ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental Evidence of a Cyclopropylcarbinyl Conjugative Electronic Effect

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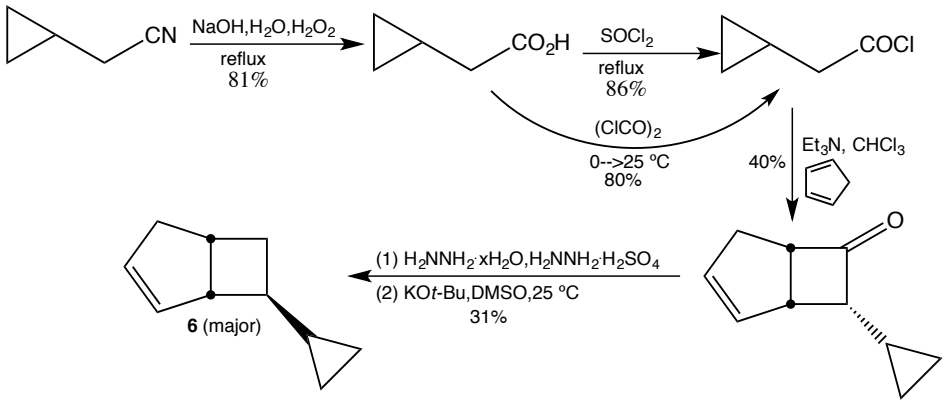
General Experimental

Kinetics. Thermal reactions of hydrocarbon **6** 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 an 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 trans-decalin. Preparative GC analysis afforded compound **6** in ca. 97% purity by GC for subsequent thermal reactions. 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 70 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: 13.6 (**8b**), 13.8 (**8a**), 14.6 (DCP), 15.7 (**6**), 16.0 (*endo*-7-cyclopropylbicyclo[3.2.0]hept-2-ene), 17.6 (ISTD).

Preparative GC. Preparative GC was accomplished on a GOW MAC® Model 350 GC equipped with a 8′ × 1/4″ DC710 column (Column A).

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.

Synthesis and Spectral Characterization



Scheme S1. Synthetic Scheme for the preparation of Compound **6** and its precursors.

Cyclopropylacetic acid. The methodology of Fenick and Falvey[1] was employed for the hydrolysis of commercially available cyclopropylacetonitrile. ^{1}H NMR (500 MHz, d_6-DMSO) δ 11.99 (br s, 1H), 2.09 (d, 2H), 0.92 (m, 1H), 0.44 (d, 2H), 0.11 (d, 2H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 174.2 (C=O), 38.9 (CH_2), 7.0 (CH), 4.2 (2 CH_2). FTIR (neat) ν_{max} 3007, 3010, 1704, 1222, 828 cm^{-1}.

Cyclopropylacetyl chloride (with thionyl chloride). Cyclopropylacetic acid (10.0 g, 100 mmol) and thionyl chloride (14.6 mL, 200 mmol) were combined and refluxed overnight at 40 ºC under argon. Short-path distillation at atmospheric pressure afforded two fractions: fraction 1 (bp ~ 75 ºC, unreacted thionyl chloride) and fraction 2 (bp 130-135 ºC, cyclopropylacetyl chloride, 10.2 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.77 (d, 2H), 1.13 (m, 1H), 0.65 (d, 2H), 0.24 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C=O), 51.9 (CH_2), 7.1 (CH), 4.6 (2 CH_2). FTIR (neat) ν_{max} 3086, 3010, 1795, 1024, 925, 830, 707 cm^{-1}.

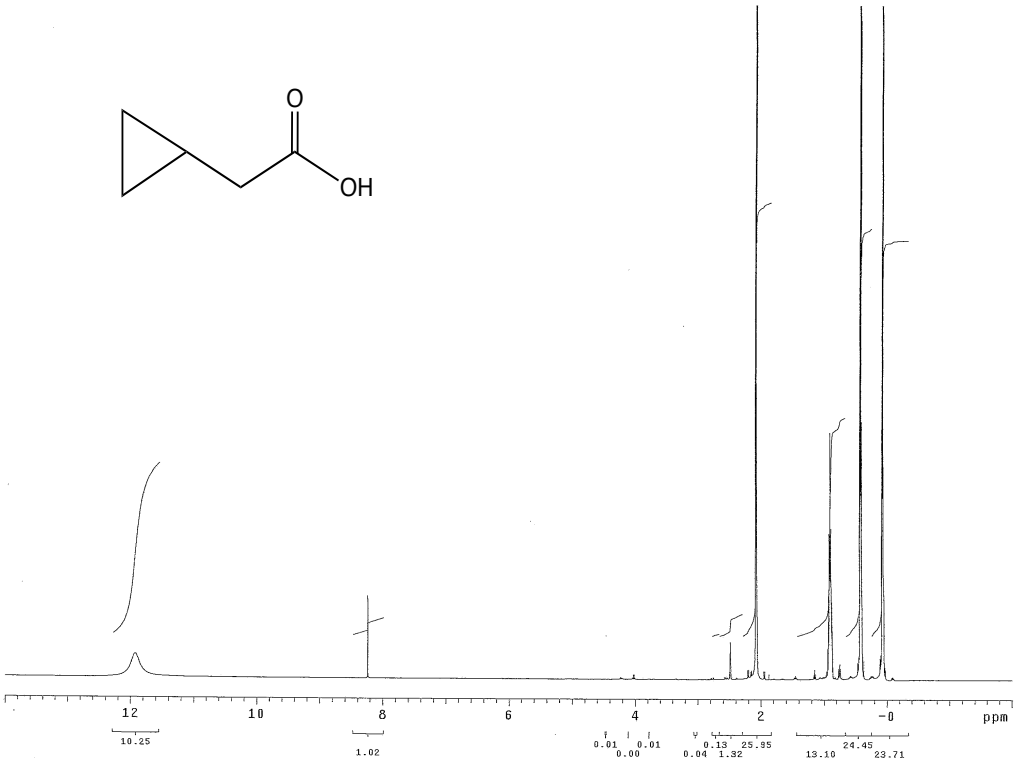
Cyclopropylacetyl chloride (with oxalyl chloride). A literature procedure for the conversion of 4-pentenoic acid to its acid chloride derivative[2] was employed for the synthesis of cyclopropylacetyl chloride with oxalyl chloride. Oxalyl chloride (5.0 g, 39.4 mmol) was added dropwise to cyclopropylcetic acid (3.5 g, 35.0 mmol) under argon at 0 ºC. As the reaction mixture was allowed to warm to rt, vigorous gas evolution occurred. After stirring overnight, the resultant cyclopropylacetyl chloride (3.3 g, 80%) was used as is in the subsequent ketene cycloaddition reaction.

