SUPPORTING INFORMATION

Ketone Enolization with Sodium Hexamethyldisilazide: Solvent-and Substrate-Dependent E-Z Selectivity and Affiliated Mechanisms

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I. NMR, IR, and GC Characterization Data

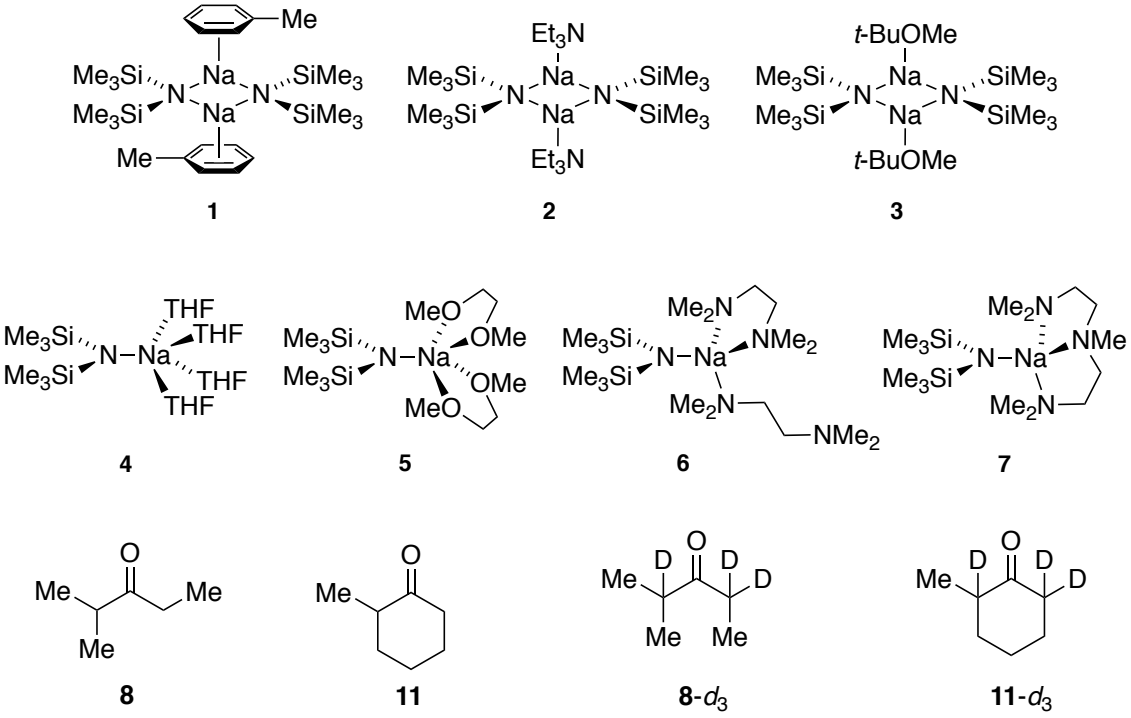
II. IR Spectroscopy Rate Studies

III. Derivations

IV. Computations

I. NMR, IR, and GC Characterization Data

Chart 1. Select solution structures of NaHMDS and substrates tested.



1 **2** **3**

4 **5** **6** **7**

8 **11** **8**-d_3 **11**-d_3

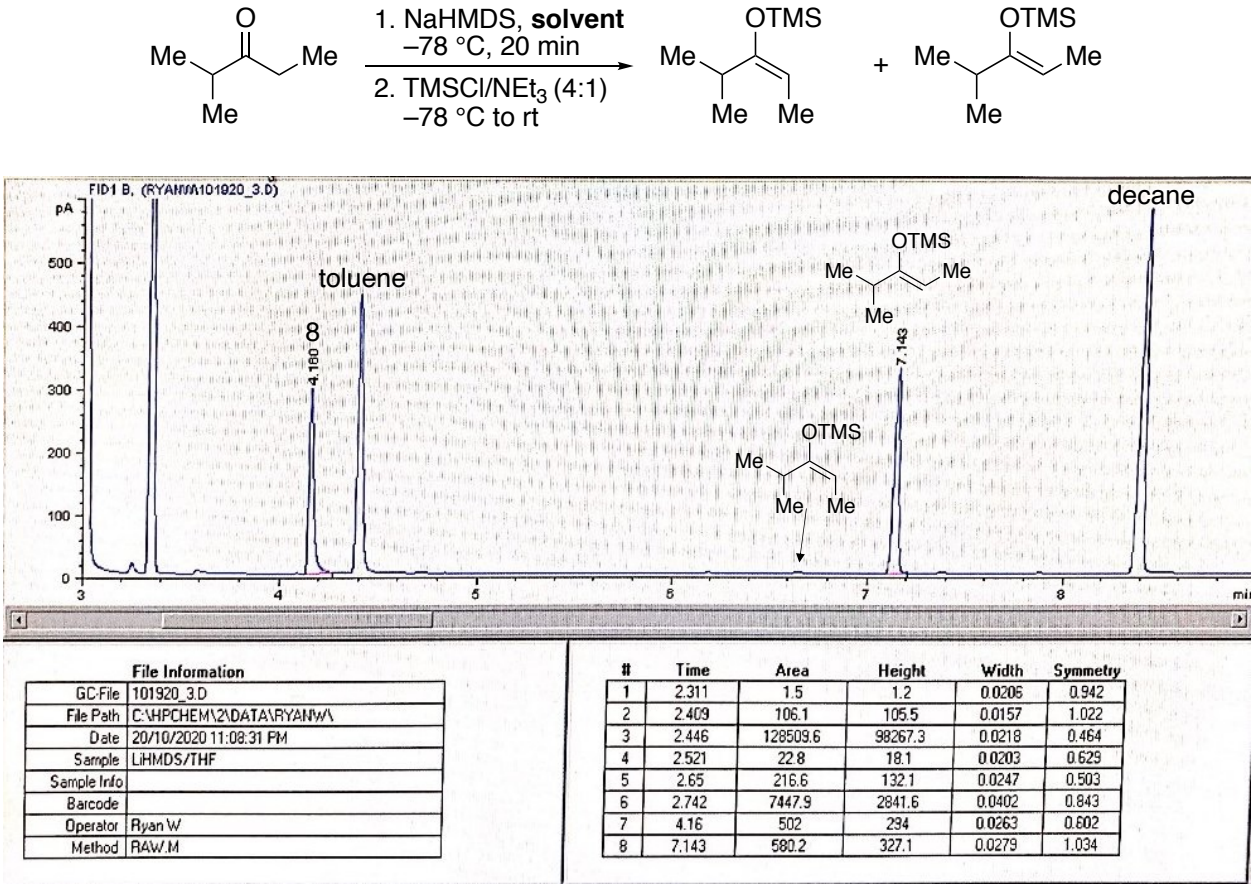
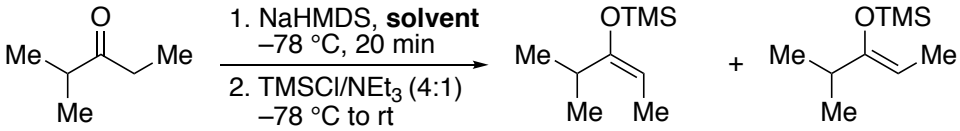
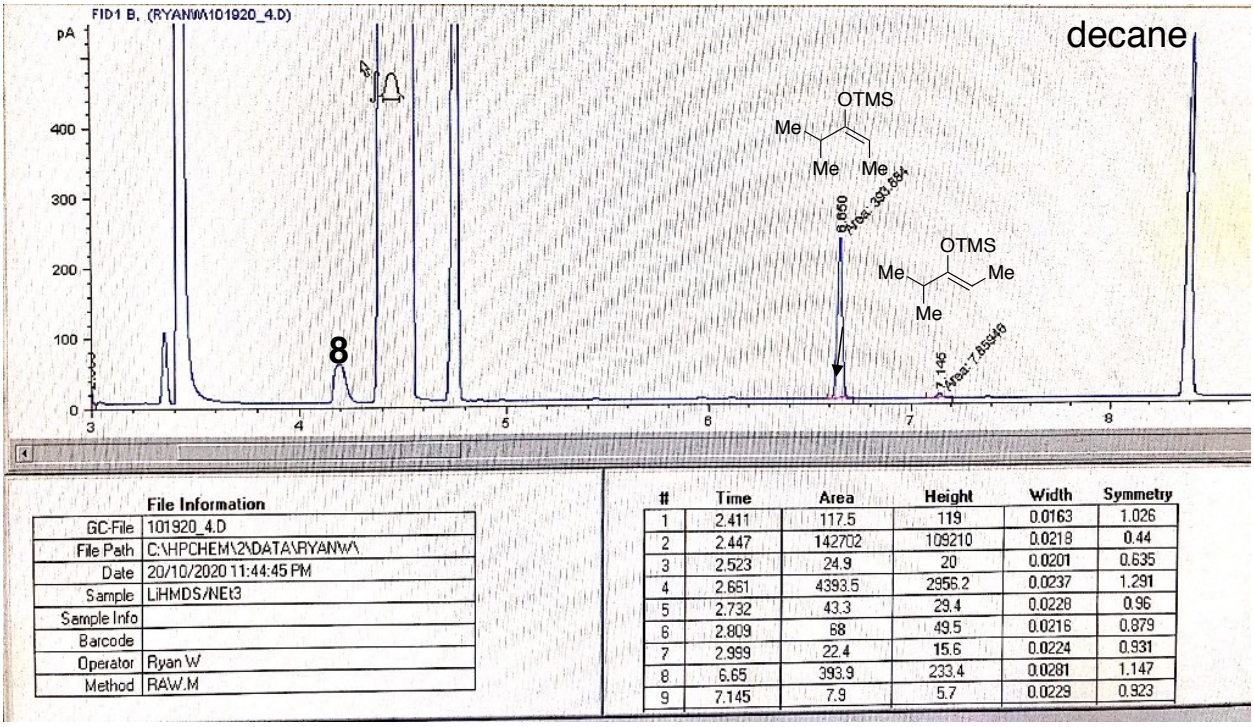


Figure S1. GC trace for the enolization of **8** (0.050 M) by 0.15 M LiHMDS in neat THF with decane internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 20 mins, standard aqueous workup, and dilution with pentane before loading sample.





#	Time	Area	Height	Width	Symmetry
1	2.411	117.5	119	0.0163	1.026
2	2.447	142702	109210	0.0218	0.44
3	2.523	24.9	20	0.0201	0.635
4	2.661	4393.5	2956.2	0.0237	1.291
5	2.732	43.3	29.4	0.0229	0.96
6	2.809	68	49.5	0.0216	0.879
7	2.999	22.4	15.6	0.0224	0.931
8	6.65	393.9	233.4	0.0281	1.147
9	7.145	7.9	5.7	0.0229	0.923

Figure S2. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M LiHMDS in 1.5 M Et_3N with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 20 mins, standard aqueous workup, and dilution with pentane before loading sample.

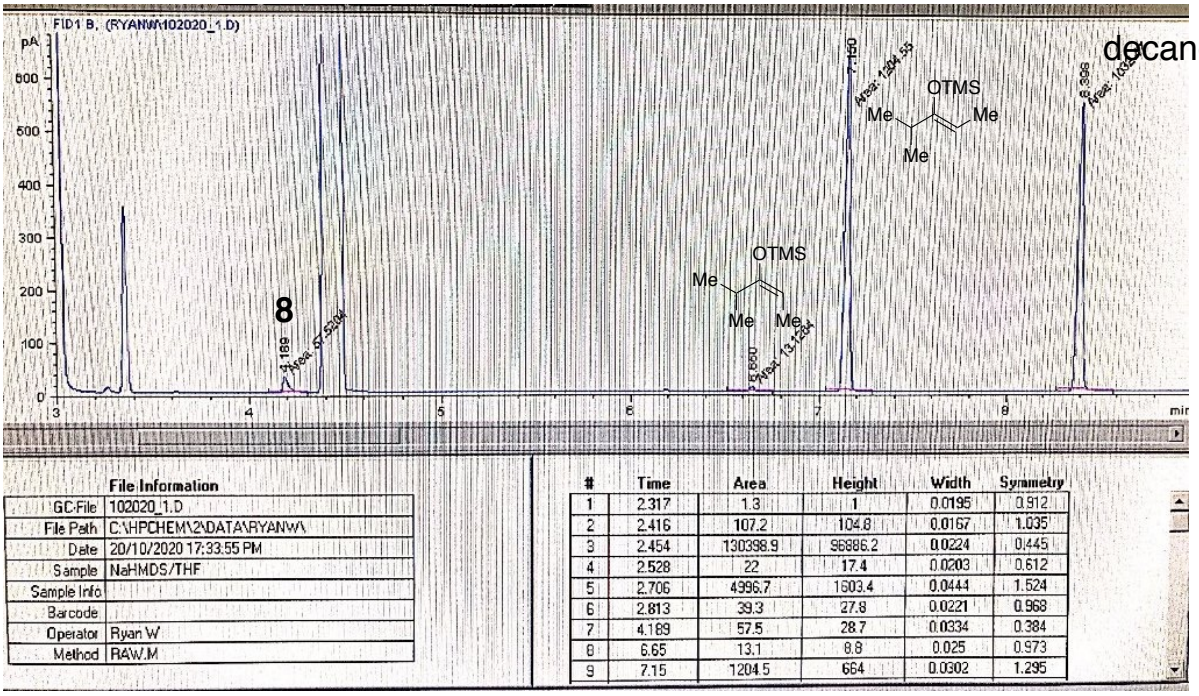


Figure S3. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 9.0 M THF with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 20 mins, standard aqueous workup, and dilution with pentane before loading sample.

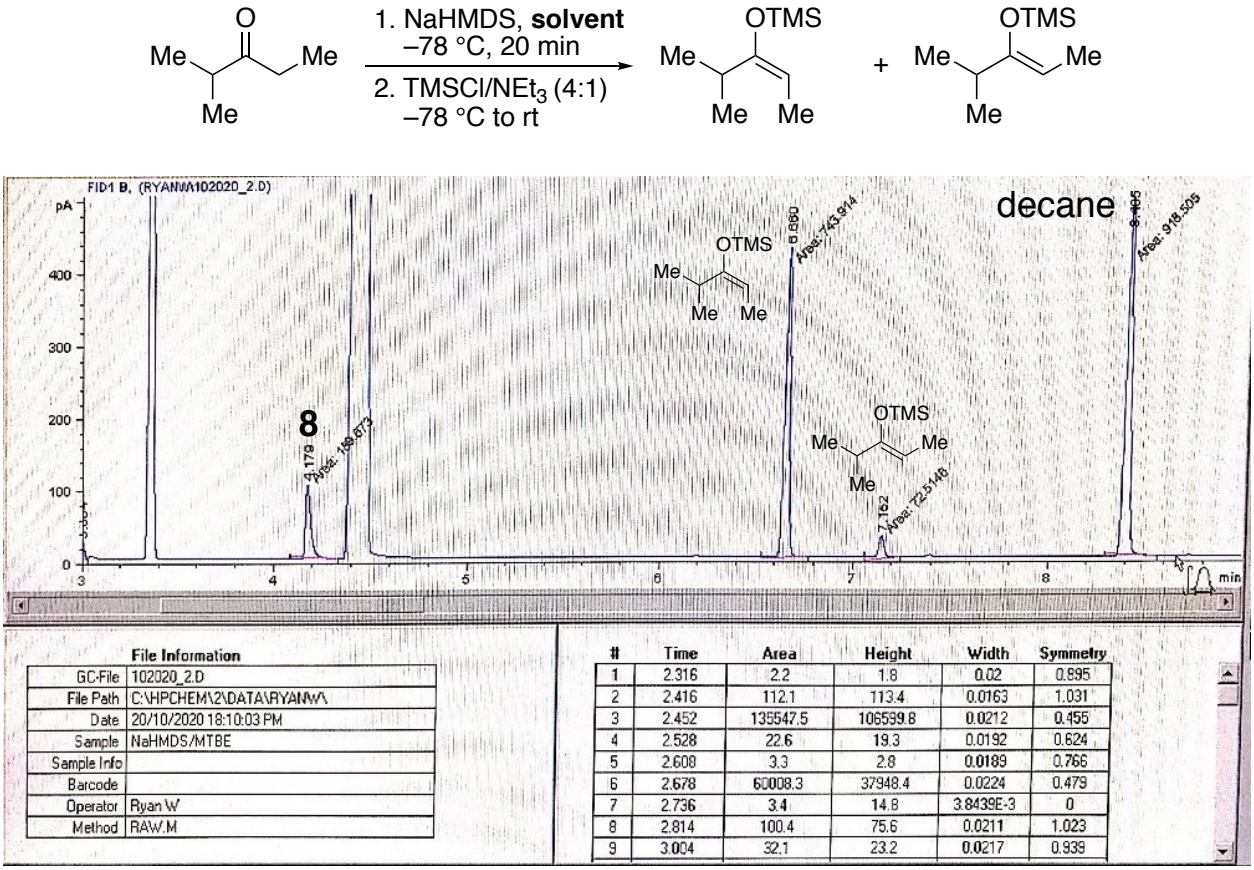
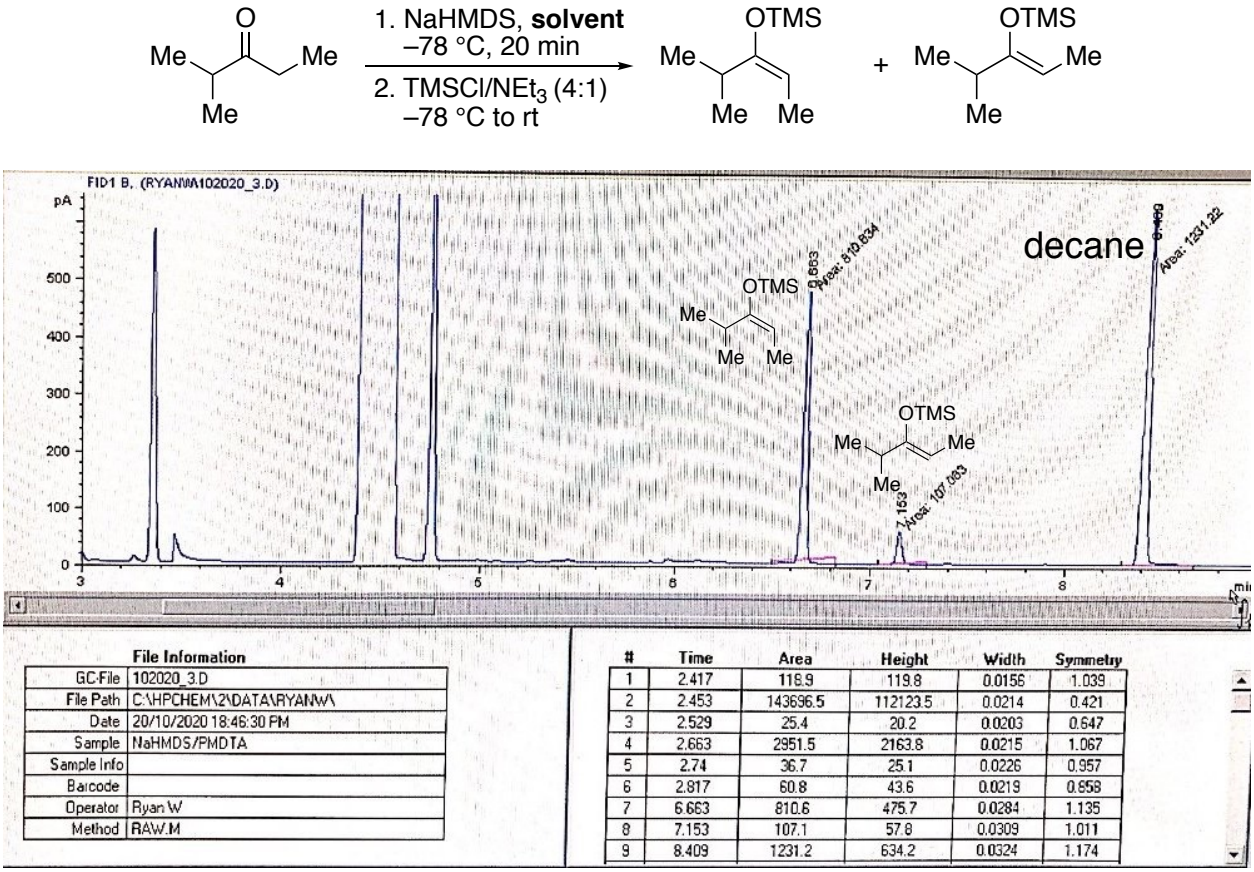
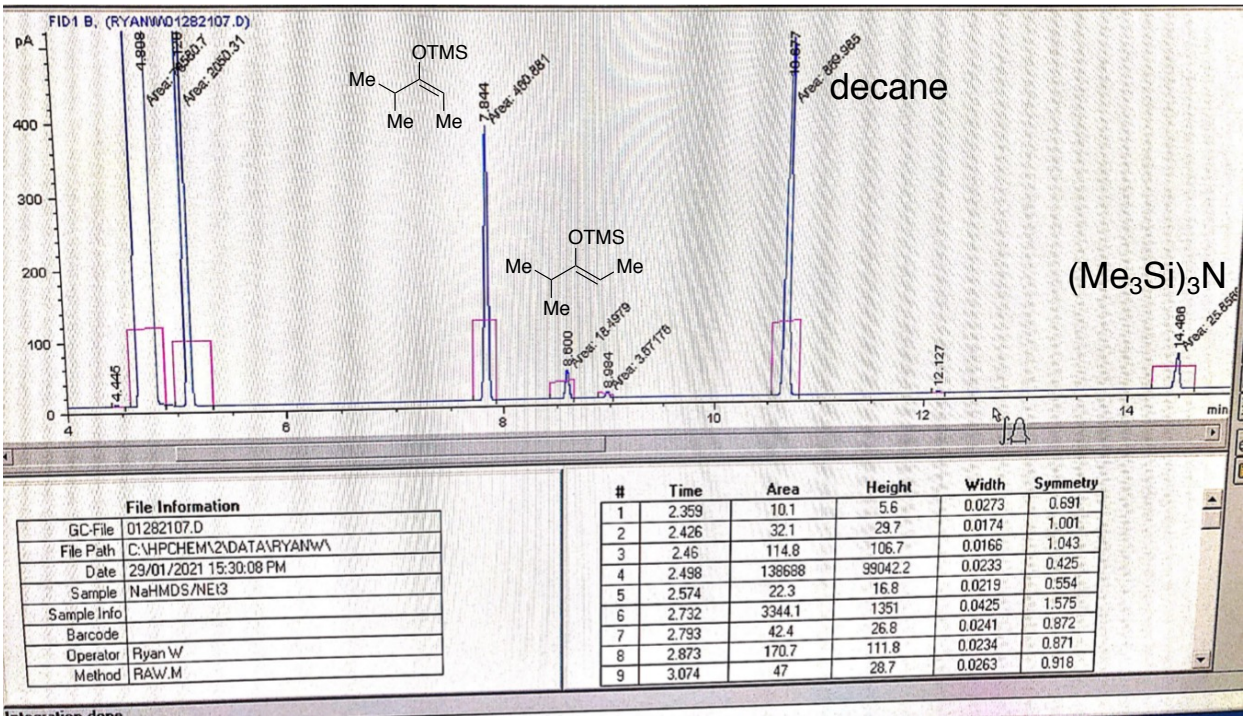


Figure S4. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 6.0 M MTBE with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 20 mins, standard aqueous workup, and dilution with pentane before loading sample.



#	Time	Area	Height	Width	Symmetry
1	2.417	119.9	119.8	0.0156	1.039
2	2.453	143696.5	112123.5	0.0214	0.421
3	2.529	25.4	20.2	0.0203	0.647
4	2.663	2951.5	2163.8	0.0215	1.067
5	2.74	36.7	25.1	0.0226	0.957
6	2.817	60.8	43.6	0.0219	0.858
7	6.663	810.6	475.7	0.0284	1.135
8	7.153	107.1	57.8	0.0309	1.011
9	8.409	1231.2	634.2	0.0324	1.174

Figure S5. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 1.5 M PMDTA with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 20 mins, standard aqueous workup, and dilution with pentane before loading sample.



#	Time	Area	Height	Width	Symmetry
1	2.359	10.1	5.6	0.0273	0.691
2	2.426	32.1	29.7	0.0174	1.001
3	2.46	114.8	106.7	0.0166	1.043
4	2.498	138688	99042.2	0.0233	0.425
5	2.574	22.3	16.8	0.0219	0.554
6	2.732	3344.1	1351	0.0425	1.575
7	2.793	42.4	26.8	0.0241	0.872
8	2.873	170.7	111.8	0.0234	0.871
9	3.074	47	28.7	0.0263	0.918

Figure S6. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 4.0 M Et_3N with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 45 mins, standard aqueous workup, and dilution with pentane before loading sample.

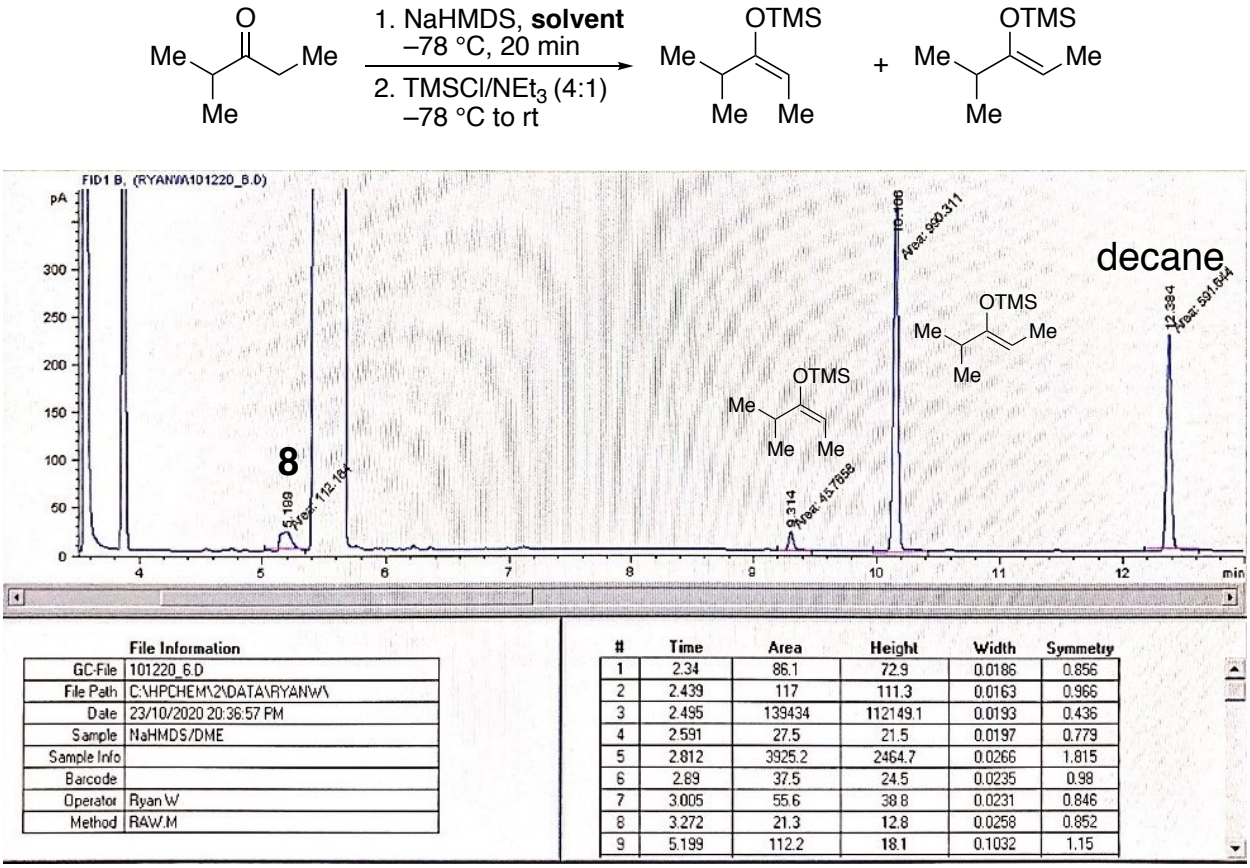


Figure S7. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 1.5 M DME with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 45 mins, standard aqueous workup, and dilution with pentane before loading sample.

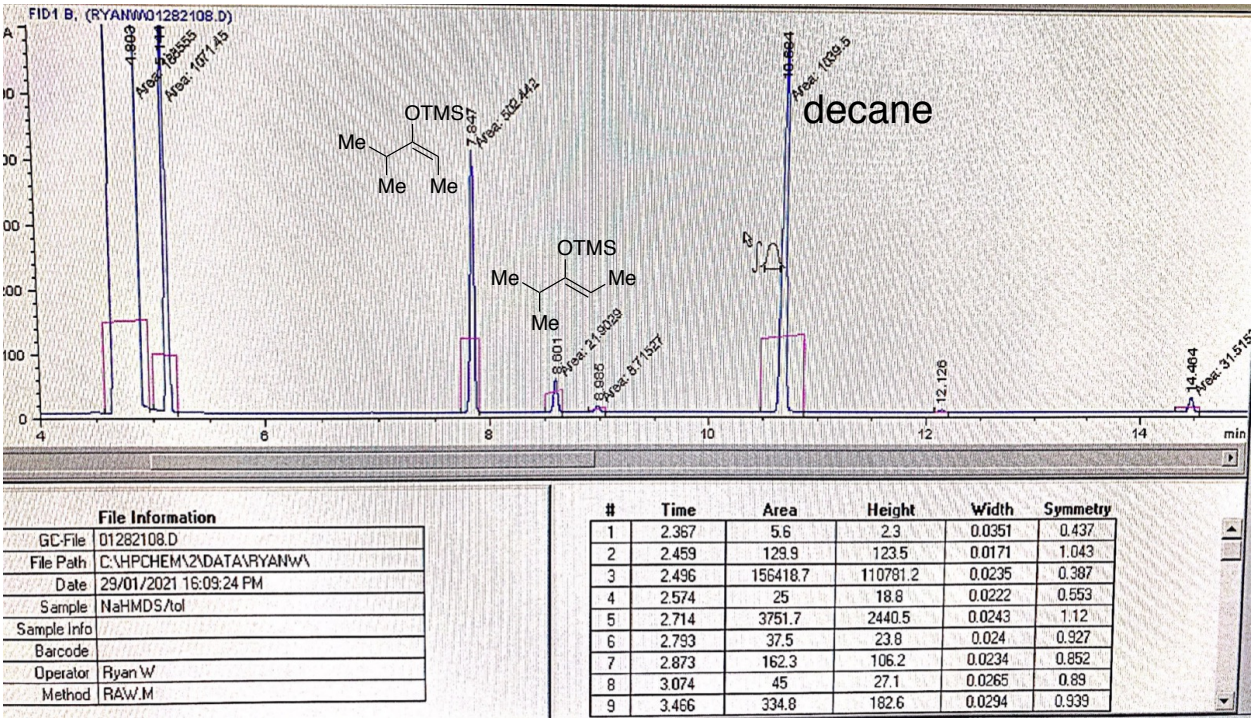
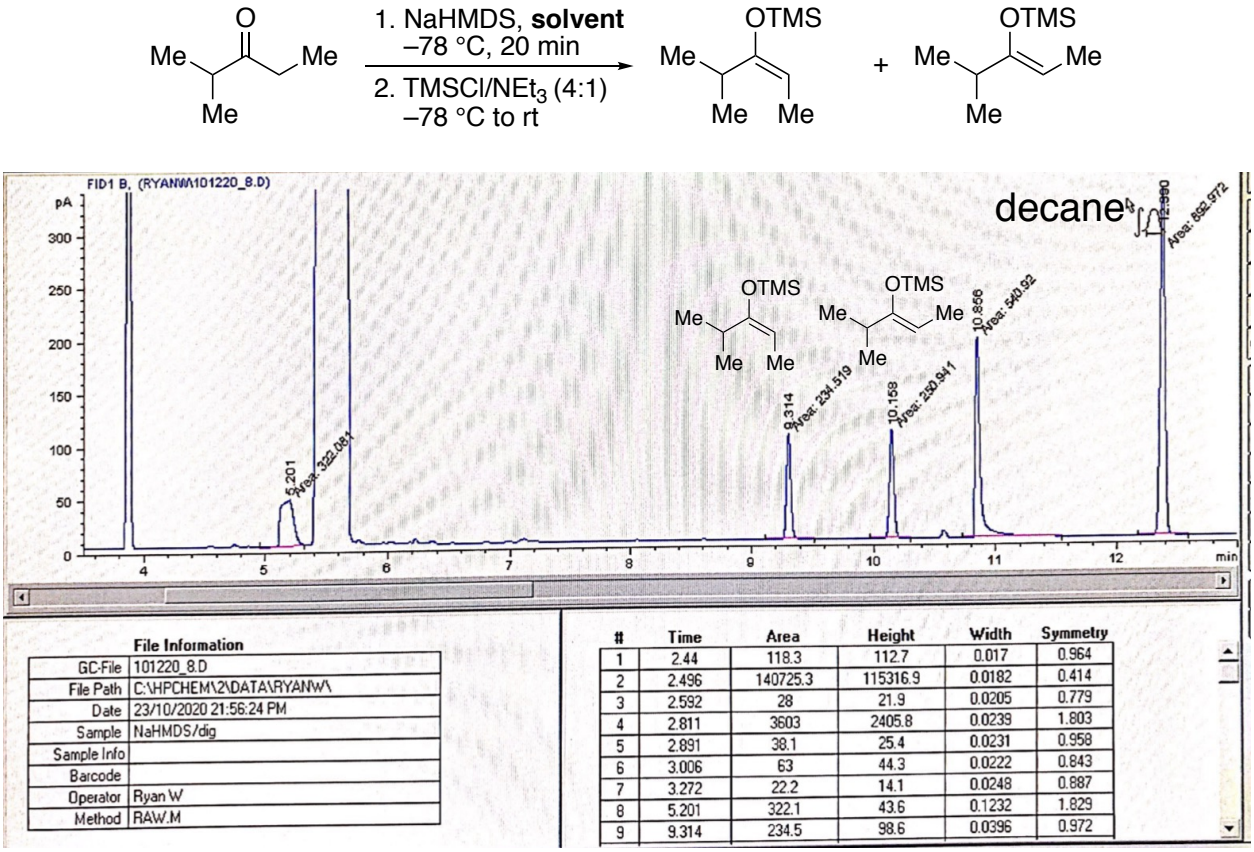
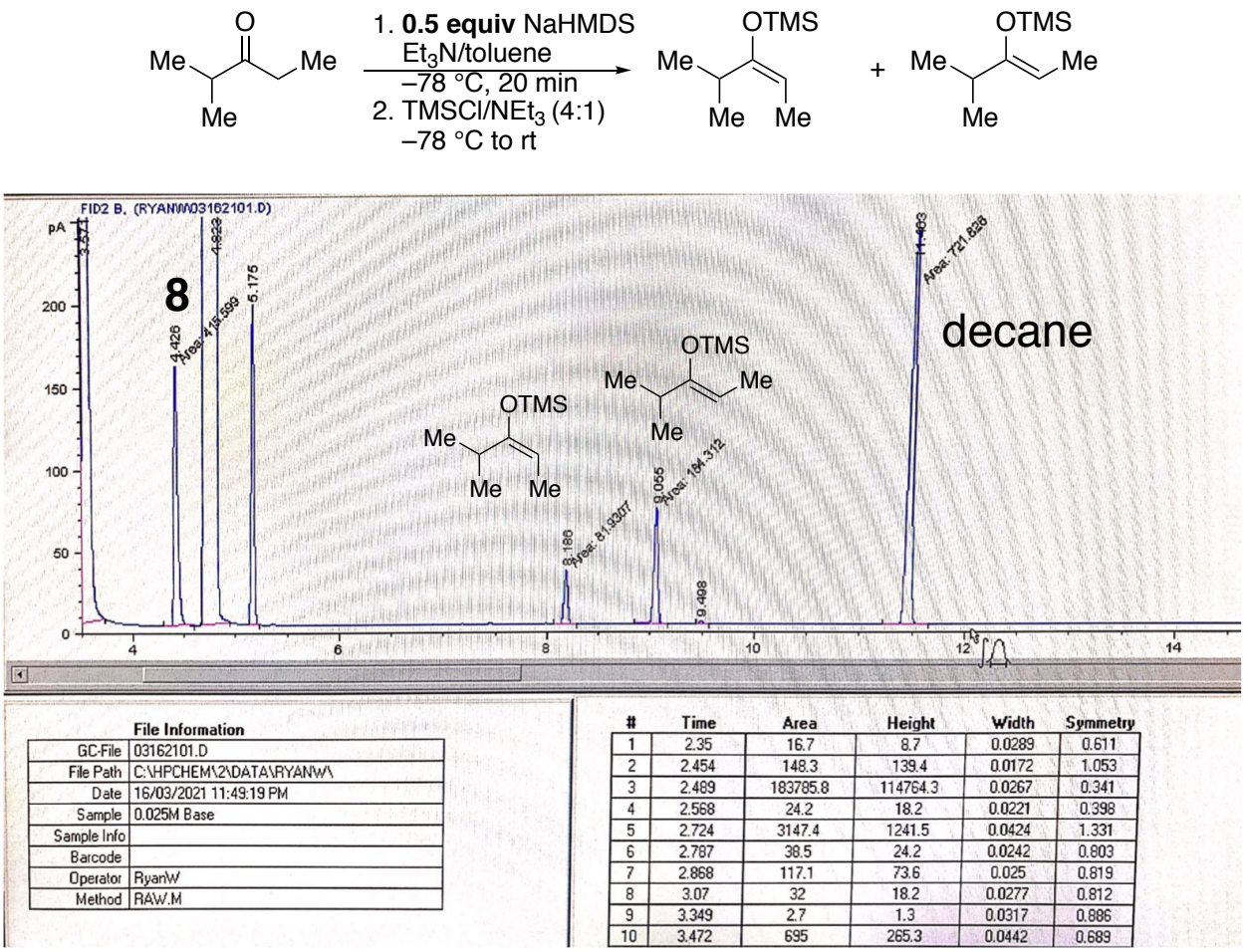


Figure S8. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in toluene using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 45 mins, standard aqueous workup, and dilution with pentane before loading sample.



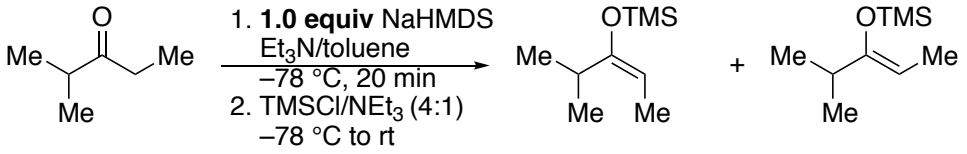
#	Time	Area	Height	Width	Symmetry
1	2.44	118.3	112.7	0.017	0.964
2	2.496	140725.3	115316.9	0.0182	0.414
3	2.592	28	21.9	0.0205	0.779
4	2.811	3603	2405.8	0.0239	1.803
5	2.891	38.1	25.4	0.0231	0.958
6	3.006	63	44.3	0.0222	0.843
7	3.272	22.2	14.1	0.0248	0.887
8	5.201	322.1	43.6	0.1232	1.829
9	9.314	234.5	98.6	0.0396	0.972

Figure S9. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 1.5 M diglyme with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 45 mins, standard aqueous workup, and dilution with pentane before loading sample.



#	Time	Area	Height	Width	Symmetry
1	2.35	16.7	8.7	0.0289	0.611
2	2.454	148.3	139.4	0.0172	1.053
3	2.489	183785.8	114764.3	0.0267	0.341
4	2.568	24.2	18.2	0.0221	0.398
5	2.724	3147.4	1241.5	0.0424	1.331
6	2.787	38.5	24.2	0.0242	0.803
7	2.868	117.1	73.6	0.025	0.819
8	3.07	32	18.2	0.0277	0.812
9	3.349	2.7	1.3	0.0317	0.886
10	3.472	695	265.3	0.0442	0.689

Figure S10. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.025 M NaHMDS in 4.0 M Et_3N with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 1 h, standard aqueous workup, and dilution with pentane before loading sample.



