Electronic Supplementary Information

Total Synthesis of Endiandric Acid J and Beilcyclone A from Cyclooctatetraene

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General Procedures

NMR analysis was conducted using either an Agilent 600 MHz DD2 console with an Oxford 600 MHz magnet and Agilent cryoprobe, a *Bruker Advance III-HD* 600 MHz, and an *Agilent* 500 MHz. Chemical shifts are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for ^1H NMR and δ = 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). The assignment of signals was assisted correlated spectroscopy (COSY), heteronuclear single quantum coherence (HSQC). High-resolution mass spectroscopy was recorded using an Agilent 6230 TOF LC/MS (ESI). Infra-red spectra were recorded using a *PerkinElmer spectrum 100* FTIR spectrometer equipped with a zinc selenide crystal. Cyclooctatetraene was obtained as a generous gift from Dr Graham Gream (The University of Adelaide). The material was manufactured by BASF, most likely sometime in the 1970s. Samples were purified by vacuum distillation using a short vigrex column (20 mbar/ 60 °C) and stored in a freezer under an atmosphere of nitrogen. All other chemicals were purchased from commercial suppliers and used as received. All reactions were performed in flame-dried glassware using conventional Schlenk techniques under static pressure of nitrogen. Liquids and solutions were transferred with syringes.

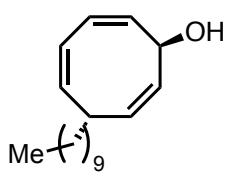
Diethyl ether (Et_2O) and tetrahydrofuran (THF) were purified by a Pure Solv^{TM} Micro solvent purification system and stored over 4 Å molecular sieves under an atmosphere of nitrogen. 1,2-dichloroethane was dried through storage over 4 Å molecular sieves under an atmosphere of nitrogen. Toluene was dried following the rapid purification procedures outlined in Purification of Laboratory Chemicals (5th Edition, by Amarego and Chai), and stored over 4 Å molecular sieves under an atmosphere of nitrogen.

Experimental Procedures

Synthesis of Cyclooctatriene oxide (3)

Cyclooctatetraene oxide was synthesized according to the work of Pineschi and colleagues[1] starting from 5g of cyclooctatetraene. Product obtained as a yellow oil (71%).

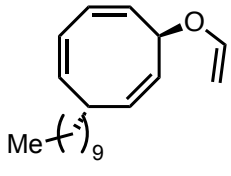
Synthesis of (2*Z*,4*Z*,7*Z*)-6-decylcycloocta-2,4,7-trien-1-ol (4)



4

Under nitrogen atmosphere, an oven dried round bottom flask was charged with magnesium powder (989 mg, 40.7 mmol, 4.90 eq), anhydrous Et_2O (5 mL), and 1,2-dibromoethane (20 µL). Upon activation of the magnesium 1-bromodecane (5.63 mL, 27.1 mmol, 3.30 eq) was added dropwise. The mixture was stirred for 2 h before being added dropwise to a stirred suspension of CuCN (2.68 g, 29.9 mmol, 3.60 eq) in anhydrous tetrahydrofuran (20 ml) at –18 °C. This was allowed to stir for an hour at –18 °C before a solution of COT-monoepoxide (1.00 g, 8.32 mmol, 1.00 eq) in anhydrous tetrahydrofuran (2 mL) was added. The resulting mixture was allowed to stir for a further hour at –18 °C. The reaction was quenched with saturated aqueous NH_4Cl solution. The aqueous layers were extracted with Et_2O and the organic layer was washed with distilled water and saturated NaCl solution. The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo. The desired product was purified through column chromatography using buffered silica and hexane/Et_2O (9:1) as eluent. **4** was obtained as a yellow oil (2.1 g, 96%). **IR** (ATR): ν/cm^{-1} = 3350, 3012, 2922, 2853, 1668, 1649, 1611, 1465, 1377, 1254, 1037, 771, 721, 669. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.13 – 6.11 (1H, m), 6.09 – 6.07 (1H, m), 5.58 – 5.55 (1H, m), 5.39 – 5.34 (2H, m), 5.18 (1H, dd, *J* = 10.2, 7.0 Hz), 4.87 (1H, brs), 2.79 – 2.75 (1H, m), 2.09 (1H, brs),1.55 – 1.51 (2H, m), 1.25 (18H, m), 0.87 (3H, t, J = 7.0 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 132.9, 132.8, 132.3, 130.9, 127.5, 126.4, 70.0, 37.4, 36.4, 32.1, 29.8, 29.7, 29.5, 27.4, 22.8, 14.3. **HRMS** (ESI, m/z) calculated for ([M]) $C_{18}H_{31}O$ 262.2297 found 262.2265.

Synthesis of (1*Z*,3*Z*,6*Z*)-5-decyl-8-(vinyloxy)cycloocta-1,3,6-triene (5)

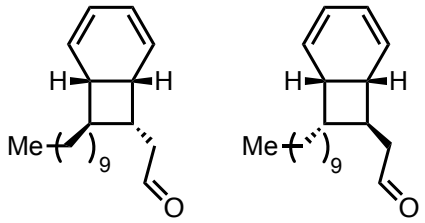


5

Under nitrogen atmosphere an oven dried round bottom flask was charged with $AuClPPh_3$ (47.1 mg, 95.3 µmol, 0.10 eq) AgOAc (15.9 mg, 95.3 µmol, 0.10 eq) and freshly distilled butyl vinyl ether (4 mL) The mixture was stirred at room temperature for 10 min before decyl alcohol **4** (250 mg, 952 µmol, 1.00 eq) and acetic acid (1.72 µL, 25.6 µmol, 0.03 eq) were added, and allowed to stir for 12 h. The reaction was diluted in diethyl ether and quenched with triethylamine (20 µL) before filtrated through a pad of Al_2O_3. The solvent was then removed at 28 °C in vacuo. Under nitrogen atmosphere another oven dried round bottom flask was

charged with $AuClPPh_3$ (23.6 mg, 47.6 μmol, 0.05 eq.) AgOAc (7.95 mg, 47.6 μmol, 0.05 eq) and freshly distilled butyl vinyl ether (4 mL). The mixture was stirred at room temperature for 10 min before the crude material and acetic acid (0.86 μL, 12.8 μmol, 0.01 eq) were added. After 12 h, the reaction was quenched with triethylamine (20 μL) before filtrated through a pad of Al_2O_3. The solvent was then removed at 28 °C in vacuo and the product was used as impurified intermediate for the next step. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.35 (1H, dd, *J* = 14.3, 6.8, Hz), 6.18 – 6.16 (2H, m), 5.60 – 5.57 (1H, m), 5.45 – 5.42 (1H, m), 5.36 – 5.34 (1H, m), 5.23 – 5.20 (1H, m), 4.98 (1H, brs), 4.19 (1H, dd, *J* = 14.3, 1.8 Hz), 4.03 (1H, dd, *J* = 6.8, 1.8 Hz), 2.79 (1H, brs), 1.58 – 1.57 (3H, m), 1.26 (27H, m), 0.88 (5H, t, *J* = 7.0 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 150.4, 132.8, 132.8, 129.7, 128.4, 127.5, 127.3, 88.9, 76.6, 37.6, 36.4, 32.1, 29.8, 29.7, 29.5, 27.4, 22.8, 14.3.

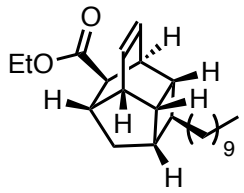
Synthesis of 2-((1*S*,6*R*)-8-decylbicyclo[4.2.0]octa-2,4-dien-7-yl)acetaldehyde (6a, 6b)



6a **6b**

Under nitrogen atmosphere an oven dried round bottom flask was charged with **5** (270 mg) and anhydrous toluene (5 mL). The solution was heated at 60 ºC overnight. Upon completion of the reaction the solvent was removed in vacuo. The crude material was purified by column chromatography using buffered silica and hexane/EtAOc (9:1) as eluent (R_f = 0.23), affording the aldehyde **6a** and **6b** as an inseparable ~2:1 mixture (**6a:6b** or **6b:6a**) as a yellow oil (134 mg, 48%, over two steps). **IR** (ATR): v/cm^{-1} = 3029, 2921, 2852, 2712, 1724, 1675, 1613, 1465, 1378, 1320, 1237, 1195, 998, 961, 814, 705, 663. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 9.77 (1H, s), 9.68 (0.5H, dd, *J* = 2.5 Hz), 5.89 - 5.85 (2H, m), 5.72 - 5.69 (1H, m,), 5.67 - 5.64 (1H, m), 5.61 – 5.57 (2H, m), 5.42 - 5.40 (1H, m), 3.24 - 3.23 (1H, m,), 3.18-3.14 (0.6H, m), 2.84 - 2.79 (2H m), 2.70 - 2.62 (2H, m), 2.60 - 2.55 (2H, m), 2.53 - 2.8 (1H, m), 2.32 – 2.27 (1H, m),1.59 – 1.42 (4H, m), 1.25 - 1.33 (33H, m), 0.88 (6H, t, *J* = 7.0 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 202.3, 201.7, 127.8, 126.5, 126.1, 125.6, 124.8, 124.3, 122.3, 121.4, 52.4, 51.5, 50.3, 45.8, 45.4, 44.5, 37.4, 36.9, 36.2, 35.1, 33.9, 32.1, 30.3, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 28.3, 28, 22.8, 14.3. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{20}H_{32}O$ 311.2345 found 311.2319.

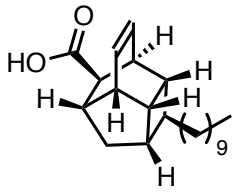
Synthesis of Endiandric acid J ester (9) in one pot starting from (6a,6b)



9

Under nitrogen atmosphere an oven dried round bottom flask was charged with **6a**,**6b** (16 mg, 91 μmol, 1.0 eq) (carbomethoxymethylene)triphenylphosphorane (79.1 mg, 227 μmol, 2.50 eq.) and anhydrous 1,2-dichloroethane (0.1 mL). The mixture was heated at 55 ºC for 3 hrs. Anhydrous toluene (30 mL) was added and the reaction mixture was heated at 120 ºC for 5 hrs. The solvent was removed in vacuo and the crude material was purified by column chromatography using hexane/Et_2O (1%) as eluents (R_f = 0.21). The desired product was obtained as a colorless oil (12 mg, 54%, over two steps). **IR** (ATR): v/cm^{-1} = 2956, 2923, 2853, 1736, 1611, 1532, 1465, 1367, 1305, 1205, 1179, 1042, 790, 691. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.21 - 6.15 (2H, m), 4.13 – 4.03 (2H, m), 3.02 – 2.99 (1H, m), 2.80 (1H, d, *J* = 3.8 Hz), 2.67 (1H, d, *J* = 5.5 Hz), 2.58 (1H, dd, *J* = 6.9 Hz), 2.36 – 2.33 (1H, m), 2.23 – 2.21 (1H, m), 1.91 – 1.87 (1H, m), 1.66 – 1.60 (2H, m), 1.53 – 1.43 (2H, m), 1.26 (21H, m), 0.88 (3H, t, *J* = 7.0 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 175, 131.9, 131.4, 60.3, 49.3, 42.1, 40.4, 40.3, 39.7, 39.6, 38.7, 38.5, 36.5, 35.3, 32.1, 29.9, 29.9, 29.8, 29.8, 29.5, 27.4, 22.8, 14.4, 14.2. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{24}H_{38}O_2$ 381.2764 found 381.2707.

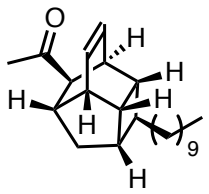
Synthesis of Endiandric acid J (1)



1

A 25 mL round bottom flask was charged with **9** (25 mg, 70 μmol, 1.0 eq), lithium hydroxide (5.00 mg, 0.21 mmol, 3.00 eq), and THF/water/methanol in a ratio of 1:1:1 (10 mL). The reaction mixture was heated at 50 ºC overnight. After reaction the solution was acidified until pH = 1 and extracted with ethyl acetate three times. The organic layer was washed with distilled water and saturated NaCl solution and dried over $MgSO_4$. The solvent was evaporated in vacuo and the crude material was purified on column chromatography using hexane/EAOc (9:1) as eluent (R_f = 0.18). The product was obtained as a colorless oil (18 mg, 72 %). **IR** (ATR): v/cm^{-1} = 3047, 2966, 2922, 2852, 1753, 1464, 1366, 1296, 1204, 1176, 1095, 1042, 855, 808, 719, 690. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.25 – 6.20 (2H, m), 3.02 – 3.00 (1H, m), 2.87 (1H, d, *J* = 3.8 Hz), 2.65 – 2.71 (1H, m), 2.54 (1H, t, *J* = 5.2 Hz), 2.34 (1H, dt, *J* = 8.9, 5.5 Hz), 2.23 (1H, t, *J* = 6.4 Hz), 1.89 (1H, ddd, *J* = 12.9, 7.6, 5.4 Hz), 1.66 – 1.68, (2H, m), 1.54 (1H, d, *J* = 12.7 Hz), 1.43 – 1.51 (2H, m), 1.26 (16H, m), 0.88 (3H, t, *J* = 6.9 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 180.3, 132.1, 131.4, 49.1, 42.0, 40.4, 40.3, 39.8, 39.6, 38.7, 38.5, 36.5, 35.2, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.5, 27.4, 22.9, 14.3. **HRMS** (ESI, m/z) calculated for ([M+K]$^+$) $C_{22}H_{34}O_2$ 367.2608 found 367.2645.

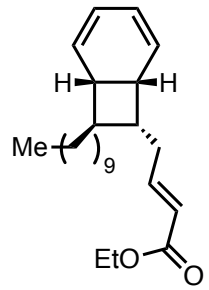
Synthesis of Beilcyclone A (2) in one pot starting from (6a,6b)



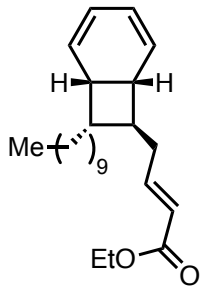
2

Under nitrogen atmosphere an oven dried round bottom flask was charged with **6a**,**6b** (16 mg, 91 μmol, 1.0 eq) acetylmethylene-triphenylphosphorane (86.7 mg, 272 μmol, 3.00 eq) and anhydrous 1,2-dichloroethane (0.1 mL). The mixture was heated at 40 ºC for 24 h. anhydrous toluene (5 mL), and heated at 120 ºC for 5 hrs. The solvent was removed in vacuo and the crude material was purified by column chromatography using hexane/Et_2O (1%) as eluents as eluent (Rf = 0.27). The desired product was obtained as a colourless oil (12 mg, 61%, over two steps). **IR** (ATR): v/cm^{-1} = 2954, 2922, 2852, 1714, 1459, 1363, 160, 1169, 1019, 966, 802, 702, 665. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.20 (1H, ddd, *J* = 8.0, 6.4, 1.0 Hz), 6.11 (1H, ddd, *J* = 8.0, 6.4, 1.0 Hz), 3.02 (1H, dt, *J* = 7.3, 4.1 Hz), 2.78 (1H, d, *J* = 3.6 Hz), 2.68 – 2.65 (2H, m), 2.35 (1H, dt, *J* = 9.8, 5.4 Hz), 2.23 (1H, dt, *J* = 6.3, 3.5 Hz), 2.12 (3H, s), 1.89 (1H, ddd, *J* = 12.7, 7.5, 5.2 Hz), 1.69 − 1.64 (2H, m), 1.53 − 1.45 (2H, m), 1.26 (16H, brs), 0.88 (3H, t, *J* = 6.9 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 209.3, 132.4, 130.5, 57.9, 42.4, 40.4, 40.4, 40.1, 39.8, 38.5, 37.0, 36.5, 35.6, 32.1, 29.9, 29.9, 29.8, 29.8, 29.5, 28.5, 27.5, 22.8, 14.3. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{24}H_{38}O_2$ 351.2658 found 351.2687.

Synthesis of ethyl (*E*)-4-((1*S*,6*R*)-8-decylbicyclo[4.2.0]octa-2,4-dien-7-yl)but-2-enoate (7a,7b)



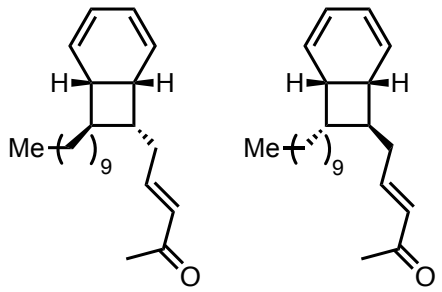
7a



7b

Under nitrogen atmosphere an oven dried round bottom flask was charged with **6a**,**6b** (60.0 mg, 208 μmol, 1.00 eq) (carbomethoxymethylene)triphenylphosphorane (181 mg, 519 μmol, 2.50 eq.) and anhydrous 1,2-dichloroethane (0.2 mL). The mixture was heated at 55 ºC for 3 hrs. After reaction the solvent was removed in vacuo. The crude material was purified by column chromatography using hexane/Et_2O (9.5:0.5) as eluent (R_f = 0.23) affording 7**a** and 7**b** as an inseparable ~1:1 mixture (**7a:7b** or 7**b:7a**) as a colorless oil (50 mg, 67%). **IR** (ATR): v/cm^{-1} =3030, 2921, 2852, 1721, 1653, 1465, 1366, 1320, 1306, 1264, 1192, 1149, 1095, 1042, 979, 850, 718. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.94 – 6.84 (2H, m), 5.85 - 5.79 (4H, m), 5.65 - 5.63 (2H, m), 5.60 - 5.50 (4H, m), 4.19 – 4.15 (4H, m), 3.18 (1H, brs), 3.11 (0.8H, brs), 2.51 - 2.47 (4H, m), 2.42 - 2.25 (6H, m), 1.49 – 1.34 (4H, m), 1.25 (33H, m), 0.88 (7H, m). **^{13}CNMR** (150 MHz, $CDCl_3$) δ: 166.8, 166.7, 148.5, 147.5, 127.6, 126.8, 126.7, 125.9, 124.6, 124.1, 122.1, 122, 121.7, 121.3, 60.3, 52.5, 51.1, 50.7, 49.5, 38.6, 37.2, 36.7, 36.3, 34.5, 34.2, 33.7, 32.1, 30.5, 30, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 28.3, 28.2, 22.8, 14.4, 14.2. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{22}H_{34}O_2$ 311.2319 found 311.2345.

