Wittig Rearrangements of Boron-Based
Oxazolidinone Enolates

Zirong Zhang and David B. Collum*
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York 14853-1301, United States
E-mail: dbc6@cornell.edu

1. IR spectroscopy

2. NMR spectroscopic structural study

3. Kinetics

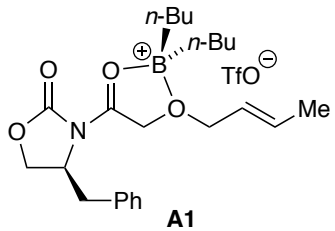
4. Syntheses of substrates

5. Wittig Rearrangements

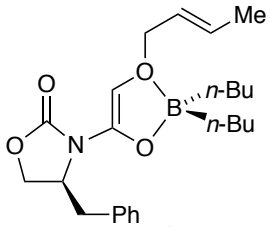
6. Product characterizations

7. Sodium- and lithium-based Wittig rearrangement attempts

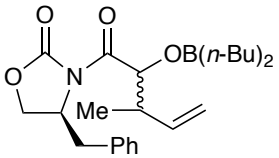
8. Computations



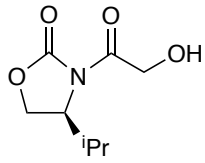
A1



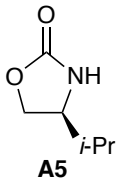
A2



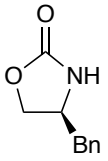
A3



A4



A5



A6

1. IR spectra

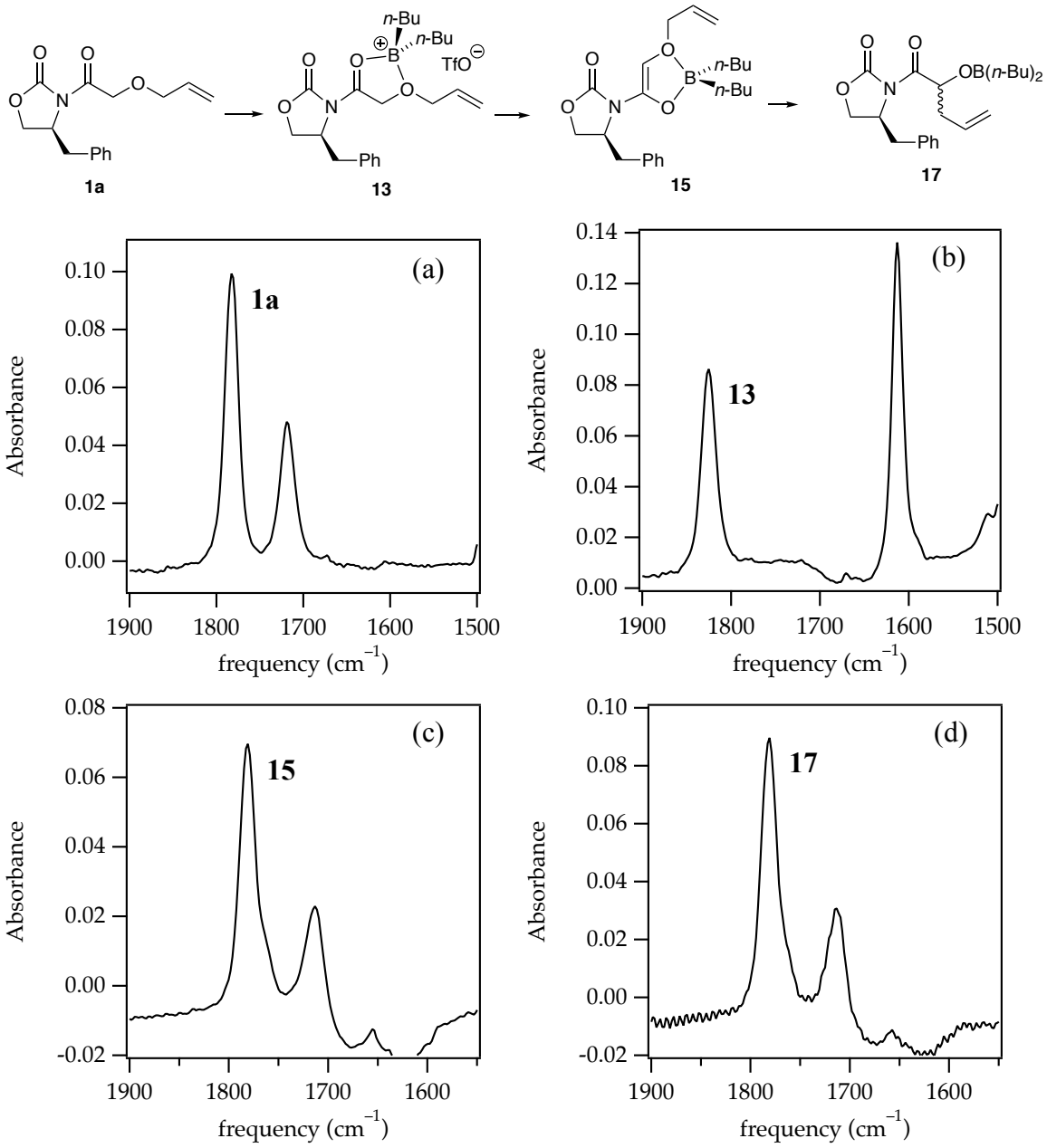


Figure S1. IR spectra of 0.030 M **1a** in CH_2Cl_2 recorded at 0 °C with (a) no additive; (b) 0.060 M *n*-Bu_2BOTf affording **13**; (c) 0.060 M *n*-Bu_2BOTf and 0.10 M Et_3N affording **15**; and (d) product **17** after warming to 25 °C.

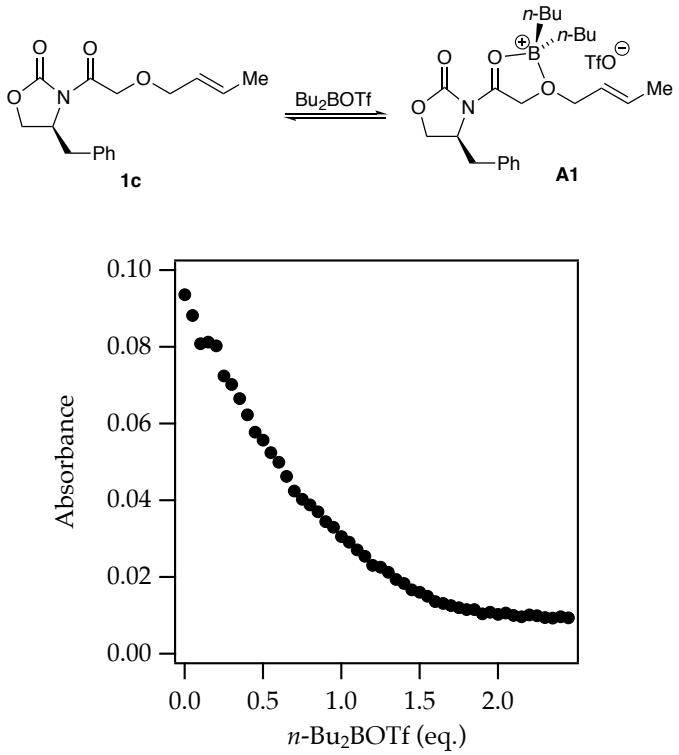


Figure S2. Loss of oxazolidinone carbonyl (1783 cm^{-1}) at –30 ºC of **1c** (0.040 M) in CH_2Cl_2. *n*-Bu_2BOTf (1.0 M) in CH_2Cl_2 via syringe pump over 13 min. The requirement of ≈2.0 equiv of *n*-Bu_2BOTf for full complexation, and the curvature of the decay suggests that the complexation is a soft equilibrium.

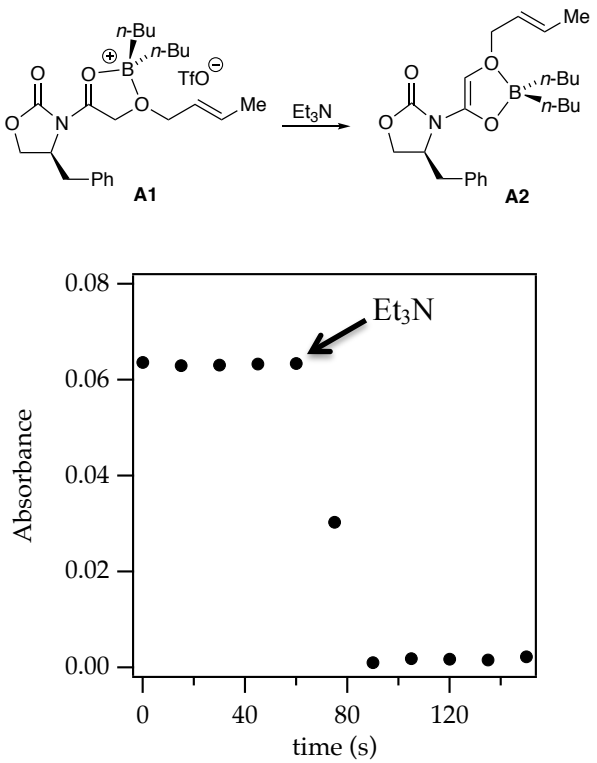


Figure S3. IR spectrum recorded at –30 ºC following the loss of the oxazolidinone carbonyl (1825 cm^{-1}) of boron complex **A1** formed from 0.040 M **1c** and 0.10 M *n*-Bu_2BOTf. Addition of Et_3N (0.12 M) causes immediate disappearance of boron complex **A1** and formation of boron enolate **A2**.

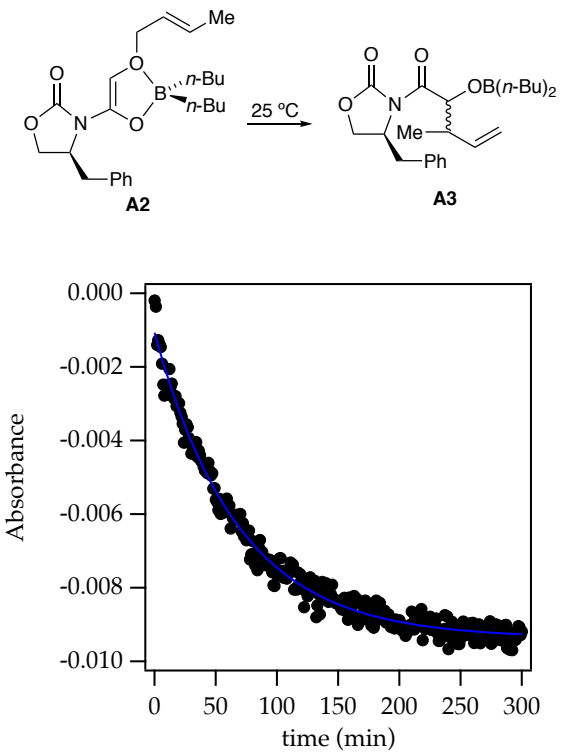
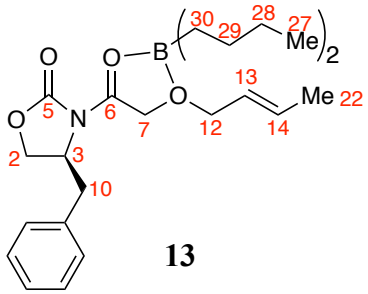


Figure S4. Loss of the oxazolidinone carbonyl of **A2** (1781 cm^{-1}) in a solution of 0.040 M **1c**, 0.10 M *n*-Bu_2BOTf, and 0.12 M Et_3N in CH_2Cl_2. The decay correlates with the enolate rearranging to the product alkoxide **A3**. The lower net absorbance loss compared to enolate is due to peak overlap between enolate and alkoxide. The curve depicts a least-squares fit to $y = a^{-bx} + c$, such that $a = 0.00829 \pm 0.00006$, $b = 0.0147 \pm 0.0002$, $c = 0.00936 \pm 0.00003$.

2. NMR structural study



13

Table S1. ^{1}H and ^{13}C chemical shift assignments for **13**.[a,b]

Atom #	δ ^{13}C, ppm	δ ^{1}H, ppm	COSY	HMBC	ROESY
2	69.8	4.42 (2')	2", 3	10, 3, 5	2", 10"
		4.64 (2")	2', 3		3, 2'
3	56.4	4.88	2', 2", 10', 10"	10, 5	2', 10'
10	36.4	3.35 (10')	10", 3	3, 2	10", 3
		3.00 (10")	10', 3		10', 2'
7	70.7	5.51		12, 6	12, 13
12	78.2	4.70	13, 22	7, 13, 14	30, 7, 13, 14
13	119.5	5.59	14, 12, 22	22, 6	7, 12, 22
14	142.2	6.21	13, 22	22, 12	12, 22
22	18.3	1.81	12, 13, 14	13, 14	13, 14
30	18.5	0.66	29	29	12
29, 28	25.7	1.25	30, 27	27, 30	
27	14.2	0.85	28	28	
5	150.8				
6	175.3				

[a] Important correlations that allowed determination of subunit arrangement are marked in red. [b] *n*-butyl groups time average.

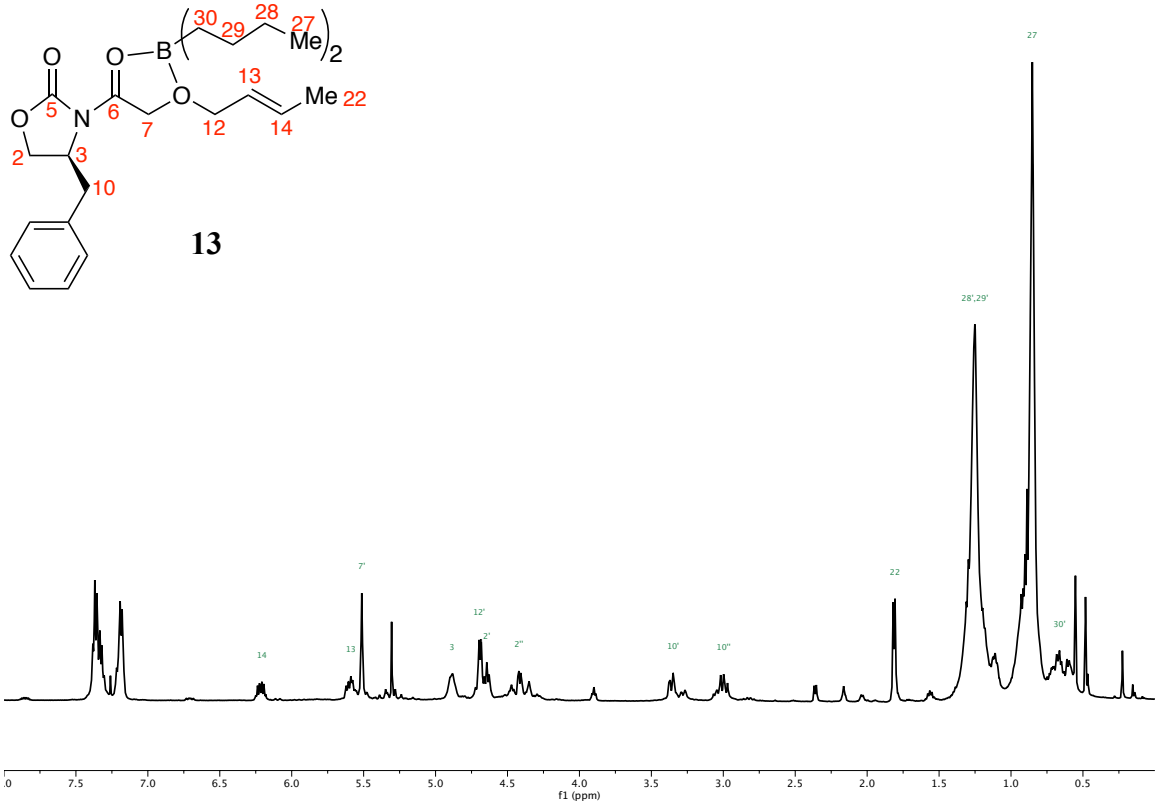


Figure S5. ^{1}H NMR spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

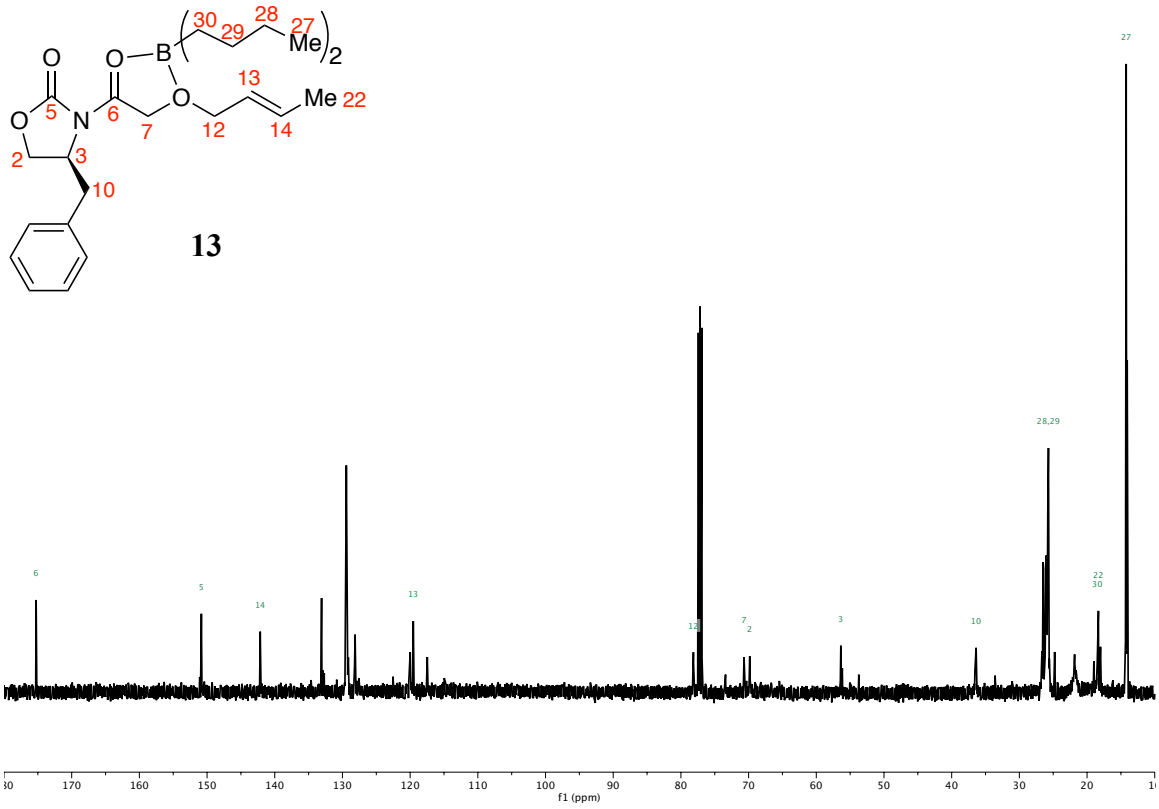
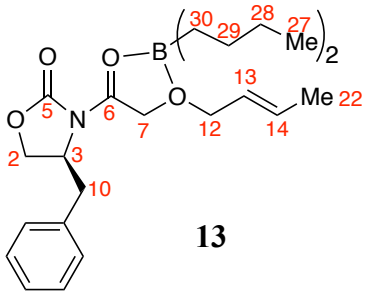


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	HSQCAD
4	Number of Scans	2
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.1501



13

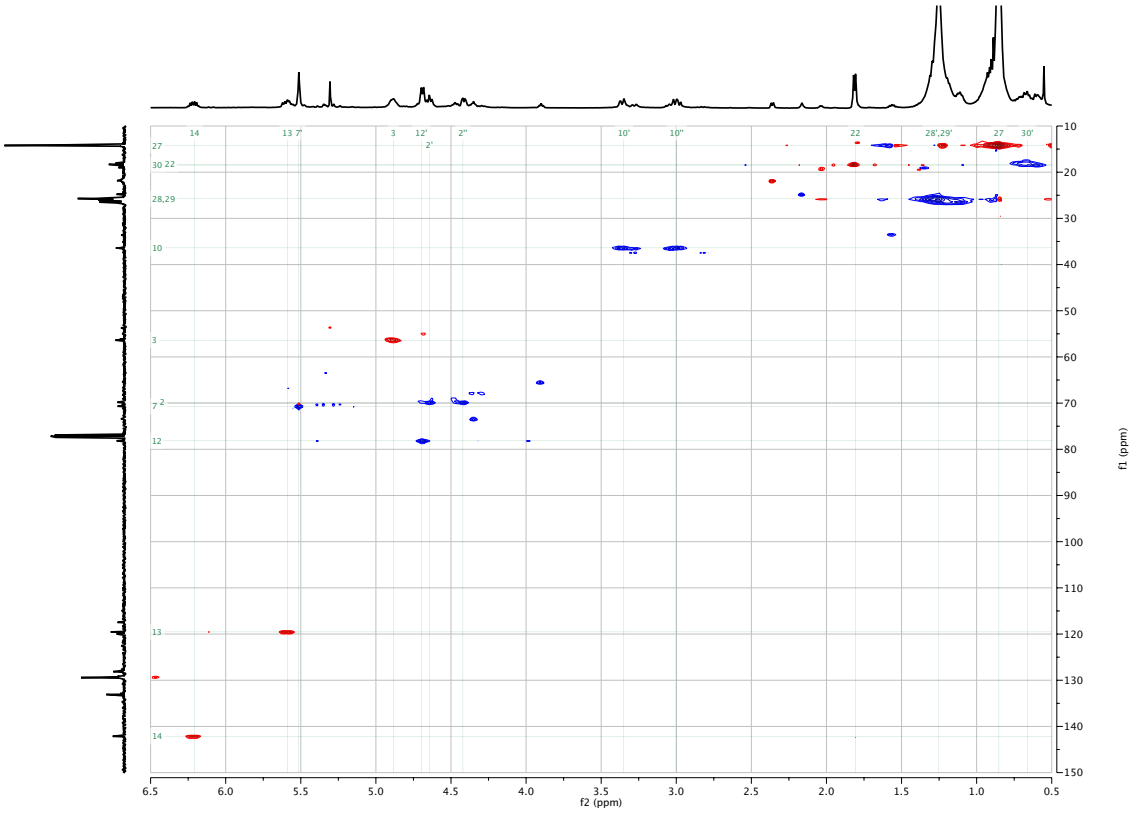
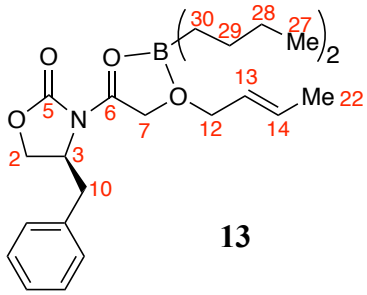


Figure S7. HSQC spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	gCOSY
4	Number of Scans	1
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.5000



13

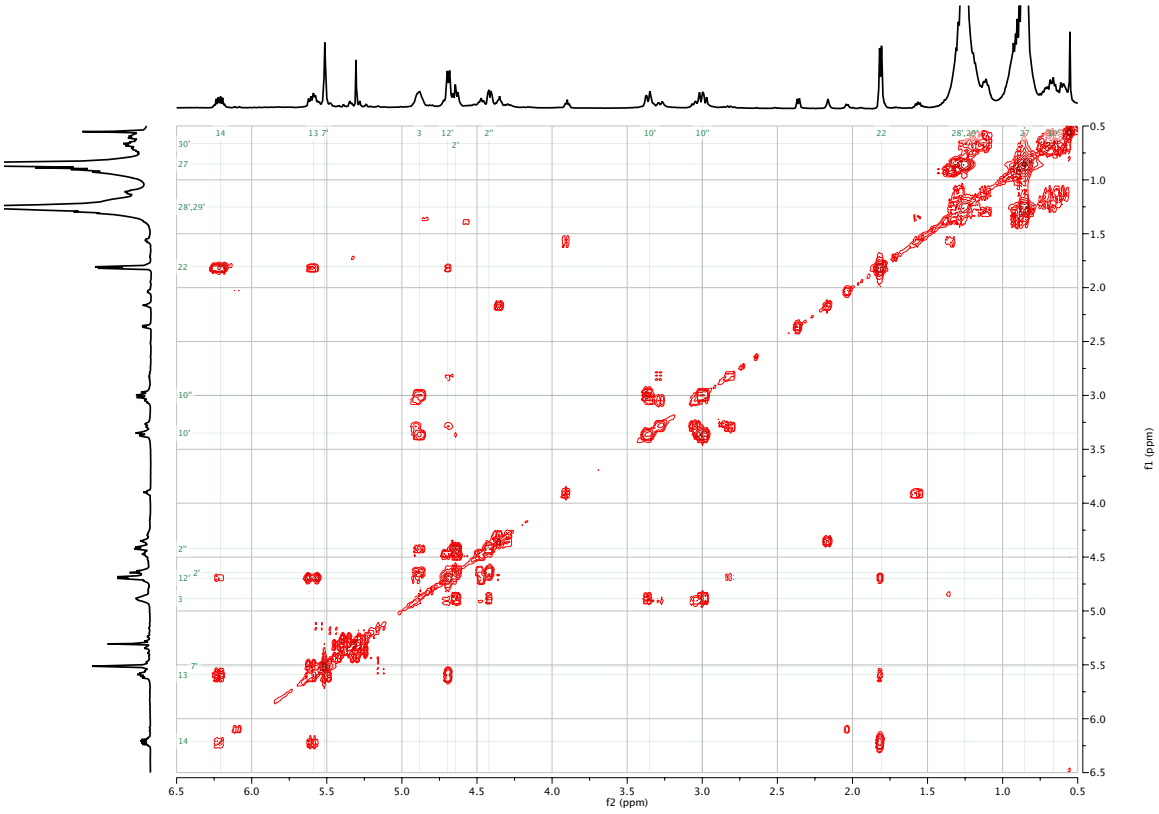
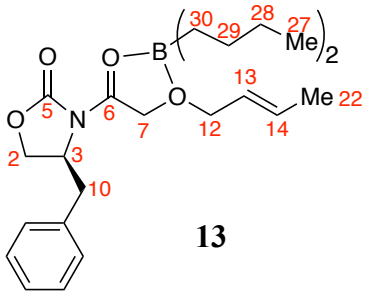


Figure S8. COSY spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

Parameter	Value
1 Solvent	cdcl3
2 Temperature	-30.0
3 Pulse Sequence	gHMBCAD
4 Number of Scans	2
5 Receiver Gain	10
6 Relaxation Delay	1.0000
7 Pulse Width	8.5000
8 Acquisition Time	0.3000



13

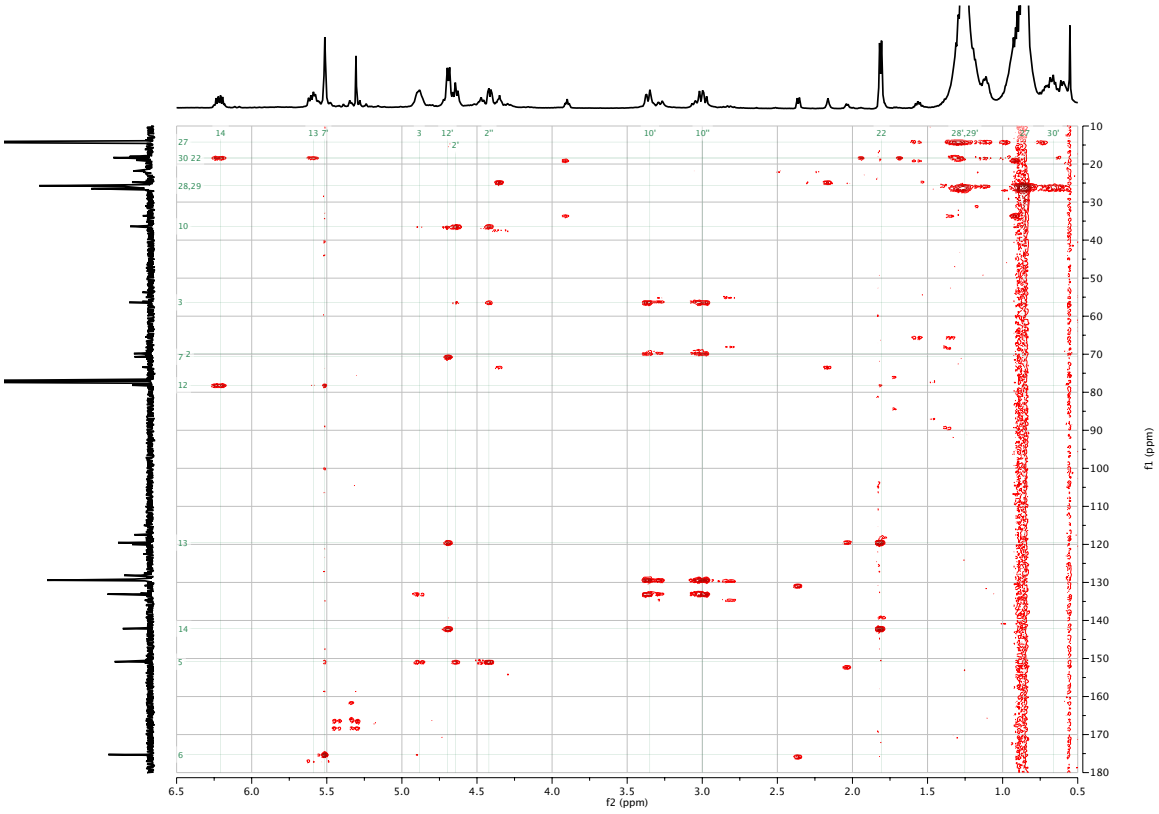
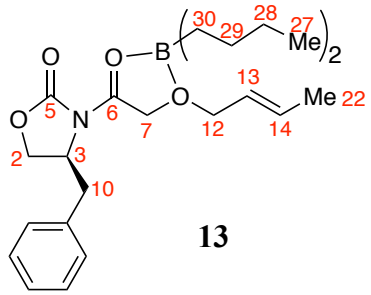


Figure S9. HMBC spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	ROESYAD
4	Number of Scans	4
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.4000



13

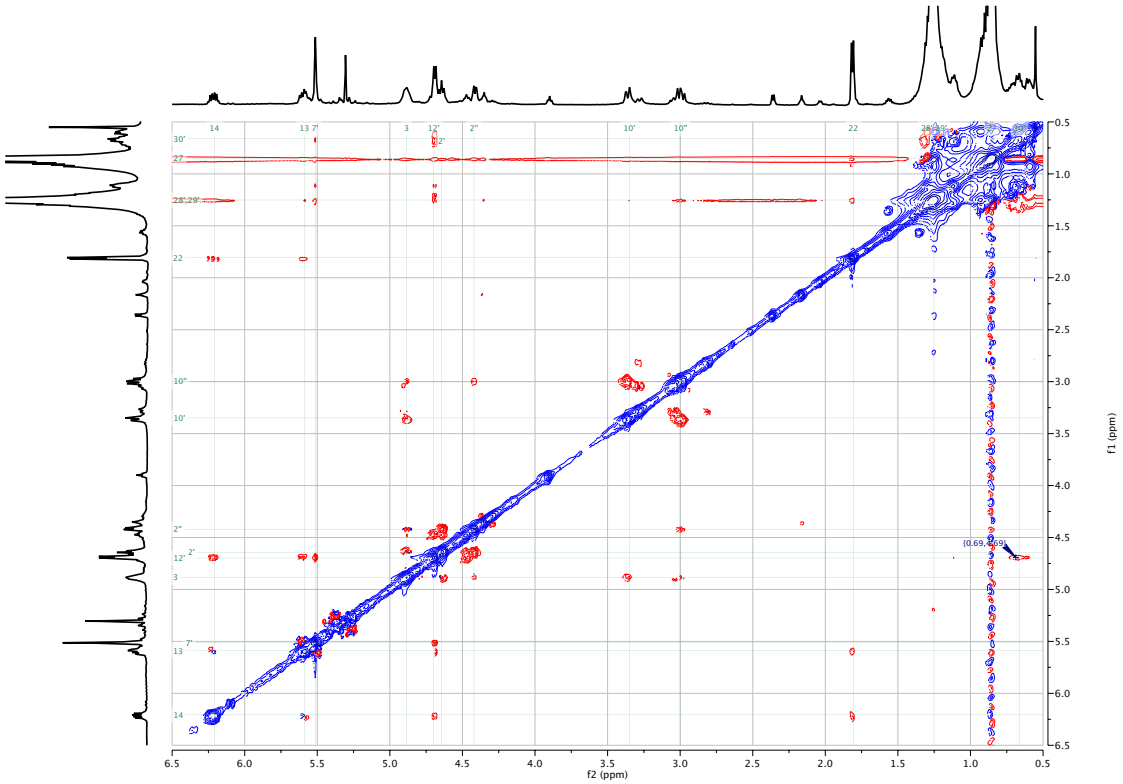
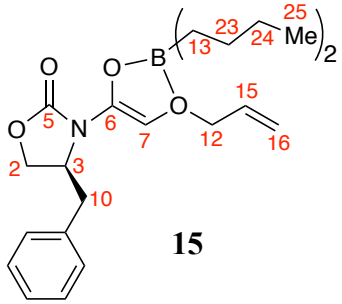


Figure S10. ROESY spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.



