SUPPORTING INFORMATION

Sodium Diisopropylamide-Mediated Dehydrohalogenations: Influence of Primary- and Secondary-Shell Solvation

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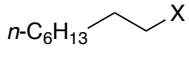
I. NMR Spectroscopic studies

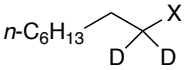
II. Rate studies

III. Calculations

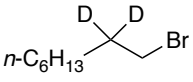
Chart I



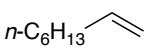
1 = Br
3 = N(*i*-Pr)$_2$
5 = Cl
6 = I
7 = F



1,1-**1**-d_2 = Br
1,1-**5**-d_2 = Cl



2,2-**1**-d_2



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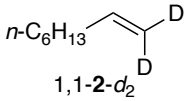

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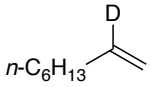
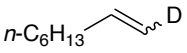
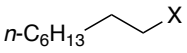


2-**2**-d_1



2-d_1



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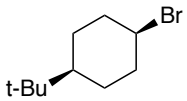
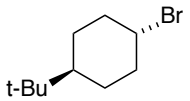


cis-**17**



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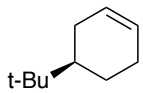

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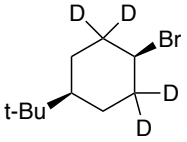
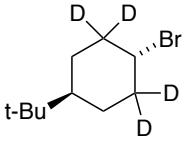


cis-**17**-d_4



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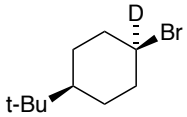

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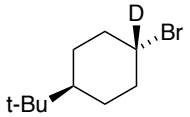
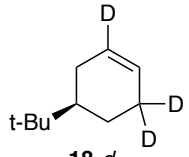


trans-**17**-d_1



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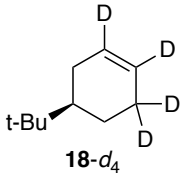

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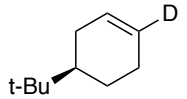
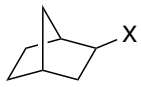


18-d_1



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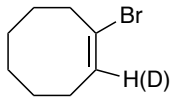
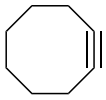
23 = Cl



26 (**26**-d_1)



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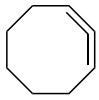

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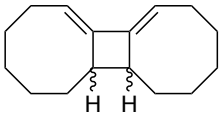

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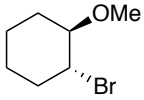

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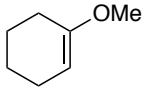

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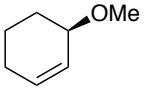

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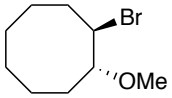

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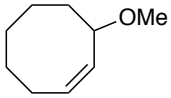

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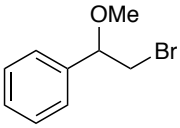

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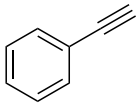

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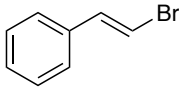

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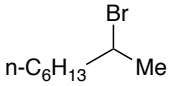
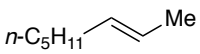


A



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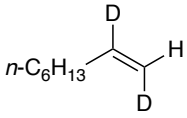
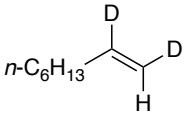
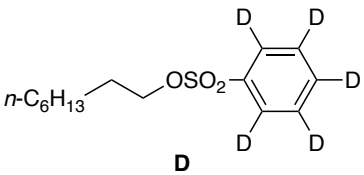


cis-1,2-**C**-d_2



trans-1,2-**C**-d_2



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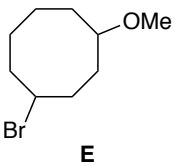

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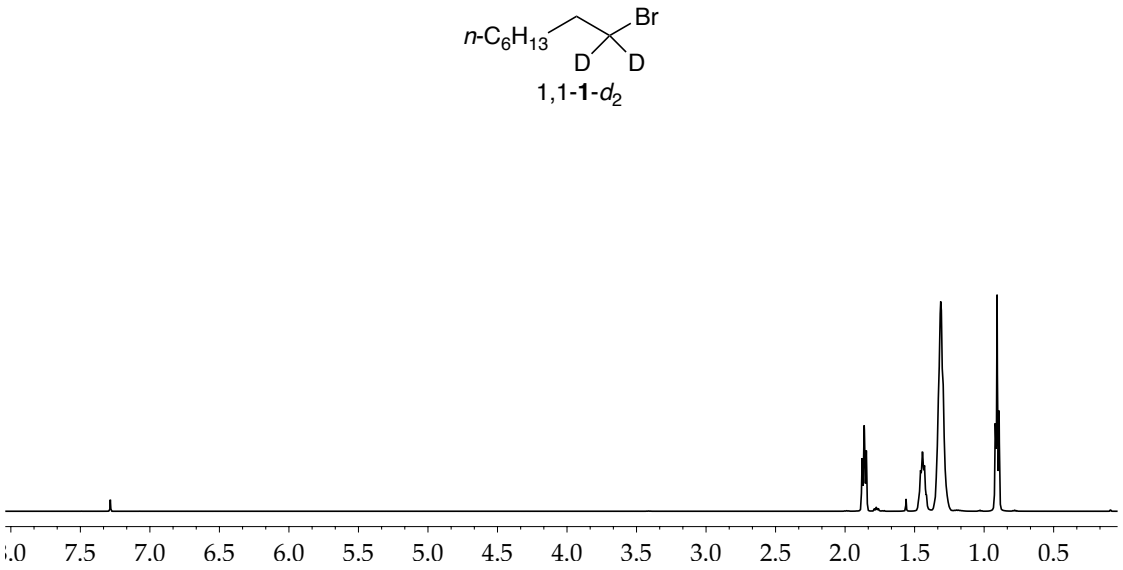


Figure S-1. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-bromooctane-1,1-d_2 (1,1-**1**-d_2): δ 1.86 (2H, t, J = 7.61 Hz), 1.44 (2H, m); 1.31 (8H, m), 0.91 (3H, t, J = 7.60 Hz).

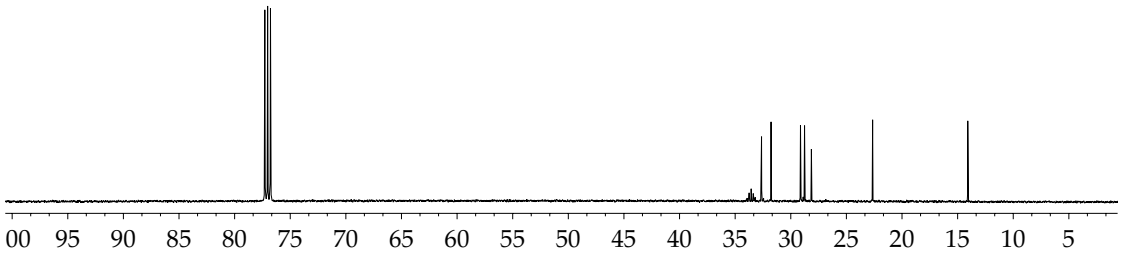


Figure S-2. ^{13}C NMR (126 MHz, $CDCl_3$) of 1-bromooctane-1,1-d_2 (1,1-**1**-d_2): δ 33.6 (q, $J_{C–D}$ = 7.6 Hz), 32.6, 31.7, 29.1, 28.7, 28.1, 22.6, 14.1.

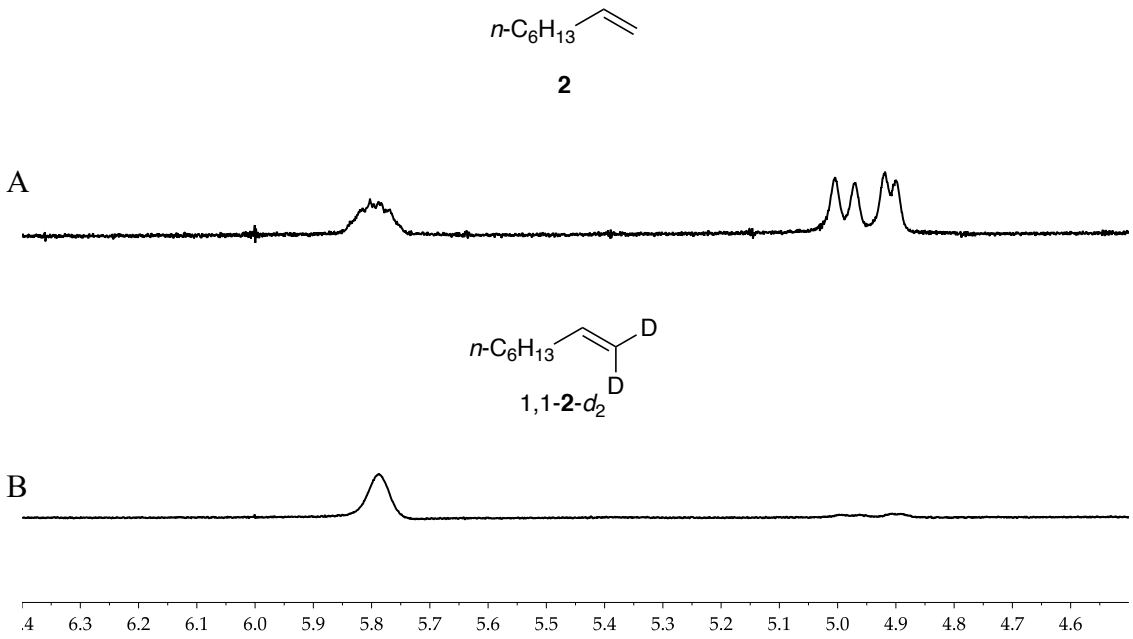
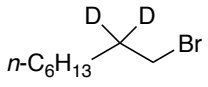


Figure S-3. ^{1}H NMR (500 MHz) of NaDA (0.12 M) with the following substrates (0.10 M) in THF/hexane: (A) 1-bromooctane (**1**) **Figure S-9.** Expanded ^{1}H NMR spectrum of 1-octene (**2**) in THF. k_H/k_D = 1.25.



2,2-**1**-d_2

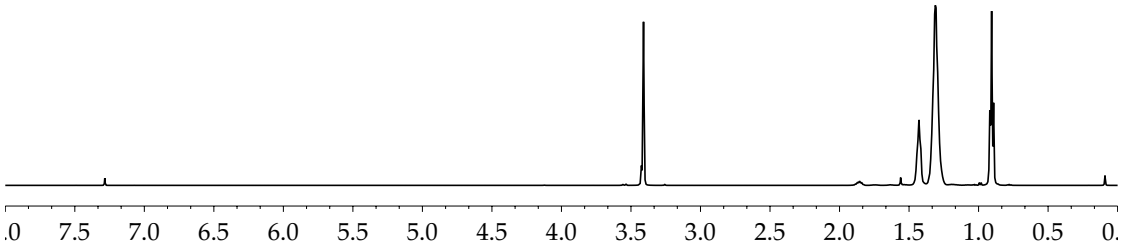


Figure S-4. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-bromooctane-2,2-d_2 (2,2-**1**-d_2): $_3$: δ 3.41 (2H, s) 1.44 (2H, m); 1.31 (8H, m), 0.91 (3H, t, J = 7.60 Hz).

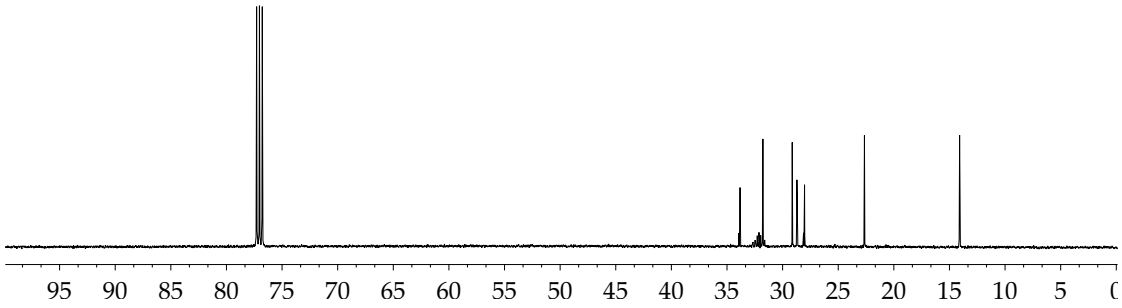


Figure S-5. ^{13}C NMR (126 MHz, $CDCl_3$) of 1-bromooctane-2,2-d_2 (2,2-**1**-d_2): δ 33.8, 32.6 (q, $J_{C–D}$ = 7.6 Hz), 31.7, 29.1, 28.7, 28.2, 22.6, 14.1.

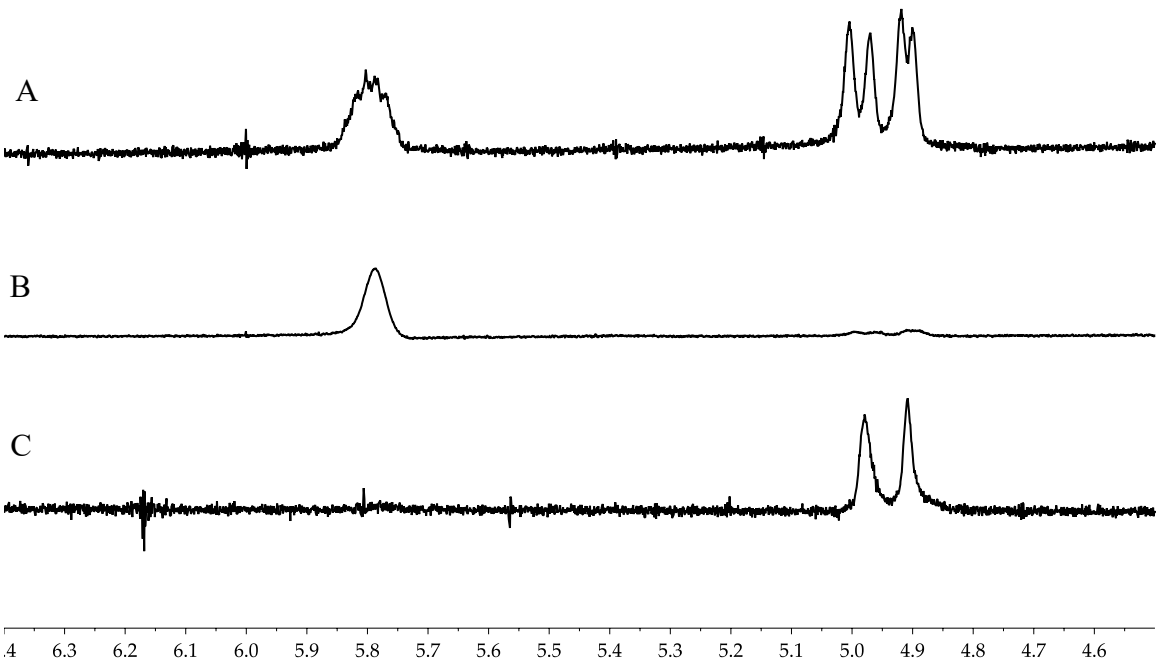


Figure S-6. ^{1}H NMR (500 MHz, 6.1 M THF/hexane) of NaDA (0.12 M) with the following substrates (0.10 M): (A) 1-bromooctane (**1**), (B) 1-bromooctane-1,1-d_2 (1,1-**1**-d_2), and (C) 1-bromooctane-2,2-d_2 (2,2-**1**-d_2).

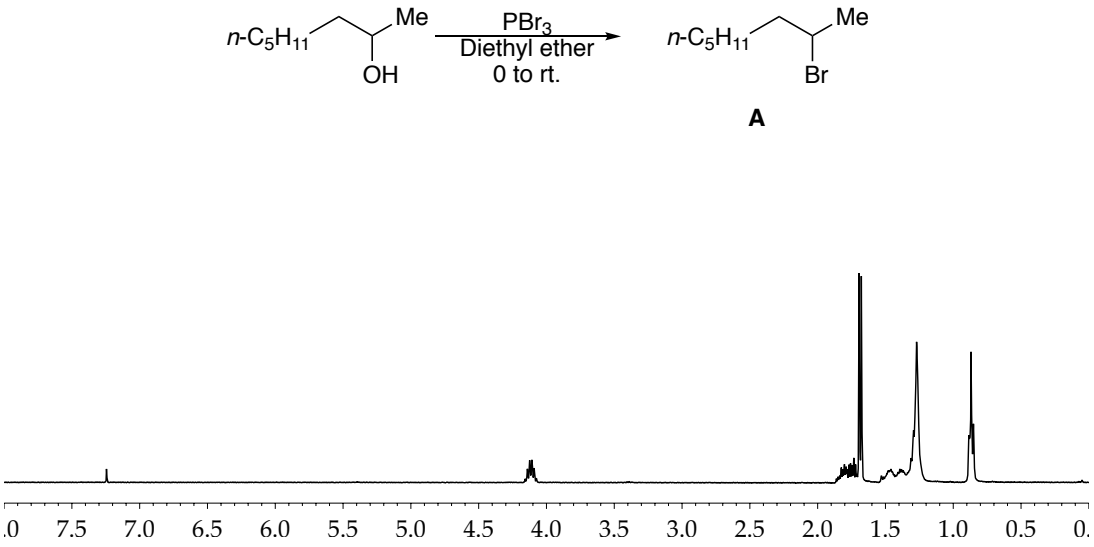


Figure S-7. ^{1}H NMR (500 MHz, $CDCl_3$) of 2-bromooctane (**A**): δ 4.16 (1H, m), 1.84 (2H, m); 1.73 (3H, d, J = 6.70 Hz), 1.48 (2H, m), 1.32 (4H, m), 0.91 (3H, t, J = 7.10 Hz).

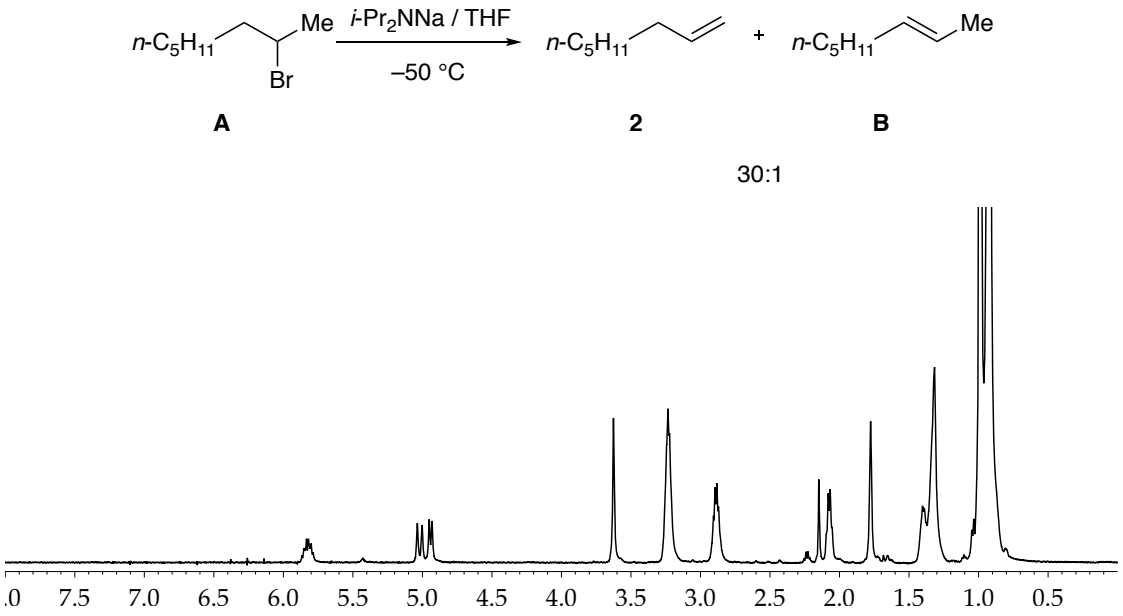


Figure S-8. ^{1}H NMR (500 MHz, THF-d_8) of 1-octene (**2**): δ: 5.83 (1H, m), 5.02 (d, J = 16.50 Hz), 1.48 (2H, m), 1.32 (4H, m), 0.91 (3H, t, J = 9.58 Hz).

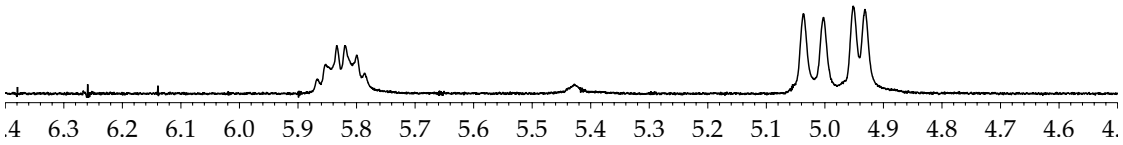
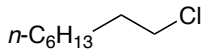


Figure S-9. Expanded ^{1}H NMR (500 MHz, THF-d_8) of 1-octene (**2**).



5

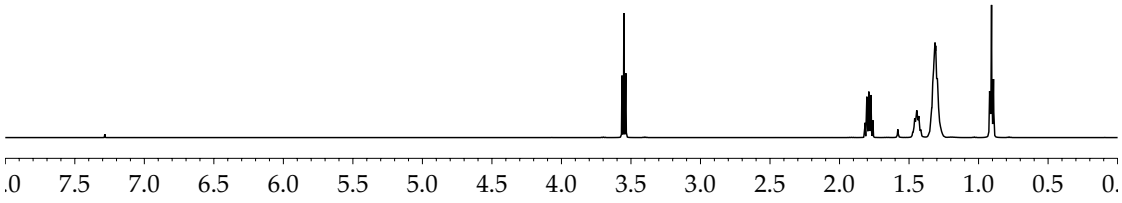


Figure S-10. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-chlorooctane (**5**): δ 3.55 (2H, t, *J* = 6.87 Hz) 1.79 (2H, m); 1.44 (2H, m), 1.31 (8H, m), 0.91 (3H, t, *J* = 7.37 Hz).

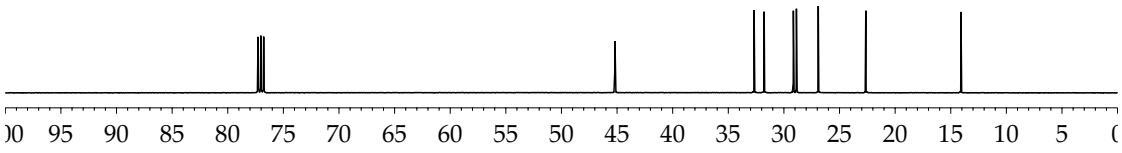


Figure S-11. ^{13}C NMR (126 MHz, $CDCl_3$) of 1-chlorooctane (**5**): δ 45.2, 32.7, 31.8, 29.1, 28.8, 26.9, 22.65, 14.1.

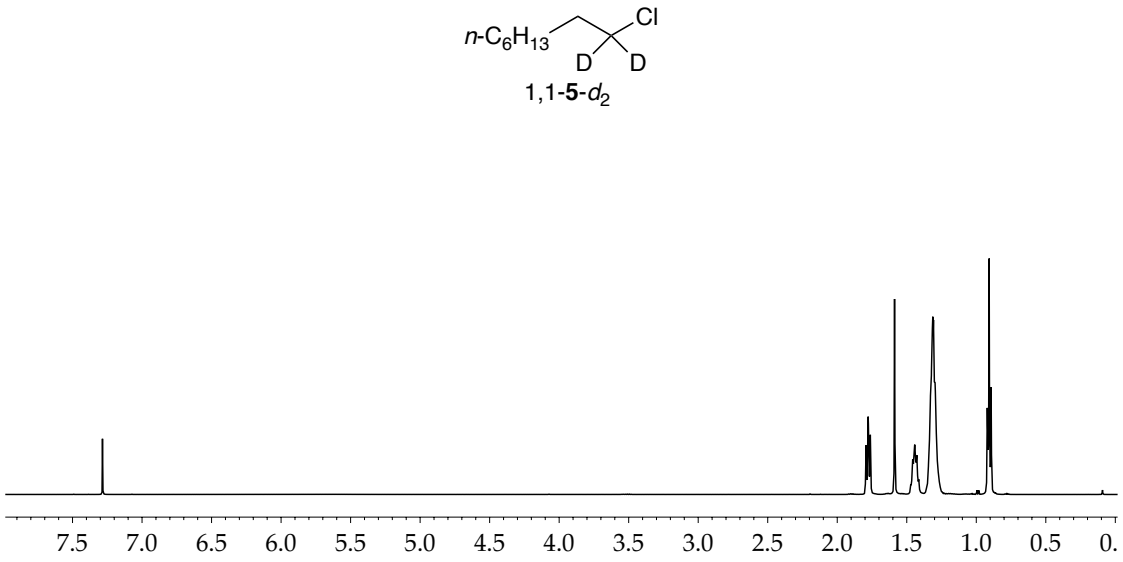


Figure S-12. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-chlorooctane-1,1-d_2 (1,1-**5**-d_2): δ 1.76 (2H, t, J = 7.27 Hz); 1.44 (2H, m), 1.31 (8H, m), 0.91 (3H, t, J = 7.37 Hz).

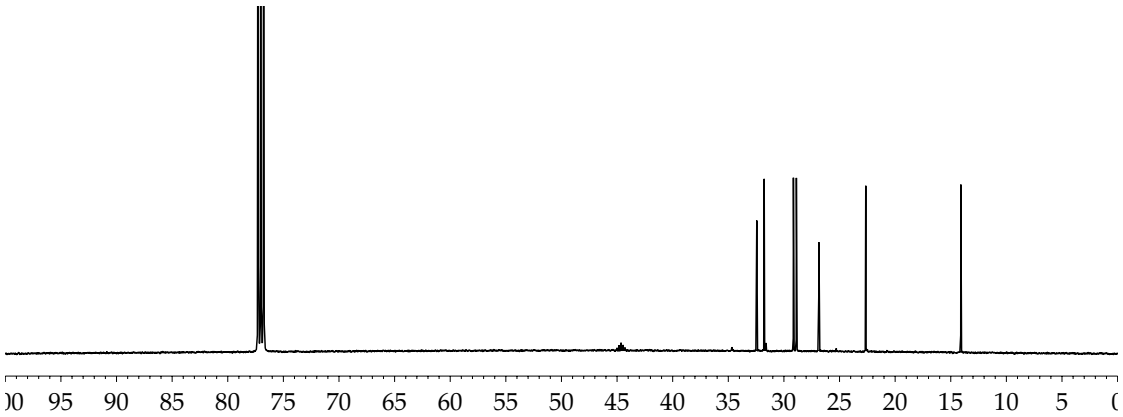


Figure S-13. ^{13}C NMR (126 MHz, $CDCl_3$) of 1-chlorooctane-1,1-d_2 (1,1-**5**-d_2): δ 44.6 (q, $J_{C–D}$ = 22.3 Hz), 32.4, 31.8, 29.1, 28.9, 26.8, 22.6, 14.1.

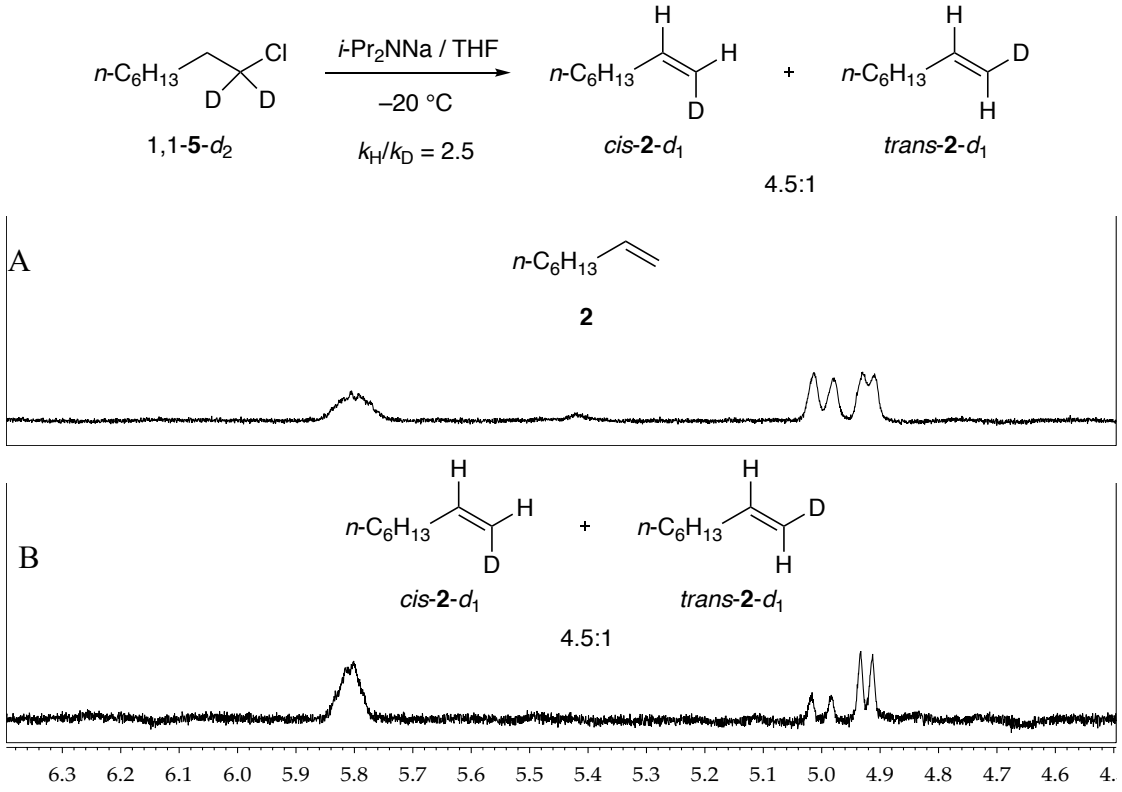


Figure S-14. ^{1}H NMR (500 MHz, 6.1 M THF/hexane) of NaDA (0.10 M) with the following substrates (0.050 M): (A) 1-octene (**2**) and (B) 1-chlorooctane-1,1-d_2 (1,1-**5**-d_2).

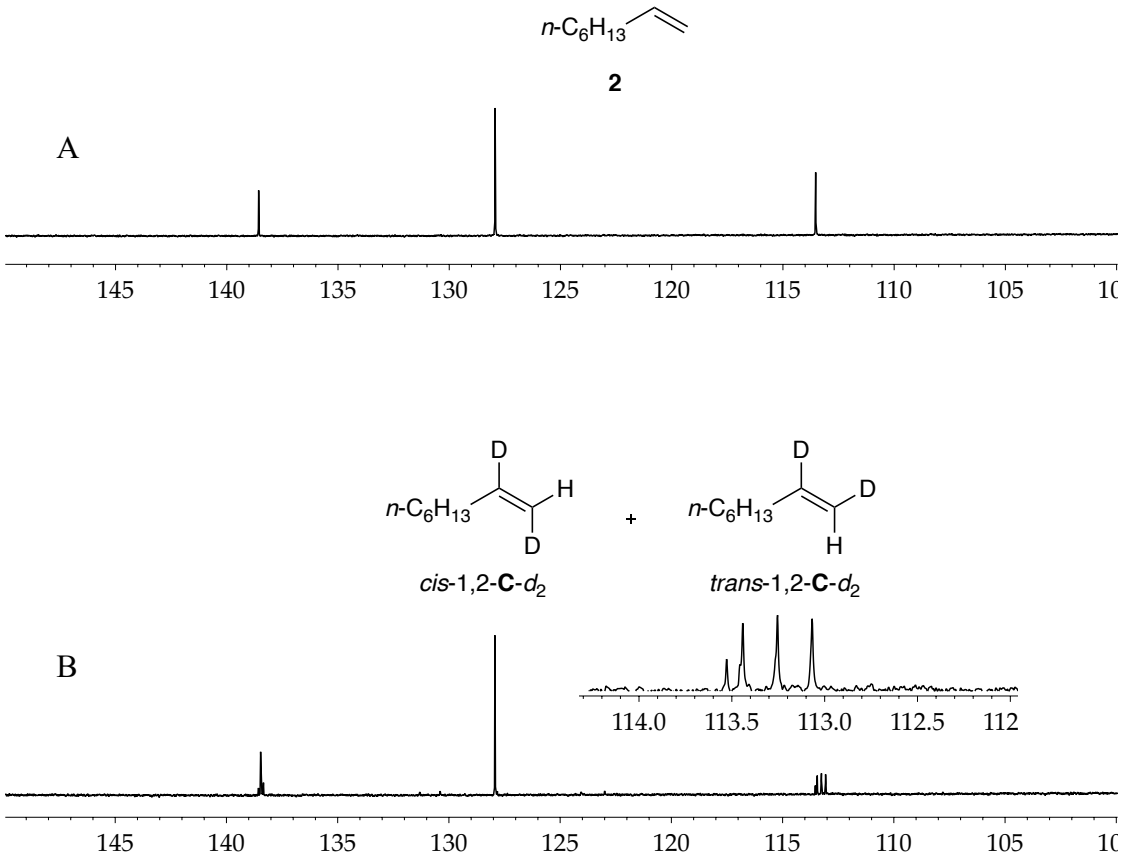


Figure S-15. ^{13}C NMR (126 MHz, 6.1 M THF/hexane) of NaDA (0.10 M) with substrates (0.050 M): (A) 1-octene (**2**): δ 138.8, 128.0, 114.7; and (B) oct-1-ene-1,2-d_2 (1,2-**C**-d_2): δ 138.2, 128.1, 113.3(t, $J_{C–D}$ = 12.2 Hz).

