SUPPORTING INFORMATION

Sodium Diisopropylamide in Tetrahydrofuran: Selectivities, Rates, and Mechanisms of Alkene and Diene Isomerizations and Metalations

Russell F. Algera, Yun Ma, and David B. Collum*

Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York 14853–1301
E-mail: dbc6@cornell.edu

I. Rate studies

II. Computations

I. Rate Studies

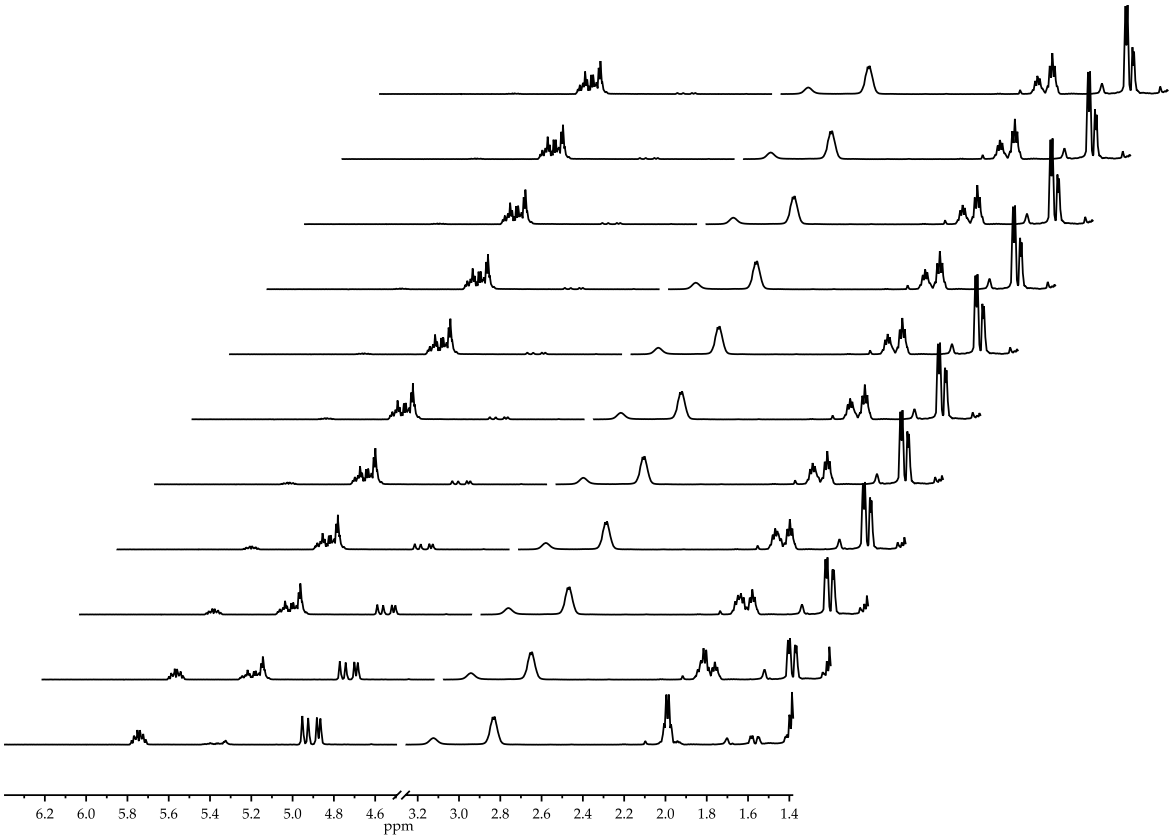


Figure S-1. Representative plot of pentene concentration versus time (^{1}H NMR) for the isomerization of 0.76 M 1-pentene with 0.18 M NaDA and 0.59 M diisopropylamine in 8.83 M THF/hexane at 25 °C. Each interval represents 300 seconds.

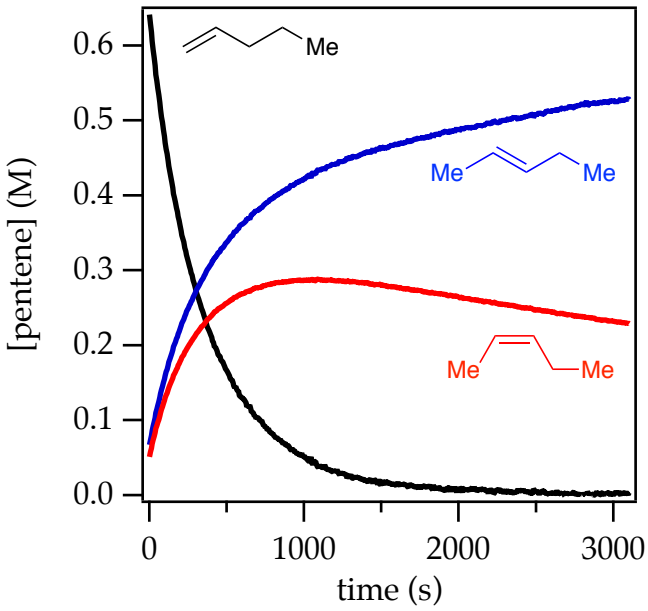


Figure S-2. Plot of alkene concentration versus time (^{1}H NMR) for the isomerization of 0.76 M 1-pentene with 0.18 M NaDA and 0.59 M diisopropylamine in 8.83 M THF/hexane at 25 °C. The black trace represents 1-pentene, the blue trace represents *trans*-2-pentene, and the red trace represents *cis*-2-pentene.

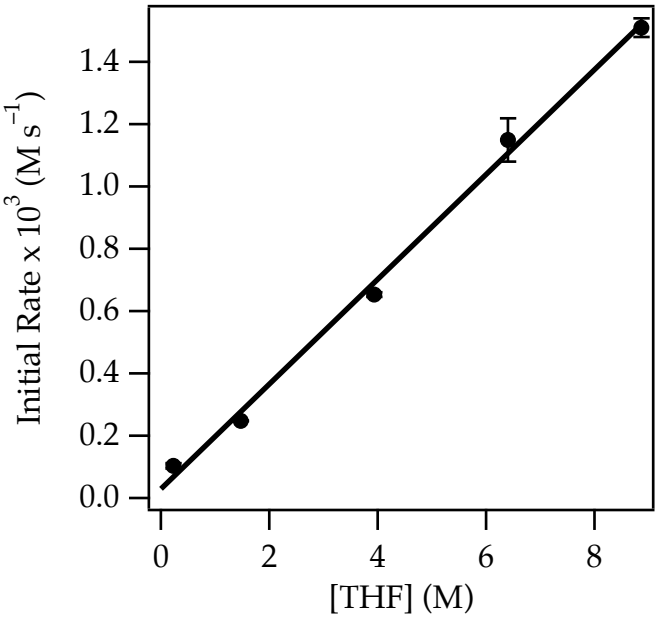


Figure S-3. Plot of initial rate versus THF concentration for the isomerization of 0.76 M 1-pentene (Equation 1) with 0.18 M NaDA and 0.59 M diisopropylamine in hexane cosolvent at 25 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax + b$: $a = 0.168 \pm 0.006$; $b = 0.03 \pm 0.03$.

[THF] (M)	Initial Rate × 10^3 (M s^{-1})	Standard deviation × 10^3 (M s^{-1})
0.23	0.104	0.008
1.47	0.248	0.0007
3.93	0.653	0.007
6.40	1.15	0.07
8.86	1.51	0.03

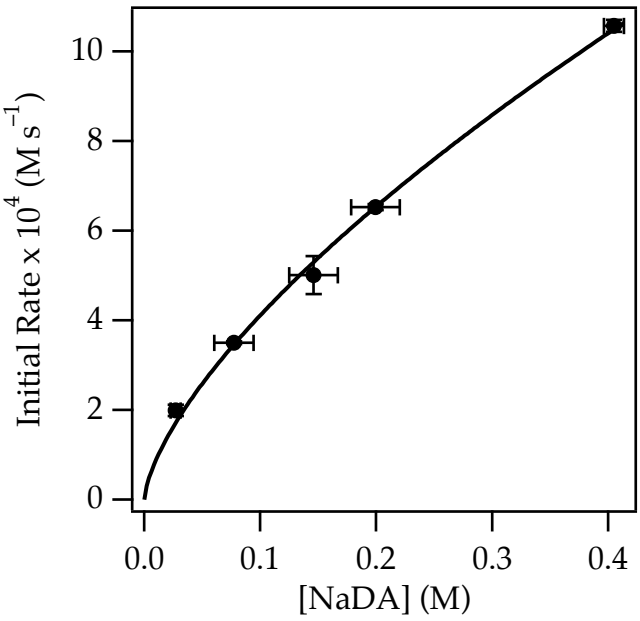


Figure S-4. Plot of initial rate versus NaDA concentration for the isomerization of 0.76 M 1-pentene (Equation 1) with 0.59 M diisopropylamine in 3.93 M THF/hexane at 25 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 19.2 \pm 0.8$; $b = 0.67 \pm 0.03$. The covariance represents measured titer of NaDA.

[NaDA] (M)	Initial Rate × 10^4 (M s^{-1})	Standard deviation × 10^4 (M s^{-1})
0.027	2.0	0.1
0.080	3.50	0.03
0.15	5.0	0.4
0.20	6.53	0.07
0.405	10.6	0.1

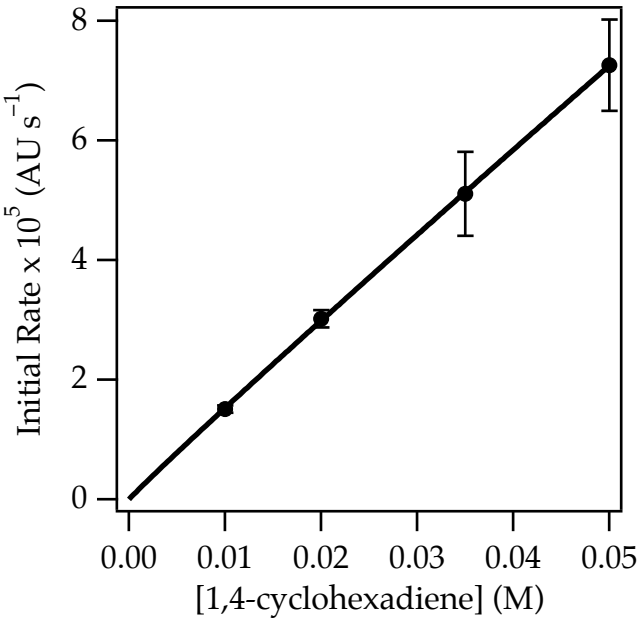


Figure S-5. Plot of initial rate versus concentration of 1,4-cyclohexadiene following product growth at 1558 cm^{-1} with 0.10 M NaDA in 6.04 M THF/DMEA at –95 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 132 \pm 4$; $b = 0.968 \pm 0.009$.

[alkene] (M)	Initial Rate × 10^5 (AU s^{-1})	Standard deviation × 10^5 (AU s^{-1})
0.010	1.51	0.06
0.020	3.0	0.1
0.035	5.1	0.7
0.050	7.3	0.8

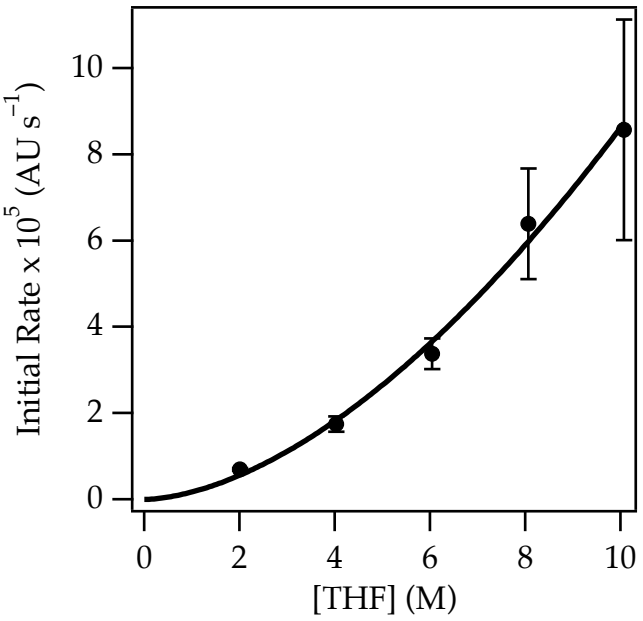


Figure S-6. Plot of initial rate versus concentration of THF following product growth at 1558 cm^{-1} with 0.10 M NaDA and 0.020 M 1,4-cyclohexadiene in DMEA cosolvent at –95 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 0.17 \pm 0.05$; $b = 1.7 \pm 0.1$.

[THF] (M)	Initial Rate × 10^5 (AU s^{-1})	Standard deviation × 10^5 (AU s^{-1})
2.01	0.696	0.03
4.03	1.75	0.2
6.04	3.38	0.4
8.06	6.39	1
10.1	8.57	3

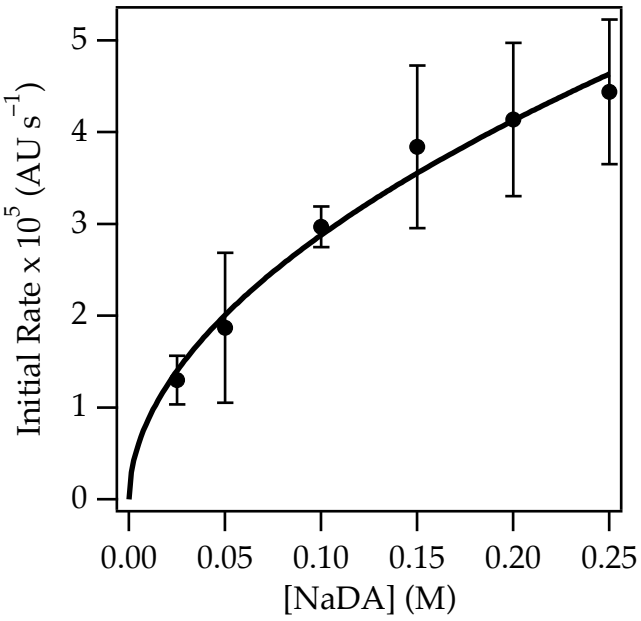


Figure S-7. Plot of initial rate versus concentration of NaDA following product growth at 1558 cm^{-1} with 0.020 M 1,4-cyclohexadiene in 6.04 M THF/DMEA at –95 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: a = 9.53 ± 0.8; b = 0.52 ± 0.05.

[NaDA] (M)	Initial Rate × 10^5 (M s^{-1})	Standard deviation × 10^5 (M s^{-1})
0.025	1.3	0.3
0.05	1.87	0.8
0.10	2.97	0.2
0.15	3.84	0.9
0.20	4.14	0.8
0.25	4.44	0.8

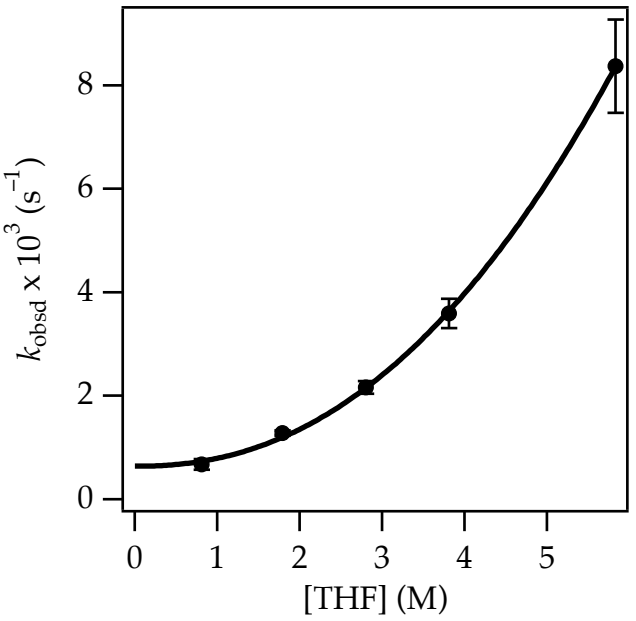


Figure S-8. Plot of k_{obsd} versus concentration of THF following product growth with 0.10 M NaDA and 0.020 M 1,4-pentadiene at –116 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b + c$: $a = 0.15 \pm 0.02$; $b = 2.23 \pm 0.07$; $c = 0.64 \pm 0.08$. The THF order depicted here is consistent with and supportive of the elevated THF order observed in the metalation of 1,4-cyclohexadiene.

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})	Standard deviation $\times 10^3$ (s^{-1})
0.81	0.7	0.1
1.79	1.28	0.05
2.80	2.2	0.1
3.81	3.6	0.3
5.83	8.4	0.9

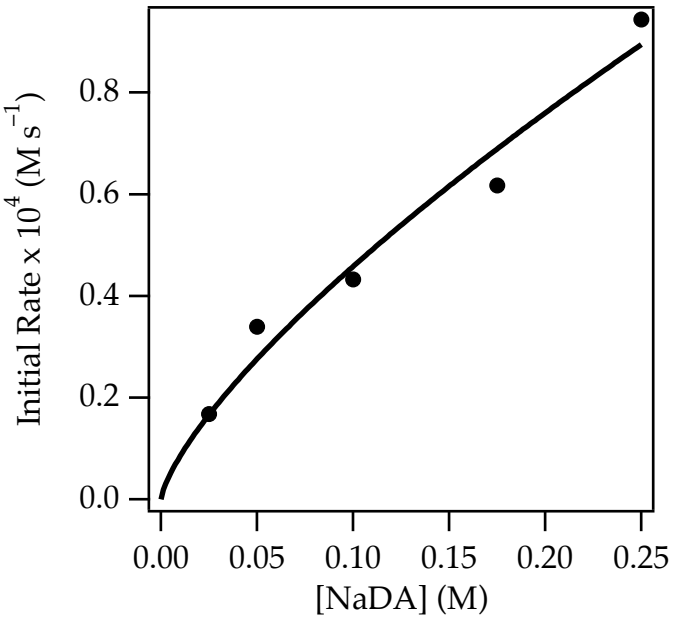


Figure S-9. Plot of initial rate versus concentration of NaDA following product growth with 0.020 M 1,4-pentadiene in 2.80 M THF/DMEA at –116 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 2.5 \pm 0.5$; $b = 0.7 \pm 0.1$.

[NaDA] (M)	Initial Rate × 10^4 (s^{-1})
0.025	0.167
0.05	0.339
0.1	0.433
0.175	0.617
0.25	0.944

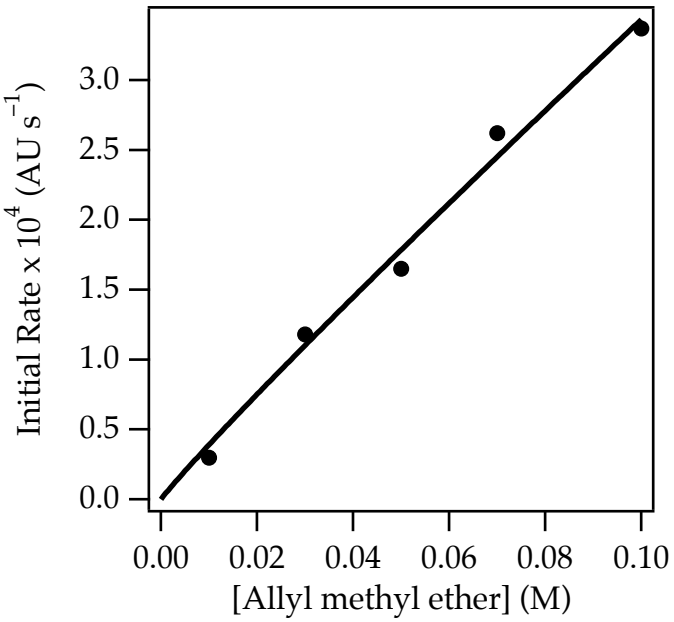


Figure S-10. Plot of initial rate versus concentration of allyl methyl ether following product growth at 1674 cm^{-1} (methyl enol ether) with 0.10 M NaDA in 5.5 M THF/DMEA at –116 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax$: $a = 35 \pm 1$.

[allyl methyl ether] (M)	Initial Rate × 10^4 (AU s^{-1})
0.010	0.299
0.030	1.18
0.050	1.65
0.070	2.62
0.10	3.37

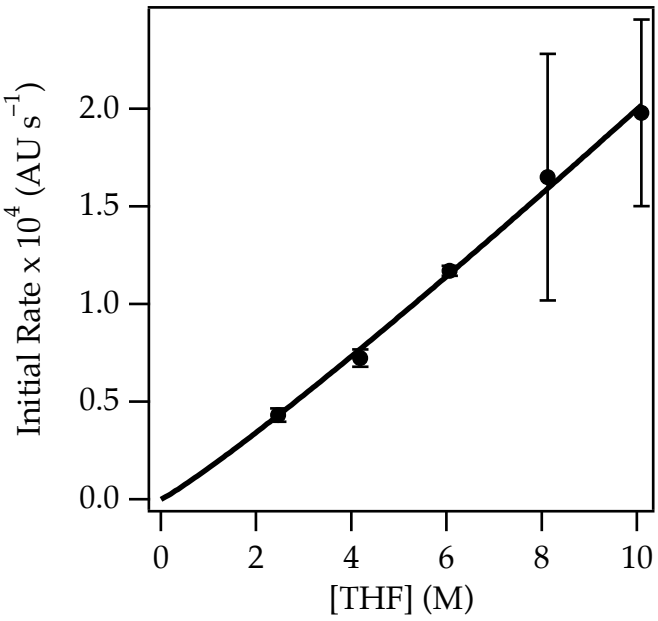


Figure S-11. Plot of initial rate versus concentration of THF following product growth at 1674 cm^{-1} (methyl enol ether) with 0.10 M NaDA and 0.030 M allyl methyl ether at –116 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 0.16 \pm 0.02$; $b = 1.10 \pm 0.05$.

