

Supporting Information

Lithiated Oppolzer Enolates: Solution Structures, Mechanism of Alkylation, and Origin of Stereoselectivity

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Contents

Substrates	S-20
Chart S1. <i>N</i> -acyl-camphorsultams studied in this work	S-20
Synthesis	S-21
Synthesis of <i>N</i>-acyl sultams	S-21
General Procedure A (GP-A)	S-21
General Procedure B (GP-B)	S-21
Synthesis of (<i>S</i>)- <i>N</i> -propionyl-camphorsultam (7b)	S-22
Figure S1. ¹ H NMR spectrum of (<i>S</i>)- 7b	S-22
Figure S2. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7b	S-23
Synthesis of (<i>R</i>)- 7b	S-23
Synthesis of (<i>S</i>)- <i>N</i> -butanoyl-camphorsultam (7c)	S-24
Figure S3. ¹ H NMR spectrum of (<i>S</i>)- 7c	S-24
Figure S4. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7c	S-25
Synthesis of (<i>S</i>)- <i>N</i> -hexanoyl-camphorsultam (7e)	S-25
Figure S5. ¹ H NMR spectrum of (<i>S</i>)- 7e	S-26
Figure S6. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7e	S-26
Synthesis of (<i>S</i>)- <i>N</i> -isovaleryl-camphorsultam (7f)	S-27
Figure S7. ¹ H NMR spectrum of (<i>S</i>)- 7f	S-27
Figure S8. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7f	S-28
Synthesis of (<i>R</i>)- 7f	S-28
Synthesis of (<i>S</i>)- <i>N</i> -cyclohexylacetyl-camphorsultam (7g)	S-28
Figure S9. ¹ H NMR spectrum of (<i>S</i>)- 7g	S-29
Figure S10. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7g	S-29
Synthesis of (<i>S</i>)- <i>N</i> -hydrocinnamoyl-camphorsultam (7l)	S-30
Figure S11. ¹ H NMR spectrum of (<i>S</i>)- 7l	S-30
Figure S12. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7l	S-31

Synthesis of (<i>R</i>)- 7l	S-31
Synthesis of (<i>S</i>)- <i>N</i> -phenylacetyl-camphorsultam (7o)	S-31
Figure S13. ¹ H NMR spectrum of (<i>S</i>)- 7o	S-32
Figure S14. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7o	S-32
Synthesis of (<i>S</i>)- <i>N</i> -(<i>o</i> -fluorophenyl)acetyl-camphorsultam (7r)	S-33
Figure S15. ¹ H NMR spectrum of (<i>S</i>)- 7r	S-34
Figure S16. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7r	S-34
Figure S17. ¹⁹ F NMR spectrum of (<i>S</i>)- 7r	S-35
Synthesis of (<i>S</i>)- <i>N</i> -(<i>m</i> -fluorophenyl)acetyl-camphorsultam (7s)	S-35
Figure S18. ¹ H NMR spectrum of (<i>S</i>)- 7s	S-36
Figure S19. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7s	S-36
Figure S20. ¹⁹ F NMR spectrum of (<i>S</i>)- 7s	S-37
Synthesis of (<i>S</i>)- <i>N</i> -(<i>p</i> -fluorophenyl)acetyl-camphorsultam (7t)	S-37
Figure S21. ¹ H NMR spectrum of (<i>S</i>)- 7t	S-38
Figure S22. ¹³ C{ ¹ H} NMR spectrum of (<i>S</i>)- 7t	S-38
Figure S23. ¹⁹ F NMR spectrum of (<i>S</i>)- 7t	S-39
Synthesis of (<i>R</i>)- 7t	S-39
Synthesis of (<i>R</i>)-1-((3<i>aS</i>,6<i>R</i>,7<i>aR</i>)-8,8-dimethyl-2,2-dioxidotetrahydro-3<i>H</i>-3<i>a</i>,6-methanobenzo[<i>c</i>]isothiazol-1(4<i>H</i>)-yl)-2-phenylpent-4-en-1-one (34)	S-40
Synthesis and purification of 34	S-40
Figure S24. ¹ H NMR spectrum of 34	S-41
Figure S25. ¹³ C{ ¹ H} NMR spectrum of 34	S-41
Structural Elucidation of Oppolzer Enolates	S-42
General procedure for sealed tube NMR spectroscopy	S-42
Alkyl-substituted enolate tetramers	S-43
Figure S26. ⁶ Li NMR spectra of mixtures of [⁶ Li]-(<i>S</i>)- 8l and [⁶ Li]-(<i>S</i>)- 8f in toluene at –80 °C.	S-43

Figure S27. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8I}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$ after aging at $0\text{ }^\circ\text{C}$ for 10 min.	S-44
Figure S28. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8I}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-45
Figure S29. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-46
Figure S30. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$ after aging at $0\text{ }^\circ\text{C}$ for 10 min.	S-47
Figure S31. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-48
Figure S32. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(R)-8b}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-49
Figure S33. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(R)-8b}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-50
Figure S34. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8f}$ and $[\text{}^6\text{Li}]\text{-(R)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-51
Figure S35. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8f}$ and $[\text{}^6\text{Li}]\text{-(R)-8f}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-52
Figure S36. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8I}$ and $[\text{}^6\text{Li}]\text{-(R)-8I}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-53
Figure S37. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8I}$ and $[\text{}^6\text{Li}]\text{-(R)-8I}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-54
Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (S)-7b in toluene at $-80\text{ }^\circ\text{C}$.	S-55
Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{}^6\text{Li}]\text{-(S)-8b}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-55
Spirocyclic aryl acetamide-derived enolate dimers	S-56
Figure S40. a ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(R)-8t}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$. b The corresponding ^{19}F NMR spectra.	S-56
Figure S41. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8s}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-57
Figure S42. ^{19}F NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8s}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-58
Figure S43. ^{19}F Job plot of $[\text{}^6\text{Li}]\text{-(S)-8s}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-59
Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (S)-7o in toluene at $-80\text{ }^\circ\text{C}$.	S-60
Figure S45. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{}^6\text{Li}]\text{-(S)-8o}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-60

THF-solvated aryl acetamide-derived enolate dimers	S-61
Figure S46. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in THF at $-80\text{ }^\circ\text{C}$.	S-61
Figure S47. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in THF at $-80\text{ }^\circ\text{C}$.	S-62
Figure S48. ^{19}F NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in THF at $-80\text{ }^\circ\text{C}$.	S-63
Figure S49. ^{19}F Job plot of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in THF at $-80\text{ }^\circ\text{C}$.	S-64
THF-solvated alkyl-substituted enolate dimers	S-65
Figure S50. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-65
Figure S51. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-66
Figure S52. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8g}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-67
Figure S53. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8i}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-68
Figure S54. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8f}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-69
Figure S55. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of pyridine.	S-70
Figure S56. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8i}$ in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of pyridine.	S-71
Figure S57. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ in THF at various temperatures.	S-72
Figure S58. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-}(S)\text{-8g}$ in THF at various temperatures.	S-73
Figure S59. ^6Li NMR spectra of a 1:1 mixture of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8g}$ in THF at various temperatures.	S-74
Figure S60. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-}(S)\text{-}N\text{-acyl-camphorsultam-enolates}$ in THF.	S-75
Figure S61. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-}(S)\text{-8b}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8f}$ in THF at $-80\text{ }^\circ\text{C}$.	S-76

Figure S62. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8f}$ in THF at $-80\text{ }^\circ\text{C}$.	S-77
Figure S63. ^{15}N NMR spectra of mixtures of $[\text{}^6\text{Li},^{15}\text{N}]\text{-(S)-8b}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{-(S)-8g}$ in neat THF at $-80\text{ }^\circ\text{C}$.	S-78
Figure S64. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8g}$ in THF at $-80\text{ }^\circ\text{C}$.	S-79
Figure S65. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8g}$ in THF at $-80\text{ }^\circ\text{C}$.	S-80
Figure S66. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8e}$ in THF at $-80\text{ }^\circ\text{C}$.	S-81
Figure S67. ^6Li Job plot of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(S)-8e}$ in THF at $-80\text{ }^\circ\text{C}$.	S-82
Figure S68. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8b}$ in THF at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine.	S-83
HMPA-solvated Oppolzer enolates	S-84
Figure S69. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8b}$ with 4.0 equiv HMPA in toluene at various temperatures.	S-84
Figure S70. ^6Li NMR spectra of 0.10 M $[\text{}^6\text{Li}]\text{-(S)-8b}$ with various concentrations of HMPA in 1:2 THF/pentane at $-90\text{ }^\circ\text{C}$.	S-85
Figure S71. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in 1:2 THF/pentane at $-90\text{ }^\circ\text{C}$.	S-86
Figure S72. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in 1:1 THF/pentane at $-90\text{ }^\circ\text{C}$.	S-87
Figure S73. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.	S-88
Figure S74. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-100\text{ }^\circ\text{C}$.	S-89
Figure S75. ^{31}P NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.	S-90
Figure S76. ^6Li NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-100\text{ }^\circ\text{C}$.	S-91
Figure S77. ^{31}P NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.	S-92
Figure S78. ^{19}F NMR spectra of various $[\text{}^6\text{Li}]\text{-(S)-N-acyl-camphorsultam-enolates}$ with 3 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.	S-93

HMPA-solvated aryl acetamide-derived enolate monomers	S-94
Figure S79. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8r}$ with 1.5 equiv HMPA in toluene at various temperatures.	S-94
Figure S80. ^{19}F NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8r}$ with 1.5 equiv HMPA in toluene at various temperatures.	S-95
Figure S81. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8t}$ and $[\text{}^6\text{Li}]\text{-(S)-8r}$ with 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$.	S-96
Figure S82. ^{19}F NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8t}$ and $[\text{}^6\text{Li}]\text{-(S)-8r}$ with 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$.	S-97
Figure S83. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(R)-8t}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$.	S-98
Figure S84. ^{19}F NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(R)-8t}$ and $[\text{}^6\text{Li}]\text{-(S)-8t}$ with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$.	S-99
Figure S85. a ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine. b The corresponding ^{19}F NMR spectra.	S-100
Figure S86. a ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in 13 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine. b The corresponding ^{19}F NMR spectra.	S-101
Figure S87. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in 13 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-102
Figure S88. ^{19}F NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in 13 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of THF.	S-103
Figure S89. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-104
Figure S90. ^{19}F NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8t}$ in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-105
Figure S91. ^6Li NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8r}$ in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-106
Figure S92. ^{19}F NMR spectra of $[\text{}^6\text{Li}]\text{-(S)-8r}$ in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-107
Figure S93. ^{19}F DOSY of 0.16 M $[\text{}^6\text{Li}]\text{-(S)-8r}$ in toluene at $-80\text{ }^\circ\text{C}$.	S-108
Figure S94. ^{19}F DOSY of 0.15 M $[\text{}^6\text{Li}]\text{-(S)-8r}$ in 0.18 M HMPA in toluene at $-80\text{ }^\circ\text{C}$.	S-109
Figure S95. ^{19}F DOSY of 0.15 M $[\text{}^6\text{Li}]\text{-(S)-8r}$ in 0.30 M HMPA in toluene at $-80\text{ }^\circ\text{C}$.	S-110

Figure S96. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8o in toluene at $-90\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-111
Figure S97. ^{31}P NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8o in toluene at $-90\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-112
HMPA-solvated alkyl-substituted enolate dimers	S-113
Figure S98. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8i in toluene at $-90\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-113
Figure S99. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8m in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-114
Figure S100. ^{19}F NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8m in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.	S-115
Figure S101. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8b and $[\text{}^6\text{Li}]$ -(<i>R</i>)- 8b with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$.	S-116
Figure S102. ^6Li Job plot of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8b and $[\text{}^6\text{Li}]$ -(<i>R</i>)- 8b with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$.	S-117
Figure S103. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8b and $[\text{}^6\text{Li}]$ -(<i>R</i>)- 8b with 3 equiv HMPA in 11.4 M THF at $-80\text{ }^\circ\text{C}$.	S-118
Figure S104. ^6Li Job plot of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8b and $[\text{}^6\text{Li}]$ -(<i>R</i>)- 8b with 3 equiv HMPA in 11.4 M THF at $-80\text{ }^\circ\text{C}$.	S-119
THF-solvated alkyl-substituted dianion tetramer	S-120
Figure S105. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8g with varying concentrations of $[\text{}^6\text{Li}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-120
Figure S106. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8e with varying concentrations of $[\text{}^6\text{Li}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-121
Figure S107. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8f with varying concentrations of $[\text{}^6\text{Li}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-122
Figure S108. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8g with 0.0, 0.6, and 1.5 equiv excess $[\text{}^6\text{Li},^{15}\text{N}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-123
Figure S109. ^{15}N and $^{15}\text{N}\{^1\text{H}\}$ NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8g with 0.6 excess $[\text{}^6\text{Li},^{15}\text{N}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-124
Figure S110. ^{15}N and $^{15}\text{N}\{^1\text{H}\}$ NMR spectra of $[\text{}^6\text{Li}]$ -(<i>S</i>)- 8g with 1.5 equiv excess $[\text{}^6\text{Li},^{15}\text{N}]$ -LDA in THF at $-80\text{ }^\circ\text{C}$.	S-125
Figure S111. DART-HRMS of $[\text{}^6\text{Li}]$ - 34 after quenching with excess TMSI.	S-126

Rate Studies	S-127
General procedure for in situ IR analyses	S-127
Figure S112. HMPA order	S-128
Table S1. Average pseudo-first-order rate constants (k_{obsd}) at various free HMPA concentrations	S-128
Figure S113. Toluene order @ 0.275 M HMPA / cyclopentane	S-129
Table S2. Average initial rate constants (k_{initial}) at various Toluene concentrations	S-129
Figure S114. THF order @ 0.275 M HMPA / Toluene	S-130
Table S3. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-130
Figure S115. THF order @ 0.275 M HMPA / 2,5-DimethylTHF	S-131
Table S4. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-131
Figure S116. THF order @ 0.275 M HMPA	S-132
Table S5. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-133
Figure S117. Toluene order @ 0.810 M HMPA / cyclopentane	S-134
Table S6. Average initial rate constants (k_{obsd}) at various Toluene concentrations	S-134
Figure S118. THF order @ 0.810 M HMPA / Toluene	S-135
Table S7. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-135
Figure S119. THF order @ 0.810 M HMPA / 2,5-DimethylTHF	S-136
Table S8. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-136
Figure S120. THF order @ 0.810 M HMPA	S-137
Table S9. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations	S-138
Figure S121. Allyl bromide order	S-139
Table S10. Average pseudo-first-order rate constants (k_{obsd}) at various allyl bromide concentrations	S-139

Single Crystal X-Ray Diffraction Data	S-140
General methods	S-140
Conditions of growth for Rnml1.	S-141
Figure S122. X-ray crystal structure of Rnml1. a Top view. b Side view.	S-141
Figure S123. X-ray crystal structure of Rnml1 with cyclohexyl groups hidden. a Top view. b Side view.	S-141
Figure S124. X-ray crystal structure of Rnml1 with cyclohexyl groups and solvent molecules hidden. a Top view. b Side view. c Rotated side view.	S-142
Table S11. Crystal data and structure refinement for Rnml1.	S-143
Table S12. Atomic coordinates and equivalent isotropic displacement parameters for Rnml1.	S-144
Conditions of growth for Rnml2.	S-148
Figure S125. X-ray crystal structure of Rnml2. a Top view. b Side view. c Rotated side view.	S-148
Table S13. Crystal data and structure refinement for Rnml2.	S-149
Table S14. Atomic coordinates and equivalent isotropic displacement parameters for Rnml2.	S-150
Conditions of growth for Rnml5.	S-153
Figure S126. X-ray crystal structure of Rnml5.	S-153
Figure S127. X-ray crystal structure of Rnml5 with outer solvent molecules hidden. a Top view. b Side view. c Rotated side view.	S-154
Table S15. Crystal data and structure refinement for Rnml5.	S-155
Table S16. Atomic coordinates and equivalent isotropic displacement parameters for Rnml5.	S-156
Conditions of growth for Rnml4.	S-158
Figure S128. X-ray crystal structure of Rnml4.	S-158
Table S17. Crystal data and structure refinement for Rnml4.	S-159
Table S18. Atomic coordinates and equivalent isotropic displacement parameters for Rnml4.	S-160

Computational Data	S-161
General computational methods	S-161
Solvent molecules	S-162
Table S19. Atomic coordinates and single point energies for THF	S-162
Table S20. Atomic coordinates and single point energies for HMPA	S-163
Table S21. Atomic coordinates and single point energies for Toluene	S-164
Anions of enolate 8o	S-165
Table S22. Atomic coordinates and single point energies for just the anion fragment of 8o with the enolate oxygen <i>syn</i> to the sultam ring.	S-165
Table S23. Atomic coordinates and single point energies for just the anion fragment of 8o anion with the enolate oxygen <i>anti</i> to the sultam ring.	S-167
Monomers of enolate 8o	S-169
Table S24. Atomic coordinates and single point energies of 8o chelated to the <i>exo</i> sulfonyl oxygen.	S-169
Table S25. Atomic coordinates and single point energies of 8o chelated to the <i>endo</i> sulfonyl oxygen.	S-171
Table S26. Atomic coordinates and single point energies of 8o .	S-173
Table S27. Atomic coordinates and single point energies of HMPA-solvated 8o chelated to the <i>exo</i> sulfonyl oxygen.	S-175
Table S28. Atomic coordinates and single point energies of HMPA-solvated 8o chelated to the <i>endo</i> sulfonyl oxygen.	S-178
Table S29. Atomic coordinates and single point energies of HMPA-solvated 8o .	S-181
Table S30. Atomic coordinates and single point energies of <i>bis</i> -HMPA-solvated 8o chelated to the <i>exo</i> sulfonyl oxygen.	S-184
Table S31. Atomic coordinates and single point energies of <i>bis</i> -HMPA-solvated 8o chelated to the <i>endo</i> sulfonyl oxygen.	S-187
Table S32. Atomic coordinates and single point energies of <i>bis</i> -HMPA-solvated 8o .	S-190
Table S33. Atomic coordinates and single point energies of <i>tris</i> -HMPA-solvated 8o chelated to the <i>exo</i> sulfonyl oxygen.	S-193
Table S34. Atomic coordinates and single point energies of <i>tris</i> -HMPA-solvated 8o chelated to the <i>endo</i> sulfonyl oxygen.	S-197

Table S35. Atomic coordinates and single point energies of <i>tris</i> -HMPA-solvated 8o with the enolate oxygen <i>syn</i> to the sultam ring.	S-201
Table S36. Atomic coordinates and single point energies of <i>tris</i> -HMPA-solvated 8o with the enolate oxygen <i>anti</i> to the sultam ring.	S-205
<i>Mixed-solvates of enolate 8o</i>	S-209
Table S37. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>exo</i> sulfonyl oxygen with an axial THF.	S-209
Table S38. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>endo</i> sulfonyl oxygen with an axial THF.	S-213
Table S39. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>exo</i> sulfonyl oxygen with an equatorial THF (higher energy conformer).	S-217
Table S40. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>endo</i> sulfonyl oxygen with an equatorial THF (higher energy conformer).	S-221
Table S41. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>exo</i> sulfonyl oxygen with an equatorial THF (lower energy conformer).	S-225
Table S42. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) chelated to the <i>endo</i> sulfonyl oxygen with an equatorial THF (lower energy conformer).	S-229
Table S43. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>syn</i> to the sultam ring (lowest energy conformer).	S-233
Table S44. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>syn</i> to the sultam ring (higher energy conformer).	S-237
Table S45. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>syn</i> to the sultam ring (higher energy conformer).	S-241
Table S46. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>anti</i> to the sultam ring (lowest energy conformer).	S-245
Table S47. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>anti</i> to the sultam ring (higher energy conformer).	S-249

Table S48. Atomic coordinates and single point energies of the 8o mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen <i>anti</i> to the sultam ring (higher energy conformer).	S-253
Dimers of enolate 8o	S-257
Table S49. Atomic coordinates and single point energies of the symmetric dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens.	S-257
Table S50. Atomic coordinates and single point energies of the symmetric dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens.	S-260
Table S51. Atomic coordinates and single point energies of the spirocyclic dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens.	S-263
Table S52. Atomic coordinates and single point energies of the spirocyclic dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens.	S-266
Table S53. Atomic coordinates and single point energies of the spirocyclic heterochiral dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens.	S-269
Table S54. Atomic coordinates and single point energies of the spirocyclic heterochiral dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens.	S-272
<i>Toluene-solvated dimers of enolate 8o</i>	S-275
Table S55. Atomic coordinates and single point energies of the toluene-solvated spirocyclic dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens.	S-275
Table S56. Atomic coordinates and single point energies of the toluene-solvated spirocyclic dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens.	S-278
<i>THF-solvated dimers of enolate 8o</i>	S-281
Table S57. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens (higher energy conformer).	S-281
Table S58. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens (higher energy conformer).	S-284

Table S59. Atomic coordinates and single point energies of the <i>bis</i> -THF-solvated spirocyclic dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens (lowest energy conformer).	S-287
Table S60. Atomic coordinates and single point energies of the <i>bis</i> -THF-solvated spirocyclic dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens (lowest energy conformer).	S-290
<i>HMPA-solvated dimers of enolate 8o</i>	S-293
Table S61. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>exo</i> -face.	S-293
Table S62. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>endo</i> -face.	S-297
Table S63. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>exo</i> -face.	S-301
Table S64. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8o with double <i>endo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>endo</i> -face.	S-305
Table S65. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8o with chelation to one <i>endo</i> and one <i>exo</i> sulfonyl oxygen; the HMPAs are aligned <i>anti</i> to each other.	S-309
<i>Solvent-bridged HMPA-solvated dimers of enolate 8o</i>	S-313
Table S66. Atomic coordinates and single point energies of the <i>tris</i> -HMPA-solvated symmetric dimer of 8o with chelation to one <i>endo</i> and one <i>exo</i> sulfonyl oxygen where the μ_2 -HMPA is on the camphor <i>endo</i> -face.	S-313
Table S67. Atomic coordinates and single point energies of the <i>tris</i> -HMPA-solvated symmetric dimer of 8o with double <i>exo</i> chelation to the sulfonyl oxygens where the μ_2 -HMPA is on the camphor <i>exo</i> -face.	S-318
Dimers of enolate 8b	S-323
Table S68. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8b with double <i>exo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>exo</i> -face.	S-323
Table S69. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8b with double <i>exo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>endo</i> -face.	S-327

Table S70. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8b with double <i>endo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>exo</i> -face.	S-331
Table S71. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8b with double <i>endo</i> chelation to the sulfonyl oxygens; both HMPAs are on the camphor <i>endo</i> -face.	S-335
Table S72. Atomic coordinates and single point energies of the <i>bis</i> -HMPA-solvated symmetric dimer of 8b with chelation to one <i>endo</i> and one <i>exo</i> sulfonyl oxygen; both HMPAs are on the camphor <i>endo</i> -face.	S-339
Table S73. Atomic coordinates and single point energies of the <i>tris</i> -HMPA-solvated symmetric dimer of 8b with chelation to one <i>endo</i> and one <i>exo</i> sulfonyl oxygen where the μ_2 -HMPA is on the camphor <i>exo</i> -face.	S-343
Tetramers of enolate 8b	S-348
Table S74. Atomic coordinates and single point energies of the S ₄ -type tetramer of 8b with all <i>endo</i> chelation to the sulfonyl oxygens.	S-348
Table S75. Atomic coordinates and single point energies of the S ₄ -type tetramer of 8b with all <i>exo</i> chelation to the sulfonyl oxygens.	S-353
Table S76. Atomic coordinates and single point energies of the S ₄ -type tetramer of 8b with <i>endo</i> chelation to the sulfonyl oxygens of the <i>syn</i> subunits and <i>exo</i> chelation to the sulfonyl oxygens of the <i>anti</i> subunits.	S-358
Table S77. Atomic coordinates and single point energies of the S ₄ -type tetramer of 8b with <i>exo</i> chelation to the sulfonyl oxygens of the <i>syn</i> subunits and <i>endo</i> chelation to the sulfonyl oxygens of the <i>anti</i> subunits.	S-363
Table S78. Atomic coordinates and single point energies of the D _{2d} -type tetramer of 8b with all <i>endo</i> chelation to the sulfonyl oxygens.	S-368
Table S79. Atomic coordinates and single point energies of the D _{2d} -type tetramer of 8b with all <i>exo</i> chelation to the sulfonyl oxygens.	S-373
Heterochiral tetramers of enolate 8b	S-378
Table S80. Atomic coordinates and single point energies of the S ₄ -type heterochiral (S₃R₁) tetramer of 8b with all <i>endo</i> chelation to the sulfonyl oxygens.	S-378
Table S81. Atomic coordinates and single point energies of the S ₄ -type heterochiral (S₃R₁) tetramer of 8b with <i>exo</i> chelation to the sulfonyl oxygens of the <i>syn</i> subunits and <i>endo</i> chelation to the sulfonyl oxygens of the <i>anti</i> subunits.	S-383

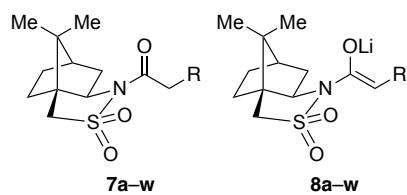
Table S82. Atomic coordinates and single point energies of the S ₄ -type heterochiral (S₂R₂) tetramer of 8b with all <i>endo</i> chelation to the sulfonyl oxygens.	S-388
Table S83. Atomic coordinates and single point energies of the S ₄ -type heterochiral (S₂R₂) tetramer of 8b with <i>exo</i> chelation to the sulfonyl oxygens of the <i>syn</i> subunits and <i>endo</i> chelation to the sulfonyl oxygens of the <i>anti</i> subunits.	S-393
Transition states	S-398
Table S84. Atomic coordinates and single point energies of the reactant ground state for the top-face allylation of 8o with π-stacking.	S-398
Table S85. Atomic coordinates and single point energies of the transition state for the top-face allylation of 8o with π-stacking.	S-400
Table S86. Atomic coordinates and single point energies of the product ground state for the top-face allylation of 8o .	S-402
Table S87. Atomic coordinates and single point energies of the reactant ground state for the top-face allylation of 8o without π-stacking.	S-404
Table S88. Atomic coordinates and single point energies of the transition state for the top-face allylation of 8o without π-stacking.	S-406
Table S89. Atomic coordinates and single point energies of the reactant ground state for the bottom-face allylation of 8o with π-stacking.	S-408
Table S90. Atomic coordinates and single point energies of the transition state for the bottom-face allylation of 8o with π-stacking.	S-410
Table S91. Atomic coordinates and single point energies of the product ground state for the bottom-face allylation of 8o .	S-412
Table S92. Atomic coordinates and single point energies of the reactant ground state for the bottom-face allylation of 8o without π-stacking.	S-414
Table S93. Atomic coordinates and single point energies of the transition state for the bottom-face allylation of 8o without π-stacking.	S-416
Table S94. Atomic coordinates and single point energies of the reactant ground state for the top-face allylation of 8b .	S-418
Table S95. Atomic coordinates and single point energies of the transition state for the top-face allylation of 8b .	S-420
Table S96. Atomic coordinates and single point energies of the product ground state for the top-face allylation of 8b .	S-422

Table S97. Atomic coordinates and single point energies of the ground state for the bottom-face allylation of 8b .	S-424
Table S98. Atomic coordinates and single point energies of the transition state for the bottom-face allylation of 8b .	S-426
Table S99. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of 8b .	S-428
Table S100. Atomic coordinates and single point energies of the transition state for the top-face methylation of 8b .	S-430
Table S101. Atomic coordinates and single point energies of the ground state for the bottom-face methylation of 8b .	S-432
Table S102. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of 8b .	S-434
Table S103. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of 8o .	S-436
Table S104. Atomic coordinates and single point energies of the transition state for the top-face methylation of 8o .	S-438
Table S105. Atomic coordinates and single point energies of the product ground state for the top-face methylation of 8o .	S-440
Table S106. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of 8o .	S-442
Table S107. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of 8o .	S-444
Table S108. Atomic coordinates and single point energies of the product ground state for the bottom-face methylation of 8o .	S-446
Table S109. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of 8o without camphor methyl groups.	S-448
Table S110. Atomic coordinates and single point energies of the transition state for the top-face methylation of 8o without camphor methyl groups.	S-450
Table S111. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of 8o without camphor methyl groups.	S-452
Table S112. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of 8o without camphor methyl groups.	S-454

Table S113. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of 8o without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.	S-456
Table S114. Atomic coordinates and single point energies of the transition state for the top-face methylation of 8o without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.	S-458
Table S115. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of 8o without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.	S-460
Table S116. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of 8o without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.	S-462
Table S117. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of <i>N</i> -phenylacetyl γ -sultam enolate.	S-464
Table S118. Atomic coordinates and single point energies of the transition state for the top-face methylation of <i>N</i> -phenylacetyl γ -sultam enolate.	S-466
Table S119. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of <i>N</i> -phenylacetyl γ -sultam enolate.	S-468
Table S120. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of <i>N</i> -phenylacetyl γ -sultam enolate.	S-470
Table S121. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of dihedrally-anchored (C-C-C-N) <i>N</i> -phenylacetyl γ -sultam enolate.	S-472
Table S122. Atomic coordinates and single point energies of the transition state for the top-face methylation of dihedrally-anchored (C-C-C-N) <i>N</i> -phenylacetyl γ -sultam enolate.	S-474
Table S123. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of dihedrally-anchored (C-C-C-N) <i>N</i> -phenylacetyl γ -sultam enolate.	S-476

Table S124. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of dihedrally-anchored (C-C-C-N) <i>N</i> -phenylacetyl γ -sultam enolate.	S-478
Table S125. Atomic coordinates and single point energies of the reactant ground state for the top-face protonation of 8o by CHF ₃ .	S-480
Table S126. Atomic coordinates and single point energies of the transition state for the top-face protonation of 8o by CHF ₃ .	S-482
Table S127. Atomic coordinates and single point energies of the reactant ground state for the bottom-face protonation of 8o by CHF ₃ .	S-484
Table S128. Atomic coordinates and single point energies of the transition state for the bottom-face protonation of 8o by CHF ₃ .	S-486
Supplementary References	S-488

Substrates



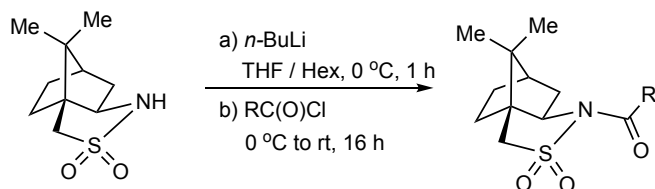
a ; H	h ; <i>t</i> -Bu	o ; Ph
b ; Me	i ; CH ₂ CF ₃	p ; <i>p</i> -Cl-Ph
c ; Et	j ; CH=CH ₂	q ; <i>p</i> -MeO-Ph
d ; <i>n</i> -Pr	k ; CH ₂ CH=CH ₂	r ; <i>o</i> -F-Ph
e ; <i>n</i> -Bu	l ; CH ₂ Ph	s ; <i>m</i> -F-Ph
f ; <i>i</i> -Pr	m ; CH ₂ - <i>m</i> -F-Ph	t ; <i>p</i> -F-Ph
g ; cyclohexyl (Cy)	n ; CH ₂ - <i>p</i> -F-Ph	u ; <i>m</i> -CF ₃ -Ph

Chart S1. *N*-acyl-camphorsultams and their enolates studied in this work

Synthesis

Synthesis of *N*-acyl sultams

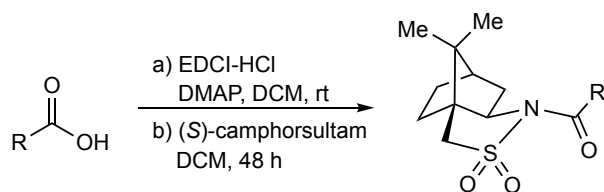
General Procedure A (GP-A)



At 0 °C, *n*BuLi (1.6 M in hexanes, 4.8 mL, 7.6 mmol, 1.5 equiv) was added to a solution of (*S*)-camphorsultam or (*R*)-camphorsultam (1.08 g, 4.7 mmol, 1.0 equiv) in dry (neutral activated alumina) THF (15 mL). The solution was stirred on ice for 1 h. The acyl chloride (6.7 mmol, 1.4 equiv) was then added slowly via syringe. The mixture was allowed to warm to room temperature and stirred vigorously overnight. The reaction was quenched with 20 mL of half-saturated NH₄Cl. The aqueous layer was separated and extracted twice with 20 mL Et₂O. The organic layers were combined and concentrated to dryness to afford the crude *N*-acyl camphorsultam derivatives.

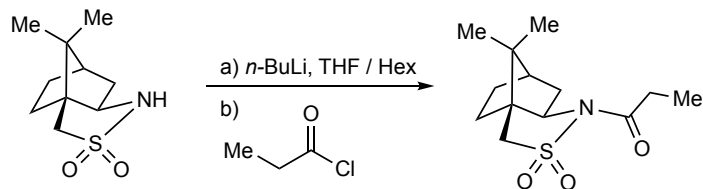
Slightly modified from the procedure of ref S1.

General Procedure B (GP-B)



To a room temperature solution of a carboxylic acid (5.2 mmol, 1.1 equiv), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI-HCl, 1.14 g, 6.0 mmol, 1.3 equiv), and 4-dimethylaminopyridine (DMAP, 0.71 g, 5.9 mmol, 1.2 equiv) in dry (4 Å molecular sieves) DCM (40 mL) was added (*S*)-camphorsultam or (*R*)-camphorsultam (1.01 g, 4.7 mmol, 1.0 equiv) in dry (4 Å molecular sieves) DCM (5 mL). The mixture left to stir at room temperature for 48 h. The reaction was quenched with 30 mL of 10 wt% aqueous citric acid. The aqueous layer was separated and extracted twice with 25 mL DCM. The organic layers were combined and concentrated to dryness to afford the crude *N*-acyl camphorsultam derivatives.

Synthesis of (*S*)-*N*-propionyl-camphorsultam (**7b**)



(*S*)-**7b** was synthesized according to **GP-A**. The crude product was recrystallized from hot MeOH (1.01 g, 79.9%) to yield thin, flat, long, white needle-like crystals identical to the product reported in ref S2.

¹H NMR (500 MHz, CDCl₃) δ 3.86 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 1H), 3.42 (d, *J* = 13.9 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.18 – 2.03 (m, 2H), 1.96 – 1.83 (m, 3H), 1.45 – 1.30 (m, 2H), 1.16 (t, *J* = 7.3 Hz, 3H), 1.15 (s, 3H), 0.96 (s, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 172.67, 65.24, 52.91, 48.44, 47.75, 44.64, 38.49, 32.84, 28.89, 26.44, 20.82, 19.88, 8.38.

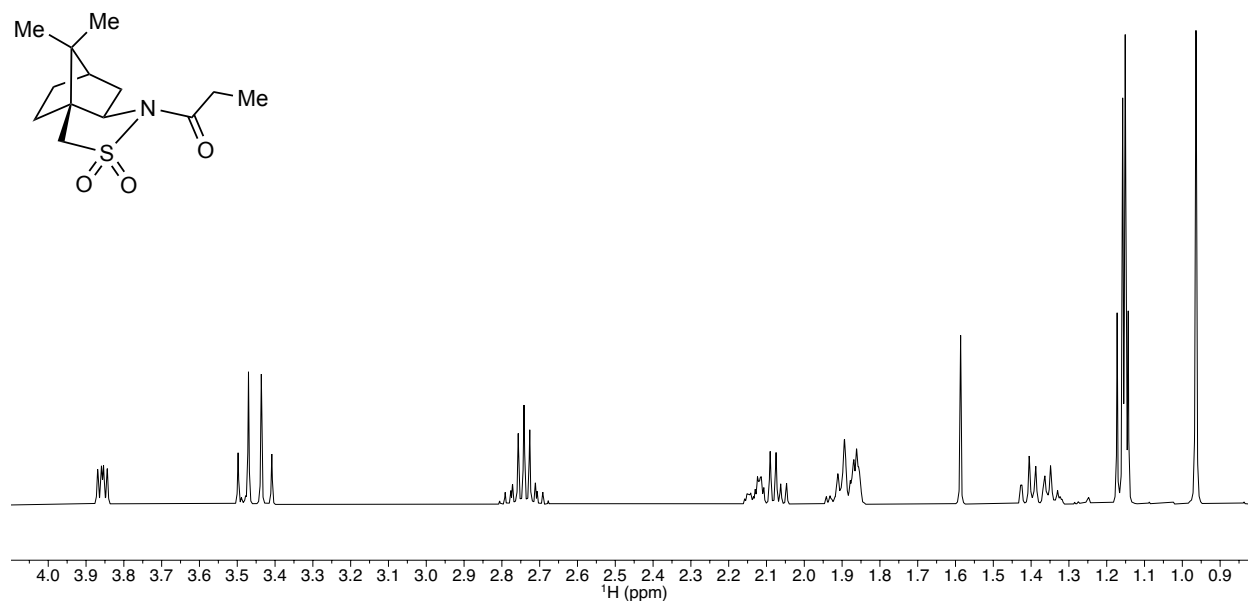


Figure S1. ¹H NMR spectrum of (*S*)-**7b** in CDCl₃ w/ 0.05% TMS at 25 °C.

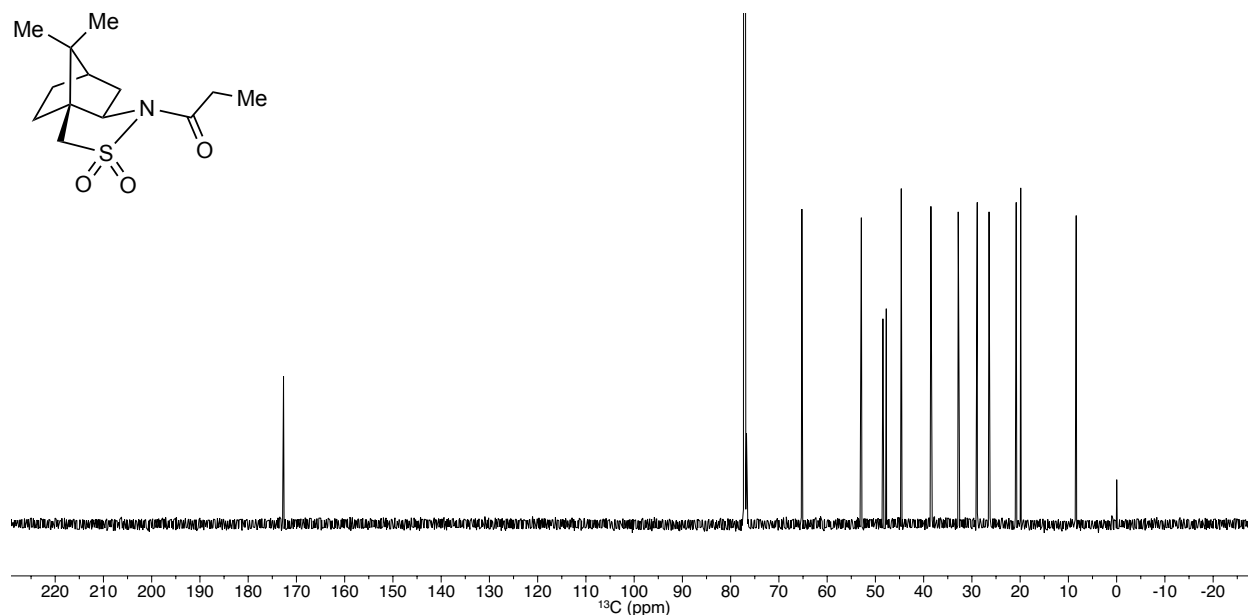
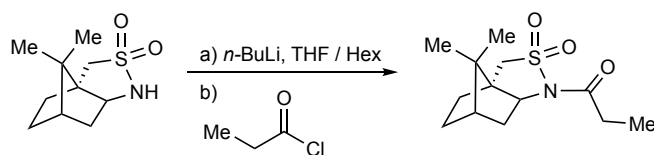


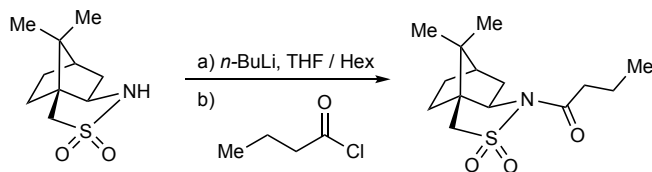
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-**7b** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*R*)-*N*-propionyl-camphorsultam (**7b**)



(*R*)-**7b** was synthesized according to **GP-A**. The crude product was recrystallized from hot MeOH (1.10 g, 86.3%) to yield thin, flat, long, white needle-like crystals. Spectral properties of (*R*)-**7b** were identical to those of (*S*)-**7b**.

Synthesis of (*S*)-*N*-butanoyl-camphorsultam (**7c**)



(*S*)-**7c** was synthesized according to **GP-A**. The crude product was purified by flash chromatography on silica (50% Et₂O in hexanes, *R_f* = 0.43) to afford a white solid (0.55 g, 80.3%) identical to the product reported in ref S2.

¹H NMR (500 MHz, None) δ 3.87 (dd, *J* = 7.6, 5.1 Hz, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 3.42 (d, *J* = 13.8 Hz, 1H), 2.76 – 2.62 (m, 2H), 2.15 – 2.05 (m, 2H), 1.95 – 1.80 (m, 3H), 1.45 – 1.30 (m, 2H), 1.16 (s, 3H), 0.97 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.96, 65.25, 53.00, 48.38, 47.76, 44.69, 38.57, 37.36, 32.87, 26.47, 20.84, 19.90, 17.97, 13.53.

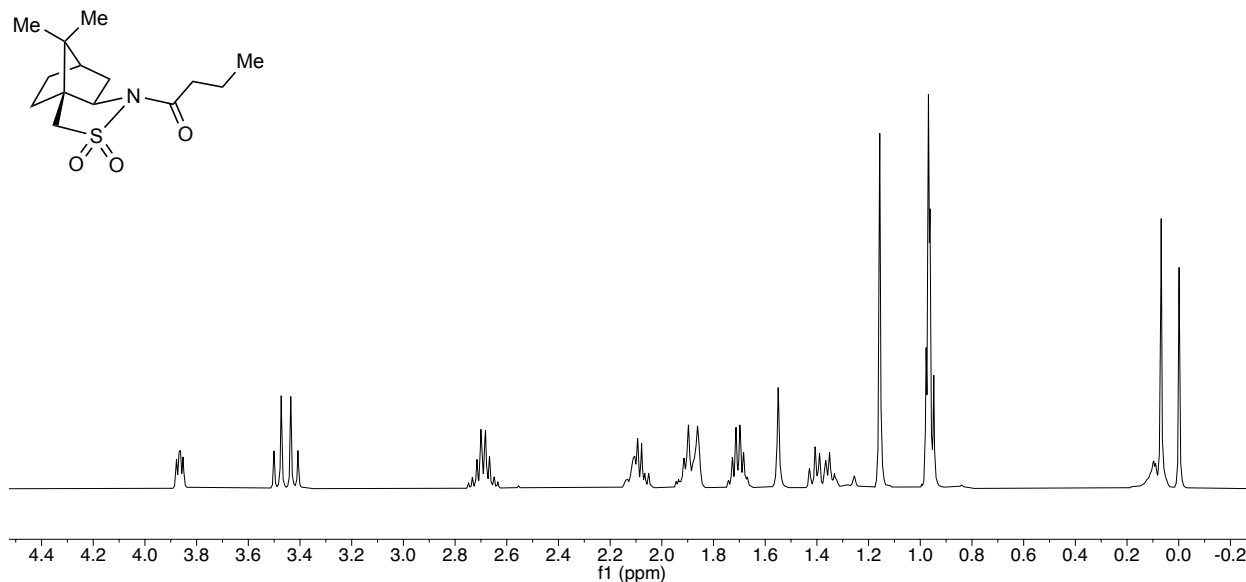


Figure S3. ¹H NMR spectrum of (*S*)-**7c** in CDCl₃ w/ 0.05% TMS at 25 °C.

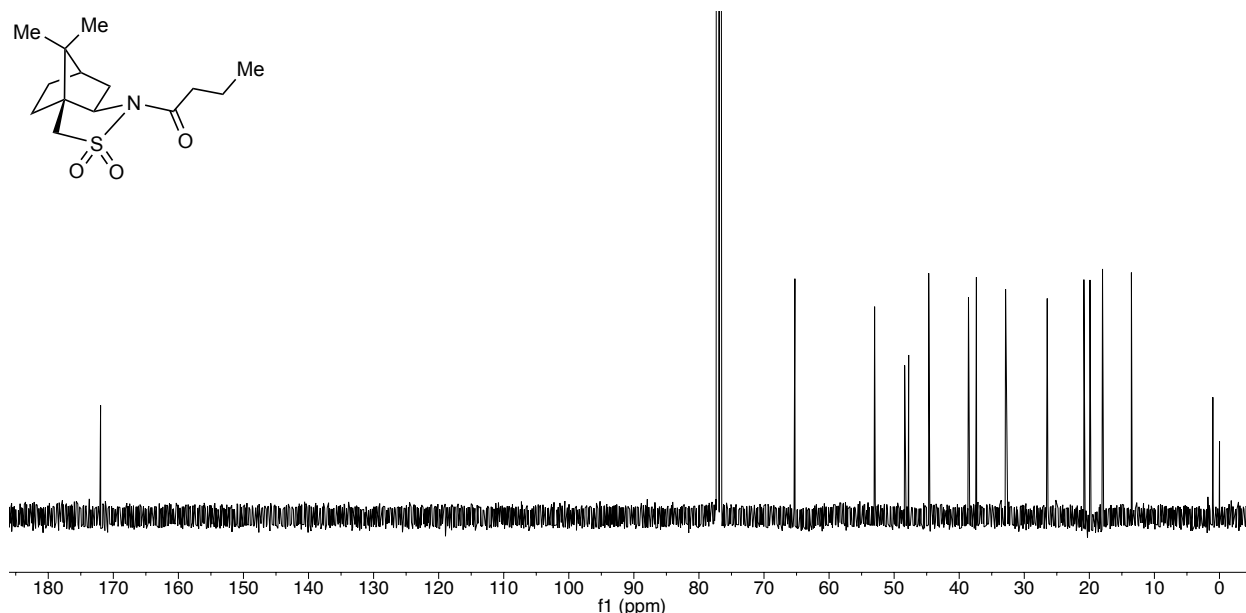
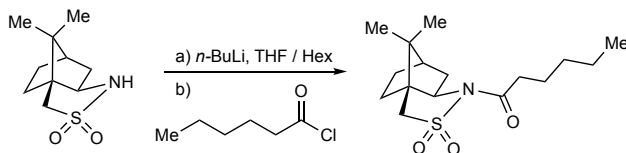


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-**7c** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-hexanoyl-camphorsultam (**7e**)



(*S*)-(**7e**) synthesized according to **GP-A**. The crude product was purified by flash chromatography on silica (40% Et_2O in hexanes, $R_f = 0.38$) to afford a clear colorless oil (1.47 g, 95.8%) that does not solidify identical to the product reported in ref S2.

^1H NMR (500 MHz, CDCl_3) δ 3.86 (dd, $J = 7.6, 5.1$ Hz, 1H), 3.49 (d, $J = 13.8$ Hz, 1H), 3.42 (d, $J = 13.8$ Hz, 1H), 2.78 – 2.63 (m, 2H), 2.35 (t, $J = 7.5$ Hz, 1H), 2.16 – 2.03 (m, 2H), 1.96 – 1.84 (m, 3H), 1.72 – 1.60 (m, 3H), 1.45 – 1.23 (m, 9H), 1.15 (s, 3H), 0.97 (s, 3H), 0.94 – 0.83 (m, 5H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.3, 65.4, 53.1, 48.5, 47.9, 44.8, 38.7, 35.6, 33.0, 31.4, 31.3, 26.6, 24.5, 24.3, 22.5, 22.4, 21.0, 20.0, 14.0, 14.0.

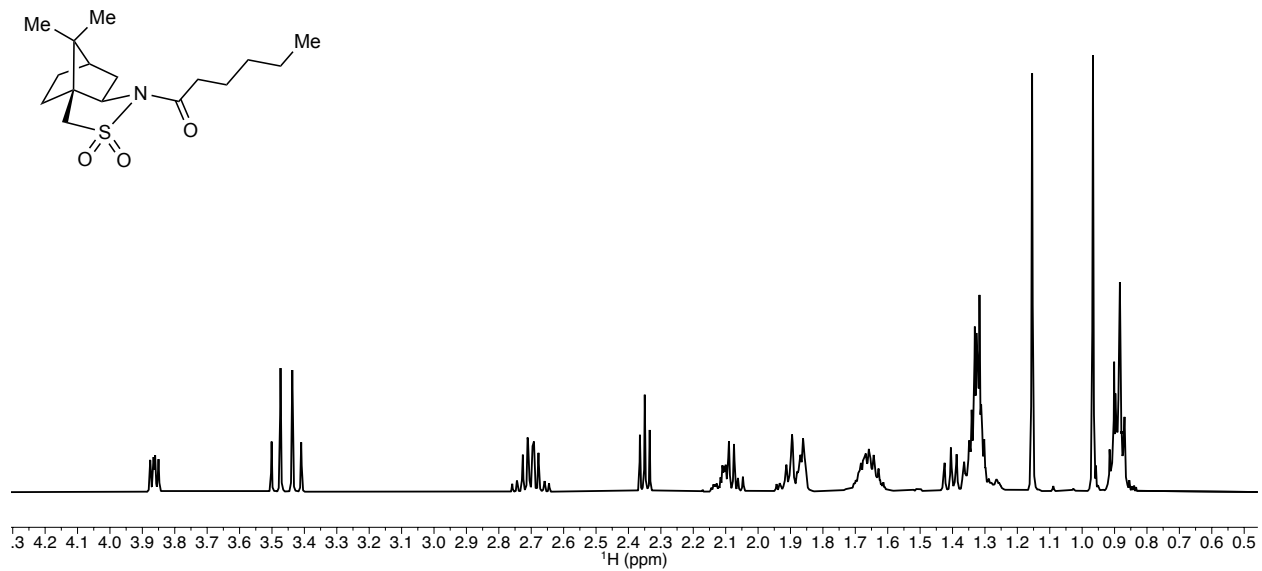


Figure S5. ¹H NMR spectrum of (S)-(**7e**) in CDCl₃ w/ 0.05% TMS at 25 °C.

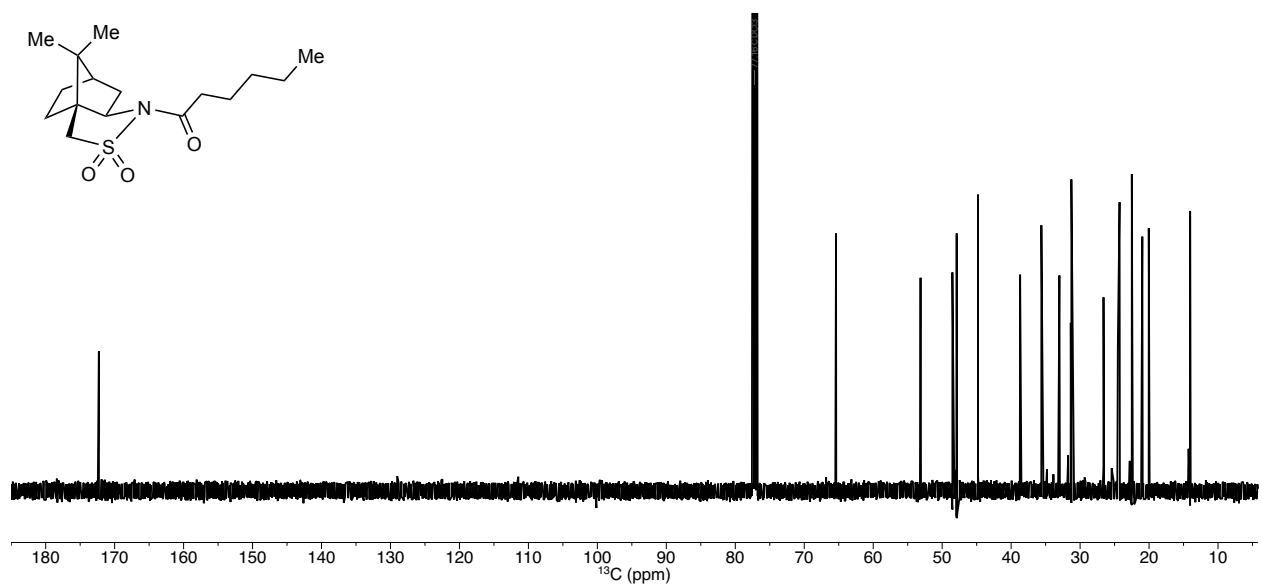
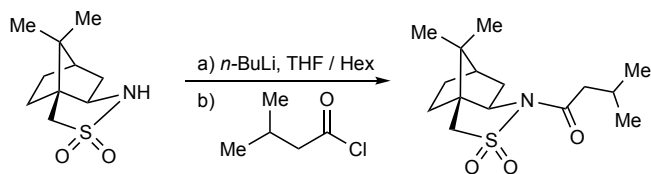


Figure S6. ¹³C{¹H} NMR spectrum of (S)-(**7e**) in CDCl₃ w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-isovaleryl-camphorsultam (**7f**)



(*S*)-**7f** was synthesized according to **GP-A**. The crude product was purified by flash chromatography on silica (40% Et₂O in hexanes, *R_f* = 0.43) to afford a white solid (1.11 g, 78.4%) identical to the product reported in ref S3.

¹H NMR (500 MHz, CDCl₃) δ 3.88 (t, *J* = 6.3 Hz, 1H), 3.49 (d, *J* = 13.7 Hz, 1H), 3.42 (d, *J* = 13.8 Hz, 1H), 2.66 (dd, *J* = 15.7, 7.1 Hz, 1H), 2.51 (dd, *J* = 15.6, 6.9 Hz, 1H), 2.23 (dh, *J* = 13.5, 6.7 Hz, 1H), 2.14 – 2.04 (m, 2H), 1.96 – 1.84 (m, 3H), 1.45 – 1.30 (m, 2H), 1.15 (s, 3H), 1.03 – 0.94 (m, 9H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 171.7, 65.4, 53.2, 48.4, 47.9, 44.8, 44.4, 38.8, 33.0, 26.6, 25.7, 22.5, 22.4, 21.0, 20.0.

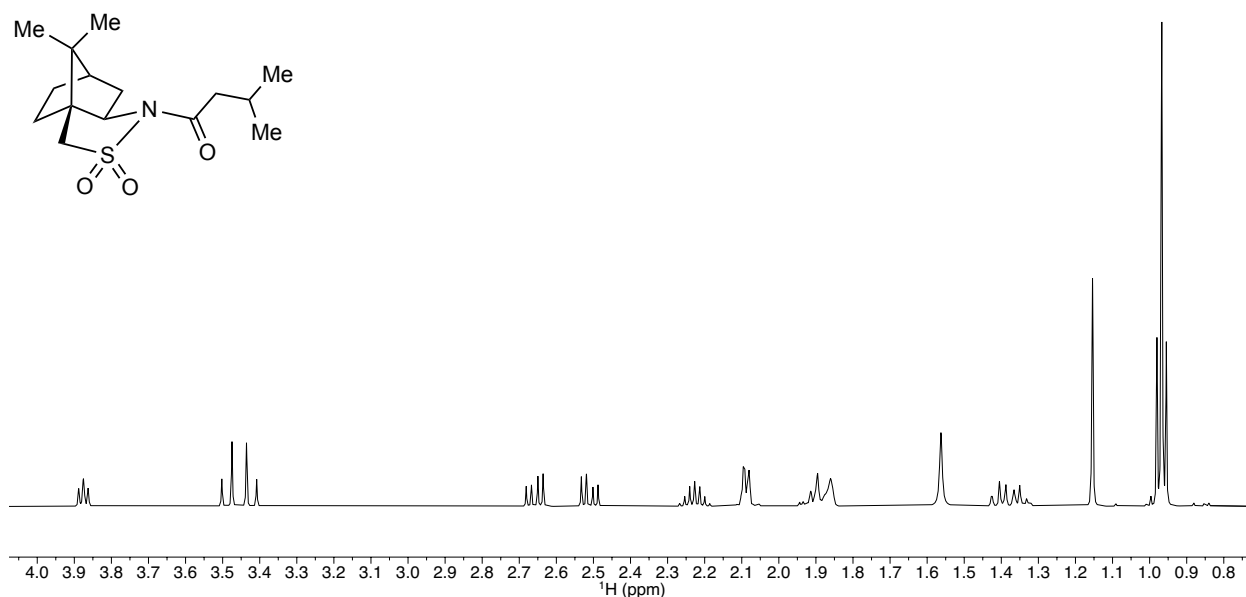


Figure S7. ¹H NMR spectrum of (*S*)-**7f** in CDCl₃ w/ 0.05% TMS at 25 °C.

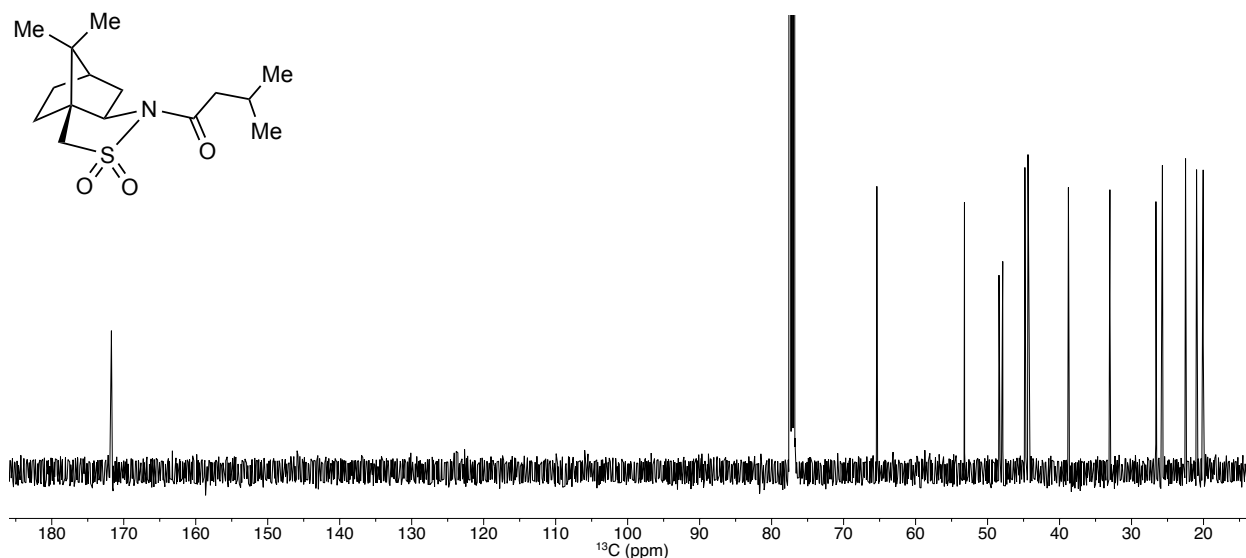
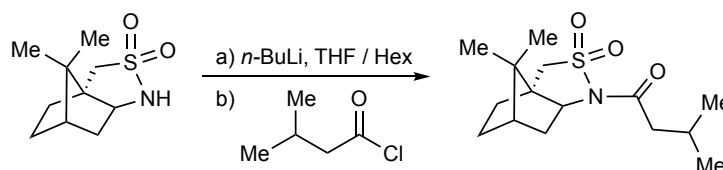


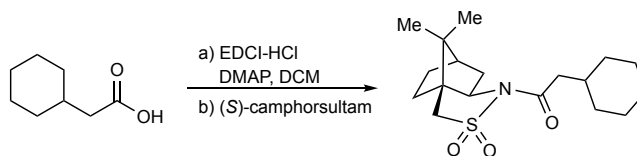
Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-**7f** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*R*)-*N*-isovaleryl-camphorsultam (**7f**)



(*R*)-**7f** was synthesized according to **GP-A**. The crude product was purified by flash chromatography on silica (10% to 40% Et_2O in hexanes) to afford a white solid (0.94 g, 66.3%). Spectra properties of (*R*)-**7f** were identical to those of (*S*)-**7f**.

Synthesis of (*S*)-*N*-cyclohexylacetyl-camphorsultam (**7g**)



(*S*)-**7g** was synthesized according to **GP-B**. The crude product was purified by flash chromatography on silica (5% to 15% EtOAc in hexanes) to afford a colorless oil that solidifies to a white solid over several days (1.24 g, 77.9%) identical to the product reported in ref S4.

^1H NMR (500 MHz, CDCl_3) δ 3.90 – 3.84 (m, 1H), 3.49 (d, $J = 13.7$ Hz, 1H), 3.42 (d, $J = 13.8$ Hz, 1H), 2.65 (dd, $J = 15.7, 7.2$ Hz, 1H), 2.51 (dd, $J = 15.7, 6.7$ Hz, 1H), 2.14 – 2.03 (m, 2H), 1.98 – 1.83 (m, 4H), 1.76 – 1.65 (m, 5H), 1.44 – 1.35 (m, 1H), 1.38 – 1.27 (m, 1H), 1.29 – 1.07 (m, 2H), 1.15 (s, 3H), 1.07 – 0.96 (m, 2H), 0.97 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 171.7, 65.4, 53.2, 48.4, 47.9, 44.8, 43.1, 38.8, 34.9, 33.1, 33.0, 32.9, 26.6, 26.3, 26.2, 26.2, 21.0, 20.1.

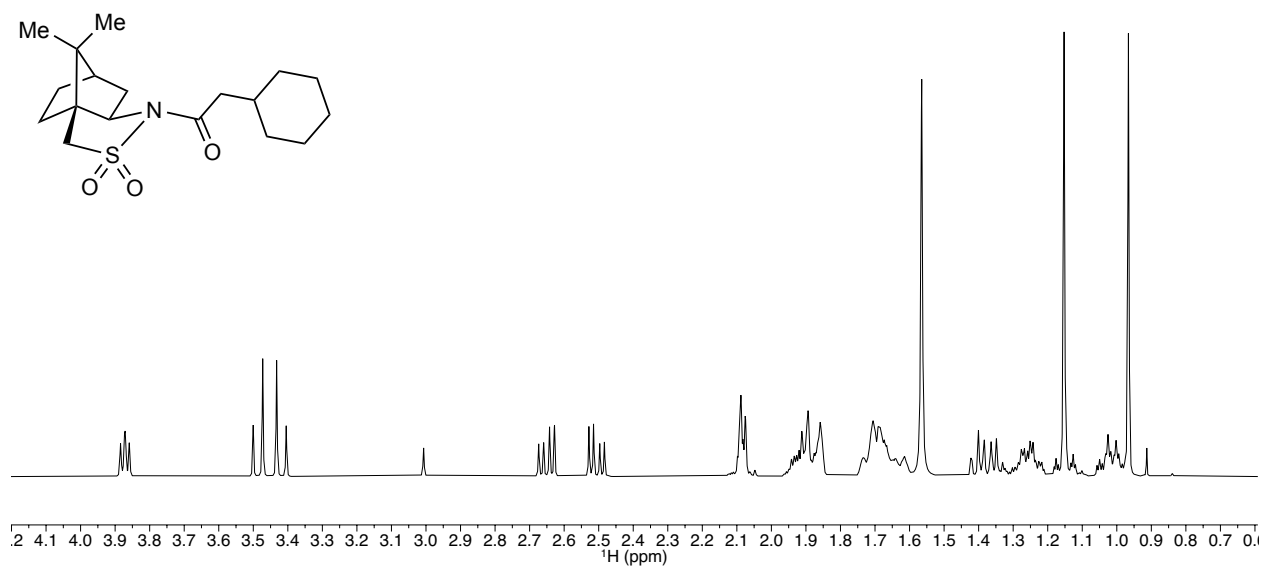


Figure S9. ^1H NMR spectrum of (*S*)-7g in CDCl_3 w/ 0.05% TMS at 25 °C.

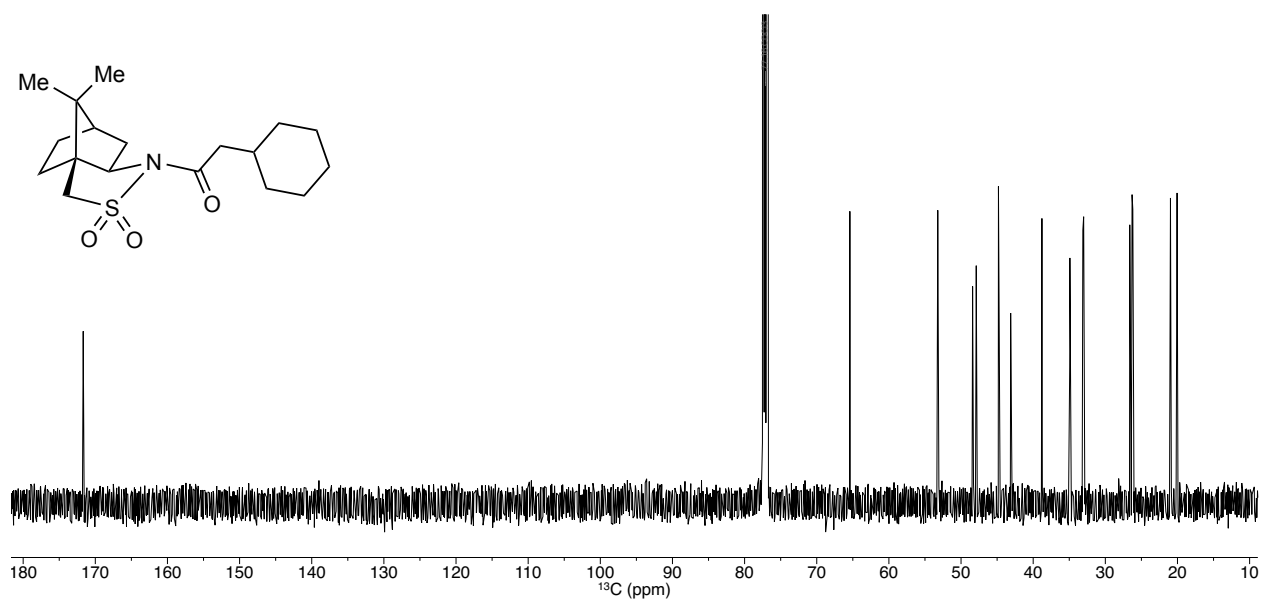
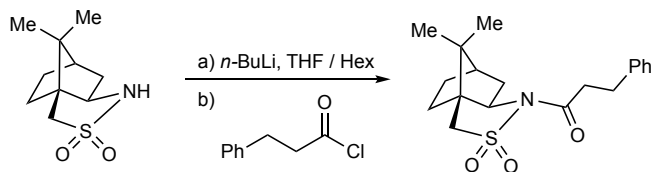


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-7g in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-hydrocinnamoyl-camphorsultam (**7I**)



(*S*)-**7I** was synthesized according to **GP-A**. The crude product was purified by trituration in Et₂O/hexanes to afford a white crystalline solid (1.35 g, 80.7%) identical to the product reported in ref S3.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.14 (m, 5H), 3.86 (t, *J* = 6.4 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 1H), 3.42 (d, *J* = 13.8 Hz, 1H), 3.12 – 2.94 (m, 4H), 2.07 (dd, *J* = 5.2, 3.0 Hz, 2H), 1.96 – 1.83 (m, 3H), 1.40 (t, *J* = 9.6 Hz, 1H), 1.34 (dd, *J* = 14.4, 5.1 Hz, 1H), 1.09 (s, 3H), 0.96 (s, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 171.2, 140.3, 128.7, 128.6, 128.6, 126.4, 65.4, 53.1, 48.6, 47.9, 44.8, 38.6, 37.1, 33.0, 30.6, 26.6, 20.9, 20.0.

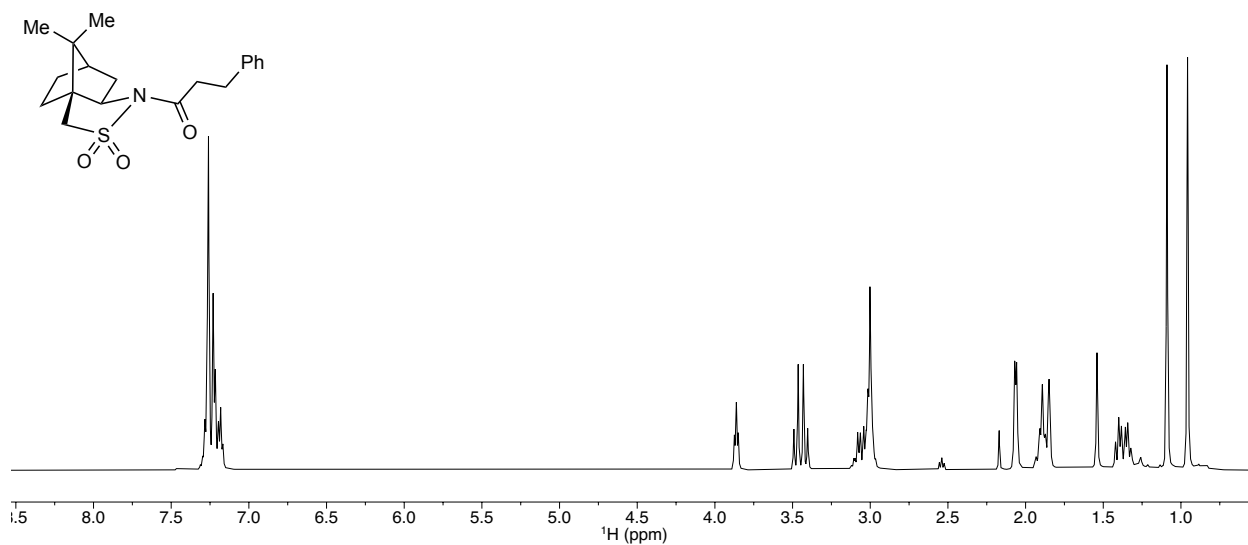


Figure S11. ¹H NMR spectrum of (*S*)-**7I** in CDCl₃ w/ 0.05% TMS at 25 °C.

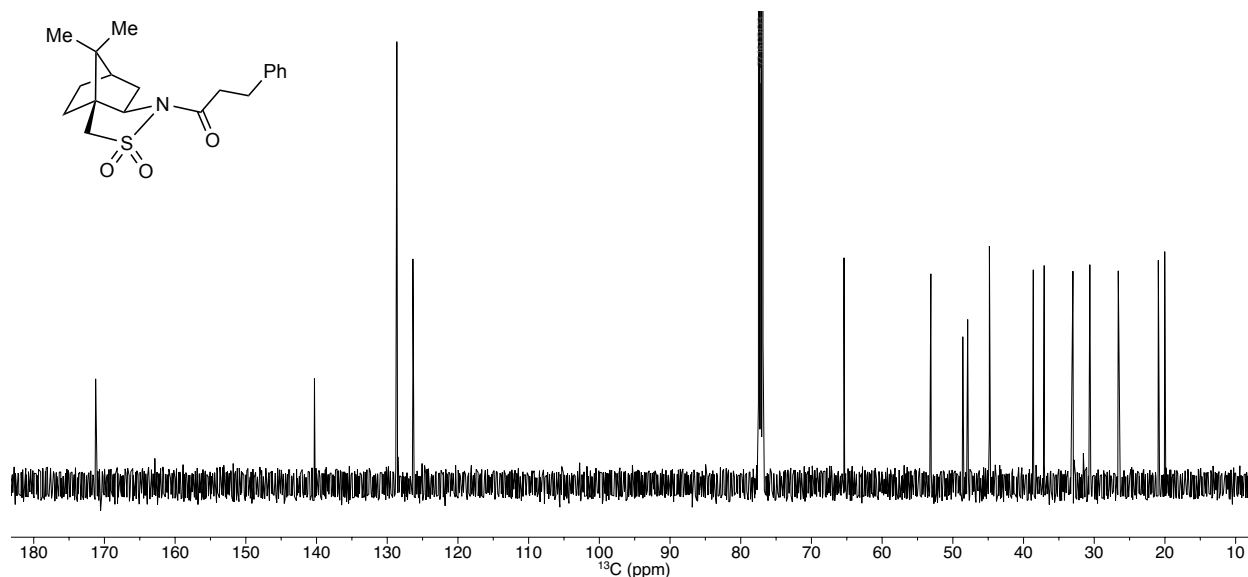
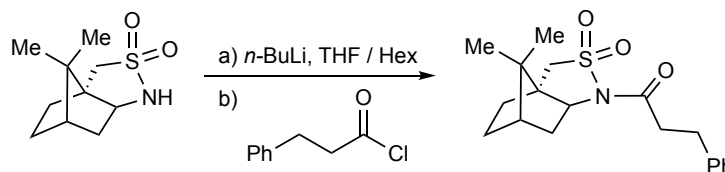


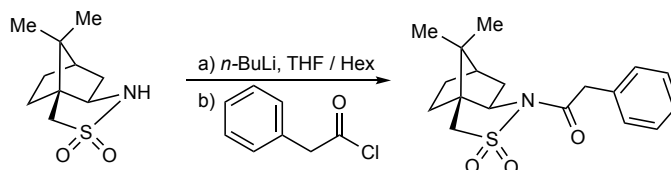
Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-**7I** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*R*)-*N*-hydrocinnamoyl-camphorsultam (**7I**)



(*R*)-**7I** was synthesized according to **GP-A**. The crude product was purified by flash chromatography on silica (10% to 40% Et_2O in hexanes) to afford a white solid (0.62 g, 39.6%). Spectral properties of (*R*)-**7I** were identical to those of (*S*)-**7I**.

Synthesis of (*S*)-*N*-phenylacetyl-camphorsultam (**7o**)



(*S*)-**7o** was synthesized according to **GP-A**. The crude product was dissolved in Et_2O , adsorbed onto celite, and purified by dry column vacuum chromatography (50:50 Tol/Hex to 45:5:50 Tol/EtOAc/Hex to 40/10/50 Tol/EtOAc/Hex, 10 step gradients) to yield the pure product as a white solid (15.6 g, 99.7%) identical to the product reported in ref S3.

^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.24 (m, 3H), 4.10 (d, $J = 15.9$ Hz, 1H), 4.02 (d, $J = 15.9$ Hz, 1H), 3.92 (dd, $J = 7.5, 5.2$ Hz, 1H), 3.56 (d, $J = 13.8$ Hz, 1H), 3.50 (d, $J = 13.8$ Hz, 1H), 2.13 – 2.00 (m, 2H), 2.00 – 1.84 (m, 3H), 1.44 (ddd, $J = 10.5, 9.0, 1.9$ Hz, 1H), 1.36 (ddd, $J = 11.5, 9.1, 3.5$ Hz, 1H), 1.15 (s, 3H), 0.99 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 169.9, 133.3, 129.8, 128.5, 127.2, 65.4, 53.1, 48.5, 47.8, 44.6, 42.0, 38.4, 32.9, 26.5, 20.8, 19.9.

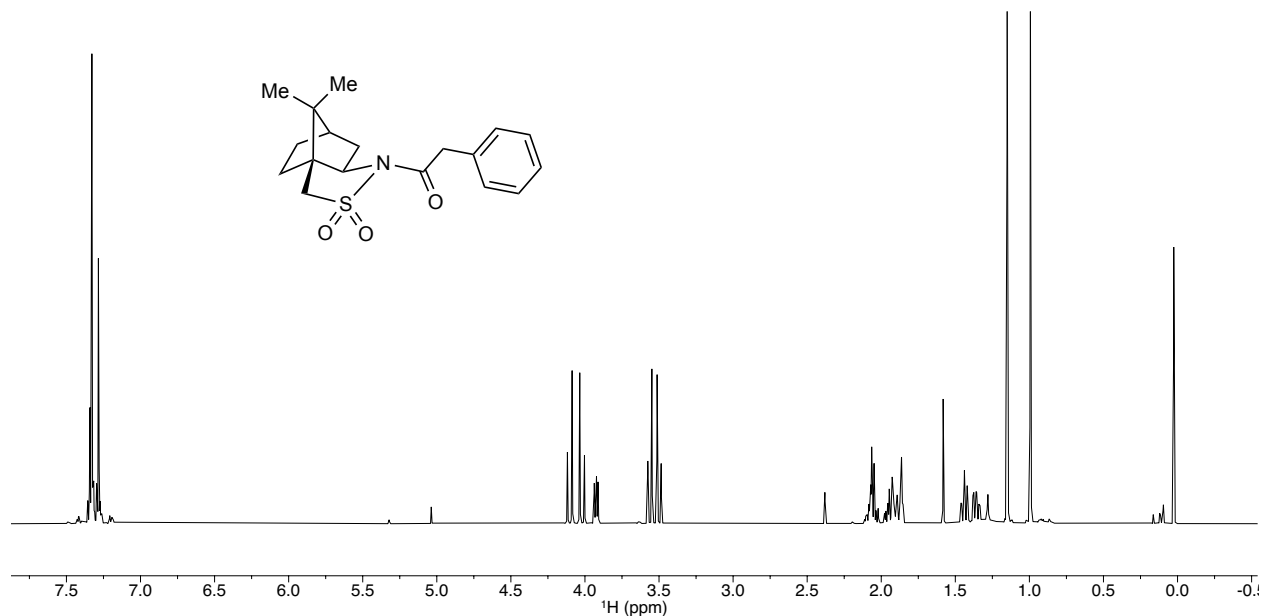


Figure S13. ^1H NMR spectrum of *(S)*-7o in CDCl_3 w/ 0.05% TMS at 25 °C.

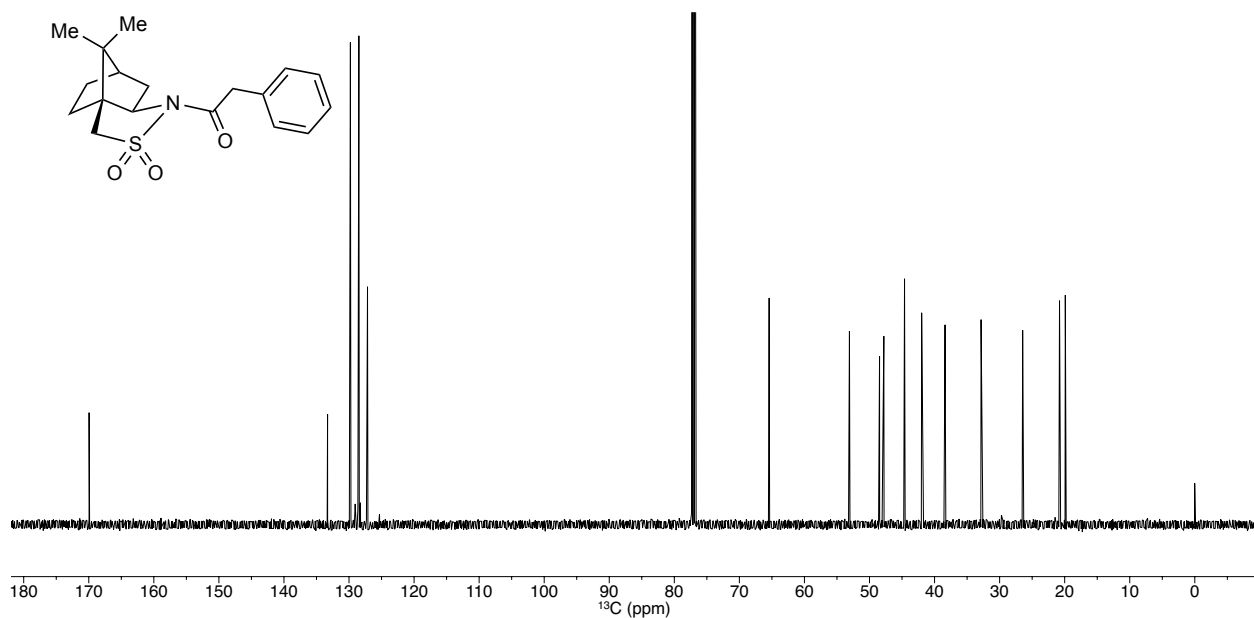
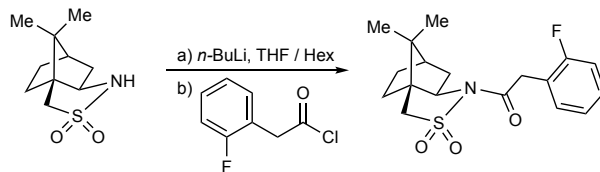


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *(S)*-7o in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-(*o*-fluorophenyl)acetyl-camphorsultam (**7r**)



Synthesis of (*S*)-**7r** and other fluorinated phenylacetyl-sultam by EDCI/DMAP coupling (**GP-B**) produced surprisingly low yields (< 15%) so fluorinated aryl-acetyl-camphorsultam derivatives were synthesized by **GP-A**. The crude product was dissolved in Et₂O, adsorbed onto celite, and purified by dry column vacuum chromatography (50:50 Tol/Hex to 45:5:50 Tol/EtOAc/Hex to 40/10/50 Tol/EtOAc/Hex, 10 step gradients) to yield the pure product as a fluorescent yellow oil (1.14 g, 38.8%).

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.01 (m)*, 5.29 (s)**, 4.15 (d, *J* = 17.0 Hz, 1H), 4.06 (dd, *J* = 17.1, 1.2 Hz, 1H), 3.91 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.58 – 3.44 (m, 2H), 2.35 (s)*, 2.16 (ddt, *J* = 14.0, 4.9, 3.4 Hz, 1H), 2.04 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.98 – 1.84 (m, 3H), 1.47 – 1.29 (m, 2H), 1.20 (s, 3H), 0.98 (s, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 168.67 (d, *J* = 0.9 Hz), 161.19 (d, *J* = 246.7 Hz), 137.88*, 131.79 (d, *J* = 4.1 Hz), 129.20 (d, *J* = 8.2 Hz), 129.04*, 128.23*, 125.30, 124.05 (d, *J* = 3.7 Hz), 120.81 (d, *J* = 16.1 Hz), 115.35 (d, *J* = 21.6 Hz), 65.47, 53.43**, 52.99, 48.61, 47.83, 44.64, 38.37, 35.67 (d, *J* = 2.5 Hz), 32.83, 26.44, 21.46*, 20.81, 19.91.

¹⁹F NMR (470 MHz, CDCl₃) δ –116.46 – –116.55 (m).

*Residual toluene signal; **Residual DCM signal

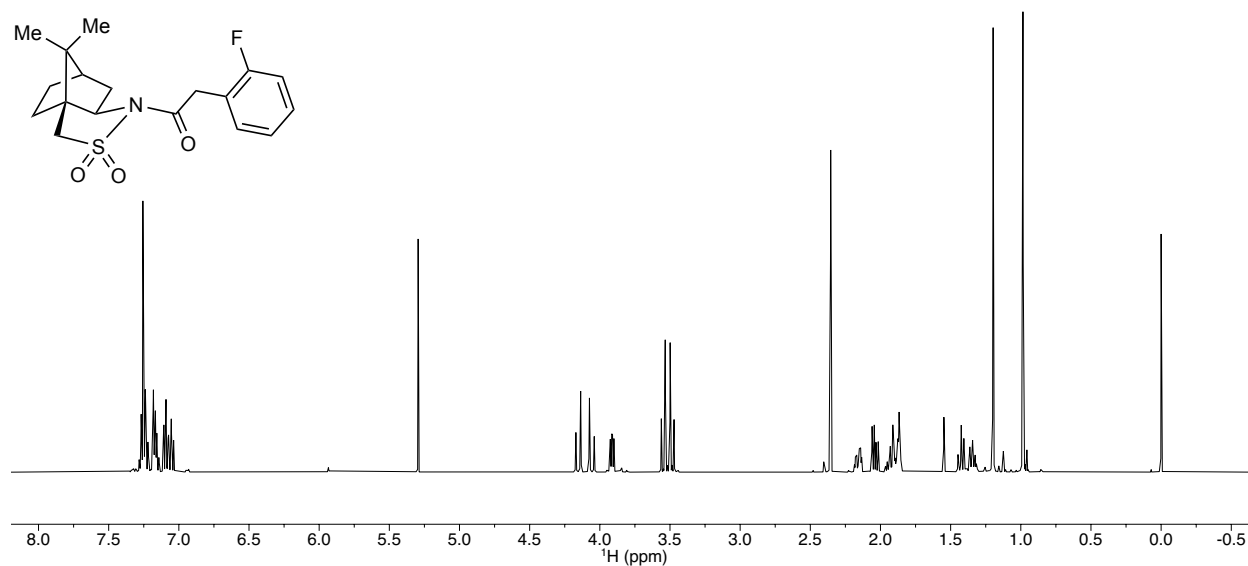


Figure S15. ¹H NMR spectrum of (S)-7r in CDCl₃ w/ 0.05% TMS at 25 °C.

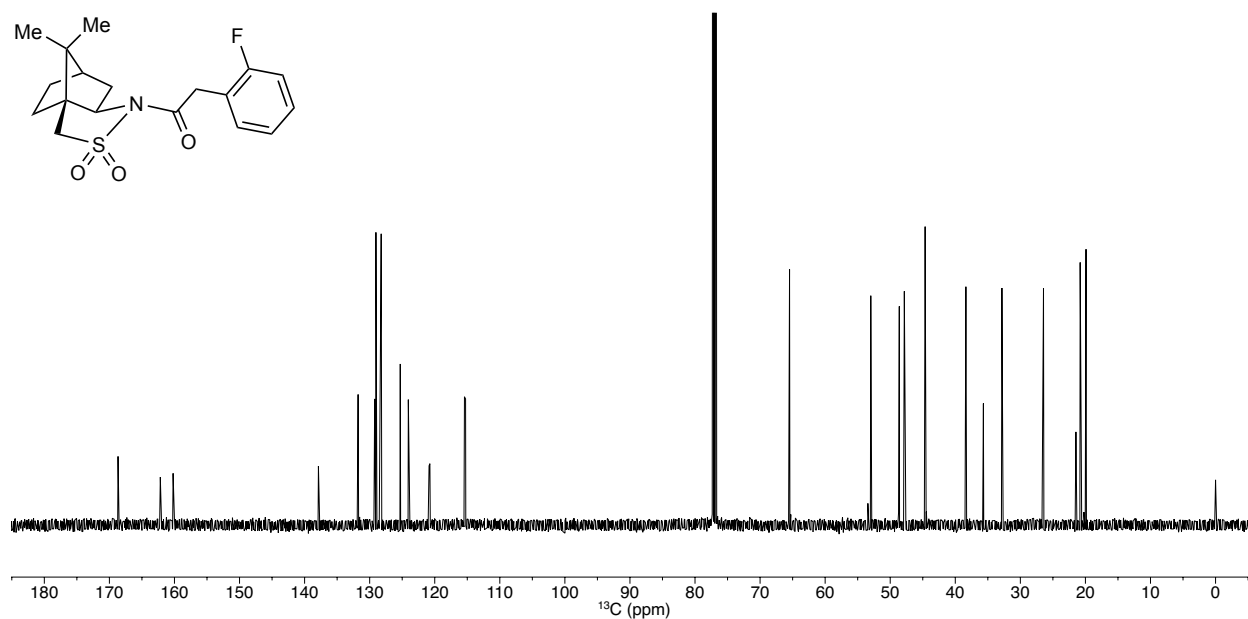


Figure S16. ¹³C{¹H} NMR spectrum of (S)-7r in CDCl₃ w/ 0.05% TMS at 25 °C.

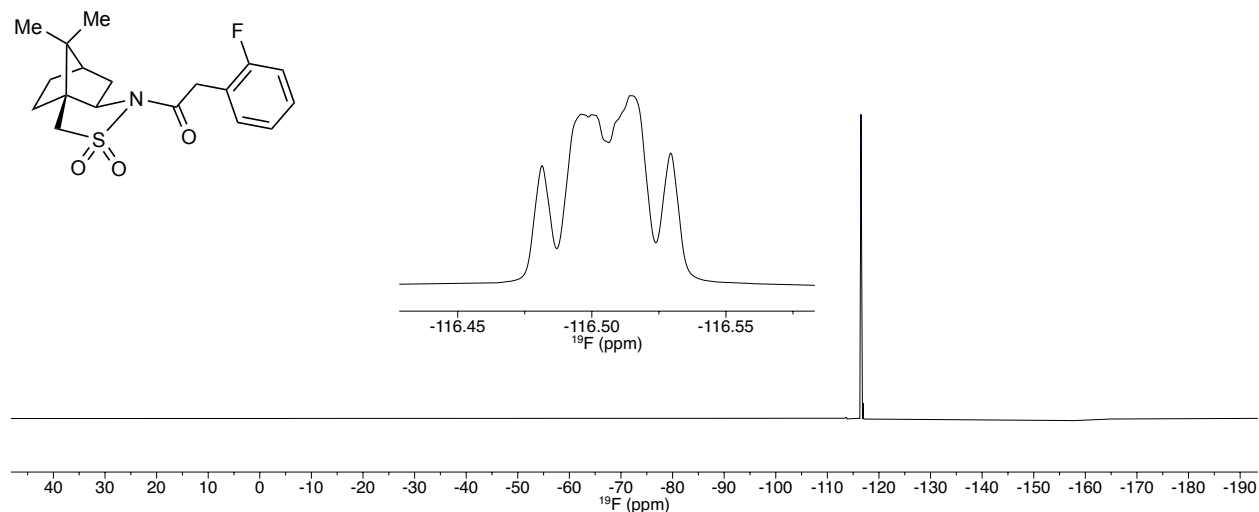
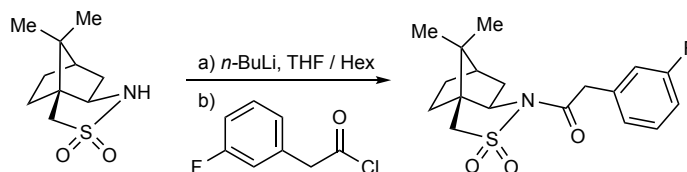


Figure S17. ^{19}F NMR spectrum of (*S*)-**7r** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-(*m*-fluorophenyl)acetyl-camphorsultam (**7s**)



(*S*)-**7s** was synthesized according to **GP-A**. The crude product was dissolved in Et_2O , adsorbed onto celite, and purified by dry column vacuum chromatography (50:50 Tol/Hex to 45:5:50 Tol/EtOAc/Hex to 40/10/50 Tol/EtOAc/Hex, 10 step gradients) to yield the pure product as a light-yellow oil (2.58 g, 78.0%).

^1H NMR (500 MHz, CDCl_3) δ 7.30 (td, $J = 8.0, 6.0$ Hz, 1H), 7.08 (ddt, $J = 21.0, 9.8, 1.7$ Hz, 2H), 6.98 (tdd, $J = 8.5, 2.7, 1.0$ Hz, 1H), 4.09 (d, $J = 15.9$ Hz, 1H), 4.01 (d, $J = 15.9$ Hz, 1H), 3.92 (dd, $J = 7.5, 5.2$ Hz, 1H), 3.57 (d, $J = 13.8$ Hz, 1H), 3.50 (d, $J = 13.8$ Hz, 1H), 2.13 – 2.01 (m, 2H), 2.01 – 1.85 (m, 3H), 1.49 – 1.40 (m, 1H), 1.36 (ddd, $J = 13.1, 9.2, 3.4$ Hz, 1H), 1.15 (s, 3H), 1.00 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 169.29, 162.74 (d, $J = 245.7$ Hz), 135.54 (d, $J = 7.9$ Hz), 129.88 (d, $J = 8.4$ Hz), 125.54 (d, $J = 3.0$ Hz), 116.82 (d, $J = 21.9$ Hz), 114.19 (d, $J = 21.0$ Hz), 65.43, 53.06, 48.50, 47.81, 44.60, 41.59 (d, $J = 1.8$ Hz), 38.34, 32.85, 26.44, 20.78, 19.89.

^{19}F NMR (470 MHz, CDCl_3) δ -113.26 (td, $J = 9.1, 6.0$ Hz).

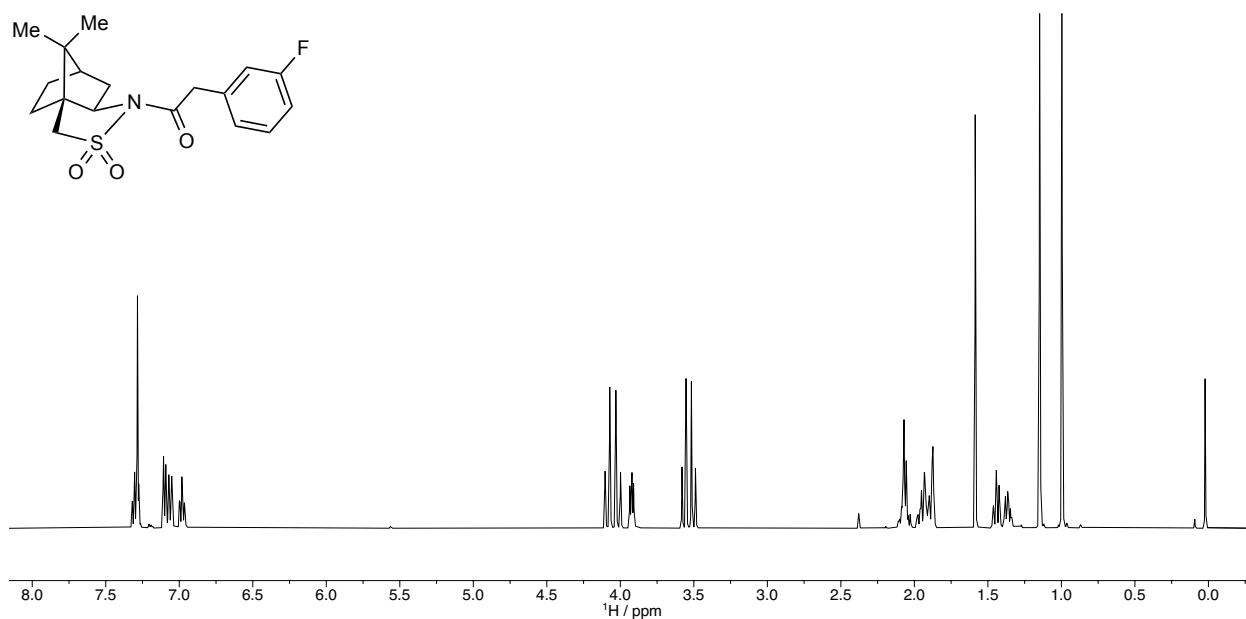


Figure S18. ¹H NMR spectrum of (*S*)-7s in CDCl₃ w/ 0.05% TMS at 25 °C.

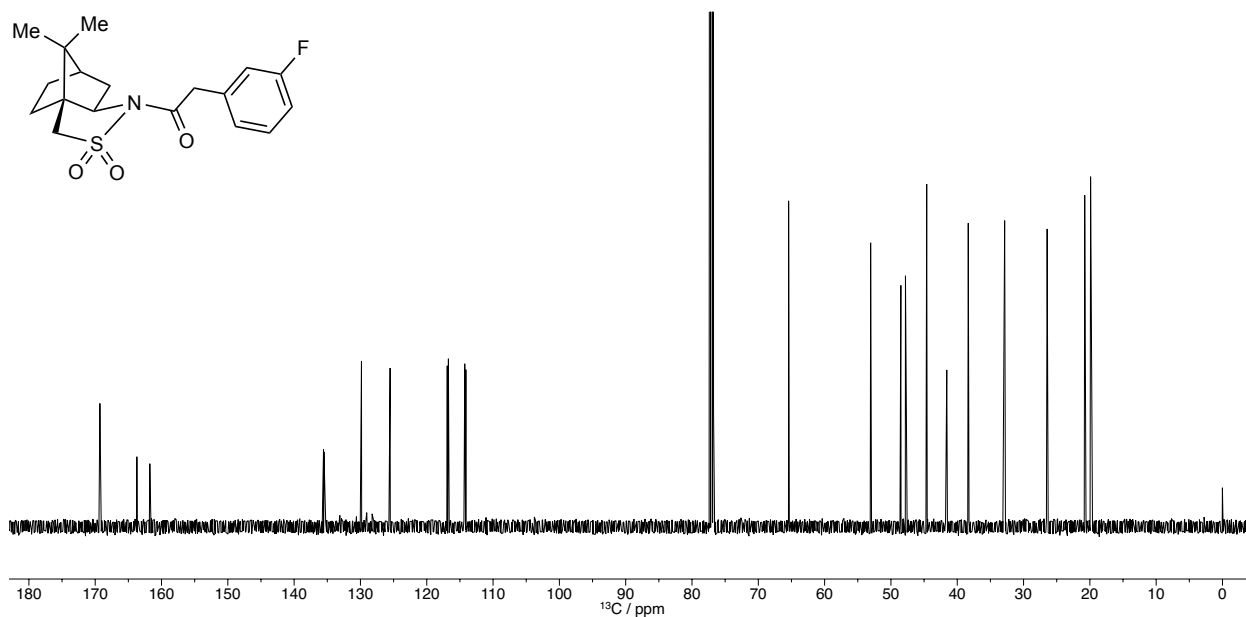


Figure S19. ¹³C{¹H} NMR spectrum of (*S*)-7s in CDCl₃ w/ 0.05% TMS at 25 °C.

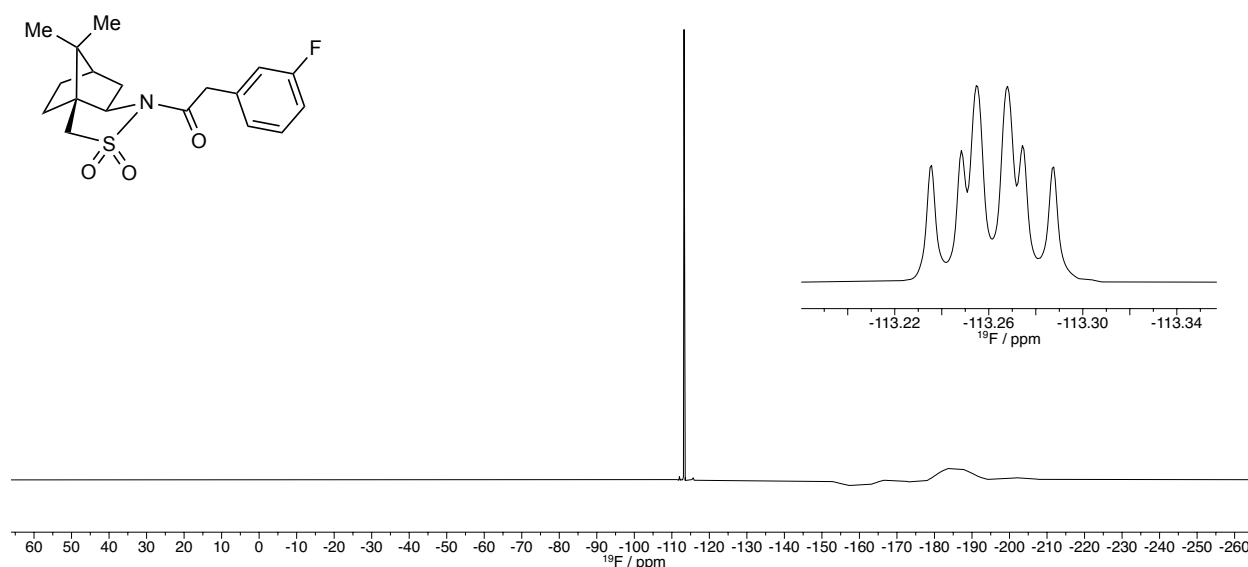
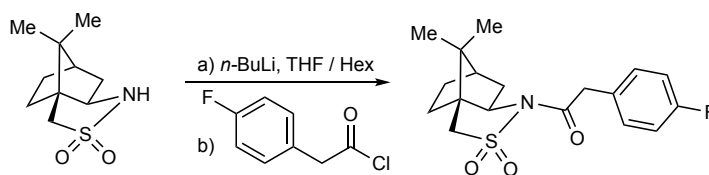


Figure S20. ^{19}F NMR spectrum of (*S*)-**7s** in CDCl_3 w/ 0.05% TMS at 25 °C.

Synthesis of (*S*)-*N*-(*p*-fluorophenyl)acetyl-camphorsultam (**7t**)



(*S*)-**7t** was synthesized according to **GP-A**. The crude product was dissolved in Et_2O , adsorbed onto celite, and purified by dry column vacuum chromatography (50:50 Tol/Hex to 45:5:50 Tol/EtOAc/Hex to 40/10/50 Tol/EtOAc/Hex, 10 step gradients) to yield the pure product as a light-yellow oil that solidifies over days (3.25 g, 96.6%) identical to the product reported in ref S5.

^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.22 (m)*, 7.20 – 7.12 (m)*, 7.00 (t, $J = 8.7$ Hz, 2H), 4.04 (d, $J = 16.0$ Hz, 1H), 3.97 (d, $J = 16.0$ Hz, 1H), 3.89 (dd, $J = 7.2, 5.4$ Hz, 1H), 3.62 – 3.51 (m, 1H), 3.47 (d, $J = 13.8$ Hz, 1H), 2.36 (s)*, 2.11 – 1.98 (m, 2H), 1.97 – 1.82 (m, 3H), 1.48 – 1.28 (m, 2H), 1.12 (s, 3H), 0.97 (s, 3H), 0.96 – 0.85 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 169.79, 162.08 (d, $J = 245.4$ Hz), 137.88*, 131.36 (d, $J = 8.0$ Hz), 129.04*, 128.23*, 125.30, 115.33 (d, $J = 21.5$ Hz), 65.41, 53.06, 48.48, 47.79, 44.59, 41.09, 38.34, 32.84, 26.43, 21.46*, 20.77, 19.88, 14.09.z

^{19}F NMR (470 MHz, CDCl_3) δ -115.70 (tt, $J = 8.7, 5.3$ Hz).

*Residual toluene

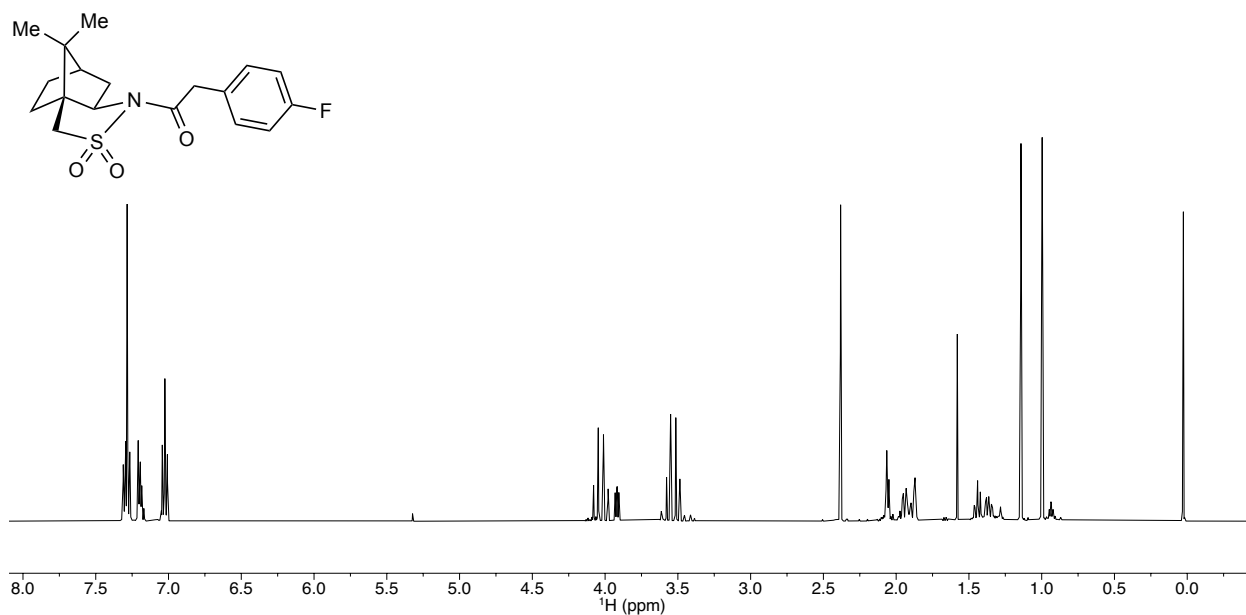


Figure S21. ¹H NMR spectrum of (S)-7t in CDCl₃ w/ 0.05% TMS at 25 °C.

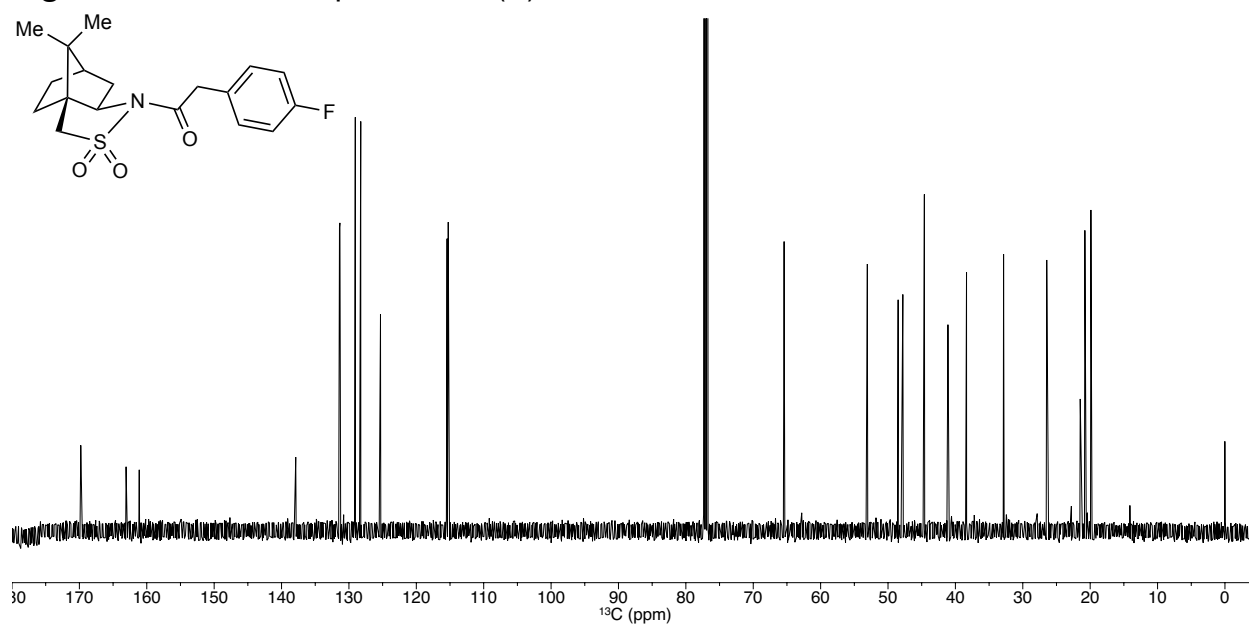


Figure S22. ¹³C{¹H} NMR spectrum of (S)-7t in CDCl₃ w/ 0.05% TMS at 25 °C.

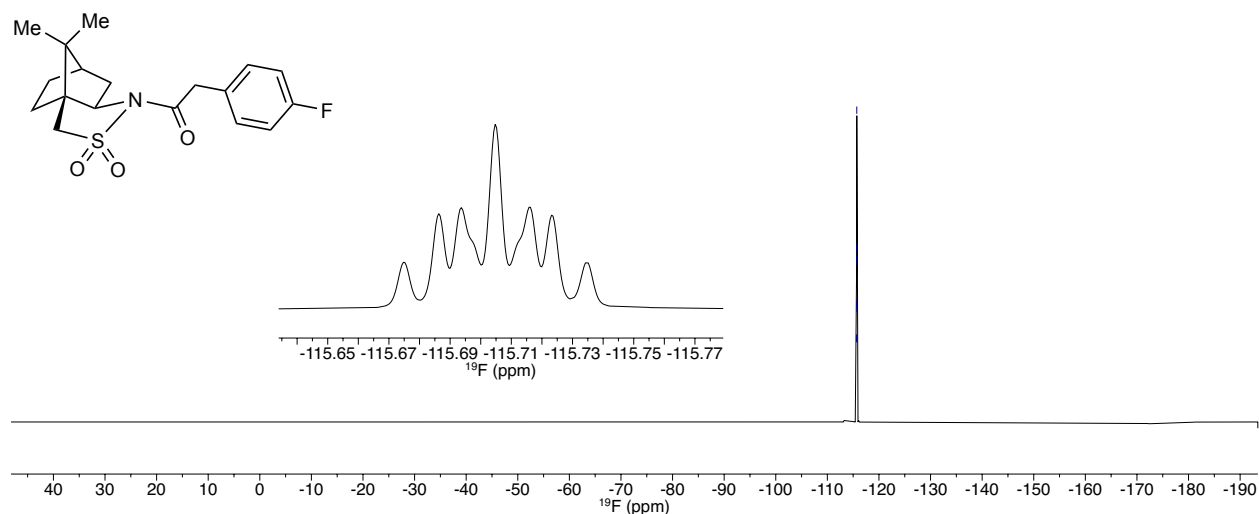
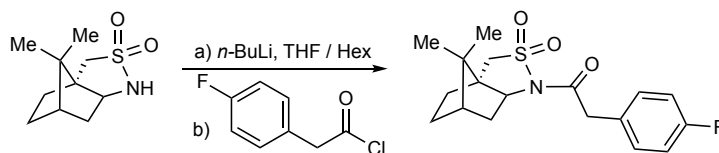


Figure S23. ^{19}F NMR spectrum of (*S*)-**7t** in CDCl_3 w/ 0.05% TMS at 25 °C.

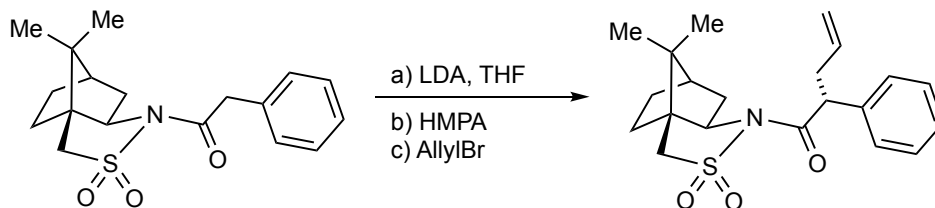
Synthesis of (*R*)-*N*-(*p*-fluorophenyl)acetyl-camphorsultam (**7t**)



(*R*)-**7t** was synthesized according to **GP-A**. The crude product was dissolved in Et_2O , adsorbed onto celite, and purified by dry column vacuum chromatography (50:50 Tol/Hex to 45:5:50 Tol/EtOAc/Hex to 40/10/50 Tol/EtOAc/Hex, 10 step gradients) to yield the pure product as a light-yellow oil that solidifies over days (3.25 g, 98.5%). Spectral properties of (*R*)-**7t** were identical to those of (*S*)-**7t**.

Synthesis of (*R*)-1-((3*aS*,6*R*,7*aR*)-8,8-dimethyl-2,2-dioxidotetrahydro-3*H*-3*a*,6-methanobenzo[*c*]isothiazol-1(4*H*)-yl)-2-phenylpent-4-en-1-one

Synthesis and purification of 34



34 was synthesized according to the general procedure for *in situ* IR analysis described later in the SI. The reaction vessel was taken off the IR probe and quenched with 5 mL 1M HCl and extracted 3x with 10 mL Et₂O. The organic fractions were combined, washed with 30 mL saturated NaCl_(aq), dried over NaSO₄, and evaporated to yield a white solid. The crude product was recrystallized from hexanes to yield the pure product as white block shaped crystals. Diffraction quality crystals were grown by slow evaporation of a supersaturated solution of hexanes.

¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.44 (m, 2H), 7.34 – 7.20 (m, 3H), 5.81 (dddd, *J* = 15.9, 10.2, 8.2, 5.6 Hz, 1H), 5.13 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.41 (dd, *J* = 9.2, 6.1 Hz, 1H), 3.84 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.52 (dd, *J* = 13.8, 2.1 Hz, 1H), 3.40 (dd, *J* = 13.8, 2.1 Hz, 1H), 2.87 (dt, *J* = 14.2, 8.8 Hz, 1H), 2.72 (d, *J* = 2.2 Hz)*, 2.63 – 2.54 (m, 1H), 2.17 – 2.02 (m, 2H), 1.94 – 1.82 (m, 3H), 1.37 – 1.27 (m, 2H), 1.20 (s, 2H), 0.97 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 172.77, 137.59, 134.86, 128.83, 128.27, 127.33, 117.63, 65.67, 53.20, 50.42, 48.24, 47.74, 44.68, 40.34, 38.47, 34.75*, 32.96, 26.39, 20.95, 19.95.

*Residual HMPA

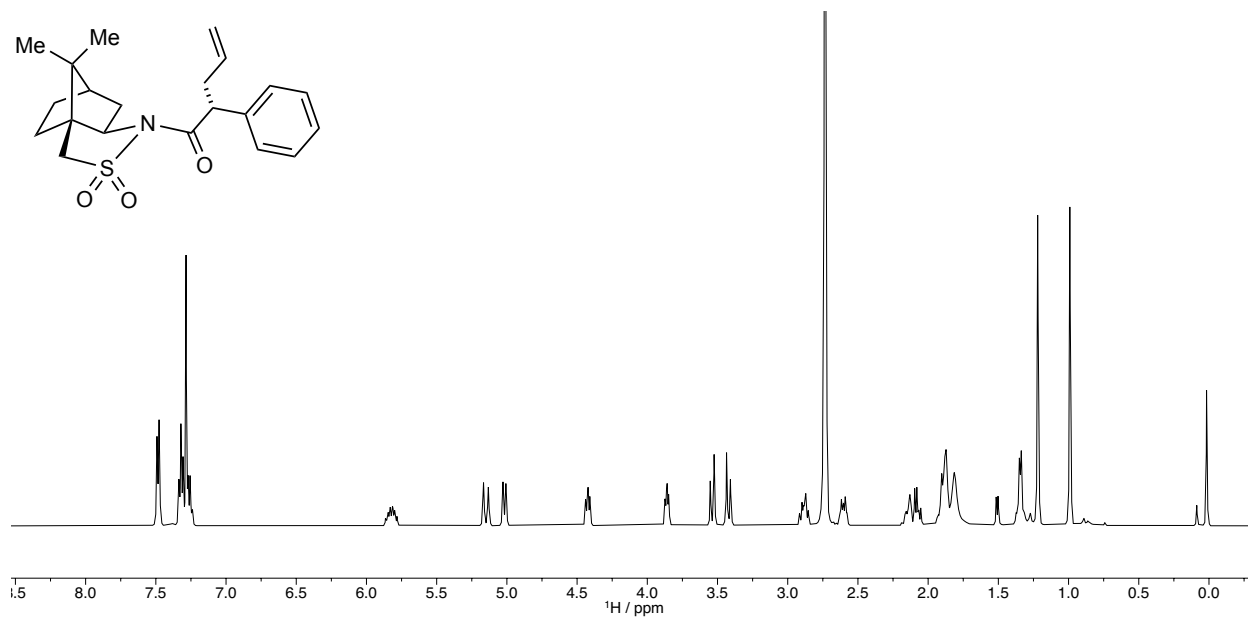


Figure S24. ^1H NMR spectrum of **34** in CDCl_3 w/ 0.05% TMS at 25 °C.

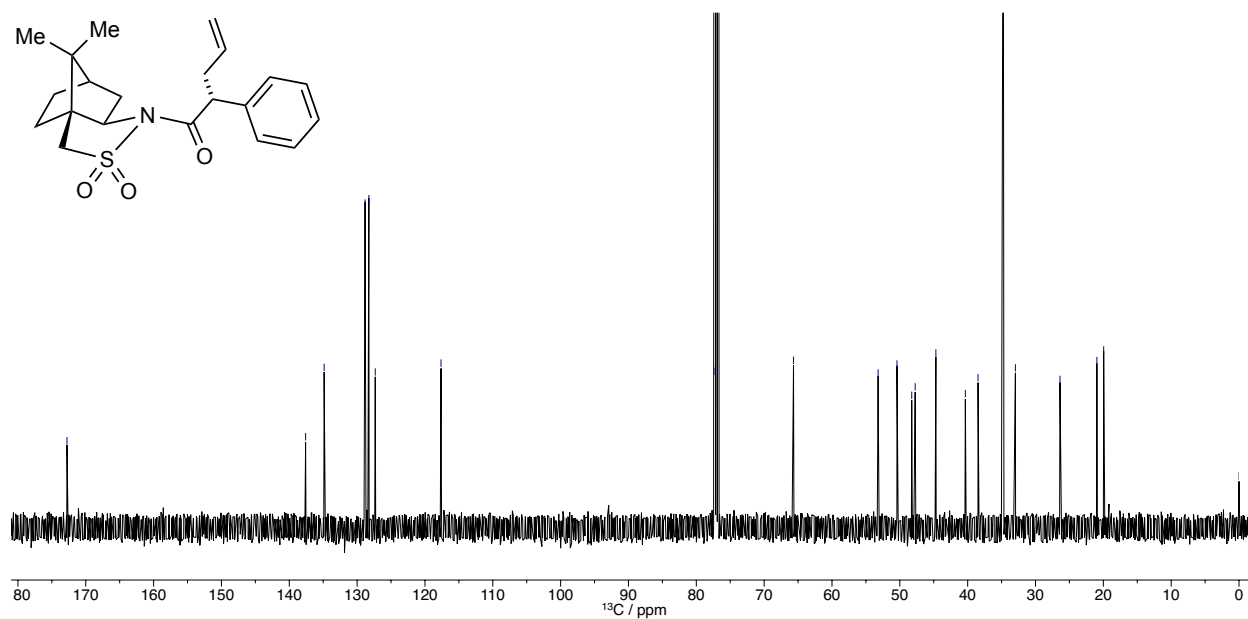


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **34** in CDCl_3 w/ 0.05% TMS at 25 °C.

Structural Elucidation

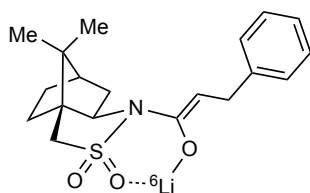
General procedure for sealed tube NMR spectroscopy

A double-stoppered NMR tube under vacuum was flame-dried on a Schlenk line and allowed to passively cool to room temperature. It was then backfilled with argon and placed in a dry ice/acetone cooling bath. Individual stock solutions of the *N*-acyl sultams and [⁶Li]-LDA were prepared at room temperature and –78 °C, respectively. The appropriate amounts of the *N*-acyl sultams, [⁶Li]-LDA, solvent, and (when applicable) co-solvent were added sequentially via gastight syringe. The tube was flame-sealed under partial vacuum while cold to minimize evaporation. The tubes were mixed on a vortex mixer and stored at –80 °C. Unless otherwise stated all tubes were sealed a total enolate concentration of 0.10 M.

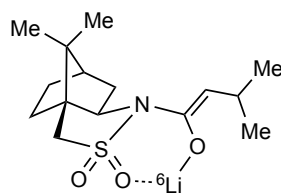
Standard ¹H, ¹⁹F, ⁶Li, ¹³C, ¹⁵N, and ³¹P direct detection spectra were recorded on a 11.8 T spectrometer at 500.1, 470.6, 73.6, 125.8, 50.7, and 202.5 MHz, respectively. ¹H, ¹³C, ¹⁵N, and ³¹P resonances are referenced to their respective standards (TMS, NH₃, H₃PO₄). ⁶Li resonances are referenced to 0.30 M [⁶Li]-LiCl/MeOH (0.0 ppm). ¹⁹F spectra are referenced to C₆H₅F (–113.15 ppm).

For quantitated ⁶Li and ¹⁹F spectra the spin-lattice relaxation (T₁) was determined by standard inversion recovery experiments on several samples. The relaxation delay (d₁) was set to seven times the average relaxation lifetime. Integration of the NMR signals were determined using the line-fitting method included in MNOVA (Mestrelab research S.L.).

Alkyl-substituted enolate tetramers



A: 8I



B: 8f

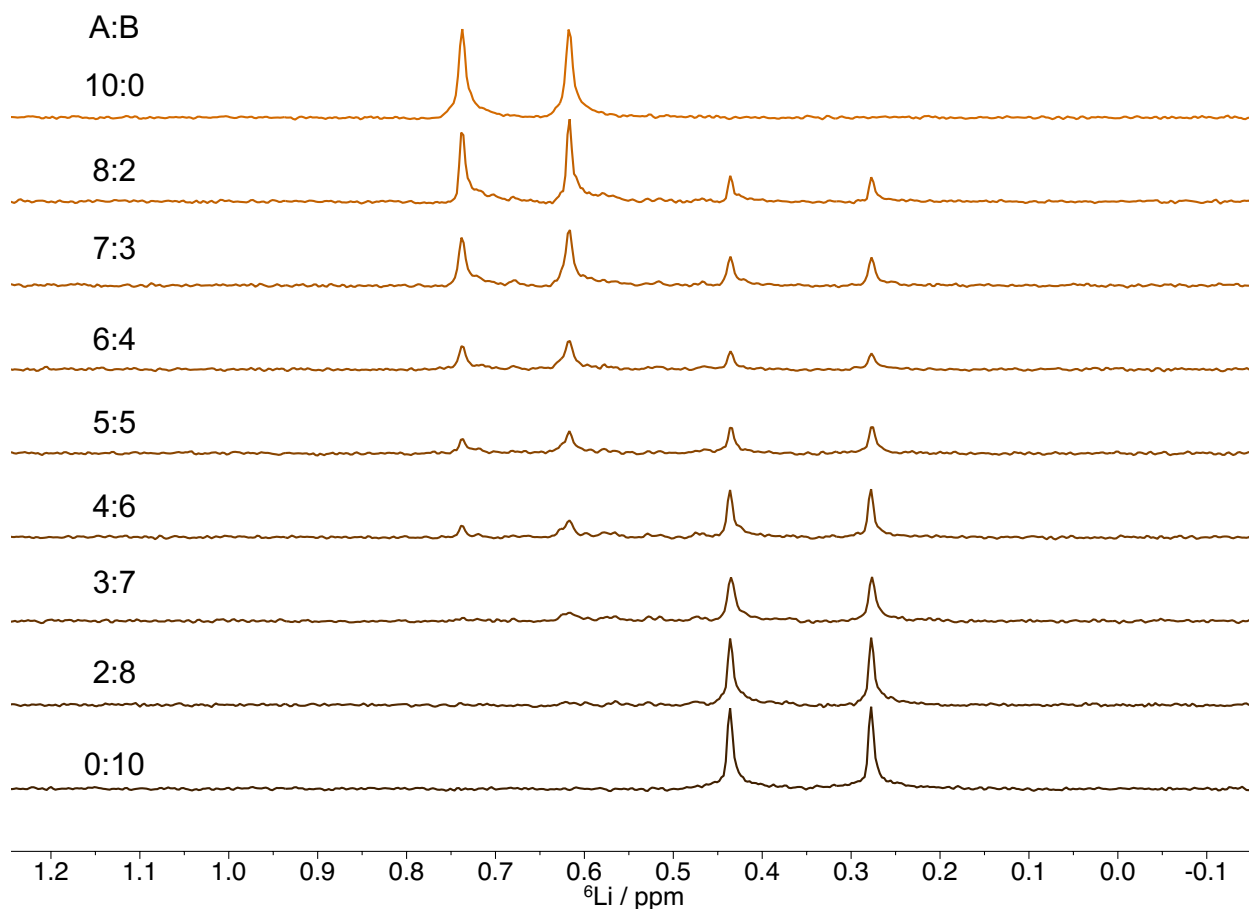


Figure S26. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(*S*)-**8I** (A) and $[\text{}^6\text{Li}]$ -(*S*)-**8f** (B) in toluene at -80°C . The sealed NMR tubes were not aged. A:B represents the total molar ratio of the two enolates.

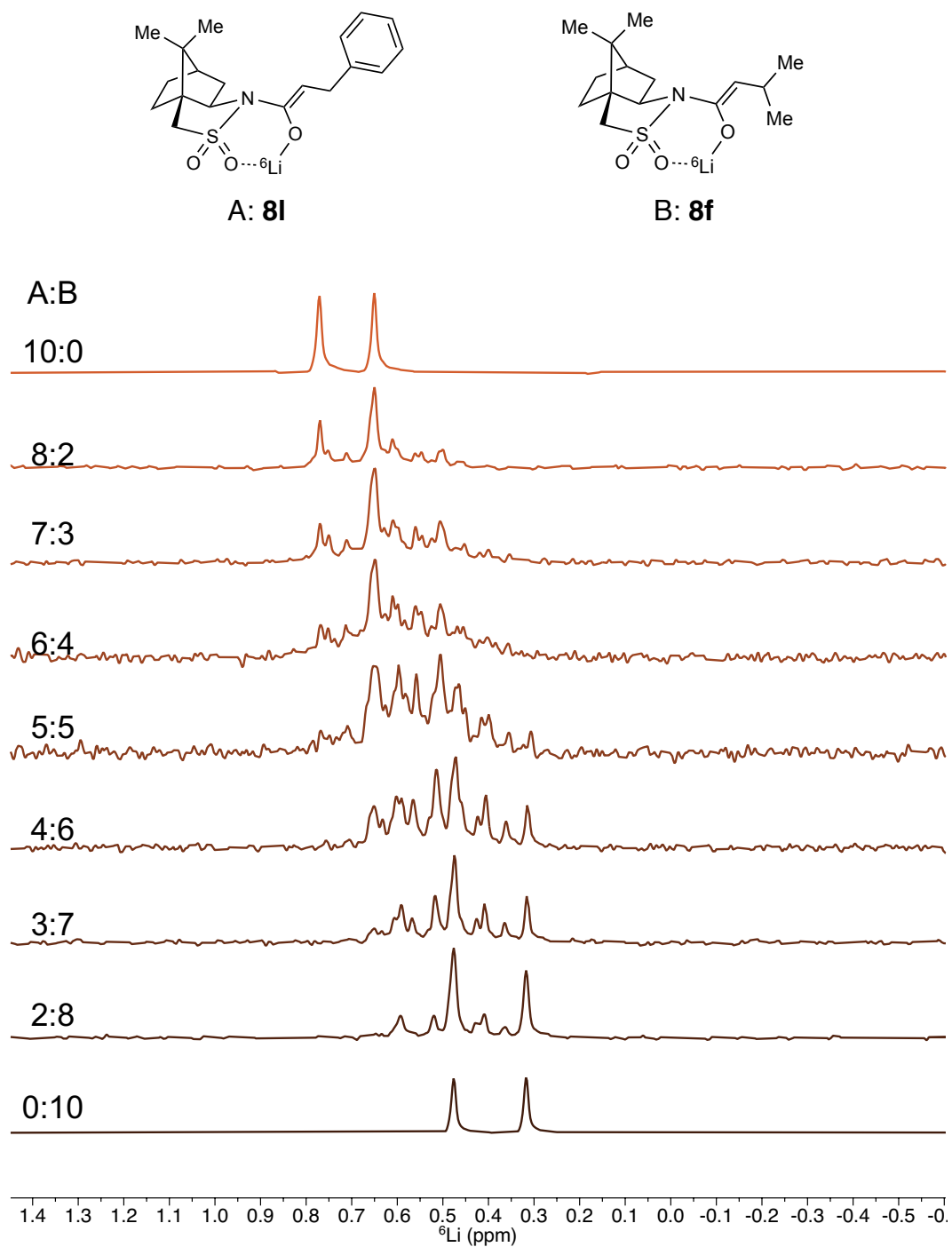


Figure S27. ${}^6\text{Li}$ NMR spectra of mixtures of $[{}^6\text{Li}]$ -(*S*)-**8I** (A) and $[{}^6\text{Li}]$ -(*S*)-**8f** (B) in toluene at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were aged at $0\text{ }^\circ\text{C}$ for 10 min. Several new overlapping resonances appear for the mixed aggregates ($\mathbf{A}_3\mathbf{B}_1$, $\mathbf{A}_2\mathbf{B}_2$, $\mathbf{A}_1\mathbf{B}_3$) consistent with a tetramer model. A:B represents the total molar ratio of the two enolates.

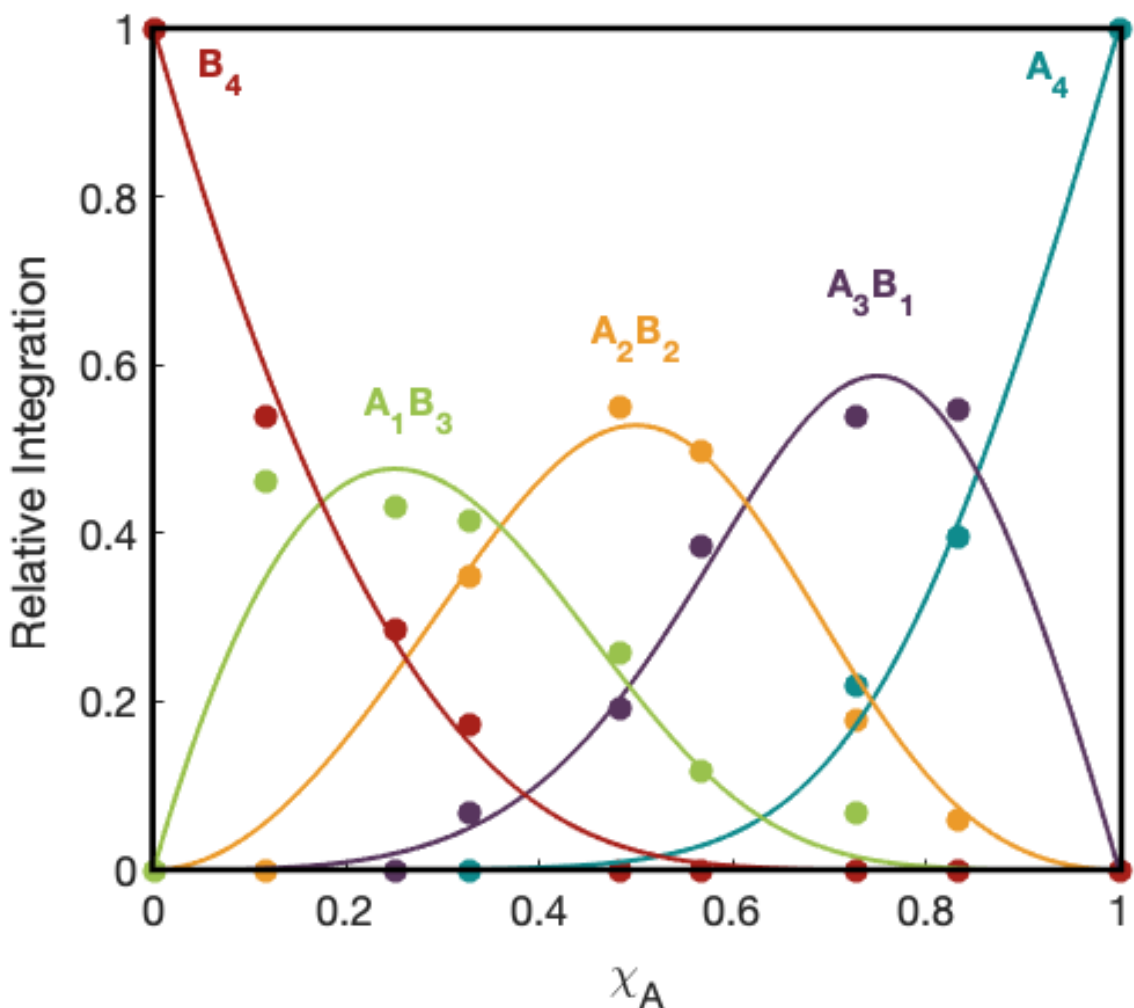
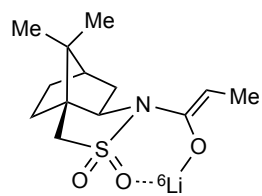
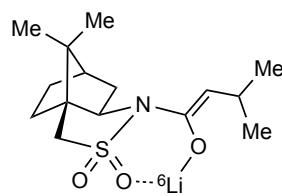


Figure S28. ^6Li Job plot showing relative integrations of the two homoaggregates of $[\text{}^6\text{Li}]$ -(*S*)-**8I** (blue) and $[\text{}^6\text{Li}]$ -(*S*)-**8f** (red), the 3:1 mixed tetramers (green and violet), and the 2:2 mixed tetramer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(*S*)-**8I** for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(*S*)-**8I** and $[\text{}^6\text{Li}]$ -(*S*)-**8f** in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S27**). The curves result from a parametric fit to a single aggregate tetramer model.



A: **8b**



B: **8f**

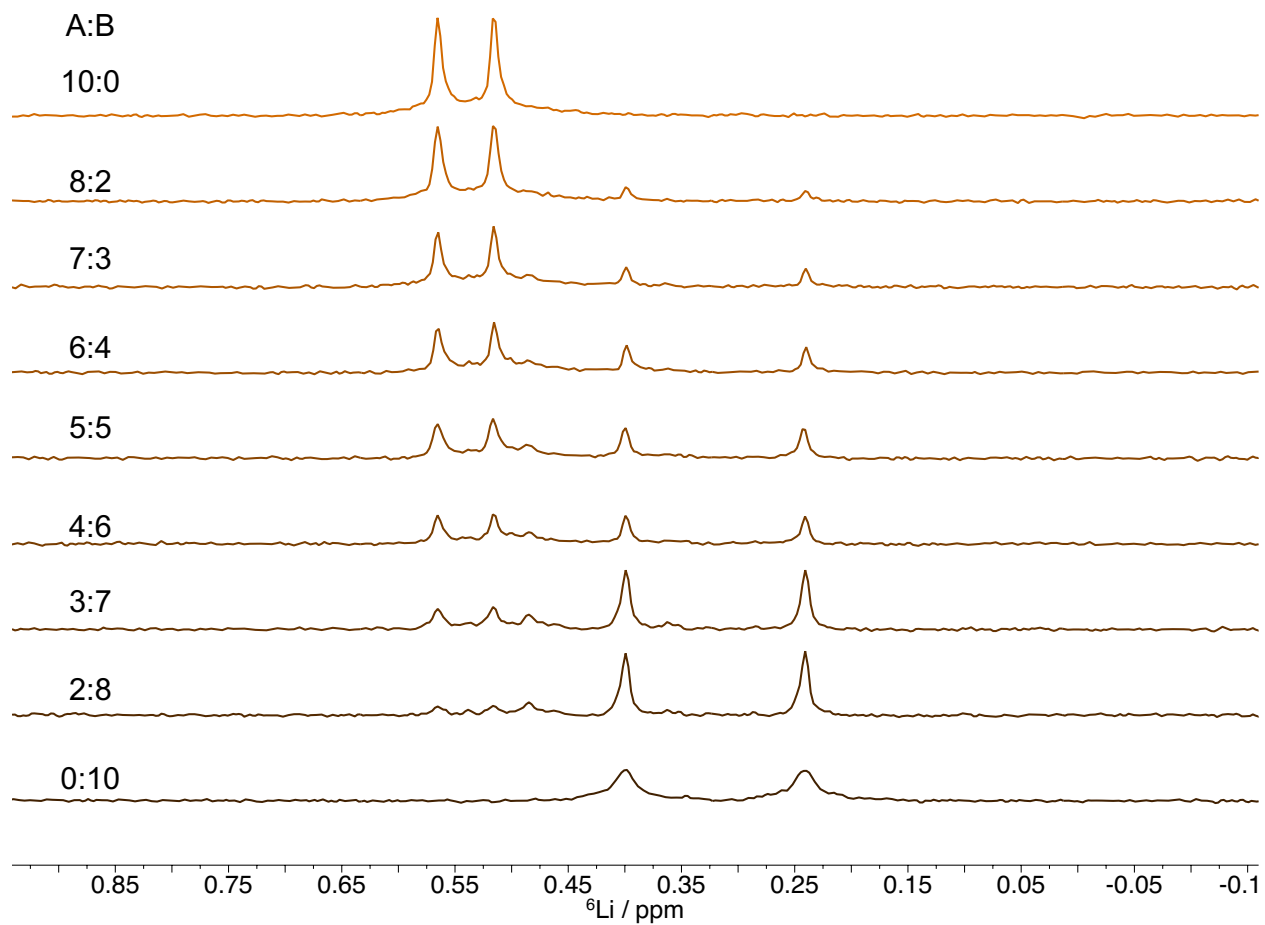
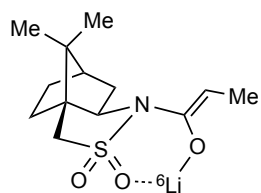
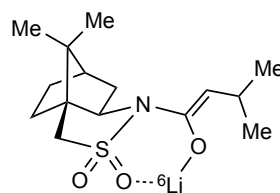


Figure S29. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(*S*)-**8b** (A) and $[\text{}^6\text{Li}]$ -(*S*)-**8f** (B) in toluene at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. A:B represents the total molar ratio of the two enolates.



A: **8b**



B: **8f**

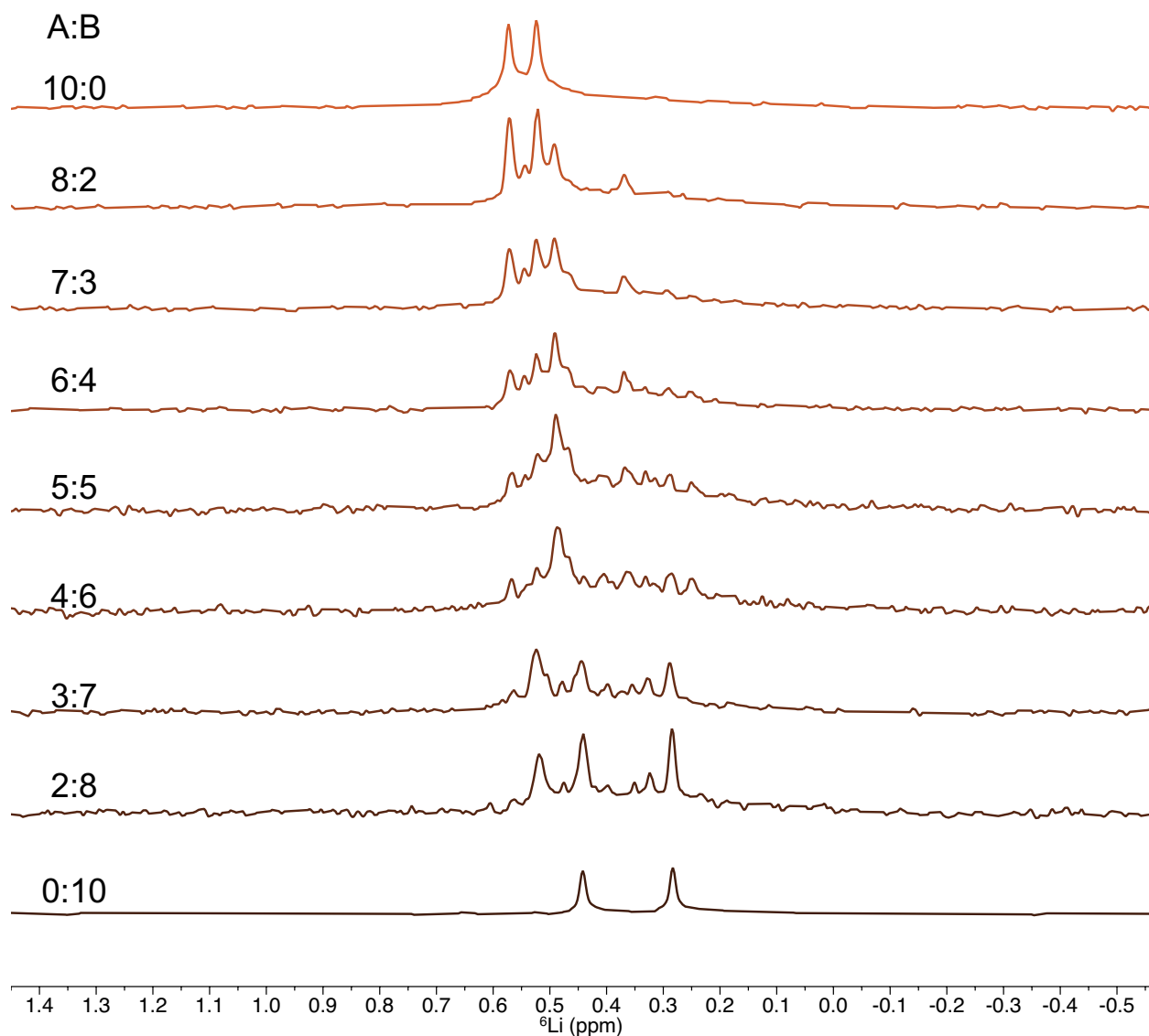


Figure S30. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(*S*)-**8b** (A) and $[\text{}^6\text{Li}]$ -(*S*)-**8f** (B) in toluene at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were aged at $0\text{ }^\circ\text{C}$ for 10 min. Several new overlapping resonances appear for the mixed aggregates ($\mathbf{A}_3\mathbf{B}_1$, $\mathbf{A}_2\mathbf{B}_2$, $\mathbf{A}_1\mathbf{B}_3$) consistent with a tetramer model. A:B represents the total molar ratio of the two enolates.

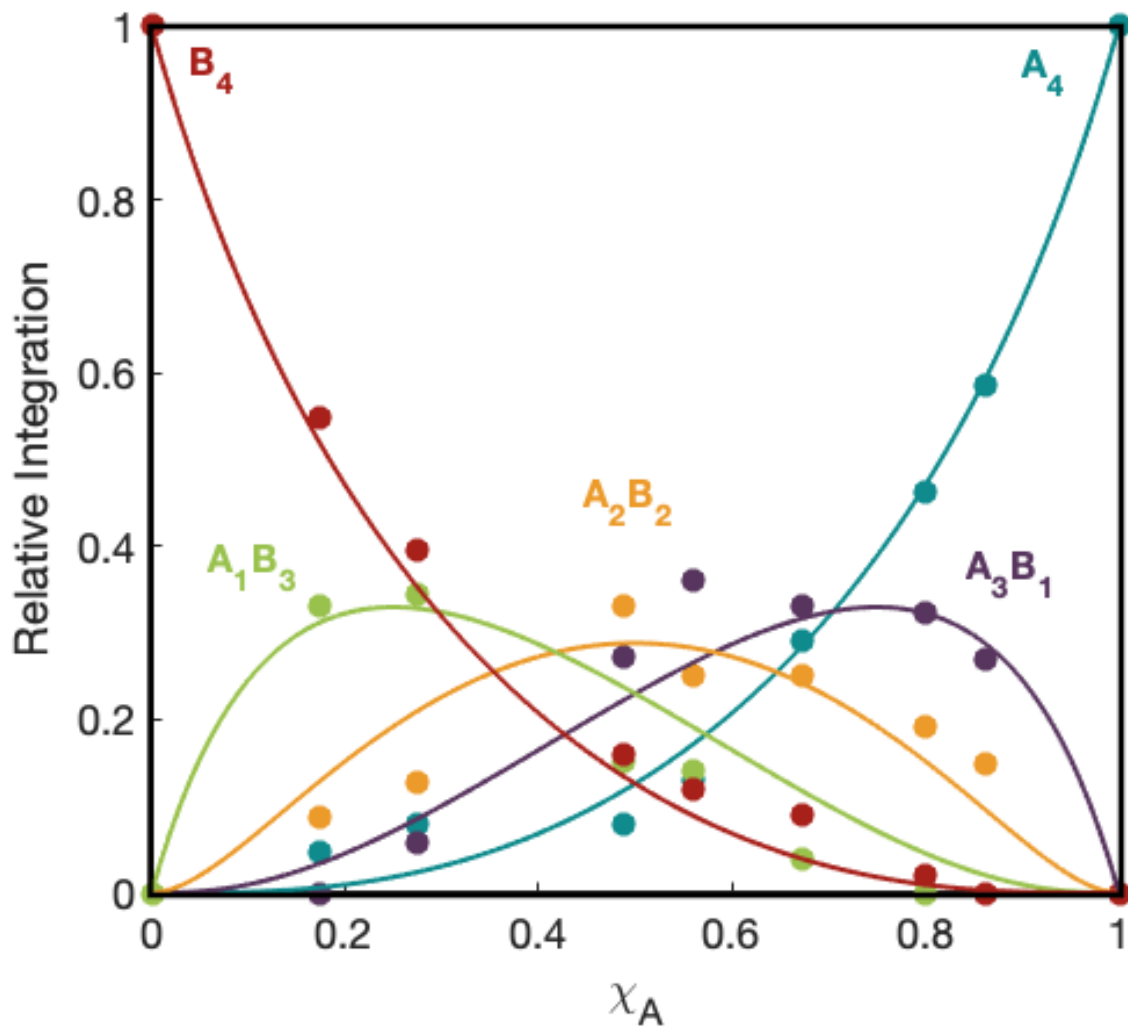


Figure S31. ^6Li Job plot showing relative integrations of the two homoaggregates of $[\text{}^6\text{Li}]$ -(S)-**8b** (blue) and $[\text{}^6\text{Li}]$ -(S)-**8f** (red), the 3:1 mixed tetramers (green and violet), and the 2:2 mixed tetramer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(S)-**8b** for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(S)-**8b** and $[\text{}^6\text{Li}]$ -(S)-**8f** in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S30**). The curves result from a parametric fit to a single aggregate tetramer model.

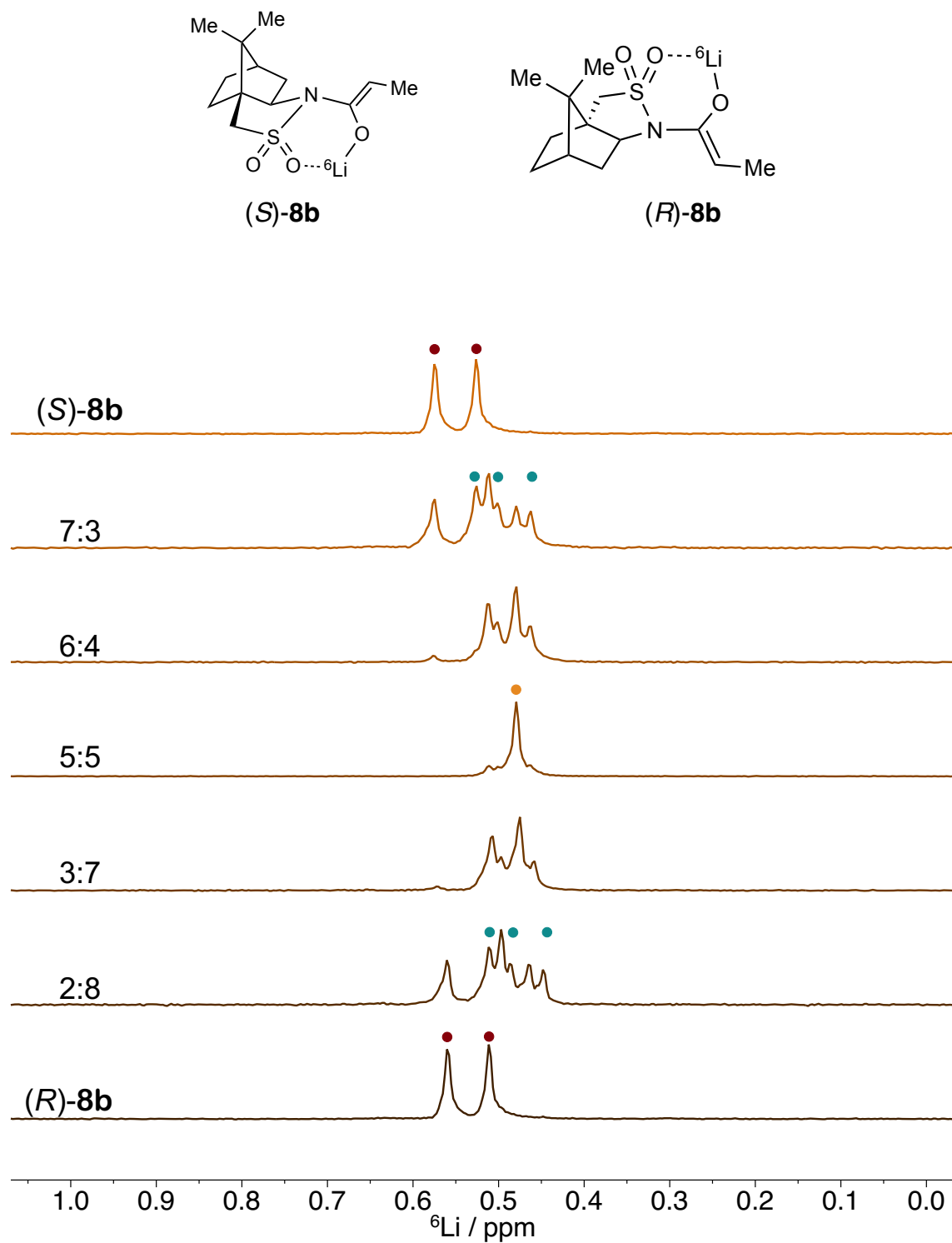


Figure S32. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -*(S)*-**8b** and $[\text{}^6\text{Li}]$ -*(R)*-**8b** in toluene at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were aged at $0\text{ }^\circ\text{C}$ for 10 min. Four new resonances appear for the mixed aggregates (R_3S_1 , R_2S_2 , R_1S_3) consistent with a heterochiral tetramer model. *R*:*S* represents the total molar ratio of the two enantiomers.

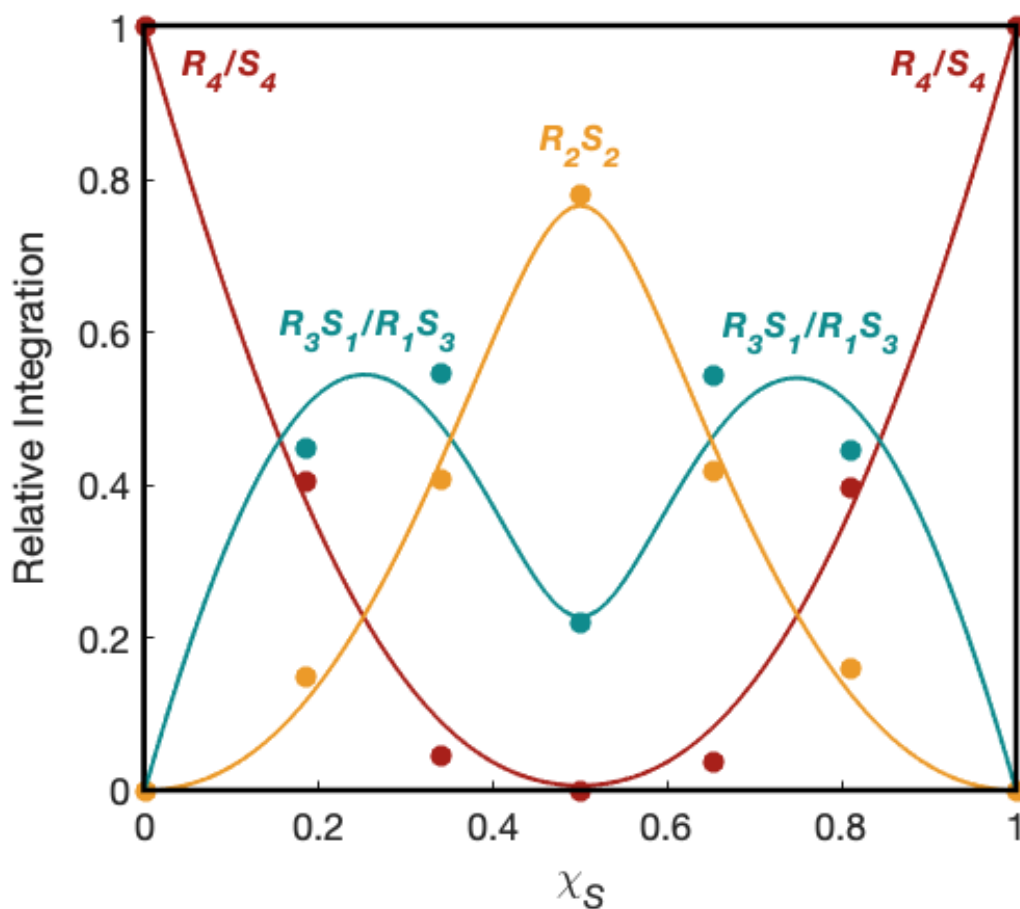


Figure S33. ^6Li Job plot showing relative integrations the two homoaggregates of $[\text{}^6\text{Li}]$ -(*S*)-**8b** and $[\text{}^6\text{Li}]$ -(*R*)-**8b** (blue), the two 3:1 mixed tetramers (violet), and the R_2S_2 mixed tetramer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(*S*)-**8b** for 0.20 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(*S*)-**8b** and $[\text{}^6\text{Li}]$ -(*R*)-**8b** in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S32**). The curves result from a parametric fit to a single aggregate tetramer model.