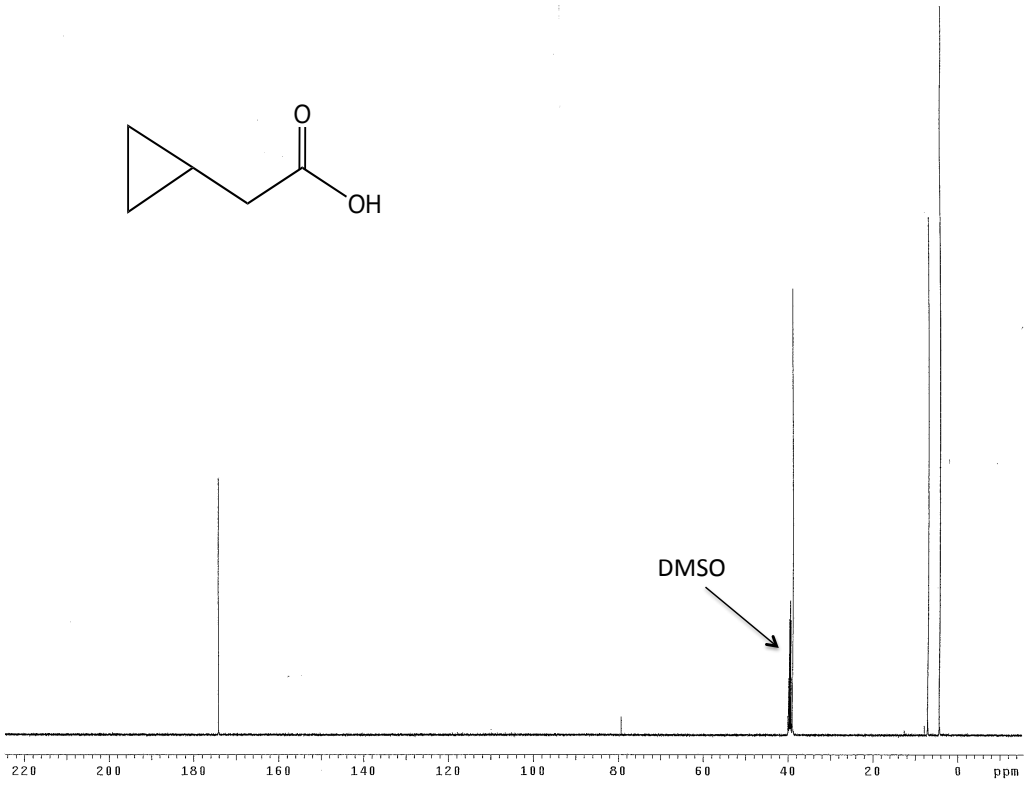
endo-7-Cyclopropylbicyclo[3.2.0]hept-2-en-6-one. Triethylamine (11.8 mL, 85 mmol), freshly distilled from CaH_2, was dissolved in 75 mL chloroform (purified by washing with conc. H_2SO_4 and distilled from CaH_2) and then added dropwise to a solution of

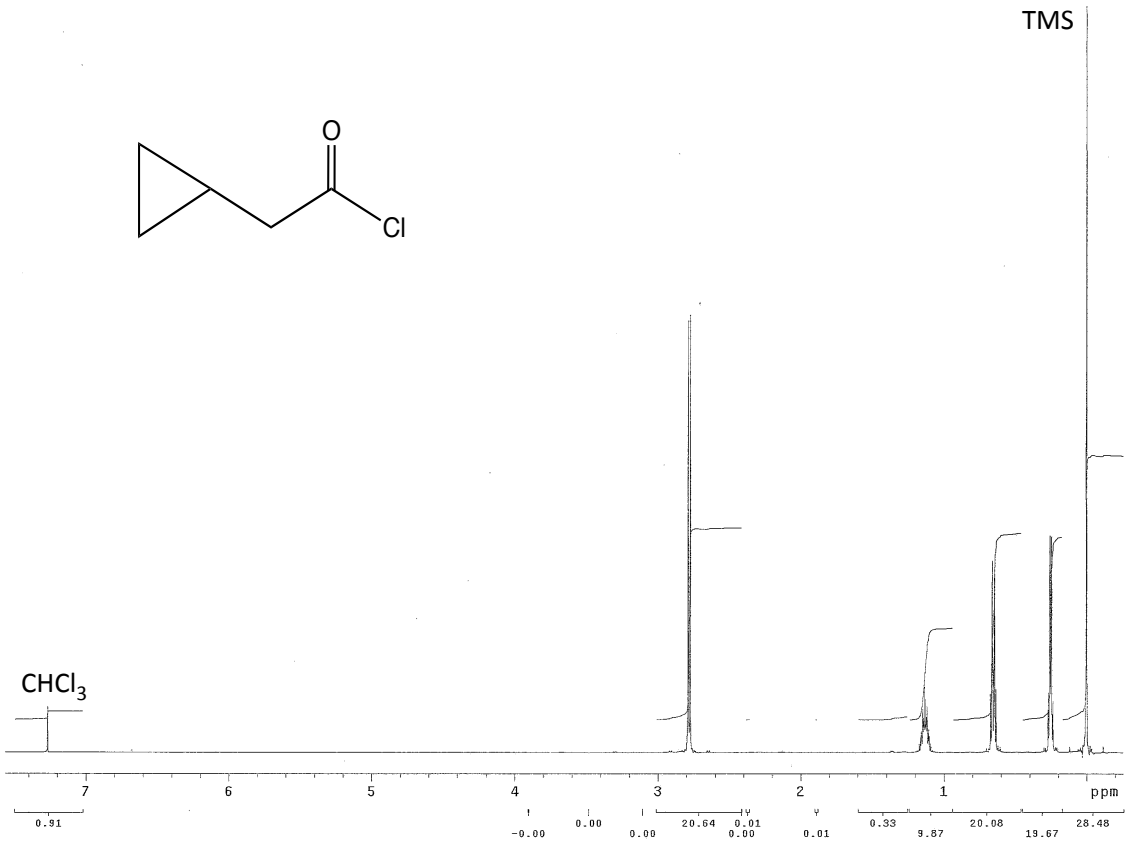
cyclopropylacetyl chloride (10. g, 84 mmol) in 1,3-cyclopentadiene (90 mL, 1680 mmol). After stirring at rt for 24 h, the chloroform was removed via simple distillation. After addition of 150 mL of ether, the suspended solid was removed via vacuum filtration. The ether layer was washed with water, dried over $MgSO_4$ (anhydrous), and concentrated under reduced pressure. Fractional distillation at 10 torr afforded two fractions: fraction 1 (bp ~ 70 ºC, dicyclopentadiene) and fraction 2 (bp ~ 85 ºC, product ketone, 5.0 g, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (m, 1H), 5.88 (m, 1H), 3.72 (m, 1H), 3.61 (m, 1H), 2.90 (t, 1H), 2.65 (dd, 1H), 2.40 (m, 1H), 0.77 (m, 1H), 0.58 (m, 1H), 0.41 (m, 1H), 0.29 (m, 1H), 0.18 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.5 (C=O), 134.1 (=CH), 130.5 (=CH), 69.8 (CH), 59.0 (CH), 42.7 (CH), 34.1 (CH_2), 6.7 (CH), 4.4 (CH_2), 2.1 (CH_2). FTIR (neat) ν_{max} 3055, 3005, 2956, 1770, 705 cm^{-1}. LRMS (EI) *m/z* 148 (M^+, $C_{10}H_{12}O$, 3), 147 (8), 130 (15), 120 (35), 105 (59), 91 (100), 82 (94), 79 (65), 77 (49), 66 (65); HRMS (EI) calcd for $C_{10}H_{11}O$ (M-1) 147.0810, found 147.0818.