[THF] (M)	Initial Rate × 10^4 (AU s^{-1})	Standard deviation × 10^4 (AU s^{-1})
2.46	0.43	0.03
4.18	0.72	0.04
6.06	1.17	0.03
8.12	1.7	0.6
10.1	2.0	0.5

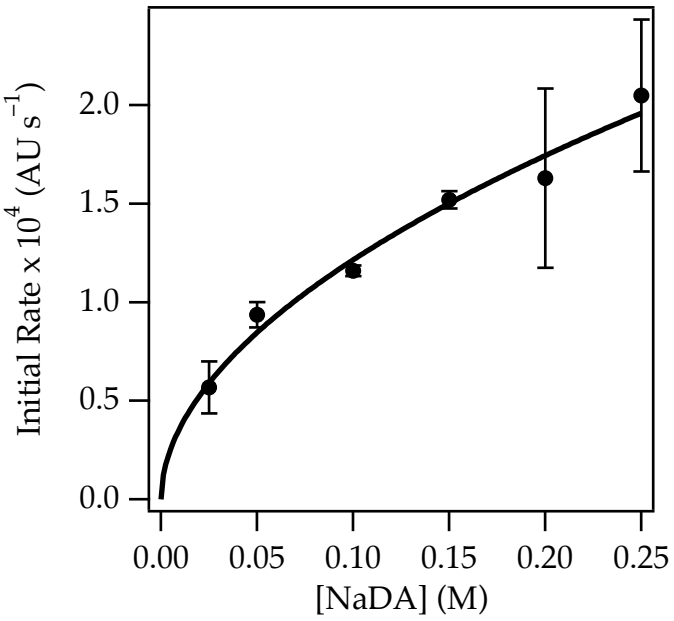


Figure S-12. Plot of initial rate versus concentration of NaDA following product growth at 1674 cm^{-1} (methyl enol ether) with 0.030 M allyl methyl ether in 5.5 M THF/DMEA at –116 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 4.0 \pm 0.3$; $b = 0.52 \pm 0.05$.

[NaDA] (M)	Initial Rate × 10^4 (AU s^{-1})	Standard deviation × 10^4 (AU s^{-1})
0.025	0.6	0.1
0.05	0.94	0.06
0.10	1.16	0.03
0.15	1.52	0.04
0.20	1.6	0.5
0.25	2.1	0.4

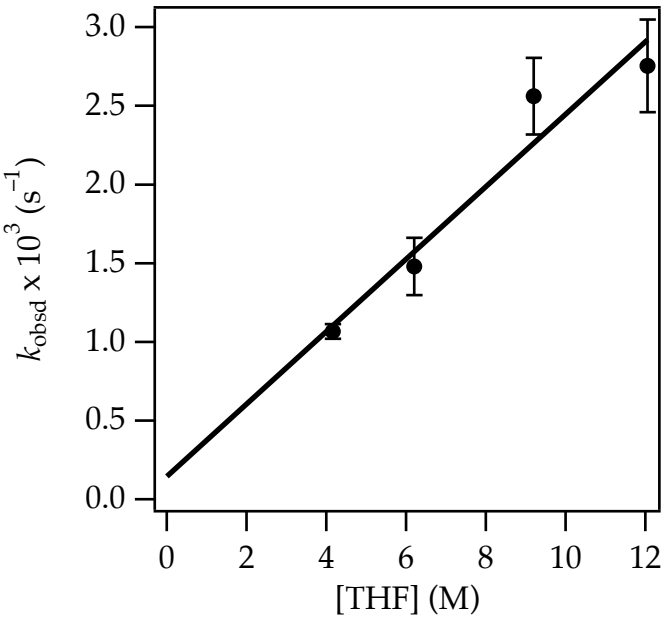


Figure S-13. Plot of k_{obsd} versus THF concentration following product growth at 1601 cm^{-1} (trimethylsilyl enol ether) with 0.010 M allyloxytrimethylsilane in hexane cosolvent at –78 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax + b$: $a = 0.23 \pm 0.04$; $b = 0.14 \pm 0.4$.

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})	Standard deviation $\times 10^3$ (s^{-1})
4.16	1.07	0.05
6.20	1.5	0.2
9.20	2.6	0.2
12.05	2.8	0.3

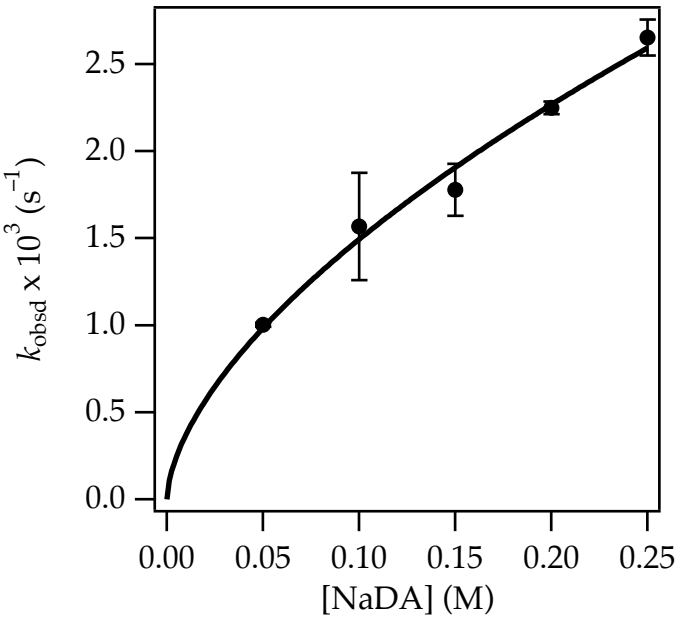


Figure S-14. Plot of k_{obsd} versus NaDA concentration following product growth at 1601 cm^{-1} (trimethylsilyl enol ether) with 0.010 M allyloxytrimethylsilane in 6.0 M THF/hexane at –78 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 6.0 \pm 0.6$; $b = 0.60 \pm 0.05$.

[NaDA] (M)	$k_{obsd} \times 10^3$ (s^{-1})	Standard deviation $\times 10^3$ (s^{-1})
0.05	1.00	0.01
0.10	1.6	0.3
0.15	1.8	0.1
0.20	2.25	0.04
0.25	2.7	0.1

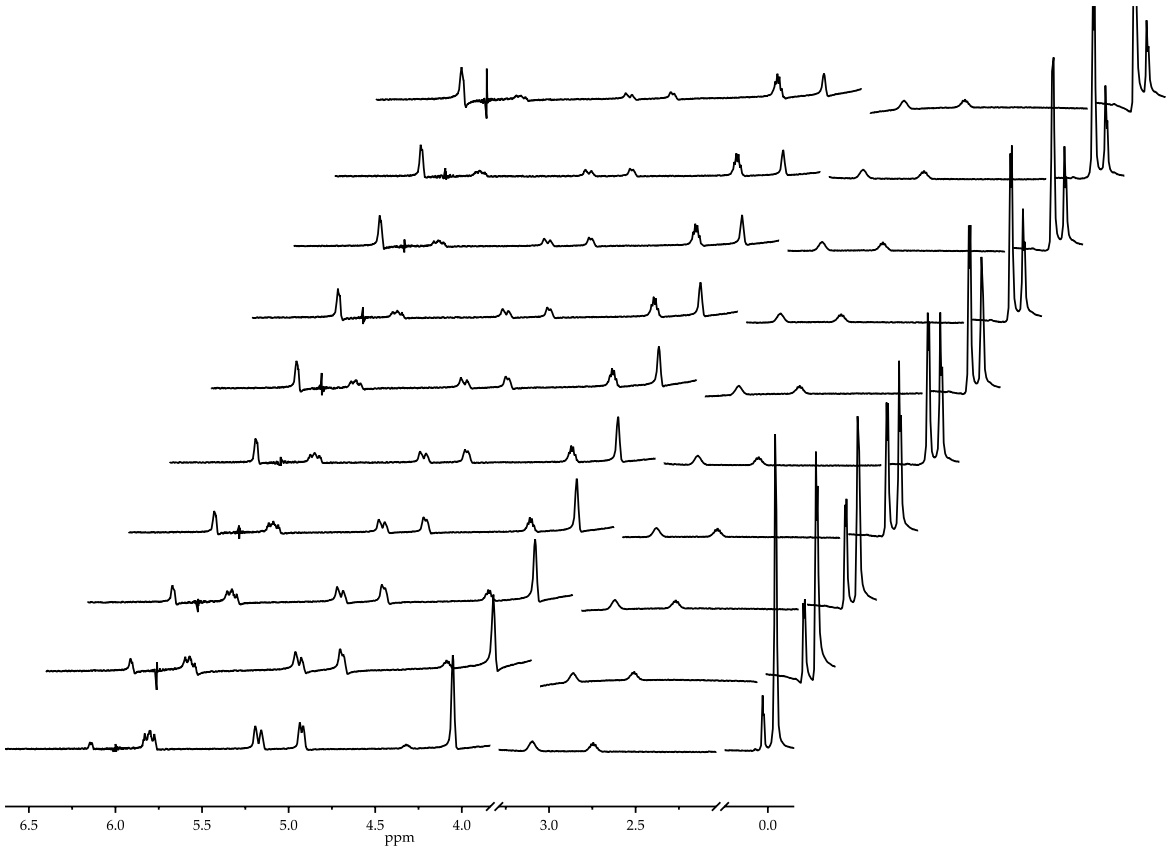


Figure S-15. ^{1}H NMR spectra of 0.78 M allyloxy-*tert*-butyldimethylsilane with 0.27 M NaDA in neat THF at –80 °C. Each spectrum corresponds to an interval of 881 seconds.

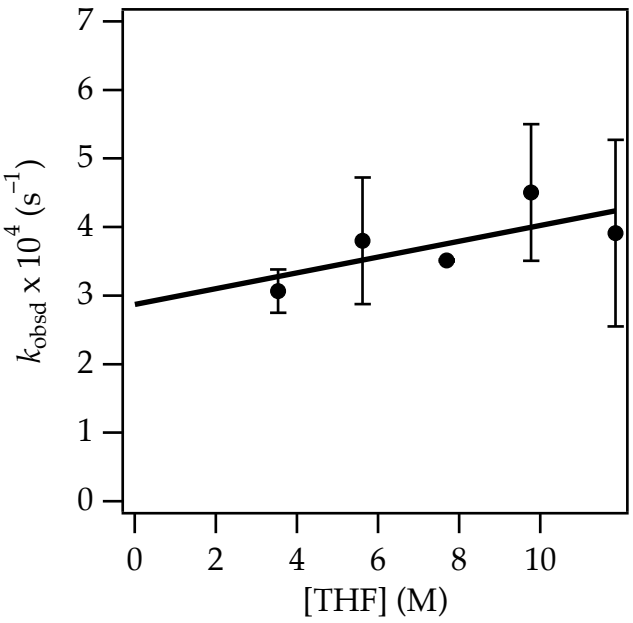


Figure S-16. Plot of k_{obsd} versus THF concentration following product growth at 1664 cm^{-1} (*tert*-butyldimethylsilyl enol ether) with 0.010 M allyloxy-*tert*-butyldimethylsilane in 6.00 M THF/hexane at –78 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax + b$: $a = 0.12 \pm 0.06$; $b = 2.9 \pm 0.5$.

[THF] (M)	$k_{obsd} \times 10^4$ (s^{-1})	Standard deviation $\times 10^4$ (s^{-1})
3.53	3.1	0.3
5.61	3.8	0.9
7.69	3.51	0.01
9.77	4.5	1
11.9	3.9	1.4

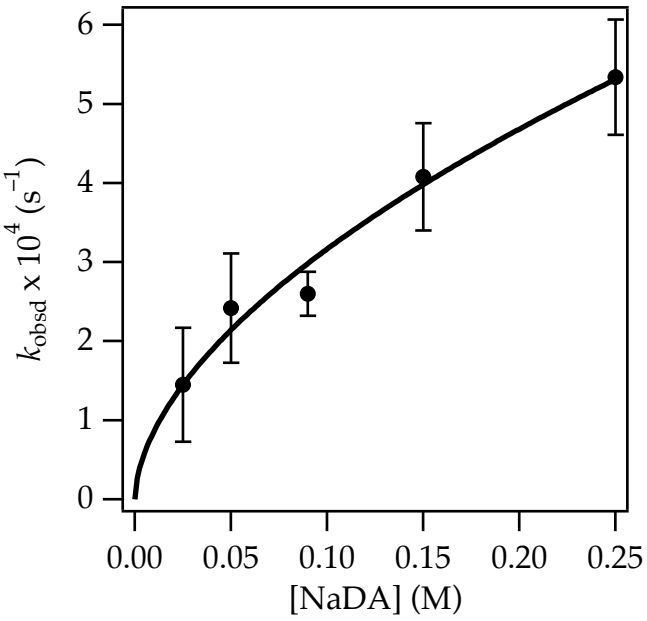


Figure S-17. Plot of initial rate versus NaDA concentration following product growth at 1664 cm^{-1} (*tert*-butyldimethylsilyl enol ether) with 0.010 M allyloxy-*tert*-butyldimethylsilane in 6.0 M THF/hexane at –78 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax^b$: $a = 12 \pm 1$; $b = 0.56 \pm 0.06$.

[NaDA] (M)	$k_{obsd} \times 10^4$ (s^{-1})	Standard deviation $\times 10^4$ (s^{-1})
0.025	1.5	0.7
0.050	2.4	0.7
0.090	2.6	0.3
0.15	4.1	0.7
0.25	5.3	0.7

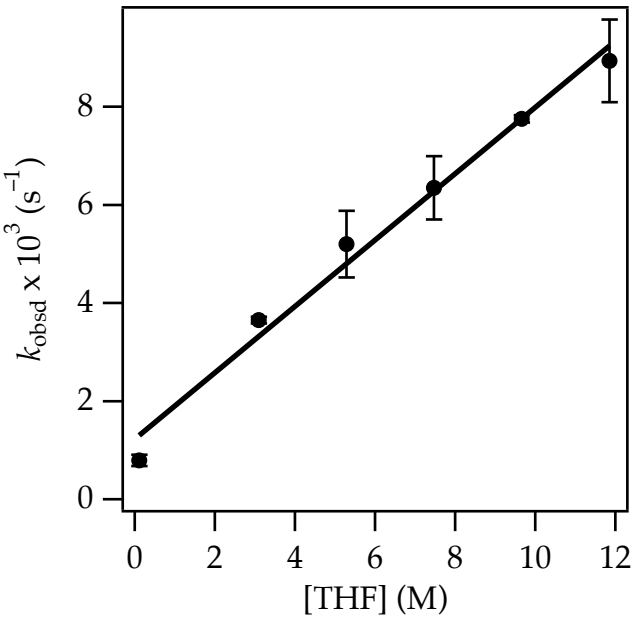


Figure S-18. Plot of k_{obsd} versus THF concentration following product growth at 1661 cm^{-1} (triisopropylsilyl enol ether) with 0.010 M allyloxytriisopropylsilane and 0.10 M NaDA with hexane cosolvent at 0 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax + b$: $a = 0.68 \pm 0.04$; $b = 1.2 \pm 0.3$.

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})	Standard deviation $\times 10^3$ (s^{-1})
0.11	0.8	0.1
3.09	3.66	0.07
5.28	5.2	0.7
7.47	6.3	0.6
9.66	7.76	0.07
11.9	8.9	0.8

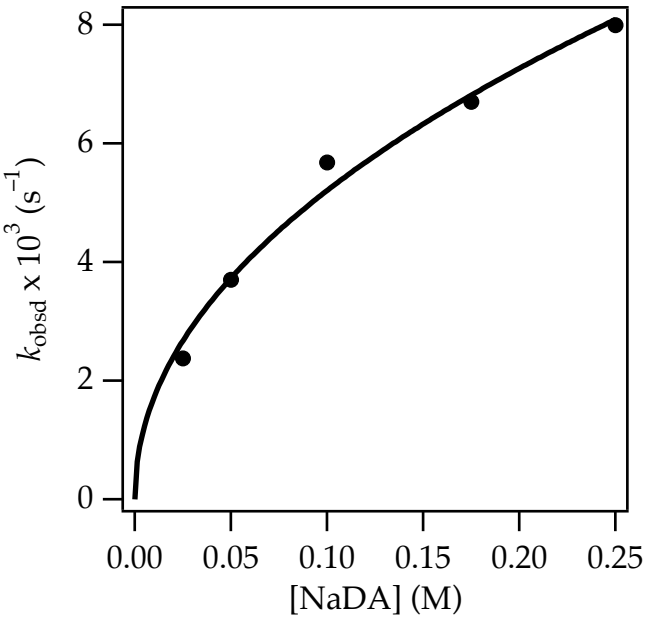


Figure S-19. Plot of k_{obsd} versus NaDA concentration following product growth at 1661 cm^{-1} (triisopropylsilyl enol ether) with 0.010 M allyloxytriisopropylsilane in 5.28 M THF/hexane at 0 °C. The curve depicts an unweighted least-squares fit to the function $f(x) = ax + b$: $a = 0.68 \pm 0.04$; $b = 1.2 \pm 0.3$.

[NaDA] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.025	2.38
0.050	3.70
0.10	5.68
0.175	6.70
0.25	7.99

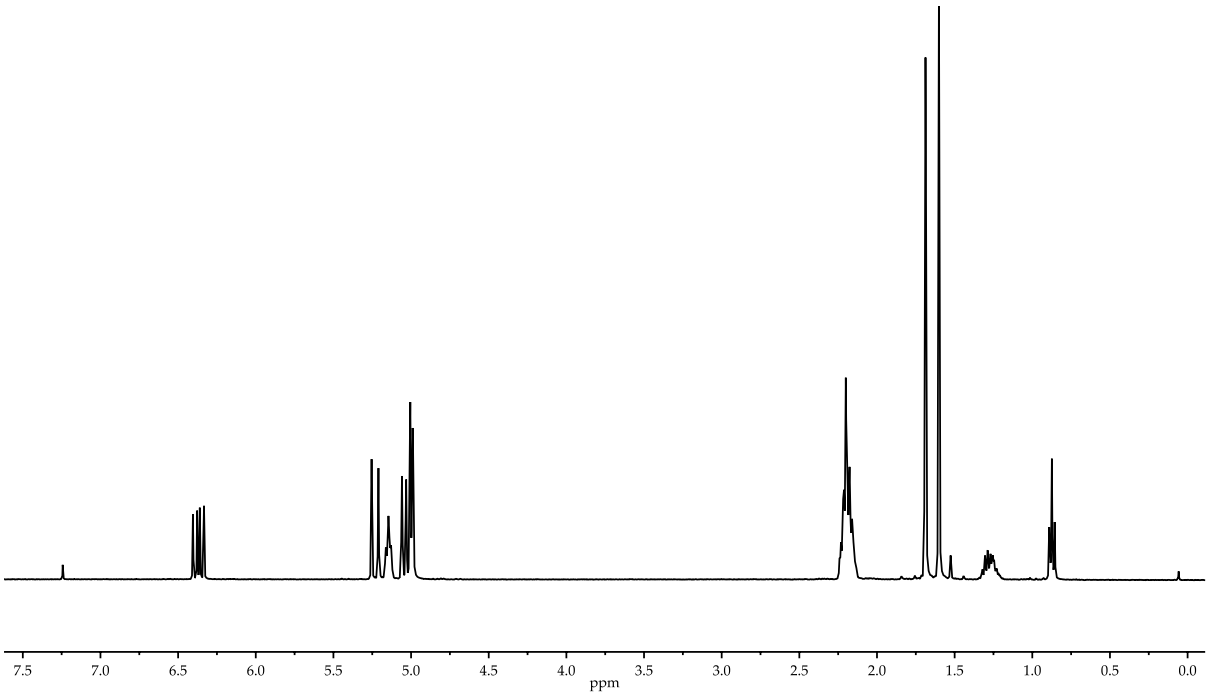


Figure S-20. ^{1}H NMR spectrum ($CDCl_3$) of myrcene recovered from reaction of NaDA/THF with trimethylsilyl ether of geraniol. Resonances at δ 0.85 ppm and δ 1.35 ppm correspond to residual pentane from chromatography.