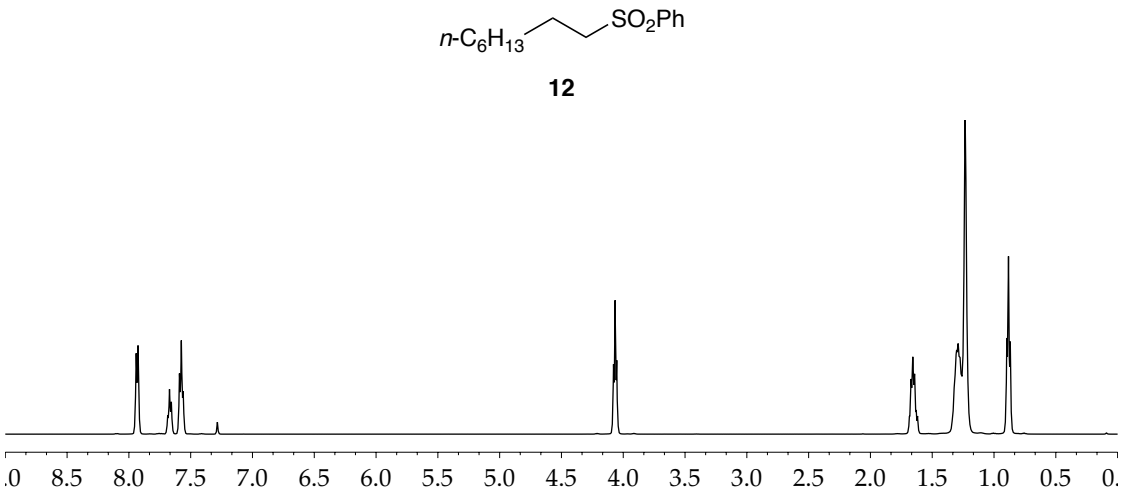


Figure S-16. ^{1}H NMR (500 MHz, $CDCl_3$) of *n*-octyl benzenesulfonate (**12**): δ 7.93 (2H, d, *J* = 8.05 Hz) 7.67 (2H, t, *J* = 7.02 Hz), 7.58 (2H, t, *J* = 7.05 Hz), 4.06 (2H, t, *J* = 6.31 Hz), 1.66 (2H, m), 1.44 (2H, m), 1.29 (2H, m), 1.23 (4H, m), 0.88 (3H, t, *J* = 7.30 Hz).

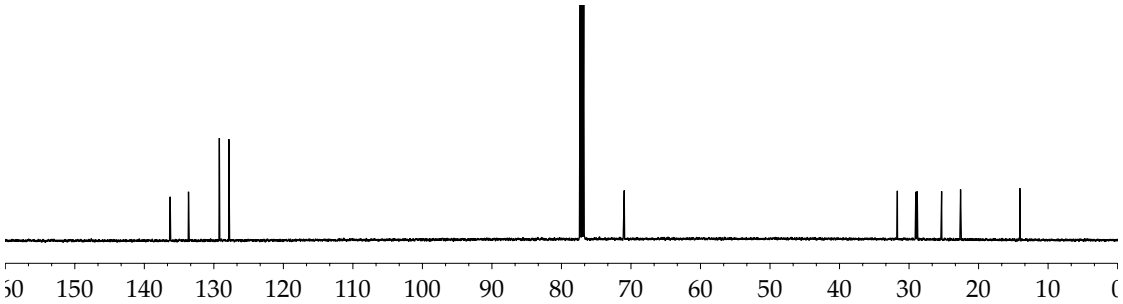


Figure S-17. ^{13}C NMR (126 MHz, $CDCl_3$) of *n*-octyl benzenesulfonate (**12**): δ 136.3, 133.6, 129.2, 127.85, 70.9, 31.6, 25.3, 22.6, 14.0.

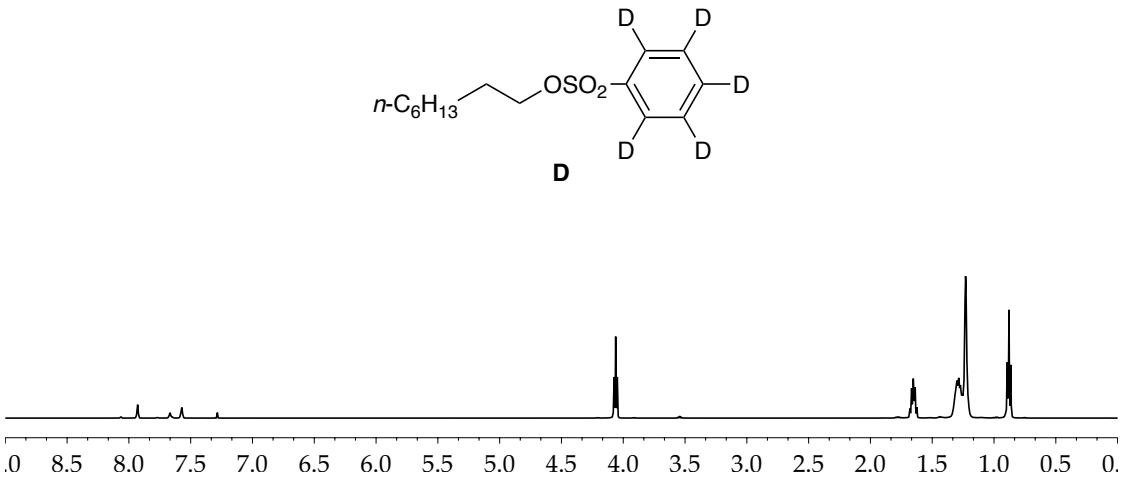


Figure S-18. ^{1}H NMR (500 MHz, $CDCl_3$) of deuterated *n*-octyl benzenesulfonate (**D**): δ 4.06 (2H, t, *J* = 6.31 Hz), 1.66 (2H, m); 1.44 (2H, m), 1.29 (2H, m), 1.23 (4H, m), 0.88 (3H, t, *J* = 7.30 Hz).

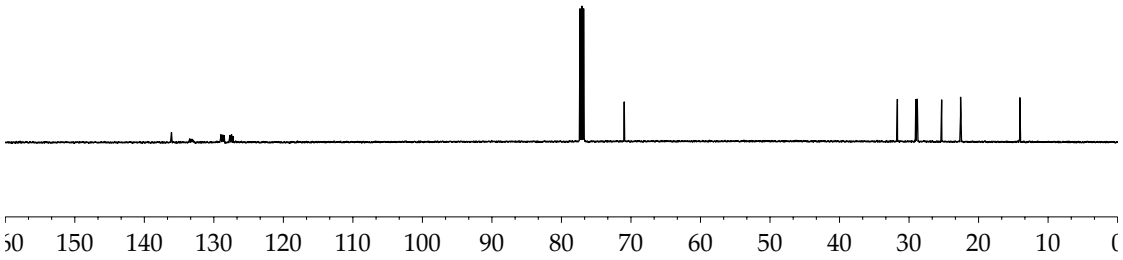
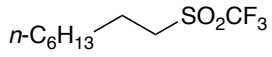


Figure S-19. ^{13}C NMR (126 MHz, $CDCl_3$) of deuterated *n*-octylbenzenesulfonate (**D**): δ 135.9, 133.2 (m), 128.8 (m), 127.5 (m), 70.7, 31.6, 25.3, 22.5, 14.0.



13

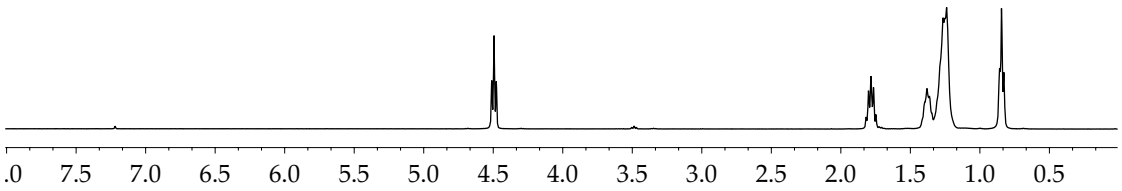


Figure S-20. ^{1}H NMR (500 MHz, $CDCl_3$) of *n*-octyl trifluoromethanesulfonate (**13**): δ 4.56 (2H, t, J = 6.71 Hz); 1.85 (2H, m), 1.45 (2H, m), 1.31 (8H, m), 0.91 (3H, t, J = 7.18 Hz).

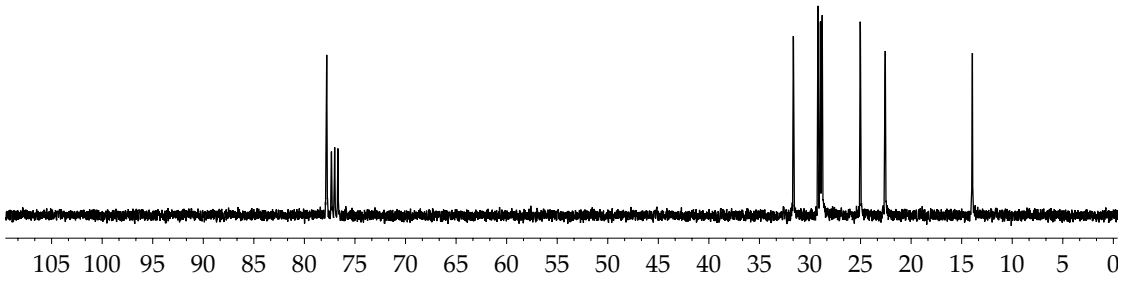


Figure S-21. ^{13}C NMR (126 MHz, $CDCl_3$) of *n*-octyl trifluoromethanesulfonate (**13**): δ 118.6 ($J_{C–D}$ = 321.4), 77.6, 29.2, 29.0, 28.7, 25.1, 22.5, 14.0.

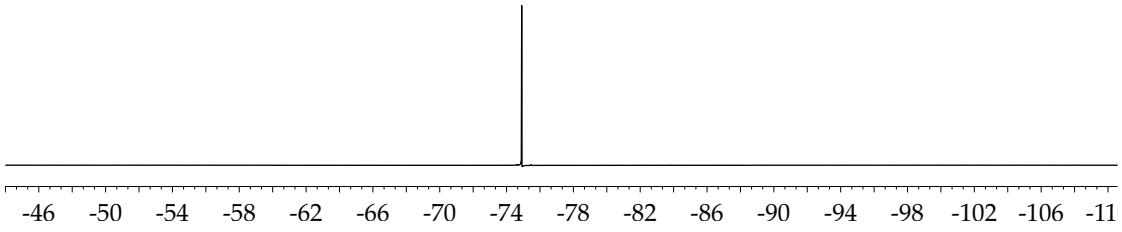
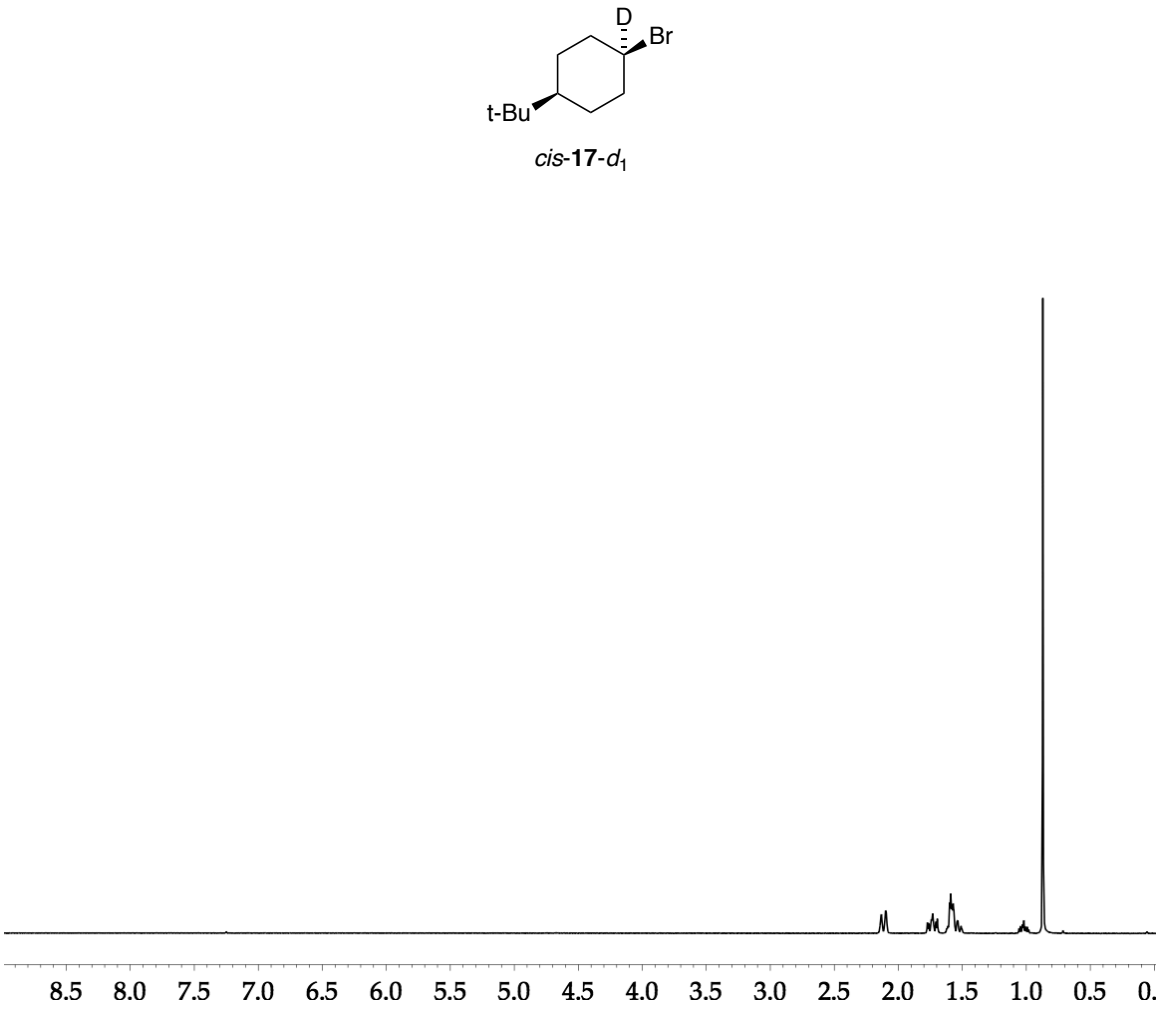


Figure S-22. ^{19}F NMR (470 MHz, $CDCl_3$) of *n*-octyl trifluoromethanesulfonate (**13**): δ –75.3.



cis-**17**-d_1

Figure S-23. ^{1}H NMR (500 MHz, $CDCl_3$) of *cis*-1-bromo-1-deuterio-4-*tert*-butylcyclohexane (*cis*-**17**-d_1): δ 2.15 (2H, m), 1.75 (2H, m), 1.61 (4H, m), 1.01 (1H, m), 0.89 (9H, s).

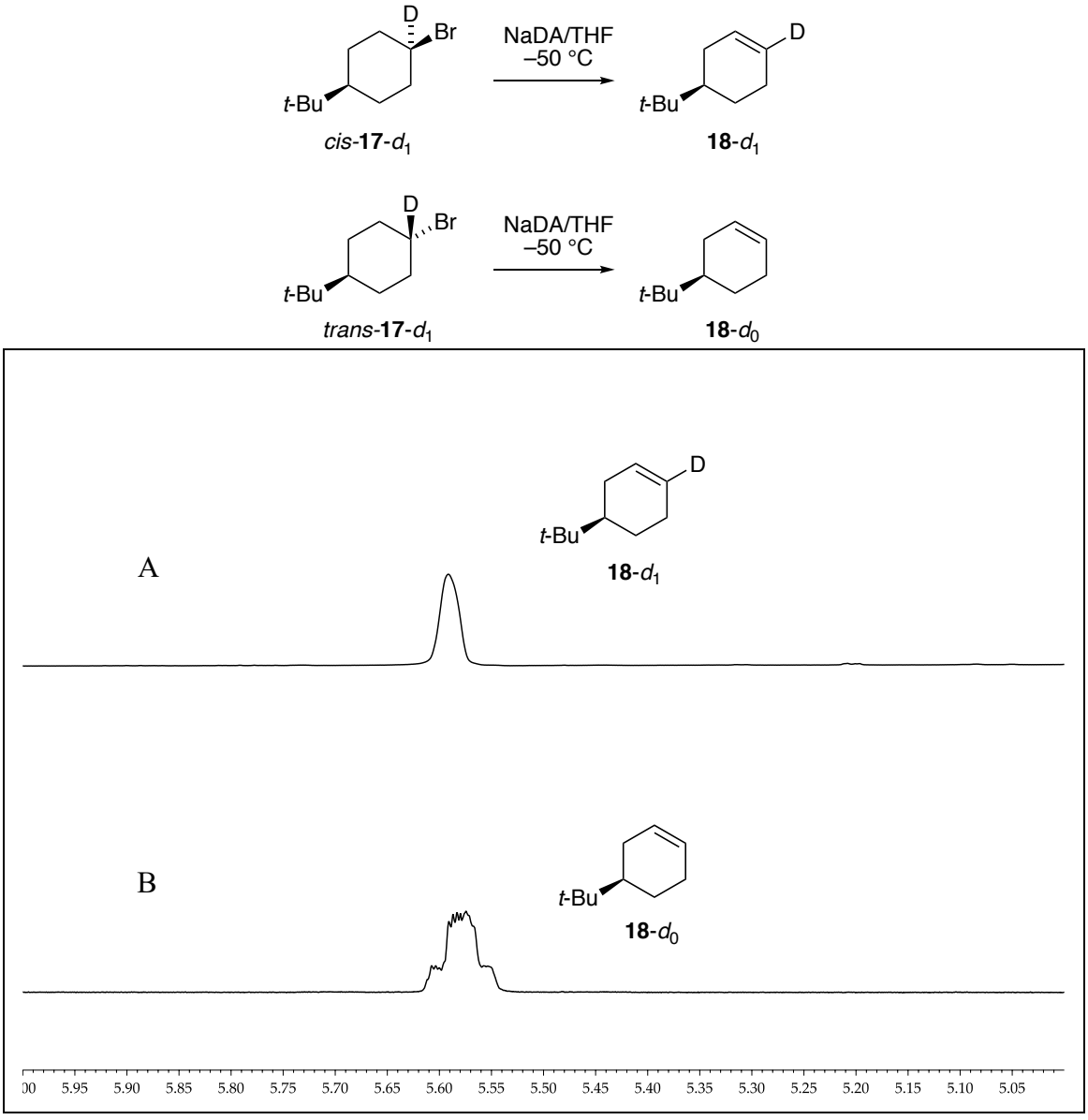


Figure S-24. ^{1}H NMR (500 MHz, 6.1 M THF/hexane) of NaDA (0.12 M) with *cis*-1-bromo-4-(*tert*-butyl)cyclohexane-1-d_1 (*cis*-**17**-d_1): (A) and *trans*-1-bromo-4-(*tert*-butyl)cyclohexane-1-d_1 (*trans*-**17**-d_1) (0.10 M) at –50 °C: (A) 4-(*tert*-butyl)-1-deuterio-cyclohex-1-ene (**18**-d_1), and (B) 4-(*tert*-butyl)cyclohex-1-ene (**18**).

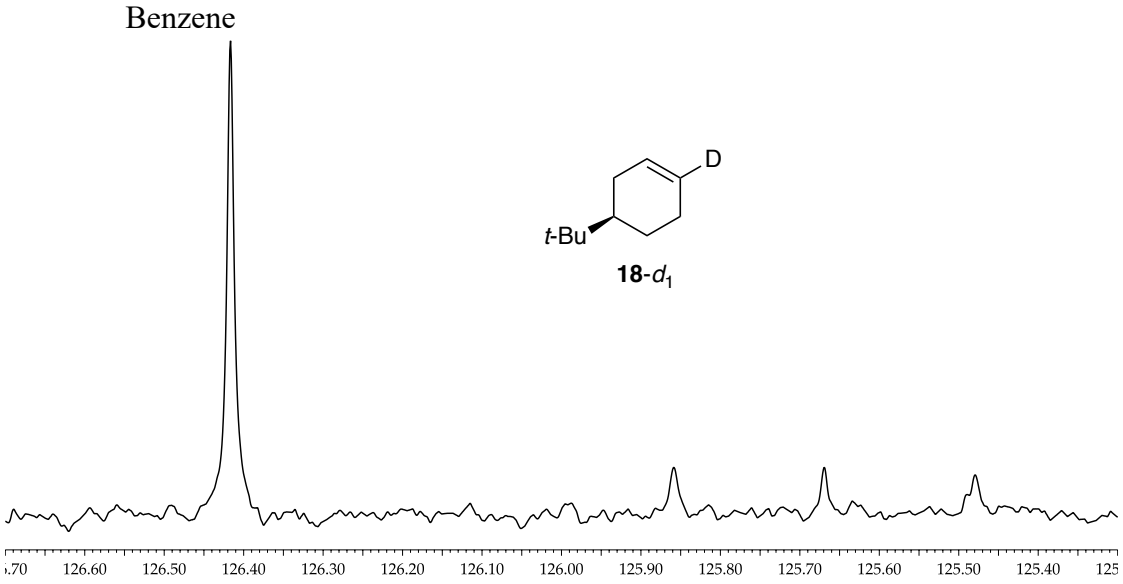


Figure S-25. ^{13}C NMR (126 MHz, 6.1 M THF/hexane) of NaDA (0.12 M) with *cis*-**17**-d_1 (0.10 M) at –50 °C: 4-(*tert*-butyl)-1-deuteriocyclohex-1-ene (**18**-d_1).

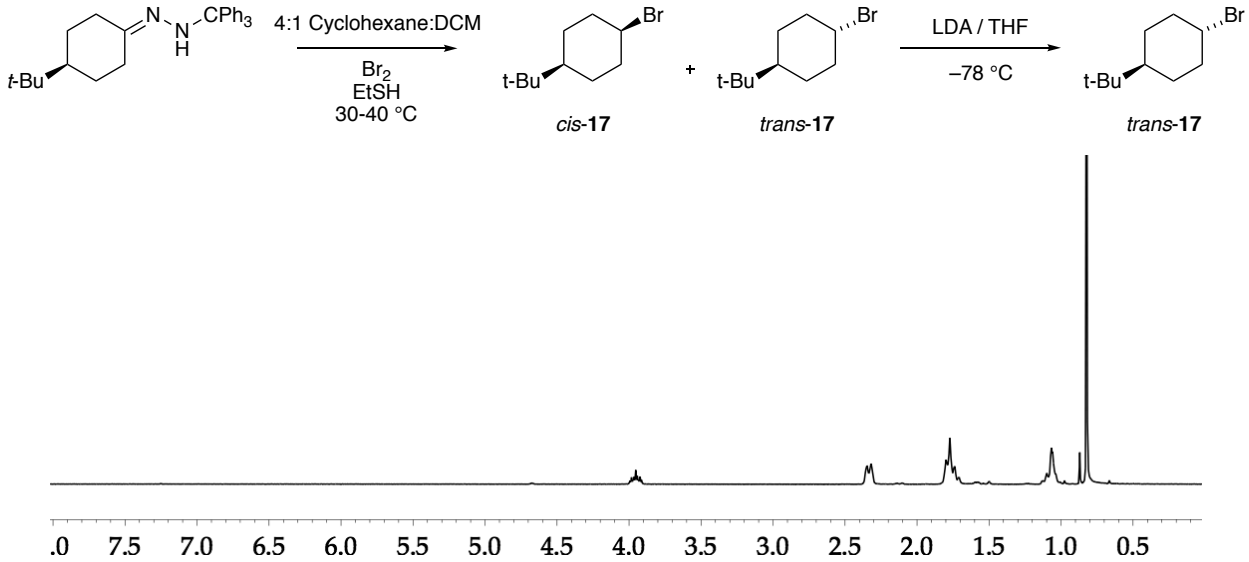


Figure S-26. ^{1}H NMR (500 MHz, $CDCl_3$) of *trans*-1-bromo-4-*tert*-butycyclohexane (*trans*-**17**): δ 3.93 (1H, m), 2.40 (4H, m), 1.78 (4H, m), 1.05 (1H, m), 0.89 (9H, s).

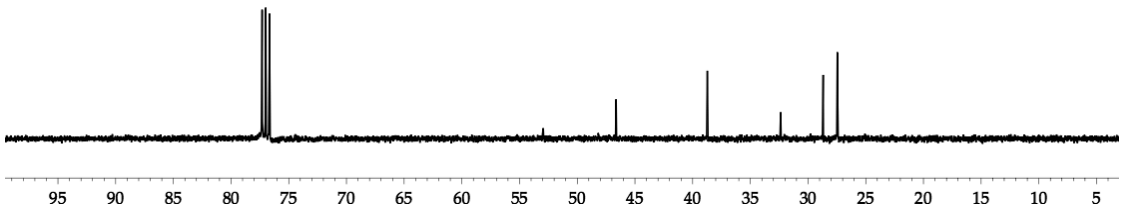
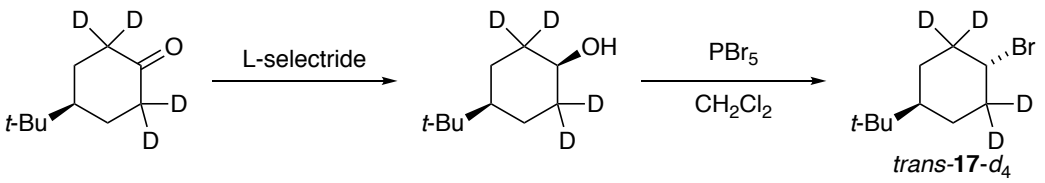


Figure S-27. ^{13}C NMR (126 MHz, $CDCl_3$) of *trans*-1-bromo-4-*tert*-butylcyclohexane (*trans*-**17**): δ 53.1, 46.8, 39.0, 32.4, 28.8, 27.8.



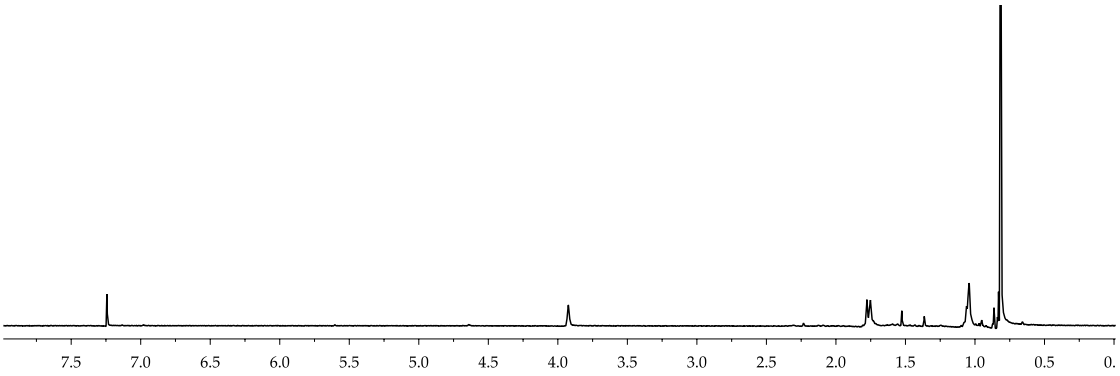


Figure S-28. ^{1}H NMR (500 MHz, $CDCl_3$) of *trans*-1-bromo-4-*tert*-butylcyclohexane (*trans*-**17**-d_4): δ 3.93 (1H, m), 1.78 (4H, m), 1.05 (1H, m), 0.89 (9H, s).

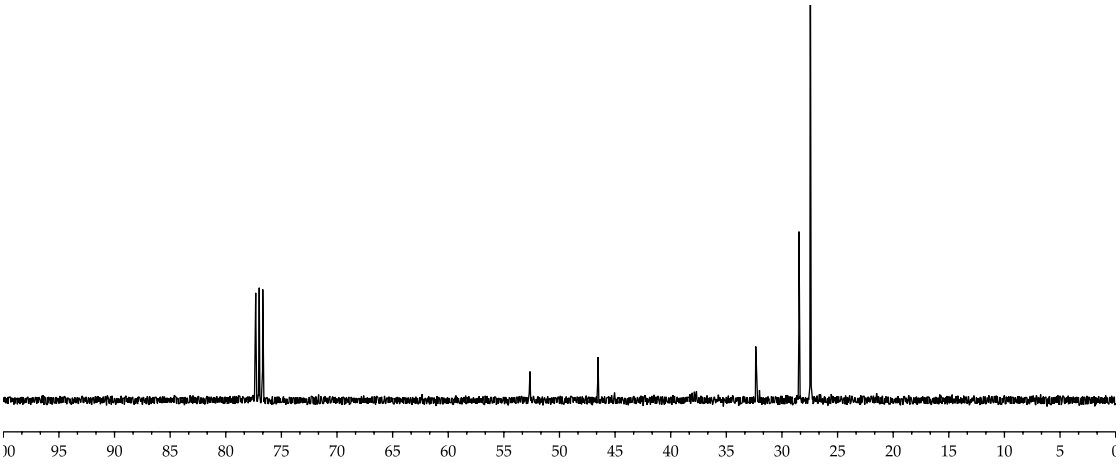


Figure S-29. ^{13}C NMR (126 MHz, $CDCl_3$) of *trans*-1-bromo-4-*tert*-butylcyclohexane (*trans*-**17**-d_4): δ 52.6, 46.5, 39.0 (m), 32.3, 28.5, 27.4.