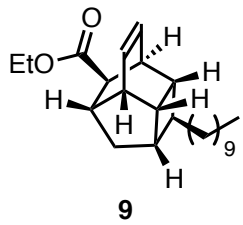
Synthesis of (*E*)-5-((1*S*,6*R*)-8-decylbicyclo[4.2.0]octa-2,4-dien-7-yl)pent-3-en-2-one (8a,8b)



8a **8b**

Under nitrogen atmosphere an oven dried round bottom flask was charged with **6a**,**6b** (10.0 mg, 34.7 μmol, 1.00 eq.), acetylmethylene-triphenylphosphorane (33.1 mg, 100 μmol, 3.00 eq) and anhydrous 1,2-dichloroethane (0.1 mL). The mixture was heated at 40 ºC for 24 h. After reaction the solvent was removed in vacuo. The crude material was purified by column chromatography using hexane/Et_2O (9.5:0.5) as eluent (R_f = 0.30) affording the desired compound as a colourless oil (6.2 mg, 57%). **IR** (ATR): v/cm^{-1} = 2921, 1721, 1653, 1465, 1192. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.81 - 6.67 (2H, m), 6.07 (2H, dd, *J* = 15.8 7.8 Hz), 5.89 – 5.84 (2H, m), 5.68 – 5.64 (2H, m), 5.62 – 5.56 (2H, m), 5.53 – 5.48 (2H, m), 3.19 (1H, brs), 3.13 (0.9H, brs), 2.57 – 2.49 (3H, m), 2.46 – 2.27 (5H, m) 2.23 (5H, s), 1.49 – 1.36 (4H, m), 1.26 (35H, m), 0.88 (7H, m). **^{13}CNMR** (150 MHz, $CDCl_3$): 198.7, 147.6, 146.7, 132.1, 131.7, 127.7, 126.9, 126.5, 125.8, 124.7, 124.2, 122.1, 121.3, 52.5, 51.3, 50.8, 49.5, 39.1, 37.2, 36.8, 36.4, 34.6, 34.2, 34.0, 32.1, 30.6, 30.0, 29.9, 29.8, 29.8, 29.5, 28.4, 28.2, 22.9, 14.3. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{24}H_{38}O_2$ 329.2839 found 329.2838.

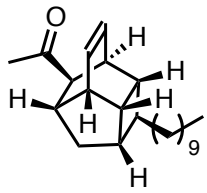
Synthesis of Endiandric ester J (9)



9

Under nitrogen atmosphere **7a**,**7b** (20 mg, 56 mmol) was dissolved in anhydrous toluene (20 mL), and heated at 120 ºC for 5 hrs. The solvent was removed in vacuo and the crude material was purified by column chromatography using hexane/Et_2O (1%) as eluents (R_f = 0.21). The desired product was obtained as a colorless oil (17 mg, 85%). **IR** (ATR): v/cm^{-1} = 2956, 2923, 2853, 1736, 1611, 1532, 1465, 1367, 1305, 1205, 1179, 1042, 790, 691. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.21 - 6.15 (2H, m), 4.13 – 4.03 (2H, m), 3.02 – 2.99 (1H, m), 2.80 (1H, d, *J* = 3.8 Hz), 2.67 (1H, d, *J* = 5.5 Hz), 2.58 (1H, dd, *J* = 6.9 Hz), 2.36 – 2.33 (1H, m), 2.23 – 2.21 (1H, m), 1.91 – 1.87 (1H, m), 1.66 – 1.60 (2H, m), 1.53 – 1.43 (2H, m), 1.26 (21H, m), 0.88 (3H, t, *J* = 7.0 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 175, 131.9, 131.4, 60.3, 49.3, 42.1, 40.4, 40.3, 39.7, 39.6, 38.7, 38.5, 36.5, 35.3, 32.1, 29.9, 29.9, 29.8, 29.8, 29.5, 27.4, 22.8, 14.4, 14.2. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{24}H_{38}O_2$ 381.2764 found 381.2707.

Synthesis of Beilcyclone A (2)



2

Under nitrogen atmosphere **8a**,**8b** (40.0 mg, 0.12 mmol) was dissolved in anhydrous toluene (30 mL), and heated at 120 ºC for 5 hrs. The solvent was removed in vacuo and the crude material was purified by column chromatography using hexane/Et_2O (1%) as eluents as eluent (Rf = 0.27). The desired product was obtained as a colourless oil (25 mg, 62%). **IR** (ATR): v/cm^{-1} = 2954, 2922, 2852, 1714, 1459, 1363, 160, 1169, 1019, 966, 802, 702, 665. **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.20 (1H, ddd, *J* = 8.0, 6.4, 1.0 Hz), 6.11 (1H, ddd, *J* = 8.0, 6.4, 1.0 Hz), 3.02 (1H, dt, *J* = 7.3, 4.1 Hz), 2.78 (1H, d, *J* = 3.6 Hz), 2.68 – 2.65 (2H, m), 2.35 (1H, dt, *J* = 9.8, 5.4 Hz), 2.23 (1H, dt, *J* = 6.3, 3.5 Hz), 2.12 (3H, s), 1.89 (1H, ddd, *J* = 12.7, 7.5, 5.2 Hz), 1.69 − 1.64 (2H, m), 1.53 − 1.45 (2H, m), 1.26 (16H, brs), 0.88 (3H, t, *J* = 6.9 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 209.3, 132.4, 130.5, 57.9, 42.4, 40.4, 40.4, 40.1, 39.8, 38.5, 37.0, 36.5, 35.6, 32.1, 29.9, 29.9, 29.8, 29.8, 29.5, 28.5, 27.5, 22.8, 14.3. **HRMS** (ESI, m/z) calculated for ([M+Na]) $C_{24}H_{38}O_2$ 351.2658 found 351.2687.

NMR spectra

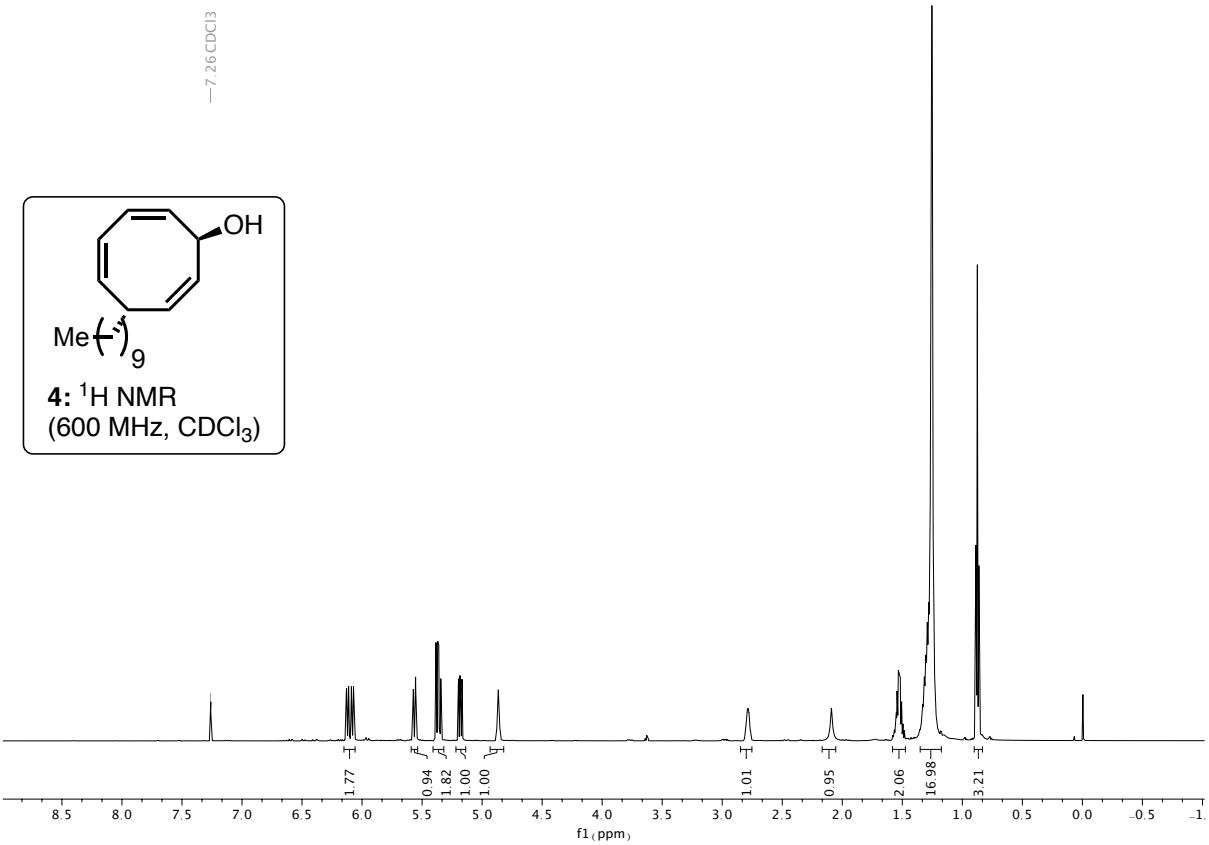


Figure 1: ^{1}H NMR of **4**.

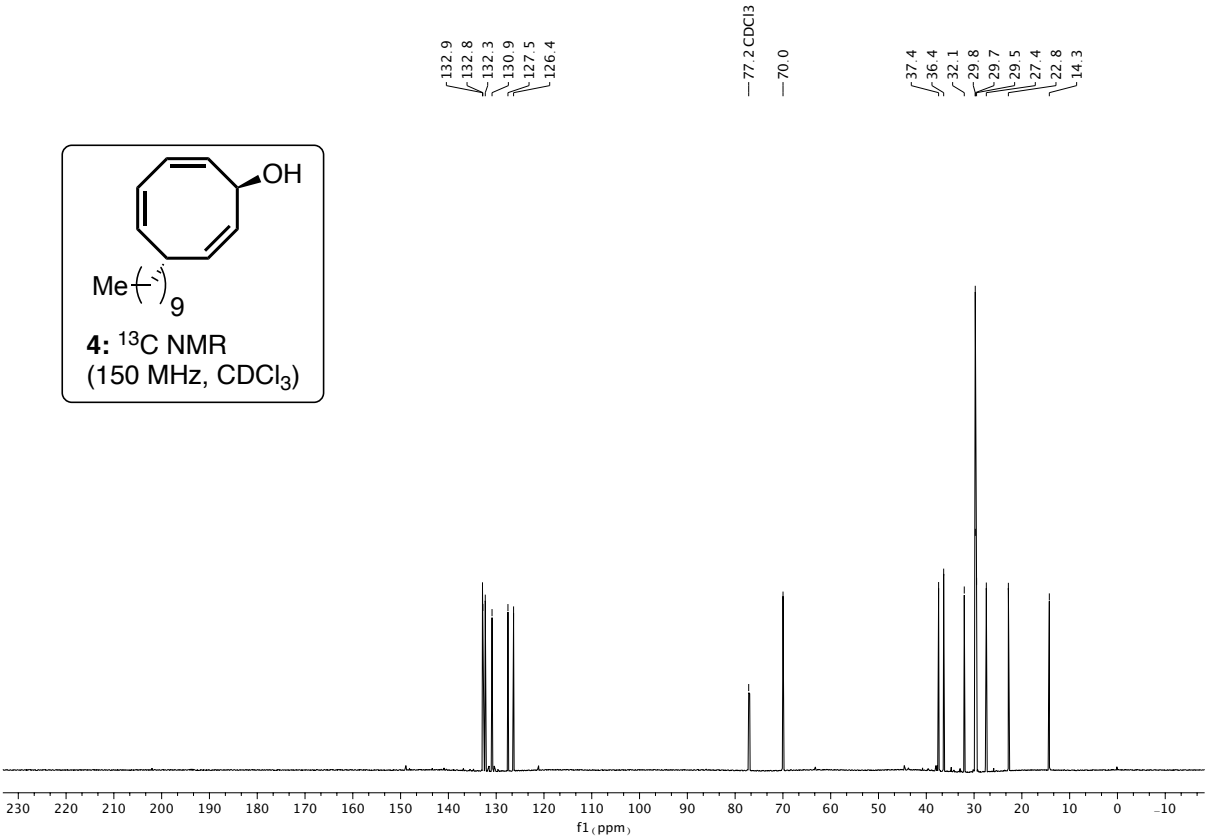


Figure 2:^{13}C NMR of **4**.

