

## Supporting Information

### Silver-Catalyzed [4+3] Cycloaddition of 1,3-Dienes with Alkenyl-*N*-triflylhydrazones: A Practical Approach to 1,4-Cycloheptadienes

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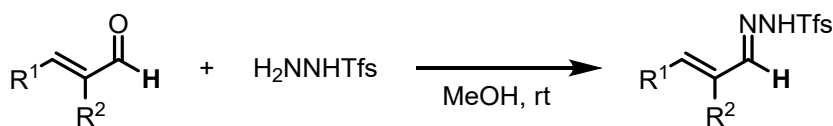
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## 1. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Dry  $\text{CHCl}_3$  was distilled over calcium hydride under nitrogen prior to use. The products were purified by column chromatography over silica gel. NMR spectra were recorded on a Bruker Advance 600 ( $^1\text{H}$ : 600 MHz,  $^{13}\text{C}$ : 150 MHz,  $^{19}\text{F}$ : 565 MHz) and Bruker Advance 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz,  $^{19}\text{F}$ : 470 MHz) at ambient temperature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were reported as chemical shifts in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent ( $\text{CHCl}_3$  at 7.26 ppm  $^1\text{H}$  NMR, 77.00 ppm  $^{13}\text{C}$  NMR; DMSO at 2.50 ppm  $^1\text{H}$  NMR, 39.52 ppm  $^{13}\text{C}$  NMR; MeOH at 3.31 ppm  $^1\text{H}$  NMR, 49.00 ppm  $^{13}\text{C}$  NMR) or tetramethylsilane as reference.  $^{19}\text{F}$  NMR spectra were reported as chemical shifts in parts per million (ppm) using  $\text{CFCl}_3$  (0 ppm) in  $\text{CDCl}_3$  as reference. Coupling constants were reported in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on Bruker microTof by using EI method.

## 2. The Synthesis of Substrates

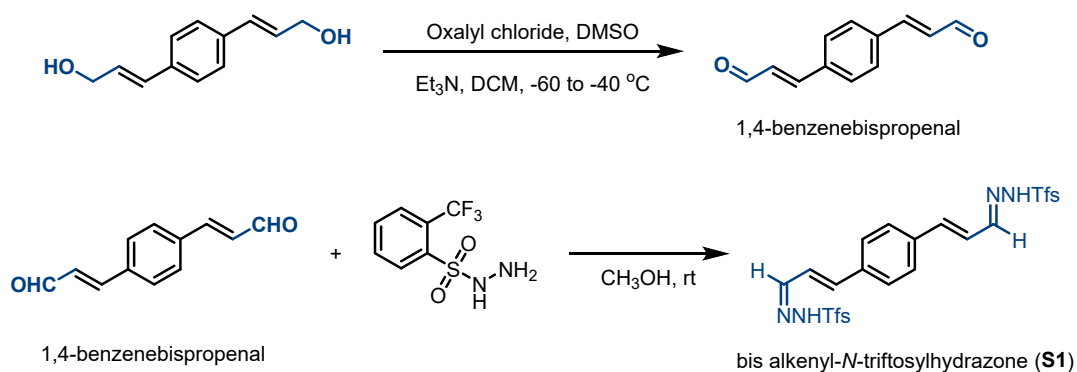
### 2.1 General Procedures for Synthesis of Alkenyl-*N*-Triftosylhydrazones



Scheme S1. Synthesis of alkenyl-*N*-triftosylhydrazones.

Alkenyl-*N*-triftosylhydrazones were prepared according to literature procedure.<sup>1</sup> To a stirred solution of ArSO<sub>2</sub>NHNH<sub>2</sub> (2.0 mmol, 1.0 equiv) in methanol (2 mL) were added carbonyl compounds (2.2 mmol, 1.1 equiv) and the mixture was stirred for 1-2 h at room temperature. If the hydrazone precipitated, the mixture was filtered and the resulting solid was washed with ice cold diethyl ether and dried under reduced pressure to give pure alkenyl *N*-Sulfonylhydrazones. If not, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to obtain the *N*-Sulfonylhydrazone. The yields were around 80% in general.

### 2.2 Preparation of bis-Alkenyl-*N*-Triftosylhydrazone (S1)



Scheme S2. Preparation of bis-alkenyl-*N*-triftosylhydrazone (S1).

**1,4-Benzenebispropenal** was prepared according to literature procedure.<sup>2</sup> To a cooled solution of oxalyl chloride (1.17 mL, 1.75 g, 13.8 mmol, 2.3 equiv) in 13.0 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added a solution of DMSO (2.00 mL, 2.16 g, 27.6 mmol, 4.6 equiv) in 5.2 mL of CH<sub>2</sub>Cl<sub>2</sub> with stirring under Ar at -60 °C. The reaction mixture was stirred for 30 min, then a solution of 1,4-benzenebis-2-propenol (1.14 g, 6.0 mmol, 1.0 equiv) dissolved in 13.0 mL of CH<sub>2</sub>Cl<sub>2</sub> and 2.6 mL of DMSO was added at -40 °C within 45 min; stirring was continued for an additional 1 h. Subsequently triethylamine (11 mL, 7.60 g, 75.0 mmol, 12.5 equiv) was added, and the reaction mixture was stirred for 5 min and then allowed to warm to room temp. Then 80 mL of water was added, and the aqueous layer was reextracted with additional CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed successively with dilute HCl, water, satd. aqueous NaHCO<sub>3</sub> solution, water, and sat. aqueous NaCl solution, then dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to yield (2*E*,2'*E*)-3,3'-(1,4-phenylene)diacrylaldehyde (1.00 g, 90% yield) as a yellow solid.

**bis-Alkenyl-*N*-triftosylhydrazone (S1)** was prepared according to the following procedure: To a

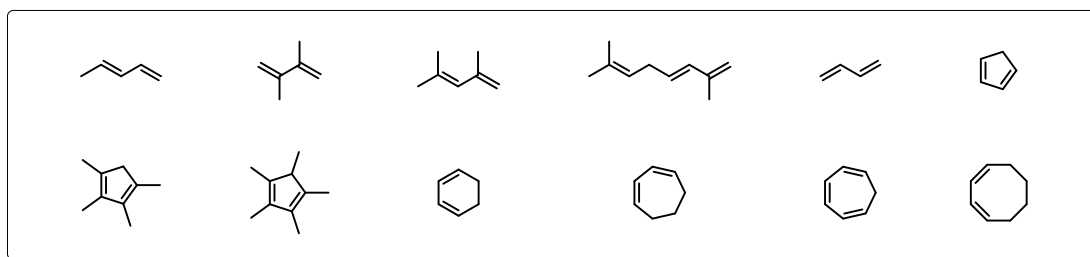
stirred solution of TfsNHNH<sub>2</sub> (1.2 g, 5.0 mmol, 2.0 equiv) in methanol (40 mL) were added (*2E,2'E*)-3,3'-(1,4-phenylene)diacrylaldehyde (0.5 g, 2.5 mmol, 1.0 equiv) and the mixture was stirred for 5 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent/EtOAc) to yield *bis*-alkenyl *N*-trifosylhydrazone (S1) (5.1 g, 81% yield) as a yellow solid.

*Spectral data were in good agreement with literature values.*<sup>3</sup>

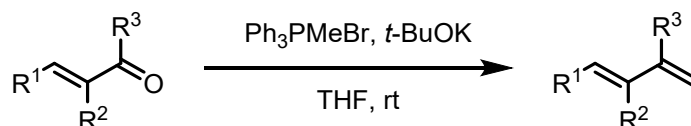
### 2.3 List and Preparation of 1,3-Butadienes

The following 1, 3-butadienes substrates were employed as received from commercial sources.

(1,3-Cyclopentadiene was obtained by cracking and distillation of its commercial dimer, and used immediately afterwards. 1,3-Butadiene was purchased from Macklin (B871825-25ml) as a 15% solution in hexane, and used as received.)



The other 1, 3-butadienes substrates were prepared according to reported procedures.<sup>4,5</sup>



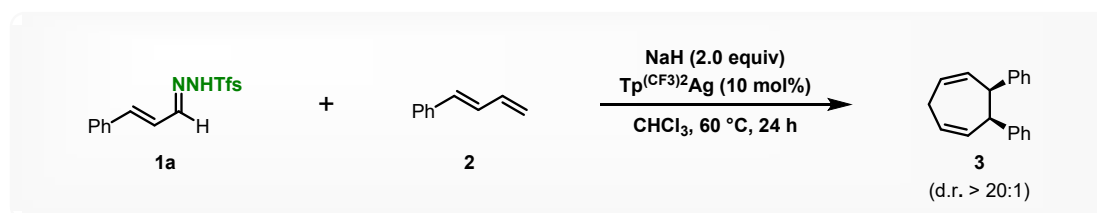
**Scheme S3.** Preparation of 1, 3-butadienes.

Methyltriphenylphosphonium bromide (1.5 equiv) and potassium *tert*-butoxide (1.5 equiv) were combined in dry THF (0.33 M relative to aldehyde or ketone) under argon atmosphere. The bright yellow solution was stirred at room temperature for 0.5-1 h, upon which the aldehyde or ketone (1.0 equiv) was added. The reaction was stirred at room temperature until consumption of the aldehyde (generally within 2-3 h). The reaction was quenched with a saturated solution of NH<sub>4</sub>Cl (1 mL/mmol) and 75% of THF was removed in vacuo. The mixture was poured into a separatory funnel and diluted with saturated sodium chloride solution and extracted with ether 3 times. Then the organic layer was collected and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to obtain the 1, 3-butadienes.

### 3. Experimental Procedures and Characterization Data

#### 3.1 Optimization of the Reaction Conditions

We found that the reaction of **1** with **2** in the presence of  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$  at 60 °C gave desired product **3** in excellent yield, as a single diastereoisomer (entry 1, Table S1). Replacing  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$  with  $\text{Tp}^{\text{Br}_3}\text{Ag}$  gave a comparable yield (entry 2). In contrast, other tested catalysts like  $\text{AgOTf}$ ,  $\text{Rh}_2(\text{S-DOSP})_4$  or  $\text{Rh}_2\text{TFA}_4$ , gave only small or trace amounts of product **3** (entries 3-5). The less polar solvent, such as DCM and  $\text{PhCF}_3$ , is also suitable for this reaction (entries 6 and 7), whereas 1,4-dioxane was ineffective for the reactions (entry 8). Increasing the reaction temperature decreased the yield of **3** slightly, while the yields diminished dramatically at low temperature (entries 9-11).

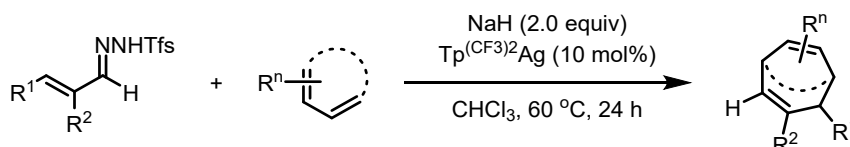


**Table 1.** Optimization of the Reaction Conditions<sup>a</sup>

entry	deviation from standard conditions	yield <sup>b</sup> (%)
1	none	99 (98)
2	$\text{Tp}^{\text{Br}_3}\text{Ag}$ instead of $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$	90
3	$\text{AgOTf}$ instead of $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$	13
4	$\text{Rh}_2(\text{S-DOSP})_4$ (1 mol%) instead of $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$	25
5	$\text{Rh}_2\text{TFA}_4$ (5 mol) instead of $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$	trace
6	DCM instead of $\text{CHCl}_3$	72
7	$\text{PhCF}_3$ instead of $\text{CHCl}_3$	95
8	1,4-dioxane instead of $\text{CHCl}_3$	8
9	80 °C instead of 60 °C	94
10	40 °C instead of 60 °C	73
11	25 °C instead of 60 °C	26

<sup>a</sup>Standard conditions: *N*-Trifosylhydrazone **1a** (0.3 mmol), NaH (0.6 mmol),  $\text{CHCl}_3$  (3.0 mL),  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$  (10 mol%) and **2** (0.6 mmol) were stirred at 60 °C for 24 h under argon atmosphere. <sup>b</sup>Yield calculated by <sup>1</sup>H NMR with  $\text{CH}_2\text{Br}_2$  as internal standard and isolated yield was given in bracket.

#### 3.2 General Procedures for 1,4-Cycloheptadienes

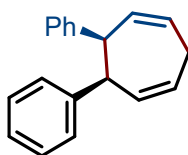


**Scheme S4.** General Procedure A for 1,4-Cycloheptadienes.

**General procedure A:** To an oven-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar were added alkenyl *N*-trifosylhydrazone (0.3 mmol, 1.0 equiv), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry  $\text{CHCl}_3$  (6.0 mL) inside a glove box with nitrogen atmosphere. Then,  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}$  (34.0 mg, 10 mol%) and 1, 3-dienes (0.6 mmol, 2.0 equiv) were

added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 24 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain the 1, 4-cycloheptadienes product.

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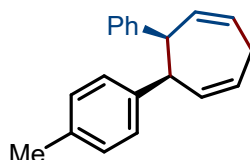
3

### *cis*-6,7-Diphenylcyclohepta-1,4-diene (3)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-buta-1,3-dien-1-ylbenzene (78.2 mg, 0.6 mmol) derived from cinnamaldehyde afforded **3** (72.5 mg, 98% yield) as a colourless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18-7.15 (m, 6H), 6.88-6.85 (m, 4H), 5.95-5.90 (m, 2H), 5.77 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 2H), 4.09 (s, 2H), 3.41-3.33 (m, 1H), 2.81 (dt, *J* = 19.5, 8.0 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.5, 133.2, 129.6, 128.1, 127.4, 126.3, 50.2, 28.0. HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>17</sub> [M-H]<sup>-</sup> 245.1330, found 245.1335.

*Spectral data were in good agreement with literature values.*<sup>6</sup>

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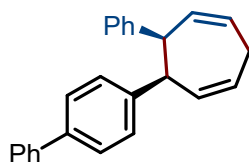


4

### *cis*-6-Phenyl-7-(*p*-tolyl)cyclohepta-1,4-diene (4)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (86.5 mg, 0.6 mmol) derived from 4-methylcinnamaldehyde afforded **4** (75.8 mg, 97% yield) as a colourless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18-7.15 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.90-6.88 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.92-5.88 (m, 2H), 5.79-5.73 (m, 2H), 4.06 (s, 2H), 3.41-3.33 (m, 1H), 2.80 (dt, *J* = 20.0, 7.5 Hz, 1H), 2.31 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.7, 138.5, 135.7, 133.5, 133.2, 129.7, 129.5, 128.1, 128.0, 127.8, 127.4, 126.2, 50.2, 49.8, 28.0, 21.0. HRMS (EI) *m/z* calcd. for C<sub>20</sub>H<sub>19</sub> [M-H]<sup>-</sup> 259.1487, found 259.1492.

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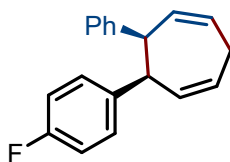


5

***cis*-4-(7-Phenylcyclohepta-2,5-dien-1-yl)-1,1'-biphenyl (5)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-4-(buta-1,3-dien-1-yl)-1,1'-biphenyl (123.8 mg, 0.6 mmol) derived from 4-phenylcinnamaldehyde afforded **5** (95.0 mg, 98% yield) as a white solid (mp: 107-108 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.47-7.43 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.22-7.20 (m, 3H), 6.97-6.93 (m, 4H), 6.00-5.93 (m, 2H), 5.85-5.81 (m, 2H), 4.15 (s, 2H), 3.46-3.36 (m, 1H), 2.85 (dt, *J* = 19.5, 7.5 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.3, 143.4, 141.2, 137.2, 137.2, 135.1, 132.9, 131.2, 129.7, 128.7, 127.7, 126.5, 117.6, 50.2, 49.8, 27.0. HRMS (EI) *m/z* calcd. for C<sub>25</sub>H<sub>21</sub> [M-H]<sup>-</sup> 321.1643, found 321.1648.

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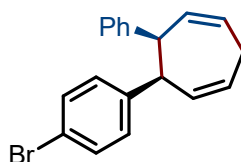


6

***cis*-6-(4-Fluorophenyl)-7-phenylcyclohepta-1,4-diene (6)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (89.0 mg, 0.6 mmol) derived from 4-fluorocinnamaldehyde afforded **6** (68.2 mg, 86% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.20-7.16 (m, 3H), 6.86-6.77 (m, 6H), 5.96-5.87 (m, 2H), 5.77-5.71 (m, 2H), 4.10 (s, 1H), 4.01 (s, 1H), 3.39-3.31 (m, 1H), 2.80 (dt, *J* = 20.0, 7.5 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.6 (d, *J* = 244.0 Hz), 141.5, 137.0, 133.0, 132.9, 131.1 (d, *J* = 7.8 Hz), 129.5, 128.3, 128.1, 127.5, 126.4, 114.1 (d, *J* = 21.0 Hz), 50.0, 49.7, 27.9. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ (-116.98)-(-117.04) (m). HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>16</sub>F [M-H]<sup>-</sup> 263.1236, found 263.1241.

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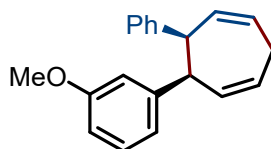
7

***cis*-6-(4-Bromophenyl)-7-phenylcyclohepta-1,4-diene (7)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (125.4 mg, 0.6 mmol) derived from 4-bromocinnamaldehyde afforded **7** (84.9 mg, 87% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.27-7.17 (m, 3H), 6.90-6.86 (m, 2H), 6.72 (d, *J* = 8.0

Hz, 2H), 5.96-5.88 (m, 2H), 5.76 (ddd,  $J = 11.0, 6.0, 3.0$  Hz, 1H), 5.70 (ddd,  $J = 11.0, 6.0, 3.0$  Hz, 1H), 4.11 (s, 1H), 3.99 (s, 1H), 3.39-3.31 (m, 1H), 2.81 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 140.3, 132.8, 132.5, 131.4, 130.4, 129.5, 128.3, 127.6, 126.5, 120.3, 49.84, 49.80, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{16}\text{Br}$   $[\text{M}-\text{H}]^-$  323.0435, found 323.0440.

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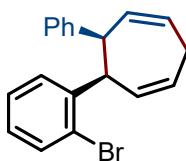


8

#### *cis*-6-(3-Methoxyphenyl)-7-phenylcyclohepta-1,4-diene (8)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (96.1 mg, 0.6 mmol) derived from 3-methoxycinnamaldehyde afforded **8** (81.3 mg, 98% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19-7.15 (m, 3H), 7.08 (t,  $J = 8.0$  Hz, 1H), 6.92-6.87 (m, 2H), 6.73 (dd,  $J = 8.0, 2.0$  Hz, 1H), 6.48 (d,  $J = 7.5$  Hz, 1H), 6.37 (s, 1H), 5.94-5.89 (m, 2H), 5.80-5.73 (m, 2H), 4.07 (s, 2H), 3.64 (s, 3H), 3.39-3.33 (m, 1H), 2.80 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 143.2, 141.6, 133.1, 129.7, 128.3, 128.2, 128.0, 127.9, 127.4, 126.3, 122.1, 114.9, 112.2, 55.0, 50.21, 50.19, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{19}\text{O}$   $[\text{M}-\text{H}]^-$  275.1436, found 275.1441.

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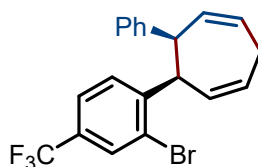
9

#### *cis*-6-(2-Bromophenyl)-7-phenylcyclohepta-1,4-diene (9)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-bromo-2-(buta-1,3-dien-1-yl)benzene (125.5 mg, 0.6 mmol) derived from 2-bromocinnamaldehyde afforded **9** (94.3 mg, 97% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.50 (m, 1H), 7.18-7.16 (m, 1H), 7.11 (t,  $J = 7.0$  Hz, 2H), 7.05-7.00 (m, 2H), 6.81 (d,  $J = 7.0$  Hz, 2H), 6.69 (d,  $J = 6.0$  Hz, 1H), 5.98-5.92 (m, 1H), 5.92-5.87 (m, 1H), 5.78 (ddd,  $J = 11.0, 5.5, 2.5$  Hz, 1H), 5.68 (ddd,  $J = 10.5, 6.0, 3.0$  Hz, 1H), 4.90-4.85 (m, 1H), 3.90-3.86 (m, 1H), 3.43-3.35 (m, 1H), 2.81 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 140.4, 133.0, 132.5, 132.3, 130.9, 130.2, 129.3, 127.8, 127.4, 127.3, 126.49, 126.45, 125.4, 48.9, 47.3, 28.1. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{16}\text{Br}$   $[\text{M}-\text{H}]^-$  323.0435, found 323.0440.

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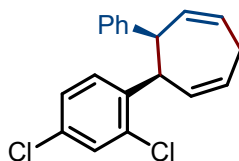


10

***cis*-6-(2-Bromo-4-(trifluoromethyl)phenyl)-7-phenylcyclohepta-1,4-diene (10)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazones (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-bromo-2-(buta-1,3-dien-1-yl)benzene (166.3 mg, 0.6 mmol) derived from (*E*)-3-(2-bromo-4-(trifluoromethyl)phenyl)acrylaldehyde afforded **10** (115.6 mg, 98% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.20-7.17 (m, 1H), 7.15-7.12 (m, 2H), 6.87 (s, 1H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.02-5.99 (m, 1H), 5.95-5.91 (m, 1H), 5.79 (ddd, *J* = 11.5, 6.0, 2.5 Hz, 1H), 5.62 (ddd, *J* = 11.0, 5.5, 2.5 Hz, 1H), 4.94-4.90 (m, 1H), 3.87-3.81 (m, 1H), 3.44-3.35 (m, 1H), 2.86 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 142.4, 139.7, 132.9, 132.4, 131.4, 130.1, 129.9, 129.0, 128.8 (q, *J* = 32.0 Hz) 127.8 (q, *J* = 3.0 Hz), 127.7, 127.6, 126.9, 124.3 (q, *J* = 3.5 Hz), 123.6 (q, *J* = 272.0 Hz), 48.8, 47.4, 28.1. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.67. **HRMS** (EI) *m/z* calcd. for C<sub>20</sub>H<sub>15</sub>BrF<sub>3</sub> [M-H]<sup>-</sup> 391.0309, found 391.0314.

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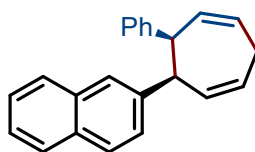


11

***cis*-6-(2,4-Dichlorophenyl)-7-phenylcyclohepta-1,4-diene (11)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazones (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-2,4-dichlorobenzene (119.4 mg, 0.6 mmol) derived from (*E*)-3-(2,4-dichlorophenyl)acrylaldehyde afforded **11** (81.3 mg, 86% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 2.0 Hz, 1H), 7.18-7.12 (m, 3H), 7.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.83 (d, *J* = 6.5 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.98-5.94 (m, 1H), 5.92-5.88 (m, 1H), 5.77 (ddd, *J* = 11.5, 6.0, 3.0 Hz, 1H), 5.61 (ddd, *J* = 10.5, 5.5, 3.0 Hz, 1H), 4.80 (s, 1H), 3.90 (s, 1H), 3.41-3.34 (m, 1H), 2.82 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 140.4, 138.1, 134.9, 132.8, 132.4, 131.74, 131.65, 129.9, 129.5, 128.7, 127.7, 127.5, 126.6, 126.1, 48.6, 44.2, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub> [M-H]<sup>-</sup> 313.0551, found 313.0556.

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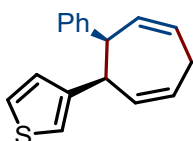


12

***cis*-2-(7-Phenylcyclohepta-2,5-dien-1-yl)naphthalene (12)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-2-(buta-1,3-dien-1-yl)naphthalene (108.2 mg, 0.6 mmol) derived from (*E*)-3-(naphthalen-2-yl)acrylaldehyde afforded **12** (87.1 mg, 86% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.77-7.75 (m, 1H), 7.65-7.64 (m, 1H), 7.61 (d, *J* = 10.2 Hz, 1H), 7.40-7.38 (m, 2H), 7.29 (d, *J* = 1.5 Hz, 1H), 7.18-7.14 (m, 1H), 7.13-7.10 (m, 2H), 6.98 (dd, *J* = 10.2, 1.8 Hz, 1H), 6.85-6.83 (m, 2H), 5.97-5.92 (m, 2H), 5.83 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 1H), 5.78 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 1H), 4.24 (s, 1H), 4.16 (s, 1H), 3.43-3.35 (m, 1H), 2.83 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.4, 139.1, 133.2, 133.1, 133.0, 132.3, 129.7, 128.3, 128.2, 127.8, 127.4, 126.7, 126.4, 125.6, 125.3, 50.3, 50.2, 28.0. **HRMS** (EI) *m/z* calcd. for C<sub>23</sub>H<sub>19</sub> [M-H]<sup>-</sup> 295.1487, found 295.1492.

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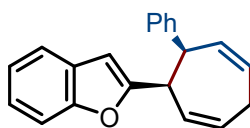


**13**

***cis*-3-(7-Phenylcyclohepta-2,5-dien-1-yl)thiophene (13)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-3-(buta-1,3-dien-1-yl)thiophene (81.7 mg, 0.6 mmol) derived from (*E*)-3-(thiophen-3-yl)acrylaldehyde afforded **13** (42.4 mg, 56% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.21-7.19 (m, 3H), 7.18-7.16 (dd, *J* = 5.4, 3.0 Hz, 1H), 6.95-6.93 (m, 2H), 6.72 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.70-6.69 (m, 1H), 5.95-5.89 (m, 2H), 5.51 (ddd, *J* = 10.8, 5.4, 2.4 Hz, 1H), 5.76 (ddd, *J* = 10.8, 6.0, 3.0 Hz, 1H), 4.27 (s, 1H), 4.08 (s, 1H), 3.39-3.32 (m, 1H), 2.81 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 142.7, 141.7, 133.3, 133.2, 129.4, 128.9, 128.0, 127.4, 126.3, 124.1, 122.0, 49.8, 45.4, 28.0. **HRMS** (EI) *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>S [M-H]<sup>-</sup> 251.0894, found 251.0900.

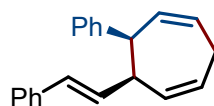
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**14**

***cis*-2-(7-Phenylcyclohepta-2,5-dien-1-yl)benzofuran (14)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-2-(buta-1,3-dien-1-yl)benzofuran (102.1 mg, 0.6 mmol) derived from benzofuran-2-carbaldehyde<sup>7</sup> afforded **14** (54.1 mg, 63% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.47-7.45 (m, 2H), 7.27-7.23 (m, 1H), 7.21-7.18 (m, 1H), 7.16-7.11 (m, 3H), 6.98-6.96 (m, 2H), 6.25 (s, 1H), 6.06-6.03 (m, 1H), 5.93-5.89 (m, 1H), 5.85 (ddd, *J* = 12.0, 6.0, 3.0 Hz, 1H), 5.75-5.71 (m, 1H), 4.65-4.60 (m, 1H), 4.29-4.25 (m, 1H), 3.37-3.32 (m, 1H), 2.84 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 159.1, 154.4, 140.2, 132.3, 130.4, 129.8, 129.5, 128.7, 127.4, 127.3, 126.5, 123.4, 122.4, 120.5, 110.8, 103.5, 47.4, 43.1, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>O [M-H]<sup>-</sup> 285.1279, found 285.1284.

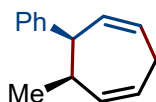


15

***cis*-6-Phenyl-7-((*E*)-styryl)cyclohepta-1,4-diene (15)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (93.7 mg, 0.6 mmol) derived from (2*E*,4*E*)-5-phenylpenta-2,4-dienal afforded **15** (67.8 mg, 83% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.33-7.28 (m, 8H), 7.25-7.20 (m, 2H), 6.31 (d, *J* = 15.5 Hz, 1H), 6.20 (dd, *J* = 15.5, 8.0 Hz, 1H), 5.88-5.82 (m, 3H), 5.62-5.58 (m, 1H), 4.03-3.97 (m, 1H), 3.66-3.59 (m, 1H), 3.30-3.25 (m, 1H), 2.84-2.76 (m, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 142.3, 137.7, 133.0, 132.9, 131.1, 130.8, 129.3, 128.4, 128.1, 127.8, 127.7, 127.0, 126.3, 126.2, 49.4, 47.5, 28.6. **HRMS** (EI) *m/z* calcd. for C<sub>21</sub>H<sub>19</sub> [M-H]<sup>-</sup> 271.1487, found 271.1492.

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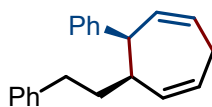


16

***cis*-6-Methyl-7-phenylcyclohepta-1,4-diene (16)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-penta-1,3-diene (40.9 mg, 0.6 mmol) afforded **16** (40.4 mg, 73% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.29-7.26 (m, 4H), 7.24-7.20 (m, 1H), 5.80-5.73 (m, 3H), 5.35-5.32 (m, 1H), 3.67-3.63 (m, 1H), 3.25-3.16 (m, 1H), 3.12-3.04 (m, 1H), 2.73-2.66 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.9, 136.5, 132.9, 129.7, 127.9, 127.6, 127.1, 126.2, 49.4, 36.8, 28.3, 18.5. **HRMS** (EI) *m/z* calcd. for C<sub>14</sub>H<sub>15</sub> [M-H]<sup>-</sup> 183.1174, found 183.1179.

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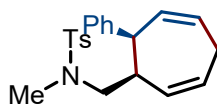
17

***cis*-6-Phenethyl-7-phenylcyclohepta-1,4-diene (17)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-hexa-3,5-dien-1-ylbenzene (94.9 mg, 0.6 mmol) derived from (*E*)-5-phenylpent-2-enal<sup>4</sup> afforded **17** (58.5 mg, 71% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.27-7.22 (m, 6H), 7.21-7.15 (m, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 5.96-5.90 (m, 1H), 5.75-5.69 (m, 1H), 5.66 (ddd, *J* = 11.5, 5.0, 3.0 Hz, 1H), 5.40-5.33 (m, 1H), 3.60-3.54 (m, 1H), 3.22-3.13 (m, 1H), 3.08-3.01 (m, 1H), 2.72-2.62 (m, 2H), 2.56 (ddd, *J* = 14.0, 10.0, 7.0 Hz, 1H), 1.70-1.61 (m, 1H), 1.56-1.48 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 142.4, 141.3, 135.2, 133.0, 129.9, 129.7, 128.4, 128.3, 127.5,

126.4, 126.3, 125.7, 48.4, 41.0, 35.7, 34.0, 27.9. **HRMS** (EI)  $m/z$  calcd. for  $C_{21}H_{21}$   $[M-H]^-$  273.1643, found 273.1648.

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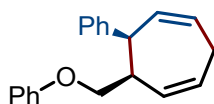


**18**

***cis*-N,4-Dimethyl-N-((7-phenylcyclohepta-2,5-dien-1-yl)methyl)benzenesulfonamide (18)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-*N*,4-dimethyl-*N*-(penta-2,4-dien-1-yl)benzenesulfonamide (150.8 mg, 0.6 mmol) derived from penta-1,4-dien-3-ol and *N*,4-dimethylbenzenesulfonamide<sup>8</sup> afforded **18** (73.9 mg, 67% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ )  $\delta$  7.57 (d,  $J = 8.5$  Hz, 2H), 7.31-7.27 (m, 6H), 7.25-7.22 (m, 1H), 5.94-5.90 (m, 1H), 5.77-5.69 (m, 2H), 5.38-5.35 (m, 1H), 3.68-3.65 (m, 1H), 3.35-3.30 (m, 1H), 3.21-3.15 (m, 1H), 2.89 (dd,  $J = 12.5, 6.5$  Hz, 1H), 2.80-2.73 (m, 2H), 2.67 (s, 3H), 2.42 (s, 3H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ )  $\delta$  143.3, 140.1, 133.7, 132.3, 131.9, 130.2, 130.0, 129.6, 127.8, 127.5, 126.8, 126.7, 53.3, 45.5, 39.7, 35.3, 28.2, 21.5. **HRMS** (EI)  $m/z$  calcd. for  $C_{22}H_{26}NO_2S$   $[M+H]^+$  368.1684, found 368.1678.

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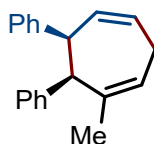


**19**

***cis*-6-(Phenoxymethyl)-7-phenylcyclohepta-1,4-diene (19)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-(penta-2,4-dien-1-yloxy)benzene (96.1 mg, 0.6 mmol) derived from penta-1,4-dien-3-ol and phenol<sup>9</sup> afforded **19** (60.5 mg, 73% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ )  $\delta$  7.35-7.25 (m, 7H), 7.01 (t,  $J = 7.5$  Hz, 1H), 6.96-6.94 (m, 2H), 6.07-6.02 (m, 1H), 5.87-5.80 (m, 2H), 5.31-5.27 (m, 1H), 4.05-4.02 (m, 1H), 3.85-3.78 (m, 2H), 3.69-3.66 (m, 1H), 3.35-3.31 (m, 1H), 2.85-2.78 (m, 1H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ )  $\delta$  158.8, 140.2, 132.5, 130.8, 130.5, 130.1, 129.4, 127.7, 126.6, 126.5, 120.7, 114.6, 68.9, 44.2, 41.1, 28.3. **HRMS** (EI)  $m/z$  calcd. for  $C_{20}H_{21}O$   $[M+H]^+$  277.1592, found 277.1586.

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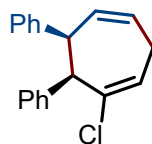
**20**

***cis*-1-Methyl-6,7-diphenylcyclohepta-1,4-diene (20)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (86.5 mg, 0.6 mmol) derived from  $\alpha$ -methylcinnamylaldehyde afforded **20** (63.3 mg, 81% yield) as a colorless oil. **<sup>1</sup>H NMR**

(500 MHz, CDCl<sub>3</sub>)  $\delta$  7.21-7.10 (m, 6H), 6.85-6.82 (m, 4H), 5.97-5.93 (m, 1H), 5.78-5.74 (m, 1H), 5.64-5.60 (m, 1H), 4.45-4.41 (m, 1H), 3.37-3.32 (m, 1H), 3.32-3.25 (m, 1H), 2.80 (dt,  $J$  = 20.0, 7.5 Hz, 1H), 1.52 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  143.3, 139.8, 138.6, 132.9, 130.7, 128.9, 128.7, 127.8, 127.0, 126.3, 126.1, 121.7, 56.5, 48.4, 27.9, 26.3. HRMS (EI)  $m/z$  calcd. for C<sub>20</sub>H<sub>19</sub> [M-H]<sup>-</sup> 259.1487, found 259.1492.

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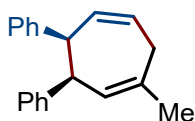


**21**

#### *cis*-1-Chloro-6,7-diphenylcyclohepta-1,4-diene (**21**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*Z*)-(2-chlorobuta-1,3-dien-1-yl)benzene (98.8 mg, 0.6 mmol) derived from  $\alpha$ -chlorocinnamaldehyde afforded **21** (62.3 mg, 74% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25-7.16 (m, 6H), 6.86-6.84 (m, 4H), 6.15 (dd,  $J$  = 8.0, 2.5 Hz, 1H), 6.02-5.98 (m, 1H), 5.86-5.82 (m, 1H), 4.46-4.44 (m, 1H), 3.76 (t,  $J$  = 3.5 Hz, 1H), 3.35-3.30 (m, 1H), 2.89 (dt,  $J$  = 20.0, 8.0 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 137.4, 136.3, 133.1, 130.4, 128.6, 128.5, 128.0, 127.2, 127.1, 126.7, 125.4, 59.1, 48.2, 27.3. HRMS (EI)  $m/z$  calcd. for C<sub>19</sub>H<sub>16</sub>Cl [M-H]<sup>-</sup> 279.0941, found 279.0946.

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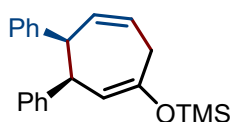


**22**

#### *cis*-2-Methyl-6,7-diphenylcyclohepta-1,4-diene (**22**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-(3-methylbuta-1,3-dien-1-yl)benzene (86.5 mg, 0.6 mmol) derived from (*E*)-4-phenylbut-3-en-2-one afforded **22** (75.8 mg, 97% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.18-7.13 (m, 6H), 6.85-6.82 (m, 4H), 5.91-5.86 (m, 1H), 5.71 (ddd,  $J$  = 11.5, 6.0, 3.0 Hz, 1H), 5.54-5.50 (m, 1H), 4.21 (s, 1H), 3.82 (s, 1H), 3.51-3.43 (m, 1H), 2.56 (dd,  $J$  = 19.0, 8.0 Hz, 1H), 1.87 (d,  $J$  = 0.5 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 142.5, 133.2, 130.0, 129.2, 127.5, 127.2, 126.9, 126.5, 126.3, 126.1, 50.7, 49.2, 32.8, 26.2. HRMS (EI)  $m/z$  calcd. for C<sub>20</sub>H<sub>19</sub> [M-H]<sup>-</sup> 259.1487, found 259.1492.

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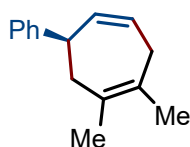


**23**

#### *cis*-((3,4-Diphenylcyclohepta-1,5-dien-1-yl)oxy)trimethylsilane (**23**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol)

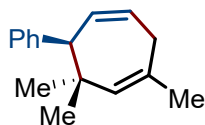
derived from cinnamaldehyde and (*E*)-trimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane (131.0 mg, 0.6 mmol) derived from (*E*)-4-phenylbut-3-en-2-one<sup>10</sup> afforded **23** (93.4 mg, 98% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.22-7.16 (m, 6H), 6.87-6.83 (m, 4H), 5.91-5.87 (m, 1H), 5.78 (ddd, *J* = 11.0, 5.5, 3.0 Hz, 1H), 5.02 (d, *J* = 6.0 Hz, 1H), 4.11 (s, 1H), 3.89 (s, 1H), 3.67-3.63 (m, 1H), 2.72 (dd, *J* = 19.5, 8.0 Hz, 1H), 0.25 (s, 9H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 156.8, 144.4, 140.1, 130.3, 129.8, 128.0, 127.8, 127.4, 126.5, 126.2, 122.8, 106.2, 43.1, 37.6, 34.3, 0.34. HRMS (EI) *m/z* calcd. for C<sub>22</sub>H<sub>27</sub>OSi [M+H]<sup>+</sup> 335.1831, found 335.1825.



**24**

#### *cis*-1,2-Dimethyl-6-phenylcyclohepta-1,4-diene (**24**)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and 2,3-dimethylbuta-1,3-diene (49.3 mg, 0.6 mmol) afforded **24** (30.9 mg, 52% yield) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30-7.27 (m, 2H), 7.24-7.20 (m, 2H), 7.21-7.17 (m, 1H), 5.84-5.79 (m, 1H), 5.56-5.51 (m, 1H), 3.54-3.49 (m, 1H), 3.01-2.97 (m, 1H), 2.71 (dd, *J* = 18.0, 6.6 Hz, 1H), 2.63 (dd, *J* = 13.2, 9.6 Hz, 1H), 2.42 (dd, *J* = 13.8, 3.0 Hz, 1H), 1.73 (s, 3H), 1.51-1.49 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 146.0, 132.9, 131.9, 129.0, 128.2, 127.8, 127.4, 126.0, 43.3, 41.5, 33.7, 20.9, 20.2. HRMS (EI) *m/z* calcd. for C<sub>15</sub>H<sub>19</sub> [M+H]<sup>+</sup> 199.1481, found 199.1482.



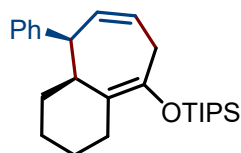
**25**  
major



**25'**  
minor

#### 2,7,7-Trimethyl-6-phenylcyclohepta-1,4-diene (**25** and **25'**)

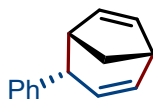
Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and 2,4-dimethylpenta-1,3-diene (57.7 mg, 0.6 mmol) afforded an inseparable mixture of **25** and **25'** (57.3 mg, 90% yield, **25** and **25'** = 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36-7.31 (m, 2H, minor), 7.30-7.27 (m, 1H, major), 7.27-7.21 (m, 3H, major, 2H, minor), 7.21-7.14 (m, 1H, major, 1H, minor), 6.50 (d, *J* = 15.5 Hz, 1H, minor), 6.03 (dd, *J* = 15.5, 9.0 Hz, 1H, minor), 5.80 (ddd, *J* = 11.0, 6.0, 2.0 Hz, 1H, major), 5.73-5.67 (m, 1H, major), 5.37-5.34 (m, 1H, minor), 5.18-5.13 (m, 1H, major), 3.49 (d, *J* = 6.0 Hz, 1H, major), 3.16-3.08 (m, 1H, major), 2.66 (dd, *J* = 21.0, 6.0 Hz, 1H, major), 1.74 (s, 3H, major), 1.72 (s, 3H, minor), 1.66 (s, 3H, minor), 1.62-1.57 (m, 1H, minor), 1.17 (s, 3H, minor), 1.02 (s, 3H, major), 0.97 (dd, *J* = 8.5, 4.5 Hz, 1H, minor), 0.93 (s, 3H, major), 0.64 (t, *J* = 5.0 Hz, 1H, minor). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.3, 138.0, 135.1, 135.0, 133.2, 132.3, 131.2, 130.4, 130.0, 129.7, 128.5, 127.5, 126.6, 126.5, 126.1, 125.7, 55.2, 38.1, 34.3, 30.3, 29.2, 27.5, 27.4, 25.2, 23.1, 22.7, 20.1, 18.8. HRMS (EI) *m/z* calcd. for C<sub>16</sub>H<sub>21</sub> [M+H]<sup>+</sup> 213.1643, found 213.1637.



**26**

***trans*-Triisopropyl((-9-phenyl-2,3,4,6,9,9a-hexahydro-1*H*-benzo[7]annulen-5-yl)oxy)silane (26)**

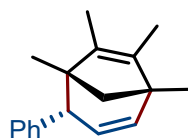
Prepared according to **General procedure A** using alkenyl *N*-triflylsilane (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and ((1-(cyclohex-1-en-1-yl)alkenyl)oxy)triisopropylsilane (168.3 mg, 0.6 mmol) derived from 1-(cyclohex-1-en-1-yl)ethan-1-one<sup>11</sup> afforded **26** (103.5 mg, 87% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.31-7.26 (m, 4H), 7.23-7.17 (m, 1H), 6.04-5.94 (m, 1H), 5.94-5.86 (m, 1H), 4.06-3.87 (m, 1H), 3.65-3.56 (m, 1H), 2.55 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.52-2.45 (m, 1H), 1.84-1.70 (m, 1H), 1.63-1.55 (m, 1H), 1.55-1.42 (m, 2H), 1.40-1.30 (m, 1H), 1.28-1.15 (m, 6H), 1.14 (d, *J* = 6.0 Hz, 18H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 142.9, 141.2, 133.5, 128.9, 128.0, 126.6, 126.1, 120.0, 47.2, 45.6, 33.4, 28.2, 27.7, 26.3, 25.7, 18.2, 13.4. **HRMS** (EI) *m/z* calcd. for C<sub>26</sub>H<sub>41</sub>OSi [M+H]<sup>+</sup> 397.2927, found 397.2921.



**27**

**(±)-(1*S*,4*R*,5*R*)-4-Phenylbicyclo[3.2.1]octa-2,6-diene (27)**

Prepared according to **General procedure A** using alkenyl *N*-triflylsilane (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and cyclopenta-1,3-diene (59.6 mg, 0.9 mmol) afforded **27** (51.4 mg, 94% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.29-7.24 (m, 2H), 7.21-7.16 (m, 1H), 7.16-7.11 (m, 2H), 6.35 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.34-6.28 (m, 1H), 5.37 (dt, *J* = 9.5, 2.0 Hz, 1H), 5.22 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.72-3.68 (m, 1H), 3.02-2.98 (m, 1H), 2.69-2.64 (m, 1H), 2.20-2.14 (m, 1H), 2.10 (d, *J* = 9.5 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 141.9, 141.3, 134.6, 129.6, 128.1, 127.8, 127.7, 126.1, 46.7, 44.3, 43.9, 38.4. **HRMS** (EI) *m/z* calcd. for C<sub>14</sub>H<sub>15</sub> [M+H]<sup>+</sup> 183.1174, found 183.1168. *Spectral data were in good agreement with literature values.*<sup>6</sup>



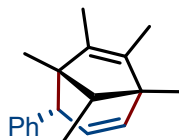
**28**

**(±)-(1*R*,4*S*,5*S*)-1,5,6,7-Tetramethyl-4-phenylbicyclo[3.2.1]octa-2,6-diene (28)**

Prepared according to **General procedure A** using alkenyl *N*-triflylsilane (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and 1,2,3,4-tetramethylcyclopenta-1,3-diene (73.3 mg, 0.6 mmol) afforded **28** (68.7 mg, 96% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.26-7.17 (m, 3H), 7.01-6.96 (m, 2H), 6.13-6.07 (m, 1H), 5.41 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.21 (t, *J* = 2.0 Hz, 1H), 1.83 (d, *J*

= 9.0 Hz, 1H), 1.62-1.60 (m, 4H), 1.13 (s, 3H), 1.12 (s, 3H), 0.84 (d,  $J = 0.5$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 141.7, 139.2, 132.5, 129.6, 128.4, 127.5, 126.2, 58.3, 50.8, 50.0, 45.0, 22.7, 21.4, 11.9, 10.3. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{23} [\text{M}+\text{H}]^+$  239.1800, found 239.1994.

Spectral data were in good agreement with literature values.<sup>6</sup>

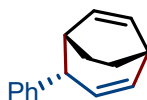


29

(±)-(1S,4S,5S,8R)-1,5,6,7,8-Pentamethyl-4-phenylbicyclo[3.2.1]octa-2,6-diene (29)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (81.7 mg, 0.6 mmol) afforded **29** (68.9 mg, 91% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.18 (m, 3H), 7.05-6.99 (m, 2H), 6.12 (dd,  $J = 9.5, 2.5$  Hz, 1H), 5.40 (dd,  $J = 9.5, 2.5$  Hz, 1H), 3.16 (t,  $J = 2.5$  Hz, 1H), 2.01 (q,  $J = 7.0$  Hz, 1H), 1.62 (d,  $J = 0.5$  Hz, 3H), 1.03 (s, 3H), 0.99 (s, 3H), 0.85 (d,  $J = 0.5$  Hz, 3H), 0.77 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 141.3, 140.3, 129.9, 129.1, 128.0, 127.4, 126.2, 57.1, 53.2, 52.5, 47.6, 18.4, 18.2, 12.3, 11.5, 10.5. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{25} [\text{M}+\text{H}]^+$  253.1956, found 253.1950.

Spectral data were in good agreement with literature values.<sup>6</sup>

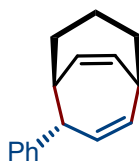


30

(±)-(1S,4R,5R)-4-Phenylbicyclo[3.2.2]nona-2,6-diene (30)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and cyclohexa-1,3-diene (48.1 mg, 0.6 mmol) afforded **30** (55.9 mg, 95% yield) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.23 (m, 2H), 7.21-7.15 (m, 3H), 6.42 (t,  $J = 8.4$  Hz, 1H), 6.16 (ddd,  $J = 10.8, 8.4, 2.4$  Hz, 1H), 5.53 (t,  $J = 8.4$ , 1H), 5.35 (ddd,  $J = 10.8, 3.6, 1.8$  Hz, 1H), 3.53-3.49 (m, 1H), 2.72-2.66 (m, 2H), 2.14-2.08 (m, 1H), 2.06-1.99 (m, 1H), 1.97-1.89 (m, 1H), 1.74-1.67 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 138.3, 133.6, 130.4, 128.9, 128.3, 127.9, 126.1, 51.5, 39.6, 32.7, 30.5, 26.2. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{15} [\text{M}-\text{H}]^-$  195.1174, found 195.1169.

Spectral data were in good agreement with literature values.<sup>6</sup>



31

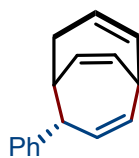
(±)-(1S,4R,5R)-4-Phenylbicyclo[3.3.2]deca-2,9-diene (31)



Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and cyclohepta-1,3-diene (56.5 mg, 0.6 mmol) afforded **31** (60.6 mg, 96% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.27-7.22 (m, 4H), 7.20-7.14 (m, 1H), 6.20 (t, *J* = 9.0 Hz, 1H), 5.87-5.76 (m, 2H), 5.61 (t, *J* = 9.0 Hz, 1H), 3.49-3.44 (m, 1H), 2.85-2.78 (m, 1H), 2.45-2.38 (m, 1H), 2.38-2.27 (m, 1H), 1.94-1.87 (m, 1H), 1.84-1.77 (m, 1H), 1.75-1.64 (m, 1H), 1.64-1.55 (m, 1H), 1.55-1.48 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.3, 139.2, 135.0, 132.4, 128.6, 128.2, 128.0, 126.0, 48.1, 42.7, 36.4, 33.1, 27.9, 23.8. **HRMS** (EI) *m/z* calcd. for C<sub>16</sub>H<sub>17</sub> [M-H]<sup>-</sup> 209.1330, found 209.1335.

*Spectral data were in good agreement with literature values.*<sup>6</sup>

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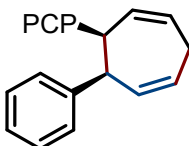


**32**

**(±)-(1*S*,4*R*,5*R*)-4-Phenylbicyclo[3.3.2]deca-2,7,9-triene (32)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and cyclohepta-1,3,5-triene (55.3 mg, 0.6 mmol) afforded **32** (44.4 mg, 71% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.35-7.29 (m, 2H), 7.28-7.24 (m, 2H), 7.24-7.20 (m, 1H), 6.10-6.02 (m, 2H), 5.93-5.81 (m, 4H), 3.53-3.44 (m, 1H), 3.24-3.14 (m, 1H), 2.81-2.75 (m, 1H), 2.07-2.00 (m, 1H), 1.53-1.48 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 143.9, 140.3, 135.4, 128.5, 128.2, 128.1, 126.3, 125.9, 125.1, 123.7, 45.5, 42.9, 35.3, 23.2. **HRMS** (EI) *m/z* calcd. for C<sub>16</sub>H<sub>17</sub> [M+H]<sup>+</sup> 209.1330, found 209.1324.

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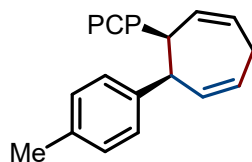


**33**

***cis*-6-(4-Chlorophenyl)-7-phenylcyclohepta-1,4-diene (33)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **33** (82.6 mg, 98% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.22-7.16 (m, 3H), 7.16-7.11 (m, 2H), 6.91-6.85 (m, 2H), 6.80-6.76 (m, 2H), 5.97-5.89 (m, 2H), 5.77 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 1H), 5.71 (ddd, *J* = 11.0, 5.5, 2.5 Hz, 1H), 4.20-4.06 (m, 1H), 4.06-3.85 (m, 1H), 3.41-3.32 (m, 1H), 2.82 (dt, *J* = 19.5, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.3, 139.8, 132.8, 132.6, 132.1, 131.0, 129.5, 128.3, 127.6, 127.5, 126.5, 49.9, 49.8, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>16</sub>Cl [M-H]<sup>-</sup> 279.0941, found 279.0946.

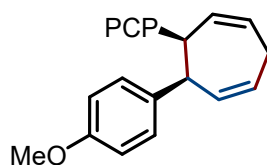
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**34**

***cis*-6-(4-Chlorophenyl)-7-(*p*-tolyl)cyclohepta-1,4-diene (34)**

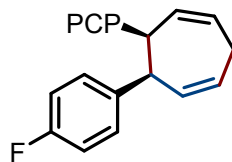
Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (110.5 mg, 0.3 mmol) derived from 4-methylcinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **34** (82.3 mg, 93% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.14-7.10 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.80-6.76 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.92-5.85 (m, 2H), 5.74-5.65 (m, 2H), 4.20-4.01 (m, 1H), 4.01-3.80 (m, 1H), 3.29-3.37 (m, 1H), 2.78 (dt, *J* = 19.8, 7.8 Hz, 1H), 2.30 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 140.0, 138.2, 135.9, 133.1, 132.7, 132.0, 131.0, 129.4, 128.3, 128.1, 127.5, 49.8, 49.5, 27.9, 21.0. **HRMS** (EI) *m/z* calcd. for C<sub>20</sub>H<sub>18</sub>Cl [M-H]<sup>-</sup> 293.1097, found 293.1102.



**35**

***cis*-6-(4-Chlorophenyl)-7-(4-methoxyphenyl)cyclohepta-1,4-diene (35)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (115.3 mg, 0.3 mmol) derived from 4-methoxycinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **35** (85.8 mg, 92% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.07-7.03 (m, 2H), 6.72-6.68 (m, 4H), 6.67-6.62 (m, 2H), 5.86-5.77 (m, 2H), 5.66-5.58 (m, 2H), 4.12-3.75 (m, 2H), 3.70 (s, 3H), 3.29-3.20 (m, 1H), 2.71 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 158.2, 140.1, 133.3, 133.2, 132.7, 132.0, 131.0, 130.5, 128.4, 127.9, 127.5, 112.9, 55.2, 49.8, 49.2, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>20</sub>H<sub>18</sub>ClO [M-H]<sup>-</sup> 309.1046, found 309.1041.



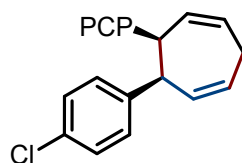
**36**

***cis*-6-(4-Chlorophenyl)-7-(4-fluorophenyl)cyclohepta-1,4-diene (36)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (111.7 mg, 0.3 mmol) derived from 4-fluorocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **36** (87.8 mg, 98% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.16-7.10 (m, 2H), 6.88-6.83 (m, 2H), 6.82-6.78 (m, 2H), 6.78-6.74 (m, 2H), 5.94-5.87 (m, 2H), 5.71-5.65 (m, 2H), 4.19-3.83 (m, 2H), 3.36-3.29 (m, 1H), 2.79 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ

161.7 (d,  $J = 243.0$  Hz), 139.8, 136.9, 132.7, 132.4, 132.2, 130.9, 128.6, 128.4, 127.6, 114.3 (d,  $J = 19.5$  Hz), 49.6, 49.3, 27.9.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  (-118.15)-(-118.21) (m). HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{ClF}$   $[\text{M}-\text{H}]^-$  297.0846, found 297.0851.

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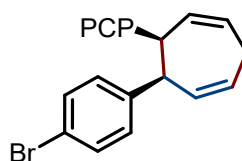


**37**

***cis*-6,7-bis(4-Chlorophenyl)cyclohepta-1,4-diene (37)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (116.6 mg, 0.3 mmol) derived from 4-chlorocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **37** (90.8 mg, 96% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (d,  $J = 8.5$  Hz, 4H), 6.78 (d,  $J = 8.5$  Hz, 4H), 5.97-5.85 (m, 2H), 5.67 (ddd,  $J = 11.0, 6.0, 3.0$  Hz, 2H), 4.08-3.77 (m, 2H), 3.38-3.28 (m, 1H), 2.80 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 132.32, 132.29, 130.9, 128.6, 127.7, 49.5, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{Cl}_2$   $[\text{M}-\text{H}]^-$  313.0551, found 313.0556.

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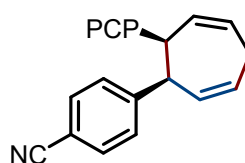


**38**

***cis*-6-(4-Bromophenyl)-7-(4-chlorophenyl)cyclohepta-1,4-diene (38)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (130.0 mg, 0.3 mmol) derived from 4-bromocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **38** (104.7 mg, 97% yield) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.27 (m, 2H), 7.16-7.12 (m, 2H), 6.80-6.76 (m, 2H), 6.74-6.71 (m, 2H), 5.94-5.88 (m, 2H), 5.69-5.64 (m, 2H), 4.22-3.80 (m, 2H), 3.36-3.29 (m, 1H), 2.80 (dt,  $J = 20.0, 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 139.6, 132.3, 132.2, 131.3, 130.9, 130.6, 128.6, 127.7, 120.5, 49.6, 49.4, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{15}\text{BrCl}$   $[\text{M}-\text{H}]^-$  357.0046, found 357.0051.

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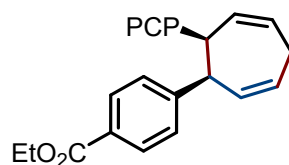
**39**

***cis*-4-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)benzonitrile (39)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (113.8 mg, 0.3 mmol) derived from 4-cyanocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6

mmol) afforded **39** (78.9 mg, 86% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.44 (m, 2H), 7.17-7.12 (m, 2H), 6.97-6.93 (m, 2H), 6.77-6.73 (m, 2H), 6.00-5.90 (m, 2H), 5.67 (ddd,  $J = 11.0, 6.0, 3.0$  Hz, 2H), 4.29-3.85 (m, 2H), 3.39-3.30 (m, 1H), 2.84 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 139.3, 132.6, 131.9, 131.3, 131.2, 130.6, 130.3, 129.3, 128.9, 127.9, 119.0, 110.4, 50.3, 49.2, 28.0. **HRMS** (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{15}\text{ClN}$   $[\text{M}-\text{H}]^-$  304.0893, found 304.0898.

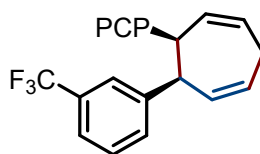
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***cis*-Ethyl-4-(7-(4-chlorophenyl)cyclohepta-2,5-dien-1-yl)benzoate (40)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (127.9 mg, 0.3 mmol) derived from ethyl (*E*)-4-(3-oxoprop-1-en-1-yl)benzoate and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **40** (99.5 mg, 94% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 8.5$  Hz, 2H), 6.93 (d,  $J = 8.5$  Hz, 2H), 6.76 (d,  $J = 8.0$  Hz, 2H), 5.99-5.88 (m, 2H), 5.76-5.64 (m, 2H), 4.37 (q,  $J = 7.0$  Hz, 2H), 4.23-4.08 (m, 1H), 4.08-3.93 (m, 1H), 3.40-3.30 (m, 1H), 2.83 (dt,  $J = 20.0, 7.5$  Hz, 1H), 1.39 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 146.6, 139.4, 132.31, 132.25, 131.9, 130.9, 129.5, 128.8, 128.7, 128.5, 127.7, 60.8, 50.0, 49.5, 27.9, 14.3. **HRMS** (EI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{20}\text{ClO}_2$   $[\text{M}-\text{H}]^-$  351.1152, found 351.1157.

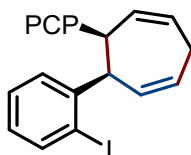
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***cis*-6-(4-Chlorophenyl)-7-(3-(trifluoromethyl)phenyl)cyclohepta-1,4-diene (41)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (126.7 mg, 0.3 mmol) derived from 3-(trifluoromethyl)cinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **41** (94.2 mg, 90% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.0$  Hz, 1H), 7.27 (t,  $J = 8.0$  Hz, 1H), 7.16-7.10 (m, 2H), 7.10 (s, 1H), 6.99 (d,  $J = 7.5$  Hz, 1H), 6.77-6.71 (m, 2H), 5.99-5.89 (m, 2H), 5.73-5.64 (m, 2H), 4.22-4.07 (m, 1H), 4.07-3.89 (m, 1H), 3.39-3.30 (m, 1H), 2.83 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 139.4, 132.9, 132.5, 132.1, 131.9, 130.8, 129.8 (q,  $J = 32.5$  Hz), 129.1, 128.7, 127.9, 127.7, 126.4, 125.1 (q,  $J = 272.0$  Hz), 123.4 (q,  $J = 3.0$  Hz), 49.9, 49.5, 28.0.  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.61. **HRMS** (EI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{15}\text{ClF}_3$   $[\text{M}-\text{H}]^-$  347.0814, found 347.0819.

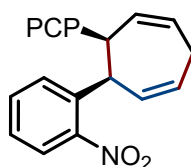
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42

***cis*-6-(4-Chlorophenyl)-7-(2-iodophenyl)cyclohepta-1,4-diene (42)**

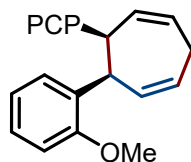
Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (144.1 mg, 0.3 mmol) derived from 2-iodocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **42** (104.9 mg, 86% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.15-7.07 (m, 3H), 6.88 (td, *J* = 7.5, 1.5 Hz, 1H), 6.77-6.71 (m, 2H), 6.69-6.61 (m, 1H), 6.00-5.88 (m, 2H), 5.75 (ddd, *J* = 11.5, 6.0, 3.0 Hz, 1H), 5.67 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 1H), 4.76-4.69 (m, 1H), 3.85-3.77 (m, 1H), 3.46-3.35 (m, 1H), 2.84 (dt, *J* = 20.5, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 143.7, 139.4, 138.6, 132.4, 132.3, 132.1, 131.6, 130.0, 129.4, 128.2, 127.7, 127.40, 127.36, 102.6, 52.3, 48.4, 28.1. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>15</sub>ClI [M-H]<sup>-</sup> 404.9907, found 404.9912.



43

***cis*-6-(4-Chlorophenyl)-7-(2-nitrophenyl)cyclohepta-1,4-diene (43)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (119.8 mg, 0.3 mmol) derived from 2-nitrocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **43** (87.0 mg, 89% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.72-7.66 (m, 1H), 7.36-7.29 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.86-6.81 (m, 1H), 6.81-6.75 (m, 2H), 6.02-5.95 (m, 1H), 5.92-5.86 (m, 1H), 5.72 (ddd, *J* = 11.4, 6.0, 3.0 Hz, 1H), 5.67-5.61 (m, 1H), 4.95-4.85 (m, 1H), 4.05-3.97 (m, 1H), 3.37-3.29 (m, 1H), 2.82 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.3, 138.7, 135.9, 132.7, 132.0, 131.7, 131.5, 131.3, 130.2, 127.8, 127.7, 127.3, 123.7, 48.8, 42.9, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>17</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> 326.0948, found 326.0942.



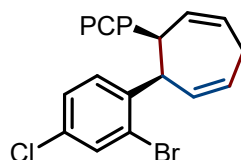
44

***cis*-6-(4-Chlorophenyl)-7-(2-methoxyphenyl)cyclohepta-1,4-diene (44)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (115.3 mg, 0.3 mmol) derived from (*E*)-3-(2-methoxyphenyl)acrylaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene

(98.8 mg, 0.6 mmol) afforded **44** (82.1 mg, 88% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.19-7.14 (m, 1H), 7.11-7.07 (m, 2H), 6.82-6.76 (m, 3H), 6.76-6.73 (m, 2H), 5.95-5.87 (m, 2H), 5.73-5.67 (m, 2H), 4.83-4.75 (m, 1H), 3.94-3.85 (m, 1H), 3.61 (s, 3H), 3.40-3.30 (m, 1H), 2.78 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 156.8, 140.3, 132.9, 132.8, 131.8, 131.0, 130.0, 129.8, 128.5, 128.0, 127.3, 127.1, 119.6, 109.8, 55.1, 48.2, 40.5, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>20</sub>H<sub>18</sub>ClO [M-H]<sup>-</sup> 309.1046, found 309.1051.

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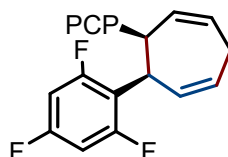


**45**

***cis*-6-(2-Bromo-4-chlorophenyl)-7-(4-chlorophenyl)cyclohepta-1,4-diene (45)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazine (140.3 mg, 0.3 mmol) derived from (*E*)-3-(2-bromo-4-chlorophenyl)acrylaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **45** (115.9 mg, 98% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 2.0 Hz, 1H), 7.16-7.09 (m, 2H), 7.07 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.79-6.73 (m, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.00-5.93 (m, 1H), 5.93-5.86 (m, 1H), 5.72 (ddd, *J* = 11.5, 6.0, 2.5 Hz, 1H), 5.60 (ddd, *J* = 10.5, 5.5, 3.0 Hz, 1H), 4.85-4.74 (m, 1H), 3.89-3.79 (m, 1H), 3.43-3.31 (m, 1H), 2.83 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 139.4, 138.6, 132.8, 132.5, 132.2, 132.1, 131.5, 131.4, 131.3, 129.7, 127.9, 127.6, 126.8, 125.5, 48.1, 46.7, 28.0. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>14</sub>BrCl<sub>2</sub> [M-H]<sup>-</sup> 390.9656, found 390.9661.

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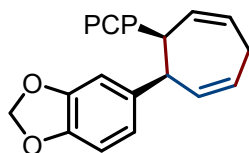


**46**

***cis*-6-(4-Chlorophenyl)-7-(2,4,6-trifluorophenyl)cyclohepta-1,4-diene (46)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazine (122.5 mg, 0.3 mmol) derived from 2,4,6-trifluorocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **46** (96.4 mg, 96% yield) as a white solid (mp: 130-132 °C). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.17-7.12 (m, 2H), 6.93-6.87 (m, 2H), 6.57-6.50 (m, 2H), 6.01-5.94 (m, 1H), 5.93-5.80 (m, 2H), 5.67 (ddd, *J* = 11.5, 5.5, 3.0 Hz, 1H), 4.85-4.78 (m, 1H), 3.63-3.55 (m, 1H), 3.39-3.29 (m, 1H), 2.82 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 161.6 (ddd, *J* = 248.0, 14.5, 11.0 Hz), 161.2 (dt, *J* = 248.0, 15.8 Hz), 139.1, 132.6, 131.9, 130.8, 130.5, 129.8 (t, *J* = 5.0 Hz), 127.7, 127.3, 114.3 (td, *J* = 17.0, 4.5 Hz), 100.5-100.0 (m), 49.5, 39.1, 27.9. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ (-107.89), (-110.35)-(-110.39) (m). **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>13</sub>ClF<sub>3</sub> [M-H]<sup>-</sup> 333.0658, found 333.0653.

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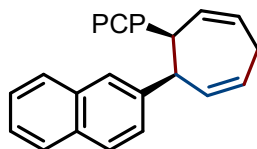


47

***cis*-5-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)benzo[*d*][1,3]dioxole (47)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (119.5 mg, 0.3 mmol) derived from 3,4-methylenedioxcinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **47** (94.5 mg, 97% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.17-7.12 (m, 2H), 6.85-6.80 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 6.25 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.96-5.84 (m, 4H), 5.74-5.65 (m, 2H), 4.15-3.82 (m, 2H), 3.39-3.28 (m, 1H), 2.79 (dt, *J* = 20.0, 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 146.9, 146.0, 140.2, 135.1, 133.0, 132.7, 132.1, 130.9, 128.5, 127.9, 127.6, 122.8, 110.0, 107.3, 100.8, 49.8, 49.7, 27.9. **HRMS** (EI) *m/z* calcd. for C<sub>20</sub>H<sub>16</sub>ClO<sub>2</sub> [M-H]<sup>-</sup> 323.0839, found 323.0844.

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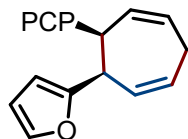


48

***cis*-2-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)naphthalene (48)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (121.3 mg, 0.3 mmol) derived from (*E*)-3-(naphthalen-2-yl)acrylaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **48** (97.3 mg, 98% yield) as a colorless oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.80-7.76 (m, 1H), 7.69-7.64 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.31 (s, 1H), 7.10-7.06 (m, 2H), 6.99 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.77-6.72 (m, 2H), 5.99-5.91 (m, 2H), 5.83 (ddd, *J* = 10.8, 6.0, 3.0 Hz, 1H), 5.71 (ddd, *J* = 11.4, 6.0, 3.0 Hz, 1H), 4.39-4.17 (m, 1H), 4.17-3.89 (m, 1H), 3.42-3.34 (m, 1H), 2.84 (dt, *J* = 19.8, 7.8 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 139.8, 138.9, 133.0, 132.8, 132.7, 132.3, 132.2, 131.1, 128.4, 128.1, 128.0, 127.8, 127.50, 127.46, 127.0, 125.7, 125.4, 50.0, 49.8, 28.0. **HRMS** (EI) *m/z* calcd. for C<sub>23</sub>H<sub>18</sub>Cl [M-H]<sup>-</sup> 329.1097, found 329.1102.

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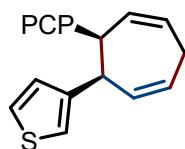


49

***cis*-2-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)furan (49)**

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (103.3 mg, 0.3 mmol) derived from 3-(2-furyl)acrolein and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **49** (45.6 mg, 53% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.36-7.32 (m, 1H),

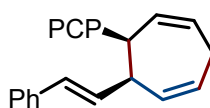
7.13-7.08 (m, 2H), 6.82-6.77 (m, 2H), 6.27-6.23 (m, 1H), 5.99-5.92 (m, 1H), 5.89-5.81 (m, 2H), 5.72 (ddd,  $J = 11.5, 6.0, 3.0$  Hz, 1H), 5.62-5.55 (m, 1H), 4.48-4.41 (m, 1H), 4.08-4.02 (m, 1H), 3.31-3.22 (m, 1H), 2.77 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 140.8, 139.0, 132.2, 131.9, 130.7, 130.2, 130.1, 127.7, 127.4, 110.2, 106.5, 47.4, 42.4, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{14}\text{ClO}$   $[\text{M}-\text{H}]^-$  269.0733, found 269.0728.



50

***cis*-3-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)thiophene (50)**

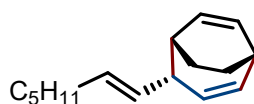
Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (108.1 mg, 0.3 mmol) derived from (*E*)-3-(thiophen-3-yl)acrylaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **50** (69.7 mg, 81% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.16-7.12 (m, 2H), 6.84-6.79 (m, 2H), 6.71 (dd,  $J = 5.0, 1.0$  Hz, 1H), 6.70-6.66 (m, 1H), 5.94-5.85 (m, 2H), 5.75-5.67 (m, 2H), 4.35-4.17 (m, 1H), 4.03-3.90 (m, 1H), 3.36-3.26 (m, 1H), 2.78 (dt,  $J = 20.0, 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 139.9, 133.0, 132.6, 132.1, 130.8, 128.7, 128.3, 128.2, 127.5, 124.5, 122.0, 49.4, 45.0, 27.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{14}\text{ClS}$   $[\text{M}-\text{H}]^-$  285.0505, found 285.0510.



51

***cis*-6-(4-Chlorophenyl)-7-((*E*)-styryl)cyclohepta-1,4-diene (51)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (114.1 mg, 0.3 mmol) derived from (*2E,4E*)-5-phenylpenta-2,4-dienal and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **51** (84.7 mg, 92% yield) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.29 (m, 4H), 7.29-7.20 (m, 5H), 6.33 (d,  $J = 16.0$  Hz, 1H), 6.15 (dd,  $J = 16.0, 8.5$  Hz, 1H), 5.90-5.82 (m, 2H), 5.77 (ddd,  $J = 11.5, 5.5, 3.0$  Hz, 1H), 5.61-5.54 (m, 1H), 3.98-3.90 (m, 1H), 3.69-3.57 (m, 1H), 3.32-3.22 (m, 1H), 2.81 (dt,  $J = 20.0, 7.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 137.5, 132.7, 132.5, 132.2, 131.1, 130.8, 130.7, 128.6, 128.4, 128.1, 127.9, 127.2, 126.2, 49.0, 47.4, 28.6. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{18}\text{Cl}$   $[\text{M}-\text{H}]^-$  305.1097, found 305.1102.