15

Table S2. ^{1}H and ^{13}C chemical shift assignments for **15**.[a, b]

Atom #	δ ^{13}C, ppm	δ ^{1}H, ppm	COSY	HMBC	ROESY
2	70.0	4.39 (2')	2"		
		4.30 (2")	2', 3		
3	58.5	4.39	2", 10', 10"	5	10', 10", 7
10	37.9	3.05 (10')	10", 3	3, 2	3
		2.98 (10")	10', 3		3
7	124.8	5.78		12	12, 3
12	75.5	4.30	15, 16', 16"	7, 15, 16	13, 7, 15, 16'
15	135.9	5.95	12, 16', 16"	12	13, 12, 16', 16"
16	120.1	5.35 (16')	12, 15, 16"	15, 12	12, 15
		5.25 (16")	12, 15, 16'		15
13	22.6	0.50	23	23	12, 15, 23
23, 24	28.5	1.24	13, 25	25, 13	13, 25
25	16.4	0.86	24	24	24
5	159.8				
6	172.0				

[a] Important correlations that allowed determination of subunit arrangement are marked in red. [b] *n*-butyl groups time average.

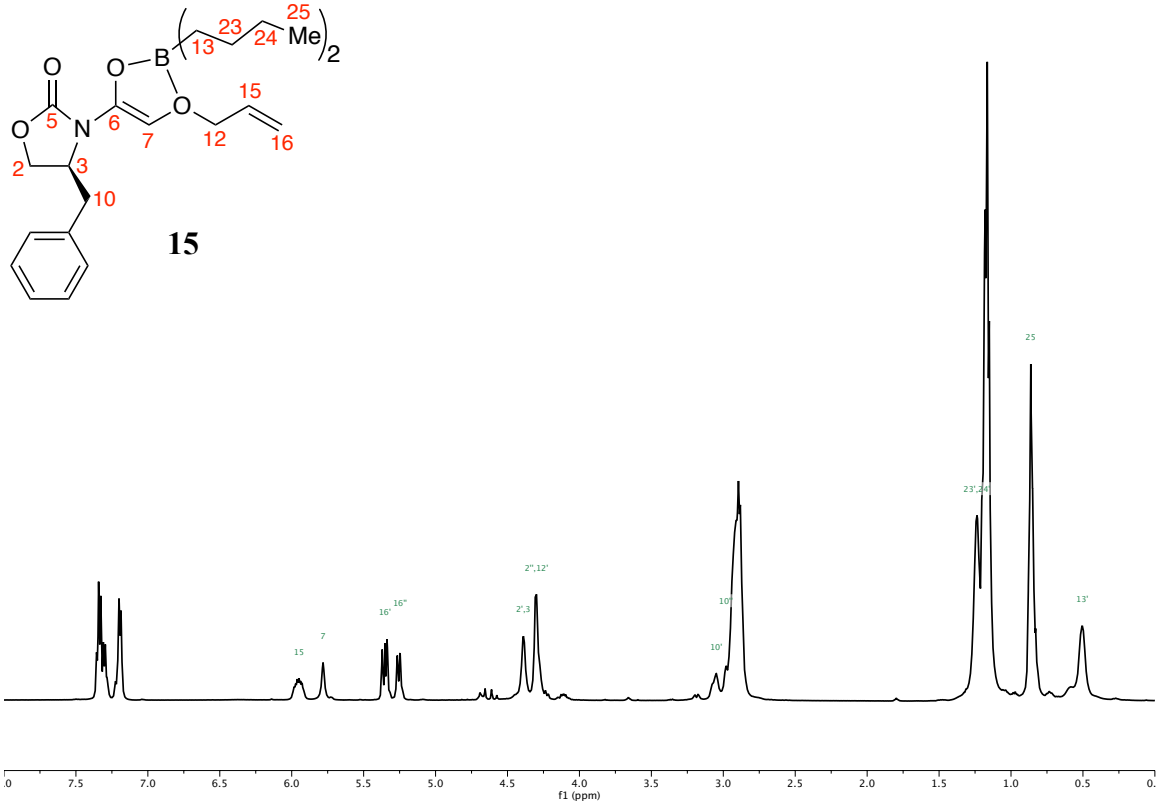


Figure S11. ^{1}H NMR spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

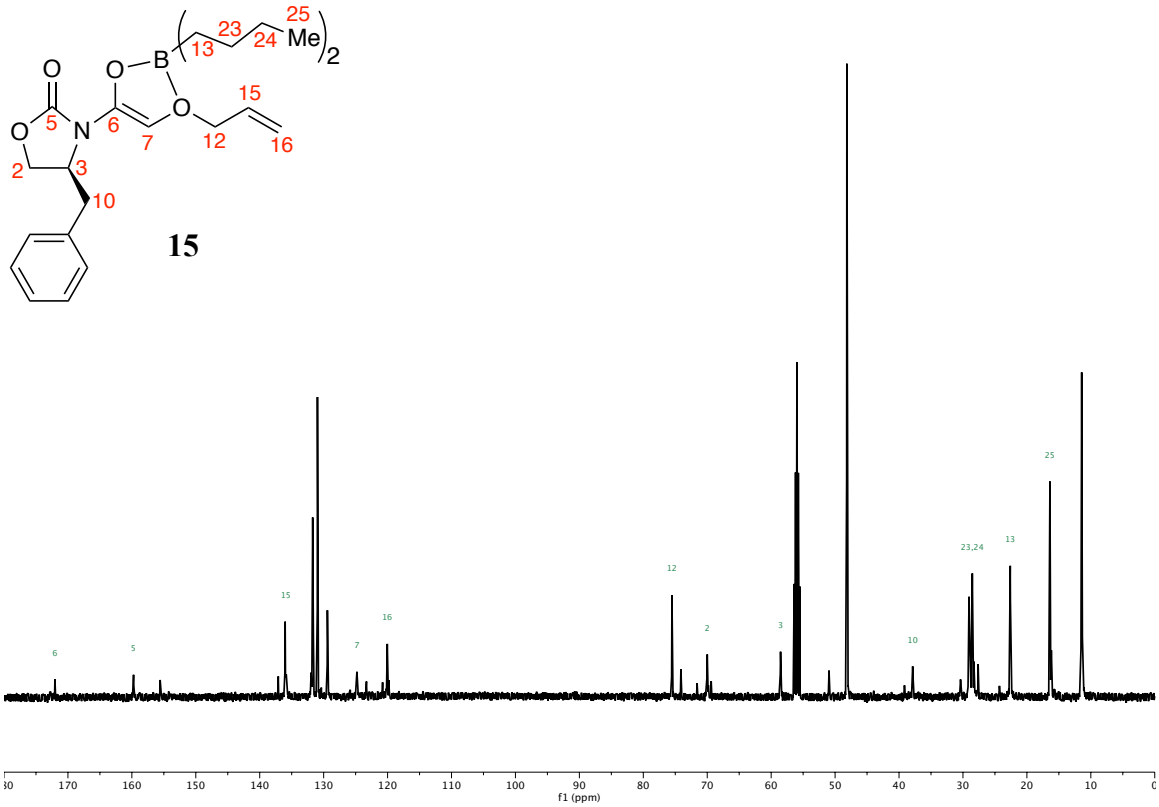
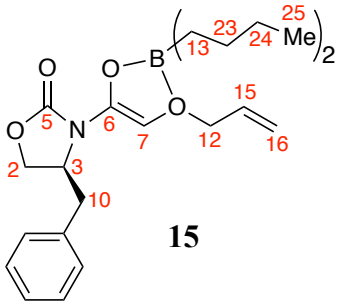


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC. Extra peaks are rearranged product alkoxide.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	HSQCAD
4	Number of Scans	2
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.1501



15

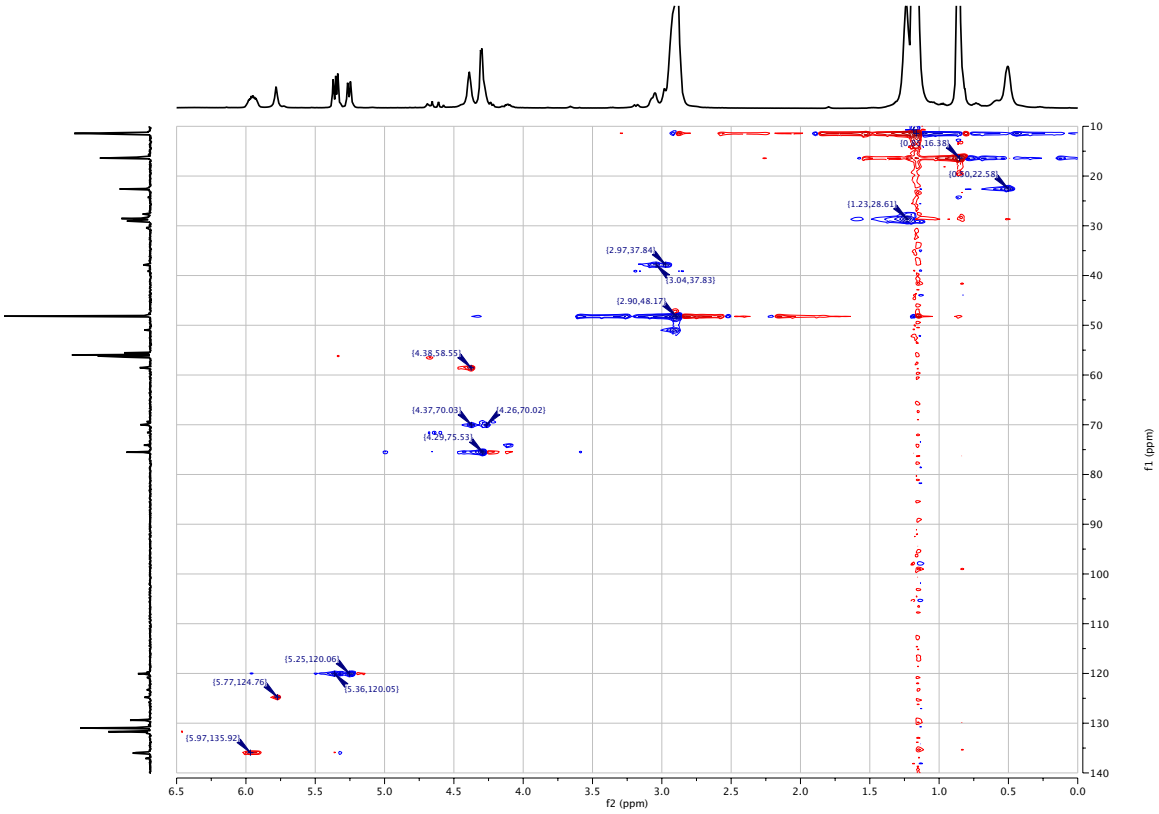
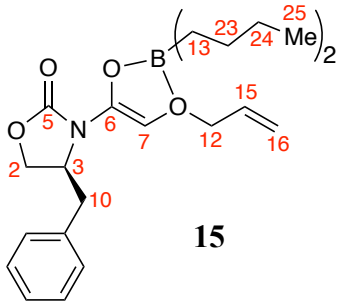


Figure S13. HSQC spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	gCOSY
4	Number of Scans	1
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.5000



15

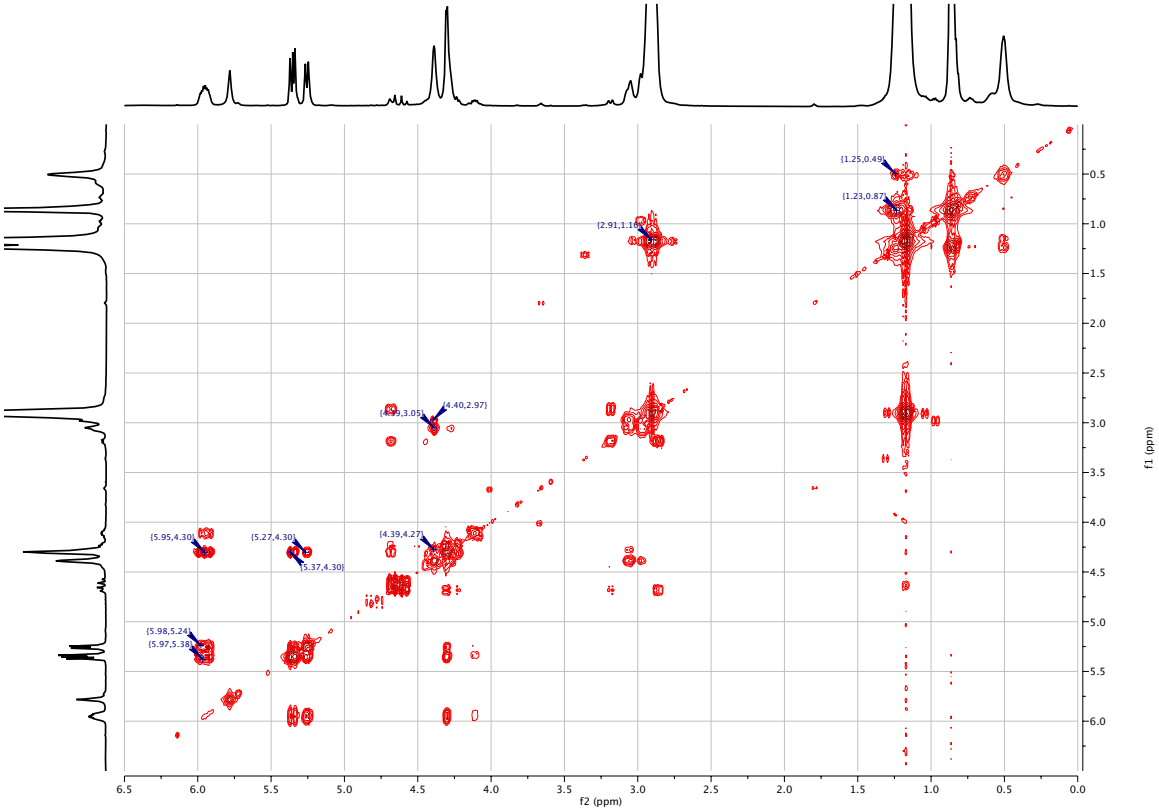
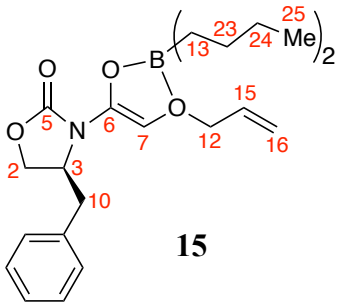


Figure S14. COSY spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	gHMBCAD
4	Number of Scans	2
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.3000



15

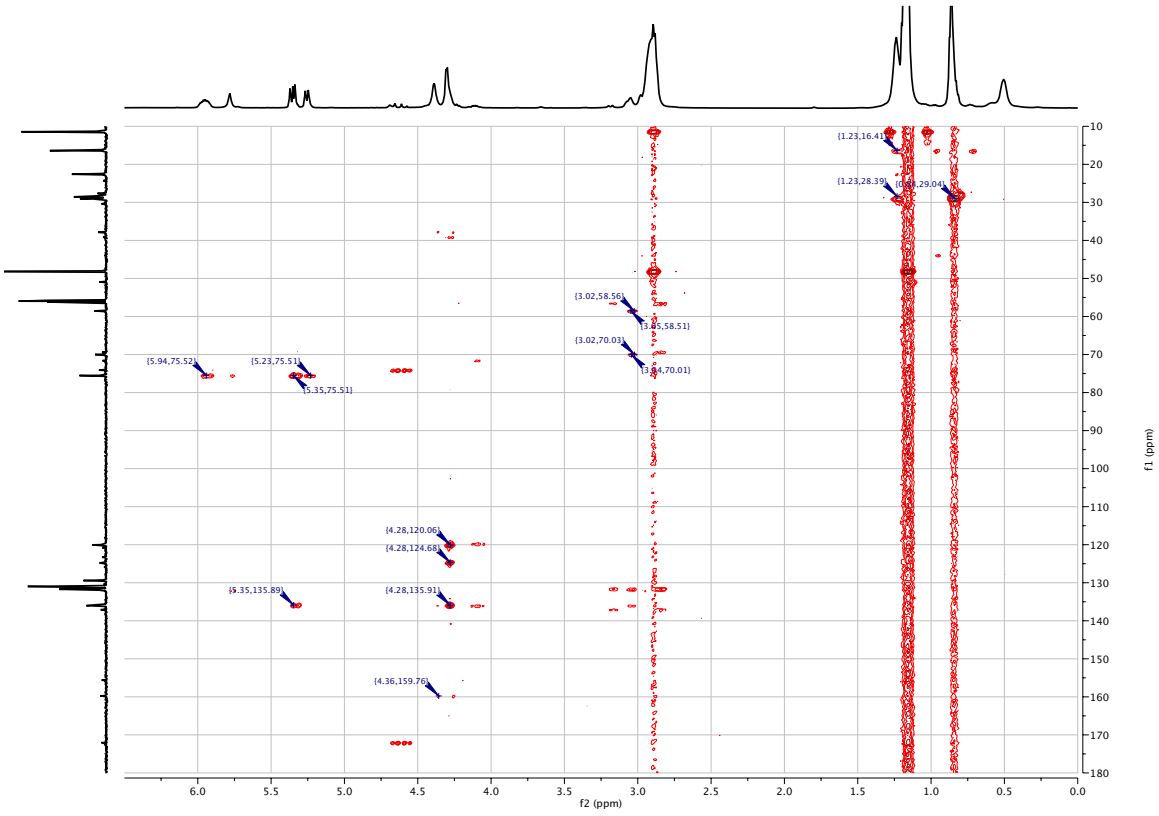
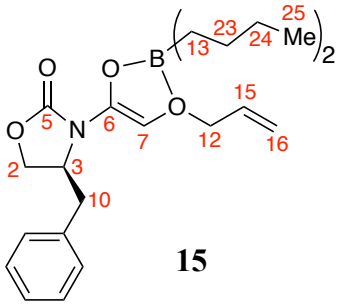


Figure S15. HMBC spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

Parameter	Value
1 Solvent	cdcl3
2 Temperature	-50.0
3 Pulse Sequence	ROESYAD
4 Number of Scans	4
5 Receiver Gain	10
6 Relaxation Delay	1.0000
7 Pulse Width	8.5000
8 Acquisition Time	0.4000



15

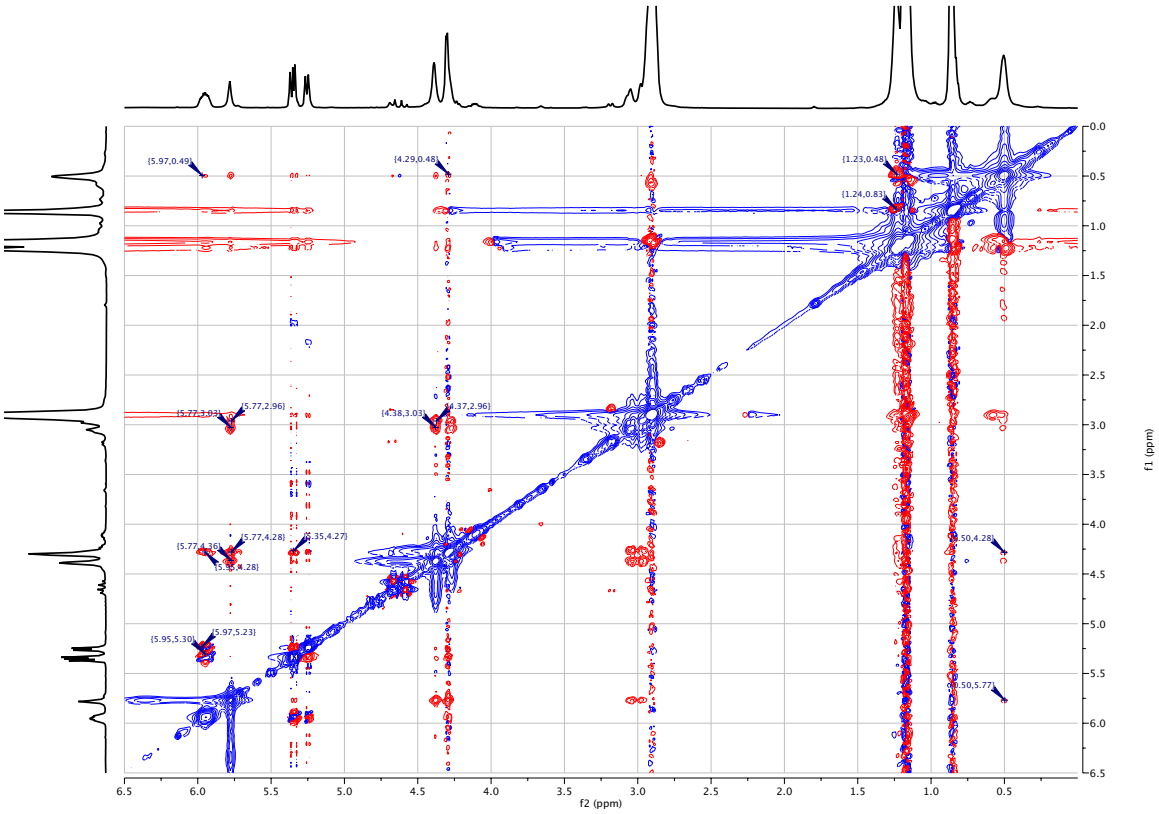


Figure S16. ROESY spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

3. Kinetics

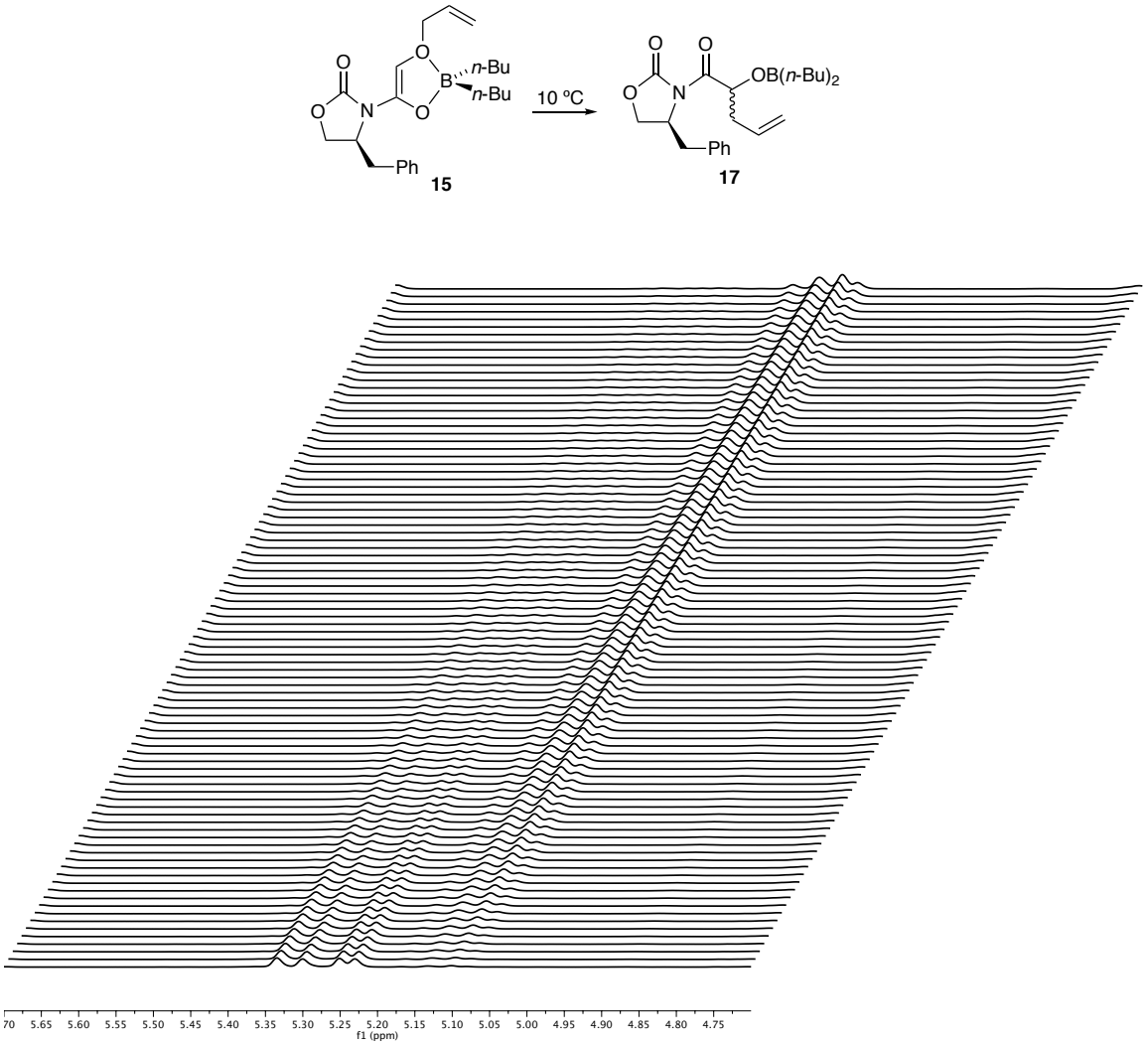


Figure S17. ^{1}H NMR spectra recorded at 10 ºC following the rearrangement of **15** generated in a solution of 0.10 M **1a**, 0.11 M *n*-Bu_2BOTf, and 0.12 M Et_3N in $CDCl_3$. The decay and growth correspond to with the allyl protons of **15** and product alkoxide **17**, respectively.

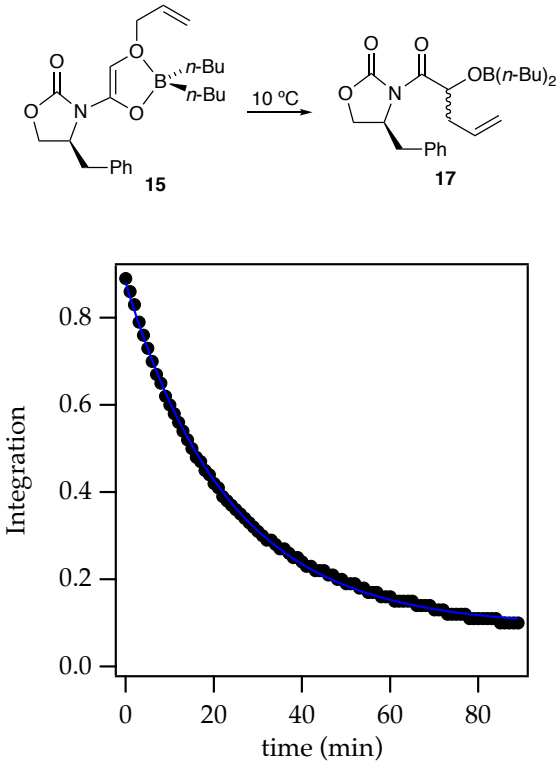


Figure S18. Plot following the loss of **15** at 10 ºC in a solution generated from 0.10 M **1a**, 0.11 M *n*-Bu_2BOTf, and 0.12 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.788 \pm 0.003$, $b = 0.0427 \pm 0.0004$, $c = 0.092 \pm 0.002$. The curvature fits a first-order decay.