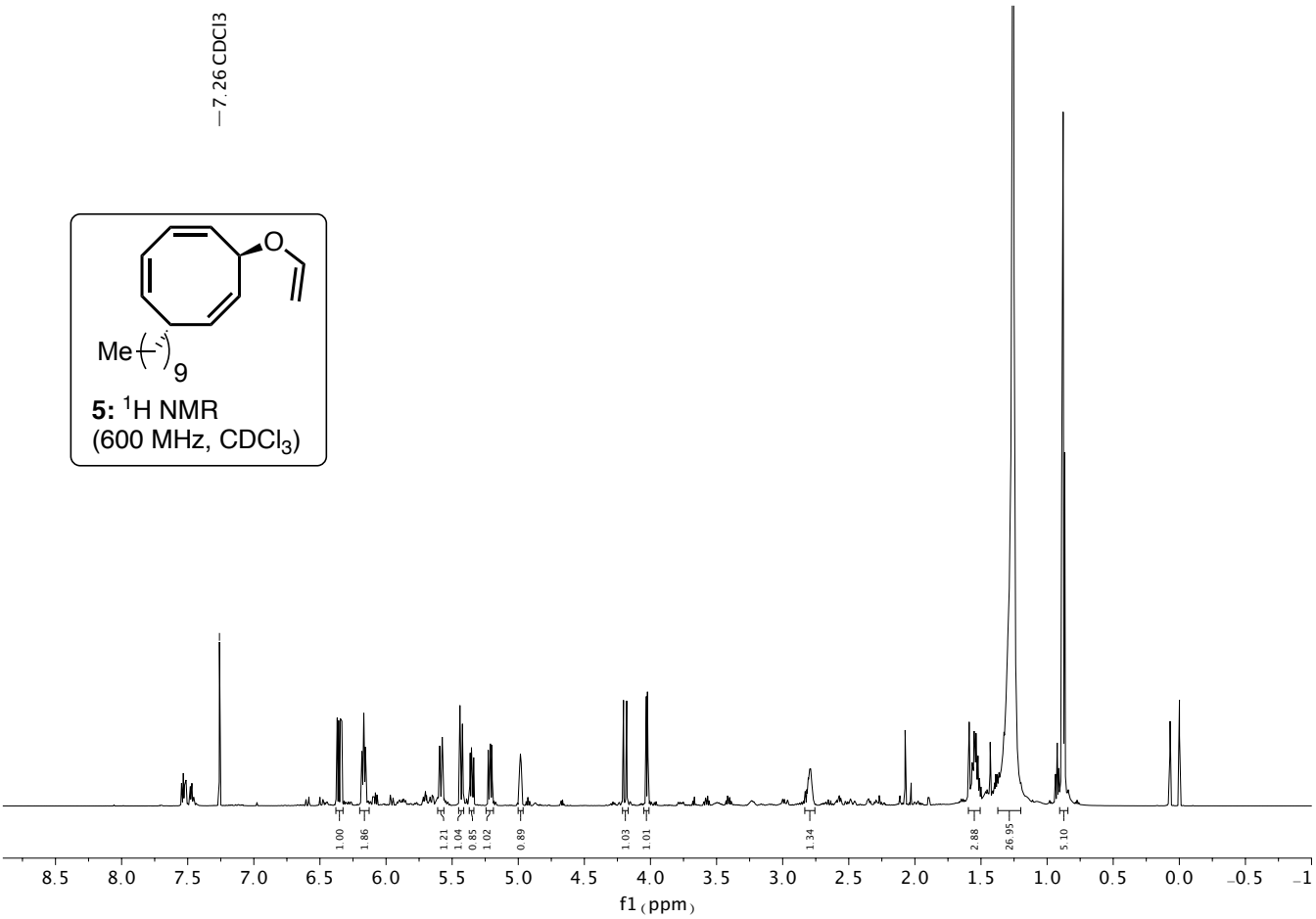


Figure 3: ^{1}H NMR of **5.**

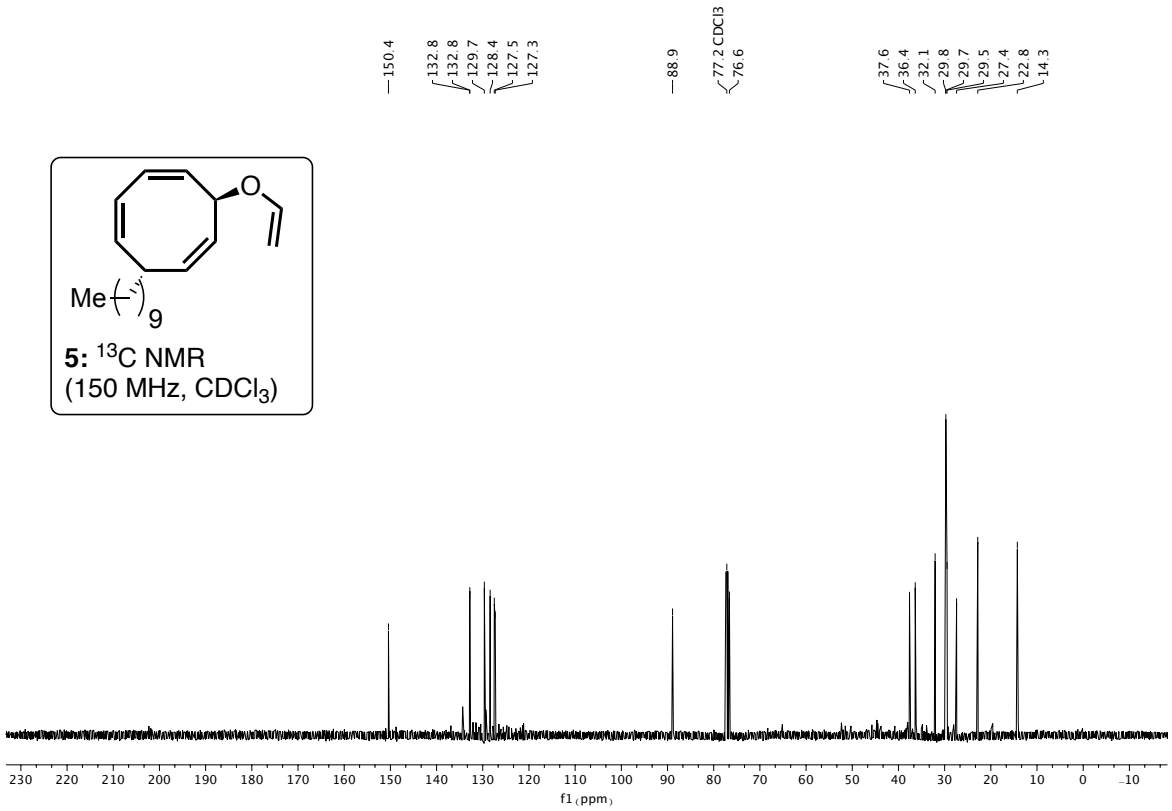


Figure 4: ^{13}C NMR of **5**.

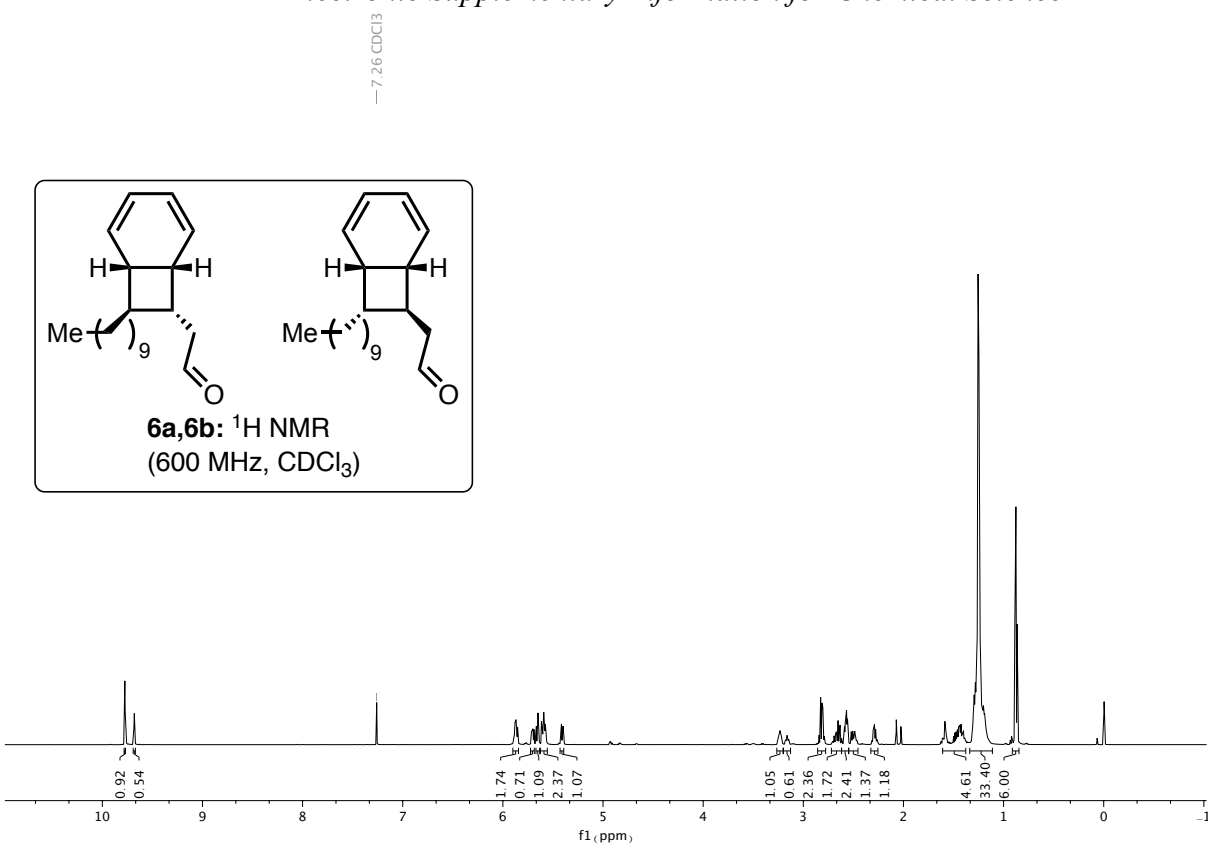


Figure 5: ^{1}H NMR of **6a**,**6b.**

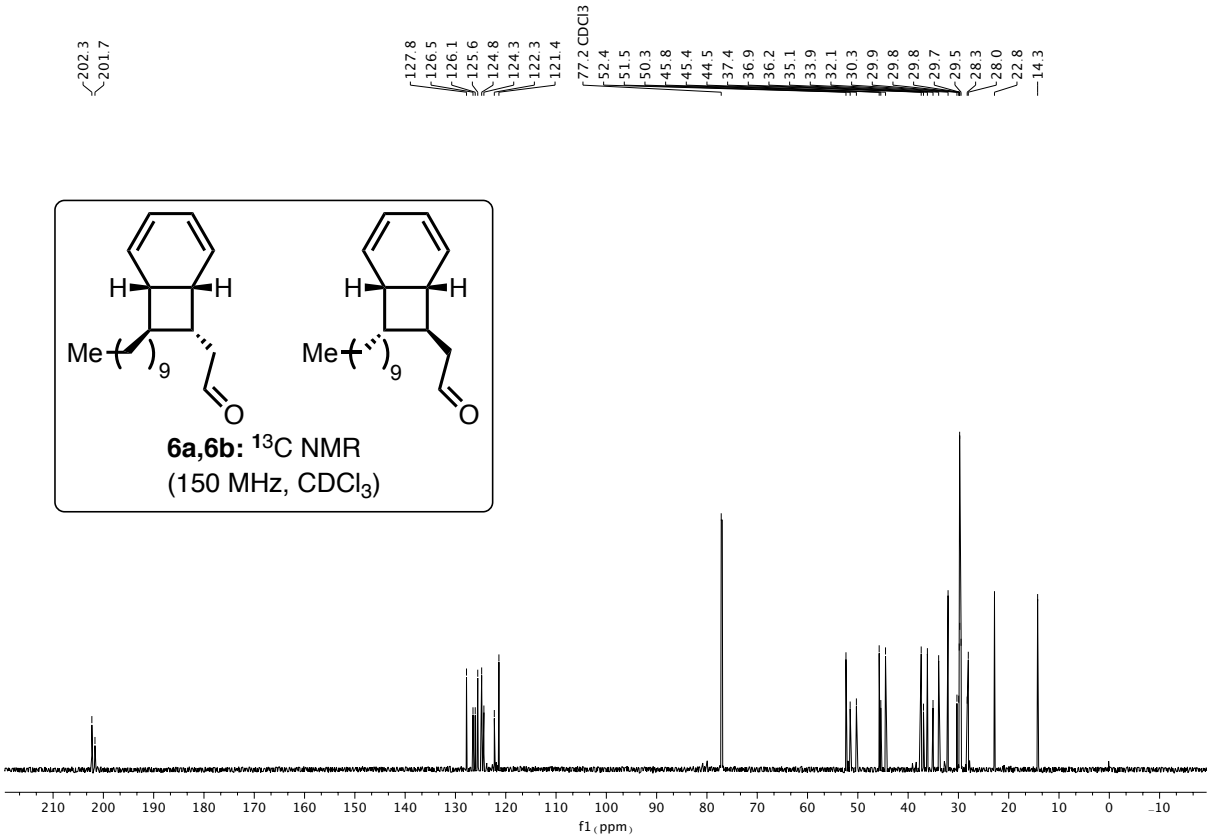


Figure 6: ^{13}C NMR of **6a**,**6b**.

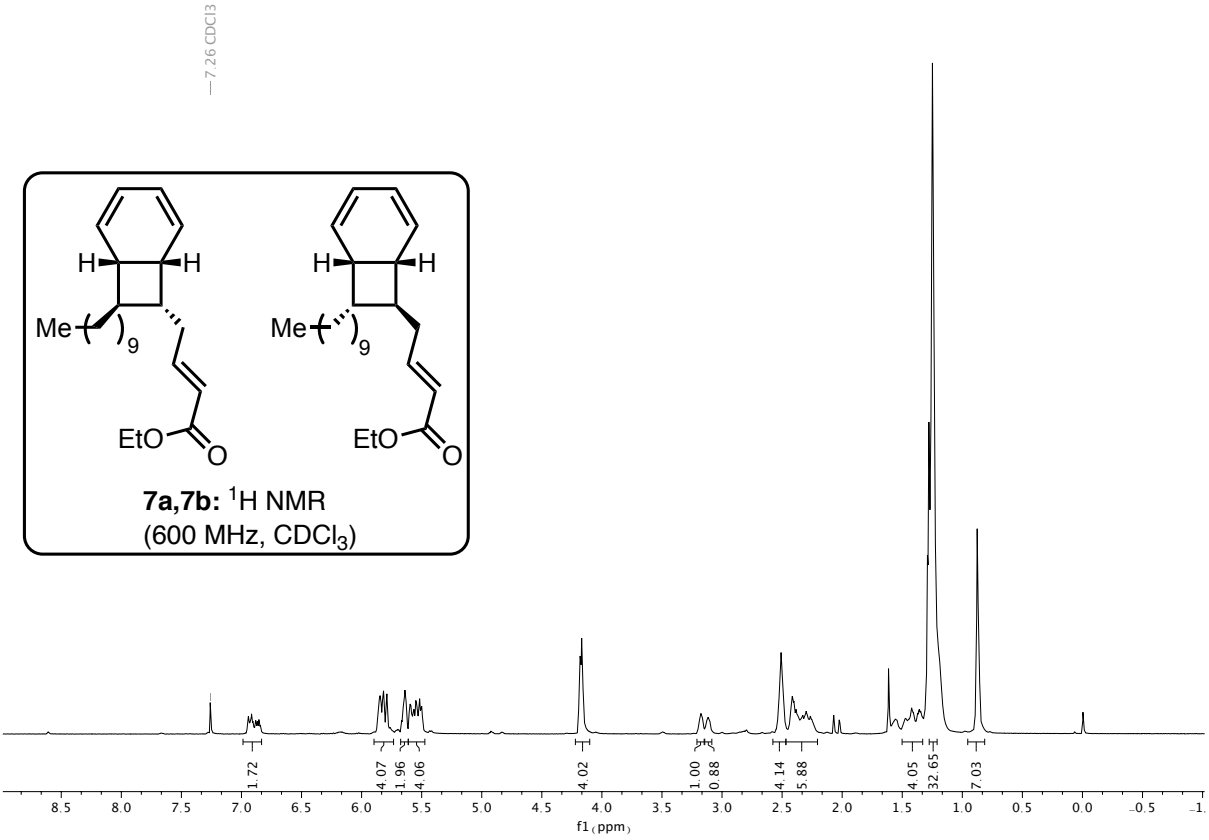


Figure 7: ^{1}H NMR of **7a**,**7b.**

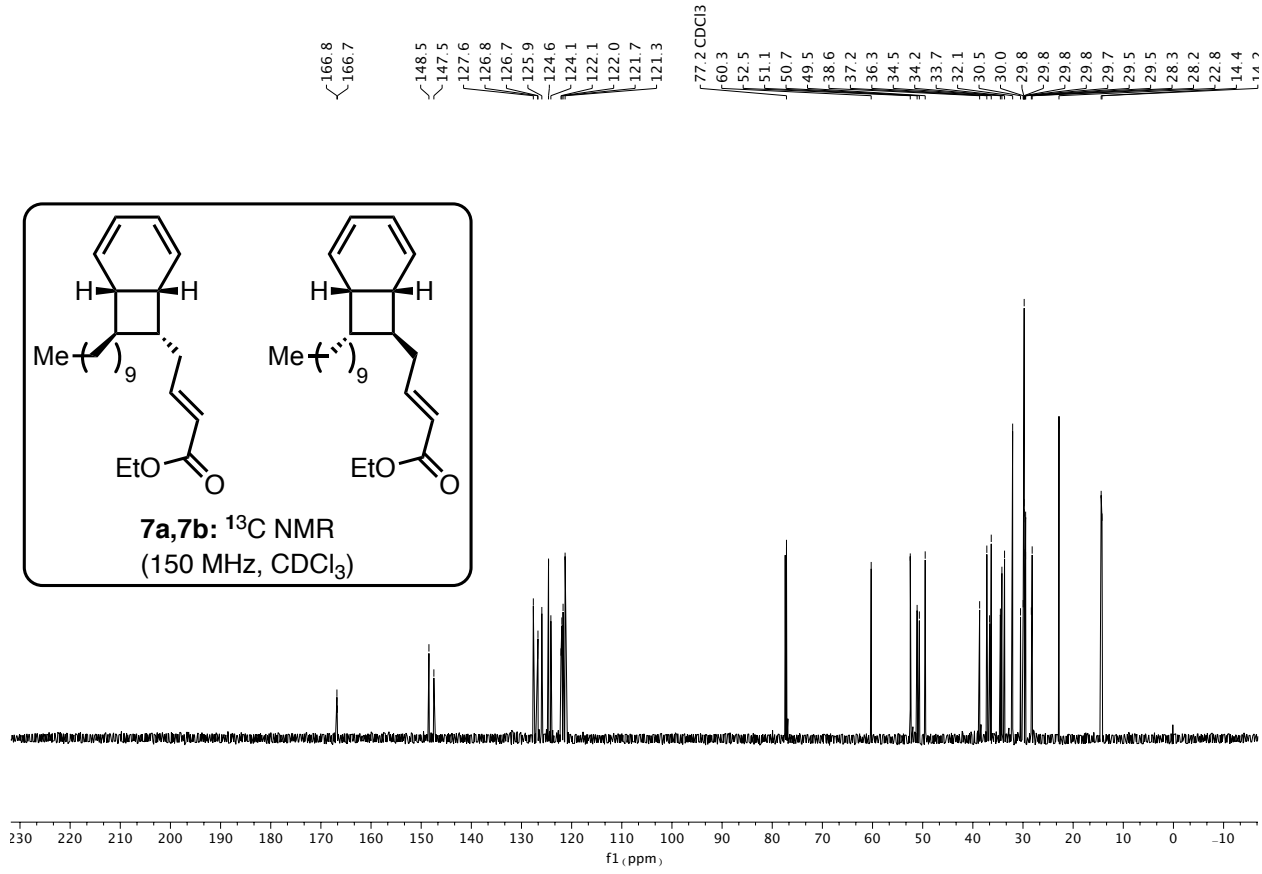


Figure 8: ^{13}C NMR of **7a**,**7b**.