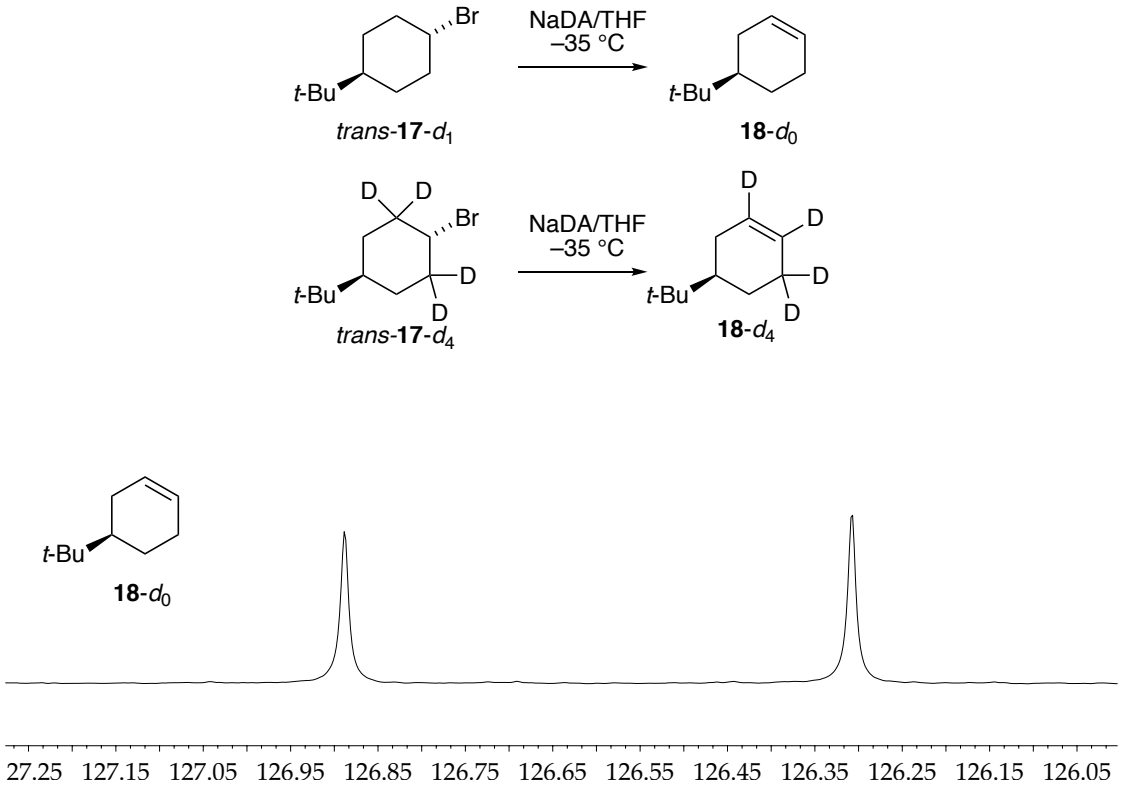


Figure S-30. Partial ^{13}C NMR (126 MHz, 6.1 M THF/hexane) of NaDA (0.12 M) with *cis*-1-bromo-4-*tert*-butylcyclohexane (*trans*-**17**, 0.10 M) at –35 °C.

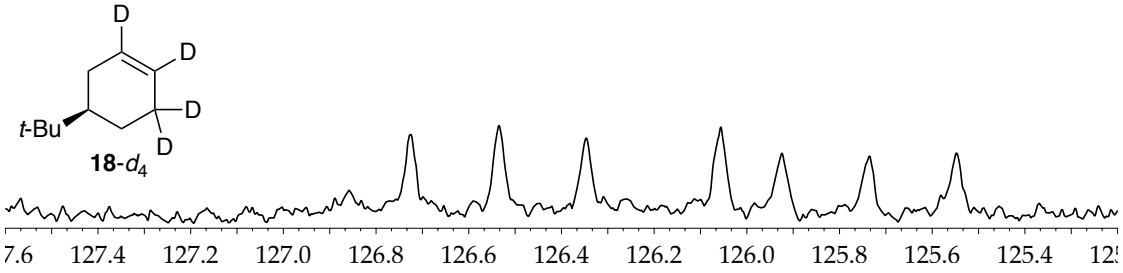
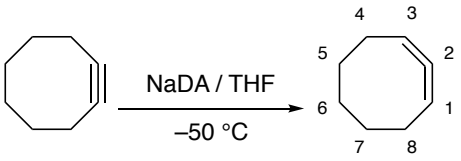


Figure S-31. ^{13}C NMR (126 MHz, 6.1 M THF/hexane) of NaDA (0.15 M) with 1-bromo-4-*tert*-butycyclohexane (*trans*-**17**-d_4, 0.10 M) at –35 °C.



27 **28**

Atom #	Chemical Shift (ppm)		HMBC correlations
	^{13}C	^{1}H	
1	95.08	5.31	3, 7eq, 8ax, 8eq
2	208.56	–	4ax, 4eq, 8ax, 8eq
3	90.51	5.11	1, 4ax, 4eq
4	31.59	1.84, 2.29	1, 5eq, 6ax, 6eq
5	27.4	1.29, 1.84	3, 6ax, 6eq
6	29.1	0.84, 1.95	5eq
7	33.35	1.33, 1.78	3, 5eq, 6ax, 6eq
8	30.05	1.91, 2.01	3, 6ax, 6eq

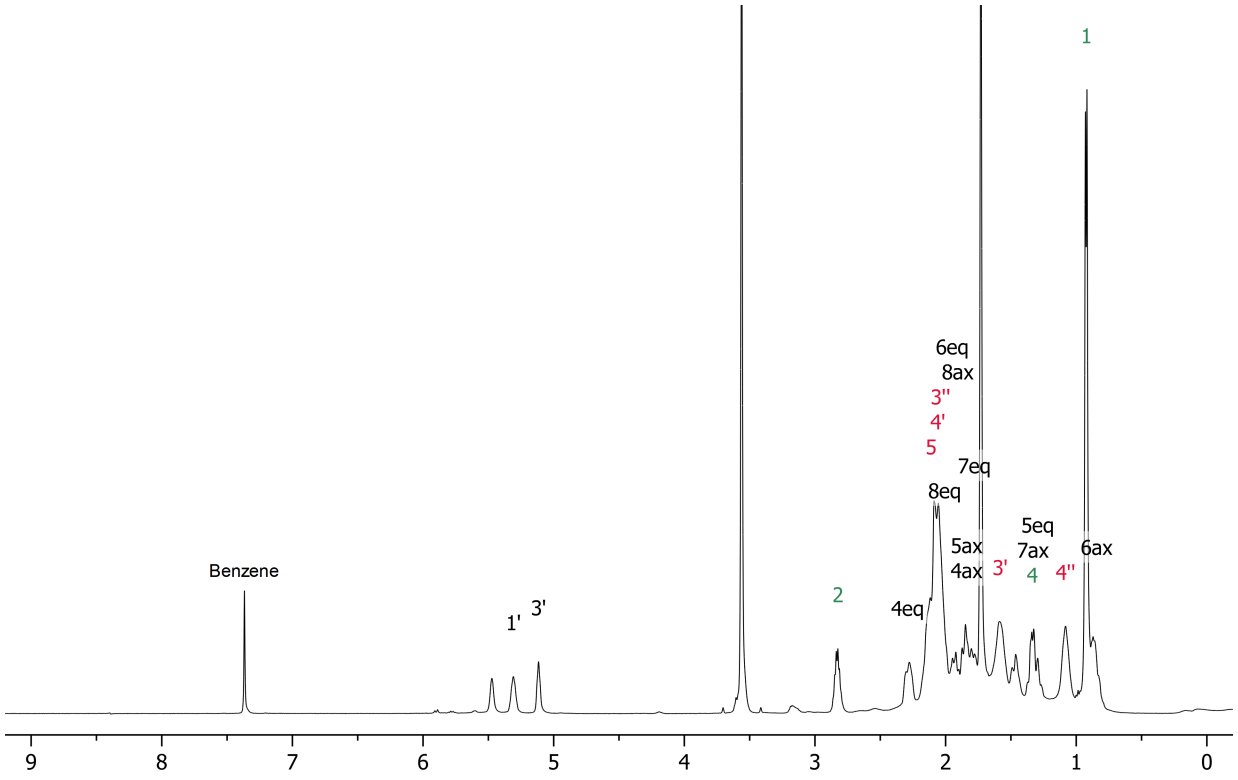


Figure S-32. ^{1}H NMR spectrum at –110 °C in THF-d_8. Numbers indicate assignments of cycloocta-1,2-diene (**28**, black), cyclooctyne (**27**, red) and diisopropylamine (green). Unassigned correlations are attributed to a minor, symmetric conformational isomer of **28**.

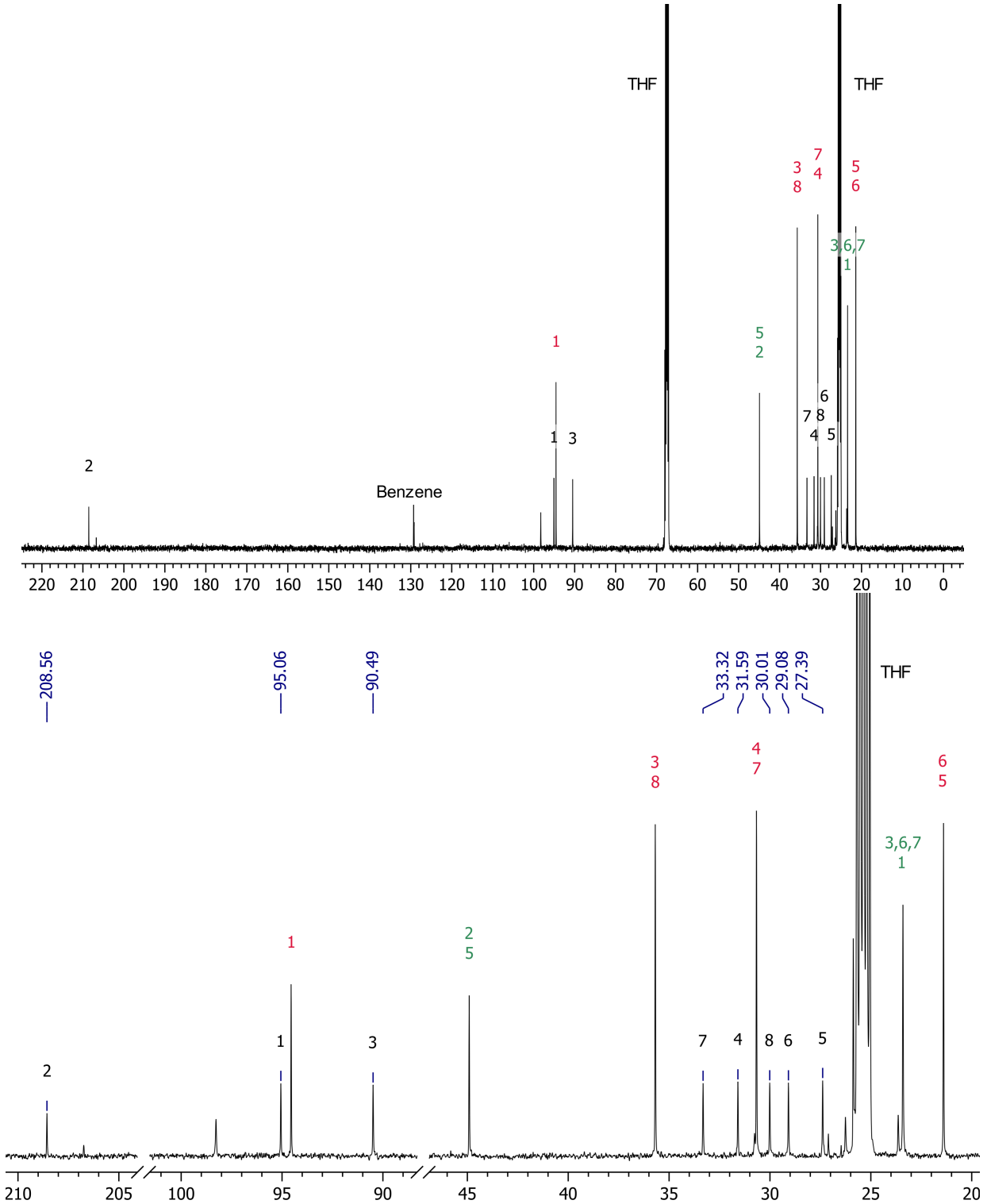


Figure S-33a and S-33b. ^{13}C NMR spectrum at –110 °C in THF-d_8. Numbers indicate assignments of cycloocta-1,2-diene (**28**, black), cyclooctyne (**27**, red) and diisopropylamine (green). Unassigned correlations are attributed to a minor, symmetric conformational isomer of **28**.

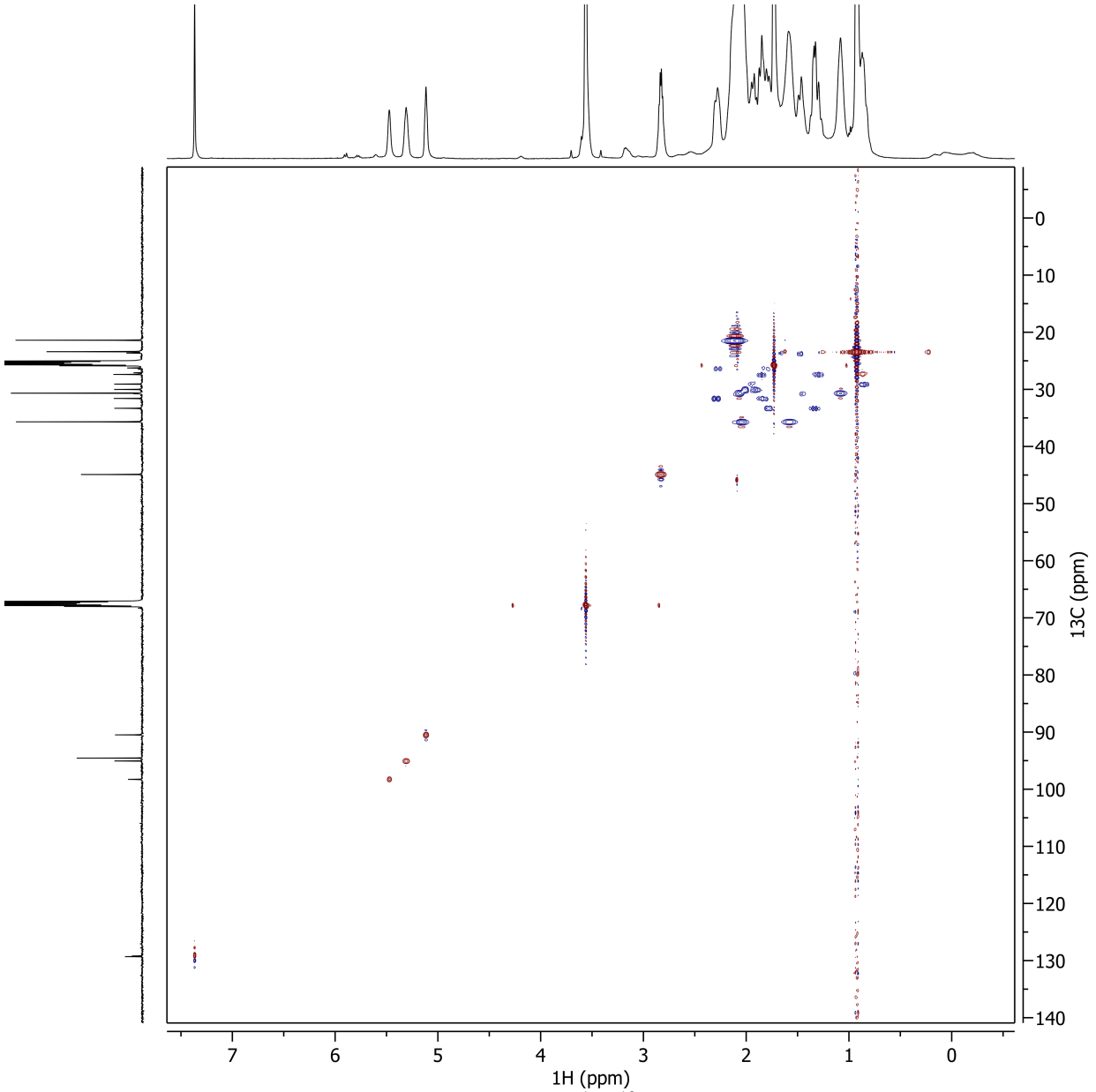


Figure S-34. Full display of multiplicity-edited 2D $^{1}H/^{13}C$ HSQC spectrum at –110 °C in THF-d_8. Red and blue contours indicate positive and negative intensities corresponding to CH/CH_3 and CH_2 groups, respectively.

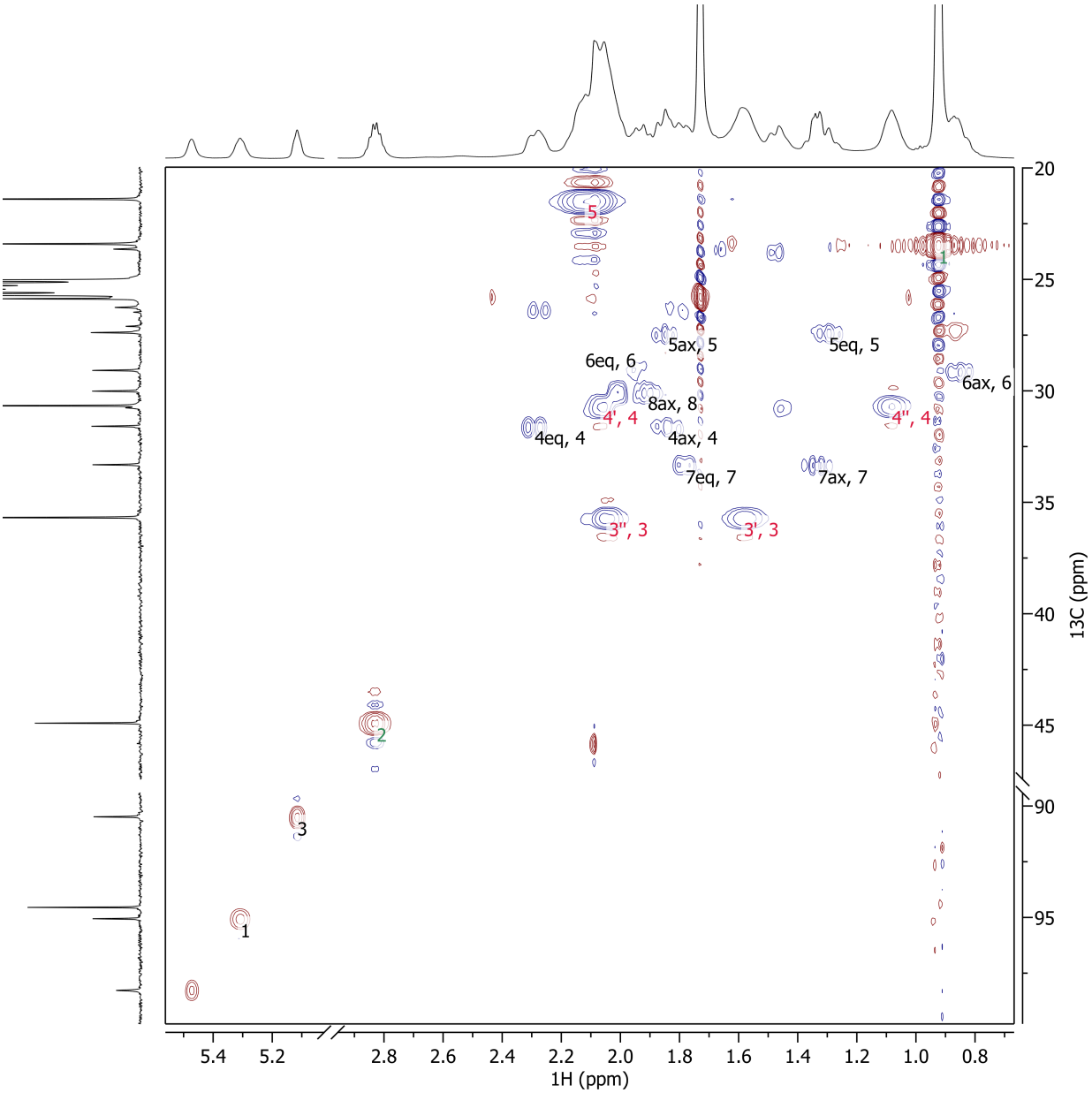


Figure S-35. Partial display of multiplicity-edited 2D $^{1}H/^{13}C$ HSQC spectrum at –110 °C in THF-d_8. Red and blue contours indicate positive and negative intensities corresponding to CH/CH_3 and CH_2 groups, respectively. Numbers indicate assignments of cycloocta-1,2-diene (**28**, black), cyclooctyne (**27**, red) and diisopropylamine (green). Unassigned correlations are attributed to a minor, symmetric conformational isomer of **28**.

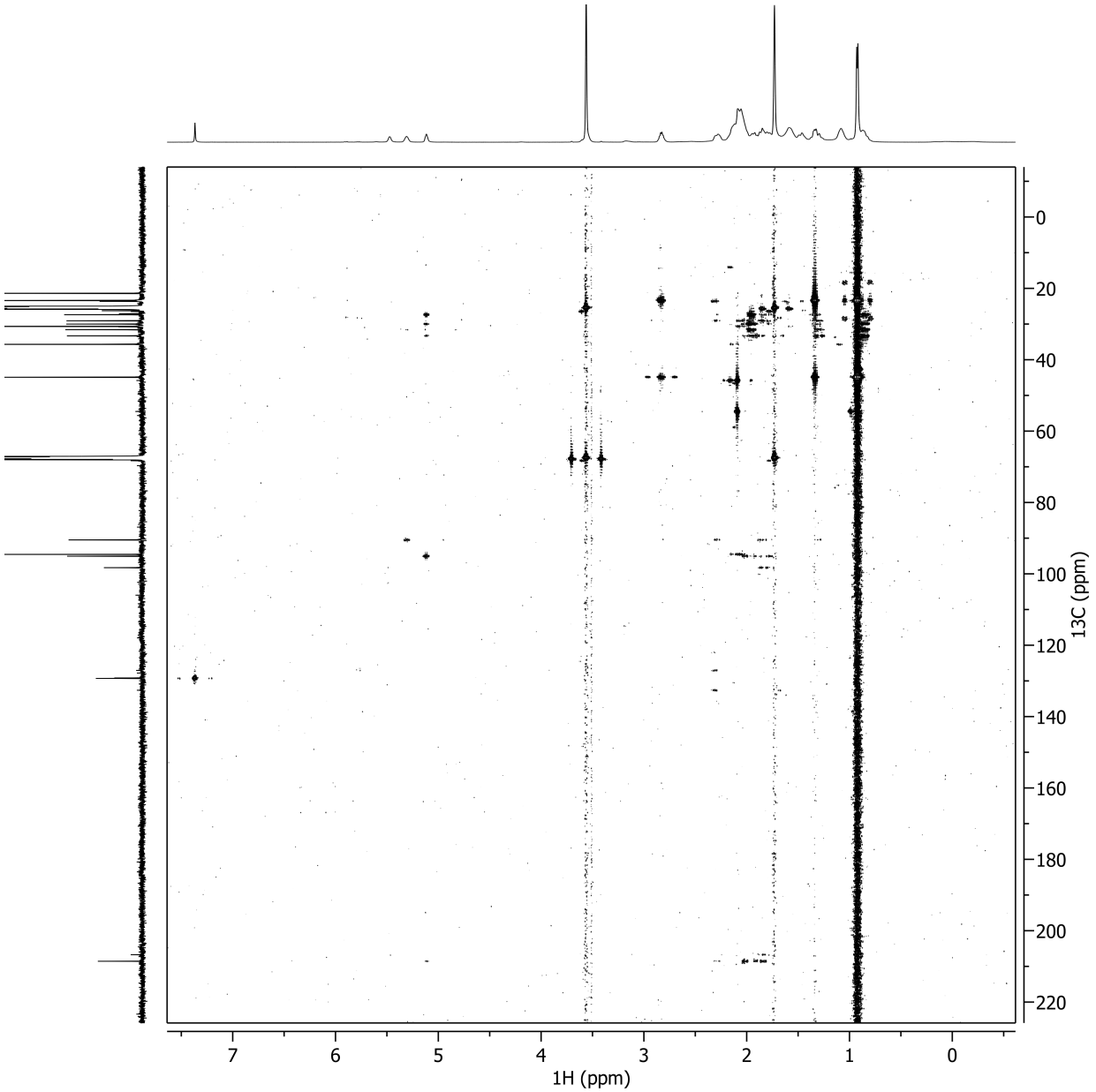


Figure S-36. Full display of 2D $^{1}H/^{13}C$ HMBC spectrum at –110 °C in THF-d_8.

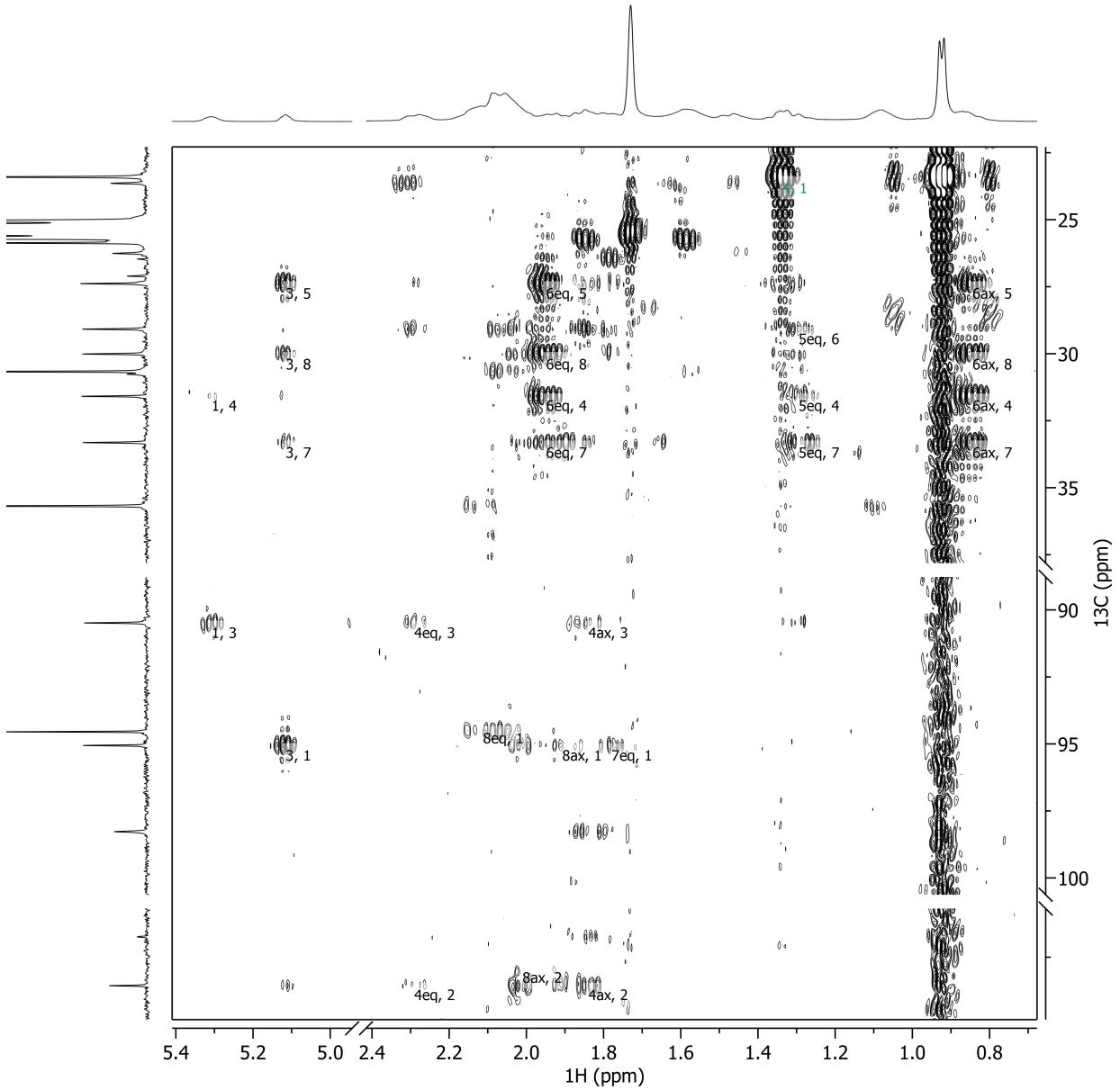


Figure S-37. Partial display of 2D $^{1}H/^{13}C$ HMBC spectrum at –110 °C in THF-d_8. Black numbers indicate crosspeak assignments for cycloocta-1,2-diene (**28**). Other assignments were omitted for clarity.

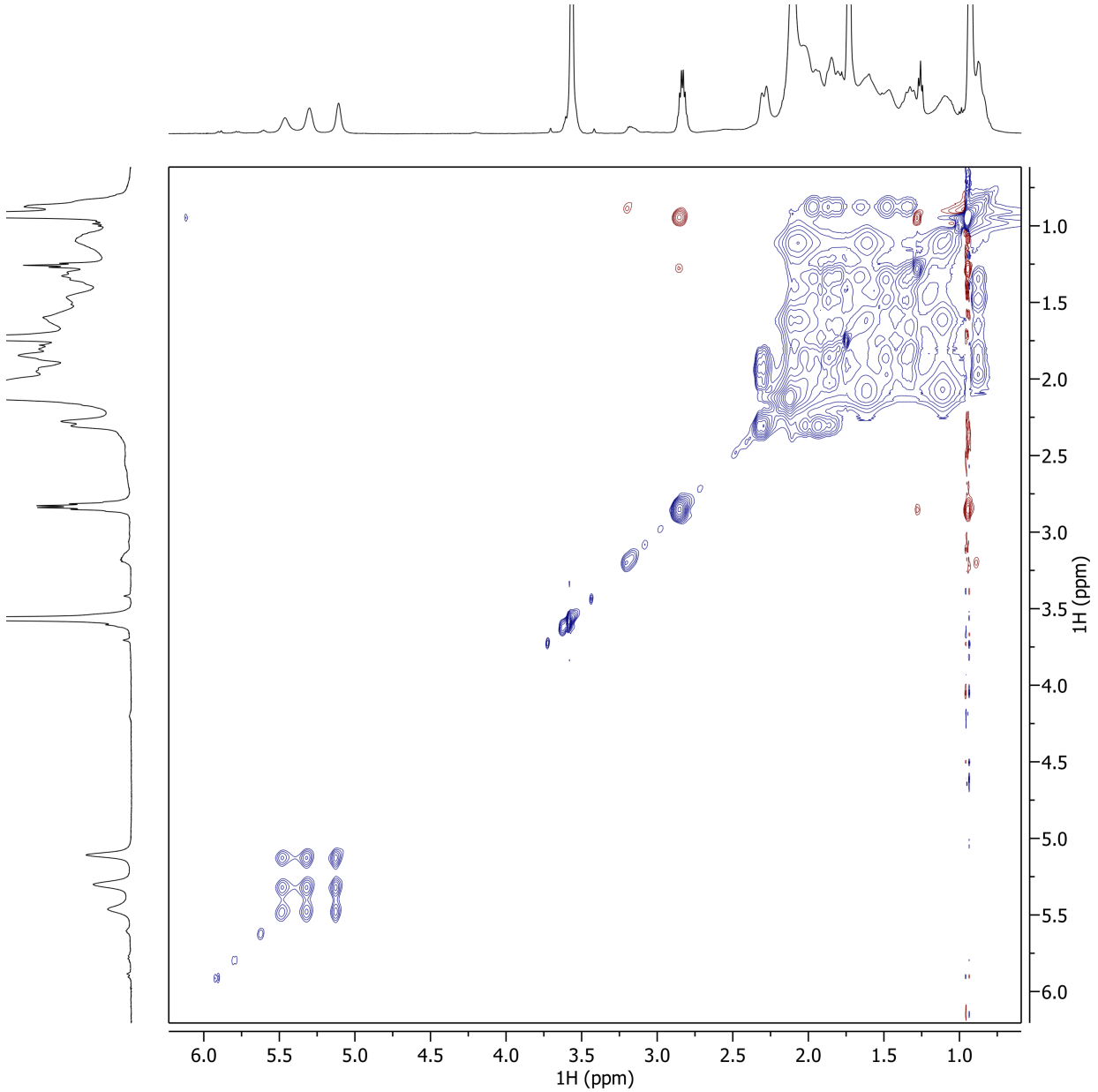


Figure S-38. Full display of 2D ^{1}H ROESY spectrum at –110 °C in THF-d_8 showing extensive exchange between symmetric and asymmetric cycloocta-1,2-diene (**28**) isomers, as well as within the major isomer. Blue contours correspond to negative intensities.

