Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information

69451 Weinheim, Germany

# Catalysis of 6p Electrocyclizations

**Lee M. Bishop, Jennifer E. Barbarow, Robert G. Bergman* and Dirk Trauner***

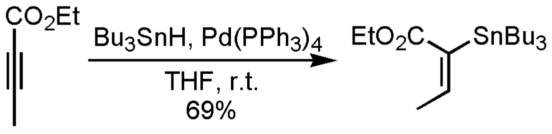
*Department of Chemistry, University of California, Berkeley, CA 94720-1460*

## Supporting Information

**General Information.** All reactions and manipulations, unless otherwise noted, were carried out in an inert atmosphere ($N_2$) glovebox or using standard Schlenk and high vacuum techniques. Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a cajon ultra-torr reducing union, then flame-sealing on a vacuum line. All glassware was dried in an oven at 150 ºC for at least 12 h prior to use or was flame-dried under reduced pressure. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on Bruker DRX-500 (500 MHz), AV-500 (500 MHz), AVB-400 (400 MHz), AVQ-400 (400 MHz), and AV-300 (300 MHz) spectrometers as indicated. $^1H$ NMR chemical shifts (d) are reported in parts per million relative to residual protiated solvent. NMR data are reported in the following format: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant; integration). Column chromatography was performed using a Biotage SP1 MPLC purification system and pre-packed silica gel columns. HPLC was performed using an Alltech Econosil C18 10u column (250mm x 22mm). IR spectra were obtained on neat samples on NaCl plates using a ThermoNicolet Avatar 370 FT-IR spectrometer. The temperatures of the kinetics experiments carried out in a circulating oil bath were measured using a calibrated mercury thermometer, and varied ±0.1 ºC. The temperatures of the kinetics and titration experiments carried out in an NMR probe were determined from the $^1H$ NMR chemical shifts of ethylene glycol and MeOH samples, and varied ±0.1 ºC. The values for $k_{obs}$ were determined by fitting the concentration versus time plots to the equation $C_t = C_8 - (C_8 - C_0)\exp(-k_{obs}t)$ using the program KaleidaGraph (where $C_t$, $C_8$, $C_0$ are the concentration at time t, time infinity, and time zero).[1] All well-resolved starting material and product $^1H$ NMR resonances were integrated and fit separately;[2] the $k_{obs}$ values shown are averages of those individual values. The reported errors in the $k_{obs}$ values are one standard deviation of the $k_{obs}$ values obtained from each integrated resonance.

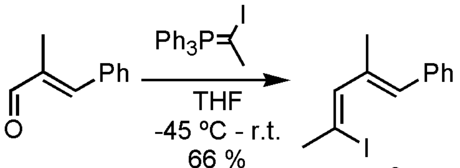
**Materials.** Tetrahydrofuran and toluene were dried and purified by passage through a column of activated alumina under $N_2$ pressure followed by sparging with $N_2$.[3] Dry DMF was obtained from EMD and used without further purification. Benzene-$d_6$ and toluene-$d_8$, obtained from Cambridge Isotope Labs, Inc., were sparged with $N_2$ and stored over activated 4 Å molecular sieve pellets overnight prior to use. Activated 4 Å molecular sieve pellets were obtained from Sigma-Aldrich and heated at 150 ºC under vacuum for 24 h. Hexamethylbenzene was obtained from Sigma-Aldrich and was sublimed prior to use. HMPA was obtained from Sigma-Aldrich and distilled from $CaH_2$ prior to use. 1,1,2,2-tetrachloroethane, obtained from Sigma-Aldrich, was sparged with $N_2$ and stored over activated 4 Å molecular sieve pellets overnight prior to use. $Pd(PPh_3)_4$ was obtained from Strem Chemicals; ethyl 2-butynoate was obtained from Fluka; $Bu_3SnH$, *n*-BuLi, NaHMDS, a-methyl-*trans*-cinnamaldehyde, $Cu(OTf)_2$, $Sc(OTf)_3$, $Me_3Al$, $Me_2AlCl$, $AlBr_3$, $BF_3{\cdot}OEt_2$, TMSOTf, $MgBr_2{\cdot}OEt_2$, $TiCl_4{\cdot}2THF$, $Yb(OTf)_3$, $Pr(OTf)_3$, and $ZnBr_2$ were obtained from Sigma-Aldrich; iodine was obtained from Fisher Scientific; these reagents were used without further purification. (Ethyl)triphenylphosphonium iodide,[4] copper(I) thiophene-2-carboxylate,[5] and iodomethyltriphenylphosphonium iodide[6] were synthesized according to literature procedures. Spectral data for these compounds agree with literature values.

# Synthesis and Characterization



**5**

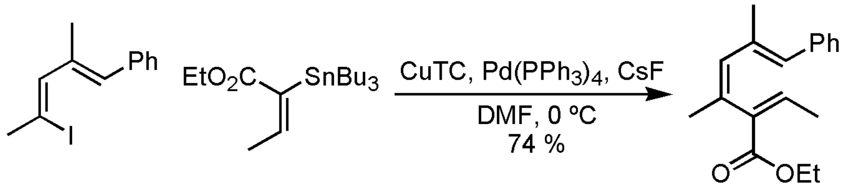
**Synthesis of ethyl 2-tributylstannyl-2-butenoate 5.** A round bottom flask was charged with $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), THF (10 mL), and ethyl 2-butynoate (0.10 mL, 0.86 mmol). To this solution was added $Bu_3SnH$ (1 mL, 0.86 M in THF, 0.86 mmol) dropwise over 2 h at room temperature. The reaction mixture was stirred for an additional 1 h, concentrated *in vacuo*, and purified by silica gel chromatography (2-4 % EtOAc in hexanes) to yield a 3:1 mixture of a :ß stannylated isomers. These isomers were separated by reverse-phase HPLC (96:4 $MeCN:H_2O$) to yield 239 mg product as a clear oil (69 %). **$^1$H NMR** ($CDCl_3$, 300 MHz): d 6.17 (q, $J_{H\text{-}H}$ = 6.1 Hz, $J_{Sn\text{-}H}$ = 31 Hz, 1H), 4.15 (q, $J$ = 7.1 Hz, 2H), 2.00 (d, $J$ = 6.9 Hz, 3H) 1.55-1.40 (m, 6H), 1.38-1.20 (m, 12H), 0.98-0.80 ppm (m, 12H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): d 171.4, 148.2, 137.1, 60.1, 29.1 ($J_{Sn\text{-}C}$ = 9.8 Hz), 27.5 ($J_{Sn\text{-}C}$ = 29 Hz), 18.4 ($J_{Sn\text{-}C}$ = 22 Hz), 14.6, 13.9, 10.4 ppm ($J_{Sn\text{-}C}$ = 170 Hz); **IR** 2957, 2926, 2872, 2853, 1708, 1608, 1464, 1183, 1035 cm$^{-1}$; **HRMS** (EI$^+$) Exact mass calcd for $C_{18}H_{35}O_2Sn$ [M-H]$^+$: 403.1659, found 403.1660.



**3**

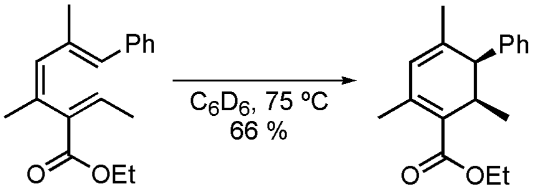
**Synthesis of 2-iodo-4-methyl-5-phenyl-2,4-pentadiene 3.** Synthesized according to the procedure developed by Zhao et. al.[7] To a Schlenk flask charged with ethyl(triphenyl)phosphonium iodide (1.5 g, 3.6 mmol) and THF (10 mL) was added *n*-BuLi

(2.25 mL, 1.6 M in hexanes, 3.6 mmol) at room temperature. The resulting suspension was stirred for 5 min, during which the reaction mixture became a red, homogeneous solution. This solution was slowly cannulated into a round bottom flask charged with iodine (0.91 g, 3.6 mmol) and THF (30 mL) at -78 ºC, resulting in an orange suspension. The temperature of this suspension was raised to -45 ºC and NaHMDS (5.60 mL, 0.6 M in toluene, 3.4 mmol) was added dropwise over 5 min. The resulting suspension was stirred for 5 min, during which the reaction mixture again became a red, homogeneous solution. To this solution was added a-methyl-*trans*-cinnamaldehyde (0.25 mL, 1.8 mmol) dropwise. The reaction mixture was allowed to warm to room temperature over 20 min. Hexanes (100 mL) was added, and the reaction mixture was filtered through a plug of Celite, concentrated *in vacuo*, and purified by silica gel chromatography (0-2 % EtOAc in hexanes), yielding 334 mg product as a yellow oil (66 %). **$^1$H NMR** ($CDCl_3$, 500 MHz): d 7.42-7.31 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.61 (s, 1H), 6.20 (s, 1H), 2.67 (s, 3H), 2.07 ppm (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$): d 138.6, 137.5, 136.3, 131.3, 129.2, 128.3, 126.9, 98.0, 35.4, 18.0 ppm; **HRMS** ($EI^+$) Exact mass calcd for $C_{12}H_{13}I$ $[M]^+$: 284.0062, found 284.0062.



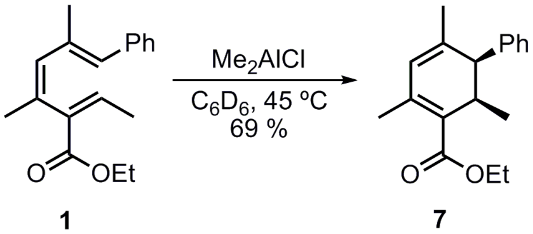
**3** **5** **1**

**Synthesis of triene 1**. A Schlenk flask was charged with ethyl 2-tributylstannyl-2-butenoate **5** (775 mg, 1.9 mmol), 2-iodo-4-methyl-5-phenyl-2,4-pentadiene **3** (600 mg, 2.1 mmol), DMF (22 mL), and $Pd(PPh_3)_4$ (111 mg, 0.1 mmol). This solution was cooled to 0 ºC and copper(I) thiophene-2-carboxylate (403 mg, 2.1 mmol) was added. The reaction mixture was stirred for 10 min, after which CsF (583 mg, 3.8 mmol) was added. After a further 50 min of stirring, the reaction mixture was diluted with $Et_2O$ and the organic phase was washed three times with 10 % aqueous KF and once with brine. The organic solution was then dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (4-5 % EtOAc in hexanes). The resulting orange oil was further purified by reverse-phase HPLC (67:33 $MeCN:H_2O$) yielding 384 mg product as a clear oil (74 %). **$^1$H NMR** (400 MHz, $C_6D_6$): d 7.26 (d, *J* = 8.0 Hz, 2H), 7.18-7.10 (m, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.54 (s, 1H), 5.99 (s, 1H), 5.80 (q, *J* = 7.2 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 2H), 1.98-1.85 (m, 9H), 0.88 ppm (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (100 MHz, $C_6D_6$): d 167.1, 138.8, 137.4, 136.3, 136.2, 135.1, 133.9, 131.5, 129.9, 128.7, 127.0, 60.5, 26.2, 18.7, 15.9, 14.5 ppm; **IR** 3021, 2977, 2922, 1715, 1444, 1243, 1222, 1184, 1031, 748, 700 $cm^{-1}$; **HRMS** ($FAB^+$) Exact mass calcd for $C_{18}H_{22}O_2$ $[M]^+$: 270.1620, found 270.1625.

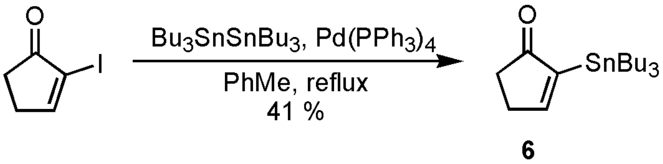


**1** **7**

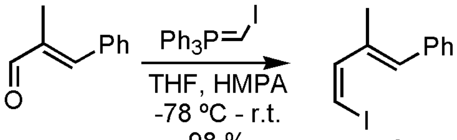
**Thermal synthesis of cyclohexadiene 7.** A solution of triene **1** (0.84 mL, 40 mM in benzene-*$d_6$*, 0.034 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was heated in a sealed NMR tube at 75 °C for 4 h. The reaction mixture was concentrated *in vacuo* and purified by silica gel chromatography (4-5 % EtOAc in hexanes) yielding 6 mg product (66 %). Quantitative conversion was observed by $^1$H NMR. **$^1$H NMR** (400 MHz, $C_6D_6$): d 7.20-7.00 (m, 5H), 5.70 (s, 1H), 4.06 (m, 2H), 3.38 (d, *J* = 7.6 Hz, 1H), 3.17 (quintet, *J* = 7.0 Hz, 1H), 2.36 (s, 3H), 1.55 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.98 ppm (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (100 MHz, $C_6D_6$): d 168.4, 143.2, 140.0, 139.9, 130.8, 129.8, 128.0, 127.3, 127.0, 60.1, 52.4, 36.2, 22.5, 21.0, 14.8, 14.0 ppm; **IR** 3028, 2967, 2934, 1701, 1575, 1444, 1366, 1259, 1222, 1071, 1048, 786, 707 cm$^{-1}$; **HRMS** (FAB$^+$) Exact mass calcd for $C_{18}H_{22}O_2$ [M]$^+$: 270.1620, found 270.1620.



**Catalyzed synthesis of cyclohexadiene 7.** A solution of triene **1** (400 µL, 48 mM in benzene-*d*$_6$, 0.019 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was combined in an NMR tube with benzene-*d*$_6$ (10 µL) and a solution of $Me_2AlCl$ (70 µL, 240 mM in benzene-*d*$_6$, 0.017 mmol). The NMR tube was sealed and heated at 45 ºC for 5 h. The reaction mixture was quenched with water and extracted three times with dichloromethane. The organic solution was then dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (4-5 % EtOAc in hexanes) yielding 3.6 mg product (69 %). Quantitative conversion was observed by $^1$H NMR. Spectral data were identical to those listed above.

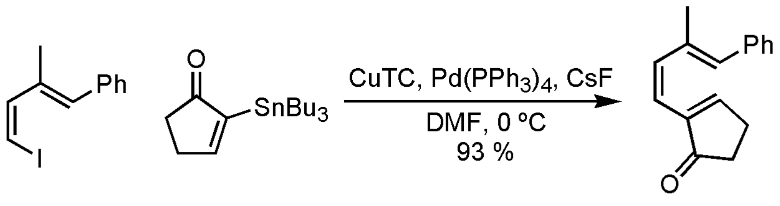


**Synthesis of 2-tributylstannyl-2-cyclopentenone 6.** A round bottom flask was charged with toluene (60 mL), 2-iodo-2-cyclopentenone (1.44 g, 6.9 mmol), $Pd(PPh_3)_4$ (800 mg, 0.7 mmol), and $Bu_3SnSnBu_3$ (7.0 mL, 13.8 mmol). The flask was equipped with a reflux condenser and the reaction mixture was heated at reflux for 16 h. The cooled reaction mixture was diluted with hexanes and washed three times with water and once with brine. The organic solution was then dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (5 % EtOAc in hexanes) yielding 1.06 g product as a clear oil (41 %). **$^1$H NMR** ($CDCl_3$, 500 MHz): d 7.74 (t, $J_{\text{H-H}}$ = 2.0 Hz, $J_{\text{Sn-H}}$ = 13.5 Hz, 1H), 2.72-2.69 (m, 2H), 2.28-2.24 (m, 2H) 1.54-1.36 (m, 6H), 1.31-1.20 (m, 6H), 1.05-0.87 (t, $J_{\text{H-H}}$ = 8.0 Hz, $J_{\text{Sn-H}}$ = 26.5 Hz, 6H), 0.84 ppm (t, $J$ = 6.0 Hz, 9H); **$^{13}$C NMR** ($CDCl_3$, 125 MHz): d 215.4, 173.6, 149.0, 33.9, 32.2, 29.3 ($J_{\text{Sn-C}}$ = 42 Hz), 27.4 ($J_{\text{Sn-C}}$ = 119 Hz), 13.9, 9.5 ppm ($J_{\text{Sn-C}}$ = 695 Hz); **IR** 2956, 2923, 2870, 2852, 1691, 1278, 1164, 696 cm$^{-1}$; **HRMS** (EI$^+$) Exact mass calcd for $C_{13}H_{23}O_1Sn_1$ [M-Bu]$^+$: 315.0771, found 315.0775.