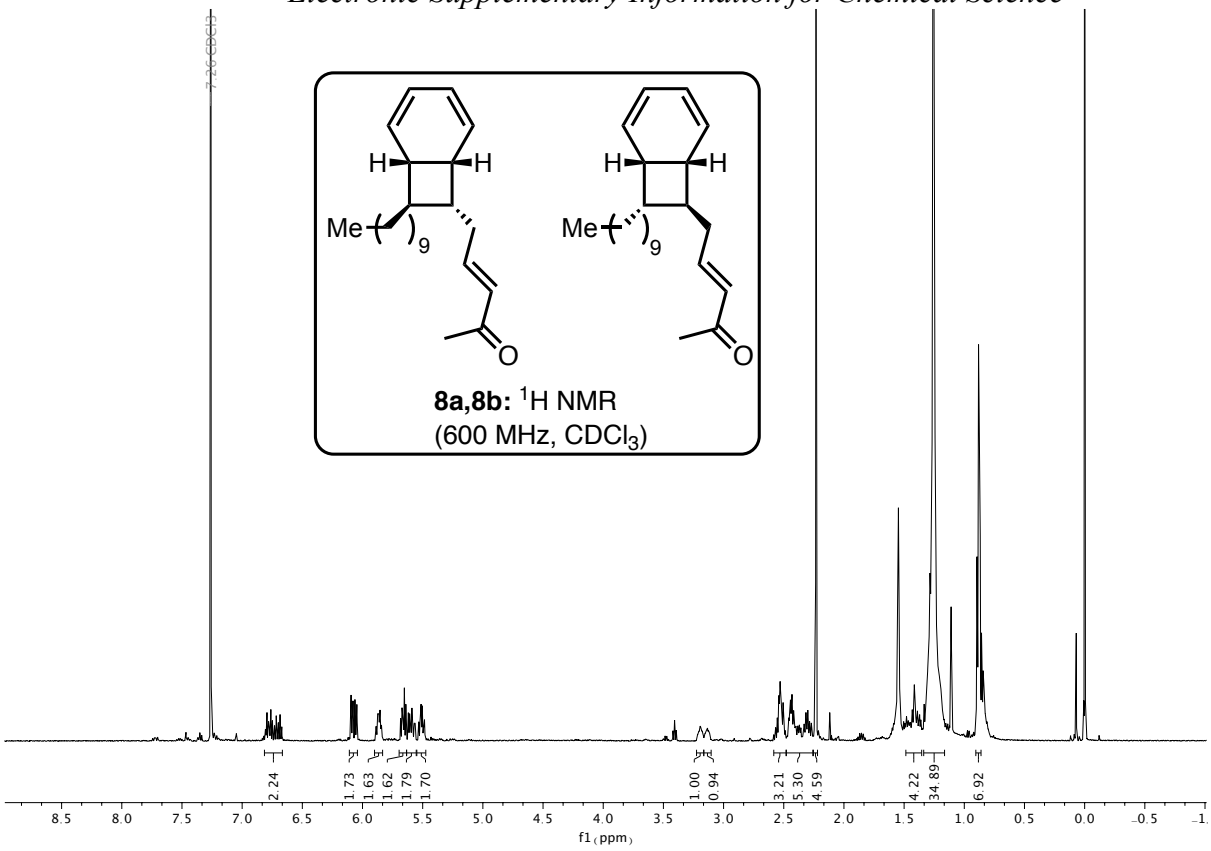


Figure 9: ^{1}H NMR of **8a**,**8b.**

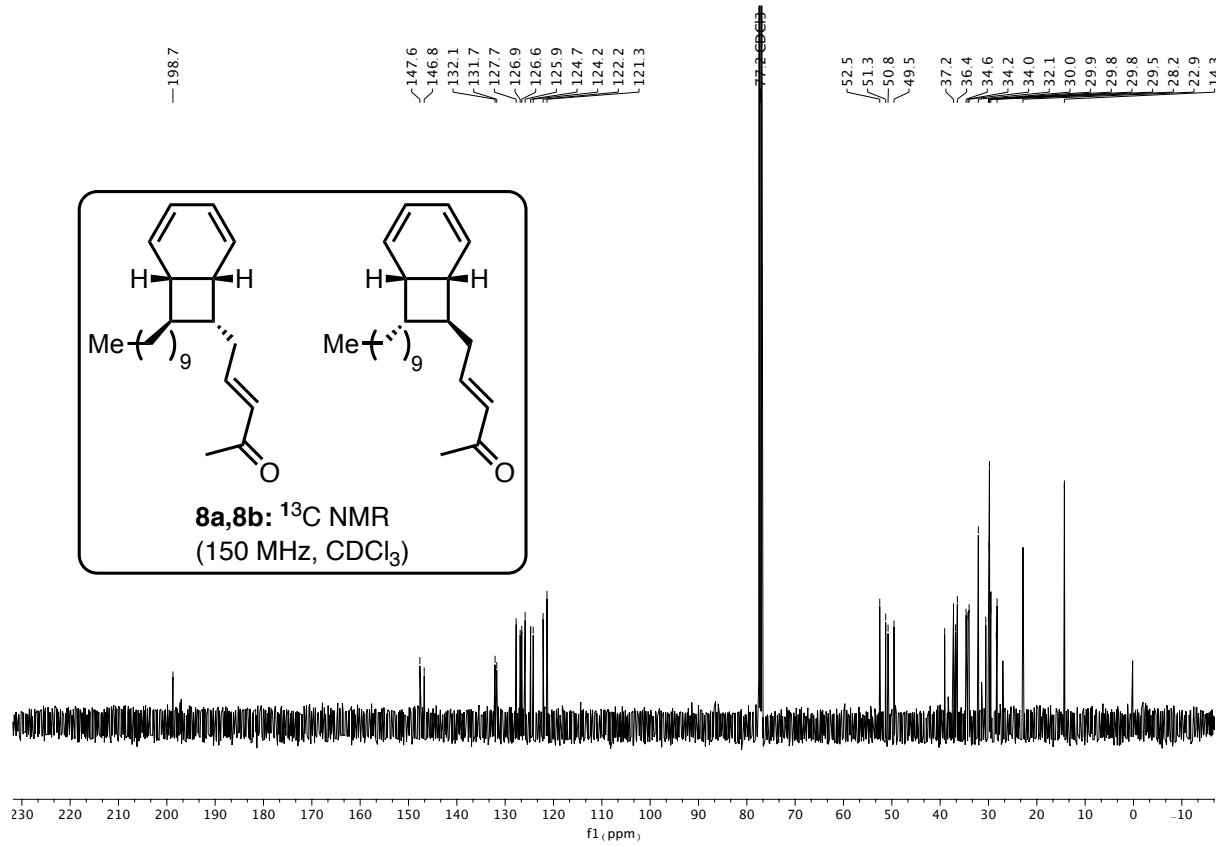


Figure 10: ^{13}C NMR of **8a**,**8b**.

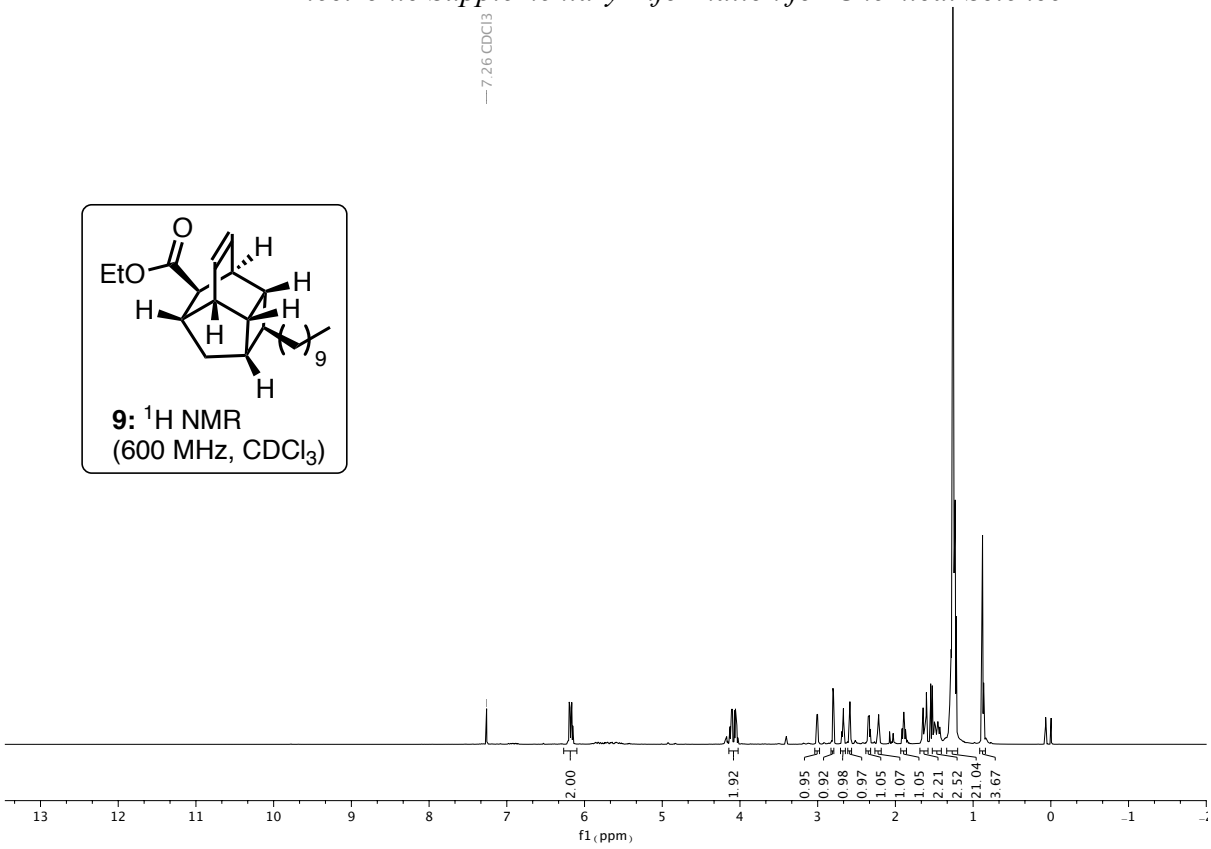


Figure 11: ^{1}H NMR of **9**.

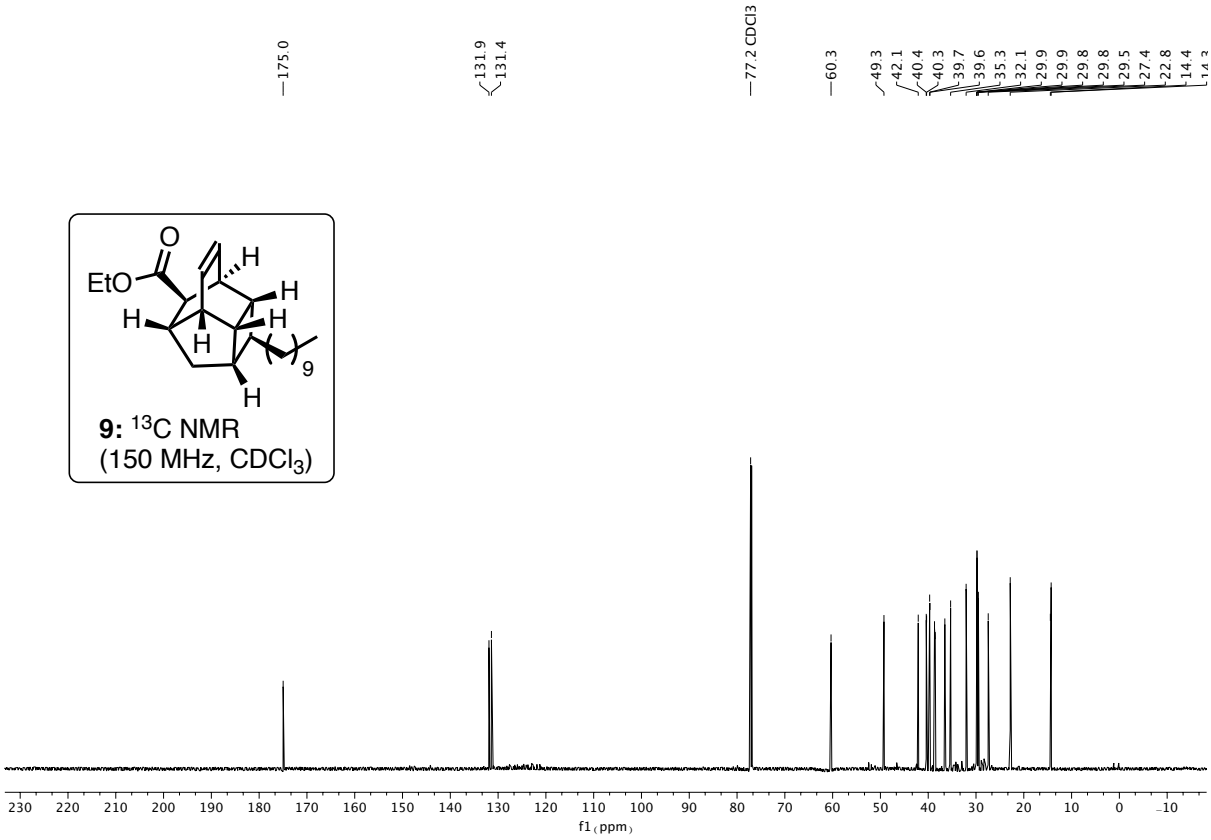


Figure 12: ^{13}C NMR of **9**.

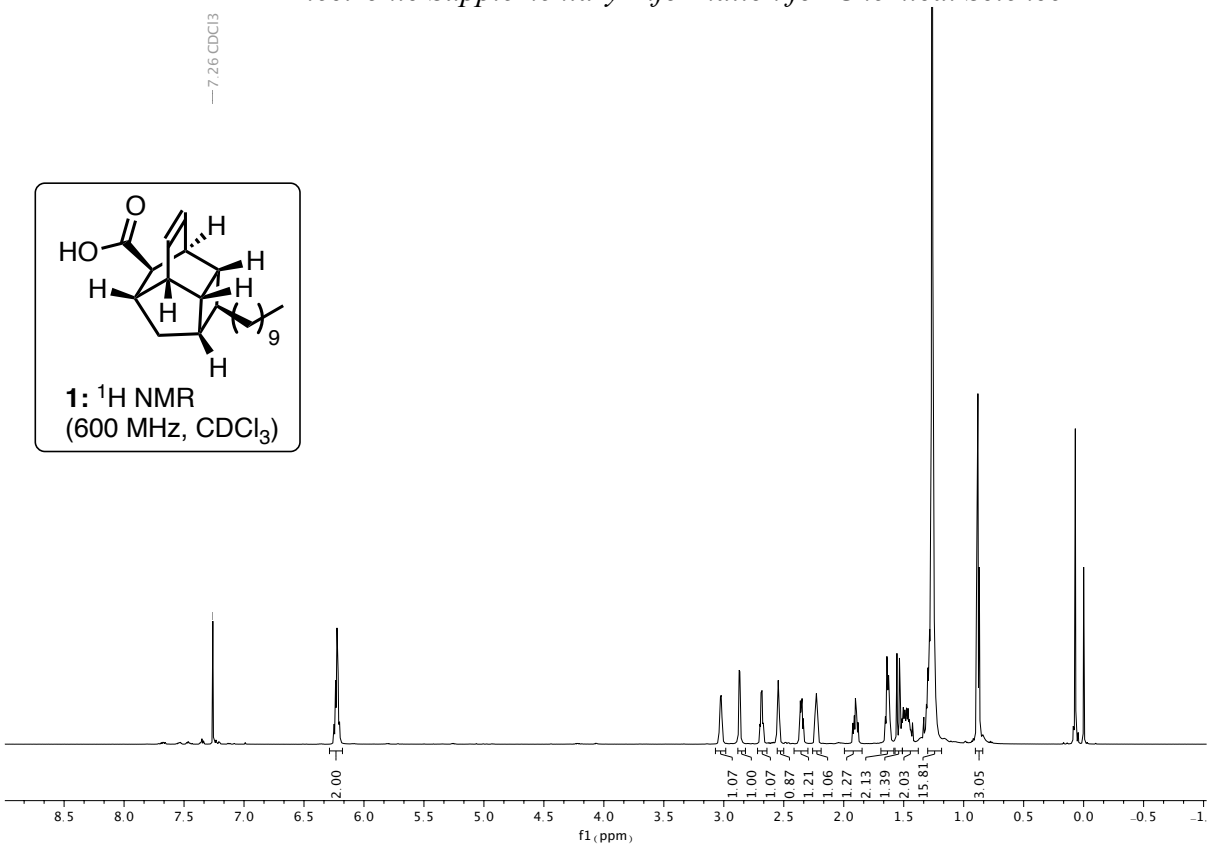


Figure 13: ^{1}H NMR of Endiandric acid J.

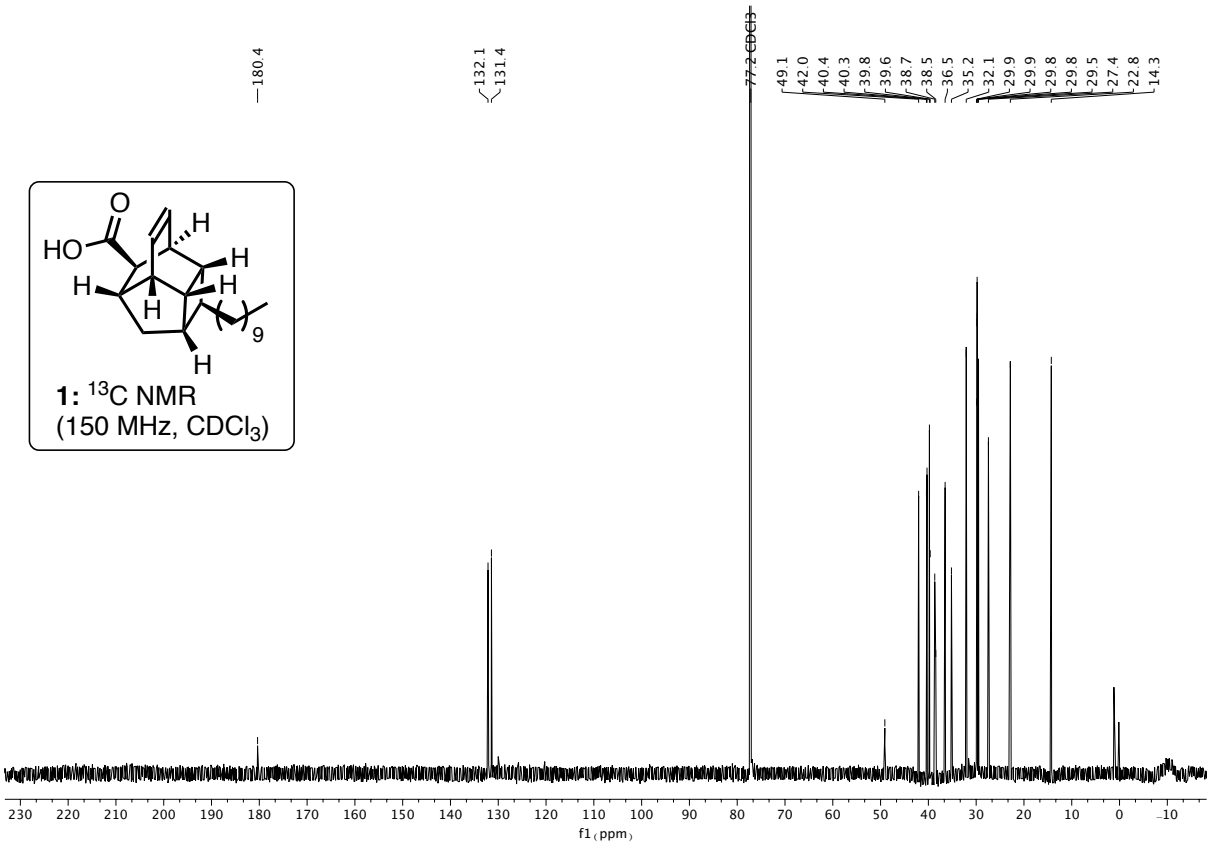


Figure 14: ^{13}C NMR of Endiandric acid J.