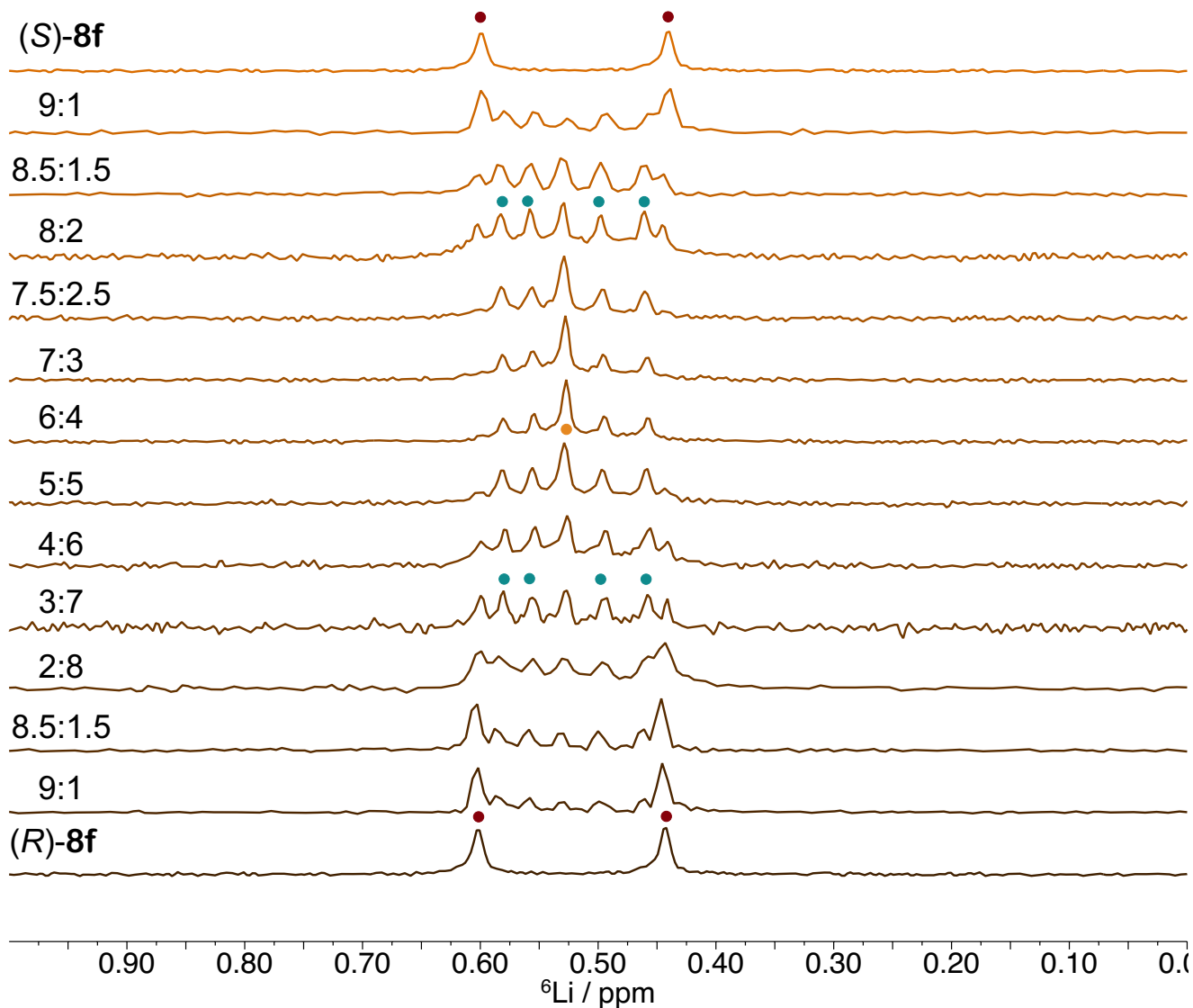
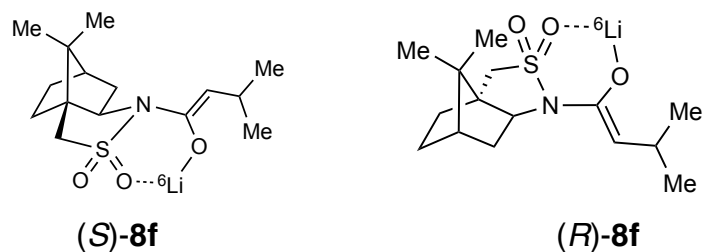


Figure S34. ${}^6\text{Li}$ NMR spectra of mixtures of $[{}^6\text{Li}]$ -(S)-8f and $[{}^6\text{Li}]$ -(R)-8f in toluene at -80 °C. The sealed NMR tubes were aged at 0 °C for 10 min. Five new resonances appear for the mixed aggregates (R_3S_1 , R_2S_2 , R_1S_3) consistent with a tetramer model. $R:S$ represents the total molar ratio of the two enantiomers.

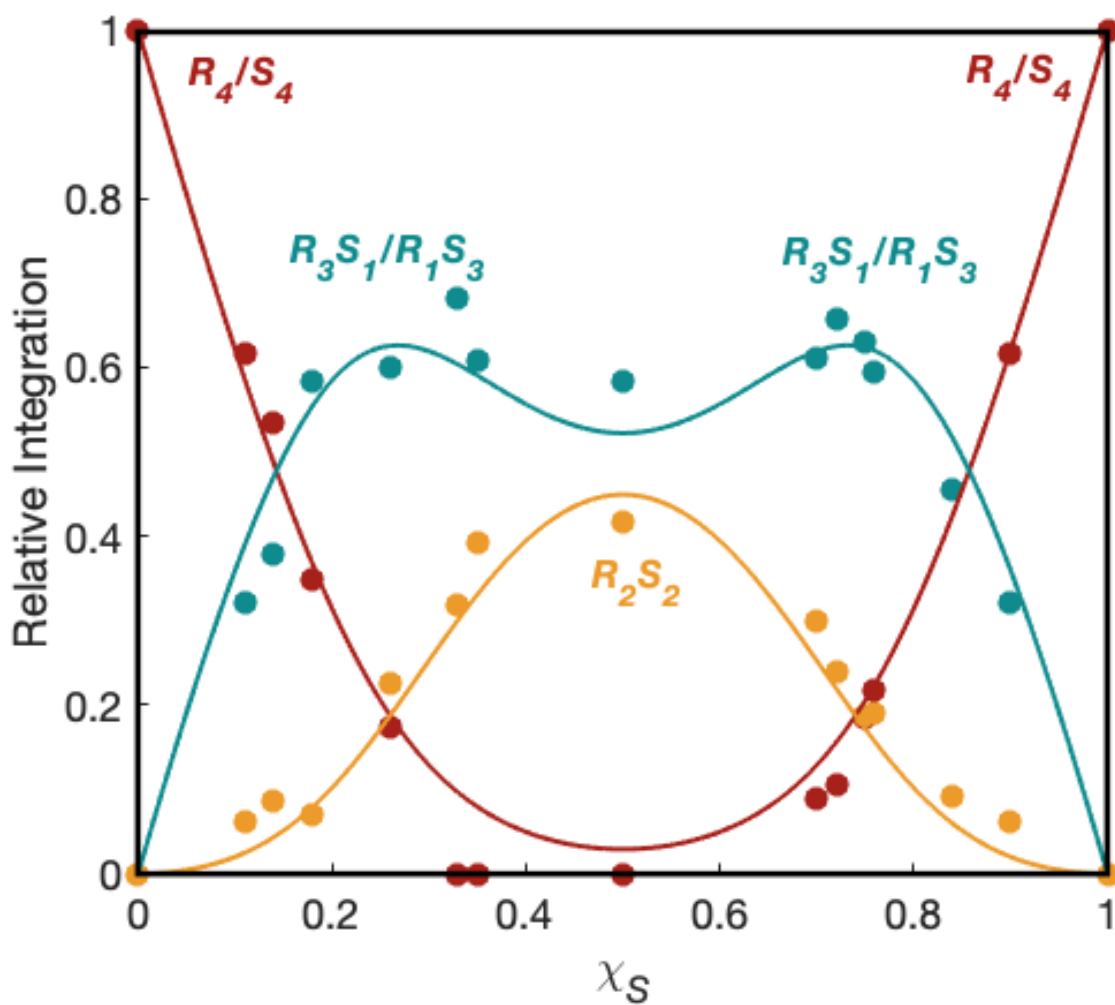


Figure S35. ^6Li Job plot showing relative integrations of the two homoaggregates of $[\text{}^6\text{Li}]$ -(*S*)-**8f** and $[\text{}^6\text{Li}]$ -(*R*)-**8f** (blue), the two 3:1 mixed tetramers (violet), and the R_2S_2 mixed tetramer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(*S*)-**8f** for 0.20 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(*S*)-**8f** and $[\text{}^6\text{Li}]$ -(*R*)-**8f** in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S34**). The curves result from a parametric fit to a single aggregate tetramer model.

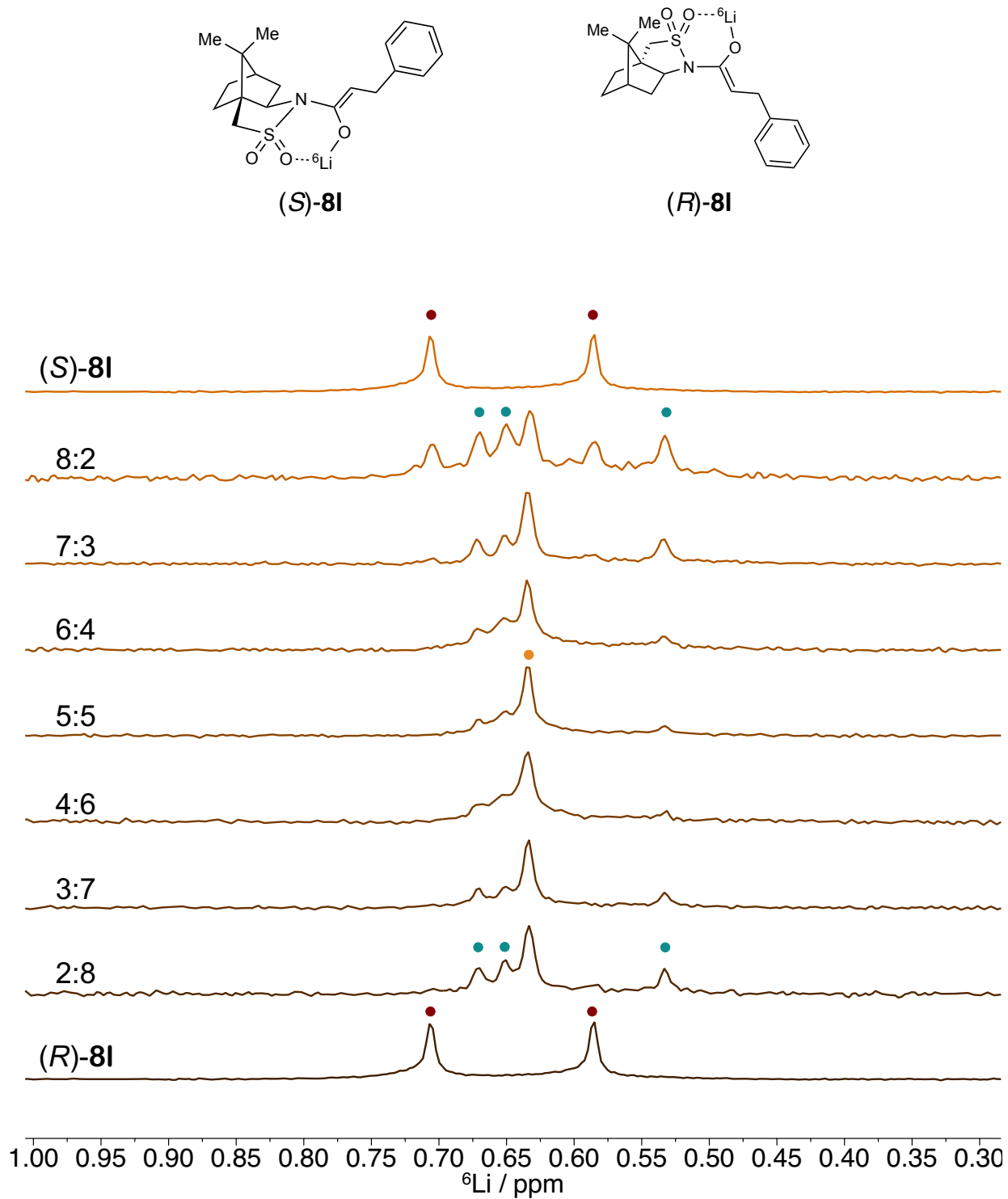


Figure S36. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-}(S)\text{-8I}$ and $[\text{}^6\text{Li}]\text{-}(R)\text{-8I}$ in toluene at -80°C . The sealed NMR tubes were aged at 0°C for 10 min. Five new resonances appear for the mixed aggregates (R_3S_1 , R_2S_2 , R_1S_3) consistent with a tetramer model. *R:S* represents the total molar ratio of the two enantiomers.

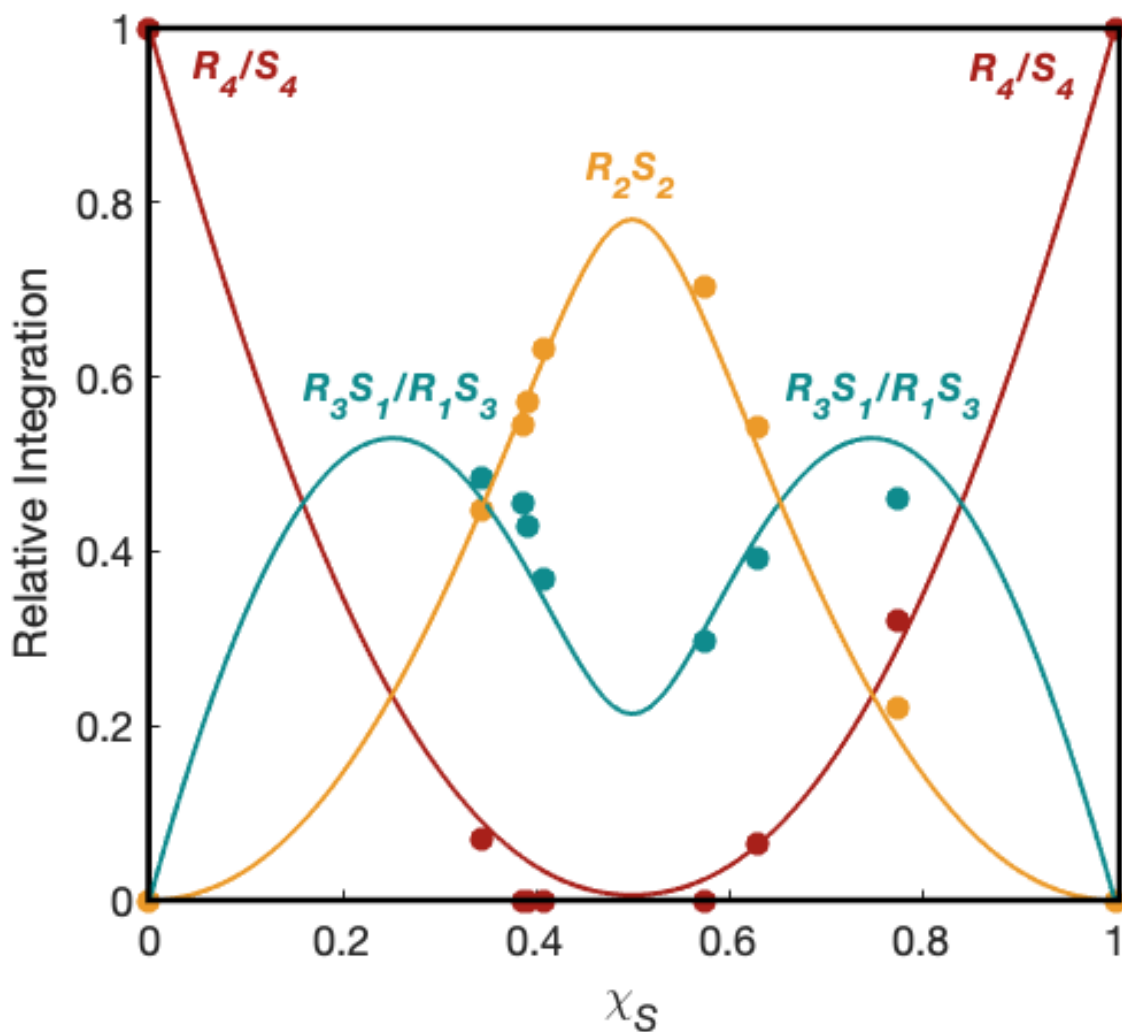


Figure S37. ^6Li Job plot showing relative integrations the two homoaggregates of $[\text{}^6\text{Li}]$ - $(S)\text{-8I}$ and $[\text{}^6\text{Li}]$ - $(R)\text{-8I}$ (blue), the two 3:1 mixed tetramers (violet), and the R_2S_2 mixed tetramer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ - $(S)\text{-8I}$ for 0.20 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ - $(S)\text{-8I}$ and $[\text{}^6\text{Li}]$ - $(R)\text{-8I}$ in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S36**). The curves result from a parametric fit to a single aggregate tetramer model.

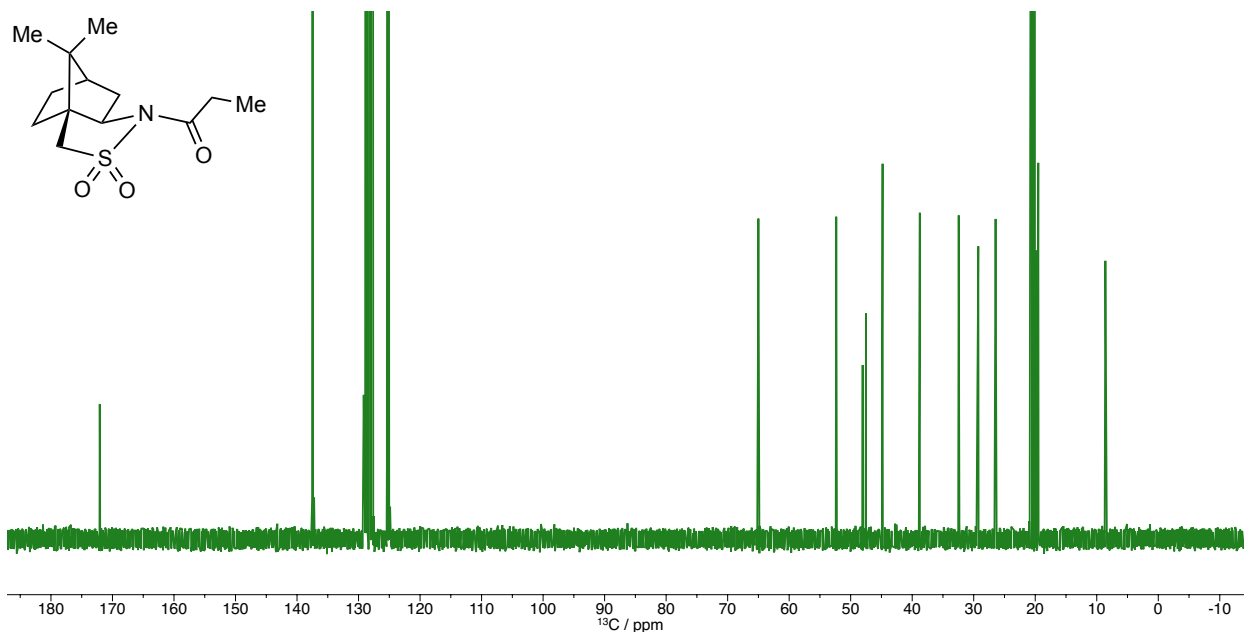


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (*S*)-**7b** in toluene at $-80\text{ }^\circ\text{C}$.

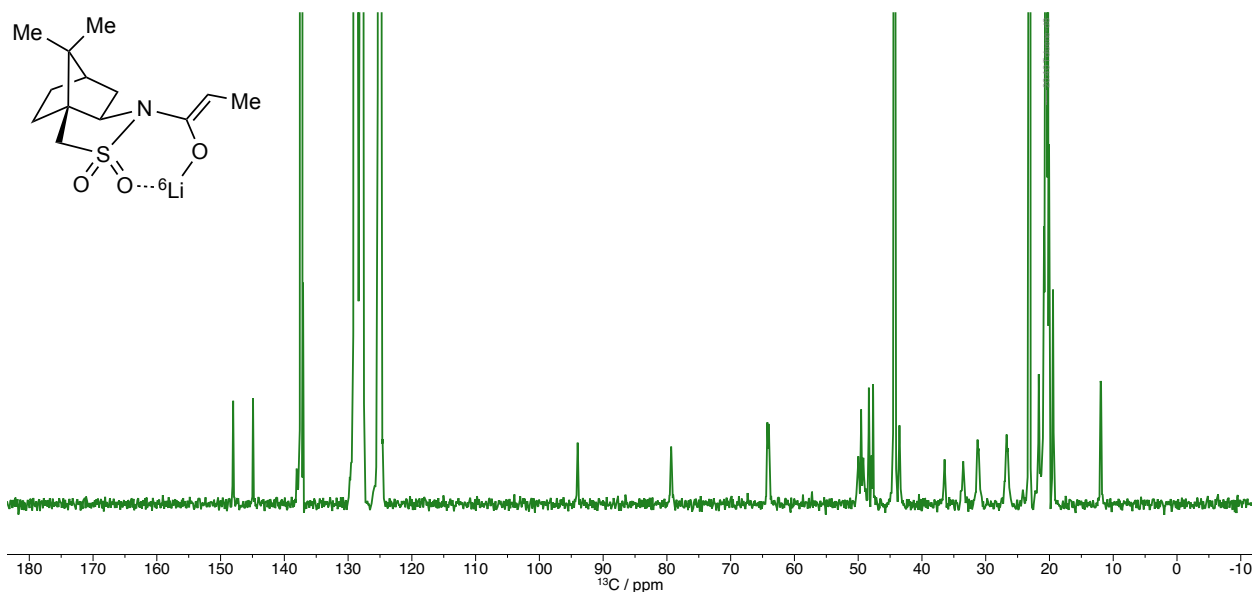


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[^6\text{Li}]$ -(*S*)-**8b** in toluene at $-80\text{ }^\circ\text{C}$ indicating that enolate $[^6\text{Li}]$ -(*S*)-**8b** possesses two subunits (two sets of ^{13}C resonances) implicating the S_4 symmetric tetramer (core type **32**).

Spirocyclic aryl acetamide-derived enolate dimers

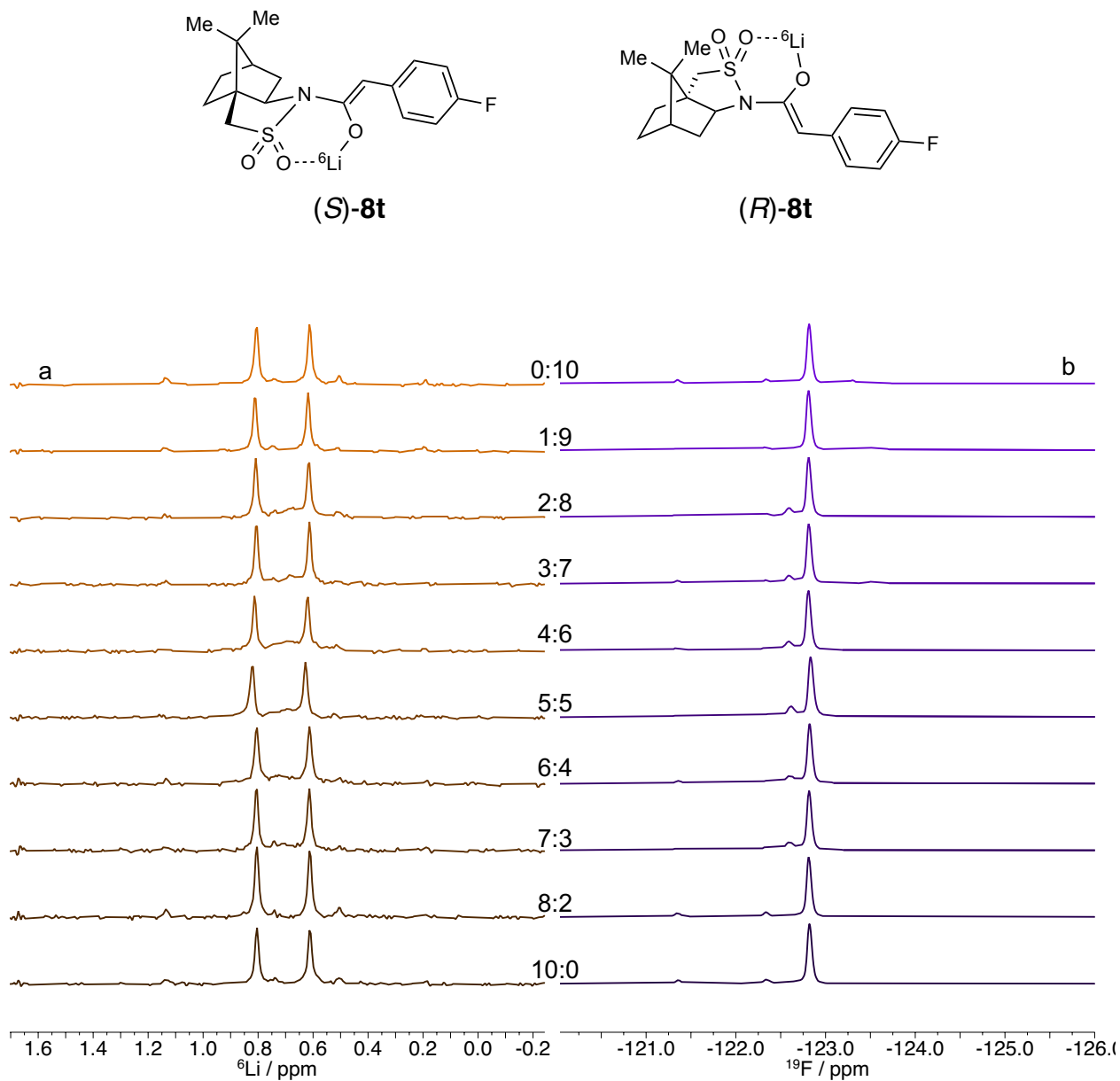


Figure S40. **a** | ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(S)-8t (A) and $[\text{}^6\text{Li}]$ -(R)-8t (B) in toluene at $-80\text{ }^\circ\text{C}$. **b** | The corresponding ^{19}F NMR spectra. R:S represents the molar ratio of the two enantiomers. Curiously, the resonances of the mixed aggregate do not visibly appear.

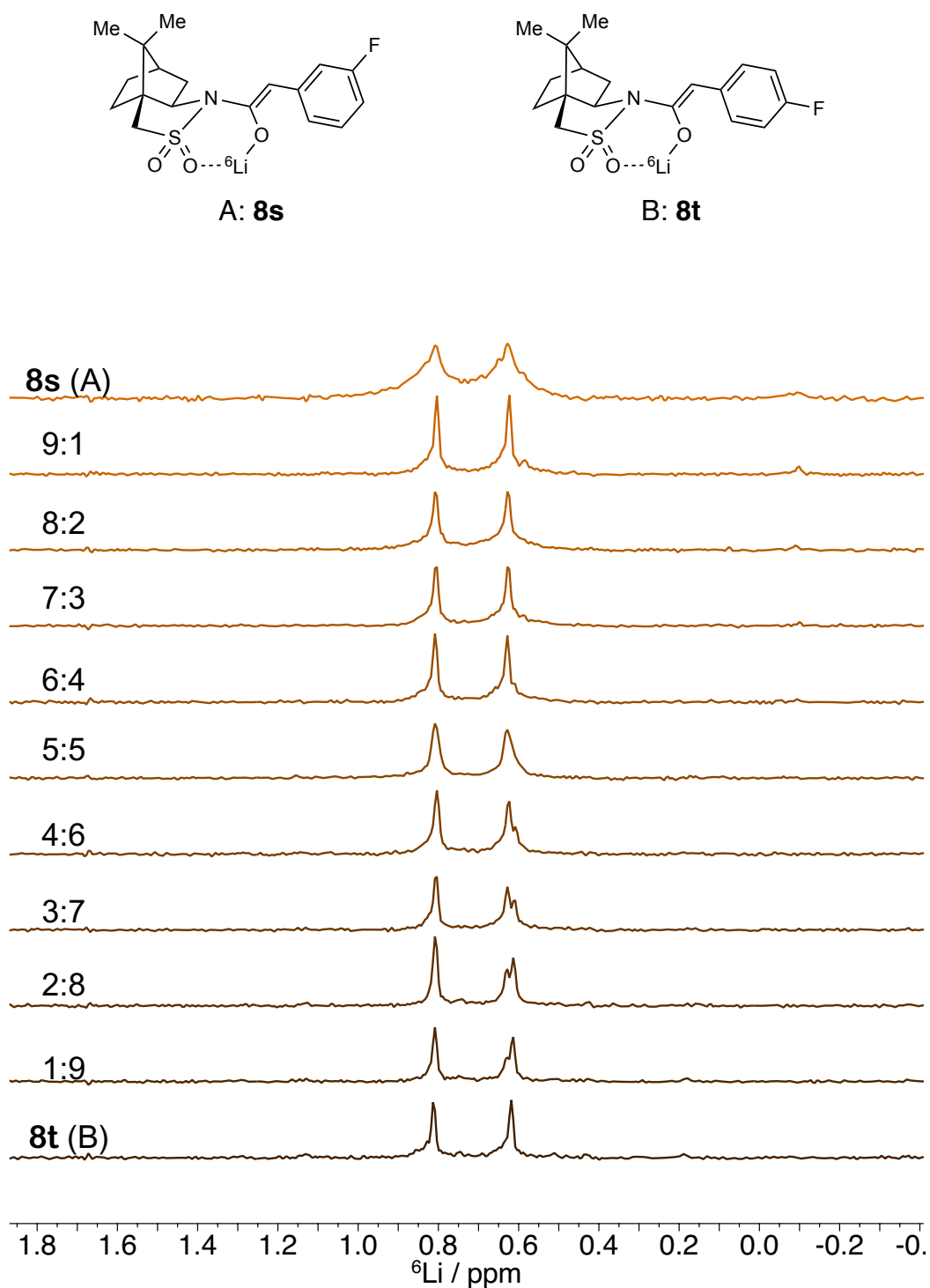


Figure S41. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]$ -(*S*)-**8s** (A) and $[\text{}^6\text{Li}]$ -(*S*)-**8t** (B) in toluene at $-80\text{ }^\circ\text{C}$. Severe overlap of the homodimers (**A**₂/**B**₂) with the heterodimer (**A**₁**B**₁) prevents accurate integration. A:B represents the molar ratio of the two enolates.

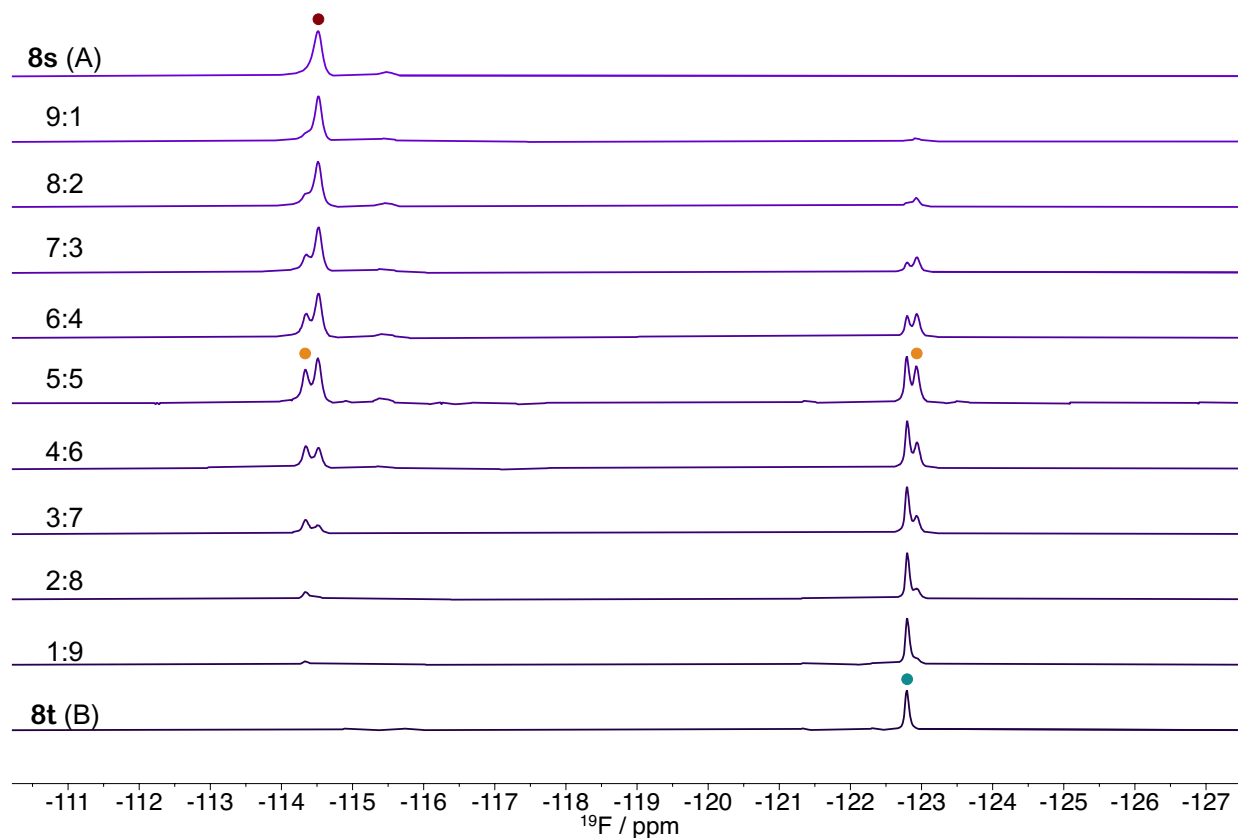
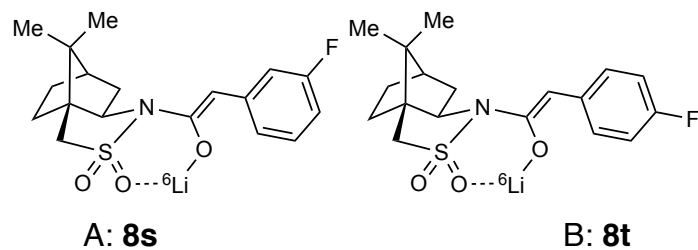


Figure S42. ^{19}F NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-(S)-8s}$ (A) and $[\text{}^6\text{Li}]\text{-(S)-8t}$ (B) in toluene at $-80\text{ }^\circ\text{C}$. Two new resonances appear for the mixed aggregate (**A₁B₁**) consistent with the dimer assignment. A:B represents the molar ratio of the two enolates.

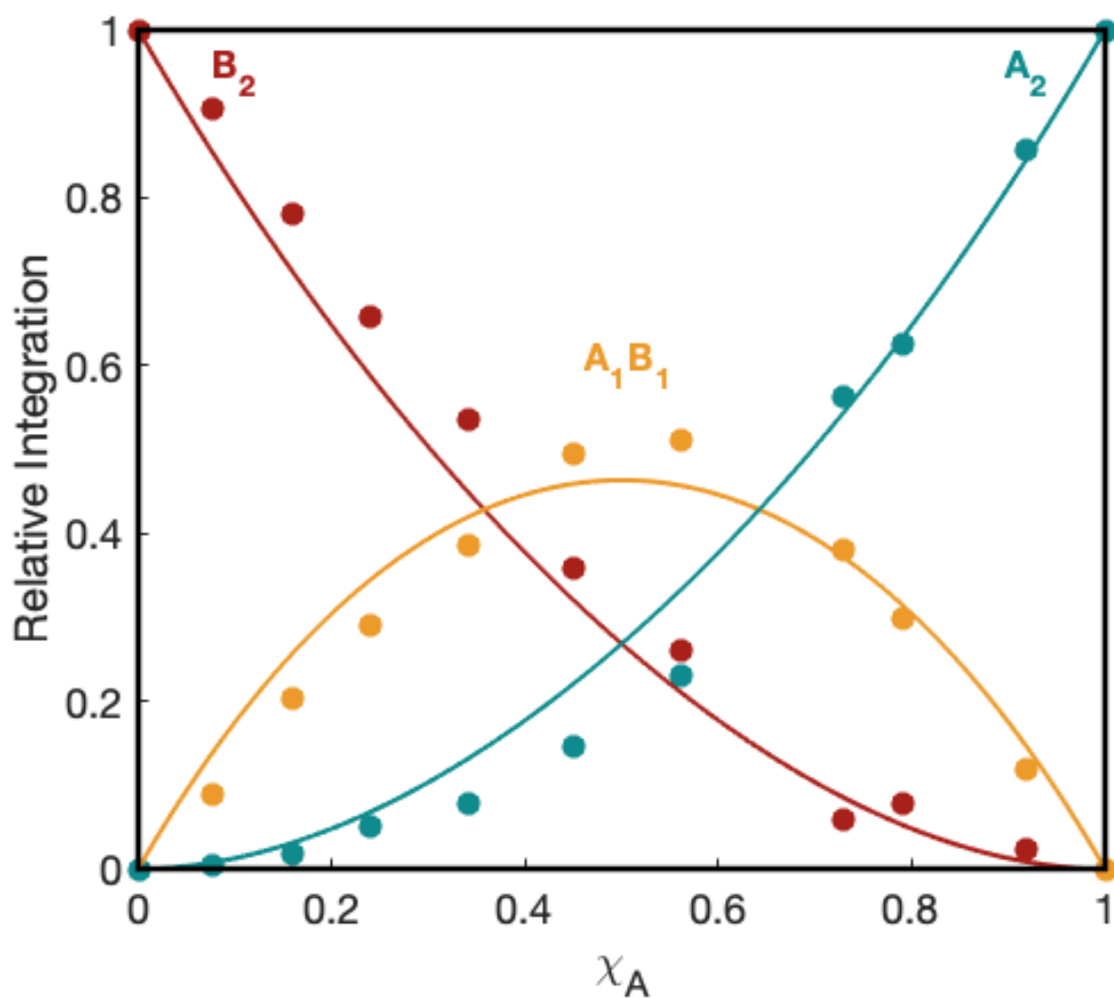


Figure S43. ^{19}F Job plot showing relative integrations the two homoaggregates of $[\text{}^6\text{Li}]-(\text{S})\text{-8s}$ (red) and $[\text{}^6\text{Li}]-(\text{S})\text{-8t}$ (blue), and the 1:1 mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]-(\text{S})\text{-8t}$ for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]-(\text{S})\text{-8s}$ and $[\text{}^6\text{Li}]-(\text{S})\text{-8t}$ in neat toluene at $-80\text{ }^\circ\text{C}$ monitored by ^{19}F NMR spectroscopy (**Figure S42**). The curves result from a parametric fit to a single aggregate dimer model.

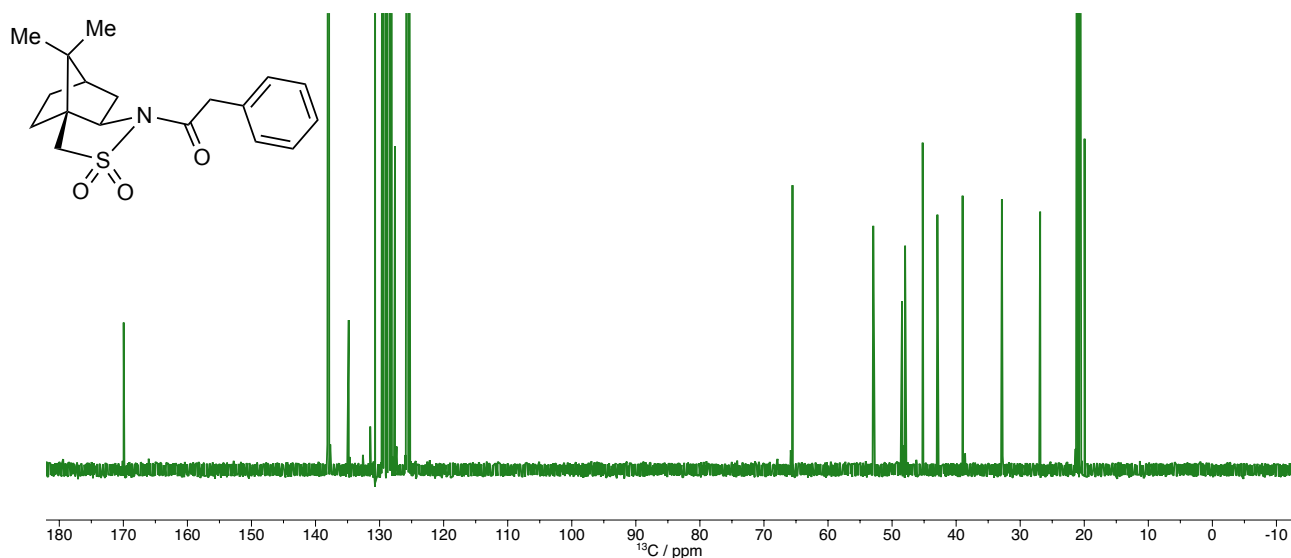


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 0.20 M (*S*)-**7o** in toluene at $-80\text{ }^\circ\text{C}$.

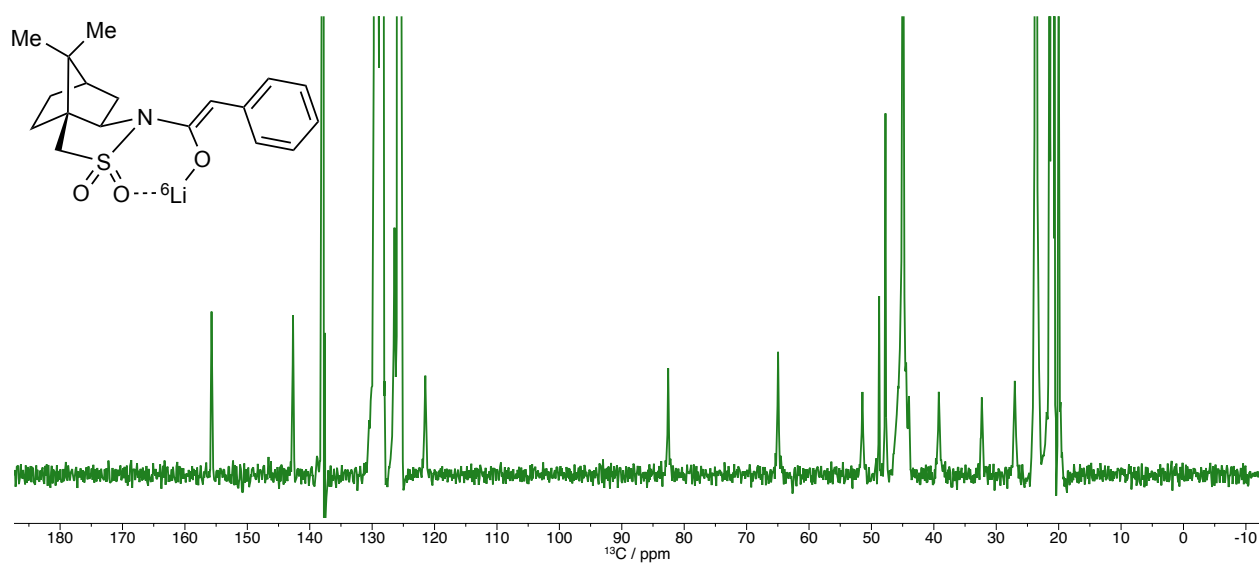


Figure S45. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 0.20 M $[^6\text{Li}]$ -(*S*)-**8o** in toluene at $-80\text{ }^\circ\text{C}$ indicating that enolate $[^6\text{Li}]$ -(*S*)-**8b** possesses a single subunit (one set of ^{13}C resonances) implicating the spirocyclic dimer (core type **36**).

THF-solvated aryl acetamide-derived enolate dimers

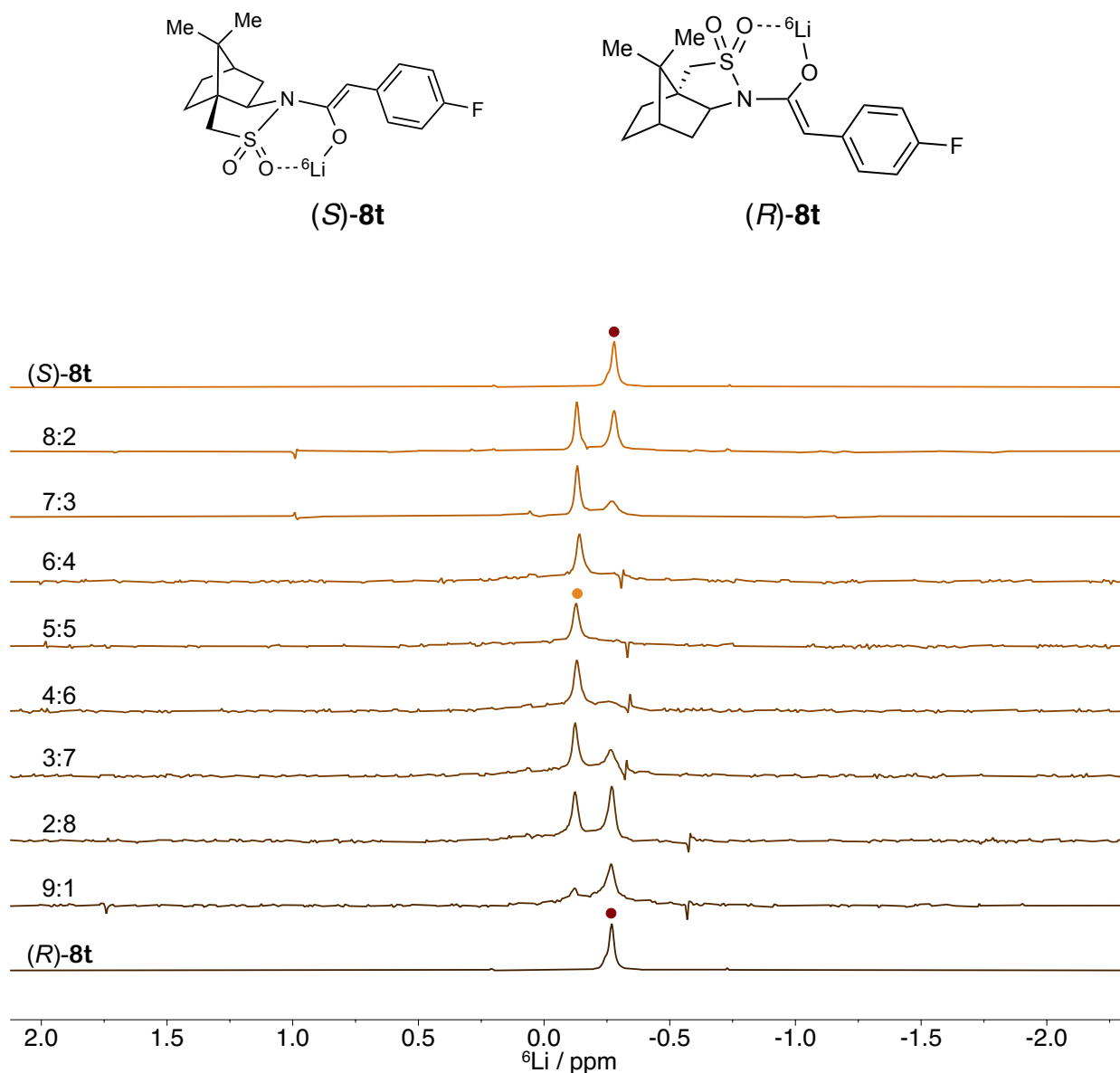


Figure S46. ^6Li NMR spectra of mixtures of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in 10.0 M THF at $-80\text{ }^\circ\text{C}$. One new resonance appears for the heterochiral aggregate (R_1S_1) consistent with a dimer model. $R:S$ represents the total molar ratio of the two enantiomers.

The dispersive peaks are the result of a slight drift of the spectrometer lock (^2H) frequency, but do not interfere with peak integration.

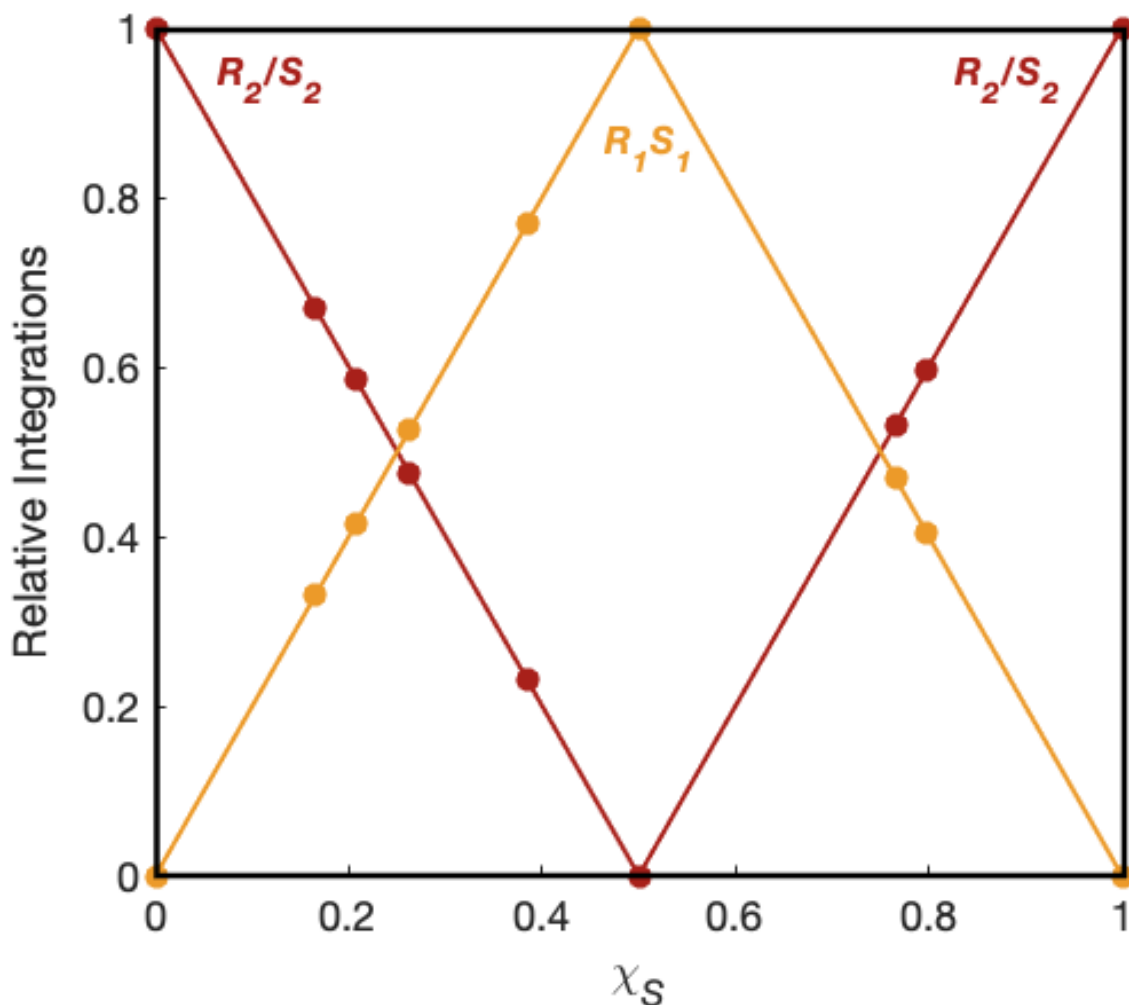


Figure S47. ^6Li Job plot showing relative integrations the two identical homochiral homoaggregates of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ (red), and the R_1S_1 heterochiral mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in 10.0 M THF at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S46**). The curves result from a parametric fit to a single aggregate dimer model.

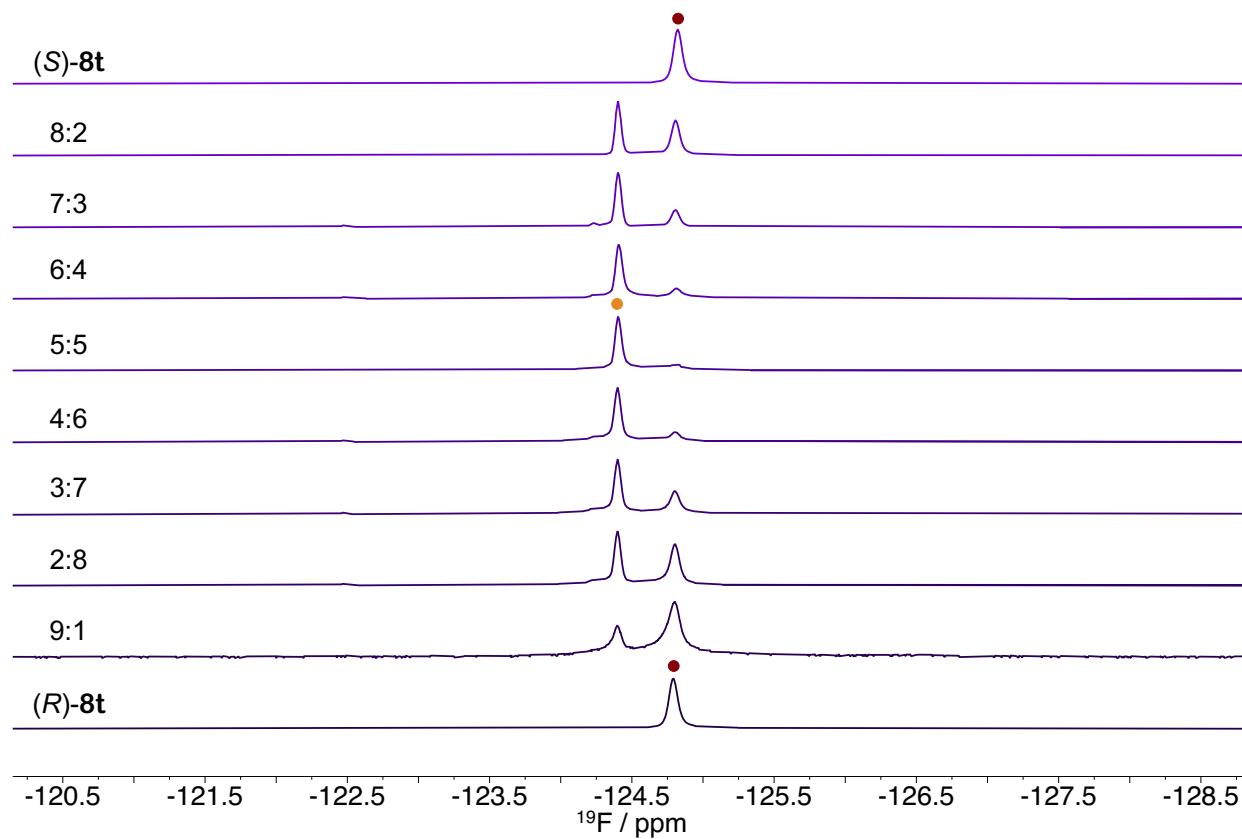
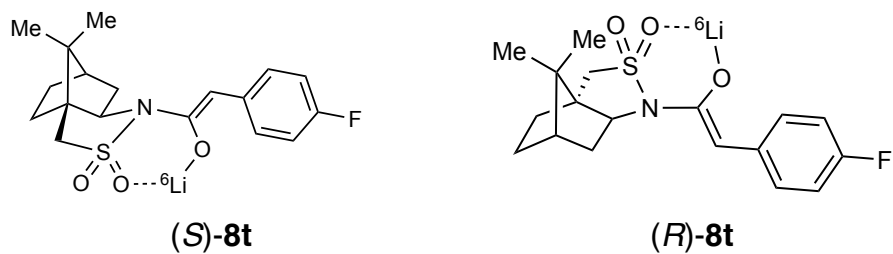


Figure S48. ^{19}F NMR spectra of mixtures of $[^6\text{Li}]$ -(*R*)-8t and $[^6\text{Li}]$ -(*S*)-8t in 10.0 M THF at -80 °C. One new resonance appears for the heterochiral aggregate (R_1S_1) consistent with a dimer model. *R*:*S* represents the total molar ratio of the two enantiomers.

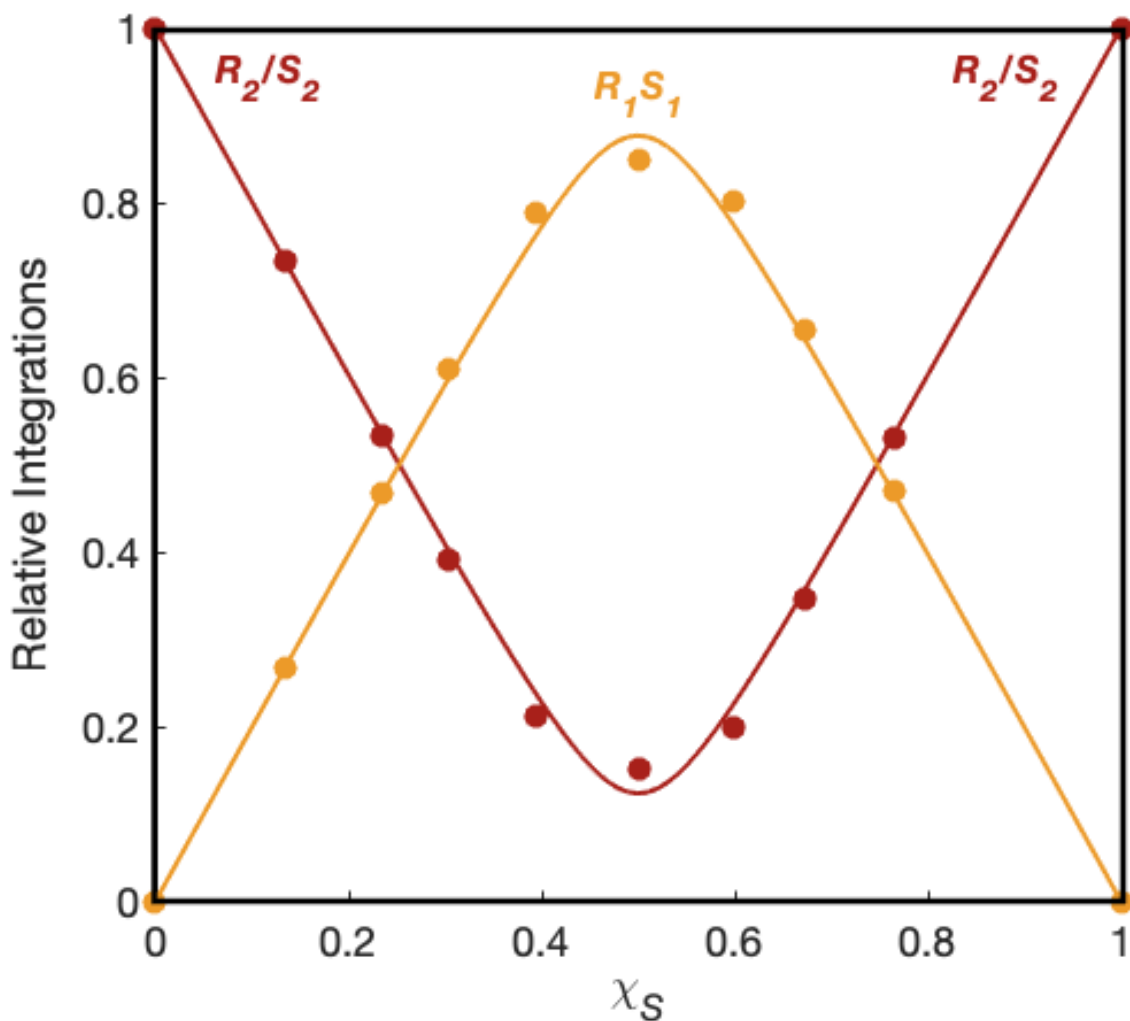


Figure S49. ^{19}F Job plot showing relative integrations of the two identical homochiral homoaggregates of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ (red), and the R_1S_1 heterochiral mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ in 10.0 M THF at $-80\text{ }^\circ\text{C}$ monitored by ^{19}F NMR spectroscopy (Figure S48). The curves result from a parametric fit to a single aggregate dimer model.

THF-solvated alkyl-substituted enolate dimers

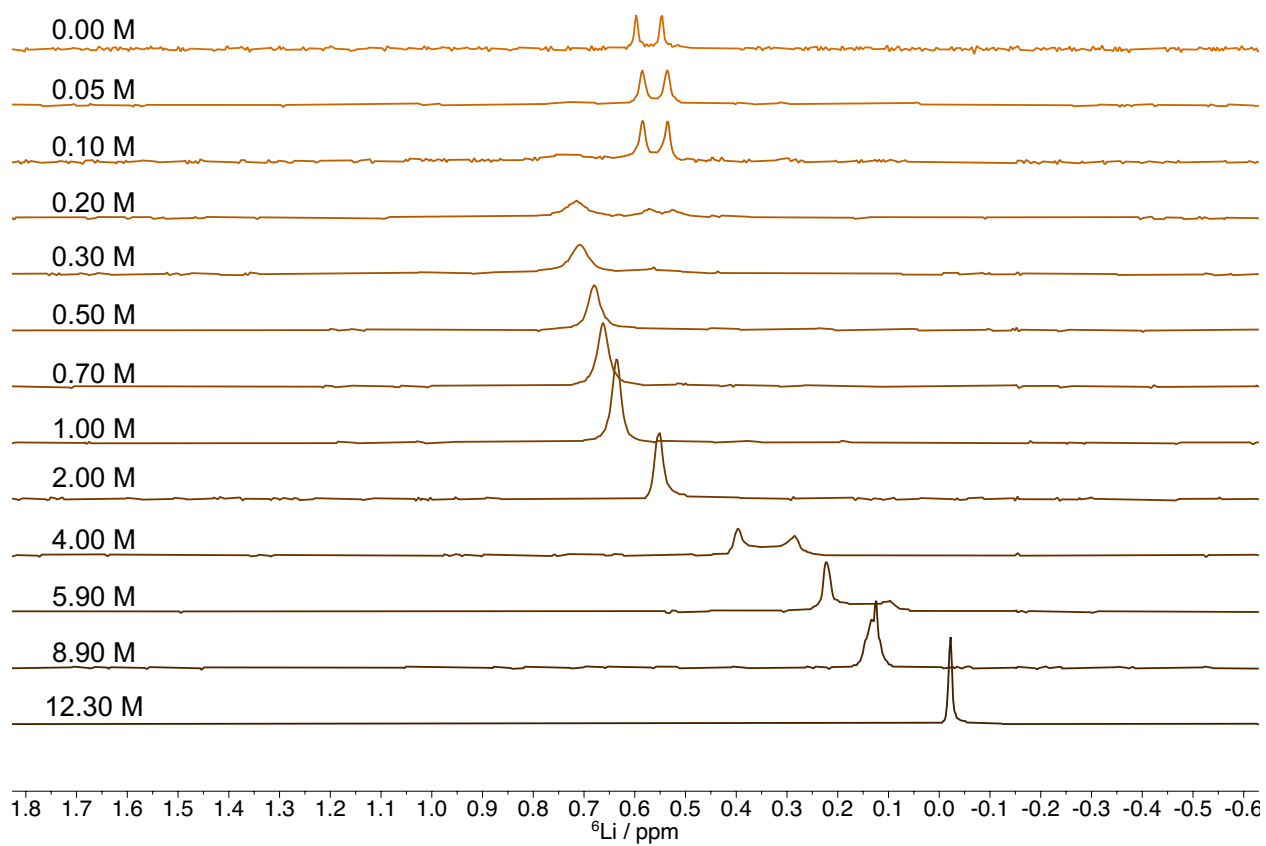
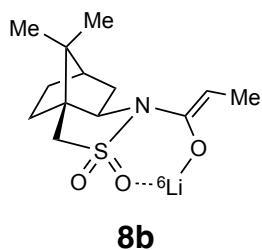


Figure S50. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8b** in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of THF.

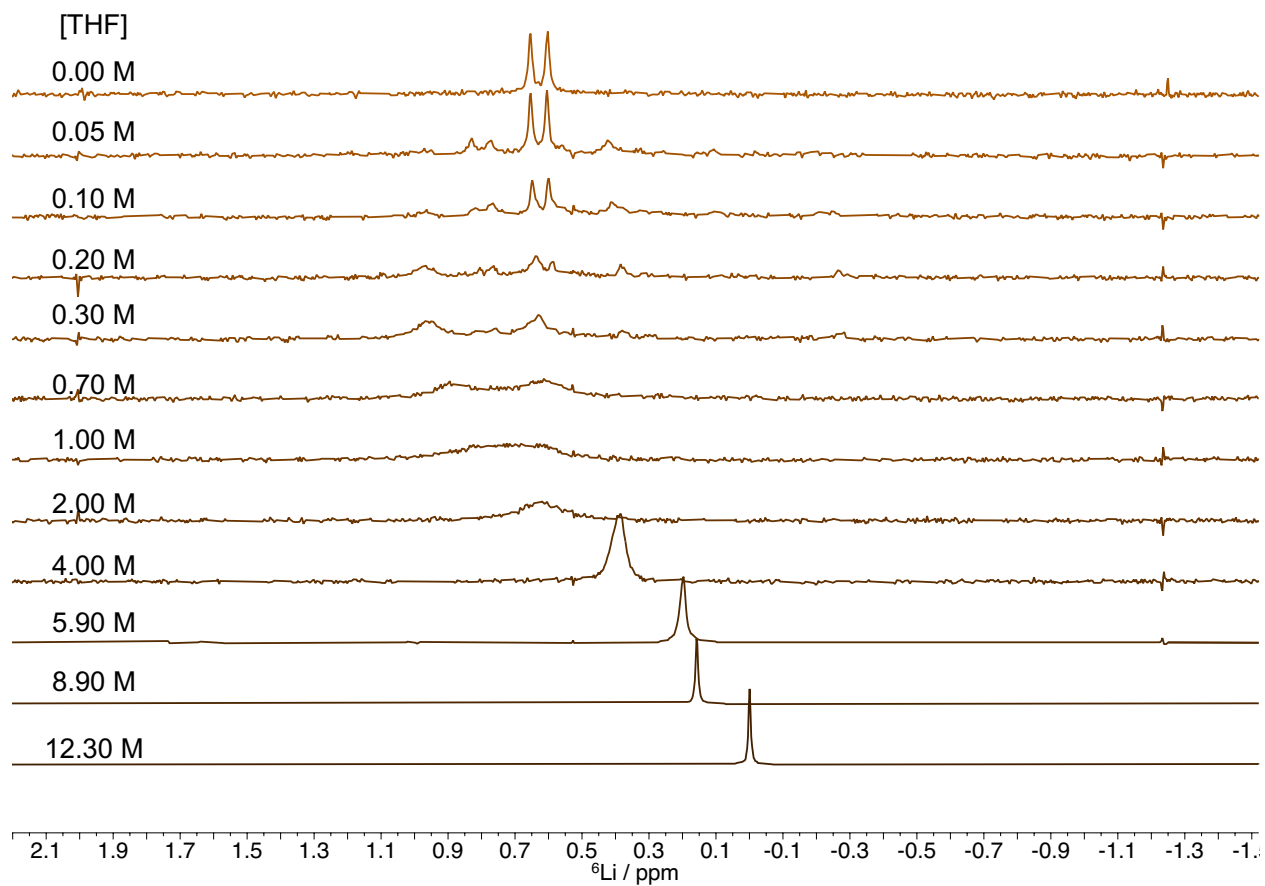
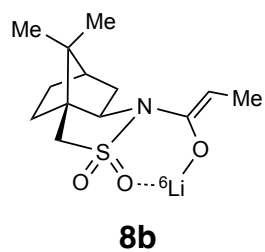


Figure S51. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8b** in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.

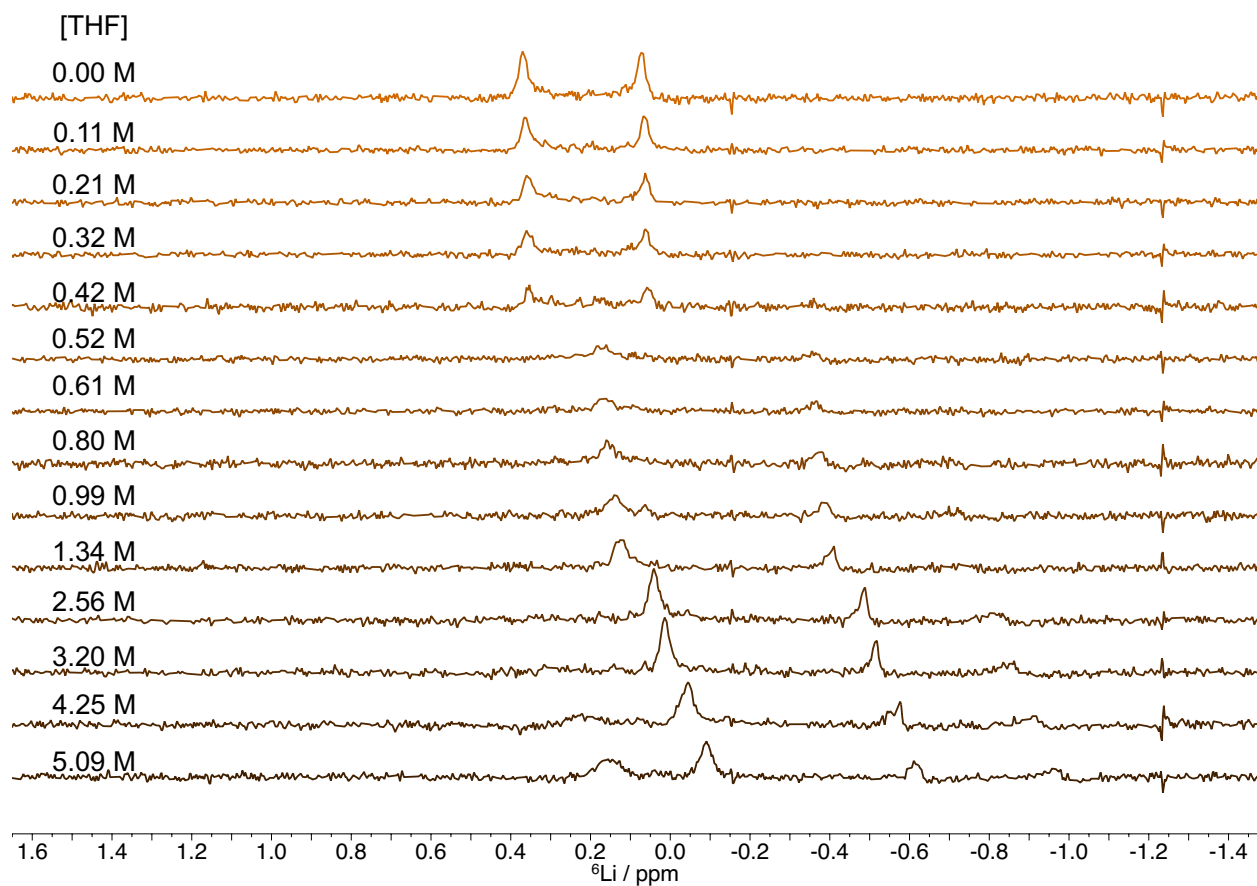
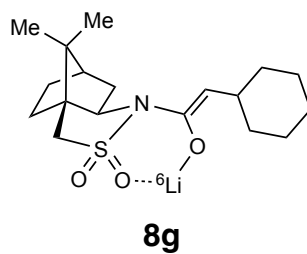
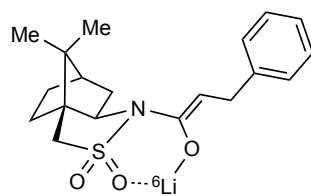


Figure S52. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8g** in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.



8I

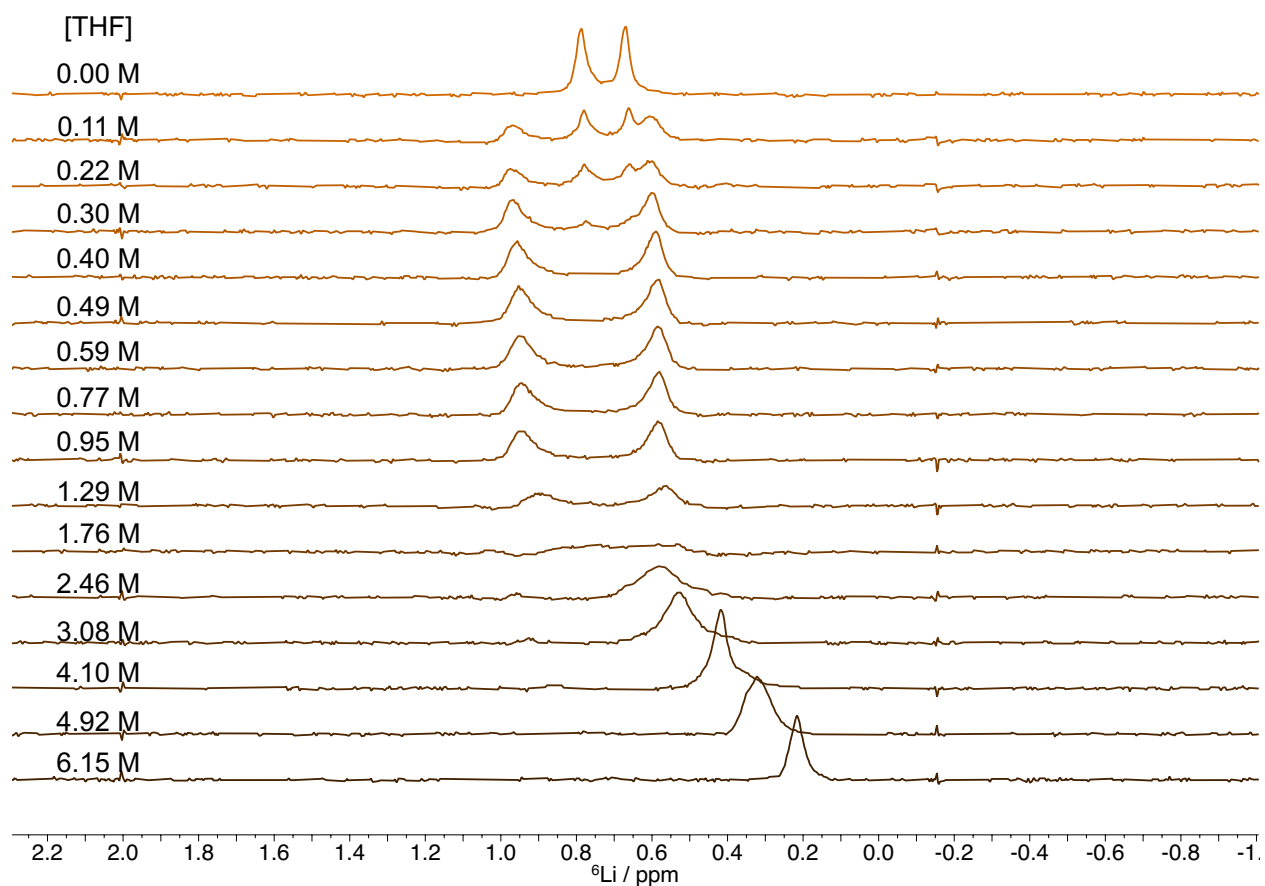


Figure S53. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8I** in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of THF.

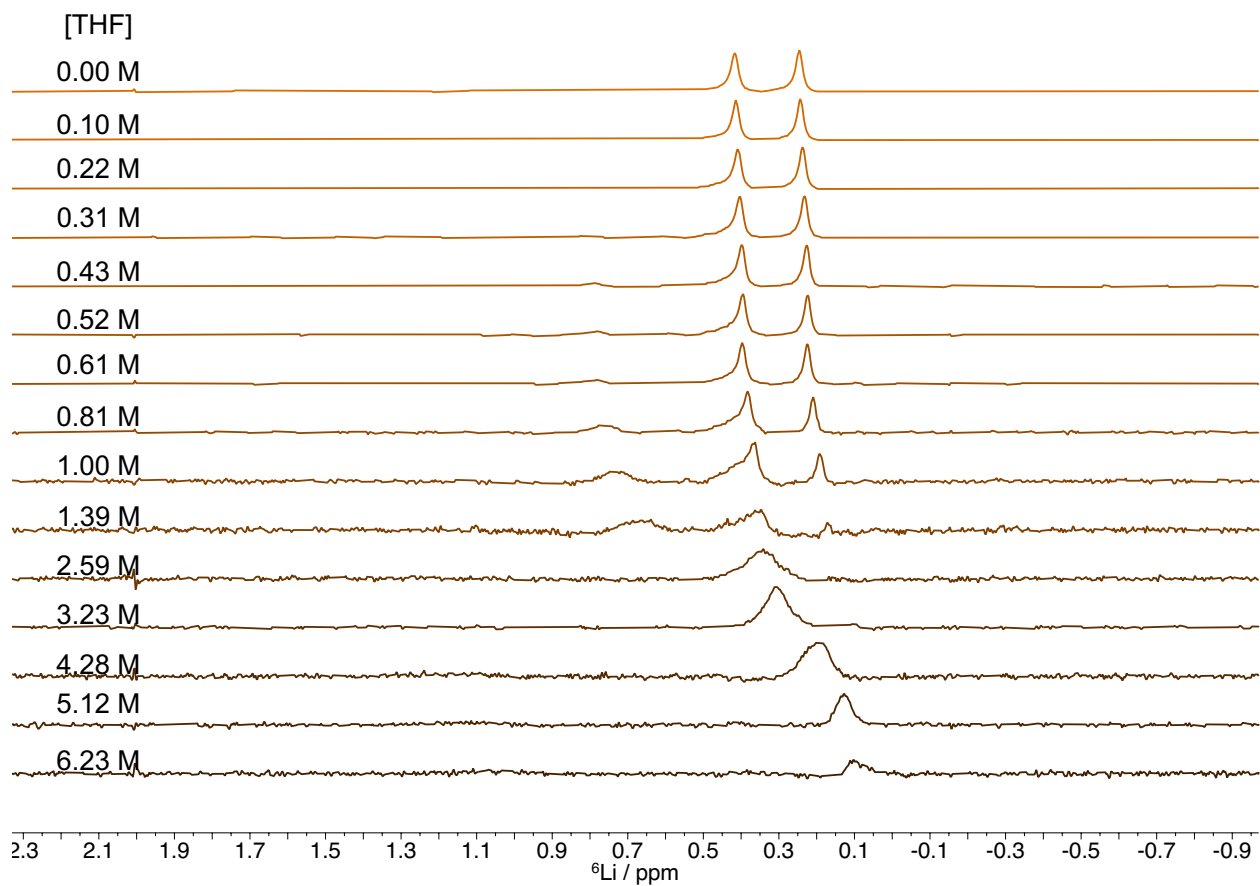
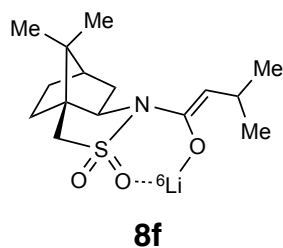


Figure S54. ⁶Li NMR spectra of [⁶Li]-(*S*)-**8f** in toluene at $-80\text{ }^{\circ}\text{C}$ with varying concentrations of THF.

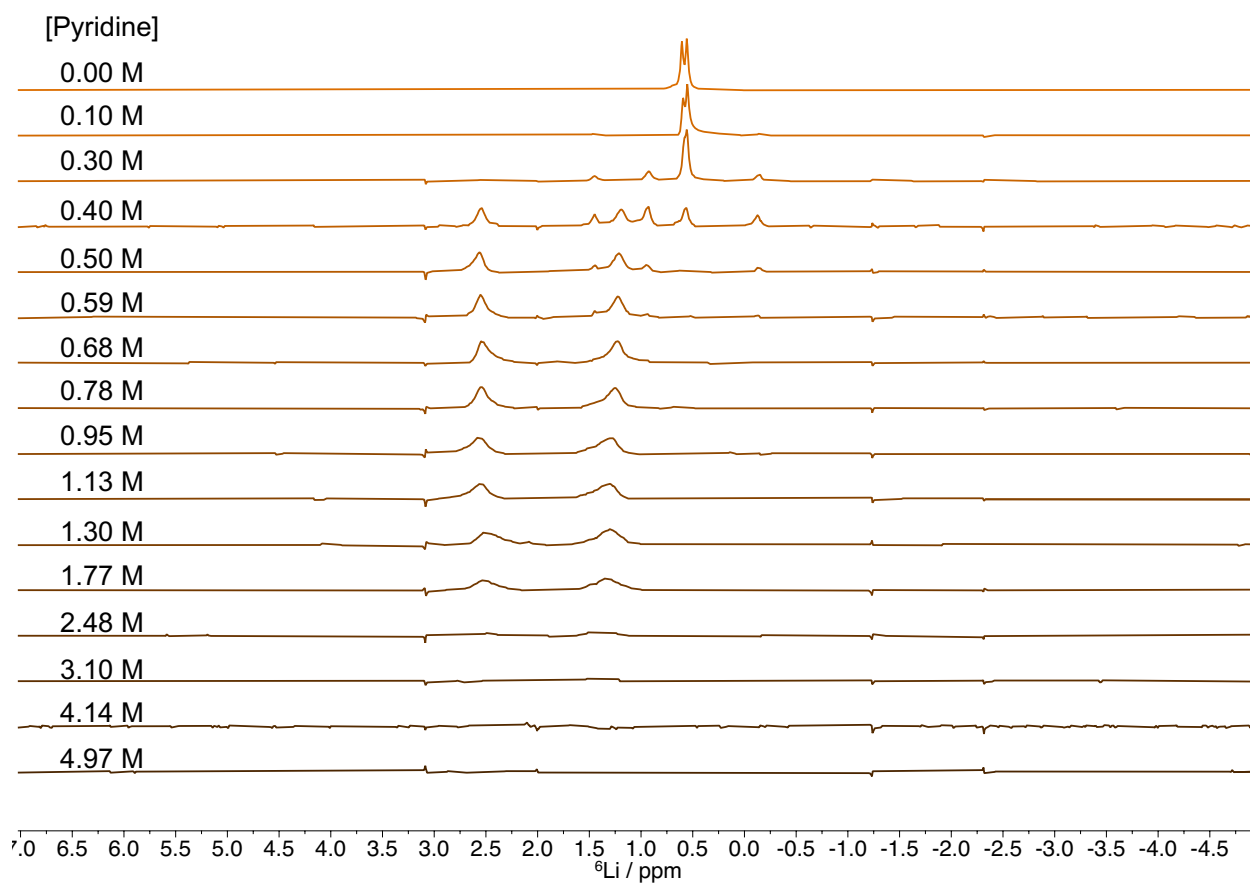
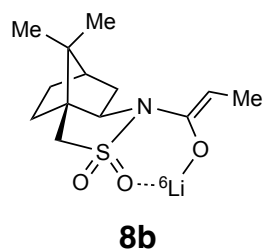


Figure S55. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8b** in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of pyridine.

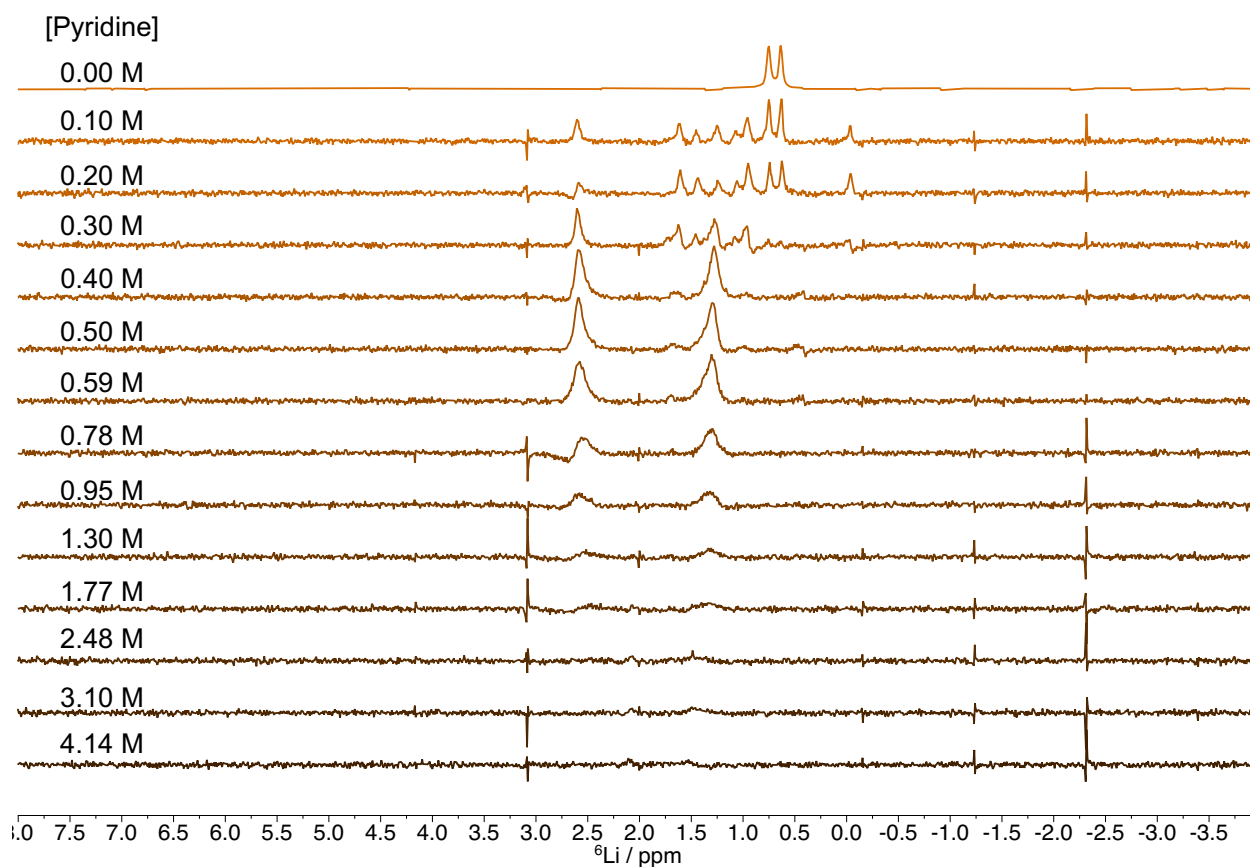
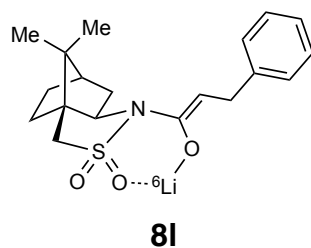


Figure S56. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8I** in toluene at $-100\text{ }^\circ\text{C}$ with varying concentrations of pyridine.

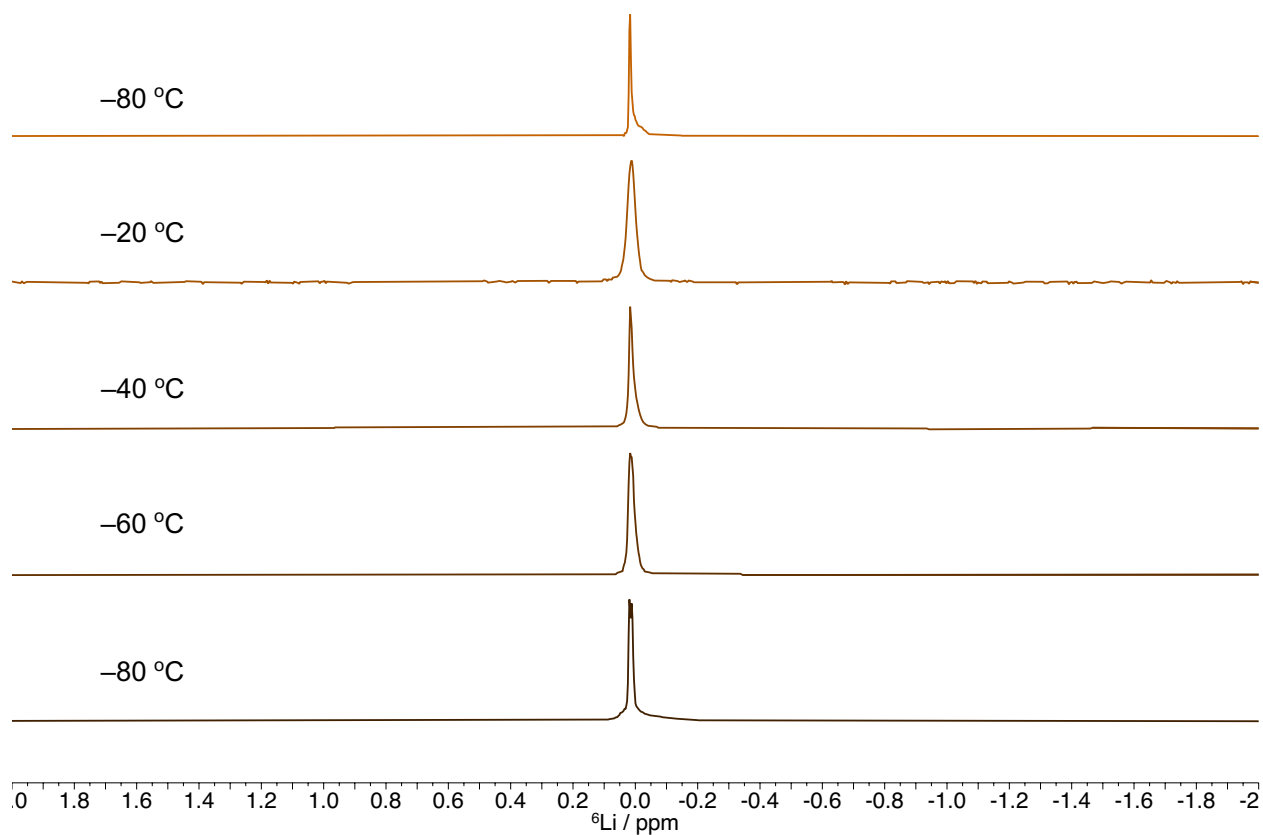
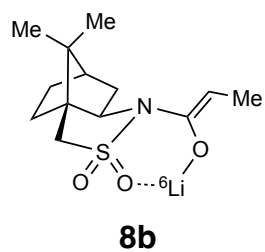


Figure S57. ^6Li NMR spectra of $[\text{}^6\text{Li}]$ -(S)-**8b** in THF at various temperatures. The top spectrum is taken at $-80\text{ }^\circ\text{C}$ after aging for 20 minutes at $-20\text{ }^\circ\text{C}$. The enolate does not appear to age from the original state.

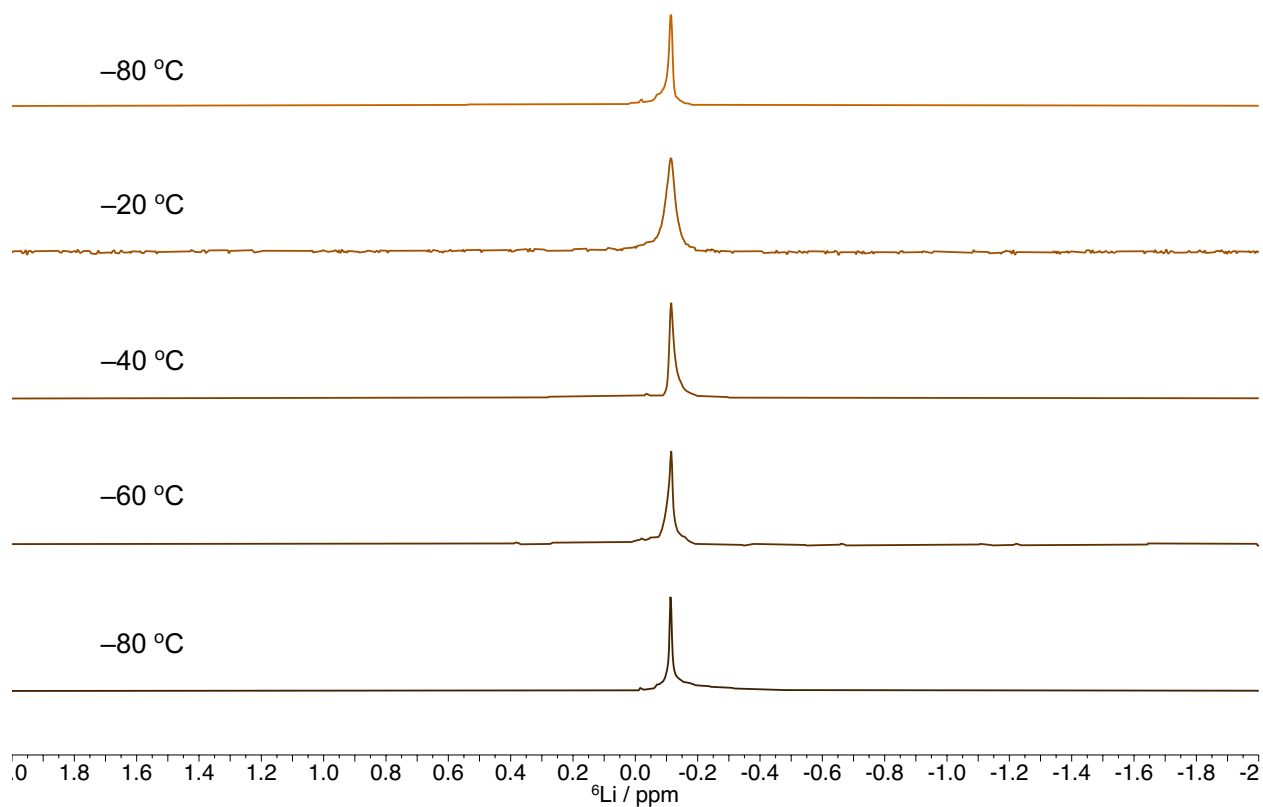
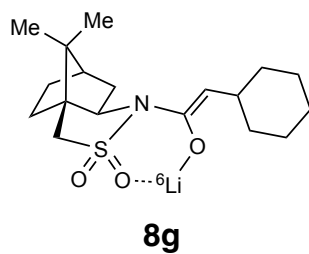


Figure S58. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8g** in THF at various temperatures. The top spectrum is taken at $-80\text{ }^\circ\text{C}$ after aging for 20 minutes at $-20\text{ }^\circ\text{C}$. The enolate does not appear to age from the original state.

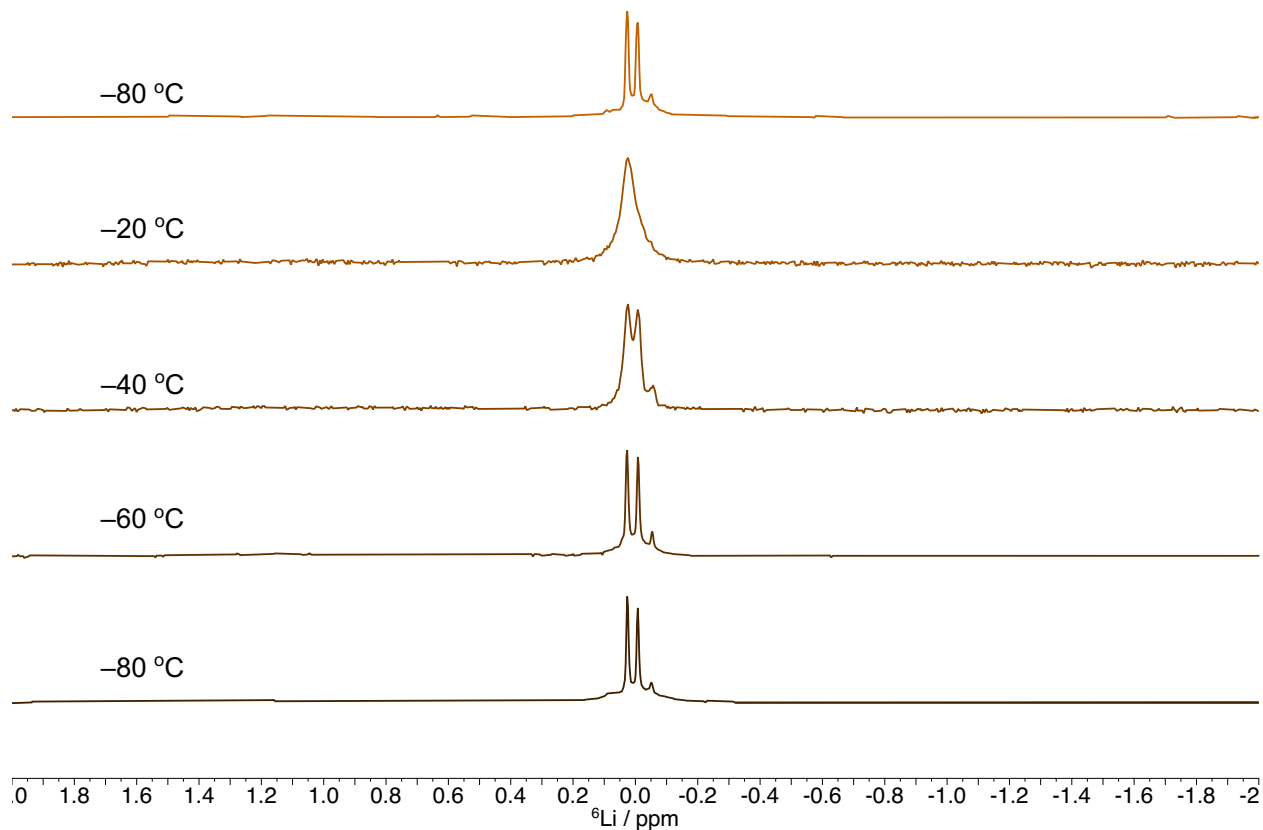
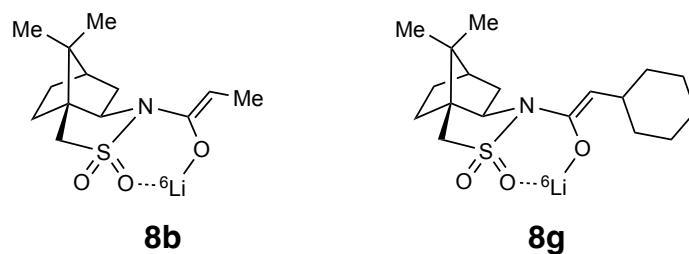


Figure S59. ^6Li NMR spectra of a 1:1 mixture of $[\text{}^6\text{Li}]$ -(*S*)-**8b** and $[\text{}^6\text{Li}]$ -(*S*)-**8g** in THF at various temperatures. The top spectrum is taken at $-80\text{ }^\circ\text{C}$ after aging for 20 minutes at $-20\text{ }^\circ\text{C}$. The enolates do not appear to age from their original state.

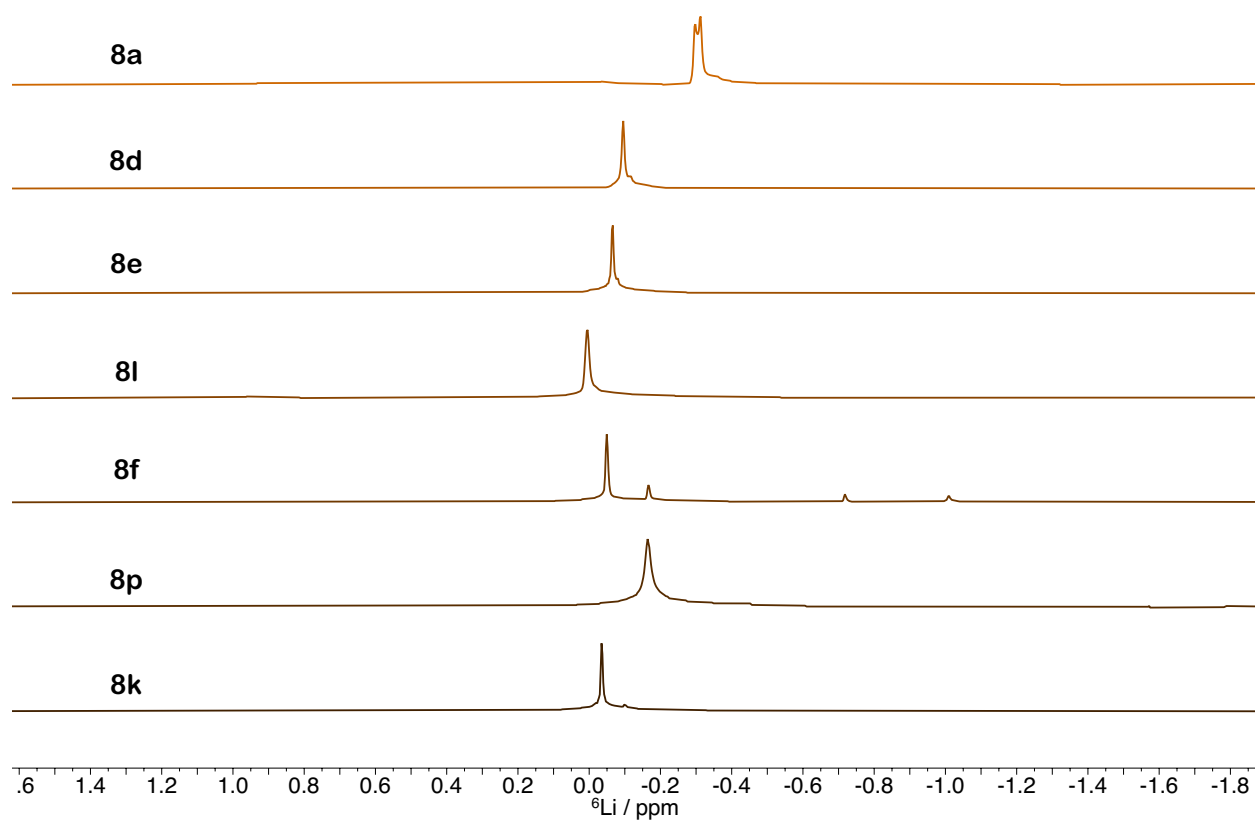


Figure S60. ^6Li NMR spectra of various $[\text{}^6\text{Li}]$ -(*S*)-*N*-acyl-camphorsultam-enolates in THF. The three small upfield peaks in **8f** are assigned to the dianion (vide infra).

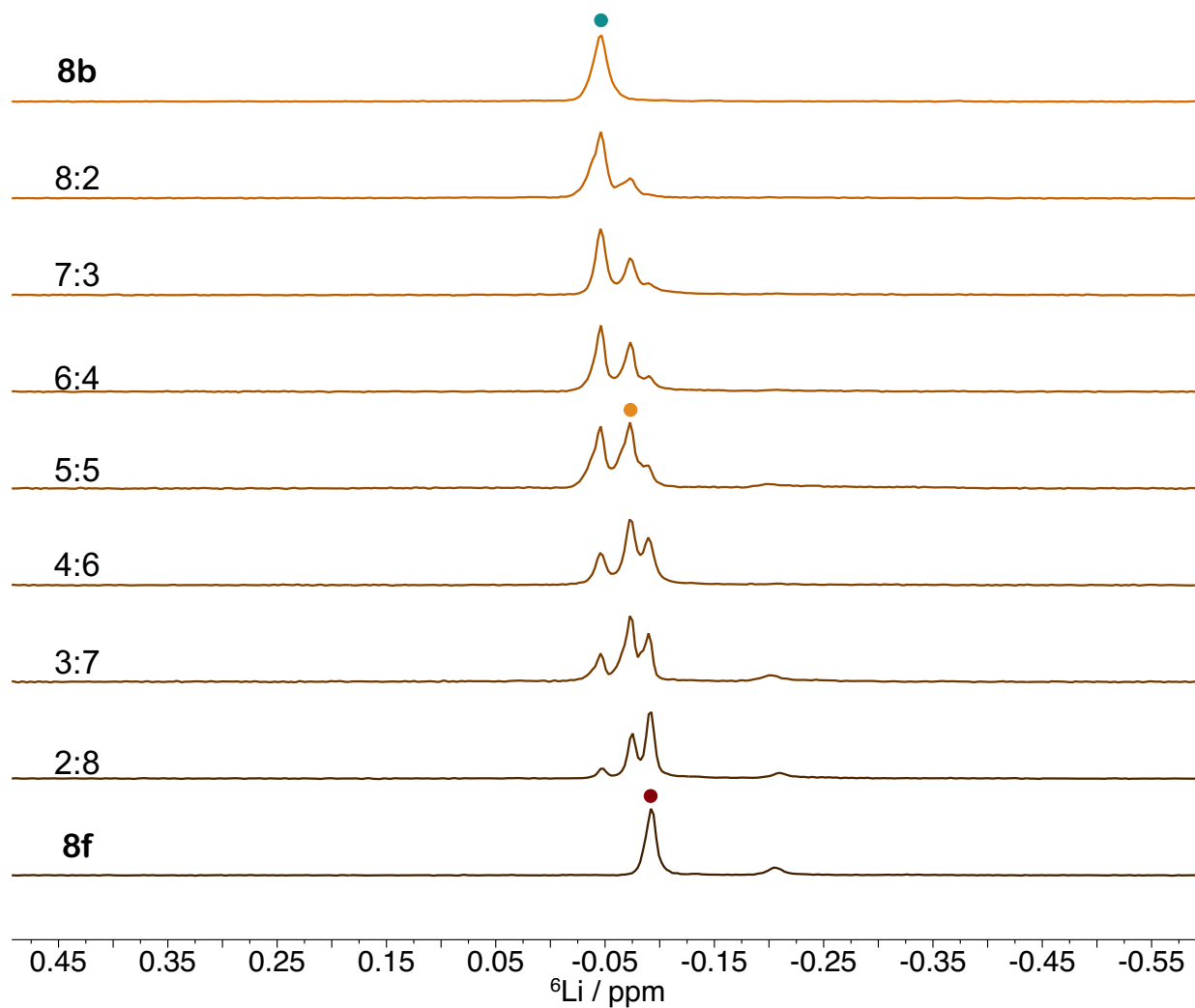
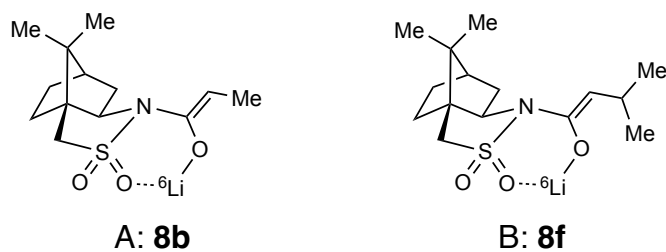


Figure S61. ^6Li NMR spectra of 0.10 M mixtures of $[\text{}^6\text{Li}]\text{-(S)-8b}$ (A) and $[\text{}^6\text{Li}]\text{-(S)-8f}$ (B) in neat THF at $-80\text{ }^\circ\text{C}$. One new resonance appears for the mixed aggregate ($\mathbf{A_1B_1}$) consistent with the dimer assignment. A:B represents the total molar ratio of the two enolates.

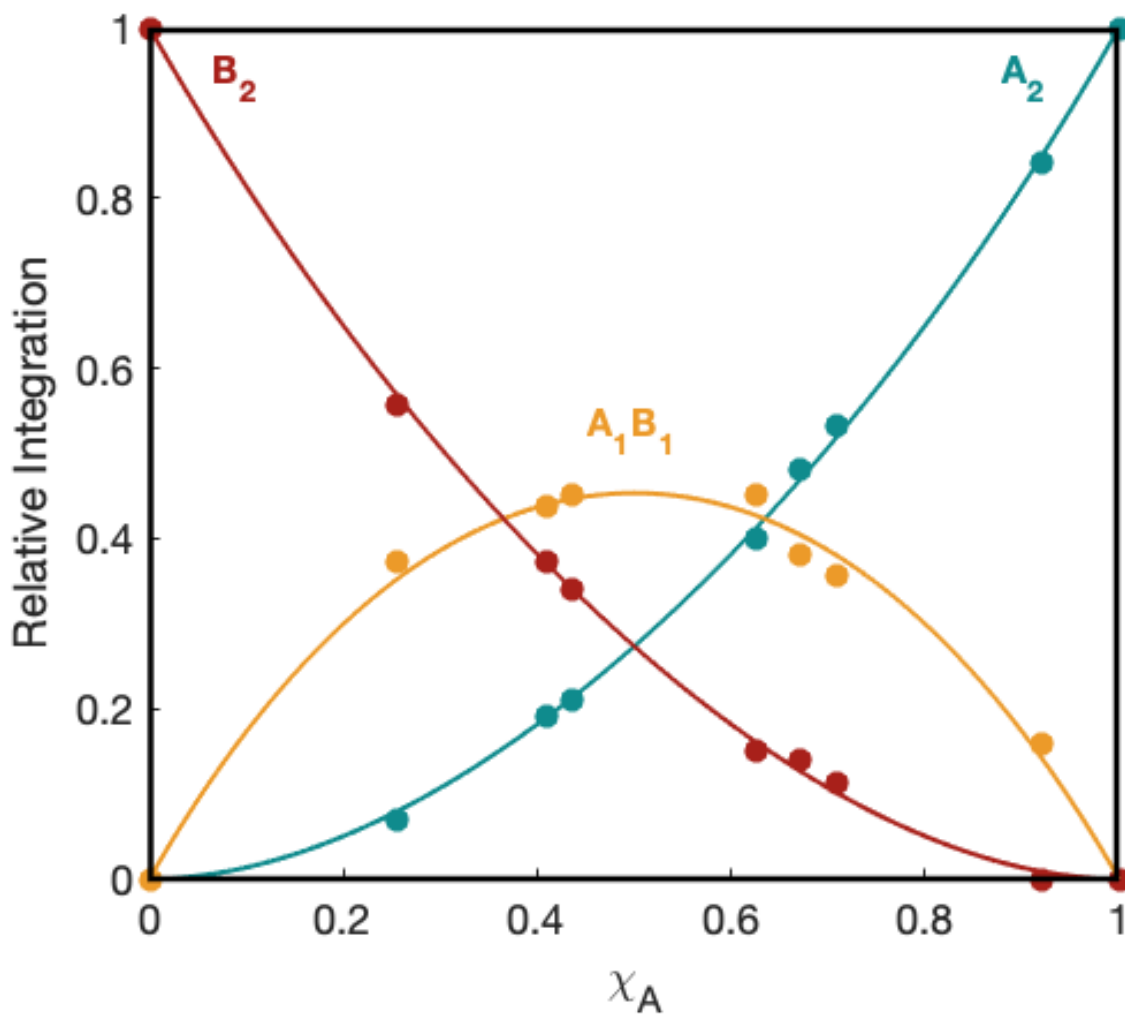


Figure S62. ^6Li Job plot showing relative integrations the two homoaggregates of $[\text{}^6\text{Li}]$ -(S)-**8b** (blue) and $[\text{}^6\text{Li}]$ -(S)-**8f** (red) and their mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(S)-**8b** for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(S)-**8b** and $[\text{}^6\text{Li}]$ -(S)-**8f** in neat THF at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (Figure S61). The curves result from a parametric fit to a single aggregate dimer model.

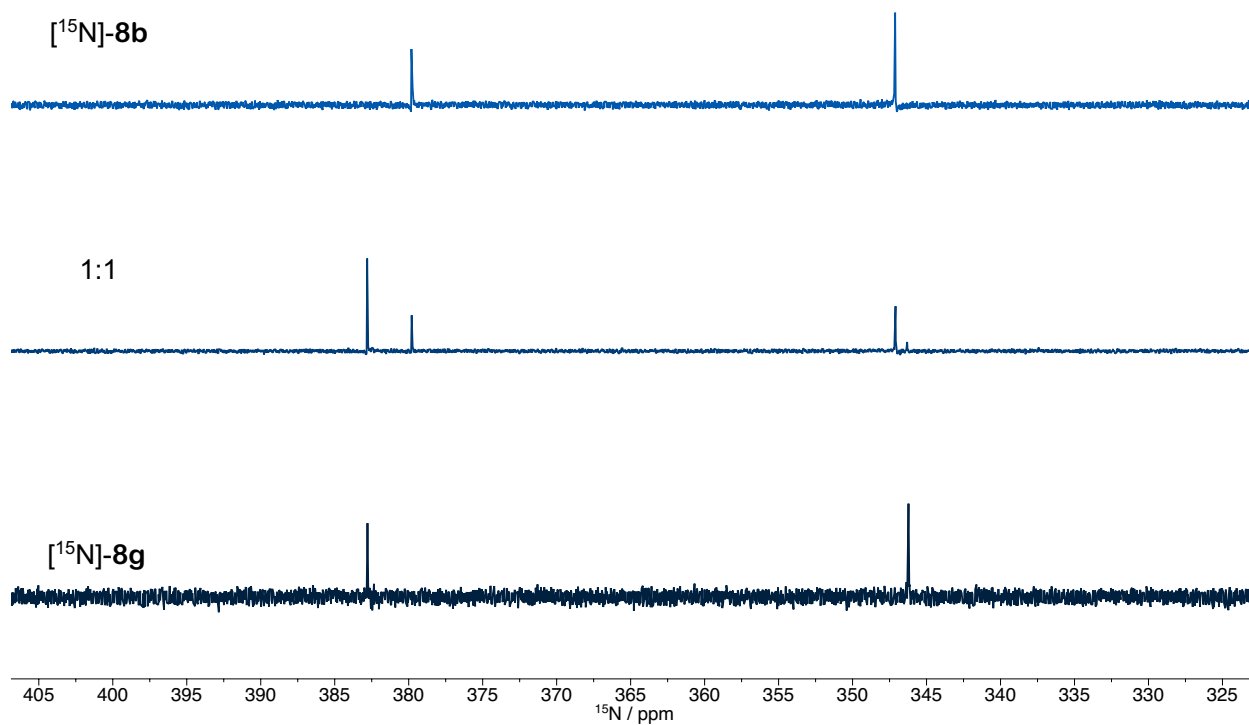
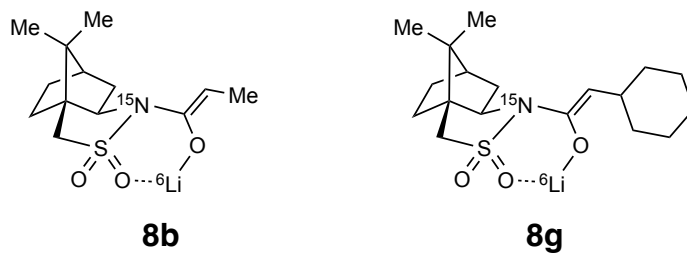


Figure S63. ¹⁵N NMR spectra of 0.10 M mixtures of [⁶Li,¹⁵N]-(*S*)-**8b** and [⁶Li,¹⁵N]-(*S*)-**8g** in neat THF at $-80\text{ }^{\circ}\text{C}$. Resolution of the new mixed aggregate (**A₁B₁**) is poor

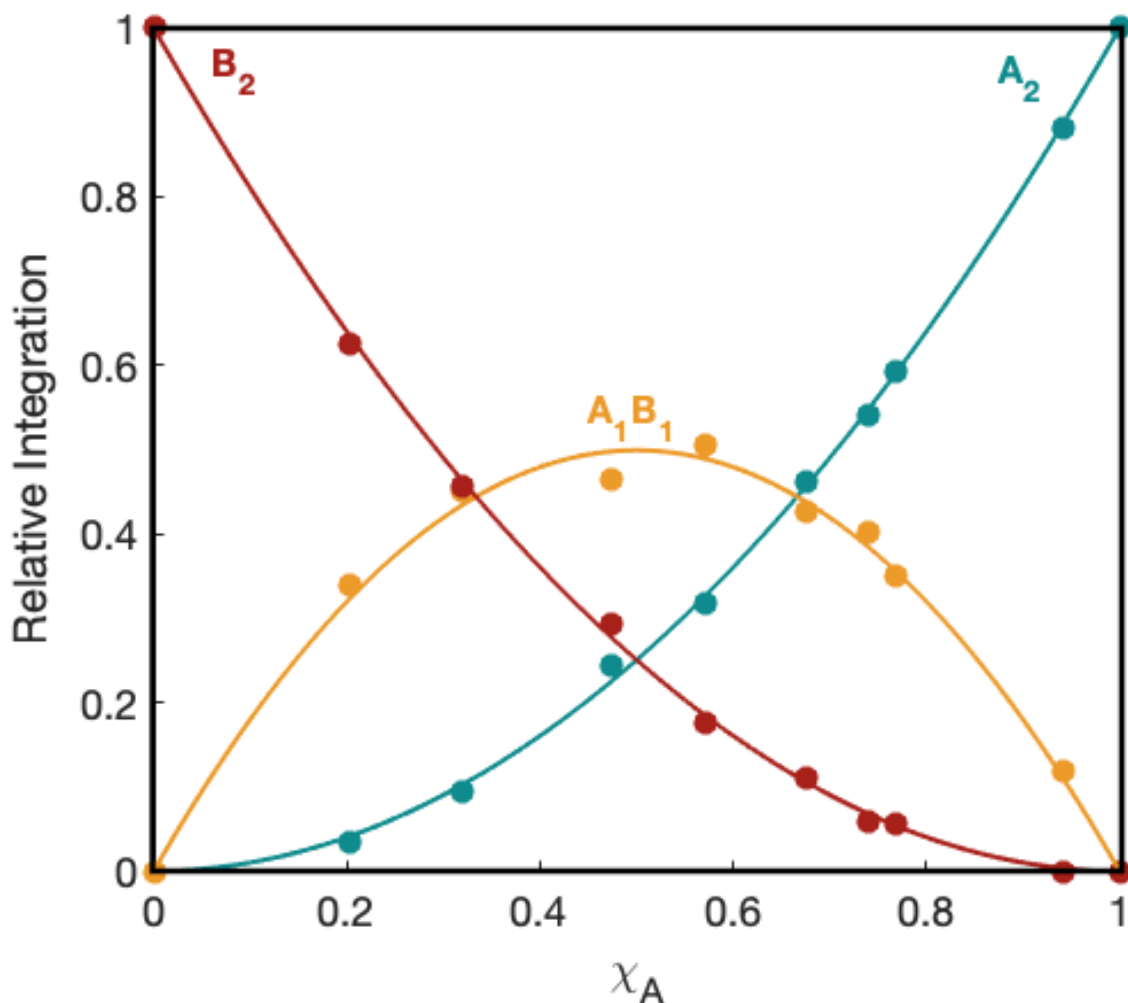


Figure S65. ^6Li Job plot showing relative integrations of the two homoaggregates of $[\text{}^6\text{Li}]$ -(S)-**8b** (blue) and $[\text{}^6\text{Li}]$ -(S)-**8g** (red) and their mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]$ -(S)-**8b** for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]$ -(S)-**8b** and $[\text{}^6\text{Li}]$ -(S)-**8g** in neat THF at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (Figure S64). The curves result from a parametric fit to a single aggregate dimer model.

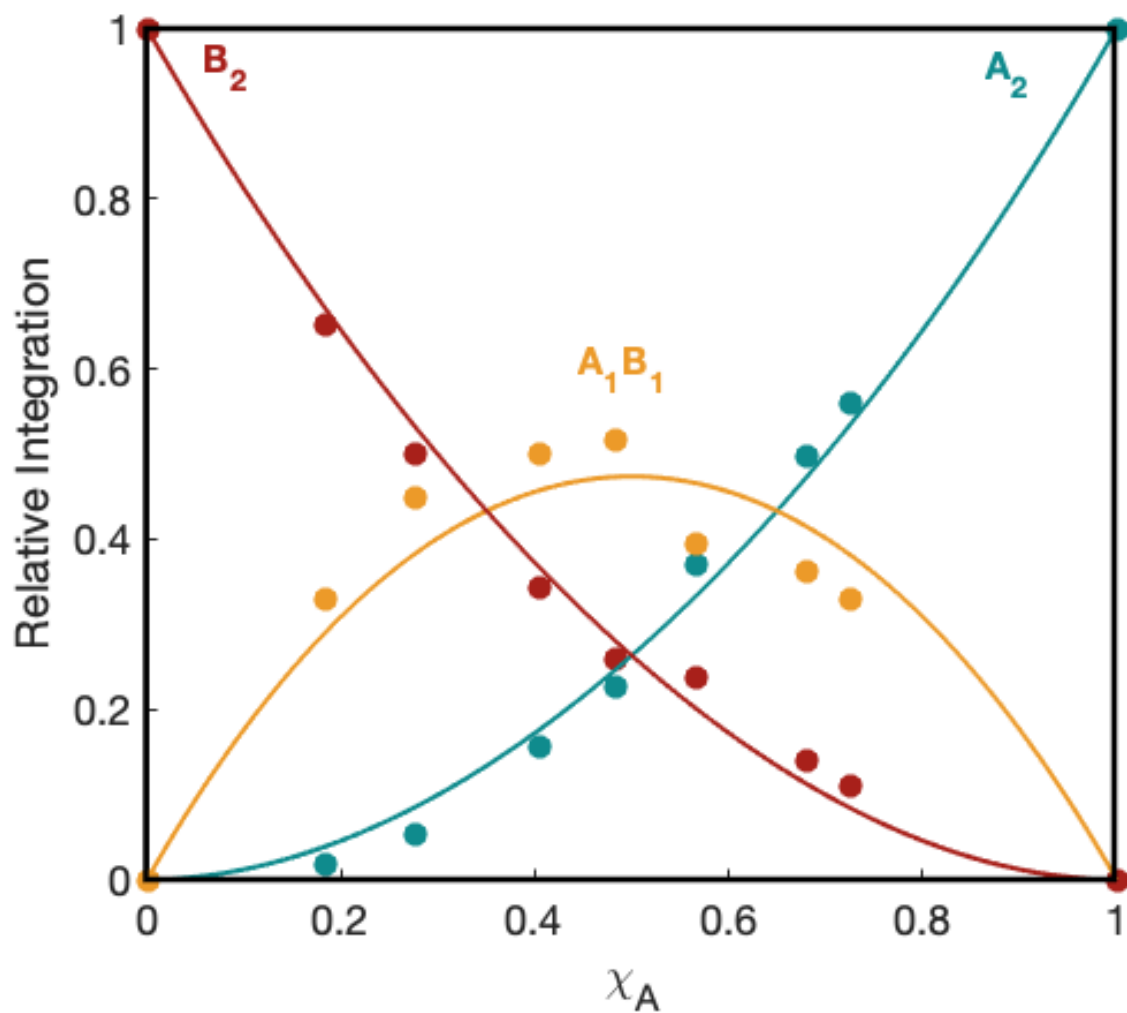


Figure S67. ^6Li Job plot showing relative integrations the two homoaggregates of $[^6\text{Li}]-(S)\text{-8b}$ (blue) and $[^6\text{Li}]-(S)\text{-8e}$ (red) and their mixed dimer (orange) against the measured mole fraction of $[^6\text{Li}]-(S)\text{-8b}$ for 0.10 M mixtures of lithium enolates $[^6\text{Li}]-(S)\text{-8b}$ and $[^6\text{Li}]-(S)\text{-8e}$ in neat THF at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (Figure S66). The curves result from a parametric fit to a single aggregate dimer model.

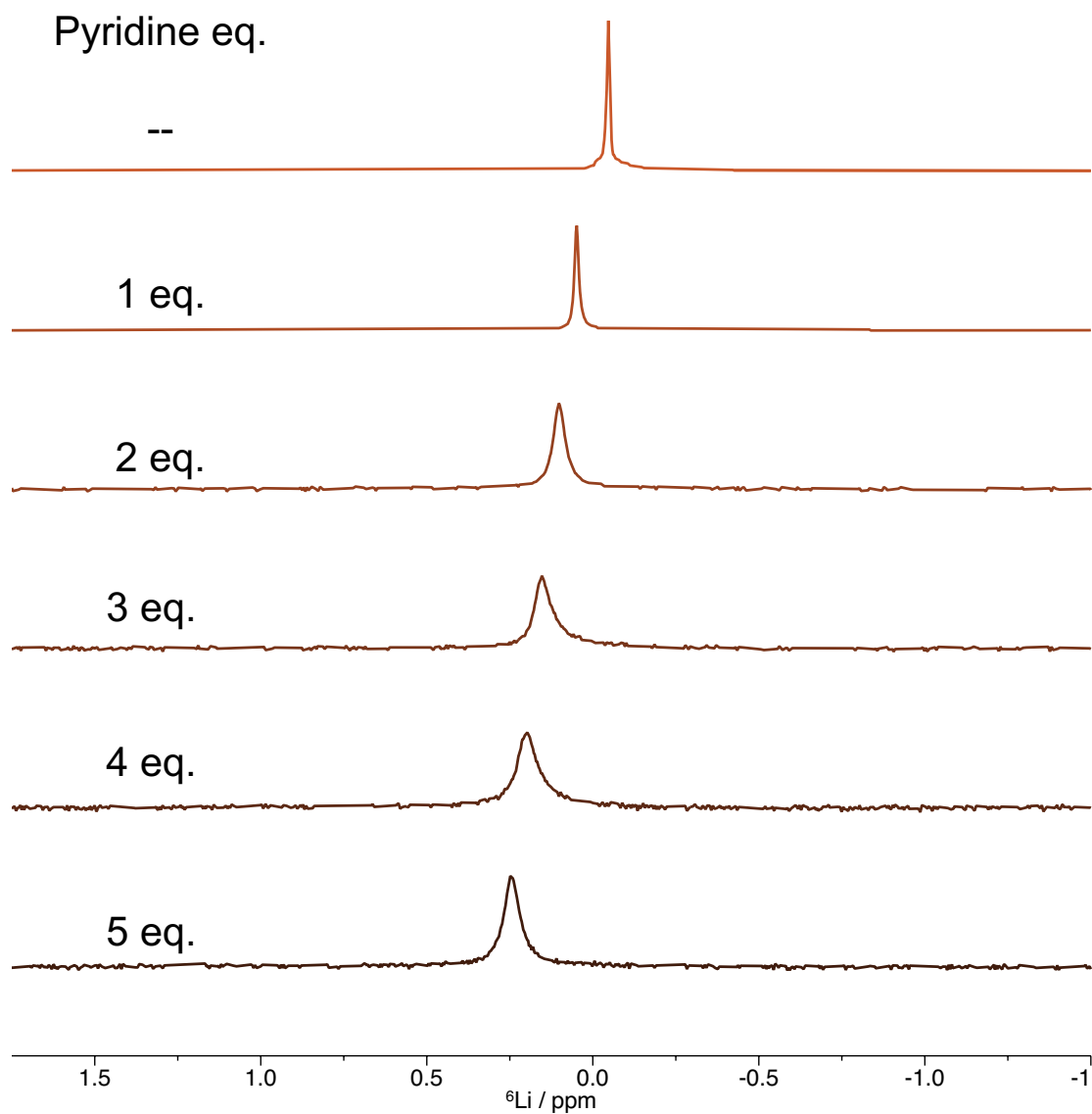
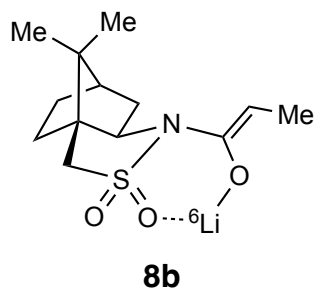


Figure S68. ${}^6\text{Li}$ NMR spectra of a 0.10 M solution of $[{}^6\text{Li}]$ -(S)-**8b** in THF at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine.

HMPA-solvated Oppolzer enolates

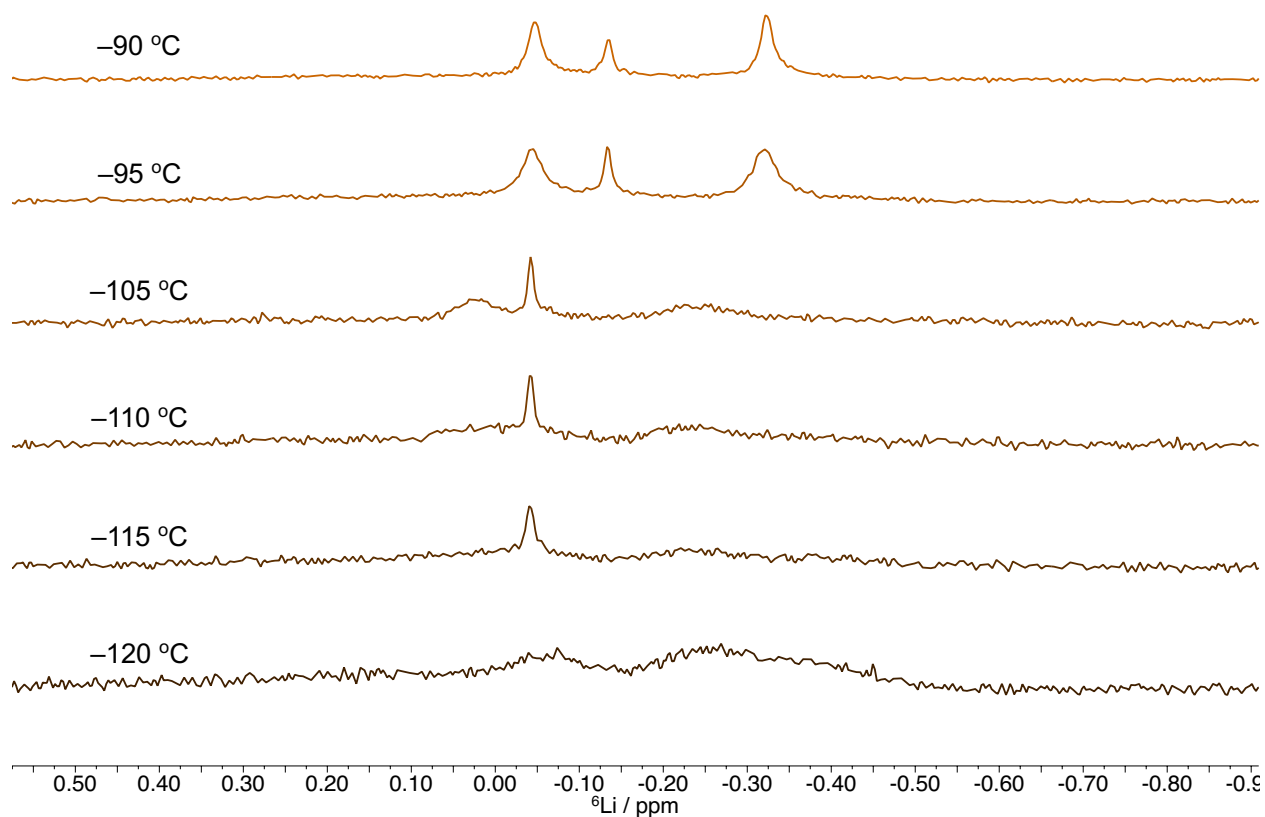
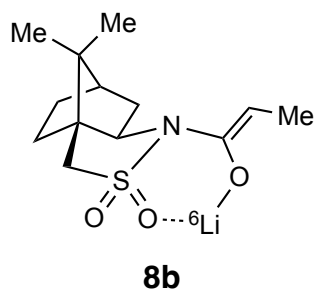


Figure S69. ${}^6\text{Li}$ NMR spectra of 0.10 M $[{}^6\text{Li}]$ -*(S)*-**8b** with 4.0 equiv HMPA in 1:2 THF/pentane at various temperatures.

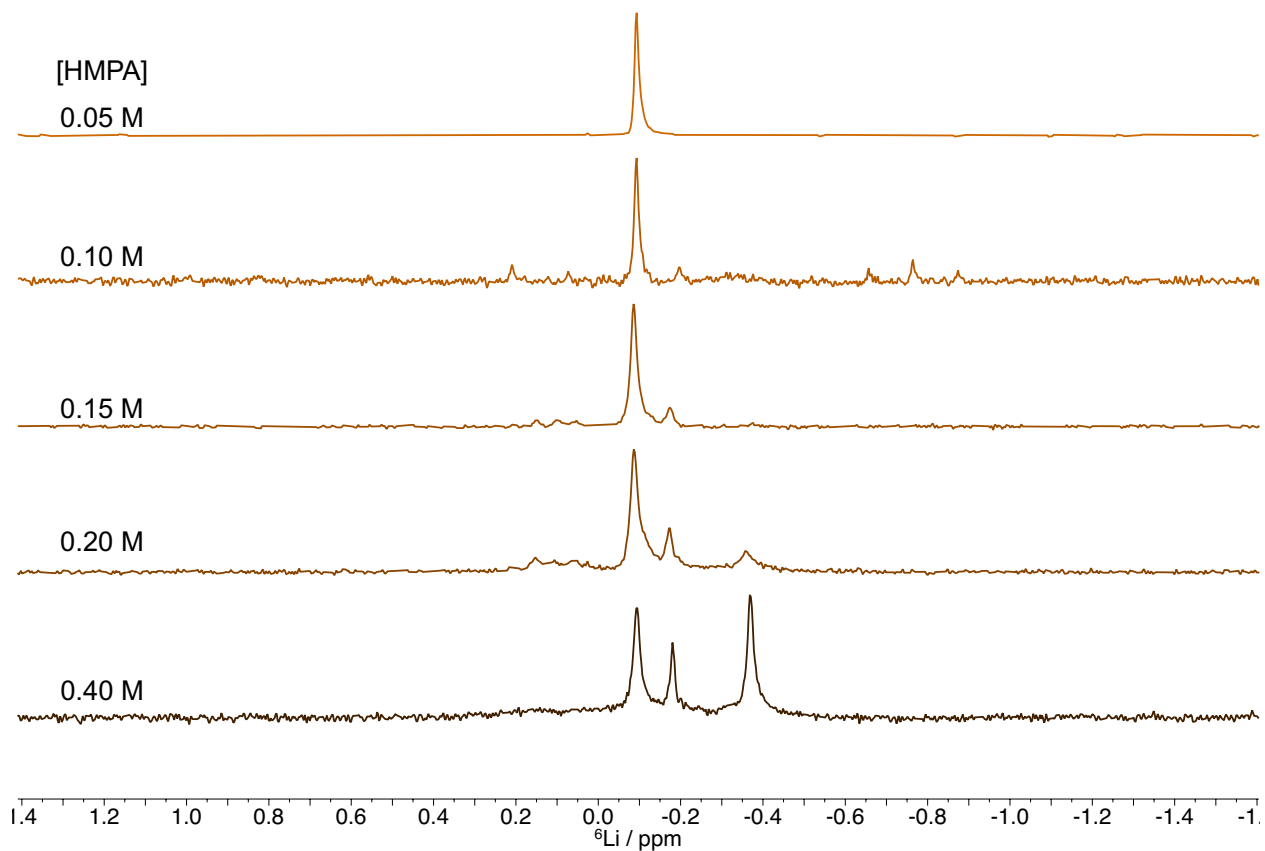
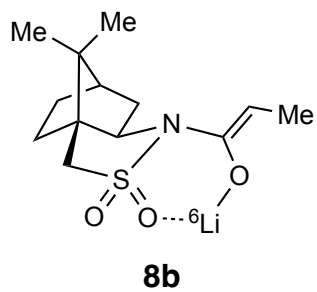


Figure S70. ${}^6\text{Li}$ NMR spectra of 0.10 M ${}^6\text{Li}$ -(*S*)-**8b** with various concentrations of HMPA in 1:2 THF/pentane at $-90\text{ }^\circ\text{C}$.

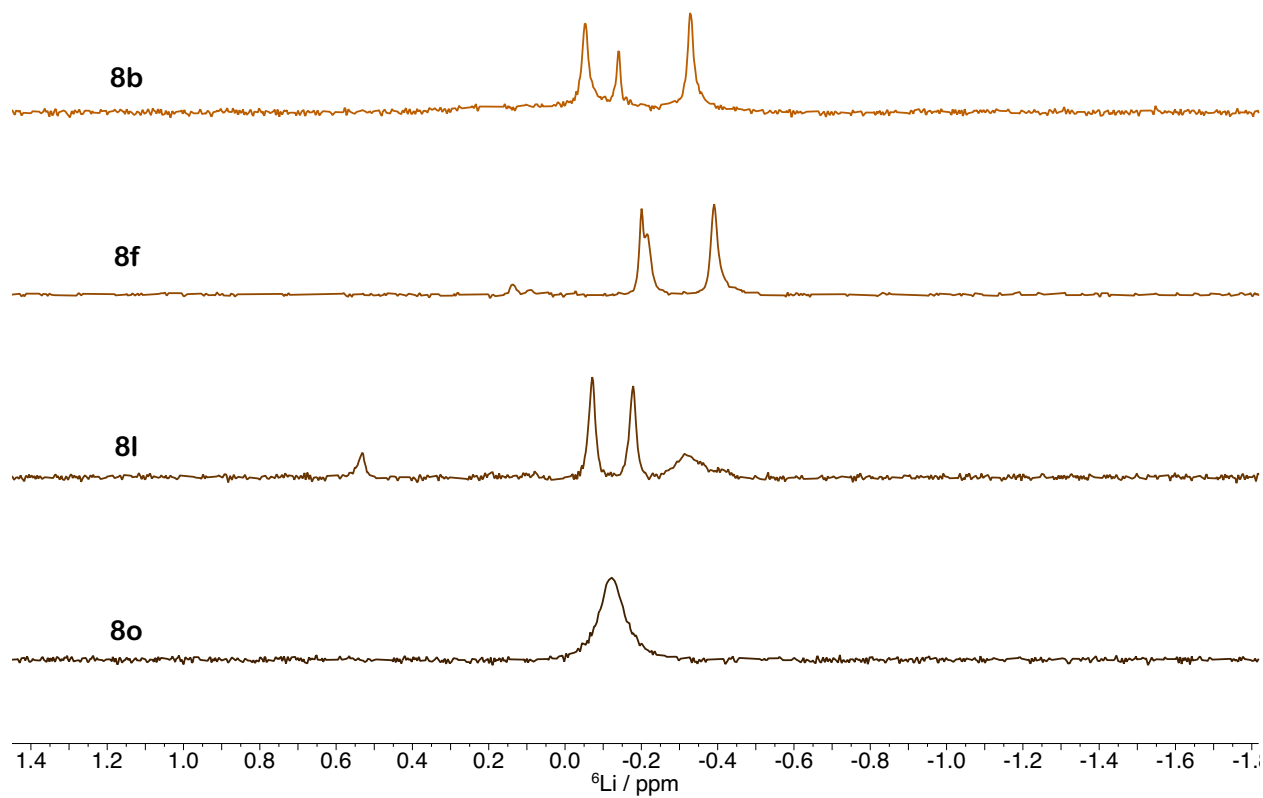


Figure S71. ^6Li NMR spectra of various $[\text{}^6\text{Li}]$ - (S) - N -acyl-camphorsultam-enolates with 3.0 equiv. HMPA in 1:2 THF/pentane.

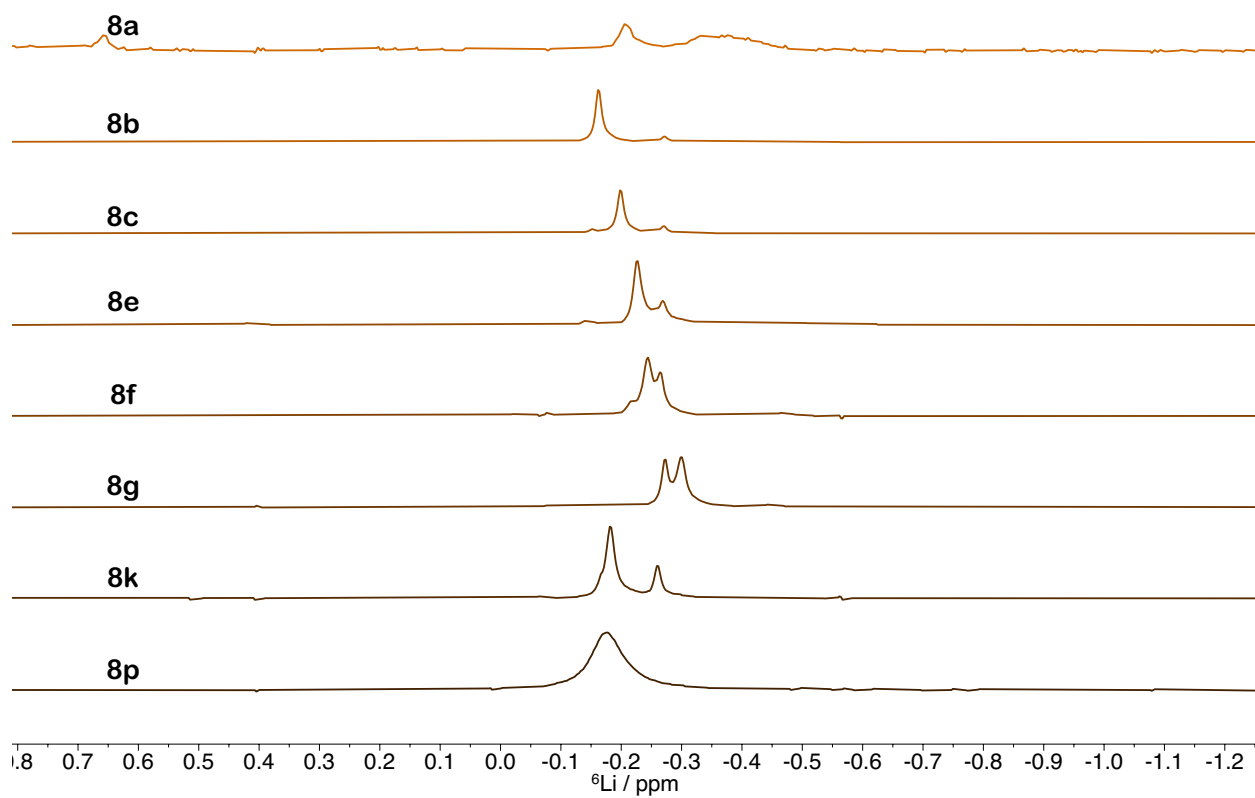


Figure S72. ^6Li NMR spectra of various [^6Li]-(*S*)-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in 1:1 THF/pentane at -90°C .

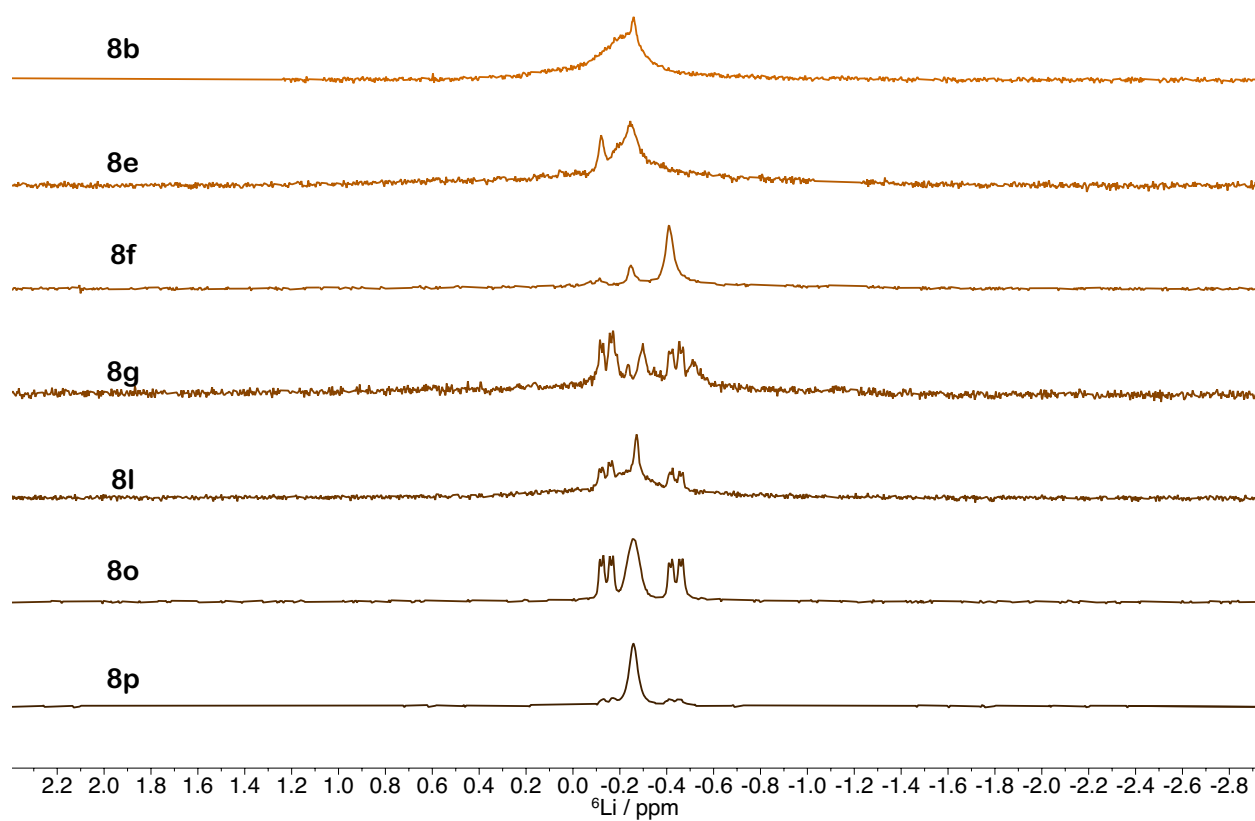


Figure S73. ^6Li NMR spectra of various $[\text{}^6\text{Li}]$ -*(S)*-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.

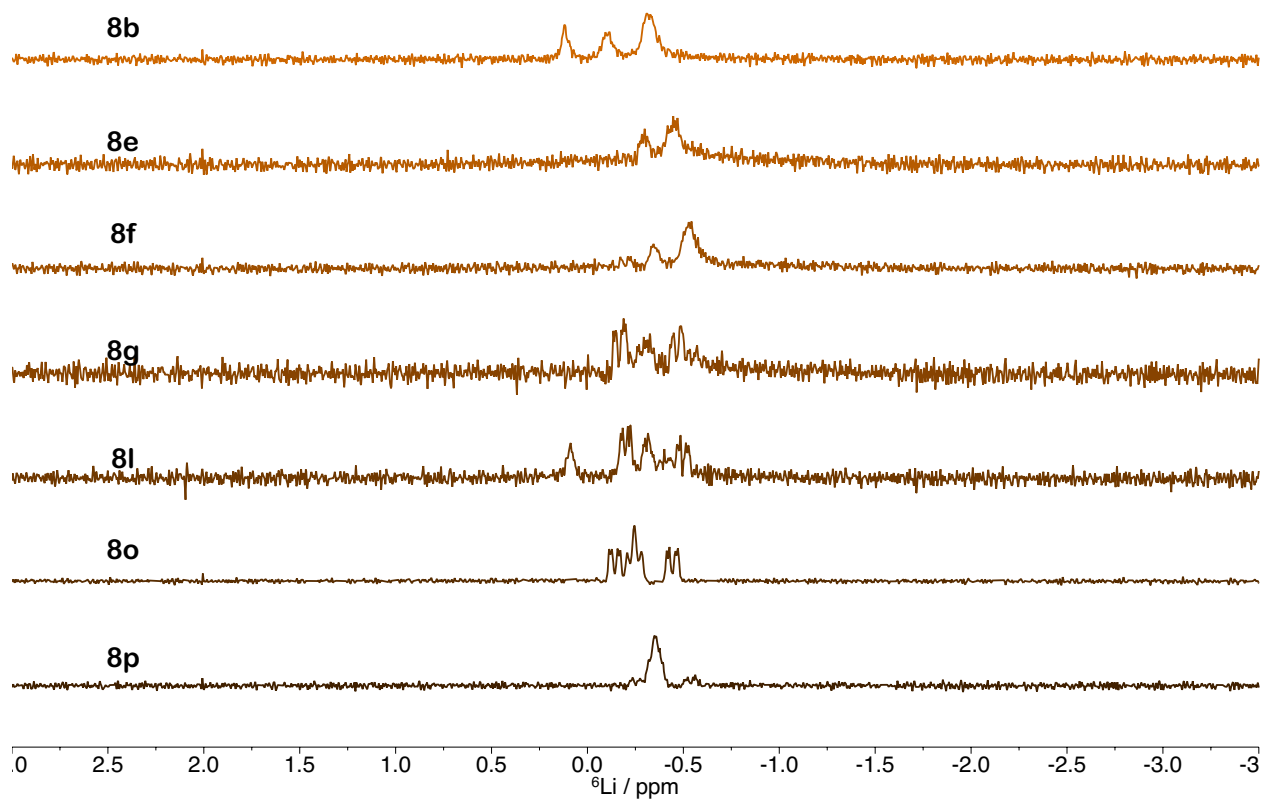


Figure S74. ^6Li NMR spectra of various ^6Li -(*S*)-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.

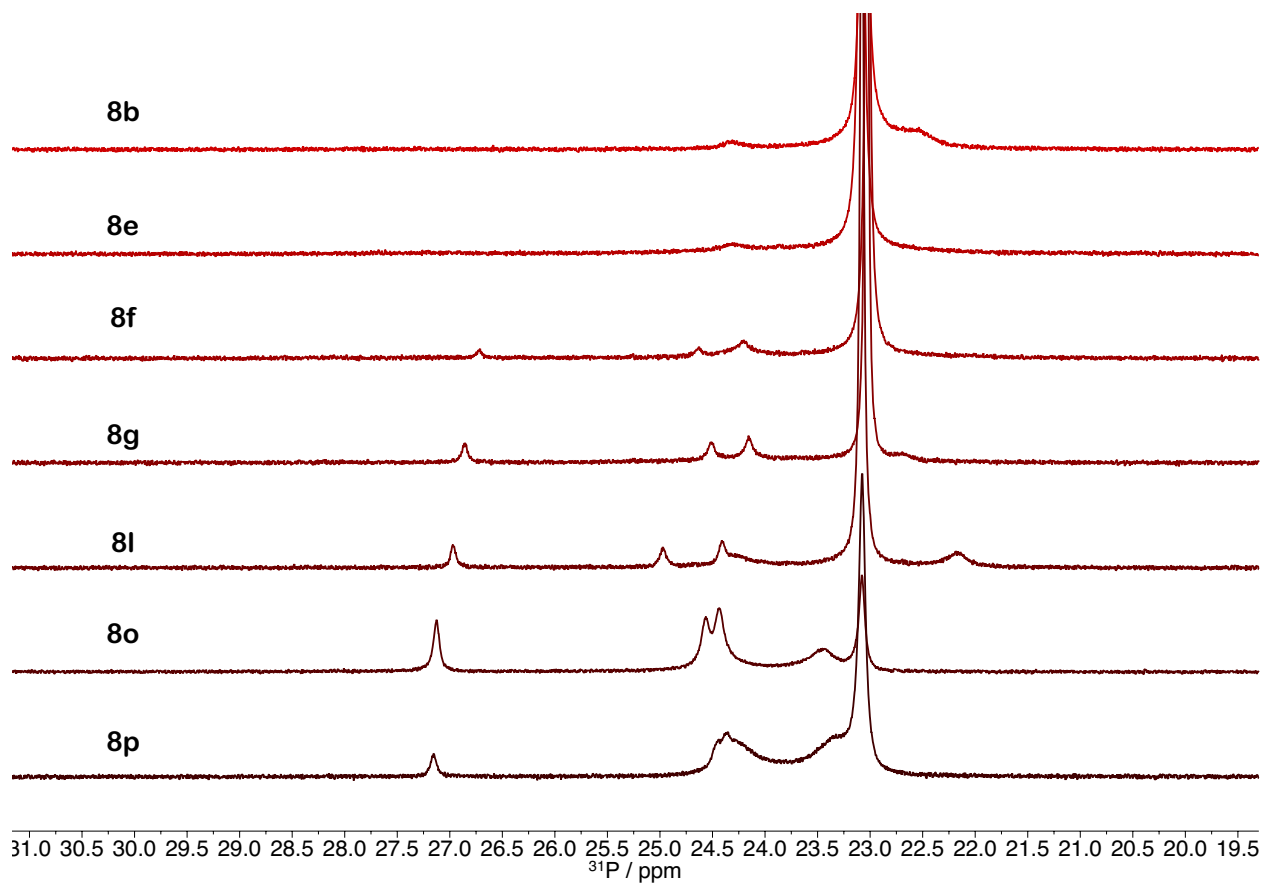


Figure S75. ^{31}P NMR spectra of various $[\text{}^6\text{Li}]$ -(*S*)-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.

