ELECTRONIC SUPPLEMENTARY INFORMATION

A Vinylcyclobutane Substrate Designed as a Cyclopropylcarbinyl Radical Probe

Ryan M. Bell, Carlton W. Christie, Joseph A. Mohrbacher III and Phyllis A. Leber*

Department of Chemistry, Franklin & Marshall College, Lancaster PA 17604-3003

General Experimental

Kinetics. Thermal reactions of hydrocarbon **9** were carried out at 275.0˚C (with temperature control to ± 0.1˚C provided by a Bayley Precision Temperature Controller Model 124) in based-treated capillary tubes immersed in a molten salt bath (composed of a eutectic mixture of $NaNO_2$ and KNO_3). Temperatures were measured with a Omega DP11 thermocouple with a digital readout to ± 0.1˚C . Run times were measured to ± 0.01 min with a Precision Solid State Time-it. The internal standard (ISTD) was *t*-butylcyclohexane. Thermolysis samples were analyzed on an HP 5890A GC equipped with an HP cross-lined methyl silicone column (50 m x 0.2 mm i.d. x 0.10 μm film thickness) operating at an initial temperature of 60 ºC held for 1 min followed by a temperature ramp of 0.1 ºC/min to a maximum temperature of 100 ºC. Retention times (min) were as follows: **4** (7.0), **3** (7.5), **8** (9.4), **10** (11.3), **7** (11.6), **9** (11.9), **12b/12c** (12.2,12.5), **11b/11c** (14.8, overlapping peaks), ISTD (16.5).

General Synthesis. All commercial materials were used as purchased except that methyltriphenylphosphonium bromide was recrystallized[1] prior to use. Preparative GC was accomplished on a GOW MAC® Model 350 GC equipped with a 12′ × 1/4″ DC710 column (Column A) or a 8′ × 1/4″ DC710 column (Column B).

NMR Analysis. NMR spectra were acquired on a Varian Inova 500 operating at 499.7 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR.

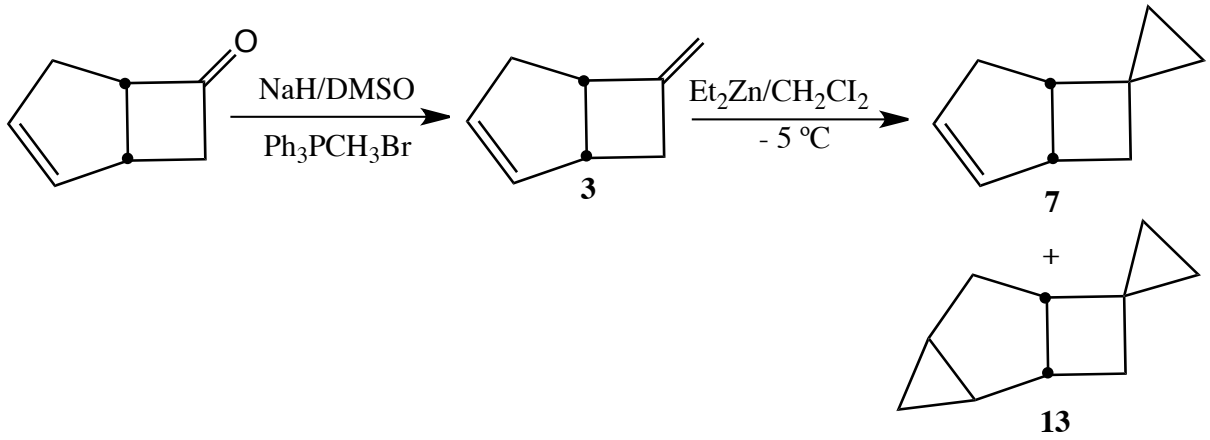
Catalytic Hydrogenation Reactions. In selected cases NMR samples of olefins or diolefins dissolved in $CDCl_3$ were subjected to catalytic hydrogenation in a medium pressure Parr hydrogenation apparatus using 10% Pd-C as a catalyst.

Selective Cyclopropanation Reactions. To 15 mL (15 mmol) of 1.0 M diethylzinc in hexanes under argon, 1.5 g (14 mmol) diolefin **3** or **4** was added extremely slowly via syringe. After cooling the flask to – 5 ºC in a salt bath, diiodomethane (1.2 mL, 15 mmol) was added via syringe. Aliquots were withdrawn periodically to monitor the course of the reaction so that

additional increments of diethylzinc and diiodomethane could be added to push the reaction to completion, thus allowing for more efficient purification by preparative GC. To quench the reaction, 2 mL of 1 M aqueous HCl were added. The reaction mixture was poured into 50 mL cold water and extracted several times with pentane. The combined organic extracts were washed with water and brine and then dried over magnesuium sulfate. The organic layer was concentrated by short-path distillation to afford a mixture of unreacted starting material as well as monocyclopropanated and dicyclopropanated products.

Classic Wittig reactions. All Wittig reactions except for the preparation of **3** from bicyclo[3.2.0]hept-2-en-6-one were accomplished using a classic Wittig protocol, but substituting CH_3Li/Et_2O for BuLi/hexanes as base and anhydrous THF for Et_2O as solvent.[2] Into an oven-dried flask under argon was first added a sample of 1.80 g (5.04 mmol) Ph_3PCH_3Br followed by 30 mL anhydrous THF. At -50 ºC, 3.1 mL of 1.6 M CH_3Li/Et_2O was added and then stirred for 30 min before allowing the reaction mixture to warm to rt. After cooling again to -50 ºC, 5.0 mmol of a selected ketone was added dropwise. The reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was quenched with cold water and extracted with pentane. The organic layer was washed extensively with water (to remove THF) and then dried over $MgSO_4$. Removal of pentane via short-path distillation afforded crude hydrocarbon product.

Synthesis and Spectral Characterization



Scheme S1. Synthetic Scheme for the preparation of compound **7,** its precursor **3**, and a side product **13**.

6-Methylenebicyclo[3.2.0]hept-2-ene (**3**). The Corey modification[3] of the Wittig reaction was employed for the conversion of cyclobutanone bicyclo[3.2.0]hept-2-en-6-one to the corresponding methylenecyclobutane 6-methylenebicyclo[3.2.0]hept-2-ene **3**. A 1.27 g (31.8 mmol) sample of 60% NaH by weight was transferred to an oven-dried apparatus under argon and rinsed with three 5-mL portions of pentane. After the addition of 14 mL of anhydrous DMSO the resultant mixture was heated at 80 ºC for 1h, during which time the reaction assumed a green coloration. Upon cooling the reaction mixture in an ice bath, a solution of 10.2 g (28.5 mmol) recrystallized methyltriphenylphosphonium bromide in 28 mL of anhydrous DMSO was added dropwise via an addition funnel. During a 1 h stirring period at rt the reaction mixture slowly assumed a milky yellow appearance as the ylid gradually formed. A sample of 2.00 g (18.5 mmol) of bicyclo[3.2.0]hept-2-en-6-one dissolved in 9 mL of anhydrous DMSO was slowly added to the reaction mixture, which was subsequently stirred at 40 ºC for 8 h and then at rt overnight. The reaction was quenched with 40 mL of water and extracted twice with pentane. The combined organic layers were washed ten times

with water and once with brine, and then dried over $MgSO_4$. Removal of pentane by short-path distillation resulted in 0.75 g (38% yield) of crude product **3**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (m, 2H), 4.90 (dd, 1H), 4.81 (dd, 1H), 3.49 (br m, 1H), 3.27 (br m, 1H), 2.97 (qt, 1H), 2.56 (m, 1H), 2.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5 (=C), 133.5 (=CH), 131.3 (=CH), 107.3 ($=CH_2$), 45.5 (CH), 42.5 (CH), 39.5 (CH_2), 38.0 (CH_2). FTIR (neat) ν_{max} 3051, 2917, 2843, 1672, 1606, 876, 708 cm^{-1}. LRMS (EI) *m/z* 106 (M^+, C_8H_{10}, 5), 105 (19), 91 (100), 78 (60), 66 (68).

Spiro[bicyclo[3.2.0]hept-2-ene-6,1′-cyclopropane] (**7**). A 0.75 g sample of compound **3** was subjected to a selective cyclopropanation procedure, as described in the general experimental section. Under optimal conditions only 10-13% of starting material **3** remained along with 45-50% of product **7**, 2-4% undesired monocyclopropanated product, and 35-40% dicyclopropanated product **13**. Preparative GC on Column B at 94 ºC afforded both compound **7** and dicyclopropanated product **13**, which was thermally stable at 275 ºC.

Compound **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.74 (m, 1H), 3.28 (br m, 1H), 2.90 (t, 1H), 2.44 (dd, 1H), 2.35 (qq, 1H), 2.10 (br d, 1H), 1.66 (dd, 1H), 0.54 (pent, 1H), 0.40 (pent, 1H), 0.33 (m, 1H), 0.12 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5 (=CH), 130.6 (=CH), 42.2 (CH), 41.8 (CH), 37.1 (CH_2), 36.3 (CH_2), 22.2 (C), 12.3 (CH_2), 8.8 (CH_2). FTIR (neat) ν_{max} 3050, 2919, 1612, 718 cm^{-1}. LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 2), 105 (33), 92 (74), 91 (100), 79 (26), 66 (20); HRMS (EI) calcd for C_9H_{12} 120.0939, found 120.0933.

Compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.81 (dd, 1H), 2.28 (br m, 1H), 2.01 (m, 1H), 1.97 (m, 2H), 1.75 (dd, 1H), 1.43 (m, 1H), 1.24 (m, 1H), 0.52 (dt, 1H), 0.46 (m, 1H), 0.42 (m, 1H), 0.31 (pent, 1H), 0.22 (pent, 1H), -0.31 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.2 (CH), 39.5 (CH), 34.2 (CH_2), 34.1 (CH_2), 24.6 (CH), 22.3 (C), 20.1 (CH), 14.5 (CH_2), 11.9

(CH_2), 9.2 (CH_2). LRMS (EI) *m/z* 134 (M^+, $C_{10}H_{14}$, 1), 119 (33), 105 (40), 93 (40), 92 (31), 91 (100).

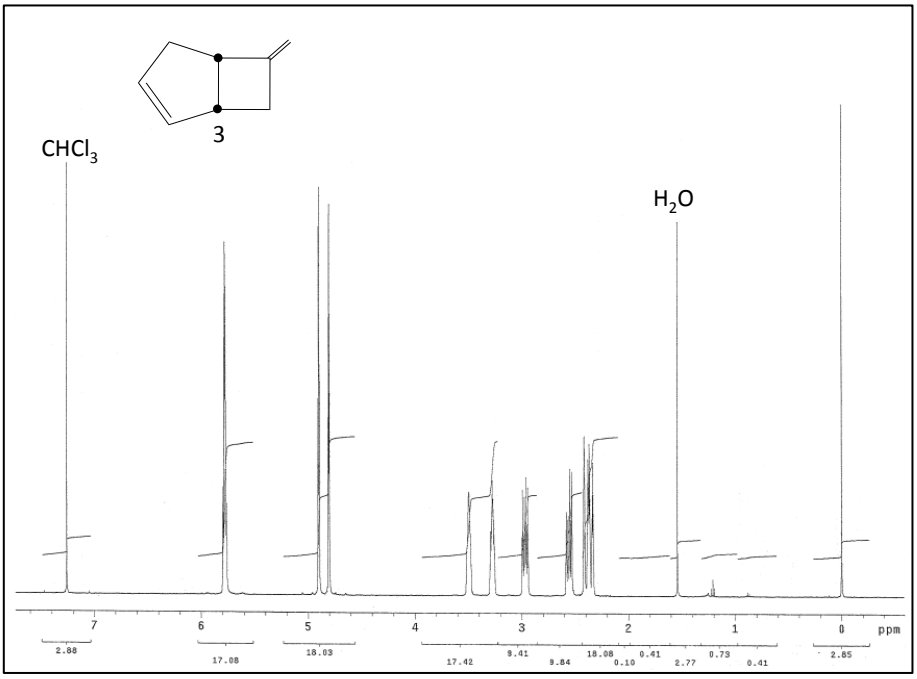


Fig S1a. ^{1}H NMR Spectrum of 6-Methylenebicyclo[3.2.0]hept-2-ene (**3**).