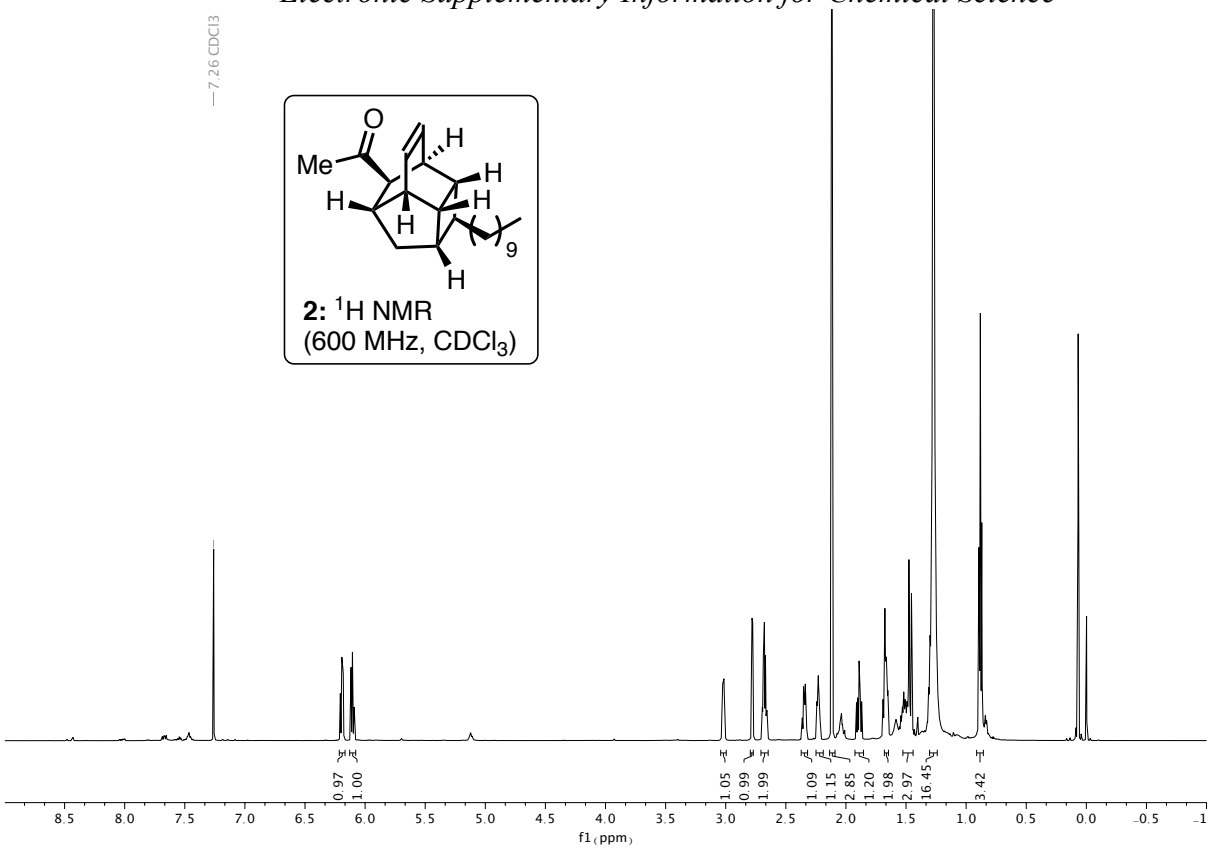


Figure 15: ^{1}H NMR of Beilcyclone A.

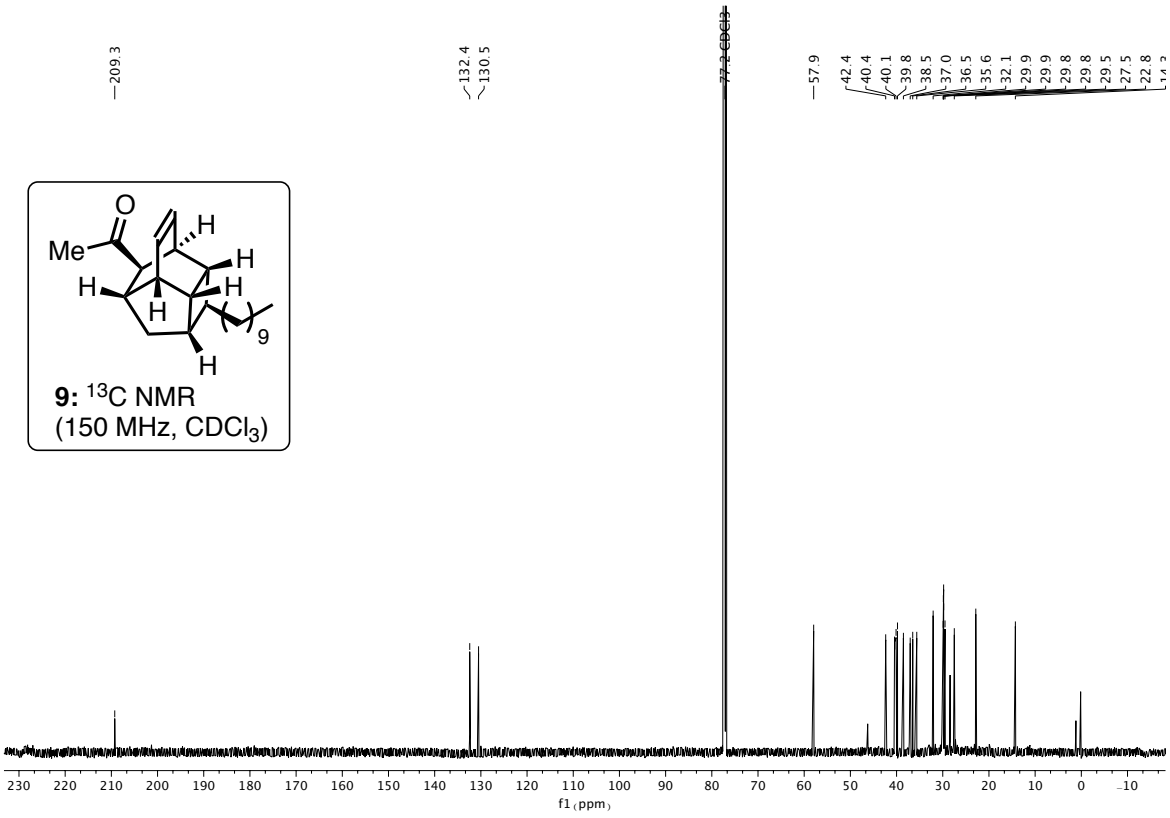
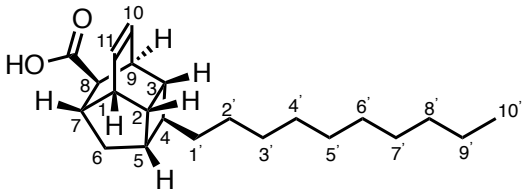


Figure 16: ^{13}C NMR of Beilcyclone A.

Tables of NMR data

Table of ^{1}H and ^{13}C NMR data of natural and synthetic Endiandric acid J (**1**).

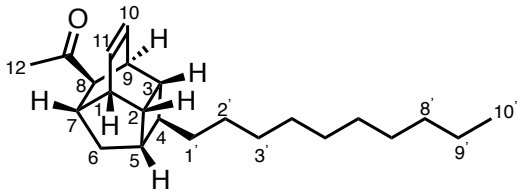


Endiandric Acid J (**1**)

^{1}H NMR of Endiandric acid J		
Assignment	**Synthetic (600 MHz)**	**Natural (400 MHz)**
11	6.19 – 6.26 (1H, m),	6.23 (ddd *J* = 10.0, 8.0, 2.0 Hz)
10	6.19 – 6.26 (1H, m)	6.23 (ddd, *J* = 10.0, 8.0, 2.0 Hz)
9	3.02 – 3.00 (1H, m)	3.02 (dt, *J* = 7.2, 4.8 Hz)
8	2.87 (1H, d, *J* = 3.8 Hz)	2.87 (d, *J* = 4.0 Hz)
1	2.65 – 2.71 (1H, m)	2.69 (ddd, *J* = 7.2, 4.8, 2.0 Hz)
7	2.54 (1H, t, *J* = 5.2 Hz)	2.54 (t, *J* = 5.2 Hz)
2	2.34 (1H, dt, *J* = 8.9, 5.5 Hz)	2.35 (dt, *J* = 8.4, 5.6 Hz)
5	2.23 (1H, br. t, *J* = 6.4 Hz)	2.23 (br. t, *J* = 6.8 Hz)
6	1.89 (1H, ddd, *J* = 12.9, 7.6, 5.4 Hz)	1.90 (ddd, *J* = 12.6, 7.6, 5.6 Hz)
3	1.66 – 1.68, (1H, m),	1.61 – 1.66 (m)
4	1.66 – 1.68, (1H, m),	1.61 – 1.66, m
6	1.54 (1H, d, *J* = 12.7 Hz),	1.54 (d, *J* = 12.6 Hz)
1’	1.43 – 1.51 (2H, m),	1.43 – 1.50 (m)
2’ – 9’	1.26 (16H, m)	1.26 (br. S)
10’	0.88 (3H, t, *J* = 6.9 Hz)	0.88 (t, *J* = 6.6 Hz)

^{13}C NMR of Endiandric acid J		
Assignement	**Synthetic**	**Natural**
C=O	180.3	180.1
H-C	132.1	131.9
H-C	131.4	131.3
H-C	49.1	48.9
H-C	42.0	41.8
H-C	40.4	40.1
H-C	40.3	39.4
H-C	39.8	39.6
H-C	39.6	38.5
H-C	38.7	38.2
CH_2	36.5	36.3
H-C	35.2	35.0
CH_2	32.1	31.9
CH_2	29.9	29.4 – 29.7
CH_2	29.9	29.4 – 29.7
CH_2	29.9	29.4 – 29.7
CH_2	29.8	29.4 – 29.7
CH_2	29.8	29.4 – 29.7
CH_2	29.8	29.4 – 29.7
CH_2	29.5	29.4 – 29.7
CH_2	27.4	27.3
CH_2	22.9	22.7
CH_3	14.3	14.1

Table of ^{1}H and ^{13}C NMR data of natural and synthetic Beilcyclone A (**2**).



Beilcyclone A (**2**)

^{1}H NMR of Bilcyclone A		
Assignement	**Synthetic (600 MHz)**	**Natural (600 MHz)**
11	6.20 (1H, ddd, *J* = 8.0. 6.4, 1.0 Hz)	6.20 (ddd, *J* = 8.0, 6.4, 0.8 Hz)
10	6.11 (1H, ddd, *J* = 8.0, 6.4, 1.0 Hz)	6.10 (ddd, *J* = 8.0, 6.0, 1.0 Hz)
9	3.02 (1H, dt, *J* = 7.3, 4.1 Hz)	3.02 (dt, *J* = 6.0, 4.0 Hz)
8	2.78 (1H, d, *J* = 3.6 Hz)	2.78 (d, *J* = 4.0 Hz)
1 and 7	2.68 – 2.65 (2H, m)	2.68 (m)
		2.66 (m)
2	2.35 (1H, dt, *J* = 9.8, 5.4 Hz)	2.35 (dt, *J* = 7.2, 6.0 Hz)
5	2.23 (1H, t, *J* = 6.3 Hz, 3.5 Hz)	2.23 (br. t, *J* = 6.0 Hz)
12	2.12 (3H, s)	2.12 (s)
6	1.89 (1H, ddd, *J* = 12.7, 7.5, 5.2 Hz)	1.89 (ddd, *J* = 12.8, 7.7, 5.0 Hz)
4 and 3	1.69 − 1.64 (2H, m)	1.64 − 1.70 (m)
6	1.53 − 1.45 (2H, m)	1.52 (m)
1‘		1.46 (d, *J* = 12.8 Hz)
2’ – 9’	1.26 (16H, br. s)	1.27 (br. s)
10‘	0.88 (3H, t, *J* = 6.9 Hz)	0.88 (t, *J* = 6.9 Hz)

^{13}C NMR of Beilcyclone A		
Assignement	**Synthetic**	**Natural**
C=O	209.3	209.2
H-C	132.4	132.3
H-C	130.5	130.3
H-C	57.9	57.8
H-C	42.4	42.2
H-C	40.4	40.3
H-C	40.1	40.2
H-C	40.1	39.9
H-C	39.8	39.6
H-C	38.5	38.3
H-C	37.0	36.9
H-C	36.5	36.3
H-C	35.6	35.5
H-C	32.1	31.9
CH_2	29.9 – 29.5	29.4 − 29.8
$COCH_3$	28.5	28.3
CH_2	27.5	27.3
CH_2	22.8	22.7
CH_3	14.3	14.1

Computational Studies

Calculations were carried out with density functional theory (DFT) using Gaussian 16 (revision A.03).[2] Geometries were optimised in the gas phase at the M06-2X/6-31G(d) level.[3] Stable ground states and transition states were identified by the number of imaginary vibrational frequencies. Zero-point energies and thermal corrections at 333.15 K (**10**-**13**), 393.15 K (**14**-**17**) and 1 atm were determined from the unscaled frequencies. The transition states were shown to connect reactants and products using intrinsic reaction coordinate calculations.[4] Single-point energy calculations of the optimised geometries were carried out in the gas phase at the M06-2X/6-311+G(d,p) level and in toluene solvent using the SMD continuum solvent model[5] at the M06-2X/6-31G(d) level. The optimised geometries are given below in Cartesian coordinates and the energies given in units of Hartree. The Gibbs free energy in toluene solution at 333.15 K (**10**-**13**), and 393.15 K (**14**-**17**) was calculated as Gsoln = EM06-2X/6-311+G(d,p) + ΔGthermal,M06-2X/6-31G(d) + GM06-2X/6-31G(d),toluene – EM06-2X/6-31G(d). The reaction free energy profiles below were calculated from the relative values of Gsoln for the various species.

Kinetic simulations were performed using the software program *KinTec Explorer* (https://kintekcorp.com).

Figure 17 shows the reaction profile of aldehyde **14**. The calculated transition structure of a thermal Claisen rearrangment in a chair-like conformation is located at 139.8 kJ/mol above the energy of the vinyl ether **17**. This activation barrier is inconsistent with the experimental reaction temperature of 60 °C, but we cannot discount the possibility of hydrogen bonding or transition metal catlaysis under the reaction conditions.