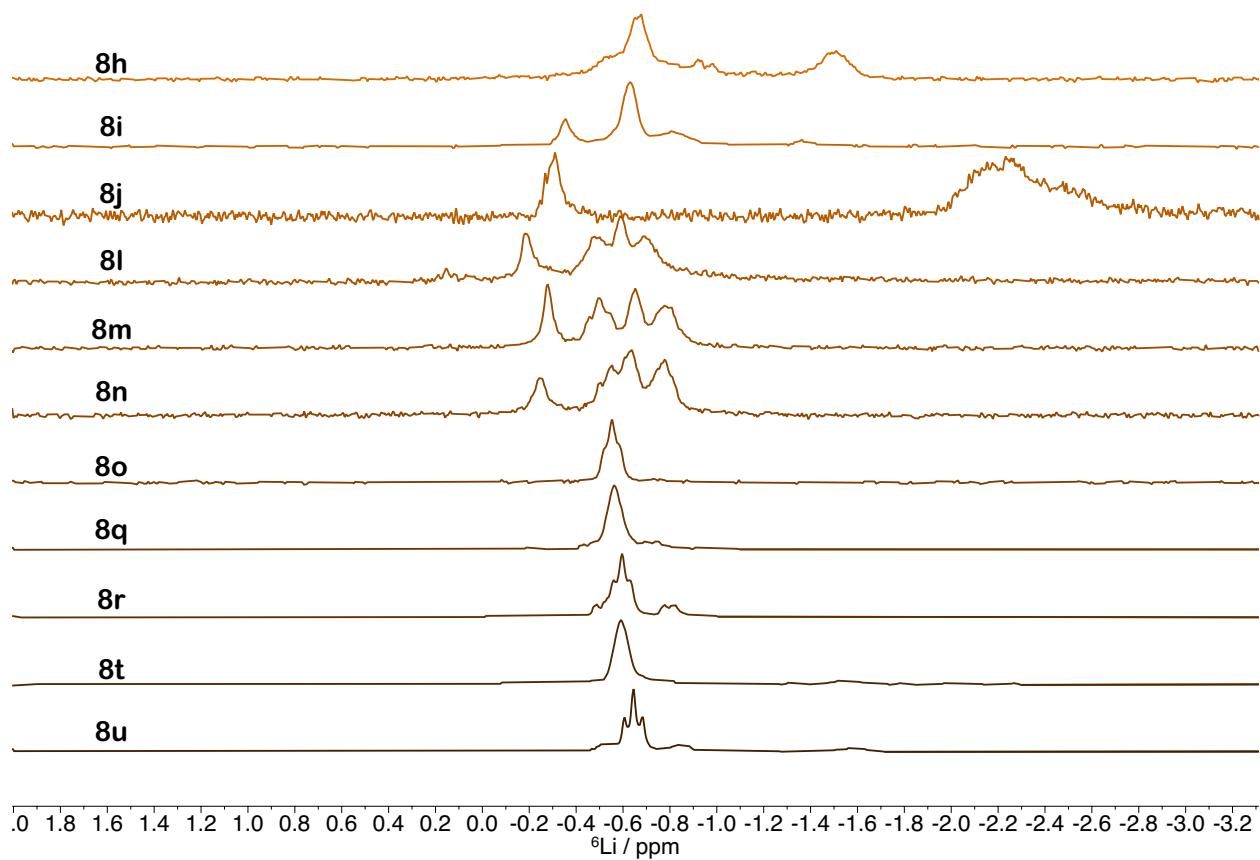


Figure S76. ^6Li NMR spectra of various $[\text{}^6\text{Li}]$ - (S) - N -acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-100\text{ }^\circ\text{C}$.

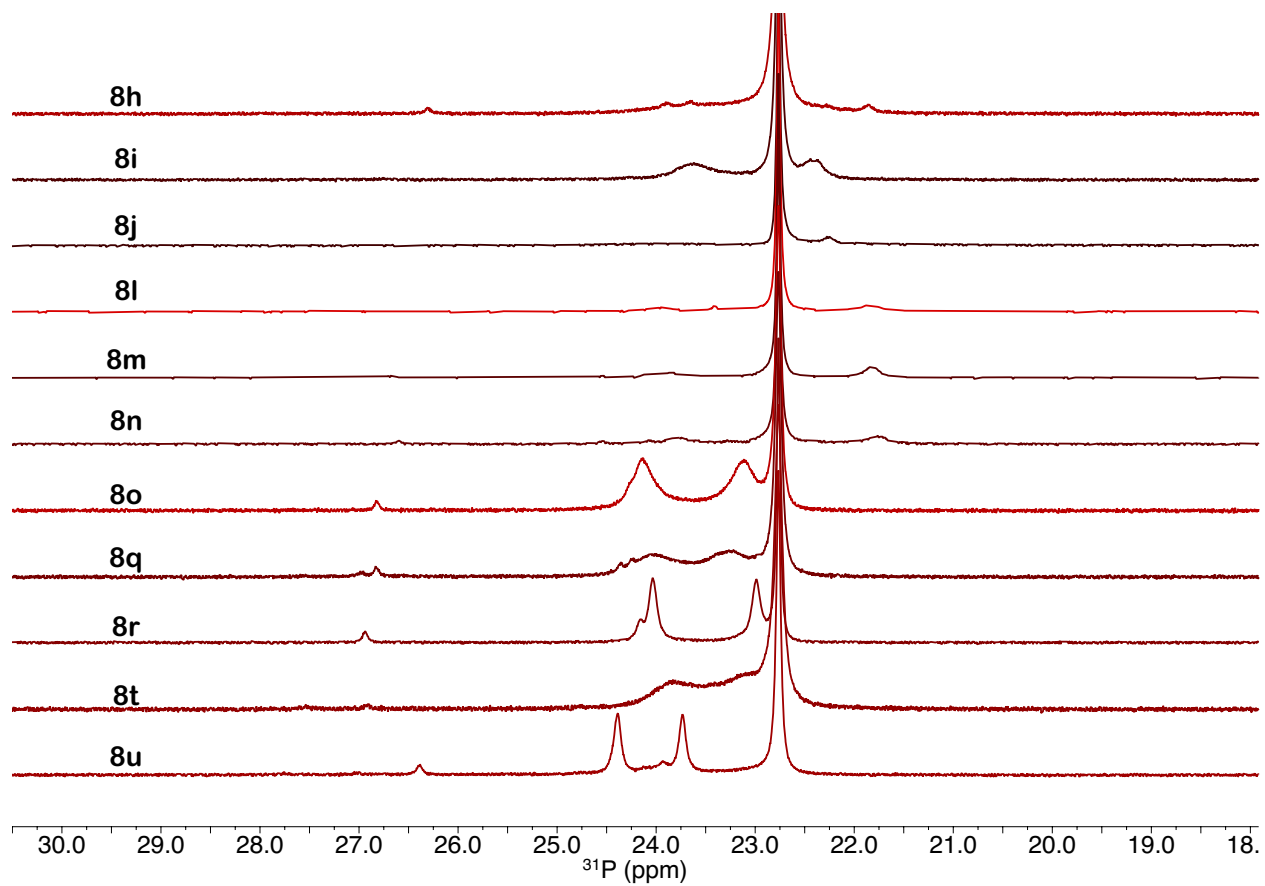


Figure S77. ^{31}P NMR spectra of various $[\text{}^6\text{Li}]$ -(*S*)-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.

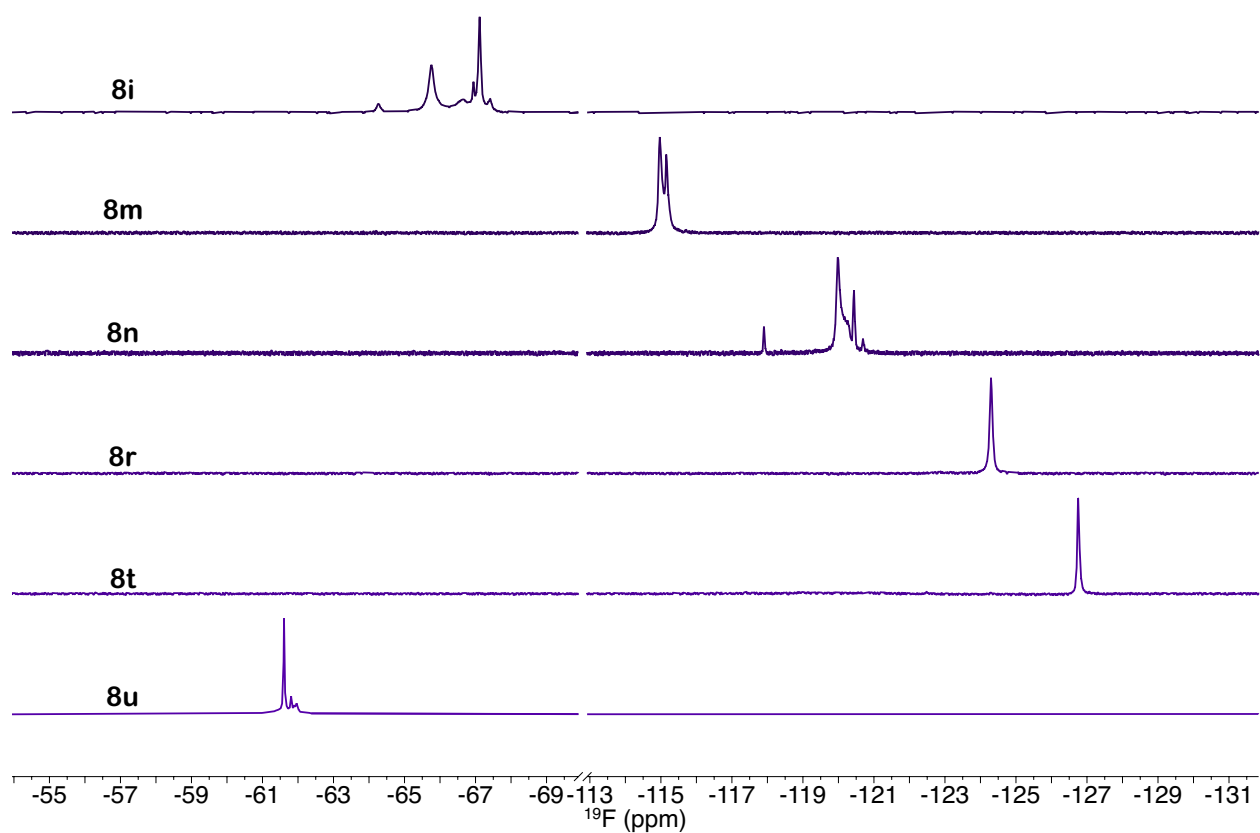


Figure S78. ^{19}F NMR spectra of various $[\text{}^6\text{Li}]$ -(*S*)-*N*-acyl-camphorsultam-enolates with 3.0 equiv. HMPA in toluene at $-90\text{ }^\circ\text{C}$.

HMPA-solvated aryl acetamide-derived enolate monomers

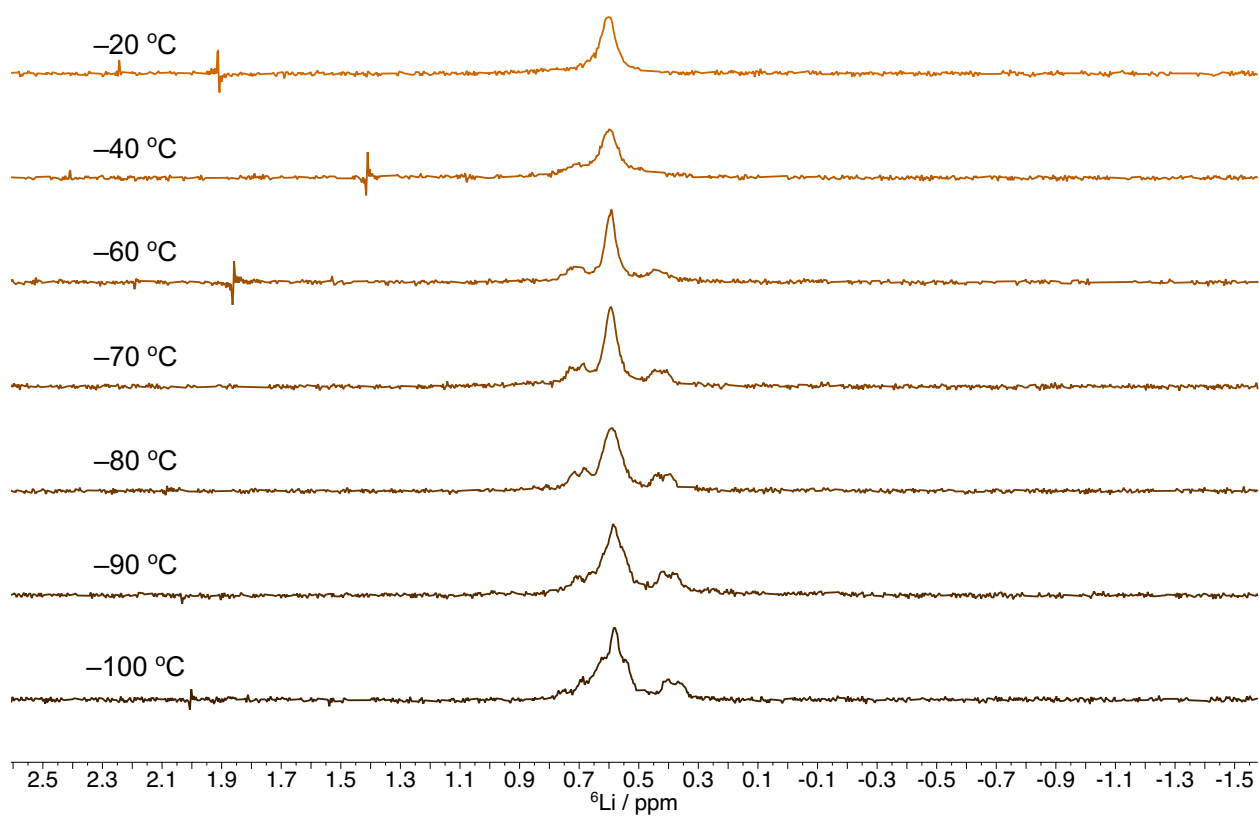
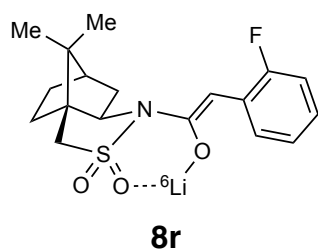


Figure S79. ⁶Li NMR spectra of [6Li]-(S)-8r with 1.5 equiv HMPA in toluene at various temperatures.

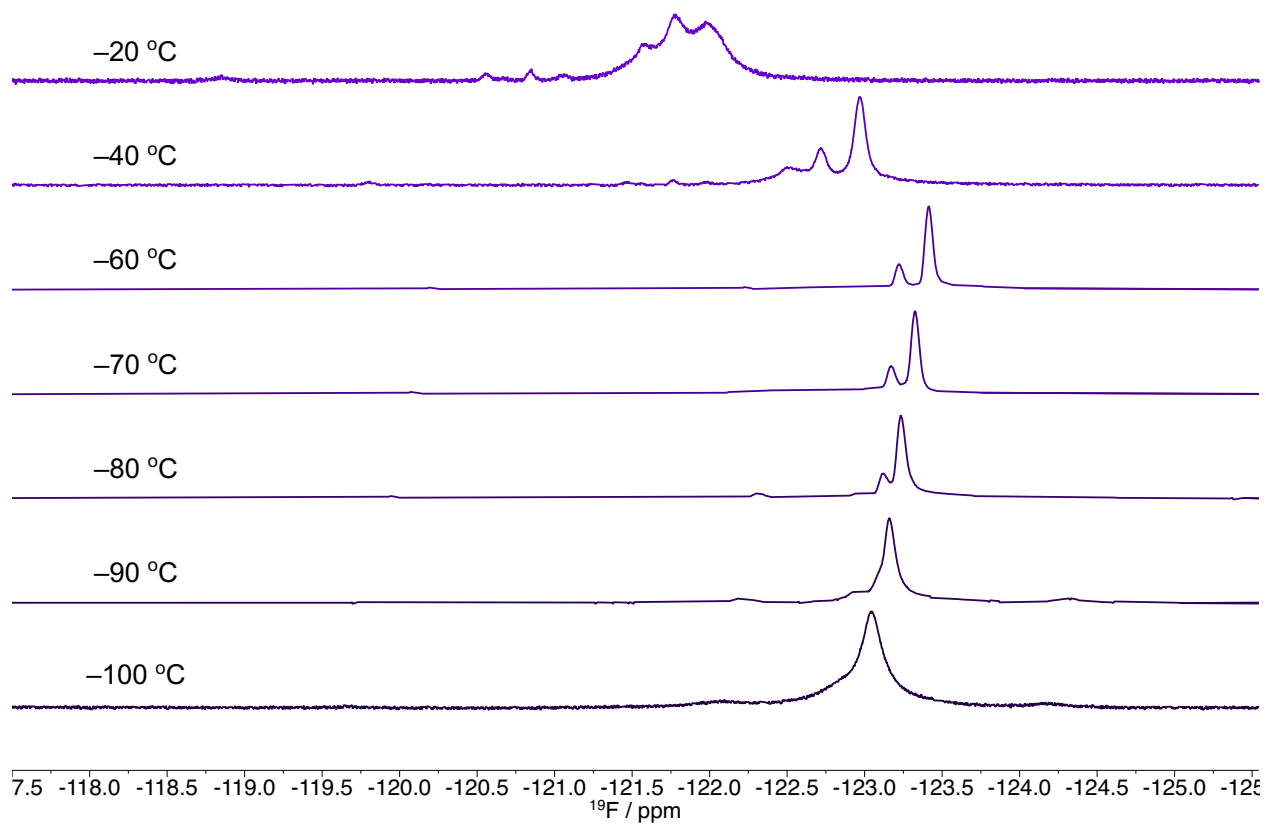
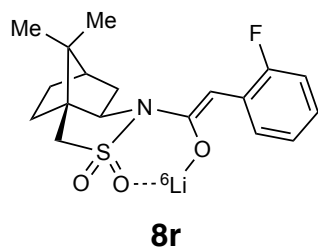


Figure S80. ¹⁹F NMR spectra of [⁶Li]-(S)-8r with 1.5 equiv HMPA in toluene at various temperatures.

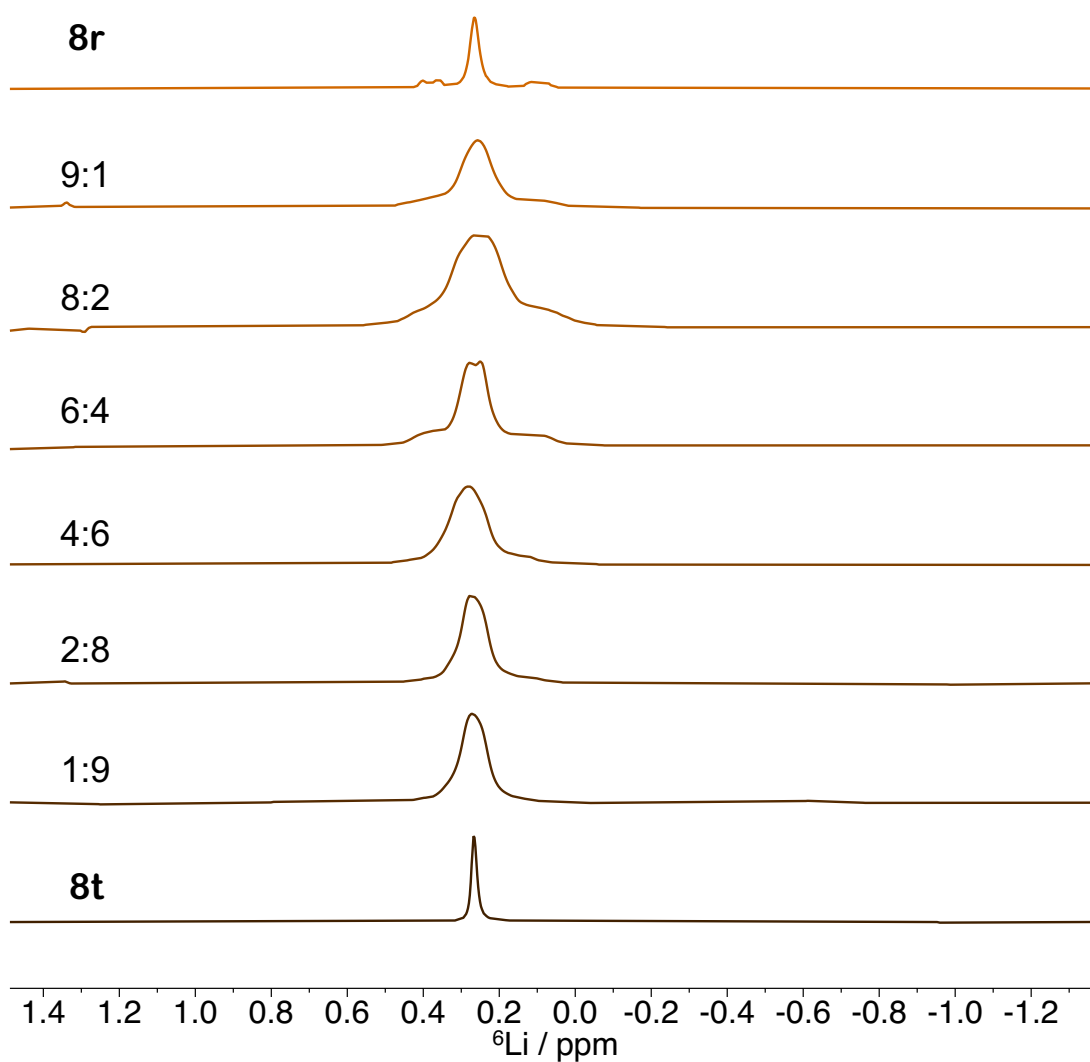
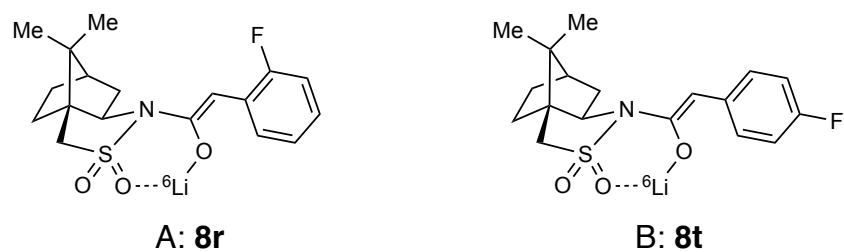
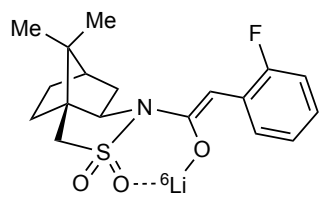
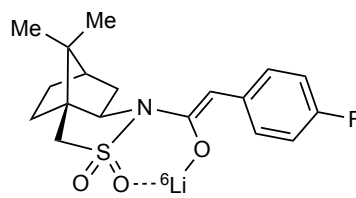


Figure S81. ^6Li NMR spectra of 0.10 M mixtures of $[\text{}^6\text{Li}]\text{-(S)-8r}$ (A) and $[\text{}^6\text{Li}]\text{-(S)-8t}$ (B) with 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$. Severe overlap of the two enolates prevents accurate integration. A:B represents the total molar ratio of the two enolates.



A: **8r**



B: **8t**

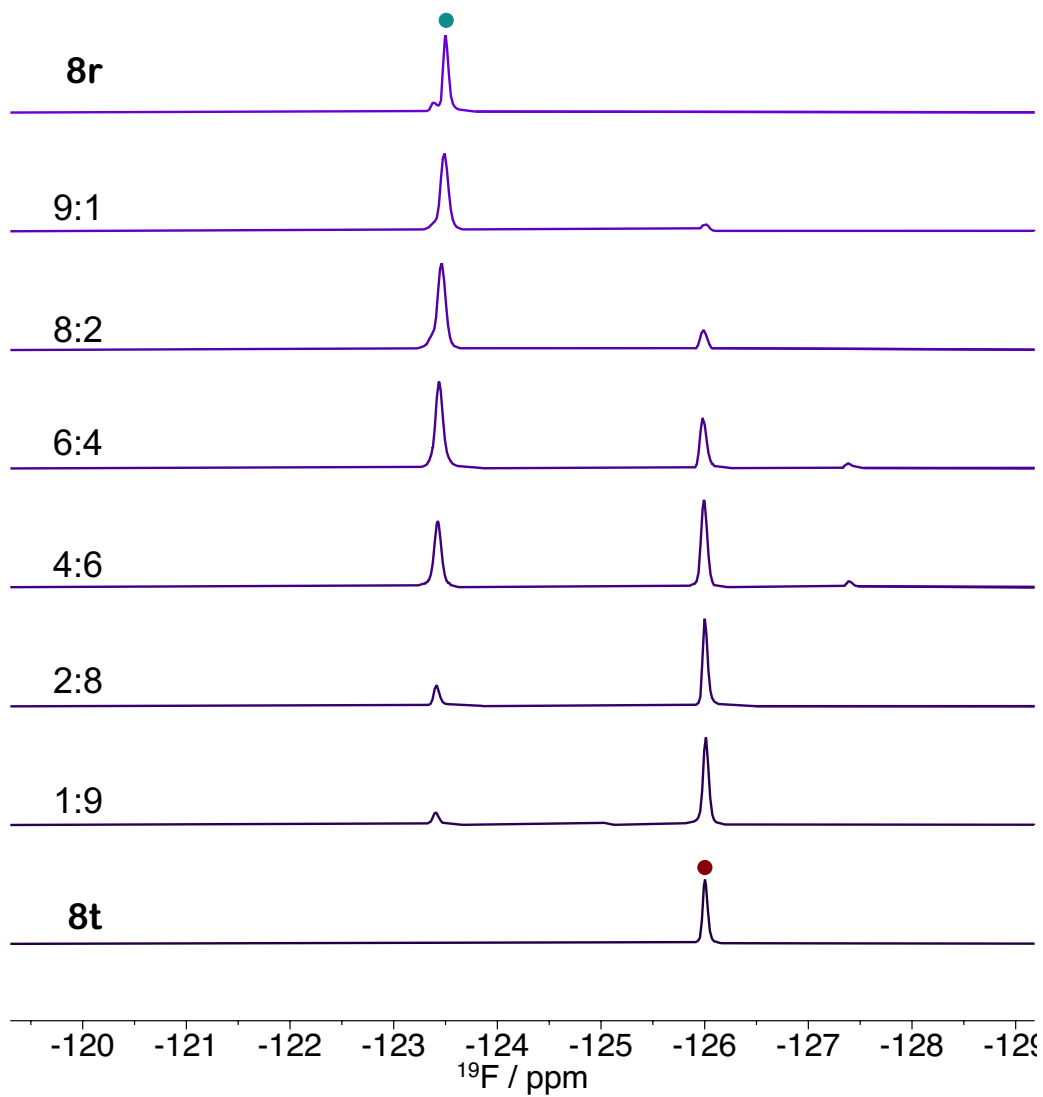


Figure S82. ^{19}F NMR spectra of 0.10 M mixtures of $[\text{}^6\text{Li}]\text{-(S)-8r}$ (A) and $[\text{}^6\text{Li}]\text{-(S)-8t}$ (B) with 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$. A:B represents the total molar ratio of the two enolates.

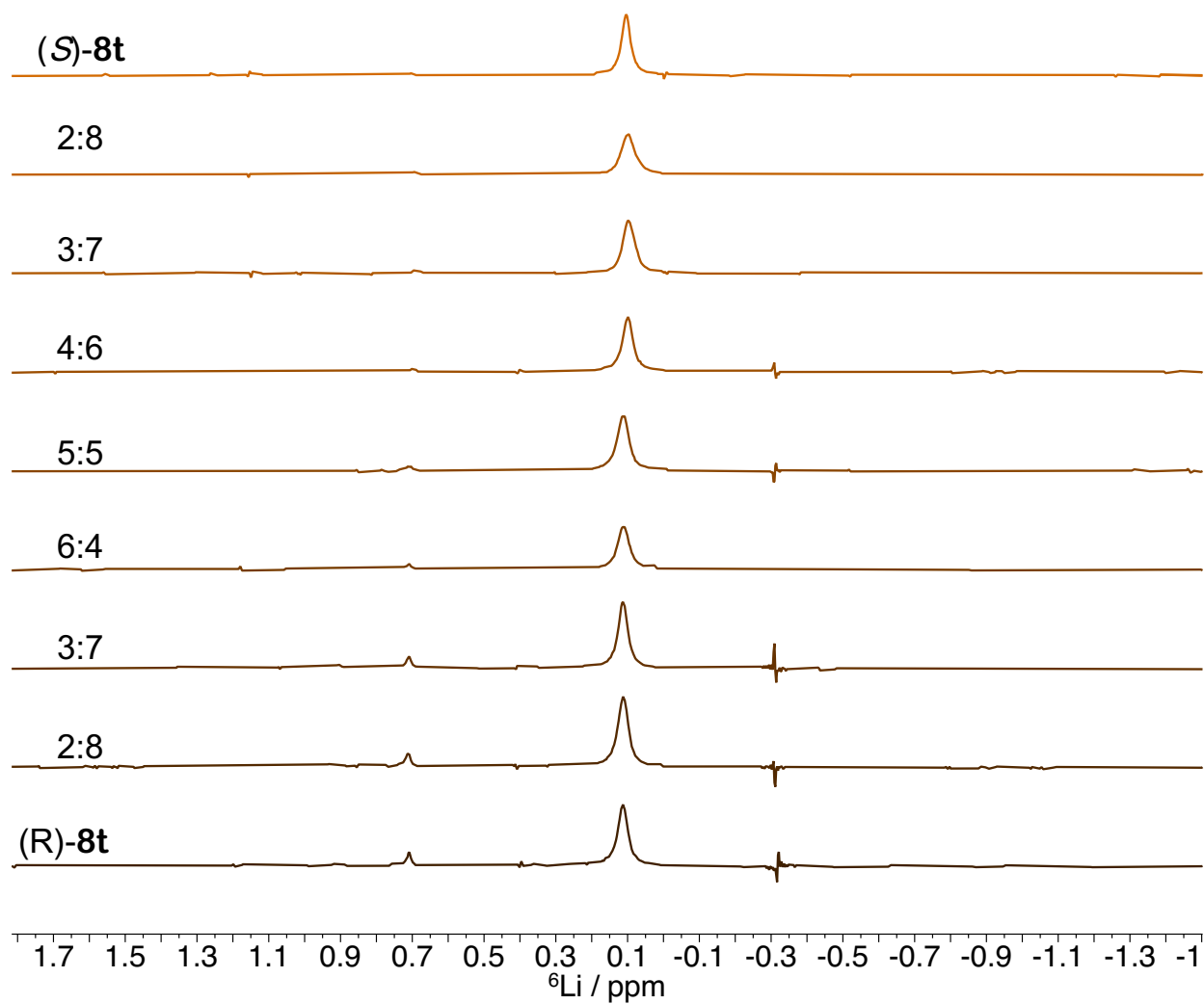
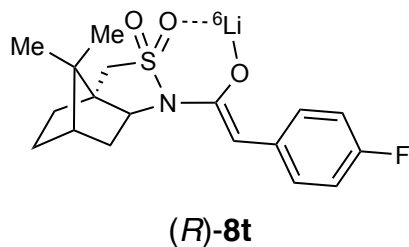
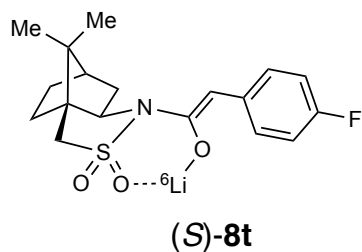


Figure S83. ${}^6\text{Li}$ NMR spectra of 0.10 M mixtures of $[{}^6\text{Li}]$ -(*R*)-8t and $[{}^6\text{Li}]$ -(*S*)-8t with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$. *R*:*S* represents the total molar ratio of the two enantiomers.

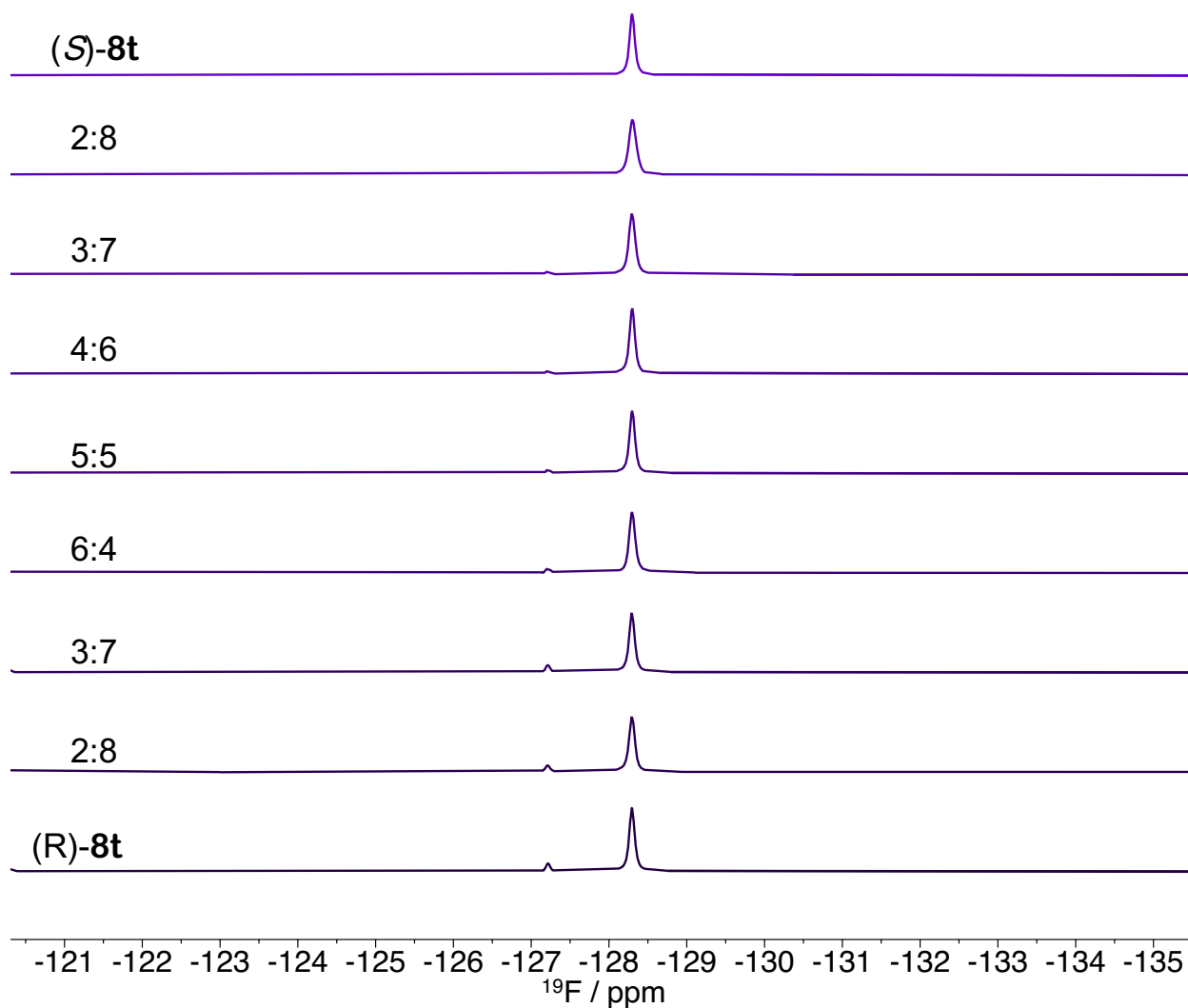
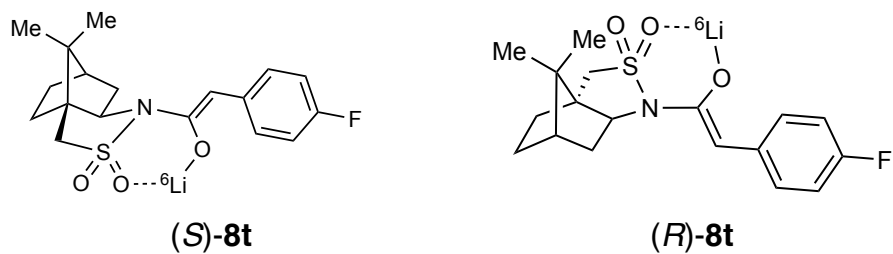


Figure S84. ^{19}F NMR spectra of 0.10 M mixtures of $[\text{}^6\text{Li}]\text{-}(R)\text{-8t}$ and $[\text{}^6\text{Li}]\text{-}(S)\text{-8t}$ with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$. *R:S* represents the total molar ratio of the two enantiomers.

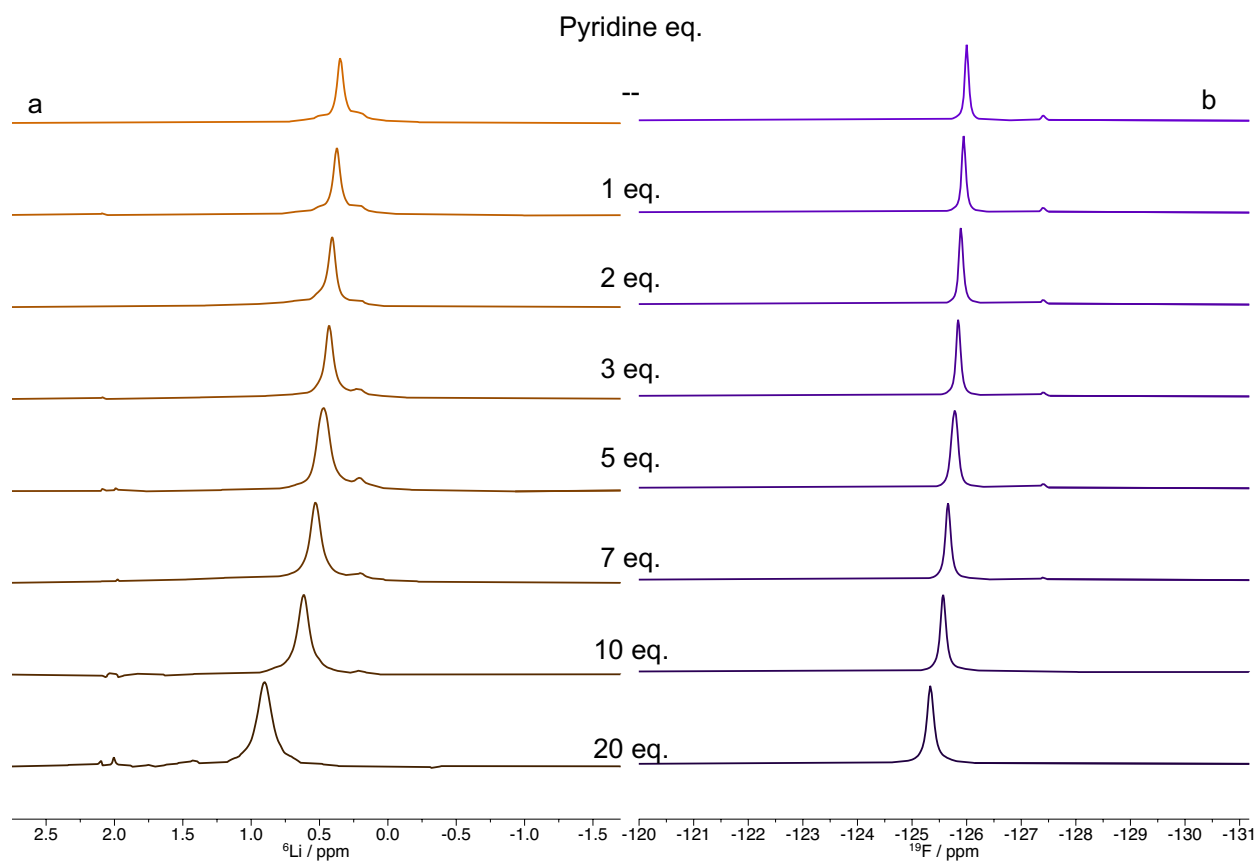
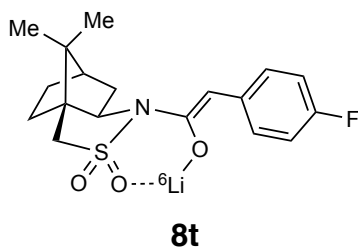


Figure S85. a | ${}^6\text{Li}$ NMR spectra of a 0.10 M solution of [${}^6\text{Li}$]-(*S*)-**8t** with 3 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine. **b** | The corresponding ${}^{19}\text{F}$ NMR spectra.

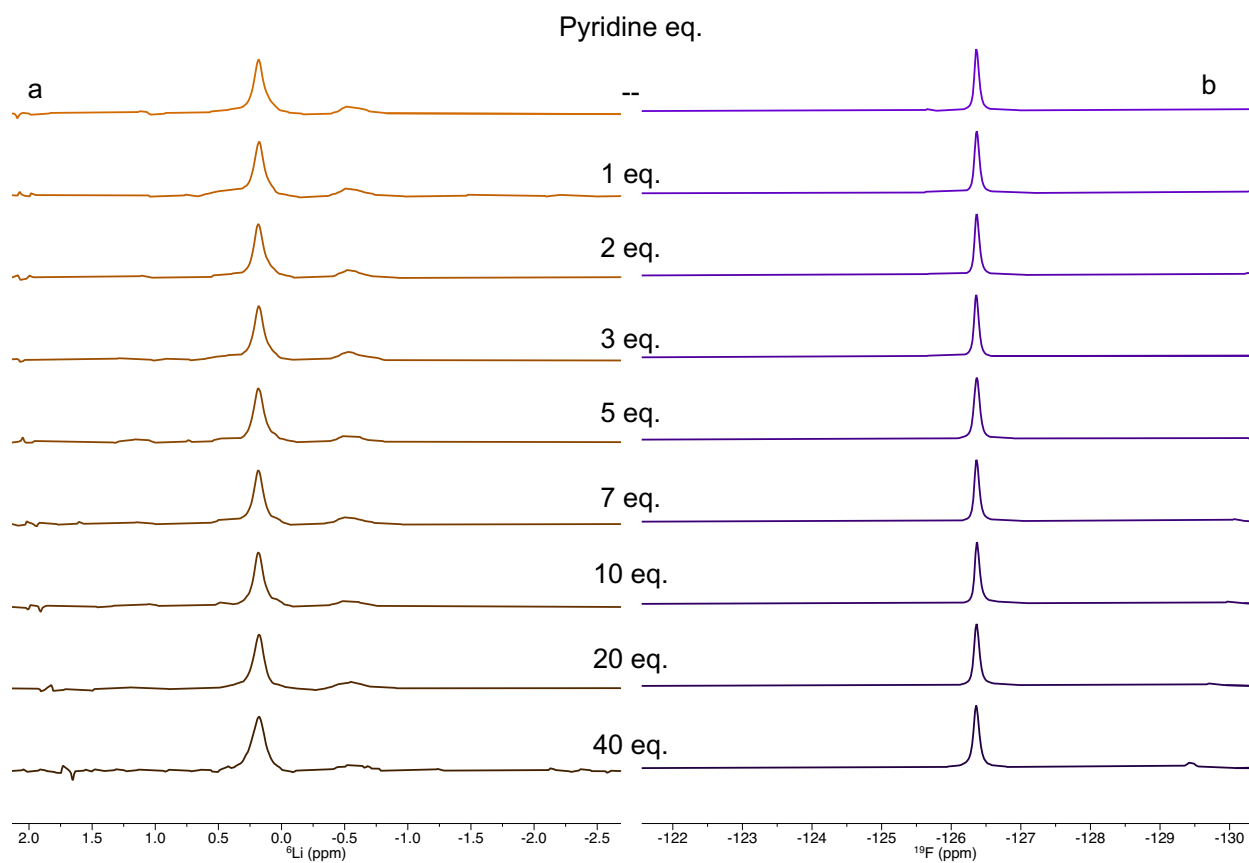
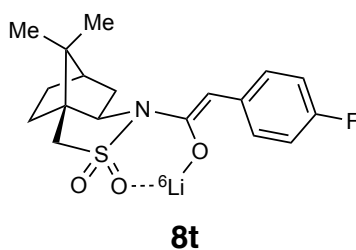


Figure S86. a | ${}^6\text{Li}$ NMR spectra of a 0.10 M solution of $[{}^6\text{Li}]\text{-}(S)\text{-8t}$ with 13 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of pyridine. **b** | The corresponding ${}^{19}\text{F}$ NMR spectra.

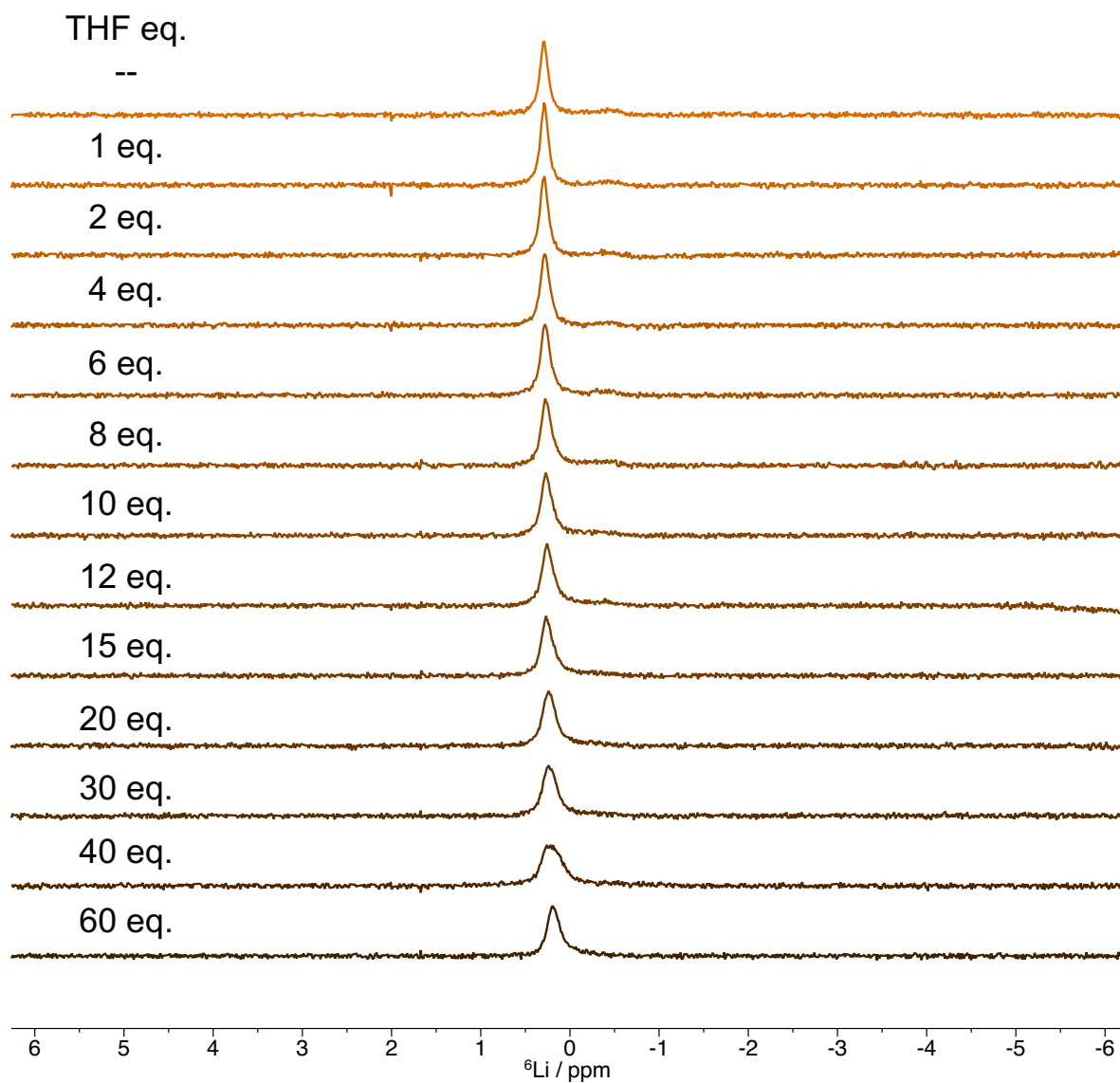
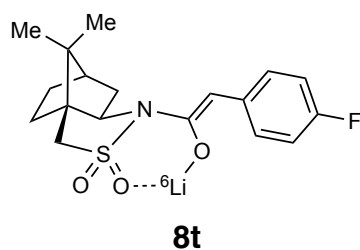


Figure S87. ⁶Li NMR spectra of a 0.10 M solution of [⁶Li]-(S)-8t in 13 equiv HMPA in toluene at -80 °C with varying concentrations of THF.

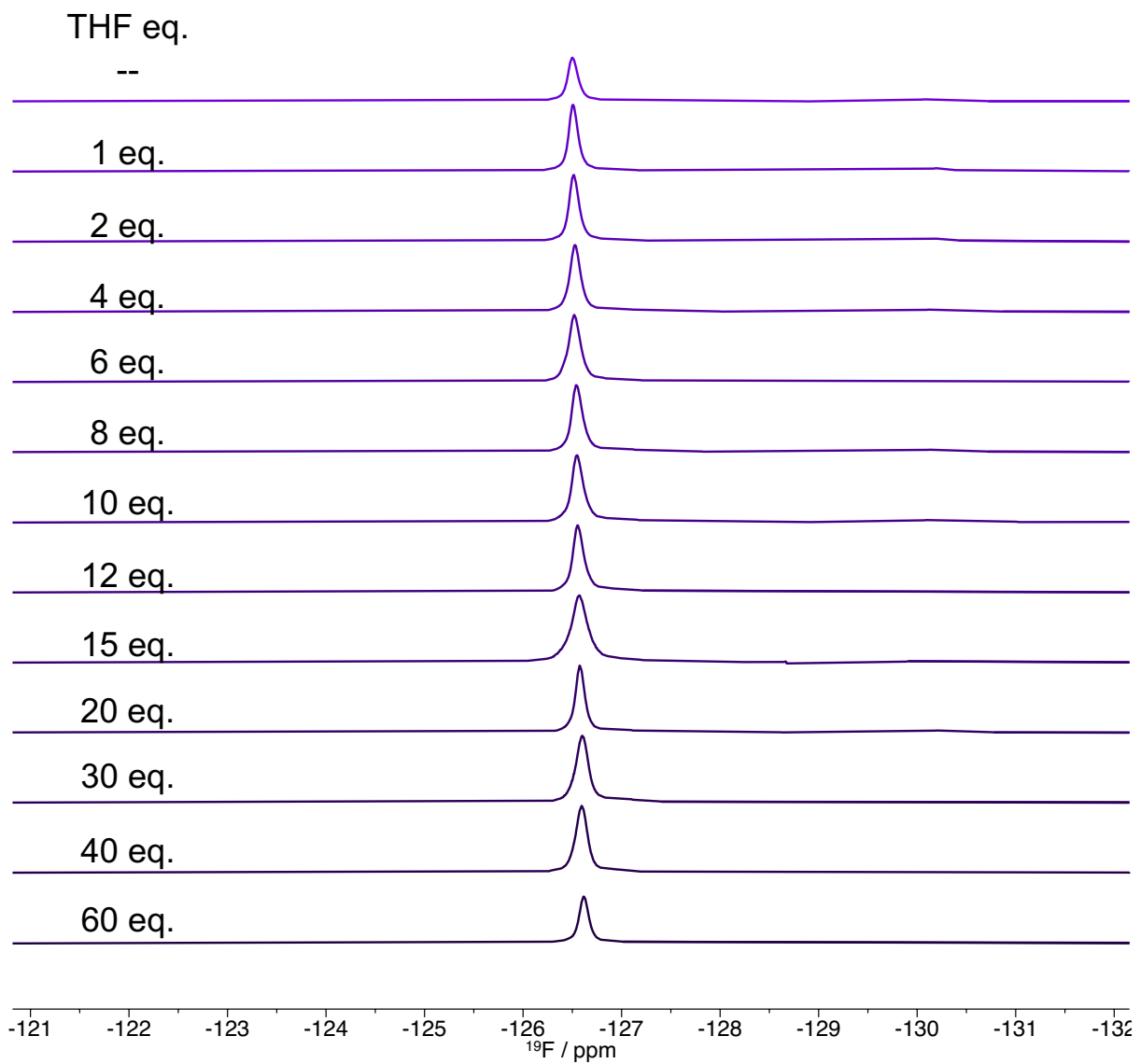
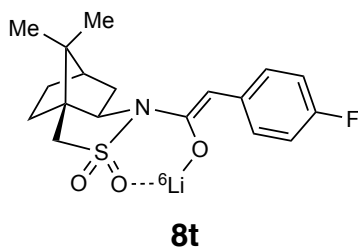


Figure S88. ^{19}F NMR spectra of a 0.10 M solution of $[^6\text{Li}]$ -(*S*)-**8t** in 13 equiv HMPA in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of THF.

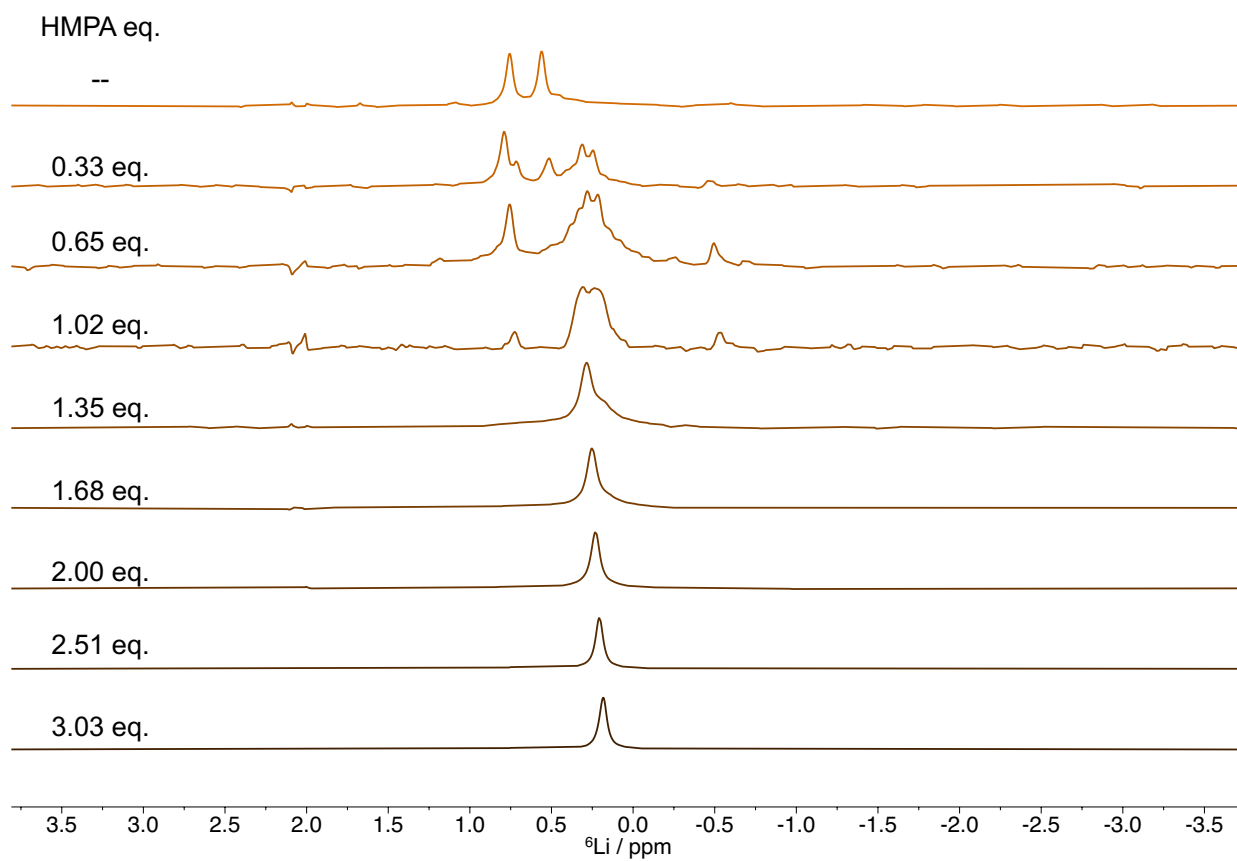
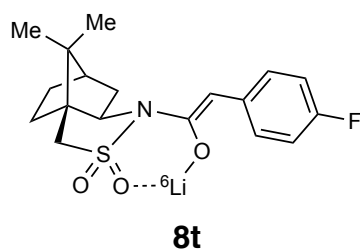


Figure S89. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(*S*)-**8t** in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.

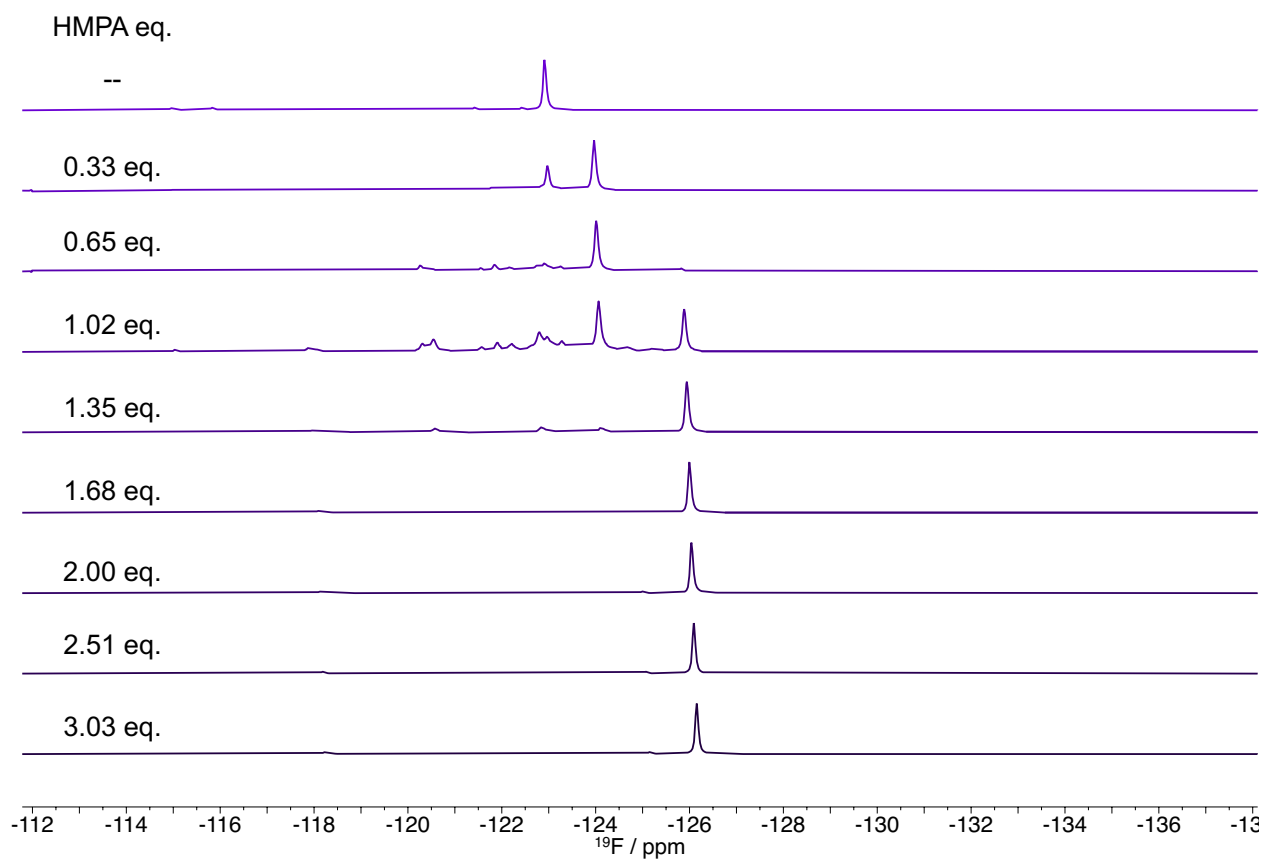
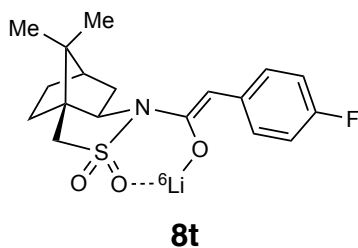


Figure S90. ^{19}F NMR spectra of $[^6\text{Li}]$ -(*S*)-**8t** in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.

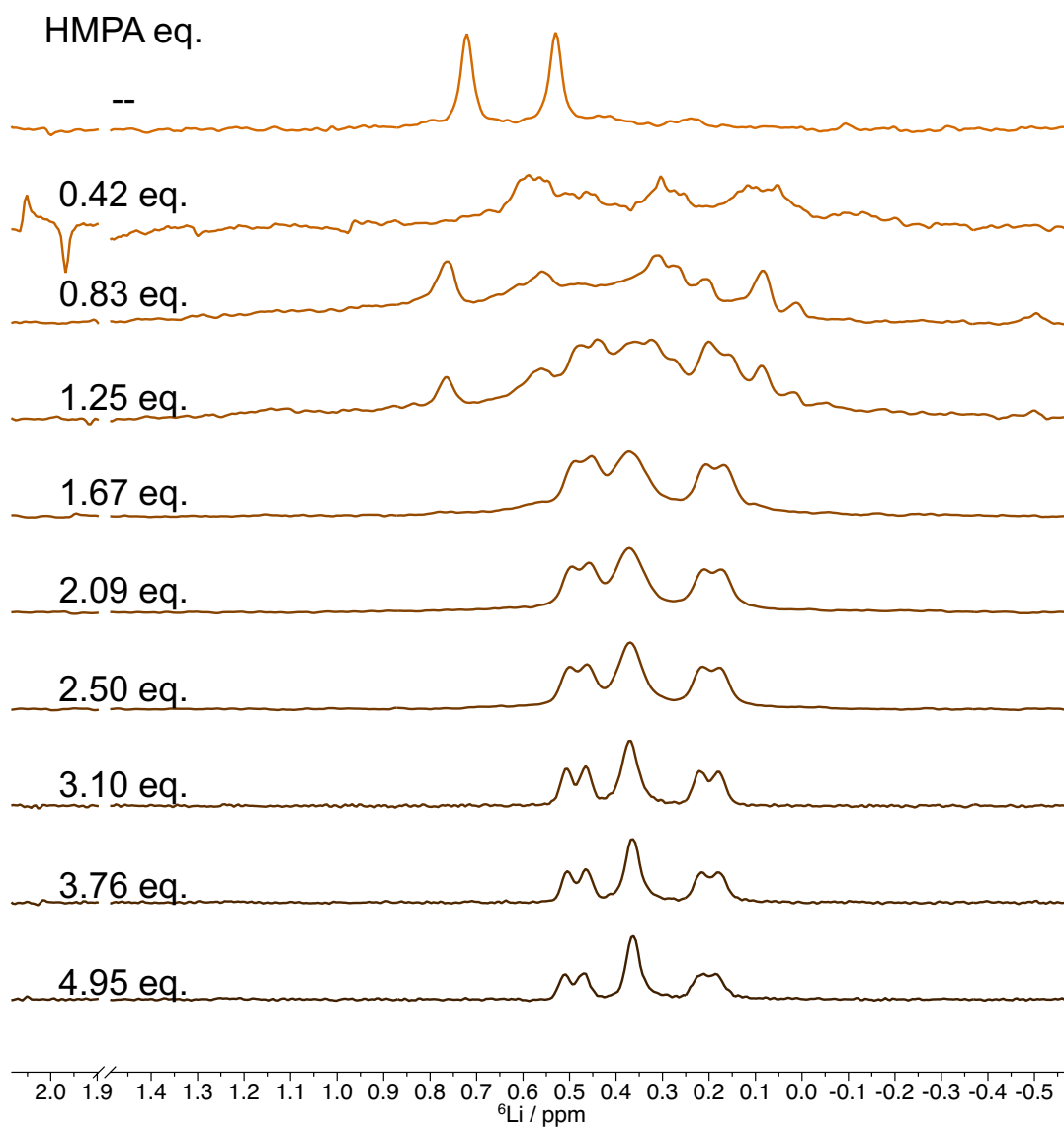
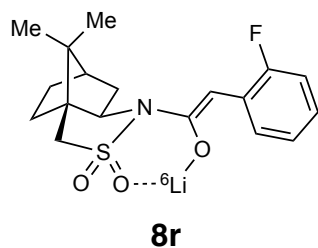


Figure S91. ⁶Li NMR spectra of [Li]-(S)-8r in toluene at -80 °C with varying concentrations of HMPA.

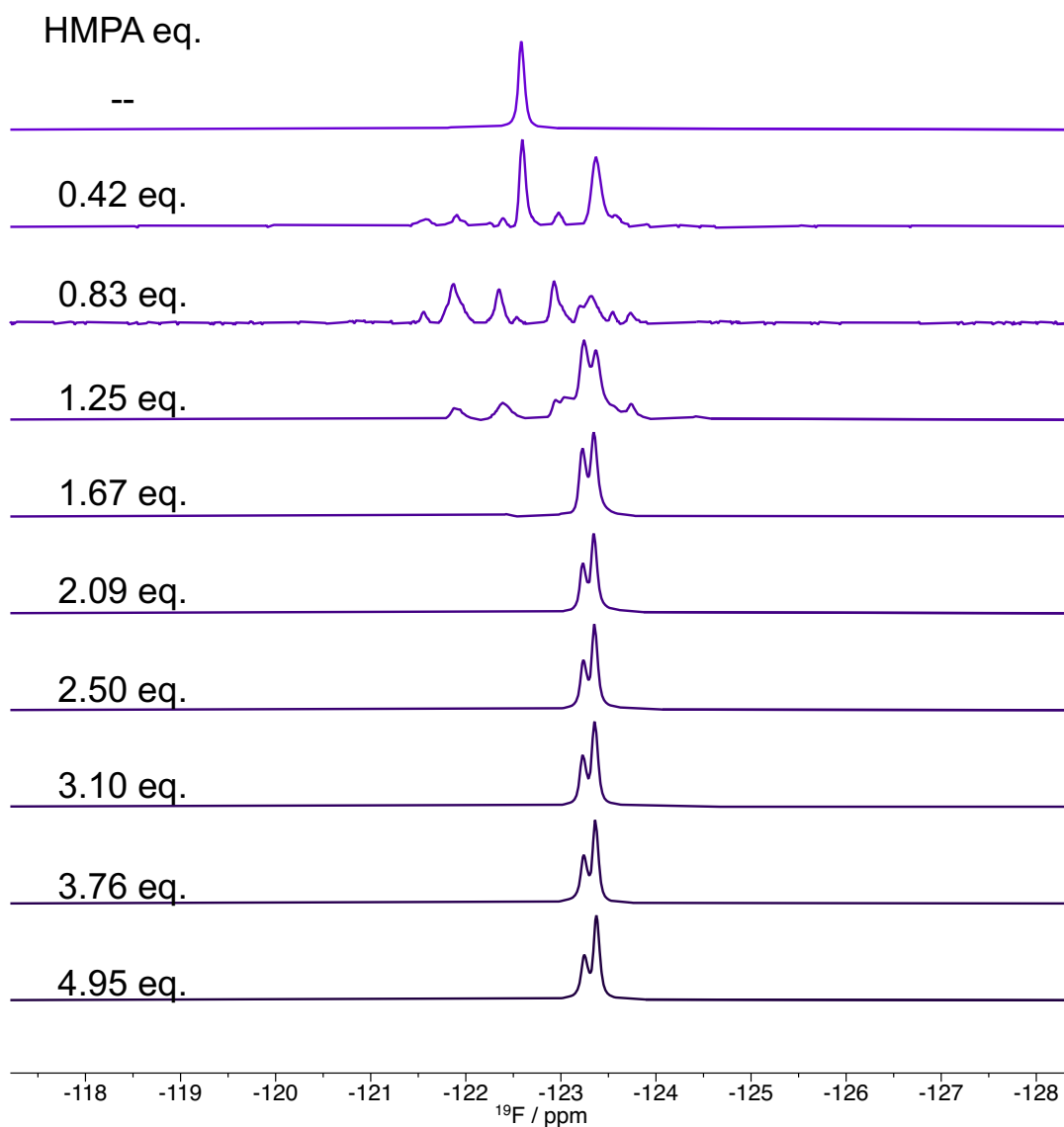
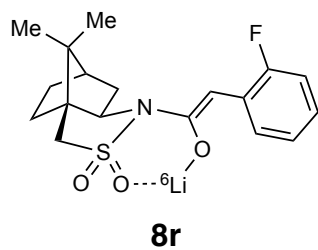


Figure S92. ^{19}F NMR spectra of $[^6\text{Li}]$ -(*S*)-**8r** in toluene at $-80\text{ }^\circ\text{C}$ with varying concentrations of HMPA.

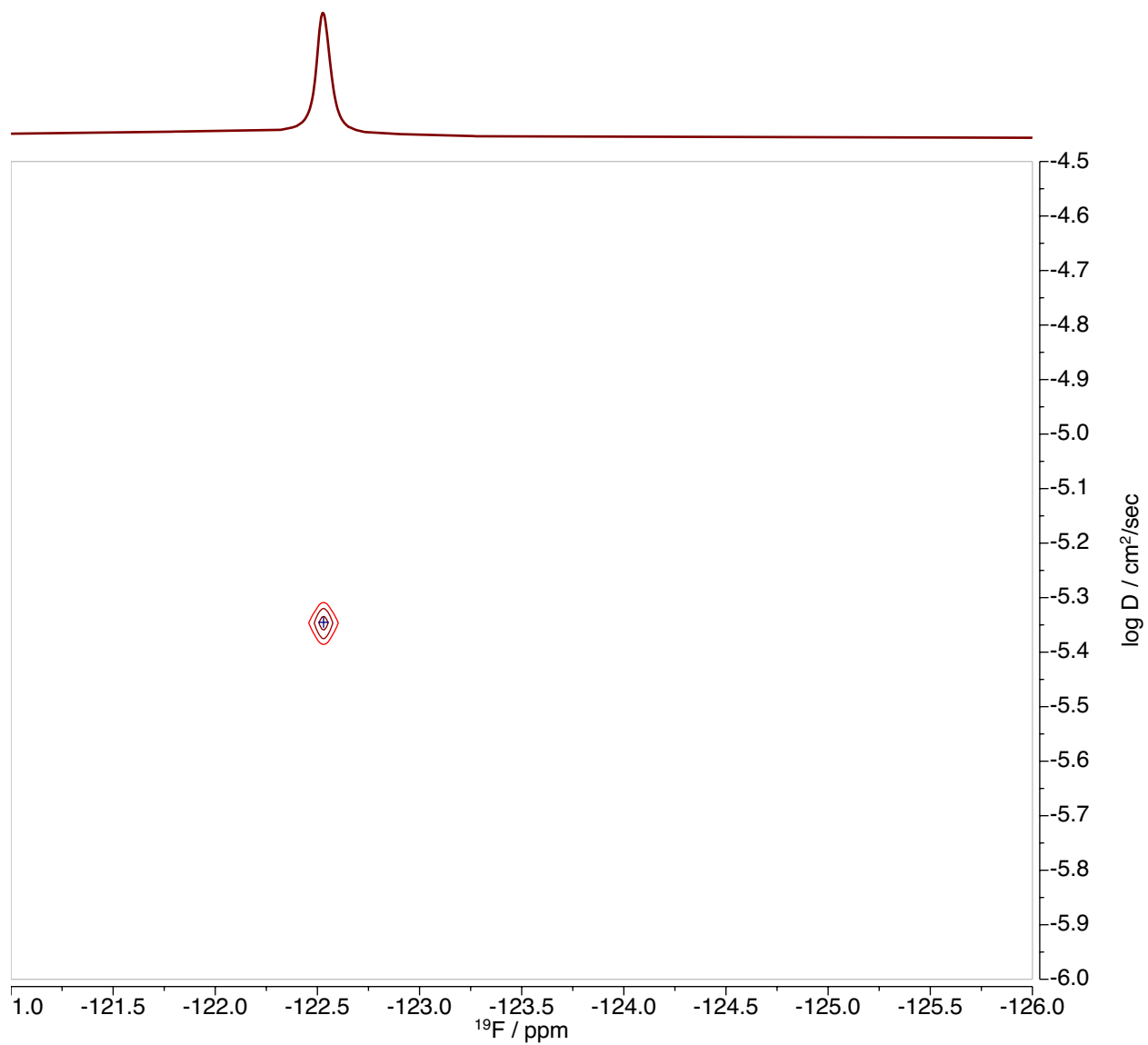
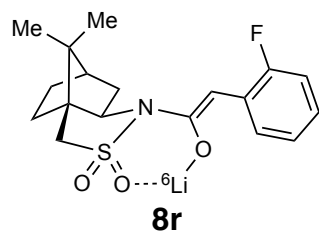


Figure S93. ^{19}F DOSY of 0.16 M [^6Li]-(*S*)-**8r** in toluene at -80 °C.

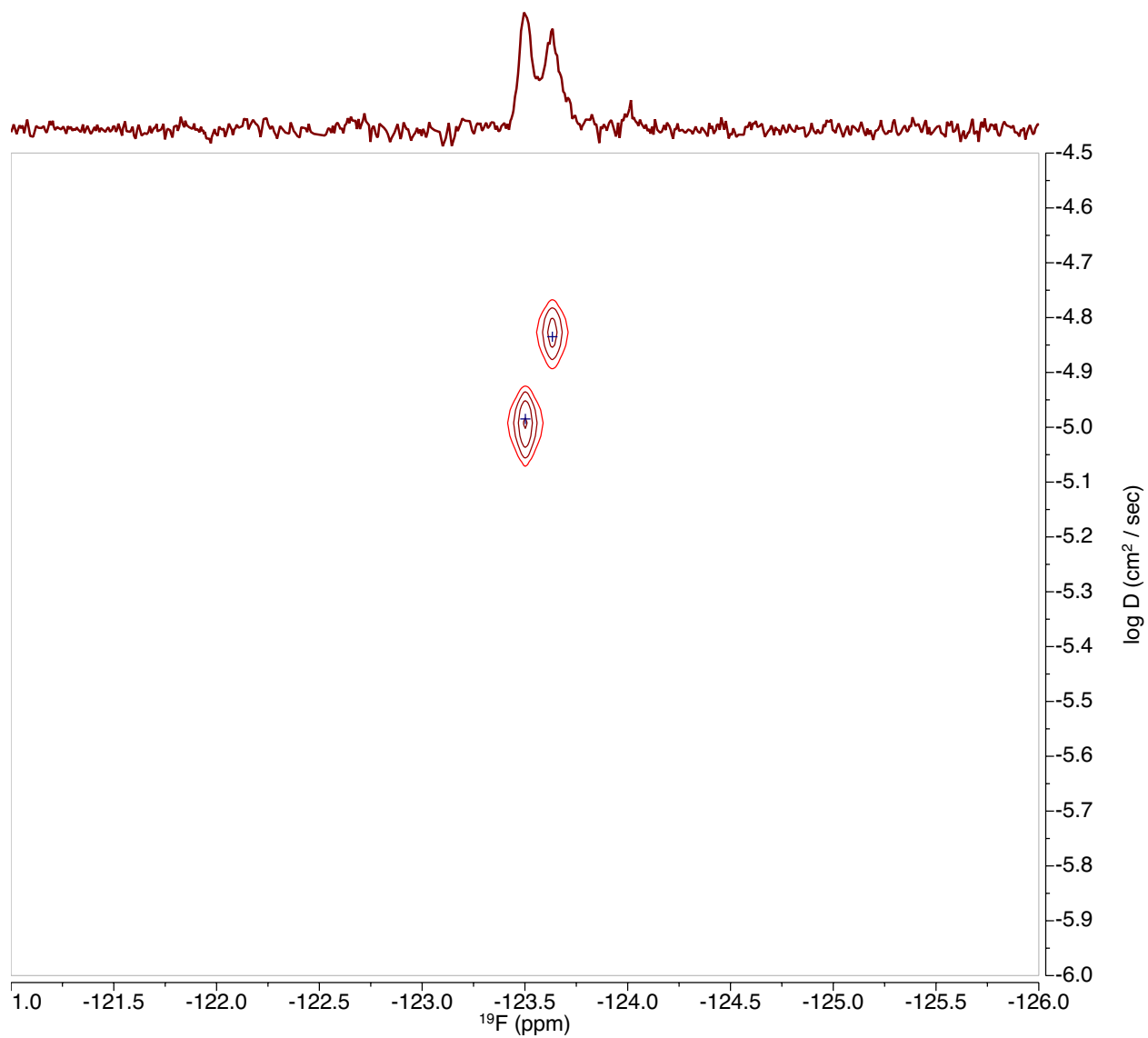
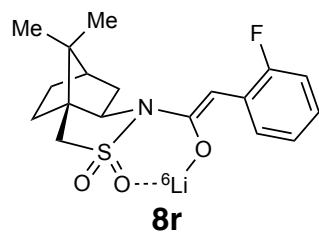


Figure S94. ¹⁹F DOSY of 0.15 M [⁶Li]-(*S*)-**8r** in 0.18 M HMPA in toluene at -80 °C.

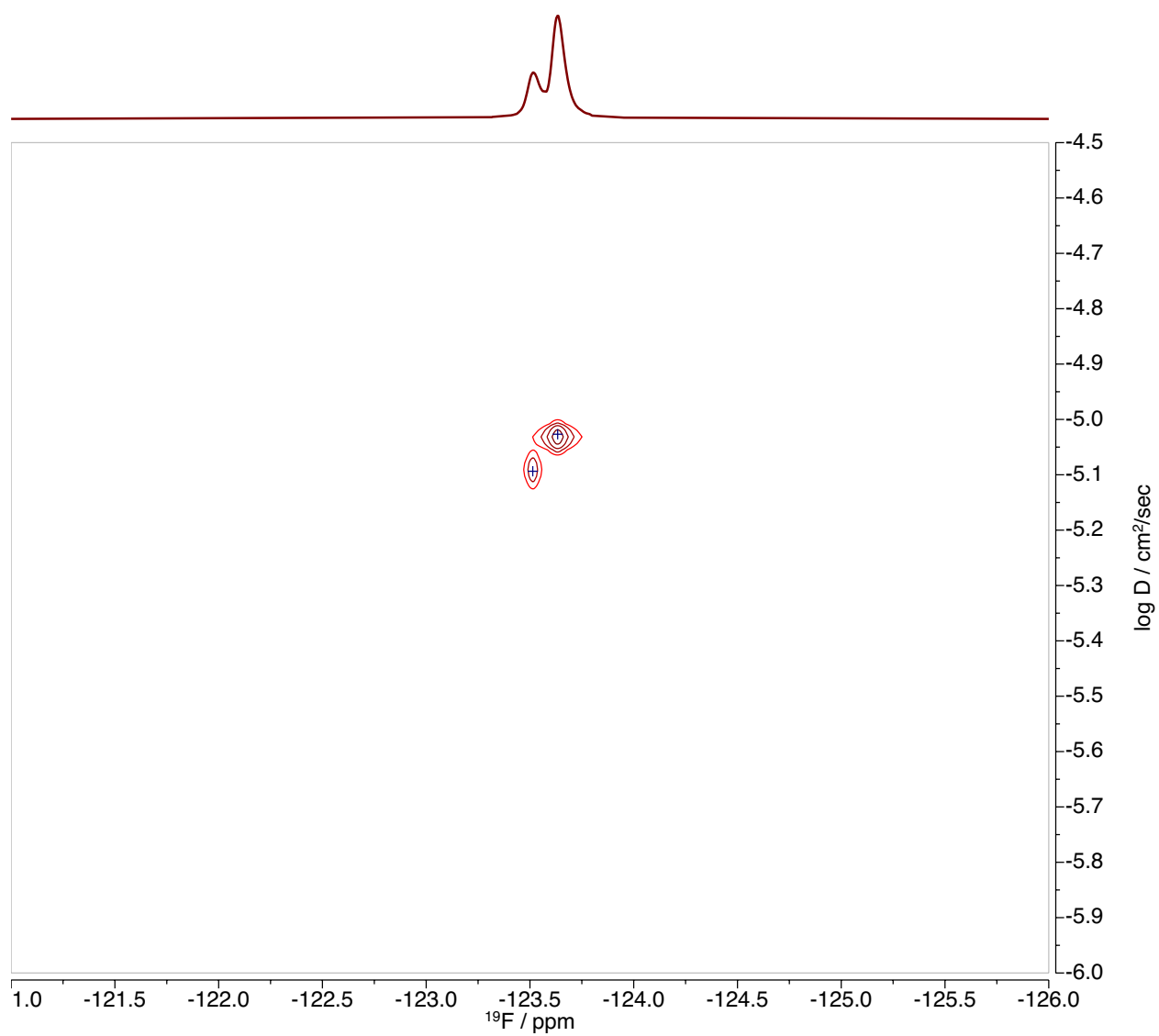
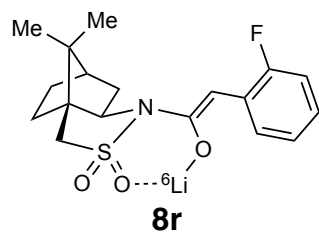


Figure S95. ¹⁹F DOSY of 0.15 M [⁶Li]-(S)-8r in 0.30 M HMPA in toluene at -80 °C.

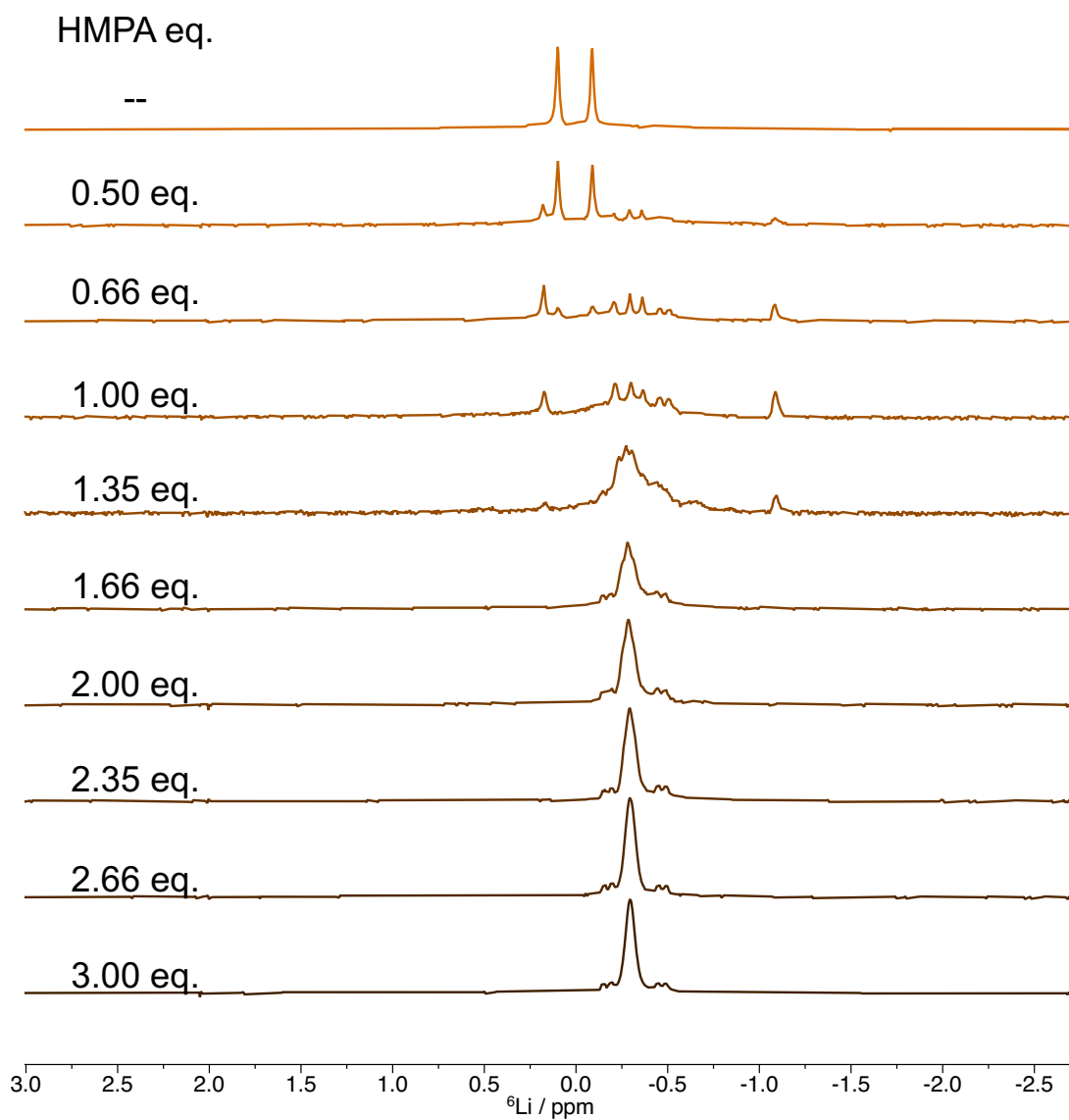
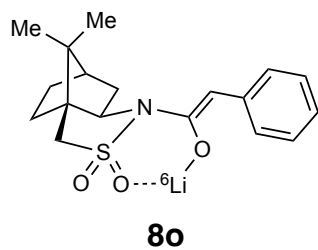


Figure S96. ${}^6\text{Li}$ NMR spectra of 0.10 M [${}^6\text{Li}$]-(*S*)-**8o** in toluene at $-90\text{ }^\circ\text{C}$ with varying concentrations of HMPA.

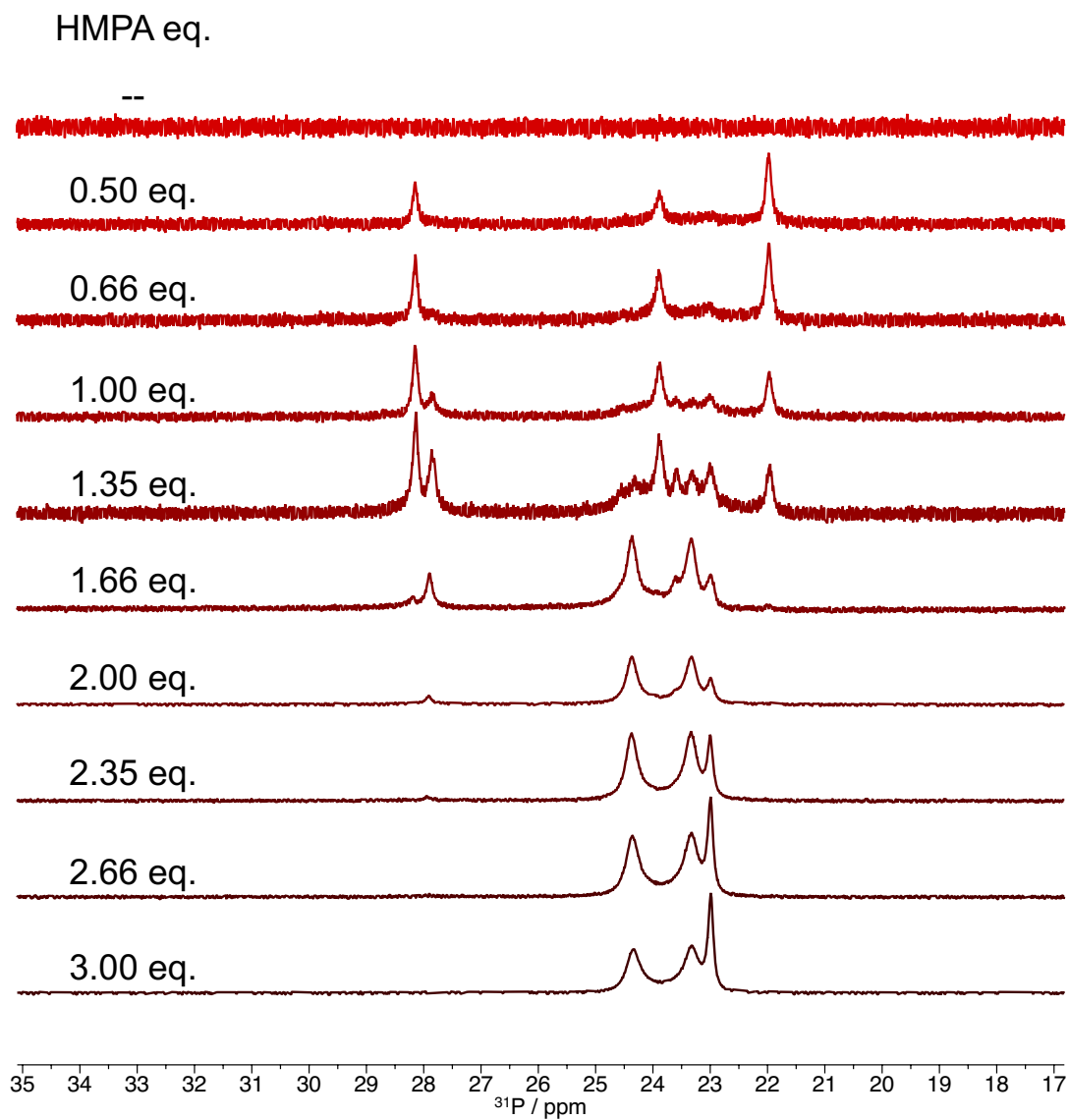
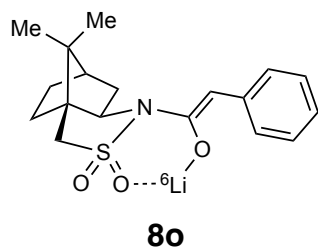


Figure S97. ³¹P NMR spectra of 0.10 M [⁶Li]-(*S*)-**8o** in toluene at -90 °C with varying concentrations of HMPA.

HMPA-solvated alkyl-substituted enolate dimers

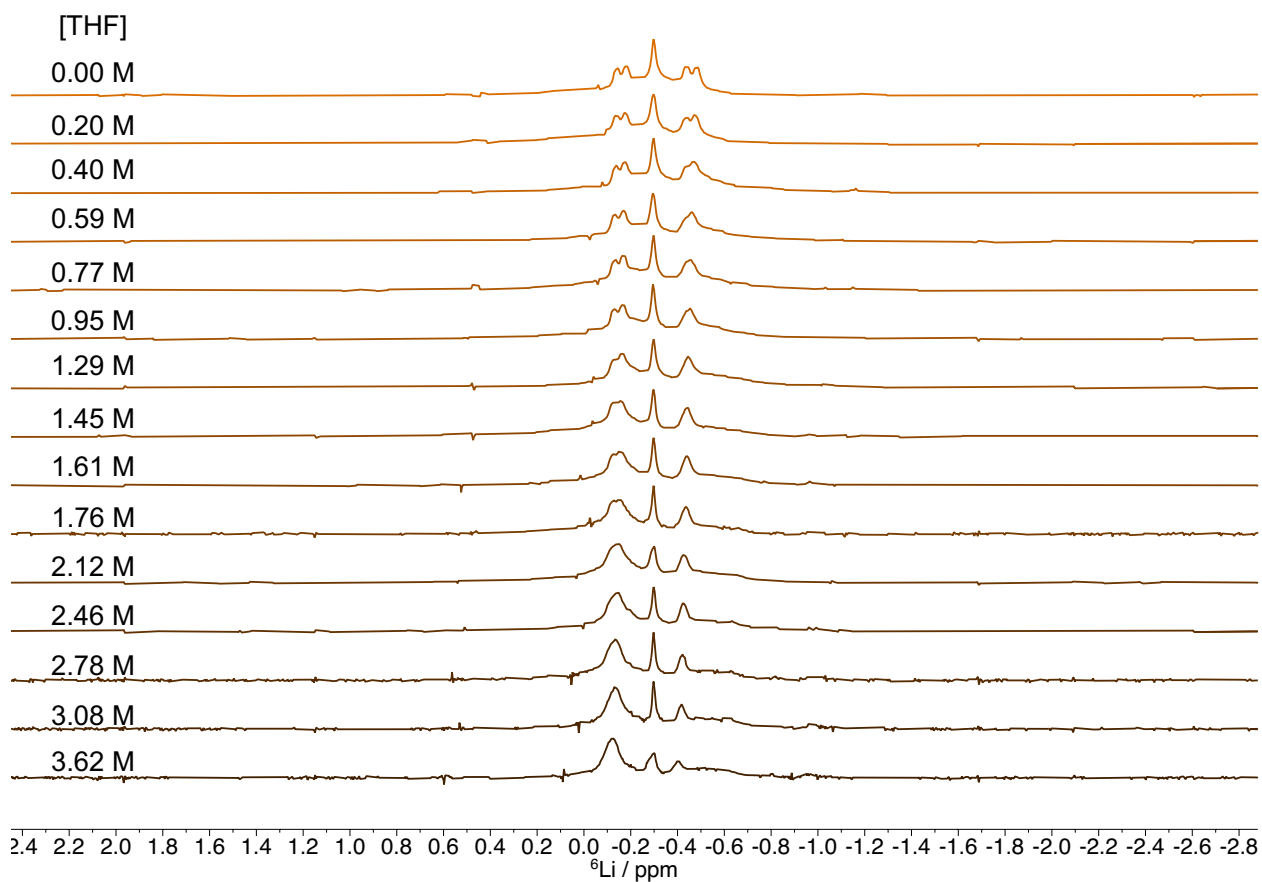
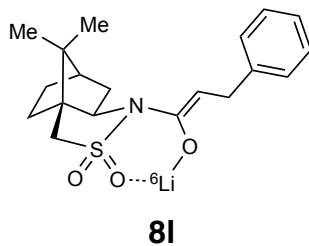


Figure S98. ⁶Li NMR spectra of [⁶Li]-(S)-**8I** with 3.0 equiv HMPA in toluene at -90 °C with varying concentrations of THF.

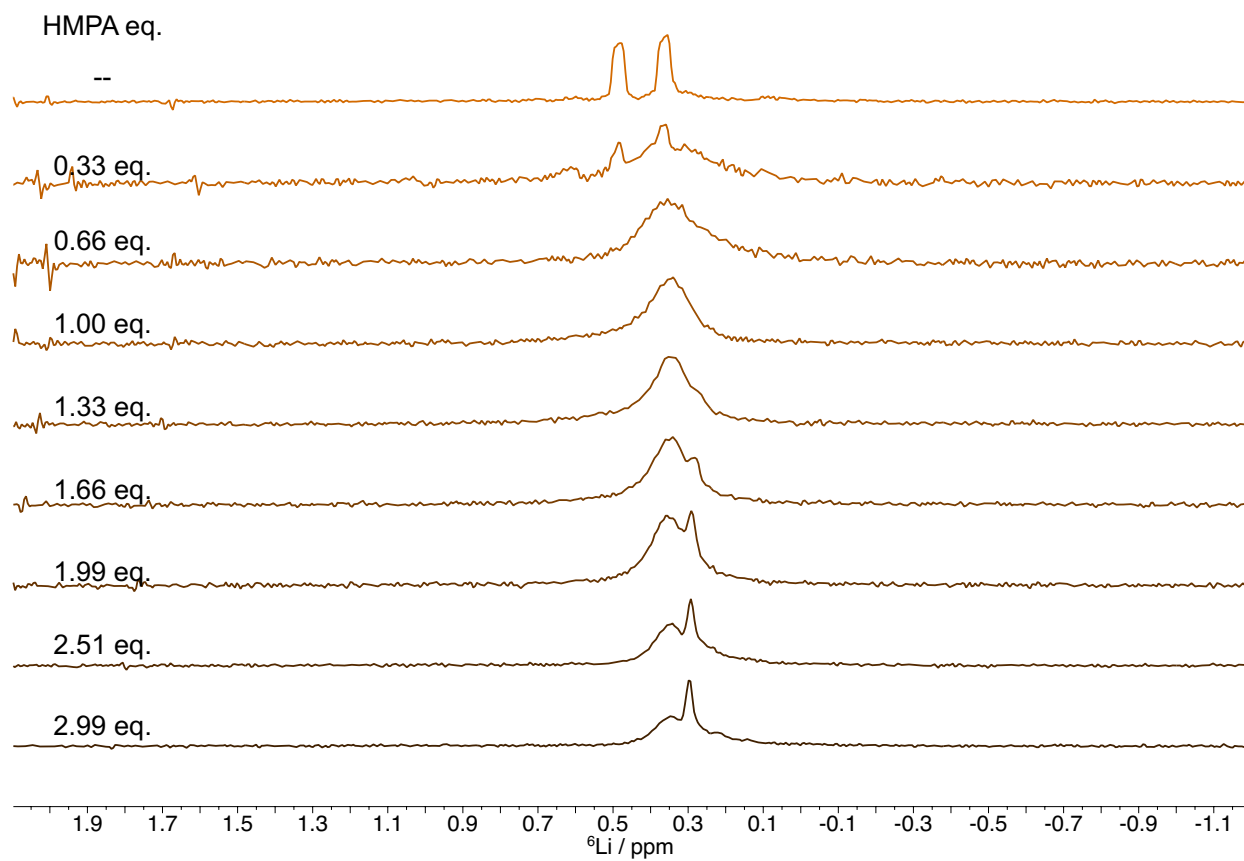
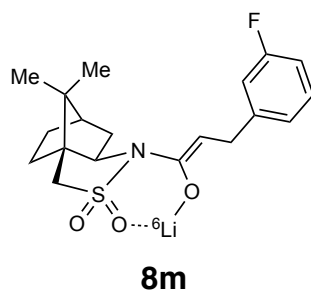


Figure S99. ${}^6\text{Li}$ NMR spectra of $[{}^6\text{Li}]$ -(S)-**8m** in toluene at -80 °C with varying concentrations of HMPA.

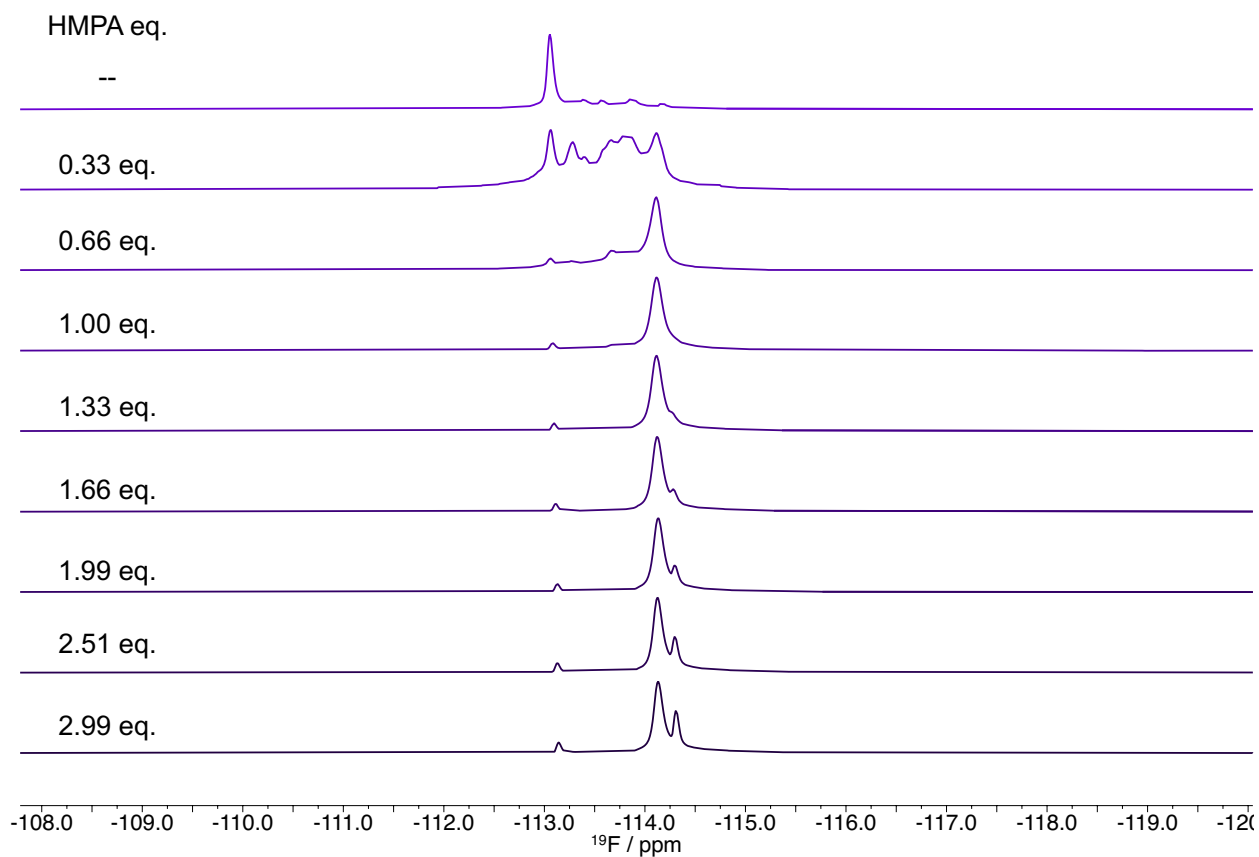
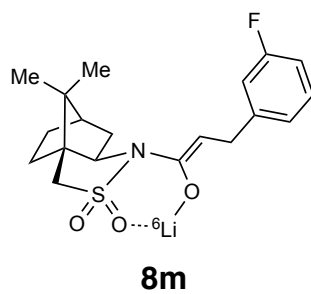


Figure S100. ¹⁹F NMR spectra of [⁶Li]-(*S*)-**8m** in toluene at -80 °C with varying concentrations of HMPA.

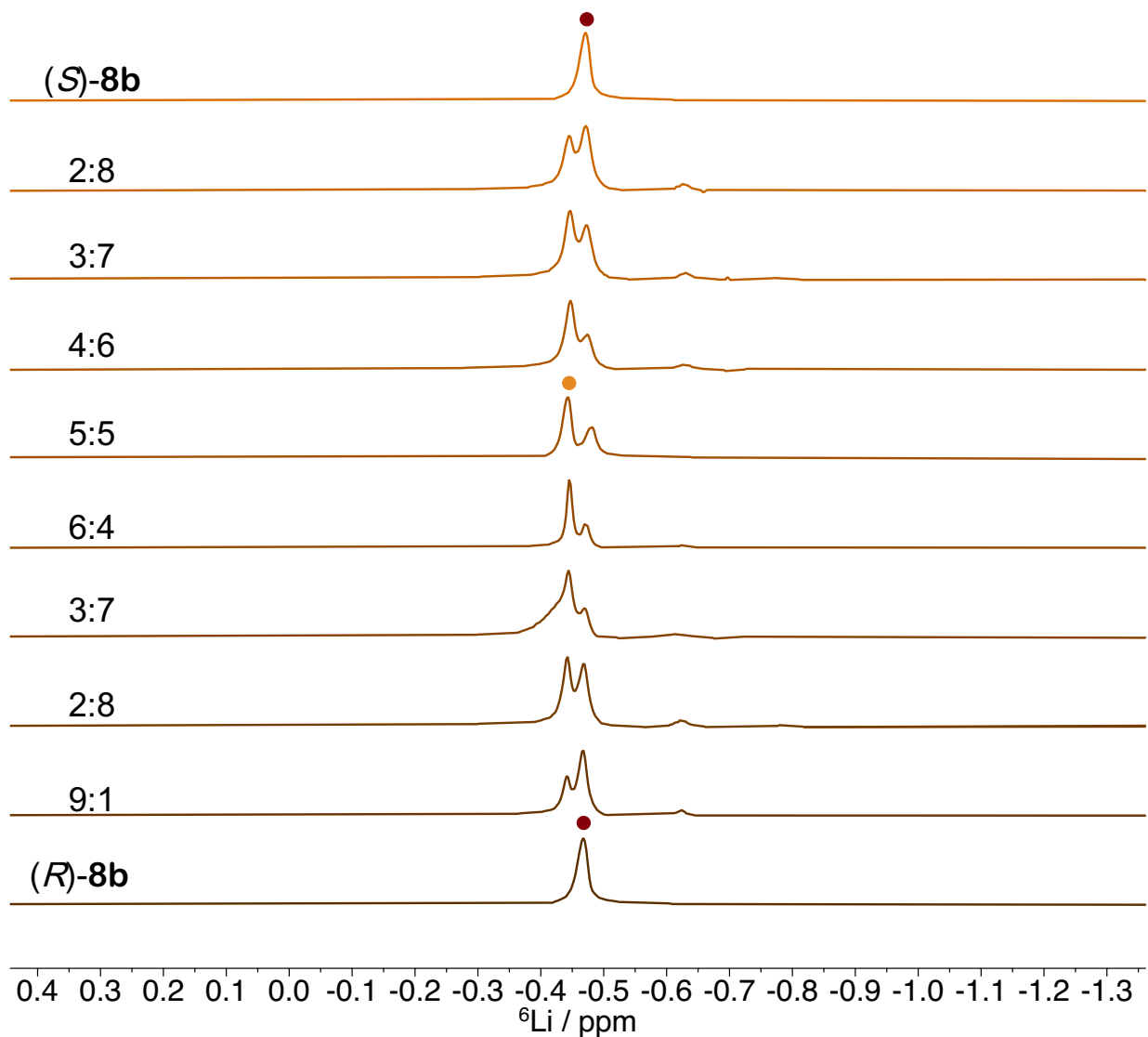
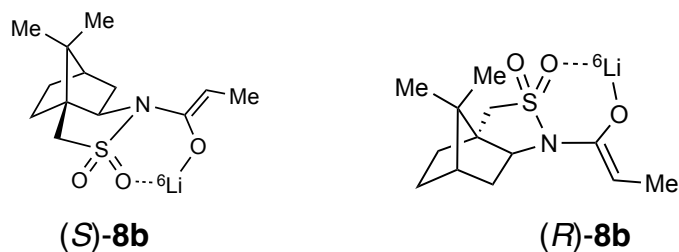


Figure S101. ⁶Li NMR spectra of 0.10 M mixtures of [⁶Li]-(S)-8b and [⁶Li]-(R)-8b with 3 equiv HMPA in 6.0 M THF at -80 °C. One new resonance appears for the heterochiral aggregate (**R₁S₁**, orange) consistent with a dimer model. R:S represents the total molar ratio of the two enantiomers.

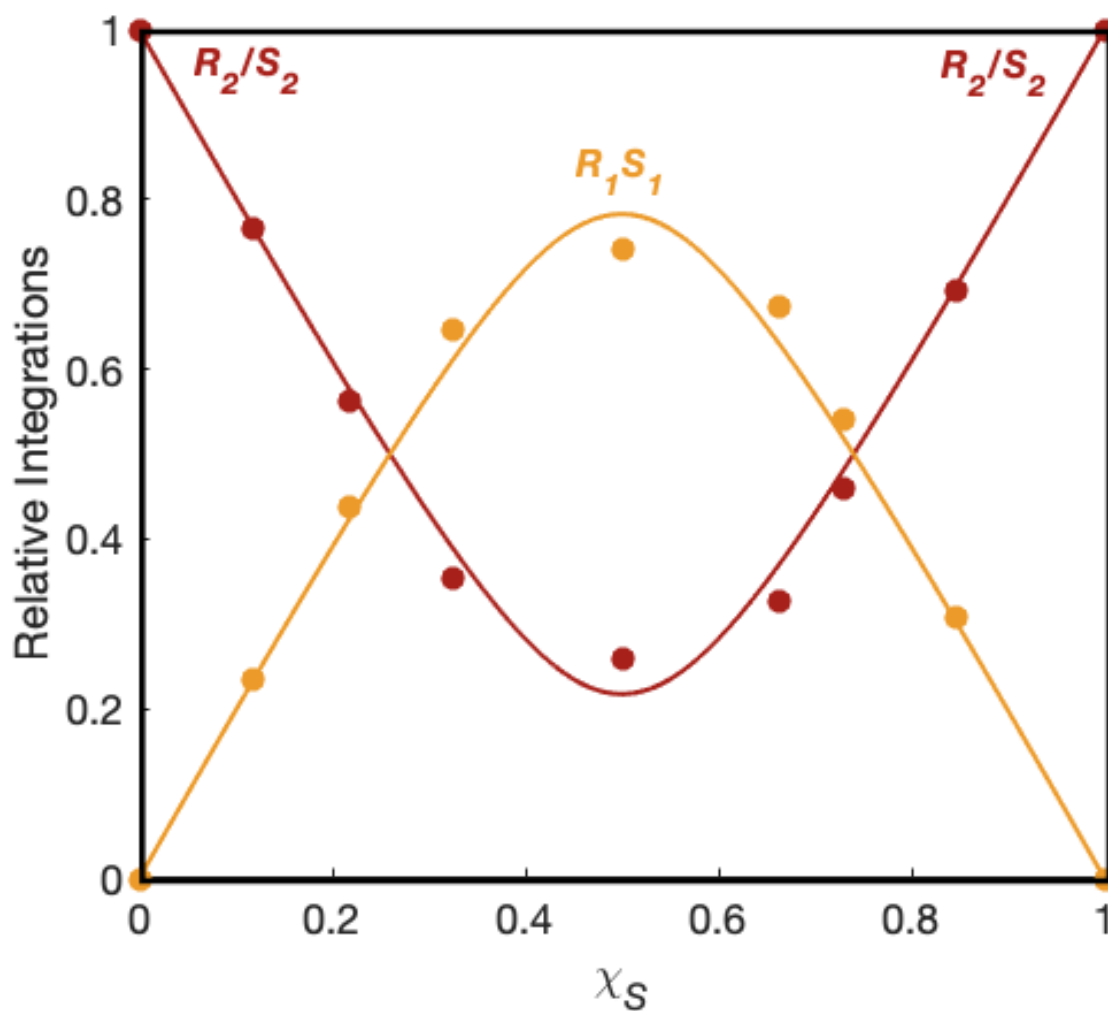


Figure S102. ^6Li Job plot showing relative integrations the two identical homochiral homoaggregates of $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(R)-8b}$ (red), and the R_1S_1 heterochiral mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]\text{-(S)-8b}$ for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]\text{-(S)-8b}$ and $[\text{}^6\text{Li}]\text{-(R)-8b}$ with 3 equiv HMPA in 6.0 M THF at $-80\text{ }^\circ\text{C}$ monitored by ^6Li NMR spectroscopy (**Figure S101**). The curves result from a parametric fit to a single aggregate dimer model.

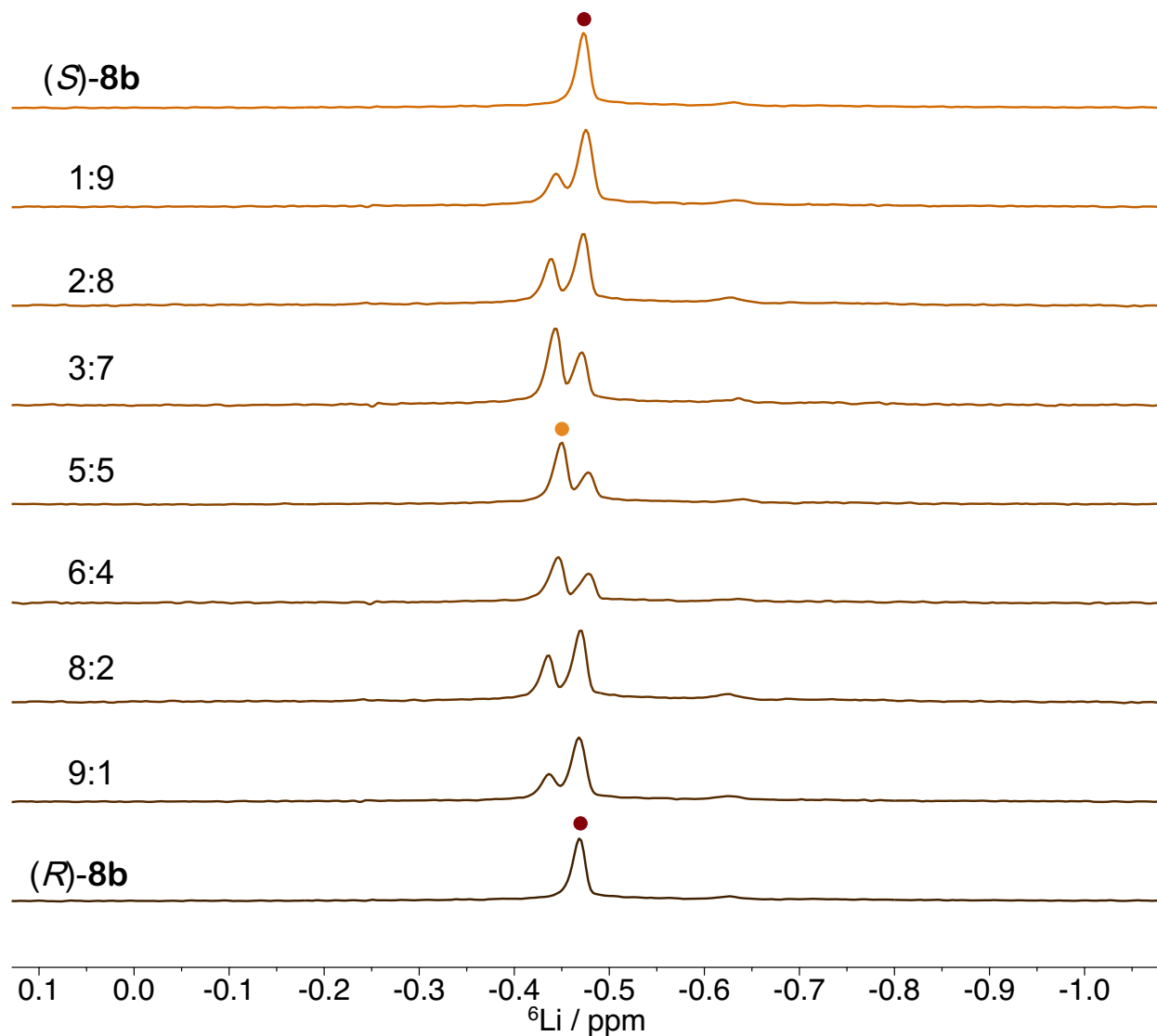
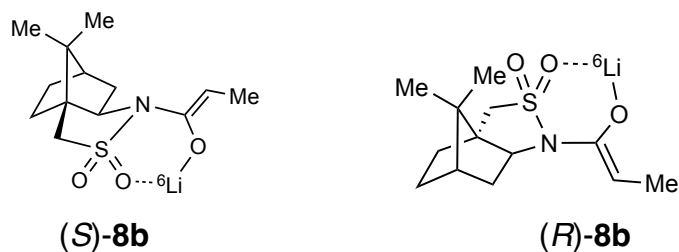


Figure S103. ⁶Li NMR spectra of 0.10 M mixtures of [⁶Li]-(*S*)-**8b** and [⁶Li]-(*R*)-**8b** with 3 equiv HMPA in 11.4 M THF at -80 °C. One new resonance appears for the heterochiral aggregate (*R₁S₁*) consistent with a dimer model. *R*:*S* represents the total molar ratio of the two enantiomers.

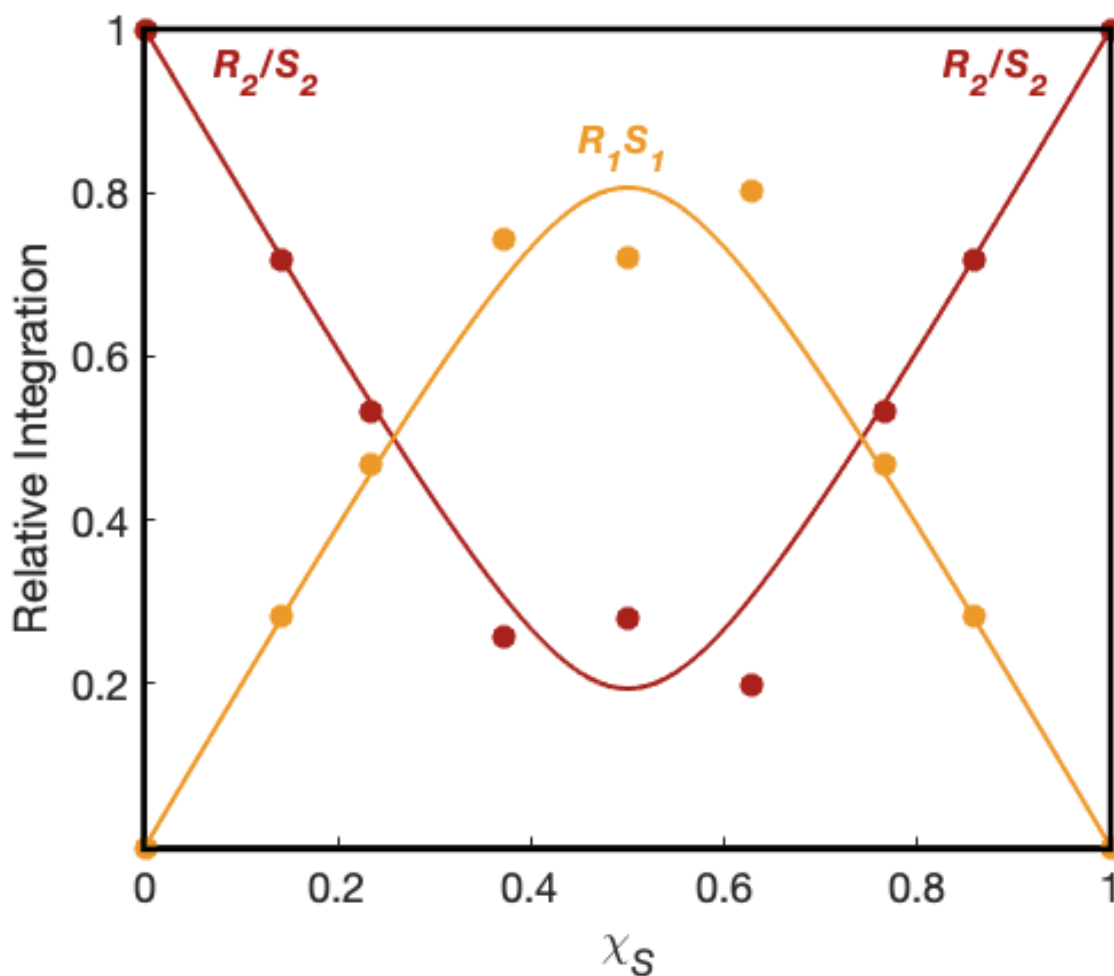


Figure S104. ^6Li mini-Job plot showing relative integrations the two identical homochiral homoaggregates of $[\text{}^6\text{Li}]-(S)\text{-8b}$ and $[\text{}^6\text{Li}]-(R)\text{-8b}$ (red), and the R_1S_1 heterochiral mixed dimer (orange) against the measured mole fraction of $[\text{}^6\text{Li}]-(S)\text{-8b}$ for 0.10 M mixtures of lithium enolates $[\text{}^6\text{Li}]-(S)\text{-8b}$ and $[\text{}^6\text{Li}]-(R)\text{-8b}$ with 3 equiv HMPA in 11.4 M THF at -80°C monitored by ^6Li NMR spectroscopy (**Figure S103**). The curves result from a parametric fit to a single aggregate dimer model.

THF-solvated alkyl-substituted dianion tetramer

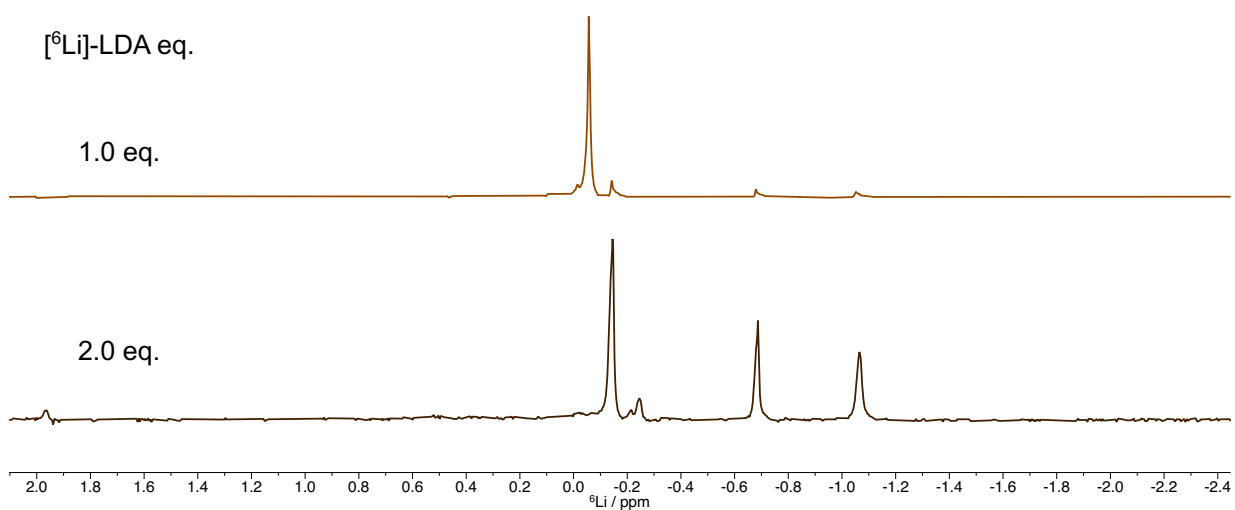
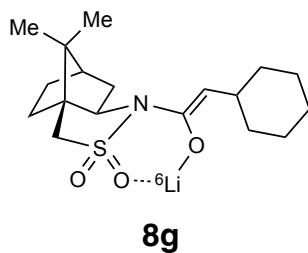


Figure S105. ⁶Li NMR spectra of 0.10 M [⁶Li]-(S)-**8g** with varying concentrations of [⁶Li]-LDA in THF at -80 °C. [⁶Li]-LDA equiv refers to the total titer of [⁶Li]-LDA in the NMR tube relative to the *N*-acyl sultam. NMR tubes with 3.0 and 4.0 equiv base precipitated out of solution.

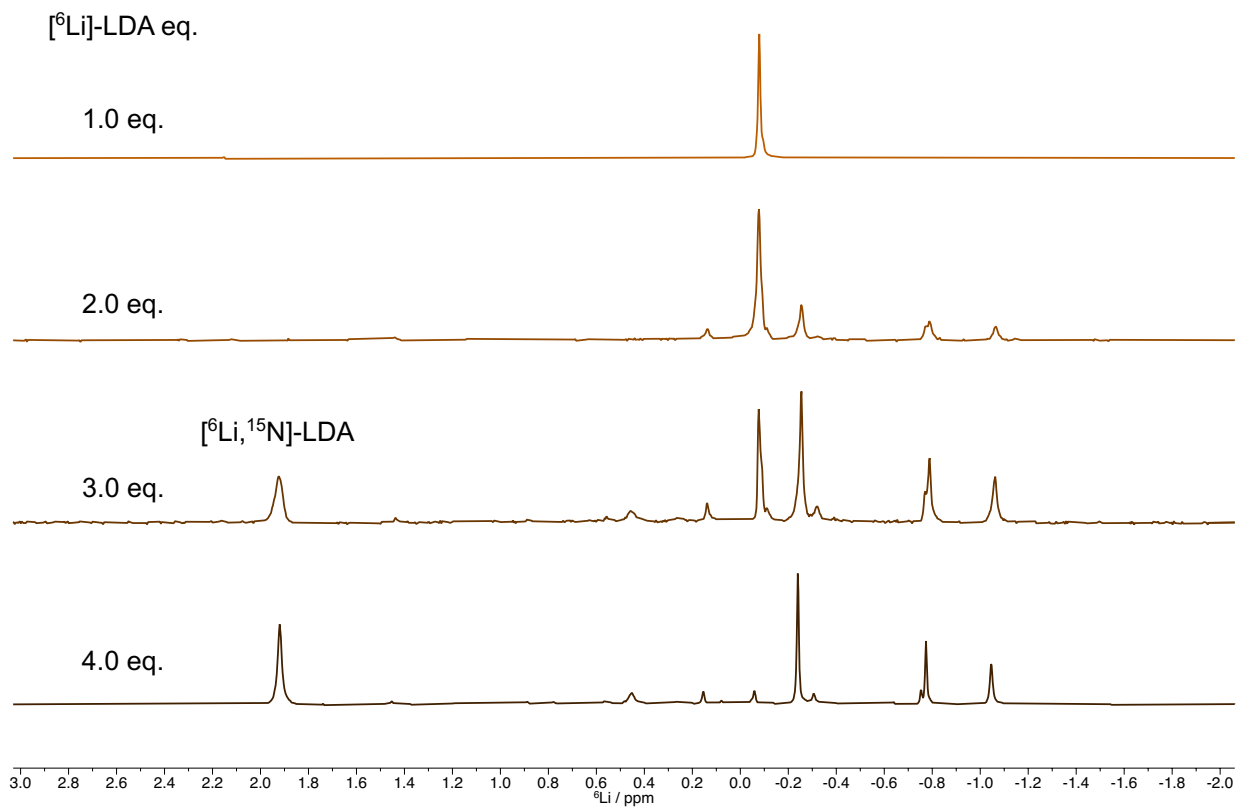
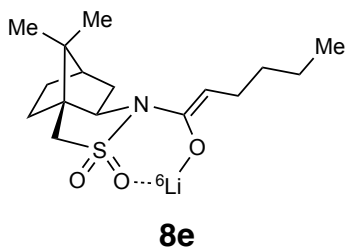


Figure S106. ⁶Li NMR spectra of mixtures of 0.10 M [⁶Li]-(*S*)-8e with varying concentrations of [⁶Li]-LDA in THF at -80 °C. [⁶Li]-LDA equiv refers to the total titer of [⁶Li]-LDA in the NMR tube relative to the *N*-acyl sulfam.

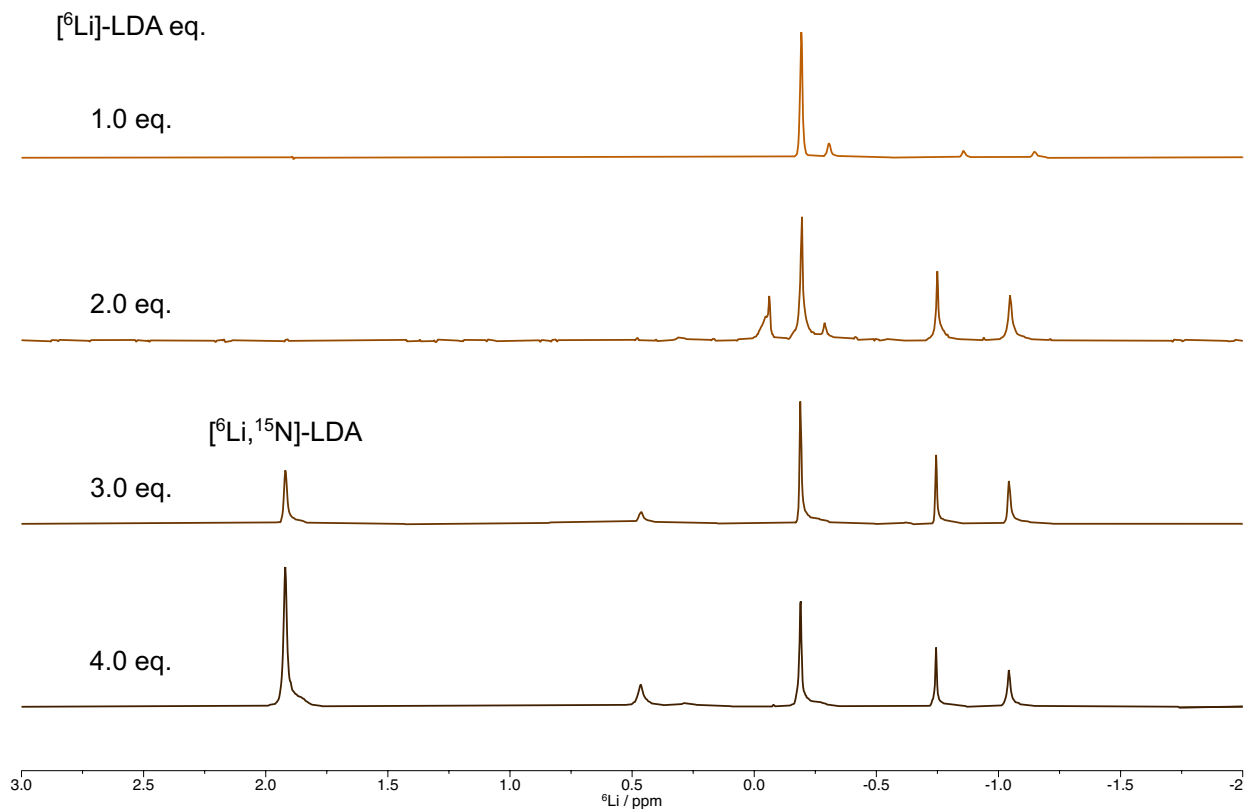
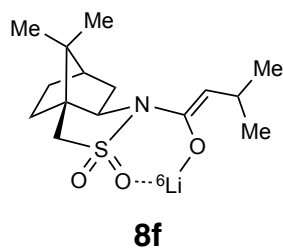


Figure S107. ⁶Li NMR spectra of mixtures of 0.10 M [⁶Li]-(*S*)-**8f** with varying concentrations of [⁶Li]-LDA in THF at $-80\text{ }^{\circ}\text{C}$. [⁶Li]-LDA equiv refers to the total titer of [⁶Li]-LDA in the NMR tube relative to the *N*-acyl sultam.

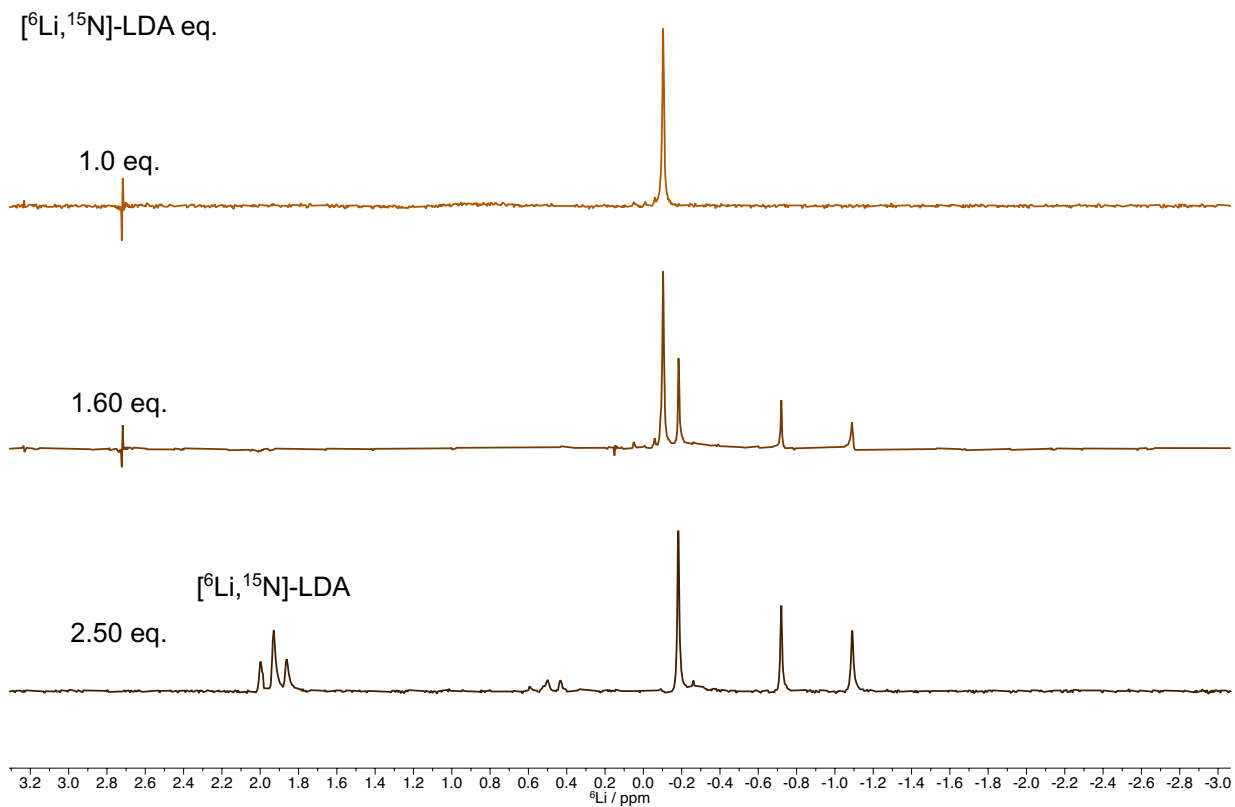
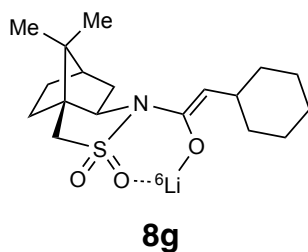


Figure S108. ${}^6\text{Li}$ NMR spectra of 0.10 M ${}^6\text{Li}$ -(S)-**8g** with 0.0, 0.6, and 1.5 equiv excess (1.0, 1.6, and 2.5 equiv total) ${}^6\text{Li}, {}^{15}\text{N}$ -LDA in THF at $-80\text{ }^\circ\text{C}$. ${}^6\text{Li}, {}^{15}\text{N}$ -LDA equiv refers to the total titer of ${}^6\text{Li}, {}^{15}\text{N}$ -LDA in the NMR tube relative to the concentration of the *N*-acyl sulfam.

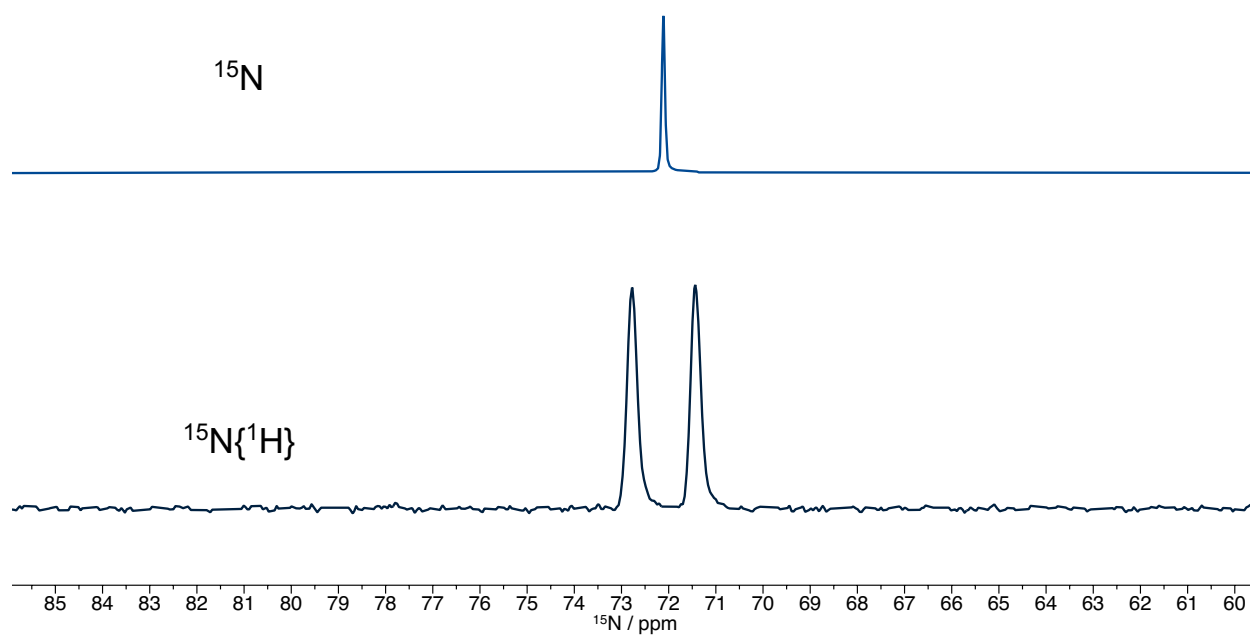
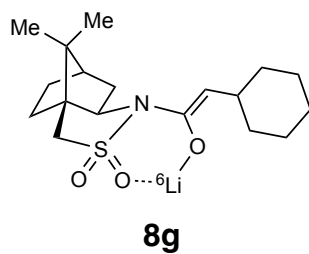


Figure S109. ¹⁵N and ¹⁵N{¹H} NMR spectra of 0.10 M [⁶Li]-(S)-**8g** with 0.6 equiv excess (1.6 equiv total) [⁶Li,¹⁵N]-LDA in THF at -80 °C.

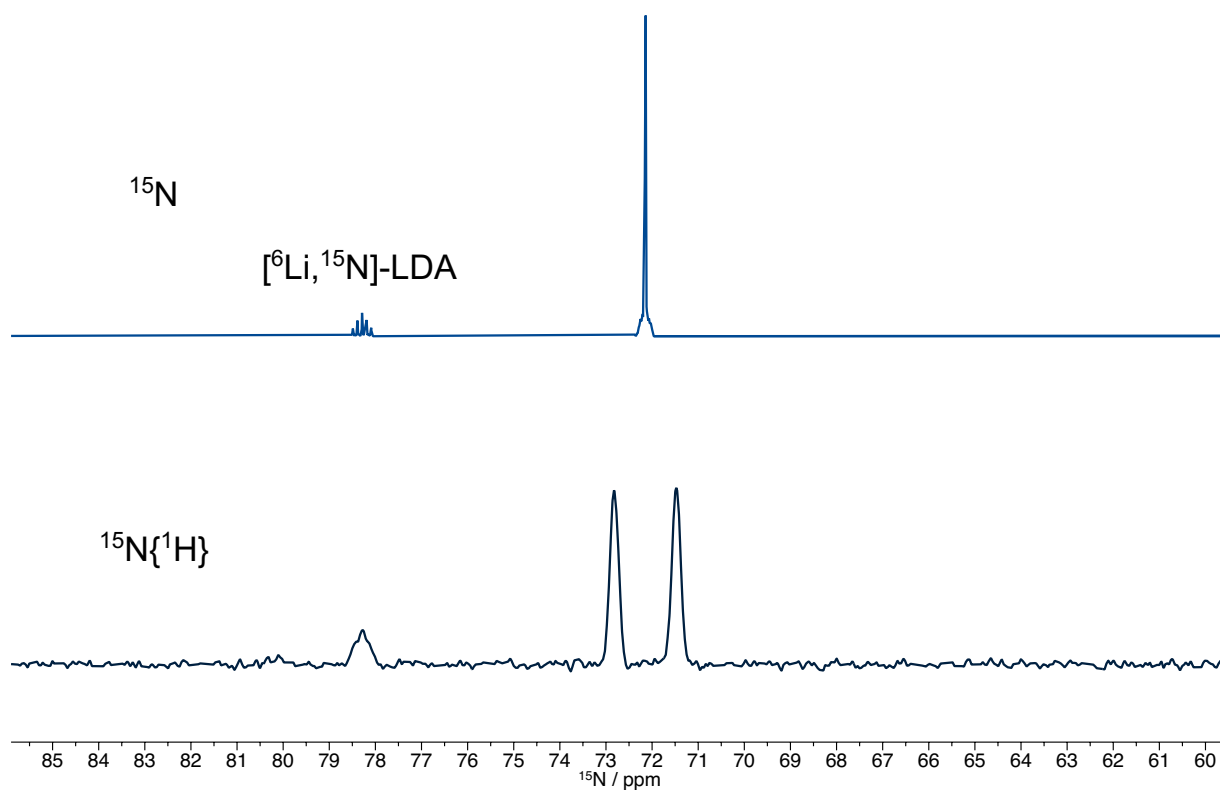
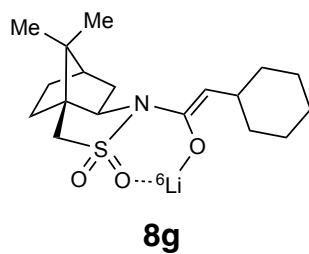
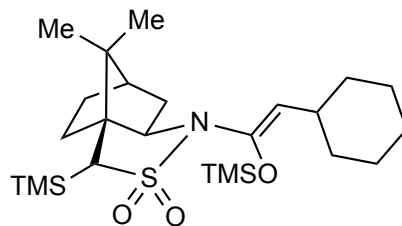


Figure S110. ^{15}N and $^{15}\text{N}\{^1\text{H}\}$ NMR spectra of 0.10 M $[^6\text{Li}]\text{-(S)-8g}$ with 1.5 equiv excess (2.5 equiv total) $[^6\text{Li}, ^{15}\text{N}]\text{-LDA}$ in THF at $-80\text{ }^\circ\text{C}$.



Monoisotopic Exact Mass (calc): 484.27314 (M+H⁺)

Monoisotopic Exact Mass (found): 484.27175 (M+H⁺)

Error: 2.87 ppm

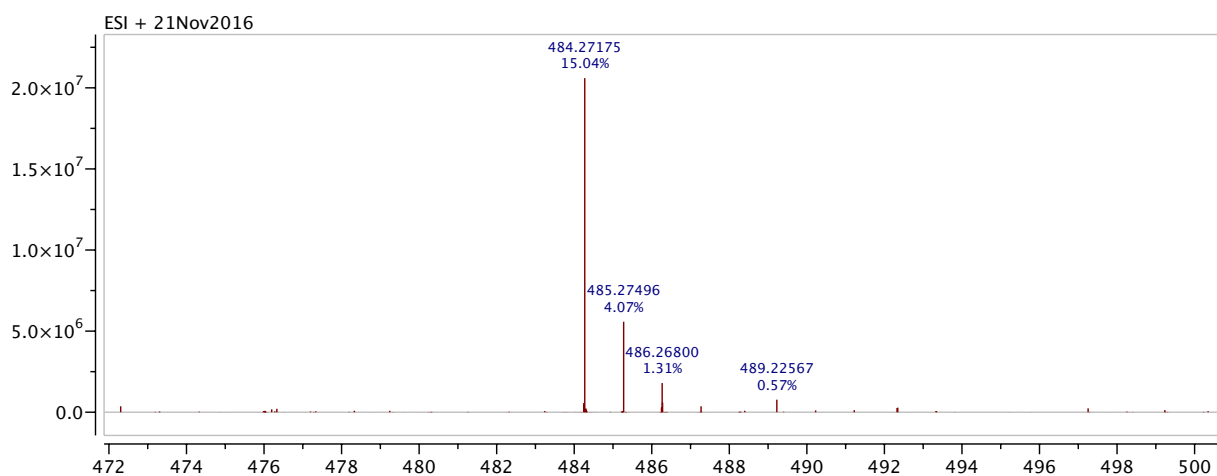


Figure S111. DART-HRMS of [⁶Li]-(*S*)-*N*-cyclohexylacetyl-camphorsultam-dianion after quenching with excess TMSCl.

Rate Studies

General procedure for in situ IR analyses

IR spectra were recorded with an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired at a gain of 1 and a resolution of 4 cm^{-1} . All tracked reactions were conducted under positive flow of argon from a Schlenk line.

A representative reaction was carried out as follows: The IR probe was inserted through a teflon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was capped with a septum for injections and an argon line. After evacuation under full vacuum, heating, and flushing with argon, the flask was charged with the THF/cosolvent mixture of choice toluene, 2,5-dimethylTHF, toluene/cyclopentane and cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice–acetone bath.

A set of 256 baseline scans were collected and IR spectra were recorded every 15 seconds from 30 scans. The reaction vessel was charged to 0.025M (*S*)-**7o** (1704 cm^{-1}). A 2.00 M stock solution of LDA was injected (0.030 M, 1.2 equiv) through the septum and enolization was tracked to completion (1616 cm^{-1}), typically ~ 10 min. Following full disappearance of the *N*-acyl sultam, HMPA was added to the reaction as a 4.70 M (75 v/v%) stock solution in toluene. The reaction was left to stir for another 10 min.

At this point spectral collection was halted and an additional 256 baseline scans were collected. The spectrometer was configured to collect spectra every 5 seconds from 16 scans. 1 set of scans was collected before addition of *neat* allyl bromide through the septum. The reaction was tracked over 5 half-lives monitoring disappearance of the enolate (1616 cm^{-1}) and appearance of the allyl adduct (1706 cm^{-1}).

The reaction was quenched by removing the vessel from the probe and adding 5 mL 1.0 M HCl. Workup and product analysis were conducted as described in the synthesis section above.

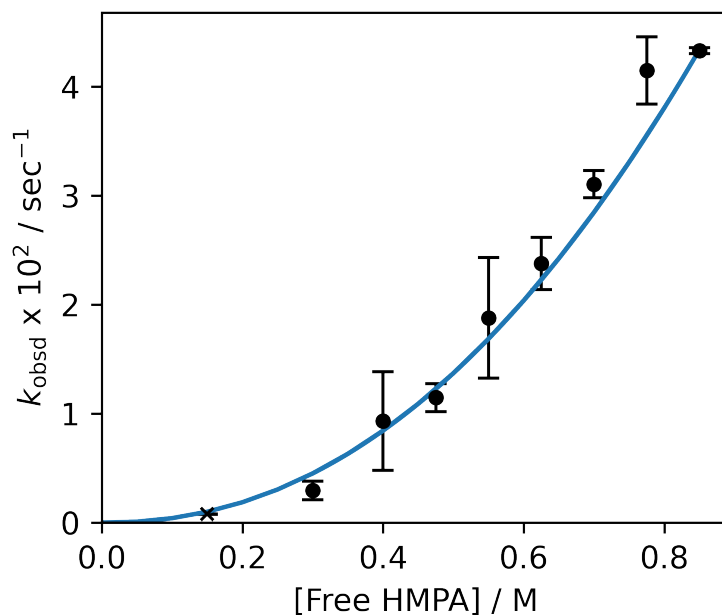


Figure S112. HMPA order I Plot of pseudo-first-order rate constants (k_{obsd}) against free HMPA concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 9.0 M THF/toluene at -78 °C. The point outside pseudo-first-order conditions is denoted by an asterisk (*) and was not included in the fit.

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = ax^b$ such that $a = 0.062 \pm 0.001$, $b = 2.2 \pm 0.1$.

Table S1. Average pseudo-first-order rate constants (k_{obsd}) at various free HMPA concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 9.0 M THF/toluene at -78 °C. Asterisks (*) denote point(s) outside pseudo-first-order restraints; these points are excluded from the fit.

[Free HMPA] / M	$k_{\text{obs}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$
0.90	4.33	0.03
0.825	4.15	0.31
0.75	3.10	0.13
0.675	2.38	0.24
0.60	1.88	0.55
0.525	1.15	0.13
0.45	0.93	0.45
0.35	0.29	0.08
0.20*	0.08	0.01

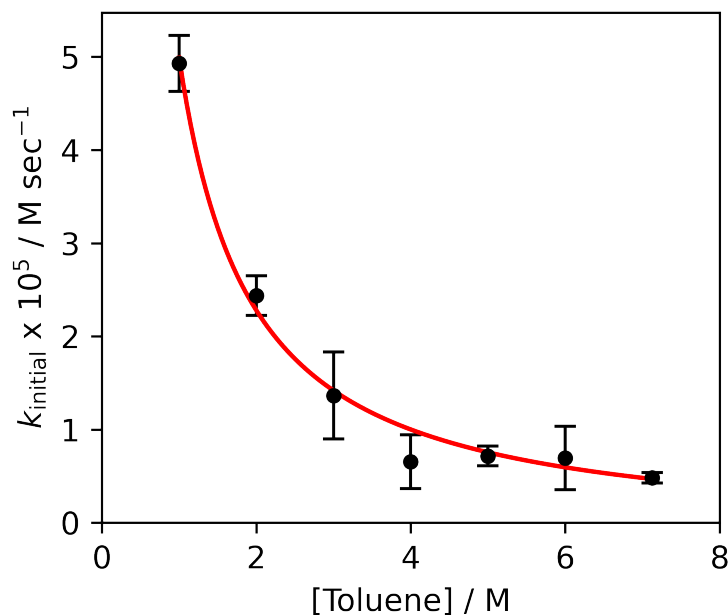


Figure S113. Toluene order @ 0.275 M free HMPA / cyclopentane | Plot of initial rate constants (k_{initial}) against toluene concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/2.0 M THF/cyclopentane at -78 °C.

The red curve depicts an error-weighted least-squares fit to the function $f(x) = y_0 + ax^b$ such that $y_0 = -1.4 \times 10^{-6} \pm 0.3 \times 10^{-6}$, $a = 5.1 \times 10^{-5} \pm 0.3 \times 10^{-5}$, $b = -1.1 \pm 0.2$.

Table S2. Average initial rate constants (k_{obsd}) at various free Toluene concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/2.0 M THF/cyclopentane at -78 °C.

[Toluene] / M	$k_{\text{initial}} \times 10^5 / \text{M sec}^{-1}$	Standard Deviation $\times 10^5 / \text{M sec}^{-1}$
7.125	0.48	0.06
6.00	0.69	0.34
5.00	0.72	0.11
4.00	0.65	0.29
3.00	1.36	0.47
2.00	2.44	0.21
1.00	4.93	0.30

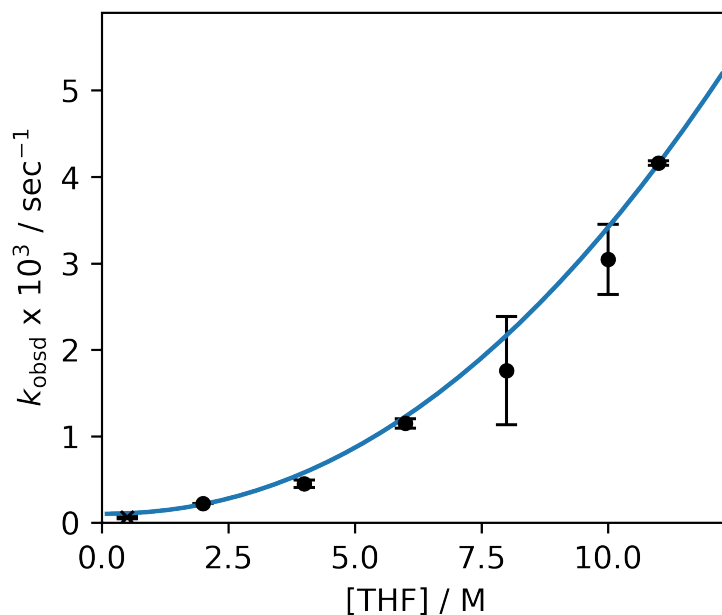


Figure S114. THF order @ 0.275 M free HMPA/Toluene | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/toluene at -78 °C. Points outside pseudo-first-order conditions are denoted by asterisks (*).