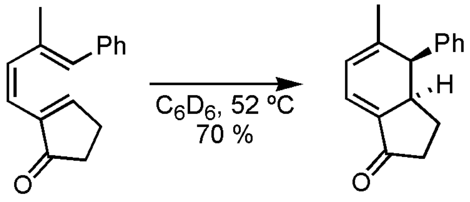
4

**Synthesis of 4-iodo-2-methyl-1-phenyl-1,3-butadiene 4.** Synthesized according to the procedure developed by Stork and Zhao.[8] A Schlenk flask was charged with THF (40 mL), iodomethyltriphenylphosphonium iodide (2.09 g, 3.9 mmol), and NaHMDS (4.30 mL, 1.0 M in THF, 4.30 mmol). This solution was stirred for 5 minutes at room temperature and cooled to -60 ºC. HMPA was then added and the reaction mixture was cooled to -78 ºC and stirred a further 15 minutes. a-Methyl-*trans*-cinnamaldehyde (0.50 mL, 3.6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 1.5 h, after which hexanes was added and the resultant suspension was filtered through Celite. The filtrate was concentrated *in vacuo*, hexanes was added, and the organic suspension was washed five times with water, once with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Hexanes was again added, the resultant suspension was filtered through Celite, and the filtrate was concentrated *in vacuo* yielding 0.95 g product as an orange oil (98 %). **$^1$H NMR** (400 MHz, $CDCl_3$): d 7.45-7.21 (m, 5H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.77 (s, 1H), 6.34 (d, *J* = 8.6 Hz, 1H) 2.21 ppm (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$): d 142.6, 137.1, 135.0, 133.3, 129.3, 128.4, 127.1, 77.0, 17.7 ppm; **HRMS** ($EI^+$) Exact mass calcd for $C_{11}H_{11}I$ $[M]^+$: 269.9903, found 269.9906.



**4** **6** **2**

**Synthesis of triene 2.** A Schlenk flask was charged with 4-iodo-2-methyl-1-phenyl-1,3-butadiene **4** (180 mg, 0.67 mmol), 2-tributylstannyl-2-cyclopentenone **6** (264 mg, 0.71 mmol), DMF (6.7 mL), and $Pd(PPh_3)_4$ (39 mg, 0.03 mmol). This solution was cooled to 0 °C and copper(I) thiophene-2-carboxylate (140 mg, 0.73 mmol) was added. The reaction mixture was stirred for 10 min, after which CsF (202 mg, 1.3 mmol) was added. After a further 50 min of stirring, the reaction mixture was diluted with $Et_2O$ and the organic phase was washed three times with 10 % aqueous KF and once with brine. The organic solution was then dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (17-20 % EtOAc in hexanes) yielding 139 mg product as a yellow oil (93 %). **$^1$H NMR** (400 MHz, $CDCl_3$): d 7.62 (m, 1H), 7.38-7.18 (m, 5H), 6.52 (s, 1H), 6.36 (d, *J* = 12.2 Hz, 1H), 5.98 (d, *J* = 12.2 Hz, 1H), 2.66-2.60 (m, 2H), 2.43-2.38 (m, 2H), 1.95 ppm (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$): d 208.5, 159.3, 142.1, 139.0, 137.6, 135.6, 131.6, 129.3, 128.4, 127.0, 117.6, 34.3, 27.1, 17.9 ppm; **IR** 2956, 2922, 1705, 1573, 1439, 737, 698 $cm^{-1}$; **HRMS** ($FAB^+$) Exact mass calcd for $C_{16}H_{17}O$ $[M+H]^+$: 225.1285, found 225.1279.



**2** **8**

**Thermal synthesis of cyclohexadiene 8.** A solution of triene **2** (0.96 mL, 40 mM in benzene-$d_6$, 0.038 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was heated in a sealed NMR tube at 52 ºC for 3 h. The reaction mixture was concentrated *in vacuo* and purified by silica gel chromatography (16-19 % EtOAc in hexanes) yielding 6 mg product (70 %). Quantitative conversion was observed by $^1$H NMR. **$^1$H NMR** (500 MHz, $CDCl_3$): d 7.28-7.19 (m, 3H), 7.10-7.01 (m, 2H), 6.88-6.84 (m, 1H), 6.20 (d, *J* = 5.5 Hz, 1H) 3.50 (d, *J* = 10.5 Hz, 1H), 3.49-3.40 (m, 1H), 2.33-2.19 (m, 2H), 2.00-1.90 (m, 1H), 1.81 (s, 3H), 1.20-1.09 ppm (m, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$): d 205.4, 147.7, 137.0, 133.6, 129.2, 128.7, 127.5, 126.8, 121.5, 49.0, 41.0, 39.3, 23.2, 22.8 ppm; **IR** 2963, 1702, 1649, 1574, 1225, 699 cm$^{-1}$; **LRMS** 224; **HRMS** (EI$^+$) Exact mass calcd for $C_{16}H_{14}O$ $[M-2H]^+$: 222.1045, found 222.1045.

**Catalyzed synthesis of cyclohexadiene 8.** A solution of triene **2** (450 µL, 48 mM in benzene-$d_6$, 0.022 mmol; containing 25 mol% 1,1,2,2-tetrachloroethane as an internal standard) was combined in an NMR tube with a solution of $Me_2AlCl$ (80 µL, 240 mM in benzene-$d_6$, 0.019 mmol). The NMR tube was sealed and kept at room temperature for 1.75 h. The reaction mixture was quenched with water and extracted three times with dichloromethane. The organic solution was then dried over $MgSO_4$, filtered, concentrated *in vacuo*, and purified by silica gel chromatography (17 % EtOAc in hexanes) yielding 4.7 mg product (97 %). Quantitative conversion was observed by $^1$H NMR. Spectral data were identical to those listed above.

## Lewis Acid Screen

**Representative procedure.** An NMR tube was charged with 2,6-di-*tert*-butyl-4-methylpyridine (2 mg, 0.0097 mmol), Lewis acid (0.0192 mmol), benzene-$d_6$ (80 µL), and triene **1** (400 µL, 48 mM in benzene-$d_6$, 0.0192 mmol; containing 5 mol% hexamethylbenzene as an internal standard). The NMR tube was then sealed under vacuum and the reaction was monitored at regular intervals *via* $^1$H NMR. The reaction mixture was kept at room temperature initially, and heated in a circulating oil bath at increasing temperatures until significant conversion was observed. Approximate half-lives at given temperatures, approximate rate accelerations, as well as any deviations made from this procedure, are noted below in Table S1.

**Table S1.**

| Lewis Acid | Approx $t_{1/2}$, temperature | Approx. rate acceleration | Notes |
|---|---|---|---|
| $Cu(OTf)_2$ | 2 h, 50 ºC | 2 | Reaction mixture heterogeneous |
| $Sc(OTf)_3$ | 2 h, 50 ºC | 2 | Reaction mixture heterogeneous |
| $Me_3Al$ | 40 min, 50 ºC | 6 | Stock solution of $Me_3Al$ used (239 mM in $C_6D_6$); no 2,6-di-*tert*-butyl-4-methylpyridine added |
| $Me_2AlCl$ | 20 min, 50 ºC | 13 | |
| $AlBr_3$ | Decomposition at r.t. | N/A | Reaction mixture heterogeneous |
| $AlBr_3$:$Me_3Al$ 6:1 | 30 min, 35 ºC | 50 | Slight decomposition observed; stock solution of $Me_3Al$ used (239 mM in $C_6D_6$); reaction initially at 0 ºC; 150 µL $C_6D_6$ added, instead of 80 µL; no 2,6-di-*tert*-butyl-4-methylpyridine added. |
| $BF_3 \cdot OEt_2$ | 2.5 h, 55 ºC | None | |
| TMSOTf | 2.5 h, 55 ºC | None | |
| $MgBr_2 \cdot OEt_2$ | 2 h, 55 ºC | 1.5 | Reaction mixture heterogeneous |
| $TiCl_4 \cdot 2THF$ | 2 h, 55 ºC | 1.5 | Reaction mixture heterogeneous |
| $Yb(OTf)_3$ | 2.5 h, 55 ºC | None | Reaction mixture heterogeneous |
| $Pr(OTf)_3$ | 2.5 h, 55 ºC | None | Reaction mixture heterogeneous |
| $ZnBr_2$ | 2.5 h, 55 ºC | None | Reaction mixture heterogeneous |

# Kinetics Experiments

**Saturation and kinetic order in $Me_2AlCl$ for triene 1.** A solution of triene **1** (400 µL, 48 mM in benzene-*d*$_6$, 0.0192 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was combined in a J-Young NMR tube with varying amounts of a solution of $Me_2AlCl$ in benzene-*d*$_6$. Benzene-*d*$_6$ was then added such that the total volume of the solution in the tube was 480 µL. A 240 mM $Me_2AlCl$ solution was used for the kinetic runs with the four lowest $Me_2AlCl$ concentrations, and a 1.44 M $Me_2AlCl$ solution was used for the remaining runs. The J-Young tube was then sealed and the reaction mixture was frozen in ice-water until ready for kinetic analysis. Once ready for analysis, the solution was thawed and agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to 50.4 ºC, and the reaction was monitored for disappearance of **1** and appearance of **7** (*via* single scan $^1H$ NMR spectroscopy). The concentration of $Me_2AlCl$ was determined by integration against the internal standard. The first order rate constants and $Me_2AlCl$ concentrations can be found numerically in Table S2 and graphically in Figure S1. A plot of the logarithm of the rate constants versus the logarithm of $Me_2AlCl$ concentration at sub-stoichiometric catalyst loadings can be found in Figure S2.

**Table S2.**

| Entry | [$Me_2AlCl$] (mM) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 6.80 | $1.27(4)\times10^{-4}$ |
| 2 | 17.2 | $2.8(1)\times10^{-4}$ |
| 3 | 21.2 | $3.51(5)\times10^{-4}$ |
| 4 | 28.8 | $4.8(2)\times10^{-4}$ |
| 5 | 38.8 | $5.6(1)\times10^{-4}$ |
| 6 | 42.8 | $5.77(4)\times10^{-4}$ |
| 7 | 102 | $6.5(1)\times10^{-4}$ |
| 8 | 162 | $6.8(3)\times10^{-4}$ |
| 9 | 232 | $7(1)\times10^{-4}$ |

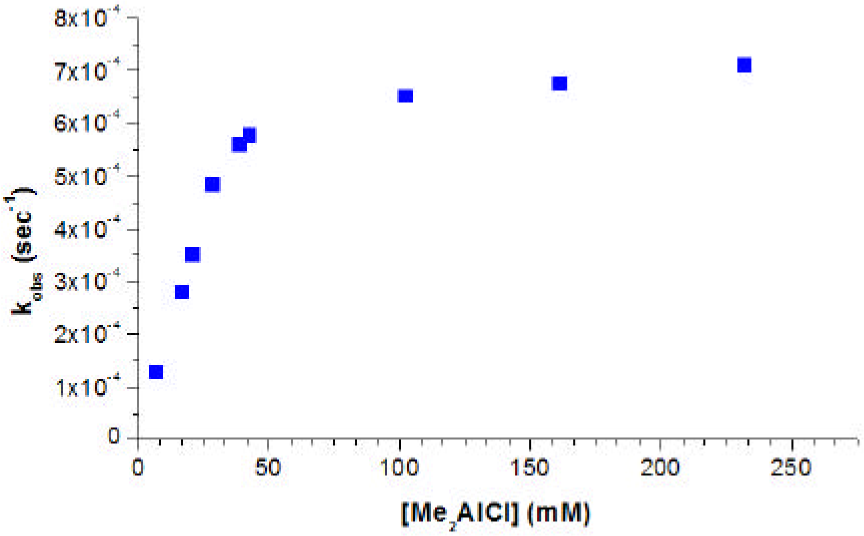


**Figure S1.** Saturation in $Me_2AlCl$.

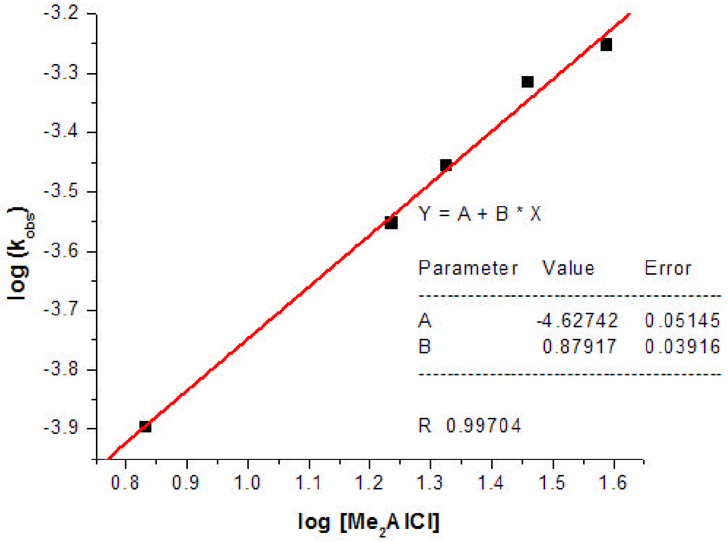


**Figure S2.** Plot showing kinetic order in $Me_2AlCl$.

**Saturation and kinetic order in 1.** A solution of $Me_2AlCl$ (80 µL, 240 mM in benzene-*d*$_6$, 0.0192 mmol) was combined in a J-Young NMR tube with varying amounts of a solution of **1** in benzene-*d*$_6$ (containing 5 mol% hexamethylbenzene as an internal standard). Benzene-*d*$_6$ was then added such that the total volume of the solution in the tube was 480 µL. A 48 mM solution of **1** was used for the kinetic runs with the seven lowest concentrations of **1**, and a 384 mM solution of **1** was used for the remainder. The J-Young tube was then sealed, the solution was agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to 50.4 ºC, and the reaction was monitored for disappearance of **1** and appearance of **7** (*via* single scan $^1$H NMR spectroscopy). The concentration of **1** was determined by integration against $Me_2AlCl$ and the internal standard. The portion of the concentration versus time plots exhibiting zero order dependence on substrate was fit to a line via the least-squares method. The slope of this line was taken as the initial velocity of the reaction. These, as well as the concentrations of **1**, can be found numerically in Table S3 and graphically in Figure S3. A plot of the logarithm of the initial reaction velocity versus the logarithm of the concentration of **1** (where [**1**] < 40 mM) can be found in Figure S4.

**Table S3.**

| Entry | [**1**] (mM) | $V_{init}$ (mM/s) |
|---|---|---|
| 1 | 2.16 | $8.01x10^{-4}$ |
| 2 | 4.85 | $1.95x10^{-3}$ |
| 3 | 9.15 | $3.73x10^{-3}$ |
| 4 | 16.5 | $6.58x10^{-3}$ |
| 5 | 24.2 | $9.72x10^{-3}$ |
| 6 | 32.6 | $1.24x10^{-2}$ |
| 7 | 39.7 | $1.40x10^{-2}$ |
| 8 | 62.4 | $1.58x10^{-2}$ |
| 9 | 132 | $1.92x10^{-2}$ |
| 10 | 199 | $2.03x10^{-2}$ |
| 11 | 276 | $2.18x10^{-2}$ |
| 12 | 298 | $2.22x10^{-2}$ |