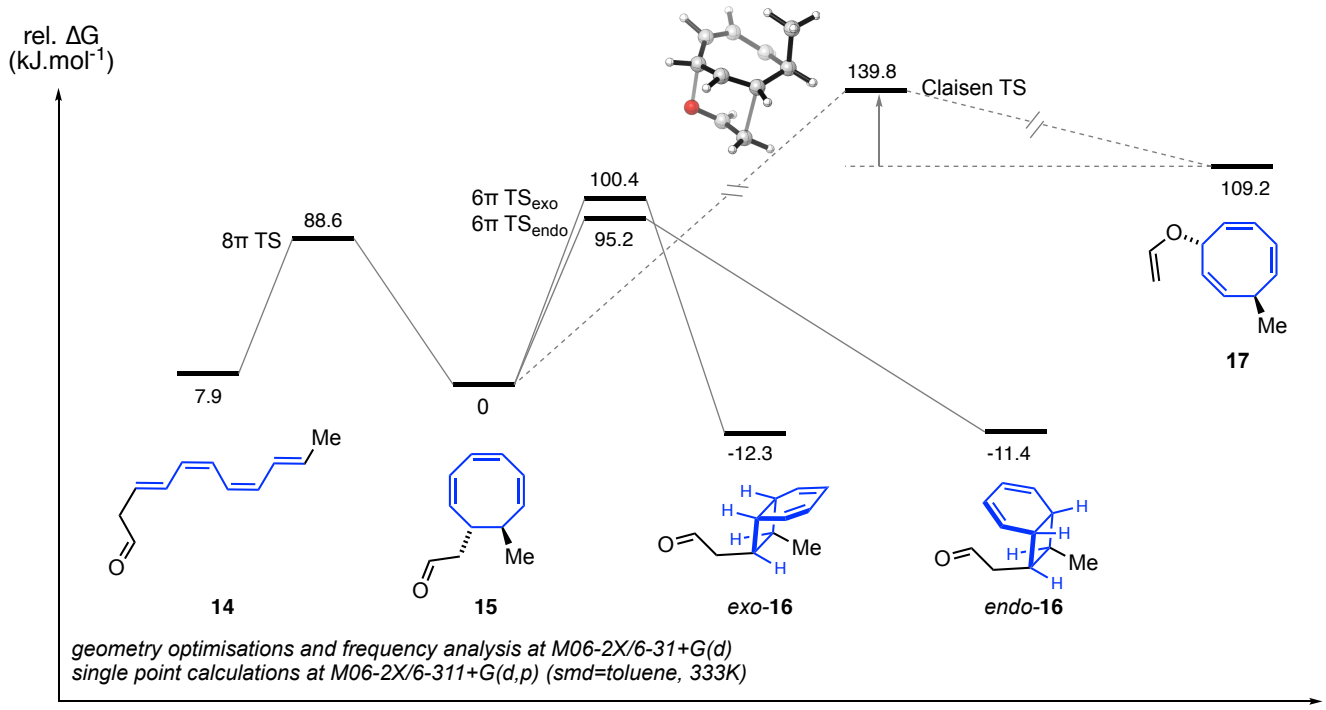


*Figure 17. Computational analysis of the 8π/6π-Claisen rearrangement sequence of vinyl ether **17**.*

Figure 18 shows a kinetic simulation starting from a population oone antipode of *endo*-**16** at 60 °C. Racemisation is predicted within hours, and equillibration between diasteroisomers within ~1.5 days.

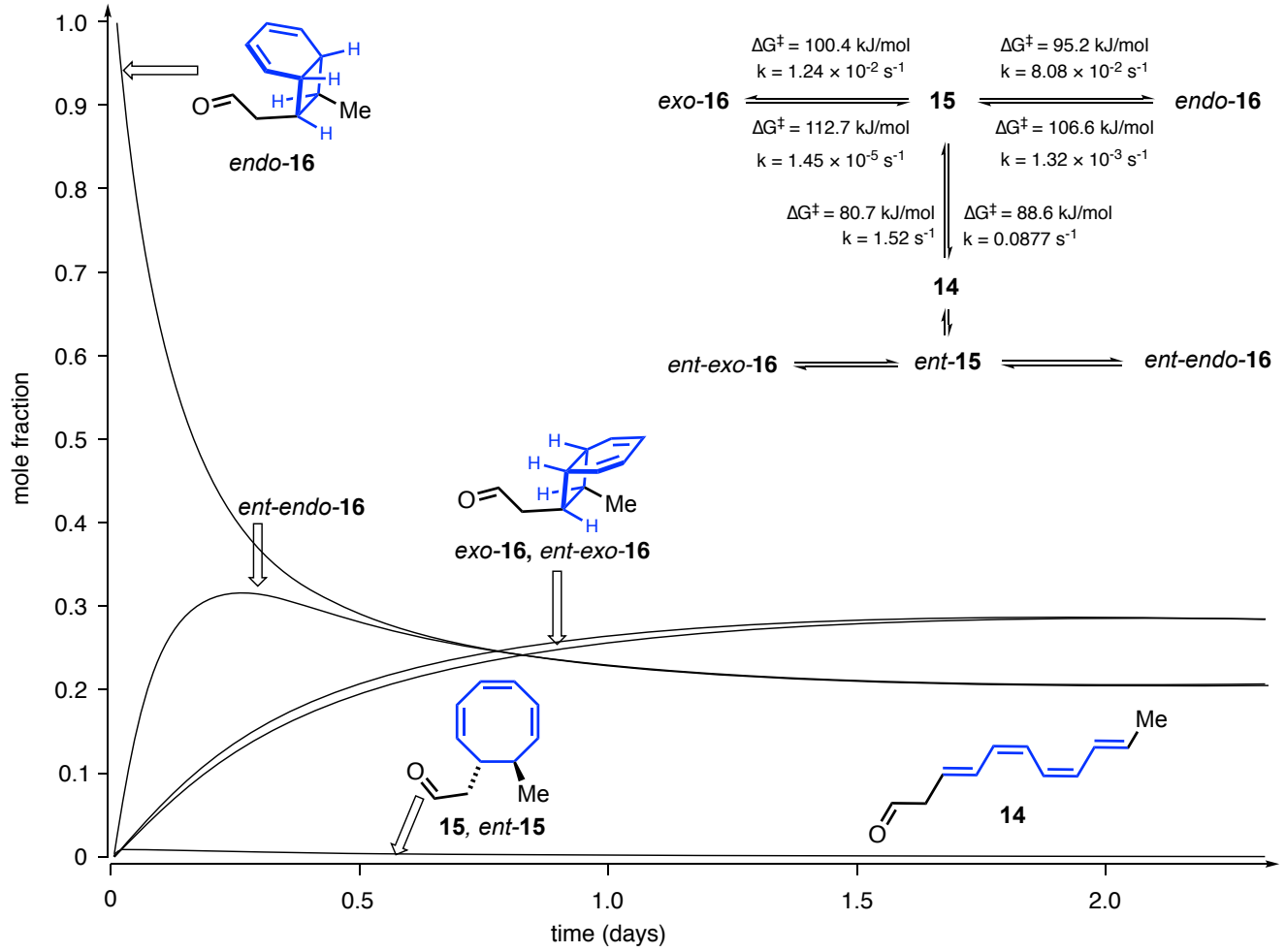


*Figure 18. Kinetic simulation from aldehyde endo-**16** at 333 K.*

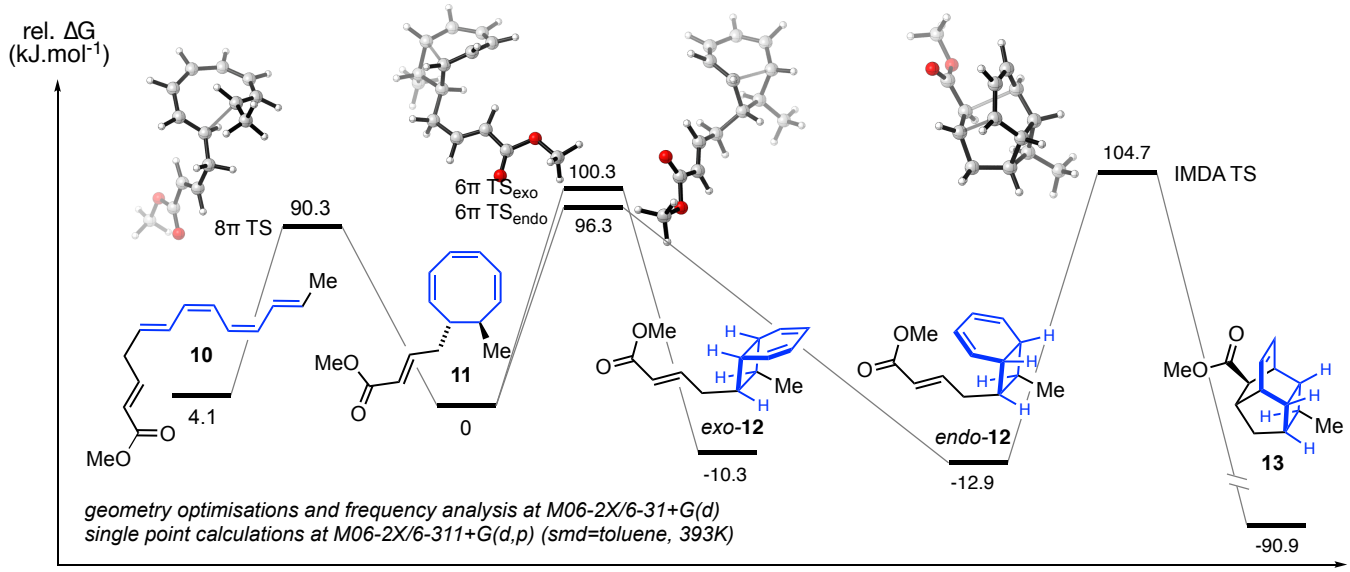


*Figure 19. Computational analysis of the 8π/6π/DA rearrangement sequence of ester **10**.*

Figure 20 shows a kinetic simulation starting from a population oone antipode of *endo*-**12** at 120 °C. Racemisation and equillibration between diasteroisomers is predicted within minutes.

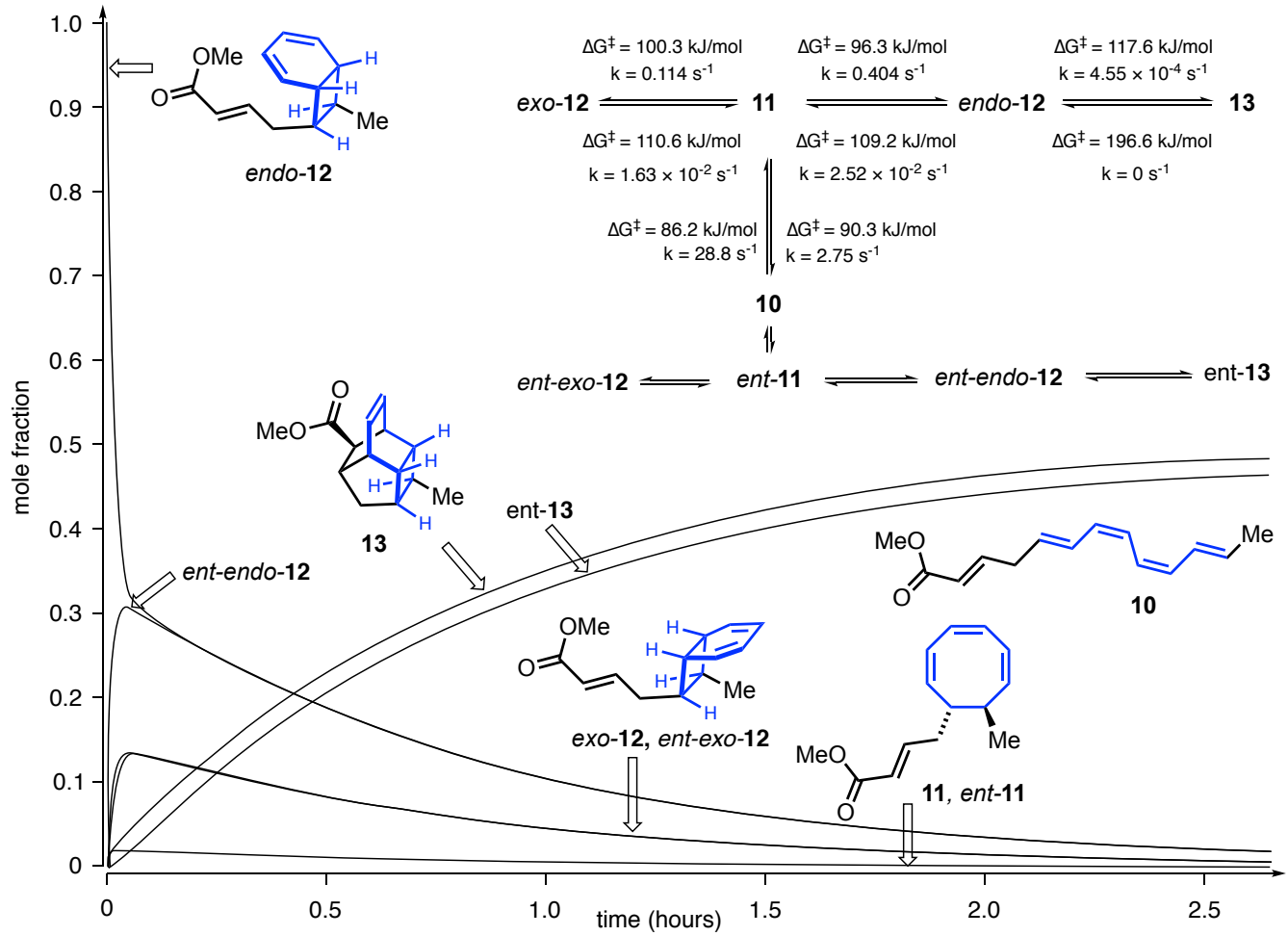
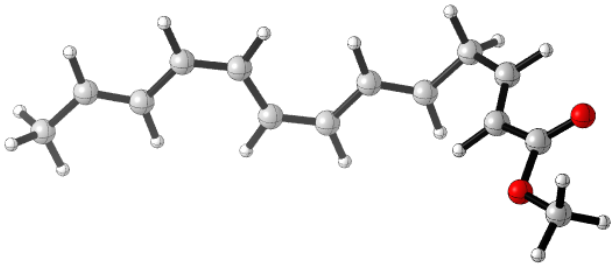
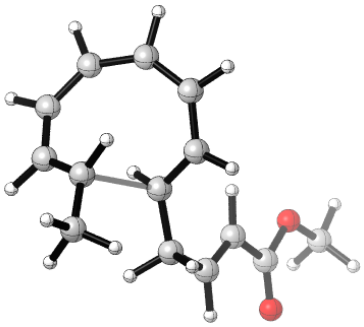


*Figure 20. Kinetic simulation of ester endo-**12** at 393 K.*



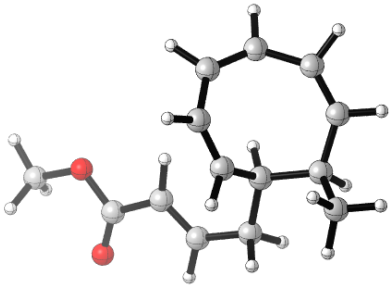
tetraene **10**
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.581874
Gibbs free energy (393K) = -694.381651

C	-1.26637300	-0.72122600	1.10092100
H	-0.96692100	-0.55518700	2.13449700
C	-2.51256200	-0.35306900	0.73692700
H	-3.14129100	0.08875000	1.50533400
C	-3.09164800	-0.49221900	-0.58682800
H	-2.46512600	-0.93224200	-1.35790000
C	-0.25385900	-1.32855500	0.25080700
H	-0.50036300	-1.52012400	-0.79217000
C	-4.33950400	-0.12253000	-0.94398400
H	-4.64088200	-0.28732900	-1.97747100
C	-5.35256000	0.48378700	-0.09428300
H	-5.11013800	0.67499000	0.94957800
C	0.96493700	-1.66473800	0.69255500
H	1.22408500	-1.46925300	1.73407200
C	-6.57058500	0.81733900	-0.54100900
H	-6.81164400	0.62506400	-1.58719400
C	-7.64542900	1.44254200	0.29161600
H	-7.31077400	1.59515900	1.32123400
H	-8.54358300	0.81460700	0.31232300
H	-7.94732800	2.41319500	-0.11838600
C	2.03248300	-2.29592200	-0.14896500
H	1.63824400	-2.52785800	-1.14788300
H	2.32631500	-3.26303200	0.28383800
C	3.27579200	-1.46336300	-0.30533100
H	4.14412300	-1.94708800	-0.75111200
C	3.39769800	-0.18374200	0.04793100
H	2.58470200	0.38514800	0.48773700
C	4.68495200	0.51618200	-0.17263800
O	5.68280700	0.02919400	-0.65138300
O	4.61438900	1.79710200	0.23452100
C	5.81363100	2.54532100	0.05498200
H	5.59905000	3.54598400	0.42695600
H	6.08850000	2.57750600	-1.00175500
H	6.63362500	2.09250400	0.61700200



*tetraene **10** 8pi-TS*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.55896
Gibbs free energy (393K) = -694.34883
imaginary frequency: -348.05

C	-3.16987200	0.95789500	-1.56686200
H	-3.43018300	1.20959200	-2.59333800
C	-2.91322400	2.06190500	-0.76199500
H	-3.18169200	2.99624100	-1.25450900
C	-2.43170100	2.30370700	0.55228700
H	-2.64911600	3.32537200	0.86322500
C	-1.72520400	1.60432200	1.52393600
H	-1.65147700	2.12129300	2.47877600
C	-3.16997700	-0.41722400	-1.27493300
H	-3.20195700	-1.10301500	-2.12187000
C	-3.06020100	-0.95077400	-0.00781300
H	-3.30750700	-0.29615600	0.82023600
C	-1.07601200	0.35818600	1.46909900
H	-0.76024600	-0.07979200	2.41655500
C	-0.88356200	-0.37322700	0.31613900
H	-0.91993100	0.16724300	-0.62339300
C	-3.18055500	-2.42523900	0.25204700
H	-2.58410200	-2.73296100	1.11651700
H	-2.86280400	-3.01170300	-0.61567900
H	-4.22258900	-2.68789900	0.47054900
C	-0.08105000	-1.64420000	0.30948700
H	-0.21405900	-2.18209300	1.25937300
H	-0.45126700	-2.32319900	-0.47031800
C	1.39409400	-1.44048500	0.08774800
H	1.99351200	-2.33609800	-0.07312000
C	2.02819300	-0.26784900	0.07680900
H	1.52201300	0.67903900	0.23504800
C	3.49244200	-0.23594500	-0.15060700
O	4.20127400	-1.19760300	-0.33829200
O	3.95842200	1.02622800	-0.12333700
C	5.36224600	1.14675800	-0.33468500
H	5.63689400	0.74344300	-1.31203900
H	5.91234900	0.60246300	0.43634300
H	5.58089800	2.21225500	-0.28326600