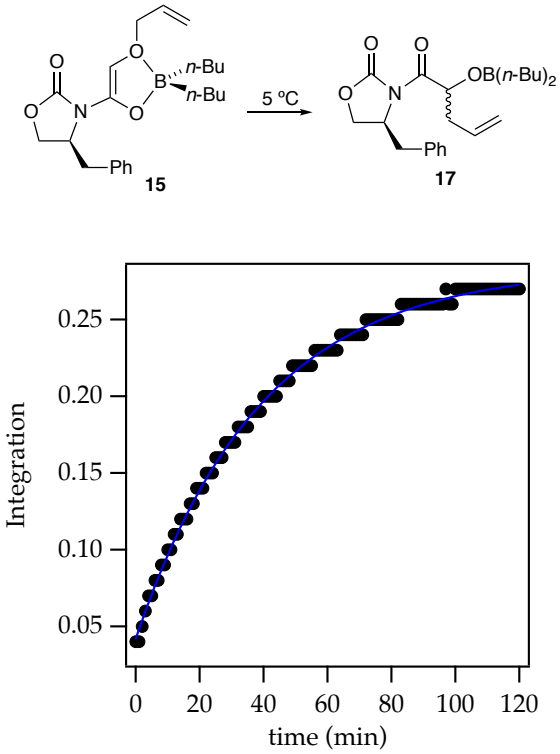
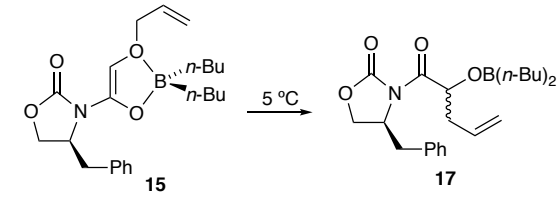


Figure S19. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 0.10 M *n*-Bu_2BOTf, and 0.10 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.242 \pm 0.001$, $b = 0.0255 \pm 0.0003$, $c = 0.042 \pm 0.001$. The curvature fits a first order growth.



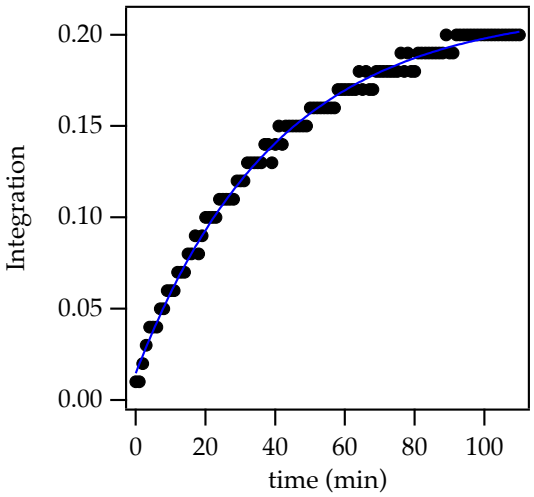


Figure S20. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 0.10 M *n*-Bu_2BOTf, and 1.0 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.200 \pm 0.001$, $b = 0.0249 \pm 0.0005$, $c = 0.015 \pm 0.001$. k_{obsd} is the same (within 10%) as using 1.0 equiv of Et_3N, confirming no dependence on amine concentration.

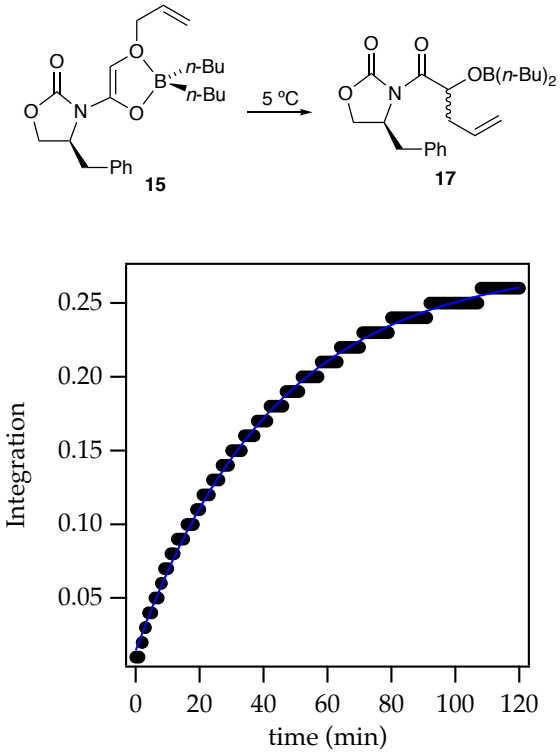


Figure S21. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 1.0 M *n*-Bu_2BOTf, and 1.0 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.263 \pm 0.001$, $b = 0.0229 \pm 0.0003$, $c = 0.015 \pm 0.001$. k_{obsd} is the same (within 10%) as using 1.0 equiv of *n*-Bu_2BOTf, confirming no dependence on the *n*-Bu_2BOTf concentration.

4. Substrate synthesis

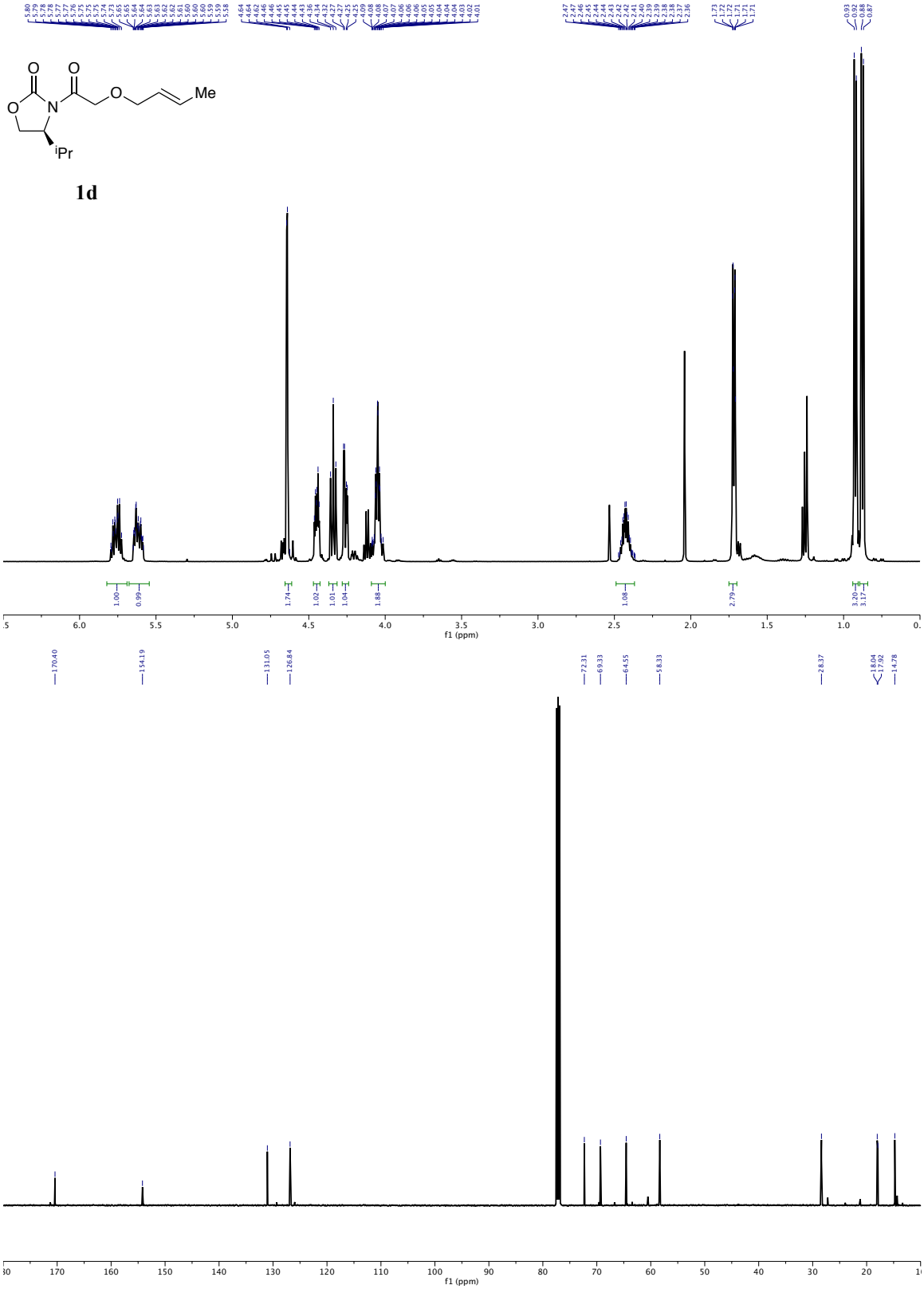


Figure S22. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1d** in $CDCl_3$.

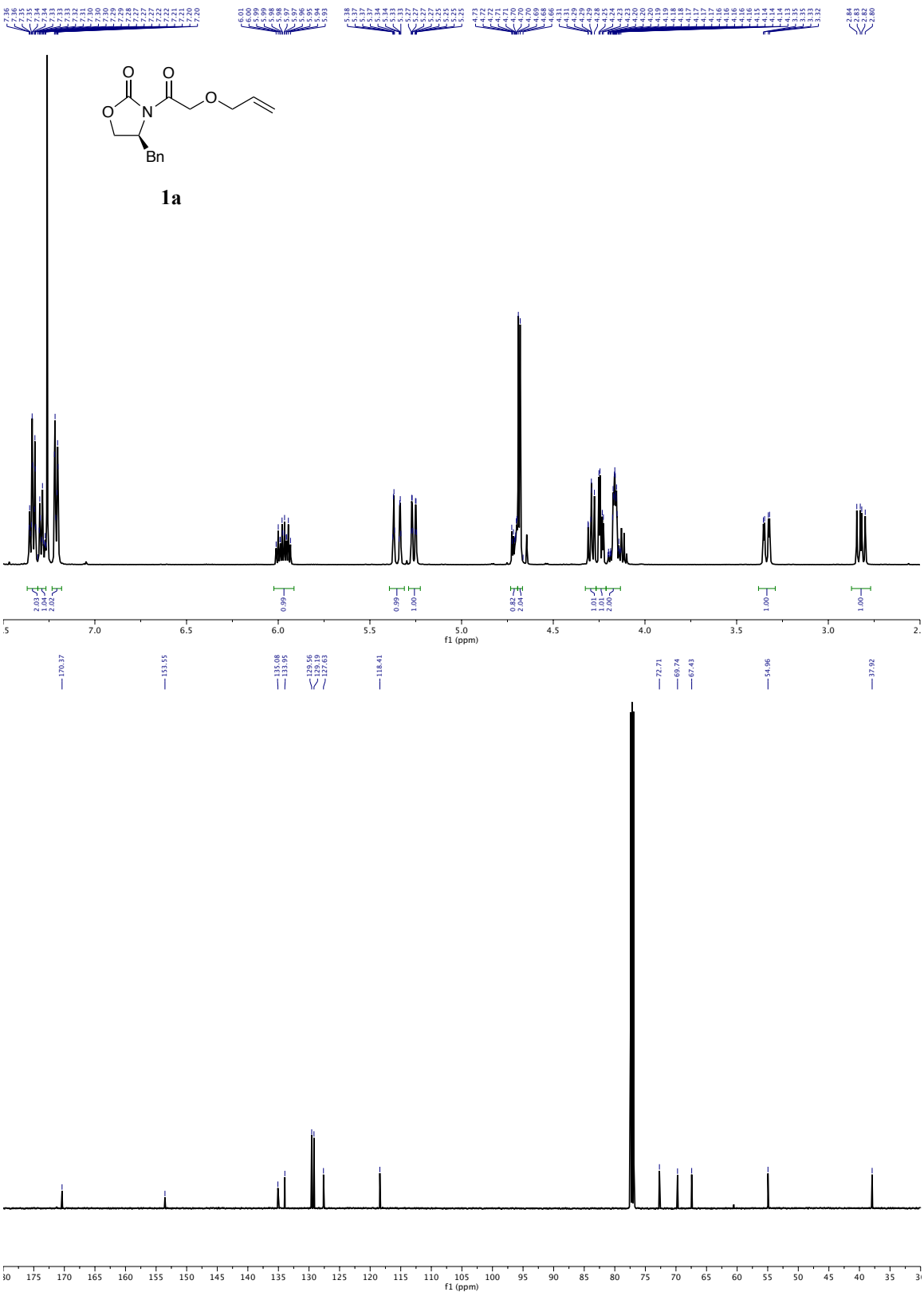


Figure S23. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1a** in $CDCl_3$.

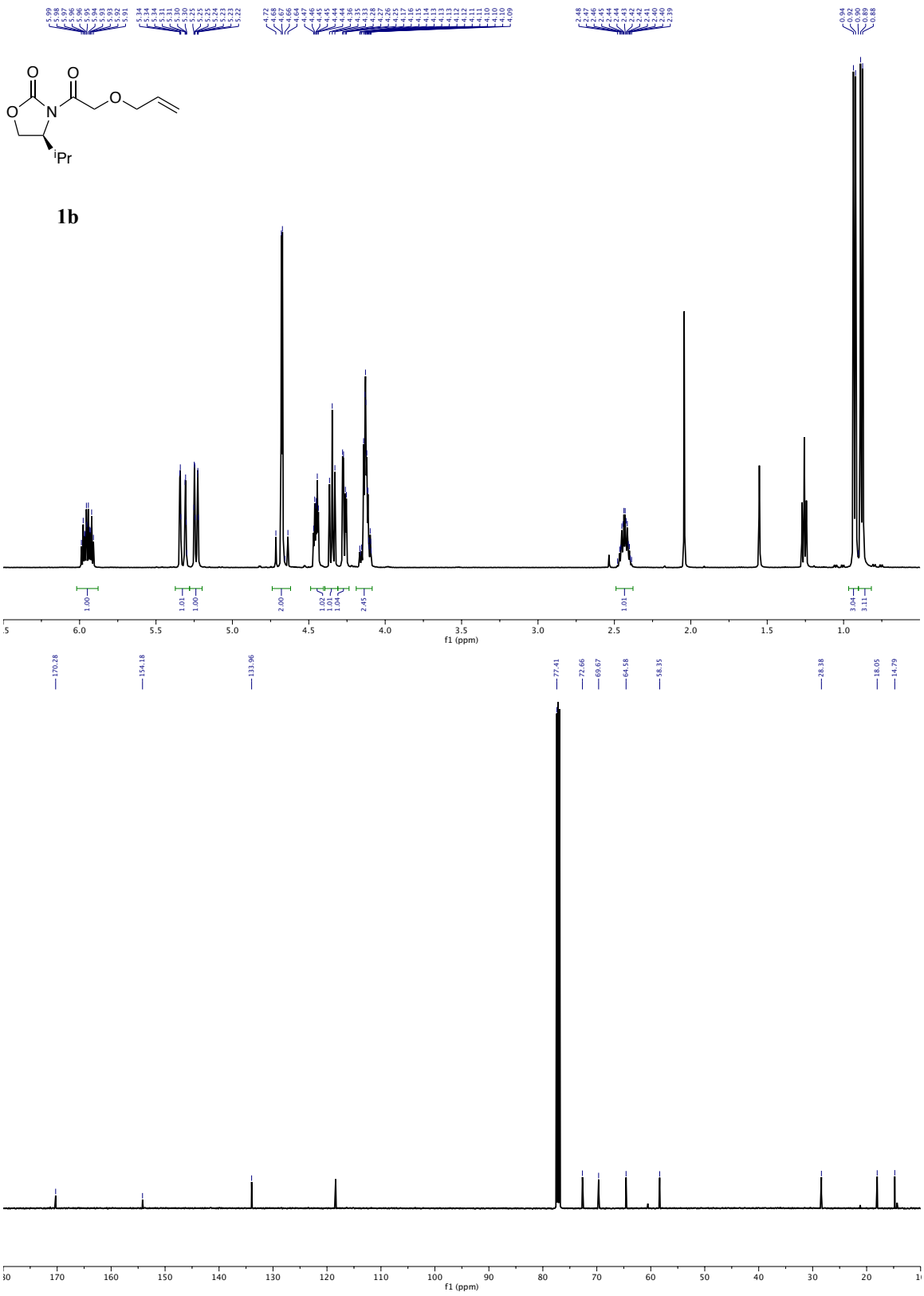


Figure S24. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1b** in $CDCl_3$.

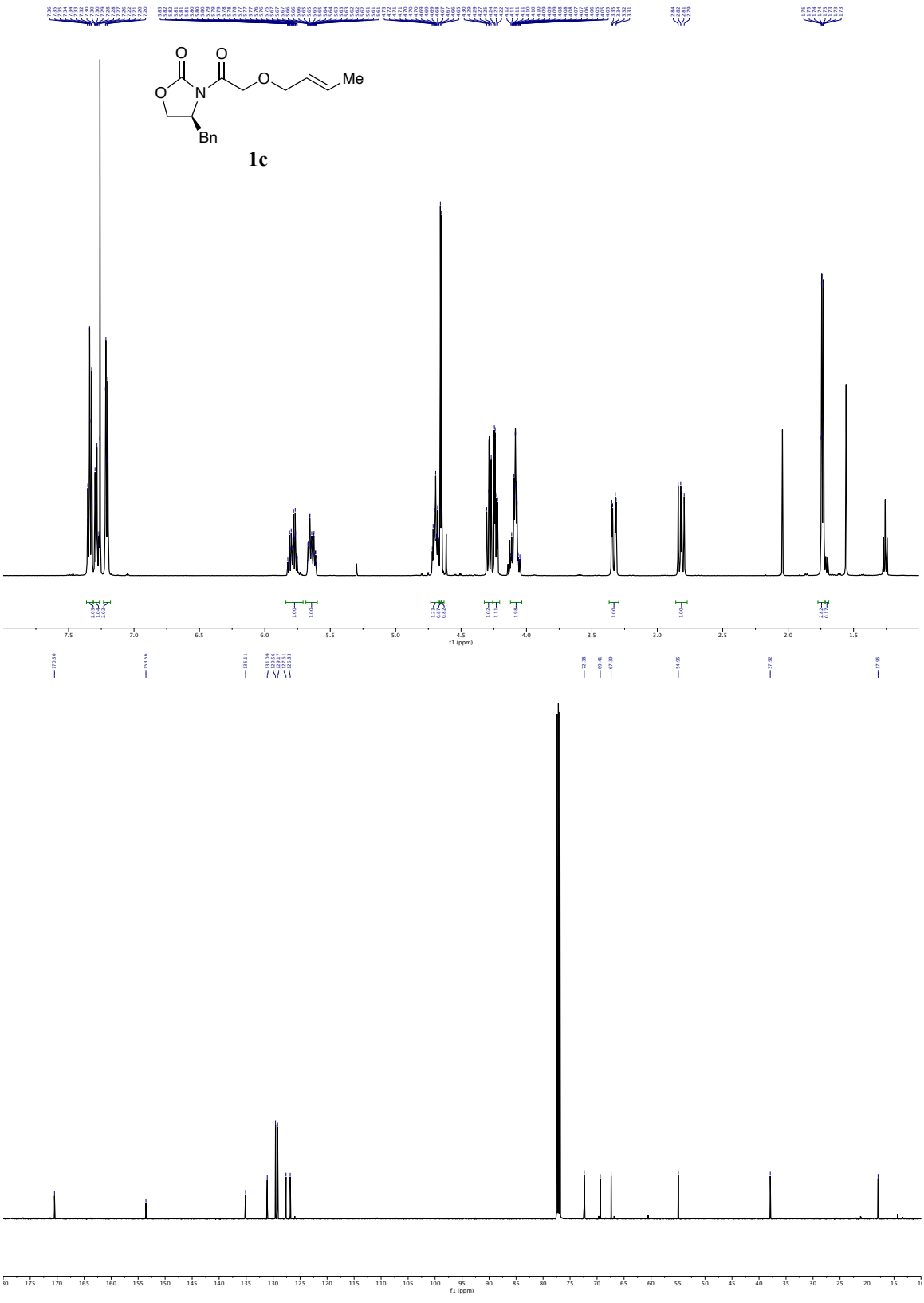


Figure S25. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1c** in $CDCl_3$.

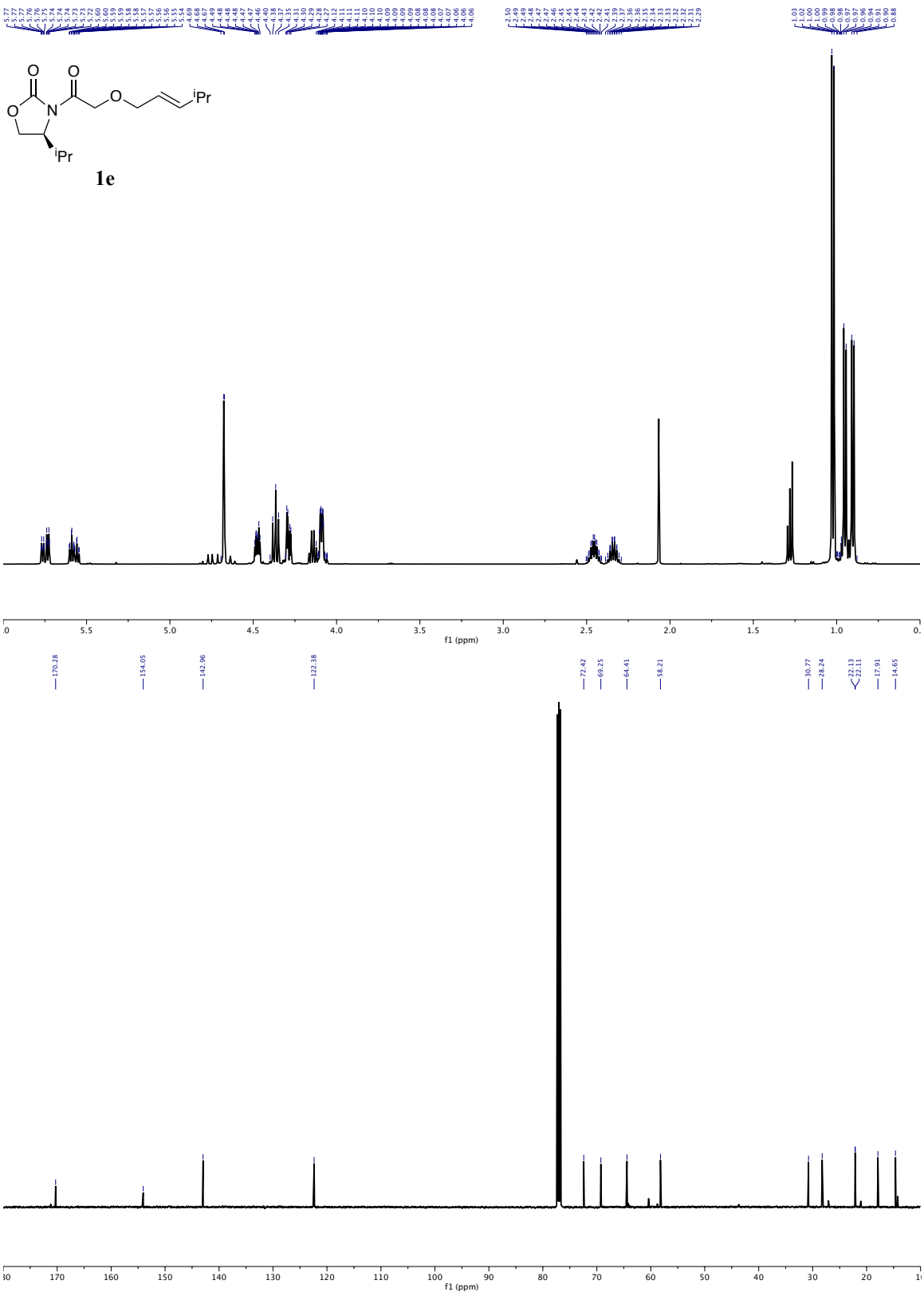


Figure S26. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1e** in $CDCl_3$.

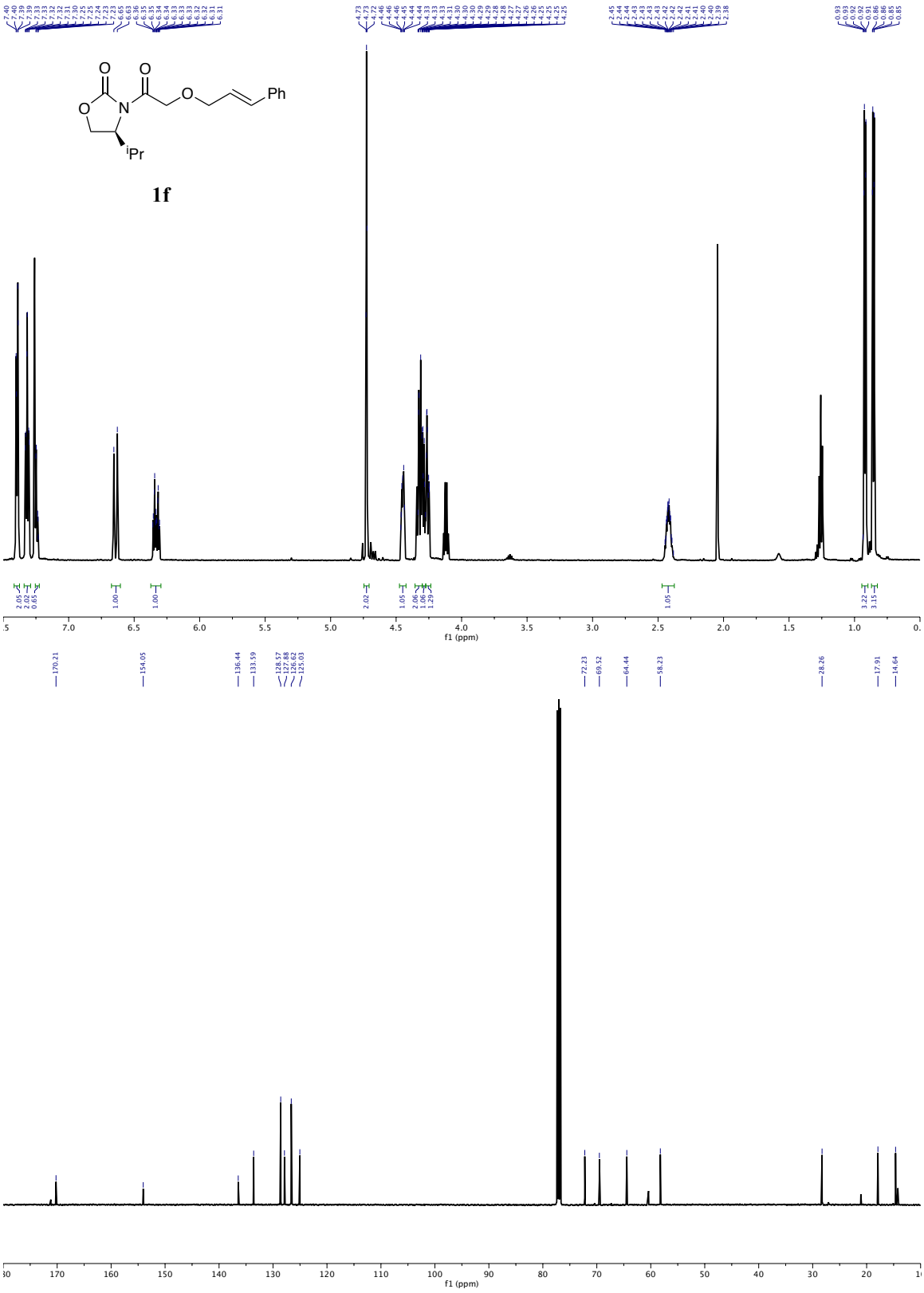


Figure S27. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1f** in $CDCl_3$.

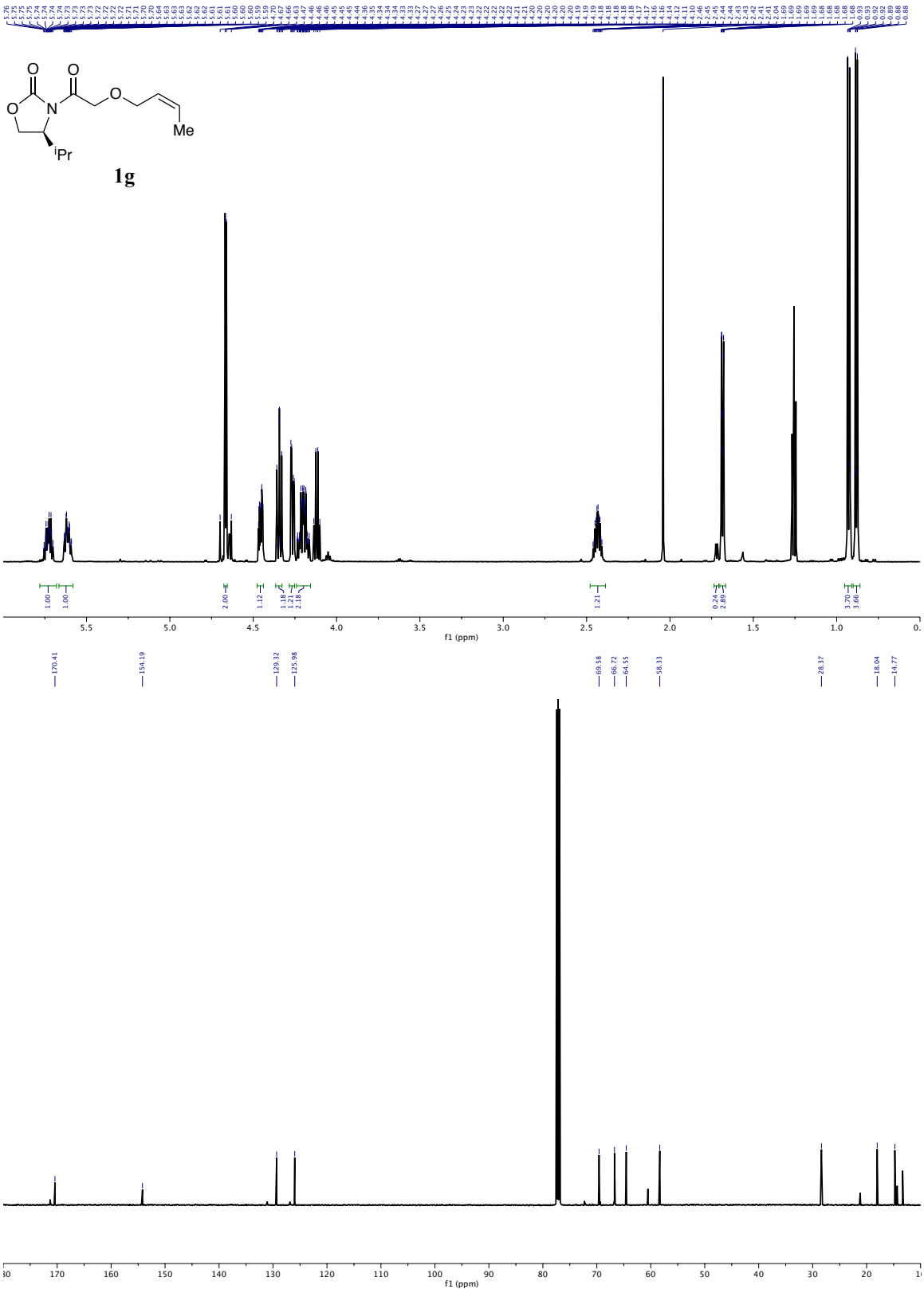


Figure S28. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectrum of **1g** in $CDCl_3$.