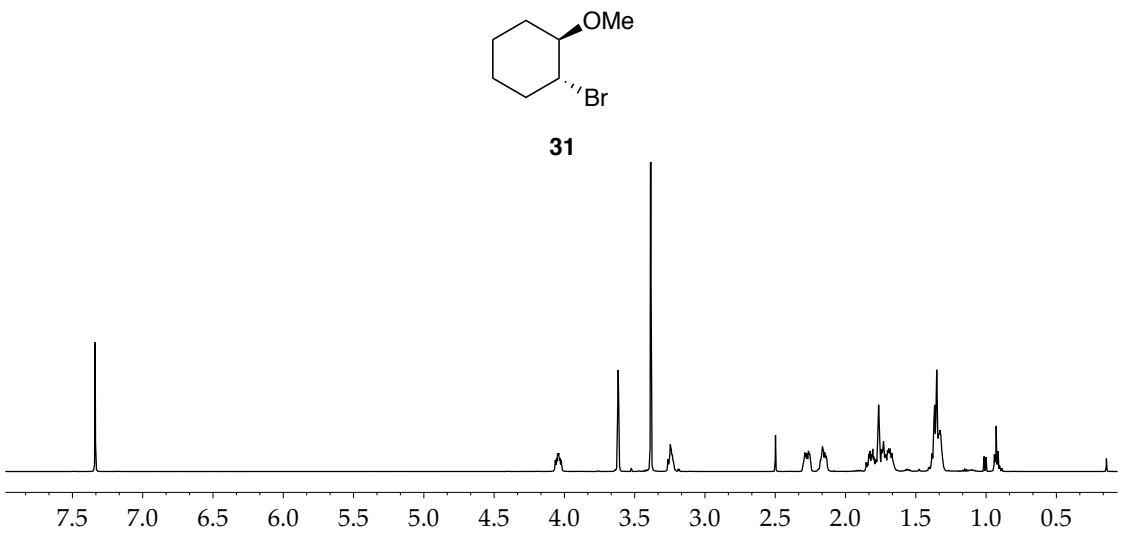


Figure S-39. ^{1}H NMR (500 MHz, THF-d_8) of *trans*-1-bromo-2-methoxycyclohexane (**31**): δ 4.05 (1H, m)), 3.38 (3H, s), 3.24 (1H, m), 2.28 (1H, m), 2.15 (1H, m), 1.72 (3H, m), 1.35 (2H, m), xxincomplete

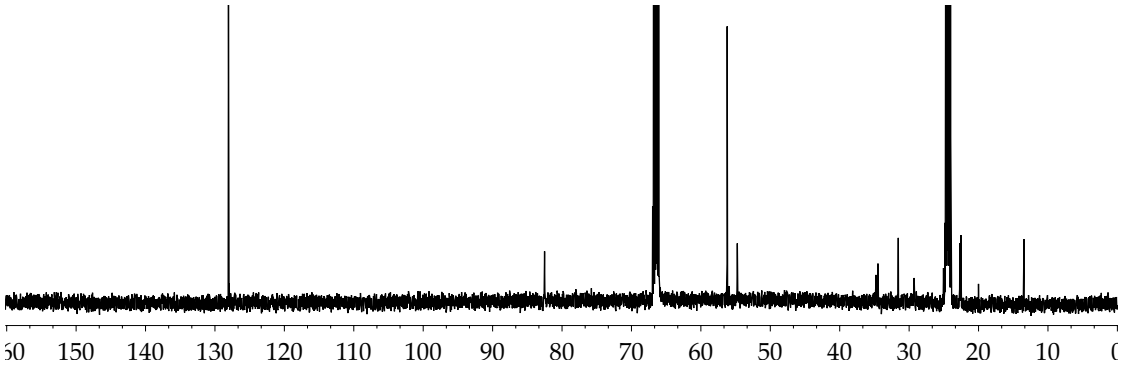


Figure S-40. ^{13}C NMR (126 MHz, THF-d_8) of *trans*-1-bromo-2-methoxycyclohexane (**31**): δ.128.2, 82.3, 56.1, 54.7, 34.4, 31.5, 29.3.

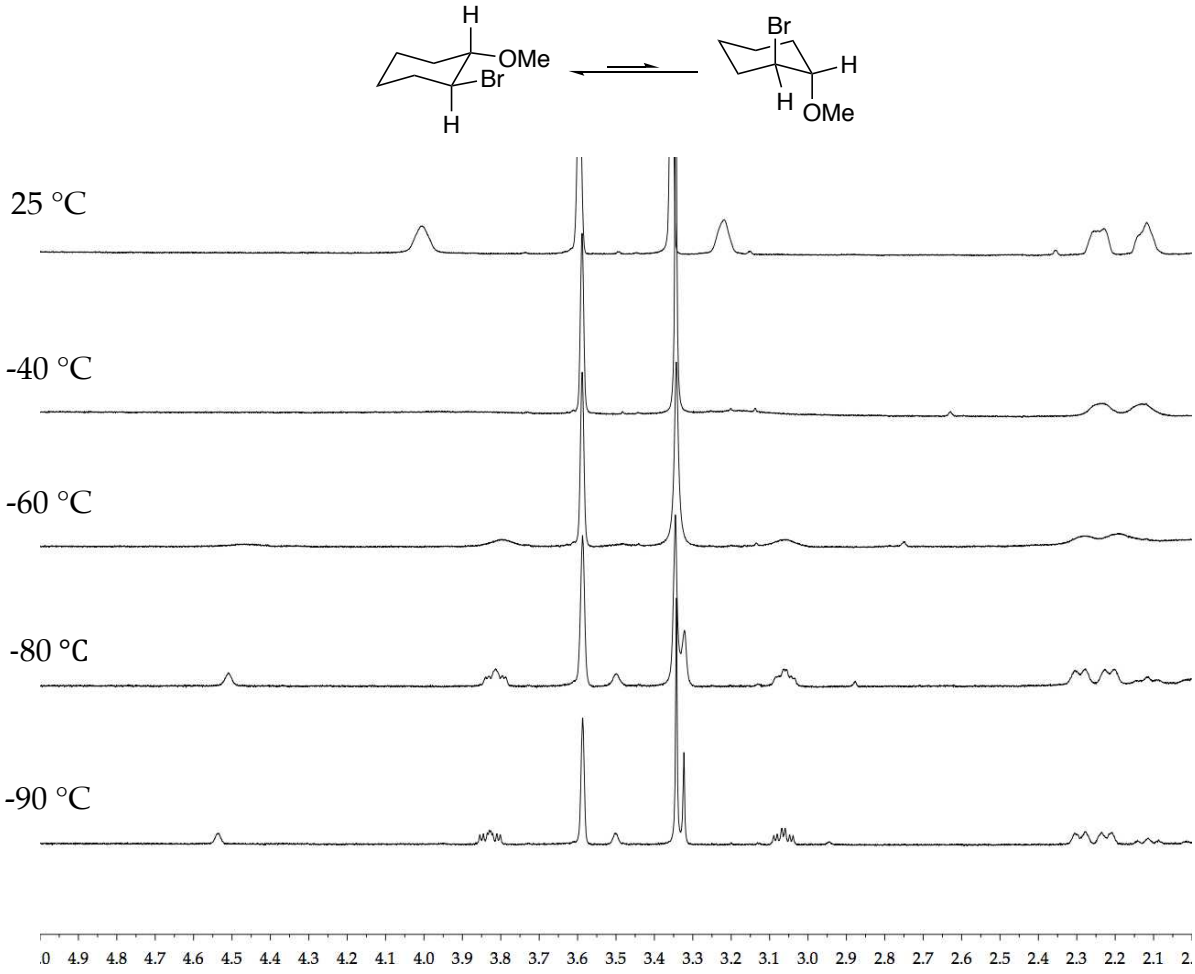


Figure S-41. ^{1}H NMR spectra of 1-bromo-2-methoxycyclohexane (**31**, 0.10 M) in 6.1 M THF/hexane, recorded at different temperatures.

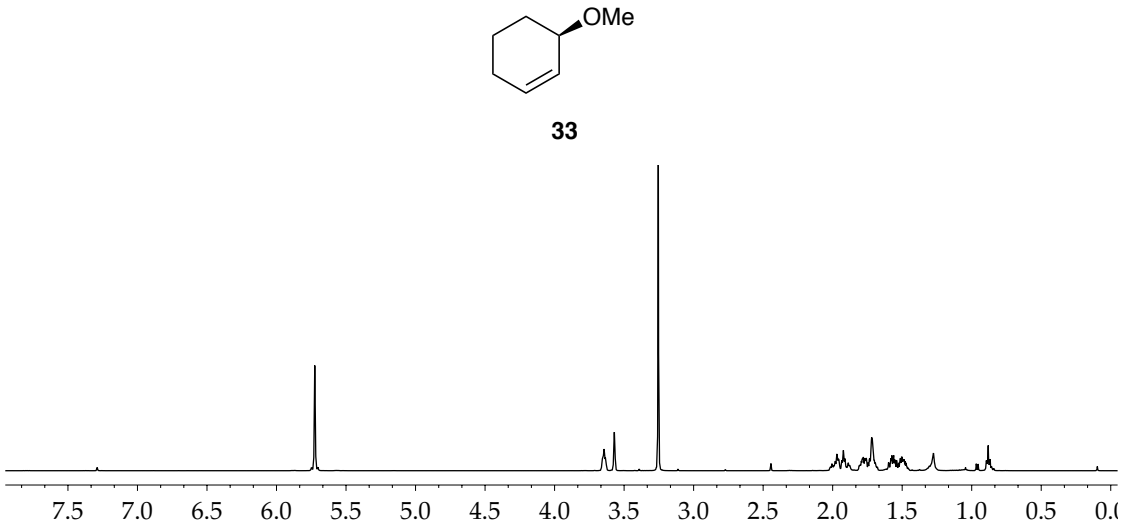


Figure S-42. ^{1}H NMR (500 MHz, THF-d_8) of 3-methoxycyclohex-1-ene (**33**): δ 5.78 (2H, m), 3.60 (1H, m), 3.25 (3H, s), 1.45–2.15 (4H, m), 0.75 (2H, m).

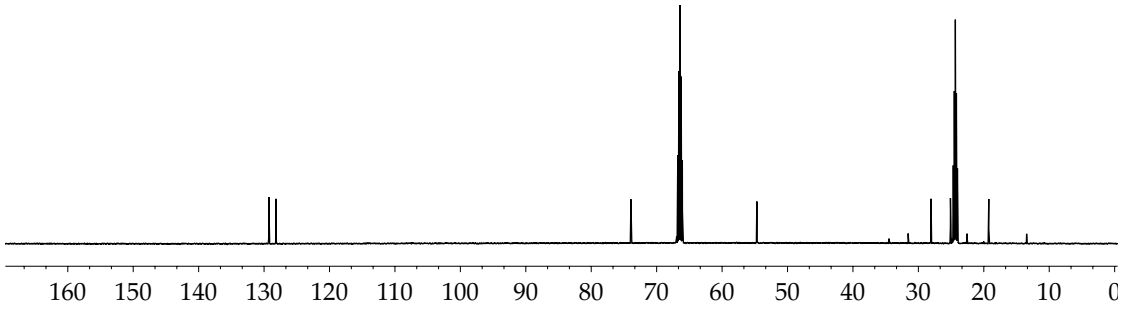


Figure S-43. ^{13}C NMR (126 MHz, THF-d_8) of 3-methoxycyclohex-1-ene (**33**): δ 129.8, 129.2, 74.6, 55.6, 35.2, 26.3, 19.8.

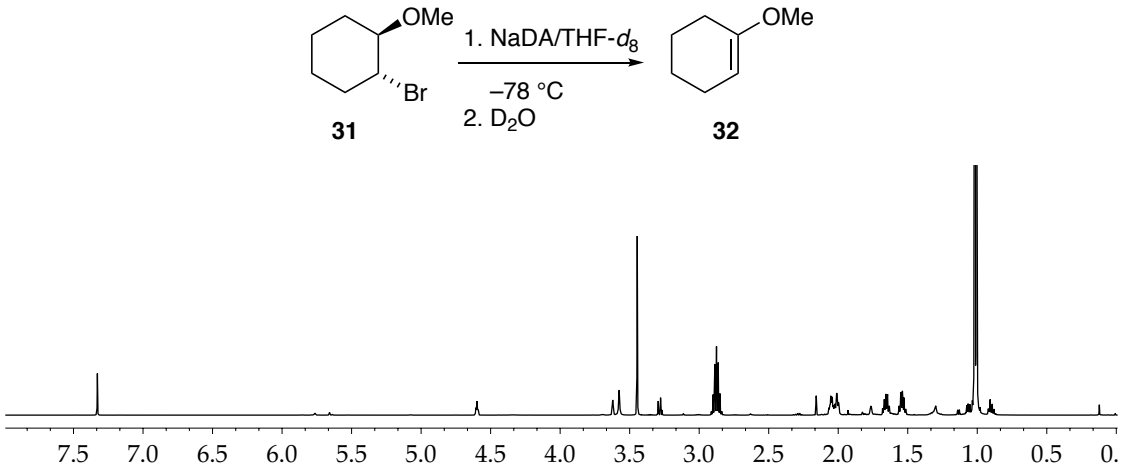


Figure S-44. ^{1}H NMR (500 MHz, THF-d_8) of 1-methoxycyclohex-1-ene (**32**): δ 4.58 (1H, m), 3.47 (3H, s), 2.15–1.85 (4H, m), 1.66–1.52 (4H, m).

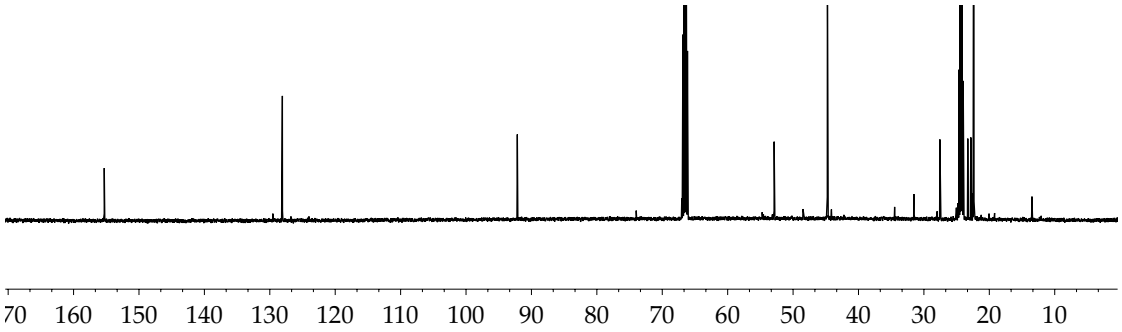


Figure S-45. ^{13}C NMR (126 MHz, THF-d_8) of 1-methoxycyclohex-1-ene (**32**): δ 155.0, 128.2, 53.1, 28.8, 23.4, 23.2, 23.0.

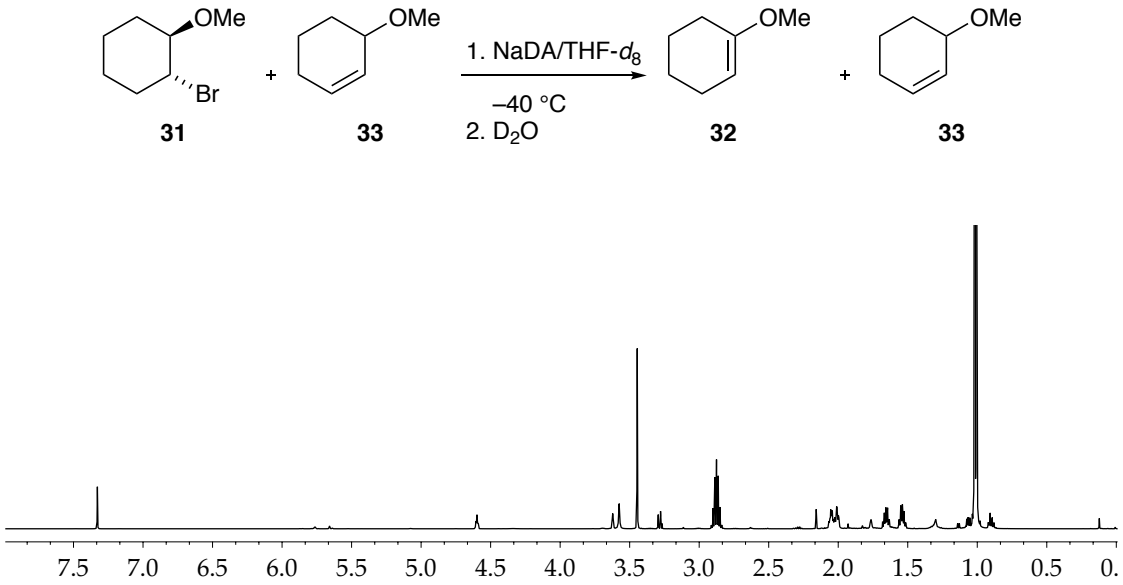


Figure S-46. ^{1}H NMR (500 MHz, THF-d_8) of 1-methoxycyclohex-1-ene (**32**) and 3-methoxycyclohex-1-ene (**33**).

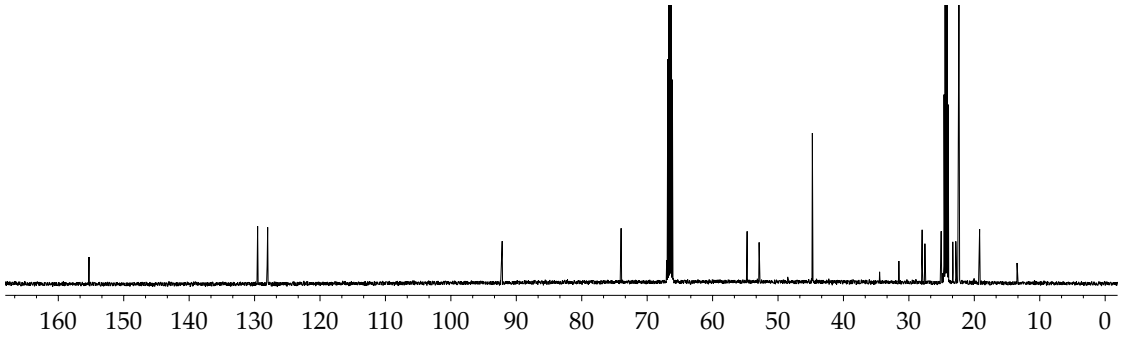


Figure S-47. ^{13}C NMR (126 MHz, THF-d_8) of 1-methoxycyclohex-1-ene (**32**) and 3-methoxycyclohex-1-ene (**33**).

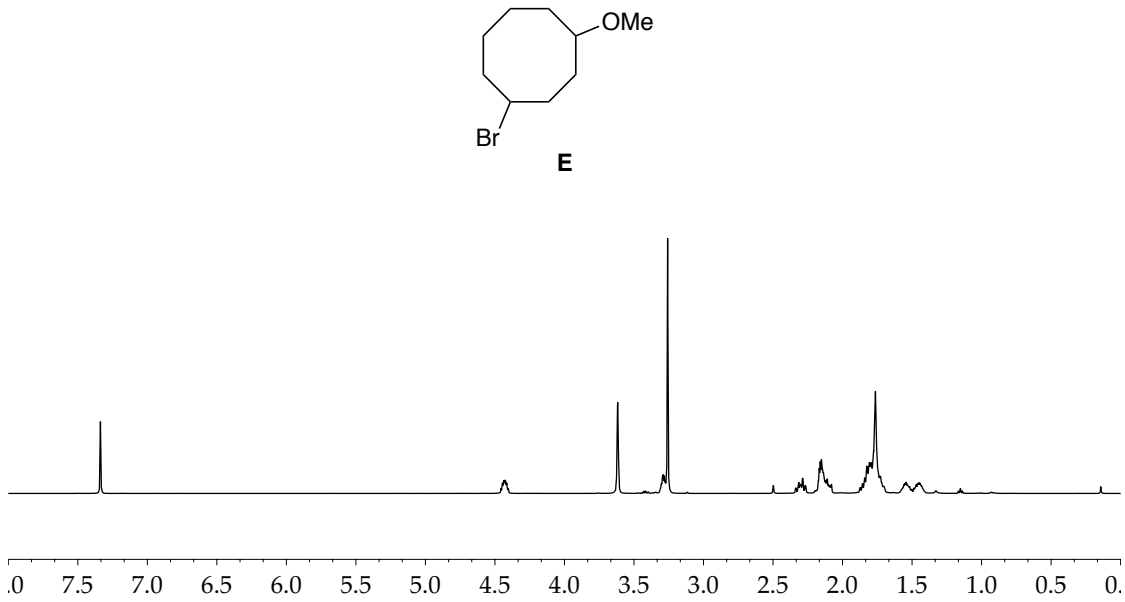


Figure S-48. ^{1}H NMR (500 MHz, THF-d_8) of 1-bromo-4-methoxycyclooctane (**E**): δ 4.45 (1H, m), 3.24 (1H, m), 3.19 (3H, s), 2.38-2.15 (6H, m), 1.86–1.50 (6H, m).

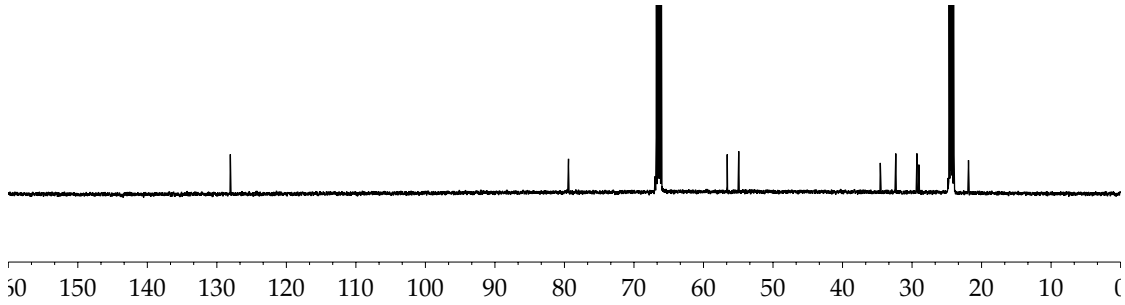


Figure S-49. ^{13}C NMR (126 MHz, THF-d_8) of 1-bromo-4-methoxycyclooctane (**E**): δ 128.2, 80.1, 56.6, 54.9, 35.0, 33.5, 28.3, 21.7.

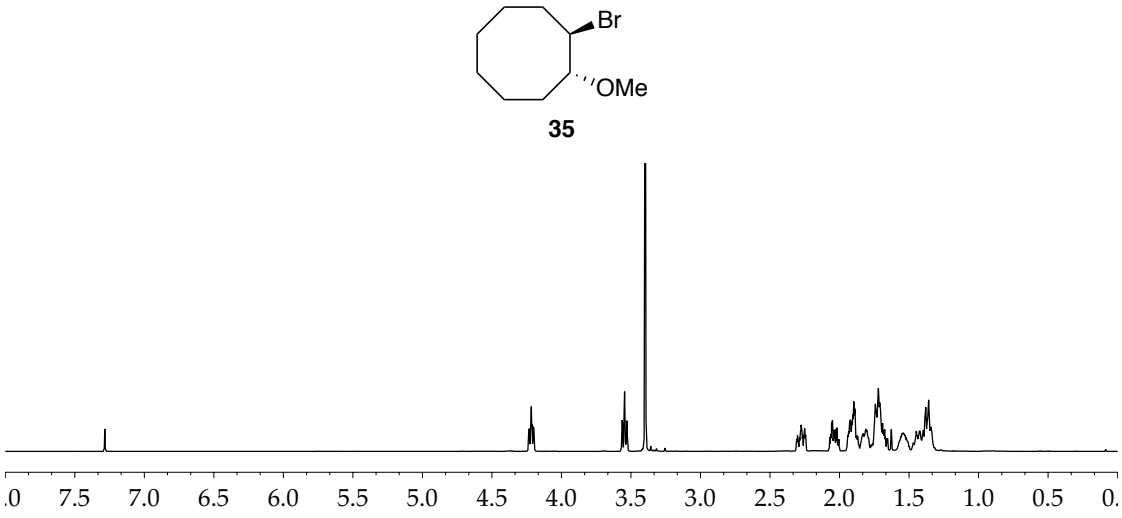


Figure S-50. ^{1}H NMR (500 MHz, $CDCl_3$) of *trans*-1-bromo-2-methoxycyclooctane (**35**): δ 5.78 (1H, m), 3.08 (1H, m), 3.46 (3H, s), 2.34–1.24 (12H, m).

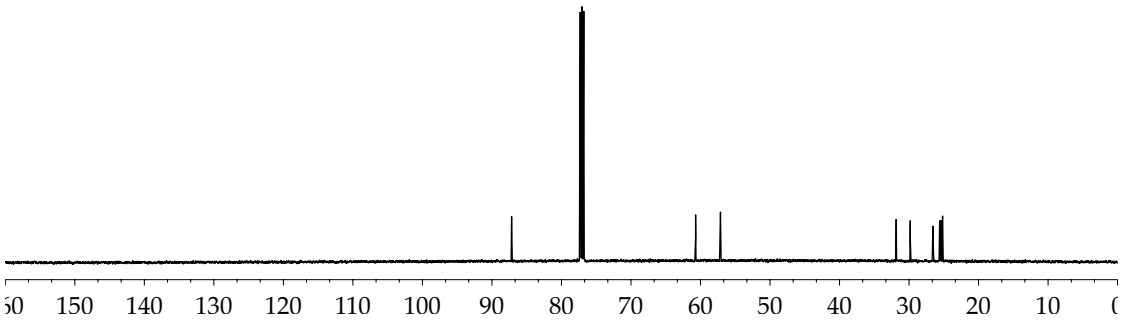


Figure S-51. ^{13}C NMR (126 MHz, $CDCl_3$) of *trans*-1-bromo-2-methoxycyclooctane (**35**): δ 86.6, 61.6, 56.7, 31.5, 29.9, 26.7, 26.0, 25.3.

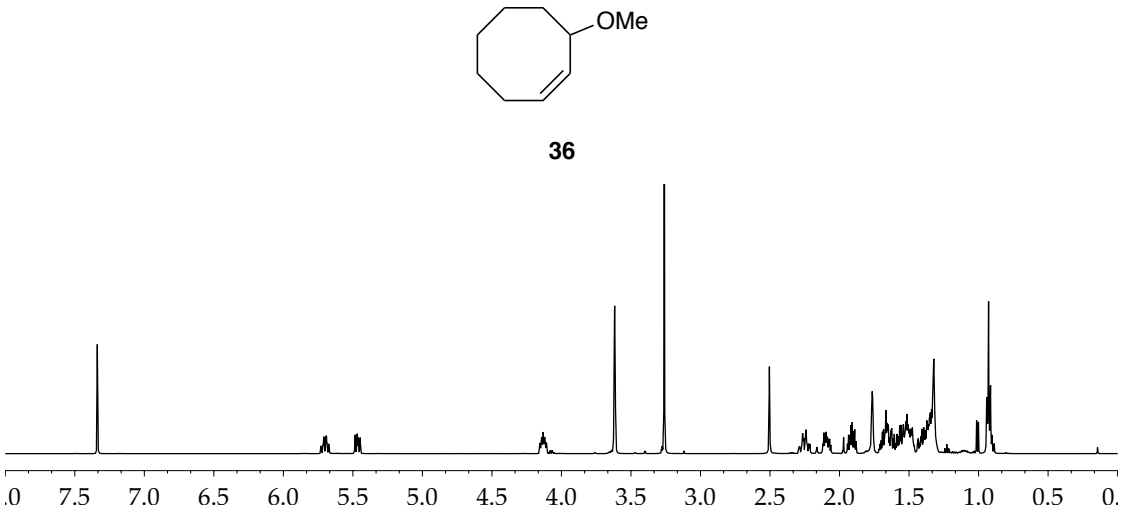


Figure S-52. ^{1}H NMR (500 MHz, THF-d_8) of (*Z*)-3-methoxycyclooct-1-ene (**36**): δ 5.65 (1H, m), 5.46 (1H, m), 4.08 (1H, m), 3.46 (3H, s), 2.45–1.2 (8H, m), 0.85 (2H, m)

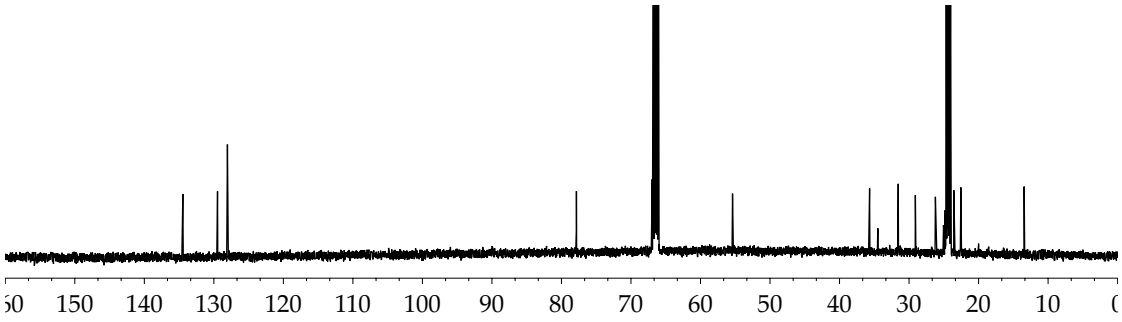


Figure S-53. ^{13}C NMR (126 MHz, THF-d_8) of (*Z*)-3-methoxycyclooct-1-ene (**36**): δ 134.8, 130.0, 126.8, 70.7, 55.1, 35.3, 31.8, 29.8, 26.7.

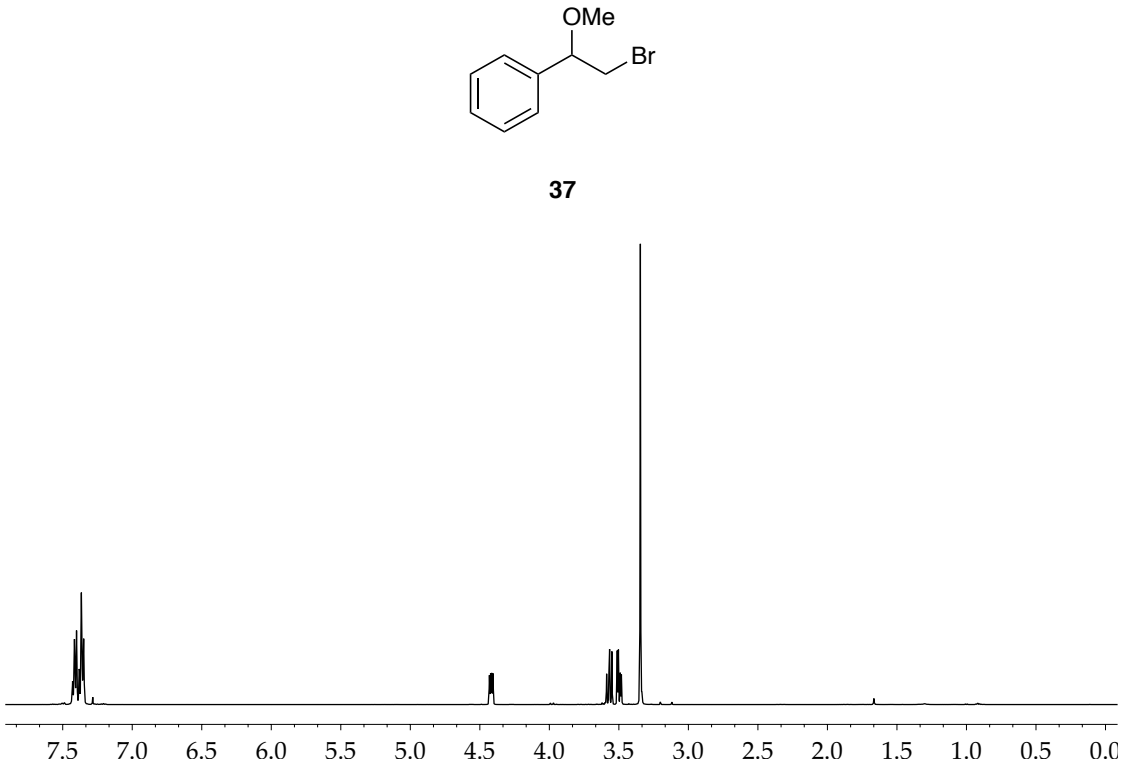


Figure S-54. ^{1}H NMR (500 MHz, $CDCl_3$) of (2-bromo-1-methoxyethyl)benzene (**37**): δ 7.47–7.33 (5H), 4.43 (1H, m), 3.09–3.45 (2H, m), 3.34 (3H, s).