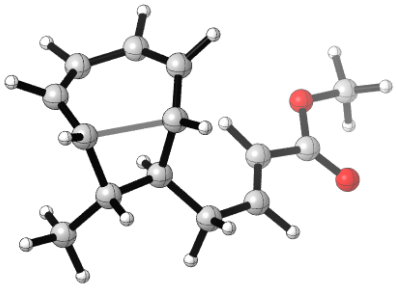
cyclooctatriene ***11***

M06-2X/6-311+G(d,p) smd toluene

Energy (0K, vacuum) = -694.597663

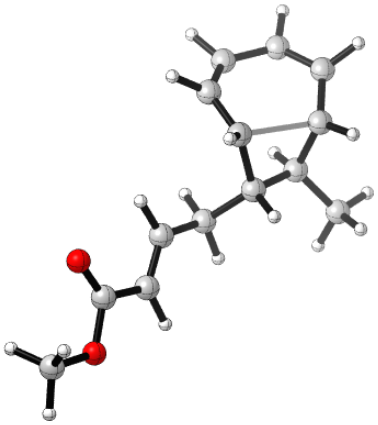
Gibbs free energy (393K) = -694.383209

C	3.52806600	0.16455800	-0.78005100
H	4.53899000	-0.12860800	-1.06826900
C	3.29169600	1.48414500	-0.83483300
H	4.13635500	2.07436900	-1.19229200
C	2.12851800	2.34055800	-0.55342500
H	2.07394300	3.21019000	-1.20766400
C	1.24728600	2.30950900	0.46134800
H	0.56871400	3.15666200	0.55445600
C	1.12424700	1.27631600	1.48843900
H	0.96574700	1.61987400	2.50940000
C	1.11443700	-0.03792100	1.24144600
H	0.99102100	-0.72353300	2.08047500
C	1.20631400	-0.66977300	-0.12231500
H	0.86969300	0.05835000	-0.87136000
C	2.66090500	-1.02866700	-0.47939100
H	2.63421100	-1.61772200	-1.41132300
C	0.29445600	-1.89966500	-0.21037600
H	0.52226500	-2.60055500	0.60566300
H	0.51113100	-2.45512000	-1.13455200
C	-1.17805600	-1.61826100	-0.18058300
H	-1.83928900	-2.48441900	-0.20465500
C	3.33732400	-1.90654500	0.58373200
H	2.78075400	-2.83373700	0.75275600
H	3.41471700	-1.36682000	1.53223000
H	4.34965400	-2.18049200	0.27079400
C	-1.76029300	-0.41843000	-0.14272300
H	-1.20859700	0.51510400	-0.10595800
C	-3.23952200	-0.33126800	-0.13942100
O	-4.00645700	-1.26607300	-0.16134200
O	-3.64788100	0.95170900	-0.10872000
C	-5.06178200	1.12517200	-0.10487400
H	-5.50294200	0.68586000	-1.00252100
H	-5.23027800	2.20079400	-0.08089200
H	-5.50295200	0.64636100	0.77236100



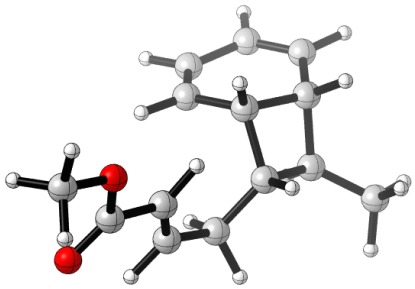
*cyclooctatriene **11** 6pi-exo-TS*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.559128
Gibbs free energy (393K) = -694.345014
imaginary frequency: -578.11

C	-1.33497900	0.20928700	1.25217300
H	-1.28733000	-0.26186300	2.23635700
C	-0.84582000	1.51281100	1.13515100
H	-0.33712400	1.98292400	1.97487100
C	-1.12957200	2.27993100	0.01257900
H	-0.58041300	3.20325200	-0.15533600
C	-2.31858600	2.11333000	-0.71987700
H	-2.55288800	2.89968400	-1.43404300
C	-3.37901300	1.30447200	-0.31043400
H	-4.36399300	1.74392600	-0.47920800
C	-3.34837700	0.13544900	0.47415700
H	-4.26745500	-0.01825800	1.04781600
C	-2.69934700	-1.17322900	0.02069800
H	-2.88771400	-1.91604600	0.80910500
C	-1.23962900	-0.77767500	0.09319700
H	-0.96561200	-0.23101400	-0.81780800
C	-0.27329300	-1.93656000	0.31683600
H	-0.47556400	-2.71777900	-0.43237200
H	-0.49538700	-2.40948100	1.28542900
C	1.19138600	-1.62266900	0.26550800
H	1.87261300	-2.44247600	0.49338400
C	-3.21947600	-1.70633700	-1.30859500
H	-2.73453800	-2.65269300	-1.57315200
H	-3.02427200	-0.97989200	-2.10437300
H	-4.29955100	-1.88200000	-1.26860300
C	1.74468500	-0.44974500	-0.04657900
H	1.16917000	0.43940700	-0.28155900
C	3.22132600	-0.32946300	-0.06842500
O	3.59990200	0.91702900	-0.41115800
O	4.01053400	-1.21104900	0.18204500
C	5.00926600	1.11779100	-0.45814500
H	5.46653600	0.44740600	-1.18952000
H	5.45554300	0.92499500	0.52019400
H	5.15306100	2.15771600	-0.74773900



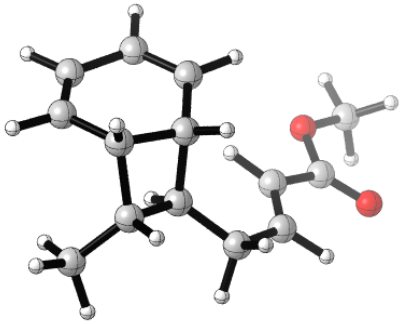
*cyclooctatriene **11** 6pi-endo-TS*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.559041
Gibbs free energy (393K) = -694.346533
imaginary frequency: -572.51

C	-3.15335400	0.50354900	0.96537600
H	-3.15249100	1.02827300	1.92310400
C	-4.27867600	-0.25760400	0.64033500
H	-5.16097200	-0.23266900	1.27741900
C	-4.23461500	-1.18190200	-0.39601300
H	-5.16185100	-1.61576500	-0.76263500
C	-3.04840500	-1.84826000	-0.75106200
H	-3.16317400	-2.70929200	-1.40585900
C	-1.86332600	-1.77469700	-0.01678200
H	-1.34445700	-2.72978900	0.08779100
C	-1.38251700	-0.71683900	0.77849700
H	-0.74059200	-1.05311800	1.59774100
C	-0.98560600	0.65015200	0.21803500
H	-0.56595100	1.23735400	1.04684000
C	-2.35140900	1.20297400	-0.12556400
H	-2.66961400	0.80097700	-1.09485100
C	0.04134500	0.60627800	-0.92357300
H	0.23511700	1.62553900	-1.28009000
H	-0.40942600	0.03856500	-1.74960100
C	-2.49539700	2.71910700	-0.12341300
H	-3.53031300	3.01588600	-0.31929500
H	-1.86129400	3.17588700	-0.89105700
H	-2.20090100	3.13328000	0.84776900
C	1.32165700	-0.04903400	-0.51529700
H	1.27589800	-1.09782200	-0.22030900
C	2.50996600	0.55422800	-0.46067000
H	2.65241200	1.59495400	-0.73654600
C	3.70346800	-0.20097400	-0.01510000
O	4.80420300	0.57448400	-0.03842800
O	3.71959500	-1.35973000	0.33015000
C	6.00030000	-0.07880500	0.37690500
H	6.21466000	-0.93107700	-0.27196400
H	5.90281600	-0.43651600	1.40447500
H	6.78915500	0.66826800	0.30325400



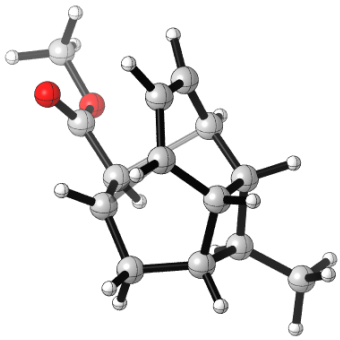
bicyclo[4.2.0]octadiene ***12****-endo*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.603461
Gibbs free energy (393K) = -694.388117

C	1.20197000	-1.51340800	0.48293300
H	0.23909800	-1.75207600	0.93231600
C	2.30937300	-2.15894200	0.86945500
H	2.25193500	-2.91792700	1.64490500
C	3.61466300	-1.91617200	0.23625200
H	4.44150200	-2.56881300	0.50150300
C	3.77830100	-0.93596600	-0.65941400
H	4.73998100	-0.77567700	-1.14057000
C	1.21119200	-0.47408400	-0.60170600
H	0.57671100	-0.80919600	-1.43248500
C	2.64735700	-0.00661200	-0.97742200
H	2.68591200	0.32978800	-2.02004000
C	0.92355100	0.97642200	-0.10640700
H	0.48785500	1.56389200	-0.92609600
C	2.45002500	1.22082000	-0.04344700
H	2.81432000	0.95872000	0.95850700
C	2.99254300	2.56966600	-0.47521300
H	2.64490400	2.81944400	-1.48405800
H	4.08742700	2.57307800	-0.48445700
H	2.66162000	3.36558900	0.20108100
C	0.13465100	1.19820600	1.17205400
H	0.22928700	2.24946700	1.48219500
H	0.59249200	0.61346100	1.98395700
C	-1.32080400	0.85035300	1.10963800
H	-1.90685200	1.00047100	2.01627200
C	-1.96581900	0.36670000	0.04591900
H	-1.48297800	0.17884800	-0.90761500
C	-3.41344400	0.06571000	0.14085100
O	-4.10483000	0.21258100	1.12177300
O	-3.88637200	-0.40572000	-1.02828300
C	-5.27579100	-0.72185900	-1.02342500
H	-5.48988900	-1.48894200	-0.27577100
H	-5.50198300	-1.08666100	-2.02418500
H	-5.86834900	0.16663700	-0.79379000



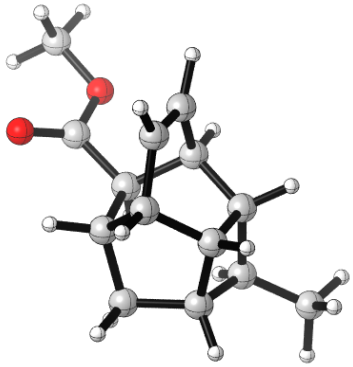
bicyclo[4.2.0]octadiene ***12****-exo*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.602865
Gibbs free energy (393K) = -694.387143

C	0.75940200	1.49822100	-0.96373500
H	-0.16627300	1.64788000	-1.51372600
C	1.24480100	2.45354800	-0.16182600
H	0.71874200	3.39620600	-0.04123300
C	2.51998100	2.27389000	0.54741900
H	2.82669300	3.04348400	1.25042000
C	3.32276800	1.23016500	0.30461500
H	4.28877800	1.15852200	0.80130000
C	1.46664000	0.18199400	-1.08234700
C	2.96929900	0.14642400	-0.67393000
C	1.19750800	-0.90403200	0.00197500
H	0.95297700	-0.41284800	0.95324000
C	2.70589900	-1.24328500	-0.02309400
H	2.88456900	-2.02226600	-0.77646700
C	3.38147900	-1.61558400	1.28383500
H	3.20448500	-0.84601300	2.04263100
H	4.46400100	-1.72751500	1.16038600
H	2.98942300	-2.56461200	1.66523700
C	0.22528600	-2.03187800	-0.29036100
H	0.39150100	-2.85250400	0.42516000
H	0.45778200	-2.46290000	-1.27569700
C	-1.23114700	-1.67870600	-0.26105200
H	-1.93282000	-2.46086700	-0.55060000
C	-1.75165800	-0.50291800	0.09499100
H	-1.15203400	0.34831900	0.40147100
C	-3.22235300	-0.32280600	0.07458200
O	-4.03648800	-1.16077900	-0.23736400
O	-3.56128300	0.92429500	0.45368100
C	-4.96230100	1.18236200	0.46340600
H	-5.38306300	1.04447000	-0.53527800
H	-5.07292900	2.21602300	0.78776600
H	-5.47032200	0.50529200	1.15394900
H	1.32382600	-0.25826700	-2.07607000
H	3.70321500	0.13509000	-1.48989200



*bicyclo[4.2.0]octadiene **12**-endo IMDA TS*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -694.567091
Gibbs free energy (393K) = -694.343315
imaginary frequency: -478.95

C	0.77474600	1.88408400	-0.38261800
H	0.99826900	2.84041000	0.08813300
C	-0.27266600	1.81211800	-1.28706700
H	-0.93195800	2.66274800	-1.42966300
C	-0.66344500	0.55284600	-1.77883500
H	-1.62095700	0.45356000	-2.28254600
C	-0.00036100	-0.56802100	-1.31807800
H	-0.40256600	-1.55754600	-1.52881600
C	1.92040100	0.91218200	-0.51095600
H	2.73414700	1.36951500	-1.08259500
C	1.48817200	-0.46738000	-1.07236900
H	1.97459300	-0.72470300	-2.02314800
C	2.38139400	0.23137800	0.80627800
H	3.41860800	0.41186600	1.11022200
C	2.17655300	-1.16016200	0.13522900
H	1.55402900	-1.86051900	0.70073900
C	3.48819100	-1.83700200	-0.23782800
H	4.13178100	-1.14995100	-0.80031700
H	3.31498900	-2.71957600	-0.86236000
H	4.03642900	-2.15164200	0.65616700
C	1.40754400	0.60785900	1.92553300
H	1.73307400	1.54856700	2.38191100
H	1.41567100	-0.15373300	2.71560400
C	0.01966300	0.78069200	1.35183200
H	-0.57097500	1.64502500	1.63702000
C	-0.68513500	-0.31727300	0.88082300
H	-0.35249000	-1.33555700	1.03465700
C	-2.10360800	-0.12744000	0.56372100
O	-2.66275500	0.94724100	0.50285600
O	-2.72910300	-1.29374700	0.28489100
C	-4.09532000	-1.15604700	-0.08727900
H	-4.46129900	-2.16685500	-0.26358500
H	-4.18709400	-0.55194900	-0.99390000
H	-4.66614900	-0.67462200	0.71019400



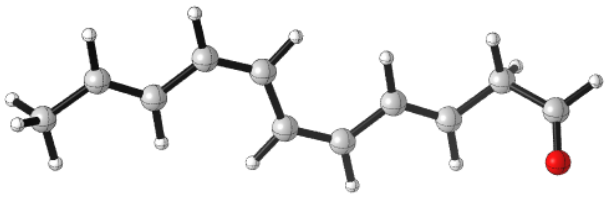
IMDA product ***13***

M06-2X/6-311+G(d,p) smd toluene

Energy (0K, vacuum) = -694.646924

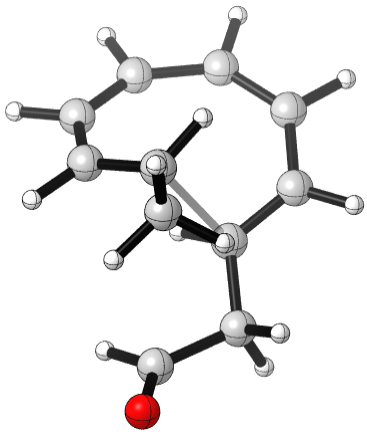
Gibbs free energy (393K) = -694.417819

C	1.91165300	-0.73632000	0.69906500
H	2.64950300	-1.05897900	1.43580000
C	1.43854300	0.73777000	0.82872000
H	1.77978300	1.26889600	1.72372400
C	2.41270700	-0.42475400	-0.74206400
H	3.43469700	-0.71462800	-1.00510100
C	2.22563900	1.08927700	-0.46210600
H	1.66297800	1.64146000	-1.22557100
C	3.53713200	1.80540500	-0.17338400
H	4.11521000	1.25944600	0.58174800
H	3.35999800	2.81642600	0.20813000
H	4.15320500	1.88160000	-1.07535100
C	1.35913900	-1.07172800	-1.65030100
H	1.69631200	-2.07319600	-1.94210100
H	1.17960500	-0.50354000	-2.57041900
C	-2.10691700	0.01305000	-0.56070900
O	-2.73062500	-0.96472500	-0.89089100
O	-2.70262900	1.15106400	-0.15461900
C	-4.12717200	1.10166900	-0.12511500
H	-4.45225600	2.08263600	0.21851200
H	-4.46578700	0.32119800	0.55996600
H	-4.52328500	0.89152300	-1.12107200
C	0.10071400	-1.20239900	-0.77716400
H	-0.61732400	-1.91769500	-1.18289500
C	-0.59522700	0.15747300	-0.56806000
H	-0.36590500	0.83464000	-1.40085200
C	-0.10648900	0.79058300	0.76818600
H	-0.47352600	1.81517400	0.85573600
C	0.68116200	-1.66827300	0.59515100
H	0.97955200	-2.71938900	0.54009800
C	-0.24408800	-1.38476300	1.74823900
H	-0.54468000	-2.16693000	2.43837600
C	-0.62495700	-0.10921000	1.86510900
H	-1.27309000	0.26396300	2.65195900



*tetraene **14***
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.648737
Gibbs free energy (393K) = -502.492141

