

# Synthesis of Benzodiquinanes *via* Tandem Palladium-Catalyzed Semipinacol Rearrangement and Direct Arylation

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## SUPPORTING INFORMATION

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## General Experimental

Reactions were conducted in flame- or oven-dried glassware under an atmosphere of argon using freshly distilled solvents unless specified otherwise. Stainless steel needles were oven-dried, cooled in a dessicator and flushed with argon prior to the handling of dry solvents and reagents. Commercial reagents were used as received. Dichloromethane (DCM) and toluene were distilled from CaH<sub>2</sub> prior to use. Tetrahydrofuran (THF) and diethyl ether (Et<sub>2</sub>O) were distilled from sodium/benzophenone.

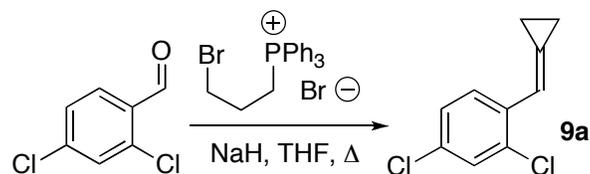
Thin-layer chromatography was performed on Merck silica gel 60 F<sub>254</sub> plates. Visualisation was carried out using UV light and KMnO<sub>4</sub>, anisaldehyde or (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> solutions. Hexanes and ethyl acetate (ACS grade) were used as received. Flash column chromatography<sup>1</sup> was carried out using Silicycle<sup>®</sup> SilaFlash<sup>®</sup> P60 silica gel (230-400 mesh, 40-63 μ, 60 Å pore size).

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker DRX-600, Bruker AV-400 or Bruker AV-300 spectrometer in chloroform-*d* (99.8 % deuterated), and using chloroform (7.28 ppm <sup>1</sup>H and 77.23 ppm <sup>13</sup>C) as a reference. Chemical shifts (δ) are reported in ppm and multiplicities are indicated by s (singlet), d (doublet), q (quartet), t (triplet), m (multiplet), br (broad). Coupling constants *J* are reported in Hertz (Hz). Infrared (IR) spectra were recorded as thin films in NaCl cells using a Mattson Genesis II FT-IR instrument or neat using a Bruker ALPHA FTIR spectrometer equipped with a ZnSe ATR crystal. Melting points were determined using a calibrated Kofler Heizmikroskop apparatus. Mass Spectrometry was conducted at the Mass Spectrometry Facility of Queen's University on either a Waters/Micromass GC-TOF instrument with an EI source or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument with and ESI source.

## Experimental Procedures

### General Procedure 1: Synthesis of Methylenecyclopropanes.

Methylenecyclopropanes were prepared using the procedure reported by Shi et al.<sup>2</sup>



**Methylenecyclopropane 9a** was prepared from 2,4-dichlorobenzaldehyde following *General Procedure 1*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:100) provided methylenecyclopropane **9a** as white crystals in 56 % unoptimized yield.

#### Data for 9a

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.77 (d, *J* = 8.5 Hz, 1 H), 7.40 (d, *J* = 2.0 Hz, 1 H), 7.22 (dd, *J* = 2.0 Hz, 8.5 Hz, 1 H),  
7.12 (d, *J* = 2.0 Hz), 1.44-1.42 (m, 2 H), 1.27-1.26 (m, 2 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 134.2, 132.8, 132.4, 129.2, 128.0, 127.74, 126.9, 3.9, 0.8

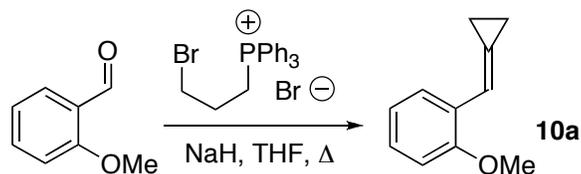
IR (thin film, NaCl)

ν = 1727, 1587, 1553, 1472, 1401, 1381, 1102, 1062, 976, 863, 827, 767 cm<sup>-1</sup>

m.p. 59-62 °C

HRMS EI

Calc'd for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub> (M<sup>+</sup>) *m/z* 198.0003, *m/z*, found 198.0011



**Methylenecyclopropane 10a** was prepared from 2-methoxybenzaldehyde following *General Procedure 1*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:90) provided methylenecyclopropane **10a** as in 40 % unoptimized yield.

Data for 10a

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.75 (d,  $J = 7.4$  Hz, 1 H), 7.20 (m, 1 H), 7.14 (s, 1 H), 6.94 (m, 1 H),

6.90 (d,  $J = 8.2$  Hz, 1 H), 3.89 (s, 3 H), 1.39 (t,  $J = 7$  Hz, 2 H), 1.17 (t,  $J = 7$  Hz, 2 H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

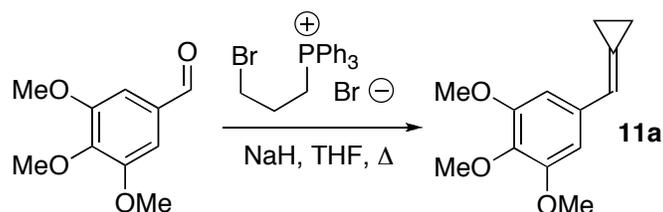
$\delta$  156.1, 127.7, 127.1, 126.6, 124.3, 120.6, 112.1, 110.8, 55.6, 3.9, 0.7

IR (thin film, NaCl)

$\nu = 2945, 2841, 1585, 1477, 1277, 1138, 1039, 727 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{11}\text{H}_{12}\text{O}$  ( $\text{M}^+$ )  $m/z$  160.0888, found 160.0891



**Methylenecyclopropane 11a** was prepared from 3,4,5-trimethoxybenzaldehyde following *General Procedure 1*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:6) provided methylenecyclopropane **11a** as in 74 % unoptimized yield.

Data for 11a

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  6.80 (s, 2 H), 6.69-6.68 (m, 1 H), 3.90 (s, 6 H), 3.87 (s, 3 H), 1.46-1.41 (m, 2 H),  
1.24-1.18 (m, 2 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

$\delta$  153.2, 137.1, 134.1, 123.7, 118.1, 103.6, 60.9, 56.0, 4.0, 0.5

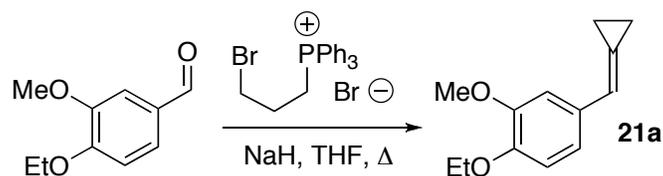
IR ATR

$\nu$  = 2999, 2959, 2936, 2834, 2349, 2322, 1575, 1508, 1410, 1348, 1326, 1237, 1126,  
1001, 841, 783, 676  $\text{cm}^{-1}$

HRMS HREI

Calc'd for  $\text{C}_{13}\text{H}_{16}\text{O}_3$  ( $\text{M}^+$ )  $m/z$  220.1106, found 220.1099

m.p. 71-75  $^\circ\text{C}$



**Methylenecyclopropane 21a** was prepared from 4-ethoxy-3-methoxybenzaldehyde following *General Procedure 1*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:90) provided methylenecyclopropane **21a** as in 52 % unoptimized yield.

Data for 21a

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.17 (s, 1 H), 7.04 (d,  $J = 8.0$  Hz, 1 H), 6.87 (d,  $J = 8.0$  Hz, 1 H),  
6.70 (t,  $J = 1.8$  Hz, 1 H), 4.13 (q,  $J = 7.0$  Hz, 2 H), 3.92 (s, 3 H),  
1.49 (t,  $J = 7.0$  Hz, 3 H), 1.42 (ddd,  $J = 8.8, 5.1, 1.8$  Hz, 2 H),  
1.19 (ddd,  $J = 8.8, 5.1, 1.8$  Hz, 2 H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  149.2, 147.3, 131.4, 121.8, 119.3, 117.8, 112.5, 109.5, 64.2, 55.7, 14.7, 3.9, 0.39

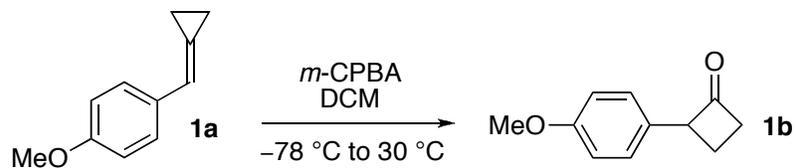
IR (thin film, NaCl)

$\nu = 2973, 2918, 2848, 1585, 1261, 1138, 1038, 802$   $\text{cm}^{-1}$

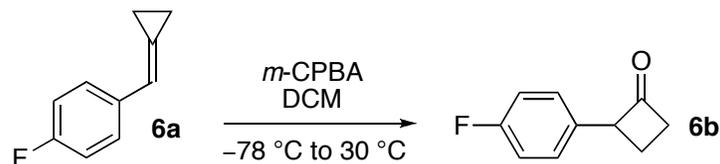
HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ )  $m/z$  204.1150, found 204.1156

m.p. 30-35  $^\circ\text{C}$

**General Procedure 2: Synthesis of  $\alpha$ -Arylcyclobutanones**

**$\alpha$ -Aryl cyclobutanone 1b.** An oven-dried 100 mL round-bottomed flask equipped with a stir bar was charged with methylenecyclopropane **1a** (0.54 g, 3.38 mmol) and 20 mL of freshly distilled dichloromethane, and the resulting solution was cooled with a dry ice/acetone bath ( $\sim -78$  °C). A solution of freshly purified<sup>3</sup> *m*-CPBA (0.58 g, 3.38 mmol, 1.0 equiv) in freshly distilled DCM (10 mL) was added dropwise over a period of five minutes. The reaction mixture was warmed to 30 °C, and the progress of the reaction was monitored by TLC. Upon completion, the reaction was worked-up by washing three times with saturated sodium bicarbonate (NaHCO<sub>3</sub>) solution, brine, dried with MgSO<sub>4</sub>, and concentrated *in vacuo*. Flash column chromatography using a solution of EtOAc in hexanes (1:7) provided cyclobutanone **1b** in 62 % unoptimized yield as a yellow oil. The spectral data of the product was consistent with that previously reported.<sup>4</sup>



Methylene cyclopropane **6a** was converted to  $\alpha$ -aryl cyclobutanone **6b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:10) provided  $\alpha$ -Aryl cyclobutanone **6b** in 59 % unoptimized yield.

Data for **6b**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.24 (dd,  $J = 8$ ,  $^4J_{\text{H-F}} = 6$  Hz, 2 H), 7.05 (dd,  $J = 8$ ,  $^3J_{\text{H-F}} = 8$  Hz, 2 H),

4.38 (dd,  $J = 8.6$ , 8.6 Hz, 1 H), 3.32-3.21 (m, 1 H), 3.05 (m, 1 H),

2.58 (dddd,  $J = 5.0$ , 10.8, 10.8, 10.8 Hz, 1 H), 2.22 (dddd,  $J = 9$  Hz, 1 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

$\delta$  207.4, 161.7 (d,  $^1J_{\text{C-F}} = 244$  Hz), 132.3 (d,  $^4J_{\text{C-F}} = 2.4$  Hz), 128.5 (d,  $^3J_{\text{C-F}} = 7.7$  Hz),

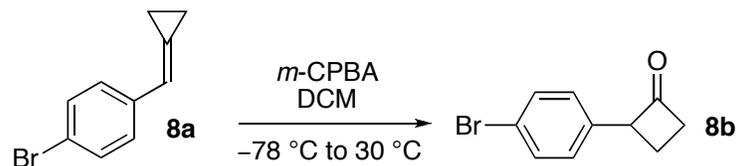
115.3 (d,  $^2J_{\text{C-F}} = 21.2$  Hz), 63.5, 44.60, 17.7

IR ATR

$\nu = 1781, 1602, 1506, 1225, 1156, 1072, 827$  cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>10</sub>H<sub>9</sub>FO (M<sup>+</sup>)  $m/z$  164.0637, found 164.0642



Methylene cyclopropane **8a** was converted to  $\alpha$ -aryl cyclobutanone **8b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:15) provided  $\alpha$ -Aryl cyclobutanone **8b** in 69 % unoptimized yield.

Data for **8b**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.47 (d,  $J$  = 8.0 Hz, 2 H), 7.15 (d,  $J$  = 8.0 Hz, 2 H), 4.51 (dd,  $J$  = 9, 9 Hz, 1 H),

3.24 (m, 1 H), 3.07 (m, 1 H), 2.56 (dddd,  $J$  = 4.5, 10.5, 10.5, 10.5 Hz, 1 H),

2.21 (dddd,  $J$  = 9, 9, 9, 9 Hz, 1 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

$\delta$  207.0, 135.4, 131.7, 128.6, 120.8, 63.7, 44.9, 17.5

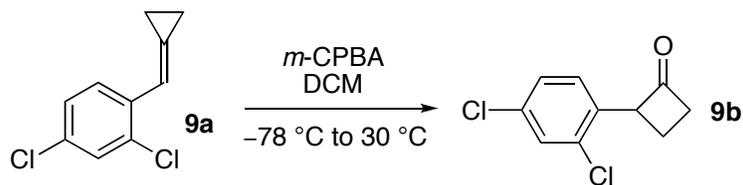
IR (thin film, NaCl)

$\nu$  = 1776, 176, 1484, 1394, 1205, 1071, 1011, 816, 726 cm<sup>-1</sup>

m.p. 34-35 °C

HRMS EI

Calc'd for C<sub>10</sub>H<sub>9</sub>BrO (M<sup>+</sup>)  $m/z$  223.9837, found 223.9841



Methylene cyclopropane **9a** was converted to  $\alpha$ -aryl cyclobutanone **9b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:12) provided  $\alpha$ -Aryl cyclobutanone **9b** in 61 % unoptimized yield.

Data for **9b**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.42 (d,  $J = 1.9$  Hz, 1 H), 7.32 (d,  $J = 8.2$  Hz, 1 H), 7.23 (dd,  $J = 1.9, 8.2$  Hz, 2 H), 4.78 (dd,  $J = 10$  Hz, 2 H), 3.26 (m, 1 H), 3.12(m, 1 H), 2.66 (dddd,  $J = 4.8, 10.8, 10.8, 10.8$  Hz, 1 H), 2.14 (dddd,  $J = 9, 9, 9, 9$  Hz, 1 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

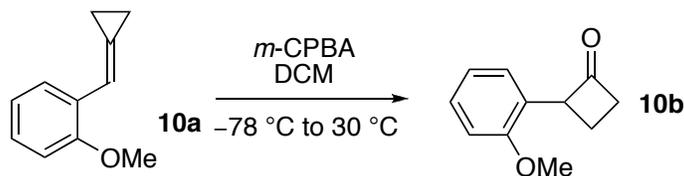
$\delta$  205.7, 133.6, 133.0, 128.9, 128.8, 126.7, 61.1, 44.5, 18.1

IR (thin film, NaCl)

$\nu = 1784, 1587, 1473, 1381, 1110, 1068, 802$  cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>O (M<sup>+</sup>)  $m/z$  213.9952, found 213.9959



Methylene cyclopropane **10a** was converted to  **$\alpha$ -aryl cyclobutanone 10b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:15) provided  $\alpha$ -Aryl cyclobutanone **10b** in 61 % unoptimized yield.

Data for 10b

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.26 (dd,  $J = 1.5, 7.4$ , 1 H), 7.15 (dd,  $J = 1.4, 7.4$  Hz, 1 H),

6.94-6.88 (m, 2 H), 4.52 (dd,  $J = 9, 9$  Hz, 1 H), 3.83 (s, 3 H), 3.16 (t,  $J = 8.5$  Hz, 2 H),

2.49-2.40 (m, 1 H), 2.28-2.19 (m, 1 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  209.1, 157.2, 129.1, 128.5, 126.0, 120.6, 110.8, 61.6, 55.3, 44.7, 18.1

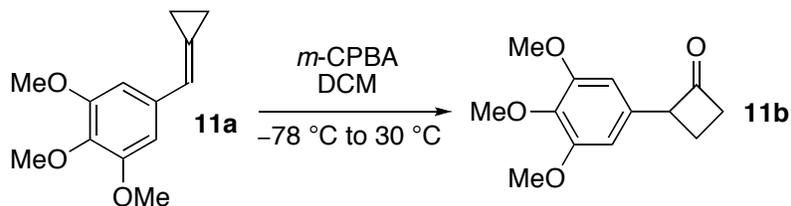
IR (thin film, NaCl)

$\nu = 2958, 1777, 1597, 1492, 1261, 1236, 1179, 1119, 1074, 1017 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{11}\text{H}_{12}\text{O}_2$  ( $\text{M}^+$ )  $m/z$  176.0837, found 176.0842

m.p. 34-35 °C



Methylene cyclopropane **11a** was converted to  $\alpha$ -aryl cyclobutanone **11b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:3) provided  $\alpha$ -Aryl cyclobutanone **11b** in 62 % unoptimized yield.

Data for **11b**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

$\delta$  6.49 (s, 2 H), 4.51 (m, 1 H), 3.88 (s, 6 H), 3.84 (s, 3 H), 3.30-3.20 (m, 1 H),  
3.10-3.01 (m, 1 H), 2.61-2.52 (m, 1 H) 2.28-2.19 (m, 1 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

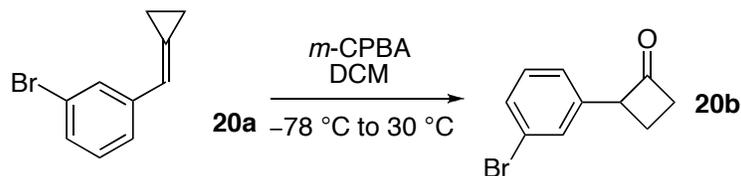
$\delta$  207.7, 153.2, 136.9, 132.0, 103.8, 64.3, 60.7, 56.0, 44.6, 17.8

IR (thin film, NaCl)

$\nu$  = 2995, 2962, 2939, 2839, 1778, 1587, 1508, 1460, 1419, 1344, 1242, 1128, 1076,  
1007, 835  $\text{cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{16}\text{O}_4$  ( $\text{M}^+$ )  $m/z$  236.1049, found 236.1057



Methylene cyclopropane **20a** was converted to  **$\alpha$ -aryl cyclobutanone 20b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:10) provided  $\alpha$ -Aryl cyclobutanone **20b** in 46 % unoptimized yield.

Data for 20b

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.40 (m, 2 H), 7.23 (m, 2 H), 4.54 (m, 1 H), 3.28 (m, 1 H), 3.07 (m, 1 H),

2.57 (dddd,  $J = 5.2, 10.8, 10.8, 10.8$  Hz, 1 H), 2.25 (m, 1 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

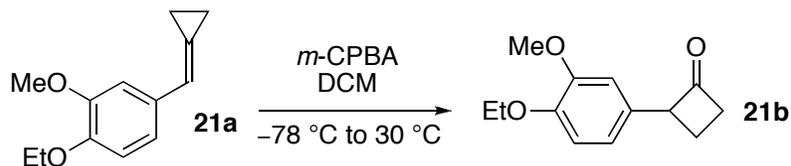
$\delta$  207.0, 135.4, 131.7, 128.6, 120.8, 63.7, 44.9, 17.5

IR ATR

$\nu = 1776, 1762, 1484, 1394, 1205, 1071, 1011, 816, 726$   $\text{cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{10}\text{H}_9\text{BrO}$  ( $\text{M}^+$ )  $m/z$  223.9837, found 223.9841



Methylene cyclopropane **21a** was converted to  $\alpha$ -aryl cyclobutanone **21b** using *General Procedure 2*. Purification using flash column chromatography using a solution of EtOAc in hexanes (1:10) provided  $\alpha$ -Aryl cyclobutanone **21b** in 76 % unoptimized yield.

Data for **21b**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  6.85 (d,  $J = 8.0$  Hz, 1 H), 6.80 (s, 1 H), 6.78 (d,  $J = 8.0$  Hz, 1 H), 4.53-4.48 (m, 1 H),  
4.10 (q,  $J = 7$  Hz, 2 H), 3.90 (s, 1H), 3.29-3.19 (m, 1 H),  
3.05 (dddd,  $J = 2.8, 5.0, 10.0, 17.2$  Hz, 1 H), 2.55 (dddd,  $J = 5, 11, 11, 11$  Hz, 1 H),  
2.27-2.17 (m, 1 H), 1.47 (t,  $J = 7$  Hz, 3 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  207.8, 149.1, 147.1, 129.1, 118.8, 112.7, 110.6, 64.1, 63.9, 55.6, 44.4, 17.8, 14.6

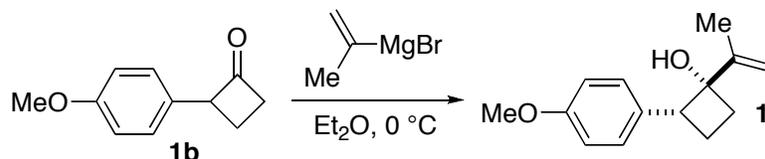
IR (thin film, NaCl)

$\nu = 2976, 2922, 1778, 1587, 1514, 1466, 1416, 1257, 1142, 1072, 1036, 802\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{16}\text{O}_3$  ( $\text{M}^+$ )  $m/z$  220.1099, found 220.1103

m.p. 36-39  $^{\circ}\text{C}$

**General Procedure 3: Synthesis of  $\alpha$ -aryl-tert-isopropenylcyclobutanols**

A dry 20 ml round-bottomed flask equipped with stir bar and a rubber septum was charged with 100 mg (0.57 mmol, 1 equiv.) of cyclobutanone **1b** and 5 ml of diethyl ether and placed under a positive pressure of argon. The solution was cooled to  $0\text{ }^\circ\text{C}$  using an ice bath. Isopropenylmagnesium bromide (0.5 M in THF, 2.27 ml, 1.14 mmol, 2 equiv.) was added dropwise over a period of 10 minutes. After the addition was complete, the ice bath was removed and the reaction was allowed to warm to room temperature. Upon completion the reaction was quenched with  $\text{NH}_4\text{Cl}$  and extracted exhaustively with EtOAc. The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. Flash column chromatography using a solution of EtOAc in hexanes (1:5) provided alcohol **1** in 64 % unoptimized yield as a colourless oil.