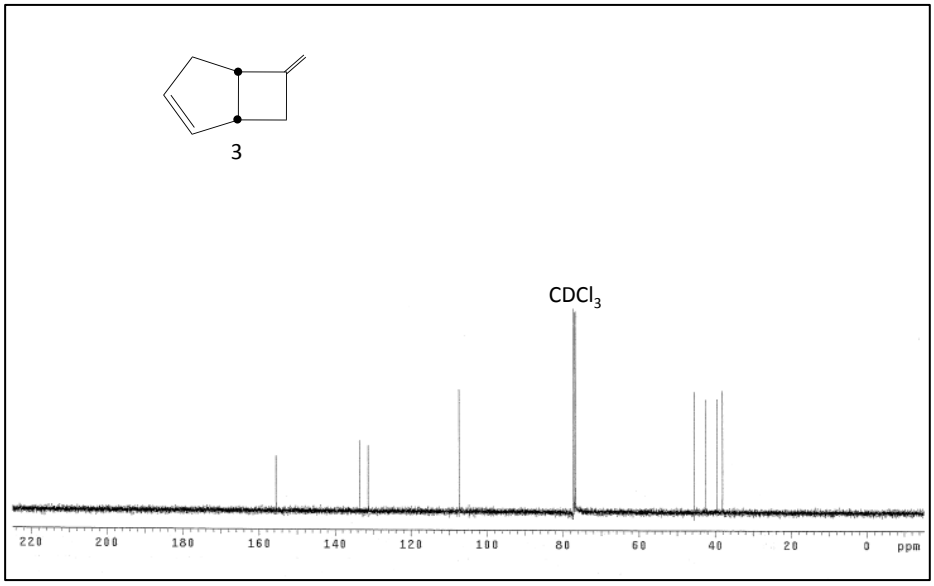


Fig S1b. ^{13}C NMR Spectrum of 6-Methylenebicyclo[3.2.0]hept-2-ene (**3**).

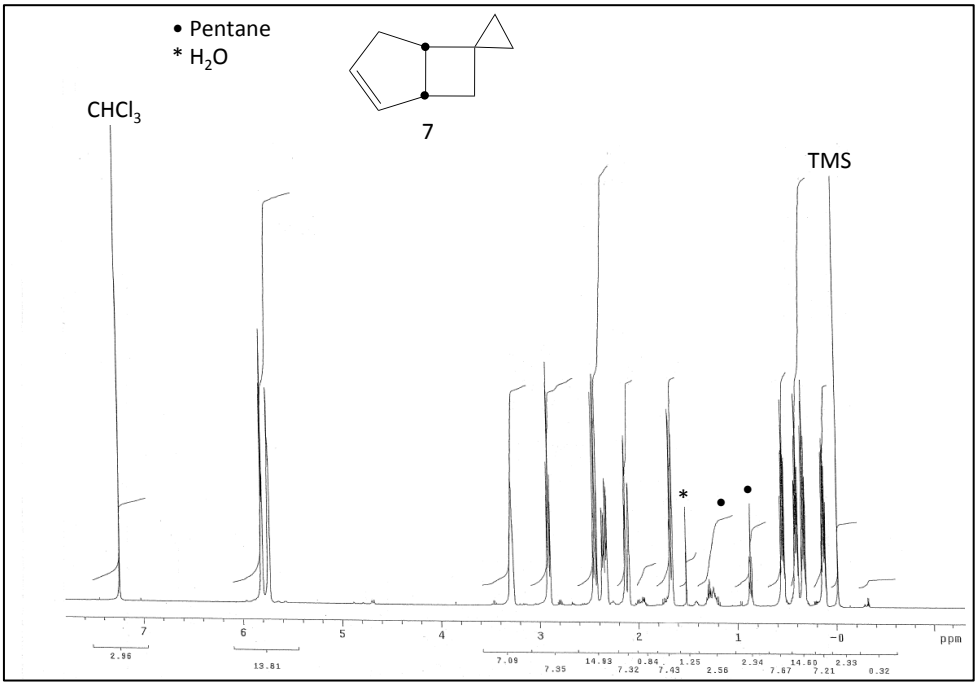


Fig S1c. ^{1}H NMR Spectrum of Spiro[bicyclo[3.2.0]hept-2-ene-6,1′-cyclo-propane] (**7**).

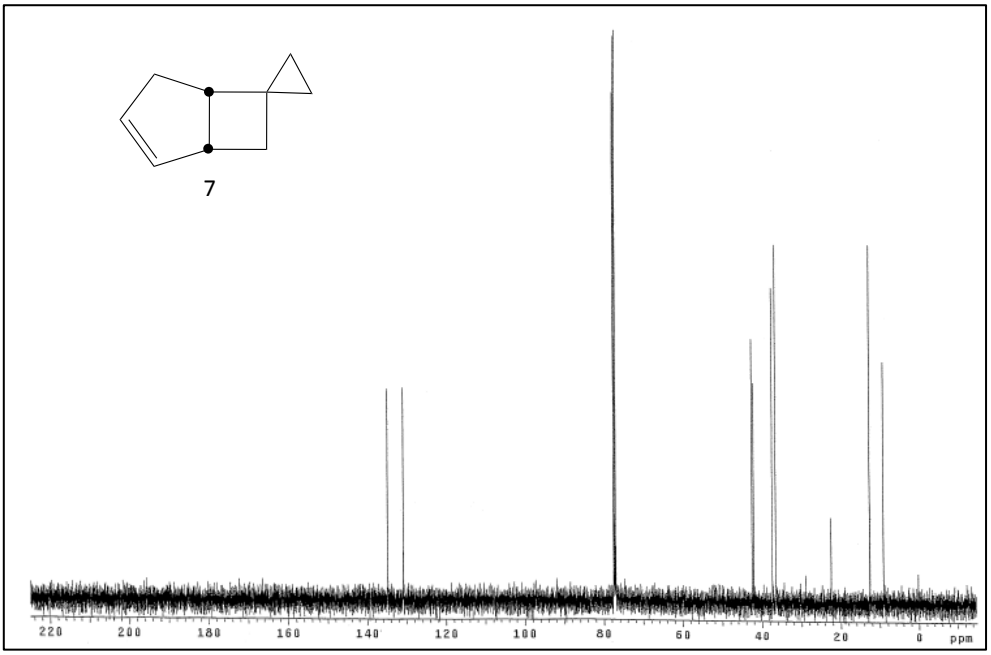


Fig S1d. ^{13}C NMR Spectrum of Spiro[bicyclo[3.2.0]hept-2-ene-6,1′-cyclo-propane] (**7**).

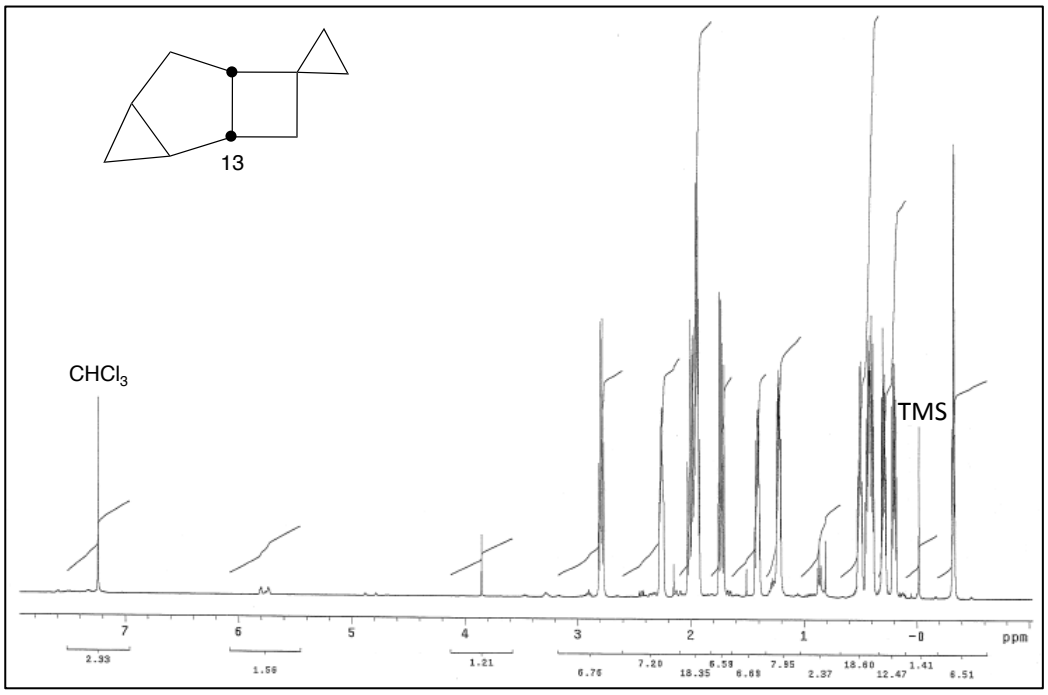


Fig S1e. ^{1}H NMR Spectrum of Compound **13**.

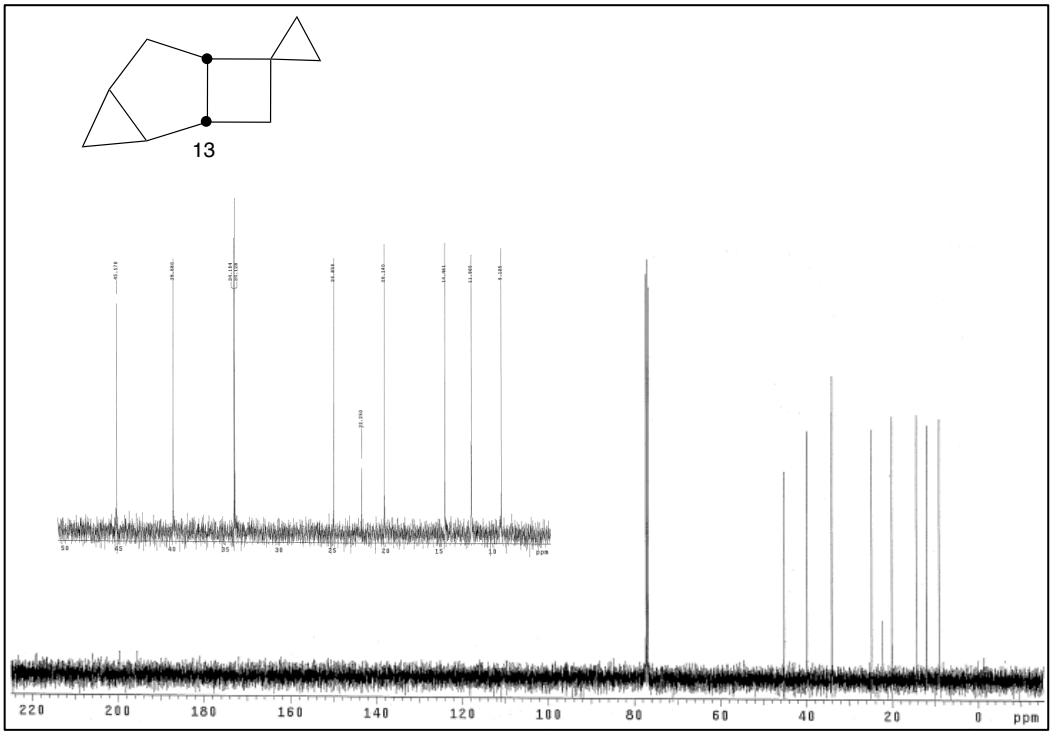
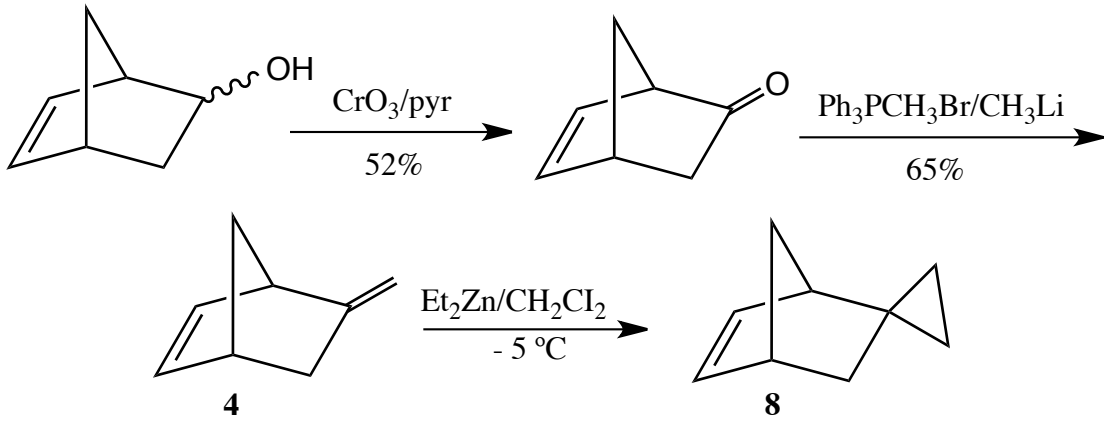


Fig S1f. ^{13}C NMR Spectrum of Compound **13**.



Scheme S2. Synthetic Scheme for the preparation of Compound **8** and its precursors.