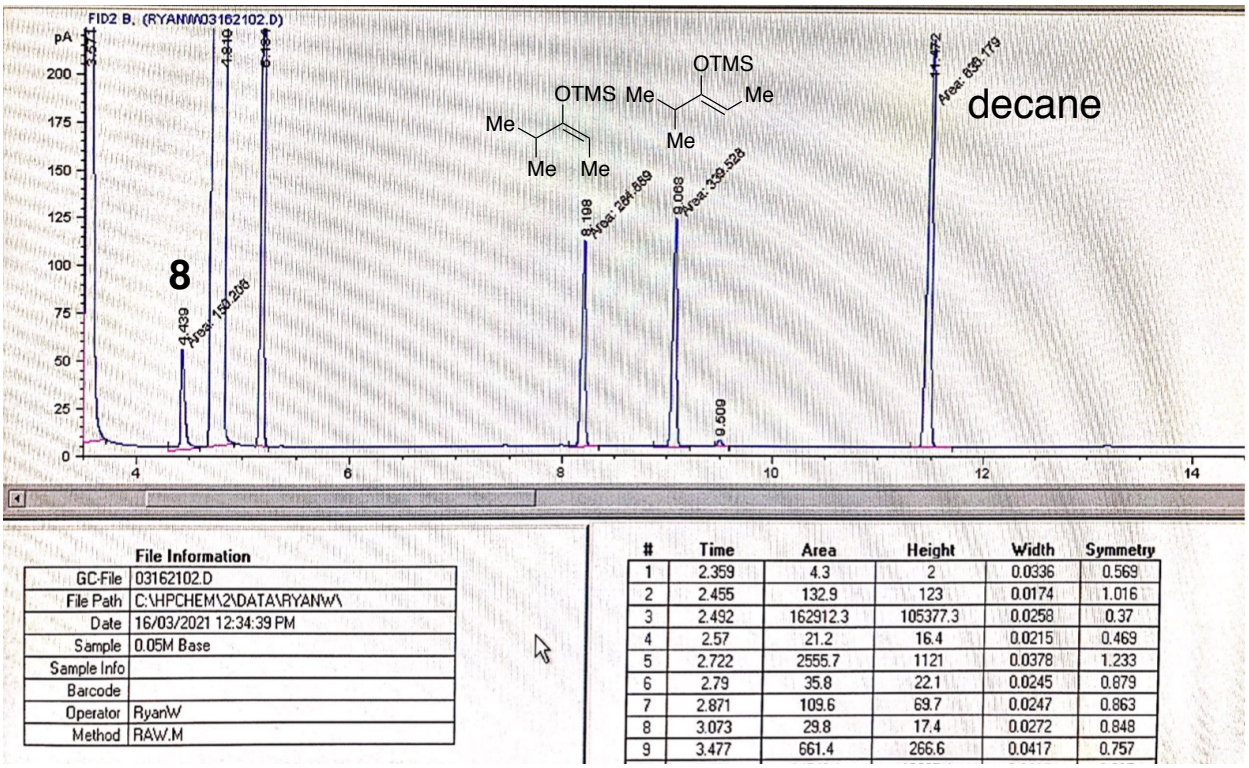
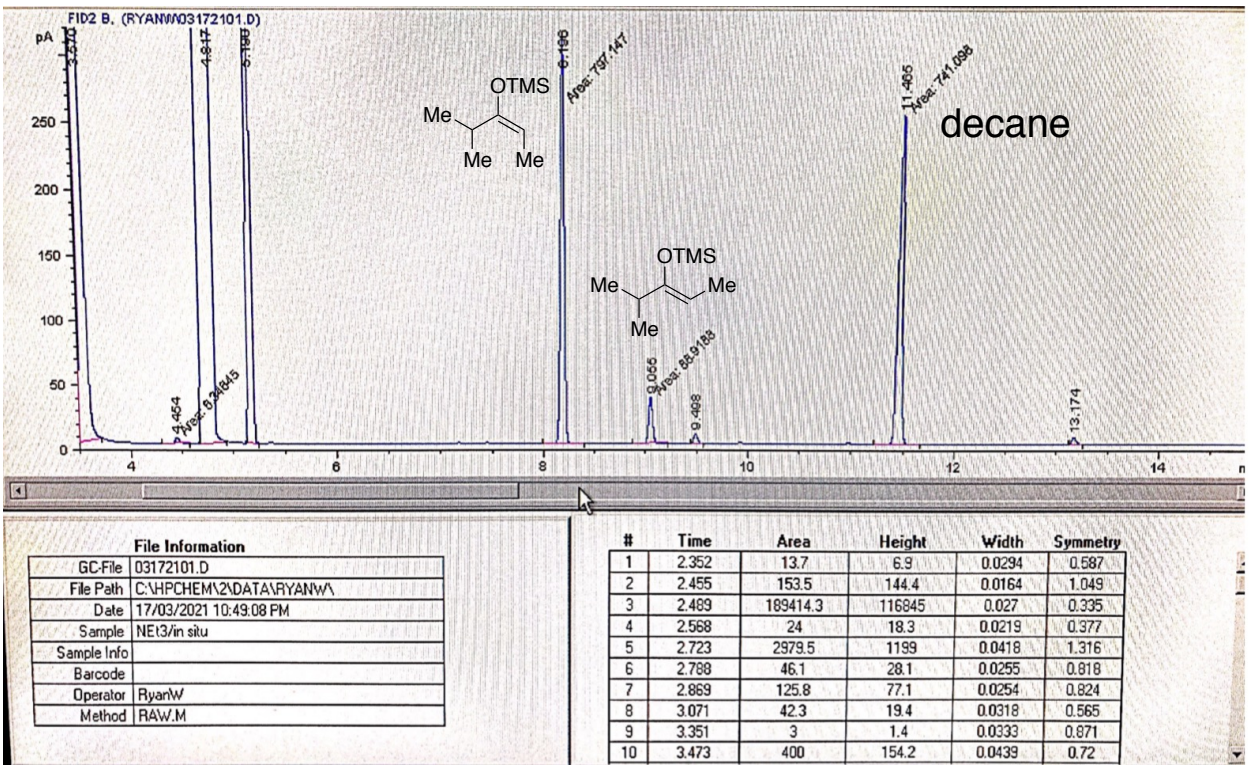


Figure S11. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.050 M NaHMDS in 4.0 M Et_3N with toluene cosolvent using decane as an internal standard at –78 °C. Samples for GC analysis were prepared by addition of TMSCl/Et_3N after 1 h, standard aqueous workup, and dilution with pentane before loading sample.



#	Time	Area	Height	Width	Symmetry
1	2.352	13.7	6.9	0.0294	0.587
2	2.455	153.5	144.4	0.0164	1.049
3	2.489	189414.3	116845	0.027	0.335
4	2.568	24	18.3	0.0219	0.377
5	2.723	2979.5	1199	0.0418	1.316
6	2.788	46.1	28.1	0.0255	0.818
7	2.869	125.8	77.1	0.0254	0.824
8	3.071	42.3	19.4	0.0318	0.565
9	3.351	3	1.4	0.0333	0.871
10	3.473	400	154.2	0.0439	0.72

Figure S12. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 4.0 M Et_3N with toluene cosolvent in the presence of 180 µL of 4:1 TMSCl/Et_3N using decane as an internal standard at –78 °C. Samples for GC analysis were prepared after stirring 1 h, standard aqueous workup, and dilution with pentane before loading sample.

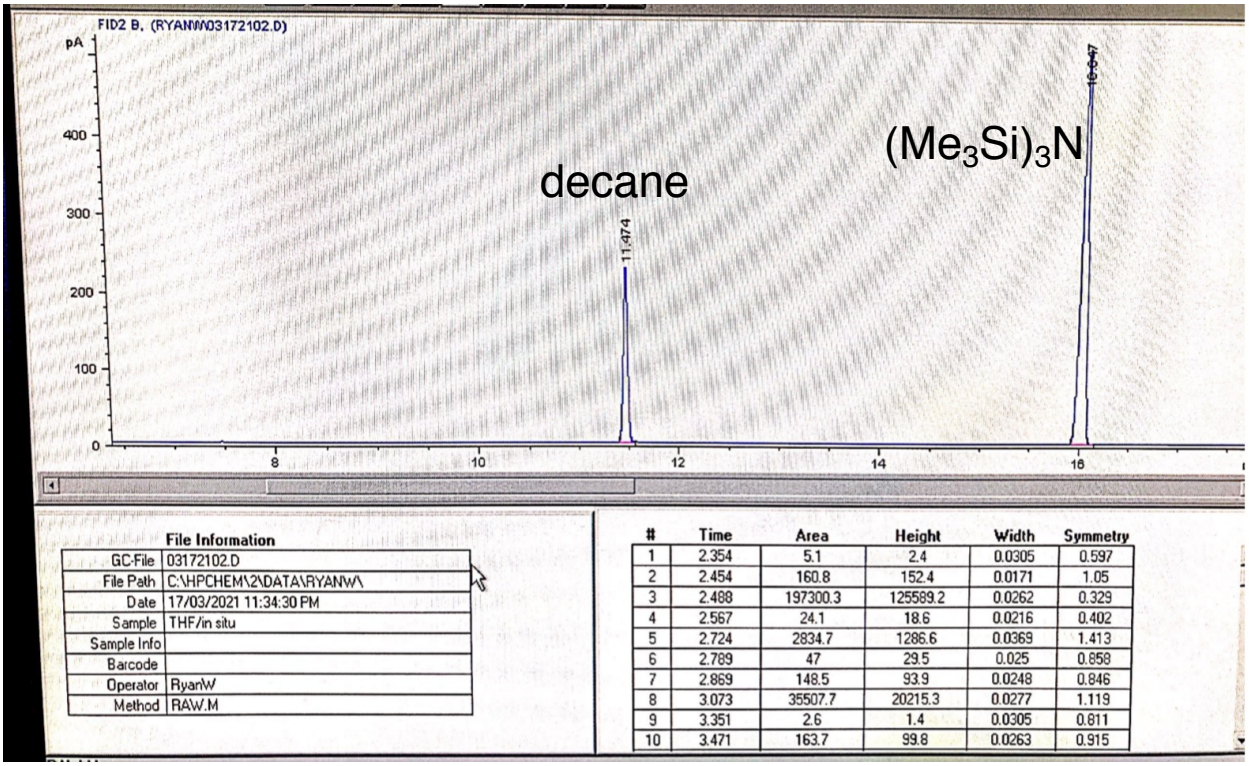
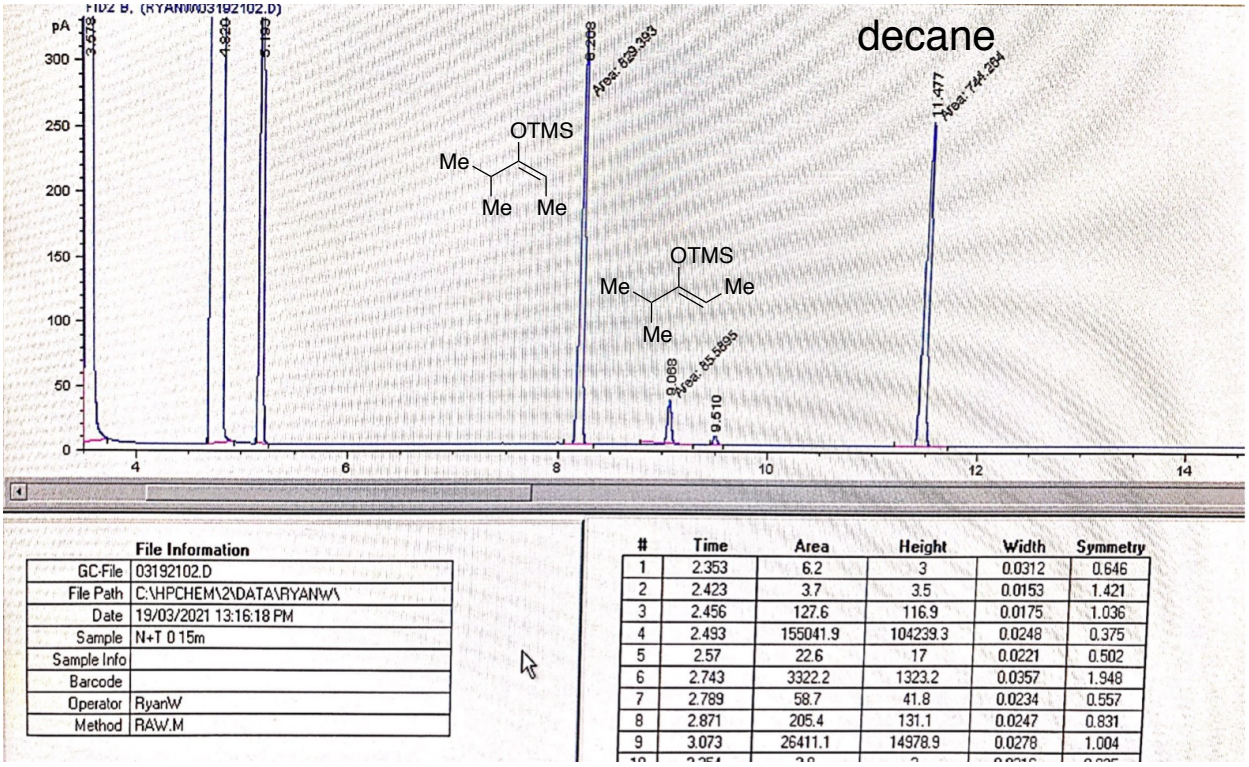


Figure S13. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in neat THF in the presence of 180 μL of 4:1 TMSCl/Et_3N using decane as an internal standard at –78 °C. Sample for GC analysis was prepared after stirring 1 h, a standard aqueous workup, and dilution with pentane before loading sample.



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Date	19/03/2021 13:16:18 PM
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Sample Info	
Barcode	
Operator	RyanW
Method	RAW.M

#	Time	Area	Height	Width	Symmetry
1	2.353	6.2	3	0.0312	0.646
2	2.423	3.7	3.5	0.0153	1.421
3	2.456	127.6	116.9	0.0175	1.036
4	2.493	155041.9	104239.3	0.0248	0.375
5	2.57	22.6	17	0.0221	0.502
6	2.743	3322.2	1323.2	0.0357	1.948
7	2.789	58.7	41.8	0.0234	0.557
8	2.871	205.4	131.1	0.0247	0.831
9	3.073	26411.1	14978.9	0.0278	1.004

Figure S14. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 4.0 M Et_3N with toluene cosolvent using decane as an internal standard. The reaction was allowed to stir for 1 h at –78 °C followed by the addition of 0.5 mL THF. The reaction was then brough to 0 °C immediately followed by stirring in an ice bath for 15 mins. Sample for GC analysis was prepared by a standard aqueous workup and dilution with pentane before loading sample.

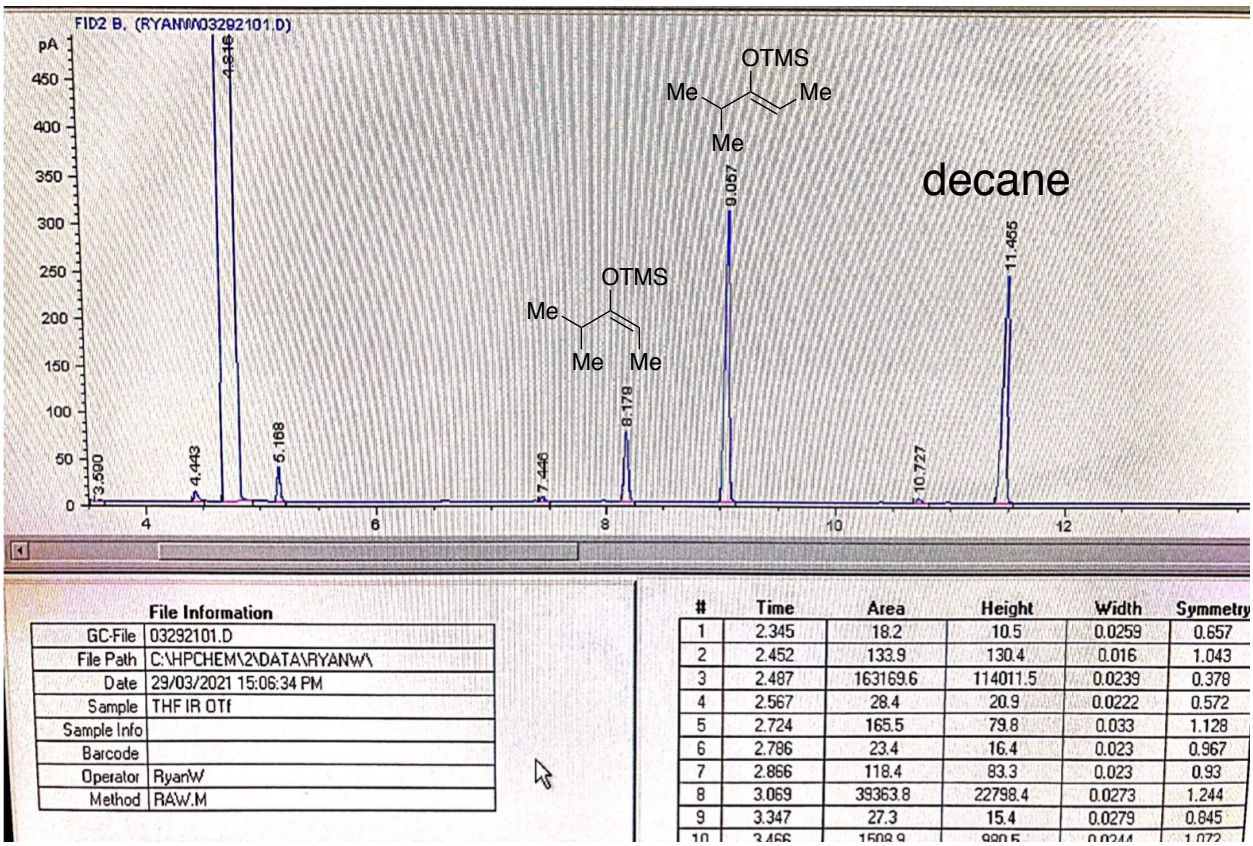


Figure S15. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in neat THF using decane as an internal standard at –78 °C. The reaction was followed using IR spectroscopy to ensure all starting ketone had been consumed before quenching the TMSOTf. After the complete disappearance of **8** (4 min), TMSOTf (200 μL) was added at –78 °C. Complete conversion of enolate to silyl enol ether was achieved after 1 min. The reaction was then brough to room temperature and allowed to stir for 15 mins. Sample for GC analysis was prepared by a standard aqueous workup and dilution with pentane before loading sample.

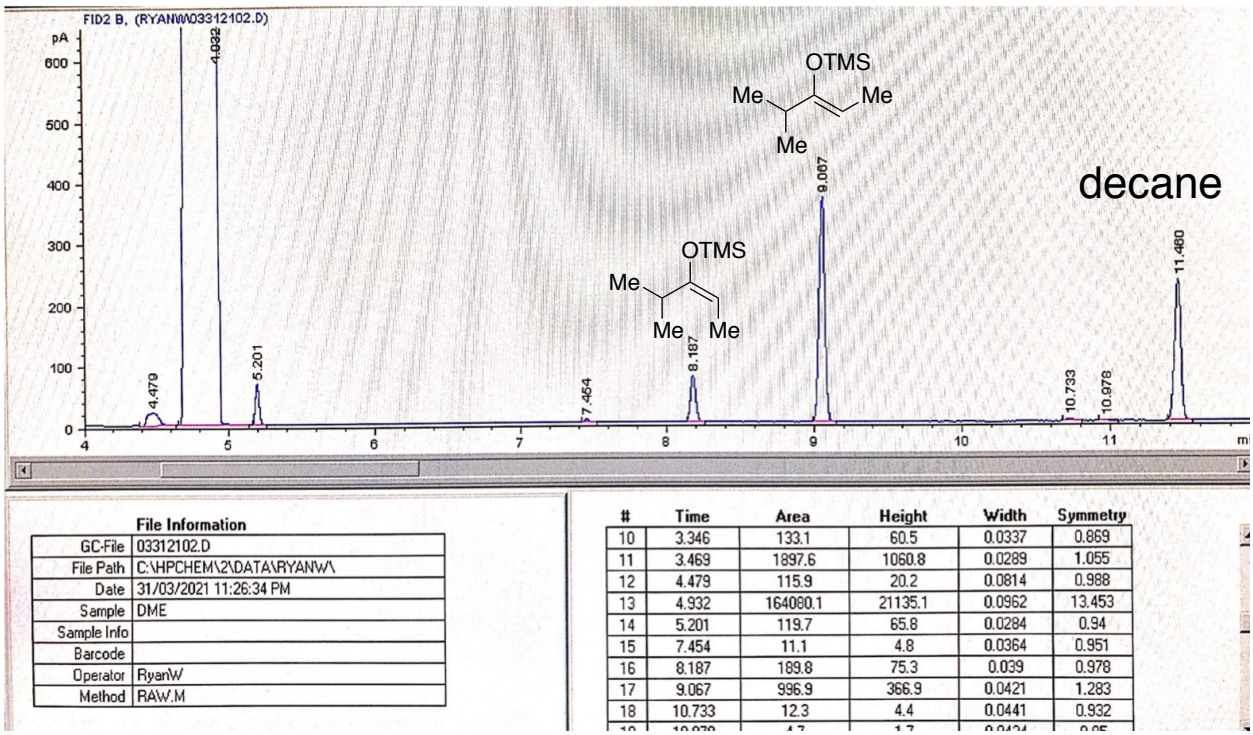


Figure S16. GC trace for the enolization of **8**-d_0 (0.050 M) by 0.15 M NaHMDS in 2.0 M DME using decane as an internal standard at –78 °C. The reaction was followed using IR spectroscopy to ensure all starting ketone had been consumed before quenching the TMSOTf. After the complete disappearance of **8**, TMSOTf (200 µL) was added at –78 °C. The reaction was then brough to room temperature and allowed to stir for 15 mins. Sample for GC analysis was prepared by a standard aqueous workup and dilution with pentane before loading sample.

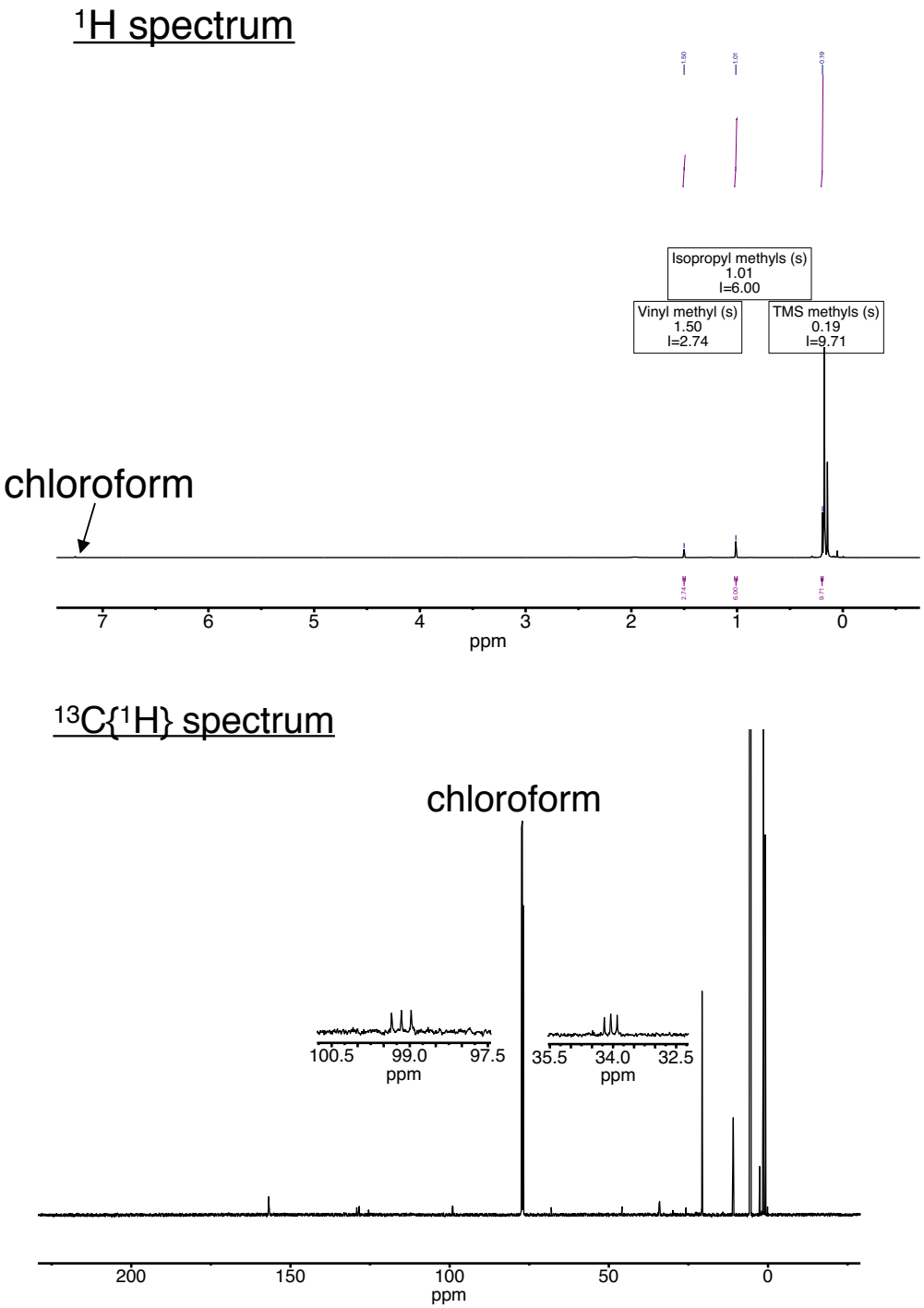


Figure S17. ^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (125 MHz) NMR spectra of the silyl enol ether resulting from the enolization of **8-***d*$_3$ (0.050 M) by 0.15 M NaHMDS in neat THF and 2.0 M hexamethyldisilazane with toluene cosolvent at –78 °C followed by the addition of TMSCl/Et_3N. The reaction was worked using standard aqueous washes, dried using Na_2SO_4, and solvent removed. The crude silyl enol ether was then dissolved in $CDCl_3$ and spectra were recorded. The insets shows clean deuterium retention.

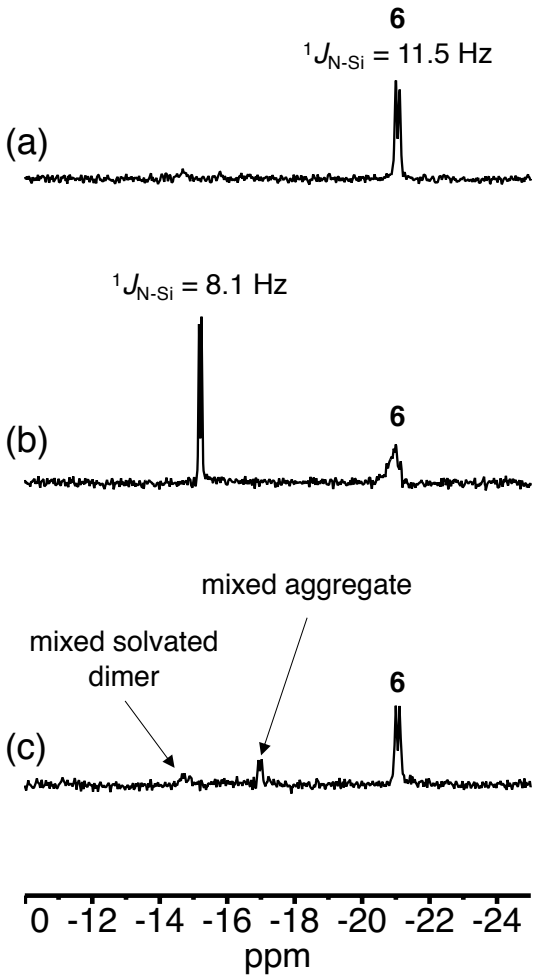


Figure S18. ^{29}Si {^{1}H} NMR spectra of showing (a) [^{15}N]NaHMDS (0.15 M) in 1.50 M TMEDA with toluene-d_8 cosolvent at –95 °C, (b) [^{15}N]NaHMDS (0.15 M) in 1.50 M TMEDA and 0.075 M DMPU with toluene-d_8 cosolvent at –95 °C, and (c) [^{15}N]NaHMDS (0.15 M) in 1.50 M TMEDA and 0.05 M **8**-d_3 with toluene-d_8 cosolvent at –95 °C.

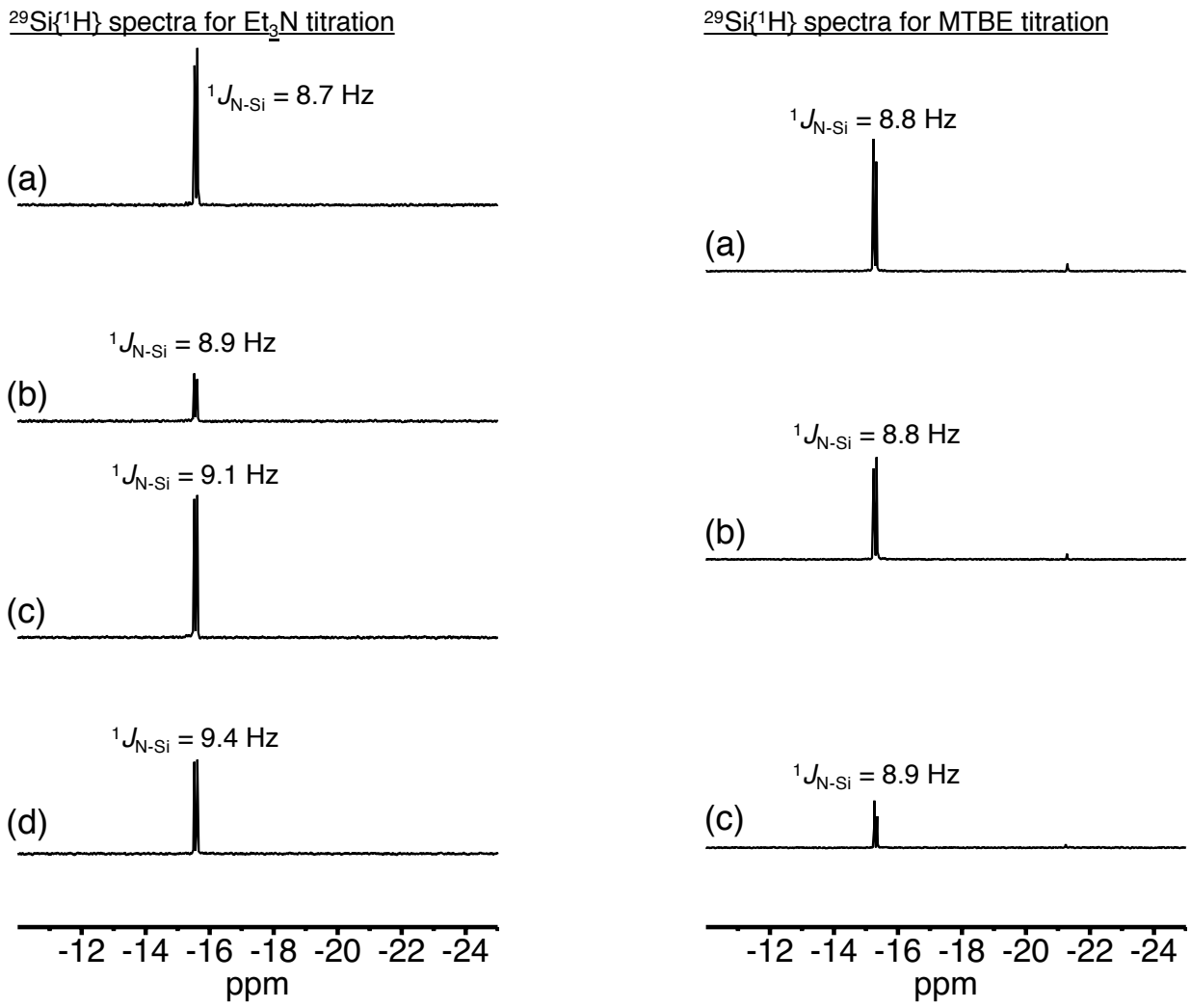


Figure S19. ^{29}Si {^{1}H} NMR spectra of titrating **8**-d_3 into an NMR tube that contains 0.10 M [^{15}N]NaHMDS in either 4.0 M Et_3N (spectra on the left) or 8.0 M MTBE (spectra on the right) with toluene-d_8 cosolvent at –100 °C. The number of equiv of **8**-d_3 for each spectra are as follows: Et_3N (a) 0.0 equiv (b) 0.5 equiv (c) 1.0 equiv and (d) 2.0 equiv; MTBE (a) 0.0 equiv (b) 0.5 equiv and (c) 1.5 equiv.

II. IR Spectroscopy Rate Studies

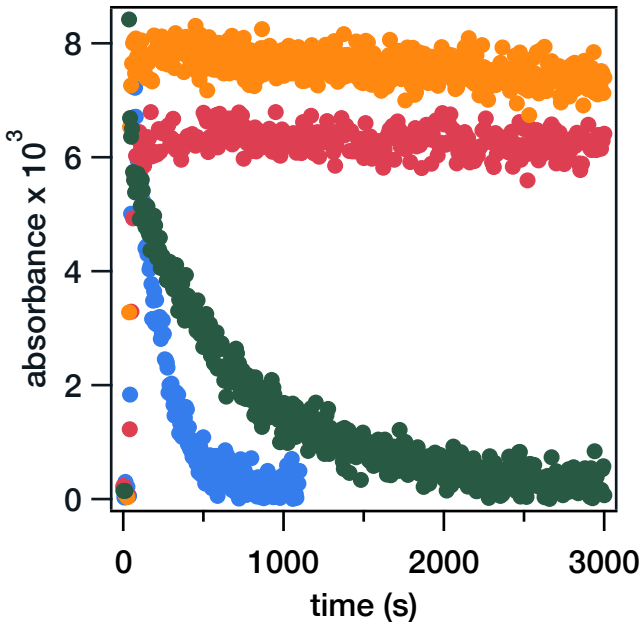


Figure S20. Plot of absorbance vs time (s) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS or LiHMDS (0.10 M) in either Et_3N or THF with toluene cosolvent at –78 °C measured with IR spectroscopy.

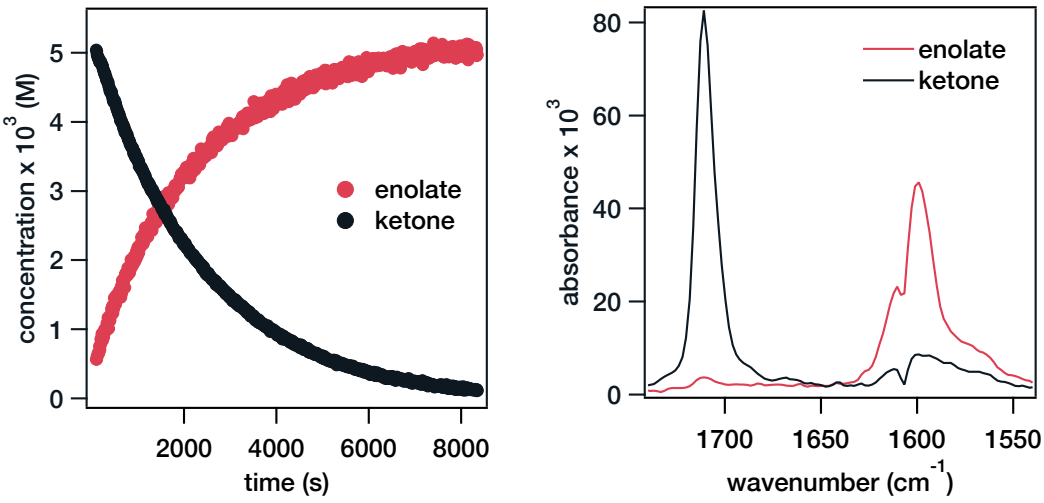


Figure S21. Emblematic enolization of **8**-d_0 (0.050 M; 1712 cm^{-1}) to form enolate **9**-d_2 (1599 cm^{-1}) by 0.15 M NaHMDS in 4.0 M Et_3N/toluene.

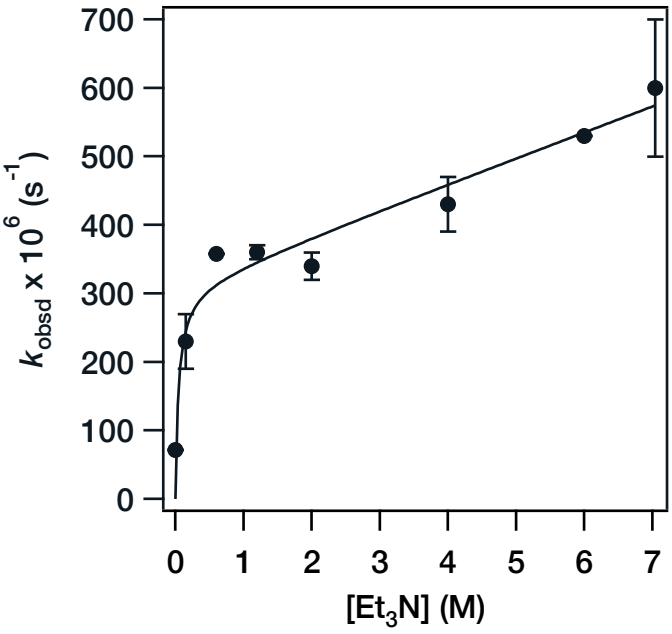


Figure S22. Plot of k_{obsd} vs [Et_3N] (M) for the enolization of 2-methyl-3-pentanone (**8**-d_0, 0.005 M) by NaHMDS (0.10 M) in toluene cosolvent at –78 °C measured with IR spectroscopy (1712 cm^{-1}). The curve is fit to the function described in the section title "Derivations".

[Et_3N] (M)	k_{obsd}^1 (s^{-1}) x 10^4	k_{obsd}^2 (s^{-1}) x 10^4	k_{obsd}^{avg} (s^{-1}) x 10^4
0.00	0.714*	–	0.714
0.15	2.63	2.08	2.3 ± 0.4
0.60	3.54	–	3.54
1.20	3.53	3.71	3.6 ± 0.1
2.00	3.54	3.27	3.4 ± 0.2
4.00	3.97	4.60	4.3 ± 0.5
6.00	5.3	–	5.3
7.04	4.97	6.53	6 ± 1

*Pseudo-first-order rate constant converted from initial rate

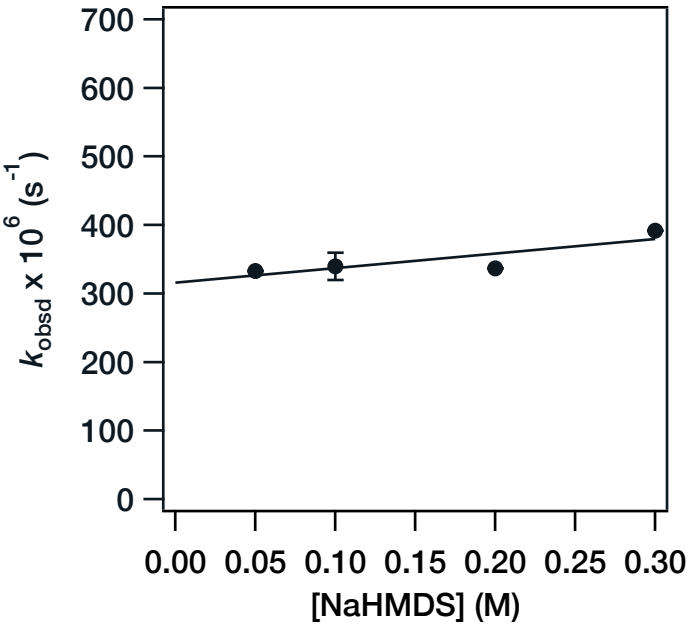


Figure S23. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone (**8**-d_0, 0.005 M) by NaHMDS in 2.0 M Et_3N with toluene cosolvent at –78 °C measured with IR spectroscopy (1712 cm^{-1}). The curve depicts an unweighted least-squares fit to y = ax + b [a = (2.1 ± 0.9) x 10^4; b = (3.2 ± 0.2) x 10^4].

[NaHMDS] (M)	k_{obsd}^1 (s^{-1}) x 10^4	k_{obsd}^2 (s^{-1}) x 10^4	k_{obsd}^{avg} (s^{-1}) x 10^4
0.05	3.33	–	3.33
0.10	3.54	3.27	3.4 ± 0.2
0.20	3.37	–	3.37
0.30	3.92	–	3.92

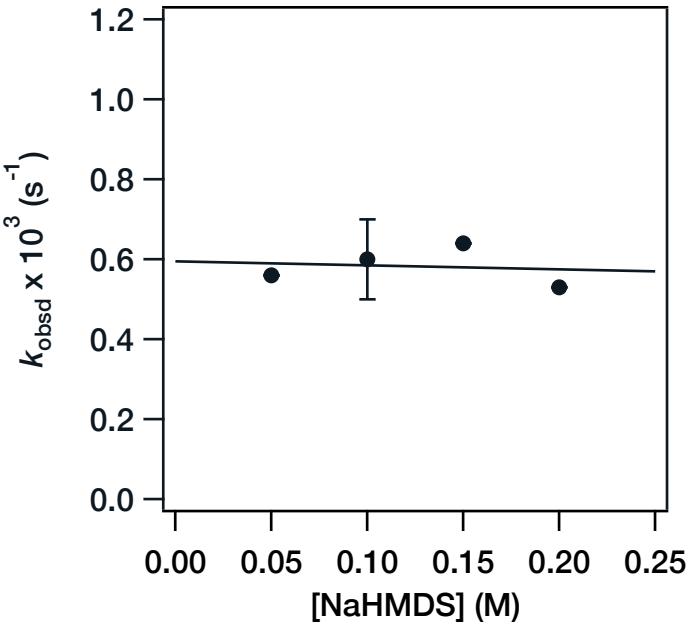


Figure S24. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone (**8**-d_0, 0.005 M) by NaHMDS in 7.04 M Et_3N with toluene cosolvent at –78 °C measured with IR spectroscopy (1712 cm^{-1}). The curve depicts an unweighted least-squares fit to y = ax + b [a = (–1 ± 5) x 10^4; b = (6.0 ± 0.7) x 10^4].

[NaHMDS] (M)	k_{obsd}^1 (s^{-1}) x 10^4	k_{obsd}^2 (s^{-1}) x 10^4	k_{obsd}^{avg} (s^{-1}) x 10^4
0.05	5.6	–	5.6
0.10	4.97	6.53	6 ± 1
0.15	6.4	–	6.4
0.20	5.3	–	5.3

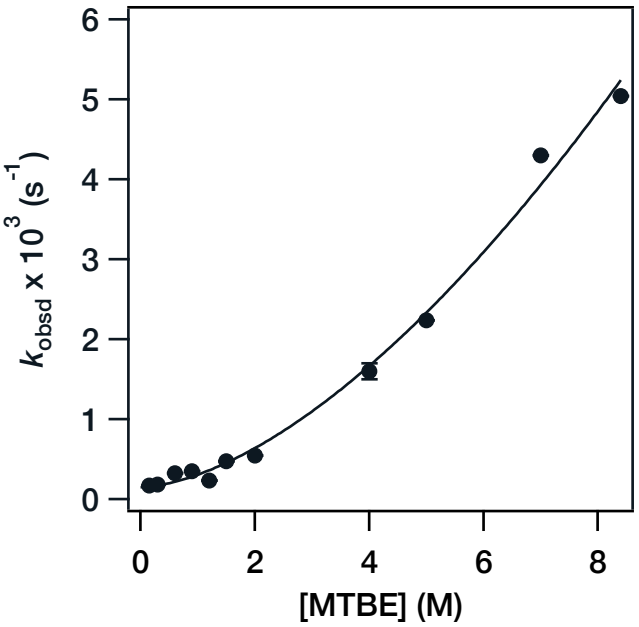


Figure S25. Plot of k_{obsd} vs [MTBE] (M) for the enolization of 2-methyl-3-pentanone (**8**-d_0, 0.005 M) by NaHMDS (0.10M) in toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b + c$ [$a = (1.9 \pm 0.5) \times 10^4$; $b = 1.6 \pm 0.1$; $c = (1.3 \pm 0.9) \times 10^4$].

[MTBE] (M)	k_{obsd}^1 (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
0.15	0.172*	–	0.172
0.30	0.182*	–	0.182
0.60	0.324*	–	0.324
0.90	0.350*	–	0.350
1.20	0.234*	–	0.234
1.50	0.474*	–	0.474
2.00	0.546*	–	0.546
4.00	1.51	1.76	1.6 ± 0.1
5.00	2.24	–	2.24
7.00	4.30	–	4.30
8.39	5.04	–	5.04

*Pseudo-first-order rate constant converted from initial rate

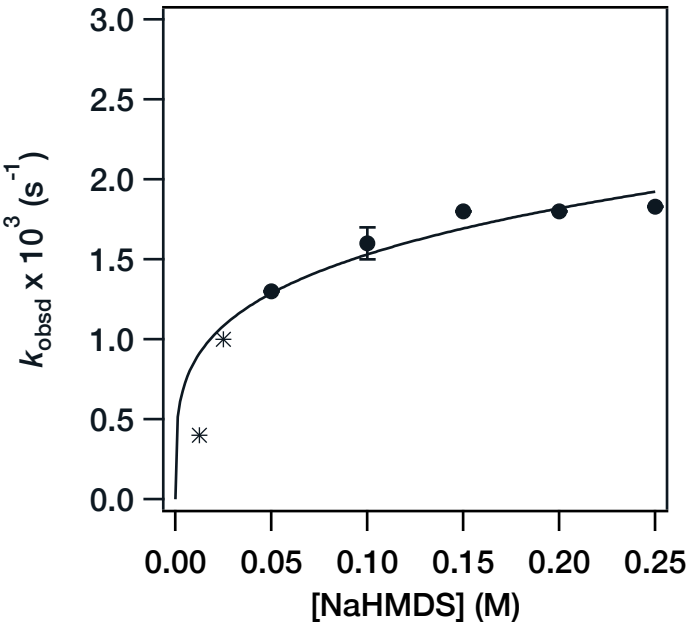


Figure S26. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone (**8**-d_0, 0.005 M) by NaHMDS in 4.0 M MTBE in toluene at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [$a = (2.7 \pm 0.2) \times 10^3$; $b = 0.25 \pm 0.03$]. The lowest concentration point (0.0125 M NaHMDS) is excluded from the fit due to the departure from pseudo-first-order conditions.