**Data for 1** **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.23 (d,  $J = 8.7$  Hz, 2 H), 6.91 (d,  $J = 8.7$  Hz, 2 H), 5.03 (s, 1 H), 4.89 (s, 1 H),  
3.82 (s, 3 H), 3.76 (dd,  $J = 8.7, 8.7$  Hz, 1 H), 2.45 (m, 1 H), 2.34 (m, 1 H), 2.13 (m, 1 H),  
1.85 (s, 3 H)

 **$^{13}\text{C NMR}$**  (75 MHz,  $\text{CDCl}_3$ )

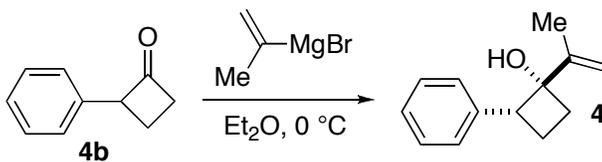
$\delta$  158.4, 148.9, 130.6, 129.5, 113.9, 109.8, 80.6, 55.2, 46.7, 30.9, 20.9, 18.5

**IR** (thin film, NaCl)

$\nu = 3529, 3460, 3082, 2985, 2947, 2835, 1610, 1512, 1456, 1250, 1178, 1124, 1037,$   
 $895, 829\text{ cm}^{-1}$

**HRMS** EI

Calc'd for  $\text{C}_{14}\text{H}_{18}\text{O}_2$  ( $\text{M}^+$ ) 218.1307, found 218.1316



**tert-Cyclobutanol 4** was prepared from ketone **4b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:15) provided alcohol **4** in 69 % unoptimized yield.

Data for 4

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.40-7.26 (m, 5 H), 5.07 (s, 1 H), 4.91 (s, 1 H), 3.84 (dd  $J = 8.8, 8.8$  Hz, 1 H),  
2.55-2.46 (m, 1 H), 2.40-2.33 (m, 1 H), 2.19-2.12 (m, 1 H), 2.04-1.98 (m, 1 H),  
1.87 (s, 3 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

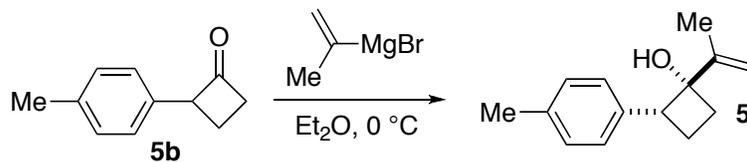
$\delta$  148.8, 138.6, 128.4, 128.3, 126.7, 109.9, 80.7, 47.2, 31.0, 20.5, 18.4

IR (thin film, NaCl)

$\nu = 3541, 3438, 3084, 3060, 3026, 2985, 2949, 2864, 1782, 1496, 1452, 1122, 897,$   
 $702\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{16}\text{O}$  ( $\text{M}^+$ )  $m/z$  188.1201, found 188.1194



**tert-Cyclobutanol 5** was prepared from ketone **5b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided alcohol **5** in 52 % unoptimized yield.

Data for 5

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.18-7.16 (m, 4 H), 5.04 (s, 1 H), 4.89 (t,  $J = 1$  Hz, 1 H),

3.79 (dd,  $J = 9, 9$  Hz, 1 H), 2.53-2.30 (m, 2 H), 2.36 (s, 3 H), 2.17-2.07 (m, 1 H),

2.02-1.95 (m, 1 H), 1.85 (s, 3 H), 1.46 (d,  $J = 1$  Hz, 1 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

$\delta$  149.0, 136.3, 135.6, 129.2, 128.4, 109.9, 80.7, 47.1, 31.0, 21.1, 20.7, 18.5

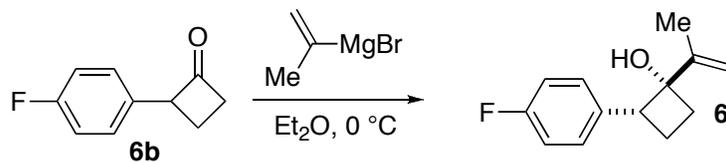
IR (thin film, NaCl)

$\nu = 3556, 3529, 3435, 3084, 2985, 2947, 2920, 2866, 1898, 1786, 1736, 1645, 1514,$

$1450, 1373, 1234, 1194, 1124, 895, 818 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{14}\text{H}_{18}\text{O}$  ( $\text{M}^+$ )  $m/z$  202.1353, found 202.1353



**tert-Cyclobutanol 6** was prepared from ketone **6b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided alcohol **6** in 51 % unoptimized yield.

Data for 6

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.26 (dd,  $J = 8.5$ ,  $^4J_{\text{H-F}} 5.4$  Hz, 2 H), 7.05 (dd,  $J = 8.5$ ,  $^3J_{\text{H-F}} 8.5$  Hz, 2 H), 5.03 (s, 1 H),  
4.90 (t,  $J = 1.2$  Hz, 1 H), 3.78 (dd,  $J = 8.5$ , 8.5 Hz, 1 H), 2.51-2.30 (m, 2 H),  
2.20-2.10 (m, 1 H), 2.02-1.94 (m, 1 H), 1.84 (s, 3 H); δ 1.43 (s, 1 H)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 161.8 (d,  $^1J_{\text{C-F}} = 243$  Hz), 148.8, 134.5 (d,  $^4J_{\text{C-F}} = 3$  Hz), 129.9 (d,  $^3J_{\text{C-F}} = 8.25$  Hz),  
115.2 ( $^2J_{\text{C-F}} = 21$  Hz), 110.0, 80.8, 46.5, 31.0, 21.1, 18.5

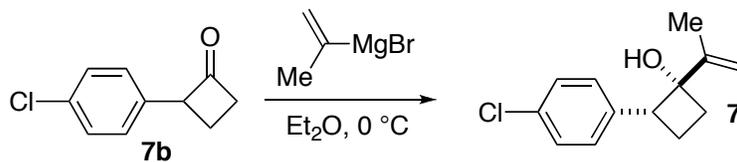
IR (thin film, NaCl)

$\nu = 3560, 3438, 3084, 3039, 2980, 2949, 2872, 1603, 1510, 1452, 1225, 1159, 1120,$   
899, 833, 816 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>13</sub>H<sub>15</sub>FO (M<sup>+</sup>)  $m/z$  206.1107, found 206.1101

m.p. 50-55 °C



**tert-Cyclobutanol 7** was prepared from ketone **7b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided alcohol **7** in 38 % unoptimized yield.

Data for 7

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.33 (d,  $J = 8.4$  Hz, 2 H), 7.23 (d,  $J = 8.4$  Hz, 2 H), 5.02 (s, 1 H), 4.90 (s, 1 H),

3.78 (dd,  $J = 8.5, 8.5$  Hz, 1 H), 2.52-2.31 (m, 2 H), 2.20-2.11 (m, 1 H),

2.05-1.95 (m, 1 H), 1.84 (s, 3 H), 1.36 (s, 1 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

$\delta$  148.7, 137.4, 132.5, 129.8, 128.5, 110.1, 80.9, 46.7, 31.0, 20.9, 18.5

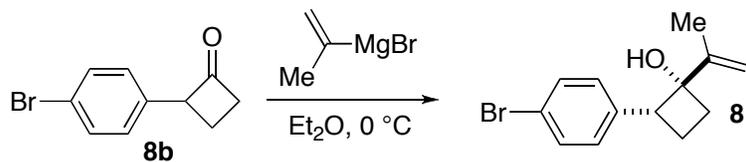
IR ATR

$\nu = 3377, 3083, 2990, 2963, 2945, 1490, 1121, 1085, 1014, 903, 832 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{15}\text{ClO}$  ( $\text{M}^+$ )  $m/z$  222.0812, found 222.0816

m.p. 49-52 °C



**tert-Cyclobutanol 8** was prepared from ketone **8b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:25) provided alcohol **8** in 43 % unoptimized yield.

Data for 8

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.48 (d,  $J = 8.6$  Hz, 2 H), 7.18 (d,  $J = 8.6$  Hz, 2 H), 5.02 (s, 1 H), 4.90 (s, 1 H),  
3.76 (dd,  $J = 9, 9$  Hz, 1 H), 2.49-2.32 (m, 2 H), 2.18-2.11 (m, 1 H), 2.01-1.95 (m, 1 H),  
1.84 (s, 3 H), 1.35 (s, 1 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

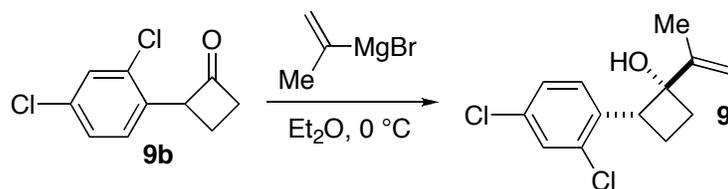
$\delta$  148.6, 137.8, 131.3, 130.1, 120.5, 110.1, 80.8, 46.6, 30.9, 20.8, 18.4

IR ATR

$\nu = 1777, 1763, 1486, 1394, 1205, 1071, 1035, 1011, 898, 816, 726\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{15}\text{BrO}$  ( $\text{M}^+$ )  $m/z$  266.0306, found 266.0311



**tert-Cyclobutanol 9** was prepared from ketone **9b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided alcohol **9** in 54 % unoptimized yield.

Data for 9

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.58 (d,  $J = 8.4$  Hz, 1 H), 7.39 (d,  $J = 2.1$ , 1 H), 7.30 (dd,  $J = 8.4, 2.1$ , 1 H), 5.06 (s, 1 H), 4.88 (s, 1 H), 4.20 (dd,  $J = 8.7, 8.7$  Hz, 1 H), 2.50-2.33 (m, 2 H), 2.22-2.10 (m, 1 H), 2.02-1.93 (m, 1 H), 1.89 (s, 3 H), 1.41 (s, 1 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

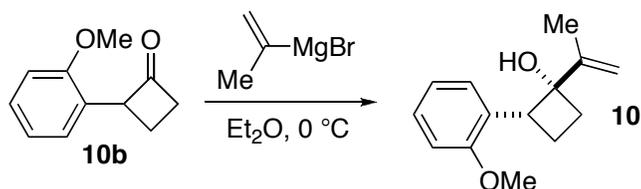
$\delta$  148.2, 135.2, 135.0, 132.8, 131.2, 129.1, 126.8, 110.1, 81.4, 43.7, 31.0, 21.4, 18.5

IR (thin film, NaCl)

$\nu = 3558, 3444, 3087, 2989, 2951, 2866, 1786, 1726, 1643, 1587, 1556, 81473, 1452, 1383, 1111, 1072, 1049, 901, 804\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{O}$  ( $\text{M}^+$ )  $m/z$  256.0422, found 256.0426



**tert-Cyclobutanol 10** was prepared from ketone **10b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided alcohol **10** in 57 % yield.

Data for 10

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.42 (dd,  $J = 8, 1$  Hz, 1 H), 7.24 (dd,  $J = 8, 1$  Hz, 1 H), 7.02 (dd,  $J = 8, 8$  Hz, 1 H), 6.88 (d,  $J = 8$  Hz, 1 H), 5.07 (s, 1 H), 4.82 (s, 1 H), 4.18 (dd,  $J = 9, 9$  Hz, 1 H), 3.79 (s, 3 H), 2.53-2.35 (m, 2 H), 2.12-1.94 (m, 2 H), 1.89 (s, 3 H), 1.69 (s, 1 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

$\delta$  157.5, 149.2, 129.4, 127.8, 127.1, 120.6, 110.3, 108.9, 81.1, 55.0, 41.6, 31.1, 20.1, 18.5

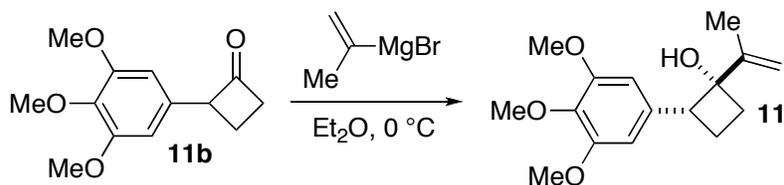
IR ATR

$\nu = 3377, 2981, 2941, 1650, 1593, 1486, 1450, 1241, 1121, 1090, 898, 823, 747\text{ cm}^{-1}$

HRMS ESI

Calc'd for  $\text{C}_{13}\text{H}_{18}\text{O}_2$  ( $\text{M}^+$ )  $m/z$  241.1204, found 241.1208

m.p. 27-29  $^\circ\text{C}$



**tert-Cyclobutanol 11** was prepared from ketone **11b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:4) provided alcohol **11** in 58 % unoptimized yield.

Data for 11

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  6.50 (s, 2 H), 5.07 (s, 1 H), 4.92 (s, 1 H), 3.88 (s, 6 H), 3.86 (s, 3 H),  
3.77 (dd,  $J = 8.8, 8.8$ , 1 H), 2.50-2.31 (m, 2 H), 2.19-2.12 (m, 1 H), 2.02-1.96 (m, 1 H),  
1.87 (s, 3 H), 1.57 (s, 1 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  153.2, 148.8, 136.7, 134.4, 109.9, 105.1, 80.7, 60.7, 56.0, 47.4, 30.7, 20.9, 18.6

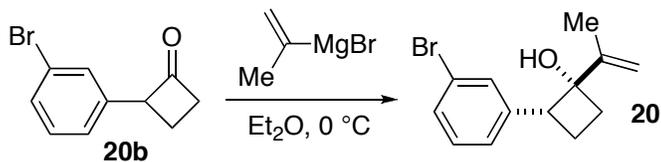
IR ATR

$\nu = 3475, 1591, 1508, 1460, 1238, 1131, 822\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{16}\text{H}_{22}\text{O}_4$  ( $\text{M}^+$ )  $m/z$  278.1518, found 278.1513

m.p. 55-58  $^\circ\text{C}$



**tert-Cyclobutanol 20** was prepared from ketone **20b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:16) provided alcohol **20** in 48 % yield.

Data for 20

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.45 (s, 1 H), 7.35 (m, 1 H), 7.23 (m, 2 H), 5.04 (s, 1 H), 4.92 (s, 1 H),

3.79 (dd,  $J = 8$  Hz, 1 H), 2.51-2.32 (m, 2 H), 2.18-2.12 (m, 1 H), 2.03-1.97 (m, 1 H),

1.85 (s, 3 H), 1.40 (s, 1 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

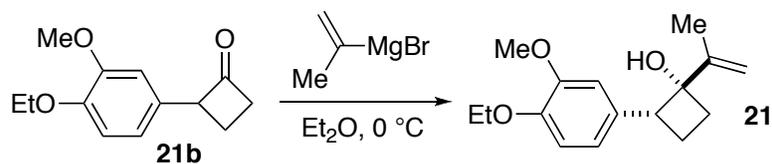
$\delta$  148.5, 141.4, 131.4, 129.8, 129.7, 127.0, 122.6, 110.2, 81.0, 46.7, 31.0, 20.8, 18.4

IR (thin film, NaCl)

$\nu = 2985, 2947, 1593, 1562, 1475, 1450, 1236, 1196, 1120, 1072, 897, 785\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{15}\text{BrO}$  ( $\text{M}^+$ )  $m/z$  266.0306, found 266.0311



**tert-Cyclobutanol 21** was prepared from ketone **21b** using *General Procedure 3*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:3) provided alcohol **21** in 56 % yield.

Data for 21

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  6.86 (d,  $J = 8$  Hz, 1 H), 6.80 (m, 2 H), 5.05 (s, 1 H), 4.90 (s, 1 H),  
4.11 (q,  $J = 7$  Hz, 2 H), 3.90 (s, 3 H), 3.76 (dd,  $J = 9, 9$  Hz, 1 H),  
2.49-2.31 (m, 2 H), 2.17-2.10 (m, 1 H), 2.01-1.95 (m, 1 H), 1.57 (s, 3 H),  
1.53 (s, 1 H), 1.48 (t,  $J = 7$  Hz, 3 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  149.1, 148.9, 147.1, 131.0, 120.3, 112.6, 111.8, 109.7, 80.5, 64.2, 55.8, 47.0, 30.7,  
20.8, 18.5, 14.7

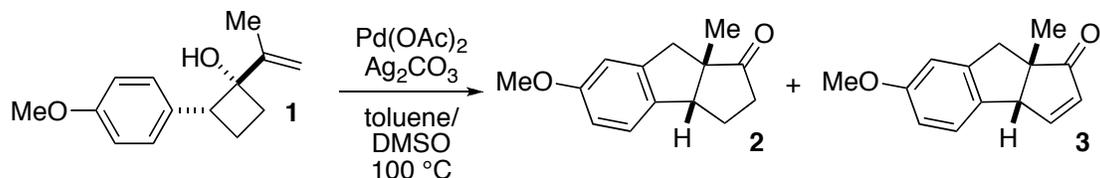
IR ATR

$\nu = 3493, 1518, 1463, 1267, 1234, 1037, 904, 813, 784\text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{16}\text{H}_{22}\text{O}_3$  ( $\text{M}^+$ )  $m/z$  285.1466, found 285.1463

m.p. 63-66  $^\circ\text{C}$

**General Procedure 4: Synthesis of Benzodiquinanes**

An oven-dried 25 mL test tube equipped with a stir bar was charged with  $\alpha$ -aryl-*tert*-isopropenyl cyclobutanol **1** (30 mg, 0.14 mmol), silver carbonate ( $\text{Ag}_2\text{CO}_3$ , 76 mg, 0.28 mmol, 2.0 equiv) and palladium acetate ( $\text{Pd}(\text{OAc})_2$ , 3.1 mg, 0.014 mmol, 0.1 equiv.). The reaction vessel was sealed with a rubber septum, an atmosphere of argon was introduced, and 950  $\mu\text{L}$  of freshly distilled toluene and 50  $\mu\text{L}$  of anhydrous DMSO were added via a syringe. The reaction vessel was placed in a hot oil bath ( $100\text{ }^\circ\text{C}$ ) and the progress of the reaction was monitored by TLC analysis. Upon completion ( $\sim 1$  h), the reaction mixture was filtered through a pad of silica gel and eluted using EtOAc. The filtrate was washed with water and brine, dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. Flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **2** in 58 % yield. Extended reaction times led to oxidation of benzodiquinane **2** to unsaturated benzodiquinane **3**.

**Data for 2** **$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )

$\delta$  7.15 (d,  $J = 8.4$  Hz, 1 H), 6.79 (dd,  $J = 8.4, 1.8$  Hz, 1 H), 6.69 (d,  $J = 1.8$  Hz, 1 H),  
3.79 (s, 3 H), 3.53 (br d,  $J = 6.6$  Hz, 1 H), 3.23 (d,  $J = 16.2$  Hz, 1 H),  
2.86 (d,  $J = 16.2$  Hz, 1 H), 2.36 (m, 1 H), 2.30 (m, 1 H), 2.22 (m, 1 H), 2.03 (m, 1 H),  
1.29 (s, 3 H)

 **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )

$\delta$  224.6, 159.3, 143.7, 136.5, 124.2, 113.3, 109.3, 56.7, 55.3, 52.8, 43.2, 36.0, 24.6, 20.4

**IR** (thin film, NaCl)

$\nu = 2963, 2927, 2846, 1736, 1608, 1491, 1460, 1259\text{ cm}^{-1}$

**HRMS** EI

Calc'd for  $\text{C}_{14}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ )  $m/z$  216.1150, found 216.1151

**m.p.** 35 – 40  $^\circ\text{C}$

Data for **3**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.75 (dd,  $J = 5.7, 3.0$  Hz, 1 H), 7.20 (d,  $J = 8.4$  Hz, 1 H),

6.79 (dd,  $J = 8.4, 2.4$  Hz, 1 H), 6.70 (d,  $J = 2.4$  Hz, 1 H),

6.07 (dd,  $J = 5.7, 1.8$  Hz, 1 H), 4.06 (dd,  $J = 1.8, 3.0$  Hz, 1 H),

3.79 (s, 3H), 3.22 (d,  $J = 17.5$ , 1 H), 2.89 (d,  $J = 17.5$ , 1 H), 1.41 (s, 3 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 214.0, 164.6, 159.7, 142.9, 132.9, 130.9, 124.9, 113.5, 110.1, 60.8, 55.3, 53.5, 41.8,

22.6

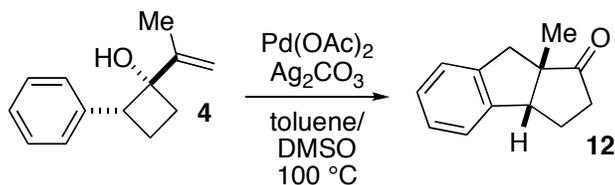
IR (thin film, NaCl)

$\nu = 2958, 2926, 2852, 2252, 1707, 1609, 1493, 1255, 910, 733$  cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> (M<sup>+</sup>)  $m/z$  214.0994, found 214.1002

m.p. 47-50 °C



**Benzodiquinane 12** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **12** in 48 % yield.

Data for 12

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.36-7.14 (m, 4 H), 3.59 (br d,  $J = 5.6$  Hz, 1 H), 3.27 (d,  $J = 16.4$  Hz, 1 H),

2.88 (d,  $J = 16.4$  Hz, 1 H), 2.42-2.24 (m, 3 H), 2.07-1.96 (m, 1 H), 1.31 (s, 3 H)

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )

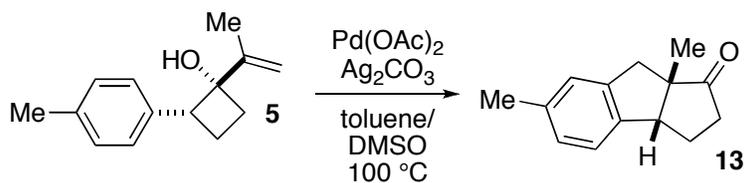
$\delta$  224.6, 144.7, 142.3, 127.2, 127.0, 124.4, 123.8, 56.3, 53.8, 43.3, 36.4, 24.8, 20.7

IR (thin film, NaCl)

$\nu = 3068, 3022, 2956, 2926, 2848, 1736, 1460, 1404, 1134, 1061, 779, 742 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{14}\text{O} (\text{M}^+)$   $m/z$  186.1045, found 186.1038



**Benzodiquinane 13** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:8) provided benzodiquinane **13** in 66 % yield.