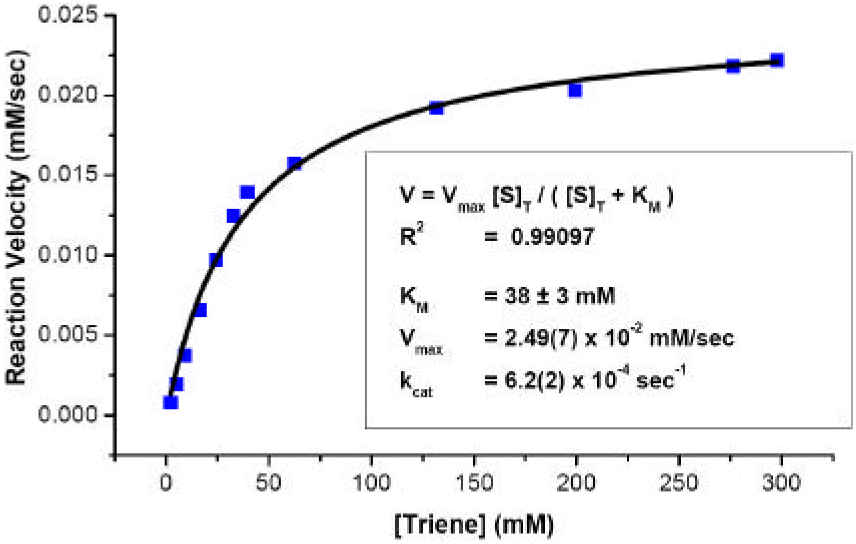


**Figure S3.** Saturation in **1**.

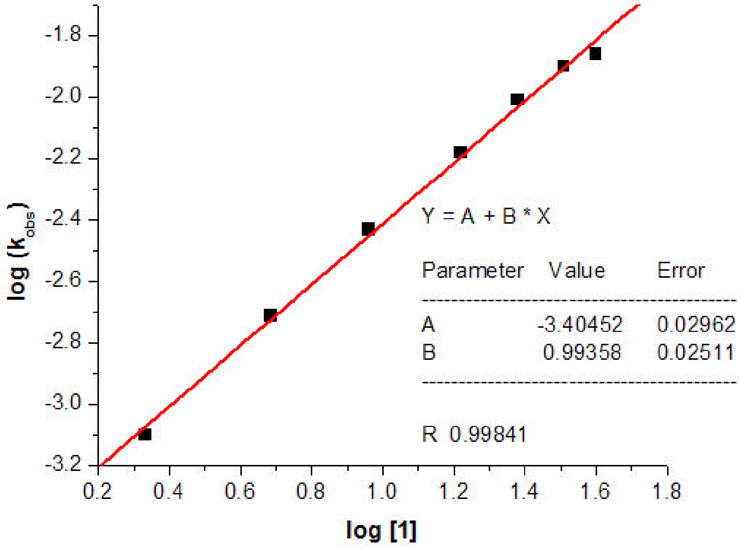


**Figure S4.** Plot showing kinetic order in **1**.

**Activation Parameter Measurements for the Thermal Cyclization of 1.** A solution of **1** (500 µL, 48 mM in benzene-$d_6$, 0.0240 mmol; containing 5 mol% hexamethylbenzene as an internal standard) and benzene-$d_6$ (100 µL) were combined in a standard or J-Young NMR tube. Kinetic analyses of the reactions monitored at 36.0 and 44.0 °C were carried out in the following fashion. The NMR tube was sealed under vacuum and completely submerged in a circulating oil bath equilibrated to the desired temperature; the tube was removed from the oil bath and cooled rapidly to room temperature under a stream of hexanes; the reaction was monitored for disappearance of **1** and appearance of **7** (via single scan $^1$H NMR spectroscopy using an AVB-400 spectrometer) and the tube was replaced in the oil bath. Only time spent in the oil bath was included in the concentration versus time plots. Kinetic analyses of the reactions monitored at 50.4 and 52.4 ºC were carried out in the following fashion: the NMR tube was sealed under vacuum and placed in an AV-500 NMR probe pre-equilibrated to the desired temperature, and the reaction was monitored for disappearance of **1** and appearance of **7** (*via* single scan $^1$H NMR spectroscopy). Kinetic analyses of the reactions monitored at 60.6, 68.7, and 76.8 ºC were carried out in the following fashion: the J-Young NMR tube was sealed and placed in an AV-500 NMR probe pre-equilibrated to the desired temperature, and the reaction was monitored for disappearance of **1** and appearance of **7** (*via* single scan $^1$H NMR spectroscopy). The first order rate constants and Eyring plot can be found in Table S4 and Figure S5, respectively.

**Table S4.**

| Entry | Temperature (ºC) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 36.0 | 8.8(1)x10$^{-6}$ |
| 2 | 44.0 | 2.26(6)x10$^{-5}$ |
| 3 | 50.4 | 4.75(4)x10$^{-5}$ |
| 4 | 52.4 | 5.05(5)x10$^{-5}$ |
| 5 | 60.6 | 1.54(1)x10$^{-4}$ |
| 6 | 60.6 | 1.51(1)x10$^{-4}$ |
| 7 | 68.7 | 3.17(5)x10$^{-4}$ |
| 8 | 76.8 | 6.61(2)x10$^{-4}$ |

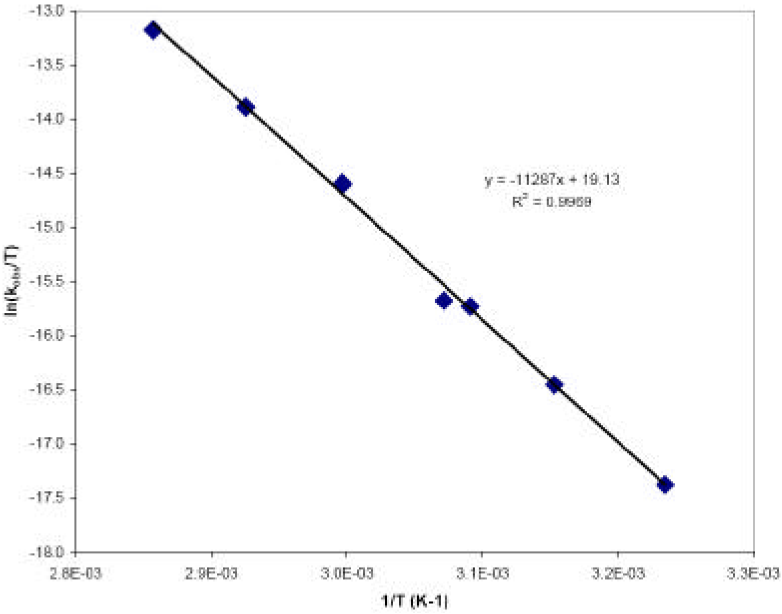


**Figure S5.** Eyring plot for the thermal cyclization of **1** to **7** in benzene-*d*$_6$.

**Activation Parameter Measurements for the Catalyzed Cyclization of 1.** A solution of **1** (400 µL, 48 mM in benzene-*d*$_6$, 0.0192 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was combined in a J-Young NMR tube with a solution of $Me_2AlCl$ (80 µL, 480 mM in benzene-*d*$_6$, 0.0384 mmol). The J-Young tube was then sealed, the solution was agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to the desired temperature, and the reaction was monitored for disappearance of **1** and appearance of **7** (*via* single scan $^1$H NMR spectroscopy). The concentration of $Me_2AlCl$ was determined to be 80(2) mM in all experiments by integration against the internal standard. The NMR probe for the above experiments was calibrated to 34.1, 42.3, 50.4, 58.5, 66.7, and 74.8 °C. The first order rate constants and the Eyring plot for these experiments are displayed in Table S5 and Figure S6, respectively.

**Table S5.**

| Entry | Temperature (ºC) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 34.1 | $1.09(9)x10^{-4}$ |
| 2 | 42.3 | $2.6(1)x10^{-4}$ |
| 3 | 50.4 | $5.59(6)x10^{-4}$ |
| 4 | 58.5 | $1.27(1)x10^{-3}$ |
| 5 | 66.7 | $2.76(4)x10^{-3}$ |
| 6 | 74.8 | $5.6(4)x10^{-3}$ |

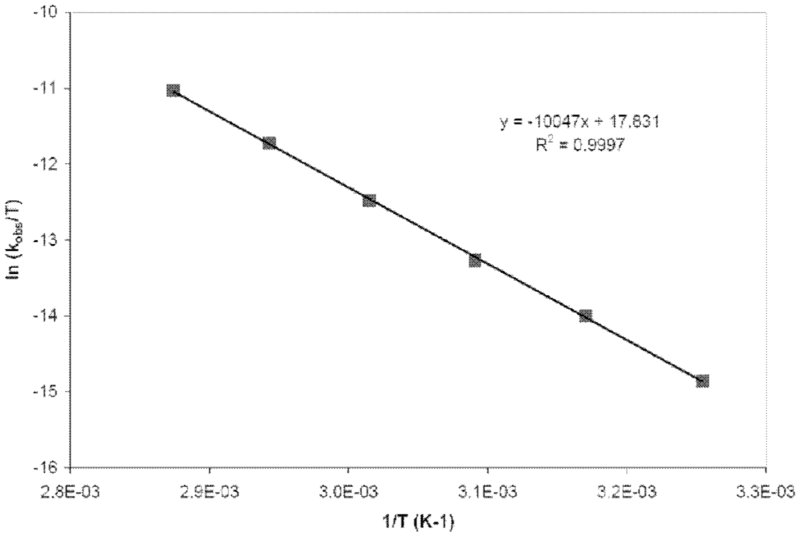


**Figure S6.** Eyring plot for the catalyzed cyclization of **1** to **7** in benzene-$d_6$.

**Activation parameter measurements for the thermal cyclization of 2.** A solution of **2** (400 µL, 48 mM in benzene-$d_6$, 0.0192 mmol; containing 25 mol% 1,1,2,2-tetrachloroethane as an internal standard) and benzene-$d_6$ (80 µL) were combined in a J-Young NMR tube. The J-Young tube was then sealed, the solution was agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to the desired temperature, and the reaction was monitored for disappearance of **2** and appearance of **8** (*via* single scan $^1$H NMR spectroscopy). The NMR probe for the above experiments was calibrated to 40.2, 52.4, 59.5, 60.6, 68.7, and 76.8 ºC. The first order rate constants and the Eyring plot for these experiments are displayed in Table S6 and Figure S7, respectively.

**Table S6.**

| Entry | Temperature (°C) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 40.2 | $9.74(5)x10^{-5}$ |
| 2 | 52.4 | $3.1(3)x10^{-4}$ |
| 3 | 59.5 | $6.7(5)x10^{-4}$ |
| 4 | 60.6 | $7.7(1)x10^{-4}$ |
| 5 | 68.7 | $1.6(1)x10^{-3}$ |
| 6 | 76.8 | $3.2(3)x10^{-3}$ |

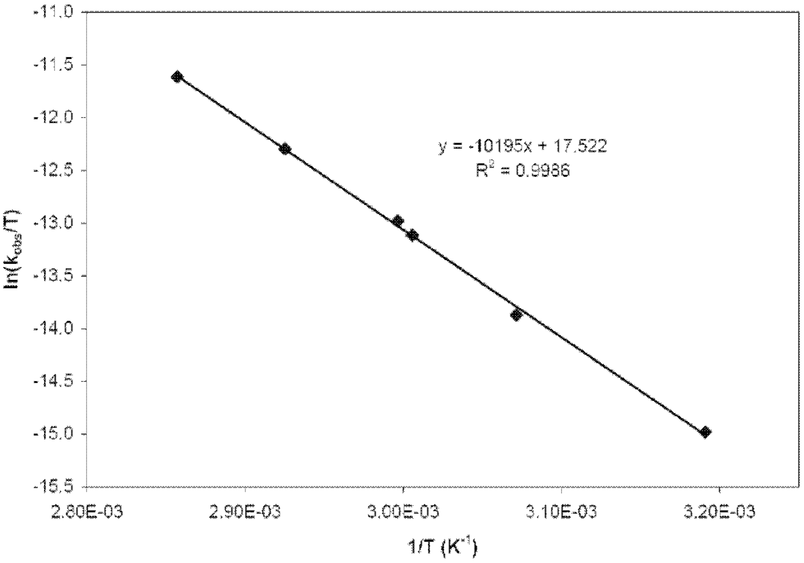


**Figure S7.** Eyring plot for the thermal cyclization of **2** to **8** in benzene-*d*$_6$.

**Activation parameter measurements for the catalyzed cyclization of 2.** A solution of **2** (400 µL, 48 mM in benzene-*d*$_6$, 0.0192 mmol; containing 25 mol% 1,1,2,2-tetrachloroethane as an internal standard) was combined in a J-Young NMR tube with a solution of $Me_2AlCl$ (80 µL, 240 mM in benzene-*d*$_6$, 0.0192 mmol). The J-Young tube was then sealed, the solution was agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to the desired temperature, and the reaction was monitored for disappearance of **2** and appearance of **8** (*via* single scan $^1$H NMR spectroscopy). The concentration of $Me_2AlCl$ was determined to be 40(5) mM in all experiments by integration against the internal standard. The NMR probe for the above experiments was calibrated to 8.7, 11.6, 14.5, 17.4, 20.4, 23.9, 28.0, 32.1, and 36.2 ºC. The first order rate constants and the Eyring plot for these experiments are displayed in Table S7 and Figure S8, respectively.

**Table S7.**

| Entry | Temperature (ºC) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 8.7 | $1.59(3)x10^{-4}$ |
| 2 | 11.6 | $2.3(1)x10^{-4}$ |
| 3 | 14.5 | $3.2(1)x10^{-4}$ |
| 4 | 17.4 | $4.32(5)x10^{-4}$ |
| 5 | 20.4 | $5.72(8)x10^{-4}$ |
| 6 | 23.9 | $8.5(2)x10^{-4}$ |
| 7 | 28.0 | $1.32(2)x10^{-3}$ |
| 8 | 32.1 | $2.11(6)x10^{-3}$ |
| 9 | 36.2 | $3.13(8)x10^{-3}$ |

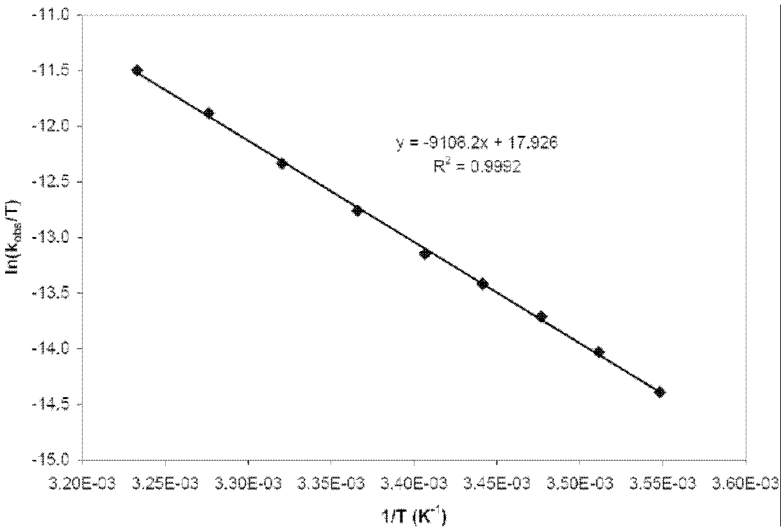


**Figure S8.** Eyring plot for the catalyzed cyclization of **2** to **8** in benzene-*d*$_6$.

**Kinetic order in $Me_2AlCl$ for triene 2.** A solution of triene **2** (400 µL, 48 mM in benzene-*d*$_6$, 0.0192 mmol; containing 25 mol% 1,1,2,2-tetrachloroethane as an internal standard) was combined in a J-Young NMR tube with varying amounts of a 240 mM solution of $Me_2AlCl$ in benzene-*d*$_6$. Benzene-*d*$_6$ was then added such that the total volume of the solution in the tube was 480 µL. The J-Young tube was then sealed and the reaction mixture was frozen in ice-water until ready for kinetic analysis. Once ready for analysis, the solution was thawed and agitated, the tube was placed in an AV-500 NMR probe pre-equilibrated to 28.0 ºC, and the reaction was monitored for disappearance of **2** and appearance of **8** (*via* single scan $^1H$ NMR spectroscopy). The concentration of $Me_2AlCl$ was determined by integration against the internal standard. The first order rate constants and $Me_2AlCl$ concentrations can be found numerically in Table S8 and graphically in Figure S9.

**Table S8.**

| Entry | [$Me_2AlCl$] (mM) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 1 | 6.51 | 2.5(4)x$10^{-4}$ |
| 2 | 10.4 | 3.5(6)x$10^{-4}$ |
| 3 | 22.4 | 7.5(3)x$10^{-4}$ |
| 4 | 30.2 | 1.1(1)x$10^{-3}$ |
| 5 | 38.4 | 1.32(2)x$10^{-3}$ |

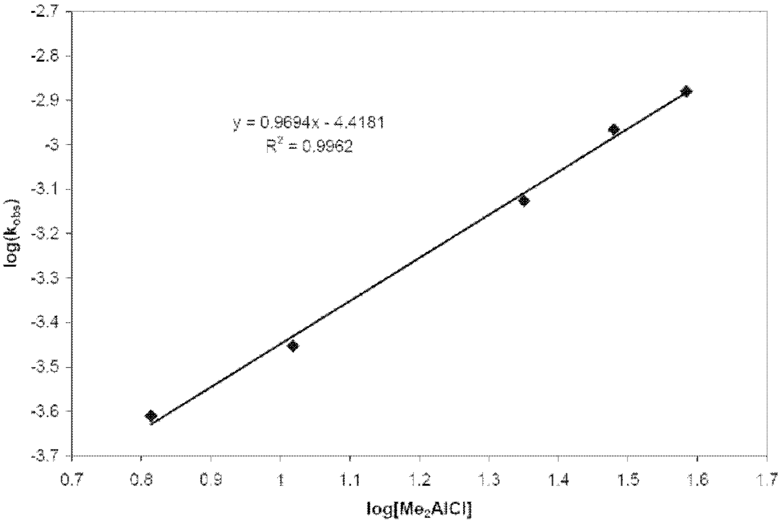


**Figure S9.** Plot showing kinetic order in $Me_2AlCl$.

# Low-Temperature NMR Titrations

**Titration of 1 with $Me_2AlCl$.** A solution of **1** (500 µL, 48 mM in benzene-$d_6$, 0.0240 mmol; containing 5 mol% hexamethylbenzene as an internal standard) was added to an NMR tube, which was subsequently sealed with a rubber septum. The NMR tube was placed in an AV-500 NMR spectrometer pre-equilibrated to 9.7 ºC and the shift of the $^1H$ NMR spectrum of **1** was monitored as a function of added $Me_2AlCl$ (240 mM in benzene-$d_6$). The $Me_2AlCl$ solution was added by ejecting the sample from the NMR probe, injecting the solution through the septum, agitating the sample, and replacing it in the NMR probe. The concentration of $Me_2AlCl$ was determined by integration against the internal standard. The graphical representations of the change in chemical shift of two representative resonances are shown in Figures S10 and S11 and stacked spectra of three representative resonances are shown in Figure S12.