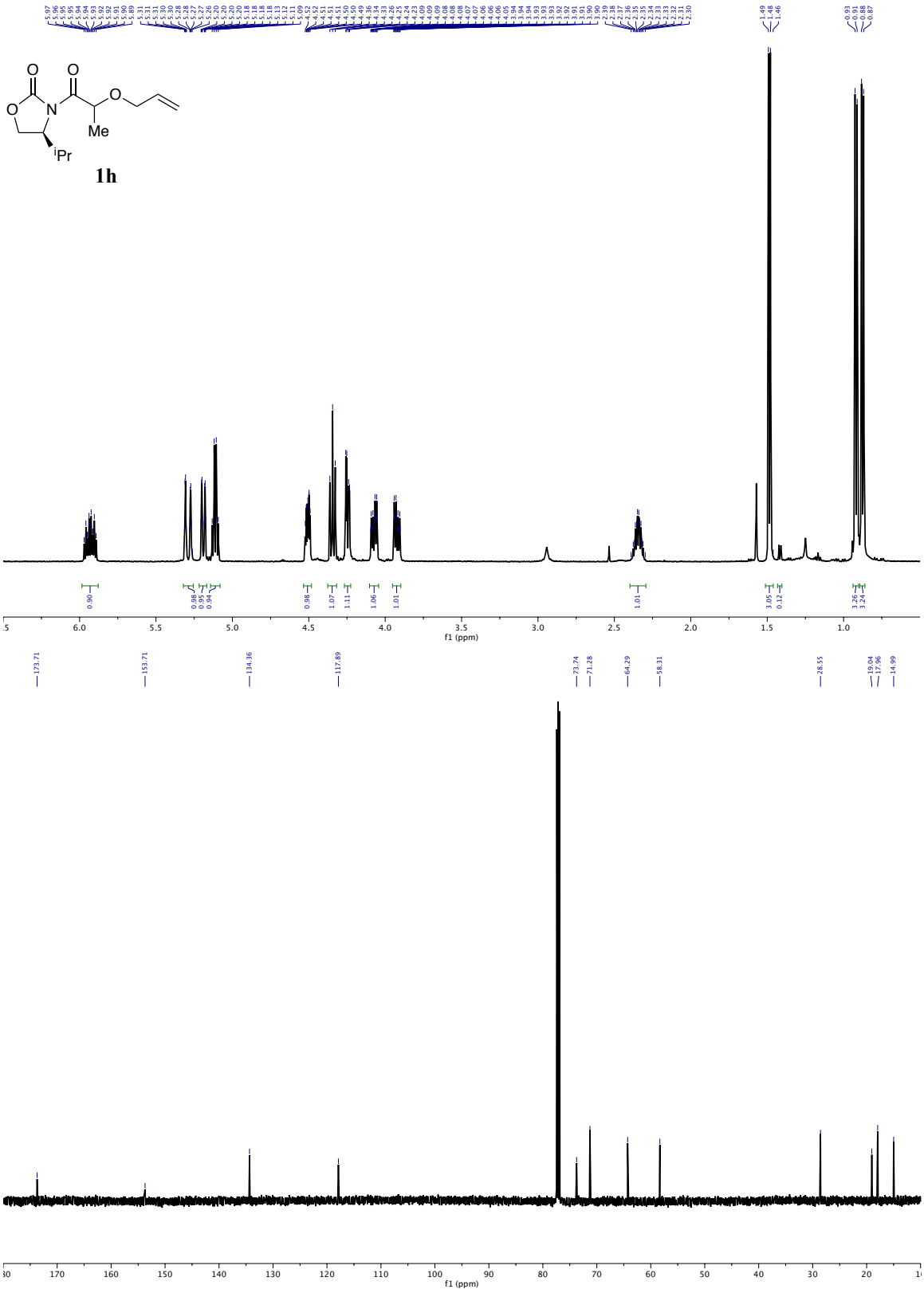


Figure S29. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1h** in $CDCl_3$.

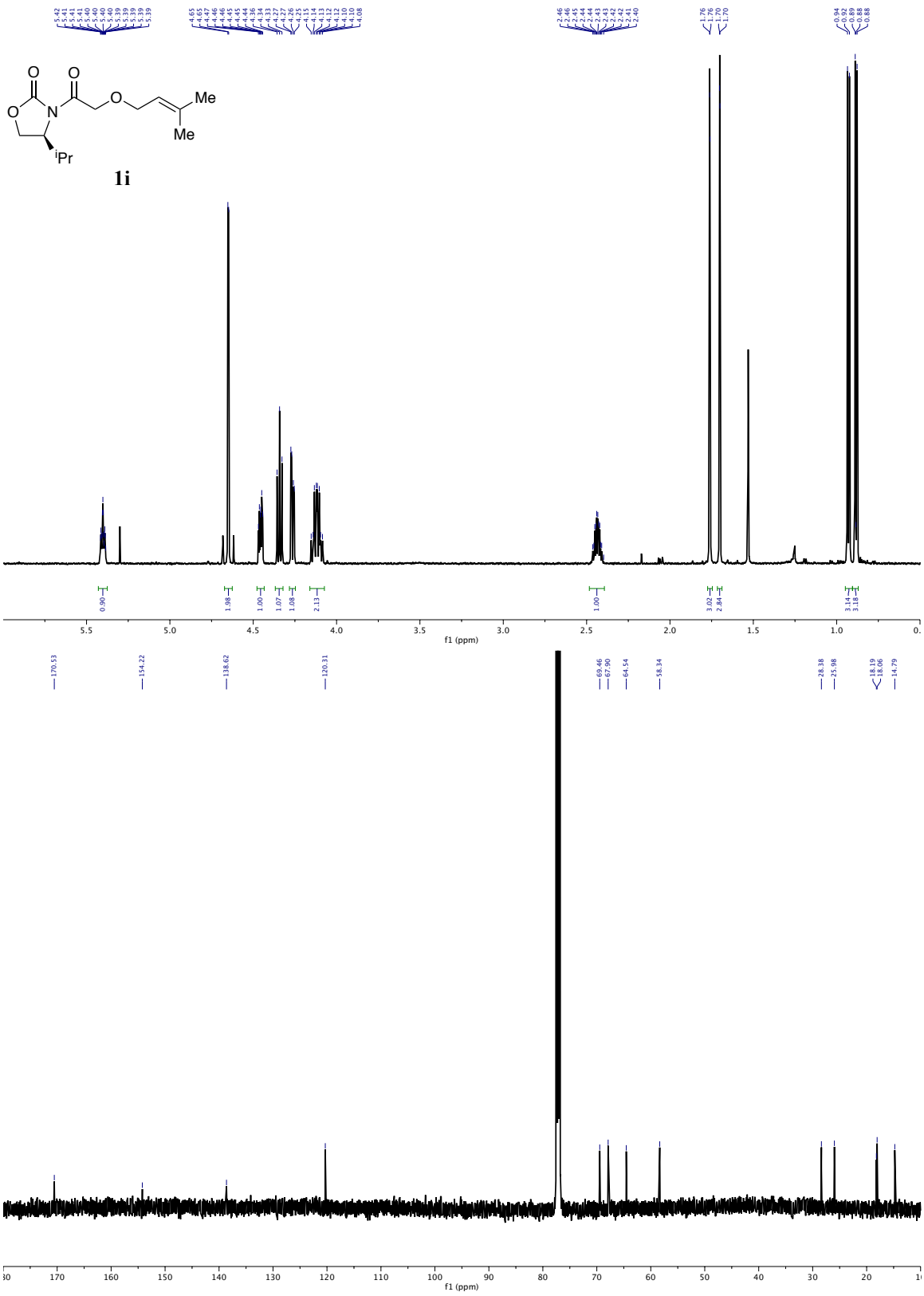


Figure S30. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1i** in $CDCl_3$.

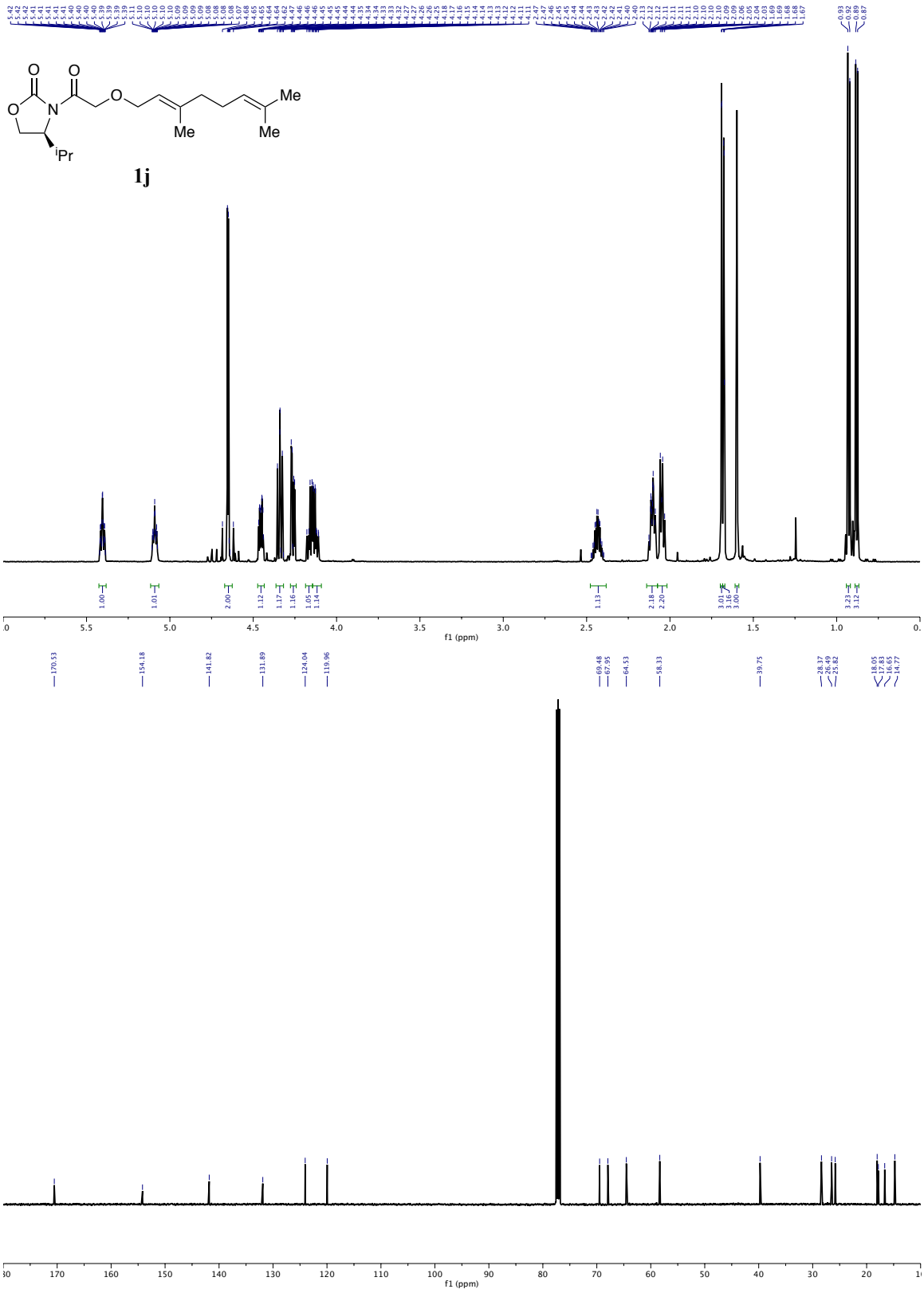


Figure S31. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1j** in $CDCl_3$.

5. Rearrangements

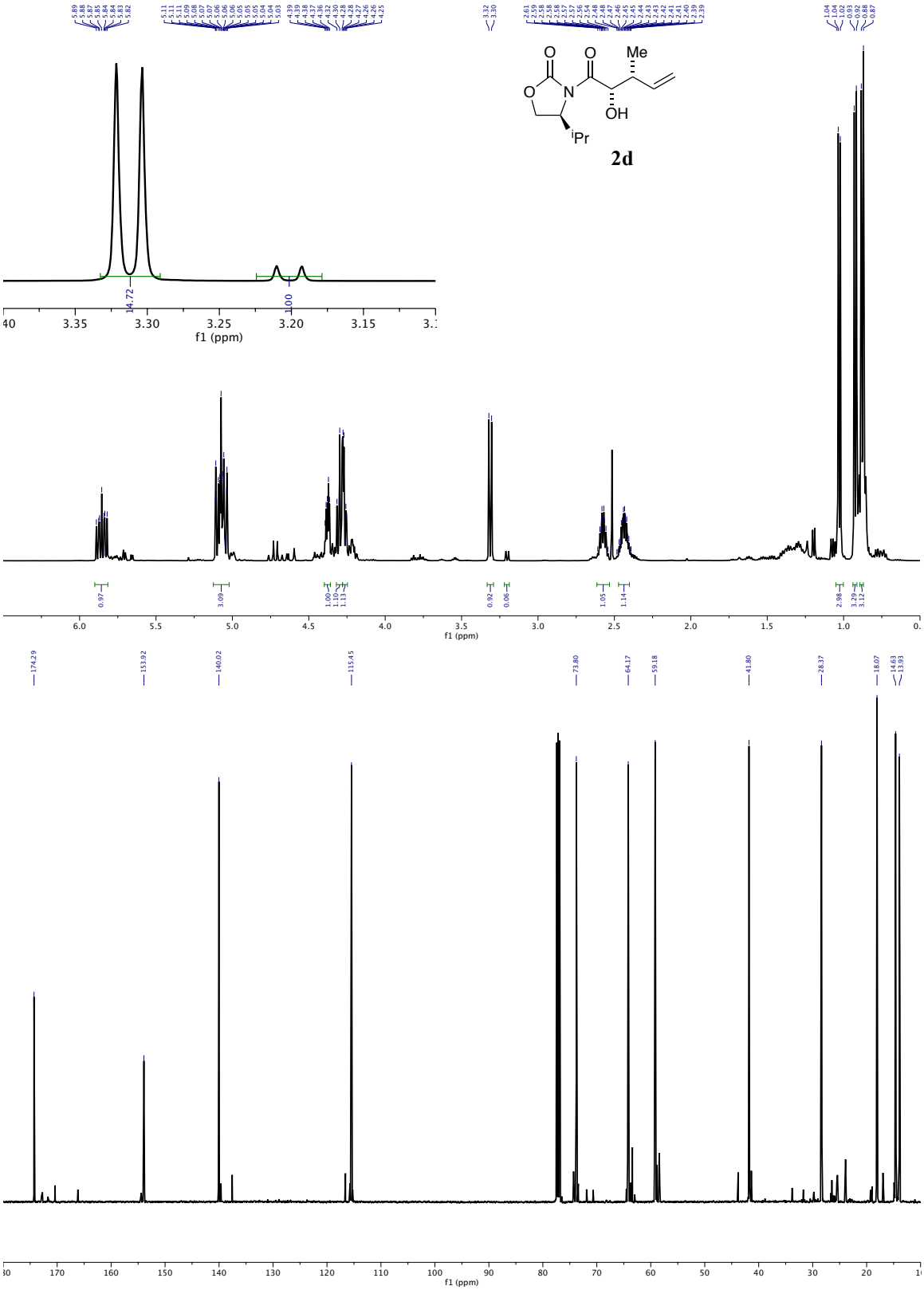


Figure S32. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2d** in $CDCl_3$.

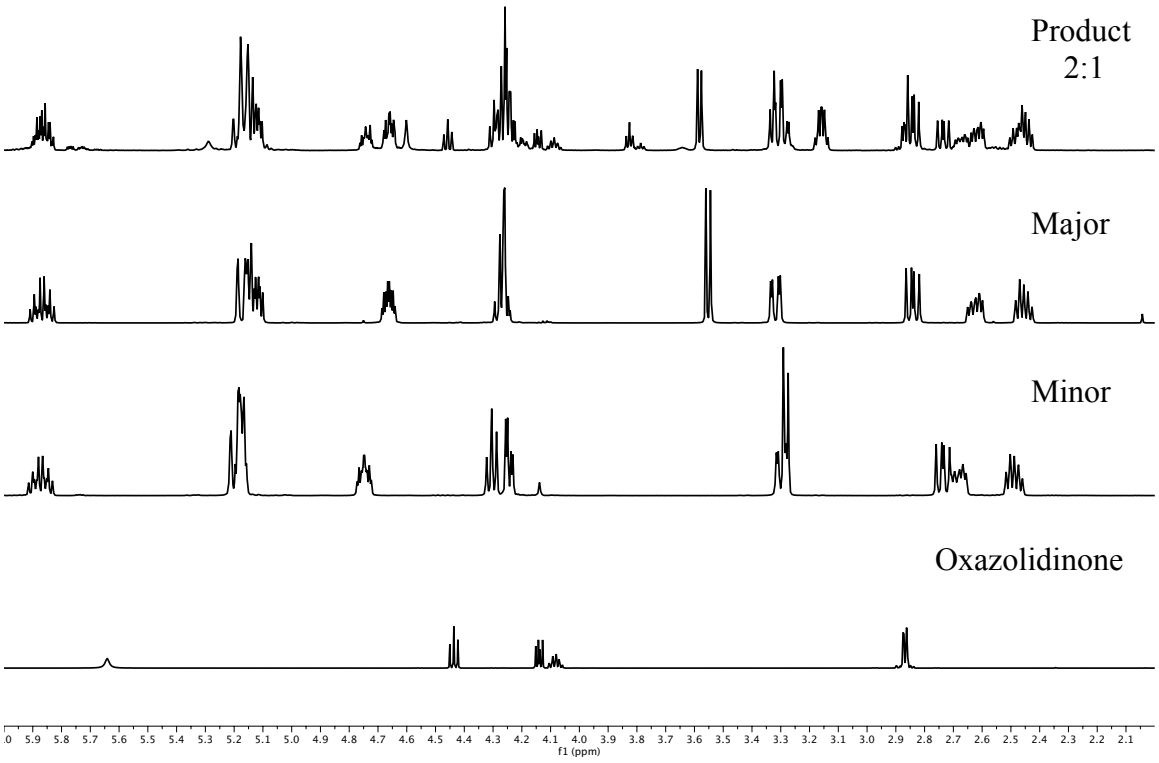


Figure S33. ^{1}H NMR spectra of **2a** and its minor isomer in $CDCl_3$.

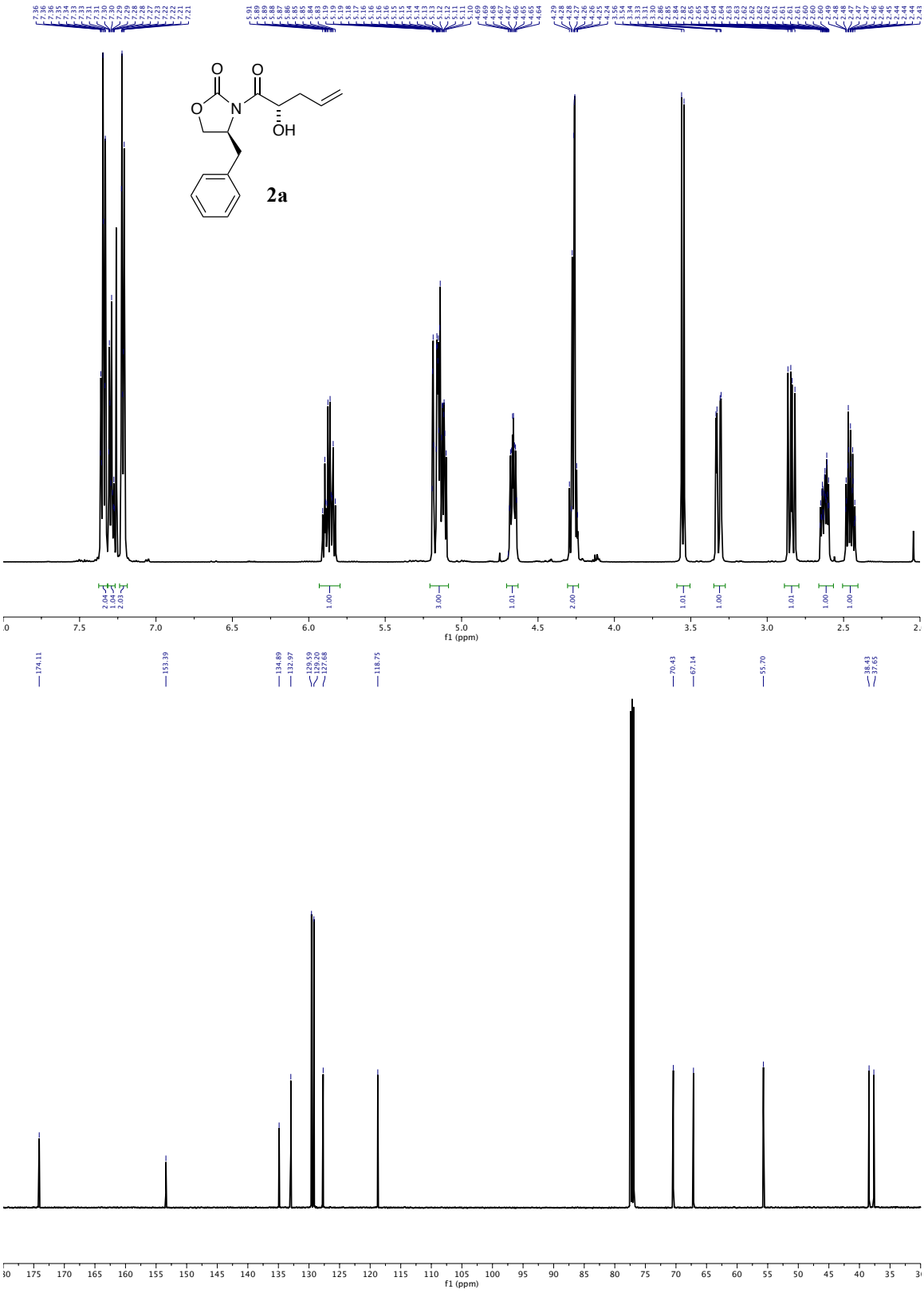


Figure S34. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a** in $CDCl_3$.

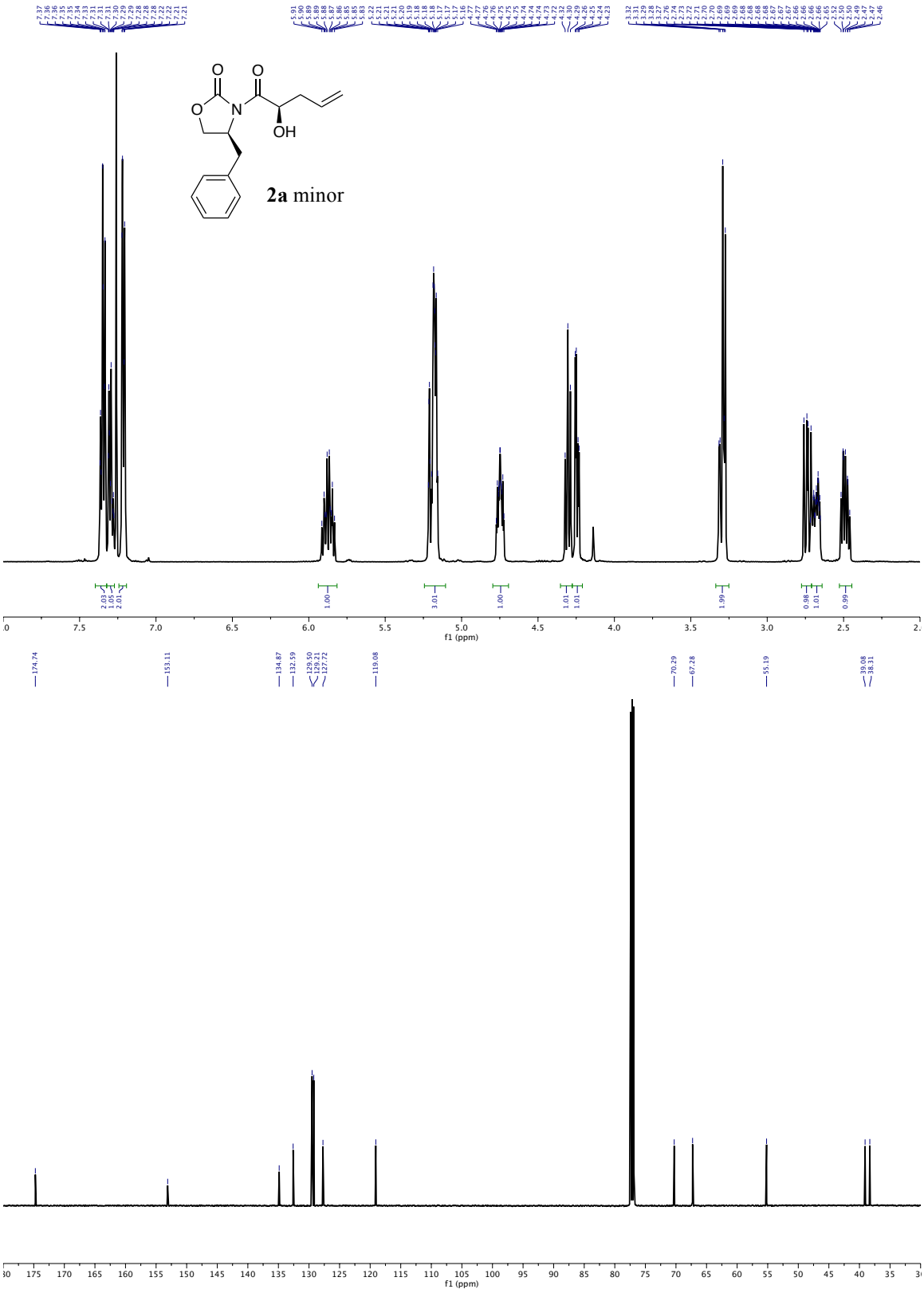


Figure S35. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a** minor isomer in $CDCl_3$.

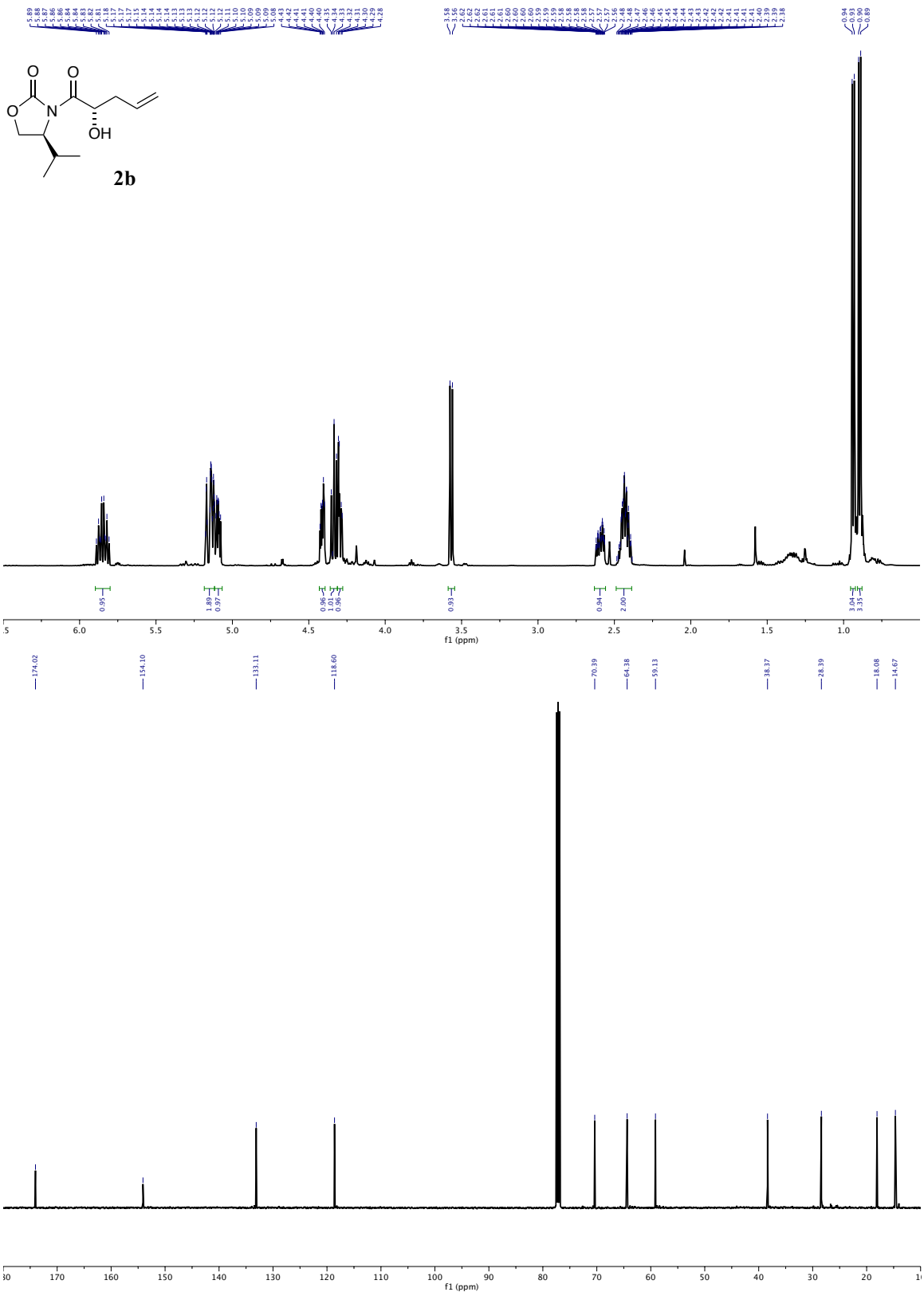


Figure S36. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2b** in $CDCl_3$.