Data for 13

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.15 (d, *J* = 8 Hz, 1 H), δ 7.04 (d, *J* = 8 Hz, 1 H), δ 6.97 (s, 1 H),  
δ 3.54 (br d, *J* = 5.7 Hz, 1 H), δ 3.23 (d, *J* = 16.5 Hz, 1 H),  
δ 2.85 (d, *J* = 16.5 Hz, 1 H), δ 2.41-2.19 (m, 3 H), δ 2.33 (s, 3 H),  
δ 2.12-1.95 (m, 1 H), δ 1.29 (s, 3 H)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

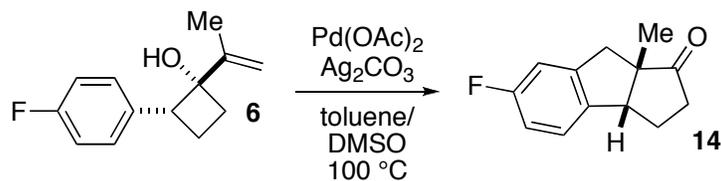
δ 224.8, 142.4, 141.7, 136.9, 127.8, 125.0, 123.4, 56.4, 53.4, 43.1, 36.3, 24.7, 21.2, 20.6

IR (thin film, NaCl)

ν = 3005, 2954, 2924, 1738, 1493, 1460, 1261, 1119, 1061, 812 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>14</sub>H<sub>16</sub>O (M<sup>+</sup>) *m/z* 200.1201, found 200.1203



**Benzodiquinane 14** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **14** in 45 % yield.

Data for 14

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.18 (dd,  $J = 8.1$ ,  $^4J_{\text{H-F}} = 5.1$  Hz, 1 H), 6.91 (ddd,  $J = 8.7$ , 2.1,  $^3J_{\text{H-F}} = 8.7$  Hz, 1 H),  
 6.83 (br d,  $J = 9$  Hz, 1 H), 3.53 (br d,  $J = 5.7$  Hz, 1 H), 3.24 (d,  $J = 16.5$  Hz, 1 H),  
 2.85 (d,  $J = 16.5$  Hz, 1 H), 2.43-2.18 (m, 3 H), 2.06-1.93 (m, 1 H), 1.29 (s, 3 H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  224.0, 162.4 (d,  $^1J_{\text{C-F}} = 243$  Hz), 144.3 (d,  $^3J_{\text{C-F}} = 8$  Hz), 140.0, 124.6 (d,  $^3J_{\text{C-F}} = 9$  Hz),  
 113.9 (d,  $^2J_{\text{C-F}} = 22$  Hz), 111.3 (d,  $^2J_{\text{C-F}} = 22$  Hz), 56.7, 52.8, 42.9, 36.0, 24.6, 20.4

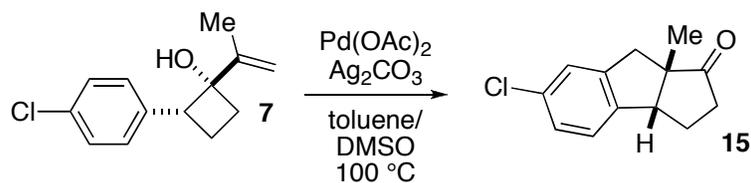
IR (thin film, NaCl)

$\nu = 2958, 2927, 2900, 1738, 1612, 15967, 1485, 1248, 1128, 1061, 812 \text{ cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{13}\text{H}_{13}\text{FO}$  ( $\text{M}^+$ )  $m/z$  204.0950, found 204.0946

m.p. 31-35 °C



**Benzodiquinane 15** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **15** in 48 % yield.

Data for 15

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.21-7.15 (m, 2 H), 7.12 (s, 1 H), 3.53 (br d, *J* = 6 Hz, 1 H), 3.24 (d, *J* = 17 Hz, 1 H),  
2.85 (d, *J* = 17 Hz, 1 H), 2.43-2.18 (m, 3 H), 2.10-1.92 (m, 1 H), 1.29 (s, 3 H)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 223.8, 144.2, 143.2, 133.0, 127.2, 124.8, 124.6, 56.5, 53.1, 42.8, 36.1, 24.6, 20.5

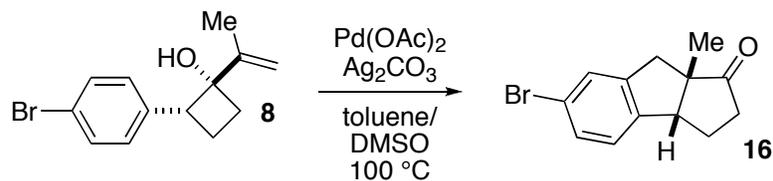
IR (thin film, NaCl)

$\nu$  = 3055, 2962, 1736, 1601, 1471, 1265, 1063, 739, 706 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>13</sub>H<sub>13</sub>ClO (M<sup>+</sup>) *m/z* 220.0655, found 220.0652

m.p. 35-38 °C



**Benzodiquinane 16** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:40) provided benzodiquinane **16** in 24 % yield.

Data for 16

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.34 (d, *J* = 8 Hz, 1 H), 7.28 (s, 1 H), 7.11 (d, *J* = 8 Hz, 1 H), 3.51 (d, *J* = 6 Hz, 1 H),  
3.24 (d, *J* = 16 Hz, 1 H), 2.85 (d, *J* = 16 Hz, 1 H), 2.42-2.18 (m, 3 H),  
2.06-1.93 (m, 1 H), 1.30 (s, 3 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

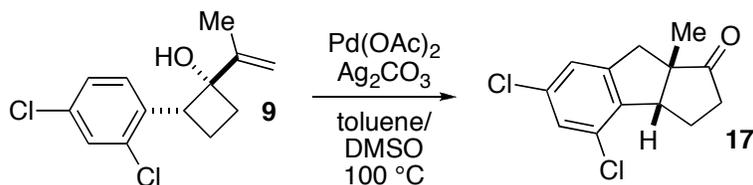
δ 223.7, 144.5, 143.7, 130.1, 127.6, 125.3, 121.0, 56.4, 53.2, 42.8, 36.1, 24.6, 20.5

IR (thin film, NaCl)

ν = 2954, 2924, 1738, 1470, 1406, 1124, 1061, 756 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>13</sub>H<sub>13</sub>BrO (M<sup>+</sup>) *m/z* 264.0150, found 264.0156



**Benzodiquinane 17** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **17** in 56 % yield.

Data for 17

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.22 (s, 1 H), 7.05 (s, 1 H), 3.65 (dd,  $J = 6.0, 5.7$  Hz, 1 H), 3.26 (d,  $J = 17$  Hz, 1 H),  
2.82 (d,  $J = 17$  Hz, 1 H), 2.51-2.30 (m, 3 H), 2.25-2.14 (m, 1 H), 1.30 (s, 3 H)

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

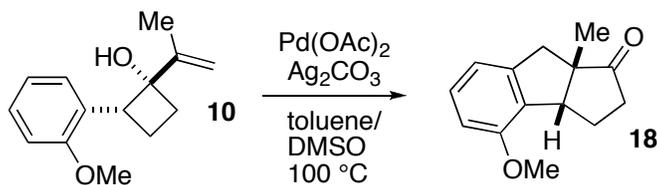
$\delta$  222.5, 145.1, 140.9, 133.7, 131.4, 127.5, 123.5, 55.6, 53.9, 43.2, 37.1, 23.9, 21.7

IR (thin film, NaCl)

$\nu = 3078, 2960, 2926, 1738, 1595, 1566, 1450, 1406, 1259, 1149, 1119, 1080, 849\text{ cm}^{-1}$

HRMS ESI

Calc'd for  $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{O}$  ( $\text{M}^+$ )  $m/z$  255.0343, found 255.0333



**Benzodiquinane 18** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:20) provided benzodiquinane **18** in 53 % yield.

Data for 18

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )

$\delta$  7.17 (dd,  $J = 8, 8$  Hz, 1 H), 6.76 (d,  $J = 8$  Hz, 1 H), 6.71 (d,  $J = 8$  Hz, 1 H),  
 3.86 (s, 1 H), 3.67 (dd,  $J = 6.2, 2.7$  Hz, 1 H), 3.25 (d,  $J = 16.5$  Hz, 1 H),  
 2.83 (d,  $J = 16.5$  Hz, 1 H), 2.55-2.45 (m, 1 H), 2.55-2.45 (m, 1 H), 2.42-2.33 (m, 1 H),  
 2.31-2.17 (m, 1 H), 2.17-2.06 (m, 1 H), 1.30 (s, 3 H)

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )

$\delta$  224.8, 156.5, 143.8, 131.7, 128.8, 116.9, 108.4, 55.6, 55.0, 52.6, 43.7, 37.0, 23.4, 21.3

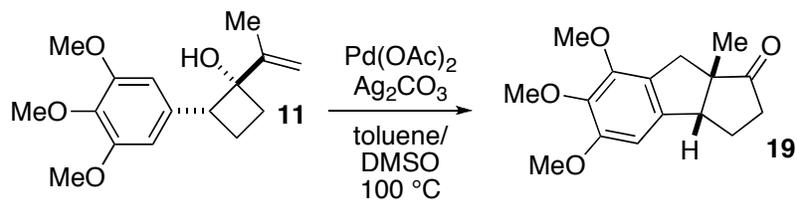
IR ATR

$\nu = 2999, 2936, 2896, 1726, 1584, 1481, 1455, 1401, 1259, 1232, 1121, 1067, 769,$   
 667  $\text{cm}^{-1}$

HRMS EI

Calc'd for  $\text{C}_{14}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ )  $m/z$  216.1150, found 216.1153

m.p. 68-71  $^\circ\text{C}$



**Benzodiquinane 19** was prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:5) provided benzodiquinane **19** in 53 % yield.

Data for 19

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 6.55 (s, 1 H), δ 3.87 (s, 6 H), δ 3.83 (s, 3 H), δ 3.51 (br d, *J* = 5.4 Hz, 1 H),  
δ 3.28 (d, *J* = 16.2 Hz, 1 H), δ 2.77 (d, *J* = 16.2 Hz, 1 H), δ 2.41-2.13 (m, 3 H),  
δ 2.11-1.97 (m, 1 H), δ 1.28 (s, 3 H)

<sup>13</sup>C NMR (MHz, CDCl<sub>3</sub>)

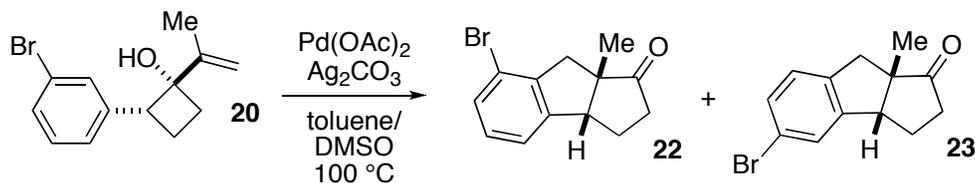
δ 224.2, 153.7, 149.3, 140.9, 140.2, 126.6, 102.5, 61.0, 60.3, 56.4, 56.3, 54.1, 40.3,  
36.2, 24.7, 20.7

IR (thin film, NaCl)

ν = 2937, 2848, 2251, 1736, 1601, 1587, 1481, 1468, 1414, 1340, 1120, 912, 731 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub> (M<sup>+</sup>) *m/z* 276.1362, found 276.1359



**Benzodiquinanes 22 and 23** were prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:40) provided benzodiquinane **22** and **23** as an inseparable mixture in 17 % yield.

Data for 22 and 23 (mixture)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.39 (s, 1 H), 7.35 (d, *J* = 8 Hz, 1 H), 7.31 (d, *J* = 8 Hz, 1 H), 7.19 (d, *J* = 8 Hz, 1 H),  
 7.11 (t, *J* = 8 Hz, 1 H), 7.01 (d, *J* = 8 Hz), 3.66 (d, *J* = 6 Hz, 1 H),  
 3.57 (d, *J* = 6 Hz, 1 H), 3.33 (d, *J* = 16 Hz, 1 H), 3.22 (d, *J* = 16 Hz, 1 H),  
 2.86 (d, *J* = 16 Hz, 1 H), 2.80 (d, *J* = 16 Hz, 1 H), 2.43-2.20 (m, 6 H),  
 2.04-2.00 (m, 2 H), 1.32 (s, 3 H), 1.30 (s, 3 H)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

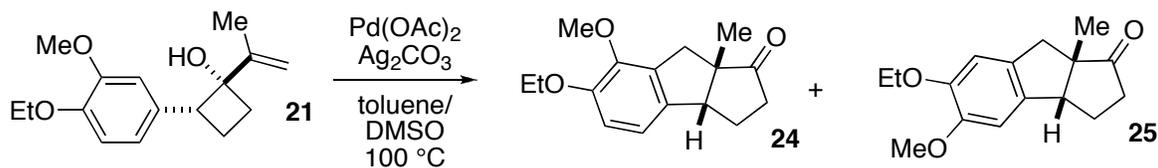
δ 223.8, 223.5, 147.1, 146.6, 142.7, 141.2, 130.4, 130.3, 128.8, 127.0, 125.9, 122.6,  
 120.7, 119.7, 56.6, 55.2, 54.8, 53.6, 44.5, 42.6, 36.2, 36.2, 25.0, 24.6, 20.7, 20.5

IR (thin film, NaCl)

$\nu$  = 2956, 2924, 1738, 1564, 1406, 1061, 754 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>13</sub>H<sub>13</sub>BrO (M<sup>+</sup>) *m/z* 264.0150, found 264.0146



**Benzodiquinane 24** and **25** were prepared following *General Procedure 4*. Purification by flash column chromatography using a solution of EtOAc in hexanes (1:7) provided benzodiquinane **24** in 11 % yield and benzodiquinane **25** in 37 % yield.

Data for 24

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 6.89 (d, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 4.05 (ddd, *J* = 7, 7, 2 Hz, 2 H),  
 3.83 (s, 3 H), 3.51 (d, *J* = 6 Hz, 1 H), 3.33 (d, *J* = 16 Hz, 1 H), 2.80 (d, *J* = 16 Hz, 1 H),  
 2.39-2.18 (m, 3 H), 2.06-2.00 (m, 1 H), 1.44 (t, *J* = 7 Hz, 3 H), 1.28 (s, 3 H)

<sup>13</sup>C NMR (MHz, CDCl<sub>3</sub>)

δ 224.4, 150.7, 145.1, 138.3, 135.3, 118.5, 113.4, 64.6, 60.0, 56.6, 53.2, 40.1, 36.1,  
 24.6, 20.5, 14.9

IR (thin film, NaCl)

ν = 1736, 1487, 1394, 1263, 1221, 1068, 1068, 1047, 754 cm<sup>-1</sup>

HRMS EI

Calc'd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub> (M<sup>+</sup>) *m/z* 260.1412, found 260.1410

Data for 25<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 6.76 (s, 2 H), 6.66 (s, 2 H), 4.05 (q,  $J = 7$  Hz, 2 H), 3.88 (s, 3 H), 3.54 (d,  $J = 6$  Hz, 1 H), 3.17 (d,  $J = 16$  Hz, 1 H), 2.82 (d,  $J = 16$  Hz, 1 H), 2.39-2.19 (m, 3 H), 2.08-1.99 (m, 1 H), 1.29 (s, 3 H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

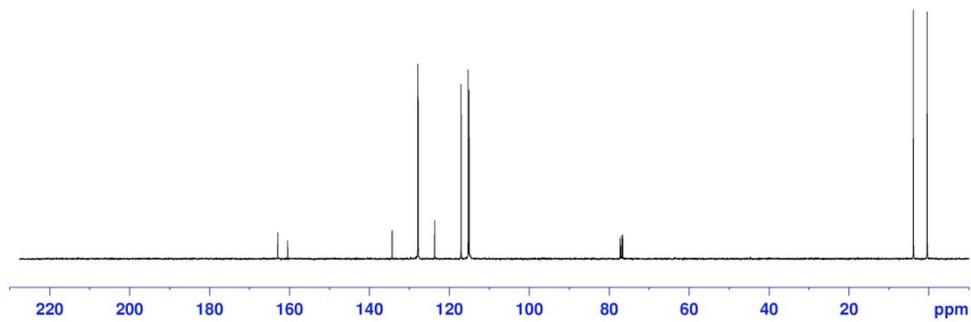
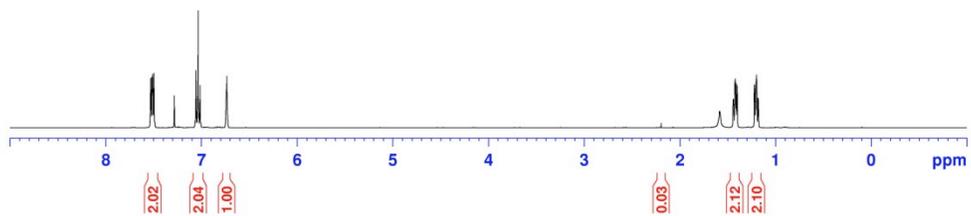
δ 224.85, 148.99, 148.07, 135.97, 133.94, 108.69, 106.91, 64.34, 56.81, 56.13, 53.72, 43.17, 36.12, 24.63, 20.49, 14.78

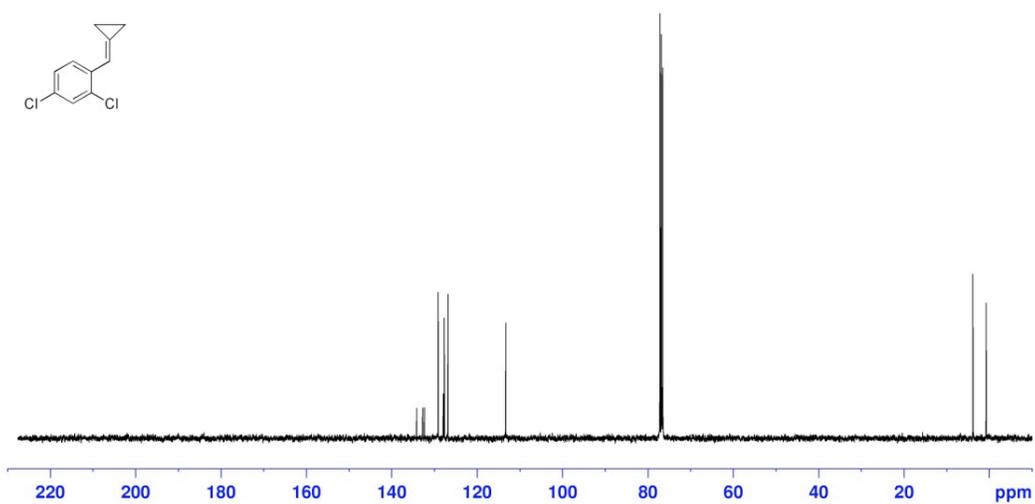
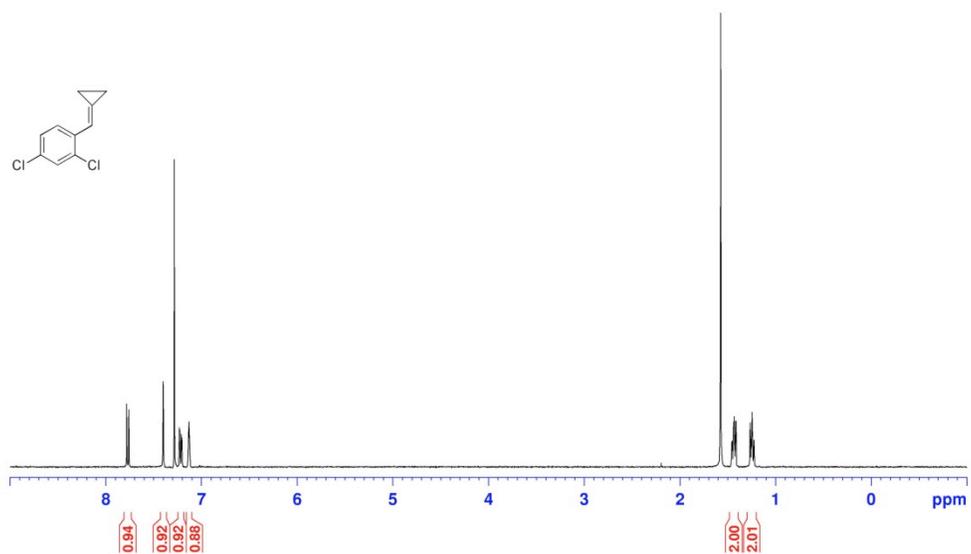
IR (thin film, NaCl)