[NaHMDS] (M)	k_{obsd}^1 (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
*0.0125	0.40	–	0.40
*0.025	1.00	–	1.00
0.05	1.30	–	1.30
0.10	1.51	1.76	1.6 ± 0.1
0.15	1.80	–	1.80
0.20	1.80	–	1.80
0.25	1.83	–	1.83

*No longer under pseudo-first-order conditions.

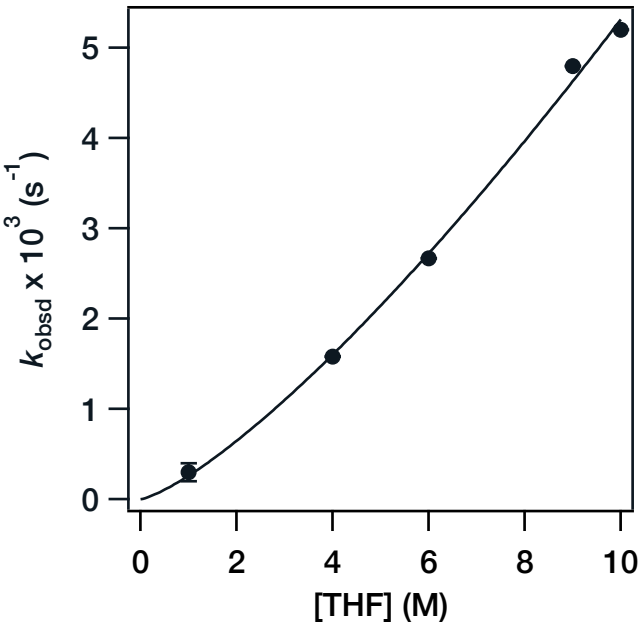


Figure S27. Plot of k_{obsd} vs [THF] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS (0.10 M) in toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [a = (0.26 ± 0.04) x 10^3; b = 1.31 ± 0.07].

[THF] (M)	k_{obsd}^1 (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
1.00	0.327*	0.222*	0.3 ± 0.1
4.00	1.58	–	1.58
6.00	2.67	–	2.67
9.00	4.80	–	4.80
10.00	5.20	–	5.20

*Pseudo-first-order rate constant converted from initial rate

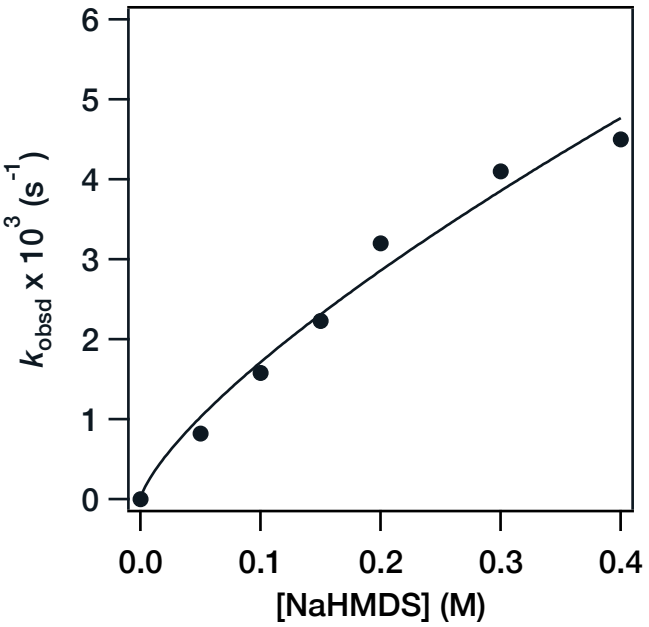


Figure S28. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS in 4.0M THF with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [$a = (9.4 \pm 0.9) \times 10^3$; $b = 0.74 \pm 0.07$].

[NaHMDS] (M)	k_{obsd} (s^{-1}) x 10^3
0.00	0
0.05	0.820
0.10	1.58
0.15	2.23
0.20	3.20
0.30	4.10
0.40	4.50

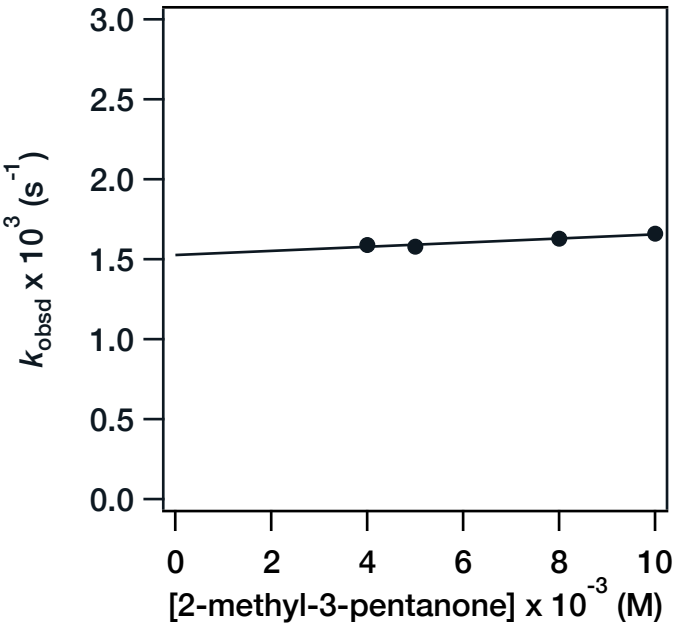


Figure S29. Plot of k_{obsd} vs [ketone] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3) by NaHMDS (0.10 M) in 4.0M THF with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to y = ax + b [a = 0.013 ± 0.003; b = (1.52 ± 0.02) x 10^3].

[ketone] (M)	k_{obsd} (s^{-1}) x 10^3
0.004	1.59
0.005	1.58
0.008	1.63
0.01	1.59

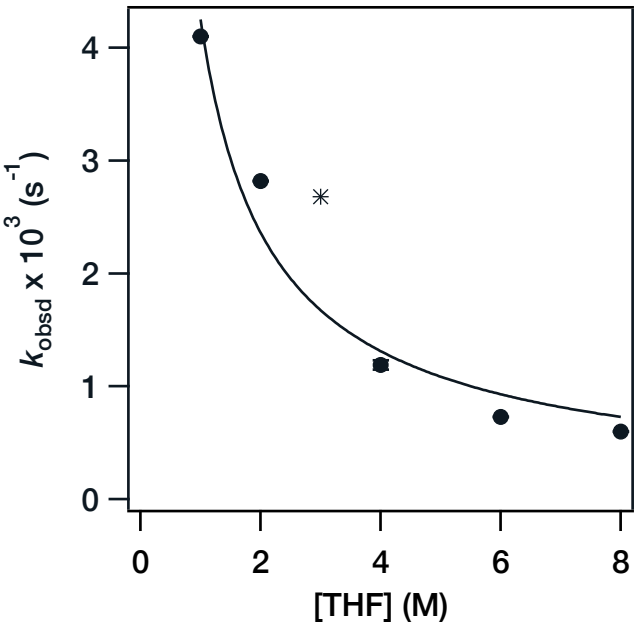


Figure S30. Plot of k_{obsd} vs [THF] (M) for the enolization of 2-methylcyclohexanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS (0.10 M) in THF with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [$a = (4.3 \pm 0.3) \times 10^3$; $b = -0.8 \pm 0.1$].

[THF] (M)	k_{obsd}^1 (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
1.00	4.10	–	4.10
2.00	2.82	–	2.82
3.00	2.68	–	2.68
4.00	1.22	1.17	1.19 ± 0.04
6.00	0.733	–	0.733
8.00	0.60	–	0.60

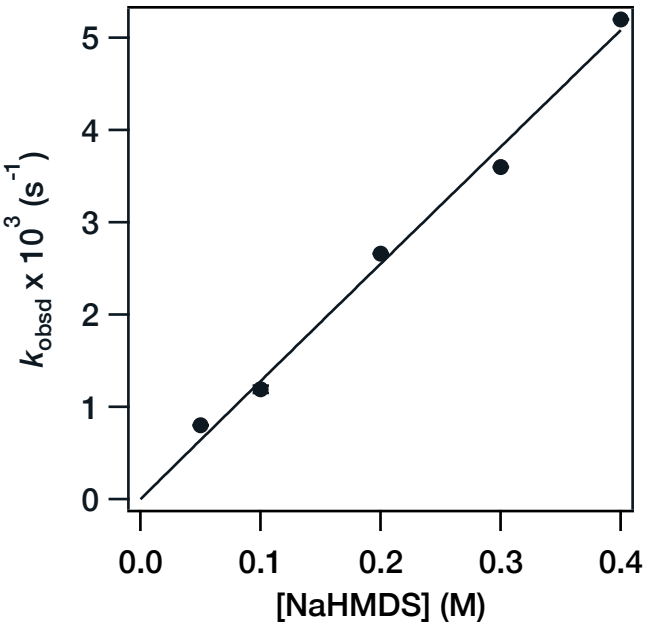


Figure S31. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methylcyclohexanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS in 4.0M THF with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [$a = 0.013 \pm 0.001$; $b = 0.99 \pm 0.07$].

[NaHMDS] (M)	k_{obsd} (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
0.05	0.800	–	0.800
0.10	1.22	1.17	1.19 ± 0.04
0.20	2.66	–	2.66
0.30	3.60	–	3.60
0.40	5.21	–	5.21

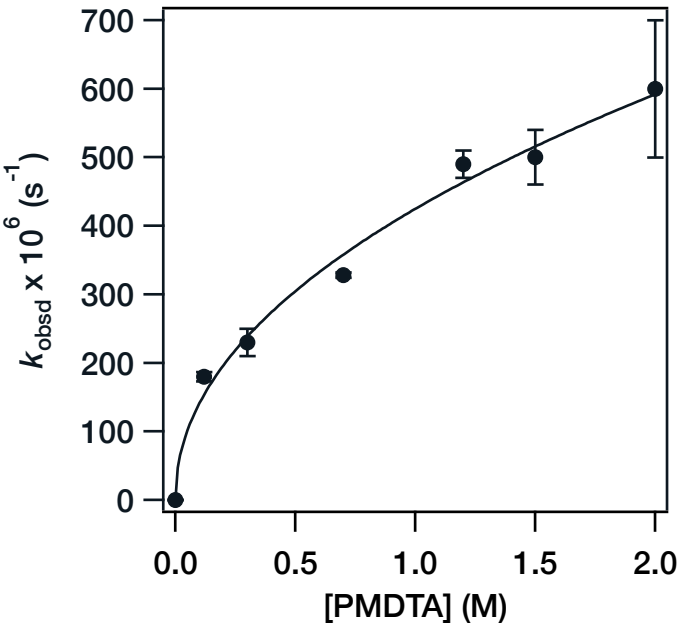


Figure 32. Plot of k_{obsd} vs [PMDTA] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS (0.10 M) with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [a =(4.1 ± 0.1) x 10^4; b = 0.48 ± 0.04].

[PMDTA] (M)	k_{obsd} (s^{-1}) x 10^4	k_{obsd}^2 (s^{-1}) x 10^4	k_{obsd}^{avg} (s^{-1}) x 10^4
0.00	0.0714	–	0.0714
0.12	1.85 ± 0.04	1.75 ± 0.03	1.80 ± 0.07
0.30	2.14 ± 0.02	2.45 ± 0.05	2.3 ± 0.2
0.70	3.30 ± 0.04	3.25 ± 0.08	3.28 ± 0.04
1.20	5.1 ± 0.1	4.8 ± 0.1	4.9 ± 0.2
1.50	5.3 ± 0.1	4.7 ± 0.1	5.0 ± 0.4
2.00	5.7 ± 0.2	7.3 ± 0.3	6 ± 1

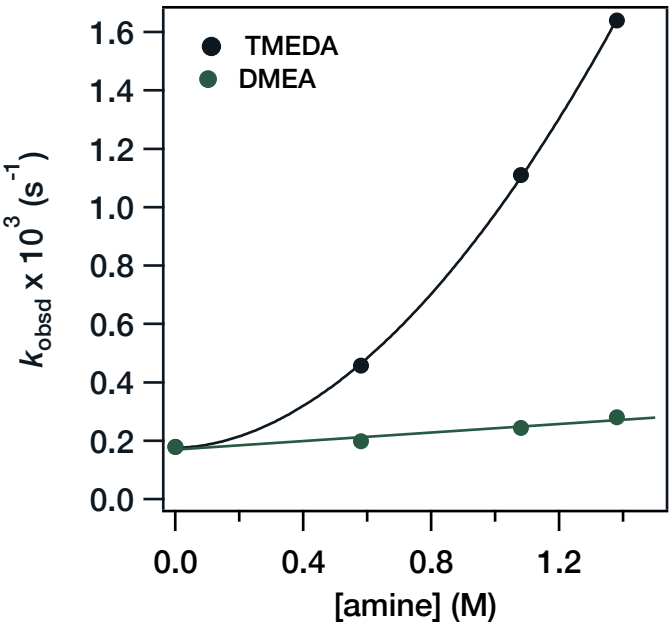


Figure 33. Plot of k_{obsd} vs [amine] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS (0.10 M) in 0.12 M PMDTA with toluene cosolvent at –78 °C measured with IR spectroscopy. The concentration of amine corresponds to the concentration of either TMEDA or DMEA. The TMEDA curve depicts an unweighted least-squares fit to $y = ax^b + c$ [$a = (8.0 \pm 0.2) \times 10^{-4}$; $b = 1.87 \pm 0.05$; $c = (1.8 \pm 0.1) \times 10^{-4}$]. The Me_2NEt curve depicts an unweighted least-squares fit to $y = ax + b$ [$a = (7 \pm 1) \times 10^{-5}$; $b = (1.7 \pm 0.1) \times 10^{-4}$].

[amine] (M)	TMEDA k_{obsd} (s^{-1}) x 10^4	DMEA k_{obsd} (s^{-1}) x 10^4
0.00	1.80	1.80
0.58	4.58	1.99
1.08	11.10	2.44
1.38	16.40	2.81

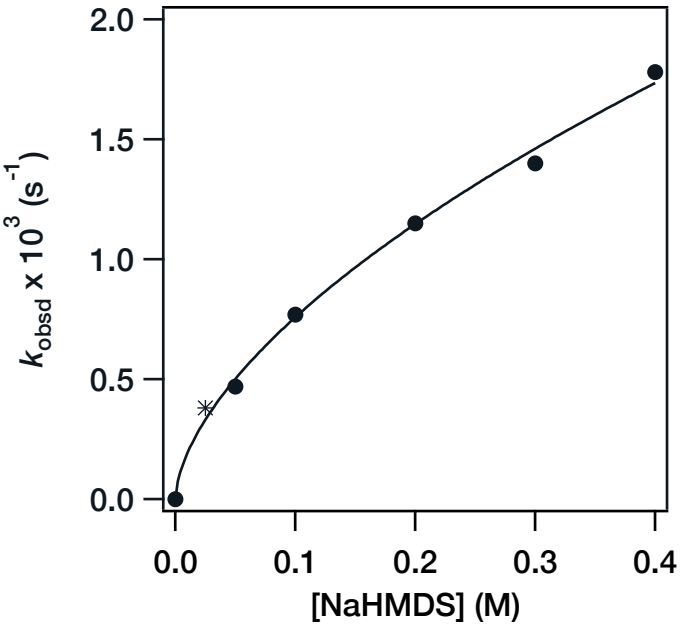


Figure S34. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS in 2.0 M PMDTA with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = ax^b$ [$a = (3.0 \pm 0.1) \times 10^3$; $b = 0.59 \pm 0.03$].

[NaHMDS] (M)	k_{obsd} (s^{-1}) x 10^3
0.00	0
0.025	0.38
0.05	0.47
0.10	0.77
0.20	1.15
0.30	1.40
0.40	1.78

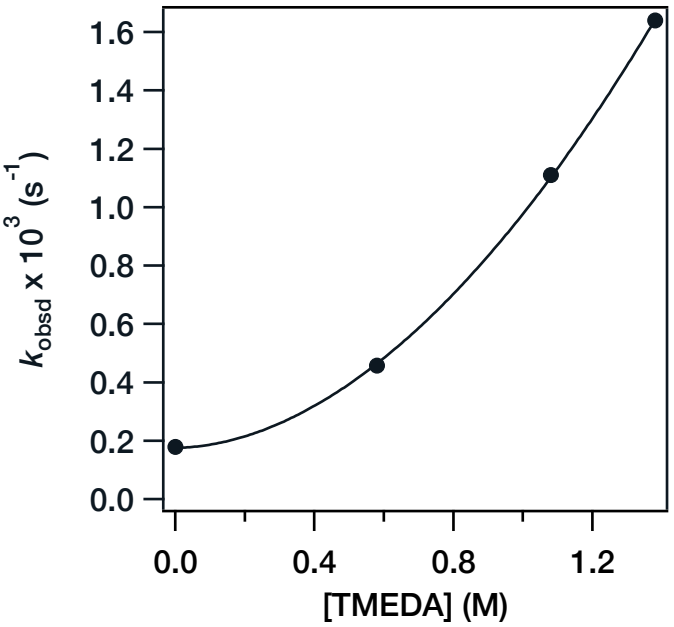


Figure S35. Plot of k_{obsd} vs [TMEDA] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS (0.10 M) in TMEDA and toluene cosolvent with 1.2 equiv PMDTA relative to [NaHMDS] at –78 °C measured with IR spectroscopy. The curve depicts a weighted least-squares fit to $y = ax^b$ [$a = 0.671 \pm 0.002$; $b = 2.067 \pm 0.003$].

[TMEDA] (M)	k_{obsd}^1 (s^{-1}) x 10^3	k_{obsd}^2 (s^{-1}) x 10^3	k_{obsd}^{avg} (s^{-1}) x 10^3
0.025	0.65	–	0.65
0.050	1.76	–	1.76
0150	13.30	–	13.30
0.200	17 ± 1	39 ± 5	30 ± 10

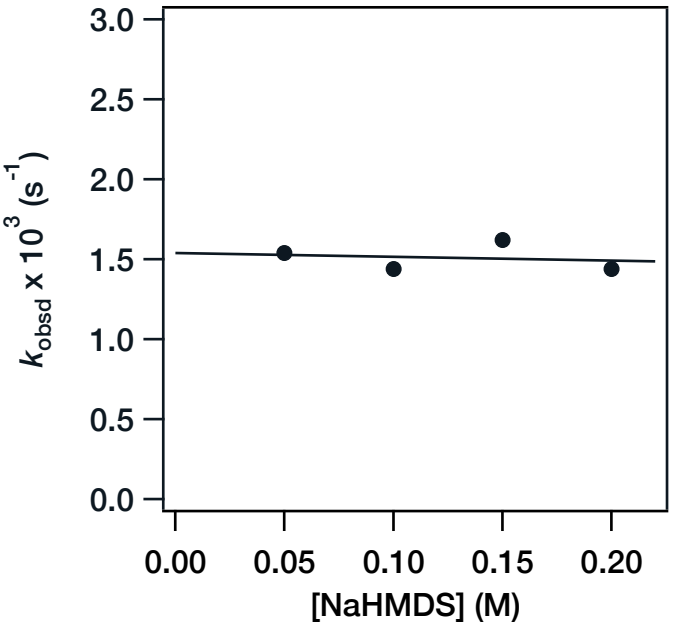


Figure 36. Plot of k_{obsd} vs [NaHMDS] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by NaHMDS in 0.75 M TMEDA with toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to y = ax + b [a = (3 ± 3) x 10^{-4} ; b = (1.57 ± 0.04) x 10^{-3}].

[NaHMDS] (M)	k_{obsd} (s^{-1}) x 10^3
0.05	1.54
0.10	1.57
0.15	1.50
0.20	1.51

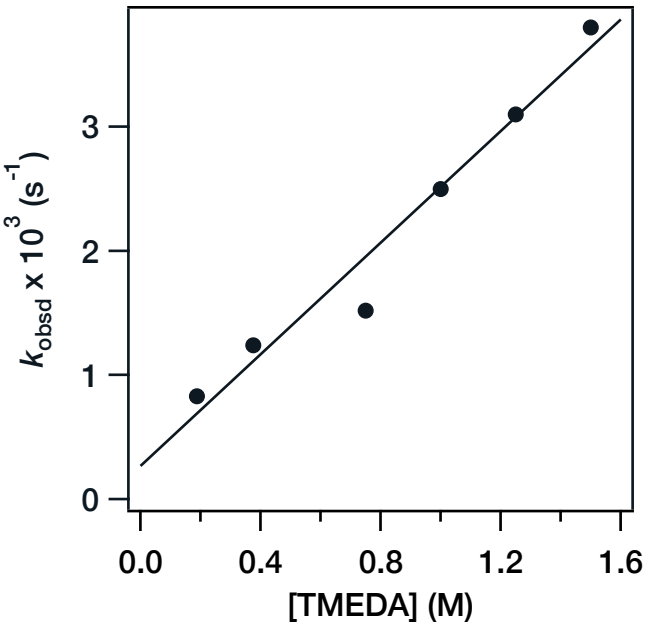


Figure 37. Plot of k_{obsd} vs [TMEDA] (M) for the enolization of 2-methyl-3-pentanone-d_3 (**8**-d_3, 0.005 M) by 0.10 M NaHMDS in toluene cosolvent at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to y = ax + b [a = (2.2 ± 0.2) x 10^{-3}; b = (3 ± 2) x 10^{-4}]. Fitting it to y = ax^n as an adjustable parameter gives an order n = 0.9 ± 0.1.

[TMEDA] (M)	k_{obsd} (s^{-1}) x 10^3
0.19	0.83
0.38	1.24
0.75	1.52
1.00	2.50
1.25	3.10
1.50	3.80

III. Derivations

Derivation 1. NaHMDS-mediated enolization: Et_3N order

The function derived to produce the fit above is based on (1) the basal rate of the toluene solvate, (2) the near quantitative displacement of toluene by Et_3N, and (3) the equilibrium between the di-ketone solvated dimer and the mixed Et_3N/ketone solvated dimer. Due to the quantitative binding of **8**-d_3 couple with being under pseudo-first-order conditions it can be assumed no free ketone is present. The equilibrium expressions and final fitting function are shown below.

$$\text{rate} = \text{toluene basal rate} + k_1[A_2NK] + k_2[A_2NK][Et_3N]$$

Where $[A_2NK]$ = Et_3N/ketone mixed solvated dimer.

The equilibrium expression below is derived from the toluene ([T] = toluene)/Et_3N equilibrium. Accounting for mass balance of the total ketone concentration $[K]_T$ one can solve for $[A_2NK]$ in terms of $[K]_T$ and $[Et_3N]$.

$$K_{eq} = [A_2NK][T]/[A_2TK][Et_3N] \quad (1)$$

$$[K]_T = [A_2NK] + [A_2TK] \quad (2)$$

Rearranging eq 2 gives:

$$[K]_T - [A_2NK] = [A_2TK] \quad (3)$$

Substituting eq 3 into eq 1 gives:

$$K_{eq} = [A_2NK][T]/([K]_T - [A_2NK])[Et_3N] \quad (4)$$

Solving for $[A_2NK]$ and assuming [T] is constant due to it being present in large excess gives:

$$[A_2NK] = [Et_3N][K]_T K_{eq} / 1 + [Et_3N]K_{eq} \quad (5)$$

Substituting eq 5 into the original rate equation above and inputting the known toluene basal rate gives the final fitting function:

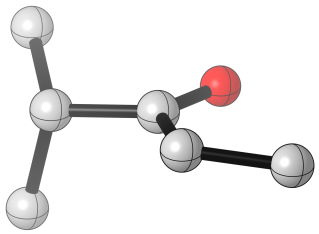
$$\text{rate} = (7.14 \times 10^{-5} + [Et_3N]K_{eq}\,(7.14 \times 10^{-5} + [K]_T\,(k_1 + k_2[Et_3N]))) / (1 + [Et_3N]K_{eq}) \quad (6)$$

IV. Computations

IV. Computations

DFT calculations were performed with the Gaussian 09 program package. Geometry optimizations and single point energies were computed at the M06-2X/def2-SVP level of theory and M06-2X/def2-TZVP level of theory respectively. A pruned (99,590) integration grid was used for all computations as well. CYLview Visualization Software was used for all ball-and-stick structures. Goodvibes (v3.0.1) was also used to streamline the extraction of thermochemical data. Thermal corrected single point energies (denoted as G(T)_SPC) are listed as well as other thermochemical data extracted using Goodvibes. For computed transition structures, the single imaginary frequency for each structure was extracted using Goodvibes and is included in the table as proof of a legitimate saddle point. All energies are in Hartrees and thermal corrections correspond to frequency calculations conducted at T = 195 K.

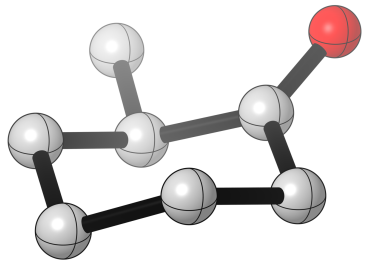
Table S1. Geometric coordinates and thermal corrected single point energies for 2-methyl-3-pentanone.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-311.0617	-310.70521	0.170173	-310.88636	0.024858	0.02444	-310.91122	-310.9108

Atom	X	Y	Z	Atom	X	Y	Z
C	1.1252130	0.2409210	0.4066130				
H	1.0398250	0.6811990	1.4140320				
C	-0.2558580	-0.2575240	-0.0081570				
C	-1.4504810	0.4637770	0.5863540				
H	-1.4417900	0.2424510	1.6682910				
H	-1.2689940	1.5493080	0.5147830				
C	-2.7679800	0.0590900	-0.0518320				
H	-2.9149990	-1.0254870	0.0313670				
H	-3.6143730	0.5692520	0.4262010				
H	-2.7713490	0.3037170	-1.1226800				
O	-0.3874450	-1.1659120	-0.7903760				
C	2.1338680	-0.9015880	0.4126020				
H	3.1392800	-0.5323510	0.6588070				
H	1.8587420	-1.6748830	1.1434360				
H	2.1605210	-1.3747880	-0.5783650				
C	1.5411320	1.3480060	-0.5723460				
H	1.6156370	0.9373430	-1.5901020				
H	0.8196380	2.1778730	-0.5892260				
H	2.5220640	1.7575790	-0.2929400				

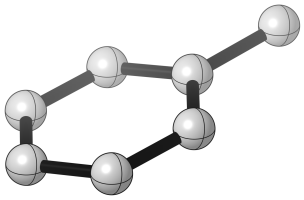
Table S2. Geometric coordinates and thermal corrected single point energies for 2-methyl-cyclohexanone.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-349.17404	-348.7793	0.179991	-348.98972	0.023135	0.023101	-349.01285	-349.01282

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-1.6223050	-1.1299090	0.0868430	H	-0.0468700	-1.3964450	-1.3688130
C	-1.9617780	0.3095390	-0.2955480	H	0.0683440	-2.4988430	0.0079380
C	-0.9972490	1.2994560	0.3704190	H	-1.1384630	1.2606650	1.4645150
C	0.4479860	0.9344210	0.0826240	O	1.2365780	1.7258580	-0.3696200
C	0.8290210	-0.5089960	0.3947820	C	2.2704160	-0.8006910	0.0113900
C	-0.1762910	-1.4634060	-0.2742330	H	2.9586140	-0.1064790	0.5101540
H	-1.1617090	2.3329230	0.0396190	H	2.5440770	-1.8303550	0.2809390
H	-1.8898430	0.4195960	-1.3903400	H	2.4085760	-0.6735320	-1.0719410
H	-2.9980090	0.5544490	-0.0207790				
H	-1.7686860	-1.2650010	1.1725980				
H	-2.3089190	-1.8287490	-0.4134370				
H	0.7014630	-0.6175770	1.4888380				

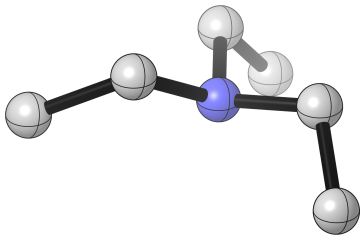
Table S3. Geometric coordinates and thermal corrected single point energies for toluene.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-271.53438	-271.23533	0.128724	-271.40194	0.022077	0.021686	-271.42402	-271.42363

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.4199700	0.0001370	0.0094220				
C	0.9133230	0.0003670	-0.0119040				
C	0.1953080	-1.2010320	-0.0090820				
C	-1.1984960	-1.2041830	0.0021120				
C	-1.9016160	-0.0002670	0.0084730				
C	-1.1991070	1.2038450	0.0021090				
C	0.1948480	1.2013150	-0.0090800				
H	0.7380160	2.1492950	-0.0181460				
H	-1.7393190	2.1521350	0.0021330				
H	-2.9926080	-0.0005390	0.0143450				
H	-1.7383390	-2.1526870	0.0021330				
H	0.7389200	-2.1487830	-0.0181610				
H	2.7962350	-0.0161780	1.0442130				
H	2.8258640	-0.8824340	-0.5032250				
H	2.8258480	0.8981050	-0.4755900				

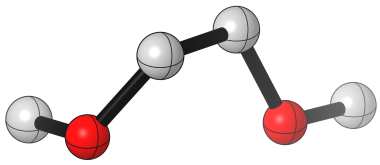
Table S4. Geometric coordinates and thermal corrected single point energies for triethylamine.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-292.36645	-292.03338	0.206426	-292.15473	0.024956	0.024794	-292.17969	-292.17953

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3428320	0.3788900	0.4447400	H	0.0341600	-2.2777240	-1.4810030
N	-0.0000020	0.0000430	0.0292400	H	-1.9811410	-0.5150910	0.3952010
C	0.9994960	0.9736150	0.4445480	H	-1.3525000	0.7017650	1.5098560
H	0.5444500	1.9733820	0.3945760	C	-1.9561180	1.4559910	-0.4392370
H	1.2837780	0.8208640	1.5097520	H	-2.9781020	1.6931880	-0.1112760
C	2.2391170	0.9658090	-0.4391700	H	-1.3751730	2.3889020	-0.4135900
H	2.9555350	1.7322610	-0.1111940	H	-1.9897120	1.1088200	-1.4810100
H	2.7564110	-0.0038350	-0.4130810				
H	1.9555780	1.1682290	-1.4810810				
C	0.3434160	-1.3523100	0.4445960				
H	1.4367600	-1.4581300	0.3945980				
H	0.0690520	-1.5221110	1.5098200				
C	-0.2830800	-2.4219900	-0.4391340				
H	0.0223940	-3.4256490	-0.1110670				
H	-1.3814650	-2.3851970	-0.4132420				

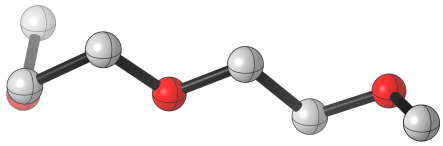
Table S5. Geometric coordinates and thermal corrected single point energies for 1,2-dimethoxyethane (DME).



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-308.83597	-308.47134	0.142981	-308.68841	0.023239	0.0231	-308.71165	-308.71151

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.8545320	1.0807780	-0.0333880	H	-2.3453150	-1.1869650	0.8423880
H	1.4082410	1.5961330	0.7787710	H	-2.9043750	-1.0569690	-0.8538690
H	0.6933360	1.8015900	-0.8470190	O	1.6140040	0.0440770	-0.5803980
C	-0.4922100	0.6499760	0.5210180	C	1.8299410	-1.0406890	0.2708620
H	-0.3631990	0.0258080	1.4291910	H	2.5777850	-1.6888460	-0.2031870
H	-1.0482120	1.5558250	0.8379540	H	2.2191200	-0.7216180	1.2575770
O	-1.1877530	-0.0582110	-0.4594400	H	0.9098240	-1.6307360	0.4289980
C	-2.4357060	-0.5086350	-0.0274660				
H	-3.0965540	0.3302800	0.2617460				

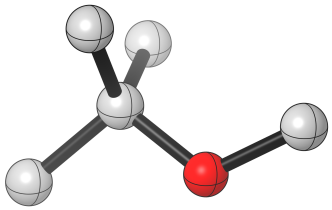
Table S6. Geometric coordinates and thermal corrected single point energies for diglyme.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-462.66143	-462.11801	0.205076	-462.44977	0.029049	0.028168	-462.47882	-462.47794

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.5518820	0.9555020	-0.3165470	O	-3.1662040	-0.7330100	0.1769020
H	3.3256950	1.4871730	0.2751590	C	-4.0359690	0.3285350	-0.0920210
H	2.4105220	1.5000100	-1.2605470	H	-4.2227440	0.4324610	-1.1767160
C	1.2557620	0.9885800	0.4744360	H	-4.9885380	0.1150090	0.4086460
H	1.3991070	0.5585950	1.4860960	H	-3.6567330	1.2958290	0.2841660
H	0.9567660	2.0461690	0.6189120	O	2.9805500	-0.3258760	-0.6693740
O	0.2766470	0.2742170	-0.2198280	C	3.1215370	-1.2144540	0.3981120
C	-0.9563050	0.2246470	0.4374950	H	3.6327440	-2.1081760	0.0188110
H	-1.3617120	1.2453200	0.5877830	H	3.7306280	-0.7839770	1.2167830
H	-0.8605200	-0.2394720	1.4385500	H	2.1446870	-1.5229410	0.8110630
C	-1.9023340	-0.6098980	-0.4127050				
H	-1.9658070	-0.1670870	-1.4242990				
H	-1.4794720	-1.6190270	-0.5186280				

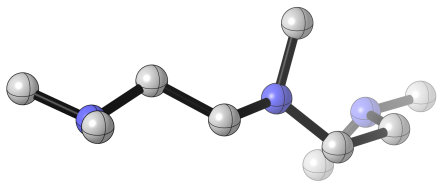
Table S7. Geometric coordinates and thermal corrected single point energies for MTBE.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-272.94329	-272.62633	0.16431	-272.77491	0.021788	0.021812	-272.7967	-272.79673

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.0151930	-0.0000340	-0.1524300	H	-0.3261930	2.1527210	0.2493820
H	2.1680520	0.8953560	0.4757110	H	-1.4374530	1.3240370	1.3750840
H	2.1676800	-0.8949840	0.4764320	C	-0.4610360	-1.2597340	0.8747900
O	0.7780070	-0.0000200	-0.8005840	H	-1.4381980	-1.3245860	1.3740070
C	-0.3938030	0.0000030	0.0075160	H	-0.3277170	-2.1529850	0.2473180
C	-1.5345800	0.0008250	-1.0039380	H	0.3112990	-1.2619400	1.6573560
H	-2.5104760	0.0007890	-0.4988920	H	2.7863910	-0.0005120	-0.9335200
H	-1.4610540	0.8911200	-1.6436950				
H	-1.4614830	-0.8888250	-1.6446410				
C	-0.4602520	1.2589600	0.8759730				
H	0.3119580	1.2598530	1.6586670				

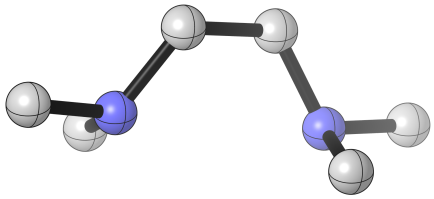
Table S8. Geometric coordinates and thermal corrected single point energies for PMDTA.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-520.95411	-520.3614	0.326472	-520.61974	0.031585	0.030796	-520.65132	-520.65053

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.6833450	-0.8495710	-0.3928530	H	-1.6367970	1.1773270	0.6878120
H	3.2989410	-1.1266260	-1.2809410	N	-3.3218030	0.4562360	-0.2956520
H	2.9230330	-1.5917790	0.3863840	C	-4.1714280	1.4056090	0.3862310
C	1.2199890	-0.9883810	-0.8035260	H	-5.0526770	1.6322550	-0.2309760
H	1.0584520	-0.4875470	-1.7719120	H	-4.5308690	1.0320940	1.3711990
H	1.0318590	-2.0728530	-0.9818120	H	-3.6248230	2.3434830	0.5592770
N	0.2743120	-0.4290910	0.1413170	C	-4.0405990	-0.7597630	-0.6056820
C	0.4679140	-0.9189630	1.4894820	H	-4.3430170	-1.3218340	0.3069280
H	-0.2552300	-0.4486120	2.1684550	H	-4.9514370	-0.5176710	-1.1715430
H	0.3415250	-2.0227500	1.5663810	H	-3.4300690	-1.4267990	-1.2291420
H	1.4706880	-0.6420920	1.8383050	N	3.0391550	0.4562450	0.1189160
C	-1.0837670	-0.6057560	-0.3358280	C	4.4337430	0.5068040	0.4880520
H	-1.3630530	-1.6846760	-0.3455120	H	5.1158940	0.3797300	-0.3824810
H	-1.1321730	-0.2510200	-1.3779180	H	4.6644970	1.4719280	0.9613350
C	-2.1054390	0.2081860	0.4552410	H	4.6612410	-0.2905080	1.2111100
H	-2.3377160	-0.2858710	1.4269520	C	2.6697610	1.5398530	-0.7636740
H	1.5790210	1.5664120	-0.8838500	H	2.9828230	2.4947980	-0.3181560
				H	3.1471210	1.4607710	-1.7666180

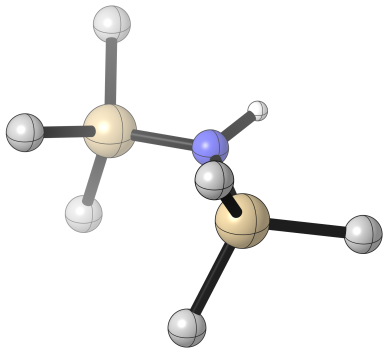
Table S9. Geometric coordinates and thermal corrected single point energies for TMEDA.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-347.69984	-347.30314	0.223895	-347.47051	0.025188	0.025127	-347.49569	-347.49563

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.7069220	0.2873500	0.9881320	N	1.4485050	0.0487130	-0.2313130
H	1.2314030	-0.1316470	1.8791130	C	2.7719560	0.6196240	-0.1542410
H	0.6634400	1.3778250	1.1455430	H	3.4050490	0.1394900	0.6255850
C	-0.7069200	-0.2873500	0.9881310	H	3.2859930	0.5139230	-1.1202870
H	-0.6634390	-1.3778260	1.1455420	H	2.7063940	1.6921760	0.0813530
H	-1.2314020	0.1316460	1.8791130	C	1.4765480	-1.3414990	-0.6259150
N	-1.4485050	-0.0487120	-0.2313130	H	2.0665940	-1.4462320	-1.5474700
C	-1.4765500	1.3415010	-0.6259150	H	1.9342340	-2.0004390	0.1464550
H	-2.0665920	1.4462310	-1.5474730	H	0.4568220	-1.6871560	-0.8389570
H	-1.9342410	2.0004380	0.1464530				
H	-0.4568250	1.6871580	-0.8389540				
C	-2.7719550	-0.6196250	-0.1542410				
H	-3.4050460	-0.1394960	0.6255900				
H	-3.2859950	-0.5139210	-1.1202840				
H	-2.7063920	-1.6921780	0.0813490				

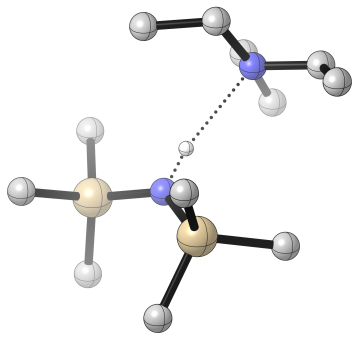
Table S10. Geometric coordinates and thermal corrected single point energies for hexamethyldisilazane.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-873.89676	-873.34731	0.238269	-873.64974	0.03226	0.031787	-873.682	-873.68152

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	0.0000050	-0.0050370	-1.8490480	H	-2.8287040	-0.0800080	-2.2510600
N	-0.0000720	-0.0015390	-0.8322730	C	-2.0795720	-1.7058960	0.5101990
Si	-1.5821150	0.0083800	-0.0889400	H	-1.3726200	-2.0777250	1.2670530
Si	1.5820250	-0.0085280	-0.0889760	H	-2.0837260	-2.4224570	-0.3250230
C	-1.5723170	1.1846380	1.3807820	H	-3.0846200	-1.6976450	0.9594890
H	-0.8349240	0.8807770	2.1400220	C	2.0796060	1.7078920	0.5037640
H	-2.5582610	1.2069090	1.8695320	H	3.0845690	1.7009450	0.9532680
H	-1.3242670	2.2071130	1.0585420	H	1.3726640	2.0827460	1.2591270
C	-2.8172520	0.5935680	-1.3802020	H	2.0841550	2.4213380	-0.3341120
H	-2.5699870	1.6056240	-1.7335790	C	1.5728200	-1.1795370	1.3849890
H	-3.8361690	0.6163900	-0.9654030	H	2.5589310	-1.1999140	1.8735060
H	3.8359460	-0.6196090	-0.9638050	H	1.3249740	-2.2031760	1.0662830
H	2.8277900	0.0709260	-2.2521110	H	0.8355730	-0.8733500	2.1434310
H	2.5696250	-1.6124340	-1.7270300	C	2.8168490	-0.5987590	-1.3782580

Table S11. Geometric coordinates and thermal corrected single point energies for triethylamine-HMDS complexation.