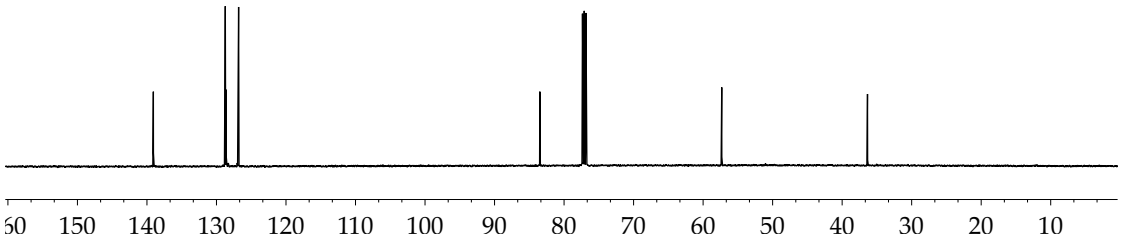


Figure S-55. ^{13}C NMR (126 MHz, $CDCl_3$) of (2-bromo-1-methoxyethyl)benzene (**37**): δ 139.8, 128.3, 126.6, 83.8, 57.1, 36.3.

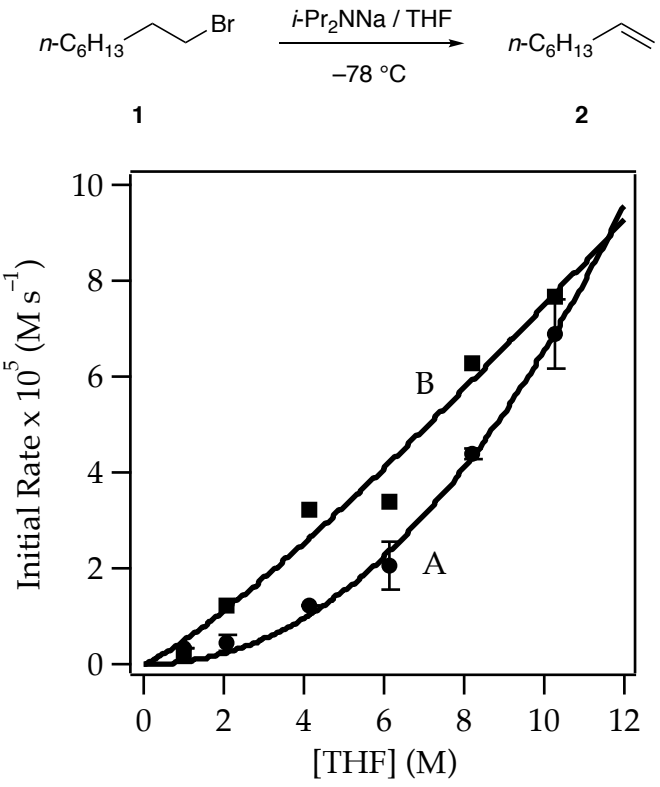


Figure S-56. Plot of initial rate versus [THF] for the dehydrobromination of 1-bromooctane (**1**) (0.050 M) with NaDA (0.10 M) at –78 °C in hexane (Curve A) or 2,5-Me_2THF (Curve B). The curves depict unweighted least-squares fits. Curve A: y = k[THF]^n: k = (5.25 ± 0.02) x 10^{-5}; n = 2.09 ± 0.16. Curve B: y = k[THF]^n: k = (0.93 ± 0.03) x 10^{-5}; n = 1.18 ± 0.17.

Curve A

[THF] (M)	y_1x10^5(Ms^{-1})	y_2x10^5(Ms^{-1})	y(avg)x10^5(Ms^{-1})
1.03	0.32	-	0.32
2.05	0.58	0.32	0.45
4.1	1.20	-	1.20
6.15	1.71	2.39	2.05
8.20	4.34	4.40	4.37
10.25	6.39	7.41	6.90

Curve B

[THF] (M)	$y_1 x 10^5 (Ms^{-1})$
1.03	0.25
2.05	1.2
4.1	3.2
6.15	3.4
8.20	6.3
10.25	7.66

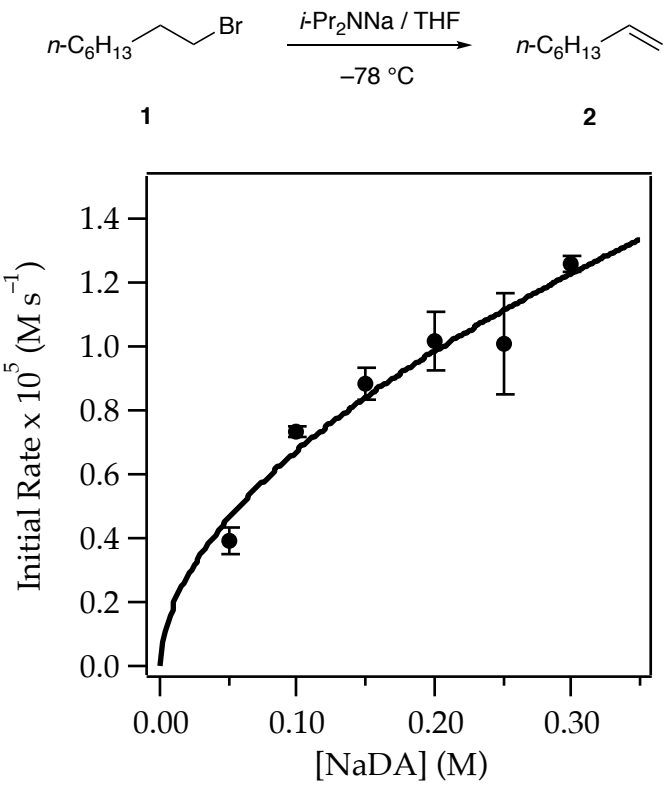


Figure S-57. Plot of initial rate versus [NaDA] in 5.10 M THF for the dehydrobromination of 1-bromooctane **1** (0.050 M) at –78 °C. The curve depicts an unweighted least-squares fit to y = k[NaDA]^n: k = (23.7 ± 3.0) x 10^{-5}; n = 0.55 ± 0.07.

[NaDA] (M)	y_1x10^5(Ms^{-1})	y_2x10^5(Ms^{-1})	y(avg)x10^5(Ms^{-1})
0.05	3.6	4.2	3.9
0.1	7.2	7.4	7.3
0.15	9.2	8.5	8.85
0.2	9.5	10.8	10.15
0.25	9.0	11.2	10.0
0.3	12.4	12.8	12.6

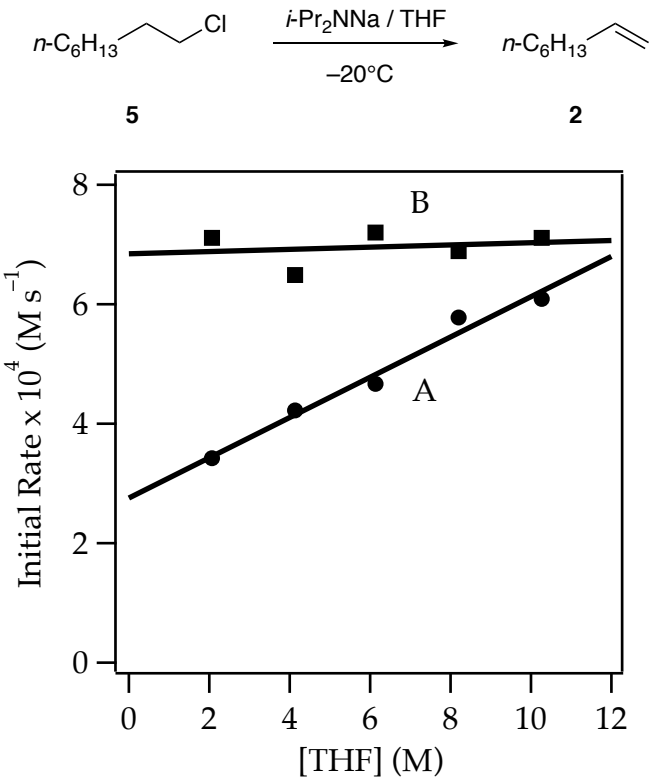


Figure S-58. Plot of initial rate versus [THF] for the dehydrochlorination of 1-chlorooctane **5** (0.050 M) with NaDA (0.10 M) at –20 °C in hexane (Curve A) or 2,5-Me_2THF (curve B). The curves depict unweighted least-squares fit to y = *k*[THF] + *k'*. Curve A: *k* = (0.37 ± 0.15) x 10^{-4}; *k'* = (2.25 ± 0.29) x 10^{-5}. Curve B: *k* = (0.02 ± 0.05) x 10^{-4}; *k'* = (6.84 ± 0.33) x 10^{-5}.

Curve A

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	3.43
4.10	4.22
6.15	4.67
8.20	5.78
10.25	6.10

Curve B

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	7.10
4.10	6.51
6.15	7.22
8.20	6.90
10.25	6.13

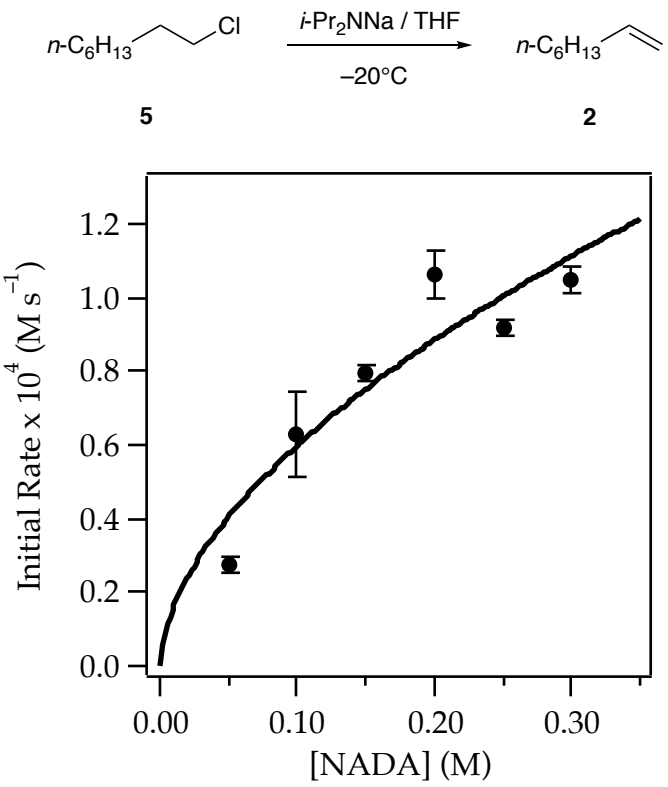
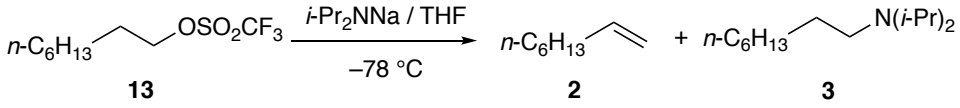


Figure S-59. Plot of initial rate versus [NaDA] in 5.10 M THF/hexane for the dehydrochlorination of 1-chlorooctane **5** (0.050 M) at –20 °C. The curve depicts an unweighted least-squares fit to $y = k[\text{NaDA}]^n$: $k = (2.2 \pm 3.0) \times 10^{-4}$; $n = 0.56 \pm 0.10$.

[NaDA] (M)	y_1 x10^4(Ms^{-1})	y_2 x10^4(Ms^{-1})	y(avg)x10^4(Ms^{-1})
0.05	0.26	0.29	0.27
0.10	0.55	0.71	0.63
0.15	0.78	0.81	0.80
0.20	1.02	1.11	1.07
0.25	0.93	0.90	0.92
0.30	1.07	1.02	1.05



13 **2** **3**

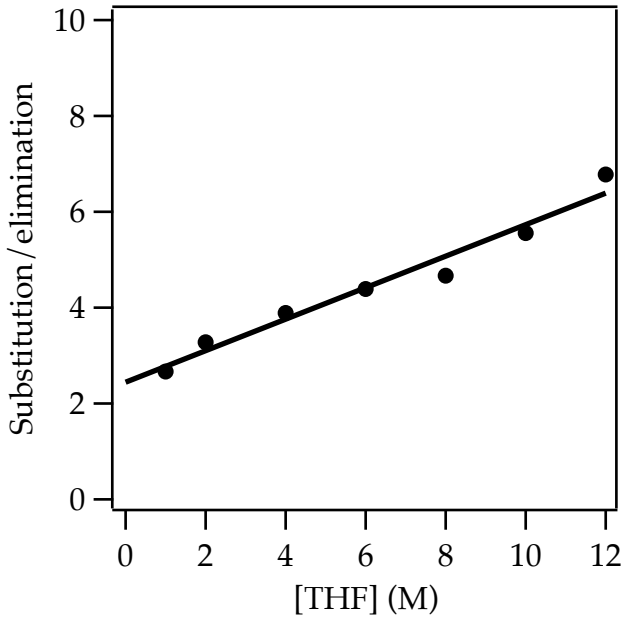
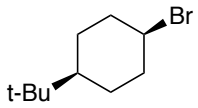


Figure S-60. Plot of [*n*-C_8H_{17}N(i-Pr)$_2$]/[1-octene] versus THF concentration in hexane for the reaction of triflate **13** (0.10 M) with NaDA (0.12 M) at –78 °C. The curve depicts an unweighted least-squares fit to y = *k*[THF] + *k'*: *k* = 0.33 ± 0.03; *k'* = 2.4 ± 0.2.

[THF] (M)	substitution/elimination
1.0	2.7
2.0	3.3
4.0	3.9
6.0	4.4
8.0	4.7
10.0	5.5
12.0	6.7



cis-**17**

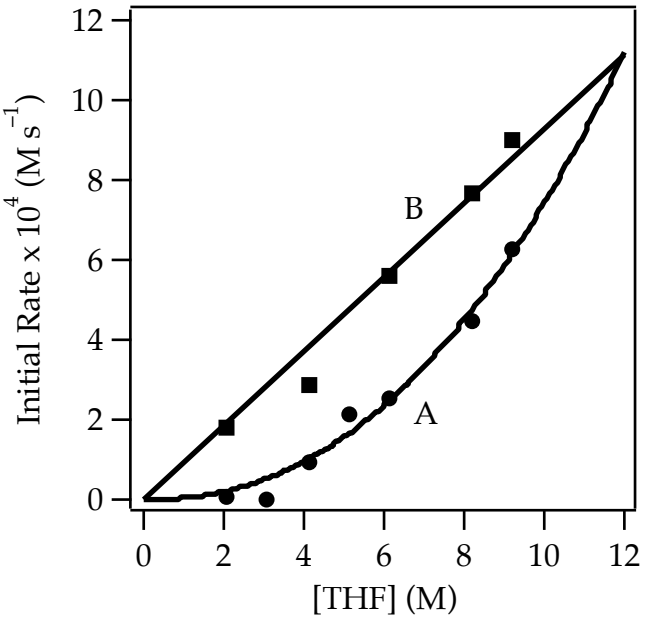


Figure S-61. Plot of initial rate versus [THF] for the dehydrobromination of *cis*-**17** (0.050 M) with NaDA (0.10 M) at –50 °C in hexane (curve A) or 2,5-Me_2THF (curve B). The curves depict unweighted least-squares fits. Curve A: $y = k[\text{THF}]^n$: $k = (3.23 \pm 0.01) \times 10^{-6}$; $n = 2.39 \pm 0.24$. Curve B: $y = k[\text{THF}]$: $k = (0.93 \pm 0.03) \times 10^{-4}$.

Curve A

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	0.042
3.08	0.032
4.10	0.95
6.15	1.25
8.20	2.54
9.23	6.30

Curve B

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	1.80
4.10	2.92
6.15	5.61
8.20	7.70
9.23	9.02

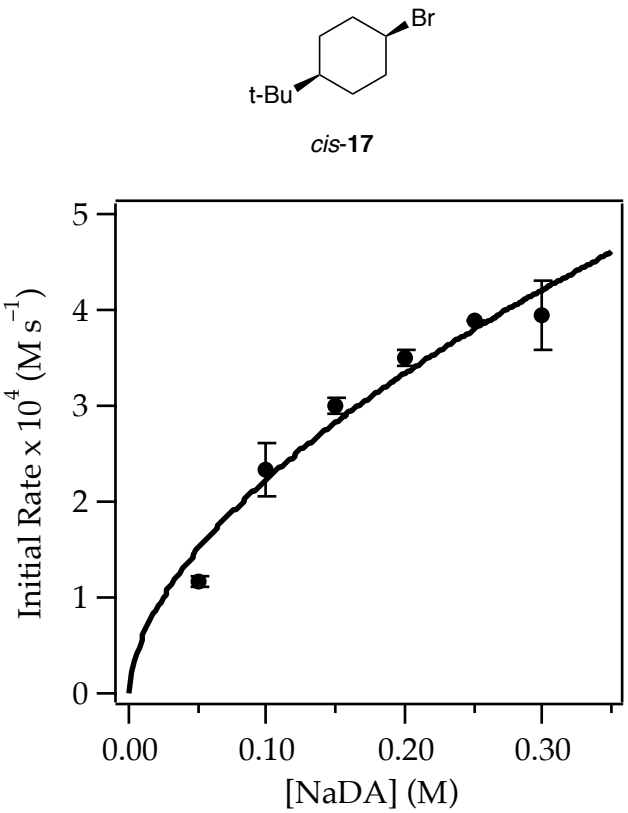


Figure S-62. Plot of initial rate versus [NaDA] in THF (5.10 M) for the dehydrobromination of *cis*-1-bromo-4-*tert*-butylcyclohexane *cis*-**17** (0.050 M) at –50 °C. The curve depicts an unweighted least-squares fit to $y = k[\text{NaDA}]^n$: $k = (8.4 \pm 0.1) \times 10^{-4}$; $n = 0.58 \pm 0.08$.

[NaDA] (M)	$y_1 \times 10^4$ (Ms^{-1})	$y_2 \times 10^4$ (Ms^{-1})	y(avg)$\times 10^4$ (Ms^{-1})
0.05	1.20	1.14	1.17
0.10	2.54	2.14	2.34
0.15	2.95	3.05	3.00
0.20	3.43	3.56	3.50
0.25	3.89	3.90	3.90
0.30	4.2	3.68	3.94

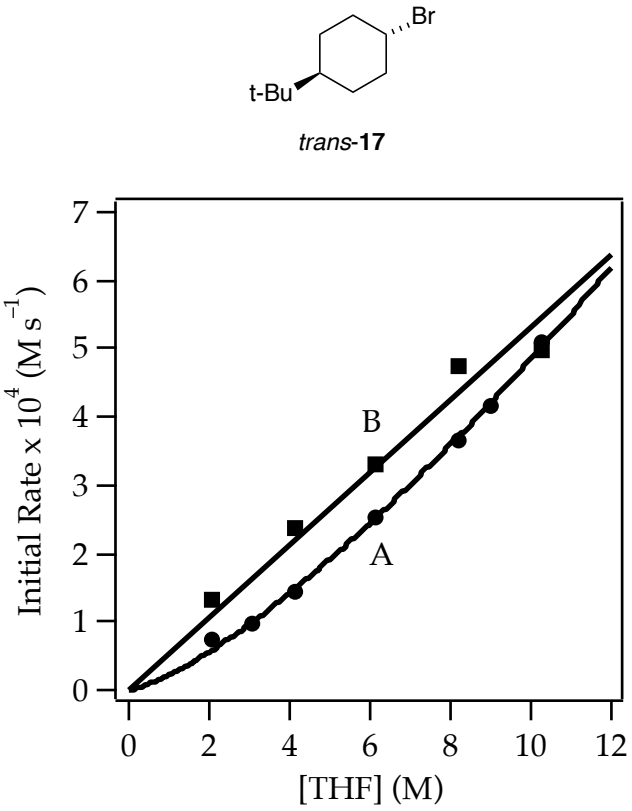


Figure S-63. Plot of initial rate versus [THF] for the dehydrobromination of *trans*-1-bromo-4-(*tert*-butyl)cyclohexane *trans*-**17** (0.050 M) with NaDA (0.13 M) at –25 °C in hexane (A) or 2,5-Me_2THF (B). The curves depict unweighted least-squares fits. Hexane: y = k[THF]^n: k = (1.11 ± 0.2) x 10^{-4}; n = 1.34 ± 0.04. Me_2THF: y = k[THF]: k = (0.53 ± 0.02) x 10^{-4}.

Curve A

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	0.75
3.08	0.98
4.10	1.44
6.15	2.51
8.20	3.66
9.00	4.16
10.25	5.10

Curve B

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	1.33
4.10	2.37
6.15	3.30
8.20	4.76
10.25	4.97

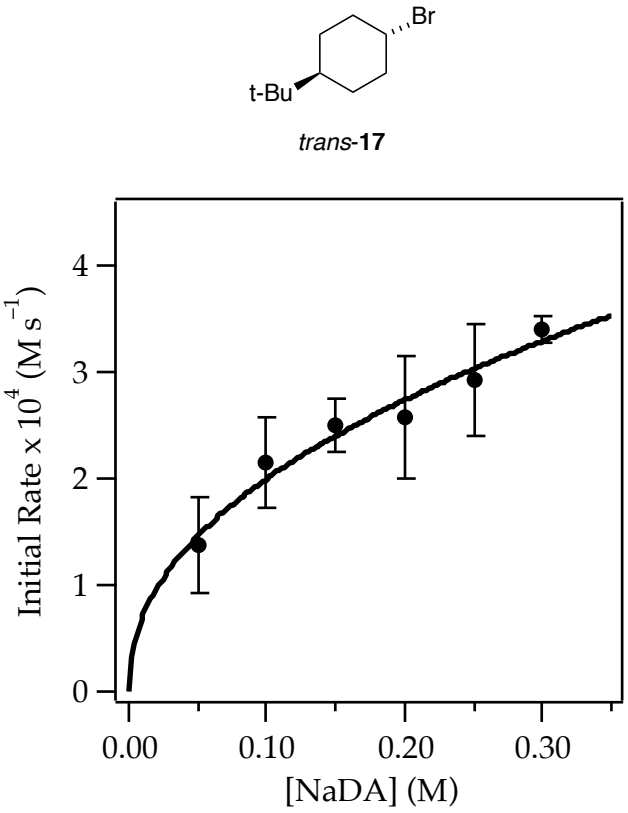


Figure S-64. Plot of initial rate versus [NaDA] in THF/hexane (5.10 M) for the dehydrobromination of *trans*-1-bromo-4-*tert*-butylcyclohexane *trans*-**17** (0.050 M) at –25 °C. The curve depicts an unweighted least-squares fit to y = k[NaDA]^n: k = (5.7 ± 0.5) x 10^{-4}; n = 0.46 ± 0.05.

[NaDA] (M)	y_1x10^4(Ms^{-1})	y_2x10^4(Ms^{-1})	y(avg)x10^4(Ms^{-1})
0.025	0.50	_	0.50
0.050	1.06	1.68	1.37
0.10	1.85	2.45	2.15
0.15	2.32	2.66	2.49
0.20	2.32	2.99	2.58
0.25	2.55	3.29	2.92
0.30	3.32	3.50	3.41

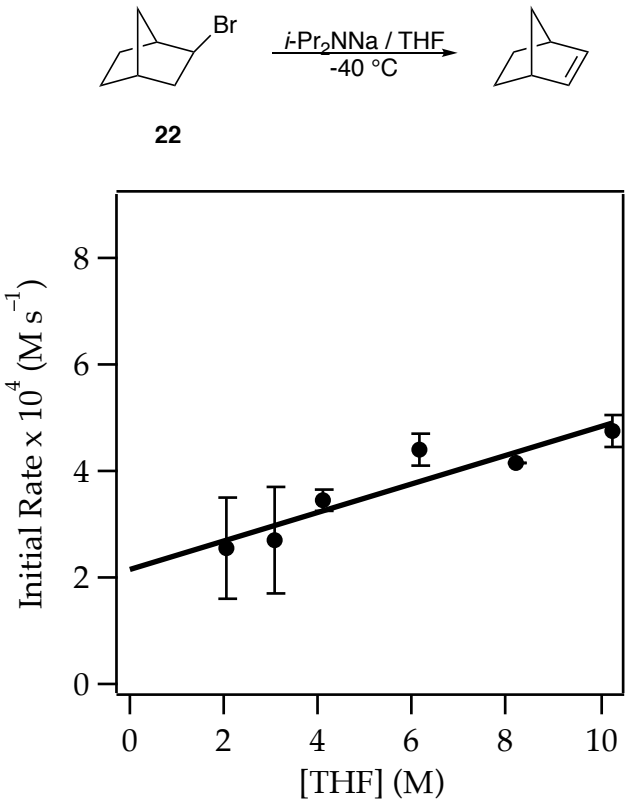


Figure S-65. Plot of initial rate versus [THF] in hexane for the dehydrobromination of *exo*-2-bromonorbornane **22** (0.040 M) with NaDA (0.10 M) at –40 °C. The curve depicts an unweighted least-squares fit to $y = k[\text{THF}] + k'$: $k = (2.6 \pm 0.5) \times 10^{-4}$; $k' = (2.2 \pm 0.3) \times 10^{-4}$.

[THF] (M)	$y_1 \times 10^4 (\text{Ms}^{-1})$	$y_2 \times 10^4 (\text{Ms}^{-1})$	$y(\text{avg}) \times 10^4 (\text{Ms}^{-1})$
2.05	3.23	1.89	2.56
3.08	2.10	3.40	2.75
4.10	3.60	3.33	3.47
6.15	4.19	4.60	4.40
8.20	4.14	4.12	4.13
10.25	4.96	4.55	4.76

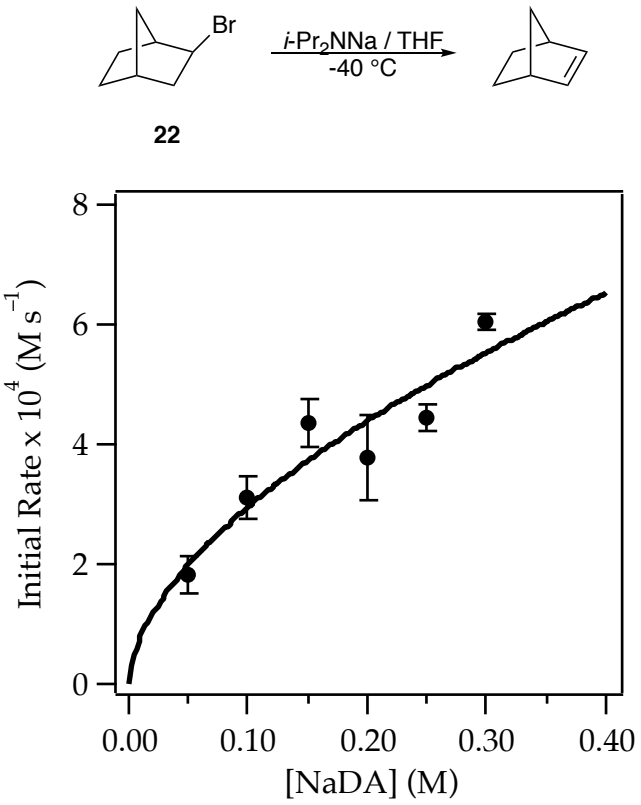
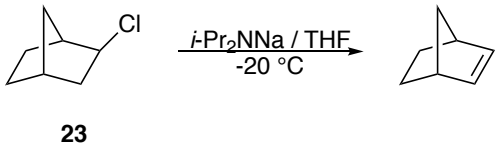


Figure S-66. Plot of initial rate versus [NaDA] in THF/hexane (5.10 M) for the dehydrobromination of *exo*-2-bromonorbornane **22** (0.040 M) at –40 °C. The curve depicts an unweighted least-squares fit to $y = k[\text{NaDA}]^n$: $k = (11.0 \pm 2.5) \times 10^{-4}$; $n = 0.57 \pm 0.10$.

[NaDA] (M)	$y_1 \times 10^4 (Ms^{-1})$	$y_2 \times 10^4 (Ms^{-1})$	$y(avg) \times 10^4 (Ms^{-1})$
0.05	2.05	1.60	1.83
0.10	3.36	2.85	3.10
0.15	4.10	4.65	4.38
0.20	4.28	3.25	3.77
0.25	4.29	4.62	4.45
0.30	6.13	5.96	6.05



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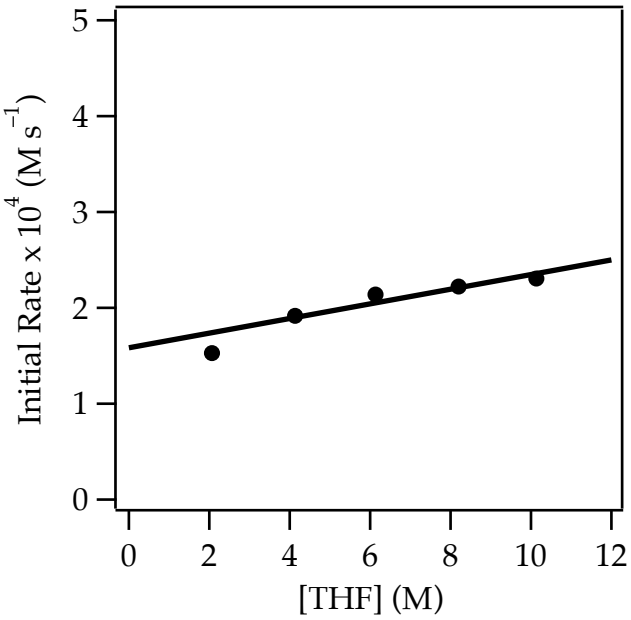
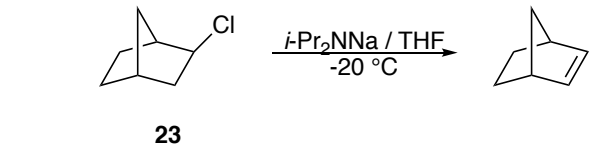


Figure S-67. Plot of initial rate versus [THF] in hexane for the dehydrochlorination of *exo*-2-chloronorbornane **23** (0.040 M) with NaDA at –20 °C. The curve depicts an unweighted least-squares fit to y = k[THF] +k': k = (1.45 ± 0.10) x 10^{-4}; k' = (9.24 ± 0.19) x 10^{-4}.

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	1.53
4.10	1.91
6.15	2.15
8.20	2.22
10.25	2.31



23

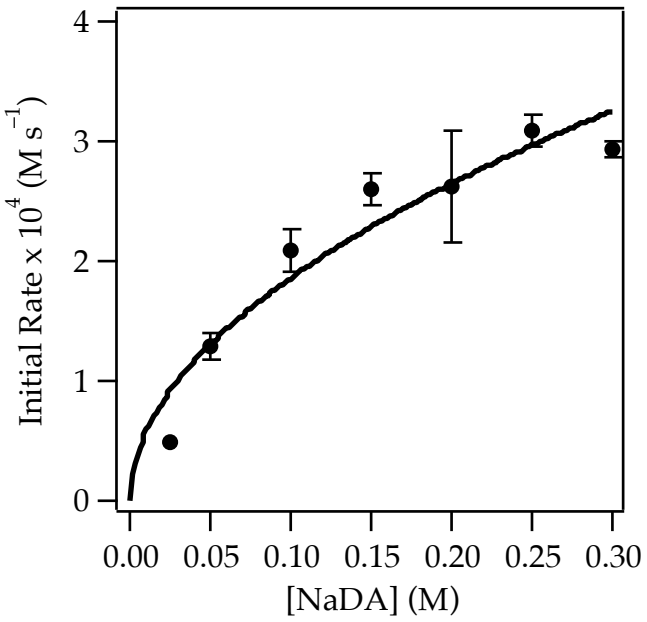


Figure S-68. Plot of initial rate versus [NaDA] in THF/hexane (5.10 M) for the dehydrochlorination of *exo*-2-chloronorbornane **23** (0.040 M) at –20 °C. The curve depicts an unweighted least-squares fit to $y = k[\text{NaDA}]^n$: $k = (6.01 \pm 0.9) \times 10^{-4}$; $n = 0.51 \pm 0.09$.