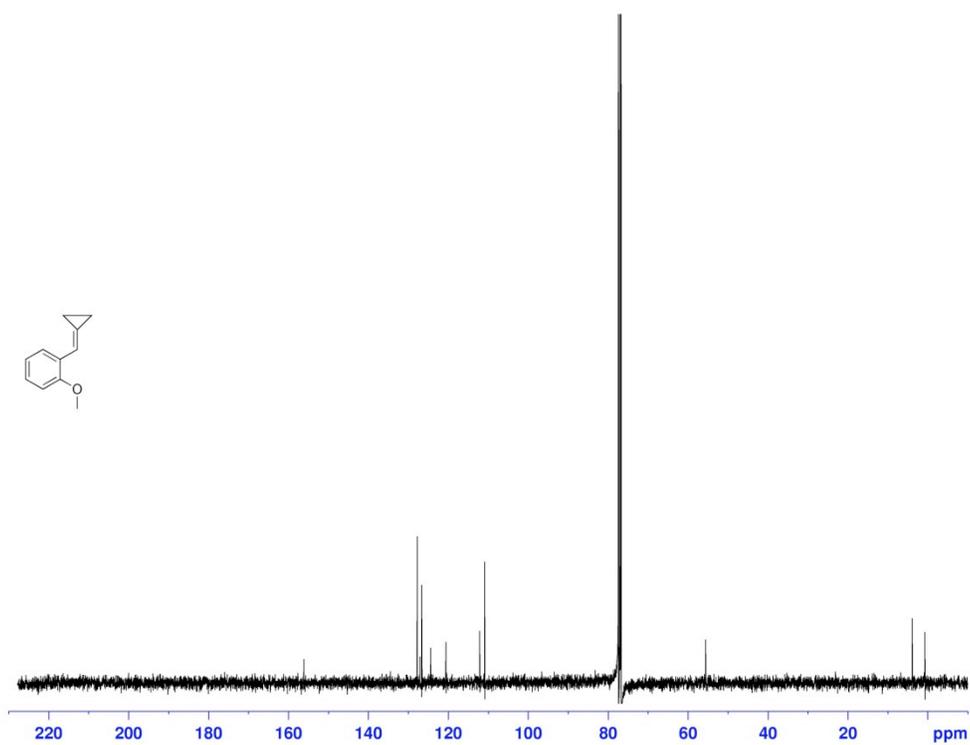
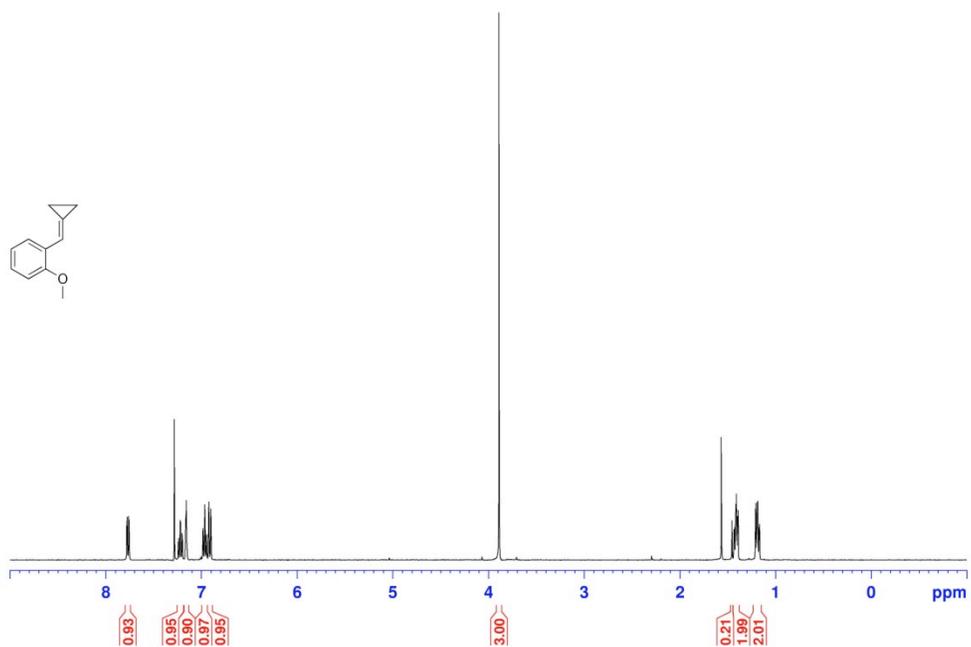
$\nu = 1732, 1504.2, 1464, 1329, 1273, 1215, 1100, 756$  cm<sup>-1</sup>

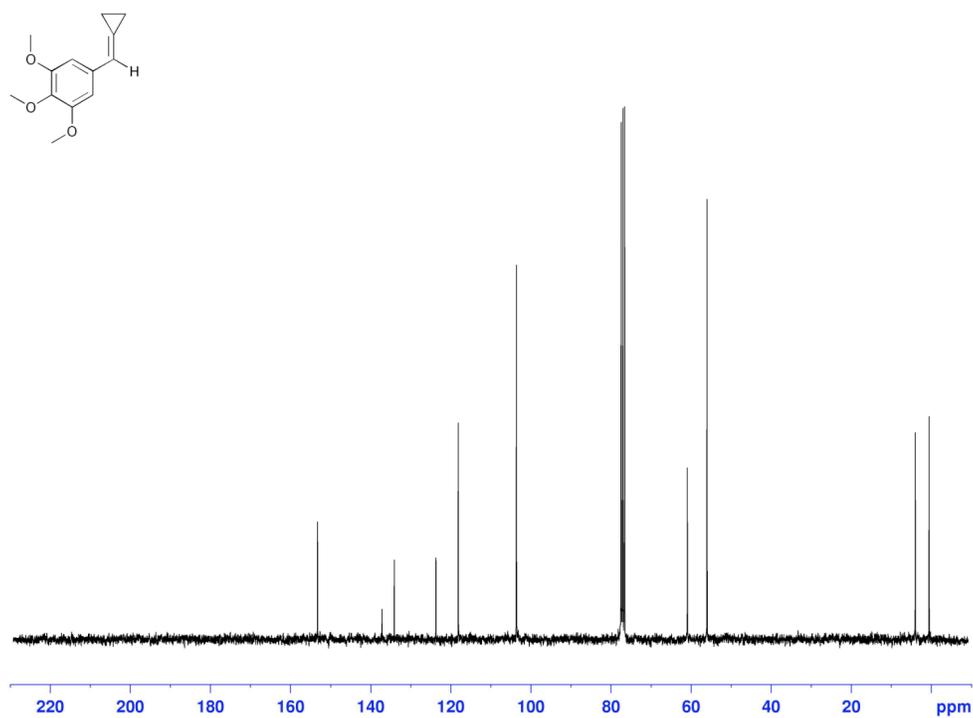
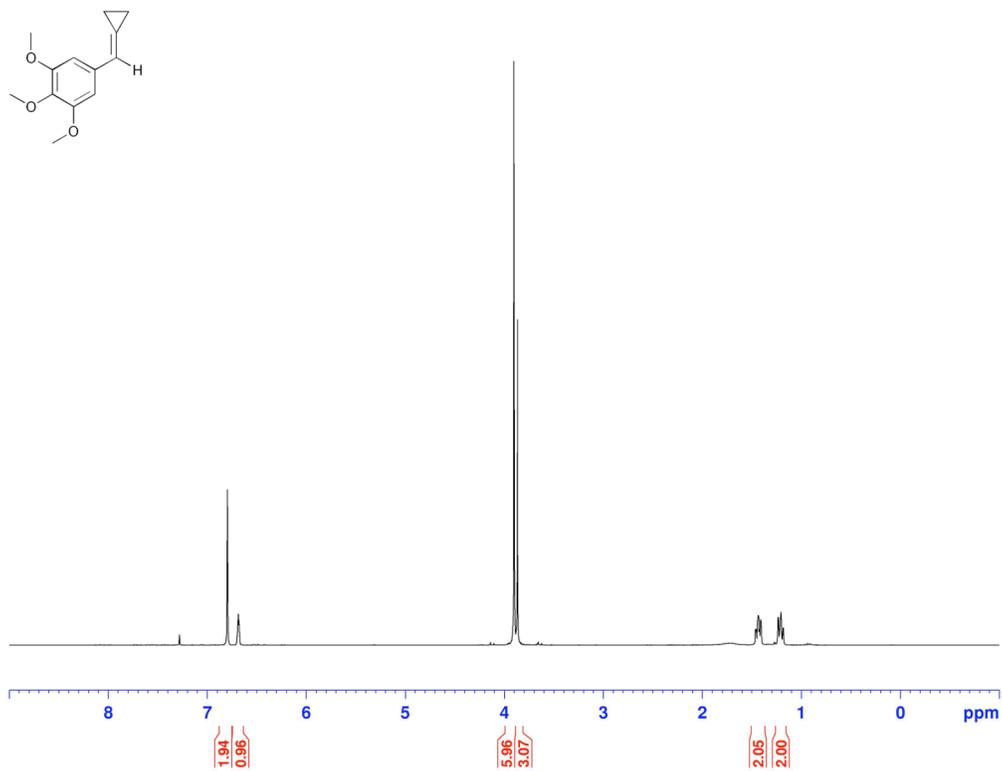
HRMS EI

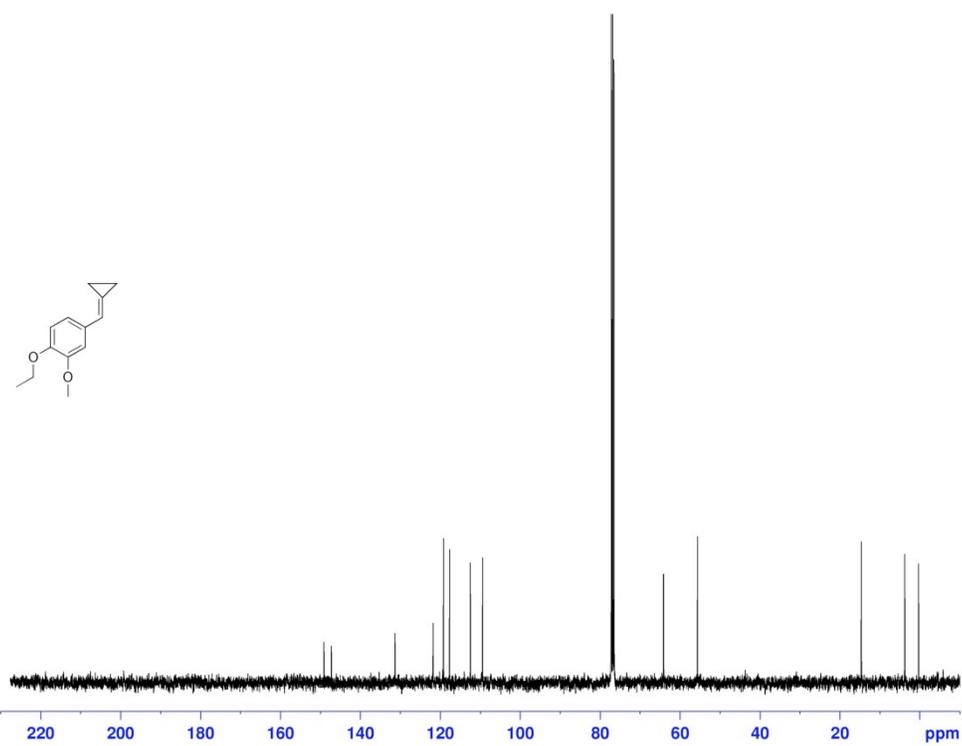
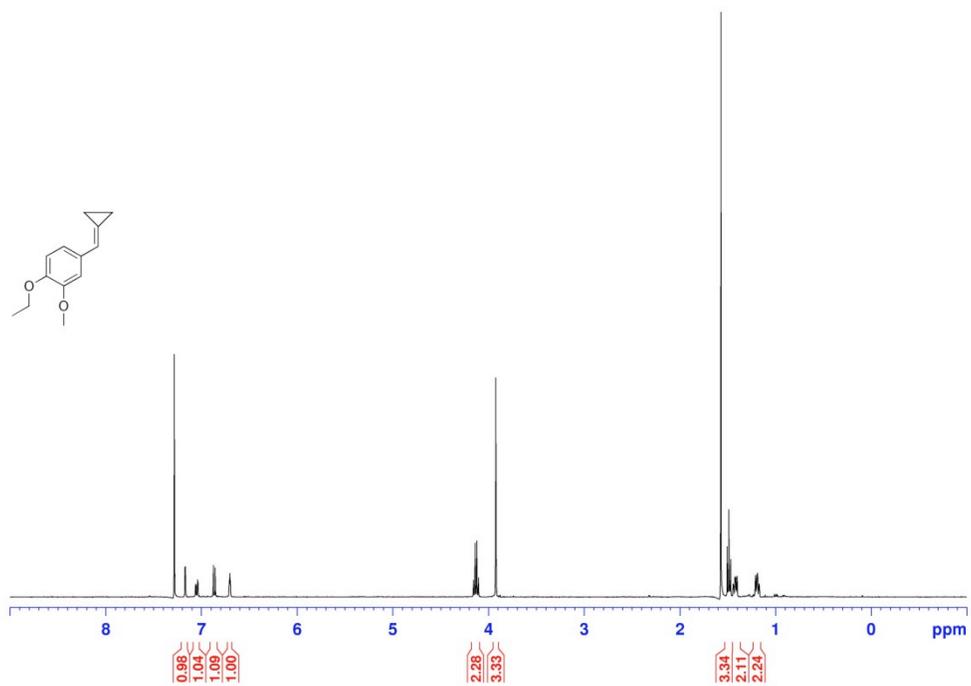
Calc'd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub> (M<sup>+</sup>)  $m/z$  260.1412, found 260.1407

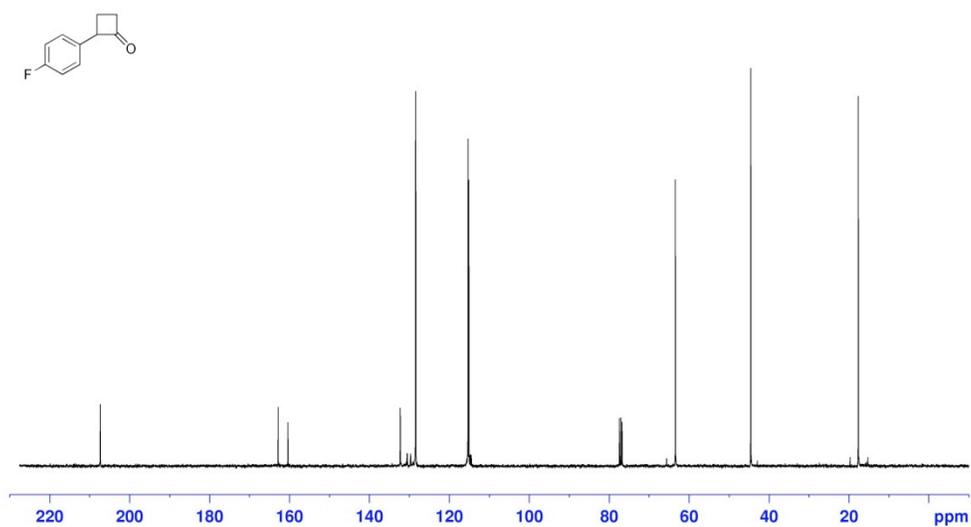
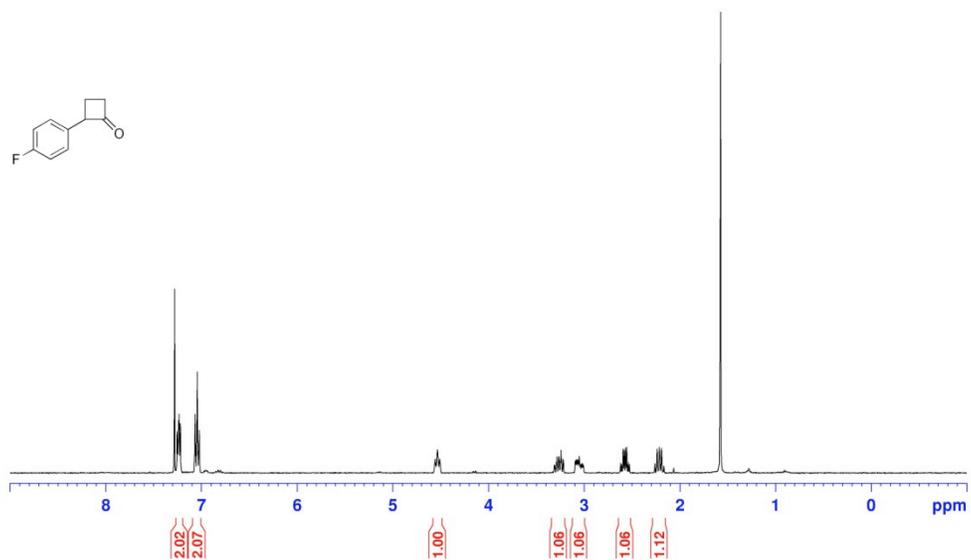
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **6a**

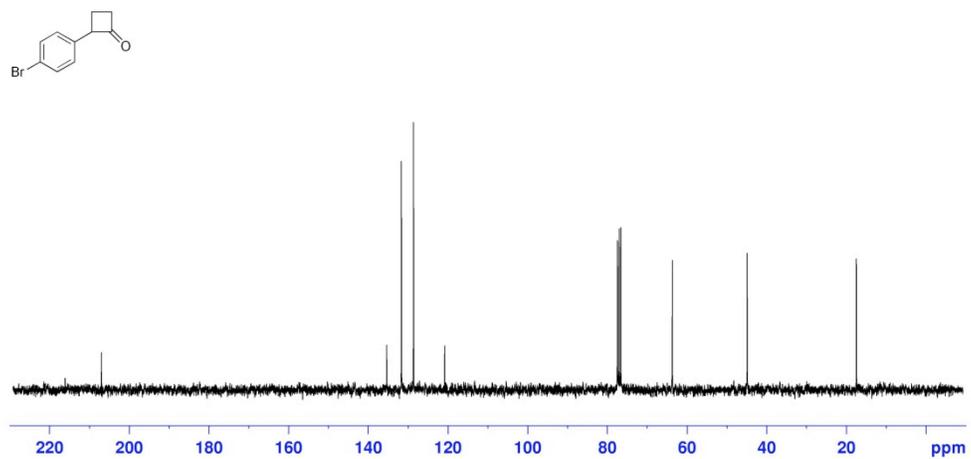
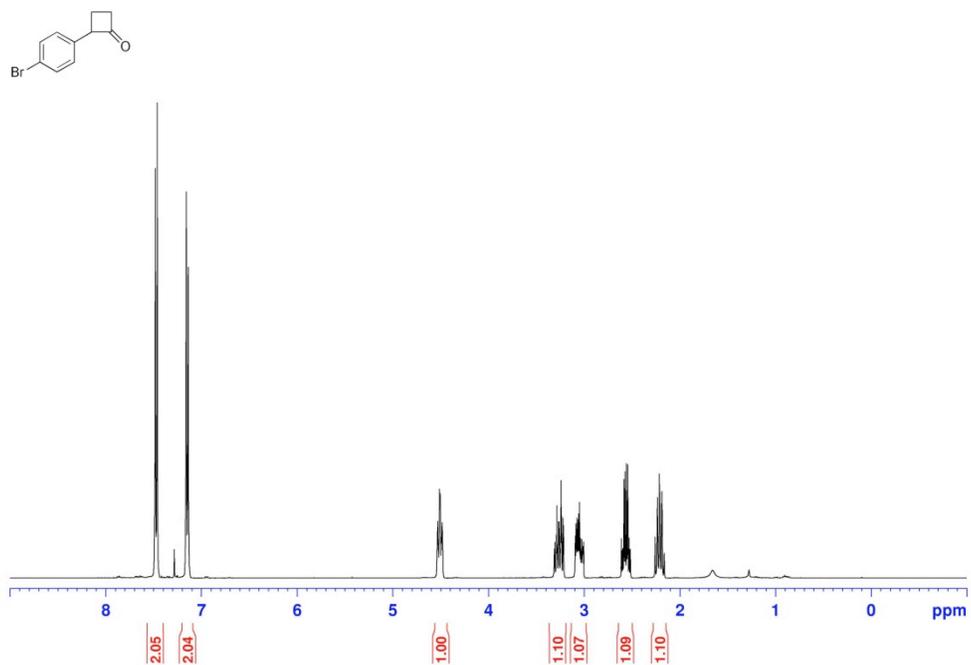
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **9a**

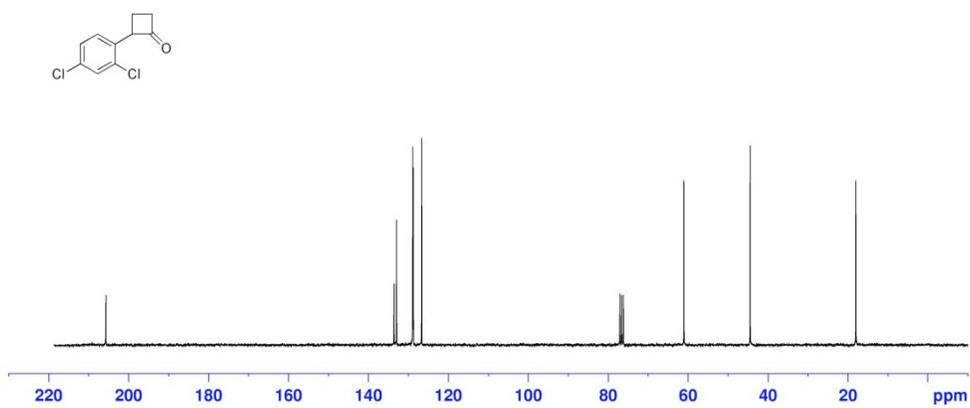
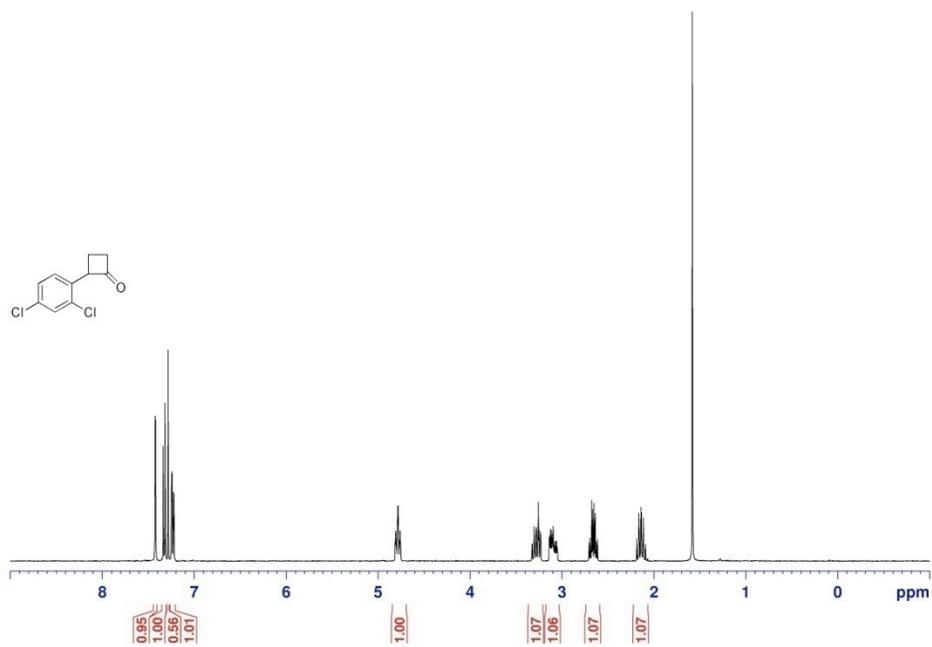
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **10a**