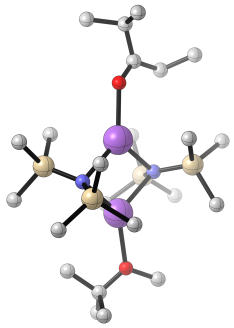


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1166.2759	-1165.3955	0.446872	-1165.8151	0.044339	0.042452	-1165.8595	-1165.8576

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
N	-2.2753640	-0.6303080	0.0016490	H	-0.0288000	-0.3598290	-0.2033040
C	-3.3890180	0.1402770	-0.5443110	N	0.8875530	0.0943650	-0.2310810
H	-4.3108460	-0.4847010	-0.5747160	Si	2.2606590	-0.9586490	-0.0244850
H	-3.1455880	0.3802810	-1.5885700	Si	0.6853190	1.8169110	-0.0444340
C	-2.0170200	-1.8177920	-0.8097290	C	2.9641180	-0.8457960	1.7224920
H	-2.9068690	-2.4874220	-0.8115410	H	3.2858780	0.1814950	1.9541520
H	-1.2063800	-2.3822370	-0.3274970	H	3.8350720	-1.5065360	1.8528520
C	-2.4993970	-0.9788150	1.4014790	H	2.2035720	-1.1328340	2.4650210
H	-2.7422070	-0.0529400	1.9400070	C	1.6708580	-2.7208580	-0.3302280
H	-3.3892510	-1.6416900	1.5006910	H	0.9533620	-3.0367590	0.4427120
C	-1.5877370	-1.5175250	-2.2411070	H	2.5166730	-3.4244830	-0.3056250
H	-2.4038110	-1.1146410	-2.8556940	H	1.1836210	-2.8095840	-1.3135620
H	-1.2455200	-2.4440260	-2.7233410	C	3.6254220	-0.5341330	-1.2476160
H	-0.7542480	-0.7984700	-2.2473000	H	4.0514880	0.4603550	-1.0505970
C	-3.6842840	1.4449740	0.1843200	H	3.2377620	-0.5411240	-2.2772790
H	-4.3835090	2.0471520	-0.4121180	H	4.4438070	-1.2675980	-1.1816450
H	-2.7631420	2.0294860	0.3225520	C	-0.0820450	2.1914010	1.6366700

H	-4.1473610	1.2888450	1.1677420	H	-0.3410320	3.2547610	1.7557940
C	-1.2991200	-1.6158790	2.0909370	H	0.6153890	1.9137210	2.4424590
H	-0.3965630	-1.0080830	1.9240060	H	-0.9990630	1.5965510	1.7699710
H	-1.1019360	-2.6398400	1.7446020	C	2.3613310	2.6640240	-0.1634010
H	-1.4812660	-1.6703200	3.1730860	H	2.2468350	3.7445300	0.0131180
H	3.0724650	2.2794720	0.5839930	H	2.8045600	2.5303960	-1.1613840
C	-0.4347530	2.4466800	-1.4191700				
H	-0.7458890	3.4907310	-1.2622900				
H	-1.3386080	1.8216770	-1.4789520				
H	0.0822490	2.3802540	-2.3884520				

Table S12. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (1x 2-methyl-3 pentanone; 1x MTBE).

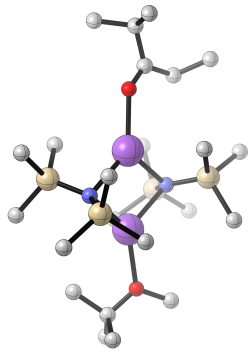


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2655.2828	-2653.4268	0.795025	-2654.4595	0.07577	0.070151	-2654.5353	-2654.5296

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	1.8629030	2.0726830	-1.8356500	H	-0.6240640	-4.5789580	-2.5420300
C	0.8673780	2.0460190	-2.3118170	H	0.4093920	-4.8373200	-1.1189900
Si	-0.4674030	2.8452260	-1.2062860	H	-1.2927980	-4.3658240	-0.9041270
N	-0.7623620	1.8311930	0.1382550	C	-1.3173820	-1.4988470	-2.4944680
Na	-1.6454490	-0.3132670	0.0139650	H	-2.2936780	-1.7158540	-2.0268170
N	0.2793560	-1.6600510	-0.0162580	H	-1.1872320	-0.4024430	-2.5318550
Na	1.1627460	0.5138670	0.1030750	H	-1.3731770	-1.8494630	-3.5361550
Si	0.8439860	-2.3886290	1.4192680	C	1.6382310	-2.2464790	-2.6458770
C	1.7388780	-1.0742030	2.4743020	H	2.0058030	-1.2077210	-2.6935940
H	2.6216150	-0.6571130	1.9607050	H	2.4489510	-2.8731660	-2.2406430
H	1.0695300	-0.2335860	2.7275570	H	1.4396230	-2.5828130	-3.6755680
H	2.0887450	-1.4982980	3.4280990	Si	-1.3620240	2.3428750	1.6538040
C	-0.5283140	-3.0955710	2.5226440	C	-2.0032980	0.8141540	2.5999270
H	-1.0427030	-3.9182860	1.9996440	H	-2.8751030	0.3473940	2.1088020
H	-0.1226220	-3.5016410	3.4627970	H	-1.2171320	0.0454770	2.6956150
H	-1.2789330	-2.3322180	2.7836260	H	-2.3174140	1.0809280	3.6205490
C	2.0645350	-3.8284970	1.1755410	C	-2.8170430	3.5595710	1.5671020
H	2.6503000	-4.0154290	2.0899010	H	-3.1698810	3.8346180	2.5735560

H	1.5197790	-4.7556640	0.9393770	H	-2.5268440	4.4877170	1.0498600
H	2.7693600	-3.6439180	0.3498900	H	-3.6688780	3.1292010	1.0166180
Si	0.0911950	-2.3798560	-1.5531480	C	-0.0462390	3.1423740	2.7589930
C	-0.3980330	-4.2115510	-1.5285520	H	0.3332720	4.0644990	2.2919210
H	-6.5875330	0.5466090	0.4738480	H	-0.4419070	3.4019910	3.7533480
H	-6.0926620	-0.8773590	1.4095330	H	0.8122010	2.4657700	2.9017790
H	-5.1212530	0.6205660	1.4853710	C	-1.9838510	3.1209710	-2.3099720
C	-5.6947350	-1.3574230	-1.3164810	H	-1.7656750	3.8276980	-3.1259430
H	-5.0521850	-1.7616610	-2.1128430	H	-2.3197360	2.1755330	-2.7645620
H	-6.1787040	-2.1935740	-0.7919330	H	-2.8215880	3.5282520	-1.7213030
H	-6.4851140	-0.7541040	-1.7837170	C	0.2110560	4.5586040	-0.7553780
C	-4.3047910	0.7165670	-1.1109810	H	-0.4951950	5.1238850	-0.1269420
H	-3.6408200	1.3057120	-0.4576060	H	1.1525740	4.4593180	-0.1918860
H	-3.7243350	0.3804670	-1.9831520	H	0.4147950	5.1609920	-1.6545980
H	-5.1056460	1.3808040	-1.4640560	H	0.9602560	2.5853470	-3.2670120
O	3.3691880	0.9245610	-0.0566900	H	0.6284220	0.9968230	-2.5578480
C	4.3720760	0.2680030	-0.2666680	O	-3.7162550	-1.1920710	0.1008830
C	5.7122210	0.9705790	-0.4035350	C	-4.8786010	-0.4831770	-0.3669980
C	4.3232780	-1.2335450	-0.3778240	C	-3.8839110	-2.4897530	0.6217840
H	6.4571930	0.2344620	-0.7439700	H	-4.6344620	-2.5164010	1.4282830
C	5.5989440	2.1008100	-1.4276010	H	-4.1682400	-3.2097770	-0.1621300
C	6.1234660	1.5058330	0.9739770	H	-2.9142890	-2.7926850	1.0390200
H	3.2696230	-1.5490830	-0.3342850	C	-5.7171610	-0.0254250	0.8247510
H	4.7105920	-1.4979720	-1.3770710	H	4.8372570	2.8229050	-1.1021680
C	5.1589910	-1.9309480	0.6997460	H	5.3701420	2.2220120	1.3320690
H	6.5604510	2.6232490	-1.5256110	H	6.2132970	0.7006080	1.7172650
H	5.3097790	1.7219120	-2.4183090	H	7.0916640	2.0209380	0.9064570
H	6.2140930	-1.6236380	0.6604390	H	4.7700150	-1.7109270	1.7044820
				H	5.1207520	-3.0190090	0.5604030

Table S13. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (1x 2-methylcyclohexanone; 1x MTBE).

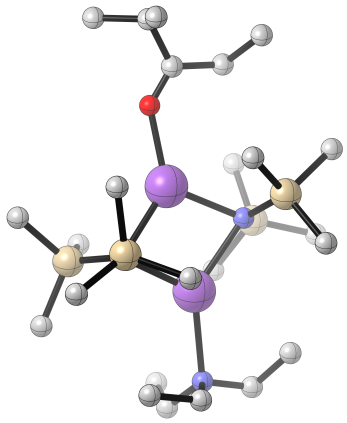


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2693.3978	-2691.5048	0.804305	-2692.566	0.073251	0.068413	-2692.6392	-2692.6344

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	-1.8956340	-0.9215900	-2.7196980	H	-1.5371590	-4.3763710	-2.6286320
C	-0.8800530	-1.2482590	-3.0013960	H	-0.9612950	-1.7134270	-3.9956020
Si	-0.1425330	-2.4762120	-1.7430340	H	-0.2497640	-0.3497220	-3.1253150
N	0.1260910	-1.6666150	-0.2600500	O	-3.2478050	0.5744590	-1.0721930
Na	1.7767840	-0.0213470	0.0094310	C	-4.1549960	-0.0680780	-0.5785300
N	0.5463370	1.9407110	-0.0452610	C	-3.9120030	-1.3559540	0.1695320
Na	-1.0332520	0.3391100	-0.6606980	C	-5.5920210	0.4083230	-0.6418680
Si	-0.2119470	2.6042470	1.3330720	C	-4.5148930	-1.2818880	1.5812750
C	-1.5868010	1.4141970	1.9293900	H	-2.8328210	-1.5755980	0.1907400
H	-2.4607790	1.4788830	1.2583790	H	-4.4110980	-2.1638090	-0.3939920
H	-1.2541810	0.3620360	1.9699960	C	-6.1548120	0.4562790	0.7934630
H	-1.9377330	1.6835150	2.9376150	H	-6.1433760	-0.3848370	-1.1809310
C	0.9667730	2.8791770	2.7929130	C	-5.7257300	1.7321290	-1.3767260
H	1.7652480	3.5804900	2.5001870	C	-5.9847450	-0.8709160	1.5290780
H	0.4473280	3.3060270	3.6650770	H	-3.9463220	-0.5437660	2.1717740
H	1.4423060	1.9375420	3.1109410	H	-4.3868260	-2.2517640	2.0818680
C	-1.1038910	4.2503040	1.0285230	H	-5.6301790	1.2547640	1.3469910

H	-1.6091240	4.6095640	1.9389800	H	-7.2143730	0.7489210	0.7468510
H	-0.4078350	5.0375970	0.6994950	H	-5.3240340	1.6643670	-2.3958560
H	-1.8654260	4.1289200	0.2415240	H	-6.7803970	2.0342980	-1.4314830
Si	1.3191920	2.8187830	-1.2903300	H	-5.1642700	2.5188930	-0.8527280
C	2.4039550	4.2553900	-0.6910130	H	-6.5681790	-1.6530640	1.0135350
H	2.9057920	4.7609500	-1.5309270	H	-6.3920300	-0.7923270	2.5474990
H	1.8084600	5.0102180	-0.1542330	O	3.9312990	0.1627700	0.6066940
H	3.1811230	3.8928190	0.0002740	C	4.9478750	-0.7893320	0.2527580
C	2.4950030	1.6421860	-2.2270220	C	4.2858870	1.2857780	1.3796860
H	3.3411260	1.3435370	-1.5848170	H	4.7492240	0.9973830	2.3371970
H	1.9797510	0.7267870	-2.5707280	H	4.9664060	1.9579120	0.8327810
H	2.9172920	2.1256450	-3.1210390	H	3.3542160	1.8300880	1.5891420
C	0.1110830	3.5181200	-2.5711150	C	5.3764410	-1.5779550	1.4886970
H	-0.5046090	2.7141340	-3.0071330	H	6.1180300	-2.3395350	1.2095040
H	-0.5737140	4.2379730	-2.0962080	H	5.8368230	-0.9275430	2.2459720
H	0.6288680	4.0327920	-3.3954630	H	4.5108250	-2.0851800	1.9387500
Si	0.3192870	-2.4553120	1.2455340	C	6.1387040	-0.0882610	-0.3973880
C	1.2854690	-1.3258950	2.4416350	H	5.8001250	0.5567360	-1.2218080
H	2.3398050	-1.1977140	2.1416380	H	6.6983490	0.5234190	0.3243970
H	0.8308430	-0.3236810	2.5185660	H	6.8303960	-0.8377180	-0.8060900
H	1.2944900	-1.7552780	3.4551790	C	4.2539230	-1.7025570	-0.7515540
C	1.3077690	-4.0765900	1.1718600	H	3.3481690	-2.1492020	-0.3097640
H	1.4028490	-4.5267070	2.1726630	H	3.9637760	-1.1318180	-1.6466920
H	0.8235500	-4.8180020	0.5171690	H	4.9148670	-2.5226450	-1.0637530
H	2.3245520	-3.9092690	0.7818460	C	1.4327920	-3.1631530	-2.5427200
C	-1.3106980	-2.8704240	2.1239470	H	1.2110820	-3.7061900	-3.4748430
H	-1.9487180	-3.5002840	1.4825920	H	2.1324650	-2.3478900	-2.7872760
H	-1.1308800	-3.4151410	3.0640330	H	1.9479030	-3.8566910	-1.8591190
H	-1.8721100	-1.9547600	2.3695310	C	-1.3785300	-3.9143170	-1.6416110
H	-2.3553010	-3.5656640	-1.2708640	H	-1.0266590	-4.7018430	-0.9568740

Table S14. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (1x 2-methyl-3-pentanone; 1x triethylamine).



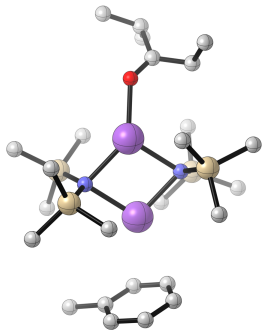
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2674.7037	-2672.8287	0.838216	-2673.837	0.074271	0.069877	-2673.9113	-2673.9069

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	0.1210780	1.3979330	-2.9727320	H	-0.8719570	2.6236380	-3.7831370
C	-0.8569850	1.9090280	-2.9453840	H	-1.6343150	1.1561260	-3.1497960
Si	-1.1649860	2.8092920	-1.2992000	N	-4.1651340	-0.8041350	0.1313020
N	-0.8600240	1.7700930	0.0268560	C	-4.4929190	-0.2347140	1.4469370
Na	-1.7101070	-0.3916960	0.0523850	H	-5.5109760	-0.5577660	1.7540540
N	0.3301840	-1.7040260	0.0044760	H	-3.7980600	-0.6720220	2.1796720
Na	1.0732230	0.4957500	-0.3318910	C	-4.3843070	1.2838020	1.5173270
Si	1.1448170	-2.2782460	1.3973470	H	-5.2391460	1.7928000	1.0530130
C	2.1387920	-0.8735850	2.2199280	H	-4.3489680	1.6039880	2.5681090
H	2.8626570	-0.4171220	1.5235470	H	-3.4654520	1.6358090	1.0201310
H	1.4909050	-0.0692710	2.6005040	C	-4.2813000	-2.2675060	0.1726730
H	2.7125570	-1.2583330	3.0781860	H	-5.2888950	-2.5487440	0.5461630
C	-0.0124790	-2.9645520	2.7342770	H	-4.2212420	-2.6392430	-0.8597420
H	-0.5556120	-3.8412510	2.3457550	C	-3.2110390	-2.9635660	1.0032420
H	0.5526890	-3.2865880	3.6233430	H	-3.3367950	-4.0527280	0.9276550
H	-0.7585240	-2.2233210	3.0610720	H	-2.1913160	-2.7350040	0.6495040

C	2.4004450	-3.6788530	1.0868580	H	-3.2653850	-2.7069400	2.0700960
H	3.1214840	-3.7434630	1.9176740	C	-5.0480310	-0.2518730	-0.9040380
H	1.8895570	-4.6515040	1.0218630	H	-5.1184320	0.8302560	-0.7421390
H	2.9697280	-3.5437610	0.1533160	H	-6.0738090	-0.6579780	-0.7723250
Si	0.1468040	-2.6071420	-1.4373960	C	-4.5727670	-0.4699490	-2.3315070
C	-0.1481550	-4.4685770	-1.2219890	H	-4.4975860	-1.5303220	-2.6085540
H	-0.4623710	-4.9219400	-2.1755300	H	-5.2799260	0.0031270	-3.0270770
H	0.7623520	-4.9889460	-0.8908550	H	-3.5873080	-0.0066890	-2.4856140
H	-0.9370240	-4.6633920	-0.4781360	O	3.2117470	0.9876660	-0.7562100
C	-1.3747070	-1.9476870	-2.3629660	C	4.3033750	0.4560760	-0.6683920
H	-2.2946430	-2.1136590	-1.7783590	C	5.5459480	1.3127900	-0.5139020
H	-1.2832770	-0.8683770	-2.5675430	C	4.4384310	-1.0469230	-0.7115050
H	-1.5184020	-2.4482740	-3.3326850	H	6.4218550	0.7090150	-0.7992190
C	1.6002480	-2.4373670	-2.6506870	C	5.4599340	2.5582050	-1.3925500
H	1.8591200	-1.3789170	-2.8235220	C	5.6613350	1.6896320	0.9722090
H	2.4989410	-2.9458730	-2.2671230	H	3.4238020	-1.4717250	-0.6800470
H	1.3569390	-2.8859710	-3.6267760	H	4.8477390	-1.2719110	-1.7137900
Si	-0.6315710	2.3280540	1.6302060	C	5.3361370	-1.6694800	0.3573580
C	-1.0702020	0.9256280	2.8422770	H	6.3530970	3.1825820	-1.2535130
H	-2.1621000	0.8415170	2.9568800	H	5.3836090	2.2964230	-2.4572250
H	-0.6889890	-0.0471950	2.4906860	H	4.5730460	3.1470750	-1.1222290
H	-0.6479770	1.0926470	3.8455350	H	4.7825750	2.2782620	1.2744710
C	-1.6640320	3.8312580	2.1523930	H	5.7229510	0.8058320	1.6224960
H	-1.4435120	4.1034910	3.1967810	H	6.5607920	2.2991640	1.1357540
H	-1.4406560	4.7083720	1.5253810	H	4.9173310	-1.5224750	1.3629080
H	-2.7436090	3.6326590	2.0763840	H	5.4155270	-2.7515010	0.1898330
C	1.1749320	2.8356790	1.9588800	H	6.3531200	-1.2525190	0.3378130
H	1.4240790	3.7102810	1.3367060	H	-3.2287320	3.9703710	-0.4594690
H	1.3326720	3.1131940	3.0132110	C	-0.0356900	4.3355990	-1.3377470
H	1.9048220	2.0450690	1.7185910	H	-0.1582410	4.9589510	-0.4381800
C	-2.9596420	3.4190900	-1.3739800	H	1.0211490	4.0248000	-1.3839910

H	-3.1341460	4.0815070	-2.2362750	H	-0.2407100	4.9692310	-2.2148110
H	-3.6463280	2.5608030	-1.4625620				

Table S15. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (1x 2-methyl-3-pentanone; 1x toluene).

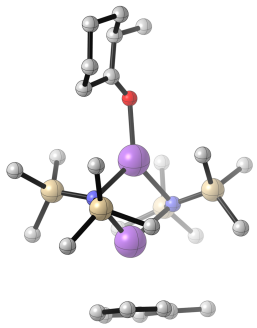


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2653.8659	-2652.0237	0.758695	-2653.0796	0.073467	0.068628	-2653.1531	-2653.1482

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	-2.2678350	-0.9664050	-2.5059530	H	-1.4165640	-2.0364740	-3.6353090
C	-1.3018090	-1.4610400	-2.7040660	H	-0.5551990	-0.6738290	-2.9077880
Si	-0.7858740	-2.5730110	-1.2424510	C	3.5306970	-2.2457380	0.9196030
N	-0.5824080	-1.5969720	0.1417000	C	4.1727950	-2.6729700	-0.2462040
Na	1.4910410	-0.5212050	0.1937720	C	5.1788580	-1.8836290	-0.7994600
N	0.9096940	1.6592620	-0.3312480	C	5.5344810	-0.6732570	-0.2016560
Na	-1.1376780	0.5733080	-0.5768020	C	4.9013940	-0.2289180	0.9637800
Si	0.5460600	2.8434520	0.8481230	C	3.8934930	-1.0351500	1.5164300
C	-1.0974780	2.4020580	1.7085410	H	2.7464860	-2.8640910	1.3660240
H	-1.9501240	2.4995340	1.0139960	H	3.8855950	-3.6141970	-0.7161220
H	-1.0968930	1.3762960	2.1139150	H	5.6846670	-2.2057210	-1.7109030
H	-1.2924630	3.0823760	2.5520740	H	6.3173680	-0.0576350	-0.6498010
C	1.8707840	2.9738130	2.1998060	H	3.3997730	-0.7102280	2.4372610
H	2.8154860	3.3263590	1.7552260	C	5.3050230	1.0541880	1.6393290
H	1.5889700	3.6783660	2.9977370	H	4.4240890	1.6610990	1.8909450
H	2.0605550	1.9923740	2.6653950	H	5.8412920	0.8431450	2.5770180
C	0.2957870	4.5906840	0.1548740	H	5.9655350	1.6519630	0.9982400
H	0.0509260	5.3094910	0.9525500	O	-3.3161680	1.1095370	-0.6732610

H	1.1979760	4.9564900	-0.3602550	C	-4.3485440	0.5614340	-0.3335530
H	-0.5299140	4.5980370	-0.5742690	C	-5.4917020	1.3569590	0.2619310
Si	1.9086460	1.9207110	-1.6946160	C	-4.5251060	-0.9265380	-0.5011030
C	3.5013850	2.8813420	-1.3251380	H	-6.4299760	0.8588320	-0.0350550
H	4.1311970	2.9856990	-2.2226000	C	-5.3637650	1.2677430	1.7924520
H	3.2896410	3.8922650	-0.9429630	C	-5.4820720	2.8031840	-0.2165390
H	4.0861800	2.3492870	-0.5575240	H	-3.5325500	-1.3951300	-0.4200930
C	2.4807680	0.2257650	-2.3537210	H	-5.1631950	-1.3199030	0.3043790
H	3.1622170	-0.2827950	-1.6481870	C	-5.1589380	-1.2268760	-1.8653200
H	1.6308960	-0.4452540	-2.5634050	H	-6.2093970	1.7842880	2.2670940
H	3.0435800	0.3327300	-3.2937720	H	-5.3490240	0.2284950	2.1507610
C	1.0241000	2.7921430	-3.1243960	H	-4.4327980	1.7542230	2.1210310
H	0.1261900	2.2294560	-3.4280020	H	-4.5417450	3.2916570	0.0737810
H	0.6970820	3.7975000	-2.8169000	H	-5.5689700	2.8657060	-1.3100640
H	1.6715650	2.8997040	-4.0085150	H	-6.3170940	3.3588440	0.2316400
Si	-0.9093250	-1.9425810	1.7789880	H	-4.5442920	-0.8224570	-2.6814020
C	0.3958950	-1.0925050	2.8826050	H	-5.2454760	-2.3117790	-2.0105500
H	1.3522690	-1.6395960	2.8326860	H	-6.1654930	-0.7914230	-1.9467980
H	0.5802800	-0.0402440	2.6049010	H	-2.7849860	-0.2745990	2.0148260
H	0.0885580	-1.0945880	3.9396590	C	0.8164110	-3.4493860	-1.7585660
C	-0.8460760	-3.7748640	2.2605650	H	0.6839350	-4.0580020	-2.6668790
H	-0.8910740	-3.8966530	3.3543980	H	1.6307600	-2.7319990	-1.9534000
H	-1.6896700	-4.3330340	1.8272560	H	1.1453680	-4.1195270	-0.9468330
H	0.0850330	-4.2455470	1.9051840	C	-2.0958400	-3.9416420	-1.1119740
C	-2.6061800	-1.3079020	2.3563390	H	-1.7318150	-4.7655790	-0.4794040
H	-3.4066880	-1.9451450	1.9480000	H	-3.0398910	-3.5805270	-0.6735410
H	-2.6966900	-1.3197240	3.4539250	H	-2.3215710	-4.3609770	-2.1053350

Table S16. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (1x 2-methylcyclohexanone; 1x toluene).

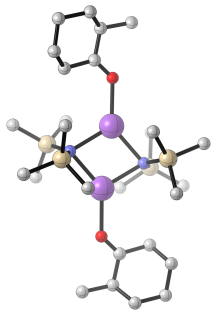


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2691.9804	-2690.1003	0.768324	-2691.1853	0.072711	0.067627	-2691.258	-2691.2529

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	-2.3720780	-0.4602080	-2.3426790	H	-2.2406030	-3.8796730	-2.7028340
C	-1.4132020	-0.8110010	-2.7574840	H	-1.6138720	-1.1703740	-3.7786610
Si	-0.6728810	-2.2064470	-1.6882190	H	-0.7522690	0.0662110	-2.8577260
N	-0.2171620	-1.5951100	-0.1562800	O	-2.9760620	1.3341480	-0.3964950
Na	1.8912720	-0.5395120	-0.1602270	C	-4.0420790	0.7512370	-0.3451690
N	1.2913070	1.6972890	0.0019440	C	-4.1291510	-0.7420150	-0.1438570
Na	-0.8244700	0.6541400	-0.2332230	C	-5.3593860	1.4904410	-0.4777390
Si	0.9781830	2.5042530	1.4786020	C	-5.0829590	-1.0888190	1.0078440
C	-0.6605780	1.8656650	2.2294950	H	-3.1182180	-1.1471300	0.0165940
H	-1.5311390	2.2067690	1.6425910	H	-4.5232370	-1.1735660	-1.0815580
H	-0.6925280	0.7650190	2.3050810	C	-6.2913700	1.0908370	0.6828100
H	-0.7961280	2.2569690	3.2493180	H	-5.8119930	1.0943160	-1.4069660
C	2.3020910	2.2410210	2.8115120	C	-5.1645400	2.9934110	-0.5972230
H	3.2028780	2.8334920	2.5894260	C	-6.4430320	-0.4229720	0.8134030
H	1.9314280	2.5572640	3.7992060	H	-4.6399570	-0.7445200	1.9567770
H	2.6019790	1.1832530	2.8856160	H	-5.1776980	-2.1810630	1.0863900
C	0.7365580	4.3802810	1.3365420	H	-5.8783730	1.5018650	1.6204040
H	0.5839920	4.8298070	2.3304840	H	-7.2685410	1.5732890	0.5319540

H	1.6069200	4.8735050	0.8766820	H	-4.5104530	3.2438340	-1.4420910
H	-0.1464850	4.6150990	0.7221160	H	-6.1319380	3.4943670	-0.7378330
Si	1.7802670	2.3966910	-1.4785540	H	-4.6955000	3.3928790	0.3134180
C	3.3556630	3.4524470	-1.4139090	H	-6.9239250	-0.8240290	-0.0952970
H	3.5409420	3.9476800	-2.3800810	H	-7.1077860	-0.6638590	1.6556070
H	3.2921570	4.2348420	-0.6419500	C	3.6911260	-2.4078400	1.0933050
H	4.2337330	2.8280680	-1.1850770	C	3.7840110	-2.7479300	-0.2578190
C	2.1653950	1.0073800	-2.7268360	C	4.3490800	-1.8388500	-1.1562370
H	3.0787270	0.4561030	-2.4513990	C	4.8090920	-0.6010540	-0.7039270
H	1.3439750	0.2774370	-2.8153040	C	4.7096750	-0.2389120	0.6478690
H	2.3353680	1.4209370	-3.7330220	C	4.1474820	-1.1642760	1.5387190
C	0.4312780	3.4609990	-2.2855720	H	3.2514140	-3.1097850	1.8035590
H	-0.5068650	2.8929480	-2.4056080	H	3.4216150	-3.7145680	-0.6100800
H	0.2061880	4.3415700	-1.6645470	H	4.4277510	-2.0950160	-2.2143430
H	0.7347020	3.8187130	-3.2819700	H	5.2517580	0.1044470	-1.4112310
Si	-0.2570530	-2.4890960	1.3018510	H	4.0636880	-0.9061040	2.5969250
C	0.7121660	-1.5864370	2.6851490	C	5.1559190	1.1208430	1.1075210
H	1.3774870	-2.2744880	3.2304470	H	4.3685180	1.8591820	0.8903160
H	1.3272460	-0.7447780	2.3253180	H	5.3416680	1.1383930	2.1891870
H	0.0159200	-1.1635050	3.4263670	H	6.0693020	1.4356260	0.5843250
C	0.4765910	-4.2377830	1.1537520	H	-2.4538590	-1.7535030	2.2535110
H	0.5678490	-4.7214390	2.1394820	C	0.8015870	-2.9186970	-2.6483810
H	-0.1607920	-4.8811670	0.5275710	H	0.5153460	-3.2664340	-3.6532880
H	1.4737790	-4.2166230	0.6881590	H	1.6046010	-2.1723380	-2.7698820
C	-2.0007650	-2.7294560	2.0140500	H	1.2195090	-3.7772820	-2.0978290
H	-2.6596520	-3.2495960	1.3005350	C	-1.9996790	-3.5656680	-1.6748890
H	-1.9718510	-3.3209170	2.9430080	H	-1.6637600	-4.4578040	-1.1247450
				H	-2.9313090	-3.2162020	-1.2032040

Table S17. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (2x 2-methylcyclohexanone).

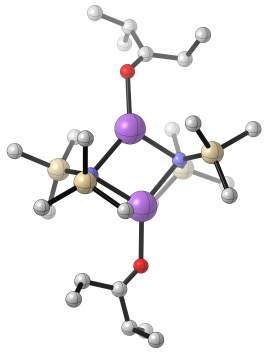


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2769.6279	-2767.655	0.81906	-2768.781	0.075244	0.069638	-2768.8562	-2768.8506

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	-2.8111160	-0.2976870	-2.3028710	H	-3.1337530	-3.6744410	-2.6326540
C	-1.9328910	-0.7966620	-2.7467920	H	-2.2255270	-1.1375190	-3.7517430
Si	-1.3074910	-2.2397710	-1.6689120	H	-1.1472720	-0.0342620	-2.8865870
N	-0.8285370	-1.6214990	-0.1528450	O	-3.4654420	1.3732610	-0.1477180
Na	1.3215010	-0.6657860	-0.2020380	C	-4.5286360	0.7822860	-0.1389970
N	0.8286680	1.6209800	-0.1532270	C	-4.6043140	-0.7236010	-0.0774730
Na	-1.3210770	0.6650040	-0.2028770	C	-5.8490430	1.5257840	-0.2032030
Si	0.7890340	2.4229710	1.3536380	C	-5.5824420	-1.1946460	1.0071800
C	-0.7511400	1.8586870	2.3276040	H	-3.5907450	-1.1267740	0.0712360
H	-1.6776050	2.2264540	1.8523280	H	-4.9629680	-1.0677720	-1.0646220
H	-0.8183620	0.7608530	2.4142920	C	-6.7934120	1.0038130	0.8960730
H	-0.7416920	2.2588710	3.3529710	H	-6.2884540	1.2271760	-1.1745510
C	2.3049580	2.0407430	2.4332860	C	-5.6608000	3.0339160	-0.1647550
H	3.1946930	2.5341820	2.0087250	C	-6.9416860	-0.5152630	0.8600400
H	2.1805640	2.4089200	3.4636610	H	-5.1587030	-0.9593130	1.9969890
H	2.5106540	0.9582040	2.4816520	H	-5.6773820	-2.2891890	0.9595650
C	0.6707750	4.3132650	1.2761620	H	-6.3935640	1.3121420	1.8777190
H	0.5004270	4.7358010	2.2791160	H	-7.7701640	1.4979470	0.7853950

H	1.5955990	4.7584670	0.8793290	H	-5.0002190	3.3728340	-0.9728010
H	-0.1628640	4.6302810	0.6296400	H	-6.6294440	3.5427310	-0.2621870
Si	1.3078530	2.2382910	-1.6696060	H	-5.2023660	3.3387630	0.7869970
C	2.6879770	3.5445180	-1.6352970	H	-7.4045930	-0.8162590	-0.0954690
H	3.1343170	3.6718260	-2.6343850	H	-7.6204410	-0.8473390	1.6589740
H	2.2861100	4.5216160	-1.3268890	O	3.4658860	-1.3736780	-0.1462160
H	3.4939250	3.2802350	-0.9324860	C	4.5287030	-0.7819990	-0.1380810
C	1.9332650	0.7944450	-2.7465160	C	4.6034650	0.7239070	-0.0762520
H	2.8116840	0.2958710	-2.3025310	C	5.8495640	-1.5246100	-0.2031530
H	1.1476830	0.0318590	-2.8855350	C	5.5816290	1.1952290	1.0082660
H	2.2255420	1.1346240	-3.7518030	H	3.5897080	1.1264350	0.0729100
C	-0.1225100	3.0347370	-2.6305240	H	4.9616350	1.0685790	-1.0633990
H	-0.9567430	2.3305100	-2.7851550	C	6.7939420	-1.0024550	0.8960440
H	-0.5166830	3.8953900	-2.0667890	H	6.2884520	-1.2252970	-1.1745140
H	0.1938610	3.3956850	-3.6218490	C	5.6623390	-3.0328800	-0.1652430
Si	-0.7895450	-2.4223790	1.3546120	C	6.9412500	0.5167280	0.8605310
C	0.7498920	-1.8568760	2.3290560	H	5.1583000	0.9593640	1.9981260
H	1.6768480	-2.2247690	1.8548340	H	5.6758860	2.2898430	0.9609330
H	0.8166750	-0.7589380	2.4147810	H	6.3945740	-1.3114100	1.8776880
H	0.7398210	-2.2561110	3.3547870	H	7.7709710	-1.4959330	0.7848900
C	-0.6709150	-4.3127180	1.2787690	H	5.0016550	-3.3719100	-0.9731590
H	-0.5004390	-4.7342450	2.2821290	H	6.6312790	-3.5410160	-0.2632760
H	-1.5957200	-4.7584330	0.8824660	H	5.2044900	-3.3384180	0.7865680
H	0.1627110	-4.6302700	0.6324990	H	7.4037140	0.8183590	-0.0949920
C	-2.3061170	-2.0396450	2.4331720	H	7.6200090	0.8489400	1.6594050
H	-3.1955970	-2.5332420	2.0082620	C	0.1229850	-3.0368800	-2.6290940
H	-2.1823700	-2.4073780	3.4637850	H	-0.1932770	-3.3984690	-3.6202220
H	-2.5118140	-0.9570760	2.4809270	H	0.9572600	-2.3327860	-2.7840880
H	-2.2855280	-4.5227690	-1.3242160	H	0.5170430	-3.8971770	-2.0647390
H	-3.4935870	-3.2812370	-0.9311570	C	-2.6875300	-3.5460490	-1.6336560

Table S18. Geometric coordinates and thermal corrected single point energies for a mixed solvated NaHMDS dimer (2x 2-methyl-3-pentanone).

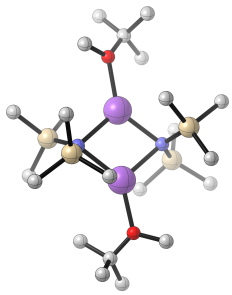


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2693.4001	-2691.5014	0.800532	-2692.5704	0.077774	0.071884	-2692.6482	-2692.6423

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	2.0198350	2.3282730	-1.4199250	H	-0.0296830	4.9545340	-1.8871830
C	1.1451550	2.0377910	-2.0276770	H	1.2642330	2.5138790	-3.0132420
Si	-0.4791590	2.5860020	-1.1914220	H	1.1844480	0.9471820	-2.1895960
N	-0.7151730	1.6767230	0.2355280	O	3.5423470	1.1677980	0.3578190
Na	-1.2829230	-0.5797730	-0.0045610	C	4.5177540	0.5271820	0.0108440
N	0.8268320	-1.6193950	0.1370130	C	5.6303410	1.1756660	-0.7868270
Na	1.3671030	0.6313740	0.5050070	C	4.6539780	-0.9292920	0.3757460
Si	1.0367670	-2.3803610	1.6480250	H	6.5753570	0.6958130	-0.4805180
C	1.5519270	-1.0530010	2.9158490	C	5.3848580	0.8496180	-2.2699790
H	2.4970050	-0.5628270	2.6243840	C	5.6940130	2.6785300	-0.5477560
H	0.7792580	-0.2709480	3.0133990	H	3.6428400	-1.3647540	0.4090690
H	1.7025090	-1.4766540	3.9204310	H	5.2362920	-1.4568540	-0.3942220
C	-0.5585760	-3.1699400	2.3089740	C	5.3484470	-1.0576770	1.7377080
H	-0.8904650	-3.9664970	1.6237690	H	6.2003940	1.2602160	-2.8812150
H	-0.4174920	-3.6179240	3.3051740	H	5.3252880	-0.2321760	-2.4558030
H	-1.3802490	-2.4389250	2.3891680	H	4.4398370	1.3046900	-2.6036520
C	2.3489960	-3.7512890	1.7212610	H	4.7479130	3.1496260	-0.8478560

H	2.5848070	-4.0102130	2.7657500	H	5.8617950	2.9102800	0.5130490
H	1.9822020	-4.6642860	1.2280780	H	6.5081670	3.1243710	-1.1354180
H	3.2871810	-3.4596100	1.2231630	H	4.7889250	-0.5189710	2.5148340
Si	0.9726670	-2.2681400	-1.4344580	H	5.4097490	-2.1133760	2.0332420
C	0.8820140	-4.1574380	-1.5560910	H	6.3705150	-0.6523190	1.7087610
H	0.8342650	-4.4801760	-2.6081900	O	-3.4124940	-1.1512410	-0.4403190
H	1.7657930	-4.6302840	-1.1015500	C	-4.4635770	-0.5606630	-0.6073430
H	-0.0117540	-4.5454580	-1.0420470	C	-5.7215480	-1.3489360	-0.9322570
C	-0.4495330	-1.6143620	-2.5257570	C	-4.5566670	0.9382970	-0.4862810
H	-1.4247570	-2.0080280	-2.1892060	H	-6.5109000	-0.6382790	-1.2230260
H	-0.5042530	-0.5121670	-2.5312050	C	-5.4469340	-2.3143570	-2.0855290
H	-0.3239710	-1.9301950	-3.5727190	C	-6.1604650	-2.1007640	0.3312160
C	2.5926910	-1.7674590	-2.2950250	H	-3.5450780	1.3331320	-0.3049000
H	2.8029240	-0.6936450	-2.1582440	H	-4.8903770	1.3165910	-1.4684540
H	3.4363200	-2.3348760	-1.8704850	C	-5.5387410	1.3911660	0.5981030
H	2.5638670	-1.9703970	-3.3771700	H	-6.3487470	-2.8980380	-2.3160850
Si	-1.4179070	2.1841580	1.7043420	H	-5.1400730	-1.7797880	-2.9957970
C	-2.2464580	0.6814530	2.5372300	H	-4.6405830	-3.0069020	-1.8075270
H	-3.0212260	0.2244900	1.8981530	H	-5.3665100	-2.7942680	0.6434880
H	-1.5020770	-0.0992800	2.7700960	H	-6.3667520	-1.4160030	1.1662860
H	-2.7266870	0.9557230	3.4893090	H	-7.0716820	-2.6806560	0.1292430
C	-2.7338280	3.5494240	1.5550520	H	-5.2132600	1.0541570	1.5928320
H	-3.4021100	3.5610920	2.4309240	H	-5.5923310	2.4871910	0.6216030
H	-2.2515900	4.5372010	1.4946740	H	-6.5537280	1.0090010	0.4166440
H	-3.3534120	3.4314660	0.6519720	H	-2.1001580	1.2782910	-2.6244630
C	-0.1465570	2.8393360	2.9514710	H	-2.7863910	2.8429820	-2.1233040
H	0.3579870	3.7266260	2.5366850	C	-0.3161260	4.4584540	-0.9462990
H	-0.6142130	3.1310210	3.9050650	H	-1.2640290	4.9041810	-0.6088460
H	0.6307470	2.0913380	3.1791780	H	0.4540130	4.6898520	-0.1933680
C	-1.8661380	2.3446380	-2.4685780	H	-1.5996410	2.7787390	-3.4450600

Table S19. Geometric coordinates and thermal corrected single point energies for a disolvated NaHMDS dimer (2x MTBE).

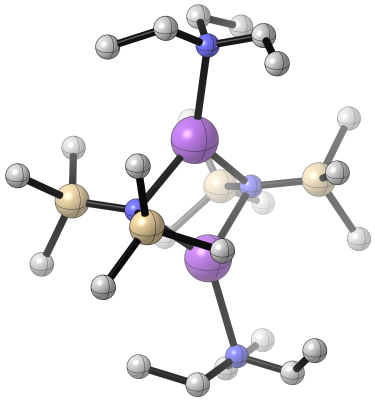


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2617.1681	-2615.3548	0.789152	-2616.3514	0.072665	0.068063	-2616.4241	-2616.4195

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-1.4433530	-0.1752760	-0.0241910	C	-1.0603300	-4.3668830	-0.9627860
N	0.2241610	-1.8108020	0.0521650	H	-1.3309320	-4.8957230	-1.8902370
Na	1.4425570	0.1778430	-0.0251580	H	-0.4278420	-5.0424090	-0.3657880
N	-0.2243980	1.8130770	0.0515340	H	-1.9857830	-4.1890600	-0.3923540
Si	-0.7965060	2.4574130	1.5277250	C	1.3023600	-3.1368960	-2.4441000
C	-2.0504610	3.8719140	1.3434880	H	2.0774500	-3.6763960	-1.8765770
H	-2.3960470	4.2281650	2.3267700	H	1.0059220	-3.7663180	-3.2977990
H	-1.6130010	4.7315660	0.8120280	H	1.7570950	-2.2174270	-2.8458750
H	-2.9359200	3.5488410	0.7728250	Si	0.7975900	-2.4548750	1.5279820
C	-1.7077890	1.0895910	2.4963820	C	1.7061740	-1.0858470	2.4973810
H	-2.6444600	0.7849160	1.9991240	H	2.6419180	-0.7784860	2.0000320
H	-1.0848670	0.1877170	2.6230670	H	1.9791570	-1.4338230	3.5053340
H	-1.9795240	1.4373470	3.5047450	H	1.0810110	-0.1856840	2.6249790
C	0.5778110	3.1020940	2.6649230	C	-0.5752260	-3.1028490	2.6650990
H	1.2802000	2.2968260	2.9345870	H	-0.1695680	-3.5215970	3.5993460
H	1.1487680	3.8972230	2.1588110	H	-1.2784250	-2.2987750	2.9362030
H	0.1733760	3.5203460	3.5999180	H	-1.1455350	-3.8981290	2.1585200
Si	0.1769640	2.7293310	-1.3342940	C	2.0541390	-3.8669610	1.3424110

C	1.3973280	1.7292950	-2.4085500	H	1.6179250	-4.7269430	0.8104270
H	2.3824020	1.6558840	-1.9167060	H	2.9388030	-3.5419530	0.7715940
H	1.0321790	0.7064040	-2.6120060	H	2.4007620	-4.2234400	2.3252420
H	1.5567710	2.2129720	-3.3842240	O	-3.6034500	-0.7769910	0.1528330
C	-1.3034150	3.1385730	-2.4443110	C	-4.6892360	0.0039960	-0.3761330
H	-2.0780330	3.6783560	-1.8764160	C	-5.5782180	-0.8522550	-1.2754040
H	-1.0076980	3.7674690	-3.2986400	H	-6.1452420	-1.5985730	-0.7009890
H	-1.7584950	2.2188550	-2.8451460	H	-6.3030000	-0.2109580	-1.7955410
C	1.0609500	4.3683090	-0.9647210	H	-4.9711610	-1.3723450	-2.0312890
H	1.3315660	4.8965400	-1.8925180	C	-3.9945300	1.0888060	-1.1910600
H	0.4292150	5.0445620	-0.3677710	H	-3.2863630	1.6549580	-0.5642840
H	1.9865390	4.1900600	-0.3946290	H	-3.4391890	0.6386490	-2.0277060
O	3.6038850	0.7758080	0.1508790	H	-4.7229310	1.8002120	-1.6037260
C	3.8979140	1.9914600	0.7986440	C	-5.4911120	0.6225610	0.7673930
H	4.6005210	1.8529750	1.6362800	H	-5.9582360	-0.1463180	1.3991580
H	4.3077490	2.7373710	0.0988840	H	-4.8422490	1.2490980	1.3961290
H	2.9488180	2.3752440	1.1981850	H	-6.2950410	1.2533680	0.3628360
C	4.6879190	-0.0084090	-0.3769690	C	-3.8944740	-1.9948100	0.7979080
C	5.5816230	0.8457790	-1.2735110	H	-4.6016020	-1.8606980	1.6324300
H	6.1508610	1.5888670	-0.6971040	H	-4.2974930	-2.7418850	0.0954050
H	6.3045410	0.2024130	-1.7936920	H	-2.9453590	-2.3743950	1.2013830
H	4.9776920	1.3695130	-2.0293900	H	5.9534660	0.1351660	1.4013120
C	3.9908590	-1.0896690	-1.1945720	H	4.8333820	-1.2569960	1.3935110
H	3.2786130	-1.6533190	-0.5701480	Si	-0.1774270	-2.7275240	-1.3332890
H	3.4395360	-0.6365410	-2.0322710	C	-1.3984920	-1.7281240	-2.4073140
H	4.7173200	-1.8038650	-1.6058530	H	-2.3834370	-1.6551090	-1.9152010
C	5.4854390	-0.6312840	0.7672560	H	-1.0337590	-0.7050670	-2.6107190
H	6.2883680	-1.2637960	0.3633720	H	-1.5579020	-2.2117300	-3.3830250

Table S20. Geometric coordinates and thermal corrected single point energies for a disolvated NaHMDS dimer (2x triethylamine).