[NaDA] (M)	$y_1 \times 10^4 (Ms^{-1})$	$y_2 \times 10^4 (Ms^{-1})$	$y(avg) \times 10^4 (s^{-1})$
0.025	0.50	_	0.50
0.05	1.20	1.36	1.28
0.10	2.21	1.95	2.08
0.15	2.70	2.52	2.61
0.20	2.95	2.30	2.63
0.25	3.18	3.01	3.09
0.30	2.89	2.98	2.94

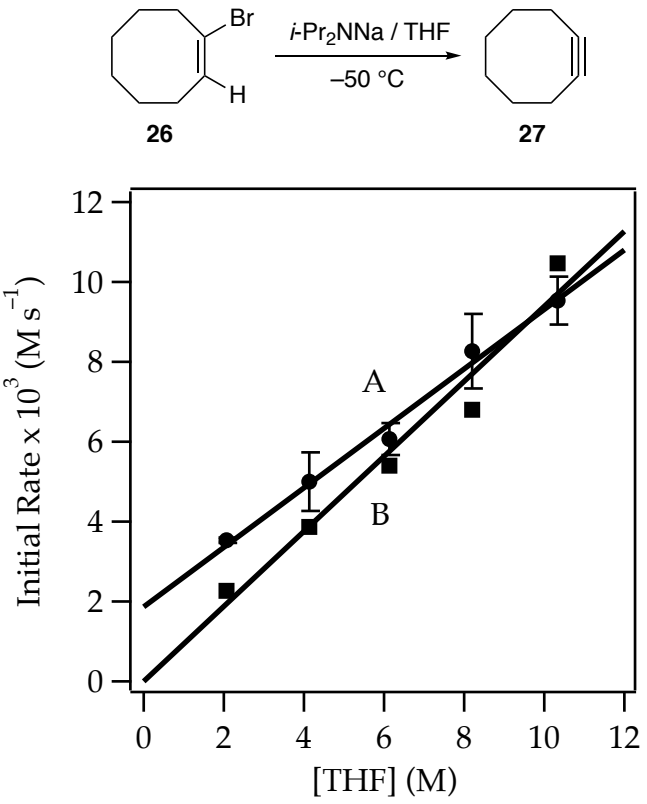


Figure S-69. Plot of initial rate versus [THF] for the dehydrobromination of 1-bromocyclooctene **26** (0.050 M) with NaDA (0.10 M) at –50 °C in (A) hexane and (B) 2,5-Me_2THF. The curve depicts an unweighted least-squares fit. Curve A: y = k[THF] + k': k = (0.74 ± 0.05) x 10^{-3}; k' = (1.90 ± 0.05) x 10^{-3}. Curve B: y = k[THF] : k = (0.89 ± 0.12) x 10^{-3}; k' = (2.61 ± 0.0.03) x 10^{-5}.

[THF] (M)	y_1x10^4(Ms^{-1})	y_2x10^4(Ms^{-1})	y(avg)x10^4(Ms^{-1})
2.05	3.47	3.55	3.51
4.10	5.55	4.48	5.02
6.15	5.80	6.35	6.08
8.20	7.59	8.92	8.26
10.25	9.97	9.13	9.55

Curve B

[THF] (M)	$y_1 x 10^4 (Ms^{-1})$
2.05	2.32
4.10	3.90
6.15	5.42
8.20	6.30
10.25	9.91

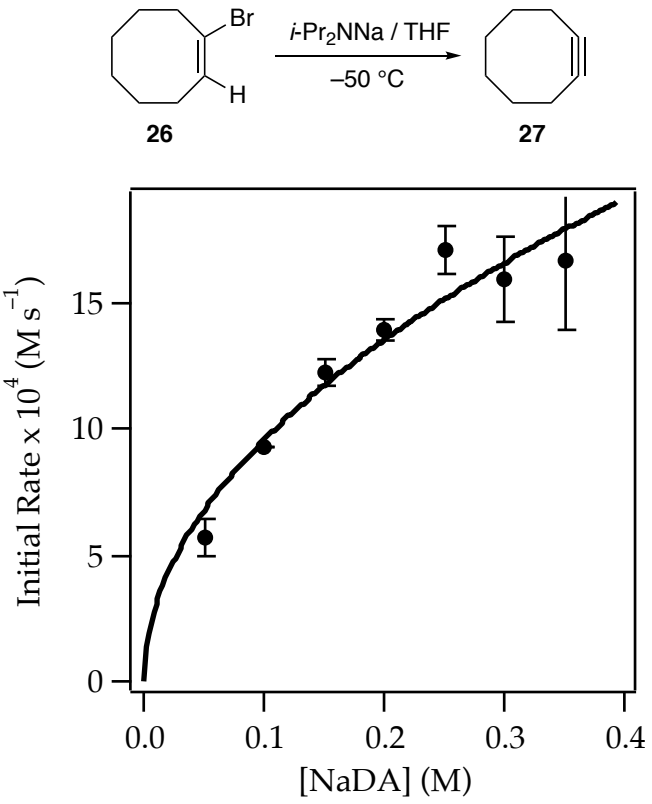


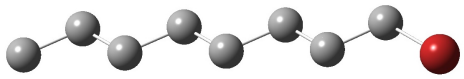
Figure S-70. Plot of initial rate versus [NaDA] in THF/hexane (5.10 M) for the dehydrobromination of 1-bromocyclooctene **26** (0.005 M) at –50 °C. The curve depicts an unweighted least-squares fit to y = k[NaDA]^n: k = (30.7 ± 3.3) x 10^{-4}; n = 0.50 ± 0.07.

[NaDA] (M)	y_1x10^4(Ms^{-1})	y_2x10^4(Ms^{-1})	y(avg)x10^4(Ms^{-1})
0.05	5.20	6.22	5.57
0.10	9.30	9.36	9.33
0.15	11.91	12.68	12.30
0.20	13.59	14.18	13.89
0.25	17.71	16.44	17.08
0.30	17.17	14.78	15.98
0.35	14.75	18.65	16.70

III. Computations

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. G_{MP2} is derived from a MP2 single point calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table S-1. Geometric coordinates and thermally corrected MP2 energies for 1-bromooctane (**1**).

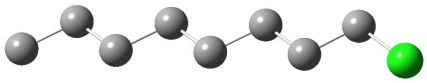


G = -1811216.896

G_{MP2} = -1809526.815

Atom	X	Y	Z	Atom	X	Y	Z
C	5.3139760	0.3880240	0.0000020	H	-1.1757650	-0.8001240	0.8797020
H	5.3449380	1.0490260	-0.8779690	H	-1.1757650	-0.8001230	-0.8797060
H	5.3449370	1.0490220	0.8779760	C	-2.3349380	0.7815040	0.0000000
C	3.9913370	-0.3892720	0.0000000	H	-2.3769890	1.4103600	-0.8904070
H	3.9602060	-1.0511170	-0.8784480	H	-2.3769880	1.4103590	0.8904070
H	3.9602040	-1.0511200	0.8784460	Br	-4.0415220	-0.2307080	0.0000010
C	2.7506850	0.5127800	0.0000000	C	6.5482420	-0.5194580	0.0000000
H	2.7827150	1.1743260	-0.8785180	H	7.4754390	0.0649280	0.0000020
H	2.7827140	1.1743240	0.8785190	H	6.5633830	-1.1680860	0.8846170
C	1.4282840	-0.2647740	-0.0000020	H	6.5633840	-1.1680820	-0.8846200
H	1.3935740	-0.9254120	0.8785730				
H	1.3935750	-0.9254100	-0.8785780				
C	0.1902200	0.6421940	-0.0000010				
H	0.2231170	1.3020030	-0.8792750				
H	0.2231170	1.3020030	0.8792730				
C	-1.1298960	-0.1463460	-0.0000010				

Table S-2. Geometric coordinates and thermally corrected MP2 energies for 1-chlorooctane (**5**).

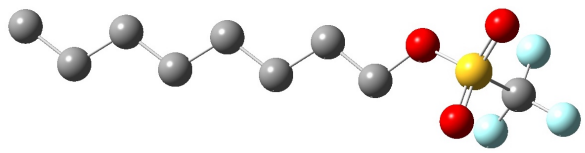


G = -486237.0121

$\mathbf{G_{MP2}}$ = -485249.1627

Atom	X	Y	Z	Atom	X	Y	Z
C	4.3884360	0.4376570	-0.0000010	Cl	-4.8136630	-0.3438930	-0.0000010
H	4.4022570	1.0990540	-0.8780230	C	5.6457680	-0.4376540	-0.0000020
H	4.4022580	1.0990530	0.8780220	H	6.5574130	0.1706020	0.0000000
C	3.0865790	-0.3740740	0.0000000	H	5.6775450	-1.0855740	0.8846170
H	3.0727830	-1.0364000	-0.8784510	H	5.6775450	-1.0855700	-0.8846240
H	3.0727840	-1.0363990	0.8784530				
C	1.8225040	0.4950040	0.0000010				
H	1.8368930	1.1570040	-0.8785650				
H	1.8368940	1.1570060	0.8785640				
C	0.5216240	-0.3181270	0.0000030				
H	0.5051630	-0.9793750	0.8785790				
H	0.5051630	-0.9793790	-0.8785700				
C	-0.7410370	0.5542680	0.0000010				
H	-0.7257350	1.2147550	-0.8792300				
H	-0.7257360	1.2147580	0.8792310				
C	-2.0381880	-0.2701310	0.0000010				
H	-2.0664270	-0.9239360	0.8804310				
H	-2.0664260	-0.9239390	-0.8804260				
C	-3.2703340	0.6241970	-0.0000010				
H	-3.3111100	1.2588470	-0.8881420				
H	-3.3111110	1.2588490	0.8881390				

Table S-3. Geometric coordinates and thermally corrected MP2 energies for octyl trifluoromethanesulfonate (**13**).

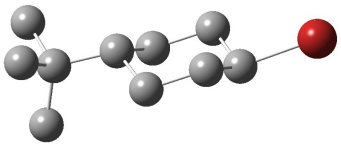


G = -800713.7399

$\mathbf{G_{MP2}}$ = -798919.1428

Atom	X	Y	Z	Atom	X	Y	Z
C	7.0176430	0.3746750	0.4607250	O	-1.7288470	-0.5719900	-0.5418120
H	6.9402020	1.4439300	0.7042060	S	-3.1891180	-0.8193910	0.1058580
H	7.0322190	-0.1556290	1.4235250	O	-3.9043940	-1.7009820	-0.7959320
C	5.7763320	-0.0533760	-0.3328510	O	-3.0851650	-1.0635760	1.5381930
H	5.7614170	0.4779640	-1.2961340	C	-3.9278730	0.8866350	-0.0993890
H	5.8542210	-1.1230670	-0.5781240	F	-5.1523860	0.8888400	0.4213650
C	4.4576800	0.2021520	0.4082150	F	-3.9861950	1.2079690	-1.3885540
H	4.3805270	1.2717000	0.6540270	F	-3.1690670	1.7819500	0.5464060
H	4.4729460	-0.3302070	1.3707300	C	8.3303770	0.1148440	-0.2852450
C	3.2174860	-0.2254290	-0.3871230	H	9.1964260	0.4338180	0.3057340
H	3.2930010	-1.2943600	-0.6338310	H	8.4547830	-0.9517610	-0.5093770
H	3.1984010	0.3085670	-1.3482410	H	8.3590730	0.6577970	-1.2379860
C	1.9009790	0.0287620	0.3591280	H	-0.6640620	-0.7149000	1.2522990
H	1.8240950	1.0976390	0.6058400	H	-0.7552900	0.9183830	0.5459440
H	1.9183520	-0.5070750	1.3190530				
C	0.6658620	-0.4024720	-0.4462640				
H	0.7250320	-1.4709370	-0.6872210				
H	0.6301930	0.1388790	-1.3997730				
C	-0.6184130	-0.1436110	0.3226440				

Table S-4. Geometric coordinates and thermally corrected MP2 energies for 1-bromo-4-(*tert*-butyl)cyclohexane (*trans*-**17**).

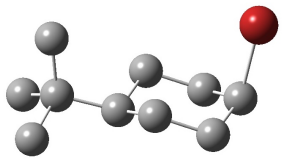


G = -1859753.221

G_{MP2} = -1857933.555

Atom	X	Y	Z	Atom	X	Y	Z
C	0.7356280	-1.2621140	-0.0964820	H	-4.5143560	0.0025900	1.5369830
C	1.4085440	0.0000390	0.4272540	H	-3.0414940	-0.8773810	1.9534000
C	0.7355540	1.2621050	-0.0966270	H	-0.8780350	1.3067460	1.3466600
C	-0.7660280	1.2552430	0.2545960	H	-1.2156350	2.1688410	-0.1476540
C	-1.4857830	-0.0001010	-0.2863120	H	1.2215860	2.1517240	0.3183000
C	-0.7660920	-1.2555910	0.2543110	H	0.8610630	1.3074110	-1.1860970
H	-0.8786580	-1.3079160	1.3463000	H	1.4371280	0.0001300	1.5199520
H	-1.2152910	-2.1689460	-0.1488940	Br	3.3442450	0.0000140	-0.0812990
H	-1.3430920	-0.0001290	-1.3800000	H	0.8612800	-1.3074990	-1.1859360
C	-3.0394320	0.0001070	-0.0659570	H	1.2217030	-2.1516670	0.3185380
C	-3.6607860	-1.2475300	-0.7320060				
H	-3.3620370	-2.1771130	-0.2366240				
H	-4.7552720	-1.1954150	-0.6898390				
H	-3.3726620	-1.3206280	-1.7884110				
C	-3.6612730	1.2424460	-0.7413820				
H	-4.7556920	1.1924650	-0.6949480				
H	-3.3594090	2.1762590	-0.2559680				
H	-3.3766780	1.3050110	-1.7994170				
C	-3.4230270	0.0054150	1.4281540				
H	-3.0468510	0.8949200	1.9458320				

Table S-5. Geometric coordinates and thermally corrected MP2 energies for 1-bromo-4-(*tert*-butyl)cyclohexane (*cis*-**17**).



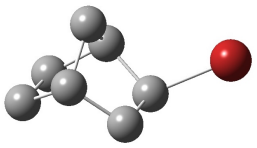
G = -1859752.247

$\mathbf{G_{MP2}}$ = -1857933.939

Atom	X	Y	Z	Atom	X	Y	Z
C	0.8254970	1.2644400	-1.2638350	H	-1.8097790	-2.1023220	-0.8853090
C	1.6681040	1.1267220	0.0001210	H	-0.0807300	-0.6861000	1.3125650
C	0.8255300	1.2641690	1.2641340	H	-0.9886370	0.5559170	2.1687670
C	-0.4138840	0.3573820	1.2585370	H	1.4390850	1.0737850	2.1509660
C	-1.2874210	0.5679160	0.0001180	H	0.5076810	2.3177440	1.3171080
C	-0.4139830	0.3577440	-1.2584390	H	2.5089260	1.8217010	0.0001800
H	-0.0809750	-0.6857650	-1.3129110	Br	2.5895950	-0.6660640	-0.0000810
H	-0.9888040	0.5567130	-2.1685330	H	0.5076900	2.3180400	-1.3165950
H	-1.5969060	1.6277100	0.0002670	H	1.4390230	1.0742180	-2.1507240
C	-2.6211220	-0.2578550	-0.0000100	H	-3.3231770	-2.3201800	-0.0006670
C	-3.4605200	0.1061030	-1.2446130				
H	-2.9873610	-0.2198320	-2.1765290				
H	-4.4438940	-0.3765260	-1.1946430				
H	-3.6257460	1.1892290	-1.3104420				
C	-3.4607180	0.1059900	1.2445020				
H	-4.4439590	-0.3769080	1.1944890				
H	-2.9875720	-0.2197420	2.1764950				
H	-3.6262330	1.1890780	1.3102170				
C	-2.3687770	-1.7795990	-0.0000920				
H	-1.8107070	-2.1025860	0.8856060				

Table S-6. Geometric coordinates and thermally corrected MP2 energies for

exo-2-bromonorbornane (**22**).

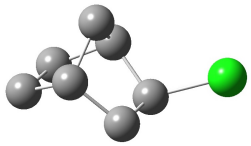


G = -1785108.188

G_{MP2} = -1783523.483

Atom	**X**	**Y**	**Z**
C	2.8023570	0.1815690	-0.3465520
C	1.7512270	1.0297340	0.4047310
C	1.1471950	-0.0108030	1.3743480
C	0.7436720	-0.9944070	0.2557720
C	2.0929030	-1.2048390	-0.4843050
H	1.9509550	-1.5091910	-1.5275410
H	2.6670440	-1.9983360	0.0061140
C	-0.1215250	-0.1010280	-0.6479200
C	0.5597930	1.2933610	-0.5507090
H	-0.1254150	2.0359410	-0.1343840
H	0.8787460	1.6537030	-1.5355530
H	-0.2255590	-0.4804430	-1.6638450
Br	-2.0104760	-0.0436680	0.0134060
H	0.2492840	-1.9193680	0.5582110
H	0.2881010	0.3614690	1.9413250
H	1.8816400	-0.4315610	2.0703060
H	2.1518340	1.9407440	0.8581940
H	3.0725990	0.6182020	-1.3144580
H	3.7236910	0.0957010	0.2402350

Table S-7. Geometric coordinates and thermally corrected MP2 energies for *exo*-2-chloronorbornane (**23**).

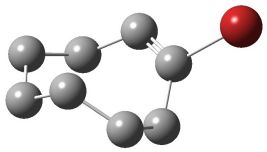


G = -459244.7103

$\mathbf{G_{MP2}}$ = -460127.524

Atom	**X**	**Y**	**Z**
C	2.2330990	0.1891480	-0.4087050
C	1.2078240	1.0421690	0.3731130
C	0.6510360	0.0145160	1.3838400
C	0.2126830	-0.9921560	0.2990560
C	1.5359420	-1.2081950	-0.4826910
H	1.3605630	-1.5436420	-1.5111640
H	2.1370180	-1.9804920	0.0089800
C	-0.6917250	-0.1239840	-0.5962620
C	-0.0265880	1.2820420	-0.5307390
H	-0.7082470	2.0085100	-0.0802540
H	0.2398440	1.6502980	-1.5276900
H	-0.7795630	-0.5168310	-1.6099060
Cl	-2.4238110	-0.0957230	0.0170780
H	-0.2645410	-1.9149170	0.6347240
H	-0.1841580	0.3943170	1.9809730
H	1.4158610	-0.3893170	2.0568290
H	1.6204230	1.9629830	0.7949880
H	2.4511030	0.6074900	-1.3976280
H	3.1828560	0.1276490	0.1341570

Table S-8. Geometric coordinates and thermally corrected MP2 energies for (*E*)-1-bromocyclooct-1-ene (**26**).

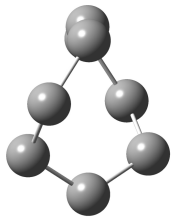


G = -1809733.726

$\mathbf{G_{MP2}}$ = -1808066.159

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.1146110	0.8015120	1.2198460	H	-0.8970570	0.4191860	1.8867140
C	-0.7130360	1.8969100	0.3099380	H	0.6596560	1.2388760	1.8589480
C	-1.6997590	1.3917860	-0.7583740				
C	-2.8668200	0.5063330	-0.2538850				
C	-2.7102890	-1.0200060	-0.4251340				
C	-1.6587310	-1.7297160	0.4611350				
C	-0.2195160	-1.4529830	0.0808160				
C	0.4425280	-0.3521050	0.4398750				
Br	2.2364970	-0.0697820	-0.2233030				
H	0.2736470	-2.1838850	-0.5550610				
H	-1.8405000	-1.4616430	1.5102950				
H	-1.8274880	-2.8111800	0.3921830				
H	-3.6838940	-1.4825240	-0.2114830				
H	-2.4942950	-1.2385240	-1.4802170				
H	-3.7733800	0.7870260	-0.8053440				
H	-3.0854840	0.7362110	0.7995630				
H	-2.1153400	2.2784370	-1.2540220				
H	-1.1444410	0.8505050	-1.5342410				
H	0.1048260	2.4278730	-0.1933300				
H	-1.2122430	2.6316250	0.9562810				

Table S-9. Geometric coordinates and thermally corrected MP2 energies for symmetrical cycloocta-1,2-diene (**28a**).

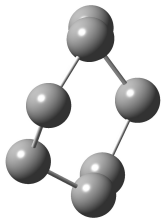


G = -195579.7717

$\mathbf{G_{MP2}}$ = -194980.1683

Atom	**X**	**Y**	**Z**
C	1.9641272	-0.1227573	0.0944600
C	1.1379571	-1.2963110	0.6072425
C	-0.0286548	-1.5422203	0.0626315
C	-1.1874122	-1.2980169	-0.4992301
C	-1.9739886	-0.0642800	-0.0726817
C	-1.1249772	0.9537735	0.7112061
C	0.0238703	1.6648582	-0.0520486
C	1.1479887	0.8639249	-0.7611907
H	1.8457560	1.6027126	-1.1788609
H	0.7323567	0.3257756	-1.6203804
H	0.4985588	2.3495074	0.6660110
H	-0.4290508	2.3115904	-0.8177389
H	-0.7261241	0.4650772	1.6071161
H	-1.7977152	1.7429255	1.0742410
H	-2.8572192	-0.3411276	0.5221997
H	-2.3674477	0.4046403	-0.9868382
H	-1.5645889	-1.8914756	-1.3316460
H	1.4962219	-1.8406017	1.4806087
H	2.3738672	0.3971789	0.9731815
H	2.8370717	-0.4702643	-0.4781036

Table S-10. Geometric coordinates and thermally corrected MP2 energies for asymmetrical cycloocta-1,2-diene (**28b**).

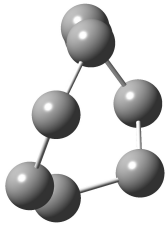


G = -195580.4394

$\mathbf{G_{MP2}}$ = -194980.247

Atom	**X**	**Y**	**Z**
C	1.9508098	-0.3501015	-0.3658589
C	1.0477736	-1.4318243	0.2050154
C	-0.1871796	-1.5154762	-0.2220103
C	-1.3908944	-1.1882561	-0.6202889
C	-2.0411713	0.0685462	-0.0620997
C	-1.0634411	0.9981615	0.6837647
C	0.1268665	1.5467498	-0.1622804
C	1.5540406	1.0447254	0.1769140
H	1.6873165	1.0586005	1.2680259
H	2.2735107	1.7721658	-0.2251943
H	0.1477206	2.6372239	-0.0402166
H	-0.0686042	1.3747644	-1.2297091
H	-1.6502428	1.8445758	1.0628202
H	-0.6796974	0.4793064	1.5703886
H	-2.8831047	-0.1857278	0.5993159
H	-2.4848793	0.6124192	-0.9097899
H	-1.9202296	-1.7461956	-1.3923361
H	1.3939556	-2.0071039	1.0635880
H	2.9994550	-0.5515322	-0.1145384
H	1.8808824	-0.3409364	-1.4604200

Table S-11. Geometric coordinates and thermally corrected MP2 energies for the isomerization of asymmetrical cycloocta-1,2-diene (**28b**) to symmetrical cycloocta-1,2-diene (**28a**).

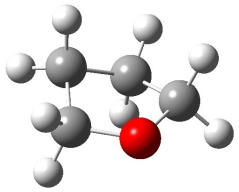


G = -195571.4341

$\mathbf{G_{MP2}}$ = -194970.5996

Atom	**X**	**Y**	**Z**				
C	1.9994747	-0.1348541	0.3249512	H	2.7828707	-0.5769275	-0.3068090
C	1.0904652	-1.1955795	0.9399226				
C	-0.0189419	-1.4831137	0.3068522				
C	-1.0326050	-1.3987288	-0.5170324				
C	-1.9369858	-0.1862120	-0.6406681				
C	-1.4786696	1.1812750	-0.0390456				
C	0.0012441	1.4908512	0.3515130				
C	1.1822767	0.9070748	-0.4775065				
H	1.8608604	1.7131762	-0.7843019				
H	0.8181082	0.4500101	-1.4040223				
H	0.1461137	1.1939117	1.3954359				
H	0.0782562	2.5857497	0.3503697				
H	-2.0693846	1.3747714	0.8648248				
H	-1.8052472	1.9436852	-0.7575873				
H	-2.9412190	-0.4156577	-0.2550769				
H	-2.0813747	-0.0573877	-1.7224172				
H	-1.1959751	-2.1869858	-1.2544878				
H	1.3112660	-1.5735594	1.9369260				
H	2.5213780	0.3734418	1.1475166				

Table S-12. Geometric coordinates and thermally corrected MP2 energies for THF.

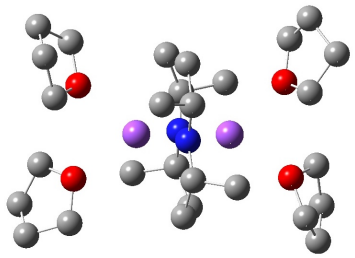


G = -145737.157

$\mathbf{G_{MP2}}$ = -145310.7976

Atom	**X**	**Y**	**Z**
C	-1.1655770	-0.4304460	-0.1316510
H	-1.5359580	-0.4831270	-1.1673560
H	-1.9488020	-0.8230080	0.5275430
C	-0.7333840	0.9970250	0.2267570
H	-0.7966490	1.1557780	1.3100440
H	-1.3434230	1.7616460	-0.2642560
C	0.7339430	0.9965910	-0.2269410
H	0.7973310	1.1548800	-1.3102840
H	1.3443500	1.7610810	0.2638280
C	1.1652710	-0.4309590	0.1320600
H	1.9488890	-0.8240060	-0.5263660
H	1.5347420	-0.4835500	1.1681130
O	-0.0002500	-1.2516200	-0.0003270

Table S-13. Geometric coordinates and thermally corrected MP2 energies for NaDA ground-state $A_2(THF)_4$.



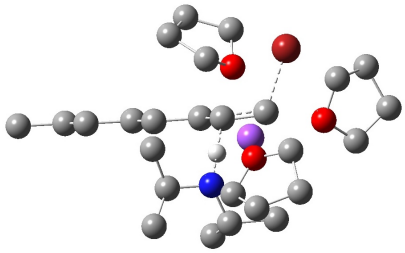
G = -1152417.329

$\mathbf{G_{MP2}}$ = -1149102.475

Atom	X	Y	Z	Atom	X	Y	Z
Na	-1.4745010	-0.0632710	-0.0235120	H	1.4159540	-2.9220130	0.0308580
Na	1.5318880	-0.0837150	-0.0153470	H	-0.2902890	-2.8883490	0.5107590
N	0.0480430	-1.1761660	-1.6084690	C	-1.3387470	-3.2360300	-2.0563500
C	0.1694240	-0.6602420	-2.9692230	H	-1.6880690	-2.8019560	-3.0002740
H	-0.4391800	-1.2515570	-3.6856630	H	-1.2901530	-4.3272000	-2.1901370
C	1.6173190	-0.7046300	-3.5272920	H	-2.0883350	-3.0173860	-1.2853010
H	1.6660960	-0.4095990	-4.5863350	N	0.0436240	0.9620520	1.6283840
H	2.2667120	-0.0262920	-2.9563270	C	0.1629600	0.3853700	2.9640200
H	2.0364470	-1.7149110	-3.4483130	H	-0.6048770	0.7831280	3.6620500
C	-0.3591310	0.7771420	-3.0699780	C	1.5227050	0.6404950	3.6656670
H	0.1590080	1.4365080	-2.3605390	H	1.5496610	0.1956660	4.6704000
H	-0.2204570	1.1961090	-4.0758830	H	2.3433580	0.2066400	3.0763150
H	-1.4296400	0.8116060	-2.8348000	H	1.7276340	1.7111730	3.7780880
C	0.0271220	-2.6365720	-1.6314440	C	-0.0808510	-1.1279190	2.9182160
H	0.7700500	-3.0423870	-2.3523090	H	-0.0389550	-1.5743730	3.9205700
C	0.4062580	-3.2286650	-0.2668280	H	-1.0667210	-1.3524080	2.4933100
H	0.3735860	-4.3267510	-0.2805270	H	0.6699010	-1.6337420	2.2966250
C	0.1180760	2.4186890	1.6539680	H	1.0966840	2.7865630	2.0449150
C	-0.9440190	3.1314560	2.5304000	H	5.3871050	-3.7911540	1.6592860

H	-0.8438370	4.2238800	2.4653710	H	5.6388130	-3.5342260	-0.7121630
H	-1.9551740	2.8575990	2.2008830	H	3.9006430	-3.7803170	-0.9305790
H	-0.8583860	2.8609410	3.5879860	O	-3.4695290	-1.4404060	0.5393580
C	0.0185850	2.9789940	0.2279000	C	-4.4738530	-1.6560670	-0.4757560
H	-0.9483170	2.7203850	-0.2233340	H	-5.2225710	-0.8558490	-0.4101070
H	0.1102680	4.0736640	0.2192520	H	-3.9887420	-1.6012620	-1.4539740
H	0.8112090	2.5716710	-0.4093050	C	-5.0889850	-3.0243470	-0.1740300
O	3.2577980	1.5416510	-0.6638420	C	-4.9638820	-3.0982440	1.3553370
C	3.9857410	2.0219660	0.4919400	C	-3.6126820	-2.4178520	1.5911700
H	3.2579640	2.3311640	1.2515300	H	-3.5447420	-1.9016160	2.5538340
H	4.5765230	1.1930680	0.8925230	H	-2.7854400	-3.1364570	1.5218640
C	4.8326480	3.2018480	0.0024160	H	-5.7700750	-2.5292250	1.8340020
C	3.9941480	3.7343840	-1.1697470	H	-4.9913180	-4.1199540	1.7458670
C	3.4510790	2.4390760	-1.7742680	H	-4.4982270	-3.8189740	-0.6439690
H	2.4928980	2.5597860	-2.2872250	H	-6.1200620	-3.1081090	-0.5312060
H	4.1689420	1.9945590	-2.4785430	O	-3.3798430	1.4669330	-0.5936400
H	3.1698500	4.3540500	-0.7984710	C	-4.2223680	1.8421640	0.5128200
H	4.5722940	4.3244270	-1.8874770	H	-5.1178640	1.2037760	0.5261900
H	5.8100450	2.8557700	-0.3553700	H	-3.6599370	1.6727060	1.4339750
H	5.0034250	3.9449820	0.7871290	C	-4.5910330	3.3033560	0.2651240
O	3.5270160	-1.3789260	0.5680030	C	-4.7116000	3.3327290	-1.2666450
C	4.4239670	-1.7202000	-0.4966710	C	-3.5995450	2.3670140	-1.7022990
H	3.9520080	-1.4221720	-1.4344730	H	-3.8647470	1.7802710	-2.5886700
H	5.3660330	-1.1612940	-0.3774660	H	-2.6598550	2.8935520	-1.9058840
C	4.6503900	-3.2324120	-0.3525370	H	-5.6935320	2.9562590	-1.5771100
C	4.4582220	-3.4859690	1.1678370	H	-4.5843960	4.3318020	-1.6940450
C	3.9634930	-2.1266860	1.7108940	H	-3.7808030	3.9593460	0.6029010
H	3.1175580	-2.1988930	2.3971970	H	-5.5108880	3.5999960	0.7785850
H	4.7769180	-1.5813150	2.2134040				
H	3.7189100	-4.2727580	1.3412860				

Table S-14. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_3$ mediated anti elimination of 1-bromooctane (**1**).