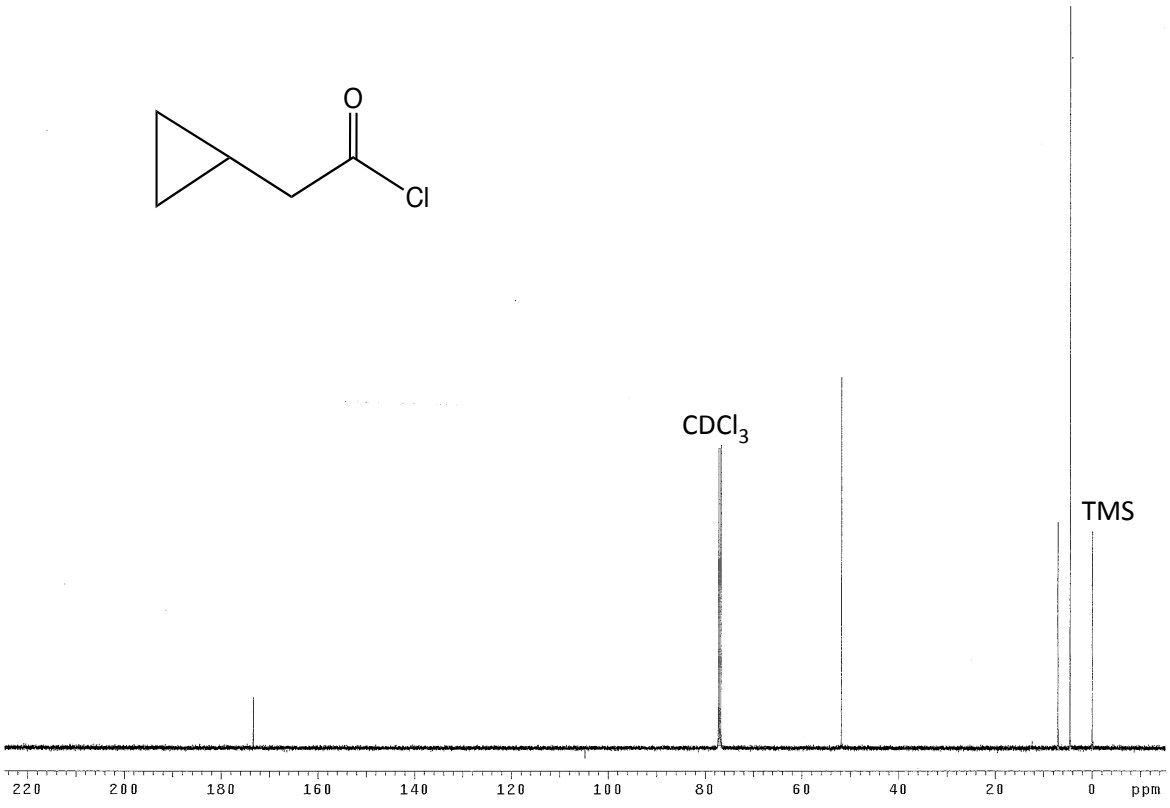
exo-7-Cyclopropylbicyclo[3.2.0]hept-2-ene (**6**). The target compound for the thermal study was prepared from the corresponding ketone using a low-temperature Wolff-Kishner reduction sequence.[3] A mixture of hydrazine sulfate (2.1 g, 15.9 mmol) dissolved in 7 mL hydrazine hydrate and *endo*-7-cyclopropylbicyclo[3.2.0]hept-2-en-6-one (2.2 g, 14.9 mmol) was refluxed overnight at 65 ºC. The reaction mixture was extracted several times with ether, and the combined organic layers were was with distilled water and brine, dried over $MgSO_4$ (anhydrous), and concentrated under reduced pressure to afford crude 7-cyclopropylbicyclo[3.2.0]hept-2-en-6-one hydrazone (1.5 g, 62%). FTIR (neat) ν_{max} 3369, 3076, 3048, 1675, 1608, 1018, 710 cm^{-1}. To a solution of potassium *tert*-butoxide (0.60 g, 5.2 mmol), sublimed under high vacuum at 190 ºC and dissolved in 25 mL anhydrous DMSO,

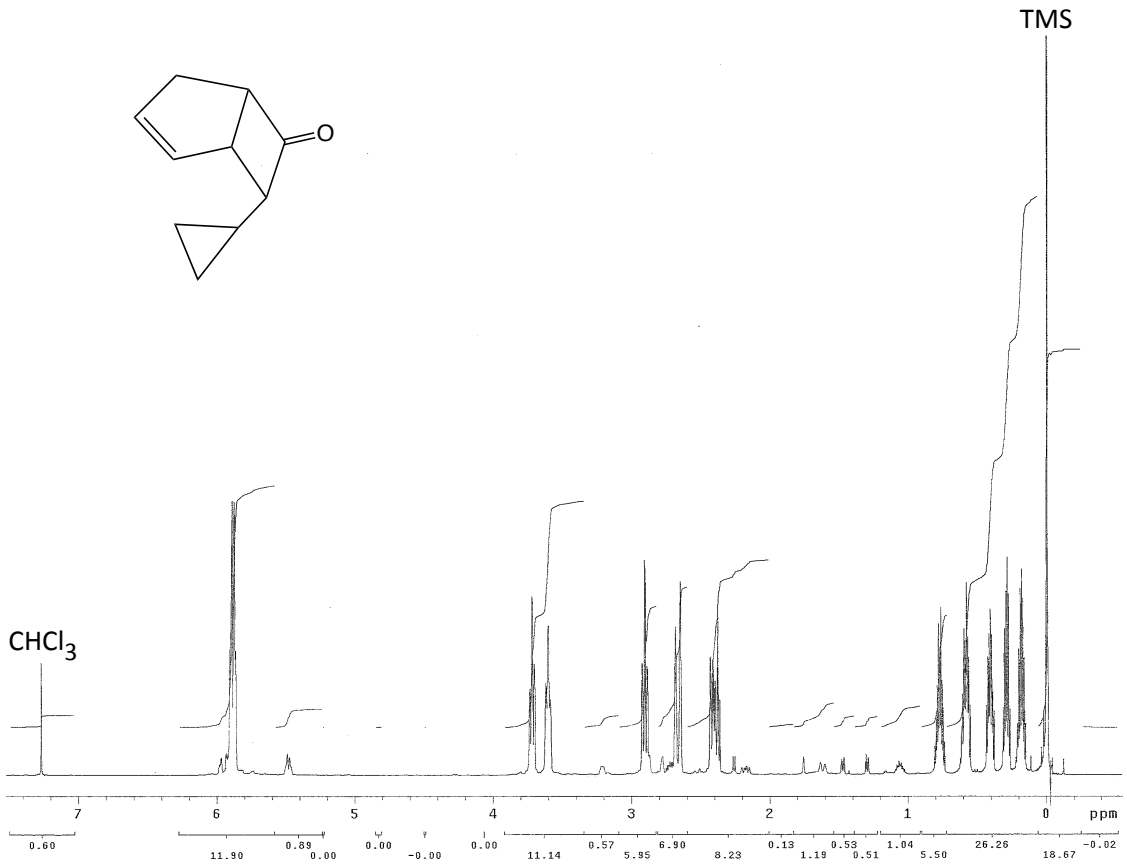
was added 7-cyclopropylbicyclo[3.2.0]hept-2-en-6-one hydrazone (0.80 g, 5.0 mmol) dropwise over 4 h. After stirring overnight, the reaction mixture was quenched with 5 mL cold water and extracted four times with pentane. The combined pentane extracts were washed ten times with water to remove DMSO and dried over $MgSO_4$ (anhydrous). The pentane was removed via simple distillation to yield crude **6** (0.34 g, 50%) in an exo:endo ratio of 3:1. The epimers were partially separated by preparative GC using Column A at 107 ºC to afford an isomeric mixture consisting of 92% **6** and a less pure mixture consisting of a ca. 3:2 exo:endo ratio. Major epimer (**6**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (m, 1H), 5.71 (m, 1H), 2.93 (br s, 1H), 2.80 (pent, 1H), 2.52 (dd, 1H), 2.12 (dq, 1H), 1.86 (m, 1H), 1.72 (m, 1H), 1.61 (m, 1H), 0.98 (m, 1H), 0.42 (m, 2H), 0.09 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.7 (=CH), 130.2 (=CH), 50.9 (CH), 45.1 (CH), 40.6 (CH_2), 33.0 (CH), 31.6 (CH_2), 16.3 (CH), 2.9 (CH_2), 2.8 (CH_2). FTIR (neat) ν_{max} 3075, 3046, 2999, 1605, 1014, 727, 700 cm^{-1}. LRMS (EI) *m/z* 134 (M^+, $C_{10}H_{14}$, <1), 119 (7), 105 (6), 91 (15), 79 (13), 67 (33), 66 (100); HRMS (EI) calcd for $C_{10}H_{14}$ 134.1096, found 134.1091. Minor epimer (*endo*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (m, 1H), 5.85 (m, 1H), 3.33 (br s, 1H), 2.64 (pent, 1H), 2.48 (dd, 1H), 2.22 (dq, 1H), 1.77 (m, 1H), 1.48 (m, 1H), 1.43 (m, 1H), 0.72 (m, 1H), 0.35 (m, 2H), 0.03 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.9 (=CH), 131.5 (=CH), 50.2 (CH), 43.6 (CH), 40.2 (CH_2), 32.6 (CH_2), 32.0 (CH), 12.1 (CH), 3.4 (CH_2), 2.3 (CH_2). LRMS (EI) *m/z* 134 (M^+, $C_{10}H_{14}$, 12), 119 (4), 105 (5), 91 (18), 79 (13), 67 (39), 66 (100).