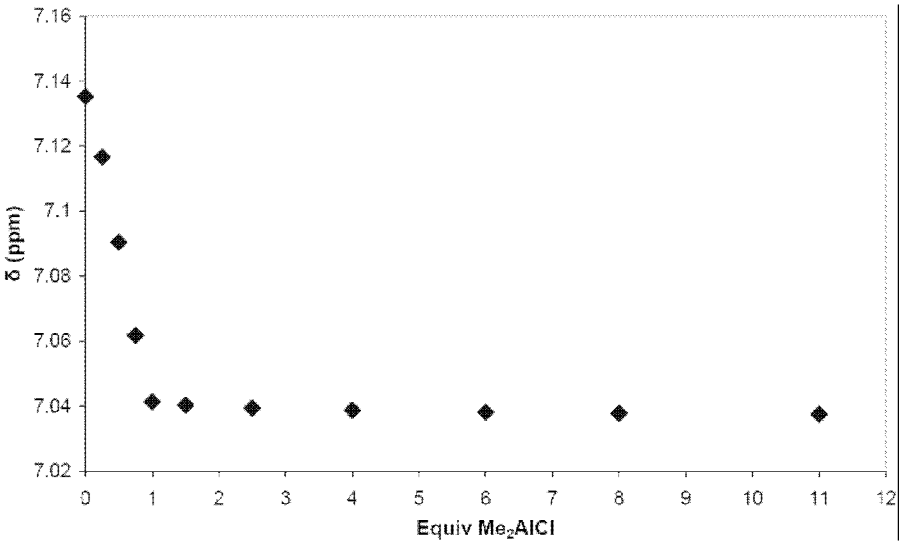


**Figure S10.** Chemical shift of a representative resonance of **1** versus added equivalents of $Me_2AlCl$ in benzene-$d_6$ at 9.7 ºC.

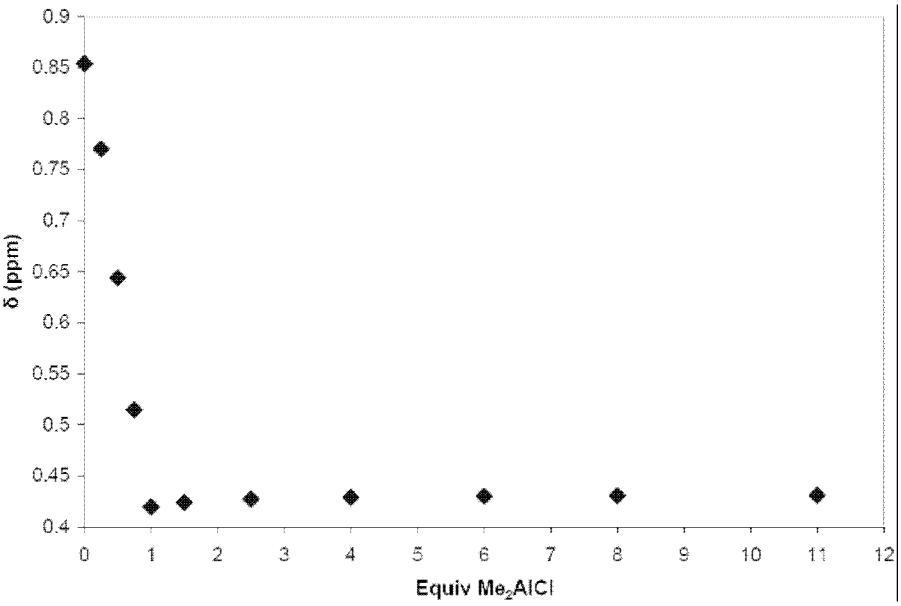


**Figure S11.** Chemical shift of a representative resonance of **1** versus added equivalents of $Me_2AlCl$ in benzene-$d_6$ at 9.7 °C.

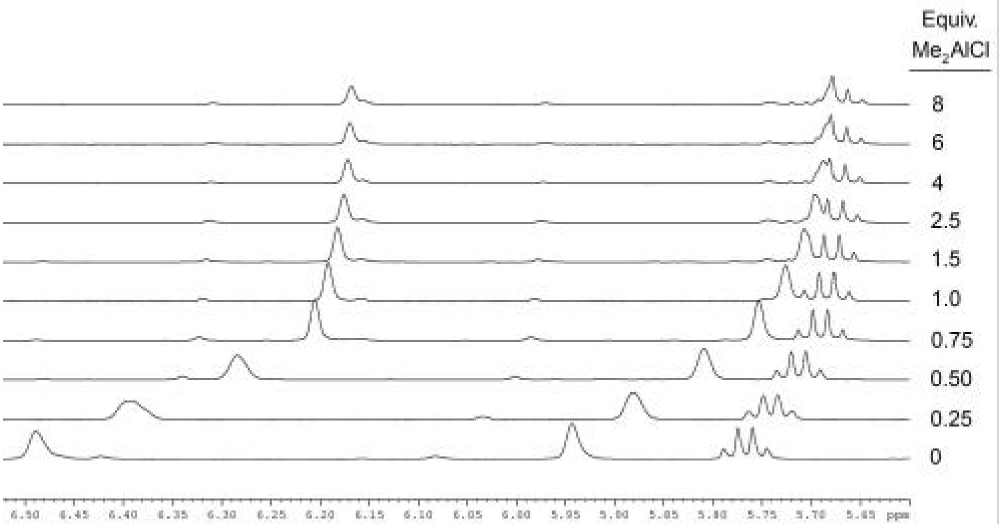


**Figure S12.** Stacked $^1H$ NMR spectra of three representative resonances of **1** versus added equivalents of $Me_2AlCl$ in benzene-$d_6$ at 9.7 °C.

**Titration of 2 with $Me_2AlCl$.** A solution of **2** (500 µL, 63 mM in toluene-$d_8$, 0.0315 mmol; containing 25 mol% 1,1,2,2-tetrachloroethane as an internal standard) was added to an NMR tube, which was subsequently sealed with a rubber septum. The NMR tube was placed in an AV-500 NMR spectrometer pre-equilibrated to -25 ºC and the shift of the $^1$H NMR spectrum of **2** was monitored as a function of added $Me_2AlCl$ (317 mM in toluene-$d_8$). The $Me_2AlCl$ solution was added by ejecting the sample from the NMR probe, injecting the solution through the septum, agitating the sample, and replacing it in the NMR probe. The concentration of $Me_2AlCl$ was determined by integration against the internal standard. The graphical representations of the change in chemical shift of two representative resonances are shown in Figures S13 and S14.

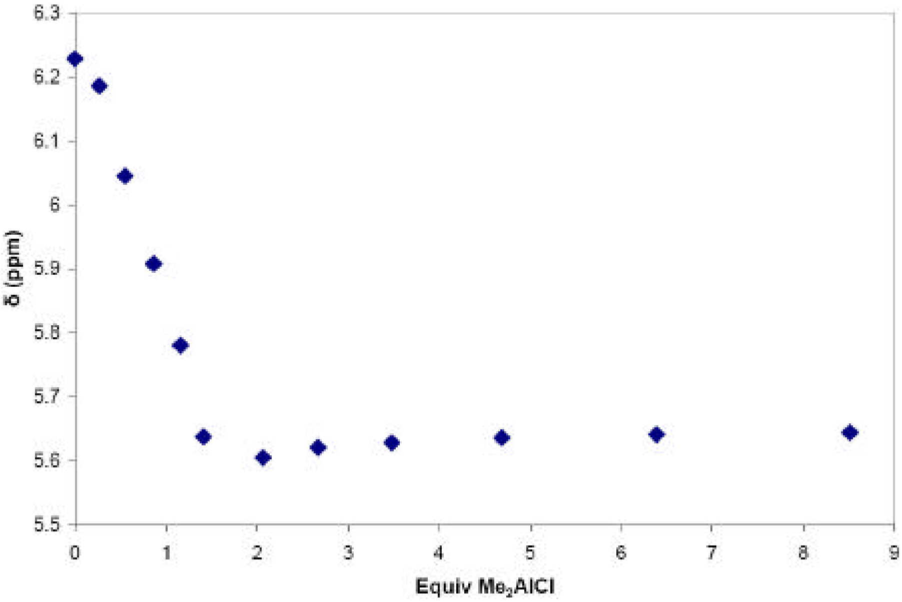


**Figure S13.** Chemical shift of a representative resonance of **2** versus added equivalents of $Me_2AlCl$ in toluene-$d_8$ at -25 ºC.

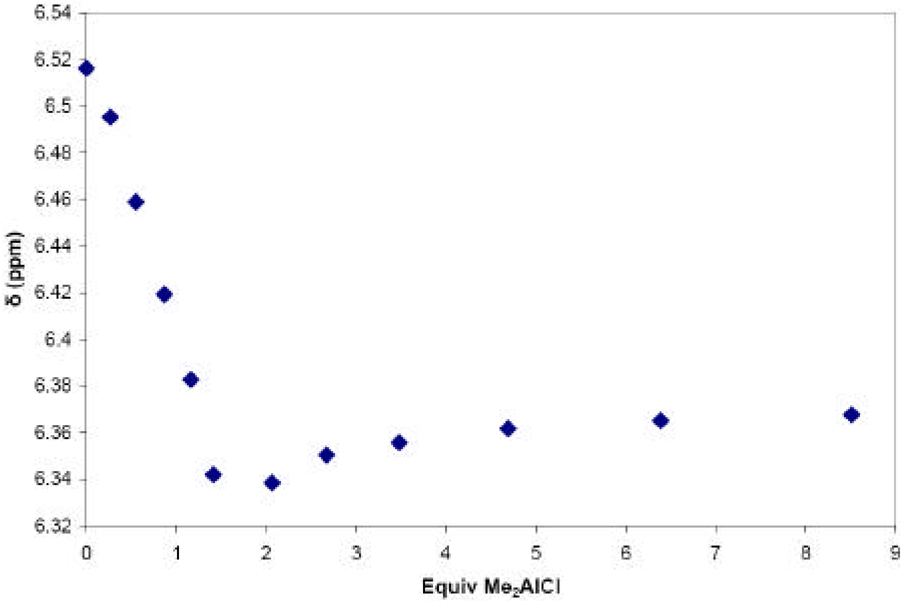
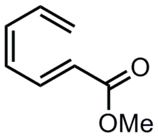


**Figure S14.** Chemical shift of a representative resonance of **2** versus added equivalents of Me$_2$AlCl in toluene-$d_8$ at -25 °C.

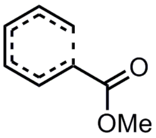
## Calculations

Molecules were first submitted to 1000-step conformational searches using the OPLS_2005 force field in the program MACROMODEL.[9] The potential energy surfaces were further investigated by performing geometry optimizations, energy minimizations, and frequency calculations, in GAUSSIAN 03 at the B3LYP/6-31G** level of theory,[10] on molecules in conformations similar to the minimum energy conformations obtained from MACROMODEL. All energies reported are those of the lowest energy conformation obtained *via* this method. Intrinsic reaction coordinate searches were performed in GAUSSIAN 03 by the method of Schlegel and Gonzalez.[11]



$E_{SCF}$ = -461.280415991 Hartrees
Zero-Point Correction = 0.162729 Hartrees
No Imaginary Frequencies

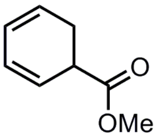
| | | | |
|---|---|---|---|
| C | -1.37343577 | -1.13728222 | -0.00027238 |
| H | -1.04710001 | -2.17571813 | -0.00050229 |
| C | -2.71006841 | -0.89562431 | -0.00014188 |
| H | -3.37607074 | -1.75740162 | -0.00027934 |
| C | -3.36763823 | 0.39688102 | 0.00017164 |
| H | -2.74557384 | 1.28844520 | 0.00031327 |
| C | -4.70321715 | 0.53760483 | 0.00029800 |
| H | -5.17342520 | 1.51509823 | 0.00053647 |
| H | -5.36487023 | -0.32487448 | 0.00016654 |
| C | -0.33123509 | -0.14017951 | -0.00013050 |
| H | -0.60033115 | 0.91296170 | 0.00005578 |
| C | 0.98957962 | -0.42631070 | -0.00022080 |
| H | 1.31941453 | -1.45945898 | -0.00041385 |
| C | 1.97686785 | 0.67826846 | -0.00009328 |
| O | 1.66640086 | 1.85185892 | -0.00022814 |
| O | 3.30593481 | 0.37028245 | -0.00000050 |
| C | 3.76479196 | -0.98140696 | 0.00043729 |
| H | 3.44041070 | -1.52326324 | 0.89568143 |
| H | 4.85396688 | -0.92099707 | 0.00079577 |
| H | 3.44102501 | -1.52362623 | -0.89481320 |



$E_{SCF}$ = -461.230263158 Hartrees
Zero-Point Correction = 0.162477 Hartrees
Single Imaginary Frequency = -515.8687 $cm^{-1}$

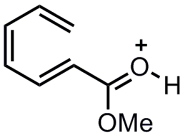
| | | | |
|---|---|---|---|
| C | 2.86206658 | 0.14819491 | -0.07905338 |
| H | 3.93374611 | 0.03083982 | 0.07069430 |
| C | 2.21098743 | 1.13784975 | 0.65201883 |
| H | 2.70719777 | 1.47656713 | 1.56205211 |
| C | 2.20687815 | -0.94999033 | -0.67672245 |
| H | 2.84564416 | -1.78741304 | -0.94990656 |
| C | 0.84690170 | -1.20516091 | -0.54831041 |
| H | 0.55534878 | -2.24103573 | -0.37978005 |
| C | -0.17000993 | -0.23385695 | -0.41638171 |
| H | -0.29138037 | 0.46206757 | -1.22839919 |
| C | 0.90627437 | 1.58085883 | 0.40254618 |

|  |  |  |  |
|---|---|---|---|
| H | 0.67818895 | 1.93896693 | -0.58891372 |
| H | 0.37967373 | 2.11530523 | 1.19181316 |
| C | -1.41087842 | -0.67739799 | 0.28483514 |
| O | -1.45624820 | -1.67400194 | 0.97365783 |
| O | -2.54017990 | 0.08206745 | 0.18313589 |
| C | -2.60174269 | 1.22573678 | -0.66719506 |
| H | -1.87682739 | 1.99323625 | -0.37673962 |
| H | -3.60802058 | 1.62926903 | -0.54531680 |
| H | -2.45500958 | 0.96026821 | -1.72027619 |



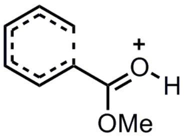
$E_{SCF}$ = -461.292089491 Hartrees
Zero-Point Correction = 0.165446 Hartrees
No Imaginary Frequencies

|  |  |  |  |
|---|---|---|---|
| C | -2.78599769 | -0.48742626 | 0.07782539 |
| H | -3.80597897 | -0.85068323 | 0.16601300 |
| C | -2.41946248 | 0.68426163 | 0.62229479 |
| H | -3.14132786 | 1.30172039 | 1.15044293 |
| C | -1.81964416 | -1.27544473 | -0.68949911 |
| H | -2.18513756 | -2.08824986 | -1.31176158 |
| C | -0.50477845 | -1.01126453 | -0.63192447 |
| H | 0.20749446 | -1.59518974 | -1.20796198 |
| C | 0.01265913 | 0.09394702 | 0.28281338 |
| H | 0.19068958 | -0.35090134 | 1.27476222 |
| C | -1.02299849 | 1.22196743 | 0.43306259 |
| H | -0.73687390 | 1.87168139 | 1.26628999 |
| H | -0.98788718 | 1.85523501 | -0.46530677 |
| C | 1.33588253 | 0.64922248 | -0.24913586 |
| O | 1.42742912 | 1.69682860 | -0.84182635 |
| O | 2.46054682 | -0.10275849 | -0.09147218 |
| C | 2.49613965 | -1.25041767 | 0.76364787 |
| H | 2.35214363 | -0.97084368 | 1.81275471 |
| H | 3.49599318 | -1.66960133 | 0.64433893 |
| H | 1.75627679 | -2.00480086 | 0.48230939 |



$E_{SCF}$ = -461.653133826 Hartrees
Zero-Point Correction = 0.176010 Hartrees
No Imaginary Frequencies