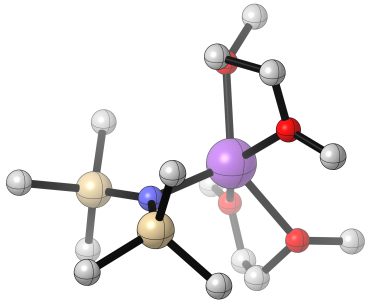
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2656.01	-2654.1576	0.875707	-2655.1063	0.072163	0.068697	-2655.1784	-2655.1749

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.4658810	-0.9428330	-3.1031770	H	-2.2612200	3.4163620	-2.9169340
C	-3.8025220	-1.7030440	-1.8268230	Si	0.6873490	-2.0120520	2.0084050
N	-3.7759630	-0.8808980	-0.6108570	C	1.5276890	-0.4778670	2.7688710
C	-4.1438690	-1.6753740	0.5710010	H	2.5940040	-0.4446130	2.4970900
H	-5.2325770	-1.8972810	0.5454100	H	1.0569810	0.4622310	2.4401030
H	-3.9785910	-1.0496200	1.4622450	H	1.4770390	-0.4892310	3.8687940
C	-3.3668130	-2.9727640	0.7302580	C	1.8091120	-3.4814230	2.4417260
H	-3.5504860	-3.3871960	1.7304830	H	1.8615620	-3.6000350	3.5357420
H	-3.6686560	-3.7308480	-0.0046820	H	1.4210180	-4.4235110	2.0239580
H	-2.2803950	-2.8144060	0.6339290	H	2.8359240	-3.3492810	2.0703490
C	-4.6759870	0.2714880	-0.7300760	C	-0.8969490	-2.3293720	3.0119630
H	-4.4676640	0.7708950	-1.6834060	H	-1.2669990	-3.3475280	2.8137020
H	-5.7289220	-0.0805790	-0.7790130	H	-0.6919820	-2.2521130	4.0916470
C	-4.5099320	1.2974280	0.3779770	H	-1.7133310	-1.6257560	2.7818920
H	-5.1185980	2.1852230	0.1560080	C	2.3900210	-3.4552200	-1.1852210
H	-4.8200640	0.9245760	1.3640620	H	2.4485290	-4.2026640	-1.9922630

H	-3.4604990	1.6266180	0.4360460	H	2.9886130	-2.5825200	-1.4930680
H	-3.0651420	-2.5081550	-1.6972640	H	2.8579290	-3.8872800	-0.2874280
H	-4.7937290	-2.1948900	-1.9347720	C	-0.3787270	-4.5487920	-0.5664060
H	-3.2292970	-1.6568030	-3.9036210	H	-0.3175170	-4.8756340	0.4835420
H	-4.2927590	-0.3126450	-3.4557380	H	-1.4449830	-4.4275860	-0.8117220
H	-2.5833820	-0.2994240	-2.9592100	H	0.0125160	-5.3636430	-1.1955260
H	-1.0309840	-1.8530140	-2.4744990	H	-0.0766270	-3.1104720	-3.2861020
C	-0.0239160	-2.2929860	-2.5496850	H	0.6455250	-1.5221040	-2.9626090
Si	0.5892630	-2.9390350	-0.8734500	N	3.8780980	0.6572240	-0.6057130
N	0.4042070	-1.7399360	0.3373000	C	4.5744880	0.2292390	0.6164570
Na	1.4327010	0.3450580	-0.0463710	H	5.6364160	0.5551210	0.5782590
N	-0.4453970	1.8408250	0.2342980	H	4.1186010	0.7621640	1.4620520
Na	-1.4606110	-0.2889920	0.1094240	C	4.4956490	-1.2672720	0.8883170
Si	-0.8628200	2.6053560	1.7167740	H	5.1833870	-1.8541970	0.2654180
C	-1.6537440	1.3638480	2.9224760	H	4.7523100	-1.4680540	1.9379860
H	-2.5708870	0.9196710	2.4988930	H	3.4755230	-1.6420550	0.7101890
H	-0.9743560	0.5444750	3.1986180	C	3.9781920	2.1156170	-0.7571060
H	-1.9496690	1.8717680	3.8539960	H	5.0486350	2.4070830	-0.8181120
C	0.6155990	3.3832350	2.6187410	H	3.5265750	2.3862570	-1.7227090
H	1.0481990	4.1931420	2.0091720	C	3.2900860	2.9157580	0.3395580
H	0.2997700	3.8188810	3.5797820	H	3.3498150	3.9868570	0.1017170
H	1.4150250	2.6553340	2.8265510	H	2.2183050	2.6700250	0.4247680
C	-2.1283140	4.0196160	1.5725220	H	3.7549300	2.7812440	1.3253130
H	-2.2825560	4.4794460	2.5616200	C	4.4630480	-0.0110940	-1.7757740
H	-1.7870300	4.8127930	0.8896420	H	4.5773030	-1.0741110	-1.5321360
H	-3.1080610	3.6709340	1.2132880	H	5.4871120	0.3830220	-1.9500640
Si	-0.5177980	2.6708170	-1.2627110	C	3.6421400	0.0829780	-3.0511730
C	0.3173780	4.3748430	-1.3186580	H	3.5101600	1.1135670	-3.4076990
H	0.1691820	4.8430990	-2.3045880	H	4.1464290	-0.4786180	-3.8497950
H	-0.0867510	5.0611730	-0.5592650	H	2.6463910	-0.3616640	-2.9068950
H	1.4008250	4.2912920	-1.1465580	H	0.3193930	2.0426430	-3.5686700

C	0.3960210	1.6199730	-2.5550890	C	-2.2743950	2.9173390	-1.9352030
H	1.4716300	1.5635100	-2.3182780	H	-2.7754770	1.9443330	-2.0598310
H	0.0042960	0.5892810	-2.5975730	H	-2.8844360	3.5261640	-1.2501010

Table S21. Geometric coordinates and thermal corrected single point energies for a disolvated NaHMDS monomer (2x DME).

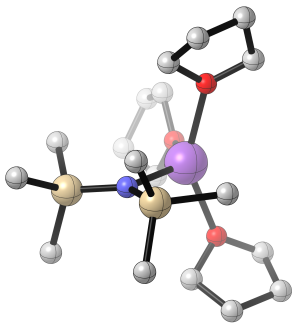


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1653.318	-1652.0066	0.517145	-1652.7825	0.053589	0.051078	-1652.8361	-1652.8336

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.9540170	-0.1797570	-0.2030820	C	1.4495280	-3.6366920	-0.5759360
N	-1.2844070	0.1294900	-0.0112860	H	0.5270910	-4.2417450	-0.5581580
Si	-1.8667250	1.3877680	0.9593030	H	1.6404440	-3.3151960	-1.6066830
C	-1.5237960	3.1097020	0.2163590	H	2.2945280	-4.2551190	-0.2256330
H	-0.4375080	3.2798060	0.1569800	H	0.8156760	-1.6332920	3.3964900
H	-1.9385060	3.1860530	-0.8020480	H	-0.1290430	-1.0821070	1.9679180
H	-1.9586580	3.9182820	0.8250700	C	3.1004850	-0.7159890	2.4036190
C	-3.7321590	1.3615760	1.3235350	H	3.6850340	0.1989620	2.2429420
H	-4.0445370	0.3826710	1.7222820	H	3.1296300	-0.9721210	3.4772340
H	-3.9960720	2.1303450	2.0675390	H	3.5671910	-1.5339240	1.8284140
H	-4.3210450	1.5557310	0.4140130	O	1.5780620	0.4958210	-2.3461680
C	-1.0208550	1.4240330	2.6673710	C	0.9935660	1.7804970	-2.2567770
H	-1.2515640	2.3535020	3.2123460	C	1.7491820	2.6657270	-1.2823990
H	-1.3622840	0.5804110	3.2899230	H	1.2094940	3.6241820	-1.1756160
H	0.0740390	1.3428130	2.5692130	H	2.7748330	2.8943980	-1.6326110
Si	-2.0923440	-1.0630320	-0.8978510	O	1.8001980	1.9793740	-0.0564310
C	-3.8176700	-0.6130620	-1.5533870	C	2.2527910	2.7466180	1.0279100
H	-4.1829560	-1.3800360	-2.2550760	H	2.2337710	2.0982550	1.9126630

H	-4.5488920	-0.5290550	-0.7353580	H	3.2802570	3.1139090	0.8545590
H	-3.7959940	0.3524380	-2.0838320	H	1.5881080	3.6097670	1.2054130
C	-2.3126460	-2.6883770	0.0746510	H	-0.0284960	1.6219200	-1.8737820
H	-2.8648280	-2.5091700	1.0112930	H	0.9413340	2.2546080	-3.2524630
H	-2.8489730	-3.4614010	-0.4986020	C	2.7103860	0.4131180	-3.1693610
H	-1.3217100	-3.0904750	0.3416670	H	3.0293100	-0.6362820	-3.1912200
C	-1.0776190	-1.5532390	-2.4355520	H	2.4717520	0.7311370	-4.1987120
H	-0.9667750	-0.6986610	-3.1217760	H	3.5465950	1.0282890	-2.7940410
H	-0.0614290	-1.8787060	-2.1591080	C	1.1444730	-2.7704070	1.5881210
H	-1.5537240	-2.3788720	-2.9883160	H	2.0562860	-3.2632730	1.9777730
O	1.7869050	-0.4589700	1.9823030	H	0.2984960	-3.4634990	1.7463840
C	0.8471530	-1.4660230	2.3048280	O	1.3093150	-2.4855800	0.2187450

Table S22. Geometric coordinates and thermal corrected single point energies for a trisolvated NaHMDS monomer (3x THF).

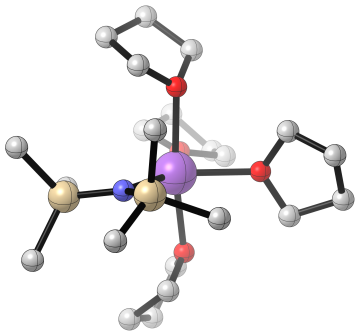


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1732.9412	-1731.5512	0.584266	-1732.3374	0.059335	0.054748	-1732.3967	-1732.3921

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Si	2.6181760	0.2198260	-0.0778390	C	-1.0667510	2.8823130	-2.3342300
N	1.2072890	0.0326850	0.8292400	H	-2.1328400	2.8974330	-2.6071440
Si	0.9450640	-0.2339740	2.4778750	H	-0.5188550	2.3218740	-3.1104070
C	0.9476500	-2.0787690	2.9487980	H	-1.2653740	4.9837760	-1.8114850
H	0.8029420	-2.2354240	4.0296130	H	-0.0328050	4.6814290	-3.0579830
H	0.1441020	-2.6180490	2.4200530	H	1.4488230	3.6035090	-1.3992240
H	1.9036260	-2.5464050	2.6620720	H	0.7888710	4.9706070	-0.4654860
C	-0.7829020	0.4112840	2.9548240	O	-0.5442310	-2.0920150	-1.3857020
H	-1.5381780	-0.0392400	2.2889110	C	-0.9168940	-2.6972090	-2.6077540
H	-1.0583720	0.1723070	3.9940650	H	-1.6133480	-3.5328620	-2.4092490
H	-0.8382780	1.5052070	2.8285600	H	-1.4341820	-1.9495460	-3.2235340
C	2.1920930	0.6121940	3.6327700	C	0.3978770	-3.2096090	-3.2088340
H	3.2085490	0.2240630	3.4556870	C	1.2918110	-3.4414160	-1.9676670
H	2.2156630	1.6981500	3.4494930	C	0.4275310	-2.9506500	-0.7946880
H	1.9503210	0.4482670	4.6948250	H	-0.0923210	-3.7946630	-0.3057780
Na	-0.5695990	0.0244650	-0.5599900	H	0.9660530	-2.3652900	-0.0358310
O	-2.7344970	-0.2461180	-0.0112950	H	1.5731420	-4.4948330	-1.8426960
C	-3.1491880	-1.4933770	0.5460960	H	2.2179860	-2.8560150	-2.0380590

H	-3.5535860	-2.1291220	-0.2596750	H	0.8377570	-2.4476650	-3.8664280
H	-2.2725350	-1.9994080	0.9781560	H	0.2468640	-4.1186620	-3.8049840
C	-4.2180570	-1.1415070	1.5773900	C	3.8684700	-1.2056140	0.0771410
C	-4.8333850	0.1196310	0.9687970	H	3.3997710	-2.1818730	-0.1248030
C	-3.5989450	0.8113210	0.4001290	H	4.7263990	-1.0889020	-0.6041310
H	-3.8065580	1.4524490	-0.4674540	H	4.2610370	-1.2421530	1.1065950
H	-3.0892950	1.4161750	1.1695190	C	2.1189960	0.3340910	-1.9208540
H	-5.5309890	-0.1458330	0.1598890	H	2.9831450	0.4383290	-2.5948380
H	-5.3693130	0.7415830	1.6969480	H	1.5565030	-0.5634760	-2.2318360
H	-3.7476170	-0.9038560	2.5431930	H	1.4658690	1.2105970	-2.0789060
H	-4.9389570	-1.9541090	1.7332540	C	3.6084720	1.7988420	0.2958920
O	-0.9050840	2.2096630	-1.0871480	H	2.9728670	2.6952830	0.2157890
C	-0.2212400	3.0480970	-0.1465210	H	3.9989130	1.7670500	1.3252850
H	-0.9630190	3.5510360	0.4995990	H	4.4640330	1.9231060	-0.3871570
H	0.4231590	2.4018360	0.4696350	C	0.5235380	4.0552170	-1.0096980
				C	-0.4824540	4.2837000	-2.1392880

Table S23. Geometric coordinates and thermal corrected single point energies for a tetrasolvated NaHMDS monomer (4x THF).

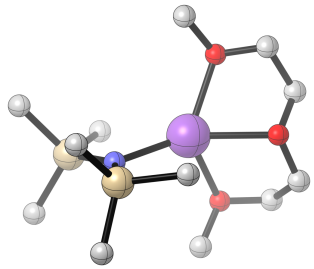


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1965.3893	-1963.7359	0.703682	-1964.6634	0.063849	0.059551	-1964.7272	-1964.7229

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.2720600	-0.0111720	0.0803480	C	2.2404100	-1.2754110	3.9934520
N	-2.0170340	0.1189060	-0.0625900	C	1.6338570	-1.5699760	2.6251780
Si	-2.4618490	0.0729410	-1.6876270	H	2.2533750	-2.2211640	1.9915160
C	-3.3094710	1.6454530	-2.3463720	H	0.6362810	-2.0306740	2.7171840
H	-2.6641450	2.5306570	-2.2246320	H	3.3365820	-1.2015010	3.9206160
H	-3.5689330	1.5606150	-3.4138630	H	1.9952420	-2.0432310	4.7382510
H	-4.2403770	1.8365570	-1.7879140	H	0.5943590	-0.0206710	4.6404120
C	-0.8650260	-0.1098500	-2.7246020	H	2.1874200	0.6613030	5.0634330
H	-1.0566410	-0.2219500	-3.8030850	O	0.5775490	-2.3113920	-0.2180660
H	-0.2428030	0.7924000	-2.5899690	C	-0.6500470	-3.0326200	-0.0781970
H	-0.2686060	-0.9761650	-2.3892710	H	-0.5807050	-3.7167340	0.7880520
C	-3.6265080	-1.3519880	-2.1711380	H	-1.4484670	-2.2944690	0.0918820
H	-3.2742380	-2.3176550	-1.7759410	C	-0.7823300	-3.8106820	-1.3794300
H	-4.6272550	-1.1749590	-1.7461590	C	0.6725340	-4.1984990	-1.6474710
H	-3.7368360	-1.4447170	-3.2636040	C	1.4344110	-2.9658430	-1.1467690
Si	-2.9042240	0.2396680	1.3698350	H	2.3820280	-3.2380940	-0.6523630
C	-3.1293510	2.0262530	1.9891950	H	1.6648630	-2.2586630	-1.9612300
H	-3.7613210	2.0696920	2.8906150	H	0.9429830	-5.0840690	-1.0532930

H	-2.1536430	2.4736830	2.2402500	H	0.8822270	-4.4203140	-2.7017620
H	-3.5970940	2.6556960	1.2147610	H	-1.1601040	-3.1472810	-2.1718820
C	-1.9747930	-0.6463120	2.7777320	H	-1.4589910	-4.6712230	-1.2979850
H	-0.9462140	-0.2511650	2.8288730	O	0.6108770	2.2795930	0.3042880
H	-2.4490440	-0.4981190	3.7608280	C	1.8142520	3.0076400	0.1502200
H	-1.9095340	-1.7305300	2.5887320	H	2.0573390	3.5306640	1.0925620
C	-4.6464450	-0.5151970	1.2957540	H	2.6151280	2.2863340	-0.0629870
H	-5.2697780	0.0207480	0.5612480	C	1.5668140	4.0223770	-0.9925200
H	-4.6015880	-1.5708670	0.9838410	C	0.0822470	3.8090200	-1.3440600
H	-5.1582150	-0.4661780	2.2700320	C	-0.4548730	3.1369880	-0.0859380
O	1.5023480	-0.2997290	1.9895600	H	-0.6458180	3.8821870	0.7096380
C	1.6688760	0.7596220	2.9301230	H	-1.3458030	2.5097980	-0.2207280
H	2.6413130	1.2527810	2.7477890	H	-0.4410450	4.7414660	-1.5914720
H	0.8715130	1.4990420	2.7686930	H	-0.0274020	3.1219380	-2.1969730
C	1.6351910	0.0943620	4.3029900	H	2.2288740	3.8523470	-1.8526920
H	2.0942180	1.5767590	-2.4300530	H	1.7467050	5.0479180	-0.6424440
H	2.1894660	-0.0732360	-3.0944770	O	2.2793230	0.0693820	-1.0340420
H	4.4636560	1.6344470	-1.9424040	C	3.4553060	-0.3707210	-0.3654930
H	4.5101760	0.5997450	-3.3906600	H	3.7431340	0.3693620	0.4033560
H	4.4105630	-1.4370960	-1.9908390	H	3.2294720	-1.3145070	0.1483110
H	5.5376900	-0.4076480	-1.0690670	C	4.5134160	-0.4796810	-1.4564920
				C	4.1154500	0.6809890	-2.3700460
				C	2.5912190	0.6003960	-2.3183910

Table S24. Geometric coordinates and thermal corrected single point energies for a monosolvated NaHMDS monomer (1x diglyme).

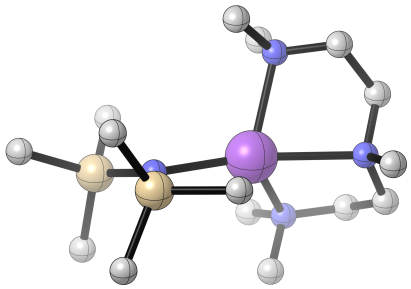


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1498.2904	-1497.1594	0.433572	-1497.8407	0.051169	0.047577	-1497.8919	-1497.8883

Atom	X	Y	Z	Atom	X	Y	Z
Si	-2.2425320	0.5847510	-1.2769620	H	1.8909050	4.1927090	0.2247870
N	-1.3870850	0.0202350	0.0641940	H	3.9164420	0.6732620	-0.9870560
Si	-1.7620900	-0.5669460	1.5996000	H	4.8792450	0.4835000	0.5121670
C	-2.7942470	0.6006230	2.6829670	H	3.0011550	-3.0176590	-1.5438930
H	-3.7967870	0.7415320	2.2487880	H	3.3485820	-1.3364330	-2.0015130
H	-2.9214130	0.2154340	3.7071400	C	0.5455350	-2.6985410	-1.1011060
H	-2.3192410	1.5926150	2.7424800	H	0.7791040	-3.1894170	-0.1403460
C	-2.6613990	-2.2413570	1.6095560	H	-0.4537770	-2.2477390	-1.0256950
H	-2.0807190	-3.0028140	1.0644330	H	0.5747080	-3.4490030	-1.9080090
H	-2.8355640	-2.6130550	2.6319140	C	-3.2725740	2.1497320	-0.9643070
H	-3.6392510	-2.1552860	1.1099380	H	-4.0665640	1.9501830	-0.2275480
C	-0.1180740	-0.8532310	2.5349350	H	-2.6415110	2.9550920	-0.5554520
H	0.4499690	0.0884210	2.6369210	H	-3.7502010	2.5218500	-1.8846620
H	-0.2716150	-1.2530830	3.5492560	C	-0.9786400	1.0397800	-2.6342870
H	0.5203990	-1.5753230	1.9947140	H	-0.3599070	0.1643020	-2.8964420
Na	0.7989960	0.2225360	-0.1968220	H	-1.4607110	1.3938080	-3.5587040
O	1.4492020	-1.6426660	-1.3747500	H	-0.3038020	1.8458200	-2.2942070
C	2.8138390	-1.9641030	-1.2718630	C	-3.4237940	-0.6844600	-2.0530900
C	3.3173220	-1.6913490	0.1403950	H	-2.8868370	-1.6094490	-2.3176410

H	2.8206680	-2.3621980	0.8566440	H	-4.2175310	-0.9568980	-1.3394330
H	4.4057440	-1.8679070	0.2076180	H	-3.9073580	-0.2980900	-2.9643530
O	2.9939190	-0.3797090	0.5527570				
C	3.8597490	0.6408430	0.1167150				
C	3.3097460	1.9522770	0.6284670				
H	3.2607910	1.9273550	1.7326930				
H	3.9760470	2.7807230	0.3264500				
O	2.0232420	2.1247650	0.0911280				
C	1.3565430	3.2822750	0.5438790				
H	0.3500730	3.2759190	0.1077510				
H	1.2693530	3.2789700	1.6433600				

Table S25. Geometric coordinates and thermal corrected single point energies for a monosolvated NaHMDS monomer (1x PMDTA).

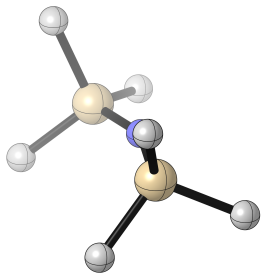


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1556.5905	-1555.4067	0.556246	-1556.0173	0.050697	0.048255	-1556.068	-1556.0656

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Si	2.6891480	0.9874910	-0.6808380	H	-2.7575290	-2.5615910	-1.0861020
N	1.6217800	-0.1072420	0.0473230	H	-3.4441650	-1.7351190	-2.4925230
Si	1.9838610	-1.4142930	1.0565060	H	-3.7101670	0.3490720	-1.1340370
C	2.8576040	-2.8770490	0.2197320	H	-4.6716880	-1.0123130	-0.5527300
H	3.8527290	-2.5767000	-0.1429740	C	-3.5010750	0.7621220	1.3234820
H	2.9903530	-3.7259920	0.9092590	C	-2.9211310	2.0509640	0.7450150
H	2.2807570	-3.2271670	-0.6509900	N	-1.4695810	2.0601370	0.6717550
C	3.0052540	-0.9837930	2.5983140	C	-0.9785440	3.2089230	-0.0703230
H	2.5137670	-0.1849450	3.1764590	H	-1.4055600	3.2142280	-1.0838850
H	3.1533310	-1.8506980	3.2615800	H	-1.2397320	4.1677740	0.4232550
H	4.0003130	-0.6119890	2.3047710	H	0.1148840	3.1481360	-0.1583110
C	0.3305660	-2.1324720	1.7177570	C	-0.8257520	1.9766180	1.9758090
H	-0.3210640	-2.4765260	0.8932980	H	-1.1234300	1.0555260	2.4993620
H	0.4971090	-3.0003620	2.3737800	H	0.2648090	1.9341630	1.8372340
H	-0.2245280	-1.3839830	2.3118540	H	-1.0803570	2.8398850	2.6246460
Na	-0.6057500	-0.0843110	0.0706470	H	-3.3029450	2.8977840	1.3567830
N	-3.0270010	-0.4558270	0.6694850	H	-3.3051420	2.2160850	-0.2745000
C	-3.6320490	-0.6345170	-0.6502710	H	-3.2365920	0.6917370	2.3886690

C	-2.8514420	-1.5757600	-1.5660940	H	-4.6089230	0.8323670	1.2903690
N	-1.5126280	-1.0938980	-1.8628660	C	-3.2688750	-1.6153520	1.5163840
C	-0.6136020	-2.1409660	-2.3234870	H	-2.8776200	-2.5262650	1.0452860
H	0.4081100	-1.7381930	-2.3828560	H	-2.7476240	-1.4961130	2.4759840
H	-0.6035160	-2.9696500	-1.6011070	H	-4.3504160	-1.7622870	1.7159920
H	-0.9075970	-2.5420050	-3.3150840	C	4.3658890	0.2419820	-1.1752220
C	-1.5051400	0.0355570	-2.7775290	H	4.9050640	-0.1351940	-0.2907420
H	-2.0888530	0.8743170	-2.3696600	H	4.2257110	-0.6053730	-1.8649950
H	-0.4736160	0.3875400	-2.9152380	H	5.0132530	0.9830110	-1.6704360
H	-1.9251700	-0.2284190	-3.7704760	C	1.9528820	1.6968780	-2.2864070
H	2.2137440	3.0638200	0.6952200	H	0.9581800	2.1412680	-2.1172470
H	3.5650530	2.1309090	1.3646910	H	2.5963030	2.4753020	-2.7258620
H	3.8198850	3.1688210	-0.0615700	H	1.8417560	0.8936710	-3.0336040
				C	3.1094590	2.4811880	0.4245210

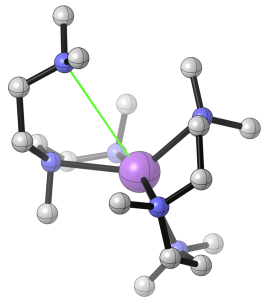
Table S26. Geometric coordinates and thermal corrected single point energies for the anionic fragment of a NaHMDS free ion.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-873.31019	-872.75122	0.223979	-873.07783	0.032322	0.031441	-873.11015	-873.10927

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Si	-1.6059210	0.0133710	0.0725470	H	3.7485460	-0.7140150	1.2439530
N	0.0000000	0.0807800	0.4430140	H	2.5370910	-0.0953990	2.4036520
Si	1.6059140	0.0133600	0.0725510	H	2.3565740	-1.7266390	1.7264860
C	2.0649960	-1.0616790	-1.4479440	C	-2.6737180	-0.6963360	1.4916370
H	1.7075810	-2.0944870	-1.3047190	H	-2.5371700	-0.0931340	2.4037030
H	1.5768870	-0.6684620	-2.3548680	H	-3.7487310	-0.7125510	1.2445420
H	3.1528410	-1.0947530	-1.6300200	H	-2.3569730	-1.7250210	1.7280120
C	2.4095610	1.7124070	-0.2986540	C	-2.4092280	1.7122440	-0.3002140
H	2.2633060	2.3929140	0.5557570	H	-3.4916120	1.6352460	-0.5000410
H	3.4919380	1.6353660	-0.4985040	H	-2.2628660	2.3935110	0.5535720
H	1.9291920	2.1781060	-1.1746840	H	-1.9287300	2.1770350	-1.1766570
C	2.6735310	-0.6978050	1.4910440	C	-2.0651380	-1.0629820	-1.4469740
H	-1.7081740	-2.0957880	-1.3025990	H	-1.5766780	-0.6709100	-2.3542010
H	-3.1529610	-1.0958170	-1.6292310				

Table S27. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3, κ^3-PMDTA.

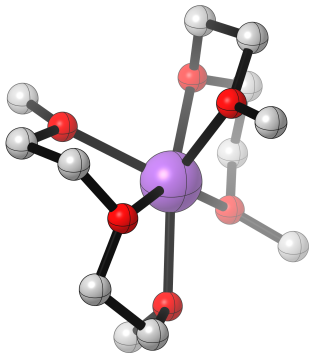


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1204.1203	-1202.8996	0.660607	-1203.4441	0.047308	0.045666	-1203.4914	-1203.4898

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.4940170	-0.1996320	0.1123120	H	4.2387940	0.5358620	-1.9134650
N	1.2943170	-1.1613720	-1.3580710	H	2.6624790	-0.8983550	-2.9566250
C	1.8726960	-2.3509430	-0.7398090	H	1.8135120	0.5573360	-2.4111900
C	0.8857040	-3.1742040	0.0740940	C	0.2495330	-1.5280930	-2.3040120
N	0.1714890	-2.4001780	1.0867160	H	-0.5675980	-2.0549330	-1.7941590
C	-0.7222840	-3.2821440	1.8257180	H	-0.1680800	-0.6220870	-2.7663850
H	-1.2937800	-2.7078230	2.5676650	H	0.6258020	-2.1817730	-3.1168440
H	-1.4282250	-3.7673840	1.1364950	N	-1.4186380	1.7510820	-1.1499810
H	-0.1659480	-4.0782280	2.3591260	C	-1.5335630	2.8029730	-0.1322420
C	1.0949280	-1.7403920	2.0039150	C	-0.3883960	2.7964840	0.8692520
H	1.6697280	-0.9546350	1.4873310	N	-0.3754470	1.6431990	1.7739980
H	0.5193390	-1.2709960	2.8135230	C	0.8853930	1.6452180	2.5135520
H	1.8072420	-2.4554030	2.4643840	H	0.8751130	0.8620890	3.2821070
H	0.1404380	-3.6570990	-0.5765340	H	1.7177530	1.4461650	1.8239700
H	1.4591080	-3.9980580	0.5493690	H	1.0550090	2.6148490	3.0226010
H	2.6843410	-2.0349270	-0.0731990	C	-1.4915560	1.6843420	2.7121710
H	2.3285750	-3.0156560	-1.5041440	H	-2.4541120	1.6622400	2.1844640
C	2.3074900	-0.3598900	-2.0523540	H	-1.4518550	0.8073880	3.3737340

C	3.5410570	0.0027030	-1.2351380	H	-1.4663220	2.5949100	3.3433720
N	3.2685040	0.7924460	-0.0410750	H	0.5680200	2.7972740	0.3242190
C	4.2788320	0.5803100	0.9829450	H	-0.4206570	3.7396550	1.4536490
H	4.3102670	-0.4806060	1.2716730	H	-2.4864730	2.6966070	0.4008190
H	5.2933670	0.8790120	0.6493590	H	-3.2877330	-0.4945330	1.8081890
H	4.0331840	1.1687460	1.8791060	C	-3.5301610	-1.1944540	0.9958450
C	3.1717610	2.2031600	-0.3707060	N	-2.9480100	-0.7341810	-0.2609880
H	2.4042680	2.3651040	-1.1409840	C	-3.5506990	0.5399450	-0.6532560
H	2.8949870	2.7890180	0.5178780	C	-2.7270600	1.3325470	-1.6586150
H	4.1292370	2.6074690	-0.7590530	H	-3.3215830	2.2075090	-1.9920950
H	4.0726240	-0.9122130	-0.9407440	H	-2.5554180	0.7208290	-2.5580630
H	-1.5736050	3.7989550	-0.6143100	H	-3.6980880	1.1366950	0.2591180
C	-0.5874930	2.2292410	-2.2497080	H	-4.5645680	0.3811310	-1.0739610
H	0.3966700	2.5415280	-1.8749210	C	-3.1604000	-1.7476390	-1.2882560
H	-0.4348360	1.4363010	-2.9943700	H	-2.7608620	-1.4156970	-2.2554300
H	-1.0465240	3.0961650	-2.7639700	H	-2.6468230	-2.6788750	-1.0070750
				H	-4.2368520	-1.9746280	-1.4207690
				H	-4.6324910	-1.2855860	0.9316740
				H	-3.1234360	-2.1793620	1.2544720

Table S28. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3, κ^3-diglyme.

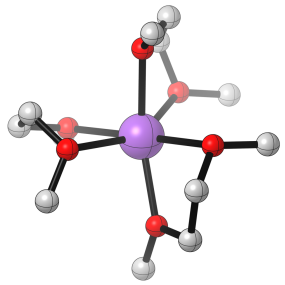


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1087.5393	-1086.431	0.415324	-1087.1107	0.04343	0.041575	-1087.1542	-1087.1523

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.0001490	0.2279490	-0.0000940	H	4.0703730	0.0242160	0.9556980
O	0.6920520	-1.3378920	-1.5404950	H	2.7212630	-1.3646440	-1.9385700
C	1.9629960	-1.9132290	-1.3488000	H	1.9746990	-2.9619810	-1.6963770
C	2.2675550	-1.8843820	0.1384450	C	0.2031710	-1.4508040	-2.8596820
H	3.2838960	-2.2700320	0.3273450	H	0.1442380	-2.5085000	-3.1658030
H	1.5428640	-2.5219630	0.6639370	H	-0.8033610	-1.0153620	-2.8679640
O	2.1048720	-0.5940810	0.6880600	H	0.8505470	-0.9115320	-3.5714190
C	3.1450260	0.3255110	0.4341300	O	-0.6926860	-1.3369500	1.5407340
C	2.6623820	1.6688250	0.9414850	C	-1.9639070	-1.9117670	1.3492880
H	2.4378610	1.5883210	2.0152480	C	-2.2685200	-1.8833630	-0.1379550
H	3.4395950	2.4385680	0.8080800	H	-3.2850190	-2.2687090	-0.3266400
O	1.4638320	2.0401540	0.2895040	H	-1.5441250	-2.5214850	-0.6632050
C	1.6338690	2.8705980	-0.8424490	O	-2.1052920	-0.5933940	-0.6881340
H	2.2580940	2.3861250	-1.6127310	C	-3.1449080	0.3268640	-0.4344770
H	0.6342060	3.0574940	-1.2530570	C	-2.6614680	1.6697840	-0.9421500
H	2.0981480	3.8283030	-0.5580650	H	-2.4368830	1.5888280	-2.0158560
H	3.3648990	0.3824730	-0.6476090	H	-3.4382790	2.4399960	-0.8090420

H	-2.7218980	-1.3626180	1.9388960	O	-1.4627390	2.0407760	-0.2903310
H	-1.9760810	-2.9603800	1.6972710	C	-1.6325990	2.8697310	0.8427320
C	-0.2038690	-1.4495260	2.8599810	H	-2.2560480	2.3839560	1.6128320
H	-0.1454200	-2.5071180	3.1665500	H	-0.6328040	3.0567430	1.2529720
H	0.8028580	-1.0145320	2.8680890	H	-2.0976560	3.8274900	0.5597980
H	-0.8510160	-0.9096620	3.5714780	H	-3.3648690	0.3841680	0.6472240
				H	-4.0704090	0.0260320	-0.9560400

Table S29. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^2, κ^2, κ^2-DME.

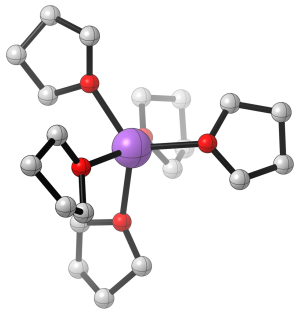


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1088.7304	-1087.6164	0.434608	-1088.281	0.046999	0.044596	-1088.328	-1088.3256

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.0145960	-0.0325590	-0.1256840	C	1.1963340	2.5252360	-1.9542150
O	1.8612670	-0.6650050	-1.3451520	O	0.7148930	2.0681630	-0.7105720
C	2.9522310	-0.2822390	-0.5258510	C	0.3854510	3.0980970	0.1926550
C	2.8248810	-0.8763770	0.8617590	C	-0.0059600	2.4531710	1.5101150
H	2.7783970	-1.9818110	0.8135010	O	-1.0217920	1.4825930	1.3505540
H	3.7049090	-0.6037100	1.4719850	C	-2.2991380	2.0201720	1.0891030
O	1.6433740	-0.3669680	1.4313160	H	-2.3532180	2.4873670	0.0915400
C	1.3197280	-0.9199570	2.6876770	H	-3.0232590	1.1971770	1.1238100
H	2.1265460	-0.7378610	3.4166570	H	-2.5712740	2.7668850	1.8532060
H	0.4003240	-0.4293380	3.0320010	H	0.8619800	1.9164620	1.9167390
H	1.1377700	-2.0041630	2.6051320	H	-0.3176540	3.2286020	2.2310550
H	3.9084570	-0.5756540	-0.9887710	H	1.2519770	3.7629090	0.3608800
H	2.9202320	0.8140730	-0.4455720	H	-0.4300700	3.7195380	-0.2218410
C	2.0908980	-1.8265390	-2.1132100	H	1.4540910	1.6388190	-2.5466560
H	1.1593780	-2.0676340	-2.6396890	H	0.4312450	3.1183060	-2.4831270
H	2.8865050	-1.6538960	-2.8557670	O	-0.8522770	-2.0731230	0.6480290
H	2.3770400	-2.6844940	-1.4819120	C	-2.2051680	-1.7399790	0.8660620
H	2.0960130	3.1495100	-1.8221890	C	-2.9012930	-1.3167580	-0.4155010

C	-0.6367510	-3.3501710	0.0920950	H	-3.9163380	-0.9505810	-0.1735460
H	0.4466570	-3.5210470	0.0728610	H	-3.0161420	-2.1626910	-1.1182610
H	-1.1076120	-4.1314160	0.7110710	O	-2.1316270	-0.2972460	-1.0105990
H	-1.0265500	-3.4257580	-0.9369290	C	-2.7390730	0.2872170	-2.1399640
H	-2.1974010	-0.8986700	1.5753130	H	-2.0512300	1.0454810	-2.5337640
H	-2.7484090	-2.5805110	1.3313810	H	-2.9323220	-0.4659990	-2.9215260
				H	-3.6930220	0.7697030	-1.8680130

Table S30. Geometric coordinates and thermal corrected single point energies for the sodium cation with 5 THF.

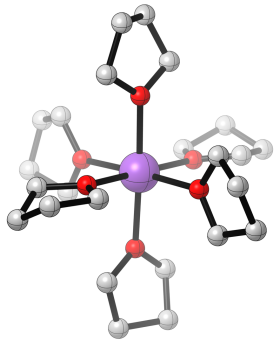


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1324.3824	-1323.0166	0.595615	-1323.7693	0.056174	0.051416	-1323.8255	-1323.8207

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.1201990	0.0299590	0.3364380	H	1.3020460	-3.3825890	-0.9385290
O	1.5192360	0.6582040	-1.1095080	H	-1.5390610	-4.1331750	-1.8177740
C	2.0095210	1.9668980	-1.4066140	H	-0.0053050	-4.8010570	-2.4248960
H	1.6183170	2.2925000	-2.3862330	H	0.5509960	-2.6662480	-3.5261630
H	1.6383710	2.6571770	-0.6354810	H	-1.1872710	-2.8141040	-3.8728810
C	3.5262880	1.8293060	-1.4510050	O	1.4232490	-0.3793150	1.9111000
C	3.6835060	0.4190080	-2.0205210	C	1.9408120	-1.6377200	2.3524800
C	2.5293920	-0.3251590	-1.3527810	H	1.3757260	-1.9722840	3.2378500
H	2.1067500	-1.1259240	-1.9770400	H	1.8021690	-2.3742720	1.5475590
H	2.8242250	-0.7665100	-0.3838480	C	3.4021180	-1.3729110	2.6941100
H	3.5464490	0.4348490	-3.1116660	C	3.3390920	0.0669820	3.2044780
H	4.6591320	-0.0354680	-1.8083290	C	2.3153050	0.6837870	2.2575340
H	3.9510540	1.8870970	-0.4371740	H	1.7372900	1.5014750	2.7111750
H	4.0042100	2.6046120	-2.0624420	H	2.7891790	1.0593170	1.3336300
O	-0.1311340	-1.8863390	-0.8924960	H	2.9647050	0.0886650	4.2383070
C	-0.6961510	-1.5318650	-2.1599090	H	4.3053350	0.5856310	3.1798120
H	-1.7750490	-1.3393550	-2.0241230	H	4.0258760	-1.4319580	1.7887400
H	-0.2133460	-0.6047720	-2.5060760	H	3.8005550	-2.0828510	3.4292240

C	-0.4473750	-2.7317910	-3.0673730	O	-2.3021520	-0.4851570	0.6390730
C	-0.4959460	-3.8873780	-2.0676810	C	-2.6990100	-1.8507960	0.8044480
C	0.2057430	-3.2733780	-0.8620370	H	-2.9305030	-2.2785150	-0.1859850
H	-0.1194550	-3.6983570	0.0987120	H	-1.8597590	-2.4158420	1.2350310
O	-0.8983860	2.1393920	0.0469280	C	-3.9301520	-1.8166920	1.7045430
C	-1.0316120	3.3940720	0.7191970	C	-4.5420080	-0.4634390	1.3434290
H	-1.7938710	3.3019820	1.5114110	C	-3.2945630	0.3939750	1.1761370
H	-0.0707330	3.6475980	1.1891310	H	-3.4276120	1.2393030	0.4863900
C	-1.4658840	4.3814950	-0.3567890	H	-2.9451910	0.7891420	2.1454070
C	-2.3156480	3.4890740	-1.2620610	H	-5.0890810	-0.5309200	0.3912670
C	-1.5192100	2.1885460	-1.2418520	H	-5.2267760	-0.0728140	2.1061250
H	-2.1380920	1.2857590	-1.3650980	H	-3.6306300	-1.8275560	2.7629010
H	-0.7343910	2.1829070	-2.0173070	H	-4.6033390	-2.6652630	1.5315150
H	-3.3127410	3.3384320	-0.8206240				
H	-2.4490670	3.8873140	-2.2752590				
H	-0.5899790	4.7584450	-0.9062010				
H	-2.0107470	5.2417190	0.0509540				

Table S31. Geometric coordinates and thermal corrected single point energies for the sodium cation with 6 THF.