52

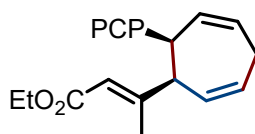
**(±)-(1*S*,4*R*,5*R*)-4-((*E*)-Hept-1-en-1-yl)bicyclo[3.2.2]nona-2,6-diene (52)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (112.3 mg, 0.3 mmol)



derived from (2*E*,4*E*)-deca-2,4-dienal and cyclohexa-1,3-diene (48.1 mg, 0.6 mmol) afforded **52** (54.5 mg, 84% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.42 (t, *J* = 8.0 Hz, 1H), 5.97-5.91 (m, 1H), 5.90-5.84 (m, 1H), 5.42-5.36 (m, 2H), 5.20-5.14 (m, 1H), 2.83-2.76 (m, 1H), 2.62-2.55 (m, 1H), 2.55-2.49 (m, 1H), 2.08-2.00 (m, 1H), 2.00-1.93 (m, 2H), 1.89-1.80 (m, 2H), 1.70-1.60 (m, 1H), 1.39-1.27 (m, 6H), 0.88 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 138.6, 132.3, 131.4, 131.1, 130.1, 129.5, 49.2, 37.2, 32.7, 32.4, 31.4, 30.6, 29.2, 25.5, 22.5, 14.1. HRMS (EI) *m/z* calcd. for C<sub>16</sub>H<sub>25</sub> [M+H]<sup>+</sup> 217.1956, found 217.1950.

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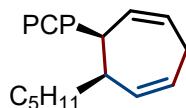


**53**

***cis*-Ethyl-(*E*)-3-(7-(4-chlorophenyl)cyclohepta-2,5-dien-1-yl)but-2-enoate (**53**)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (117.1 mg, 0.3 mmol) derived from (2*E*,4*E*)-3-methyl-6-oxohexa-2,4-dienoate and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **53** (81.7 mg, 86% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.22-7.18 (m, 2H), 7.10-7.06 (m, 2H), 5.92-5.85 (m, 1H), 5.86-5.80 (m, 1H), 5.75 (ddd, *J* = 11.5, 6.0, 3.0 Hz, 1H), 5.52 (ddd, *J* = 11.0, 6.0, 3.0 Hz, 1H), 5.37 (s, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.93-3.83 (m, 1H), 3.73-3.63 (m, 1H), 3.26-3.17 (m, 1H), 2.74 (dt, *J* = 20.0, 7.5 Hz, 1H), 2.04 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.6, 158.3, 139.3, 132.5, 132.1, 130.7, 130.4, 129.3, 127.9, 127.8, 118.6, 59.5, 52.8, 47.2, 27.7, 19.7, 14.3. HRMS (EI) *m/z* calcd. for C<sub>19</sub>H<sub>20</sub>ClO<sub>2</sub> [M+H]<sup>+</sup> 315.1152, found 315.1157.

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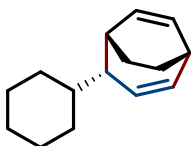


**54**

***cis*-6-(4-Chlorophenyl)-7-pentylcyclohepta-1,4-diene (**54**)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (104.5 mg, 0.3 mmol) derived from (*E*)-2-octenal and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **54** (50.3 mg, 61% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24-7.20 (m, 2H), 7.20-7.15 (m, 2H), 5.91-5.83 (m, 1H), 5.77-5.70 (m, 1H), 5.66-5.59 (m, 1H), 5.25-5.17 (m, 1H), 3.58-3.50 (m, 1H), 3.24-3.15 (m, 1H), 3.04-2.95 (m, 1H), 2.66 (dt, *J* = 19.5, 7.5 Hz, 1H), 1.34-1.20 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 139.9, 135.6, 132.7, 132.0, 131.2, 129.3, 127.5, 126.8, 47.7, 41.4, 33.9, 31.9, 28.0, 27.4, 22.7, 14.1. HRMS (EI) *m/z* calcd. for C<sub>18</sub>H<sub>22</sub>Cl [M-H]<sup>-</sup> 273.1410, found 273.1415.

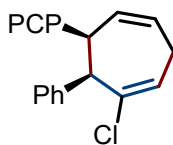
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55

**(±)-(1*S*,4*R*,5*R*)-4-Cyclohexylbicyclo[3.2.2]nona-2,6-diene (55)**

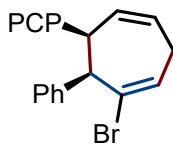
Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (108.1 mg, 0.3 mmol) derived from (*E*)-3-cyclohexylacrylaldehyde and cyclohexa-1,3-diene (48.1 mg, 0.6 mmol) afforded **55** (52.2 mg, 86% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 6.39 (t, *J* = 8.0 Hz, 1H), 5.96-5.86 (m, 2H), 5.40-5.34 (m, 1H), 2.68-2.61 (m, 1H), 2.60-2.50 (m, 1H), 2.05-1.97 (m, 1H), 1.91-1.79 (m, 4H), 1.77-1.66 (m, 3H), 1.66-1.58 (m, 2H), 1.37-1.27 (m, 1H), 1.22-1.08 (m, 3H), 1.04-0.93 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 138.4, 132.5, 130.8, 129.9, 51.7, 41.7, 33.6, 33.1, 31.5, 31.4, 30.8, 26.8, 26.6, 26.0. **HRMS** (EI) *m/z* calcd. for C<sub>15</sub>H<sub>23</sub> [M+H]<sup>+</sup> 203.1800, found 203.1794.



56

***cis*-1-Chloro-6-(4-chlorophenyl)-7-phenylcyclohepta-1,4-diene (56)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (116.6 mg, 0.3 mmol) derived from  $\alpha$ -chlorocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **56** (76.7 mg, 93% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.25-7.22 (m, 1H), 7.21-7.15 (m, 4H), 6.88-6.84 (m, 2H), 6.78-6.74 (m, 2H), 6.13 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.03-5.97 (m, 1H), 5.77-5.72 (m, 1H), 4.44-4.37 (m, 1H), 3.73-3.66 (m, 1H), 3.35-3.25 (m, 1H), 2.88 (dt, *J* = 19.5, 8.0 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 140.2, 137.1, 136.1, 132.7, 130.4, 130.0, 128.9, 128.1, 127.4, 127.3, 126.9, 125.4, 59.0, 47.6, 27.3. **HRMS** (EI) *m/z* calcd. for C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub> [M-H]<sup>-</sup> 313.0551, found 313.0556.

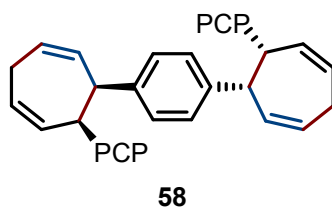


57

***cis*-1-Bromo-6-(4-chlorophenyl)-7-phenylcyclohepta-1,4-diene (57)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (130.0 mg, 0.3 mmol) derived from  $\alpha$ -bromocinnamaldehyde and (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (98.8 mg, 0.6 mmol) afforded **57** (84.2 mg, 78% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.26-7.22 (m, 1H), 7.22-7.14 (m, 4H), 6.88-6.81 (m, 2H), 6.77-6.73 (m, 2H), 6.38 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.03-5.96 (m, 1H), 5.76-5.71 (m, 1H), 4.49-4.43 (m, 1H), 3.84-3.79 (m, 1H), 3.37-3.28 (m, 1H), 2.82 (dt, *J* = 19.5, 8.0 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 140.2, 137.2, 132.8, 130.4, 130.0, 129.4, 128.80,

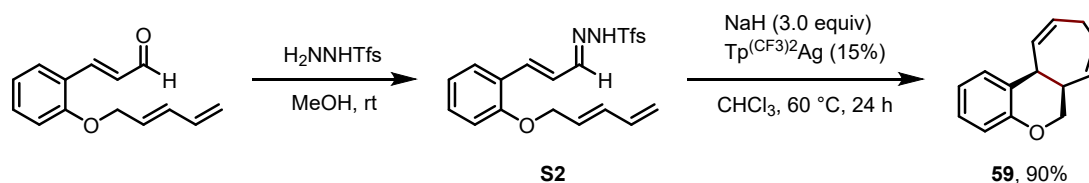
128.2, 127.7, 127.44, 127.35, 127.0, 60.8, 48.3, 28.9. **HRMS** (EI)  $m/z$  calcd. for  $C_{19}H_{15}BrCl$   $[M-H]^-$  357.0046, found 357.0041.



**(±)-1-(7-(4-Chlorophenyl)cyclohepta-2,5-dien-1-yl)-4-(7-(4-chlorophenyl)cyclohepta-2,5-dien-1-yl)benzene (58)**

Prepared according to **General procedure A** with some modification using alkenyl *N*-triflylhydrazone (189.2 mg, 0.3 mmol) derived from (*2E,2'E*)-3,3'-(1,4-phenylene)diacrylaldehyde and (*E*)-1-(buta-1, 3-dien-1-yl)-4-chlorobenzene (197.6 mg, 1.2 mmol) afforded **58** (75.4 mg, 52% yield) as a pale yellow solid (mp: 130-131 °C). **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ )  $\delta$  7.15-7.10 (m, 4H), 6.79-6.74 (m, 4H), 6.69 (s, 4H), 5.94-5.86 (m, 4H), 5.75-5.65 (m, 4H), 4.16-4.00 (m, 2H), 4.00-3.87 (m, 2H), 3.37-3.27 (m, 2H), 2.78 (dt,  $J = 20.0, 7.5$  Hz, 2H). **<sup>13</sup>C NMR** (150 MHz,  $CDCl_3$ )  $\delta$  139.9, 139.7, 132.92, 132.90, 132.64, 132.62, 132.2, 131.0, 128.7, 128.4, 128.3, 127.5, 49.9, 49.4, 27.9. **HRMS** (EI)  $m/z$  calcd. for  $C_{32}H_{29}Cl_2$   $[M+H]^+$  483.1646, found 483.1640.

**Intramolecular Reactions**



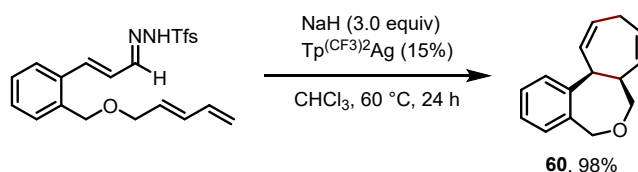
**Scheme S5.** Preparation of **59**.

***N'*-((1*Z*,2*E*)-3-(2-(((*E*)-Penta-2,4-dien-1-yl)oxy)phenyl)allylidene)-2-(trifluoromethyl)benzenesulfonylhydrazone (S2)**

Alkenyl *N*-Sulfonylhydrazones **S2** were prepared according to literature procedure.<sup>1</sup> To a stirred solution of 2-(trifluoromethyl)benzenesulfonylhydrazone (480.0 mg, 2.0 mmol, 1.0 equiv) in methanol (2 mL) were added (*E*)-3-(2-(((*E*)-penta-2,4-dien-1-yl)oxy)phenyl) acrylaldehyde (471.4 mg, 2.2 mmol, 1.1 equiv) and the mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to obtain the **S2** (707.1 mg, 81% yield) as a colorless oil. **<sup>1</sup>H NMR** (500 MHz,  $DMSO-d_6$ )  $\delta$  11.96 (s, 1H), 8.02 (dd,  $J = 11.5, 8.0$  Hz, 2H), 7.92 (t,  $J = 7.5$  Hz, 1H), 7.88-7.85 (m, 2H), 7.60 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.30-7.26 (m, 1H), 7.18 (d,  $J = 16.0$  Hz, 1H), 7.03 (d,  $J = 8.0$  Hz, 1H), 6.92 (t,  $J = 7.5$  Hz, 1H), 6.86 (dd,  $J = 16.0, 9.5$  Hz, 1H), 6.46-6.36 (m, 2H), 6.00-5.95 (m, 1H), 5.27-5.24 (m, 1H), 5.15-5.13 (m, 1H), 4.69 (d,  $J = 5.5$  Hz, 2H). **<sup>13</sup>C NMR** (150 MHz,  $DMSO-d_6$ )  $\delta$  156.3, 150.5, 138.7, 136.7, 134.8, 133.8, 133.8, 133.7, 131.4, 130.8, 129.4, 128.9, 128.0, 127.0, 126.8, 125.6, 124.7, 124.2, 122.4, 121.4, 118.8, 113.3, 68.4. **<sup>19</sup>F NMR** (470 MHz,  $DMSO-d_6$ )  $\delta$  -56.28. **HRMS** (EI)  $m/z$  calcd. for  $C_{21}H_{19}F_3N_2O_3S$   $[M+H]^+$  436.1068, found 436.1062.

### *cis*-6,6a,9,11a-Tetrahydrocyclohepta[*c*]chromene (59)

**General Procedure B:** To an oven-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar were added **S2** (130.9 mg, 0.3 mmol), NaH (36.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 3.0 equiv), dry CHCl<sub>3</sub> (15.0 mL) and Tp<sup>(CF<sub>3</sub>)<sub>2</sub>Ag</sup> (34.0 mg, 15 mol%) inside a glove box with nitrogen atmosphere. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 24 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **59** (53.5 mg, 90% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.17-7.07 (m, 2H), 6.89-6.83 (m, 1H), 6.82-6.78 (m, 1H), 5.81-5.68 (m, 3H), 5.63-5.56 (m, 1H), 4.10 (d, *J* = 6.5 Hz, 2H), 4.01-3.94 (m, 1H), 3.11-3.01 (m, 1H), 2.95-2.85 (m, 1H), 2.65 (dt, *J* = 20.0, 6.0 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.6, 133.9, 130.1, 129.3, 129.1, 128.1, 127.7, 126.8, 120.3, 116.5, 67.7, 38.7, 37.4, 28.5. HRMS (EI) *m/z* calcd. for C<sub>14</sub>H<sub>13</sub>O [M-H]<sup>+</sup> 197.0966, found 197.0971.

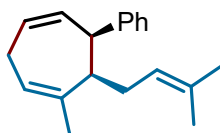


Scheme S6. Preparation of **60**.

### *cis*-7,7a,10,12a-Tetrahydro-5*H*-benzo[*c*]cyclohepta[*e*]oxepine (60)

Prepared according to **General procedure B** using alkenyl *N*-triflylhydrazone (135.2 mg, 0.3 mmol) derived from (*E*)-3-(2-(((*E*)-penta-2,4-dien-1-yl)oxy)methyl)phenyl)acrylaldehyde afforded **60** (62.4 mg, 98% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25-7.19 (m, 2H), 7.19-7.14 (m, 2H), 5.83-5.72 (m, 2H), 5.64-5.55 (m, 2H), 4.78 (d, *J* = 13.5 Hz, 1H), 4.64 (d, *J* = 13.5 Hz, 1H), 4.27-4.22 (m, 1H), 4.10 (dd, *J* = 12.0, 8.5 Hz, 1H), 3.93 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.21-3.12 (m, 1H), 3.03-2.87 (m, 1H), 2.86-2.76 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.6, 139.0, 132.7, 130.6, 129.5, 129.2, 128.3, 127.9, 127.7, 126.3, 74.4, 48.7, 43.6, 30.1. HRMS (EI) *m/z* calcd. for C<sub>15</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 213.1279, found 213.1273.

### 3.3 Late-Stage Modification of Complex Natural Products



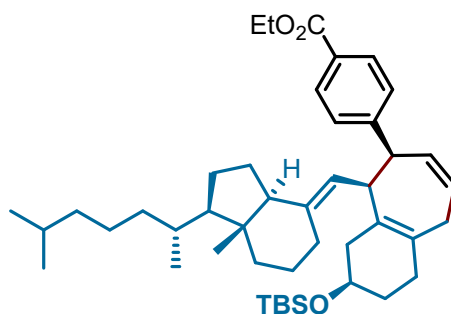
**61**

### *cis*-1-Methyl-7-(3-methylbut-2-en-1-yl)-6-phenylcyclohepta-1,4-diene (61)

Prepared according to **General procedure A** using alkenyl *N*-triflylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and Ocimene (81.7 mg, 0.6 mmol) afforded **13** (43.9 mg, 58% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31-7.23 (m, 4H), 7.19-7.14 (m, 1H), 5.81-5.75 (m, 1H), 5.65-5.58 (m, 1H), 5.43-5.37 (m, 1H), 5.23-5.17 (m, 1H), 3.63-3.58 (m, 1H), 3.12-3.01 (m, 1H), 2.82 (dt, *J* = 22.0, 6.5 Hz, 1H), 2.46-2.32 (m, 2H), 2.27-2.21 (m, 1H), 1.74 (s, 3H), 1.66 (s, 3H), 1.31 (s, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 140.2, 132.6, 128.8, 128.6, 128.2, 127.8, 125.8, 123.5, 122.1, 52.3, 47.5, 31.3, 30.3, 27.6, 25.9, 17.9. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{25}$   $[\text{M}+\text{H}]^+$  253.1956, found 253.1950.

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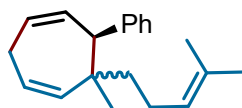


62

**Ethyl-4-((3*R*,5*S*,6*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-(((1*R*,3*aS*,7*aR*,*E*)-7*a*-methyl-1-((*R*)-6-methylheptan-2-yl)octahydro-4*H*-inden-4-ylidene)methyl)-2,3,4,5,6,9-hexahydro-1*H*-benzo[7]annulen-6-yl)benzoate (62)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (127.9 mg, 0.3 mmol) derived from ethyl (*E*)-4-(3-oxoprop-1-en-1-yl)benzoate and *tert*-butyldimethyl(((*S,Z*)-3-(2-((1*R*,3*aS*,7*aR*,*E*)-7*a*-methyl-1-((*R*)-6-methylheptan-2-yl)octahydro-4*H*-inden-4-ylidene)ethylidene)-4-methylenecyclohexyl)oxy)silane (299.3 mg, 0.6 mmol) derived from Vitamin D<sub>3</sub> afforded **63** (105.1 mg, 51% yield, dr = 4:1) as a pale yellow solid (mp: 140-142 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.0$  Hz, 2H), 7.24 (d,  $J = 7.5$  Hz, 2H), 5.83-5.77 (m, 1H), 5.51 (dd,  $J = 11.5, 5.0$  Hz, 1H), 5.10 (d,  $J = 9.0$  Hz, 1H), 4.35 (q,  $J = 7.0$  Hz, 2H), 3.75-3.66 (m, 1H), 3.50-3.43 (m, 1H), 3.43-3.36 (m, 1H), 2.91-2.83 (m, 2H), 2.52-2.45 (m, 1H), 2.12-1.65 (m, 9H), 1.42-1.36 (m, 7H), 1.33-1.29 (m, 5H), 1.25-1.21 (m, 3H), 1.16-1.06 (m, 4H), 0.89-0.85 (m, 9H), 0.84 (s, 9H), 0.48 (s, 3H), 0.00 (s, 3H), -0.02 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 149.7, 139.0, 131.4, 131.3, 130.4, 129.2, 128.6, 128.1, 127.6, 121.0, 68.9, 60.7, 56.5, 55.7, 49.4, 46.9, 45.3, 40.5, 40.3, 39.5, 36.1, 34.3, 32.0, 29.1, 28.0, 27.6, 25.9, 23.8, 23.6, 22.8, 22.5, 22.2, 18.8, 18.2, 14.3, 11.9, -4.62, -4.70. HRMS (EI)  $m/z$  calcd. for  $\text{C}_{45}\text{H}_{69}\text{O}_3\text{Si}$   $[\text{M}-\text{H}]^-$  685.5016, found 685.5021.

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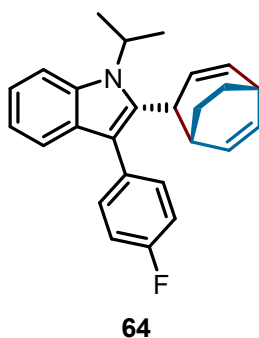
63

***cis*-6-Methyl-6-(4-methylpent-3-en-1-yl)-7-phenylcyclohepta-1,4-diene (63)**

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*E*)-4,8-dimethylnona-1,3,7-triene (90.2 mg, 0.6 mmol) derived from Citral afforded **13** (43.9 mg, 58% yield, d.r. = 1:1) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.24 (m, 4H, major, 4H, minor), 7.23-7.18 (m, 1H, major, 1H, minor), 5.86-5.76 (m, 1H, major, 1H, minor), 5.76-5.68 (m, 1H, major, 1H, minor), 5.68-5.61 (m, 1H, major, 1H, minor), 5.51-5.44 (m, 1H, major), 5.29 (dd,  $J = 12.0, 3.0$  Hz, 1H, minor), 5.10-5.00 (m, 1H, major, 1H, minor), 3.66-3.56 (m,

1H, major, 1H, minor), 3.17-3.06 (m, 1H, major, 1H, minor), 2.89-2.78 (m, 1H, major, 1H, minor), 2.12-2.00 (m, 2H, minor), 2.00-1.91 (m, 2H, major), 1.67 (s, 3H, minor), 1.66 (s, 3H, major), 1.61 (s, 3H, minor), 1.57 (s, 3H, major), 1.55-1.42 (m, 2H, minor), 1.34-1.21 (m, 2H, major), 1.03 (s, 3H, major), 0.95 (s, 3H, minor). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.1, 139.3, 139.0, 133.5, 132.9, 131.1, 131.0, 130.2, 130.1, 127.7, 127.6, 127.3, 127.0, 126.19, 126.15, 126.11, 126.06, 125.2, 125.1, 55.2, 53.6, 42.3, 41.8, 39.3, 30.1, 29.8, 26.9, 25.9, 25.7, 23.2, 23.1, 17.6. HRMS (EI) m/z calcd. for C<sub>20</sub>H<sub>25</sub> [M-H]<sup>-</sup> 265.1956, found 265.1961.

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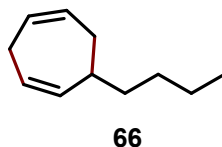
#### Bicyclo[3.2.2]nona-3,6-dien-2-yl-3-(4-fluorophenyl)-1-isopropyl-1H-indol (**64**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (158.9 mg, 0.3 mmol) derived from (*E*)-3-(3-(4-fluorophenyl)-1-isopropyl-1H-indol-2-yl)acrylaldehyde and cyclohexa-1, 3-diene (48.1 mg, 0.6 mmol) afforded **64** (74.7 mg, 67% yield) as a white solid (mp: 159-160 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37-7.32 (m, 2H), 7.17-7.08 (m, 3H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.43 (t, *J* = 8.0 Hz, 1H), 6.09 (t, *J* = 7.5 Hz, 1H), 6.06-5.98 (m, 1H), 5.44 (d, *J* = 10.5 Hz, 1H), 5.08-4.96 (m, 1H), 4.02-3.96 (m, 1H), 2.81-2.70 (m, 2H), 2.08-2.00 (m, 1H), 1.87-1.79 (m, 2H), 1.76-1.68 (m, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.53 (d, *J* = 6.2 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 161.57 (d, *J* = 244.5 Hz), 138.9, 136.9, 134.0, 132.9, 132.0 (d, *J* = 7.5 Hz), 131.8 (d, *J* = 3.0 Hz), 129.2, 129.0, 128.7, 120.8, 119.4, 119.3, 115.1 (d, *J* = 21.0 Hz), 113.4, 112.3, 47.4, 43.2, 40.1, 32.5, 29.8, 28.4, 22.1, 21.3. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ (-117.22)-(117.27) (m). HRMS (EI) m/z calcd. for C<sub>26</sub>H<sub>25</sub>FN [M-H]<sup>-</sup> 370.1971, found 370.1966.

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### 3.4 The Synthesis of Natural Products and Analogues

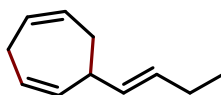
#### 3.4.1 Total Synthesis of (±)-Dictyopterene C' (**66**)



Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and 1,3-butadiene (216.4 mg, 15% w/w solution in hexane, 0.6 mmol) afforded **66** (25.2 mg, 56% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.74-5.66 (m, 1H), 5.66-5.56 (m, 3H), 3.00-2.89 (m, 1H), 2.70 (dt, *J* = 20.0, 5.5 Hz, 1H), 2.50-2.40 (m, 1H), 2.25-2.17 (m, 1H), 2.14-2.05 (m, 1H), 1.31-1.28 (m, 6H), 0.90-0.87 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 136.9, 129.9, 128.1, 127.3, 37.2, 36.0, 32.9, 29.7, 28.3, 22.9, 14.1. HRMS (EI) m/z calcd. for C<sub>11</sub>H<sub>17</sub> [M-H]<sup>-</sup> 149.1330, found 149.1325.

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### 3.4.2 Synthesis of Analogues of Natural Products

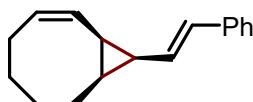


**68**

#### (*E*)-6-(But-1-en-1-yl)cyclohepta-1,4-diene (**68**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from (*2E,4E*)-hepta-2, 4-dienal and 1,3-butadiene (216.4 mg, 15% w/w solution in hexane, 0.6 mmol) afforded **67** (31.6 mg, 71% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.76-5.65 (m, 2H), 5.65-5.56 (m, 2H), 5.53-5.40 (m, 2H), 3.13-3.05 (m, 1H), 2.96-2.87 (m, 1H), 2.80-2.69 (m, 1H), 2.34-2.20 (m, 2H), 2.05-1.97 (m, 2H), 0.97 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 132.5, 130.9, 129.5, 128.7, 126.8, 40.4, 33.2, 28.0, 25.3, 13.7. **HRMS** (EI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{17}$   $[\text{M}+\text{H}]^+$  149.1330, found 149.1325.

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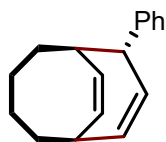
**69**

#### (*endo,Z*)-9-((*E*)-Styryl)bicyclo[6.1.0]non-2-ene (**69**)

Prepared according to **General procedure A** using alkenyl *N*-trifosylhydrazone (106.3 mg, 0.3 mmol) derived from cinnamaldehyde and (*1Z, 3Z*)-cycloocta-1,3-diene (64.9 mg, 0.6 mmol) afforded **68** (52.5 mg, 78% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.29 (m, 2H), 7.29-7.24 (m, 2H), 7.18-7.13 (m, 1H), 6.54 (d,  $J = 16.0$  Hz, 1H), 5.92 (dd,  $J = 16.0, 10.0$  Hz, 1H), 5.85-5.78 (m, 1H), 5.42-5.38 (m, 1H), 2.50-2.40 (m, 1H), 2.10-1.93 (m, 2H), 1.90-1.70 (m, 4H), 1.68-1.58 (m, 1H), 1.52-1.42 (m, 1H), 1.39-1.28 (m, 1H), 1.25-1.15 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 136.2, 130.3, 128.6, 128.4, 126.4, 125.6, 123.4, 30.9, 30.0, 25.1, 23.03, 23.95, 21.7. **HRMS** (EI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{19}$   $[\text{M}-\text{H}]^-$  223.1487, found 223.1482.

*Spectral data were in good agreement with literature values.*<sup>6</sup>

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**70**

#### (±)-(1*R*,6*S*,9*R*,*Z*)-9-Phenylbicyclo[4.3.2]undeca-7,10-diene (**70**)

Prepared according to dissolving **68** (50 mg, 0.2 mmol) in xylenes and heating at 160 °C for 24 h, afforded **69** (37.7 mg, 84% yield) as a colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.28 (m, 2H), 7.28-7.23 (m, 2H), 7.20-7.14 (m, 1H), 5.79 (dd,  $J = 11.0, 8.0$  Hz, 1H), 5.72 (dd,  $J = 12.0, 6.5$  Hz, 1H), 5.67-5.59 (m, 2H), 3.54-3.48 (m, 1H), 3.16-3.07 (m, 1H), 2.68-2.61 (m, 1H), 2.16-2.06 (m, 1H), 1.96-1.89 (m, 2H), 1.83-1.66 (m, 4H), 1.61-1.56 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 134.0, 132.5, 131.5, 129.7, 128.7, 127.8, 125.9, 51.1, 44.6, 40.1, 38.9, 33.1, 27.2, 24.1. **HRMS** (EI)  $m/z$  calcd.

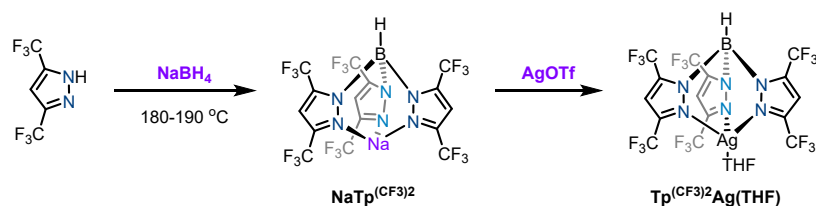
for  $C_{17}H_{19} [M-H]^-$  223.1487, found 223.1482.

*Spectral data were in good agreement with literature values.*<sup>6</sup>

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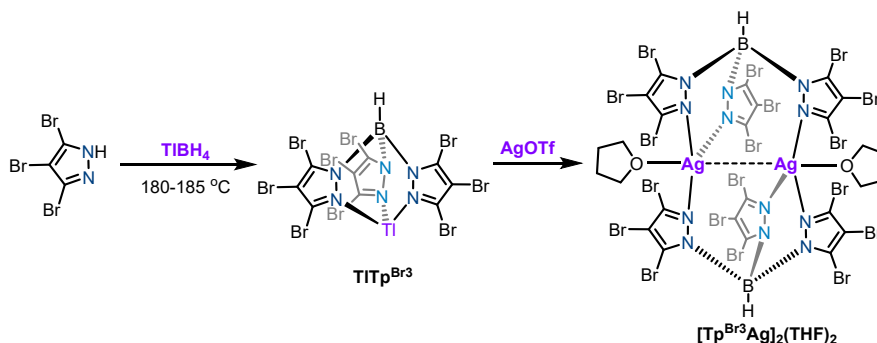
## 4. The Synthesis of Catalysts



Scheme S7. Synthesis of catalyst  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}(\text{THF})$ .

Synthesis of  $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{Na}(\text{H}_2\text{O})$ :

$\text{NaBH}_4$  (0.40 g, 10.6 mmol) and 3,5-bis(trifluoromethyl)pyrazole (7.55 g, 37 mmol) were mixed in a minimum amount of kerosene. The mixture was slowly heated to  $180\text{--}190\text{ }^\circ\text{C}$  and kept for 4 h at  $190\text{ }^\circ\text{C}$ . During this period, a white solid slowly precipitated. The mixture was allowed to cool to room temperature, and the resulting white solid was collected by suction filtration (in air). It was washed several times with petroleum ether and sucked dry in air to obtain **4** as a white solid (yield 76% based on  $\text{NaBH}_4$ ).



Scheme S8. Synthesis of catalyst  $[\text{Tp}^{\text{Br}_3}\text{Ag}]_2(\text{THF})_2$ .

Synthesis of  $\text{Tp}^{(\text{CF}_3)_2}\text{Ag}\cdot\text{THF}$ :

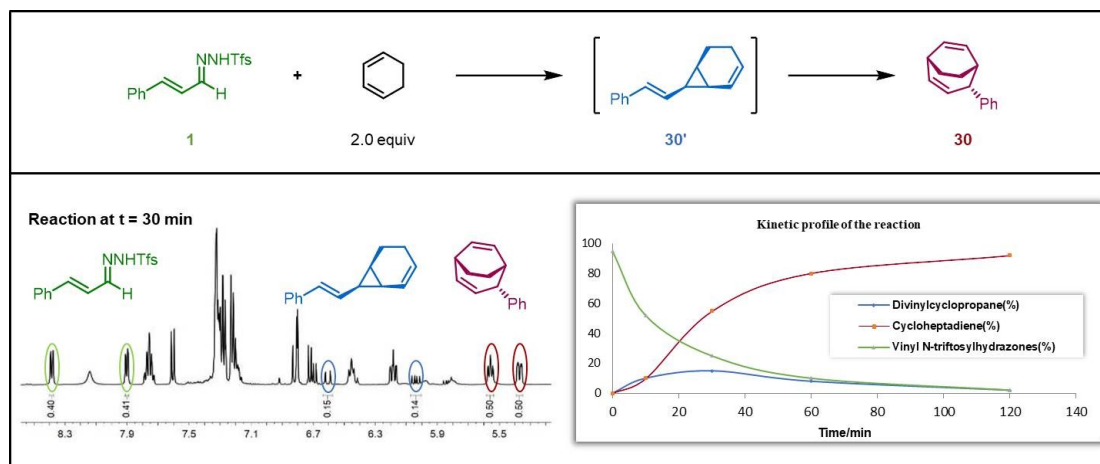
$\text{AgOTf}$  (0.463 g, 1.8 mmol) was treated with  $\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3\text{Na}$  (1.16 g, 1.8 mmol) in thf at room temperature. The mixture was stirred overnight, and the solvent was removed under reduced pressure. The residue was extracted into hexane and filtered through Celite, and the hexane was removed from the filtrate to obtain **1** as a white solid: 92% yield.

*Spectral data were in good agreement with literature values<sup>12,13</sup>.*

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## 5. Mechanistic Studies on the Silver-catalyzed Tandem Cyclopropanation/Cope Rearrangement

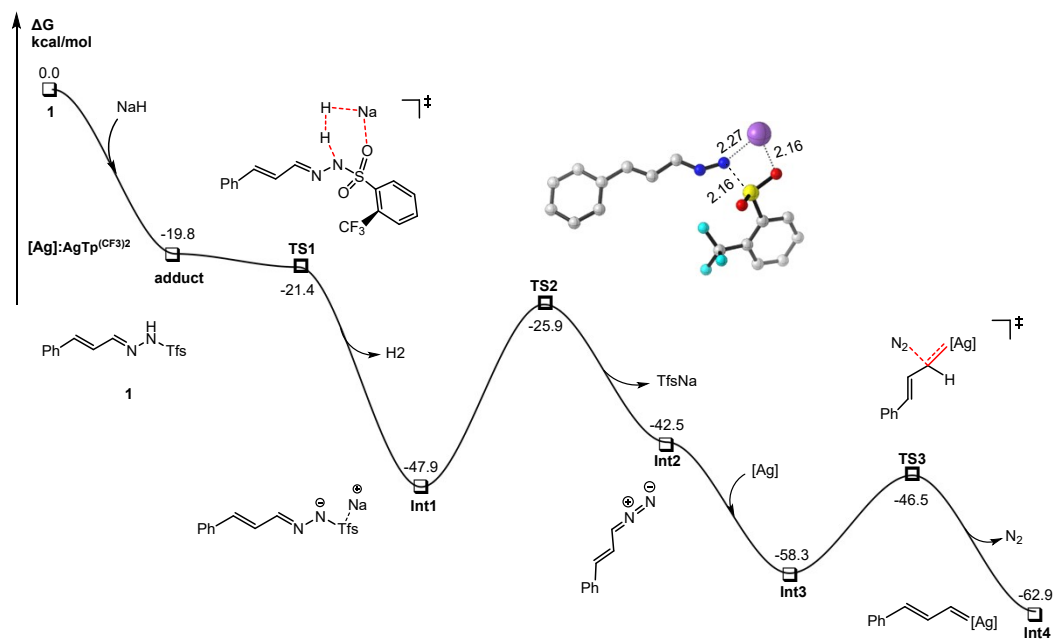
Kinetic profile of the reaction of alkenyl *N*-sulfonylhydrazones with cyclohexa-1,3-diene, followed by  $^1\text{H}$  NMR, showing accumulation and consumption of *cis*-dialkenylcyclopropane intermediate **30'**, and then consumption to give rise cleanly to cycloheptadiene **30**.



**Figure S1.** Kinetic profile of the overall reaction

## 6. Computational Details

All the calculations in this work were performed on the basis of density functional theory (DFT) using the B3LYP<sup>[15,16]</sup> functional and GD3BJ empirical dispersion<sup>[17]</sup> in the Gaussian 16 package<sup>[18]</sup>. Geometry optimizations and vibrational frequency calculations were carried out with a mixed basis set that utilizes the 6-31g(d,p)<sup>[19-22]</sup> basis set for main-group atoms (B, C, H, N, F) and the SDD<sup>[23,24]</sup> basis set for Ag atom. All of the optimized geometries had been characterized as minima (zero imaginary frequencies) or transition state structures (a single imaginary frequency) at the same level of theory in solvent (chloroform). Intrinsic reaction coordinate (IRC)<sup>[25,26]</sup> calculations were also carried out to inspect whether each of the transition structures actually connected the proposed reactant and product. We performed single-point energy calculations for all the optimized structures at the B3LYP-D3(BJ)/def2tzvp<sup>[27]</sup> level with solvent effects simulated by the SMD solvent model<sup>[28]</sup> (solvent = chloroform). 3D structures of optimized geometries were generated using CYLview visualization software.<sup>[29]</sup>



**Fig. S2.** Gibbs-free energy profile for silver-catalyzed decomposition of alkenyl-*N*-trifosylhydrazone to form silver carbene.

### Cartesian coordinates of the computed structures

1

Zero-point correction= 0.266644 (Hartree/Particle)

Thermal correction to Energy= 0.287114

Thermal correction to Enthalpy= 0.288058

Thermal correction to Gibbs Free Energy= 0.217034

Sum of electronic and zero-point Energies= -1575.468484

Sum of electronic and thermal Energies= -1575.448015

Sum of electronic and thermal Enthalpies= -1575.447071

Sum of electronic and thermal Free Energies= -1575.518094

S	-2.12843400	-1.54635200	-0.09615800
O	-2.96348200	-2.41560000	-0.93028000
O	-2.20536100	-1.57581800	1.36000000
N	0.45375900	-1.25408800	0.05290800
N	-0.55907300	-1.98475600	-0.52059400
C	1.61672300	-1.36207100	-0.49296200

C	-3.39751600	2.32849000	-0.61683000
C	-2.53314500	2.77913200	-1.61289400
C	-1.57428800	1.91992100	-2.13811300
C	-1.47180800	0.61639500	-1.65506000
C	-2.32099000	0.16873400	-0.64290000
C	-3.31075200	1.02553100	-0.12325500
H	-0.46089500	-2.32539500	-1.48011400
H	1.77899500	-1.98753200	-1.37881500
H	-4.15567400	2.99135700	-0.21957900
H	-0.90177400	2.25474700	-2.92054500
H	-0.72102000	-0.04246200	-2.07003800
H	-2.61899600	3.79692600	-1.97790100
C	-4.29146100	0.62272700	0.95664800
F	-3.73492500	0.62742600	2.18315800
F	-4.80924400	-0.60597000	0.74210800
F	-5.33918500	1.47804800	1.00507000
C	2.74577800	-0.65825100	0.06287000
H	2.54449900	-0.05302700	0.94231200
C	3.98041600	-0.74829600	-0.47789400
H	4.10443400	-1.37900700	-1.35767000
C	5.19840900	-0.09012200	-0.01320700
C	6.39690900	-0.31737400	-0.71470800
C	5.23351000	0.76315800	1.10751700
C	7.58858800	0.28259100	-0.31479700
H	6.38458500	-0.97365200	-1.58068100
C	6.42370300	1.36184900	1.50506700
H	4.32657900	0.95776700	1.67037000
C	7.60676900	1.12535100	0.79722700
H	8.50196600	0.09203900	-0.87018600
H	6.43179600	2.01609400	2.37169100

H	8.53351400	1.59490500	1.11244600
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**Adduct**

Zero-point correction=			0.270091 (Hartree/Particle)
Thermal correction to Energy=			0.293173
Thermal correction to Enthalpy=			0.294117
Thermal correction to Gibbs Free Energy=			0.216891
Sum of electronic and zero-point Energies=			-1738.382549
Sum of electronic and thermal Energies=			-1738.359466
Sum of electronic and thermal Enthalpies=			-1738.358522
Sum of electronic and thermal Free Energies=			-1738.435749

S	-1.97707600	1.09821600	-0.68665200
Na	-2.51650000	3.72535600	1.24768200
O	-2.91268100	2.19613200	-0.32590000
O	-2.04005500	0.52381000	-2.02553900
N	0.56218200	0.86509000	-0.58707200
N	-0.47616900	1.76737600	-0.42440100
C	1.72739900	1.30171000	-0.24331900
C	-3.21806700	-2.20433700	1.42886300
C	-2.40045600	-2.13221500	2.55585500
C	-1.48887800	-1.09005300	2.68628000
C	-1.38183500	-0.13032400	1.68033900
C	-2.18504300	-0.21349800	0.54266300
C	-3.12944800	-1.25002500	0.41386500
H	-0.55566800	3.29919200	1.59099400
H	-0.45062300	2.45601000	0.42246600
H	1.87198500	2.31457600	0.14283200
H	-3.94104700	-3.00476300	1.33591800

H	-0.85401000	-1.01724800	3.56280500
H	-0.67510300	0.68232600	1.79216300
H	-2.48653500	-2.88787300	3.32939100
C	-4.06318400	-1.39606500	-0.76734700
F	-3.44533100	-1.89233500	-1.85571400
F	-4.62916900	-0.21838900	-1.11409100
F	-5.08119800	-2.24076100	-0.48172800
C	2.87720700	0.43917600	-0.36677800
H	2.68823400	-0.55321900	-0.76746200
C	4.11542400	0.83932400	-0.00435100
H	4.22732200	1.85015100	0.38636100
C	5.35047500	0.06223000	-0.07464600
C	6.55434300	0.67036700	0.32687300
C	5.39726300	-1.27200000	-0.52543900
C	7.76150200	-0.02298900	0.27891400
H	6.53384900	1.69854500	0.67764100
C	6.60294700	-1.96295200	-0.57271600
H	4.48607500	-1.77116800	-0.83825400
C	7.79110500	-1.34329900	-0.17174900
H	8.67811400	0.46728900	0.59290100
H	6.61883900	-2.99055700	-0.92346700
H	8.72985400	-1.88737100	-0.21058500

## TS1

Zero-point correction=	0.267420 (Hartree/Particle)
Thermal correction to Energy=	0.290294
Thermal correction to Enthalpy=	0.291238
Thermal correction to Gibbs Free Energy=	0.214096
Sum of electronic and zero-point Energies=	-1738.384938

Sum of electronic and thermal Energies=	-1738.362065
Sum of electronic and thermal Enthalpies=	-1738.361121
Sum of electronic and thermal Free Energies=	-1738.438262

S	-1.94812000	1.10861000	-0.64369500
Na	-2.43598200	3.71483400	1.29310900
O	-2.88577100	2.20280300	-0.26341100
O	-2.01178800	0.57242400	-2.00100100
N	0.57173900	0.84375000	-0.48625200
N	-0.45641800	1.75862300	-0.32750200
C	1.74888900	1.29928400	-0.21086400
C	-3.29620800	-2.22981300	1.35428400
C	-2.48422600	-2.21870800	2.48742800
C	-1.54491600	-1.20730600	2.65721500
C	-1.40530500	-0.21797200	1.68443200
C	-2.20302700	-0.23900300	0.54001700
C	-3.17464400	-1.24452700	0.37252800
H	-0.49246400	3.13265600	1.62807100
H	-0.44166900	2.44867700	0.61112300
H	1.90612700	2.33613100	0.09923800
H	-4.04033200	-3.00637800	1.23071100
H	-0.91326700	-1.18216200	3.53884100
H	-0.67444200	0.56811800	1.82470500
H	-2.59600200	-2.99732100	3.23449200
C	-4.10403000	-1.32747100	-0.81823700
F	-3.49393400	-1.81223900	-1.91650400
F	-4.63288600	-0.12510200	-1.13565000
F	-5.14962800	-2.14934500	-0.56357000
C	2.89397300	0.42789800	-0.31446600
H	2.68957800	-0.58934100	-0.63827400

C	4.14612400	0.84596100	-0.02749400
H	4.27526800	1.88072700	0.28818600
C	5.37585300	0.05964400	-0.09128400
C	6.59643800	0.68732800	0.21997400
C	5.40216800	-1.30296800	-0.44969500
C	7.79907200	-0.01403200	0.17360300
H	6.59249900	1.73743100	0.49923200
C	6.60334200	-2.00196200	-0.49539800
H	4.47823500	-1.81785700	-0.69179600
C	7.80802800	-1.36260200	-0.18493800
H	8.72845100	0.49219900	0.41702200
H	6.60266200	-3.05157100	-0.77409000
H	8.74315400	-1.91301000	-0.22208700

### Int1

Zero-point correction=	0.254807 (Hartree/Particle)
Thermal correction to Energy=	0.276950
Thermal correction to Enthalpy=	0.277894
Thermal correction to Gibbs Free Energy=	0.202641
Sum of electronic and zero-point Energies=	-1737.250760
Sum of electronic and thermal Energies=	-1737.228617
Sum of electronic and thermal Enthalpies=	-1737.227673
Sum of electronic and thermal Free Energies=	-1737.302926

S	-2.45288400	1.20602900	-0.69273800
Na	-2.00731100	3.95016500	0.15042700
O	-3.44205100	2.29542200	-0.38971800
O	-2.51873300	0.62837700	-2.04299200
N	0.01988400	1.06397300	-0.33985600



N	-1.03575800	1.92166700	-0.26119100
C	1.18087200	1.56056500	-0.06020400
C	-2.74870800	-2.34327500	1.42178900
C	-3.27553800	-1.88051500	2.62467700
C	-3.57070000	-0.52904400	2.77606300
C	-3.32528200	0.34946400	1.72475800
C	-2.79328100	-0.10781500	0.51599700
C	-2.49529900	-1.47539800	0.35317800
H	1.29515800	2.61948500	0.20599400
H	-2.53137500	-3.39660800	1.30423500
H	-3.99138900	-0.15517100	3.70379400
H	-3.56191500	1.40119800	1.82801800
H	-3.45780700	-2.57942100	3.43420300
C	-1.98930500	-2.10756000	-0.93048800
F	-0.88216600	-1.52664200	-1.42004600
F	-2.93099600	-2.09698400	-1.89729000
F	-1.67018100	-3.41363200	-0.73158300
C	2.34754500	0.71680300	-0.09402900
H	2.16137900	-0.31892100	-0.36846300
C	3.59487800	1.15543300	0.19010300
H	3.71808000	2.20541100	0.45499500
C	4.82665300	0.36975100	0.18311100
C	6.04245200	1.00787300	0.49536200
C	4.86448700	-1.00646900	-0.12132500
C	7.24604400	0.30647600	0.50329800
H	6.03376700	2.06844100	0.73280400
C	6.06666800	-1.70559800	-0.11300200
H	3.94706800	-1.53201600	-0.36576200
C	7.26512900	-1.05534000	0.19881000
H	8.16940900	0.82389700	0.74719800

H	6.07103200	-2.76538300	-0.35105800
H	8.20093600	-1.60585900	0.20384300

## TS2

Zero-point correction=	0.251755 (Hartree/Particle)		
Thermal correction to Energy=	0.274183		
Thermal correction to Enthalpy=	0.275127		
Thermal correction to Gibbs Free Energy=	0.198605		
Sum of electronic and zero-point Energies=	-1737.214703		
Sum of electronic and thermal Energies=	-1737.192276		
Sum of electronic and thermal Enthalpies=	-1737.191332		
Sum of electronic and thermal Free Energies=	-1737.267853		

S	2.28255400	1.10401800	0.73452200
Na	2.38926300	3.90606300	-0.17119500
O	3.31512900	2.21343000	0.89349500
O	1.65429100	0.60031000	1.98870100
N	-0.23411400	1.71973300	-0.38454000
N	0.89105000	2.17044600	-0.51987100
C	-1.46620100	1.95083600	-0.74013600
C	3.54999600	-2.52778100	-0.78959800
C	4.86958300	-2.24000400	-1.13546900
C	5.38455800	-0.96640000	-0.90933900
C	4.57911800	0.01770000	-0.33677300
C	3.26505100	-0.27251500	0.02813700
C	2.73321300	-1.55280500	-0.21246900
H	-1.69146500	2.82874500	-1.35100800
H	3.14575300	-3.51593800	-0.97168500
H	6.41082000	-0.73376700	-1.17533400

H	4.96307000	1.01281000	-0.14853600
H	5.48682700	-3.01122100	-1.58417400
C	1.32416100	-1.94642500	0.15905400
F	0.42534300	-0.98665100	-0.16008700
F	1.19026500	-2.20460000	1.47537200
F	0.93671100	-3.06690600	-0.49530400
C	-2.51204600	1.05210400	-0.34010800
H	-2.18432400	0.19608200	0.24609400
C	-3.81807700	1.21619100	-0.65928400
H	-4.09374300	2.08890500	-1.25097800
C	-4.92566400	0.33777500	-0.29489300
C	-6.22794500	0.66719200	-0.72100400
C	-4.76632000	-0.83804500	0.46854800
C	-7.32065200	-0.13598200	-0.40252200
H	-6.37515100	1.56882400	-1.31008200
C	-5.85824700	-1.63897100	0.78580800
H	-3.77959000	-1.12644500	0.81646800
C	-7.14348000	-1.29586900	0.35342900
H	-8.31249000	0.14480100	-0.74567800
H	-5.70692100	-2.53900000	1.37521600
H	-7.99262000	-1.92455200	0.60368600

## Int2

Zero-point correction=	0.147483 (Hartree/Particle)
Thermal correction to Energy=	0.156664
Thermal correction to Enthalpy=	0.157608
Thermal correction to Gibbs Free Energy=	0.112829
Sum of electronic and zero-point Energies=	-457.278500
Sum of electronic and thermal Energies=	-457.269319

Sum of electronic and thermal Enthalpies= -457.268375

Sum of electronic and thermal Free Energies= -457.313154

N	3.94707700	0.11343500	-0.00008300
N	4.87776000	0.78339600	-0.00022400
C	2.88792800	-0.64448900	0.00008400
H	3.08214900	-1.71088700	0.00019300
C	1.56924400	-0.07069600	0.00007800
H	1.52480400	1.01547900	-0.00008800
C	0.43768000	-0.81264800	0.00020300
H	0.53664800	-1.89707900	0.00031100
C	-0.93449600	-0.31221300	0.00013100
C	-1.99332400	-1.24132000	-0.00006700
C	-1.26544600	1.05861500	0.00017000
C	-3.32246800	-0.82453800	-0.00018800
H	-1.76064100	-2.30292300	-0.00014400
C	-2.59305000	1.47321100	0.00004000
H	-0.47968700	1.80740200	0.00032000
C	-3.63140600	0.53639300	-0.00011600
H	-4.11789900	-1.56426300	-0.00031700
H	-2.82116700	2.53528100	0.00006800
H	-4.66604400	0.86528900	-0.00020100

### Int3

Zero-point correction= 0.372887 (Hartree/Particle)

Thermal correction to Energy= 0.420007

Thermal correction to Enthalpy= 0.420952

Thermal correction to Gibbs Free Energy= 0.287953

Sum of electronic and zero-point Energies= -3330.048037

Sum of electronic and thermal Energies=	-3330.000916
Sum of electronic and thermal Enthalpies=	-3329.999972
Sum of electronic and thermal Free Energies=	-3330.132971

Ag	0.84325400	1.03441500	-0.32344700
N	-1.48178100	1.67159100	-0.49177500
N	-2.39410700	0.68321200	-0.50015200
N	-0.05075400	-0.92488300	-1.35022300
N	-1.13306100	-1.49436400	-0.78394000
N	-0.10070700	-0.10022300	1.59235300
N	-1.39214100	-0.47046800	1.51434200
B	-2.08387200	-0.69338100	0.14402300
C	-2.00930400	2.69036400	-1.17254100
C	-3.29455900	2.37918300	-1.63974300
C	-3.49949500	1.08561000	-1.18635900
C	0.56937200	-1.88123600	-2.04389700
C	-0.10570300	-3.10639500	-1.93727500
C	-1.18563300	-2.81228500	-1.12216600
C	0.17162700	0.07549200	2.88675000
C	-0.95252800	-0.18359500	3.68451900
C	-1.92935300	-0.52843400	2.76420800
H	-3.08900700	-1.29565000	0.29640400
C	-3.34854800	-0.90989500	3.02954700
C	1.53445000	0.52659000	3.28592100
C	-2.25525900	-3.74135200	-0.64815200
C	1.86597200	-1.59122800	-2.72107100
C	-4.70121700	0.22207500	-1.38656100
C	-1.19328100	3.92091900	-1.37536100
H	-1.04275100	-0.13688200	4.75797900
H	0.14627600	-4.05474700	-2.38460900

H	-3.97306200	2.99532500	-2.20771300
F	-3.61046700	-0.82170900	4.34908100
F	-3.62363600	-2.17371900	2.64364000
F	-4.21892200	-0.10042600	2.38505000
F	2.50231000	-0.26442800	2.76513400
F	1.67833300	0.53427900	4.62173200
F	1.79955100	1.78661200	2.84178000
F	-1.92240000	4.90957700	-1.92089300
F	-0.66750300	4.37667800	-0.21515300
F	-0.13612900	3.69242600	-2.20245900
F	-5.30063600	-0.10782000	-0.22337100
F	-5.61118700	0.86708400	-2.14427500
F	-4.39220400	-0.93436300	-2.01525500
F	-3.47858000	-3.40034900	-1.10422200
F	-1.99790400	-4.99402200	-1.07476200
F	-2.33028600	-3.77673400	0.70130400
F	1.93384200	-0.31050100	-3.15907900
F	2.05711400	-2.40134000	-3.77962100
F	2.91766100	-1.77007800	-1.88639800
C	7.07408600	-2.02123900	-0.78237100
C	6.15804600	-1.04954700	-1.17999900
C	5.36293200	-0.37104700	-0.23780600
C	5.50250500	-0.71664400	1.12127800
C	6.41828000	-1.68701500	1.51606700
C	7.21207600	-2.34236400	0.56906900
H	7.67838200	-2.52914100	-1.52852300
H	6.05209200	-0.80388400	-2.23333000
H	4.87621600	-0.24338700	1.87001000
H	6.50826700	-1.94100100	2.56843000
H	7.92285600	-3.10100900	0.88261200

C	4.42339700	0.64277900	-0.71474300
C	3.70270400	1.48244300	0.05487500
H	4.29257300	0.69004900	-1.79386200
H	3.79249200	1.47950900	1.13615000
C	2.70575500	2.40719800	-0.50041000
H	2.68603400	2.63625000	-1.56398400
N	2.37733600	3.47052400	0.24315100
N	2.05914200	4.33764300	0.89903600

### TS3

Zero-point correction=	0.370931 (Hartree/Particle)
Thermal correction to Energy=	0.418131
Thermal correction to Enthalpy=	0.419075
Thermal correction to Gibbs Free Energy=	0.284757
Sum of electronic and zero-point Energies=	-3330.027925
Sum of electronic and thermal Energies=	-3329.980726
Sum of electronic and thermal Enthalpies=	-3329.979782
Sum of electronic and thermal Free Energies=	-3330.114100

Ag	0.82557400	0.97115400	-0.36501600
N	-1.46755600	1.71514400	-0.30326800
N	-2.45457700	0.80465600	-0.38687800
N	-0.26098000	-0.84857600	-1.45377500
N	-1.36592200	-1.41011600	-0.93060700
N	-0.18079800	-0.34676400	1.52277000
N	-1.49648200	-0.61843100	1.46127300
B	-2.23831300	-0.65123700	0.10126900
C	-1.94232500	2.84598500	-0.83070400
C	-3.26390300	2.68687600	-1.27251100

C	-3.54957200	1.36508100	-0.96956400
C	0.30503100	-1.76762900	-2.23851000
C	-0.43362900	-2.96009800	-2.23834300
C	-1.49269800	-2.68573100	-1.38815800
C	0.13945300	-0.30662400	2.81751900
C	-0.97715600	-0.55671300	3.63071700
C	-2.00248600	-0.74969700	2.71924800
H	-3.28216700	-1.19259100	0.22150900
C	-3.43683700	-1.05486800	2.99606700
C	1.54060900	0.00999800	3.21271100
C	-2.61531300	-3.58854700	-0.99506600
C	1.60148800	-1.46358100	-2.90989500
C	-4.81866700	0.61811100	-1.21663900
C	-1.05728400	4.04296400	-0.91074600
H	-1.03183400	-0.60043800	4.70671800
H	-0.23538500	-3.87458800	-2.77399100
H	-3.91301400	3.41520900	-1.73167400
F	-3.65596900	-1.07959900	4.32634400
F	-3.81438500	-2.25251200	2.49940100
F	-4.26480600	-0.12755700	2.46320700
F	2.43854400	-0.78066300	2.57422200
F	1.72333900	-0.14381300	4.53605300
F	1.88126200	1.29054600	2.90384900
F	-1.74591200	5.13264000	-1.29572200
F	-0.47067700	4.31801100	0.27768000
F	-0.04481900	3.86902400	-1.80137900
F	-5.41398600	0.21625000	-0.07390100
F	-5.69454900	1.40280200	-1.87638500
F	-4.61532700	-0.48794700	-1.96748900
F	-3.81728200	-3.12236200	-1.39503500



F	-2.44552000	-4.80466500	-1.55219300
F	-2.68258000	-3.75878700	0.34466000
F	1.59946500	-0.24222300	-3.49348400
F	1.88218600	-2.37622100	-3.85906200
F	2.63580900	-1.46351200	-2.03083800
C	8.05092800	-1.41527700	-0.64160500
C	7.05559800	-0.52084200	-1.02610800
C	5.93119200	-0.29546300	-0.20870600
C	5.82142500	-1.01505600	0.99941000
C	6.81681800	-1.90829400	1.37934200
C	7.93576700	-2.11037100	0.56395700
H	8.91307900	-1.57300100	-1.28252800
H	7.14357400	0.01963800	-1.96459100
H	4.94787100	-0.88998200	1.63018600
H	6.71806600	-2.45821100	2.31043200
H	8.70752400	-2.81283500	0.86386200
C	4.93721900	0.67787100	-0.64218000
C	3.87334900	1.11599100	0.07807200
H	5.05275500	1.04933100	-1.65994400
H	3.73190200	0.80507500	1.10759900
C	2.78071900	1.80211500	-0.57135900
H	3.03339500	2.22577100	-1.54570800
N	2.62780200	3.35718800	0.30272700
N	2.30598700	4.00356700	1.14868800

#### Int4

Zero-point correction=	0.363724 (Hartree/Particle)
Thermal correction to Energy=	0.408793
Thermal correction to Enthalpy=	0.409737

Thermal correction to Gibbs Free Energy=	0.280421
Sum of electronic and zero-point Energies=	-3220.487377
Sum of electronic and thermal Energies=	-3220.442308
Sum of electronic and thermal Enthalpies=	-3220.441363
Sum of electronic and thermal Free Energies=	-3220.570679

Ag	0.91163200	-1.09340900	-0.01551200
N	-1.07612600	-1.33190900	-1.25830400
N	-2.23676900	-0.80250900	-0.82757400
N	-0.70194900	-0.68229500	1.67491000
N	-1.77770200	0.10149800	1.48180300
N	0.02967400	1.41437700	-0.40582800
N	-1.30383300	1.53117800	-0.54304500
B	-2.25885400	0.47158400	0.05651900
C	-1.38931400	-2.41732500	-1.97214200
C	-2.77642100	-2.61602500	-2.01108100
C	-3.27768300	-1.56190400	-1.26469000
C	-0.51485900	-0.76356000	2.99452700
C	-1.48027900	-0.02080100	3.68980300
C	-2.26577200	0.51540500	2.68246800
C	0.56630100	2.42455700	-1.09345500
C	-0.42000700	3.22452500	-1.69445200
C	-1.60347700	2.61481500	-1.31545100
H	-3.35976300	0.89963200	0.10216800
C	-2.99658800	3.02339400	-1.65741700
C	2.04723300	2.55608900	-1.18908500
C	-3.46192000	1.39884600	2.81921000
C	0.64661300	-1.52613300	3.53777300
C	-4.70568300	-1.27091400	-0.93627500
C	-0.30924100	-3.26898000	-2.55082600

H	-0.29541900	4.10814700	-2.29969100
H	-1.59577600	0.10184900	4.75480800
H	-3.32989800	-3.39786200	-2.50583500
F	-2.97709400	4.11017100	-2.45652500
F	-3.72754700	3.33665800	-0.56557800
F	-3.66597600	2.04864500	-2.31378900
F	2.64944700	2.50673700	0.02851100
F	2.39604900	3.72253600	-1.76526500
F	2.60303300	1.56141300	-1.92416200
F	-0.81189600	-4.13166300	-3.45559200
F	0.64748800	-2.53574000	-3.16150200
F	0.31872900	-4.00654500	-1.59958800
F	-5.13659200	-0.10585700	-1.46218800
F	-5.49638100	-2.25034700	-1.42058800
F	-4.91058300	-1.20346200	0.39866800
F	-4.58947600	0.81500500	2.36020300
F	-3.66293000	1.70437900	4.11710100
F	-3.31491400	2.56098300	2.14431100
F	0.77231700	-2.74429300	2.96439600
F	0.52329000	-1.70584700	4.86744400
F	1.82066800	-0.87877100	3.32731800
C	8.83585700	0.11551100	-0.06704600
C	7.70703200	-0.69322800	-0.05918000
C	6.41366300	-0.12315200	-0.03066800
C	6.28408300	1.28739800	-0.02405500
C	7.41573000	2.08806500	-0.03585700
C	8.69056700	1.50605300	-0.05469600
H	9.82540500	-0.32922100	-0.08487300
H	7.80535600	-1.77461800	-0.06987200
H	5.30083000	1.74416900	-0.02294900

H	7.31379900	3.16832600	-0.03378400
H	9.57163000	2.14061500	-0.06387300
C	5.27836700	-1.00157300	-0.00735400
C	3.94734700	-0.63044200	0.08219700
H	5.49623500	-2.06738800	-0.07855700
H	3.70100700	0.41977900	0.18353900
C	2.91113300	-1.56618400	-0.00519500
H	3.28631400	-2.59615400	-0.05923000

### Int5-cis

Zero-point correction=	0.532151 (Hartree/Particle)
Thermal correction to Energy=	0.587067
Thermal correction to Enthalpy=	0.588012
Thermal correction to Gibbs Free Energy=	0.438378
Sum of electronic and zero-point Energies=	-3607.585790
Sum of electronic and thermal Energies=	-3607.530874
Sum of electronic and thermal Enthalpies=	-3607.529930
Sum of electronic and thermal Free Energies=	-3607.679563

Ag	0.30038900	-0.60602600	-1.16953700
N	0.77189300	0.73231200	1.43504700
N	2.01928700	0.25955400	1.61565800
N	2.34289700	-1.53028200	-0.69661000
N	3.37409700	-0.79845900	-0.23306800
N	1.79735700	1.35313800	-1.37116300
N	2.68591400	1.61766000	-0.39821000
B	3.13973400	0.50920900	0.56921500
C	0.07272400	0.34114100	2.50509500
C	0.85787100	-0.40722600	3.39872300

C	2.09952500	-0.43403200	2.78874300
C	2.87316100	-2.58899900	-1.32093600
C	4.27256600	-2.55667900	-1.27106100
C	4.54726100	-1.39476000	-0.56823100
C	1.52771900	2.51519000	-1.96771100
C	2.24689700	3.56963200	-1.38150900
C	2.97368600	2.94769500	-0.38045000
H	4.14671700	0.81651000	1.11302100
C	3.93959500	3.55585900	0.57972700
C	0.50577300	2.57447100	-3.05148300
C	5.88469900	-0.84591500	-0.19030400
C	1.99281800	-3.61788600	-1.94713700
C	3.34287700	-1.09711800	3.27766200
C	-1.37320700	0.67108000	2.62774100
H	2.24825700	4.61428300	-1.64893600
H	4.97486500	-3.26810100	-1.67460800
H	0.57558400	-0.84540600	4.34302800
F	3.97973800	4.89339800	0.41555200
F	5.19583000	3.08769200	0.41092200
F	3.59893600	3.31204200	1.86602300
F	0.56829300	1.50230600	-3.87245300
F	0.66107500	3.68326700	-3.80354400
F	-0.75628800	2.60565900	-2.55380700
F	-1.73531100	0.82701500	3.91727800
F	-1.69688500	1.80519900	1.96528000
F	-2.17290200	-0.31019300	2.12256300
F	4.36121000	-0.22996900	3.46006900
F	3.11108500	-1.70488000	4.45893800
F	3.78713100	-2.04515300	2.41720100
F	6.08571400	-0.84941500	1.14400300

F	6.86001100	-1.59138800	-0.74865500
F	6.04968400	0.42661800	-0.61494400
F	1.15733300	-4.18514100	-1.04334900
F	2.72544100	-4.60256400	-2.49814300
F	1.20590600	-3.09998300	-2.92292400
C	-7.33638800	1.86135200	-1.01391100
C	-6.30301300	1.05132800	-1.46728200
C	-5.02316700	1.11199000	-0.87422400
C	-4.81704300	1.99935700	0.20736100
C	-5.85347100	2.80480100	0.65732600
C	-7.11294800	2.74032800	0.04849300
H	-8.31626900	1.80116000	-1.47545700
H	-6.47032900	0.35993100	-2.28723200
H	-3.85277500	2.04233200	0.69957900
H	-5.68771600	3.48223000	1.48904900
H	-7.92028600	3.37074400	0.40854800
C	-3.98819300	0.24572400	-1.37834300
C	-2.66025300	0.21929100	-0.99093000
H	-4.28329600	-0.42925700	-2.17947100
H	-2.32747300	0.88955300	-0.20678600
C	-1.72670300	-0.63992700	-1.58461000
H	-2.16103700	-1.26244200	-2.37361400
C	-9.01991400	-1.16886500	0.31122900
C	-7.89948100	-1.83390500	-0.17945900
C	-6.63252000	-1.65804300	0.41137600
C	-6.52616200	-0.78361200	1.51304100
C	-7.64525400	-0.12059600	2.00041000
C	-8.89678000	-0.30764300	1.40312000
H	-9.98722400	-1.31965300	-0.15878200
H	-7.99453600	-2.50249000	-1.03092400

H	-5.56284500	-0.61531400	1.98176200
H	-7.54330800	0.55481700	2.84423700
H	-9.76718900	0.21588300	1.78699100
C	-5.49189300	-2.36098300	-0.15621100
H	-5.71012400	-2.97937900	-1.02659300
C	-4.20774800	-2.31704100	0.28150500
H	-3.94527700	-1.71212300	1.14457200
C	-3.13006900	-3.01565000	-0.36320000
H	-3.38069300	-3.62640400	-1.22984100
C	-1.83671000	-2.90144100	0.01863400
H	-1.55754900	-2.32168500	0.89163500
H	-1.04608900	-3.43955100	-0.48885900

### Int5-trans

Zero-point correction=	0.531460 (Hartree/Particle)
Thermal correction to Energy=	0.586779
Thermal correction to Enthalpy=	0.587723
Thermal correction to Gibbs Free Energy=	0.436320
Sum of electronic and zero-point Energies=	-3607.583159
Sum of electronic and thermal Energies=	-3607.527841
Sum of electronic and thermal Enthalpies=	-3607.526897
Sum of electronic and thermal Free Energies=	-3607.678299

Ag	0.05596300	-0.57655800	-0.49734900
N	1.55157400	-1.14919500	1.25687200
N	2.73044600	-0.52263700	1.43275300
N	2.17348200	-0.66877900	-1.68170300
N	3.33516300	-0.53919400	-1.01697500
N	1.30238100	1.65674200	0.17727400

N	2.64519000	1.61674600	0.11082500
B	3.40669600	0.28211600	0.29245200
C	1.21940600	-1.67683500	2.43878800
C	2.18747500	-1.39569500	3.41308000
C	3.13398900	-0.65474500	2.72512600
C	2.41499200	-1.46977900	-2.72241100
C	3.75656600	-1.88044100	-2.74895900
C	4.30736200	-1.26205100	-1.63829400
C	0.95139800	2.91979000	-0.07235500
C	2.07396600	3.73124100	-0.30891200
C	3.13755600	2.85387500	-0.18142800
H	4.53714600	0.49296900	0.56770400
C	4.59433600	3.14427800	-0.31374400
C	-0.49019300	3.29329700	-0.12708800
C	5.71270100	-1.34550200	-1.14180900
C	1.29814400	-1.86803300	-3.62712400
C	4.40209700	-0.06835900	3.25320700
C	-0.07084800	-2.40582800	2.59957600
H	2.10945000	4.78665900	-0.52699100
H	4.25102600	-2.51866100	-3.46378000
H	2.20293000	-1.68994200	4.45012700
F	4.78121000	4.43380800	-0.66250300
F	5.18177900	2.37682600	-1.26013500
F	5.26980900	2.93430600	0.83764500
F	-0.64712000	4.63142700	-0.07847800
F	-1.19723600	2.75993900	0.90133600
F	-1.08804600	2.86252600	-1.26482500
F	-0.11377500	-3.05654200	3.77769300
F	-1.13686300	-1.56170700	2.57043100
F	-0.27219200	-3.31278200	1.61758000



F	4.46037900	1.26930300	3.06450500
F	4.49646100	-0.29611100	4.57915400
F	5.49882300	-0.59829500	2.67157900
F	5.77364400	-1.81645700	0.12485500
F	6.42829900	-2.18221700	-1.92097300
F	6.33935600	-0.15015600	-1.14831900
F	0.48283700	-2.78874600	-3.04970100
F	1.77088600	-2.41612200	-4.76432200
F	0.51344400	-0.82096500	-3.96424300
C	-7.49306700	2.02611300	-1.28268700
C	-6.44910100	1.14817500	-1.54508600
C	-5.20113700	1.29858600	-0.90179400
C	-5.02705500	2.36519000	0.01065900
C	-6.07299400	3.23966100	0.26713500
C	-7.30679200	3.07107500	-0.37485700
H	-8.45086500	1.89381000	-1.77393100
H	-6.58542500	0.33001300	-2.24494500
H	-4.06771200	2.51743700	0.49269600
H	-5.93286900	4.05948900	0.96444300
H	-8.12137800	3.75791300	-0.16617500
C	-4.15734400	0.35495000	-1.20136500
C	-2.89540100	0.29073300	-0.63664000
H	-4.38143200	-0.36516800	-1.98673900
H	-2.65100300	0.95612800	0.18428700
C	-1.91486300	-0.58586200	-1.11533600
H	-2.27585100	-1.20104400	-1.94576100
C	-8.64821000	0.39615900	1.63560000
C	-7.34953600	-0.09893500	1.71978000
C	-6.90587900	-1.12204800	0.86180000
C	-7.81432500	-1.63950500	-0.08362400

C	-9.11287000	-1.14743600	-0.16362200
C	-9.53650700	-0.12663400	0.69383400
H	-8.96675700	1.19116700	2.30313000
H	-6.65750800	0.31243800	2.44907800
H	-7.50439500	-2.43874600	-0.74939000
H	-9.80084800	-1.56217100	-0.89467200
H	-10.55102300	0.25486700	0.62805700
C	-5.52858600	-1.58630600	0.98184000
H	-4.97264500	-1.17094600	1.82161100
C	-4.87513100	-2.44594300	0.16461700
H	-5.37336500	-2.86556000	-0.70785500
C	-3.49410800	-2.81415400	0.37119900
H	-3.01478500	-2.43500000	1.27034700
C	-2.77235900	-3.55008200	-0.49487700
H	-3.21017700	-3.93682800	-1.41249500
H	-1.73128700	-3.78295100	-0.30579500

#### TS4-cis

Zero-point correction=	0.532068 (Hartree/Particle)
Thermal correction to Energy=	0.586144
Thermal correction to Enthalpy=	0.587088
Thermal correction to Gibbs Free Energy=	0.439255
Sum of electronic and zero-point Energies=	-3607.584455
Sum of electronic and thermal Energies=	-3607.530379
Sum of electronic and thermal Enthalpies=	-3607.529435
Sum of electronic and thermal Free Energies=	-3607.677268