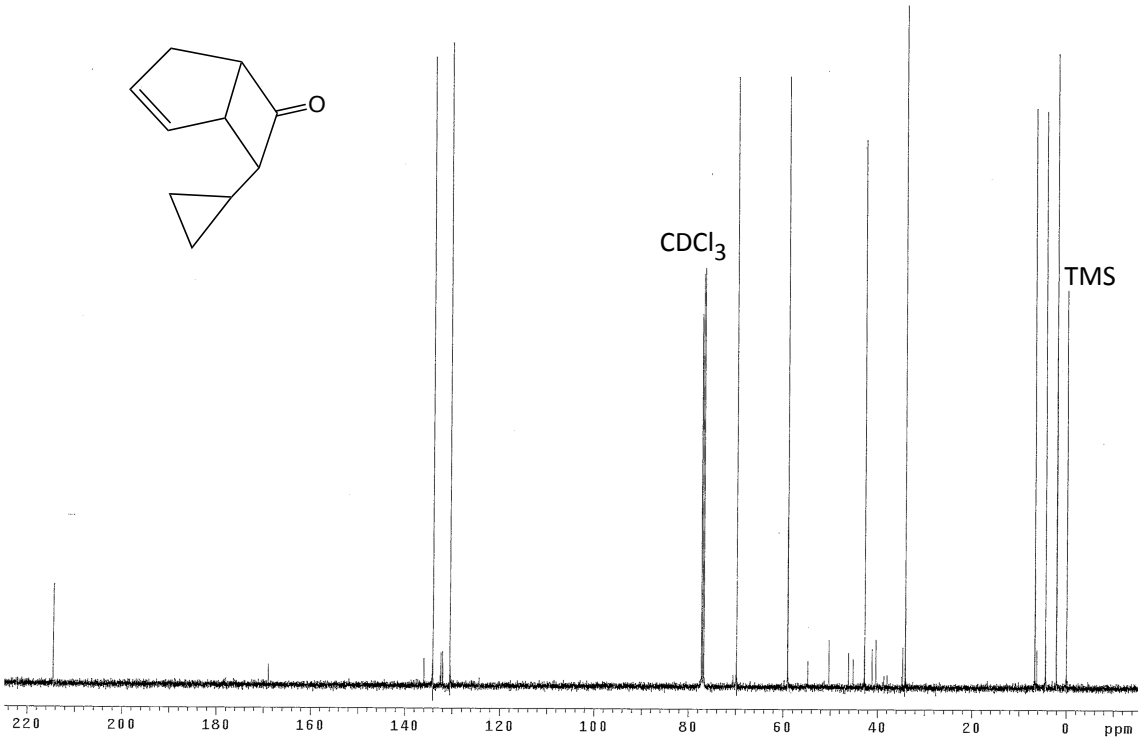


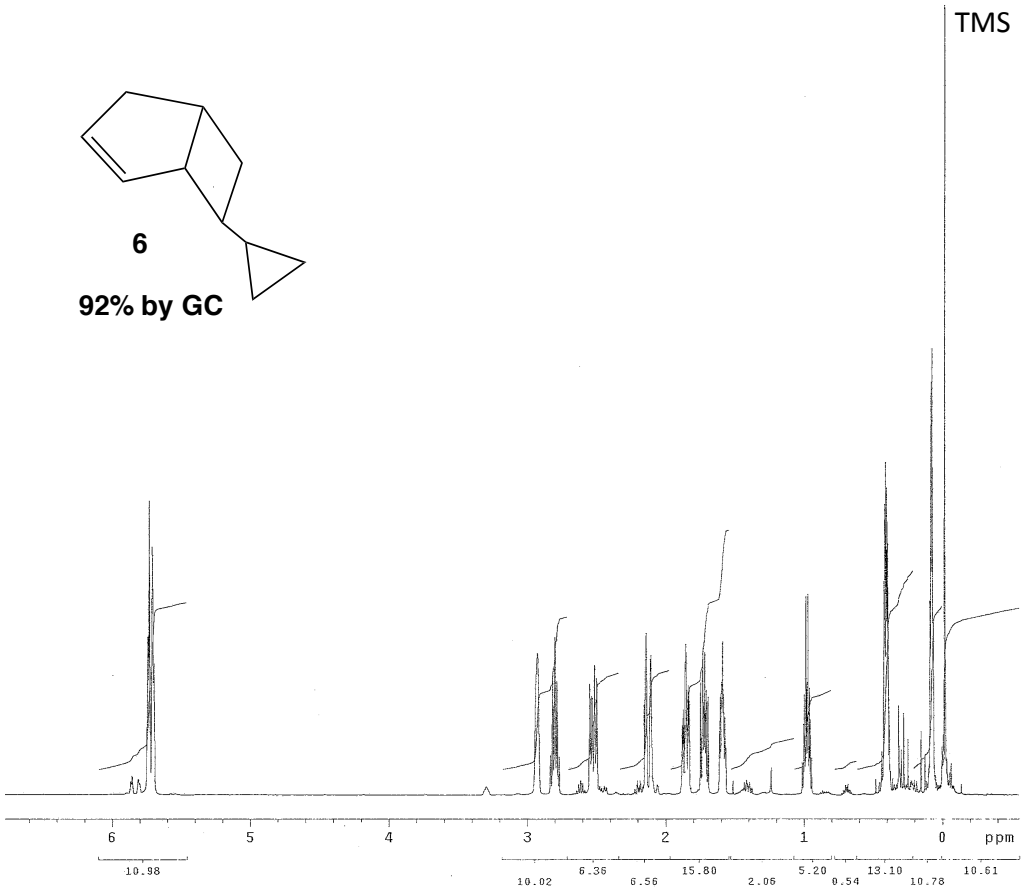


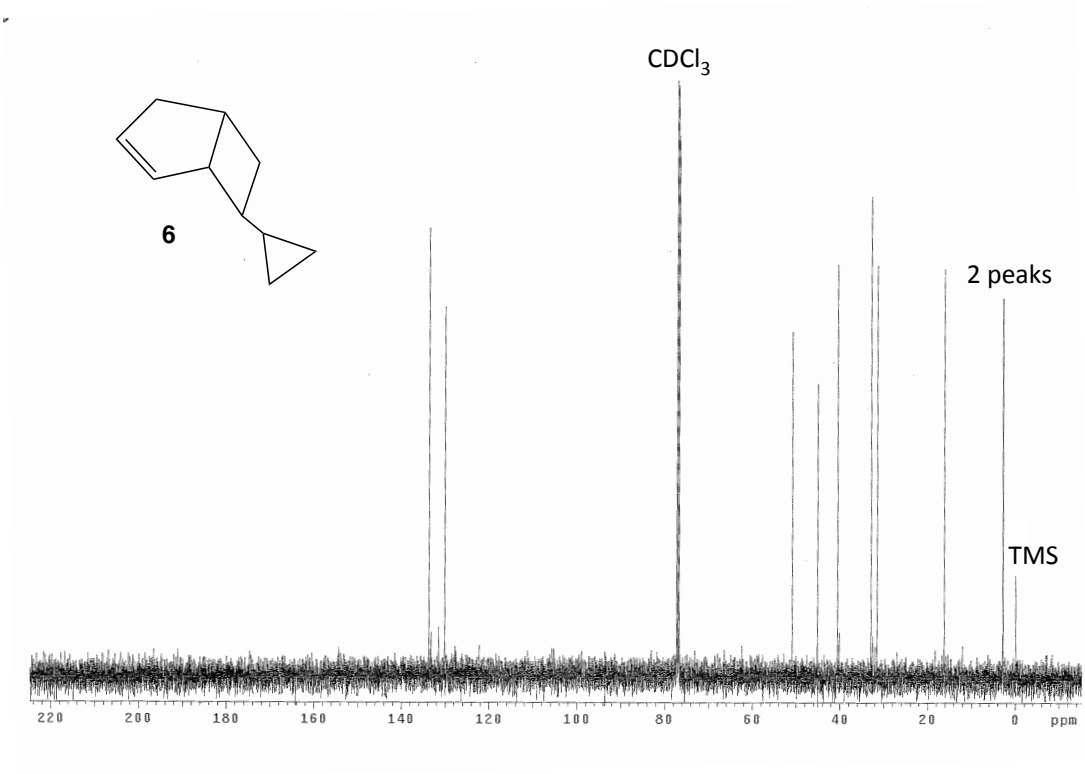


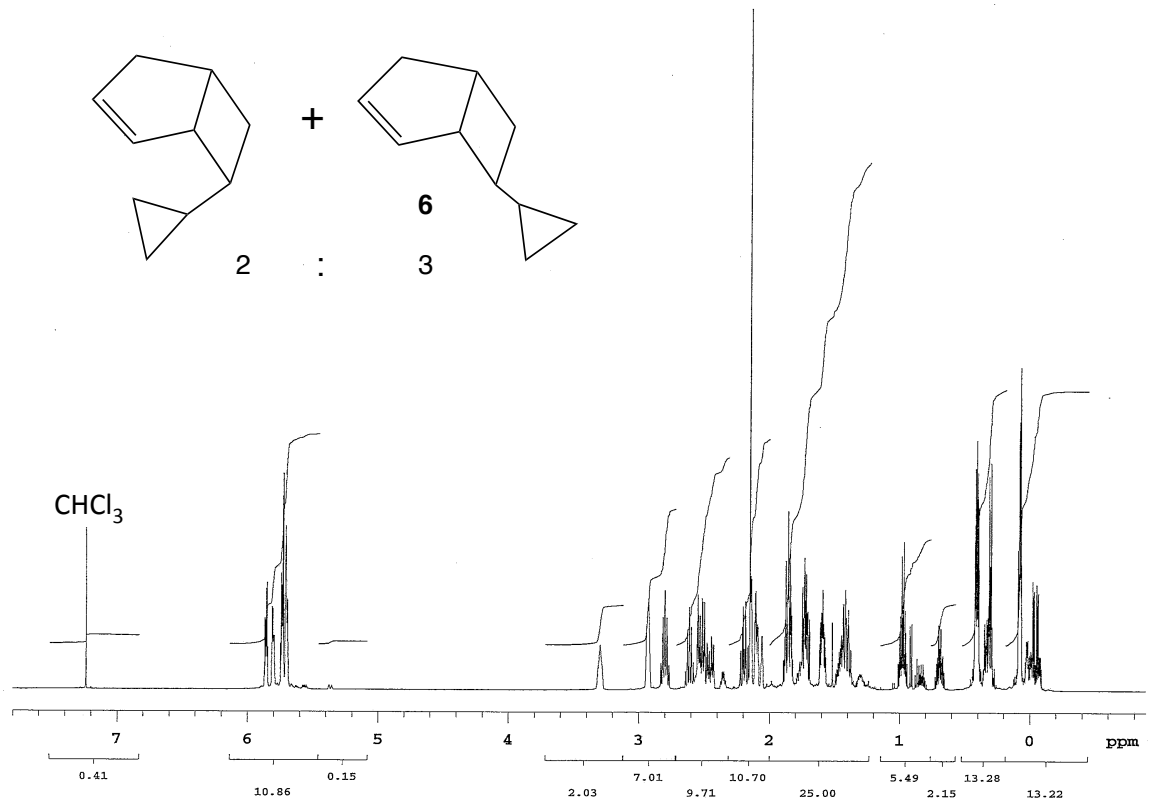


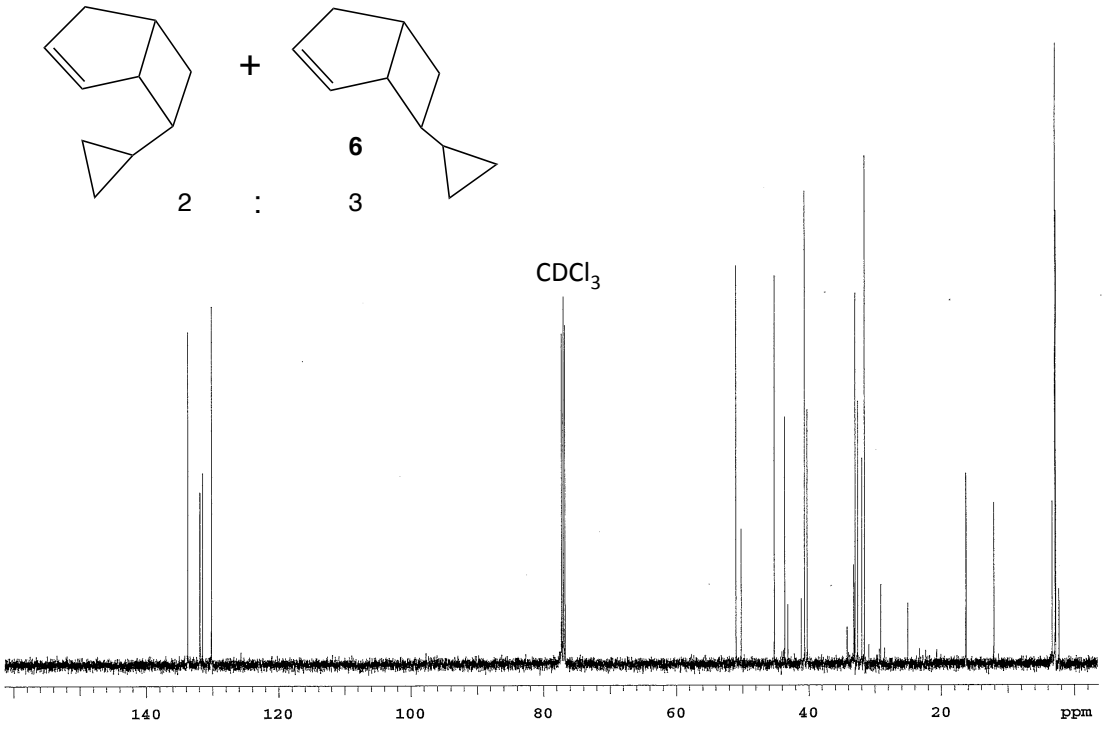


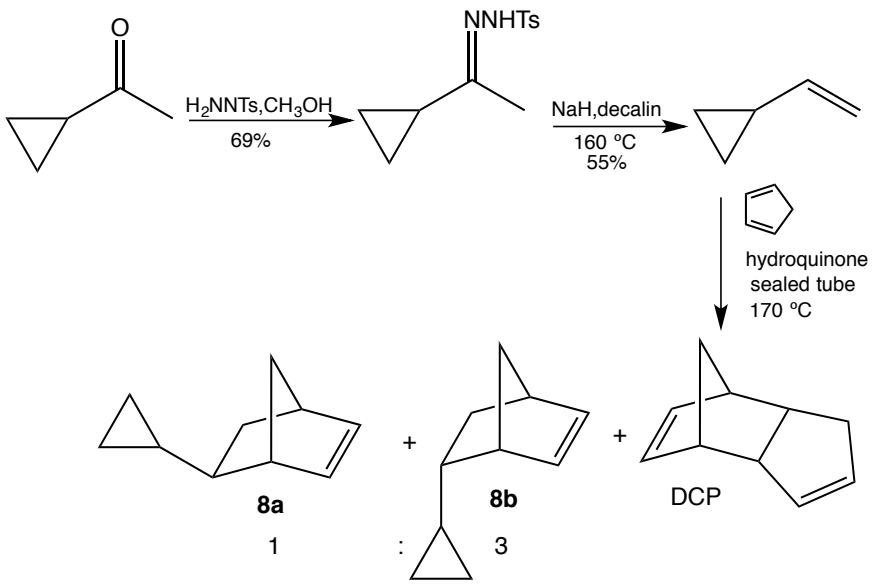












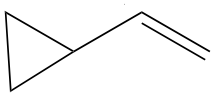
Scheme S2. Synthetic Scheme for the preparation of Compounds **8a**/**8b** and their precursors.

Cyclopropyl methyl ketone tosylhydrazone. To a solution of 17.7 g (95.1 mmol) p-toluenesulfonylhydrazide in 280 mL methanol was added 5.0 g (5.5 mL, 59 mmol) of cyclopropyl methyl ketone. Due to evaporative loss overnight, as indicated by