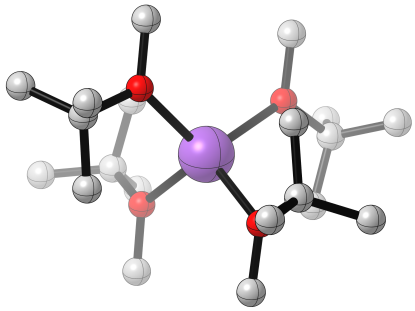


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1556.8368	-1555.2078	0.713877	-1556.1021	0.063462	0.05802	-1556.1656	-1556.1602

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.0455590	0.0002590	-0.0013920	C	-3.0571730	0.4681580	3.3298850
O	1.3007950	1.8457170	0.3907730	C	-2.4385670	-0.2819950	2.1498830
C	2.4165340	1.9036730	1.2769300	H	-2.1397550	-1.3118820	2.4017580
H	2.0557450	2.0735690	2.3071920	H	-3.1268500	-0.3299920	1.2885690
H	2.9367860	0.9342740	1.2483220	H	-2.6335250	0.1058010	4.2783110
C	3.2564090	3.0791540	0.7912920	H	-4.1470170	0.3541500	3.3798100
C	2.1712960	4.0291210	0.2834740	H	-3.2244720	2.3720550	2.2914480
C	1.1885010	3.0554730	-0.3602640	H	-2.6195040	2.5418130	3.9586520
H	0.1428210	3.3957990	-0.3339440	O	-1.2573120	-1.7887500	-0.4826960
H	1.4543510	2.8498990	-1.4115580	C	-1.1469920	-3.0451750	0.1806870
H	1.6972480	4.5493810	1.1293290	H	-0.4161460	-3.6820520	-0.3501520
H	2.5406480	4.7861930	-0.4191810	H	-0.7702600	-2.8645390	1.1978260
H	3.9103750	2.7671840	-0.0375640	C	-2.5434330	-3.6479500	0.1142730
H	3.8856270	3.5090890	1.5803200	C	-3.0029100	-3.1693820	-1.2639550
O	-1.2787740	1.2894300	-1.3070800	C	-2.4093870	-1.7617820	-1.3229480
C	-2.4380770	1.9907010	-0.8618460	H	-2.1118580	-1.4608650	-2.3398390
H	-3.1384370	1.2685660	-0.4078960	H	-3.1129290	-1.0037590	-0.9375850

H	-2.1491400	2.7161430	-0.0849480	H	-2.5632450	-3.8033980	-2.0481920
C	-3.0315500	2.6493800	-2.1071530	H	-4.0921170	-3.1756110	-1.3935450
C	-2.5632210	1.7058290	-3.2161540	H	-3.1811060	-3.2192940	0.9028300
C	-1.1658500	1.3519250	-2.7264780	H	-2.5461500	-4.7394080	0.2241990
H	-0.7831320	0.3849880	-3.0837660	O	1.3204520	-1.2412050	1.4032670
H	-0.4388330	2.1358330	-3.0064140	C	1.2028760	-1.2031150	2.8261900
H	-3.1952470	0.8048900	-3.2472680	H	1.4462780	-0.1854310	3.1770500
H	-2.5660990	2.1634770	-4.2131120	H	0.1606870	-1.4189010	3.1038560
H	-2.5970320	3.6491740	-2.2552610	C	2.2050150	-2.2289970	3.3475610
H	-4.1215420	2.7583600	-2.0501000	C	3.2907190	-2.1719330	2.2725460
O	-1.2840250	0.4661640	1.7738190	C	2.4494640	-2.0187370	1.0111020
C	-1.1917130	1.6667330	2.5358470	H	2.9616220	-1.4995760	0.1869620
H	-0.4752120	1.5252930	3.3654470	H	2.1062600	-3.0019360	0.6422290
H	-0.8061520	2.4606140	1.8798630	H	3.9278890	-1.2860890	2.4185330
C	-2.5987210	1.9034770	3.0667710	H	3.9367180	-3.0582120	2.2499280
H	2.1034390	0.9695940	-2.9266830	H	1.7499930	-3.2305450	3.3734860
H	3.9492150	-1.4045350	-2.3133000	H	2.5683900	-1.9930920	4.3553370
H	3.9524150	-0.3772340	-3.7670230	O	1.3294020	-0.5745660	-1.7811120
H	1.7789860	-1.2913550	-4.4842480	C	1.2287770	-1.8296860	-2.4552760
H	2.6108770	-2.7491720	-3.8945800	H	1.4777490	-2.6372590	-1.7454900
				H	0.1897560	-1.9756980	-2.7853420
				C	2.2353550	-1.7614220	-3.6001780
				C	3.3085050	-0.8446590	-3.0119010
				C	2.4526380	0.1644220	-2.2555870
				H	2.9554790	0.6272520	-1.3929500

Table S32. Geometric coordinates and thermal corrected single point energies for the sodium cation with 4 MTBE.

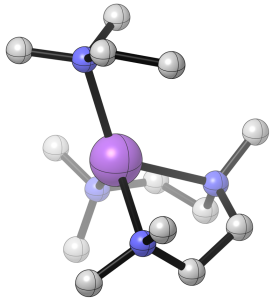


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1253.9841	-1252.6915	0.665043	-1253.2997	0.055789	0.052752	-1253.3555	-1253.3525

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
O	1.8815750	-0.4866990	-1.2419770	H	-1.4072370	3.7090890	0.8877610
O	0.4868180	1.8814540	1.2418980	C	-3.7014520	2.0697310	-0.8820320
O	-1.8815880	0.4867400	-1.2419720	H	-3.9812190	2.1994990	-1.9361750
O	-0.4867890	-1.8813970	1.2419150	H	-4.6049510	2.2488140	-0.2832980
C	-0.6722520	-3.1592610	0.5885050	H	-2.9558020	2.8339610	-0.6192600
C	-0.4446130	-1.8816390	2.6529950	C	-2.8417750	0.5332320	0.8954780
H	-1.1973120	-2.5557050	3.0867910	H	-2.0870250	1.2811810	1.1894220
H	0.5505110	-2.1676370	3.0309590	H	-3.7423630	0.6981590	1.5014620
H	-0.6769480	-0.8621550	2.9891840	H	-2.4549430	-0.4742980	1.1098400
C	-1.8819310	0.4446950	-2.6530550	C	-4.1406070	-0.4063880	-1.0372960
H	-2.5557520	1.1976760	-3.0867440	H	-4.4117060	-0.2959100	-2.0966480
H	-0.8623850	0.6767050	-2.9892770	H	-3.7091970	-1.4072890	-0.8879000
H	-2.1682910	-0.5502920	-3.0311020	H	-5.0665060	-0.3382250	-0.4500960
C	-3.1594040	0.6721860	-0.5884630	C	3.7013330	-2.0698430	-0.8821640
C	0.6722720	3.1593170	0.5884830	H	4.6048080	-2.2490420	-0.2834270
C	0.4446550	1.8817060	2.6529780	H	2.9556240	-2.8340430	-0.6194720
H	-0.5504560	2.1677370	3.0309510	H	3.9811130	-2.1995400	-1.9363120
H	0.6769630	0.8622170	2.9891700	C	2.8417560	-0.5334470	0.8954690

H	1.1973810	2.5557530	3.0867600	H	3.7423300	-0.6984970	1.5014410
C	1.8819100	-0.4445620	-2.6530580	H	2.4549920	0.4740870	1.1099230
H	2.1683620	0.5504220	-3.0310420	H	2.0869510	-1.2813720	1.1893380
H	2.5556520	-1.1975810	-3.0868040	C	4.1406630	0.4062570	-1.0372130
H	0.8623370	-0.6764490	-2.9892840	H	5.0665400	0.3379960	-0.4499890
C	3.1593790	-0.6722860	-0.5884820	H	4.4117890	0.2958330	-2.0965640
C	0.5334420	2.8418040	-0.8954970	H	3.7093130	1.4071750	-0.8877630
H	1.2814760	2.0871420	-1.1894490	C	-2.0697670	-3.7012950	0.8822290
H	-0.4740410	2.4549160	-1.1099750	H	-2.2488840	-4.6048600	0.2836050
H	0.6983440	3.7424560	-1.5013930	H	-2.1994560	-3.9809470	1.9364130
C	2.0697860	3.7013570	0.8822090	H	-2.8340210	-2.9556780	0.6194350
H	2.1994870	3.9809640	1.9364040	C	-0.5334230	-2.8417470	-0.8954730
H	2.8340450	2.9557620	0.6193710	H	0.4740880	-2.4549350	-1.1099590
H	2.2488820	4.6049510	0.2836220	H	-0.6983980	-3.7423830	-1.5013730
C	-0.4063470	4.1404680	1.0373190	H	-1.2814040	-2.0870260	-1.1894100
H	-0.2959810	4.4114340	2.0967170	C	0.4063660	-4.1404150	1.0373360
H	-0.3381140	5.0664390	0.4502400	H	0.3381380	-5.0663810	0.4502480
				H	1.4072550	-3.7090310	0.8877880
				H	0.2959950	-4.4113910	2.0967300
				Na	-0.0000060	0.0000260	-0.0001250

Table S33. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3-PMDTA, κ^1-DMEA.

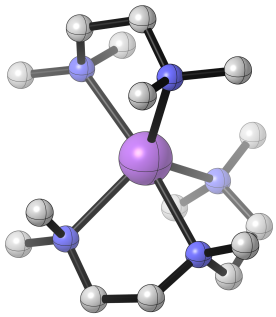


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-896.89774	-896.0209	0.480908	-896.40437	0.041467	0.039747	-896.44583	-896.44411

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.2618810	-0.0936250	-0.4150200	H	0.5428160	-3.2715060	-0.1949310
C	2.5718950	1.6656520	1.0611830	H	-0.8735990	-4.1636630	-0.8160670
C	3.1718260	0.8458500	-0.0711950	C	-2.2197110	-1.9603460	-1.5601390
N	2.6043290	-0.5037120	-0.1887160	H	-2.8353760	-1.0686110	-1.3814960
C	3.1831870	-1.1865750	-1.3433960	H	-1.8055440	-1.8884060	-2.5753540
H	2.9973770	-0.6058130	-2.2581250	H	-2.8819180	-2.8470720	-1.5207980
H	4.2770770	-1.3181390	-1.2375710	H	-0.8132670	-2.4553660	1.4339280
H	2.7289820	-2.1802290	-1.4608720	H	-2.4176180	-2.9364800	0.8609590
C	2.8309550	-1.2887560	1.0221700	H	-3.0022090	-0.4757350	0.6209540
H	2.2985880	-0.8514030	1.8777610	H	-1.6545480	0.8879880	-2.6022420
H	2.4593410	-2.3123250	0.8745550	C	-1.1750110	1.8595320	-2.4116340
H	3.9072020	-1.3512320	1.2770890	N	-0.8306860	1.9857850	-0.9964700
H	2.9966220	1.3580800	-1.0311660	C	-2.0362060	1.9106920	-0.1641200
H	4.2720730	0.7856350	0.0547790	C	-1.7555720	1.5603990	1.2936290
H	2.8667020	1.2899720	2.0503260	H	-2.6868340	1.6916280	1.8795220
H	1.4695010	1.6759800	1.0105220	H	-1.0309130	2.2766060	1.7107250
N	-1.2047980	0.2131630	1.4722180	H	-2.7005820	1.1500530	-0.6028060
C	-2.2227810	-0.8327780	1.3077080	H	-2.5986040	2.8647790	-0.2029430

C	-1.6465600	-2.1434900	0.7841110	C	-0.1181460	3.2429190	-0.7791280
N	-1.1341320	-2.0539360	-0.5875400	H	0.1110260	3.3847030	0.2845500
C	-0.3045840	-3.2172670	-0.8933390	H	0.8309360	3.2397840	-1.3336130
H	0.0885970	-3.1393000	-1.9165860	H	-0.7162030	4.1098760	-1.1203480
H	-0.1660570	-0.9289750	2.9113730	H	-1.8679810	2.6562350	-2.7437690
H	0.2870440	0.7901490	2.8502520	H	-0.2652150	1.9260120	-3.0247870
H	-1.2573320	0.2978080	3.6063630	H	-2.7365830	-1.0273300	2.2684960
H	2.9144880	2.7066340	0.9918080	C	-0.5562370	0.0892420	2.7755300

Table S34. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3-PMDTA, κ^2-TMEDA.

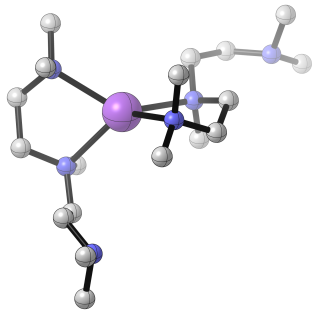


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1030.8614	-1029.8352	0.556351	-1030.2913	0.043604	0.042136	-1030.3349	-1030.3335

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.1170130	0.0213390	-0.0615590	H	-0.6249820	0.1460520	3.1761550
N	-1.7307860	0.9501430	1.5704990	H	-2.3241670	0.5271030	3.5753520
C	-3.0654830	0.8526200	0.9752620	N	2.1326980	0.3299110	1.0027880
C	-3.2836100	-0.4186280	0.1682490	C	2.9401990	0.8953010	-0.0824350
N	-2.3611970	-0.5758680	-0.9577450	C	2.2295970	1.9721240	-0.8891850
C	-2.6309570	-1.8384110	-1.6354500	N	1.0470740	1.5102210	-1.6205050
H	-1.9171350	-1.9851130	-2.4578290	C	0.4176730	2.6555500	-2.2708780
H	-2.5335110	-2.6767900	-0.9309430	H	-0.4578850	2.3321770	-2.8479760
H	-3.6547200	-1.8684170	-2.0575240	H	0.0909570	3.3850420	-1.5164620
C	-2.4836410	0.5249930	-1.9065040	H	1.1140400	3.1659560	-2.9645480
H	-2.1402880	1.4704450	-1.4628460	C	1.3878930	0.4957220	-2.6130780
H	-1.8593240	0.3190830	-2.7871640	H	1.7420420	-0.4246480	-2.1268650
H	-3.5274580	0.6628260	-2.2537270	H	0.4933570	0.2381390	-3.1975450
H	-3.1767610	-1.3031230	0.8166260	H	2.1693260	0.8442870	-3.3175180
H	-4.3346900	-0.4201990	-0.1891700	H	1.9109240	2.7910230	-0.2257030
H	-3.2224720	1.7297950	0.3315960	H	2.9665760	2.4109380	-1.5938850
H	-3.8483220	0.9095780	1.7576180	H	3.2526110	0.0872880	-0.7562460
C	-1.4093720	2.3402750	1.8778220	H	1.4034970	-2.7960970	-1.9961280

H	-0.4227450	2.3966660	2.3559910	C	0.8205560	-3.1460000	-1.1324570
H	-1.3839360	2.9361830	0.9538090	N	0.9464010	-2.2050280	-0.0261350
C	-1.6520940	0.1424020	2.7833200	C	2.3474380	-2.0883220	0.3710040
H	-1.9341100	-0.8979800	2.5738860	C	2.6204380	-0.9937050	1.3954590
H	0.3937630	-3.6156300	1.4854380	H	3.7112670	-0.9729250	1.5951940
H	1.1833810	-4.1561520	-0.8587040	H	2.1465080	-1.2540030	2.3538280
H	-0.2310540	-3.2298860	-1.4343600	H	2.9365240	-1.9121800	-0.5423440
H	3.8771940	1.3281370	0.3211310	H	2.7200440	-3.0464640	0.7899400
C	2.1552540	1.2238060	2.1559190	C	0.1037660	-2.6231600	1.0862910
H	1.8242950	2.2302770	1.8682340	H	0.1583060	-1.8975710	1.9102520
H	1.4816320	0.8520440	2.9407850	H	-0.9435730	-2.6793640	0.7531240
H	3.1714900	1.3102930	2.5879600				
H	-2.1487280	2.7954180	2.5653680				

Table S35. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^2,κ^2-PMDTA.

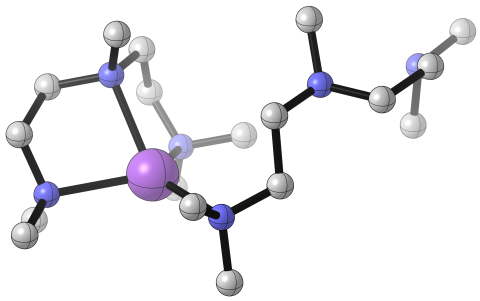


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1204.104	-1202.8817	0.657858	-1203.4295	0.051629	0.048457	-1203.4812	-1203.478

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.1626820	0.5699480	0.2483880	H	-2.1956490	-0.9304350	-1.9050230
N	-1.9703170	1.0293420	-1.2446340	C	-1.1571000	1.3992110	-2.3991790
C	-2.7155820	2.1810040	-0.7358750	H	-0.3625380	2.1051670	-2.1119370
C	-1.8171980	3.2734840	-0.1633990	H	-0.6822980	0.5010510	-2.8168660
N	-0.8817180	2.7945140	0.8559590	H	-1.7588760	1.8700130	-3.2009050
C	0.0854470	3.8360450	1.1877110	N	1.9860790	-0.3038970	-0.3726800
H	0.8103170	3.4558780	1.9210940	C	2.2220090	-1.4317110	0.5393860
H	0.6325000	4.1402140	0.2848520	C	0.9410990	-2.1576640	0.9374480
H	-0.4016120	4.7329290	1.6165480	N	-0.0223110	-1.3359530	1.6774230
C	-1.5818830	2.3497590	2.0570180	C	-1.2708560	-2.0740640	1.8537870
H	-2.2244300	1.4822220	1.8394020	H	-1.9835300	-1.4583640	2.4222810
H	-0.8510460	2.0494130	2.8213600	H	-1.7216570	-2.3173130	0.8784640
H	-2.2195070	3.1460710	2.4886780	H	-1.1149680	-3.0165640	2.4146080
H	-1.2287950	3.7391870	-0.9675620	C	0.5062830	-0.9250880	2.9744160
H	-2.4670690	4.0737980	0.2458940	H	1.3602250	-0.2423550	2.8573860
H	-3.4108330	1.8336670	0.0404360	H	-0.2736710	-0.3968370	3.5395410
H	-3.3406980	2.6312530	-1.5342420	H	0.8378020	-1.7921750	3.5793070
C	-2.8431670	-0.0962170	-1.5894770	H	0.4309580	-2.5381400	0.0378880

C	-3.6905650	-0.5885580	-0.4160040	H	1.2217600	-3.0498110	1.5345280
N	-3.9265260	-2.0169970	-0.4722250	H	2.7257310	-1.0525850	1.4395680
C	-4.6715800	-2.4606350	0.6907170	H	5.4577930	-1.2445080	-2.5103290
H	-4.1365970	-2.1863820	1.6113720	C	5.9474840	-1.0870870	-1.5385640
H	-5.6868760	-2.0143000	0.7393220	N	4.9753990	-0.6483340	-0.5539580
H	-4.7799120	-3.5533730	0.6700520	C	4.3059370	0.5716060	-0.9570540
C	-4.5972960	-2.4237100	-1.6948930	C	2.9620630	0.7889020	-0.2580820
H	-3.9875620	-2.1876460	-2.5772720	H	2.5134230	1.7037580	-0.6864700
H	-4.7526130	-3.5105590	-1.6819770	H	3.1086740	0.9924990	0.8145030
H	-5.5878840	-1.9357780	-1.8145970	H	4.1322010	0.5211160	-2.0425850
H	-3.1448170	-0.3765420	0.5213210	H	4.9348350	1.4747110	-0.7918710
H	-4.6483430	-0.0230010	-0.3636150	C	5.5818290	-0.5391930	0.7580220
H	-3.4868900	0.1646160	-2.4541750	H	4.8399150	-0.2371270	1.5108740
C	1.8364140	-0.7685200	-1.7484680	H	5.9900610	-1.5120580	1.0651610
H	0.9563050	-1.4236210	-1.8381200	H	6.4067000	0.2036740	0.7803580
H	1.6928210	0.0891340	-2.4223250	H	6.7714960	-0.3573350	-1.6794140
H	2.7184770	-1.3393330	-2.0916040	H	6.3905440	-2.0415220	-1.2232140
				H	2.9213500	-2.1582420	0.0927940

Table S36. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3,κ^1-PMDTA.

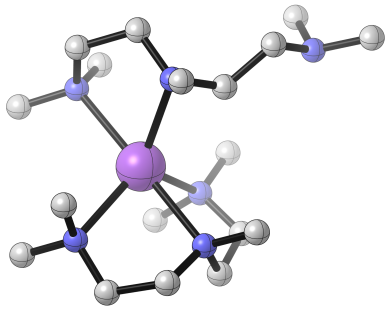


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1204.1057	-1202.8829	0.657707	-1203.4314	0.051249	0.048228	-1203.4827	-1203.4796

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	1.5841300	0.3123470	-0.4596790	C	-2.6278750	-0.2196600	2.0547050
N	-2.4831610	0.6029070	0.8702880	H	-3.4355800	-0.9449000	1.8999610
C	-3.6732430	1.3900060	0.5803440	H	-1.6992530	-0.7877030	2.2200260
C	-4.9574610	0.5653720	0.5362580	H	-2.8298560	0.3724120	2.9724890
N	-4.8326840	-0.6726830	-0.2037170	N	1.8806270	-1.1809010	1.4095600
C	-6.0539180	-1.4482570	-0.1295470	C	3.3112460	-1.5004420	1.3439700
H	-5.9132550	-2.4185430	-0.6257920	C	4.2001160	-0.2826220	1.1164850
H	-6.3151190	-1.6378330	0.9214710	N	3.9657830	0.3975040	-0.1601970
H	-6.9161450	-0.9381130	-0.6094900	C	4.6666070	1.6778830	-0.1832570
C	-4.4085950	-0.4720410	-1.5709370	H	4.4520520	2.2085130	-1.1216230
H	-3.4084510	-0.0156520	-1.5929930	H	4.3356450	2.3030910	0.6572320
H	-4.3463770	-1.4429690	-2.0827190	H	5.7635560	1.5493250	-0.1055080
H	-5.1059480	0.1719850	-2.1506010	C	4.3864440	-0.4217450	-1.2934210
H	-5.2718930	0.3152130	1.5618170	H	3.8009520	-1.3509660	-1.3440500
H	-5.7564160	1.2210310	0.1216830	H	4.2231780	0.1292000	-2.2307210
H	-3.5319120	1.8887110	-0.3906320	H	5.4591760	-0.6915730	-1.2358010
H	-3.8167650	2.1989910	1.3310090	H	4.0364590	0.4512920	1.9199420
C	-1.2863490	1.4127780	0.9292070	H	5.2590390	-0.6030450	1.1976720

C	-1.0128030	2.1538600	-0.3802210	H	3.4808540	-2.2267990	0.5388780
N	0.4147130	2.3914280	-0.6110140	H	2.1766160	-2.4110090	-2.7354940
C	0.6142400	3.0064860	-1.9204350	C	1.0980350	-2.2092850	-2.6769980
H	0.1997430	2.3592900	-2.7065180	N	0.7359150	-1.7681460	-1.3323750
H	0.1208510	3.9945770	-1.9930520	C	1.0979410	-2.7964090	-0.3550000
H	1.6880190	3.1468930	-2.1106560	C	1.0386770	-2.3411990	1.0999020
C	0.9905270	3.2335540	0.4351660	H	1.3013100	-3.2065250	1.7416700
H	0.9370760	2.7318250	1.4120050	H	0.0020260	-2.0739030	1.3568780
H	2.0471060	3.4336820	0.2084150	H	2.1111220	-3.1486310	-0.6015290
H	0.4656920	4.2055910	0.5163790	H	0.4379950	-3.6819720	-0.4588150
H	-1.3923510	1.5317440	-1.2065970	C	-0.6945160	-1.4632100	-1.2856240
H	-1.5659720	3.1145020	-0.4122130	H	-1.0066210	-1.0373590	-0.3203530
H	-1.3100290	2.1273460	1.7831830	H	-0.9352920	-0.7246640	-2.0644730
H	-0.4367520	0.7295430	1.1229350	H	-1.3125780	-2.3632640	-1.4732060
H	2.1417500	0.2410810	2.9514700	H	0.5586920	-3.1318160	-2.9663460
H	0.4848080	-0.3714880	2.7713100	H	0.8511940	-1.4270850	-3.4081820
H	1.7341260	-1.3989720	3.5277380	H	3.6382100	-2.0018580	2.2761410
				C	1.5451830	-0.6543670	2.7303550

Table S37. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^3,κ^2-PMDTA.

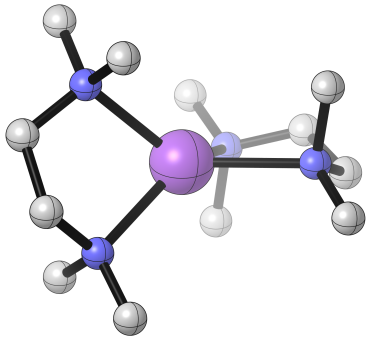


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1204.1165	-1202.8958	0.658911	-1203.4414	0.049722	0.047214	-1203.4911	-1203.4886

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.8206810	0.2285290	0.0931070	H	-1.7935040	0.4417630	0.3638620
N	-0.9336430	1.0543750	-1.4202850	C	-0.8124050	0.7548770	-2.8388440
C	-1.2254940	2.4648510	-1.1534500	H	-0.0336380	1.3873930	-3.2893980
C	-0.0168500	3.2111620	-0.6024650	H	-0.5139480	-0.2953710	-2.9721140
N	0.5034050	2.6546560	0.6486640	H	-1.7503300	0.9216720	-3.4015830
C	1.7371290	3.3416820	1.0149550	N	1.1898180	-2.1874180	-0.6386660
H	2.1900270	2.8651040	1.8963410	C	1.2183210	-2.8395850	0.6746140
H	2.4539750	3.2983430	0.1834690	C	0.0397130	-2.4843710	1.5694830
H	1.5598670	4.4094200	1.2506390	N	-0.0083540	-1.0809850	1.9821230
C	-0.4578840	2.7902420	1.7378050	C	-1.2858710	-0.8205970	2.6389810
H	-1.3664160	2.2048310	1.5432680	H	-1.3584680	0.2415540	2.9127790
H	-0.0118030	2.4230080	2.6727460	H	-2.1130800	-1.0678170	1.9566530
H	-0.7550530	3.8463320	1.8955110	H	-1.4019580	-1.4219480	3.5620550
H	0.7917630	3.1657070	-1.3501980	C	1.0970110	-0.7331460	2.8682560
H	-0.2777440	4.2827620	-0.4743980	H	2.0634900	-0.8161460	2.3481320
H	-2.0724250	2.5462490	-0.4535470	H	0.9874050	0.3094150	3.1995540
H	-1.5555730	2.9791350	-2.0714600	H	1.1325530	-1.3774010	3.7692930
C	-1.7973740	0.1324060	-0.6920020	H	-0.9058330	-2.7076370	1.0519320

C	-3.2513510	0.0014690	-1.1504620	H	0.0706510	-3.1467720	2.4595990
N	-4.0179500	-0.6732410	-0.1172470	H	2.1516690	-2.5702970	1.1860370
C	-4.4847530	0.2498200	0.8986810	H	4.3712660	0.2340250	1.3109350
H	-3.6469040	0.8330740	1.3111760	C	4.2534130	0.7066490	0.3257840
H	-5.2351610	0.9669760	0.5046290	N	3.2055000	0.0286140	-0.4296710
H	-4.9434900	-0.3032060	1.7302850	C	3.5730750	-1.3743390	-0.6103160
C	-5.1137550	-1.4663450	-0.6437280	C	2.5068930	-2.2311010	-1.2781780
H	-4.7329990	-2.2132700	-1.3536320	H	2.8889340	-3.2719220	-1.3227110
H	-5.6100750	-2.0012620	0.1775260	H	2.3792370	-1.9143510	-2.3242770
H	-5.8780770	-0.8506890	-1.1609530	H	3.8305670	-1.7799460	0.3796940
H	-3.6754860	0.9987490	-1.4020870	H	4.4970550	-1.4584740	-1.2201260
H	-3.2926350	-0.5957030	-2.0738040	C	2.9857280	0.6941490	-1.7085300
H	-1.3443310	-0.8727000	-0.7095440	H	2.1289850	0.2510700	-2.2390850
C	0.2280200	-2.8608060	-1.5076990	H	2.7617120	1.7568920	-1.5359430
H	-0.7679420	-2.8872990	-1.0475830	H	3.8707360	0.6335620	-2.3728240
H	0.1478670	-2.3310640	-2.4668320	H	5.2294790	0.6644380	-0.1959220
H	0.5331220	-3.9049630	-1.7166500	H	3.9906040	1.7604110	0.4777280
				H	1.2456150	-3.9415540	0.5549070

Table S38. Geometric coordinates and thermal corrected single point energies for the sodium cation with κ^2,κ^2-TMEDA.

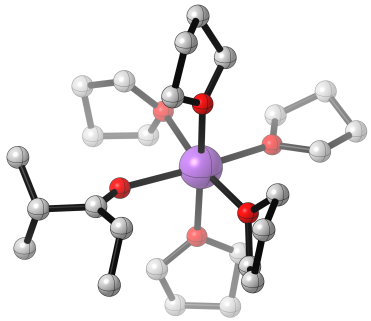


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-857.58799	-856.75533	0.451784	-857.12384	0.042891	0.040035	-857.16673	-857.16387

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.0000520	0.0013590	-0.0003650	C	1.8195080	2.5811450	-1.1195860
N	-1.8766230	1.1272330	0.9933240	H	0.9218510	2.8730250	-1.6824840
C	-3.0491270	0.7326840	0.2085520	H	1.7709490	3.0436520	-0.1240920
C	-3.0484740	-0.7326800	-0.2110400	H	2.7039440	2.9865190	-1.6475110
N	-1.8750770	-1.1265260	-0.9948130	C	1.8897060	0.5067540	-2.3147170
C	-1.8150260	-2.5801320	-1.1226290	H	1.8154680	-0.5883420	-2.2368980
H	-0.9160310	-2.8705480	-1.6841570	H	1.0328320	0.8661650	-2.9013660
H	-1.7676190	-3.0432210	-0.1273530	H	2.8129400	0.7474850	-2.8771350
H	-2.6980440	-2.9862590	-1.6523550	H	3.0921690	1.3763250	0.6831690
C	-1.8858270	-0.5050490	-2.3165030	H	3.9828170	0.9273190	-0.7732250
H	-1.8132690	0.5901000	-2.2378200	H	3.0916320	-1.3786530	-0.6792580
H	-1.0274510	-0.8628540	-2.9019400	C	1.8131110	-2.5816540	1.1204360
H	-2.8077510	-0.7466690	-2.8806900	H	0.9137310	-2.8721460	1.6813120
H	-3.0919180	-1.3779970	0.6789420	H	1.7658690	-3.0437800	0.1247010
H	-3.9808810	-0.9288620	-0.7784550	H	3.9799560	-0.9309150	0.7789430
H	-3.0922440	1.3779830	-0.6814570	C	1.8846000	-0.5077980	2.3163740
H	-3.9821220	0.9282760	0.7751870	H	1.8127940	0.5874730	2.2387380

C	-1.8171000	2.5809100	1.1206020	H	1.0257590	-0.8656280	2.9011090
H	-2.7007760	2.9870480	1.6492240	H	2.8061500	-0.7506030	2.8806570
H	-0.9187870	2.8718020	1.6829790	H	-1.7687530	3.0436330	0.1251940
C	-1.8885880	0.5062920	2.3152580	H	2.6956920	-2.9887680	1.6501390
H	-1.8158810	-0.5888730	2.2370490	C	3.0479320	-0.7339740	0.2111700
H	-1.0308040	0.8643860	2.9013830	C	3.0493660	0.7316900	-0.2073400
H	-2.8110820	0.7481090	2.8784220	N	1.8775690	1.1273620	-0.9926150
N	1.8739790	-1.1279630	0.9940490				

Table S39. Geometric coordinates and thermal corrected single point energies for the sodium cation with 5 THF and 2-methyl-3-pentanone.

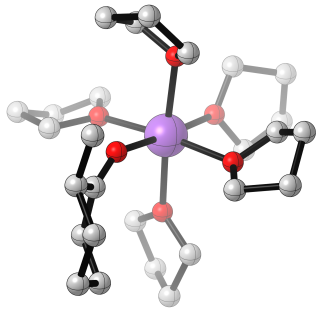


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1635.4694	-1633.7515	0.768039	-1634.679	0.065414	0.060394	-1634.7445	-1634.7394

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	0.4678500	0.0420120	-0.1354730	O	0.0018230	-1.7029750	-1.5007170
O	0.7930030	-1.5146280	1.5198980	C	1.0538930	-2.5906640	-1.8804020
C	1.3925160	-1.3130550	2.7895470	H	1.6355670	-2.1380290	-2.7025150
H	2.3851100	-1.8003440	2.8154850	H	1.7226640	-2.7207480	-1.0179300
H	1.5214490	-0.2317830	2.9295010	C	0.3519830	-3.8646690	-2.3317800
C	0.4333440	-1.9849250	3.7710070	C	-0.9167480	-3.2962810	-2.9697800
C	-0.1321810	-3.1625570	2.9479150	C	-1.2497880	-2.1447490	-2.0245170
C	0.3075360	-2.8483520	1.5021840	H	-1.7497960	-1.2966440	-2.5159800
H	1.1157610	-3.5302600	1.1811350	H	-1.8912570	-2.4780540	-1.1886160
H	-0.5016160	-2.8969030	0.7598790	H	-0.6943400	-2.9120660	-3.9763860
H	0.2764240	-4.1253130	3.2796360	H	-1.7328740	-4.0241560	-3.0558690
H	-1.2241850	-3.2263790	3.0342350	H	0.0971220	-4.4886280	-1.4609920
H	-0.3669030	-1.2860240	4.0547560	H	0.9589040	-4.4666840	-3.0191960
H	0.9346520	-2.3074800	4.6917420	C	-4.1554020	0.6045310	0.1916980
O	0.7389270	1.6105430	1.4636170	H	-4.8350840	0.4852720	1.0494410
C	-0.1905950	2.0773310	2.4370150	C	-2.7767660	0.1116840	0.5978940
H	-1.1204540	2.3905010	1.9278070	C	-2.6352710	-0.6344860	1.9018860
H	-0.4342130	1.2500530	3.1220820	H	-1.5709050	-0.8788230	2.0353060

C	0.4943790	3.2544950	3.1256890	H	-2.9313550	0.0662190	2.7027310
C	1.3577440	3.8116880	1.9927780	C	-3.5134730	-1.8867500	1.9788760
C	1.8202530	2.5318350	1.3058720	H	-3.2132910	-2.6313550	1.2268700
H	2.0238590	2.6411390	0.2305170	H	-3.4273580	-2.3525110	2.9693700
H	2.7208000	2.1198670	1.7946230	H	-4.5755630	-1.6524530	1.8211440
H	0.7425370	4.4138040	1.3070880	O	-1.8183750	0.3200580	-0.1218750
H	2.1917560	4.4333970	2.3409080	C	-4.0837970	2.0799650	-0.2009410
H	1.1312100	2.8966820	3.9485940	H	-5.0756440	2.4452990	-0.4991360
H	-0.2179140	3.9806630	3.5362960	H	-3.7253770	2.7046740	0.6306290
O	2.6788550	-0.1219570	-0.6307100	H	-3.3954830	2.2060620	-1.0485980
C	3.3604230	0.5658350	-1.6826020	C	-4.6628490	-0.2570490	-0.9716920
H	3.2885590	-0.0277690	-2.6112680	H	-3.9927030	-0.1482910	-1.8373860
H	2.8580320	1.5287810	-1.8448260	H	-4.7134310	-1.3228170	-0.7052730
C	4.8058830	0.6775910	-1.2154790	H	-5.6685290	0.0665180	-1.2722880
C	4.9704210	-0.6284870	-0.4384350	O	0.4352800	1.7960040	-1.6325500
C	3.6132770	-0.7465700	0.2486160	C	-0.3546000	2.9421220	-1.3079540
H	3.2968980	-1.7851250	0.4295640	H	-0.9800390	2.6922040	-0.4347530
H	3.6048650	-0.2149170	1.2161700	H	0.3100680	3.7781280	-1.0409950
H	5.1215170	-1.4672060	-1.1344330	C	-1.2016760	3.2372450	-2.5477850
H	5.8060980	-0.6195810	0.2722580	C	-1.2884100	1.8597660	-3.2065850
H	4.9233220	1.5408310	-0.5424710	C	0.1126130	1.3276670	-2.9417300
H	5.5150450	0.7900520	-2.0448690	H	0.1858110	0.2303510	-2.9373920
				H	0.8363510	1.7309910	-3.6723870
				H	-2.0229370	1.2319900	-2.6783750
				H	-1.5440020	1.8960000	-4.2729820
				H	-0.6801760	3.9404340	-3.2134320
				H	-2.1776860	3.6729990	-2.2982900

Table S40. Geometric coordinates and thermal corrected single point energies for the sodium cation with 5 THF and 2-methylcyclohexanone.

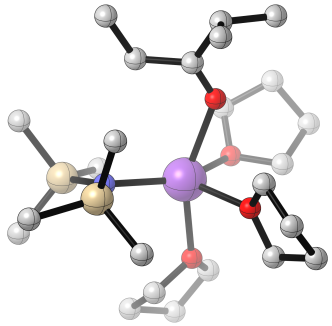


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1673.5838	-1671.8283	0.777339	-1672.7849	0.063705	0.058988	-1672.8486	-1672.8439

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.5724630	0.1493160	0.1712630	O	-1.1410290	-1.2659590	1.8567440
O	-0.6679220	-1.6750450	-1.2059330	C	-2.4682240	-1.6022430	2.2573080
C	-0.2048450	-1.7245140	-2.5545610	H	-2.8217810	-0.8796850	3.0155600
H	-0.8416680	-1.0791260	-3.1833130	H	-3.1205970	-1.5202740	1.3768090
H	0.8209720	-1.3295660	-2.5866710	C	-2.3532670	-2.9997090	2.8486560
C	-0.3050840	-3.1893820	-2.9646090	C	-0.9922410	-2.9141580	3.5420370
C	-1.5237670	-3.6443330	-2.1616610	C	-0.1858010	-2.0607410	2.5617080
C	-1.3177830	-2.8943240	-0.8499480	H	0.5396300	-1.3979390	3.0574270
H	-2.2527620	-2.6553420	-0.3223420	H	0.3604490	-2.6800080	1.8295940
H	-0.6686840	-3.4634690	-0.1601480	H	-1.0939030	-2.3957830	4.5067800
H	-2.4492870	-3.3082580	-2.6537590	H	-0.5308750	-3.8914140	3.7302510
H	-1.5840440	-4.7311570	-2.0256840	H	-2.3315960	-3.7520640	2.0451340
H	0.5921330	-3.7388360	-2.6391410	H	-3.1773940	-3.2464430	3.5293490
H	-0.4137230	-3.3225990	-4.0479990	C	4.9225860	-1.6404230	-1.0473830
O	0.0849550	1.4163850	-1.6141380	C	3.5003570	-2.0644490	-1.4047820
C	1.3815130	1.6118930	-2.1741520	C	2.5726660	-1.9825390	-0.1825410
H	2.1023710	1.8083300	-1.3597040	C	2.6518200	-0.6256010	0.4786830
H	1.6908960	0.6916180	-2.6915480	C	4.0447820	-0.1170570	0.7972870

C	1.2499100	2.8113400	-3.1063720	C	4.9345490	-0.2333750	-0.4561620
C	0.1841940	3.6379090	-2.3867070	H	4.5763770	0.4886270	-1.2116320
C	-0.7504380	2.5481180	-1.8723450	H	5.9570930	0.0730020	-0.1921910
H	-1.2768880	2.8106710	-0.9417960	H	4.4458890	-0.8300500	1.5426250
H	-1.4996580	2.2773520	-2.6365030	C	4.0265250	1.2840440	1.3863580
H	0.6337750	4.1873800	-1.5462070	H	3.4000020	1.3295530	2.2870070
H	-0.3249780	4.3610470	-3.0356720	H	5.0434510	1.6021320	1.6514860
H	0.8829660	2.4898130	-4.0923450	H	3.6213080	2.0043410	0.6589080
H	2.1980750	3.3439410	-3.2503380	O	1.6564480	0.0234940	0.7373280
O	-2.7794910	0.4145680	-0.3124800	H	1.5214910	-2.1854110	-0.4327340
C	-3.6103980	1.4192940	0.2717970	H	2.9035780	-2.7251990	0.5649260
H	-4.2703700	0.9578810	1.0279390	H	3.1163110	-1.3990530	-2.1968280
H	-2.9573010	2.1492090	0.7697650	H	3.4821650	-3.0846270	-1.8138040
C	-4.4202220	1.9828090	-0.8879350	H	5.3467490	-2.3502320	-0.3173410
C	-4.6377460	0.7294890	-1.7367410	H	5.5660060	-1.6823460	-1.9374710
C	-3.3072880	-0.0063410	-1.5707520	H	1.1929860	2.5187230	0.5590400
H	-3.4208650	-1.1014420	-1.5721250	H	0.0751050	3.9070160	0.7566950
H	-2.5839310	0.2613220	-2.3593330	C	1.0805890	3.2885030	2.6134850
H	-5.4608970	0.1308390	-1.3198760	C	0.6244530	2.0830970	3.4373030
H	-4.8734300	0.9432690	-2.7867220	C	-0.7596160	1.8427110	2.8545380
H	-3.8263880	2.7262590	-1.4410260	H	-1.1313920	0.8183400	2.9860890
H	-5.3534530	2.4608510	-0.5653210	H	-1.4961210	2.5530420	3.2711660
O	-0.5985050	2.0722780	1.4556580	H	1.2639170	1.2116230	3.2286710
C	0.4702350	2.9981560	1.2372110	H	0.6136200	2.2697250	4.5185120
				H	0.6603440	4.2125650	3.0358230
				H	2.1710230	3.4045650	2.5703700

Table S41. Geometric coordinates and thermal corrected single point energies for NaHMDS tetrasolvated monomer with 3x THF and 1x 2-methyl-3-pentanone bound.