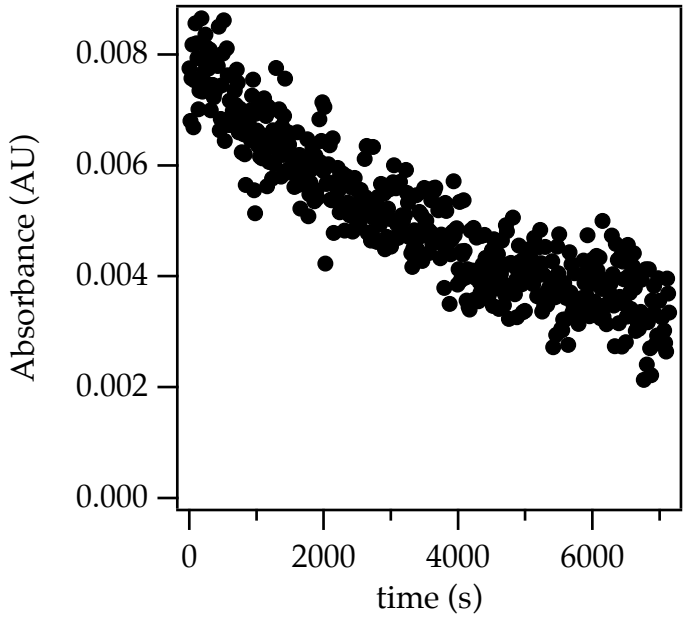


Figure S-21. Representative concentration trace showing loss of 0.050 M geraniol TMS ether **6** with 0.10 M NaDA in neat THF at –78 °C (monitored by ReactIR).

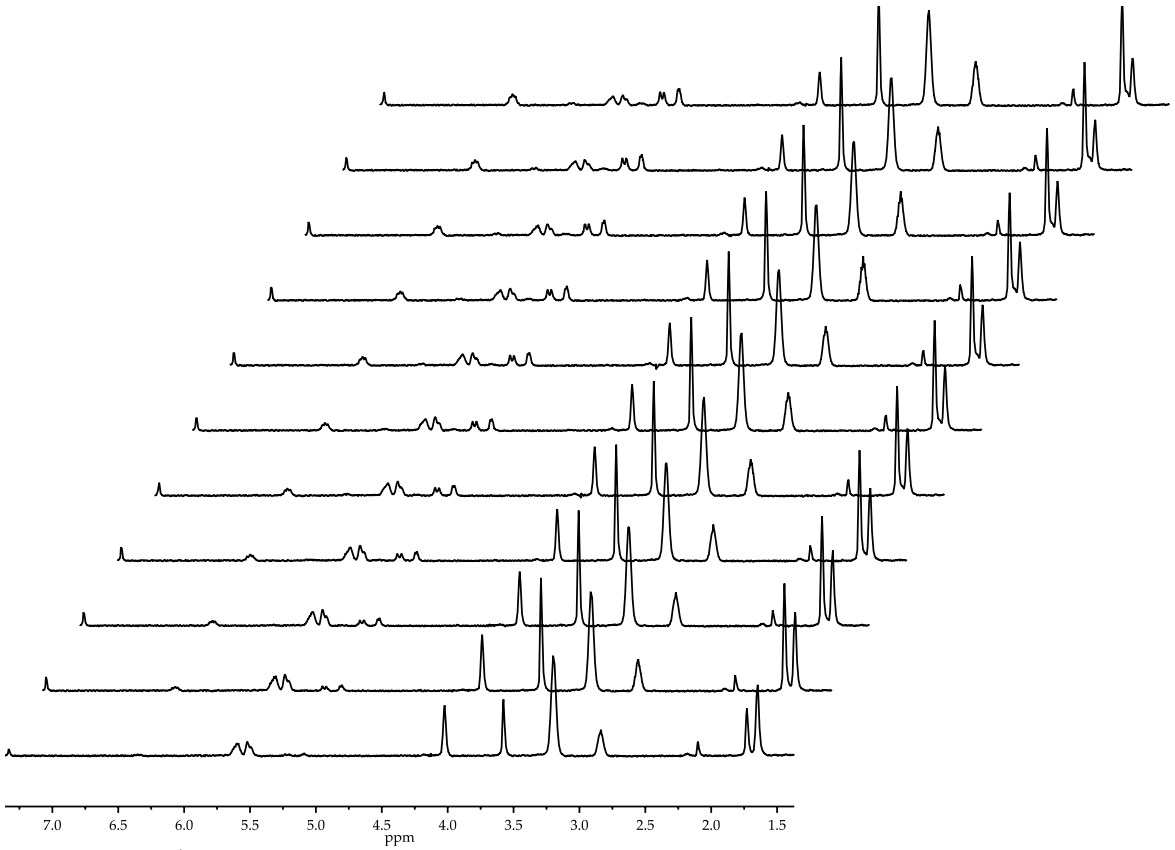


Figure S-22. ^{1}H NMR spectra of 0.090 M trimethylsilyl ether of crotyl alcohol with 0.32 M NaDA in neat THF at –60 °C. Each spectrum corresponds to an interval of 263 seconds. These spectra are consistent with stoichiometric consumption of NaDA to give 1,3-butadiene.

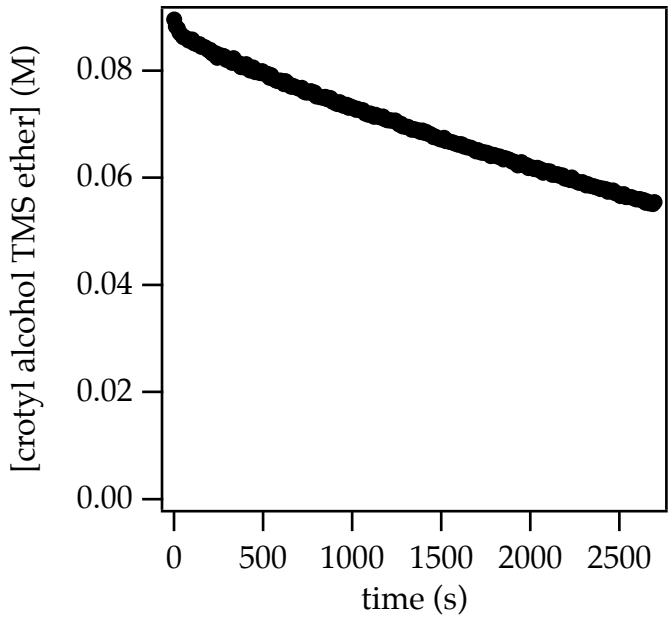


Figure S-23. Concentration of 0.090 M trimethylsilyl ether of crotyl alcohol with 0.32 M NaDA in neat THF at –60 °C.

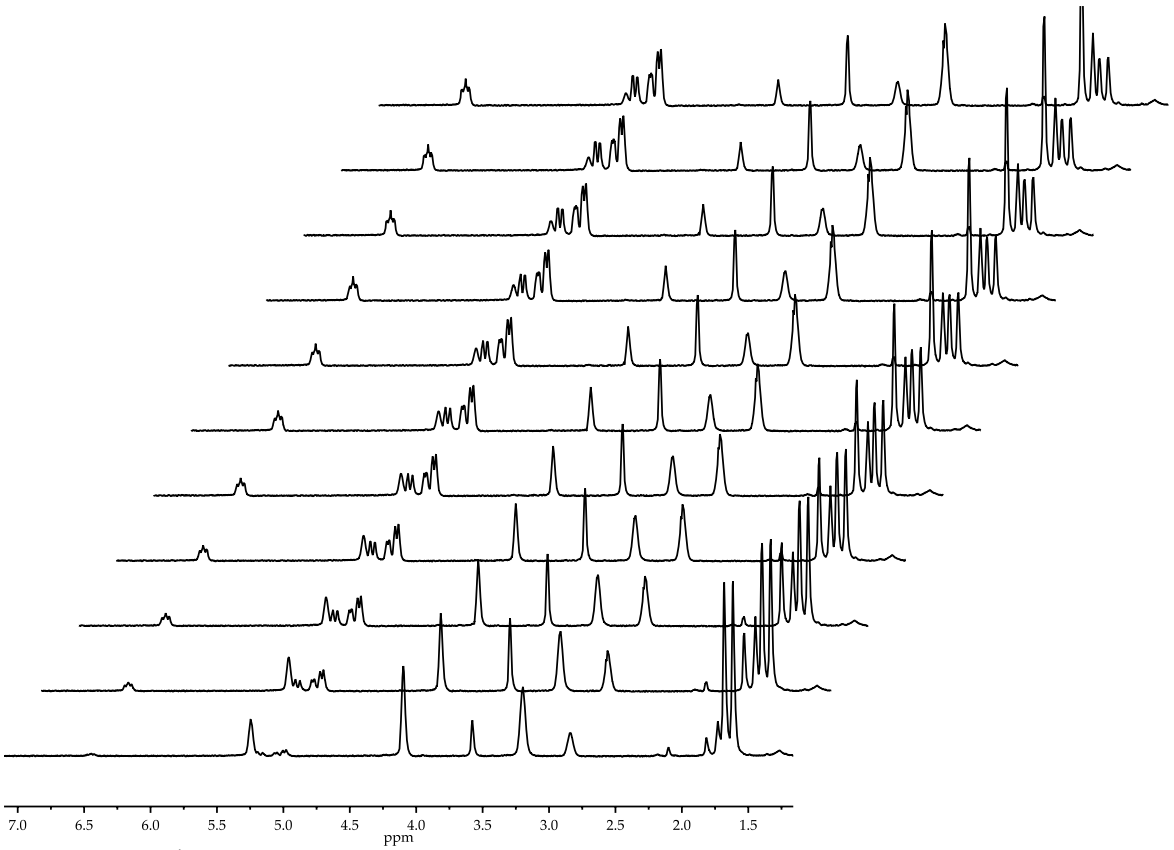


Figure S-24. ^{1}H NMR spectra of 0.23 M trimethylsilyl ether of prenol with 0.30 M NaDA in neat THF at –60 °C. Each spectrum corresponds to an interval of 131 seconds. These spectra are consistent with stoichiometric consumption of NaDA to give isoprene.

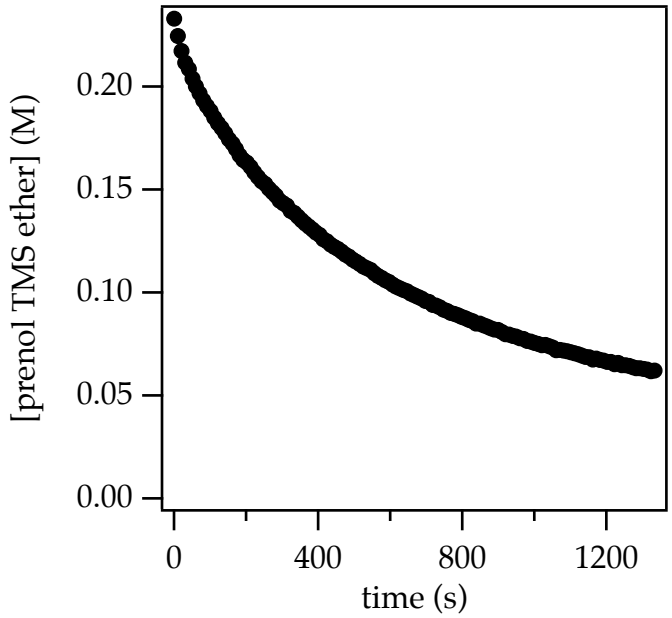


Figure S-25. Concentration of 0.23 M trimethylsilyl ether of prenol with 0.30 M NaDA in neat THF at –60 °C.

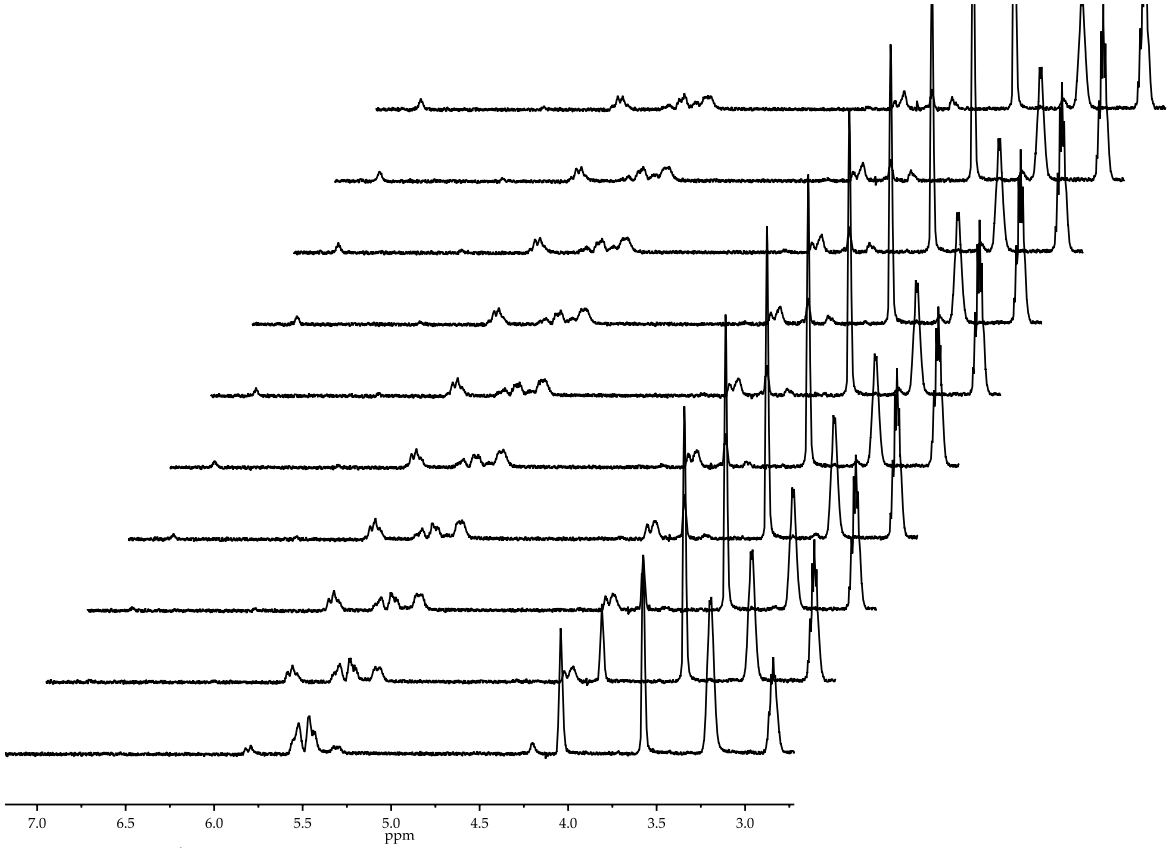


Figure S-26. ^{1}H NMR spectra of 0.080 M trimethylsilyl ether **8** with 0.19 M NaDA in neat THF at –40 °C. Each spectrum corresponds to an interval of 626 seconds. These spectra are consistent with stoichiometric consumption of NaDA to give several products.

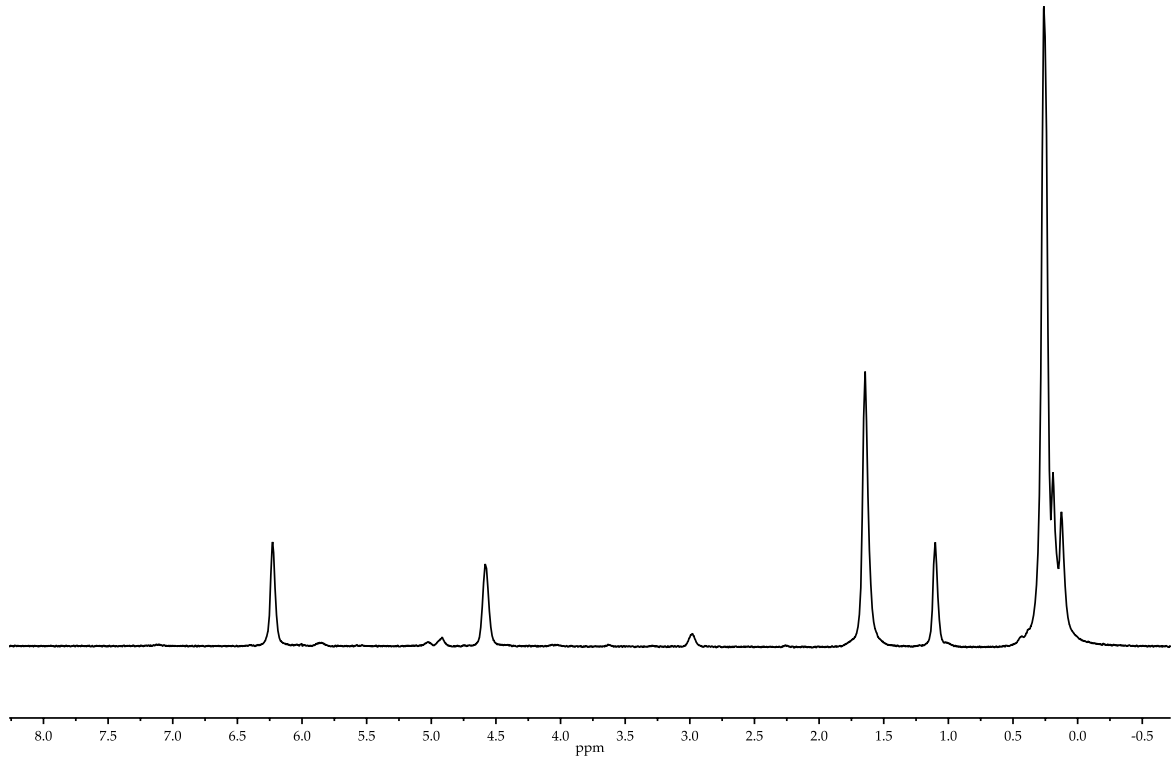


Figure S-27. ^{1}H NMR spectrum of isomerization of 1.5 mL neat allyloxytrimethylsilane with 7 mol % NaDA at room temperature after one minute. The resonances at 2.9 ppm and 1.1 ppm are consistent with diisopropylamine.

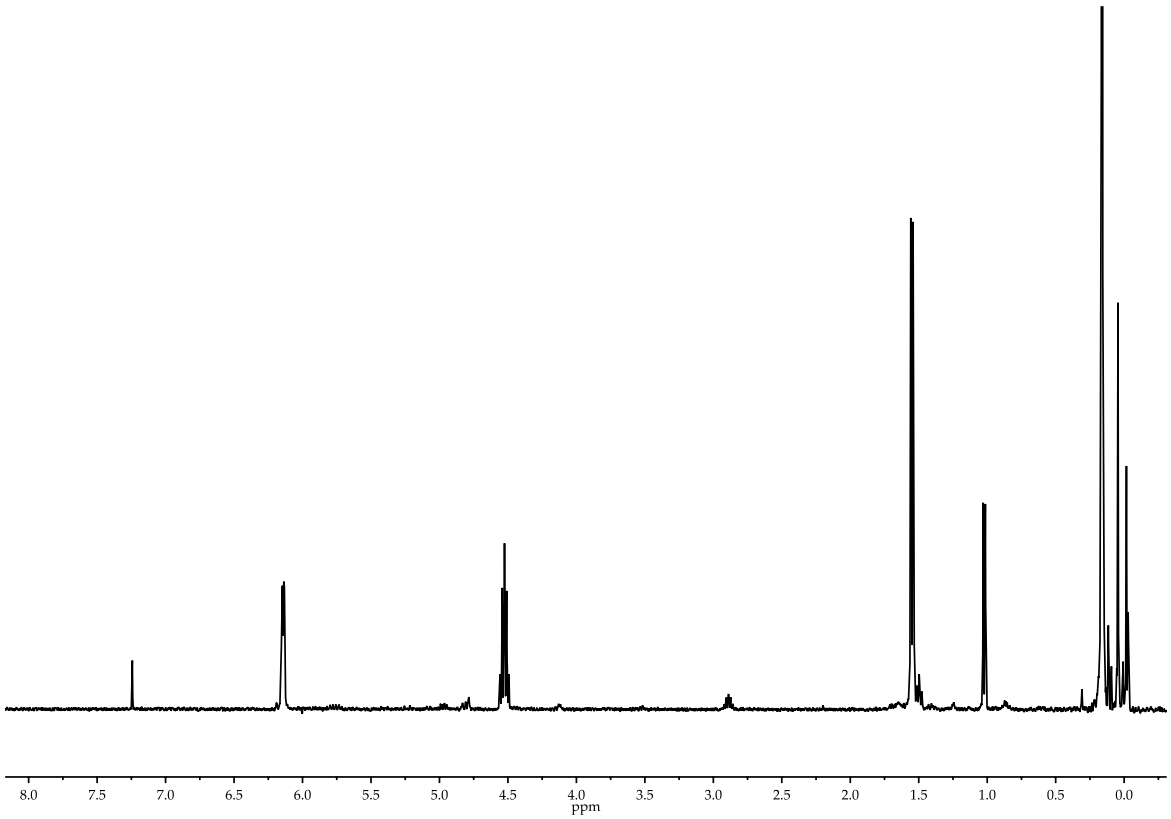


Figure S-28. ^{1}H NMR spectrum ($CDCl_3$) of isolated material (distillation) from isomerization of 1.5 mL neat allyloxytrimethylsilane with 7 mol % NaDA at room temperature after one minute.