Ag	0.23936900	-0.67809800	-1.02105800
N	0.84551500	0.74132000	1.46096300

N	2.12345500	0.34510200	1.61008800
N	2.33149600	-1.59520400	-0.58398000
N	3.37951100	-0.82298900	-0.24246100
N	1.67773900	1.23106000	-1.41442600
N	2.63935800	1.56478600	-0.53618400
B	3.17084300	0.53391400	0.47953100
C	0.22789700	0.42812500	2.60448300
C	1.09881900	-0.19190500	3.51671500
C	2.30375100	-0.22447100	2.83723800
C	2.83425000	-2.67964100	-1.18527400
C	4.23313600	-2.62404200	-1.24374400
C	4.53691800	-1.41914100	-0.63065300
C	1.37708900	2.33905600	-2.09370400
C	2.14988400	3.42780000	-1.65998300
C	2.94223100	2.88528300	-0.66223700
H	4.20294900	0.89551500	0.93549800
C	3.98308400	3.56393100	0.16361600
C	0.27974400	2.31626700	-3.10310500
C	5.88614900	-0.82239700	-0.39515500
C	1.92336600	-3.74225400	-1.70004600
C	3.60674000	-0.77481900	3.31032300
C	-1.22085600	0.71785200	2.78649700
H	2.14255600	4.44429800	-2.01963000
H	4.91755700	-3.34625000	-1.65893800
H	0.89310800	-0.54400800	4.51525600
F	4.01601900	4.88108800	-0.12224500
F	5.22003100	3.06875500	-0.05929800
F	3.74154800	3.43930300	1.48848200
F	0.30617200	1.19638600	-3.86109600
F	0.36102800	3.37844600	-3.92949200

F	-0.94373300	2.35702600	-2.51926100
F	-1.51259400	0.96747200	4.07902100
F	-1.62314700	1.78304200	2.05647000
F	-2.01337200	-0.32587400	2.41112100
F	4.57678100	0.16196400	3.37600600
F	3.46835300	-1.30117800	4.54412500
F	4.06749100	-1.75834100	2.50063200
F	6.18714500	-0.72250900	0.91641300
F	6.83403500	-1.58975800	-0.97074100
F	5.98933800	0.41820000	-0.92211900
F	1.10630400	-4.22227600	-0.73067500
F	2.62444900	-4.77854200	-2.19401400
F	1.11280700	-3.29042400	-2.69073900
C	-7.26301100	2.04875800	-0.99251600
C	-6.26019000	1.18944500	-1.42779700
C	-5.00760400	1.15124200	-0.78221100
C	-4.79604800	1.99781700	0.32813300
C	-5.79997800	2.85566100	0.75914000
C	-7.03516300	2.88597800	0.10157900
H	-8.22347700	2.05985200	-1.49763200
H	-6.43683800	0.53096700	-2.27288100
H	-3.85007700	1.97538200	0.85669000
H	-5.62465600	3.50174900	1.61396000
H	-7.81711700	3.55605900	0.44587900
C	-4.01317000	0.20675800	-1.25014100
C	-2.73587300	0.04660200	-0.77301800
H	-4.31690000	-0.42104500	-2.08582600
H	-2.40424000	0.65945200	0.05725900
C	-1.82152600	-0.88916700	-1.31743200
H	-2.23166800	-1.44762200	-2.16389800

C	-9.06740200	-1.11469500	0.07438900
C	-7.92739600	-1.80823800	-0.32178100
C	-6.70895600	-1.65741700	0.37012500
C	-6.67073900	-0.78141200	1.47527300
C	-7.80977500	-0.09157800	1.86927500
C	-9.01189000	-0.25239800	1.17111600
H	-9.99685200	-1.24395200	-0.47189200
H	-7.96752900	-2.47654800	-1.17782500
H	-5.74527800	-0.63620500	2.02118700
H	-7.76166600	0.58457000	2.71707500
H	-9.89777300	0.29358600	1.48111200
C	-5.54139600	-2.37300400	-0.11294700
H	-5.70791400	-3.00224300	-0.98670300
C	-4.27748900	-2.31804700	0.38914500
H	-4.05578500	-1.69149600	1.24865000
C	-3.17454600	-2.98162400	-0.22580300
H	-3.38662100	-3.62508200	-1.07835300
C	-1.87129100	-2.74610100	0.12353500
H	-1.63017000	-2.18475900	1.01827900
H	-1.06610100	-3.30406200	-0.33474900

#### TS4-trans

Zero-point correction=	0.532005 (Hartree/Particle)
Thermal correction to Energy=	0.586284
Thermal correction to Enthalpy=	0.587228
Thermal correction to Gibbs Free Energy=	0.437878
Sum of electronic and zero-point Energies=	-3607.579554
Sum of electronic and thermal Energies=	-3607.525276
Sum of electronic and thermal Enthalpies=	-3607.524332

Sum of electronic and thermal Free Energies= -3607.673682

g	-0.04056500	-0.55179000	0.31300300
N	1.89629900	-0.64980300	1.64635800
N	3.04787500	-0.05951800	1.27315600
N	1.68951900	-1.22530900	-1.35572200
N	2.97774000	-0.94614700	-1.09095800
N	1.23329100	1.62645300	-0.21693700
N	2.50753800	1.49593000	-0.62780600
B	3.35470300	0.27040200	-0.21269100
C	1.92156200	-0.72920200	2.98051500
C	3.10235900	-0.18256600	3.50111700
C	3.79075500	0.23487900	2.37365000
C	1.68157100	-2.36576900	-2.04884200
C	2.98349400	-2.85284000	-2.24896000
C	3.78086700	-1.91252900	-1.61782500
C	0.77132400	2.74991000	-0.76950200
C	1.75001900	3.37457000	-1.56072000
C	2.84526700	2.53581400	-1.44058700
H	4.50607900	0.50996400	-0.33610900
C	4.19812600	2.68764200	-2.05013300
C	-0.64811100	3.15345400	-0.55594800
C	5.26793700	-1.89939800	-1.49411300
C	0.38279400	-2.99714700	-2.41736300
C	5.12265000	0.90838400	2.30981600
C	0.76862000	-1.32448900	3.71457400
H	1.67916100	4.29296000	-2.12144400
H	3.29780000	-3.74011500	-2.77521700
H	3.41200000	-0.10673600	4.53106000
F	4.22047000	3.75785900	-2.87048200

F	4.55026100	1.60519200	-2.78104100
F	5.16470000	2.86731000	-1.12320000
F	-0.82826200	4.46157400	-0.82962000
F	-1.04987100	2.93917000	0.72029300
F	-1.49891200	2.46043600	-1.35101200
F	1.03449900	-1.42637900	5.02941200
F	-0.36104700	-0.58272200	3.58569300
F	0.46344300	-2.56427700	3.25814500
F	5.05883000	2.09685500	1.66819900
F	5.57834000	1.14323600	3.55724100
F	6.05027600	0.16353500	1.67288400
F	5.66830400	-1.88105500	-0.20195400
F	5.78967200	-3.00455200	-2.06479400
F	5.82855400	-0.82860100	-2.09550700
F	-0.16623400	-3.66605400	-1.36647700
F	0.54005500	-3.89272500	-3.41176400
F	-0.53738600	-2.09053400	-2.81329100
C	-7.10550200	2.83297400	-0.56297000
C	-6.22750400	1.76660800	-0.73478300
C	-4.98206500	1.74622300	-0.07432700
C	-4.62476000	2.84770700	0.73238100
C	-5.50125000	3.91441700	0.89246000
C	-6.74680600	3.90776900	0.25333700
H	-8.06679200	2.82576000	-1.06731400
H	-6.50443900	0.93069400	-1.36879200
H	-3.64603200	2.87978800	1.19803900
H	-5.21251000	4.76074500	1.50848600
H	-7.42746200	4.74404400	0.38237800
C	-4.12486800	0.58669500	-0.24077900
C	-2.99925700	0.27985300	0.48162900

H	-4.38735200	-0.07760400	-1.06103200
H	-2.73716700	0.87719200	1.35065900
C	-2.10855400	-0.73269200	0.04248000
H	-2.51329100	-1.28789200	-0.80759000
C	-9.15501500	-0.47069300	-0.12421700
C	-8.03392300	-0.74497800	0.65584500
C	-6.97484000	-1.52572300	0.15510200
C	-7.07326400	-2.01994600	-1.16187700
C	-8.19075800	-1.74083500	-1.94094100
C	-9.23669200	-0.96487700	-1.42682600
H	-9.95926200	0.13564800	0.28132900
H	-7.96352800	-0.34583200	1.66364700
H	-6.26692100	-2.61355800	-1.58030700
H	-8.24872100	-2.12498300	-2.95503000
H	-10.10546400	-0.74711800	-2.04063500
C	-5.80101600	-1.72554400	0.99304100
H	-5.82300200	-1.20637500	1.94998300
C	-4.68804500	-2.45245000	0.70598000
H	-4.59563700	-2.98968900	-0.23537400
C	-3.54385800	-2.40649800	1.55865200
H	-3.67289300	-1.90695900	2.51772800
C	-2.28226700	-2.79104900	1.20123400
H	-2.09360900	-3.32975600	0.27868700
H	-1.46890600	-2.73973000	1.91141400

## Int6

Zero-point correction=	0.535771 (Hartree/Particle)
Thermal correction to Energy=	0.589504
Thermal correction to Enthalpy=	0.590448



Thermal correction to Gibbs Free Energy=	0.443827
Sum of electronic and zero-point Energies=	-3607.642046
Sum of electronic and thermal Energies=	-3607.588314
Sum of electronic and thermal Enthalpies=	-3607.587370
Sum of electronic and thermal Free Energies=	-3607.733991

Ag	0.21339600	0.82292400	0.41821400
N	-0.34793000	-0.85895200	-1.22304500
N	-1.52160600	-1.49345400	-1.03641000
N	-1.41291300	-0.52983500	1.83224800
N	-2.56241300	-0.87153300	1.21589800
N	-1.88824600	1.59710100	-0.30004300
N	-2.76550900	0.68494000	-0.76616900
B	-2.71310500	-0.80222600	-0.32041800
C	0.39950800	-1.65529800	-1.99234400
C	-0.27949000	-2.84156200	-2.30896400
C	-1.50199700	-2.69470200	-1.67705400
C	-1.67196200	-0.54426400	3.14301600
C	-3.00192600	-0.90935800	3.40180100
C	-3.53578900	-1.10755600	2.14161500
C	-2.18853800	2.75711200	-0.88903000
C	-3.27335300	2.61651500	-1.76486700
C	-3.60811000	1.27667300	-1.65625900
H	-3.71723200	-1.33728500	-0.63769500
C	-4.68045100	0.54268200	-2.39471000
C	-1.33776400	3.95593500	-0.63795400
C	-4.94239800	-1.47835400	1.80277300
C	-0.62272000	-0.19329200	4.14175900
C	-2.64900400	-3.65216400	-1.66978100
C	1.77452900	-1.25244300	-2.40357200

H	-3.74431400	3.36837700	-2.37758400
H	-3.49755900	-1.01134600	4.35374600
H	0.05843400	-3.67002600	-2.91106100
F	-5.27651000	1.36990800	-3.27713100
F	-5.64054500	0.05847600	-1.58137700
F	-4.18238600	-0.50509000	-3.08973100
F	-0.97648800	4.05315100	0.66181100
F	-1.98159100	5.08924100	-0.97667400
F	-0.19397300	3.90961500	-1.36102600
F	2.07506700	-1.72857000	-3.62527400
F	1.92268500	0.09074600	-2.42948200
F	2.72592600	-1.73132900	-1.55584000
F	-3.71570800	-3.19049700	-2.35547700
F	-2.27747700	-4.81717900	-2.23783200
F	-3.06852700	-3.92275400	-0.41430100
F	-5.02360300	-2.62174500	1.09108900
F	-5.65428000	-1.65434000	2.93510400
F	-5.56079500	-0.51601000	1.08226000
F	0.29958800	-1.17221900	4.30161800
F	-1.17125800	0.03440300	5.35047500
F	0.05905900	0.92575600	3.78637600
C	2.41496300	5.47323600	0.12444300
C	2.19360700	4.34464700	0.91168300
C	2.44484300	3.05599700	0.41315600
C	2.92966000	2.92763700	-0.90149200
C	3.14491400	4.05483900	-1.68763700
C	2.88904800	5.33303900	-1.18006900
H	2.21381100	6.46054100	0.52967000
H	1.81719400	4.45416500	1.92502000
H	3.12554800	1.94538500	-1.31692100

H	3.51575300	3.93752300	-2.70175400
H	3.05945400	6.20958800	-1.79783900
C	2.20127900	1.90498600	1.30162100
C	2.50830900	0.59094200	1.04915500
H	1.89173200	2.16370700	2.31286600
H	2.93068300	0.32333200	0.08562500
C	2.52253500	-0.44883700	2.09759200
H	2.20413100	-0.10173600	3.07325600
C	9.45507300	-1.84770800	-0.17087500
C	8.40778200	-1.80989900	0.74887800
C	7.06826000	-1.73914400	0.32646100
C	6.81341500	-1.71535000	-1.05943100
C	7.85894700	-1.75277000	-1.97686200
C	9.18616200	-1.81798300	-1.53973700
H	10.48088900	-1.90043300	0.18268900
H	8.62327000	-1.83194500	1.81411600
H	5.79128900	-1.67378300	-1.42356700
H	7.63885500	-1.73399900	-3.04060500
H	9.99861100	-1.84789800	-2.25968900
C	6.00597900	-1.69079400	1.33903400
H	6.34299500	-1.78067100	2.37152600
C	4.69234500	-1.54227900	1.10124400
H	4.34332600	-1.45215100	0.07752900
C	3.65175600	-1.50688200	2.14238300
H	3.99437300	-1.73342500	3.14886900
C	2.23536800	-1.89807500	1.79815000
H	2.04138900	-2.16345600	0.76424400
H	1.65226500	-2.44584800	2.53020500

Zero-point correction=	0.536359 (Hartree/Particle)
Thermal correction to Energy=	0.589941
Thermal correction to Enthalpy=	0.590885
Thermal correction to Gibbs Free Energy=	0.444604
Sum of electronic and zero-point Energies=	-3607.637484
Sum of electronic and thermal Energies=	-3607.583902
Sum of electronic and thermal Enthalpies=	-3607.582958
Sum of electronic and thermal Free Energies=	-3607.729239

C	4.46203300	-2.77773000	-1.08673800
C	3.84524900	-1.66084900	-0.52622300
C	3.31612100	-0.64488700	-1.33950200
C	3.42456800	-0.77970200	-2.73472300
C	4.03234100	-1.89914100	-3.29317000
C	4.55501300	-2.90396000	-2.47304500
H	4.87551600	-3.54392800	-0.43764600
H	3.78878700	-1.55998900	0.55121300
H	3.02863200	-0.00967200	-3.38845700
H	4.10237500	-1.98835500	-4.37342600
H	5.03455300	-3.77317800	-2.91328400
C	2.74865500	0.54824400	-0.68359300
C	2.38927500	1.71707700	-1.31361200
H	2.84593600	0.55327400	0.39510100
H	2.39221800	1.72924600	-2.40133900
C	2.32370100	3.05906600	-0.70274300
H	1.86547100	3.80277900	-1.34104500
C	6.64114500	-1.24138700	2.50640300
C	5.73761300	-0.18692300	2.38316800
C	5.89114900	0.78872300	1.38095400

C	6.98722700	0.67564800	0.50577400
C	7.89082700	-0.37505600	0.63150000
C	7.72243900	-1.34044700	1.62976800
H	6.49818500	-1.98629700	3.28394600
H	4.88679900	-0.11966900	3.05623000
H	7.12725900	1.40771200	-0.28323200
H	8.72850700	-0.44726900	-0.05629200
H	8.42704900	-2.16188500	1.71933400
C	4.85726300	1.82070700	1.25968900
H	4.07422600	1.75083700	2.00913600
C	4.73743700	2.76199300	0.30779900
H	5.51260600	2.87526800	-0.44869900
C	3.54564500	3.61203000	0.11876800
H	3.75160100	4.65270600	-0.12191200
C	2.22786100	3.32547500	0.77472900
H	2.15422400	2.46914800	1.43379900
H	1.61476300	4.16930600	1.07615500
Ag	0.36184400	0.50120200	-0.70582000
N	-1.20896400	-1.26520400	-1.27155200
N	-2.28322500	-1.42756800	-0.47413400
N	-0.51972600	-0.30095400	1.53979100
N	-1.85387900	-0.15292400	1.65969100
N	-1.72317400	1.69825100	-0.72757800
N	-2.84176100	1.03237300	-0.37561900
B	-2.79583600	-0.28540100	0.43542100
C	-1.02170200	-2.42779400	-1.89993000
C	-1.97588800	-3.37920900	-1.50976200
C	-2.76023200	-2.69686000	-0.59584700
C	-0.02466700	-0.26176800	2.78062400
C	-1.03722600	-0.07363200	3.73400700

C	-2.19048200	-0.00938000	2.97229000
C	-2.11884400	2.73114500	-1.47971800
C	-3.51159800	2.75308500	-1.62709000
C	-3.93287700	1.64845500	-0.90778500
H	-3.88597200	-0.54130700	0.81154800
C	-5.33522500	1.15734800	-0.74546900
C	-1.13089200	3.69595200	-2.03928800
C	-3.59350000	0.16833800	3.45221100
C	1.43609500	-0.42078000	3.02527000
C	-3.93188700	-3.21631700	0.17159800
C	0.14271100	-2.61363400	-2.81215100
H	-4.11849300	3.46039200	-2.16876600
H	-0.94834600	-0.01019800	4.80683800
H	-2.08316100	-4.39935100	-1.84240600
F	-6.17979400	1.96188600	-1.42294400
F	-5.73830600	1.14009700	0.54137900
F	-5.49097700	-0.09461900	-1.22966400
F	-0.47967400	4.37827200	-1.06854100
F	-1.73861900	4.59910500	-2.83082100
F	-0.17951100	3.07774200	-2.78435500
F	-0.12101400	-3.54324400	-3.75317500
F	0.47394000	-1.46537000	-3.44640400
F	1.23883000	-3.02848600	-2.13901200
F	-5.08391300	-2.59015900	-0.14674300
F	-4.10169600	-4.52951600	-0.08323700
F	-3.76166300	-3.07827600	1.50608900
F	-4.35485200	-0.92804400	3.25164300
F	-3.59745700	0.42460800	4.77615600
F	-4.21036000	1.19977300	2.83374600
F	2.01564400	-1.22885000	2.11164100

F	1.67306000	-0.93479300	4.24608700
F	2.10511400	0.76544700	2.97042700

## TS5

Zero-point correction=	0.535108 (Hartree/Particle)		
Thermal correction to Energy=	0.588234		
Thermal correction to Enthalpy=	0.589178		
Thermal correction to Gibbs Free Energy=	0.444035		
Sum of electronic and zero-point Energies=	-3607.625149		
Sum of electronic and thermal Energies=	-3607.572023		
Sum of electronic and thermal Enthalpies=	-3607.571079		
Sum of electronic and thermal Free Energies=	-3607.716223		

C	4.81548100	-3.14133900	0.59860000
C	4.12485800	-1.95483700	0.82740100
C	3.85837000	-1.05557900	-0.22461300
C	4.33994000	-1.37625400	-1.51040900
C	5.02899600	-2.56267600	-1.73613200
C	5.27115800	-3.45180300	-0.68440900
H	5.00697700	-3.82064400	1.42415600
H	3.77480100	-1.71444000	1.82579300
H	4.19037900	-0.68119000	-2.32991100
H	5.39475300	-2.78932400	-2.73345500
H	5.81773400	-4.37291800	-0.86314400
C	3.17827200	0.19468600	0.06604100
C	2.53910300	1.00510200	-0.87744700
H	3.01727600	0.40729600	1.11357700
H	2.54206800	0.68411400	-1.91690000
C	2.13045800	2.34414100	-0.64207600

H	1.65386000	2.87734400	-1.45488000
C	7.76124800	-0.79522900	1.60267600
C	6.69255100	0.09389300	1.67211900
C	6.33481800	0.89099300	0.56651200
C	7.07649600	0.74232100	-0.62373600
C	8.14581600	-0.14468300	-0.69041000
C	8.49418400	-0.91926400	0.42058200
H	8.01752500	-1.39872300	2.46862400
H	6.12082800	0.18266800	2.59199400
H	6.79647400	1.30925500	-1.50567500
H	8.70072600	-0.24735700	-1.61857500
H	9.32283000	-1.61848400	0.36099700
C	5.18213600	1.77099700	0.66748400
H	4.62115300	1.69295500	1.59142300
C	4.89588900	2.82429800	-0.18673900
H	5.60804400	3.06318700	-0.97421100
C	3.69291900	3.53574200	-0.19668200
H	3.59401700	4.37700000	-0.87523700
C	2.47160500	3.15418000	0.57215200
H	2.64089400	2.58481900	1.48300900
H	1.77968800	3.97330300	0.75701100
Ag	0.24699800	0.64120200	-0.29496300
N	-1.14741700	-0.97789200	-1.41497600
N	-2.28510800	-1.35230500	-0.79899200
N	-0.91296400	-0.29150200	1.61541500
N	-2.25354700	-0.39967200	1.55256700
N	-1.94478900	1.80943300	-0.38925700
N	-3.03901700	1.02304500	-0.38650400
B	-3.00692000	-0.41158700	0.19837700
C	-0.79322500	-1.98699900	-2.21304300



C	-1.70224600	-3.05155800	-2.12365300
C	-2.63890100	-2.60208900	-1.20794100
C	-0.59225600	-0.27380100	2.91171800
C	-1.73163800	-0.37047000	3.72231600
C	-2.77165000	-0.44742700	2.81090800
C	-2.29620800	2.94378300	-1.00072700
C	-3.63662800	2.91225900	-1.41217900
C	-4.07245600	1.66491600	-0.99921400
H	-4.11181400	-0.79381200	0.36867700
C	-5.42909100	1.06629600	-1.17767200
C	-1.29072300	4.02060200	-1.21912100
C	-4.23318800	-0.55544100	3.10090600
C	0.83456900	-0.15453200	3.32010400
C	-3.84602800	-3.32351000	-0.70463700
C	0.47850400	-1.90983700	-2.98611500
H	-4.20225100	3.67699900	-1.91997500
H	-1.79200900	-0.38856300	4.79857400
H	-1.68686500	-3.99537700	-2.64492400
F	-6.21737900	1.91292400	-1.87077000
F	-6.04355300	0.81010400	-0.00371900
F	-5.38057200	-0.09802600	-1.86308300
F	-0.53695700	4.24400300	-0.11873200
F	-1.88513100	5.17963400	-1.55677200
F	-0.42609500	3.70938700	-2.22233100
F	0.45790100	-2.74342800	-4.04361900
F	0.71796700	-0.65838000	-3.44644200
F	1.54605000	-2.25122000	-2.22606500
F	-4.99961700	-2.71570700	-1.05222200
F	-3.87887000	-4.57284800	-1.21090000
F	-3.84354500	-3.42840800	0.64326600

F	-4.76891800	-1.70761000	2.64712100
F	-4.44053400	-0.50906800	4.43267000
F	-4.93558200	0.45625800	2.54365100
F	1.60072600	-1.12794200	2.77446300
F	0.96747800	-0.22448900	4.65578900
F	1.37993400	1.02640700	2.92005900

**Pro**

Zero-point correction=	0.311919 (Hartree/Particle)
Thermal correction to Energy=	0.326888
Thermal correction to Enthalpy=	0.327832
Thermal correction to Gibbs Free Energy=	0.270000
Sum of electronic and zero-point Energies=	-734.879632
Sum of electronic and thermal Energies=	-734.864663
Sum of electronic and thermal Enthalpies=	-734.863719
Sum of electronic and thermal Free Energies=	-734.921551

C	0.45766900	3.26247900	-0.58704100
C	0.32576600	1.94448100	-1.02476900
C	-0.72528100	1.13644400	-0.57275000
C	-1.65414800	1.68597900	0.32074600
C	-1.52305500	3.00223000	0.76475600
C	-0.46547500	3.79503600	0.31421500
H	1.28131100	3.87124500	-0.94878800
H	1.05204800	1.53035100	-1.71805500
H	-2.48242800	1.07706800	0.66515500
H	-2.25159600	3.41098800	1.45928100
H	-0.36616000	4.82069800	0.65736500
C	-0.81691000	-0.31428500	-1.02049900

C	-2.22396600	-0.69303600	-1.42198600
H	-0.20913000	-0.39508500	-1.93138500
H	-2.56071400	-0.17923300	-2.32214100
C	-3.08591900	-1.54925400	-0.86198100
H	-4.03575400	-1.68288400	-1.37870600
C	3.57864600	-1.58247200	-0.68011500
C	2.20263100	-1.81119200	-0.70908600
C	1.32899500	-1.07661200	0.10287200
C	1.87195700	-0.09826900	0.94735400
C	3.24749600	0.13232800	0.98177600
C	4.10675700	-0.60831700	0.16859700
H	4.23683900	-2.16790400	-1.31568900
H	1.79626600	-2.57258800	-1.37033900
H	1.21810200	0.49918500	1.57334700
H	3.64681300	0.89629100	1.64261000
H	5.17742900	-0.42871100	0.19681500
C	-0.16543400	-1.31414000	-0.00150200
H	-0.30406200	-2.30145900	-0.46070000
C	-0.87223000	-1.32485200	1.33303200
H	-0.34025100	-0.92893500	2.19316000
C	-2.10243600	-1.81280700	1.50030400
H	-2.53904900	-1.81006500	2.49697000
C	-2.95097200	-2.38704700	0.39124600
H	-2.56591900	-3.38345900	0.11395400
H	-3.95828600	-2.57567300	0.77613600

**Int6'**

Zero-point correction= 0.309191 (Hartree/Particle)

Thermal correction to Energy= 0.325229

Thermal correction to Enthalpy=	0.326173
Thermal correction to Gibbs Free Energy=	0.264583
Sum of electronic and zero-point Energies=	-734.866393
Sum of electronic and thermal Energies=	-734.850355
Sum of electronic and thermal Enthalpies=	-734.849410
Sum of electronic and thermal Free Energies=	-734.911001

C	-5.47781800	-1.31946100	-0.83753100
C	-4.65963200	-0.19932000	-0.97351500
C	-3.47470900	-0.06548600	-0.22761100
C	-3.13596400	-1.10447300	0.66096400
C	-3.95270400	-2.22253700	0.79711600
C	-5.12908700	-2.33785700	0.04996700
H	-6.38779100	-1.39604700	-1.42562200
H	-4.93712600	0.59083200	-1.66621200
H	-2.22445200	-1.04068100	1.24680900
H	-3.66986400	-3.01158200	1.48803400
H	-5.76294400	-3.21269200	0.15834600
C	-2.65572600	1.13817300	-0.41150100
C	-1.53801800	1.46619500	0.25847400
H	-3.01737000	1.82757700	-1.17411800
H	-1.15924800	0.80538500	1.03502000
C	-0.77383000	2.70108900	0.01848100
H	-1.21152700	3.36818000	-0.71971600
C	5.47782100	-1.31948900	-0.83749500
C	4.65965900	-0.19933000	-0.97347900
C	3.47471400	-0.06549100	-0.22760900
C	3.13592400	-1.10449300	0.66093200
C	3.95264100	-2.22257500	0.79708400
C	5.12904300	-2.33790100	0.04996700

H	6.38780900	-1.39608100	-1.42556300
H	4.93718800	0.59083300	-1.66614800
H	2.22439700	-1.04070000	1.24675300
H	3.66976800	-3.01163000	1.48797800
H	5.76287600	-3.21275400	0.15834200
C	2.65575800	1.13818700	-0.41150200
H	3.01742900	1.82758700	-1.17411000
C	1.53804600	1.46622700	0.25845600
H	1.15925700	0.80542200	1.03499500
C	0.77386200	2.70112100	0.01845400
H	1.21152000	3.36819000	-0.71978400
C	0.00002400	3.35989000	1.13480800
H	0.00006000	2.85923200	2.09918000
H	0.00000000	4.44410400	1.18905200

### Int7'

Zero-point correction=	0.309488 (Hartree/Particle)
Thermal correction to Energy=	0.325417
Thermal correction to Enthalpy=	0.326361
Thermal correction to Gibbs Free Energy=	0.265307
Sum of electronic and zero-point Energies=	-734.862892
Sum of electronic and thermal Energies=	-734.846963
Sum of electronic and thermal Enthalpies=	-734.846019
Sum of electronic and thermal Free Energies=	-734.907072

C	-3.08181600	-2.33320400	1.04006900
C	-2.45521500	-1.09985500	1.20805200
C	-2.33523900	-0.19050500	0.14205700
C	-2.85916900	-0.56913200	-1.10873500

C	-3.48743900	-1.79923200	-1.27636900
C	-3.60387700	-2.68889300	-0.20390600
H	-3.16058700	-3.01666500	1.88058200
H	-2.04868500	-0.82837500	2.17871500
H	-2.76626500	0.09958100	-1.95846200
H	-3.88355900	-2.07023200	-2.25085400
H	-4.09135500	-3.64948000	-0.34023500
C	-1.66555800	1.09248500	0.38403900
C	-1.54217000	2.11541100	-0.47874500
H	-1.24324900	1.19669500	1.38042700
H	-1.99007900	2.03539400	-1.46782100
C	-0.78552200	3.35955200	-0.24838500
H	-1.19560300	4.22935500	-0.75549200
C	3.08181000	-2.33321000	1.04006900
C	2.45520700	-1.09986100	1.20805200
C	2.33523600	-0.19050800	0.14205900
C	2.85917300	-0.56913100	-1.10873100
C	3.48744500	-1.79923000	-1.27636600
C	3.60387700	-2.68889400	-0.20390500
H	3.16057600	-3.01667300	1.88058000
H	2.04867200	-0.82838400	2.17871400
H	2.76627300	0.09958500	-1.95845700
H	3.88357000	-2.07022700	-2.25084900
H	4.09135600	-3.64948100	-0.34023400
C	1.66555500	1.09248200	0.38404200
H	1.24323600	1.19668700	1.38042500
C	1.54217600	2.11541200	-0.47873900
H	1.99009500	2.03539900	-1.46781100
C	0.78552600	3.35955300	-0.24838200
H	1.19560900	4.22935600	-0.75548700

C	-0.00000100	3.63785800	1.00157000
H	-0.00000200	2.88446700	1.78239200
H	-0.00000100	4.65641400	1.37738700

**TS5'**

Zero-point correction=	0.309133 (Hartree/Particle)
Thermal correction to Energy=	0.324028
Thermal correction to Enthalpy=	0.324972
Thermal correction to Gibbs Free Energy=	0.267484
Sum of electronic and zero-point Energies=	-734.847278
Sum of electronic and thermal Energies=	-734.832383
Sum of electronic and thermal Enthalpies=	-734.831439
Sum of electronic and thermal Free Energies=	-734.888927

C	2.42049400	-2.02569100	1.05693900
C	1.07416200	-1.73217600	1.25254400
C	0.19857500	-1.56422100	0.16246700
C	0.73358200	-1.67631900	-1.13633000
C	2.07911100	-1.97213600	-1.33091800
C	2.93092800	-2.14773500	-0.23693100
H	3.07452000	-2.15316300	1.91477100
H	0.68218900	-1.63498400	2.26139900
H	0.09168300	-1.50644600	-1.99477400
H	2.47079500	-2.05021500	-2.34106900
H	3.98237300	-2.36960800	-0.39236700
C	-1.19497100	-1.21449500	0.40394200
C	-2.24327800	-1.52952600	-0.48637800
H	-1.45730000	-1.09336400	1.44778900
H	-1.99638300	-2.06561500	-1.40124400

C	-3.53921900	-1.09650600	-0.33392800
H	-4.27631800	-1.37032800	-1.08343900
C	2.42727400	1.93222900	1.07588200
C	1.09103300	1.61417200	1.30083300
C	0.16643600	1.55882500	0.23996300
C	0.64258000	1.81297900	-1.06213400
C	1.97768900	2.13431900	-1.28551800
C	2.87884100	2.19466600	-0.21912500
H	3.12012800	1.96893300	1.91160100
H	0.74639700	1.40805600	2.31035900
H	-0.03625500	1.73144300	-1.90498400
H	2.32247100	2.32108600	-2.29861000
H	3.92261000	2.43486000	-0.39744600
C	-1.21424800	1.17126700	0.49649800
H	-1.44597000	0.95462300	1.53210000
C	-2.28718000	1.54695300	-0.34066100
H	-2.06687300	2.17732800	-1.20038400
C	-3.57053400	1.06933400	-0.22288700
H	-4.31961400	1.40167200	-0.93613800
C	-3.96554300	-0.06811700	0.67660700
H	-3.41341600	-0.10736200	1.61785100
H	-5.03543400	-0.09385700	0.88939000



## 7. NMR Spectra of Products

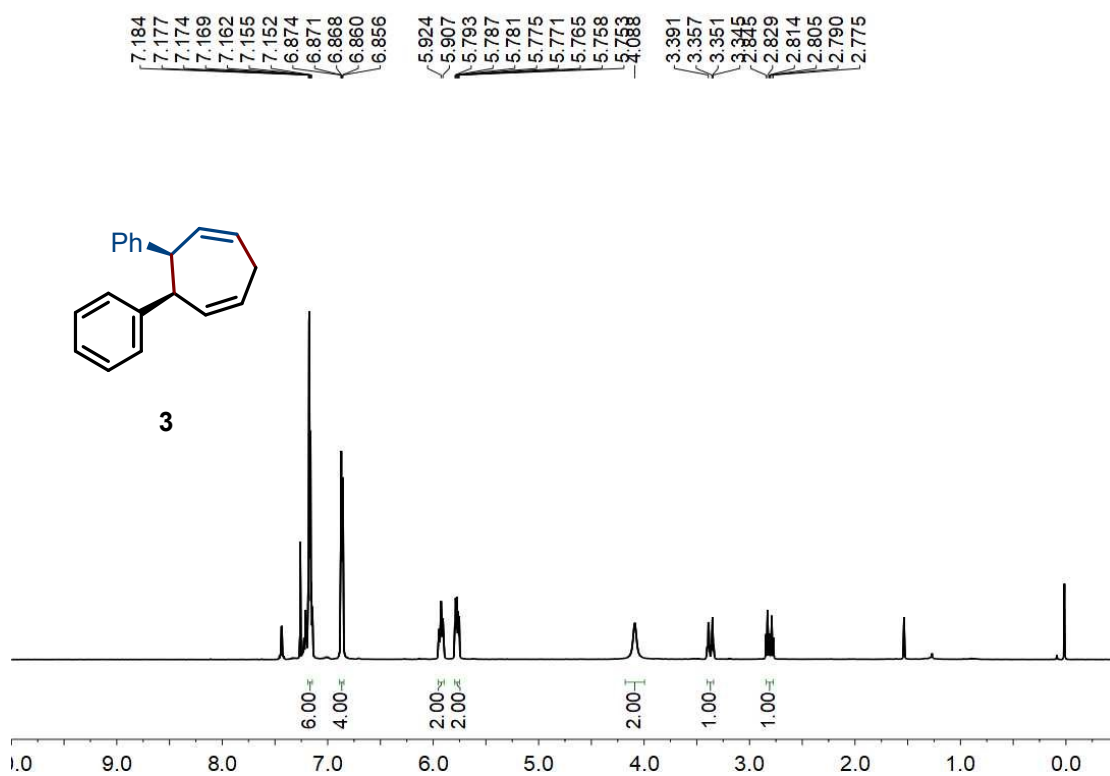


Figure S3.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) spectrum of **3**.

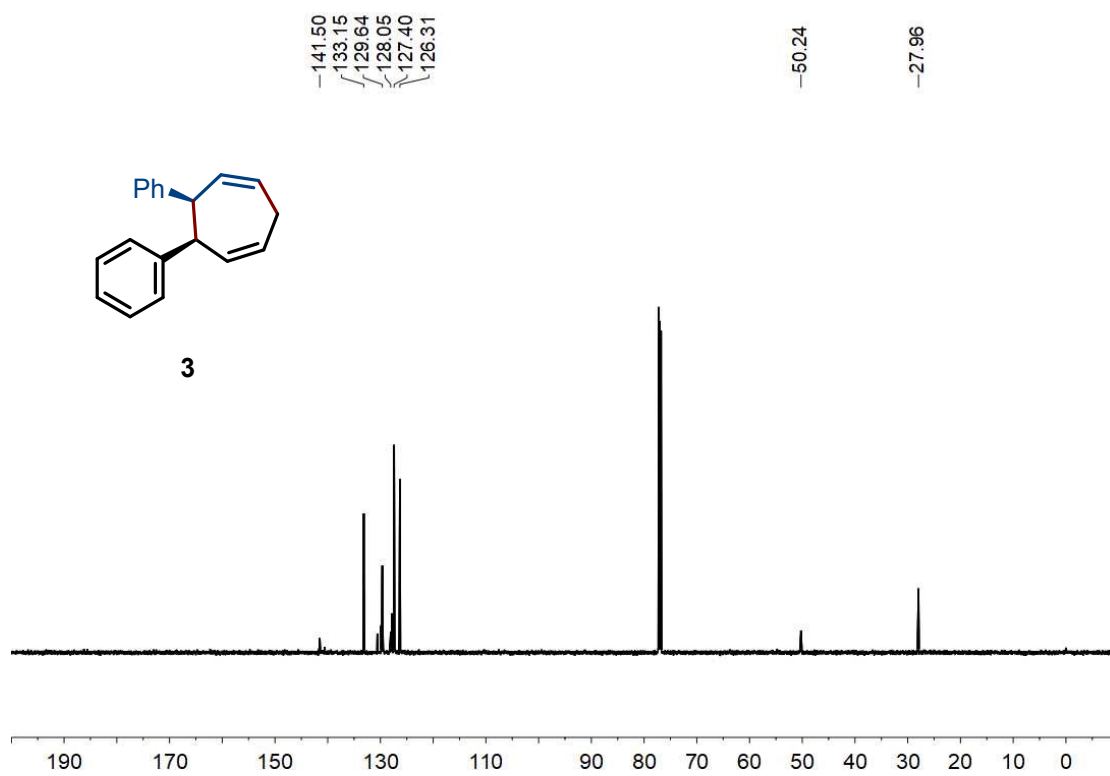


Figure S4.  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ) spectrum of **3**.

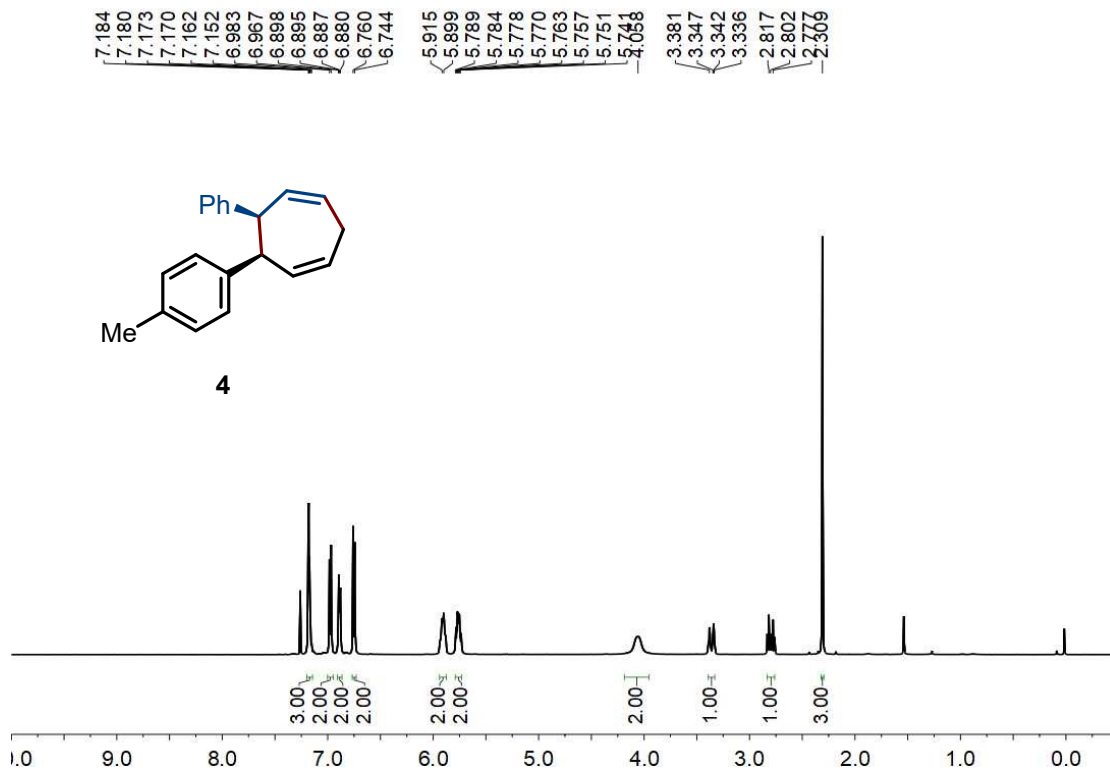


Figure S5. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **4**.

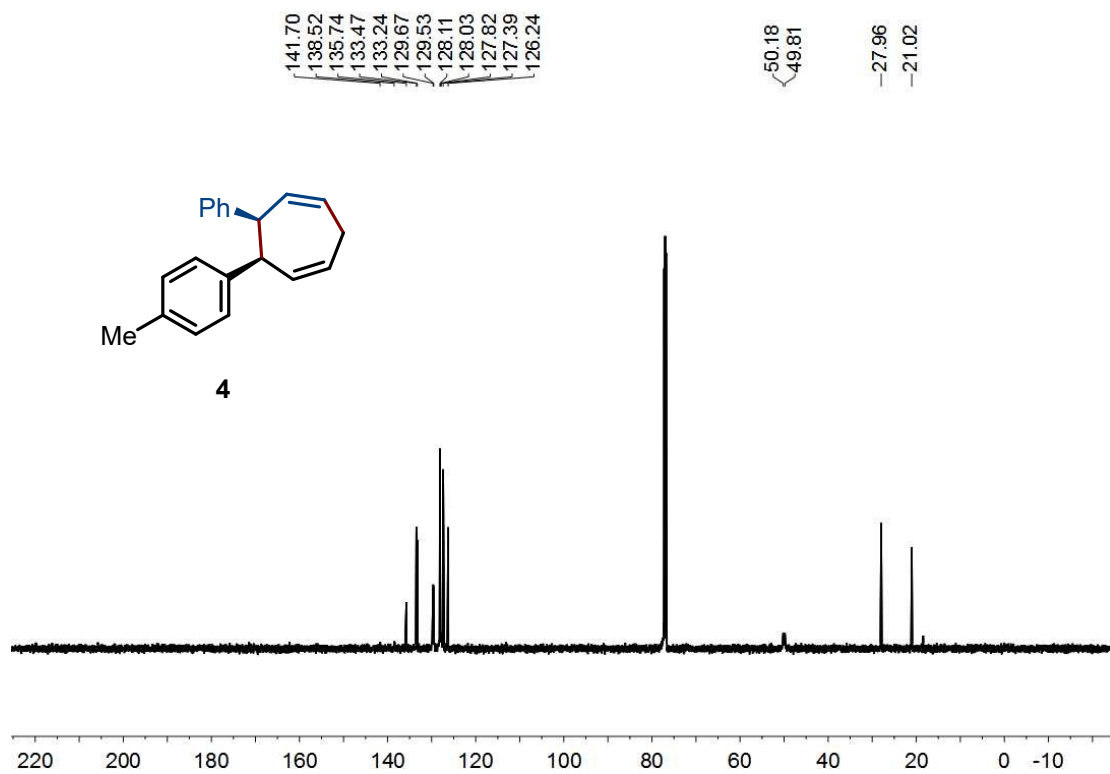


Figure S6. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **4**.

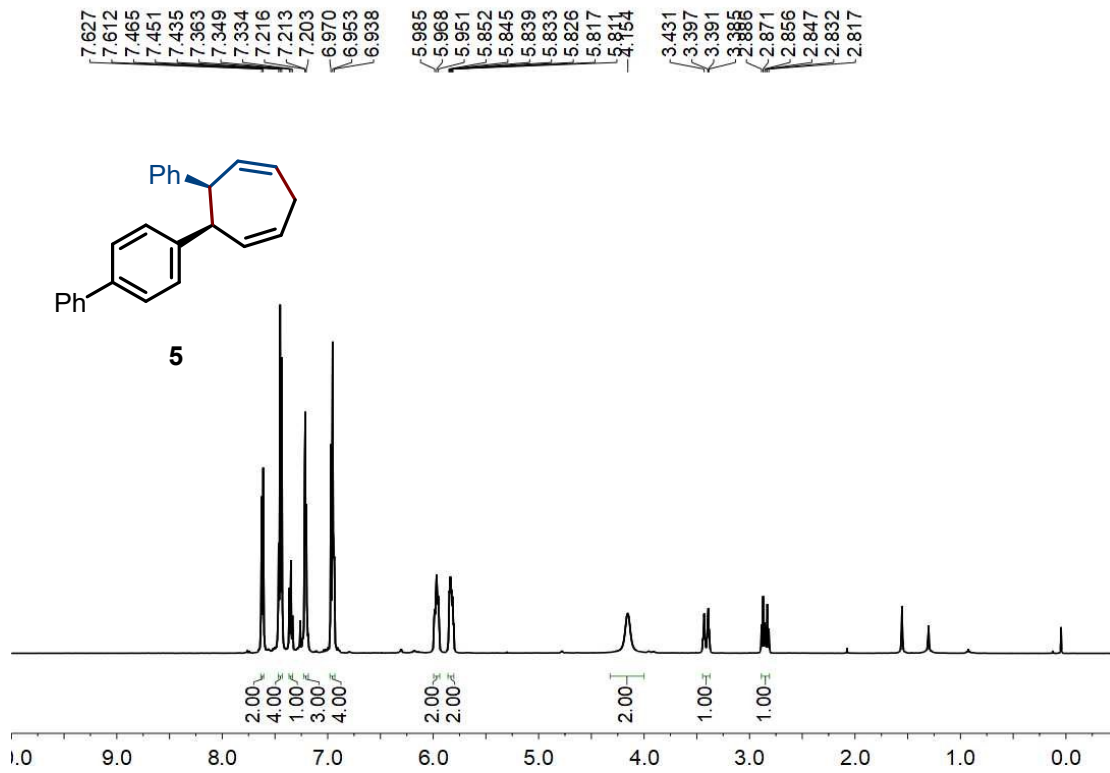


Figure S7. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **5**.

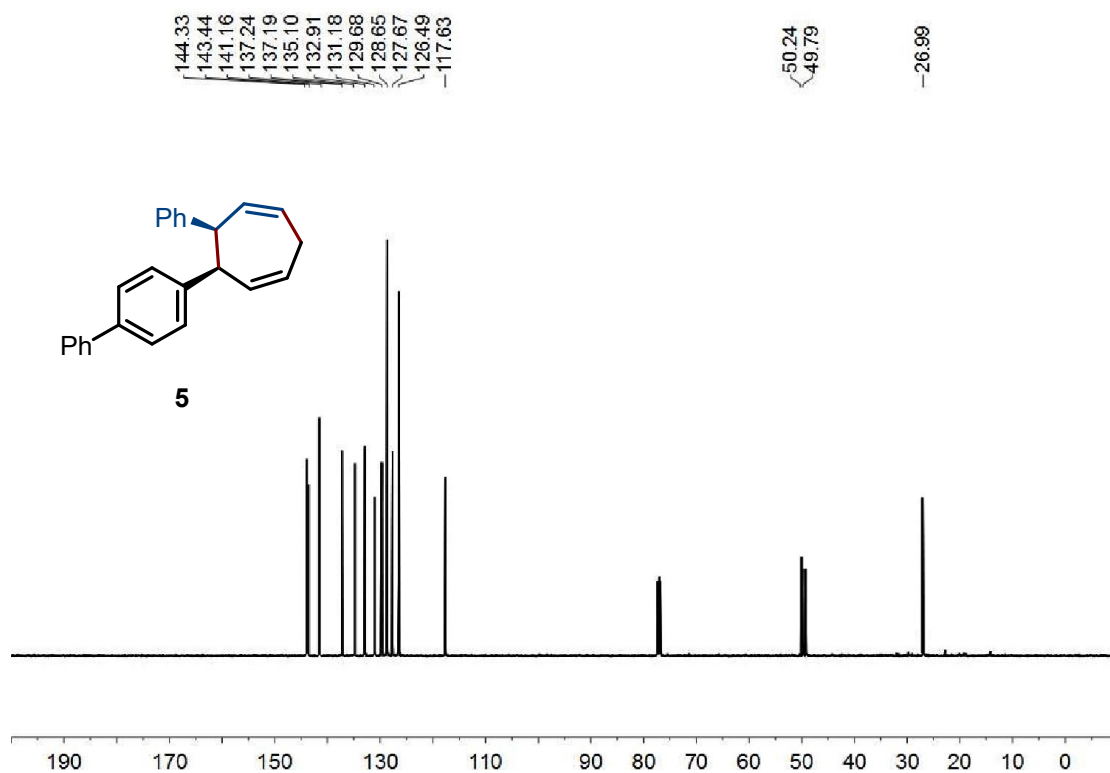


Figure S8. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **5**.

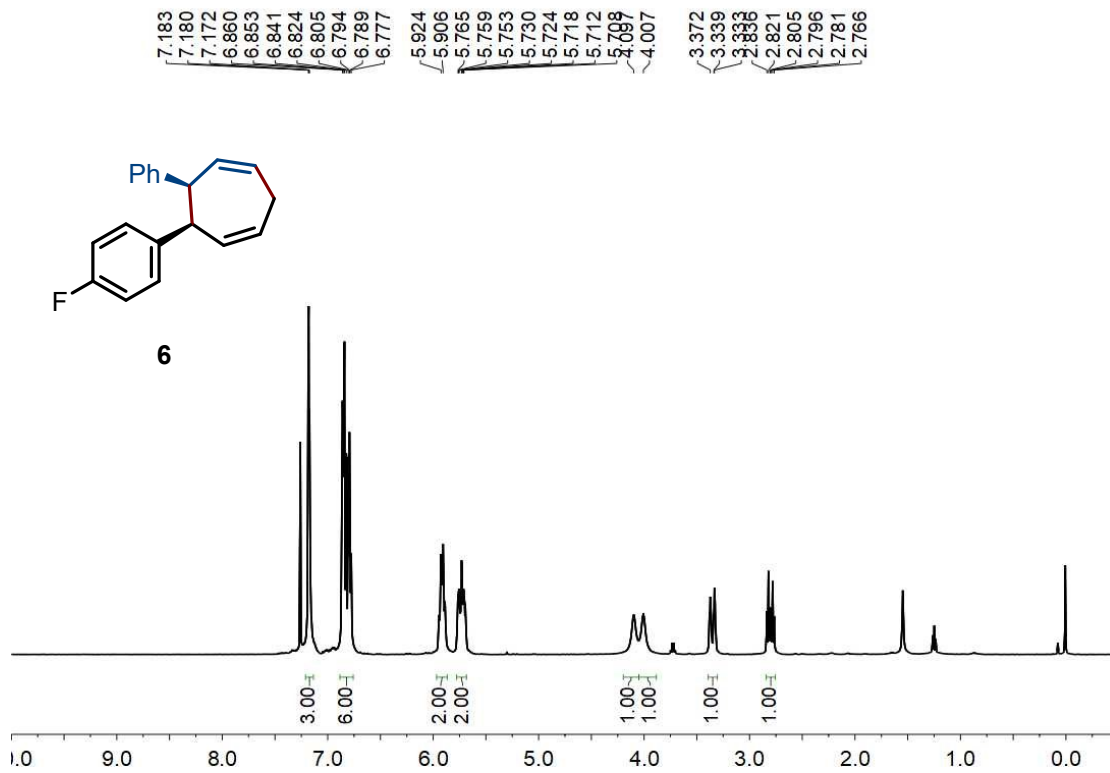


Figure S9. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **6**.

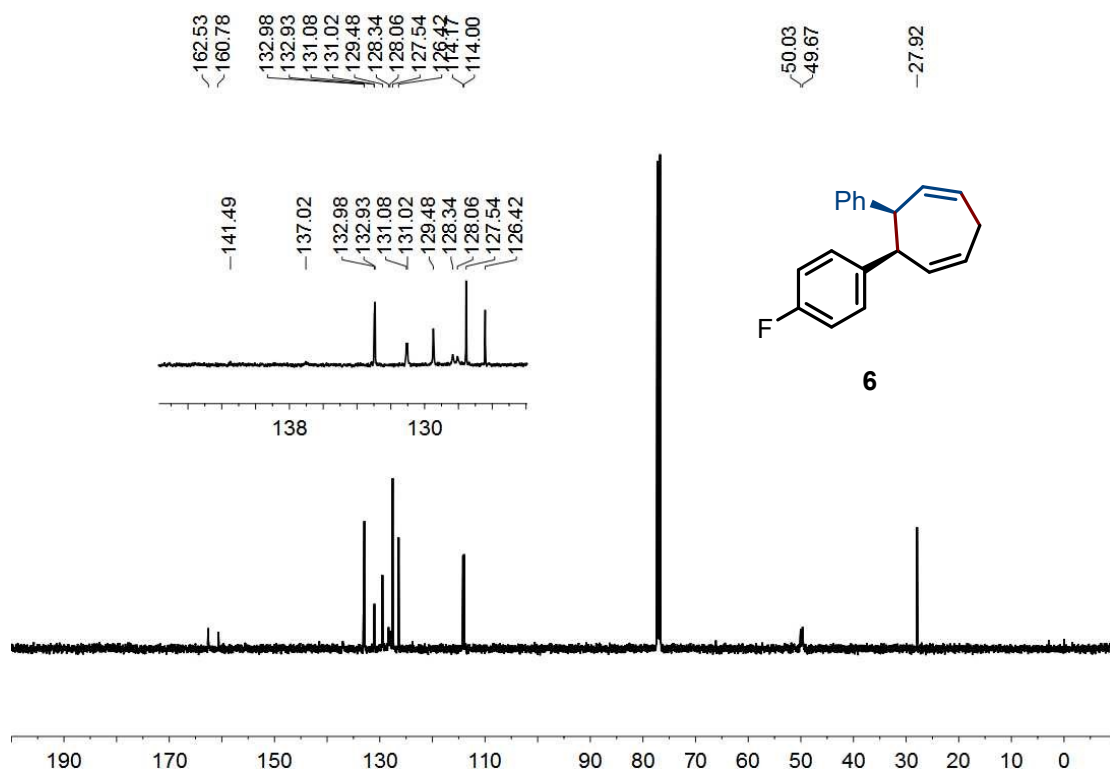


Figure S10. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **6**.

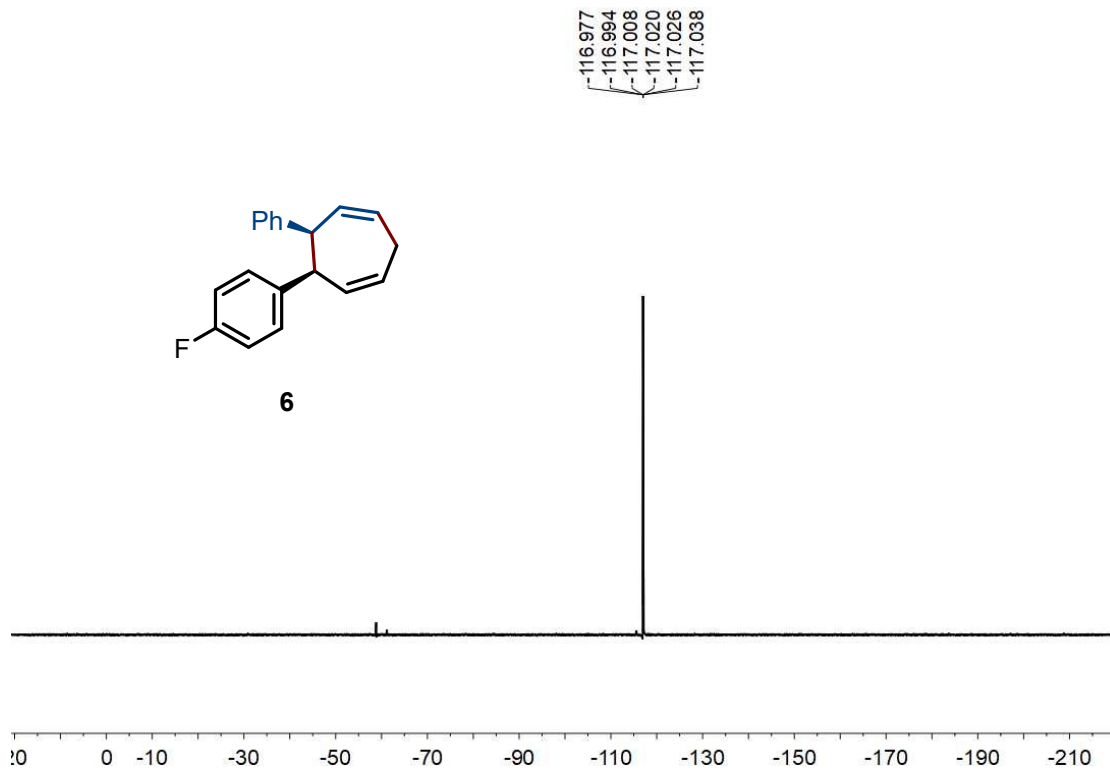


Figure S11.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of **6**.

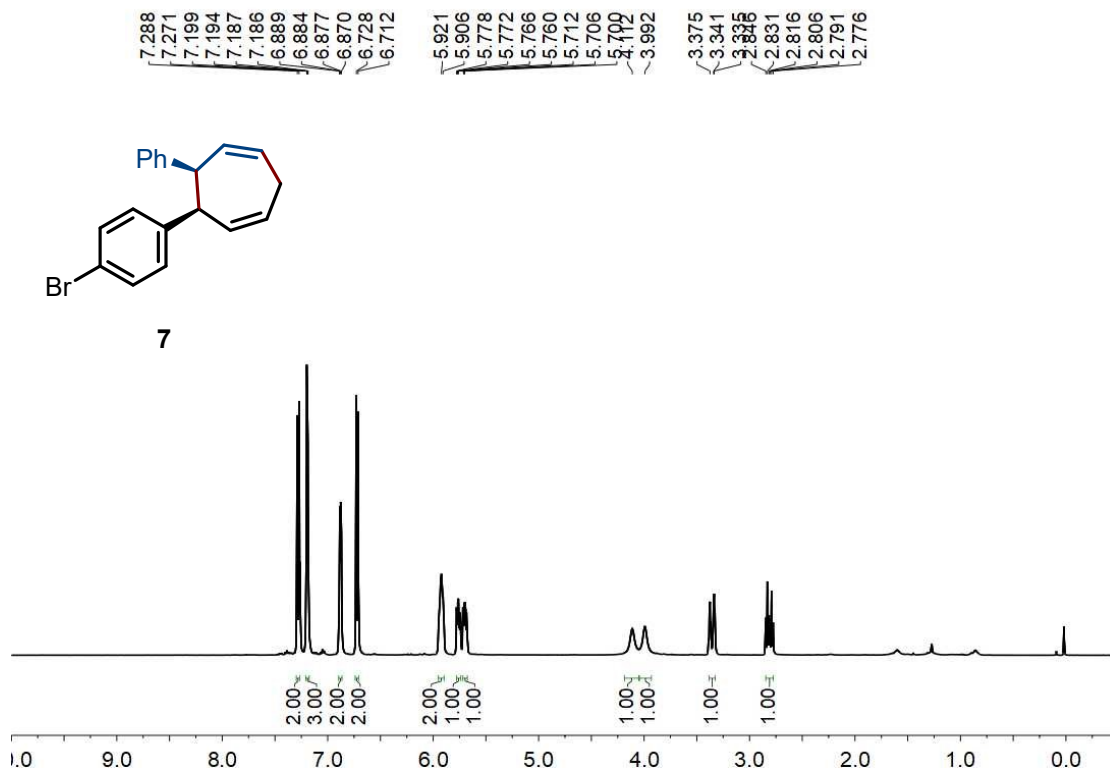


Figure S12.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **7**.

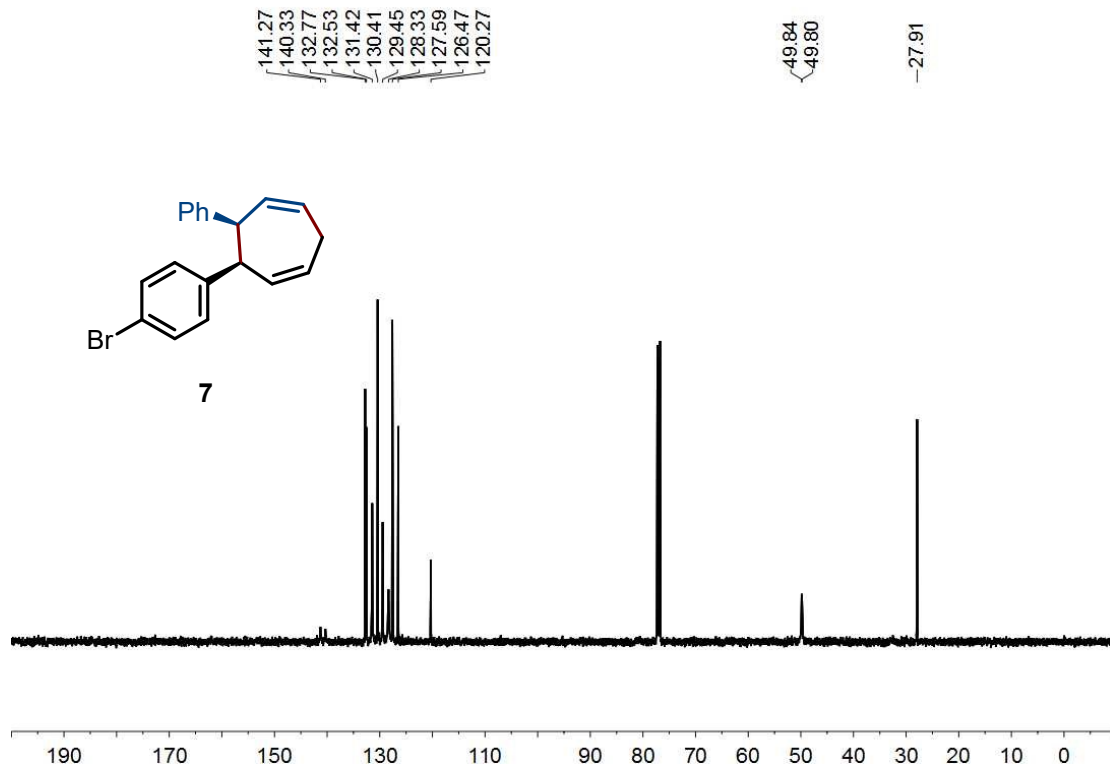


Figure S13.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **7**.

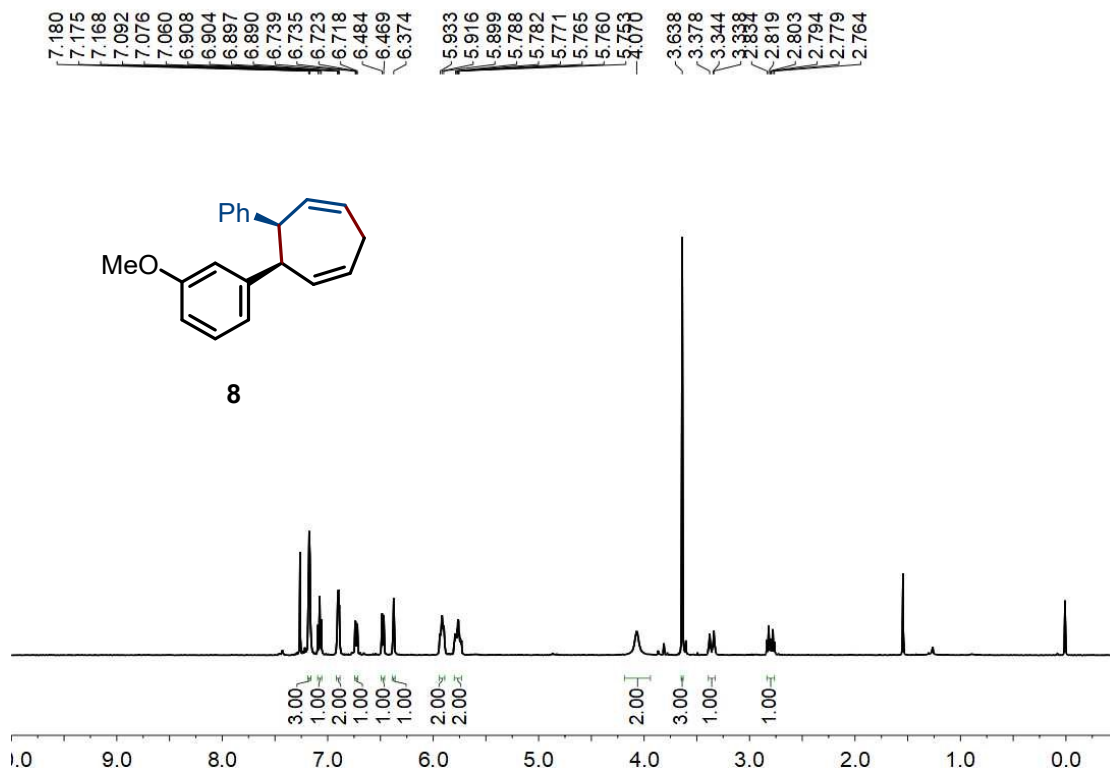


Figure S14.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **8**.

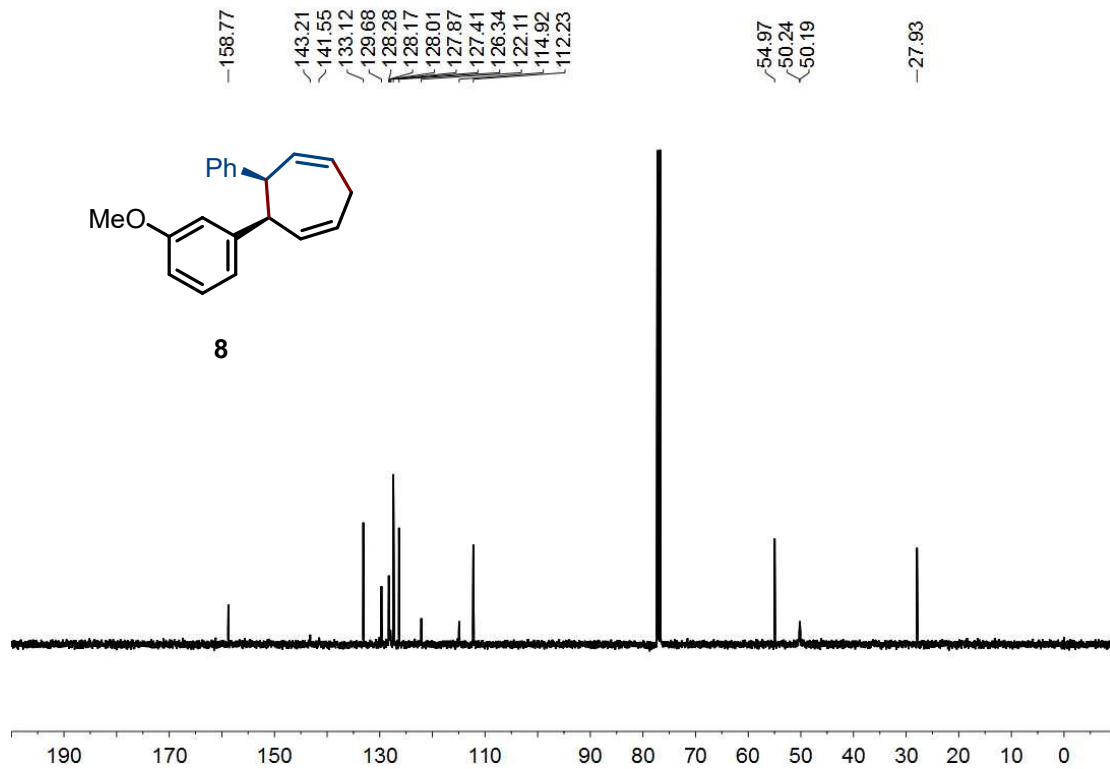


Figure S15. <sup>1</sup>H NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **8**.