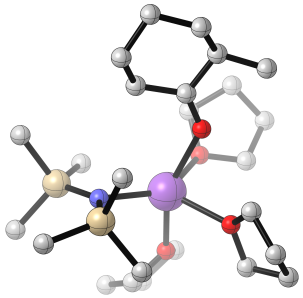


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2044.0198	-2042.2783	0.756136	-2043.2394	0.067372	0.06293	-2043.3068	-2043.3024

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.1313880	-0.5642580	-0.2054850	H	-5.0369550	-2.0810420	0.1318630
N	-1.3767380	1.3680660	0.0070210	O	0.7308420	-2.1414050	-1.6613000
Si	-2.2773450	1.5820240	-1.4064980	C	1.5243180	-3.0824420	-0.9401460
C	-1.8881190	3.1706820	-2.3832310	H	1.9366170	-2.5921910	-0.0417790
H	-0.8525330	3.1647650	-2.7593830	H	0.8750160	-3.9120660	-0.6232050
H	-2.5580060	3.2938690	-3.2493290	C	2.6263410	-3.5052560	-1.9050250
H	-2.0045210	4.0565990	-1.7379390	C	2.8523890	-2.2052350	-2.6760870
C	-1.8679580	0.1532120	-2.6057730	C	1.4274040	-1.6779650	-2.8155320
H	-2.4931540	0.1718120	-3.5121170	H	1.3814530	-0.5793380	-2.8415770
H	-0.8169040	0.2318840	-2.9334820	H	0.9290980	-2.0708130	-3.7177010
H	-1.9908610	-0.8330280	-2.1271560	H	3.4422020	-1.5088340	-2.0629320
C	-4.1652080	1.6104630	-1.1676610	H	3.3531950	-2.3422340	-3.6431450
H	-4.5080360	0.7944990	-0.5122470	H	2.2654090	-4.2958870	-2.5803800
H	-4.4670440	2.5583640	-0.6945220	H	3.5229810	-3.8727230	-1.3895320
H	-4.7015770	1.5307240	-2.1269690	O	2.0995220	0.2293040	-0.4738360
Si	-1.3789510	2.1903530	1.4839700	C	2.4940850	1.3524510	-0.7373160
C	0.2611750	3.1226810	1.7659130	C	1.5573660	2.3323720	-1.4038480

H	0.3310400	3.5691470	2.7704570	C	3.9169360	1.7578920	-0.3759580
H	1.1149760	2.4365770	1.6372720	C	2.0191540	3.7713110	-1.5870800
H	0.3712310	3.9313260	1.0240550	H	0.6048550	2.2681290	-0.8416410
C	-1.5481260	0.9827040	2.9484290	H	1.3161200	1.8778650	-2.3828430
H	-0.8950010	0.1103270	2.7856100	C	3.9037500	2.3637660	1.0362370
H	-1.2865460	1.4449530	3.9139350	H	4.2413830	2.5374850	-1.0810090
H	-2.5827070	0.6100050	3.0225720	C	4.8649910	0.5657250	-0.4505730
C	-2.7541320	3.4810270	1.7088440	H	2.2972030	4.2341640	-0.6296950
H	-2.7303790	4.2312980	0.9020400	H	1.1981000	4.3670170	-2.0086220
H	-3.7449370	3.0005150	1.6889860	H	3.5771560	1.6066590	1.7649030
H	-2.6554600	4.0131230	2.6684700	H	4.9157290	2.6931230	1.3112050
O	0.7375810	-1.4049730	1.7368270	H	4.9363490	0.1718250	-1.4745070
C	1.6915610	-0.6850410	2.5136730	H	5.8736280	0.8573370	-0.1262830
H	2.6997640	-0.8708620	2.1038640	H	4.5056950	-0.2437280	0.2003700
H	1.4738490	0.3905960	2.4300400	H	3.2257530	3.2237530	1.1189460
C	1.5478350	-1.2209720	3.9355940	H	2.8761870	3.8572920	-2.2706670
C	1.1157290	-2.6650130	3.6770200	H	2.4736440	-1.1322860	4.5183590
C	0.1865370	-2.4877100	2.4807390	O	-1.7445430	-2.1756800	0.1676820
H	0.1242200	-3.3674520	1.8244730	C	-2.9580920	-1.6528470	0.7029140
H	-0.8364880	-2.2254190	2.8002720	H	-3.1456070	-2.0851290	1.7046800
H	1.9853020	-3.2807230	3.3994340	H	-2.8355280	-0.5633810	0.7903300
H	0.6181550	-3.1364920	4.5341470	C	-4.0235780	-2.0945800	-0.2902630
H	0.7502730	-0.6763760	4.4630020	C	-3.5352910	-3.4994870	-0.6553900
H	-3.8938230	-4.2281540	0.0863470	C	-2.0059010	-3.3610070	-0.5768800
H	-3.8734060	-3.8328760	-1.6448430	H	-1.5444960	-4.2263680	-0.0704110
H	-4.0069830	-1.4322540	-1.1684620	H	-1.5312620	-3.2466410	-1.5632810

Table S42. Geometric coordinates and thermal corrected single point energies for NaHMDS tetrasolvated monomer with 3x THF and 1x 2-methylcyclohexanone bound.

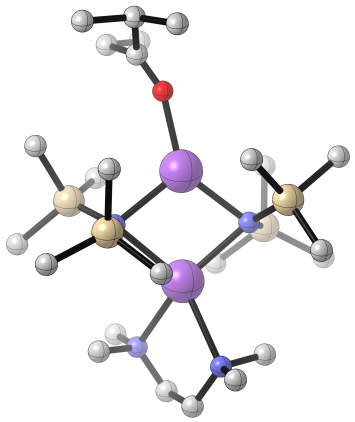


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2082.134	-2080.3549	0.765046	-2081.3451	0.067836	0.062749	-2081.4129	-2081.4078

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.4640540	-0.4962710	-0.1207960	H	-5.5302770	-0.3341000	-0.9249230
N	-1.0516910	1.7049010	0.1451770	O	0.2104360	-2.0066930	-1.7446250
Si	-1.5671150	2.4062910	-1.3008270	C	0.6598960	-3.2117620	-1.1274350
C	-0.5421240	3.9034790	-1.8807210	H	1.1207110	-2.9683540	-0.1557930
H	0.5141850	3.6266640	-2.0299490	H	-0.2146790	-3.8549930	-0.9510380
H	-0.9185930	4.3217880	-2.8280580	C	1.6735200	-3.8046040	-2.0995000
H	-0.5714430	4.7037970	-1.1237330	C	2.3129000	-2.5365880	-2.6660820
C	-1.3935390	1.1119710	-2.6945790	C	1.1109770	-1.6002180	-2.7698030
H	-1.8743520	1.4275790	-3.6338210	H	1.3775610	-0.5432640	-2.6174320
H	-0.3242580	0.9495930	-2.9118700	H	0.6053280	-1.6861630	-3.7460320
H	-1.8233870	0.1389680	-2.4002150	H	3.0409300	-2.1337120	-1.9460160
C	-3.3686890	3.0194550	-1.3068190	H	2.8200510	-2.6855110	-3.6279490
H	-4.0647170	2.2522980	-0.9327040	H	1.1624640	-4.3651010	-2.8969570
H	-3.4648340	3.8971180	-0.6480280	H	2.3901480	-4.4761370	-1.6089320
H	-3.6974040	3.3196860	-2.3148120	O	1.8933030	-0.5042440	0.0933710
Si	-0.9935070	2.2767920	1.7339840	C	2.7354850	0.2936890	-0.2698990
C	0.7961490	2.5892200	2.3117990	C	2.3604270	1.6521660	-0.8133250
H	0.8655020	2.8092120	3.3889200	C	4.2116030	-0.0810690	-0.2623530

H	1.4327390	1.7137030	2.0949430	C	3.3131170	2.7680780	-0.3711790
H	1.2129000	3.4491370	1.7623300	H	1.3112680	1.8534870	-0.5344300
C	-1.7171510	0.9980790	2.9480140	H	2.4036820	1.5575280	-1.9160190
H	-1.2986310	0.0012670	2.7353560	C	5.0860840	1.0956620	0.1982940
H	-1.5063890	1.2479570	4.0003580	H	4.4449720	-0.2538550	-1.3327180
H	-2.8107770	0.9290130	2.8290650	C	4.4694140	-1.3557240	0.5282180
C	-1.9329800	3.8952610	2.0615740	C	4.7747350	2.3777390	-0.5682880
H	-1.5718340	4.7026380	1.4042300	H	3.1395480	2.9792840	0.6953540
H	-3.0093500	3.7639850	1.8683150	H	3.0675270	3.6899960	-0.9173250
H	-1.8142350	4.2298700	3.1045020	H	4.9130060	1.2637290	1.2757240
O	-0.2178400	-1.9067480	1.6646710	H	6.1446080	0.8146570	0.0895660
C	0.8032990	-1.7083250	2.6410530	H	3.8477610	-2.1870430	0.1690650
H	1.7156590	-2.2396020	2.3185750	H	5.5264390	-1.6467280	0.4565950
H	1.0329560	-0.6340850	2.6981830	H	4.2259770	-1.1985830	1.5895560
C	0.2399940	-2.2812130	3.9382530	H	4.9831960	2.2250250	-1.6417520
C	-0.6509320	-3.4081340	3.4144140	H	5.4352720	3.1895710	-0.2303130
C	-1.2403930	-2.7646580	2.1632270	C	-3.5987640	-0.6781620	0.0655640
H	-1.5134910	-3.4818650	1.3762960	H	-4.1241230	-1.1273790	0.9296580
H	-2.1335640	-2.1625090	2.4026940	H	-3.1759870	0.2947520	0.3567560
H	-0.0405580	-4.2838760	3.1446480	C	-4.5005330	-0.6336380	-1.1597970
H	-1.4203680	-3.7302660	4.1277200	C	-4.3852530	-2.0715830	-1.6721070
H	-0.3718050	-1.5224200	4.4490840	C	-2.9313760	-2.4331460	-1.3338930
H	1.0232750	-2.6193040	4.6288000	H	-2.8414580	-3.4648390	-0.9535750
O	-2.5126270	-1.5154180	-0.3280680	H	-2.2519070	-2.3244370	-2.1932950
				H	-5.0813530	-2.7236650	-1.1240620
				H	-4.6017830	-2.1715850	-2.7434150
				H	-4.0923420	0.0775480	-1.8933660

Table S43. Geometric coordinates and thermal corrected single point energies for NaHMDS disolvated dimer with 1x TMEDA and 1x 2-methyl-3-pentanone bound.



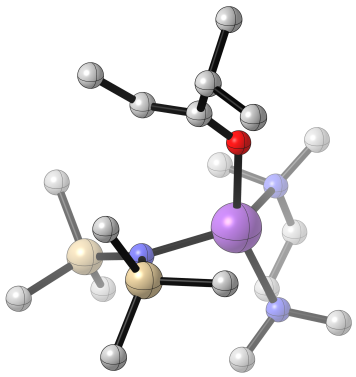
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2730.0505	-2728.1131	0.855373	-2729.1664	0.074515	0.070314	-2729.2409	-2729.2367

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
N	0.8699980	1.9055090	-0.1058750	H	0.6355680	5.2254030	0.0663660
Na	1.7681910	-0.3303540	0.0156010	H	-1.0361860	4.6238000	0.1403980
Na	-1.0579860	0.6076720	-0.0908850	H	-0.2700030	5.3057020	1.5935200
N	-0.2964390	-1.5898310	0.1719620	N	4.1887210	-0.1755870	0.9382900
Si	-0.3267130	-1.9497250	1.8446730	C	4.4632560	-0.0505260	2.3603160
C	-0.0936260	-3.7806730	2.2863880	H	3.7923230	0.6959520	2.8055930
H	-0.0890460	-3.9273060	3.3781350	H	4.2925950	-1.0108130	2.8669810
H	-0.9100530	-4.3935800	1.8720470	H	5.5102800	0.2642060	2.5516810
H	0.8544720	-4.1738350	1.8870420	C	5.0326070	-1.2041050	0.3448740
C	1.0946900	-1.0266580	2.7131360	C	4.5918530	-1.6357730	-1.0487490
H	2.0658980	-1.4635610	2.4296900	N	3.1856140	-2.0018890	-1.1230260
H	1.1265690	0.0483370	2.4659300	C	2.8417130	-3.0815880	-0.2086640
H	1.0109250	-1.1063600	3.8078930	H	1.7799810	-3.3312350	-0.3305060
C	-1.9534510	-1.4298460	2.6948770	H	3.4555310	-3.9893220	-0.3902630
H	-2.3377840	-0.4762040	2.2955180	H	2.9841470	-2.7679130	0.8357830
H	-2.7256550	-2.1958260	2.5201330	C	2.8150960	-2.3579920	-2.4823550

H	-1.8341500	-1.3155220	3.7839130	H	1.7245760	-2.4796090	-2.5466550
Si	-1.2270890	-2.4713310	-0.9577170	H	3.1118460	-1.5611970	-3.1771760
C	-1.4586670	-1.4640640	-2.5555770	H	3.2954150	-3.3046100	-2.8070850
H	-1.9031820	-0.4714870	-2.3662770	H	5.2433000	-2.4814040	-1.3621970
H	-0.4985500	-1.3032230	-3.0709600	H	4.7684730	-0.8253740	-1.7747130
H	-2.1248890	-1.9871910	-3.2605810	H	6.0908270	-0.8690130	0.2875370
C	-0.5345210	-4.1610120	-1.4854550	H	5.0246030	-2.0760340	1.0157320
H	-0.3251870	-4.7829040	-0.6005490	C	4.3660150	1.1128660	0.2833300
H	-1.2745410	-4.6958790	-2.1019680	H	4.1616210	1.0318110	-0.7925080
H	0.3936670	-4.0916700	-2.0714130	H	3.6540090	1.8406820	0.6957880
C	-2.9780880	-2.8816930	-0.3221240	H	5.3992650	1.4996970	0.4094650
H	-3.6227940	-3.2871120	-1.1191600	O	-3.2571740	0.8516650	-0.2441110
H	-2.9311880	-3.6369120	0.4795570	C	-4.4178080	0.5230390	-0.4003340
H	-3.4632620	-1.9898430	0.1038900	C	-5.4362950	0.6799790	0.7080160
Si	1.2745700	2.4249270	-1.6831020	C	-4.8699720	-0.0517160	-1.7249460
C	-0.2128270	3.0980620	-2.6554180	H	-6.3362850	1.1096880	0.2330160
H	-1.0126460	2.3398500	-2.7125500	C	-5.8014540	-0.7148720	1.2430860
H	-0.6324460	3.9912030	-2.1679820	C	-4.9371060	1.5945080	1.8174130
H	0.0602280	3.3703300	-3.6870960	H	-4.2806780	-0.9676640	-1.8921420
C	1.8834980	0.9320660	-2.6942240	H	-5.9301820	-0.3361010	-1.6764720
H	2.8605400	0.5596290	-2.3468510	C	-4.6184440	0.9418550	-2.8614000
H	1.1680680	0.0947310	-2.6304180	H	-6.6266470	-0.6312500	1.9634490
H	1.9931620	1.1902710	-3.7589560	H	-6.1118050	-1.4038320	0.4445050
C	2.6399770	3.7383940	-1.7984690	H	-4.9374940	-1.1562860	1.7615680
H	2.8812020	3.9624100	-2.8496720	H	-4.0509940	1.1609950	2.3026800
H	2.3333170	4.6809070	-1.3201830	H	-4.6555240	2.5828910	1.4290660
H	3.5644220	3.4029030	-1.3035400	H	-5.7164620	1.7269320	2.5802740
Si	0.5158250	2.9590280	1.1957630	H	-3.5584610	1.2267360	-2.8946060
C	-0.9183840	2.2557650	2.2401030	H	-4.8867390	0.4967330	-3.8279400
H	-1.8646440	2.2424350	1.6703380	H	-5.2128900	1.8572170	-2.7289420
H	-1.0959740	2.8896700	3.1228400	H	1.6775250	3.8757760	3.2291440

H	-0.7247010	1.2363920	2.6113330	H	2.3054210	2.2645800	2.8140230
C	1.9643010	3.2224030	2.3905330	H	2.8173910	3.6915010	1.8745930
				C	-0.0887870	4.6897310	0.6984570

Table S44. Geometric coordinates and thermal corrected single point energies for NaHMDS disolvated monomer with 1x κ^2-TMEDA and 1x 2-methyl-3-pentanone bound.

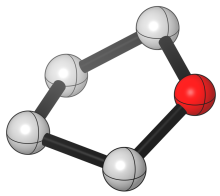


E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1694.4051	-1693.0613	0.625409	-1693.7601	0.056116	0.053313	-1693.8162	-1693.8134

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	2.7390840	-1.8777160	-1.8802310	C	3.1177210	2.2768320	2.1386240
Si	0.9559680	-2.2488670	-1.3098190	H	2.7048920	1.9976840	3.1179930
N	0.4452790	-1.2982320	0.0008130	H	4.2086470	2.4462380	2.2584920
Si	-0.2564150	-1.8082830	1.4568870	H	2.6505800	3.2259500	1.8411230
C	0.6209380	-3.2230070	2.3683130	C	0.9405020	-4.1243510	-0.9990740
H	0.2110820	-3.3565560	3.3820880	H	-0.0496100	-4.4658490	-0.6555210
H	0.5074800	-4.1763300	1.8312780	H	1.1853350	-4.6761650	-1.9205100
H	1.6997200	-3.0182630	2.4586020	H	1.6764410	-4.4067530	-0.2302920
C	-2.0868890	-2.3223580	1.3133060	C	-0.1009520	-2.0044460	-2.8773440
H	-2.2167240	-3.0946080	0.5375850	H	0.3172530	-2.5684450	-3.7261540
H	-2.4814840	-2.7213360	2.2614310	H	-1.1292920	-2.3646840	-2.7107620
H	-2.7147390	-1.4602070	1.0304710	H	-0.1606990	-0.9444760	-3.1743610
C	-0.2902100	-0.3635170	2.7201000	H	2.8478510	-0.8835350	-2.3433460
H	0.7184110	0.0297020	2.9334860	H	3.4533510	-1.9426690	-1.0439400
H	-0.9307900	0.4750320	2.3973680	H	3.0490390	-2.6147300	-2.6383150
H	-0.7019300	-0.7188950	3.6774560	O	-1.6751850	1.5389830	0.2229190
Na	0.5144300	0.9366710	0.4554000	C	-2.6404720	0.9172890	-0.1874300

N	2.8285000	1.2291440	1.1756030	C	-3.9899720	1.0736350	0.4886540
C	3.3870830	1.5093400	-0.1436530	C	-2.4948110	0.0485400	-1.4161490
C	2.7830910	2.7295590	-0.8322840	H	-4.5338630	0.1219750	0.3908580
N	1.3469930	2.6100750	-1.0582880	C	-3.8422590	1.4381890	1.9600090
C	0.6921160	3.9001710	-1.1801130	C	-4.7590190	2.1532190	-0.2916420
H	-0.3935030	3.7517100	-1.2657600	H	-2.2463860	0.7364350	-2.2435690
H	0.8831000	4.5059660	-0.2831780	H	-1.5746260	-0.5373310	-1.2288410
H	1.0406610	4.4679990	-2.0673640	C	-3.6568040	-0.8564990	-1.8019340
C	1.0405890	1.7637180	-2.2025750	H	-4.8297320	1.5909210	2.4172100
H	-0.0480830	1.6275480	-2.2757640	H	-3.3240190	0.6422210	2.5136720
H	1.4089800	2.2003250	-3.1536350	H	-3.2569720	2.3617860	2.0666550
H	1.4858470	0.7662040	-2.0807480	H	-4.2388170	3.1186800	-0.2045700
H	3.3259850	2.8978250	-1.7857340	H	-4.8507920	1.9076680	-1.3595780
H	2.9602130	3.6253470	-0.2191480	H	-5.7711720	2.2685680	0.1201360
H	3.2262570	0.6123720	-0.7616430	H	-4.5849070	-0.2971680	-1.9893620
H	4.4878220	1.6545950	-0.0817590	H	-3.4075590	-1.4019940	-2.7219490
C	3.3062170	-0.0653160	1.6473070	H	-3.8563000	-1.6035460	-1.0207610
H	4.4140770	-0.0999780	1.6998070				
H	2.9090400	-0.2661860	2.6520680				
H	2.9378130	-0.8547980	0.9768820				

Table S45. Geometric coordinates and single point energies for THF.

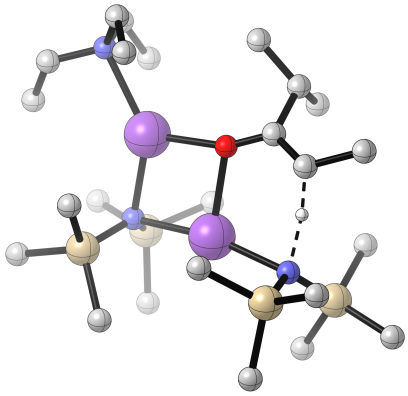


G = -232.060313 Hartrees

$\mathbf{G_{SP}}$ = -232.329161 Hartrees

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.1561140	-0.4302150	-0.1364250				
H	-1.5191120	-0.4680640	-1.1798190				
H	-1.9521560	-0.8248280	0.5124330				
C	-0.7265970	0.9879550	0.2364880				
H	-0.7694920	1.1264360	1.3276930				
H	-1.3464000	1.7629510	-0.2329060				
C	0.7269230	0.9876820	-0.2366390				
H	0.7698960	1.1257440	-1.3278950				
H	1.3469340	1.7626540	0.2325220				
C	1.1559260	-0.4304830	0.1367540				
H	1.9523400	-0.8254160	-0.5114370				
H	1.5181460	-0.4681940	1.1804400				
O	-0.0001230	-1.2351150	-0.0002630				

Table S46. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a monosolvated triethylamine closed dimer transition structure poised to generate the *E* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2674.6735	-2672.8041	0.832028	-2673.813	0.074402	0.069974	-2673.8874	-2673.883018

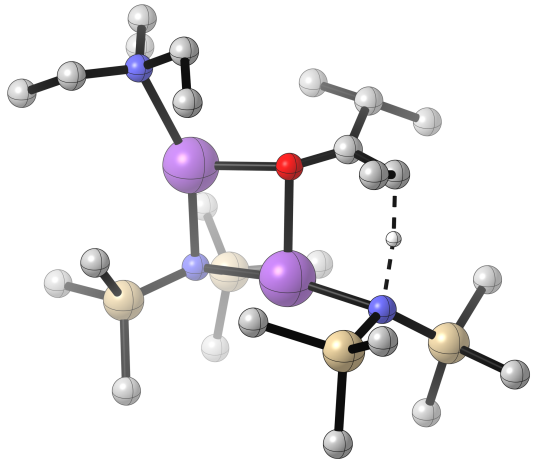
Imaginary frequency: -1073.49 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
H	-2.8207080	0.9839920	-2.5105820	H	1.0518420	3.0282430	-1.4375630
C	-1.8138710	1.4209100	-2.6357460	H	0.1099550	3.9851720	-2.6017910
Si	-1.4422810	2.5873070	-1.1759090	H	-1.0826990	0.5968690	-2.7042460
N	-1.2713020	1.6097390	0.2207200	H	-1.8091630	1.9398890	-3.6061960
Na	-2.0115760	-0.5024810	-0.2607390	N	-4.1261350	-1.6407870	-0.5448400
N	3.0396030	-0.0546350	-0.1397780	C	-4.6534590	-2.0513370	0.7687930
Na	0.8181450	0.5528670	-0.0088170	H	-5.7410250	-1.8548970	0.8202830
Si	3.5119620	0.3772780	-1.7428360	H	-4.5366210	-3.1404120	0.8685550
C	4.3083450	2.0886740	-1.8586290	C	-3.9419580	-1.3766870	1.9361070
H	3.6284670	2.8680430	-1.4805400	H	-3.9686560	-0.2819190	1.8549690
H	5.2363600	2.1407520	-1.2684540	H	-4.4057340	-1.6554540	2.8926790
H	4.5601640	2.3355740	-2.9018970	H	-2.8884880	-1.6905540	1.9849860
C	4.7081910	-0.8687760	-2.5161530	C	-3.9337100	-2.7617000	-1.4771300
H	4.2647820	-1.8759650	-2.5565780	H	-3.6439580	-3.6446310	-0.8915820

H	4.9806920	-0.5788500	-3.5429730	H	-4.8891370	-3.0147920	-1.9792520
H	5.6339330	-0.9341270	-1.9242540	C	-2.8496150	-2.4880350	-2.5120030
C	1.9624450	0.4108040	-2.8490670	H	-2.7746330	-3.3273120	-3.2173060
H	1.3213830	1.2828620	-2.6398380	H	-3.0539920	-1.5831170	-3.1024640
H	2.2435090	0.4793100	-3.9114480	H	-1.8643740	-2.3720460	-2.0304890
H	1.3472990	-0.4962880	-2.7275850	C	-4.9652960	-0.6070120	-1.1676810
Si	4.0086850	0.1988680	1.2635370	H	-5.9863740	-1.0116140	-1.3299080
C	3.4471550	-0.9952130	2.6187030	H	-4.5544150	-0.4009050	-2.1674330
H	2.3827890	-0.8518690	2.8641160	C	-5.0530040	0.6965080	-0.3876980
H	3.5855120	-2.0381300	2.2908110	H	-4.0586200	1.1227090	-0.1698440
H	4.0254990	-0.8524540	3.5444210	H	-5.6098780	1.4384080	-0.9766930
C	5.8550130	-0.1195190	0.9870140	H	-5.5848160	0.5700140	0.5660630
H	6.4276760	0.0424670	1.9134920	O	-0.0818260	-1.5953490	-0.3027820
H	6.0215640	-1.1589520	0.6628830	C	0.6944260	-2.5489610	-0.0521820
H	6.2744740	0.5435840	0.2143750	C	0.2094780	-3.6188050	0.9213590
C	3.8142620	1.9571660	1.9367410	C	2.0245500	-2.5896060	-0.5995580
H	4.1091490	2.6996100	1.1789940	H	0.8264140	-4.5166430	0.7770440
H	2.7640130	2.1554900	2.2076700	C	0.3928190	-3.1371970	2.3633620
H	4.4272240	2.1252550	2.8359080	C	-1.2440960	-3.9800020	0.6233830
Si	-1.3784600	2.2083760	1.8237680	H	2.5286310	-1.4596990	-0.2409870
C	-0.7237850	0.8751160	3.0069810	H	-0.0085780	-3.8791960	3.0688170
H	-0.7865620	1.1913580	4.0594820	H	1.4532400	-2.9767930	2.6001840
H	-1.3061900	-0.0554970	2.9057560	H	-0.1323720	-2.1846470	2.5310890
H	0.3337930	0.6318120	2.8065600	H	-1.8968370	-3.1050060	0.7635410
C	-3.1415420	2.6330730	2.3845860	H	-1.3639150	-4.3318840	-0.4122070
H	-3.7970240	1.7490840	2.4130080	H	-1.5891570	-4.7737420	1.3014060
H	-3.1366060	3.0735720	3.3940830	H	1.9956080	-2.3018060	-1.6607900
H	-3.5990510	3.3639950	1.6999540	C	2.9579060	-3.7460490	-0.2991800
C	-0.3527190	3.7761280	2.1114090	H	3.0305000	-3.9371580	0.7822870
H	0.6914120	3.6375970	1.7882090	H	2.6647220	-4.6901910	-0.7869430
H	-0.7651180	4.6224420	1.5384230				

H	-0.3439630	4.0669660	3.1734550	H	3.9732540	-3.4997560	-0.6429330
C	-2.8478260	3.8580390	-1.1270470	H	-2.6787750	4.5948860	-0.3256900
C	0.1179580	3.5978090	-1.5707580	H	-2.9058240	4.4103620	-2.0782500
H	0.1734630	4.4606500	-0.8885550	H	-3.8255320	3.3860880	-0.9470690

Table S47. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a monosolvated triethylamine closed dimer transition structure poised to generate the *Z* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2674.6704	-2672.8002	0.833173	-2673.8093	0.07242	0.068649	-2673.8817	-2673.877914

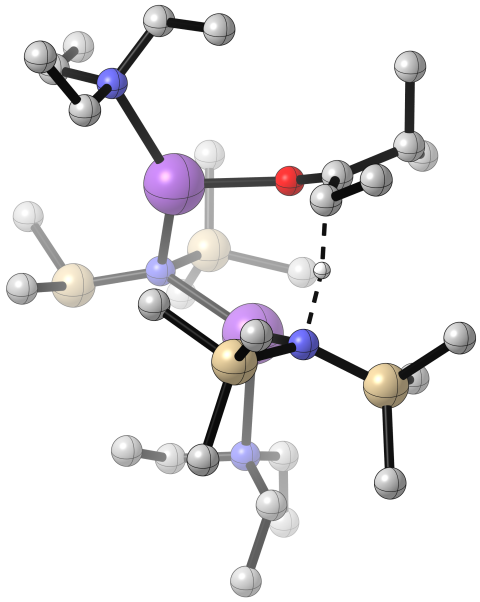
Imaginary frequency: -1296.43 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Symbol	X	Y	Z	H	-5.6464080	-2.5549800	0.1749400
H	-3.0458500	0.7964240	-2.1311280	H	-4.1710920	-3.0887220	0.9692070
C	-2.2471910	1.4999310	-2.4234340	C	-4.7553690	-1.1001420	1.5228460
Si	-1.7772870	2.6723610	-0.9960640	H	-5.1359900	-0.1671230	1.0883040
N	-1.0960910	1.7375640	0.2663720	H	-5.4330530	-1.3957970	2.3360990
Na	-2.1163390	-0.3084000	0.0166220	H	-3.7794920	-0.8858300	1.9846130
N	3.0217390	-0.3244990	-0.3520890	C	-2.9923290	-2.9857790	-1.1100860
Na	0.8654430	0.5253260	-0.0486230	H	-2.3749530	-3.2662180	-0.2428220
Si	3.1527580	0.0386140	-2.0405460	H	-3.6272200	-3.8633160	-1.3536150
C	4.0416140	1.6786820	-2.3755820	C	-2.0660540	-2.6847900	-2.2793480
H	3.5671790	2.5073070	-1.8268880	H	-1.3476870	-3.5080760	-2.3916840
H	5.1028080	1.6455990	-2.0844090	H	-2.6025580	-2.5806150	-3.2313880
H	3.9989790	1.9153600	-3.4505770	H	-1.4779160	-1.7709510	-2.1017210

C	4.0259660	-1.2567780	-3.1083800	C	-4.6866260	-1.4107860	-1.8078170
H	3.3978180	-2.1375740	-3.3001280	H	-5.2985290	-2.2665880	-2.1661820
H	4.2955010	-0.8174020	-4.0816200	H	-4.0276660	-1.1253060	-2.6388900
H	4.9530960	-1.5979740	-2.6230300	C	-5.6019320	-0.2376670	-1.4938620
C	1.4044640	0.2957270	-2.7620830	H	-5.0356200	0.6306680	-1.1238080
H	0.9753850	1.2640710	-2.4492530	H	-6.1198370	0.0711450	-2.4119830
H	1.4449210	0.3224900	-3.8617270	H	-6.3703820	-0.4934250	-0.7516200
H	0.6970640	-0.5026800	-2.4824850	O	-0.2649660	-1.5217280	0.1681690
Si	4.3278680	0.0219310	0.7353870	C	0.4903930	-2.2842940	0.8152540
C	4.0149800	-0.8268480	2.3918630	C	0.0196560	-2.7782260	2.1866400
H	3.0665490	-0.4909870	2.8383320	C	1.7591710	-2.7041940	0.2869410
H	3.9729970	-1.9204130	2.2760760	H	-0.1000840	-3.8677660	2.0373640
H	4.8237720	-0.5903740	3.1003720	C	1.0433400	-2.5885770	3.3090200
C	5.9941930	-0.6134550	0.0955320	C	-1.3358680	-2.1952970	2.5696780
H	6.8006420	-0.4196280	0.8198710	H	2.4160370	-1.5639480	0.0998360
H	5.9477820	-1.6999000	-0.0797930	H	2.2982190	-3.3887180	0.9524490
H	6.2767390	-0.1333480	-0.8546700	C	1.7554060	-3.1715910	-1.1629850
C	4.5415240	1.8697000	1.0979990	H	0.6977160	-3.1040500	4.2162890
H	4.8974280	2.4208400	0.2158970	H	2.0294930	-2.9893590	3.0456170
H	3.5962690	2.3334350	1.4220630	H	1.1668760	-1.5244880	3.5549660
H	5.2776190	2.0157880	1.9044170	H	-1.2777190	-1.1002310	2.6800980
Si	-0.8571310	2.2763140	1.8737100	H	-2.0978620	-2.4272940	1.8119170
C	0.5988710	1.2957750	2.6222100	H	-1.6785400	-2.6086800	3.5286200
H	0.6805980	1.4439980	3.7099020	H	1.2589950	-2.4347840	-1.8096540
H	0.4842530	0.2109740	2.4537890	H	2.7860300	-3.2891610	-1.5229700
H	1.5662740	1.6046450	2.1897390	H	1.2378470	-4.1366610	-1.2918740
C	-2.3596650	1.9599330	2.9889130	C	-3.3822910	3.5568350	-0.4996940
H	-2.5938960	0.8846760	3.0567820	H	-3.2000620	4.2945900	0.2977330
H	-2.1983410	2.3277970	4.0141290	H	-3.8377850	4.0893910	-1.3492500
H	-3.2470350	2.4689840	2.5799490	H	-4.1219660	2.8360310	-0.1136740
C	-0.4057060	4.1055270	2.0486140	C	-0.6158150	3.9847850	-1.7079180

H	0.5174220	4.3295380	1.4912400	H	-0.3684170	4.7328930	-0.9391710
H	-1.2003600	4.7593060	1.6563640	H	0.3306430	3.5400810	-2.0540920
H	-0.2395060	4.3759340	3.1029800	H	-1.0729990	4.5126670	-2.5592770
				H	-1.3802220	0.9105050	-2.7630740
				H	-2.6292090	2.0581960	-3.2920530
				N	-3.8387190	-1.8539860	-0.6928570
				C	-4.6408200	-2.2161340	0.4900790

Table S48. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a disolvated triethylamine open dimer transition structure poised to generate the *E* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2927.7321	-2925.5772	1.014317	-2926.6858	0.080544	0.076158	-2926.7664	-2926.761978

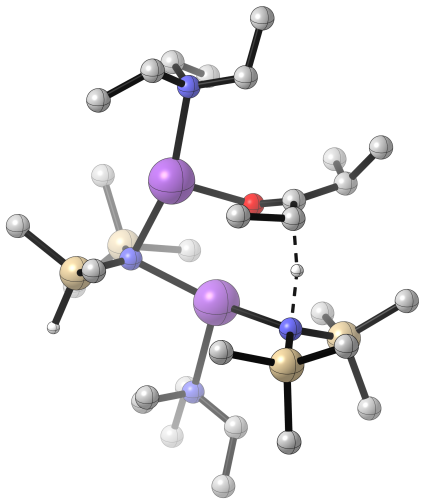
Imaginary frequency: -1257.63 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-1.1753710	-2.1613450	1.5146220	H	2.1940880	-1.5416810	-4.4050450
C	-1.0153320	-2.9902440	0.3537980	H	2.8230010	-0.4264080	-3.1756830
H	-1.4932130	-2.5226300	-0.5202270	H	3.3747350	-2.1185190	-3.2059320
Na	-1.9971310	0.5591900	-0.0356450	C	0.4817200	-3.6542030	-2.8687450
Na	1.2216670	0.3305130	0.2470370	H	0.3342800	-3.6384210	-3.9599750
N	-0.3515160	2.1826740	0.1598620	H	-0.4699100	-3.9527500	-2.4038590
N	1.3962510	-1.9518960	-0.5410980	H	1.2255350	-4.4349380	-2.6414190
O	-1.2951770	-0.9218330	1.4134680	C	-0.3608450	-0.7472930	-2.5460240
H	0.2026500	-2.5568960	0.0162610	H	-1.3039970	-1.1600120	-2.1531570
C	-1.1864800	-4.4967120	0.3841680	H	-0.1817990	0.2252060	-2.0574890
H	-0.8034870	-4.9481680	1.3092350	H	-0.5146290	-0.5467390	-3.6179870

H	-0.6362530	-4.9673810	-0.4436120	C	0.6301590	4.3156540	2.1018760
H	-2.2430060	-4.7993310	0.2854630	H	0.8036710	4.4846580	3.1763250
C	-1.1591580	-2.7803990	2.9093880	H	0.0067790	5.1433640	1.7305580
H	-0.4843960	-3.6503700	2.8936570	H	1.6005270	4.3870820	1.5863580
C	-2.5824900	-3.2813930	3.1986500	C	0.8140150	1.3289060	2.7579440
H	-2.6243380	-3.7723970	4.1814740	H	0.3235310	0.3499890	2.6415320
H	-2.9284200	-3.9987030	2.4410240	H	0.8308660	1.5573060	3.8347300
H	-3.2813440	-2.4303640	3.2123490	H	1.8636030	1.2548700	2.4341360
C	-0.6994700	-1.8043410	3.9841630	C	-1.8606200	2.6852530	2.7318040
H	-0.7797100	-2.2680750	4.9777110	H	-1.7237240	2.9317160	3.7966480
H	-1.3187120	-0.8964620	3.9677030	H	-2.5322520	3.4413130	2.2956400
H	0.3451190	-1.4982170	3.8363420	H	-2.3615800	1.7027990	2.6854620
Si	-0.1964340	2.6310250	1.8169250	C	-1.1832580	2.7077690	-2.6883590
Si	-0.6704770	3.4058820	-0.9977450	H	-0.3661230	2.1921960	-3.2119660
H	0.4981220	4.3148800	-1.2740370	H	-2.0191310	1.9916230	-2.6006000
Si	2.6751670	-2.7333980	0.3160900	H	-1.5272630	3.5333660	-3.3309150
Si	1.0646220	-1.9687650	-2.2324010	C	-2.0874080	4.5821100	-0.5276390
C	2.1743300	-4.4431970	0.9568370	H	-1.9103710	5.0851050	0.4350020
H	1.8378290	-5.0977130	0.1379990	H	-3.0403370	4.0364160	-0.4441820
H	1.3539560	-4.3689370	1.6864770	H	-2.2110810	5.3622780	-1.2950360
H	3.0247710	-4.9322210	1.4573980	N	-4.2920220	0.2120670	-0.8295400
C	4.2616920	-3.0288720	-0.6751730	C	-5.0727430	-0.6012720	0.1125330
H	5.0332570	-3.4622490	-0.0191500	H	-4.9687210	-0.1453920	1.1076630
H	4.0691540	-3.7560350	-1.4806590	H	-6.1529740	-0.5550160	-0.1404030
H	4.6758100	-2.1206990	-1.1349590	C	-4.8442900	1.5675400	-0.9460790
C	3.0459110	-1.7103540	1.8670370	H	-4.1916680	2.1289190	-1.6358600
H	2.1381930	-1.6727500	2.4928550	H	-5.8504410	1.5431230	-1.4098710
H	3.8532300	-2.1430380	2.4775260	C	-4.1407740	-0.4149520	-2.1506040
H	3.3255070	-0.6725380	1.6289400	H	-3.5622120	-1.3421190	-2.0221090
C	2.5035750	-1.4628900	-3.3508570	H	-3.5107810	0.2536460	-2.7596200
H	3.2285460	2.7900240	1.6623090	C	-5.4307440	-0.7298340	-2.9074530

H	4.0691120	1.2756140	1.9881610	H	-6.0740190	-1.4234370	-2.3465480
C	3.0863630	2.6689290	-0.8960630	H	-6.0142130	0.1743380	-3.1288680
H	2.3507250	3.2752660	-0.3455190	H	-5.1850660	-1.2069380	-3.8660590
H	3.9270590	3.3413260	-1.1607570	C	-4.9369150	2.3119680	0.3778200
C	5.5525570	1.0863280	-1.4864170	H	-3.9802710	2.2977990	0.9229700
H	6.2792740	1.6799070	-0.9188300	H	-5.1927370	3.3637300	0.1912440
H	6.0808560	0.2148500	-1.9004000	H	-5.7122720	1.8971310	1.0353440
H	5.2133540	1.6956900	-2.3354910	C	-4.6242180	-2.0509070	0.2026230
C	2.4382800	2.1742230	-2.1782630	H	-4.8374380	-2.6173470	-0.7147180
H	2.0181010	3.0275550	-2.7272980	H	-5.1534880	-2.5467800	1.0276170
H	3.1493030	1.6637720	-2.8416010	H	-3.5457970	-2.1174270	0.4080190
H	1.6062720	1.4828850	-1.9719070	N	3.5145740	1.5946960	0.0007370
C	5.3493430	2.8549110	1.2853630	C	4.3837750	0.5938400	-0.6278800
H	5.3920920	3.6456190	0.5225510	H	4.7729500	-0.0495910	0.1766980
H	6.1943580	2.1718110	1.1252200	H	3.7503230	-0.0619810	-1.2486780
H	5.4941290	3.3313910	2.2653300	C	4.0088540	2.1159160	1.2768510

Table S49. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a disolvated triethylamine open dimer transition structure poised to generate the *Z* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2927.735	-2925.5809	1.01481	-2926.6885	0.079136	0.0754	-2926.7677	-2926.763944

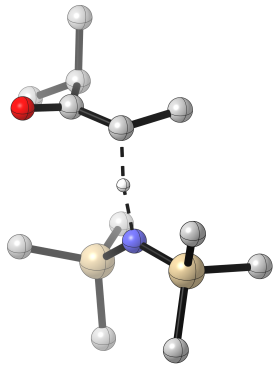
Imaginary frequency: -1170.34 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	1.0755370	-2.1497740	-0.6261320	H	3.6053600	1.1377390	2.4390090
C	0.6541130	-2.5443820	0.6936440	H	5.1888800	1.2391820	3.2105530
Na	2.3263810	0.5364100	0.3160330	H	4.9817160	1.8635410	1.5670810
Na	-0.9233260	0.4363850	-0.2687820	C	4.7072570	-0.1432720	-2.0662400
N	0.6868870	2.1588730	0.3209280	H	4.9883210	-1.1412580	-2.4316670
N	-1.9921260	-1.6627680	0.5155790	H	5.1194670	0.5963020	-2.7654450
O	1.2448200	-0.9426960	-0.8969010	H	3.6074640	-0.0746070	-2.1035220
H	-0.6169140	-2.2525220	0.5853690	N	-3.0066710	1.9306360	-0.8263540
C	1.1718580	-3.1656380	-1.7662730	C	-4.1312970	0.9902640	-0.7468370
H	0.1244320	-3.3839970	-2.0349010	H	-4.2456560	0.5421900	-1.7467700
C	1.8239870	-4.4863350	-1.3506430	H	-3.8363280	0.1640670	-0.0806250
H	1.9111010	-5.1502710	-2.2223130	C	-2.9174210	2.6443930	-2.1001920

H	1.2409360	-5.0188940	-0.5879900	H	-1.9866140	3.2300560	-2.0738250
H	2.8371870	-4.3212110	-0.9511820	H	-2.7848450	1.8925800	-2.8966120
C	1.8451370	-2.5649730	-2.9971250	C	-2.8994370	2.8242490	0.3266430
H	1.7861990	-3.2682840	-3.8393190	H	-2.0014530	3.4440520	0.1800080
H	2.9093570	-2.3569800	-2.8064900	H	-3.7639010	3.5146310	0.3926680
H	1.3706480	-1.6207050	-3.2934360	C	-5.4858010	1.5272550	-0.2766190
Si	1.0479500	2.9285670	-1.1696410	H	-5.8644470	2.3473600	-0.8997000
Si	0.6824000	3.0276920	1.7963040	H	-6.2222200	0.7105030	-0.3070590
H	-0.4943100	3.9532170	1.9566630	H	-5.4448570	1.8866990	0.7616160
Si	-2.5803520	-2.3956280	-0.9385370	C	-2.7586610	2.0791520	1.6435050
Si	-2.7723450	-1.9557110	2.0372510	H	-2.6739290	2.7931240	2.4741520
C	-2.0510480	-4.2216690	-1.0953190	H	-3.6109920	1.4159390	1.8477490
H	-2.8114150	-4.8617220	-0.6218820	H	-1.8465740	1.4643510	1.6608980
H	-1.0964660	-4.4311820	-0.5914660	C	-4.0739930	3.5688440	-2.4871630
H	-1.9661880	-4.5385640	-2.1475100	H	-4.3067700	4.2917150	-1.6917040
C	-4.4588370	-2.4944990	-1.1835660	H	-4.9875770	3.0059670	-2.7226530
H	-4.6560610	-2.8202410	-2.2181090	H	-3.7989270	4.1406190	-3.3849250
H	-4.8926520	-3.2544330	-0.5158450	C	1.0555870	-1.6203590	1.8331060
H	-4.9943980	-1.5506360	-1.0147030	H	0.5231830	-0.6544390	1.7891380
C	-1.8935450	-1.4128700	-2.4157620	H	0.7974630	-2.0690340	2.8009390
H	-0.8014020	-1.2741610	-2.3719540	H	2.1425640	-1.4137810	1.8620720
H	-2.1271040	-1.9036790	-3.3732640	H	0.7498010	-3.6114370	0.9143210
H	-2.3540370	-0.4104310	-2.4452470	C	2.1952750	4.1504410	2.0545610
C	-4.6204280	-1.5215020	2.0843890	H	2.2601700	4.9256570	1.2753020
H	-4.9946650	-1.6767100	3.1090090	H	3.1364930	3.5775990	2.0328460
H	-4.8112140	-0.4691060	1.8215720	H	2.1347320	4.6619750	3.0278970
H	-5.2219500	-2.1481260	1.4117830	N	4.4915030	-0.5898830	0.3855520
C	-2.6428190	-3.7874760	2.5153220	C	5.2379490	0.1175940	-0.6629860
H	-3.0670980	-3.9812050	3.5127860	H	5.1754920	1.1955440	-0.4493470
H	-1.5901290	-4.1140980	2.5236840	H	6.3160940	-0.1390300	-0.6170030
H	-3.1787570	-4.4227000	1.7923590	C	5.0588360	-0.3210820	1.7107610

C	-2.0379720	-0.9790050	3.4833800	H	4.6792110	-1.0910630	2.4008200
H	-2.5291730	-1.3198890	4.4088290	H	6.1617020	-0.4275910	1.6952790
H	-0.9568820	-1.1183450	3.6131500	C	4.3555650	-2.0269660	0.1174210
H	-2.2346470	0.0986990	3.3899860	H	3.7817310	-2.1406760	-0.8137390
C	0.3471350	4.6783950	-1.3779540	H	3.7216860	-2.4537620	0.9110510
H	0.4911620	5.0394520	-2.4084860	C	5.6607960	-2.8138780	0.0237180
H	0.8705280	5.3759940	-0.7051360	H	6.2946560	-2.4612420	-0.8030520
H	-0.7244910	4.7450190	-1.1394430	H	6.2442470	-2.7482400	0.9535940
C	0.5025140	1.8229920	-2.6132880	H	5.4424340	-3.8757610	-0.1567160
H	1.0399550	0.8615300	-2.5649060	C	4.6878420	1.0541480	2.2508150
H	0.7280180	2.2911800	-3.5840790	C	0.6410980	1.8600140	3.2887820
H	-0.5750290	1.5973850	-2.6053380	H	-0.2378340	1.1990810	3.2779750
C	2.9309280	3.1252410	-1.4247350	H	1.5346790	1.2137790	3.3295300
H	3.1589110	3.7046960	-2.3334900	H	0.6135180	2.4365430	4.2264930
H	3.3930900	3.6418010	-0.5682380				
H	3.4279310	2.1483340	-1.5481400				

Table S50. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a free ion transition structure poised to generate the *E* enolate. Only the anionic fragment is present at the transition state.