5-Methylenebicyclo[2.2.1]hept-2-ene (**4**). Oxidation of 5-norbornen-2-ol to norbornenone was accomplished using chromium oxide in pyridine.[4] Subjecting norbornenone to the classic Wittig methodology, as described in the general experimental section, afforded 5-methylene-2-norbornene **4** in good yield. Compound **4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (dd, 1H), 6.06 (dd, 1H), 4.98 (dd, 1H), 4.71 (dd, 1H), 3.15 (br s, 1H), 2.96 (br s, 1H), 2.24 (m, 1H), 1.75 (m, 1H), 1.59 (m, 1H), 1.41 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7 (=C), 136.2 (=CH), 134.1 (=CH), 103.2 ($=CH_2$), 50.8 (CH), 50.0 (CH_2), 41.9 (CH), 33.5 (CH_2). LRMS (EI) *m/z* 106 (M^+, C_8H_{10}, 46), 91 (100), 78 (52), 66 (87).

Spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane] (**8**). A selective cyclopropanation reaction performed on compound **4** resulted in product **8** in lesser selectivity than observed for compound **7**. The ratio of desired monocyclopropanated product **8** to undesired monocyclopropanated product to dicyclopropanated product was 30:9:54 with 7% unreacted **4**. Preparative GC on Column B at 94 ºC afforded compound **8** in high purity. Compound **8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (dd, 1H), 6.14 (dd, 1H), 2.88 (br s, 1H), 2.00 (br s, 1H), 1.69 (m, 2H), 1.50 (m, 1H), 1.11 (dd, 1H), 0.54 (m, 1H), 0.52 (m, 1H), 0.43 (pent, 1H), 0.31 (m, 1H), 0.12 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6 (=CH), 135.4 (=CH), 50.6 (CH),

49.7 (CH_2), 43.7 (CH), 38.0 (CH_2), 23.4 (C), 11.8 (CH_2), 9.6 (CH_2). FTIR (neat) ν_{max} 3150, 3070, 2980, 720 cm^{-1}. LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 13), 105 (45), 92 (38), 91 (67), 79 (28), 66 (100).

Samples of compound **8** that were heated up to 40 h at 275 ºC under identical conditions to those described in the General Experimental SI section for the thermal reactions of compound **7** showed that compound **8** was thermally stable at 275 ºC. The ratio of compound **8** to ISTD (**8:**ISTD) was invariant over 40 h at 275 ºC: 2.99±0.06.

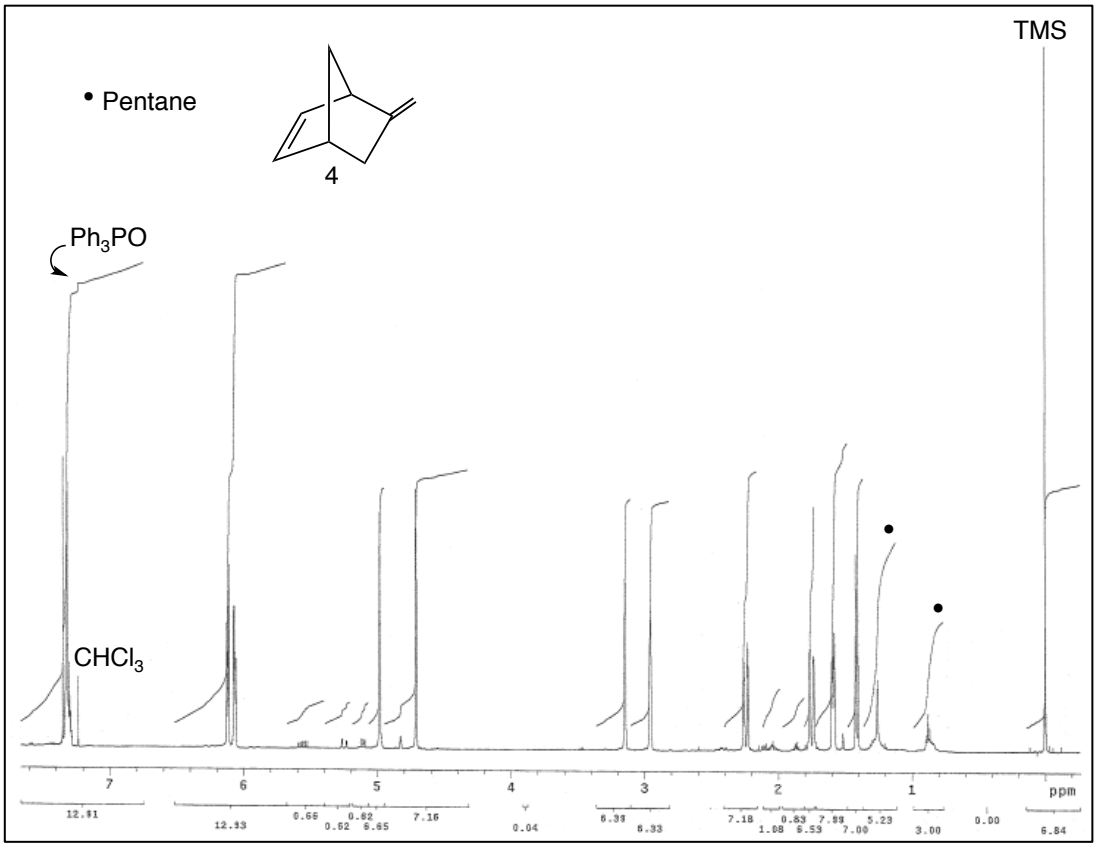


Fig S2a. ^{1}H NMR Spectrum of 2-Methylenebicyclo[2.2.1]hept-5-ene (**4**).

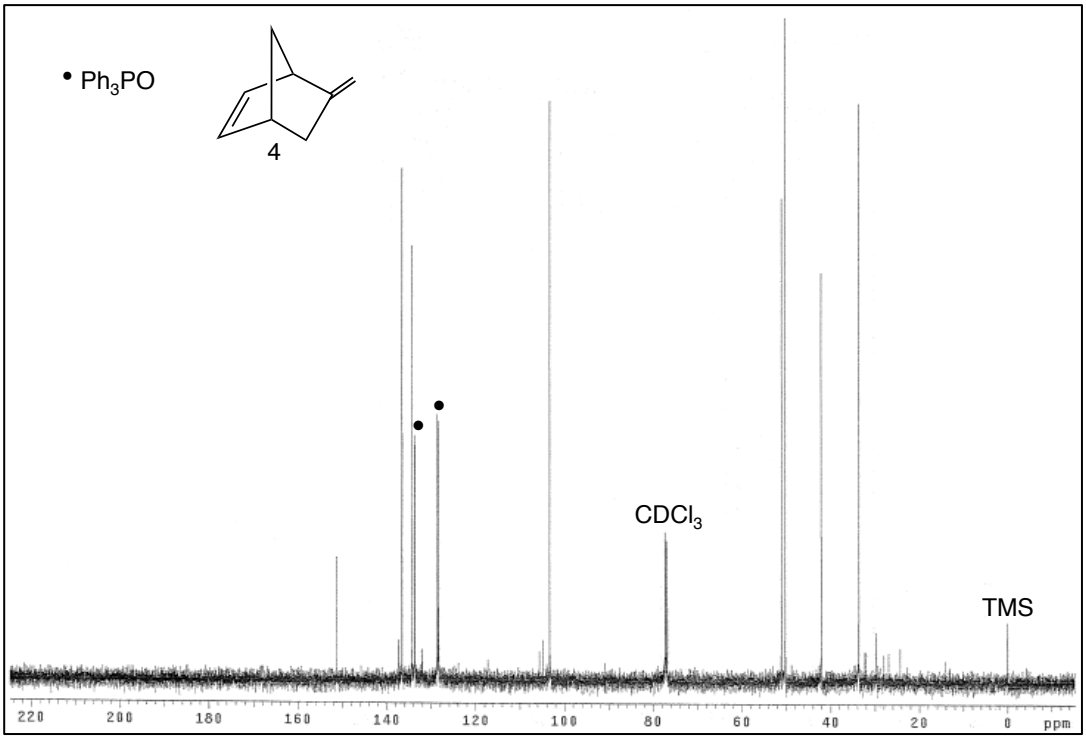


Fig S2b. ^{13}C NMR Spectrum of 2-Methylenebicyclo[2.2.1]hept-5-ene (**4**).

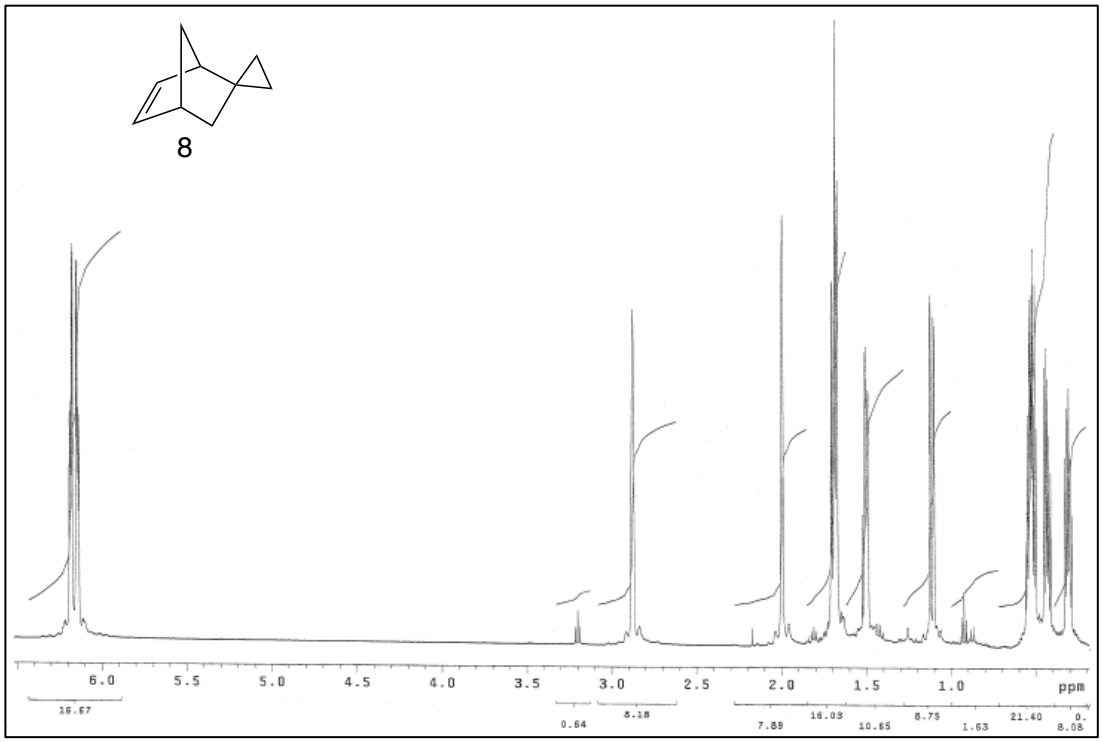


Fig S2c. ^{1}H NMR Spectrum of Spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane] (**8**).