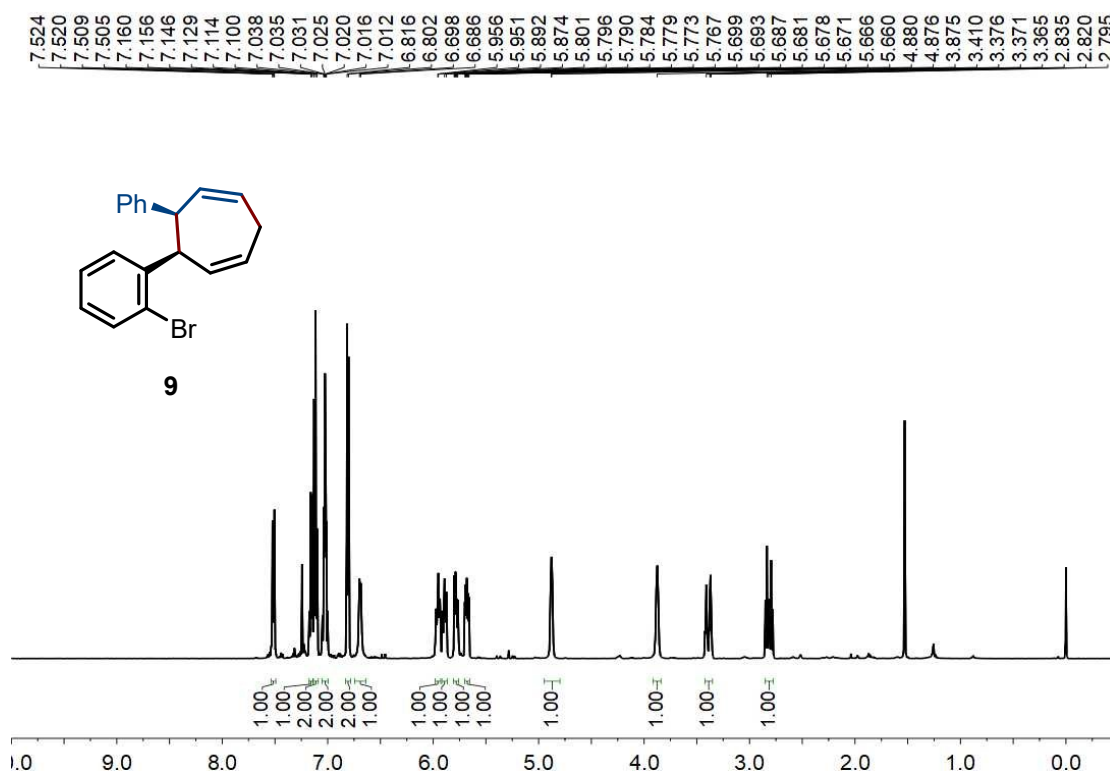
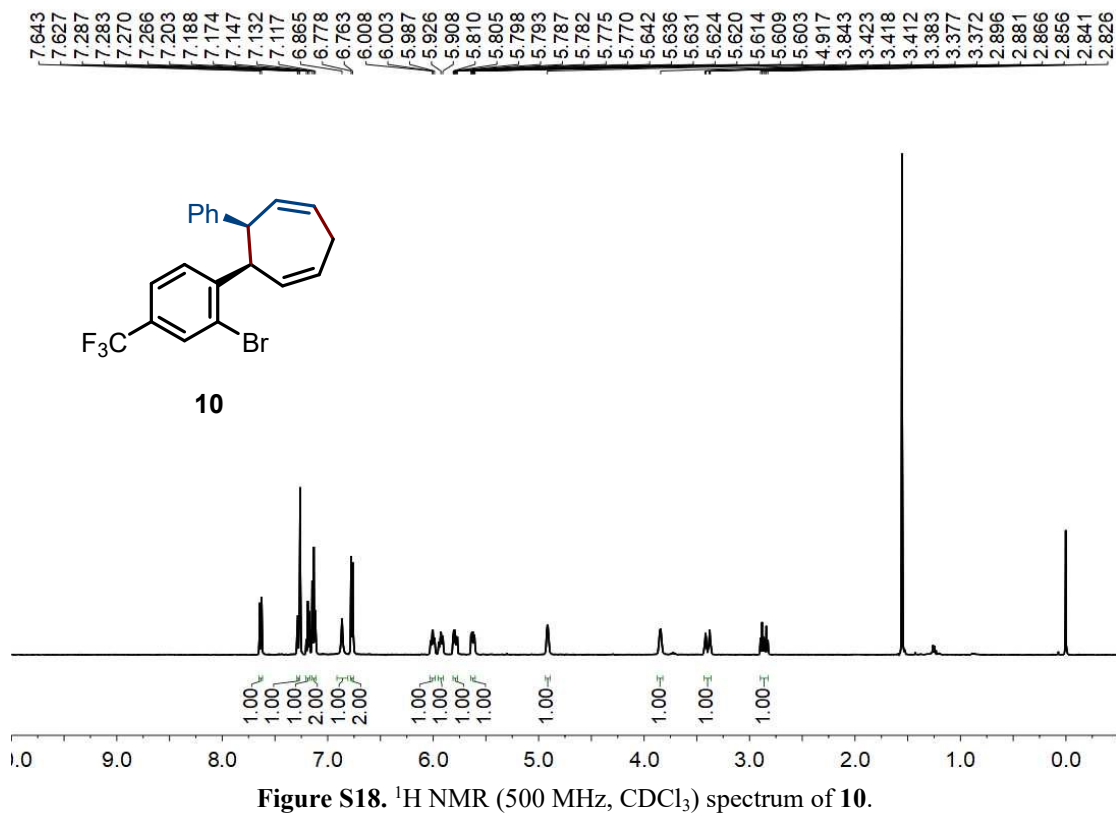
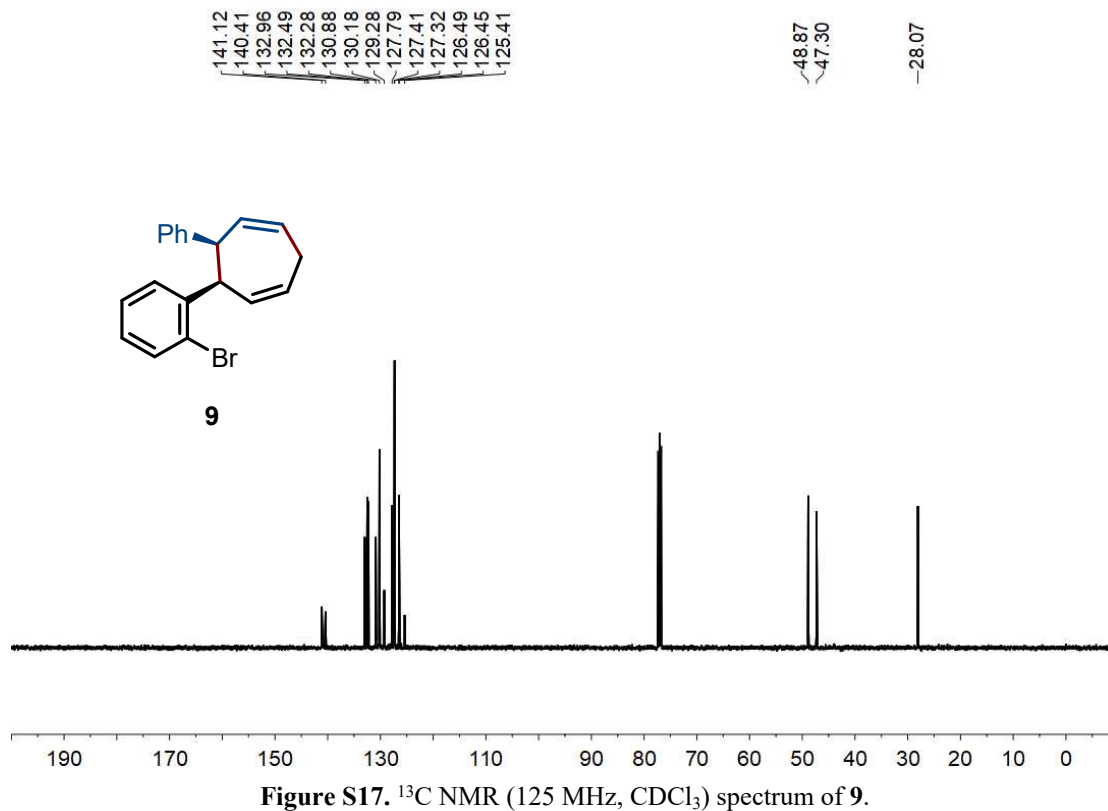


Figure S16. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **9**.





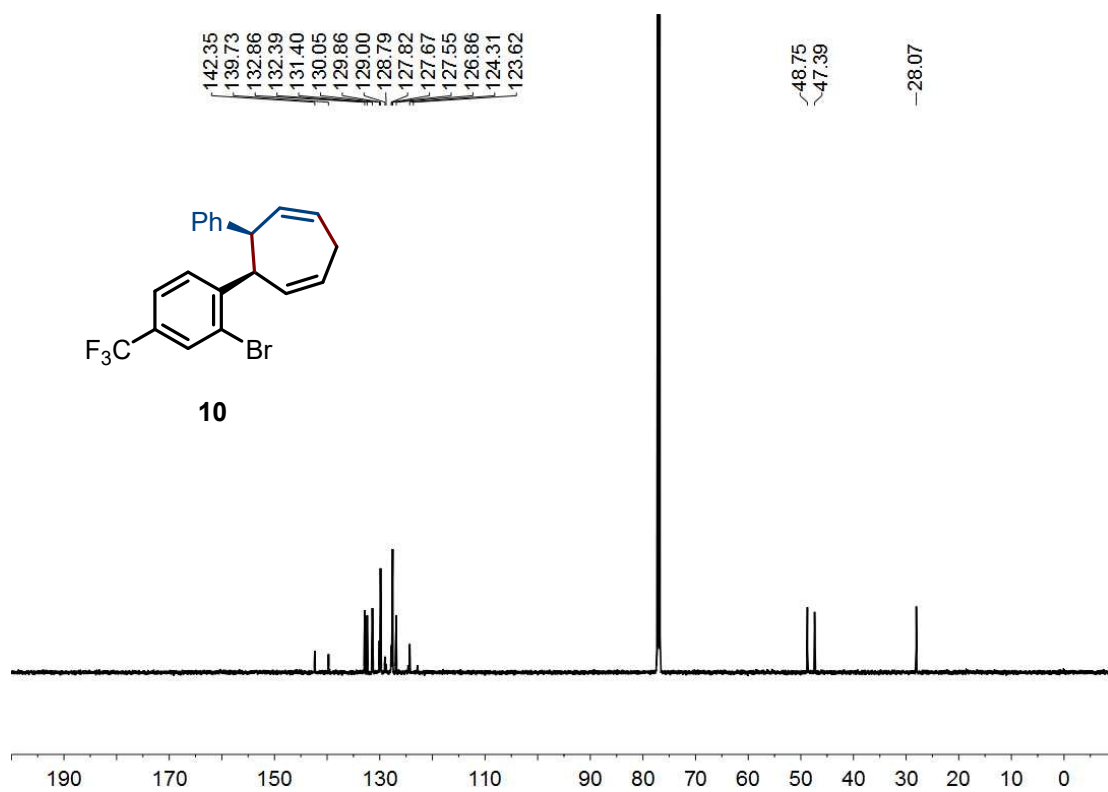


Figure S19. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **10**.

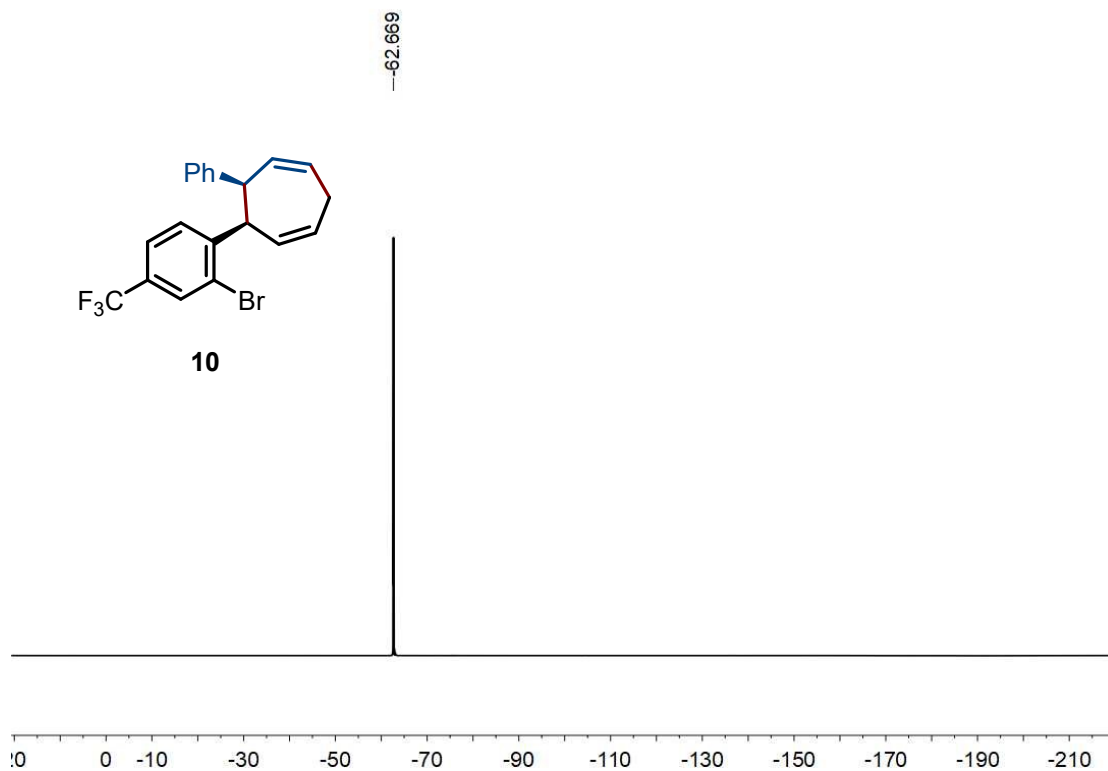


Figure S20. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of **10**.

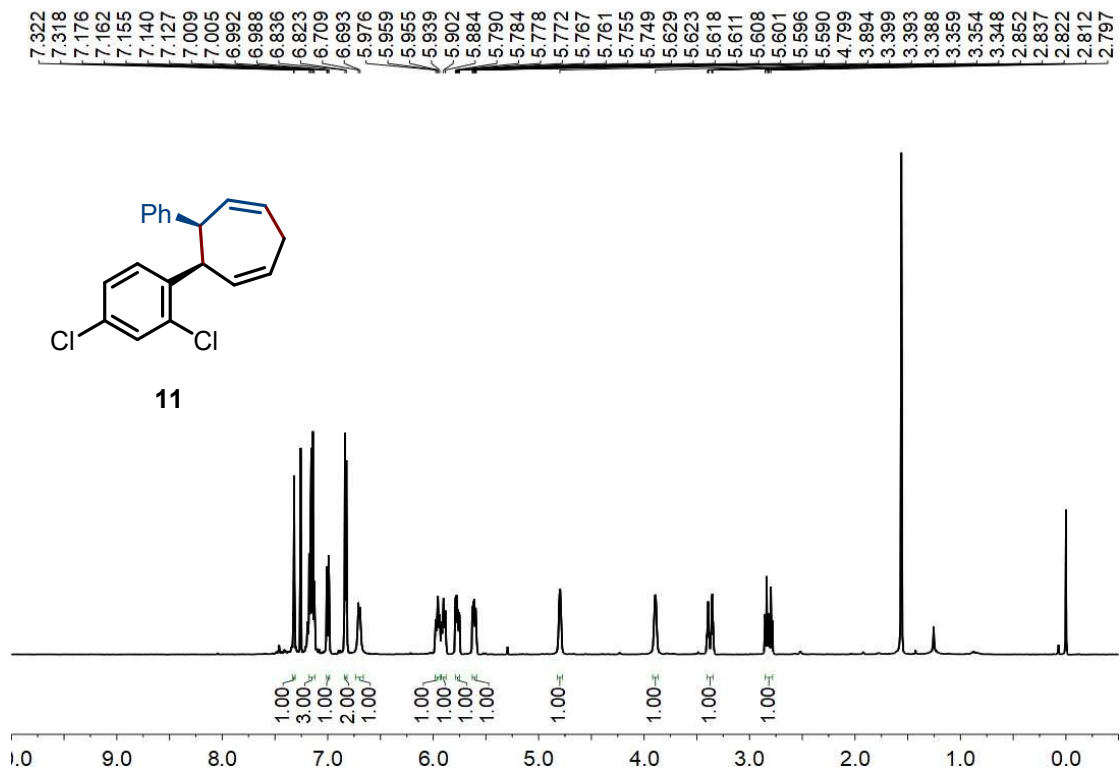


Figure S21.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **11**.

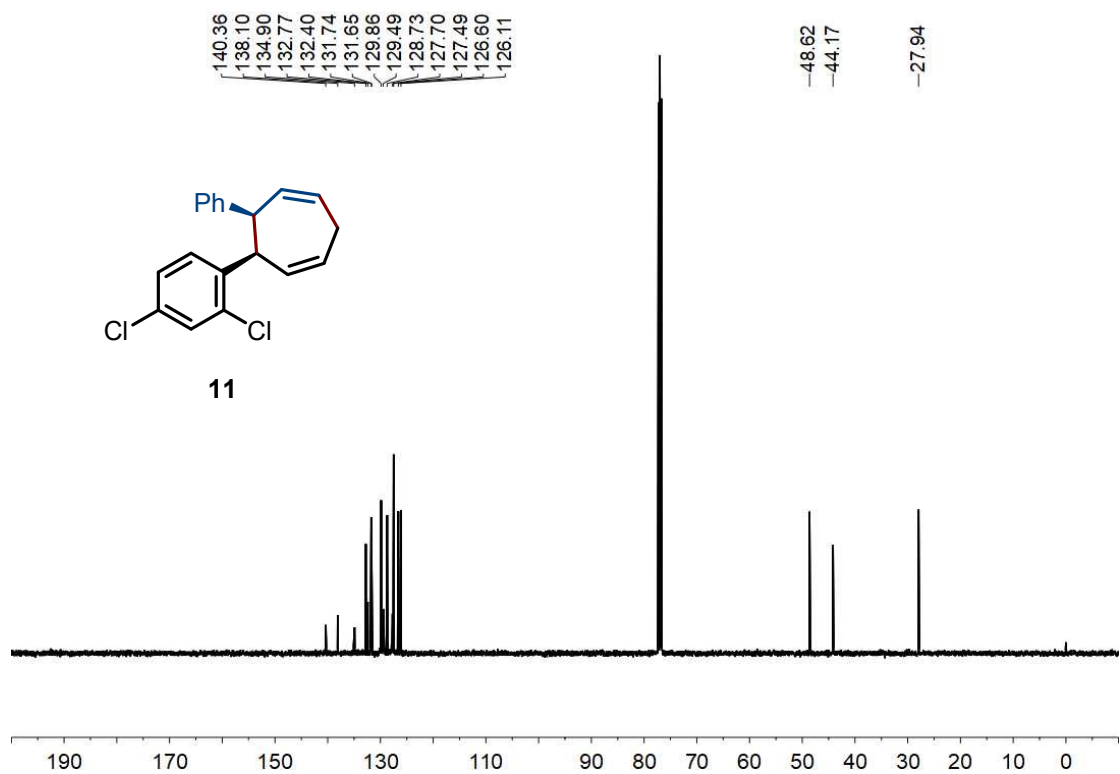


Figure S22.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **11**.

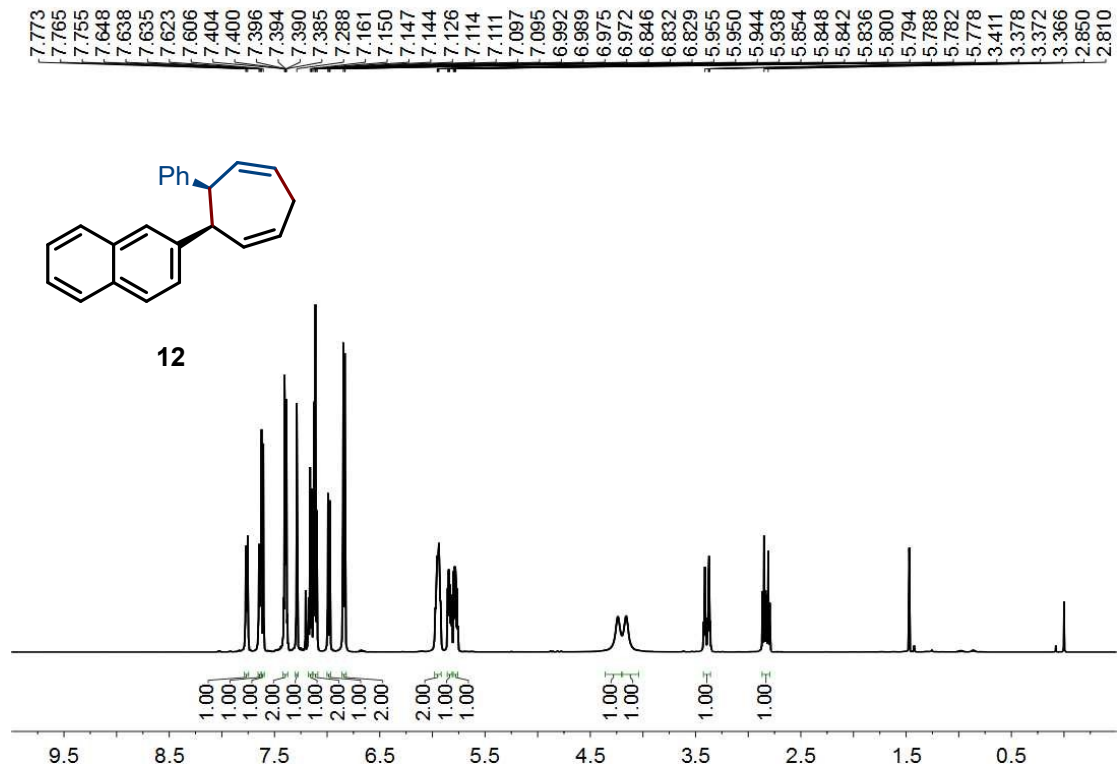


Figure S23.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **12**.

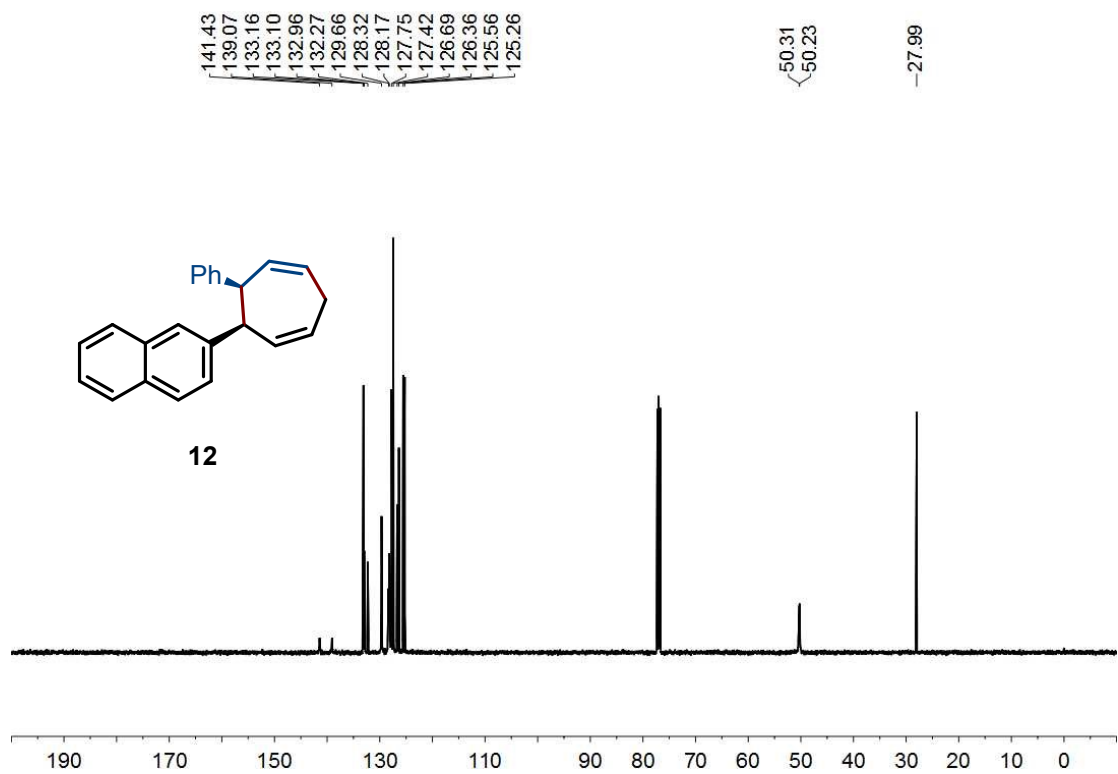


Figure S24.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **12**.

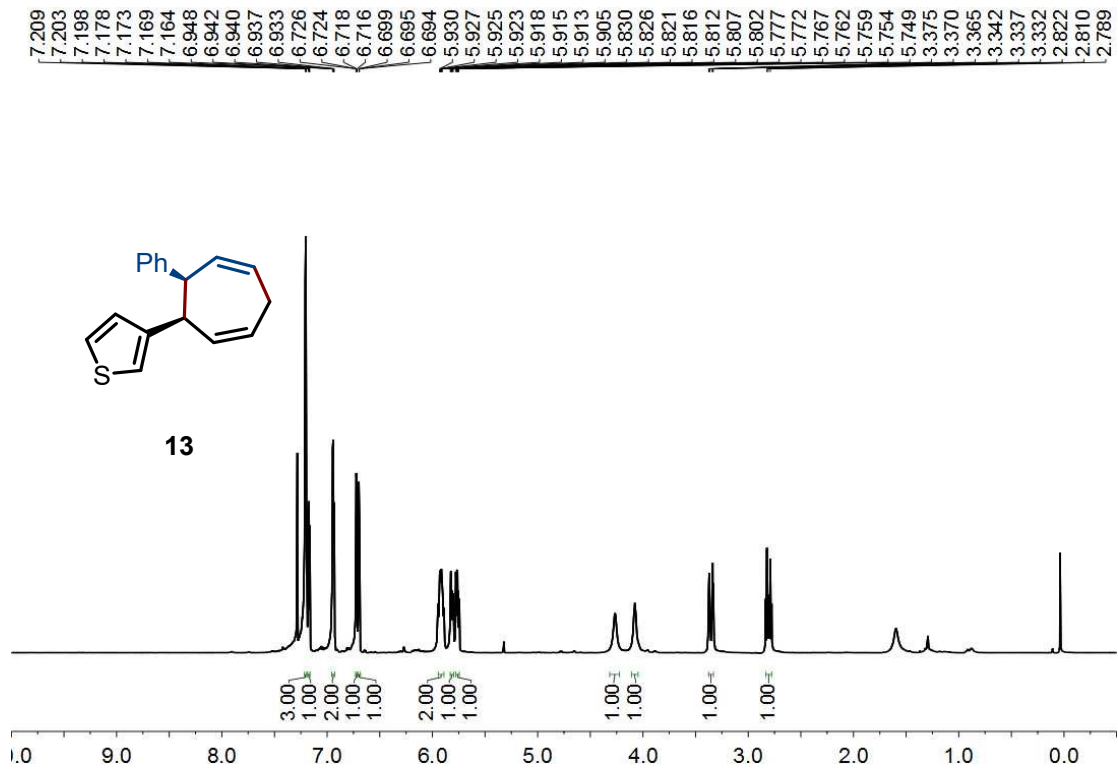


Figure S25.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **13**.

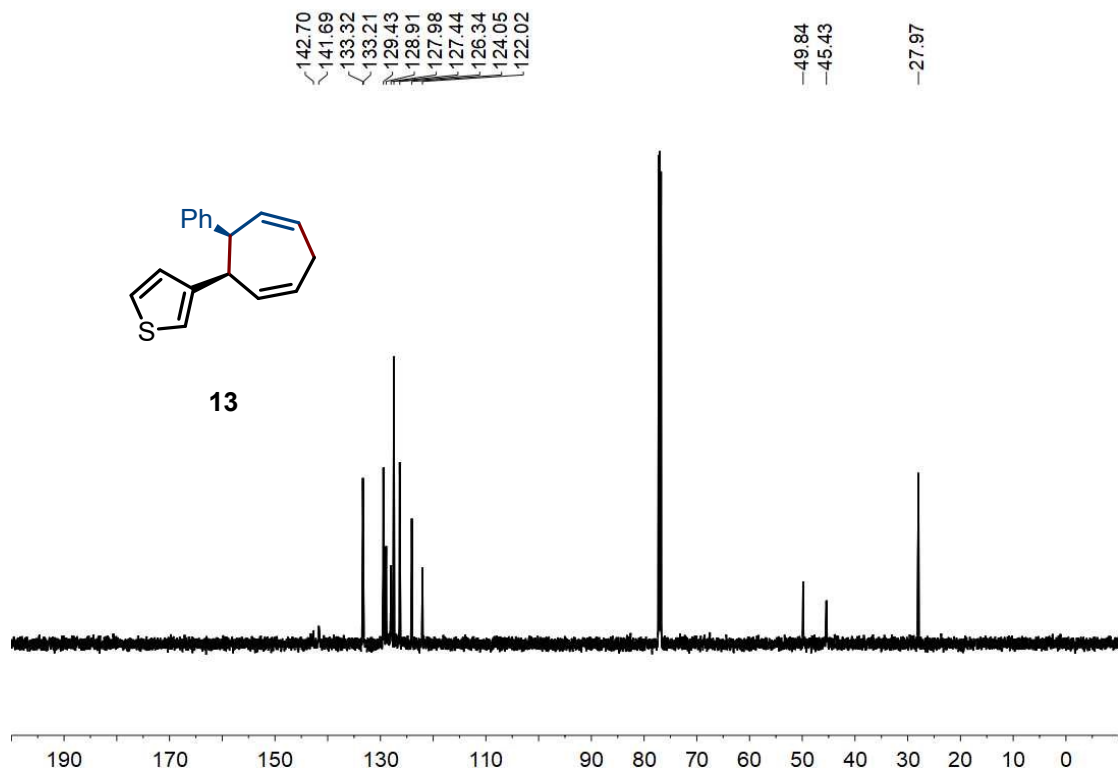


Figure S26.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **13**.

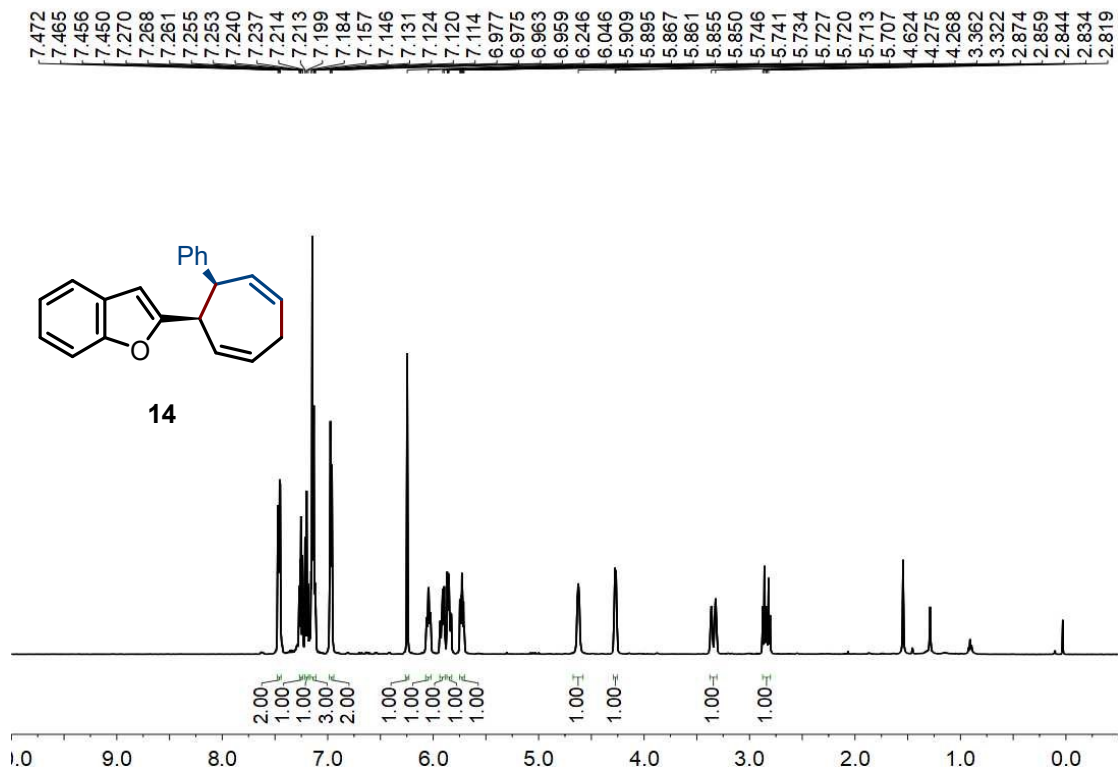


Figure S27.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 14.

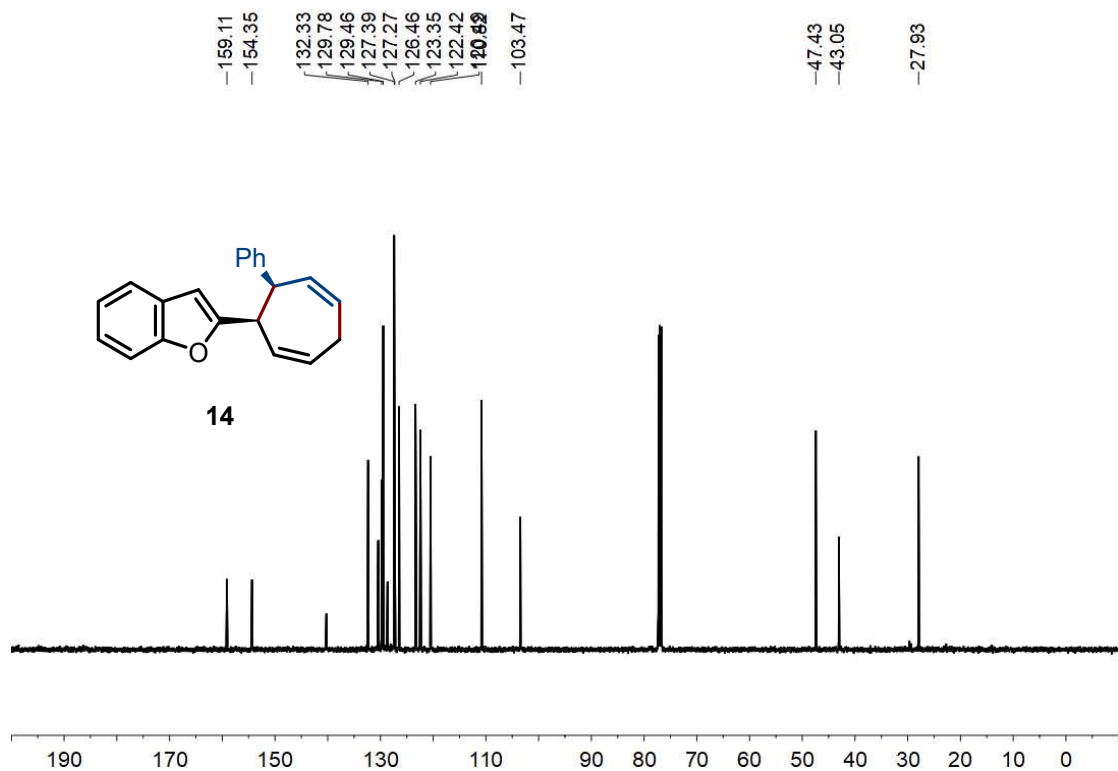


Figure S28.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 14.

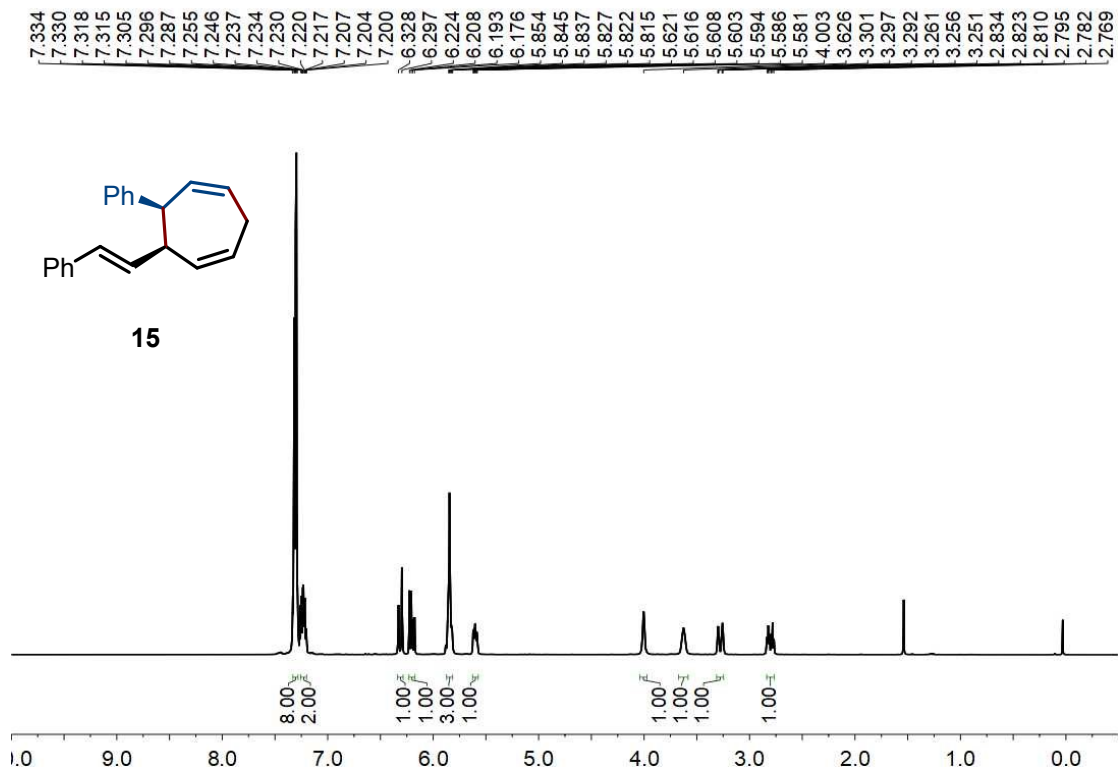


Figure S29.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **15**.

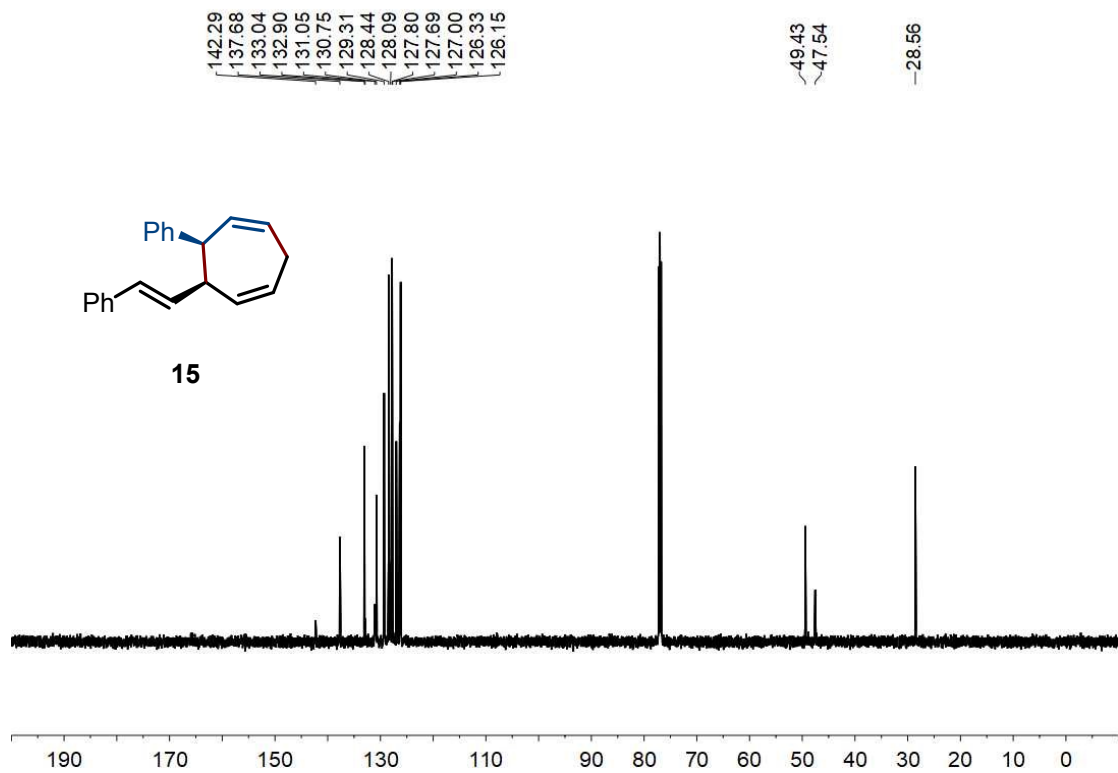


Figure S30.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **15**.

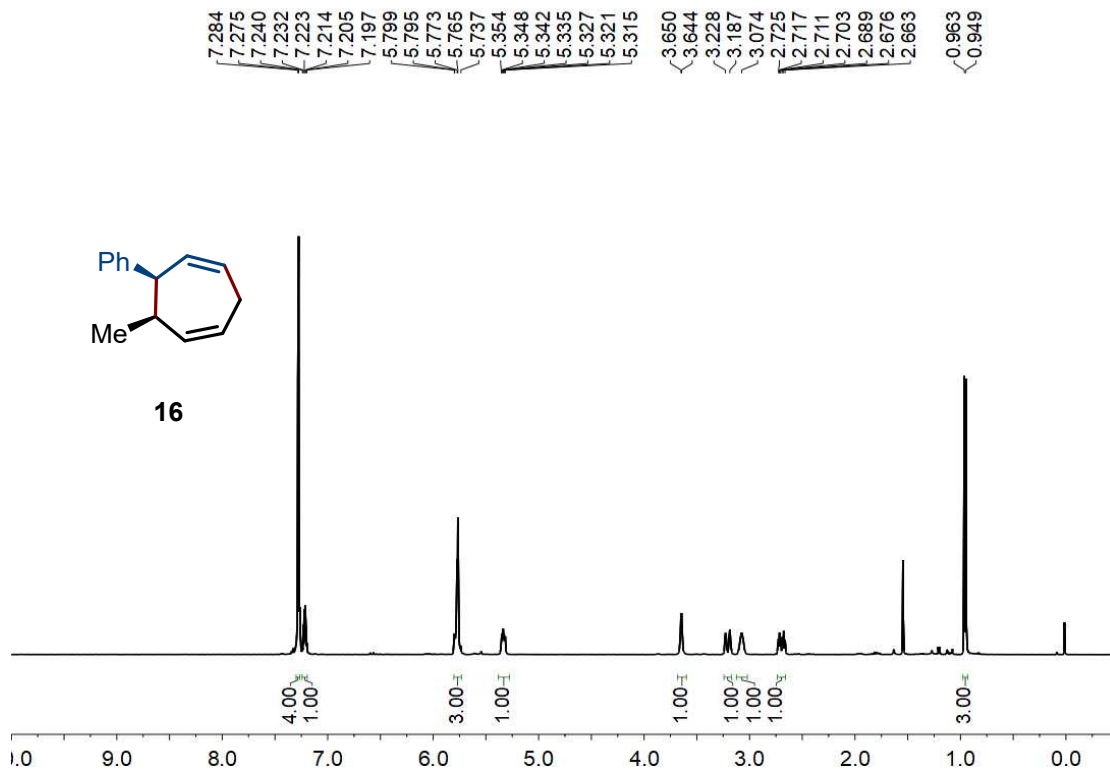


Figure S31. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **16**.

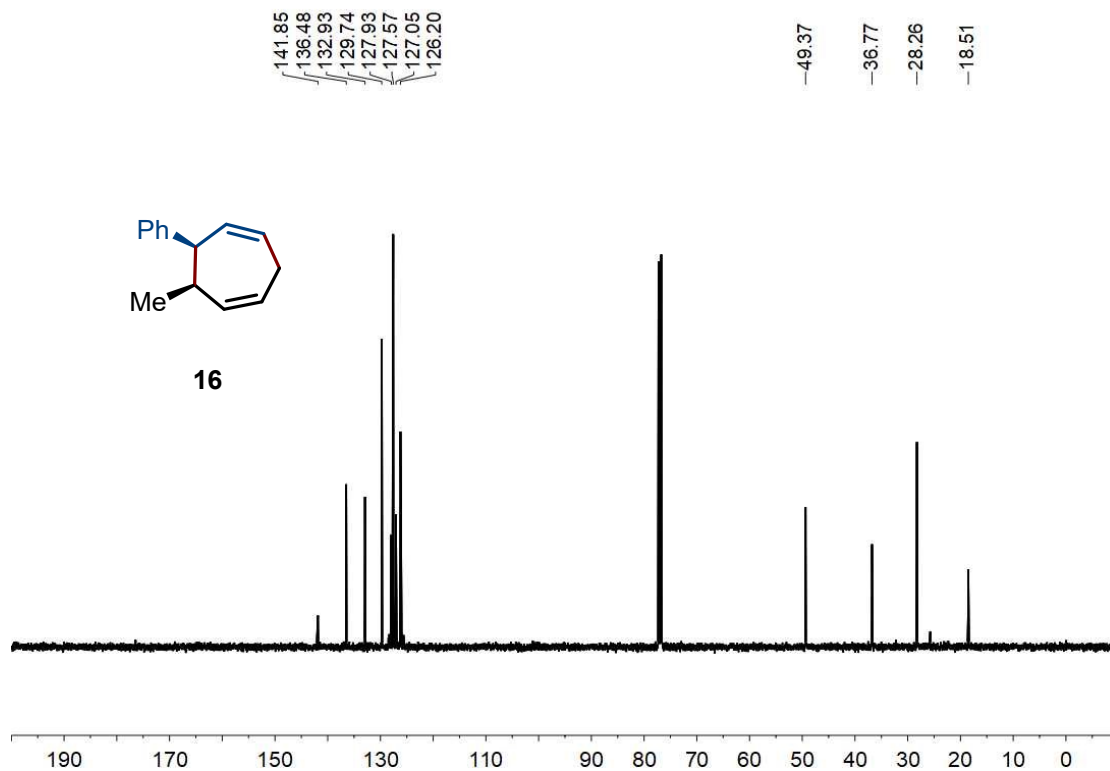
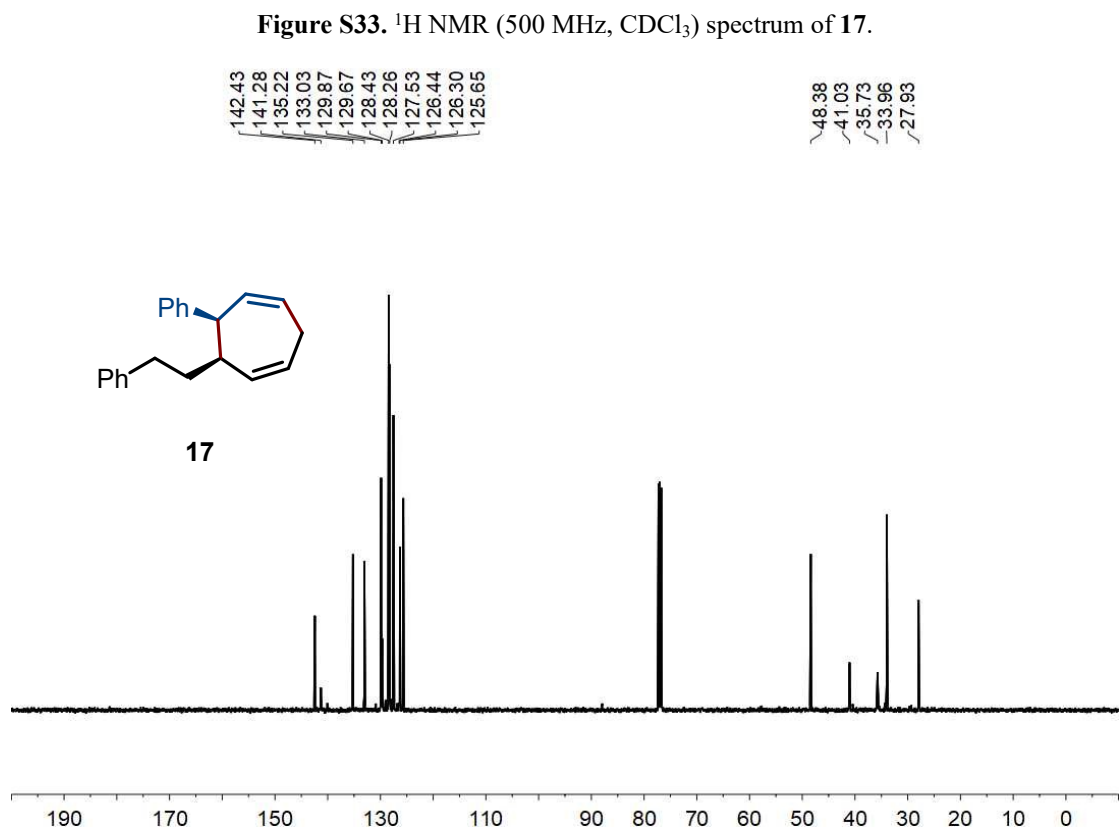
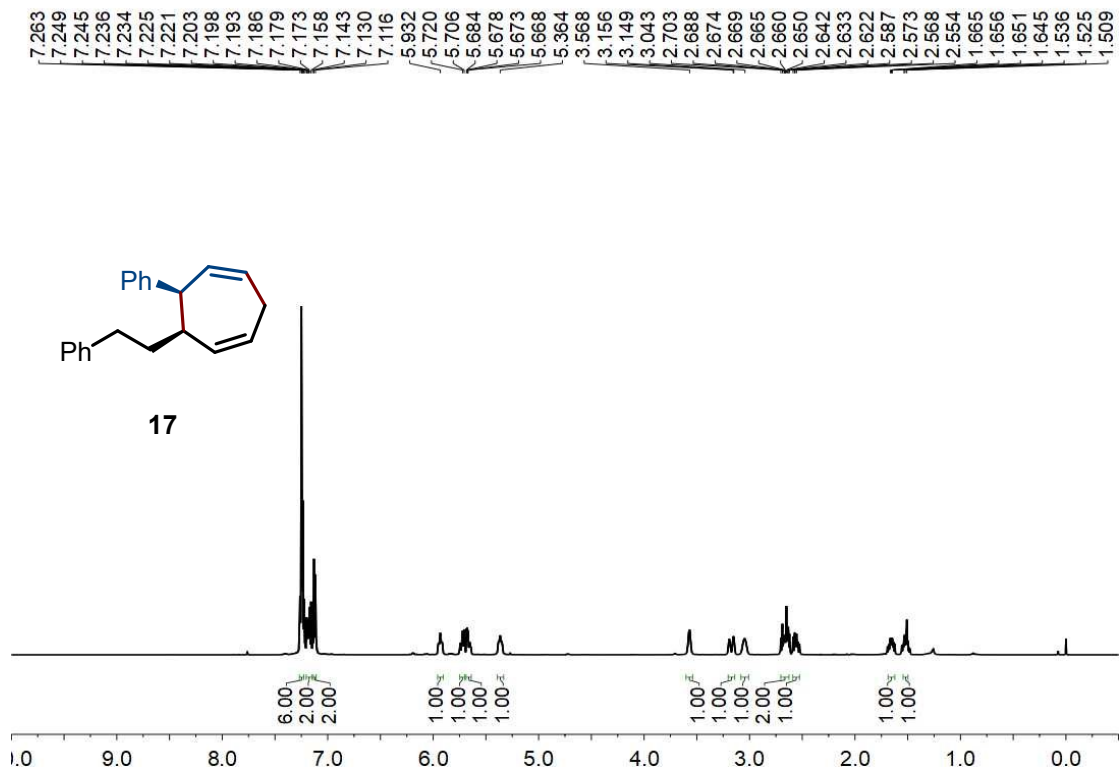


Figure S32. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **16**.





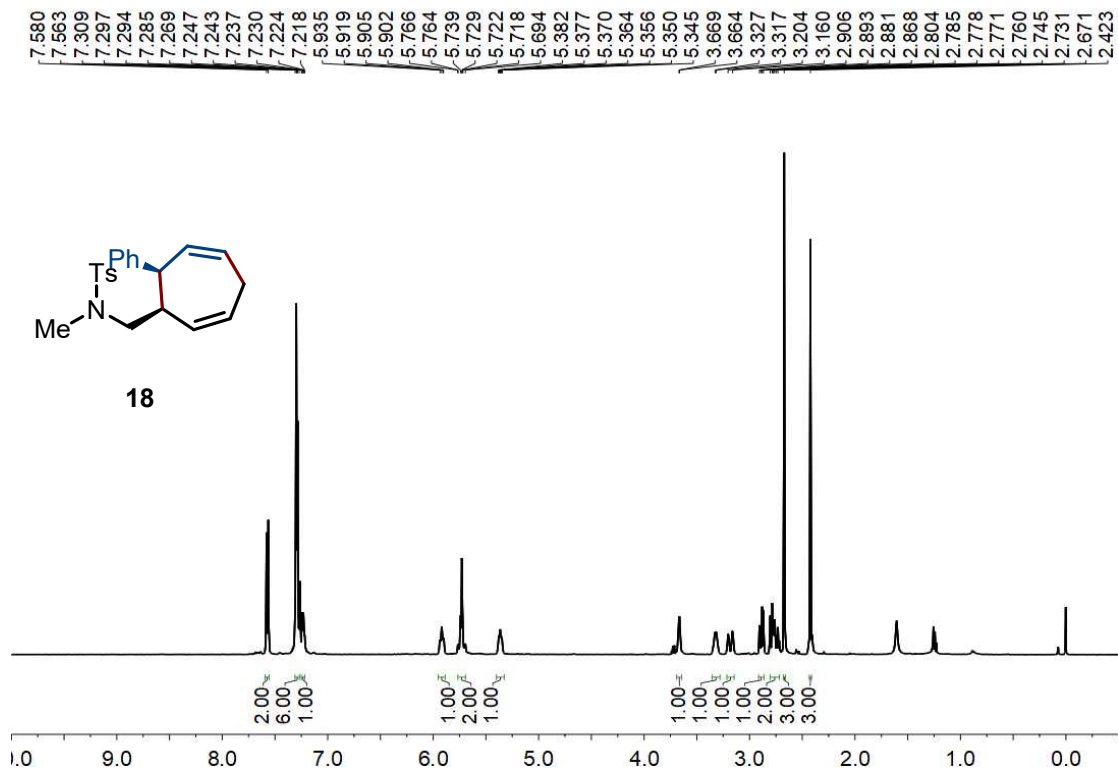


Figure S35.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **18**.

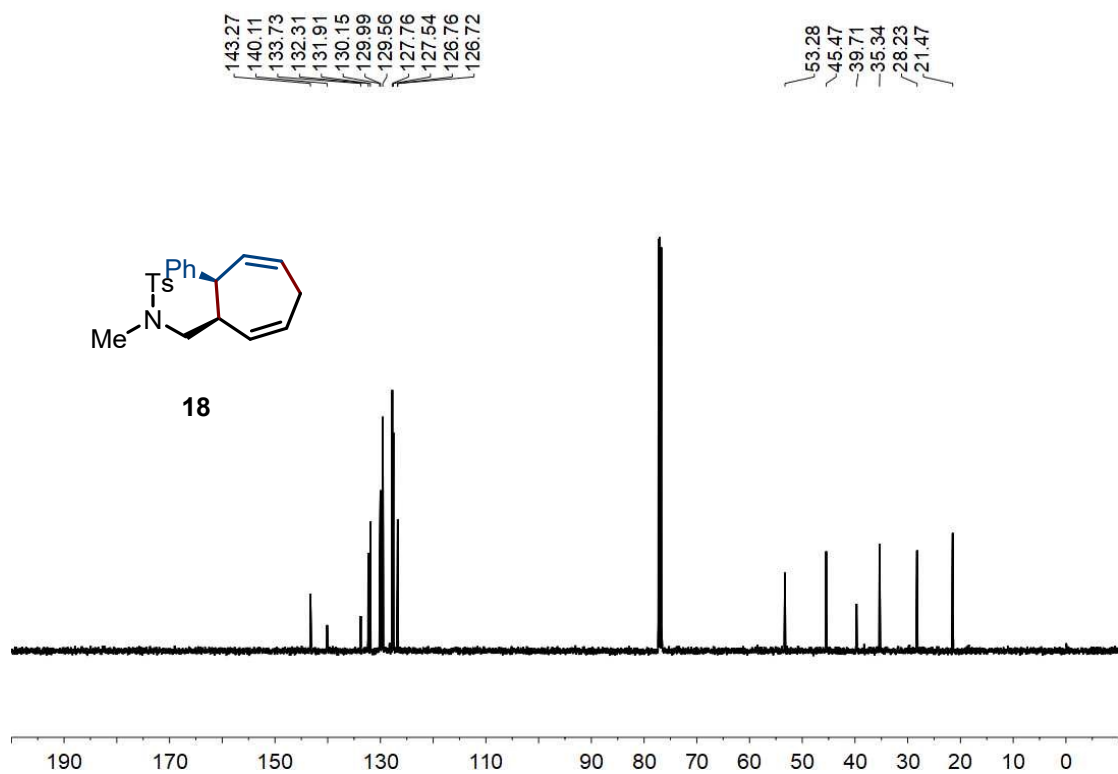


Figure S36.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **18**.

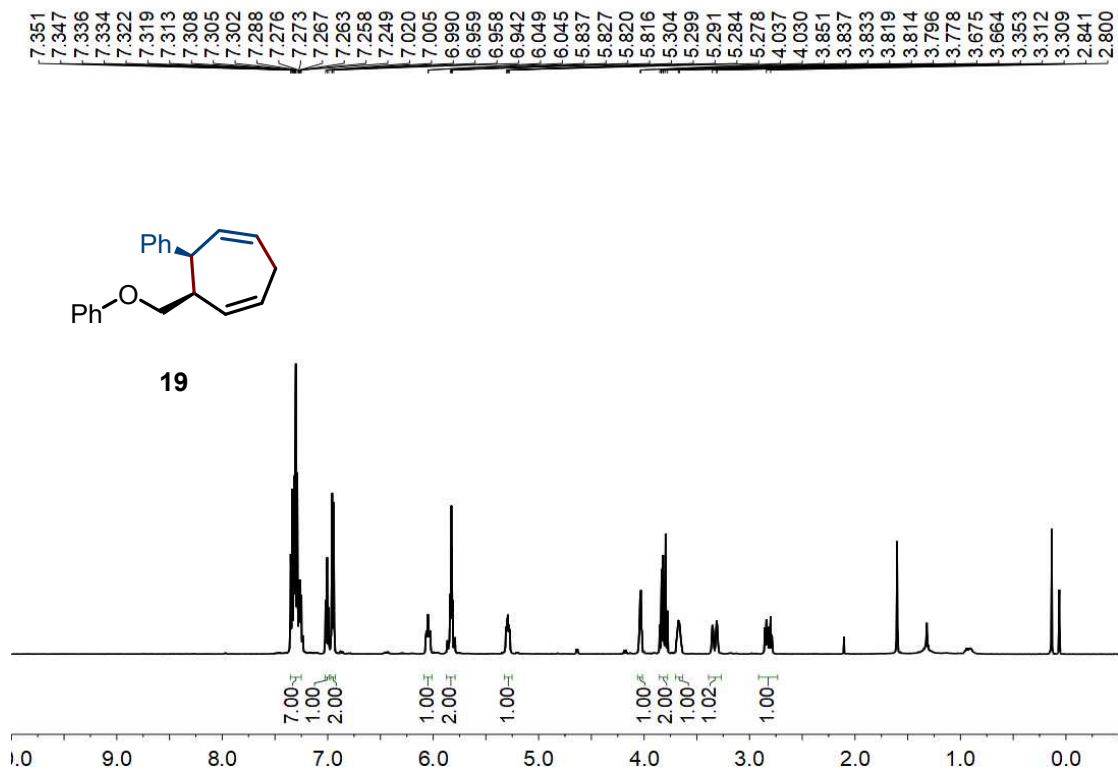


Figure S37.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **19**.

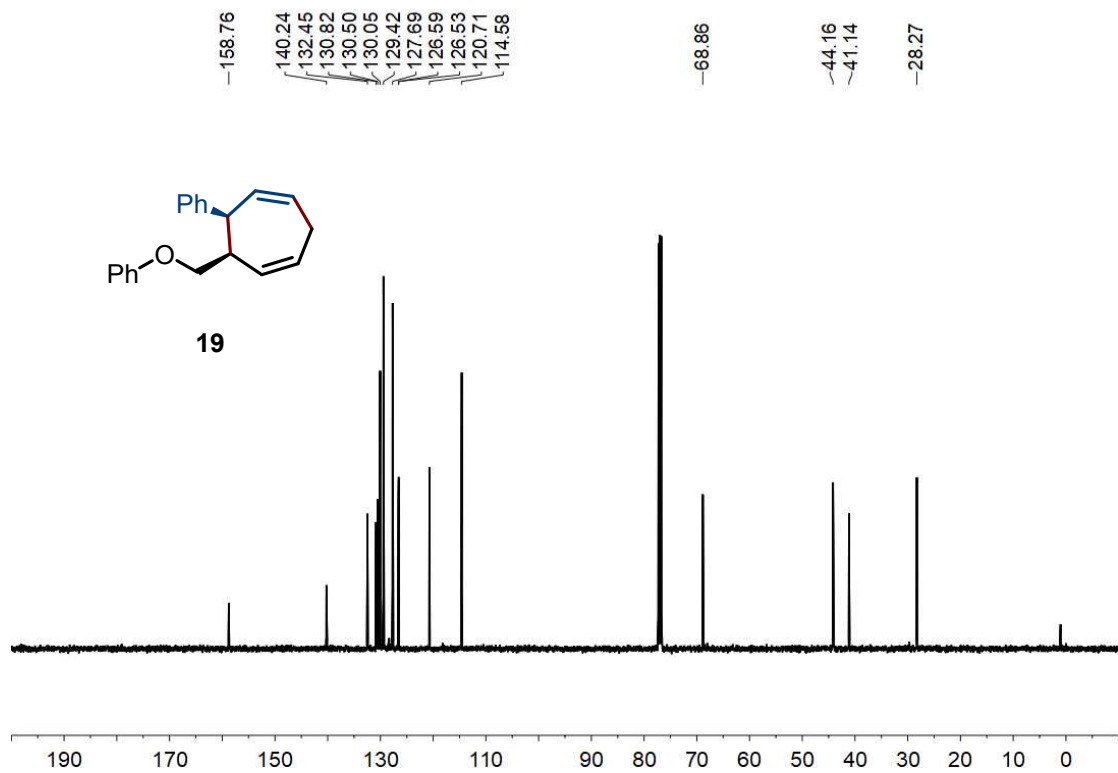


Figure S38.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **19**.

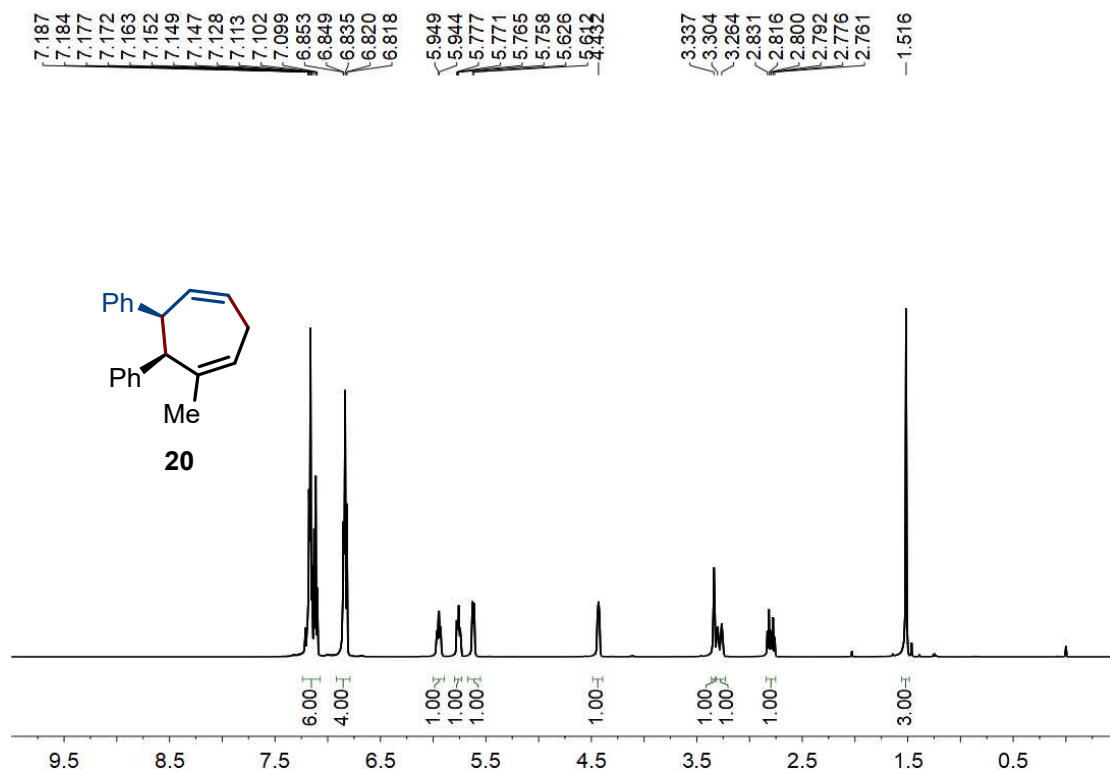


Figure S39. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **20**.

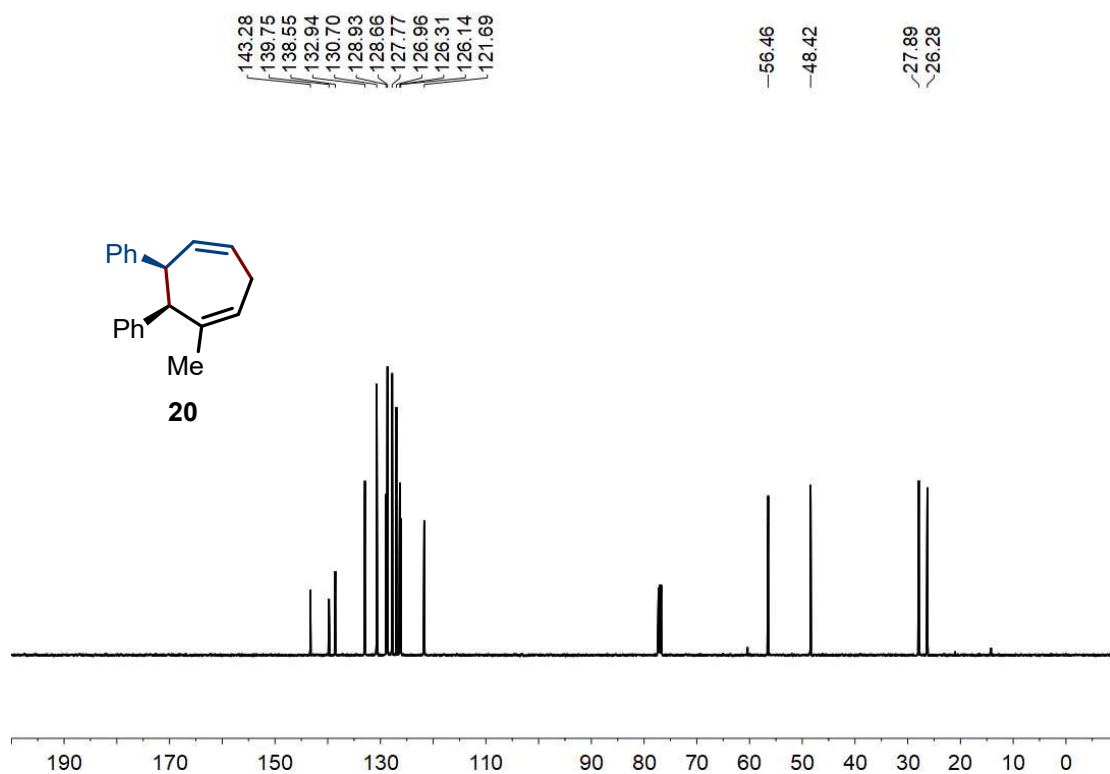


Figure S40. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **20**.

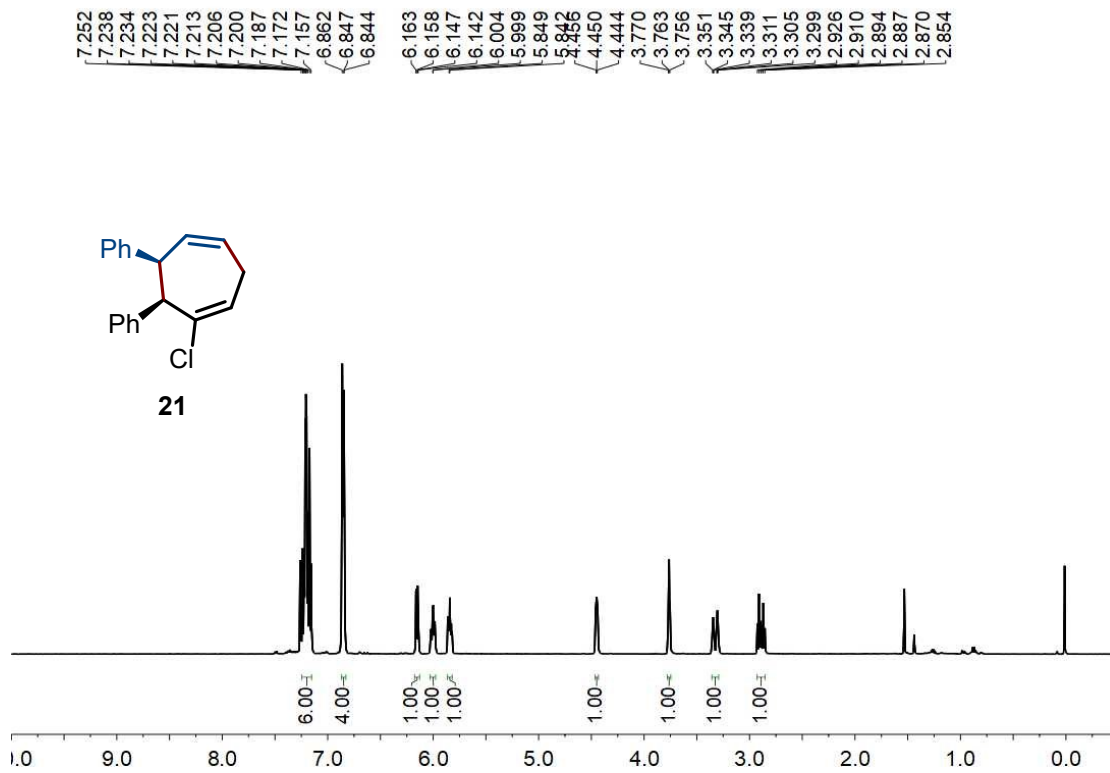


Figure S41.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **21**.

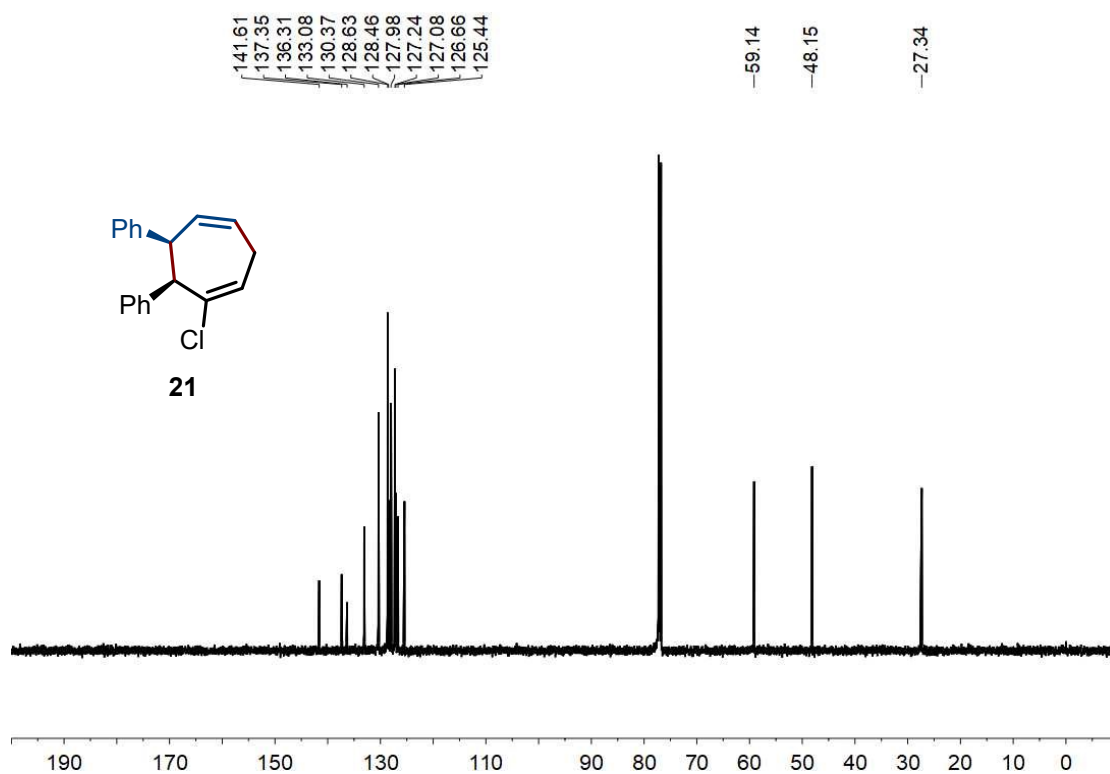


Figure S42.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **21**.