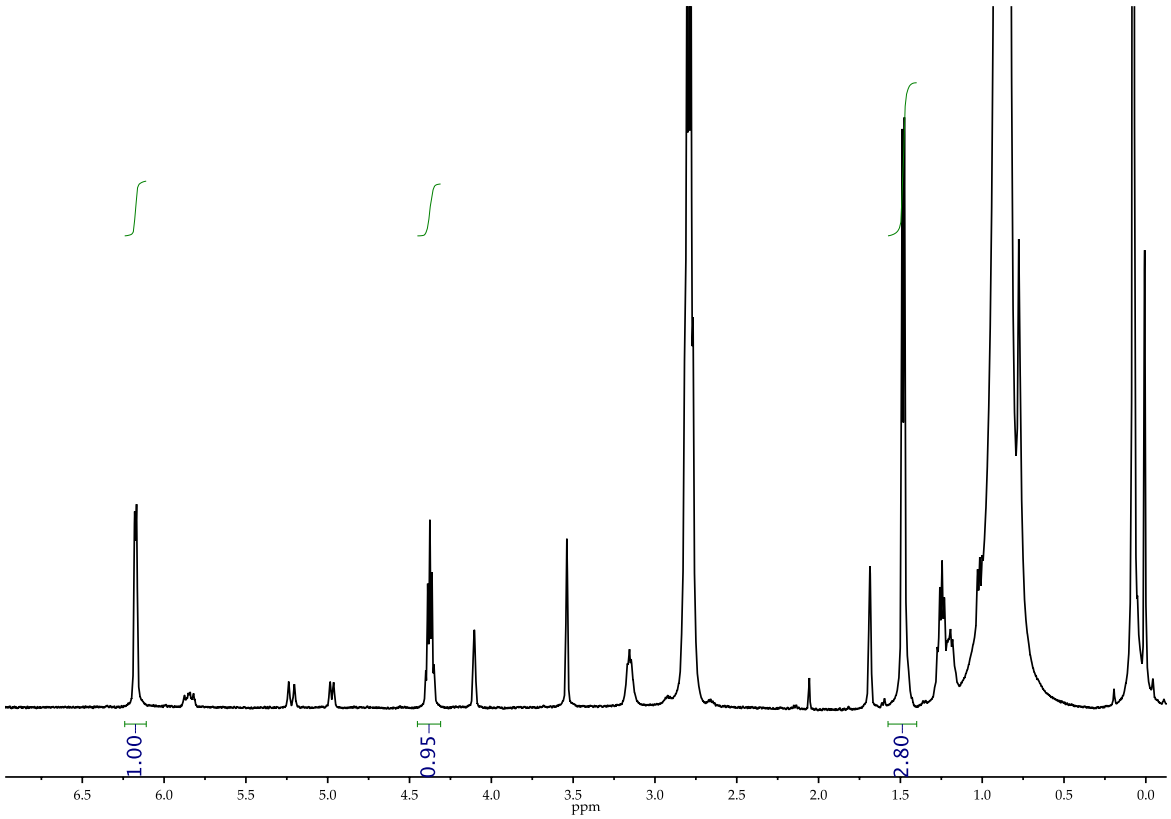
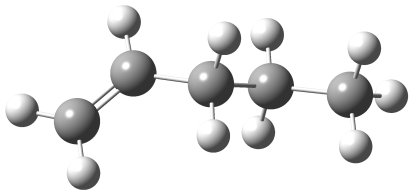


Figure S-29. ^{1}H NMR spectrum of partial isomerization of 0.47 M allyloxy-*tert*-butyldimethylsilane with 0.094 M NaDA and 1.43 M DN*i*-Pr_2 in THF-d_8. That the relative integration of the terminal methyl (~1.4 ppm) is significantly above 2 is consistent with predominant retention of protons from substrate without trapping of the allylsodium intermediate by DN*i*-Pr_2.

II. 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 (T = 195 K). G_{MP2} is derived from a MP2 single point calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT optimization.

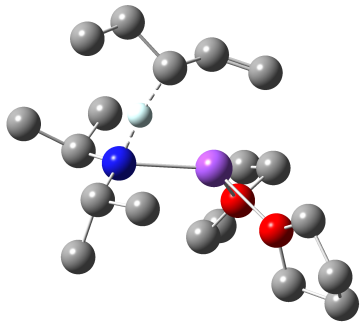
Table S-1. Geometric coordinates and thermally corrected MP2 energies for 1-pentene.



G = –196.427062 Hartree
G_{MP2} = –195.6789852 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-1.34505100	0.65407700	-0.16177800
C	-2.41055200	0.09604400	-0.73768800
H	-2.37937500	-0.91648900	-1.13602800
H	-3.35559300	0.62465400	-0.83136300
H	-1.42477700	1.67371300	0.22098000
H	-0.04326100	-1.03222700	-0.37274100
H	0.24798500	-0.06478100	1.07124600
C	1.13172800	0.76137100	-0.71658500
H	1.15496900	1.79890600	-0.35477500
H	0.90064400	0.81671400	-1.78845700
C	2.50583800	0.11609400	-0.51279000
H	2.52118500	-0.91250900	-0.89360800
H	3.29061900	0.67579600	-1.03417400
H	2.77298800	0.07870800	0.55060700

Table S-2. Geometric coordinates and thermally corrected MP2 energies for [A(THF)$_2$(1-pentene)]‡.

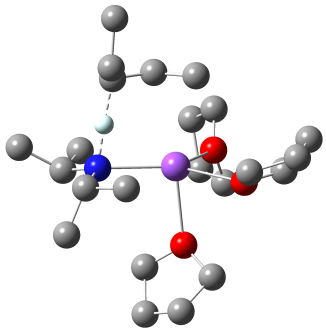


G = –1115.07229 Hartree
G_{MP2} = –1111.273063 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-1.49330000	-0.22641000	0.25981600
C	-2.40677500	0.46614700	-0.62462100
C	-3.64942800	0.08905100	-1.05336800
H	-4.01271700	-0.93019300	-0.91481500
H	-4.24898000	0.73199500	-1.69350600
H	-2.09247400	1.47583700	-0.91588800
H	-1.72487400	-1.30219700	0.31459300
H	0.24201000	1.06639000	0.13815200
H	0.27461300	-0.22877100	-1.04384000
C	0.89422700	-0.83882200	0.92092400
H	0.71446600	-1.91050800	0.76443500
H	1.95872200	-0.65191700	0.73183000
H	0.69458900	-0.62359900	1.97672700
H	-1.78085900	0.24358600	1.58894300
N	-2.25168400	0.66378500	2.80586900
Na	-4.21830800	0.49496900	1.51962400
O	-5.85479100	2.19753000	1.74938000
C	-6.01805400	3.02390700	2.92802600
H	-5.02593800	3.19016200	3.36176500
H	-6.63018400	2.48118900	3.65684300
C	-6.67163600	4.33138200	2.45416100
H	-7.76093200	4.28119900	2.56598500
H	-6.31618000	5.19870300	3.01775000
C	-6.29182500	4.37841600	0.96493000
H	-5.27402000	4.76408800	0.83727000
H	-6.97041400	4.99219200	0.36514200
C	-6.34558600	2.89950500	0.58837300
H	-7.37549900	2.57824100	0.37393100
H	-5.70942600	2.62406400	-0.25743300
O	-5.82157600	-1.20240500	1.83235400
C	-6.97271100	-1.04118500	2.68635100
H	-7.37053900	-0.03551100	2.52427700
H	-6.65509500	-1.13129300	3.73473900
C	-7.93480900	-2.16557500	2.29965100
H	-8.60789100	-2.44173000	3.11679600
H	-8.54566300	-1.86864100	1.43872800
C	-6.96067800	-3.28710200	1.90582500
H	-7.40802300	-4.04301300	1.25382100
H	-6.57994700	-3.79235300	2.80104500
C	-5.83876200	-2.50851200	1.21253900
H	-4.85121500	-2.96278400	1.33720600
H	-6.03417600	-2.38252600	0.13995700
C	-1.99683400	-0.34531600	3.83782500
C	-2.60817600	0.00743100	5.20927900
H	-2.43908900	-0.80100000	5.93253000
H	-3.69272200	0.15937800	5.11186000
H	-2.18035400	0.92108600	5.63524900
C	-2.54283500	-1.70881800	3.38625600
H	-2.31227300	-2.48339900	4.12835800
H	-2.10592500	-2.01535100	2.43155700
H	-3.63492300	-1.67160000	3.26950400
H	-0.91111100	-0.48991000	4.00758100
C	-1.73105100	1.99834000	3.13094700
C	-0.21320100	2.06801800	3.41475800
H	0.08988900	3.09445200	3.65963100

H	0.36213900	1.74377600	2.53967200
H	0.07579100	1.43299900	4.25906900
C	-2.07406400	2.98533100	2.00322400
H	-1.76727900	4.00428400	2.27034900
H	-3.15320800	3.00302900	1.80287400
H	-1.56369000	2.71642000	1.07215600
H	-2.23200400	2.38421800	4.03935100

Table S-3. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* $[A(THF)_3(1\text{-pentene})]^{‡}$.

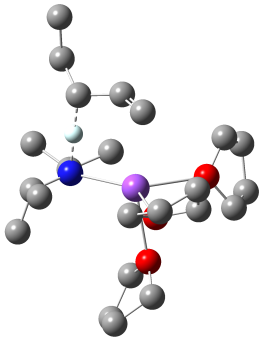


G = –1347.419378 Hartree
G_{MP2} = –1342.854422 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	1.87182400	-1.56019900	-0.21990600
C	2.38464500	-1.81767100	-1.57232200
C	1.94030900	-3.15395800	-2.19923800
H	2.33031000	-3.24513100	-3.22116800
H	0.84502300	-3.21152200	-2.25069900
H	2.29694000	-4.02265600	-1.63629400
C	1.94411400	-0.67275300	-2.49522300
H	2.41510600	-0.74997300	-3.48353000
H	2.21365900	0.29907100	-2.07043800
H	0.85423900	-0.69699500	-2.64047100
H	3.49337700	-1.82565200	-1.58543700
C	2.08631200	-2.66248300	0.72787100
C	3.56408700	-3.06349400	0.94488300
H	3.64265600	-3.90697900	1.64345900
H	4.13960900	-2.22635800	1.35486500
H	4.04307600	-3.36837900	0.00793600
C	1.44788000	-2.30399000	2.07935900
H	1.54153200	-3.13282700	2.79247300
H	0.37946800	-2.07888700	1.96286200
H	1.93168300	-1.42551200	2.52122600
H	1.56705200	-3.57354300	0.37397400
O	-1.86683700	-1.55864700	-0.66739100
C	-2.71532300	-1.36455200	-1.81001500
H	-2.48722600	-0.37562200	-2.21149500
H	-3.77347100	-1.39603600	-1.50304200
C	-2.38069900	-2.52794800	-2.74043300
H	-3.16640300	-2.72577100	-3.47635100
H	-1.44930400	-2.31920000	-3.27828700
C	-2.18443600	-3.68405800	-1.74192700
H	-1.48822800	-4.44415700	-2.10781100
H	-3.14071100	-4.17895600	-1.53894400
C	-1.65666400	-2.97750700	-0.47423200
H	-2.19195800	-3.30211300	0.42778000
H	-0.58478300	-3.11732600	-0.31946700
O	-1.52112100	0.48999600	1.94106300
C	-2.76331700	-0.19034000	2.17842600
H	-2.91050400	-0.88258600	1.34961700
H	-3.58204000	0.54669400	2.18532100
C	-2.61064000	-0.85061100	3.56294900
H	-3.55260300	-0.83465400	4.11962100
H	-2.30209500	-1.89564100	3.46487900
C	-1.49657200	-0.01102900	4.24944500
H	-0.61773900	-0.62945400	4.45272300
H	-1.82137200	0.42997100	5.19653700
C	-1.16340900	1.06826300	3.20463000
H	-1.76157100	1.97807300	3.36969100
H	-0.10948200	1.34285700	3.15850200
O	-1.12014300	1.56497500	-1.55027600
C	-2.08396000	2.43891600	-0.92259100
H	-2.08556200	2.21656200	0.14721400
H	-3.08269500	2.22556000	-1.33245100
C	-1.63769600	3.85820800	-1.26905800
H	-2.45949700	4.57985900	-1.22909300
H	-0.85347500	4.18664500	-0.57826800
C	-1.06468100	3.66633800	-2.68196200

H	-0.35340500	4.44574100	-2.97062800
H	-1.87312800	3.65502000	-3.42274700
C	-0.40288300	2.28655400	-2.58043300
H	-0.45630800	1.71179500	-3.51093000
H	0.64617000	2.36170100	-2.27454100
C	3.28754300	0.60428000	0.83020200
C	2.20682600	1.41003500	1.36032900
C	1.47767800	2.40391400	0.77121100
H	1.77322400	2.85359700	-0.17433700
H	0.64437800	2.87408500	1.28822700
H	1.85328300	1.08738100	2.34654800
C	4.19081100	1.22154300	-0.23653800
H	3.58285900	1.62769000	-1.05889200
H	4.80957600	0.43443400	-0.69157400
C	5.11364500	2.33989000	0.27930000
H	5.78622700	1.95932500	1.05849600
H	5.73655900	2.76209000	-0.52162800
H	4.52761100	3.15479700	0.71936000
H	3.88071700	0.15406800	1.63709700
H	2.59317400	-0.51968400	0.27651100

Table S-4. Geometric coordinates and thermally corrected MP2 energies for pro-*E* [A(THF)$_3$(1-pentene)]‡.

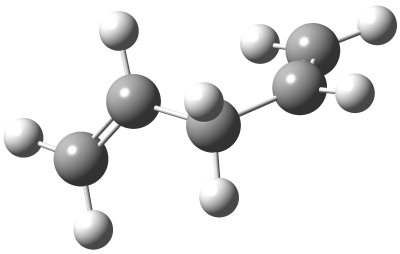


G = –1347.422632 Hartree
G_{MP2} = –1342.856104 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	1.44643100	-0.07906100	-0.48436200
C	2.31927200	-0.97962100	0.23351100
C	3.44352800	-1.62159500	-0.20050800
H	3.69011300	-1.66968300	-1.26050000
H	4.05432100	-2.22171000	0.46982200
H	2.10078200	-1.06562800	1.30655400
H	1.49086700	-0.23689900	-1.57266400
H	-0.49291700	0.87367400	-0.45114900
H	-0.01411200	0.18191300	1.08718100
C	-0.85467700	-1.24424400	-0.29814100
H	-0.43292000	-2.13494200	0.18381400
H	-1.89028200	-1.12768700	0.05123700
H	-0.88682800	-1.44315200	-1.37714600
H	2.12313000	1.17888900	-0.36441800
N	2.88750400	2.30276000	-0.34715300
Na	4.77452900	0.84811100	0.13801100
O	6.60449300	2.56645500	0.45898200
C	7.80598500	2.63770400	-0.32237100
H	7.82841200	1.74575900	-0.95049200
H	8.68796700	2.63854300	0.33932700
C	7.68873500	3.95956500	-1.07794500
H	8.65115400	4.32963100	-1.44503900
H	7.01666100	3.83791400	-1.93437000
C	7.05413100	4.87953900	-0.01526600
H	6.41305700	5.64747800	-0.45709300
H	7.83092900	5.38937900	0.56490000
C	6.25599900	3.90360400	0.88151800
H	6.51199100	4.02684700	1.94252000
H	5.17456300	3.99972300	0.76653300
O	5.54954900	0.03549200	2.32611900
C	6.65885600	0.54211100	3.07937100
H	7.07784900	1.37135500	2.50904400
H	7.41947800	-0.24818700	3.18609900
C	6.07175400	0.92703600	4.44760600
H	6.79921600	0.79409000	5.25416100
H	5.76178500	1.97641200	4.44886600
C	4.83705000	-0.00676400	4.58972200
H	3.92444900	0.57614100	4.74183800
H	4.93168300	-0.69957400	5.43127100
C	4.78950000	-0.76280800	3.24567400
H	5.25525000	-1.75630500	3.33313600
H	3.78893300	-0.87926000	2.82819100
O	6.51917000	-0.29923800	-1.21604600
C	7.20783300	-1.34692200	-0.49814000
H	6.72987000	-1.44960700	0.47919700
H	8.25664900	-1.04881100	-0.35174200
C	7.10401200	-2.59023400	-1.38070800
H	7.90955300	-3.30692600	-1.19360700
H	6.14624200	-3.09493700	-1.21297500
C	7.14993100	-1.97642300	-2.78901800
H	6.71592900	-2.62211500	-3.55803800
H	8.18533400	-1.75679400	-3.07571000
C	6.35392500	-0.68013800	-2.60203100
H	6.70905400	0.14122900	-3.23330700
H	5.28525900	-0.82914900	-2.79396600
C	2.79517000	2.85658500	-1.70407700

C	3.37128100	4.27660900	-1.86634100
H	3.30208100	4.60152600	-2.91255900
H	4.43044800	4.29557500	-1.57644100
H	2.84277000	5.01865400	-1.25894000
C	3.52211400	1.91901900	-2.68024800
H	3.36932400	2.23293900	-3.72083400
H	3.16395400	0.88970500	-2.58176300
H	4.60491600	1.92905200	-2.48628800
H	1.74097100	2.90714500	-2.04524200
C	2.35185200	3.17784200	0.70352100
C	0.87948400	3.61473500	0.52582600
H	0.57969100	4.30091200	1.32902100
H	0.20641200	2.75137000	0.54828100
H	0.72130700	4.13527300	-0.42494600
C	2.51901800	2.48796100	2.06668600
H	2.15751600	3.12889000	2.88082400
H	3.57242000	2.25255300	2.26598700
H	1.95228500	1.55039000	2.09895800
H	2.94127500	4.11389700	0.75472700

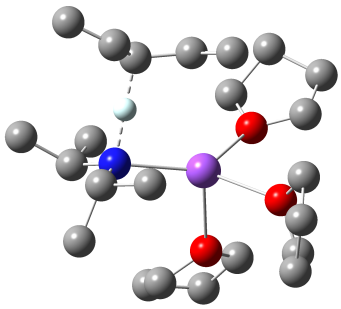
Table S-5. Geometric coordinates and thermally corrected MP2 energies for 1,4-pentadiene.



G = –195.196301 Hartree
G_{MP2} = –194.4806266 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	0.28469200	0.45255400	-0.96181500
H	-0.01737200	0.83380800	0.72058300
C	1.04547400	-0.99523000	0.42429700
H	0.89593800	-1.44602700	1.40627700
C	2.10802900	-1.34793500	-0.29944800
H	2.29239800	-0.92933100	-1.28710800
H	2.83764000	-2.06577900	0.06619400
C	-1.40497100	-0.55318800	-0.10755400
H	-2.18830900	0.19915300	-0.20887600
C	-1.74339700	-1.84261800	-0.09728700
H	-0.99966800	-2.63043400	-0.00881500
H	-2.77995700	-2.15642400	-0.18562600

Table S-6. Geometric coordinates and thermally corrected MP2 energies for [A(THF)$_3$·(1,4-pentadiene)]‡.

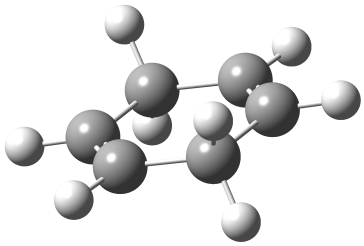


G = –1346.169909 Hartree
G_{MP2} = –1341.634158 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
N	-0.71360800	-0.29172100	-1.25047400
Na	-2.79623700	-1.42128000	-1.06212000
O	-3.95910900	-2.39810400	0.79412900
C	-3.50013300	-3.49286900	1.60556200
C	-3.35188000	-2.91951300	3.02878500
C	-4.25213900	-1.65216200	3.01719700
C	-4.88157500	-1.66707500	1.61363200
H	-5.00588700	-0.68400100	1.15725000
H	-5.85224000	-2.18818000	1.62280000
H	-3.64908200	-0.75009000	3.15762300
H	-5.01455900	-1.66745200	3.80193100
H	-2.31149100	-2.65367500	3.23356000
H	-3.66419300	-3.64666000	3.78435800
H	-4.25176700	-4.29699800	1.58015500
H	-2.57316700	-3.85816600	1.15972700
O	-4.15755600	-2.56073100	-2.70558600
C	-4.85092500	-3.75686500	-2.27466800
C	-5.29573200	-4.47389900	-3.55323000
C	-4.22002800	-4.03675900	-4.55974600
C	-3.96972300	-2.58893300	-4.13775400
H	-4.69203500	-1.90491000	-4.60606100
H	-2.95984800	-2.23173800	-4.35513400
H	-4.54036000	-4.12030800	-5.60248800
H	-3.30971700	-4.63340200	-4.43158400
H	-6.28320900	-4.11903700	-3.87204400
H	-5.35196900	-5.55858700	-3.42290600
H	-4.15346100	-4.36565000	-1.68765200
H	-5.68101000	-3.45961000	-1.62654200
O	-4.45544700	0.37498300	-1.05364700
C	-5.74716400	0.29936200	-1.69580600
C	-6.00106500	1.67337800	-2.35347800
C	-4.61951200	2.35226800	-2.30642900
C	-4.01514800	1.74567000	-1.04255900
H	-2.92427100	1.73090200	-1.01800700
H	-4.39083400	2.25098000	-0.13909800
H	-4.68035600	3.44401800	-2.26679000
H	-4.01651200	2.07357400	-3.17754400
H	-6.72790600	2.24955400	-1.77026600
H	-6.39424900	1.57944700	-3.37009100
H	-5.69613500	-0.52299100	-2.41455500
H	-6.51171400	0.05781000	-0.94578300
C	-0.45042500	0.66604000	-2.33033200
C	1.03851900	0.84479300	-2.70763100
H	1.14730200	1.55401900	-3.53895000
H	1.48793700	-0.10864000	-3.00569300
H	1.62391500	1.23309800	-1.86768000
C	-1.24960100	0.25129800	-3.57626400
H	-1.11686900	0.97132800	-4.39356000
H	-2.32304300	0.19193300	-3.35190800
H	-0.92236900	-0.73055700	-3.93963500
H	-0.81811300	1.67470100	-2.05349300
C	-0.23400600	1.41646300	0.56225000
H	0.10301600	2.19994200	-0.12489100
H	0.31004500	1.55397900	1.50583000
H	-1.30252600	1.57949700	0.76209300

C	-0.41364300	-1.02589000	1.06534300
H	0.19817000	-0.92467600	1.97080300
H	-0.30690500	-2.05063900	0.69562600
H	-1.46392000	-0.87532300	1.35561700
H	1.09289900	-0.11197600	-0.13234500
C	0.35180400	-2.73715300	-2.10809000
H	0.55386200	-2.52585500	-3.16624700
C	1.59616900	-2.97547600	-1.35348800
H	1.47644200	-3.34760500	-0.33310100
C	2.84909700	-2.72707700	-1.77112700
H	3.05614900	-2.36741700	-2.77788000
H	3.70866700	-2.87202100	-1.12196000
C	-0.76483500	-3.67615900	-1.95835700
H	-1.51666100	-3.59471800	-2.75028200
C	-1.05263600	-4.55017700	-0.96291500
H	-0.36266800	-4.75736700	-0.14845200
H	-1.95647400	-5.15415500	-0.99041700
H	-0.15960900	-1.53746400	-1.68933600

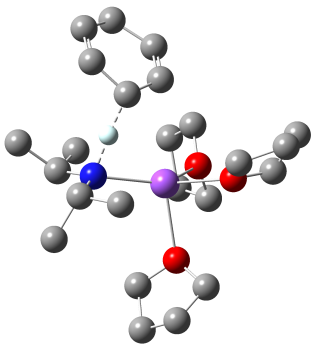
Table S-7. Geometric coordinates and thermally corrected MP2 energies for 1,4-cyclohexadiene.