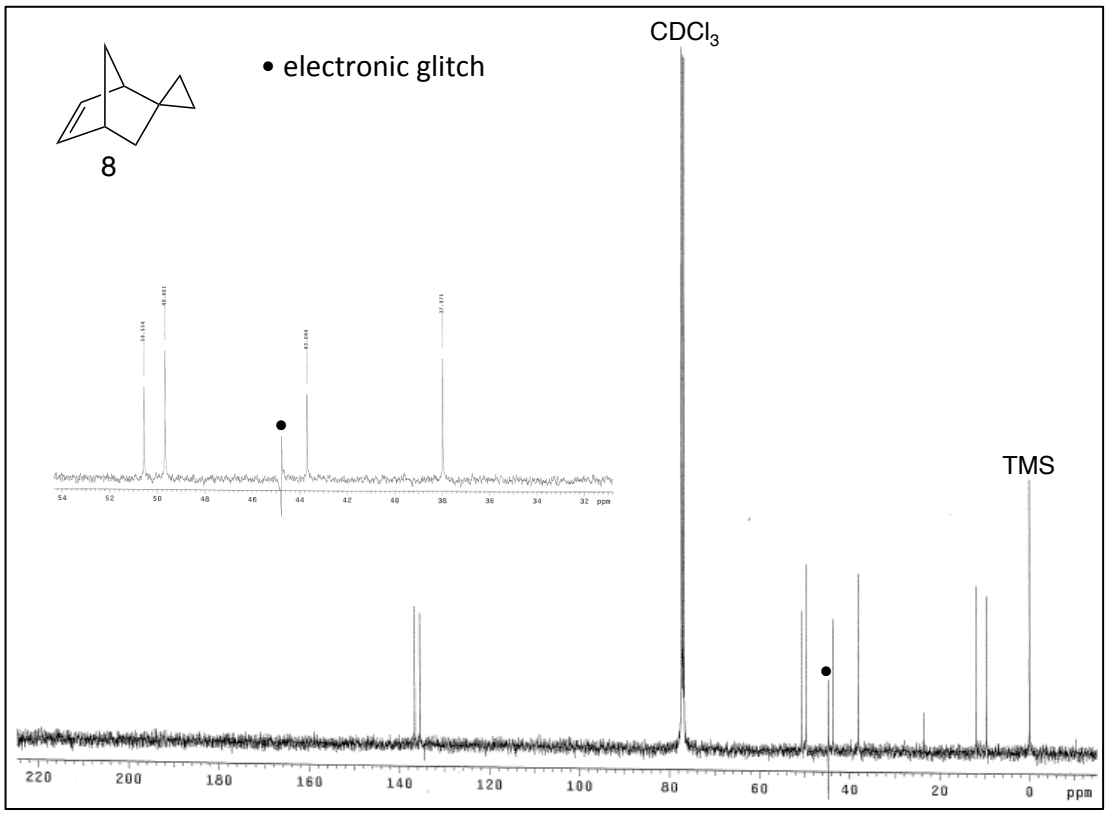
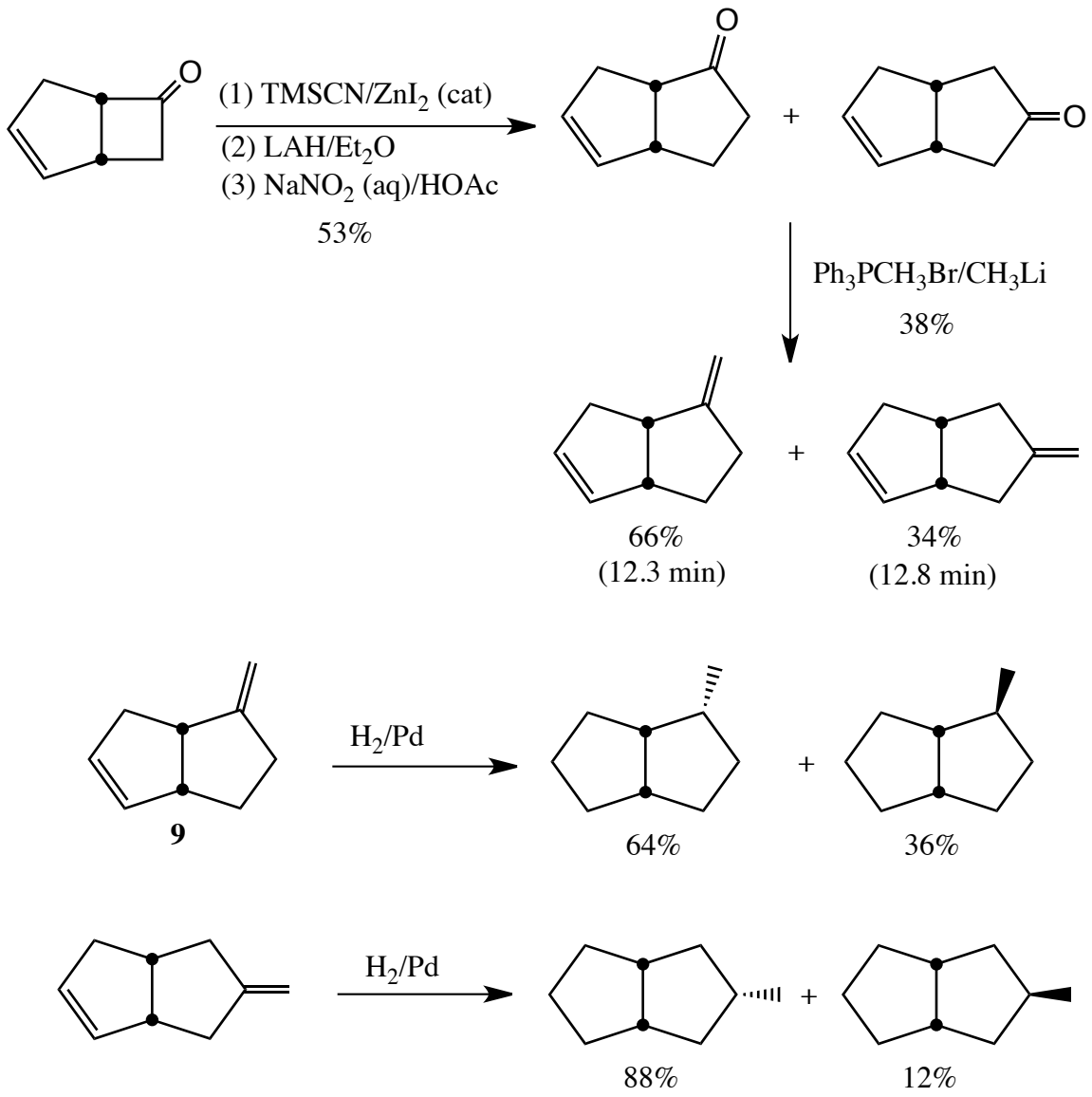


Fig S2d. ^{13}C NMR Spectrum of Spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane] (**8**).



Scheme S3. Synthetic Scheme for the preparation of Compound **9**, its precursors, and its hydrogenation products.

cis-Bicyclo[3.3.0]oct-6-en-2-one. The Tiffeneau-Demjanov rearrangement conditions devised by Della and Pigou for the ring expansion of bicyclo[2.1.1]hexan-2-one[5] was successfully applied to 2.05 g (19.0 mmol) of bicyclo[3.2.0]hept-2-en-6-one to yield a mixture of *cis*-bicyclo[3.3.0]oct-6-en-2-one and *cis*-bicyclo[3.3.0]oct-6-en-3-one, 1.22 g (10.0 mmol). FTIR (neat) ν_{max} 3046, 2933, 1735, 721, 685 cm^{-1}. Preparative GC on Column A at 90 ºC afforded *cis*-bicyclo[3.3.0]oct-6-en-2-one, the first eluting peak, in 99% purity, and *cis*-

bicyclo[3.3.0]oct-6-en-3-one in 90% purity. *cis*-Bicyclo[3.3.0]oct-6-en-2-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (m, 1H), 5.61 (m, 1H), 3.52 (br m, 1H), 2.63 (br d, 1H), 2.62 (m, 1H), 2.55 (m, 1H), 2.25 (m, 1H), 2.10 (m, 2H), 1.99 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 224.1 (C=O), 133.7 (=CH), 131.1 (=CH), 48.4 (CH), 47.7 (CH), 37.4 (CH_2), 36.4 (CH_2), 25.3 (CH_2). LRMS (EI) *m/z* 122 (M^+, $C_8H_{10}O$, 78), 94 (38), 79 (35), 66 (100); HRMS (EI) calcd for $C_8H_{10}O$ 122.0732, found 122.0723.

cis-Bicyclo[3.3.0]oct-6-en-3-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (br s, 1H), 5.63 (br s, 1H), 3.42 (br s, 1H), 2.97 (br pent, 1H), 2.72 (m, 1H), 2.51 (sextet, 2H), 2.23 (br dd, 2H), 1.99 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.2 (C=O), 134.1 (=CH), 130.5 (=CH), 46.3 (CH), 44.9 (CH_2), 42.6 (CH_2), 40.1 (CH_2), 37.1 (CH). LRMS (EI) *m/z* 122 (M^+, $C_8H_{10}O$, 81), 80 (60), 79 (100).

2-Methylene-*cis*-bicyclo[3.3.0]oct-6-ene (**9**). A classic Wittig reaction on 0.60 g (4.92 mmol) of the isomeric ketone mixture afforded 0.20 g (1.66 mmol) of the corresponding hydrocarbons. FTIR (neat) ν_{max} 3054, 2923, 1636, 721, 695 cm^{-1}. Preparative GC on Column B at 110 ºC afforded 2-methylene-*cis*-bicyclo[3.3.0]oct-6-ene, the first eluting peak, in 97% purity and 3-methylene-*cis*-bicyclo[3.3.0]oct-6-ene in 90% purity. Compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (m, 1H), 5.53 (m, 1H), 4.86 (d, 1H), 4.81 (d, 1H), 3.30 (br m, 1H), 3.08 (br m, 1H), 2.77 (qq, 1H), 2.30 (m, 1H), 2.27 (m, 2H), 1.80 (m, 1H), 1.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8 (=C), 133.9 (=CH), 130.1 (=CH), 104.6 ($=CH_2$), 51.1 (CH), 45.3 (CH), 41.9 (CH_2), 32.9 (CH_2), 30.8 (CH_2). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 82), 105 (96), 92 (70), 91 (100), 79 (59); HRMS (EI) calcd for C_9H_{12} 120.0939, found 120.0935. Hydrogenation of the NMR sample of compound **9** gave an isomeric mixture of *endo*-2-methylbicyclo[3.3.0]octane and *exo*-2-methylbicyclo[3.3.0]octane in a 64:36 ratio, respectively. ^{13}C NMR data for these two saturated hydrocarbons match those reported in the literature.[6] *endo*-2-Methylbicyclo[3.3.0]octane: ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.8 (CH), 43.0 (CH), 37.7 (CH), 35.5 (CH_2), 33.0 (CH_2), 32.3 (CH_2), 27.7 (CH_2, 2 overlapping peaks), 15.4 (CH_3). LRMS (EI) *m/z* 124 (M^+, C_9H_{16}, 14), 109 (6), 96 (39), 82 (87), 81 (68), 67 (100).

exo-2-Methylbicyclo[3.3.0]octane: ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.8 (CH), 43.3 (CH), 42.3 (CH), 36.0 (CH_2), 33.9 (CH_2), 33.6 (CH_2), 32.3 (CH_2), 25.5 (CH_2), 19.8 (CH_3). LRMS (EI) *m/z* 124 (M^+, C_9H_{16}, 20), 109 (10), 96 (44), 82 (94), 81 (99), 67 (100).

3-Methylene-*cis*-bicyclo[3.3.0]oct-6-ene: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (m, 1H), 5.55 (m, 1H), 4.78 (m, 1H), 4.76 (m, 1H), 3.24 (br t, 1H), 2.77 (br pent, 1H), 2.54 (m, 3H), 2.13 (dd, 2H), 2.01 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0 (=C), 134.6 (=CH), 129.4 (=CH), 104.9 ($=CH_2$), 50.0 (CH), 41.5 (CH_2), 40.4 (CH_2), 40.2 (CH), 38.2 (CH_2). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 50), 105 (100), 92 (25), 91 (37), 79 (41); HRMS (EI) calcd for C_9H_{12} 120.0939, found 120.0930.

Hydrogenation of the NMR sample of 3-methylene-*cis*-bicyclo[3.3.0]oct-6-ene gave an isomeric mixture of *endo*-3-methylbicyclo[3.3.0]octane and *exo*-3-methylbicyclo[3.3.0]-octane in an 88:12 ratio, respectively. *endo*-3-Methylbicyclo[3.3.0]octane (first eluting peak): ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.6 ($2CH_2$), 43.5 (2CH), 36.8 (CH), 33.3 ($2CH_2$), 24.8 (CH_2), 19.2 (CH_3). LRMS (EI) *m/z* 124 (M^+, C_9H_{16}, 9), 109 (10), 96 (36), 82 (31), 81 (100), 67 (46). *exo*-3-Methylbicyclo[3.3.0]octane (second eluting peak): ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.9 (2CH), 42.3 ($2CH_2$), 35.5 (CH), 34.9 ($2CH_2$), 27.7 (CH_2), 19.4 (CH_3). LRMS (EI) *m/z* 124 (M^+, C_9H_{16}, 15), 109 (6), 96 (28), 82 (85), 81 (71), 67 (100).