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = y_0 + ax^b$ such that $y_0 = 1.0 \times 10^{-4} \pm 0.1 \times 10^{-4}$, $a = 2.5 \times 10^{-5} \pm 0.4 \times 10^{-5}$, $b = 2.1 \pm 0.1$.

Table S3. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/toluene at -78 °C. Asterisks (*) denote point(s) outside pseudo-first-order restraints; these points are excluded from the fit.

[THF] / M	$k_{\text{obsd}} \times 10^3 / \text{sec}^{-1}$	Standard Deviation $\times 10^3 / \text{sec}^{-1}$
11.00	4.16	0.02
10.00	3.04	0.41
8.00	1.76	0.62
6.00	1.15	0.05
4.00	0.45	0.04
2.00	0.22	0.001
0.50*	0.061	0.016

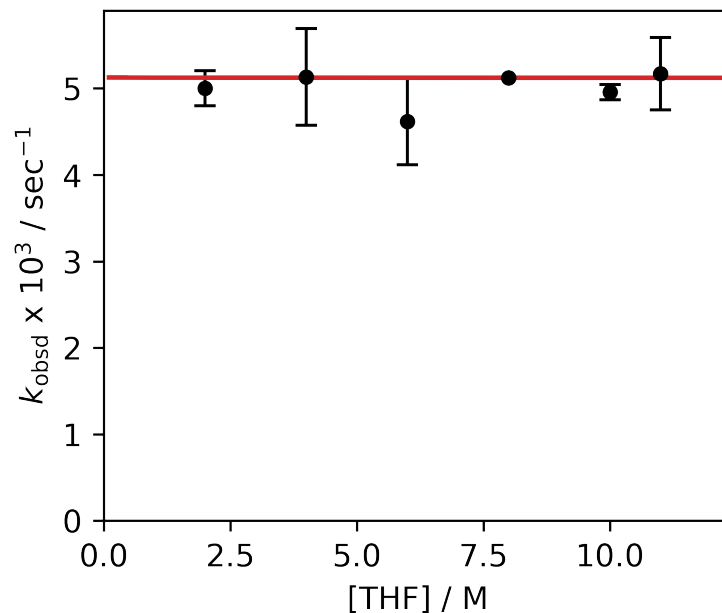


Figure S115. THF order @ 0.275 M free HMPA/2,5-DimethylTHF | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/2,5-DimethylTHF at -78 °C.

The red curve depicts an error-weighted least-squares fit to the function $f(x) = y_0 + ax$ such that $y_0 = 4.9 \times 10^{-3} \pm 0.2 \times 10^{-3}$, $a = 1.1 \times 10^{-5} \pm 2.9 \times 10^{-5}$.

Table S4. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA/2,5-DimethylTHF at -78 °C.

[THF] / M	$k_{\text{obsd}} \times 10^3 / \text{sec}^{-1}$	Standard Deviation $\times 10^3 / \text{sec}^{-1}$
11.00	5.17	0.41
10.00	4.96	0.08
8.00	5.12	0.01
6.00	4.62	0.50
4.00	5.13	0.56
2.00	5.00	0.20

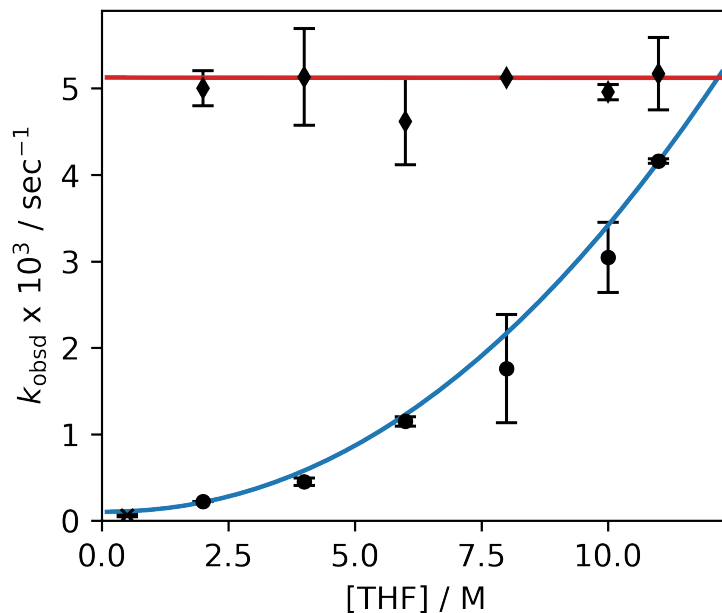


Figure S116. THF order @ 0.275 M free HMPA | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA at -78 °C in toluene (●) or 2,5-DimethylTHF (◆) co-solvent. The point denoted by an asterisk (0.5 M THF) falls outside pseudo-first-order conditions.

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = y_0 + ax^b$ such that $y_0 = 1.0 \times 10^{-4} \pm 0.1 \times 10^{-4}$, $a = 2.5 \times 10^{-5} \pm 0.4 \times 10^{-5}$, $b = 2.1 \pm 0.1$. The red curve depicts an error-weighted least-squares fit to the function $f(x) = y_0 + ax$ such that $y_0 = 4.9 \times 10^{-3} \pm 0.2 \times 10^{-3}$, $a = 1.1 \times 10^{-5} \pm 2.9 \times 10^{-5}$. Asterisks (*) denote point(s) outside pseudo-first-order restraints; these points are excluded from the fit.

Table S5. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.275 M free HMPA at -78 °C in toluene or 2,5-DimethylTHF co-solvent.

Cosolvent:	Toluene		2,5-DimethylTHF	
[THF] / M	$k_{\text{obsd}} \times 10^3 / \text{sec}^{-1}$	Standard Deviation $\times 10^3 / \text{sec}^{-1}$	$k_{\text{obsd}} \times 10^3 / \text{sec}^{-1}$	Standard Deviation $\times 10^3 / \text{sec}^{-1}$
11.00	4.16	0.02	5.17	0.41
10.00	3.04	0.41	4.96	0.08
8.00	1.76	0.62	5.12	0.01
6.00	1.15	0.05	4.62	0.50
4.00	0.45	0.04	5.13	0.56
2.00	0.22	0.001	5.00	0.20
0.50*	0.061	0.016		

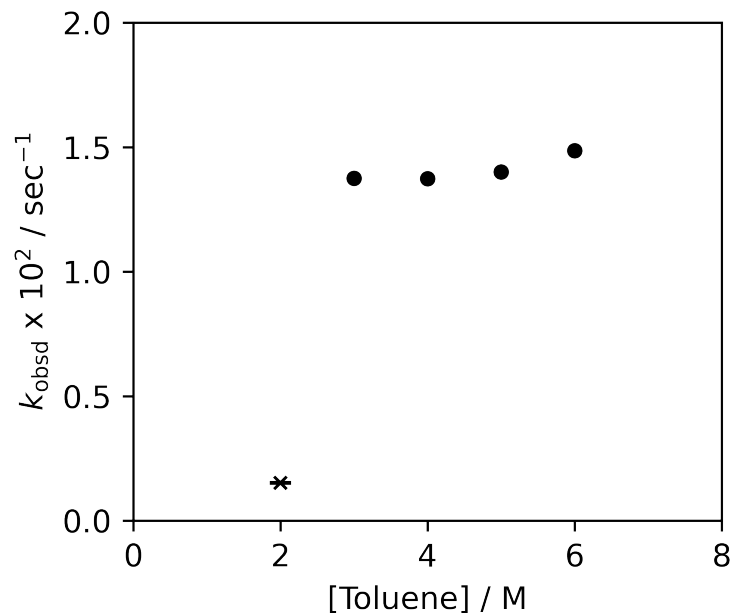


Figure S117. Toluene order @ 0.810 M HMPA/cyclopentane | Plot of pseudo-first-order rate constants (k_{obsd}) against toluene concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/2.0 M THF/cyclopentane at -78 °C. Points denoted by asterisks (*) indicate solubility issues.

Table S6. Average initial rate constants (k_{obsd}) at various Toluene concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/2.0 M THF/cyclopentane at -78 °C. Points denoted by asterisks (*) indicate solubility issues.

[Toluene] / M	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$
6.25	1.77
6.00	1.49
5.00	1.40
4.00	1.37
3.00	1.37
2.00*	0.15

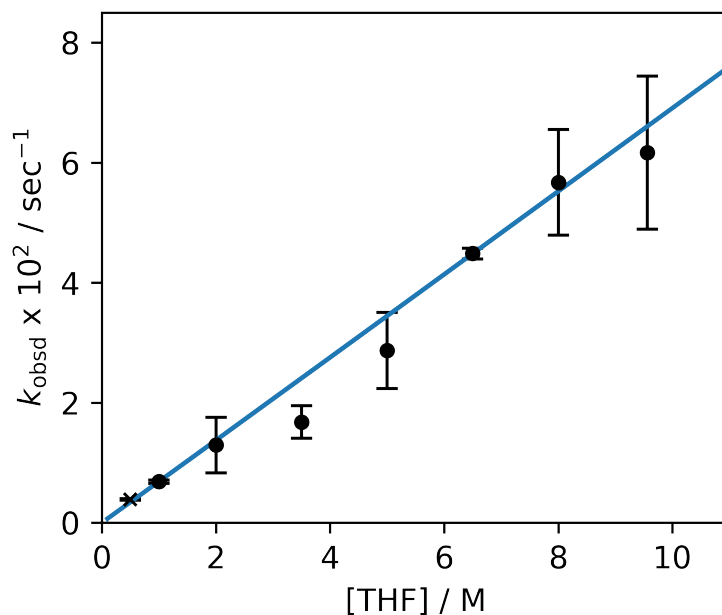


Figure S118. THF order @ 0.810 M free HMPA/Toluene | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/toluene at -78 °C. Points outside pseudo-first-order conditions are denoted by asterisks (*).

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = ax^b$ such that $a = 0.684 \pm 0.004$, $b = 1.00 \pm 0.01$.

Table S7. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/toluene at -78 °C. Asterisks (*) denote point(s) outside pseudo-first-order restraints; these points are excluded from the fit.

[THF] / M	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$
9.56	6.17	1.28
8.00	5.67	0.88
6.50	4.48	0.08
5.00	2.87	0.63
3.50	1.68	0.27
2.00	1.29	0.46
1.00	0.68	0.03
0.50*	0.39	0.01

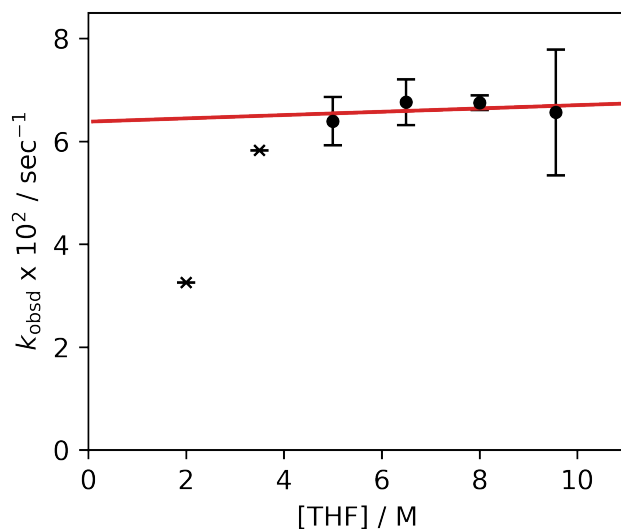


Figure S119. THF order @ 0.810 M free HMPA/2,5-DimethylTHF | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/2,5-DimethylTHF at -78 °C. Points denoted by asterisks (*) indicate ones where solubility issues prevented full measurement of the first-order decay.

The red curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = y_0 + ax$ such that $y_0 = 0.064 \pm 0.004$, $a = 3.2 \times 10^{-4} \pm 5.9 \times 10^{-4}$.

Table S8. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (*S*)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA/2,5-DimethylTHF at -78 °C. Points denoted by asterisks (*) indicate ones where solubility issues prevented full measurement of the first-order decay.

[THF] / M	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$
9.56	6.56	1.22
8.00	6.75	0.14
6.50	6.76	0.44
5.00	6.39	0.47
3.50*	5.82	<i>not replicated</i>
2.00*	3.25	<i>not replicated</i>

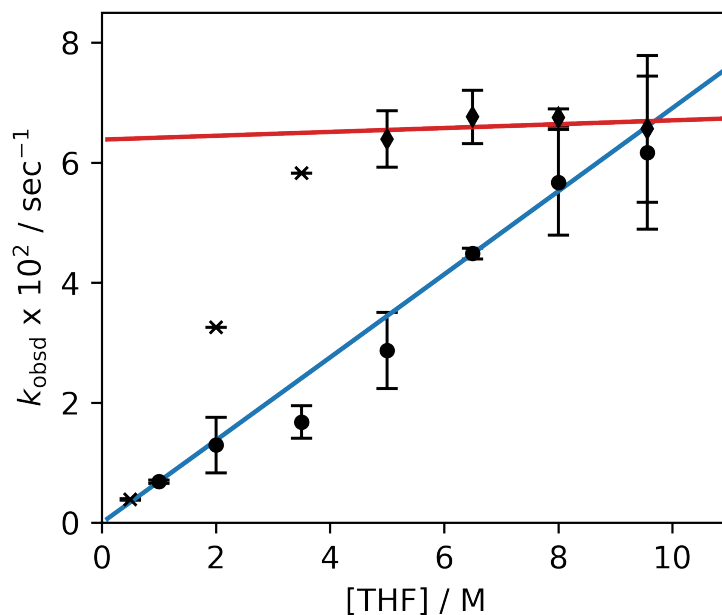


Figure S120. THF order @ 0.810 M free HMPA | Plot of pseudo-first-order rate constants (k_{obsd}) against THF concentration for alkylation of 0.025 M (S)-**8o** with 0.275 M allyl bromide in 0.810 M free HMPA at -78 °C in toluene (blue ●) or 2,5-DimethylTHF (red ◆) co-solvent. Points denoted by asterisks (*) indicate solubility issues (in DimethylTHF) or those outside pseudo-first-order conditions (in toluene).

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = ax^b$ such that $a = 0.684 \pm 0.004$, $b = 1.00 \pm 0.01$.

The red curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = y_0 + ax$ such that $y_0 = 0.064 \pm 0.004$, $a = 3.2 \times 10^{-4} \pm 5.9 \times 10^{-4}$.

Table S9. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M (S)-**8o** with 0.275 M allyl bromide in 0.810 M HMPA at -78 °C in toluene or 2,5-DimethylTHF co-solvent. Points denoted by asterisks (*) indicate solubility issues (DimethylTHF) or those outside pseudo-first-order conditions (toluene).

Cosolvent:	Toluene		2,5-DimethylTHF	
[THF] / M	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$
9.56	6.17	1.28	6.56	1.22
8.00	5.67	0.88	6.75	0.14
6.50	4.48	0.08	6.76	0.44
5.00	2.87	0.63	6.39	0.47
3.50	1.68	0.27	5.82	<i>not replicated</i>
2.00	1.29	0.46	3.25	<i>not replicated</i>
1.00	0.68	0.03		
0.50	0.39	0.01		

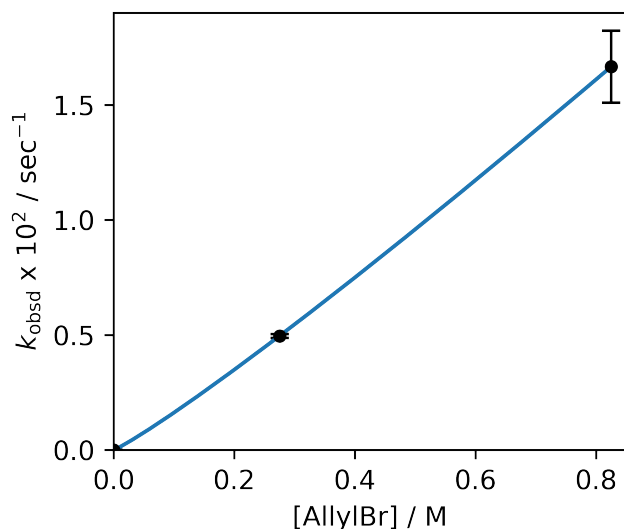


Figure S121. Allyl bromide order I Plot of pseudo-first-order rate constants (k_{obsd}) against allyl bromide concentration for alkylation of 0.025 M (*S*)-**8o** with allyl bromide in 0.275 M free HMPA/9.0 M THF/toluene at -78 °C.

The blue curve depicts an error-weighted least-squares fit of only the bulleted points to the function $f(x) = ax^b$ such that $a = 0.021 \pm 0.002$, $b = 1.1 \pm 0.1$.

Table S10. Average pseudo-first-order rate constants (k_{obsd}) at various allyl bromide concentrations for alkylation of 0.025 M (*S*)-**8o** with allyl bromide in 0.275 M free HMPA/9.0 M THF/toluene at -78 °C.

[AllylBr] / M	$k_{\text{obsd}} \times 10^2 / \text{sec}^{-1}$	Standard Deviation $\times 10^2 / \text{sec}^{-1}$
0.825	1.66	0.16
0.275	0.50	0.01
0	0	0

Single Crystal X-Ray Diffraction Data

General methods

Low-temperature X-ray diffraction data for **Rnml1**, **Rnml2**, **Rnml4** and **Rnml5** were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$), from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.^{S6} The structures were solved through intrinsic phasing using SHELXT^{S7} and refined against F^2 on all data by full-matrix least squares with SHELXL^{S8} following established refinement strategies.^{S9} All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). **Rnml1** and **Rnml2** were refined as inversion twins. Both **Rnml1** and **Rnml2** contain disordered solvent molecules of THF that were included in the unit cell but could not be satisfactorily modeled. Therefore, those solvents were treated as diffuse contributions to the overall scattering without specific atom positions using the solvent mask routine in Olex2.^{S10} Details of the data quality and a summary of the residual values of the refinements are listed below.

All structures have been deposited with the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 2202043-2202046.

Conditions of growth for Rnm11

To a flame dried NMR tube was added 200 μL 0.30 M (*S*)-**7g** in THF, 250 μL 0.66 M [^6Li - ^{15}N]-LDA in THF, and 150 μL THF at $-78\text{ }^\circ\text{C}$. The tube was sealed under reduced Ar atmosphere and mixed by sequential 5 second vortex/cooling cycles and stored in a $-80\text{ }^\circ\text{C}$ freezer. Several months later it was observed that a white precipitate had formed. Crystals were grown by warming the tube in a water bath until fully dissolved and allowing the solution to cool to room temperature slowly and then further to $-20\text{ }^\circ\text{C}$.

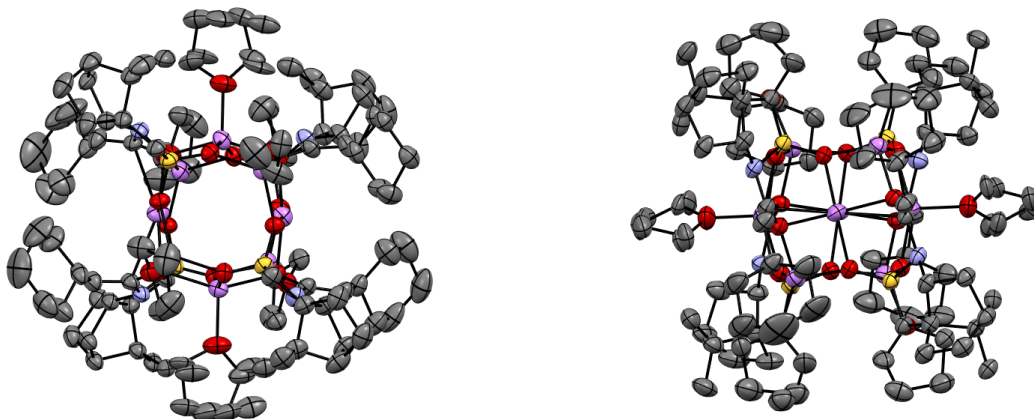


Figure S122. X-ray crystal structure of Rnm11. **a** | Top view. **b** | Side view.

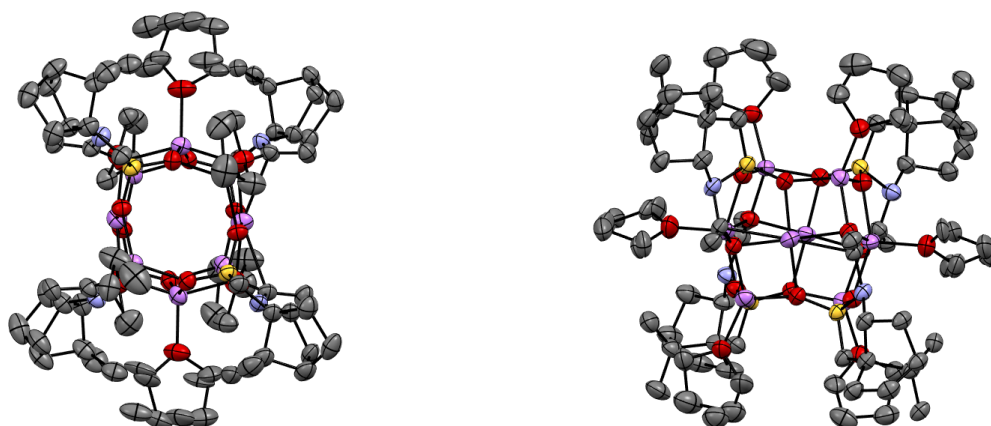


Figure S123. X-ray crystal structure of Rnm11 with cyclohexyl groups hidden. **a** | Top view. **b** | Side view.

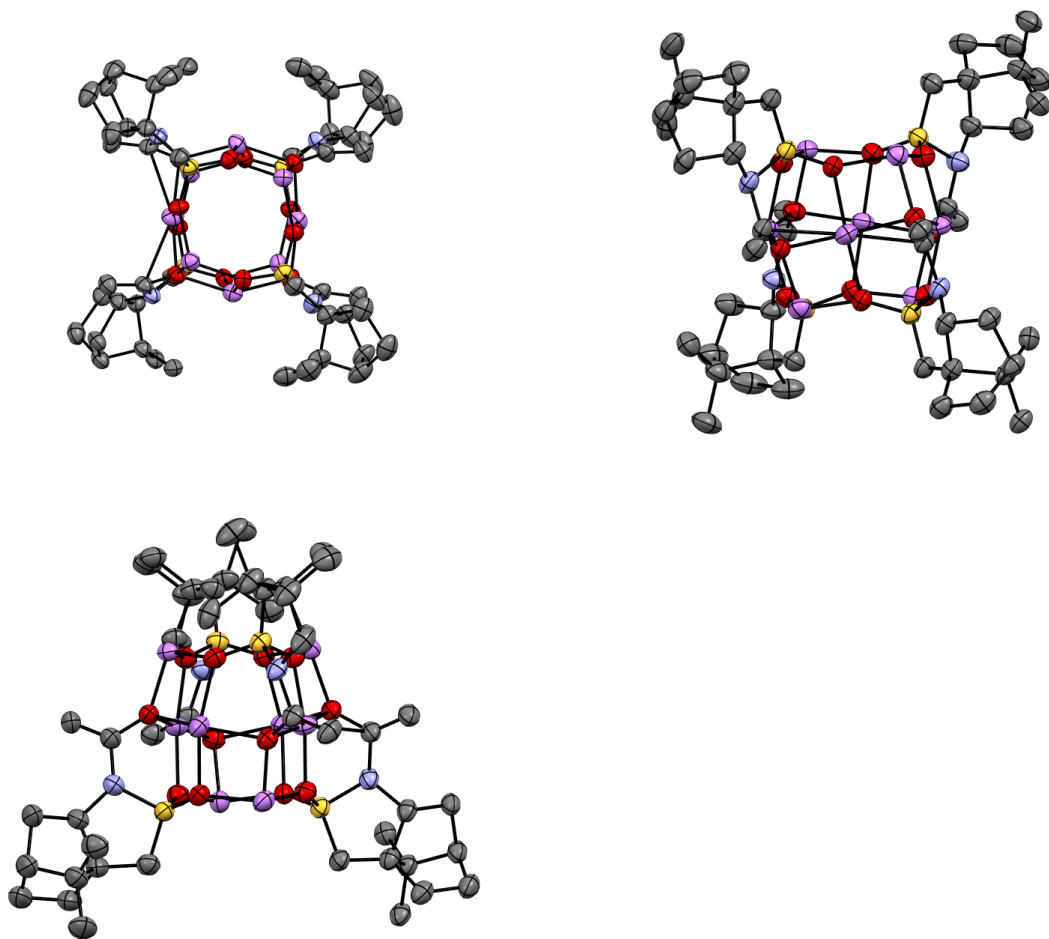


Figure S124. X-ray crystal structure of Rnml1 with cyclohexyl groups and solvent molecules hidden. **a** | Top view. **b** | Side view. **c** | Rotated side view.

Table S11. Crystal data and structure refinement for Rnml1.

Identification code	rnml1_abs	
CCDC Deposition Number	2202046	
Empirical formula	C124 H220 Li8 N4 O25 S4	
Formula weight	2350.79	
Temperature	100.0(5) K	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	P 41 21 2	
Unit cell dimensions	a = 25.17460(10) Å	a = 90°.
	b = 25.17460(10) Å	b = 90°.
	c = 43.1549(3) Å	g = 90°.
Volume	27349.9(3) Å ³	
Z	8	
Density (calculated)	1.142 Mg/m ³	
Absorption coefficient	1.156 mm ⁻¹	
F(000)	10240	
Crystal size	0.503 x 0.361 x 0.267 mm ³	
Theta range for data collection	2.482 to 77.229°.	
Index ranges	-31<=h<=31, -30<=k<=29, -38<=l<=54	
Reflections collected	208334	
Independent reflections	28635 [R(int) = 0.0838]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.223	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	28635 / 494 / 1268	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1448	
R indices (all data)	R1 = 0.0568, wR2 = 0.1496	
Absolute structure parameter	0.043(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.341 and -0.298 e.Å ⁻³	

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rnml1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
S(1)	2190(1)	6341(1)	4154(1)	40(1)
S(2)	1600(1)	8212(1)	4900(1)	38(1)
S(3)	3486(1)	6779(1)	4943(1)	40(1)
S(4)	2952(1)	8610(1)	4157(1)	41(1)
O(1)	2668(1)	6673(1)	4086(1)	44(1)
O(2)	2021(1)	6482(1)	4471(1)	44(1)
O(3)	1784(1)	7392(1)	4072(1)	40(1)
O(4)	865(1)	6962(1)	4516(1)	68(1)
O(5)	1540(1)	8005(1)	4584(1)	42(1)
O(6)	2180(1)	8201(1)	4973(1)	44(1)
O(7)	1838(1)	7113(1)	4982(1)	41(1)
O(8)	2196(1)	5736(1)	5028(1)	55(1)
O(9)	3562(1)	6974(1)	4626(1)	44(1)
O(10)	2906(1)	6793(1)	5006(1)	43(1)
O(11)	3246(1)	7879(1)	5001(1)	40(1)
O(12)	2886(1)	9260(1)	5003(1)	56(1)
O(13)	2481(1)	8274(1)	4087(1)	45(1)
O(14)	3114(1)	8484(1)	4474(1)	43(1)
O(15)	3371(1)	7563(1)	4097(1)	41(1)
O(16)	3861(1)	6214(1)	4092(1)	50(1)
O(17)	4259(1)	8011(1)	4565(1)	67(1)
O(18)	1300(1)	8741(1)	4021(1)	47(1)
N(1)	1720(1)	6526(1)	3901(1)	45(1)
N(2)	1312(1)	7798(1)	5154(1)	40(1)
N(3)	3764(1)	7205(1)	5194(1)	42(1)
N(4)	3426(1)	8420(1)	3906(1)	44(1)
C(1)	2218(1)	5705(1)	4075(1)	48(1)
C(2)	1869(1)	5587(1)	3804(1)	48(1)
C(3)	2084(2)	5251(1)	3533(1)	57(1)
C(4)	1585(2)	5157(1)	3324(1)	66(1)
C(5)	1131(2)	5413(1)	3516(1)	63(1)
C(6)	1184(1)	6026(1)	3485(1)	55(1)

C(7)	1723(1)	6130(1)	3651(1)	47(1)
C(8)	1316(1)	5317(1)	3851(1)	54(1)
C(9)	1343(2)	4729(1)	3941(1)	63(1)
C(10)	960(1)	5593(1)	4102(1)	59(1)
C(11)	1712(1)	7083(1)	3824(1)	42(1)
C(12)	1620(1)	7249(1)	3532(1)	47(1)
C(13)	1565(1)	7812(1)	3430(1)	48(1)
C(14)	1010(2)	7916(2)	3291(1)	67(1)
C(15)	951(2)	8486(2)	3169(1)	83(1)
C(16)	1378(3)	8616(2)	2951(1)	96(2)
C(17)	1934(3)	8540(2)	3098(1)	99(2)
C(18)	2007(2)	7972(2)	3215(1)	74(1)
C(19)	1272(1)	8755(1)	4983(1)	42(1)
C(20)	909(1)	8648(1)	5248(1)	41(1)
C(21)	863(1)	9058(1)	5517(1)	50(1)
C(22)	375(1)	8847(1)	5706(1)	53(1)
C(23)	181(1)	8364(1)	5515(1)	45(1)
C(24)	582(1)	7912(1)	5561(1)	45(1)
C(25)	1089(1)	8129(1)	5402(1)	42(1)
C(26)	303(1)	8543(1)	5180(1)	41(1)
C(27)	8(1)	9038(1)	5067(1)	46(1)
C(28)	193(1)	8108(1)	4938(1)	44(1)
C(29)	1606(1)	7321(1)	5229(1)	40(1)
C(30)	1634(1)	7147(1)	5521(1)	48(1)
C(31)	1875(1)	6630(1)	5619(1)	52(1)
C(32)	2327(2)	6701(2)	5850(1)	81(1)
C(33)	2570(2)	6163(2)	5946(1)	106(2)
C(34)	2147(3)	5790(3)	6075(1)	122(2)
C(35)	1678(2)	5712(2)	5854(1)	86(1)
C(36)	1458(2)	6252(2)	5750(1)	74(1)
C(37)	3800(1)	6238(1)	5036(1)	45(1)
C(38)	4152(1)	6350(1)	5312(1)	46(1)
C(39)	4170(2)	5961(2)	5591(1)	59(1)
C(40)	4641(2)	6171(2)	5789(1)	65(1)
C(41)	4863(1)	6632(2)	5590(1)	58(1)
C(42)	4472(1)	7099(2)	5618(1)	52(1)

C(43)	3971(1)	6882(1)	5452(1)	46(1)
C(44)	4757(1)	6438(2)	5255(1)	56(1)
C(45)	5046(2)	5927(2)	5165(1)	73(1)
C(46)	4893(1)	6857(2)	5007(1)	60(1)
C(47)	3462(1)	7680(1)	5255(1)	42(1)
C(48)	3431(1)	7880(1)	5542(1)	53(1)
C(49)	3177(1)	8402(2)	5623(1)	58(1)
C(50)	2681(2)	8328(2)	5826(1)	85(1)
C(51)	2432(3)	8852(3)	5911(2)	116(2)
C(52)	2833(4)	9240(4)	6061(2)	150(3)
C(53)	3334(2)	9319(2)	5859(2)	106(2)
C(54)	3567(2)	8782(2)	5779(1)	90(2)
C(55)	2924(1)	9240(1)	4072(1)	47(1)
C(56)	3244(1)	9348(1)	3789(1)	48(1)
C(57)	3009(2)	9663(1)	3518(1)	63(1)
C(58)	3500(2)	9755(1)	3304(1)	74(1)
C(59)	3957(2)	9527(1)	3487(1)	67(1)
C(60)	3927(2)	8909(1)	3473(1)	62(1)
C(61)	3393(1)	8805(1)	3646(1)	49(1)
C(62)	3789(2)	9636(1)	3823(1)	57(1)
C(63)	4157(2)	9385(1)	4070(1)	64(1)
C(64)	3746(2)	10235(1)	3904(1)	71(1)
C(65)	3452(1)	7857(1)	3847(1)	44(1)
C(66)	3552(1)	7677(1)	3557(1)	48(1)
C(67)	3631(1)	7101(1)	3476(1)	48(1)
C(68)	4183(1)	7011(1)	3333(1)	46(1)
C(69)	4272(1)	6430(1)	3244(1)	50(1)
C(70)	3836(1)	6239(1)	3032(1)	56(1)
C(71)	3286(2)	6307(1)	3179(1)	64(1)
C(72)	3197(1)	6892(1)	3264(1)	61(1)
C(73)	668(6)	6651(7)	4786(3)	63(3)
C(74)	58(5)	6651(5)	4739(5)	77(4)
C(75)	4(6)	6697(8)	4408(6)	84(5)
C(76)	431(7)	7091(11)	4312(5)	70(4)
C(77)	551(5)	6622(5)	4697(4)	78(3)
C(78)	-11(5)	6710(7)	4564(5)	94(4)

C(79)	60(4)	6801(4)	4231(4)	80(3)
C(80)	547(5)	7140(8)	4249(4)	72(3)
C(81)	1751(2)	5410(2)	4930(1)	67(1)
C(82)	1985(2)	4881(2)	4852(1)	90(1)
C(83)	2595(3)	4960(2)	4893(1)	97(2)
C(84)	2626(2)	5396(2)	5109(1)	70(1)
C(85)	3337(2)	9589(2)	4927(1)	64(1)
C(86)	3093(2)	10122(2)	4841(1)	94(2)
C(87)	2468(3)	10020(3)	4859(2)	76(2)
C(88)	2439(2)	9589(2)	5073(1)	84(1)
C(89)	2615(5)	10155(5)	5051(3)	76(2)
C(90)	3690(2)	5671(2)	4063(1)	84(1)
C(91)	4189(3)	5357(2)	4028(2)	61(2)
C(92)	4584(2)	5654(2)	4197(1)	77(1)
C(93)	4422(1)	6222(1)	4156(1)	55(1)
C(94)	4044(5)	5343(5)	4228(5)	105(5)
C(95)	4679(4)	7925(5)	4339(2)	60(2)
C(96)	5123(3)	8316(4)	4437(3)	70(3)
C(97)	5061(4)	8344(3)	4789(3)	75(3)
C(98)	4455(4)	8327(5)	4830(2)	69(3)
C(99)	4561(9)	7869(11)	4283(6)	77(6)
C(100)	5067(6)	8204(6)	4265(7)	75(5)
C(101)	5083(6)	8327(10)	4616(8)	92(6)
C(102)	4521(7)	8405(8)	4745(6)	70(5)
C(103)	1489(1)	9261(1)	3942(1)	53(1)
C(104)	1164(2)	9624(2)	4139(1)	70(1)
C(105)	627(2)	9369(2)	4138(1)	72(1)
C(106)	748(1)	8774(1)	4093(1)	50(1)
Li(1)	2576(2)	7474(2)	4046(1)	43(1)
Li(2)	2542(2)	7504(2)	5033(1)	49(1)
Li(3)	3528(2)	7785(2)	4554(1)	45(1)
Li(4)	1600(2)	7186(2)	4527(1)	40(1)
Li(5)	2860(2)	8508(2)	4894(1)	46(1)
Li(6)	1745(2)	8138(2)	4160(1)	42(1)
Li(7)	3393(2)	6817(2)	4197(1)	39(1)
Li(8)	2237(2)	6480(2)	4894(1)	44(1)

Conditions of growth for Rnml2

To a flame dried NMR tube was added 200 μL 0.30 M (*S*)-**7c** in THF, 42 μL 4.31 M HMPA in toluene, 100 μL 0.66 M [^6Li]-LDA in THF-*d*₈, and 258 μL pentane at $-78\text{ }^\circ\text{C}$. The tube was sealed under reduced Ar atmosphere and mixed by sequential 5 second vortex/cooling cycles and stored in a $-80\text{ }^\circ\text{C}$ freezer. White crystals formed over several days.

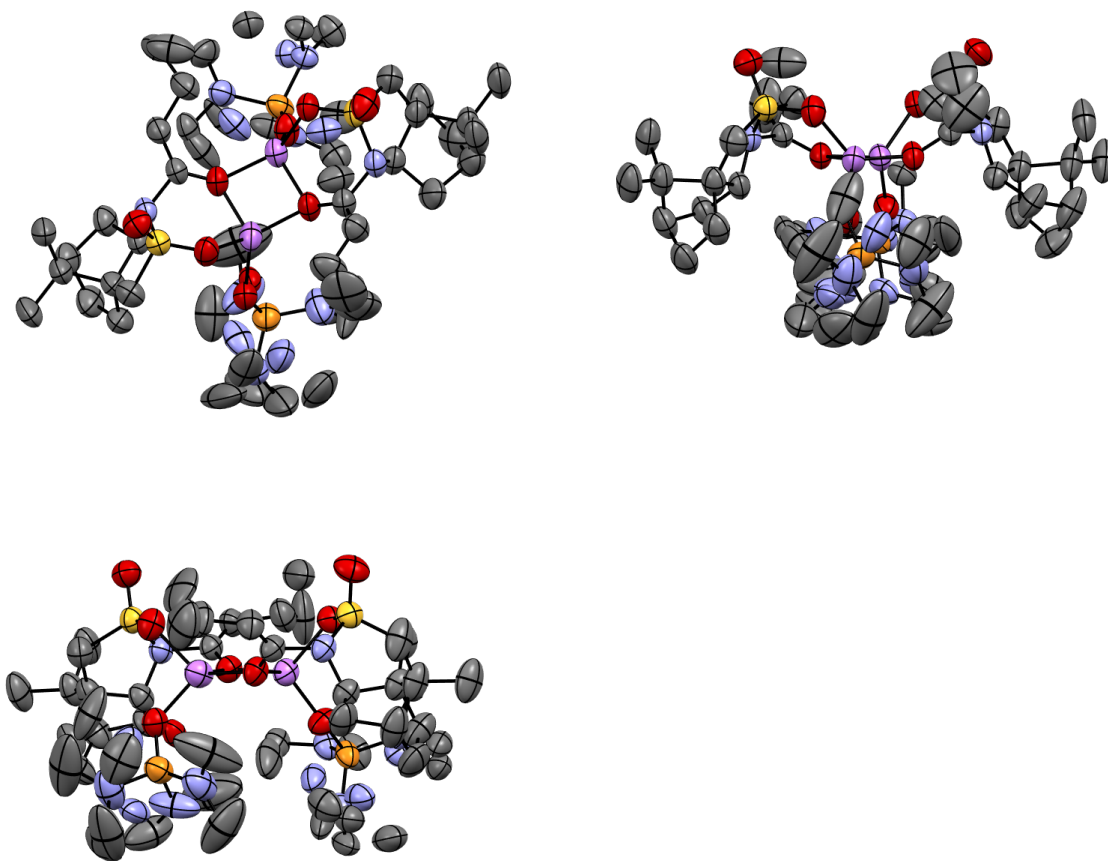


Figure S125. X-ray crystal structure of Rnml2. **a** | Top view. **b** | Side view. **c** | Rotated side view.

Table S13. Crystal data and structure refinement for Rnml2.

Identification code	rnml2_abs	
CCDC Deposition Number	2202044	
Empirical formula	C _{52.35} H _{105.05} Li ₂ N ₈ O ₁₁ P ₂ S ₂	
Formula weight	1162.63	
Temperature	100.0(5) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	P 31 2 1	
Unit cell dimensions	a = 17.3618(2) Å	a = 90°.
	b = 17.3618(2) Å	b = 90°.
	c = 37.1890(4) Å	g = 120°.
Volume	9708.1(2) Å ³	
Z	6	
Density (calculated)	1.193 Mg/m ³	
Absorption coefficient	1.682 mm ⁻¹	
F(000)	3787	
Crystal size	0.353 x 0.212 x 0.192 mm ³	
Theta range for data collection	2.939 to 77.110°.	
Index ranges	-21<=h<=21, -20<=k<=21, -46<=l<=46	
Reflections collected	83559	
Independent reflections	13432 [R(int) = 0.0615]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.313	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13432 / 1007 / 745	
Goodness-of-fit on F ²	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1404	
R indices (all data)	R1 = 0.0580, wR2 = 0.1476	
Absolute structure parameter	0.018(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.355 and -0.296 e.Å ⁻³	

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rnml2. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	5878(1)	794(1)	7192(1)	62(1)
S(2)	6175(1)	-1173(1)	5630(1)	60(1)
P(1)	5419(1)	2496(1)	6164(1)	64(1)
P(2)	8704(1)	2134(1)	5646(1)	73(1)
O(1)	5366(2)	466(2)	6868(1)	62(1)
O(2)	5731(2)	130(2)	7451(1)	86(1)
O(3)	7092(2)	1116(2)	6502(1)	64(1)
O(4)	6768(2)	-690(2)	5920(1)	73(1)
O(5)	5582(2)	-2091(2)	5698(1)	74(1)
O(6)	5843(2)	325(2)	5943(1)	62(1)
O(7)	5774(2)	1948(2)	6294(1)	72(1)
O(8)	8061(7)	1198(9)	5723(2)	66(2)
O(8B)	7868(16)	1466(19)	5741(3)	65(7)
N(1)	6946(2)	1415(2)	7109(1)	60(1)
N(2)	5621(2)	-690(2)	5486(1)	57(1)
N(3)	4651(4)	1865(4)	5837(2)	67(2)
N(3B)	5340(7)	2460(6)	5739(2)	86(3)
N(4)	4804(4)	2533(4)	6485(2)	60(1)
N(4B)	4632(5)	2664(5)	6317(2)	65(2)
N(5)	6082(4)	3410(4)	5995(2)	68(2)
N(5B)	6299(6)	3555(6)	6252(3)	81(2)
N(6)	8208(5)	2575(6)	5398(2)	130(3)
N(6B)	8892(9)	2527(7)	5264(3)	96(4)
N(7)	9497(4)	2223(5)	5398(2)	114(3)
N(7B)	9404(8)	1772(9)	5756(5)	113(5)
N(8)	9059(4)	2879(3)	5963(1)	111(2)
C(1)	5717(3)	1634(3)	7377(1)	83(1)
C(2)	6596(3)	2509(3)	7332(1)	69(1)
C(3)	6560(4)	3327(3)	7201(2)	94(1)
C(4)	7550(5)	4076(4)	7264(2)	117(2)
C(5)	7971(3)	3596(4)	7451(2)	104(2)
C(6)	8122(3)	3043(3)	7164(2)	90(1)

C(7)	7166(3)	2340(2)	7062(1)	66(1)
C(8)	7215(3)	2886(3)	7668(1)	83(1)
C(9)	7411(4)	2230(4)	7865(1)	102(2)
C(10)	6823(4)	3253(4)	7955(2)	105(2)
C(11)	7291(2)	1048(2)	6831(1)	61(1)
C(12)	7754(3)	686(3)	6954(1)	73(1)
C(13)	8137(4)	263(5)	6724(2)	103(2)
C(14)	9013(11)	510(20)	6839(7)	168(11)
C(14B)	8580(30)	-150(30)	6899(7)	158(11)
C(15)	6813(3)	-999(3)	5229(1)	76(1)
C(16)	6594(2)	-448(3)	4979(1)	68(1)
C(17)	7353(3)	324(3)	4779(1)	80(1)
C(18)	6845(3)	596(4)	4503(1)	94(1)
C(19)	5865(3)	-112(4)	4570(1)	83(1)
C(20)	5582(3)	131(3)	4926(1)	74(1)
C(21)	6147(2)	-40(2)	5206(1)	62(1)
C(22)	5902(3)	-933(3)	4666(1)	78(1)
C(23)	6280(4)	-1270(4)	4372(1)	104(2)
C(24)	5020(3)	-1721(4)	4786(1)	88(1)
C(25)	5261(2)	-377(2)	5775(1)	56(1)
C(26)	4383(3)	-854(2)	5819(1)	66(1)
C(27)	3895(3)	-641(4)	6101(1)	90(1)
C(28)	3049(6)	-755(9)	5982(3)	147(6)
C(28B)	3078(17)	-1359(15)	6226(10)	123(11)
C(29)	4903(7)	1441(8)	5560(3)	71(2)
C(29B)	5396(18)	1768(17)	5550(5)	131(8)
C(30)	3866(5)	1917(8)	5767(2)	91(3)
C(30B)	5250(13)	3099(11)	5512(3)	124(6)
C(31)	4183(5)	1747(4)	6684(2)	64(2)
C(31B)	3768(6)	2097(7)	6168(3)	84(3)
C(32)	4726(6)	3303(6)	6561(3)	72(2)
C(32B)	4644(8)	2960(8)	6684(2)	74(2)
C(33)	5844(7)	3862(6)	5725(2)	88(3)
C(33B)	6333(9)	4425(7)	6230(4)	108(4)
C(34)	6838(9)	3960(6)	6202(2)	85(2)
C(34B)	7199(8)	3669(11)	6216(4)	103(4)

C(35)	7336(7)	2425(8)	5500(5)	238(7)
C(35B)	9822(17)	3030(20)	5120(8)	172(10)
C(36)	8293(7)	2725(5)	5048(2)	159(3)
C(37)	10320(8)	3108(11)	5354(5)	198(10)
C(37B)	10314(12)	2243(18)	5917(8)	160(10)
C(38)	9562(7)	1489(11)	5241(7)	226(11)
C(38B)	9194(14)	872(14)	5637(8)	149(10)
C(39)	9255(6)	3750(5)	5944(4)	204(6)
C(40)	9279(7)	2610(7)	6292(2)	235(7)
Li(1)	5928(4)	968(4)	6375(1)	62(1)
Li(2)	7049(4)	567(4)	6050(2)	68(1)

Conditions of growth for Rnm15

To a flame dried NMR tube was added 20 μL of 0.60 M (*S*)-**7t** in toluene, 80 μL 0.60 M (*R*)-**7t** in toluene, 100 μL 0.66 M [^6Li]-LDA in THF- d_8 , and 400 μL THF at $-78\text{ }^\circ\text{C}$. The tube was mixed by sequential 5 second vortex/cooling cycles and stored in a $-80\text{ }^\circ\text{C}$ freezer. White crystals formed overnight.

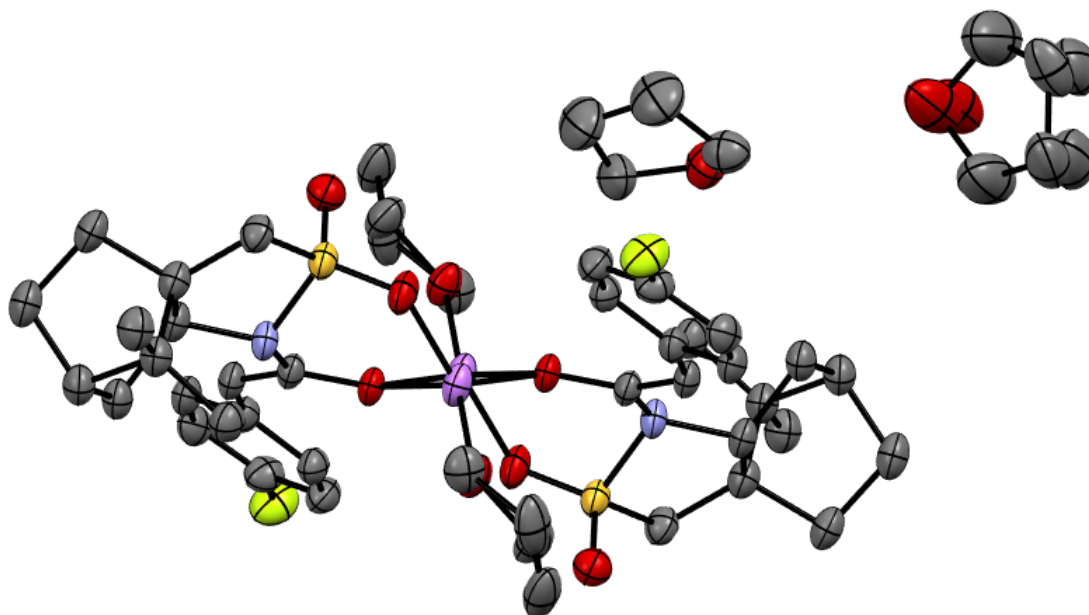


Figure S126. X-ray crystal structure of Rnm15.

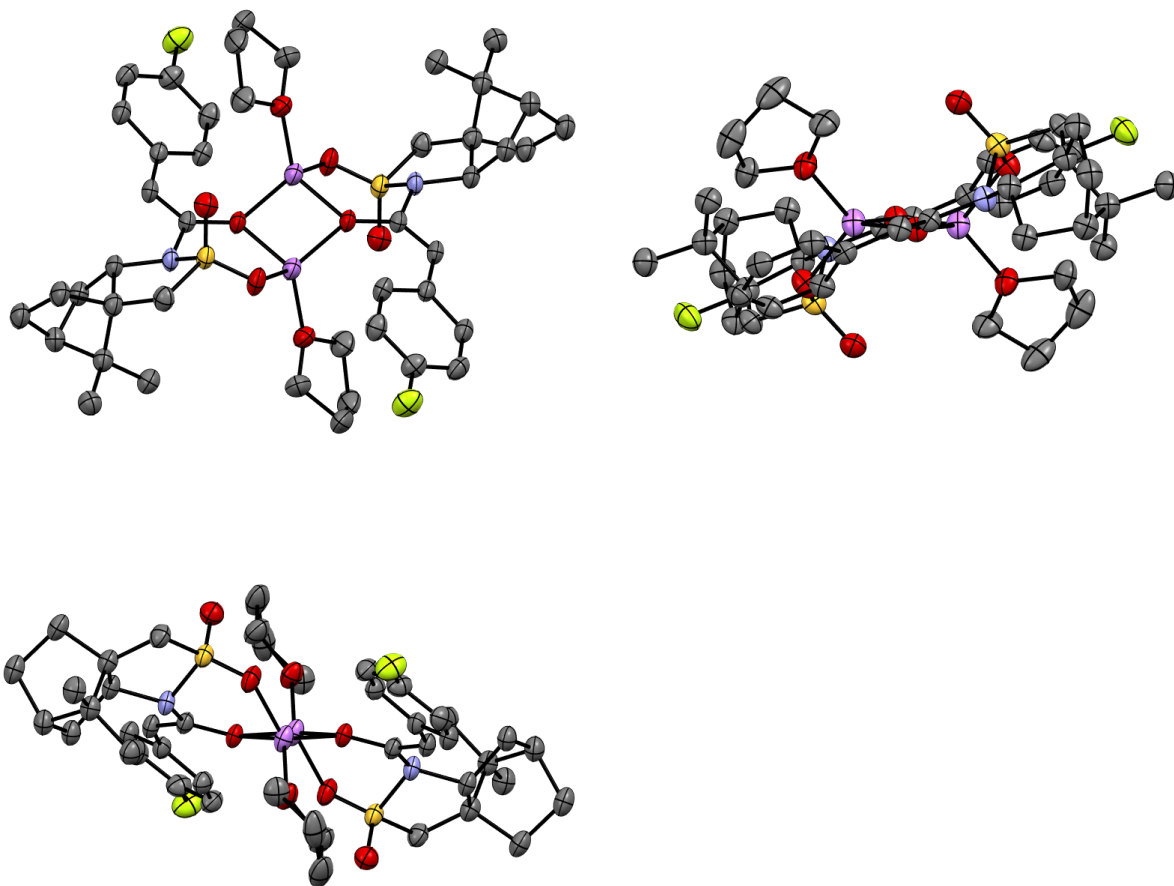


Figure S127. X-ray crystal structure of Rnml5 with outer solvent molecules hidden. **a** | Top view. **b** | Side view. **c** | Rotated side view.

Table S15. Crystal data and structure refinement for Rnm15.

Identification code	rnm15_abs
CCDC Deposition Number	2202043
Empirical formula	C60 H90 F2 Li2 N2 O12 S2
Formula weight	1147.33
Temperature	99.9(8) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 11.13210(10) Å a = 90°. b = 13.8801(2) Å b = 100.2770(10)°. c = 19.6841(3) Å g = 90°.
Volume	2992.69(7) Å ³
Z	2
Density (calculated)	1.273 Mg/m ³
Absorption coefficient	1.363 mm ⁻¹
F(000)	1232
Crystal size	0.262 x 0.095 x 0.089 mm ³
Theta range for data collection	3.918 to 70.072°.
Index ranges	-13<=h<=10, -16<=k<=16, -23<=l<=23
Reflections collected	40579
Independent reflections	5681 [R(int) = 0.0466]
Completeness to theta = 67.684°	99.9 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.604
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5681 / 85 / 385
Goodness-of-fit on F ²	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1770
R indices (all data)	R1 = 0.0687, wR2 = 0.1804
Extinction coefficient	n/a
Largest diff. peak and hole	0.625 and -0.483 e.Å ⁻³

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rnml5. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
S	3162(1)	5559(1)	3453(1)	32(1)
F	1566(2)	3202(1)	7443(1)	52(1)
O(1)	3882(1)	4548(1)	4748(1)	30(1)
O(2)	2606(2)	6341(1)	3757(1)	41(1)
O(3)	4481(2)	5552(2)	3567(1)	40(1)
O(4)	3648(2)	6073(2)	5914(1)	40(1)
N	2654(2)	4494(2)	3677(1)	31(1)
C(1)	2835(2)	3588(2)	5894(1)	34(1)
C(2)	2761(2)	3389(2)	6574(2)	39(1)
C(3)	1640(3)	3402(2)	6770(1)	39(1)
C(4)	582(2)	3594(2)	6314(2)	39(1)
C(5)	671(2)	3809(2)	5636(1)	36(1)
C(6)	1792(2)	3817(2)	5404(1)	31(1)
C(7)	1814(2)	4045(2)	4682(1)	32(1)
C(8)	2790(2)	4354(2)	4420(1)	30(1)
C(9)	2540(2)	5488(2)	2557(1)	36(1)
C(10)	1657(2)	4643(2)	2476(1)	35(1)
C(11)	346(2)	4798(2)	2080(1)	40(1)
C(12)	-129(2)	3750(2)	1988(2)	42(1)
C(13)	978(2)	3125(2)	2301(1)	38(1)
C(14)	1167(2)	3215(2)	3093(1)	36(1)
C(15)	1492(2)	4289(2)	3203(1)	33(1)
C(16)	2056(2)	3718(2)	2123(1)	36(1)
C(17)	3325(2)	3335(2)	2433(2)	41(1)
C(18)	2037(3)	3848(2)	1349(2)	43(1)
C(19)	2635(3)	6496(2)	5448(2)	51(1)
C(20)	1930(3)	7049(3)	5906(2)	62(1)
C(21)	2110(3)	6431(3)	6550(2)	61(1)
C(22)	3423(3)	6119(2)	6615(2)	46(1)
Li	4650(4)	5127(4)	5589(2)	36(1)
O(6)	241(7)	52(6)	4005(7)	93(2)
C(27)	-213(5)	-910(4)	3993(4)	127(3)

C(28)	-1330(9)	-809(7)	4144(7)	69(3)
C(29)	-1755(9)	172(8)	3938(9)	84(4)
C(30)	-737(5)	571(4)	3555(4)	114(2)
O(6B)	163(5)	-78(4)	3581(5)	93(2)
C(28B)	-1404(6)	-969(5)	3651(6)	100(3)
C(29B)	-1846(6)	15(6)	3493(7)	106(3)
O(5)	3360(2)	1578(2)	3820(1)	52(1)
C(23)	2792(3)	1419(3)	4405(2)	54(1)
C(24)	3809(4)	1184(4)	4967(2)	80(1)
C(25)	4875(4)	1733(3)	4795(2)	75(1)
C(26)	4456(3)	2087(3)	4077(2)	58(1)

Conditions of growth for Rnml4

Crystals of **34** were grown by slow evaporation from a supersaturated solution in hexanes in a 20 mL scintillation vial at room temperature.

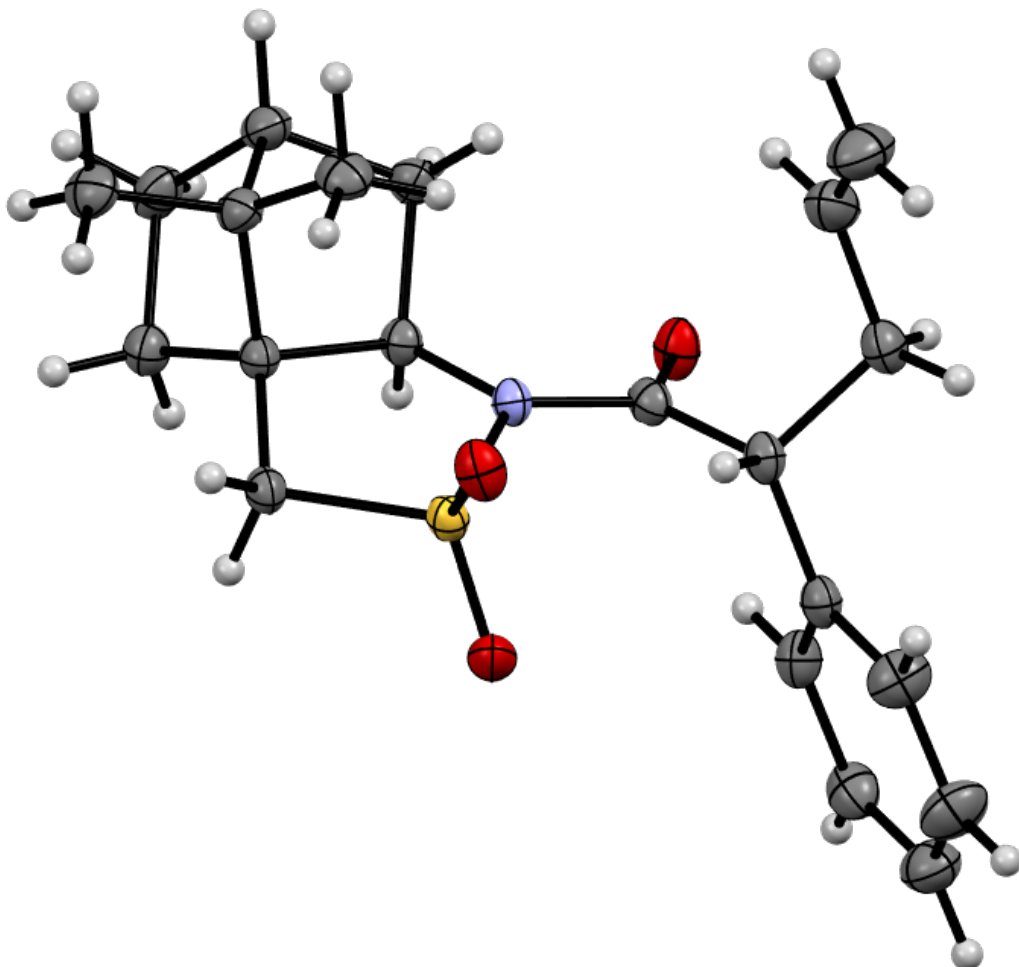


Figure S128. X-ray crystal structure of Rnml4.

Table S17. Crystal data and structure refinement for Rnml4.

Identification code	rnml4_abs	
CCDC Deposition Number	2202045	
Empirical formula	C ₂₁ H ₂₇ N O ₃ S	
Formula weight	373.49	
Temperature	100.0(5) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 1 2 1	
Unit cell dimensions	a = 12.1055(3) Å	a = 90°.
	b = 7.69960(10) Å	b = 102.420(2)°.
	c = 20.9494(5) Å	g = 90°.
Volume	1906.94(7) Å ³	
Z	4	
Density (calculated)	1.301 Mg/m ³	
Absorption coefficient	1.670 mm ⁻¹	
F(000)	800	
Crystal size	0.299 x 0.089 x 0.05 mm ³	
Theta range for data collection	3.895 to 70.075°.	
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -25 ≤ l ≤ 25	
Reflections collected	17098	
Independent reflections	3618 [R(int) = 0.0378]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.535	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3618 / 1 / 237	
Goodness-of-fit on F ²	1.065	
Final R indices [I > 2σ(I)]	R1 = 0.0282, wR2 = 0.0751	
R indices (all data)	R1 = 0.0287, wR2 = 0.0755	
Absolute structure parameter	-0.015(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.228 and -0.245 e.Å ⁻³	

Table S18. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rnml4. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S	4669(1)	3589(1)	3857(1)	19(1)
O(1)	5464(1)	8345(2)	3780(1)	26(1)
O(2)	3939(1)	3921(2)	4297(1)	26(1)
O(3)	4160(1)	2884(2)	3231(1)	26(1)
N	5384(2)	5432(2)	3758(1)	18(1)
C(1)	3845(2)	7308(4)	1655(1)	40(1)
C(2)	4244(2)	7915(4)	2244(1)	32(1)
C(3)	3532(2)	8447(3)	2719(1)	25(1)
C(4)	3644(2)	7143(3)	3296(1)	21(1)
C(5)	2865(2)	7639(3)	3749(1)	21(1)
C(6)	3254(2)	8369(3)	4365(1)	24(1)
C(7)	2500(2)	8787(3)	4755(1)	28(1)
C(8)	1356(2)	8503(4)	4537(1)	34(1)
C(9)	959(2)	7782(4)	3923(1)	38(1)
C(10)	1711(2)	7352(3)	3533(1)	31(1)
C(11)	4882(2)	7047(3)	3639(1)	20(1)
C(12)	6597(2)	5334(3)	4066(1)	18(1)
C(13)	7410(2)	6085(3)	3657(1)	23(1)
C(14)	8216(2)	4543(3)	3638(1)	24(1)
C(15)	8881(2)	4238(3)	4345(1)	27(1)
C(16)	8000(2)	3350(3)	4684(1)	24(1)
C(17)	6916(2)	3386(3)	4136(1)	18(1)
C(18)	5893(2)	2379(3)	4245(1)	20(1)
C(19)	7397(2)	2983(3)	3512(1)	22(1)
C(20)	6545(2)	3047(3)	2853(1)	27(1)
C(21)	7978(2)	1209(3)	3546(1)	28(1)

Computational details

General computational methods

All density functional theory (DFT) calculations were performed using Gaussian 16.^{S11} Geometries were optimized with the M06-2X functional^{S12} along with Grimme's zero-dampened D3 dispersion correction^{S13} (M06-2X-D3(0)) using the double- ζ pcseg-1 basis set from Jensen and co-workers.^{S14} For improved accuracy single point energies were calculated with the same dispersion corrected M06-2X-D3(0) functional^{S12,S13} using the slightly larger (triple- ζ) basis sets of the same family; pcseg-2.^{S14}

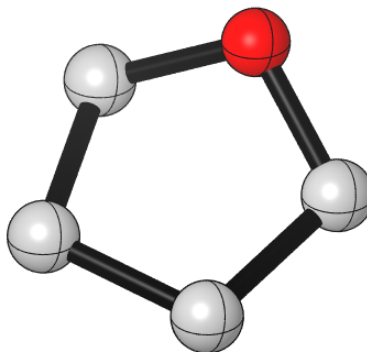
A pruned (99, 590) integration grid (equivalent to Gaussian's "UltraFine" option) was used for all calculations. Jensen's segment-contracted polarization-consistent basis sets were obtained from the Basis Set Exchange^{S15} and included in Gaussian using the "gen" keyword. CYLview^{S16} was used to render all ball-and-stick models.

A vibrational frequency analysis was conducted at the same level of theory as the geometry optimizations (M06-2X-D3(0)/pcseg-1). The optimized geometries characterized as local minima on the potential energy surface have no imaginary frequencies, while each transition state possesses exactly one. Transition structures were verified with bi-directional IRC calculations.

The energies in this section are defined as follows: G is the sum of electronic and thermal free energies calculated at the M06-2X-D3(0)/pcseg-1 level of theory (T = 195.15 K) and G_{SP} is a thermally corrected single point energy at the M06-2X-D3(0)/pcseg-2 level of theory. Atomic coordinates are given in the standard cartesian (.xyz) format.

Solvent Molecules

Table S19. Atomic coordinates and single point energies for THF



$G = -232.191075$

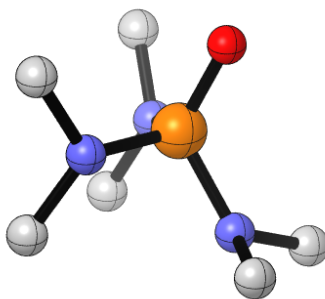
$G_{SP} = -232.334336$

13

THF: optimized structure

C	-0.151515138697	-0.069728800366	0.099971474024
O	0.108544701087	-0.030026489506	1.489280813372
C	1.514989942862	-0.110349626010	1.611767968719
C	1.951422782223	-1.161849858821	0.578722855850
H	2.926523464137	-0.924897619331	0.141924394793
H	2.027410453715	-2.149674524702	1.043237726867
H	1.965562743746	0.870441875449	1.385262726968
H	1.749188716443	-0.373843185045	2.646129229660
C	0.806923562202	-1.132965084425	-0.461100956344
H	1.154953141087	-0.878439182251	-1.467002411257
H	0.311307035918	-2.106840501768	-0.518324074249
H	-1.210125997759	-0.302724624240	-0.038619331005
H	0.055414227934	0.917344004711	-0.346272198931

Table S20. Atomic coordinates and single point energies for HMPA



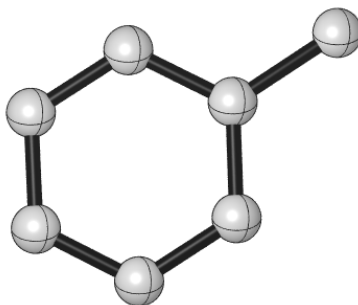
G = -819.772185
G_{SP} = -820.114861

29

HMPA: optimized structure

P	0.063866957531	0.204112836212	-0.189076231430
O	0.447084423330	0.947266777350	1.040679541833
N	1.437247566422	-0.296420944901	-1.022447811405
N	-0.791308718300	-1.242449201498	-0.084042832667
N	-0.979507645615	1.127081650817	-1.130000718386
C	-2.177461451857	-1.179292682228	0.370428499000
H	-2.707342257730	-2.073950729272	0.020082358944
H	-2.243122404268	-1.139963276823	1.468290567046
H	-2.667689827964	-0.293828586914	-0.040788785327
C	-0.093706544446	-2.412743190327	0.441043639529
H	-0.607107980203	-3.317647192418	0.092525542826
H	0.936912214307	-2.427598923450	0.079733502653
H	-0.081762846644	-2.418269988883	1.541539636871
C	1.350714740934	-0.998926900826	-2.289103020621
H	1.345747023241	-0.311084507979	-3.150742621172
H	2.217925611378	-1.665512799431	-2.393803701061
H	0.444973780738	-1.611998261758	-2.318487797804
C	2.675509649224	0.442275289007	-0.824587821725
H	2.660554839675	0.909924745594	0.162217251866
H	3.523646549044	-0.253070454426	-0.878383764705
H	2.816493681621	1.220059259375	-1.592330007266
C	-1.547727803766	0.652188913750	-2.377118667554
H	-2.572169645515	1.037620451605	-2.482011265221
H	-0.968933673375	0.987492820975	-3.252964976906
H	-1.593568065838	-0.440658757479	-2.378789605077
C	-0.979818158749	2.573041832178	-0.972471892695
H	-2.010892766326	2.946837643118	-1.035556473551
H	-0.570141299638	2.827628594605	0.007432726996
H	-0.384402255903	3.068447592027	-1.755651447017

Table S21. Atomic coordinates and single point energies for Toluene



G = -271.28241

G_{SP} = -271.439476

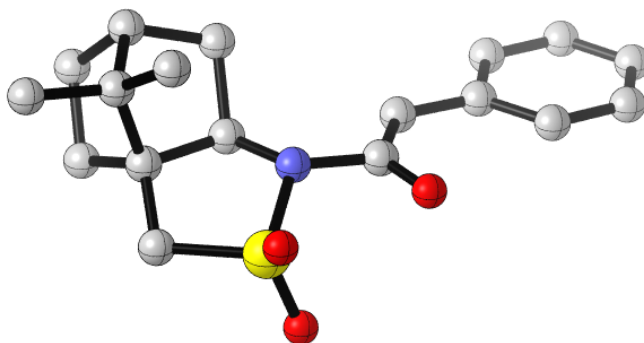
15

Toluene: optimized structure // E(RM062X) = -271.549811187 A.U. after 10 cycles

C	0.001499914796	-0.003742138196	-0.000830439381
C	0.000242917684	-0.008926139097	1.393210381156
C	1.197027042916	-0.018064213248	2.112189042434
C	2.400333340087	-0.022932021056	1.397347200234
C	2.406600042504	-0.017552748967	0.006743216022
C	1.204466483159	-0.007764879987	-0.699067842891
H	-0.942848755323	0.002729452498	-0.541245865008
H	-0.946380168301	-0.006637614411	1.931823275818
H	3.343981979634	-0.031927026927	1.942102665770
H	3.353281958463	-0.021950519304	-0.529820792484
H	1.207649328193	-0.004835690205	-1.786826849998
C	1.206529499522	-0.015892460393	3.617713282622
H	1.796209526652	-0.853825465763	4.007194874768
H	1.651249533733	0.909322916913	4.003722021343
H	0.191932158247	-0.097269778388	4.020201167580

Anions of enolate 8o

Table S22. Atomic coordinates and single point energies of **8o** anion with the enolate oxygen *syn* to the sultam ring.



G = -1376.799945

G_{SP} = -1377.438335

45

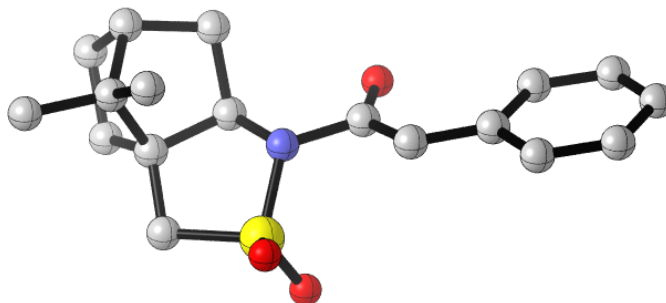
monomer_anion_oxy_front_THF: optimized structure // E(RM062X) = -1377.786447

A.U. after 13 cycles

O	-0.019614096269	0.036801510866	-0.001577605389
C	0.003921627746	0.034540180509	1.241522335737
N	1.336854815833	0.035480815265	1.829030127612
S	2.512767583756	-0.785318116486	0.911545335596
O	2.051681227087	-2.122978795530	0.509326059287
C	3.688677092918	-0.975912464048	2.282961811552
C	3.132177147835	-0.189969427932	3.446931205928
C	1.595156453231	-0.066987376235	3.264699213260
C	1.248193556551	1.197549793874	4.095073626577
C	2.588470770834	1.539391154757	4.773731480633
C	2.906522891944	0.403675454073	5.773454250307
C	3.330748696607	-0.778643311205	4.854406681745
H	2.714473583520	-1.673744529519	4.993675805025
H	4.374155673961	-1.070690301715	5.015854517321
H	2.030317251604	0.158940371881	6.384967433831
H	3.711777020075	0.684502822693	6.460722484892
C	3.607352077825	1.286037237012	3.635830970553
C	3.437902400338	2.203383209803	2.422680253371

H	4.121506178762	1.903367303168	1.617614764540
H	2.429918751415	2.206231444872	2.004012537204
H	3.697495872534	3.230854024478	2.712092881676
C	5.071775080328	1.390990186689	4.070026635928
H	5.733148753387	1.028221276323	3.271078543817
H	5.327268442728	2.443340858090	4.249543893809
H	5.309587742633	0.833623261307	4.980403306387
H	2.616364995930	2.542460598121	5.214074448190
H	0.894914288481	2.000680137977	3.440956802451
H	0.459543807785	0.995682218280	4.828146572734
H	1.093407719139	-0.960953266256	3.664544782806
H	4.662633132197	-0.628453205979	1.923449273230
H	3.726857385584	-2.052069727968	2.480097793143
O	3.084239136860	0.080492724335	-0.126428269142
C	-1.065491140684	0.045237758192	2.145997994986
H	-0.862110312059	0.011410765933	3.211366390901
C	-2.454245769336	0.103349386768	1.767805538408
C	-3.448150284882	0.104067378059	2.781746935654
C	-2.926431322593	0.160970094536	0.430364408218
C	-4.803120116574	0.153665131290	2.487774534800
H	-3.129376068868	0.060561247607	3.823641296732
C	-4.288039202322	0.212585119033	0.148438506209
H	-2.197296992376	0.159137064563	-0.373533094906
C	-5.245811694939	0.209360201728	1.163325410558
H	-5.525704896955	0.149848623225	3.303459104662
H	-4.607245056532	0.255590213754	-0.892812479649
H	-6.307857698764	0.248374006634	0.930799143629

Table S23. Atomic coordinates and single point energies of **8o** anion with the enolate oxygen *anti* to the sultam ring.



G = -1376.805924

G_{SP} = -1377.444564

45

monomer_anion_oxy_back_THF: optimized structure // E(RM062X) = -1377.791898

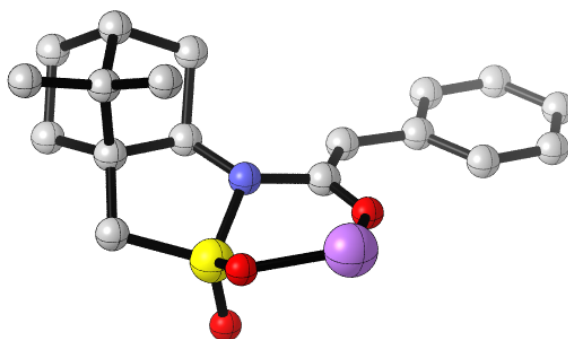
A.U. after 13 cycles

O	-0.047695995008	-0.065663790773	-0.011171444004
C	-0.017521152240	-0.065018716400	1.231797147579
N	1.334276531859	-0.086892317220	1.821985153906
S	1.742964701194	1.010808621805	3.034938709124
O	1.360892284595	2.389299727593	2.683254628403
C	3.540038195879	0.827112378572	2.844592912784
C	3.746516112738	-0.196448473293	1.747961820568
C	2.453972351935	-0.273997651790	0.897427569843
C	2.530381022266	-1.682786035528	0.261550932876
C	3.919329828534	-2.181351631373	0.707849507768
C	4.976685767625	-1.306110192190	-0.004003579783
C	4.883978429243	0.056522689090	0.743681868177
H	4.637451149986	0.892922892465	0.080274678494
H	5.818787207192	0.308402146566	1.256240180395
H	4.753545075434	-1.207926098386	-1.072634043002
H	5.979682263329	-1.738692433231	0.078459221706
C	3.997742628162	-1.678912577137	2.171809146096
C	2.953009139357	-2.291089190118	3.108547360979
H	2.950025603429	-1.767129427966	4.074402390939
H	1.933512967853	-2.257999365448	2.721103032161
H	3.217196921476	-3.339171914615	3.304347356413
C	5.361789752051	-1.884186098793	2.836268834331
H	5.390883185384	-1.375095294502	3.809798564916

H	5.523445495273	-2.953451634361	3.024737063475
H	6.206950385022	-1.521279008695	2.244661380377
H	4.070256691661	-3.258585347181	0.573550105808
H	1.719594218690	-2.316592215539	0.634071810580
H	2.435437159054	-1.633809757729	-0.827712769839
H	2.434145722635	0.509297079310	0.128741291275
H	3.942407075740	0.536644177216	3.820623690980
H	3.902656500592	1.824123046885	2.575009823979
O	1.294734432110	0.517692561293	4.346391890459
C	-1.057774021697	-0.090718435997	2.160609005861
H	-0.794209962872	-0.159351950216	3.213107098004
C	-2.457425496632	-0.017130522630	1.830743417180
C	-3.418763908799	-0.004292276416	2.874839934800
C	-2.968416913100	0.040680642575	0.508035016834
C	-4.781238608023	0.062499463945	2.620666875666
H	-3.067104275418	-0.044804623815	3.905895529529
C	-4.336852321313	0.108904947862	0.265888472281
H	-2.263691726837	0.028677713409	-0.317808301550
C	-5.262850499440	0.120011704945	1.309883389894
H	-5.479366309282	0.070729422460	3.457330585741
H	-4.687140510384	0.152790533043	-0.765315063236
H	-6.330862531422	0.172324381611	1.109474889085

Monomers of enolate **8o**

Table S24. Atomic coordinates and single point energies of **8o** chelated to the *exo* sulfonyl oxygen.



G = -1384.37817

G_{SP} = -1385.018443

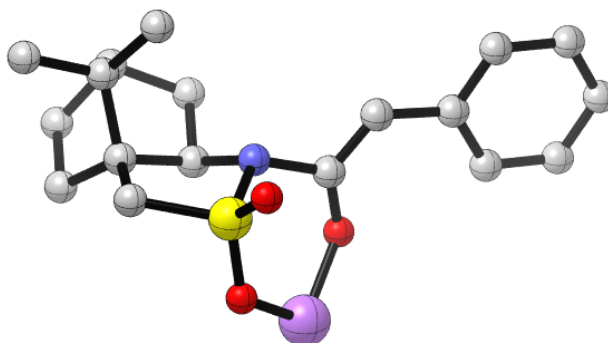
46

0000m_syn_thf: optimized structure // E(RM062X) = -1385.36893994 A.U. after 12 cycles

Li	-0.001771397800	0.161629116657	-0.023995662060
O	-0.004706835862	-0.008185940457	1.773170535203
C	0.948722289028	-0.002319687160	2.627263759912
N	2.265180919200	-0.036813591742	2.030256310655
S	2.430346844223	-1.078524996634	0.718643819307
O	2.028330323517	-2.455287699653	1.021542715514
C	4.227149296478	-0.949376005329	0.594335176531
C	4.654446032273	-0.015182706148	1.711191904007
C	3.524270415374	0.059163926616	2.775169171618
C	3.775656193802	1.425551437004	3.460660853312
C	5.100599142251	1.884911423695	2.821241048885
C	6.208432450953	0.917310829093	3.296914396001
C	5.924751990157	-0.386359775072	2.494606844318
H	5.746826893214	-1.255789421881	3.136639760920
H	6.746554667504	-0.640323805731	1.817245712110
H	6.154392815527	0.756762125141	4.379525892907
H	7.206500409688	1.310170668152	3.077599854324
C	4.911401281736	1.479986161410	1.338749244975

C	3.764170243341	2.197825492366	0.622559407378
H	3.589103098736	1.749449929743	-0.365613072862
H	2.817264888509	2.182312893748	1.165000021943
H	4.047549673453	3.245627066931	0.457545507621
C	6.159570726364	1.668426396579	0.472289929084
H	6.010924746831	1.213709953821	-0.516865868670
H	6.336315409752	2.739708989175	0.313980046090
H	7.070214044034	1.243107589704	0.902250103038
H	5.327097701303	2.942397511128	2.994043163425
H	2.953458235429	2.118508147989	3.258519170064
H	3.858991762652	1.317802225243	4.547107858149
H	3.600580851137	-0.777767680596	3.484264258080
H	4.459927078074	-0.591252507799	-0.413792945972
H	4.589939722171	-1.974497308467	0.720862390927
O	1.759971160279	-0.462366020534	-0.465429156351
C	0.869031802810	0.057826719930	3.993401995580
H	1.791223586424	0.014307121586	4.565457705097
C	-0.354605106241	0.211498587747	4.765919219946
C	-0.253329091827	0.330517042811	6.169043124736
C	-1.651654896542	0.248886653350	4.210264823585
C	-1.376233982558	0.483059363659	6.972154773164
H	0.734502280021	0.302088151484	6.628276905227
C	-2.772184125285	0.404938836838	5.021865040915
H	-1.763909946387	0.149054986979	3.135827829628
C	-2.650587487165	0.523650717123	6.405255189234
H	-1.255715508673	0.571320776423	8.050712556740
H	-3.759282187609	0.429647948069	4.562303746733
H	-3.532004289029	0.642904076185	7.031594678027

Table S25. Atomic coordinates and single point energies of **8o** chelated to the *endo* sulfonyl oxygen.



G = -1384.374237

G_{SP} = -1385.014619

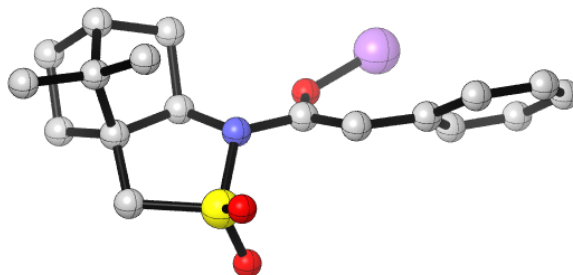
46

0000m_anti_thf: optimized structure // E(RM062X) = -1385.36487829 A.U. after 12 cycles

Li	-0.191577324898	-0.246655374370	0.005270051919
O	-0.015434716253	0.005789320862	1.786825061305
C	1.113308965411	0.004767176383	2.392447282995
N	2.071190933582	-1.048535604509	1.990556725049
S	2.670792378855	-0.891934707131	0.430651636551
O	1.547604860332	-0.767599419050	-0.557423781909
C	3.309139837698	-2.577130569897	0.298934216546
C	2.684465962200	-3.329440830874	1.465664464706
C	1.595520423826	-2.438933953462	2.124576225174
C	1.524211911353	-2.958372988132	3.577394517468
C	2.449342551330	-4.191224764014	3.528461614345
C	1.780069925337	-5.242349283033	2.611617157578
C	1.989087396302	-4.669867901694	1.178018526944
H	1.048963691782	-4.516233790706	0.636364197862
H	2.619889397532	-5.320022404388	0.563008449550
H	0.719269263350	-5.363077472237	2.858595632748
H	2.250822947038	-6.224952744790	2.718621837550
C	3.627949206484	-3.686903410867	2.659418141565
C	4.407874037426	-2.517557871512	3.264569635512
H	5.132535924004	-2.121860605536	2.538487855346
H	3.783718099123	-1.685357151747	3.592822505203

H	4.983039838407	-2.880367798022	4.126511010774
C	4.652798313737	-4.765275658247	2.298543084133
H	5.345222363717	-4.389323664328	1.532321767167
H	5.251267462051	-5.014147773972	3.183875734164
H	4.212008872955	-5.693999294102	1.926063239161
H	2.725785609999	-4.574158587961	4.516601796772
H	1.878156854625	-2.197609516757	4.280723874796
H	0.499478856361	-3.220446509686	3.858911822275
H	0.630537099029	-2.551414584077	1.609264762951
H	4.401144529732	-2.511478486420	0.344808860943
H	2.998319461660	-2.932704056067	-0.687997301059
O	3.684533517956	0.157423505920	0.358271581834
C	1.573673584282	0.819463397653	3.383183836217
H	2.582590172507	0.633915916673	3.741952377493
C	0.840344025701	1.922654046089	3.993273718790
C	1.480984643881	2.690857768389	4.986175085913
C	-0.481885093706	2.273022666712	3.652291279336
C	0.839321774011	3.755487125081	5.606846389404
H	2.503124711917	2.439766246355	5.267532543399
C	-1.119150741223	3.340853082181	4.278742605071
H	-0.998492719741	1.694101981921	2.893220729147
C	-0.468983916889	4.090714199453	5.257228160769
H	1.364390445389	4.328819516201	6.368950201558
H	-2.141057922677	3.589623940801	3.996594318738
H	-0.973705589848	4.923996957161	5.741462108938

Table S26. Atomic coordinates and single point energies of **8o**.



G = -1384.358308

G_{SP} = -1385.000052

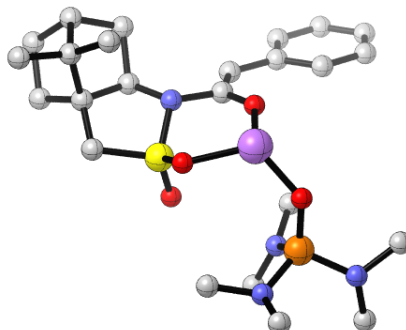
46

0000m_pend_thf: optimized structure // E(RM062X) = -1385.34971406 A.U. after 13 cycles

Li	-0.320892211543	-0.082329184036	0.028648015011
O	-0.026857811101	-0.138895258698	1.802339365711
C	1.132907453381	-0.066655987062	2.341207977466
N	1.121197916689	0.224239038537	3.742268023492
S	2.070836927452	-0.715011355886	4.789252305739
O	1.838434680606	-2.149513794881	4.565954445515
C	1.220235376147	-0.184717377299	6.300726606584
C	0.177626642031	0.828702405868	5.874450101298
C	-0.141266716127	0.614659374905	4.373882849037
C	-0.687321282739	1.991009463674	3.924786811409
C	-0.753025739136	2.776710998487	5.249760366115
C	-1.844072283849	2.117687533951	6.124821562946
C	-1.183018047219	0.787096594840	6.590744145649
H	-1.751471218364	-0.101502514597	6.294906963543
H	-1.056949734898	0.749742695064	7.677923551737
H	-2.761424659894	1.945432294043	5.550309155912
H	-2.111240274755	2.749829464929	6.978127975218
C	0.554855775547	2.342580633324	5.958514818999
C	1.837802224913	2.753821607744	5.231025989398
H	2.711184969047	2.272024593239	5.691440524833
H	1.851147182455	2.502212872509	4.168936118087
H	1.972279691556	3.839243505965	5.330183820235

C	0.685190549593	2.841115035168	7.400160897803
H	1.547397052702	2.367032689099	7.889394028872
H	0.865808992991	3.923595744502	7.400828951714
H	-0.195973092143	2.652311614493	8.019416726636
H	-0.878863591537	3.857306796916	5.119411671466
H	-0.012284264895	2.455128553526	3.198574888977
H	-1.669146244915	1.894010428244	3.450564610313
H	-0.884241244067	-0.180465438752	4.234643250535
H	1.984789594121	0.208925576338	6.978476751627
H	0.785480925111	-1.097960947848	6.719394831348
O	3.462537006684	-0.249616120913	4.758188896976
C	2.357824236810	-0.170737991297	1.720484735235
H	3.243637585619	0.123914328311	2.276566536625
C	2.516696541104	-0.539970789465	0.324064317758
C	3.619294927715	-0.057865818166	-0.414886080984
C	1.623529276330	-1.397271404744	-0.361730244224
C	3.790463927111	-0.373678572715	-1.755739463656
H	4.344658085499	0.581564441967	0.086301056549
C	1.795258490893	-1.704824039471	-1.712123525434
H	0.838412149401	-1.907249636269	0.201725024376
C	2.871528214497	-1.185654928049	-2.425426205395
H	4.652068519872	0.022804006769	-2.290432185325
H	1.092032732381	-2.379287663336	-2.198482435873
H	3.007564158992	-1.425616690841	-3.477216503124

Table S27. Atomic coordinates and single point energies of HMPA-solvated **8o** chelated to the *exo* sulfonyl oxygen.



G = -2204.18913

G_{SP} = -2205.168380

75

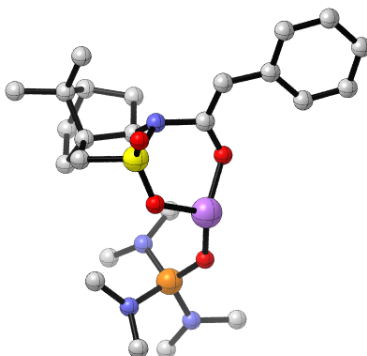
10010m_syn_thf: optimized structure // E(RM062X) = -2205.76743203 A.U. after 12 cycles

Li	-0.007253476450	-0.119107457403	0.099148738561
O	0.005435662303	-0.172248757465	1.934425838667
C	0.891164184869	-0.071882236596	2.841187507876
N	2.134860560857	0.530603365335	2.391618373914
S	2.751922337118	-0.103458901627	0.961039755802
O	3.021325721824	-1.546314490141	1.058620379755
C	4.306077259737	0.815304917881	1.004477905721
C	4.336651609912	1.504986540786	2.357853319572
C	3.248520259172	0.881873090008	3.277884866131
C	2.947750548665	2.015085522951	4.289517739405
C	4.006877559535	3.075250278089	3.929777186785
C	5.393261431759	2.489205980839	4.284301893376
C	5.641524176875	1.432951753897	3.167625611182
H	5.803088054501	0.422831521463	3.559681952334
H	6.506706802393	1.686857010819	2.546536537230
H	5.388178096097	2.040750304688	5.284200584065
H	6.169098194824	3.261767524294	4.280511845371
C	4.005848229990	3.031476741108	2.382125083956
C	2.679695425442	3.436680897014	1.733544833417
H	2.705286748196	3.236900467689	0.652788790651
H	1.805270699909	2.927014948002	2.140894173858
H	2.537594962328	4.518338592094	1.857823061384
C	5.097046378723	3.882473704792	1.727350310826
H	5.146805097567	3.673711222734	0.649583512466
H	4.851088400253	4.945722421852	1.841497702071

H	6.095364275426	3.726973017445	2.145067420065
H	3.811724597750	4.057963289851	4.372161419690
H	1.926525281133	2.387118051120	4.164178257497
H	3.049018180027	1.665928506553	5.322309174747
H	3.632905653235	-0.020399973143	3.776049949464
H	4.304289841226	1.500717823375	0.150485521746
H	5.086299826417	0.059042417947	0.876018232914
O	1.896718639314	0.313101148449	-0.180605150035
C	0.808705308348	-0.445026790839	4.160200760926
H	1.683382695848	-0.319032847676	4.791563473078
O	-0.759512484067	-1.474571171708	-0.912398400086
P	-0.140488407323	-2.806238788754	-1.283794119004
N	-1.367747877000	-3.818102211736	-1.806043513665
N	0.953358505817	-2.846909835289	-2.537896936720
N	0.731329390639	-3.420117752068	-0.011250272730
C	-1.043157180413	-5.231846919566	-1.947784704719
C	-2.731660791744	-3.567061026742	-1.354863675509
C	2.235024178521	-2.166114626722	-2.354089689517
C	0.492302271196	-2.824832432280	-3.922273916934
C	1.799729541494	-4.399566525147	-0.123229294589
C	0.236020268966	-3.252955323810	1.350934416981
H	-1.096922420520	-5.765815514715	-0.985001518461
H	-1.754270791690	-5.696038612936	-2.642063100365
H	-0.036278357776	-5.350714824214	-2.361908815789
H	-2.913589092808	-2.491464823273	-1.313697370319
H	-3.428325879716	-4.018373959747	-2.071862134314
H	-2.925059160414	-4.001992542128	-0.361355940291
H	3.010530973868	-2.706862668052	-2.912300534009
H	2.189510352756	-1.132079717440	-2.726433627077
H	2.509526528432	-2.139212530629	-1.295486154439
H	1.262052666200	-3.284963414067	-4.553735365977
H	-0.434593321902	-3.393254419456	-4.023803792001
H	0.321568974701	-1.796997497680	-4.276440630317
H	2.678612886814	-4.033235045670	0.425890617141
H	1.490514132252	-5.362949085576	0.309585473604
H	2.075594135646	-4.558766309611	-1.168230621992
H	1.062730267426	-2.931489915242	1.999159450944
H	-0.533742940399	-2.479435769189	1.387389178316
H	-0.174925298719	-4.200261695463	1.733330252547
C	-0.370644429063	-0.999802947290	4.805094643844
C	-0.297996917906	-1.327164390706	6.177313051049
C	-1.599573683299	-1.244421330765	4.152597762952
C	-1.380803067351	-1.867636230842	6.858650451865
H	0.636100928943	-1.149919708286	6.709932289049

C	-2.681127978714	-1.784467345981	4.843883782380
H	-1.689675931851	-1.003318122564	3.098447682404
C	-2.587295618511	-2.102791835592	6.197646094909
H	-1.282755064917	-2.106849439110	7.916432788951
H	-3.614686736635	-1.959670211935	4.310866701739
H	-3.437056885401	-2.525931207701	6.728955281131

Table S28. Atomic coordinates and single point energies of HMPA-solvated **8o** chelated to the *endo* sulfonyl oxygen.



G = -2204.187073

G_{SP} = -2205.167238

75

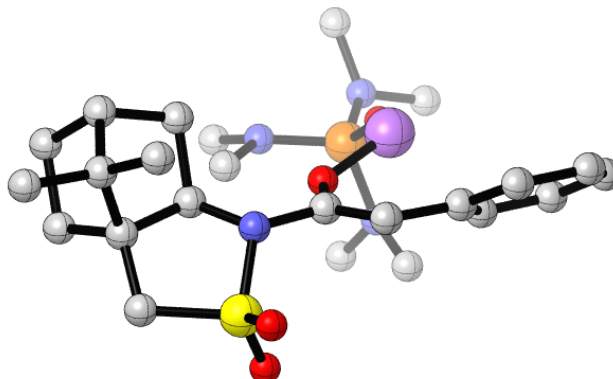
10010m_anti_thf: optimized structure // E(RM062X) = -2205.76749054 A.U. after 12 cycles

Li	-0.079402375941	-0.099647873308	0.047557825420
O	0.019954608497	0.158509153540	1.874359425618
C	1.113341111463	0.097183293223	2.527880456088
N	2.027644280261	-1.013635822217	2.170669189399
S	2.777232913931	-0.836288267212	0.676771376789
O	1.760727837851	-0.586895761499	-0.392158110195
C	3.303140231318	-2.561940586466	0.531462427343
C	2.488983211979	-3.310477004786	1.578630799400
C	1.414199142773	-2.354165513574	2.156983137619
C	1.113471302143	-2.938451530192	3.553514585386
C	1.940443644579	-4.241714208222	3.550624500607
C	1.306654803079	-5.193706690467	2.511536538267
C	1.706288230570	-4.562559976501	1.144413160858
H	0.835800111436	-4.275976648646	0.543649333215
H	2.325112474728	-5.236998391628	0.542458945431
H	0.219273681174	-5.253493886131	2.640224388112
H	1.699334841725	-6.211107355417	2.610244021377
C	3.251193942646	-3.804912344911	2.849355620963
C	4.045421213296	-2.740726617915	3.609801529414
H	4.850027062962	-2.335142751225	2.980050091479
H	3.444098898889	-1.898890205665	3.955460753098
H	4.522654147079	-3.207199075817	4.481708699559
C	4.218711536765	-4.950546972384	2.543348574393
H	5.056842815987	-4.583937444079	1.934509111947
H	4.641701025979	-5.337967354849	3.478898404732

H	3.762528904514	-5.790443041821	2.012150465037
H	2.066297600104	-4.686459763084	4.543622288844
H	1.427409578922	-2.244928087917	4.340571617076
H	0.043043304509	-3.127715843481	3.687217516955
H	0.521872434754	-2.345965333515	1.515062742044
H	4.383557486984	-2.584232012782	0.709048408119
H	3.090055196004	-2.849103514322	-0.502810191389
O	3.875465395496	0.126003956339	0.748902435162
C	1.583155238361	0.888257889374	3.537054316670
H	2.559853220142	0.638925717434	3.943078972652
O	-1.417346592963	-0.900636769956	-0.928123569701
P	-1.593953964279	-2.269532307451	-1.543755827154
N	-3.088901340366	-2.328757602086	-2.268535376141
N	-0.557640956514	-2.757506926994	-2.748518796445
N	-1.351180173136	-3.431067025567	-0.351692704868
C	-3.539207185390	-3.476251647465	-3.043381767945
C	-4.151661407323	-1.415376015034	-1.870073515408
C	0.821812916316	-3.118056112756	-2.421878006253
C	-0.674659649158	-2.143564060577	-4.070613683171
C	-1.509913375589	-4.841270651873	-0.700571953926
C	-1.902609337423	-3.120867615697	0.967945500827
H	-4.254851723334	-4.088300148468	-2.475102412487
H	-4.037899016505	-3.125451029443	-3.957594740222
H	-2.689800532344	-4.100857070485	-3.333878801748
H	-3.726835607564	-0.561786652515	-1.338309993767
H	-4.670360231330	-1.050404096313	-2.766433452663
H	-4.886107492630	-1.916379616863	-1.222707204882
H	1.188747470848	-3.819469219153	-3.181442921619
H	1.472885154733	-2.232097611267	-2.407079025276
H	0.866881158101	-3.603950303212	-1.444685279909
H	-0.348019192778	-2.867398053377	-4.826954924007
H	-1.711370944756	-1.865452035102	-4.274296697690
H	-0.044473215773	-1.245834208674	-4.149393368844
H	-1.011120375729	-5.450768380994	0.064151569330
H	-2.569399173822	-5.140534677898	-0.736810228409
H	-1.046173237612	-5.052069317076	-1.668729298523
H	-1.421749884372	-3.775775853942	1.706234175622
H	-1.693473860195	-2.080949585833	1.235009309311
H	-2.990703198201	-3.294209752530	1.009748927742
C	0.896064050252	2.040171749417	4.105472865800
C	1.537084974036	2.777205487898	5.122528696221
C	-0.385851704405	2.469285560728	3.702934296426
C	0.935527668324	3.885055988434	5.706402416370
H	2.527969728362	2.466052837959	5.451860154414

C	-0.982601595761	3.580536001773	4.292951586141
H	-0.902344636660	1.915976348247	2.924625311728
C	-0.332453949211	4.298032222221	5.295573042062
H	1.460535179926	4.431368753000	6.488283923507
H	-1.973133683157	3.889393778608	3.962215857061
H	-0.805512527446	5.165478217305	5.750944359259

Table S29. Atomic coordinates and single point energies of HMPA-solvated **8o**



G = -2204.173391

G_{SP} = -2205.156548

75

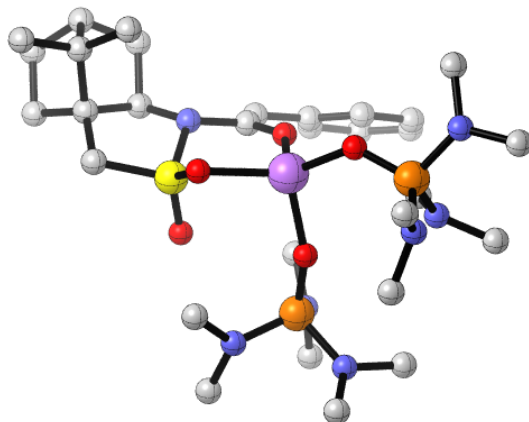
10010m_pend_thf: optimized structure // E(RM062X) = -2205.75237848 A.U. after 13 cycles

Li	1.113898416147	0.801545880155	-0.489890336638
O	0.707045181296	0.597016899620	1.267158627369
C	1.379293510456	0.122025791131	2.242208491906
N	0.839337887324	0.427842175487	3.543006061914
S	0.525553799761	-0.858446475296	4.602825280291
O	-0.265398778688	-1.908189249916	3.940744780318
C	-0.553992694498	0.095772987450	5.706479108430
C	-0.667003481173	1.481489851605	5.100786937548
C	-0.242288110261	1.413427671092	3.613142696536
C	0.193019423706	2.862999423043	3.295647253442
C	-0.173384843864	3.614702030684	4.591008961264
C	-1.715318045711	3.615740614130	4.704970316301
C	-2.053783357689	2.146954602660	5.096475206022
H	-2.719770097007	1.654079552125	4.379067327210
H	-2.528345763225	2.083359071711	6.081358041148
H	-2.181881079966	3.911019105745	3.757960797258
H	-2.061280643930	4.320687768986	5.468243250773
C	0.243894880681	2.605366988523	5.690581995507
C	1.742158453771	2.293637166791	5.731673156545
H	1.938666779672	1.443849648327	6.400322486725
H	2.174683173373	2.049399262609	4.760082903151
H	2.277546931370	3.160635059198	6.141181086270
C	-0.162326064616	3.014634134327	7.108679019403
H	0.032983951902	2.192898258915	7.811633085484

H	0.443820320177	3.870043995455	7.433216042791
H	-1.214001887710	3.296993920938	7.208889133109
H	0.279458959459	4.609140379698	4.670987422534
H	1.265294789861	2.904223340918	3.078504640107
H	-0.335609486819	3.256752793579	2.421451076980
H	-1.076952175030	1.092904995863	2.975616379317
H	-0.099590768150	0.074745467409	6.702357434239
H	-1.502313259353	-0.450338253370	5.719310369233
O	1.765616470035	-1.271371606344	5.270327527920
C	2.561571674010	-0.579760269902	2.196632857526
H	3.097871586223	-0.745253061941	3.127222377304
C	3.181615077097	-1.008906405341	0.953902641521
C	4.581424817892	-1.169079373616	0.875416878697
C	2.444750182476	-1.302253386378	-0.216525040115
C	5.204430684690	-1.551966201559	-0.305795650242
H	5.181206715436	-0.977567851339	1.764326448189
C	3.073374894275	-1.678411490957	-1.401903994767
H	1.355206694275	-1.318441543319	-0.162045431711
C	4.460245417198	-1.793802651474	-1.462429185609
H	6.287911258969	-1.657978612702	-0.327066529027
H	2.468719293466	-1.903251033862	-2.279702418858
H	4.952447617535	-2.085844438990	-2.387146951994
O	-0.156329411334	1.121323387632	-1.736499565892
P	-1.608192397417	1.096920289696	-2.160175592673
N	-2.539563978193	1.951323017391	-1.071092493244
N	-1.994579129324	1.813770805076	-3.608464796426
N	-2.079044688714	-0.492773916665	-2.352722470627
C	-3.903002524752	2.385177737492	-1.353141835475
C	-2.273323547208	1.779755219595	0.355045152561
C	-1.766333873530	1.106437875156	-4.865780542012
C	-1.817193949656	3.260256354211	-3.730320603582
C	-3.504178796280	-0.773679747091	-2.481478831178
C	-1.309188682452	-1.550806656334	-1.706428791446
H	-4.641888572291	1.691712866133	-0.924350920343
H	-4.061974597624	3.375361839676	-0.905370568272
H	-4.070553133812	2.459238008217	-2.430181287041
H	-1.233693351119	1.488006003776	0.531414365387
H	-2.462035478390	2.732315151963	0.868034590064
H	-2.934699257892	1.015901757286	0.793669962237
H	-2.451432270924	1.509897023306	-5.620746428084
H	-0.734653973684	1.239869046027	-5.223625270293
H	-1.965432719122	0.039914562267	-4.742231081721
H	-2.557450136104	3.654088822283	-4.437429247534
H	-1.963258783321	3.747507559563	-2.762705332459

H	-0.811397038833	3.506317733551	-4.101167274540
H	-3.635724455048	-1.714157252004	-3.030175418568
H	-3.996856141077	-0.870431512836	-1.501237142000
H	-3.996928467484	0.021420181811	-3.050938114911
H	-1.564398831302	-2.503386560092	-2.185244668320
H	-0.240966341782	-1.372696517381	-1.848564113955
H	-1.523731185863	-1.633189953484	-0.629588832099

Table S30. Atomic coordinates and single point energies of *bis*-HMPA-solvated **8o** chelated to the *exo* sulfonyl oxygen.



G = -3023.959948

G_{SP} = -3025.303331

104

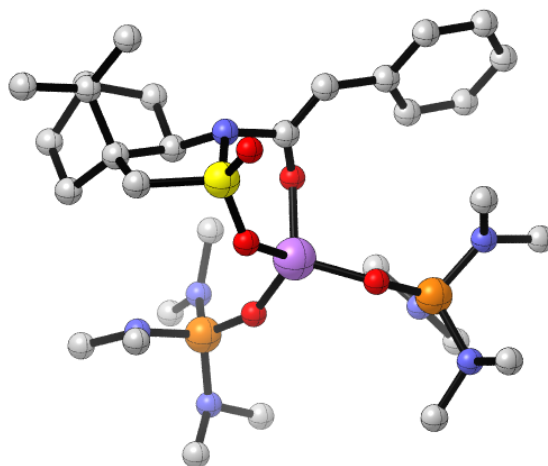
20020m_syn_THF2: optimized structure // E(RM062X) = -3026.15591054 A.U. after 13 cycles

Li	0.043224794855	0.178815535926	-0.076349627405
O	0.033394168467	0.206138136420	1.809963515747
C	0.862161914943	0.097071214000	2.763453919633
N	2.221749912671	0.476475588931	2.392207801178
S	2.716937759554	-0.204031999654	0.933969420233
O	2.616230649165	-1.670500924830	0.949428797342
C	4.455879618370	0.282665629878	1.098547990160
C	4.582802998293	0.907371472921	2.476082187237
C	3.344055814540	0.502160791325	3.322850129540
C	3.262675109984	1.620970151691	4.390388837267
C	4.531011758527	2.450320959985	4.108995957055
C	5.750351291549	1.574949986194	4.476585454084
C	5.805906515283	0.526446534770	3.327059382510
H	5.728757891957	-0.506308313229	3.685208678101
H	6.733946151812	0.597316108009	2.749579044506
H	5.623056187025	1.106897735029	5.459108666828
H	6.671191553582	2.165443279404	4.524196338669
C	4.582066484244	2.468201633179	2.560641673321
C	3.399256514998	3.174255270605	1.892048677190
H	3.392736388490	2.983490377356	0.809853355470
H	2.421814260678	2.871646602267	2.268448300331
H	3.505952185919	4.258433923632	2.028812920329
C	5.855160595497	3.094220745523	1.984296516970

H	5.884562274978	2.973048883157	0.892752800235
H	5.859241140723	4.172917168240	2.184376034563
H	6.784188853898	2.683321547794	2.388535926761
H	4.530200275868	3.434715709369	4.589260887380
H	2.341495202154	2.197514452527	4.267191623662
H	3.254625250640	1.211081667657	5.405795668620
H	3.490153644594	-0.491735523955	3.774590820753
H	4.683009786042	0.961492490965	0.270499183570
H	5.022122113699	-0.647105506440	0.986230855989
O	2.080525314755	0.493426106208	-0.203558526751
C	0.659268184614	-0.364869621965	4.037809520965
H	1.514741621228	-0.488591426670	4.694862191372
O	-0.189033247733	-1.601241186625	-0.761531452540
P	0.107038326470	-3.072281100255	-0.796022832149
N	-0.130721414872	-3.780518906405	0.690977905418
N	-0.877169091292	-4.044300707289	-1.754514048884
N	1.609079585505	-3.331481178967	-1.469144336220
C	-0.148514028515	-5.215533307856	0.904551538152
C	-0.003569887763	-3.006217357663	1.924548012998
C	-0.589965864149	-4.361265172244	-3.140492404324
C	-2.241870255849	-4.344856581814	-1.361110662559
C	2.278441713949	-4.607809582027	-1.336274536844
C	2.427120399322	-2.257080700493	-1.997540841842
H	0.800002115904	-5.572834631020	1.334989046121
H	-0.952909546725	-5.465164585429	1.611180149845
H	-0.338000870908	-5.750326176166	-0.030381550027
H	-0.101816974140	-1.942159473764	1.707586216038
H	-0.810406406234	-3.296666438204	2.612897275758
H	0.965967938437	-3.181962588150	2.409992688177
H	-0.662653595523	-5.447175634828	-3.303653640853
H	-1.305674057504	-3.871151376711	-3.818426958733
H	0.419099884467	-4.036116949909	-3.403958477989
H	-2.437556974764	-5.424194246994	-1.453143233698
H	-2.410632204911	-4.049783001880	-0.321572111498
H	-2.965322055165	-3.814988971273	-2.001263373302
H	2.834763636188	-4.831923462189	-2.257671662628
H	2.987993425027	-4.606850512001	-0.494133704926
H	1.554795807962	-5.415627717839	-1.186643744008
H	2.661327140486	-2.446406669056	-3.057744388944
H	1.898008784866	-1.306468874753	-1.906741854840
H	3.368615697613	-2.181823814536	-1.436627772199
O	-1.476576852336	1.058671080626	-0.780505959213
P	-2.688253894105	0.506127664626	-1.469809260945
N	-3.839150475611	1.722785187705	-1.552313390430

N	-2.588738135288	0.030207688864	-3.068331795013
N	-3.239371919082	-0.883691837911	-0.713818169534
C	-5.075382551610	1.610552486637	-2.302176280978
C	-3.822115163478	2.794630761406	-0.569973986283
C	-1.984885159891	-1.252237582899	-3.408332055164
C	-2.372802856726	1.046377246564	-4.090164835546
C	-4.517974879499	-1.444063693509	-1.114657333157
C	-2.918860484461	-1.090971599558	0.695027420796
H	-5.939150847520	1.422088757487	-1.645495533377
H	-5.265821986551	2.548251394366	-2.845459185352
H	-5.006463212715	0.801699047770	-3.034968203345
H	-2.840681087831	2.836897533279	-0.092670530531
H	-4.012259131048	3.754167638807	-1.070666484755
H	-4.594049346269	2.648038245512	0.201287327705
H	-2.505464939393	-1.673271400708	-4.280437655899
H	-0.917515022546	-1.137838468721	-3.652925810337
H	-2.059242110971	-1.931748725906	-2.557687220062
H	-2.843035122936	0.722448978079	-5.027918275396
H	-2.817348383337	1.996739597072	-3.784376655524
H	-1.300076861997	1.206535582995	-4.274870581207
H	-4.571633450633	-2.486117059950	-0.774366622810
H	-5.373715901085	-0.905525432438	-0.673335120052
H	-4.617848279066	-1.436469521487	-2.205831629403
H	-2.817215200014	-2.167380356168	0.891625450660
H	-1.971638325626	-0.613599722508	0.952763077043
H	-3.713018796307	-0.693384481989	1.348749300315
C	-0.621697796305	-0.825584906704	4.546502379190
C	-1.857322595693	-0.531775147363	3.933635129123
C	-0.653834254035	-1.629814761618	5.702793000832
C	-3.045299275714	-1.042732598812	4.443213182202
H	-1.862891436765	0.109293405174	3.058195137214
C	-1.844153894116	-2.138000264256	6.204868067733
H	0.284602929244	-1.868776025089	6.202139578007
C	-3.054248783196	-1.855772833864	5.574652184580
H	-3.984885450806	-0.795422065809	3.950585893927
H	-1.826659984847	-2.763923859239	7.095508223086
H	-3.987948613548	-2.255380334229	5.963636147436

Table S31. Atomic coordinates and single point energies of *bis*-HMPA-solvated **8o** chelated to the *endo* sulfonyl oxygen.



G = -3023.992071

G_{SP} = -3025.311247

104

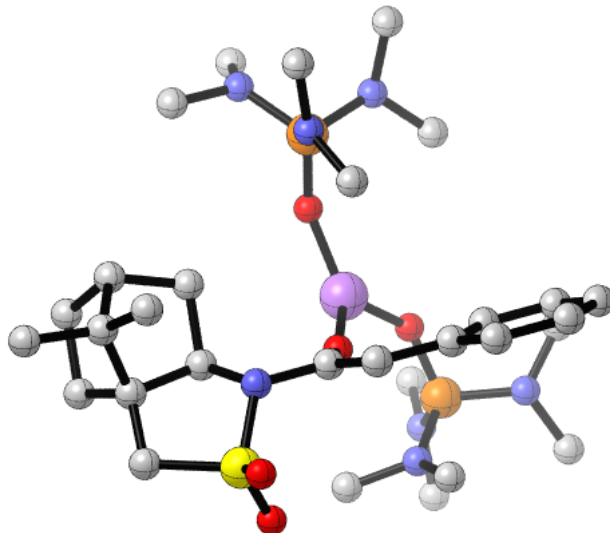
20020m_anti_thf: optimized structure // E(RM062X) = -3026.16212540 A.U. after 12 cycles

Li	-0.057179149228	-0.000883839665	0.103378605745
O	-0.000030088934	0.012680955878	2.047046963068
C	1.174170383757	0.000981647069	2.527248261476
N	1.955276789327	-1.237264971749	2.273317425014
S	2.691000987118	-1.267122217484	0.759316558472
O	1.714703912753	-0.874198369301	-0.294414149825
C	2.907328531198	-3.065883359653	0.688930877307
C	2.073265363514	-3.613725702913	1.836913888970
C	1.170430519199	-2.479647507998	2.379276162536
C	0.871721044656	-2.911501314037	3.831787333734
C	1.529685673040	-4.306049148902	3.906480059858
C	0.722012718677	-5.249004784175	2.987330160714
C	1.110133721074	-4.781744979193	1.553040158611
H	0.244361758752	-4.431844674005	0.979313159994
H	1.598366322895	-5.577043975787	0.978461913324
H	-0.354629721628	-5.160350535210	3.174404096651
H	0.993916801362	-6.296914981957	3.152397462349
C	2.841279767493	-4.102353238458	3.106352387499
C	3.809725536626	-3.094837067632	3.730941721888
H	4.603721232639	-2.829543041359	3.018173223939
H	3.337956270898	-2.165617775798	4.052854107989

H	4.296133315549	-3.557640244856	4.599843468669
C	3.636207169801	-5.385664959178	2.853184213838
H	4.480916799798	-5.179026710776	2.181282486248
H	4.055434276807	-5.754914517532	3.797856225316
H	3.048858207858	-6.195419915562	2.411418529469
H	1.657467671745	-4.680668898038	4.927997483629
H	1.309291586414	-2.202971895421	4.543094252679
H	-0.205297608855	-2.953665817281	4.025880264231
H	0.255369708127	-2.388026948440	1.776114707696
H	3.980099459891	-3.265557659614	0.781564561574
H	2.558053827876	-3.364463181154	-0.303994719621
O	3.956762207794	-0.531981505796	0.773358202565
C	1.845654714017	0.948519317157	3.252695000461
H	2.865895661154	0.719012329318	3.548934727944
O	-1.467225655063	-1.062983485229	-0.493854130172
P	-2.333650661315	-2.289640289031	-0.506238272744
N	-3.195291294821	-2.459385262290	0.899914969469
N	-3.544028960020	-2.321625887389	-1.669244020586
N	-1.366820772296	-3.628790626079	-0.776038236661
C	-4.407217968375	-3.251027203394	1.049252531948
C	-2.559304596345	-2.090613948806	2.159153537210
C	-3.131552539743	-2.594783948949	-3.044174437454
C	-4.552296111692	-1.264997272915	-1.590495151493
C	-1.951183207388	-4.960361501681	-0.749100966785
C	-0.147118816800	-3.507870717005	-1.565891934762
H	-4.214576316495	-4.157226188112	1.643127582683
H	-5.170939855300	-2.657688842087	1.571370802850
H	-4.796442312738	-3.543402425681	0.071068122066
H	-1.715511113683	-1.413575134243	1.985387992024
H	-3.291924517738	-1.572688971092	2.793399245188
H	-2.208177125517	-2.983998498099	2.699841954015
H	-4.027604194408	-2.804989841565	-3.639433825360
H	-2.604546086183	-1.741890021439	-3.500360487221
H	-2.485794841799	-3.475822190855	-3.083913257479
H	-5.440620699998	-1.579822854152	-2.151309534619
H	-4.843187629109	-1.093694610439	-0.550106022395
H	-4.184432399305	-0.318375833937	-2.016106018117
H	-2.354161896277	-5.265741643332	-1.728427957767
H	-1.178280284417	-5.682569073272	-0.455675478344
H	-2.755383305474	-5.009441124531	-0.008741512168
H	-0.322752002650	-3.694088900242	-2.637588751224
H	0.280370336770	-2.509307710248	-1.434496825910
H	0.577056113912	-4.252397372363	-1.209020952390
O	-0.150056183064	1.753999210399	-0.540954847646

P	-1.088579468805	2.928959573076	-0.535681713419
N	-0.458134953628	4.117116035194	0.444030724810
N	-1.372439184774	3.636174299186	-2.033704937268
N	-2.623834258896	2.524368682740	-0.045719872922
C	-1.218944250355	5.320908573858	0.723190329861
C	0.974137514346	4.213665208208	0.688286871468
C	-1.946284866435	2.771468045988	-3.062762291079
C	-0.332303531819	4.515854365078	-2.559962805477
C	-3.839303355412	3.237411908858	-0.403032619430
C	-2.786688361245	1.582914616473	1.055213543307
H	-0.946159971515	5.691377079543	1.719762750424
H	-1.022656915260	6.122692258039	-0.007944815436
H	-2.292018835581	5.103338919482	0.724529469902
H	1.439686633446	3.238689728723	0.521128476325
H	1.450163048554	4.961603101299	0.032920203352
H	1.139682510797	4.505713514634	1.733824779770
H	-2.441030149457	3.392427990814	-3.819895475499
H	-1.174905350964	2.160964150905	-3.557326336453
H	-2.689727680060	2.100228181715	-2.622408182212
H	-0.752144566017	5.093451834657	-3.392045874301
H	-0.000007808119	5.218751513909	-1.791180001564
H	0.539474143081	3.955184996540	-2.932623730080
H	-4.594088721355	2.525541713985	-0.767771798785
H	-4.258671801040	3.758612761303	0.471108525051
H	-3.637418714325	3.970080859912	-1.187761683111
H	-3.507125213212	0.801931903883	0.773074140645
H	-1.837027992405	1.096600104219	1.295039288322
H	-3.159845945351	2.099435043085	1.953502295265
C	1.301061066674	2.241473162191	3.640642389620
C	2.153590836184	3.201931352480	4.224758129001
C	-0.055090857276	2.595259526035	3.479749146161
C	1.683428196558	4.449800962392	4.615756196666
H	3.205839066457	2.954989875151	4.363814208069
C	-0.521479785967	3.843544407746	3.879971736631
H	-0.731924104673	1.873597208735	3.034418514808
C	0.338441211310	4.784581145514	4.445417008947
H	2.372004220947	5.168069112425	5.058286034788
H	-1.575419720969	4.085100341550	3.743511434947
H	-0.031575608394	5.760696199253	4.753156981282

Table S32. Atomic coordinates and single point energies of *bis*-HMPA-solvated **8o**.



G = -3023.987062

G_{SP} = -3025.307062

104

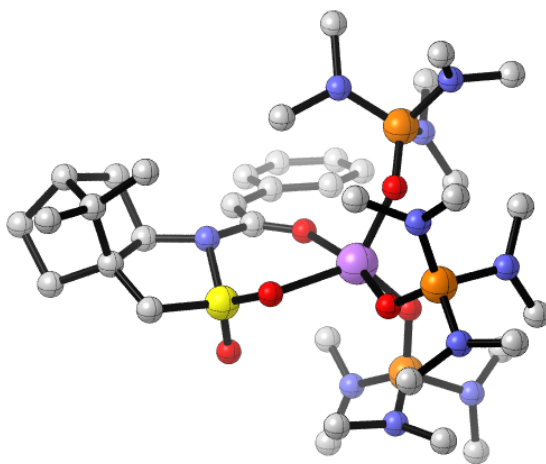
20020m_pend_thf: optimized structure // E(RM062X) = -3026.15640610 A.U. after 12 cycles

Li	0.015125291383	-0.021758162072	-0.004101845077
O	0.004986312903	0.016601587767	1.796093231162
C	0.487605999010	0.001675850054	2.967097440795
N	0.767310221067	1.311535897399	3.535926650619
S	-0.089317614602	1.786275508293	4.909719917379
O	-1.542332416610	1.643735083779	4.705485046981
C	0.365885240033	3.540428226735	4.782391785513
C	1.126542584218	3.684016422432	3.475851538256
C	0.850440231728	2.436629398529	2.602327957885
C	2.068535522167	2.380933781069	1.649327042711
C	2.826979935397	3.676193067588	2.003731817144
C	1.952362204781	4.864382744961	1.541706435002
C	0.794317767869	4.891639840672	2.582862140077
H	-0.194872444895	4.776447256487	2.125872893003
H	0.782357877997	5.822533408110	3.159694263992
H	1.586865418942	4.712373472714	0.519524566223
H	2.514836005649	5.804098227714	1.548532745434
C	2.687229354939	3.735928988719	3.546549811061
C	3.363039263559	2.579323607434	4.288509605440
H	3.047253976836	2.560979150640	5.341270010201
H	3.149777613778	1.594254043500	3.870097539061

H	4.450314117008	2.734146326816	4.277642938459
C	3.208141900908	5.030001424232	4.177721914943
H	2.952996369652	5.059786473766	5.246253701425
H	4.302791985458	5.061681755918	4.104497431171
H	2.818972478817	5.941523931321	3.715667313078
H	3.855595414239	3.707976452721	1.626046150151
H	2.665012748463	1.480261518929	1.834923867289
H	1.757495276363	2.344797775510	0.600041988907
H	-0.092697826558	2.538280129159	2.048593141857
H	0.951610953697	3.789684468434	5.673205401268
H	-0.582286133170	4.086529702782	4.796450552257
O	0.481670525884	1.153632979063	6.105351916813
C	0.821315664773	-1.081205645865	3.744941986006
H	1.279088749740	-0.876395398863	4.709559802428
C	0.657406514322	-2.472987396980	3.366432912464
C	1.092063008147	-3.471675856550	4.267798012915
C	0.103124576653	-2.918009210799	2.143109854610
C	0.985322860836	-4.824124411113	3.972934774729
H	1.520761824176	-3.162472445934	5.220631858583
C	-0.001928918304	-4.276768723557	1.856163214640
H	-0.262326998352	-2.189430306122	1.424674009542
C	0.436784288042	-5.243428789472	2.759446406208
H	1.332374329166	-5.559060781378	4.697718471224
H	-0.437821100956	-4.582569693491	0.906026183412
H	0.351168416699	-6.302355231164	2.525360348278
O	1.545918488438	0.289674727639	-0.964694343003
P	2.953355310140	-0.098841623147	-1.337710874032
N	2.879275363248	-1.337995799183	-2.458463478452
N	3.901856840158	1.047424593266	-2.086040776676
N	3.839919123356	-0.461732586452	0.030315294470
C	4.116926547032	-1.987259171437	-2.872402443427
C	1.718579487721	-2.223700613338	-2.443588708607
C	4.325442926022	2.208283265855	-1.303576857955
C	3.664218376950	1.372836872625	-3.490204030801
C	5.280543047407	-0.682386976034	-0.010666628116
C	3.177141329711	-1.174006163279	1.119829469822
H	4.392936371566	-2.814619244837	-2.199858426451
H	3.988678730389	-2.393278252223	-3.883839793955
H	4.935702914078	-1.260455757376	-2.897351012341
H	0.816468732215	-1.653283772815	-2.208303557218
H	1.604665413530	-2.668028481527	-3.440191060447
H	1.830464488066	-3.038888456201	-1.710831262004
H	5.271105358268	2.586362711684	-1.711627774007
H	3.578807279350	3.016079638980	-1.350004602700

H	4.481153614912	1.929347568450	-0.258118171942
H	4.589203419315	1.778713903543	-3.916979687090
H	3.383248729298	0.475410349064	-4.045666877844
H	2.869066858839	2.125278659367	-3.601587368184
H	5.726697865355	-0.293168356801	0.914354357666
H	5.524893424674	-1.752836076623	-0.084399097048
H	5.726334473611	-0.157342601948	-0.859211320280
H	3.647280605966	-0.887344300223	2.069628227070
H	2.119704405485	-0.900822118177	1.166567389996
H	3.267879059963	-2.266499950588	1.006561076450
O	-1.463660163438	-0.893716591505	-0.704228311914
P	-2.793796535084	-1.176898706504	-0.039629274169
N	-2.981959303570	-2.839751063138	0.066339329013
N	-3.102718611901	-0.652696764588	1.496188417634
N	-3.977819056983	-0.403970657060	-0.933449061466
C	-4.283133775458	-3.365221149598	0.464438013553
C	-2.318172973442	-3.657021725316	-0.944115862208
C	-3.181698562521	0.783226127882	1.755309050628
C	-2.802163643369	-1.421947541755	2.700545317984
C	-5.357759394212	-0.283064188382	-0.489099441092
C	-3.794630270039	-0.195088785238	-2.362454436479
H	-4.968669912374	-3.455851174879	-0.393634650958
H	-4.147095335020	-4.360534631918	0.905668163799
H	-4.743875513658	-2.719275352817	1.218079541231
H	-1.303177832437	-3.289438796083	-1.112623393795
H	-2.269720038436	-4.690187945718	-0.579617165828
H	-2.863973047925	-3.657471174476	-1.902469851981
H	-4.027513654976	0.986796932792	2.426482171784
H	-2.257440164141	1.126297348725	2.239731583858
H	-3.336657318362	1.333610625449	0.822299959055
H	-3.634619739329	-1.306198389668	3.408830139319
H	-2.679551866385	-2.480621402653	2.464059447215
H	-1.882203483205	-1.052247444550	3.172181758041
H	-5.726677497194	0.726837172052	-0.717343869711
H	-6.011899944806	-1.008538563351	-0.996330151985
H	-5.426713516046	-0.438817252265	0.590561376155
H	-4.174287902922	0.798443013079	-2.636811037532
H	-2.732280692075	-0.242926579395	-2.610848526421
H	-4.339931732942	-0.946823996908	-2.953454375840

Table S33. Atomic coordinates and single point energies of *tris*-HMPA-solvated **8o** chelated to the *exo* sulfonyl oxygen.



G = -3843.780807

G_{SP} = -3845.434724

133

30030m_open_exo_THF: optimized structure // E(RM062X) = -3846.53457275 A.U.
after 14 cycles

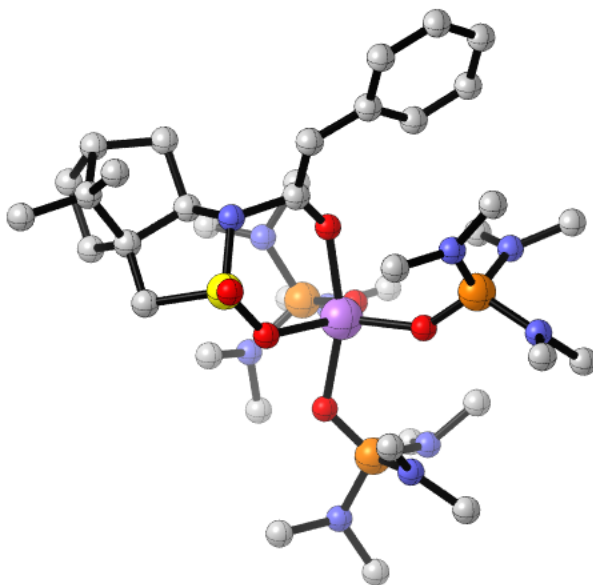
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C	-0.003955751688	0.008941136297	1.261824664138
N	1.329548727900	0.013641517161	1.862621307972
S	2.370705528540	-1.082937787785	1.100433659296
O	1.826243207911	-2.451388095527	1.157690517287
C	3.699161002066	-0.951497014875	2.321081056700
C	3.103247310667	-0.206463280624	3.502782371436
C	1.561968381501	-0.072962170909	3.308088264689
C	1.211312109597	1.197261375459	4.122329542970
C	2.540433113175	1.515328277997	4.832915554018
C	2.827522781442	0.362727569484	5.824690955773
C	3.280209078582	-0.809911989943	4.905075024500
H	2.669965768956	-1.711717513084	5.025856017589
H	4.323530431755	-1.090868904700	5.084316091676
H	1.932425721517	0.111407335127	6.405116634388
H	3.611040652100	0.632882149156	6.540469797157
C	3.579463998738	1.265095102677	3.713652746200
C	3.424945473534	2.174517681627	2.495312810899
H	4.146672265241	1.898518959527	1.712822888551
H	2.430518449603	2.132293619548	2.053442677967
H	3.639525721849	3.212788087209	2.783096888810

C	5.035911572332	1.363743384141	4.172136958015
H	5.706202422280	0.959167909641	3.400868267880
H	5.304671089868	2.418085771698	4.316019126498
H	5.245497702102	0.838540805851	5.108202384672
H	2.569842756475	2.511763695003	5.287237711987
H	0.888345010151	2.006605833936	3.459695004354
H	0.400782882604	1.007452813818	4.833651608523
H	1.052131586068	-0.960655070185	3.711331264630
H	4.533138931601	-0.428451912622	1.842126117566
H	3.986073779632	-1.983240887064	2.543754706971
O	2.781490180992	-0.573227992812	-0.219046060343
C	-1.075827932935	0.021504344441	2.139871873727
H	-0.880617997833	-0.026776994597	3.206076151146
O	0.768626441413	1.557600530374	-2.437039094575
P	-0.213710172548	2.676385355716	-2.241561239328
N	0.151347537207	3.547116161514	-0.872813966398
N	-0.243975454667	3.898182066408	-3.392605058897
N	-1.770902054791	2.076875820150	-2.224041321998
C	-0.367511890243	4.867879075017	-0.564071843565
C	0.945331915957	2.960205187143	0.194868273387
C	-1.126388666655	3.888782669920	-4.546526550298
C	0.881577041938	4.806468721123	-3.532309696925
C	-2.898714957143	2.939758536777	-1.926646281549
C	-2.093299611184	0.845877382149	-2.929202561712
H	-1.058115717114	4.831179594194	0.291739202678
H	0.463431777264	5.540131409101	-0.302267690621
H	-0.893247915005	5.288025720184	-1.425463471476
H	1.355722278592	1.999028900960	-0.122654398905
H	1.767324643223	3.647017773046	0.448156752609
H	0.335882100567	2.792325734705	1.097115263697
H	-1.664757350954	4.845494605714	-4.619158936029
H	-0.556143256297	3.749848026797	-5.477267127699
H	-1.860548169351	3.083557135024	-4.470970702343
H	0.516561794222	5.830243287702	-3.699614921522
H	1.491197331439	4.802371575991	-2.623922927801
H	1.519341084208	4.527497848604	-4.387181490807
H	-3.356964402813	3.365393524360	-2.835043070628
H	-3.663273200909	2.360607690573	-1.393705212846
H	-2.594532578336	3.759764462394	-1.270349802961
H	-2.466636317803	1.039446673108	-3.951065321413
H	-1.215039082420	0.195009735328	-2.966556252089
H	-2.884919606181	0.316118744458	-2.381790271227
O	2.709392131031	-0.537558759749	-2.978615906546
P	2.987977656728	0.216229578933	-4.243175136154

N	4.158717056289	-0.637853980274	-5.110340611662
N	1.805344168009	0.376703405098	-5.410731075655
N	3.476068872968	1.774788151341	-3.909885813216
C	4.523753659139	-0.319754965554	-6.480734756912
C	5.249725706825	-1.220251850736	-4.343576408943
C	0.876203884132	1.495300612231	-5.429289234745
C	1.238869383607	-0.849048257753	-5.965892916663
C	4.021873070431	2.634037292908	-4.942529328180
C	3.696699890075	2.215717101292	-2.543497010952
H	5.368940272190	0.385955907898	-6.533399409946
H	4.823105234712	-1.242670146373	-6.996970366514
H	3.669993402929	0.111085911445	-7.010656489604
H	4.893516803085	-1.498258388869	-3.348076350552
H	5.611775322065	-2.124063571751	-4.852449167284
H	6.098199113328	-0.522495308359	-4.239579642246
H	0.696348294316	1.790994553818	-6.473401090750
H	-0.083072482874	1.223804965534	-4.964920935530
H	1.290288670093	2.335702409107	-4.869001172537
H	0.742410287748	-0.607847865842	-6.914480089853
H	2.029571866132	-1.576937600277	-6.168951217644
H	0.503941837627	-1.301524694214	-5.280259104798
H	3.689300509154	3.668822075595	-4.776748775057
H	5.124112454239	2.628167979935	-4.945719906045
H	3.667263481719	2.322549356613	-5.931077445409
H	3.158049459271	3.156419318567	-2.357950143784
H	3.318897281251	1.461341564937	-1.849536670746
H	4.770423428226	2.380458302520	-2.357414066265
Li	1.164153010431	-0.205609098064	-1.695501217470
O	0.025572562824	-1.553037498184	-2.559231124444
P	0.254906425412	-3.038274892235	-2.576227180605
N	-0.626378186112	-3.677095739630	-3.871766335823
N	1.767787073064	-3.679564426901	-2.844423455965
N	-0.177533771914	-3.698824143658	-1.110397395092
C	-0.722485287391	-5.127818414793	-3.967809108010
C	-1.887132515413	-3.008694149734	-4.174751780884
C	2.781987455817	-3.515853242306	-1.803444075687
C	2.349235045722	-3.705988428683	-4.180933062484
C	0.188830526636	-5.029218659396	-0.664597100322
C	-1.052956514212	-2.978829868316	-0.194237009725
H	-1.434818684456	-5.547531683554	-3.237140224366
H	-1.066019589608	-5.397887519062	-4.974321682611
H	0.258601571615	-5.585778998987	-3.806902530715
H	-1.748545990765	-1.925502107543	-4.137455947182
H	-2.205469892322	-3.293923221336	-5.185315388223

H	-2.687862249719	-3.289002040394	-3.468687131349
H	3.469365858360	-4.373028525451	-1.844227886457
H	3.336036543144	-2.578672038623	-1.954404986032
H	2.314398458132	-3.477526237798	-0.816269819388
H	3.026893018548	-4.568589028413	-4.251751911726
H	1.567208550018	-3.814466852880	-4.936818030263
H	2.920759529116	-2.787448186676	-4.378434682744
H	0.727835755599	-4.962793531036	0.293149859467
H	-0.705792982779	-5.652186570187	-0.512253410856
H	0.837232211430	-5.519464057431	-1.395593613010
H	-0.592721713167	-2.962002718523	0.803060501611
H	-1.163603408958	-1.943050282709	-0.523024670890
H	-2.038650881610	-3.467108635980	-0.130626385702
C	-2.470347372619	0.033914211991	1.752247843351
C	-2.924943488042	0.142406035204	0.416913631915
C	-3.460830920139	-0.082568914001	2.756432156507
C	-4.285457000313	0.103049211803	0.122600885376
H	-2.185876742903	0.261036425825	-0.371511842607
C	-4.815066048767	-0.111572688084	2.451708788774
H	-3.144476635391	-0.160761428911	3.796645155447
C	-5.245693137451	-0.025844185003	1.126467172012
H	-4.606481344980	0.173848609593	-0.916876241996
H	-5.542799255646	-0.207269209130	3.256493142236
H	-6.305300347223	-0.057523467956	0.882252334950

Table S34. Atomic coordinates and single point energies of *tris*-HMPA-solvated **8o** chelated to the *endo* sulfonyl oxygen.



G = -3843.779104

G_{SP} = -3845.430947

133

30030m_open_endo_THF: optimized structure // E(RM062X) = -3846.53434373 A.U.
after 14 cycles

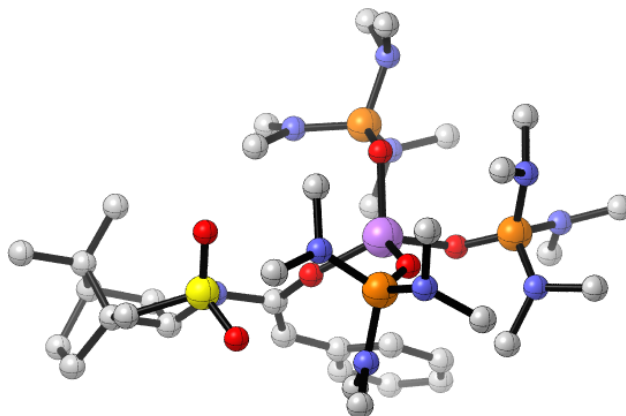
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N	1.346202626930	0.035521852351	1.950957007469
S	2.460777352470	1.196757148320	1.486644341972
O	2.555529260473	1.351809636847	0.016247461258
C	3.930090395582	0.297612649465	2.068333072449
C	3.415958127830	-1.014007941365	2.630381027970
C	2.000367129746	-1.279473314619	2.052384311586
C	1.366300182876	-2.228488931967	3.099331835082
C	2.528143646313	-2.485166029739	4.081924121301
C	3.594335730399	-3.316886550825	3.337026336613
C	4.227776154923	-2.293188642268	2.350768857343
H	4.128910347867	-2.600900619324	1.305173334341
H	5.294402212965	-2.138515928295	2.546287718863
H	3.141265385150	-4.169428813618	2.816971643249
H	4.342686442158	-3.720939760747	4.027180591759
C	3.197277704275	-1.092432067008	4.177484744240
C	2.307650819690	-0.008542227291	4.791563302410

H	2.746377558010	0.986785867204	4.635246907425
H	1.295821057289	0.018227997023	4.384860703340
H	2.244427385428	-0.172277659856	5.875677133898
C	4.513742114896	-1.075134496588	4.959890290666
H	4.986429218445	-0.086050448620	4.883366789377
H	4.312331053199	-1.256438927950	6.023424636404
H	5.242869674224	-1.819796981464	4.629243550782
H	2.209998843624	-2.918948374263	5.036403322743
H	0.507173675841	-1.751776352517	3.581179459672
H	1.010592319874	-3.157290954619	2.638931312357
H	2.045271142889	-1.743505246445	1.055111874108
H	4.431477823289	0.936247277358	2.803352973371
H	4.565935482050	0.180031957502	1.184725040613
O	2.223801655287	2.438006820469	2.238172661596
C	-1.017162642045	0.211852350329	2.086770046756
H	-0.782238957897	0.381317597234	3.134399100099
O	0.066902696836	1.909032014886	-2.323198139264
P	-1.339497502342	2.424551560376	-2.225253572410
N	-1.664295548037	2.856788618564	-0.653029418134
N	-1.737180506896	3.786056730127	-3.125767632549
N	-2.428442903949	1.312259029234	-2.822984526103
C	-2.994904313142	3.248389810236	-0.234297826274
C	-0.593976421187	3.182619328069	0.274973989481
C	-1.951272781357	3.740144548002	-4.562754307533
C	-1.552101500385	5.133235321619	-2.612193320705
C	-3.786500246572	1.612908537370	-3.240026367874
C	-2.065000398211	-0.092837432828	-2.937510629515
H	-3.205881340122	2.819896648098	0.756288931248
H	-3.104165369498	4.344734515699	-0.172832417112
H	-3.748486154444	2.861779795762	-0.927428947470
H	0.337694190988	2.719244963882	-0.060108825318
H	-0.447399417336	4.273697784780	0.363540146899
H	-0.842210287632	2.783558309686	1.265948793891
H	-2.876142710471	4.277437327450	-4.821544691315
H	-1.119644445971	4.214375870699	-5.106039830192
H	-2.043855729228	2.706179924144	-4.906267638923
H	-2.469089538049	5.722881780332	-2.760034900309
H	-1.322092756854	5.112157276799	-1.543960863287
H	-0.729595459696	5.646550847403	-3.133245030204
H	-3.945522039659	1.276027465403	-4.276122109938
H	-4.517385551686	1.098672333849	-2.599162052502
H	-3.979569908986	2.687434212046	-3.192744419051
H	-2.097203107605	-0.401237511321	-3.994988153873
H	-1.054845490457	-0.263180620093	-2.552562162518

H	-2.780182865852	-0.719749961241	-2.384179028617
O	2.941133683246	1.088149385733	-2.674113854251
P	2.912226619662	1.786104596475	-3.999821640331
N	4.467258157369	1.709946125540	-4.666238095448
N	2.000838581168	1.188585769186	-5.267334710690
N	2.392217903144	3.358080196885	-3.818353731686
C	4.726220760326	2.386375026678	-5.930182497037
C	5.563700838072	1.863404946391	-3.717443477114
C	0.551553689379	1.363650423276	-5.227908261487
C	2.385056850946	-0.089338628482	-5.860989768043
C	2.082778435122	4.245447936979	-4.921689384830
C	2.211089947363	3.938675275195	-2.497934502510
H	4.844391032451	3.476075518535	-5.804364127848
H	5.655544787219	1.991749353543	-6.360489991133
H	3.912371134828	2.197477981778	-6.636482573317
H	5.348867342625	1.294637590384	-2.809308617906
H	6.484862231886	1.475972128509	-4.171095176360
H	5.732196724815	2.919689644096	-3.444235322392
H	0.170727544835	1.361691891479	-6.258848429510
H	0.073600573237	0.561208478371	-4.646940885089
H	0.308734123525	2.311816368022	-4.746835089594
H	1.914891573412	-0.167254395250	-6.850051970359
H	3.469514324279	-0.142205229069	-5.987358845326
H	2.050448702621	-0.936352593738	-5.242346976920
H	1.054517897658	4.628198257116	-4.817673562135
H	2.764569521862	5.109335698183	-4.942334899547
H	2.156275192703	3.717901357636	-5.877121929723
H	1.177470076705	4.297689224697	-2.389104659450
H	2.387870450641	3.179910673406	-1.730722003178
H	2.901720065689	4.784216021761	-2.352910970094
Li	1.278353078702	0.609315880255	-1.562173638470
O	1.024117609661	-1.043378070454	-2.695566650603
P	1.928483456319	-2.227445605474	-2.503443905531
N	1.763037047075	-3.239771814358	-3.834576384155
N	3.580713053525	-2.039120990933	-2.394266307577
N	1.567549647903	-2.973681662761	-1.043013589522
C	2.413002045032	-4.541557791121	-3.841412387241
C	0.522744627819	-3.197497524249	-4.596347560563
C	4.131307724624	-1.352850639340	-1.226781259204
C	4.397674408937	-1.831680332102	-3.584714859132
C	2.361348373936	-4.061993807898	-0.495938580489
C	0.164928256709	-3.020629986933	-0.644041376837
H	1.767650888735	-5.325860121621	-3.414063011416
H	2.653002574988	-4.823012327473	-4.875573584796

H	3.347332104769	-4.503995359394	-3.272527847991
H	0.098849501573	-2.191158194291	-4.551438330074
H	0.734189530655	-3.449762646864	-5.644218974419
H	-0.219731750587	-3.916333327095	-4.212353196509
H	5.098680679865	-1.806368893355	-0.965804830022
H	4.252555958784	-0.280879857188	-1.431841453447
H	3.453068399648	-1.460778955761	-0.377333005353
H	5.407603620868	-2.214993924965	-3.383898210766
H	3.983094854595	-2.377010999588	-4.436168996773
H	4.466765957901	-0.763527154955	-3.836905340390
H	2.315601235574	-4.018644783578	0.603023791551
H	1.984420047990	-5.049339739650	-0.808209929018
H	3.407112814463	-3.969765946638	-0.802906287554
H	0.100853111148	-2.986116790153	0.452862272391
H	-0.354796344291	-2.141612324073	-1.029868303296
H	-0.321220567434	-3.947099467856	-0.993044674717
C	-2.413532208522	0.236468277031	1.704003315797
C	-2.866635180816	-0.105173265964	0.411507601821
C	-3.391574628023	0.613779529451	2.650500025414
C	-4.220353752874	-0.074000227757	0.097496174337
H	-2.126486260685	-0.381986046441	-0.333212255015
C	-4.742406830714	0.657573238472	2.324379707846
H	-3.072142552693	0.881975892912	3.657572735741
C	-5.172822634988	0.313464749068	1.042312120477
H	-4.541789738855	-0.361276168202	-0.903680644239
H	-5.466791128488	0.960670062364	3.079210219607
H	-6.230032133737	0.340271154450	0.786395317867

Table S35. Atomic coordinates and single point energies of *tris*-HMPA-solvated **8o** with the enolate oxygen *syn* to the sultam ring.



G = -3843.78183

G_{SP} = -3845.435170

133

30030m_pendant_front: optimized structure // E(RM062X) = -3846.53842016 A.U. after 14 cycles

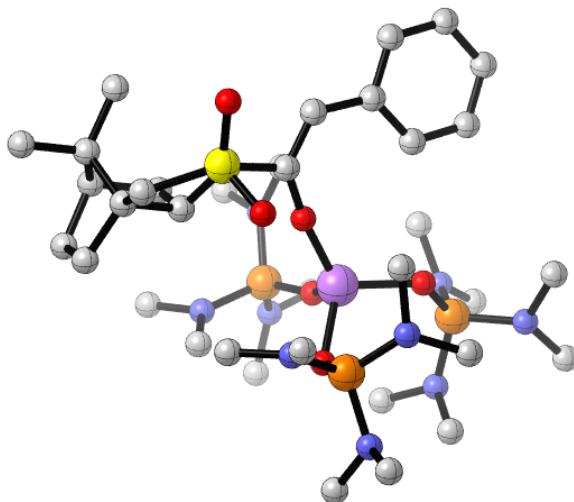
O	-0.051719309072	0.015231641955	0.054233460044
C	-0.027828141219	-0.029214478062	1.317673820041
N	1.306070452086	0.017648828111	1.902430948818
S	2.492582799527	-0.879510519075	1.048276487242
O	1.974693247429	-2.184446638521	0.616434502517
C	3.591700473442	-1.130424345914	2.471048073629
C	3.016242973655	-0.328210000172	3.613247462692
C	1.501909526221	-0.127077682814	3.351402974636
C	1.169353745303	1.130650002150	4.196640147065
C	2.489362629063	1.399817073855	4.947087704394
C	2.703045152573	0.235337168087	5.939762107794
C	3.105325812566	-0.952169986322	5.018275681100
H	2.432260896999	-1.812049262471	5.106203916796
H	4.120215036285	-1.307794915294	5.225830458412
H	1.790504598725	0.027662345717	6.510086591540
H	3.492440026538	0.464166560616	6.663594971820
C	3.554933788919	1.116688269828	3.859193873525
C	3.487833447854	2.063337139659	2.661234655094
H	4.132588365028	1.706066726487	1.846849477079
H	2.483339935679	2.175621479953	2.252863411120

H	3.851474327655	3.054839814090	2.963897445153
C	4.998880485762	1.138636317749	4.366301507174
H	5.682912708783	0.799491093455	3.576076752616
H	5.283019609734	2.167509881483	4.621984071473
H	5.173762026935	0.517755137111	5.249258237343
H	2.539666707321	2.393593125109	5.405787008075
H	0.878002631073	1.963502898616	3.548346815273
H	0.340697362065	0.944669451013	4.888545674165
H	0.943597893871	-1.007558850106	3.700507451600
H	4.594985792537	-0.824654860791	2.157478388224
H	3.570520598476	-2.208474275317	2.659918717475
O	3.166604770499	-0.038873441204	0.051926080710
C	-1.086486229541	-0.082313116880	2.209791065902
H	-0.878981542546	-0.032352763057	3.272422474966
O	-0.353007330944	-1.221934031745	-2.766875069887
P	0.694453733050	-2.300392007905	-2.819971990112
N	0.342504885482	-3.542307598718	-1.781878990012
N	0.814570324542	-3.111112871371	-4.296407550060
N	2.195958796019	-1.651120869761	-2.547079943812
C	0.819812499156	-4.905935768202	-1.910343897292
C	-0.440001776066	-3.280552028141	-0.580096168203
C	1.618438543500	-2.517261871684	-5.356518744187
C	-0.382411055047	-3.779156798069	-4.789411876426
C	3.328151979057	-2.488215214668	-2.211949374202
C	2.513648849773	-0.299874338969	-2.979402931449
H	1.474929212153	-5.170556530117	-1.066499232217
H	-0.030513063604	-5.605098350265	-1.911109941977
H	1.374756848232	-5.031450871047	-2.843585755474
H	-0.548523078690	-2.203054406813	-0.431033155905
H	-1.431867248637	-3.753744313834	-0.659026152088
H	0.081869630138	-3.681605253544	0.296127439272
H	1.802734193661	-3.279393106540	-6.123823569530
H	1.123659957194	-1.658837024858	-5.840827175122
H	2.585731761435	-2.193114680882	-4.964052489305
H	-0.092790808043	-4.552569873337	-5.512696669865
H	-0.908667333457	-4.265084993798	-3.961778659841
H	-1.075372782365	-3.079591434060	-5.286297067820
H	3.899841406183	-2.801667112352	-3.103390942428
H	3.992476755724	-1.923834397424	-1.545802102440
H	2.991232638989	-3.374796946161	-1.667271235517
H	3.064182674617	-0.292306875053	-3.936369114613
H	1.592819308783	0.283851273906	-3.086908656583
H	3.130438610747	0.173165794753	-2.207395255887
O	-2.634962964631	0.514527237749	-2.191518144474

P	-3.161892183498	0.293755191111	-3.582928026305
N	-4.634783510904	1.098576810353	-3.715899148259
N	-2.343443881535	0.881676230596	-4.911667505516
N	-3.270335724050	-1.342469795625	-3.905323262663
C	-5.393828119358	1.111097893232	-4.956975423959
C	-5.465062363355	1.224243363855	-2.526816371209
C	-1.105518033604	0.225846100593	-5.329928306755
C	-2.320844091887	2.319468489742	-5.167438874255
C	-3.867486320899	-1.832164200859	-5.134969380487
C	-3.244504787958	-2.303670991299	-2.816172964600
H	-6.124844593139	0.288219153766	-5.002367474122
H	-5.944914595892	2.058742069550	-5.032355703068
H	-4.723090611126	1.035197817327	-5.817363435974
H	-4.832529468220	1.279477738630	-1.636764958292
H	-6.057462333329	2.146791379197	-2.598601496457
H	-6.163882209591	0.377272614729	-2.419595234842
H	-0.994434344718	0.345146495992	-6.416714690931
H	-0.240643089879	0.670214032467	-4.815422691792
H	-1.141413086658	-0.834288521523	-5.070494984342
H	-2.118199884905	2.478975915296	-6.234984808304
H	-3.287834670633	2.769653582428	-4.929062327672
H	-1.537450574644	2.818168930182	-4.579075016513
H	-3.378331135298	-2.772384872252	-5.425689507667
H	-4.945431814687	-2.033051299412	-5.024483667565
H	-3.722179581997	-1.109663411212	-5.944138745940
H	-2.701903076289	-3.202157808443	-3.140210708489
H	-2.711499392423	-1.874688560991	-1.966409641178
H	-4.260860644024	-2.604825366489	-2.512189954027
Li	-0.722327503426	0.312777053184	-1.727837060740
O	-0.071343452774	1.947769000877	-2.602203854987
P	-0.360422016391	3.255014784693	-1.906969329123
N	-0.238038046181	4.498402680708	-3.042320108606
N	-1.849049492761	3.533986577368	-1.225860804110
N	0.696850100335	3.470643408491	-0.638808423544
C	-0.265433204743	5.862681177367	-2.527181756537
C	0.778515683012	4.312612348597	-4.073573200204
C	-2.222554262791	2.754318247650	-0.042642709163
C	-2.999787212945	3.932104424236	-2.027642692431
C	0.453063905870	4.340551218951	0.497080639925
C	1.842375305020	2.585146832375	-0.476651237728
H	0.680208602862	6.134999758841	-2.028351064171
H	-0.427225574751	6.555072552904	-3.362207621137
H	-1.087611864585	5.985632299100	-1.815073785804
H	0.740738987559	3.287578899484	-4.450422299075

H	0.574186168016	5.004762814011	-4.899700879567
H	1.794794380673	4.516036196103	-3.694518361080
H	-2.658193077515	3.417695379454	0.718479082662
H	-2.946856707385	1.978035100012	-0.320447600125
H	-1.348280963231	2.248121365120	0.383192537415
H	-3.690012964031	4.500818067318	-1.389802981154
H	-2.686644038794	4.570167675582	-2.857925680778
H	-3.527386837405	3.053911175960	-2.425645399371
H	0.284039352753	3.746089748644	1.409974328518
H	1.322132060884	4.992148679484	0.668453495533
H	-0.426095456508	4.967302423842	0.327090961727
H	1.690843622990	1.908976315974	0.369745399734
H	1.968696183528	1.964068747708	-1.364075002841
H	2.753891532957	3.180837274000	-0.314527928252
C	-2.494126175894	-0.164630309709	1.864671027858
C	-2.974738287100	-0.560637639142	0.600766879424
C	-3.464486639247	0.127604828199	2.850436777029
C	-4.337255363748	-0.643806451055	0.339392617316
H	-2.268030488408	-0.787452403403	-0.188698730845
C	-4.826021456184	0.045180473257	2.584697752452
H	-3.129899154324	0.431816107211	3.842430767526
C	-5.279977775085	-0.339980616550	1.321492646620
H	-4.659599454404	-0.947353286247	-0.655672185597
H	-5.540531656284	0.285149191716	3.370978438156
H	-6.345582690587	-0.404198864147	1.110311516037

Table S36. Atomic coordinates and single point energies of *tris*-HMPA-solvated **8o** with the enolate oxygen *anti* to the sultam ring.