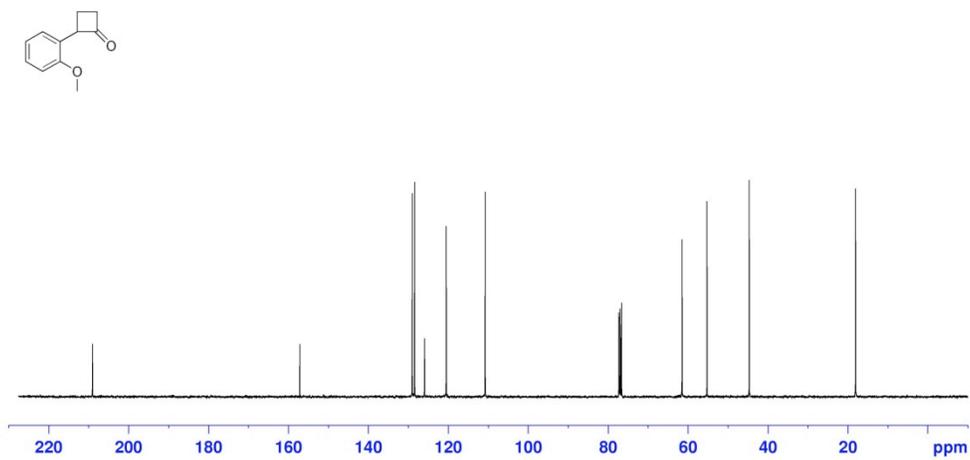
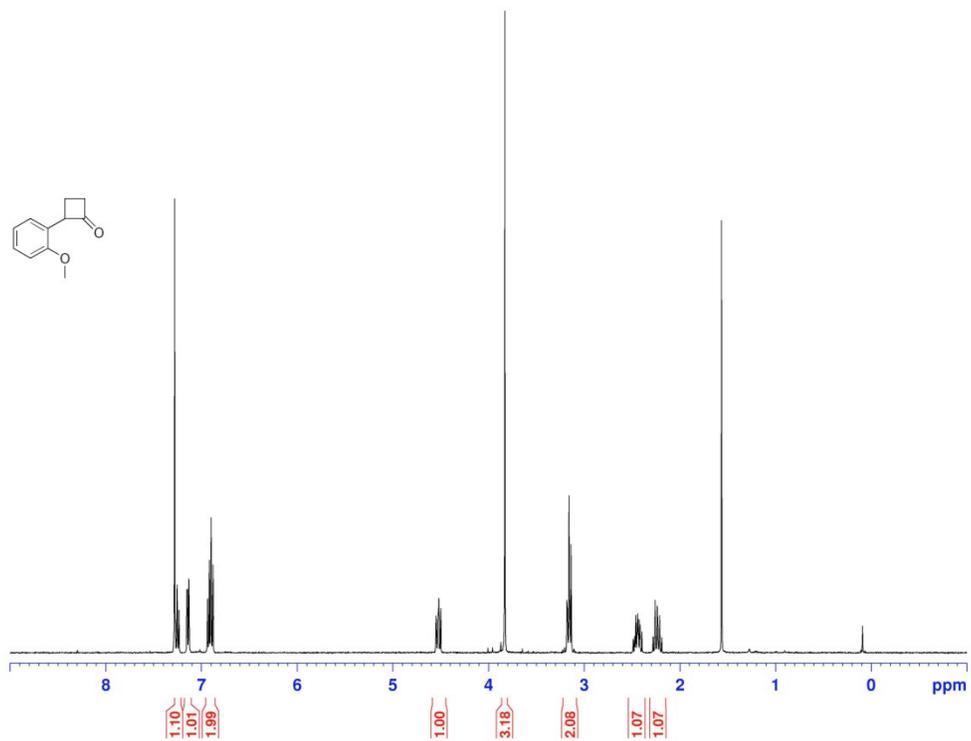
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **11a**

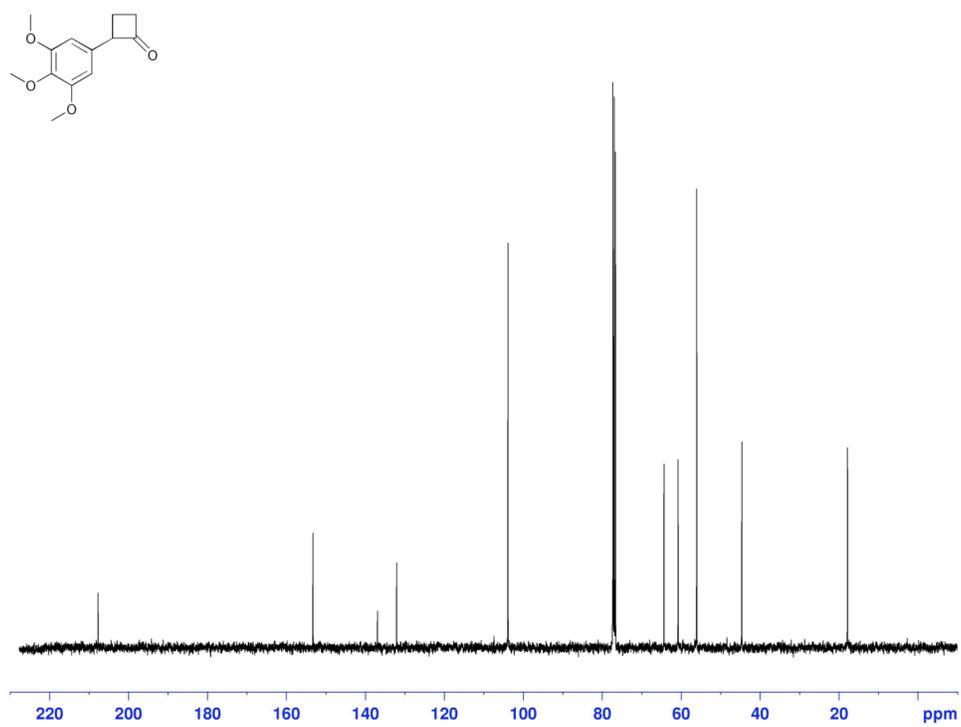
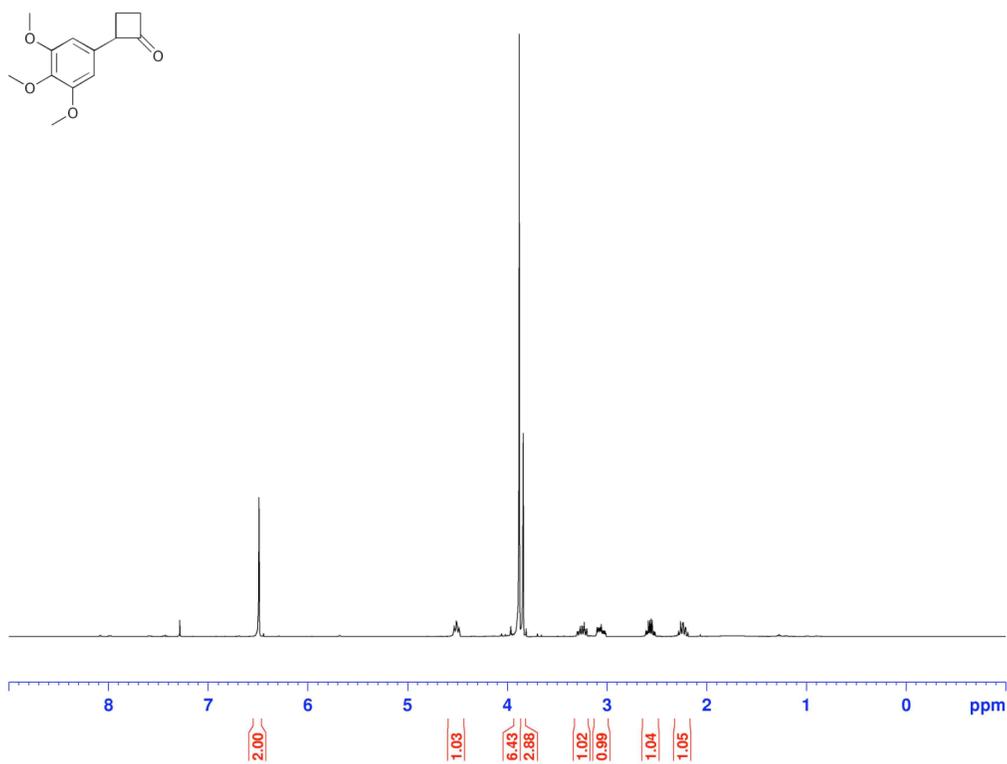
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **21a**

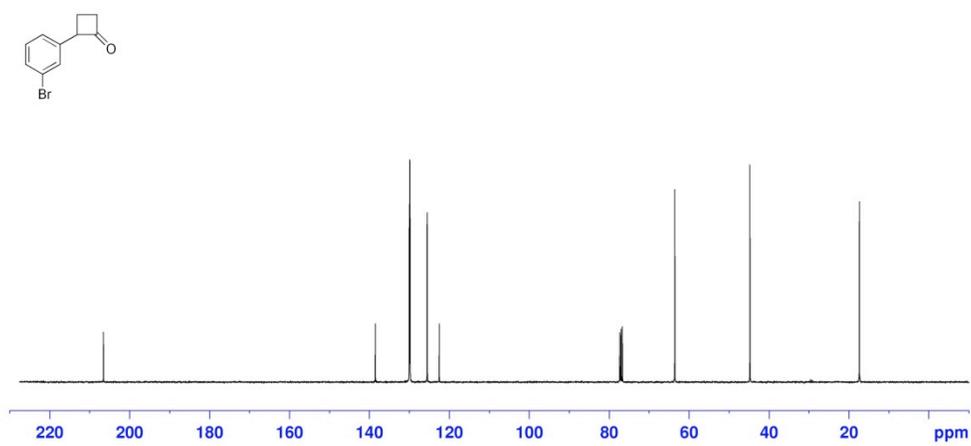
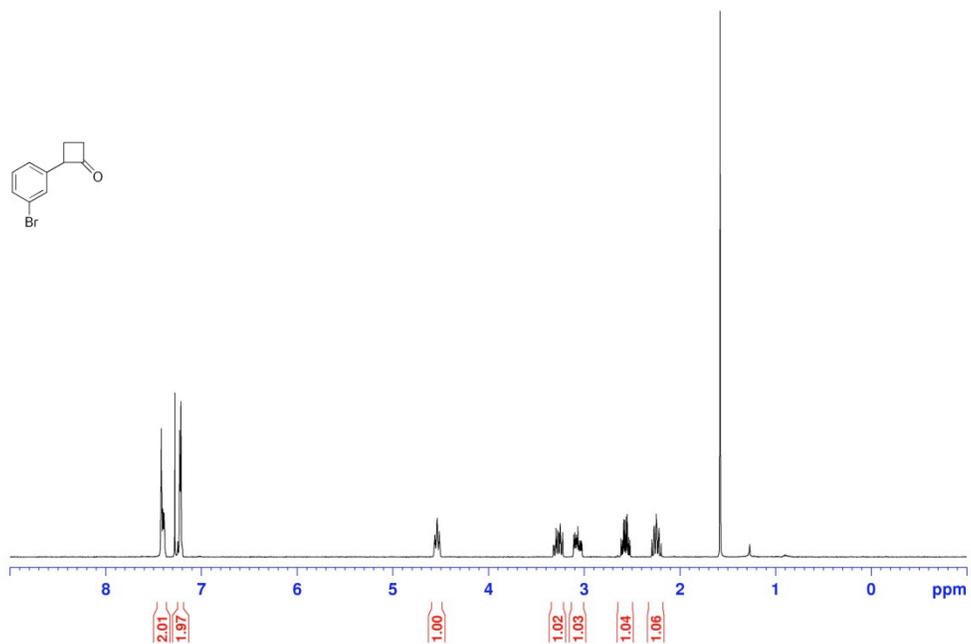
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **6b**

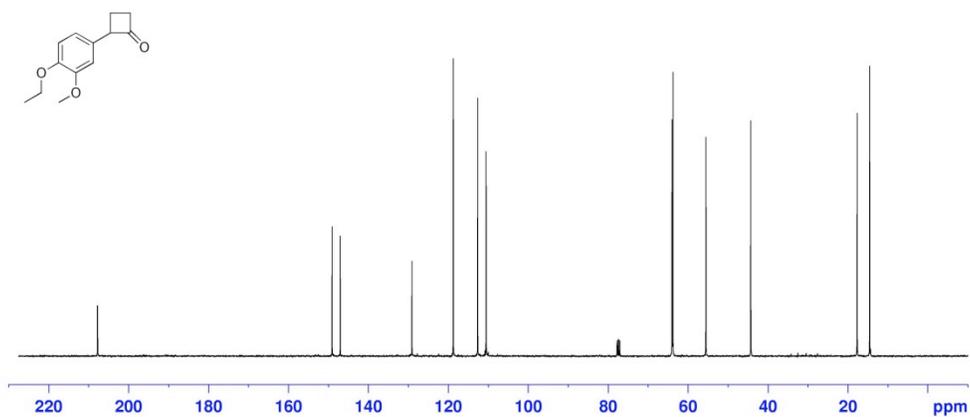
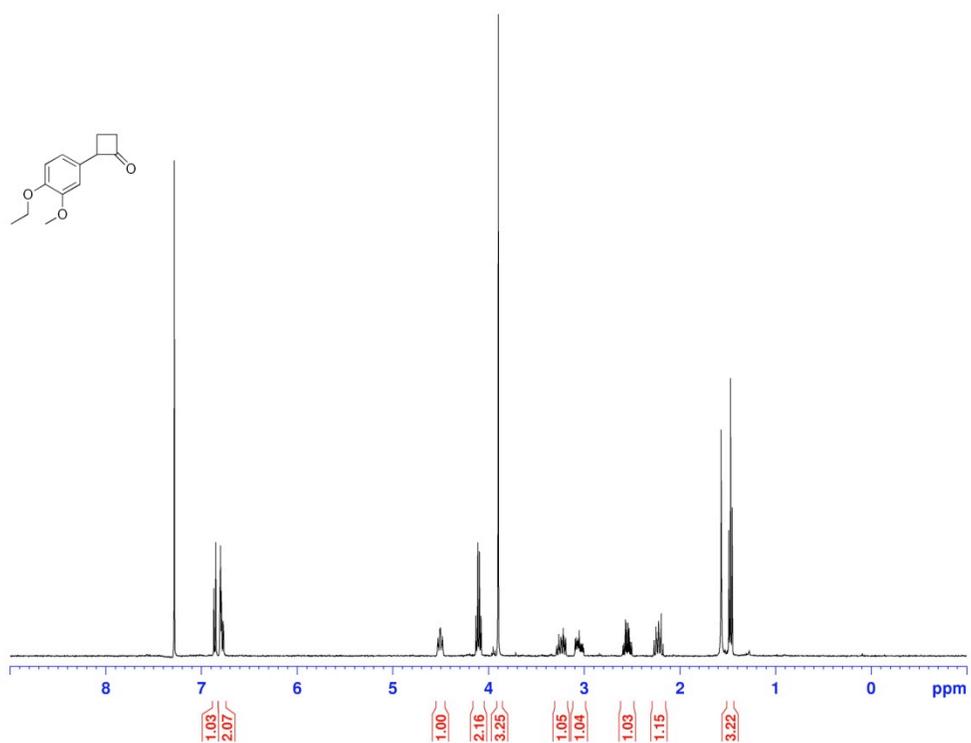
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **8b**

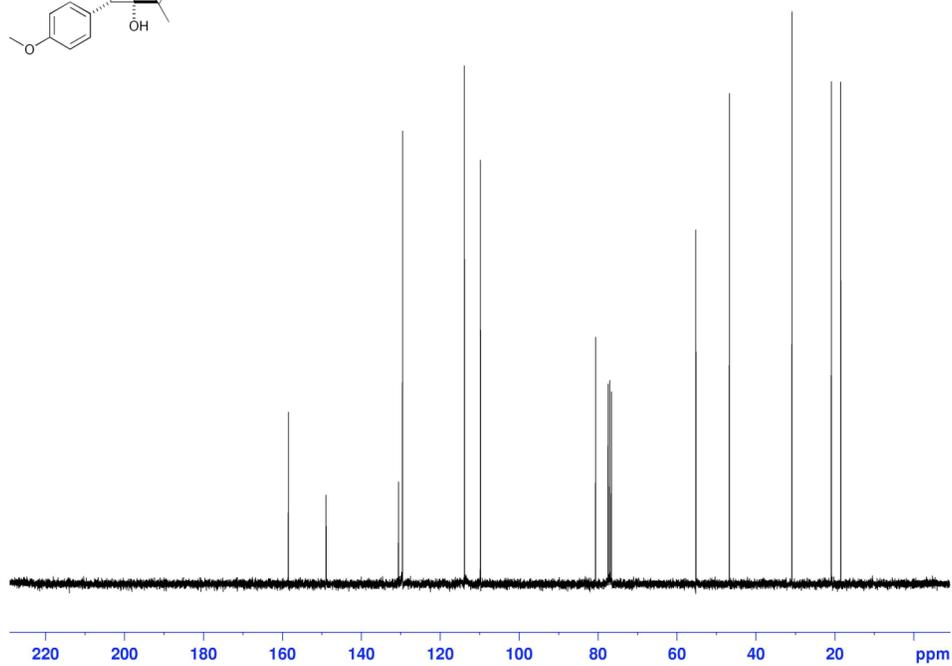
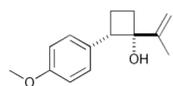
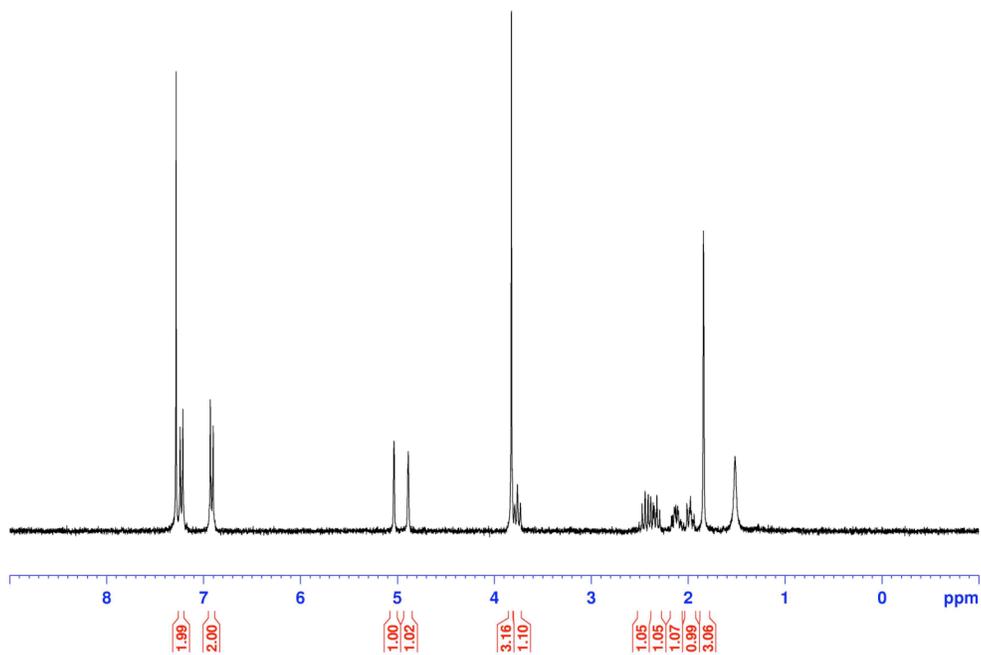
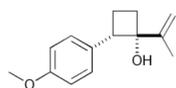
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **9b**