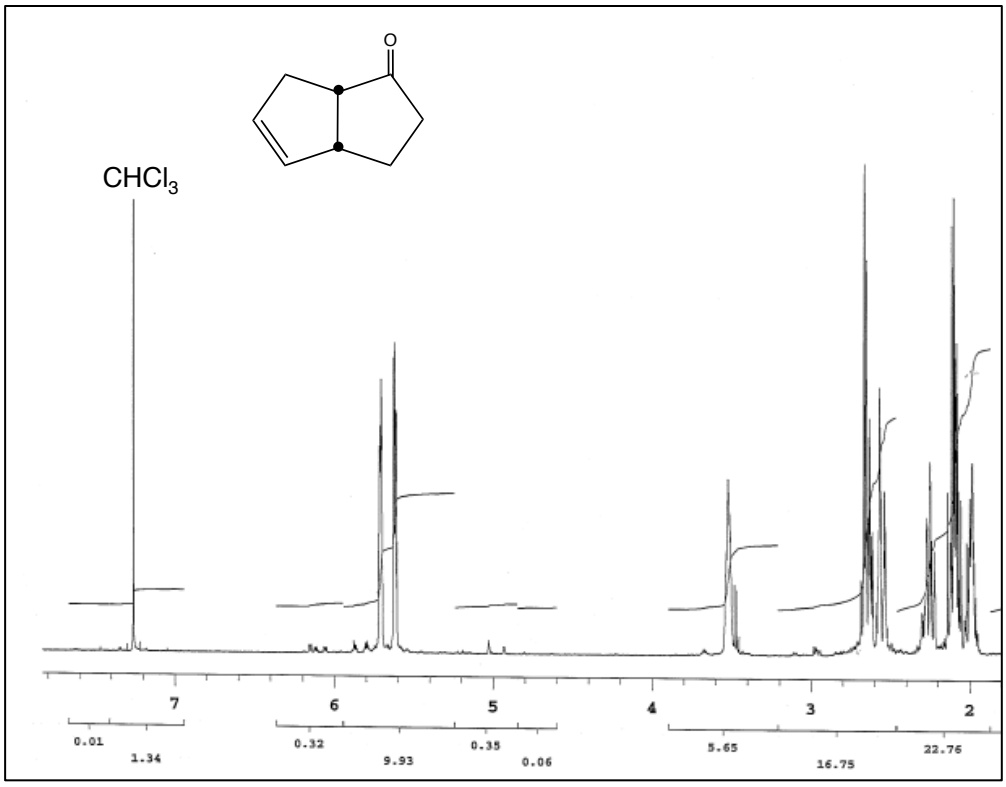


Fig S3a. ^{1}H NMR Spectrum of *cis*-Bicyclo[3.3.0]oct-6-en-2-one.

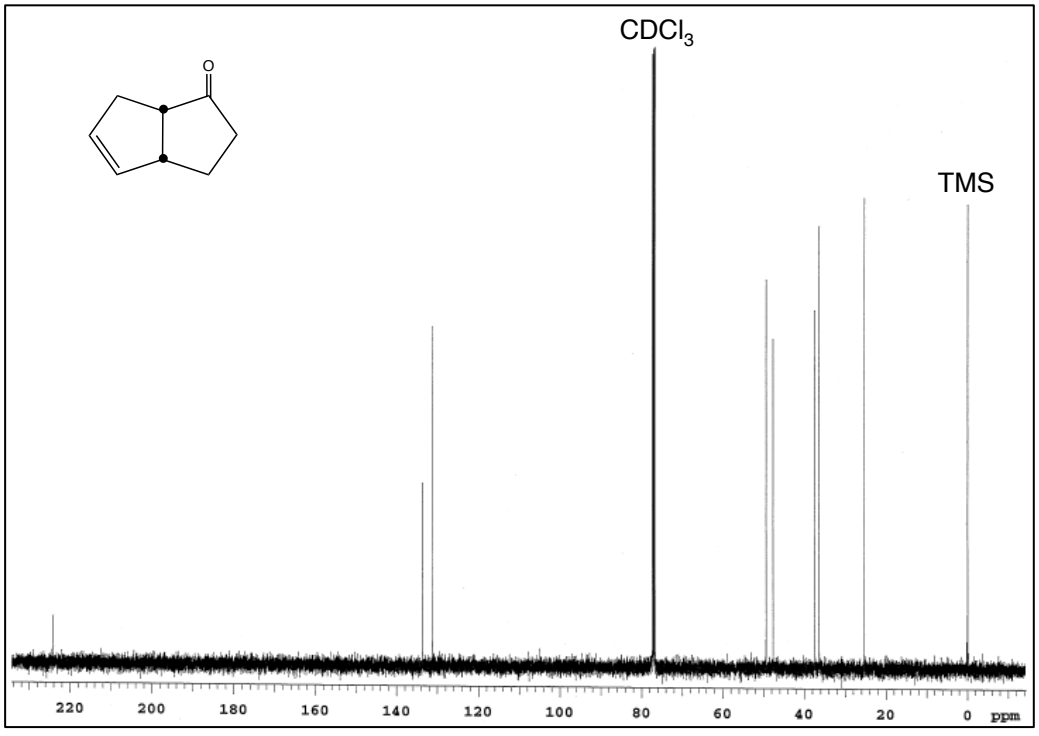


Fig S3b. ^{13}C NMR Spectrum of *cis*-Bicyclo[3.3.0]oct-6-en-2-one.

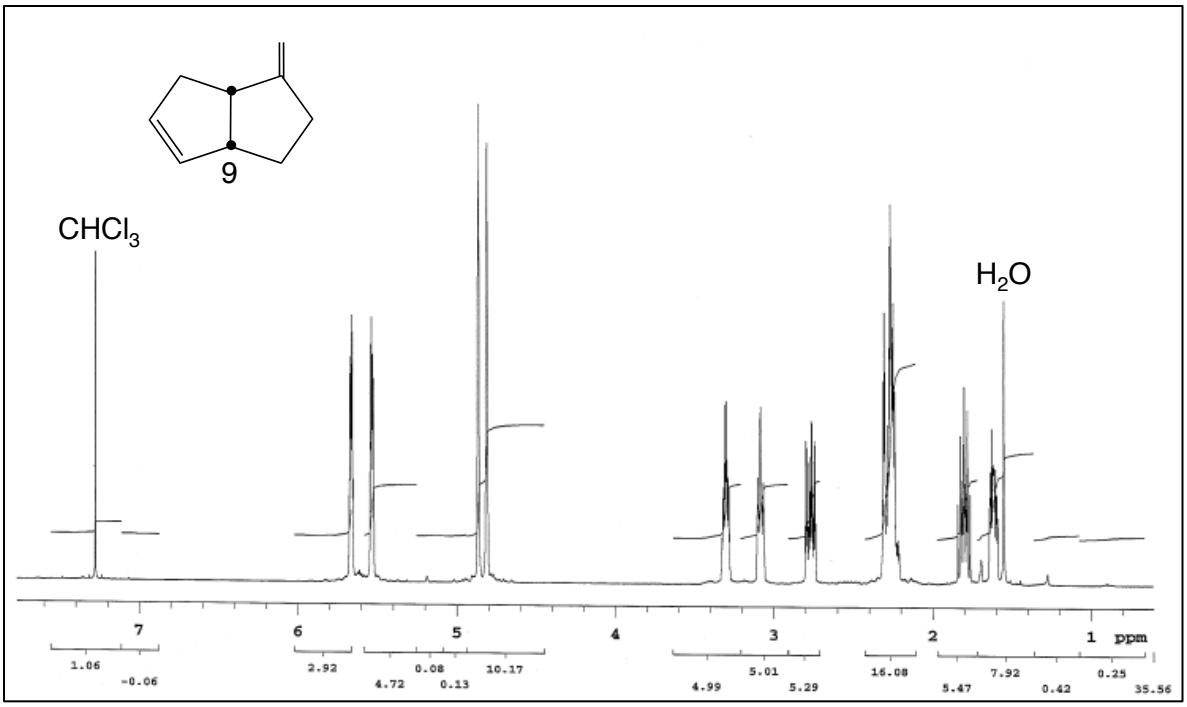


Fig S3c. [1]H NMR Spectrum of 2-Methylene-*cis*-bicyclo[3.3.0]oct-6-ene (**9**).

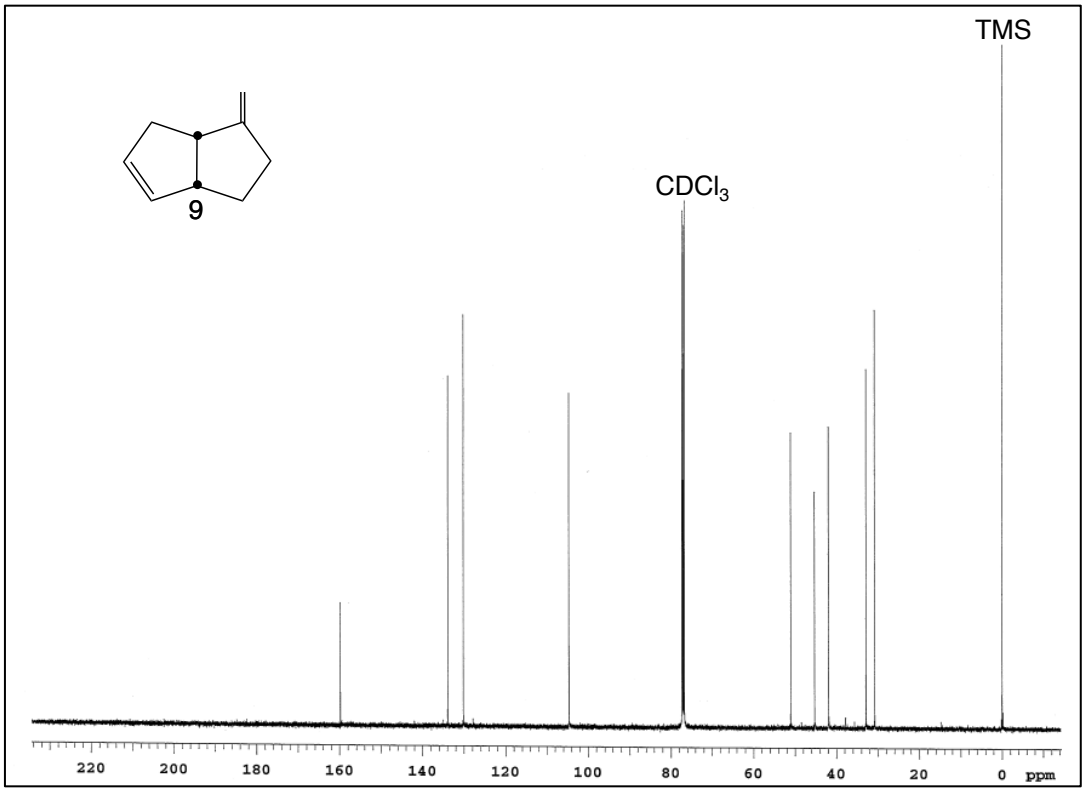
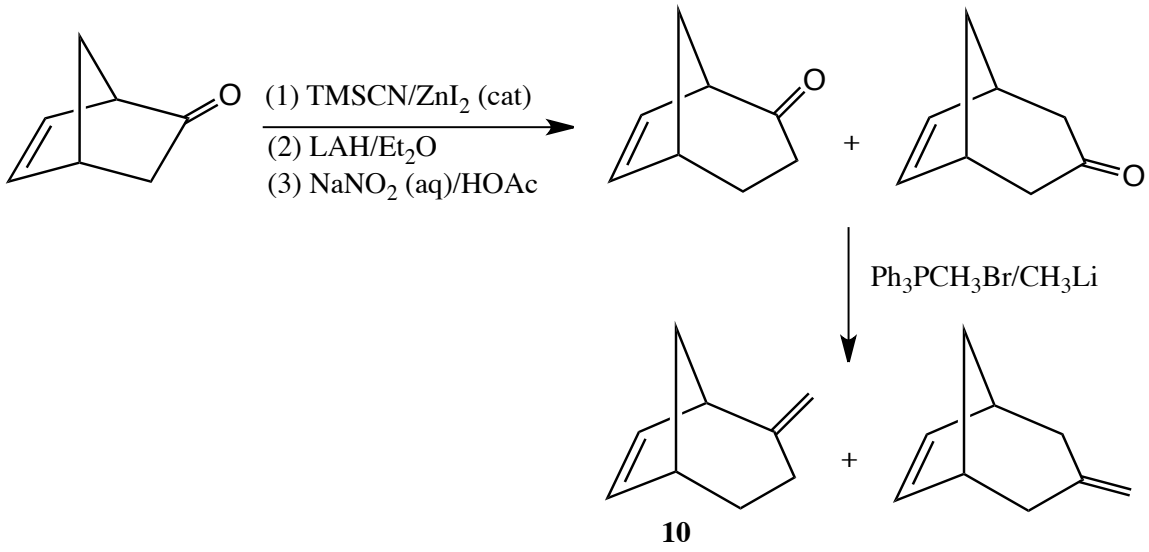


Fig S3d. [13]C NMR Spectrum of 2-Methylene-*cis*-bicyclo[3.3.0]oct-6-ene (**9**).



10

Scheme S4. Synthetic Scheme for the preparation of Compound **10** and its precursor.