G = –233.310874 Hartree
G_{MP2} = –232.4838718 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	1.25515400	-0.83325500	-0.00004200
C	1.25515400	-2.16801300	-0.00004200
C	0.00000000	-3.00126800	0.00000000
C	-1.25515400	-2.16801300	-0.00004200
C	-1.25515400	-0.83325500	-0.00004200
H	-2.20112300	-0.29343500	-0.00006700
H	-2.20112300	-2.70783300	-0.00006700
H	0.00000000	-3.67865300	-0.87080500
H	0.00000000	-3.67858500	0.87085100
H	2.20112300	-2.70783300	-0.00006700
H	2.20112300	-0.29343500	-0.00006700
H	0.00000000	0.67731700	0.87085100
H	0.00000000	0.67738500	-0.87080500

Table S-8. Geometric coordinates and thermally corrected MP2 energies for [A(THF)$_3$·(1,4-cyclohexadiene)]‡.

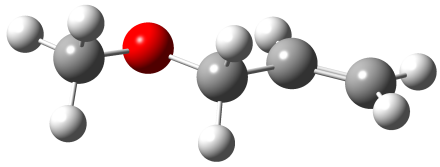


G = –1384.281914 Hartree
G_{MP2} = –1379.639054 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-1.19409600	2.03014500	-0.21291100
C	-0.91557800	3.00583900	-1.27507500
C	-0.04379700	4.20223100	-0.84706600
H	0.14820600	4.86246200	-1.70278800
H	0.92605500	3.85740100	-0.46301500
H	-0.51695700	4.80669600	-0.06703500
C	-0.23697100	2.29506800	-2.45574100
H	-0.09446700	2.98005800	-3.30143100
H	-0.83696000	1.45030000	-2.80567700
H	0.75238900	1.91619000	-2.15970000
H	-1.85637000	3.43715000	-1.67359900
C	-1.72603700	2.62250200	1.02579500
C	-3.03254100	3.43161700	0.86576500
H	-3.32812500	3.87801300	1.82460500
H	-3.85017900	2.79085100	0.51831900
H	-2.91716900	4.25096200	0.14721400
C	-1.93782300	1.51108200	2.06484000
H	-2.34913100	1.91685800	2.99750100
H	-0.98846100	1.01565300	2.31279400
H	-2.63310700	0.75208200	1.68758400
H	-0.97974700	3.31402600	1.45934200
O	2.29695800	0.53386900	0.54639800
C	3.36031200	0.31888700	-0.39854700
H	2.93780100	-0.24233900	-1.23560600
H	4.15810000	-0.27975500	0.06789300
C	3.85632900	1.71825000	-0.75452000
H	4.87135700	1.71775200	-1.16355400
H	3.18736800	2.17743100	-1.49053600
C	3.75152100	2.44182400	0.59998500
H	3.61736000	3.52217100	0.49511900
H	4.65792100	2.27330400	1.19229900
C	2.53472200	1.76989300	1.26576000
H	2.71377500	1.53834900	2.32275800
H	1.62247700	2.36760400	1.18388400
O	0.10653400	-1.70991600	1.71684100
C	1.21174200	-1.84539600	2.62269800
H	1.99416000	-1.16782100	2.27869600
H	1.58623400	-2.88086800	2.58628400
C	0.63128700	-1.51903100	4.00785200
H	1.14388400	-2.06852600	4.80327100
H	0.73411300	-0.45064700	4.22184200
C	-0.86827500	-1.90704300	3.87492400
H	-1.51293500	-1.05872300	4.11964000
H	-1.14381700	-2.73490800	4.53504100
C	-1.01978100	-2.30269400	2.39210200
H	-0.97192000	-3.39539600	2.26875100
H	-1.92387100	-1.92940700	1.90834100
O	0.64801500	-1.51613600	-1.74493200
C	1.01032300	-2.86989900	-1.39542900
H	0.72974000	-3.02267600	-0.35098600
H	2.09963200	-2.99137000	-1.49424800
C	0.26611300	-3.75547400	-2.39179900
H	0.72867100	-4.74025400	-2.50865400
H	-0.77254900	-3.89747400	-2.07205400
C	0.32581400	-2.90034500	-3.66762600

H -0.45925500 -3.14527300 -4.38860800
H 1.29395400 -3.02861000 -4.16599500
C 0.18168900 -1.47403600 -3.11945900
H 0.77826100 -0.73823900 -3.66808100
H -0.86190800 -1.14283700 -3.11085500
C -3.06961800 0.29917700 -1.36911700
C -4.43507400 0.85112800 -1.26499100
C -5.37791600 0.38340000 -0.42530600
C -5.15023200 -0.80864500 0.48184400
C -3.88146800 -1.54600000 0.10512500
C -2.97232800 -1.03533400 -0.75551700
H -2.10324600 -1.65176400 -1.00785600
H -3.74107000 -2.54386800 0.52190500
H -5.12239000 -0.49255800 1.54410500
H -6.01412200 -1.49642200 0.43301600
H -6.35549500 0.86198400 -0.37874900
H -4.67562400 1.71155100 -1.89178500
H -2.69316100 0.31196000 -2.40282000
H -2.14702000 1.20469100 -0.74074700

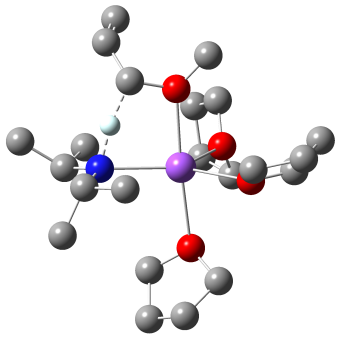
Table S-9. Geometric coordinates and thermally corrected MP2 energies for allyl methyl ether.



G = –232.316236 Hartree
G_{MP2} = –231.5298026 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.76316100	-0.78262600	-0.00015300
H	-0.13659800	0.63226600	0.89297300
H	-0.13651100	0.63252900	-0.89279900
O	1.25529000	-0.64147500	-0.00003400
C	2.33503700	0.27428800	0.00015400
H	2.27760500	0.93251000	-0.88578100
H	2.27751100	0.93225000	0.88627700
C	3.62214700	-0.51204900	0.00010800
H	3.48782200	-1.59248700	0.00022700
C	4.84346100	0.01906400	-0.00004400
H	5.00828100	1.09534300	-0.00016900
H	5.73301500	-0.60403300	-0.00004800

Table S-10. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* [A(THF)$_3$·(allyl methyl ether)]‡.

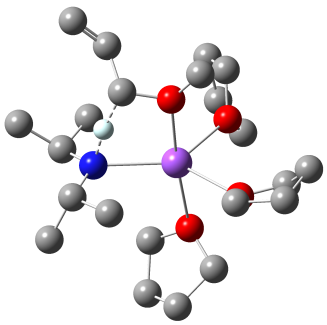


G = –1383.296497 Hartree
G_{MP2} = –1378.692455 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-2.02382300	1.08297800	-0.79721800
C	-1.99530400	1.91826600	-2.00311500
C	-2.03192500	3.43501300	-1.73958300
H	-1.96738100	3.99116700	-2.68388500
H	-1.18376600	3.73775300	-1.11080400
H	-2.95216500	3.74992300	-1.23690700
C	-0.73456600	1.58132000	-2.81356400
H	-0.72820100	2.10882300	-3.77607600
H	-0.67302700	0.50732900	-3.01588100
H	0.16784400	1.87988700	-2.26047500
H	-2.85786800	1.69610700	-2.66477900
C	-3.14175700	1.36386600	0.11626400
C	-4.54818000	1.25252500	-0.51566300
H	-5.32523100	1.50002900	0.21931700
H	-4.73178700	0.23314200	-0.87232800
H	-4.67063500	1.93495500	-1.36405800
C	-3.05372400	0.42261400	1.32736000
H	-3.83894700	0.65100200	2.05934900
H	-2.08510100	0.52619300	1.83475700
H	-3.17435000	-0.62248600	1.01804900
H	-3.05301000	2.39339500	0.51172500
O	1.05060400	1.89739700	1.24125900
C	2.28182900	2.50749100	0.82197500
H	2.71047600	1.86596500	0.04925800
H	2.98089500	2.56603700	1.67170200
C	1.88436700	3.90205000	0.34325500
H	2.72425500	4.60387200	0.32938200
H	1.46489200	3.84518400	-0.66752400
C	0.79473700	4.28178100	1.36133400
H	0.07347200	5.00188600	0.96419900
H	1.24841300	4.72218800	2.25654400
C	0.13650300	2.92755500	1.69272500
H	-0.03828700	2.80426300	2.76882400
H	-0.80410800	2.77175800	1.15857200
O	0.50340200	-1.29413300	1.97655100
C	0.91845400	-0.79194300	3.25342500
H	1.20041300	0.25212700	3.11007800
H	1.79503400	-1.36111600	3.60283600
C	-0.28730800	-1.01548500	4.17975900
H	0.02075600	-1.18965000	5.21530500
H	-0.94230900	-0.13897400	4.16939800
C	-1.00869200	-2.23996900	3.55044800
H	-2.05559000	-2.00897500	3.33746500
H	-0.98842800	-3.11542700	4.20663000
C	-0.22726700	-2.50370100	2.24588400
H	0.48605000	-3.33263400	2.37296000
H	-0.85244500	-2.69568000	1.37370700
O	2.21933700	-0.34408600	-1.00100800
C	3.14364300	-1.20203500	-0.29547800
H	2.60538100	-1.65081800	0.54308200
H	3.96779300	-0.59025100	0.09984000
C	3.65017300	-2.20548000	-1.33176700
H	4.63417700	-2.61145600	-1.07821100
H	2.94805900	-3.04132400	-1.42861100
C	3.65056200	-1.35685800	-2.61296700

H 3.61555800 -1.95307900 -3.52955900
H 4.54754200 -0.72735300 -2.65223900
C 2.39568400 -0.49714400 -2.42852200
H 2.48029800 0.49788700 -2.87670600
H 1.50334400 -0.98672900 -2.83552400
C -2.14345400 -1.51230700 -1.71394200
C -3.31350700 -2.31562300 -1.38329200
C -3.52727700 -3.16644500 -0.35509000
H -2.74369100 -3.43179000 0.35028200
H -4.49743700 -3.62817700 -0.19631200
H -4.15667200 -2.12103800 -2.05314000
H -1.97080800 -1.46612600 -2.80176700
O -0.91148300 -1.92950300 -1.05898500
C -0.37654100 -3.14169600 -1.56625400
H -0.04046100 -3.01951900 -2.60888400
H 0.48592000 -3.41849900 -0.94694800
H -1.11844100 -3.94810600 -1.53212500
H -2.20209500 -0.14485600 -1.25106400

Table S-11. Geometric coordinates and thermally corrected MP2 energies for pro-*E* [A(THF)$_3$·(allyl methyl ether)]‡.

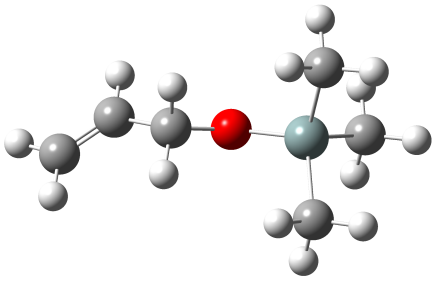


G = –1383.294895 Hartree
G_{MP2} = –1378.689974 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-2.02751600	1.17882600	-0.67558400
C	-2.06054100	1.82638800	-1.99389000
C	-1.97603600	3.36283500	-1.95711600
H	-1.95721900	3.77144500	-2.97573600
H	-1.06023300	3.68802100	-1.44514900
H	-2.82859100	3.81464900	-1.43971600
C	-0.90742000	1.27579400	-2.84545300
H	-0.95469100	1.65756700	-3.87336700
H	-0.94048100	0.18239700	-2.88870500
H	0.06143300	1.57611000	-2.42012600
H	-2.99412000	1.57759500	-2.53752800
C	-3.04262400	1.66970900	0.27015900
C	-4.50627100	1.51083700	-0.20114800
H	-5.20032100	1.91094300	0.54998900
H	-4.75160100	0.45557600	-0.36800200
H	-4.69191400	2.05181000	-1.13602900
C	-2.85554300	0.95477300	1.61710300
H	-3.57436500	1.31905200	2.36175800
H	-1.84547700	1.12261400	2.01292400
H	-3.00625000	-0.12496700	1.50576800
H	-2.88496600	2.74648500	0.46239200
O	1.32912800	1.92015000	0.89319700
C	2.55784300	2.35453800	0.28731100
H	2.84502300	1.59082000	-0.43821700
H	3.34430000	2.43982600	1.05420500
C	2.23591900	3.71761900	-0.32109400
H	3.12784200	4.32694600	-0.49785200
H	1.71145400	3.58785800	-1.27452400
C	1.29413600	4.31592800	0.73830900
H	0.60565800	5.05927900	0.32600800
H	1.87496800	4.80141400	1.53093000
C	0.55207200	3.08042600	1.28405100
H	0.46317600	3.09961500	2.37741400
H	-0.44201500	2.95536300	0.84715400
O	0.59603300	-1.14638500	2.04867200
C	1.19045500	-0.54729400	3.20807100
H	1.54175900	0.44208700	2.91148600
H	2.04935100	-1.15635500	3.53223900
C	0.08274900	-0.54580800	4.27626900
H	0.49137100	-0.68108300	5.28234800
H	-0.46195000	0.40287400	4.26353400
C	-0.84807500	-1.71377300	3.84330400
H	-1.86314800	-1.35072500	3.66189100
H	-0.90631900	-2.50422200	4.59756300
C	-0.21193600	-2.22999900	2.53735000
H	0.43261200	-3.10189700	2.72933500
H	-0.92413600	-2.47591600	1.74903200
O	2.07427200	-0.64354400	-1.16147300
C	3.04555100	-1.44497700	-0.45560300
H	2.60635100	-1.72797300	0.50429400
H	3.94436000	-0.83848900	-0.26999000
C	3.35840200	-2.62377100	-1.37763700
H	4.34753800	-3.05294500	-1.19080600
H	2.61172200	-3.41609800	-1.25091500
C	3.22571100	-1.97865000	-2.76612100

H 3.02981700 -2.70137200 -3.56366700
H 4.14238300 -1.43382700 -3.02154700
C 2.05789600 -1.00676500 -2.56221100
H 2.14524700 -0.09363600 -3.15959300
H 1.09191500 -1.47472400 -2.78262400
O -1.11997200 -1.93248700 -0.76983900
C -2.44806000 -1.49777200 -1.21181500
C -3.52891300 -2.19405500 -0.51899500
C -4.76026700 -2.49294200 -0.98509300
H -5.03202400 -2.33046400 -2.02676600
H -5.54095300 -2.87604000 -0.33364600
H -3.33045700 -2.39853700 0.53978900
H -2.50521200 -1.60677200 -2.30736900
C -0.79172900 -3.25856900 -1.14239600
H -0.75711500 -3.36741900 -2.23857400
H 0.19673900 -3.49530800 -0.72817600
H -1.52770600 -3.97699400 -0.75571700
H -2.32845200 -0.05600000 -0.91412600

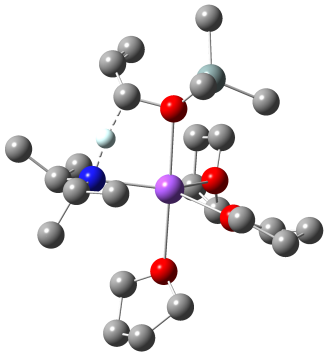
Table S-12. Geometric coordinates and thermally corrected MP2 energies for allyloxytrimethylsilane.



G = –601.664955 Hartree
G_{MP2} = –600.0511662 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	0.05666200	1.04776400	-0.33103700
H	-0.15535000	0.00852600	1.09195800
C	1.28718400	-0.70631600	-0.31609100
H	1.28161000	-1.77998100	-0.13002000
C	2.38488800	-0.10519900	-0.77249900
H	2.40903900	0.96361000	-0.97682600
H	3.30402600	-0.65426200	-0.95821300
O	-1.07830300	-0.67941500	-0.63431700
Si	-2.69405000	-0.24700300	-0.49355100
C	-2.97013000	1.49386900	-1.17508900
H	-4.03086100	1.77048400	-1.12537300
H	-2.41060500	2.25231400	-0.61427900
H	-2.65873100	1.55930100	-2.22428000
C	-3.62283100	-1.51752900	-1.52155400
H	-3.45599400	-2.53136000	-1.14032600
H	-4.70315600	-1.32795500	-1.50866500
H	-3.29129100	-1.49641900	-2.56587300
C	-3.24426000	-0.31922600	1.31351500
H	-4.31154500	-0.08073300	1.40362300
H	-3.09181500	-1.32037100	1.73386600
H	-2.69876000	0.39301700	1.94438800

Table S-13. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* [A(THF)$_3$·(allyloxytrimethylsilane)]‡.

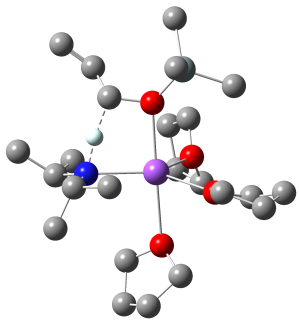


G = –1752.641904 Hartree
G_{MP2} = –1747.217566 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-0.21848100	-2.08640500	-1.19752800
C	-0.44656800	-1.99564700	-2.64421300
C	-1.89021300	-2.29360100	-3.08850400
H	-1.99768700	-2.14949600	-4.17146300
H	-2.59340400	-1.61644000	-2.58468800
H	-2.19502700	-3.32096700	-2.86402700
C	-0.05865800	-0.58798700	-3.12112900
H	-0.09749900	-0.51280900	-4.21538000
H	0.95414400	-0.32605300	-2.79923800
H	-0.75541400	0.15751400	-2.71034200
H	0.20445300	-2.70241200	-3.19956900
C	-0.64887000	-3.35248200	-0.58749000
C	-0.01158300	-4.62284000	-1.19698500
H	-0.40095100	-5.52549800	-0.70839700
H	1.07610800	-4.61211800	-1.06840000
H	-0.22243800	-4.71286600	-2.26842700
C	-0.36727600	-3.31162400	0.92232500
H	-0.72939800	-4.22434400	1.41281600
H	-0.87455800	-2.45727900	1.38931700
H	0.70717900	-3.22310400	1.12063900
H	-1.74330400	-3.46829700	-0.69786100
O	-2.57029500	0.31521400	0.46885000
C	-3.34507700	1.33569900	-0.18478900
H	-2.67696100	1.87672700	-0.85913900
H	-3.73241200	2.04066000	0.56741200
C	-4.48956000	0.60489000	-0.88711900
H	-5.35713600	1.24844600	-1.06323500
H	-4.15263300	0.20894700	-1.85192800
C	-4.76940900	-0.54208800	0.09594200
H	-5.26700100	-1.39863100	-0.36826200
H	-5.40148000	-0.18961300	0.91979400
C	-3.36278200	-0.89088000	0.59935000
H	-3.35188400	-1.20441900	1.64939900
H	-2.88833800	-1.66919200	-0.00448000
O	0.23957200	0.55653400	2.33641500
C	-0.79836300	0.54276100	3.32582800
H	-1.74900100	0.51888300	2.79124700
H	-0.74285900	1.46779500	3.92211700
C	-0.50802300	-0.69112100	4.19932000
H	-0.79595300	-0.52372600	5.24181400
H	-1.06459000	-1.56011900	3.83576900
C	1.02129400	-0.91238400	4.02568400
H	1.22892900	-1.90198500	3.61030900
H	1.56639300	-0.82510800	4.97045000
C	1.44266500	0.18529900	3.03058300
H	1.84135300	1.06788400	3.55450600
H	2.15707500	-0.14234700	2.27571800
O	-0.14999600	2.41576400	-0.57451100
C	-0.36183400	3.37531600	0.48704500
H	0.19111100	3.03001700	1.36331000
H	-1.43175600	3.39649800	0.73509900
C	0.10522000	4.72188800	-0.06838300
H	-0.39973900	5.56831100	0.40697400
H	1.18489100	4.84270400	0.07672200
C	-0.22208400	4.57729200	-1.56315300

H	0.35566600	5.25096000	-2.20283600
H	-1.28682500	4.77044200	-1.74121700
C	0.10825600	3.10413200	-1.81841800
H	-0.50412300	2.64604600	-2.60109000
H	1.16454000	2.96934400	-2.08126700
O	2.47415000	-0.38807900	-0.34402400
C	2.50051200	-1.74984100	-0.91190000
C	3.18188700	-2.73678300	-0.09138800
C	3.53476700	-2.71277900	1.21413300
H	3.43825200	-1.81945500	1.82394800
H	3.96291100	-3.58638100	1.69700000
H	3.34196400	-3.67569500	-0.63104100
H	2.89783200	-1.71590100	-1.93667100
Si	3.76682900	0.64453100	-0.65792700
C	3.82003400	1.08537900	-2.50119500
H	4.61091900	1.81961200	-2.70195600
H	4.02820000	0.20434200	-3.11932100
H	2.87152300	1.51204300	-2.84902200
C	3.41715000	2.20455400	0.35128400
H	3.54203700	2.02129200	1.42493300
H	4.09581300	3.02034700	0.07242000
H	2.38842300	2.54155400	0.18632600
C	5.44881400	-0.06279800	-0.17585000
H	6.24343200	0.65145900	-0.43062100
H	5.50946000	-0.27452100	0.89631900
H	5.65492300	-1.00107400	-0.70045100
H	1.09010100	-2.02982600	-1.06298600

Table S-14. Geometric coordinates and thermally corrected MP2 energies for pro-*E* [A(THF)$_3$·(allyloxytrimethylsilane)]‡.