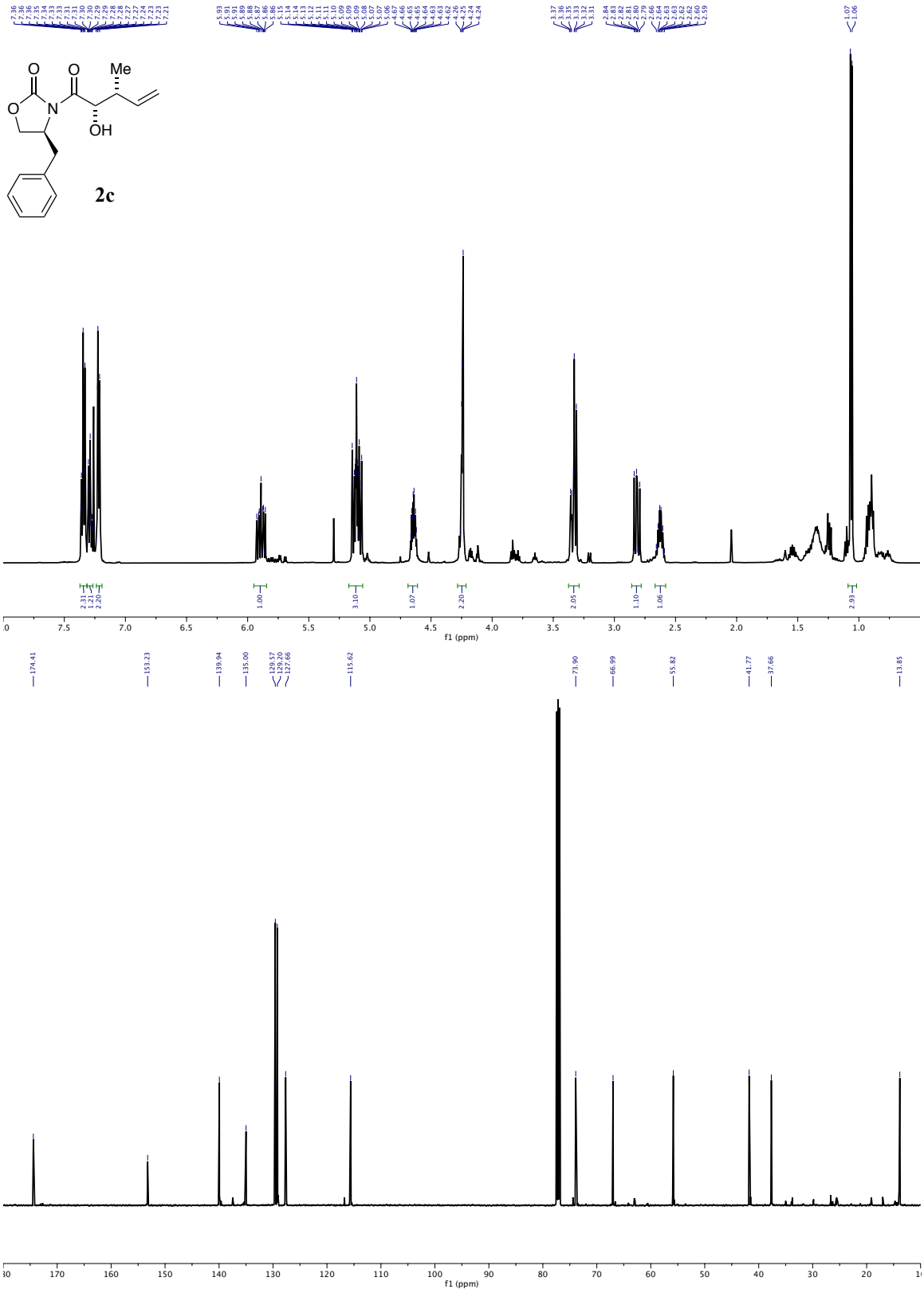


Figure S37. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2c** in $CDCl_3$.

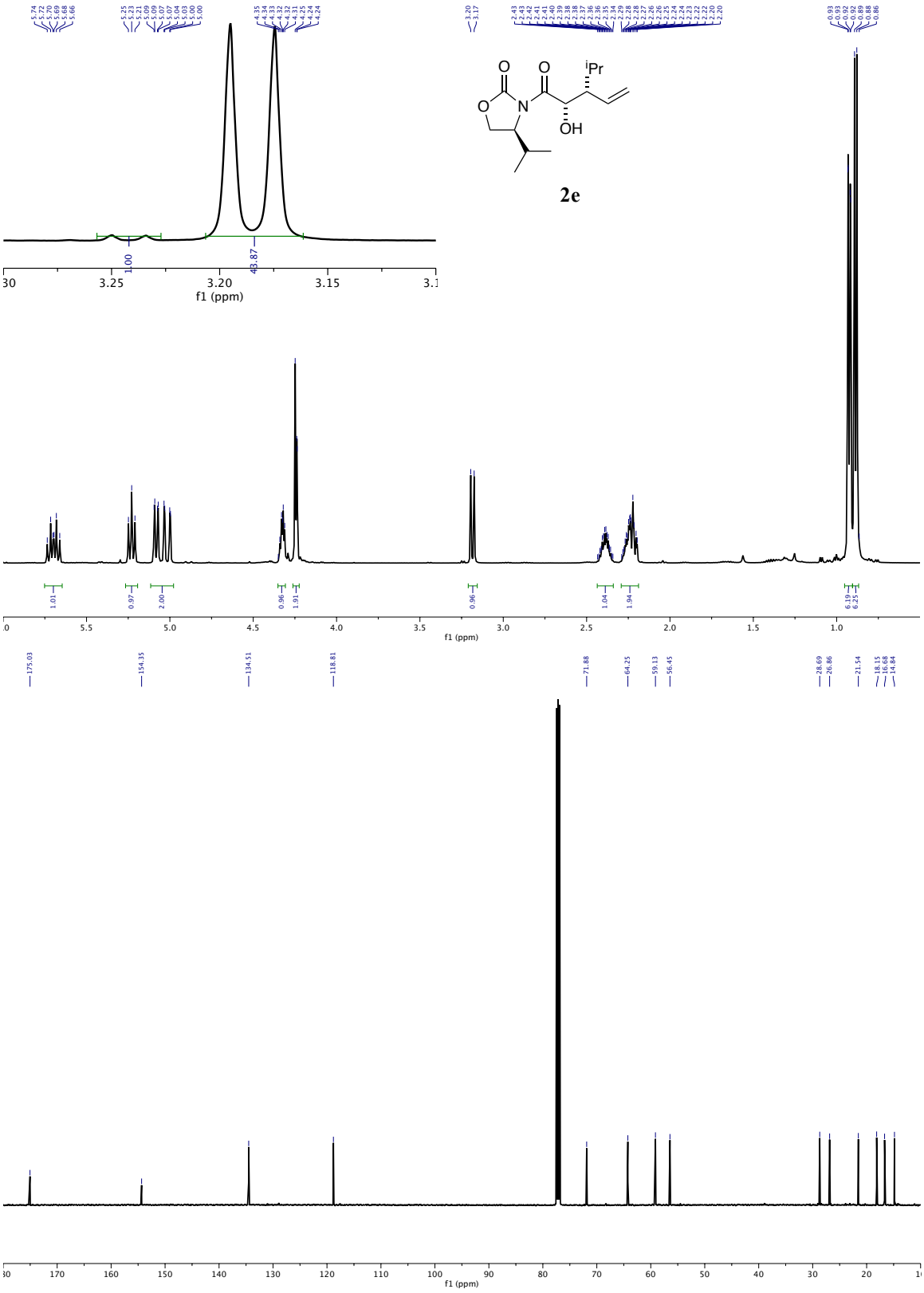
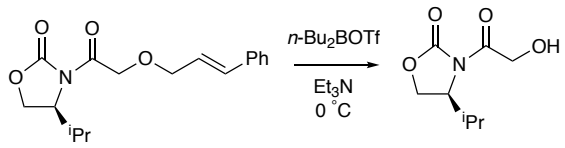


Figure S38. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2e** in $CDCl_3$.



Decomposition of 1f. Following the procedure for **1d** except using **1f** afforded a decomposition product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (dt, *J* = 5.3, 1.8 Hz, 2H), 4.46 (dt, *J* = 8.5, 3.5 Hz, 1H), 4.38 (td, *J* = 8.8, 1.3 Hz, 1H), 4.30 (ddd, *J* = 9.2, 3.1, 1.3 Hz, 1H), 3.06 (td, *J* = 5.4, 1.3 Hz, 1H), 2.43 (dqd, *J* = 8.3, 7.1, 5.0 Hz, 1H), 0.95 (dd, *J* = 7.0, 1.4 Hz, 3H), 0.90 (dd, *J* = 6.9, 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.52, 153.81, 64.73, 63.25, 58.53, 28.43, 18.01, 14.76. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_8H_{13}NO_4$ 188.09173, found 188.09181.

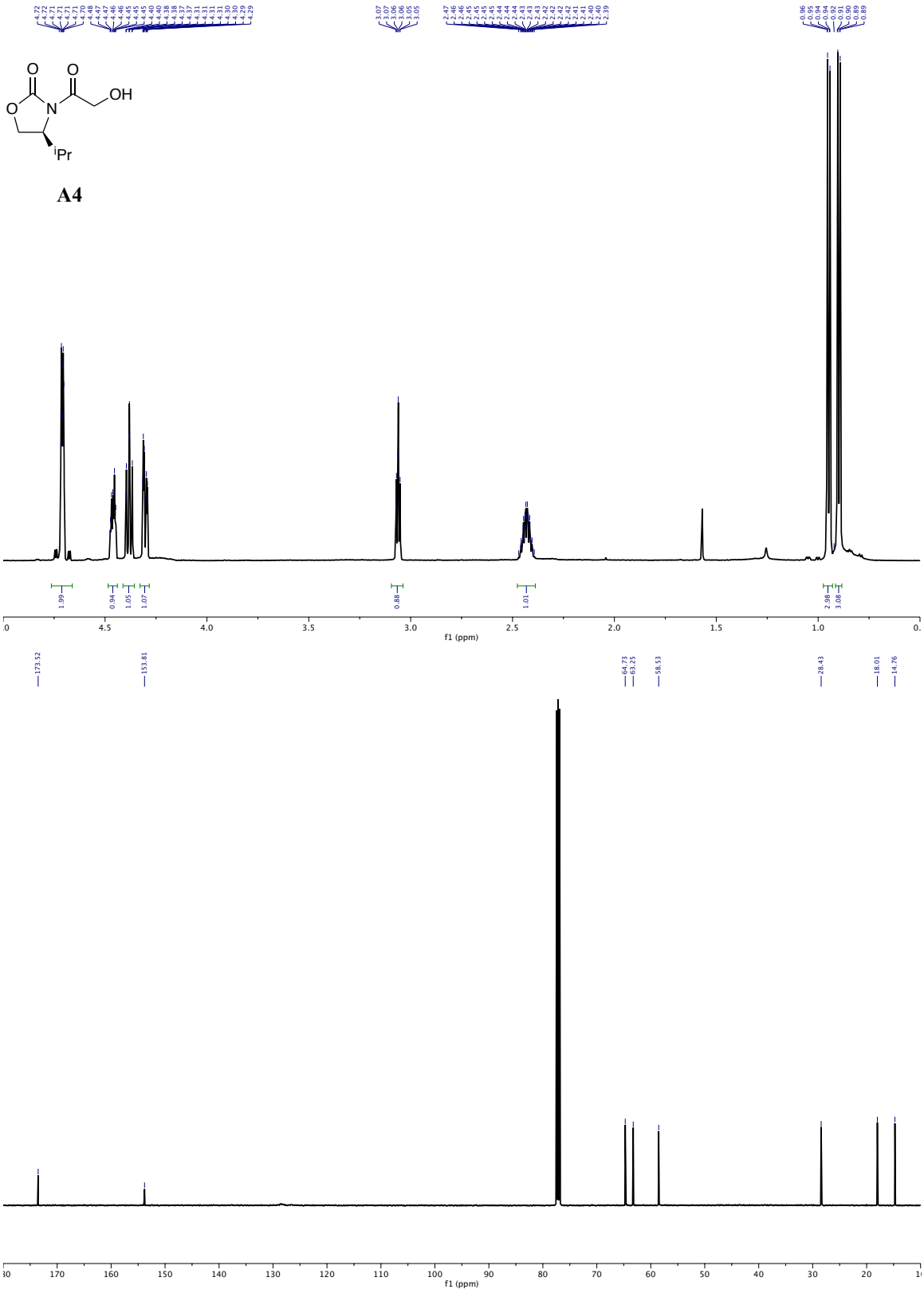


Figure S39. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1f** decomposition in $CDCl_3$.

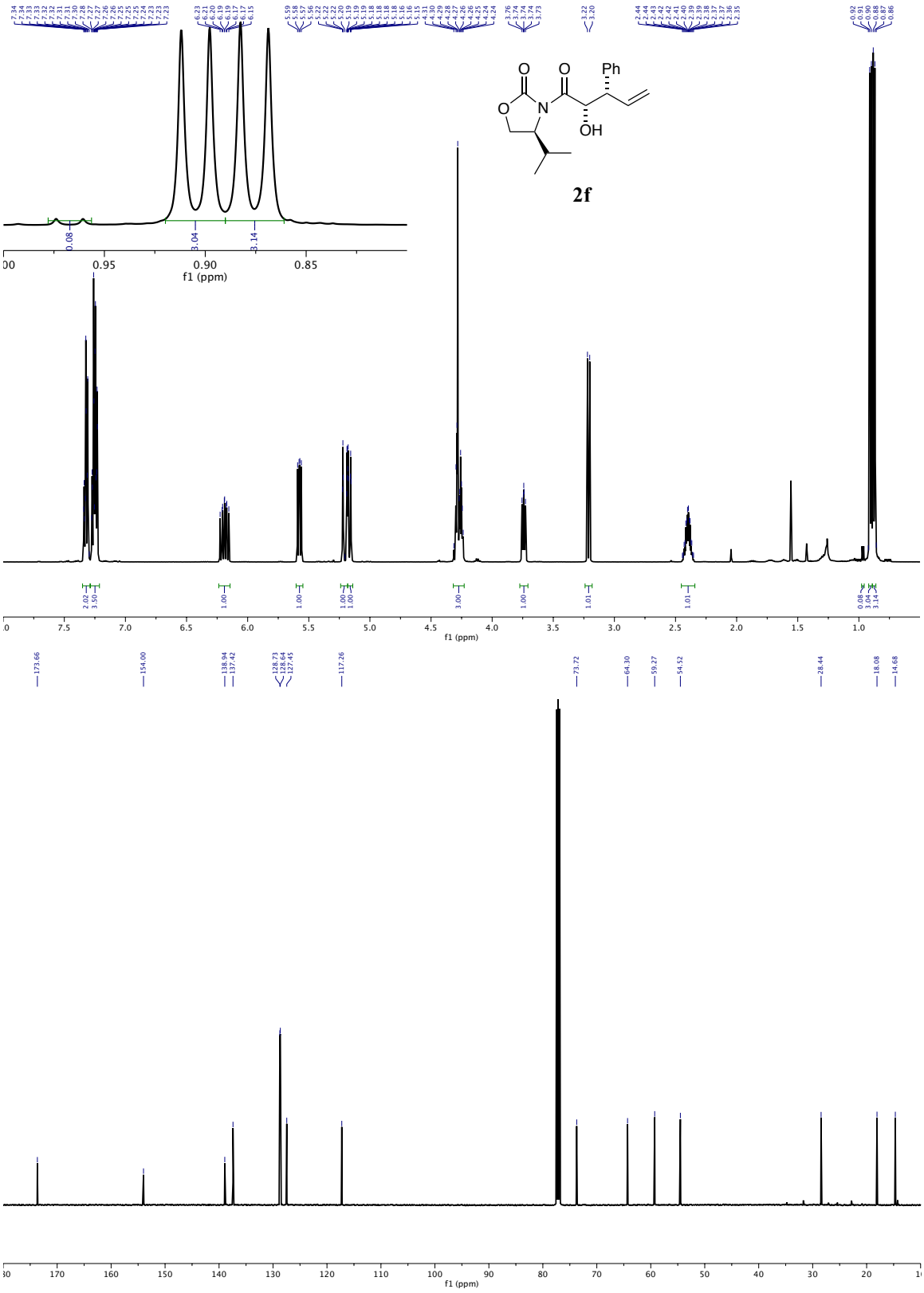


Figure S40. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2f** in $CDCl_3$.

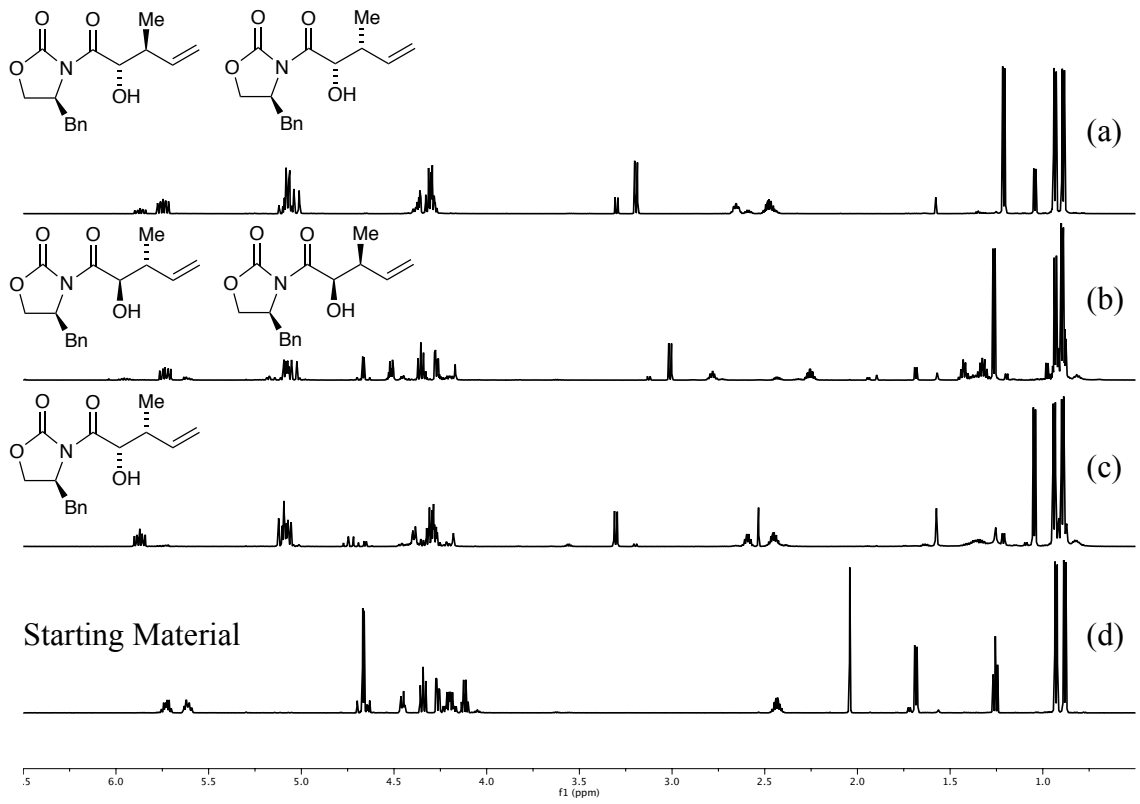


Figure S41. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) **1g** rearrangement major product; (b) **1g** minor product; (c) **2d**; (d) **1g**.

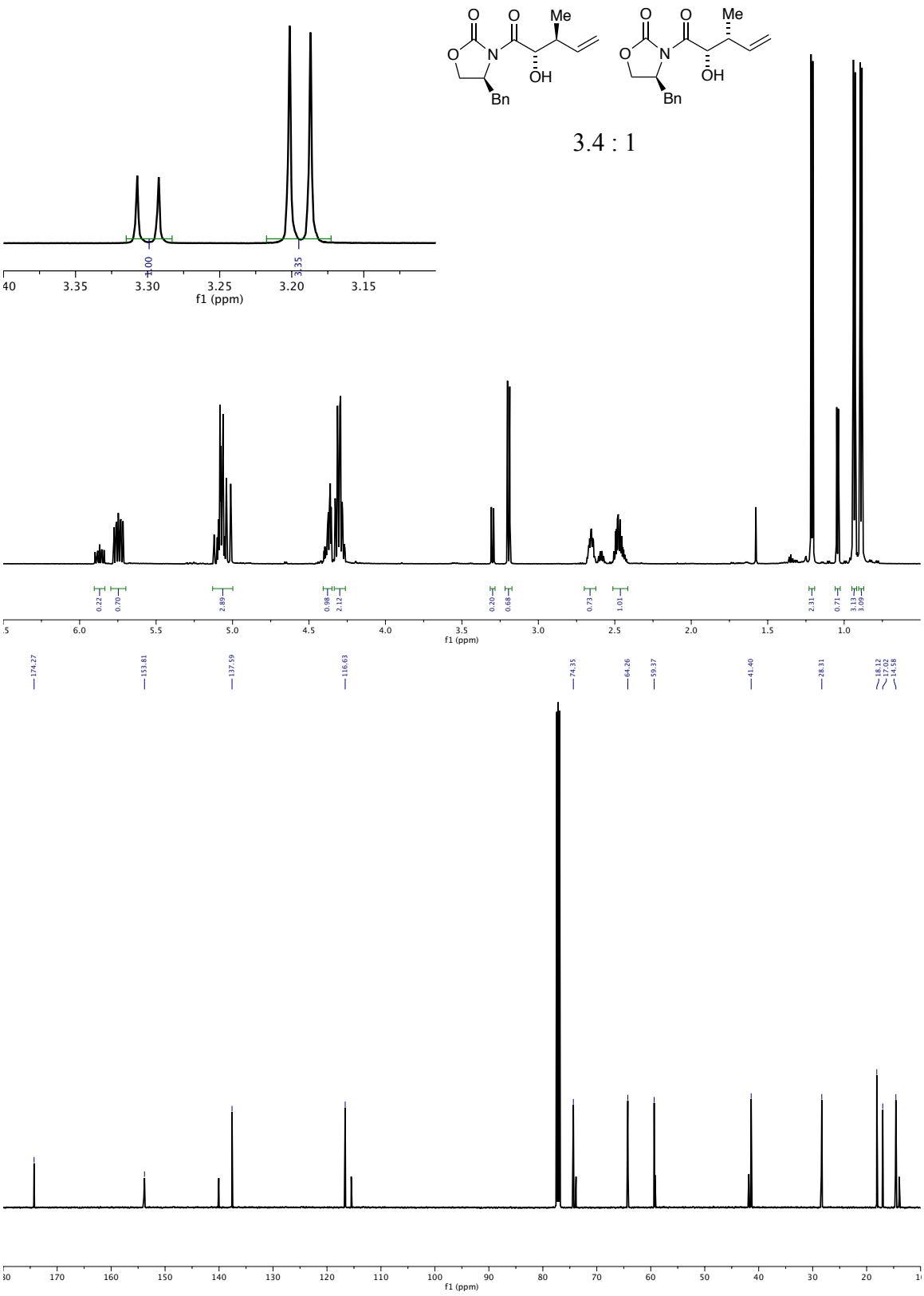


Figure S42. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1g** major product in $CDCl_3$.

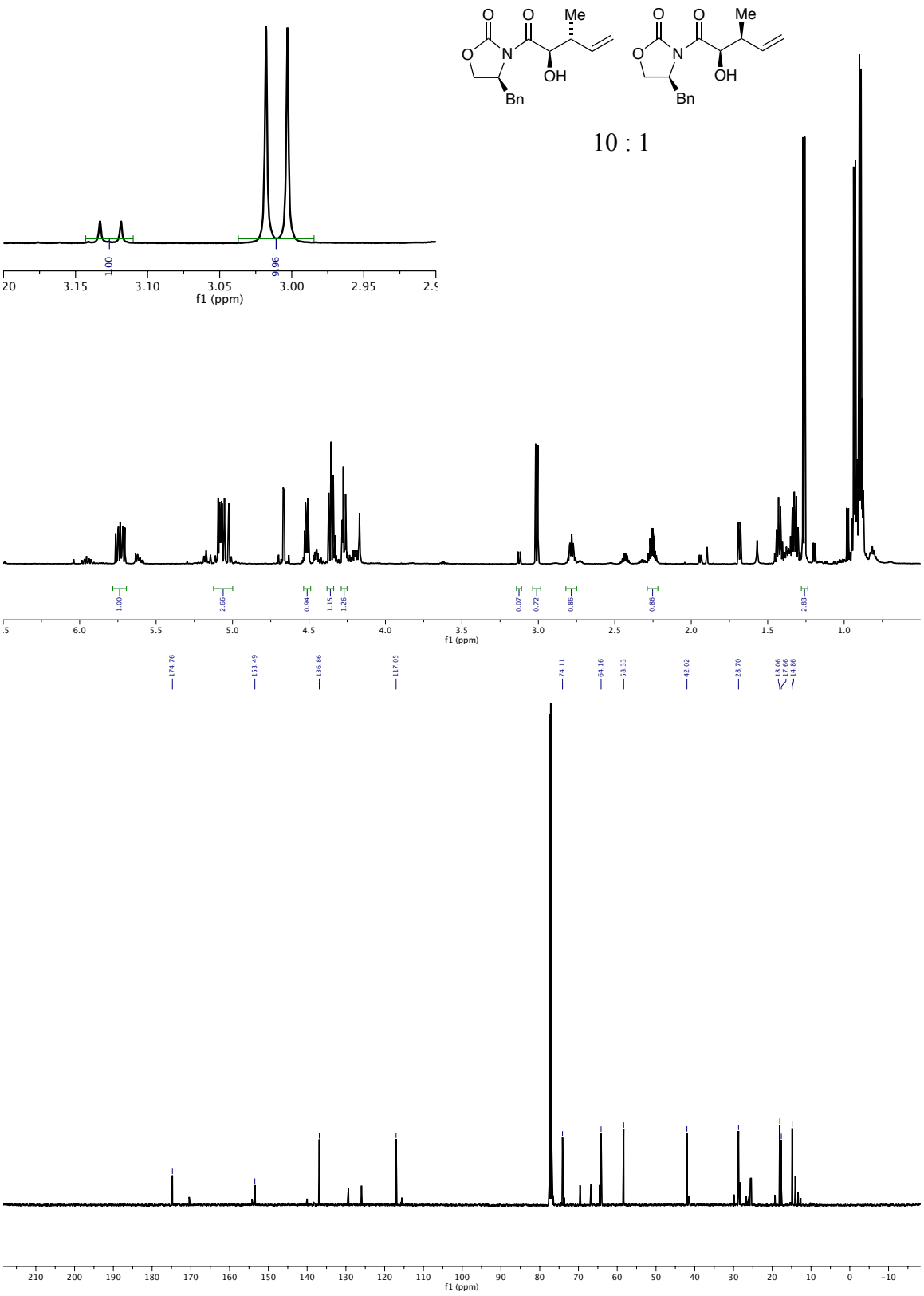
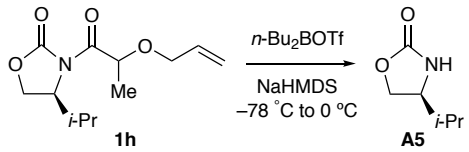


Figure S43. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1g** minor product in $CDCl_3$.



Rearrangement of 1h. Following the procedure for **1d** except using **1h** showed no reactivity even with heating to 60 ºC. Using NaHMDS in place of Et_3N afforded the deacylated product.

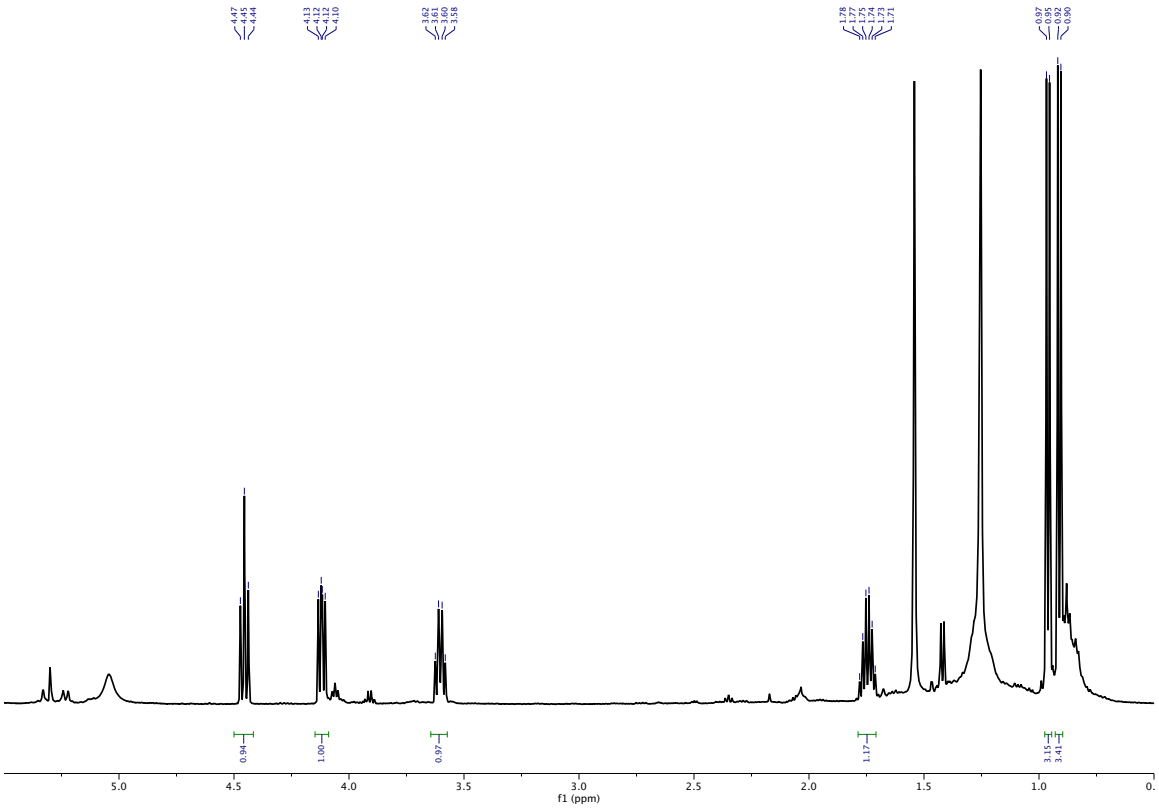
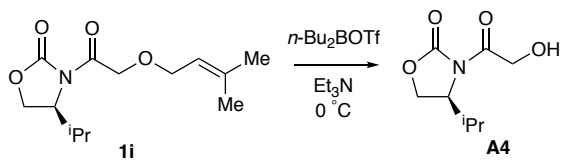


Figure S44. ^1H NMR spectrum of **1h** decomposition product in $CDCl_3$.



Decomposition of 1i. Following the procedure for **1d** except using **1i** afforded a decomposition product.