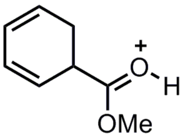
| | | | |
|---|---|---|---|
| C | 1.40764995 | -1.14970499 | 0.00001473 |
| H | 1.10844629 | -2.19434597 | 0.00003875 |
| C | 2.75603699 | -0.86997604 | 0.00002006 |
| H | 3.42855622 | -1.72626289 | 0.00005004 |
| C | 3.39756126 | 0.41489211 | -0.00000806 |
| H | 2.79380183 | 1.31795277 | -0.00003688 |
| C | 4.74271329 | 0.52269349 | -0.00000069 |
| H | 5.23593838 | 1.48876670 | -0.00002385 |
| H | 5.38270663 | -0.35540668 | 0.00002797 |
| C | 0.38376691 | -0.17594843 | -0.00001838 |
| H | 0.66044010 | 0.87486594 | -0.00004258 |
| C | -0.96441931 | -0.48281447 | -0.00003108 |
| H | -1.29004372 | -1.51521375 | 0.00000085 |
| C | -1.94876271 | 0.52123926 | -0.00005932 |
| O | -3.24134605 | 0.33337091 | 0.00002297 |
| C | -3.82270077 | -1.00129047 | 0.00000362 |
| H | -3.52030262 | -1.53563037 | -0.90221833 |
| H | -4.89703981 | -0.83345478 | -0.00008626 |
| H | -3.52044295 | -1.53559214 | 0.90229612 |
| O | -1.59715145 | 1.78896538 | 0.00001996 |
| H | -2.38515403 | 2.36108815 | 0.00012560 |



$E_{SCF}$ = -461.597697796 Hartrees
Zero-Point Correction = 0.175567 Hartrees
Single Imaginary Frequency = -407.1270 $cm^{-1}$

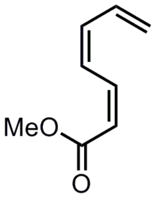
| | | | |
|---|---|---|---|
| C | 2.84523581 | 0.11763171 | 0.13417271 |
| H | 3.84352982 | -0.11773712 | 0.49567468 |
| C | 2.14021038 | 1.13130043 | 0.75429975 |
| H | 2.46584523 | 1.46906315 | 1.73602360 |
| C | 2.25206343 | -0.86317949 | -0.71497891 |
| H | 2.90011285 | -1.67277571 | -1.03761008 |
| C | 0.89848694 | -1.08203657 | -0.80512939 |
| H | 0.59191877 | -2.10945705 | -0.99810204 |
| C | -0.16944676 | -0.12452601 | -0.56101837 |
| H | -0.41710454 | 0.58491681 | -1.33490796 |
| C | 0.96003168 | 1.65225607 | 0.20862766 |

| | | | |
|---|---|---|---|
| H | 0.96206080 | 1.88940239 | -0.84604257 |
| H | 0.31574853 | 2.28121284 | 0.81847624 |
| C | -1.28275204 | -0.56354491 | 0.20637845 |
| O | -2.45560531 | 0.00188517 | 0.28742983 |
| C | -2.84124993 | 1.09679288 | -0.59188863 |
| H | -2.20930828 | 1.96489474 | -0.39796700 |
| H | -3.87325555 | 1.31324130 | -0.32617193 |
| H | -2.77437816 | 0.77727555 | -1.63312678 |
| O | -1.12767676 | -1.59771707 | 0.99627906 |
| H | -1.95438998 | -1.80154629 | 1.47130311 |



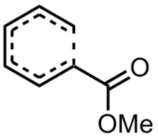
$E_{SCF}$ = -461.640920445 Hartrees
Zero-Point Correction = 0.178140 Hartrees
No Imaginary Frequencies

| | | | |
|---|---|---|---|
| C | -2.83464941 | -0.41310578 | -0.15875259 |
| H | -3.86860547 | -0.66935825 | -0.36440403 |
| C | -2.05646899 | -1.22555984 | 0.57227628 |
| H | -2.42961181 | -2.15690247 | 0.98614759 |
| C | -2.30647716 | 0.85446858 | -0.66448693 |
| H | -3.00202999 | 1.59950808 | -1.03849614 |
| C | -0.98867957 | 1.10287983 | -0.69993521 |
| H | -0.58816387 | 2.02987485 | -1.09493502 |
| C | -0.02823138 | 0.00256281 | -0.27470175 |
| H | 0.13720822 | -0.68760944 | -1.11385432 |
| C | -0.64280084 | -0.82310928 | 0.91654415 |
| H | -0.02458848 | -1.69935962 | 1.13391488 |
| H | -0.64772396 | -0.19088749 | 1.81610067 |
| C | 1.28860141 | 0.50778723 | 0.17483454 |
| O | 2.43136241 | -0.05420749 | -0.00923231 |
| C | 2.61009282 | -1.29210064 | -0.78476332 |
| H | 2.01333652 | -2.08853753 | -0.34193238 |
| H | 3.67177100 | -1.50743283 | -0.69492950 |
| H | 2.33778936 | -1.10443152 | -1.82332197 |
| O | 1.31093199 | 1.59962929 | 0.86948752 |
| H | 2.21394183 | 1.82882430 | 1.16757761 |



$E_{SCF}$ = -461.277110556 Hartrees
Zero-Point Correction = 0.162893 Hartrees
No Imaginary Frequencies

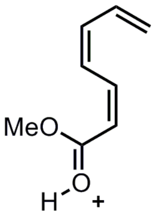
| | | | |
|---|---|---|---|
| C | 2.54036342 | 0.61868143 | 0.00007920 |
| H | 3.03056367 | 1.59147677 | 0.00029480 |
| C | 1.18079329 | 0.61216643 | -0.00021535 |
| H | 0.64999491 | 1.55615351 | -0.00011856 |
| C | 0.36298387 | -0.57838060 | -0.00063847 |
| H | 0.88723914 | -1.53200156 | -0.00111579 |
| C | -0.99253146 | -0.65882678 | -0.00060357 |
| H | -1.42582485 | -1.65152539 | -0.00104677 |
| C | 3.43997749 | -0.51918882 | 0.00018955 |
| H | 3.01057540 | -1.51837834 | 0.00016984 |
| C | 4.77734170 | -0.39431840 | 0.00037057 |
| H | 5.25487980 | 0.58210513 | 0.00043523 |
| H | 5.43216216 | -1.25923169 | 0.00045246 |
| C | -1.91163468 | 0.50029780 | -0.00011640 |
| O | -1.56505287 | 1.66523576 | -0.00001683 |
| O | -3.25621529 | 0.25382794 | 0.00020484 |
| C | -3.79447629 | -1.06754551 | 0.00052714 |
| H | -3.50451156 | -1.62834114 | -0.89491256 |
| H | -4.87825699 | -0.94179162 | 0.00108373 |
| H | -3.50358053 | -1.62828860 | 0.89569751 |



$E_{SCF}$ = -461.222944393 Hartrees
Zero-Point Correction = 0.162355 Hartrees
Single Imaginary Frequency = -485.0193 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.66046775 | 0.19875581 | 0.20087930 |
| H | 3.74193713 | 0.22245224 | 0.32176180 |
| C | 1.98535031 | 1.41500587 | 0.14384841 |
| H | 2.57270859 | 2.29431225 | -0.12240088 |
| C | 2.12842336 | -1.02343695 | -0.25794169 |

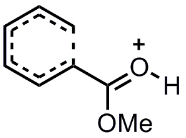
| | | | |
|---|---|---|---|
| H | 2.85116986 | -1.82343994 | -0.40518641 |
| C | 0.91792926 | -1.13918539 | -0.93246965 |
| H | 0.93408918 | -1.80533279 | -1.79773576 |
| C | -0.25252891 | -0.36857678 | -0.76208004 |
| H | -0.83794327 | -0.25524499 | -1.67403887 |
| C | 0.59989814 | 1.53887412 | 0.26862462 |
| H | 0.12429438 | 2.46842299 | -0.04003059 |
| H | 0.14559401 | 1.05426172 | 1.11710783 |
| C | -1.08782885 | -0.53278318 | 0.46040031 |
| O | -0.72081432 | -1.04969401 | 1.49249745 |
| O | -2.37641988 | -0.07440400 | 0.40571232 |
| C | -2.88801884 | 0.63745792 | -0.71970659 |
| H | -2.23930520 | 1.47041484 | -1.00925578 |
| H | -3.85506813 | 1.03181519 | -0.40313615 |
| H | -3.04175629 | -0.02154584 | -1.58209143 |



$E_{SCF}$ = -461.648353678 Hartrees
Zero-Point Correction = 0.176257 Hartrees
No Imaginary Frequencies

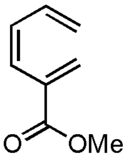
| | | | |
|---|---|---|---|
| C | 2.59910104 | 0.58965823 | 0.00009245 |
| H | 3.09569046 | 1.55882231 | 0.00034716 |
| C | 1.22012371 | 0.61395733 | 0.00017999 |
| H | 0.73673528 | 1.58199031 | 0.00029987 |
| C | 0.41984806 | -0.55188264 | 0.00022225 |
| H | 0.94761853 | -1.50229881 | 0.00014032 |
| C | -0.96254975 | -0.68428714 | 0.00025785 |
| H | -1.36545665 | -1.68800017 | 0.00033415 |
| C | 3.48057980 | -0.54403762 | -0.00023483 |
| H | 3.07051344 | -1.54986353 | -0.00063719 |
| C | 4.82049842 | -0.38180591 | -0.00009923 |
| H | 5.27286443 | 0.60616717 | 0.00026495 |
| H | 5.49623621 | -1.23034405 | -0.00035323 |
| C | -1.90846736 | 0.35589013 | -0.00002532 |
| O | -3.20711535 | 0.20080071 | -0.00022420 |
| C | -3.83241555 | -1.11377882 | -0.00001005 |
| H | -3.54825151 | -1.65802093 | -0.90220404 |
| H | -4.90038264 | -0.90907471 | -0.00009907 |
| H | -3.54837194 | -1.65766705 | 0.90243111 |

|  |  |  |  |
|---|---|---|---|
| O | -1.53753962 | 1.61764447 | -0.00012129 |
| H | -2.32026610 | 2.19844661 | -0.00005872 |



$E_{SCF}$ = -461.595323975 Hartrees
Zero-Point Correction = 0.175350 Hartrees
Single Imaginary Frequency = -347.5207 $cm^{-1}$

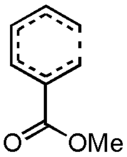
|  |  |  |  |
|---|---|---|---|
| C | 2.78295995 | 0.26453320 | 0.00781738 |
| H | 3.85926437 | 0.34791684 | -0.12585207 |
| C | 2.04701005 | 1.42248247 | 0.18209391 |
| H | 2.49624816 | 2.37587172 | -0.08778936 |
| C | 2.22243043 | -1.00401483 | -0.32054100 |
| H | 2.92973205 | -1.80912092 | -0.49666833 |
| C | 0.95665031 | -1.18071294 | -0.82751763 |
| H | 0.84230911 | -2.01595501 | -1.52042879 |
| C | -0.20726684 | -0.31592539 | -0.73369819 |
| H | -0.64937429 | -0.05108391 | -1.69432703 |
| C | 0.72166235 | 1.38945120 | 0.61931336 |
| H | 0.10781071 | 2.28483695 | 0.56474295 |
| H | 0.47520565 | 0.69142799 | 1.40673933 |
| C | -1.16290878 | -0.45843498 | 0.28399595 |
| O | -2.38949656 | 0.00431551 | 0.26243850 |
| C | -2.89598832 | 0.77359409 | -0.86123911 |
| H | -2.26000328 | 1.64320736 | -1.03692813 |
| H | -3.89302886 | 1.08435176 | -0.55772874 |
| H | -2.95089158 | 0.13887214 | -1.74805730 |
| O | -0.87383354 | -1.11892897 | 1.38790567 |
| H | -1.63792625 | -1.11925422 | 1.99219611 |



$E_{SCF}$ = -461.282039183 Hartrees
Zero-Point Correction = 0.162560 Hartrees
No Imaginary Frequencies

|  |  |  |  |
|---|---|---|---|
| H | 2.41269506 | 0.80343701 | 0.92855585 |
| C | 2.84929608 | -0.04426606 | 0.40582081 |

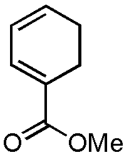
| | | | |
|---|---|---|---|
| C | 1.96150399 | -0.85188113 | -0.41583121 |
| C | 4.15444118 | -0.31113707 | 0.56760078 |
| H | 2.39398701 | -1.77632320 | -0.79693824 |
| C | 0.66545588 | -0.61334912 | -0.71503619 |
| H | 0.12502682 | -1.38475618 | -1.25601020 |
| C | -0.12604817 | 0.57629597 | -0.36325615 |
| C | -1.56574727 | 0.39541196 | 0.03480093 |
| C | 0.32009285 | 1.84400407 | -0.41658819 |
| H | -0.33850319 | 2.66040914 | -0.14145115 |
| H | 1.32245392 | 2.07967909 | -0.75423425 |
| H | 4.63218920 | -1.14499414 | 0.05934973 |
| H | 4.78520725 | 0.29631799 | 1.20809580 |
| O | -2.31703831 | 1.29116902 | 0.36269897 |
| O | -1.94330329 | -0.90258714 | -0.01399504 |
| C | -3.31095438 | -1.15480516 | 0.34624503 |
| H | -3.50459336 | -0.82458713 | 1.36951611 |
| H | -3.44393238 | -2.23277824 | 0.25857004 |
| H | -3.99003845 | -0.62670013 | -0.32762000 |



$E_{SCF}$ = -461.243865583 Hartrees
Zero-Point Correction = 0.162468 Hartrees
Single Imaginary Frequency = -528.5674 $cm^{-1}$

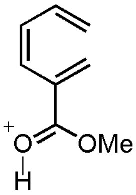
| | | | |
|---|---|---|---|
| H | 3.22932103 | -0.98395604 | 1.48693261 |
| C | 2.77002224 | -0.57049002 | 0.58645407 |
| C | 1.90848584 | -1.44871026 | -0.09232391 |
| C | 2.92432908 | 0.79434855 | 0.35291610 |
| H | 2.08042624 | -2.51513070 | 0.04177939 |
| C | 0.64051999 | -1.09474108 | -0.56291742 |
| H | -0.05596766 | -1.90906301 | -0.73551596 |
| C | 0.12005814 | 0.21166367 | -0.46899718 |
| C | -1.28586870 | 0.41928058 | -0.01779338 |
| C | 0.92017470 | 1.35220047 | -0.59087238 |
| H | 3.19867554 | 1.14201629 | -0.62848739 |
| H | 3.33389527 | 1.40677108 | 1.15543662 |
| H | 0.51878588 | 2.29553562 | -0.23136242 |
| H | 1.55633580 | 1.42131120 | -1.45720491 |
| O | -1.74316093 | 1.48187073 | 0.35944653 |
| O | -2.02951662 | -0.71408060 | -0.08570801 |
| C | -3.40408060 | -0.56205489 | 0.29576916 |

| | | | |
|---|---|---|---|
| H | -3.48265333 | -0.23961692 | 1.33697716 |
| H | -3.85612739 | -1.54536368 | 0.16530974 |
| H | -3.90311514 | 0.17619305 | -0.33718328 |



$E_{SCF}$ = -461.316767056 Hartrees
Zero-Point Correction = 0.165806 Hartrees
No Imaginary Frequencies

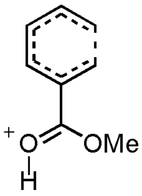
| | | | |
|---|---|---|---|
| H | -4.03545257 | -0.62129757 | 0.04658302 |
| C | -2.96518732 | -0.42970503 | 0.04903990 |
| C | -2.09139903 | -1.43537667 | -0.13912067 |
| C | -2.47717523 | 0.96461181 | 0.35815457 |
| H | -2.43827934 | -2.45101089 | -0.30738607 |
| C | -0.65450898 | -1.19311262 | -0.06430107 |
| H | 0.02057700 | -2.03959130 | 0.00505473 |
| C | -0.15919108 | 0.06446893 | -0.08673966 |
| C | 1.28957037 | 0.35719850 | -0.03934707 |
| C | -1.09769152 | 1.24022619 | -0.25959543 |
| H | -2.43047118 | 1.07673430 | 1.45419451 |
| H | -3.19801399 | 1.71272117 | 0.01172383 |
| H | -1.20897537 | 1.43585818 | -1.33744206 |
| H | -0.64931992 | 2.14078231 | 0.16590392 |
| O | 1.76057290 | 1.47947728 | -0.10070235 |
| O | 2.05968803 | -0.75480243 | 0.08101104 |
| C | 3.47239373 | -0.51183919 | 0.13005432 |
| H | 3.81218240 | -0.01456207 | -0.78202281 |
| H | 3.93696965 | -1.49335144 | 0.22559196 |
| H | 3.72783022 | 0.11748689 | 0.98646020 |