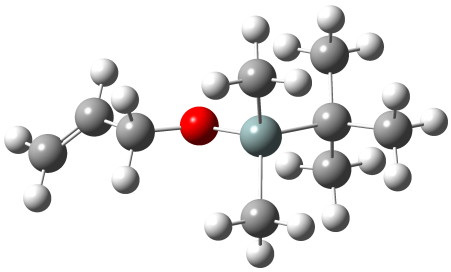


G = –1752.64151 Hartree
G_{MP2} = –1747.216122 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	0.03283800	-2.19033500	-1.04755400
C	-0.18941100	-2.21652900	-2.49952200
C	-1.56252100	-2.76623500	-2.92427100
H	-1.68715900	-2.69397200	-4.01249400
H	-2.36814600	-2.18933600	-2.45040300
H	-1.69525200	-3.81742200	-2.64916800
C	-0.02390700	-0.79314900	-3.05362000
H	-0.05982000	-0.78689100	-4.15058400
H	0.93208600	-0.35672000	-2.74521100
H	-0.83502600	-0.14560400	-2.68940300
H	0.57190500	-2.84040500	-3.00976600
C	-0.18874000	-3.47760100	-0.37152500
C	0.67302700	-4.65067700	-0.89119000
H	0.43272000	-5.57497200	-0.34912400
H	1.74050200	-4.44176900	-0.75445000
H	0.49819700	-4.84313200	-1.95585100
C	0.04979600	-3.29617100	1.13529400
H	-0.15684700	-4.22453500	1.68246600
H	-0.59799700	-2.50996100	1.54312800
H	1.09153400	-3.01740700	1.32851000
H	-1.24453100	-3.78342000	-0.49054700
O	0.15104100	0.60796200	2.31585700
C	-0.91526400	0.67930900	3.27178400
H	-1.84999900	0.61457300	2.71286100
H	-0.87014200	1.64794400	3.79494100
C	-0.66281600	-0.48401000	4.24735300
H	-0.98068600	-0.23461400	5.26435700
H	-1.21697700	-1.37427400	3.93516600
C	0.86858700	-0.72974900	4.13939900
H	1.07379900	-1.75541600	3.82144200
H	1.38651500	-0.56565400	5.08911400
C	1.33034400	0.27744200	3.06735000
H	1.72974400	1.19285900	3.53062400
H	2.06140700	-0.11304900	2.35861500
O	-0.48165200	2.30363300	-0.78021700
C	-0.76910400	3.31470500	0.21421500
H	-0.16479400	3.10057500	1.09942900
H	-1.82966100	3.24105900	0.48888300
C	-0.45441100	4.66065200	-0.44511300
H	-1.06485300	5.47469000	-0.04263800
H	0.59971100	4.92220500	-0.29930300
C	-0.73153400	4.36616700	-1.92777700
H	-0.21793800	5.05013200	-2.60991600
H	-1.80682800	4.42232800	-2.13595500
C	-0.23314600	2.92515200	-2.05998300
H	-0.75368900	2.34602300	-2.82798500
H	0.84374600	2.89156100	-2.27032100
O	2.44310500	-0.04677600	-0.25869500
C	2.66708900	-1.42242600	-0.79469100
C	3.52737700	-2.23219500	0.05696400
C	4.34724400	-3.24242100	-0.31258900
H	4.53498500	-3.47314400	-1.35981800
H	4.82454100	-3.88677800	0.42033200
H	3.40472200	-2.05213100	1.13044700
H	3.03601400	-1.34539600	-1.82676800

Si	3.67851500	1.08443600	-0.42573500
C	4.04913800	1.39002900	-2.25725300
H	4.79387200	2.18683000	-2.37942300
H	4.44554800	0.49135900	-2.74276200
H	3.14663800	1.68940700	-2.80494300
C	3.03073200	2.68030100	0.35647000
H	2.87644100	2.55997000	1.43535900
H	3.73807800	3.50642100	0.21128400
H	2.07245900	2.96908600	-0.08629600
C	5.26719300	0.56997300	0.45736000
H	6.05711000	1.31470100	0.29283000
H	5.11157100	0.48543400	1.54001600
H	5.62631900	-0.40093800	0.10247000
O	-2.61588800	0.04972200	0.43434400
C	-3.51430000	0.91264200	-0.28276900
H	-2.90739300	1.55235300	-0.92719700
H	-4.06620800	1.54670500	0.42933800
C	-4.46588700	-0.01634500	-1.03484400
H	-5.41434100	0.46607800	-1.29120200
H	-3.99799600	-0.37020900	-1.96046700
C	-4.62165800	-1.17180400	-0.03337500
H	-4.91835500	-2.11357300	-0.50421700
H	-5.37646100	-0.91962800	0.72090900
C	-3.22431300	-1.25544800	0.59974000
H	-3.26026200	-1.49482800	1.66917800
H	-2.58063700	-1.98143500	0.09623100
H	1.28652300	-1.92152800	-0.91004100

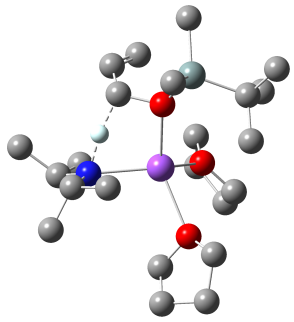
Table S-15. Geometric coordinates and thermally corrected MP2 energies for allyloxy-*tert*-butyldimethylsilane.



G = –719.514504 Hartree
G_{MP2} = –717.4643974 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.20510000	0.55381700	0.92820000
H	-0.04023500	0.72417200	-0.83075400
C	-1.04586300	-1.05787000	-0.20712300
H	-0.86340500	-1.72931000	-1.04577900
C	-2.14006100	-1.19236800	0.54070100
H	-2.33583700	-0.54006100	1.38968600
H	-2.88534400	-1.95580200	0.33454900
O	1.28544400	-0.61037600	0.04382700
Si	2.74073000	0.21570700	0.20868600
C	2.74290500	1.20389000	1.82242600
H	3.69978600	1.71835700	1.97275400
H	1.96104900	1.97338200	1.82008700
H	2.56957600	0.55946300	2.69164300
C	4.06537700	-1.16209700	0.21556300
C	3.99581400	-1.95820200	-1.10558600
H	4.74338600	-2.76498400	-1.10508900
H	3.01051300	-2.41517400	-1.24820300
H	4.20239400	-1.32461800	-1.97704500
C	5.47389400	-0.54650200	0.36223800
H	5.58435800	0.01514400	1.29837200
H	6.23689000	-1.33834600	0.36795700
H	5.71754100	0.13079400	-0.46593200
C	3.80720500	-2.12536200	1.39428900
H	4.54724600	-2.93912100	1.39181500
H	3.88672700	-1.61686400	2.36313000
H	2.81132900	-2.57744900	1.33306200
C	2.97624400	1.41000600	-1.24063000
H	3.94066400	1.92818900	-1.17462800
H	2.94247400	0.88865400	-2.20389400
H	2.19706000	2.18197400	-1.25497200

Table S-16. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* [A(THF)$_2$·(allyloxy-*tert*-butyldimethylsilane)]‡.

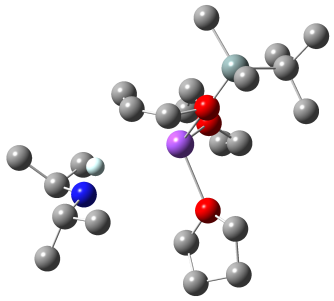


G = –1638.147241 Hartree
G_{MP2} = –1633.055742 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	0.93392300	2.17820300	-0.00532400
C	1.04559600	2.98232500	-1.22862900
C	2.48784300	3.21856200	-1.71380400
H	2.48723500	3.76248700	-2.66708600
H	3.00578400	2.26226800	-1.86867400
H	3.07868100	3.80606800	-1.00359800
C	0.24185000	2.30265200	-2.34750700
H	0.21901400	2.92219600	-3.25298700
H	-0.79026400	2.11719100	-2.03618500
H	0.69716100	1.33686700	-2.60831600
H	0.59719100	3.98828200	-1.08994500
C	1.75867800	2.64938900	1.11564200
C	1.42115000	4.07324100	1.61410600
H	2.09741400	4.37744900	2.42366000
H	0.39483900	4.11956300	1.99603700
H	1.51245000	4.81510800	0.81285600
C	1.65726300	1.65360700	2.28134600
H	2.28897200	1.96548600	3.12259200
H	1.99098100	0.65447700	1.96748000
H	0.62568100	1.57687800	2.64692000
H	2.82085400	2.66226700	0.81479300
O	1.37939500	-1.29348900	-1.49961700
C	1.17437600	-1.81637700	-2.83138000
H	0.61656200	-1.07549200	-3.41845200
H	0.57067600	-2.72622700	-2.75498000
C	2.57178600	-2.05411100	-3.41007200
H	2.93922700	-3.04891500	-3.13128100
H	2.58843100	-1.97982400	-4.50140400
C	3.39631600	-0.96208400	-2.71056500
H	3.25417600	0.00390700	-3.20845900
H	4.46857700	-1.17769600	-2.68475100
C	2.77261000	-0.93683900	-1.31490200
H	3.23881500	-1.68035300	-0.65311400
H	2.80192200	0.04421500	-0.83222000
O	0.02523500	-1.83441000	1.48399700
C	0.53971800	-3.14192700	1.18923400
H	1.03775100	-3.07932400	0.22061200
H	-0.29933200	-3.85007600	1.11714600
C	1.46673200	-3.50078000	2.37088300
H	1.35398400	-4.55118100	2.65584200
H	2.51773100	-3.34164700	2.11161600
C	1.02107800	-2.52952700	3.49981500
H	1.80895900	-1.80173500	3.71583500
H	0.77928900	-3.04652700	4.43309200
C	-0.20463700	-1.82253800	2.90373400
H	-1.13071100	-2.37544500	3.12219100
H	-0.33562800	-0.78391600	3.21075400
O	-2.13998400	0.89443400	-0.03770200
C	-1.77236700	2.17500800	0.59899200
C	-2.06169100	2.22058700	2.02365000
C	-2.34251800	1.21455800	2.88297500
H	-2.51443900	0.19925000	2.53764500
H	-2.45655800	1.39825300	3.94755200
H	-1.93463500	3.22249200	2.44468800
H	-2.22033300	3.01087800	0.04493400

Si	-3.67931500	0.66915200	-0.69128500
C	-3.87274100	1.76482200	-2.22528200
H	-4.85737300	1.63345700	-2.69066900
H	-3.78045500	2.82405200	-1.95717500
H	-3.11103500	1.55232700	-2.98400800
C	-3.78690600	-1.18952000	-1.17656800
C	-2.74058800	-1.53750300	-2.25540200
H	-1.71634100	-1.35961000	-1.90555600
H	-2.81114000	-2.60052500	-2.53273600
H	-2.88311600	-0.95105100	-3.17116200
C	-5.19328200	-1.48999800	-1.74083400
H	-5.27339000	-2.54958700	-2.02571800
H	-5.98102500	-1.29090700	-1.00467400
H	-5.41515300	-0.89571600	-2.63600600
C	-3.54647600	-2.07982900	0.06162300
H	-4.28098300	-1.88333900	0.85199900
H	-3.63503700	-3.14348500	-0.20865200
H	-2.54897100	-1.92585100	0.48958400
C	-5.04893200	1.12083900	0.52851500
H	-6.03171800	1.08621100	0.04175500
H	-5.06939600	0.45529100	1.39687900
H	-4.89790600	2.13639000	0.90919600
H	-0.35182400	2.27426800	0.35090600

Table S-17. Geometric coordinates and thermally corrected MP2 energies for IRC of pro-*Z* [A(THF)$_2$·(allyloxy-*tert*-butyldimethylsilane)]‡.

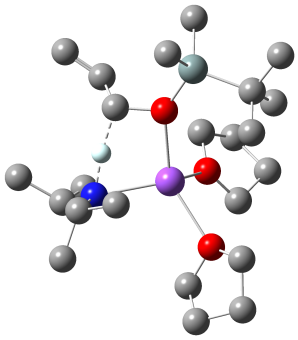


G = –1638.162218 Hartree
G_{MP2} = –1633.063992 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	3.36272100	-0.93377000	-0.53662500
C	3.86728400	-2.23563900	-0.06200000
C	5.24250600	-2.09800200	0.60249700
H	5.54401600	-3.05370800	1.04611200
H	5.20712000	-1.34420900	1.39883000
H	6.02404100	-1.80570100	-0.10659400
C	2.85584100	-2.82462400	0.92866400
H	3.14749800	-3.84137800	1.21750800
H	1.84868200	-2.86739300	0.49993200
H	2.80896700	-2.21186600	1.83728500
H	3.97103300	-2.95667400	-0.89362700
C	4.19014300	-0.21770700	-1.52835300
C	4.42928600	-0.99399500	-2.83712200
H	5.05146600	-0.41163300	-3.52790600
H	3.47533900	-1.20578900	-3.33551800
H	4.93810800	-1.94804800	-2.66118200
C	3.52916800	1.13494500	-1.81881000
H	4.12404800	1.71783600	-2.53217300
H	3.42205100	1.71691500	-0.89635600
H	2.53057800	0.97964500	-2.24527800
H	5.16429100	-0.02169000	-1.06239300
O	0.71294700	0.49318500	2.16314200
C	0.10805900	-0.06388100	3.35165300
H	0.02129200	-1.15145100	3.22948900
H	-0.89772000	0.35546900	3.45325200
C	1.04605900	0.30062700	4.50385100
H	0.81408400	1.30226500	4.88539500
H	0.97677900	-0.40471100	5.33734500
C	2.41705600	0.29401400	3.80954500
H	2.78973100	-0.73220800	3.71233400
H	3.17409100	0.88051600	4.33879300
C	2.08753700	0.87507200	2.43263800
H	2.14468700	1.97273900	2.44015600
H	2.71140500	0.48431600	1.62240300
O	-0.42207000	2.24632700	-0.47570100
C	-0.48686100	3.36964600	0.41340900
H	-0.14553700	3.02434200	1.39156900
H	-1.53134500	3.70344700	0.49855300
C	0.39726500	4.46385500	-0.22599400
H	-0.07877700	5.44628400	-0.15219100
H	1.36866100	4.53092600	0.27255600
C	0.56170700	3.99763600	-1.69962900
H	1.59286100	3.68733300	-1.89150100
H	0.30637200	4.77876400	-2.42179800
C	-0.38071500	2.78975500	-1.80412400
H	-1.39473600	3.09468800	-2.10356700
H	-0.03456000	1.99455900	-2.46732900
O	-1.94331000	-1.33467200	-0.03660300
C	-1.08554900	-2.43441200	-0.38043000
C	-0.15051800	-2.29414200	-1.36899800
C	0.16882300	-1.16930600	-2.18959500
H	-0.65200700	-0.48332200	-2.42271700
H	0.79522100	-1.37322800	-3.05688300
H	0.50119500	-3.16793000	-1.46055400
H	-1.16778300	-3.28938800	0.28148000

Si	-3.58715300	-1.52646400	-0.39027000
C	-4.23676300	-3.07017200	0.49119700
H	-5.30478900	-3.22565300	0.29745800
H	-3.70554600	-3.96110800	0.13816100
H	-4.09822300	-3.00992500	1.57713000
C	-4.45029500	0.04875000	0.29253600
C	-4.09139600	0.24805500	1.78019600
H	-3.01089500	0.37139900	1.91907100
H	-4.58667700	1.14600100	2.18000400
H	-4.41016600	-0.60141100	2.39682500
C	-5.98201200	-0.10123700	0.16287900
H	-6.48826400	0.80277400	0.53310500
H	-6.29445900	-0.24281700	-0.87945200
H	-6.36403700	-0.94867500	0.74469000
C	-4.00840700	1.29761200	-0.50027200
H	-4.28191400	1.22426700	-1.55996200
H	-4.50126900	2.19708700	-0.09975300
H	-2.92566800	1.45889300	-0.44427000
C	-3.83991100	-1.71803600	-2.24982000
H	-4.88045200	-1.95912000	-2.49977200
H	-3.55801500	-0.81325200	-2.79870800
H	-3.20511500	-2.53270500	-2.61500000
H	2.44081500	-1.08079400	-0.96824800

Table S-18. Geometric coordinates and thermally corrected MP2 energies for pro-*E* [A(THF)$_2$·(allyloxy-*tert*-butyldimethylsilane)]‡.

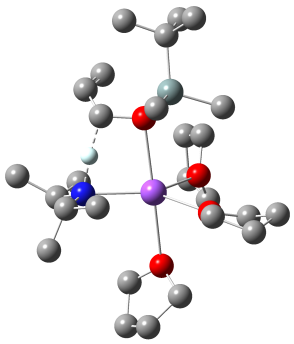


G = –1638.147473 Hartree
G_{MP2} = –1633.054489 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	1.15685700	2.04165700	-0.21493200
C	1.58614600	2.49530000	-1.54376200
C	3.11026600	2.47569400	-1.76085800
H	3.35615300	2.75926200	-2.79228600
H	3.51217000	1.46941900	-1.57910600
H	3.63618400	3.16955100	-1.09724100
C	0.91334500	1.61967500	-2.61296200
H	1.12964700	1.99083800	-3.62269700
H	-0.17380800	1.60078500	-2.48602600
H	1.28451900	0.58644900	-2.54858400
H	1.25535700	3.53546800	-1.73872900
C	1.79085500	2.74548900	0.90978600
C	1.53011200	4.26777600	0.95165800
H	2.06105200	4.73088600	1.79388600
H	0.45951100	4.47563700	1.06739000
H	1.87515000	4.76268200	0.03668800
C	1.33002500	2.10954500	2.23026500
H	1.82722100	2.57953000	3.08796200
H	1.56000600	1.03605700	2.25255600
H	0.24899400	2.23601100	2.36414800
H	2.88509200	2.60783500	0.86228600
O	1.37557100	-1.78082600	-0.78033300
C	1.27897500	-2.63562300	-1.94270700
H	0.91236000	-2.03793700	-2.78689900
H	0.54989700	-3.42514100	-1.73372100
C	2.69365600	-3.16324700	-2.20056600
H	2.87101300	-4.08356700	-1.63155900
H	2.87007600	-3.37974600	-3.25826100
C	3.56659900	-2.02154700	-1.65674700
H	3.63616900	-1.20796100	-2.38778800
H	4.58183500	-2.33695500	-1.39858000
C	2.76694100	-1.56891600	-0.43546900
H	3.00755600	-2.17571100	0.44879900
H	2.89017700	-0.51043800	-0.18902200
O	-0.44470600	-1.19871100	1.96518000
C	0.13880900	-2.44964300	2.36753400
H	1.08012700	-2.26547900	2.90785000
H	0.36051000	-3.01380600	1.45873200
C	-0.90231200	-3.08931400	3.28231300
H	-1.69642500	-3.55045100	2.68382800
H	-0.47795100	-3.85335100	3.94070900
C	-1.43529600	-1.86199700	4.04118000
H	-0.77897000	-1.62602700	4.88641400
H	-2.44639100	-2.00414100	4.43329100
C	-1.37333100	-0.74667400	2.98206000
H	-2.33715800	-0.57783800	2.49164700
H	-1.01761800	0.20525500	3.38933900
O	-2.03177400	0.96590200	-0.49066900
C	-1.59707700	2.37416600	-0.22308700
C	-2.20406600	2.93327700	0.98088500
C	-2.52109200	4.22518900	1.21761500
H	-2.45682900	4.98178000	0.43766500
H	-2.81807800	4.56875900	2.20459200
H	-2.31045900	2.22731800	1.81119800
H	-1.80203800	2.97377500	-1.11934500

Si	-3.58669300	0.65335700	-1.06617200
C	-3.94583700	1.73079200	-2.57956900
H	-4.91988800	1.48617800	-3.01998900
H	-3.96773900	2.79094900	-2.30428000
H	-3.18402100	1.60787200	-3.35832400
C	-3.60986000	-1.21005400	-1.55623800
C	-2.53309400	-1.49758400	-2.62294400
H	-1.52547600	-1.25720400	-2.26354800
H	-2.54080500	-2.56177700	-2.90448300
H	-2.69936300	-0.91688200	-3.53833000
C	-4.99173700	-1.57734000	-2.14123500
H	-5.02048900	-2.64183600	-2.41815300
H	-5.80183800	-1.40827500	-1.42135900
H	-5.22275600	-1.00118300	-3.04526100
C	-3.35002500	-2.10076600	-0.32240300
H	-4.12843500	-1.97174500	0.43979000
H	-3.35047200	-3.16392800	-0.60913600
H	-2.38465800	-1.88637800	0.15189400
C	-4.89784700	0.99862000	0.25320600
H	-5.91031600	0.84313700	-0.13997700
H	-4.77929200	0.35474300	1.13290000
H	-4.82149900	2.03692600	0.59270100
H	-0.12961200	2.28374600	-0.16058100

Table S-19. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* [A(THF)$_3$·(allyloxy-*tert*-butyldimethylsilane)]‡.