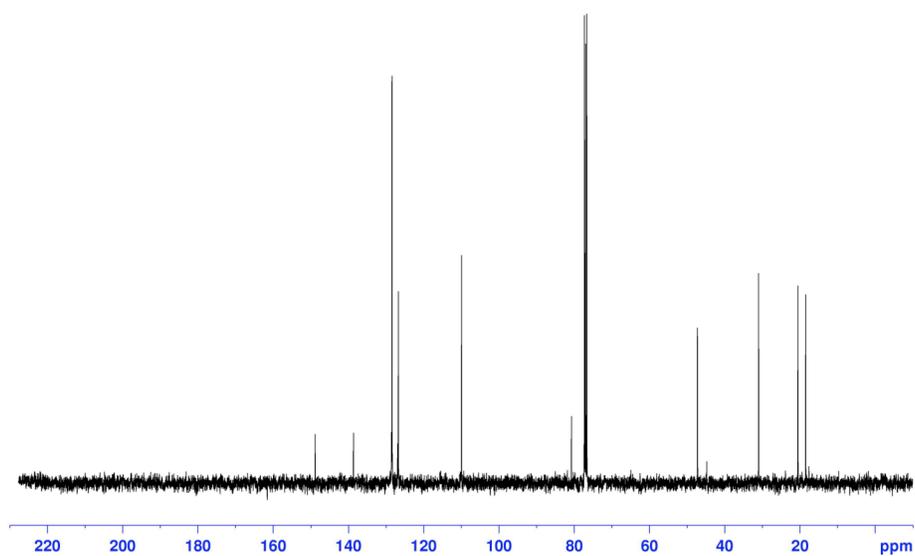
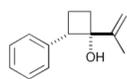
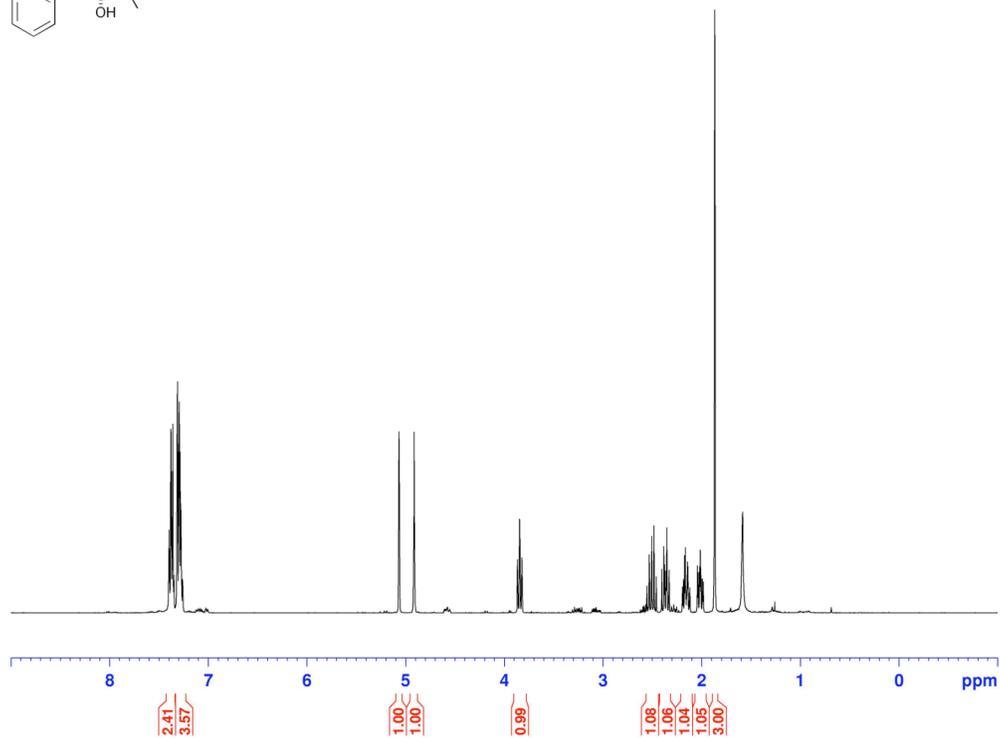
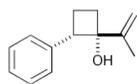
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **10b**

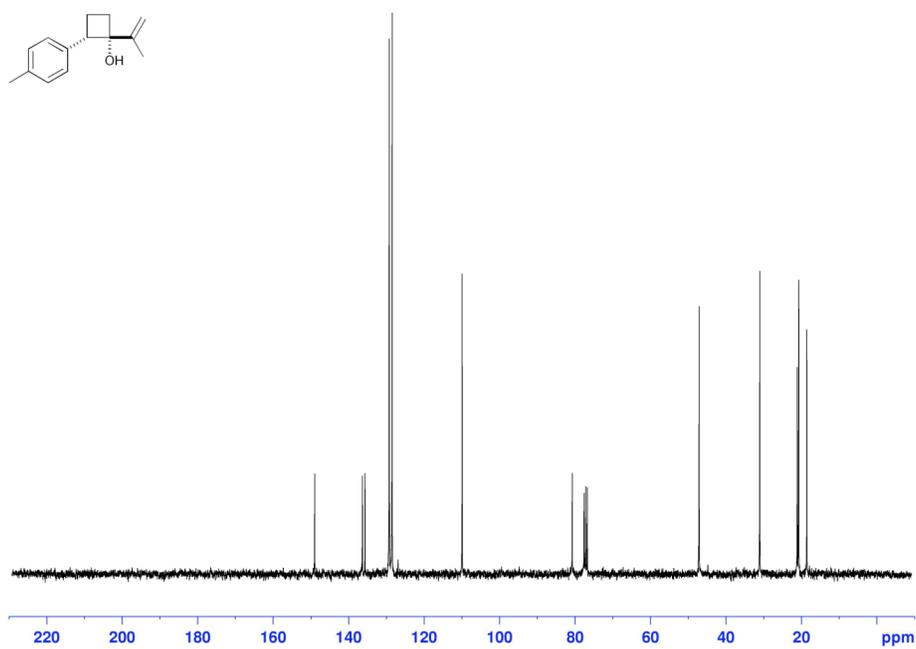
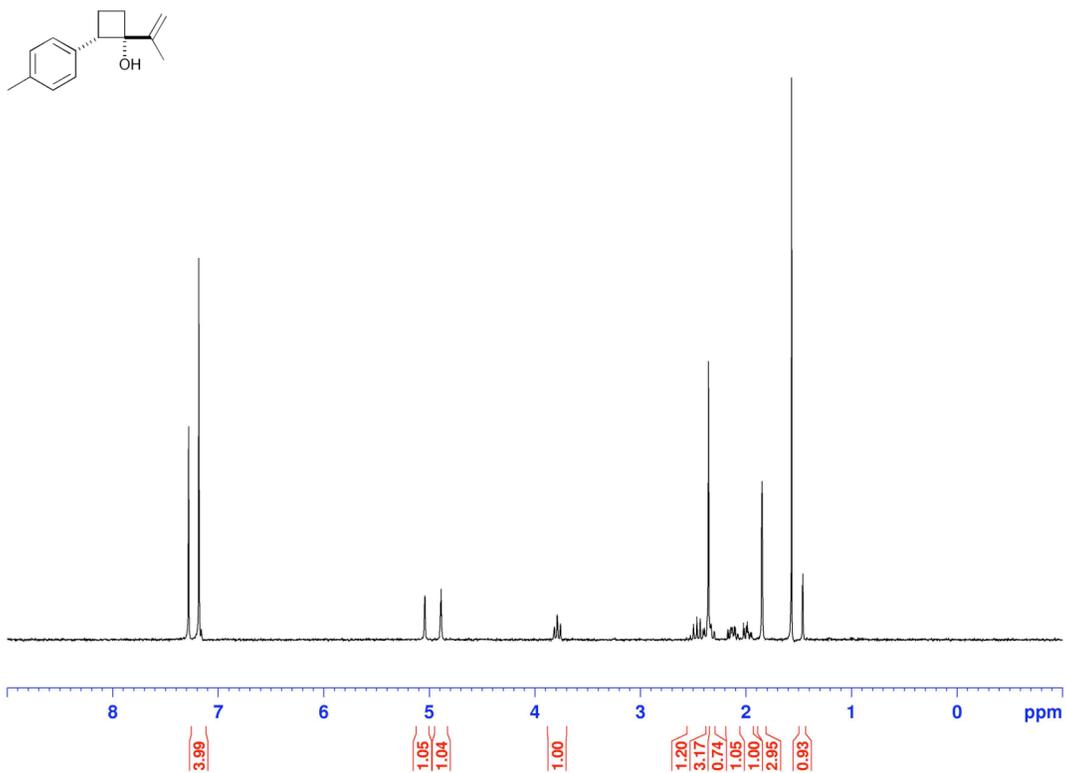
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **11b**

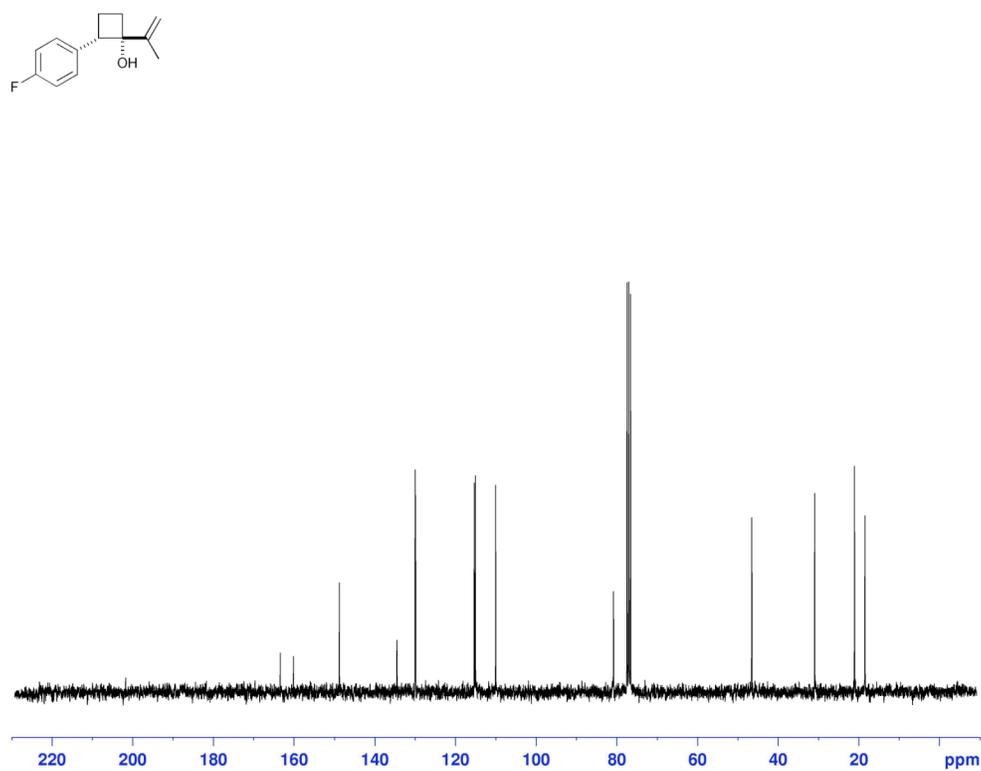
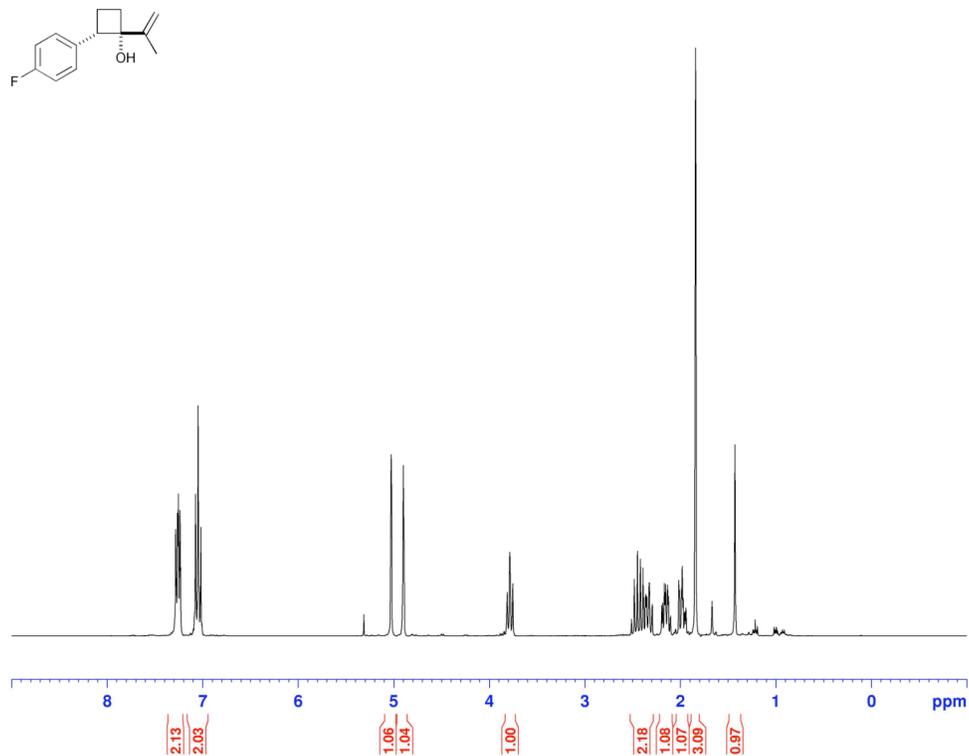
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **20b**

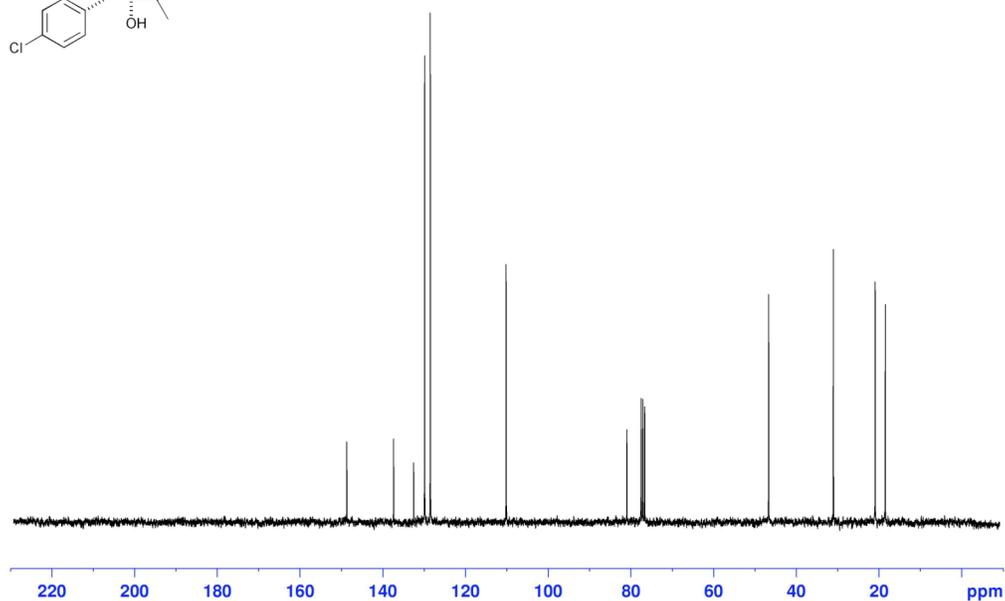
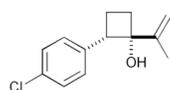
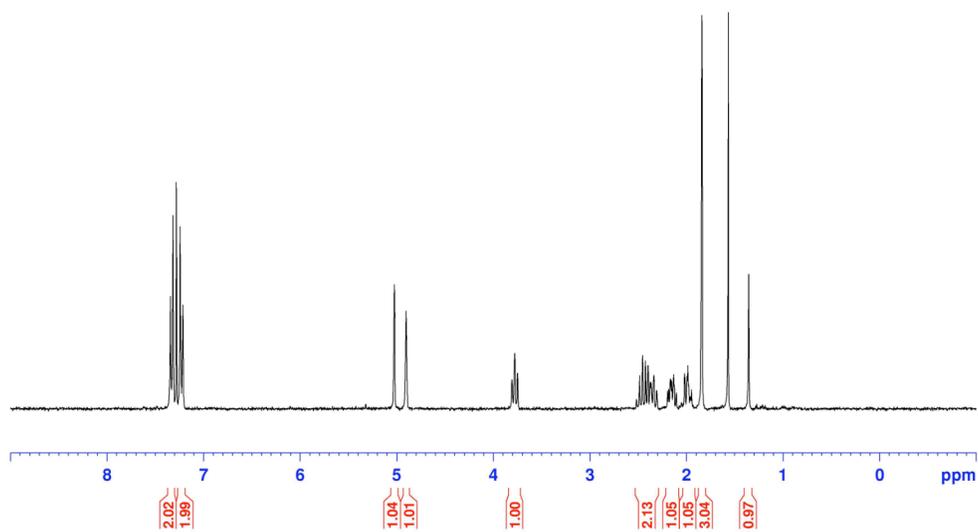
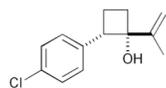
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **21b**

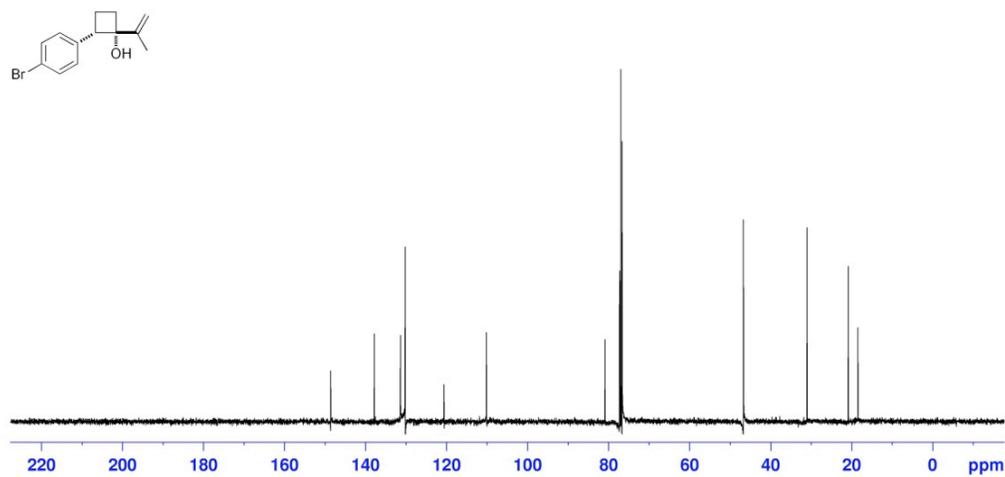
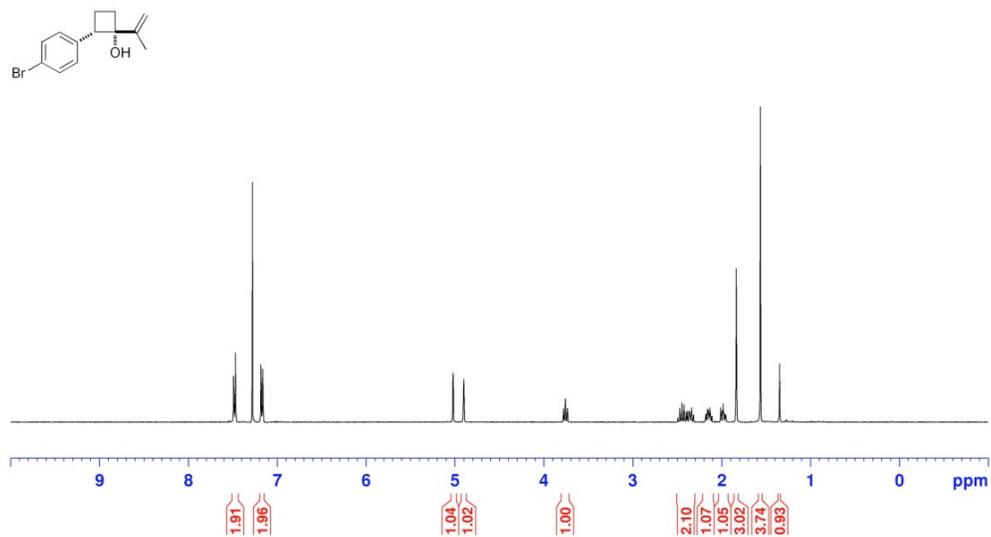
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **1**

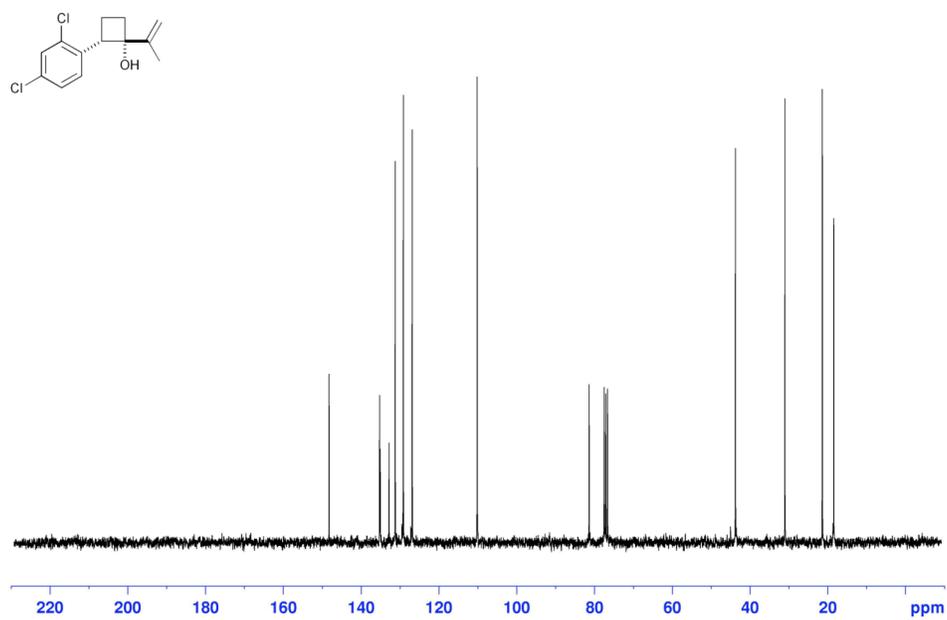
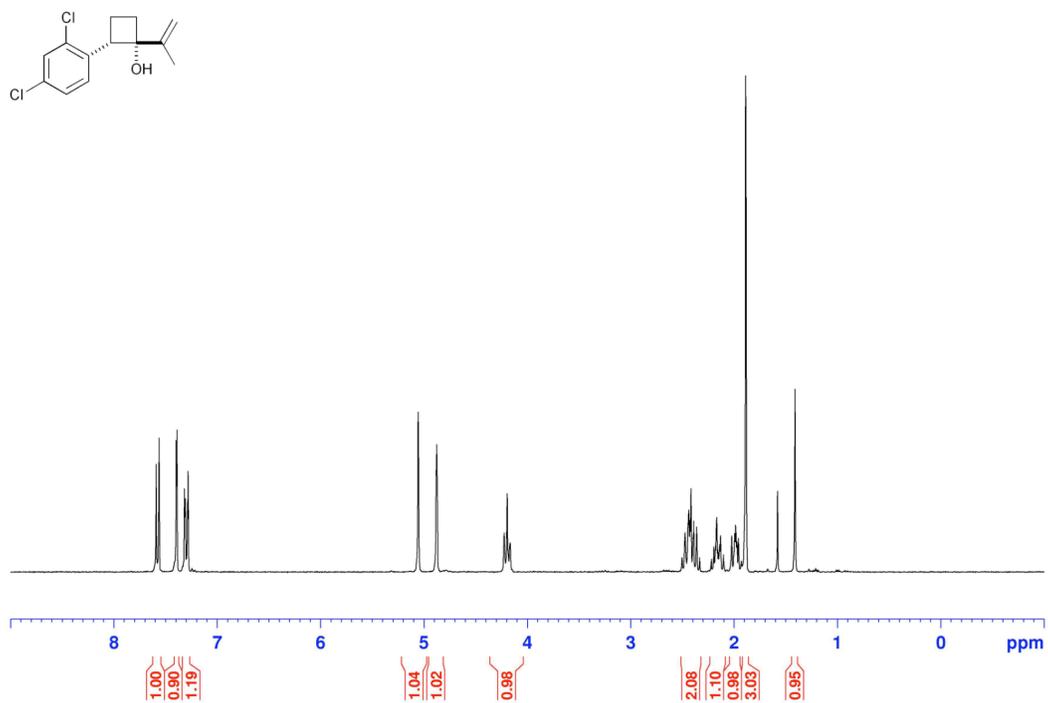
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **4**