$E_{SCF}$ = -461.617780626 Hartrees
Zero-Point Correction = 0.174701 Hartrees
No Imaginary Frequencies

| | | | |
|---|---|---|---|
| H | 2.47190529 | 0.82585837 | 0.93748709 |

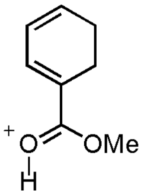
| | | | |
|---|---|---|---|
| C | 2.89192108 | -0.02558882 | 0.40705286 |
| C | 2.01416371 | -0.82974618 | -0.42313800 |
| C | 4.19347042 | -0.31537023 | 0.56526925 |
| H | 2.46080398 | -1.73880748 | -0.82200826 |
| C | 0.71199133 | -0.62523791 | -0.72872222 |
| H | 0.19460681 | -1.39308655 | -1.29517382 |
| C | -0.09202467 | 0.55192652 | -0.36369603 |
| C | -1.48456701 | 0.31749424 | -0.00401281 |
| C | 0.32903477 | 1.84357796 | -0.36630567 |
| H | -0.30901826 | 2.66239425 | -0.05458369 |
| H | 1.33237771 | 2.08863403 | -0.69312632 |
| H | 4.65626972 | -1.15412487 | 0.05247660 |
| H | 4.83498721 | 0.28011778 | 1.20559659 |
| O | -1.90420201 | -0.90290703 | 0.02968165 |
| C | -3.28684784 | -1.25208316 | 0.34761558 |
| H | -3.51828491 | -0.94639954 | 1.37131351 |
| H | -3.32032535 | -2.33592582 | 0.26985658 |
| H | -3.96147380 | -0.80420492 | -0.38674167 |
| O | -2.26240001 | 1.33130105 | 0.25783810 |
| H | -3.17188306 | 1.09855797 | 0.51036771 |



$E_{SCF}$ = -461.594966929 Hartrees
Zero-Point Correction = 0.174555 Hartrees
Single Imaginary Frequency = -392.0461 $cm^{-1}$

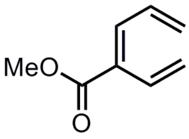
| | | | |
|---|---|---|---|
| H | 3.07716277 | -0.98821499 | 1.58796776 |
| C | 2.72820340 | -0.56749710 | 0.64294355 |
| C | 1.92383162 | -1.44616113 | -0.13830439 |
| C | 2.98339162 | 0.76479811 | 0.40059895 |
| H | 2.15256416 | -2.50853477 | -0.09528504 |
| C | 0.69202395 | -1.10168503 | -0.64627619 |
| H | 0.04522565 | -1.89988284 | -0.99644744 |
| C | 0.13844973 | 0.21687056 | -0.47103466 |
| C | -1.21013369 | 0.33399467 | -0.04246017 |
| C | 0.93076770 | 1.37097600 | -0.57234280 |
| H | 3.22325691 | 1.10055991 | -0.59591905 |
| H | 3.39048565 | 1.38077276 | 1.19827412 |
| H | 0.61221456 | 2.30515813 | -0.12114351 |
| H | 1.57494207 | 1.45980071 | -1.43091443 |

| | | | |
|---|---|---|---|
| O | -1.94385446 | -0.74253708 | 0.05979893 |
| C | -3.37812846 | -0.67324450 | 0.28850368 |
| H | -3.58044527 | -0.31589016 | 1.30258700 |
| H | -3.72470008 | -1.69965538 | 0.19387488 |
| H | -3.85492417 | -0.04752394 | -0.47056202 |
| O | -1.70313649 | 1.53033868 | 0.19842076 |
| H | -2.59028979 | 1.52268828 | 0.59204245 |



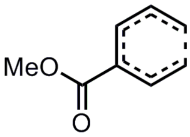
$E_{SCF}$ = -461.667677047 Hartrees
Zero-Point Correction = 0.178148 Hartrees
No Imaginary Frequencies

| | | | |
|---|---|---|---|
| H | 4.09968617 | -0.16887860 | 0.07873184 |
| C | 3.01575728 | -0.09108391 | 0.04400399 |
| C | 2.43514227 | 1.12303786 | -0.13714180 |
| C | 2.20894068 | -1.32688371 | 0.30102538 |
| H | 3.03427448 | 2.01857014 | -0.25799256 |
| C | 1.00994851 | 1.24643165 | -0.06245644 |
| H | 0.57757325 | 2.24053541 | 0.00561537 |
| C | 0.18705883 | 0.14120933 | -0.06774549 |
| C | -1.21454502 | 0.32086316 | 0.01182941 |
| C | 0.78233463 | -1.24109671 | -0.26929292 |
| H | 2.19067517 | -1.48078567 | 1.39256554 |
| H | 2.71977385 | -2.20474609 | -0.10602362 |
| H | 0.80639059 | -1.44985548 | -1.34744628 |
| H | 0.15258141 | -2.01004293 | 0.18192725 |
| O | -1.97857996 | -0.73722478 | -0.06951728 |
| C | -3.42617133 | -0.64891330 | 0.01416303 |
| H | -3.72587075 | -0.24013057 | 0.98344768 |
| H | -3.77341535 | -1.67587941 | -0.07157043 |
| H | -3.81854403 | -0.06024971 | -0.82020852 |
| O | -1.71732419 | 1.52855519 | 0.16606740 |
| H | -2.68668673 | 1.55943343 | 0.18224176 |



$E_{SCF}$ = -461.284504052 Hartrees
Zero-Point Correction = 0.162432 Hartrees
No Imaginary Frequencies

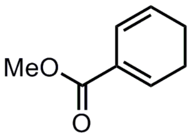
| | | | |
|---|---|---|---|
| C | -0.16543043 | 0.16038579 | -0.06707443 |
| C | -1.24692719 | -0.66098554 | -0.00424621 |
| H | -1.03290485 | -1.71484253 | 0.16254084 |
| C | -2.63772613 | -0.30287468 | -0.18716849 |
| H | -2.86133113 | 0.71653976 | -0.48979545 |
| C | -3.64049619 | -1.18138491 | -0.01956343 |
| H | -4.67593662 | -0.90132791 | -0.18305744 |
| H | -3.45242644 | -2.20528250 | 0.29265804 |
| C | -0.19382249 | 1.62159344 | -0.24965936 |
| H | 0.56954129 | 2.02691177 | -0.90960131 |
| C | -1.03368871 | 2.46839169 | 0.35880662 |
| H | -0.98883510 | 3.53535839 | 0.16393411 |
| H | -1.76669959 | 2.13354085 | 1.08614174 |
| C | 1.16502608 | -0.51703041 | 0.03277923 |
| O | 1.33970151 | -1.70708185 | 0.21402857 |
| O | 2.18894756 | 0.36032386 | -0.10378495 |
| C | 3.50117138 | -0.21659506 | -0.02679558 |
| H | 3.65057444 | -0.70411262 | 0.93959163 |
| H | 4.19540177 | 0.61468009 | -0.14852788 |
| H | 3.64478566 | -0.95640324 | -0.81830346 |



$E_{SCF}$ = -461.242282722 Hartrees
Zero-Point Correction = 0.162062 Hartrees
Single Imaginary Frequency = -567.7264 $cm^{-1}$

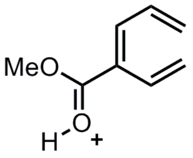
| | | | |
|---|---|---|---|
| C | 0.68042053 | -1.14709511 | 0.02782572 |
| H | -0.05894015 | -1.93125428 | -0.10169091 |
| C | 2.00640327 | -1.45215668 | -0.27717532 |
| H | 2.14222516 | -2.28919853 | -0.96480904 |
| C | 0.16420707 | 0.16624492 | 0.09380255 |
| C | 0.95898731 | 1.30545319 | -0.11684162 |
| H | 0.50367786 | 2.08893311 | -0.72012246 |
| C | 2.29486912 | 1.41817635 | 0.25679910 |
| H | 2.89351506 | 2.21350108 | -0.18327032 |
| H | 2.55715461 | 1.19248788 | 1.27750053 |
| C | 3.13540357 | -0.68955375 | 0.04186286 |
| H | 4.03365561 | -0.83264438 | -0.55859683 |

|  |  |  |  |
|---|---|---|---|
| H | 3.35000303 | -0.47012020 | 1.07411955 |
| C | -1.31046268 | 0.37490682 | -0.03308424 |
| O | -1.83629744 | 1.43834199 | -0.30253716 |
| O | -2.02546986 | -0.75107146 | 0.21032245 |
| C | -3.44928817 | -0.60038364 | 0.11319315 |
| H | -3.73941798 | -0.30811792 | -0.89924177 |
| H | -3.80481972 | 0.16061804 | 0.81206856 |
| H | -3.86615520 | -1.57592156 | 0.36346722 |



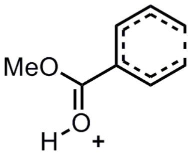
$E_{SCF}$ = -461.295210321 Hartrees
Zero-Point Correction = 0.165060 Hartrees
No Imaginary Frequencies

|  |  |  |  |
|---|---|---|---|
| C | -0.49063558 | -0.89629614 | -0.79185319 |
| H | 0.16168671 | -1.47090255 | -1.44300491 |
| C | -1.76221112 | -1.27206787 | -0.58759963 |
| H | -2.15199695 | -2.17333267 | -1.05343141 |
| C | 0.04297069 | 0.32917778 | -0.16936707 |
| C | -0.80464208 | 1.23659331 | 0.35609158 |
| H | -0.41014534 | 2.17097666 | 0.74492622 |
| C | -2.29332479 | 1.01330047 | 0.33112226 |
| H | -2.77581191 | 1.52666815 | 1.16934048 |
| H | -2.68766313 | 1.48892227 | -0.58245746 |
| C | -2.65743561 | -0.48181440 | 0.33794175 |
| H | -2.55384908 | -0.88359457 | 1.35907404 |
| H | -3.71017435 | -0.61276540 | 0.06768184 |
| C | 1.50737716 | 0.65213248 | -0.19396840 |
| O | 1.93488673 | 1.76421769 | -0.40375136 |
| O | 2.39877722 | -0.36313427 | -0.00030191 |
| C | 2.04563039 | -1.53640999 | 0.74260675 |
| H | 1.75372698 | -2.35379759 | 0.07702447 |
| H | 1.23569037 | -1.34149605 | 1.45014298 |
| H | 2.94285085 | -1.82703952 | 1.29328551 |



$E_{SCF}$ = -461.628708815 Hartrees
Zero-Point Correction = 0.175269 Hartrees
No Imaginary Frequencies

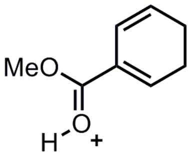
| | | | |
|---|---|---|---|
| C | 0.05661094 | 0.02073461 | 0.14873345 |
| C | 1.29930354 | -0.54801164 | -0.06602786 |
| H | 1.32782898 | -1.59577565 | -0.35414929 |
| C | 2.57180061 | 0.09450469 | 0.07225023 |
| H | 2.60814725 | 1.11605947 | 0.43462091 |
| C | 3.71370467 | -0.56827606 | -0.21555301 |
| H | 4.68547552 | -0.10362439 | -0.08590443 |
| H | 3.70455717 | -1.58851504 | -0.58987132 |
| C | -0.15404415 | 1.44453789 | 0.51218444 |
| H | -0.75673999 | 1.62792930 | 1.40028350 |
| C | 0.37468491 | 2.48340832 | -0.14228593 |
| H | 0.22012979 | 3.49869907 | 0.20770641 |
| H | 0.96506029 | 2.36065717 | -1.04562829 |
| C | -1.06320655 | -0.87824631 | 0.08921343 |
| O | -2.32717699 | -0.58918121 | 0.01515592 |
| C | -2.90231503 | 0.69943655 | -0.38296887 |
| H | -3.02700342 | 1.31915511 | 0.50320299 |
| H | -3.87040155 | 0.43468666 | -0.80349101 |
| H | -2.26786128 | 1.18309279 | -1.12191822 |
| O | -0.83593641 | -2.16982801 | 0.15227470 |
| H | -1.66351921 | -2.66881907 | 0.02242853 |



$E_{SCF}$ = -461.589710442 Hartrees
Zero-Point Correction = 0.174857 Hartrees
Single Imaginary Frequency = -513.5010 $cm^{-1}$

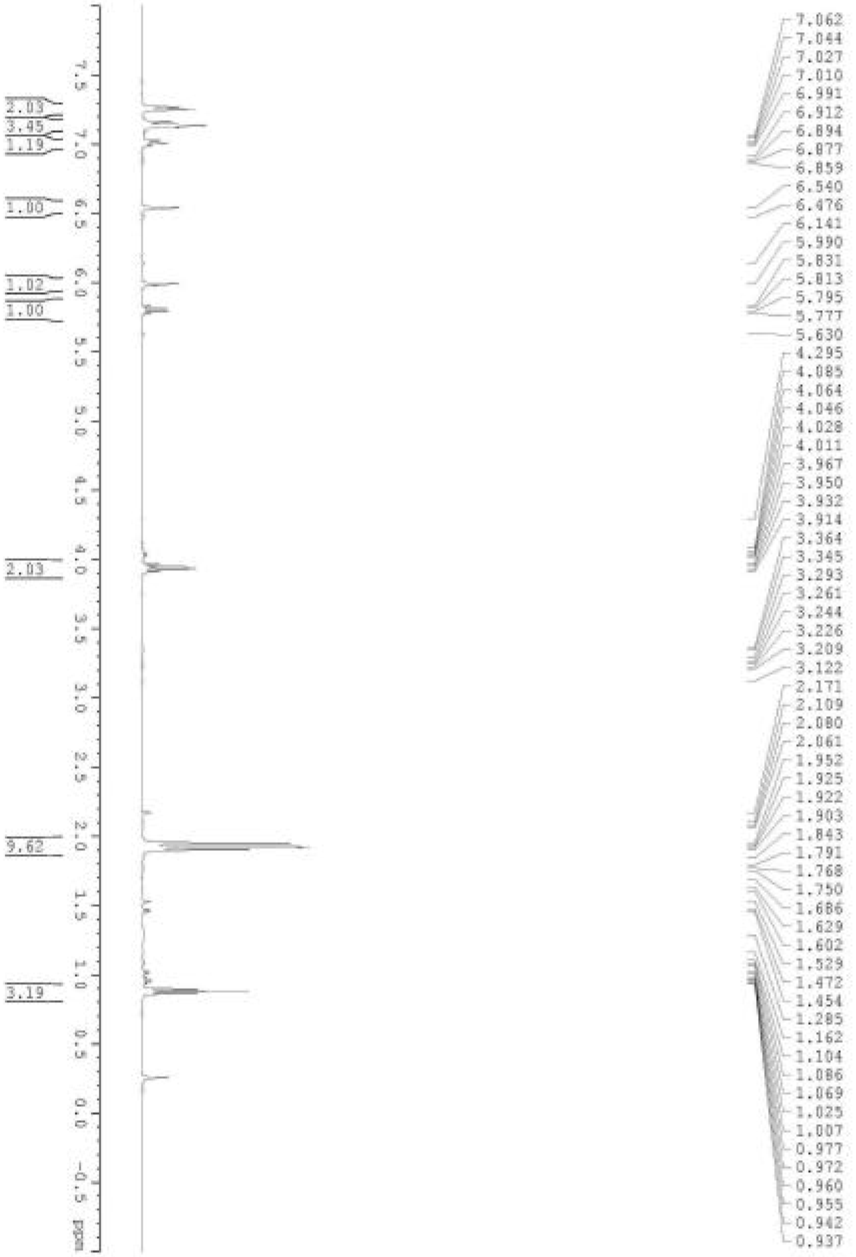
| | | | |
|---|---|---|---|
| C | -1.02938094 | -1.18911367 | 0.27141109 |
| H | -0.67278397 | -2.20540338 | 0.39784291 |
| C | -2.36741735 | -1.02040990 | -0.04453127 |
| H | -2.83277566 | -1.90008797 | -0.49567684 |
| C | -0.03078663 | -0.18484459 | 0.06940876 |
| C | -0.38555045 | 1.13633081 | -0.33368286 |
| H | 0.16706276 | 1.58759656 | -1.15538254 |
| C | -1.53256040 | 1.75079421 | 0.12359531 |
| H | -1.77363899 | 1.62995723 | 1.17043406 |
| H | -1.88497105 | 2.66654175 | -0.33990739 |

|  |  |  |  |
|---|---|---|---|
| C | -3.14412860 | 0.14734803 | -0.04375266 |
| H | -3.36019801 | 0.67158281 | 0.87329635 |
| H | -3.94049167 | 0.22919962 | -0.78313684 |
| C | 1.32147500 | -0.64437223 | -0.03869334 |
| O | 2.41024549 | 0.06427272 | -0.11108638 |
| C | 2.54695267 | 1.49498637 | 0.15565323 |
| H | 1.78020751 | 1.82402199 | 0.85568622 |
| H | 2.48234730 | 2.03348746 | -0.78891150 |
| H | 3.54374900 | 1.59694651 | 0.58080790 |
| O | 1.55327532 | -1.93503928 | -0.04492909 |
| H | 2.51170633 | -2.11202429 | -0.02337823 |