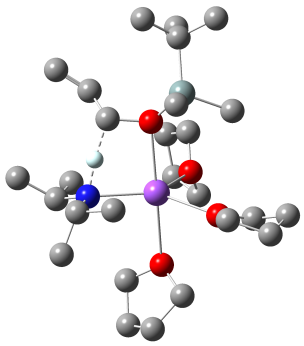


G = –1870.485032 Hartree
G_{MP2} = –1864.62615 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-0.22669800	-2.06796000	-1.20570800
C	-0.42094400	-1.98669100	-2.65846700
C	-1.85971700	-2.25647200	-3.13636600
H	-1.93771600	-2.10788600	-4.22118600
H	-2.56197400	-1.56711300	-2.64817500
H	-2.18924800	-3.27833600	-2.92276000
C	0.00918200	-0.59318000	-3.13703300
H	-0.00555700	-0.52312900	-4.23219000
H	1.02182100	-0.35769900	-2.79697600
H	-0.67668900	0.17125700	-2.74284300
H	0.22687800	-2.71316800	-3.19187900
C	-0.73031100	-3.30679200	-0.59455100
C	-0.12348800	-4.61189600	-1.16012900
H	-0.57837400	-5.49001000	-0.68349300
H	0.95540000	-4.65085800	-0.97819600
H	-0.28594000	-4.70341500	-2.23984400
C	-0.51812100	-3.25861000	0.92603700
H	-0.94126800	-4.15008100	1.40678900
H	-1.01084500	-2.37950700	1.36226500
H	0.54846500	-3.21456400	1.17473700
H	-1.82240400	-3.37894900	-0.75254100
O	0.22166700	0.54629600	2.32668200
C	-0.84231100	0.53522000	3.28938700
H	-1.77809800	0.47845100	2.73133100
H	-0.82138000	1.47680100	3.86116500
C	-0.55188800	-0.66935700	4.20390200
H	-0.85056900	-0.46894200	5.23748000
H	-1.09959200	-1.55350300	3.86478900
C	0.98066400	-0.88582800	4.05320600
H	1.19515900	-1.87591000	3.64244500
H	1.51296400	-0.79515200	5.00487400
C	1.41150700	0.20887700	3.06038800
H	1.77356200	1.10541300	3.58739700
H	2.15814000	-0.10857100	2.33235600
O	-0.10688200	2.43050300	-0.54664300
C	-0.28779900	3.39142900	0.52078300
H	0.27294700	3.03635500	1.38790100
H	-1.35341700	3.42644300	0.78459400
C	0.19051100	4.73243000	-0.03868100
H	-0.29851500	5.58448400	0.44313400
H	1.27306100	4.83879100	0.09490600
C	-0.15427900	4.59453600	-1.53021100
H	0.42506700	5.26216400	-2.17474300
H	-1.21844700	4.80040000	-1.69731800
C	0.15643900	3.11856300	-1.79040600
H	-0.46440100	2.66893100	-2.57126300
H	1.21019200	2.97178600	-2.05639500
O	2.58521300	-0.49011300	-0.26933800
C	2.50901300	-1.84018200	-0.85300000
C	3.05587000	-2.89236900	-0.01641400
C	3.29923300	-2.92384900	1.31497200
H	3.19239300	-2.04270800	1.93964600
H	3.62180400	-3.83612200	1.80821100
H	3.19037400	-3.82796300	-0.56809800
H	2.95050900	-1.83650800	-1.85872400

Si	3.81981900	0.58642700	-0.67693100
C	3.70754700	0.98177200	-2.53171100
H	4.39896900	1.78489100	-2.81314400
H	3.94303200	0.11211100	-3.15554300
H	2.69507300	1.30609500	-2.79840800
C	3.39395700	2.14630000	0.30842500
H	3.56298700	2.00807200	1.38231500
H	3.98828800	3.00905800	-0.01490200
H	2.33558100	2.38673200	0.16583400
C	5.63463400	0.05620200	-0.27866900
C	5.83215800	-0.20379400	1.22952400
H	5.23316600	-1.05346300	1.57012300
H	6.88767300	-0.43532700	1.43778900
H	5.56935000	0.67170900	1.83741400
C	6.56551200	1.22123700	-0.69600900
H	7.60979200	0.96242300	-0.46766400
H	6.51418800	1.43235800	-1.77088400
H	6.33938100	2.15080800	-0.15876300
C	6.05747400	-1.20600400	-1.06058500
H	5.47576300	-2.08006800	-0.75451100
H	5.94198400	-1.07771400	-2.14419100
H	7.11921000	-1.42720100	-0.87225400
O	-2.60192100	0.37804500	0.38193300
C	-3.33298500	1.45353500	-0.22547700
H	-2.61320900	2.06812500	-0.76975300
H	-3.81120900	2.07038700	0.55272100
C	-4.38269800	0.78105700	-1.10735900
H	-5.22884900	1.43627900	-1.33708700
H	-3.93026800	0.45729500	-2.05149900
C	-4.77106500	-0.43347600	-0.24791700
H	-5.16791400	-1.26599500	-0.83600000
H	-5.53345800	-0.14879400	0.48649600
C	-3.44790300	-0.79633100	0.45082300
H	-3.59410600	-1.06976900	1.50294400
H	-2.91727300	-1.60733800	-0.05252800
H	1.08721900	-2.04639600	-1.04236700

Table S-20. Geometric coordinates and thermally corrected MP2 energies for pro-*E* [A(THF)$_3$·(allyloxy-*tert*-butyldimethylsilane)]‡.

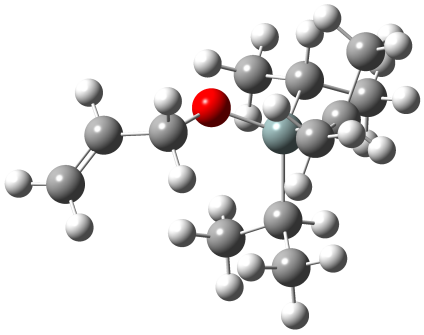


G = –1870.484508 Hartree
G_{MP2} = –1864.62501 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-0.20162000	-2.14573100	-1.07431100
C	-0.40993100	-2.15307700	-2.52796400
C	-1.85352700	-2.46050700	-2.96474400
H	-1.95092000	-2.38139600	-4.05522100
H	-2.55133400	-1.74516500	-2.50822300
H	-2.17299100	-3.46879400	-2.68177000
C	0.00580800	-0.78896600	-3.09744500
H	-0.01943700	-0.79146400	-4.19456800
H	1.01959400	-0.52199300	-2.78323000
H	-0.68303600	-0.00473600	-2.75030700
H	0.23611600	-2.90719300	-3.02080200
C	-0.64064500	-3.37265800	-0.39118400
C	0.02167500	-4.67753000	-0.88802200
H	-0.38114800	-5.54388900	-0.34672100
H	1.10610000	-4.65039200	-0.72933200
H	-0.16281300	-4.84660800	-1.95492700
C	-0.40404900	-3.22388200	1.11983500
H	-0.78223500	-4.09833000	1.66427600
H	-0.91258600	-2.33487600	1.51374800
H	0.66532500	-3.13226900	1.33690600
H	-1.72991400	-3.50194100	-0.52739100
O	0.27416200	0.61823700	2.29480900
C	-0.75736800	0.77402200	3.27944900
H	-1.71140100	0.72995200	2.75209700
H	-0.65396400	1.76115900	3.75729900
C	-0.52529600	-0.35637200	4.30182800
H	-0.74408900	-0.02360400	5.32113800
H	-1.17031200	-1.21378200	4.08838900
C	0.97052200	-0.73344300	4.10449000
H	1.06388000	-1.76484500	3.75337000
H	1.55390100	-0.64040800	5.02536000
C	1.45624600	0.24863700	3.02414700
H	1.89589900	1.15094400	3.47718700
H	2.16033600	-0.17123200	2.30540100
O	-0.26186300	2.36685400	-0.73986800
C	-0.46205400	3.38603000	0.26709600
H	0.10445200	3.09312700	1.15422800
H	-1.52871000	3.42102900	0.52686300
C	-0.00144200	4.69806000	-0.36958900
H	-0.50076900	5.57044500	0.06278000
H	1.07958600	4.82459700	-0.24388800
C	-0.34692800	4.47015200	-1.84965600
H	0.22703700	5.10321600	-2.53265600
H	-1.41245900	4.65929400	-2.02678200
C	-0.02726200	2.98277800	-2.02711400
H	-0.65872200	2.48454300	-2.76893400
H	1.02262400	2.82564400	-2.30312100
O	2.51881500	-0.37616200	-0.27180000
C	2.51822000	-1.78499500	-0.75428700
C	3.15118700	-2.70199000	0.18067200
C	3.77807400	-3.86980100	-0.09360200
H	3.98293700	-4.18254000	-1.11597800
H	4.07106800	-4.55881200	0.69349600
H	2.99060300	-2.45529400	1.23528700
H	2.95474500	-1.82350600	-1.76144300

Si	3.76950400	0.69024500	-0.64303800
C	3.86500700	0.92204500	-2.52354400
H	4.64224100	1.64358300	-2.80358000
H	4.08563600	-0.01748000	-3.04183800
H	2.90967700	1.29383100	-2.91440400
C	3.21183100	2.32080700	0.14442600
H	3.33046900	2.31543800	1.23440400
H	3.77406500	3.17661300	-0.24749800
H	2.15105500	2.47656100	-0.07368800
C	5.51735800	0.23450000	0.03445500
C	5.44168900	-0.18888000	1.51624000
H	4.88454600	-1.12247400	1.63617100
H	6.45281400	-0.35140600	1.91884200
H	4.96489100	0.57841300	2.14072600
C	6.40713700	1.49732300	-0.06787000
H	7.42473600	1.26577200	0.27962100
H	6.49530700	1.86328900	-1.09878000
H	6.03306900	2.32249400	0.54989500
C	6.18764700	-0.89537700	-0.77735300
H	5.63392000	-1.83685800	-0.70471500
H	6.28563600	-0.63249400	-1.83800500
H	7.20367200	-1.07953000	-0.39581200
O	-2.61978600	0.30906400	0.50089300
C	-3.39371800	1.27980000	-0.22765900
H	-2.72322600	1.77413500	-0.93426600
H	-3.78631700	2.03367400	0.47248300
C	-4.53342200	0.50075700	-0.88411300
H	-5.40299400	1.12825900	-1.10299100
H	-4.19292000	0.04468400	-1.82078900
C	-4.81030800	-0.58248900	0.16933300
H	-5.30953100	-1.46654700	-0.23803600
H	-5.43799200	-0.17893200	0.97295100
C	-3.40107300	-0.89713000	0.68529400
H	-3.38407700	-1.16400600	1.74792400
H	-2.92418900	-1.69869000	0.11391000
H	1.07936400	-2.06226400	-0.91498600

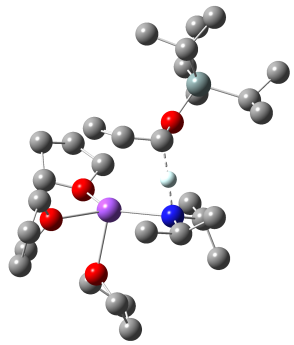
Table S-21. Geometric coordinates and thermally corrected MP2 energies for allyloxytriisopropylsilane.



G = –837.366923 Hartree
G_{MP2} = –834.8750592 Hartree

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.14497500	0.40850000	1.00933000
H	0.04571700	0.85558200	-0.69123900
C	-1.16098100	-0.88232700	-0.36627100
H	-1.03415900	-1.44960500	-1.28801500
C	-2.28862300	-0.97906500	0.33789900
H	-2.43453400	-0.42527300	1.26363400
H	-3.11425200	-1.60765600	0.01543100
O	1.21846000	-0.72650100	-0.11490300
Si	2.52198800	-0.81371000	0.94471300
C	3.62804500	-2.15119100	0.14728700
H	3.98183300	-1.67897200	-0.78182000
C	4.86992400	-2.49269500	0.99494500
H	4.59042300	-2.99908800	1.92765800
H	5.54093200	-3.17105600	0.45092700
H	5.45487600	-1.60510300	1.26636000
C	2.88166200	-3.43391900	-0.26585200
H	1.98192200	-3.20865500	-0.84633400
H	3.52866800	-4.07851700	-0.87689600
H	2.57772300	-4.02411800	0.60700000
C	1.98258100	-1.31814600	2.71929200
H	2.90159600	-1.74615800	3.15382300
C	1.55871300	-0.16201700	3.64706300
H	0.63521300	0.32047400	3.30269000
H	1.36279200	-0.53448100	4.66198600
H	2.32858200	0.61268700	3.72530300
C	0.91059600	-2.42756800	2.73202300
H	1.23077200	-3.32090700	2.18684600
H	0.68332100	-2.73392900	3.76259500
H	-0.02621600	-2.09044200	2.27403800
C	3.47109300	0.85823300	0.98917700
H	4.08028200	0.83759000	1.90788800
C	4.43402100	1.03913600	-0.20167300
H	4.94281300	2.01129600	-0.14498300
H	5.20863000	0.26629100	-0.23529400
H	3.89611300	1.01110600	-1.15785400
C	2.54178000	2.08773600	1.07786700
H	3.12878800	3.00900300	1.19499000
H	1.95119500	2.19907500	0.16063100
H	1.84228000	2.03787100	1.91864600

Table S-22. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* μ-allyl [A(THF)$_3$·(allyloxytriisopropylsilane)]‡.

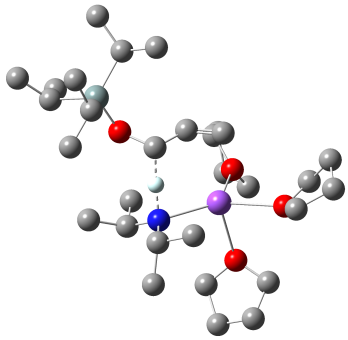


G = –1988.359903 Hartree
G_{MP2} = –1982.055175 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	-1.06450500	2.18843700	-0.07206800
C	-1.65303500	2.67678500	-1.32825800
C	-0.80782200	3.71822400	-2.08673100
H	-1.29845800	3.99002300	-3.03004100
H	0.18347200	3.31266400	-2.32865000
H	-0.66282700	4.64296900	-1.51842000
C	-1.92227200	1.48061000	-2.25011600
H	-2.45682400	1.79215000	-3.15711100
H	-2.53238200	0.73415200	-1.73349500
H	-0.97554900	1.01641900	-2.56388600
H	-2.63692400	3.15525400	-1.14603200
C	-0.63768300	3.25622500	0.84362800
C	-1.76423500	4.20514300	1.31608000
H	-1.36478800	4.99794300	1.96238000
H	-2.52445600	3.65683500	1.88451500
H	-2.26671800	4.69056500	0.47250100
C	0.05795600	2.64172800	2.06832800
H	0.43418900	3.42310300	2.74073600
H	0.90864600	2.01692100	1.76703400
H	-0.63525300	2.01546200	2.64198500
H	0.11993900	3.89403000	0.35205800
O	2.11918100	0.44757800	-1.24252000
C	2.42403900	-0.12520600	-2.52471100
H	1.67044900	-0.89095400	-2.71793300
H	3.41989900	-0.59649600	-2.49833900
C	2.40340200	1.05691900	-3.49061000
H	2.94910200	0.85932800	-4.41856600
H	1.36900600	1.31231100	-3.74517000
C	3.04318500	2.16922400	-2.63912700
H	2.70494600	3.16897100	-2.92613100
H	4.13422600	2.14524400	-2.73835700
C	2.61911800	1.80513300	-1.20039100
H	3.46086000	1.85773000	-0.49772900
H	1.80429400	2.42941200	-0.82496400
O	1.52787900	-0.92269000	1.68086600
C	2.93640900	-1.13898900	1.51649400
H	3.20898000	-0.73148800	0.54305000
H	3.14170400	-2.22140200	1.52912600
C	3.59788600	-0.44256500	2.72031800
H	4.48781200	-0.98215200	3.05819400
H	3.90704200	0.57365300	2.45762800
C	2.47156200	-0.41348400	3.79170500
H	2.22941500	0.61579200	4.07115600
H	2.74582100	-0.94961100	4.70516400
C	1.27647400	-1.08059400	3.08410800
H	1.22088600	-2.15326500	3.32485900
H	0.31076800	-0.62238800	3.29971700
O	-0.18652800	-1.94592500	-1.43218200
C	0.32567900	-3.17790300	-0.87629000
H	0.57976000	-2.99525400	0.17145600
H	1.23997600	-3.45538500	-1.42026800
C	-0.77791200	-4.21982500	-1.07066100
H	-0.38340600	-5.23790800	-1.14472300
H	-1.48360600	-4.18425400	-0.23384500
C	-1.45360400	-3.73174900	-2.36148000

H -2.48094000 -4.09027300 -2.47448200
H -0.88197700 -4.05599200 -3.23953500
C -1.38499500 -2.21103700 -2.20254800
H -1.30417300 -1.67547200 -3.15323500
H -2.24660400 -1.81855800 -1.65130500
C -3.07793300 0.70374900 1.16163000
C -2.36632900 -0.30758700 1.91810500
C -2.09337600 -1.59453100 1.57490800
H -2.56586900 -2.05034300 0.71006800
H -1.47938600 -2.23336500 2.20365500
H -1.90498700 0.08265500 2.83078800
H -3.64359200 1.38633400 1.80897700
O -3.89622400 0.15563600 0.10571500
Si -5.57171300 0.13076900 0.01826300
C -6.28957100 -0.25932600 1.75429800
H -5.74943700 0.43135700 2.42093200
C -7.79390500 0.02226800 1.93814200
H -8.10232200 -0.19142000 2.97158800
H -8.05138500 1.06691900 1.73287900
H -8.41445200 -0.60374600 1.28520100
C -5.94409200 -1.68743000 2.22455000
H -4.86751600 -1.88092900 2.18225400
H -6.27186400 -1.84323400 3.26248700
H -6.44837500 -2.44678000 1.61299000
C -5.90830300 -1.27014100 -1.24897400
H -5.27956000 -2.09393600 -0.87530300
C -7.35529700 -1.79563100 -1.30795800
H -8.05855800 -1.02859900 -1.65290700
H -7.43375700 -2.63933100 -2.00872600
H -7.70742500 -2.14897700 -0.33311700
C -5.40431200 -0.92084300 -2.66328200
H -4.35881700 -0.59505200 -2.65668600
H -5.48278700 -1.78856700 -3.33463500
H -5.99575200 -0.11423300 -3.11462500
C -6.13911400 1.84135500 -0.64762400
H -5.44429100 2.01907600 -1.48394500
C -7.56713200 1.90703600 -1.22363700
H -7.77440200 2.90706900 -1.63086100
H -7.71895300 1.18845200 -2.03639700
H -8.33107000 1.70813500 -0.46249300
C -5.91367600 2.98085800 0.36662000
H -4.87399600 3.02531400 0.70692700
H -6.15441000 3.95570600 -0.08096700
H -6.55096900 2.86922500 1.25318100
H -2.06055800 1.50717800 0.55105000

Table S-23. Geometric coordinates and thermally corrected MP2 energies for pro-*E* μ-allyl [A(THF)$_3$·(allyloxytriisopropylsilane)]‡.