2-Methylenebicyclo[3.2.1]oct-6-ene (**10**). Norbornenone was subjected to a Tiffeneau-Demjanov rearrangement using the Della and Pigou methodology[5] to afford a 1:1 mixture of two known isomeric ketones ($C_9H_{10}O$).[7] Treatment of the isomeric mixture under classic Wittig conditions resulted in compound **10**[8] and its symmetric isomer,[9] both known compounds. Preparative GC separation on column A at 115 ºC gave 2-methylenebicyclo[3.2.1]oct-6-ene (**10**) in ca. 91% purity by GC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dd, 1H), 5.89 (dd, 1H), 4.64 (t, 1H), 4.51 (t, 1H), 3.02 (dd, 1H), 2.65 (sextet, 1H), 2.39 (m, 1H), 2.10 (m, 2H), 1.53 (m, 1H), 1.48 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9 (=C), 133.6 (=CH), 133.3 (=CH), 105.8 ($=CH_2$), 49.0 (CH), 46.6 (CH_2), 39.2 (CH), 27.6 (CH_2), 25.5 (CH_2). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 49), 105 (48), 92 (100), 91 (86), 79 (38).

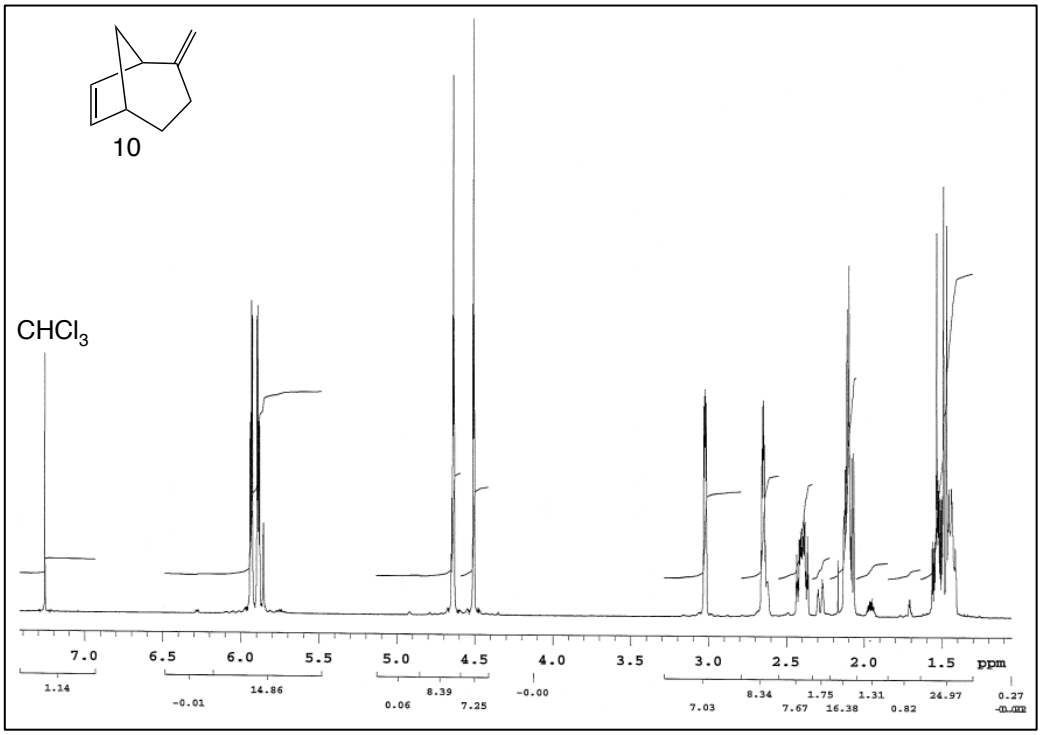


Fig S4a. ^{1}H NMR Spectrum of 2-Methylenebicyclo[3.2.1]oct-6-ene (**10**).

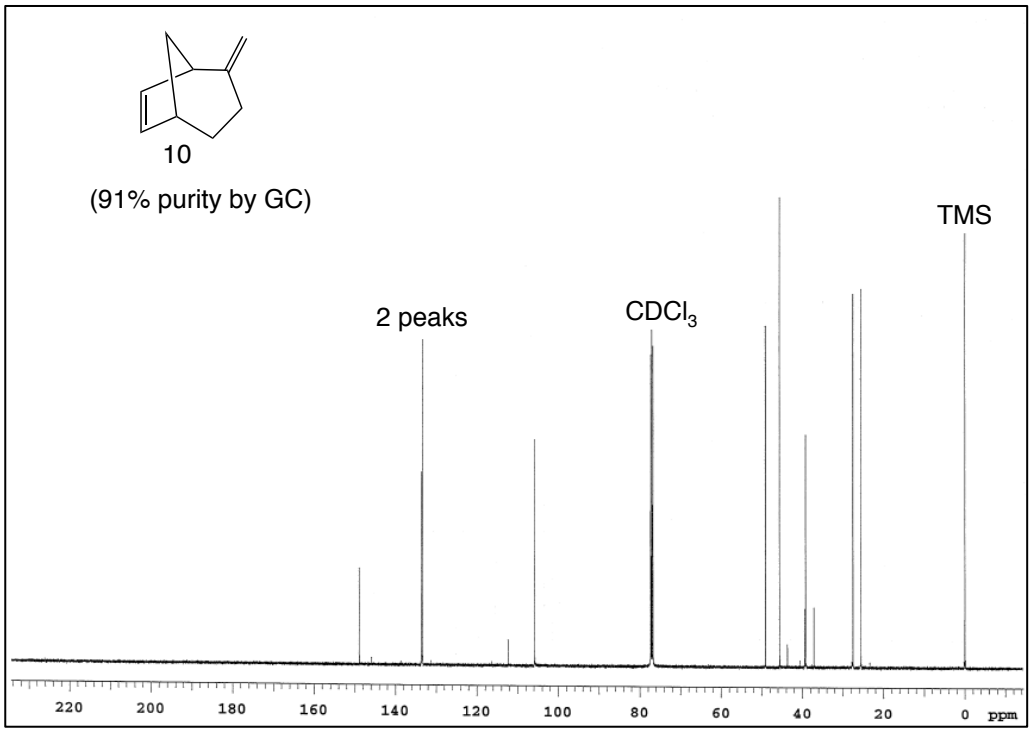
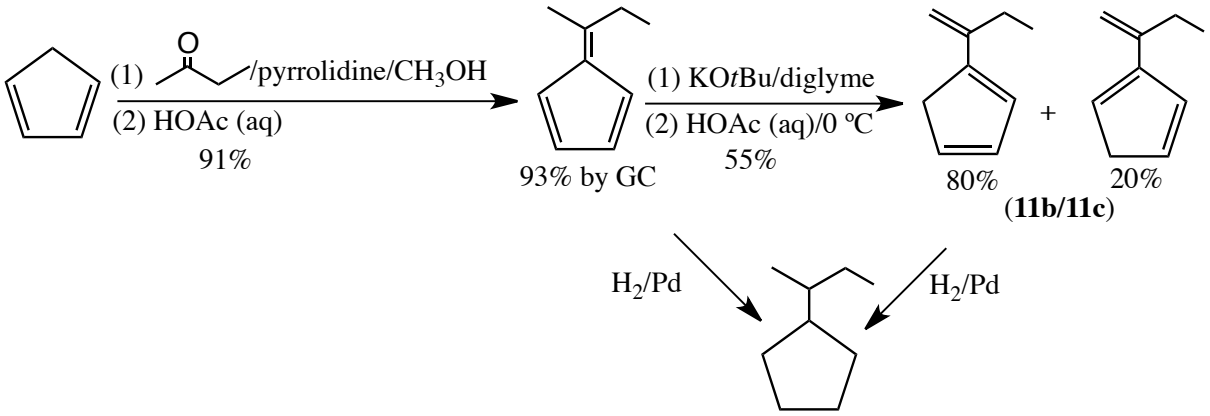


Fig S4b. ^{13}C NMR Spectrum of 2-Methylenebicyclo[3.2.1]oct-6-ene (**10**).



Scheme S5. Synthetic Scheme for the preparation of Compounds **11b** and **11c**, their precursor 6-ethyl-6-methylfulvene, and their hydrogenation product.

6-Ethyl-6-methylfulvene. The method of Stone and Little for the preparation of 6,6-dimethylfulvene[10] gave 6-ethyl-6-methylfulvene in excellent yield (91%) with 5% dicyclopentadiene impurity. FTIR (neat) ν_{max} 3069, 2970, 1638, 761, 633 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (m, 2H), 6.62 (m, 2H), 2.68 (q, 2H), 2.32 (s, 3H), 1.30 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2 (=C), 142.1 (=C), 130.9 (=CH), 130.7 (=CH), 120.8 (=CH), 120.2 (=CH), 30.0 (CH_2), 20.4 (CH_3), 14.0 (CH_3). The ^{13}C NMR data match those reported in the literature.[11] LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 60), 105 (100), 91 (30).

1- and 2-(But-1-en-2-yl)-1,3-cyclopentadiene. Base-catalyzed isomerization of 6-ethyl-6-methylfulvene to an isomeric mixture of **11b** and **11c** was accomplished as per the method of Hine and Knight for isomerization of 6,6-dimethylfulvene.[12] The crude product mixture also contained 19% 6-ethyl-6-methylfulvene and 8% dicyclopentadiene. Major isomer: ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9 (=C), 145.1 (=C), 132.8(=CH), 131.9 (=CH), 127.7 (=CH), 108.4 (=CH_2), 40.7 (ring CH_2), 26.6 (CH_3), 13.2 (CH_3). Minor isomer: ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2 (=C), 144.5 (=C), 133.6 (=CH), 131.6 (=CH), 126.6 (=CH), 110.0 (=CH_2), 41.9 (ring CH_2), 26.9 (CH_3), 13.0 (CH_3). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 42), 105 (48), 91 (100) due to overlapping peaks on GC/MS column.

sec-Butylcyclopentane. Catalytic hydrogenation of the isomeric mixture of **11b** and **11c** and independently of 6-ethyl-6-methylfulvene afforded the same single product, *sec*-

butylcyclopentane. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73 (m, 2H), 1.59 (m, 3H), 1.51 (m, 3H), 1.18 (m, 1H), 1.11 (m, 3H), 0.87 (t, 3H), 0.86 (d, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.0 (CH), 39.8 (CH), 30.8 (CH_2), 30.3 (CH_2), 28.1 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 17.2 (CH_3), 11.3 (CH_3). LRMS (EI) *m/z* 126 (M^+, C_9H_{18}, 1), 98 (8), 97 (100).

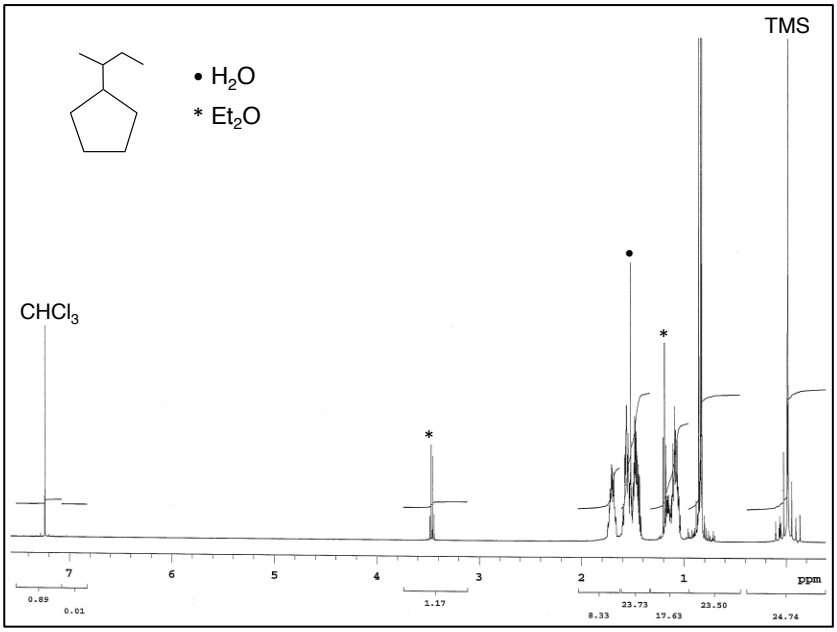


Fig S5a. ^{1}H NMR Spectrum of *sec*-Butylcyclopentane.