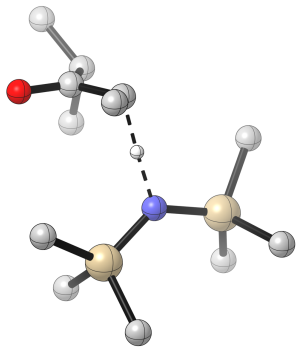
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1184.3703	-1183.4607	0.391309	-1183.9657	0.042754	0.041213	-1184.0084	-1184.006902

Imaginary frequency: -1212.13 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
O	-2.6692270	-0.3840580	-1.8489370	C	2.2540920	-2.5166140	-1.0245760
C	-2.3381210	-0.7121990	-0.7100130	H	3.1618890	-3.1383310	-0.9622240
C	-3.2198240	-0.2036460	0.4525650	H	1.4066720	-3.1051080	-0.6411500
H	-2.6562670	-0.2561950	1.3961730	H	2.0506490	-2.3019770	-2.0852700
C	-3.6739440	1.2291050	0.1963780	C	4.0174420	-0.0672650	-0.7894540
H	-4.3950360	1.5626820	0.9598550	H	4.8683520	-0.7685400	-0.7941860
H	-2.8193980	1.9217670	0.1978990	H	3.8323450	0.2573050	-1.8256790
H	-4.1420530	1.2810440	-0.7966660	H	4.3115890	0.8197980	-0.2076110
C	-4.4234770	-1.1475090	0.5522390	C	2.2001070	2.8142970	0.1828870
H	-4.9735550	-1.1316780	-0.4012690	H	2.8508700	2.5216410	1.0230850
H	-4.1071940	-2.1840490	0.7432560	H	2.7989040	2.7683950	-0.7401240
H	-5.1090700	-0.8402230	1.3582130	H	1.8925370	3.8612430	0.3407550
C	-1.1800020	-1.5213100	-0.4014220	C	-0.2694170	1.9433530	1.6947830
H	-0.1037180	-0.6719080	-0.3616320	H	0.3837850	1.6899250	2.5456770

N	1.0509830	0.0397450	-0.1792610	H	-0.6195550	2.9810890	1.8210420
Si	0.6774440	1.6773440	0.0653990	H	-1.1449460	1.2776980	1.7434020
Si	2.4594790	-0.8910690	-0.0663900	C	-0.3858950	2.3513200	-1.3497040
C	2.9279840	-1.3642100	1.7193620	H	-1.1952450	1.6487040	-1.6051220
H	3.8181780	-2.0129010	1.7668030	H	-0.8278320	3.3336470	-1.1146100
H	3.1345770	-0.4545190	2.3069340	H	0.2402870	2.4635930	-2.2496470
H	2.0898140	-1.8872470	2.2060880	C	-1.0465970	-2.2207190	0.9409880
				H	-0.9407430	-1.4979370	1.7675660
				H	-1.8763990	-2.9049670	1.2003680
				H	-0.1235480	-2.8219990	0.9552710
				H	-0.8999590	-2.1321670	-1.2711890

Table S51. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a free ion transition structure poised to generate the *Z* enolate. Only the anionic fragment is present at the transition state.



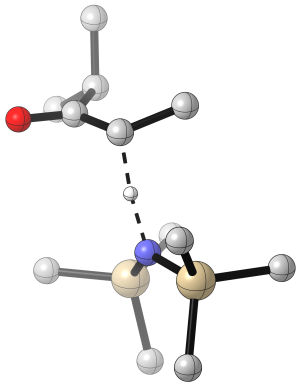
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1184.3781	-1183.4696	0.391429	-1183.9734	0.042845	0.041199	-1184.0163	-1184.01461

Imaginary frequency: -1207.91 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
O	-3.0383570	1.2420940	-0.3473620	H	0.2125120	-2.9194430	-1.4639300
C	-2.5540880	0.1186560	-0.4938390	C	3.1407210	-1.5383560	-1.4117810
C	-2.8676280	-0.9379350	0.5830240	H	3.6759020	-2.5007730	-1.3575190
H	-2.5412540	-1.9245090	0.2158960	H	2.7353040	-1.4236000	-2.4294180
C	-2.0639040	-0.5852470	1.8375060	H	3.8708940	-0.7290120	-1.2527850
H	-2.2504090	-1.3052870	2.6508680	C	2.5572970	-1.6950680	1.5593170
H	-0.9866060	-0.5644090	1.6109240	H	3.1057070	-2.6503960	1.6038170
H	-2.3575460	0.4190470	2.1812050	H	3.2715360	-0.8842950	1.7778430
C	-4.3657960	-0.9585310	0.8706290	H	1.7980780	-1.6930250	2.3576850
H	-4.6886410	0.0612060	1.1252160	C	2.9941440	2.0807560	-0.1401110
H	-4.9397840	-1.2821860	-0.0113400	H	3.1484470	2.0019950	-1.2280270
H	-4.6057180	-1.6334490	1.7075690	H	3.2098520	3.1177230	0.1657710
C	-1.5898440	-0.2505070	-1.5013630	H	3.7318870	1.4242690	0.3506430
H	-0.4192720	-0.1326120	-0.8061670	C	1.1037040	1.7640430	2.2035650
H	-1.5819620	-1.3272010	-1.7195300	H	1.3964870	2.7773570	2.5247340

C	-1.4373870	0.6600700	-2.7012650	H	0.0723960	1.5815800	2.5433570
H	-1.7594520	1.6742430	-2.4247630	H	1.7583340	1.0389130	2.7127680
H	-0.3864670	0.7156240	-3.0336160	C	0.0487560	2.8491510	-0.4368080
H	-2.0469460	0.3436700	-3.5663660	H	-1.0034460	2.5556480	-0.2835030
N	0.8195420	0.0002470	-0.2313670	H	0.2102480	3.8412090	0.0157810
Si	1.2138210	1.5662490	0.3120890	H	0.2153420	2.9343640	-1.5221400
Si	1.7307660	-1.4272140	-0.1367870				
C	0.6241860	-2.9376410	-0.4430650				
H	1.1842210	-3.8779430	-0.3147440				
H	-0.2247500	-2.9400370	0.2591490				

Table S52. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a free ion transition structure poised to generate the *E* enolate. Only the anionic fragment is present at the transition state. The latest functionals from Head-Gordon (ωB97X-D), which include dispersion corrections and Dunning's diffuse function augmented basis set (aug-cc-pVTZ) were used to see if the standard conditions were inadequate.



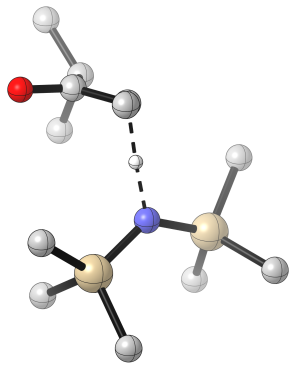
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1184.5288	-1184.3313	0.39061	-1184.1248	0.04394	0.041839	-1184.1687	-1184.166639

Imaginary frequency: -1304.95 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
O	-2.6847570	-0.4272820	-1.8830680	H	3.7318390	-2.0015490	1.8121640
C	-2.3471490	-0.7248860	-0.7255050	H	3.0604360	-0.4283470	2.3113680
C	-3.1980100	-0.1560720	0.4291190	H	2.0003370	-1.8482320	2.2150500
H	-2.5995720	-0.1529630	1.3492450	C	2.2337980	-2.5502540	-1.0000790
C	-3.6659300	1.2681200	0.1424910	H	3.1424450	-3.1662750	-0.9150230
H	-4.3286450	1.6253240	0.9457170	H	1.3877580	-3.1363520	-0.6154200
H	-2.8149310	1.9566370	0.0696300	H	2.0433770	-2.3602740	-2.0664400
H	-4.2075730	1.2999530	-0.8112220	C	4.0083720	-0.1077340	-0.7775750
C	-4.3898410	-1.0976240	0.6468560	H	4.8477580	-0.8208030	-0.7513540
H	-5.0027750	-1.1386990	-0.2648590	H	3.8523530	0.1981760	-1.8227240
H	-4.0555820	-2.1176100	0.8803920	H	4.3069030	0.7840560	-0.2087770
H	-5.0223890	-0.7452520	1.4759560	C	2.2634620	2.7718300	0.1860650

C	-1.1975900	-1.5336570	-0.4103500	H	2.9156830	2.4497040	1.0118480
H	-0.1230460	-0.6695910	-0.3693660	H	2.8526690	2.7394830	-0.7415550
N	1.0155710	0.0301060	-0.2446520	H	1.9784240	3.8194130	0.3718290
Si	0.7059120	1.6837340	0.0587370	C	-0.2145420	1.9458650	1.7044900
Si	2.4294820	-0.9061790	-0.0721530	H	0.4229350	1.6352130	2.5461500
C	2.8518650	-1.3432490	1.7351760	H	-0.5034410	2.9969810	1.8597820
C	-1.0832320	-2.2514470	0.9272650	H	-1.1264700	1.3344510	1.7402080
H	-1.1158420	-1.5504740	1.7748540	C	-0.3591600	2.4209270	-1.3231870
H	-1.8540190	-3.0225500	1.1021050	H	-1.1831170	1.7423080	-1.5859610
H	-0.1076110	-2.7543200	0.9938600	H	-0.7811850	3.4014510	-1.0518520
H	-0.9071430	-2.1500360	-1.2700610	H	0.2517180	2.5510040	-2.2292160

Table S53. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a free ion transition structure poised to generate the *Z* enolate. Only the anionic fragment is present at the transition state. The latest functionals from Head-Gordon (ωB97X-D), which include dispersion corrections and Dunning's diffuse function augmented basis set (aug-cc-pVTZ) were used to see if the standard conditions were inadequate.



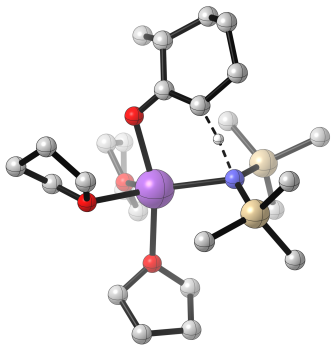
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-1184.5364	-1184.3393	0.390864	-1184.1323	0.042722	0.041132	-1184.175	-1184.173438

Imaginary frequency: -1265.9 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
O	-3.0106390	1.3486510	-0.1855460	Si	1.6353750	-1.4584140	-0.2174580
C	-2.5360060	0.2297280	-0.4434200	C	0.4662970	-2.9010470	-0.6061060
C	-2.8018250	-0.9135950	0.5535780	H	0.9915900	-3.8661140	-0.5406530
H	-2.4501720	-1.8525640	0.1018850	H	-0.3743940	-2.9195410	0.1024430
C	-1.9967140	-0.6660780	1.8334210	H	0.0470960	-2.8082070	-1.6180110
H	-2.1680550	-1.4703240	2.5651770	C	3.0889550	-1.5977490	-1.4399800
H	-0.9239150	-0.6131570	1.6083060	H	3.5802790	-2.5825930	-1.3885240
H	-2.3008920	0.2880800	2.2857460	H	2.7359350	-1.4425110	-2.4704840
C	-4.2976570	-1.0304960	0.8451970	H	3.8463270	-0.8275730	-1.2304490
H	-4.6723140	-0.0790160	1.2458950	C	2.3823430	-1.8199440	1.4983910
H	-4.8643030	-1.2587220	-0.0693120	H	2.8727510	-2.8057150	1.5251120
H	-4.4922460	-1.8274980	1.5793180	H	3.1341210	-1.0635080	1.7704710
C	-1.6320270	-0.0587210	-1.5230890	H	1.6002680	-1.8040150	2.2718880

H	-0.4335860	-0.0199200	-0.8611080	C	3.1099040	1.9405210	-0.0387010
H	-1.6437670	-1.1122270	-1.8271760	H	3.7889260	1.2044340	0.4189160
C	-1.5222360	0.9301220	-2.6663030	H	3.2869310	1.9272090	-1.1244430
H	-1.7070200	1.9468570	-2.2979580	H	3.3878540	2.9354160	0.3433510
H	-0.5141070	0.9063850	-3.1097330	C	1.1457420	1.6199140	2.2452980
H	-2.2503450	0.7352000	-3.4721920	H	1.7506320	0.8386970	2.7289360
N	0.7937860	0.0227080	-0.3061080	H	1.4819770	2.5971040	2.6266200
Si	1.2885190	1.5268600	0.3478920	H	0.1011190	1.4754010	2.5565010
H	0.4823490	3.8857750	0.1360970	C	0.2232840	2.9261940	-0.3376760
H	0.3634230	3.0306420	-1.4232700	H	-0.8427220	2.7225030	-0.1559530

Table S54. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methylcyclohexanone via a trisolvated THF monomer transition structure.



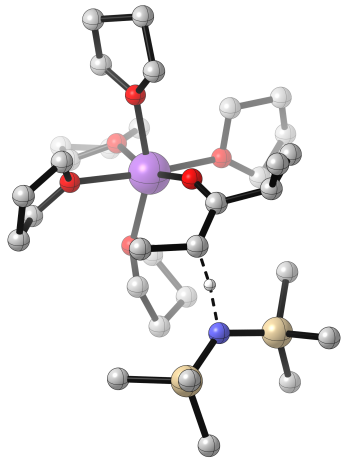
E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2082.1135	-2080.3391	0.762245	-2081.3286	0.063087	0.059787	-2081.3917	-2081.388427

Imaginary frequency: -1281.14 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	-0.6589340	-0.4534900	-0.2032840	C	-4.1475860	2.1001920	-0.4460120
N	0.4843790	1.6520360	0.0610110	C	-4.6379610	0.9082670	-1.3017430
Si	-0.0040090	2.7943910	-1.1357840	C	-3.9792520	-0.3105490	-0.6382570
C	1.4600730	3.5494100	-2.0677880	H	-4.6603580	-0.7709440	0.1029240
H	2.0152910	2.7805860	-2.6256660	H	-3.6305830	-1.0762150	-1.3416470
H	1.1221990	4.3112700	-2.7880250	H	-5.7317800	0.8191780	-1.3195820
H	2.1636920	4.0277130	-1.3684360	H	-4.2938620	1.0099290	-2.3396070
C	-1.0636340	1.9065900	-2.4354830	H	-3.5808050	2.8133710	-1.0596750
H	-1.4966810	2.6080500	-3.1660050	H	-4.9705540	2.6487950	0.0297320
H	-0.4417170	1.1901940	-2.9972170	O	-1.4561080	-1.8906690	-1.8406110
H	-1.8845550	1.3396400	-1.9695210	C	-1.4766570	-3.2006650	-1.2750790
C	-0.9746260	4.2733150	-0.4492810	H	-0.7028440	-3.2712090	-0.4941240
H	-1.8825490	3.9910120	0.1034440	H	-2.4655110	-3.3640570	-0.8227010
H	-0.3390780	4.8596170	0.2339400	C	-1.1483320	-4.1293810	-2.4350110
H	-1.2745490	4.9403560	-1.2732010	C	-0.0952010	-3.2972450	-3.1677850

Si	0.9398650	2.0200110	1.6799500	C	-0.6473430	-1.8791750	-3.0191740
C	2.3091570	3.3233460	1.7996800	H	0.1566270	-1.1379920	-2.9001950
H	2.6241240	3.4884320	2.8419820	H	-1.2808870	-1.5854490	-3.8718800
H	3.1937760	3.0146470	1.2210420	H	0.8653380	-3.3694420	-2.6383600
H	1.9682950	4.2901990	1.3955660	H	0.0502090	-3.5870950	-4.2163170
C	1.5833870	0.4184660	2.4501390	H	-2.0352980	-4.2848970	-3.0683800
H	2.5086620	0.1085880	1.9398030	H	-0.7793580	-5.1086360	-2.1036470
H	1.8020650	0.5165210	3.5247010	O	1.2154960	-1.7281290	-0.5325890
H	0.8443080	-0.3877070	2.3097380	C	2.2995200	-1.1237470	-0.6390650
C	-0.4763840	2.6536470	2.7727890	C	2.3885580	0.1698910	-1.2706280
H	-0.9337130	3.5632510	2.3542160	C	3.5566990	-1.7914570	-0.0745360
H	-1.2718350	1.9028590	2.8957090	C	3.7232750	0.9006590	-1.4117730
H	-0.0944060	2.9019910	3.7758190	H	1.5269930	0.8891010	-0.5307810
O	-1.2095240	-1.7517660	1.6068400	H	1.7383560	0.2132060	-2.1571640
C	-0.4242880	-2.8184230	2.1325290	C	4.7019790	-0.8037100	0.1502500
H	-0.8623710	-3.7861340	1.8252150	H	3.8696420	-2.4491700	-0.9098670
H	0.5820440	-2.7339770	1.7023950	C	3.2678800	-2.6839580	1.1264640
C	-0.4953250	-2.6515040	3.6447140	C	4.9398800	0.0283860	-1.1044430
C	-1.9323090	-2.1558940	3.8181680	H	3.7374830	1.7719680	-0.7306580
C	-2.1092220	-1.2538790	2.5951040	H	3.8220200	1.3222910	-2.4233030
H	-3.1321900	-1.2604810	2.1911710	H	4.4652090	-0.1377510	0.9995920
H	-1.8368040	-0.2085110	2.8192320	H	5.6089250	-1.3605460	0.4335620
H	-2.6315910	-3.0043950	3.7728780	H	2.5122620	-3.4370620	0.8694990
H	-2.1045240	-1.6223410	4.7616170	H	4.1832490	-3.2017580	1.4474500
H	0.2209170	-1.8836420	3.9738590	H	2.8921060	-2.0949440	1.9766610
H	-0.2825750	-3.5815250	4.1873240	H	5.1310810	-0.6570160	-1.9483120
O	-2.8422700	0.2072580	0.0270440	H	5.8379930	0.6546470	-0.9939140
C	-3.2311670	1.4425120	0.5976680	H	-3.7766640	1.2561940	1.5429040
				H	-2.3170710	2.0076940	0.8227930

Table S55. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a pentasolvated THF contact ion pair transition structure that is poised to form the *Z* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-2508.8846	-2506.6152	0.991016	-2507.8643	0.078435	0.073061	-2507.9427	-2507.937319

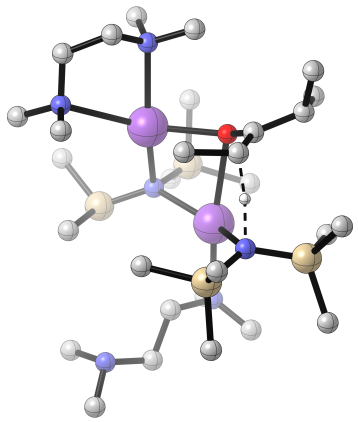
Imaginary frequency: -1088.66 cm^{-1}

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Na	1.5389930	-0.1563480	0.0709410	H	3.0537980	4.1065820	2.1593560
O	1.7352720	-2.4285440	-0.3751670	H	1.7476770	5.2458360	1.7447100
C	1.4437420	-3.5977650	0.3688250	O	3.1114090	-0.0988130	-1.6006950
H	2.3664980	-4.1903730	0.5276210	C	4.4175920	-0.6151040	-1.3747110
H	1.0515910	-3.2815920	1.3441660	H	4.9529860	0.0585060	-0.6838640
C	0.4503730	-4.3631980	-0.4944910	H	4.3287240	-1.5984180	-0.8868310
C	0.9841260	-4.0881680	-1.9070170	C	5.0866620	-0.6696760	-2.7489130
C	1.7071400	-2.7338640	-1.7676750	C	4.3615420	0.4530130	-3.4927390
H	2.7395260	-2.7819040	-2.1579580	C	2.9446460	0.2844630	-2.9598780
H	1.1833620	-1.9077720	-2.2684430	H	2.3228870	1.1890860	-2.9926970
H	1.6909470	-4.8739510	-2.2095590	H	2.4044940	-0.5086780	-3.5072550
H	0.1823400	-4.0515320	-2.6554740	H	4.7654030	1.4332120	-3.1948660
H	-0.5566660	-3.9396490	-0.3683550	H	4.4225370	0.3709530	-4.5854300

H	0.4053430	-5.4323300	-0.2501240	H	4.8819240	-1.6346320	-3.2376300
O	0.4381440	-0.9677590	1.8946510	H	6.1750890	-0.5386210	-2.6963830
C	-0.9338400	-1.3084670	1.6186380	O	0.1993820	0.4565520	-1.6091180
H	-1.2841150	-0.7618320	0.7274150	C	-0.9203330	0.7050000	-2.0841980
H	-0.9991360	-2.3883990	1.4169830	C	-1.2161670	2.1172710	-2.5933580
C	-1.7268820	-0.8757960	2.8461530	H	-2.2085850	2.3890960	-2.1951740
C	-0.8780880	0.2858230	3.3674820	C	-0.1787300	3.1238450	-2.1128990
C	0.5304860	-0.2339000	3.1067720	H	-0.5109010	4.1522450	-2.3192170
H	1.2874690	0.5545240	2.9712760	H	0.0059540	3.0138470	-1.0357680
H	0.8633980	-0.9019140	3.9245680	H	0.7787280	2.9659580	-2.6346020
H	-1.0633810	1.1839480	2.7586570	C	-1.2996610	2.1130310	-4.1253550
H	-1.0583600	0.5313300	4.4224380	H	-0.3453600	1.7729620	-4.5584910
H	-1.7730190	-1.6825420	3.5943970	H	-2.0952810	1.4513610	-4.4919820
H	-2.7461270	-0.5867370	2.5593730	H	-1.4978370	3.1276900	-4.5010800
O	3.4043380	-0.3506060	1.4989290	C	-1.9932610	-0.2577120	-2.1435290
C	4.0646690	0.6198360	2.3001580	H	-2.6958920	-0.0742600	-1.0693430
H	5.0027510	0.9339760	1.8050530	H	-2.7436860	-0.0087660	-2.9067630
H	3.4088680	1.4972260	2.3916980	C	-1.5847900	-1.7164900	-2.1219870
C	4.3582810	-0.0760910	3.6243980	H	-0.9210030	-1.9123240	-1.2650750
C	4.6237140	-1.5054350	3.1531390	H	-2.4619000	-2.3718610	-2.0237360
C	3.5858410	-1.6580920	2.0437890	H	-1.0441330	-2.0153740	-3.0371650
H	3.8978190	-2.3393800	1.2389920	N	-3.6137430	-0.0495820	0.0993600
H	2.6162530	-2.0096800	2.4317040	Si	-3.9071600	1.5618460	0.5509860
H	5.6421860	-1.5852350	2.7434280	Si	-4.6736660	-1.3842890	0.0811020
H	4.5119830	-2.2593100	3.9428010	C	-5.3953440	-1.7090700	-1.6464890
H	3.4681400	-0.0479710	4.2712710	H	-6.0454880	-2.5983260	-1.6596090
H	5.1971210	0.3760900	4.1689000	H	-5.9973630	-0.8418590	-1.9619850
O	1.7043040	2.0916850	0.7866490	H	-4.6079000	-1.8523130	-2.4024450
C	1.1925520	3.1256680	1.6239320	C	-3.7957940	-2.9811280	0.6305060
H	0.1904540	3.4224570	1.2732840	H	-4.4479950	-3.8597590	0.5031710
H	1.0961420	2.7340220	2.6479700	H	-2.8757780	-3.1532150	0.0507220

C	2.1889870	4.2719800	1.4974950	H	-3.5176400	-2.9202640	1.6952490
C	2.6048280	4.1401740	0.0319260	C	-6.1728260	-1.2173370	1.2345310
C	2.6412760	2.6240860	-0.1514270	H	-6.7994220	-2.1223850	1.1872100
H	2.3490650	2.2966840	-1.1576970	H	-5.8606210	-1.0741730	2.2809230
H	3.6387510	2.2045990	0.0713980	H	-6.8013580	-0.3582410	0.9498790
H	1.8354080	4.5813090	-0.6191320	C	-4.7084750	1.8003060	2.2574990
H	3.5663400	4.6165410	-0.1987950	H	-5.7272770	1.3885500	2.2992110
C	-2.2471800	2.5115190	0.6520370	H	-4.1148780	1.3119020	3.0474540
H	-1.4003510	1.8537530	0.3894570	H	-4.7676710	2.8745050	2.4979910
H	-2.2185330	3.3882320	-0.0146580	C	-5.0117170	2.5059870	-0.6742380
H	-2.0865970	2.8805420	1.6782340	H	-6.0185670	2.0584500	-0.6974120
				H	-5.1187810	3.5710200	-0.4128420
				H	-4.6045450	2.4413150	-1.6964480

Table S56. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a disolvated $\kappa^1\kappa^2$-TMEDA dimer-based transition structure that is poised to form the *Z* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3038.4127	-3036.1308	1.049042	-3037.331	0.081583	0.077246	-3037.4126	-3037.4083

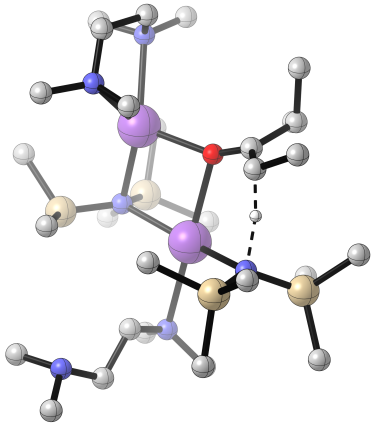
Imaginary frequency: -1238.1 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3102580	2.6207540	-0.1840600	H	-2.4822090	-3.6376690	2.2938810
C	-0.7955020	2.7337610	1.1539650	H	-4.0911970	-3.6173990	1.5399430
Na	-2.3121720	-0.4959070	0.1217880	C	-4.9307560	0.2200520	1.9272290
Na	0.8169290	0.2342140	-0.8426060	H	-5.9805010	0.5413350	2.1025960
N	-0.6702920	-1.6001640	-1.1811750	H	-4.3032910	0.8606960	2.5661040
N	1.8001400	1.8893180	0.6499980	N	2.8787920	-0.9765140	-1.7549400
O	-1.5106300	1.5009980	-0.6971850	C	4.0218210	-0.0964690	-1.9106640
H	0.4698130	2.4241570	0.9070660	H	3.9078750	0.5072740	-2.8233360
C	-1.5087750	3.8827770	-1.0287100	H	4.0717900	0.5851320	-1.0488340
H	-0.5208200	4.3738830	-1.0638810	C	2.7253760	-1.8863990	-2.8769660
C	-2.4820040	4.8663710	-0.3657660	H	1.8124180	-2.4829080	-2.7347000
H	-2.5394230	5.7905910	-0.9582020	H	2.6263490	-1.3149910	-3.8115480
H	-2.1740150	5.1375010	0.6523820	C	2.8790290	-1.6772670	-0.4762530
H	-3.4966810	4.4424660	-0.3163990	H	2.0139600	-2.3537800	-0.4771410

C	-1.9506330	3.5606110	-2.4511900	H	3.5850140	-2.5756380	-2.9961340
H	-2.0794000	4.4877740	-3.0270880	H	4.9837990	-0.6425620	-1.9887240
H	-2.9090370	3.0198770	-2.4497870	H	2.7145570	-0.9483910	0.3341560
H	-1.2239390	2.9290910	-2.9768440	C	4.1328900	-2.4731080	-0.1008670
Si	-1.1251630	-1.2498400	-2.8011800	H	4.4919700	-3.0880560	-0.9543850
Si	-0.5737110	-3.2093290	-0.6254440	H	4.9494020	-1.7764130	0.1437460
H	0.4256080	-4.0675270	-1.3669870	N	3.8556220	-3.2915020	1.0682750
Si	2.4922230	3.2057680	-0.2355440	C	5.0055180	-3.4670030	1.9274450
Si	2.4447210	1.2651290	2.1301940	H	4.7146690	-4.0337200	2.8237780
C	1.9168620	4.8986940	0.4053860	H	5.8349950	-4.0179920	1.4324650
H	2.2667530	5.0398730	1.4403420	H	5.3863230	-2.4884360	2.2529290
H	0.8243940	5.0198640	0.4137300	C	3.2605510	-4.5626440	0.7119120
H	2.3441460	5.7092290	-0.2061770	H	3.9803390	-5.2292120	0.1878380
C	4.3811450	3.3533500	-0.1991250	H	2.9060180	-5.0807540	1.6149780
H	4.6871360	4.1287140	-0.9198050	H	2.3943810	-4.4149430	0.0510460
H	4.7233670	3.6780800	0.7958900	H	-3.9458250	-3.5683000	3.3233080
H	4.9156460	2.4274160	-0.4526800	H	-1.6155250	-1.6196370	3.3506940
C	1.9554240	3.0416560	-2.0441500	N	-4.5532150	0.4568060	0.5379840
H	0.8602600	2.9576460	-2.1279450	C	-4.5381540	1.8854300	0.2582180
H	2.2690970	3.9032250	-2.6535070	H	-3.8464280	2.3958950	0.9447170
H	2.3881040	2.1351350	-2.4967450	H	-4.1816580	2.0587890	-0.7666200
C	4.2876170	0.8154700	2.0717940	H	-5.5439110	2.3404040	0.3720090
H	4.5606130	0.3201510	3.0179260	C	-5.4526610	-0.2258140	-0.3843610
H	4.5163420	0.1149200	1.2534660	H	-6.5146060	0.0238310	-0.1798050
H	4.9347560	1.6956280	1.9546950	H	-5.2166560	0.0711130	-1.4135880
C	2.2710600	2.5073350	3.5516030	H	-5.3324880	-1.3167490	-0.3207580
H	2.5554590	2.0626360	4.5181970	C	-1.1874380	1.6159460	2.0996340
H	1.2383180	2.8807340	3.6355440	H	-2.2825740	1.4943470	2.1681410
H	2.9228360	3.3786840	3.3784250	H	-0.7596820	0.6504020	1.7840410
C	1.5475820	-0.3410680	2.6287970	H	-0.8082600	1.7958620	3.1155480
H	0.9119220	-0.1977090	3.5168160	H	-0.8293990	3.7387890	1.5864560

H	0.9052580	-0.7227890	1.8197500	H	0.9993450	-3.0080680	1.3539800
H	2.2721170	-1.1405520	2.8522360	H	-0.6647710	-2.6063940	1.7962360
C	-0.9452660	-2.6800030	-4.0347110	H	-0.1870600	-4.3132890	1.5955340
H	-1.2300930	-2.3417650	-5.0435140	C	-2.2297760	-4.1345810	-0.7824900
H	-1.5910800	-3.5324320	-3.7751110	H	-2.4548170	-4.3493360	-1.8379990
H	0.0888180	-3.0524720	-4.0847900	H	-3.0498200	-3.5058700	-0.3974500
C	-0.1290850	0.2081650	-3.4953050	H	-2.2418970	-5.0896370	-0.2339630
H	-0.3528740	1.1076890	-2.9026610	N	-3.4458840	-1.7638210	2.3099070
H	-0.4178030	0.4255670	-4.5351500	C	-2.6534170	-1.2671890	3.4299710
H	0.9572180	0.0303740	-3.4778930	H	-2.6344730	-0.1710790	3.4429470
C	-2.9392130	-0.6832110	-2.8908870	H	-3.0655070	-1.6175740	4.3990430
H	-3.2640840	-0.4788690	-3.9231070	C	-4.8051940	-1.2312210	2.3643850
H	-3.6089070	-1.4540400	-2.4741440	H	-5.4439590	-1.8600710	1.7275730
H	-3.0536540	0.2518480	-2.3154680	H	-5.2174230	-1.3212310	3.3920930
C	-0.0512680	-3.2956160	1.1947200	C	-3.4941140	-3.2205780	2.3711850

Table S57. Geometric coordinates and thermal corrected single point energies for NaHMDS-mediated enolization of 2-methyl-3-pentanone via a disolvated $\kappa^1\kappa^2$-TMEDA dimer-based transition structure that is poised to form the *E* enolate.



E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
-3038.4124	-3036.1297	1.048201	-3037.331	0.08246	0.077811	-3037.4137	-3037.4091

Imaginary frequency: -1018.02 cm^{-1}

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.1260670	2.5614690	0.0400920	H	-2.5338230	0.8158680	3.9062110
C	-0.2915030	2.9783850	1.1355590	C	-4.7077880	-0.0602360	2.5370200
H	-0.2977590	2.2259710	1.9384200	H	-5.3956290	-0.9144580	2.6115550
Na	-2.5138840	-0.4974610	0.0973670	H	-4.8777140	0.5492500	3.4492180
Na	0.7516160	0.0402010	-0.7359970	C	-3.2232240	-1.7112410	3.4162130
N	-0.7912180	-1.7919840	-0.8703390	H	-2.2011620	-2.1080010	3.3953780
N	2.0954320	1.8667570	0.2034470	H	-3.9068800	-2.5147630	3.1075780
O	-1.3029610	1.3492740	-0.2098100	C	-5.0875620	0.7784650	1.3264540
H	0.8237070	2.5728840	0.6324420	H	-6.1384610	1.1120010	1.4711900
C	-0.2475610	4.4109570	1.6345750	H	-4.4739100	1.6933080	1.2835090
H	-0.3398700	5.1432850	0.8212230	N	2.7370340	-1.4426270	-1.6744750
H	0.7128060	4.6152260	2.1279930	C	3.9183310	-0.6701920	-2.0102720
H	-1.0428110	4.6267020	2.3667500	H	3.8015070	-0.2212460	-3.0077150
C	-1.7368800	3.5982930	-0.8988420	H	4.0372230	0.1420060	-1.2788370

H	-0.9945110	4.4007470	-1.0355110	C	2.4870820	-2.5081700	-2.6276580
C	-2.9688740	4.2045360	-0.2120220	H	1.5700080	-3.0404700	-2.3368410
H	-3.4305700	4.9675770	-0.8547800	H	2.3404750	-2.0873750	-3.6335030
H	-2.7194180	4.6707520	0.7501140	C	2.7537370	-1.9307160	-0.3024070
H	-3.7213600	3.4225850	-0.0259420	H	1.8452520	-2.5315150	-0.1625110
C	-2.0961770	3.0118730	-2.2574000	H	3.3176390	-3.2397640	-2.6889720
H	-2.5701520	3.7755830	-2.8900980	H	4.8457190	-1.2786730	-2.0245580
H	-2.7920440	2.1680210	-2.1456950	H	2.6815870	-1.0729960	0.3867720
H	-1.2082930	2.6371840	-2.7842080	C	3.9651040	-2.7525930	0.1493470
Si	-1.2524870	-1.7539160	-2.5174340	H	4.2209370	-3.5369540	-0.5950330
Si	-0.7888220	-3.2091160	0.0735040	H	4.8470860	-2.0987110	0.2245930
H	0.0063830	-4.3495850	-0.5163410	N	3.6993380	-3.3260840	1.4594220
Si	2.7547380	2.9131120	-0.9953120	C	4.8798060	-3.4274940	2.2888670
Si	2.8112220	1.4607250	1.7183130	H	4.6009990	-3.7990670	3.2855340
C	2.2298270	4.7211820	-0.7509510	H	5.6435580	-4.1189060	1.8704470
H	2.4932590	5.0843320	0.2546200	H	5.3403230	-2.4370090	2.4120040
H	1.1431030	4.8428500	-0.8761510	C	3.0051750	-4.5934400	1.3666260
H	2.7236360	5.3725450	-1.4892300	H	3.6506580	-5.3941330	0.9434690
C	4.6472310	2.9791570	-1.0804190	H	2.6673310	-4.9136310	2.3631580
H	4.9565690	3.6023720	-1.9344650	H	2.1153620	-4.5030800	0.7272650
H	5.0489930	3.4480160	-0.1676980	H	-3.4668720	-1.4247890	4.4597180
H	5.1254780	1.9952440	-1.1882800	H	-1.3562310	0.0771510	2.7771480
C	2.0588940	2.4179090	-2.6845180	N	-4.9448770	0.0836100	0.0496510
H	0.9634300	2.5470850	-2.6743590	C	-5.4193870	0.9438340	-1.0248510
H	2.4549580	3.0399370	-3.5018850	H	-4.8490830	1.8828990	-1.0343480
H	2.2658340	1.3641360	-2.9250350	H	-5.2815140	0.4465460	-1.9938310
C	4.5783620	0.7773600	1.6285230	H	-6.4940130	1.1925570	-0.9050760
H	4.8810140	0.4345470	2.6315060	C	-5.6627770	-1.1838720	0.0311160
H	4.6632610	-0.0792720	0.9435590	H	-6.7261060	-1.0629370	0.3268150
H	5.2978710	1.5427880	1.3032030	H	-5.6360010	-1.5996510	-0.9843970
C	2.9164990	2.9241990	2.9219110	H	-5.1912260	-1.9144150	0.7033370

H	3.4871630	2.6451820	3.8220150	H	0.8074870	-0.5698700	-3.3862870
H	1.9162500	3.2450360	3.2502800	C	-3.0681880	-1.1952620	-2.7037730
H	3.4174280	3.7903970	2.4603350	H	-3.3961320	-1.2017730	-3.7550290
C	1.7372450	0.1324840	2.5659210	H	-3.7447040	-1.8552010	-2.1351670
H	0.8087710	-0.0388220	1.9947960	H	-3.1879010	-0.1623110	-2.3352780
H	2.2573720	-0.8362530	2.6399230	C	-0.0876530	-2.9043060	1.8073210
H	1.4464910	0.4347120	3.5848570	H	1.0031080	-2.7605790	1.8261450
C	-1.1438820	-3.3995330	-3.4506910	H	-0.5307190	-1.9856870	2.2239060
H	-1.4810380	-3.2735050	-4.4914990	H	-0.3323190	-3.7390150	2.4841320
H	-1.7920300	-4.1547650	-2.9777640	C	-2.5454950	-3.8942140	0.3497520
H	-0.1246650	-3.8109740	-3.4728570	H	-3.0465040	-4.1067730	-0.6081940
C	-0.2809490	-0.4237840	-3.4545750	H	-3.1548970	-3.1472320	0.8895770
H	-0.5231690	0.5638570	-3.0270130	H	-2.5476010	-4.8181500	0.9487630
H	-0.5550020	-0.3886880	-4.5200950	N	-3.3432140	-0.5776730	2.5078950
				C	-2.3833320	0.4610170	2.8660270
				H	-2.4718490	1.3238530	2.1905560