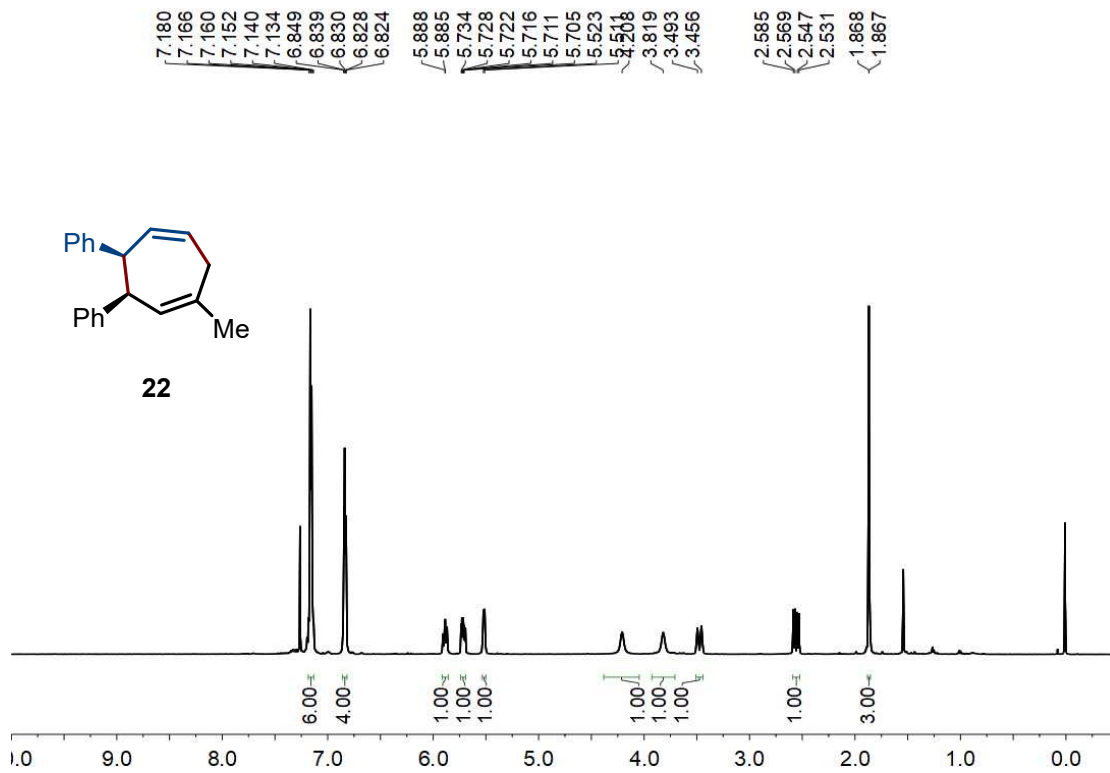


Figure S43. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **22**.

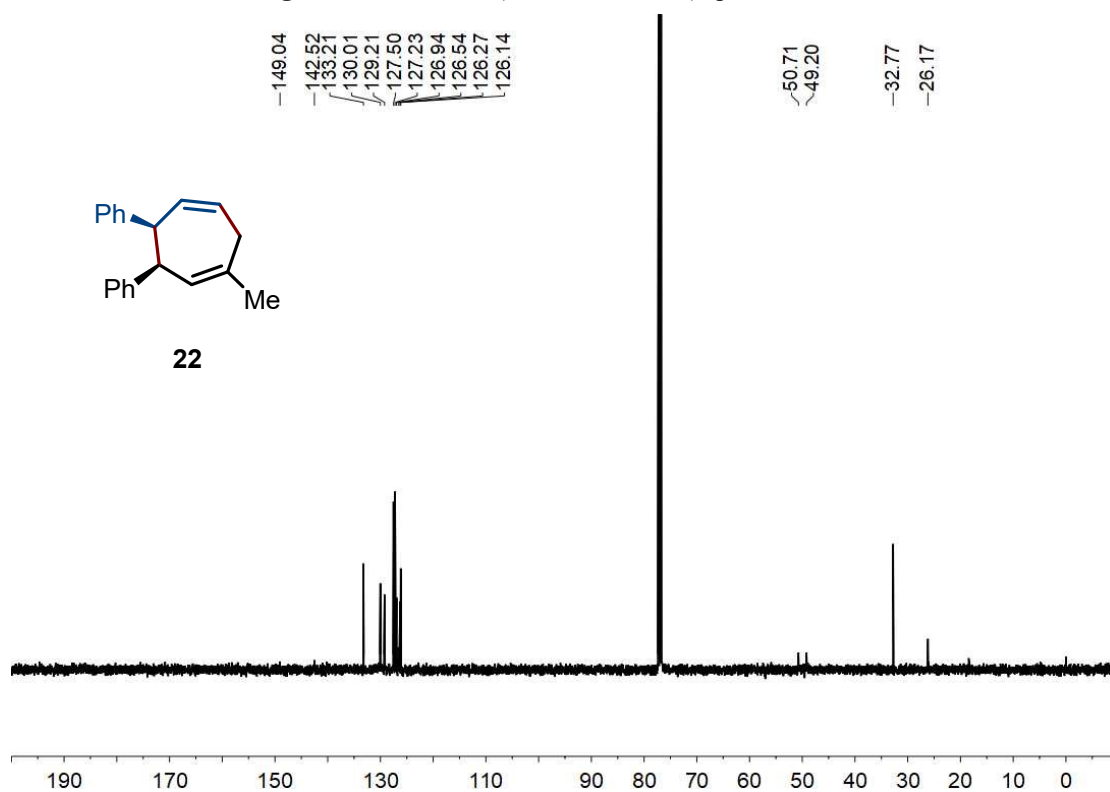


Figure S44. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **22**.

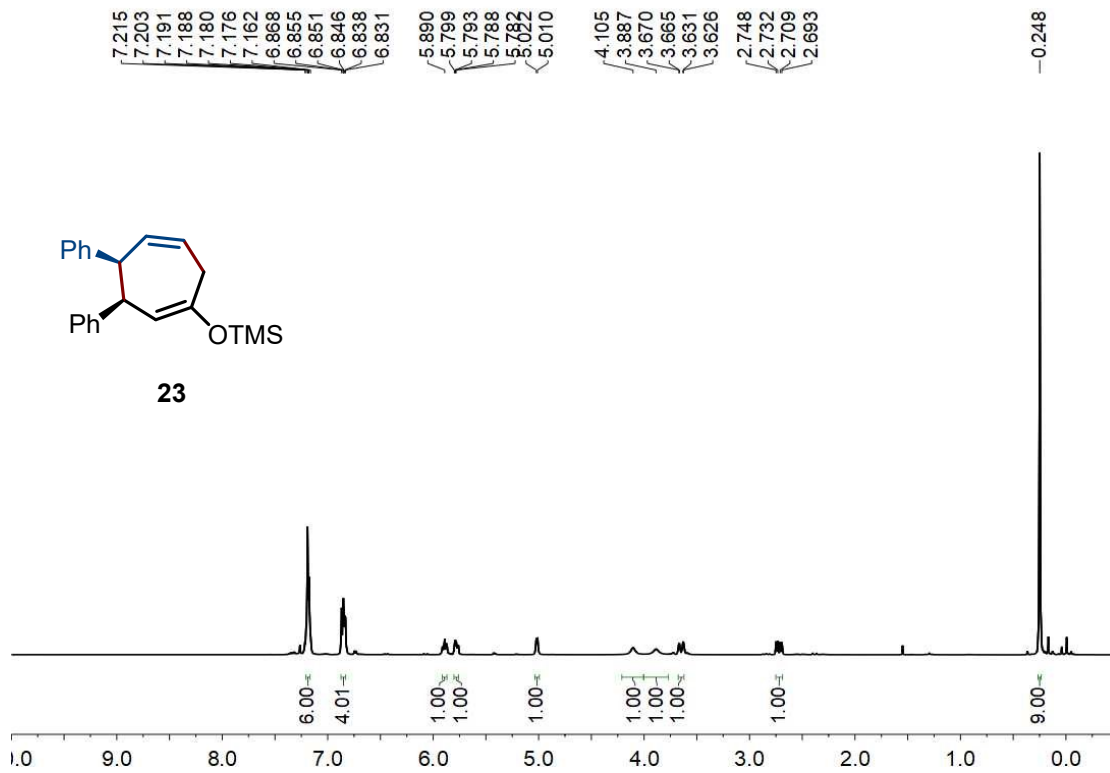


Figure S45. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **23**.

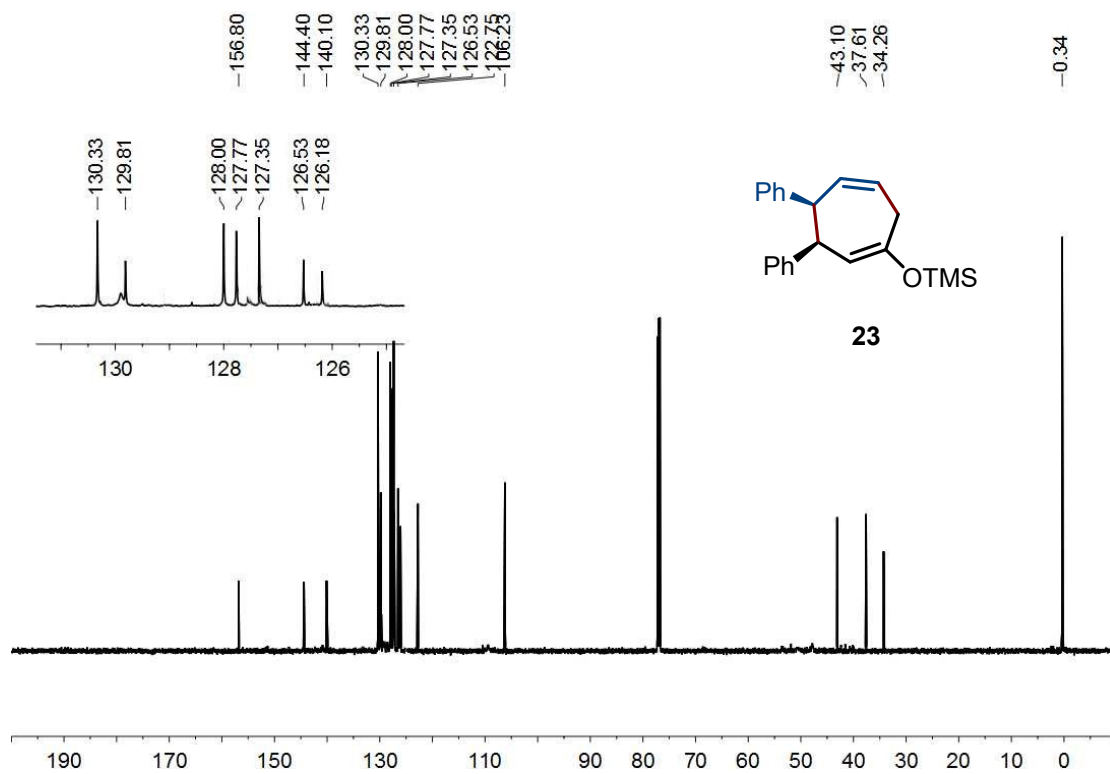


Figure S46. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **23**.

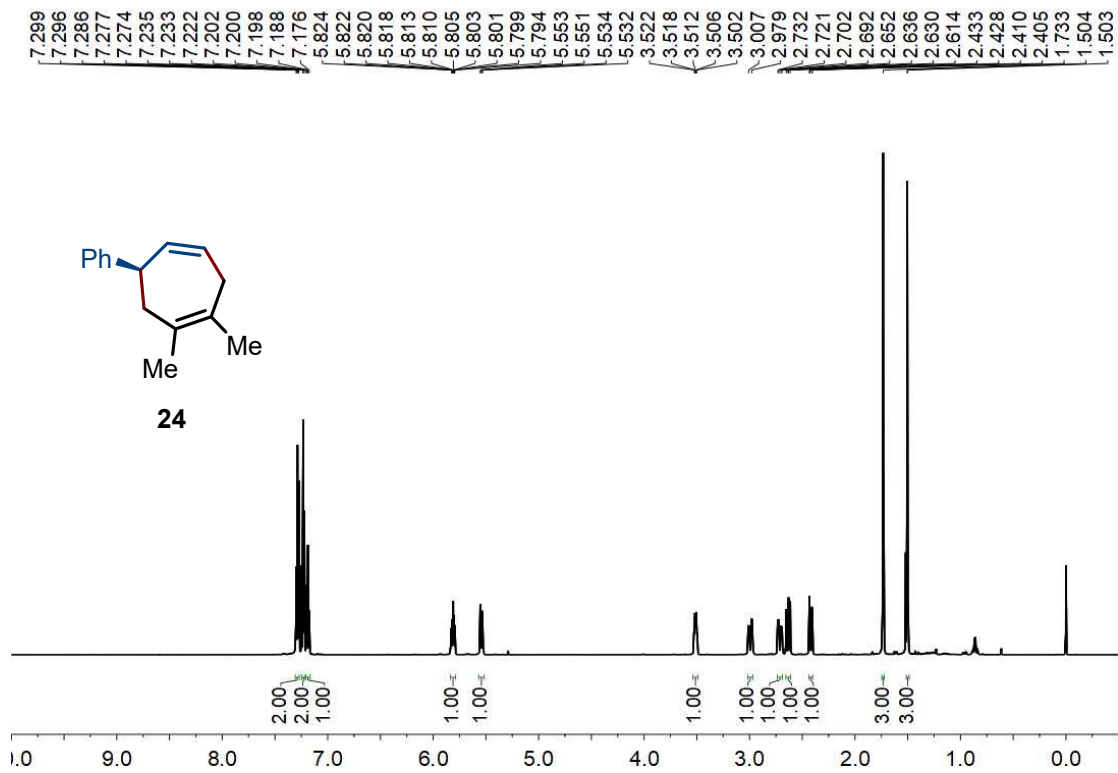


Figure S47.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **24**.

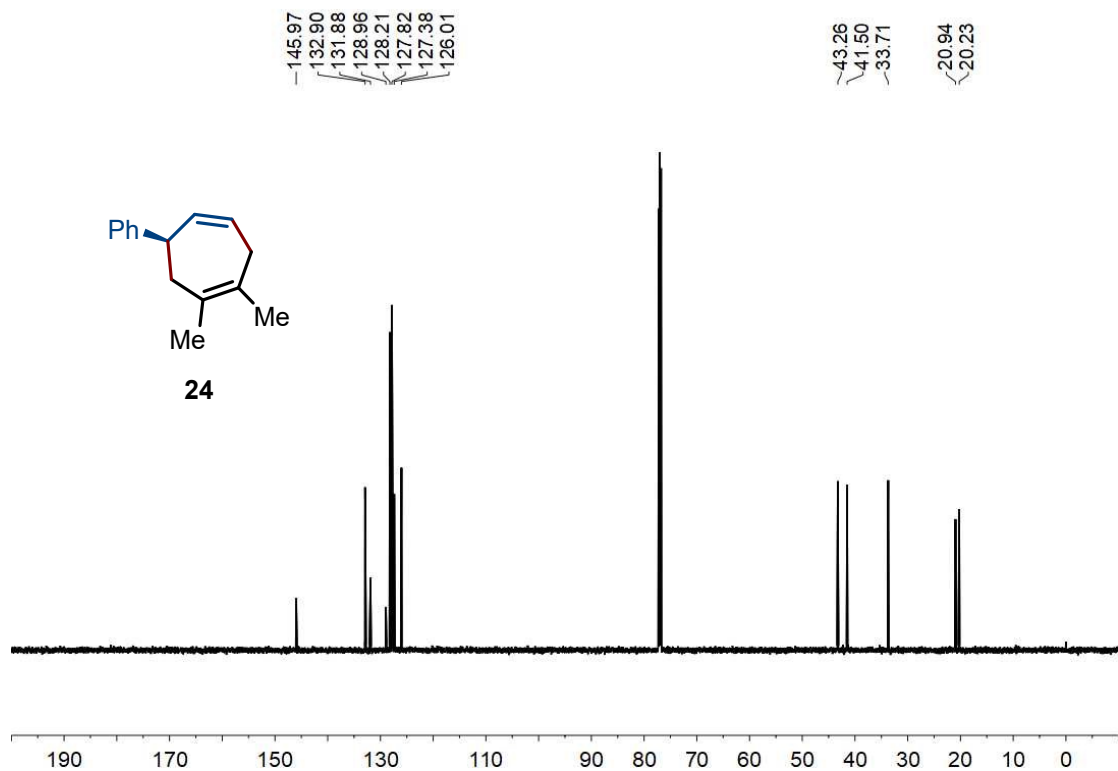
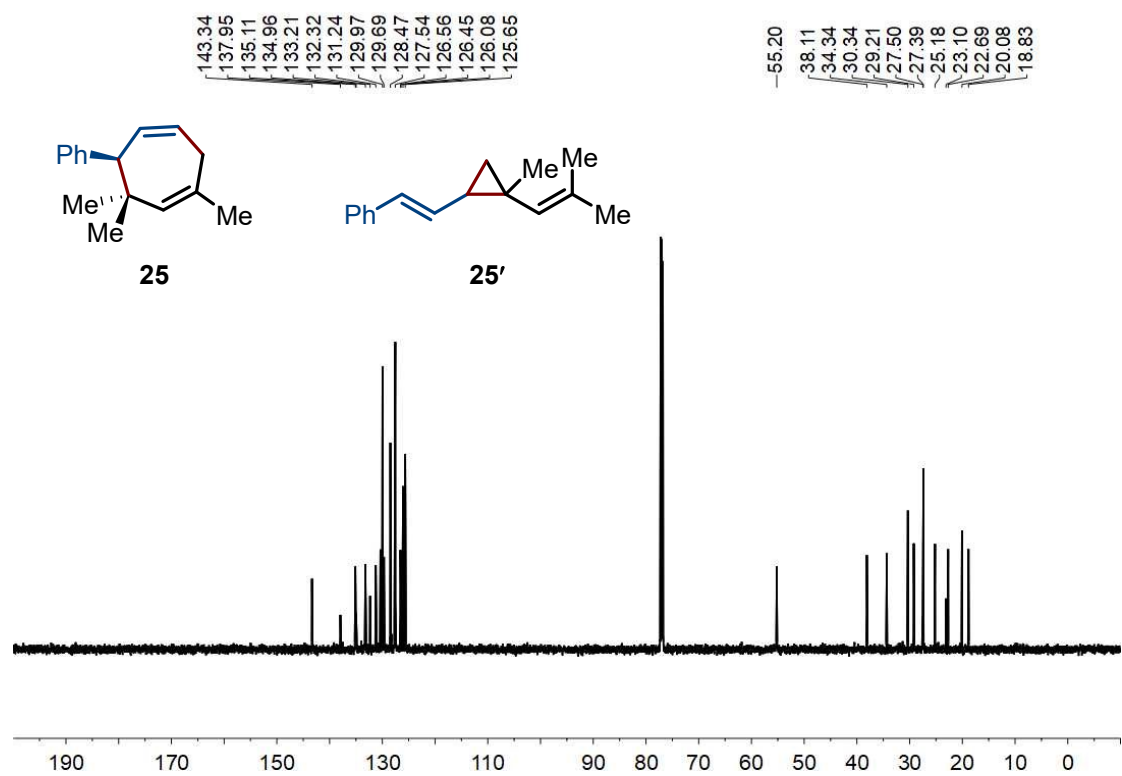
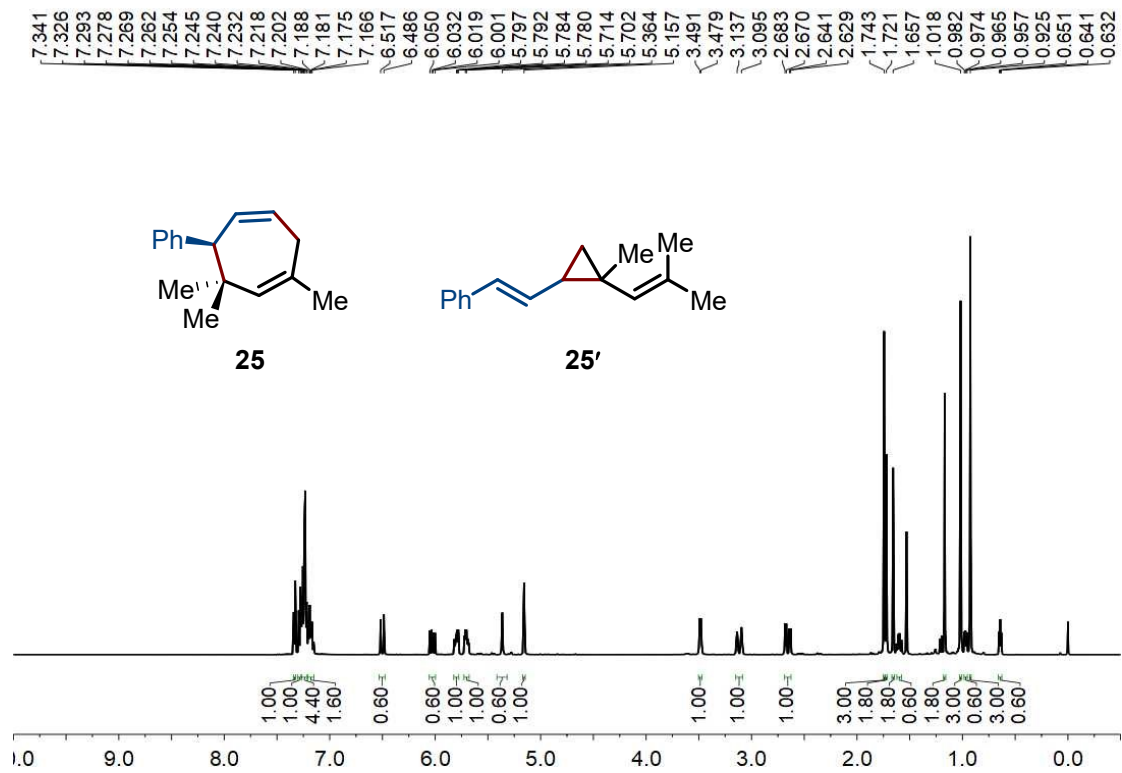


Figure S48.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **24**.





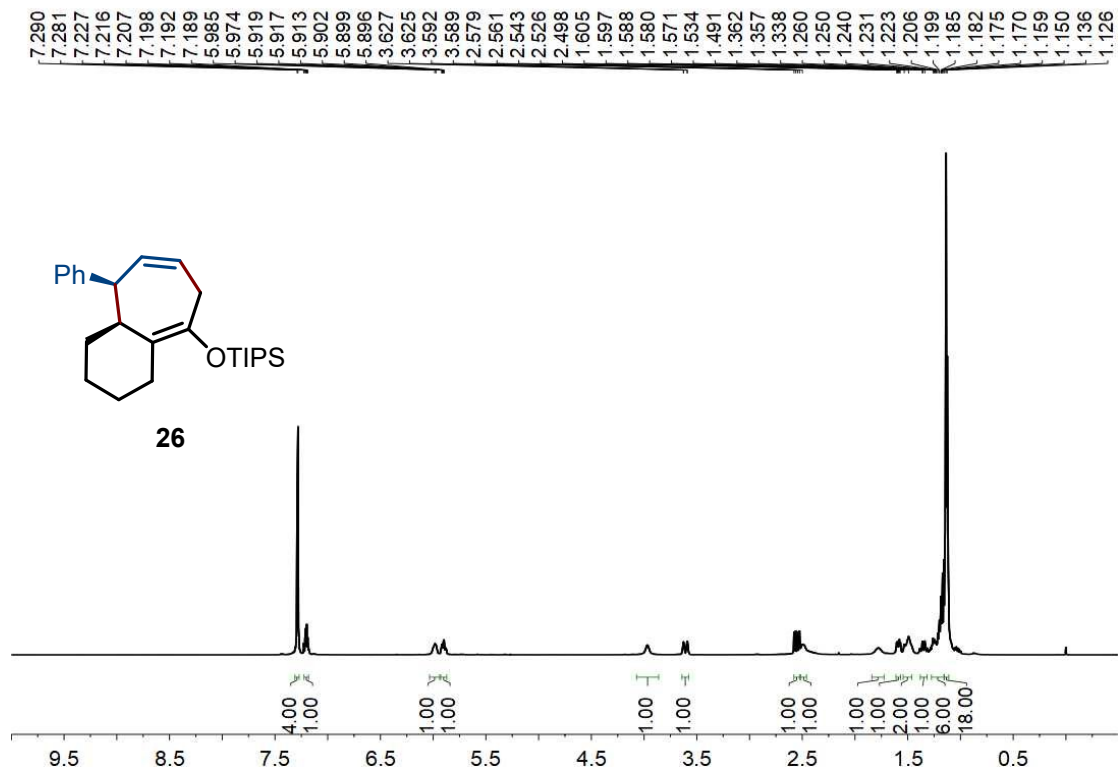


Figure S51.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **26**.

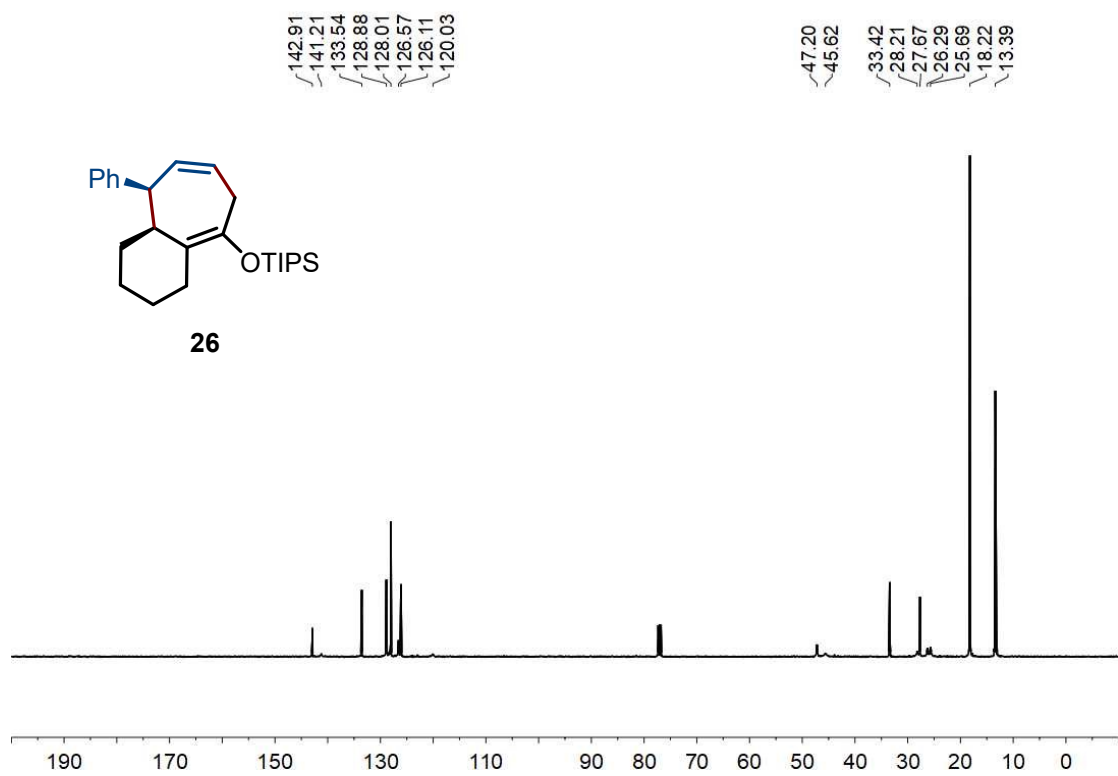


Figure S52.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **26**.

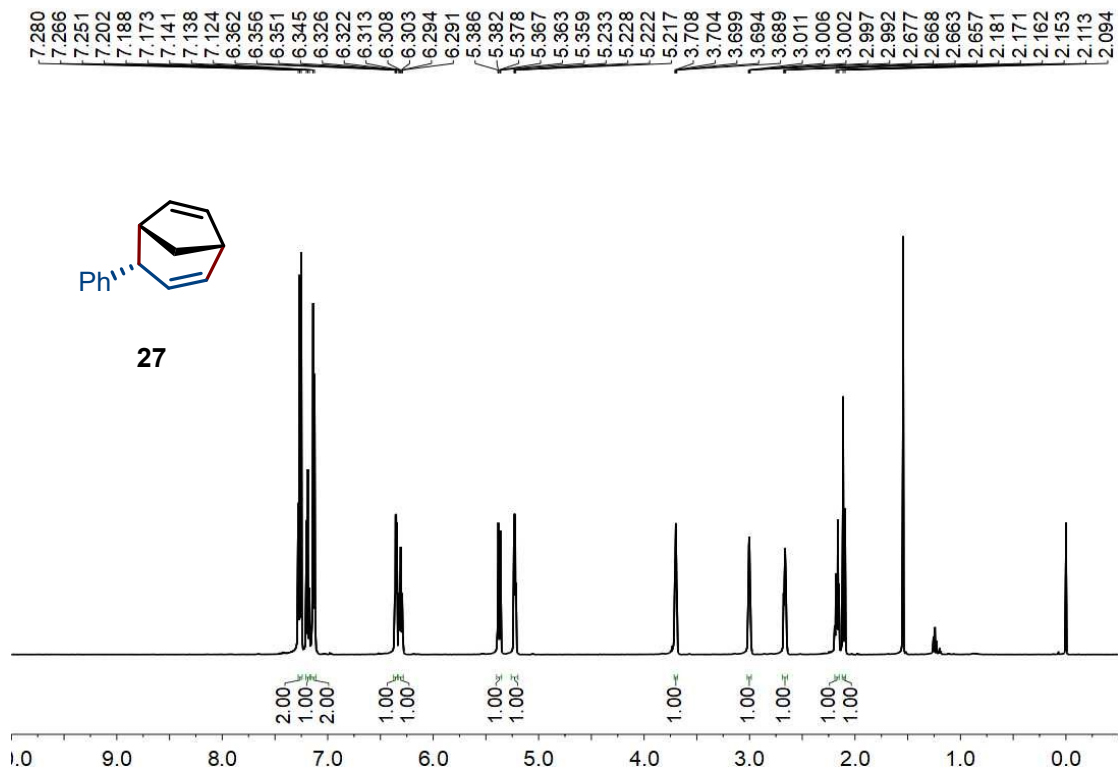


Figure S53. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 27.

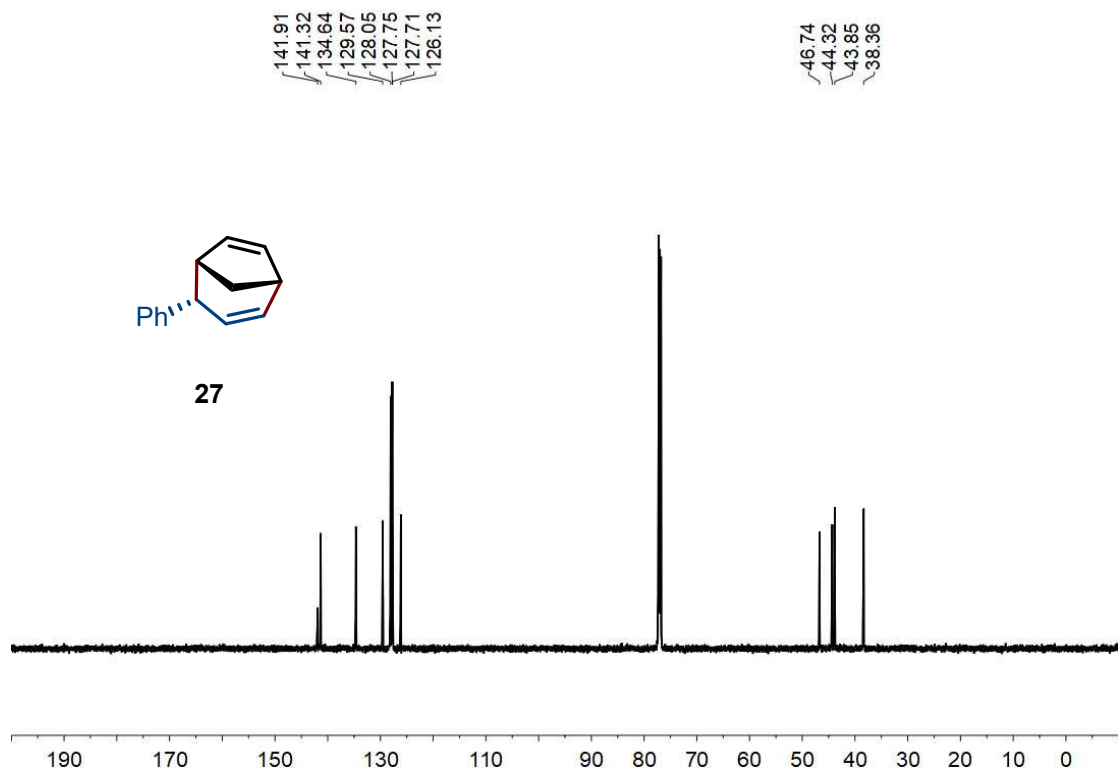


Figure S54. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 27.

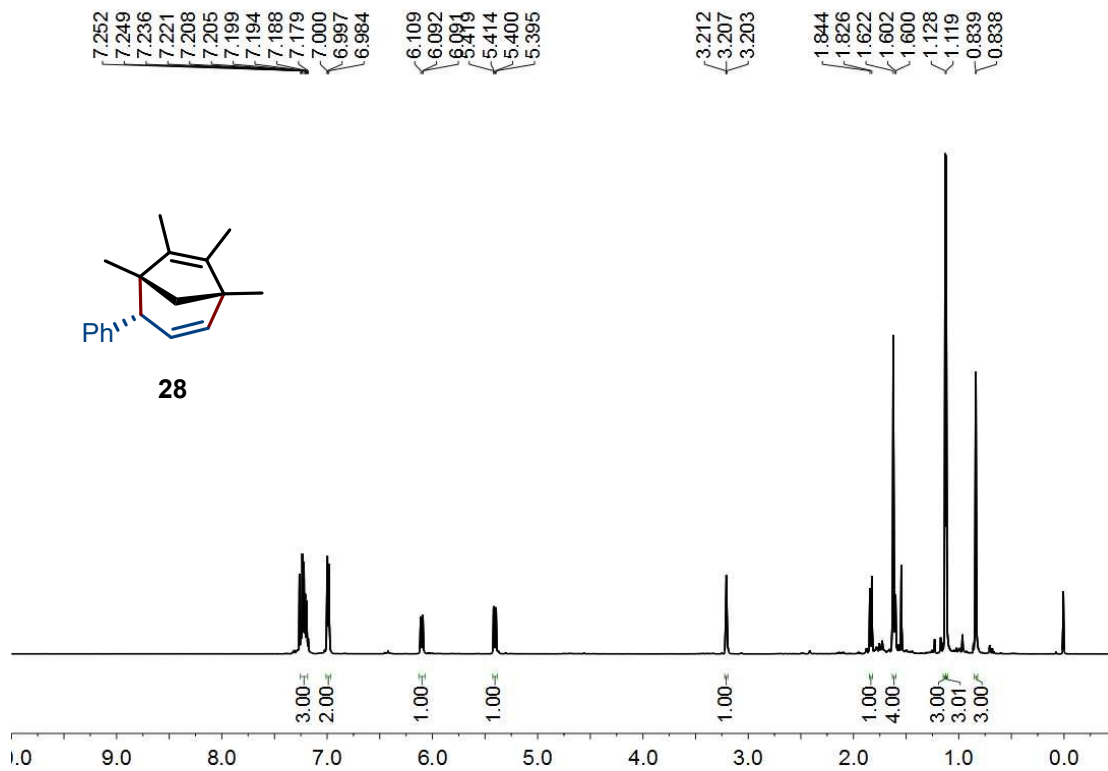


Figure S55. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **28**.

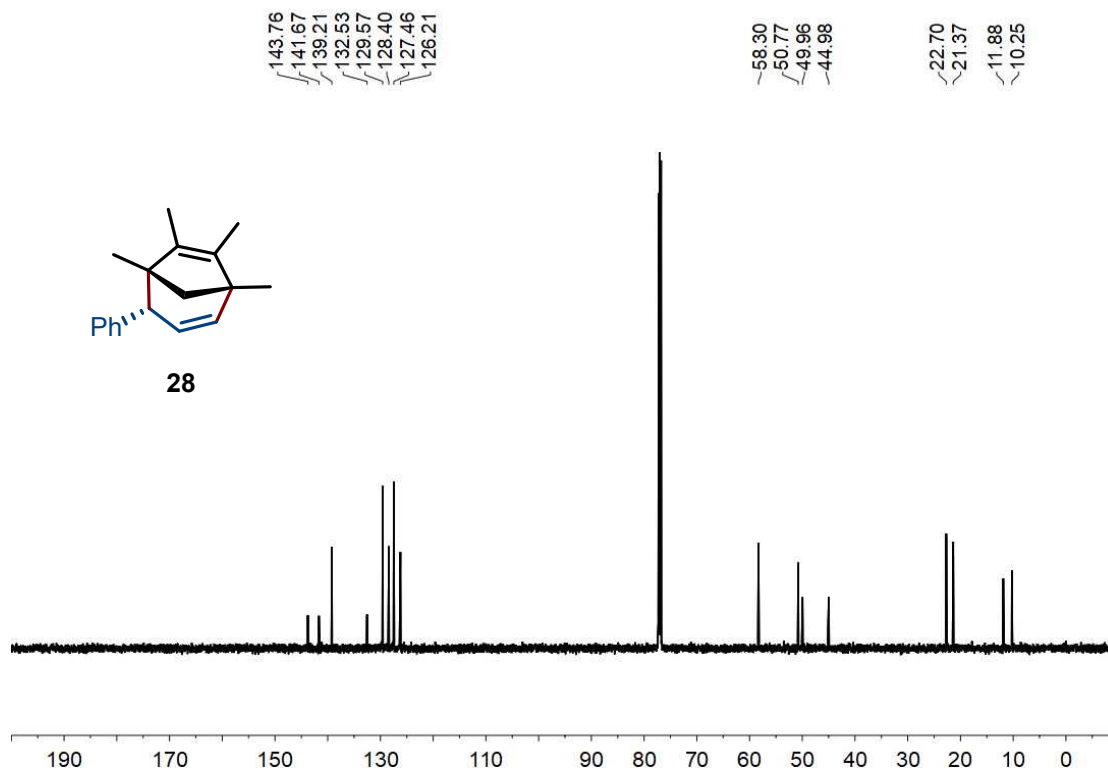


Figure S56. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **28**.

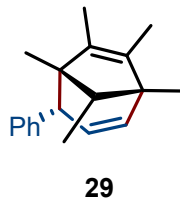
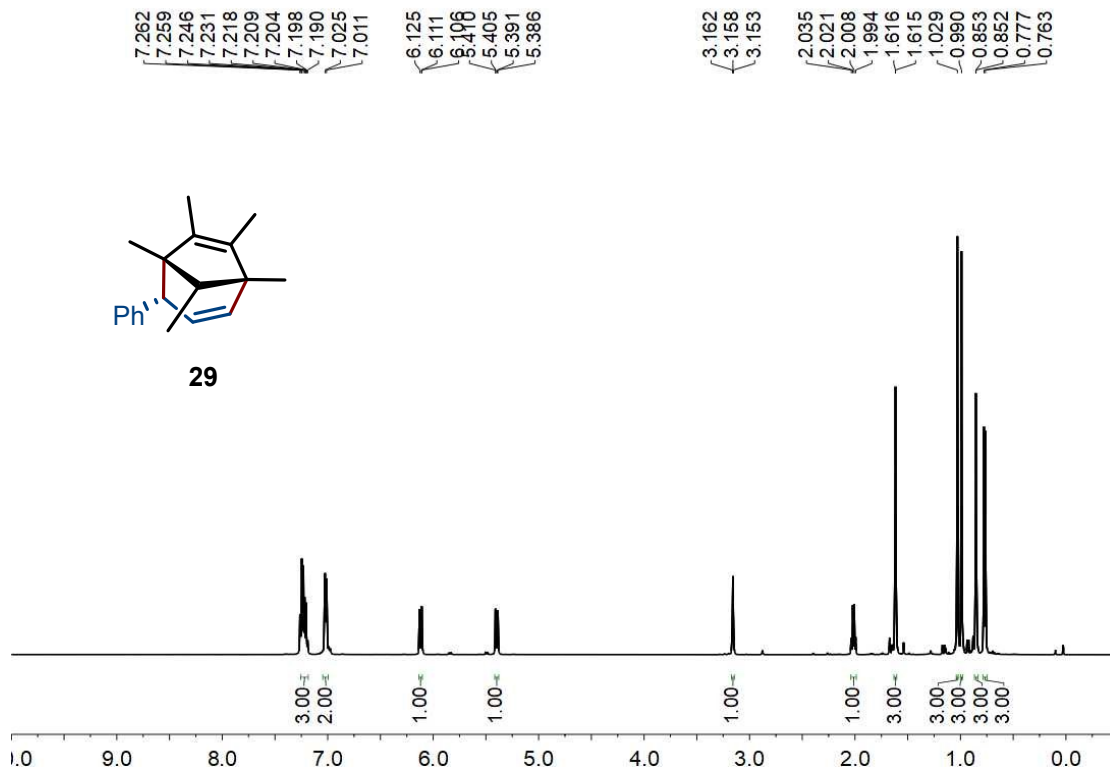


Figure S57. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **29**.

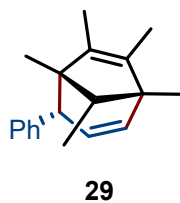
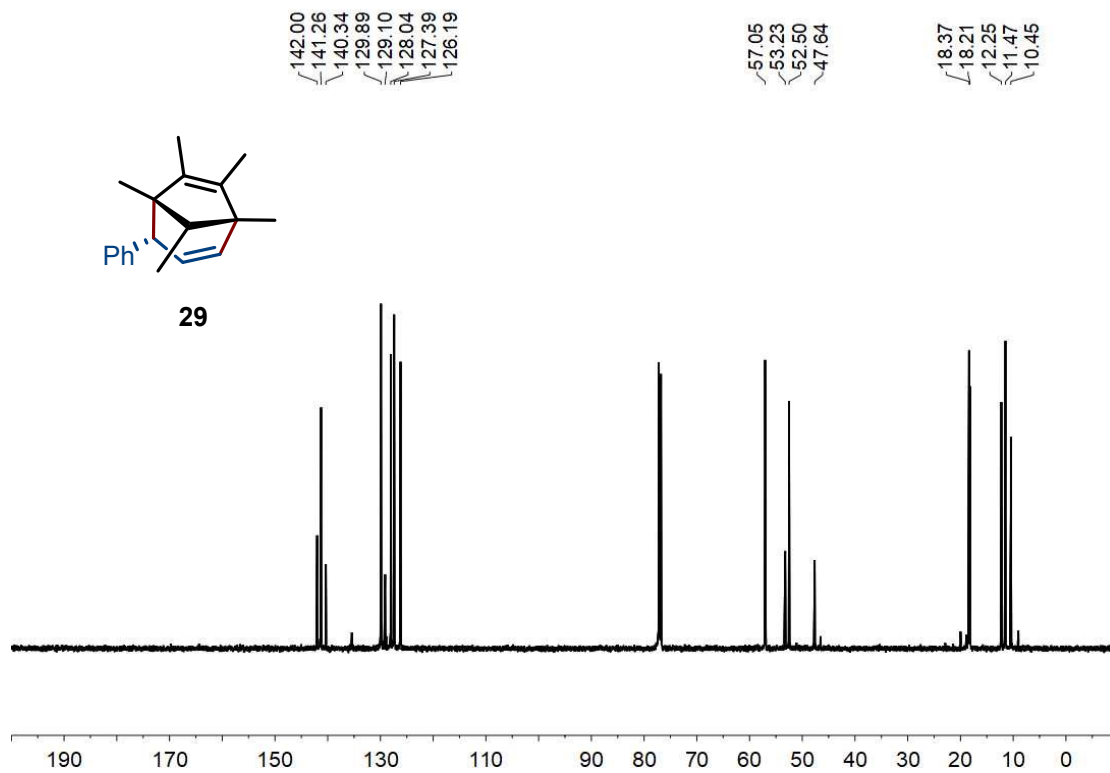


Figure S58. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **29**.

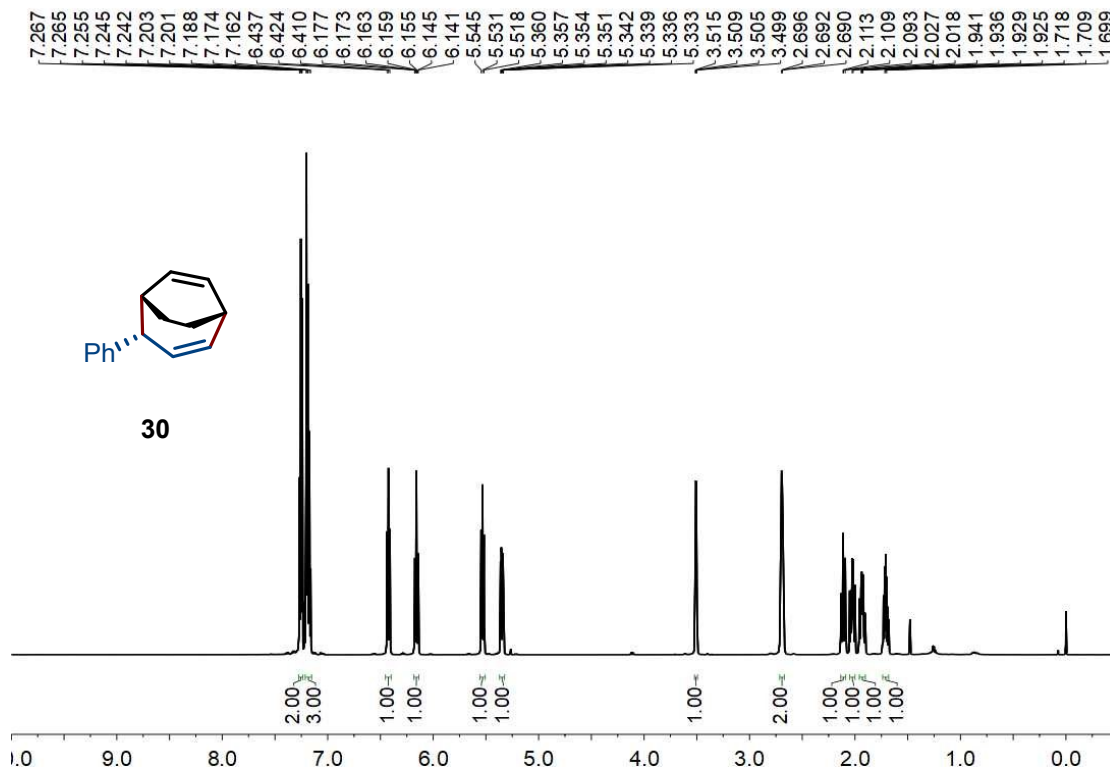


Figure S59.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum of **30**.

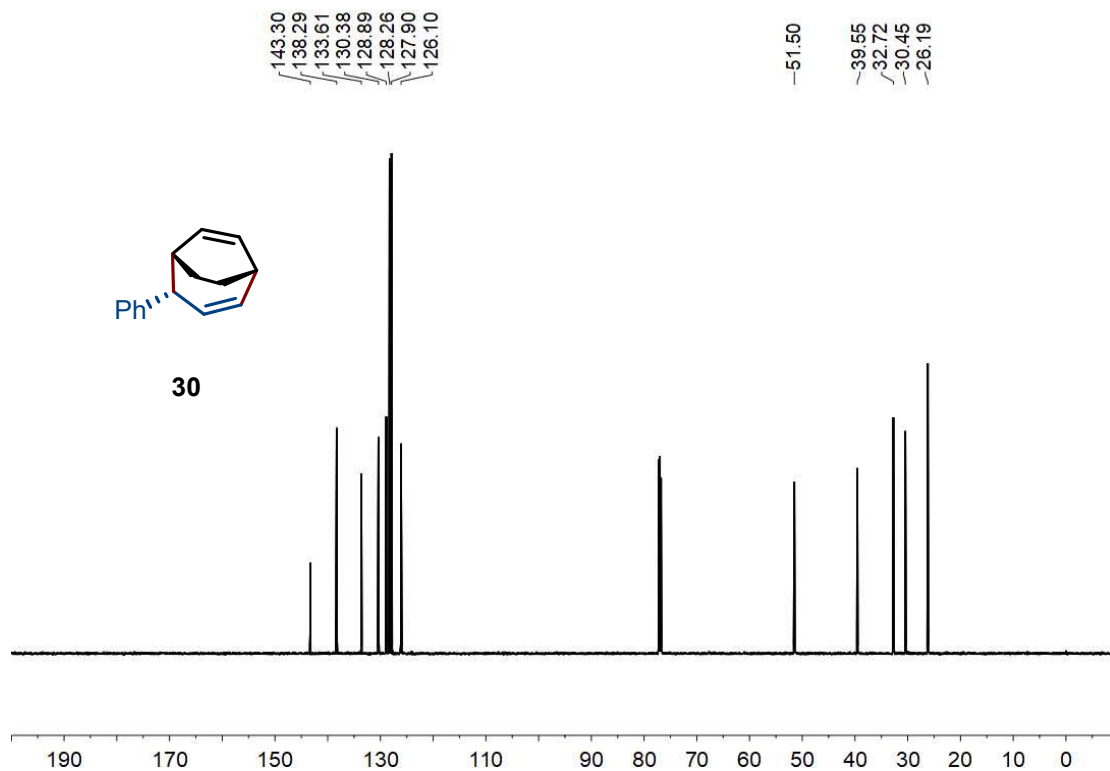


Figure S60.  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ) spectrum of **30**.

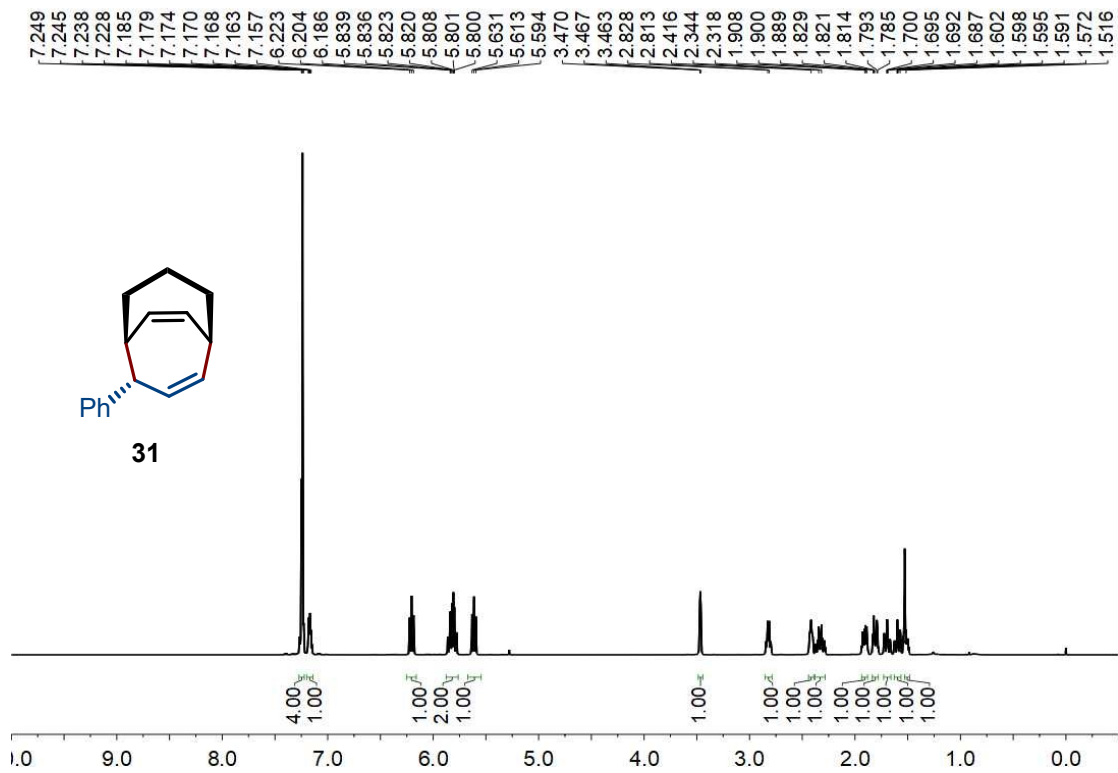


Figure S61.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) spectrum of **31**.

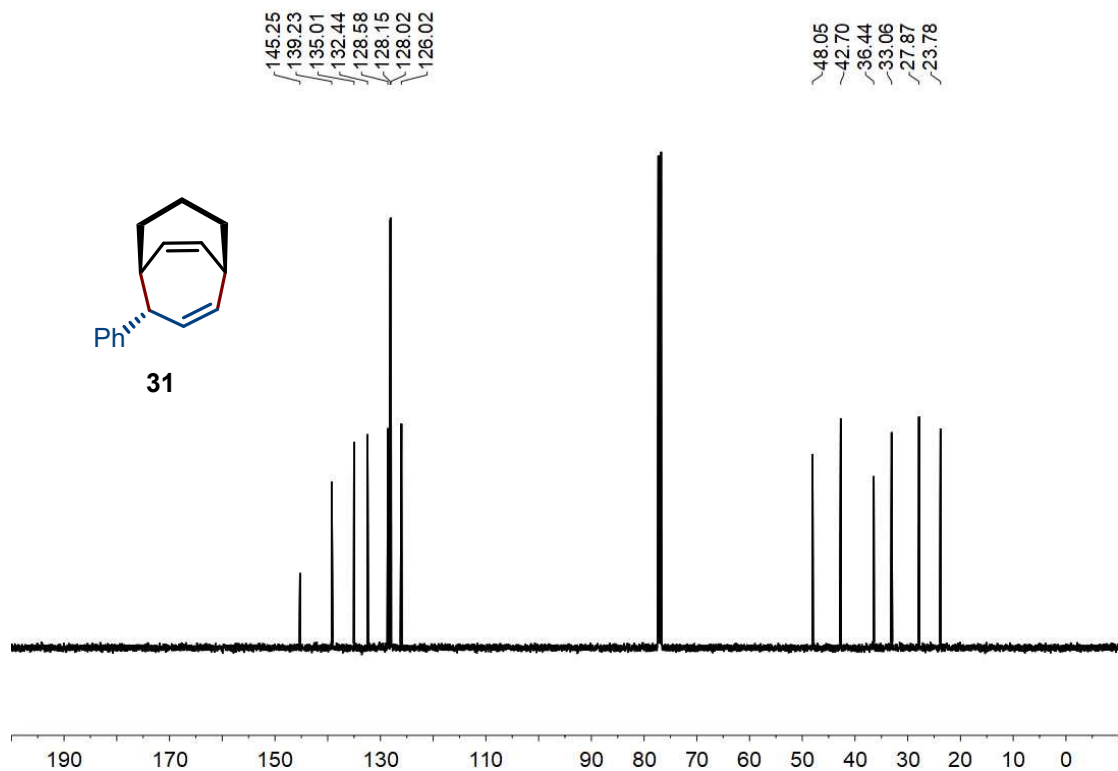
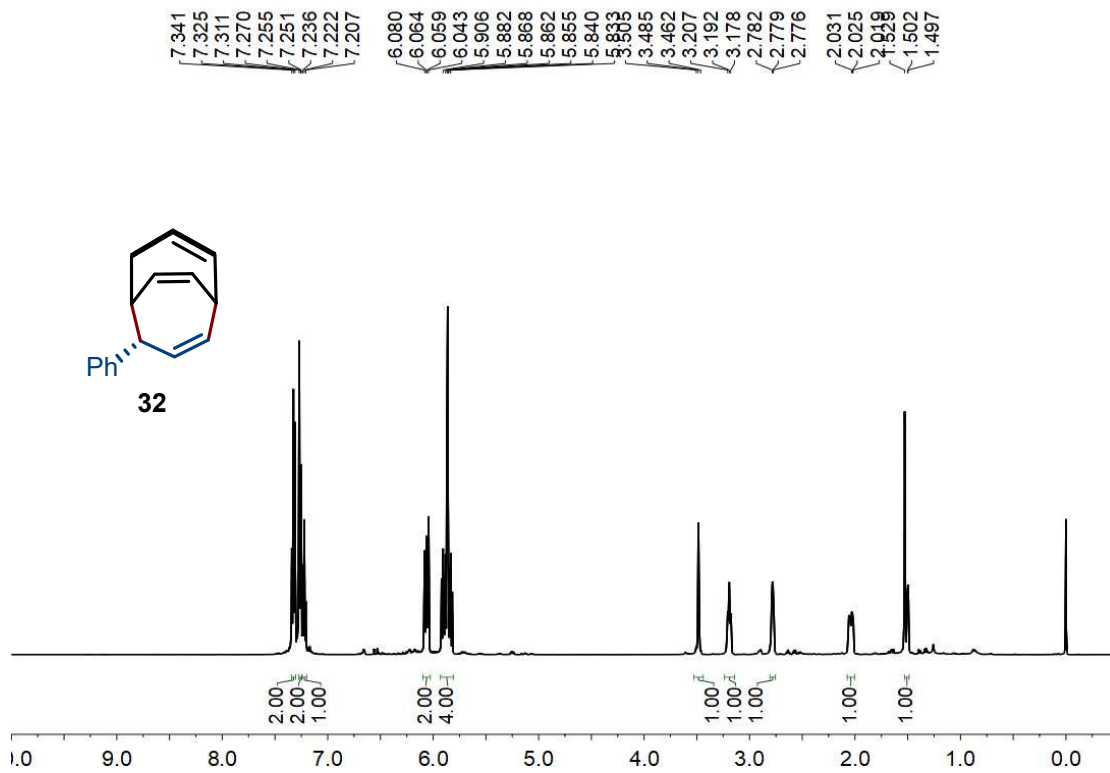
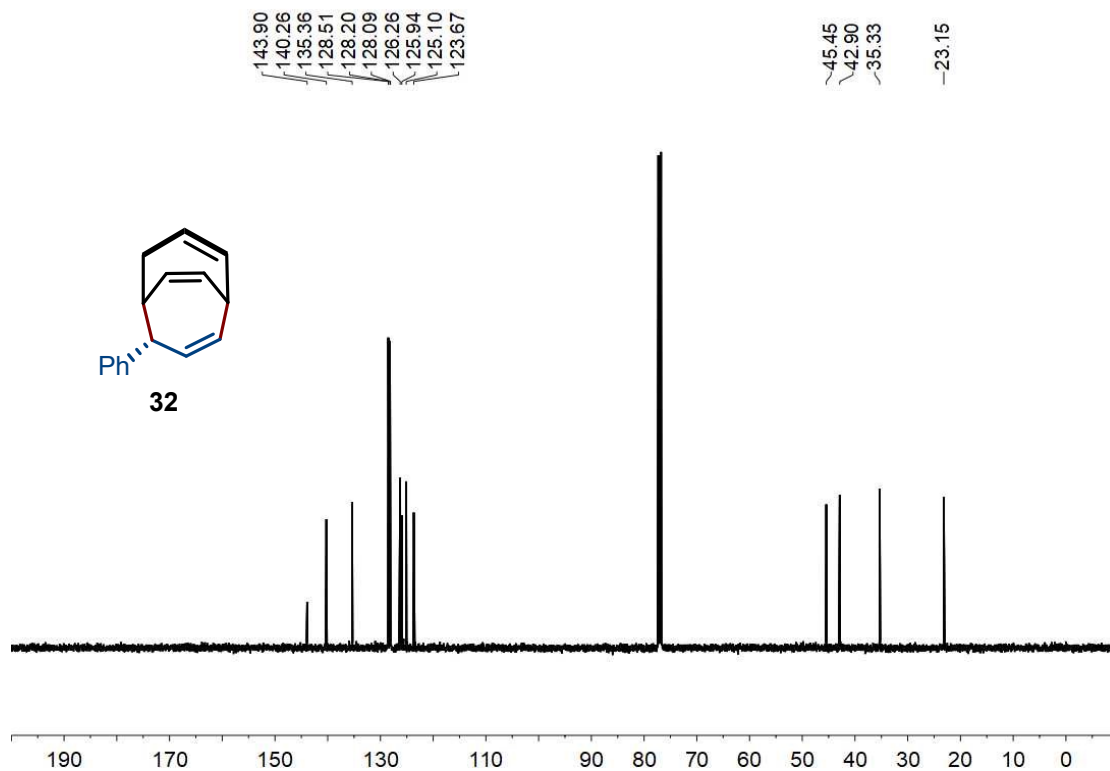


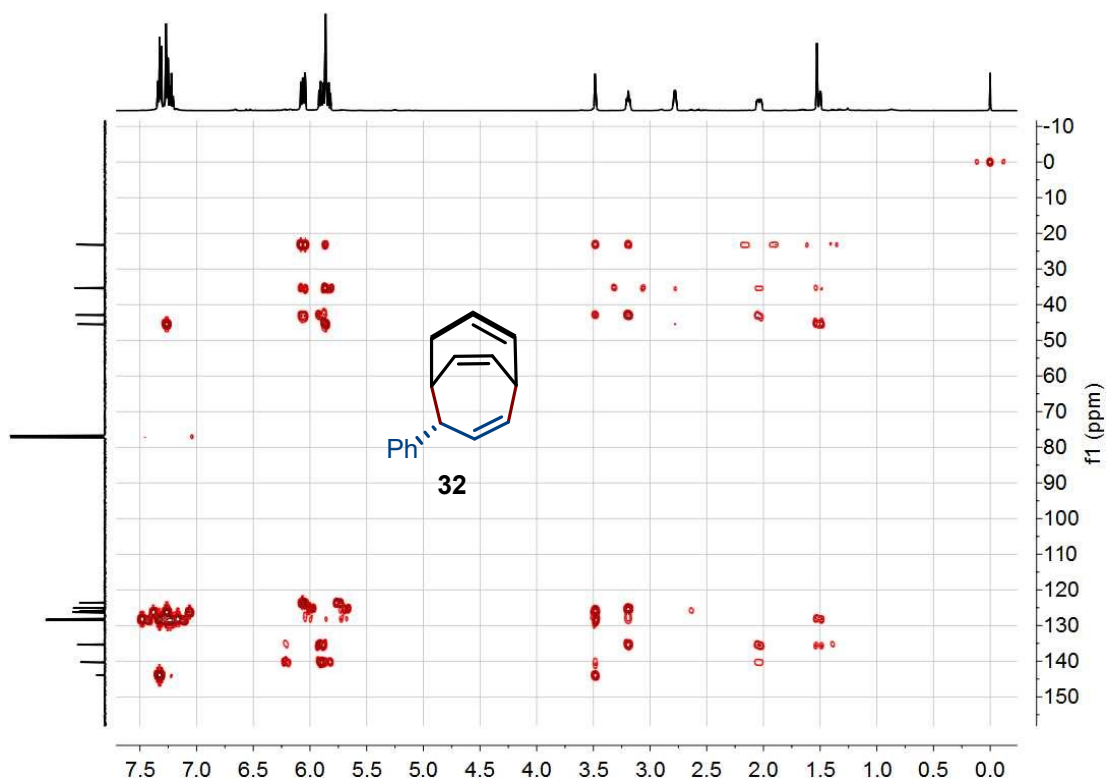
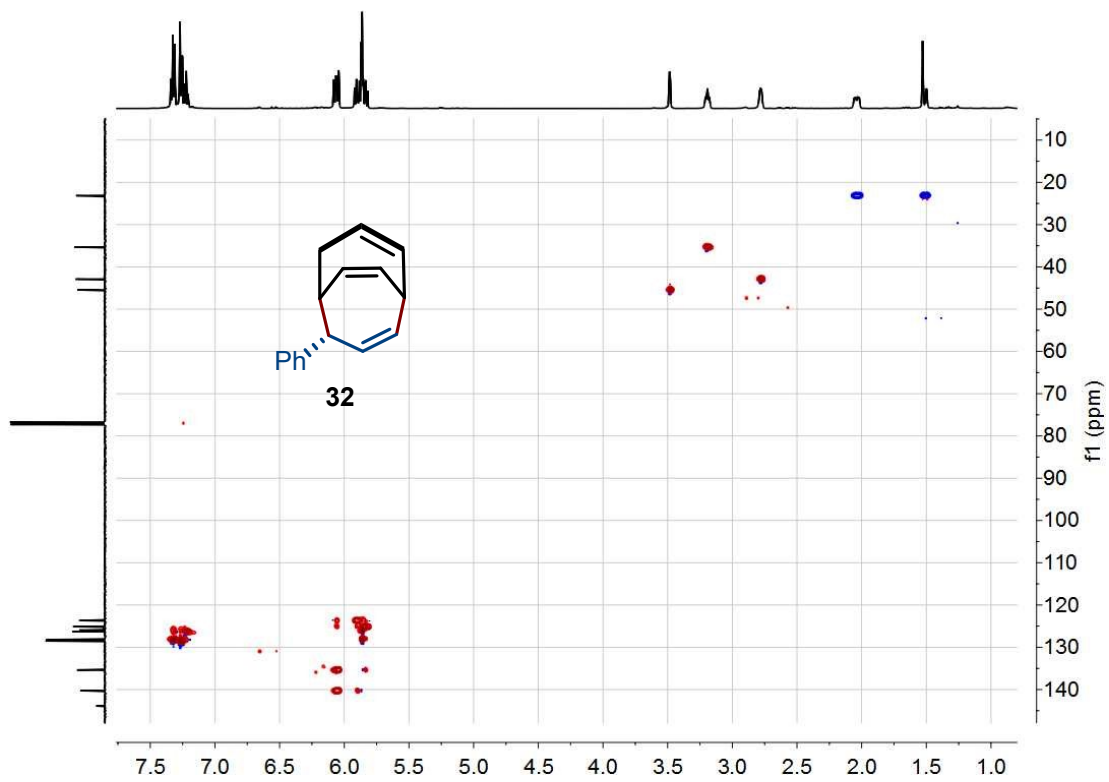
Figure S62.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ) spectrum of **31**.



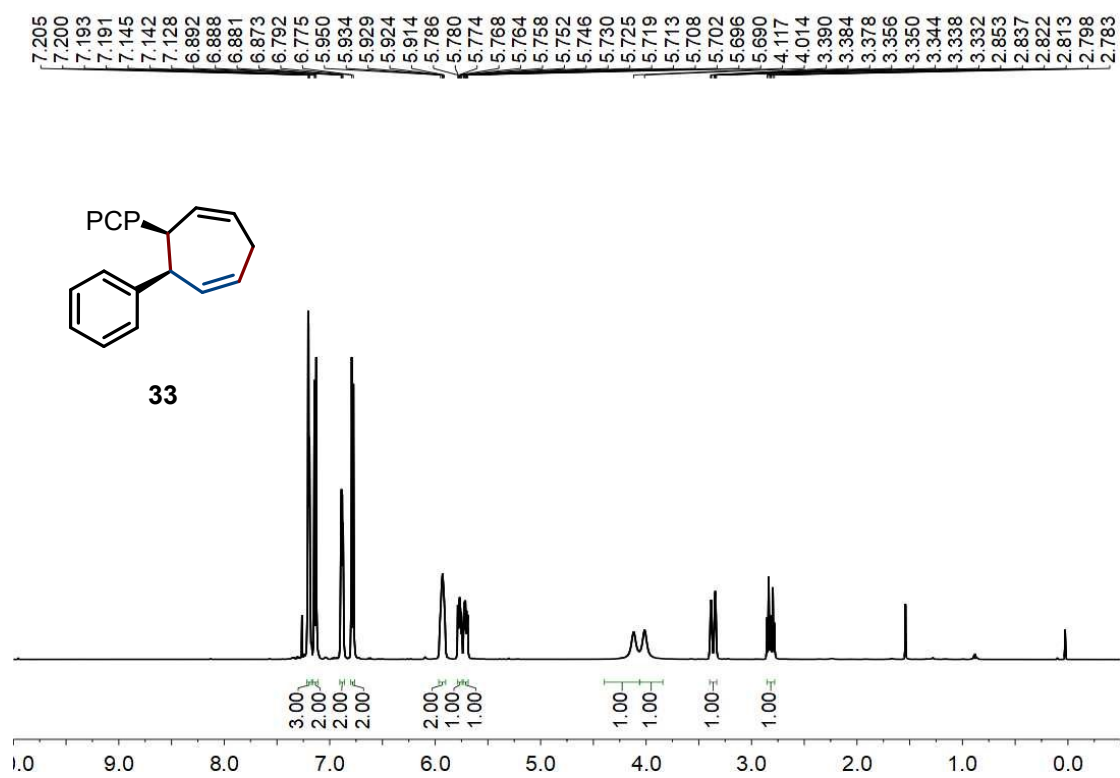
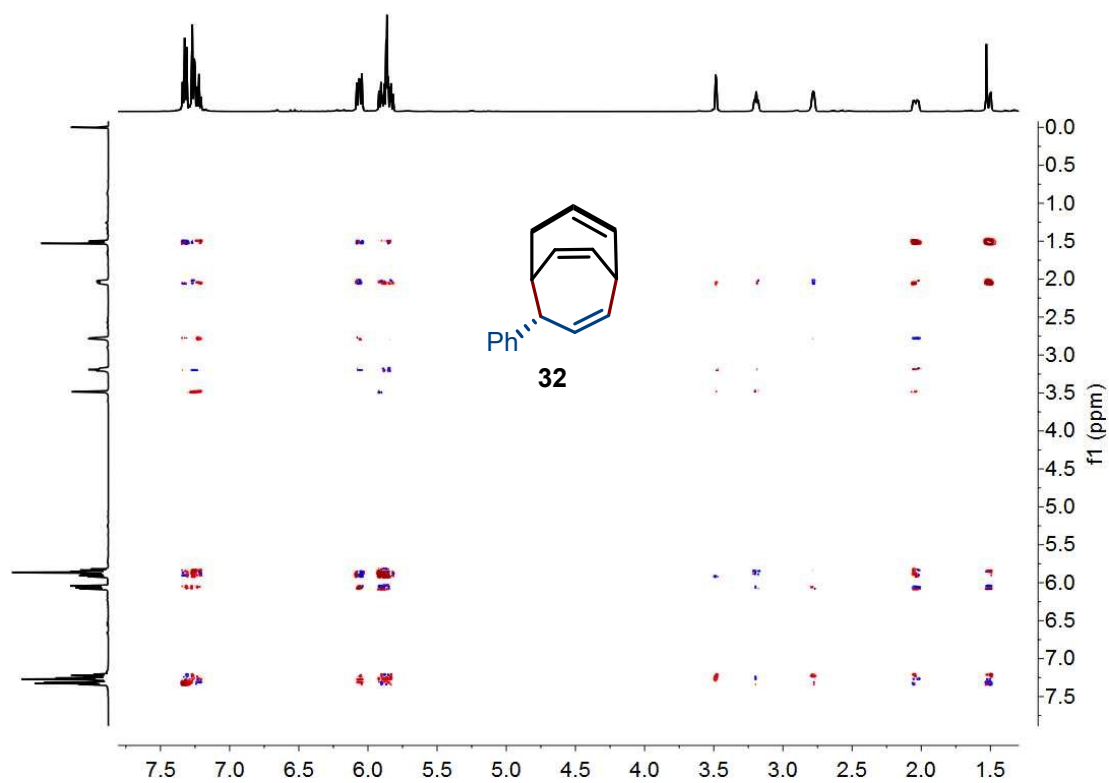
**Figure S63.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **32**.