G = -3843.753644
 G_{SP} = -3845.439461

133

30030m_pendant_back: optimized structure // E(RM062X) = -3846.54627989 A.U. after 14 cycles

O	0.078682243047	0.134672207581	-0.039271465381
C	0.052064272985	0.003998819331	1.221317035797
N	1.366168419358	0.010480469839	1.889730190381
S	1.806839126665	1.434581761823	2.670905807575
O	1.596357156454	2.617557984910	1.816283997248
C	3.590880966992	1.059165895320	2.705890770032
C	3.756544652376	-0.266340772584	1.988907248367
C	2.490409754424	-0.525766040149	1.131772118128
C	2.463512387894	-2.067034934159	0.992357909092
C	3.790612302951	-2.491131867260	1.653546284708
C	4.951812407267	-1.973776131428	0.774976720307
C	4.944954221510	-0.436897385655	1.025880378959
H	4.792722361529	0.143604315066	0.107511017224
H	5.883251560911	-0.090016492513	1.472578368540
H	4.801730912919	-2.222859861450	-0.281591566624
H	5.906676513487	-2.422075003792	1.069438128439
C	3.859973787720	-1.547171533255	2.880746117225
C	2.733128788772	-1.742617070224	3.899004513813
H	2.735359802065	-0.931927543247	4.640563546445
H	1.733639128707	-1.762395281315	3.462816645083
H	2.899619086129	-2.682384430885	4.442566178945

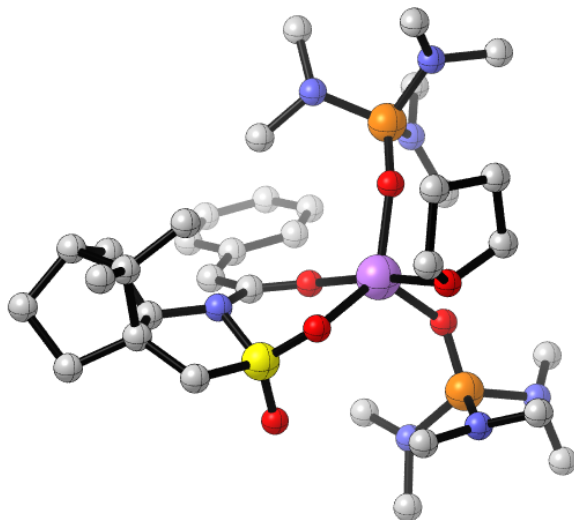
C	5.176542993277	-1.626123639966	3.658799629476
H	5.204999639236	-0.857403028039	4.443045464166
H	5.251718526388	-2.598034312081	4.162721959335
H	6.073279539021	-1.505032386223	3.044995674099
H	3.851904722339	-3.561281603613	1.882903644861
H	1.598088281597	-2.471969982193	1.525800097260
H	2.380760914888	-2.380841886605	-0.055277672871
H	2.548042687625	-0.033792126111	0.152470479029
H	3.890755434823	1.039587504874	3.758784219445
H	4.080976186307	1.898784708017	2.203133368668
O	1.248477022783	1.466370347187	4.022549187703
C	-0.986952435319	-0.201819007871	2.090005656733
H	-0.715091278188	-0.344452067934	3.132421036084
O	-0.017742171401	-1.401707253010	-2.699376118449
P	0.627794708439	-2.750510078464	-2.648270952783
N	-0.041103896333	-3.680551310843	-1.442915377652
N	0.466124546866	-3.754609710926	-3.984896492104
N	2.283616025098	-2.572691252008	-2.532959972993
C	0.231384373188	-5.095414028510	-1.269121021332
C	-0.699923542146	-3.050618150068	-0.297997791150
C	1.287592468426	-3.546755772662	-5.168514031942
C	-0.822840835483	-4.356260797886	-4.289576282177
C	3.165473058293	-3.715610487615	-2.402322617271
C	2.924927214057	-1.268802081548	-2.547480573181
H	0.981920855476	-5.270725978477	-0.482060894522
H	-0.693590630627	-5.609845644526	-0.972644657465
H	0.585007989357	-5.541308771059	-2.203381834081
H	-0.666320080960	-1.960307546862	-0.381832113674
H	-1.748275408268	-3.377514761567	-0.237782789728
H	-0.197028497870	-3.339442895723	0.634263556785
H	1.569183807032	-4.518331869393	-5.596904307724
H	0.748822263596	-2.975936077524	-5.940290789785
H	2.199942712536	-3.003471514379	-4.910047728574
H	-0.664007172731	-5.296379034067	-4.834571056307
H	-1.366334259731	-4.579752066400	-3.368093421636
H	-1.443526015254	-3.694119179041	-4.915451299366
H	4.038024698504	-3.592133330520	-3.060230613017
H	3.530891878265	-3.840742375983	-1.370571177678
H	2.652428890124	-4.635440452972	-2.701842635923
H	3.634611463223	-1.204879415250	-3.388198465368
H	2.178287160907	-0.476357302671	-2.658629222155
H	3.486326639219	-1.100120789808	-1.615976511218
O	-1.941007202208	0.782022490044	-2.467977504022
P	-2.499000596270	0.389377763317	-3.806959084134

N	-3.781573481850	1.418655442385	-4.154367570950
N	-1.571133301184	0.542542049828	-5.184319472679
N	-2.936012500385	-1.225199128497	-3.823429514063
C	-4.436846001839	1.478908143504	-5.447863363625
C	-4.579883935958	1.943961926101	-3.058186577618
C	-0.539966506661	-0.448109103689	-5.483033454756
C	-1.186356170459	1.888279581068	-5.603463011973
C	-3.749277864932	-1.727547977459	-4.914900278300
C	-3.088968509544	-1.941970422044	-2.566086398657
H	-5.382421773031	0.913987823430	-5.457969858375
H	-4.668669336274	2.525642411364	-5.693289332969
H	-3.780301080747	1.082698932039	-6.227195851592
H	-4.002940375688	1.914895916349	-2.129893302475
H	-4.850367478378	2.988268527757	-3.269324636050
H	-5.511706538817	1.370933784314	-2.922046223558
H	-0.414867537050	-0.502525357785	-6.573479703661
H	0.415897251307	-0.176936887262	-5.010513405736
H	-0.842398369887	-1.422483403591	-5.092870020748
H	-0.949444311111	1.867701424907	-6.675491725132
H	-2.011214879545	2.588654229092	-5.446387091022
H	-0.308779458564	2.246263731655	-5.047974576186
H	-3.610999503976	-2.813674325558	-4.998908765444
H	-4.825072482182	-1.539634010443	-4.760664568364
H	-3.440596758125	-1.273696998130	-5.862912130338
H	-2.747551786327	-2.978151150084	-2.695934154218
H	-2.474116209569	-1.470802883587	-1.798431154593
H	-4.138018721471	-1.960602415110	-2.229805984425
Li	-0.163705202038	0.288750508782	-1.860063068924
O	1.039709074012	1.484659081004	-2.810190839902
P	1.004244102488	2.949045926277	-2.447424972584
N	1.268707673577	3.834298573294	-3.863205127853
N	-0.376985208787	3.633525470260	-1.844615799537
N	2.136930361789	3.273644022116	-1.273735682197
C	1.420499503534	5.277390932111	-3.761004017412
C	2.163540563236	3.238938018811	-4.845753543255
C	-0.808272839639	3.269883499407	-0.488582033469
C	-1.481110845780	4.027415644673	-2.710495820758
C	2.225949725794	4.541677240684	-0.567772271844
C	3.243678488608	2.370411742756	-1.032087118884
H	2.439134951843	5.569124362043	-3.454982679203
H	1.215388521988	5.731467876939	-4.739290902331
H	0.706972682167	5.686731537319	-3.039423143554
H	2.004462882345	2.158473532019	-4.882899085414
H	1.947455148123	3.665414098219	-5.834209318437

H	3.224576616749	3.433981088127	-4.612214024171
H	-1.223401970963	4.161351428836	0.000828820216
H	-1.578343939548	2.486827180014	-0.529577778302
H	0.033114557313	2.900750135917	0.106704115669
H	-1.986640169458	4.893135564157	-2.260557250924
H	-1.111994817541	4.312717242191	-3.698922869842
H	-2.204218365820	3.208298249803	-2.819657252516
H	2.312338915055	4.347298792814	0.508266558040
H	3.099290290680	5.123289154761	-0.903314925572
H	1.321406110516	5.132061955326	-0.736069018515
H	3.328006482375	2.196201422894	0.048550021893
H	3.054433349234	1.417509004995	-1.533233339709
H	4.193963989525	2.790683513620	-1.400547440734
C	-2.399404166565	-0.258382944816	1.761347332112
C	-2.918956888615	-0.010792522303	0.475719253548
C	-3.322490677437	-0.591447773597	2.774150451098
C	-4.284329861261	-0.106131898427	0.228331633324
H	-2.248293795755	0.264953787484	-0.330943324512
C	-4.683219510680	-0.683121726664	2.519420701933
H	-2.948813120175	-0.780894432066	3.779504247627
C	-5.180670270705	-0.444352475945	1.238940305092
H	-4.651819572673	0.089480506860	-0.778731843600
H	-5.364015513382	-0.944251631362	3.328003192151
H	-6.246688944602	-0.517235674487	1.035662702374

Mixed-solvates of enolate **8o**

Table S37. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *exo* sulfonyl oxygen with an axial THF.



G = -3256.194422

G_{SP} = -3257.645462

117

31020m_ax: optimized structure // E(RM062X) = -3258.61148285 A.U. after 14 cycles

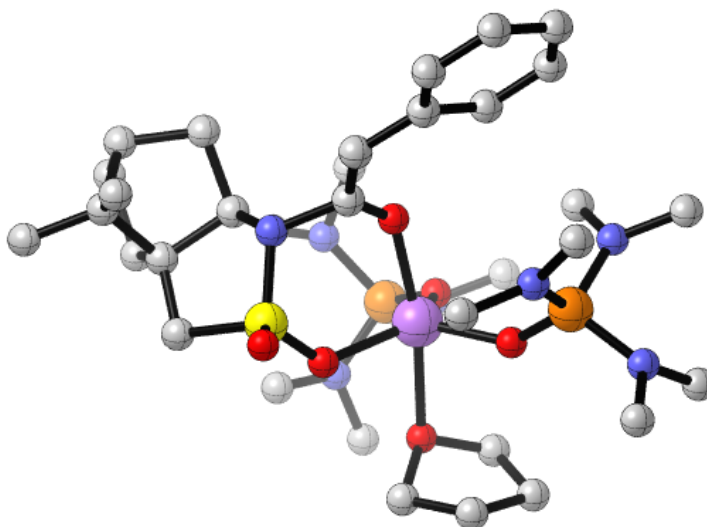
O	0.020631279631	-0.194627677354	0.131674404116
C	0.077590682845	-0.350307995105	1.380451036741
N	1.421785642023	-0.320262450338	1.919236754727
S	2.579454754813	-1.051499127795	0.940239146034
O	2.260084081302	-2.457585937610	0.645597808195
C	3.914062315504	-0.994748546082	2.162981502590
C	3.325620612159	-0.353058500755	3.403838630728
C	1.772971192249	-0.434436119479	3.333562620946
C	1.319258095519	0.753417422342	4.220559973963
C	2.645879783988	1.243897627185	4.829950290516
C	3.175720496091	0.125338934886	5.758078546173
C	3.699942222529	-0.956087739227	4.767516304318
H	3.225727374596	-1.933595252680	4.907882850230
H	4.782265319364	-1.099897185389	4.851941544101
H	2.379609846568	-0.258806353680	6.406027410718
H	3.976276143771	0.489157562182	6.410513748620
C	3.610968951523	1.167094478724	3.622460518899
C	3.245213921579	2.083367514546	2.452942651462
H	3.918814681501	1.905639708395	1.602822338615
H	2.224773689086	1.956367214105	2.090582583583
H	3.377301929750	3.129978558021	2.759067599903

C	5.073817309122	1.454497305137	3.970640185281
H	5.726341979549	1.188170809330	3.127544649989
H	5.202029136898	2.528996615667	4.153360936222
H	5.435229320924	0.923666595550	4.855651181211
H	2.572805766259	2.225121745663	5.311563556479
H	0.831231547484	1.522132762103	3.612491370218
H	0.606144304161	0.433540102018	4.987531731828
H	1.418662806138	-1.397358324208	3.730235203586
H	4.742500443990	-0.434543681444	1.717168929562
H	4.206253636507	-2.038955733319	2.310334336943
O	2.868394810297	-0.184557514172	-0.222392122339
C	-0.957962715550	-0.499739382386	2.285305781093
H	-0.720684842462	-0.681086300676	3.329421309613
O	0.520421544675	2.220736498774	-1.537420272943
P	-0.612655615481	3.194490620448	-1.381997051100
N	-0.658737188288	3.785970992013	0.180967579925
N	-0.546605066542	4.612448688020	-2.267685168422
N	-2.048585173155	2.474772856159	-1.828135149692
C	-1.554196730048	4.859621914196	0.587500086955
C	-0.391072980986	2.829423135741	1.250972249259
C	-1.039016468979	4.676004243615	-3.635525129034
C	0.403171880849	5.665510896900	-1.936523150656
C	-3.304515822164	3.206244297609	-1.821487762155
C	-2.081036480002	1.222545829985	-2.567480553781
H	-2.527670644369	4.472414607864	0.928010205220
H	-1.094638454469	5.406120173426	1.421721020797
H	-1.716635248994	5.560605601797	-0.236068449050
H	0.332550758946	2.089834237963	0.901278509621
H	0.023558583091	3.372515370315	2.111131886674
H	-1.306682478394	2.305435628206	1.568877757202
H	-1.679159469721	5.560133148025	-3.765529560075
H	-0.206116658907	4.747647620170	-4.351219519506
H	-1.623522189551	3.784347371328	-3.878855534934
H	-0.083866364860	6.646647328702	-2.026185967178
H	0.760132012504	5.545297183816	-0.910216988130
H	1.269238535204	5.648444691010	-2.616645355162
H	-3.704966980918	3.298150346242	-2.843321046198
H	-4.048965527453	2.684390030171	-1.204213668598
H	-3.170494105499	4.214747454359	-1.420932776811
H	-2.208601939160	1.403916485608	-3.649311363468
H	-1.165031552433	0.650474084661	-2.401758588281
H	-2.935675609208	0.623604621299	-2.224086362942
Li	1.194793658073	0.405432380875	-1.371544210222
O	0.443698484509	-0.786573800791	-2.711875242242

P	1.012646590973	-2.087315703251	-3.208500780831
N	0.300530198055	-2.417336753755	-4.704470336722
N	2.630204353018	-2.242076813628	-3.565018647929
N	0.756801461145	-3.280437638293	-2.078454634865
C	0.548967224138	-3.723722758305	-5.299967311467
C	-1.077583520349	-1.970828823346	-4.875660916752
C	3.602844155452	-2.303693603459	-2.479512166557
C	3.197483255348	-1.691583909498	-4.787830265634
C	1.387385559295	-4.586485052411	-2.105824158022
C	-0.280856815624	-3.133999512041	-1.065761760621
H	-0.053254430075	-4.518423739028	-4.828010362576
H	0.289659531813	-3.685763947234	-6.365436252490
H	1.608248361336	-3.986079102706	-5.215291656926
H	-1.190953111771	-0.964051977317	-4.467507178306
H	-1.311442775240	-1.949743557590	-5.947261638412
H	-1.798500875824	-2.641385782458	-4.378161383997
H	4.412325237763	-2.992255873117	-2.761927803072
H	4.019667972051	-1.305234751548	-2.284968211648
H	3.129920806938	-2.657786460423	-1.559682636500
H	3.949445890269	-2.388090849355	-5.185129755043
H	2.419362275947	-1.546420485476	-5.541124895984
H	3.685143726013	-0.727689651377	-4.581595881005
H	1.888115287279	-4.773537010865	-1.143694702610
H	0.642494381857	-5.381062183661	-2.265185937751
H	2.133919389722	-4.642437833929	-2.902815302543
H	0.125329466081	-3.443599517643	-0.094514628355
H	-0.570672974098	-2.083764839688	-0.979814922797
H	-1.156751642631	-3.757288254625	-1.307088012870
C	-2.360059802450	-0.357131307560	1.955787534812
C	-2.847361729835	-0.065199431866	0.658440287112
C	-3.323321325103	-0.487170251524	2.984010002622
C	-4.212272066183	0.081863710387	0.425348452544
H	-2.132389939564	0.038135933326	-0.152786721573
C	-4.681925371426	-0.337868009820	2.739660384329
H	-2.982407727084	-0.709688677887	3.995179384073
C	-5.144971691804	-0.050433488596	1.454076010657
H	-4.555686258727	0.298578502575	-0.586231497889
H	-5.388356690230	-0.447126799190	3.561504256397
H	-6.209098984195	0.063446946083	1.258913938781
O	2.717142378778	0.854406559791	-2.846097852783
C	3.865782224746	1.610466735218	-2.489015862660
C	2.100697058601	1.543361007241	-3.934210987499
C	3.398123460552	3.060871937642	-2.553674323373
H	4.187816210170	1.276595502561	-1.499598504771

H	4.673263168507	1.422835782041	-3.218941494282
C	2.411073378745	3.040036682203	-3.735191147153
H	2.529247367390	1.174843241216	-4.879728779935
H	1.035895252769	1.301030420441	-3.901837415372
H	4.227831441043	3.761939294726	-2.694457411936
H	2.868134649355	3.311788761127	-1.628651040819
H	2.854988156779	3.469332296137	-4.640949479911
H	1.502060970000	3.594995839390	-3.492360692397

Table S38. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *endo* sulfonyl oxygen with an axial THF.



G = -3256.192736

G_{SP} = -3257.642187

117

31020m_ax_endo: optimized structure // E(RM062X) = -3258.60983592 A.U. after 12 cycles

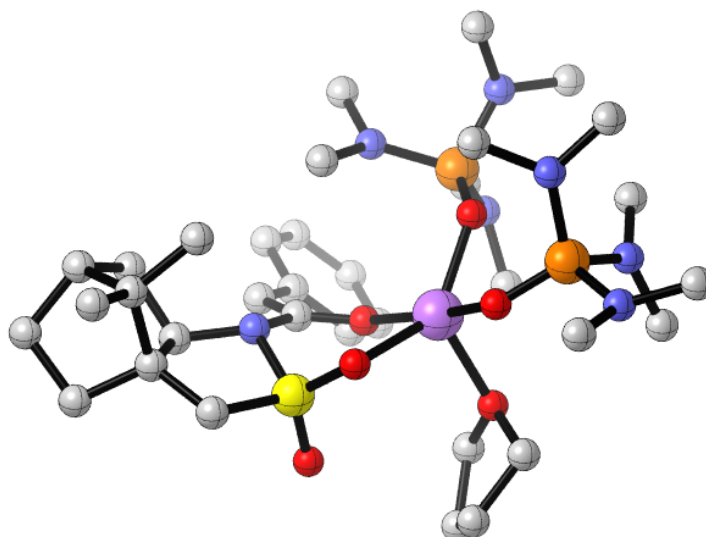
O	-0.121713795498	0.381001489422	0.200050313619
C	0.014336536361	0.715012950749	1.408264415103
N	1.297326730705	0.331855482739	2.066074008833
S	2.650127146715	1.093525471111	1.442105680805
O	2.677580454414	1.044555464392	-0.043816909786
C	3.856841397629	-0.112136313326	2.066386123098
C	3.029341081645	-1.263575019049	2.614575134863
C	1.571649060061	-1.115040392533	2.106417292416
C	0.743150716349	-1.876959974496	3.167034835319
C	1.831600462111	-2.483621978113	4.076656410337
C	2.586368511381	-3.549062612734	3.251849214842
C	3.436539881194	-2.705844882331	2.256703286300
H	3.197912007365	-2.932689898133	1.212471182757
H	4.511609922542	-2.865895240380	2.392809895803
H	1.888115239321	-4.218780937839	2.735114125353
H	3.221125628191	-4.174123315393	3.888804685788
C	2.868089606000	-1.337139249958	4.168404901076
C	2.347165484571	-0.070321248535	4.851164853683
H	3.043490065053	0.766155144076	4.696529019613

H	1.366889234481	0.252617939040	4.498645502292
H	2.288515290783	-0.246711827638	5.933452250990
C	4.171197262776	-1.716921515092	4.877063551805
H	4.897641519737	-0.896119691829	4.797264198723
H	3.977657760442	-1.875792674959	5.945623881225
H	4.645425742747	-2.621842197380	4.487396661024
H	1.451069787676	-2.849748859501	5.036543267258
H	0.083914240590	-1.188231028552	3.705600499194
H	0.111688019750	-2.647793737586	2.713351927489
H	1.458767489146	-1.541196736274	1.098025993380
H	4.461910727856	0.399736577270	2.822133397226
H	4.482686914899	-0.374668171006	1.207661532804
O	2.804929951483	2.427729010710	2.033343421035
C	-0.835239193360	1.362565233465	2.274790246141
H	-0.452168818770	1.580415796570	3.268337555030
O	0.352214390871	2.100524185025	-2.320705455866
P	-0.845367780621	3.007494859034	-2.300178670465
N	-0.926403777016	3.775847172518	-0.830993130636
N	-0.888351160701	4.245179674019	-3.431976624331
N	-2.236175860656	2.168393138623	-2.660070128521
C	-2.059611276355	4.603380190778	-0.468610670710
C	0.228514006180	3.871219169965	0.046064720428
C	-1.123541293856	3.963829177074	-4.841676953586
C	-0.147819629672	5.476593881872	-3.201956707253
C	-3.465866212107	2.757944362123	-3.158724212426
C	-2.256838061743	0.714903933911	-2.564900157284
H	-2.328383706354	4.413292449651	0.580628448366
H	-1.840347024337	5.678139441461	-0.586691683587
H	-2.930989255080	4.356514290525	-1.083334544529
H	0.954018680727	3.094922268487	-0.210804377135
H	0.715156759870	4.859096450661	-0.026667746375
H	-0.092533497208	3.715799066475	1.083732096464
H	-1.877712047301	4.654606071216	-5.245358560407
H	-0.200705162840	4.084786536082	-5.428059649875
H	-1.482999649505	2.939069317347	-4.975145141817
H	-0.701167183251	6.322882142741	-3.630757409005
H	-0.023745613084	5.654196362990	-2.130166842910
H	0.848261786622	5.444124941810	-3.671615522389
H	-3.727017464008	2.323338450740	-4.136173850570
H	-4.298502935140	2.565352642364	-2.466792813716
H	-3.355832558273	3.838457596136	-3.279549979996
H	-2.337044247925	0.271267473229	-3.570201210406
H	-1.343656308085	0.344984419533	-2.088686633850
H	-3.127927593725	0.389565493406	-1.978143840566

Li	1.163652065333	0.653331478342	-1.370969487491
O	0.734347564770	-0.966692549521	-2.345788741931
P	1.548361424815	-2.229365635496	-2.378367047846
N	1.146982466072	-3.093503576275	-3.750504368269
N	3.209579840548	-2.181549512739	-2.436040347904
N	1.272642458491	-3.066042156303	-0.941040542361
C	1.763143863340	-4.365699139134	-4.089979143452
C	-0.079778432154	-2.804144283304	-4.476760058470
C	3.941993764198	-1.679947883282	-1.278902377968
C	3.937200973154	-1.991671478316	-3.683534073684
C	1.868060261051	-4.382114799530	-0.749681873862
C	-0.087669740972	-2.960649279110	-0.412443945033
H	1.089873042739	-5.209626137001	-3.876502041388
H	2.004189830044	-4.384571914108	-5.162687891617
H	2.691802766616	-4.505977797278	-3.529272931170
H	-0.452306355484	-1.818543807684	-4.189162986919
H	0.124407708876	-2.805807563820	-5.556501811020
H	-0.855456875478	-3.557235778937	-4.270797039730
H	4.813401545278	-2.321261655449	-1.079540051135
H	4.273632961275	-0.648448990615	-1.460237752238
H	3.293678808842	-1.675262702592	-0.400189276301
H	4.810833222331	-2.658462140410	-3.702530196288
H	3.301803005305	-2.222028892343	-4.542327883520
H	4.281692119987	-0.951339365815	-3.765659579512
H	1.861298372782	-4.622565765134	0.321676210897
H	1.313410057699	-5.175711427157	-1.277531592685
H	2.906514883792	-4.383117421116	-1.095767722807
H	-0.093643032151	-3.364621907958	0.607443689233
H	-0.387058152558	-1.907864235328	-0.379152062258
H	-0.811741620641	-3.540706625633	-1.010785790577
C	-2.170806324271	1.830035516261	1.952648002184
C	-2.841938555925	1.481784697716	0.761211246897
C	-2.856018290475	2.667560169802	2.858562178896
C	-4.126307333367	1.946558051308	0.501957609671
H	-2.326000867494	0.845401361240	0.048981001736
C	-4.136859629796	3.137075268572	2.588307026380
H	-2.363327869084	2.951416153090	3.788475029525
C	-4.786248926613	2.781355122161	1.405486123287
H	-4.624149490471	1.648145084787	-0.420729224728
H	-4.633669266924	3.785189144898	3.308914843895
H	-5.790307250981	3.143919590142	1.194695563315
O	2.885275824483	0.848413709431	-2.846203274403
C	3.874048794874	1.854210613922	-2.674605470205
C	2.319035550158	1.064007674746	-4.138766358739

C	3.213949857549	3.118358359228	-3.211610409332
H	4.132763813796	1.891793053443	-1.614654283598
H	4.771285864541	1.596809385874	-3.266925002704
C	2.398627575275	2.582159948083	-4.401720657905
H	2.909659666776	0.506225367424	-4.884390946941
H	1.300531783471	0.672413266138	-4.108332433614
H	3.941802228357	3.886989455271	-3.493319220344
H	2.540685520625	3.522264874792	-2.447125593699
H	2.897581105492	2.786885713169	-5.356353228880
H	1.400511245197	3.025849004551	-4.423148213341

Table S39. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *exo* sulfonyl oxygen with an equatorial THF (higher energy conformer).



G = -3256.187972

G_{SP} = -3257.637213

117

31020m_eq1_THF: optimized structure // E(RM062X) = -3258.60397023 A.U. after 14 cycles

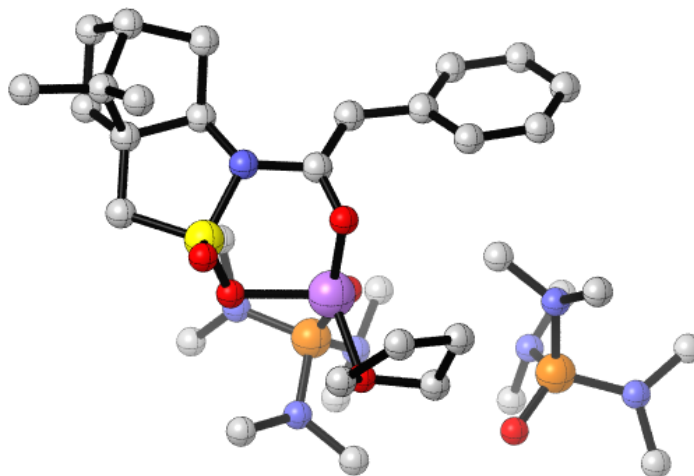
O	0.023812983380	-0.063045803315	0.021043678318
C	0.021376928178	-0.055182984447	1.285339937016
N	1.353855803290	-0.019132633622	1.875076188312
S	2.451677043902	-0.933385047387	0.959369848320
O	1.955169093472	-2.295703766418	0.705436131554
C	3.736893719963	-1.014316706837	2.229842204932
C	3.150136690591	-0.365428942210	3.467752949441
C	1.607145006571	-0.240542930977	3.302679603793
C	1.254942547890	0.941137519763	4.244072076886
C	2.594575922991	1.232037728466	4.946023421886
C	2.926719004535	0.012692074023	5.836996000388
C	3.358176761747	-1.078594149682	4.814084275728
H	2.750382594033	-1.988007111755	4.873876402402
H	4.404634337154	-1.373484687969	4.945933681446
H	2.055333457538	-0.293595702526	6.426802727184
H	3.732679193347	0.237632423377	6.543328719209
C	3.610135714651	1.092105425292	3.786601910128
C	3.422016672939	2.099556927223	2.651245024478
H	4.090226415422	1.860360214916	1.811731638392
H	2.405326015796	2.131196889618	2.259192263813

H	3.692259954483	3.102905678241	3.007106370600
C	5.075557774189	1.174469522777	4.220051598267
H	5.734832595257	0.882735892633	3.390813697051
H	5.322750424325	2.211065047935	4.482351046401
H	5.322971763114	0.547695275867	5.081313700914
H	2.614145477690	2.190659500415	5.475960498931
H	0.893478042757	1.801461694858	3.673360194611
H	0.471966977387	0.663253617874	4.957676864328
H	1.106708714308	-1.167124932085	3.621262518464
H	4.619960951940	-0.502810908294	1.833299337108
H	3.947188602497	-2.080846489429	2.352106187326
O	2.900441647630	-0.152060047663	-0.209381215521
C	-1.050336165076	-0.047079553656	2.156027734043
H	-0.875398925010	0.097700602198	3.217600795836
O	0.390072161854	2.174624532467	-1.939429369845
P	-0.942151511739	2.708604635278	-1.487865644476
N	-0.863147567327	3.095223275679	0.133961374764
N	-1.506698936730	4.142337974571	-2.156038108731
N	-2.161476003134	1.657839520209	-1.906105932518
C	-1.902662783658	3.821611300736	0.838451136336
C	0.388318777157	2.997614183093	0.862446162466
C	-2.315767386945	4.232561056594	-3.359162330332
C	-0.922276287341	5.413394334747	-1.761456728816
C	-3.498919240589	1.844599457162	-1.360280464721
C	-1.850742724636	0.324812653778	-2.407745854242
H	-2.258777214748	3.239993520557	1.701702552447
H	-1.518496083344	4.786822812115	1.206439830146
H	-2.752055339597	4.025584416167	0.181470951355
H	1.065674185319	2.303116115414	0.362739494906
H	0.874547483534	3.985628380449	0.951879710629
H	0.189034100862	2.616414261850	1.871718364430
H	-3.158997576291	4.917717272135	-3.186293153961
H	-1.731550898149	4.623065555252	-4.206914923960
H	-2.711221373721	3.250139308490	-3.626208862889
H	-1.714889687480	6.138653578873	-1.524541196730
H	-0.290304270877	5.291079001530	-0.876979517401
H	-0.306723975785	5.834954162432	-2.571492893463
H	-4.205759709378	1.245688538710	-1.947999777381
H	-3.569488893504	1.531776058822	-0.307244885583
H	-3.802290052093	2.895835850391	-1.442976335446
H	-2.563502435028	0.074654016723	-3.207788415906
H	-0.836571596145	0.311214689222	-2.816323555968
H	-1.901617507389	-0.429176453819	-1.616772896963
O	2.831457741232	1.120333708619	-2.708374067458

P	2.660893951460	1.954616392004	-3.944324205936
N	3.891074235559	1.522417562270	-5.014490301561
N	1.323532579736	1.775952733312	-4.921426737069
N	2.710285842463	3.573470468254	-3.560887065147
C	3.953232321456	2.024197056885	-6.378015205274
C	5.204887296957	1.269934860218	-4.438473748067
C	0.142582077935	2.616555401782	-4.825217326106
C	1.081423714938	0.501242796523	-5.582677729884
C	2.689679340666	4.615912567014	-4.568730592148
C	2.756159164448	4.033759382249	-2.185052678069
H	4.509306569712	2.973746014194	-6.447500128207
H	4.466795276373	1.285645119199	-7.008373070316
H	2.945541470297	2.174206522059	-6.775721770274
H	5.092269770065	0.824612533294	-3.447293364573
H	5.751608499790	0.567616119605	-5.080978875314
H	5.800984321574	2.193888327997	-4.352997411508
H	-0.134327502736	2.980324859358	-5.826875852182
H	-0.703793111081	2.051751097613	-4.407893110635
H	0.333617803394	3.463048004413	-4.162912021153
H	0.640055013680	0.681520843776	-6.572983057347
H	2.021590023897	-0.041077675648	-5.716600480420
H	0.391516675722	-0.125335912401	-4.996236934181
H	1.899563922992	5.348217380146	-4.342386336993
H	3.649886042165	5.152241228189	-4.611387490843
H	2.481944879790	4.196573263508	-5.558255590126
H	1.862581156375	4.631192021242	-1.950069940659
H	2.776829294193	3.172484112528	-1.515022629285
H	3.650942470575	4.653211934949	-2.020944685694
Li	1.367911212850	0.483483260976	-1.506755028754
C	-2.437182694940	-0.167798436521	1.726250024072
C	-2.816527373279	-0.999266829371	0.653180894270
C	-3.473618580787	0.483231048993	2.425782412253
C	-4.149309866188	-1.157007906965	0.291516035586
H	-2.037670588249	-1.542905950302	0.123384134331
C	-4.808496438265	0.325649353698	2.062475984434
H	-3.218161719032	1.124842189102	3.269317734219
C	-5.159514267039	-0.492314145348	0.988463008441
H	-4.404255316227	-1.813681181572	-0.539806365846
H	-5.582213749784	0.847055257535	2.624486675075
H	-6.202932329431	-0.617329881123	0.706193032279
O	1.062917815632	-1.233305311755	-2.550916279787
C	0.244693052454	-2.302217933313	-2.047350896370
C	2.150128310404	-1.822480498949	-3.264290271160
C	1.137689067283	-3.556975390787	-2.001668026652

H	-0.106674382919	-1.985399866697	-1.063137795055
H	-0.611155596475	-2.440527380387	-2.725217632140
C	2.515918734690	-3.040106802076	-2.433139474271
H	1.808566077587	-2.124417611015	-4.269244607705
H	2.932875594624	-1.065531389391	-3.349953987129
H	0.772105125688	-4.316647596911	-2.702887693949
H	1.160995965459	-3.990690428034	-0.998600360737
H	3.096475409940	-3.777524521136	-2.998074396691
H	3.091261546124	-2.721706763134	-1.557528836350

Table S40. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *endo* sulfonyl oxygen with an equatorial THF (higher energy conformer).



G = -3256.181315

G_{SP} = -3257.636252

117

31020m_eq2_endo: optimized structure // E(RM062X) = -3258.60317520 A.U. after 12 cycles

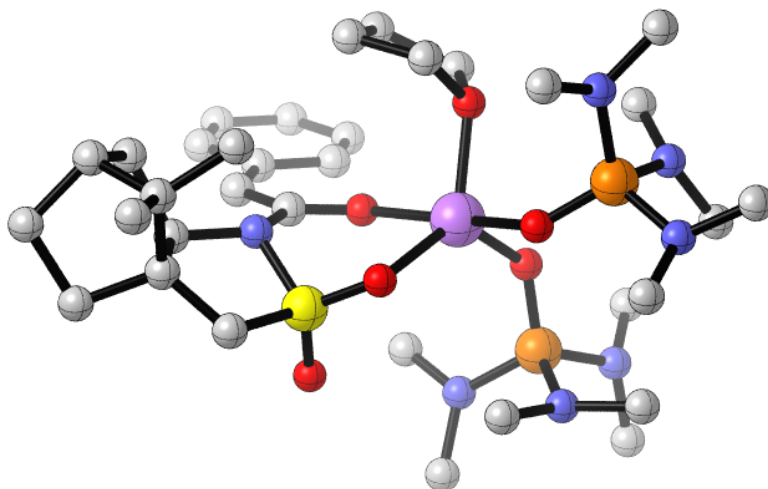
O	1.060094363186	1.185881003023	0.637418312143
C	0.289331798153	0.487280384919	1.376856505475
N	0.968143224353	-0.177690323265	2.459493815386
S	2.639550560194	-0.354299675688	2.273285561740
O	2.964710205857	-0.901288883391	0.927500541319
C	2.819930692885	-1.669567016802	3.500848665311
C	1.495618124045	-1.754200061155	4.229325033752
C	0.370849600662	-1.216374229555	3.300825067703
C	-0.716356141266	-0.745225087862	4.302291621847
C	-0.171240797542	-1.254721794166	5.649207326036
C	-0.177962233032	-2.801066195093	5.605636944193
C	1.019473796790	-3.147367863432	4.672439421237
H	0.728927905414	-3.757033080421	3.809332021845
H	1.812773589698	-3.683801149377	5.203647291977
H	-1.129017820562	-3.180577001402	5.214843489879
H	-0.043066703137	-3.232926042448	6.602606106701
C	1.334312745584	-0.916355094714	5.538882640173
C	1.635292733328	0.579289983980	5.415656220540

H	2.713893702139	0.745587599453	5.298593769150
H	1.138618238816	1.069332630913	4.575610478228
H	1.322885833116	1.082555142790	6.340423600785
C	2.182622014026	-1.448314929852	6.696601402783
H	3.251763091182	-1.371191778767	6.455248130022
H	2.006592830449	-0.835326671357	7.589588784190
H	1.971757766811	-2.487671444648	6.963229847008
H	-0.683735911389	-0.830856979879	6.519491652476
H	-0.819242363798	0.343805518729	4.280603146483
H	-1.693779290020	-1.178038893627	4.064440669986
H	-0.010316076161	-2.018545303898	2.652451051624
H	3.668340626960	-1.391726730059	4.134907066895
H	3.062256027062	-2.571979556268	2.931281547660
O	3.374772427429	0.849516142943	2.669085590068
C	-1.069155455650	0.298964067291	1.251543026645
H	-1.569515177802	-0.420808026126	1.892233881048
O	1.829785509406	0.251650216329	-5.522485097250
P	0.340591087095	0.364830363068	-5.629361766820
N	-0.333181353932	-1.182495552346	-5.685915883283
N	-0.550209552478	1.083339348720	-4.420734691491
N	-0.056716517181	1.288469346701	-6.971819296502
C	-1.774294251986	-1.344449332627	-5.816034582111
C	0.423750052552	-2.155733062548	-6.462940718759
C	-0.692050419606	2.529437060300	-4.328805125421
C	-0.784645400495	0.395567742351	-3.153955560546
C	-1.425874470783	1.614084631211	-7.330589386820
C	0.915232995632	1.522626940322	-8.025960412532
H	-2.118852195964	-1.226904531256	-6.857023949837
H	-2.050833774043	-2.352913858865	-5.480661317574
H	-2.297842477740	-0.619795055773	-5.185451394784
H	1.482295223184	-2.099457622330	-6.195924274171
H	0.051531709658	-3.161565519316	-6.232769390021
H	0.316666433468	-1.996811081693	-7.550682449735
H	-1.744189257686	2.787864718612	-4.142398696646
H	-0.090441162142	2.926372115970	-3.498743907303
H	-0.369923150593	3.009304758684	-5.256688450610
H	-1.828145744644	0.543187404487	-2.836449797259
H	-0.576349290710	-0.670338726004	-3.258010703202
H	-0.126834661768	0.784387657522	-2.362642803144
H	-1.495412125513	2.676183195185	-7.609043205360
H	-1.773530870690	1.015222491967	-8.186616048802
H	-2.097445688419	1.439410903736	-6.485049702935
H	0.890376224131	2.580054664803	-8.325787676827
H	1.916056798926	1.284394078227	-7.659501009966

H	0.701686675047	0.908922580651	-8.914873991159
Li	1.964734299309	0.002126649473	-0.542841074493
O	1.142626531656	-1.374590842671	-1.507952109841
P	2.011156812643	-2.535099089942	-1.930413315423
N	1.335850682294	-3.234570443696	-3.303571059459
N	3.576295229419	-2.244378415032	-2.388998786106
N	2.131255638429	-3.604024335912	-0.657393709667
C	2.042246467872	-4.298026989149	-4.009105839135
C	-0.098696447657	-3.489048389765	-3.205418282907
C	4.647973295152	-2.108533212008	-1.407753836331
C	3.838010590217	-1.520141604969	-3.632921344732
C	2.875827403001	-4.847154264718	-0.758424285515
C	1.250167637669	-3.504731052991	0.493276301797
H	1.917711427207	-5.277439329072	-3.518985472853
H	1.636541796968	-4.376123714052	-5.025015993631
H	3.108839538371	-4.068941057539	-4.080645973856
H	-0.591521905780	-2.662422291763	-2.687453687045
H	-0.519678217755	-3.570042216616	-4.214224015756
H	-0.308253515629	-4.427345267839	-2.663024040232
H	5.564880506501	-2.554227754228	-1.817034321007
H	4.830621066400	-1.047938973546	-1.183728251036
H	4.382606162965	-2.614974305336	-0.477356557383
H	4.616377181408	-2.040943296168	-4.209022757027
H	2.933380398097	-1.428966856945	-4.241741780535
H	4.187676210899	-0.504686696101	-3.401956506964
H	3.463662124102	-5.001381373583	0.157998348290
H	2.207468855318	-5.712536428233	-0.886371061090
H	3.570645584710	-4.810382167035	-1.603305702401
H	1.836624001487	-3.622813475010	1.415926436734
H	0.766892881513	-2.524017077910	0.503397468122
H	0.476860693209	-4.289030816076	0.473392792706
C	-1.899408863782	1.021774222532	0.300188686987
C	-1.518726986445	2.248150089464	-0.289080497224
C	-3.178358462924	0.525404628346	-0.030062983246
C	-2.370278210153	2.925545340390	-1.154408928907
H	-0.543228098256	2.660941614319	-0.047774161166
C	-4.022905843178	1.203501907172	-0.902751161949
H	-3.506276076878	-0.415826967762	0.410970617232
C	-3.627300044500	2.411613703659	-1.477072390661
H	-2.047221289078	3.874665587706	-1.581173523666
H	-5.000770071187	0.783967240237	-1.135135098484
H	-4.287864579320	2.945113870665	-2.157636739819
O	3.283873931006	0.962694422255	-1.551901108508
C	3.950011815367	1.908262931675	-0.703129740369

C	2.714846011260	1.726148147392	-2.622080343975
C	3.084762192094	3.179224574999	-0.735531352883
H	4.036854739242	1.457294048374	0.289755424249
H	4.954115630132	2.090930548664	-1.112328470029
C	2.122594355282	2.945352945337	-1.920860471086
H	3.517336737940	2.011766365772	-3.320125403047
H	2.003435629044	1.088929819910	-3.158805370401
H	3.706874610440	4.068486457723	-0.880440197964
H	2.526132720360	3.288373336578	0.197703286724
H	2.046349635455	3.808173636798	-2.590604521185
H	1.122749990071	2.701946339588	-1.543545345443

Table S41. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *exo* sulfonyl oxygen with an equatorial THF (lower energy conformer).



G = -3256.189237

G_{SP} = -3257.638597

117

31020m_eq2: optimized structure // E(RM062X) = -3258.60808109 A.U. after 14 cycles

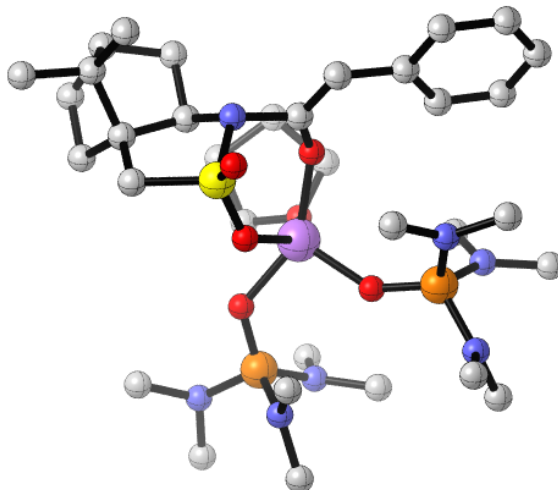
O	0.057349491243	0.167563034043	-0.016678703368
C	0.053639915770	0.050078327895	1.236336632894
N	1.380983386797	0.067841245735	1.830585920846
S	2.503132473659	-0.812942581981	0.925518183143
O	2.047882079044	-2.190356076395	0.669167695655
C	3.784633976072	-0.852732806190	2.205674241295
C	3.201969894821	-0.142034788854	3.410960021347
C	1.654293413514	-0.065757193025	3.260518049716
C	1.278682516963	1.171670483123	4.114305968692
C	2.615940760969	1.532553282818	4.789225292552
C	2.978001394734	0.375755721666	5.751007407630
C	3.439441635905	-0.765133054342	4.796400387051
H	2.860160112983	-1.687007562809	4.917125827582
H	4.495188051625	-1.018325143290	4.939519042789
H	2.113313029258	0.082884285582	6.357348012486
H	3.776185332258	0.662674324837	6.443531658432
C	3.632274477819	1.341743738658	3.636865455259
C	3.431004921016	2.273272309888	2.440180005077
H	4.115935480543	1.999356758514	1.625160356807

H	2.419398471383	2.257959405622	2.035190482544
H	3.671526993504	3.303009582781	2.737403233483
C	5.096389775157	1.480713679528	4.062859059107
H	5.761891111906	1.142379343676	3.256415766894
H	5.324068243605	2.537984347800	4.249284205541
H	5.354399844119	0.923225807278	4.967314430329
H	2.619144880530	2.521411823092	5.260568640169
H	0.902852431747	1.978697490325	3.476286591953
H	0.499305466973	0.935780540162	4.846567807077
H	1.187954662503	-0.984371954163	3.646272710554
H	4.676567157682	-0.373117424785	1.790027844371
H	3.978242798530	-1.915742132949	2.378007830166
O	2.923181702790	-0.021659812051	-0.247330596706
C	-1.019730146513	-0.072388456245	2.102837188528
H	-0.822561572700	-0.178000342373	3.165420824137
O	2.885131183711	1.204012571576	-2.754198177600
P	2.826002699833	2.104507632979	-3.954669252706
N	4.084684156676	1.683689598660	-4.991076501141
N	1.512569726385	2.115811935252	-4.980448805630
N	2.921096911120	3.713798118788	-3.472743164374
C	4.362295256915	2.515361642657	-6.151962341936
C	5.264112399998	1.026658492314	-4.447298976424
C	0.234302728874	2.635473726026	-4.499696222305
C	1.330366444633	1.044042828481	-5.955114217502
C	2.674876423162	4.830192499368	-4.373666194742
C	3.912366578207	4.018610023552	-2.449313550438
H	5.067528332603	3.329516280840	-5.917383906625
H	4.806953444968	1.897815987786	-6.944021990812
H	3.436055912630	2.951720279595	-6.538897047084
H	4.983411440680	0.425788228990	-3.579260798744
H	5.696813780849	0.367292558637	-5.212307568185
H	6.037038991606	1.752789547110	-4.145187531806
H	-0.328905931859	3.022179293214	-5.359919537477
H	-0.342696983918	1.840545602945	-4.005669444371
H	0.397423614193	3.440525990106	-3.780486978769
H	0.692161987084	1.423543798237	-6.764029386198
H	2.289694132473	0.744305553708	-6.382894603967
H	0.844396392667	0.167044958938	-5.503209733310
H	2.220301378266	5.656023806823	-3.808238256744
H	3.606450092174	5.203529526495	-4.828388226125
H	1.987948153108	4.538402706987	-5.171536044940
H	3.563484014000	4.860565784291	-1.836464073518
H	4.057075079611	3.151043838493	-1.799883071285
H	4.881460912376	4.299595018570	-2.895474777895

Li	1.333350126947	0.624741256521	-1.559964259782
O	0.382924225659	-0.410818333306	-2.930534557344
P	0.779802455565	-1.817198241410	-3.298686447843
N	-0.006563725619	-2.217018894518	-4.738582224069
N	2.368356614865	-2.177934494264	-3.651960977006
N	0.438540974719	-2.873785096131	-2.060662215257
C	0.044967578429	-3.612507139236	-5.154235258010
C	-1.307333624341	-1.600184120741	-4.972286898975
C	3.340181012217	-2.097909038758	-2.559763007058
C	2.951536413553	-1.817703573288	-4.938945405671
C	1.019518676883	-4.194047300691	-1.902252921310
C	-0.642699097451	-2.585512646378	-1.129045838585
H	-0.654464033511	-4.243051220849	-4.579807448377
H	-0.222997393460	-3.680755017884	-6.215926695433
H	1.058323376518	-4.008425311325	-5.031217964848
H	-1.277764486810	-0.551362746446	-4.667159969579
H	-1.538297729632	-1.654579761742	-6.043788065293
H	-2.114947417313	-2.109139567190	-4.419101969095
H	4.167216799298	-2.788239012008	-2.776729378151
H	3.720981043135	-1.072863265862	-2.451134421421
H	2.874471019765	-2.385434153545	-1.612664209547
H	3.792995968413	-2.494671969166	-5.139745081788
H	2.215050839137	-1.929882720997	-5.738469243365
H	3.326083085488	-0.783560264590	-4.936726434997
H	1.473698521198	-4.272777462585	-0.903182393196
H	0.247975104474	-4.973663279540	-1.995873945891
H	1.791451818479	-4.373102090817	-2.654950069233
H	-0.273946471973	-2.699508679915	-0.100803243042
H	-0.960697039597	-1.549623354613	-1.247138537290
H	-1.490765718688	-3.269601969492	-1.293417245175
C	-2.414456077769	-0.083435110720	1.709895618457
C	-2.869472855880	-0.022612336206	0.371355925405
C	-3.408693312613	-0.165620766506	2.712702575965
C	-4.228163446715	-0.038840552919	0.071035754514
H	-2.133220352283	0.039829633790	-0.424022092530
C	-4.762803084437	-0.183157950570	2.404313376850
H	-3.096678411092	-0.215332667840	3.755930654043
C	-5.190976152189	-0.118777079026	1.077048012065
H	-4.538808186001	0.009909584282	-0.972192856544
H	-5.493254197513	-0.246871654420	3.209746049149
H	-6.251165745550	-0.132198805518	0.833667680549
O	0.534529738575	2.460464953865	-1.570358986626
C	1.150497386754	3.383523647011	-0.683415962353
C	-0.877357640495	2.590032311537	-1.417379998030

C	0.285733076836	3.347358591638	0.572810193071
H	2.183469438890	3.056234749456	-0.529373013516
H	1.157484827134	4.386875273899	-1.143544299934
C	-1.124899129784	3.069079540491	0.023552045287
H	-1.246859363635	3.326270467914	-2.148561450235
H	-1.312516418056	1.611679858635	-1.636952760271
H	0.350918269651	4.276927541355	1.148708055542
H	0.601831513075	2.517607629654	1.211979542783
H	-1.747023335606	3.970896105803	0.028826349771
H	-1.630832225769	2.302569455251	0.617976879055

Table S42. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) chelated to the *endo* sulfonyl oxygen with an equatorial THF (lower energy conformer).



G = -3256.188042

G_{SP} = -3257.639825

117

31020m_eq1_endo_THF: optimized structure // E(RM062X) = -3258.60920805 A.U.
after 12 cycles

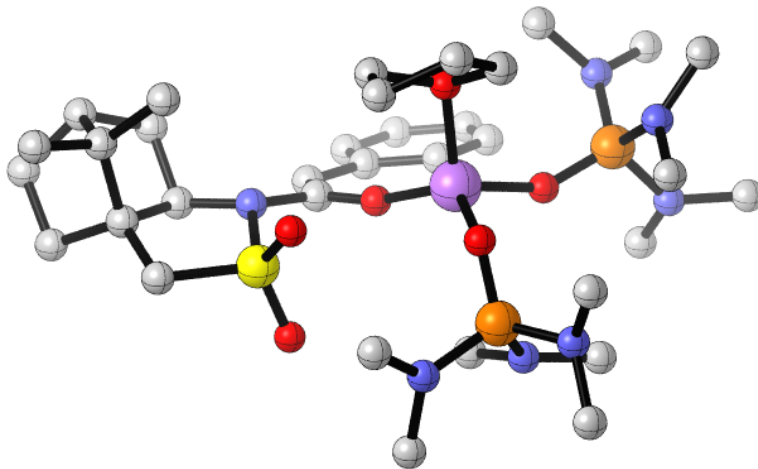
O	-0.085146950342	-0.480967654421	0.160817916067
C	-0.156169445837	-0.221525358162	1.394235978562
N	1.137215646751	0.017938385875	2.090157987439
S	1.705688313669	1.590480601869	1.819032712249
O	1.575664424332	1.948924476850	0.389913870347
C	3.450282051562	1.233553034877	2.155435497892
C	3.542970583427	-0.278852018517	2.242190573872
C	2.223763277496	-0.899051202686	1.708779334770
C	2.170491513584	-2.279714290695	2.404928826680
C	3.529193744533	-2.342465321945	3.132293537682
C	4.627406694634	-2.422490792732	2.046546061033
C	4.663288291206	-0.981741897804	1.456354911110
H	4.459504568942	-0.952217061201	0.379113405906
H	5.630823059123	-0.495548449293	1.620865990117
H	4.380348538906	-3.176186247217	1.289516176478
H	5.596164468463	-2.700919951848	2.474814709536
C	3.688822702788	-0.899199470209	3.668078497936
C	2.623782936136	-0.482750985348	4.684888617965
H	2.689934080243	0.595050305120	4.891278784797
H	1.601532935638	-0.691358649631	4.366622773961

H	2.808612762562	-1.005537000169	5.632834406918
C	5.050396801801	-0.607838788478	4.303970666942
H	5.144568085483	0.465118999456	4.522119939171
H	5.133995252654	-1.142012604354	5.259088172846
H	5.903770396628	-0.899224205276	3.685389065017
H	3.590093233433	-3.133904093094	3.887419508345
H	1.319718287332	-2.333275094526	3.092838244191
H	2.066841527287	-3.096017063617	1.682685908248
H	2.249185846245	-0.992410294209	0.613170862584
H	3.720111450430	1.751825027108	3.081229621125
H	3.997609825152	1.664404226116	1.311483886650
O	1.116741853141	2.519568188790	2.790548950815
C	-1.254592445842	-0.119373291736	2.211283876992
H	-1.077097186421	0.106069868598	3.259523312757
O	-0.484822338199	1.633704624958	-2.206438212534
P	-1.923729140613	2.073319677781	-2.277201965705
N	-2.468879734887	2.440570497499	-0.750715687695
N	-2.304672673459	3.423521036818	-3.194403073509
N	-2.845324456442	0.898607916093	-3.019749549472
C	-3.866227308802	2.713320122660	-0.483510575745
C	-1.558741131468	2.855143747498	0.303557147512
C	-2.395353719695	3.408380041046	-4.645444846886
C	-2.239255521394	4.765670032705	-2.636639018835
C	-4.202196727350	1.085597064366	-3.504535718716
C	-2.355705528670	-0.466478318077	-3.118965300296
H	-4.117579607266	2.323162624610	0.513130572394
H	-4.089564543043	3.793920053970	-0.502826136399
H	-4.512012322696	2.207580326119	-1.206821527836
H	-0.534937086728	2.582360428269	0.040364029912
H	-1.614628566522	3.944260197642	0.475253306752
H	-1.828061810482	2.343882342262	1.237265261730
H	-3.320817405087	3.910379322612	-4.964274440264
H	-1.546202368799	3.938318909929	-5.103307337336
H	-2.410399794093	2.381814516504	-5.020796565039
H	-3.166433093636	5.311789415552	-2.862942458724
H	-2.113240294363	4.729036319985	-1.551793193977
H	-1.397149364171	5.329984679079	-3.063970623798
H	-4.274764939623	0.742563106510	-4.547400089239
H	-4.921246361072	0.507865889189	-2.904206281795
H	-4.484128472581	2.141140235612	-3.467561269766
H	-2.448856474954	-0.815374231372	-4.158798832298
H	-1.301735744606	-0.500106413887	-2.832825106090
H	-2.932075825774	-1.150907262213	-2.477635336209
O	2.402414156359	0.931022754888	-2.217966498693

P	2.488012405176	1.483375920359	-3.613132625061
N	4.026470322137	1.129624360796	-4.198873704746
N	1.533031983988	0.881425268031	-4.836780265300
N	2.171922131330	3.117884248598	-3.594971429945
C	4.422173777260	1.466879127133	-5.558537027393
C	5.127064014954	1.223273424769	-3.247596620844
C	0.221588604270	1.433998652817	-5.133665757886
C	1.722082975875	-0.468351161140	-5.348244932513
C	2.183954705470	3.929656370093	-4.797762097469
C	1.691770850180	3.795226144587	-2.400988463963
H	4.799966762243	2.499570345032	-5.636902508483
H	5.224755949873	0.787570308297	-5.874622697065
H	3.578910705231	1.344478642535	-6.244315806824
H	4.790347370750	0.895167729637	-2.261587545198
H	5.943586569324	0.569546505943	-3.579371442211
H	5.517188674654	2.251557598646	-3.170513284669
H	0.129992664081	1.612322061186	-6.216208088572
H	-0.572504704665	0.742639081971	-4.817576877473
H	0.077820685469	2.369341248224	-4.591949188846
H	1.582966465409	-0.468280511660	-6.438767544414
H	2.732728264651	-0.821086346338	-5.126457024755
H	0.995561399465	-1.160278166823	-4.896987867765
H	1.204500988003	4.412326925739	-4.943559801983
H	2.946373853786	4.719584098128	-4.731573373903
H	2.392247428815	3.318282924170	-5.680897860904
H	0.651175069076	4.127210498061	-2.542098527791
H	1.719901372866	3.113348953278	-1.548319199052
H	2.320787734543	4.673732220805	-2.194011418691
Li	0.763905256199	0.436956787703	-1.309597604712
C	-2.634091000985	-0.220090544177	1.763998981717
C	-3.010444429374	-0.521894837741	0.435192804880
C	-3.676849866048	0.005305789170	2.689083855640
C	-4.350966123905	-0.605736723783	0.072513046154
H	-2.227305420601	-0.673467589676	-0.302095527996
C	-5.014149967564	-0.075752385921	2.317842025805
H	-3.419455898306	0.247368629268	3.720089940962
C	-5.366297722374	-0.386663503726	1.003714154481
H	-4.608294190703	-0.843718488380	-0.960192777841
H	-5.788678772729	0.103846968547	3.062073416073
H	-6.412228674579	-0.454981365968	0.711537168537
O	0.860638239538	-1.505203010898	-2.292922065249
C	-0.005272993230	-2.552749093933	-1.860021070711
C	2.132166533415	-2.126684916644	-2.473877155620
C	0.818367956590	-3.354688510423	-0.855284202960

H	-0.890177900352	-2.100328976640	-1.412172681938
H	-0.291477235798	-3.163081862925	-2.733550960417
C	2.274433956485	-3.122868654863	-1.312356348676
H	2.133787801315	-2.662515121890	-3.436240387413
H	2.885332766511	-1.335637449515	-2.495668426400
H	0.536520549868	-4.412569129231	-0.844238590881
H	0.649700009738	-2.935001449828	0.140953564831
H	2.762625218197	-4.044719127116	-1.645766221058
H	2.882615641503	-2.702555607916	-0.502751705379

Table S43. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *syn* to the sultam ring (lowest energy conformer).



G = -3256.19651

G_{SP} = -3257.649507

117

31020m_pendant_front_eq2: optimized structure // E(RM062X) = -3258.61453810 A.U.
after 14 cycles

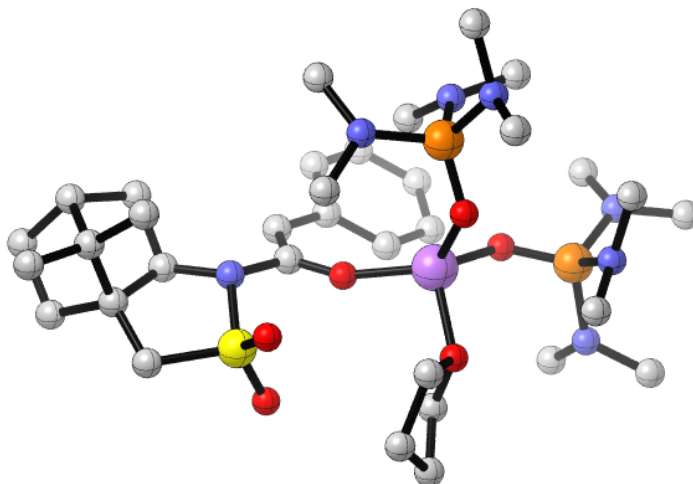
O	-0.146412676845	-0.273635843045	0.042921758196
C	-0.095681664977	-0.106024736584	1.291760606798
N	1.241488670747	-0.088468102247	1.832241650647
S	2.346359234850	-1.122350028517	1.048382453204
O	1.802850101033	-2.482236755205	0.894797513231
C	3.556646027590	-1.125874070800	2.400057906320
C	3.072597978241	-0.114408457327	3.413975488508
C	1.537084834824	0.037852632943	3.260126150714
C	1.264264238463	1.437333495423	3.872198235304
C	2.644978945525	1.846106386687	4.423359636828
C	2.974448393831	0.901887091692	5.600808649971
C	3.303436712682	-0.447449106059	4.898819567359
H	2.651598012153	-1.267952678620	5.218544924994
H	4.337002356526	-0.763040387544	5.076467353790
H	2.126186211955	0.815413970695	6.289350310468
H	3.827521983104	1.267554405410	6.182141452896
C	3.604780569821	1.351521637769	3.313071572963
C	3.410826122734	2.049403770673	1.964037923178
H	3.984364075759	1.540212502163	1.177898412396
H	2.371340656609	2.087835220166	1.634413016486

H	3.787836327198	3.078455166035	2.038402019393
C	5.090198959626	1.469731248295	3.664156084822
H	5.702975730688	0.986071248139	2.890959593862
H	5.378307914313	2.528481430350	3.691201461385
H	5.358906344042	1.029046744478	4.628203187780
H	2.721997857625	2.910944973570	4.669512029129
H	0.898389201894	2.127620358850	3.106066956877
H	0.507451450308	1.389728729606	4.662669830678
H	1.016197910896	-0.757295045676	3.813855517184
H	4.532242392397	-0.898309863331	1.958395807427
H	3.551270443675	-2.149077478251	2.789038024865
O	2.905553007092	-0.471905753138	-0.140666078805
C	-1.140494117226	0.082755521771	2.179792314556
H	-0.916311563194	0.165862855407	3.238491293017
O	-1.748628579672	-0.344786729240	-2.565564370996
P	-2.766169664423	0.244225447610	-3.500196931657
N	-3.542302319180	1.553457029447	-2.835320992327
N	-2.060295722323	0.731627464509	-4.927012141116
N	-3.925669980343	-0.889520753285	-3.881340104605
C	-4.922646896511	1.904470412904	-3.112169290002
C	-2.756873834416	2.595417694135	-2.188935402481
C	-1.171678797292	-0.201043180244	-5.604940898216
C	-2.523152552278	1.849609727605	-5.727631210493
C	-4.625483029811	-0.944298350209	-5.151108134448
C	-4.510257726449	-1.693171908948	-2.819216125222
H	-5.414660838848	2.205691655917	-2.176693606703
H	-4.999472587313	2.744281705422	-3.821332443348
H	-5.462691583550	1.046955338363	-3.524169673384
H	-1.754673109019	2.222272326272	-1.952831681373
H	-2.668616798850	3.486702412359	-2.831682660465
H	-3.246879909097	2.890778478645	-1.250756510241
H	-1.707046567381	-0.824896188185	-6.340561341265
H	-0.395272122279	0.365490779286	-6.136298539417
H	-0.681430269375	-0.844857974709	-4.866030518750
H	-3.072174944712	1.517151355339	-6.622909666577
H	-3.177260628163	2.496591370815	-5.136419664030
H	-1.660943414612	2.444219382221	-6.059901022355
H	-4.611036509598	-1.972694624732	-5.538771677595
H	-5.676821165009	-0.633363156683	-5.047695253007
H	-4.142116358597	-0.293936896073	-5.885080504393
H	-4.606215744665	-2.734981883603	-3.155840050113
H	-3.860977755152	-1.673938397046	-1.937815360411
H	-5.510811672644	-1.328098121784	-2.536464122326
Li	-0.034675018385	-0.075259426566	-1.791948190510

O	1.196520254843	-0.972584863414	-2.989728304256
P	1.111507123555	-2.471442294195	-3.140482653184
N	2.268563267974	-3.222066263142	-2.209814129444
N	-0.283302896948	-3.257617728682	-2.704978090210
N	1.279134990900	-2.843956888544	-4.774069052276
C	2.191227143813	-4.575388225629	-1.694093706863
C	3.588785007000	-2.622668189779	-2.121077184443
C	-1.400631824040	-3.445609485267	-3.621675540774
C	-0.693411484199	-3.180116376341	-1.300429601419
C	1.541458416558	-4.235367694358	-5.112780327148
C	1.950311766292	-1.892133534735	-5.648226817080
H	2.952250643391	-5.219084524378	-2.163035731796
H	2.362474672476	-4.557897481051	-0.607998328323
H	1.205493842974	-5.005462057358	-1.885989792692
H	3.526544883182	-1.554339840660	-2.339989466695
H	3.965288474287	-2.724998413468	-1.095703518938
H	4.297595926464	-3.113107857467	-2.809329954577
H	-1.926250106468	-4.369731599950	-3.343566467882
H	-2.103438572167	-2.603795319251	-3.565710519524
H	-1.042766360200	-3.544907508563	-4.649623948193
H	-1.111729120448	-4.149282702621	-0.992875141207
H	0.161384263998	-2.937841400100	-0.658457542178
H	-1.451412532818	-2.395050818976	-1.167416944730
H	1.237030688117	-4.421002041818	-6.150744150336
H	2.609947211874	-4.490102214445	-5.013947373095
H	0.962084457045	-4.901568781017	-4.464266007941
H	1.564748208136	-2.005093364003	-6.670457859932
H	1.753192591915	-0.874641245343	-5.302833749319
H	3.040922697799	-2.053522604604	-5.671533704532
C	-2.533845924073	0.238864833120	1.815780000445
C	-3.031293147147	0.213137240730	0.490685464899
C	-3.481098528727	0.451422677364	2.846995100828
C	-4.387816596439	0.405371415923	0.236247933132
H	-2.347760105710	0.046229565520	-0.338676371374
C	-4.831296672187	0.633719011313	2.580927154878
H	-3.132496601538	0.474789053850	3.879604403129
C	-5.303484483590	0.616043265288	1.266697503374
H	-4.727405284783	0.393021408775	-0.799221410060
H	-5.522257176259	0.794593719344	3.407531925841
H	-6.360317332352	0.762271959652	1.053186299677
O	0.475250038872	1.793069036855	-2.127271166060
C	0.769042442555	2.019916646508	-3.516396713308
C	1.622522541282	2.128835002654	-1.332986482790
C	2.273446119856	2.317397779201	-3.595282319999

H	0.494599054846	1.107265064866	-4.053636810814
H	0.154707485567	2.855997697945	-3.878554863071
C	2.797308058453	1.824354985522	-2.243065222124
H	1.577121951345	3.196028674068	-1.061747565866
H	1.585419275762	1.508004469492	-0.433759717853
H	2.446358276564	3.395559367842	-3.700924095904
H	2.744583571345	1.815509910709	-4.446722608258
H	3.719499686170	2.324682717303	-1.927608193614
H	2.951061390906	0.739685709909	-2.253088006941

Table S44. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *syn* to the sultam ring (higher energy conformer).



G = -3256.192892

G_{SP} = -3257.644618

117

31020m_pendant_front_eq1: optimized structure // E(RM062X) = -3258.61304949 A.U.
after 14 cycles

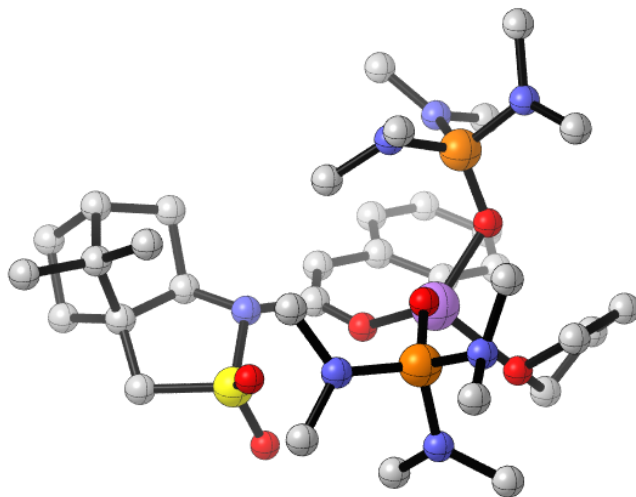
O	-0.065630824869	-0.086545773495	0.041851051144
C	-0.046966754525	-0.056382532020	1.307570893311
N	1.288336234438	-0.030030053041	1.880421413843
S	2.425491294376	-0.969056724620	1.012892265766
O	1.865758877392	-2.273039911948	0.621569793787
C	3.559844732180	-1.216787374379	2.406877003109
C	3.017840616917	-0.403827800843	3.559384635831
C	1.502345765245	-0.166987756388	3.326476203040
C	1.218313318070	1.105150375744	4.168305151961
C	2.557531070537	1.342616397447	4.894081742832
C	2.759576272961	0.175903278594	5.887138511064
C	3.118375211867	-1.024776139201	4.964532305331
H	2.427303392825	-1.868425216871	5.068237022812
H	4.128258257022	-1.402788416845	5.155944550226
H	1.851600642350	-0.007734133974	6.472736245097
H	3.565777320864	0.388009947895	6.597242731140
C	3.594770198882	1.028895290500	3.788079512659
C	3.526957548523	1.968580834568	2.584443324538
H	4.153066616420	1.594281568005	1.762760011628
H	2.518510045125	2.097189269788	2.190883941359

H	3.914491933635	2.954987624491	2.873593994223
C	5.047903105286	1.018912432257	4.268890273396
H	5.708720830912	0.646184468855	3.474062161125
H	5.365008872479	2.043724749349	4.500829459206
H	5.220442789012	0.409723126923	5.160445483509
H	2.641300026616	2.335989287980	5.348566922199
H	0.938989587364	1.942715071297	3.520669136315
H	0.397059416653	0.944702921380	4.875150133333
H	0.924124264803	-1.028105313449	3.691579928345
H	4.555313321883	-0.916085091592	2.064799963667
H	3.540451830170	-2.294019946943	2.599928132777
O	3.073494682023	-0.169610279111	-0.034536149084
C	-1.107879080860	-0.014714828186	2.193005691300
H	-0.908298395018	0.114668690623	3.251060238997
O	-2.537220783240	0.192987460941	-2.231335497920
P	-2.988456643665	0.042960282339	-3.660405565115
N	-4.516175534502	0.717362665526	-3.797471679097
N	-2.152932745909	0.757770263612	-4.906884473169
N	-2.946850967436	-1.584444424636	-4.081066029353
C	-5.260893661684	0.615808883842	-5.042677243507
C	-5.347090008288	0.918372631201	-2.619985265720
C	-0.820602036292	0.266063624161	-5.259222995448
C	-2.303295308971	2.184849170181	-5.175903910279
C	-3.194708962068	-2.033629388730	-5.444934437280
C	-3.456249113502	-2.510325530786	-3.075410206818
H	-5.951776687395	-0.242082698516	-5.036615458657
H	-5.853114585695	1.529502492770	-5.189689687165
H	-4.576923967390	0.512947053414	-5.890774828949
H	-4.716536571595	0.993750002501	-1.730637649446
H	-5.918540959351	1.850474216635	-2.733330831214
H	-6.064061920430	0.092382025918	-2.482257036840
H	-0.684304170821	0.362105973749	-6.345326677536
H	-0.054195992740	0.851778746828	-4.733006029129
H	-0.709017250470	-0.780013811950	-4.965086104376
H	-2.067561757716	2.362791101583	-6.233566567693
H	-3.331331396443	2.506856199728	-4.992200270909
H	-1.620376144514	2.782903022933	-4.555321956010
H	-2.652898990972	-2.973804811068	-5.613449812553
H	-4.264639536463	-2.218612961446	-5.631402312994
H	-2.833654581982	-1.293604430565	-6.163500104612
H	-3.042080122901	-3.508864465549	-3.264245411818
H	-3.144642457113	-2.185949409031	-2.078668213105
H	-4.556971903067	-2.586228004995	-3.105637702775
Li	-0.690280357366	0.311977035719	-1.697998217377

O	-0.118697793006	1.951963698515	-2.582857538167
P	-0.452673641584	3.235609009124	-1.863148608927
N	-0.360521772029	4.508274103707	-2.963711949436
N	-1.965505938575	3.437171429627	-1.203423370847
N	0.580148662474	3.441166473002	-0.574611111444
C	-0.449476024148	5.857238573236	-2.415536146171
C	0.665710305187	4.387196619786	-3.995151397751
C	-2.329457955269	2.584167688006	-0.067059026320
C	-3.109533086652	3.759107213379	-2.050657906447
C	0.289209175191	4.236812576173	0.604159470794
C	1.776788485993	2.614106275393	-0.465008758901
H	0.481441078049	6.157590981750	-1.905745059258
H	-0.638687224163	6.561865546190	-3.234235651309
H	-1.278958891549	5.925637808915	-1.704549537416
H	0.673758679060	3.368685421174	-4.391141473701
H	0.432002406564	5.084606611182	-4.808876514034
H	1.670694563189	4.628843780285	-3.609482125950
H	-2.858945999650	3.180531224850	0.689574677441
H	-2.970192779563	1.758800891218	-0.404070735011
H	-1.438102507550	2.141012594502	0.391515806808
H	-3.892573605797	4.201783590711	-1.421402564721
H	-2.827936355955	4.483151458842	-2.819440290546
H	-3.515032102085	2.857701220520	-2.533334565178
H	0.150498280133	3.587863109407	1.484448897421
H	1.121026431183	4.925250350257	0.811175830424
H	-0.622571761437	4.822516309934	0.461059475284
H	1.649845065919	1.841237933313	0.300190322667
H	1.971779337753	2.107451558817	-1.412096240064
H	2.639504247362	3.248031946089	-0.212159436192
C	-2.510944534861	-0.100231801127	1.821195368588
C	-2.964199329499	-0.696667721999	0.627070035863
C	-3.495596390346	0.395677882603	2.703188828386
C	-4.320302523634	-0.772491280953	0.332391300491
H	-2.237984105596	-1.085637004512	-0.080506879399
C	-4.850847539347	0.321514933323	2.402033376195
H	-3.178206533570	0.857476623189	3.638354768823
C	-5.278632952187	-0.261339732240	1.208145912432
H	-4.631183919427	-1.235256009765	-0.603212286257
H	-5.579429885596	0.723795466276	3.104630268911
H	-6.338559566482	-0.319934340813	0.968049013634
O	0.232228672129	-1.043362344314	-2.712395254436
C	0.067451293835	-2.372588885042	-2.206848261598
C	1.632135020994	-0.769633703061	-2.893774623943
C	1.231566078867	-3.141739451095	-2.808805997670

H	0.126955960266	-2.351068412226	-1.109868929577
H	-0.915967292143	-2.721219973501	-2.535185470342
C	2.358791908874	-2.109023503767	-2.718478666621
H	1.750447362583	-0.350545042486	-3.900984350936
H	1.954624797101	-0.034666382238	-2.148114831134
H	1.012869390711	-3.395664042521	-3.854567819581
H	1.451023297048	-4.065517220273	-2.263714298980
H	3.137599303083	-2.256866139730	-3.473923106533
H	2.818879348540	-2.148093673156	-1.726490923037

Table S45. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *syn* to the sultam ring (higher energy conformer).



G = -3256.190362

G_{SP} = -3257.643962

117

31020m_pendant_front_ax: optimized structure // E(RM062X) = -3258.61312043 A.U.
after 14 cycles

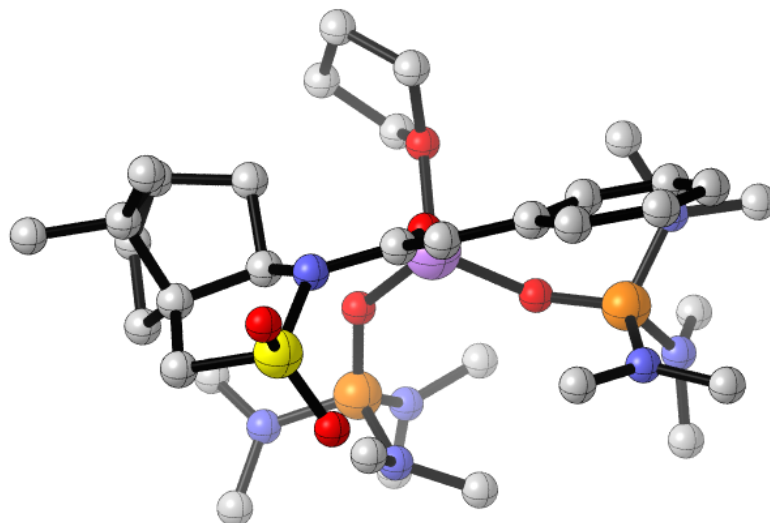
O	0.053639313729	-0.088624865763	0.014681680053
C	0.053890901308	-0.075912500586	1.278671911597
N	1.370710029471	-0.063622649450	1.879998804553
S	2.561394488454	-0.938490079169	1.030430381878
O	2.055907885854	-2.224590482568	0.530948853001
C	3.622751663516	-1.239886461551	2.470541563402
C	3.087559810995	-0.378314096014	3.589247972944
C	1.576199775553	-0.132864452800	3.329782832344
C	1.298106750448	1.184386325488	4.098986058201
C	2.620873690370	1.418352724569	4.852637596133
C	2.775412560697	0.278213267385	5.886305267274
C	3.162536026627	-0.951955304242	5.014706838074
H	2.476406566543	-1.797494964114	5.133894364453
H	4.172213946569	-1.312463815275	5.239325846628
H	1.841799558298	0.116876325576	6.437416627429
H	3.551430349400	0.504461015990	6.624911175800
C	3.679093841824	1.053204274809	3.782687262147
C	3.657221908140	1.947552094657	2.542011078173
H	4.449466719039	1.644481742442	1.845091317492
H	2.715543288172	1.910853822820	1.992293387423
H	3.854484011668	2.987143938004	2.839119912242

C	5.117903762235	1.047994997889	4.304480216739
H	5.784603843809	0.558669843797	3.581127129407
H	5.467953558727	2.081831086231	4.420846919089
H	5.242099286750	0.547590674958	5.268873297194
H	2.714416007147	2.423261378079	5.279020982467
H	1.071960553607	1.995335488096	3.398238793613
H	0.447755016175	1.085220134565	4.782440796589
H	0.990684612427	-0.970367380283	3.734636014485
H	4.649505708569	-1.013450667900	2.165348250496
H	3.522099942054	-2.309853358558	2.679759170043
O	3.247934661585	-0.062239230497	0.070212293522
C	-1.019333415170	-0.049496296957	2.152768036495
H	-0.820434691613	-0.025848776684	3.218518124875
O	-1.591877055127	2.275779258396	-1.473939646638
P	-1.551990014655	3.539352580374	-0.651923003814
N	-2.458794119616	3.417008802614	0.732232412548
N	-0.056694108710	4.036463140991	-0.093324549361
N	-2.180859609445	4.786065076127	-1.568022879359
C	-2.168999099887	4.037128588613	2.012452569728
C	-3.828176123339	2.943385678722	0.586689458396
C	0.780043787706	4.858542333777	-0.963171593304
C	0.707626576505	3.085661203807	0.714679646672
C	-2.529980808235	6.053496882926	-0.952078739559
C	-1.972223239578	4.837785558226	-3.005813492097
H	-2.927206193922	4.797950245452	2.255763677307
H	-2.178727220365	3.275850789533	2.806714751863
H	-1.187856294515	4.516465526290	1.992120602894
H	-3.939668002060	2.412541678315	-0.363213492881
H	-4.067652966186	2.241752145655	1.396152890854
H	-4.539784173446	3.784666697234	0.617844269378
H	1.557476225877	5.326879991989	-0.345706038025
H	1.260603030679	4.258219787048	-1.748197762483
H	0.188113464145	5.658652107838	-1.418359803004
H	1.376257123009	3.651143536708	1.378937162755
H	0.027331984383	2.488246129901	1.333356624967
H	1.304709929933	2.400448549421	0.091352259977
H	-1.721212890996	6.796761554340	-1.043075932986
H	-3.426035116678	6.460909544675	-1.438424720863
H	-2.754341156665	5.909788954138	0.109513176672
H	-1.207701955915	5.583349009191	-3.277937006864
H	-1.655577888833	3.854184511577	-3.363418789251
H	-2.910529177248	5.108671705725	-3.509162648325
Li	-0.165302712508	0.980342209465	-1.525467516061
O	1.257830989651	1.968811768747	-2.361703414142

P	2.328194530779	1.409905167977	-3.266573508090
N	3.797222666301	1.453643368872	-2.485165125443
N	2.220448693682	-0.150370412252	-3.814514520622
N	2.347655676414	2.312146564102	-4.689320340627
C	4.902239984565	0.544430219294	-2.715732954092
C	4.042916991570	2.445342234042	-1.450971635169
C	1.646679830406	-0.550943384452	-5.088466208249
C	2.196684815780	-1.211320898518	-2.811992991618
C	3.538122150466	2.188764481965	-5.520273753794
C	1.806257393661	3.664402034503	-4.652393344381
H	5.810434333058	1.102732569555	-2.989256946488
H	5.106311281228	-0.032750645731	-1.801161024238
H	4.665410774315	-0.151727218402	-3.524117973651
H	3.142162781994	3.041632282169	-1.283693752688
H	4.299259913410	1.944074315489	-0.508727653415
H	4.866425353413	3.114096324794	-1.745422151568
H	2.294666349505	-1.305929112273	-5.556673972218
H	0.651043264189	-0.991095313292	-4.933856386885
H	1.558025715801	0.305613569224	-5.759986138722
H	2.802556087692	-2.060712744073	-3.158722917137
H	2.597975666037	-0.849773741744	-1.861846786566
H	1.163465291639	-1.550404597839	-2.646516099454
H	3.301690380578	2.509714707167	-6.542381339802
H	4.370269225195	2.806560329686	-5.143014304374
H	3.870080869253	1.145543512774	-5.560273773233
H	1.552476696560	3.972222846015	-5.674807820694
H	0.900546307978	3.683820313734	-4.041258445209
H	2.527863988054	4.391788968400	-4.243388853804
C	-2.420495881749	-0.120146300960	1.794656705448
C	-2.911449881774	-0.303326412608	0.482651679890
C	-3.383746158911	-0.059771541727	2.830654938190
C	-4.274084042124	-0.456229377707	0.243384712684
H	-2.200715954265	-0.326228689244	-0.337176560971
C	-4.742703178547	-0.197409256973	2.581040223744
H	-3.040308060183	0.086052302143	3.855104269497
C	-5.205226138764	-0.405721221288	1.280347914565
H	-4.619214295400	-0.613731596651	-0.777946870006
H	-5.447408725424	-0.147991004801	3.410157571913
H	-6.267731339956	-0.525746420832	1.079751336730
O	-0.786005974503	0.066618784838	-3.201102902673
C	-1.167194254092	1.062902962067	-4.160023550976
C	-1.869354250041	-0.856715605146	-3.113493889212
C	-2.705149674597	1.138171252331	-4.126199968729
H	-0.671814666201	1.990076767638	-3.862042899732

H	-0.804913916532	0.754872171301	-5.151279140215
C	-3.106612564941	0.029891996237	-3.139005747001
H	-1.842205134711	-1.536519524421	-3.981329993153
H	-1.737597395141	-1.443696353994	-2.199021751863
H	-3.121391990181	0.958890287103	-5.123698285104
H	-3.048553821311	2.116049397256	-3.776348642015
H	-4.009126866757	-0.513563681695	-3.437637364625
H	-3.254319151999	0.468849490070	-2.147826510761

Table S46. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *anti* to the sultam ring (lowest energy conformer).



G = -3256.200219

G_{SP} = -3257.655054

117

31020m_pendant_back_eq2: optimized structure // E(RM062X) = -3258.62286238 A.U.
after 13 cycles

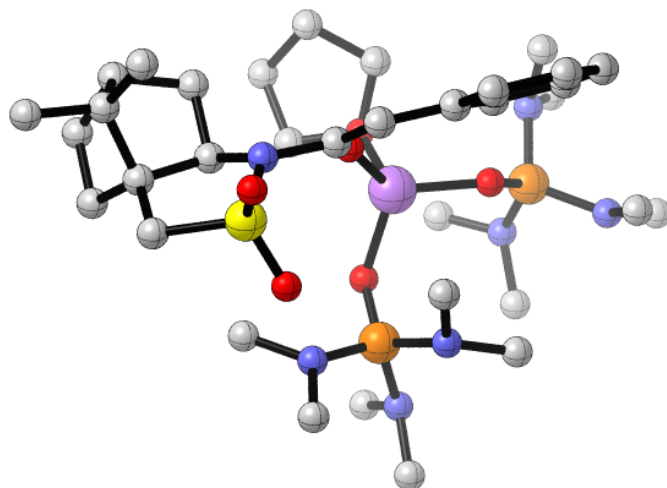
O	-0.505920404930	-0.448342189298	-0.169381739365
C	-0.628333678426	-0.254006281149	1.074392988774
N	0.629393965774	-0.113399450999	1.783616083486
S	0.833822171091	1.060930349215	2.979769686984
O	0.383270905627	2.388116064483	2.527488436049
C	2.648958411417	1.008453930735	2.969962818481
C	3.046658032449	-0.072388956186	1.985687296332
C	1.861795982836	-0.329380694976	1.021620899592
C	2.088703308209	-1.779056013924	0.540896225849
C	3.472156023303	-2.107868947379	1.132431904632
C	4.500448291402	-1.190048006808	0.427936248383
C	4.247712501831	0.207679069061	1.066707543213
H	3.997809262113	0.973025837649	0.321026212373
H	5.113281134295	0.561114897495	1.638435862825
H	4.331074888933	-1.178834323190	-0.655226791566
H	5.529355735873	-1.527022848028	0.595365985803
C	3.377686566273	-1.489157528328	2.550882296305
C	2.297013590448	-2.104370954514	3.443011526959
H	2.231135417141	-1.557735714199	4.393681730830

H	1.299889989044	-2.103038065305	2.998687495231
H	2.570494318795	-3.141384206864	3.680273429718
C	4.688329728548	-1.529804053153	3.339691813443
H	4.614732731837	-0.898250415462	4.236052589475
H	4.881489168663	-2.555136855756	3.680454836713
H	5.561648377432	-1.201886046466	2.768481629458
H	3.731881582183	-3.172505157993	1.102846263164
H	1.304353725217	-2.443982947440	0.918341305655
H	2.071532146244	-1.820374840238	-0.553290044863
H	1.899521588890	0.354273879127	0.168193123616
H	2.968995568286	0.823941923266	4.001043573863
H	2.961499440495	2.011475822307	2.661806907107
O	0.287308792178	0.581961544951	4.257239811172
C	-1.789639803100	-0.196419931704	1.818673051726
H	-1.697213720141	-0.080009778613	2.895960817974
O	-0.921956124378	0.903302518939	-2.840352355941
P	-2.293861390675	1.349317930618	-3.270004365494
N	-2.947720389455	2.340370630515	-2.106604970345
N	-2.419141208953	2.279627483961	-4.651567652642
N	-3.213022434990	0.010913646965	-3.660245400149
C	-4.280922026101	2.905825109584	-2.235341779535
C	-2.372679651738	2.450925777751	-0.769543159139
C	-2.227547943545	1.669849196799	-5.960708790706
C	-2.244628447233	3.724506539297	-4.660161463741
C	-4.479305911435	0.083477856786	-4.367774388527
C	-2.744275115881	-1.342261806046	-3.406878277407
H	-5.022015143721	2.316403590078	-1.672729391878
H	-4.282278543868	3.929497440305	-1.836565441331
H	-4.585640919124	2.952637184065	-3.285669913036
H	-1.552720292987	1.737180496750	-0.650696311365
H	-2.003149686889	3.473788476914	-0.596566637831
H	-3.136687762787	2.221075617947	-0.015256364216
H	-3.026187123057	1.986868895148	-6.646028240472
H	-1.262273087797	1.971552617588	-6.393668806668
H	-2.245261796371	0.579034005433	-5.884689485395
H	-2.991854284567	4.179166835711	-5.325625260583
H	-2.375270993276	4.134183410527	-3.655878498736
H	-1.244642976786	4.001802702473	-5.028264769449
H	-4.419180890030	-0.478307408828	-5.312679694751
H	-5.291775300459	-0.351548375274	-3.767516395168
H	-4.736839679738	1.119324676705	-4.602808251688
H	-2.626383618891	-1.884882866503	-4.359085904714
H	-1.776533367503	-1.316652440668	-2.902116389370
H	-3.465649316640	-1.892735148229	-2.785566735605

Li	0.275504008033	-0.126044152961	-1.813207773796
O	2.018029933016	0.555058021085	-2.200020409442
P	2.478468568725	1.968906894829	-2.462414323527
N	2.473560938402	2.272659072829	-4.100137656350
N	1.609539226262	3.171552564740	-1.694468922280
N	4.026873423761	2.189583355963	-1.894258095385
C	3.239595306100	3.367736032456	-4.670519818518
C	1.376425851824	1.794201425165	-4.932216435656
C	1.319763172252	2.946332044508	-0.278308932884
C	0.550544274570	3.874453501367	-2.414375436211
C	4.569970660521	3.433059939653	-1.375893579182
C	5.028835106891	1.199156054134	-2.258740054399
H	3.636441419722	3.060309032343	-5.646747025343
H	2.625991605470	4.270746215557	-4.819312590775
H	4.084560909308	3.621289407775	-4.023559763354
H	0.812987108048	1.022625732839	-4.400019103569
H	0.682573004427	2.613683484671	-5.183125184917
H	1.778810117292	1.380902696818	-5.867362221120
H	1.006295286419	3.891229858786	0.180022742589
H	0.523768194941	2.202494794038	-0.123525583959
H	2.223929277459	2.603106903147	0.240251564528
H	0.324811962092	4.801723708770	-1.873206023029
H	0.891668902146	4.145812515017	-3.417875900994
H	-0.364795887327	3.273204967159	-2.493750848417
H	5.077611025732	3.243083977616	-0.418892597370
H	5.305940254593	3.865799270102	-2.071326473761
H	3.767584284456	4.156128532904	-1.213856371058
H	5.663199792244	0.973200793319	-1.390245502822
H	4.541222727812	0.274042142130	-2.579561873980
H	5.672645783106	1.566093545806	-3.073790873090
C	-3.128800731073	-0.245249496570	1.271123882798
C	-3.428143009242	-0.459315743365	-0.096082239524
C	-4.230022099561	-0.041727664919	2.135623408706
C	-4.740310452785	-0.434064167805	-0.556559729926
H	-2.607352824945	-0.611756381648	-0.790818754424
C	-5.537702263289	-0.026290602000	1.667865335822
H	-4.037853019009	0.123189984432	3.195612966474
C	-5.810707116147	-0.217091525699	0.311684391725
H	-4.925087181056	-0.580722419423	-1.620745308141
H	-6.353821025004	0.141703702780	2.369456807870
H	-6.833838268960	-0.199162331451	-0.057906076852
O	0.458808496474	-1.908661110232	-2.554409097395
C	0.075485009514	-3.129460973205	-1.921027099481
C	1.400645228086	-2.231657314197	-3.571784323894

C	1.311511333354	-4.046959948987	-1.995310300383
H	-0.246013788192	-2.872298971398	-0.907693690685
H	-0.773338113562	-3.564875089246	-2.469778904673
C	2.283232404570	-3.298707833565	-2.932502576424
H	0.866234598029	-2.625826328764	-4.451221840041
H	1.923983802593	-1.308686459337	-3.835291378084
H	1.037631441766	-5.026835356118	-2.399407433542
H	1.753208069684	-4.208705848555	-1.006809582363
H	2.745662785554	-3.953901605582	-3.677371193913
H	3.084746328173	-2.818521462022	-2.359012208439

Table S47. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *anti* to the sultam ring (higher energy conformer).



G = -3256.193353

G_{SP} = -3257.647442

117

31020m_pendant_back_eq1: optimized structure // E(RM062X) = -3258.61560529 A.U.
after 14 cycles

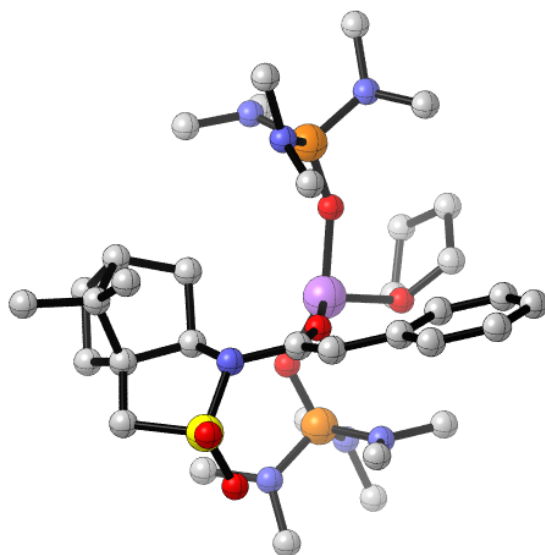
O	-0.133562398416	0.034692584536	0.078108625191
C	-0.088879501977	0.011447530633	1.341711478181
N	1.256632415812	0.022942593731	1.919023989008
S	1.653189842517	1.211360411969	3.045540020765
O	1.253492197823	2.552020261918	2.578008504921
C	3.450999145070	1.023437845636	2.886360327046
C	3.669386538280	-0.122590722922	1.921089881435
C	2.392735062749	-0.303651890479	1.058450806974
C	2.469783725663	-1.786915454703	0.623067609064
C	3.848199077571	-2.227138418650	1.152981954015
C	4.919384824869	-1.453994821143	0.349266749583
C	4.827160500850	-0.005905259585	0.914999971908
H	4.602840666693	0.739748087869	0.143465781728
H	5.754953392423	0.301768229344	1.408878520856
H	4.710615151793	-1.491732145583	-0.726728735405
H	5.918515595414	-1.876832386714	0.498764022771
C	3.902515604850	-1.540024416030	2.538191774829
C	2.834710427965	-2.024206943402	3.522760111292
H	2.835985280580	-1.402468578547	4.428221023699
H	1.818848964846	-2.010730312866	3.123234377079

H	3.072924430185	-3.051442140304	3.829942420131
C	5.251149617892	-1.664738090735	3.251538445263
H	5.265236754304	-1.034582994553	4.151594493612
H	5.398131519068	-2.701549927612	3.580215901596
H	6.111503700482	-1.388229524151	2.635708424700
H	3.994921102647	-3.312892881563	1.161715728413
H	1.647434207844	-2.363826243005	1.059106415317
H	2.406581267732	-1.885450561180	-0.463821754610
H	2.399569776827	0.365689640387	0.189819740721
H	3.843856106006	0.845425346095	3.893008600486
H	3.817526721536	1.985846316258	2.515524044279
O	1.196728846756	0.827685041484	4.388689724810
C	-1.102525992608	-0.058739642559	2.274106045794
H	-0.799700457271	-0.126472910815	3.316092908618
O	-2.385548686062	1.119591750434	-2.036557217420
P	-2.966487401990	1.199524000616	-3.425072208525
N	-4.356123282143	2.128933173509	-3.351621184977
N	-2.097765823925	1.903061196082	-4.657307863080
N	-3.243053242672	-0.347699743391	-4.010955932959
C	-5.201844050567	2.265041496924	-4.527724714652
C	-5.057432019426	2.313462841670	-2.088483136495
C	-0.870576470878	1.250487456282	-5.118243872502
C	-2.019070853242	3.359269327997	-4.751576412483
C	-3.590929416439	-0.611508204725	-5.400741362570
C	-3.865382500331	-1.281253977898	-3.080091413312
H	-6.001715534562	1.507807558012	-4.545289662644
H	-5.671199239130	3.257953245022	-4.525672235460
H	-4.605634491973	2.171670561028	-5.440998225563
H	-4.370571221469	2.149633727831	-1.254170357875
H	-5.446761297523	3.339719969487	-2.034283021611
H	-5.907490292738	1.618628757982	-1.995514247930
H	-0.710010327570	1.517505919392	-6.171333077229
H	-0.010848281790	1.573555093927	-4.513619969863
H	-0.958069685556	0.165272324519	-5.028973123342
H	-1.777730889016	3.622800186626	-5.789632742620
H	-2.978571902846	3.814129504053	-4.492633260561
H	-1.240195723560	3.766917791109	-4.092062519115
H	-3.197022772763	-1.596894073792	-5.685556794643
H	-4.681283113792	-0.623275529503	-5.555723600592
H	-3.149082060758	0.141348360474	-6.057916205388
H	-3.579173286305	-2.306773988119	-3.348034174911
H	-3.519604271016	-1.081658159198	-2.062446094244
H	-4.966027786227	-1.213098659946	-3.109454739536
Li	-0.546685674681	0.858999560289	-1.565541055439

O	0.477878551634	2.367742207079	-2.204243754454
P	0.359070340594	3.701576020547	-1.504027438671
N	0.434984460835	4.921989955570	-2.658199082537
N	-1.035027748087	4.057212132975	-0.671870195965
N	1.535620067931	3.820230894123	-0.331658295500
C	0.461912766873	6.311968381624	-2.219543908455
C	1.257892730944	4.677742649594	-3.836618026741
C	-1.339630212821	3.227558068222	0.501887578376
C	-2.233686725369	4.493428241290	-1.384266845569
C	1.609398184656	4.931089803426	0.605312480631
C	2.756103765523	3.041290845144	-0.431325160463
H	1.482824778754	6.647376794633	-1.976621216273
H	0.074180115696	6.948895832064	-3.025103093491
H	-0.172601040946	6.447742455955	-1.338522314513
H	1.164130255063	3.633125992281	-4.143854539494
H	0.907601540127	5.321292556002	-4.654064486781
H	2.321401627382	4.903998751144	-3.652004604797
H	-1.934987428368	3.822453886092	1.206641463519
H	-1.919046768425	2.335910895920	0.214248149198
H	-0.416371788408	2.916939369874	1.002321544177
H	-2.903999670532	4.973225831729	-0.659878978714
H	-1.981070063656	5.221689915546	-2.158959050596
H	-2.759877493055	3.645602898699	-1.842704274485
H	1.895957213855	4.541646048326	1.589185045700
H	2.348896283164	5.681736718373	0.285022602452
H	0.631736943807	5.411823127117	0.699352133653
H	2.999829054358	2.635896114152	0.559866155810
H	2.609877664686	2.211612689398	-1.128347660911
H	3.603338036588	3.656721806283	-0.775143069443
C	-2.528599918817	-0.067129271097	2.017356504824
C	-3.109309540664	-0.130788320025	0.731506718308
C	-3.416368146445	-0.030393559115	3.117945989131
C	-4.492267459871	-0.150268833557	0.571404606705
H	-2.469684892499	-0.147941186123	-0.144769660340
C	-4.794462261810	-0.051513791408	2.948646441466
H	-2.999742128264	0.018896666615	4.123735602155
C	-5.351059074084	-0.111458094462	1.669321710601
H	-4.905748824149	-0.198164486578	-0.435567029405
H	-5.441671566089	-0.019891017557	3.824087954402
H	-6.430333684463	-0.128328323956	1.533064566829
O	-0.003744177619	-0.515001522018	-2.819151396411
C	-0.639482604181	-1.791241934137	-2.655366243077
C	1.420952719692	-0.658427883597	-2.841918217101
C	0.481674916631	-2.784866488682	-2.379226240775

H	-1.358586895351	-1.714641854790	-1.832822308830
H	-1.178807841657	-2.022912446466	-3.584152292106
C	1.668805013930	-2.139322540309	-3.096332726679
H	1.817212673048	-0.000640154832	-3.622829913857
H	1.819076250652	-0.338130145089	-1.867673749839
H	0.245233131227	-3.787919174107	-2.747901102345
H	0.669891518999	-2.848059929457	-1.301860959718
H	1.625344862107	-2.350419989221	-4.172542187020
H	2.642342888038	-2.473191698503	-2.721115507825

Table S48. Atomic coordinates and single point energies of the **8o** mixed-solvate (2 HMPA, 1 THF) with the enolate oxygen *anti* to the sultam ring (higher energy conformer).



G = -3256.189873

G_{SP} = -3257.642465

117

31020m_pendant_back_ax: optimized structure // E(RM062X) = -3258.61170204 A.U.
after 13 cycles

O	-0.144550131073	-0.049356752471	0.044382261539
C	-0.073127592682	0.003452204181	1.300334141199
N	1.280266700805	0.027503263266	1.837251167403
S	1.751431616286	1.215378809770	2.930803452013
O	1.549890152633	2.570905610787	2.381797258190
C	3.519511196576	0.811881418242	2.861825492091
C	3.663706335377	-0.261995392411	1.799499033138
C	2.387391052604	-0.269789244999	0.919226433727
C	2.369520597532	-1.701606736865	0.333774191006
C	3.697330998597	-2.297312883217	0.844356214597
C	4.846205875383	-1.547833866632	0.134246618617
C	4.850357440491	-0.153711715664	0.826377717907
H	4.706851725855	0.669087791423	0.120732283825
H	5.786106477080	0.035150425800	1.363321801926
H	4.661149968107	-1.471370274690	-0.943799662822
H	5.805185795809	-2.060990962709	0.263940846146
C	3.772939782399	-1.743672736574	2.288892518902
C	2.652911496587	-2.234064895912	3.211080710593
H	2.642263395673	-1.655810134500	4.145934284185
H	1.653624277861	-2.166028084069	2.777783819877

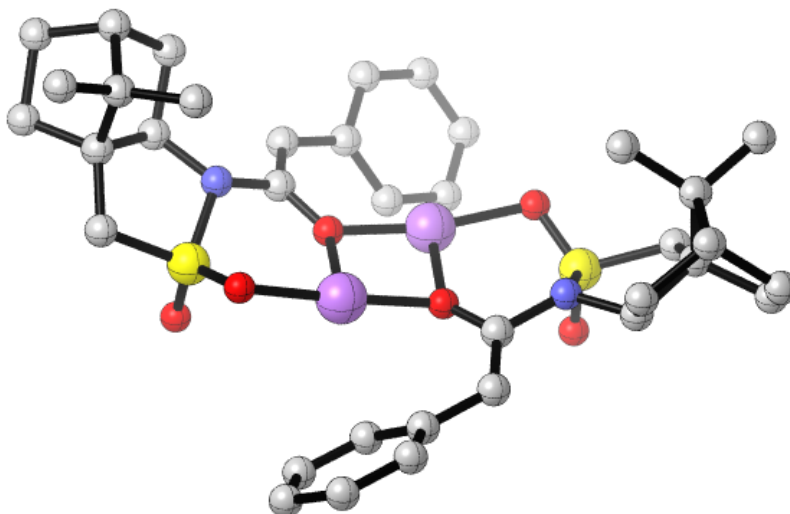
H	2.844602242862	-3.281882307706	3.479370355946
C	5.093371095169	-2.034956299606	3.007435004414
H	5.130726661885	-1.498455499764	3.965810317171
H	5.161400317856	-3.106845598201	3.233397981302
H	5.984358259463	-1.760045482429	2.436406783723
H	3.758745244083	-3.388370697882	0.762613207966
H	1.499403906616	-2.260629520379	0.686929770793
H	2.315920153387	-1.678358403869	-0.761058231714
H	2.421345877438	0.481458245973	0.119932435717
H	3.814901770546	0.491168813706	3.866552299438
H	4.023945918712	1.750312706723	2.610897673086
O	1.178806020870	0.949547731447	4.257271735306
C	-1.108810852840	-0.020604249421	2.213030142920
H	-0.855686549068	-0.018741596070	3.269814788290
O	-0.232851990466	-2.171604278555	-2.079149324809
P	-0.086339104080	-3.661849160611	-1.930285778178
N	-1.308061471981	-4.432409565499	-2.799521178020
N	1.292570290469	-4.372214627295	-2.538554955820
N	-0.111076193567	-4.100078883689	-0.319148755293
C	-1.239933882246	-5.841230341207	-3.171244120428
C	-2.662829183504	-4.017954398578	-2.440651853997
C	2.520446788064	-4.443151604769	-1.754439445508
C	1.537645252979	-4.236839350863	-3.972428894449
C	-0.122271665897	-5.515712903113	0.026871306263
C	-0.831638855373	-3.253794538016	0.630067065168
H	-1.650898309106	-6.494309425901	-2.385642661209
H	-1.831321199709	-5.993715318237	-4.083674411121
H	-0.208501632151	-6.139245738698	-3.371991541938
H	-2.668008876572	-2.968351061540	-2.131796037598
H	-3.323900644237	-4.127665245474	-3.309988486720
H	-3.068291055553	-4.631333290314	-1.619437002474
H	3.073519812431	-5.345689310948	-2.045487140705
H	3.164949858946	-3.568474897441	-1.931634839981
H	2.288555108696	-4.498220084690	-0.688637509016
H	2.100856287405	-5.110185441631	-4.325237660960
H	0.592511052883	-4.189175133595	-4.521123205144
H	2.122662527677	-3.331126000660	-4.193120652909
H	0.359335275242	-5.649692465982	1.004281876057
H	-1.147684466452	-5.912645408187	0.092457920965
H	0.436235671807	-6.098313958139	-0.713014769629
H	-0.343643531006	-3.319561987589	1.612252647854
H	-0.806832935496	-2.214779277783	0.290539482250
H	-1.878645745235	-3.578040964344	0.745455836545
Li	0.198046266205	-0.310939898389	-1.747881058865

O	1.492634906961	1.143984881717	-2.123293626111
P	0.987446298696	2.557142720254	-1.939354182553
N	0.987507109585	3.300764931742	-3.457975388971
N	-0.534935722396	2.889348436620	-1.383241801093
N	1.969122988740	3.342014475453	-0.840998666207
C	0.656842426614	4.719603097055	-3.528340081419
C	2.097394525727	2.961181376482	-4.342156807364
C	-0.854600964562	2.884418949858	0.041674981955
C	-1.717956613925	2.942599790966	-2.229630504732
C	1.660831951758	4.632858217059	-0.247544416603
C	3.324958392995	2.891160085621	-0.589741946612
H	1.507513673978	5.355645341012	-3.231191264860
H	0.387381863284	4.971629006976	-4.561874329639
H	-0.196640479602	4.952791567586	-2.885823571766
H	2.362034883187	1.908092442744	-4.226711066442
H	1.798065930933	3.142387997477	-5.382692841340
H	2.989781256039	3.574538031826	-4.129661314119
H	-1.307963347472	3.848458111418	0.319006409089
H	-1.566308349115	2.079595690054	0.262814067047
H	0.042463656387	2.725781558630	0.644734477296
H	-2.251139899030	3.888658670604	-2.050728722181
H	-1.445273406287	2.874908331413	-3.284612244113
H	-2.392860009342	2.109970415207	-1.988893480140
H	1.692034083503	4.550223932821	0.848214171340
H	2.393621416579	5.388900460720	-0.567555157772
H	0.664685023020	4.969901365484	-0.544323346404
H	3.467316847059	2.716640945859	0.487532978516
H	3.510757801935	1.961319179311	-1.131542758909
H	4.053072891018	3.648199589698	-0.920385893157
C	-2.512415454428	-0.078740891576	1.859191860976
C	-3.005380785688	-0.169402173896	0.533520149928
C	-3.479806795329	-0.063804663102	2.892164072941
C	-4.372494171308	-0.234207890275	0.275981011872
H	-2.295189729028	-0.190838688810	-0.287318861784
C	-4.840477662803	-0.131493415505	2.625549790501
H	-3.138391566949	0.004891961364	3.924746052924
C	-5.305853914998	-0.216449466890	1.311184012359
H	-4.712168565978	-0.300699693388	-0.757729206912
H	-5.548072799176	-0.115780469211	3.453399028692
H	-6.372023963666	-0.267813373240	1.101225532470
O	-0.995168949658	0.307628914733	-3.237185609563
C	-2.234264899146	-0.374143266479	-3.420004875874
C	-0.421326685671	0.448543626915	-4.533894556859
C	-2.021221338630	-1.343720421275	-4.596397918117

H	-2.476326541551	-0.870102761971	-2.475668079339
H	-3.014901474349	0.367746687008	-3.650399370940
C	-0.679573037719	-0.894370351416	-5.207165835939
H	-0.926547911485	1.271465864383	-5.067312969469
H	0.632199827798	0.697938456368	-4.401761478361
H	-2.845406477788	-1.268551463612	-5.313785655539
H	-1.954168190204	-2.378471678462	-4.251044274261
H	-0.708681132455	-0.810054827878	-6.298216050005
H	0.113782370892	-1.597920623649	-4.932954815959

Dimers of enolate 8o

Table S49. Atomic coordinates and single point energies of the symmetric dimer of **8o** with double *exo* chelation to the sulfonyl oxygens.



G = -2768.785257

G_{SP} = -2770.060970

92

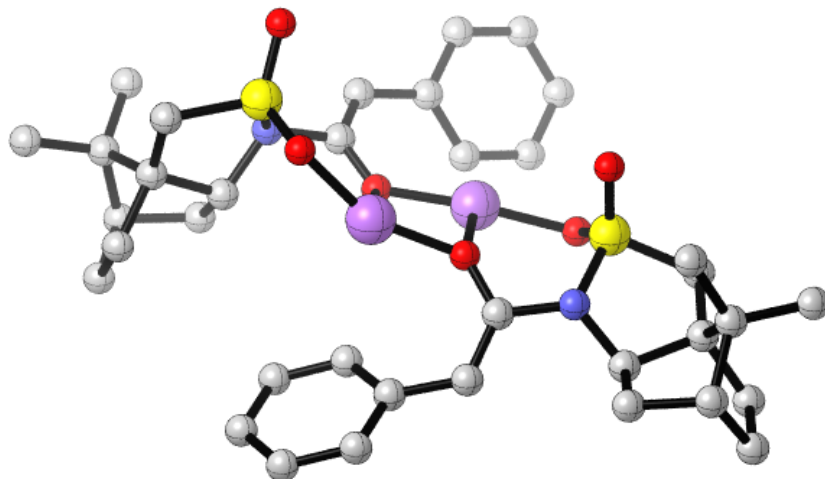
0000a_exo_ss: optimized structure // E(RM062X) = -2770.78454249 A.U. after 12 cycles

O	-0.264098502967	-0.634114407157	0.073147822925
C	-0.197472532855	-0.313629189181	1.326631027906
N	1.148259972306	-0.202779227440	1.803976440320
S	2.201236810205	-1.390936123050	1.216971139905
O	1.707132928012	-2.747784172063	1.462702712324
C	3.555733332025	-1.002576298278	2.348938563362
C	3.048520602040	0.111201005857	3.245949149220
C	1.496002734014	0.156850309569	3.177981587260
C	1.171807191426	1.620521596843	3.574781554509
C	2.553406210355	2.181234432197	3.963283043065
C	3.009596004638	1.451798961341	5.247496743988
C	3.388487035658	0.028123704582	4.743846737972
H	2.814833676808	-0.767306747441	5.232122137720
H	4.449409323114	-0.194133240100	4.898582912094
H	2.209989335665	1.427459176222	5.996264469163
H	3.866822123054	1.951839049747	5.709686109923
C	3.474879472621	1.569380273790	2.879954260096

C	3.162363666130	2.017877357220	1.449495341925
H	3.729887930411	1.420170226481	0.722556401087
H	2.109192649219	1.944091933803	1.174752859254
H	3.478215244136	3.061968932470	1.325849955354
C	4.967198248355	1.825335186146	3.107541518056
H	5.568569560597	1.254548221311	2.386681597236
H	5.187020510296	2.886892191162	2.938956646478
H	5.318503896643	1.571833674170	4.111318432186
H	2.577634025582	3.273488760993	4.038584740266
H	0.723343872477	2.159255885925	2.734900883653
H	0.463564122645	1.661129036714	4.409163723988
H	1.047473877174	-0.566503353795	3.875505253638
H	4.422769290819	-0.732774541562	1.737414052652
H	3.750090831213	-1.939445526746	2.880222664774
O	2.560053436603	-1.069291824195	-0.186635118830
C	-1.239788342834	-0.038772908444	2.158111367135
H	-1.041950791475	0.282506107104	3.176111649443
O	-0.424628894713	-0.783101387655	-2.601039009424
C	-0.338736488648	-0.664560585287	-3.888258630508
C	0.610250159688	-1.207864170725	-4.699156379617
H	0.604717593238	-0.975671044811	-5.759697568944
N	-1.350280242898	0.186365365911	-4.439440803837
S	-2.882584811326	-0.004965692053	-3.746396071209
C	-3.760801682090	0.977383817562	-4.983553887566
C	-2.717772595984	1.405628726192	-5.998991060274
C	-3.107107835519	1.346891409877	-7.485978564978
C	-1.954976885449	2.147998068328	-8.160446276891
C	-1.085787953206	2.607053456070	-6.967473356254
C	-0.327851086516	1.373072931451	-6.441190412020
H	0.396536200465	1.628496417048	-5.662231163236
H	0.214154898197	0.853964373551	-7.238815209936
C	-1.466690995204	0.492539056005	-5.864508245361
H	-1.593586519435	-0.439870182074	-6.435005355800
H	-0.434601383660	3.458415986218	-7.192003254541
C	-2.135860257683	2.848842615777	-5.855726900992
C	-1.545926577710	3.198621193487	-4.486544174770
H	-1.143768440123	4.219514415219	-4.521520430965
H	-2.326167516124	3.184834441239	-3.712715611648
H	-0.751301408208	2.528942078592	-4.154582047694
C	-3.161147549422	3.936824120343	-6.186482610517
H	-3.951787162549	3.963338301218	-5.424071301763
H	-2.671084929551	4.918321169608	-6.174358171106
H	-3.640774506202	3.820448657309	-7.162014882306
H	-2.341785539894	3.001411430615	-8.726624080705

H	-1.377266708022	1.533738886030	-8.860128335140
H	-3.170379070871	0.309902211943	-7.833612109239
H	-4.084979215336	1.808121356487	-7.658994500604
H	-4.516630499181	0.298671583842	-5.390779183323
H	-4.246527471848	1.804719085148	-4.456209979082
O	-2.899454424734	0.657059169540	-2.418316355414
O	-3.343118960020	-1.395024457638	-3.781117585127
Li	0.942947738157	-1.042592710160	-1.325898363767
Li	-1.558655985604	-0.164457317846	-1.218132815673
C	-2.633818910818	-0.036381789215	1.707765188031
C	-3.551805252921	0.867351664149	2.271951454813
C	-3.120005600439	-0.925818750731	0.729763964223
C	-4.876703492093	0.906004068103	1.854497031977
H	-3.208267663783	1.555289856115	3.043467448141
C	-4.444880896457	-0.876356040800	0.304132446890
H	-2.456341400481	-1.695285365607	0.336331023056
C	-5.330315070586	0.044336688443	0.856827367663
H	-5.560795760740	1.621683125024	2.306881969706
H	-4.784672175785	-1.571535891450	-0.461374816582
H	-6.364764213221	0.082920063237	0.523554792467
C	1.728205819122	-2.004613365228	-4.187731057212
C	2.980344105872	-1.947054439825	-4.825344064497
C	1.607540072896	-2.860923413397	-3.075916656669
C	4.064743835147	-2.677539417424	-4.354604208832
H	3.098497838311	-1.306825573970	-5.698647904467
C	2.698971836395	-3.581886146688	-2.598538046982
H	0.629980820856	-2.994480495325	-2.613456029152
C	3.936546250664	-3.489538414195	-3.228637457928
H	5.022398508880	-2.606281071694	-4.867098681177
H	2.573135179038	-4.226182023767	-1.730329997699
H	4.788757741205	-4.052354817272	-2.854982650570

Table S50. Atomic coordinates and single point energies of the symmetric dimer of **8o** with double *endo* chelation to the sulfonyl oxygens.



G = -2768.790104

G_{SP} = -2770.066419

92

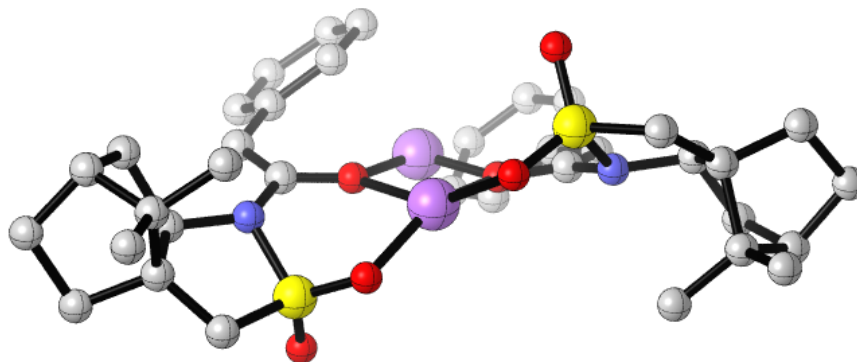
0000a_endo_rr: optimized structure // E(RM062X) = -2770.78005140 A.U. after 12 cycles

O	-0.023191049167	-0.001723053555	0.004416838505
C	-0.019328088181	-0.005659951156	1.302816157426
N	1.300487190555	0.009711066543	1.931157947946
S	2.160420204993	1.449001212688	1.711613696899
O	2.341433770939	1.724194380974	0.254889153865
C	3.728895175301	0.785799841883	2.310375705662
C	3.592976697961	-0.725606589817	2.164336691762
C	2.224848419137	-1.053657929121	1.499353361759
C	1.890575071574	-2.471982225750	2.003741787019
C	3.194096853075	-2.866147040483	2.726176366277
C	4.312378745142	-2.961271653602	1.658699154762
C	4.634914462291	-1.475100411249	1.320478836122
H	4.525491212251	-1.238960179756	0.255246912595
H	5.654252328020	-1.201184923060	1.612598894281
H	3.972639508402	-3.523933027671	0.780479971140
H	5.194459224250	-3.481863163165	2.045698893458
C	3.556586355911	-1.563073829180	3.482702506859
C	2.517039402135	-1.119887314830	4.514329554085
H	2.793334897890	-0.148032206235	4.946722041247

H	1.506417952400	-1.020907068002	4.115977348697
H	2.496969746756	-1.843373592034	5.339795693443
C	4.909286078629	-1.607994128745	4.197276518457
H	5.203327338517	-0.601170066784	4.525143920394
H	4.830774919893	-2.230701068517	5.097147859777
H	5.722264960996	-2.011615434610	3.587686470156
H	3.099947754654	-3.760227306422	3.351473965130
H	1.025914052294	-2.457253634647	2.675018309931
H	1.652503301227	-3.146951724451	1.174564285048
H	2.317192372222	-1.034079173572	0.404503767994
H	3.841657383947	1.123540870368	3.345561257356
H	4.502545928954	1.237023895176	1.682265609516
O	1.599834659973	2.523460491687	2.520382872662
C	-1.074261599654	-0.011870587099	2.151127903777
H	-0.865073437021	0.083702051863	3.213009046527
O	0.012701271710	0.995113609457	-2.499075714014
C	0.027756294614	0.793722185508	-3.776047750944
C	0.916678815080	0.030784245512	-4.476169236466
H	0.886647163106	0.037947812056	-5.560770169092
N	-1.009781008706	1.487849852187	-4.471077779901
S	-2.359791643453	1.906016266619	-3.530284772541
C	-3.527427681451	1.957525805119	-4.907976431218
C	-2.690116853886	1.932240504053	-6.168118737245
C	-3.286501082046	1.206521719469	-7.386753532072
C	-2.308188402022	1.617350869294	-8.525523909979
C	-1.329804624413	2.590043388035	-7.828288620681
C	-0.392943345196	1.751798226127	-6.937817978147
H	0.391939290405	2.356937801230	-6.473844321875
H	0.092982633719	0.946244798284	-7.498911866514
C	-1.360131812837	1.191204399750	-5.862253979564
H	-1.486594292833	0.103054598129	-5.960809187962
H	-0.800095311810	3.259063595517	-8.514589040963
C	-2.229810258724	3.293877749498	-6.783488725563
C	-1.474400113027	4.239763848205	-5.846008751978
H	-1.053065178079	5.062959949320	-6.438015673309
H	-2.155479581104	4.682214447632	-5.108367119200
H	-0.661032163931	3.769442561047	-5.289570168048
C	-3.383892801816	4.096294046274	-7.389975181828
H	-4.092414391066	4.402011062031	-6.608093607168
H	-2.991322122704	5.014785212626	-7.843683748894
H	-3.945494591113	3.562876880253	-8.161719219275
H	-2.838103853150	2.101591689884	-9.351929966991
H	-1.778469171896	0.755090411509	-8.946026203094
H	-3.323737983248	0.124334372420	-7.220625449560

H	-4.310164995372	1.542550961269	-7.582572698449
H	-4.151021380525	1.065123500995	-4.790011987153
H	-4.132988343163	2.859834456751	-4.774811558935
O	-2.190807505262	3.207968824529	-2.893488784901
O	-2.739551077032	0.783357844314	-2.625973810669
Li	1.247094186199	0.885687981765	-1.107942433772
Li	-1.348648739801	0.479915736754	-1.255185681263
C	-2.471318826162	-0.025716176080	1.707254517238
C	-3.450125248815	0.648545768156	2.455164987645
C	-2.887598607316	-0.705160646459	0.548335797697
C	-4.777457753309	0.672117750466	2.044309429907
H	-3.153225858587	1.171166083362	3.363008987171
C	-4.216853284799	-0.675693268286	0.135096604769
H	-2.163426078640	-1.305524761293	-0.003312149298
C	-5.167987127813	0.019934045575	0.875862259415
H	-5.513396714177	1.210965879243	2.637828022507
H	-4.508800613394	-1.206155606033	-0.768947347429
H	-6.205737405907	0.046780868760	0.551787461999
C	2.000444493486	-0.727865016985	-3.852740302937
C	3.196819741475	-0.937439212038	-4.564812275474
C	1.897625543407	-1.324974865441	-2.579155150111
C	4.240846955783	-1.683387115525	-4.032370170746
H	3.301430095941	-0.496750308764	-5.555277911812
C	2.944974622749	-2.079089589406	-2.053673680232
H	0.965350740149	-1.250353211955	-2.019501635828
C	4.126894686573	-2.257909296433	-2.767189426788
H	5.152521627660	-1.818738022079	-4.611269095807
H	2.822296263632	-2.557677970703	-1.082276209546
H	4.940061687868	-2.849155424753	-2.351543291870

Table S51. Atomic coordinates and single point energies of the spirocyclic dimer of **8o** with double *exo* chelation to the sulfonyl oxygens.



G = -2768.793992

G_{SP} = -2770.067830

92

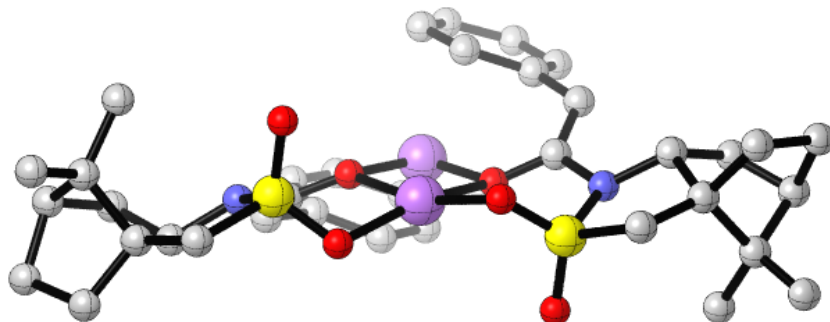
0000s_exo_ss: optimized structure // E(RM062X) = -2770.78610562 A.U. after 12 cycles

O	0.896680875330	-0.229924250933	0.447773541961
C	0.498740206482	-0.279214160558	1.675383043209
N	1.561692572662	-0.545896768456	2.585915871934
S	2.701709146299	-1.668268510841	2.018833179966
O	2.080863827121	-2.946889979785	1.663867476652
C	3.573442399263	-1.825030022129	3.597575647759
C	2.810793903501	-0.967830320540	4.591683369680
C	1.391781907162	-0.672774052860	4.030574794028
C	0.988093128466	0.634225876117	4.759481546210
C	2.152991294890	0.843944834767	5.746523064447
C	2.092067527352	-0.293934054344	6.790817730761
C	2.581699699575	-1.542531222228	5.999759366843
H	1.844532850900	-2.352779423370	5.977141399061
H	3.506312714737	-1.956733595334	6.414992032676
H	1.075895300115	-0.422005746364	7.180289839892
H	2.740215280822	-0.086487473274	7.648477433767
C	3.384835683804	0.454242226463	4.892921134637
C	3.626289852588	1.348866983924	3.673702455208
H	4.385281117713	0.907851768401	3.012569360297
H	2.739316236508	1.533033280945	3.066161106735

H	4.016856171883	2.317212045942	4.012578601402
C	4.700976727535	0.408673849236	5.674391018363
H	5.506045825672	0.004715732917	5.045256958944
H	4.995106415090	1.427313568446	5.956431111104
H	4.660834170485	-0.187610023659	6.589939505152
H	2.182404189902	1.847972838943	6.182731854788
H	0.888035144113	1.458993172493	4.048249678110
H	0.027166462367	0.525778632366	5.273257601614
H	0.699873980832	-1.499430021321	4.253793227575
H	4.607909329425	-1.508008641800	3.430310377698
H	3.542851686087	-2.894432049274	3.827738589729
O	3.558455757710	-1.031039427921	0.992698844017
C	-0.781248680617	-0.125588696994	2.121424859339
H	-1.022612072840	-0.344228974063	3.157623073766
O	1.445065625928	-0.197933937652	-2.118614872056
C	1.560067635492	-0.048743275570	-3.395789551334
C	0.580358270157	-0.229709646225	-4.328041631125
H	0.751861005556	0.075981976574	-5.355977439003
N	2.864920106593	0.377005558742	-3.785785364800
S	3.550080256459	1.537886803585	-2.752322153213
C	4.956950430330	1.905905249796	-3.828901158441
C	4.731785068789	1.115856506411	-5.106302023135
C	4.990087505845	1.829375704855	-6.443898411921
C	4.979235434206	0.645952320083	-7.455891782796
C	4.775557467946	-0.597402960545	-6.559594146603
C	3.308157137912	-0.595825862798	-6.088940463459
H	3.044451861614	-1.500297574717	-5.533421029898
H	2.607448941802	-0.508711097078	-6.925887943541
C	3.250095395609	0.649183669017	-5.168341853500
H	2.607331081357	1.439668519979	-5.585353181965
H	5.085713793912	-1.538446562441	-7.025908789791
C	5.538323980288	-0.212947842092	-5.268197098908
C	5.401146260295	-1.217393072865	-4.120640056715
H	5.991183307005	-2.112770697784	-4.355534235150
H	5.806992319583	-0.798867145969	-3.188949584953
H	4.376313580617	-1.528296436820	-3.913751084170
C	7.037115653884	0.025301856289	-5.471894727874
H	7.488708058985	0.432738575858	-4.556912219734
H	7.535786756510	-0.930035319028	-5.677556768237
H	7.276930004589	0.705024674639	-6.293970102059
H	5.919910758509	0.589910322338	-8.013177792925
H	4.174458485825	0.738911518442	-8.193715582975
H	4.214436938125	2.576091197052	-6.647074203257
H	5.951103583493	2.353999540373	-6.434326238741

H	4.924770754995	2.990489076936	-3.970294450297
H	5.863616654894	1.626677273848	-3.282398408437
O	3.989781933608	0.888966216624	-1.496570925578
O	2.697496081701	2.722775834798	-2.625054654840
Li	-0.102313014838	-0.278143485780	-1.105315483393
Li	2.558387419756	-0.157151434784	-0.533561887736
C	-0.761156987348	-0.685841972994	-3.961902288764
C	-1.886615313210	-0.195656470051	-4.648390960058
C	-0.996918994913	-1.616978412995	-2.927363351411
C	-3.174904527452	-0.582125059291	-4.295717392899
H	-1.739224583271	0.511680487864	-5.463319305498
C	-2.289657005556	-1.988235856831	-2.563833338385
H	-0.145284545775	-2.093772222875	-2.439531074475
C	-3.389249966014	-1.467429941006	-3.240918333163
H	-4.022846638001	-0.177691690659	-4.845697772571
H	-2.432986968428	-2.702193134668	-1.754295346012
H	-4.398503096433	-1.755633862267	-2.956423497529
C	-1.879324913149	0.189202436071	1.205191090074
C	-3.152310595436	-0.375281569467	1.399082548764
C	-1.723084785203	1.055936747561	0.101937861415
C	-4.198942177815	-0.119323499357	0.519543923941
H	-3.311053370968	-1.036604171553	2.249673907457
C	-2.767342907624	1.295645321417	-0.788444936415
H	-0.778256994141	1.587375905011	-0.024749939553
C	-4.011951428380	0.703003524079	-0.589740400327
H	-5.169940391411	-0.578249147380	0.697165183058
H	-2.607298344929	1.963710707741	-1.633349404413
H	-4.827210190831	0.888546587235	-1.285087410967

Table S52. Atomic coordinates and single point energies of the spirocyclic dimer of **8o** with double *endo* chelation to the sulfonyl oxygens.



G = -2768.785235

G_{SP} = -2770.059402

92

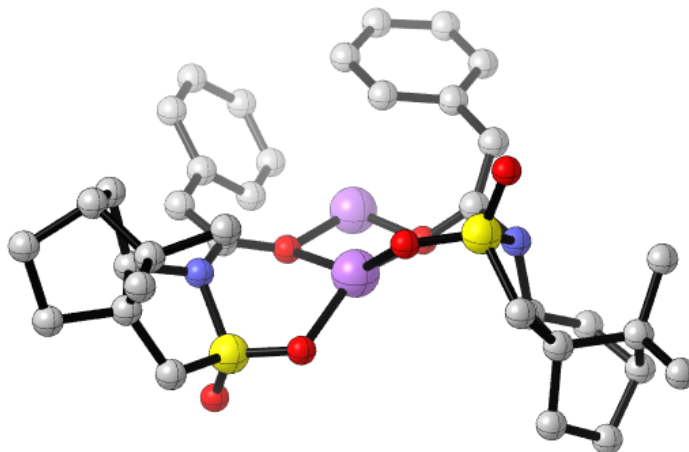
0000s_endo_rr: optimized structure // E(RM062X) = -2770.77920168 A.U. after 12 cycles

O	0.103666326244	0.099029044516	-0.016000686319
C	0.068820418418	0.086577433894	1.277539356808
N	1.352351717514	-0.034139589440	1.886064566750
S	2.599441844156	-0.610577692636	0.890345953316
O	2.140944861600	-1.751916461961	0.060938702315
C	3.617507543287	-1.244051689385	2.242008185130
C	3.047088045522	-0.654127298502	3.512996386212
C	1.531452320983	-0.383809549519	3.296364701349
C	1.228576664546	0.736335584848	4.327294690001
C	2.540404967828	0.819446235851	5.129157634975
C	2.711237279722	-0.513698086355	5.893382402051
C	3.125443200201	-1.520965210854	4.781413140317
H	2.454796208520	-2.384132500025	4.710676592300
H	4.139285342347	-1.906596368946	4.932535363350
H	1.780025851642	-0.807449936407	6.390976787411
H	3.479015091824	-0.438045796927	6.670044814303
C	3.607902774303	0.717127257630	4.013433842409
C	3.569223046455	1.871269958324	3.008017827450
H	4.333521034962	1.737059454946	2.232705357318

H	2.612128286420	1.990801315176	2.495851806150
H	3.795701299151	2.807797477733	3.534981342518
C	5.045824719519	0.623768634141	4.530529783090
H	5.730045400888	0.341950009534	3.718674812446
H	5.367860936363	1.607545684262	4.894152276031
H	5.183373142930	-0.089151821222	5.348096681274
H	2.611335555616	1.709626675910	5.763189377100
H	0.994220771026	1.676989021411	3.819956699345
H	0.375018957643	0.475569277073	4.962260843664
H	0.938660832276	-1.286940931795	3.502195315130
H	4.650874461398	-0.955923581688	2.023396193345
H	3.512617377569	-2.333067350733	2.191323574125
O	3.248173389049	0.483836806797	0.171029596466
C	-1.042078373680	0.220725299246	2.062487675315
H	-0.942145903192	0.339184221655	3.135928439716
O	-0.728272940733	-0.756830364227	-2.472352778652
C	-0.923125868959	-0.592747941538	-3.741069548634
C	-1.583163555941	0.446608960270	-4.334683172592
H	-1.813835890473	0.414234146689	-5.393945801335
N	-0.418196184001	-1.657918958922	-4.542810902327
S	0.730025500118	-2.667121351512	-3.806012315602
C	1.492397044854	-3.213537710422	-5.350309945701
C	0.547526064759	-2.800554463726	-6.457331163309
C	1.179436446359	-2.404774458262	-7.802896121263
C	-0.063554435234	-2.314701337261	-8.735347727434
C	-1.231664851639	-2.760721165536	-7.825898304504
C	-1.533063840625	-1.608641456720	-6.849857942891
H	-2.405203666146	-1.816090566464	-6.222569766022
H	-1.713128761946	-0.663497880480	-7.373333418166
C	-0.241343407682	-1.544394340221	-5.991615375629
H	0.328153533861	-0.625900202220	-6.195266373112
H	-2.112491749849	-3.114744767068	-8.372029063004
C	-0.567016006539	-3.805216964019	-6.897325461039
C	-1.485478957749	-4.324877443191	-5.787914088652
H	-2.333969238911	-4.849422809109	-6.247236568206
H	-0.957534727383	-5.046629226045	-5.152594791985
H	-1.880368191539	-3.548411750916	-5.129285518084
C	-0.013985082981	-5.030722175314	-7.629476464526
H	0.625212736426	-5.623374241630	-6.960975426546
H	-0.844545101613	-5.678540318225	-7.936443136191
H	0.565934889561	-4.794159595047	-8.525759202735
H	0.042238521386	-2.969151955591	-9.606498529384
H	-0.222456787641	-1.299027170467	-9.115092039682
H	1.724347972500	-1.458280581039	-7.718951266519

H	1.893085874868	-3.163684520076	-8.140819744263
H	2.454738705296	-2.692382314142	-5.392868164781
H	1.653572191169	-4.292714753761	-5.260536877187
O	0.083884810485	-3.762925917522	-3.086525108304
O	1.722389208943	-1.878857759757	-3.034917578951
Li	-1.346591051374	0.354839805311	-1.131970826144
Li	0.861636517593	-1.106100525295	-1.371177046845
C	-2.181438964849	1.520889291897	-3.531798748702
C	-1.467195878739	2.171850277967	-2.506556084491
C	-3.506853664101	1.933724610470	-3.751231932739
C	-2.073181236323	3.122036274857	-1.684818090037
H	-0.408591964339	1.940361338272	-2.370252440207
C	-4.102144755568	2.903591835143	-2.951835669938
H	-4.079770220626	1.462768307363	-4.548679617980
C	-3.399791853113	3.487322920139	-1.898666911245
H	-1.495929552023	3.587673776207	-0.887651029067
H	-5.134625778804	3.192563764929	-3.140324313090
H	-3.876528065590	4.226614024852	-1.259301341150
C	-2.369641406036	0.423001409811	1.467990074844
C	-3.214865990263	1.450091845640	1.921859374153
C	-2.847975917061	-0.385653869335	0.418070804794
C	-4.445693698014	1.690232259550	1.320660951827
H	-2.881737447479	2.081037206439	2.744587068632
C	-4.068237879395	-0.125852388484	-0.205444151919
H	-2.256854987310	-1.248489622442	0.103514052031
C	-4.871353821674	0.921506916809	0.238513132387
H	-5.071605104867	2.501487422089	1.688275480419
H	-4.394941332455	-0.758776537023	-1.028955666407
H	-5.822724169750	1.128490377303	-0.245909649769

Table S53. Atomic coordinates and single point energies of the spirocyclic heterochiral dimer of **8o** with double *exo* chelation to the sulfonyl oxygens.



G = -2768.770541

G_{SP} = -2770.062308

92

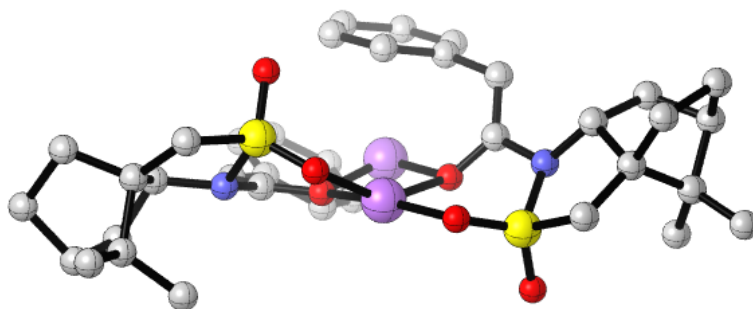
0000s_het_exo_ss: optimized structure // E(RM062X) = -2770.78069176 A.U. after 12 cycles

O	-0.089424808735	0.081854323354	-0.042352242937
C	-0.071984344119	0.047184226320	1.255010843969
N	1.254056825050	-0.032419527439	1.857574252967
S	1.808592377936	-1.635997252724	1.898484419876
O	1.376454727817	-2.315422659427	3.111206560600
C	3.577501665586	-1.227107411318	1.917479723886
C	3.654279474619	0.283533017399	1.792135920670
C	2.298185302942	0.806319714511	1.252544314588
C	2.262436095021	2.278043470078	1.725354421148
C	3.656326584226	2.458284648366	2.360380993061
C	4.696814471610	2.380766687407	1.219819350905
C	4.720156129531	0.868765989137	0.848977039047
H	5.702130633314	0.417097121947	1.026195105728
H	4.463205854405	0.679200756738	-0.199265464748
H	5.681814950527	2.726882325651	1.549549460237
H	4.406739887315	3.011029201614	0.371918227004
H	3.746609616623	3.354060037146	2.984109324858
H	2.095596280852	2.966355865879	0.890757309438

H	1.449427694414	2.427518044319	2.443046967267
H	4.002577492140	-1.759900305049	1.060983200660
H	3.988612291035	-1.627153598645	2.849706416633
O	1.500352507491	-2.295782361610	0.601602649429
C	-1.120372619119	0.044223151467	2.110104674197
H	-0.917744891104	0.104358935784	3.175421921537
O	-0.703705132342	-1.318870552413	-2.261853475259
C	-1.060493986306	-2.237091390264	-3.100861848836
C	-2.280387712296	-2.401525206599	-3.680035508516
H	-2.457413363669	-3.257043373116	-4.324624031010
N	-0.008484794774	-3.174259716717	-3.349977973301
S	1.515006454117	-2.471549951098	-3.621370097223
C	2.296947397159	-4.006377704571	-4.183589536137
C	1.222826509136	-5.075609913873	-4.128447070536
C	1.186246497466	-6.104929194828	-5.271937410175
C	0.218646024033	-7.189251249765	-4.714242700035
C	-0.147581064964	-6.656998342758	-3.311312686722
C	-1.093366641427	-5.454794910140	-3.502944296082
H	-1.505887322576	-5.088523709830	-2.558491324332
H	-1.938877109296	-5.698572961586	-4.155262904610
C	-0.168615420603	-4.387379428221	-4.143190044631
H	-0.475486324445	-4.131482359064	-5.169334652733
H	-0.542202532775	-7.421456306488	-2.633873772981
C	1.166624516818	-5.977912335555	-2.851623424996
C	1.070787233593	-5.248755822776	-1.506901873234
H	1.071749392279	-5.988912307974	-0.696685341989
H	1.938235021300	-4.594564549121	-1.345181166726
H	0.181539295037	-4.627908177515	-1.392147621313
C	2.361212140759	-6.931042138967	-2.750751058591
H	3.275221173261	-6.376622014551	-2.498329420159
H	2.191851625785	-7.648617999996	-1.938590906230
H	2.560961814503	-7.505228326410	-3.659396919626
H	0.705624169086	-8.168083811781	-4.657505768828
H	-0.671484908561	-7.313625617569	-5.340826847998
H	0.827363768941	-5.646893532470	-6.200450592257
H	2.182825680911	-6.508890931075	-5.478839287990
H	2.642002671801	-3.788357338657	-5.199230863461
H	3.153684812001	-4.190279854828	-3.527727103786
O	2.086359469243	-2.045865897816	-2.323584257146
O	1.495458760347	-1.493357181077	-4.705198939547
Li	-1.536629731197	-0.084033583855	-1.184479206481
Li	0.758651693592	-1.377570428493	-1.002432233406
C	-3.407806020841	-1.509664925987	-3.409959554955
C	-3.242043944322	-0.125402695446	-3.203685214342

C	-4.720289585020	-2.010190477589	-3.383739469411
C	-4.328218121705	0.701181098448	-2.933213991995
H	-2.249611516010	0.305461193362	-3.341564961697
C	-5.805766232653	-1.181000060277	-3.123988014074
H	-4.882428757105	-3.071990391697	-3.563223277408
C	-5.617020642356	0.177312333546	-2.879361477246
H	-4.169423329690	1.767720263400	-2.784131424971
H	-6.809514902498	-1.601258970306	-3.108129641906
H	-6.465555781481	0.823808051192	-2.669116923948
C	-2.509835934867	-0.010731752073	1.633930708922
C	-3.498291093020	0.820606414761	2.177271224911
C	-2.896753171726	-0.912623951846	0.625002925674
C	-4.808448064067	0.774035722094	1.711821548750
H	-3.225689929840	1.516860283843	2.968254534072
C	-4.204944788133	-0.950617314283	0.149841656665
H	-2.165287024533	-1.635892626506	0.254458832484
C	-5.166285905160	-0.099705232249	0.688517610158
H	-5.556197974398	1.433419449172	2.147852893460
H	-4.473709497957	-1.651586758234	-0.639153609255
H	-6.188277065472	-0.127182984411	0.318103773244
C	3.866482199190	1.112191920463	3.100291248955
C	2.867076093973	0.844479820389	4.228751354035
H	1.825526703018	1.005187290414	3.949329535432
H	2.945016898782	-0.193393335478	4.581842706282
H	3.104510819047	1.493971954883	5.081302051146
C	5.266239097736	0.937505741402	3.695679915790
H	5.399985746798	1.630715097346	4.535396357157
H	5.389894714650	-0.077276544480	4.098043154138
H	6.082265979746	1.116480226615	2.990540436470
H	2.247553024191	0.729718791375	0.157721926702

Table S54. Atomic coordinates and single point energies of the spirocyclic heterochiral dimer of **8o** with double *endo* chelation to the sulfonyl oxygens.



G = -2768.790902

G_{SP} = -2770.062529

92

0000s_het_endo_rr: optimized structure // E(RM062X) = -2770.78175348 A.U. after 12 cycles

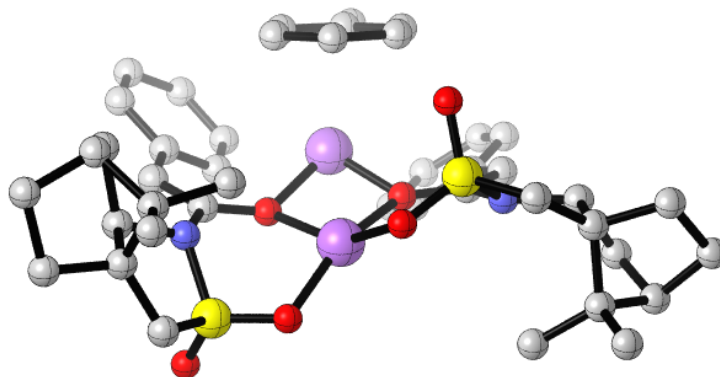
O	0.011659954778	-0.046935373890	0.005679568344
C	0.015551466970	-0.042424857953	1.294641599206
N	1.337659372166	-0.046087843887	1.844087092298
S	2.377265254061	1.052046797646	1.073587296511
O	2.778324166349	0.522476935011	-0.247511987543
C	3.711253420179	0.900480024096	2.285505225504
C	3.161276656080	0.034422357421	3.406305290502
C	1.61455552510	-0.047791295176	3.279397198485
C	1.266334890720	-1.369941738626	4.006506263938
C	2.628508341928	-1.804439432608	4.582846174781
C	3.022405458947	-0.778360884242	5.670174909119
C	3.427907156472	0.483641139171	4.852940526817
H	4.480731007542	0.747165688275	4.998634398188
H	2.833102736948	1.368555283735	5.105172162394
H	3.854774165454	-1.140885424937	6.282057297849
H	2.186614704066	-0.580783887462	6.350678955725
H	2.649197816716	-2.844847811662	4.923833228595
H	0.518893855545	-1.212025819456	4.790937448361
H	0.854816004660	-2.100224875051	3.303704560165
H	3.932842556788	1.927955939592	2.589961355798

H	4.573294526372	0.469318711351	1.766402559302
O	1.828676587941	2.413358412952	1.102030586145
C	-1.068861970879	0.007739740185	2.122930746419
H	-0.915056264323	0.139132877732	3.189979062146
O	-0.233128968877	0.517936855347	-2.613033783366
C	-0.116606832353	1.452220066682	-3.508395278061
C	-0.622884970542	2.710729356897	-3.402296337567
H	-0.578452673773	3.425402897343	-4.217638234273
N	0.600532400091	1.035344701186	-4.667490447208
S	1.627303068438	-0.300728120168	-4.440359788275
C	2.755451088222	0.125249037500	-5.789786169230
C	2.075067064580	1.218317362159	-6.584990182677
C	2.980853372128	2.288230835605	-7.219299467799
C	1.991180633734	3.049071392408	-8.148935176531
C	0.668436560236	2.264912456834	-7.988567199763
C	0.084534475068	2.612591769011	-6.605906539867
H	-0.901938528591	2.166716798620	-6.446085130239
H	-0.009999223095	3.694160800423	-6.460825849914
C	1.126360412318	1.997811998456	-5.635008338613
H	1.674029549347	2.777584788213	-5.084859605797
H	-0.038129889439	2.408284284371	-8.813035278028
C	1.155255094171	0.809429431269	-7.781570539006
C	0.034823769158	-0.184405336111	-7.463749479538
H	-0.635678885003	-0.252344104887	-8.330795541763
H	0.444211865205	-1.186785769742	-7.285960019619
H	-0.563158532888	0.076409546917	-6.588294083479
C	1.934950753575	0.236033085231	-8.967687963095
H	2.413614387342	-0.713270767222	-8.690896535984
H	1.241977306704	0.017862591777	-9.789907389541
H	2.709907294717	0.900601760798	-9.359157573514
H	2.337264492381	3.047397216208	-9.187565307654
H	1.869427504920	4.097319822865	-7.853497591236
H	3.428929665269	2.928432758221	-6.451592880676
H	3.801120628162	1.828297285834	-7.780676983145
H	3.673214147571	0.464870843583	-5.298278200429
H	2.947350479224	-0.797367644595	-6.346675662383
O	0.930799165104	-1.559727230673	-4.689689726203
O	2.372128009668	-0.192972521911	-3.158873111548
Li	-1.282632362411	0.711599391632	-1.089335060302
Li	1.273224823324	-0.019711905990	-1.483056830661
C	-1.340421323099	3.043901524768	-2.147560964236
C	-0.643776061026	3.063037041231	-0.924182500251
C	-2.727433566900	3.251438412111	-2.113341288830
C	-1.311055857673	3.241601787088	0.286712155413

H	0.436311606739	2.920297080541	-0.919731242517
C	-3.393930781358	3.453072451820	-0.904365128061
H	-3.287809252946	3.228266750470	-3.046673036590
C	-2.692274837608	3.438116664877	0.298971711103
H	-0.738379014937	3.221824450363	1.212360361239
H	-4.472488779869	3.598805426496	-0.901369444693
H	-3.218830259700	3.573238611347	1.240847682352
C	-2.443829232810	0.056216992146	1.635625279296
C	-3.427561879292	0.699055445155	2.410687340413
C	-2.859244374435	-0.493417453832	0.403661308565
C	-4.733229262649	0.837291325041	1.958279664084
H	-3.145922844717	1.113782829988	3.377868415471
C	-4.168055981076	-0.343106038070	-0.051622561425
H	-2.160873202216	-1.102147281557	-0.171344676122
C	-5.111984846285	0.336270386883	0.713155742737
H	-5.463434452279	1.350333574164	2.581840131112
H	-4.451512430815	-0.780043989897	-1.007708573361
H	-6.131693585850	0.455855934317	0.355018630919
C	3.602853886257	-1.464427416731	3.427957722874
C	3.360640497710	-2.249036806784	2.135681310941
H	2.319116208748	-2.273969914017	1.813195034738
H	3.946484309903	-1.823967336622	1.308394916410
H	3.703143907568	-3.282590284209	2.274957922677
C	5.081938389831	-1.639987857831	3.782303154434
H	5.308832133384	-2.707552829754	3.893636891041
H	5.717744272324	-1.259258977252	2.971130066704
H	5.384250461958	-1.140407516543	4.706564662780
H	1.138264848474	0.823637677717	3.754311544280

Toluene-solvated dimers of enolate 8o

Table S55. Atomic coordinates and single point energies of the toluene-solvated spirocyclic dimer of **8o** with double *exo* chelation to the sulfonyl oxygens.