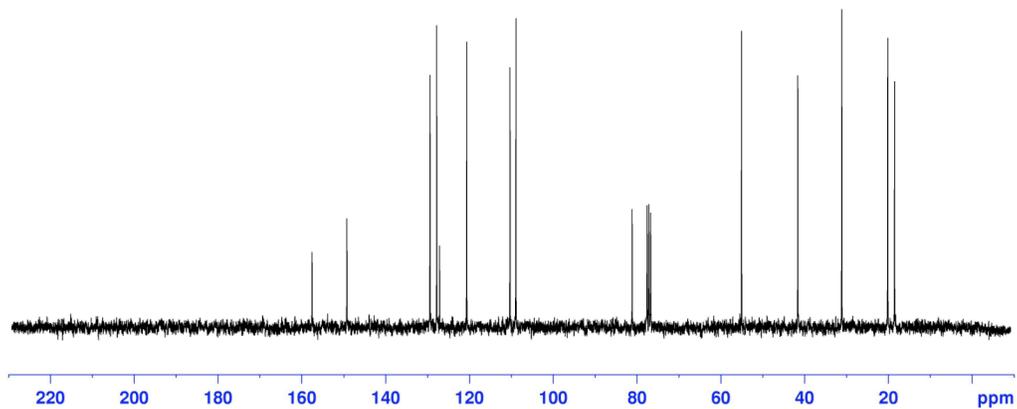
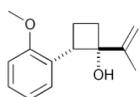
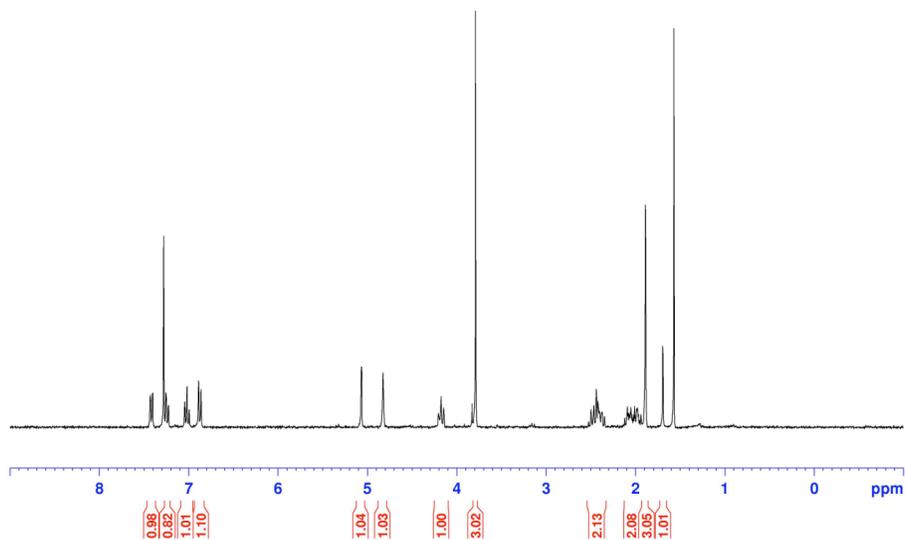
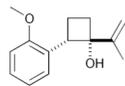
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **5**

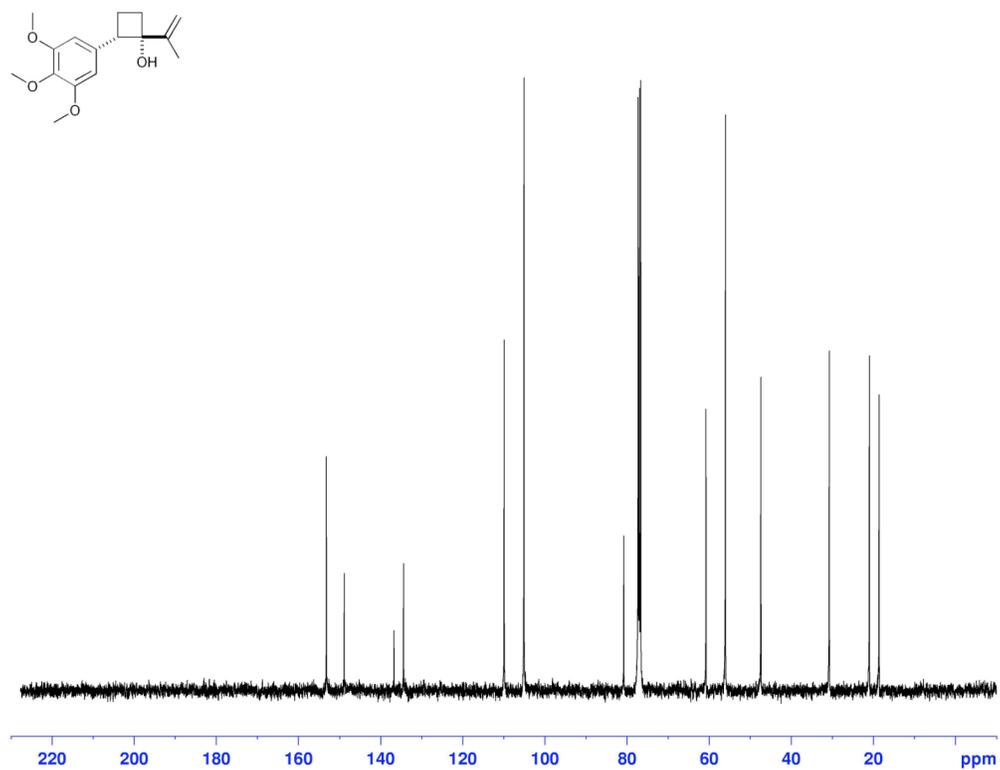
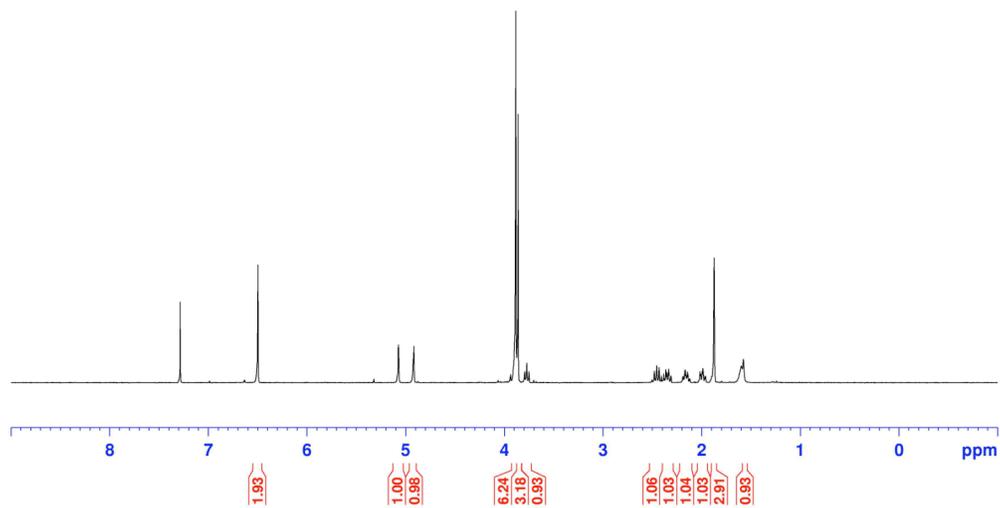
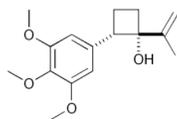
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **6**

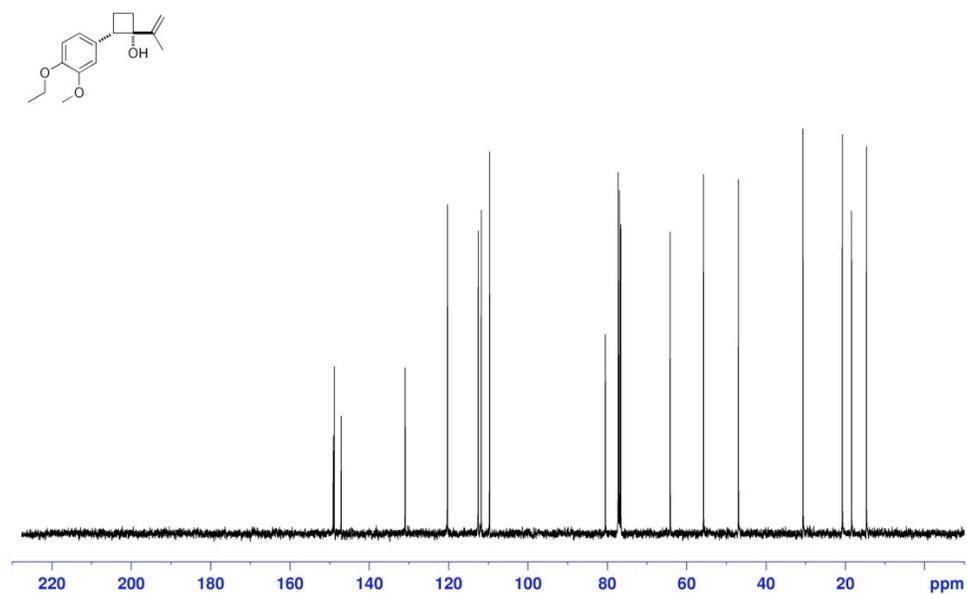
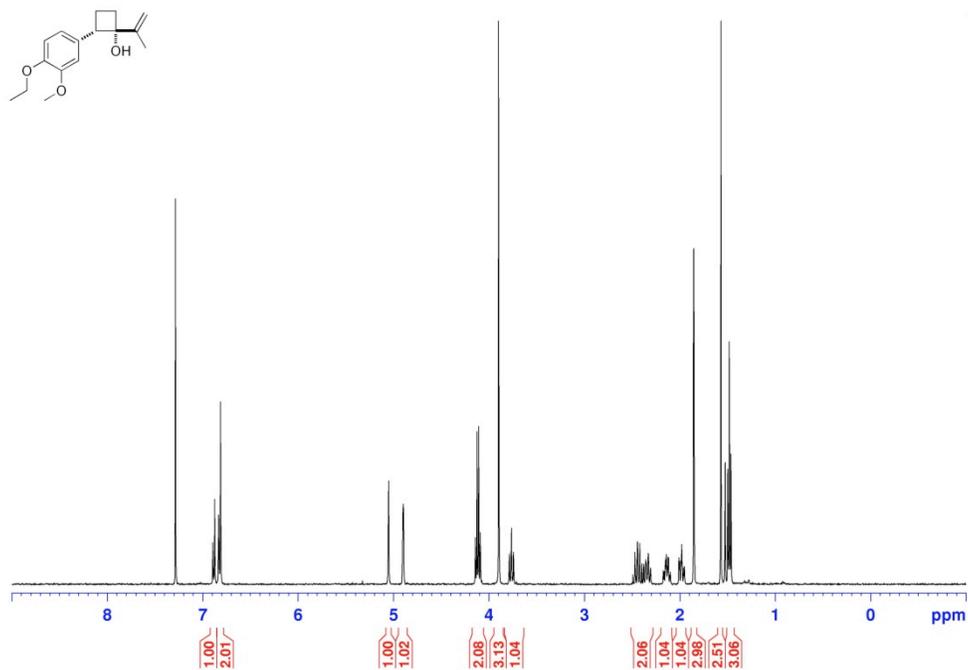
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound 7

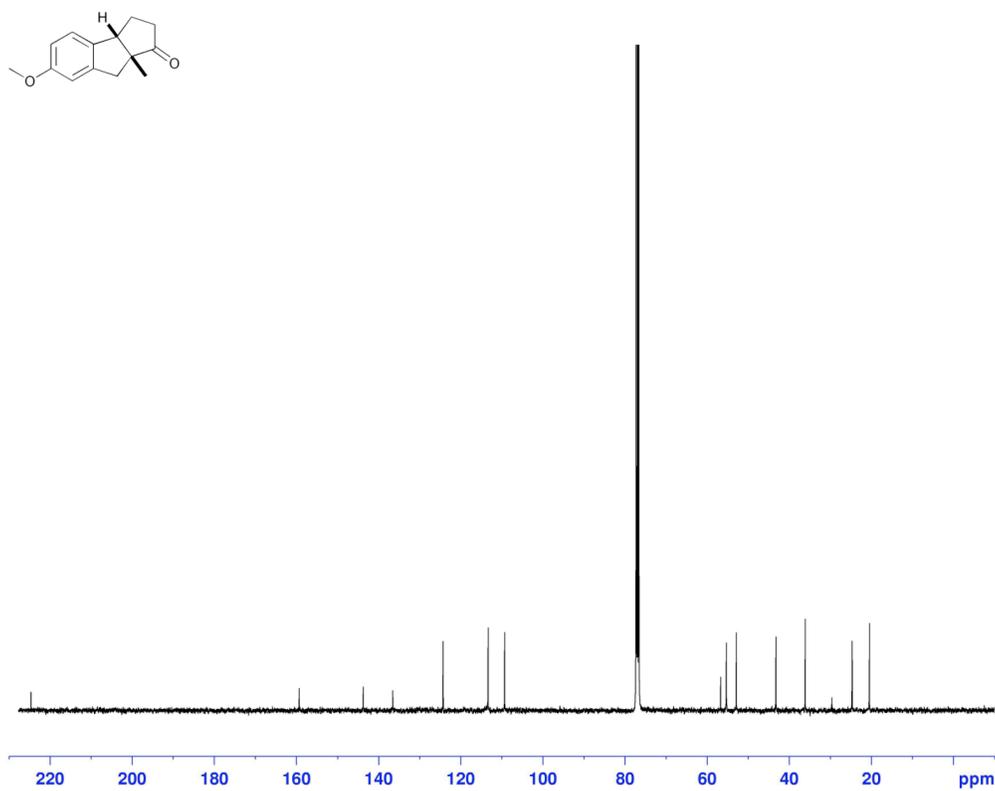
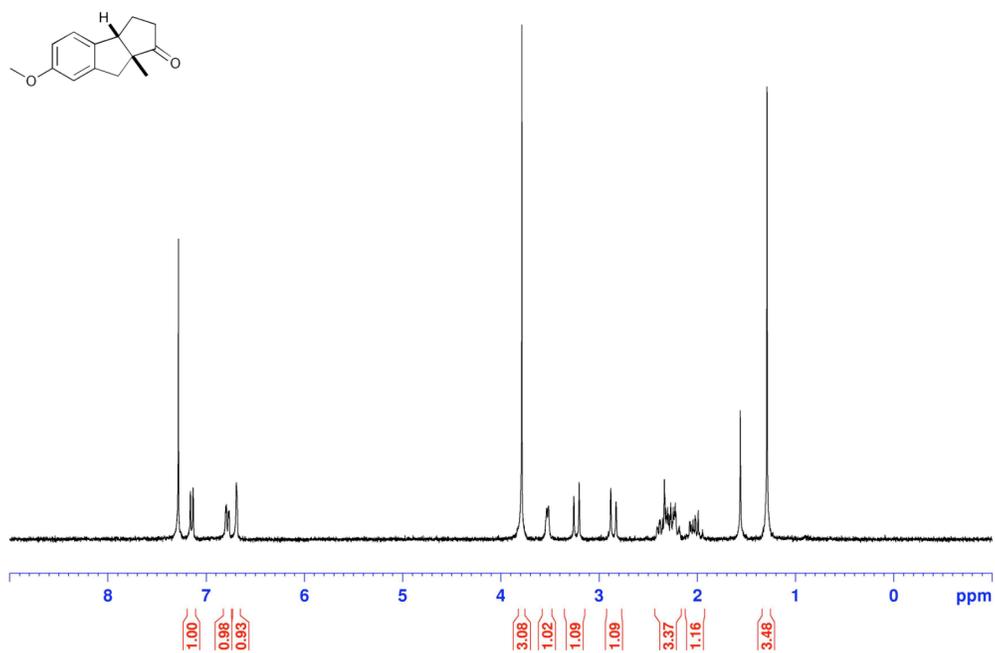
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **8**

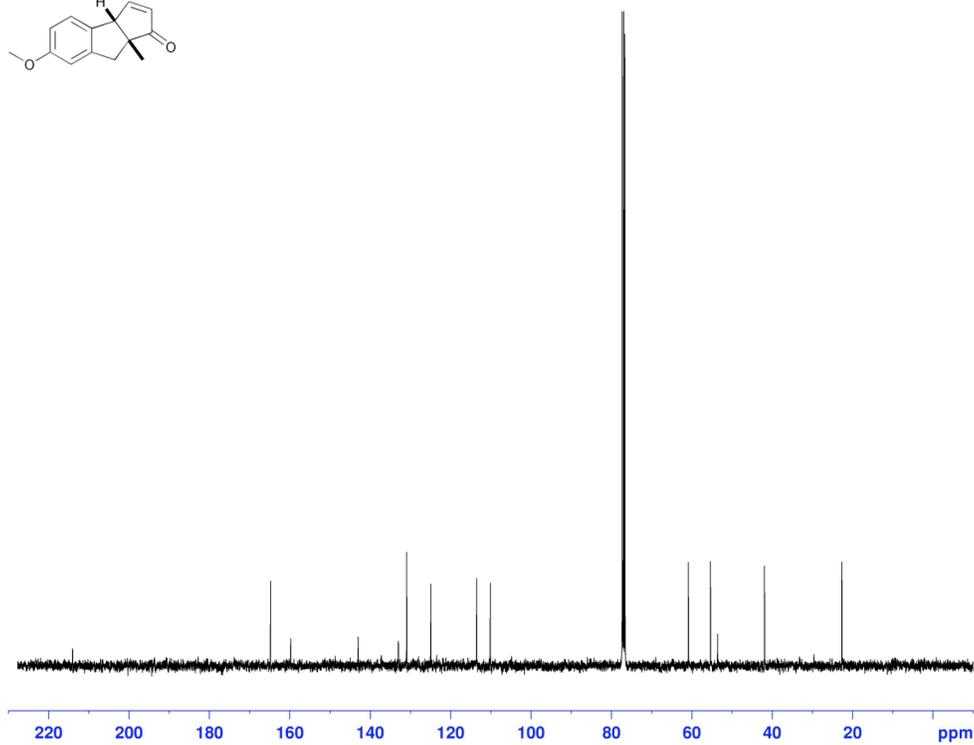
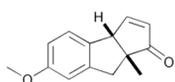
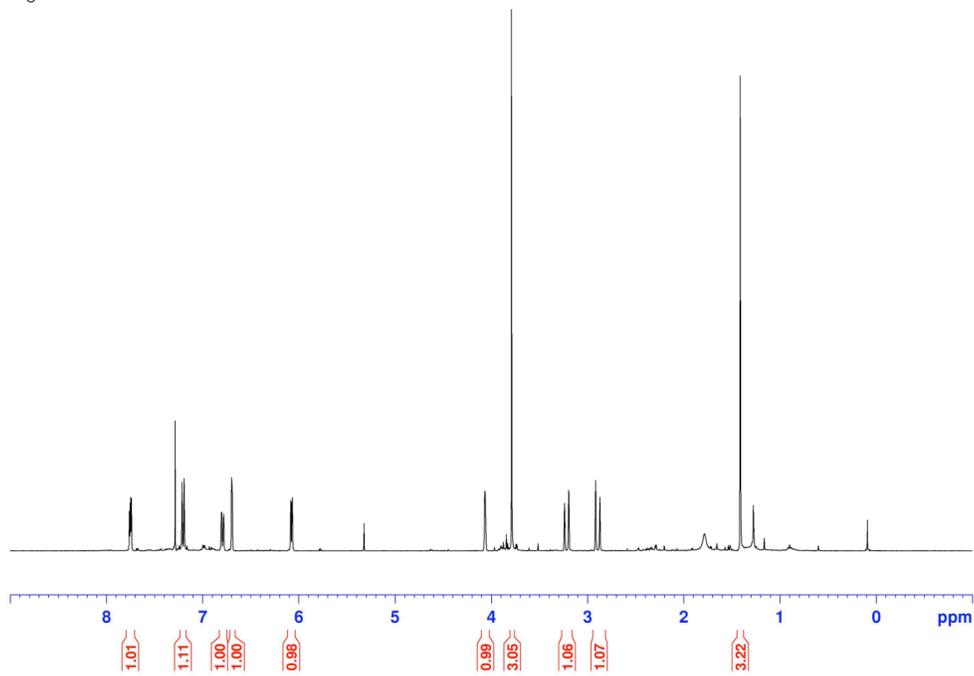
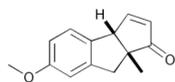
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **9**