**Figure S64.** <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **32**.







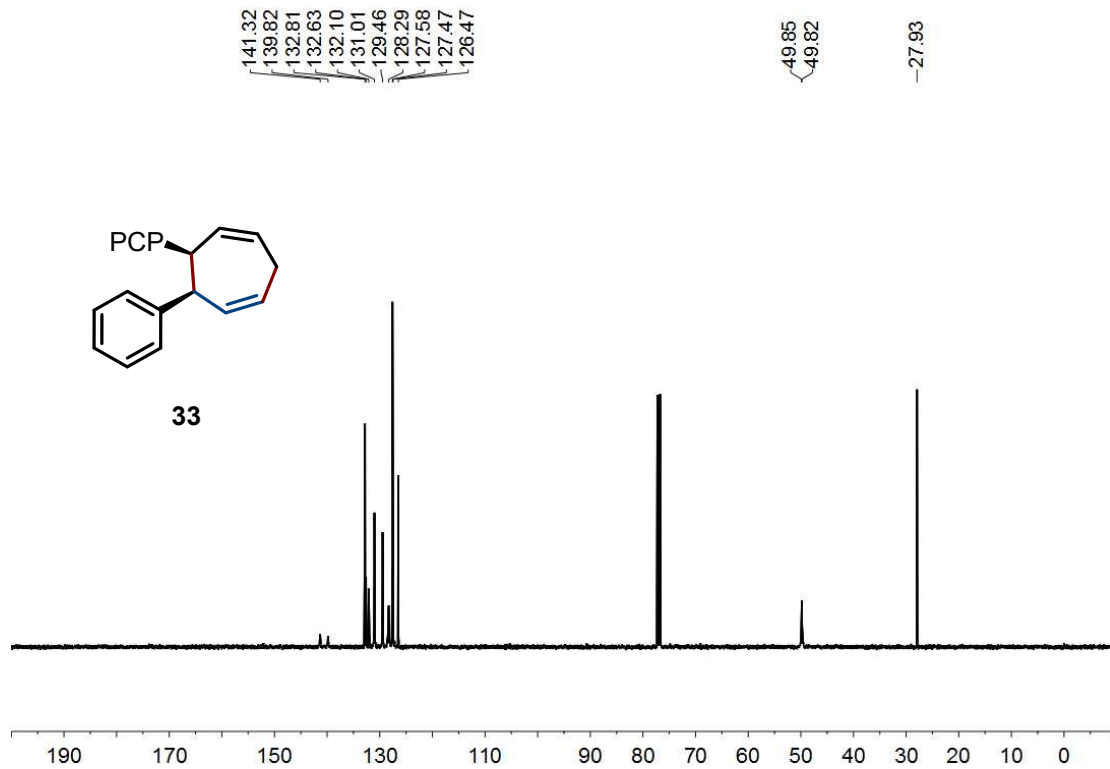


Figure S69.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 33.

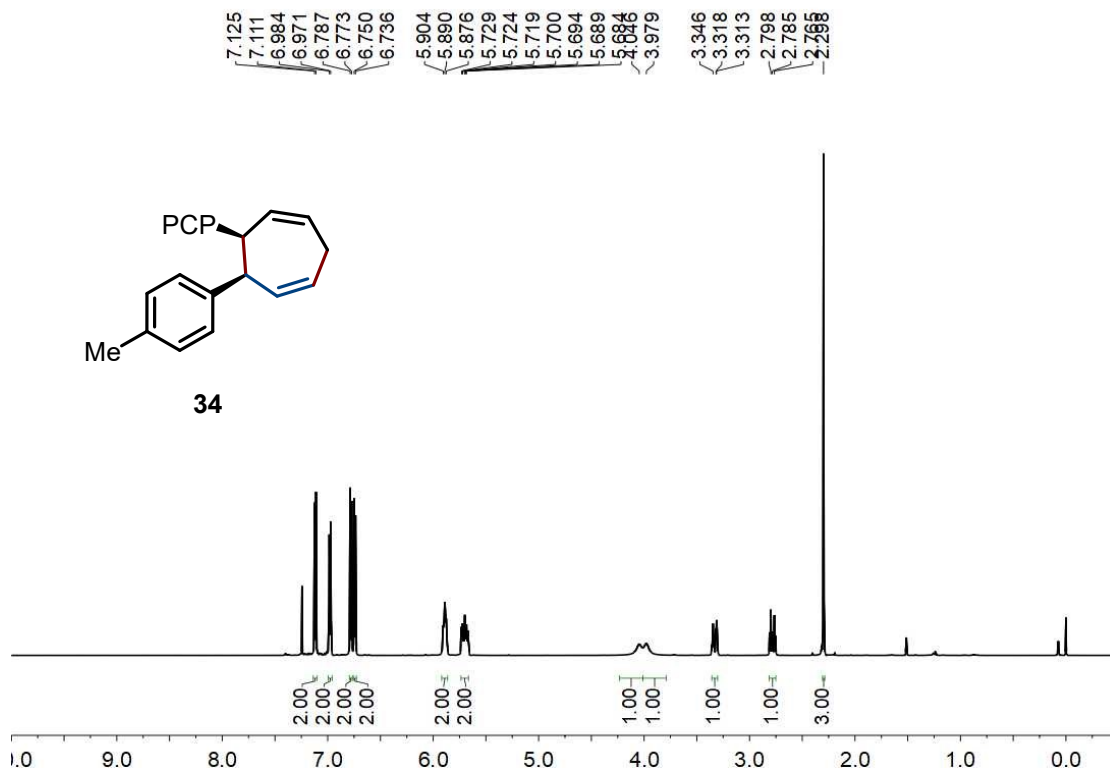


Figure S70.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 34.

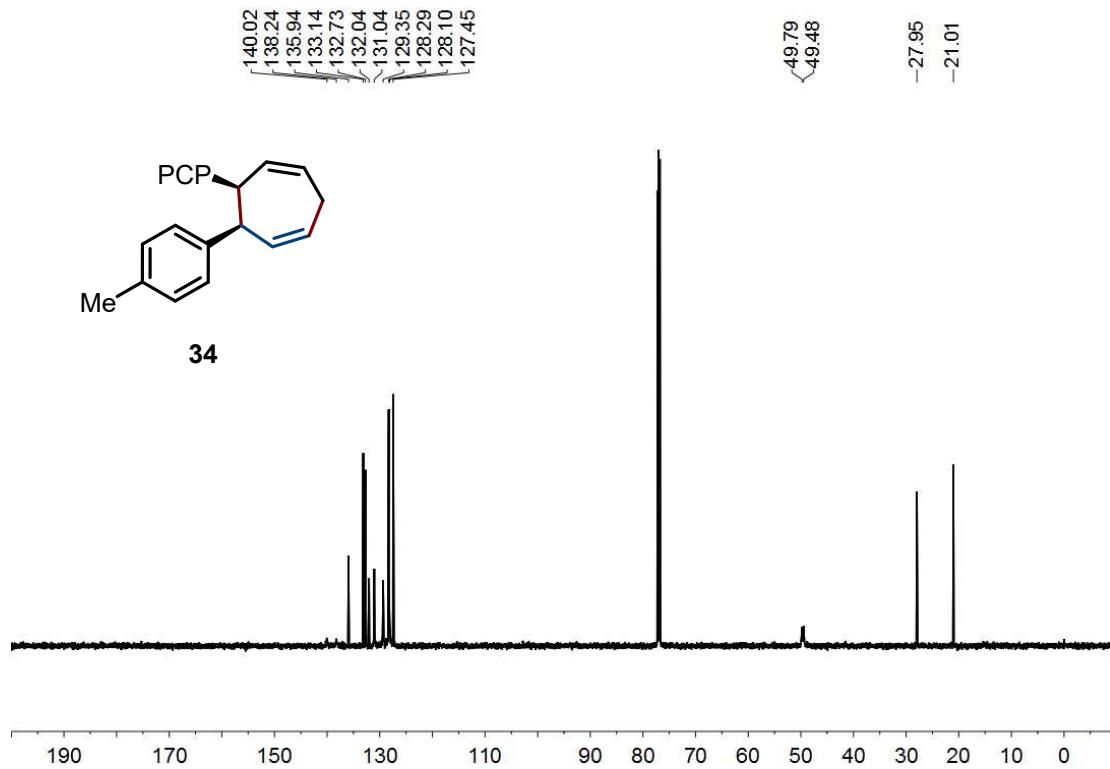


Figure S71. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **34**.

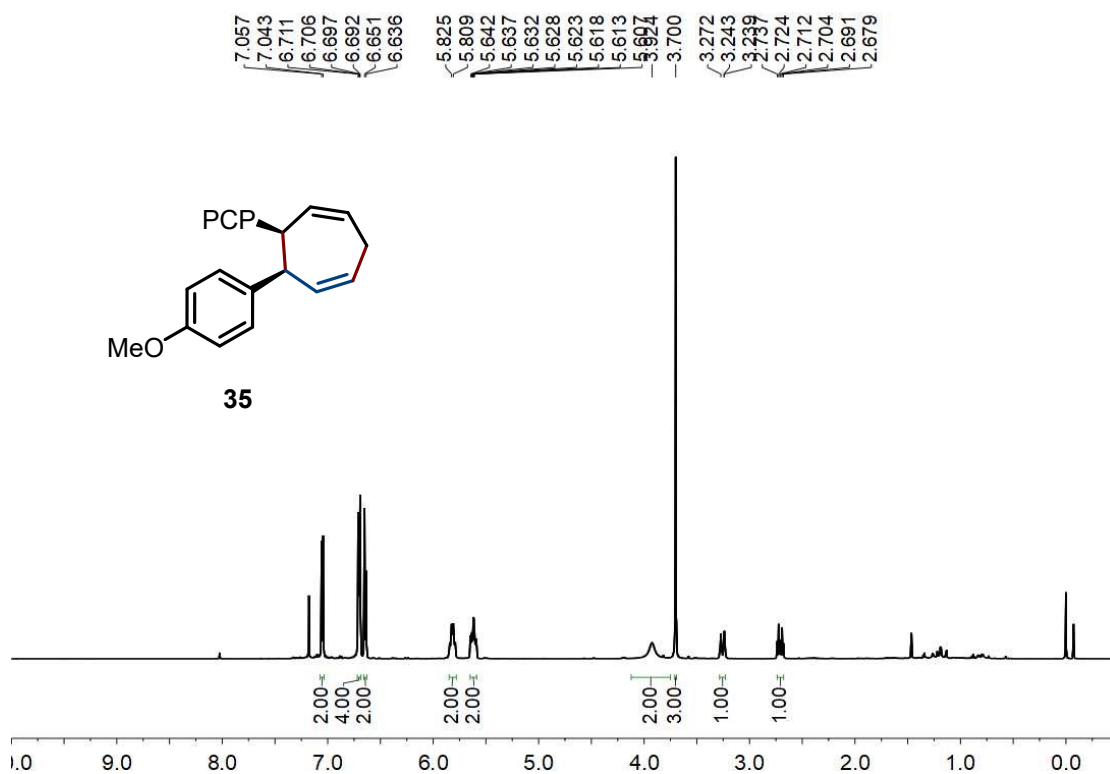


Figure S72. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **35**.

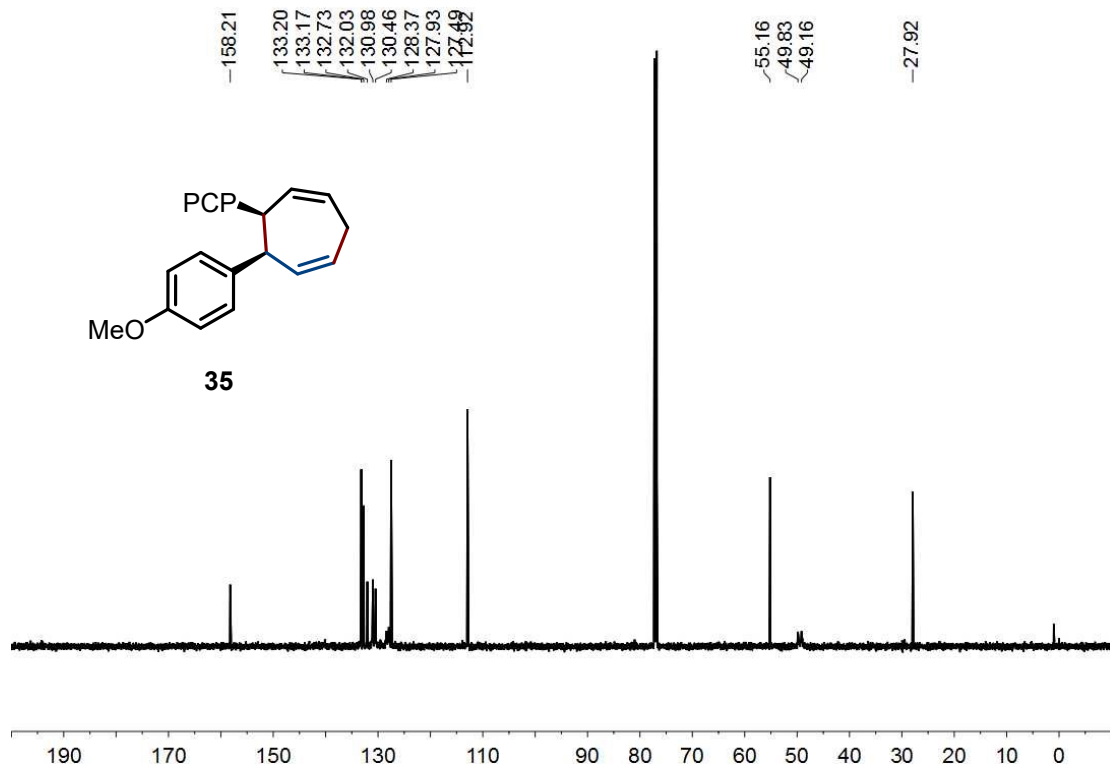


Figure S73. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **35**.

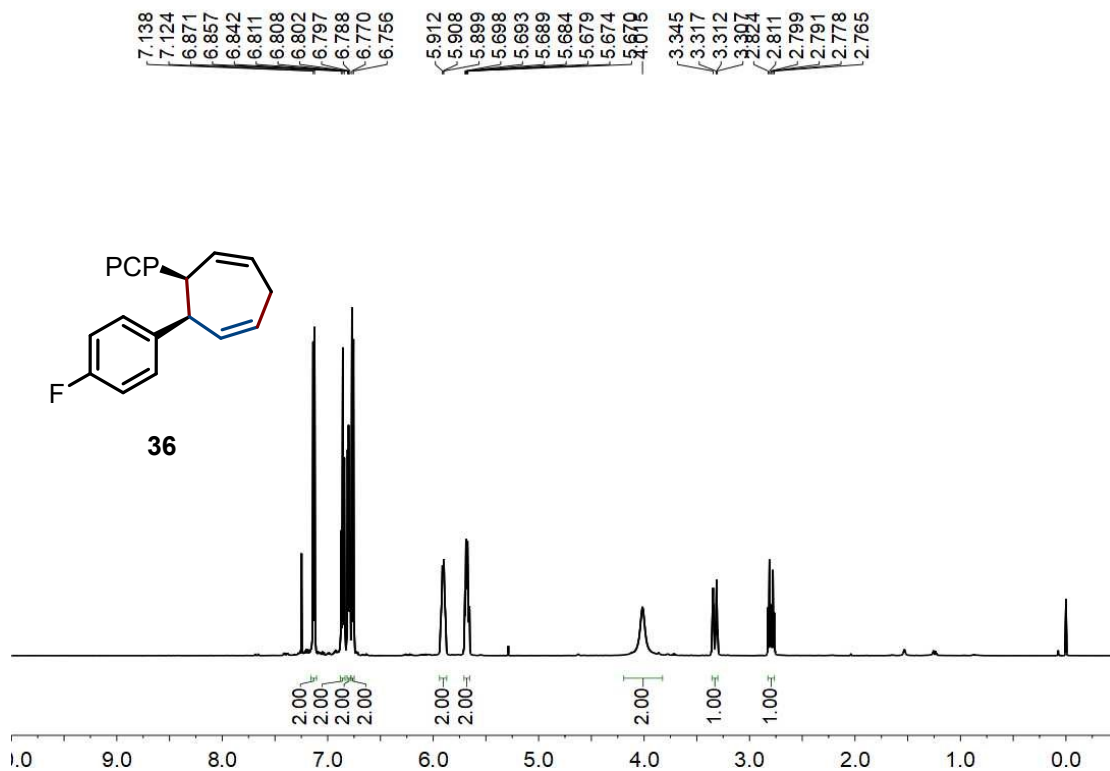


Figure S74. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **36**.

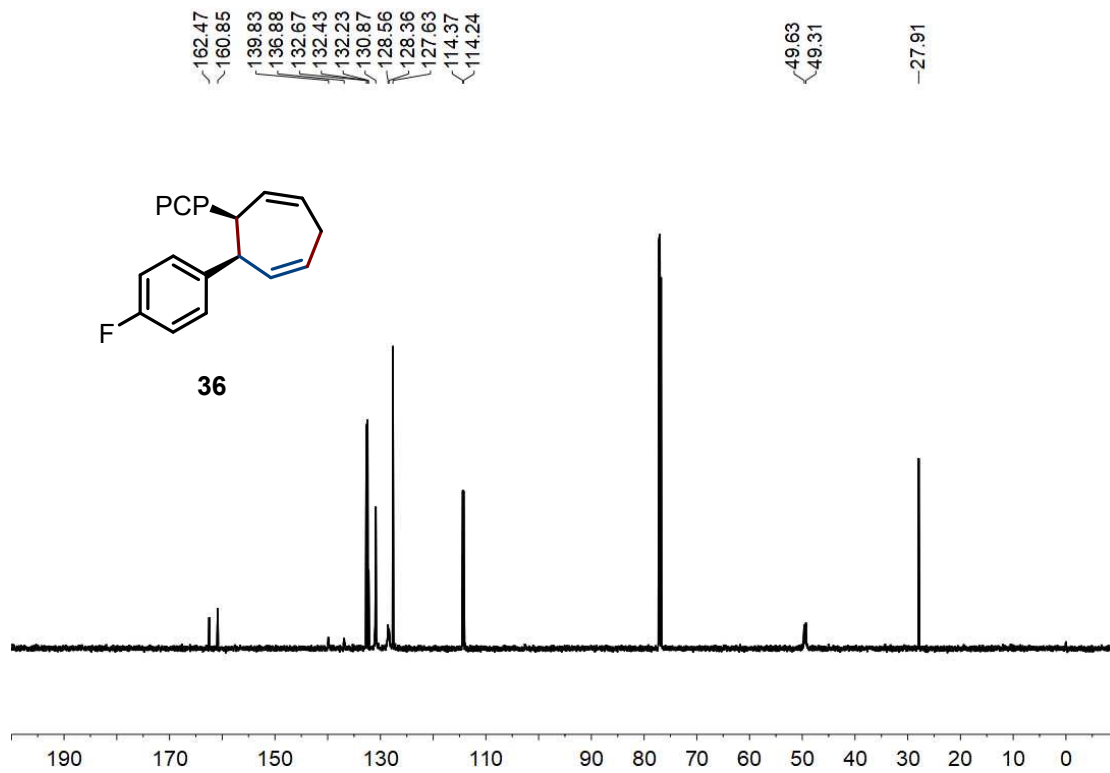


Figure S75. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **36**.

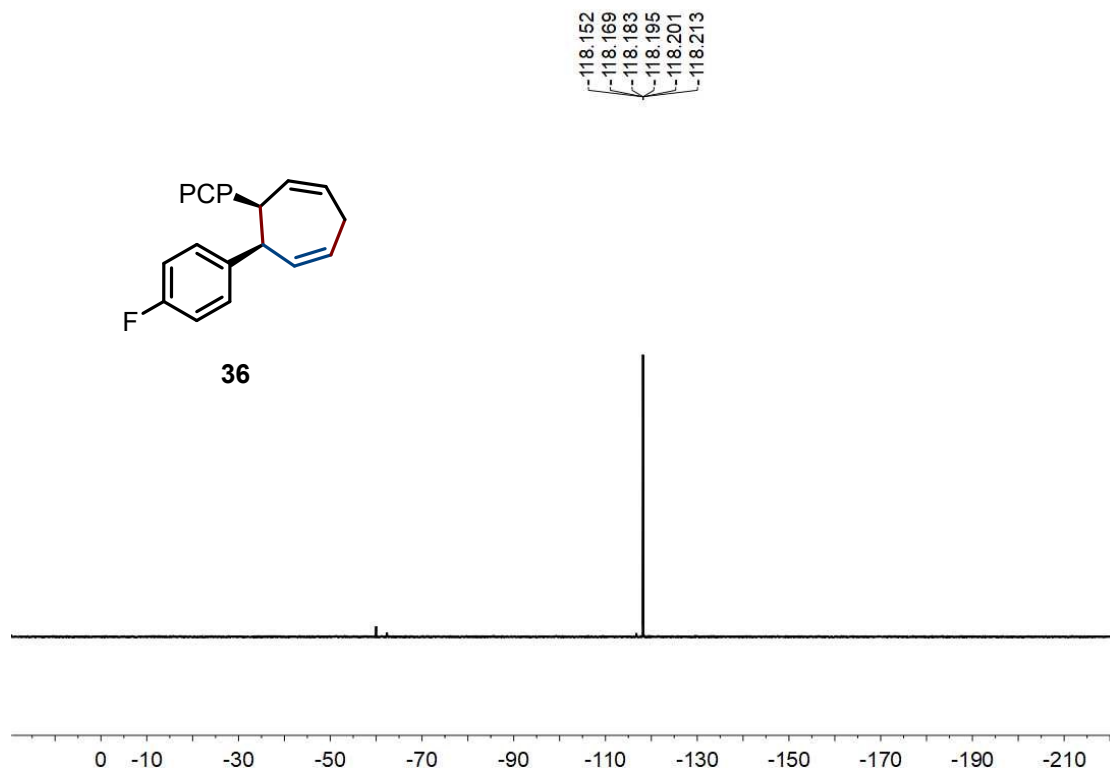


Figure S76. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of **36**.

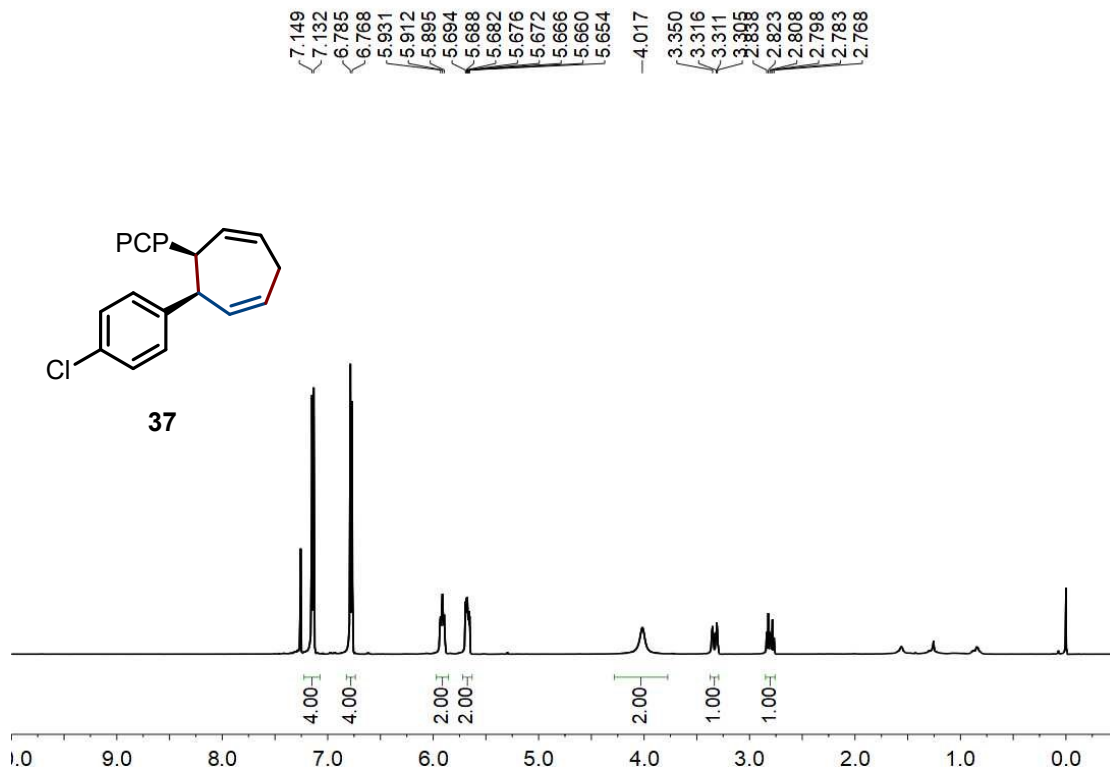


Figure S77.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **37**.

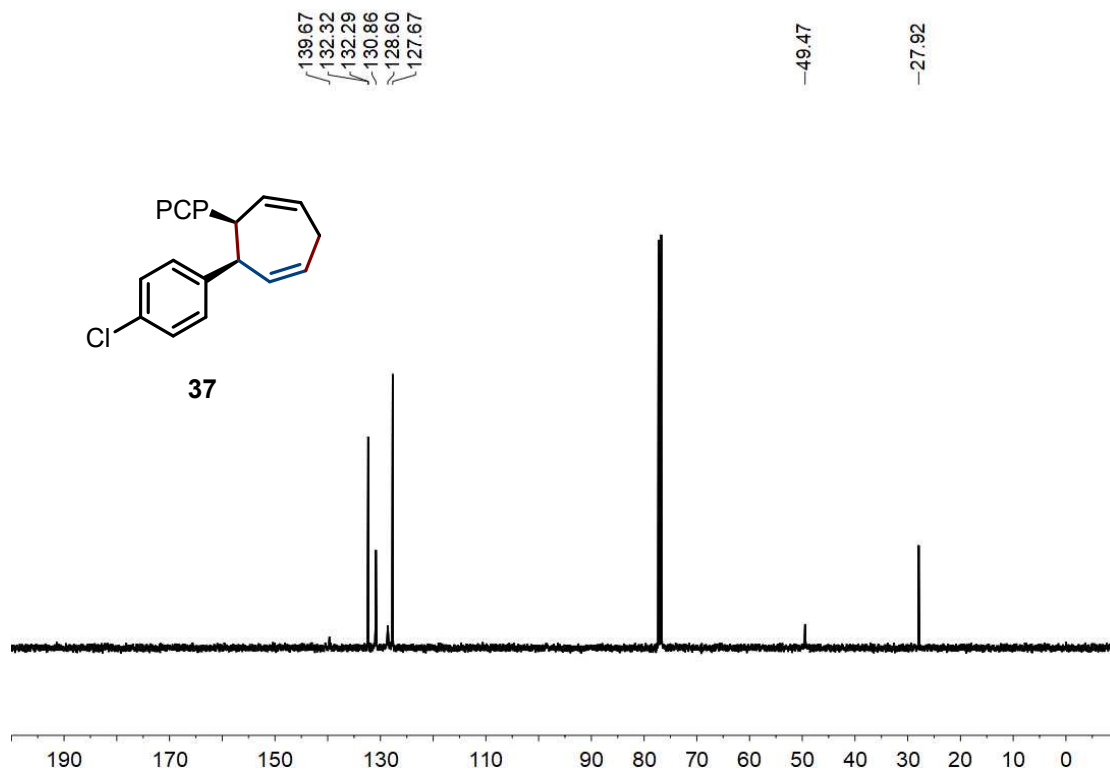


Figure S78.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **37**.

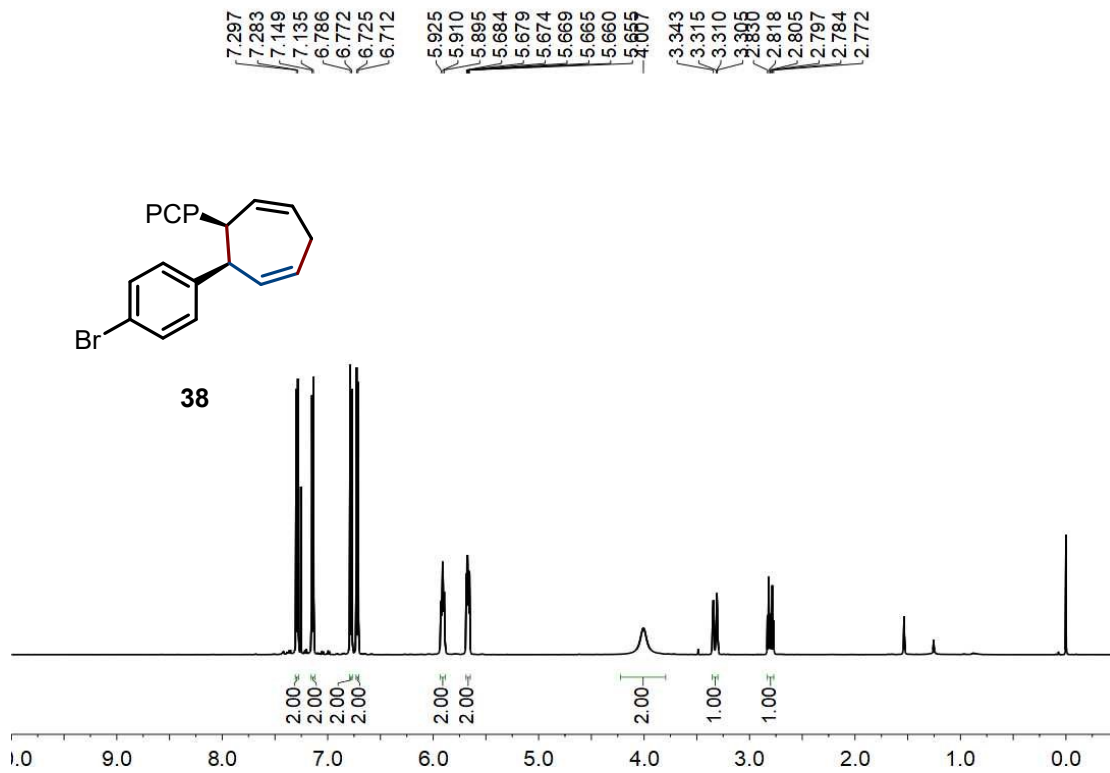


Figure S79.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **38**.

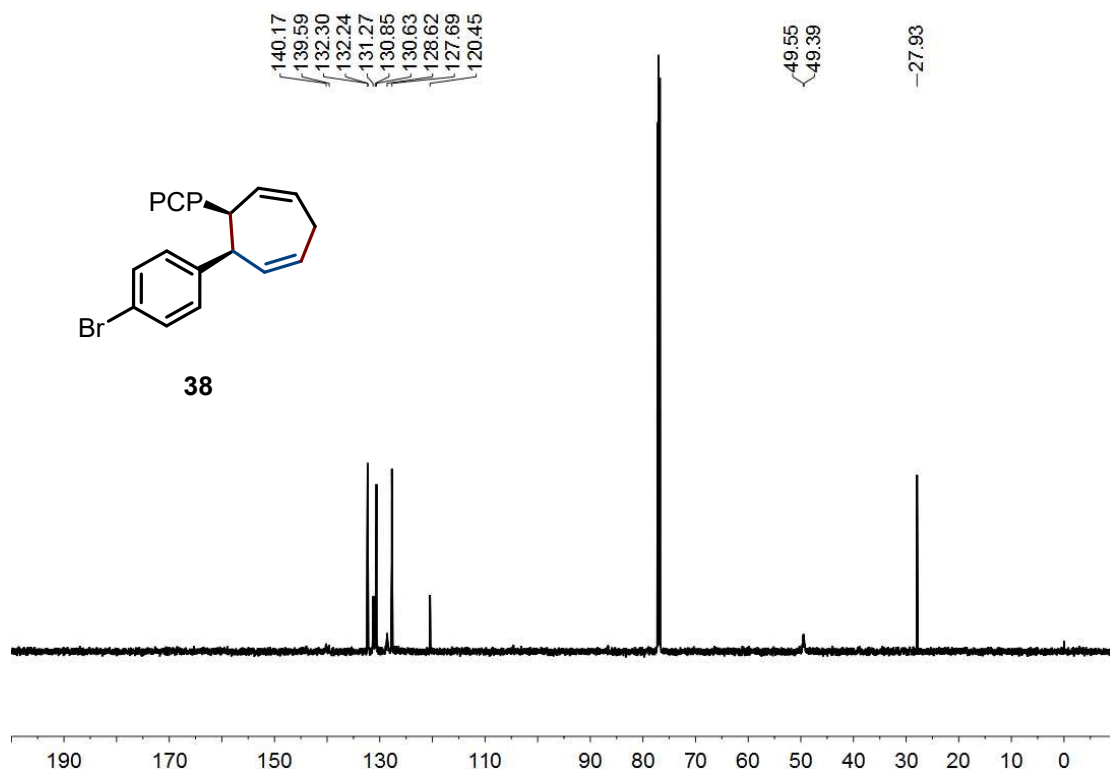


Figure S80.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **38**.

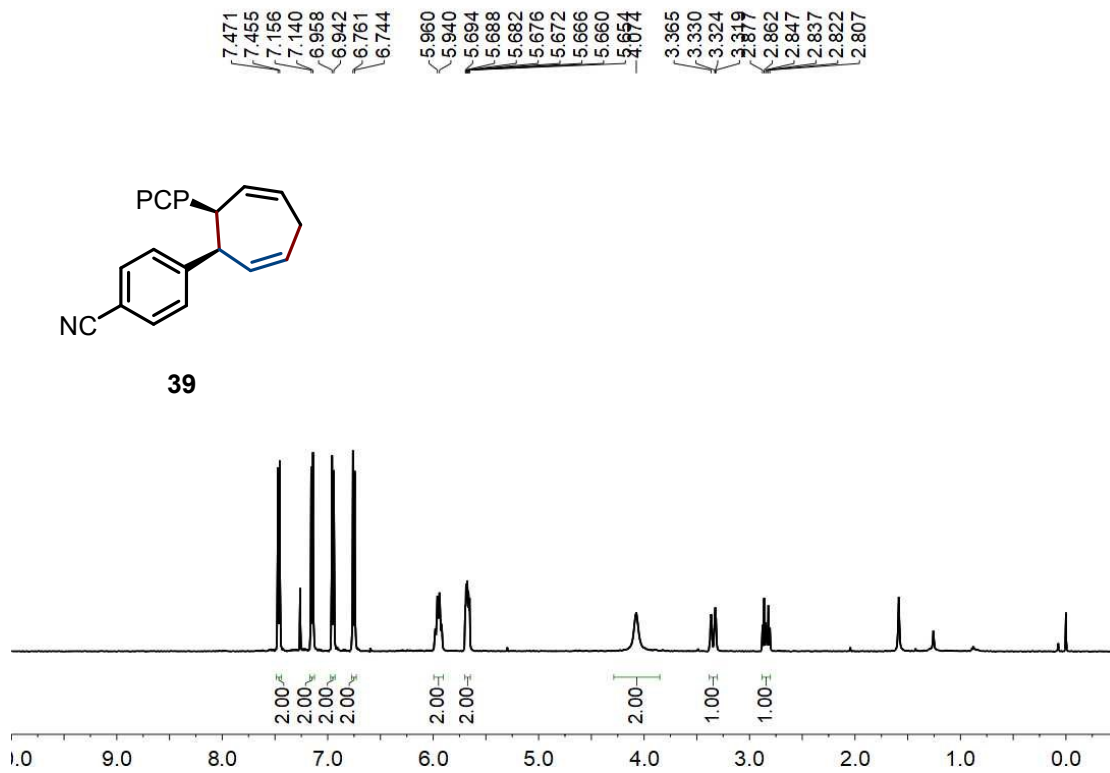


Figure S81. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **39**.

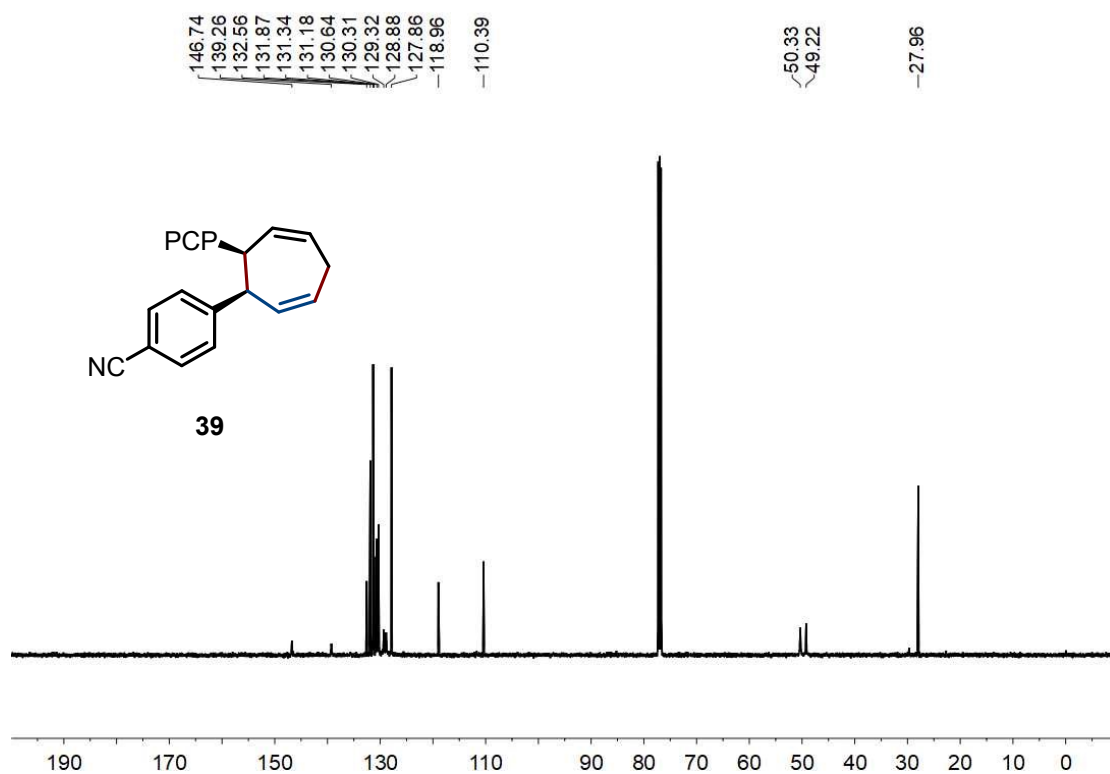


Figure S82. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **39**.



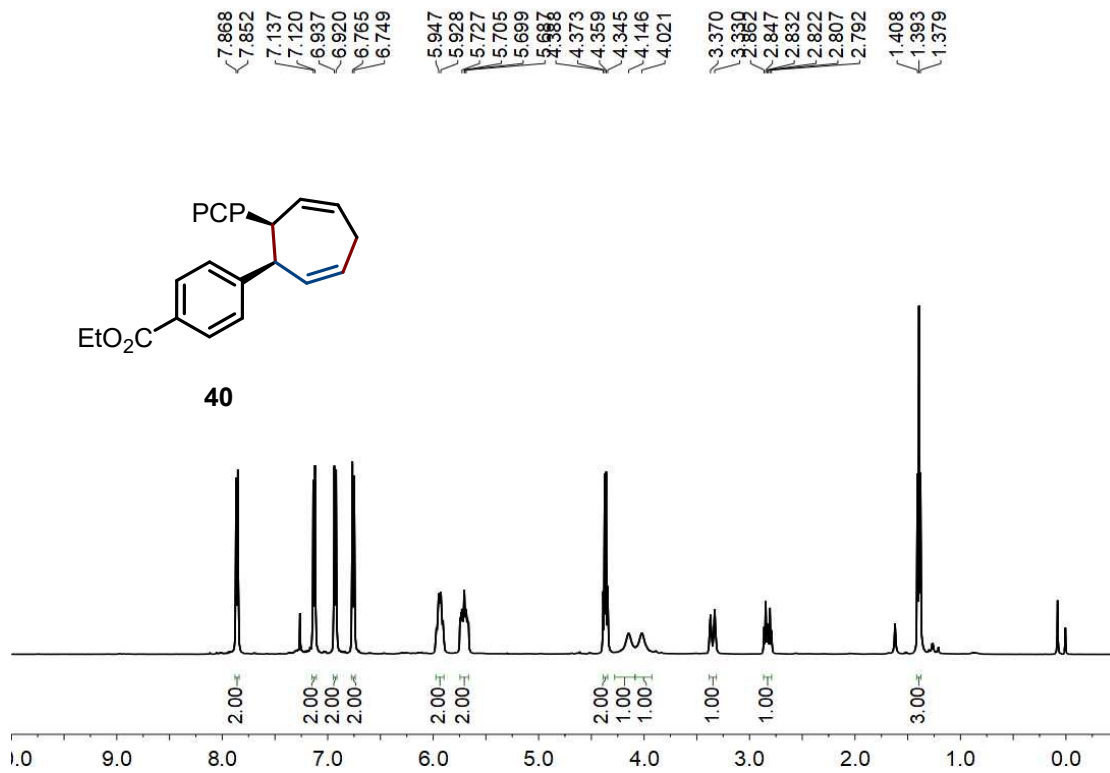


Figure S83. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **40**.

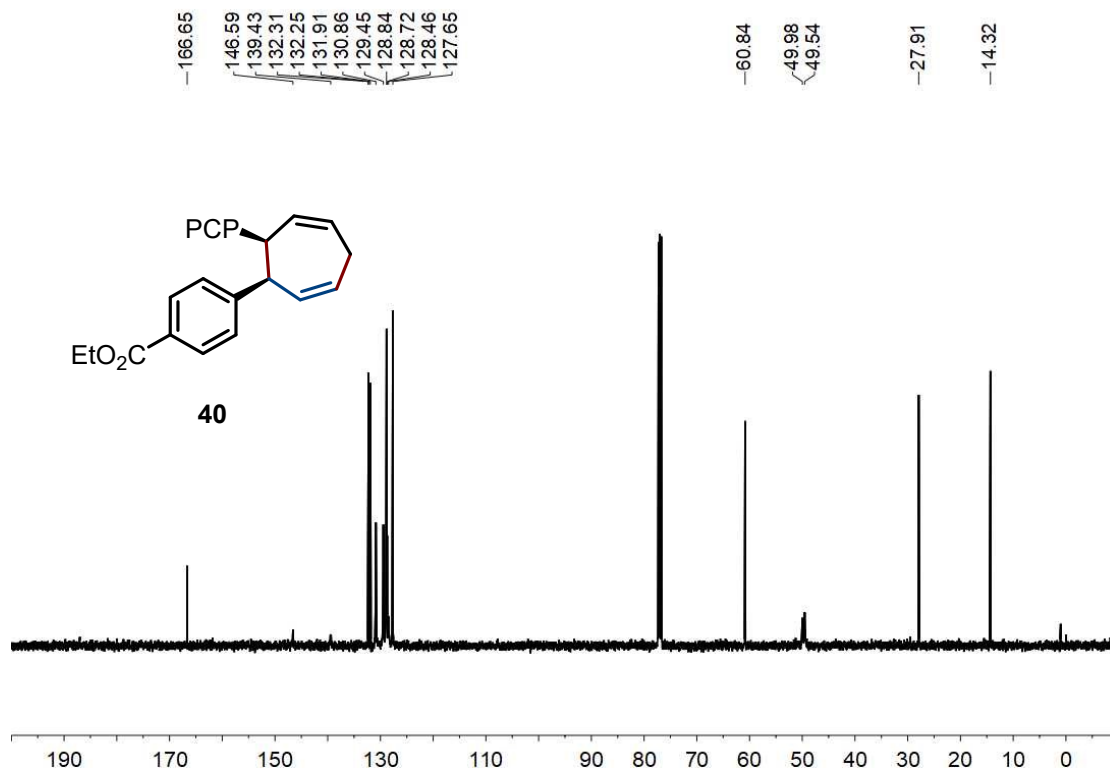


Figure S84. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **40**.

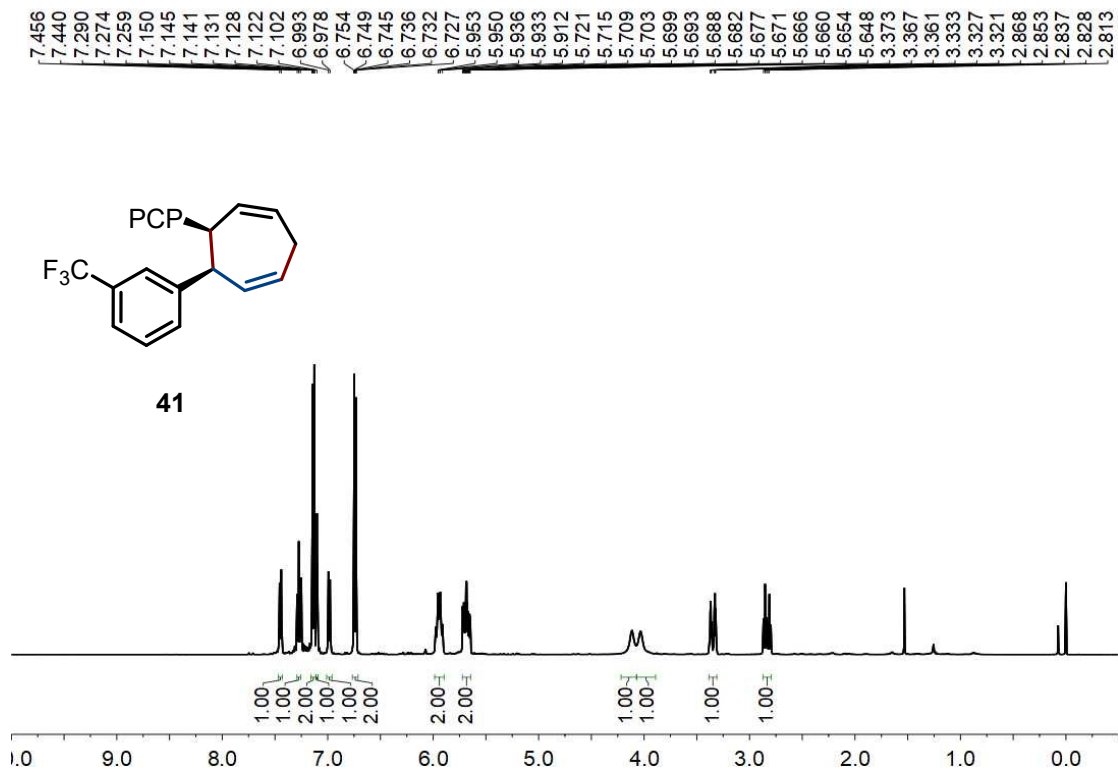


Figure S85.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **41**.

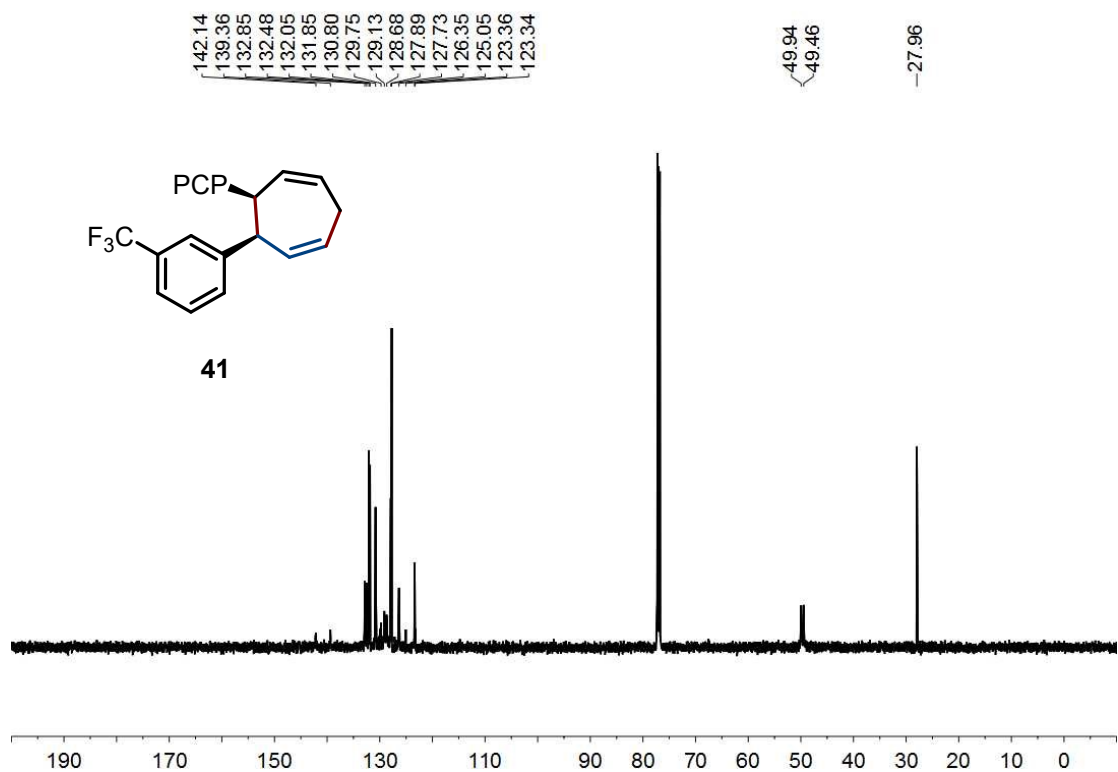
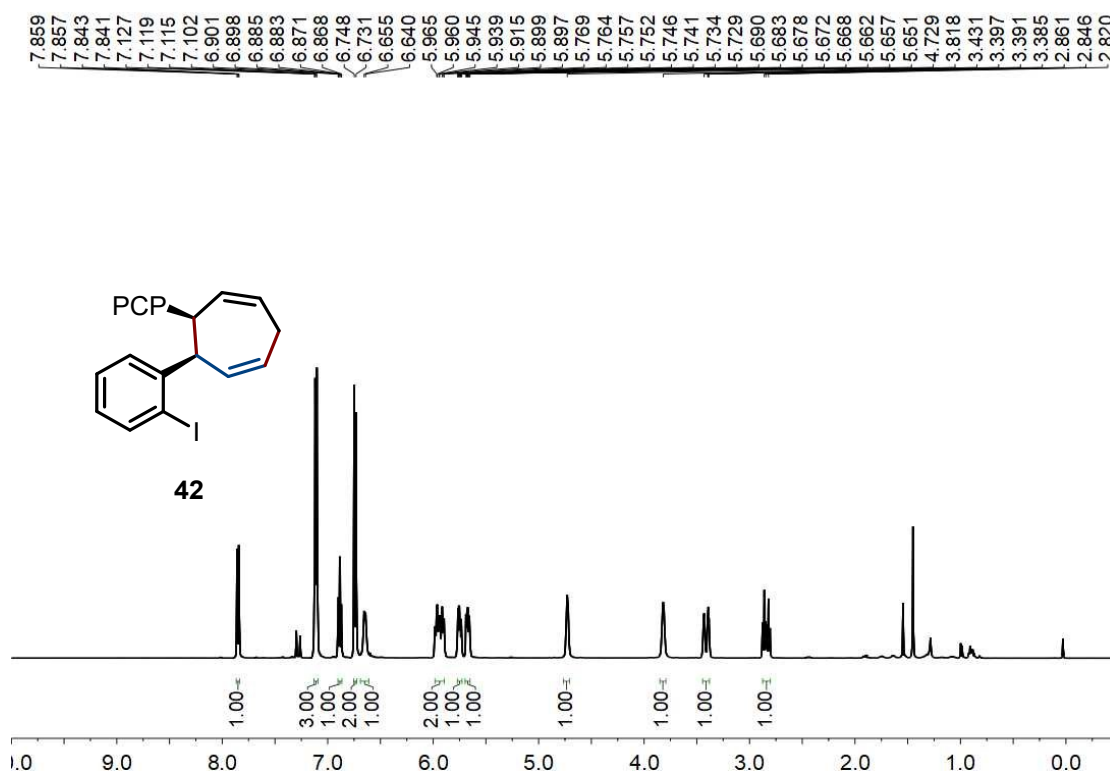
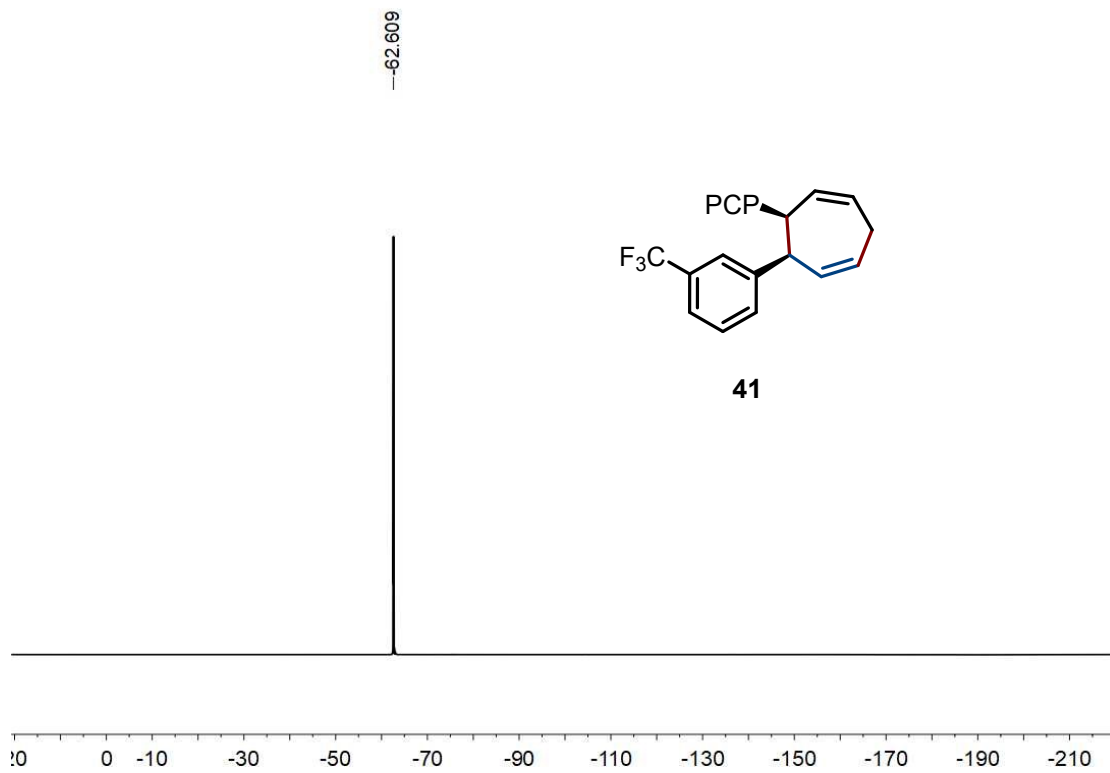


Figure S86.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **41**.



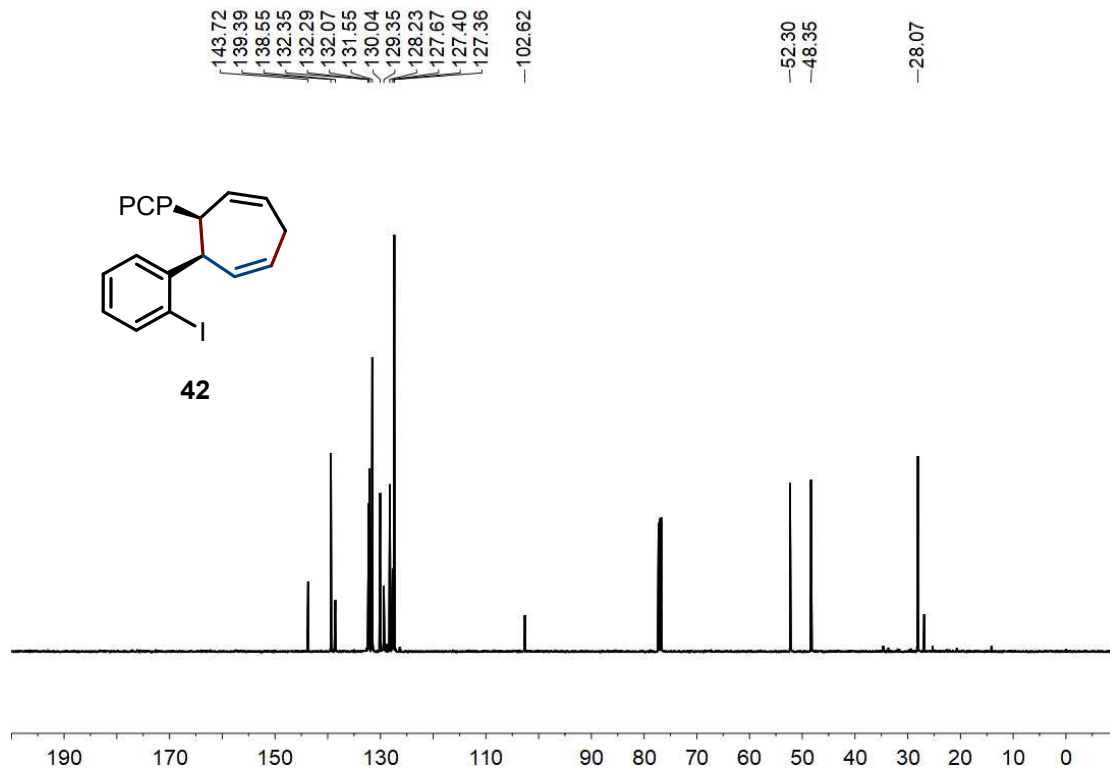


Figure S89. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **42**.

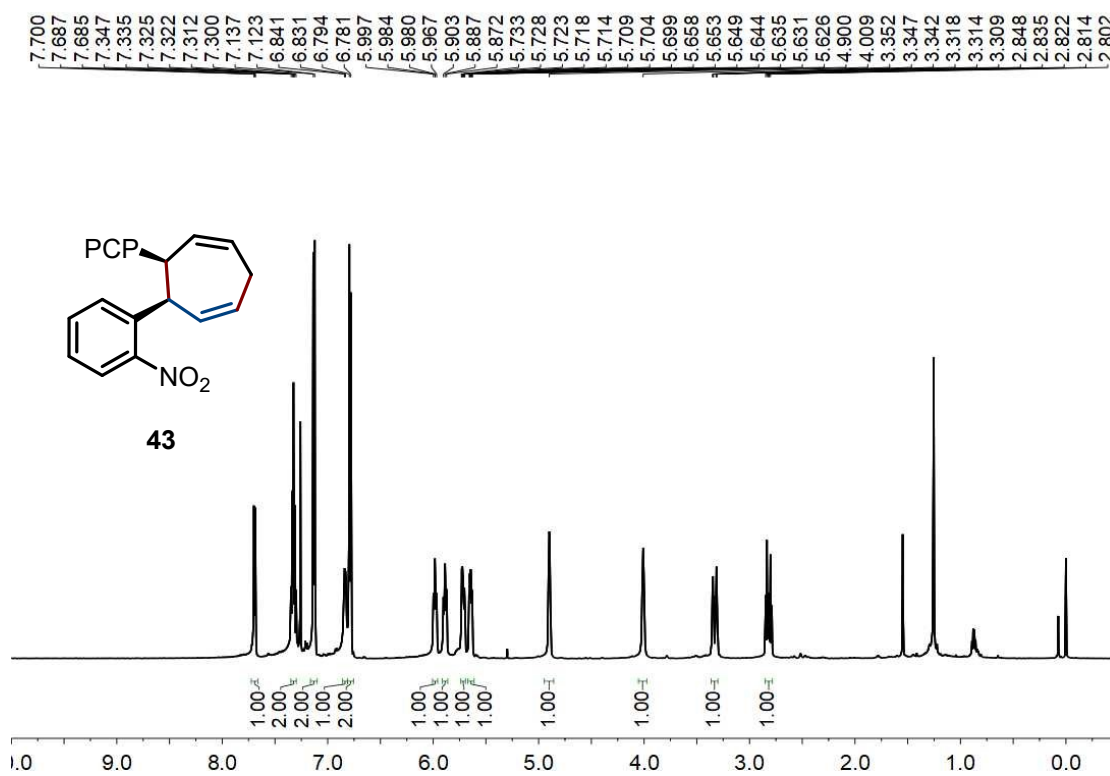


Figure S90. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **43**.

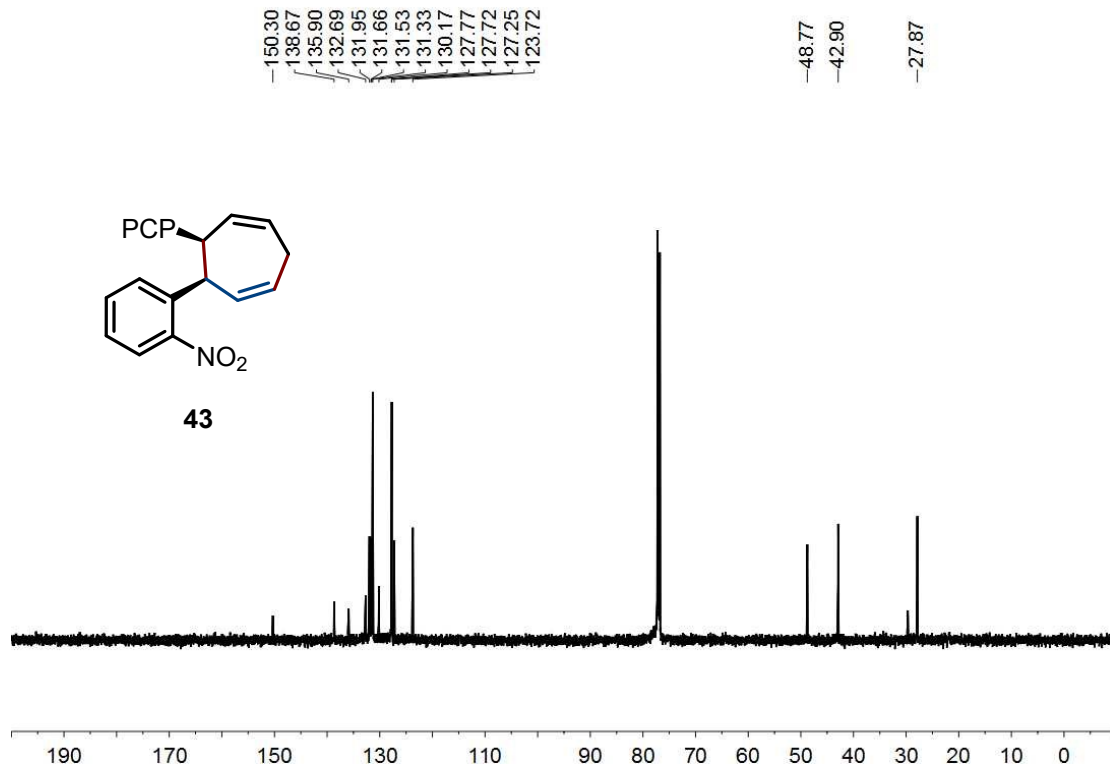


Figure S91. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 43.

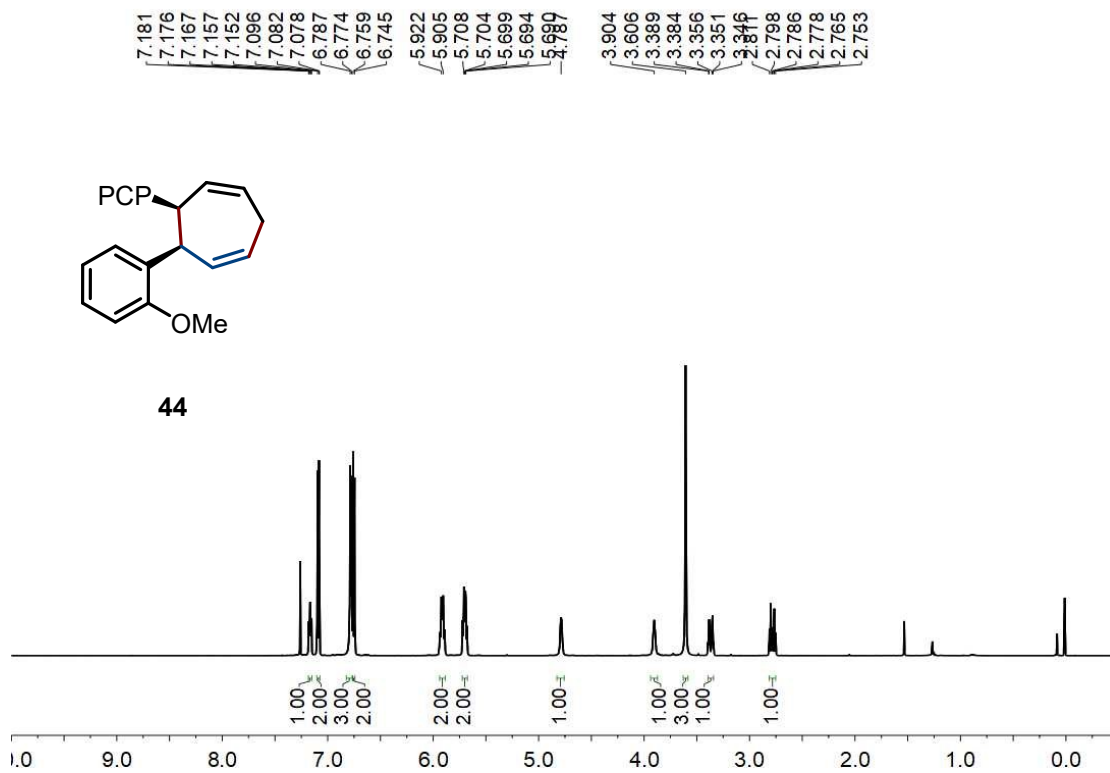


Figure S92. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 44.

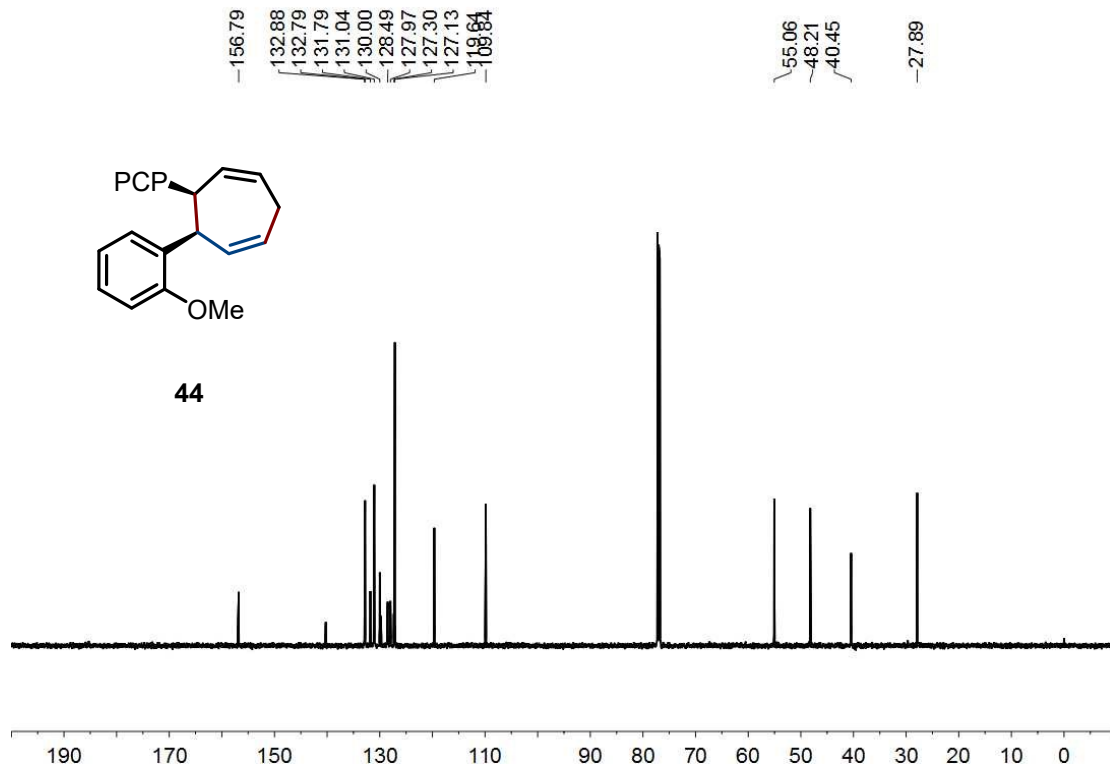


Figure S93. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **44**.

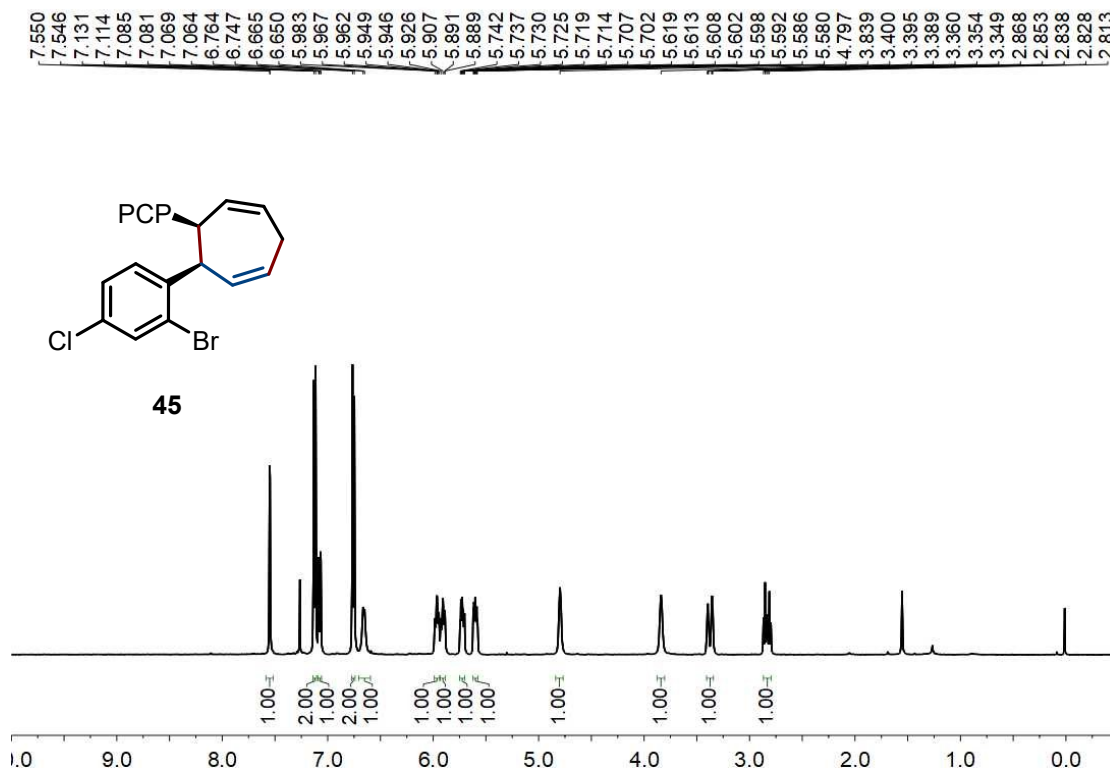


Figure S94. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **45**.