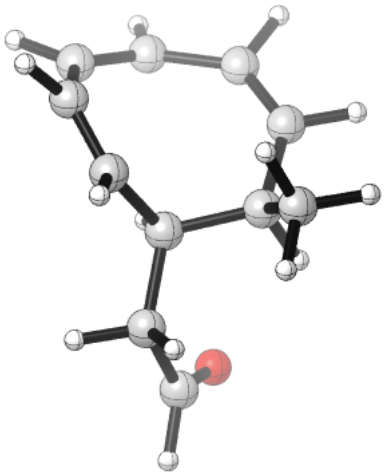
C	0.59773100	-0.83334900	-0.42156600
H	0.90186600	-1.85632200	-0.63617200
C	-0.71987800	-0.58236100	-0.27353800
H	-1.39800000	-1.42495600	-0.37868700
C	-1.31606700	0.70976500	0.01298600
H	-0.64055400	1.55453500	0.11744800
C	1.68460800	0.12861600	-0.32351300
H	1.43844800	1.16487500	-0.09727900
C	-2.63493100	0.95479500	0.16119300
H	-2.93989200	1.97815200	0.37538100
C	-3.72201400	-0.00715900	0.06711300
H	-3.47955600	-1.04693000	-0.14521500
C	2.96893800	-0.20590300	-0.49777900
H	3.23254500	-1.24099000	-0.70771100
C	-5.00787100	0.33069600	0.23074100
H	-5.24898900	1.37286100	0.44381300
C	-6.15979400	-0.62074900	0.14459800
H	-5.81913300	-1.63666900	-0.07280600
H	-6.86272600	-0.31930100	-0.64054900
H	-6.72460100	-0.64219000	1.08373800
C	4.10725100	0.76083300	-0.41452800
H	3.78896900	1.72976100	-0.00887100
H	4.52008900	0.98139400	-1.41288500
C	5.26986500	0.24928800	0.41021400
H	6.09584700	0.97658500	0.55859500
O	5.34108300	-0.86220500	0.86821000



*tetraene **14** 8pi-TS*

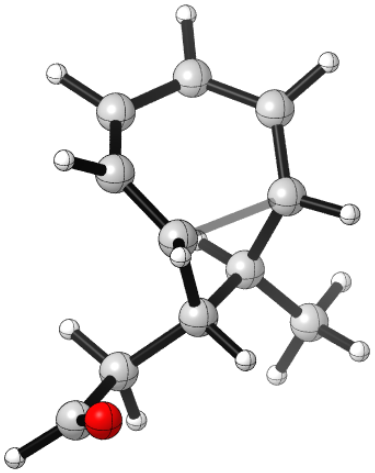
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.626711
Gibbs free energy (393K) = -502.461417
imaginary frequency: -348.05

C	-3.16987200	0.95789500	-1.56686200
H	-3.43018300	1.20959200	-2.59333800
C	-2.91322400	2.06190500	-0.76199500
H	-3.18169200	2.99624100	-1.25450900
C	-2.43170100	2.30370700	0.55228700
H	-2.64911600	3.32537200	0.86322500
C	-1.72520400	1.60432200	1.52393600
H	-1.65147700	2.12129300	2.47877600
C	-3.16997700	-0.41722400	-1.27493300
H	-3.20195700	-1.10301500	-2.12187000
C	-3.06020100	-0.95077400	-0.00781300
H	-3.30750700	-0.29615600	0.82023600
C	-1.07601200	0.35818600	1.46909900
H	-0.76024600	-0.07979200	2.41655500
C	-0.88356200	-0.37322700	0.31613900
H	-0.91993100	0.16724300	-0.62339300
C	-3.18055500	-2.42523900	0.25204700
H	-2.58410200	-2.73296100	1.11651700
H	-2.86280400	-3.01170300	-0.61567900
H	-4.22258900	-2.68789900	0.47054900
C	-0.08105000	-1.64420000	0.30948700
H	-0.21405900	-2.18209300	1.25937300
H	-0.45126700	-2.32319900	-0.47031800
C	1.39409400	-1.44048500	0.08774800
H	1.99351200	-2.33609800	-0.07312000
C	2.02819300	-0.26784900	0.07680900
H	1.52201300	0.67903900	0.23504800
C	3.49244200	-0.23594500	-0.15060700
O	4.20127400	-1.19760300	-0.33829200
O	3.95842200	1.02622800	-0.12333700
C	5.36224600	1.14675800	-0.33468500
H	5.63689400	0.74344300	-1.31203900
H	5.91234900	0.60246300	0.43634300
H	5.58089800	2.21225500	-0.28326600



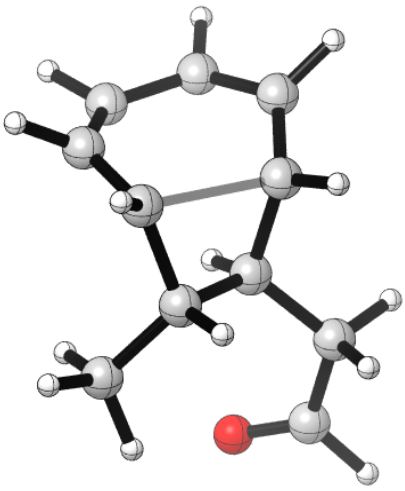
cyclooctatriene ***15***
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.664644
Gibbs free energy (393K) = -502.495162

C	-0.8102020000	1.7048200000	-0.4296120000
H	-0.7845080000	2.7937720000	-0.4957570000
C	-1.8948000000	1.1384700000	-0.9802260000
H	-2.5797850000	1.8481690000	-1.4455320000
C	-2.3732800000	-0.2430470000	-1.1477430000
H	-2.9346820000	-0.3840910000	-2.0709350000
C	-2.3687730000	-1.2867170000	-0.3005530000
H	-2.9355230000	-2.1674490000	-0.5997660000
C	-1.7208160000	-1.3606050000	1.0078330000
H	-2.2915570000	-1.8317940000	1.8068280000
C	-0.4740470000	-0.9500420000	1.2627690000
H	-0.0894790000	-1.0562080000	2.2778870000
C	0.4760510000	-0.3891580000	0.2404460000
H	0.1733330000	-0.7352910000	-0.7542890000
C	0.4338940000	1.1513060000	0.2106760000
H	1.2689230000	1.4932900000	-0.4178450000
C	1.8901270000	-0.9183570000	0.4985790000
H	1.8656050000	-2.0015620000	0.6892280000
H	2.3405520000	-0.4819100000	1.4014950000
C	2.8484810000	-0.7096710000	-0.6483970000
H	3.8857010000	-1.0629750000	-0.4651060000
O	2.5525000000	-0.2191960000	-1.7097510000
C	0.6107190000	1.7797760000	1.6013060000
H	1.5418980000	1.4574060000	2.0791340000
H	-0.2254240000	1.5101850000	2.2533320000
H	0.6408210000	2.8713780000	1.5288700000



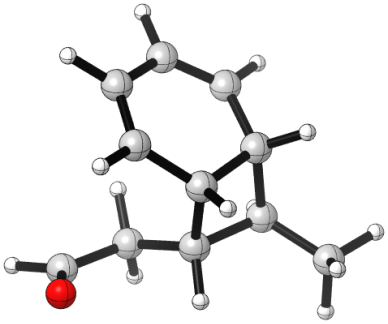
*bicyclo[4.2.0]octadiene **15**-endo*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.627819
Gibbs free energy (393K) = -502.45891
imaginary frequency: -574.49

C	-1.42753200	0.69328700	0.85223600
H	-1.39313600	1.26718900	1.78069400
C	-2.63010100	0.06652300	0.51708800
H	-3.52448700	0.23933500	1.11313100
C	-2.66807400	-0.91264700	-0.46780200
H	-3.62932000	-1.24597000	-0.85172900
C	-1.56475300	-1.74289600	-0.73465400
H	-1.76646700	-2.61959200	-1.34663300
C	-0.40634000	-1.77735300	0.04409900
H	-0.01962100	-2.78309500	0.22085000
C	0.18052200	-0.74831400	0.80481800
H	0.75146700	-1.11079600	1.66156900
C	0.76738400	0.52600200	0.19513500
H	1.22798900	1.09589700	1.01259900
C	-0.50302400	1.22360200	-0.23734900
H	-0.83658800	0.81140800	-1.19710700
C	1.81671900	0.28524800	-0.88266900
H	2.11996700	1.23038300	-1.35919400
H	1.40199600	-0.34000700	-1.68660500
C	-0.45252400	2.74368000	-0.31978300
H	-1.43245600	3.15642000	-0.57835000
H	0.26436900	3.07425800	-1.07981100
H	-0.14562200	3.17201000	0.64128100
C	3.06629700	-0.38078000	-0.36540000
H	3.83584000	-0.62010600	-1.12964700
O	3.25932900	-0.64818100	0.79557900



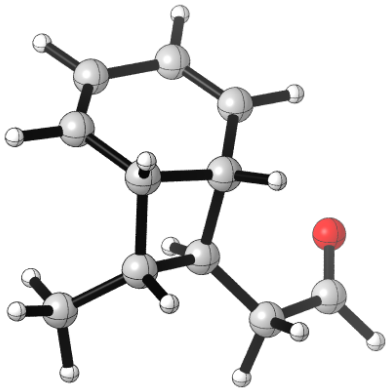
bicyclo[4.2.0]octadiene ***15****-exo*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.625871
Gibbs free energy (393K) = -502.456922
imaginary frequency: -574.83

C	-0.73602200	-0.93321800	-1.02551200
H	-0.54019200	-1.19626100	-2.06747300
C	-1.70409000	-1.66960500	-0.33863500
H	-2.16644000	-2.53878300	-0.80326100
C	-2.21858300	-1.20594800	0.86572400
H	-2.81870300	-1.87107200	1.48197600
C	-2.29890100	0.16599600	1.15923500
H	-2.91290900	0.43537400	2.01572700
C	-2.03320300	1.18145200	0.23892900
H	-2.73008400	2.02005100	0.29300400
C	-1.16295200	1.17465700	-0.86776300
H	-1.48859100	1.84535000	-1.66919500
C	0.35994700	1.06955500	-0.76232100
H	0.75253200	1.11688000	-1.78888600
C	0.47065000	-0.36679800	-0.28940400
H	0.28725200	-0.41159800	0.78913700
C	1.76127200	-1.11374100	-0.60150100
H	2.08981400	-0.93437900	-1.63614400
H	1.60518200	-2.20109000	-0.52945700
C	2.90630600	-0.78066300	0.32342000
H	3.87564800	-1.26045400	0.06951200
O	2.81696300	-0.06707600	1.29162600
C	0.99736800	2.17363400	0.07256700
H	2.08893400	2.11653700	0.04706100
H	0.67772000	2.08556800	1.11542300
H	0.69338400	3.15855800	-0.29887100



bicyclo[4.2.0]octadiene ***16****-endo*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.671214
Gibbs free energy (393K) = -502.499491

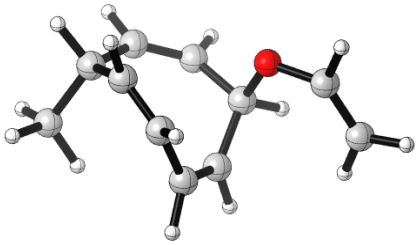
C	-0.79194300	1.19641500	-1.07019400
H	-1.65209400	1.09971600	-1.72665100
C	-0.64034300	2.27193800	-0.28826500
H	-1.37147000	3.07535600	-0.30726900
C	0.52141500	2.41265200	0.60428500
H	0.54983300	3.26540500	1.27718600
C	1.53546300	1.53939200	0.58323300
H	2.39687600	1.67997300	1.23417500
C	1.56061400	0.35281100	-0.33672300
H	2.42985500	0.42484700	-1.00501000
C	0.19858200	0.07147000	-1.03501600
H	0.34464300	-0.33000400	-2.04193600
C	1.45130800	-1.02378200	0.38062600
H	1.60818400	-0.97601300	1.46639200
C	-0.04349100	-1.10903100	-0.03586900
H	-0.32746200	-2.04757400	-0.52378700
C	2.32377400	-2.10760900	-0.23257800
H	3.38564200	-1.91232300	-0.05072000
H	2.17304300	-2.15547400	-1.31762700
H	2.08064500	-3.09129000	0.18231900
C	-1.01931100	-0.81921600	1.09014400
H	-0.81661600	0.15146800	1.56326500
H	-0.91806900	-1.56798500	1.89052500
C	-2.45743700	-0.82967900	0.63997100
H	-3.20701600	-0.58203900	1.42121100
O	-2.81347300	-1.09577900	-0.48247000



bicyclo[4.2.0]octadiene ***16****-exo*

M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.670072
Gibbs free energy (393K) = -502.499858

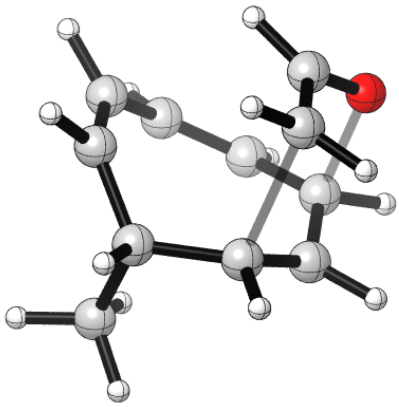
C	2.37393300	-0.03532000	-0.02076400
H	3.22039500	0.62365400	-0.20601100
C	2.33432700	-1.25206900	-0.57663600
H	3.14399200	-1.57906700	-1.22362200
C	1.24083500	-2.19724400	-0.30726800
H	1.33069700	-3.20817800	-0.69392800
C	0.16601500	-1.83269200	0.39984100
H	-0.64257400	-2.53042000	0.59304900
C	1.30178900	0.46404200	0.90530300
H	1.73755200	0.66332800	1.89266500
C	0.01944200	-0.42115600	0.88262200
H	-0.49699700	-0.38377900	1.84971600
C	0.44790100	1.63732700	0.33813900
H	0.05985900	2.23023500	1.17730700
C	-0.62113500	0.60564000	-0.09357700
H	-0.43974100	0.27739400	-1.12430600
C	1.02756800	2.55500800	-0.72291600
H	1.84476100	3.16593500	-0.32471200
H	0.26002100	3.23488300	-1.10875300
H	1.41915100	1.97204300	-1.56313200
C	-2.07591900	0.98820700	0.08946700
H	-2.26269000	1.33026600	1.11956900
H	-2.35259200	1.83810900	-0.55248600
C	-3.04404200	-0.13414900	-0.18938100
H	-4.11928400	0.12635100	-0.08849900
O	-2.71585400	-1.25329000	-0.49698000



vinyl ether ***17***
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.625837
Gibbs free energy (393K) = -502.453576

C	1.52431300	1.50811600	-0.21502400
H	2.19448300	2.36044900	-0.33299800
C	0.30637100	1.80204300	0.24055200
H	0.09559000	2.85198400	0.43004100
C	-0.86223700	0.87317500	0.49368600
H	-1.61856600	1.44250900	1.05207200
O	-1.43107700	0.55582400	-0.77547300
C	-2.68646700	0.05246600	-0.78346900
H	-3.02220000	-0.06668900	-1.80986400
C	-3.46793300	-0.26414700	0.24848900
H	-4.46504900	-0.63668400	0.05143400

H	-3.15587100	-0.18754900	1.28271100
C	-0.52200800	-0.34665400	1.32463300
H	-0.77893200	-0.27693800	2.38030700
C	0.00771700	-1.47987300	0.85998200
H	0.10828900	-2.32446100	1.54136400
C	0.44696100	-1.67507800	-0.52840400
H	-0.00159700	-2.50514600	-1.07313900
C	1.34303600	-0.90994200	-1.15597900
H	1.54296900	-1.13354400	-2.20209900
C	2.19759400	0.19363100	-0.56172000
H	2.92317700	0.45162500	-1.34280600
C	3.03060500	-0.28812500	0.64415400
H	3.72372400	0.49611700	0.96493900
H	3.61152000	-1.17441600	0.37345300
H	2.38337300	-0.53753300	1.48696700



*vinyl ether **17** Claisen rearrangement TS*
M06-2X/6-311+G(d,p) smd toluene
Energy (0K, vacuum) = -502.572019
Gibbs free energy (393K) = -502.400323
imaginary frequency: -537.48

C	0.10432900	-1.40846000	-0.63085500
H	0.06231400	-2.46279900	-0.90431100
C	-0.63239800	-0.59922300	-1.47302600
H	-1.29840800	-1.13100600	-2.14900300
C	-1.03667000	0.73027500	-1.21859200
H	-1.77353900	1.08692100	-1.93273300
O	-2.27906900	0.42445000	0.10486800
C	-1.74831700	-0.24785800	1.06685300
H	-1.33429100	0.31136500	1.91237800
C	-1.48740100	-1.60058600	0.95545900
H	-1.03001700	-2.12911200	1.78879400
H	-2.06316000	-2.19588200	0.25722900
C	-0.20492000	1.86308400	-0.74735000
H	-0.37449500	2.75787700	-1.34380200
C	0.66325300	2.02577100	0.26497300
H	1.05977600	3.03587700	0.36464000
C	1.11075400	1.12598100	1.32927000
H	1.24043200	1.62151400	2.29130200
C	1.39907900	-0.17795400	1.28567300
H	1.68960000	-0.64050000	2.22739700

C	1.41918700	-1.09705900	0.09285600
H	1.76796200	-2.06388100	0.47180300
C	2.44580600	-0.62484700	-0.95504700
H	2.50283000	-1.33605900	-1.78460300
H	3.43716800	-0.53185800	-0.50206200
H	2.15016600	0.34719300	-1.35725100

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