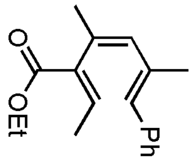


$E_{SCF}$ = -461.657937455 Hartrees
Zero-Point Correction = 0.177606 Hartrees
No Imaginary Frequencies

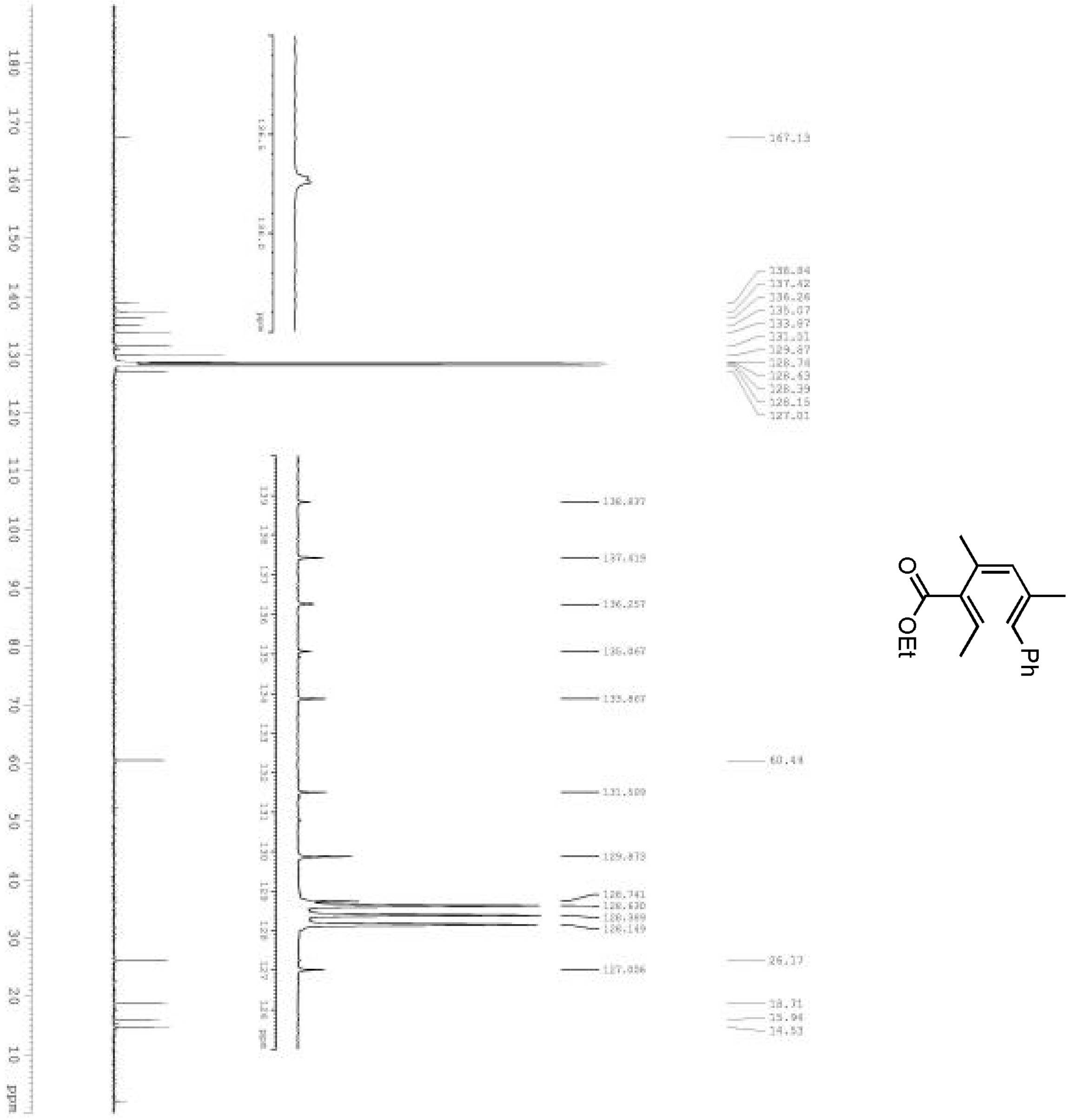
|  |  |  |  |
|---|---|---|---|
| C | -0.73156060 | -1.25023587 | -0.17541556 |
| H | -0.05800908 | -2.07579075 | -0.36939038 |
| C | -2.04686146 | -1.44326748 | -0.00643204 |
| H | -2.45182992 | -2.44975290 | -0.05484188 |
| C | -0.17423994 | 0.11055899 | -0.06874848 |
| C | -0.99267410 | 1.20586783 | -0.05449458 |
| H | -0.57348558 | 2.20651394 | -0.00042541 |
| C | -2.46767985 | 1.04617785 | -0.19025426 |
| H | -2.98770675 | 1.88163612 | 0.28797996 |
| H | -2.67783595 | 1.15363237 | -1.27021273 |
| C | -2.98943582 | -0.31198711 | 0.31635512 |
| H | -3.13573345 | -0.27910460 | 1.40604347 |
| H | -3.97825220 | -0.50248365 | -0.10975405 |
| C | 1.24489329 | 0.31013851 | 0.00416473 |
| O | 2.01136458 | -0.73689088 | -0.02286370 |
| C | 3.46407515 | -0.64350726 | 0.04515604 |
| H | 3.84408239 | -0.09036607 | -0.81808713 |
| H | 3.80913754 | -1.67367946 | 0.00218866 |
| H | 3.76549970 | -0.19263091 | 0.99459006 |
| O | 1.72726001 | 1.52500658 | 0.09423267 |
| H | 2.69603652 | 1.57462746 | 0.13897169 |

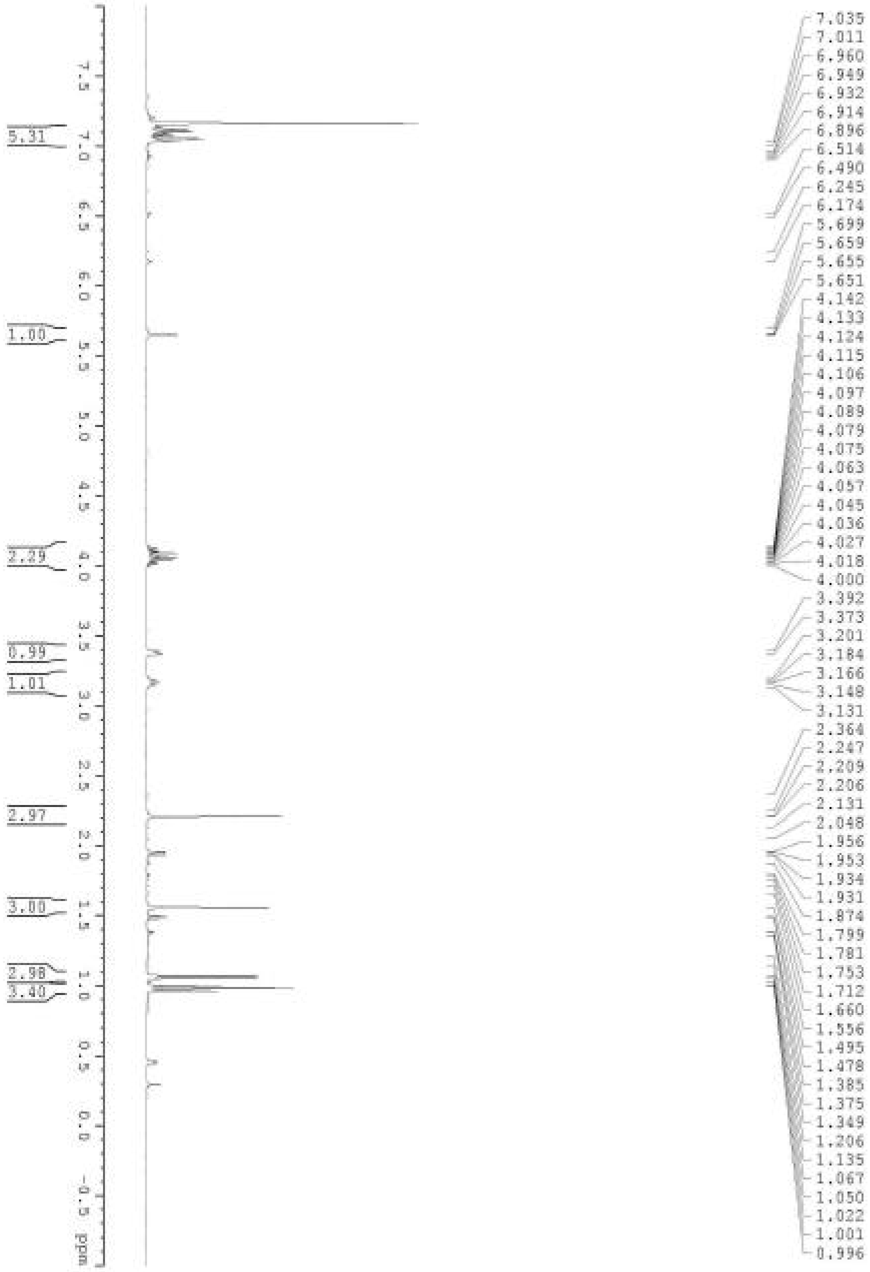


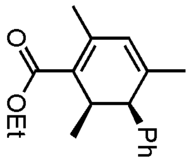
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5 ppm
2.03
3.45
1.19
1.00
1.02
1.00
2.03
9.62
3.19
7.062
7.044
7.027
7.010
6.991
6.912
6.894
6.877
6.859
6.540
6.476
6.141
5.990
5.831
5.813
5.795
5.777
5.630
4.295
4.085
4.064
4.046
4.028
4.011
3.967
3.950
3.932
3.914
3.364
3.345
3.293
3.261
3.244
3.226
3.209
3.122
2.171
2.109
2.080
2.061
1.952
1.925
1.922
1.903
1.843
1.791
1.768
1.750
1.686
1.629
1.602
1.529
1.472
1.454
1.285
1.162
1.104
1.086
1.069
1.025
1.007
0.977
0.972
0.960
0.955
0.942
0.937