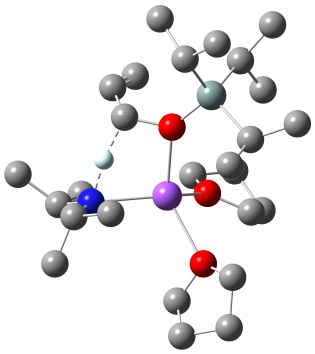


G = –1988.358474 Hartree
G_{MP2} = –1982.051409 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	1.46349800	-1.93113800	-0.13205900
C	1.42315300	-2.72814500	-1.36366800
C	0.53683900	-3.98571700	-1.28854100
H	0.53001300	-4.51191600	-2.25187800
H	-0.49851400	-3.71041100	-1.04575500
H	0.88350300	-4.69520400	-0.53034000
C	0.93251500	-1.84174700	-2.51780800
H	1.00023200	-2.36568600	-3.47977100
H	1.52410200	-0.92314700	-2.59099100
H	-0.12049700	-1.56238100	-2.36547500
H	2.43689100	-3.07699800	-1.64808100
C	1.83554000	-2.69092600	1.07194800
C	3.18672300	-3.43497000	0.98727600
H	3.39235000	-3.97229500	1.92261300
H	3.99783800	-2.72018700	0.81157700
H	3.19648500	-4.17468400	0.17870500
C	1.86070900	-1.73644900	2.27580900
H	2.07401700	-2.27990000	3.20497900
H	0.89613200	-1.22570900	2.39930500
H	2.64162700	-0.97885400	2.14224600
H	1.06640500	-3.45712400	1.28938000
O	-2.13747300	-1.10162300	0.71465300
C	-3.37143600	-1.03697700	-0.01502400
H	-3.23895700	-0.28563100	-0.79544200
H	-4.19066600	-0.72645100	0.65416900
C	-3.58921500	-2.46143500	-0.52098800
H	-4.62972000	-2.66462700	-0.79305600
H	-2.96138700	-2.64283400	-1.40042000
C	-3.10341500	-3.30254600	0.67641700
H	-2.67935200	-4.26240900	0.36864500
H	-3.93305700	-3.51016500	1.36097000
C	-2.05041500	-2.39576400	1.35480500
H	-2.24437000	-2.28132500	2.42950000
H	-1.02626300	-2.74595300	1.21489300
O	-0.33149800	1.47722300	1.91415300
C	-1.52419300	1.47838400	2.72204900
H	-2.09728100	0.59024200	2.45015300
H	-2.12322800	2.37431700	2.49462600
C	-1.02523300	1.51100700	4.16451300
H	-1.77971400	1.87787500	4.86724900
H	-0.71740700	0.50760300	4.48100800
C	0.19425000	2.43963700	4.04286100
H	0.93155400	2.29207300	4.83722500
H	-0.12486900	3.48798600	4.07240300
C	0.75629300	2.08158000	2.65709400
H	1.12096500	2.95529100	2.10641000
H	1.56532500	1.34722600	2.71761600
O	-1.49850700	1.25429200	-1.54391200
C	-1.83269100	2.58014100	-1.07684300
H	-1.24202100	2.77491100	-0.17806800
H	-2.90022700	2.60577800	-0.81313700
C	-1.52753300	3.51966200	-2.24311200
H	-2.11467500	4.44227000	-2.20446600
H	-0.46491400	3.78621100	-2.24719100
C	-1.86284900	2.63397300	-3.45318200

H	-1.36978600	2.95459500	-4.37553100
H	-2.94462800	2.62559800	-3.63242400
C	-1.38104600	1.25613500	-2.98578700
H	-1.97908100	0.42955700	-3.38382400
H	-0.33072700	1.08433400	-3.24713200
C	3.46652300	-0.07120600	-0.58408700
C	2.81721500	1.19144400	-0.31039600
C	1.92838300	1.87677800	-1.08582300
H	1.76806000	1.62433300	-2.13283600
H	1.43272800	2.77160900	-0.71860900
H	2.97260400	1.55367200	0.70969500
O	4.58947000	-0.35755500	0.27616500
Si	6.20723300	0.00106300	0.01338400
C	6.69989700	-0.69149800	-1.70642000
H	5.97090500	-0.23336600	-2.39468400
C	8.10079700	-0.30239800	-2.21811000
H	8.26939400	-0.70147800	-3.22865700
H	8.23862000	0.78319800	-2.27063400
H	8.89720600	-0.70360000	-1.58003700
C	6.49741100	-2.21787400	-1.78632800
H	5.48489500	-2.51219800	-1.48991200
H	6.66776600	-2.58353800	-2.80901200
H	7.20010200	-2.75083700	-1.13285000
C	7.02042800	-0.95474700	1.46007000
H	6.56084100	-1.95172100	1.37483400
C	8.54646500	-1.15174400	1.39851200
H	9.09041000	-0.20079500	1.44049800
H	8.89312600	-1.75670500	2.24865400
H	8.86001900	-1.66872800	0.48478100
C	6.59239800	-0.38458100	2.82685600
H	5.50272300	-0.30863300	2.90318100
H	6.94332900	-1.02584400	3.64805900
H	7.01120000	0.61550600	2.99885600
C	6.48900400	1.90201800	0.12111200
H	5.84301000	2.20924600	0.95915700
C	7.92482800	2.33778700	0.47623000
H	7.98854100	3.43306300	0.55004000
H	8.25932800	1.92718000	1.43474400
H	8.65018900	2.02732200	-0.28554400
C	5.99627900	2.65906600	-1.12941000
H	4.94434600	2.45096500	-1.34870500
H	6.09666200	3.74542300	-0.98965300
H	6.58441000	2.39650600	-2.01778000
H	2.46580800	-1.04442400	-0.32571400
H	3.71884200	-0.23236700	-1.64075300

Table S-24. Geometric coordinates and thermally corrected MP2 energies for pro-*Z* κ-O [A(THF)$_2$·(allyloxytriisopropylsilane)]‡.

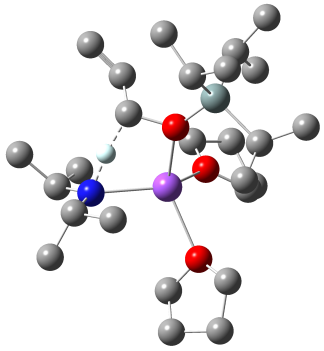


G = –1756.012449 Hartree
G_{MP2} = –1750.479449 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	0.87448200	-2.13517900	-0.55844800
C	1.08164000	-3.22808500	0.39771000
C	2.55508900	-3.47444300	0.77677400
H	2.62940600	-4.25271200	1.54726300
H	3.00784300	-2.55592700	1.17469000
H	3.15908500	-3.80190200	-0.07552700
C	0.27704400	-2.94149900	1.67234400
H	0.35523300	-3.77020600	2.38734100
H	-0.78129600	-2.79065600	1.44242100
H	0.65261300	-2.03294600	2.16365300
H	0.70015800	-4.19130000	0.00012100
C	1.61956400	-2.29133100	-1.81652000
C	1.22438000	-3.52889300	-2.65364100
H	1.84647600	-3.60820200	-3.55469800
H	0.17711800	-3.46781300	-2.97026300
H	1.34941300	-4.45775700	-2.08627600
C	1.47800600	-1.02030300	-2.66619600
H	2.04646000	-1.10581300	-3.60100400
H	1.86690800	-0.14853100	-2.12178400
H	0.42969300	-0.83110600	-2.92955600
H	2.69698200	-2.38965200	-1.59784300
O	1.26476600	0.92781200	1.79440800
C	0.98433300	1.09877300	3.20225400
H	0.41744500	0.22826000	3.55386900
H	0.36302500	1.99205500	3.32662600
C	2.34590000	1.20429200	3.89694400
H	2.68691900	2.24615200	3.92065200
H	2.31694700	0.83429300	4.92603500
C	3.24465600	0.36792300	2.97264000
H	3.11957500	-0.70115600	3.17893600
H	4.30722700	0.61192000	3.06381800
C	2.68168900	0.70947100	1.59343700
H	3.12894700	1.63041800	1.19310200
H	2.79328800	-0.09242500	0.85782200
O	0.06173700	2.12957600	-1.03265500
C	0.10521300	3.36367700	-0.28055600
H	0.87586500	3.27008700	0.48975100
H	-0.86639900	3.50065800	0.21197400
C	0.37575400	4.47530600	-1.30016200
H	-0.06466800	5.43082400	-1.00009400
H	1.45414100	4.62525800	-1.43084900
C	-0.24096200	3.89332800	-2.58196600
H	0.15827700	4.34019100	-3.49735000
H	-1.32877700	4.02827600	-2.58012200
C	0.11255300	2.41282400	-2.45123600
H	-0.58239000	1.73533700	-2.95305100
H	1.12733400	2.21076400	-2.81948900
O	-2.17910200	-0.77974200	-0.08128600
C	-1.87590500	-1.92324600	-0.95870500
C	-2.21742700	-1.73112400	-2.35939300
C	-2.45545100	-0.59690300	-3.05794100
H	-2.52628000	0.37084100	-2.57184200
H	-2.60644200	-0.61911000	-4.13330000
H	-2.16972900	-2.66576800	-2.92627900
H	-2.32318100	-2.83174300	-0.53807700

Si	-3.68351700	-0.38099500	0.60023800
C	-4.74355300	-1.96894100	0.78487700
H	-4.02325300	-2.74072000	1.09970700
C	-5.83052200	-1.89106600	1.87665100
H	-6.37708700	-2.84231200	1.94155400
H	-5.41656300	-1.68641600	2.86931000
H	-6.57086500	-1.11168500	1.66094600
C	-5.36919100	-2.44293900	-0.54474100
H	-4.63322200	-2.51626900	-1.35036300
H	-5.83567300	-3.43014900	-0.41977700
H	-6.15621700	-1.75763100	-0.88239200
C	-3.15741500	0.36986800	2.29087900
H	-2.33138300	1.04865800	2.01552900
C	-4.21388400	1.22619800	3.01606300
H	-3.80586500	1.63371800	3.95219500
H	-4.54672600	2.07471600	2.40988600
H	-5.10345100	0.64365500	3.28287600
C	-2.56999700	-0.68243600	3.25148500
H	-1.77460800	-1.26759400	2.78068700
H	-2.15167500	-0.20446200	4.14930600
H	-3.33589400	-1.38721600	3.59621400
C	-4.54817300	0.93153300	-0.50222600
H	-4.54939500	0.46394200	-1.49676600
C	-6.01353100	1.26177700	-0.15321700
H	-6.42981000	1.97160000	-0.88210100
H	-6.65438700	0.37403200	-0.16619400
H	-6.11305100	1.72509100	0.83529000
C	-3.71849900	2.22693300	-0.61012500
H	-3.71187000	2.77989900	0.33860800
H	-2.67648000	2.02540700	-0.88299900
H	-4.13985300	2.90088700	-1.36987400
H	-0.44923900	-2.11564600	-0.82782600

Table S-25. Geometric coordinates and thermally corrected MP2 energies for pro-*E* κ-O [A(THF)$_2$·(allyloxytriisopropylsilane)]‡.

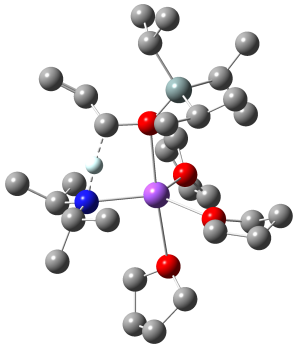


G = –1756.011312 Hartree
G_{MP2} = –1750.477393 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	0.77602100	2.23156000	0.21075300
C	0.90250800	3.13123400	-0.94285000
C	2.35338700	3.49068200	-1.31325700
H	2.37757300	4.09809000	-2.22711500
H	2.94215600	2.58058900	-1.49307700
H	2.85664400	4.06411800	-0.52813200
C	0.21455200	2.48964000	-2.15696600
H	0.21181400	3.17088500	-3.01715400
H	-0.82242800	2.22507500	-1.92938500
H	0.74347500	1.57282600	-2.45424500
H	0.37991600	4.09225400	-0.76055400
C	1.44822100	2.70651900	1.42938100
C	0.89768400	4.03189800	2.00106400
H	1.47580000	4.34702000	2.87986100
H	-0.15009500	3.91943300	2.30467100
H	0.95365600	4.84242500	1.26565500
C	1.37588300	1.61183800	2.50370600
H	1.88979200	1.92154100	3.42223100
H	1.84981200	0.68682800	2.14791400
H	0.33338100	1.39411000	2.76593200
H	2.51964000	2.86729900	1.22067300
O	1.46155100	-1.18541400	-1.45923900
C	1.27603700	-1.65545800	-2.81438500
H	0.65325800	-0.93134700	-3.35340900
H	0.74546000	-2.61283900	-2.77923500
C	2.67772200	-1.75853100	-3.42371800
H	3.11430100	-2.74400100	-3.22248100
H	2.67154500	-1.60589200	-4.50695500
C	3.44220200	-0.66709700	-2.65820000
H	3.23102500	0.32064700	-3.08341200
H	4.52616900	-0.81501700	-2.65932900
C	2.83858000	-0.78006400	-1.25859000
H	3.34870000	-1.54856900	-0.66107600
H	2.82954100	0.16214600	-0.70288300
O	0.02070100	-1.82838700	1.51237200
C	0.17495900	-3.17655800	1.02084800
H	0.84924200	-3.13771100	0.16175300
H	-0.80344800	-3.55333900	0.68963900
C	0.70246100	-3.98333100	2.20607500
H	0.48326900	-5.05177400	2.11916600
H	1.78842100	-3.86207500	2.29854800
C	-0.01907800	-3.30723400	3.38259200
H	0.47915400	-3.46065600	4.34427500
H	-1.04353800	-3.68757100	3.46738700
C	-0.02575600	-1.83307300	2.96047100
H	-0.92309600	-1.29599700	3.28242900
H	0.85427000	-1.29638600	3.33231400
O	-2.19388300	0.67042500	-0.16534600
C	-1.96244700	1.94027000	0.57554500
C	-2.43635000	1.89158400	1.95487900
C	-2.89067000	2.91796300	2.70834300
H	-3.05880300	3.90685900	2.28575500
H	-3.07384000	2.80746100	3.77345800
H	-2.30422300	0.92392800	2.45090900
H	-2.40043800	2.76500900	-0.00053100

Si	-3.70627800	0.09489600	-0.66598000
C	-4.73968800	1.54519000	-1.38533400
H	-3.98944600	2.16450000	-1.90324100
C	-5.79055200	1.12829800	-2.43566600
H	-6.31170400	2.01286100	-2.82782200
H	-5.35007900	0.60557900	-3.29091100
H	-6.55781700	0.47142900	-2.00705100
C	-5.40583900	2.43447200	-0.31335100
H	-4.70904200	2.75956300	0.46374700
H	-5.83988200	3.33121200	-0.77749800
H	-6.22676400	1.90684700	0.18798700
C	-3.18445400	-1.18956900	-1.99681900
H	-2.39421100	-1.76699100	-1.48644500
C	-4.26306600	-2.19877600	-2.43427500
H	-3.85513500	-2.91331800	-3.16371500
H	-4.65100100	-2.78044800	-1.59163200
H	-5.11660800	-1.70543300	-2.91312300
C	-2.53017000	-0.52870800	-3.22683500
H	-1.72547300	0.15794300	-2.94298200
H	-2.10703200	-1.28667800	-3.90202500
H	-3.25751900	0.04717700	-3.81140600
C	-4.56866500	-0.73875000	0.83083200
H	-4.54825500	0.04579900	1.60223400
C	-6.04261900	-1.14188100	0.62855500
H	-6.46977500	-1.52942000	1.56426800
H	-6.66441500	-0.29733600	0.31401300
H	-6.15513500	-1.93128700	-0.12433600
C	-3.75327800	-1.93119900	1.36905000
H	-3.78293700	-2.78133100	0.67433100
H	-2.70057700	-1.67024900	1.52500500
H	-4.15956700	-2.28696000	2.32678900
H	-0.51369500	2.16019200	0.46404600

Table S-26. Geometric coordinates and thermally corrected MP2 energies for pro-*E* κ-O [A(THF)$_3$·(allyloxytriisopropylsilane)]‡. The pro-*Z* isomer does not converge without THF extrusion.



G = –1988.34947 Hartree
G_{MP2} = –1982.049537 Hartree

Atom	X	Y	Z
Na	0.00000000	0.00000000	0.00000000
N	0.60164300	1.96298100	-1.26448300
C	0.75387600	1.78999700	-2.71469700
C	2.20956600	1.83613200	-3.21457900
H	2.25381600	1.62528600	-4.29093600
H	2.81369700	1.08026400	-2.69437700
H	2.67987000	2.81127000	-3.05309300
C	0.13508100	0.44658400	-3.12343700
H	0.10098000	0.33683000	-4.21493000
H	-0.88748100	0.34970700	-2.74493200
H	0.73267300	-0.38417500	-2.72254600
H	0.20382700	2.57393600	-3.27328400
C	1.26298300	3.16452900	-0.73173600
C	0.83005700	4.50074400	-1.37588100
H	1.38382600	5.33838500	-0.93118800
H	-0.24082100	4.67830300	-1.22225500
H	1.02670000	4.51724500	-2.45375700
C	1.04599900	3.23779700	0.78720600
H	1.60714700	4.07487000	1.22170400
H	1.37647500	2.31436200	1.27770400
H	-0.01318000	3.39074200	1.01938300
H	2.35466600	3.08185100	-0.88793400
O	2.53022500	-0.85141900	0.43673400
C	3.14160200	-1.94637500	-0.26779400
H	2.39845200	-2.36024000	-0.95354900
H	3.42733300	-2.72848200	0.45258100
C	4.37415200	-1.36681200	-0.96361200
H	5.14295200	-2.12124800	-1.15767500
H	4.09251800	-0.90900700	-1.91878200
C	4.81376000	-0.28682700	0.03636700
H	5.42802500	0.49783600	-0.41512300
H	5.38714700	-0.73719400	0.85572000
C	3.46870000	0.24694100	0.54136400
H	3.50185200	0.57558700	1.58600900
H	3.09323000	1.06895500	-0.07526900
O	-0.02665900	-0.02363700	2.38561100
C	0.83629000	-0.71239500	3.30119200
H	1.65897600	-1.12275000	2.71420500
H	0.27836900	-1.53571700	3.77429900
C	1.25384800	0.33959000	4.34980100
H	1.29936800	-0.09568700	5.35272400
H	2.24345500	0.74762000	4.12328600
C	0.16270800	1.44034400	4.22747400
H	0.59848200	2.37719000	3.86945000
H	-0.33682700	1.64629200	5.17885500
C	-0.81472800	0.87188300	3.18599800
H	-1.62651500	0.30670100	3.66716100
H	-1.25190300	1.61167200	2.51477100
O	-0.20014400	-2.42384600	-0.65109500
C	-0.16490100	-3.46383100	0.34170700
H	-0.56011400	-3.04756700	1.27039900
H	0.87405000	-3.78509800	0.51113600
C	-1.00086300	-4.59656300	-0.24720600
H	-0.78553900	-5.56678200	0.21082800
H	-2.06732900	-4.38232700	-0.11716300
C	-0.60772200	-4.52749900	-1.73281600

H	-1.38031600	-4.92137000	-2.39916200
H	0.30861600	-5.10200300	-1.90963800
C	-0.35715600	-3.02371700	-1.96011100
H	0.54581500	-2.83736800	-2.55289300
H	-1.19847600	-2.52640300	-2.45043900
C	-2.14335900	2.05074900	-0.82906700
C	-2.55723400	3.24688600	-0.10535900
C	-2.93586300	4.43759400	-0.62037000
H	-3.09485000	4.57434000	-1.68866100
H	-3.07134500	5.31431300	0.00678300
H	-2.43453900	3.18525200	0.98129100
H	-2.58419600	1.99750100	-1.83431400
O	-2.45321300	0.79266800	-0.09259800
Si	-3.98416500	0.06033000	-0.06852900
C	-5.38128400	1.34303700	-0.38364100
H	-4.97196700	2.00791900	-1.15727900
C	-6.69271300	0.74765700	-0.93757800
H	-7.42284800	1.54699200	-1.12685600
H	-6.54713400	0.21314900	-1.88187600
H	-7.16213700	0.04933000	-0.23384900
C	-5.68629100	2.23172400	0.84000000
H	-4.79214900	2.74025900	1.20810400
H	-6.41247900	3.01140000	0.57183200
H	-6.12109000	1.65752900	1.66716400
C	-4.16463700	-0.70707700	1.68633800
H	-3.97161600	0.14850300	2.35318200
C	-5.56885800	-1.24169800	2.03518500
H	-5.83792800	-2.11404500	1.42883600
H	-5.60877200	-1.55951500	3.08696000
H	-6.35198500	-0.49102900	1.89307300
C	-3.10471400	-1.77709200	2.00591900
H	-2.08777000	-1.39238200	1.88431400
H	-3.20549800	-2.13051800	3.04329900
H	-3.21628400	-2.65769300	1.35985600
C	-3.91303200	-1.30311500	-1.42539200
H	-2.93133400	-1.76331700	-1.23117200
C	-4.96356600	-2.42759000	-1.34542300
H	-4.80533900	-3.16445600	-2.14688600
H	-4.92181100	-2.96967400	-0.39452400
H	-5.98491200	-2.04771400	-1.46100900
C	-3.86262200	-0.72387100	-2.85419600
H	-3.09104600	0.04448400	-2.96364100
H	-3.65098100	-1.51287900	-3.59108200
H	-4.81827000	-0.27011800	-3.14218600
H	-0.68028000	2.06834300	-1.04886700

III. Full reference (Gaussian):

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.