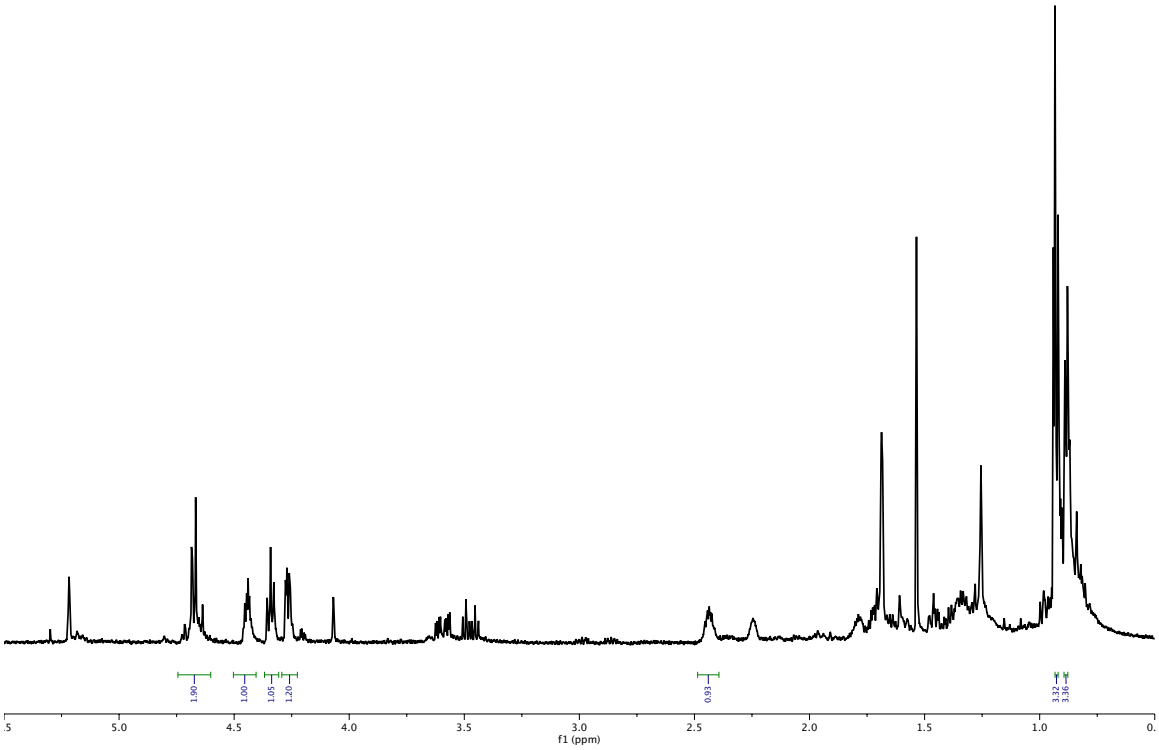
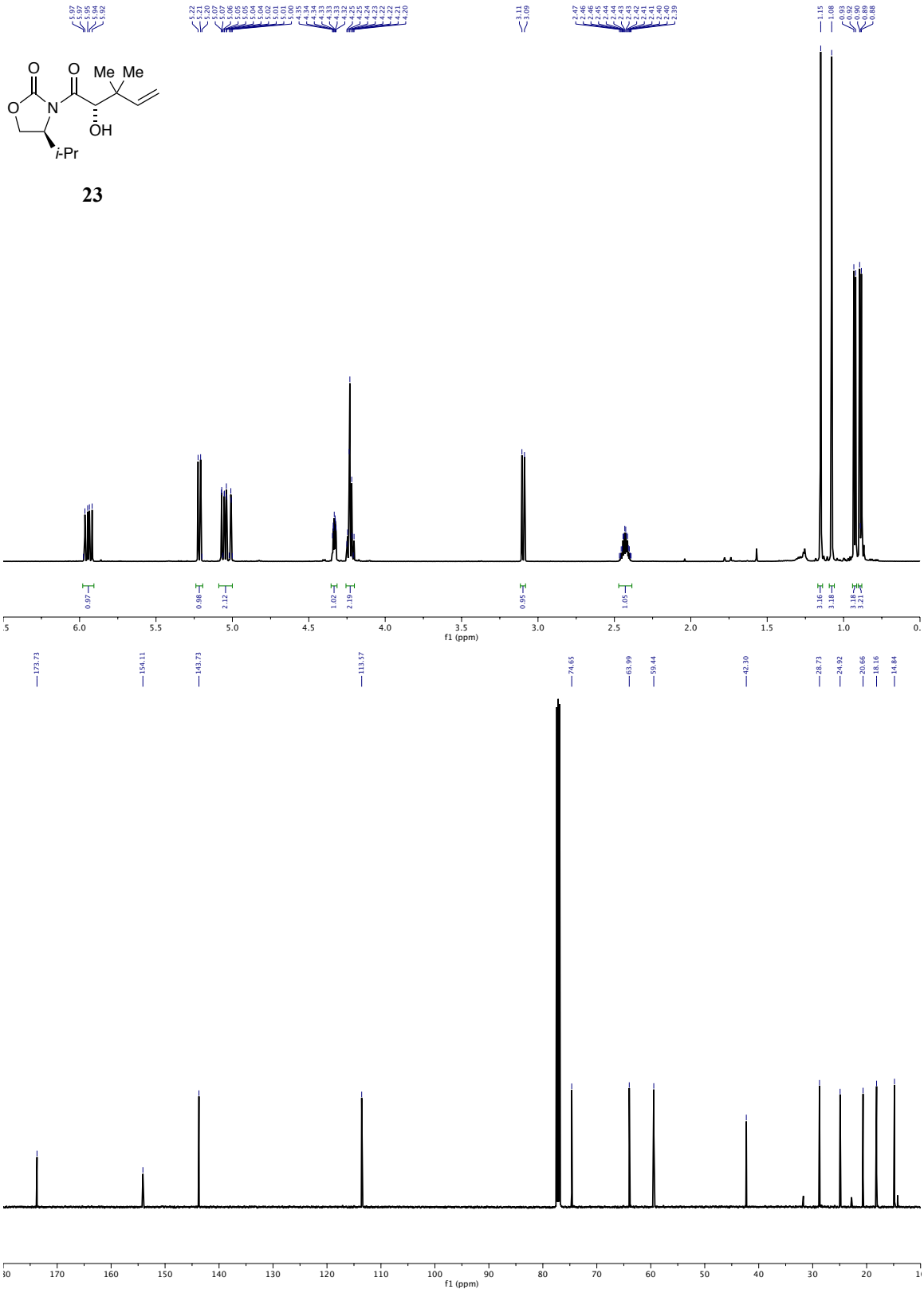


Figure S45. ^{1}H NMR spectrum of **1i** decomposition product in $CDCl_3$.



23

Figure S46. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **23** in $CDCl_3$.

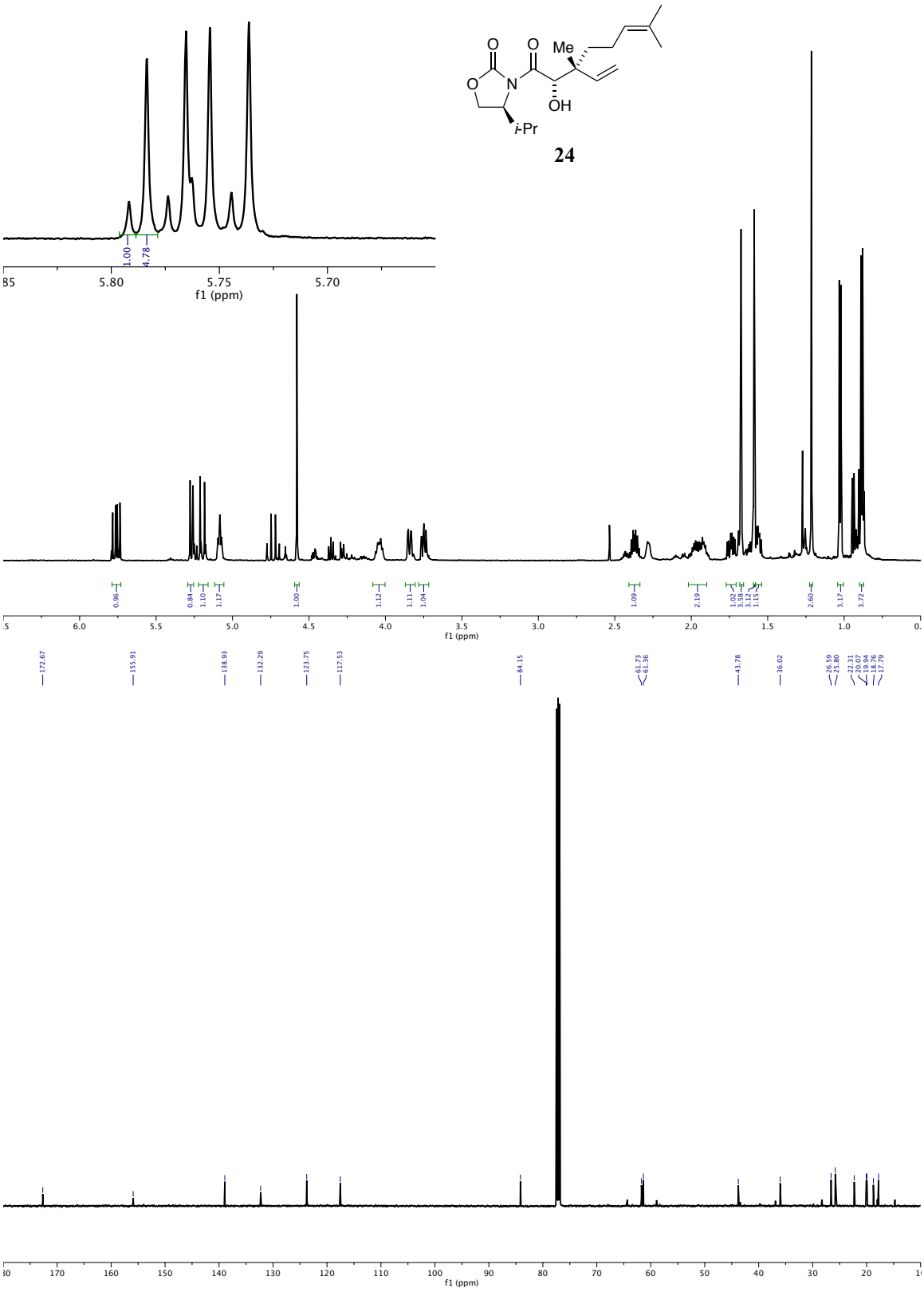


Figure S47. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **24** major in $CDCl_3$.

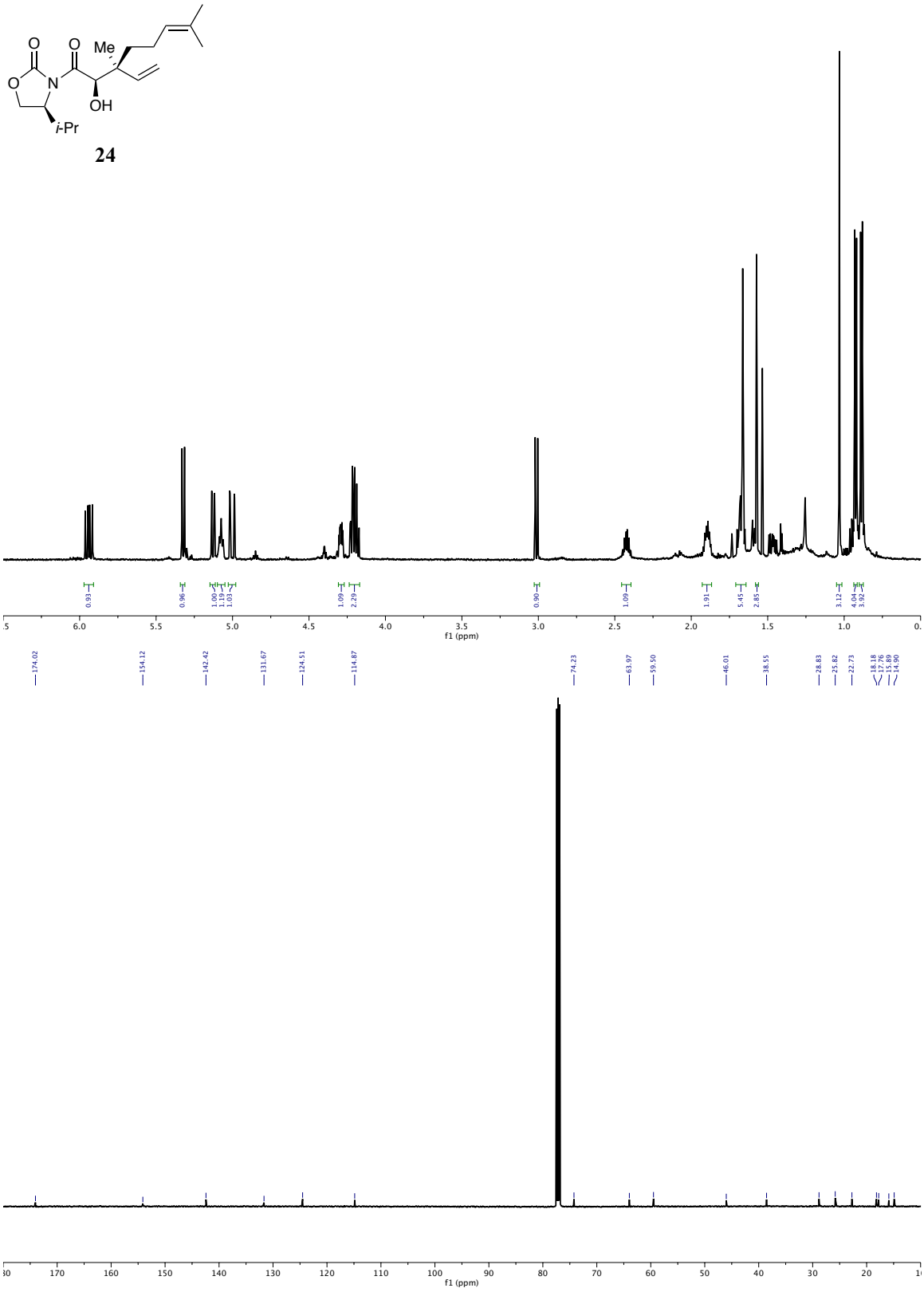
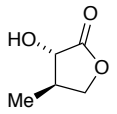


Figure S48. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **24** minor in $CDCl_3$.

6. Products characterization



6

Figure S49. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **6** in $CDCl_3$.

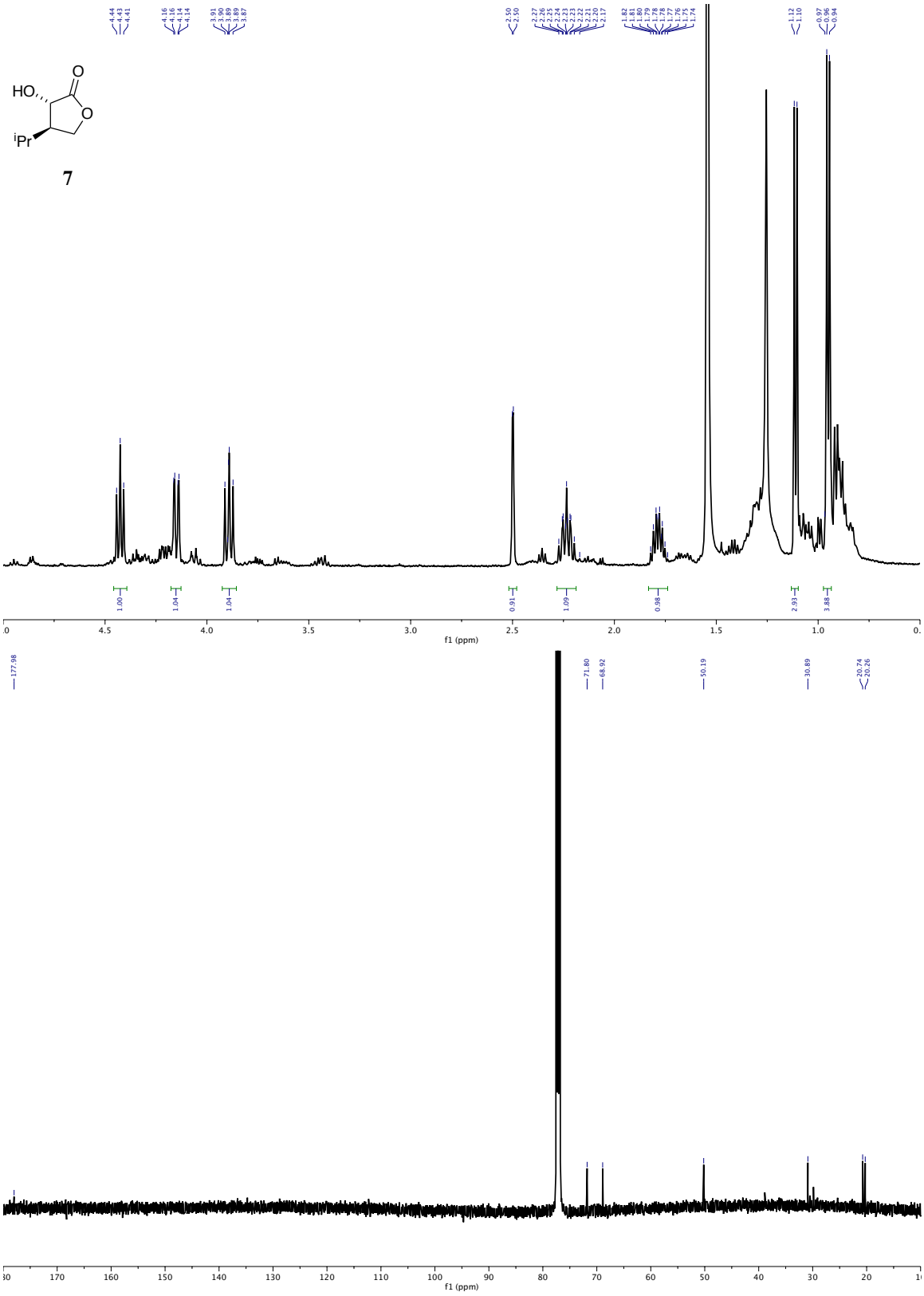


Figure S50. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **7** in $CDCl_3$.

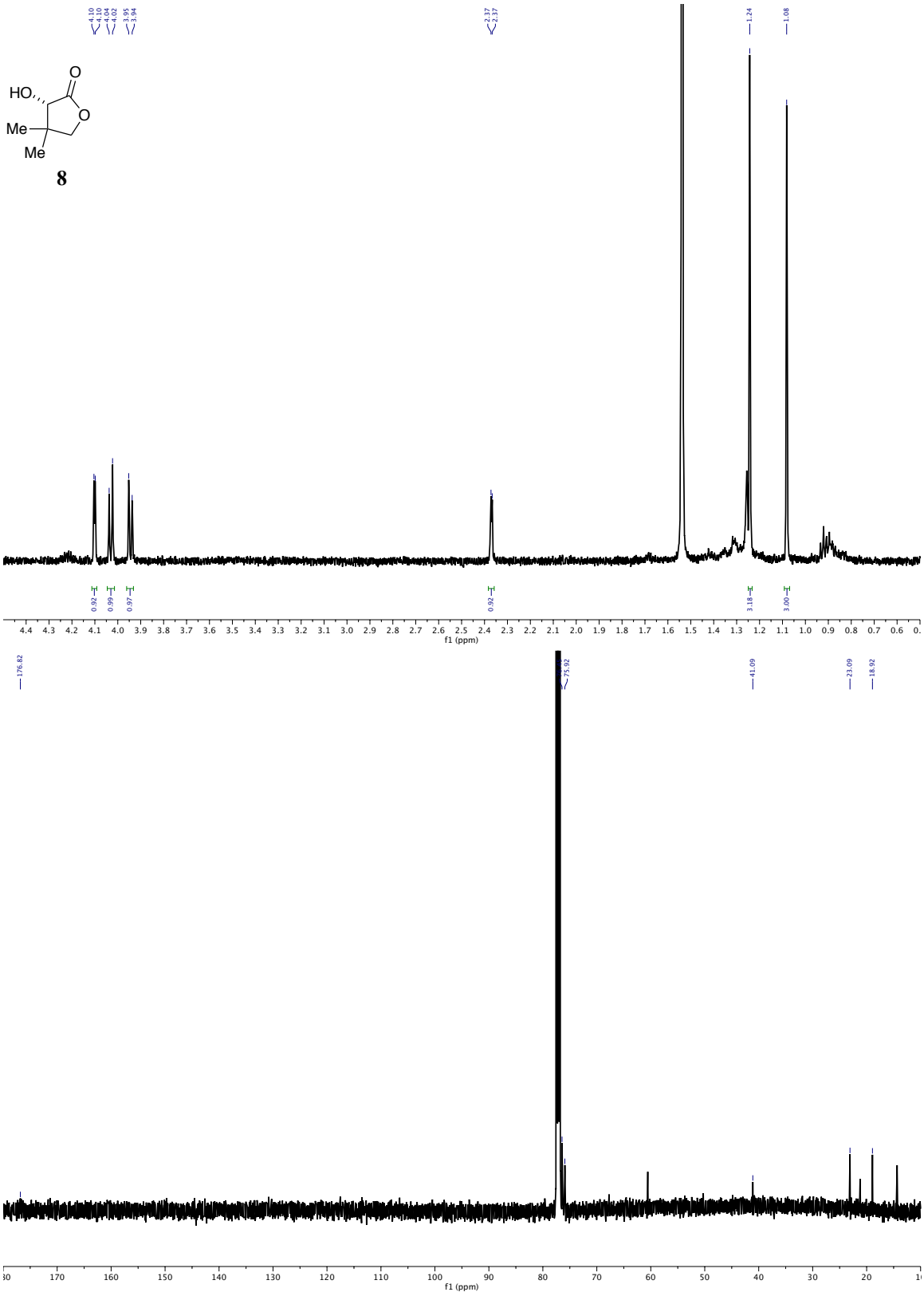


Figure S51. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **8** in $CDCl_3$.

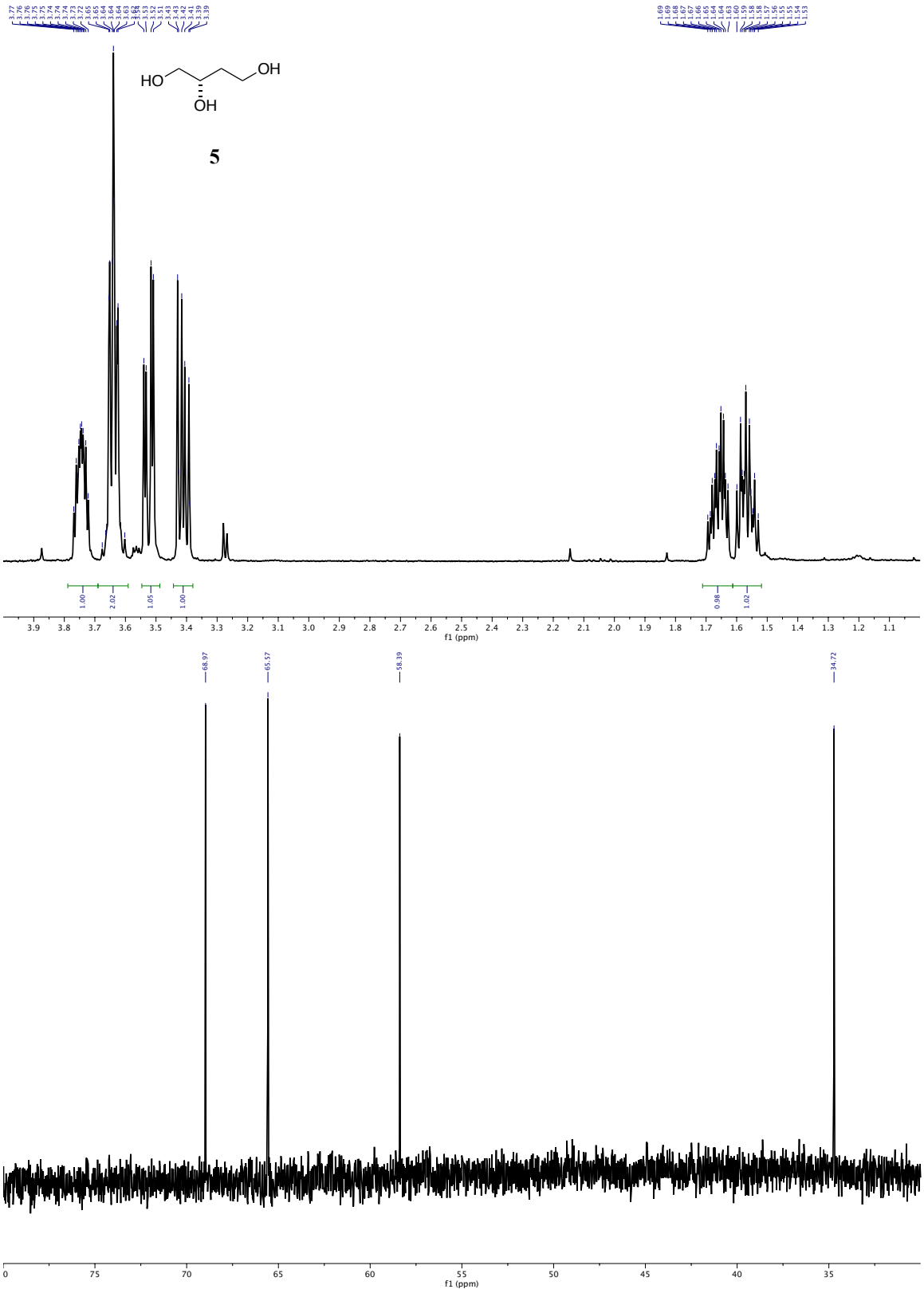


Figure S52. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **5** in D_2O.

7. Using sodium and lithium

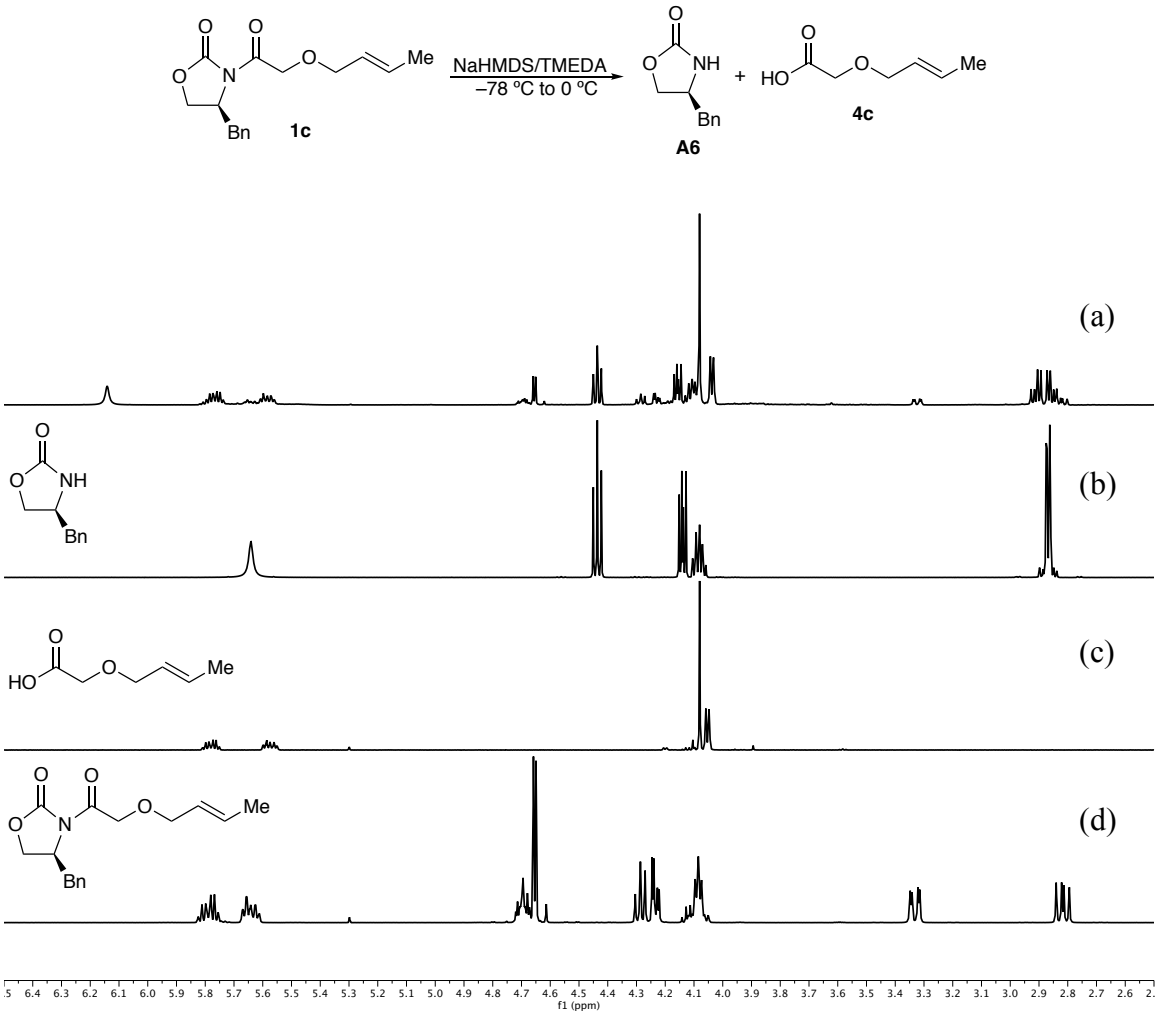


Figure S53. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) products of **1c** reacting with NaHMDS; (b) (*S*)-4-benzyl-2-oxazolidinone; (c) **4c**; (d) **1c**. Using NaHMDS resulted in deacylation prior to rearrangement.