G = -3040.085474

G_{SP} = -3041.510326

107

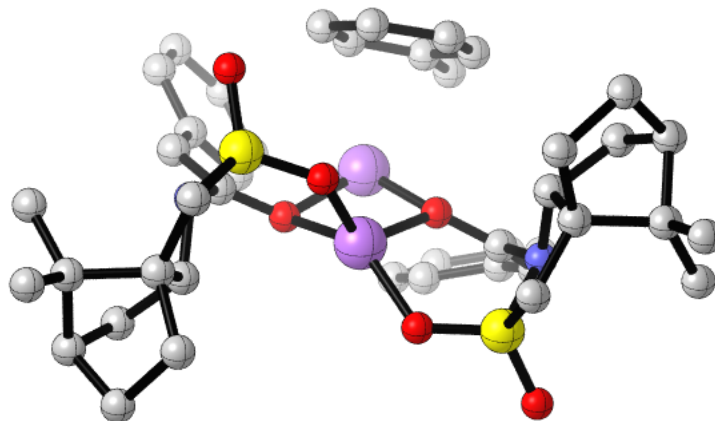
10000s_exo_ss_tol_tol: optimized structure // E(RM062X) = -3042.35606779 A.U. after 12 cycles

O	0.029750784870	0.007391744800	0.039122629409
C	0.005585091035	0.022195058166	1.330860203274
N	1.324499141384	0.014665582957	1.909518426511
S	2.321601093347	-1.252075497197	1.388136328167
O	1.722038622025	-2.566529554236	1.622761772939
C	3.633286778851	-0.939358029172	2.596647183384
C	3.131664911742	0.195620598815	3.470360731410
C	1.591477020741	0.303111034563	3.317662133225
C	1.296742169906	1.766329728823	3.732125244619
C	2.681131534841	2.280100575785	4.177268821652
C	3.057918116511	1.533432409642	5.475843665237
C	3.389630897748	0.094380023544	4.983777832916
H	2.751241814115	-0.671751941403	5.437486485092
H	4.427700832011	-0.183730294492	5.193544089014
H	2.233438070195	1.546235557122	6.197338259670
H	3.921153195325	1.995255631077	5.965978486987
C	3.628213058749	1.639199169333	3.131817052255
C	3.403066448507	2.111268514056	1.690830504745
H	3.896748446257	1.440908725807	0.973415135125

H	2.354048615260	2.173781333756	1.397619987721
H	3.850981039580	3.105744369305	1.565386627223
C	5.117575110230	1.833746345874	3.430889634678
H	5.727653226238	1.283747840245	2.701380067541
H	5.377061318389	2.895099599789	3.331061967536
H	5.421835557768	1.512091157142	4.430582320878
H	2.739233553716	3.370804489332	4.257035793955
H	0.893736493101	2.331151257411	2.885954699056
H	0.560374172777	1.815173713175	4.541268815325
H	1.080269412478	-0.426136989908	3.964104810350
H	4.544085138613	-0.708782241310	2.034729254025
H	3.753561569971	-1.884621421295	3.135071247292
O	2.787037113073	-0.961737128890	0.012925126324
C	-1.077799661517	0.076824082501	2.154412825859
H	-0.914186588337	0.127245616063	3.227181154165
O	0.419464113777	0.668664947702	-2.501969915268
C	0.531224816409	0.970951602776	-3.749442314109
C	-0.454274773806	0.923719010456	-4.693870814959
H	-0.260808595791	1.335631275625	-5.680576603620
N	1.850179505930	1.369508532620	-4.116559485918
S	2.758388565039	2.204904380164	-2.963888728501
C	4.182510500842	2.481667150104	-4.044404921892
C	3.849590394174	1.822799804953	-5.368399580223
C	4.268078688794	2.557019679419	-6.653456174578
C	4.070060315951	1.459461192765	-7.739760543925
C	3.617880581294	0.224088484364	-6.928443168675
C	2.164922806976	0.465881755869	-6.476973705803
H	1.728491659529	-0.409540058322	-5.989064933290
H	1.511744229321	0.732296450617	-7.314560168317
C	2.309428787853	1.643130271194	-5.476562222029
H	1.832140498758	2.560613598586	-5.852473307155
H	3.759987026383	-0.728307300287	-7.449783561936
C	4.403206853129	0.380121200447	-5.603799737673
C	4.055061922573	-0.655122719771	-4.529580931172
H	4.475100212273	-1.626433913256	-4.821113135023
H	4.506423877750	-0.383495143652	-3.565406261721
H	2.985474766683	-0.788029615588	-4.358786836842
C	5.925148367223	0.350334850817	-5.768062922930
H	6.418464866814	0.600866343640	-4.818868893134
H	6.244770428587	-0.664010397275	-6.037301713510
H	6.307936538501	1.030107287405	-6.533953681127
H	4.999970456970	1.265204892505	-8.283886606287
H	3.316776661020	1.743178536424	-8.483207718214
H	3.645179996086	3.443019049993	-6.819560409540

H	5.307367044481	2.897069202234	-6.595969161562
H	4.276115065515	3.570175293863	-4.109283637165
H	5.057571868598	2.060395626629	-3.538737758602
O	3.097928834667	1.301297976412	-1.842001808076
O	2.161982666411	3.496512955943	-2.603122351321
Li	-0.959638654240	0.939940947343	-1.258215682142
Li	1.608808911174	0.157196397891	-1.105277119396
C	-1.762309095526	0.317761325027	-4.467946590110
C	-2.833437986964	0.641644611197	-5.323909247428
C	-2.013914366907	-0.641388493220	-3.462636570962
C	-4.079889468431	0.040957422364	-5.192891565069
H	-2.670616518765	1.372919679017	-6.115215815242
C	-3.261709040042	-1.246946732268	-3.341964098169
H	-1.198591593304	-0.967618080799	-2.819572385112
C	-4.307278625227	-0.910979310142	-4.199935830890
H	-4.880784488960	0.315320514639	-5.877220746620
H	-3.406222684559	-2.010821650939	-2.579138247638
H	-5.279020329939	-1.389959967907	-4.103580746500
C	-2.466327580420	0.108517974136	1.702456758417
C	-2.897432175903	-0.451288144591	0.482764472200
C	-3.444852080192	0.691285840107	2.528507772799
C	-4.234351717374	-0.390757552006	0.100479394458
H	-2.175421456432	-0.971887909297	-0.144789584535
C	-4.779958836248	0.746672172653	2.145099739008
H	-3.141638095926	1.113769957414	3.485870232857
C	-5.183717373868	0.215855315726	0.920783799505
H	-4.541543933863	-0.830179753822	-0.846914118697
H	-5.510369387457	1.209785950591	2.806032446243
H	-6.227091452960	0.260120562120	0.616536200243
C	-0.540168363084	3.535246407782	-0.865546093614
C	-0.867620879515	3.565947739528	-2.222797022723
C	-2.129384733184	3.164016264087	-2.649580957301
C	-3.097651085824	2.730927446200	-1.733695206667
C	-2.767525560139	2.726312313401	-0.372757910368
C	-1.498485816428	3.120595079061	0.060502821498
H	0.458096712467	3.828096883168	-0.548470864156
H	-0.118439678344	3.877064108982	-2.945475989706
H	-2.366660873969	3.171075370718	-3.712517978685
H	-3.509849451069	2.402969338064	0.355187822299
H	-1.263882083398	3.090148971742	1.123291045723
C	-4.442934111624	2.259492474444	-2.208900154084
H	-4.386878546240	1.214160507499	-2.541316651544
H	-5.187776625074	2.321473253265	-1.408313699264
H	-4.789074311785	2.857679325894	-3.059634255443

Table S56. Atomic coordinates and single point energies of the toluene-solvated spirocyclic dimer of **8o** with double *endo* chelation to the sulfonyl oxygens.



G = -3040.078882

G_{SP} = -3041.504668

107

10000s_endo_rr_tol_tol: optimized structure // E(RM062X) = -3042.34957868 A.U. after 12 cycles

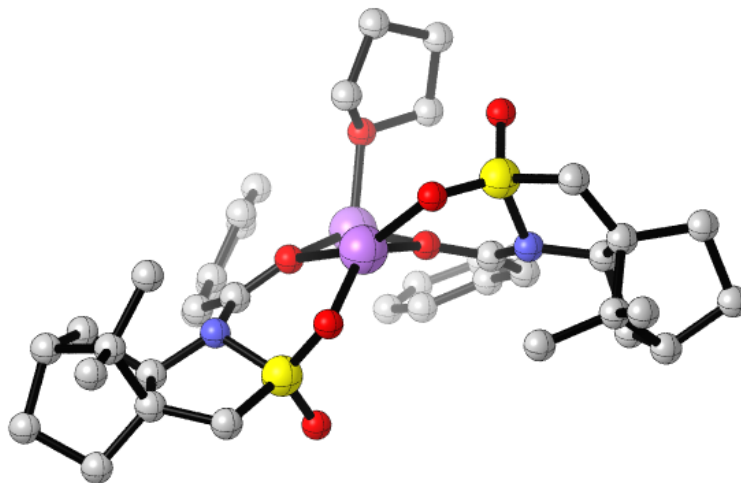
O	-0.213617891582	0.214962010017	0.052401734781
C	-0.199516889311	0.558743431746	1.299504335573
N	1.124218330130	0.677674839345	1.911798893713
S	2.077139685684	1.919446617553	1.283614905809
O	2.305803579873	1.726663952506	-0.177059770357
C	3.588876479467	1.390564636419	2.120358930079
C	3.345738403600	-0.071991850700	2.477026089984
C	1.975148047459	-0.524766620824	1.893663124444
C	1.528420310347	-1.666631390249	2.830813457374
C	2.778349291362	-1.864425808878	3.711065515337
C	3.917821158818	-2.383703186664	2.800544387981
C	4.352605526461	-1.125534249829	1.990588900433
H	4.282312758605	-1.267842477009	0.906114706006
H	5.381983637124	-0.827392605011	2.216419800808
H	3.566260868515	-3.192059136936	2.149807435479
H	4.749402979565	-2.785140059607	3.388631553120
C	3.211908798771	-0.405663384056	3.998289067208
C	2.179919759856	0.420969994205	4.768554606659
H	2.503535110394	1.468424193190	4.847385242973
H	1.185242800757	0.422591457105	4.321376379988

H	2.100480839496	0.032715623800	5.792362601342
C	4.539358695300	-0.278904003141	4.749841876475
H	4.890779872102	0.762319600097	4.732374421489
H	4.395613430497	-0.553395215171	5.802251110963
H	5.339372821633	-0.909073177897	4.351862455848
H	2.600802984347	-2.483593535180	4.596717507348
H	0.646898936071	-1.375803291303	3.410870793598
H	1.270089014315	-2.567128232574	2.265323135659
H	2.094099492072	-0.889353287527	0.861762584207
H	3.720142250231	2.042148310262	2.990487013187
H	4.397804315390	1.556089987010	1.402822334048
O	1.566960055165	3.224042119536	1.698770354982
C	-1.238172732724	0.841416636016	2.125603388597
H	-0.989731496786	1.203834860556	3.119423026643
O	0.106908548801	0.808528703342	-2.581679714060
C	0.291622228710	0.432890152769	-3.800877497825
C	-0.591811622208	-0.161653900165	-4.639055461674
H	-0.288053851926	-0.333364306989	-5.667999518116
N	1.626447789542	0.696083478273	-4.338839700854
S	2.798574735287	-0.361299052693	-3.722146123057
C	4.205865869102	0.771536855208	-3.890749904579
C	3.635465705097	2.061984899952	-4.445689949783
C	4.156393084281	3.385810801733	-3.859629969445
C	3.586375849916	4.433875728772	-4.860646483611
C	2.870459466470	3.569759397808	-5.924988053577
C	1.572323844988	3.035519711598	-5.287173273310
H	0.949472335008	2.486056885293	-6.000796873937
H	0.961514399537	3.842603238593	-4.869892879392
C	2.105517265658	2.081190896166	-4.192295363327
H	1.876076210065	2.437499443604	-3.177537646233
H	2.715143264406	4.079306097532	-6.881938407740
C	3.758608737944	2.301785297179	-5.984423857252
C	3.213545117630	1.184219596931	-6.877108762444
H	3.294458535050	1.491829543934	-7.927903783659
H	3.812117187280	0.269797341084	-6.761524216740
H	2.176124137691	0.916801459050	-6.672710362736
C	5.198917638117	2.565048085935	-6.431807695260
H	5.814331926949	1.665930684976	-6.289170956691
H	5.214474239383	2.798133101243	-7.503768271949
H	5.687787520321	3.391145984184	-5.908429435126
H	4.384949168137	5.037606111397	-5.303874258063
H	2.889584733328	5.129983945003	-4.379675699208
H	3.796043892963	3.528748266083	-2.834776785383
H	5.250989563977	3.402759848118	-3.826678654370

H	4.611879649953	0.873013837374	-2.879244437095
H	4.936646752860	0.282017621537	-4.542663127248
O	2.915071206225	-1.548497095046	-4.563156239527
O	2.575946796730	-0.607370700915	-2.269895744404
Li	-1.234192303733	1.002018145745	-1.333628396914
Li	1.272582964009	0.379511854568	-1.176518472844
C	-1.930237654303	-0.583365036692	-4.212948804527
C	-3.012002451030	-0.541112944144	-5.106221930038
C	-2.164401842214	-1.104307458382	-2.925803597299
C	-4.276048911998	-0.983641404639	-4.728945846068
H	-2.851031776980	-0.155290728082	-6.111828326153
C	-3.425075766438	-1.563309107909	-2.557148384585
H	-1.324913038064	-1.219634908279	-2.238810697343
C	-4.492677760637	-1.495617993349	-3.451142998573
H	-5.097452957818	-0.935192819673	-5.441255251087
H	-3.564615565232	-2.004525042664	-1.571543040843
H	-5.477504696186	-1.855739041524	-3.161615691712
C	-2.648220245239	0.821457590205	1.740092607408
C	-3.159559986141	0.017729811887	0.703457938464
C	-3.548252265615	1.660081217828	2.420987350857
C	-4.505260625087	0.083153756886	0.349482346756
H	-2.493191121055	-0.676875426687	0.193584775321
C	-4.889503836778	1.724829291524	2.062512510349
H	-3.176509683274	2.280427407252	3.235525050336
C	-5.375935072189	0.942339968692	1.016132038643
H	-4.881808473460	-0.541320577429	-0.457958360044
H	-5.558715120171	2.392997073055	2.601011186116
H	-6.424031874275	0.992907140521	0.730372971074
C	-0.480051143625	3.880298250481	-0.894427205750
C	-0.531726379742	3.860985062478	-2.285865210063
C	-1.657055701821	3.374380383673	-2.947868830758
C	-2.767355010246	2.913274430936	-2.229795890056
C	-2.719067722939	2.968358073259	-0.827241877054
C	-1.582253595866	3.436628888538	-0.164410498916
H	0.407063889847	4.231664746711	-0.372965794772
H	0.321544567645	4.215129108230	-2.859747505030
H	-1.674269658150	3.335993829136	-4.036851454856
H	-3.585028448621	2.646311404930	-0.249683632813
H	-1.558028522820	3.453876499287	0.923464397446
C	-3.976822341057	2.349913085323	-2.927121846815
H	-3.956771718892	1.250861411048	-2.924359657155
H	-4.898637204957	2.666075187447	-2.425670338776
H	-4.017581366307	2.675763838453	-3.971723601540

THF-solvated dimers of enolate 8o

Table S57. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of **8o** with double *exo* chelation to the sulfonyl oxygens (higher energy conformer).



G = -3001.008835

G_{SP} = -3002.417606

105

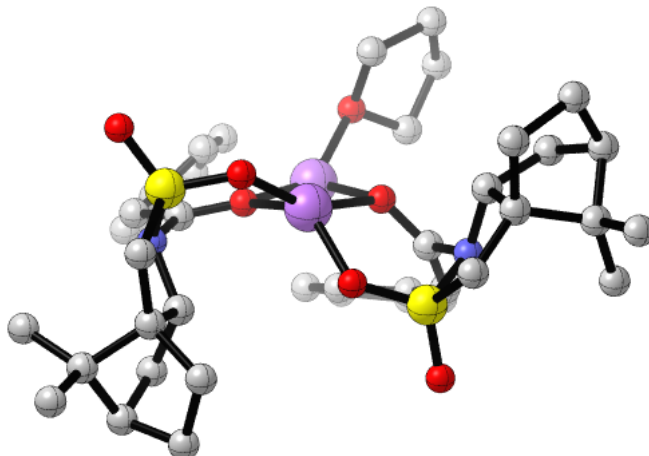
11000s_exo_ss_tol: optimized structure // E(RM062X) = -3003.25446798 A.U. after 12 cycles

O	-0.048725091976	-0.559230516216	0.143224854603
C	-0.022498355969	-0.118410580184	1.352372457796
N	1.305387332683	-0.065415630834	1.877969215831
S	2.266146863297	-1.381942718929	1.425292710165
O	1.650818793368	-2.664042303774	1.796973541064
C	3.621730778211	-0.994379308747	2.560698637996
C	3.190971625815	0.245186712941	3.324029355185
C	1.648431523146	0.394656246411	3.219541997481
C	1.421375704858	1.908162129702	3.461904585297
C	2.836985261537	2.410113892601	3.809493685259
C	3.229754033770	1.792974478788	5.170884558078
C	3.506864639833	0.299428205652	4.828440118478
H	2.868687142763	-0.394012112810	5.387276580936
H	4.545925636348	0.016955655590	5.027606831984
H	2.425075096455	1.907120280741	5.905797407579
H	4.117835908705	2.276869176847	5.590226691070
C	3.723242426805	1.623367261695	2.812268724566

C	3.460076957311	1.939872296992	1.336552461062
H	3.959628875787	1.208774136680	0.685660941014
H	2.405951886970	1.950847414394	1.055850782746
H	3.885244025351	2.924564367503	1.102513562542
C	5.228026238080	1.795360599537	3.038695117124
H	5.793347232739	1.125269319625	2.376460744748
H	5.522323083591	2.821157314233	2.784189671154
H	5.553782884942	1.604003427618	4.064608926779
H	2.937950442957	3.499724391909	3.768047635873
H	1.014474843213	2.385003196673	2.565664615388
H	0.711266912918	2.081223103688	4.277234151787
H	1.139232003426	-0.227182190744	3.972027076004
H	4.522761021407	-0.861810089197	1.953216009334
H	3.722164105376	-1.883534755872	3.190983295458
O	2.687239320609	-1.236211922580	0.012899306856
C	-1.092546134857	0.234688758373	2.120706815535
H	-0.951538712999	0.454000141513	3.175471763385
O	-0.283588049567	-0.794939685580	-2.502292254118
C	-0.591129099349	-0.275937004361	-3.642592546384
C	-1.804340590731	-0.272319423737	-4.269214983949
H	-1.929718216223	0.335987837694	-5.159815125779
N	0.511347510063	0.401405872024	-4.275583800712
S	1.332866588833	1.491928081428	-3.272407141653
C	2.319642226447	2.236447907142	-4.593022612654
C	1.815672876844	1.622236259536	-5.886963372974
C	1.594147137392	2.564191819017	-7.082901545811
C	1.406283611781	1.564513147067	-8.261608353811
C	1.594733445893	0.181875382797	-7.596928097688
C	0.335702580959	-0.102503760030	-6.753510049879
H	0.330369521083	-1.112131052602	-6.332564613728
H	-0.585125303372	0.014680328419	-7.334104967136
C	0.437008420191	0.955781352462	-5.627948245013
H	-0.368348554957	1.703246409950	-5.687492435874
H	1.842674819457	-0.620377672070	-8.299964732562
C	2.664448534733	0.469543369942	-6.513801530479
C	2.971060868098	-0.713099266350	-5.590604104586
H	3.562118386606	-1.454709740392	-6.143696306148
H	3.578868098463	-0.389106087314	-4.734043991866
H	2.087533071628	-1.209639091970	-5.187886498885
C	4.006364082145	0.957157828718	-7.067363320290
H	4.668144985425	1.266893641561	-6.246653624600
H	4.508538323542	0.134954029220	-7.592215399110
H	3.927471427259	1.794209950876	-7.766158837538
H	2.145285878962	1.735288344439	-9.051214335381

H	0.417025726380	1.650707868432	-8.724796531123
H	0.720369162469	3.204755870934	-6.919569478755
H	2.455666575386	3.222940635819	-7.234713959875
H	2.129619465052	3.311285810362	-4.514036486133
H	3.370504474942	2.024350689548	-4.371159707637
O	2.190841762777	0.740771485320	-2.326604730224
O	0.431079327167	2.490091082117	-2.691687872625
Li	-1.389315628460	-1.213039685640	-1.009962811175
Li	1.223499303463	-0.597094669390	-1.261193637035
C	-2.999653442190	-0.920378090380	-3.739532772423
C	-4.272021986526	-0.394019597122	-4.034716775487
C	-2.951426241958	-2.066903099256	-2.925106802551
C	-5.427558848384	-0.962201492849	-3.511641895082
H	-4.344227386426	0.485137356728	-4.673780312485
C	-4.107946152650	-2.622698682959	-2.385981783171
H	-1.994878318030	-2.549487699529	-2.742757260024
C	-5.355100011178	-2.072474235455	-2.669653899923
H	-6.395247449978	-0.527017079969	-3.755299319584
H	-4.023016770097	-3.498168371789	-1.744635478345
H	-6.259306162714	-2.505720855200	-2.248132027882
C	-2.457200327945	0.161005915202	1.597841739871
C	-3.513599436136	-0.231188735777	2.437735537833
C	-2.773635568432	0.437684818400	0.250778983647
C	-4.805473623652	-0.392759712323	1.947834899988
H	-3.305296023898	-0.433958945077	3.487619131395
C	-4.064141599991	0.259852986108	-0.240998454911
H	-2.001454374480	0.844148476641	-0.404778620268
C	-5.087486126507	-0.170288744513	0.601294491593
H	-5.598086358475	-0.709022128836	2.623817117294
H	-4.269197662999	0.465696924572	-1.291581584111
H	-6.093737418195	-0.314924317505	0.214483706421
O	-1.379732628124	-3.082783432742	-0.467100477041
C	-0.140773904896	-3.713913075514	-0.806108602833
C	-1.583031149080	-3.275551179635	0.943934201376
C	-0.153318322008	-5.003131264534	0.001844748178
H	-0.126986365527	-3.857987897137	-1.890683966602
H	0.695016008255	-3.068141019549	-0.502926627377
C	-0.879051114887	-4.597347813642	1.298615501171
H	-1.137326914266	-2.433112222701	1.486865092082
H	-2.665290457277	-3.283749534658	1.108069141918
H	0.856764636331	-5.382292279511	0.182588189510
H	-0.719938159683	-5.770749786728	-0.537149915393
H	-0.166199690580	-4.431458461971	2.110576680623
H	-1.591426418459	-5.364988754510	1.615775591397

Table S58. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of **8o** with double *endo* chelation to the sulfonyl oxygens (higher energy conformer).



G = -3001.002138

G_{SP} = -3002.411207

105

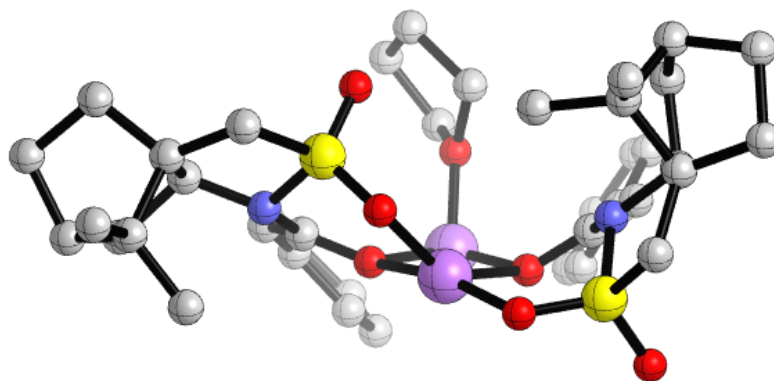
11000s_endo_rr_tol: optimized structure // E(RM062X) = -3003.24556448 A.U. after 12 cycles

O	0.088354332050	-0.532402542290	-0.129978881340
C	0.018336594257	-0.295163910702	1.138408216960
N	1.304832430341	-0.088904297656	1.805116242382
S	1.827675882203	1.511641370458	1.645547188099
O	1.673062776798	1.940540345251	0.225259063499
C	3.581631377700	1.170611285402	1.949557794451
C	3.702938678225	-0.344319044942	1.971612087449
C	2.410601609112	-0.959868125656	1.376858466814
C	2.365249665992	-2.378026453146	1.989405396801
C	3.706393758836	-2.453746611816	2.749141532184
C	4.836309813784	-2.452931964094	1.693705374275
C	4.858402753945	-0.982570476181	1.181585545623
H	4.686719102286	-0.901341198012	0.102452665159
H	5.810621429609	-0.486608849247	1.397170204199
H	4.630176643328	-3.168693047494	0.890026455239
H	5.797590464410	-2.735372293384	2.135261578279
C	3.821848499880	-1.037080221380	3.367488408488
C	2.724666313015	-0.696154593004	4.379038768112
H	2.748974807844	0.373061201865	4.633072823337

H	1.714297922916	-0.921449670304	4.036082707592
H	2.909113443453	-1.251172756454	5.308081463237
C	5.161453154858	-0.757276717038	4.054003114742
H	5.229664757082	0.301774650949	4.338774662189
H	5.232542545264	-1.343889160098	4.978414837438
H	6.036931114561	-0.996030409317	3.444327520007
H	3.764166787511	-3.282381000987	3.462973646201
H	1.499802132113	-2.483701251166	2.651969121508
H	2.287996584983	-3.148296799971	1.214847511234
H	2.455616151074	-0.991772853646	0.279723998678
H	3.843404434779	1.656014361010	2.895430480071
H	4.117949340389	1.647099698837	1.123058595939
O	1.225991924813	2.376902042823	2.654238559144
C	-1.075075495013	-0.193368114482	1.937462610352
H	-0.911906811204	-0.092167682139	3.007036886809
O	-0.665161636009	0.845459916672	-2.335621848608
C	-0.998692303589	1.701771768798	-3.245938704815
C	-2.121933258808	1.742016519715	-4.004250482168
H	-2.245189429579	2.583229131026	-4.680749576466
N	-0.082558392411	2.829797148126	-3.405494518606
S	1.516478897190	2.397896059440	-3.760520157609
C	2.184531674580	4.049887870085	-3.461252573504
C	1.160008794819	4.734089294002	-2.562869889995
C	1.610413497577	5.257425615871	-1.190407633170
C	0.374190797612	6.098697897154	-0.751239282119
C	-0.574128664363	6.038508387253	-1.975162048586
C	-1.218464447945	4.639199113356	-2.001594653187
H	-1.951302336313	4.532892458394	-2.807695375948
H	-1.719709517435	4.390011104829	-1.060920450745
C	0.007860328912	3.735196297336	-2.242497747062
H	0.249032840835	3.161338038551	-1.335644205299
H	-1.298186208537	6.859312048690	-2.016961881243
C	0.411234948924	5.963975312068	-3.167543785087
C	-0.252843507571	5.722961647925	-4.525094848905
H	-0.913578297735	6.567685977944	-4.761271256862
H	0.503997874965	5.677423903147	-5.320428673588
H	-0.833595708681	4.800786806038	-4.578524860875
C	1.307097103262	7.195956650516	-3.315982548703
H	2.133990690815	6.988498268454	-4.009772341755
H	0.727430547197	8.024113344305	-3.742956616589
H	1.739023344577	7.547399700604	-2.374943045719
H	0.656878641930	7.129253890729	-0.512315031734
H	-0.107380951465	5.683148876557	0.141206443811
H	1.828386092725	4.427979666780	-0.508055037483

H	2.513958162339	5.871049260680	-1.275685527451
H	3.163633563078	3.893116706439	-2.999593929337
H	2.302940331160	4.526435556848	-4.439767451502
O	1.627454930585	1.932947600324	-5.139230434833
O	2.085898424195	1.515191875563	-2.704241232707
Li	-1.310136184658	-0.620029986872	-1.393330165871
Li	0.909826921775	0.824630572812	-1.260349951279
C	-3.218283475140	0.779558831907	-3.864031072604
C	-4.552222328522	1.202574725123	-3.993901944876
C	-2.990773383987	-0.576303037835	-3.576289945832
C	-5.608353992367	0.318078891559	-3.802127396647
H	-4.755929235830	2.245709079688	-4.231989082689
C	-4.046947310603	-1.459013001900	-3.372010627420
H	-1.969171520928	-0.949080820864	-3.553623412941
C	-5.363150514294	-1.015821185234	-3.475701229048
H	-6.631990196591	0.674614924677	-3.900843137188
H	-3.828292958005	-2.498367446053	-3.133265915793
H	-6.190671835962	-1.703501167342	-3.315392898024
C	-2.450365787613	-0.265154599981	1.429483918313
C	-3.438742149895	-0.965515183428	2.138089114627
C	-2.826808463154	0.354505425500	0.224388342654
C	-4.730200937092	-1.087427082481	1.635587859222
H	-3.178555290669	-1.433982771254	3.086296886739
C	-4.115987252696	0.220723727860	-0.287252536083
H	-2.107578497556	0.993511534511	-0.293552530753
C	-5.072082781661	-0.512975246784	0.411602020564
H	-5.476073390317	-1.642856974236	2.201347970307
H	-4.373959105550	0.701285846514	-1.230829519818
H	-6.079083826110	-0.618654921484	0.014116319616
O	-1.608378279108	-2.521526183695	-1.553427617134
C	-0.438003583581	-3.292128564870	-1.876681950398
C	-2.195926627117	-3.088649716404	-0.376405197376
C	-0.634209382550	-4.664587606114	-1.204808975216
H	-0.381563814598	-3.343134066852	-2.968144112002
H	0.445972581265	-2.767953844899	-1.490566286158
C	-2.044068840489	-4.581928300262	-0.601679331567
H	-1.633214868389	-2.755026297463	0.510281712835
H	-3.226992868599	-2.724100969416	-0.311828535286
H	0.110065727987	-4.810072257332	-0.414656337992
H	-0.530504933251	-5.488822625374	-1.916159479134
H	-2.150902868901	-5.161802944864	0.319660246783
H	-2.798820190646	-4.924992637374	-1.318876537784

Table S59. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of **8o** with double *exo* chelation to the sulfonyl oxygens (lowest energy conformer).



G = -3001.012542

G_{SP} = -3002.420396

105

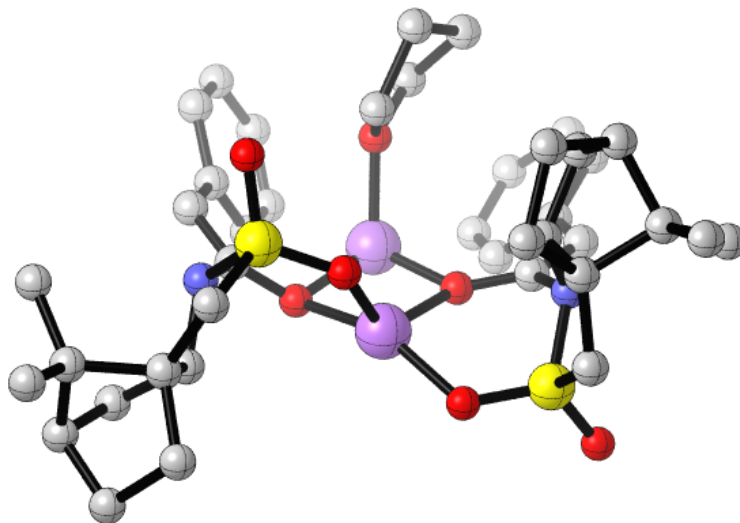
11000s_exo_ss_2_tol: optimized structure // E(RM062X) = -3003.25697343 A.U. after 12 cycles

O	-0.077947944402	-0.921697497108	-0.025619465475
C	-0.142745082621	-0.533530563941	1.204714607048
N	1.157152000728	-0.418200325237	1.807037683708
S	2.185268135926	-1.736903125464	1.511185374493
O	1.584091037327	-3.012950446078	1.901258719655
C	3.438602341910	-1.245516834602	2.722776474452
C	2.916068792047	0.016810515583	3.382395988230
C	1.384197468837	0.107935676221	3.151700261299
C	1.095404597951	1.622998355211	3.308344920232
C	2.465353056893	2.189998939805	3.730739771659
C	2.773685766338	1.654850868055	5.146970729951
C	3.110999071385	0.154797861468	4.902547496879
H	2.447054931254	-0.527905513399	5.444303902788
H	4.137276450237	-0.089636224269	5.196083181316
H	1.916527058321	1.783586565909	5.817327436716
H	3.617975617351	2.184554374737	5.600293098538
C	3.446325242765	1.385106988189	2.842856610080
C	3.284668729157	1.621264201346	1.338203915604

H	3.808540001458	0.851575867320	0.755301882896
H	2.250596520441	1.626985900416	0.990302323301
H	3.731681375610	2.589998935932	1.076544127077
C	4.924228777014	1.614467159930	3.170874660928
H	5.556610963092	0.943780648033	2.573206988752
H	5.204330339676	2.641408144201	2.904626745884
H	5.180320952009	1.464889333670	4.223312300949
H	2.535893773634	3.279162541861	3.639879042595
H	0.739442260253	2.046090385973	2.363962489269
H	0.324702072766	1.808444609810	4.064243871472
H	0.837163400647	-0.497148014041	3.890517004632
H	4.379857552396	-1.115987825683	2.178941977500
H	3.515342383077	-2.094979030784	3.408779330655
O	2.716953360167	-1.633212854101	0.133452199112
C	-1.244335817223	-0.192126058744	1.932791527253
H	-1.103930898215	0.163494236943	2.949168452001
O	0.361924116030	-0.124922540827	-2.587812117359
C	0.396965548197	0.636197086571	-3.625777180888
C	-0.640557346284	0.966670485540	-4.451612171291
H	-0.483652237572	1.723068333344	-5.214966359598
N	1.696271993262	1.182695774271	-3.885353419917
S	2.508043700208	1.752566180024	-2.516076409584
C	3.872123979867	2.512489374278	-3.428027193071
C	3.524870955693	2.366623516258	-4.899361642685
C	3.752880164510	3.583887226085	-5.811394677840
C	3.608174744873	2.963211910935	-7.232167940632
C	3.372358912180	1.461609582821	-6.950037733665
C	1.937131546590	1.309667759625	-6.409659715806
H	1.644325807208	0.263370401450	-6.284346179431
H	1.197603190316	1.780228055089	-7.065840796905
C	2.014709324794	2.024548285422	-5.037402689128
H	1.403241589447	2.939683476159	-5.013687536940
H	3.591575295971	0.808418185406	-7.801144165855
C	4.231226599440	1.215108939478	-5.685085023273
C	4.094079028982	-0.185954090099	-5.082703984776
H	4.613179791917	-0.905223443494	-5.729334577102
H	4.575912052247	-0.233742892502	-4.096025755812
H	3.064838848626	-0.523228936058	-4.954030196345
C	5.728266912543	1.466680517583	-5.885073630935
H	6.258920572088	1.409457837004	-4.924633596117
H	6.148524112988	0.685453806111	-6.530533877477
H	5.964066685570	2.432304079185	-6.340234820793
H	4.510853424628	3.123082963179	-7.830648288048
H	2.771914790649	3.397889549134	-7.791110160311

H	3.016870131639	4.369814934033	-5.608225410598
H	4.745184242319	4.018725672664	-5.651905564151
H	3.898633331588	3.550431106562	-3.082281817478
H	4.789249806501	1.994606353081	-3.128838690922
O	2.964269504400	0.610930651469	-1.695787178943
O	1.739784580021	2.793999065430	-1.820853628430
Li	-1.124058820147	-0.242318636105	-1.423127336617
Li	1.514864613478	-0.700739298377	-1.158251971939
C	-1.986108224206	0.421365508689	-4.331427834627
C	-3.069127512236	1.131964564436	-4.885381635378
C	-2.282600201166	-0.803764840387	-3.696024540695
C	-4.376277241162	0.677709417140	-4.763003371456
H	-2.871563236839	2.065688003296	-5.410665599593
C	-3.594024234309	-1.255625510707	-3.577586051462
H	-1.465688078159	-1.434502145375	-3.347821515378
C	-4.654413998713	-0.512765296156	-4.091449919896
H	-5.188142673392	1.260819811616	-5.193964382611
H	-3.782976676878	-2.212031057581	-3.092810828311
H	-5.678103581293	-0.865337008978	-3.990368078382
C	-2.616392860006	-0.196857483463	1.432517262747
C	-3.069282600649	-1.053121602497	0.409194882777
C	-3.562759437410	0.665230662688	2.015962823553
C	-4.390220916892	-1.015903190108	-0.024679197806
H	-2.379248856452	-1.783060973123	-0.012817827646
C	-4.885681437250	0.692206411973	1.587221031315
H	-3.245548577948	1.324338449847	2.823799329989
C	-5.308277094255	-0.140376232573	0.553636173295
H	-4.714503530798	-1.694265614613	-0.811426478868
H	-5.590547804539	1.372295059856	2.062576919320
H	-6.340805040840	-0.119606420027	0.212551535717
O	-1.846032437109	1.437868433721	-1.060929270461
C	-3.082797535551	2.024645144707	-1.456574787448
C	-1.117043266229	2.464621789306	-0.393030318547
C	-2.674100313682	3.390520741466	-2.008259635962
H	-3.560344717535	1.359706530625	-2.182846092639
H	-3.726171568007	2.117065414924	-0.567914804547
C	-1.385290857783	3.728961266047	-1.220344511746
H	-1.506953322837	2.554327722092	0.633309143650
H	-0.063386357875	2.170857562691	-0.369543719745
H	-3.465927418036	4.134650746821	-1.876322102972
H	-2.457911444872	3.306460208611	-3.078875666587
H	-1.506329401413	4.604619899779	-0.574540499107
H	-0.545129260656	3.915940266770	-1.895386542600

Table S60. Atomic coordinates and single point energies of the THF-solvated spirocyclic dimer of **8o** with double *endo* chelation to the sulfonyl oxygens (lowest energy conformer).



G = -3001.00608

G_{SP} = -3002.413436

105

11000s_endo_rr_2_tol: optimized structure // E(RM062X) = -3003.24977207 A.U. after 12 cycles

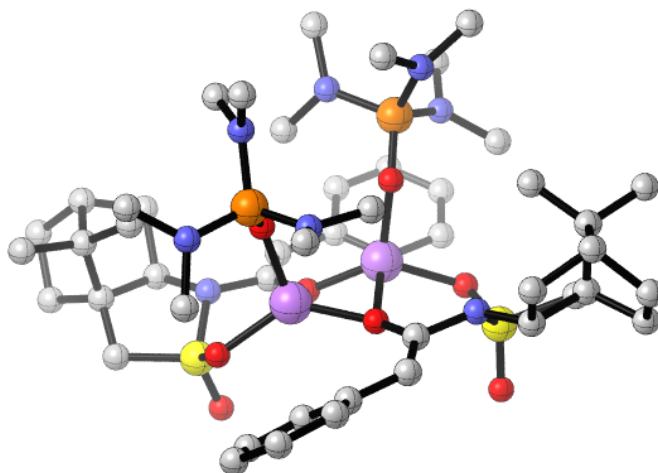
O	-0.055670118488	-0.432482511125	0.086110889798
C	-0.147480777619	0.293300742305	1.151841204569
N	1.122749671473	0.666059133452	1.782877045334
S	2.019690490371	1.789402101545	0.906817457562
O	2.241598460997	1.305356843596	-0.486581217248
C	3.561361145309	1.529361426098	1.817295253008
C	3.361547782689	0.220803594132	2.570135208970
C	2.039360108269	-0.443901826104	2.096059957290
C	1.610742471491	-1.315901340891	3.295959629413
C	2.823030562199	-1.185475789533	4.239971531334
C	4.026853461382	-1.872396414455	3.551898321284
C	4.433520830557	-0.871634582420	2.429490983685
H	4.413537028293	-1.317174630782	1.428473820136
H	5.438579904933	-0.465845632921	2.585540575206
H	3.746156763621	-2.852376344422	3.150142704551
H	4.849957266500	-2.038540690897	4.254472499596
C	3.176587806258	0.318179514311	4.119317989140
C	2.076355572611	1.267659913329	4.599500000928
H	2.329891765540	2.309729158735	4.358138359320

H	1.093817498946	1.066857040426	4.170947375316
H	1.998948898561	1.202380555128	5.692641369434
C	4.463136759134	0.722265597846	4.844057028055
H	4.752176874828	1.746274361008	4.568827603472
H	4.293775549303	0.715632494658	5.927990794678
H	5.315786064060	0.068796506057	4.640448656308
H	2.630441167112	-1.541384899532	5.257592280652
H	0.686519414880	-0.935281251080	3.742361121236
H	1.429621014507	-2.351747510675	2.992875204445
H	2.207029532385	-1.055707238512	1.197282231279
H	3.702876441433	2.399287395960	2.466586431463
H	4.347876640249	1.497316716900	1.057099657192
O	1.458846335865	3.131750109351	1.043712957098
C	-1.256590430236	0.779529015795	1.765103231862
H	-1.107021643581	1.453628436720	2.604198784569
O	0.071372200093	-0.249579003372	-2.629172108899
C	0.201581637071	0.035577709186	-3.879253655350
C	-0.755703519353	0.091055288636	-4.839747719191
H	-0.453437876459	0.390442858522	-5.839533911775
N	1.550792819482	0.408615460045	-4.306925768320
S	2.749917923920	-0.715083233504	-3.891887702111
C	4.121715921795	0.376815324606	-4.322518040626
C	3.548546471178	1.785990122734	-4.220012841703
C	4.168040955235	2.772851198882	-3.220146859796
C	3.479563572945	4.109299839036	-3.632746797568
C	2.658033240883	3.736915061421	-4.893901322076
C	1.412198202646	2.959216890486	-4.430866824821
H	0.752197360879	2.697087037610	-5.264035696227
H	0.820077014748	3.517516643907	-3.698284147571
C	2.046693050162	1.702919163376	-3.801767449224
H	1.963877684649	1.729083898489	-2.706375124650
H	2.432411291464	4.588821088498	-5.544377175684
C	3.511577269022	2.618591922481	-5.540021228171
C	2.847831836659	1.918644923379	-6.728353139181
H	2.639624101913	2.654774976235	-7.516277742351
H	3.527926890314	1.172165951249	-7.160973317106
H	1.918771386735	1.403536863916	-6.476838439263
C	4.896514033174	3.079895027808	-5.999983226529
H	5.544018929157	2.214249355542	-6.198409660055
H	4.805395799194	3.637858124191	-6.940499910019
H	5.410482385782	3.726027192912	-5.282715969745
H	4.217378132862	4.888885658669	-3.849178029540
H	2.828769001721	4.495912536222	-2.839578213356
H	3.944221771595	2.476559816932	-2.188940843962

H	5.256920910373	2.822100189059	-3.329968523392
H	4.917522078004	0.152328351537	-3.606518808142
H	4.438261331056	0.103620870339	-5.334351839701
O	2.633164817249	-1.911799168933	-4.718116479766
O	2.828591522507	-0.915706668915	-2.418138920004
Li	-1.292668781791	-0.131953196363	-1.356550388746
Li	1.352163406395	-0.312424523901	-1.241969200114
C	-2.171936337007	-0.183656184470	-4.592047890361
C	-3.157076245986	0.481121165367	-5.342022246369
C	-2.604356889712	-1.123175179114	-3.636904415413
C	-4.510762718583	0.250919172286	-5.121875601223
H	-2.847203268704	1.196123558821	-6.103263495340
C	-3.959831483388	-1.359248052056	-3.425559963084
H	-1.859786580857	-1.713516210415	-3.103699435883
C	-4.922938127654	-0.663967406673	-4.153979441878
H	-5.250537197760	0.788333864888	-5.712246204869
H	-4.265863335725	-2.107426150622	-2.697357979368
H	-5.981332869132	-0.846671678764	-3.983134810344
C	-2.622676805863	0.535801389688	1.299469954881
C	-2.999014787905	-0.655082752025	0.651451180805
C	-3.610625447440	1.513731579871	1.495129645497
C	-4.296847050208	-0.832890573637	0.180918603433
H	-2.267316924055	-1.455782869875	0.547333736609
C	-4.906152440276	1.332274750903	1.024113091203
H	-3.345741720346	2.435192869317	2.012212806419
C	-5.255859888895	0.163728138808	0.350037045808
H	-4.567096098359	-1.768468981504	-0.304857565961
H	-5.649179793311	2.112471720107	1.180295734384
H	-6.267857031898	0.023482940062	-0.023010825173
O	-1.964353463048	1.630389199841	-1.439374552435
C	-3.124269206119	2.116742949059	-2.128235938569
C	-0.961259491426	2.661444042795	-1.356204017209
C	-2.591606746678	3.246259613309	-2.991846011988
H	-3.565898013348	1.284718972693	-2.685157615364
H	-3.850432947682	2.483005361820	-1.387597339663
C	-1.574764317735	3.881387385164	-2.042407354005
H	-0.718166651066	2.833330546551	-0.301671112337
H	-0.065211829229	2.293616868186	-1.876024221822
H	-3.376222542253	3.935360457516	-3.320179079367
H	-2.090035784883	2.830233541108	-3.876840478308
H	-2.090460738470	4.510796366317	-1.306723505370
H	-0.823194812590	4.498096308765	-2.544563574031

HMPA-solvated dimers of enolate **8o**

Table S61. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with double *exo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *exo*-face.



G = -4408.415925

G_{SP} = -4410.366788

150

20020a_nit_xt_thf: optimized structure // E(RM062X) = -4411.58970908 A.U. after 13 cycles

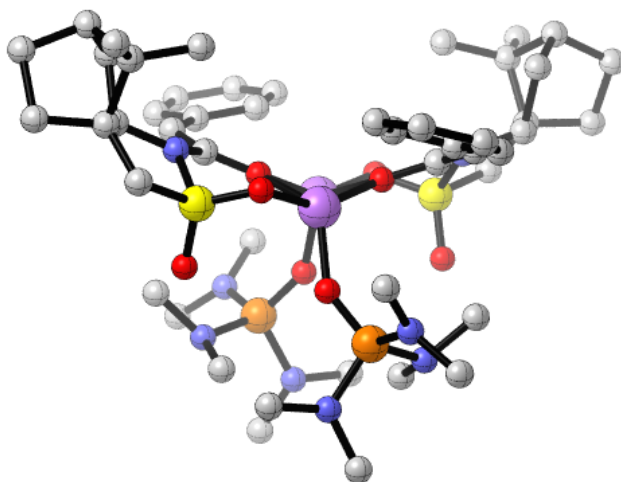
O	-0.077380185247	0.017746987403	0.010372415695
C	-0.081581122237	0.107121849969	1.288075185719
N	1.248773223684	0.094607658188	1.866136084251
S	2.210945735245	-1.187271660390	1.292949537917
O	1.591313283110	-2.486498451662	1.579822208969
C	3.579787098200	-0.894922689066	2.428587975235
C	3.034714532736	0.044670318103	3.489299531183
C	1.494699514315	0.186061735422	3.315350101345
C	1.197698452627	1.552582856766	3.984910923727
C	2.564265891455	1.953508523745	4.573342991888
C	2.891562514098	0.964883480344	5.713826822305
C	3.251693820274	-0.347492024954	4.960245953473
H	2.612308763592	-1.192917130703	5.237271422090
H	4.289385861849	-0.649888174835	5.136210525048
H	2.034494750821	0.837234912759	6.384516860096
H	3.730405051176	1.317327037101	6.323176828762
C	3.539624269697	1.523434839809	3.451290126768
C	3.342768654669	2.264416140810	2.124480140732

H	3.982860236237	1.829626126004	1.344537034087
H	2.323265086170	2.239988635709	1.738187321524
H	3.648810132522	3.312392996020	2.252166769556
C	5.020915749107	1.649466792097	3.814495050411
H	5.641151333927	1.170588086952	3.043468361341
H	5.303622798059	2.709488963286	3.846683825702
H	5.284835142530	1.206325228446	4.778905148900
H	2.620598002173	3.007741986737	4.865624559745
H	0.842133071902	2.286291651886	3.259667855390
H	0.430265539301	1.452772908850	4.759867212171
H	0.968963585778	-0.632013620452	3.829438742607
H	4.399552526220	-0.471021757498	1.838665873578
H	3.862123645951	-1.881771735004	2.807481821271
O	2.635962570005	-0.945307028602	-0.102176993427
C	-1.154705982267	0.242031140259	2.128058738286
H	-0.978850737338	0.368155949298	3.192391404921
O	0.282016454191	-0.461190769666	-2.686500786113
C	0.254571450786	-0.586967566630	-3.962206457913
C	1.278088729255	-0.916942947917	-4.811122254649
H	1.087379604218	-0.928772049135	-5.880224194658
N	-1.028700067065	-0.282956025298	-4.539553711092
S	-2.359929057673	-0.925345191027	-3.720344397289
C	-3.566282165146	-0.545271536750	-5.012802645283
C	-2.790202042073	0.137717382273	-6.120515285156
C	-3.173337669692	-0.217747365343	-7.567251332644
C	-2.431691143321	0.876177218388	-8.388852417932
C	-1.752912262257	1.739746589905	-7.303080958526
C	-0.577038409661	0.924043471126	-6.729060450270
H	0.036359374441	1.508365565222	-6.037237755137
H	0.081107613513	0.542925921646	-7.517458759600
C	-1.290241732986	-0.230836319531	-5.980043439542
H	-1.081104789885	-1.209491180701	-6.436886122149
H	-1.466956445391	2.741351262444	-7.643016206993
C	-2.778738586692	1.700148070961	-6.143329514647
C	-2.300082966474	2.384017389363	-4.860402742784
H	-2.332795067438	3.473503537848	-5.005739808905
H	-2.959785682354	2.144278855559	-4.013225989993
H	-1.295870980341	2.106072904614	-4.539317611675
C	-4.146471544449	2.294851508546	-6.486714703030
H	-4.856977276530	2.110014056588	-5.668790194886
H	-4.056724630677	3.383098569694	-6.599041062058
H	-4.588328258751	1.901953330386	-7.406847129538
H	-3.131868619064	1.465386467336	-8.990334342987
H	-1.692743107828	0.449041307059	-9.076064649032

H	-2.850712536608	-1.234685367852	-7.816084302756
H	-4.258261670023	-0.173977598128	-7.709543758342
H	-3.981106054661	-1.513270049005	-5.311168107583
H	-4.345943515787	0.072479422067	-4.555225686986
O	-2.633488947140	-0.127998258686	-2.502674621121
O	-2.251035330465	-2.377666096209	-3.538360167425
Li	1.428765911654	0.141700965138	-1.248574530540
Li	-0.997298450397	0.543215409797	-1.592894806802
O	-0.827270916173	2.358225960074	-2.094185244873
P	-1.454554498025	3.561186665409	-1.441492730987
N	-0.710877286210	4.938551960046	-2.017266019410
N	-3.097924894959	3.757132700700	-1.632980243757
N	-1.270807335928	3.508392149981	0.209001945932
C	-0.897758940507	6.220910372994	-1.365548550613
C	-0.169334216394	4.997868732247	-3.362486122398
C	-3.980770736214	2.703354460165	-1.149921489099
C	-3.698108795052	4.657353946922	-2.601531901996
C	-2.152668518837	4.122319528675	1.185091299116
C	0.078463899759	3.262047660542	0.699561844297
H	0.056631754946	6.766278662249	-1.350599062717
H	-1.641227737963	6.846260834197	-1.885619932035
H	-1.225661195192	6.080424928230	-0.331009749336
H	-0.041421435011	3.981106446284	-3.740323691038
H	-0.827248727402	5.564233805787	-4.042798212693
H	0.812423240316	5.493042404031	-3.340788652808
H	-4.902116354307	3.150724793901	-0.750856047669
H	-4.242720252840	1.995395906057	-1.952218050117
H	-3.494840644411	2.140613771275	-0.345578171121
H	-4.457999497561	5.283812012836	-2.112331074253
H	-2.941605166412	5.312030089742	-3.043358388421
H	-4.185839231390	4.096091965857	-3.412156113186
H	-2.324239019000	3.418110205602	2.011237626586
H	-1.708170501226	5.040166768539	1.603308544829
H	-3.115466594748	4.373559963976	0.732873377521
H	0.008034338844	2.648066596267	1.601478814537
H	0.669097451925	2.714460752051	-0.044228778926
H	0.584845109385	4.208506202245	0.956443407765
O	2.285031482091	1.802130918552	-1.308572488045
P	3.339349329308	2.644326813568	-1.966768941342
N	2.810270489523	3.204221374343	-3.440658035889
N	3.703821562273	4.024168515184	-1.101647351427
N	4.752845146035	1.775052290822	-2.152593901283
C	3.449367008453	4.303926187266	-4.142934995874
C	1.966442348172	2.344109776736	-4.261377998356

C	5.039846307070	4.465578969467	-0.750312851382
C	2.672463337858	5.040414480339	-0.958187111213
C	5.744711821440	2.125659739331	-3.157080666365
C	5.237050239527	0.984956111671	-1.027157849995
H	4.009991487699	3.952081856751	-5.022066428909
H	2.688465292646	5.017099005483	-4.491264837231
H	4.142759805183	4.832866199780	-3.480408506351
H	1.267168631100	1.796717426827	-3.617288608535
H	1.391367884982	2.980686683207	-4.946866228211
H	2.557648497805	1.634748847785	-4.861064487216
H	5.388387554921	5.275209945167	-1.412627972646
H	5.040863901894	4.846950639331	0.280088373858
H	5.751199937371	3.639040878002	-0.804452302716
H	2.883598171061	5.910901974350	-1.602168316070
H	1.692326976649	4.631166840910	-1.227822919339
H	2.629604384564	5.386726305687	0.084132504563
H	6.420116077294	2.937913418593	-2.841101933215
H	6.352141553746	1.236988874247	-3.365150998006
H	5.252200938859	2.413322710187	-4.090331118178
H	5.845587404579	1.575083931042	-0.320556053789
H	4.381716343422	0.544352685722	-0.504794199450
H	5.858874074916	0.170039848212	-1.415164024611
C	-2.544817945013	0.280613592999	1.683656369764
C	-3.514085618640	0.949166633389	2.459276067087
C	-2.994652875506	-0.388678481195	0.528901956955
C	-4.855497402097	0.961741873336	2.092785345473
H	-3.200283133894	1.460825461144	3.369305388447
C	-4.338136012214	-0.377503988832	0.166527022753
H	-2.284913466546	-0.951530605878	-0.071059703247
C	-5.279776275880	0.298996500780	0.939737469057
H	-5.576850514626	1.489765764140	2.714833665502
H	-4.642709112154	-0.905259633363	-0.735449515152
H	-6.330004421752	0.305797233879	0.654516031436
C	2.657842258785	-1.118322936415	-4.391216522940
C	3.704234096909	-0.889575689555	-5.308596664001
C	3.015469220742	-1.555886409283	-3.101474141146
C	5.034991144273	-1.074788763162	-4.952926766262
H	3.457597512340	-0.558696051691	-6.317756442848
C	4.348490700366	-1.735839933437	-2.747454546721
H	2.236447178280	-1.796285883862	-2.384472111765
C	5.369973883318	-1.496354673589	-3.665303831373
H	5.818123800288	-0.888144107745	-5.686684677355
H	4.580624546406	-2.074640854300	-1.738972867318
H	6.412148472865	-1.644199703245	-3.387238548699

Table S62. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with double *exo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *endo*-face.



G = -4408.40518

G_{SP} = -4410.354363

150

20020a_nit_thf: optimized structure // E(RM062X) = -4411.57504449 A.U. after 13 cycles

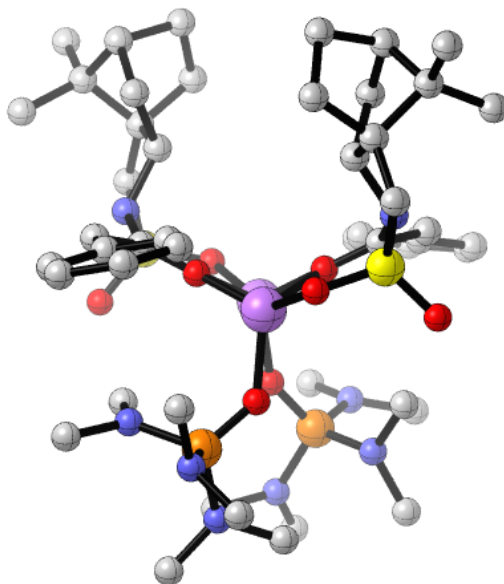
O	-0.013289191382	0.048364641054	0.012872804670
C	-0.001535745856	0.065908182029	1.293264485530
N	1.306600847269	0.062299574896	1.873822381725
S	2.549319606029	-0.679375478030	1.006920457953
O	2.279183037830	-2.101019404162	0.752811471290
C	3.793051754708	-0.524231650407	2.310675352087
C	3.145471315038	0.269419438646	3.425619608592
C	1.600189845021	0.149358344549	3.305181607279
C	1.096677817918	1.431402295765	4.020915477436
C	2.391472219421	2.023752461591	4.606685333885
C	2.906198408105	1.049992318600	5.691456321565
C	3.474094598896	-0.144139293003	4.869956454396
H	3.002259485876	-1.100857103321	5.119569863026
H	4.553518743761	-0.263868533296	5.010062260705
H	2.095730846143	0.742497715901	6.362071402864
H	3.681523679115	1.511469926499	6.311805553248
C	3.397939280946	1.810650532744	3.451191640285
C	3.057775331581	2.561514438299	2.161312320613
H	3.742933134303	2.259494793037	1.358470482062

H	2.040609838095	2.401354493534	1.798028812277
H	3.198317273276	3.638155565785	2.324998168632
C	4.843820260245	2.170676717899	3.802247352696
H	5.524867437820	1.837095822439	3.007228575583
H	4.941027167830	3.261249709768	3.875514085253
H	5.194412072050	1.743705387917	4.745835916988
H	2.282907466245	3.058139478059	4.950089044212
H	0.615843505958	2.109793466091	3.311004830661
H	0.363668574344	1.192530805291	4.798629021586
H	1.242672216699	-0.761375268543	3.807877280177
H	4.672098300025	-0.047459991692	1.864801780820
H	4.030941147321	-1.553926379739	2.595667331332
O	2.889247659504	0.158640868544	-0.164113576349
C	-1.070382888305	0.097421763703	2.157031661504
H	-0.879986571065	-0.061414699330	3.214388473266
O	-0.100422478483	0.941726519783	-2.551948523357
C	-0.157570416236	1.751273763298	-3.542515874070
C	0.872977496274	2.417655338381	-4.161726130149
H	0.662983459500	2.933957243053	-5.093827388609
N	-1.478210166687	1.982360468073	-4.043337066738
S	-2.612400950487	0.745665709461	-3.869480242168
C	-3.909139979794	1.556376921812	-4.834847184105
C	-3.380409673900	2.929741589478	-5.190740744839
C	-3.716265508517	3.475360404311	-6.588826391200
C	-3.295843609540	4.969393394148	-6.468729861275
C	-2.841756016583	5.100773609030	-4.996855446371
C	-1.476162196168	4.402360412305	-4.863176570999
H	-1.039797182973	4.534308786337	-3.869413948504
H	-0.750335608071	4.772277457173	-5.594981059316
C	-1.827582075398	2.912137771117	-5.118519989157
H	-1.400360871919	2.552495884582	-6.066201487463
H	-2.846300999095	6.128441612023	-4.617978147518
C	-3.782601611881	4.118082118088	-4.260201627900
C	-3.473343329251	3.931716404124	-2.772611401747
H	-3.723857901809	4.856011408478	-2.235376396098
H	-4.097800770907	3.130586959675	-2.356132829617
H	-2.433541197478	3.680616711481	-2.553491761655
C	-5.267846319275	4.475202177645	-4.359981511040
H	-5.885533813023	3.655009073734	-3.968952621556
H	-5.473317624937	5.358409639962	-3.742007159101
H	-5.607252168014	4.696482075115	-5.375567649788
H	-4.133192159894	5.638287718700	-6.693120182585
H	-2.482643915388	5.226913605437	-7.156860402956
H	-3.162201292090	2.933636312797	-7.363289027654

H	-4.783022511355	3.364341939738	-6.809790435800
H	-4.055219937211	0.910841704522	-5.706642498174
H	-4.814686386342	1.563548157669	-4.219403802635
O	-2.992154679255	0.634540477532	-2.443796781762
O	-2.196531147651	-0.490241997983	-4.546385324653
O	1.914875982166	-1.488744630052	-2.308278690132
P	2.330188472880	-2.153615154554	-3.588928318543
N	2.619345951645	-3.778016604700	-3.267997667960
N	1.246164945175	-2.218099717256	-4.854562293226
N	3.648320081367	-1.357932735626	-4.225897525004
C	2.942484118152	-4.698174245018	-4.349591136841
C	3.358692066804	-4.054080831949	-2.039594508575
C	0.969906196811	-0.961462904477	-5.558138061005
C	0.006196838437	-2.957366085392	-4.574049361967
C	4.237158761973	-1.721706312619	-5.503167808773
C	4.511052830315	-0.566036979799	-3.360881045287
H	4.013234876927	-4.675525717888	-4.610995875270
H	2.692456110935	-5.719065624611	-4.032133443121
H	2.354568485388	-4.459835896090	-5.240229591391
H	3.059881078367	-3.350308051352	-1.255955292554
H	3.128210484406	-5.074667980112	-1.706907006532
H	4.449083429141	-3.984980513671	-2.197128480737
H	0.566627455848	-1.201102874347	-6.550436723700
H	0.230146976578	-0.360537984453	-5.014047929242
H	1.887742354799	-0.379541451699	-5.680579193500
H	-0.535116434104	-3.079138890845	-5.520507239607
H	0.238678116788	-3.948795251245	-4.172269072149
H	-0.631545637552	-2.412552521384	-3.863125270463
H	4.504021374343	-0.809483040746	-6.055900404587
H	5.151111732239	-2.321912321218	-5.372539859709
H	3.522981938581	-2.291323484115	-6.105541805108
H	3.998511817837	-0.348858715961	-2.418765701557
H	5.451736886958	-1.098559297336	-3.145635281667
H	4.753303279485	0.383506025200	-3.856076860857
Li	1.267469192926	0.048720465444	-1.485052144953
Li	-1.323193866042	-0.114924528634	-1.423881402283
O	-1.789372651235	-1.884347909732	-1.758889812504
P	-2.093764129178	-3.238251857401	-1.185382688090
N	-2.233976581723	-4.328219564479	-2.457241103107
N	-0.965961305791	-3.970360565769	-0.198902864600
N	-3.460633314200	-3.145356494940	-0.237033473533
C	-2.429332875198	-5.747384024868	-2.194962247112
C	-2.984355551996	-3.850068681266	-3.614892862740
C	-0.789591162345	-3.405623923030	1.142900190806

C	0.329789782409	-4.249203738296	-0.836059151380
C	-3.966885412366	-4.279951913190	0.515888364847
C	-4.425630915448	-2.076228323159	-0.450096864578
H	-3.487693000619	-5.996350087017	-2.012623927638
H	-2.092533453658	-6.318520380937	-3.070102749563
H	-1.837219549697	-6.059476259764	-1.330271099615
H	-2.782271659869	-2.786717337064	-3.779550760018
H	-2.667167283308	-4.413329687720	-4.502318280818
H	-4.070301374200	-4.000464957922	-3.485857996648
H	-0.331878210170	-4.170355811622	1.783532023658
H	-0.130365660547	-2.528618605087	1.116909237663
H	-1.754956466486	-3.118735488973	1.569287994324
H	0.912449530847	-4.879882451024	-0.153140057927
H	0.181380703175	-4.792028592697	-1.775064678327
H	0.886740190317	-3.321521998139	-1.031416660645
H	-4.301774743869	-3.941212524337	1.506844598211
H	-4.822232794761	-4.753938979842	0.009598719452
H	-3.180419958153	-5.027648989672	0.656535227570
H	-4.742065012136	-1.670396008416	0.519806986566
H	-3.969376081671	-1.271335084212	-1.034412484135
H	-5.316803046687	-2.447743454442	-0.981679211726
C	-2.452618472876	0.353293950590	1.787700892542
C	-3.486490551130	-0.020264159119	2.675504317568
C	-2.836049950200	1.044978735872	0.620587760715
C	-4.816235744083	0.289038914525	2.418369654143
H	-3.224416427213	-0.549875027576	3.591321255626
C	-4.170961193643	1.338574546311	0.358842135777
H	-2.071523023463	1.422449680411	-0.056888136563
C	-5.173802967593	0.969942682551	1.253062804551
H	-5.582484080634	-0.007705293508	3.133281639268
H	-4.418860063459	1.866991454772	-0.559462216267
H	-6.215206559204	1.208555158703	1.047985477279
C	2.235500646529	2.521149902501	-3.666445938594
C	3.270006873212	2.884244081187	-4.557836068547
C	2.589208485154	2.369353858729	-2.310188251179
C	4.571251318639	3.093994216845	-4.118775658826
H	3.029756689379	3.017318015579	-5.612568770589
C	3.897284347026	2.564534492865	-1.877118670765
H	1.815039517483	2.166411919018	-1.571648007018
C	4.900226058890	2.932453532192	-2.771516180140
H	5.337984205242	3.383087175642	-4.836298407289
H	4.123637787785	2.427593082393	-0.821670064867
H	5.919791402241	3.091617490935	-2.427032998907

Table S63. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with double *endo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *exo*-face.



G = -4408.398435

G_{SP} = -4410.350058

150

20020a_endo_H-exo_thf: optimized structure // E(RM062X) = -4411.57066474 A.U.
after 12 cycles

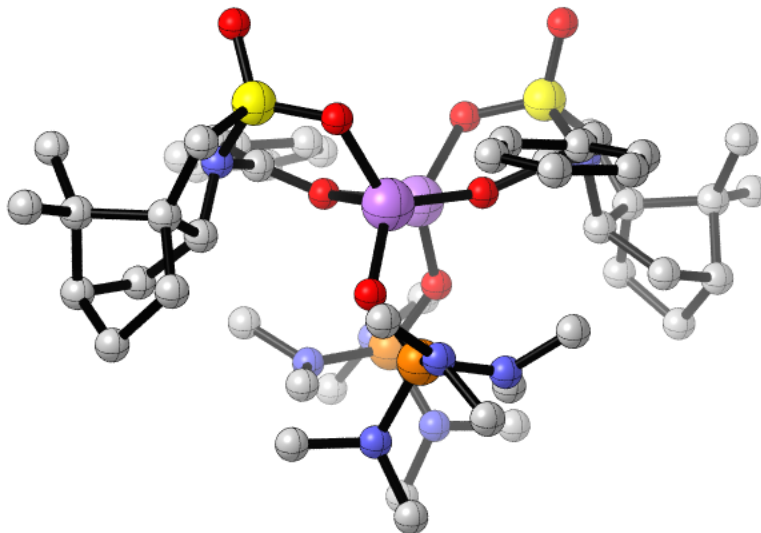
O	0.036910167390	1.198773999972	-0.208599957469
C	-0.205303484641	0.671529253624	0.927424169031
N	0.893378656248	-0.075471220105	1.556632569184
S	2.428562379943	0.628168728590	1.508891792459
O	2.903893733041	0.820856312728	0.113935843022
C	3.275617142330	-0.840665542369	2.117339916672
C	2.375239578717	-1.995961127553	1.690605896344
C	1.101643025777	-1.426976167952	0.989628523084
C	0.013358070176	-2.481227284899	1.276290467487
C	0.844453716262	-3.632584334301	1.872696569888
C	1.814279416579	-4.141553655064	0.776624025556
C	2.921776992316	-3.046650205023	0.714275262737
H	3.055025494180	-2.626252289718	-0.289147419905
H	3.893467233218	-3.428238321039	1.045170381728
H	1.295918189798	-4.258342189483	-0.182345466996
H	2.235934440592	-5.118439521494	1.035021260889
C	1.788314510840	-2.876137591688	2.838836254999
C	1.072293409461	-2.101488144877	3.947233477780
H	1.804505202841	-1.607207240079	4.600483711612

H	0.389066417013	-1.332964630945	3.580267316722
H	0.505218089812	-2.803735546971	4.572925702728
C	2.837765762696	-3.764010495444	3.511307010841
H	3.625057282087	-3.147042907067	3.966871051240
H	2.367920415748	-4.341024084459	4.318065102351
H	3.317749912946	-4.475089668085	2.832868787092
H	0.239301162094	-4.421785585144	2.331888228496
H	-0.733003401049	-2.102839765502	1.980702107472
H	-0.511515979501	-2.771405280017	0.359868857445
H	1.273978856073	-1.328914327907	-0.093189839657
H	3.368192113143	-0.734960914542	3.203005961454
H	4.266332369718	-0.833600205248	1.653322889662
O	2.477056168332	1.789148349566	2.399485302224
C	-1.372580756881	0.620719538073	1.636250310497
H	-1.322146622038	0.247341045658	2.656231626068
O	0.708069521318	0.988324901874	-2.758279436884
C	0.736721698619	0.390589687572	-3.889561451199
C	1.799268586771	0.071322357376	-4.682452907926
H	1.578337116688	-0.337275462453	-5.665355262215
N	-0.548989567640	-0.106372959988	-4.398177107230
S	-1.813589331490	1.004241312726	-4.493673433554
C	-3.068568456190	-0.238327540956	-4.857257817664
C	-2.505993454528	-1.527102020470	-4.264268879628
C	-3.292890944144	-2.249259189534	-3.160916548763
C	-2.534749030015	-3.608301292626	-3.068244252698
C	-1.486501353060	-3.530816473300	-4.205877382609
C	-0.360341957258	-2.582818008829	-3.750275653663
H	0.452455435664	-2.522018650908	-4.480763023025
H	0.075854464048	-2.880590638174	-2.790825062788
C	-1.109128017654	-1.239449790505	-3.633587417622
H	-1.213436210949	-0.941194236904	-2.578986596944
H	-1.129278827913	-4.508210095073	-4.547904847676
C	-2.210651284095	-2.679412724176	-5.276646313040
C	-1.338144530663	-2.292903558439	-6.472487733960
H	-1.037904204311	-3.202968675943	-7.008855139278
H	-1.909829083211	-1.676389221616	-7.179864762510
H	-0.438839740338	-1.735553044462	-6.204956836479
C	-3.482244502255	-3.321948769694	-5.835469816007
H	-4.070613859068	-2.580218785239	-6.393677373682
H	-3.212287861807	-4.119980617170	-6.538836707983
H	-4.131032220095	-3.759883105803	-5.071763584615
H	-3.216814999456	-4.453369910806	-3.207926701410
H	-2.049776082227	-3.743900012347	-2.094652706996
H	-3.271636547255	-1.684286728716	-2.221680580381

H	-4.342572956576	-2.383812192667	-3.443020256316
H	-3.991679901774	0.119588089967	-4.391724256298
H	-3.187078964369	-0.272729681025	-5.945053068671
O	-1.556825413991	1.968541195447	-5.564117118813
O	-2.162770142302	1.554602925722	-3.155953657560
Li	1.682058173680	1.670521043946	-1.218885440786
Li	-0.742327117682	1.925876993367	-1.819265722596
O	-0.633954005353	3.795419662773	-1.735178857681
P	-1.161477171702	4.816559029772	-0.762845167290
N	-0.313841282454	6.237350553657	-0.971471037784
N	-2.791566897236	5.200957019488	-0.919784780796
N	-1.034260447176	4.336570555483	0.819695049027
C	-0.497286373179	7.338925156788	-0.045409532294
C	0.248129670675	6.595013718967	-2.263759798579
C	-3.709681428171	4.066236785880	-0.824343865547
C	-3.140715534461	6.105656416046	-2.012402789314
C	-1.939080841254	4.698917042110	1.897825816934
C	0.289048460726	3.920167957824	1.273911756511
H	0.457465318816	7.865284087786	0.088264330579
H	-1.242985908367	8.066511258244	-0.405693560913
H	-0.820189979232	6.965838196888	0.931999310625
H	0.354189551574	5.693036399572	-2.872370865936
H	-0.380146864201	7.332530198155	-2.790055317121
H	1.247628262017	7.031302343200	-2.120718707428
H	-4.719876174175	4.439226813450	-0.611237791301
H	-3.730377566201	3.482474082047	-1.757888245592
H	-3.404696239882	3.402152152038	-0.009216092679
H	-4.187152160260	6.407626652038	-1.887431936762
H	-2.522176612016	7.006795485237	-1.978990281455
H	-3.034746091391	5.631771613703	-3.001792792829
H	-2.182625021913	3.802087137851	2.485104162804
H	-1.470922567130	5.434173171308	2.571675920125
H	-2.862614998318	5.126517051907	1.501804743567
H	0.188684914389	3.075003949656	1.964538551956
H	0.904324502414	3.604064076385	0.425150957585
H	0.796385865979	4.745072459016	1.802278535042
O	2.544673922051	3.330970886575	-1.364580645068
P	3.383655404401	4.254103121667	-2.201495297905
N	2.609722117575	4.690204021418	-3.605921988228
N	3.745821863080	5.635385107886	-1.342129260292
N	4.851880497072	3.588644138022	-2.642962660462
C	2.899742388256	5.915553772789	-4.322832199096
C	1.861055313639	3.692586850942	-4.356105753171
C	4.957045139564	6.410521399448	-1.533830915449

C	2.926911839384	6.049957551302	-0.214943262605
C	5.448440800399	3.754169468012	-3.957270190884
C	5.779594121287	3.252292127192	-1.573752873363
H	3.536404398851	5.738146132285	-5.204588203861
H	1.958096455413	6.365171167393	-4.669904898128
H	3.398020601455	6.636533946465	-3.667700335120
H	1.592701380533	2.859436196435	-3.700531610546
H	0.931759578648	4.144417234727	-4.730308595069
H	2.435720684936	3.314282306128	-5.217984358268
H	4.710870880092	7.463964826587	-1.733971432486
H	5.591840962703	6.373564612543	-0.635382643699
H	5.533134666560	6.029139768225	-2.381507976995
H	2.755327562026	7.135143424628	-0.259862230602
H	1.960966505778	5.541134281078	-0.245146782123
H	3.424682739963	5.816713947862	0.739253387757
H	6.065001851637	4.666309539184	-4.034658412488
H	6.092577612189	2.890418423882	-4.160373133472
H	4.672847906912	3.782770596855	-4.727691392668
H	6.470465731593	4.080877624391	-1.346407828710
H	5.222234760367	2.992818757832	-0.667001101245
H	6.374446463943	2.380393245215	-1.870008877953
C	-2.691413524546	0.927708676206	1.085835818908
C	-3.743591641885	1.348969668841	1.920046792391
C	-2.992453583483	0.700106734632	-0.270025094302
C	-5.029656884113	1.534708766754	1.420588538371
H	-3.544489529728	1.518963185676	2.977803369122
C	-4.277270397592	0.882401671414	-0.767613721685
H	-2.210722155334	0.332334154899	-0.931985114597
C	-5.307574637562	1.302859034709	0.073096460877
H	-5.823511852928	1.860542724094	2.090912010402
H	-4.466996708207	0.698211453381	-1.824360024794
H	-6.313944565356	1.446818191613	-0.314703922480
C	3.202383284334	0.174806286836	-4.289394558327
C	4.208570427048	0.229024339284	-5.271722648130
C	3.610518826762	0.120158424955	-2.943981812159
C	5.555759400339	0.220879839912	-4.925333694266
H	3.919810580834	0.261704173432	-6.321904600520
C	4.956877542400	0.118911044211	-2.599012227599
H	2.865315057225	0.015980202119	-2.160717156645
C	5.941296591412	0.166769593466	-3.585933404036
H	6.311755740479	0.256949733153	-5.708331241630
H	5.231616514298	0.068002766773	-1.546381693057
H	6.995923527923	0.158025806180	-3.316518331216

Table S64. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with double *endo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *endo*-face.



G = -4408.415253

G_{SP} = -4410.365572

150

20020a_endo_H-endo_thf: optimized structure // E(RM062X) = -4411.58869636 A.U.
after 12 cycles

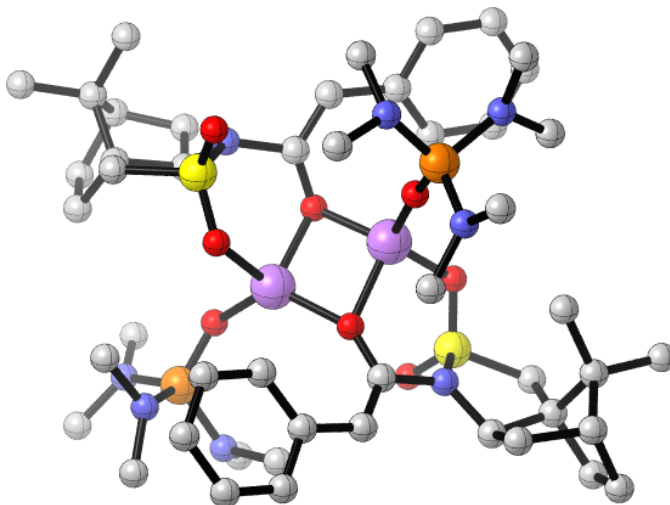
O	-0.286432534917	0.414769613405	0.250512037108
C	-0.203655275539	0.505448884184	1.532251685814
N	1.150321040332	0.470767125418	2.102856841690
S	2.125071084057	1.782960117118	1.730761749701
O	2.176577164867	2.012343319194	0.261310737238
C	3.683043874784	1.001049330779	2.222516215894
C	3.348871020636	-0.464902742146	2.446179011804
C	1.934159468512	-0.758673525940	1.876892461467
C	1.463737603708	-1.983626848385	2.693381187480
C	2.721028364721	-2.340025300825	3.514557760388
C	3.803369528778	-2.829043464797	2.524691600617
C	4.260260746970	-1.525473872769	1.805020139706
H	4.104055274320	-1.555145856675	0.720321083052
H	5.318715036232	-1.306960508553	1.983643083207
H	3.396996523740	-3.571892539116	1.827973822818
H	4.637824795416	-3.304925073888	3.050596377834
C	3.252535070242	-0.946203736081	3.928956931756
C	2.303879281030	-0.150455033212	4.827997107712
H	2.647839902019	0.888766499233	4.927904965050

H	1.273937783793	-0.119113997707	4.469988242436
H	2.309914342347	-0.590343845265	5.834120134194
C	4.613442906657	-0.971089609552	4.629703787064
H	4.986990084982	0.053094451447	4.767446291909
H	4.506751423780	-1.414470890205	5.627916046354
H	5.381201034285	-1.537281229946	4.095215358650
H	2.527287743826	-3.033491990053	4.340209400923
H	0.608144412362	-1.728006620683	3.327806024033
H	1.155696635756	-2.806662384751	2.038450061884
H	1.986117781023	-0.973558831237	0.801605952486
H	4.036330180545	1.518527443001	3.120621276416
H	4.373445082453	1.182170831304	1.393066832850
O	1.759032736796	2.941864145330	2.545780900595
C	-1.169617549581	0.548026529360	2.495021544519
H	-0.818158413477	0.557653590439	3.523620629125
O	0.153673284667	1.438786014966	-2.462885983965
C	0.003425388139	2.325101809237	-3.384759395448
C	0.913578808881	3.094609442960	-4.049046794713
H	0.518383274795	3.723765735938	-4.842525611168
N	-1.360909435207	2.505272428103	-3.900657084460
S	-2.466071852469	3.140592429858	-2.811918781935
C	-3.942019274669	2.675724764206	-3.753337049969
C	-3.446782657174	1.756611585845	-4.858015789086
C	-4.194974238072	0.433226658880	-5.093288991760
C	-3.620360124935	-0.029168093801	-6.465112398778
C	-2.651172981545	1.109608408718	-6.858014061972
C	-1.408228140936	0.999168528163	-5.949698566169
H	-0.619535755259	1.704938025463	-6.232078680271
H	-0.974417260190	-0.007146351053	-5.970027872559
C	-1.982219173945	1.338170689760	-4.555409738507
H	-1.958092564282	0.475389199247	-3.877143827059
H	-2.415136382220	1.143892858549	-7.927240562573
C	-3.363316994236	2.363670348148	-6.294705419611
C	-2.559206620263	3.658952356843	-6.425563101114
H	-2.559736712978	3.976840961244	-7.476640848910
H	-3.028968477049	4.464950558123	-5.844189661875
H	-1.524768670940	3.575844449046	-6.089447578819
C	-4.742848398712	2.633312436939	-6.901276028006
H	-5.241701386643	3.448797329028	-6.359438873869
H	-4.630877774410	2.957369610049	-7.943793685957
H	-5.411875382800	1.768435396973	-6.892432229954
H	-4.415895476903	-0.148904250658	-7.208172800860
H	-3.096436404929	-0.990073649362	-6.397459087317
H	-3.986259421994	-0.271032482897	-4.279499734338

H	-5.279022567777	0.585909979287	-5.132371098591
H	-4.606199805048	2.191112761951	-3.031180799066
H	-4.399681680687	3.601754469869	-4.116923488111
O	-2.279985756921	4.585655641143	-2.675700067759
O	-2.473170628060	2.364732915574	-1.542122273478
O	2.396870315448	-0.662446789593	-1.319348728047
P	2.807075931139	-1.427910862641	-2.555274394502
N	2.542455789117	-3.061316136458	-2.261246318685
N	2.003088365055	-1.200047903440	-3.984226764254
N	4.389405536407	-1.047979020824	-2.929152368713
C	2.779839732520	-4.056416948599	-3.298134075647
C	2.807763059197	-3.555513468684	-0.917284450749
C	2.312016122484	-0.079725736525	-4.869676625532
C	0.602473361976	-1.609206905818	-4.068438618270
C	5.058506742961	-1.634894626925	-4.081260869503
C	5.297315074237	-0.628888045211	-1.870969300334
H	3.818932826900	-4.422223729325	-3.292149254317
H	2.116131742023	-4.914614884769	-3.125844277797
H	2.556055824751	-3.639625782670	-4.283875757923
H	2.472307590216	-2.821173435750	-0.180427366404
H	2.249990935967	-4.488579112732	-0.765128747904
H	3.878513034219	-3.767942132908	-0.753959227386
H	2.333032650723	-0.435612350298	-5.909848338100
H	1.543776038136	0.697922903732	-4.773951851106
H	3.283493498018	0.357403275986	-4.621313667495
H	0.361069678772	-1.790450015185	-5.123922094949
H	0.429859661649	-2.533440245082	-3.509618328324
H	-0.062168905345	-0.824494392326	-3.670057654467
H	5.713729963193	-0.881867772950	-4.540658892527
H	5.675465880855	-2.500498354361	-3.794247776307
H	4.327929574235	-1.955063340634	-4.829611332438
H	4.735077572222	-0.125192583456	-1.081080201214
H	5.844960094700	-1.483523193272	-1.441406225695
H	6.030708886908	0.074275701227	-2.287269773463
Li	1.216748794885	0.797570043288	-1.008147275330
Li	-1.327992836162	0.736604399542	-1.321115791235
O	-2.316165294909	-0.703721048245	-2.075914784164
P	-2.575385449359	-2.127926273597	-1.644021328025
N	-2.129787405370	-3.139543117975	-2.909946671092
N	-1.741074836284	-2.779869396037	-0.371736638845
N	-4.173450183475	-2.272989687612	-1.182633213876
C	-2.200033470186	-4.587759172463	-2.770368727964
C	-2.392700139868	-2.678384257667	-4.266051851636
C	-2.142616329877	-2.544820089042	1.013149090187

C	-0.299279762344	-2.975323581808	-0.510379390111
C	-4.714855284294	-3.539112132413	-0.710016124989
C	-5.171841607617	-1.384093551468	-1.759481897723
H	-3.187235856581	-4.984796679167	-3.055610697531
H	-1.446994603051	-5.045031783881	-3.426501925707
H	-1.983691121354	-4.881632833391	-1.739675120419
H	-2.180156443913	-1.608824536646	-4.340583442505
H	-1.734433394492	-3.218302148141	-4.958893472175
H	-3.436430485139	-2.861632741247	-4.574836060298
H	-2.075404840884	-3.487859711309	1.574613290616
H	-1.477637679234	-1.805290919242	1.476837602826
H	-3.169268973826	-2.170673549217	1.063546992934
H	0.008251837510	-3.765553618206	0.186862470697
H	-0.042217173707	-3.289656305093	-1.525941785149
H	0.248676943255	-2.047135352628	-0.277120077246
H	-5.433077246984	-3.345422187040	0.098732712902
H	-5.237251321459	-4.081516250908	-1.513229377914
H	-3.918055424069	-4.175687923924	-0.314860983799
H	-5.964610559519	-1.209624666824	-1.020091319466
H	-4.710251982992	-0.427013045895	-2.013793644818
H	-5.632031403159	-1.818796532845	-2.661744712140
C	-2.607921516167	0.416398284937	2.281380951558
C	-3.395786568548	-0.212743831818	3.262770614647
C	-3.247159571253	0.855717789634	1.112895552583
C	-4.751141495991	-0.444521362487	3.057179618003
H	-2.924868598507	-0.544034605303	4.188026712934
C	-4.605983657415	0.632768807447	0.912261927055
H	-2.685993942187	1.420234580389	0.377511555971
C	-5.364663889243	-0.036424327439	1.871214484087
H	-5.334593214441	-0.947040295266	3.826954178679
H	-5.076365942609	0.999918127830	0.001812921404
H	-6.426368364593	-0.214982526111	1.711264257320
C	2.365308663885	3.029241171970	-3.907536663187
C	3.179394460405	3.279312558357	-5.027482450798
C	2.997461467985	2.685400105395	-2.703739268185
C	4.560372358769	3.133205485310	-4.959659250197
H	2.711830461857	3.568338303686	-5.968474614812
C	4.380555089146	2.549426639918	-2.633853694306
H	2.405140609762	2.572281499281	-1.803301206155
C	5.171477601077	2.751238103941	-3.763796127469
H	5.165844525274	3.318374127986	-5.845442631796
H	4.842567782501	2.296839016494	-1.681113022795
H	6.252825410677	2.639668351022	-3.709695208151

Table S65. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with chelation to one *endo* sulfonyl oxygen and one *exo* sulfonyl oxygen; the HMPAs are aligned *anti* to each other.



G = -4408.420644

G_{SP} = -4410.370707

150

20020a_mis_c_thf: optimized structure // E(RM062X) = -4411.59162060 A.U. after 13 cycles

O	-0.106228568846	-0.005223919999	-0.035999676284
C	-0.062722613237	-0.055639993782	1.245670215457
N	1.277600014391	-0.177163590904	1.843601652879
S	2.255509089070	1.176264255704	1.649488664592
O	2.347857483227	1.580341246839	0.220501532144
C	3.799321276937	0.342648072320	2.090107186750
C	3.495127378577	-1.144240880493	1.967430763193
C	2.071920095638	-1.330953108528	1.369999948850
C	1.618205124330	-2.700077172760	1.920973569314
C	2.902029866888	-3.217878241140	2.600898588714
C	3.954749569805	-3.456400686244	1.492644014220
C	4.401752592151	-2.019353601525	1.084619314899
H	4.234690807233	-1.804530943694	0.021401798965
H	5.462008201006	-1.843351628256	1.298382965054
H	3.519131828666	-4.010236270382	0.653621940496
H	4.800924979521	-4.044790772855	1.863363417676
C	3.437308030784	-1.948174260811	3.305288518799
C	2.505629770891	-1.379534614167	4.377738762935
H	2.887110707780	-0.416996464077	4.747248644360

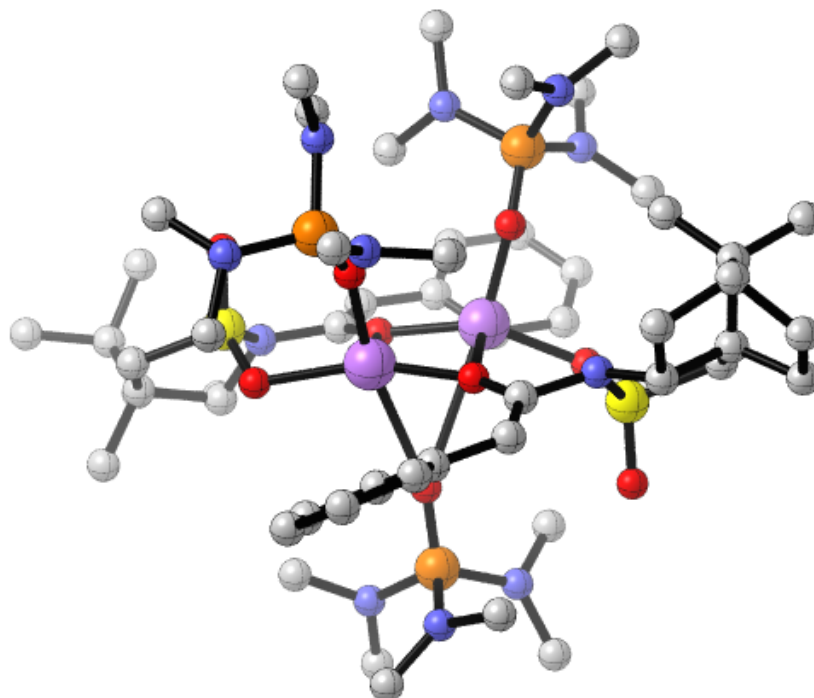
H	1.482036279730	-1.216898010830	4.037017587209
H	2.482514709574	-2.066402987845	5.234278529343
C	4.813733758244	-2.118035253325	3.952554752553
H	5.211507541006	-1.140767037949	4.260319660782
H	4.723662371091	-2.732153970482	4.857683983163
H	5.555067234772	-2.592030097805	3.303217834208
H	2.739690282291	-4.083300878638	3.252755259024
H	0.789626128990	-2.584882535285	2.627624849406
H	1.279291862994	-3.361261529068	1.116697971290
H	2.109247890501	-1.326656567302	0.272610141432
H	4.050203667021	0.657237455734	3.108644797463
H	4.555770072824	0.718240938442	1.394651864770
O	1.866380370063	2.228174898595	2.593914947205
C	-1.075881006869	-0.044057364323	2.157342784822
H	-0.789262969571	-0.030003455210	3.206037819194
O	0.154399614417	1.759545710334	-2.284412390659
C	-0.058298816402	2.420814826082	-3.364625741905
C	0.766011532634	3.307971893021	-4.007941808411
H	0.450562903340	3.692945812519	-4.973341700631
N	-1.359760878387	2.196653528904	-3.921809457897
S	-2.026253051544	0.662773986675	-3.691595777948
C	-3.443623477723	0.921603224088	-4.782710076467
C	-3.367074148640	2.364292563033	-5.237360702599
C	-3.782899882836	2.656714528625	-6.688947857034
C	-3.879220119513	4.209539575051	-6.702813385844
C	-3.561135047785	4.600834469937	-5.242799306820
C	-2.051656819151	4.391168896797	-5.021150461450
H	-1.724932572528	4.749275384496	-4.042253291203
H	-1.447981806785	4.900301778676	-5.779983822276
C	-1.898448042662	2.850932581172	-5.116536232404
H	-1.311268897352	2.551844580300	-5.997559988312
H	-3.909816250470	5.600449467217	-4.961340369157
C	-4.174484918504	3.434005688213	-4.431719121366
C	-3.899395145170	3.500942210863	-2.924971231135
H	-4.447738833529	4.354592840324	-2.502768686748
H	-4.270413802132	2.593080227054	-2.430550491274
H	-2.845883934261	3.605708416415	-2.657414001320
C	-5.688694001180	3.281035512346	-4.596506241241
H	-6.030547479330	2.348819460906	-4.126318045961
H	-6.197529686907	4.107818830472	-4.084804119116
H	-6.027635589139	3.276435687552	-5.636280815379
H	-4.878153279248	4.544423559631	-7.000864237026
H	-3.164324453373	4.662842909051	-7.398771986058
H	-3.040505152967	2.264862529612	-7.392931815479

H	-4.741278725852	2.182659804016	-6.924977687830
H	-3.309571582883	0.207084732329	-5.601204936737
H	-4.341836156105	0.670398019125	-4.209412661514
O	-2.471659972266	0.523081390575	-2.286037057207
O	-1.167618037295	-0.406709004318	-4.217059069753
O	2.469327690976	-0.709399498269	-1.878086224952
P	3.539765414979	-0.758482242689	-2.942012260368
N	4.422415405269	-2.156253133698	-2.723977010423
N	3.012275587032	-0.724111866222	-4.527566219984
N	4.565257238993	0.540716891040	-2.849008405363
C	5.652302067613	-2.366163060839	-3.468903409778
C	3.805689522310	-3.365642099922	-2.200261808402
C	2.169055464770	0.422309776285	-4.879368807658
C	2.540790474088	-1.978346386866	-5.108989797244
C	5.259818562864	1.168197243337	-3.962824119643
C	5.120347794770	0.830699341088	-1.534127245578
H	6.369692802661	-2.906735709573	-2.838161655204
H	5.487775100681	-2.953291857964	-4.386321929784
H	6.097816274725	-1.405375717478	-3.745161774925
H	2.905894122572	-3.103553182623	-1.636160997507
H	3.533621498645	-4.067411297113	-3.004988727264
H	4.511957468747	-3.869574926401	-1.527075948219
H	2.240986195697	0.602423634445	-5.960427258012
H	1.117811644289	0.243308780991	-4.608945771199
H	2.514623611170	1.318770962091	-4.355650543906
H	2.444400661666	-1.839129421413	-6.192046875193
H	3.264997241916	-2.779234945310	-4.933968761338
H	1.560315425590	-2.282755249641	-4.711327209746
H	5.090012235955	2.254104933214	-3.933136306365
H	6.343139830971	0.980490141107	-3.904002007407
H	4.887918502142	0.775414332948	-4.911729284475
H	5.346296101700	1.901355069294	-1.470424220938
H	4.377092465714	0.595504671072	-0.766649535589
H	6.046643451897	0.261885909384	-1.347986515564
Li	1.293637274280	0.624054319870	-1.234936296613
Li	-1.203909791107	1.281724785247	-0.941123857784
O	-1.707199069042	2.655349958769	0.140384891761
P	-2.094479850469	3.911529422600	0.864590221081
N	-3.640479265089	3.797501144223	1.461773368370
N	-1.218519226331	4.335875091687	2.219150154176
N	-1.977661090001	5.185682322774	-0.210115225293
C	-4.184068336273	4.595410516290	2.548776930237
C	-4.646068260271	3.188101668937	0.603128121522
C	0.057129342661	5.028041932730	2.048157309663

C	-1.223248410871	3.415303399763	3.356677197746
C	-2.471814173146	6.502316532256	0.151180960773
C	-0.970516873204	5.172835212651	-1.262979241530
H	-4.903307752377	5.340050572101	2.173866781372
H	-4.709798034944	3.939209189399	3.257296385147
H	-3.382568805156	5.114965459907	3.079110417275
H	-4.175749745036	2.439025125934	-0.041363598072
H	-5.392389274729	2.683549044226	1.228161471937
H	-5.158128437752	3.940684738019	-0.018154276816
H	0.306272370607	5.528320897545	2.992498543496
H	0.871008037479	4.333357028592	1.798520997266
H	-0.023757089881	5.793609931242	1.271862093214
H	-2.154235768821	2.839545940975	3.369925487785
H	-0.372567472540	2.722056454307	3.305080907038
H	-1.156931157751	3.994749641137	4.287888790982
H	-1.691193421069	7.135837301633	0.602900297835
H	-2.843404637558	7.007290956849	-0.749983691100
H	-3.304195439981	6.416858104946	0.856342521314
H	-0.066934708868	5.736116088392	-0.977745214344
H	-0.686022384402	4.140361819035	-1.490068076798
H	-1.389912872829	5.638201501309	-2.164565511367
C	2.054764012847	3.770298716188	-3.521300104652
C	2.897443302752	4.494593614672	-4.393023727540
C	2.517480164346	3.563375330121	-2.204960271317
C	4.126839238792	4.989574663232	-3.974562421363
H	2.566701475700	4.672691736929	-5.416225420668
C	3.748664853327	4.064256963229	-1.792287879379
H	1.895816503301	3.035473793633	-1.490697060435
C	4.567120348451	4.778767814079	-2.666839317768
H	4.746953876353	5.546125944991	-4.675841418834
H	4.061188671525	3.896553966940	-0.762298552508
H	5.527880770487	5.168475048372	-2.336408240274
C	-2.502379119040	-0.050750355200	1.851045722234
C	-3.427134460378	0.288126679224	2.858017727428
C	-3.020348916348	-0.441459020476	0.601815663492
C	-4.798465154078	0.232454105759	2.633343049691
H	-3.054069731137	0.581428199602	3.839227509601
C	-4.393231617770	-0.493818699200	0.379880705891
H	-2.339380749220	-0.731094525058	-0.193457925415
C	-5.294140003313	-0.162989510209	1.390841597805
H	-5.485354641528	0.495748094630	3.436610612150
H	-4.758863344839	-0.805130160405	-0.597609043488
H	-6.367000930280	-0.208390823061	1.213678606715

Solvent-bridged HMPA-solvated dimers of enolate **8o**

Table S66. Atomic coordinates and single point energies of the *tris*-HMPA-solvated symmetric dimer of **8o** with chelation to one *endo* and one *exo* sulfonyl oxygen where the μ_2 -HMPA is on the camphor *endo*-face.



G = -5228.179723

G_{SP} = -5230.481504

179

30031_1-1_O_Tol: optimized structure // E(RM062X) = -5231.9531623 A.U. after 14 cycles

O	-0.929196173161	0.966468605561	0.428995286457
C	-1.911770919733	1.596799062920	0.918411990977
N	-3.136162503764	1.430317464148	0.150225315898
S	-2.972129499076	1.810825477928	-1.487677937286
O	-2.630522464551	3.226385119870	-1.685680888819
C	-4.722798340391	1.577171940513	-1.877915569891
C	-5.440356992679	1.551238996175	-0.537869056878
C	-4.436044216542	1.932402640563	0.592206863742
C	-5.021755408191	1.227139752979	1.838818579575
C	-6.375100083497	0.707178668689	1.323266531787
C	-7.258513862210	1.932848255598	0.990295822725

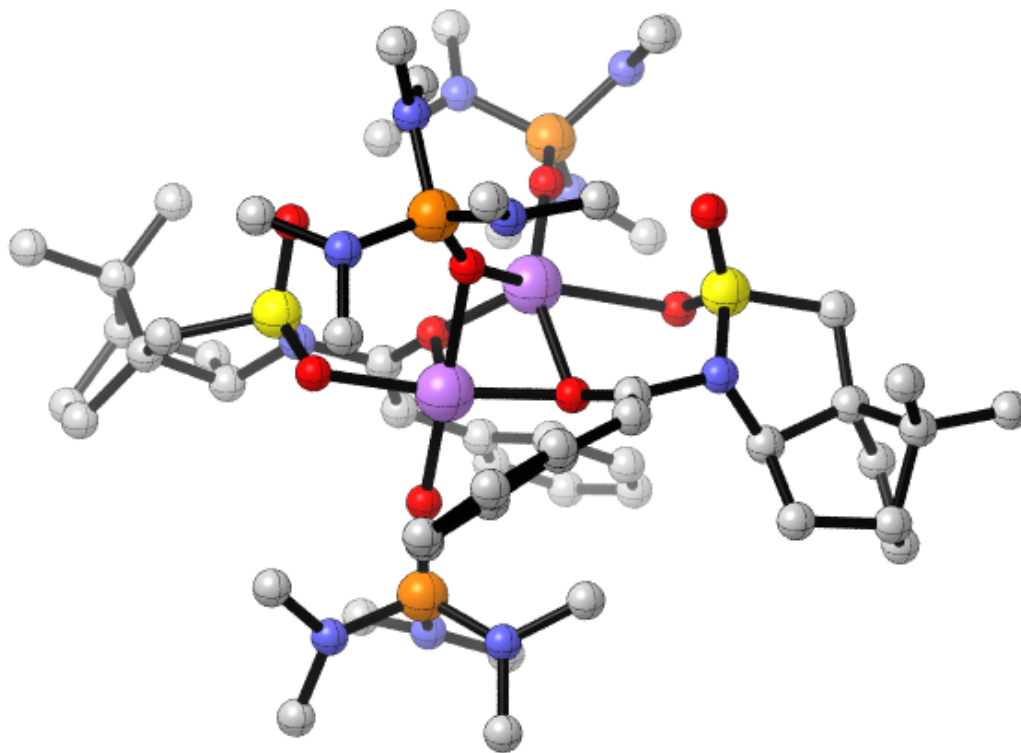
C	-6.649072066634	2.477854771474	-0.335512178679
H	-6.335700705852	3.525427689766	-0.265966419182
H	-7.352832576723	2.401681444401	-1.171419584805
H	-7.225290634010	2.674253623779	1.796729610880
H	-8.308309803543	1.649587448896	0.860410543552
C	-5.995419999185	0.166160543013	-0.074967255745
C	-4.984206907698	-0.983144044497	-0.060522907445
H	-4.765982064541	-1.310799441516	-1.085397482985
H	-4.020419966180	-0.755129347535	0.399980949031
H	-5.432997077039	-1.840668322366	0.459359821122
C	-7.188775824994	-0.305095966859	-0.910265005125
H	-6.884679407607	-0.467182002808	-1.954300481441
H	-7.549063049393	-1.268538617982	-0.527088963858
H	-8.036356661988	0.386094415999	-0.912700835030
H	-6.852635565885	-0.016793169284	1.992526300735
H	-4.367276039472	0.411745258814	2.157723510412
H	-5.133512092940	1.918520759976	2.680962408855
H	-4.397210556987	3.024573953114	0.723694809225
H	-4.802157050953	0.638027644457	-2.435727441221
H	-4.995707736425	2.419124607430	-2.520711865755
O	-2.135164095974	0.811750129026	-2.177988598376
C	-1.957245913068	2.355705787884	2.059957505447
H	-2.905364464898	2.771009850594	2.388968918594
O	1.255421402117	-0.543203352170	-0.790634085328
C	2.277990441871	-0.969339035575	-1.412448408493
C	2.339371382445	-1.493425859110	-2.680522634546
H	3.219304778289	-2.064096631389	-2.954837188502
N	3.538483620458	-0.990095647776	-0.664746991881
S	3.385830768602	-1.041190889651	1.009659445206
C	5.150717092058	-0.855079042695	1.361552847524
C	5.812424428520	-0.537096255331	0.036122529239
C	6.809846620216	0.635276069794	0.019269010694
C	7.523750418265	0.452755260672	-1.350133876796
C	6.866367833966	-0.820352004912	-1.925023067646
C	5.432621768017	-0.458686377066	-2.358363812015
H	4.962793058792	-1.272232217054	-2.908083625877
H	5.402433639429	0.422355649426	-3.008061376163
C	4.718845626926	-0.173504350651	-1.011759161832
H	4.472472310677	0.891177022243	-0.930920932640
H	7.450318952581	-1.307013130655	-2.713871157757
C	6.614495225471	-1.678396673164	-0.659874058507
C	5.830882354059	-2.969122045507	-0.910717106577
H	6.478163518736	-3.692376814881	-1.424284027006
H	5.524712400528	-3.424651577981	0.041577407110

H	4.923584715611	-2.834054475963	-1.501899707100
C	7.884478681463	-2.065161513928	0.101474469356
H	7.627278207515	-2.568716906550	1.043641697319
H	8.471201803473	-2.776393864237	-0.493729469316
H	8.535525432174	-1.220220141726	0.342630322839
H	8.604402027961	0.327444564180	-1.223018510865
H	7.376002966529	1.310590522381	-2.016009709075
H	6.285438199542	1.594251936793	0.108634795312
H	7.509938772639	0.571573380499	0.859512198410
H	5.204211273406	-0.032654126099	2.081156680969
H	5.497375293661	-1.783226071882	1.827282534249
O	2.869280311492	-2.347931488605	1.426183749353
O	2.736676902519	0.175758574931	1.557432788847
Li	-0.684147656564	-0.226130809391	-1.046030050630
Li	0.772523206971	0.295130790815	0.923383004339
O	0.256479953176	-1.138336287297	2.030222925729
P	0.127438138307	-1.645299466129	3.428345431530
N	-0.172424891302	-3.288701885525	3.367450358152
N	1.410746222862	-1.410701308478	4.471730458788
N	-1.117670147157	-0.903009245099	4.246183751699
C	-0.572280013458	-4.029026223280	4.544709161415
C	0.345161954927	-4.078684413303	2.262634754900
C	1.800005304758	-0.034073552341	4.752343676757
C	2.483222614195	-2.377313448332	4.607201420748
C	-1.217908261600	-0.727703513468	5.680702529594
C	-2.341406739209	-0.636399456375	3.510264334480
H	-1.315250644467	-4.789800547269	4.267038580584
H	0.276287725151	-4.541994932739	5.027672113151
H	-1.034787906124	-3.359730180911	5.277077909032
H	0.598744543871	-3.403180519789	1.442793742450
H	1.246934813290	-4.645149976564	2.550172369779
H	-0.424386274673	-4.790060522934	1.928915333950
H	2.113920274546	0.059057973884	5.802682877412
H	2.620609812697	0.287659230931	4.094298667200
H	0.952844923885	0.638753635850	4.580958608459
H	2.772262889408	-2.466536934488	5.664459699819
H	2.164185056955	-3.359076394465	4.247209085009
H	3.367566715943	-2.079762369705	4.024405790657
H	-1.369210737163	0.336044087539	5.920403405537
H	-2.070299351202	-1.295156129111	6.087955980708
H	-0.302672529179	-1.068371079359	6.171396274972
H	-2.730618536024	0.347017663655	3.803312754122
H	-2.124545487894	-0.607885173121	2.435844098926
H	-3.110204823331	-1.401356661627	3.717780806997

O	-1.678208178284	-1.790176653862	-0.810917159995
P	-2.050448438398	-3.177562268248	-1.220324768998
N	-0.813519745626	-4.259002269438	-0.959384627254
N	-3.320179132383	-3.783195903271	-0.319736581434
N	-2.499052566526	-3.223180810553	-2.829592407105
C	-1.014436885793	-5.689239745980	-0.844090219745
C	0.555458909443	-3.834308580253	-1.216545471723
C	-4.485641746325	-4.456089659118	-0.845196331838
C	-3.175239657054	-3.797278808228	1.125897360598
C	-2.322925603803	-4.397927076707	-3.661800279206
C	-3.393644973884	-2.192871405160	-3.339956089516
H	-0.665215668123	-6.226771108062	-1.740110584524
H	-0.450844150489	-6.076232468873	0.017363417244
H	-2.074665448839	-5.918193132996	-0.694022954634
H	0.632638044219	-2.756165487123	-1.053502005304
H	1.230126678273	-4.342970971497	-0.514896521455
H	0.872322484557	-4.069805873488	-2.244899956665
H	-4.501382089373	-5.520964796522	-0.558724816008
H	-5.405783434219	-3.990483418640	-0.460497737924
H	-4.504120212994	-4.393511108553	-1.936479721476
H	-3.032556259565	-4.823926951846	1.503945934860
H	-2.314047109810	-3.187554338005	1.424963094881
H	-4.073900874278	-3.378911552650	1.601494215117
H	-3.171554370140	-5.101986693267	-3.614167876370
H	-2.205660597402	-4.072513869067	-4.702758316861
H	-1.407508612236	-4.925941346233	-3.379008374915
H	-4.459302234867	-2.467148929040	-3.240012277034
H	-3.194791190394	-1.255715777201	-2.807262577587
H	-3.176499486623	-2.030143313683	-4.402074286307
C	-0.792182859057	2.609278844087	2.896090144931
C	-0.951660342862	2.919470641048	4.261804647222
C	0.519104629221	2.652290261133	2.373771872183
C	0.133678875013	3.265166716462	5.061340169028
H	-1.953585424552	2.906857536196	4.692132188588
C	1.600490469795	2.991889246021	3.179814654370
H	0.666943314350	2.495526561798	1.303955905411
C	1.421439430522	3.304852720318	4.527646279875
H	-0.028854818528	3.507442357837	6.110711924524
H	2.597027771441	3.018929213254	2.740437235152
H	2.270048224306	3.576061857430	5.152490030121
C	1.240170931069	-1.474739845891	-3.631269914557
C	1.157490065190	-2.463432574406	-4.632502015835
C	0.244151556674	-0.477792170340	-3.630987970806
C	0.132294549174	-2.464418646822	-5.571004003913

H	1.921955907285	-3.239592660147	-4.669041388582
C	-0.785465321923	-0.485116011475	-4.567354821040
H	0.324866820205	0.347676056985	-2.922217960630
C	-0.851510933778	-1.476856077247	-5.545462721826
H	0.105183412502	-3.241272022053	-6.334252974464
H	-1.535042078979	0.303561773050	-4.526379482768
H	-1.648240756184	-1.472362157997	-6.287335939177
O	0.982202329868	2.412963849481	-0.939206451011
P	1.197071953508	3.845087334906	-1.300308258774
N	0.245814089467	4.299308445814	-2.587427885895
N	0.850809236577	4.981247076049	-0.124097170232
N	2.810669829738	4.094697003334	-1.693761417398
C	-0.109169701186	5.665191579154	-2.905638275847
C	-0.209786532301	3.279610264434	-3.522320663136
C	1.809895261186	5.824548138292	0.553081439334
C	-0.521713275749	5.131348269850	0.330333218712
C	3.266984074089	5.182505005166	-2.529440106104
C	3.824692174359	3.404820451782	-0.923533353334
H	0.277247556007	5.963787030061	-3.893232480674
H	-1.203649603257	5.779251151039	-2.916975825552
H	0.300240466153	6.348180900987	-2.154411320778
H	-0.356169739581	2.339143260412	-2.984602373104
H	-1.181960852957	3.586902465021	-3.926480853339
H	0.493430341595	3.131048127743	-4.357093214285
H	1.586624641238	6.890268219070	0.380169602698
H	1.781114420900	5.643804716249	1.638906298106
H	2.823615906578	5.622275304135	0.198531378108
H	-0.894571244806	6.145682610931	0.108622477204
H	-1.169598228850	4.404652583778	-0.170714534130
H	-0.585402057388	4.962983469440	1.414901532082
H	3.538412875495	6.086878827915	-1.957116113201
H	4.153664567922	4.858525026113	-3.090742490632
H	2.494250337679	5.446887087287	-3.257589087647
H	4.364639442349	4.080750752523	-0.237805777107
H	3.338696869023	2.615808817858	-0.338284156926
H	4.557188610132	2.937395352673	-1.597775144934

Table S67. Atomic coordinates and single point energies of the *tris*-HMPA-solvated symmetric dimer of **8o** with double *endo* chelation to the sulfonyl oxygens where the μ_2 -HMPA is on the camphor *exo*-face.



G = -5228.168532

G_{SP} = -5230.468532

179

30031_endo_C_Tol: optimized structure // E(RM062X) = -5231.94610535 A.U. after 14 cycles

O	0.270276351193	-0.235026543240	0.302799972611
C	0.260854418051	0.355385978231	1.433596526785
N	1.571002004046	0.768564354044	1.976889165079
S	2.630631201731	1.482970338350	0.868987593528
O	3.013370807074	0.554442984855	-0.206624506253
C	4.015313981365	1.523660179984	2.031919753336
C	3.727304793456	0.389441472633	3.008316391267
C	2.365935711682	-0.283194030108	2.627756712983
C	1.835355683696	-0.824736330673	3.972465053942
C	3.047710648457	-0.621802153762	4.898681011218
C	4.198080987930	-1.521793951968	4.380895649932

C	4.726293850076	-0.769597082113	3.122663327236
H	4.725459177456	-1.387975250351	2.218062206830
H	5.749319565734	-0.403515927077	3.264030564855
H	3.832079939869	-2.526082193045	4.137354213836
H	4.984848502725	-1.647060704266	5.132315749104
C	3.519565019276	0.797279414326	4.501545959818
C	2.479676930125	1.896315599711	4.733112561039
H	2.903546708159	2.881903021764	4.496786679870
H	1.577323766523	1.781136765133	4.130003465583
H	2.198201146946	1.917299090186	5.794509022454
C	4.811126986647	1.240136446224	5.193303331184
H	5.243257025049	2.113657995118	4.685125408924
H	4.592178778203	1.543760303194	6.224846456102
H	5.581864811292	0.465478225510	5.237701055254
H	2.821713632377	-0.759938993921	5.961701514385
H	0.953753566025	-0.268299990765	4.303605936120
H	1.547314242729	-1.877618030123	3.894603981890
H	2.530818980384	-1.103747656875	1.911821235510
H	4.018215260053	2.513625165116	2.498388989047
H	4.917482255149	1.387843115710	1.428559331768
O	2.123315122403	2.806058814819	0.499222344399
C	-0.765496389545	0.642324265592	2.288400939838
H	-0.523679928848	1.281318314361	3.133602776226
O	0.170761249252	-0.643219251823	-2.614504928106
C	0.136749411743	-1.611921955288	-3.435742965127
C	0.984415368252	-2.681499644823	-3.558286876446
H	0.850852732941	-3.365654628205	-4.389006548479
N	-0.961220796152	-1.502311153803	-4.374998578201
S	-2.233650634932	-0.502854159054	-3.861635792822
C	-3.486279424749	-1.257881376894	-4.937440231672
C	-2.749215151178	-2.181937808919	-5.878872825443
C	-3.443405446161	-3.492547093243	-6.285225524819
C	-2.530691775716	-4.005007406783	-7.437718419964
C	-1.487740123821	-2.874837606254	-7.603446729687
C	-0.512826976718	-2.963827069972	-6.416229305097
H	0.312267093895	-2.249081375072	-6.495929546446
H	-0.074982895643	-3.963325224090	-6.320235087478
C	-1.416399497890	-2.614059404346	-5.202159391792
H	-1.572477988243	-3.490983274855	-4.554526476442
H	-0.993706420856	-2.865378718275	-8.580956874158
C	-2.302869473194	-1.604942673192	-7.260978154995
C	-1.472938940967	-0.321623188448	-7.198318252373
H	-1.041292472664	-0.117752942123	-8.187792857666
H	-2.103121955587	0.535908164187	-6.929320306284

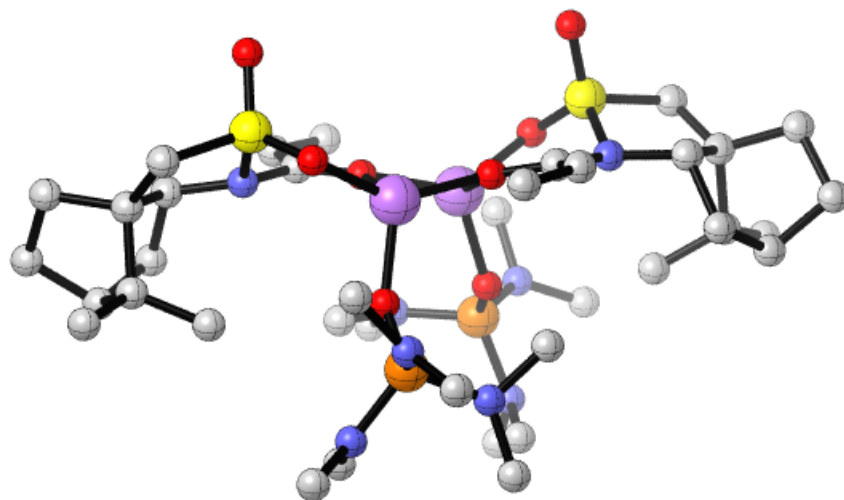
H	-0.664716252121	-0.360768448191	-6.467638680888
C	-3.471981089668	-1.339887896861	-8.212654224957
H	-4.130811213032	-0.558420478795	-7.810214451808
H	-3.087256202155	-0.969051916110	-9.170848211829
H	-4.087530904655	-2.218068761771	-8.426167073588
H	-3.100655647554	-4.169687296782	-8.357848057410
H	-2.047299824066	-4.957084079422	-7.190599342984
H	-3.500976784054	-4.189718465592	-5.441929263962
H	-4.468995673867	-3.309469606696	-6.623887954892
H	-4.163808548920	-1.784755361223	-4.257806056764
H	-4.016199618409	-0.437043631877	-5.431407986212
O	-1.985553202447	0.888096788008	-4.243339414720
O	-2.657974317909	-0.768102013505	-2.469716731817
Li	0.799421882479	0.735025969746	-1.456734314802
Li	-1.098649723793	-0.663285833030	-1.085077239642
O	-1.090759520082	1.451510746550	-1.311536211259
P	-2.172963244370	2.495068753064	-1.341115197887
N	-1.864721169625	3.616834256085	-2.529445733751
N	-3.749548076511	2.020846498530	-1.599781600533
N	-2.287508445901	3.236480773614	0.155373928231
C	-2.589928410166	4.867809904758	-2.557085098629
C	-0.749412211701	3.506609944418	-3.452785511279
C	-4.404052796928	1.154199354548	-0.630744102814
C	-4.413761117116	2.074301288404	-2.884431924051
C	-3.454276962856	3.933467418119	0.654729439918
C	-1.042841016759	3.645965022902	0.787953810497
H	-1.977633771330	5.703452966998	-2.181102900000
H	-2.893687760455	5.105083170711	-3.587531206598
H	-3.499450177088	4.803982403107	-1.949593633836
H	-0.235672179294	2.558816469193	-3.293345508759
H	-1.113135843082	3.551472756897	-4.490217055112
H	-0.030996430403	4.324460307934	-3.288021484270
H	-5.432468301047	1.503623053569	-0.450456700318
H	-4.436173070474	0.119410466105	-0.999994614120
H	-3.862577746227	1.169389346133	0.319383512007
H	-5.377306186648	2.599047920819	-2.786829875711
H	-3.789169819341	2.583289023558	-3.621087560286
H	-4.619297985026	1.055895134108	-3.251341139207
H	-3.629698648041	3.654801861999	1.704487211830
H	-3.319516750012	5.027658595227	0.610750859560
H	-4.343522791058	3.667431964591	0.078064461334
H	-1.104936235621	3.478497982101	1.870946928565
H	-0.206399848953	3.056299015114	0.407325800608
H	-0.838311633060	4.715138817895	0.606892090802

O	1.827454257940	1.844868553868	-2.523955190542
P	2.918143792506	1.970072418343	-3.538803709188
N	2.211672543690	2.159162636585	-5.046631301254
N	3.878302364729	3.279199647617	-3.176798806125
N	4.036499968526	0.743664592681	-3.725198136109
C	2.953594297243	2.697429478729	-6.164470651426
C	1.056906100928	1.343288416802	-5.398762479692
C	5.217475056265	3.493259049042	-3.683838076427
C	3.343778641406	4.349016395350	-2.348058036954
C	3.717494303119	-0.378061272473	-4.605671649437
C	4.853617161007	0.360678121641	-2.575357097097
H	3.497327766865	1.924722710557	-6.736107604903
H	2.256773688463	3.197588108940	-6.849922821509
H	3.671415599352	3.446965944409	-5.817859030305
H	0.601399512184	0.918165712016	-4.496654454660
H	0.301594718199	1.960249421247	-5.905180646528
H	1.343483617019	0.520389396994	-6.076175819518
H	5.271041892438	4.407444391724	-4.296335047566
H	5.926550373722	3.606804015102	-2.849384274852
H	5.532592172006	2.639156854184	-4.289368284079
H	3.129293823406	5.249331757403	-2.944177659016
H	2.435949571075	4.005070573985	-1.845874947534
H	4.077594634095	4.609420246519	-1.572724569944
H	4.619842521687	-0.992087000211	-4.711982890822
H	2.913366028768	-1.015292271352	-4.210887945561
H	3.441565377650	-0.015191513443	-5.600432776426
H	5.855168742766	0.076575049766	-2.928502919520
H	4.942851374284	1.204294558356	-1.884884672764
H	4.406187718632	-0.478457564332	-2.026112751852
C	-2.144215454934	0.193196172224	2.183706413057
C	-3.146968952950	0.865471181502	2.909738308371
C	-2.532505993195	-0.945939209715	1.453673830021
C	-4.464473830241	0.424716879797	2.907760747111
H	-2.872513529099	1.743165841839	3.494503709443
C	-3.847048383477	-1.397396277786	1.473896260992
H	-1.786363845477	-1.514839515323	0.907882809680
C	-4.827444254732	-0.715184824720	2.191024390553
H	-5.213910826744	0.970027285634	3.478922774974
H	-4.101430855333	-2.301954201911	0.924155853325
H	-5.855248851744	-1.070508398099	2.201692205221
C	2.113467207123	-2.939313856594	-2.682194235413
C	3.109301777295	-3.846701280204	-3.103561286588
C	2.286638609722	-2.335362588498	-1.418626192351
C	4.221575586402	-4.132084139068	-2.321183764549

H	3.006545530217	-4.323206173844	-4.079155532826
C	3.409204090078	-2.620024354329	-0.648338838735
H	1.539914506249	-1.647619737495	-1.034090772112
C	4.385384271673	-3.515636104031	-1.081742917936
H	4.969122964597	-4.834295471441	-2.686427989632
H	3.521777966846	-2.108808855092	0.306332906195
H	5.259668711481	-3.725527919442	-0.469514968482
O	-1.002999064071	-2.620537347939	-0.990571603129
P	-1.102607973943	-4.010422172683	-0.449304057487
N	-2.580373105205	-4.674651536149	-0.864383513258
N	-0.046565168382	-5.189891976783	-0.975484700250
N	-0.939411849422	-3.968513215654	1.213026414543
C	-2.877456013712	-6.091859424607	-0.861980713541
C	-3.649844793515	-3.832557101629	-1.369256380590
C	1.202534961435	-5.505276762991	-0.299037613510
C	-0.106029518893	-5.675911230952	-2.343520981394
C	-1.420098432547	-5.039140127315	2.057745903404
C	0.010936561449	-3.058832476861	1.838013700018
H	-3.745663688344	-6.308506839095	-0.220777170243
H	-3.116100547669	-6.441364657385	-1.879671771546
H	-2.019553083851	-6.662951960557	-0.496987707146
H	-3.322354370867	-2.789630759354	-1.406510722648
H	-3.921584646951	-4.146139071890	-2.391089578544
H	-4.549613027688	-3.921013854237	-0.742299422955
H	1.314214994337	-6.597844587431	-0.232562105760
H	2.064893061463	-5.091669272509	-0.839251849441
H	1.201943475609	-5.099536284380	0.715004889998
H	-0.164368489993	-6.775860523579	-2.350950465070
H	-0.988327436387	-5.273991954821	-2.851194441124
H	0.786002615321	-5.364943934923	-2.903030552654
H	-0.658668193973	-5.817718774787	2.238376859885
H	-1.718977416372	-4.618306310998	3.026482204958
H	-2.306004083157	-5.505094491733	1.616640188160
H	0.879159463472	-3.608234919971	2.243224397406
H	0.357478508409	-2.320027778985	1.105472545517
H	-0.480596688368	-2.518806996037	2.661472962565

Dimers of enolate **8b**

Table S68. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8b** with double *exo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *exo*-face.



G = -4025.16528

G_{SP} = -4026.913843

136

20020a_oxy: optimized structure // E(RM062X) = -4028.03143455 A.U. after 12 cycles

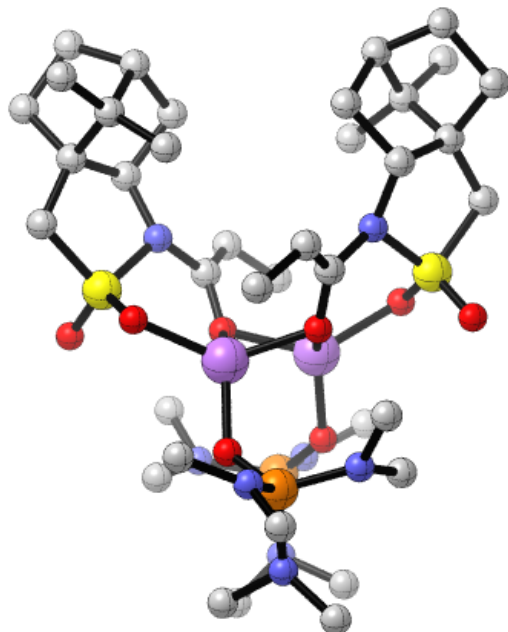
O	0.088047107715	-0.051899491570	-0.052650187015
C	0.034068292545	-0.038485401465	1.234820536480
N	1.354788508378	-0.008684974454	1.854571951965
S	2.392640191452	-1.262534560881	1.404652734162
O	1.845488766103	-2.588634573894	1.675434084305
C	3.663923574675	-0.877574198803	2.642392058038
C	3.081730122647	0.223543821446	3.508915575788
C	1.547432370368	0.285243004909	3.268975399789
C	1.185962702394	1.737391613974	3.666752529896
C	2.518615827036	2.280965426158	4.216329825161
C	2.828262066053	1.520786916513	5.526068229108
C	3.255027097460	0.106547604947	5.032860634122
H	2.627534194731	-0.695469547011	5.437033171319
H	4.290770010795	-0.127225069660	5.302016386487
H	1.950210008301	1.484445669648	6.180564647075

H	3.629473869230	2.005247786487	6.094058224898
C	3.550543193718	1.687868063518	3.225399609701
C	3.401222409750	2.171703058764	1.779673105754
H	4.040615515732	1.579529784168	1.109446814932
H	2.394711531102	2.105458903923	1.363274506106
H	3.745863982346	3.213428442327	1.715488247186
C	5.010165362459	1.931406533720	3.622819317386
H	5.684206487768	1.375624391050	2.956546081612
H	5.249390069358	2.995990627837	3.506924285385
H	5.249547284388	1.649127191933	4.651523943553
H	2.541346679448	3.371710502206	4.320543507091
H	0.842585219685	2.291816599401	2.789283819253
H	0.384025093085	1.768057101666	4.412048615859
H	1.027495912090	-0.457179099329	3.894962155321
H	4.569834560576	-0.590956526106	2.098800709900
H	3.827868316402	-1.816415995307	3.179542155581
O	2.916527553517	-0.996669619592	0.045757180698
C	-1.060580978425	-0.009714955780	2.028349424336
C	-2.438095461597	0.028111513254	1.441845251804
H	-2.876058385764	1.040960565101	1.441633862357
H	-2.416770060551	-0.328600404390	0.404753369826
H	-3.125013929680	-0.620201208757	1.999921558329
H	-0.947623530849	-0.041769454050	3.108146076649
O	0.691256727871	-0.493679524109	-2.710420972163
C	0.753358267593	-0.825515398298	-3.955382651076
C	1.864022142131	-1.128919069976	-4.663692224765
H	1.785552657343	-1.456787206933	-5.695878078034
N	-0.532869612778	-0.760141257125	-4.613106633653
S	-1.827719199700	-1.465570310684	-3.792020608387
C	-2.996850757032	-1.294830939858	-5.171670398332
C	-2.218354995959	-0.661570098660	-6.307763673720
C	-2.487536893962	-1.174665258713	-7.732690835515
C	-1.786288887028	-0.10008909331	-8.614966992405
C	-1.237575821405	0.908815748882	-7.581406468762
C	-0.038709752508	0.244279902597	-6.876818001087
H	0.496653368756	0.928481633727	-6.213355595274
H	0.691010328096	-0.152692011040	-7.590756492666
C	-0.704516910941	-0.888402564662	-6.052922272313
H	-0.388667067269	-1.887704132685	-6.393618862977
H	-1.011188920943	1.895620853859	-8.000915934845
C	-2.321873745900	0.890106140226	-6.476036691133
C	-1.979007058320	1.718074690588	-5.232774700329
H	-2.158893559427	2.782779273230	-5.441446267728
H	-2.614549710389	1.433529982629	-4.382159354358

H	-0.957025558013	1.602441751927	-4.872590162167
C	-3.708827965098	1.338321040870	-6.946814757071
H	-4.451645009353	1.173738087829	-6.153942254516
H	-3.696227912930	2.414812393836	-7.158525604404
H	-4.065218642273	0.827700662051	-7.845693445810
H	-2.492219438032	0.373193596153	-9.305666073276
H	-0.979920424900	-0.524199721911	-9.223534563788
H	-2.071903308170	-2.179110050532	-7.870258819553
H	-3.561401257341	-1.239092485960	-7.939292598429
H	-3.327603330523	-2.314993868079	-5.389299222202
H	-3.837881378850	-0.694104151148	-4.810308217870
O	-2.248551418823	-0.587231669481	-2.675401518576
O	-1.623216347290	-2.881452990087	-3.501188201569
Li	1.645688899336	-0.070160526378	-1.162442997843
Li	-0.728647535750	0.289782796721	-1.712000300339
O	-0.981908964367	2.128776921126	-2.267330020452
P	-2.056924211581	3.076556741811	-1.827553737341
N	-1.819375247854	4.557541293476	-2.582924752001
N	-3.658303120397	2.753605813194	-2.157082776773
N	-2.053312702658	3.172608887480	-0.159415003656
C	-2.598974711950	5.712714932518	-2.176662441247
C	-0.513983573998	4.876124699387	-3.137405818044
C	-4.294880113166	1.605326255402	-1.517418338546
C	-4.376223854356	3.241432214518	-3.322254761462
C	-3.096152913612	3.827616011026	0.608149945681
C	-0.774123076436	3.079072018341	0.539570313833
H	-2.094257977835	6.290360748080	-1.384968725555
H	-2.752693118672	6.375972319322	-3.039040058649
H	-3.582043132887	5.401639133999	-1.808911022305
H	0.069612967300	3.957632399958	-3.237411086534
H	-0.631944055318	5.350605117840	-4.122828212267
H	0.037031972645	5.572179194707	-2.483154435435
H	-5.313665952184	1.876908993731	-1.207227106032
H	-4.335302613809	0.748852684012	-2.204505565504
H	-3.727288537296	1.301511845729	-0.634310253021
H	-5.321396365088	3.709304832190	-3.008506060785
H	-3.774590387254	3.973595549419	-3.864650559209
H	-4.614049230300	2.414033298750	-4.006043359997
H	-3.249458903714	3.277756612823	1.547287295629
H	-2.829183801747	4.866329598005	0.863200138097
H	-4.037384672327	3.828845185183	0.051378007381
H	-0.935306340161	2.557196884036	1.491089262310
H	-0.057666878526	2.491144279718	-0.048027555221
H	-0.363411887279	4.082762869122	0.747892199683

O	2.270225054069	1.725793273930	-1.210997161573
P	3.200882692144	2.638506896771	-1.942859354591
N	2.505608581258	3.251924212499	-3.330179975867
N	3.608629364341	3.993589952328	-1.057916670772
N	4.616518868071	1.862432810590	-2.349383980386
C	2.894476478934	4.501846441412	-3.952622765652
C	1.803312574557	2.309388808558	-4.198683236610
C	4.951747444359	4.445466003524	-0.771900527664
C	2.531759777251	4.811146623775	-0.531557297226
C	5.427392595230	2.207738079055	-3.498728035906
C	5.159118505048	0.807625538886	-1.506714239483
H	3.484563107742	4.339760014113	-4.869036188451
H	1.996881747979	5.071913643852	-4.233393840719
H	3.485116734431	5.106233714748	-3.257248472798
H	1.277885799300	1.568534475821	-3.584603111284
H	1.057999865271	2.862396319248	-4.786725263594
H	2.487963985033	1.796229624682	-4.894266145624
H	5.150633617760	5.427429088219	-1.230856789144
H	5.100988364046	4.539849215030	0.314118748649
H	5.679732373078	3.725768181337	-1.155390706593
H	2.532320055486	5.814882717243	-0.987131312577
H	1.571395702927	4.327728167604	-0.738050417206
H	2.630071519028	4.922152815760	0.558348049892
H	6.409260897698	2.605714772819	-3.196335540522
H	5.593716370398	1.313338552164	-4.115978047910
H	4.925431121592	2.956840606278	-4.115313146005
H	6.064057089755	1.145229107610	-0.975004806910
H	4.405199026073	0.479450377782	-0.786330984302
H	5.421970107094	-0.057553082911	-2.131128738319
C	3.206028264834	-1.062558095400	-3.994112747930
H	3.380568784088	-1.912545306601	-3.317332874295
H	4.018617720752	-1.052884472905	-4.731316865325
H	3.293866614619	-0.149521219119	-3.384181468590

Table S69. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of N-propionyl camphorsultam enolate with double *exo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *endo*-face.



G = -4025.182128

G_{SP} = -4026.925204

136

20020a_nit: optimized structure // E(RM062X) = -4028.04409830 A.U. after 12 cycles

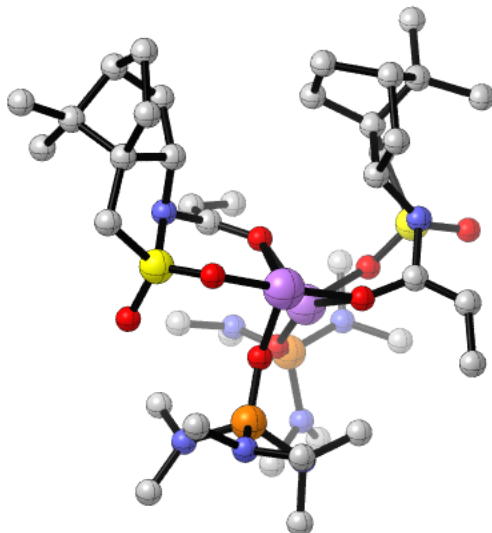
O	-0.227171986384	-0.663660499646	-0.769119905469
C	-0.414130675538	0.337594741384	0.033045285596
N	0.815719258911	0.787700676791	0.654342573315
S	1.892998752059	-0.468652898508	0.994297296726
O	1.276442150837	-1.568238365574	1.741886356676
C	2.936619725263	0.487366628914	2.128960993136
C	2.324663866443	1.872263865109	2.203057928472
C	0.852983059708	1.801221398742	1.699426975272
C	0.584172051475	3.244365138416	1.204187096849
C	1.853630980304	3.995689340613	1.641079453632
C	1.866101281950	4.021485071242	3.188563748779
C	2.250102934618	2.561273315648	3.575585578229
H	1.507426343861	2.079217056732	4.220798497372
H	3.212338757859	2.515411578582	4.096843832808
H	0.886993856356	4.310599757906	3.586828593737
H	2.592939455527	4.742557261702	3.576411202632

C	2.971602790919	2.977579940556	1.310249736621
C	3.107647705600	2.616442055593	-0.169876486805
H	3.868786355078	1.834461978109	-0.299986457788
H	2.195034808673	2.238568176403	-0.633715524768
H	3.447421391269	3.495344710292	-0.734470245506
C	4.361332900592	3.405214916882	1.793176593551
H	5.069671239021	2.569514645964	1.713140692459
H	4.739002373681	4.207502121355	1.147639189709
H	4.387281316946	3.769917296656	2.823510899810
H	1.964827809314	4.982911204876	1.178007217513
H	0.448615666253	3.246010625070	0.119736168226
H	-0.323039269325	3.667443146490	1.649809960474
H	0.171436193304	1.516082619957	2.517025318603
H	3.954332405324	0.466048251723	1.727079998972
H	2.890529128116	-0.062830461255	3.073383186798
O	2.636049648827	-0.808321309200	-0.239992498683
C	-1.583479791866	0.953798467519	0.326868873457
C	-2.861778526464	0.545181108301	-0.342697021174
H	-3.674832942297	0.418172244881	0.386201333769
H	-3.204570071565	1.270399708676	-1.095636455367
H	-2.730605644664	-0.415484075251	-0.855860916085
H	-1.601811449170	1.770332611856	1.042950801631
O	0.801524759002	-0.036467540909	-3.277229162469
C	1.283230792275	1.160011976935	-3.408642794690
C	2.585239733760	1.531651790016	-3.401977970316
H	2.853022925337	2.573795012460	-3.550550878278
N	0.247524725079	2.158540765752	-3.586290789988
S	-1.073900942537	1.600817090630	-4.479246056783
C	-1.769985243677	3.241051603893	-4.819527211415
C	-0.836499785323	4.241702066769	-4.167361134902
C	-0.497089169919	5.528360937546	-4.937706180265
C	0.200604832182	6.391018440290	-3.842913930869
C	0.093299269198	5.517916485566	-2.569418540414
C	1.107133524689	4.369674037644	-2.712694906119
H	1.159309214089	3.742725949816	-1.819009315603
H	2.119974211671	4.733142133758	-2.919184892320
C	0.533297738290	3.552292643574	-3.897095257154
H	1.183157109605	3.608433035012	-4.785241699331
H	0.191353934850	6.080492451826	-1.633842837080
C	-1.259361973915	4.792491100061	-2.769135483256
C	-1.586743699773	3.723764685385	-1.725005784686
H	-1.742654448430	4.198813850854	-0.746897303994
H	-2.522740803962	3.211745273671	-1.988632564012
H	-0.829871782289	2.945377405809	-1.615249277882

C	-2.464673734832	5.736228009196	-2.832589367901
H	-3.358431268866	5.195408166749	-3.172090420032
H	-2.682767259902	6.114648117632	-1.826479136282
H	-2.325813042337	6.600209406281	-3.487966717692
H	-0.299031902018	7.356877579189	-3.715857418198
H	1.247024939513	6.603703617631	-4.089134114814
H	0.151379281118	5.317162799349	-5.795099008375
H	-1.401029536260	6.010847058040	-5.324762151463
H	-1.791124399018	3.308793766275	-5.911189548602
H	-2.788584120512	3.248976323815	-4.419415620755
O	-1.964815495755	0.829173328419	-3.583675173699
O	-0.688913628178	0.984443502852	-5.752009382037
O	1.723591373292	-2.803891675171	-2.533596062649
P	2.065307792213	-3.176775298274	-3.950550924526
N	1.439202953769	-4.709492170829	-4.243736762820
N	1.509957166608	-2.331291086521	-5.255673889547
N	3.730442086340	-3.109834055326	-4.117488187095
C	1.354959146135	-5.303274449891	-5.564229856876
C	1.420381256208	-5.675111470625	-3.158287954311
C	2.205486607317	-1.185880669248	-5.836343939480
C	0.067452029746	-2.298538283716	-5.500278653871
C	4.372952324529	-3.638913407905	-5.304230668685
C	4.599887982964	-2.950061599883	-2.962946885318
H	2.206170246045	-5.974345575248	-5.767173984926
H	0.432844706991	-5.897337109026	-5.641560733136
H	1.325599614979	-4.523405833062	-6.328895158045
H	1.646597750078	-5.173446114102	-2.215320619973
H	0.423039680165	-6.132203935141	-3.075703337413
H	2.160469785494	-6.473617362057	-3.326910437106
H	2.121129301314	-1.243937663262	-6.930918101420
H	1.753025914626	-0.249058577016	-5.490249328878
H	3.261896327554	-1.199582692448	-5.558811156812
H	-0.131165654455	-2.511426324887	-6.561432070042
H	-0.436901719940	-3.035526005456	-4.872883773742
H	-0.326868330505	-1.306273576790	-5.254601399970
H	5.227646968942	-3.004788395599	-5.578724126577
H	4.742725961329	-4.665637207707	-5.147418188855
H	3.671795879014	-3.641601211500	-6.145180909964
H	4.023569223341	-2.567292245529	-2.116937392950
H	5.064223622413	-3.907244646370	-2.676390144937
H	5.397985032198	-2.233277033985	-3.202358929837
Li	1.358316496920	-1.124204263124	-1.777516221341
Li	-0.916864747131	-0.578530376589	-2.574459317560
O	-1.732474617016	-2.250321644649	-2.841633454919

P	-2.262567360795	-3.239162978228	-1.839363758378
N	-2.055586966298	-4.781409617974	-2.480745642384
N	-1.615703093751	-3.413727688324	-0.330513051873
N	-3.868269665717	-2.868460938451	-1.543065325809
C	-2.244637270214	-5.995454293563	-1.709199795423
C	-2.230187947063	-4.962477596022	-3.911757505618
C	-2.051318143117	-2.646534504079	0.833293573838
C	-0.231077209653	-3.874141373435	-0.217114287311
C	-4.709127664623	-3.771039023571	-0.781952597901
C	-4.581029707663	-1.889809599607	-2.348427755591
H	-3.262967252151	-6.403004374164	-1.824882994975
H	-1.535683749572	-6.761581060138	-2.054849276759
H	-2.054906066752	-5.804410715439	-0.650243476400
H	-2.194401043396	-3.992885699419	-4.412245604211
H	-1.421009561152	-5.591097435920	-4.311953378613
H	-3.192972478897	-5.449026103690	-4.138000722971
H	-2.070876932123	-3.315155673056	1.705761716344
H	-1.355982972341	-1.821556257271	1.028061486029
H	-3.053016803239	-2.241935166442	0.671735839822
H	-0.169937347960	-4.677364173504	0.532520365653
H	0.123735414975	-4.239223169792	-1.182384597116
H	0.410134753895	-3.042738048077	0.096065249914
H	-5.382981104570	-3.194369785518	-0.132562382779
H	-5.325409631820	-4.407690541057	-1.437768188384
H	-4.094374985509	-4.413694167475	-0.143382120008
H	-5.183755551123	-1.245118619195	-1.693204365889
H	-3.865790364729	-1.268766063763	-2.893574855023
H	-5.253118757813	-2.380487822897	-3.070397009453
C	3.674181468353	0.527820344032	-3.165187029523
H	3.277529932480	-0.490874396707	-3.257072640920
H	4.483390646424	0.631099694857	-3.901998148665
H	4.126241582713	0.610675434038	-2.165611800288

Table S70. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of N-propionyl camphorsultam enolate with double *endo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *exo*-face.



G = -4025.17483

G_{SP} = -4026.915891

136

20020a_endo_H_exo: optimized structure // E(RM062X) = -4028.03645139 A.U. after 12 cycles

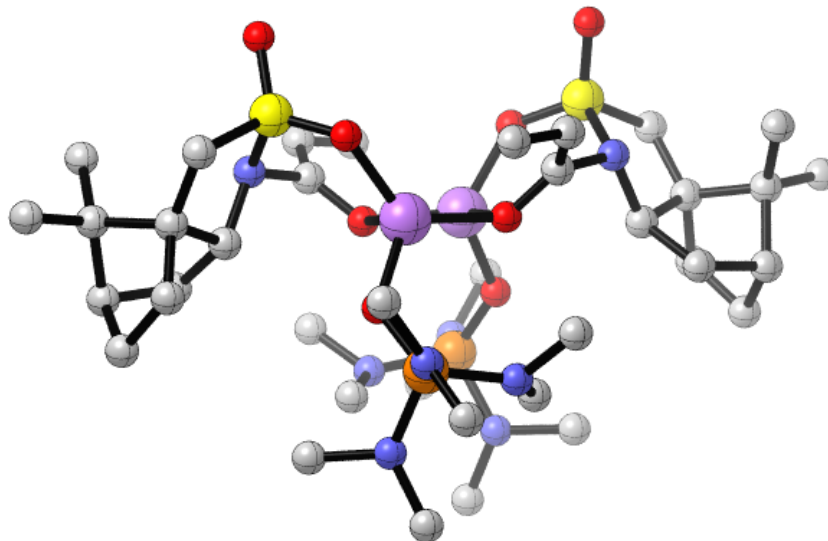
O	0.559162820090	-1.267556475952	-0.499474772667
C	0.399908036593	-0.655372648923	0.625239026329
N	1.638151790849	-0.281814930612	1.340987275180
S	2.836643761992	0.488080937096	0.435150663771
O	3.353961838527	-0.369619505822	-0.668432337063
C	4.091125040420	0.370539322698	1.728227061436
C	3.657332038729	-0.817120864184	2.578132521043
C	2.335831969652	-1.407514409267	1.991970556742
C	1.637002544373	-2.030922445410	3.219406275872
C	2.730304093667	-1.927459078351	4.297980424053
C	3.910073357878	-2.831438633908	3.860847479036
C	4.599324560044	-2.021122916556	2.720858819698
H	4.674117487905	-2.578198471219	1.780019029770
H	5.612445061832	-1.708013822106	2.996153395219
H	3.549388994484	-3.807273948873	3.514840880744
H	4.601227539562	-3.023792305888	4.688101779813
C	3.283717628538	-0.503275001376	4.061803001220

C	2.252059468180	0.611872127137	4.251870070656
H	2.715166508127	1.594396681188	4.087964277984
H	1.397413608552	0.540087281419	3.577438851058
H	1.891261527310	0.597029096162	5.288680613728
C	4.497130381163	-0.152686781813	4.927428171925
H	4.988481860558	0.755417839769	4.551412203581
H	4.168248977732	0.058627596731	5.952371135020
H	5.249301243795	-0.944580087781	4.978551340476
H	2.370978278321	-2.128669293627	5.313197280641
H	0.729990826150	-1.476341350367	3.477367934455
H	1.343772051266	-3.068464434478	3.030256421542
H	2.560362699053	-2.175026532741	1.232786516422
H	4.082733142742	1.321781835039	2.269054426994
H	5.042118526567	0.236397357371	1.205737223679
O	2.451838165906	1.857594627988	0.101263993761
C	-0.744439387405	-0.422480409581	1.305300562661
C	-2.061575501725	-0.964139833683	0.836105825807
H	-2.883292773224	-0.256845102005	1.003840211263
H	-2.024980061550	-1.186880455516	-0.238343406386
H	-2.330307573082	-1.891976894204	1.369559709195
H	-0.682215636729	0.128286172615	2.240646464647
O	1.160690013803	-2.099723172910	-3.167036388648
C	0.798136568164	-3.244250244567	-3.647867449069
C	0.937149807071	-3.726600276960	-4.898694387222
H	0.546192728020	-4.720050805394	-5.100605153936
N	0.105964195718	-4.146783929728	-2.697682513219
S	-1.515177848708	-3.749051048320	-2.512847887415
C	-1.704012236989	-4.370438120486	-0.818476795385
C	-0.322995832929	-4.817306136317	-0.382549989092
C	0.162000926945	-4.364791541345	1.002141628920
C	1.460899255963	-5.208918815197	1.173000968635
C	1.488315056050	-6.110760480514	-0.090289180583
C	1.910168257260	-5.224379613312	-1.277757364240
H	2.017020237747	-5.790684664840	-2.208471107593
H	2.857917063018	-4.706054422625	-1.093606339292
C	0.728459723576	-4.235009448827	-1.368184462267
H	1.008378285149	-3.231926243834	-1.038156745670
H	2.089675265987	-7.019247627500	0.028309371943
C	-0.017905753238	-6.344299153994	-0.376056924161
C	-0.316182864024	-7.059182939540	-1.696547764072
H	0.081306883074	-8.082070747119	-1.659049974889
H	-1.401585683955	-7.136755793366	-1.849367159395
H	0.092954858106	-6.551639891760	-2.571883245860
C	-0.746927357539	-7.106339763073	0.733244734613

H	-1.834564086135	-7.049368793571	0.587851255554
H	-0.471375319711	-8.167600604232	0.694648246133
H	-0.524054485478	-6.741990619781	1.739999601025
H	1.439302228484	-5.802361677343	2.094103050436
H	2.360576621845	-4.580145556879	1.219465985769
H	0.333398011801	-3.281459782151	1.002218459023
H	-0.576014870816	-4.586460770754	1.782509941154
H	-2.080563883855	-3.518410970735	-0.244347785757
H	-2.449338775809	-5.171502414983	-0.854999556478
O	-2.361480365252	-4.476668350427	-3.459042675050
O	-1.716795396660	-2.275220971525	-2.489221038518
Li	1.947243000277	-1.093854165092	-1.842316599139
Li	-0.349395447472	-0.831333877524	-2.211050381473
O	-1.689592981590	0.563143859196	-2.298353276890
P	-3.175034504330	0.711652470727	-2.453069281536
N	-3.470674092524	1.674766071095	-3.800863937322
N	-4.183562701785	-0.575633883198	-2.737917646046
N	-3.797216716639	1.359656341657	-1.033933939115
C	-4.812484179020	1.940373051567	-4.291459850191
C	-2.516989219499	2.729910500295	-4.109811713766
C	-4.647496352177	-1.440139372767	-1.660527587405
C	-4.176438222541	-1.245967908475	-4.039374454476
C	-5.187737773139	1.774181269715	-0.967918627290
C	-2.910274724288	2.096173546080	-0.143303340188
H	-5.224311525566	2.876736555392	-3.881314351280
H	-4.784998688672	2.032594999915	-5.385988245293
H	-5.482119724311	1.115850618118	-4.034280808508
H	-1.510901814641	2.422270613270	-3.808498302005
H	-2.522749478630	2.905447324524	-5.194284348018
H	-2.779463339609	3.678931915937	-3.611614185546
H	-5.689453448785	-1.727999829298	-1.857429772539
H	-4.033677256933	-2.349381935761	-1.607061296821
H	-4.594459845516	-0.917018290980	-0.703072517745
H	-5.212733881428	-1.453804772611	-4.341204257728
H	-3.713285047898	-0.602376336418	-4.791335671825
H	-3.616440626300	-2.187562454979	-3.985054066376
H	-5.555879510624	1.649932483084	0.059565166954
H	-5.320571327263	2.831096088649	-1.252290277140
H	-5.800762010686	1.151158279902	-1.626356612048
H	-3.317730936884	2.051224506214	0.875677045313
H	-1.919821566790	1.633763370019	-0.139490558525
H	-2.822838110718	3.156954919872	-0.431847362733
O	1.170335967444	0.523357342170	-2.482100134813
P	1.472347910971	1.684798613427	-3.383742377766

N	0.579572783931	1.539349698055	-4.779731876171
N	1.169427396410	3.127257388523	-2.626238645042
N	3.060660327285	1.857513597703	-3.890534887578
C	0.560961465491	2.608510033448	-5.755877365879
C	-0.043471108809	0.285482410021	-5.189569142105
C	1.799449667825	4.395553767727	-2.933075688996
C	0.210046239831	3.160266512974	-1.529035857569
C	3.536552608260	0.962187622330	-4.940100481787
C	4.067830697960	2.102424952623	-2.857480612814
H	1.301367070528	2.453998423457	-6.558275603488
H	-0.433622832701	2.665759882817	-6.216345365456
H	0.765148493021	3.571263415119	-5.275490299548
H	0.263258195612	-0.530691705024	-4.526117892032
H	-1.140108517463	0.381677376017	-5.166787822482
H	0.273787684821	0.027597957502	-6.211098071111
H	1.048159627388	5.138602991226	-3.242085864319
H	2.316952835003	4.783966126702	-2.042675903176
H	2.530508349796	4.272766771569	-3.736516685012
H	-0.625999115001	3.832515535033	-1.776836086938
H	-0.177096188990	2.152763659142	-1.353948220866
H	0.705689666524	3.508294451335	-0.613645198633
H	4.425872348171	1.404286578187	-5.405643060816
H	3.803637146333	-0.029739782649	-4.544083677965
H	2.768762591836	0.835446680074	-5.708245646767
H	4.887060008662	2.695371899593	-3.285527422134
H	3.623112687082	2.646716373826	-2.019208080661
H	4.469639555970	1.156796662133	-2.464587810357
C	1.604451948779	-2.946069475490	-5.987925519596
H	2.421019660214	-3.516066289805	-6.451874740922
H	0.904406620274	-2.678382547095	-6.792633653949
H	2.024113623744	-2.020644275629	-5.578102088163

Table S71. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of N-propionyl camphorsultam enolate with double *endo* chelation to the sulfonyl oxygens; both HMPAs are on the camphor *endo*-face.