G = -2533131.623

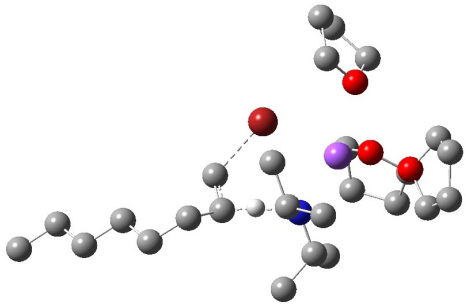
$\mathbf{G_{MP2}}$ = -2529373.821

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.5333060	-0.5832620	0.0551840	C	-0.8252510	-2.5028480	1.1832420
N	-0.2261390	-1.7551790	-1.0752910	H	-1.0782790	-1.4694150	1.4384490
C	-0.1863270	-2.0120450	-2.5221690	H	-1.4763580	-3.1628930	1.7700920
H	0.2319070	-3.0154380	-2.7177450	H	0.2112750	-2.6923750	1.4997100
C	-1.5637370	-1.9672380	-3.2225930	O	1.3752390	0.4278970	2.2243360
H	-1.4721560	-2.2036680	-4.2908490	C	1.6341500	-0.3966440	3.3713090
H	-2.2625610	-2.6889560	-2.7855120	H	1.8656390	-1.4015120	3.0114570
H	-2.0158300	-0.9721320	-3.1329820	H	2.5130520	-0.0033940	3.9051390
C	0.7673130	-1.0198330	-3.2027690	C	0.3665290	-0.3016310	4.2442130
H	1.7725930	-1.0826710	-2.7648070	C	-0.3112200	1.0133320	3.7660680
H	0.8574600	-1.2292350	-4.2760320	C	0.6804600	1.5830010	2.7415660
H	0.4098750	0.0111050	-3.0975140	H	0.2257810	2.1193390	1.9061900
C	-0.9810140	-2.7654980	-0.3221000	H	1.4133330	2.2447390	3.2295240
H	-2.0668860	-2.7001100	-0.5371580	H	-1.2714950	0.8031950	3.2863830
C	-0.5833740	-4.2282700	-0.6091640	H	-0.4950310	1.7167690	4.5832940
H	-1.1219220	-4.9089310	0.0625160	H	0.6194560	-0.2808030	5.3086070
H	-0.8148610	-4.5345600	-1.6341910	H	-0.2876180	-1.1611340	4.0742670
H	0.4931270	-4.3739160	-0.4501520	O	3.0297700	1.1980040	-0.7387950
C	3.2082420	1.6813500	-2.0960720	C	-5.3184830	0.2020830	-0.4044110

H	3.9633350	1.0642670	-2.5977040	H	-5.5766870	1.2356900	-0.1297260
H	2.2551840	1.5530700	-2.6160210	H	-5.4809230	0.1286170	-1.4902690
C	3.6261510	3.1614500	-1.9919370	C	-3.8359210	-0.0477820	-0.0991220
C	3.2549740	3.5308430	-0.5450630	H	-3.5753030	-1.0770010	-0.3825730
C	3.5014520	2.2121190	0.1778040	H	-3.6765920	0.0183040	0.9884780
H	4.5734400	2.0546120	0.3768820	C	-2.8952680	0.9359300	-0.8052160
H	2.9471630	2.0872970	1.1087150	H	-3.1735350	1.9632440	-0.5175150
H	3.8605280	4.3505470	-0.1458080	H	-3.0626430	0.8743550	-1.8924070
H	2.1965890	3.8038140	-0.4686000	C	-1.4123570	0.7203040	-0.5064370
H	3.1132260	3.7830400	-2.7310710	H	-1.2411110	0.6229860	0.5757020
H	4.7049480	3.2685250	-2.1535350	C	-0.5270110	1.6949740	-1.0931880
O	3.3522710	-2.0080010	0.6091160	H	-0.7353630	1.9736970	-2.1256700
C	3.3338830	-3.4308190	0.3330050	H	0.5396380	1.5787780	-0.9189940
H	2.7948390	-3.9373390	1.1401880	Br	-0.6368830	3.7479060	-0.2034110
H	2.7835060	-3.5877460	-0.6012080	C	-8.6900420	-1.4963290	0.7155330
C	4.8003420	-3.8657380	0.2207130	H	-9.7391350	-1.3003830	0.4647660
C	5.4957020	-2.5678130	-0.2181410	H	-8.4715790	-2.5368150	0.4443020
C	4.7097810	-1.5181070	0.5659080	H	-8.5867850	-1.4115070	1.8045860
H	5.0926670	-1.4192310	1.5920210	H	-0.9091600	-0.4955230	-0.8931500
H	4.6869030	-0.5322240	0.0962490				
H	6.5658640	-2.5502900	0.0088470				
H	5.3709180	-2.4103960	-1.2961560				
H	4.9344590	-4.6905250	-0.4851550				
H	5.1829620	-4.1901560	1.1955120				
C	-7.7487840	-0.5267660	-0.0067330				
H	-8.0145960	0.5066530	0.2581310				
H	-7.9010730	-0.6094520	-1.0923770				
C	-6.2676440	-0.7655810	0.3138400				
H	-6.1154820	-0.6852860	1.4009250				
H	-6.0026940	-1.8000770	0.0475570				

Table S-15. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_3$

mediated *syn* elimination of 1-bromooctane (**1**).



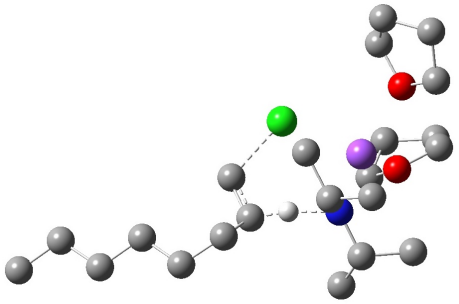
G = -2533134.885

$\mathbf{G_{MP2}}$ = -2529375.904

Atom	X	Y	Z	Atom	X	Y	Z
C	-7.9973900	-0.8952690	0.2320520	H	-2.6214570	-1.2781400	1.1748740
H	-7.9332150	-1.5931600	-0.6150470	Br	-0.5951950	-1.9341970	-0.3649240
H	-7.5280160	-1.4086380	1.0835080	C	-9.4695370	-0.6172080	0.5532550
C	-7.1981140	0.3722010	-0.0961180	H	-10.0127000	-1.5420030	0.7799500
H	-7.6686550	0.8867140	-0.9473980	H	-9.5675740	0.0474650	1.4206490
H	-7.2635590	1.0703290	0.7521040	H	-9.9749660	-0.1328030	-0.2914530
C	-5.7216860	0.1028630	-0.4173700	N	0.0078300	1.7917990	-0.3861760
H	-5.6571090	-0.5879530	-1.2719660	C	-0.0154660	2.8554550	0.6199070
H	-5.2611620	-0.4206090	0.4326730	H	0.8834070	3.4998400	0.5220570
C	-4.9269910	1.3761420	-0.7310820	C	-1.2142030	3.8345130	0.5590120
H	-4.9875460	2.0569820	0.1318100	H	-1.1118010	4.6166520	1.3227100
H	-5.4178570	1.9025750	-1.5633560	H	-1.2799000	4.3350800	-0.4129610
C	-3.4439560	1.1675700	-1.0942700	H	-2.1654380	3.3197350	0.7330520
H	-3.0366790	2.1386880	-1.3996490	C	0.0670750	2.2297060	2.0212580
H	-3.3698750	0.5192810	-1.9799970	H	0.9820580	1.6350820	2.1311970
C	-2.5659640	0.5865190	0.0280190	H	0.0691270	2.9998460	2.8032980
H	-2.7666410	1.0719120	0.9927370	H	-0.7836690	1.5630800	2.2041040
C	-2.6019150	-0.8502890	0.1780820	C	-0.0239880	2.2826370	-1.7666270
H	-3.1362050	-1.4439180	-0.5553970	H	4.3240020	-3.0662810	-0.7224180
C	1.1446640	3.2260800	-2.1337870	H	-0.9496680	2.8537750	-1.9787050

H	1.1403180	4.1469840	-1.5401420	H	1.4181720	-4.0261330	-0.8750800
H	2.1047930	2.7188020	-1.9677110	H	2.8827890	-5.0299990	-1.0504020
H	1.0912650	3.5179720	-3.1909120	H	3.4215680	-3.9689580	-3.1954610
C	-0.0162810	1.0930250	-2.7374830	H	1.6575340	-4.0898100	-3.3117110
H	-0.7641670	0.3446040	-2.4609680	O	3.7149600	1.1174840	0.2057120
H	-0.2081200	1.4214190	-3.7669590	C	3.9362550	2.4886980	0.5701130
H	0.9641820	0.5954880	-2.7299510	H	2.9634760	2.9819020	0.5793000
Na	1.5248300	-0.0552310	-0.0223860	H	4.3660240	2.5305330	1.5828610
O	2.1031100	-1.1262030	2.1539070	C	4.9248910	3.0628100	-0.4730540
C	1.1813510	-1.9680380	2.8675410	C	5.4320300	1.8101190	-1.2345030
H	0.3525220	-2.1730430	2.1890710	C	4.9457700	0.6485510	-0.3603520
H	1.6811910	-2.9148950	3.1288360	H	4.7189300	-0.2687790	-0.9044880
C	0.8252960	-1.1628440	4.1219240	H	5.6658450	0.4305090	0.4455520
C	2.1222420	-0.3587200	4.4111410	H	4.9693540	1.7495810	-2.2247480
C	2.9847570	-0.5825820	3.1458560	H	6.5179900	1.8038880	-1.3696960
H	3.4204780	0.3252270	2.7254490	H	5.7422830	3.5995940	0.0185510
H	3.7938380	-1.3019170	3.3447610	H	4.4289790	3.7643690	-1.1491770
H	1.9017590	0.7015240	4.5634110	H	-1.4200420	1.0039020	-0.1739620
H	2.6394570	-0.7203140	5.3053460				
H	0.5271960	-1.8038820	4.9570880				
H	-0.0048530	-0.4847790	3.9026330				
O	2.8561650	-1.7277680	-1.3595740				
C	2.3853020	-2.1198930	-2.6747670				
H	1.3525870	-1.7731660	-2.7745290				
H	3.0036430	-1.6240550	-3.4320320				
C	2.4778350	-3.6526610	-2.7349910				
C	2.4468480	-4.0458350	-1.2493540				
C	3.2393690	-2.9050290	-0.6181240				
H	3.0069430	-2.7174870	0.4324720				

Table S-16. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_2$ mediated *syn* elimination of 1-chlorooctane (**5**).



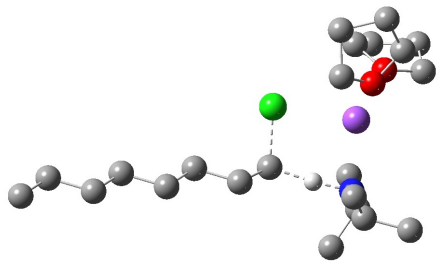
G = -1062420.29

G_{MP2} = -1059766.456

Atom	X	Y	Z	Atom	X	Y	Z
C	-7.4078370	0.8812370	1.4136980	H	-2.3643060	0.0418850	1.7868010
H	-7.3225150	0.2390860	2.3019810	H	-2.2695920	1.6745740	0.9943520
H	-6.8663440	1.8068560	1.6560310	Cl	0.0011460	1.0077310	1.7448790
C	-6.7243520	0.1930680	0.2251190	Na	1.6647800	0.0774620	-0.1202140
H	-7.2674800	-0.7322210	-0.0189790	N	0.2970780	-1.3396110	-1.3304850
H	-6.8094760	0.8365770	-0.6634510	C	0.3260200	-1.2424140	-2.7960910
C	-5.2457680	-0.1362130	0.4719570	H	-0.0815490	-2.1648570	-3.2525570
H	-5.1619210	-0.7857140	1.3565210	C	-0.5350320	-0.0823000	-3.3281380
H	-4.7113960	0.7913920	0.7236700	H	-0.4038980	0.0371470	-4.4110960
C	-4.5678950	-0.8164430	-0.7232110	H	-1.5994420	-0.2484910	-3.1371050
H	-4.6414650	-0.1590920	-1.6026390	H	-0.2476900	0.8641620	-2.8507270
H	-5.1346940	-1.7243830	-0.9782520	C	1.7641190	-1.0609270	-3.3421650
C	-3.0945880	-1.2115220	-0.5162370	H	2.4329520	-1.8472320	-2.9801270
H	-2.7801840	-1.8197770	-1.3739550	H	1.7860630	-1.0728130	-4.4414120
H	-3.0105130	-1.8645470	0.3642990	H	2.1687360	-0.0931830	-3.0127880
C	-2.1023050	-0.0353700	-0.3789960	C	0.1548990	-2.7177920	-0.8552090
H	-2.2531330	0.7019720	-1.1761050	H	-0.7947530	-3.1624560	-1.2233060
C	-2.0728890	0.6125010	0.9100470	C	1.2648390	-3.6906010	-1.3194230
H	1.3109690	-3.7748060	-2.4095700	H	2.5814100	4.0511270	0.9321550
H	2.2491400	-3.3517840	-0.9659790	H	2.3159760	5.3040350	-0.2976070
H	1.0871650	-4.6976550	-0.9182270	C	-8.8834010	1.2052400	1.1583480

C	0.1000810	-2.7475520	0.6794270	H	-9.3421020	1.6967830	2.0240730
H	-0.6569530	-2.0667960	1.0765390	H	-8.9989750	1.8735270	0.2959600
H	-0.1202810	-3.7587620	1.0438880	H	-9.4586030	0.2948170	0.9488660
H	1.0671350	-2.4455600	1.1068740	H	-1.0323670	-0.5448670	-0.7005820
O	3.5820480	-0.4514920	1.1635110				
C	3.5204390	-0.2084880	2.5859810				
H	4.2413290	0.5779800	2.8557010				
H	2.5098820	0.1383290	2.8155540				
C	3.8950920	-1.5435640	3.2217650				
C	4.9917790	-2.0454550	2.2666140				
C	4.5269550	-1.5147890	0.8973600				
H	5.3540280	-1.1175260	0.2971050				
H	4.0084120	-2.2796300	0.3090360				
H	5.9597750	-1.6097650	2.5390630				
H	5.1022230	-3.1336570	2.2712400				
H	3.0313890	-2.2181350	3.2128450				
H	4.2395380	-1.4391730	4.2550160				
O	2.5041670	2.0759420	-1.0061110				
C	1.7142010	3.2766760	-0.8890060				
H	1.4572640	3.6466580	-1.8925160				
H	0.7988960	3.0142230	-0.3529140				
C	2.6105480	4.2616270	-0.1430320				
C	3.9932940	3.9303470	-0.7297950				
C	3.9100880	2.4120480	-0.9712000				
H	4.3722950	2.1112310	-1.9186520				
H	4.3645200	1.8316420	-0.1607360				
H	4.1401760	4.4619020	-1.6769010				
H	4.8193170	4.1992520	-0.0646840				

Table S-17. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_2$ mediated carbene generation of 1-chlorooctane (**5**).



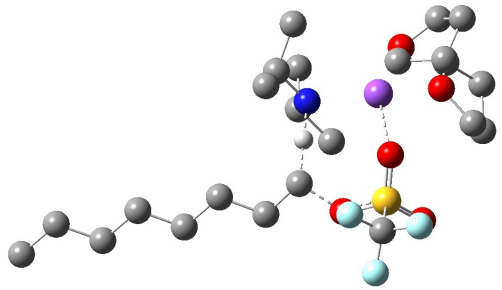
G = -1062425.683

G_{MP2} = -1059776.791

Atom	X	Y	Z	Atom	X	Y	Z
C	-8.4476500	0.7729700	-1.0779880	H	-1.0870240	-1.6722280	-1.3643180
H	-8.1812380	1.7160680	-1.5764400	Cl	-0.3090020	0.5930830	-1.1655120
H	-8.5665300	0.0301740	-1.8798370	Na	1.9535950	0.0478970	0.2603960
C	-7.2957240	0.3443570	-0.1598350	N	1.2480950	-2.0675260	0.9685990
H	-7.1789800	1.0862720	0.6445900	C	1.6855440	-3.2841400	0.2678240
H	-7.5621860	-0.6004950	0.3374870	H	2.5842960	-3.6982180	0.7563920
C	-5.9576310	0.1737060	-0.8905180	C	0.6334240	-4.4159550	0.2361370
H	-5.6911570	1.1198020	-1.3850450	H	1.0233220	-5.3014680	-0.2826030
H	-6.0773200	-0.5648910	-1.6973000	H	0.3437980	-4.7286670	1.2451930
C	-4.8045580	-0.2601290	0.0240970	H	-0.2738280	-4.0882700	-0.2857540
H	-5.0699900	-1.2084360	0.5160170	C	2.1001740	-2.9255340	-1.1679900
H	-4.6879220	0.4767060	0.8334390	H	2.9227950	-2.1988760	-1.1664170
C	-3.4663910	-0.4219640	-0.7096780	H	2.4387880	-3.8140810	-1.7153210
H	-3.1976690	0.5267130	-1.1927590	H	1.2625010	-2.4868320	-1.7226190
H	-3.5803030	-1.1577530	-1.5199460	C	0.9760260	-2.2517960	2.3987810
C	-2.3106000	-0.8648150	0.2042230	H	0.1795410	-3.0044410	2.5649280
H	-2.5792090	-1.8309850	0.6677070	C	2.1995700	-2.7210600	3.2079950
H	-2.2154500	-0.1552280	1.0402760	H	1.9576510	-2.7883640	4.2765740
C	-0.9532650	-1.1176400	-0.4236600	H	2.5563420	-3.7069470	2.8917690
H	3.0286970	-2.0095040	3.0884630	C	-9.7799050	0.9443950	-0.3408790
C	0.4531270	-0.9334190	2.9897970	H	-10.5812830	1.2479190	-1.0246010
H	-0.4132510	-0.5657180	2.4306290	H	-10.0897590	0.0084530	0.1404800
H	0.1487050	-1.0671190	4.0352150	H	-9.7039340	1.7082460	0.4429960

H	1.2315400	-0.1574530	2.9689630	H	0.1788960	-1.6495030	0.3759180
O	3.7255980	0.5595300	-1.2094880				
C	5.0724910	0.0282050	-1.2040460				
H	5.6745970	0.5996390	-0.4889150				
H	5.0244560	-1.0134080	-0.8650900				
C	5.5880910	0.1390990	-2.6467240				
C	4.2875940	0.1626340	-3.4664080				
C	3.3622190	0.9601270	-2.5516820				
H	3.5255000	2.0419240	-2.6625160				
H	2.2981410	0.7485040	-2.6839640				
H	4.4065630	0.6241220	-4.4511450				
H	3.8985660	-0.8522480	-3.6059620				
H	6.2530510	-0.6876450	-2.9125580				
H	6.1416290	1.0748090	-2.7868320				
O	2.1414080	2.0355830	1.4777230				
C	0.9742590	2.8450370	1.7324660				
H	0.1300590	2.3711540	1.2265360				
H	0.7774710	2.8768730	2.8139150				
C	1.3382150	4.2236350	1.1892240				
C	2.8232990	4.3303400	1.5782300				
C	3.3176190	2.8754220	1.4636280				
H	3.8430790	2.6806950	0.5226680				
H	3.9726130	2.5904150	2.2957970				
H	3.3884870	5.0116980	0.9354700				
H	2.9196240	4.6880450	2.6094580				
H	0.7242060	5.0231190	1.6144190				
H	1.2173220	4.2390810	0.0999590				

Table S-18. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_2$ mediated carbene generation from *n*-octyl trifluoromethanesulfonate **(13)**.



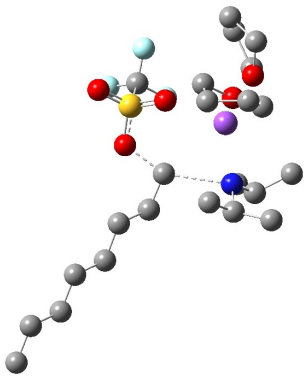
G = -1376904.647

G_{MP2} = -1373454.118

Atom	X	Y	Z	Atom	X	Y	Z
C	8.8212710	-0.7585490	0.7084320	O	0.4972270	1.6040020	-1.2317030
H	8.8227130	-0.2016890	1.6564290	S	-0.9273280	2.1292790	-0.9405480
H	8.5761120	-1.7983070	0.9682290	O	-1.6330080	2.3772960	-2.1933350
C	7.7263960	-0.1949590	-0.2065020	O	-1.6249660	1.3766530	0.1213140
H	7.9722530	0.8458910	-0.4656910	Na	-1.8852820	-0.8942030	0.3324470
H	7.7267400	-0.7508500	-1.1561440	N	0.2952290	-1.7279400	0.3136300
C	6.3225330	-0.2458500	0.4100140	C	0.7370490	-2.2276110	1.6281300
H	6.3245670	0.3059150	1.3620240	H	1.6678980	-2.8166780	1.5184430
H	6.0751740	-1.2872870	0.6643870	C	1.0583250	-1.0634360	2.5844640
C	5.2311750	0.3258090	-0.5040810	H	1.2922400	-1.4399650	3.5876860
H	5.2291920	-0.2246440	-1.4564150	H	1.9089480	-0.4709650	2.2378520
H	5.4777350	1.3677460	-0.7562400	H	0.1975800	-0.3865880	2.6749270
C	3.8262200	0.2726390	0.1119360	C	-0.3027960	-3.1409080	2.3175470
H	3.8320920	0.8194280	1.0668010	H	-0.6043200	-3.9760020	1.6797590
H	3.5756870	-0.7689390	0.3545950	H	0.0939220	-3.5569050	3.2544770
C	2.7459350	0.8622670	-0.8112710	H	-1.2055790	-2.5663680	2.5688460
H	3.0290440	1.8958720	-1.0718340	C	0.7761760	-2.5295470	-0.8203160
C	1.3756350	0.7894880	-0.1574680	H	1.8875130	-2.5125190	-0.8489660
H	1.3536200	1.4643450	0.7090870	C	0.3808940	-4.0179720	-0.8023700
H	0.7922900	-4.5467310	0.0629560	H	-4.6506000	1.6878760	2.1134710
H	-0.7123420	-4.1302120	-0.7788240	H	-4.7048740	1.7724180	3.8866900
H	0.7549500	-4.5230450	-1.7028650	C	-0.6182710	3.8043350	-0.1728270

C	0.2839140	-1.8988860	-2.1324380	F	0.0390280	3.6675450	0.9851320
H	0.5632750	-0.8447350	-2.2064710	F	-1.7933410	4.3955920	0.0629510
H	0.7007410	-2.4248920	-3.0002540	F	0.1004300	4.5625610	-0.9986410
H	-0.8121640	-1.9614450	-2.2007720	C	10.2191590	-0.7048500	0.0834260
O	-3.5892240	-1.3906900	-1.2130310	H	10.9779290	-1.1138360	0.7606430
C	-4.0645290	-0.3811520	-2.1351920	H	10.2588510	-1.2820710	-0.8486960
H	-5.0684460	-0.0529830	-1.8275850	H	10.5071080	0.3265250	-0.1554330
H	-3.3819570	0.4694970	-2.0853120	H	2.7396120	0.2978480	-1.7547030
C	-4.1003260	-1.0799260	-3.4903900	H	0.7945500	-0.5430700	0.1015490
C	-4.5694410	-2.4915120	-3.1008830				
C	-3.9054740	-2.7064770	-1.7297040				
H	-4.5606910	-3.2210100	-1.0171960				
H	-2.9681560	-3.2685560	-1.8079210				
H	-5.6612080	-2.5162470	-3.0077060				
H	-4.2780150	-3.2583410	-3.8243280				
H	-3.0944630	-1.1087290	-3.9241630				
H	-4.7673010	-0.5851350	-4.2024350				
O	-3.2524030	-0.6871990	2.2146870				
C	-3.1374530	0.4730730	3.0627420				
H	-2.8568760	0.1602720	4.0789480				
H	-2.3478390	1.1043610	2.6495450				
C	-4.5244630	1.1091160	3.0355510				
C	-5.4349670	-0.1312820	3.0327050				
C	-4.6201030	-1.1587630	2.2241420				
H	-4.6499360	-2.1603610	2.6689310				
H	-4.9453710	-1.2287450	1.1806070				
H	-5.5933570	-0.4872980	4.0568500				
H	-6.4173080	0.0584370	2.5903540				

Table S-19. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_2$ mediated substitution of *n*-octyl trifluoromethanesulfonate (**13**).



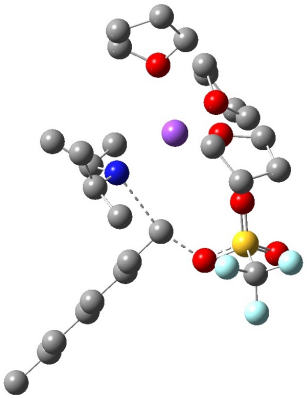
G = -1376903.394

G_{MP2} = -1373453.623

Atom	X	Y	Z	Atom	X	Y	Z
C	8.5673940	-0.0631130	-1.0206400	H	0.7893100	-0.2859510	-0.2007950
H	8.3975040	-0.9975750	-1.5742350	H	0.2805090	0.7107150	1.2422090
H	8.4653280	0.7477380	-1.7559910	C	9.9895710	-0.0585570	-0.4507280
C	7.4834660	0.0909150	0.0539710	H	10.7393540	-0.1661650	-1.2429770
H	7.5842610	-0.7215740	0.7891880	H	10.1999020	0.8772340	0.0818630
H	7.6549290	1.0249940	0.6096820	H	10.1351550	-0.8818920	0.2595490
C	6.0571050	0.0914320	-0.5106100	O	1.0468040	1.8838900	-0.4693790
H	5.8872960	-0.8408840	-1.0694010	S	-0.2612330	2.1302590	-1.2412210
H	5.9567010	0.9062460	-1.2427300	O	-0.0442530	2.7417380	-2.5452060
C	4.9723150	0.2414860	0.5635140	O	-1.1808750	0.9714820	-1.1546050
H	5.1476500	1.1687840	1.1289780	C	-1.0895660	3.4260740	-0.1876720
H	5.0622730	-0.5798770	1.2899440	F	-2.2890560	3.7278100	-0.7028300
C	3.5505180	0.2614310	-0.0119070	F	-0.3512880	4.5307790	-0.1219980
H	3.3735870	-0.6648270	-0.5763730	F	-1.2718440	2.9495000	1.0590570
H	3.4523140	1.0865480	-0.7268120	N	-0.1102370	-1.7196980	1.6072150
C	2.4761130	0.4048830	1.0760810	Na	-1.8159930	-0.8756050	0.2432740
H	2.6480510	1.3160000	1.6637100	O	-3.8463670	0.0526980	0.9916510
H	2.5446960	-0.4367450	1.7779480	C	-1.7244590	-2.1762660	3.4894310
C	1.0638140	0.4060600	0.5729390	H	-1.8719550	-3.2091580	3.1642130
H	-3.0580480	1.4291270	2.2911110	C	-4.0431550	1.1292590	1.9287590

C	-4.7898480	2.2491570	1.1619380	H	-4.6318700	0.7609450	2.7794740
C	-5.1122990	1.6093940	-0.2112830	H	-1.8528990	-2.1408130	4.5814510
C	-4.9415840	0.1148710	0.0643510	H	-2.5258450	-1.5722610	3.0401210
H	-5.8431450	-0.3149440	0.5287620	C	0.6913860	-2.8856070	1.2570920
H	-4.6645870	-0.4861610	-0.8040980	H	1.6983850	-2.8304970	1.7377600
H	-6.1131050	1.8604490	-0.5752200	C	0.1194760	-4.2591250	1.6969430
H	-4.3819800	1.9322550	-0.9592730	H	-0.0055270	-4.3245640	2.7817170
H	-4.1701840	3.1410370	1.0469580	H	-0.8628590	-4.4318000	1.2340680
H	-5.7001590	2.5403180	1.6949670	H	0.7897460	-5.0757920	1.3952910
O	-2.7364550	-2.0314410	-1.5945550	C	0.9393800	-2.9579180	-0.2597210
C	-2.5053810	-1.6297620	-2.9624980	H	1.5130900	-2.1042450	-0.6330940
H	-3.4369180	-1.2290100	-3.3895590	H	1.4988570	-3.8632490	-0.5246920
H	-1.7562360	-0.8360980	-2.9484810	H	-0.0158190	-2.9854700	-0.8034620
C	-2.0782160	-2.9102680	-3.6729660				
C	-2.9865700	-3.9552300	-3.0018190				
C	-3.1149060	-3.4295880	-1.5598410				
H	-4.1359640	-3.5138050	-1.1699590				
H	-2.4351860	-3.9372010	-0.8672400				
H	-3.9664520	-3.9755240	-3.4920430				
H	-2.5750020	-4.9679180	-3.0360910				
H	-1.0230010	-3.1216830	-3.4658310				
H	-2.2122980	-2.8575800	-4.7575040				
C	-0.3391260	-1.6305500	3.0528400				
H	0.4232110	-2.2166610	3.6039210				
C	-0.2177660	-0.1889060	3.5852730				
H	-0.4449730	-0.1402090	4.6577350				
H	0.7902220	0.2129240	3.4395860				
H	-0.9281430	0.4800600	3.0766660				

Table S-20. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_3$ mediated substitution of *n*-octyl trifluoromethanesulfonate (**13**).



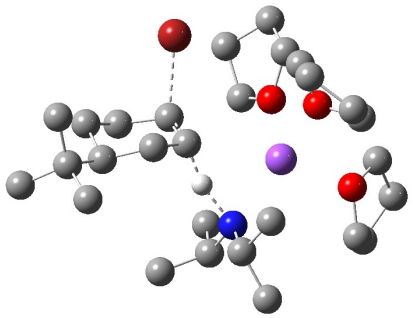
G = -1522627.836

G_{MP2} = -1518767.013

Atom	X	Y	Z	Atom	X	Y	Z
C	-8.7474590	-1.6202950	0.5833520	H	-2.5534130	-0.8099720	-1.6435250
H	-8.4333630	-2.4375120	1.2483430	C	-1.4075890	0.4353090	-0.3941400
H	-8.9168190	-0.7493780	1.2325380	H	-1.1061830	-0.0442370	0.5206360
C	-7.6126440	-1.3047840	-0.3995180	H	-0.6130740	0.8162660	-1.0073910
H	-7.4440120	-2.1769240	-1.0490830	C	-10.0595310	-2.0024920	-0.1093680
H	-7.9279410	-0.4878040	-1.0658030	H	-10.8484290	-2.2223720	0.6192150
C	-6.2950180	-0.9203320	0.2853520	H	-10.4186570	-1.1906860	-0.7540400
H	-5.9818780	-1.7361710	0.9538250	H	-9.9310430	-2.8914360	-0.7394040
H	-6.4626730	-0.0460870	0.9315660	O	-1.8806820	2.0184020	0.3718400
C	-5.1607680	-0.6106340	-0.6999230	S	-0.7374130	2.8998110	0.9035760
H	-5.4755340	0.2030920	-1.3702300	O	-1.1407840	3.7025740	2.0531020
H	-4.9891270	-1.4863890	-1.3435900	O	0.5426670	2.1653320	0.9626580
C	-3.8465350	-0.2201830	-0.0128480	C	-0.5088160	4.0998470	-0.5044090
H	-3.5271630	-1.0346200	0.6528050	F	0.4799780	4.9589230	-0.2174970
H	-4.0057820	0.6602420	0.6206000	F	-1.6268810	4.7880990	-0.7312750
C	-2.7226420	0.0743100	-1.0171810	F	-0.1785080	3.4317870	-1.6256600
H	-3.0215290	0.8845390	-1.6949130	N	0.0311680	-1.6145310	-1.1292820
C	0.0666990	-1.6456440	-2.5924860	H	3.9153020	3.2686160	-2.9182040
H	-0.8417130	-2.1342130	-3.0027580	H	4.5994260	3.8921450	-0.6985230
C	0.1047430	-0.2319670	-3.2087590	H	2.8619280	4.0369910	-0.4050880

H	0.3207280	-0.2747660	-4.2836150	O	3.7262630	-2.2847320	0.1065100
H	-0.8423440	0.3026900	-3.0906790	C	5.0817180	-1.8468890	0.3143990
H	0.8934180	0.3720110	-2.7383380	H	5.0950450	-0.7716880	0.1275810
C	1.2833860	-2.4187680	-3.1692050	H	5.3665260	-2.0283900	1.3603050
H	2.2141140	-1.9080010	-2.8821850	C	5.9673680	-2.6667860	-0.6587140
H	1.3378170	-3.4416320	-2.7911390	C	4.9668410	-3.6104790	-1.3661510
H	1.2510440	-2.4657520	-4.2675500	C	3.7834340	-3.6247900	-0.3987400
C	-0.7458560	-2.7082190	-0.5538480	H	2.8196780	-3.8391440	-0.8627090
H	-1.8375050	-2.5596360	-0.7419250	H	3.9520160	-4.3320840	0.4297570
C	-0.4804970	-4.1445980	-1.0745810	H	4.6487770	-3.1913980	-2.3264600
H	-0.6529980	-4.2364540	-2.1510580	H	5.3771770	-4.6081200	-1.5491040
H	0.5505540	-4.4609810	-0.8647430	H	6.7220860	-3.2352320	-0.1058560
H	-1.1550810	-4.8539230	-0.5761450	H	6.4965140	-2.0266060	-1.3704470
C	-0.5632930	-2.7463900	0.9734500	O	2.1797310	-0.6143490	2.4768380
H	-0.7353050	-1.7712580	1.4416290	C	1.7140820	0.3252330	3.4623430
H	-1.2503820	-3.4641010	1.4392200	H	2.5836670	0.8144590	3.9287610
H	0.4609360	-3.0577920	1.2226440	H	1.1174830	1.0763440	2.9457130
Na	1.8590660	-0.7345230	0.0979510	C	0.9458630	-0.5239130	4.4890060
O	3.3821500	0.9652200	-0.6226390	C	1.5893210	-1.9329660	4.3556580
C	3.7120070	2.1049540	0.2020720	C	2.6201590	-1.7568290	3.2230800
H	2.9855490	2.1332130	1.0135590	H	3.6233620	-1.5571780	3.6315010
H	4.7196650	1.9630010	0.6178630	H	2.6862670	-2.5971630	2.5303710
C	3.6495080	3.3484230	-0.7174200	H	2.0679210	-2.2661540	5.2816190
C	3.3609900	2.7637040	-2.1211910	H	0.8371230	-2.6789430	4.0836600
C	3.7629010	1.2970000	-1.9648140	H	-0.1183060	-0.5597950	4.2378180
H	3.2439510	0.6100860	-2.6374730	H	1.0333280	-0.1123570	5.4988390
H	4.8499650	1.1634130	-2.0886730				
H	2.2932780	2.8340020	-2.3485010				

Table S-21. Geometric coordinates and thermally corrected MP2 energies for the $A(THF)_3$ mediated anti elimination of 1-bromo-4-(*tert*-butyl)cyclohexane (*cis*-**17**).