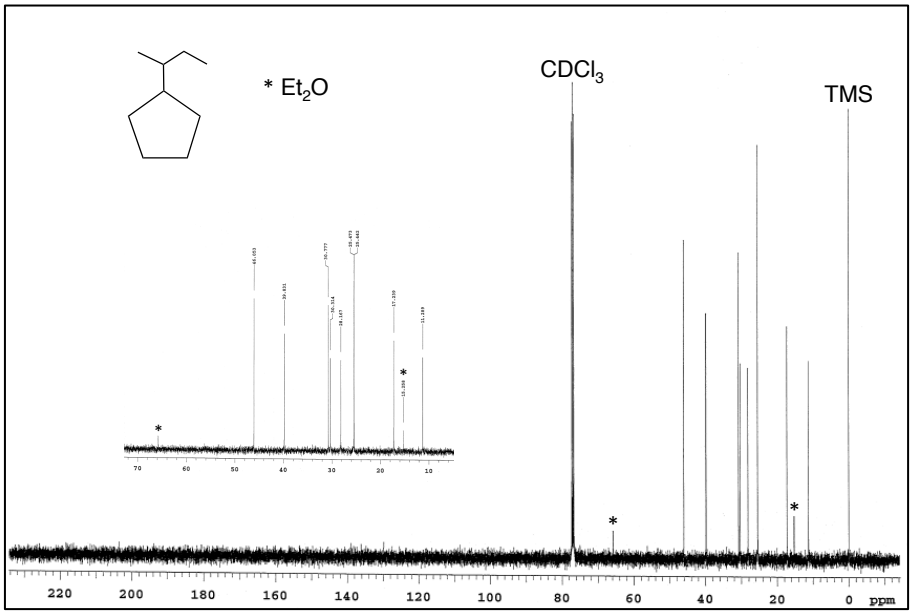
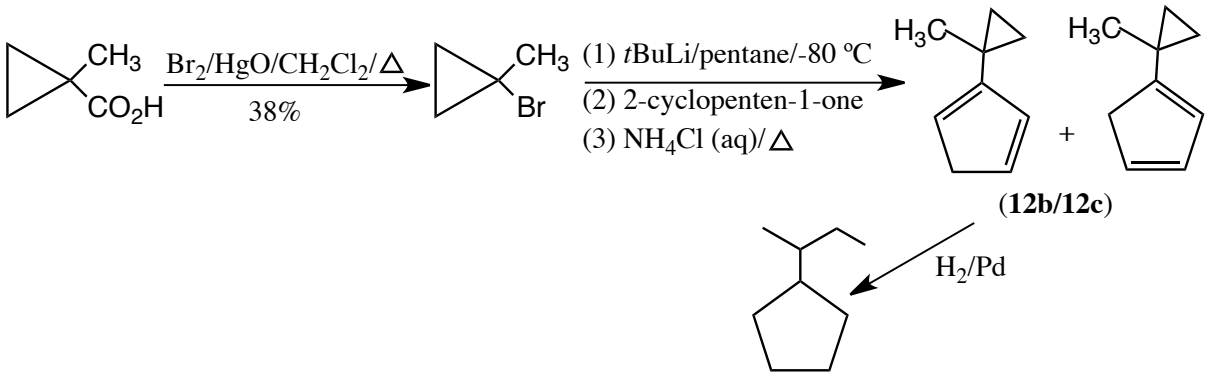


Fig S5b. ^{13}C NMR Spectrum of *sec*-Butylcyclopentane.



Scheme S6. Synthetic Scheme for the preparation of Compounds **12b/12c**, their precursor, and their hydrogenation product.

1-Bromo-1-methylcyclopropane. The Hunsdiecker methodology for the conversion of cyclopropane-1,1-dicarboxylic acid to 1,1-dibromocyclopropane[13] gave 5.1 g (38% yield) of 1-bromo-1-methylcyclopropane (in 93% purity by GC after fractional distillation) from 10.0 g of 1-methylcyclopropanecarboxylic acid. FTIR (neat) ν_{max} 3006, 2971, 1183, 758, 718 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.78 (s, 3H), 1.17 (t, 2H), 0.79 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.8 (CH_3), 29.0 (C), 17.1 ($2CH_2$). LRMS (EI) *m/z* 136 ($M+2^+$, $C_4H_7{}^{81}Br$, 5), 134 (M^+, $C_4H_7{}^{79}Br$, 5), 55 (100).

1- and 2-(Spiro[1-ethyl-1,1′-cyclopropane])-1,3-cyclopentadienes (**12b** and 1**2c**). Using the general methodology of Neuenschwander,[14] 1-bromo-1-methylcyclopropane in anhydrous Et_2O at -70 ºC was treated with 2 equiv of 1.7 M *t*-BuLi/pentane, which had been cooled in a conical vial with dry ice/acetone. The transfer of *t*-BuLi via cannula caused the internal temperature to rise to – 30 ºC. After stirring for 1 h, cyclopent-2-en-1-one (1.5 equiv) dissolved in Et_2O was added to the reaction mixture dropwise via syringe at -70 ºC. After stirring for 1 h, the reaction mixture was allowed to warm gradually to 0 ºC before the reaction was diluted with 1:1 pentane:Et_2O and quenched with aqueous NH_4Cl. A ca. 2:1 mixture of **12b** and **12c** formed almost immediately, with the more abundant peak eluting at 12.2 min. Preparative GC on column B at 110 ºC afforded an isomeric mixture of **12b** and **12c** in 97% purity. The NMR spectral data were acquired under VT-NMR conditions at 0ºC in order to suppress Diels-Alder dimerization reactions; slow isomerization in the $CDCl_3$ resulted

in a 54:46 mixture of the two isomers. Major isomer (12.2 min): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (m, 2H), 6.18 (m, 1H), 2.98 (s, 2H), 1.32 (s, 3H), 0.80 (t, 2H), 0.63 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4 (=C), 132.4 (=CH), 131.0 (=CH), 123.6 (=CH), 40.3 (CH_2), 23.5 (CH_3), 15.5 (C), 14.7 ($2CH_2$). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 38), 105 (100), 91 (44), 79 (28). Minor isomer (12.5 min): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.17 (br s, 2H), 6.03 (m, 1H), 2.71 (s, 2H), 1.31 (s, 3H), 0.71 (t, 2H), 0.67 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (=C), 134.4 (=CH), 129.2 (=CH), 124.4 (=CH), 41.4 (CH_2), 22.9 (CH_3), 17.5 ($2CH_2$), 17.2 (C). LRMS (EI) *m/z* 120 (M^+, C_9H_{12}, 40), 105 (100), 91 (44), 79 (27). Catalytic hydrogenation of the isomer mixture afforded *sec*-butylcyclopentane.

Safety Note: For a 3.0 mmol scale reaction, 3.5 mL (6.0 mmol, 2 equiv) of cold 1.7 M *t*-BuLi/pentane was dispensed in a 5.0 mL BD syringe with a Luer-Lok™ tip. Transfer of the 1.7 M *t*-BuLi/pentane solution was uneventful when the contents of the bottle were kept at < 10 ºC.

Thermal Reactions of a Mixture of **12b**/**12c**: Capillary tubes pyrolyses are fundamentally liquid-phase thermal reactions. Facile interconversion of isomers **12b** and **12c** is observed in early thermal runs, but over time the early eluting peak disappears faster. Diminution in the concentration of **12b** and **12c** over time can be attributed to slow Diels-Alder dimerization reactions.

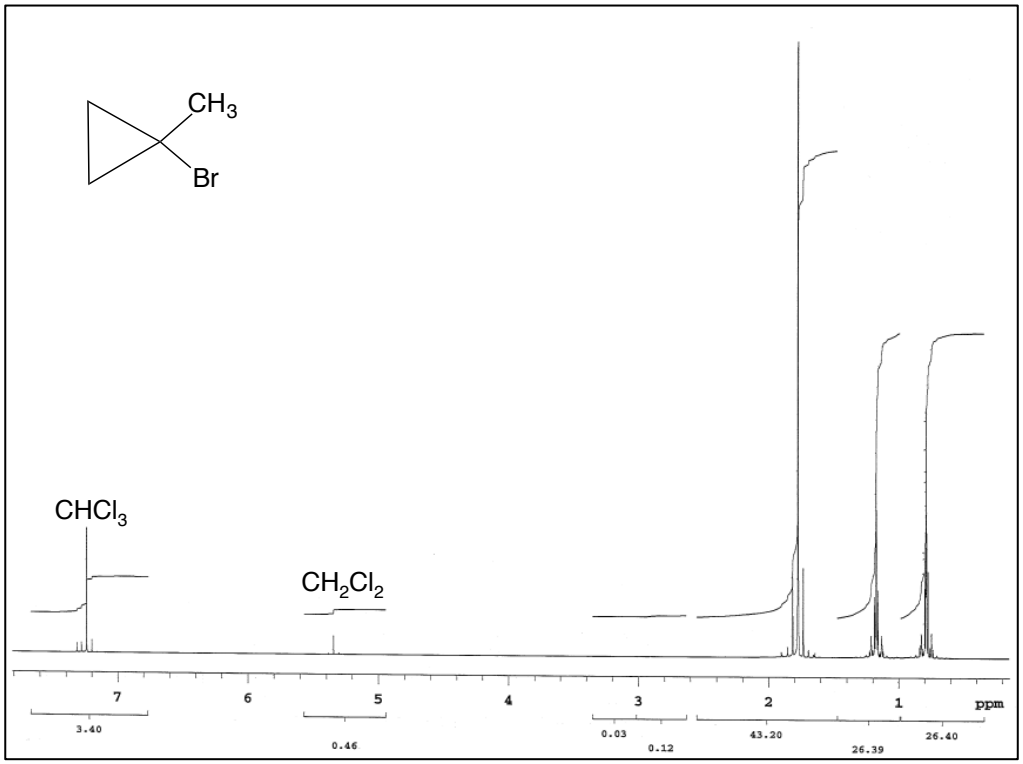


Fig S6a. ^{1}H NMR Spectrum of 1-Bromo-1-methylcyclopropane.

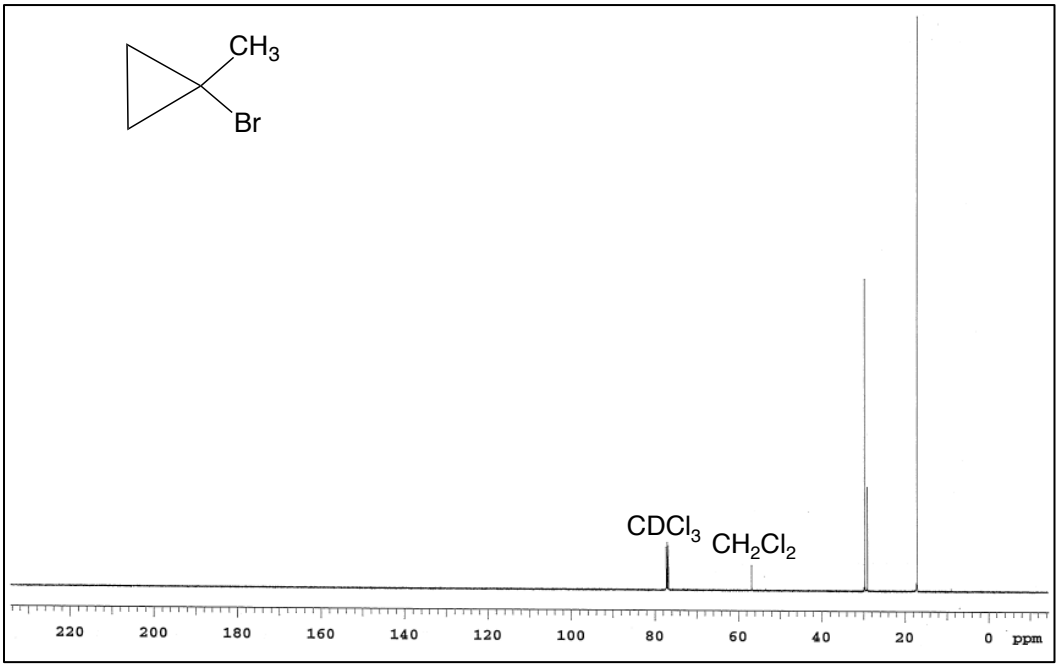


Fig S6b. ^{13}C NMR Spectrum of 1-Bromo-1-methylcyclopropane.