G = -4025.181716

G_{SP} = -4026.927889

136

20020a_endo-endo: optimized structure // E(RM062X) = -4028.04735666 A.U. after 12 cycles

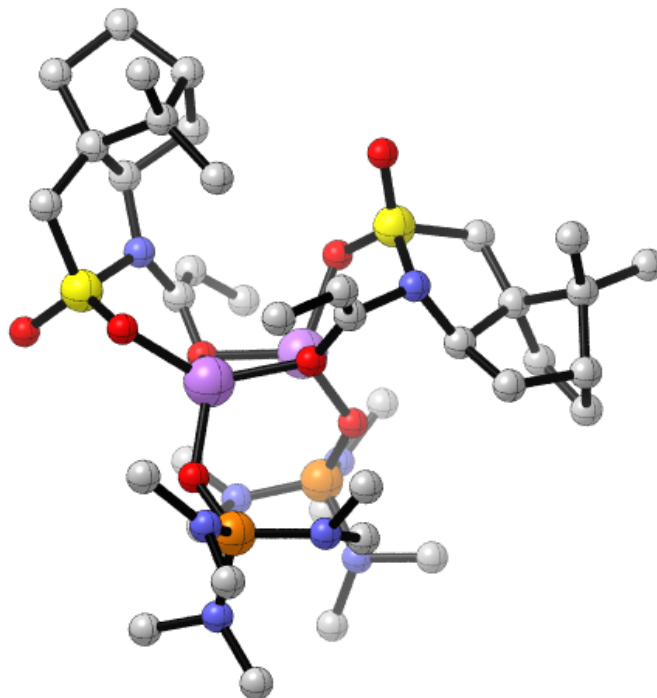
O	0.143524465343	0.088129124865	0.342186055321
C	0.223011341795	-0.108926390401	1.627784457512
N	1.575368180187	-0.378682117586	2.135579124592
S	2.531931507562	1.008223071205	2.277526703909
O	2.509120454200	1.793078105204	1.015518938468
C	4.116916913568	0.123102010961	2.317682571749
C	3.801609245818	-1.300010254369	1.887271153917
C	2.346722088308	-1.349912179495	1.345485163302
C	1.924339283201	-2.819935333397	1.563475778613
C	3.238604531417	-3.471240961907	2.037774104639
C	4.231253481844	-3.428711568770	0.850303865458
C	4.657614624616	-1.931359119383	0.776897212563
H	4.436938571826	-1.460791148644	-0.189495143294
H	5.728624039537	-1.803086526654	0.970264983354
H	3.754050548038	-3.774436830464	-0.074971873186
H	5.093324956531	-4.081649529104	1.023529962704
C	3.812320610531	-2.398514608325	2.996693899486
C	2.935750585722	-2.108265968976	4.218247524823

H	3.327711782882	-1.246487293102	4.776005172852
H	1.897961295853	-1.880280021388	3.973355563793
H	2.962738645471	-2.972311389218	4.894963914390
C	5.218705366391	-2.712176966403	3.515392722425
H	5.630185129723	-1.845099619061	4.049874724354
H	5.171680721380	-3.540321908479	4.233263369718
H	5.930205702030	-2.991111399752	2.733397242150
H	3.110530395063	-4.469025567759	2.472316681278
H	1.124872212369	-2.885544188998	2.309617655662
H	1.551500388791	-3.274335137755	0.638205648377
H	2.320612182432	-1.071398844917	0.283637378623
H	4.503332004545	0.205161170972	3.338399360557
H	4.766522899986	0.664851637259	1.624366752437
O	2.248926901903	1.716706529958	3.517075826530
C	-0.774329869796	-0.144863129652	2.531689397158
C	-2.200746371940	0.106464233726	2.146504185461
H	-2.506473921253	1.142480777579	2.346675438112
H	-2.348770978568	-0.063630941696	1.070233866178
H	-2.884792928295	-0.557705303951	2.691516994492
H	-0.508810753260	-0.317521368905	3.570875189504
O	0.261369712807	2.229193092674	-1.567206804354
C	0.158466229108	3.527072059834	-1.620133679962
C	1.137022309602	4.447905558675	-1.533239733426
H	0.852934049408	5.494743968810	-1.593479052748
N	-1.198969378983	4.036541257748	-1.859608558650
S	-2.184530722963	4.002395905684	-0.486150931193
C	-3.752846807623	4.113000521094	-1.394602159349
C	-3.401621507241	3.851771905178	-2.850055611962
C	-4.221714940348	2.803577765935	-3.620122429593
C	-3.768802160409	3.053474368163	-5.090383178579
C	-2.801030636781	4.256856396178	-4.978218857483
C	-1.489490001861	3.737301766230	-4.356630142937
H	-0.705069905630	4.501227145746	-4.320965581459
H	-1.088410840923	2.876521632004	-4.904171200120
C	-1.934861708192	3.346770160278	-2.929733798687
H	-1.891555652538	2.260942270535	-2.772031458250
H	-2.663441910859	4.803475820431	-5.917940942263
C	-3.415199864668	5.077593059675	-3.816947827723
C	-2.570471176264	6.275048214542	-3.372744093069
H	-2.595255500323	7.044177817814	-4.155732034915
H	-2.990622875664	6.724673874882	-2.462410958102
H	-1.532280611689	6.025725819869	-3.151483713967
C	-4.826130763882	5.601484793863	-4.100051738161
H	-5.265455440431	6.026309040040	-3.187179879266

H	-4.778729720878	6.409320731088	-4.840673390410
H	-5.515238169310	4.842638799495	-4.480633440731
H	-4.621877673239	3.282719224653	-5.737848632336
H	-3.265505149071	2.182365592589	-5.527696538554
H	-3.989425334860	1.794652133390	-3.256576463248
H	-5.298826005395	2.960875770672	-3.493647408509
H	-4.398232634243	3.351232930429	-0.948114356096
H	-4.161695092190	5.110700722635	-1.206601663847
O	-1.941110256624	5.158685408265	0.363714910247
O	-2.150239804692	2.660169971633	0.151368172606
O	2.605524063327	0.114683162190	-1.589118106674
P	2.856914146167	0.106946317112	-3.071857726202
N	2.725037604305	-1.480810999059	-3.606639786813
N	1.855270636718	0.897361801753	-4.133607596080
N	4.356547342907	0.781907403338	-3.345664435637
C	2.827140696581	-1.837630981968	-5.011416981079
C	3.143532842193	-2.534478968292	-2.694573053861
C	1.984416233632	2.339337816449	-4.348384707866
C	0.467953632776	0.444594829344	-4.256696364593
C	4.944904422593	0.862139634460	-4.668485030031
C	5.199463678874	1.245982681838	-2.254310755112
H	3.863406770503	-2.066002422829	-5.309809851939
H	2.214996749029	-2.730379414290	-5.199729146696
H	2.446976775319	-1.022071096608	-5.632540297798
H	2.892440466393	-2.247892527908	-1.669707265988
H	2.604281424716	-3.457487488899	-2.945373292253
H	4.226074972394	-2.738412470240	-2.757539725755
H	1.729979934940	2.560376432469	-5.394210809203
H	1.313164986645	2.896284420428	-3.683415355887
H	3.011541950158	2.663296392637	-4.161473909294
H	0.093243580621	0.758258435283	-5.240960819807
H	0.412101323876	-0.646392570100	-4.199195178585
H	-0.155456073347	0.881827812270	-3.460611417629
H	5.307836443718	1.882828554402	-4.858559969755
H	5.794660452936	0.170757938709	-4.773751406463
H	4.197966400720	0.624124883090	-5.431885087961
H	5.488159553704	2.293056715453	-2.424984846025
H	4.644445577623	1.184959441755	-1.314996748184
H	6.112991339921	0.637571050397	-2.179096129127
Li	1.451626772997	1.201151043374	-0.540247720381
Li	-1.048381041792	1.201762501331	-0.588787043769
O	-2.158623025736	0.260840678441	-1.810977139168
P	-2.379375790792	-1.215982279427	-1.989966371240
N	-2.207076482879	-1.566274496899	-3.624573416879

N	-1.370955977428	-2.341333465430	-1.302939892201
N	-3.885195296469	-1.591402352981	-1.380881586368
C	-2.272477026891	-2.923603576894	-4.138867607901
C	-2.624429882136	-0.549346757722	-4.577923189494
C	-1.522554759743	-2.719868089228	0.102712017026
C	0.026878447358	-2.386573111731	-1.737457205029
C	-4.448427679694	-2.924932149429	-1.464023464912
C	-4.759702245708	-0.574306512492	-0.817243118603
H	-3.297517809770	-3.213730841689	-4.421960676443
H	-1.639004027530	-2.998759741930	-5.033442148962
H	-1.895492502234	-3.625363172365	-3.389958738213
H	-2.400149365388	0.441240581546	-4.172983102260
H	-2.062743349319	-0.684651357740	-5.511647878218
H	-3.701376544964	-0.609006522308	-4.810476372214
H	-1.250071466123	-3.778915204230	0.210017961015
H	-0.876169000456	-2.109350921840	0.744906326850
H	-2.559335784689	-2.590320159978	0.423886684603
H	0.416212607183	-3.392724951635	-1.528589092491
H	0.101974301591	-2.205303147159	-2.813647922769
H	0.625118474711	-1.633314415029	-1.200527824307
H	-4.829750279307	-3.235093368851	-0.480158022563
H	-5.280517262682	-2.966637111098	-2.183128479646
H	-3.681145954605	-3.643406789687	-1.768076969862
H	-5.067180266415	-0.867079648804	0.196922084204
H	-4.222491065754	0.375499443431	-0.759262083696
H	-5.661381727528	-0.446976847686	-1.434624390875
C	2.566265263812	4.063714248187	-1.296882501304
H	2.739870440379	3.016286349114	-1.583134433682
H	3.251015658771	4.692485623788	-1.881576763054
H	2.848447182428	4.152091805134	-0.238851712420

Table S72. Atomic coordinates and single point energies of the *bis*-HMPA-solvated symmetric dimer of **8o** with chelation to one *endo* and one *exo* sulfonyl oxygen; both HMPAs are on the camphor *endo*-face.



G = -4025.180523

G_{SP} = -4026.925805

136

20020a_mis: optimized structure // E(RM062X) = -4028.04686134 A.U. after 12 cycles

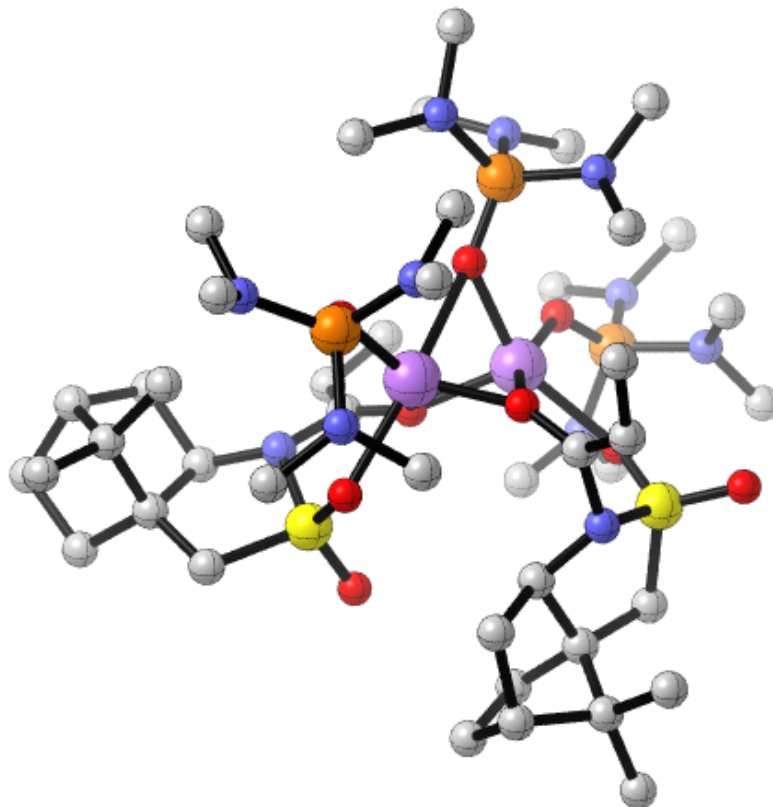
O	-0.227549612974	0.209485215004	-1.302997997974
C	-0.455344078225	0.847503098996	-0.196165289636
N	0.748068604670	1.201633644150	0.580955747440
S	1.641612475164	2.470222971899	-0.079594507888
O	1.911307187608	2.238985812642	-1.524098630382
C	3.178390977857	2.090115483306	0.808491507402
C	2.983268446037	0.693416156807	1.377997253948
C	1.683394741506	0.083578486056	0.784640346215
C	1.232069821754	-0.934971078730	1.854882351777
C	2.420380600785	-0.922306491972	2.836212586657
C	3.644186164476	-1.507141946215	2.089691704124
C	4.064677625881	-0.367623331412	1.112208299892
H	4.049628663976	-0.673890052565	0.058521741630
H	5.068052562524	0.011932181369	1.335630458012
H	3.378501996924	-2.431303368171	1.562577966865

H	4.454409223978	-1.759895759345	2.781760034630
C	2.763383742211	0.585594375739	2.919595703320
C	1.640062841796	1.459832691710	3.483791854987
H	1.907620994302	2.523093492898	3.410194883785
H	0.684989554250	1.336142493584	2.972062135997
H	1.506928484197	1.233176692874	4.549672992356
C	4.026683961981	0.895303341629	3.727659422499
H	4.313087599646	1.948343816440	3.600814933297
H	3.828968751071	0.741791442526	4.795690802453
H	4.889072726623	0.279621343623	3.458033126240
H	2.211545447251	-1.409638132291	3.795123742257
H	0.293081288179	-0.616423973126	2.320392298963
H	1.066445819386	-1.927406025182	1.421053629868
H	1.893459564311	-0.412006159818	-0.173308935722
H	3.311723181943	2.866301292625	1.568508658075
H	3.966787571438	2.161084872924	0.053647449133
O	1.068172820913	3.763967985310	0.277835385975
C	-1.633537469746	1.168096011089	0.375540982359
C	-2.946270018012	0.821561914988	-0.255347089035
H	-3.528960758661	1.715760517958	-0.517503407033
H	-2.789309943666	0.244865461054	-1.175792279744
H	-3.573380606806	0.220094437633	0.419549778419
H	-1.604455915828	1.705436768543	1.319757338363
O	0.551102040657	0.860135241902	-4.019726350994
C	0.788091615114	2.079709169999	-4.421511982131
C	1.970373505442	2.639037284645	-4.764011304507
H	1.973274481109	3.662922668077	-5.126719787110
N	-0.372467613131	2.930020530750	-4.390989136507
S	-1.852254516041	2.316977228250	-4.875454882726
C	-2.731640612896	3.898569015549	-4.748408140400
C	-1.757401185463	4.872563636131	-4.116393331300
C	-1.811649956955	6.336107332933	-4.588331843406
C	-0.911061431028	7.057233586620	-3.541386501249
C	-0.502528825854	5.921920293993	-2.575704762747
C	0.526234344336	5.033946157688	-3.300468148153
H	0.953685596984	4.265553902726	-2.648860161141
H	1.358209904696	5.617899297331	-3.709710289654
C	-0.319126891609	4.386672176519	-4.429303546483
H	-0.002518667660	4.725659452081	-5.428553899221
H	-0.163571992952	6.262284512632	-1.591671136645
C	-1.758580492910	5.018795366515	-2.558788499695
C	-1.586570194019	3.731311577119	-1.748520304338
H	-1.516224079276	3.981486477706	-0.682781392292
H	-2.451362240186	3.070281289099	-1.887961960999

H	-0.696332323823	3.153213143328	-2.006286388512
C	-3.020171300762	5.707703190426	-2.028630819615
H	-3.896837879352	5.060699327275	-2.169742227820
H	-2.915110102367	5.874030637481	-0.949764706485
H	-3.236353664209	6.673332483642	-2.494559912394
H	-1.459566371394	7.851615189092	-3.024144176380
H	-0.032974891085	7.523285589243	-4.002864403892
H	-1.437368909855	6.431000345037	-5.614208627571
H	-2.837780683375	6.719749279315	-4.582128727705
H	-2.994779947009	4.162491290720	-5.777980829751
H	-3.636388668943	3.710856356814	-4.161683382162
O	-2.369992459853	1.383366284466	-3.844812633703
O	-1.859288150669	1.834788462126	-6.256930159630
O	2.652118464555	-0.834954108633	-2.294883641203
P	3.068586461266	-1.735771911691	-3.432086577861
N	2.914344221807	-3.322412116805	-2.898528768929
N	2.254565181929	-1.769551803695	-4.869052045523
N	4.634392593802	-1.343604115977	-3.855928234368
C	3.034655491288	-4.469793930840	-3.780763859465
C	3.278123527608	-3.596215683278	-1.516927146817
C	2.536361500029	-0.839861076072	-5.963993010907
C	0.866837482430	-2.236668353949	-4.902216997910
C	5.379634970963	-2.142615547810	-4.809504732257
C	5.414883397975	-0.369884979516	-3.111381550262
H	4.058455148968	-4.878347738075	-3.792507595029
H	2.355930050398	-5.262814537591	-3.435304001547
H	2.749899656039	-4.192076354415	-4.798630108145
H	3.012535610377	-2.737549448181	-0.893766861496
H	2.719633373662	-4.473528471493	-1.165233413479
H	4.355305885288	-3.807100539244	-1.405335612039
H	2.368703294099	-1.369710102293	-6.911187633875
H	1.869788943634	0.031335728777	-5.907010399999
H	3.574911457423	-0.505846983926	-5.923732848853
H	0.721010337611	-2.844401611651	-5.807001059438
H	0.636315643576	-2.849016383663	-4.025432573555
H	0.182432895512	-1.379719899676	-4.917688191863
H	5.921413558816	-1.486335880011	-5.505239540242
H	6.113350996929	-2.793633831367	-4.308429724939
H	4.697389792197	-2.765235898392	-5.396944380670
H	5.883462928911	0.339705100212	-3.807803783847
H	4.756842499718	0.184475684897	-2.438649365887
H	6.205652171821	-0.861621969068	-2.523553291373
Li	1.351004249812	0.542615951545	-2.348906857477
Li	-1.011612922152	0.211887964263	-3.050023312692

O	-1.731272197821	-1.497725670657	-3.325749799037
P	-2.116842739402	-2.679810039728	-2.490488903545
N	-1.759162275701	-4.070041136699	-3.365621209322
N	-1.340157260438	-2.997603863870	-1.051683558473
N	-3.724768780249	-2.550027830238	-2.071268077053
C	-1.798890192426	-5.403789422998	-2.793745492271
C	-1.973999461362	-4.034824078013	-4.805563270037
C	-1.769049386122	-2.366035619344	0.194041624541
C	0.112886915230	-3.152314051841	-1.120252118435
C	-4.423886966743	-3.640364806360	-1.419775402668
C	-4.570465953151	-1.510179252158	-2.642420835533
H	-2.772745549163	-5.895214365072	-2.953311412218
H	-1.026417856117	-6.023188504067	-3.270816692340
H	-1.592921364355	-5.356996867750	-1.721178309912
H	-1.891613458404	-3.005111878830	-5.162312116978
H	-1.206053938878	-4.643928852865	-5.301268963525
H	-2.963361335524	-4.435990094622	-5.079287543760
H	-1.517397313037	-3.037013788980	1.027045394866
H	-1.270667134207	-1.400337487520	0.342362252562
H	-2.849393329009	-2.205092572388	0.185874852433
H	0.444258421911	-3.709720714294	-0.233078479328
H	0.397421690641	-3.721183047692	-2.011961334539
H	0.613187724430	-2.169870646773	-1.151341136496
H	-5.093584167440	-3.242691318098	-0.644208249130
H	-5.031019855557	-4.220362295515	-2.132963256084
H	-3.709356691944	-4.314018713846	-0.935131898806
H	-5.145875189208	-1.024013693135	-1.842396582869
H	-3.948980421231	-0.760235922971	-3.139722656071
H	-5.274178938313	-1.935028058440	-3.374203903870
C	3.293330713708	1.990186369508	-4.504829517313
H	3.154230628202	1.003845027229	-4.050899107847
H	3.892037712354	1.856776464133	-5.418633290859
H	3.893819204414	2.589694821274	-3.804215430169

Table S73. Atomic coordinates and single point energies of the *tris*-HMPA-solvated symmetric dimer of N-propionyl camphorsultam enolate with chelation to one *endo* and one *exo* sulfonyl oxygen where the μ_2 -HMPA is on the camphor *exo*-face.



G = -4844.959974

G_{SP} = -4847.038155

165

30031a-free: optimized structure // E(RM062X) = -4848.41230864 A.U. after 12 cycles

O	-0.840649383052	-0.358989830622	-0.266467268355
C	-0.642388058975	-0.300404173205	1.008169581519
N	0.652551395669	-0.862947962096	1.373492836353
S	1.109328321048	-2.181362336921	0.435092381636
O	0.104170921393	-3.252757073311	0.400343484415
C	2.456797405602	-2.718780719557	1.528613836908
C	2.477305796142	-1.739543723664	2.683209631592
C	1.102295808078	-1.020576310347	2.751129164104
C	1.440201524046	0.304813213673	3.483430271998
C	2.923405605017	0.121613161334	3.858476121030
C	3.002722978582	-1.000865100162	4.918009992086
C	2.722417536833	-2.294649266094	4.096888323689

H	1.848859820475	-2.849432195799	4.456794374325
H	3.572935803896	-2.984691252128	4.114644124302
H	2.267684501394	-0.848370414499	5.716280588804
H	3.988450631910	-1.036136670500	5.393938286649
C	3.499851738543	-0.563297651285	2.596438401111
C	3.427648581888	0.279500275024	1.322186962723
H	3.587113912737	-0.341688727801	0.430840593782
H	2.475650413633	0.786898075609	1.160277125830
H	4.230381564578	1.027866969399	1.343889452334
C	4.952768215412	-1.027840148709	2.739148779077
H	5.263931864691	-1.582481092039	1.842802153564
H	5.610373077783	-0.153357384100	2.818538627754
H	5.140093445526	-1.663821122377	3.608687912757
H	3.420848243245	1.050907102714	4.157811606854
H	1.270367578572	1.156453600824	2.819207696666
H	0.808654860912	0.448338156001	4.366815247576
H	0.370970485250	-1.622351471724	3.314186678521
H	3.377251030002	-2.729979990183	0.935664496414
H	2.185599303697	-3.736357956478	1.825405379408
O	1.642692266438	-1.714534333613	-0.860836321225
C	-1.415541755243	0.201476753086	2.000477675228
C	-2.684654049854	0.953533611640	1.749044768723
H	-2.724890420066	1.873563655349	2.351314553646
H	-2.768034075951	1.224009089053	0.690900983867
H	-3.577850530207	0.364899276740	2.015536781864
H	-1.091172041363	0.078253287519	3.029408448406
O	-0.256363382384	-0.452284524637	-3.141943042297
C	-0.413380879921	-1.243933390184	-4.148732298577
C	-0.027811982567	-1.107445484104	-5.438780501728
H	-0.310636744722	-1.901799153003	-6.123751437501
N	-1.169551036056	-2.489387387407	-3.905092078604
S	-2.814057270673	-2.232481413114	-3.824713856826
C	-3.222442438620	-3.859693870635	-3.148594272036
C	-1.889915324840	-4.437660980016	-2.699342780589
C	-1.795267620044	-5.060369897377	-1.295870998930
C	-0.442275030470	-5.827494892963	-1.366628032444
C	0.045600273626	-5.569300024576	-2.810362469927
C	0.506770150975	-4.098506979412	-2.894450869349
H	0.978590148381	-3.863116053024	-3.855027380979
H	1.211196159498	-3.838321169372	-2.099288586500
C	-0.814394451062	-3.312728114477	-2.735685749329
H	-0.824148169635	-2.702769666452	-1.820609084682
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C	-1.276782370956	-5.549383379332	-3.613352932401

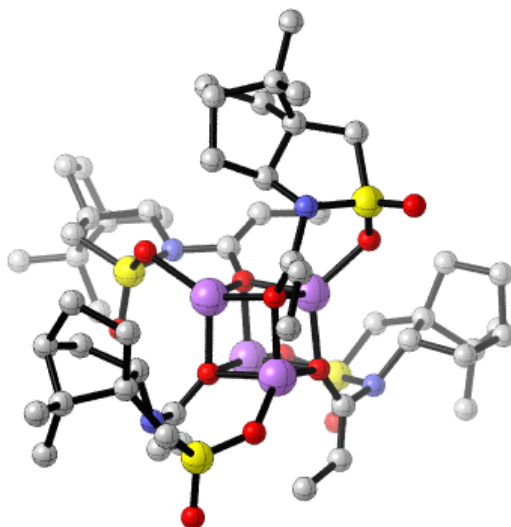
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C	-2.068573993426	-6.860047272725	-3.558818483524
H	-3.036618394699	-6.741351918453	-4.065402416092
H	-1.520283652602	-7.645329261944	-4.094305854721
H	-2.263360860443	-7.221781368432	-2.546045514974
H	-0.576793007442	-6.898843422622	-1.179020785883
H	0.266918600011	-5.444118452897	-0.627197132443
H	-1.783450827214	-4.286126146638	-0.522774423885
H	-2.640144225031	-5.730641962681	-1.098164187559
H	-3.933653871432	-3.675810916938	-2.338016336400
H	-3.705095235905	-4.426654007372	-3.951134587557
O	-3.402486786715	-2.014480866098	-5.148143954535
O	-3.129586654129	-1.216749103334	-2.789182430763
O	-0.837578203922	1.976607653071	-1.758088200923
P	-1.327209797933	3.334803652374	-2.159144703688
N	-1.957250483514	3.293353467089	-3.702338496445
N	-2.523772154025	4.142615056360	-1.312115883360
N	-0.014345978702	4.385190901891	-2.038945483139
C	-2.655885715181	4.390978385016	-4.345602386754
C	-1.419124787820	2.307244465817	-4.637857516586
C	-2.205201654629	4.601753781750	0.034112487190
C	-3.952128514668	3.927682914908	-1.492557208583
C	-0.173095708600	5.790126746698	-2.354876724012
C	1.092907200904	4.091411836235	-1.142922015938
H	-2.008709911223	4.903040013985	-5.075647591660
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H	-3.001108532141	5.118545158535	-3.606606702488
H	-0.940209348279	1.483602759928	-4.094396912250
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H	-0.687489264830	2.771372590263	-5.317668183959
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H	0.779457570499	6.184738916716	-2.732216048962
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H	1.143000519324	3.015793138502	-0.954686074263

H	2.035277563939	4.405328825504	-1.614374971563
Li	0.570421613904	0.096921044199	-1.550482817228
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H	-7.215063533503	1.624753959677	1.155468530340
H	-5.595343506542	0.888001394019	1.261844458849
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H	-3.861186270975	1.494580213389	-3.647584938409
H	-4.317881329804	0.116520822507	-4.676032907321
O	2.206396921329	1.122022930205	-1.518368581277
P	3.386251828099	0.885575222637	-2.415882410091
N	4.759328845997	1.515476573057	-1.664704498943
N	3.876973923621	-0.650154112785	-2.815862028822
N	3.084052604916	1.580567826539	-3.906878716839
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C	4.574551883175	2.700726822361	-0.839353552882
C	3.013945188033	-1.446875505771	-3.695067593091
C	4.635885006210	-1.471723248032	-1.880139686874
C	4.006603530910	1.477430500791	-5.022740704628
C	2.128033163084	2.676019272190	-3.993525935199
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H	6.848518551480	1.511832505672	-1.615595568018
H	6.134451581570	0.575201594652	-2.945781842127
H	3.606611325428	2.645827542889	-0.336328348081
H	5.368657432475	2.738262789980	-0.081817288544
H	4.624551457812	3.628537195750	-1.435337025926
H	3.642646295863	-2.146666509479	-4.261674884952
H	2.271586957570	-2.004756908897	-3.110695007793
H	2.482138289698	-0.800734568169	-4.395140684756
H	5.338178685429	-2.098081041706	-2.447254965196
H	5.200515144312	-0.840576220837	-1.188803184216
H	3.958409355864	-2.122264887070	-1.309571908269
H	3.434138786390	1.349543906289	-5.952274913160
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H	1.722213958231	2.704995571503	-5.012792672284
H	1.305138715736	2.503583849893	-3.293948954294
H	2.591118154438	3.654830434941	-3.783033692157
C	0.711874923295	0.083158816324	-5.959134509381
H	0.088080609999	0.705532882135	-6.619489068138
H	1.050372723470	0.701236448090	-5.121628234477
H	1.592880011229	-0.214517296519	-6.548061290764

Tetramers of enolate **8b**

Table S74. Atomic coordinates and single point energies of the S₄-type tetramer of **8b** with all *endo* chelation to the sulfonyl oxygens.



G = -4771.272512

G_{SP} = -4773.395279

156

baseball-sfn4r: optimized structure // E(RM062X) = -4774.65137504 A.U. after 12 cycles

O	0.453156665046	0.980746539931	0.212605419463
C	0.333677172294	1.167242509159	1.515395769331
N	1.026102425652	0.199376854912	2.353108354675
S	2.677263642768	0.450537099007	2.512380207874
O	3.325863531119	0.434683717077	1.166511443230
C	3.004990799637	-1.140410705278	3.313054782941
C	1.750511158741	-1.973424200390	3.079277987101
C	0.833294531226	-1.231766604159	2.068081859607
C	-0.581584438380	-1.759682519732	2.392678684956
C	-0.287443968311	-2.854942888977	3.438597741138
C	0.483871251505	-3.987076158830	2.719274447773
C	1.910419665863	-3.395217910013	2.517898823339
H	2.210935920585	-3.370790431634	1.464445431880
H	2.670855989783	-3.958412854799	3.069874197505

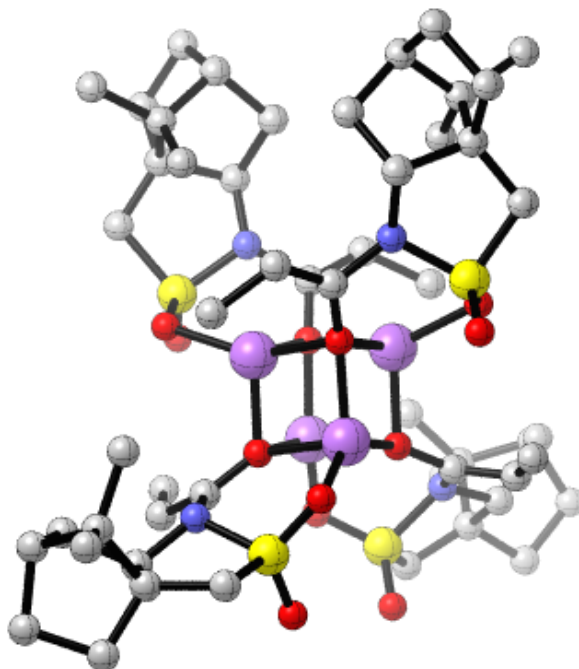
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C	0.811468275456	-2.197383654683	4.310525247705
C	0.358515202731	-0.935181593950	5.048914093526
H	1.218499131617	-0.415004430841	5.494241862664
H	-0.164447986817	-0.213429953737	4.420670533934
H	-0.305157542040	-1.222814277605	5.874938256137
C	1.427695314945	-3.127652691568	5.358774051777
H	2.299385484001	-2.649109996862	5.826843293366
H	0.699633907175	-3.320580269481	6.156537374054
H	1.749792928413	-4.095226346645	4.964745446597
H	-1.174922499646	-3.196205437498	3.982360275660
H	-1.210252181237	-0.956738745686	2.792455678169
H	-1.069633540501	-2.158929706003	1.498310606956
H	1.127980242802	-1.464859910924	1.031520264792
H	3.202837534199	-0.924577952271	4.368367523265
H	3.909483897269	-1.536338777286	2.841484388387
O	2.968124049711	1.604464618034	3.355945034780
C	-0.338071289630	2.128228690447	2.170923698901
H	-0.281835411504	2.104929929881	3.256371561399
O	1.536151188398	-1.194538948876	-1.406427088916
C	1.876490956200	-2.459615351809	-1.454391104715
C	3.006287721468	-3.011759879276	-0.960858637303
H	3.167102516636	-4.080570995254	-1.047677056073
N	0.934597343970	-3.300000998319	-2.144322315676
S	-0.678103353385	-2.808751449482	-2.188444691415
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C	-0.233308475114	-5.359958820800	-2.712560084837
C	-0.274885322387	-6.811695470478	-2.202222145375
C	0.880689364717	-7.477527346852	-3.003573888340
C	1.380071029457	-6.341918681788	-3.924544671792
C	2.171141899832	-5.345251201029	-3.055065317386
H	2.637935522941	-4.550707909104	-3.645295916887
H	2.960337667430	-5.841111034094	-2.479693311215
C	1.072660936611	-4.759820394191	-2.131266452872
H	1.208332262145	-5.080059502409	-1.087271234662
H	1.931476374344	-6.690250656988	-4.804193024524
C	0.084873397346	-5.550975762105	-4.233528699799
C	0.328930663336	-4.282916601371	-5.057652230507
H	0.748119555373	-4.574062919594	-6.029929840163
H	-0.611579526557	-3.753071755439	-5.248547098873
H	1.012923487460	-3.568384070674	-4.594451321893
C	-0.985155752285	-6.360983705628	-4.969699287858
H	-1.935293350710	-5.810124292460	-4.991467914612

H	-0.677733606006	-6.510107446380	-6.012197943623
H	-1.177343057815	-7.347476931343	-4.539049414838
H	0.522674313495	-8.336172906929	-3.580586388074
H	1.681651345744	-7.841416287458	-2.350119840234
H	-0.125572486799	-6.850270084232	-1.117216549715
H	-1.243842750398	-7.275572162971	-2.415053983640
H	-1.756950363794	-4.697125168023	-1.295012948250
H	-2.211973653353	-4.411525105009	-3.009832108112
O	-0.970024758070	-2.024137812803	-3.384864779164
O	-1.068074989656	-2.173599495118	-0.895516545992
Li	2.231939485036	0.402060183303	-0.466907807831
Li	-0.189857860906	-0.394066120866	-0.939463952925
C	-1.094250367851	3.225188490203	1.495683024656
O	-0.248570438281	0.672167811353	-2.508183075262
C	-1.160338006190	1.008822370943	-3.392738972766
Li	1.546482807610	0.028213085881	-2.920356712771
Li	0.488257773643	2.120947648760	-1.395578392569
C	-1.040097930607	0.908909145859	-4.724790740492
N	-2.370100372337	1.611693114337	-2.848577717230
H	-1.865230539561	1.243164045985	-5.346789970647
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C	-2.930087097900	0.992752464445	-1.639666024488
C	-3.585727049848	3.394935948320	-1.393242380587
O	-2.316248436081	4.061388758360	-3.729216470612
O	-0.928913162193	3.466340192266	-1.727887873841
C	-4.021382422725	1.963727411415	-1.116089564302
C	-3.700184435439	-0.322640005198	-1.895396370882
H	-2.142077447170	0.876604654743	-0.876929459695
H	-3.215091434361	3.933440980544	-0.515535274779
H	-4.342352615928	3.998362128758	-1.905604644991
C	-4.265541026789	1.542155429564	0.344285402745
C	-5.316855420995	1.467142657564	-1.836313196600
C	-5.107379008107	0.009398220156	-1.357187691908
H	-3.696112941743	-0.562826310377	-2.963595790729
H	-3.241507566518	-1.161022805674	-1.363471682840
C	-4.988204463369	0.172515928475	0.175745424317
H	-3.320332657909	1.456888617002	0.892904404344
H	-4.886114471271	2.273510137937	0.873365147546
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C	-6.584369917113	2.133958426440	-1.295606738795
H	-5.879673393544	-0.701395476399	-1.670849051853
H	-5.971590044263	0.178551353220	0.657410752288
H	-4.417312312379	-0.651327496980	0.619347591810
H	-6.282695991271	1.232791388895	-3.748705790462

H	-5.301570596794	2.696905682517	-3.633606186145
H	-4.512649845603	1.139809010594	-3.871568116284
H	-6.595890711301	3.201024922566	-1.558058956942
H	-7.468460259233	1.678993746540	-1.759723541568
H	-6.703473462825	2.056565756156	-0.211509717857
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C	3.096334691484	2.177050044413	-2.808049945039
C	2.789888430803	3.094350383761	-3.743399146316
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H	3.601334720822	3.424980532464	-4.386786308870
S	4.552457112049	0.268502958221	-3.825580866472
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H	5.988713762799	-0.375638462967	0.061071774402
H	7.557021769695	-0.815043692858	-0.627113141877
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H	7.996642629786	3.198420412904	-0.858736940375
H	8.518534497263	1.104296528606	0.382769997222
H	6.948060879017	1.565277842300	1.040474989202
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H	-1.353795604870	2.944322733074	0.471510296138
H	-2.014123927161	3.464435909669	2.044483308747
H	-0.503443161655	4.151400432566	1.435490470531
C	1.412740100700	3.648073431371	-3.934633408085
H	1.263436458482	3.974806842242	-4.970029739413

H	0.645310965608	2.895027218238	-3.721237180292
H	1.209291242939	4.513541000931	-3.287533234486
C	0.216975177099	0.356471017033	-5.325678861520
H	0.429757335190	-0.649343195251	-4.930980730973
H	0.139464013816	0.264361056044	-6.413486526419
H	1.091278246689	1.001442173077	-5.128462437113
C	4.090513041735	-2.178433225367	-0.358955919375
H	4.077673076855	-1.163635965665	-0.774705008330
H	4.008613400606	-2.070764144507	0.733809082057
H	5.077718934128	-2.613325458621	-0.563013530149

Table S75. Atomic coordinates and single point energies of the S₄-type tetramer of **8b** with all *exo* chelation to the sulfonyl oxygens.



G = -4771.261773

G_{SP} = -4773.390520

156

baseball-sfn4s-exo: optimized structure // E(RM062X) = -4774.64665228 A.U. after 12 cycles

O	0.001462102706	0.006220205805	-0.004160566029
C	0.009329095383	0.002301677485	1.313974648262
N	1.350414783268	-0.002721030693	1.868489563975
S	2.345693501551	-1.250634791771	1.275379223215
O	1.776000607885	-2.574090467449	1.532586009695
C	3.698184124782	-0.946336303552	2.430322119151
C	3.083833975766	-0.130951026722	3.558476354588
C	1.548612614503	0.003745635476	3.323872555959
C	1.187628984887	1.318870040785	4.055087045745
C	2.504036127974	1.666601974284	4.776544092613
C	2.762669578000	0.569988394134	5.837528373126
C	3.222884875026	-0.657178121838	4.995797403474
H	2.600869283922	-1.545201117244	5.152950084089
H	4.257791826591	-0.940203354087	5.215660451797

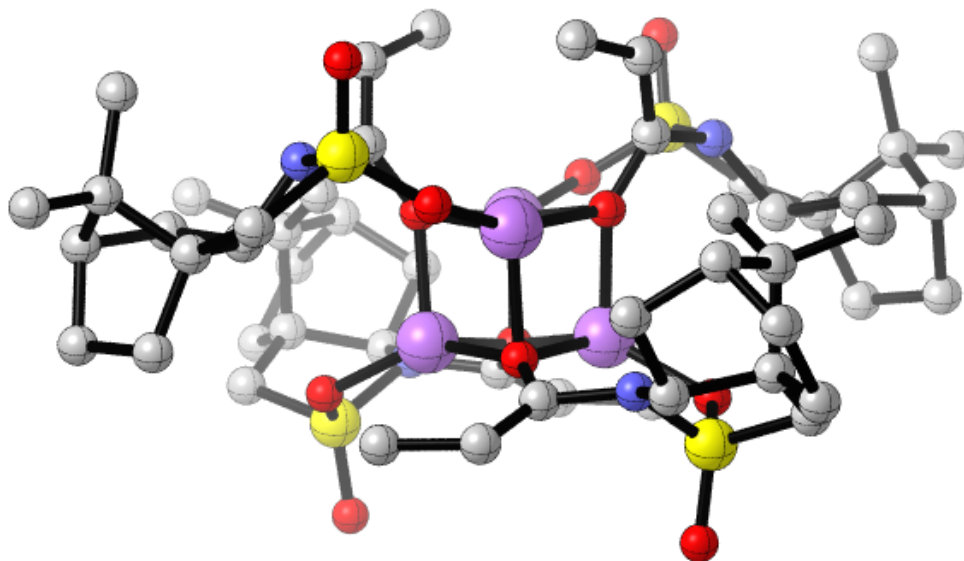
H	1.856575529607	0.358595572551	6.416667927233
H	3.534663470995	0.875533896223	6.551521223140
C	3.564573876782	1.348566856482	3.695223998953
C	3.439349526044	2.190545026507	2.426541235069
H	4.126293535866	1.827321826640	1.648961298783
H	2.437632058759	2.189638173011	1.997552973037
H	3.722712433381	3.228483317908	2.648539446852
C	5.012774502266	1.464560531008	4.176546308918
H	5.700185934784	1.043660203410	3.429491281196
H	5.277121173266	2.522585737383	4.297974173143
H	5.208669049595	0.965091378334	5.129449617968
H	2.531705556177	2.686420018259	5.175489864885
H	0.878983070151	2.090363441849	3.343534361446
H	0.361054442337	1.171561538543	4.757809362232
H	1.022090079052	-0.855759838085	3.765581400442
H	4.484180735033	-0.421957960168	1.878070316258
H	4.049726812663	-1.938159990724	2.729420688656
O	2.750151192065	-0.944234279233	-0.115463216824
C	-1.058584010582	0.029971473630	2.131555363074
H	-0.901750035104	-0.033486413101	3.203946916310
O	-0.142996367720	-1.600793641787	-2.306192278530
C	-0.408079829015	-2.710491916323	-2.968640658608
C	0.423305601076	-3.416805957100	-3.755114860530
H	0.053859157356	-4.327521524810	-4.218921132325
N	-1.786375427771	-3.134206678119	-2.794653932735
S	-2.212023311872	-3.427120950356	-1.173959452418
C	-3.730167383584	-4.346508504972	-1.532899252743
C	-3.777952314044	-4.501726422235	-3.041422014865
C	-4.144714383755	-5.881699792361	-3.612551526062
C	-4.373875670425	-5.560297982659	-5.119552796549
C	-4.191986738780	-4.025063674449	-5.196647938530
C	-2.682888548147	-3.736183487774	-5.076859198820
H	-2.449451067607	-2.674142161976	-5.203724903115
H	-2.093672515325	-4.294476280514	-5.811778528768
C	-2.372489551831	-4.183552263344	-3.629329757843
H	-1.745483979981	-5.086671449316	-3.598893590424
H	-4.661725054356	-3.564989459344	-6.072885366647
C	-4.738238524623	-3.553294061431	-3.825170463493
C	-4.565888982761	-2.062835891065	-3.528667944634
H	-5.172635120793	-1.474428741957	-4.229923963245
H	-4.928662699635	-1.829319479200	-2.517861798532
H	-3.535373050152	-1.716169170988	-3.585930819898
C	-6.217571212756	-3.879394363161	-3.599504097783
H	-6.487012143484	-3.724278308570	-2.545653384252

H	-6.837335911099	-3.195433942409	-4.192878330442
H	-6.500852090307	-4.899874946750	-3.871125404247
H	-5.373151632590	-5.866629664638	-5.445585541082
H	-3.654328547305	-6.075579565985	-5.765929857432
H	-3.339770826432	-6.605755953412	-3.444866296637
H	-5.046822826857	-6.279896478170	-3.136019118686
H	-3.615755236317	-5.293549814749	-0.996851753263
H	-4.562888915638	-3.775088135527	-1.110837250033
O	-2.524201433807	-2.125046771241	-0.539469425312
O	-1.260686782328	-4.302961783059	-0.491923036721
Li	1.269572281464	-0.649125722608	-1.348636295437
Li	-1.416730672242	-0.650592145475	-1.151402324142
C	-2.466926380957	0.145151336879	1.641125875579
O	-1.556340034486	0.894721318548	-2.327514591369
C	-2.153856875297	1.727410298417	-3.147185461568
Li	-0.134354015619	-0.009455471980	-3.388995236243
Li	-0.151462166806	1.549183735586	-1.092816625494
C	-2.535517734975	1.479911938404	-4.419434358159
N	-2.308176826008	3.037884774419	-2.580952380194
H	-3.018874167909	2.267413566848	-4.991172343079
S	-2.639528482281	3.061031129369	-0.922081417340
C	-2.964958484760	4.144585312006	-3.271505996116
C	-3.173409791090	4.789939770385	-0.865933296790
O	-1.357553520699	2.875147947615	-0.199001821828
O	-3.758274920098	2.192811895705	-0.551650697537
C	-2.992262483940	5.332778752756	-2.268716601035
C	-2.172992689628	4.722481739428	-4.471516618540
H	-3.985550181374	3.847118947649	-3.556873280601
H	-4.220188740363	4.746311319865	-0.549170887198
H	-2.572309634184	5.293373246262	-0.101854973165
C	-4.066360526993	6.293096448652	-2.806896739794
C	-1.668871395646	6.106402917036	-2.570393899312
C	-1.990198382794	6.200731796310	-4.081764309564
H	-1.218956689892	4.199923553406	-4.578445199666
H	-2.720986000270	4.607415481291	-5.413225248279
C	-3.389073383872	6.859824316100	-4.089804299465
H	-5.001434797716	5.761433998171	-3.014246073764
H	-4.294154305154	7.080087376872	-2.080338153461
C	-0.375548598390	5.360954941710	-2.230839834470
C	-1.594633804519	7.461595741916	-1.861936348889
H	-1.245174743248	6.727386045732	-4.688841253494
H	-3.320868180355	7.951938957606	-4.055521001503
H	-3.943433496042	6.601098763355	-4.998856261341
H	0.485491554020	5.960943323173	-2.554853414986

H	-0.287154398764	5.227869775240	-1.143576579745
H	-0.291118175781	4.371090277276	-2.683839517642
H	-1.530827997380	7.323024376582	-0.773991828398
H	-0.682766719812	7.986961685085	-2.172204340259
H	-2.440988058779	8.122620797487	-2.066679430893
O	1.216398540405	0.975995897514	-2.413062954427
C	1.858313536310	2.032005820718	-2.857932582836
C	2.334205803761	3.047294023151	-2.108987444062
N	1.956065585216	2.050226584062	-4.288918042275
H	2.838899590780	3.881700369337	-2.587676737435
S	2.242928959246	0.532376853299	-4.979622578826
C	2.644352017367	3.105379781799	-5.025028570685
C	2.767626115801	1.160836736715	-6.595229534366
O	0.943025676153	-0.176357348791	-5.073944295325
O	3.356462988358	-0.177603339864	-4.348176454084
C	2.653064593845	2.670706403906	-6.519227751888
C	1.891668287095	4.458815485717	-5.057789070799
H	3.671022739246	3.213118198652	-4.643219209122
H	3.796781879414	0.806136452427	-6.708606087104
H	2.125756964945	0.695495582737	-7.350272599284
C	3.758872582107	3.513161913146	-7.176709407533
C	1.355283613733	3.311482946041	-7.104798928297
C	1.723861364630	4.715581407327	-6.566478489995
H	0.932131237101	4.366788062582	-4.540438233226
H	2.460519323321	5.253765098673	-4.563210624045
C	3.136636547274	4.941523887305	-7.156068643858
H	4.696053676353	3.444824437234	-6.613708617348
H	3.964047097917	3.170142198044	-8.196125533880
C	0.044093255004	2.730235812047	-6.571768260203
C	1.283943341875	3.229615404891	-8.632284982641
H	1.009253574198	5.512210852457	-6.802045317061
H	3.091249057972	5.371981694298	-8.161610751755
H	3.716203027833	5.635082593318	-6.536516501387
H	-0.799138781095	3.325186760936	-6.947765857793
H	-0.091104001767	1.705063380030	-6.944161472104
H	-0.021541279193	2.686453909846	-5.483021854536
H	1.223355300096	2.182441700385	-8.959164268346
H	0.371569319479	3.728437313670	-8.982428980463
H	2.130052818187	3.692204969612	-9.147365983196
H	-2.511553686268	0.438684682439	0.588302561115
H	-3.015048744690	-0.800698537345	1.746179553387
H	-3.018736739283	0.913694114271	2.198816734748
C	2.160137584564	3.047454874519	-0.618110684485
H	3.039079160027	3.475919625013	-0.122098706126

H	1.289973404029	3.634757381736	-0.280630987855
H	2.047501941226	2.020917633142	-0.239625453126
C	-2.277809839651	0.165493539260	-5.095898783139
H	-1.984140243042	-0.605785237570	-4.369216703335
H	-3.181717928343	-0.210611184930	-5.593170052302
H	-1.487958846691	0.226070150150	-5.858175508331
C	1.851197843135	-3.041941136428	-3.989238367713
H	2.126215718821	-2.139211408934	-3.437935381538
H	2.521641804441	-3.849723527220	-3.664230283343
H	2.060143302136	-2.849873173304	-5.050201027755

Table S76. Atomic coordinates and single point energies of the S₄-type tetramer of **8b** with *endo* chelation to the sulfonyl oxygens of the *syn* subunits and *exo* chelation to the sulfonyl oxygens of the *anti* subunits.



G = -4771.275661

G_{SP} = -4773.401430

156

baseball-2exo2endo-matched: optimized structure // E(RM062X) = -4774.65736772

A.U. after 12 cycles

O	-0.022668011353	0.010297284064	0.059904804860
C	0.003215553251	-0.003186512501	1.373591093764
N	1.344728956963	-0.023359229055	1.912394702693
S	2.264857341656	-1.406862886818	1.657357416474
O	1.679911384705	-2.605978880048	2.260998404765
C	3.679080108959	-0.847616839959	2.639128584671
C	3.219712399210	0.431188192011	3.320370838778
C	1.673498263148	0.519846399712	3.232370796116
C	1.391494387063	2.033585888589	3.384099384243
C	2.798424171176	2.615209611766	3.640641970913
C	3.258099931749	2.128377173527	5.032622457680
C	3.563445707216	0.617953942780	4.807838081282
H	2.951560047061	-0.040586382934	5.434567123498
H	4.611981450251	0.375504214132	5.010315219054

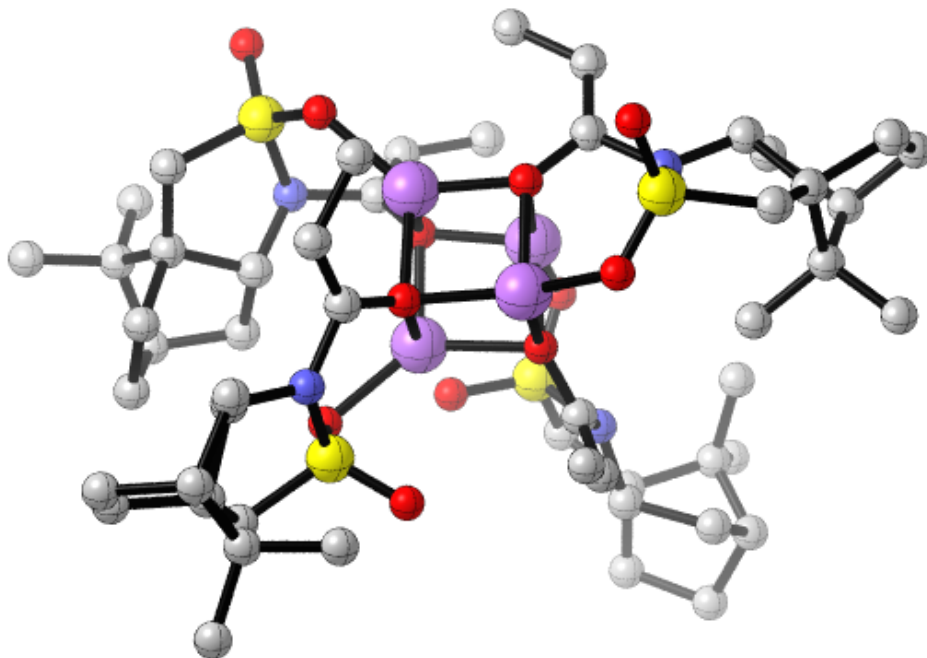
H	2.481040933486	2.287433796109	5.788450726641
H	4.149605846100	2.667888524323	5.369115165511
C	3.686461786444	1.780535854899	2.683977450874
C	3.364760841199	1.971526593484	1.198880962809
H	3.732231185221	1.132445482607	0.591274994994
H	2.297870930170	2.054430921273	0.992139153101
H	3.857349688534	2.882175536358	0.833438145551
C	5.190776242930	2.016134809208	2.844682946540
H	5.752844385860	1.353718810514	2.171134555078
H	5.434713320659	3.046108683150	2.556259012865
H	5.565794171378	1.857072763850	3.859617507309
H	2.854968382368	3.700445545284	3.505550610419
H	0.919969029350	2.435093320606	2.480816937983
H	0.709640850104	2.229328659351	4.218234990001
H	1.200011583915	-0.074733194978	4.027819379191
H	4.520481297534	-0.711494297404	1.950915506393
H	3.890007786244	-1.667454406395	3.332596106104
O	2.612895740149	-1.498961112325	0.215899739207
C	-1.057066266174	0.059981397803	2.195710116014
H	-0.905211240747	-0.009648185797	3.269514058502
O	0.159570354034	-1.141960952298	-2.428707452317
C	-0.081744080039	-2.022653151415	-3.373222686773
C	0.723663255513	-3.027651972446	-3.754374690569
H	0.386995555590	-3.721502945610	-4.519938653178
N	-1.325910870883	-1.776953474585	-4.062182570122
S	-2.742243710194	-1.954760402993	-3.172433764261
C	-3.851356174368	-1.667265605029	-4.573993190001
C	-2.952749341935	-1.623403664956	-5.799141494191
C	-3.417205955129	-2.375413107667	-7.058144174941
C	-2.461973859909	-1.814818102184	-8.152729022472
C	-1.582969405998	-0.805917240049	-7.381825291622
C	-0.620431292094	-1.613912450243	-6.484647281916
H	0.141837324471	-0.991866141181	-6.003322168444
H	-0.094877538692	-2.392469329045	-7.047679248780
C	-1.573613091429	-2.229312172405	-5.432560461555
H	-1.599367750281	-3.328208075590	-5.482389220009
H	-1.075896742439	-0.074815675092	-8.020238603921
C	-2.578661591191	-0.210732628696	-6.354743955181
C	-1.944076118286	0.765595924018	-5.358006330249
H	-1.903431723934	1.765192713306	-5.809175197018
H	-2.530812855939	0.846573086700	-4.431677138656
H	-0.929958580212	0.489998318608	-5.063440282370
C	-3.778907932553	0.509550295345	-6.975423342004
H	-4.452721246874	0.873514135891	-6.186830534747

H	-3.432832628191	1.390208395767	-7.530659450819
H	-4.368497409965	-0.105672545559	-7.660855448803
H	-3.022680085293	-1.323128531814	-8.954605906168
H	-1.856089829279	-2.600196205562	-8.617995643150
H	-3.322008712464	-3.458457686912	-6.920696169612
H	-4.468663465944	-2.168944393352	-7.283892875211
H	-4.547889271321	-2.511335869643	-4.566439149558
H	-4.390691032929	-0.733747434411	-4.381060863827
O	-2.832018057953	-0.856593440521	-2.175941248375
O	-2.928387209305	-3.313431876746	-2.658210923668
Li	1.396640187295	-0.688157580772	-1.056631285953
Li	-1.173129206215	-0.117414735894	-1.463813270968
C	-2.438699674532	0.214532533603	1.642844067303
O	-0.735893786999	1.564863184226	-2.354784422814
C	-1.207764821503	2.751106921695	-2.669022999274
Li	0.694971641814	0.580829529052	-3.123796718957
Li	0.419014810798	1.728189691533	-0.734654822270
C	-0.807328252927	3.583853468264	-3.648213902914
N	-2.276367914864	3.242578777124	-1.812201273619
H	-1.331271403317	4.534537832504	-3.716770483377
S	-1.734869652742	3.888247833952	-0.356207985666
C	-3.419522718336	2.354973079839	-1.569793567096
C	-3.294668350678	3.666208347085	0.545035734380
O	-1.362131960955	5.293034365935	-0.514570400596
O	-0.693314201010	3.010230958669	0.251117491214
C	-4.249770835571	3.017069328826	-0.444048288556
C	-4.411048626377	2.272778099941	-2.752111390670
H	-3.075046155176	1.355665968999	-1.275826090139
H	-3.047884081593	3.033556206907	1.403329395419
H	-3.605946457735	4.658318496222	0.888642533611
C	-5.193656762964	1.914467844324	0.074000021344
C	-5.226424788239	3.957289211507	-1.226658405321
C	-5.722619115520	2.801420405935	-2.131669413856
H	-4.060295102128	2.880367796393	-3.593601464458
H	-4.511011848501	1.238605927144	-3.100444999562
C	-6.200142271297	1.754102116222	-1.102632509781
H	-4.646429868345	0.989722340572	0.280879369340
H	-5.688425711800	2.215974012722	1.003539538131
C	-4.582661719349	5.119120948597	-1.988526936450
C	-6.307986683242	4.563056063366	-0.327602070348
H	-6.480911594986	3.080108191680	-2.871526501344
H	-7.228002489722	1.949558928659	-0.779618454578
H	-6.180009948367	0.741956042433	-1.522235040618
H	-5.373052363044	5.716021379707	-2.462228128814

H	-4.039444241178	5.784453182219	-1.303149328498
H	-3.876336542573	4.808145013592	-2.759302237084
H	-5.867314414721	5.311207965726	0.345681522962
H	-7.051207284372	5.084482231525	-0.943869611509
H	-6.842051730126	3.834291027206	0.287920919468
O	1.958847750681	1.062502839736	-1.658578576857
C	2.931832605131	1.763075971034	-2.197459133856
C	3.087551442167	3.099064429591	-2.170082817452
N	3.924138780104	0.998293465437	-2.936062711212
H	3.951094672853	3.506587775934	-2.689287574060
S	3.439598188759	0.590086285383	-4.495628278830
C	4.521963175232	-0.165008166716	-2.266897700293
C	4.484982434349	-0.884053692926	-4.652454052361
O	3.793217868524	1.643208937968	-5.445652671999
O	2.006521608688	0.172927506551	-4.507611482616
C	5.277631459312	-0.961598617409	-3.358506236041
C	5.632026267972	0.192242803323	-1.250574815530
H	3.739423892448	-0.774164978602	-1.797005714212
H	3.789978035323	-1.717504119762	-4.795554102726
H	5.096964018305	-0.746414248195	-5.550083508326
C	5.533366660516	-2.353256112348	-2.746546236382
C	6.706244371024	-0.322346320131	-3.349558531888
C	6.866589748403	-0.536082363681	-1.824046514599
H	5.764543935015	1.277961378201	-1.188389892651
H	5.377699465235	-0.172450048787	-0.248737836016
C	6.618181863797	-2.052230467716	-1.671485603090
H	4.619522930682	-2.767242661293	-2.309752012212
H	5.886048132055	-3.063407711373	-3.502195032082
C	6.797413129076	1.141263696442	-3.789602037193
C	7.707865424034	-1.104399940946	-4.204120292917
H	7.817362858691	-0.193139685898	-1.401726795551
H	7.531604207703	-2.628433448105	-1.851822491515
H	6.272958647843	-2.302075734809	-0.661730079470
H	7.844329877827	1.466399740487	-3.728266214908
H	6.482377533485	1.255570697792	-4.835889855290
H	6.188597641796	1.823369664314	-3.194534048632
H	7.472963791580	-0.985516066751	-5.270745452955
H	8.717001520085	-0.701448343971	-4.051303854883
H	7.743773842290	-2.175529443242	-3.988291384282
H	-2.886588705143	-0.747543411034	1.350870904474
H	-3.114533984844	0.683258527487	2.368849606236
H	-2.407797907215	0.846801177335	0.745575643507
C	2.117342946778	4.017486167777	-1.490217720317
H	1.183635169251	4.143168993417	-2.059434044591

H	1.838945052651	3.663005753306	-0.488555307741
H	2.547102886348	5.016526644646	-1.360296716050
C	0.315823096468	3.313959662112	-4.597866823504
H	0.612320559070	2.260147206664	-4.623294025271
H	0.040228909546	3.590251992773	-5.623930873185
H	1.216175057031	3.894395166223	-4.345394285638
C	2.068547936246	-3.204336557062	-3.122846701734
H	2.022244427172	-3.773786512704	-2.182436974543
H	2.763014768408	-3.729896612639	-3.789992906382
H	2.500114046564	-2.222904740871	-2.883899401399

Table S77. Atomic coordinates and single point energies of the S₄-type tetramer of **8b** with *exo* chelation to the sulfonyl oxygens of the *syn* subunits and *endo* chelation to the sulfonyl oxygens of the *anti* subunits.



G = -4771.275657

G_{SP} = -4773.397529

156

baseball-2exo2endo-matched-anti_endo-syn_exo: optimized structure // E(RM062X) = -4774.65293710 A.U. after 12 cycles

O	0.005716864197	-0.000430637448	-0.028537708116
C	0.010802713768	-0.002038584294	1.284479514152
N	1.340697180519	-0.009645239798	1.894402029107
S	1.994034539698	1.543282992853	2.001876787607
O	1.723570090439	2.289365694220	0.742074156293
C	3.737251131777	1.032961972961	2.008204418083
C	3.720241412594	-0.474534207279	1.832498793658
C	2.339719421219	-0.882488556621	1.267665911282
C	2.203340425759	-2.369000237044	1.659831383185
C	3.576912988224	-2.667411981164	2.299040715724
C	4.622561663654	-2.610130803669	1.162365199246
C	4.739951038609	-1.088953657181	0.854403777995
H	4.464082783684	-0.841067169136	-0.178276440619

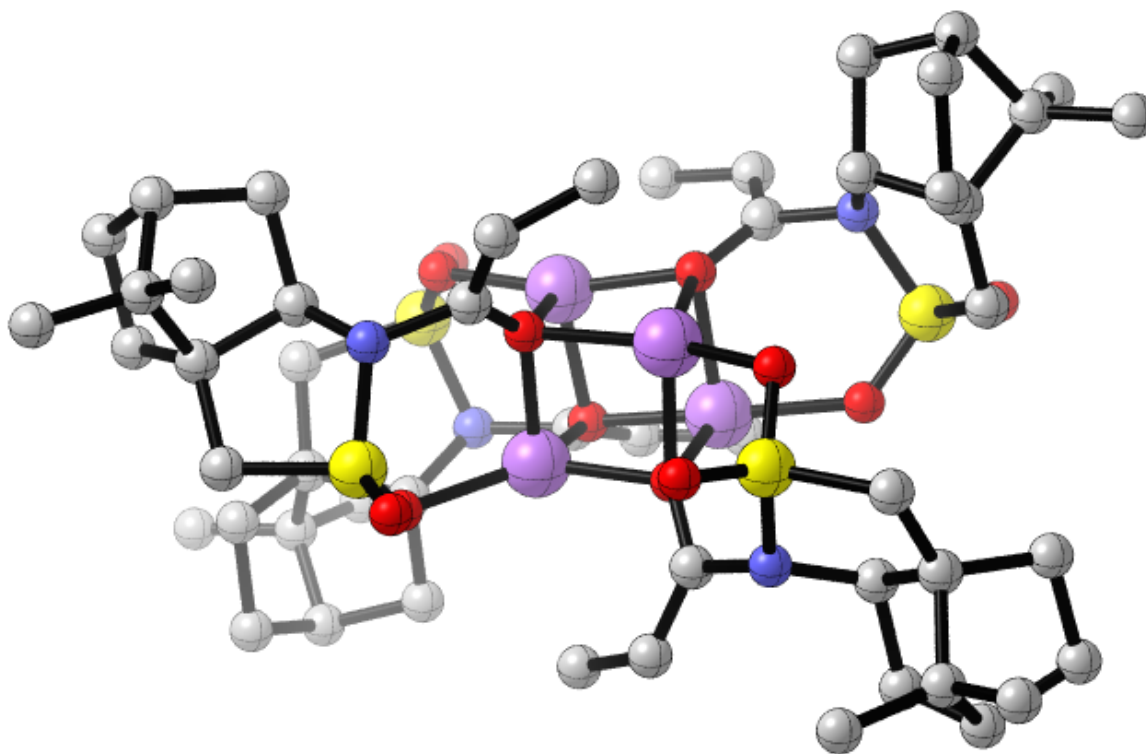
H	5.750623052798	-0.704347107822	1.033565706456
H	4.268952162168	-3.178563883958	0.294884506513
H	5.584348371173	-3.033429019167	1.472540618298
C	3.875169034951	-1.372694833627	3.099114417500
C	2.889855556702	-1.092123221085	4.236276066040
H	3.026312933119	-0.073372307477	4.625826554722
H	1.842457357633	-1.187553260095	3.947234024805
H	3.088882167326	-1.785258293337	5.064345826878
C	5.281799505389	-1.314051046825	3.700031570607
H	5.463493536433	-0.328162556388	4.149942038663
H	5.373368212880	-2.056033276640	4.503428220599
H	6.083553919398	-1.504973346683	2.981225909537
H	3.604570333202	-3.594772882563	2.881569434076
H	1.373085590431	-2.501649791071	2.361396920938
H	2.008625592355	-2.993365337190	0.782438896537
H	2.335322326699	-0.734839661391	0.182504049992
H	4.173738694478	1.379627922850	2.950525265491
H	4.191508814129	1.561594454830	1.163133850753
O	1.594295361722	2.204749509088	3.241277161138
C	-1.020705930531	0.085149955498	2.144198252582
H	-0.763270970080	0.062556549754	3.200443319894
O	1.795576983793	0.433316360691	-2.285774740657
C	3.068084433781	0.738249626558	-2.399694836904
C	3.630659635075	1.951935408851	-2.195485829291
H	4.704419012283	2.060981772208	-2.307062349289
N	3.891535972713	-0.361467168273	-2.819286120079
S	3.266401755563	-1.924234958784	-2.782062397048
C	4.875595583892	-2.741870952905	-2.745829423205
C	5.873226780727	-1.712701567706	-3.226412290131
C	7.294674532129	-1.795696313608	-2.645411918608
C	8.067355094973	-0.773547758413	-3.529121200012
C	7.015227221424	-0.324063421942	-4.569961017269
C	6.028982041080	0.627537146562	-3.868983037297
H	5.289726068080	1.044233513549	-4.559048979374
H	6.541557831046	1.465419462078	-3.384905054674
C	5.353403156675	-0.303507702177	-2.825950795806
H	5.685257747272	-0.044031779829	-1.809526323177
H	7.445732291700	0.088982708648	-5.488438806369
C	6.152258133947	-1.593347816240	-4.761858483288
C	4.936406106958	-1.373214677449	-5.666814930754
H	5.289349822357	-1.054952374451	-6.657064503034
H	4.374043477774	-2.305022515086	-5.797667701544
H	4.230228477030	-0.624891429638	-5.300282836567
C	6.918976039643	-2.791622206774	-5.326967432729

H	6.323415063652	-3.709992727792	-5.232724914214
H	7.101257579179	-2.636035696508	-6.397651706975
H	7.887879891715	-2.967699042661	-4.851405652725
H	8.936512960240	-1.236474805439	-4.007505847431
H	8.438163014149	0.078193994748	-2.947386530930
H	7.300584180996	-1.536709313192	-1.580377012039
H	7.699544251038	-2.809113769215	-2.737662054451
H	5.037230661081	-3.031628831433	-1.701688594830
H	4.792014381796	-3.634948212845	-3.373779527765
O	2.526248388218	-2.247265612196	-3.999216953332
O	2.544873331575	-2.198654991713	-1.512758424670
Li	0.892515387231	1.513956648304	-0.869510106155
Li	0.788594446228	-1.167021786187	-1.447085277286
C	-2.457622092990	0.249297534617	1.760668498440
O	-0.669890119948	-0.789784957869	-2.813977794724
C	-1.054547022395	-1.789008756333	-3.583221636048
Li	0.222226634085	0.815194813611	-3.348087352199
Li	-1.394390615611	0.192986765847	-1.286854352450
C	-0.673343368887	-2.048453558848	-4.846867435041
N	-2.010151528442	-2.636497823658	-2.916819180726
H	-1.078490051079	-2.925218163173	-5.344308856822
S	-1.839566013029	-2.632903058862	-1.242395129354
C	-2.397356720864	-3.955831157824	-3.411610714786
C	-2.768473213669	-4.151685412212	-0.943993591145
O	-2.535184095210	-1.444076945115	-0.704114965303
O	-0.435270549135	-2.827520804871	-0.823740032623
C	-3.277316761979	-4.598300725497	-2.301178764175
C	-3.340934712176	-3.950583362875	-4.641932853341
H	-1.491086611664	-4.552853894161	-3.595679159885
H	-2.043356310471	-4.842104797456	-0.501901186021
H	-3.552188267694	-3.915907655602	-0.216871491735
C	-3.267056030582	-6.107565059111	-2.596412132405
C	-4.733124683400	-4.189201524418	-2.694964384714
C	-4.566444288597	-4.733535168638	-4.134786447329
H	-3.590121264701	-2.924850239950	-4.928412445736
H	-2.874365413724	-4.432576283611	-5.507578489473
C	-4.119419996372	-6.194345059703	-3.896390586494
H	-2.243595712590	-6.475018203874	-2.727916968582
H	-3.714929187029	-6.674267560272	-1.773251884881
C	-5.050060016821	-2.693339484807	-2.613167907008
C	-5.800192766914	-4.915272728848	-1.871628380095
H	-5.447866952351	-4.636745476940	-4.777735400820
H	-4.976749768151	-6.862800740779	-3.767131608761
H	-3.540830722254	-6.574732304301	-4.745594581499

H	-6.052096390004	-2.516483550873	-3.026932873672
H	-5.066349391986	-2.358936965319	-1.566761636585
H	-4.339056473650	-2.056564250466	-3.142058173589
H	-5.743393566558	-4.613382368036	-0.816825013982
H	-6.796965528035	-4.633067787890	-2.232966774300
H	-5.732312328881	-6.005716405674	-1.912325265709
O	-0.588662920056	1.933136488339	-1.962763556366
C	-1.727707333743	2.583801890962	-1.983892484480
C	-2.325821375476	3.214440596659	-0.952772770128
N	-2.356057878081	2.501025679218	-3.276846153610
H	-3.261947277071	3.737759294683	-1.132387709546
S	-1.359226818484	2.985090110214	-4.555386218626
C	-3.735768928835	2.907745223734	-3.518704128318
C	-2.692260981272	3.095604954404	-5.778226595853
O	-0.427629483004	1.879769840094	-4.884381430300
O	-0.763735870219	4.304863454170	-4.335058782899
C	-3.965304925275	2.721253543829	-5.042137301390
C	-4.788237297148	1.965719574829	-2.882360506193
H	-3.884432605888	3.958592011407	-3.227328890867
H	-2.677092946407	4.135853647372	-6.118684448795
H	-2.432180206646	2.426691686128	-6.605012760617
C	-5.240140795718	3.520541774483	-5.363950434644
C	-4.451585331722	1.240762346582	-5.157302812285
C	-5.571480055026	1.456858346804	-4.109013465532
H	-4.297192794584	1.153603258214	-2.335668510636
H	-5.431215653212	2.496458625103	-2.172558859659
C	-6.349849579921	2.657326379416	-4.693608187122
H	-5.179673632249	4.534344722426	-4.953027919796
H	-5.389359035580	3.616851505390	-6.444459129470
C	-3.421684540548	0.167011263363	-4.793349152428
C	-4.963749918754	0.895144370345	-6.559004754027
H	-6.194601475537	0.580486564394	-3.899557273125
H	-7.097187945529	2.332203675959	-5.424843483380
H	-6.884137951754	3.205156185243	-3.909438444690
H	-3.854036445093	-0.820820117645	-4.998293723263
H	-2.521486144392	0.255774835011	-5.417989352648
H	-3.085600567956	0.185417425556	-3.754443149587
H	-4.126117725039	0.838872034668	-7.267597967674
H	-5.436472442009	-0.094978669170	-6.542993096026
H	-5.693908759392	1.603239073370	-6.960132706576
H	-2.573842610094	0.662374643306	0.751451077032
H	-3.006431574154	-0.701632686487	1.778109622023
H	-2.958035379991	0.934227352902	2.456883044555
C	-1.694288223158	3.303724364285	0.404545484485

H	-2.444416132293	3.251697569451	1.202682699259
H	-0.972978174684	2.495595445684	0.572677812990
H	-1.148674306992	4.250324173123	0.531587868005
C	0.257225901012	-1.158144847061	-5.612623020877
H	0.933224912374	-0.612966753991	-4.944273525648
H	0.903671711749	-1.752082225252	-6.269608333916
H	-0.274110172563	-0.424791741263	-6.237532021827
C	2.825229228482	3.200786289664	-1.975265692499
H	1.761568047575	3.049226247906	-2.206791491787
H	2.893278574995	3.588600691678	-0.951282344912
H	3.166925677486	3.996224415617	-2.650683457048

Table S78. Atomic coordinates and single point energies of the D_{2d} -type tetramer of **8b** with all *endo* chelation to the sulfonyl oxygens.



G = -4771.238804

G_{SP} = -4773.383918

156

drum_sfn4r_endo: optimized structure // E(RM062X) = -4774.63964878 A.U. after 13 cycles

O	-0.003174566076	-0.107900766867	-0.047914967107
C	-0.022350987473	-0.057216113902	1.264991176548
N	1.273178307950	-0.028081689969	1.923423992989
S	2.424658430382	0.974889290170	1.231938923347
O	2.733702794412	0.590872502764	-0.182522118138
C	3.809447158966	0.354265533462	2.225121751861
C	3.282408451182	-0.880759494319	2.938913053579
C	1.929471222242	-1.296623217439	2.297358425546
C	1.234402894541	-2.089052734493	3.429117057119
C	2.307835659165	-2.128236187744	4.535803860773
C	3.462396138003	-3.023771315348	4.039751087721
C	4.150142873991	-2.153383678113	2.947897747175
H	4.149213830481	-2.643378602321	1.969479956149
H	5.193187468009	-1.927092981632	3.194715377370

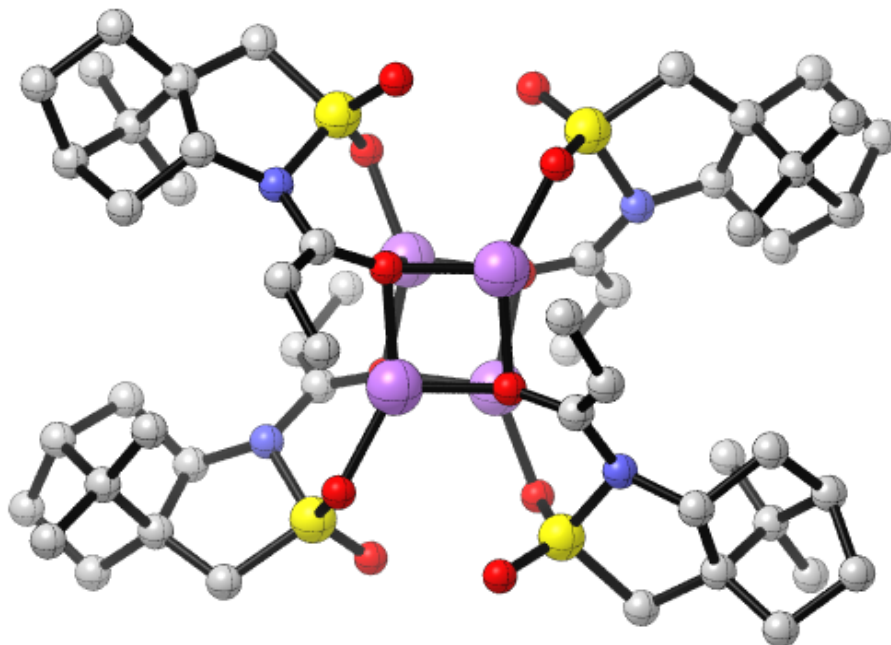
H	3.089504187512	-3.971966430040	3.637659921778
H	4.156585849269	-3.271741682360	4.849226520945
C	2.923305741636	-0.709992270349	4.452784720659
C	1.950152004900	0.422622657047	4.789356338813
H	2.364105618413	1.398673912169	4.500096630945
H	0.979081246163	0.338839669874	4.302105099396
H	1.793787016163	0.448712909769	5.875560236977
C	4.159924057569	-0.506214389780	5.332993204547
H	4.598973262373	0.485297026761	5.156395633630
H	3.870494809937	-0.540834059113	6.390606025514
H	4.948448699487	-1.248775115285	5.185002383240
H	1.916271861008	-2.411925406558	5.518480480737
H	0.318699440260	-1.587126817696	3.750054936938
H	0.949784409484	-3.090534181838	3.090988948796
H	2.068584265365	-1.915071148727	1.398377587458
H	4.102277604997	1.166300198263	2.898930070780
H	4.618570010641	0.160364904446	1.513117278870
O	2.096554493629	2.375407860861	1.457956618649
C	-1.117622336500	-0.049796689252	2.043201905352
H	-0.993470846581	0.120972221612	3.108664432101
O	-0.285226349863	1.687839396750	-2.187747434204
C	-0.015671943387	2.973154888019	-2.251881854733
C	1.182387132211	3.535283711344	-2.482288736241
H	1.259224083410	4.616458509921	-2.411059316740
N	-1.144319636782	3.871172633403	-2.089327137004
S	-2.038960012721	3.689231611975	-0.678356360482
C	-3.363578682851	4.811937491170	-1.203858635098
C	-3.173825182587	4.982706058749	-2.706022782694
C	-4.389214122201	4.800715764997	-3.631358086680
C	-3.877065715347	5.379614508578	-4.982272932098
C	-2.444921119337	5.850587120265	-4.650617101802
C	-1.564670905993	4.593459172087	-4.488965582541
H	-0.501589457491	4.828863022045	-4.379825601704
H	-1.658486401057	3.907909497777	-5.337544720851
C	-2.115502522764	3.956431796538	-3.194928865569
H	-2.555410045909	2.963001282136	-3.383628101057
H	-2.043336913519	6.582479405740	-5.359428530753
C	-2.587714672919	6.351176636201	-3.191573477122
C	-1.270207733309	6.791869609855	-2.548923516357
H	-1.002409518466	7.785807211856	-2.930136038230
H	-1.369809342197	6.879550471632	-1.458190107018
H	-0.436908385204	6.115278578716	-2.735181241888
C	-3.575244561230	7.508386791077	-3.013244671626
H	-3.688537075007	7.754648348538	-1.948495698441

H	-3.186852700783	8.407204738543	-3.507953282795
H	-4.573385333278	7.318049063672	-3.416504041813
H	-4.504594066009	6.208822719504	-5.324758227428
H	-3.875693153590	4.630697872409	-5.782604571145
H	-4.665973642495	3.746023674891	-3.703053478602
H	-5.269537485173	5.334545811865	-3.256301954584
H	-4.301627485692	4.330542514186	-0.912145663985
H	-3.231955058676	5.736874298499	-0.632816209318
O	-1.290908272888	4.150437806982	0.480393719064
O	-2.647022511842	2.325056959771	-0.595345036706
Li	-1.474014309007	0.742915763386	-0.971148204819
Li	1.168121154306	0.623509208229	-1.412792705623
O	0.986362315220	-0.629087998243	-2.854120522683
C	1.636894817487	-1.563654852424	-3.514896942273
Li	-0.685038662017	0.230817661077	-3.347408342070
Li	-0.006481590323	-1.531411881471	-1.332717226943
C	1.213006857281	-2.207060830245	-4.615349592510
N	2.930690544807	-1.937414607116	-2.976025732979
H	1.868871055526	-2.959743249340	-5.042860747603
S	2.839022101730	-2.920982510744	-1.612373581646
C	3.918081952546	-0.862304124330	-2.801404638082
C	4.298522422733	-2.233426091043	-0.781317187480
O	3.026899600999	-4.326414485558	-1.958279107722
O	1.613987156186	-2.607453471548	-0.827960511616
C	4.997557324192	-1.380478607916	-1.819878260415
C	4.722324416752	-0.528059032057	-4.078967241172
H	3.423013631851	0.021967764464	-2.383728841706
H	3.894042809880	-1.615865325859	0.027098356436
H	4.881501236850	-3.074851791038	-0.393255251785
C	5.722779886390	-0.120059526872	-1.311649324249
C	6.070012060173	-2.028333927309	-2.756153157625
C	6.179446730910	-0.745167575017	-3.620897495457
H	4.433898964230	-1.197064740409	-4.895891495104
H	4.542773646287	0.499496060311	-4.413365253611
C	6.505016013350	0.344173997696	-2.574378144570
H	4.999039897546	0.620488196430	-0.957066581449
H	6.396271212246	-0.358960696042	-0.479660827184
C	5.634013771257	-3.269481646568	-3.539436973830
C	7.361559484927	-2.397922811421	-2.021496151475
H	6.899290423611	-0.800296177616	-4.444729775508
H	7.580569673879	0.409928619935	-2.380597888119
H	6.182193363807	1.334264037381	-2.915818374951
H	6.417734890158	-3.524818868702	-4.265117107364
H	5.510897409783	-4.131155626745	-2.871389387328

H	4.691548778387	-3.149187992528	-4.076172744175
H	7.177574071716	-3.207545964097	-1.302090530073
H	8.100197600329	-2.773907907337	-2.740363529939
H	7.825959728377	-1.569518268198	-1.479827233235
O	-1.714210448319	-0.874384484455	-2.026038577846
C	-2.635600671286	-1.657059301901	-2.542594601495
C	-2.580610311340	-2.995194813154	-2.638399966339
N	-3.807848658464	-0.989415483828	-3.081070602349
H	-3.408225242143	-3.507392260419	-3.119450911517
S	-3.521766965809	-0.198764375044	-4.541988611286
C	-4.488196253972	-0.053582105734	-2.178131746488
C	-4.974384683778	0.885503965586	-4.438202676718
O	-3.575845936768	-1.134654306211	-5.658178031055
O	-2.308245568697	0.661754142285	-4.448121815280
C	-5.542654401032	0.686393169216	-3.040007613954
C	-5.328271313258	-0.745822242895	-1.081969295818
H	-3.771329510996	0.664201809529	-1.756755019170
H	-4.592378620857	1.891724353644	-4.635097629605
H	-5.651568266528	0.585138590665	-5.244297630416
C	-5.920795404937	1.926785722309	-2.209802182546
C	-6.813359352855	-0.213875900531	-2.908478590405
C	-6.744877665030	-0.203953424886	-1.360114859573
H	-5.261630729616	-1.834263131127	-1.179794076400
H	-4.978410746595	-0.482653522920	-0.078520690739
C	-6.728404150338	1.305801463626	-1.032448995886
H	-5.015852574107	2.442191963709	-1.867342486924
H	-6.518138939019	2.640497147580	-2.787924114114
C	-6.711381753774	-1.606264471743	-3.535961459967
C	-8.067830330172	0.447043463854	-3.485861981088
H	-7.540149246587	-0.760256361748	-0.852779476229
H	-7.740888469653	1.719121121694	-0.981243841893
H	-6.253058421329	1.498050004071	-0.064060364680
H	-7.651513294493	-2.146951573369	-3.365929257024
H	-6.572831487425	-1.536993958132	-4.624104927474
H	-5.889099510901	-2.208986720186	-3.149777239851
H	-7.999783754272	0.511739617510	-4.580556813460
H	-8.948916332251	-0.165403925349	-3.257552709272
H	-8.261153655092	1.453947726131	-3.106023691720
C	-1.389936870007	-3.752535022843	-2.133120623171
H	-0.476177230143	-3.531689920588	-2.710453037059
H	-1.183840393644	-3.532206979726	-1.073543668534
H	-1.542747411817	-4.833798862639	-2.198112751089
C	-2.496570303804	-0.228877279709	1.481753793981
H	-3.014346434821	0.732125142797	1.347130692837

H	-2.457657716455	-0.742678418537	0.509260967587
H	-3.115589705967	-0.845316631141	2.145468669566
C	2.402662175919	2.721219870051	-2.789802117841
H	2.119994178325	1.742025804089	-3.203851795812
H	3.030817623767	3.219698892756	-3.538238027205
H	3.028307356284	2.559010385242	-1.898731830459
C	-0.115023452220	-1.898350745115	-5.237929555291
H	-0.939392602188	-2.004064406719	-4.517733229370
H	-0.155527624437	-0.876127905116	-5.645043704275
H	-0.340759931246	-2.575596838190	-6.066922670785

Table S79. Atomic coordinates and single point energies of the D_{2d} -type tetramer of **8b** with all *exo* chelation to the sulfonyl oxygens.



G = -4771.232444

G_{SP} = -4773.382735

156

drum_sfn4s_exo: optimized structure // E(RM062X) = -4774.64025426 A.U. after 11 cycles

O	-0.101676077459	-0.009146368872	-0.020417166288
C	-0.126405533868	0.022863693729	1.293203484390
N	1.188917931085	-0.029205147584	1.862791193022
S	2.279996244284	-1.037251476392	1.037155549532
O	1.742692661578	-2.368798269141	0.787858781736
C	3.491659992398	-1.117871052003	2.382883079093
C	2.979458463528	-0.201321241004	3.474580174093
C	1.444275848086	-0.015871787039	3.295024343717
C	1.177457647756	1.347535540024	3.982495496181
C	2.540382509372	1.686147309952	4.611851973325
C	2.808667417360	0.645609921118	5.724294276663
C	3.164848588183	-0.648874364783	4.934507328869
H	2.508925723056	-1.492558748815	5.175810180858
H	4.193088224263	-0.975579610369	5.123111131466

H	1.927927775388	0.511480911805	6.362392522957
H	3.629756566403	0.954519230597	6.379184406420
C	3.532758691435	1.259675334251	3.502563271621
C	3.411019679728	2.035998751117	2.188663980749
H	4.085286551827	1.611317968485	1.432847024285
H	2.410961268442	2.034672282831	1.750717376118
H	3.718841656855	3.077893369774	2.350109795349
C	5.003385789516	1.336169826664	3.923232445189
H	5.646041934088	0.855595892947	3.173223329050
H	5.313586262034	2.386893211334	3.980924569794
H	5.221586583417	0.877694517182	4.891468500195
H	2.626821380379	2.726663643260	4.944629477785
H	0.867159875328	2.085163851740	3.237733369099
H	0.380231272949	1.280970384619	4.731197760314
H	0.891969587762	-0.835978567470	3.781027922248
H	4.460491120640	-0.830414930397	1.962525200113
H	3.509945889539	-2.172377047174	2.675186075302
O	2.824928180658	-0.253799206200	-0.093131044112
C	-1.213507773097	0.161601057221	2.080407356192
H	-1.085652047359	0.165443654897	3.159434287292
O	0.388703727126	2.301229433469	-1.433554632126
C	0.967984601108	3.320308259596	-0.839237600615
C	2.284377179345	3.616565391957	-0.837733592255
H	2.624966932319	4.500376238534	-0.305246490344
N	0.039349967197	4.104893566962	-0.078112095689
S	-1.497121959622	4.269071643692	-0.785723346663
C	-2.016233071170	5.661985877797	0.251532592355
C	-0.897764718550	5.894208482152	1.246184649337
C	-0.552200209930	7.347576059363	1.612742989580
C	0.389905077911	7.163469766010	2.839468975502
C	0.399406096522	5.632933899283	3.062168288147
C	1.254743325182	5.009562887737	1.944969899691
H	1.385339252475	3.931650973608	2.071888218900
H	2.253214755237	5.457261865942	1.888612697028
C	0.418090709263	5.293033236823	0.671264211104
H	0.917658668480	6.012950255704	0.003456189234
H	0.702759544833	5.331243027129	4.071050804944
C	-1.035186116537	5.221655746506	2.649829811456
C	-1.299694802215	3.713788338917	2.635303813267
H	-1.261914625582	3.326378103076	3.662363553416
H	-2.306525150638	3.508630266509	2.247414860981
H	-0.605300151610	3.136253230911	2.021970273599
C	-2.132949012009	5.851828352549	3.512010984652
H	-3.122338349735	5.675576816734	3.068708770178

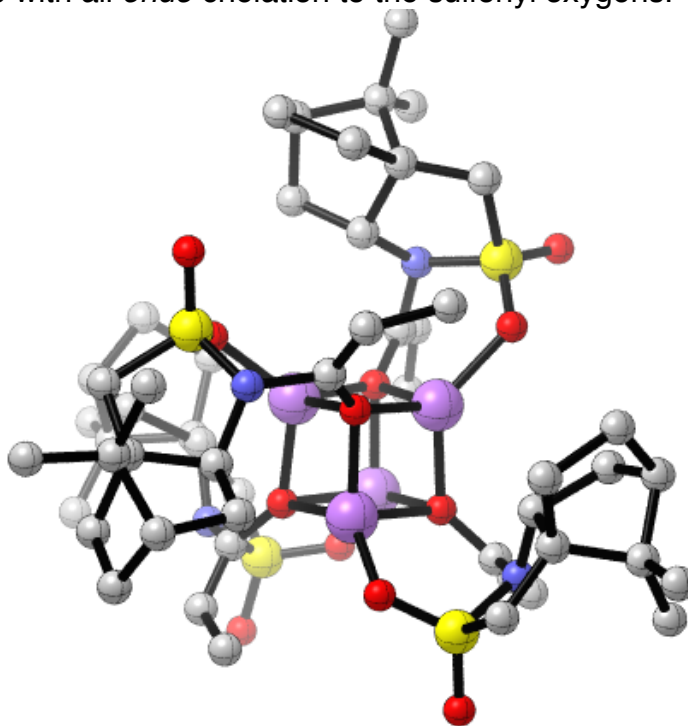
H	-2.139104704235	5.377602274459	4.501275374485
H	-2.024597558402	6.928668987536	3.666822446949
H	0.014325264844	7.698804862421	3.717449055443
H	1.399819792068	7.542137158405	2.645702742189
H	-0.069548306506	7.862663955627	0.774890283350
H	-1.451595900152	7.918444435180	1.867267133350
H	-2.152976893336	6.491841666866	-0.448751672227
H	-2.976947469137	5.390065883095	0.699920905040
O	-2.268674043226	3.056747076861	-0.434671306218
O	-1.436312074705	4.696943754543	-2.177519918616
Li	-1.262096360944	1.397519218525	-0.760361636262
Li	1.421627250798	0.653352808074	-1.132260070990
O	0.940266581715	-0.127920379976	-2.791828028470
C	1.309966265218	-0.612831854955	-3.956077357598
Li	-0.182664834272	1.469369813545	-3.039111303722
Li	-0.465753917307	-0.944579831145	-1.629463175674
C	1.760838723128	0.085623287087	-5.018876641034
N	1.112942993798	-2.030992949768	-4.041207856585
H	2.038185705517	-0.450378066330	-5.922450758497
S	1.434199814736	-2.879064002411	-2.603852561446
C	1.446690166680	-2.818211873098	-5.218317458840
C	1.526412581653	-4.512259216552	-3.384711580775
O	0.220867140775	-2.783833096483	-1.763008803104
O	2.729562444529	-2.543666860729	-2.026432281668
C	1.185332259984	-4.307035717877	-4.846140162055
C	0.505549680284	-2.593668997478	-6.429312239232
H	2.504079542054	-2.661856643609	-5.485332527232
H	2.558382979563	-4.838293553975	-3.221936759429
H	0.838020970747	-5.168401297551	-2.842900583696
C	1.964727264448	-5.127335403278	-5.888115762837
C	-0.297426279724	-4.546331977624	-5.276953342328
C	-0.040596667727	-4.005796515602	-6.704917493406
H	-0.283582694116	-1.886331002637	-6.160974017679
H	1.038521433493	-2.179610201070	-7.292476662483
C	1.144123347123	-4.874966485370	-7.187818685270
H	3.003130998826	-4.786331605685	-5.963613127884
H	1.992591705968	-6.188706518485	-5.619227460218
C	-1.349831169621	-3.779537219233	-4.471774480909
C	-0.703065647916	-6.022597374584	-5.236327228574
H	-0.907023047322	-4.021030124913	-7.375705809263
H	0.802478075341	-5.813985451255	-7.635049411747
H	1.731282134954	-4.354887930926	-7.953079508557
H	-2.337908352605	-3.927056363329	-4.928181214211
H	-1.403468226986	-4.171061580240	-3.447036482552

H	-1.164686889437	-2.706970194372	-4.386758235812
H	-0.694490552390	-6.398125852543	-4.204156370661
H	-1.730727678917	-6.130272962777	-5.604959719318
H	-0.070310754266	-6.682474167434	-5.835890847629
O	-1.716317865697	0.411381212042	-2.315279817168
C	-2.640281760228	-0.154398063178	-3.059207623228
C	-3.320083015974	-1.287358722811	-2.785364474251
N	-2.830001850908	0.531127776082	-4.304716032583
H	-4.065608988182	-1.638713689564	-3.493461350058
S	-2.705364891341	2.223359950528	-4.209062491363
C	-3.797559496248	0.117129542549	-5.309271412690
C	-3.489927143062	2.544389329125	-5.811247106965
O	-1.265490113160	2.556941141222	-4.270640535508
O	-3.523761727868	2.791897059952	-3.145647026990
C	-3.755220198258	1.190367977571	-6.436118652157
C	-3.426405473231	-1.187491874738	-6.059541923923
H	-4.802099390769	0.061147594435	-4.860292345164
H	-4.403276572053	3.095226149263	-5.566033915708
H	-2.809609833116	3.184942614751	-6.381181393697
C	-5.065278871776	1.005119945901	-7.220650435407
C	-2.688506397770	0.641047100311	-7.437023829683
C	-3.387639326521	-0.737235698207	-7.530624807485
H	-2.457880224243	-1.554806456042	-5.710129504516
H	-4.160618325512	-1.982653110954	-5.888641812051
C	-4.830788599244	-0.357768325611	-7.937488345618
H	-5.930356995841	0.992845824196	-6.548523533385
H	-5.221727103430	1.822467452361	-7.932726007426
C	-1.250172662304	0.605513708481	-6.913792687049
C	-2.655457121534	1.410804611641	-8.760631843933
H	-2.911146271898	-1.460926854350	-8.201527945988
H	-4.934481813227	-0.262888793104	-9.023186066899
H	-5.547176085147	-1.122387238696	-7.616538695924
H	-0.607468338488	0.098605955545	-7.646144877142
H	-0.864164919441	1.626802426595	-6.794554986060
H	-1.129863536978	0.111643933282	-5.947595847832
H	-2.317142494470	2.443319415117	-8.599609622330
H	-1.932114803983	0.941719036776	-9.439091325486
H	-3.614448406047	1.452532774814	-9.283974055464
C	-2.602675111538	0.318633152715	1.538081324045
H	-2.644631858384	0.160814681988	0.452772011409
H	-3.285582251156	-0.420534129117	1.978067427536
H	-3.026536063265	1.311819923092	1.741538733164
C	-3.093574749203	-2.098711098118	-1.544814536004
H	-4.036007714588	-2.274327744164	-1.008820508004

H	-2.654231522929	-3.083204354341	-1.757486557833
H	-2.430503139099	-1.591220375589	-0.832520131627
C	3.313311264632	2.777386240549	-1.534592255251
H	2.858926299755	1.995497291640	-2.156476766169
H	3.926915888557	3.385311785428	-2.212991395868
H	3.999860791143	2.281610729728	-0.834354119508
C	1.894488831541	1.579166501617	-5.020157630418
H	2.906066539487	1.886053817572	-5.318211475704
H	1.192146450509	2.066273666105	-5.710751650123
H	1.728095575211	2.011325651413	-4.025113609006

Heterochiral tetramers of enolate **8b**

Table S80. Atomic coordinates and single point energies of the S₄-type heterochiral (S₃R₁) tetramer of **8b** with all *endo* chelation to the sulfonyl oxygens.



G = -4771.287925

G_{SP} = -4773.409953

156

baseball-3s1r-bridge: optimized structure // E(RM062X) = -4774.66554205 A.U. after 12 cycles

O	-0.180350873319	0.130906882626	-0.004003101431
C	-0.149824984848	0.103293825040	1.317008764599
N	1.174098276956	0.173786312819	1.915255173058
S	1.774928279199	1.729586074027	2.091892770644
O	1.742257313927	2.438775821541	0.775811028656
C	3.482421102778	1.227498322349	2.426949483566
C	3.519497210223	-0.273206666068	2.179053334813
C	2.247636987080	-0.683987910114	1.394103419833
C	2.078430595194	-2.181462570632	1.737408186884
C	3.333425041941	-2.475414190805	2.588403214059
C	4.559618420862	-2.386688900188	1.654357707135
C	4.696288314647	-0.860464662616	1.376650792568
H	4.601549489720	-0.628120563684	0.308791374601

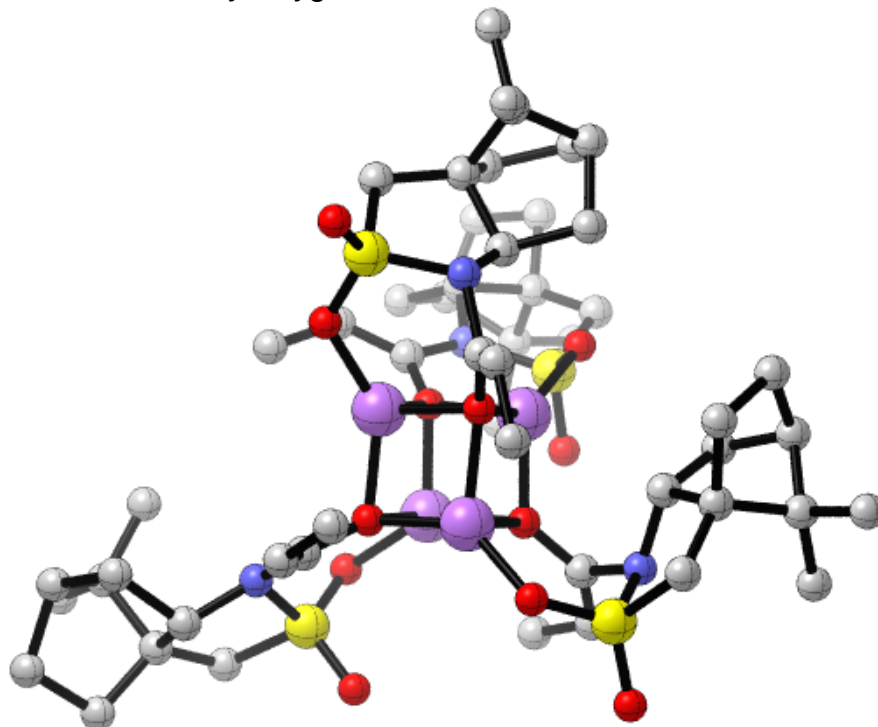
H	5.656407969457	-0.460032841459	1.720803858579
H	4.408442082133	-2.948316242873	0.727407112027
H	5.457391947479	-2.784461932866	2.139631478077
C	3.470231308560	-1.192622621671	3.443961911365
C	2.308464370727	-0.952029118824	4.412181975800
H	2.316097926894	0.081350594626	4.787571115054
H	1.323432649672	-1.129699736525	3.978836887416
H	2.427521637822	-1.611614703154	5.281846613367
C	4.757133446908	-1.117988216595	4.270699900592
H	4.817184333049	-0.154469295714	4.795753932405
H	4.748891699644	-1.901628186055	5.038872906464
H	5.672762003811	-1.236907385150	3.685474626916
H	3.269906398245	-3.410979753871	3.154804940901
H	1.148081895306	-2.341355352685	2.293960585259
H	2.044816313174	-2.790055694411	0.829241148810
H	2.388105342429	-0.517945339342	0.313197899721
H	3.698717993871	1.514888616873	3.461242207193
H	4.100799134755	1.814153268869	1.741974934642
O	1.142076778040	2.427064316802	3.206540209297
C	-1.171674746254	0.058585306988	2.189838858228
H	-0.901772966818	0.056051720513	3.243207580193
O	1.850021238537	0.578838045064	-2.075801858182
C	3.073568164904	0.209838586191	-2.391239708104
C	4.249400435532	0.760179093187	-2.037803492728
H	5.141989463055	0.267622965176	-2.416775159018
O	1.818515883152	-2.394188060385	-1.508706816813
O	4.285755063095	-2.738056859878	-1.666622563248
Li	0.905506113225	1.634622848167	-0.768608697952
Li	0.649606103564	-0.856409369841	-1.419874928969
C	-2.617608990724	0.075903702567	1.820259345434
O	-0.687367875771	-0.552563146705	-2.748287222773
C	-1.576847586349	-1.306152828021	-3.364801287819
Li	0.337309800529	0.992114038418	-3.239534247111
Li	-1.494940952240	0.679611059027	-1.355691483250
C	-1.875672537489	-1.342013363360	-4.675078208157
N	-2.405581017894	-2.133239464043	-2.497469305363
H	-2.665399529358	-2.027503537743	-4.972626977210
S	-3.772054090462	-1.289807565821	-1.973761528549
C	-1.786818121139	-2.774635604885	-1.330231582420
C	-4.133749958176	-2.359288219633	-0.557857297732
O	-4.826808734629	-1.300327046771	-2.980649041285
O	-3.355048460091	0.050263446520	-1.468932688054
C	-2.950904997895	-3.307787414205	-0.450333009889
C	-0.969267761726	-4.045507074931	-1.660379269525

H	-1.203012928195	-2.037426362580	-0.755984007616
H	-4.253679553315	-1.689710011927	0.298741336058
H	-5.084884301012	-2.856419499431	-0.775123363280
C	-2.325508580464	-3.537424816452	0.936818810760
C	-3.165535670408	-4.763963449082	-0.975132682774
C	-1.668712931709	-5.119631699054	-0.803064154359
H	-1.026944094170	-4.263527359267	-2.732816123156
H	0.083976470147	-3.922951299877	-1.393968631057
C	-1.405163891172	-4.767962512086	0.679936153335
H	-1.770508657301	-2.651740377894	1.270753457260
H	-3.092065554180	-3.748200525387	1.690461551332
C	-3.685138477893	-4.881537708849	-2.410190771720
C	-4.111740505325	-5.578903932100	-0.089883284828
H	-1.396563873519	-6.146018604690	-1.072017272177
H	-1.660576144322	-5.601470083223	1.342337086434
H	-0.347895645084	-4.535284112374	0.849353197541
H	-3.739364683611	-5.942650969672	-2.687084569444
H	-4.704698131931	-4.477870696890	-2.486856723488
H	-3.075847611772	-4.360494772991	-3.149918213140
H	-5.129967990242	-5.168687592678	-0.139048580066
H	-4.163101501228	-6.611561327977	-0.457201342064
H	-3.817925587021	-5.617466826056	0.962504527978
O	-0.475750946510	2.191211937825	-1.945705627391
C	-0.867009706574	3.395366612678	-2.324426065044
C	-2.019832117366	4.000267665339	-2.007714599803
N	0.078036324311	4.121334456283	-3.155993190499
H	-2.201892428724	4.988410195753	-2.421741801886
S	0.187330952834	3.582335727710	-4.746696575670
C	1.465915046854	4.207825735284	-2.666177915113
C	1.673520537165	4.534367383983	-5.140099808274
O	-0.993394363710	3.955489179439	-5.517165990887
O	0.575284676075	2.138748452556	-4.778994093442
C	2.248783411572	4.939822262581	-3.788997845239
C	1.661450837358	5.109146273159	-1.428373994173
H	1.873248133204	3.194259759151	-2.512840030094
H	2.311722784374	3.860511185104	-5.719386154648
H	1.358403300724	5.379335935820	-5.760989234266
C	3.730434448205	4.639160146101	-3.510335385226
C	2.120020322408	6.444653344333	-3.385120470738
C	2.646681702228	6.175004522194	-1.953374225653
H	0.706305146005	5.537741365119	-1.107601362975
H	2.065898223122	4.545746571837	-0.580490281973
C	3.996440586046	5.470111731033	-2.219848849579
H	3.886870939036	3.561994224951	-3.373351608529

H	4.366884236820	4.958283985482	-4.342677257226
C	0.708958604766	7.035557108721	-3.435265275745
C	3.015380324335	7.356958047629	-4.227883629897
H	2.725662171402	7.056677042827	-1.308600917340
H	4.802723913114	6.195129684185	-2.373222850200
H	4.286308077576	4.842006439909	-1.370321677183
H	0.752880485243	8.090442921288	-3.134306669193
H	0.310433641889	7.009098724427	-4.459428477683
H	-0.011520684641	6.524788187540	-2.795911670532
H	2.651465716362	7.396100985668	-5.264098048844
H	2.976001596930	8.380328513869	-3.834226952297
H	4.065617464748	7.054110593401	-4.254684643507
H	-2.760518479831	0.005829545215	0.738242290097
H	-3.159674242390	-0.752601408936	2.298054873323
H	-3.100943588605	1.003502079028	2.158455047855
C	-3.040559198419	3.339730777320	-1.132819410317
H	-3.683053329157	4.082159595021	-0.647586544962
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H	-2.555727396040	2.755741819838	-0.337086327707
C	-1.278085934380	-0.432691136981	-5.702104565500
H	-0.264544578567	-0.107618407226	-5.441391403673
H	-1.233901427637	-0.923227251174	-6.681956635085
H	-1.877355881097	0.481784728918	-5.824063161294
C	4.412912598813	1.953406693942	-1.155561570487
H	3.453451201605	2.425797939383	-0.916147860514
H	4.897623483141	1.674729484010	-0.207785507506
H	5.066372748341	2.700845557106	-1.623741860247
S	3.042840191541	-2.417982242330	-2.366259488236
C	2.712839629636	-3.472598081557	-3.801801933665
C	2.581395984601	-2.518193939616	-4.977011161458
H	1.786450865791	-4.005158082527	-3.563292630983
H	3.544229791314	-4.180874782272	-3.881814907978
C	2.339950201171	-1.088828581044	-4.429363493143
C	1.439490785998	-2.771479464141	-5.977508413948
C	3.823991677812	-2.340107841801	-5.908279511856
C	2.796439975532	-0.175084386517	-5.589004917127
H	1.277768644287	-0.959732605285	-4.169347457479
C	1.824357167643	-1.838284563391	-7.163008395726
H	0.468897281679	-2.524980483511	-5.529976962981
H	1.400807339063	-3.823750041424	-6.278717963541
C	3.147503948330	-1.191219526307	-6.697949050256
C	4.117401593835	-3.591712902275	-6.740439907244
C	5.135408739753	-1.947242148489	-5.222022517280
H	3.656533390543	0.429826981443	-5.280617366861

H	2.001090451003	0.513717782071	-5.891863163130
H	1.059591437175	-1.079493236807	-7.359771341036
H	1.961163869348	-2.406907414923	-8.088743153816
H	3.745596896956	-0.765787471274	-7.510896452344
H	3.251240342680	-3.988779861354	-7.276272876354
H	4.892547218555	-3.367413035271	-7.483823025186
H	4.509578168715	-4.392900969052	-6.098721225915
H	5.100548917055	-0.981508283023	-4.716428148917
H	5.426139958747	-2.696197875331	-4.471431946213
H	5.935332855590	-1.915398621696	-5.973207918920
N	3.173254570775	-0.986139389701	-3.220280996527

Table S81. Atomic coordinates and single point energies of the S₄-type heterochiral (S₃R₁) tetramer of **8b** with *exo* chelation to the sulfonyl oxygens of the *syn* subunits and *endo* chelation to the sulfonyl oxygens of the *anti* subunits.



G = -4771.25415

G_{SP} = -4773.400284

156

baseball-3s1r-loopRestart: optimized structure // E(RM062X) = -4774.65701742 A.U.
after 13 cycles

O	-0.028896288523	0.014610185585	-0.009712542407
C	-0.022652895426	0.019413680819	1.308983390067
N	1.301923394656	0.016148235893	1.923896387625
S	1.996809218950	1.547747709776	2.043157243036
O	1.739604384349	2.308147034649	0.790570460856
C	3.726026537824	0.980596055191	2.031259315332
C	3.663981278550	-0.532958280938	1.941483741171
C	2.283326586286	-0.913649747557	1.360196399992
C	2.081088505674	-2.375810366939	1.811218917858
C	3.428425365037	-2.698903640354	2.492577416305
C	4.498912581250	-2.727049236514	1.377853200555
C	4.682299702039	-1.225597975425	1.016023568710
H	4.443214451607	-1.004552888439	-0.029936658008
H	5.702478148697	-0.871682826253	1.204463484687

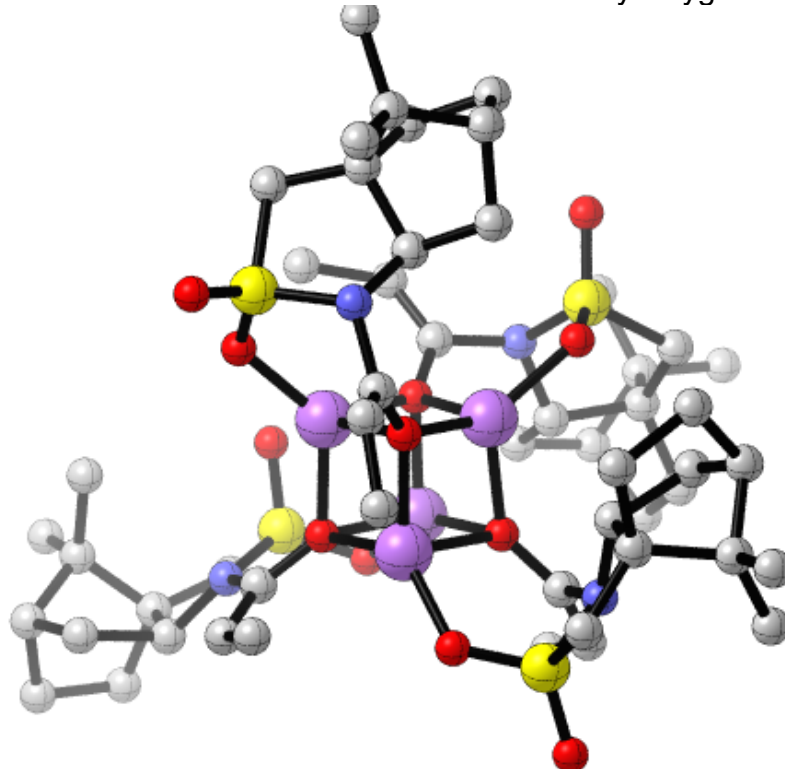
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H	5.434681355759	-3.177541794678	1.725793247265
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C	2.755507042717	-1.020993394125	4.349016483900
H	2.930734037593	0.000140810557	4.714844190525
H	1.712202407979	-1.069511677280	4.034567010122
H	2.895894834588	-1.699717313959	5.200457021338
C	5.149029340371	-1.356526456164	3.879868242933
H	5.363484928422	-0.363170001585	4.296855783198
H	5.191921607522	-2.068392319153	4.713615989315
H	5.959722518827	-1.608989522399	3.190904095460
H	3.406849208847	-3.601299477372	3.112846154878
H	1.233180777015	-2.445608449666	2.501151364553
H	1.888675610609	-3.033783255644	0.956871565177
H	2.321762089320	-0.812872038390	0.269803752727
H	4.200333236872	1.373037161737	2.936394716191
H	4.169091405631	1.433332196691	1.135742563974
O	1.632340287636	2.203153362964	3.292033429888
C	-1.059707390860	0.045832269611	2.163825933862
H	-0.807926515169	0.052357668136	3.221492672297
O	2.098770430780	0.345750231243	-2.020748203206
C	3.405697914259	0.417409255433	-2.113106288222
C	4.183909078454	1.483328586625	-1.828013894774
H	5.261000888539	1.390519639721	-1.925917611200
N	3.998265107112	-0.794199409019	-2.605754075545
S	3.051838546116	-2.178896779374	-2.680938476291
C	4.447318641908	-3.317346160615	-2.815858970624
C	5.627397232107	-2.473822329054	-3.246112608555
C	7.018263708118	-2.915680379115	-2.761645172573
C	7.958444886187	-1.988004088376	-3.585220438144
C	6.989465145706	-1.215474358472	-4.510576377596
C	6.258312611581	-0.160976312781	-3.660856363909
H	5.601696777212	0.476451084817	-4.259275974604
H	6.956345313196	0.492274584853	-3.126661459491
C	5.435645557368	-1.038144691133	-2.678619332374
H	5.848223209534	-0.966490525060	-1.660809868093
H	7.464916152912	-0.803721939748	-5.406993264568
C	5.866510812729	-2.245768023229	-4.776685346097
C	4.691215352204	-1.678711261155	-5.579210671034
H	5.062414335827	-1.344778989657	-6.557217317261
H	3.931142704289	-2.447406756015	-5.760529852135
H	4.180947709517	-0.837099059494	-5.105827746622
C	6.336713833580	-3.507255831810	-5.505363484240
H	5.561145683436	-4.284554090787	-5.478660642515

H	6.514225137932	-3.273623727861	-6.562206826610
H	7.258930978117	-3.940162013245	-5.108462394701
H	8.689538466293	-2.567040635283	-4.158170439138
H	8.528279043883	-1.304390633762	-2.945654095979
H	7.120729726475	-2.781955073213	-1.678523758338
H	7.194800458084	-3.975313944353	-2.974461478993
H	4.572127379741	-3.748434844965	-1.816399276676
H	4.150815066237	-4.096325418324	-3.525496035285
O	2.199544130678	-2.206094373792	-3.864749734017
O	2.351846014696	-2.420913984422	-1.387090568916
Li	1.055779821346	1.494618098513	-0.832261230932
Li	0.883539628479	-1.046738381906	-1.331006237515
C	-2.496789496801	0.106299420878	1.761584960060
O	-0.375552544377	-0.786767309147	-2.686535525521
C	-1.155613428257	-1.652548523749	-3.308607848786
Li	0.697153591202	0.667215423701	-3.332868828662
Li	-1.267974956131	0.478775068638	-1.483339587587
C	-1.237088264877	-1.866179324461	-4.627596128380
N	-2.049817859731	-2.408238243020	-2.439885634546
H	-1.955105880980	-2.605517580098	-4.971131006701
S	-3.457690720806	-1.557235917152	-2.054940600059
C	-1.486427950333	-2.912650233112	-1.180426257857
C	-3.890366359496	-2.568402619658	-0.611012056838
O	-4.443886731920	-1.641932211750	-3.121639111408
O	-3.102648291904	-0.196755404006	-1.561823070804
C	-2.681442862121	-3.453698646434	-0.354091297640
C	-0.566963873081	-4.144076483434	-1.347805783402
H	-1.002215752598	-2.093691580474	-0.624355026749
H	-4.100398481216	-1.856967036902	0.193439974398
H	-4.801408380028	-3.117037528482	-0.870467274854
C	-2.152965121263	-3.563656346758	1.087871250983
C	-2.777184983772	-4.947611496751	-0.802778408340
C	-1.282166176868	-5.208436720035	-0.489768648484
H	-0.496061210346	-4.422003196055	-2.404761891436
H	0.450943701323	-3.943399543759	-0.997083918407
C	-1.166936274793	-4.765222740725	0.986540613262
H	-1.660639768741	-2.632918675937	1.398138548713
H	-2.963308736169	-3.756132201373	1.799917537456
C	-3.165893141245	-5.181298552901	-2.264913784399
C	-3.749661098003	-5.762289295568	0.054335161027
H	-0.936632711828	-6.231290487255	-0.675245191700
H	-1.448337954633	-5.572555983394	1.670922984489
H	-0.139513137983	-4.479071556536	1.237888228825
H	-3.201880001848	-6.261337321295	-2.459255779189

H	-4.169189726081	-4.782940291874	-2.471734843296
H	-2.489020569944	-4.720471276201	-2.984821071075
H	-4.785784952201	-5.454101730179	-0.142146017986
H	-3.677687706325	-6.824752060877	-0.210069617513
H	-3.578192660878	-5.678982231385	1.130876110631
O	-0.241472588698	1.962811287428	-2.144227189912
C	-0.691339722415	3.198276678752	-2.227448987434
C	-1.539215827319	3.783387712025	-1.363911698656
N	-0.144767578503	3.902408026883	-3.356770042589
H	-1.890192906487	4.793936066795	-1.546796495592
O	-1.443557497938	2.433351787081	-5.111264221256
O	1.005685021501	2.029212732653	-4.744522161366
H	-2.621772367002	0.017169071977	0.677878546947
H	-3.075144128012	-0.693679246558	2.247125743723
H	-2.956899663003	1.055494780870	2.071162542036
C	-2.034434973208	3.042103729563	-0.155451032956
H	-2.311027419552	3.734162766697	0.647717854847
H	-2.924527965149	2.434217523062	-0.381034748396
H	-1.262279485323	2.375291715375	0.254744184601
C	-0.419194504919	-1.076947071830	-5.602070679074
H	0.612978385982	-0.965277538823	-5.244848651010
H	-0.373004209009	-1.577589478097	-6.575190167474
H	-0.841801498912	-0.074365761874	-5.764459176993
C	3.612006760426	2.846539549707	-1.569053909049
H	2.562469639868	2.896569141913	-1.891883233963
H	3.650781455247	3.164188281280	-0.519319145159
H	4.156203438830	3.596484786740	-2.157928456039
S	-0.127330520841	2.982144667767	-4.784811207896
C	0.241775052095	4.376248946127	-5.878427181583
C	0.131910976875	5.623632324832	-5.019533283704
H	-0.512364371991	4.315188062802	-6.668774225226
H	1.237858407594	4.204162900969	-6.297858263438
C	-0.574117235470	5.261190175023	-3.682250604402
C	-0.653056606345	6.819945258877	-5.584393702371
C	1.470136252212	6.283641754519	-4.555965964529
C	-0.073823903956	6.359199623805	-2.710006917432
H	-1.669460862708	5.283980402265	-3.796560220342
C	-0.261805166169	7.965174660894	-4.604743748273
H	-1.729034875047	6.614018495830	-5.596191923363
H	-0.357017794258	7.041324022844	-6.615318507047
C	0.734895728248	7.288824120710	-3.635988486509
C	2.243693882541	6.932683640425	-5.706532020315
C	2.444240875355	5.357015380083	-3.825552332514
H	0.531742252369	5.921217496874	-1.911426043098

H	-0.908541466623	6.883383314422	-2.232849075202
H	-1.128663486604	8.367197267259	-4.068670916791
H	0.199735131678	8.804489844314	-5.135233958061
H	1.379742304579	7.992302003817	-3.098738990388
H	1.654080740375	7.626311964146	-6.311947790507
H	3.099513118391	7.490922125518	-5.307204005113
H	2.649963770431	6.165144563734	-6.379520260699
H	2.035651461774	4.917123739267	-2.916662144673
H	2.756461463216	4.522638524698	-4.470115486189
H	3.349026238391	5.920226053421	-3.561125414016

Table S82. Atomic coordinates and single point energies of the S₄-type heterochiral (**S**₂**R**₂) tetramer of **8b** with all *endo* chelation to the sulfonyl oxygens.



G = -4771.281735

G_{SP} = -4773.403919

156

baseball-2s2r-combo: optimized structure // E(RM062X) = -4774.66025556 A.U. after 12 cycles

O	4.298886532475	6.318509135910	-2.347105111744
C	4.787278980830	6.996366135080	-1.327175923488
N	3.933937362280	7.058392800422	-0.149598453739
S	4.105985093733	5.750021081701	0.887979092679
O	3.972355457535	4.476897131422	0.121317285701
C	2.570271987752	6.037286921222	1.806570178080
C	1.888082236906	7.198923779888	1.103223111653
C	2.503049821924	7.354458100039	-0.310029589879
C	2.203661492356	8.827357487600	-0.672540578703
C	1.369184661402	9.310016448413	0.535018935185
C	0.009533655141	8.580945192852	0.479116047433
C	0.366182172938	7.119185785386	0.879018621268
H	0.123468786747	6.401373525326	0.085860014846
H	-0.156094479633	6.797837966068	1.787045225440

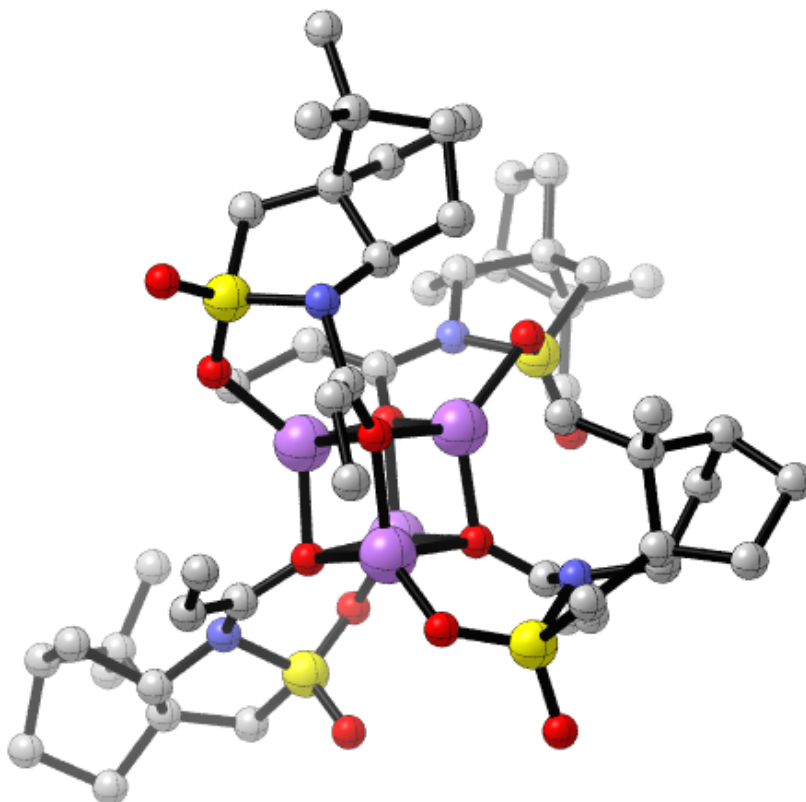
H	-0.436383696056	8.624769408634	-0.519222414001
H	-0.705920935184	9.022366946470	1.181423769220
C	2.071242454240	8.620247489059	1.730642831593
C	3.512927415902	9.080770107527	1.966016059192
H	4.044767974344	8.386263292506	2.631774256710
H	4.105951518139	9.169108113126	1.054804924330
H	3.497170597625	10.058861444023	2.464909214263
C	1.337639244091	8.768281124639	3.066880776774
H	1.856380004239	8.198905040989	3.850630816765
H	1.343576742634	9.820780674719	3.377723674661
H	0.296804816108	8.434890168550	3.046465781509
H	1.289515999480	10.400500445950	0.605100796187
H	3.138061806369	9.388042566190	-0.788500626936
H	1.644870045216	8.894156557185	-1.610845623150
H	2.036346400549	6.647464598585	-1.015522919842
H	2.854205051940	6.242165518482	2.844037836651
H	2.014418666189	5.096409553818	1.749328229883
O	5.303762660717	5.874570214102	1.713251502369
C	5.980233583977	7.607337510798	-1.204437576621
H	6.171511796436	8.101276115151	-0.254743803463
O	1.934218768701	4.702354715853	-2.732899722626
C	0.644574064976	4.636234488091	-2.479037339600
C	0.007072384908	4.128975935368	-1.410566030599
H	-1.078951170892	4.191621813616	-1.426866280263
N	-0.215858780890	5.219142031129	-3.506564565168
O	1.089925377559	7.472282403643	-3.473974655807
O	-1.171205380528	7.369588896075	-2.419108694768
Li	3.565469106019	4.441218100623	-1.767101969897
Li	2.681708352383	6.367867558317	-3.375531456765
C	7.055863237474	7.601726362453	-2.240644870128
O	3.423218978381	5.581022056317	-4.968791417527
C	3.656681045271	5.999402024338	-6.194899493970
Li	2.901615172062	3.912508228425	-4.233975747958
Li	5.070352506970	5.322358479170	-3.825901329338
C	3.382223308200	5.367391909945	-7.349280115396
N	4.389970960494	7.254147127978	-6.300240182434
H	3.672332834190	5.872520377602	-8.267000287174
S	6.057112412503	6.970042235431	-6.268072950459
C	4.092088789607	8.317665734077	-5.330715426233
C	6.538096300172	8.641997833274	-5.768008197187
O	6.561814905610	6.601809242455	-7.586245883170
O	6.367327595612	6.029291412955	-5.154274775149
C	5.238967107177	9.359708215718	-5.441232217073
C	2.822070405283	9.138234780784	-5.654907690930

H	4.077165085398	7.903801107993	-4.310278701382
H	7.209677293629	8.515256835394	-4.913749564303
H	7.085790001106	9.075893880733	-6.610923185481
C	5.162799959800	10.169471938655	-4.135005411600
C	4.709508617530	10.374091405157	-6.504379675704
C	3.373924264562	10.575263120278	-5.747175188616
H	2.383398536809	8.797003424858	-6.599339526330
H	2.067043496745	9.032036547190	-4.871411090544
C	3.845511374316	10.978386995581	-4.329949120594
H	5.132503252178	9.507207439909	-3.260645065836
H	6.033543354203	10.824349201136	-4.021507740634
C	4.558831976418	9.822625324954	-7.924096648058
C	5.574161053233	11.633369146527	-6.602618622249
H	2.678161577280	11.287396795301	-6.203974104772
H	4.024918775949	12.056054085913	-4.257224195937
H	3.091334477290	10.726531300134	-3.576098641913
H	4.120349459848	10.597084632128	-8.567163231044
H	5.541653483818	9.572242654279	-8.347978343316
H	3.941336372261	8.925846232725	-7.990470064128
H	6.570834463180	11.383811303517	-6.992582746611
H	5.119726311514	12.339665528375	-7.308712891672
H	5.709659673566	12.157406964845	-5.652684577127
O	4.501253428816	3.572814227677	-3.166862025670
C	5.292873634096	2.519412120114	-3.128708497768
C	6.639152553143	2.551059705344	-3.122309344593
N	4.580752455460	1.279195894684	-3.041863048207
H	7.201806550893	1.623798552413	-3.114193632864
O	2.609297255280	2.019797227954	-4.616843781389
O	2.171707107327	1.708866744645	-2.181431231896
H	6.717432436954	7.138683821352	-3.172275306476
H	7.397288742462	8.623067024512	-2.463607817768
H	7.938444089662	7.043408800790	-1.896607457259
C	7.381549360295	3.854757379948	-3.046509627409
H	8.333499514294	3.724422242624	-2.518611711739
H	7.611219733500	4.288729727094	-4.029244756501
H	6.808927290365	4.596744857635	-2.467866399106
C	2.813557209905	3.984327228370	-7.421560272162
H	2.154493317282	3.755718283727	-6.574717744114
H	2.231765284188	3.844357557927	-8.340187217777
H	3.607461205438	3.222710845364	-7.420959378578
C	0.672445941786	3.494584958968	-0.234096881525
H	1.758550706140	3.625083298715	-0.254376693240
H	0.281191802147	3.913032836498	0.704796081180
H	0.483160891448	2.413059244065	-0.208893437547

S	2.932437832836	1.286579955099	-3.358023079180
C	2.806571134093	-0.485827394001	-3.673527834711
C	4.086531168531	-1.091925063333	-3.140921572053
H	2.709267538239	-0.579152885120	-4.760385999810
H	1.891203969926	-0.832092332796	-3.182444295741
C	5.213439490743	-0.025353941253	-3.236365068429
C	4.633418007509	-2.326975174430	-3.876564660430
C	4.126022584976	-1.551305646232	-1.645817055541
C	6.214523658991	-0.480831113573	-2.140304531935
H	5.681058038300	-0.034707027477	-4.232196599246
C	5.758688470799	-2.808141118030	-2.914775124748
H	5.003132285139	-2.060114225708	-4.872617419930
H	3.853510454101	-3.084360494201	-4.009193528293
C	5.643781166890	-1.844659015433	-1.711016381611
C	3.260700513187	-2.785187425676	-1.376371616080
C	3.742841924507	-0.501865545265	-0.597934487048
H	6.240108484664	0.235703983736	-1.314482365956
H	7.231059222254	-0.567053241183	-2.538659150225
H	6.750418000953	-2.747906155500	-3.377212569925
H	5.608640665012	-3.850117386244	-2.614197268604
H	6.084037908628	-2.231896760474	-0.786040204075
H	3.522246433672	-3.657831273060	-1.981094218167
H	3.356121714904	-3.074413776930	-0.322368031663
H	2.200247635266	-2.557996346953	-1.551922374916
H	4.222966664900	0.469887832066	-0.731822445111
H	2.659991906103	-0.327290231700	-0.599944734653
H	4.013687363588	-0.881860778920	0.396140607842
S	-0.287175011603	6.889545572194	-3.480001861770
C	-0.974435307200	7.080480743966	-5.146161624466
C	-0.956957713673	5.684443385351	-5.747825603881
C	-0.012567318551	4.795832144936	-4.901331506300
C	-0.467568785150	5.534038887617	-7.199962458761
C	-2.296745634119	4.879290331196	-5.748376700604
C	-0.498731795935	3.360162719344	-5.199280207762
H	1.033571995402	4.968929732816	-5.199021602835
C	-0.902640056321	4.079782775918	-7.547673754211
H	0.617197265614	5.686605361552	-7.262352247962
H	-0.938021916046	6.272405517893	-7.858157924208
C	-1.598958411374	3.592838588546	-6.258076718492
C	-3.331274329067	5.463398276929	-6.714581604784
C	-2.994307764190	4.723649038191	-4.393897418237
H	-0.877607475578	2.890683267827	-4.285076363871
H	0.314300272454	2.729431701843	-5.574477014120
H	-0.050951251483	3.440967390557	-7.804790411272

H	-1.587729011291	4.063281542422	-8.401924539784
H	-2.257553662814	2.730183568097	-6.405539668575
H	-2.950792875232	5.646660111000	-7.722929971233
H	-4.184530057610	4.778965702725	-6.800870182870
H	-3.720154754217	6.414527115556	-6.325250124741
H	-2.413391835260	4.170308279373	-3.655175646763
H	-3.224076992758	5.705312482700	-3.955548985626
H	-3.949943241889	4.204206359722	-4.542849852920
H	-0.312535913297	7.788138906605	-5.655493789544
H	-1.973899549613	7.513693426247	-5.034821075114

Table S83. Atomic coordinates and single point energies of the S_4 -type heterochiral (S_2R_2) tetramer of **8b** with *exo* chelation to the sulfonyl oxygens of the *syn* subunits and *endo* chelation to the sulfonyl oxygens of the *anti* subunits.



G = -4771.271711

G_{SP} = -4773.397580

156

baseball-2s2r-loop: optimized structure // E(RM062X) = -4774.65454621 A.U. after 12 cycles

O	-0.291603893751	0.162010506190	-0.165024019120
C	-0.424494011113	0.020046843035	1.138876093385
N	0.792331356385	-0.353595189595	1.856831428150
S	1.799411658670	0.946312157313	2.214604466375
O	1.876754260867	1.864688447600	1.044041392948
C	3.342624600682	-0.007718777318	2.304859097099
C	2.948169107987	-1.447980081392	2.039571569629
C	1.592321420915	-1.448638570587	1.295566397966
C	1.021476172688	-2.855456750853	1.581263811696
C	2.175356758126	-3.534255008058	2.350373507697
C	3.334765966703	-3.728675234252	1.347856039588
C	3.881945389572	-2.286249787599	1.146756084564
H	3.809033216536	-1.940586304526	0.109983842628

H	4.928801678905	-2.191016711277	1.456404574057
H	2.968360577920	-4.166979871521	0.411886024842
H	4.104242205562	-4.398768798685	1.746066360217
C	2.700517713300	-2.391469564024	3.257595608575
C	1.689049873901	-1.894653028681	4.293535276441
H	2.043539403103	-0.970225738902	4.770227872825
H	0.700198618506	-1.685359692350	3.882730414938
H	1.585724719288	-2.648767318118	5.084890960835
C	3.987661924851	-2.728993838575	4.014638005958
H	4.359423874788	-1.842659555756	4.546773685042
H	3.782244263305	-3.496055376605	4.771985886381
H	4.797141842744	-3.099045453138	3.379123968387
H	1.880125128301	-4.450048438927	2.873860335334
H	0.105925025196	-2.781110940722	2.177823417965
H	0.784968129413	-3.380735414247	0.650621044034
H	1.762678370093	-1.281272988496	0.225111899826
H	3.781302863946	0.175662712547	3.291139649786
H	3.982288327687	0.408874555775	1.518057138144
O	1.439463658474	1.565050591072	3.487341057955
C	-1.516050233197	0.194005483530	1.904344633614
H	-1.387010950353	0.023406848317	2.970631515323
O	2.021146863566	0.121741582894	-1.973405302940
C	3.299953342256	-0.171745619960	-1.952016987662
C	4.301237640942	0.619786167869	-1.507369646154
H	5.320875273265	0.247915335522	-1.531812942254
N	3.593544318030	-1.465684134204	-2.497197442965
S	2.333192221048	-2.536641788086	-2.794058267351
C	3.381575373811	-4.002615736524	-2.870887904963
C	4.785014064746	-3.492528606809	-3.113681212720
C	5.940396258862	-4.315642521023	-2.520370296674
C	7.184132492360	-3.639785907758	-3.168204037455
C	6.572327424477	-2.597993640604	-4.134617633876
C	6.047089793996	-1.419724586994	-3.294677547448
H	5.654047316758	-0.609289172464	-3.914934349901
H	6.823190328330	-0.997891843155	-2.647392841344
C	4.917807359289	-2.085923355011	-2.463669876835
H	5.223416065003	-2.177523631901	-1.411680835077
H	7.243816517479	-2.294011584242	-4.944542551597
C	5.258168740678	-3.275306147474	-4.589623811493
C	4.380030965711	-2.378012077834	-5.467083042161
H	4.945182135620	-2.109344802564	-6.369618976083
H	3.476481211395	-2.908968937168	-5.788592694437
H	4.051493724863	-1.454205431348	-4.985584227388
C	5.460489739808	-4.586341315468	-5.353196788093

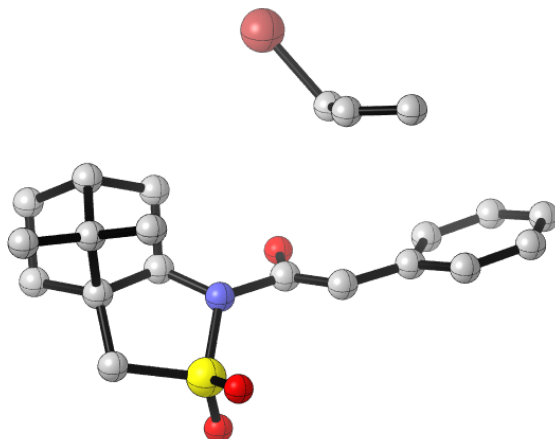
H	4.509632627295	-5.128141590667	-5.447907655922
H	5.806285887080	-4.365864914257	-6.370713193340
H	6.189544766292	-5.262552187163	-4.898303196327
H	7.802766293617	-4.369406771328	-3.700415912869
H	7.827469638091	-3.158717890264	-2.422480050899
H	5.940329030237	-4.261686847734	-1.425564520423
H	5.855470538295	-5.371897069730	-2.796263617102
H	3.268665248220	-4.496253822936	-1.899396981359
H	2.977057143539	-4.639365093172	-3.664431410186
O	1.660724726816	-2.268115658386	-4.063060616951
O	1.418859256355	-2.642748157511	-1.620625223602
Li	1.205835540325	1.364068194946	-0.696563193670
Li	0.385285066173	-0.937665228428	-1.573387888797
C	-2.856435207869	0.620627317931	1.401367165763
O	-0.516881443568	-0.125846352824	-3.042307697812
C	-1.342969980568	-0.755307712836	-3.849700464001
Li	0.947724200757	1.060400169609	-3.282936360388
Li	-1.207486461330	1.079727048581	-1.656047911061
C	-1.213745247054	-0.963625577877	-5.168755909051
N	-2.502648968294	-1.273079276847	-3.148603478736
H	-2.035207386508	-1.457789902278	-5.684919499506
O	-4.516204212115	0.225491899190	-3.930814445201
O	-3.129885567596	0.893760003358	-1.952802587127
O	0.212637838855	2.343429072301	-1.984869419929
C	0.126948592293	3.654520048107	-1.873557050000
C	-0.530797866295	4.334674239353	-0.916036184064
N	0.867980971541	4.332467513218	-2.901783640477
H	-0.558902071025	5.419702265666	-0.958824346446
O	-0.721924928945	3.485671418195	-4.819761040196
O	1.544175719895	2.443850554834	-4.550650570042
H	-2.869844752531	0.731806746652	0.313123444486
H	-3.632395356490	-0.106533929458	1.682988549351
H	-3.157052938208	1.582245140323	1.840892967729
C	-1.229604705389	3.646431191085	0.218833573603
H	-0.978644890551	4.106578381861	1.183339439941
H	-2.323154092129	3.690078261970	0.110782380583
H	-0.939016719706	2.590879961374	0.289787024143
C	-0.028647347163	-0.506305183500	-5.958551045185
H	0.834437133048	-0.334978841550	-5.307673296023
H	0.271008809700	-1.260101224604	-6.697885474418
H	-0.243478572128	0.424140835036	-6.503148856034
C	4.078433126111	2.057486536019	-1.135521269464
H	3.113132860154	2.418654406423	-1.518045530246
H	4.094969465644	2.249906247246	-0.054609437526

H	4.851870122263	2.689335556997	-1.591752255847
S	0.684124885962	3.648252039590	-4.443970902972
C	1.413434916318	5.038475784132	-5.342485756711
C	1.668379189779	6.119426052991	-4.307622479510
H	0.661732328269	5.313628692034	-6.088737067648
H	2.315233885069	4.666857042365	-5.839432788421
C	0.865461880430	5.791314916929	-3.018347951050
C	1.280879474011	7.562205518214	-4.674178523058
C	3.134438516678	6.282185983915	-3.792924047512
C	1.652612067236	6.539453429255	-1.912673023737
H	-0.171358916515	6.152929623316	-3.098653829002
C	1.975652555239	8.387423883788	-3.551588973002
H	0.192202406987	7.684217849904	-4.686041179032
H	1.649012026302	7.831206177252	-5.669867880321
C	2.713763862779	7.314868021273	-2.718305277161
C	4.081660839245	6.834378035212	-4.861062820724
C	3.784257432743	5.017038808409	-3.228422206359
H	2.093891688523	5.831036592853	-1.205369284027
H	1.001608032492	7.209996435332	-1.341965231235
H	1.256122915977	8.941282694777	-2.938218552679
H	2.672548338220	9.121407248390	-3.969645473414
H	3.528944500539	7.710989519605	-2.103368431908
H	3.735099383403	7.756578678649	-5.335319904381
H	5.061299636619	7.041091616643	-4.412099696221
H	4.241516467219	6.089576276057	-5.652875193848
H	3.239666410458	4.577660025635	-2.393160822606
H	3.871644103236	4.240046629003	-4.001607998600
H	4.801745028801	5.256172980275	-2.891162752742
S	-3.716861101963	-0.190546163216	-2.776597350899
C	-4.673925993662	-1.385448214264	-1.808955981269
C	-4.095594446337	-2.745042858341	-2.187906591223
H	-5.716972883119	-1.241787641686	-2.105088638477
H	-4.545202582460	-1.130992596043	-0.751117621971
C	-3.123084291650	-2.572733723618	-3.391465266567
C	-5.063493056005	-3.866730386692	-2.596445449577
C	-3.195017761686	-3.437300276172	-1.112840825650
C	-2.171867951567	-3.783999540880	-3.267953821832
H	-3.670563884657	-2.576562243829	-4.345854742364
C	-4.147555184126	-5.126391917792	-2.548026923060
H	-5.478801305495	-3.678718930301	-3.592841063359
H	-5.907443071672	-3.945032346083	-1.903337751977
C	-2.781754994889	-4.568543124916	-2.086693162628
C	-3.995007274124	-3.905697908172	0.105886389610
C	-2.021427388775	-2.607518080890	-0.578446430290

H	-1.143698605754	-3.456660880192	-3.079713435925
H	-2.158689589213	-4.372981354381	-4.190538408023
H	-4.068424132889	-5.620569628270	-3.522787728580
H	-4.532107523550	-5.869139954289	-1.841084638554
H	-2.110325139657	-5.326180311927	-1.667909597143
H	-4.898781768061	-4.470596998833	-0.138883605655
H	-3.364696787995	-4.542820583632	0.738876247059
H	-4.293819516989	-3.042624669150	0.717134217348
H	-1.220098268539	-2.485609000998	-1.309746172767
H	-2.336636760524	-1.604200964336	-0.260699944008
H	-1.598496720305	-3.107470114811	0.301888422121

Transition structure analysis

Table S84. Atomic coordinates and single point energies of the reactant ground state for the top-face allylation of **8o** with π -stacking.



G = -4067.963199

G_{SP} = -4069.022264

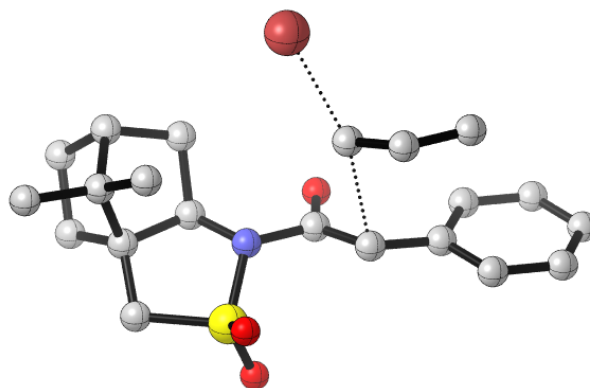
54

StartGeom: optimized structure // E(RM062X) = -4069.35810402 A.U. after 12 cycles

O	0.155515901453	-0.473585179618	0.020842629272
C	0.038478767902	0.121514490320	1.110255392566
N	1.305649669529	0.255956897466	1.869791350142
S	1.872273863790	1.742553379466	2.395724803208
O	1.995639571807	2.727030393450	1.313805088689
C	3.548446681874	1.129644153043	2.791388173509
C	3.562280766928	-0.338501726244	2.416876719632
C	2.402199517739	-0.591343791220	1.422114393692
C	2.115396726726	-2.103429941078	1.579806847812
C	3.225339080266	-2.560241231202	2.544708444167
C	4.571317905553	-2.440282472864	1.792553486884
C	4.820719217690	-0.903048130537	1.735539925003
H	4.908292921139	-0.523623893170	0.711220652137
H	5.734170905853	-0.614211831966	2.268761093136
H	4.504317915002	-2.886239869537	0.793765217035
H	5.379678731406	-2.957420104882	2.322461727063
C	3.296639060303	-1.382521604819	3.550347103281
C	2.019917445464	-1.168031554907	4.370917880626
H	2.053715713989	-0.201398921266	4.892401181165
H	1.105541127103	-1.165234194808	3.776227080011

H	1.947738928893	-1.957542302458	5.131462342226
C	4.453096831983	-1.481044265938	4.551051341479
H	4.519549901453	-0.559890703409	5.146616211168
H	4.264851203973	-2.305341190355	5.250976658127
H	5.430206896067	-1.653404684625	4.090474917897
H	3.049424045229	-3.547947111136	2.986566660304
H	1.115538965350	-2.263874224223	1.995802926459
H	2.141852565349	-2.624995259029	0.618190671124
H	2.681004197407	-0.341808082462	0.389002513165
H	3.721200036624	1.328099691332	3.854221980136
H	4.224185279162	1.735458778429	2.179926105913
O	1.175025484514	2.152195829083	3.619798048675
C	-1.081238560175	0.582339791689	1.784610332988
H	-0.933430843416	0.990979336798	2.780875966282
C	-2.428006631205	0.478249247003	1.292377957359
C	-3.503615918462	0.852025155161	2.133521681046
C	-2.774862011024	-0.040071759063	0.019564791535
C	-4.827347326900	0.690766387267	1.751941938475
H	-3.272002968433	1.264970838479	3.114972543936
C	-4.105122331888	-0.202285752320	-0.350193292010
H	-1.974425836269	-0.316575419955	-0.660625974287
C	-5.149800943001	0.150199912503	0.505612089009
H	-5.620826967719	0.987274232597	2.437778522058
H	-4.330775576825	-0.609482798122	-1.335929057710
H	-6.187314287646	0.018624244666	0.205396753328
C	-1.996184931331	-2.627243345091	2.472483824691
H	-1.210508964739	-2.595624013862	3.229275557014
C	-3.253198421742	-2.330362971209	2.790144230402
H	-4.040148610093	-2.306955914520	2.033929537063
H	-3.522345934166	-2.033264253794	3.801893725866
C	-1.573341880899	-2.934369659427	1.084514860430
H	-2.420101091648	-3.035354843493	0.403602539022
H	-0.838857104540	-2.232698649523	0.673173625961
Br	-0.642119453835	-4.705586616845	1.027044808752

Table S85. Atomic coordinates and single point energies of the transition state for the top-face allylation of **8o** with π -stacking.



TS frequency: -396.493

G = -4067.867274

G_{SP} = -4068.924572

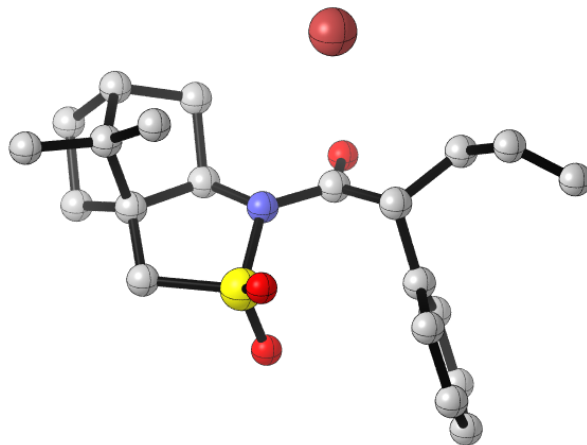
54

TS_spe: optimized structure // E(RM062X) = -4069.34051410 A.U. after 16 cycles

O	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.229592320000
N	1.318317975853	0.000000000000	1.854491577759
S	1.624927238240	0.980745963110	3.204187615680
O	1.115715607077	2.341746737488	3.011709521336
C	3.433477000543	1.004649664643	2.985676275843
C	3.740404125230	0.117014489318	1.798022698540
C	2.458370567162	-0.020981761677	0.937252948294
C	2.668386169581	-1.361079569211	0.192344653137
C	4.110851664961	-1.738366990501	0.583892303470
C	5.058290030083	-0.694263633599	-0.052890048980
C	4.830066704816	0.581190584860	0.814146163017
H	4.485546981788	1.440540529404	0.227880882449
H	5.741076328409	0.890237713350	1.339499708018
H	4.810069448252	-0.526171213303	-1.107123493869
H	6.104677249823	-1.018622374954	-0.016458799360
C	4.160383884840	-1.359908452677	2.085524727001
C	3.208226989024	-2.162121247657	2.973288630313
H	3.075909625658	-1.676532691880	3.950106712501
H	2.222680989376	-2.312349474001	2.536074765140

H	3.625710000696	-3.162044507886	3.143819532695
C	5.553056926374	-1.469617328683	2.716630264171
H	5.535548256915	-1.082586575536	3.745179867491
H	5.841235861786	-2.526471829407	2.776439862117
H	6.340093576425	-0.940278075915	2.171676791578
H	4.367522438758	-2.778798690197	0.356730264675
H	1.945502389834	-2.120743681950	0.511613194919
H	2.542995043961	-1.232918159931	-0.887099549880
H	2.359598908035	0.813770449357	0.230575377596
H	3.870949473318	0.664410547288	3.929812027798
H	3.676576246143	2.057613934467	2.812926464494
O	1.255705655062	0.272244643780	4.432896918191
C	-1.091821042352	-0.177770445811	2.119469949593
H	-0.883986690030	-0.093954266108	3.184743472509
C	-2.474982814679	-0.065292897031	1.715369955336
C	-3.472964189203	-0.045765465910	2.713272523246
C	-2.912081689465	-0.062582976091	0.371471924692
C	-4.824476046211	-0.019306985312	2.396311108843
H	-3.163317341130	-0.054714864109	3.757431947481
C	-4.267735589785	-0.041400965146	0.064550597430
H	-2.169170424166	-0.077456496023	-0.419429027748
C	-5.238597752190	-0.020985361335	1.065585822355
H	-5.561830805739	-0.003336866983	3.197751848053
H	-4.571059058049	-0.041539061165	-0.981621323606
H	-6.296807162654	-0.006081054837	0.813164438844
C	-1.690127505733	-2.983225760647	2.837012253747
H	-1.414782353902	-3.216035718883	3.865612853304
C	-2.956864254460	-3.115888177738	2.432209800166
H	-3.253035824378	-2.875023281557	1.410677912950
H	-3.734737482405	-3.450438714443	3.115663994537
C	-0.617333146954	-2.506995666037	1.980633645139
H	-0.779557868595	-2.362034960389	0.917199079516
H	0.316359048674	-2.195398433319	2.421287272645
Br	0.578817406350	-4.629487141224	1.508468494593

Table S86. Atomic coordinates and single point energies of the product ground state for the top-face allylation of **8o**.



G = -4068.01407

G_{SP} = -4069.073826

54

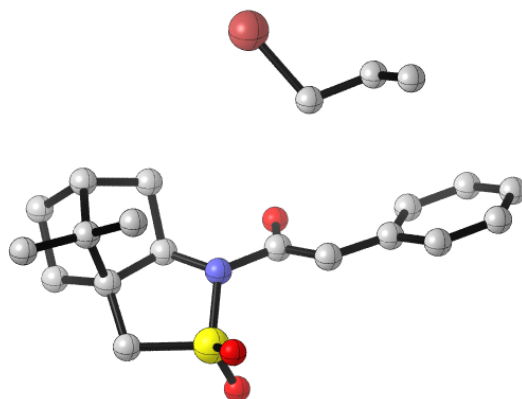
Anion_protoR_noPiStack_End: optimized structure // E(RM062X) = -4069.49314233

A.U. after 12 cycles

O	-0.076754809233	0.283659358785	0.045062175088
C	-0.069843898937	-0.121920618044	1.181913647792
N	1.159857480031	-0.250128947188	1.856703281139
S	1.325085403014	0.195966365848	3.505236535388
O	0.866809114769	1.581671777892	3.673020925100
C	3.134295000786	0.134447788018	3.504545778764
C	3.551873806428	-0.228162756719	2.092913875789
C	2.391921656702	0.088079267755	1.121992274625
C	2.692146507708	-0.810872818340	-0.099809268966
C	4.040669792215	-1.457985956206	0.279319818436
C	5.118542966219	-0.353206511782	0.259056223080
C	4.781757427125	0.498177808926	1.517974761712
H	4.539046517152	1.539854216676	1.279338972041
H	5.605978316895	0.511944060238	2.238959962094
H	5.069022973533	0.234631855013	-0.664367884799
H	6.128241612097	-0.773354445858	0.323704782470
C	3.865761663860	-1.729752492828	1.794382041888
C	2.752191572601	-2.730901104225	2.122158425821
H	2.432959946015	-2.634094400186	3.170524057205
H	1.868753133395	-2.654484281277	1.481016379322
H	3.148804892953	-3.747886838050	2.000363531362
C	5.131412780876	-2.213760079936	2.506873304676
H	4.939286237043	-2.330288961559	3.582717015646

H	5.414703001652	-3.201199452753	2.120668824585
H	5.994301112271	-1.551359436671	2.391663715268
H	4.286436504519	-2.337861120610	-0.325326317022
H	1.897100285315	-1.549180064697	-0.263281522876
H	2.770234271772	-0.207067420010	-1.010241560470
H	2.365329563595	1.154053334551	0.858812565625
H	3.425794708310	-0.596880875886	4.265510670983
H	3.449607069948	1.137756319199	3.808290161707
O	0.737287956837	-0.818561912530	4.383179973286
C	-1.305186208023	-0.563116309360	1.959600230060
H	-1.326626972558	0.020198306535	2.892935092536
C	-2.563733859969	-0.262210321806	1.179785564594
C	-3.521053453320	0.616082231056	1.685801980921
C	-2.795029338271	-0.898905100291	-0.045904009679
C	-4.701379407408	0.861382076264	0.982557993731
H	-3.343604139046	1.110226134201	2.640525061838
C	-3.971853099119	-0.651519983499	-0.745759045316
H	-2.042531673473	-1.583895521878	-0.446250575557
C	-4.928719750709	0.227686475471	-0.234995854451
H	-5.441351931051	1.547596010197	1.390012256549
H	-4.144325594595	-1.147890757722	-1.699072885270
H	-5.847919522412	0.416303617105	-0.786449081083
C	-1.213194965476	-2.064462807136	2.336522155853
C	-2.356906353926	-2.472880295681	3.214077571502
C	-2.225506557842	-2.873798496544	4.477274008746
H	-3.089480499214	-3.167128758930	5.073277624751
H	-1.244565518451	-2.920541594921	4.953218384803
H	-3.356156988178	-2.430479975948	2.770953520428
H	-1.194295689169	-2.654200208767	1.408611182912
H	-0.269017651474	-2.249381332019	2.857444481300
Br	0.051151380190	-3.499063826132	-0.798978178711

Table S87. Atomic coordinates and single point energies of the reactant ground state for the top-face allylation of **8o** without π -stacking.