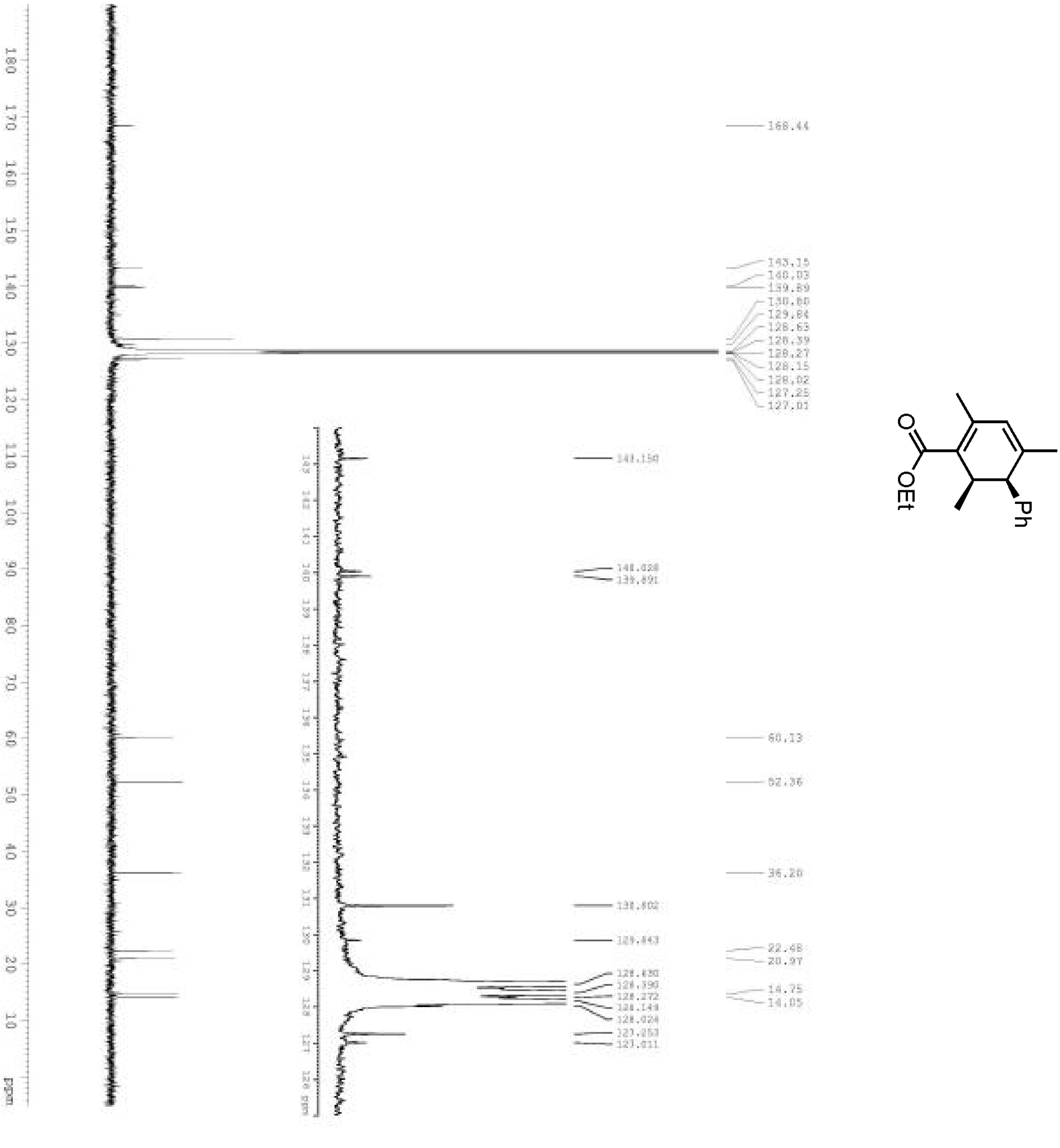


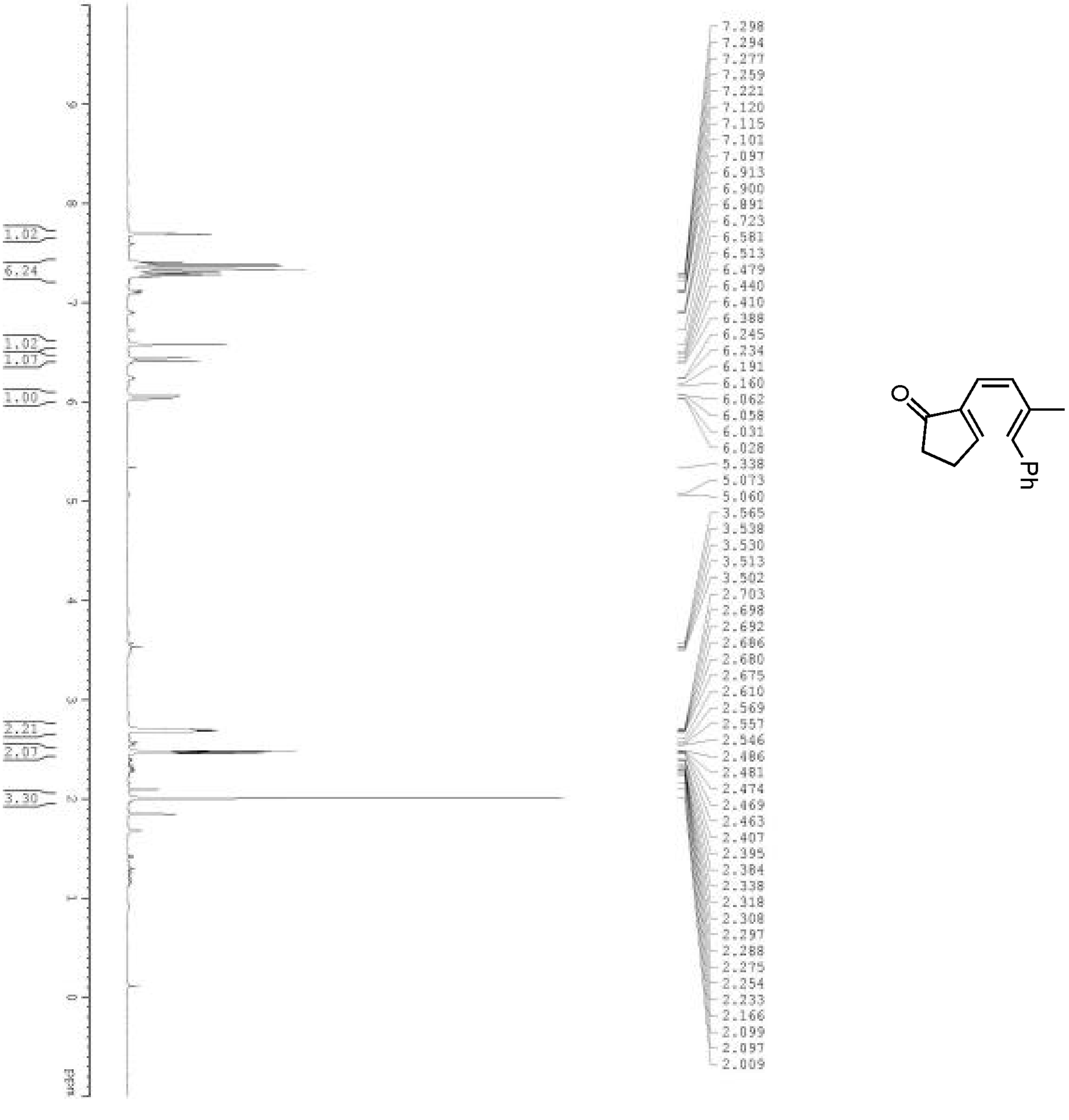
O
OEt
Ph

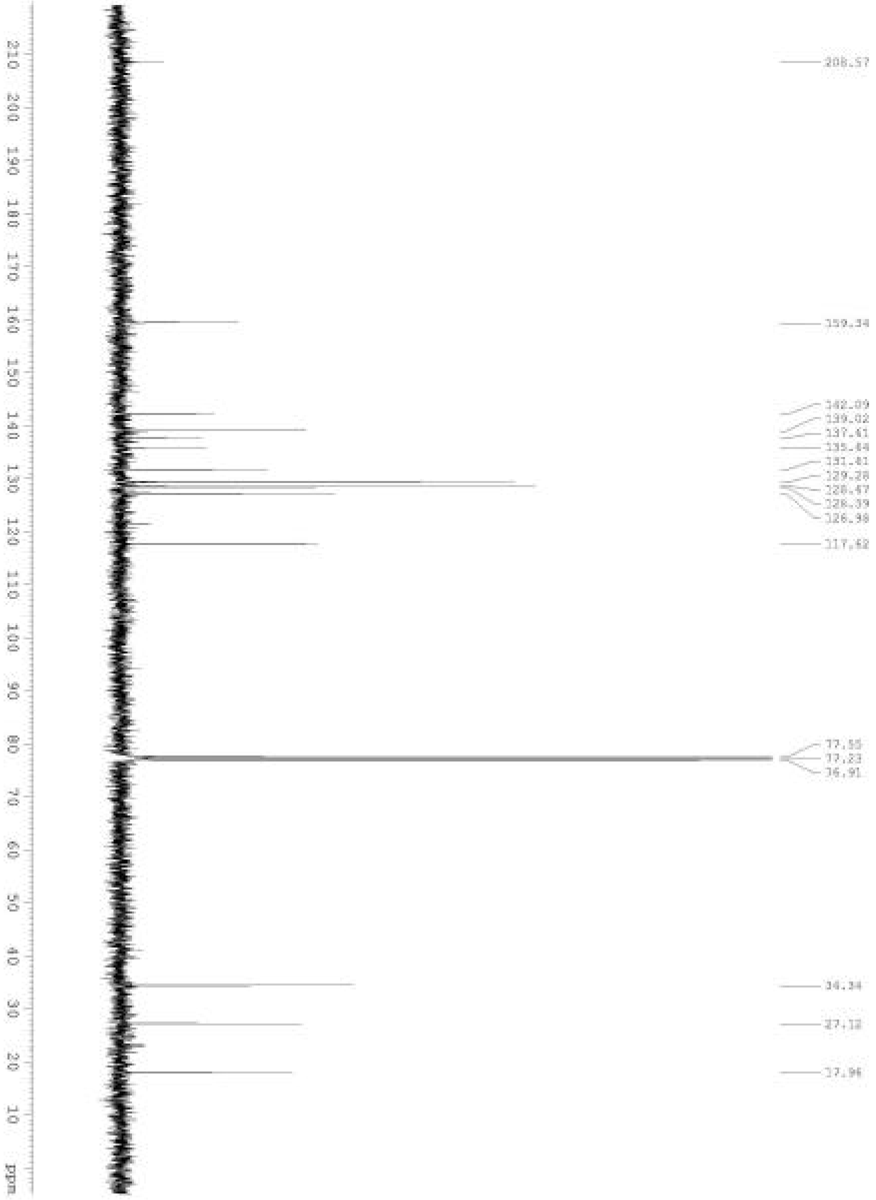

167.13
138.84
137.42
136.26
135.07
133.87
131.51
129.87
128.74
128.63
128.39
128.15
127.01
60.44
26.17
18.71
15.94
14.53
138.837
137.419
136.257
135.067
133.867
131.509
129.873
128.741
128.630
128.389
128.149
127.036
OEt
Ph
ppm

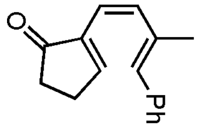

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
5.31
1.00
2.29
0.99
1.01
2.97
3.00
2.98
3.40
7.035
7.011
6.960
6.949
6.932
6.914
6.896
6.514
6.490
6.245
6.174
5.699
5.659
5.655
5.651
4.142
4.133
4.124
4.115
4.106
4.097
4.089
4.079
4.075
4.063
4.057
4.045
4.036
4.027
4.018
4.000
3.392
3.373
3.201
3.184
3.166
3.148
3.131
2.364
2.247
2.209
2.206
2.131
2.048
1.956
1.953
1.934
1.931
1.874
1.799
1.781
1.753
1.712
1.660
1.556
1.495
1.478
1.385
1.375
1.349
1.206
1.135
1.067
1.050
1.022
1.001
0.996

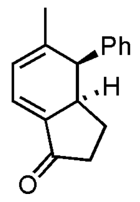

O
OEt
Ph

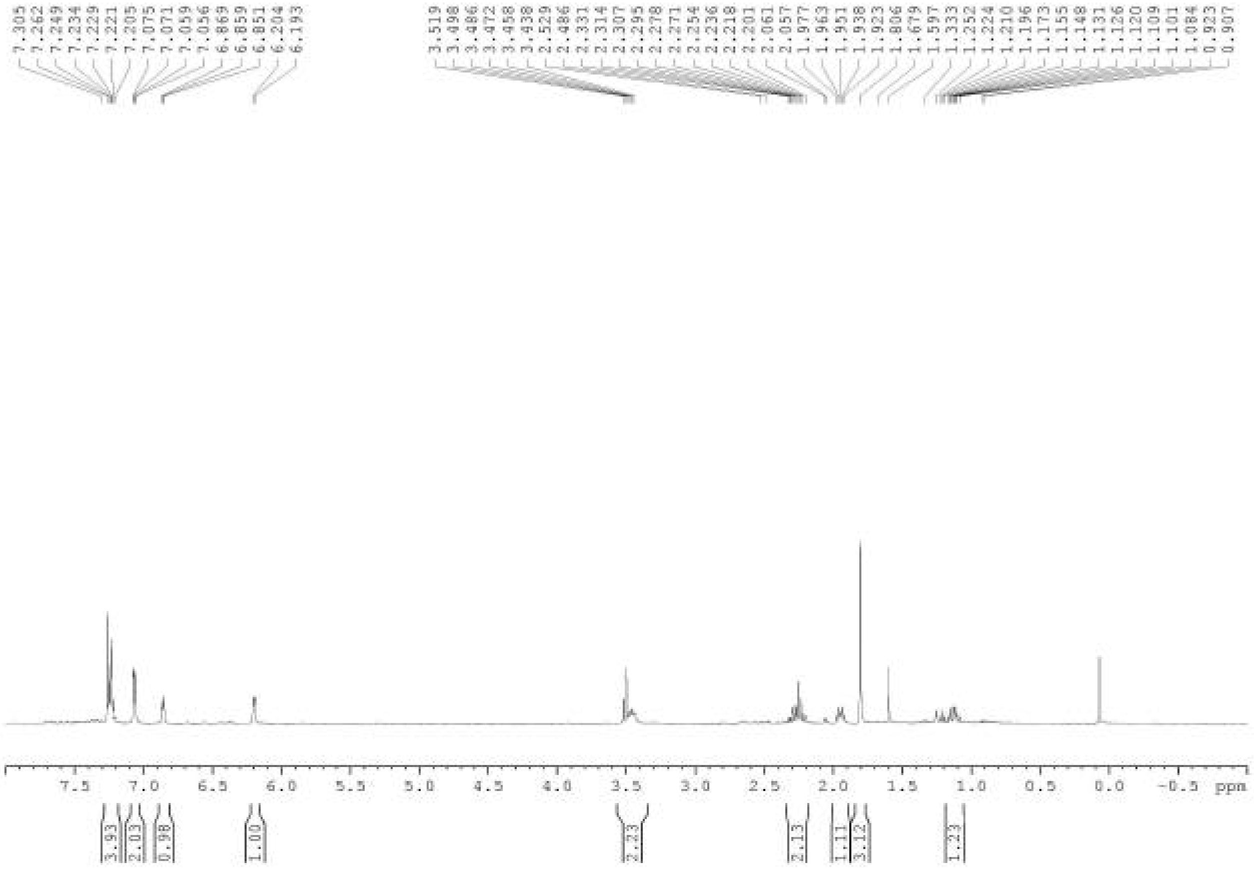

168.44
143.15
140.03
139.89
130.80
129.84
128.63
128.39
128.27
128.15
128.02
127.25
127.01
60.13
52.36
36.28
22.48
20.97
14.75
14.05
143.150
140.028
139.891
130.802
129.843
128.630
128.390
128.272
128.149
128.024
127.253
127.011
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
O
OEt
Ph

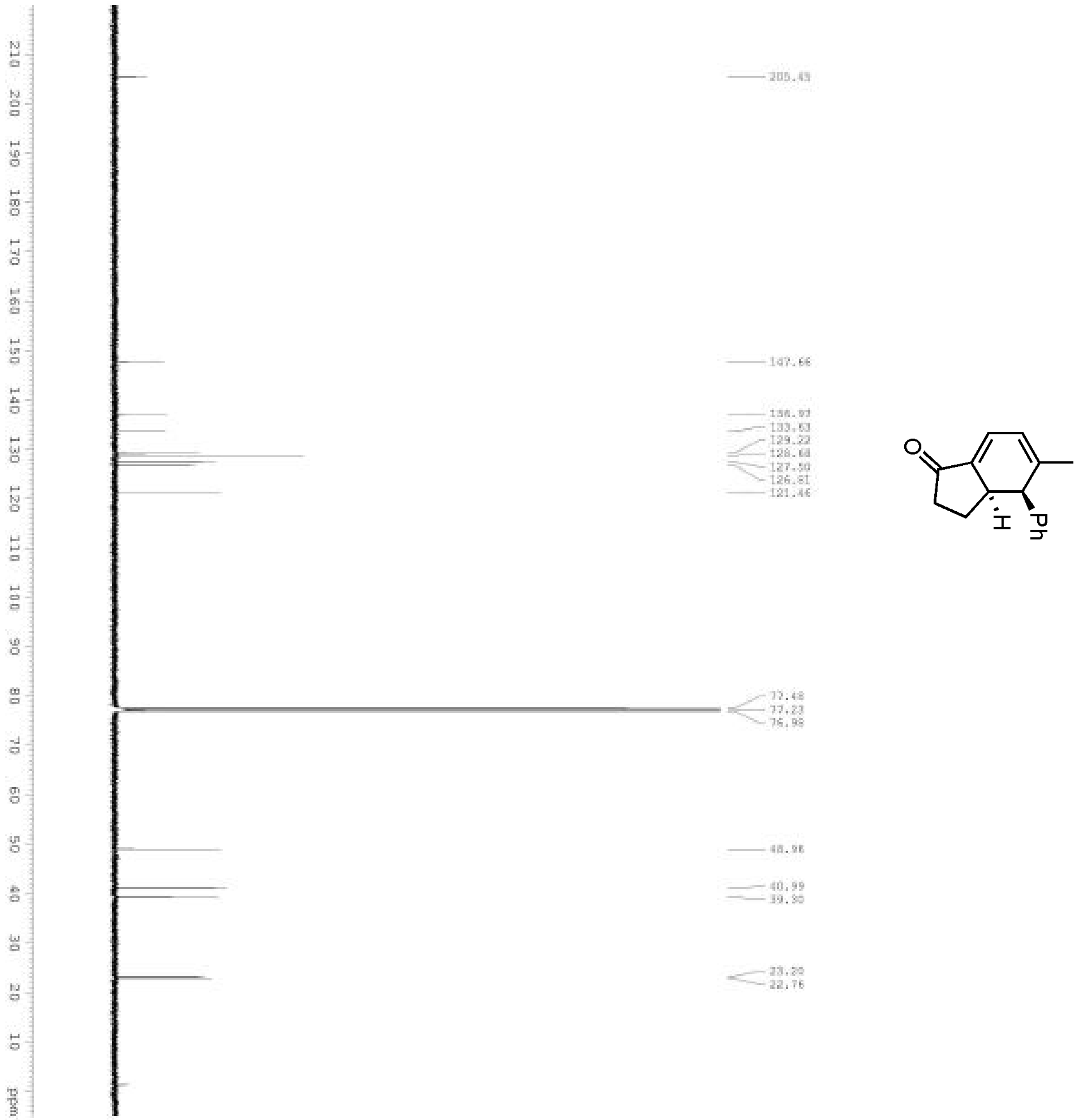

9
8
7
6
5
4
3
2
1
0
ppm
1.02
6.24
1.02
1.07
1.00
2.21
2.07
3.30
7.298
7.294
7.277
7.259
7.221
7.120
7.115
7.101
7.097
6.913
6.900
6.891
6.723
6.581
6.513
6.479
6.440
6.410
6.388
6.245
6.234
6.191
6.160
6.062
6.058
6.031
6.028
5.338
5.073
5.060
3.565
3.538
3.530
3.513
3.502
2.703
2.698
2.692
2.686
2.680
2.675
2.610
2.569
2.557
2.546
2.486
2.481
2.474
2.469
2.463
2.407
2.395
2.384
2.338
2.318
2.308
2.297
2.288
2.275
2.254
2.233
2.166
2.099
2.097
2.009
O
Ph


208.57
159.34
142.09
139.02
137.41
135.64
131.41
129.28
128.47
128.39
126.98
117.62
77.55
77.23
76.91
34.34
27.12
17.96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
Ph


Ph
H
O


7.305
7.262
7.249
7.234
7.229
7.221
7.205
7.075
7.071
7.059
7.056
6.869
6.859
6.851
6.204
6.193
3.519
3.498
3.486
3.472
3.458
3.438
2.529
2.486
2.331
2.314
2.307
2.295
2.278
2.271
2.254
2.236
2.218
2.201
2.061
2.057
1.977
1.963
1.951
1.938
1.923
1.806
1.679
1.597
1.333
1.252
1.224
1.210
1.196
1.173
1.155
1.148
1.131
1.126
1.120
1.109
1.101
1.084
0.923
0.907
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
3.93
2.03
0.98
1.00
2.23
2.13
1.11
3.12
1.23


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
205.45
147.66
136.93
133.63
129.22
128.68
127.50
126.81
121.46
77.48
77.23
76.98
48.96
40.99
39.30
23.20
22.76
O
H
Ph

# References

(1) *KaleidaGraph*: *KaleidaGraph*, Synergy Software: Reading, PA, **2003**.

(2) Which $^1$H NMR resonances are well-resolved depends on the $Me_2AlCl$:Triene ratio (see $^1$H NMR titrations). However, the vinyl proton resonances of the starting materials and products for the cyclizations of **1** and **2** were well-resolved in all cases.

(3) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001,** *78*, 64.

(4) (a) Roubelakis, M. M.; Vougioukalakis, G. C.; Angelis, Y. S.; Orfanopoulos, M. *Org. Lett.* **2006,** *8*, 39. (b) Appel, M.; Blaurock, S.; Berger, S. *Eur. J. Org. Chem.* **2002**, 1143.

(5) Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996,** *118*, 2748.

(6) Conway, J. C.; Quayle, P.; Regan, A. C.; Urch, C. J. *Tetrahedron* **2005,** *61*, 11910.

(7) Chen, J.; Wang, T.; Zhao, K. *Tetrahedron Lett.* **1994,** *35*, 2827.

(8) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989,** *30*, 2173.

(9) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990,** *11*, 440.

10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Wallingford CT, 2004.

11) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.