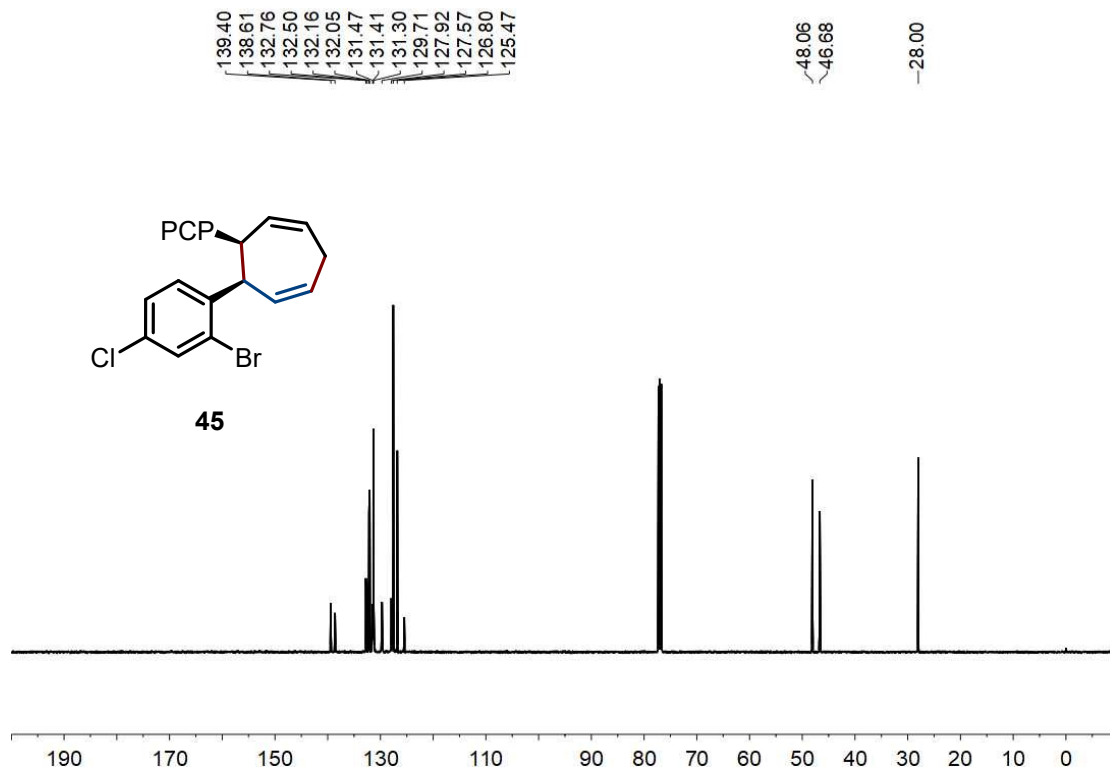


Figure S95.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **45**.

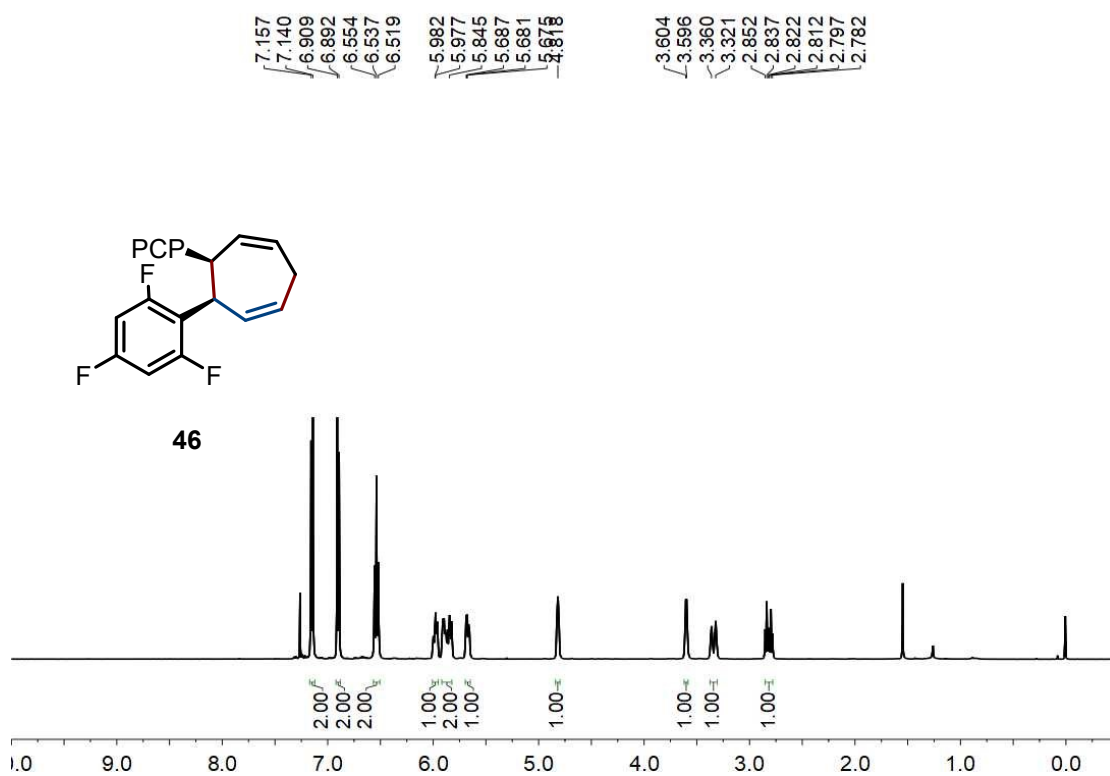


Figure S96.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **46**.

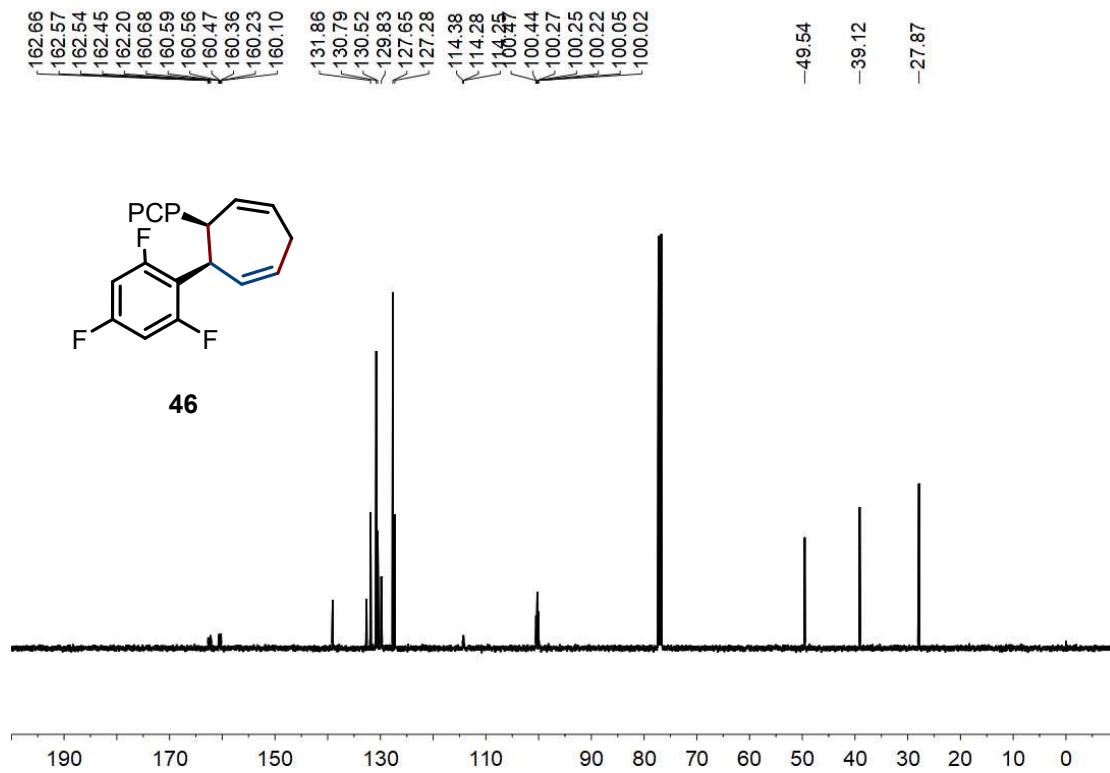


Figure S97. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 46.

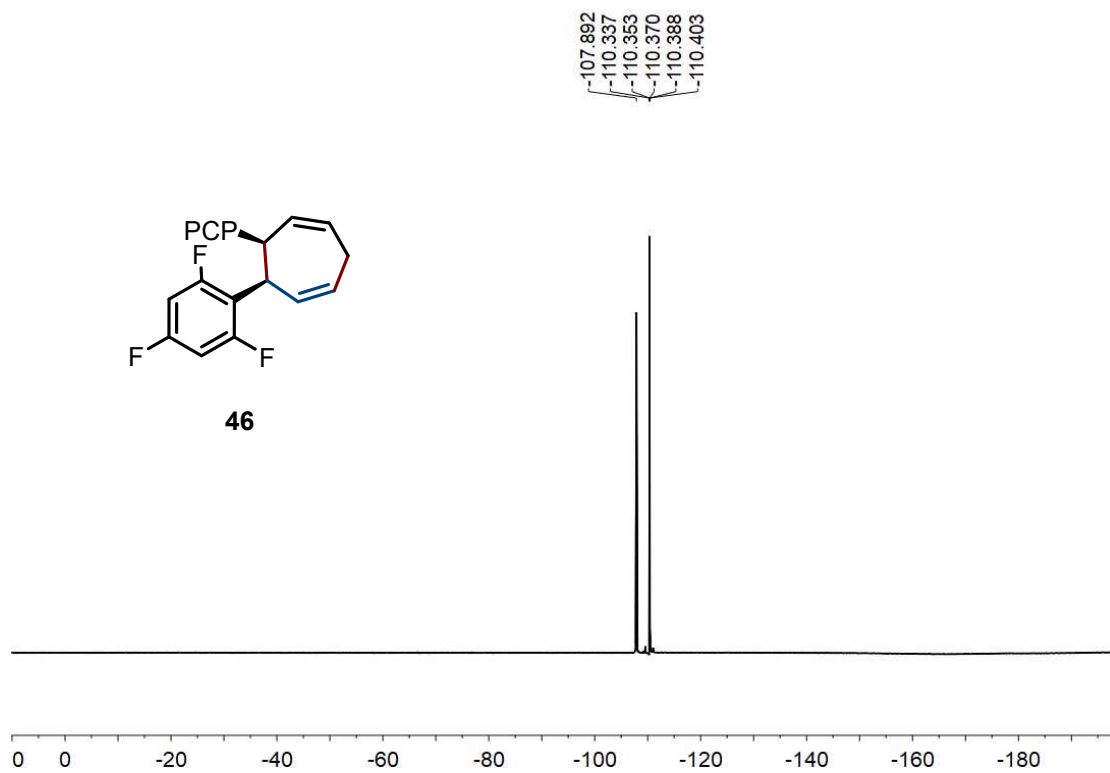


Figure S98. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of 46.



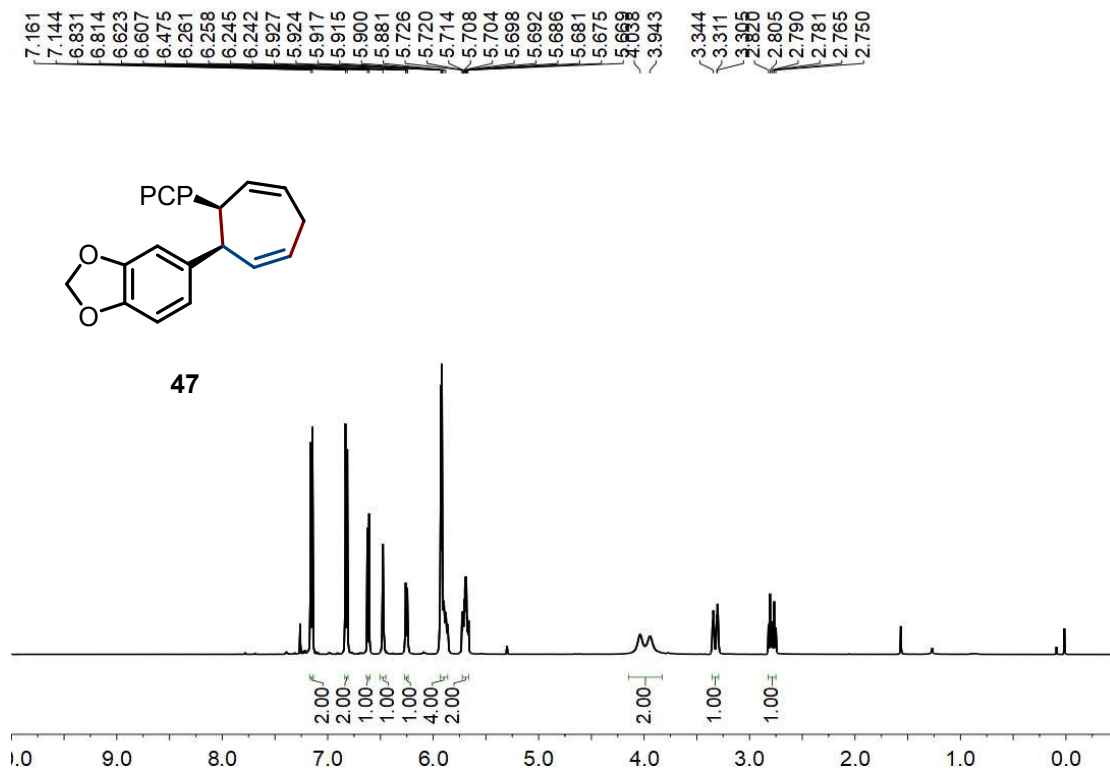


Figure S99.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **47**.

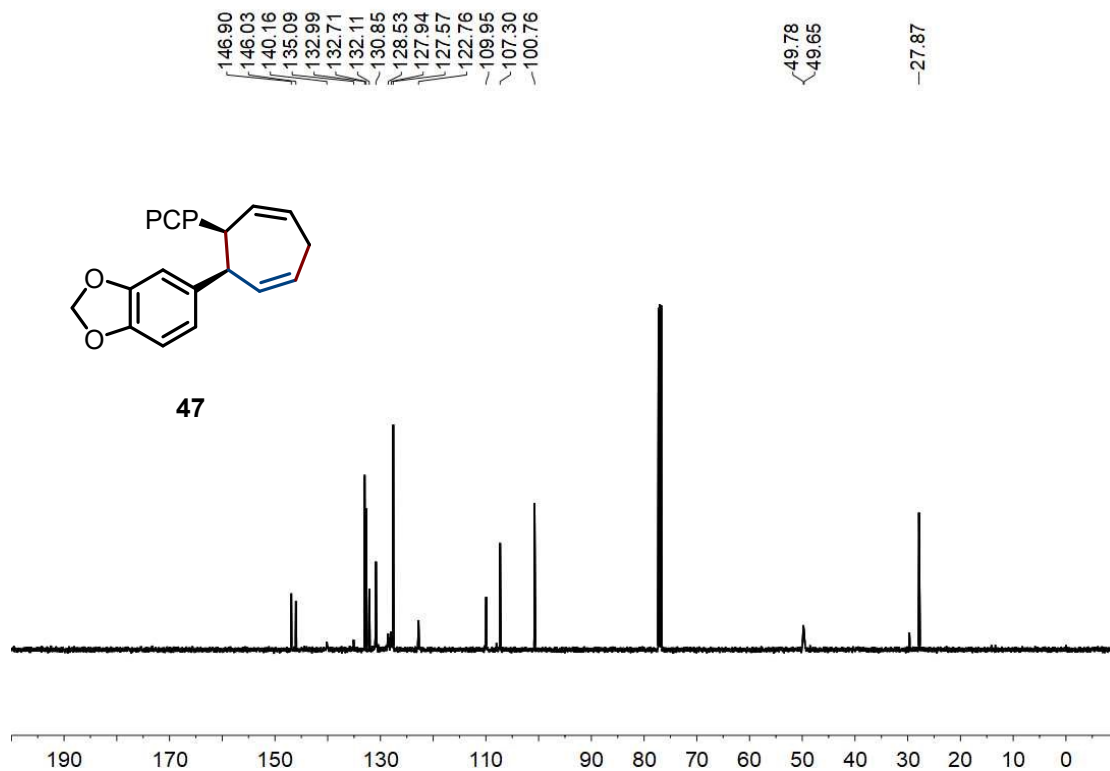


Figure S100.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **47**.

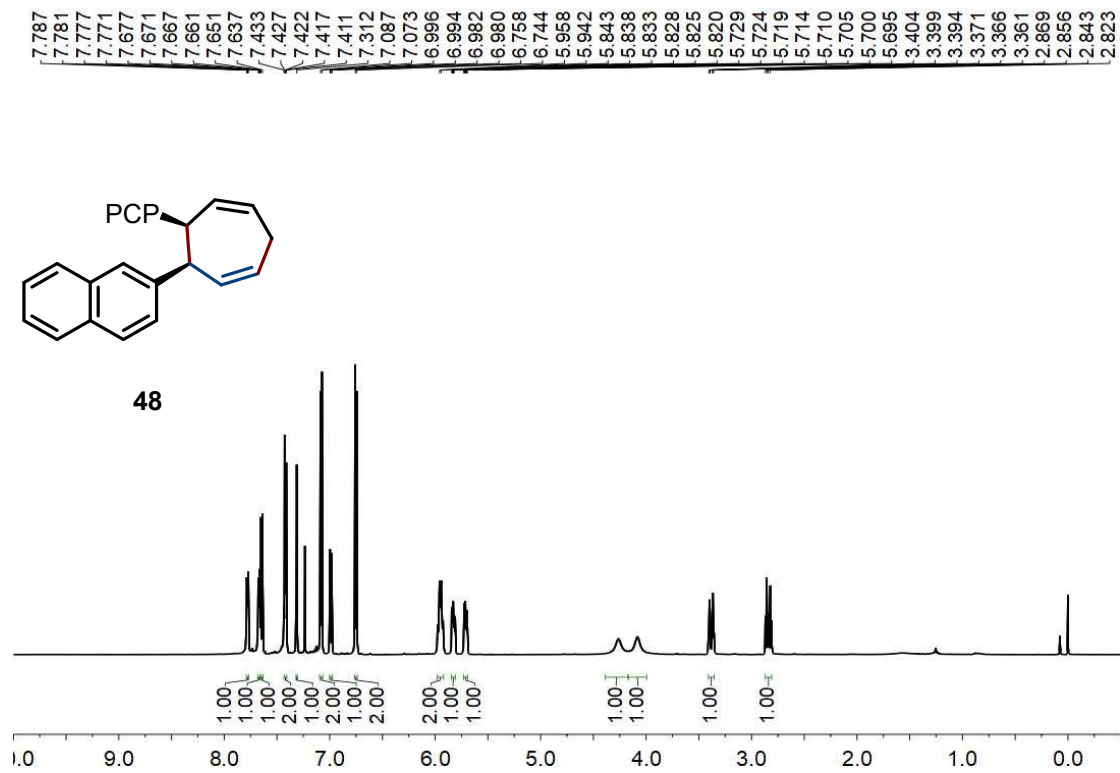


Figure S101.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **48**.

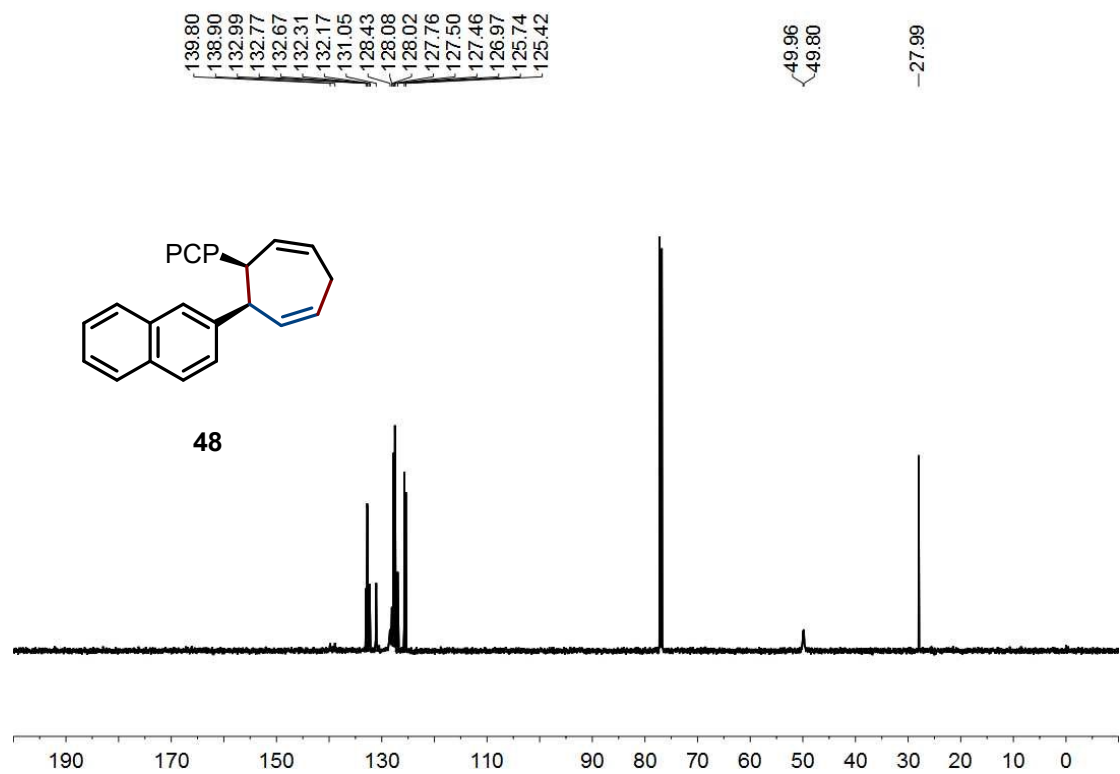


Figure S102.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **48**.

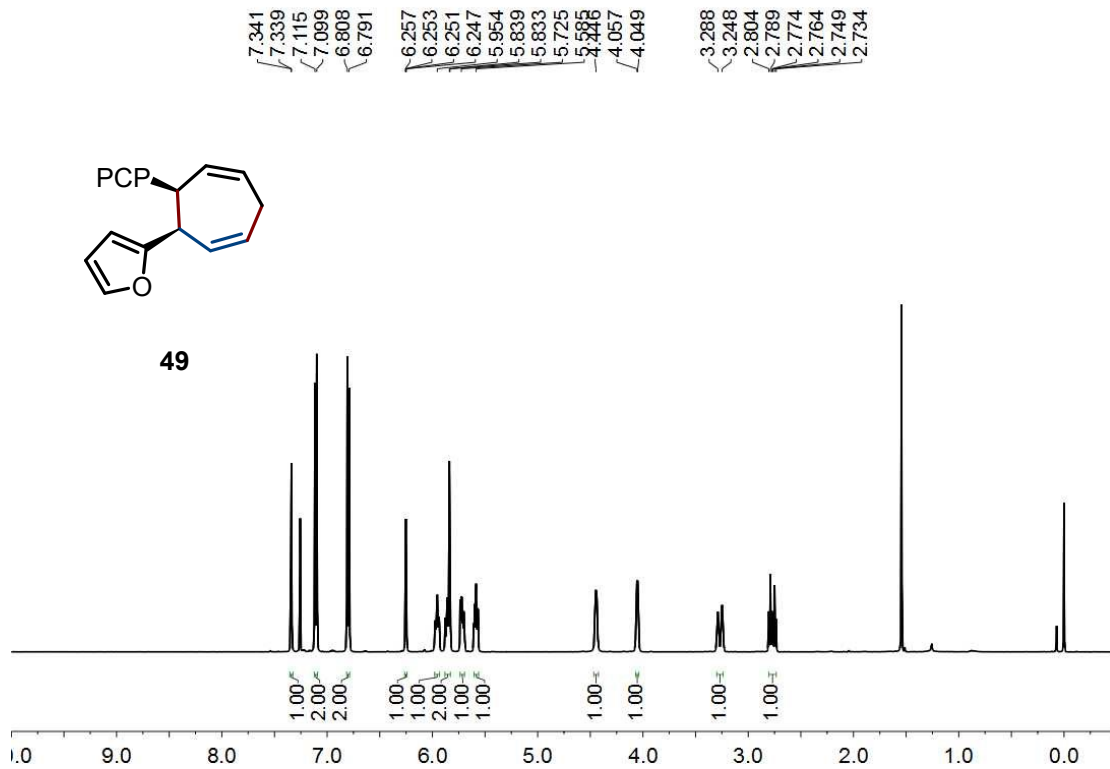


Figure S103.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **49**.

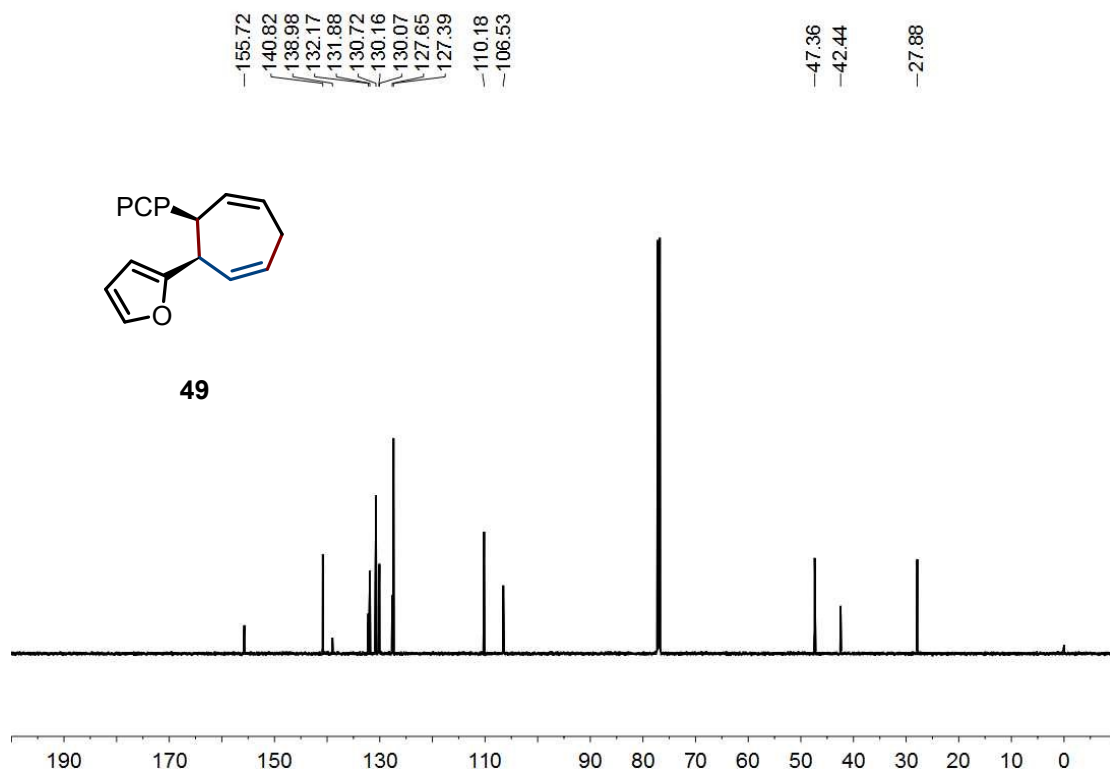


Figure S104.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **49**.

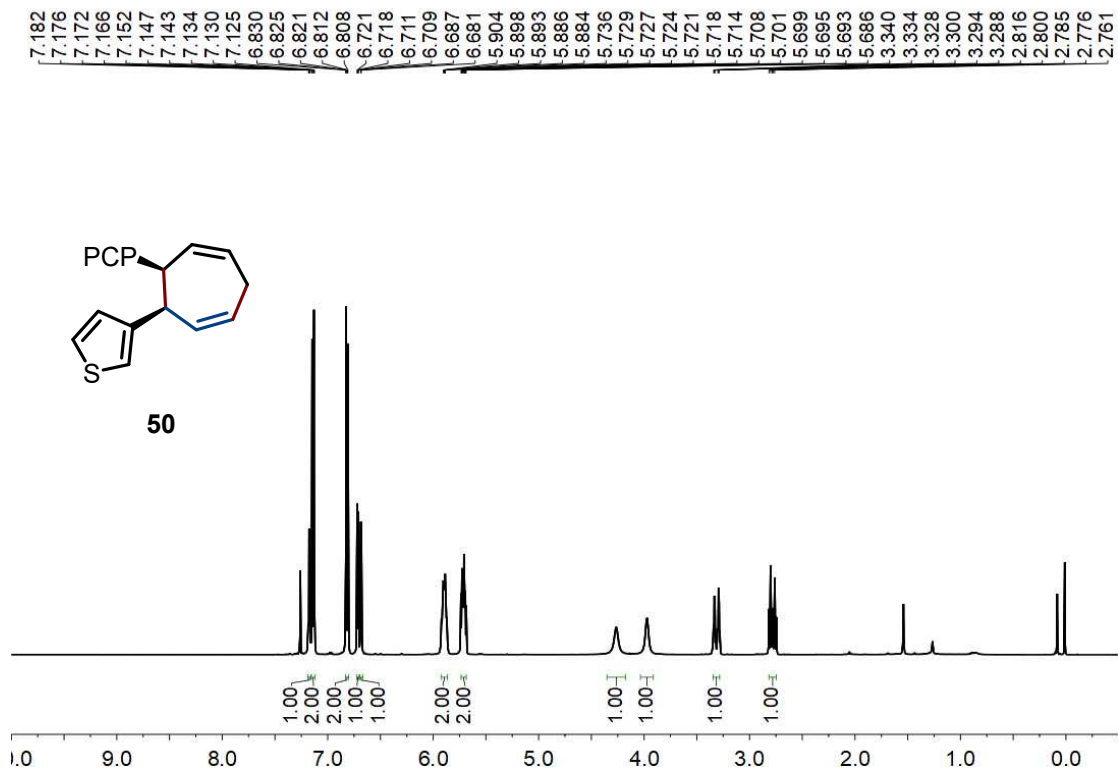


Figure S105.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **50**.

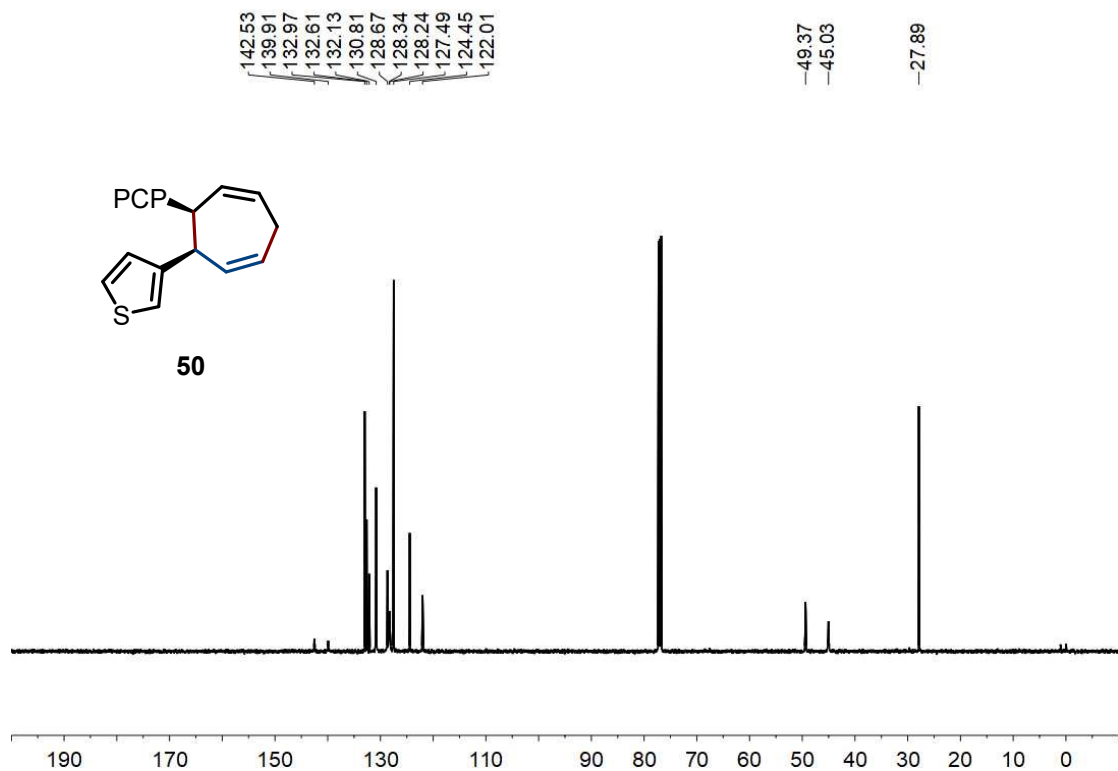
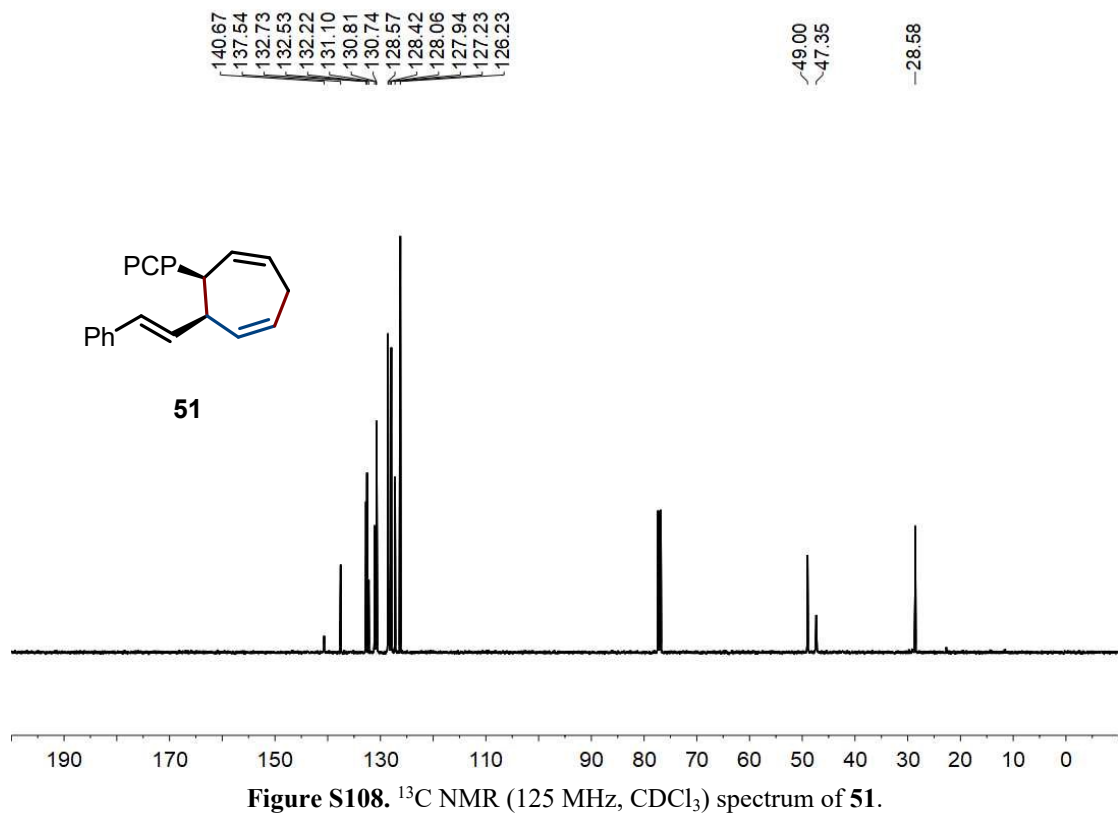
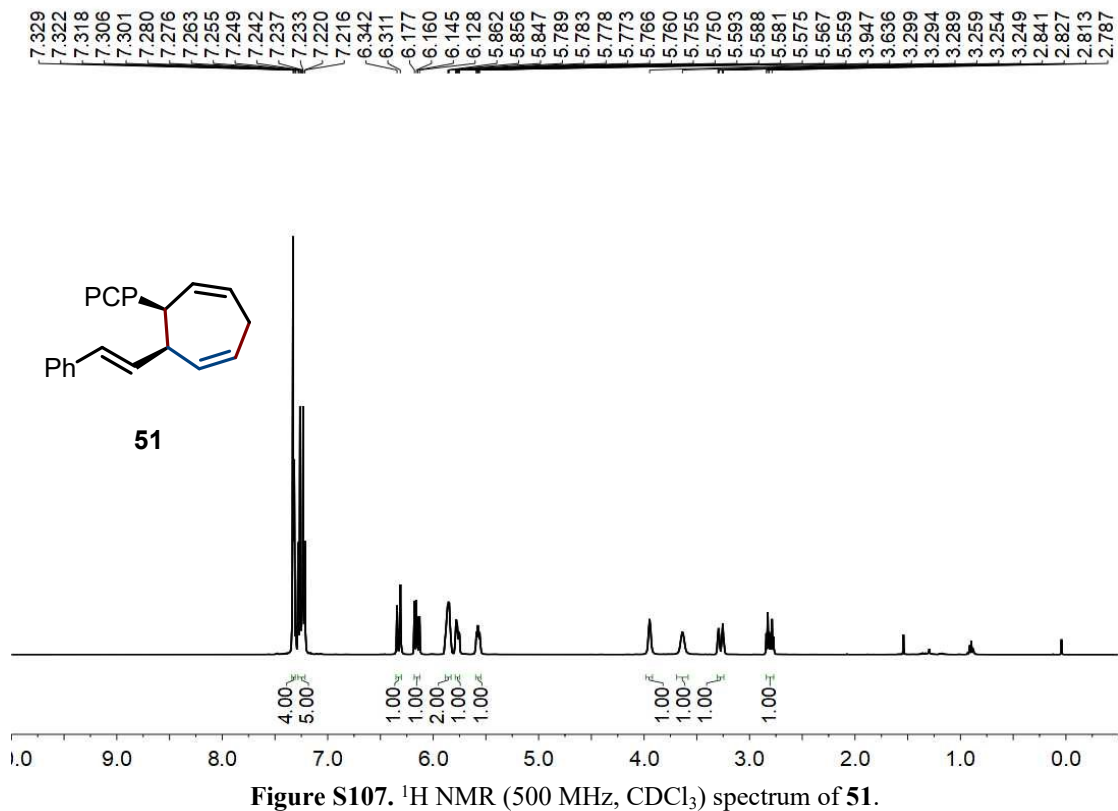


Figure S106.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **50**.



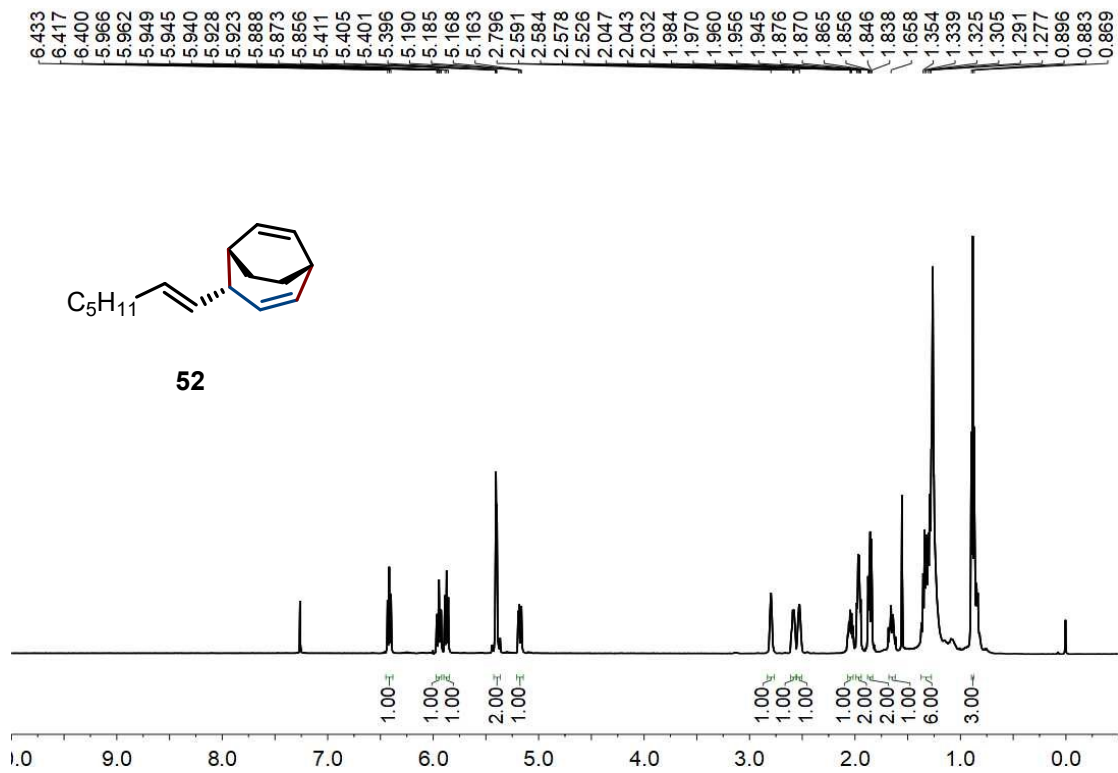


Figure S109.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **52**.

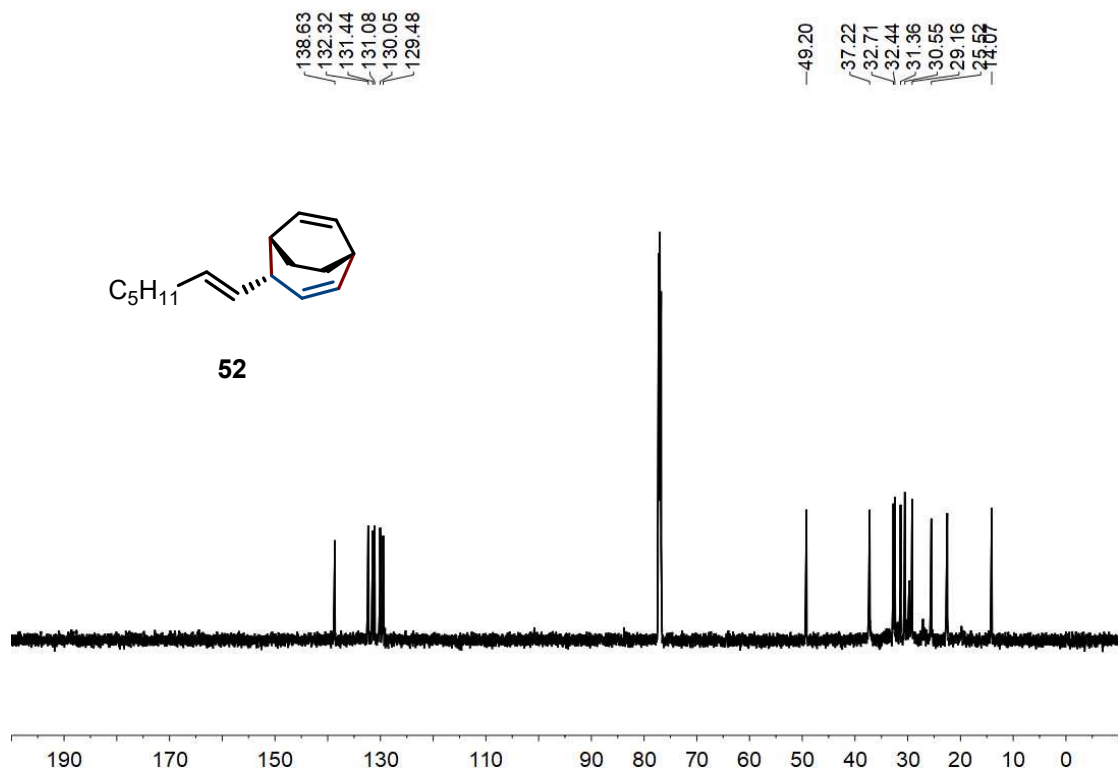


Figure S110.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **52**.

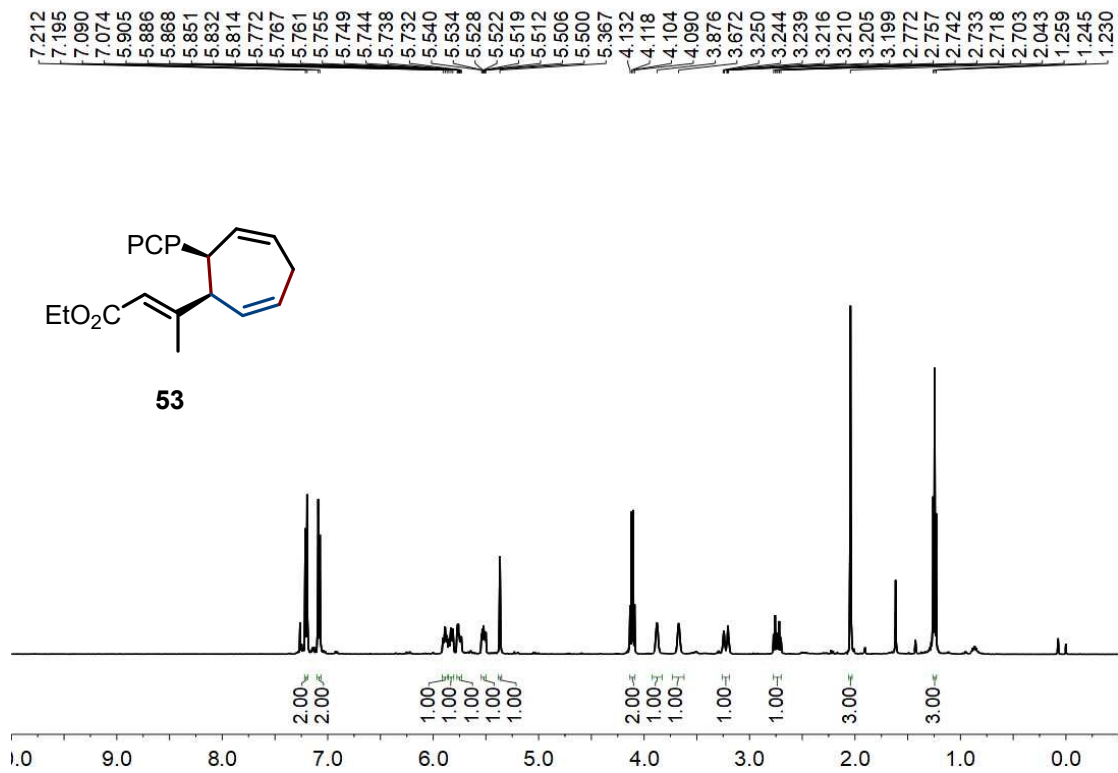


Figure S111. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **53**.

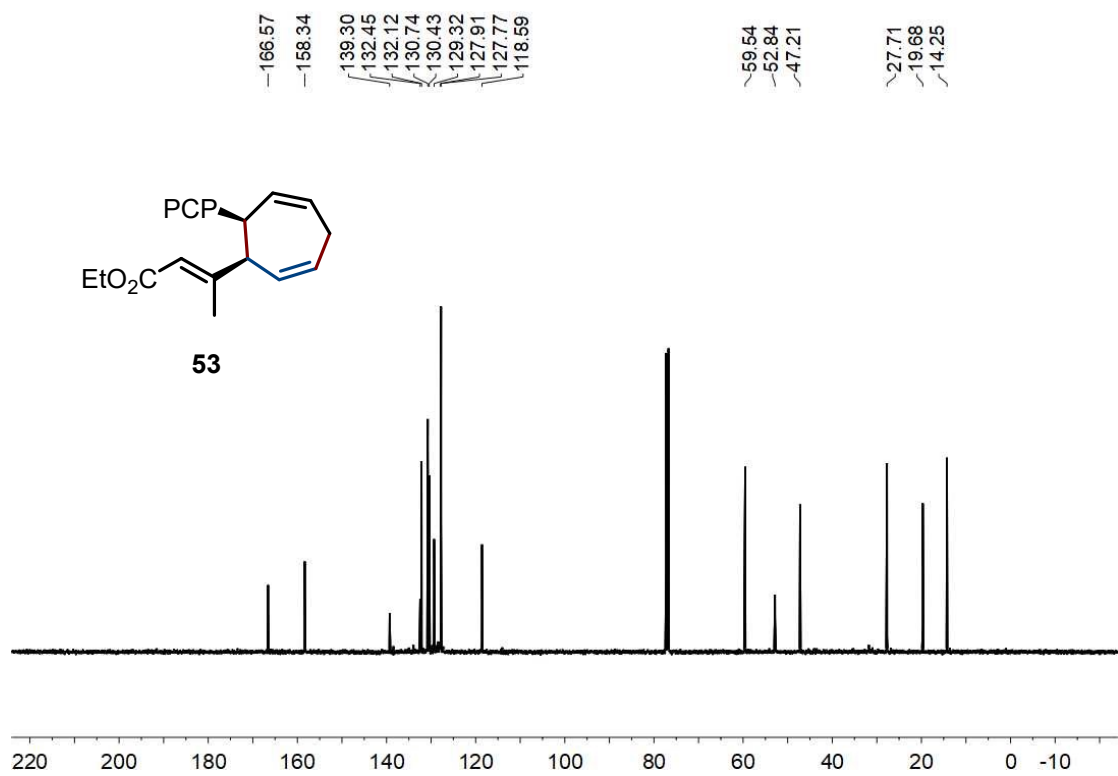


Figure S112. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **53**.

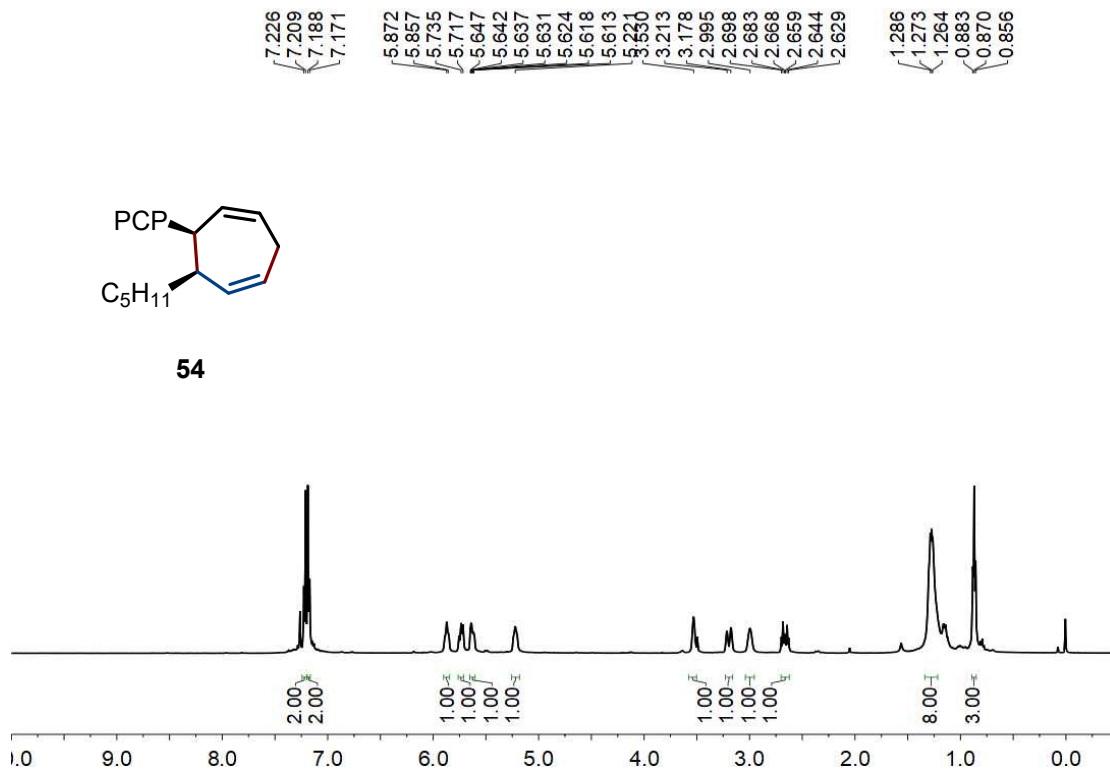


Figure S113. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **54**.

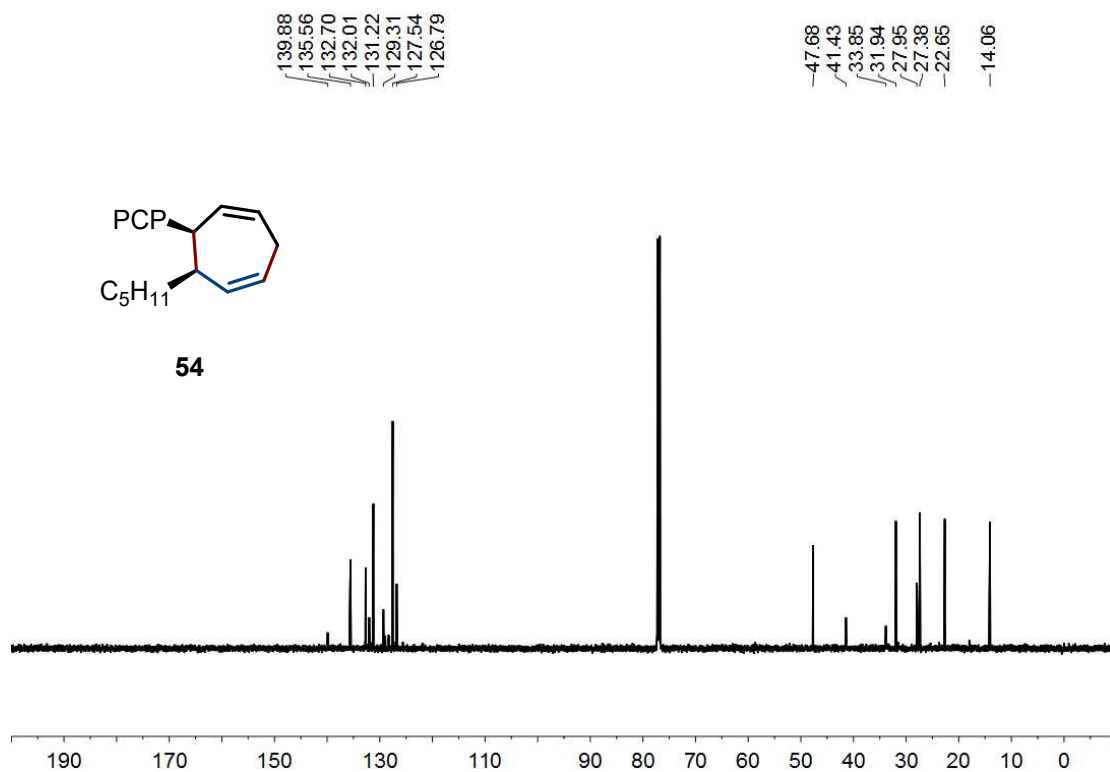


Figure S114. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **54**.



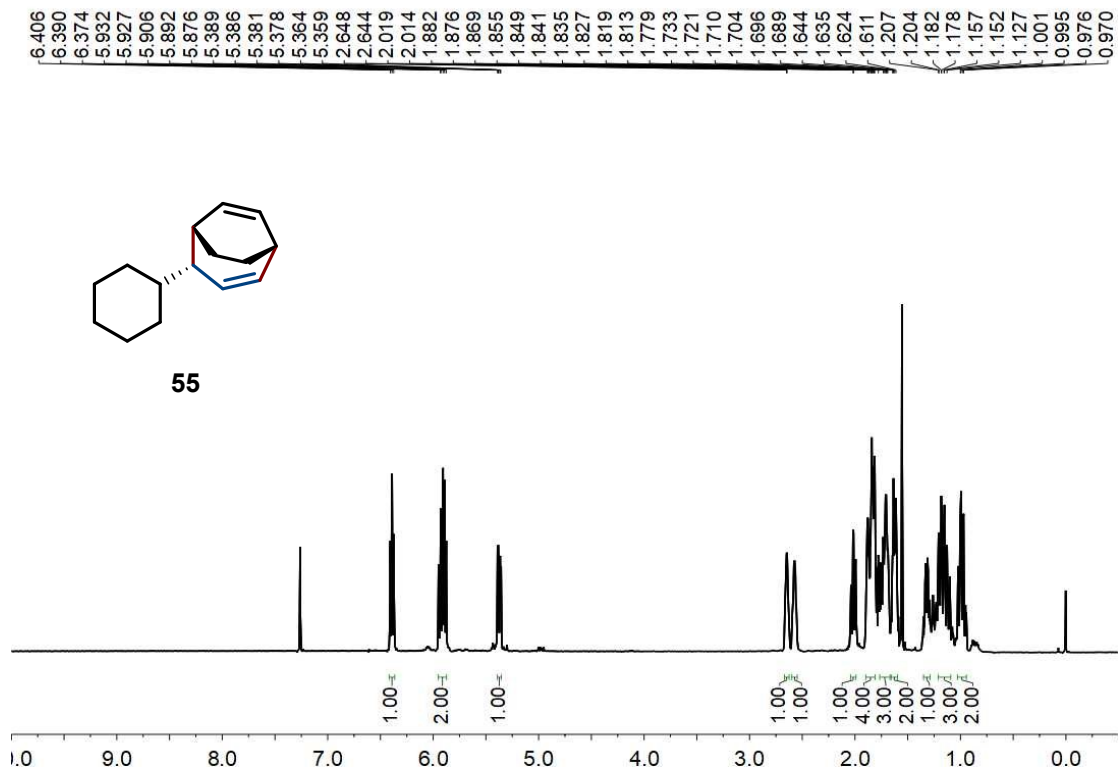


Figure S115.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **55**.

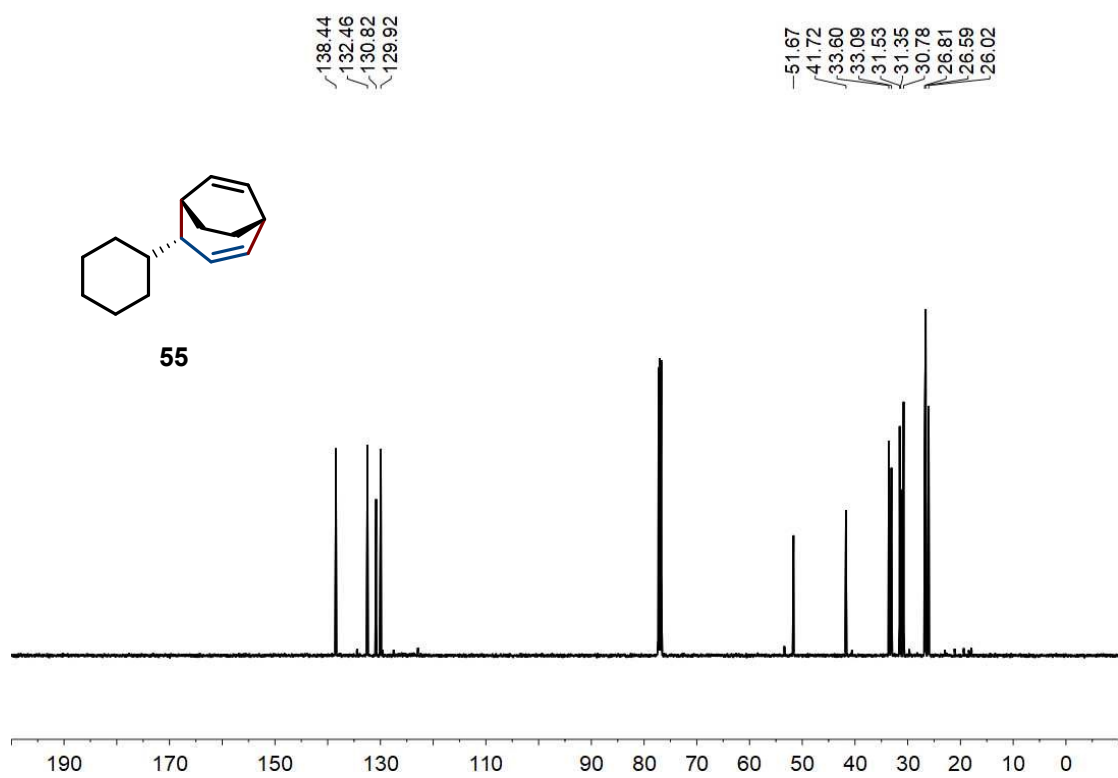


Figure S116.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **55**.

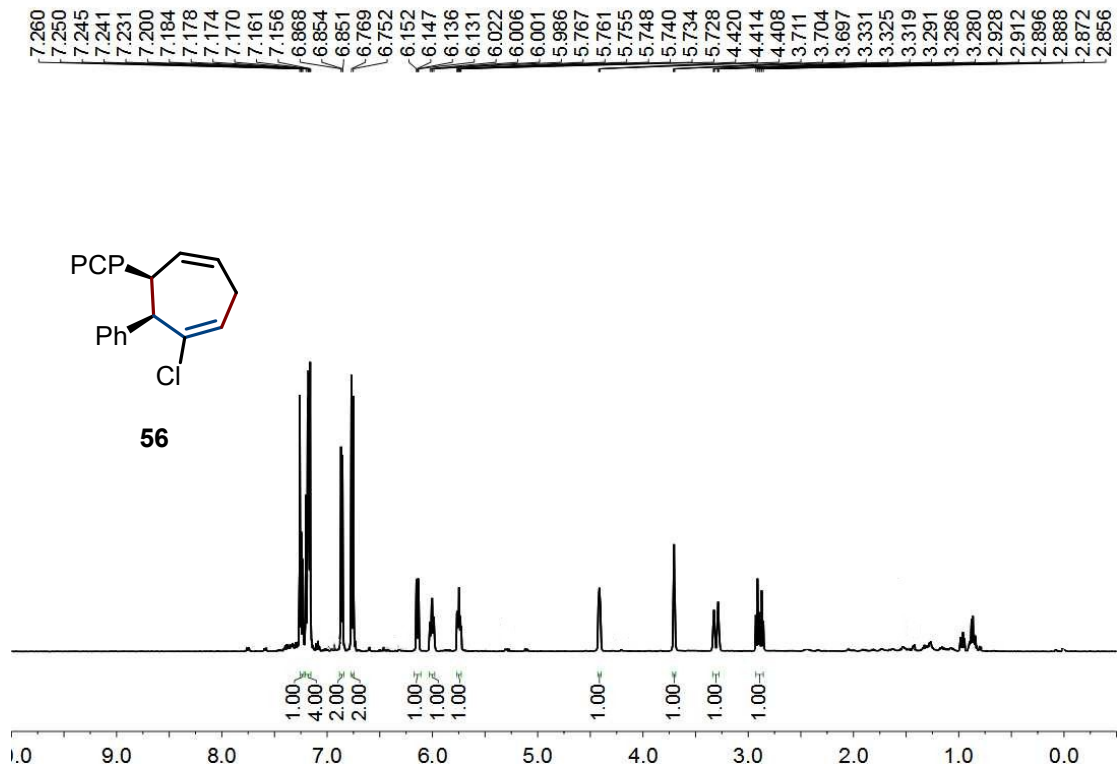


Figure S117.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **56**.

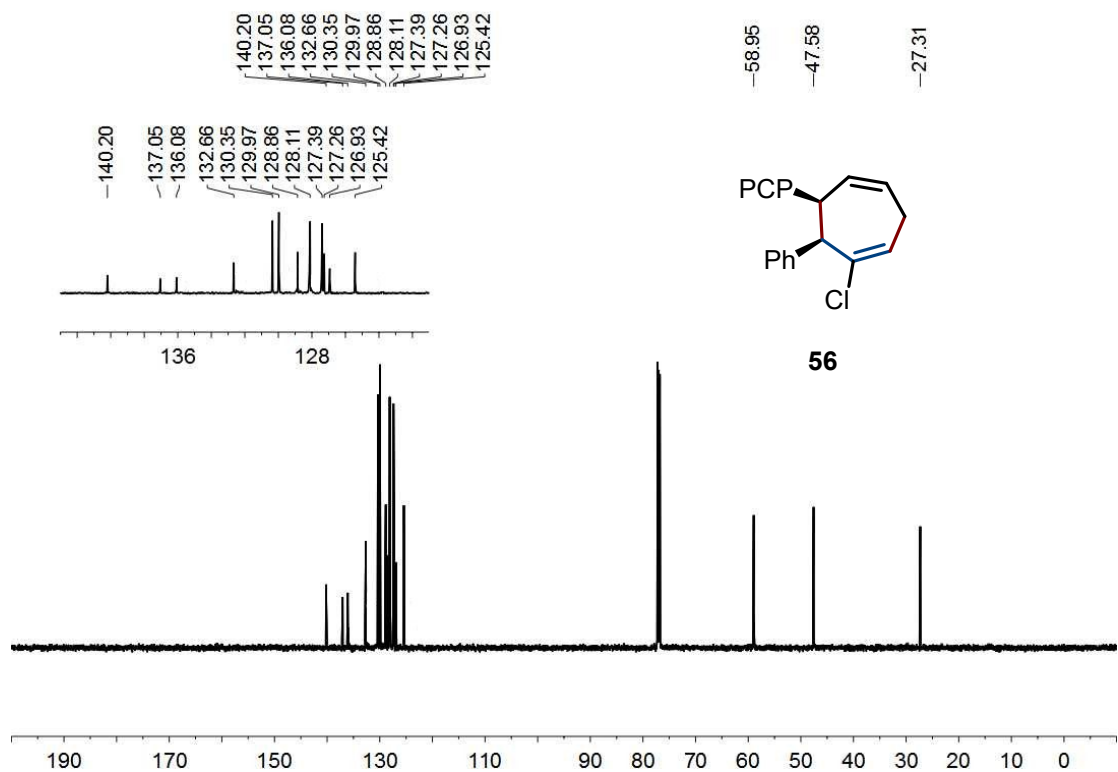


Figure S118.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **56**.

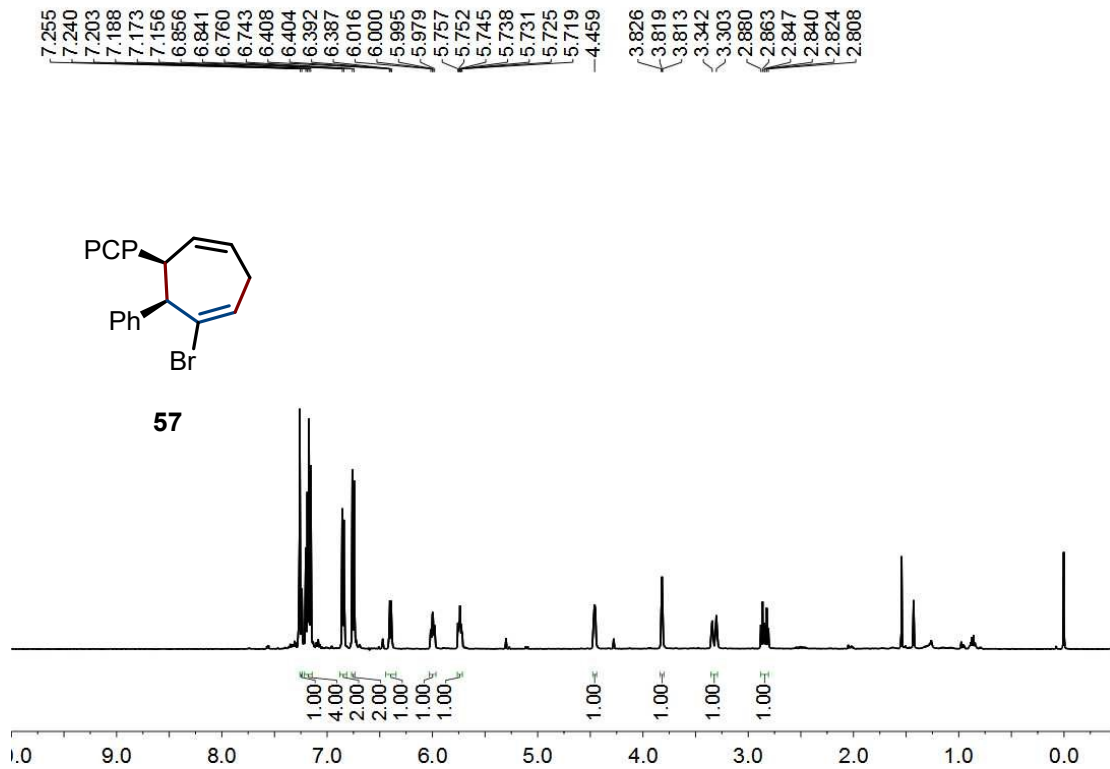


Figure S119.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **57**

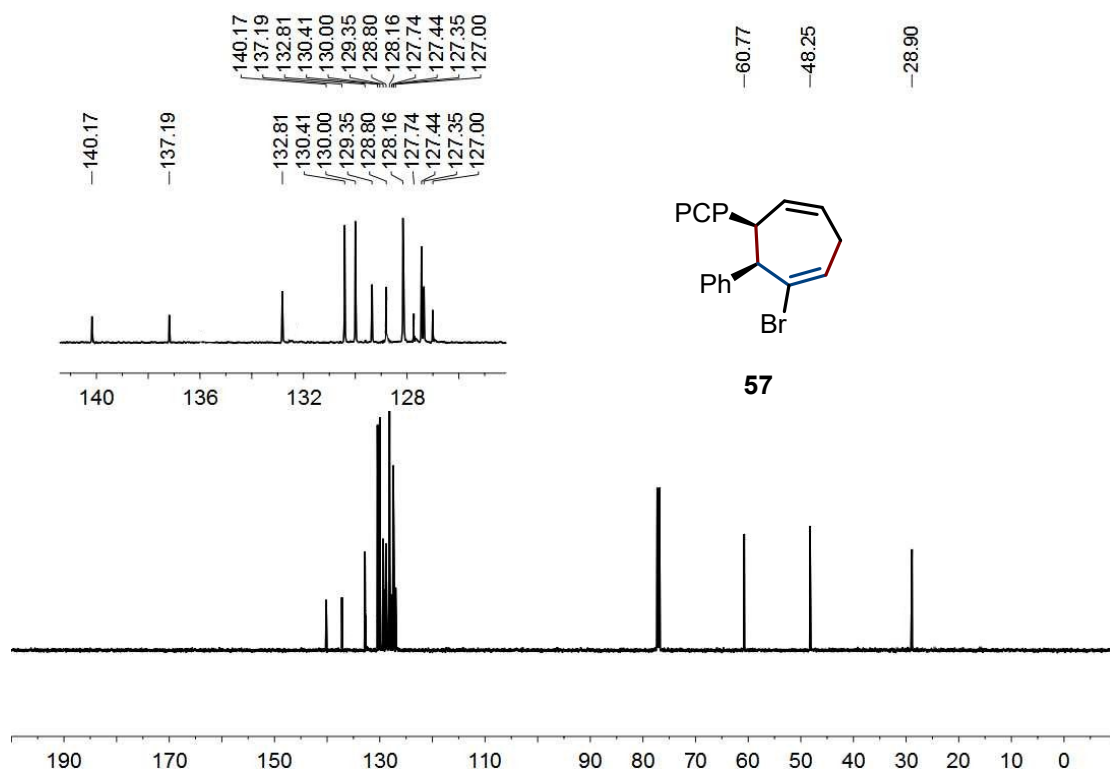


Figure S120.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **57**.