G = -4067.963447

G_{SP} = -4069.022073

54

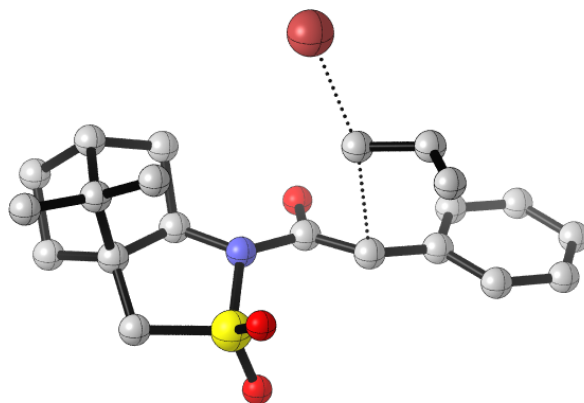
Anion_protoR_noPiStack_Start: optimized structure // E(RM062X) = -4069.43689910

A.U. after 13 cycles

O	0.010428296892	-0.060354209161	0.205036250134
C	0.136360699130	0.155378578475	1.427032830015
N	1.521924728982	0.322736979159	1.885790669086
S	1.952124013955	1.611490332152	2.878531424533
O	1.478374966821	2.900982534132	2.346390954809
C	3.739357134101	1.466343957412	2.585357989418
C	3.920334356668	0.283226969517	1.656969285724
C	2.581985300632	0.030023801254	0.920247792663
C	2.675008148787	-1.458911985920	0.511758339763
C	4.106626148213	-1.838747001557	0.938593031598
C	5.083472983534	-1.060639047631	0.027056766624
C	4.982145971082	0.402570336125	0.550266408497
H	4.660662834844	1.111341085540	-0.220981660535
H	5.936075480446	0.763448315939	0.950022952312
H	4.792134152941	-1.144246916328	-1.026185367893
H	6.106135070942	-1.443960775837	0.111669482260
C	4.255710598332	-1.103746660386	2.294955986474
C	3.297480941485	-1.589780800799	3.385666127193
H	3.328173277643	-0.915984284630	4.253081978804
H	2.256110268907	-1.655803806139	3.066025890669
H	3.619652825095	-2.582489555509	3.728216305902

C	5.665480063453	-1.158084128403	2.889840842051
H	5.733723807336	-0.501380158260	3.768398906571
H	5.883003089091	-2.178677151963	3.230473333622
H	6.456440888117	-0.866622786260	2.193124918717
H	4.289498407670	-2.919036182358	0.968155331396
H	1.912954806070	-2.051581961291	1.028078214146
H	2.510615442913	-1.590783958386	-0.562427760788
H	2.477618035329	0.681145228672	0.042529330353
H	4.221113371101	1.358039767117	3.562638801246
H	4.033518563799	2.417160782266	2.129640011425
O	1.616290210092	1.313801834394	4.279534756010
C	-0.827024463003	0.180473480602	2.431949547677
H	-0.486282862414	0.280939119658	3.459539160431
C	-2.239797091421	0.000651445887	2.212569157371
C	-3.107378747593	-0.089386018623	3.330300829216
C	-2.843500128278	-0.129251416933	0.935922856153
C	-4.465310698137	-0.336907993124	3.188961932077
H	-2.683174734444	0.019353349245	4.328676318943
C	-4.207550915795	-0.371409076001	0.805600512784
H	-2.214511129366	-0.051368589304	0.054321671122
C	-5.035412627286	-0.490831074393	1.921848259131
H	-5.089598909267	-0.412068023600	4.079023773376
H	-4.631318994793	-0.473119827510	-0.193513225669
H	-6.099458224202	-0.688834197082	1.809922584432
C	-0.930948847475	-3.043111221192	1.365176230582
C	-2.366189281903	-3.416103883106	1.441222130163
C	-3.018837036529	-3.575166485644	2.590053917725
H	-4.082012813648	-3.811906473708	2.607536926178
H	-2.512278295061	-3.457126168300	3.549477524107
H	-2.889625746263	-3.529768443937	0.489877946875
H	-0.735006688135	-2.182033638367	0.719416196095
H	-0.476431497143	-2.904111997731	2.347489520785
Br	0.111742508825	-4.524477287543	0.515826127690

Table S88 Atomic coordinates and single point energies of the transition state for the top-face allylation of **8o** without π -stacking.



TS frequency: -463.6303

G = -4067.943105

G_{SP} = -4069.000481

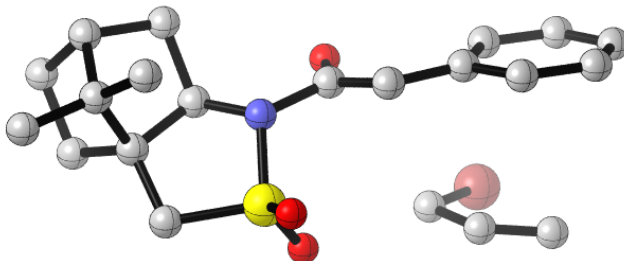
54

Anion_protoR_noPiStack: optimized structure // E(RM062X) = -4069.41600648 A.U.
after 13 cycles

O	-0.010961624608	-0.011866915050	0.009169433770
C	0.016233130992	-0.025094714983	1.243539576088
N	1.330573787254	-0.023791493181	1.840630823563
S	1.632682813523	0.779107656460	3.304563526936
O	1.017693567147	2.114397543982	3.314745216168
C	3.422644944111	0.933218641863	3.056555386929
C	3.756994990031	0.132536719455	1.816349373368
C	2.484540382070	0.019063923034	0.936226448983
C	2.728927693519	-1.270921319934	0.117505255026
C	4.186296869167	-1.620237148131	0.478441173875
C	5.091116155724	-0.499347458208	-0.086194759954
C	4.838252748693	0.697265826541	0.878483023781
H	4.479631640004	1.595363380430	0.363761058485
H	5.739969280086	0.974505299640	1.434913714976
H	4.821863407235	-0.258766467620	-1.121124010014
H	6.145999972895	-0.793877673727	-0.086935964607
C	4.223528434227	-1.346373524769	2.002669462412
C	3.294149822289	-2.237885456203	2.826103049850
H	3.270635465380	-1.908933500009	3.873786222262

H	2.267279023847	-2.266236063399	2.460602897310
H	3.672205195257	-3.268349852878	2.808977176295
C	5.616371461604	-1.459022600391	2.628428444681
H	5.604600646182	-1.072921162696	3.657291493193
H	5.907853902587	-2.515676608360	2.682442663885
H	6.399326347235	-0.928101003449	2.079799375005
H	4.486052966820	-2.630308820753	0.177789364448
H	2.030782730491	-2.062793199025	0.413225521424
H	2.593068200511	-1.092007508837	-0.953553089387
H	2.384007485233	0.892472876280	0.280133482140
H	3.906182634523	0.580487949589	3.973666828959
H	3.596842334386	2.006946326002	2.932207239773
O	1.312810447729	-0.106145681219	4.433464204238
C	-1.070742978383	-0.205133512515	2.138438920848
H	-0.862407380202	-0.129845645957	3.203601594994
C	-2.463080769482	-0.081097623582	1.756314768177
C	-3.437077733568	0.025890438938	2.775483844095
C	-2.931831777868	-0.127675561536	0.423612369723
C	-4.794330354683	0.079024700277	2.485500741750
H	-3.105769402509	0.066958330923	3.812832792809
C	-4.294253109301	-0.070686013125	0.142954070136
H	-2.210639256976	-0.208386059174	-0.383606812373
C	-5.239611871904	0.030734703220	1.163349066823
H	-5.512521039349	0.161598745094	3.300126576990
H	-4.621755864360	-0.109066517281	-0.895287712074
H	-6.302257802347	0.073033584463	0.933844106804
C	-0.599041958094	-2.533358636003	2.063381689810
C	-1.823564999429	-2.976675880398	2.724320464701
C	-1.971595147016	-3.008645875538	4.050706907025
H	-2.906981076286	-3.328644778212	4.507168686505
H	-1.157347495261	-2.714548564089	4.715423682441
H	-2.647314827625	-3.272208024385	2.073222890998
H	-0.587612699859	-2.361635638908	0.995186286007
H	0.260710140492	-2.251224440035	2.659679987526
Br	0.441498208941	-4.693820992000	1.572771482460

Table S89. Atomic coordinates and single point energies of the reactant ground state for the bottom-face allylation of **8o** with π -stacking.



G = -4067.96198

G_{SP} = -4069.019258

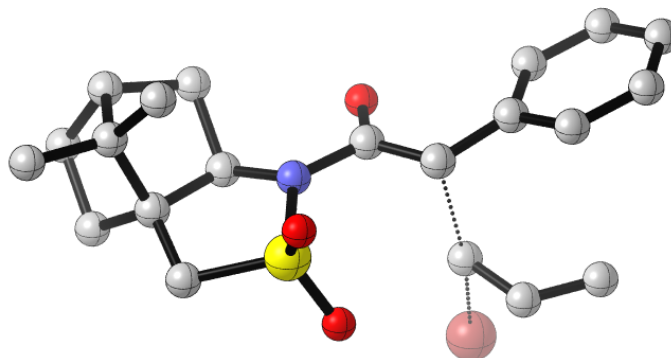
54

Anion_protoS_PiStack_start: optimized structure // E(RM062X) = -4069.43586134 A.U.
after 14 cycles

O	0.041385746905	-0.188905039413	-0.246891710331
C	0.006536655214	-0.221650193046	0.998334743733
N	1.321729408619	-0.205195734087	1.676191250362
S	1.621848951066	1.097879898512	2.707030530258
O	1.210087182698	2.376644336789	2.094062321528
C	3.433344094672	0.966541173620	2.647917551757
C	3.738278520473	-0.177689400753	1.701928116566
C	2.490203998450	-0.434034164223	0.822475811136
C	2.663635424156	-1.903034492606	0.371202327316
C	4.052702252952	-2.266999837009	0.934236814250
C	5.098134272049	-1.434548606993	0.156830867304
C	4.903437094514	0.006380171167	0.714130079989
H	4.641844080209	0.733541514071	-0.062546035703
H	5.801528254036	0.376004794810	1.220760332732
H	4.921960681410	-1.487964304174	-0.923615524786
H	6.115882662204	-1.797207225052	0.337173358767
C	4.042512066977	-1.578424284486	2.323148186737
C	2.989784935742	-2.121483428162	3.292892929266
H	2.900605967583	-1.465019690491	4.169888398781
H	1.993182237487	-2.219265671640	2.859985641339
H	3.310221528181	-3.107957956195	3.654363863996

C	5.385251841662	-1.623312389341	3.057765952852
H	5.343585991132	-1.001664125686	3.963048825918
H	5.595922087986	-2.651342886675	3.379799643119
H	6.234905810485	-1.284031017289	2.458706706886
H	4.260625541363	-3.342978221805	0.946423389326
H	1.866798070964	-2.528840307196	0.786269173431
H	2.621367375091	-1.993928297008	-0.718805323783
H	2.457483053882	0.247960590173	-0.036177289179
H	3.782873987802	0.814169359175	3.674294293625
H	3.779588117085	1.936451789126	2.277201972461
O	1.108143831305	0.820405242311	4.056080217819
C	-1.075992613661	-0.262554288205	1.869259170148
H	-0.862440829948	-0.352253783786	2.931677964797
C	-2.452804006470	-0.074071642398	1.479148700721
C	-3.451162032596	-0.011819377614	2.482497041781
C	-2.884823349893	0.113362953969	0.142995425639
C	-4.776934861221	0.265541624794	2.181477391400
H	-3.155688269827	-0.158735933926	3.521624311040
C	-4.215221500443	0.397087527668	-0.147469080885
H	-2.150168022837	0.057422279438	-0.654823621517
C	-5.176180996321	0.484856840533	0.860293100949
H	-5.508432655027	0.319244345922	2.987345883897
H	-4.503790317946	0.561555385399	-1.185215890786
H	-6.213546277689	0.712478441121	0.623294097341
C	-1.128884263209	3.000025664169	0.216816534869
H	-0.225530156235	3.609734896480	0.287338158296
H	-0.835562047611	1.961449250600	0.036682636160
Br	-2.014474365475	3.571388331283	-1.452171245753
C	-3.235068908872	3.535917220686	1.533964534422
H	-3.728226942951	3.573069566021	2.504302585362
C	-1.970493582237	3.140515209621	1.438951131058
H	-1.420265649738	2.842440081052	2.337103094923
H	-3.813117795905	3.825008596030	0.656774405168

Table S90. Atomic coordinates and single point energies of the transition state for the bottom-face allylation of **8o** with π -stacking.



TS frequency: -446.88

G = -4067.941851

G_{SP} = -4068.999865

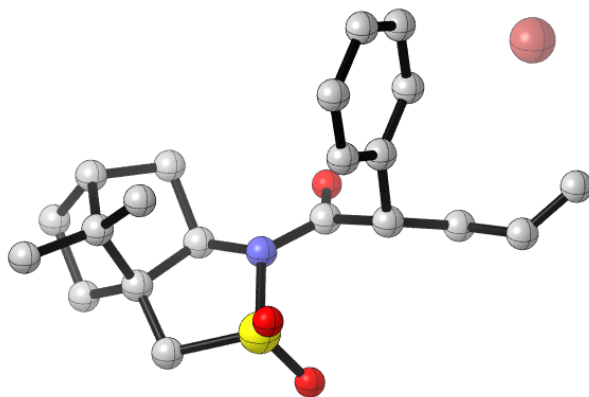
54

Anion_protoS_PiStack: optimized structure // E(RM062X) = -4069.41514591 A.U. after 14 cycles

O	-0.029750870650	-0.452859047444	-0.135177571352
C	-0.005194679293	0.022382403148	1.002466389037
N	1.294915794234	0.099646791812	1.612012967649
S	1.664328784391	1.070284609123	2.955859726632
O	1.239033741004	2.462305317351	2.743240531802
C	3.460112064746	0.953132706841	2.761362003295
C	3.712490264116	-0.123293399370	1.730340479993
C	2.474578798483	-0.225270721402	0.799300480953
C	2.556056016212	-1.676713273991	0.264492466895
C	3.923156719446	-2.151366279400	0.789857109376
C	5.016309861858	-1.310305122446	0.090467848800
C	4.910761712330	0.077773235639	0.787229230912
H	4.722709976435	0.898007722006	0.085941503877
H	5.817481230047	0.326209634860	1.349132076279
H	4.832955440134	-1.244935064373	-0.988168494690
H	6.011172942518	-1.748439057796	0.223266992093
C	3.928503040444	-1.587300392861	2.231751328135
C	2.828984750032	-2.155841930034	3.132623278054
H	2.860064574987	-1.682319229620	4.122273591159
H	1.817028236087	-2.024904556426	2.743818607570

H	3.005589244740	-3.230737374146	3.274659282995
C	5.253282483990	-1.777400420352	2.974683082426
H	5.263730288672	-1.183563937550	3.899190984232
H	5.361665632626	-2.830378403162	3.264953194811
H	6.136203693317	-1.504239148858	2.390069667911
H	4.075736872223	-3.233706549086	0.711895548417
H	1.730385058542	-2.278936581572	0.651579527214
H	2.490847847028	-1.696649946074	-0.827372660811
H	2.542032247164	0.501535214571	-0.020943696991
H	3.876310001052	0.747268222536	3.753101907992
H	3.771949063621	1.947009210704	2.423810386873
O	1.201960982539	0.425945618788	4.191428591142
C	-1.103259789641	0.538118761794	1.747972121379
H	-0.909119785464	0.848274327312	2.772189258050
C	-2.485527332054	0.228739978912	1.457771077619
C	-3.458508898620	0.507114730508	2.444692160408
C	-2.955495350676	-0.259918836881	0.216208548685
C	-4.813792599023	0.300390648935	2.215761186255
H	-3.128648278542	0.889201256674	3.410299054472
C	-4.314479734943	-0.459991074258	-0.005222052224
H	-2.236599627741	-0.480447534573	-0.566802405914
C	-5.257973346742	-0.183769258322	0.985487597859
H	-5.529889586641	0.524173259435	3.005302202466
H	-4.641994569204	-0.837238089363	-0.973213590608
H	-6.318464524200	-0.342681587601	0.801470515777
C	-0.905189131122	2.568118259591	0.496061411202
H	0.163623332434	2.508393657009	0.638404598868
H	-1.372651834955	1.970722547971	-0.279622705014
Br	-0.428174115739	4.313916654186	-1.200710930873
C	-3.041230150462	3.395634805281	1.388633089393
H	-3.610970028585	3.951705310943	2.132214679587
C	-1.706487079752	3.324497897157	1.443553021947
H	-1.154341860873	3.823997664937	2.240426626575
H	-3.599635242289	2.910871154218	0.585951917911

Table S91. Atomic coordinates and single point energies of the product ground state for the bottom-face allylation of **8o**.



G = -4068.014965
 G_{SP} = -4069.075890

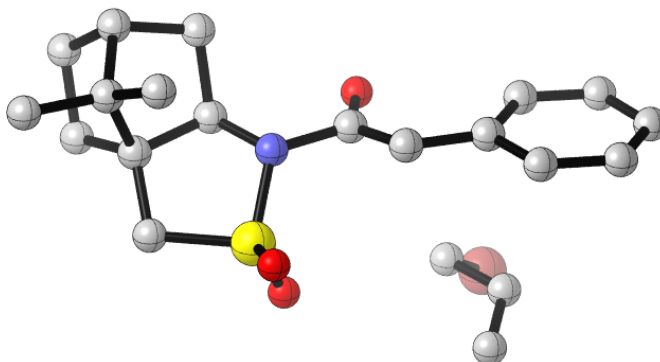
54

Anion_protoS_PiStack_end: optimized structure // E(RM062X) = -4069.49412386 A.U.
 after 12 cycles

O	0.543059517298	1.701286377448	0.134841899508
C	0.494503039206	1.552658959164	1.335039785789
N	1.531499468181	0.873341289609	1.983968101990
S	2.024414789133	1.261257688995	3.586049506664
O	2.157770293485	2.717095713469	3.704935633093
C	3.644244675562	0.465661085818	3.444699909733
C	3.628275857174	-0.323571644783	2.152766979982
C	2.639504270446	0.349984059189	1.171534121281
C	2.254128505646	-0.793664443285	0.203357617632
C	3.195967279617	-1.931087249333	0.645373075331
C	4.641206788348	-1.498846036830	0.309024452715
C	4.957904479910	-0.418522882646	1.383858885861
H	5.228138482074	0.551536001142	0.952687797052
H	5.774382085453	-0.723148574237	2.046784836610
H	4.707644093190	-1.099818521738	-0.709345784756
H	5.338281734611	-2.340686175443	0.373493734329
C	3.155541460455	-1.813369028715	2.189803668977
C	1.774045614762	-2.073225884413	2.797672827606
H	1.790328467649	-1.903231415599	3.882025373654
H	0.974063782798	-1.457260816698	2.380955559555
H	1.508715532976	-3.126202745062	2.633513444444

C	4.139834133893	-2.732264796020	2.917369562168
H	4.186123853874	-2.473316423779	3.984135801945
H	3.789020165162	-3.769864295922	2.850241489093
H	5.158029444336	-2.701315218428	2.519871774299
H	2.918388016688	-2.912295735108	0.245828668089
H	1.198506473115	-1.060643939222	0.316267272501
H	2.410736749311	-0.500078379000	-0.838723775811
H	3.110069797699	1.190422174239	0.646287938679
H	3.780075767576	-0.134770443451	4.350166052883
H	4.364105675526	1.290978156157	3.428421253053
O	1.169938386796	0.581455765664	4.562740480127
C	-0.714255337205	1.935024851911	2.174671371954
H	-0.418571639464	2.040998001624	3.225517227928
C	-1.670324277106	0.750461083994	2.082525438905
C	-1.634085535549	-0.251237887008	3.056864527523
C	-2.559078784644	0.633143059895	1.009542265888
C	-2.476803964359	-1.357941394247	2.962840784295
H	-0.936221617851	-0.162547969969	3.888816169869
C	-3.403505799020	-0.471504537531	0.924684096760
H	-2.624450338113	1.401374816854	0.234817870508
C	-3.364912761360	-1.471185561528	1.895464587450
H	-2.439924134039	-2.129945132742	3.729298436465
H	-4.098473568075	-0.538724800595	0.089364584805
H	-4.027196574780	-2.331964151562	1.823576108643
C	-1.309781662224	3.265375230820	1.688287580732
H	-0.508727746132	4.018187740379	1.727299478895
H	-1.641474727148	3.187029281458	0.644560368641
Br	-3.692178862839	3.038657936108	-1.589396559541
C	-3.696868165795	3.867542646974	2.143091269181
H	-4.481861676226	4.177484493790	2.834237163567
C	-2.446339635984	3.698061253050	2.567921184555
H	-2.203902609636	3.862608867902	3.622826460299
H	-3.958014481780	3.698778954993	1.092495747493

Table S92. Atomic coordinates and single point energies of the reactant ground state for the bottom-face allylation of **8o** without π -stacking.



G = -4067.961718

G_{SP} = -4069.020227

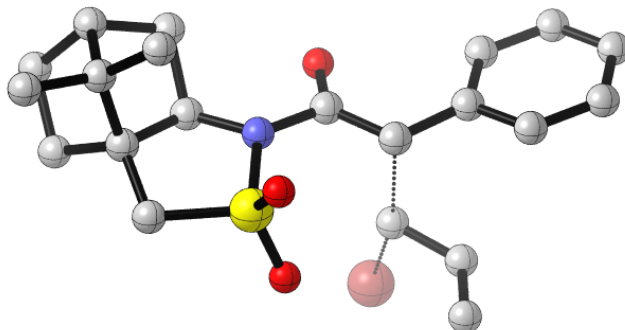
54

StartGeom: optimized structure // E(RM062X) = -4069.43655150 A.U. after 13 cycles

O	0.123570191676	-0.386618111782	-0.007001016310
C	-0.166628746277	-0.327935139925	1.202891551895
N	0.982790574122	-0.267297798110	2.128327121423
S	1.099804063934	1.016799442282	3.210935195218
O	0.927087140686	2.320617394450	2.540008205792
C	2.863315543787	0.777734710867	3.577784287379
C	3.318713806899	-0.378941012353	2.710857255995
C	2.299072441013	-0.562558611144	1.559500071879
C	2.490781117613	-2.040206815571	1.143459932069
C	3.686436446266	-2.483187993340	2.010812358251
C	4.930428990546	-1.712690358468	1.511991196287
C	4.692443308109	-0.263046118263	2.028362950741
H	4.663867740959	0.478732652041	1.222501735509
H	5.465259848392	0.052735459638	2.737573593288
H	5.010408566102	-1.755426984907	0.419729015867
H	5.855115998025	-2.134401476665	1.920658996882
C	3.387129357949	-1.795435753924	3.366973577570
C	2.106050882500	-2.278127849804	4.052925028827
H	1.852862592111	-1.622913709346	4.898325405034
H	1.233790959277	-2.311416790817	3.398217802685
H	2.274984226387	-3.284543018464	4.459248089378
C	4.512374887241	-1.917863518830	4.397998524050

H	4.291049303675	-1.296531710939	5.277044792684
H	4.583569428759	-2.956743492736	4.745278723598
H	5.497385054744	-1.626393943817	4.022881999265
H	3.824815741655	-3.569411118467	2.056760427692
H	1.585308866891	-2.619064784519	1.352350514339
H	2.698358899614	-2.129402218084	0.072490770816
H	2.506609787076	0.119700502324	0.725149413020
H	2.950258390926	0.599503613884	4.654607242009
H	3.342104758939	1.727078828344	3.318372496450
O	0.264709133676	0.774637136513	4.396136259358
C	-1.408038837011	-0.333586289371	1.831919766860
H	-1.421987746371	-0.318439548167	2.918743490111
C	-2.675659592175	-0.278185406960	1.149380094256
C	-3.861892318003	-0.137542028888	1.912637553472
C	-2.832283271409	-0.311490010726	-0.259057207319
C	-5.106745701220	0.000377675516	1.317498073712
H	-3.780278886444	-0.109597305788	2.999380043595
C	-4.085999174872	-0.164833806708	-0.846968491072
H	-1.948224833780	-0.439774855098	-0.876815372492
C	-5.236202575591	-0.000999124914	-0.075022830785
H	-5.989317002103	0.118636250542	1.945512424861
H	-4.163234755184	-0.180667859162	-1.933958577794
H	-6.211126198888	0.114838472887	-0.543947014006
C	-2.580938686614	2.886265825471	0.953720032395
H	-3.479739501541	2.537126242292	0.439095745585
C	-2.655571930921	3.377601996613	2.187991154432
H	-1.760597336203	3.707553191586	2.717559248068
H	-3.607771251141	3.437746878659	2.714068430231
C	-1.294664608935	2.730423573926	0.230514125265
H	-0.436930051057	3.078246155873	0.807218125368
H	-1.119211876187	1.716269877811	-0.135298058542
Br	-1.317603056454	3.832966746515	-1.436926248663

Table S93. Atomic coordinates and single point energies of the transition state for the bottom-face allylation of **8o** without π -stacking.



TS frequency: -476.8646

G = -4067.939173

G_{SP} = -4068.996952

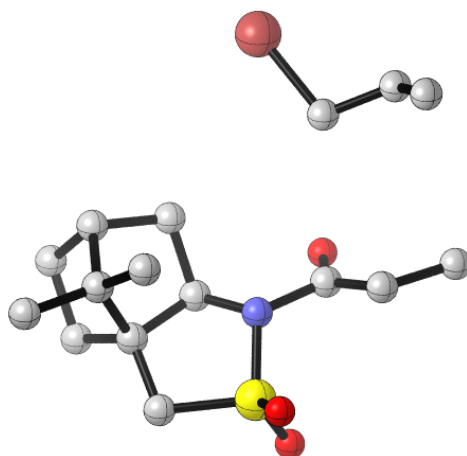
54

TS-SPE: optimized structure // E(RM062X) = -4069.41253759 A.U. after 15 cycles

O	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.234653150000
N	1.301053967296	0.000000000000	1.850456002809
S	1.590380955286	0.368289661164	3.481189537281
O	0.990653520610	1.659640668088	3.856591565731
C	3.378630871286	0.576350239031	3.296781729966
C	3.731634266946	0.068284730057	1.917762114332
C	2.484539646270	0.194774179581	1.001271586087
C	2.735771617660	-0.883467128439	-0.082314370231
C	4.171989743134	-1.342611519668	0.227721925614
C	5.118535780899	-0.148834333499	-0.038154582483
C	4.858040663921	0.799776615513	1.168344851071
H	4.539021006822	1.803104206612	0.865835249620
H	5.744357641884	0.912928714792	1.801792871591
H	4.887805031235	0.330591986332	-0.996434396995
H	6.166600605345	-0.463928166825	-0.078450784293
C	4.155976592496	-1.428276485200	1.773431434342
C	3.173207031542	-2.458167691331	2.336605728328
H	3.179670895229	-2.434557393120	3.433955158147
H	2.139001979272	-2.314534951228	2.016819653569

H	3.492127608522	-3.462407781473	2.025919588816
C	5.520441235866	-1.728088976214	2.399152963064
H	5.487766557035	-1.570676674925	3.486210539240
H	5.775101845389	-2.782633592853	2.232342340873
H	6.338479732997	-1.123997099046	1.996830093447
H	4.462632547359	-2.264927778001	-0.287701996441
H	2.011699192844	-1.696959128387	0.005382717994
H	2.632168487453	-0.461477144485	-1.086270355875
H	2.429084431176	1.196420167689	0.554999742602
H	3.850378952718	0.032842337872	4.122151929665
H	3.549290918548	1.651775047232	3.411408471103
O	1.251607748187	-0.779196726073	4.331660997798
C	-1.131956146884	0.063393091487	2.091359731950
H	-0.955457564508	0.014321879393	3.163430734943
C	-2.473033949040	-0.305938912810	1.678019081539
C	-3.442783053460	-0.545944170541	2.678971046278
C	-2.906590971290	-0.378979130050	0.335036655882
C	-4.762229392055	-0.839456568749	2.361587510099
H	-3.138196095219	-0.495391763380	3.724043740562
C	-4.231794922032	-0.676940071068	0.026936391124
H	-2.188301120677	-0.200920227658	-0.459081956439
C	-5.173389569006	-0.907610317868	1.028739940813
H	-5.478004615556	-1.018168702323	3.162814601247
H	-4.532232944131	-0.725739418922	-1.019032361630
H	-6.206855511561	-1.136999321245	0.777781117984
C	-2.402633061262	2.603203604999	2.604991487616
H	-3.383795009261	2.611019991254	2.128016826128
C	-2.291679320751	2.759072644746	3.925930101823
H	-1.312620162120	2.737798812346	4.407724295420
H	-3.170815824257	2.900697918395	4.553021377816
C	-1.253037976491	2.390765043709	1.725914935348
H	-0.254454992989	2.477473393032	2.136508711134
H	-1.386160153140	2.064453519671	0.702165955639
Br	-1.091241054721	4.674900088917	0.819927815336

Table S94. Atomic coordinates and single point energies for the ground state of the top-face allylation of lithium N-propionyl camphorsultam enolate.



G = -3876.356682

G_{SP} = -3877.314974

47

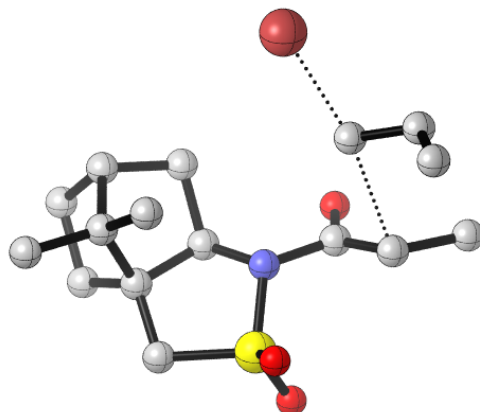
PropAnion_topFace_AllylBr_Start: optimized structure // E(RM062X) = -3877.67752966

A.U. after 12 cycles

O	-0.071521777772	0.055009641765	0.009320503155
C	-0.101260782970	-0.014571066825	1.265879206570
N	1.244341916880	-0.102946202622	1.912716090129
S	1.636182762398	1.042134141195	3.077268700203
O	1.331507801750	2.418588572377	2.642248896154
C	3.434665212963	0.792520616397	2.987416144700
C	3.660234675526	-0.223314280017	1.886132848988
C	2.382899449659	-0.291616107813	1.010618682084
C	2.465140995412	-1.696284155089	0.371458849719
C	3.843293682538	-2.203887772408	0.837412259414
C	4.916917114753	-1.329171762432	0.149759580076
C	4.817192337279	0.029440920822	0.904232794520
H	4.586258191275	0.870362987488	0.240884837323
H	5.744745502184	0.273703218495	1.433755157477
H	4.711745676536	-1.223719897881	-0.921750069620
H	5.916677311965	-1.766705588070	0.246318875519
C	3.897548866051	-1.709272173209	2.305687232112
C	2.832735538659	-2.318822753923	3.220988669792
H	2.813666317938	-1.796203688098	4.187817457024
H	1.821311732906	-2.277463877230	2.813891115758
H	3.087767829277	-3.368486493628	3.421152701123

C	5.248287379141	-1.926267830565	2.993215096077
H	5.263392244395	-1.423013413229	3.970197238935
H	5.401325979119	-2.997574760038	3.177928885867
H	6.105405946146	-1.564303336044	2.418358704880
H	3.990903796404	-3.281250573462	0.698732310006
H	1.651835327383	-2.330658592855	0.733196137979
H	2.379145484144	-1.650168743612	-0.718750841652
H	2.380874461859	0.492253041705	0.242611009555
H	3.771391403170	0.469638696009	3.977985440505
H	3.851125539036	1.778286620561	2.758126315348
O	1.110549795928	0.640215156557	4.392881256235
C	-1.166763971785	-0.083006465650	2.127648701351
H	-0.970187206391	-0.183502198747	3.193147855954
C	-0.900190262943	-3.015413718734	0.402755691463
C	-2.357718329531	-3.269214703816	0.517620721978
C	-2.955830045934	-3.550215109689	1.672572878451
H	-4.034450992422	-3.690954658416	1.730822717728
H	-2.385744233207	-3.626802738354	2.599938697638
H	-2.942580846120	-3.184517538760	-0.400376104751
H	-0.652131785868	-2.064306755674	-0.080032809456
H	-0.384654015826	-3.108752928320	1.359915680024
Br	-0.065713986689	-4.401277465205	-0.775686559462
C	-2.573845315460	0.104413886673	1.639632581245
H	-2.618575350243	-0.051321537908	0.553686319301
H	-3.276965613832	-0.602723334613	2.104227085516
H	-2.973793280822	1.114842913188	1.835054141988

Table S95. Atomic coordinates and single point energies of the transition state for the top-face allylation of N-propionyl camphorsultam enolate.



TS frequency: -453.3862

G = -3876.342605

G_{SP} = -3877.298342

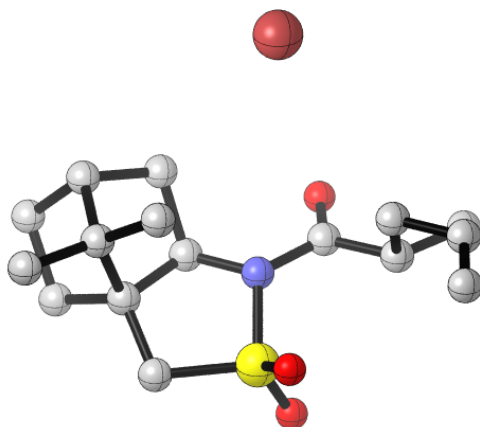
47

PropAnion_topFace_AllylBr_QST2: optimized structure // E(RM062X) = -3877.66190098 A.U. after 13 cycles

O	0.102395924767	0.213494934638	-0.307519135394
C	-0.062563074308	-0.006239590951	0.905959870886
N	1.167592901041	-0.243287397040	1.679440782945
S	1.357292266535	0.580022910818	3.143908920600
O	0.996003859054	2.002627433921	3.016736442996
C	3.166240135806	0.436136852202	3.209045898507
C	3.578439618412	-0.301645571715	1.951831046087
C	2.423287521069	-0.218282360611	0.921272024505
C	2.661291538852	-1.450981877627	0.017945205007
C	4.007255090949	-1.995546557266	0.538156610899
C	5.096621763325	-0.952950887497	0.195692249192
C	4.823297727114	0.204337028207	1.201836566383
H	4.618021421609	1.160772854506	0.708430050298
H	5.664418579899	0.362058080249	1.885597140333
H	5.014952295299	-0.623107013678	-0.846361383853
H	6.103270377112	-1.364647420924	0.327115077976
C	3.861759922838	-1.832664962828	2.072443644084
C	2.740538947581	-2.666425580987	2.694250547797

H	2.510379727172	-2.313994655462	3.709781359498
H	1.814694248544	-2.655638557188	2.118980611131
H	3.067782228607	-3.711554699251	2.772904505586
C	5.135298887096	-2.141380823729	2.864472904958
H	4.992252577580	-1.893102908544	3.925568320141
H	5.350382805485	-3.216304832429	2.809735732787
H	6.022872246804	-1.607764948006	2.513276947222
H	4.236788955635	-3.010645991836	0.194720931947
H	1.851480415257	-2.182042711002	0.124634666051
H	2.708275836108	-1.164686147334	-1.037469169335
H	2.476353933061	0.712348141248	0.342358511577
H	3.418143108926	-0.080694903159	4.140940455436
H	3.531717359663	1.467162523602	3.245843384212
O	0.718205793721	-0.170842863841	4.235784032932
C	-1.261128011110	-0.212823116479	1.586379360853
H	-1.228870046580	-0.360872091431	2.664162076642
C	-0.901433798908	-2.609568008875	1.076367542398
C	-2.280962000554	-2.977388225025	1.406088798790
C	-2.704669251486	-3.234276923817	2.644980837219
H	-3.741454641555	-3.501012079398	2.843899096789
H	-2.023106150661	-3.181710306227	3.495652123516
H	-2.975843518167	-3.040099061138	0.567312496400
H	-0.676133440718	-2.176916969619	0.110022797482
H	-0.177358290813	-2.499385232968	1.873629917477
Br	-0.018198072353	-4.678825203451	0.384158102370
C	-2.560672222841	0.151615556626	0.934062344550
H	-2.555871638464	-0.127147127738	-0.128671885351
H	-3.401315052387	-0.364299092207	1.416564827000
H	-2.780586329155	1.231878575558	0.976696495395

Table S96. Atomic coordinates and single point energies of the product ground state for the top-face allylation of N-propionyl camphorsultam enolate.



G = -3876.427988

G_{SP} = -3877.387144

47

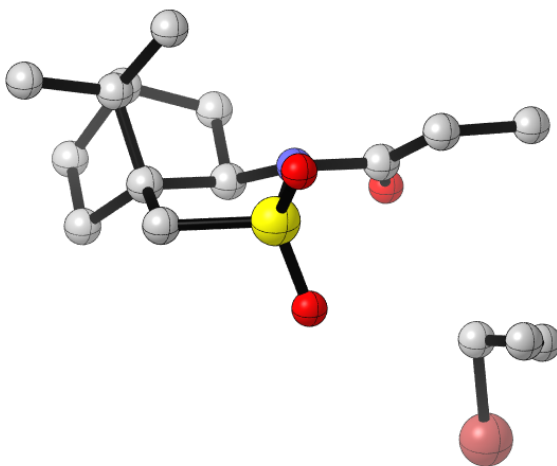
PropAnion_topFace_AllylBr_End: optimized structure // E(RM062X) = -3877.75478960

A.U. after 12 cycles

O	0.129507503925	0.105474548130	-0.361790321119
C	0.077885027639	0.052968450840	0.846508511854
N	1.273523099034	0.017015071619	1.582020004233
S	1.417727423018	0.813954406347	3.093115369442
O	1.002338781136	2.215245110457	2.940475181450
C	3.224690435916	0.706521732151	3.158456971949
C	3.657326240120	-0.068257032888	1.930432180415
C	2.552282759662	0.030783539398	0.853283771161
C	2.810026148583	-1.204812389045	-0.039482957523
C	4.104207607471	-1.790089235894	0.561531440025
C	5.253105201241	-0.799195109502	0.273381783688
C	4.950835673094	0.390012599772	1.232235000282
H	4.792504330572	1.337465393643	0.704776601860
H	5.755983695600	0.550022286300	1.957144242078
H	5.258736704534	-0.491461746672	-0.778412129811
H	6.232127039685	-1.241617513372	0.487774092350
C	3.877214245009	-1.607754062508	2.082988350613
C	2.693201672450	-2.403986689597	2.639210995785
H	2.390296524160	-2.016493022397	3.622926741739
H	1.817785621076	-2.435137354004	1.984594197630
H	3.006977378716	-3.446359945274	2.783656113924

C	5.092976728278	-1.942840761285	2.951491351356
H	4.879203877530	-1.719636536384	4.006230819892
H	5.302946222650	-3.018008230900	2.885705184429
H	6.006501343103	-1.408328144027	2.675054989793
H	4.303269971181	-2.818599432413	0.241268739778
H	1.976281101566	-1.917426586013	-0.000076246725
H	2.942416580255	-0.905117711018	-1.084594192057
H	2.624359462866	0.972538637638	0.292761786207
H	3.479149536780	0.229473039388	4.110650521800
H	3.566477046870	1.746561738170	3.156368445069
O	0.774345094649	0.034551421881	4.153638022646
C	-1.211539095047	-0.055008839527	1.639251285225
H	-1.173889097401	0.678884553635	2.458169685546
C	-1.285868581315	-1.466527848337	2.268773835254
C	-2.503639057552	-1.637197871830	3.126800119814
C	-2.471523189022	-1.699786157566	4.456817572240
H	-3.381058721969	-1.823893555526	5.044378981461
H	-1.526250231240	-1.630101561457	4.998241153124
H	-3.468665617199	-1.710883297907	2.618295135941
H	-1.257673488786	-2.217779962705	1.464883032976
H	-0.392945026348	-1.630854122728	2.881733835147
Br	0.313800410943	-4.094422932612	0.095600116128
C	-2.400405302088	0.261210383792	0.741481245736
H	-2.503428722711	-0.499005657467	-0.041181065564
H	-3.324243508795	0.289660664086	1.328681956936
H	-2.276235495989	1.234513140712	0.254455184002

Table S97. Atomic coordinates and single point energies of the product ground state for the top-face allylation of N-propionyl camphorsultam enolate.



G = -3876.356625

G_{SP} = -3877.314279

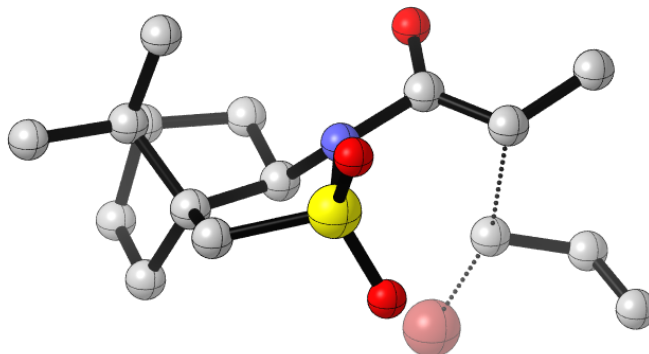
47

PropAnion_bottomFace_AllylBr_Start: optimized structure // E(RM062X) = -3877.67761124 A.U. after 12 cycles

O	-0.023053482959	-0.047476687803	0.072577759676
C	-0.038330560985	-0.052688721561	1.329414594309
N	1.319430568047	-0.057815138423	1.961169011064
S	1.727626842181	1.135980399694	3.057265435973
O	1.462653196036	2.498100651939	2.541625836627
C	3.520585977161	0.840459864703	2.991202748865
C	3.725164822595	-0.229624414102	1.937172478087
C	2.447557337102	-0.308697348223	1.063491169083
C	2.495748066582	-1.742636400558	0.487209249991
C	3.859321684179	-2.262024749824	0.984694040218
C	4.957130154001	-1.447940704698	0.261020780127
C	4.889682857768	-0.052084642213	0.948404716789
H	4.680484373112	0.761186596471	0.244544016768
H	5.821973036403	0.195361843651	1.467887560100
H	4.759887010028	-1.388762092393	-0.815593065316
H	5.944920779214	-1.905443638877	0.384166391565
C	3.922252263099	-1.699885356094	2.427639494176
C	2.840042957907	-2.240102923893	3.366312607446
H	2.817628971692	-1.659544316892	4.299378515737
H	1.832714410335	-2.215589196255	2.947734894152
H	3.082019033121	-3.277965247201	3.633232983675

C	5.265112724512	-1.917815501454	3.130440302387
H	5.284603565672	-1.379277960787	4.088338460507
H	5.395700065888	-2.984353879146	3.355520392778
H	6.132658080249	-1.594220037409	2.548391879877
H	3.982815321356	-3.347846072099	0.898881052794
H	1.657001146943	-2.335992434526	0.864509483334
H	2.425084520105	-1.734001288625	-0.604909552492
H	2.461029764838	0.440987279234	0.261543658746
H	3.841046014745	0.551471184922	3.997618275697
H	3.963293305764	1.804811432926	2.723508130299
O	1.182175468558	0.837027543925	4.390932692195
C	-1.088539972612	-0.080833528084	2.212259052966
H	-0.875836228976	-0.126625121228	3.278114815681
C	-2.040282125221	3.405522881399	1.349811454869
H	-3.056709323453	3.516518084005	0.965651659038
C	-1.761082404625	3.694604231396	2.618985040257
H	-0.748582055458	3.567706807666	3.007999410235
H	-2.537278126161	4.035535539249	3.303559744537
C	-1.016335320243	2.883827781765	0.411283181336
H	-0.020984656251	2.844532729103	0.856397788037
H	-1.255339734831	1.915569945086	-0.033116890797
Br	-0.856214933162	4.111044909638	-1.161130884026
C	-2.508747660714	-0.069958176293	1.728048802529
H	-2.524397263258	-0.115609644192	0.631603949130
H	-3.089365106127	-0.931164465906	2.096278447845
H	-3.069072815421	0.831295396322	2.029651782981

Table S98. Atomic coordinates and single point energies for the transition state of the bottom-face allylation of N-propionyl camphorsultam enolate.



TS frequency: -455.7783

G = -3876.336624

G_{SP} = -3877.292100

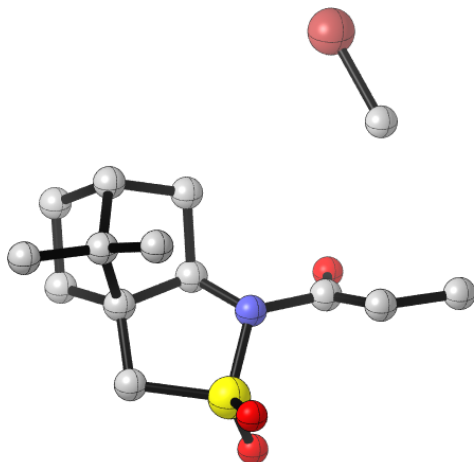
47

PropAnion_bottomFace_AllylBr_TS: optimized structure // E(RM062X) = -3877.65635314 A.U. after 13 cycles

O	-0.032438917196	0.221116377057	-0.015225185087
C	-0.012447172541	0.130969359746	1.225431255471
N	1.332925498597	0.118634916719	1.820807571675
S	1.627319741254	-0.476191931290	3.357860689310
O	1.140992279928	0.430068553722	4.419580606785
C	3.424493418854	-0.279470529762	3.256996660298
C	3.673754329550	0.648531492035	2.079139324258
C	2.312742107775	1.189852970327	1.551284304892
C	2.616808955426	1.541673783955	0.073014552292
C	4.138039104993	1.316324063794	-0.015999074398
C	4.831590940118	2.379195138504	0.866362647290
C	4.545993544979	1.891606115968	2.316630525752
H	4.011849698529	2.634828413951	2.919831017289
H	5.466799629738	1.633306816604	2.851216714677
H	4.418585666082	3.377036045414	0.678288000048
H	5.907790503404	2.430585133690	0.667728203531
C	4.317844339749	0.015981705048	0.805553328961
C	3.575804598666	-1.194464831937	0.233024445799
H	3.630062167940	-2.043016671887	0.930109322508

H	2.519946986211	-1.009065926919	0.024245317552
H	4.065725482444	-1.509757318968	-0.698395000174
C	5.774354330920	-0.400697721793	1.018977258752
H	5.834191673854	-1.217117017922	1.752535818000
H	6.193285056817	-0.778528159316	0.077234451825
H	6.420890042835	0.410144892487	1.367397467683
H	4.516231174254	1.275986447640	-1.043947445847
H	2.051293019684	0.902747984241	-0.604111537869
H	2.338363809332	2.580940954479	-0.135658445577
H	2.029121676234	2.097800026717	2.103818747050
H	3.849626875512	-1.280226638858	3.128279137009
H	3.730680348023	0.132677281595	4.222835201683
O	1.212326782307	-1.882527798533	3.440470131524
C	-1.106108536273	0.157755894547	2.091462996045
H	-0.951448959926	0.006987325596	3.156967797795
C	-1.943029362014	2.940793867260	2.708662693225
H	-2.566545278083	3.326661654321	1.900886680581
C	-2.438627891168	2.829255465178	3.943236124621
H	-1.825566599916	2.448412562657	4.761895290085
H	-3.465530514067	3.112397740619	4.169011672051
C	-0.574539536359	2.569075351420	2.352232142207
H	0.083359472390	2.169039389460	3.115146274140
H	-0.303927910707	2.475917050625	1.309189992555
Br	0.529647178416	4.687260016280	2.388680439983
C	-2.491096164831	-0.004317614842	1.542937717678
H	-3.234991218350	0.445472508325	2.214100258419
H	-2.577497872563	0.479856112539	0.561838127552
H	-2.779995033602	-1.060116622062	1.407186615713

Table S99. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of N-propionyl camphorsultam enolate.



G = -3799.040313

G_{SP} = -3799.955393

43

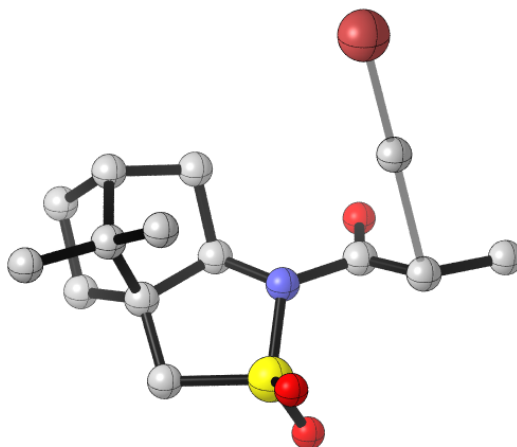
PropAnion_topFace_MeBr_Start: optimized structure // E(RM062X) = -3800.28551478

A.U. after 12 cycles

O	0.003753472875	-0.016756592362	-0.011799657878
C	-0.002033506355	0.014244576344	1.247188897954
N	1.347409578147	0.037669570382	1.881108673162
S	1.789961567377	1.379662343342	2.775484514524
O	1.483063975768	2.649327389733	2.089414618911
C	3.582045647623	1.070166847661	2.684581868287
C	3.744946448656	-0.199434525495	1.872748948156
C	2.457089698959	-0.404646705331	1.039459541583
C	2.452213058960	-1.924157172179	0.750073005817
C	3.802460994212	-2.383172188242	1.337600559779
C	4.918917612054	-1.766042821388	0.463866487381
C	4.903098477533	-0.260319204053	0.861880634050
H	4.710254754702	0.403554907058	0.011793878079
H	5.849280896509	0.054409916204	1.315832025904
H	4.713837684703	-1.914802696643	-0.602523567770
H	5.892252316247	-2.223385760368	0.672940097801
C	3.900929849856	-1.551013712097	2.642200470290
C	2.815119291257	-1.864688403664	3.675248815562
H	2.817893210312	-1.111784666959	4.475723511003
H	1.804538043788	-1.890820202936	3.264430698998
H	3.031013758703	-2.837774580827	4.137309825430

C	5.244808977140	-1.671790835655	3.366338924785
H	5.289521743134	-0.961590108626	4.203918876717
H	5.347424925836	-2.679350432183	3.790153134284
H	6.115383930448	-1.491046860705	2.729571608654
H	3.887218491268	-3.468525380247	1.465860750475
H	1.597660401410	-2.406266913556	1.238278917625
H	2.373379918243	-2.131878074769	-0.322070224741
H	2.477660613731	0.179330850769	0.110528982366
H	3.957931884955	1.006580084189	3.711024931127
H	4.004038798708	1.950535036928	2.189291681280
O	1.302128223614	1.259448011169	4.160003226003
C	-1.042114528852	-0.034570203017	2.137878604391
H	-0.812269301266	-0.058906172612	3.201301474283
C	-1.180629972416	-2.950554294140	0.272476220330
H	-0.694558382326	-2.031301701602	-0.066526019986
H	-1.041099399197	-3.119638854353	1.339777758669
Br	-0.323137801573	-4.457097864283	-0.657165290760
C	-2.468902468222	-0.026241356838	1.672949249017
H	-2.495784175929	0.029124867586	0.577554148087
H	-3.026263471009	-0.929812783160	1.970922704620
H	-3.044552054736	0.830515129675	2.059588432009
H	-2.236844181927	-2.981299136995	0.002932774847

Table S100. Atomic coordinates and single point energies of the transition state for the top-face methylation of N-propionyl camphorsultam enolate.



TS frequency: -515.5161

G = -3799.025372

G_{SP} = -3799.938961

43

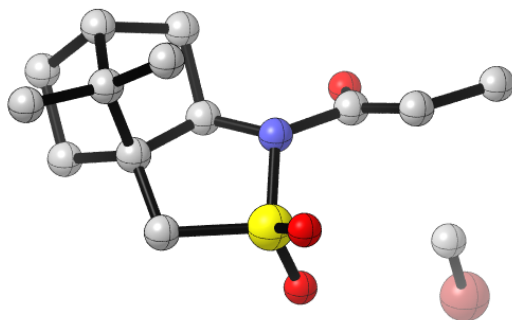
PropAnion_topFace_MeBr_TS: optimized structure // E(RM062X) = -3800.26945534

A.U. after 13 cycles

O	-0.011716717929	-0.000507398961	0.014642728374
C	0.001622321343	-0.000358119750	1.258517668688
N	1.336262759328	0.004901841547	1.875644234543
S	1.640512801335	1.052964161935	3.164293206094
O	1.100909835517	2.400136468136	2.911871292428
C	3.443966247130	1.087377316875	2.956862586639
C	3.759928334930	0.137114486389	1.821629760611
C	2.482327692763	-0.050859750766	0.963318457805
C	2.706420139627	-1.424667012798	0.286958471555
C	4.148991081555	-1.773633911523	0.704254235938
C	5.089864458291	-0.754004065252	0.020159824200
C	4.855951449704	0.557316516350	0.827088736553
H	4.516064135267	1.390210845166	0.201750757416
H	5.761572292599	0.885954839521	1.348521550742
H	4.840095745978	-0.636808353021	-1.040633046714
H	6.136517293308	-1.072864826492	0.072248644606
C	4.185281905178	-1.320856244422	2.185842172445
C	3.227027643823	-2.081269299725	3.103780728648
H	3.191004180418	-1.613301405396	4.097093994580

H	2.204075212478	-2.126523454605	2.729115602716
H	3.589874827691	-3.109476997972	3.235100136851
C	5.570465410088	-1.395586079395	2.833658150886
H	5.556149504391	-0.911313827277	3.820085634114
H	5.845679045078	-2.446190785894	2.992603098669
H	6.366188415458	-0.931078997198	2.244666840280
H	4.421928075147	-2.820129938410	0.527740996474
H	1.980155019102	-2.160978181325	0.648280406354
H	2.590850065850	-1.356645350850	-0.799199560619
H	2.387594978471	0.746583363671	0.215780219019
H	3.887580145635	0.812050668101	3.919277709597
H	3.682374065237	2.129687553841	2.722160003556
O	1.260598146456	0.419155997371	4.436392014627
C	-1.074710550594	-0.167996733346	2.130404353824
H	-0.894334391363	-0.078752466009	3.200418917116
C	-0.732508411137	-2.509752961610	1.983026407672
H	-0.708893329106	-2.313450863419	0.918211747087
H	0.150063023710	-2.333652337327	2.581390776213
Br	-0.384462964815	-4.769060393955	1.790758388012
C	-2.476183367782	-0.032285272082	1.610827577552
H	-3.194277163169	-0.545608259150	2.264486720661
H	-2.815105859329	1.013685100231	1.523950624067
H	-2.558638894330	-0.475447321697	0.609540029630
H	-1.690105050558	-2.583265935072	2.483522705178

Table S101. Atomic coordinates and single point energies of the ground state for the bottom-face methylation of N-propionyl camphorsultam enolate.



G = -3799.040937

G_{SP} = -3799.955717

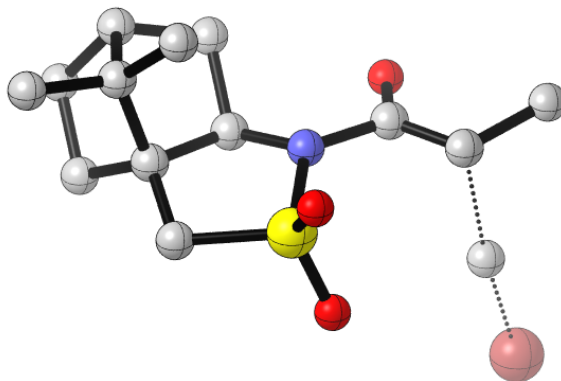
43

PropAnion_bottomFace_MeBr_Start: optimized structure // E(RM062X) = -3800.28503899 A.U. after 12 cycles

O	0.046069803501	0.034568931503	-0.079531786261
C	0.038662411023	0.019486600008	1.178271071898
N	1.395443919186	0.000268719491	1.808558892332
S	1.817906714128	1.226087118368	2.865524783947
O	1.542117543954	2.570155543054	2.316447414572
C	3.609829284935	0.929771818136	2.785308779710
C	3.799976073188	-0.191751962926	1.784328554873
C	2.518278675698	-0.298251021280	0.919939156400
C	2.551619408844	-1.757353071242	0.409013140658
C	3.912165403760	-2.266685831498	0.926093308585
C	5.015140594487	-1.497313855432	0.162397894484
C	4.962719018402	-0.070956520435	0.784901934063
H	4.758611227701	0.711178267965	0.045202888136
H	5.898952175414	0.191130622659	1.290048511523
H	4.815346488628	-1.486137596390	-0.915297934108
H	5.998991209703	-1.957918298517	0.304029074700
C	3.985733564763	-1.639608903897	2.341699011229
C	2.902789600232	-2.127572469054	3.307876081112
H	2.896388026808	-1.512477685697	4.218693951849
H	1.893163771204	-2.102538849817	2.894768673526
H	3.131319256587	-3.158373658110	3.611528270621

C	5.329469647322	-1.836625672734	3.048870772236
H	5.358727893894	-1.251324392812	3.978679493398
H	5.450408828516	-2.891886302020	3.326334677281
H	6.197454348645	-1.551213827163	2.447855999934
H	4.025103872396	-3.356429099975	0.889717674342
H	1.709010442975	-2.325184893089	0.816750268441
H	2.478777420357	-1.799210151276	-0.682363627694
H	2.533954189670	0.415283186765	0.086220352971
H	3.949416999841	0.695501768638	3.799628987601
H	4.045295967769	1.879172336626	2.458701236230
O	1.293013255988	0.955302632460	4.213966224224
C	-1.005707458990	0.003278436137	2.067394369693
H	-0.782894153308	-0.069880342582	3.129786772232
C	-1.136165870781	2.960955409829	0.462468787853
H	-0.356353721335	3.212167406941	1.180633458456
H	-0.867938662117	2.068052276178	-0.104583713756
Br	-1.257404048558	4.460603808563	-0.812802245666
C	-2.432344735408	0.032252368086	1.601710435478
H	-2.464979971849	0.168987083268	0.513644790488
H	-2.977547053716	-0.900073589490	1.825666245765
H	-3.018833067811	0.845770965804	2.058072698003
H	-2.115968411503	2.879489175194	0.931713899650

Table S102. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of N-propionyl camphorsultam enolate.



TS frequency: -522.9402

G = -3799.021406

G_{SP} = -3799.934753

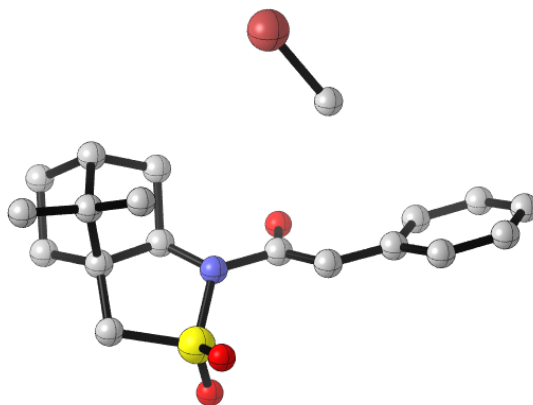
43

PropAnion_bottomFace_MeBr_TS: optimized structure // E(RM062X) = -3800.26583423 A.U. after 13 cycles

O	0.146654056222	1.535519035963	0.250754101817
C	0.142358829110	0.771239811523	1.232746840167
N	1.464701927836	0.483784387523	1.780219348623
S	1.719243793403	-0.082872520479	3.345322590221
O	1.074838468933	0.773360845837	4.356754834050
C	3.503426770178	0.236457947383	3.367098859165
C	3.879792824638	0.651919184308	1.962963682507
C	2.619377615969	1.220147939632	1.255163942482
C	2.932631149547	0.998301935771	-0.245372408950
C	4.393761040173	0.514088070278	-0.219148226121
C	5.269503229378	1.683775563452	0.288063468741
C	4.956096816471	1.739966324263	1.812055141357
H	4.574998857317	2.714483317065	2.136519887969
H	5.837378387758	1.512039113616	2.421495396554
H	5.009731372651	2.619112092561	-0.221158120661
H	6.334283270633	1.501844993262	0.106394816083
C	4.391145409447	-0.456112425829	0.987796207374
C	3.473775260753	-1.670407551037	0.822307279977
H	3.461559148179	-2.268917503803	1.742788399473

H	2.437918533087	-1.418828932725	0.587523010053
H	3.865855980336	-2.308817855184	0.018785984225
C	5.774183929316	-0.993835100308	1.364349520288
H	5.734278331677	-1.508029673031	2.334730250830
H	6.095713501175	-1.732887582825	0.619112896885
H	6.550879017613	-0.226179624216	1.423481966161
H	4.735357909063	0.081221705711	-1.166388001605
H	2.254235506679	0.256115769477	-0.672553229278
H	2.802036600171	1.922961681205	-0.815508894377
H	2.495920382288	2.288454691222	1.478168572168
H	3.991779544047	-0.677321905231	3.722007035965
H	3.637087856624	1.038653693668	4.100003530875
O	1.420631658939	-1.520563352639	3.426959001415
C	-0.975992378598	0.224488119884	1.871652218791
H	-0.818108838860	-0.525771193551	2.644884637929
C	-1.416255038317	2.251158881571	3.017599001510
H	-0.566544131567	2.078968826165	3.664778533132
H	-1.266439304530	2.664717301448	2.027764663713
Br	-2.021112417358	4.264818721306	3.978745072949
C	-2.284318136442	0.197961961872	1.130026751771
H	-2.346823019972	-0.610733702607	0.382211363588
H	-3.129537936097	0.060636099149	1.818155685832
H	-2.444632724630	1.140019522452	0.589717755645
H	-2.353109258305	1.762349049084	3.249850911285

Table S103. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of **8o**.



G = -3990.610412

G_{SP} = -3991.660107

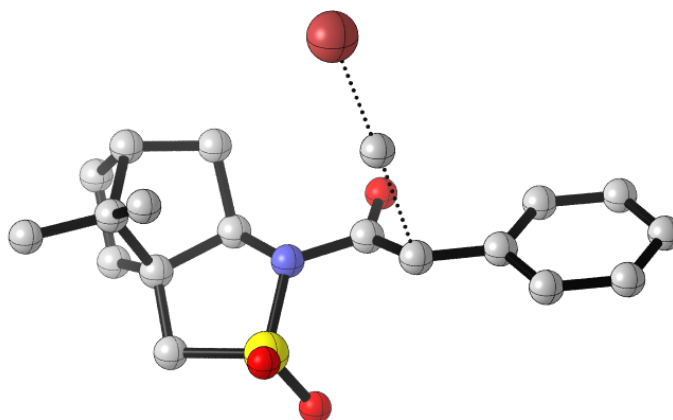
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QST_start: optimized structure // E(RM062X) = -3992.04201915 A.U. after 13 cycles

O	0.059928405928	0.228551738863	0.036194645623
C	0.088766858047	0.187081918841	1.280848805558
N	1.447334707619	0.278153423113	1.863370716858
S	1.828706203097	1.377250653146	3.070186654209
O	1.559416885242	2.767694866124	2.678434394417
C	3.629403387687	1.101760843900	2.957286973974
C	3.838233715415	0.130820409449	1.813007040308
C	2.561702287650	0.135808228123	0.933894724375
C	2.613631669173	-1.236140881252	0.222602238109
C	3.968541830876	-1.808157639397	0.678303668925
C	5.079742628746	-0.941985225397	0.043094544326
C	5.008529436028	0.388853662496	0.848793414087
H	4.804573973450	1.259995375894	0.215844380032
H	5.940221170773	0.593706378936	1.388842745230
H	4.898387782330	-0.788556966605	-1.026884646362
H	6.064886503699	-1.413388088607	0.135284446952
C	4.021232433963	-1.381535425614	2.167581937180
C	2.927714858437	-2.002579118400	3.042386095115
H	2.874687143799	-1.496393884395	4.016582787552
H	1.927104826638	-1.954510434253	2.610911143912
H	3.174046183964	-3.056932282110	3.228203007630
C	5.357359458922	-1.671709072462	2.857390489168

H	5.364515810194	-1.251417199019	3.872870860152
H	5.493988787908	-2.756116792488	2.959281633624
H	6.232027094641	-1.279125988200	2.330561546972
H	4.078484338072	-2.882952288144	0.494006609815
H	1.775997481471	-1.866436277199	0.533133355427
H	2.540500912905	-1.126755499726	-0.863777460359
H	2.563719124113	0.963221461095	0.210634450747
H	3.961410923199	0.731168883948	3.932616415773
H	4.058721009031	2.090776546658	2.769476858272
O	1.317147552365	0.921312659721	4.367624644541
C	-0.921458735517	-0.032908272839	2.206822536088
H	-0.637877414600	-0.123387255637	3.251785584181
C	-2.302394740349	-0.240625140979	1.862799303738
C	-3.223331945143	-0.611408114230	2.873986122605
C	-2.822862079078	-0.142259261684	0.546659998044
C	-4.554616721971	-0.878916950595	2.596242552079
H	-2.860684182953	-0.691255283891	3.898388260920
C	-4.159940679113	-0.413719304425	0.281549417704
H	-2.149381278162	0.151426298852	-0.252842348151
C	-5.044239548941	-0.788532505214	1.292174513750
H	-5.222402541626	-1.165203216449	3.408501857668
H	-4.520206149577	-0.327937455201	-0.743696698788
H	-6.088020690438	-1.001892248893	1.071951113882
C	-0.978920362038	-2.864368595673	0.386495298479
Br	0.262830997726	-4.351928482390	0.025254566468
H	-1.946929039289	-3.159287487099	-0.017666954003
H	-1.016684465576	-2.736473034231	1.467003883937
H	-0.582126523052	-1.972703294545	-0.104234253513

Table S104. Atomic coordinates and single point energies of the transition state for the top-face methylation of **8o**.



TS frequency: -530.418

G = -3990.623519

G_{SP} = -3991.639275

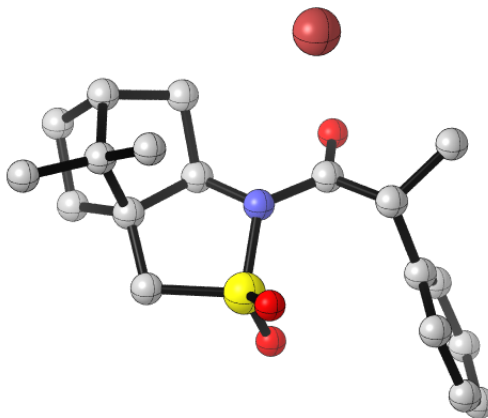
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Anion_protoR_MeBr: optimized structure // E(RM062X) = -3992.02189690 A.U. after 12 cycles

O	0.037911303818	-0.072482158899	-0.120286354712
C	0.029799716303	-0.163009684231	1.110578286622
N	1.326527469552	-0.147831758447	1.754529333328
S	1.553244975817	0.698385752766	3.209133162670
O	0.929452583946	2.028469823925	3.146692640071
C	3.352264439878	0.860259708441	3.043388583527
C	3.743264918278	0.070541620626	1.812542380051
C	2.505623934119	-0.054330040484	0.887038112360
C	2.805741905670	-1.325570935287	0.057197909223
C	4.248591145818	-1.666372143531	0.479725864436
C	5.164962988514	-0.532245409498	-0.036589203047
C	4.853368548138	0.654786986582	0.922006788911
H	4.502270173021	1.549992260847	0.397138676042
H	5.726718545022	0.943082850150	1.516819418897
H	4.941034612430	-0.288949117437	-1.081546413014
H	6.222011879621	-0.814977240761	0.010177312143
C	4.217947588812	-1.404934001554	2.006658613737
C	3.264582071915	-2.313163636908	2.784440063416

H	3.198228980050	-1.996234474399	3.833879943572
H	2.250308427146	-2.332810309136	2.384583953601
H	3.653518253820	-3.340068527004	2.772812268796
C	5.583942257324	-1.508758982564	2.690052281114
H	5.522768071305	-1.137991502452	3.722735326146
H	5.888529779118	-2.561901849999	2.741302423704
H	6.381251091688	-0.958449485829	2.182835000753
H	4.571444071522	-2.670552007801	0.183565094503
H	2.100991230228	-2.127368037023	0.303184461615
H	2.718818525111	-1.129425710150	-1.015786597051
H	2.405261725518	0.827601869705	0.242285363602
H	3.795566394652	0.500327378705	3.977753707340
H	3.530003812090	1.935222378322	2.936130262440
O	1.191633725033	-0.155252483080	4.349024957009
C	-1.070090530970	-0.441980560554	1.962479919191
H	-0.883416936442	-0.420023113688	3.034274258622
C	-2.459257225216	-0.292198028605	1.561911404715
C	-3.456824791613	-0.322459960451	2.562455778599
C	-2.897222144475	-0.176933656043	0.224068799800
C	-4.806998981651	-0.233049919415	2.251125161695
H	-3.150328477278	-0.413608199090	3.604414955829
C	-4.253676659179	-0.083688362246	-0.078536979409
H	-2.157477772441	-0.154887200272	-0.569936459938
C	-5.222037843877	-0.110853050840	0.923556301457
H	-5.543706249056	-0.257066087949	3.052885813492
H	-4.556858957805	0.009046312900	-1.120712636226
H	-6.279243882595	-0.039784463928	0.676919523121
C	-0.717689587658	-2.674789001011	1.732987363233
Br	-0.279344382962	-4.983223498240	1.476836188839
H	-1.659418653874	-2.835286385490	2.242952372077
H	0.182934825270	-2.538174542433	2.314948291642
H	-0.715507607772	-2.506947034324	0.663130198686

Table S105. Atomic coordinates and single point energies of the product ground state for the top-face methylation of **8o**.



G = -3990.698859

G_{SP} = -3991.714831

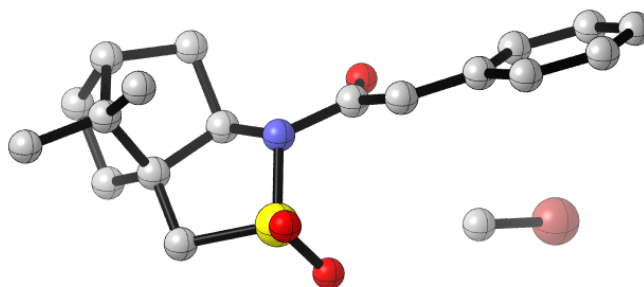
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Anion_protoR_MeBr_end: optimized structure // E(RM062X) = -3992.10177424 A.U.
after 12 cycles

O	0.110046990171	-2.720909518506	0.425886385152
C	-0.080954115164	-1.897155832070	1.292804000462
N	0.988312369939	-1.077923528505	1.695041781447
S	0.804780002469	0.570825773113	2.124378340865
O	0.241466775188	1.324157342402	0.998349834920
C	2.580363718113	0.925408005646	2.195270394149
C	3.301440330582	-0.348593321707	1.805622963989
C	2.311006608102	-1.317160343662	1.102002985778
C	2.907630003812	-2.715282586132	1.390163450079
C	4.262728743158	-2.363885960187	2.032345121926
C	5.129761856341	-1.661793586188	0.958647810018
C	4.496928618476	-0.241989872673	0.844605579129
H	4.166183225432	0.000873718878	-0.171423316335
H	5.190427885928	0.544052586429	1.161745816823
H	5.094711499837	-2.205763704649	0.007574852367
H	6.181586750282	-1.604420484678	1.258939607328
C	3.887373474548	-1.196416648632	2.976644198827
C	2.886479483198	-1.548347840493	4.076454634141
H	2.585485431681	-0.638323183811	4.617230109036
H	1.983592289265	-2.062905747311	3.737909763871
H	3.369925007950	-2.211149692978	4.806832352470
C	5.087242695785	-0.527477701205	3.653303702054
H	4.778590940080	0.406621802769	4.143826889616

H	5.476611544159	-1.189400951171	4.437336957623
H	5.915113121964	-0.293811732271	2.977566797829
H	4.754246844876	-3.215847236329	2.514926310350
H	2.257756708403	-3.282577061533	2.069215297937
H	3.020486872227	-3.290817715190	0.465633967983
H	2.258107040012	-1.106647738562	0.025337396618
H	2.797138908516	1.267285332986	3.212615168992
H	2.720547568642	1.747295733167	1.486831067157
O	0.144721726628	0.674836965685	3.427555861449
C	-1.421323698678	-1.714046105463	1.992649954317
H	-1.205538890995	-1.497815009876	3.044782572684
C	-2.202458426625	-0.556866068649	1.389773701037
C	-2.794652739288	0.402781868245	2.211563893976
C	-2.397600702040	-0.477672508926	0.007848793650
C	-3.565401631844	1.426200172243	1.663898574923
H	-2.633458120948	0.353686339920	3.287003348006
C	-3.161116613208	0.547340446380	-0.542268918738
H	-1.939911259623	-1.222099384730	-0.643971579172
C	-3.748340749252	1.503535496418	0.285305228220
H	-4.019078953442	2.169164446524	2.317202815552
H	-3.298345037762	0.600278967164	-1.620654058883
H	-4.345491112618	2.305745664494	-0.143806060233
C	-2.235505467916	-3.005073808426	1.893320204677
Br	0.452191151990	-4.329242529131	3.968102622863
H	-3.188796430785	-2.866750327711	2.417925980749
H	-1.675791244369	-3.824267840607	2.357807743085
H	-2.446036759696	-3.245815624790	0.845231622989

Table S106. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of **8o**.



G = -3990.644584

G_{SP} = -3991.660479

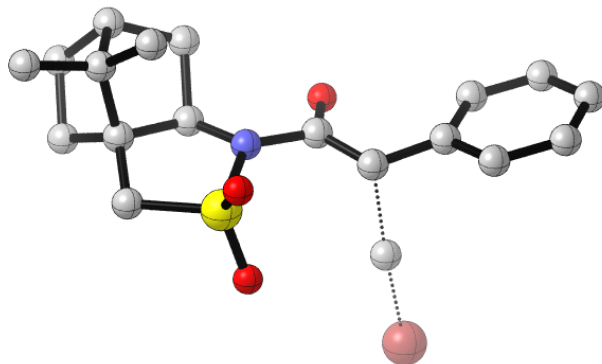
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QST_start: optimized structure // E(RM062X) = -3992.04247242 A.U. after 13 cycles

O	0.286976970385	0.150930944896	0.154875351317
C	-0.069030798246	-0.222552858219	1.289625868352
N	1.029519504118	-0.514429990951	2.233382552953
S	1.058441524495	0.326637192316	3.696273260977
O	0.828160205447	1.769871475757	3.496348573533
C	2.822093052289	0.044462897635	4.031304515710
C	3.352095702333	-0.745206108113	2.851601997491
C	2.377691522613	-0.562691305445	1.662679092955
C	2.647738499029	-1.805691939157	0.783076574051
C	3.832722336579	-2.479367863965	1.504363965988
C	5.057552437527	-1.549561448429	1.347646992523
C	4.739775944279	-0.364833600433	2.306633584804
H	4.702656622271	0.602503452286	1.793424509195
H	5.475975587230	-0.280037654645	3.113310931360
H	5.174713684743	-1.221416870921	0.308497684864
H	5.985805308045	-2.055815449492	1.633802919614
C	3.462012764476	-2.296783208922	2.998621722739
C	2.181492718685	-3.019286009125	3.425535138616
H	1.865710247036	-2.685131756904	4.423799137085
H	1.337411474656	-2.863651275916	2.751953460086
H	2.382230569386	-4.097328311401	3.489118888058
C	4.559156714581	-2.725632691027	3.976606191842

H	4.281269786299	-2.450659380352	5.003707619133
H	4.669127827239	-3.817575425939	3.952213216558
H	5.540386345516	-2.289809424210	3.768575755381
H	4.015985739294	-3.513263406524	1.190341819775
H	1.761856403674	-2.447650214110	0.744028277411
H	2.894140357413	-1.521139829688	-0.244658378307
H	2.581805582541	0.366587089788	1.115980491766
H	2.891252776506	-0.472827487005	4.993813097657
H	3.262887931607	1.042953917472	4.113445923153
O	0.214136689291	-0.345117100392	4.695122538417
C	-1.341277922875	-0.423650930418	1.814275434343
C	-2.573714852469	-0.095241547034	1.140070413915
C	-2.649262209499	0.460654011846	-0.161737398887
C	-3.806194617036	-0.306738002835	1.807774511632
C	-3.874738045103	0.781905669026	-0.736775998988
H	-1.725762909723	0.636667684677	-0.705159173665
C	-5.023405191411	0.012674425417	1.222457485808
H	-3.788350043161	-0.727722104186	2.813125582438
C	-5.075217468745	0.563910975903	-0.060536801518
H	-3.889176825661	1.217361819018	-1.735566184732
H	-5.944929001748	-0.166615719595	1.775506567617
H	-6.028468406733	0.818457846509	-0.519050338070
H	-1.411471810351	-0.827694944428	2.821251225145
C	-0.997158857427	3.057556342579	1.297399157352
Br	-1.558543343680	4.367697125653	-0.058443982934
H	-0.351830185561	3.580671214383	2.001195643348
H	-0.469186704857	2.261343141983	0.772182401653
H	-1.903904601196	2.690376794802	1.777464316078

Table S107. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of **8o**.



TS frequency: -537.0338

G = -3990.621042

G_{SP} = -3991.636467

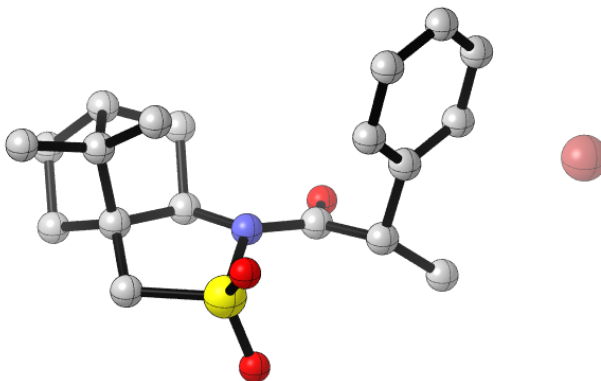
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Anion_protoS_MeBr: optimized structure // E(RM062X) = -3992.01845535 A.U. after 12 cycles

O	0.288658903735	-0.029760740883	0.101899476678
C	-0.009086446085	0.044976052525	1.297725380203
N	1.069520759354	-0.218166245990	2.214355022627
S	1.069598382989	0.249227938231	3.844402653470
O	0.760483329233	1.680413174820	3.988205989752
C	2.843718474496	-0.006855832921	4.098248208374
C	3.352559342107	-0.730740216587	2.872696535888
C	2.422860561529	-0.401007674171	1.673939700929
C	2.620129903028	-1.615355892574	0.732985429874
C	3.774113753618	-2.379427768708	1.407786528572
C	5.037962360553	-1.491492496544	1.330228906523
C	4.771465729552	-0.383584815556	2.390883151361
H	4.806125566987	0.628719012298	1.973608066820
H	5.489303508960	-0.423958081408	3.217190683226
H	5.166438402878	-1.076466782384	0.323909545641
H	5.945763827798	-2.057612453194	1.564501664211
C	3.387653705861	-2.292260667530	2.904505579816
C	2.067519937434	-2.983639953044	3.254791994124
H	1.830886619155	-2.842737404266	4.317290615265

H	1.208355824492	-2.627408441348	2.682779748169
H	2.173023829561	-4.062987622493	3.080078116518
C	4.445829604558	-2.847308724281	3.861239076433
H	4.210327936793	-2.566003777480	4.897003429131
H	4.442495886511	-3.943910597167	3.814671641414
H	5.463950582231	-2.511375454880	3.645526336759
H	3.918650978192	-3.394592433910	1.021340550000
H	1.705940877559	-2.211390608646	0.673816266478
H	2.863392006938	-1.289347693291	-0.282580757838
H	2.732525187095	0.531804319639	1.185204395760
H	2.956988606361	-0.557119628090	5.038337655321
H	3.261167729260	1.000074088732	4.201967137865
O	0.260317304607	-0.680003015598	4.642941172470
C	-1.272971277336	0.396099304840	1.849770787579
C	-2.522672152501	0.233660452734	1.121972373165
C	-2.624874622845	0.113150832266	-0.281729285728
C	-3.734147011900	0.257458899293	1.850105158694
C	-3.866879507984	0.005333406929	-0.903363927952
H	-1.715992806441	0.097546260006	-0.874654501334
C	-4.968030333171	0.154417142908	1.221425613456
H	-3.690980747140	0.355681181535	2.934783048390
C	-5.049547804036	0.024693454819	-0.166419231130
H	-3.907081297620	-0.091218442964	-1.987727176917
H	-5.876695343580	0.174009984108	1.821584745231
H	-6.015116195395	-0.056410752223	-0.661031169184
H	-1.372277232567	0.335761666376	2.931977863557
C	-1.017682357150	2.631338920268	1.497226223624
Br	-0.833462599250	4.952062627555	1.020867238675
H	-0.218627813216	2.670375284442	2.225608383027
H	-0.818506304807	2.358119756181	0.467997514110
H	-2.041938536297	2.735320619790	1.830612576498

Table S108. Atomic coordinates and single point energies of the product ground state for the bottom-face methylation of **8o**.



G = -3990.696607

G_{SP} = -3991.716230

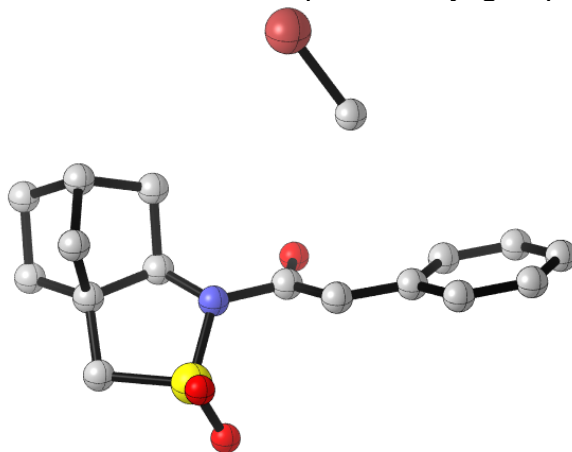
50

QST_end: optimized structure // E(RM062X) = -3992.10266469 A.U. after 13 cycles

O	0.242304935887	2.041616251672	1.177922019464
C	0.333044689104	1.375528190817	2.184867249937
N	1.484275934193	0.606491386795	2.389467877509
S	2.107248228546	0.283774514155	3.961227390629
O	2.108693722408	1.525269806962	4.741761675813
C	3.774339396799	-0.125671511955	3.386866948149
C	3.699748050066	-0.235187789582	1.878685697956
C	2.544158158789	0.660565125363	1.371293892166
C	2.173250753921	0.035639594744	0.005752865741
C	3.274722627455	-1.026338955431	-0.179615345204
C	4.618968311249	-0.281927887323	-0.347924079834
C	4.938947806439	0.222806146559	1.089365370082
H	5.057477194586	1.310243521145	1.147377504276
H	5.850974042925	-0.229881502863	1.492104308970
H	4.527089886274	0.542568627271	-1.063829980152
H	5.404215464011	-0.948130419249	-0.719744032402
C	3.395101628470	-1.630058606158	1.242301067222
C	2.125107400220	-2.333170230798	1.729119177791
H	2.247273797044	-2.680494897825	2.763362640826
H	1.226418619717	-1.713435965667	1.694029753185
H	1.948975106236	-3.218272014204	1.103227443965
C	4.545384792363	-2.625819407011	1.407999978645

H	4.685702851759	-2.873764585551	2.469097882425
H	4.298151151524	-3.559314730414	0.886752698493
H	5.502899914041	-2.272184174540	1.015904619007
H	3.060902344305	-1.747996463645	-0.975226265164
H	1.172000372526	-0.405598457213	0.038618288064
H	2.176753538539	0.788335694912	-0.788016662262
H	2.866813557265	1.704019449412	1.267989030852
H	4.067856972116	-1.046245221817	3.902096713889
H	4.400496467886	0.708608948885	3.720762930299
O	1.432384636876	-0.879071545161	4.543298994487
C	-0.805270120954	1.218941358201	3.185242931560
C	-1.706372584359	0.127106066971	2.614996598030
C	-2.814038667420	0.446410780374	1.824895890891
C	-1.399791876915	-1.216807098070	2.857640909057
C	-3.601937578177	-0.572470887970	1.290620397836
H	-3.096303353780	1.483342839601	1.623377943839
C	-2.187973657761	-2.229728300880	2.316081436097
H	-0.539665922303	-1.465729960884	3.479245971002
C	-3.293055876930	-1.909811437937	1.528653215812
H	-4.466530821836	-0.305467532667	0.685026634003
H	-1.940356906238	-3.270825076227	2.515447133078
H	-3.912367312288	-2.699868096065	1.107982254207
H	-0.409559529457	0.851976099999	4.138849572712
C	-1.504670675936	2.556099543316	3.404383570802
Br	-4.518655538460	3.657810024398	1.061404163946
H	-0.809965654012	3.268342908415	3.865892534633
H	-1.882349205050	2.981890402169	2.469023972175
H	-2.359274403630	2.419796942678	4.076051757593

Table S109. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of **8o** without camphor methyl groups.



G = -3912.127319

G_{SP} = -3913.099698

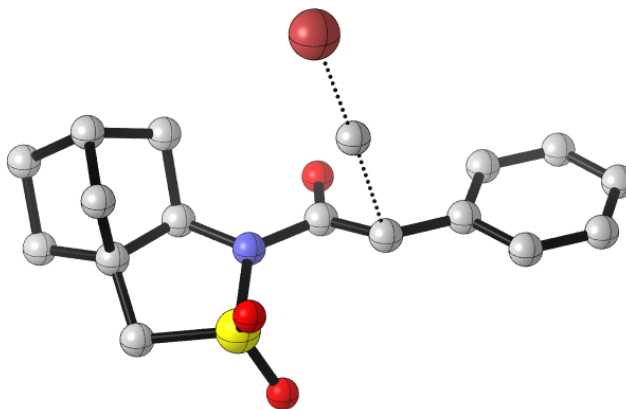
44

QST_start: optimized structure // E(RM062X) = -3913.42570570 A.U. after 13 cycles

O	-0.027977987410	0.016672457929	0.003410914588
C	0.008263274873	-0.063624395077	1.247636656360
N	1.356879538829	-0.075048210522	1.830124904558
S	1.768971279062	0.994982297774	3.061023331365
O	1.276982852268	2.358011788699	2.800743735190
C	3.554746329167	0.911310010560	2.756846784810
C	3.736386085587	-0.251840426957	1.807772835172
C	2.476528502324	-0.323287145292	0.918306518142
C	2.484673189418	-1.778944359723	0.396014422702
C	3.775924902534	-2.355868742814	1.007324149741
C	4.987240980848	-1.685531612137	0.325109120892
C	4.966028616668	-0.234779319686	0.889203884842
H	4.873124123523	0.532216105609	0.111651538010
H	5.870221871775	-0.016393071593	1.470127849088
H	4.904603975907	-1.712647938887	-0.767599615352
H	5.917227354813	-2.197094043216	0.598942587429
C	3.789693820136	-1.678125873938	2.386275091901
H	3.814876013065	-3.449145893940	1.002826812558
H	1.597870026608	-2.310227878211	0.762319680418
H	2.473206956782	-1.826062343627	-0.698302630058
H	2.490547175335	0.418714312228	0.110103002480
H	4.051646200420	0.803885860869	3.725626868502
H	3.822202453908	1.868616197234	2.296635511571

O	1.436670541015	0.411798031677	4.370673218597
C	-1.022539791375	-0.217559073774	2.168879380406
H	-0.748525573980	-0.372792186206	3.210000717553
C	-2.424089433476	-0.259732667189	1.836438081376
C	-3.372312636117	-0.515520736214	2.859501973636
C	-2.943299066034	-0.085899524499	0.527767595824
C	-4.731953568576	-0.605471484464	2.597199682810
H	-3.013240324602	-0.649063018491	3.879959441893
C	-4.309261206490	-0.177161063967	0.276546120290
H	-2.249045113902	0.118032729841	-0.282036380370
C	-5.221550103918	-0.440343506715	1.298681407697
H	-5.420912541909	-0.807377015666	3.416786832027
H	-4.667406733477	-0.037752473511	-0.743323352580
H	-6.287144568252	-0.512115727757	1.091463101649
C	-1.375644807832	-2.986917521902	0.062411455616
Br	-0.281490563238	-4.533741912285	-0.467323196857
H	-2.322000854333	-3.076953317273	-0.470866149220
H	-1.517979606823	-3.051945497243	1.140706432197
H	-0.828630911649	-2.085118581748	-0.220002454977
H	2.919797224968	-1.925541328231	3.005842576751
H	4.711173765557	-1.858931745939	2.955008286103

Table S110. Atomic coordinates and single point energies of the transition state for the top-face methylation of **8o** without camphor methyl groups.



TS frequency: -531.6884

$G = -3912.107499$

$G_{SP} = -3913.079241$

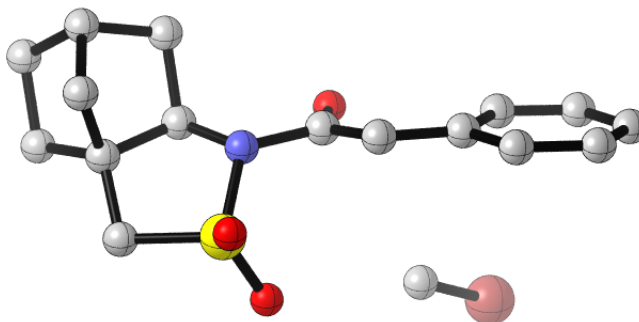
44

Anion_protoR_MeBr: optimized structure // $E(\text{RM062X}) = -3913.40599208$ A.U. after 12 cycles

O	-0.033758712658	0.237728023842	-0.067462635965
C	-0.005244089885	0.221904513711	1.167447154052
N	1.304506347543	0.267261252051	1.752413015822
S	1.634442551188	0.804575103281	3.318703516330
O	0.960763153024	2.079034034871	3.598779789520
C	3.395149780697	1.043043737894	3.013794238790
C	3.696537024577	0.120626211106	1.856398974330
C	2.488814968573	0.168485482720	0.890452640204
C	2.598266066259	-1.171117929732	0.120848552500
C	3.914027033750	-1.767616134339	0.652771701128
C	5.092976092782	-0.893443365829	0.175019869650
C	4.963038708582	0.397361228651	1.035661565027
H	4.863707415733	1.310953143016	0.438612512129
H	5.823615816261	0.522618528974	1.703477049144
H	5.035911891901	-0.687434227770	-0.900130775665
H	6.049101133551	-1.394149206913	0.364803784064
C	3.825925493296	-1.389189544262	2.136981846145
H	4.031997912206	-2.832103259069	0.431733166556
H	1.749352956943	-1.817270594002	0.371376757794

H	2.598290840174	-1.020018454511	-0.963436934482
H	2.529376759906	1.039938900229	0.225626688538
H	3.924213337619	0.814557915182	3.944077108793
H	3.517912397615	2.099773447581	2.750623037888
O	1.420323181336	-0.285697561432	4.283235098317
C	-1.083449439359	0.004964753806	2.067137749259
H	-0.889702149739	0.151138057722	3.127659541461
C	-2.481951576973	0.068442032097	1.680105473504
C	-3.463327650404	0.101945557222	2.697299756191
C	-2.945490462214	0.030933490856	0.345881880751
C	-4.820499361719	0.106208571755	2.404141423358
H	-3.138315940197	0.127322724507	3.737401936320
C	-4.309023676838	0.039107596592	0.061529411252
H	-2.219437237870	0.001948910837	-0.460300788127
C	-5.260620020279	0.076412716746	1.079343237443
H	-5.543249960436	0.134740084560	3.218407034963
H	-4.631158062335	0.012935517337	-0.978797940390
H	-6.323483926161	0.080419027021	0.847233736030
C	-0.640922915197	-2.228703286007	2.115943147472
Br	-0.111108112725	-4.530126264300	2.143144087329
H	-1.557015805273	-2.358036536298	2.679503468309
H	0.273198037229	-1.975292133681	2.637416023849
H	-0.690463748658	-2.206477907543	1.034404255712
H	2.954789765509	-1.819900804579	2.645576886541
H	4.733288483569	-1.621985074442	2.708985020329

Table S111. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of **8o** without camphor methyl groups.



G = -3912.125946

G_{SP} = -3913.097800

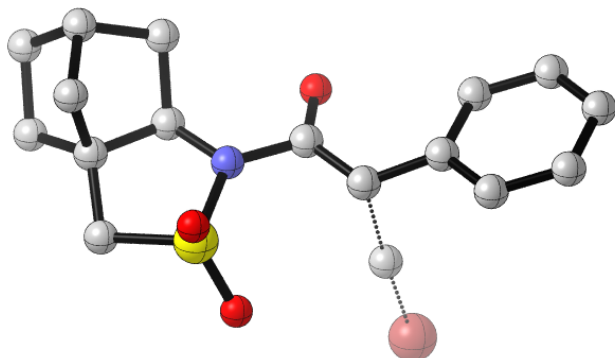
44

QST_start: optimized structure // E(RM062X) = -3913.42548585 A.U. after 12 cycles

O	0.013595442940	0.074824102754	-0.100737131102
C	0.029705999435	0.025437537324	1.144516821505
N	1.369048202369	0.039219828560	1.758391960854
S	1.720263351905	1.198777304391	2.933260565348
O	1.158257404095	2.518690799469	2.596055939911
C	3.508513902915	1.199968718298	2.641510719756
C	3.759694584717	-0.005288395234	1.764914791050
C	2.514154674886	-0.195933531324	0.872800788222
C	2.612246549844	-1.674583028172	0.430076822446
C	3.922601146523	-2.146255235028	1.090507832162
C	5.106402946609	-1.453641914885	0.383441728340
C	4.996589994556	0.025116035222	0.856328092318
H	4.869062624431	0.736390777932	0.032131088948
H	5.880242273504	0.330256137915	1.429636063852
H	5.043498694707	-1.552288504028	-0.706444916241
H	6.058017987096	-1.895347840564	0.700963386601
C	3.881924723422	-1.389701969854	2.427193476481
H	4.019684237323	-3.234129363248	1.151448573534
H	1.748526769146	-2.230273609436	0.812663227272
H	2.626074445762	-1.776924912776	-0.660199089063
H	2.494575216248	0.500747964656	0.025522656012
H	4.004263091178	1.179062361733	3.616495127528

H	3.723990500721	2.141372995162	2.124764042936
O	1.413231892739	0.670553034061	4.271824062295
C	-1.016345647421	-0.049461987846	2.058089768811
C	-2.414226862653	0.078112896649	1.728468680175
C	-2.915206067559	0.233471040175	0.411470022629
C	-3.372953216144	0.088316706007	2.772776685319
C	-4.274899621625	0.410209555203	0.175698000318
H	-2.211317358787	0.226054754139	-0.415593491234
C	-4.728023154261	0.257809923945	2.525373417374
H	-3.025613975415	-0.026941348320	3.799618204618
C	-5.199164927743	0.425334137527	1.220486407048
H	-4.617991900385	0.542081028422	-0.850150292716
H	-5.426625867542	0.264777049968	3.361497038183
H	-6.260302221154	0.564879340334	1.025024023040
H	-0.758343163046	-0.158091540598	3.109409219578
C	-1.289316913126	3.139009111415	0.706640796855
Br	-2.318901466189	4.088801726038	-0.675486137893
H	-0.521835862936	3.824935266107	1.061486914840
H	-0.860947235011	2.254592191666	0.234458125619
H	-1.990476029320	2.872353218180	1.496548305277
H	3.018070649284	-1.645015927160	3.052099173539
H	4.804237653388	-1.487357091016	3.014481267689

Table S112. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of **8o** without camphor methyl groups.



TS frequency: -535.52

G = -3912.103356

G_{SP} = -3913.075059

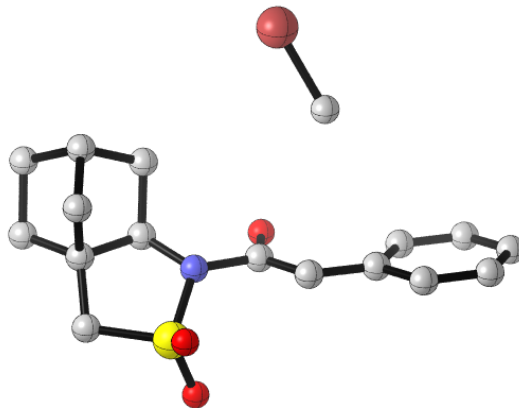
44

AnionSansMe_protoS_MeBr: optimized structure // E(RM062X) = -3913.40296997 A.U.
after 13 cycles

O	-0.014401057554	0.092049502390	-0.036722375366
C	0.000669556679	0.060662510143	1.198013691072
N	1.306657023609	0.132291145712	1.789614812964
S	1.645442027450	0.369971895761	3.430657476291
O	0.888884381264	1.505111318012	3.976984347331
C	3.364401281298	0.826568929175	3.149460165484
C	3.717507807563	0.145783362023	1.850204908049
C	2.485996844913	0.239852774535	0.916359120448
C	2.689754413069	-0.951267216775	-0.052119194138
C	4.074487457069	-1.489710908086	0.348280310932
C	5.148006060302	-0.435315021731	0.002041273971
C	4.930260861713	0.673504673157	1.072799028847
H	4.734581370801	1.662340787022	0.643252903915
H	5.795003325689	0.760620418154	1.741363742174
H	5.030093202066	-0.058067003190	-1.020458004996
H	6.153782668537	-0.863052727507	0.081710213275
C	3.996835890453	-1.369372372366	1.875399540823
H	4.288964108525	-2.485886491085	-0.049159907637
H	1.912120409915	-1.702619740213	0.117579011174

H	2.629385870553	-0.636986625448	-1.098682903428
H	2.449651174185	1.201858285960	0.390425398108
H	3.937967050580	0.498019739571	4.021603647383
H	3.376960427758	1.919412151667	3.069392873298
O	1.553962141518	-0.899897777022	4.164441898436
C	-1.120315313687	0.025272331542	2.072682536877
C	-2.436435198184	-0.431895410908	1.656533624692
C	-2.861213566997	-0.549533607737	0.314154918755
C	-3.392484000160	-0.726462940804	2.655860702141
C	-4.158140416633	-0.954114947770	0.005840024765
H	-2.156683743148	-0.326180443336	-0.480465958671
C	-4.684316596862	-1.124554309957	2.338925543035
H	-3.099407284789	-0.639503151151	3.702119237647
C	-5.083367661400	-1.245947413761	1.006329931560
H	-4.449117708210	-1.038149584599	-1.040626533159
H	-5.387671187995	-1.343641125683	3.141139395758
H	-6.094917970310	-1.558011578872	0.755497533170
H	-0.920607009633	-0.077296886562	3.137129643974
C	-1.481913646100	2.269085351228	1.929561645648
Br	-1.938528613595	4.584928025727	1.707566314048
H	-0.547743678742	2.453341236269	2.443218777925
H	-1.506200893944	2.114067411057	0.857766809038
H	-2.377537569875	2.097631825620	2.512309829362
H	3.183757544054	-1.955978246226	2.319262448505
H	4.938254436673	-1.600912263156	2.390126186762

Table S113. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of **8o** without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.



G = -3912.127001

G_{SP} = -3913.099463

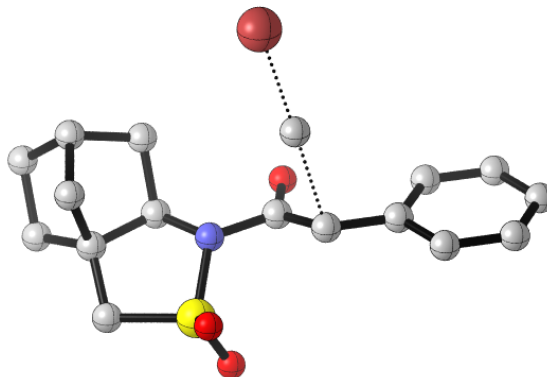
44

SansMe_Anc_protoR_MeBr_Start: optimized structure // E(RM062X) = -3913.42579677 A.U. after 13 cycles

O	-0.006783154606	0.119952820398	0.005598351751
C	0.005044061315	0.043520215709	1.250704127077
N	1.340059544471	0.046693634695	1.855697259725
S	1.717115403572	1.027917042407	3.167352388486
O	1.176800254560	2.388650991922	3.018512753324
C	3.502068806393	1.022816899198	2.859711290295
C	3.722398969196	-0.120180528743	1.895924883907
C	2.486081371971	-0.186925190423	0.973534667123
C	2.520042226780	-1.634989202558	0.430278181143
C	3.803275628780	-2.209087127212	1.060391325504
C	5.023041092101	-1.514384050928	0.418981129012
C	4.974315085269	-0.074607153865	1.009231450166
H	4.893975131912	0.705893316148	0.243877081154
H	5.861466496245	0.140587037158	1.616960339643
H	4.965696151157	-1.521754432497	-0.675645354228
H	5.951644434789	-2.021932248054	0.704678533778
C	3.776403621655	-1.556136462452	2.450809349345
H	3.853878771068	-3.301676185086	1.037742455290
H	1.631782719939	-2.179782777042	0.771767136783
H	2.530446030150	-1.666960567943	-0.664549008258

H	2.517656060904	0.566200638597	0.176377355725
H	4.005228316264	0.924104350832	3.826274976156
H	3.730307196591	1.994769328257	2.408532414662
O	1.410806797414	0.333213757888	4.428708359815
C	-1.045402480803	-0.122263543377	2.147918567287
H	-0.795483285622	-0.277442364532	3.195378024547
C	-2.436828903031	-0.190343465107	1.780876295825
C	-3.405889811431	-0.462078044053	2.780386787298
C	-2.926923801712	-0.025124297018	0.459536329435
C	-4.757213290939	-0.572949112671	2.485104421074
H	-3.069990096127	-0.589484400084	3.809507285217
C	-4.284675670198	-0.137885219282	0.175414403051
H	-2.216624034378	0.189185131276	-0.333317032051
C	-5.217673574376	-0.415254655620	1.175062732979
H	-5.462576906659	-0.785584122623	3.287868214213
H	-4.619851706349	-0.004792530190	-0.853069152115
H	-6.276669961957	-0.503506726101	0.941940303018
C	-1.205509773310	-2.972366841702	0.218310783791
Br	-0.128722714407	-4.449460747161	-0.508343874606
H	-2.220384514383	-3.110890127080	-0.154950936875
H	-1.165873788556	-3.055969264219	1.303802432165
H	-0.761863309299	-2.039524248625	-0.134908786087
H	4.685337742185	-1.737148887980	3.039310794233
H	2.894417148554	-1.824002611304	3.044395040067

Table S114. Atomic coordinates and single point energies of the transition state for the top-face methylation of **8o** without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.



TS frequency: -530.6304

G = -3912.105659

G_{SP} = -3913.077833

44

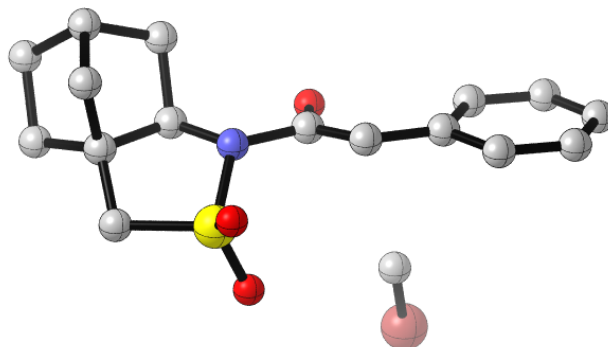
SansMe_Anc_protoR_MeBr_TS: optimized structure // E(RM062X) = -3913.40526670

A.U. after 12 cycles

O	-0.023230405459	0.147394718963	-0.024574285000
C	0.001255542574	0.104337376701	1.207987573605
N	1.316365660818	0.125968308634	1.819209301320
S	1.608510334896	1.093671947209	3.182388744195
O	1.104137066847	2.459596605672	2.973294328239
C	3.412092778652	1.080237628585	3.008556870946
C	3.706144488798	0.132212640536	1.865864002689
C	2.480571859511	0.109424263347	0.923577432650
C	2.635208133688	-1.231948934353	0.168012928076
C	3.966156730828	-1.783029844888	0.711848696554
C	5.119154920968	-0.893415519658	0.201167467104
C	4.949256308166	0.423476666925	1.013005833546
H	4.803304066408	1.308125810934	0.382571416779
H	5.814405094804	0.610978473005	1.660128270837
H	5.057562382897	-0.730371614805	-0.880990731047
H	6.089091086785	-1.358689569498	0.410527888817
C	3.883059082338	-1.362281572684	2.185211287438
H	4.109218213886	-2.850025637875	0.519640688084

H	1.802169738267	-1.900120849645	0.413939092291
H	2.640591525111	-1.088620372598	-0.917364059868
H	2.456519453178	0.974908736044	0.248811052092
H	3.834653042350	0.780527478368	3.972117997695
H	3.684985084297	2.115749342474	2.780673684480
O	1.168679372022	0.403725181705	4.402327105233
C	-1.073590881340	-0.129679486560	2.103374153027
H	-0.853193990202	-0.065384745577	3.166634458045
C	-2.474113774763	0.002948317900	1.735770485781
C	-3.444194407908	0.006590849930	2.763125504073
C	-2.947377353130	0.068769030730	0.406959437713
C	-4.802550194417	0.080784205400	2.484627266298
H	-3.109845237619	-0.045950258822	3.799167776220
C	-4.311671007986	0.147403765596	0.137063706920
H	-2.228876867524	0.063586373900	-0.406652663378
C	-5.252756829242	0.153940693029	1.165028400231
H	-5.517826292732	0.083495102446	3.305896257988
H	-4.642637441886	0.201463688761	-0.899340186618
H	-6.316417299534	0.212845887840	0.944266907055
C	-0.724663285892	-2.368132587052	1.969399750298
Br	-0.311770397111	-4.695121310867	1.799344211742
H	-1.598978206863	-2.500938537016	2.594529285889
H	0.240547061522	-2.203265423434	2.429040658962
H	-0.849539841629	-2.266783824403	0.898441057885
H	4.803005431602	-1.555031563964	2.752028641802
H	3.027893554931	-1.797553161478	2.717185365474

Table S115. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of **8o** without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.



G = -3912.12762

G_{SP} = -3913.099632

44

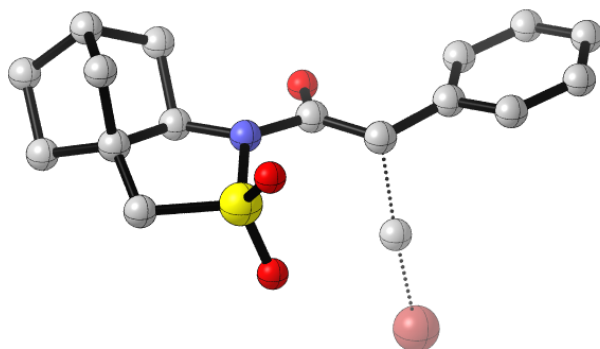
SansMe_Anc_botS_MeBr_Start: optimized structure // E(RM062X) = -3913.42568152

A.U. after 13 cycles

O	-0.016220647593	0.251501150617	0.038239628735
C	0.027440121309	-0.136375801329	1.221504333411
N	1.368294480652	-0.112268693846	1.831608925264
S	1.598435401604	0.570648222489	3.356880229549
O	0.906724170278	1.865178712718	3.496820398852
C	3.374880676958	0.863153498111	3.148615829096
C	3.743922568206	0.166867102672	1.858550965001
C	2.499407375175	0.177936450523	0.942868579712
C	2.777922182187	-0.972678653157	-0.052293268998
C	4.171183055493	-1.471536333644	0.375996102164
C	5.213025151183	-0.387931627419	0.027284177163
C	4.924657477744	0.738725574634	1.061094005271
H	4.666437550495	1.698168497385	0.598226231032
H	5.782687187764	0.905572670585	1.723419294869
H	5.110382727929	-0.043980759361	-1.008447276486
H	6.230852825879	-0.776688797895	0.147077938405
C	4.085339645502	-1.333258782330	1.903245671180
H	4.421338064816	-2.464661646738	-0.008353537813
H	2.019816520162	-1.754424172975	0.067218002964
H	2.747859570765	-0.629431687582	-1.091686553230

H	2.357606945180	1.143772499936	0.441356817079
H	3.879981169330	0.482987920388	4.041465690396
H	3.485416636082	1.950693850099	3.084168685840
O	1.343596209692	-0.428298383884	4.406011814807
C	-0.988391629574	-0.607003921383	2.049086694500
C	-2.383250021120	-0.660174766681	1.690058160454
C	-2.891972104264	-0.356527589109	0.400884043131
C	-3.338134387212	-1.028417454894	2.671452429670
C	-4.257077789844	-0.403382712728	0.135986396334
H	-2.190314904647	-0.081058976479	-0.380653720499
C	-4.697453018195	-1.074149928738	2.395139398739
H	-2.986609172437	-1.271650935222	3.674210411068
C	-5.178753410011	-0.757575083543	1.121960778743
H	-4.607274354053	-0.157528726047	-0.866378116602
H	-5.392909946651	-1.357619617508	3.184567454329
H	-6.244277604482	-0.789762870808	0.904665547348
H	-0.716974847350	-0.939545763023	3.048579274810
C	-1.783550046195	2.596118551025	1.714948785113
Br	-2.120013713679	4.455015393514	1.154913279085
H	-1.041021920916	2.627818157425	2.511804581738
H	-1.404531323797	2.062886728030	0.842748212734
H	-2.738019205320	2.193293130605	2.053259709601
H	3.293750778946	-1.942525809959	2.355495537948
H	5.036591633062	-1.524681692267	2.416674665863

Table S116. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of **8o** without camphor methyl groups anchoring the relative angle of the bridgehead and the sultam ring.



TS frequency: -534.2013

G = -3912.102894

G_{SP} = -3913.074483

44

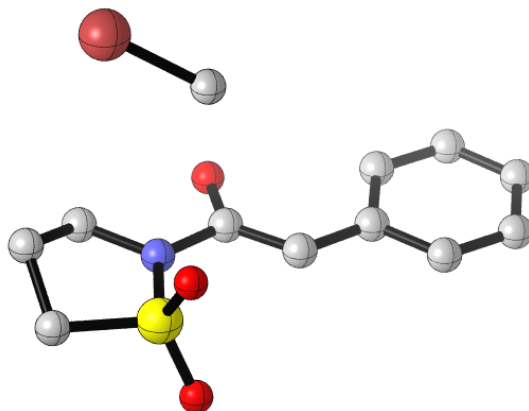
SansMe_Anc_botS_MeBr_TS: optimized structure // E(RM062X) = -3913.40144463

A.U. after 12 cycles

O	-0.000789772425	0.096534448496	-0.009351610650
C	0.010968657367	0.049387037073	1.223513804208
N	1.323177318292	0.039620804702	1.825513251416
S	1.622034543697	0.499099348641	3.431743465209
O	1.043280008169	1.820754048774	3.723179085449
C	3.409169018136	0.678265760300	3.225488433747
C	3.729195869942	0.079882400494	1.876318474969
C	2.493684221520	0.237797366167	0.956194529963
C	2.695171216668	-0.883761696701	-0.092859585601
C	4.072496265928	-1.461401176693	0.274245629342
C	5.157373730348	-0.399507325382	-0.005455591422
C	4.942306059721	0.647099573521	1.125820044632
H	4.747078741439	1.658971747698	0.753201513661
H	5.808318614856	0.696332619700	1.796660517467
H	5.048336591108	0.036306878942	-1.005329022187
H	6.158773285288	-0.840482633953	0.055071683318
C	3.994834572104	-1.432549775089	1.805231252969
H	4.275661825851	-2.433454887601	-0.184065622391

H	1.910397250463	-1.637814995486	0.018314146872
H	2.642756940962	-0.495103277840	-1.114517622802
H	2.448900386179	1.234891761816	0.498624355701
H	3.889730614022	0.182162072993	4.074083120902
H	3.589397493657	1.757488213015	3.264376061491
O	1.262434816126	-0.585579315160	4.353564983106
C	-1.113997818437	0.042743808835	2.094552519588
C	-2.427358848869	-0.429321704803	1.680215572797
C	-2.848262973192	-0.560416790004	0.338342187785
C	-3.381472739891	-0.725552887416	2.680146593570
C	-4.140379948533	-0.980570928113	0.030451127775
H	-2.145104217276	-0.335049241681	-0.457070327482
C	-4.668942773618	-1.138580950889	2.363918195880
H	-3.090953003575	-0.628036865106	3.726154903715
C	-5.064271534426	-1.273795789048	1.031640060772
H	-4.428667632272	-1.074933622085	-1.015843863585
H	-5.371582882697	-1.358633376698	3.166451370313
H	-6.072384849598	-1.597272120432	0.781436094377
H	-0.912378169291	-0.069221660266	3.158239462167
C	-1.532061074370	2.265890288093	1.869743565839
Br	-2.082036312539	4.555665939587	1.535226830708
H	-0.604395177140	2.514157842320	2.368184827722
H	-1.553565219598	2.063006308177	0.805822128887
H	-2.421114917915	2.095250573794	2.462661882920
H	3.173819909069	-2.036298289249	2.212156382578
H	4.932806133166	-1.705953652663	2.305379774546

Table S117. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of N-phenylacetyl γ -sultam enolate.



G = -3718.188387

G_{SP} = -3719.052814

33

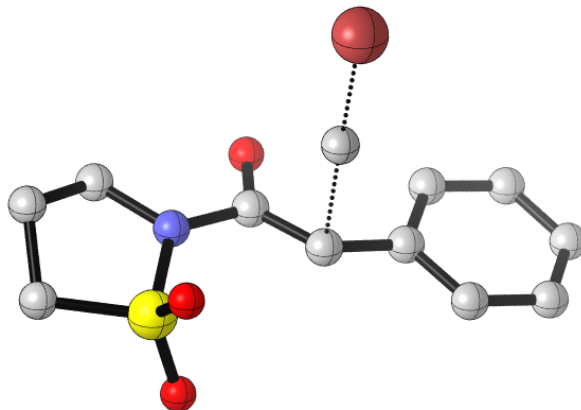
PhAcBurylSultam_TopFace_Start: optimized structure // E(RM062X) = -3719.28218446

A.U. after 14 cycles

O	0.004030539586	-0.008289662646	0.008123629510
C	0.003271596345	0.014360511451	1.254893922003
N	1.336484450605	0.023112190421	1.837991170809
S	1.707076809755	0.017079224444	3.470383563351
O	1.159105770759	1.190807784547	4.164106570525
C	3.471376544273	0.182516085854	3.182761030833
C	3.669489249702	-0.531947998879	1.857978970783
C	2.513780418625	-0.083628441102	0.964980337939
H	2.722012534302	0.889299323352	0.500105404087
H	3.989295603989	-0.255012699590	4.040399864014
H	3.674916131028	1.257215328535	3.121942390511
O	1.419803530216	-1.297178429399	4.074319521518
C	-1.079094810239	-0.013560151580	2.135810193659
H	4.637713881138	-0.283675128433	1.413861739471
H	2.304022922956	-0.806909101353	0.172857591194
H	3.626363666349	-1.617415193542	2.007767852057
H	-0.891410483274	0.025576166356	3.205482311932
C	0.553863857723	-3.093322904238	1.255225701527
H	0.237363070679	-2.360143152874	0.512819484948
H	0.772712271165	-2.634551383132	2.220410441024
Br	2.231421242441	-3.882005699002	0.597555920434

H	-0.161188088782	-3.911033335901	1.347912725438
C	-2.459077653757	-0.079682050510	1.731931553721
C	-3.470011685116	-0.094885816207	2.729350184323
C	-2.909140455756	-0.143525804832	0.386532319228
C	-4.818554605660	-0.168896246928	2.412597287507
H	-3.168543779044	-0.047062791115	3.775882823221
C	-4.265164878257	-0.218495564639	0.082166189352
H	-2.168977798554	-0.129552628087	-0.407029265633
C	-5.239110510392	-0.232981189481	1.080988229652
H	-5.554168181927	-0.177026960966	3.216457136674
H	-4.566082088401	-0.266090938714	-0.964428337295
H	-6.296293529575	-0.291202201888	0.831067344177

Table S118. Atomic coordinates and single point energies of the transition state for the top-face methylation of N-phenylacetyl γ -sultam enolate.



TS frequency: -530.1447

G = -3718.167575

G_{SP} = -3719.032504

33

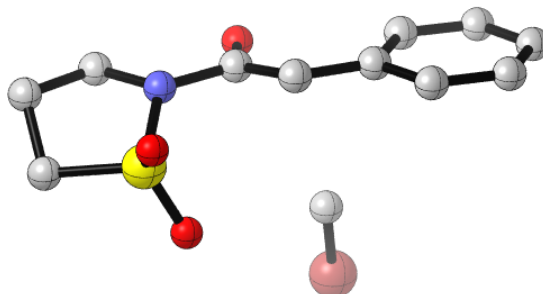
PhAcBurylSultam_TopFace_TS: optimized structure // E(RM062X) = -3719.26181891

A.U. after 13 cycles

O	0.249840011339	0.087186554494	-0.103660608711
C	0.153408543307	-0.056783535163	1.119216926315
N	1.396865943818	-0.090575790820	1.831616933773
S	1.574095682088	0.064058462295	3.501672625607
O	0.898747517401	1.265708312427	4.007612358954
C	3.353629121608	0.300058952299	3.403252209389
C	3.743047158764	-0.396716439448	2.110444240819
C	2.666407455244	-0.017861849323	1.098034348707
H	2.821940234045	0.995905981731	0.705828153116
H	3.790667595106	-0.114419004137	4.315517320669
H	3.513273204059	1.382849287721	3.363730286388
O	1.255581861842	-1.209457778843	4.164459326774
C	-1.018171180397	-0.320390625574	1.880002295178
H	4.735563531144	-0.079518936784	1.778977979189
H	2.622481098343	-0.712405612592	0.256937755376
H	3.757173076054	-1.482467090604	2.257892545234
H	-0.930675846505	-0.283285612216	2.963709805025
C	-0.774021048361	-2.578698648371	1.699832112323

H	-0.700253458365	-2.428278146126	0.629850639207
H	0.103440186714	-2.500417006156	2.330201863400
Br	-0.557822101366	-4.922103120486	1.497723367587
C	-2.364458211486	-0.124792570412	1.370912702935
C	-3.438095574531	-0.108381738850	2.290624390097
C	-2.695926026421	-0.018322372922	0.001510417115
C	-4.756804875391	0.018135777931	1.874384280655
H	-3.216939830157	-0.194202454433	3.354528525412
C	-4.021413558381	0.111782004312	-0.406465749640
H	-1.897630519146	-0.032330427676	-0.733534445295
C	-5.064873203469	0.132413667388	0.517375941212
H	-5.553137244543	0.029289397918	2.617314666911
H	-4.240060504532	0.195267103567	-1.470448764381
H	-6.097120577193	0.232171560445	0.188652793506
H	-1.752690259253	-2.652720154941	2.155885526529

Table S119. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of N-phenylacetyl γ -sultam enolate.



G = -3718.188654

G_{SP} = -3719.053898

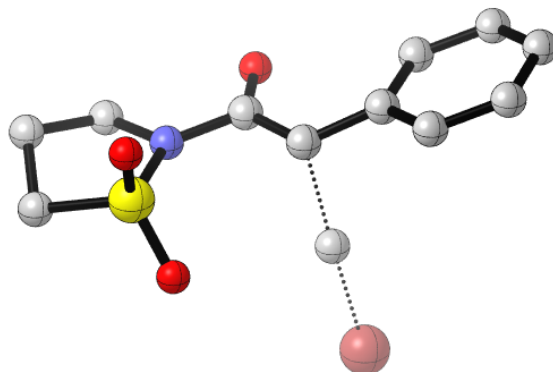
33

PhButrylStultam_BottomFace_Start: optimized structure // E(RM062X) = -3719.28259486 A.U. after 13 cycles

O	-0.016270412974	-0.235130853510	-0.064274036760
C	-0.028416775451	-0.112393892765	1.175522907009
N	1.297303972649	-0.017011475177	1.793147671197
S	1.622542782070	1.042744436029	3.059270465443
O	1.033059154151	2.374761393778	2.838026928303
C	3.398916672423	1.090046469708	2.746035376442
C	3.666066835577	-0.136658802330	1.889494337699
C	2.474271407735	-0.233477477514	0.944577120756
H	2.528516253953	0.517206969363	0.144312705256
H	3.905199475142	1.113483467343	3.714361851616
H	3.578078836171	2.023996346059	2.203595561070
O	1.335169662370	0.402721033860	4.352087745647
C	-1.104050437978	-0.065121665148	2.059949170986
H	4.609014631381	-0.035813282189	1.344494155818
H	2.388961437533	-1.219293152605	0.482249286010
H	3.719179126388	-1.032845770736	2.517588519620
H	-0.889169219597	-0.004655146891	3.124974250815
C	-1.313852065766	2.813567469386	0.542888265267
H	-2.338072153811	2.731992668109	0.906469696111
H	-1.038420605548	1.964678027123	-0.083295875400
Br	-1.242127143827	4.419181522062	-0.597492665015

H	-0.599356093824	2.960529010008	1.352282390873
C	-2.489752704504	-0.058469899960	1.669490681389
C	-3.488276447693	0.127051385455	2.660030095170
C	-2.950396334341	-0.211827851353	0.335867717226
C	-4.838930435185	0.173094905876	2.344836531745
H	-3.175934133014	0.248035264920	3.697382009683
C	-4.307265081535	-0.161534588799	0.031754847911
H	-2.217784771594	-0.368222111330	-0.450208088854
C	-5.270111462230	0.032829812005	1.022834569064
H	-5.566969195289	0.323865765322	3.141433128705
H	-4.618399623186	-0.279660678876	-1.006068211550
H	-6.328485697458	0.071737529221	0.774184376979

Table S120. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of N-phenylacetyl γ -sultam enolate.



TS frequency: -533.4466

G = -3718.167255

G_{SP} = -3719.031997

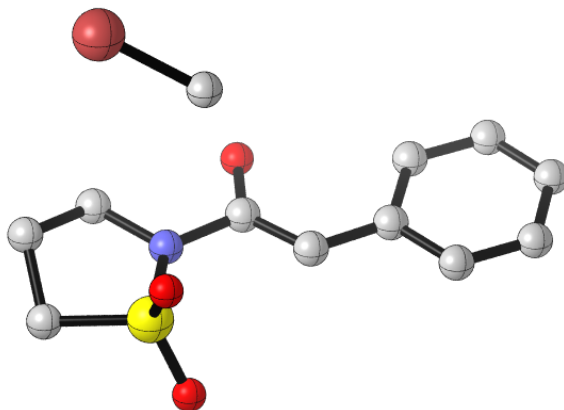
33

PhAcBurylSultam_BottomFace_TS: optimized structure // E(RM062X) = -3719.26113243 A.U. after 13 cycles

O	0.012618153199	0.022252000217	-0.013617291493
C	0.005721520460	0.007540609553	1.221111795006
N	1.300178552762	-0.015629393159	1.840645156503
S	1.611817004732	-0.172906726924	3.491072865044
O	1.068173971490	0.964657513560	4.245703304841
C	3.387656288573	-0.027607653545	3.272998449448
C	3.621514329284	-0.617860377385	1.894090802502
C	2.511452556555	-0.057763387021	1.006913198176
H	2.752337014231	0.954622605169	0.657943165639
H	3.864637421943	-0.556422621121	4.102446475915
H	3.615781601605	1.042527234570	3.322124022995
O	1.258770006520	-1.517719721452	3.967110640849
C	-1.120115941631	0.114862843372	2.082830301300
H	4.610500323695	-0.348403241281	1.513595562757
H	2.316771131874	-0.688098601858	0.137790986931
H	3.555542824818	-1.710757617792	1.940011125250
H	-0.956181911279	-0.037382797036	3.147017874468
C	-1.050595524779	2.391698909558	2.108887146687
H	-1.056295461877	2.340607312211	1.027108724573

H	-0.121537033733	2.335673174002	2.661630761746
Br	-1.033680856268	4.756679341827	2.104022087914
C	-2.486761680313	-0.105809954344	1.640432597839
C	-3.490655979294	-0.279777044150	2.620950024496
C	-2.908216722670	-0.094598114178	0.291803434941
C	-4.826961735716	-0.441836746596	2.280440195402
H	-3.199752311135	-0.288609710856	3.671401772320
C	-4.250742282877	-0.261564507278	-0.040376521391
H	-2.166163186866	0.040084505083	-0.488412829880
C	-5.223848501575	-0.436923217095	0.941778458674
H	-5.566844618216	-0.575693050961	3.068402732775
H	-4.539155842396	-0.250980293035	-1.090861919272
H	-6.270058531869	-0.564587959883	0.672126025559
H	-1.988957770077	2.346042756761	2.646001459340

Table S121. Atomic coordinates and single point energies of the reactant ground state for the top-face methylation of dihedrally-anchored (C-C-C-N) N-phenylacetyl γ -sultam enolate.



G = -3718.188512

G_{SP} = -3719.053047

33

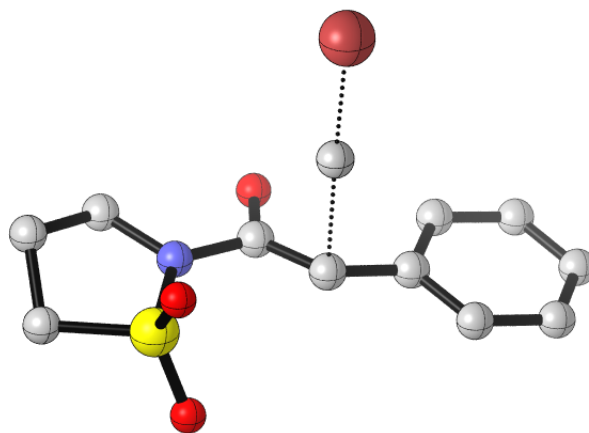
PhAcBurylSultam_TopFace_Start: optimized structure // E(RM062X) = -3719.28216948

A.U. after 14 cycles

O	0.123846215661	-0.508870067657	0.186188416850
C	0.108039909588	0.066384016214	1.292374793841
N	1.436418483310	0.315879020428	1.836057241571
S	1.785552076866	0.969197134698	3.336652250172
O	1.241163573160	2.326278051612	3.478357619329
C	3.552366363660	0.987828169402	3.034120400511
C	3.761607817407	-0.230328105010	2.152073493806
C	2.609931833543	-0.238857525388	1.144655229457
H	2.840797697810	0.381575231755	0.269289965650
H	4.057271210302	0.960716158188	4.003365632259
H	3.766732515850	1.930718634084	2.519305551979
O	1.479212620028	0.020006255762	4.423181252987
C	-0.985306011993	0.454976386906	2.068105884071
H	4.731294353222	-0.193805831053	1.647969728584
H	2.382435626025	-1.249912418621	0.796820045215
H	3.727300149547	-1.139856076820	2.763909724596
H	-0.809727333848	0.966555670091	3.010456921912
C	0.596685546770	-2.763799992056	2.646010651514
H	0.318571549512	-2.420972692684	1.648712746723
H	0.810784482202	-1.935739795594	3.323050084017

Br	2.260064885035	-3.795727546684	2.455349219003
H	-0.147544131281	-3.443410715468	3.061754114227
C	-2.361655091717	0.247971399453	1.700501280052
C	-3.384672976580	0.701230770086	2.575086525870
C	-2.796840845848	-0.394907202594	0.511460695591
C	-4.730940085350	0.527572189654	2.289107722113
H	-3.094539766402	1.200877287577	3.499516795464
C	-4.150773070577	-0.563909912124	0.236810805436
H	-2.046861497049	-0.752104105438	-0.186897356784
C	-5.136874971266	-0.109885917581	1.113100589934
H	-5.476287053713	0.894982782361	2.993976145362
H	-4.440253187838	-1.063298785634	-0.687838528741
H	-6.192247778122	-0.246831535126	0.887446119178

Table S122 Atomic coordinates and single point energies of the transition state for the top-face methylation of dihedrally-anchored (C-C-C-N) N-phenylacetyl γ -sultam enolate.



TS frequency: -529.4113

G = -3718.167687

G_{SP} = -3719.032718

33

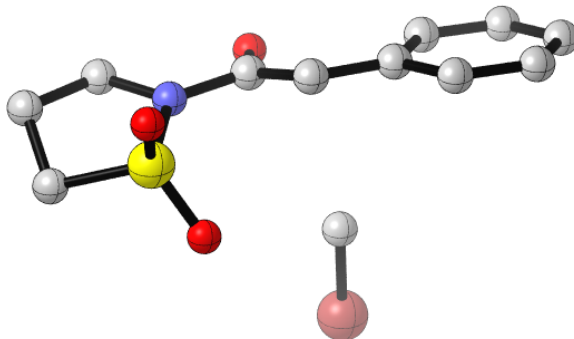
PhAcBurylSultam_TopFace_TS: optimized structure // E(RM062X) = -3719.26150362

A.U. after 13 cycles

O	0.250326823231	0.086520934263	-0.096184099513
C	0.152552335433	-0.030858233615	1.129454712222
N	1.396663123865	-0.018252613804	1.841082899637
S	1.588090430097	-0.001303767283	3.513174119560
O	0.858504620131	1.118738760301	4.119175122882
C	3.346739284203	0.325888726278	3.407068379949
C	3.763014928191	-0.353108812350	2.113246496777
C	2.659870953454	-0.068354633685	1.091412855456
H	2.818579163442	0.893223091586	0.588794413463
H	3.814691020272	-0.066346592602	4.313797269123
H	3.448575253707	1.415837218274	3.368734418791
O	1.351161012757	-1.338488179431	4.079665625559
C	-1.019433371605	-0.292251371628	1.890698127270
H	4.730107903947	0.021228417129	1.767813609857
H	2.595294376585	-0.848290002371	0.329238666725
H	3.854065794580	-1.432416404377	2.278805553481
H	-0.936163769582	-0.235303368578	2.973769606667
C	-0.786697456068	-2.551018043129	1.701531002056
H	-0.731252825071	-2.391413447216	0.631757062655

H	0.102528076825	-2.491861807272	2.317302390059
Br	-0.599389510844	-4.895467094605	1.471564673277
C	-2.365164176853	-0.108149971140	1.374485079408
C	-3.442027332844	-0.086591056249	2.290208442608
C	-2.692545821550	-0.019360723746	0.002813382012
C	-4.760018474828	0.027601550944	1.868042874678
H	-3.224224466147	-0.159144565671	3.355793479151
C	-4.017363200013	0.098682436083	-0.411161345085
H	-1.891835797469	-0.037948257209	-0.729448956180
C	-5.064090568752	0.124227088735	0.508775570104
H	-5.558940436567	0.042888328388	2.608107652868
H	-4.232661940182	0.168339781130	-1.476820000128
H	-6.095754049303	0.214065048867	0.175386150381
H	-1.757133701663	-2.620614289366	2.175507533602

Table S123. Atomic coordinates and single point energies of the reactant ground state for the bottom-face methylation of dihedrally-anchored (C-C-C-N) N-phenylacetyl γ -sultam enolate.



G = -3718.188619
 G_{SP} = -3719.054459

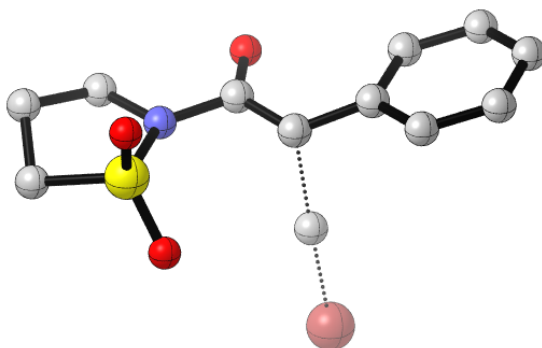
33

PhButrylStultam_BottomFace_Start: optimized structure // E(RM062X) = -3719.28220355 A.U. after 13 cycles

O	-0.053320792853	-0.294905625592	-0.081058667900
C	-0.054028467758	-0.088537906552	1.148317182451
N	1.270997082517	0.111837104469	1.717086436205
S	1.612662849188	0.955604109100	3.115848318892
O	0.905602541779	2.245500282427	3.149874169265
C	3.343943981842	1.168955309759	2.696067790221
C	3.666496852890	-0.053444340822	1.853377462607
C	2.453340542871	-0.297140651098	0.951581953823
H	2.512200806838	0.297389418840	0.032401743595
H	3.909458555977	1.258774994792	3.627028469125
H	3.401862325756	2.102756843528	2.126449099125
O	1.488108461486	0.106335561169	4.312070471904
C	-1.125606105624	-0.015801990477	2.037893747125
H	4.574482929253	0.101993279726	1.264729372459
H	2.361484856475	-1.350428174820	0.672396361093
H	3.829076079702	-0.916338108279	2.509062766383
H	-0.913697560686	0.120441906333	3.096361830940
C	-1.202763869216	2.830238195560	0.570314480285
H	-2.236186781210	2.792518258709	0.914801956399
H	-0.971200341714	2.002013832102	-0.099913457233

Br	-1.010826167628	4.490788896981	-0.474953043362
H	-0.498532928252	2.887918330744	1.400174687677
C	-2.511896465250	-0.037290288417	1.653778385575
C	-3.508001702582	0.178483015613	2.641665416884
C	-2.978251163854	-0.244201119478	0.328806823707
C	-4.860468561010	0.197817616958	2.332483078671
H	-3.191812289648	0.342631524721	3.671934512404
C	-4.337492436724	-0.219882506832	0.031210483646
H	-2.247981339746	-0.424023118353	-0.454173979772
C	-5.297419404115	0.000998392759	1.019397287560
H	-5.585795106192	0.371638259763	3.126875997051
H	-4.652711310478	-0.380982656472	-0.999636089333
H	-6.357485619298	0.017748179582	0.775548438758

Table S124. Atomic coordinates and single point energies of the transition state for the bottom-face methylation of dihedrally-anchored (C-C-C-N) N-phenylacetyl γ -sultam enolate.



TS frequency: -532.8458

G = -3718.167039

G_{SP} = -3719.031890

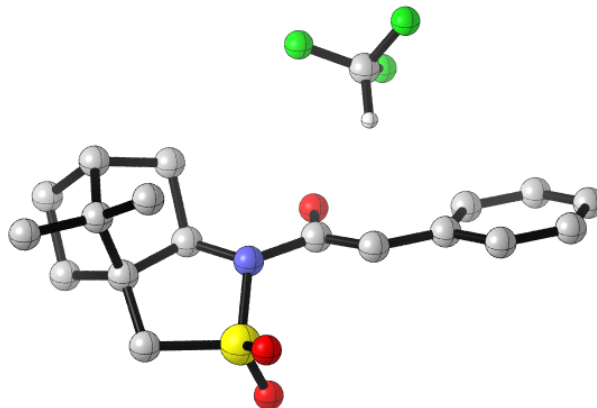
33

PhAcBurylSultam_BottomFace_TS: optimized structure // E(RM062X) = -3719.26112503 A.U. after 13 cycles

O	0.010981324360	0.007402399177	-0.011563955638
C	0.002775204477	0.004709816144	1.223202905572
N	1.298876822624	0.002390810566	1.842626719102
S	1.609805585790	-0.206840745081	3.486691091871
O	1.025915544560	0.885508679629	4.276541253760
C	3.377269754870	0.001929844880	3.276465790295
C	3.637631986305	-0.580218457222	1.898600761806
C	2.501091005728	-0.091147435433	0.998176553397
H	2.721396169093	0.898847533341	0.580540529011
H	3.872668740475	-0.510254291136	4.105485172172
H	3.565472288977	1.079701088776	3.328188609845
O	1.302929906742	-1.579021132360	3.915069336626
C	-1.124018734794	0.114031544537	2.083083010596
H	4.611126148602	-0.263200197460	1.515502133854
H	2.305353335454	-0.778493781128	0.173312446131
H	3.632276091450	-1.674504419426	1.954567893729
H	-0.962529230556	-0.030704931929	3.148413492134
C	-1.039198240778	2.389346032063	2.117271388212

H	-1.038092282683	2.346099089016	1.035112404961
H	-0.113958417233	2.320772345641	2.674905645313
Br	-1.001530452241	4.754188608438	2.130778512486
C	-2.490748709039	-0.102966030763	1.639144633373
C	-3.497142100507	-0.263370606556	2.619513815248
C	-2.910051498169	-0.101120380776	0.289838131307
C	-4.833763959381	-0.421025895819	2.278401686184
H	-3.207893700685	-0.264581573191	3.670466243199
C	-4.253039591712	-0.263460851672	-0.042950025958
H	-2.166108999577	0.022814685599	-0.490317942098
C	-5.228545340454	-0.425370919611	0.939088182689
H	-5.575578487439	-0.543929109458	3.066332164227
H	-4.539806837086	-0.260385977592	-1.093929949381
H	-6.275038363855	-0.549536054301	0.668905757558
H	-1.981578154144	2.348706382039	2.647658196267

Table S125. Atomic coordinates and single point energies of the reactant ground state for the top-face protonation of **8o** by CHF₃.



G = -1714.948376

G_{SP} = -1715.787591

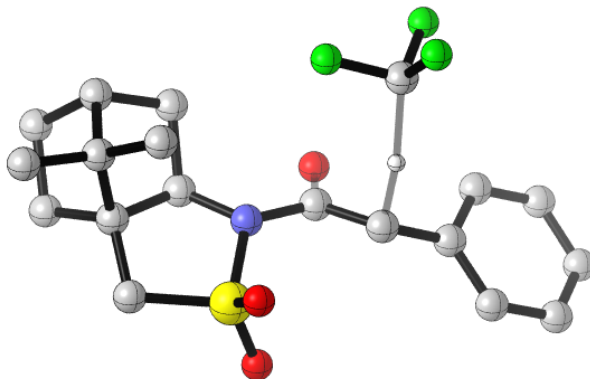
50

Anion_topFace_F3CH_Start: optimized structure // E(RM062X) = -1716.15832487 A.U.
after 13 cycles

O	-0.075663271225	-0.217590633021	0.201047963784
C	-0.014180736843	-0.024915251401	1.432328806677
N	1.341857203393	0.102297747469	1.978542155655
S	1.714002859898	1.394820537811	2.998936471428
O	1.290749161152	2.682675095905	2.423676296396
C	3.515282404574	1.238883939820	2.830757690594
C	3.753510065577	0.099650386840	1.860481231954
C	2.451889288068	-0.150059200706	1.056933019925
C	2.586418033472	-1.623453430166	0.606537665047
C	4.009521950454	-1.989406156975	1.071455512527
C	5.002694586003	-1.157459973763	0.226936132513
C	4.856681336400	0.281270605086	0.804261155904
H	4.555580251692	1.016746592204	0.050068751521
H	5.787343916620	0.638562570057	1.258365462143
H	4.748889998958	-1.203159355875	-0.838330448436
H	6.028723984394	-1.526595795141	0.331231058045
C	4.090658579104	-1.303631657561	2.458747133074
C	3.098101970961	-1.842769683807	3.492149831890
H	3.098405905725	-1.210113705764	4.390867466042
H	2.068317081809	-1.897911014854	3.135673698946

H	3.413016196993	-2.848641412134	3.801326006036
C	5.476438393259	-1.357128991975	3.107334404342
H	5.501053978292	-0.724749374378	4.005839573103
H	5.693996482005	-2.384192203805	3.427896645636
H	6.290141751712	-1.036731521836	2.450672078759
H	4.215711163000	-3.065757575200	1.068024948041
H	1.819537175481	-2.241990299000	1.082239173831
H	2.458900663225	-1.723287997436	-0.476019151848
H	2.378414640280	0.526116522933	0.195337610440
H	3.921849752940	1.072218424535	3.833663163754
H	3.851565719243	2.208436139766	2.450281704702
O	1.277059154691	1.104442597123	4.372433779514
C	-1.040377569792	0.017035465665	2.375601662997
H	-0.761108489523	0.082364631496	3.424040096542
C	-2.450112891314	0.010214430336	2.064318931827
C	-3.391572044150	0.022546412001	3.124757643831
C	-2.983663938883	-0.018302034436	0.750338909213
C	-4.759299275794	0.000385483931	2.893811385815
H	-3.020778073505	0.050312299480	4.149280079601
C	-4.358177941864	-0.041479464537	0.530746444895
H	-2.297566238780	-0.021416523888	-0.091966635845
C	-5.263914980424	-0.035567901340	1.590887221262
H	-5.443200163622	0.009539551174	3.741855331454
H	-4.726156849984	-0.064606959898	-0.494663317401
H	-6.336284661669	-0.057188510494	1.409101392184
C	-1.364512622124	-2.876759309304	0.229847230466
F	-1.771513583796	-2.482791007896	-0.981004289906
F	-2.223766175078	-3.821781217544	0.649891313345
F	-0.169938283014	-3.470208616456	0.079133105670
H	-1.310140882323	-2.049365798687	0.934017963494

Table S126. Atomic coordinates and single point energies of the transition state for the top-face protonation of **8o** by CHF₃.



TS frequency: -1045.6052

G = -1714.907856

G_{SP} = -1715.745310

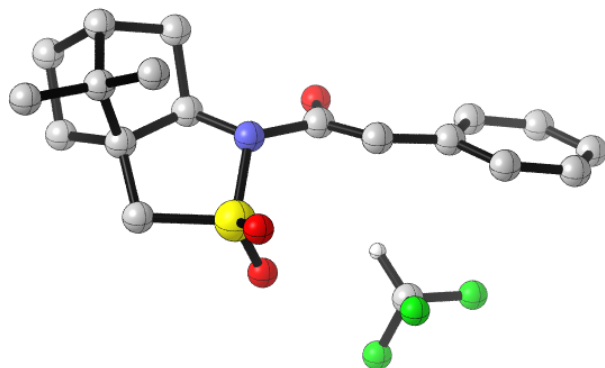
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Anion_topFace_F3CH_TS: optimized structure // E(RM062X) = -1716.10881836 A.U.
after 12 cycles

O	-0.129791778706	-0.294274240207	0.102497477450
C	-0.071187932428	-0.238615805374	1.322004537602
N	1.217181446016	-0.119917074993	1.907717364665
S	1.465018840299	0.751041815508	3.354005874283
O	0.781815547408	2.050026109500	3.284351661220
C	3.248544150968	0.963567523784	3.112624992483
C	3.628439239375	0.105581978303	1.924787286297
C	2.384122259330	-0.067764316262	1.019119987348
C	2.679425238534	-1.376646182896	0.248097261085
C	4.125376597189	-1.694436681939	0.676666392802
C	5.039689653524	-0.589336382650	0.099405872409
C	4.731880986371	0.644311085778	0.997875481682
H	4.375874568149	1.511285146157	0.430421193973
H	5.608029643607	0.964266575133	1.571981935968
H	4.811081268285	-0.398821894080	-0.955451169582
H	6.097094623777	-0.868796415260	0.155762303120
C	4.101377469560	-1.360365859861	2.189338230648
C	3.149489887745	-2.235239018096	3.008814778356

H	3.125725895793	-1.901647615200	4.054642494860
H	2.120417688001	-2.247342159680	2.644921470730
H	3.522685154282	-3.268473293728	3.001865047268
C	5.470425052732	-1.431458940520	2.870280431437
H	5.416441139814	-1.005462725875	3.881744459210
H	5.771852104096	-2.481413821446	2.976730359928
H	6.267100786370	-0.912529792792	2.329737755194
H	4.445124270620	-2.712816887731	0.429869708391
H	1.975289411599	-2.162818169235	0.537436015910
H	2.586116925568	-1.227831597616	-0.832132492836
H	2.268790413383	0.785345617397	0.338587846937
H	3.732816363519	0.683908975724	4.054020996731
H	3.384838634022	2.033796889137	2.924802930436
O	1.176967121305	-0.093751911109	4.517562415624
C	-1.183359887888	-0.470894625937	2.239077397856
H	-0.967464960130	-0.212717615760	3.277873972221
C	-2.536999427630	-0.045458916612	1.805869706772
C	-3.357688780535	0.696717008372	2.669119440169
C	-3.069914646463	-0.440463908478	0.567505714394
C	-4.653822018163	1.049608167452	2.305274153293
H	-2.963945892831	1.004788974361	3.637213815316
C	-4.365174006344	-0.079542332834	0.202265269119
H	-2.455234682010	-1.029148889227	-0.108144708600
C	-5.164627008160	0.667275413436	1.065355570723
H	-5.266675183326	1.630195637550	2.992857425437
H	-4.755144929236	-0.393713041671	-0.764580942308
H	-6.176777636334	0.944644046895	0.777616224383
C	-1.098030121636	-3.288564045274	1.741605392537
F	-1.526064046322	-3.762390706134	0.510387734233
F	-1.461870580635	-4.315592276868	2.598090665036
F	0.289589569792	-3.460710628770	1.651136099370
H	-1.224746183718	-1.757743450230	2.135565320132

Table S127. Atomic coordinates and single point energies of the reactant ground state for the bottom-face protonation of **8o** by CHF₃.



G = -1714.948782

G_{SP} = -1715.786162

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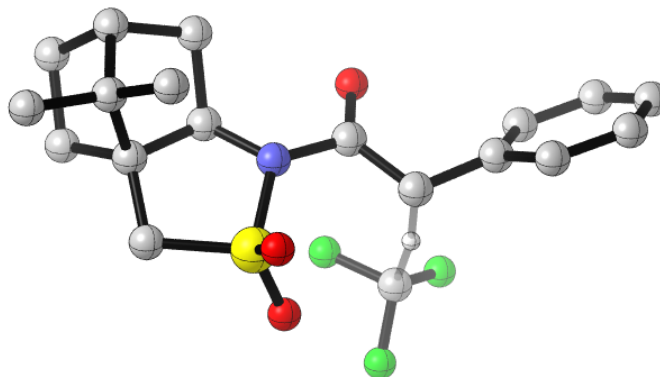
Anion_bottomFace_F3CH_Start: optimized structure // E(RM062X) = -1716.15848610

A.U. after 13 cycles

O	0.007446228344	0.003309753350	-0.018943098614
C	0.002985669809	-0.215392693753	1.205272327840
N	1.329314962592	-0.213030839604	1.858659258268
S	1.541527516570	0.867034940419	3.141724740452
O	0.922492069773	2.173404059592	2.841617385332
C	3.344522095168	1.006131884662	2.979653850473
C	3.735557001458	0.071250952030	1.854356136114
C	2.491025486186	-0.171694985631	0.966243338828
C	2.803904367797	-1.517836992035	0.271568624147
C	4.244386650908	-1.811770091402	0.738330251615
C	5.164165742321	-0.749679711055	0.093126906618
C	4.838317610555	0.546321249400	0.892049019238
H	4.474204492625	1.361043738321	0.256412822725
H	5.709717045717	0.921504768581	1.439716452648
H	4.952571765981	-0.640813675677	-0.976764135361
H	6.221021992073	-1.021282957812	0.187835277591
C	4.211850584731	-1.369607634582	2.223998144188
C	3.259316830709	-2.182037741611	3.104787683995
H	3.161070671429	-1.715994176082	4.094957911033
H	2.253074689108	-2.282601109992	2.695081951317

H	3.677871534797	-3.186515300143	3.254321649907
C	5.577766093922	-1.385916262939	2.915342369449
H	5.506458495713	-0.921582529895	3.908801781535
H	5.903676182968	-2.423354016766	3.065047418287
H	6.365725078153	-0.868560089839	2.360886742111
H	4.567160385925	-2.844597965789	0.564590078720
H	2.094954382971	-2.287841874680	0.593030924504
H	2.730042167847	-1.433030314149	-0.817331814980
H	2.358766367802	0.635249620835	0.235400065228
H	3.779399079091	0.758443456145	3.953400759871
H	3.530904659768	2.058953766988	2.744747062710
O	1.173014076290	0.237533755598	4.417427982348
C	-1.057015943872	-0.459159268357	2.075841344426
H	-0.818089977211	-0.686181614504	3.112144755467
C	-2.449367396077	-0.309243721567	1.731422489405
C	-3.430643685781	-0.414690546502	2.749167100599
C	-2.921485094702	-0.014624350221	0.427365818464
C	-4.779909857326	-0.220986460306	2.490775608350
H	-3.105004324040	-0.637186345185	3.765300886685
C	-4.277378072756	0.182602470876	0.180837912357
H	-2.198691494441	0.062384370537	-0.379187093986
C	-5.222855208368	0.088251812465	1.201764093786
H	-5.496832370044	-0.303926448080	3.306972085172
H	-4.600426439451	0.415551821588	-0.833593977489
H	-6.280087958703	0.246172874244	0.999472099144
C	-1.891589520692	2.749332274378	2.579299005159
F	-1.924012590290	2.228834310010	3.809721098248
F	-3.162835632260	2.855987077598	2.156751034551
F	-1.408936503269	3.997915036523	2.680983740742
H	-1.290274473064	2.141886362326	1.905474193313

Table S128. Atomic coordinates and single point energies of the transition state for the bottom-face protonation of **8o** by CHF₃.



TS frequency: -1021.6046

G = -1714.903907

G_{SP} = -1715.741943

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Anion_bottomFace_F3CH_TS: optimized structure // E(RM062X) = -1716.10624679

A.U. after 12 cycles

O	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.221729950000
N	1.262211217143	0.000000000000	1.866007618892
S	1.473082357869	0.441129037146	3.505276144107
O	0.779428416603	1.695371638139	3.807147991742
C	3.254528508566	0.735416091589	3.364618579713
C	3.680171529462	0.203864763212	2.014100550964
C	2.462100212137	0.236107327293	1.053758007775
C	2.802958889363	-0.855552794947	0.010274478889
C	4.247935995840	-1.233870364889	0.384336904782
C	5.142459488963	-0.001616204982	0.112119449641
C	4.792245699399	0.969837606157	1.277294865493
H	4.432855157132	1.944995969054	0.931298839936
H	5.649218939808	1.149115691874	1.935230632849
H	4.920661387282	0.435636352336	-0.868173644536
H	6.205773976747	-0.263926636259	0.116726845642
C	4.184764735324	-1.272541186804	1.930694722303
C	3.237383169041	-2.332687781278	2.496856294286
H	3.183929558582	-2.255815262317	3.590178799475

H	2.215081090391	-2.267161242653	2.118770660094
H	3.630304161604	-3.329287658248	2.253821002930
C	5.541725793027	-1.485496729136	2.606279606258
H	5.455399384641	-1.343344549877	3.692356490690
H	5.874134497265	-2.518343084489	2.440113980497
H	6.331409917393	-0.822288868168	2.242464015465
H	4.602477187088	-2.155450158040	-0.090734895817
H	2.116387113744	-1.701868860972	0.095559962384
H	2.717693344620	-0.465342587619	-1.008241229696
H	2.361997772942	1.222230757954	0.581719343760
H	3.725442590783	0.238560115904	4.219482635732
H	3.369340317950	1.820721516128	3.451616757718
O	1.178829643918	-0.712865657249	4.364533273930
C	-1.180371318241	0.084429610223	2.084803914073
H	-1.014649555688	-0.331668706132	3.082064401011
C	-2.473890471763	-0.350676787293	1.502351702533
C	-2.949906248287	0.196811412535	0.299315517304
C	-3.302587330367	-1.251622136593	2.187244745561
C	-4.194913095022	-0.167261795538	-0.207204818352
H	-2.328656741834	0.909006814025	-0.237832656980
C	-4.550126230573	-1.610461151815	1.683029841815
H	-2.957133071741	-1.677104025221	3.128988527704
C	-5.002147763209	-1.073743292301	0.478637710007
H	-4.540754841553	0.268793532732	-1.143009189469
H	-5.170903436304	-2.315327521782	2.233678226257
H	-5.975654739865	-1.354465245312	0.081546289600
C	-1.228537272822	2.936281204748	1.907087346289
F	-2.081452156485	3.563576999466	0.993127791194
F	0.007003694392	3.052241627656	1.265212204163
F	-1.133506764589	3.889575439672	2.905743857617
H	-1.288186826314	1.366079762762	2.176456341626

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