the absence of a strong C=O peak in the IR of the solution, an additional 3.0 g (3.3 mL, 36 mmol) cyclopropyl methyl ketone was added to the solution. Crystals gradually formed as the methanol evaporated in the hood. When the volume had decreased to 150 mL, the beaker was placed in an ice bath to encourage further crystallization. The crystals were then filtered, rinsed with methanol, and dried for 30 minutes using an aspirator. The crystals were further dried in a vacuum oven for 2 h: 14.2 g (60%), mp 118-119 ºC. FTIR (neat) ν_{max} 3221, 1062, 585 cm^{-1}.

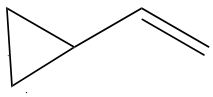
Vinylcyclopropane. A literature-based Bamford-Stevens reaction[4] was employed to prepare vinylcyclopropane. Cyclopropyl methyl ketone tosylhydrazone (6.7 g, 26.6 mmol) was added to 60% NaH (7.0 g, 180 mmol) suspended in 100 mL of decalin (a mixture

of cis and trans isomers). The mixture was heated slowly to 180 ºC, at which temperature vinylcyclopropane (1.0 g, 14.7 mmol, 55%) gradually collected over 2 h in an attached conical tube cooled in a dry ice/acetone bath. ^{1}H NMR (500 MHz, $CDCl_3$) 5.33 (ddd, 1H), 5.05 (dd, 1H), 4.84 (dd, 1H), 1.40 (m, 1H), 0.70 (m, 2H), 0.38 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 142.5 (=CH), 111.5 (=CH_2), 14.7 (CH), 6.7 (2CH_2).