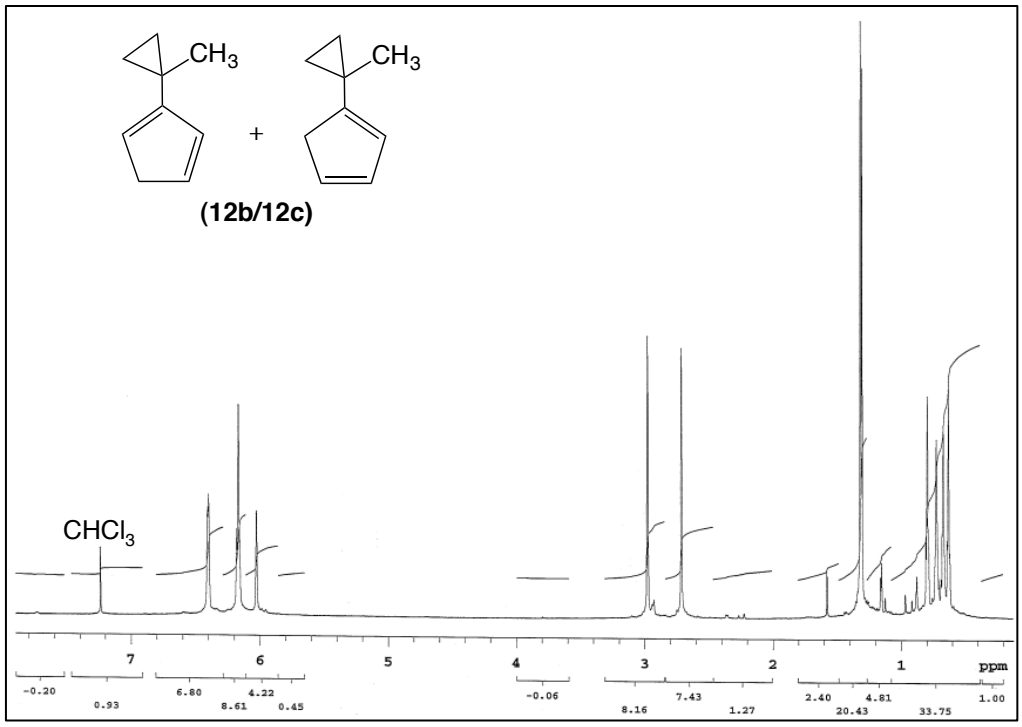


Fig S6c. ^{1}H NMR Spectrum of 1- and 2-(Spiro[1-ethyl-1,1′-cyclopropane]-1,3-cyclopentadienes (**12b** and 1**2c**).

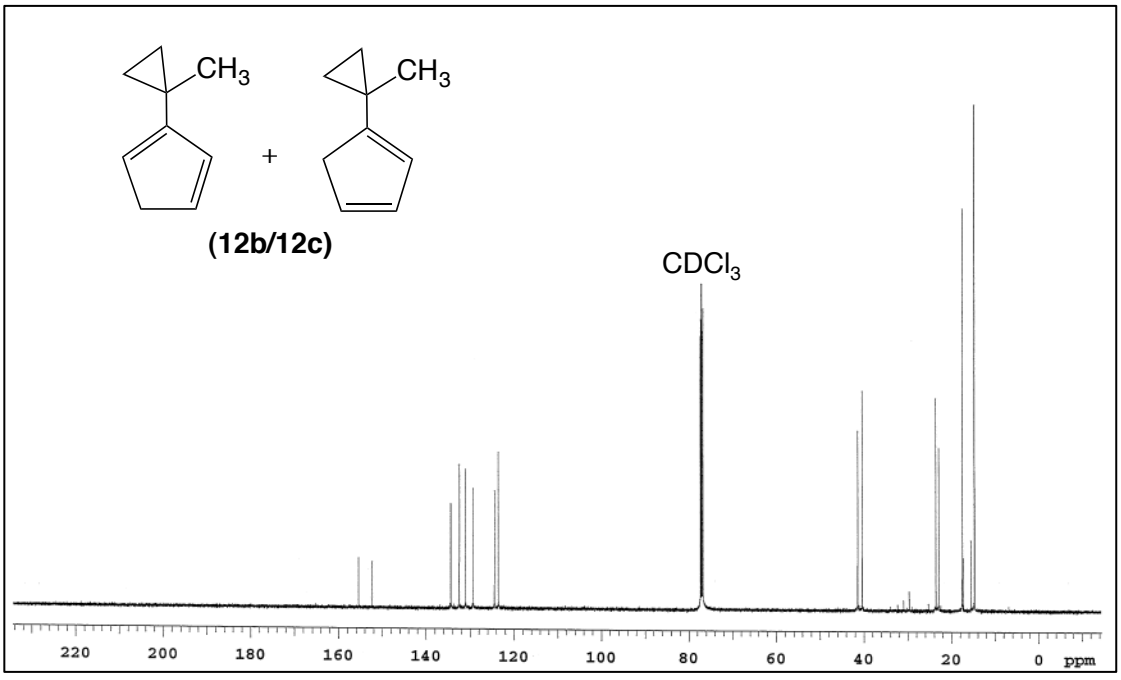
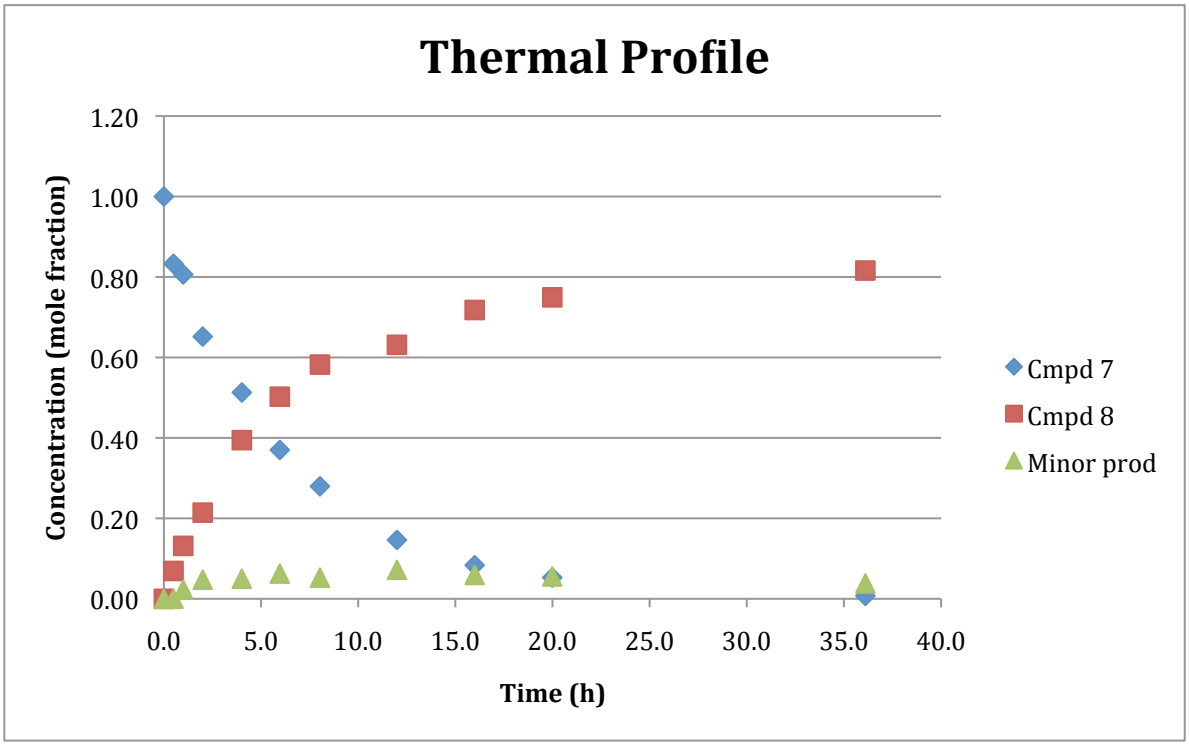
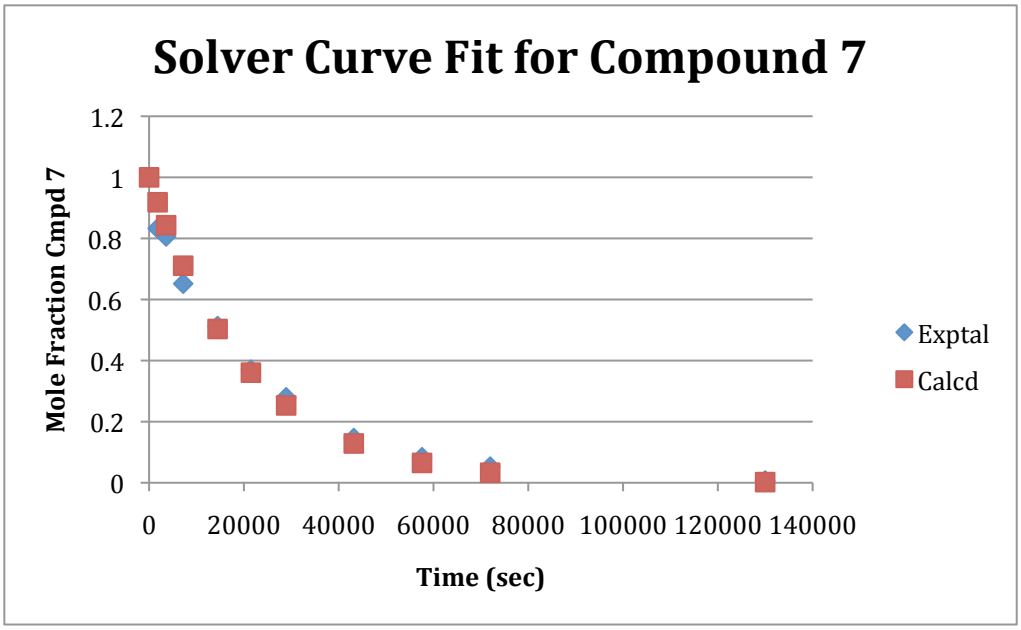


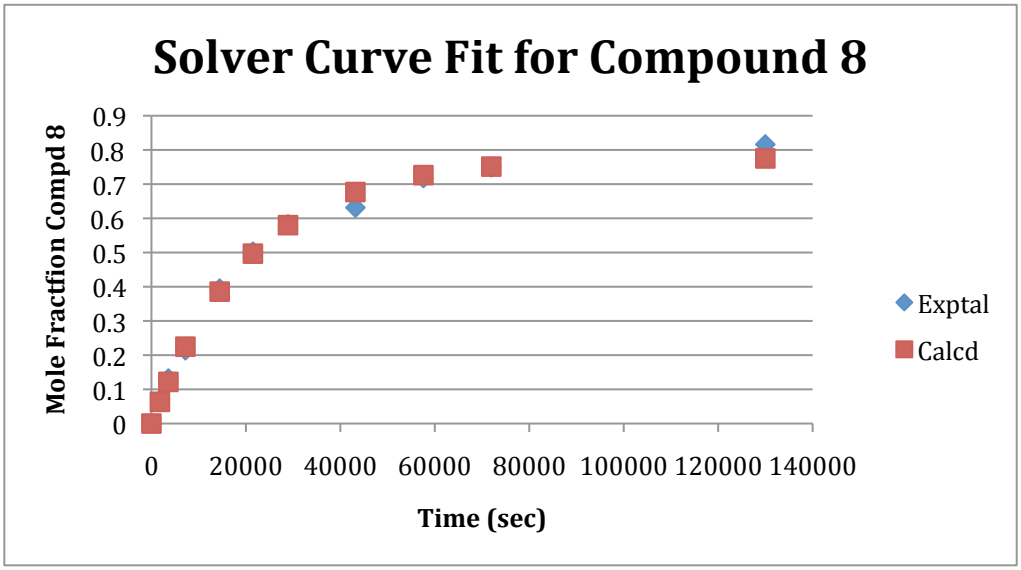
Fig S6d. ^{13}C NMR Spectrum of 1- and 2-(Spiro[1-ethyl-1,1′-cyclopropane]-1,3-cyclopentadienes (**12b** and 1**2c**).

Time-dependent Concentration Kinetics @ 275 ºC

Time (sec)	Time (h)	Mole fraction **7**	Mole fraction **8**	Mole fraction minor isomers
0.0	0.0	1.00000	0.00000	0.00000
1,791.9	0.5	0.83284	0.06925	0.00000
3,589.6	1.0	0.80643	0.13159	0.02281
7,191.9	2.0	0.65186	0.21424	0.04745
14,446.5	4.0	0.51287	0.39440	0.04989
21,482.0	6.0	0.36999	0.50241	0.06267
28,915.5	8.0	0.27968	0.58225	0.05273
43,184.2	12.0	0.14626	0.63134	0.07215
57,584.6	16.0	0.08350	0.71789	0.05929
71,966.2	20.0	0.05278	0.74939	0.05552
129,978.1	36.1	0.00731	0.81600	0.03818







Equations for Solver Curve Fit:

$[7]_t = [7]_0\ e^{(-k_d t)}$, where $[7]_0$ = 1.0 mol fraction of **7** at time 0, $[7]_t$ = mol fraction of **7** at time t, and k_d = rate of decomposition of **7**.

$[8]_t = [7]_0 * (k_{13}/k_d)\ (1 - e^{(-k_d t)})$, where k_{13} = rate of formation of **8**.

$k_d = 4.7 \times 10^{-5}\ s^{-1}$
$k_{13} = 3.7 \times 10^{-5}\ s^{-1}$

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