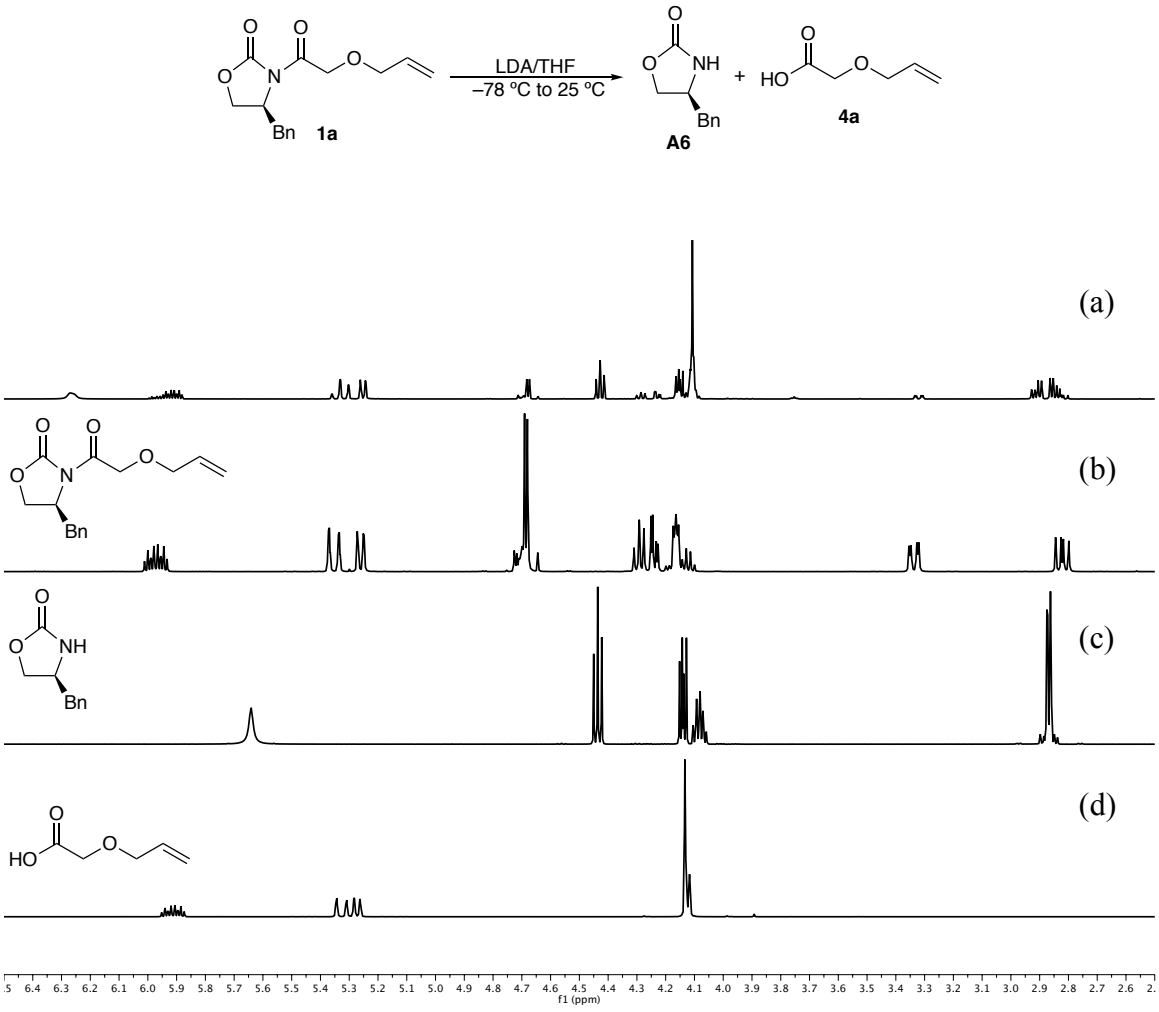
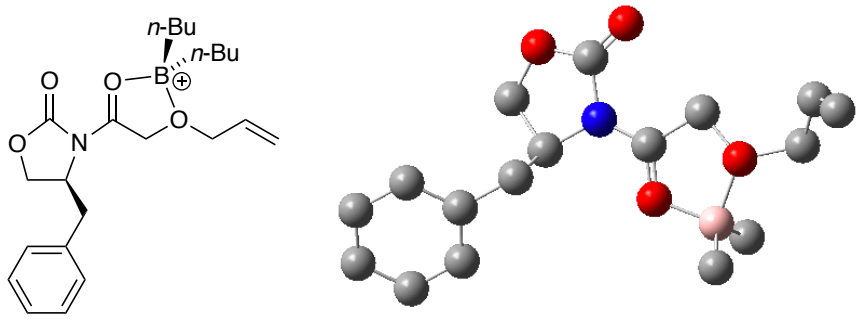


Figure S54. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) products of **1a** reacting with NaHMDS; (b) **1a**; (c) (*S*)-4-benzyl-2-oxazolidinone; (d) **4a**. Using LDA resulted in deacylation prior to rearrangement.

8. Computation

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 273 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table S3. Geometric coordinates and thermally corrected MP2 energies for boron complex **13** (5 member ring chelation).



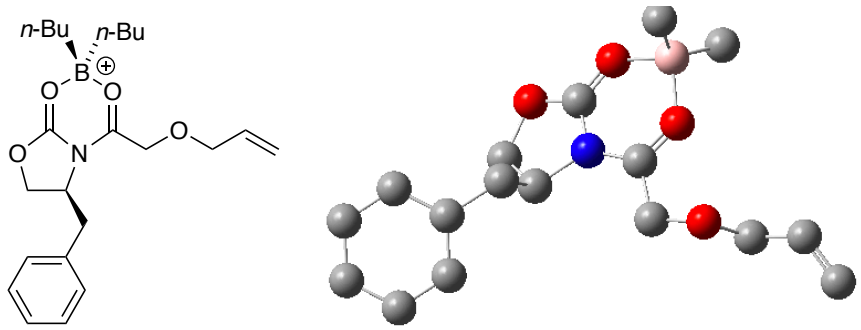
G = –1041.643803 Hartree

G_{MP2} = –651581.3129 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.96758800	0.17667100	0.46728000
H	-0.08745200	0.09270400	-1.08511500	C	0.64542400	-1.33013900	0.44145200
H	0.59396200	-2.08155100	-0.34896800	C	0.08494500	-1.90151600	1.76354100
H	0.71614500	-2.74409800	2.06743600	H	0.16436500	-1.13401600	2.54285100
C	-1.35482900	-2.34740100	1.60542600	C	-1.65754100	-3.53126500	0.91707400
C	-2.98158200	-3.93320700	0.74557800	C	-4.02164800	-3.15638600	1.26188200
C	-3.73135700	-1.98014300	1.95363200	C	-2.40486700	-1.57809000	2.12358000
H	-2.18612300	-0.67002400	2.68189900	H	-4.53437300	-1.37782900	2.36815700
H	-5.05259800	-3.47183700	1.13210700	H	-3.20150300	-4.85595900	0.21662000
H	-0.85353600	-4.15231400	0.52608500	N	2.05249000	-0.87747400	0.58735300
C	3.11697100	-1.66861900	0.66414600	O	3.00121500	-2.92336400	0.54964600
B	4.34245600	-3.73510000	0.53680100	C	4.72733000	-4.10375500	-0.95745500
H	5.71201700	-4.58227300	-1.02224200	H	4.00997300	-4.83527800	-1.35078600
H	4.72528900	-3.25299800	-1.65254800	C	4.36233300	-4.80503300	1.69931900
H	3.65875900	-5.61735900	1.47654000	H	5.34743900	-5.27800300	1.79878500
H	4.09165100	-4.39281900	2.67860700	O	5.24446800	-2.39896600	1.05171400
C	6.72366100	-2.34927800	0.86437600	H	7.02936700	-3.38016000	1.03956900
H	6.89296500	-2.08565600	-0.18485300	C	7.36844700	-1.39938400	1.81950500
H	7.30549500	-0.33753500	1.58708800	C	8.04930500	-1.81101600	2.89116300

H	8.15378700	-2.86542600	3.13709900	H	8.54110200	-1.10684800	3.55557100
C	4.52882000	-1.16859900	0.87222200	H	4.62248200	-0.53423900	1.75482200
H	4.88467800	-0.61136600	-0.00327900	C	2.12461000	0.56209300	0.68338700
O	0.90901300	1.04047400	0.45633900	O	3.12390900	1.18054300	0.92566000

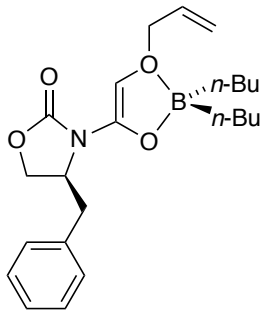
Table S4. Geometric coordinates and thermally corrected MP2 energies for boron complex **12** (6 member ring chelation).

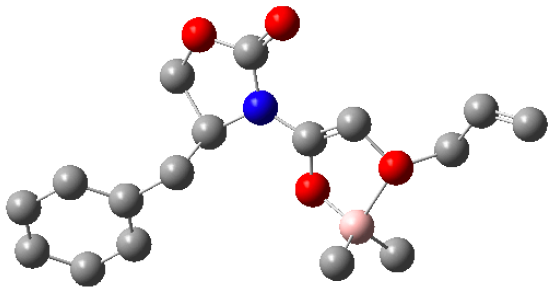


G = –1041.631708 Hartree
G_{MP2} = –651569.4126 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.01385600	-0.26887800	0.29022900
H	-0.06364400	0.13859100	-1.08090800	C	-0.57399600	1.18075300	0.81273600
H	-0.61168300	2.08581100	0.20300200	C	0.17172000	1.44054300	2.14044600
H	-0.38913800	2.18000800	2.72451800	H	0.18073800	0.51402700	2.72715600
C	1.58691700	1.92387500	1.89161700	C	1.82207600	3.23285900	1.44665500
C	3.12093100	3.67278700	1.19471600	C	4.20179900	2.80843600	1.38579700
C	3.97918200	1.50608800	1.83400100	C	2.67789800	1.06607800	2.08503500
H	2.51463200	0.05668100	2.45746800	H	4.81626400	0.83405200	1.99772600
H	5.21359600	3.15298400	1.19473400	H	3.29042000	4.69153300	0.85900600
H	0.98951900	3.92204100	1.31471000	N	-1.96111500	0.66896900	1.03345400
C	-3.10737900	1.33797800	1.38148300	O	-4.14576400	0.70243700	1.64350500
B	-4.32936100	-0.89576900	1.78812800	O	-2.96090100	-1.43652900	1.05731800
C	-1.99196100	-0.70506200	0.82733100	O	-0.86702900	-1.13945400	0.33119600
C	-4.22380200	-1.25248500	3.32526100	H	-3.31272900	-0.88095800	3.81370100
H	-5.07845300	-0.84153000	3.87571100	H	-4.24876600	-2.33991000	3.46493100
C	-5.54400500	-1.33003200	0.88099300	H	-6.48473300	-0.93184700	1.27976900
H	-5.45938500	-0.99782200	-0.16126400	H	-5.64128900	-2.42211600	0.86928300
C	-3.10637500	2.86270800	1.41522500	O	-4.29491000	3.38876500	1.87687300
C	-5.31777900	3.58398600	0.86503800	H	-4.94084500	4.28160800	0.10403800
H	-5.53103400	2.61921600	0.38259600	C	-6.53942400	4.12520300	1.53535700
H	-6.96671100	3.49971900	2.31687900	C	-7.10876400	5.28229500	1.20068600
H	-6.69680800	5.92302500	0.42393800	H	-8.01589000	5.63067700	1.68518100
H	-2.82827200	3.21721700	0.40539500	H	-2.30402700	3.17884400	2.09608000

Table S5. Geometric coordinates and thermally corrected MP2 energies for enolate **15** (5 member ring chelation).

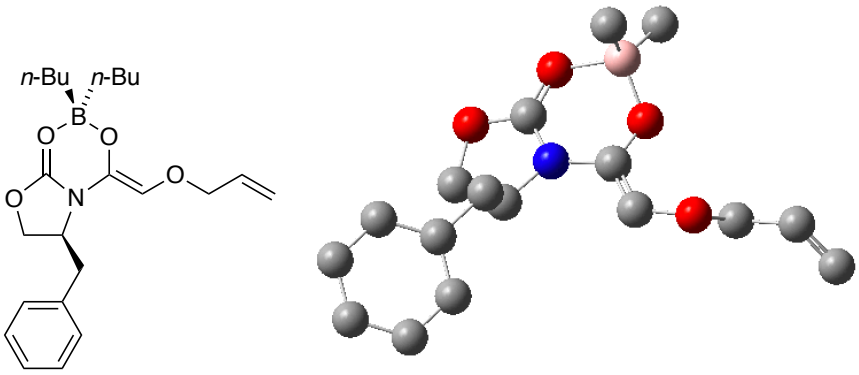




G = –1041.249187 Hartree
G_{MP2} = –651337.4921 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.01422700	0.14153800	0.37614500
H	0.01076000	0.15153700	-1.08498600	C	0.61152500	-1.35589600	0.39922300
H	0.58082000	-2.06584500	-0.42968800	C	-0.03226900	-1.99403200	1.65247100
H	0.61764000	-2.81329900	1.97746900	H	-0.04686000	-1.24883700	2.45723500
C	-1.42945700	-2.51017100	1.38324900	C	-1.61867400	-3.68522100	0.63990700
C	-2.90122000	-4.15383200	0.35735400	C	-4.02060300	-3.45524400	0.81643000
C	-3.84680600	-2.28871200	1.56131800	C	-2.56057600	-1.82143500	1.84071700
H	-2.43311000	-0.91730200	2.43248500	H	-4.71099500	-1.74239200	1.92996300
H	-5.02024700	-3.82176000	0.59934500	H	-3.02740200	-5.06822300	-0.21644800
H	-0.75119600	-4.24057000	0.28914700	N	1.99268400	-0.92523800	0.63789800
C	3.06064700	-1.80824200	0.79610400	C	4.29341300	-1.53681900	1.26129700
H	4.69857600	-0.62536600	1.66189700	O	5.09554300	-2.71063200	1.25393800
C	6.29645000	-2.62021200	0.41757500	H	6.66930700	-3.64291200	0.34861700
H	5.98579300	-2.27674200	-0.57619600	C	7.32309100	-1.71222900	1.02277200
H	7.06729900	-0.65586600	1.08642800	C	8.51680000	-2.13491300	1.43925500
H	8.80513900	-3.18252700	1.38200600	H	9.25478200	-1.45021700	1.84781000
B	3.82491500	-4.01291900	0.92018400	O	2.80549400	-3.06635900	0.41090500
C	4.37306600	-4.99770300	-0.20455600	H	5.22393800	-5.60620200	0.12640800
H	3.57031100	-5.70632300	-0.45437500	H	4.64677600	-4.49754900	-1.14191200
C	3.55324900	-4.55869800	2.39258200	H	2.73733700	-5.29580700	2.37145200
H	4.42918400	-5.06908000	2.81195500	H	3.26056000	-3.77059400	3.09763500
C	2.07462000	0.44091500	0.86189300	O	0.85251600	0.99028900	0.60843100
O	3.03669400	1.07415100	1.22546000				

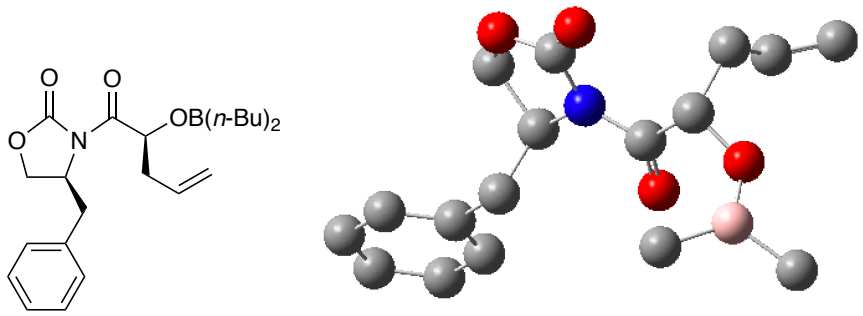
Table S6. Geometric coordinates and thermally corrected MP2 energies for enolate **14** (6 member ring chelation).



G = –1041.252377 Hartree
G_{MP2} = –651335.8477 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.01796900	-0.26678000	0.28286400
H	-0.05694100	0.15631700	-1.08116400	C	-0.56958200	1.18900500	0.80032400
H	-0.58493500	2.09721700	0.19138100	C	0.15791800	1.45437200	2.13969500
H	-0.45121700	2.15287100	2.72302000	H	0.19195900	0.51547300	2.70533300
C	1.55528200	2.00064000	1.93889100	C	1.74984000	3.33357000	1.54670700
C	3.03289800	3.83599300	1.33275700	C	4.14698600	3.01207200	1.50945200
C	3.96834100	1.68616300	1.90447700	C	2.68173200	1.18623400	2.11651800
H	2.55191200	0.15553800	2.44013100	H	4.82916200	1.04010300	2.05403800
H	5.14711100	3.40398300	1.34663200	H	3.16346200	4.87282300	1.03485800
H	0.88979100	3.98848600	1.42071500	N	-1.94341400	0.70942600	1.00049200
C	-3.09585900	1.46651200	1.39360400	C	-3.01240900	2.80145600	1.56072700
H	-2.07280700	3.33237300	1.43644900	O	-4.06330200	3.59480600	1.94105000
C	-5.19266900	3.63268500	1.04362800	H	-4.87710700	4.01290600	0.06138000
H	-5.57968000	2.61528500	0.91163800	C	-6.23358700	4.51949700	1.65441700
H	-6.51064500	4.27193500	2.67855700	C	-6.83078400	5.52684400	1.01894500
H	-6.56653400	5.79700700	-0.00169100	H	-7.61345000	6.11638100	1.48869300
O	-4.21539600	0.75290700	1.44239900	B	-4.23560200	-0.65830600	1.93617100
O	-2.97786200	-1.36731500	1.06474000	C	-2.01032000	-0.62319900	0.81649100
O	-0.86385200	-1.11902400	0.33398100	C	-3.79726900	-0.81426100	3.47346300
H	-2.84818100	-0.31658800	3.72299500	H	-4.56130700	-0.37015000	4.12557600
H	-3.69869300	-1.86721300	3.76655200	C	-5.55992300	-1.39208300	1.43602000
H	-6.44156300	-0.98621000	1.95012000	H	-5.72672300	-1.26697400	0.35830000
H	-5.53370400	-2.46857600	1.64699400				

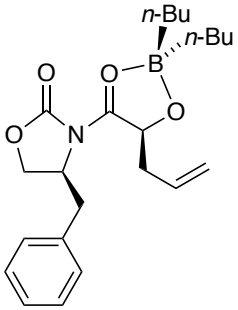
Table S7. Geometric coordinates and thermally corrected MP2 energies for rearrangement product **17** (no chelation).

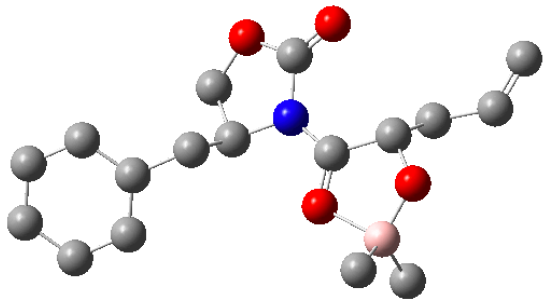


G = –1041.307135 Hartree
G_{MP2} = –651375.0352 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.02873900	0.02587400	-0.36052800
H	-0.09401800	0.63400200	0.88800600	C	-0.52814700	-1.42193700	0.23514100
H	-0.51373600	-1.69522300	1.29178500	C	0.20238700	-2.50478600	-0.59216400
H	-0.39301400	-3.42041400	-0.53282600	H	0.22407600	-2.19053200	-1.64300800
C	1.60697000	-2.75988400	-0.08857300	C	1.81008600	-3.47563200	1.10116200
C	3.09694700	-3.69541400	1.59099700	C	4.20552900	-3.20364500	0.89725200
C	4.01748500	-2.49473900	-0.28927100	C	2.72695300	-2.27506200	-0.77640000
H	2.58903900	-1.73343400	-1.71001400	H	4.87387500	-2.11543100	-0.84044400
H	5.20863200	-3.37775000	1.27686900	H	3.23527200	-4.25630600	2.51151700
H	0.95125000	-3.87162000	1.63928000	N	-1.92425100	-1.23930900	-0.19872500
C	-2.89986000	-2.19156200	0.13326200	C	-4.35287300	-1.93356500	-0.30024700
H	-4.35296900	-1.61576100	-1.34617600	C	-5.00778100	-0.81236000	0.54234900
H	-4.47007200	0.12114300	0.33686000	H	-6.02543300	-0.68208600	0.15822700
C	-5.04967100	-1.09111300	2.02057600	H	-4.09178700	-1.27383200	2.50944000
C	-6.16245400	-1.11462700	2.75291100	H	-7.14193900	-0.94879300	2.30905500
H	-6.13911200	-1.30284400	3.82286600	O	-5.11402400	-3.10969700	-0.11883400
B	-4.95608900	-4.26536300	-0.83712400	C	-5.90003900	-5.46054300	-0.41475300
H	-6.61472200	-5.68762300	-1.21951000	H	-5.32419500	-6.38341100	-0.26052500
H	-6.46973500	-5.25068700	0.49606200	C	-3.91714000	-4.41913600	-2.02630800
H	-4.30609000	-5.07611100	-2.81340000	H	-3.59760800	-3.48229400	-2.49886800
H	-3.01071900	-4.90810900	-1.64002300	O	-2.56964700	-3.16888100	0.78096700
C	-2.03241300	-0.13076000	-1.05631100	O	-0.85371200	0.53822800	-1.03394500
O	-2.97711000	0.20778200	-1.72478600				

Table S8. Geometric coordinates and thermally corrected MP2 energies for rearrangement product **16** (chelated).

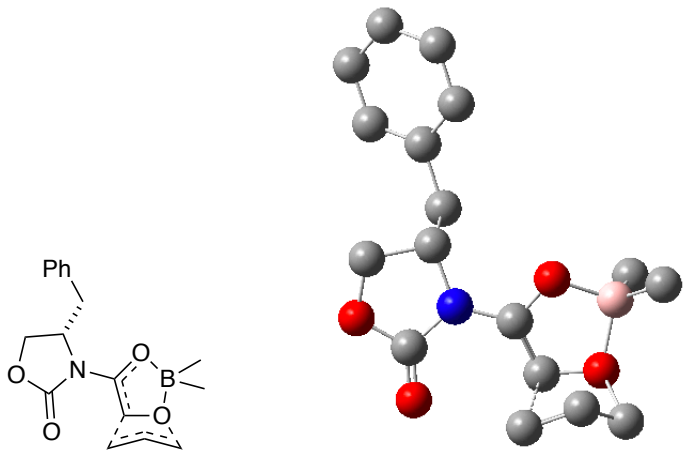




G = –1041.296955 Hartree
G_{MP2} = –651370.1006 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.01034800	0.29279500	0.28541500
H	0.14731600	0.17908000	-1.06966000	C	0.35434200	-1.43808300	0.41025100
H	0.29894400	-2.12683900	-0.43473100	C	-0.48274300	-1.98294700	1.58947000
H	-0.00330700	-2.90027000	1.94487600	H	-0.45143400	-1.25577900	2.40999700
C	-1.91498300	-2.26255100	1.18487900	C	-2.22108800	-3.38970700	0.40754500
C	-3.53178500	-3.64363700	0.00539700	C	-4.56042200	-2.77410500	0.37625800
C	-4.26986500	-1.65335400	1.15427700	C	-2.95573500	-1.40062700	1.55436200
H	-2.73986500	-0.53291900	2.17453400	H	-5.06486200	-0.97679100	1.45598100
H	-5.58231700	-2.97381800	0.06605200	H	-3.75140700	-4.52446900	-0.59179800
H	-1.42762200	-4.07950500	0.12713300	N	1.77020900	-1.23925700	0.78052400
C	2.64262500	-2.27265400	0.93157300	C	4.12547800	-2.16040800	1.28424700
H	4.24631600	-1.52415700	2.17052300	O	4.49350000	-3.47132700	1.56613300
B	3.61264600	-4.50872100	1.01770200	O	2.23313900	-3.43672400	0.74457700
C	3.12404600	-5.56588100	2.11529300	H	2.32972200	-6.22847300	1.74729800
H	3.96513300	-6.21279700	2.40264600	H	2.76879600	-5.08528800	3.03657400
C	3.95389900	-5.06625000	-0.45093200	H	4.85377200	-5.69555200	-0.40007500
H	3.15149700	-5.69984300	-0.85190000	H	4.16021400	-4.28656500	-1.19740400
C	4.94581500	-1.52039400	0.12441600	H	4.60879800	-0.49299100	-0.04501400
H	4.75788600	-2.10294800	-0.78715100	C	6.41495800	-1.53721100	0.44540400
H	6.83476700	-2.51909300	0.65508900	C	7.18859300	-0.45259300	0.49600500
H	6.79564800	0.54372100	0.30252400	H	8.24722800	-0.51903900	0.73295500
C	2.02340900	0.12435600	1.08388400	O	0.93101800	0.83253700	0.72947200
O	3.01256000	0.58993900	1.57987200				

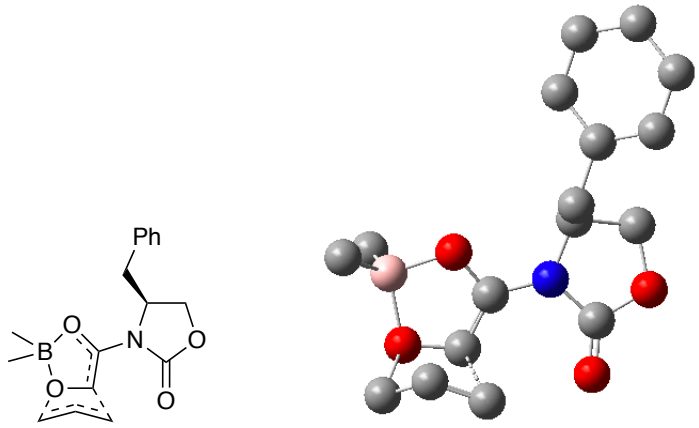
Table S9. Geometric coordinates and thermally corrected MP2 energies for transition structure **18**$_A$.



G = –1041.231479 Hartree
G_{MP2} = –651325.2492 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.03561400	0.16126400	0.30201500
H	0.10540400	0.21886900	-1.06792100	C	0.52449600	-1.40432800	0.35928900
H	0.57376700	-2.04799500	-0.52137900	N	1.88191200	-1.04918800	0.78931300
C	2.89768900	-1.97320900	0.95660400	C	4.10591700	-1.81955400	1.60147500
H	4.47701500	-0.96214500	2.13727900	O	4.82468800	-2.96179200	1.53749400
B	3.75472400	-4.10882700	1.10969300	O	2.68115200	-3.18224400	0.48908500
C	4.31967900	-5.15090400	0.03444500	H	4.62023700	-4.70458400	-0.92127900
H	5.17493600	-5.71702100	0.42759100	H	3.54358000	-5.89346200	-0.19563200
C	3.21394400	-4.74307400	2.48905900	H	4.00702700	-5.29442000	3.01102800
H	2.82794400	-3.99140000	3.19066300	H	2.40448800	-5.45978800	2.29365300
C	6.36106100	-2.71651100	0.30410200	C	5.77136500	-2.02152200	-0.77311100
H	5.42893300	-2.59513800	-1.63129800	C	5.36810300	-0.72697300	-0.62988000
H	4.77216100	-0.22748300	-1.38830100	H	5.71305700	-0.10623500	0.19009700
H	6.89537600	-2.15896500	1.06656700	H	6.65122800	-3.75500400	0.20152700
C	2.00066000	0.30771000	1.07660200	O	0.83461900	0.91856300	0.73560600
O	2.95355100	0.87780400	1.54916300	C	-0.27335100	-2.11561700	1.47612200
H	-0.34953800	-1.44108300	2.33767600	H	0.30852700	-2.98764400	1.79274600
C	-1.65035500	-2.54222500	1.01458800	C	-2.79886200	-1.84723900	1.41550600
C	-4.06325500	-2.23020900	0.96237500	C	-4.19645500	-3.31656300	0.09754200
C	-3.05940500	-4.02033600	-0.30708300	C	-1.79874700	-3.63614900	0.14849200
H	-0.91871000	-4.19649900	-0.16052200	H	-3.15527700	-4.87349200	-0.97345800
H	-5.17928300	-3.61770200	-0.25463500	H	-4.94249300	-1.68160100	1.28960600
H	-2.70406200	-1.00678400	2.09999200				

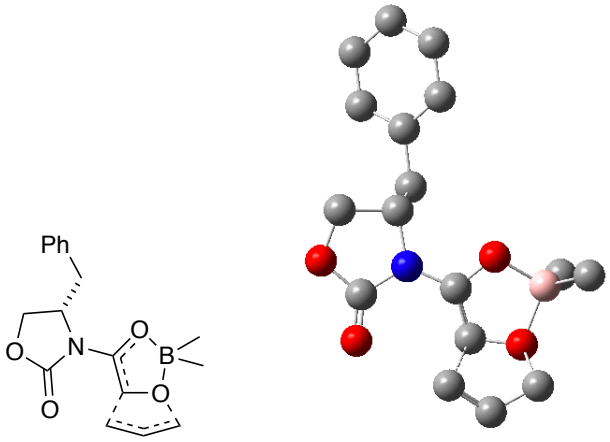
Table S10. Geometric coordinates and thermally corrected MP2 energies for transition structure **18$_B$**.



G = –1041.23127 Hartree
G_{MP2} = –651324.9035 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.98670200	0.16551600	-0.43400200
H	0.06570100	0.05835700	1.09168900	C	-0.66065800	-1.30737400	-0.47296200
H	-0.58201600	-2.09482000	0.27985000	N	-2.05082800	-0.84449600	-0.56244700
C	-2.12367900	0.54307100	-0.66636700	O	-0.87847400	1.04944100	-0.45967200
O	-3.09954800	1.21241700	-0.90193300	C	-3.13513900	-1.69276200	-0.69950100
C	-4.47687000	-1.37874800	-0.70223300	H	-4.94282500	-0.41423700	-0.58960200
O	-5.22443700	-2.49795600	-0.82437900	B	-4.21196200	-3.72018900	-0.47493300
O	-2.87959800	-2.98124200	-0.75505000	C	-4.37499600	-3.99200500	1.10470900
H	-5.37162800	-4.38907600	1.33823200	H	-3.64594100	-4.74026600	1.44437300
H	-4.23292800	-3.09220700	1.71779100	C	-4.38492100	-4.99446500	-1.42746900
H	-5.38411300	-5.44085700	-1.33269800	H	-4.20229700	-4.79825500	-2.49106000
H	-3.67382500	-5.77494200	-1.12446300	C	-6.04933300	-2.55575700	-2.62572300
H	-6.78985800	-1.82325100	-2.32113200	H	-6.38566100	-3.58537800	-2.61511800
C	-4.98326800	-2.15284700	-3.45851400	C	-4.53467900	-0.86554600	-3.44111000
H	-5.12163400	-0.05952900	-3.01417900	H	-3.62128000	-0.57171200	-3.95018100
H	-4.37731700	-2.92345700	-3.92950000	C	-0.12750400	-1.82738900	-1.82894500
H	-0.16882400	-1.00838600	-2.55787300	H	-0.81248400	-2.60925800	-2.17090900
C	1.28157300	-2.37016400	-1.72542400	C	2.37988600	-1.63716900	-2.19392000
C	3.67907100	-2.13477500	-2.07109600	C	3.89848900	-3.37647400	-1.47441400
C	2.81174900	-4.11899000	-1.00588700	C	1.51580300	-3.61978700	-1.13169900
H	0.67286000	-4.20884500	-0.77621500	H	2.97321000	-5.09107700	-0.54754400
H	4.90813300	-3.76677200	-1.37982600	H	4.51719600	-1.55327200	-2.44594600
H	2.21567500	-0.67380500	-2.67246500				

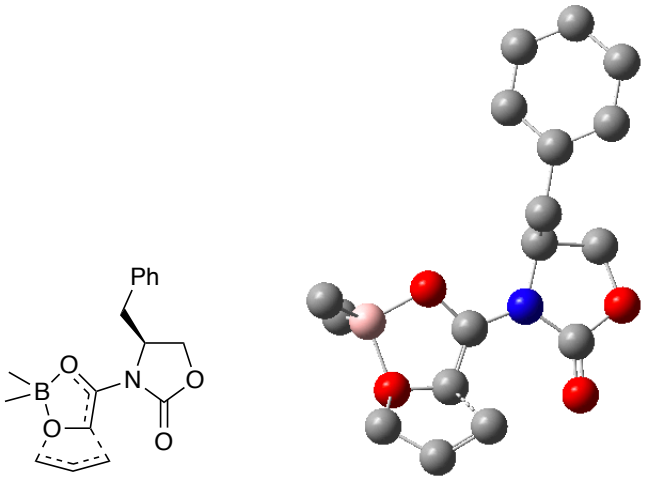
Table S11. Geometric coordinates and thermally corrected MP2 energies for transition structure **18**$_C$.