5-Cyclopropylnorbornenes (**8a**/**8b**). Hydroquinone (ca. 15 mg), vinylcyclopropane (mL, mmol), and freshly-cracked 1,3-cyclopentadiene (mL, mmol) were combined in a thick-walled 20 mL tube, which was immersed in an ice bath while the solution was degassed for 2 min. After the tube was sealed with a Teflon cap, it was heated at 170 ºC for 66 h. Upon cooling, the contents of the thick-walled tube were rinsed with pentane and purified by passing through a silica Sep-Pak to yield a ratio of **8a**:**8b**:DCP of ca. 9:3:1. The product epimers were separated from DCP by preparative GC on Column A at 107 ºC to yield a 13:87 ratio of **8a**:**8b**. *exo*-5-Cyclopropylnorbornene (**8a**): ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8 (=CH), 136.5 (=CH), 47.2 (CH), 45.7 (CH_2), 44.6 (CH), 41.7 (CH), 32.7 (CH_2), 16.5 (CH), 4.5 (CH_2), 4.2 (CH_2). LRMS (EI) *m/z* 134 (M^+, $C_{10}H_{14}$, 47), 119 (16), 105 (10), 92 (15), 91 (25), 79 (18), 77 (15), 67 (13), 66 (100). *endo*-5-Cyclopropylnorbornene (**8b**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (dd, 1H), 6.05 (dd, 1H), 2.79 (br s , 1H), 2.77 (br s, 1H), 1.84 (dq, 1H), 1.35 (m, 2H), 1.29 (m, 1H), 1.15 (d, 1H), 0.76 (dq, 1H), 0.32 (m, 2H), 0.06 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9 (=CH), 133.3 (=CH), 49.5 (CH_2), 46.3 (CH), 44.9 (CH), 42.7 (CH), 32.1 (CH_2), 14.7 (CH), 4.0 (CH_2), 3.8 (CH_2). LRMS (EI) *m/z* 134 (M^+, $C_{10}H_{14}$, 3), 119 (6), 105 (5), 92 (11), 91 (12), 79 (10), 77 (12), 67 (30), 66 (100).



- toluene



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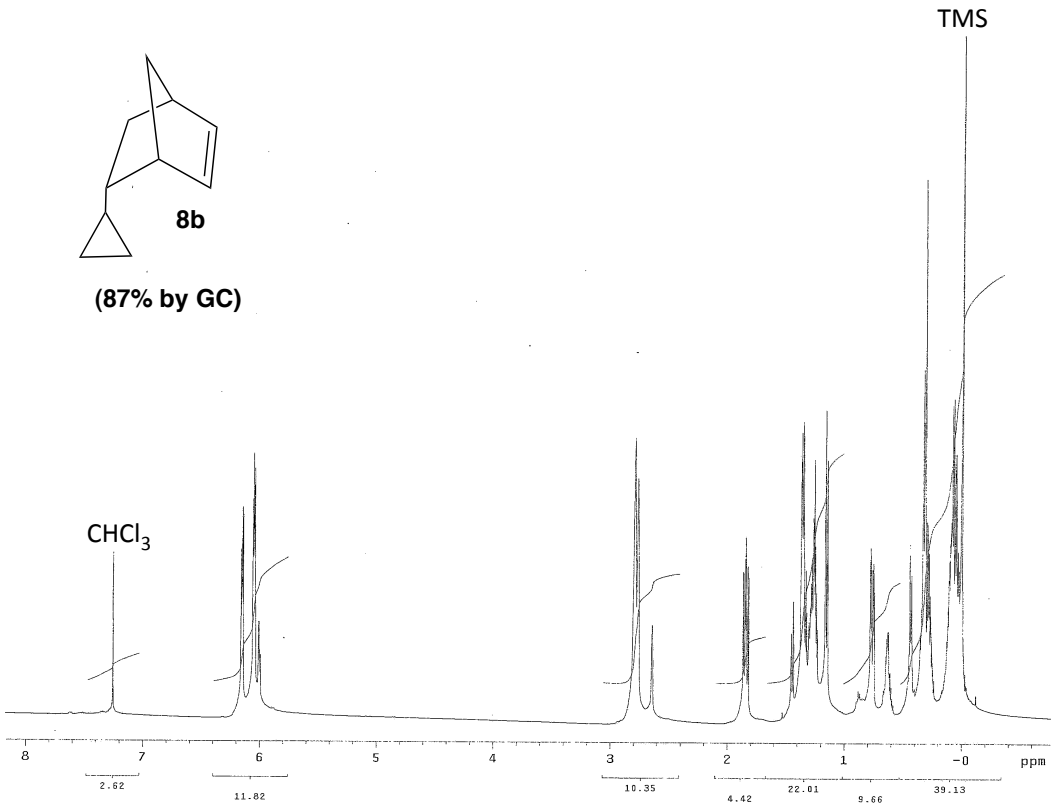
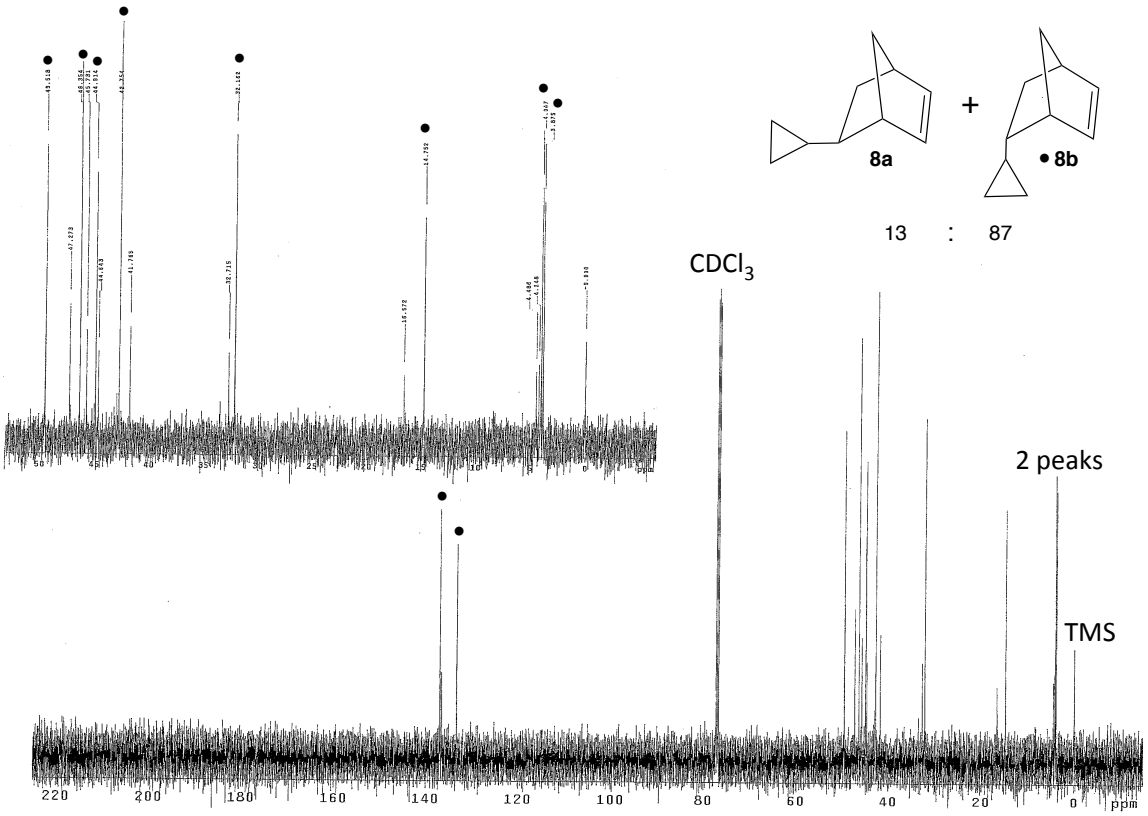
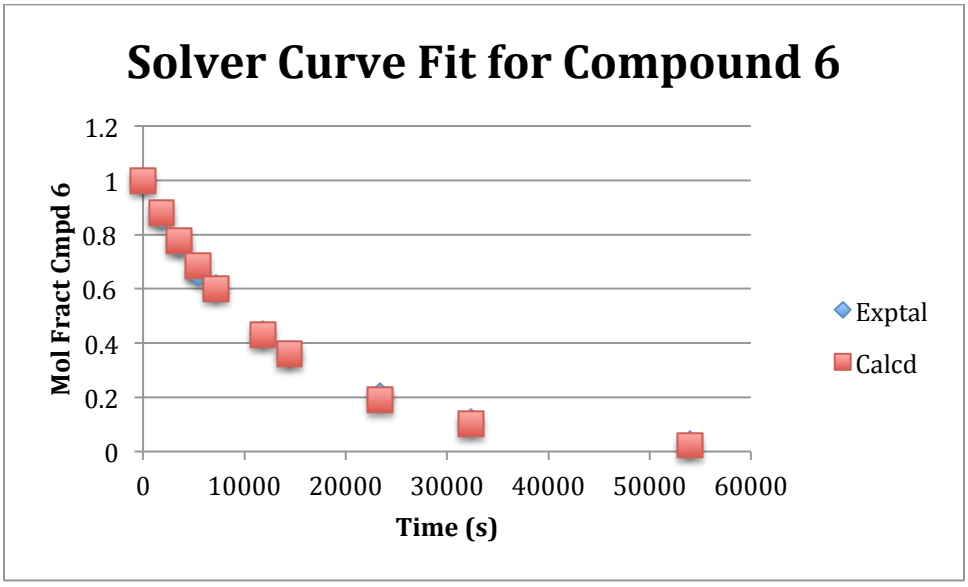