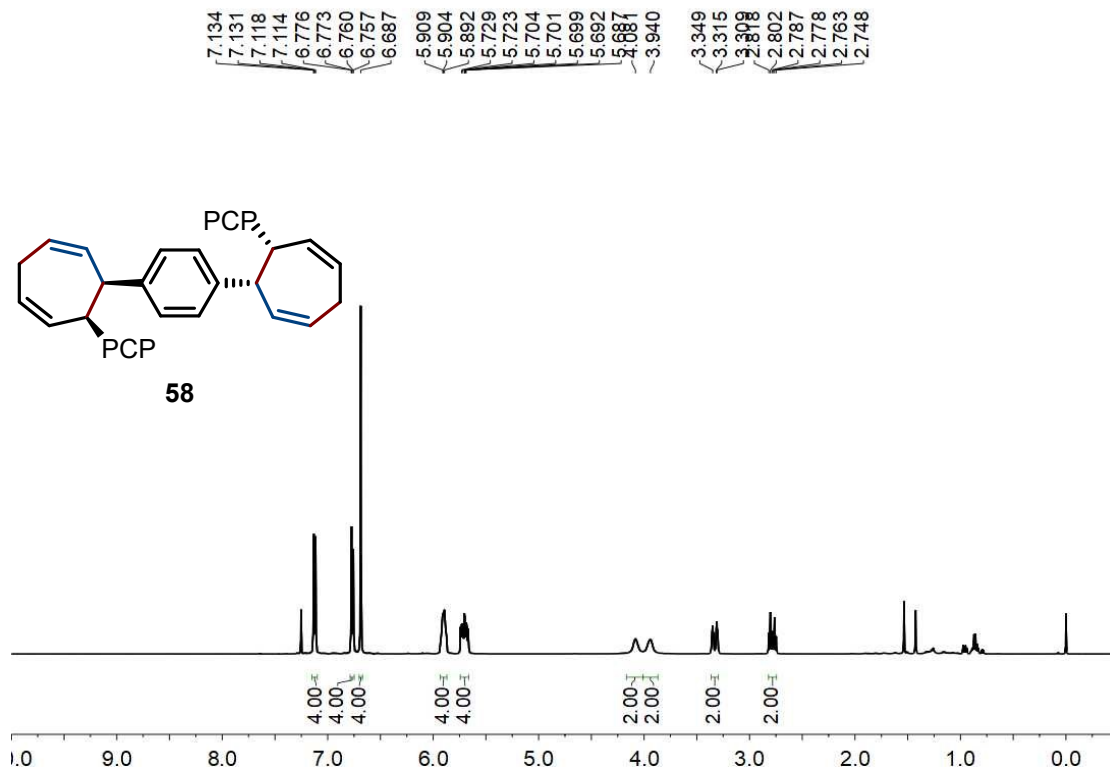


Figure S121.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **58**.

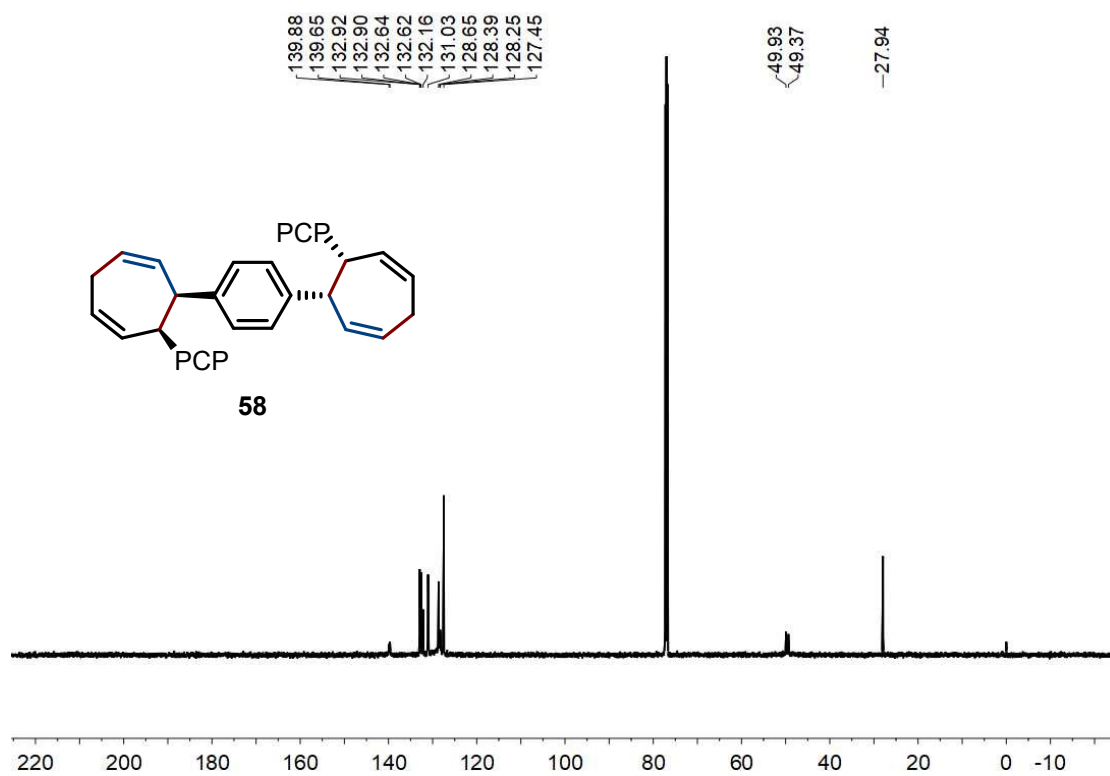


Figure S122.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **58**.

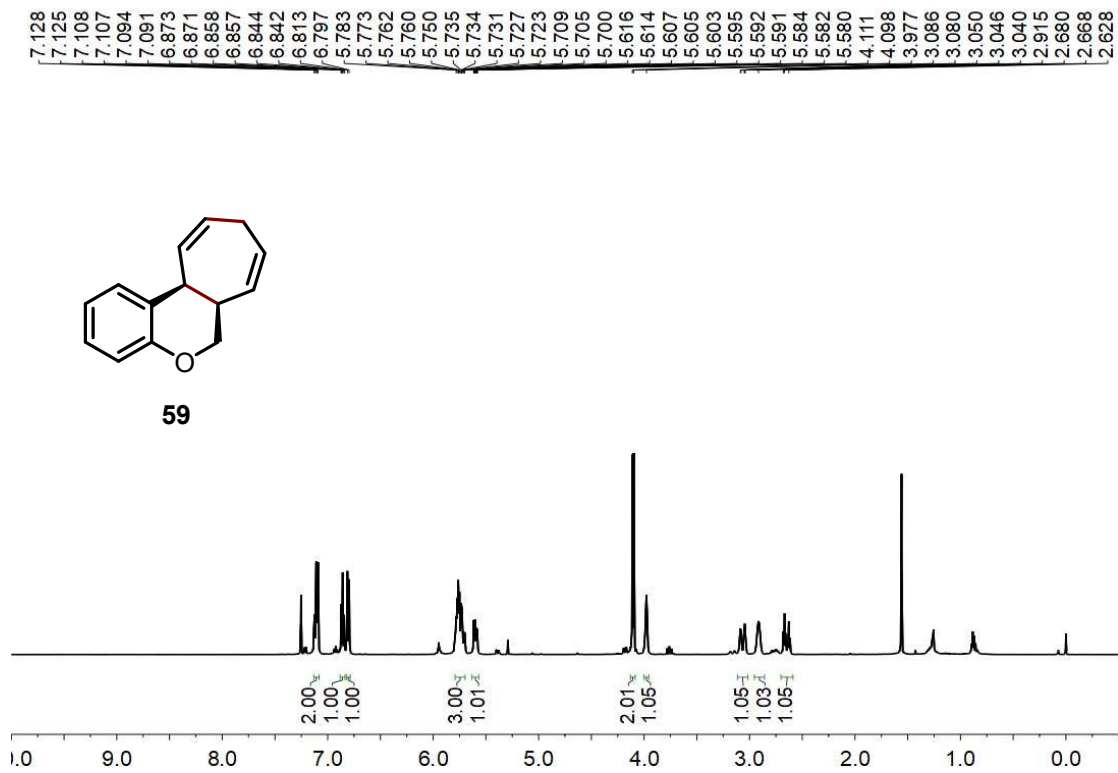


Figure S123.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **59**.

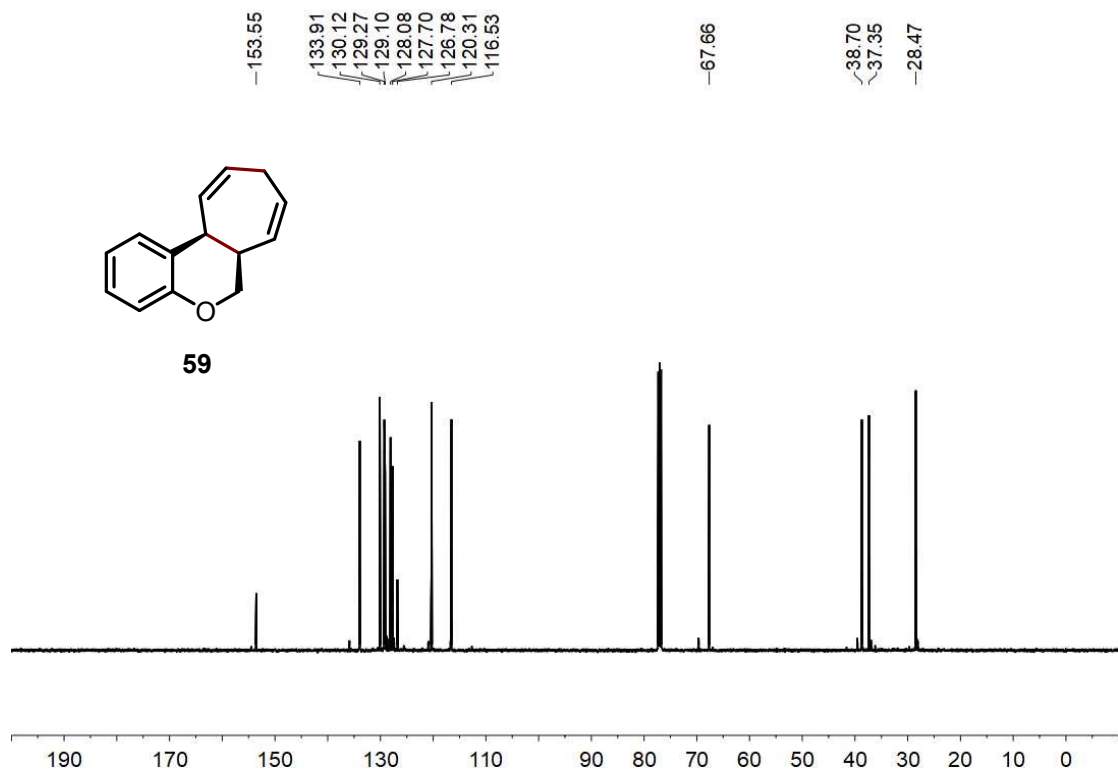


Figure S124.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **59**.

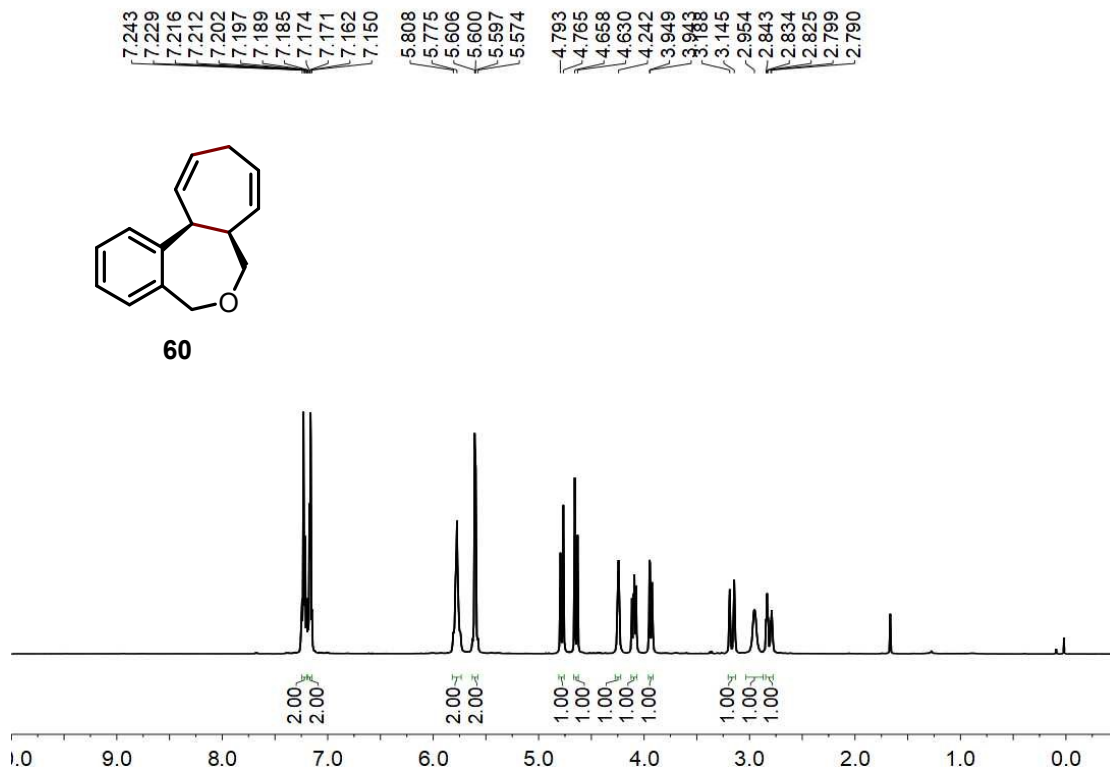


Figure S125.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **60**.

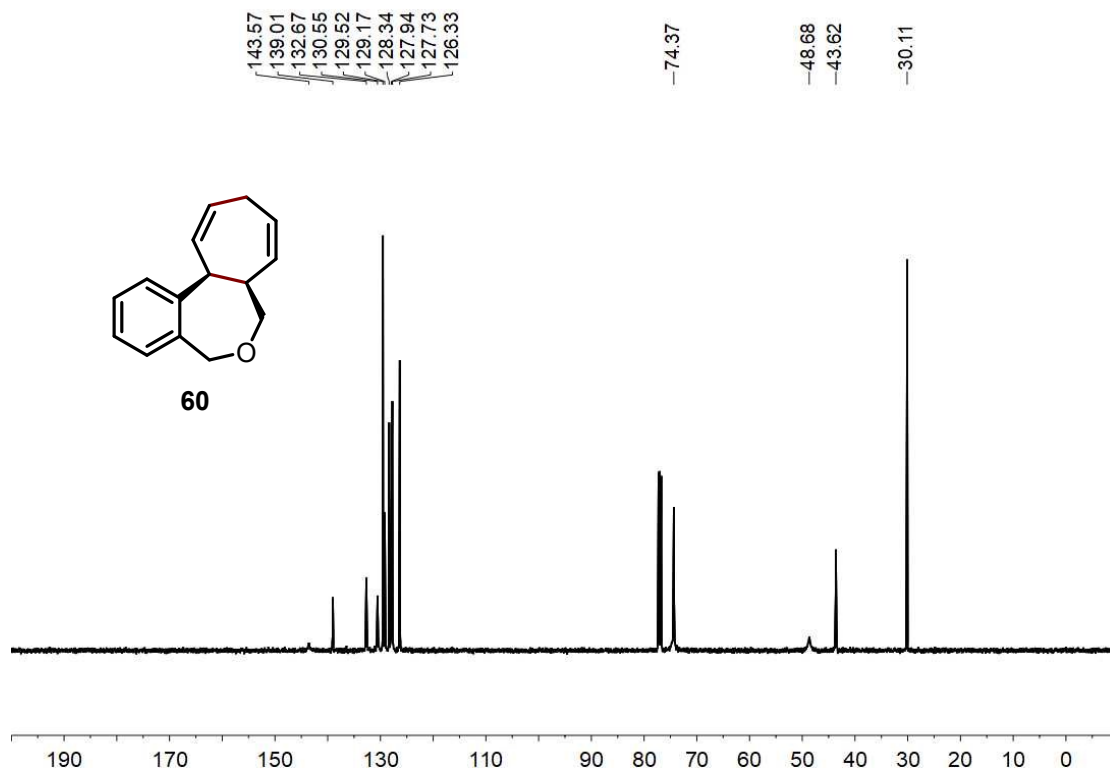


Figure S126.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **60**.

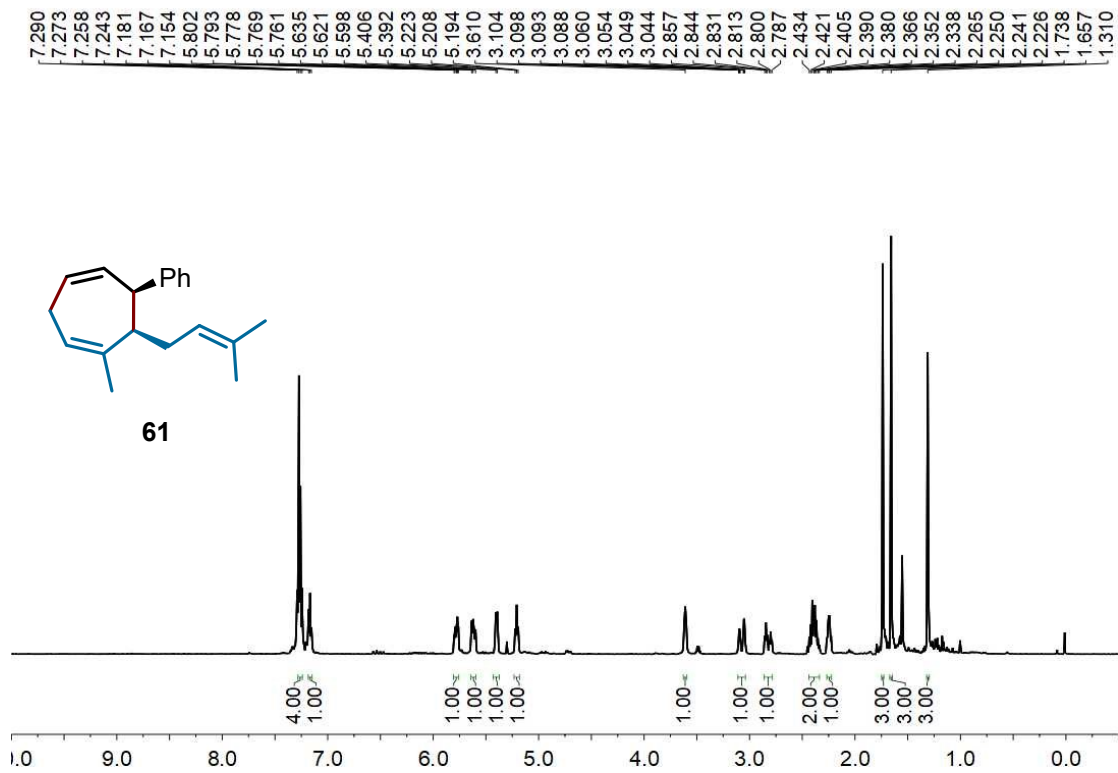


Figure S127.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **61**.

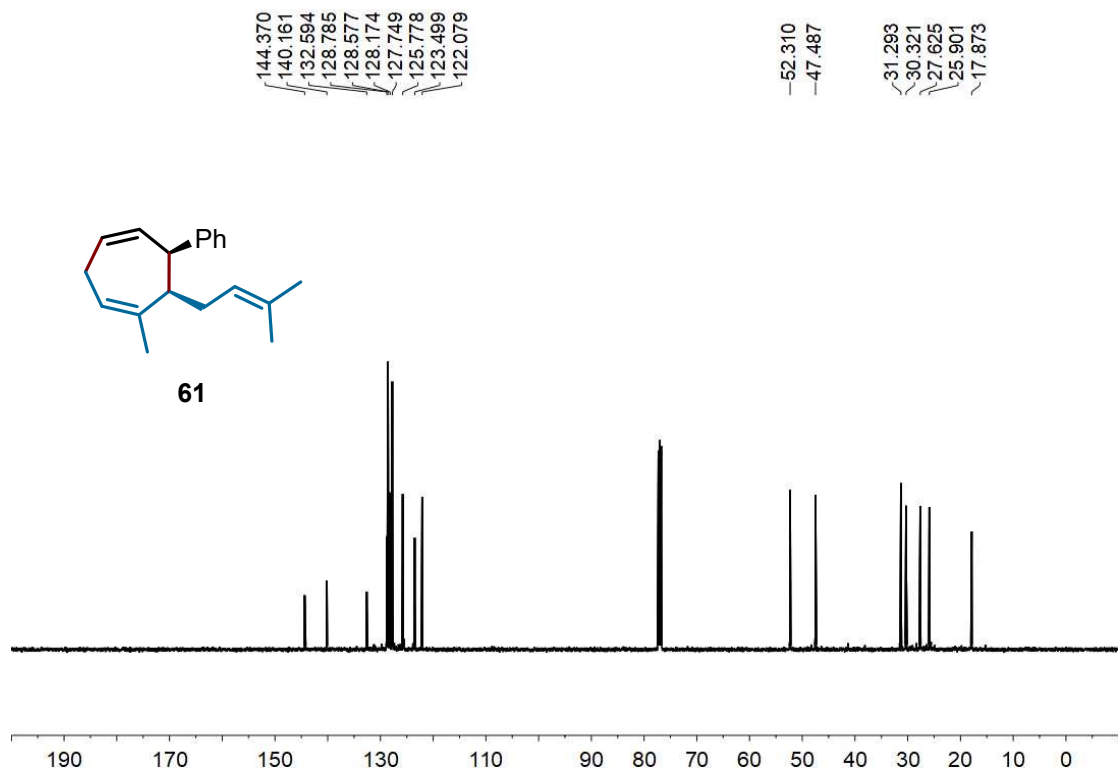
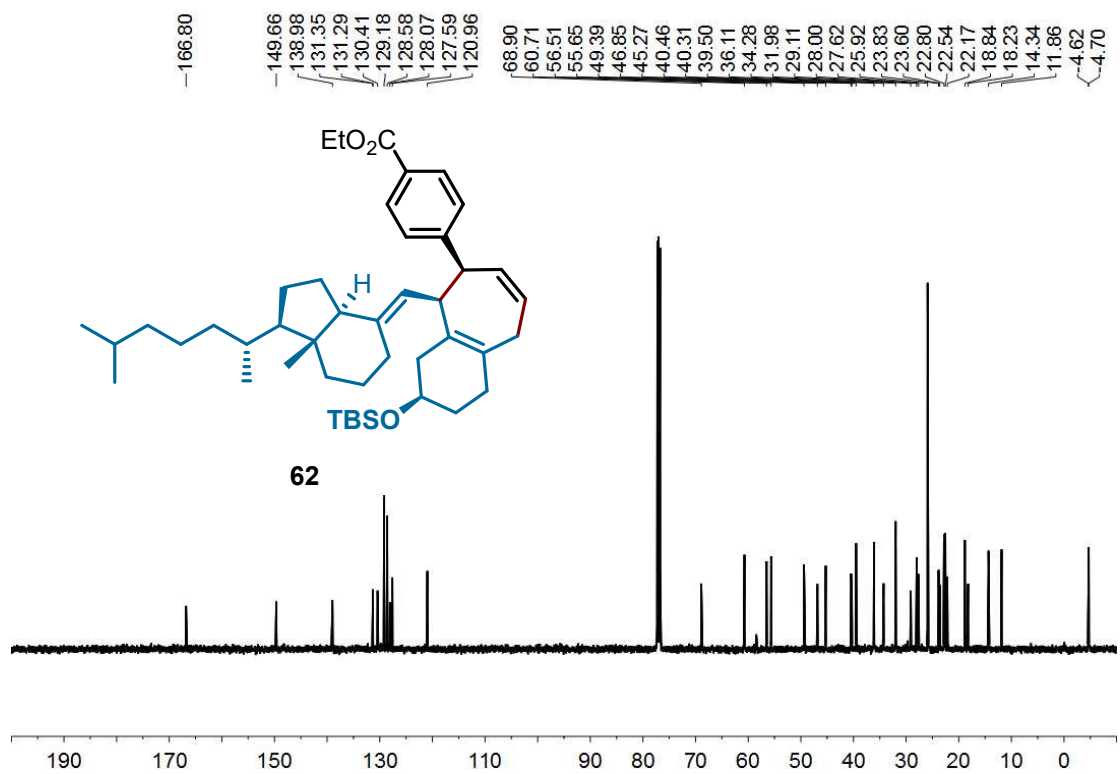
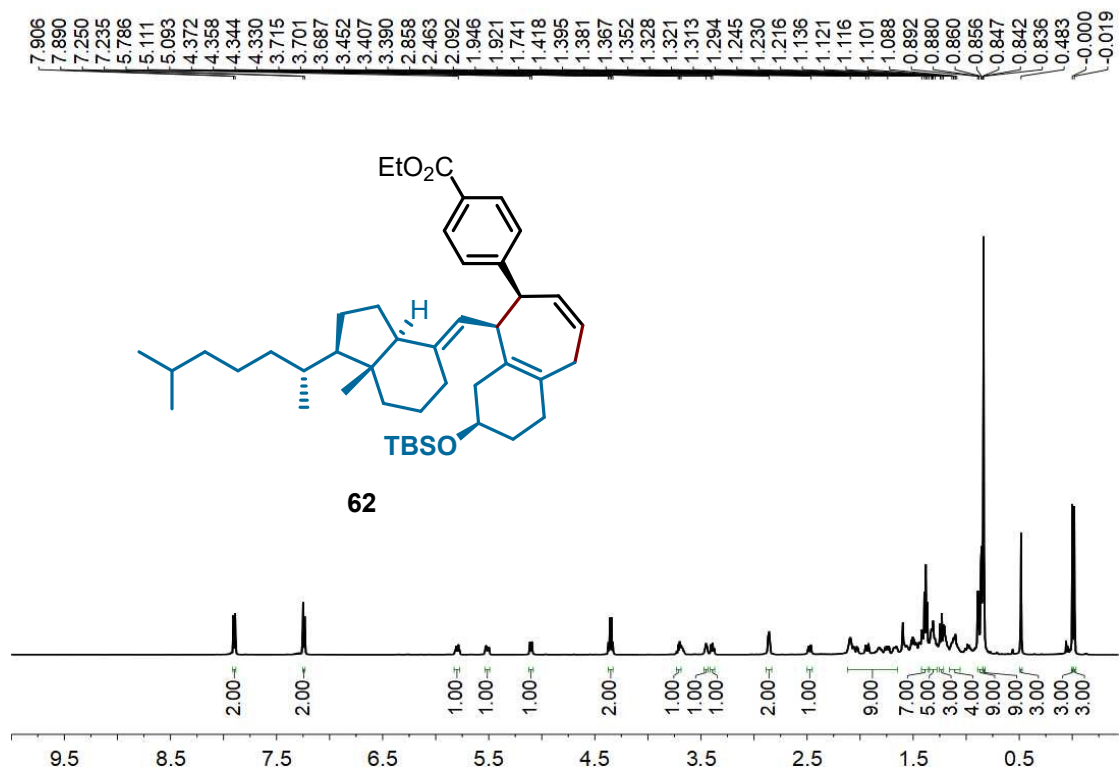
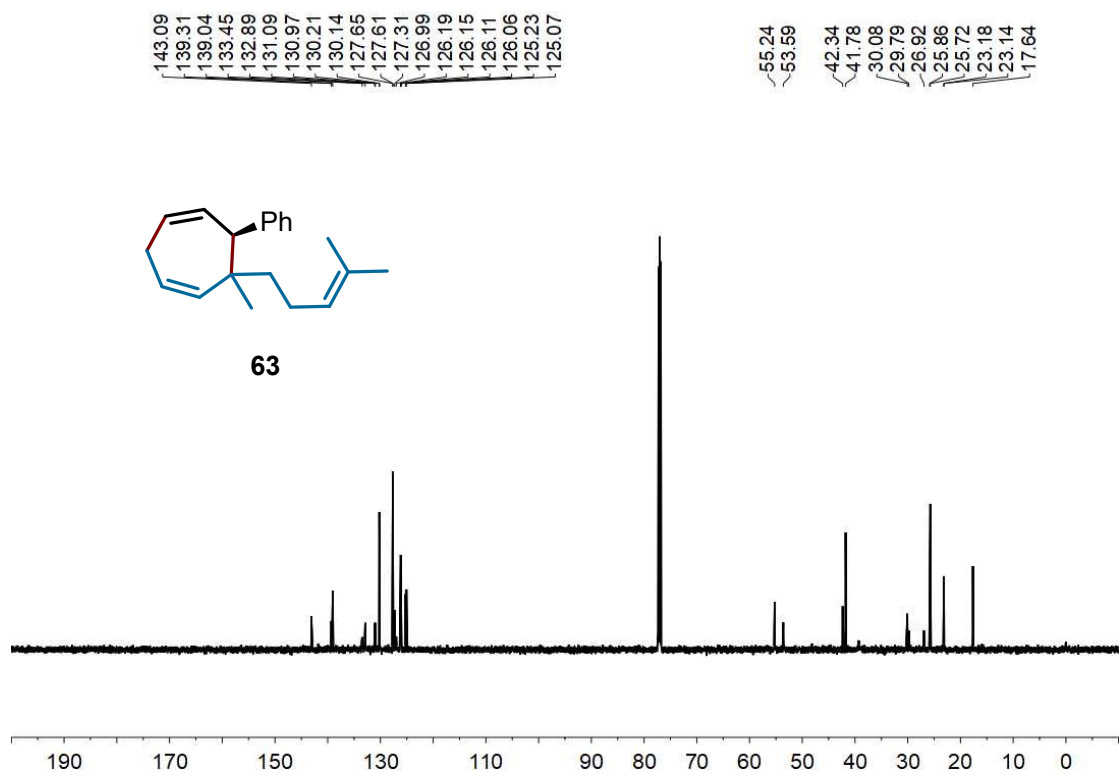
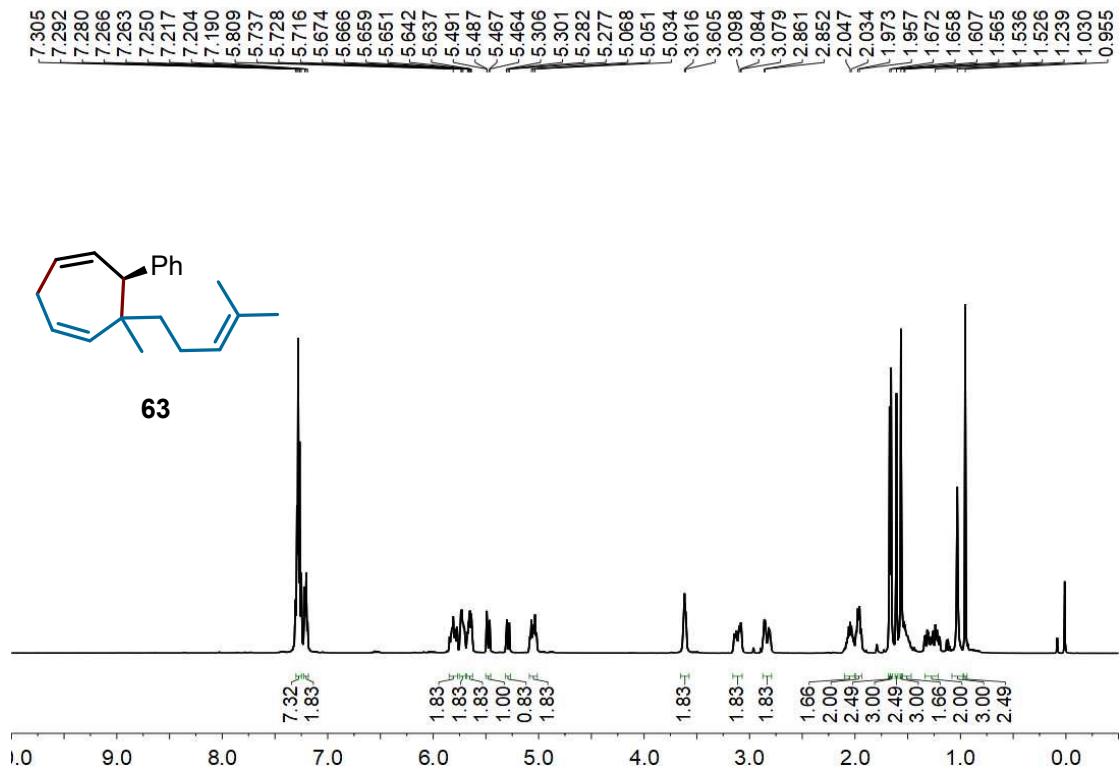


Figure S128.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **61**.







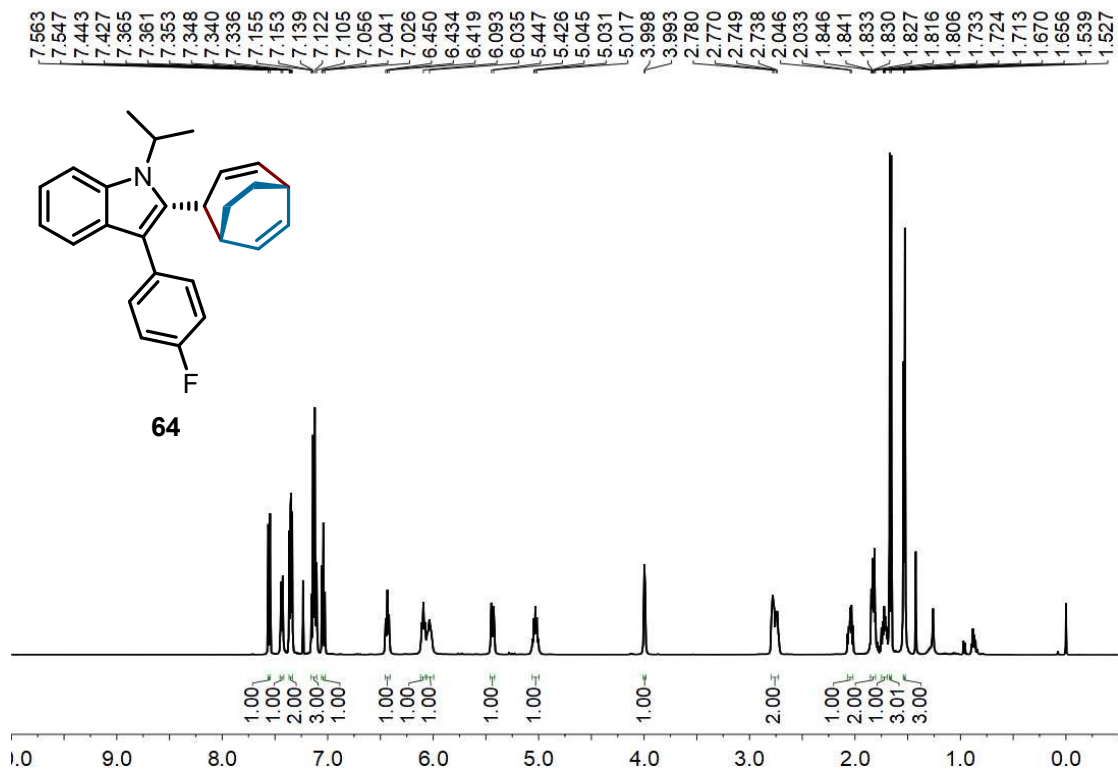


Figure S133.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **64**.

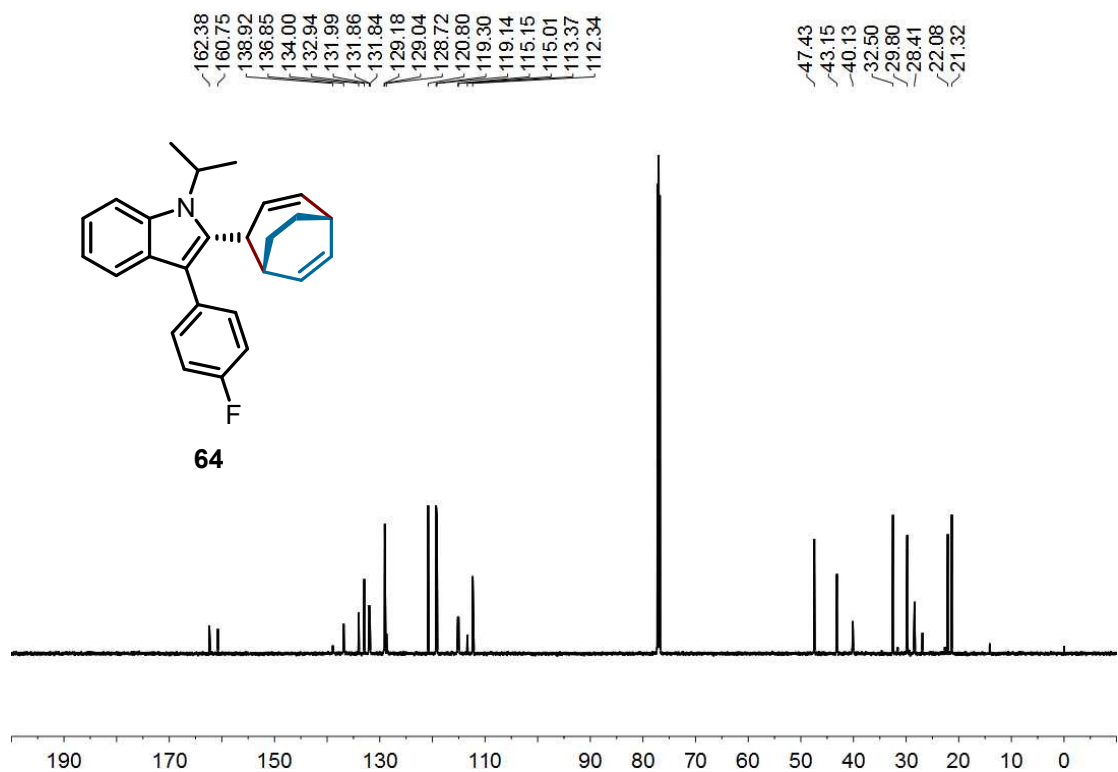


Figure S134.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **64**.

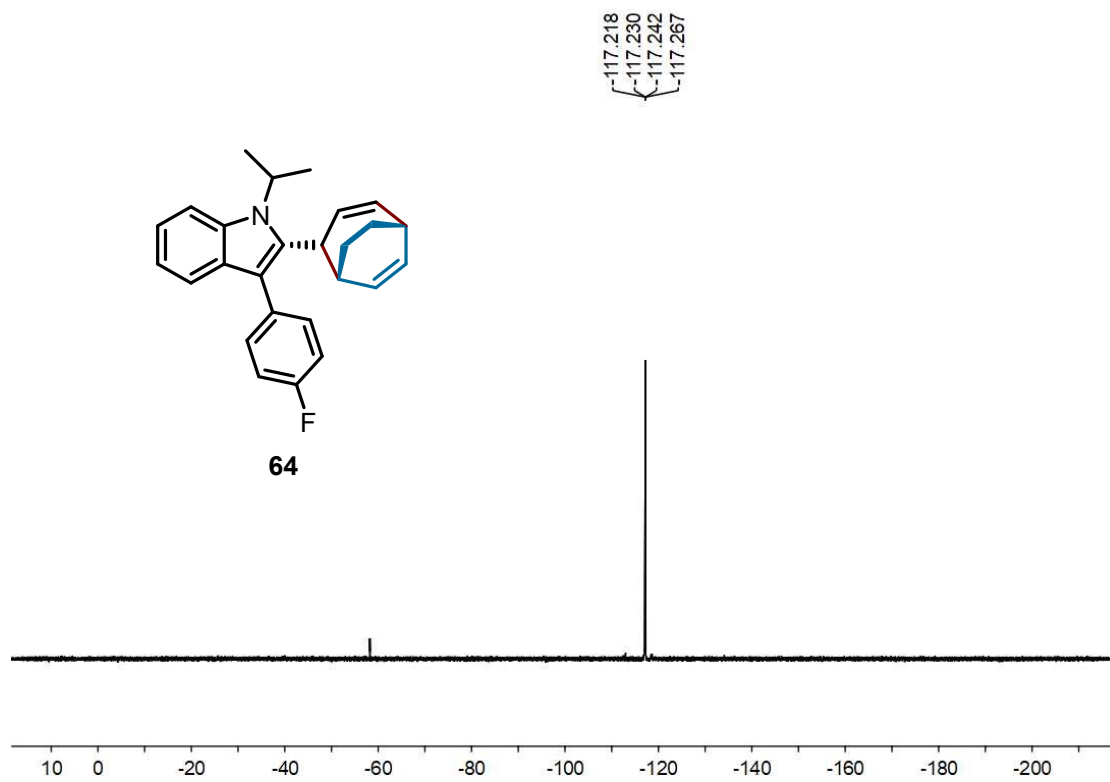


Figure S135. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of **64**.

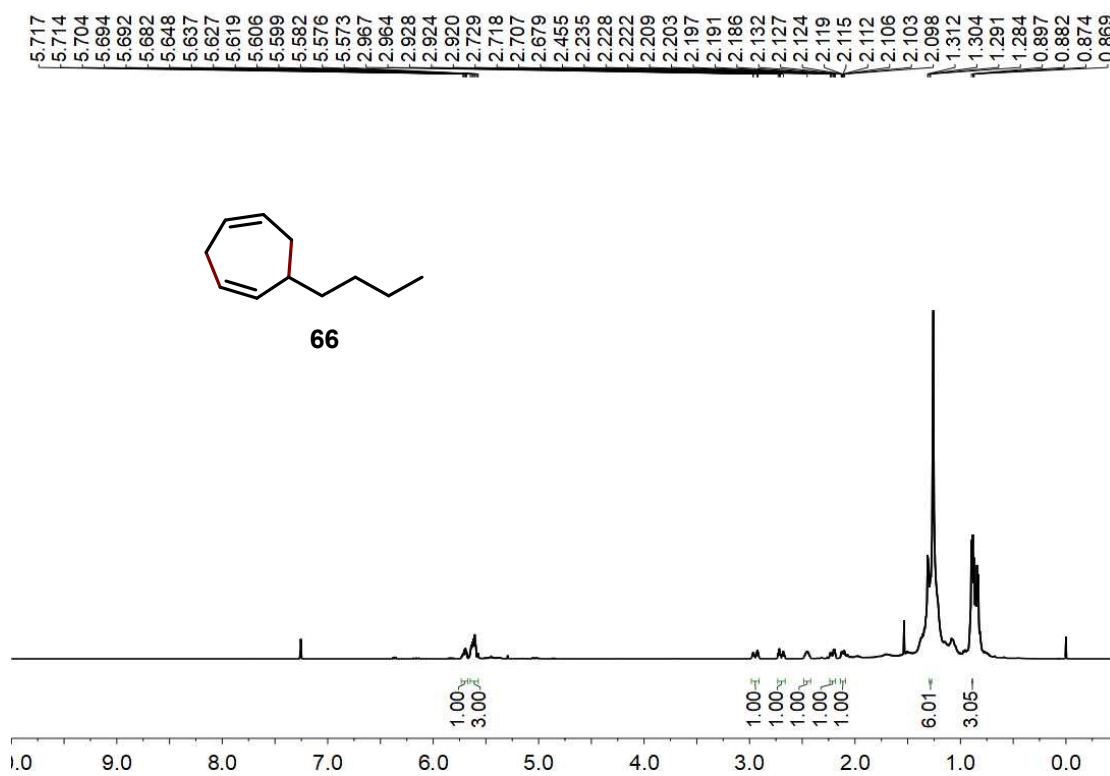


Figure S136. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **66**.

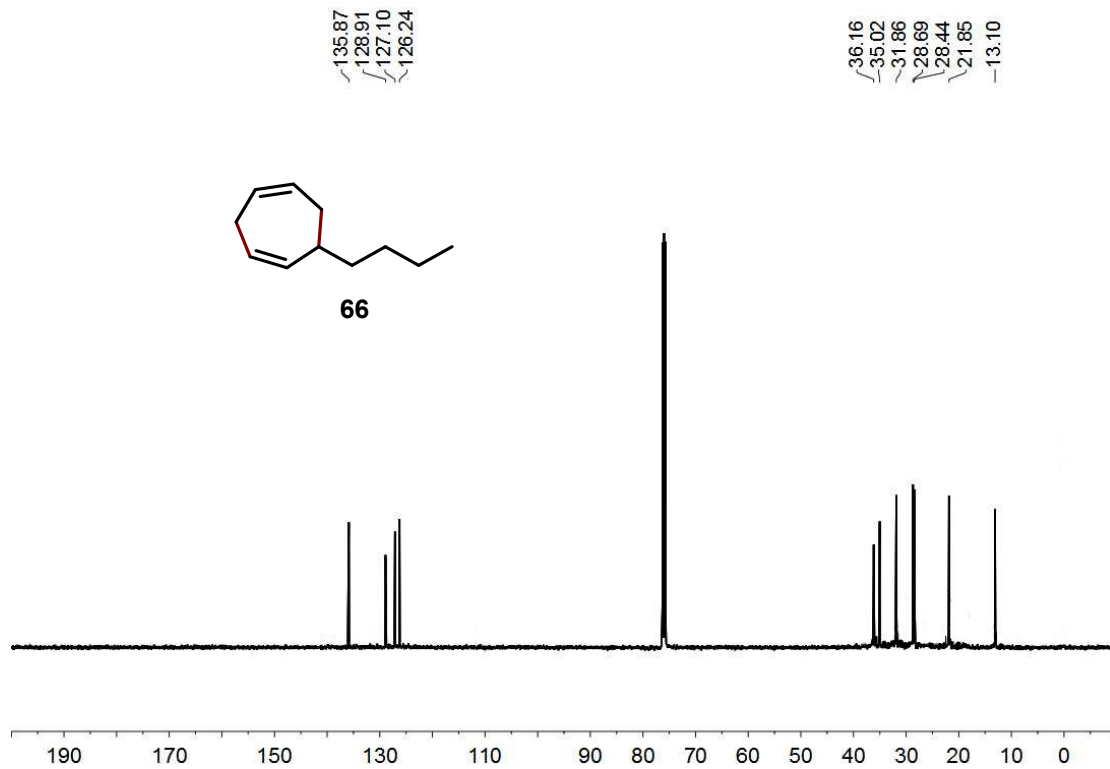


Figure S137. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **66**.

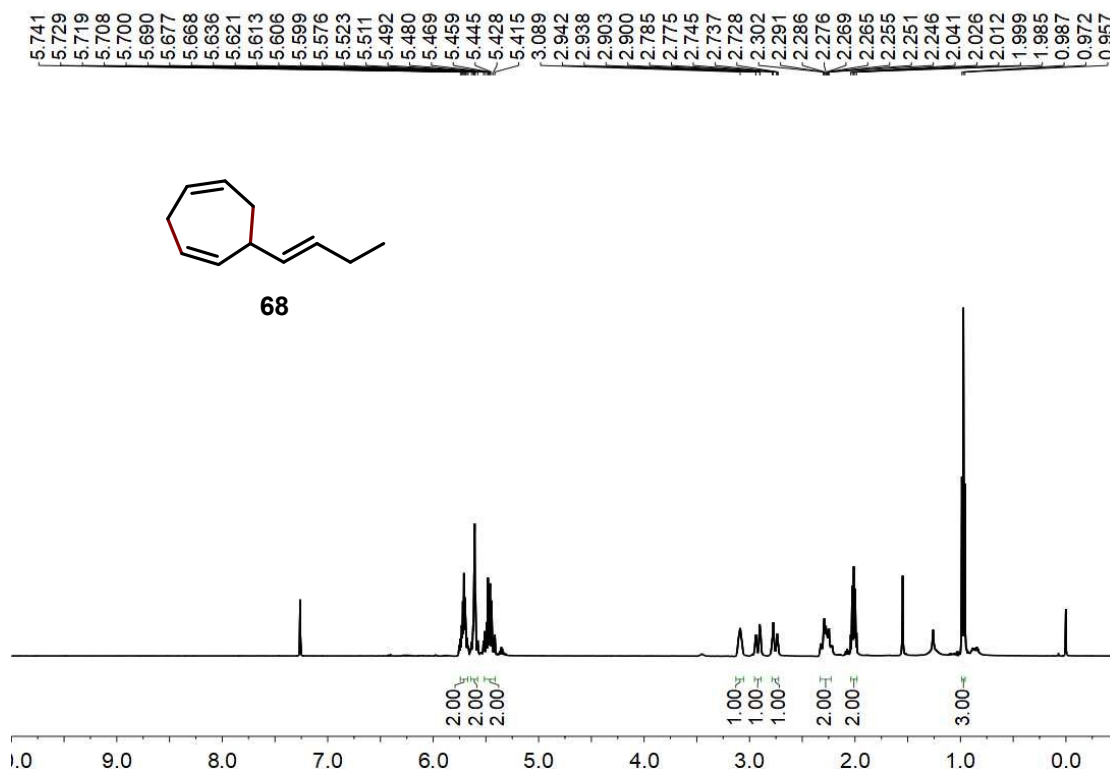


Figure S138. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **68**.

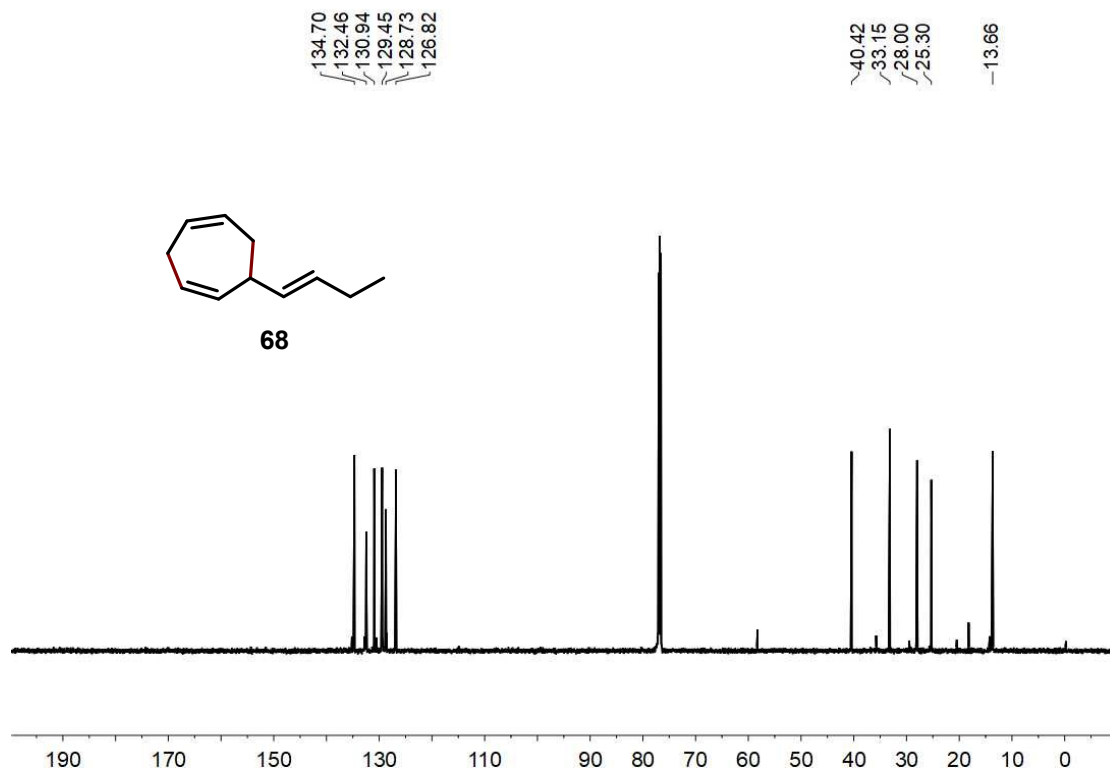


Figure S139. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **68**.

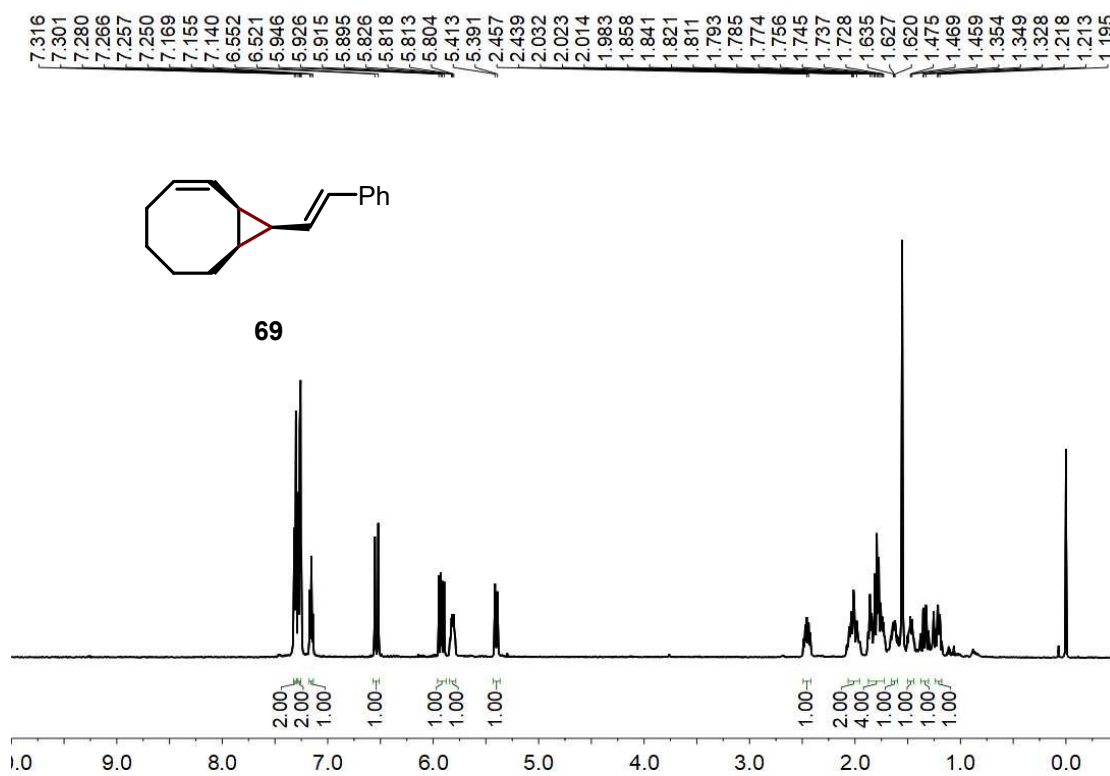


Figure S140. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **69**.

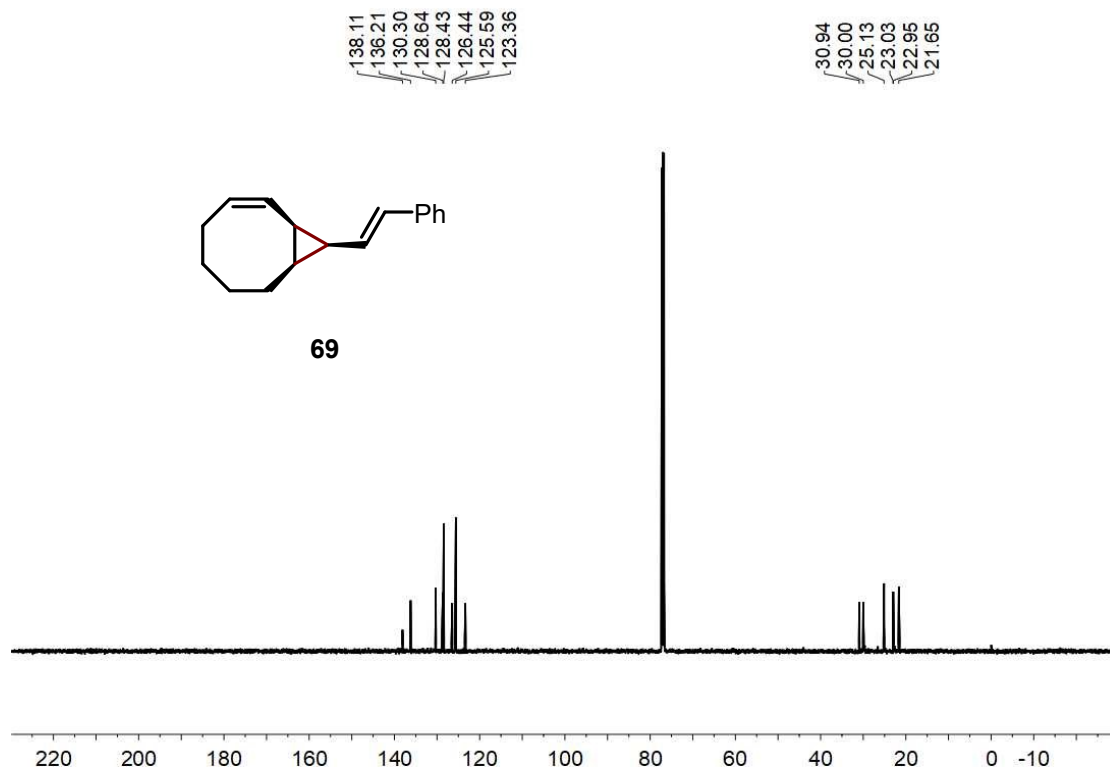


Figure S141. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **69**.

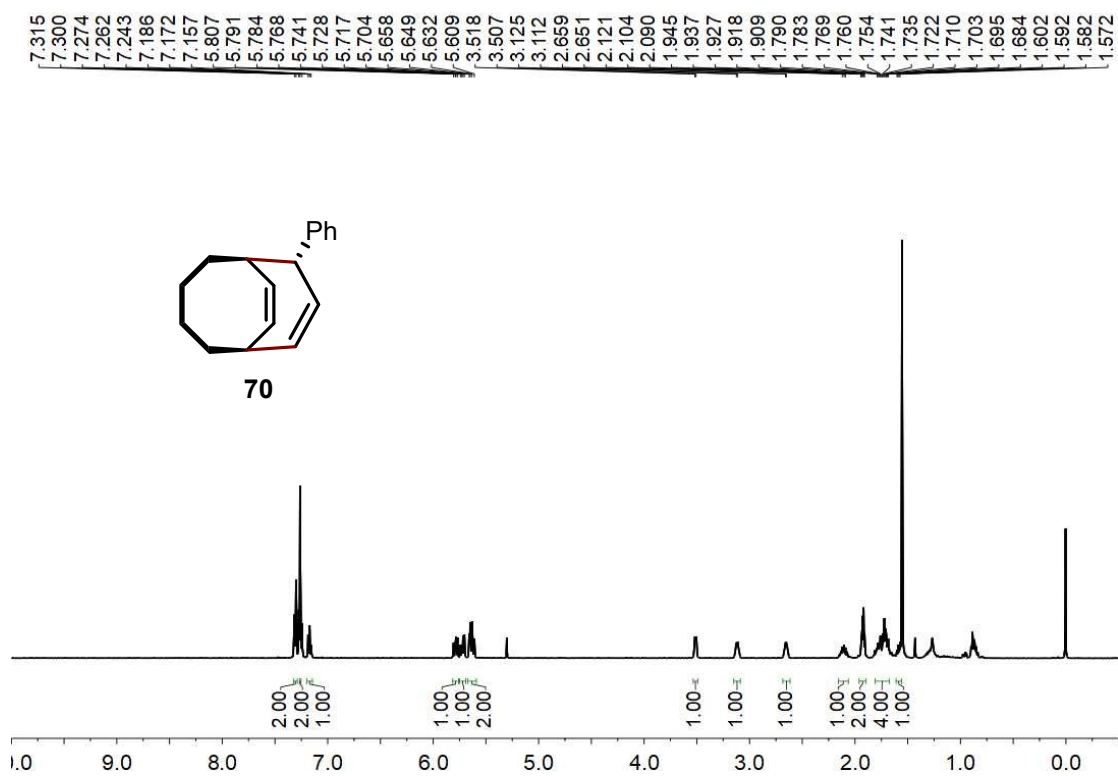


Figure S142. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **70**.

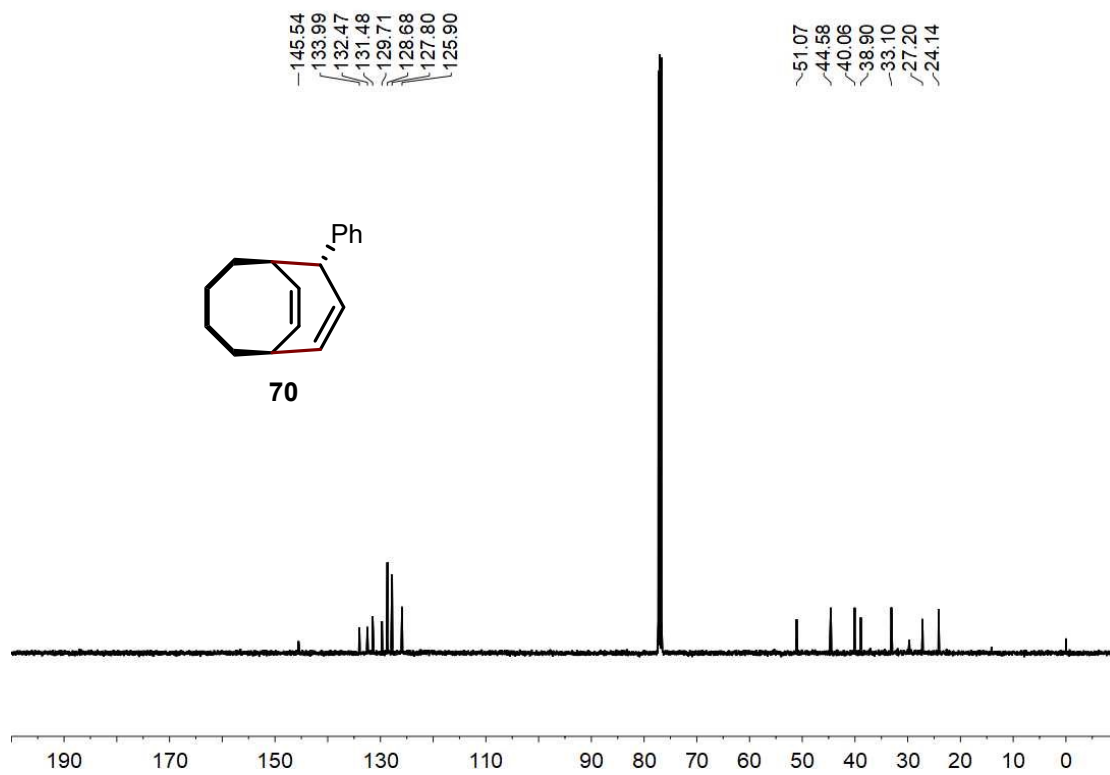


Figure S143. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **70**.

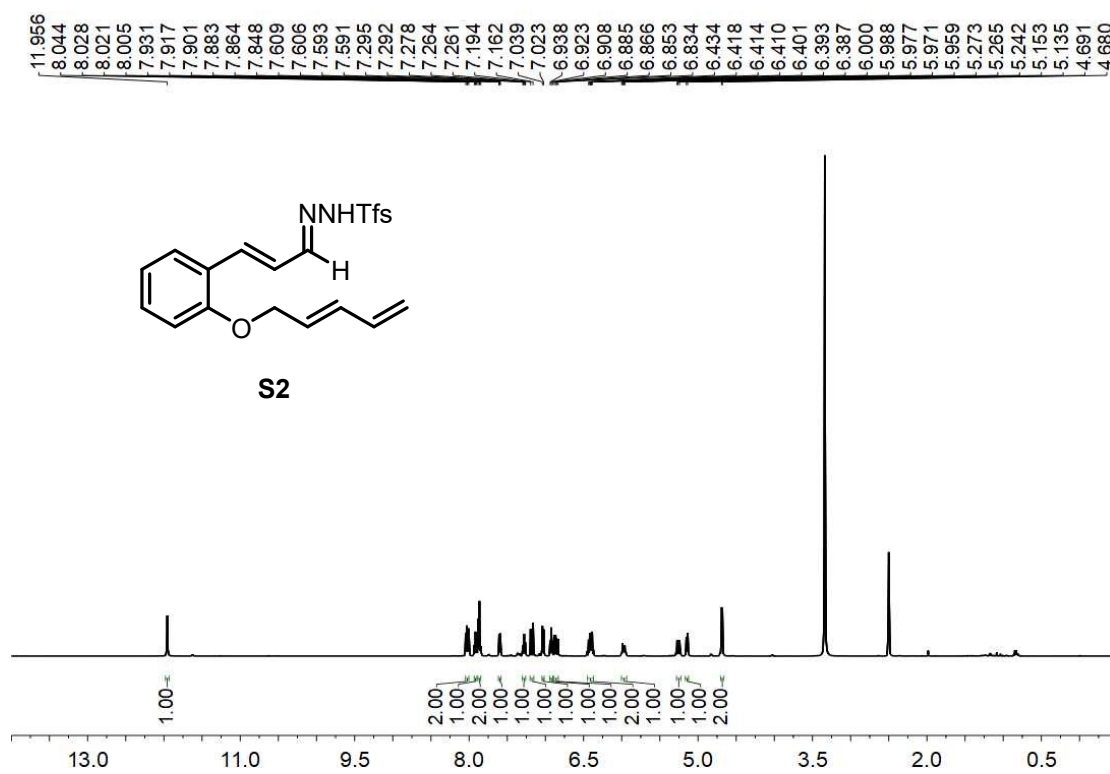


Figure S144. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) spectrum of **S2**.

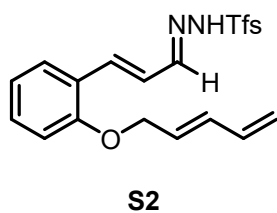
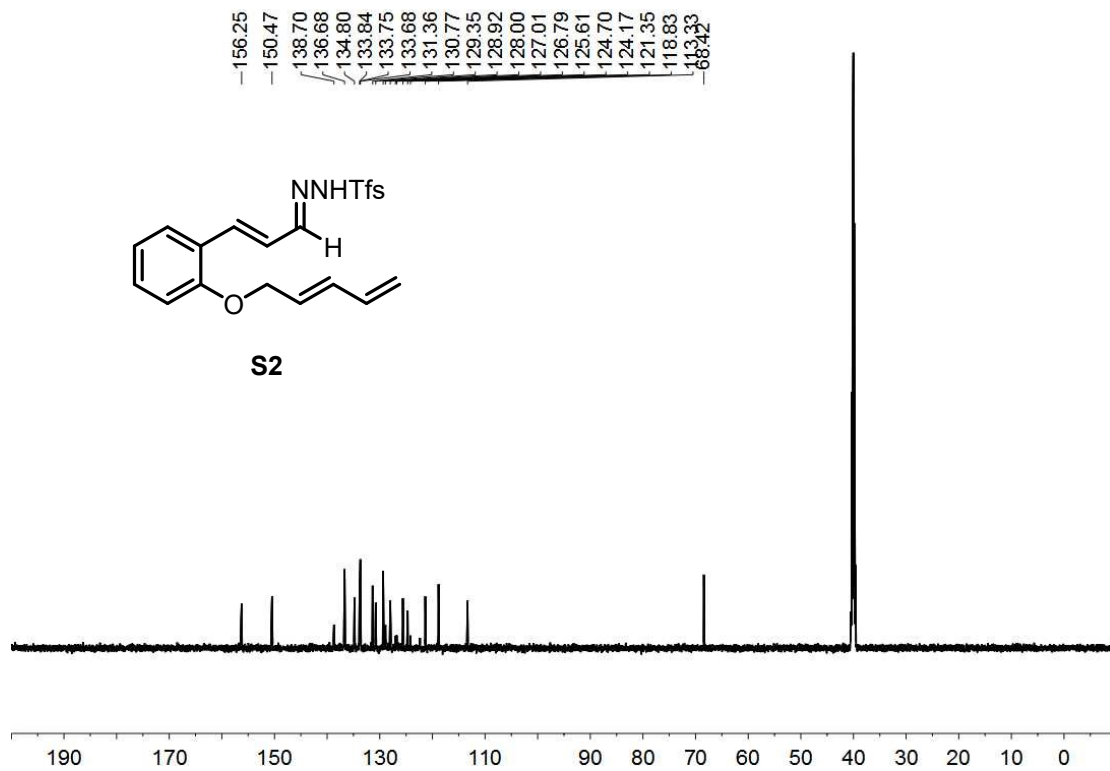


Figure S145.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectrum of S2.

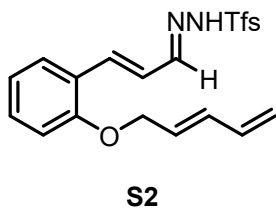
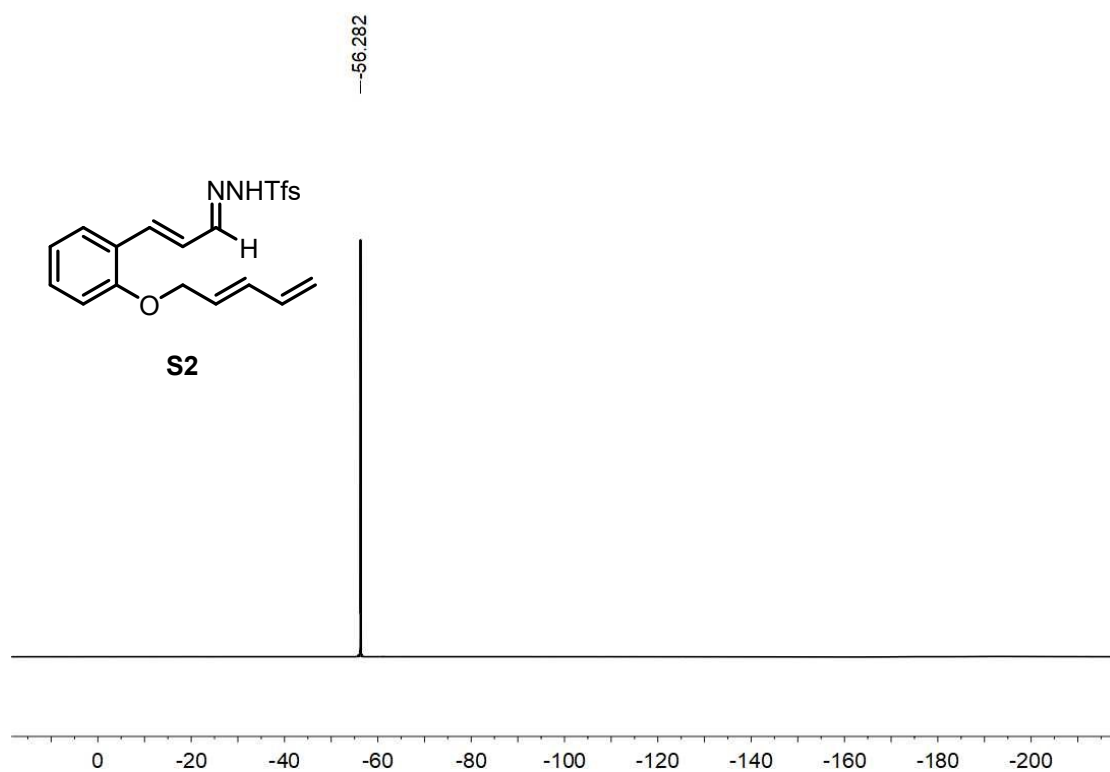


Figure S146.  $^{19}\text{F}$  NMR (565 MHz,  $\text{DMSO-}d_6$ ) spectrum of S2.



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