G = –1041.228303 Hartree
G_{MP2} = –651321.3575 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.02474100	0.19097500	0.32124300
H	0.08966700	0.20825700	-1.07152200	C	0.49360900	-1.41521000	0.35937800
H	0.50590100	-2.06688700	-0.51657100	N	1.86943500	-1.09469200	0.75755100
C	2.85998400	-2.04857300	0.91385300	C	4.07754800	-1.92738900	1.54073800
H	4.46016700	-1.09005000	2.09672900	O	4.77376200	-3.08951900	1.45442700
C	6.32629600	-2.91196900	0.24046300	H	7.00300300	-3.53841300	0.81093200
H	5.83015800	-3.39976200	-0.58774100	C	6.51336100	-1.51025400	0.19628200
H	7.22870500	-1.05646800	0.87974300	C	5.61569600	-0.71991600	-0.45301400
H	4.89431000	-1.14523700	-1.14483600	H	5.62579200	0.36182800	-0.36398200
B	3.66295200	-4.20378800	1.02071700	O	2.60712300	-3.24638900	0.42796700
C	4.17397600	-5.24509100	-0.08515900	H	4.34532100	-4.80922400	-1.07853200
H	5.09595500	-5.75669400	0.22161900	H	3.41801500	-6.03045000	-0.21963300
C	3.13660700	-4.84371600	2.40250400	H	3.92341900	-5.43278600	2.89186600
H	2.79834200	-4.09186900	3.12794900	H	2.29656800	-5.52720300	2.21718700
C	2.02944000	0.26029400	1.03579400	O	0.87339200	0.90024300	0.71226800
O	3.00454000	0.80810100	1.48860400	C	-0.29785800	-2.09591300	1.49966000
H	-0.33835100	-1.41185600	2.35606800	H	0.26870100	-2.97954200	1.81209900
C	-1.69453200	-2.49242500	1.07181500	C	-2.81586600	-1.75853600	1.48035900
C	-4.09849500	-2.11429100	1.05729700	C	-4.27763400	-3.21235000	0.21581900
C	-3.16811000	-3.95492300	-0.19576500	C	-1.88909300	-3.59754300	0.22945300
H	-1.03051100	-4.18736600	-0.08492200	H	-3.29975800	-4.81731800	-0.84389500
H	-5.27476100	-3.49245200	-0.11272900	H	-4.95607300	-1.53548700	1.38996500
H	-2.68548000	-0.90894600	2.14752400				

Table S12. Geometric coordinates and thermally corrected MP2 energies for transition structure **18$_D$**.

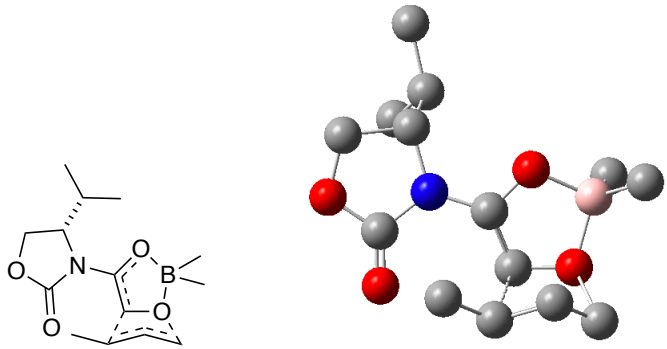


G = –1041.210713 Hartree

G_{MP2} = –651321.2071 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.97677700	0.21524600	-0.43458000
H	0.07520000	0.00993500	1.09263000	C	-0.62515800	-1.30402600	-0.52738300
H	-0.51682900	-2.12216600	0.18810700	N	-2.02975500	-0.88098800	-0.58736400
C	-2.14633800	0.50745700	-0.62213500	O	-0.91433300	1.04163200	-0.40283400
O	-3.14414300	1.15776900	-0.81416500	C	-3.08858900	-1.75794300	-0.74904000
C	-4.43559500	-1.48577900	-0.72656500	H	-4.92384500	-0.54673300	-0.53522200
O	-5.15403800	-2.62504000	-0.90135400	B	-4.08630000	-3.83093600	-0.63639400
O	-2.78693900	-3.03350600	-0.88430500	C	-4.23436300	-4.19936900	0.92437800
H	-5.21264700	-4.65210900	1.13305600	H	-3.47286500	-4.93322000	1.22174800
H	-4.13177000	-3.33016400	1.58719200	C	-4.20879600	-5.05519400	-1.66366200
H	-5.22440400	-5.47150400	-1.69557500	H	-3.90938700	-4.81871400	-2.69354100
H	-3.55375000	-5.87178100	-1.33157700	C	-6.04849400	-2.65195600	-2.65992300
C	-6.05034700	-1.28355000	-3.02185900	C	-4.88662800	-0.66435100	-3.35878400
H	-3.99630500	-1.23974700	-3.59593200	H	-4.81442900	0.41277200	-3.47125300
H	-6.92897500	-0.68310600	-2.79331600	H	-6.96231600	-3.13278200	-2.32882700
H	-5.31635400	-3.30949700	-3.10890800	C	-0.08590000	-1.74544300	-1.90856000
H	-0.15655700	-0.89542500	-2.59874800	H	-0.74943200	-2.53138400	-2.28193100
C	1.33909300	-2.25068400	-1.83708400	C	2.41319600	-1.46527400	-2.27576400
C	3.72697000	-1.92961600	-2.18061700	C	3.98548000	-3.19020600	-1.64209400
C	2.92318500	-3.98504600	-1.20438700	C	1.61265000	-3.51887000	-1.30238300
H	0.78901900	-4.14804300	-0.97128900	H	3.11523900	-4.97195000	-0.79176500
H	5.00653800	-3.55455700	-1.56890200	H	4.54590500	-1.30723600	-2.53146200
H	2.21856500	-0.48636200	-2.70916600				

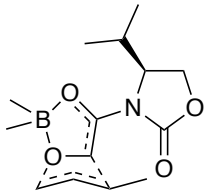
Table S13. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_A}$.

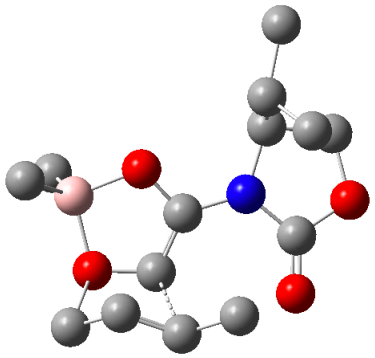


G = –928.130041 Hartree
G_{MP2} = –580544.4903 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.06876800	0.18547700	0.11509200
H	-0.16887400	-0.57744417	-0.91630091	C	-0.86190609	1.28424800	0.04148874
H	-1.23589891	1.53294591	-0.95056626	C	-0.16466417	2.53231700	0.63890391
H	-0.95111826	3.29719500	0.71306583	C	0.41546774	2.30531109	2.03953891
H	0.84611766	3.23489209	2.42183491	H	-0.35145626	1.98075600	2.75280991
H	1.21531183	1.54961909	2.04086700	C	0.89648683	3.05613509	-0.33858200
H	1.72321783	2.34970317	-0.46441200	H	0.46725783	3.25804017	-1.32818600
H	1.32438374	3.99277409	0.03318509	N	-1.97532217	0.78888591	0.86411857
C	-3.16126000	1.47164991	1.01191040	C	-4.18366360	1.28043891	1.94827131
H	-4.18079326	0.58942291	2.77937140	O	-5.09894997	2.22144103	1.84242278
B	-4.56546809	3.31414834	0.85825469	O	-3.35816657	2.50276043	0.24410934
C	-5.58101309	3.75789291	-0.29838548	H	-5.13166652	4.54891817	-0.91901557
H	-5.87786483	2.94969074	-0.97385131	H	-6.50173934	4.18938648	0.12825860
C	-3.97287366	4.50943378	1.76795991	H	-3.46254874	5.26788760	1.16025166
H	-4.78172357	5.01957486	2.30972900	H	-3.25954857	4.15496495	2.52449891
C	-7.02105914	1.05609828	0.99981445	C	-6.27384621	0.25206583	0.16747591
H	-6.22620295	0.50470731	-0.89324726	C	-5.41462222	-0.74605997	0.63665569
H	-5.52100009	-1.06097540	1.67371852	C	-4.63765114	-1.65891488	-0.26148440
H	-5.17568274	-2.61461053	-0.37739109	H	-4.50038162	-1.23354953	-1.25802314
H	-3.65851840	-1.91399983	0.16337478	H	-7.10521490	0.81997691	2.06551440
H	-7.57432288	1.91241028	0.63416102	C	-1.65445809	-0.38894100	1.53939791
O	-0.43474909	-0.80271091	1.11815709	O	-2.31988109	-0.96241674	2.36861009

Table S14. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_B}$.

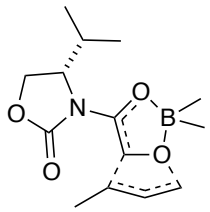


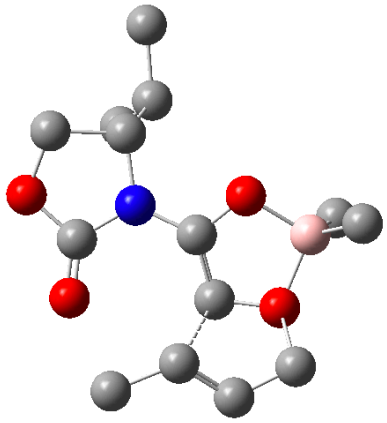


G = –928.12871 Hartree
G_{MP2} = –580542.881 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.93522500	-0.07646100	0.55591800
H	0.17443100	0.56314000	-0.92277700	C	-1.16422300	0.58674800	0.82861200
H	-1.39998300	1.60426800	0.50375700	C	-0.94902300	0.60340400	2.36143600
H	-1.91455600	0.90154500	2.78525800	C	0.08056900	1.68148400	2.73396700
H	0.17100700	1.76307000	3.82231900	H	1.07959700	1.44855700	2.34284100
H	-0.21089400	2.66621000	2.34960200	C	-0.57043400	-0.76518800	2.94365400
H	0.40319900	-1.11653500	2.57997000	H	-0.50522500	-0.70287700	4.03549700
H	-1.31596400	-1.52939600	2.70180100	N	-2.24483100	-0.31020100	0.38970200
C	-1.75924200	-1.45057400	-0.24012300	O	-0.41047300	-1.33509600	-0.35765300
O	-2.39077000	-2.40658500	-0.62424100	C	-3.59086700	-0.00622300	0.52149500
C	-4.67389900	-0.60790500	-0.08344200	H	-4.67879100	-1.41313000	-0.79955500
O	-5.81701100	0.02142100	0.25607000	B	-5.36635300	1.41375100	0.92290900
O	-3.89253700	1.04442500	1.24942400	C	-5.40216400	2.51539400	-0.25431300
H	-6.43065000	2.70400800	-0.58941400	H	-4.99890600	3.47485300	0.09731300
H	-4.82300400	2.21858400	-1.13923100	C	-6.17258300	1.78127000	2.25695400
H	-7.24324200	1.92577600	2.05772700	H	-6.07605600	1.03817400	3.05851400
H	-5.80558300	2.73403200	2.66214000	C	-6.93687700	-1.23394100	1.45234700
H	-7.26997400	-1.73924400	0.55226300	H	-7.61669200	-0.49292800	1.85371000
C	-5.94944400	-1.81930500	2.25740800	C	-5.05809900	-2.72446900	1.74285800
H	-5.26812700	-3.16302800	0.76963700	C	-3.89313400	-3.30139300	2.48074900
H	-3.00014000	-3.30345000	1.84626500	H	-3.67943500	-2.75366000	3.40437800
H	-4.08733300	-4.35167700	2.74585200	H	-5.76020400	-1.39316000	3.24138900

Table S15. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21}_{\mathbf{C}}$.



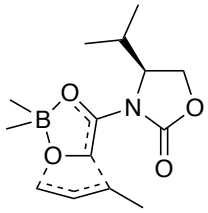


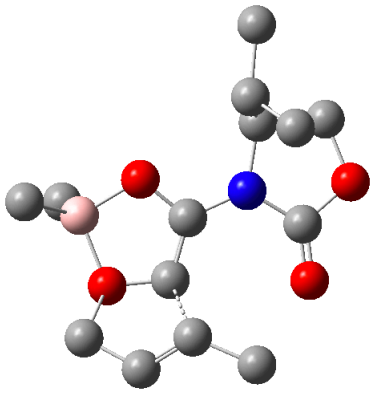
G = –928.127504 Hartree

G_{MP2} = –580539.5605 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.07223500	0.04612100	0.19475800
H	-0.16699000	-0.42593900	-0.99503600	C	-0.71777100	1.35514400	0.17943600
H	-0.98915000	1.78152400	-0.78996100	C	0.05816400	2.42357900	0.98700000
H	-0.64700300	3.25119500	1.12684200	C	0.50588100	1.93850700	2.37334800
H	1.22447300	1.11189200	2.31125600	H	0.99504600	2.75547800	2.91472000
H	-0.34130200	1.60502100	2.98189700	C	1.23943300	2.95471700	0.16047900
H	1.73556500	3.77557800	0.68898700	H	1.99730500	2.18114700	-0.01979600
H	0.90977300	3.33717800	-0.81290600	N	-1.93722700	0.88782500	0.85763500
C	-3.06030100	1.68259200	1.03042500	C	-4.15038500	1.48656300	1.85463000
H	-4.30057000	0.70966100	2.58444200	O	-5.01329100	2.51797300	1.74729900
C	-6.79854200	1.86114800	0.80112500	H	-7.47036400	2.47169300	1.39336500
H	-6.46831900	2.28991400	-0.13456000	C	-6.70469100	0.48093200	1.01352000
H	-7.23212800	0.04184100	1.85991500	C	-5.78303200	-0.28467500	0.34544500
H	-5.26172900	0.16246700	-0.49989000	C	-5.54107200	-1.73860700	0.59830600
H	-6.14712100	-2.10793700	1.43180400	H	-5.78614100	-2.33170300	-0.29487100
H	-4.48848800	-1.92738700	0.83472800	B	-4.21879500	3.67491300	0.97639500
O	-3.08856100	2.80854000	0.35396600	C	-5.05942000	4.40832900	-0.17700700
H	-5.27848000	3.77499900	-1.04712800	H	-6.01199500	4.80736800	0.19649400
H	-4.49181800	5.26871600	-0.55582700	C	-3.60338900	4.63832000	2.11586300
H	-2.94140200	5.39491400	1.67253400	H	-4.39768000	5.18044100	2.64610900
H	-3.02437800	4.09351400	2.87403600	C	-1.78488000	-0.38791600	1.38525300
O	-0.58853800	-0.88423700	0.97398000	O	-2.55572500	-0.99003700	2.09512900

Table S16. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_D}$.

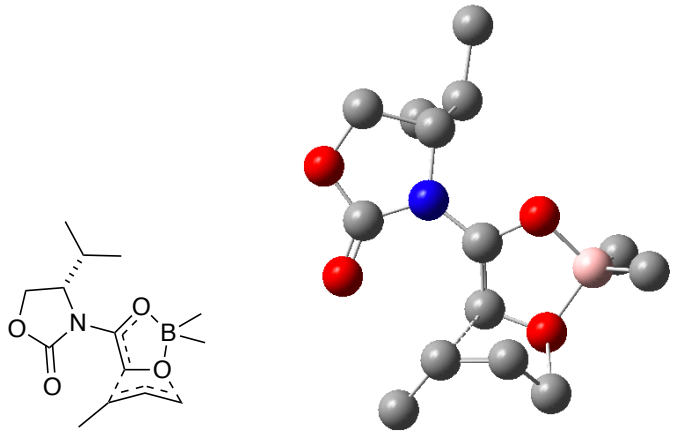




G = –928.127379 Hartree
G_{MP2} = –580539.744 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.92560700	0.12885500	0.56242200
H	-0.22157600	-0.50096800	-0.94818000	C	1.10959700	-0.72292500	0.79379600
H	1.25166900	-1.74330900	0.42727700	C	0.90507600	-0.77779200	2.32759500
H	1.83474900	-1.19833900	2.72792300	C	-0.23402700	-1.74875400	2.67411300
H	-0.31955100	-1.86475000	3.75977700	H	-1.20538400	-1.39027700	2.30948800
H	-0.05879700	-2.74296700	2.24610900	C	0.68795400	0.60224500	2.96480100
H	-0.23768500	1.07757700	2.61822700	H	0.61629600	0.50588300	4.05369000
H	1.51712600	1.28455400	2.74877100	N	2.26336100	0.09353500	0.38765000
C	1.87689000	1.30460900	-0.17338300	O	0.52347200	1.31053300	-0.29372300
O	2.58621100	2.22444900	-0.50644500	C	3.57846900	-0.32172500	0.53480800
C	4.73573200	0.28120800	0.08873300	H	4.83595300	1.16981200	-0.51036600
O	5.80970800	-0.48453900	0.38332200	B	5.21963800	-1.91877500	0.79740200
O	3.76273500	-1.48549600	1.11828300	C	5.23961800	-2.81829800	-0.54154000
H	4.74281200	-2.33425800	-1.39311000	H	6.26932200	-3.04052000	-0.85161700
H	4.74098300	-3.78223500	-0.37160000	C	5.90950800	-2.57366700	2.08948800
H	6.99985200	-2.64876900	1.98119000	H	5.70190800	-2.04615000	3.03038600
H	5.54195200	-3.59993600	2.22267100	C	6.97810800	0.45802000	1.84305000
C	6.55046100	1.78657300	1.70937900	C	5.30228100	2.17626100	2.11948400
H	4.72877200	1.48869000	2.73974300	C	4.71255600	3.53119500	1.88941200
H	5.39145000	4.17363800	1.31952200	H	3.77032800	3.45752400	1.33500900
H	4.49054200	4.02588800	2.84593000	H	7.13300700	2.46693400	1.08888800
H	7.93465400	0.13974400	1.44480200	H	6.55505300	-0.17034500	2.61429400

Table S17. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from favor face forming anti product.

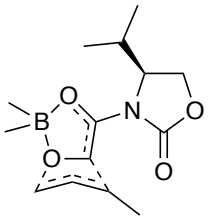


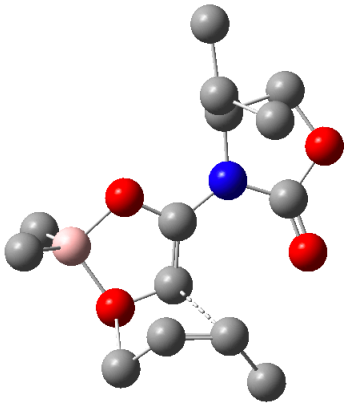
G = –928.119238 Hartree

G_{MP2} = –580536.7388 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.06873000	0.06331300	0.20930300
H	-0.14462800	-0.35814100	-1.02469400	C	-0.75824100	1.31913100	0.26631000
H	-1.05135500	1.79404600	-0.67375100	C	-0.00890600	2.36174500	1.13064500
H	-0.73433300	3.16360200	1.31373700	C	0.44870300	1.81187300	2.48923900
H	0.92486700	2.60645900	3.07387700	H	-0.39286700	1.43194300	3.07794400
H	1.18054100	1.00137100	2.38290800	C	1.16001400	2.96526000	0.33707200
H	1.94079100	2.22273600	0.12718700	H	0.82455200	3.38247700	-0.61990500
H	1.62893000	3.77479900	0.90626700	N	-1.95606500	0.77738400	0.92498900
C	-3.10789300	1.51968000	1.13597900	C	-4.16321500	1.26285700	1.98422900
H	-4.27982400	0.45131000	2.68266100	O	-5.09010600	2.23764900	1.89933800
B	-4.36257800	3.45502900	1.13698200	O	-3.20511700	2.65570900	0.48244700
C	-5.26807700	4.16039900	0.01919000	H	-4.70311600	4.97689800	-0.45052400
H	-5.58616100	3.49146300	-0.79053400	H	-6.16750500	4.61996500	0.45133100
C	-3.78018400	4.42515100	2.28736800	H	-3.17672900	5.23122600	1.84773800
H	-4.59179100	4.90490600	2.85023600	H	-3.14900800	3.89927000	3.01663600
C	-6.78762400	1.49016000	0.95494200	C	-6.18931900	0.65191600	0.00381500
H	-5.95683600	1.08957300	-0.96473500	C	-5.63540000	-0.57021400	0.29479700
C	-5.91003100	-1.44665700	1.47876800	H	-6.49651500	-2.32029200	1.15628100
H	-4.97445100	-1.82675900	1.90054600	H	-6.47304000	-0.94326100	2.26895200
H	-5.04093400	-1.04113900	-0.48784200	H	-7.14184100	1.10009600	1.90155100
H	-7.20381400	2.44440600	0.65972400	C	-1.77878300	-0.53375300	1.34521400
O	-0.57011800	-0.96919400	0.90110600	O	-2.53812400	-1.20984300	1.99822700

Table S18. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from nonfavor face forming anti product.



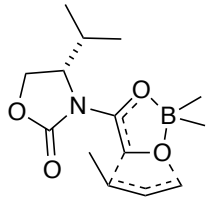


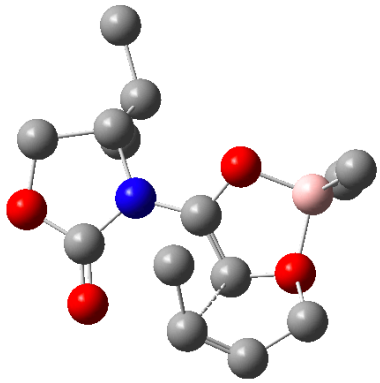
G = –928.118502 Hartree

G_{MP2} = –580536.5739 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.91083400	0.06307200	0.59677900
H	-0.24386000	-0.40011300	-0.98972100	C	1.13205800	-0.79535600	0.68528400
H	1.26089400	-1.77464500	0.21551500	C	0.97142600	-1.00208600	2.21143200
H	1.90708100	-1.46750100	2.54056200	C	-0.16847000	-1.99299700	2.49340400
H	-0.21944800	-2.22069700	3.56342800	H	-1.14674300	-1.58974700	2.20150300
H	-0.02070200	-2.93919800	1.95934900	C	0.78908000	0.30877300	2.99024200
H	-0.13397800	0.83271300	2.71297100	H	0.73568800	0.10162600	4.06470000
H	1.62696600	0.99577500	2.82924500	N	2.27207300	0.06080800	0.32460200
C	1.86724900	1.32634200	-0.08163900	O	0.51088100	1.33741600	-0.16642600
O	2.56365000	2.28337800	-0.32407200	C	3.59486400	-0.33914200	0.43437400
C	4.73475300	0.31218100	0.01495500	O	5.82971800	-0.43096000	0.27398200
B	5.27686600	-1.91100300	0.59017200	O	3.81169600	-1.53418900	0.93698500
C	5.31986500	-2.71745300	-0.80621700	H	4.86182500	-3.70982700	-0.69583900
H	4.79420100	-2.20028200	-1.62005900	H	6.35389900	-2.87773600	-1.13895600
C	5.99283900	-2.62529100	1.83243000	H	7.06584200	-2.77734500	1.65236200
H	5.88280700	-2.09437500	2.78665600	H	5.56346600	-3.62585400	1.97773100
C	6.90889600	0.44895800	1.80402800	H	7.39212200	1.10395000	1.08900400
H	7.47583800	-0.42802700	2.08819400	C	5.86324300	0.91140400	2.61698800
C	5.09470900	2.01171900	2.32987000	C	5.42515400	3.15743200	1.42207700
H	4.57609400	3.39037900	0.77168900	H	5.62439200	4.05537000	2.02624400
H	6.30410800	2.97576800	0.79832900	H	4.20468900	2.16299000	2.94086300
H	5.50493200	0.23825400	3.39296700	H	4.82054800	1.25498400	-0.49814300

Table S19. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from favor face forming syn product.



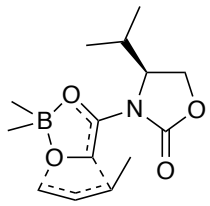


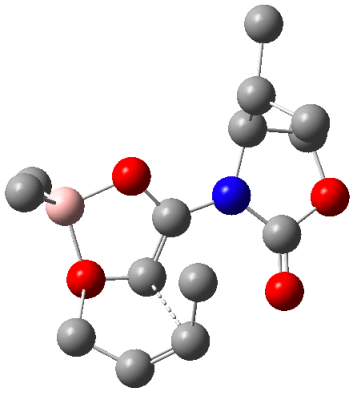
G = –928.11662 Hartree

G_{MP2} = –580534.9285 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.06765400	0.14360300	-0.17268400
H	0.14392900	-0.47578400	0.97603600	C	0.82659800	1.29845400	-0.13848600
H	1.16755700	1.64571800	0.84051800	C	0.12013500	2.47365800	-0.85521700
H	0.88631800	3.25086900	-0.96555200	C	-0.39769600	2.11300800	-2.25462600
H	-1.17471900	1.33932600	-2.22199600	H	-0.83717200	2.99623600	-2.73061000
H	0.40730700	1.75648600	-2.90558800	C	-0.99395600	3.04380400	0.03618400
H	-0.61252200	3.33141700	1.02326900	H	-1.43165400	3.93605900	-0.42378500
H	-1.80906000	2.32385800	0.18577400	N	1.97594300	0.77097500	-0.88839900
C	3.15703700	1.47376000	-1.06726400	C	4.15777200	1.25557300	-1.98161900
H	4.19414800	0.52748600	-2.77319400	O	5.16814100	2.13939200	-1.80136800
C	6.82806100	1.19786600	-1.06719100	H	7.52130600	1.70873700	-1.72524500
H	6.72771300	1.62467300	-0.08011500	C	6.50076600	-0.15090200	-1.30730500
H	6.80902200	-0.57862800	-2.25975700	C	5.60019000	-0.86337800	-0.56193400
H	5.29906800	-1.83712800	-0.94508100	C	5.08480800	-0.53269300	0.80536100
H	5.62458500	-1.12566200	1.55933900	H	5.18598000	0.52267500	1.06836400
H	4.02734100	-0.80625000	0.89484100	B	4.53723100	3.30466000	-0.87333800
O	3.36053900	2.50413300	-0.26974300	C	5.52024900	3.83201000	0.27869400
H	6.47893500	4.18259600	-0.12645200	H	5.06471400	4.69513000	0.78227200
H	5.73703000	3.09636500	1.06556300	C	3.98844400	4.42948600	-1.89179100
H	3.44488100	5.21340400	-1.34668300	H	4.81436400	4.92329100	-2.42066700
H	3.31086600	4.02626100	-2.65632300	C	1.71795500	-0.47683800	-1.44411000
O	0.49555300	-0.89295000	-1.01527100	O	2.42631000	-1.11472300	-2.18523700

Table S20. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from nonfavor face forming syn product.





G = –928.116483 Hartree

G_{MP2} = –580534.3017 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.95022300	-0.04400600	0.53374000
H	0.16951300	0.40155500	-1.00480600	C	-1.09891600	0.77619800	0.75722200
H	-1.27595600	1.75252000	0.29658500	C	-0.83964600	0.99083900	2.26815100
H	-1.78030300	1.38318100	2.67049900	C	0.24192400	2.06443600	2.46564000
H	0.38185300	2.27478400	3.53130700	H	1.21435100	1.74528200	2.06803000
H	-0.03100700	3.00531300	1.97344600	C	-0.49204900	-0.29959600	3.02406400
H	-1.26023600	-1.06934900	2.89569800	H	0.46511300	-0.72461500	2.69878300
H	-0.40853900	-0.09402300	4.09684500	N	-2.24676500	-0.09733900	0.46813100
C	-1.85059300	-1.35242900	0.01581200	O	-0.49730700	-1.34664600	-0.12881200
O	-2.55024100	-2.30898500	-0.21309800	C	-3.56725100	0.31424500	0.56164600
C	-4.68709100	-0.27474700	0.02739400	H	-4.74974400	-1.15762100	-0.58519300
O	-5.79185800	0.45519300	0.30781300	B	-5.23436000	1.88293100	0.81951500
O	-3.79577600	1.44990400	1.19067900	C	-5.20975400	2.83806400	-0.47999600
H	-4.66134800	2.40056400	-1.32488600	H	-6.22693900	3.05528500	-0.83178600
H	-4.73938900	3.80239800	-0.24413700	C	-6.00145200	2.46588600	2.10174000
H	-7.08064500	2.56847800	1.92592200	H	-5.86528600	1.87797600	3.02008600
H	-5.62874300	3.47470200	2.32430600	C	-7.04390000	-0.56629700	1.57203500
C	-6.49041800	-1.85898600	1.50193200	C	-5.32468300	-2.22314700	2.12060900
H	-4.90448700	-3.19308300	1.86004700	C	-4.62850200	-1.50371500	3.23486500
H	-3.54315000	-1.61549800	3.14321600	H	-4.85866400	-0.43646400	3.27472900
H	-4.90944100	-1.94904000	4.20159600	H	-6.88733800	-2.53395800	0.74561800
H	-7.94463400	-0.33597600	1.01491900	H	-6.84349000	0.08019400	2.41395600