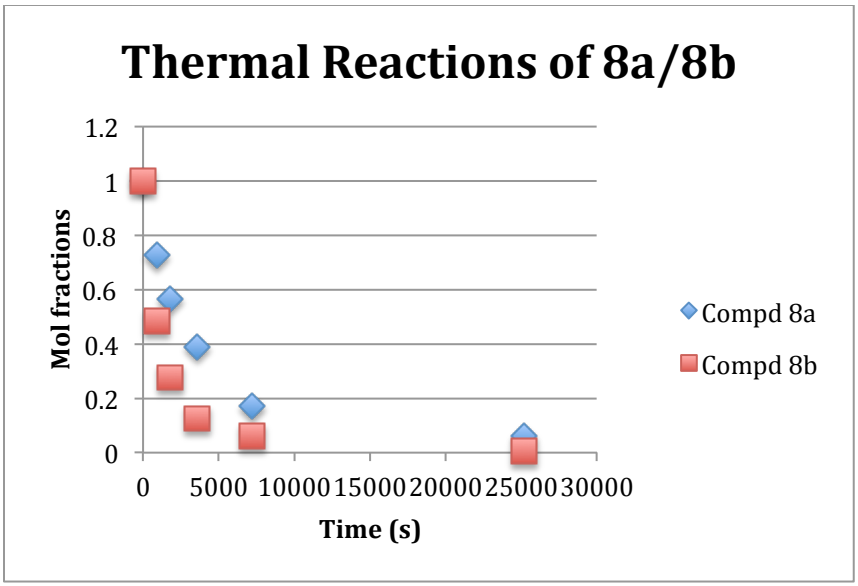
Time-dependent Concentration Kinetics for Compound **6** @ 275 ºC

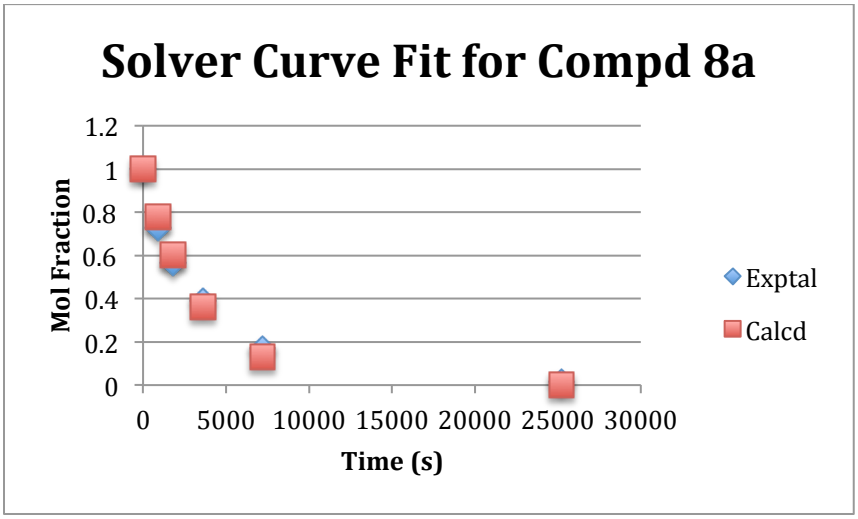
Time (sec)	Time (min)	Time (h)	Mole fraction **6**
0	0	0.0	1.0000
1800	30	0.5	0.8699
3600	60	1.0	0.7618
5400	90	1.5	0.6605
7200	120	2.0	0.6016
11880	198	3.3	0.4328
14460	241	4.0	0.3582
23400	390	6.5	0.2065
32400	540	9.0	0.1105
54000	900	15.0	0.0273

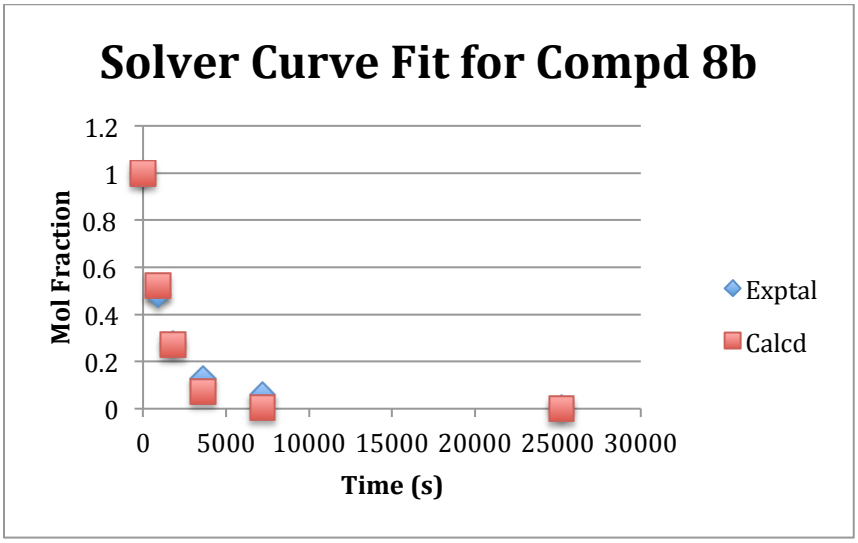


Time-dependent Concentration Kinetics for Compounds **8a**/**8b** @ 275 ºC

Time (s)	Time (min)	Time (h)	Mol fraction **8a**	Mol fraction **8b**
0	0	0.0	1.0000	1.0000
900	15	0.5	0.7260	0.4843
1800	30	1.0	0.5669	0.2760
3600	60	1.5	0.3899	0.1268
7200	120	2.0	0.1706	0.0600
25200	420	3.3	0.0161	0.0057







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