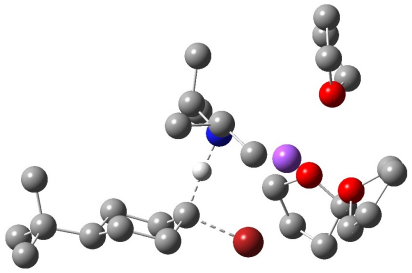
G = -2581668.122

G_{MP2} = -2577781.99

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.6717260	-0.3698210	0.1282320	H	1.8086820	-4.3788110	0.5675420
N	0.2685800	-2.2492900	-0.4046290	C	0.1200510	-2.6944190	2.0100850
C	0.2449810	-2.7534650	-1.7827610	H	-0.4441550	-1.7688950	2.1550560
H	0.9442510	-3.6041190	-1.8860100	H	-0.2095290	-3.4106070	2.7731160
C	-1.1282470	-3.2661630	-2.2730970	H	1.1829830	-2.4790930	2.1904480
H	-1.8672650	-2.4559920	-2.2854040	O	1.7567540	0.7448230	2.2293750
H	-1.0574010	-3.6752190	-3.2895360	C	2.5423750	0.1875040	3.2937770
H	-1.5179050	-4.0595840	-1.6262710	H	2.9396950	-0.7684720	2.9453830
C	0.7621650	-1.6742300	-2.7458440	H	3.3867410	0.8604300	3.5084040
H	1.7778280	-1.3563780	-2.4733190	C	1.5932110	0.0846370	4.5070750
H	0.7975270	-2.0469310	-3.7770390	C	0.4317930	1.0540430	4.1504080
H	0.1141580	-0.7898430	-2.7384800	C	0.9053550	1.7257390	2.8549480
C	-0.0746670	-3.2680660	0.5985050	H	0.1100560	1.9873150	2.1536420
H	-1.1420550	-3.5603290	0.5245780	H	1.4999440	2.6277090	3.0683680
C	0.7313010	-4.5804930	0.4957520	H	-0.4932410	0.4987730	3.9692950
H	0.4603810	-5.2588030	1.3147150	H	0.2319860	1.7859420	4.9384260
H	0.5509880	-5.1162170	-0.4416270	H	2.1046890	0.3685330	5.4318500
H	1.2248030	-0.9372830	4.6324110	C	-3.8727920	-0.5744610	-0.4313800
O	3.9285410	-1.0607460	0.1741380	C	-2.8265060	-0.4167000	0.6947420
C	4.2690680	-2.3824320	-0.2855310	H	-3.1452230	0.3921550	1.3708330
H	4.8195090	-2.9200260	0.5014440	H	-2.7784600	-1.3304720	1.2970940

H	3.3313770	-2.9054360	-0.4860470	H	-3.5574300	-1.4366110	-1.0418510
C	5.1460290	-2.1477190	-1.5121630	C	-5.3169970	-0.9246810	0.0738500
C	5.9744090	-0.9265860	-1.0733200	C	-5.2665400	-2.1475190	1.0160960
C	5.0014890	-0.1486780	-0.1627630	H	-4.7704670	-1.9172590	1.9643550
H	5.4840910	0.1957290	0.7598220	H	-6.2821150	-2.4882700	1.2530310
H	4.5431410	0.7097550	-0.6625210	H	-4.7333510	-2.9872590	0.5521970
H	6.8549020	-1.2502200	-0.5072960	C	-6.2079730	-1.3055730	-1.1289860
H	6.3249820	-0.3228330	-1.9154910	H	-7.2039140	-1.6125540	-0.7865320
H	4.5201180	-1.9033690	-2.3782850	H	-6.3468760	-0.4712910	-1.8243170
H	5.7617640	-3.0152070	-1.7678620	H	-5.7764120	-2.1438960	-1.6905220
O	2.1781820	1.6733840	-1.0837610	C	-5.9759190	0.2500820	0.8265360
C	2.2632220	2.8924310	-0.2868200	H	-6.1247350	1.1200550	0.1778200
H	1.3324550	2.9925530	0.2773300	H	-6.9611040	-0.0483150	1.2067670
H	3.1086370	2.7871470	0.3996700	H	-5.3759080	0.5728250	1.6845960
C	2.4066920	4.0377060	-1.2887120	H	-4.0653110	1.5691050	-0.7588990
C	1.6014540	3.5002260	-2.4803030	H	-4.5412930	0.6014030	-2.1565930
C	2.0012680	2.0253980	-2.4766740	H	-2.3761060	1.7960000	-2.5267370
H	1.2451500	1.3621220	-2.9053990	H	-2.1789170	0.0446640	-2.6151340
H	2.9501200	1.8617090	-3.0078200	H	-0.3477650	1.1310940	-1.2276970
H	0.5312250	3.6022570	-2.2688630	H	-0.7521630	0.1363480	1.0072210
H	1.8304080	3.9960380	-3.4285550	Br	-1.5308560	3.0566330	0.0473100
H	3.4568710	4.1954310	-1.5652490	H	-0.7514870	-1.1703430	-0.2522810
H	2.0091720	4.9763010	-0.8920770	C	-1.4227190	-0.0960870	0.1705920
C	-1.3441530	0.8961960	-0.8650850				
C	-2.4154490	0.8785300	-1.9320000				
C	-3.8153940	0.6730750	-1.3392120				

Table S-22. Geometric coordinates and thermally corrected MP2 energies for the A(THF)$_3$ mediated carbene generation of 1-bromo-4-(*tert*-butyl)cyclohexane (*trans*-**17**).



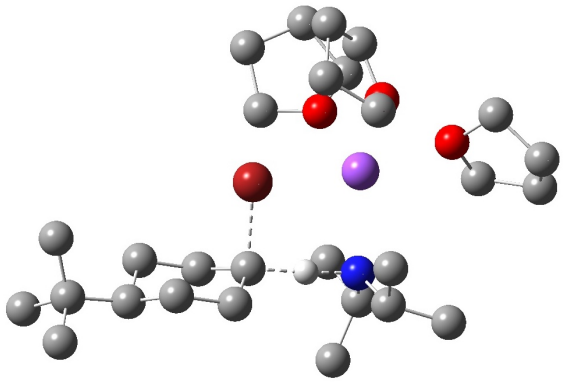
G = -2581671.815

G$_{MP2}$ = -2577789.192

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.6444110	0.0128870	-0.0953500	H	1.0087910	3.7297990	-1.1380300
N	-0.2047820	1.5665580	0.1779880	C	-0.3960620	1.6009190	-2.2617030
C	-0.1831900	2.2933660	1.4567300	H	-0.7626220	0.5728730	-2.2045560
H	0.4795450	3.1736700	1.3695190	H	-0.8756950	2.0842180	-3.1227150
C	-1.5484630	2.8294080	1.9451640	H	0.6861050	1.5662570	-2.4544910
H	-1.4238540	3.4568070	2.8377350	O	2.3592510	-1.4063440	-1.9873960
H	-2.0459590	3.4372030	1.1815630	C	1.3346400	-1.7960820	-2.9376620
H	-2.2205650	2.0058420	2.2070730	H	0.3601930	-1.6279430	-2.4688620
C	0.4301310	1.4065280	2.5513230	H	1.4229380	-1.1594080	-3.8243500
H	1.4618420	1.1241170	2.3067440	C	1.5590730	-3.2840820	-3.2284160
H	0.4500950	1.9319150	3.5147670	C	2.2186440	-3.7682560	-1.9282130
H	-0.1465190	0.4836320	2.6801960	C	3.1018840	-2.5749890	-1.5693630
C	-0.6842730	2.3637690	-0.9601220	H	3.3034040	-2.4733600	-0.4999010
H	-1.7863600	2.4978140	-0.9135680	H	4.0579270	-2.6053940	-2.1132920
C	-0.0865590	3.7779310	-1.0783600	H	1.4577740	-3.9119770	-1.1542640
H	-0.4516240	4.2677760	-1.9899420	H	2.7878070	-4.6956370	-2.0460210
H	-0.3498670	4.4230000	-0.2342660	H	2.2382830	-3.4190050	-4.0790290
H	0.6229930	-3.8027140	-3.4556060	C	-6.9677050	-0.3327250	-1.3690970
O	3.1569770	-1.0341460	1.5756310	H	-7.0411370	-1.4272640	-1.3323820

C	4.4816970	-0.6120090	1.9200350	H	-7.9876590	0.0665570	-1.4310160
H	5.1858630	-1.4427080	1.7516390	H	-6.4558930	-0.0614460	-2.2981760
H	4.7378110	0.2140740	1.2557140	C	-6.1117030	1.7516830	-0.2706440
C	4.4101470	-0.2477200	3.4130160	H	-5.5083420	2.0238730	-1.1436850
C	3.2420090	-1.1248160	3.9458080	H	-7.1008130	2.2090070	-0.3999910
C	2.7041890	-1.8305520	2.6853050	H	-5.6520570	2.2106440	0.6114530
H	3.1219260	-2.8443110	2.5884780	H	-3.8564100	0.9942070	1.2756790
H	1.6181140	-1.8896020	2.6141710	H	-4.6993350	-0.2283460	2.2208760
H	3.5726260	-1.8494170	4.6960660	H	-3.0365800	-1.9355040	1.6448710
H	2.4666320	-0.5044370	4.4035160	H	-2.2711320	-0.5463310	2.4182510
H	4.1799420	0.8150080	3.5366100	O	3.5902400	1.4318720	-0.5841470
H	5.3568820	-0.4443390	3.9254160	C	4.3024470	1.3424780	-1.8284350
Br	-0.2679020	-2.0318960	0.5261310	H	5.3748790	1.1758700	-1.6359470
C	-1.8861710	-0.6621750	0.2798550	H	3.8957020	0.4850140	-2.3674270
C	-2.7728340	-0.8740150	1.4981490	C	4.0654690	2.6974960	-2.4923870
C	-4.0880920	-0.0764090	1.3239400	C	4.1261300	3.6648050	-1.2910520
C	-4.8600670	-0.4898890	0.0533580	C	3.7310950	2.7777930	-0.0846590
C	-3.9142600	-0.3543950	-1.1583560	H	4.5027470	2.7965990	0.6972810
C	-2.6179990	-1.1697920	-0.9552300	H	2.7731410	3.0532540	0.3624750
H	-1.9944480	-1.0906840	-1.8549350	H	5.1392550	4.0600870	-1.1617980
H	-2.8978000	-2.2338760	-0.8638900	H	3.4519250	4.5172770	-1.4115890
H	-3.6537410	0.7008930	-1.3146910	H	3.0710640	2.7143950	-2.9511470
H	-4.4005240	-0.7023260	-2.0767430	H	4.8048640	2.9292600	-3.2651680
H	-5.0910790	-1.5638440	0.1542140	H	-1.0488050	0.5550600	0.2419360
C	-6.2473200	0.2223400	-0.1203690				
C	-7.1448000	-0.0768850	1.1007060				
H	-8.1559830	0.3161280	0.9379680				
H	-7.2321640	-1.1572330	1.2739550				
H	-6.7626680	0.3802690	2.0190380				

Table S-23. Geometric coordinates and thermally corrected MP2 energies for the A(THF)$_3$ mediated carbene generation of 1-bromo-4-(*tert*-butyl)cyclohexane (*cis*-**17**).



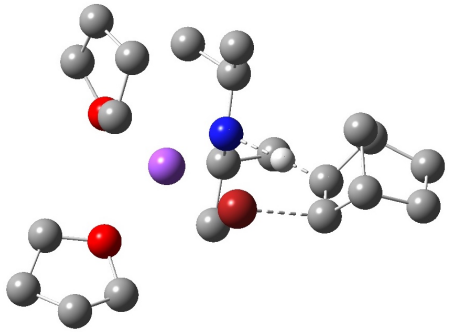
G = -2581674.681

G$_{MP2}$ = -2577790.712

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.6448180	-0.0185260	-0.0202930	H	-7.9672780	-0.4910620	1.2271820
Br	-1.0672330	-0.9470300	-0.5182780	H	-6.4506170	-0.6422220	2.1179910
C	-1.7867530	1.0142620	0.0396580	H	-7.0507710	0.9610340	1.6620750
C	-2.7197750	1.4409180	-1.0822670	C	-6.0571120	-1.6491390	-0.4130640
C	-4.0336170	0.6484660	-1.2337320	H	-5.4866360	-2.2123930	0.3335600
C	-4.8173050	0.5611110	0.0940400	H	-7.0447870	-2.1201240	-0.4965730
C	-3.8888140	-0.0194650	1.1825490	H	-5.5530810	-1.7669880	-1.3785460
C	-2.5789000	0.7828620	1.3173330	H	-3.7846010	-0.3602520	-1.5865730
H	-1.9483130	0.3335270	2.0953900	H	-4.6425500	1.1188630	-2.0151680
H	-2.8275870	1.7959100	1.6816110	H	-2.9687170	2.4906750	-0.8429120
H	-3.6296290	-1.0561250	0.9341900	H	-2.1933050	1.4738710	-2.0434710
H	-4.3952890	-0.0401680	2.1551270	N	0.7130270	2.2191420	0.0966250
H	-5.0536380	1.5974600	0.3938740	C	0.8188480	3.0569570	1.2999680
C	-6.2046590	-0.1642740	-0.0219630	H	1.7910330	3.5834450	1.3096510
C	-7.0795670	0.5407250	-1.0814390	C	-0.2686790	4.1488360	1.4299620
H	-6.6793270	0.4230710	-2.0934840	H	-0.1131950	4.7514910	2.3343450
H	-8.0935750	0.1218130	-1.0804850	H	-0.2638690	4.8327080	0.5742140

H	-7.1639950	1.6156760	-0.8758740	H	3.1062530	-1.0908660	3.5468740
C	-6.9549600	-0.0795390	1.3256880	C	2.5807490	-3.1934420	3.2156220
H	1.6105200	1.4230400	2.5180680	H	-1.2673470	3.7004840	1.4907950
H	0.9172830	2.7586530	3.4618140	C	0.8008300	2.1618140	2.5482110
H	-0.1452220	1.6144710	2.6229740	C	1.0276260	-3.2331870	3.1345470
C	0.7755330	2.9663630	-1.1689050	C	0.6516400	-1.8104720	2.6912000
H	-0.1389830	3.5767570	-1.3165570	H	-0.2011270	-1.7448980	2.0146930
C	1.9675350	3.9325960	-1.2938990	H	0.4843320	-1.1520110	3.5569390
H	1.9832260	4.3952840	-2.2890000	H	0.6965260	-3.9621830	2.3882610
H	1.9337050	4.7421680	-0.5576130	H	0.5614070	-3.5000160	4.0875690
H	2.9135860	3.3910620	-1.1576020	H	2.9502590	-3.3530990	4.2331380
C	0.8252780	1.9674880	-2.3366550	H	3.0255670	-3.9655950	2.5803640
H	0.0548350	1.1973130	-2.2326020	O	4.0716310	0.3043700	0.2104820
H	0.6813530	2.4728440	-3.3002550	C	5.0427490	-0.0609480	-0.7807650
H	1.8056290	1.4677830	-2.3704700	H	5.8543880	-0.6452230	-0.3167610
O	2.3058500	-1.7131180	-1.7195870	H	4.5278420	-0.6811520	-1.5163190
C	1.7551970	-1.7811420	-3.0480210	C	5.5625120	1.2734010	-1.3110030
H	1.2381300	-0.8383430	-3.2368370	C	5.6204620	2.1274120	-0.0278500
H	2.5689530	-1.8978620	-3.7810630	C	4.5351660	1.4984700	0.8790330
C	0.8397260	-3.0013300	-3.0262610	H	4.9366160	1.2294450	1.8649930
C	1.6390330	-3.9836450	-2.1498020	H	3.6637150	2.1423370	1.0169940
C	2.4305030	-3.0569870	-1.2003920	H	6.6070540	2.0501360	0.4416340
H	2.0327210	-3.0456330	-0.1815680	H	5.4288870	3.1863020	-0.2229310
H	3.4936080	-3.3281560	-1.1554040	H	4.8437950	1.6937500	-2.0230010
H	0.9939610	-4.6779140	-1.6034490	H	6.5318280	1.1865810	-1.8117320
H	2.3242080	-4.5791220	-2.7634420	H	-0.4748230	1.6815500	0.1097300
H	0.6290170	-3.3935430	-4.0259450				
H	-0.1050330	-2.7307630	-2.5458680				
O	1.7969470	-1.3448440	1.9581270				
C	2.9377540	-1.7803130	2.7053970				
H	3.8006160	-1.7359940	2.0387190				

Table S-24. Geometric coordinates and thermally corrected MP2 energies for the A(THF)$_2$ mediated *syn* elimination of *exo*-2-bromonorbornane (**22**).



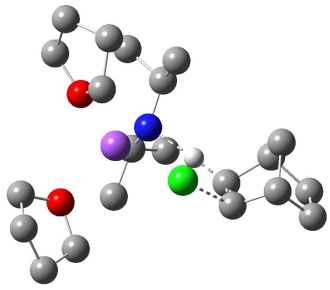
G = -2361307.377

G_{MP2} = -2358060.153

Atom	X	Y	Z	Atom	X	Y	Z
C	5.1984600	-0.5168800	0.3874120	C	2.2617680	1.0868050	-3.6404560
C	3.8952280	0.3230100	0.3469290	H	2.2447800	0.8324690	-4.7080470
C	3.3956450	0.1595040	1.7998690	H	2.5494270	2.1406780	-3.5605900
C	3.3286880	-1.3795320	1.7283410	H	3.0517790	0.4922620	-3.1680880
C	4.7961870	-1.7240500	1.2917120	C	0.4788250	-0.6507190	-3.2090110
H	4.8614950	-2.6888650	0.7769660	H	-0.5615600	-0.8254970	-2.9093340
H	5.4287520	-1.7909130	2.1844960	H	0.5707530	-0.9346120	-4.2649770
C	2.5103220	-1.5757660	0.4789370	H	1.1138250	-1.3263570	-2.6234500
C	2.8323950	-0.4925190	-0.4377540	C	1.0644290	2.5651590	-1.2832680
H	3.1693700	-0.8715990	-1.4103360	H	2.1125370	2.8192710	-1.5448010
H	2.2893950	-2.5764370	0.1246560	C	0.1802810	3.5785920	-2.0472020
Br	0.2232810	-1.4570330	1.3782270	H	0.4098590	4.6077020	-1.7413830
Na	-1.0191570	0.1918170	-0.4384090	H	0.3208710	3.5193400	-3.1313150
N	0.7532980	1.1671320	-1.5773650	H	-0.8827190	3.3875330	-1.8396760
C	0.8781780	0.8196520	-2.9978510	C	0.9232360	2.8240520	0.2234700
H	0.1579570	1.4130750	-3.5958250	H	1.5497480	2.1429370	0.8048790
H	1.2107090	3.8524930	0.4762860	H	4.0284730	1.3474150	-0.0103070
H	-0.1158010	2.6779770	0.5499400	H	5.5220230	-0.8251490	-0.6125240

O	-2.6366290	1.2548920	0.9613200	H	6.0206510	0.0527990	0.8372130
C	-2.6728160	0.8171480	2.3323460	H	1.9060550	0.2172400	-0.7982300
H	-3.6977190	0.5115350	2.5952830				
H	-2.0003320	-0.0394160	2.4160410				
C	-2.2269930	2.0453290	3.1257160				
C	-2.8334820	3.2201620	2.3197490				
C	-3.1504590	2.5987200	0.9361860				
H	-4.2331830	2.5690520	0.7499810				
H	-2.6679710	3.1146140	0.1019240				
H	-3.7469580	3.5984740	2.7893660				
H	-2.1341610	4.0567460	2.2383380				
H	-1.1337140	2.0991800	3.1262630				
H	-2.5671140	2.0215280	4.1653060				
O	-2.5966450	-1.3287620	-1.3086890				
C	-2.3935040	-2.7388660	-1.0651920				
H	-2.1932300	-3.2478840	-2.0191500				
H	-1.5229360	-2.8304180	-0.4115060				
C	-3.6995480	-3.2181620	-0.4373290				
C	-4.7400000	-2.3825880	-1.2010410				
C	-4.0098380	-1.0456760	-1.4120100				
H	-4.2136610	-0.6025000	-2.3938430				
H	-4.2570050	-0.3106560	-0.6374810				
H	-4.9690690	-2.8522480	-2.1646220				
H	-5.6813340	-2.2595020	-0.6569610				
H	-3.7127910	-2.9732280	0.6313370				
H	-3.8502070	-4.2967200	-0.5436290				
H	2.9837460	-1.9197060	2.6107980				
H	2.4147390	0.6022740	1.9882730				
H	4.1115120	0.5220710	2.5464840				

Table S-25. Geometric coordinates and thermally corrected MP2 energies for the A(THF)$_2$ mediated *syn* elimination of *exo*-2-chloronorbornane (**23**).



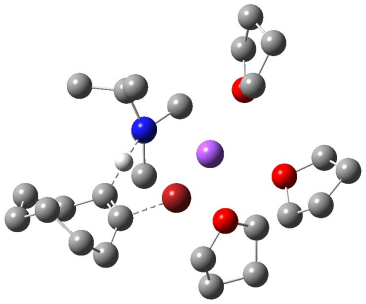
G = -1036317.92

G_{MP2} = -1033769.169

Atom	X	Y	Z	Atom	X	Y	Z
C	5.1609640	-0.5191440	0.7387950	H	2.7899070	1.9486270	-3.2867250
C	3.8960170	0.3560220	0.5418960	H	3.2500910	0.3135700	-2.7981690
C	3.3876170	0.4732310	1.9956720	C	0.7059230	-0.8464120	-3.0966830
C	3.2539460	-1.0499830	2.1975240	H	-0.3525310	-1.0248630	-2.8708690
C	4.7091970	-1.5231720	1.8455230	H	0.8816940	-1.1495100	-4.1366290
H	4.7413820	-2.5685650	1.5196010	H	1.3033700	-1.5035710	-2.4526800
H	5.3342270	-1.4452570	2.7425570	C	1.0307980	2.4330700	-1.2185790
C	2.4413220	-1.4382750	0.9922690	H	2.1061700	2.6965350	-1.3005660
C	2.7962720	-0.5373860	-0.0937800	C	0.2860170	3.4027680	-2.1650840
H	3.1087100	-1.0865880	-0.9903380	H	0.4251850	4.4427260	-1.8424240
H	2.2031550	-2.4808110	0.8145620	H	0.6372370	3.3315570	-3.1994320
Cl	0.2500870	-1.1701380	1.7639670	H	-0.7912470	3.1834850	-2.1636320
Na	-0.9366060	-0.0073820	-0.3274380	C	0.6184730	2.7471220	0.2266900
N	0.7944970	1.0155650	-1.4951900	H	1.0832870	2.0517010	0.9307680
C	1.0722280	0.6309930	-2.8827300	H	0.9044660	3.7676920	0.5111840
H	0.4184590	1.2020860	-3.5704690	H	-0.4706380	2.6609840	0.3453160
C	2.5177570	0.8911070	-3.3735050	O	-2.8152920	1.0886910	0.6692130
H	2.6252960	0.6110810	-4.4296010	C	-2.9216900	0.9964650	2.1063500
H	-3.8068370	0.3988320	2.3719560				

H	-2.0257960	0.4856230	2.4677240
C	-3.0685090	2.4414150	2.5734660
C	-3.9606420	3.0371400	1.4699570
C	-3.5218430	2.2646040	0.2102830
H	-4.3729350	1.9543520	-0.4079020
H	-2.8317440	2.8411120	-0.4148680
H	-5.0165670	2.8438910	1.6904420
H	-3.8367860	4.1177560	1.3546960
H	-2.0882780	2.9306020	2.5887660
H	-3.5094500	2.5216360	3.5716150
O	-2.2430330	-1.8250010	-1.0831530
C	-3.6767600	-1.8457200	-0.9775490
H	-3.9849450	-0.8891620	-0.5484200
H	-4.1220470	-1.9521270	-1.9785860
C	-3.9903640	-3.0571460	-0.1020480
C	-2.9314580	-4.0639710	-0.5814290
C	-1.7215840	-3.1662890	-0.8943690
H	-1.0076010	-3.1230400	-0.0656860
H	-1.1941300	-3.4702390	-1.8051890
H	-2.6957810	-4.8270780	0.1658970
H	-3.2790880	-4.5754990	-1.4864440
H	-5.0165410	-3.4172170	-0.2250890
H	-3.8342680	-2.8081260	0.9539640
H	2.8832560	-1.4131020	3.1566350
H	2.4310660	0.9909330	2.0929010
H	4.1185330	0.9292030	2.6734930
H	4.0722260	1.2948160	0.0108410
H	5.4658440	-1.0180460	-0.1874020
H	6.0099790	0.0853430	1.0801310
H	1.8978910	0.1450970	-0.5657230

Table S-26. Geometric coordinates and thermally corrected MP2 energies for the A(THF)$_3$ mediated *syn* elimination of (*E*)-1-bromocyclooct-1-ene (**26**).



G = -2531655.352

G_{MP2} = -2527921.345

Atom	X	Y	Z	Atom	X	Y	Z
Na	-0.9677510	0.1946220	0.5051790	H	4.6221550	-1.6295280	-3.3864860
Br	0.5287270	-0.5662750	-1.7572850	H	4.0077720	-2.1432980	-1.1059630
C	2.4320230	-0.7932000	-0.8505440	H	2.6349450	-2.5070790	-2.1471650
C	3.2360740	-1.6850370	-1.7423350	N	0.8428750	1.4165310	1.5970250
C	3.9278360	-0.9324850	-2.8956080	C	0.8378370	1.1982750	3.0494180
C	4.6850930	0.3356120	-2.4636180	H	1.5806600	1.8402240	3.5580610
C	5.6705770	0.1697520	-1.2793180	C	-0.5279720	1.5432950	3.6858970
C	5.1784970	0.6415130	0.1067560	H	-0.4938800	1.4791960	4.7825880
C	4.0922660	-0.1924450	0.8270890	H	-0.8468810	2.5585560	3.4231360
C	2.6925770	-0.1006670	0.2269580	H	-1.3044990	0.8459540	3.3361760
H	4.4403740	-1.2376430	0.8812730	C	1.2108580	-0.2496540	3.3979470
H	4.0526910	0.1649200	1.8657420	H	2.2291490	-0.4864450	3.0746900
H	6.0533940	0.6759170	0.7725280	H	1.1509480	-0.4158790	4.4813360
H	4.8295260	1.6787910	0.0158200	H	0.5295870	-0.9516240	2.9043990
H	6.5737800	0.7538780	-1.5008730	C	1.0659060	2.8279890	1.2480480
H	6.0106980	-0.8746570	-1.2132820	H	0.3547310	3.4699480	1.8060360
H	5.2357910	0.7007000	-3.3407890	C	2.4805230	3.3616380	1.5808360
H	3.9598470	1.1198670	-2.2166430	H	2.5505590	4.4389200	1.3789150

H	3.1766010	-0.6562360	-3.6464450	H	2.7455820	3.2102330	2.6325720
H	3.2338590	2.8545940	0.9682000	O	-0.8752010	-2.1246030	1.3461050
C	0.7951830	3.0489580	-0.2467820	C	0.1654020	-3.0644090	0.9985260
H	-0.2420960	2.8048020	-0.4946570	H	-0.0605680	-3.5030060	0.0166500
H	0.9821100	4.0922460	-0.5335700	H	1.1020120	-2.5082930	0.9262970
H	1.4413500	2.4062200	-0.8537880	C	0.1308880	-4.1217660	2.1005820
O	-2.5937000	1.9491290	-0.1316640	C	-1.3718950	-4.1956280	2.4148860
C	-2.9400170	3.1231360	0.6393580	C	-1.8064870	-2.7310950	2.2617060
H	-3.7336750	2.8424440	1.3435830	H	-2.8175760	-2.6171470	1.8568550
H	-2.0627270	3.4406390	1.2106460	H	-1.7513250	-2.1933010	3.2178190
C	-3.4166800	4.1791690	-0.3691930	H	-1.8825230	-4.8277210	1.6783060
C	-3.8758340	3.3216820	-1.5600180	H	-1.5915740	-4.5935790	3.4101950
C	-2.8526240	2.1880770	-1.5294850	H	0.6898020	-3.7752320	2.9776320
H	-3.1992700	1.2475180	-1.9637610	H	0.5538600	-5.0790080	1.7805010
H	-1.9201460	2.4812880	-2.0317720	H	1.7810550	0.6776510	0.9269970
H	-4.8868720	2.9318530	-1.3886360	H	-3.4787030	-1.3915640	-3.1681240
H	-3.8754950	3.8650160	-2.5097930				
H	-2.5832770	4.8247150	-0.6685950				
H	-4.2070630	4.8166900	0.0379890				
O	-3.0625100	-1.0580890	-0.4227990				
C	-2.8738660	-2.2059120	-1.2576710				
H	-1.8332770	-2.2000820	-1.5853020				
H	-3.0686950	-3.1258820	-0.6824670				
C	-3.9001430	-2.0271760	-2.3824700				
C	-5.0806790	-1.3127300	-1.6730290				
C	-4.4752450	-0.8572510	-0.3205420				
H	-4.6315470	0.1982840	-0.0890320				
H	-4.8754390	-1.4610000	0.5089120				
H	-5.4463380	-0.4651890	-2.2605660				
H	-5.9280890	-1.9868690	-1.5136840				
H	-4.1909080	-2.9770740	-2.8411220				