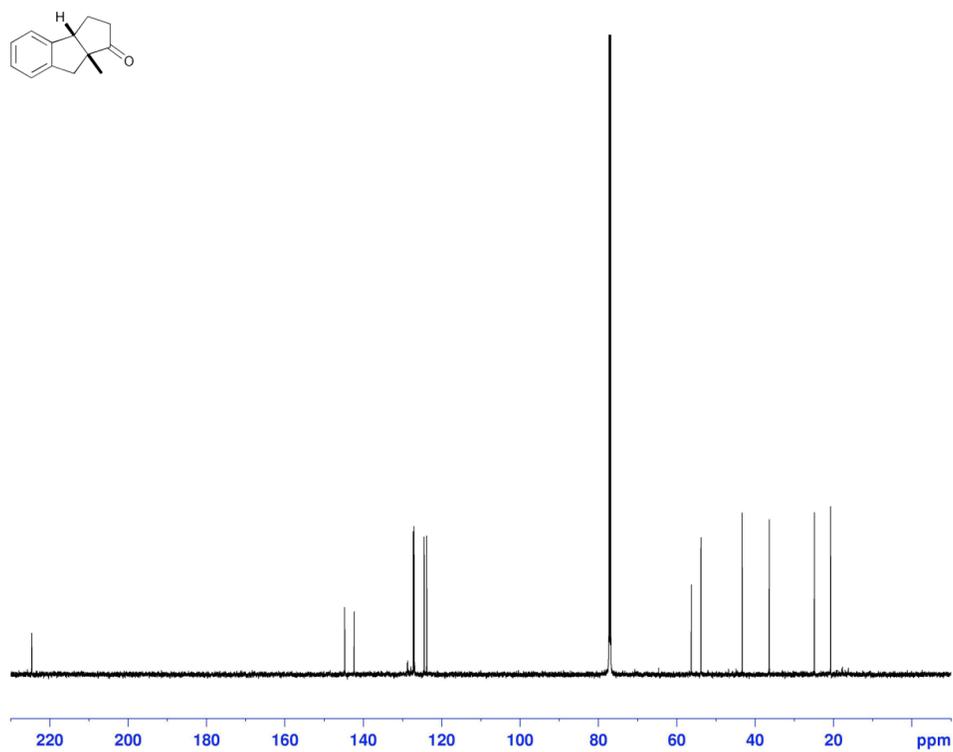
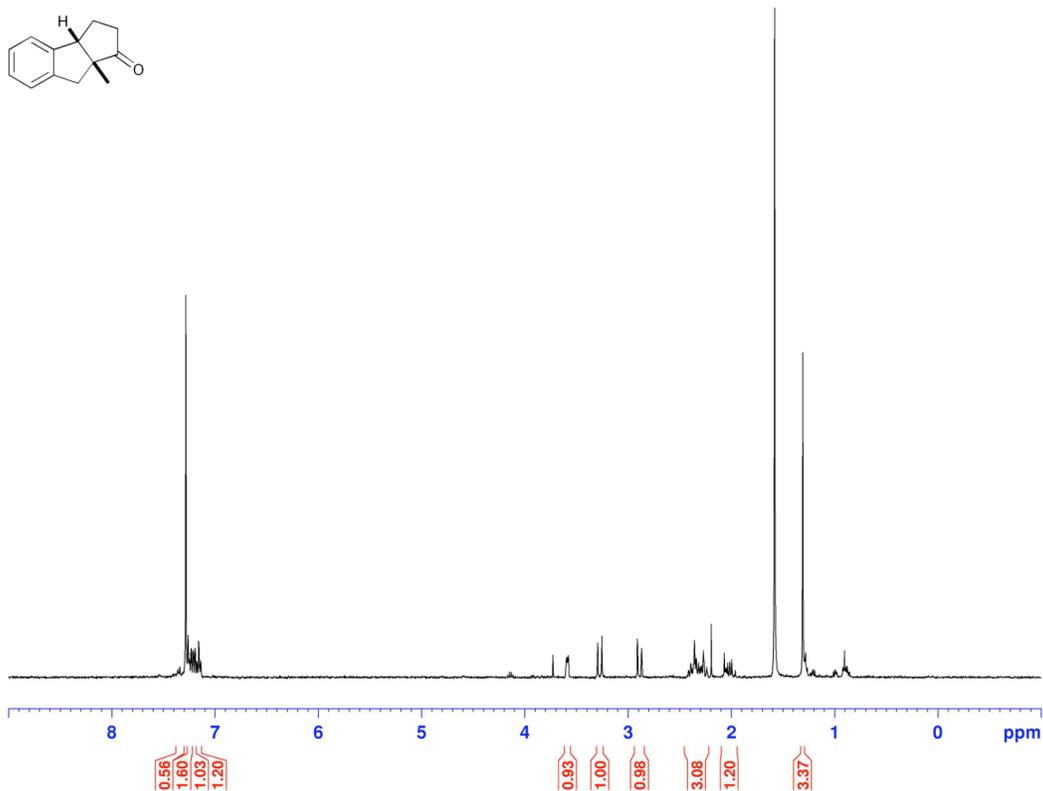
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **10**

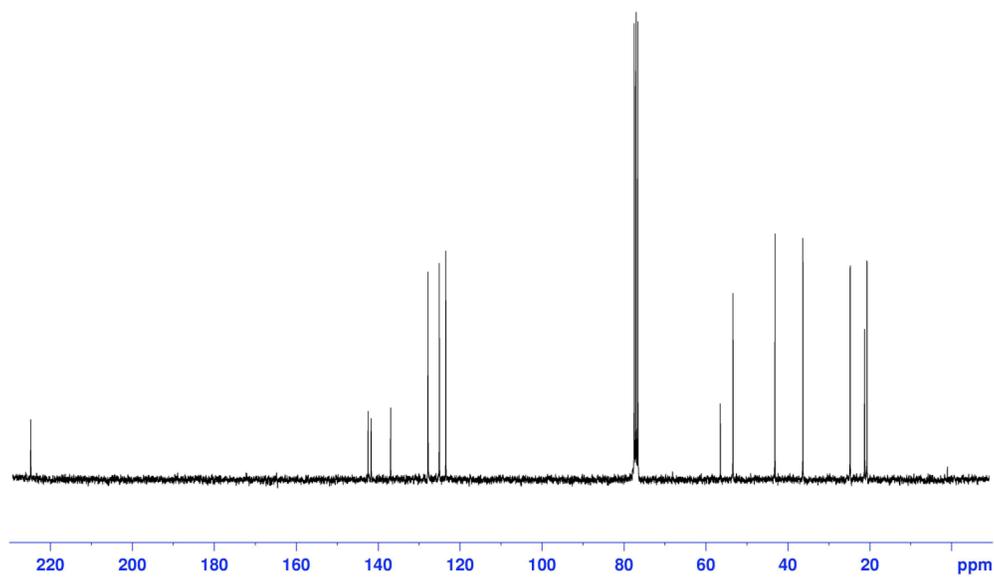
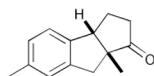
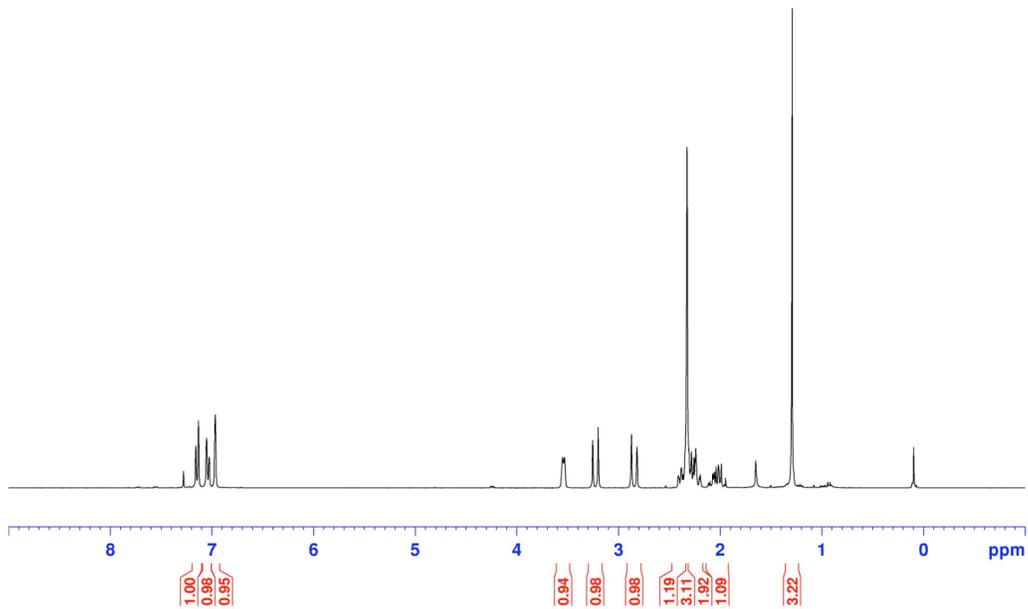
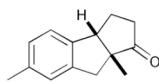
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **11**

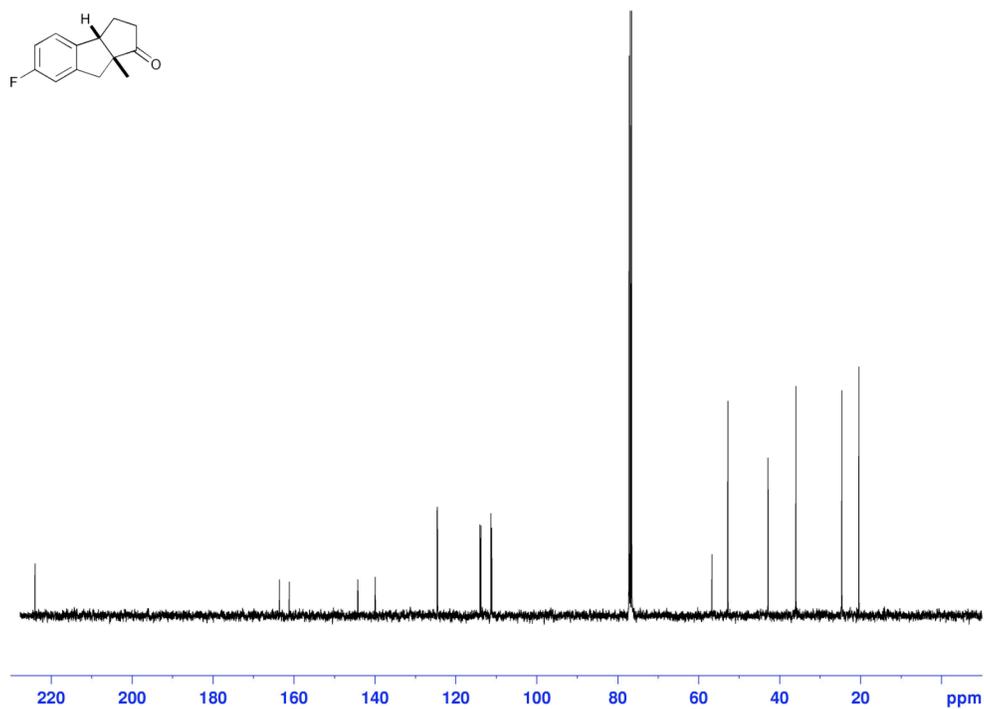
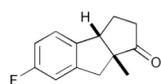
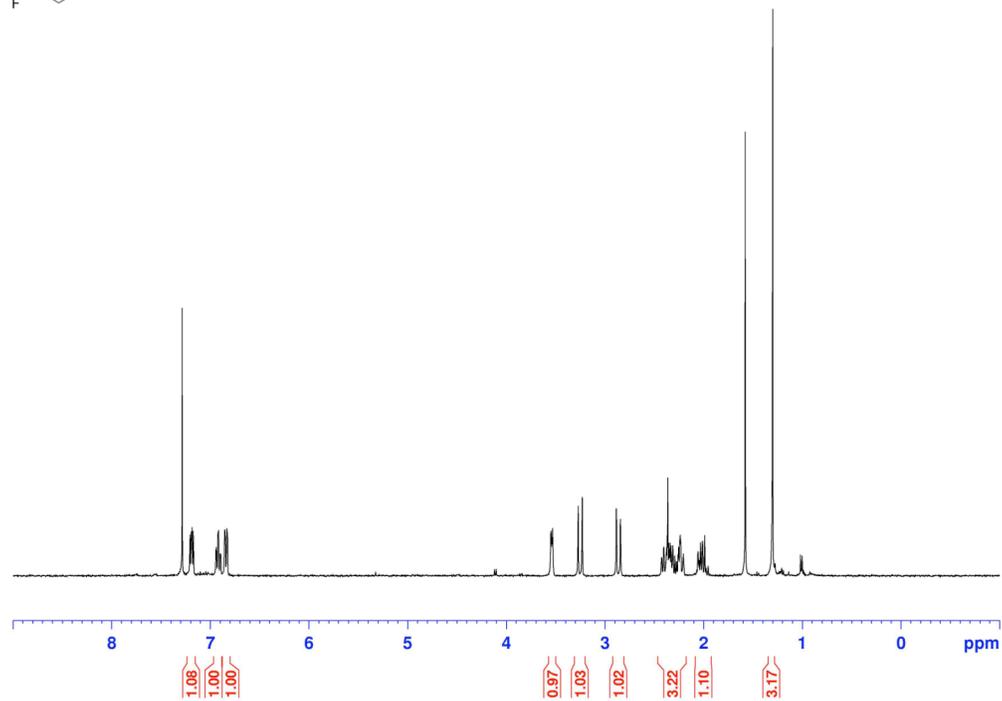
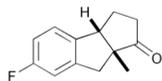
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **21**

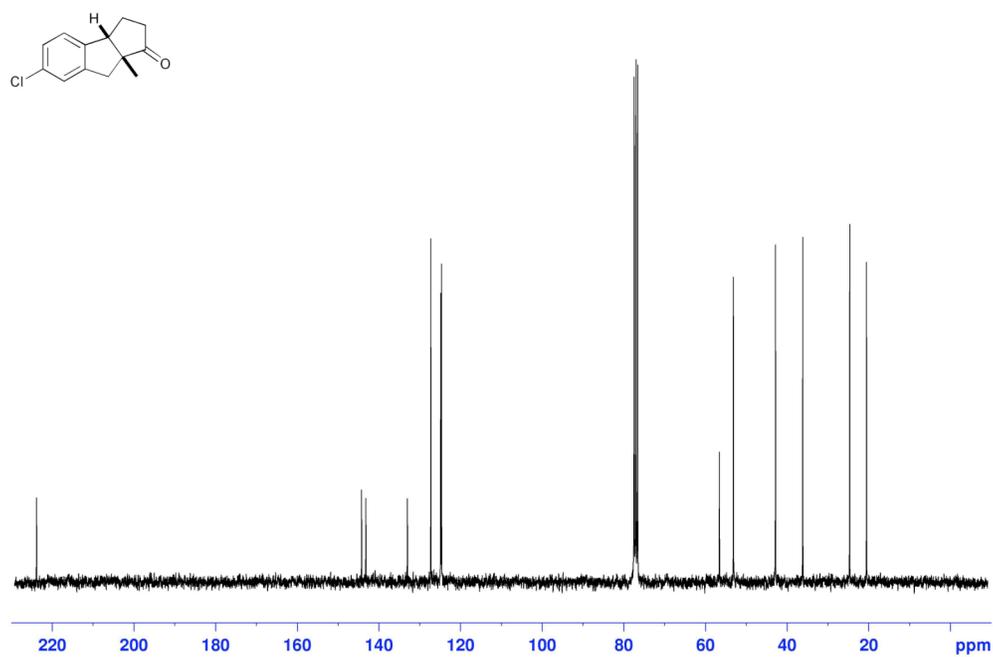
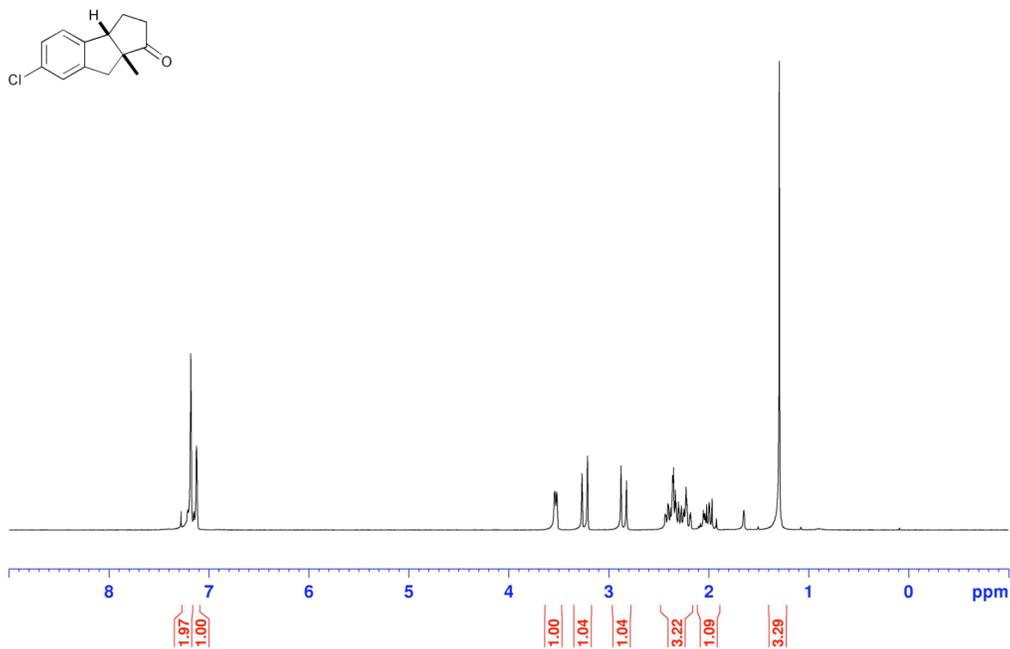
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **2**

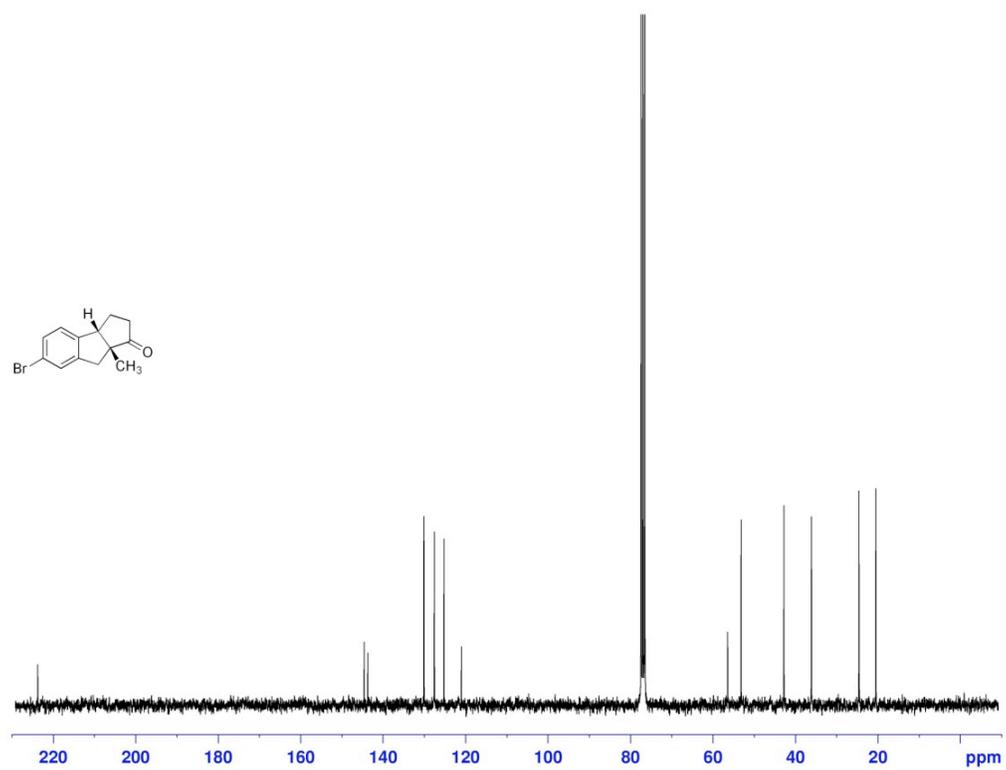
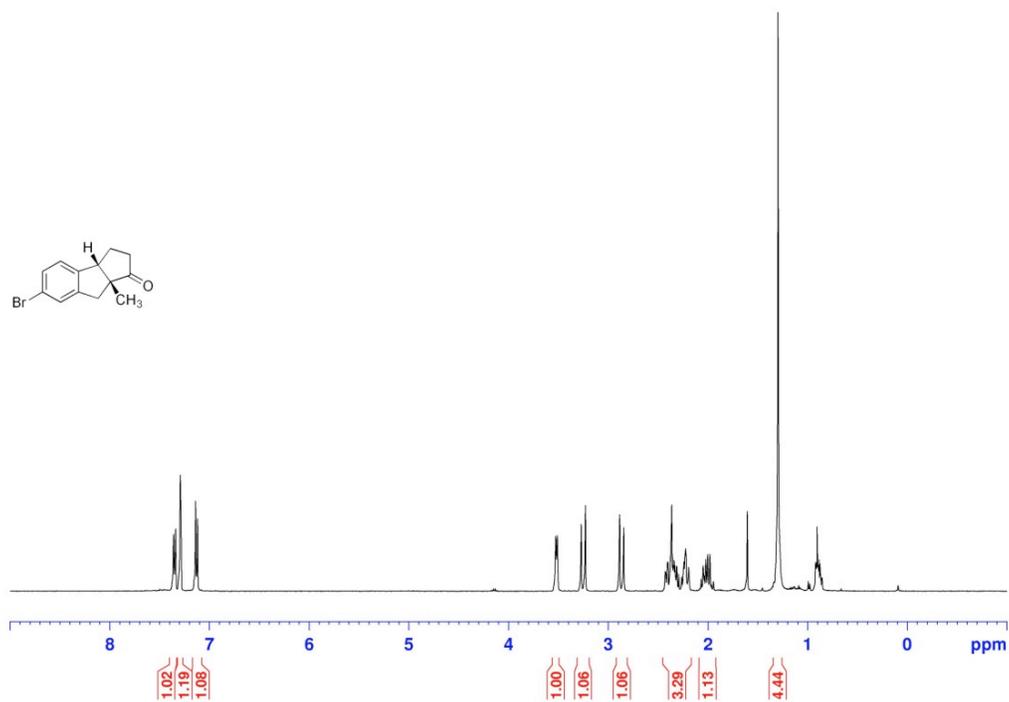
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **3**

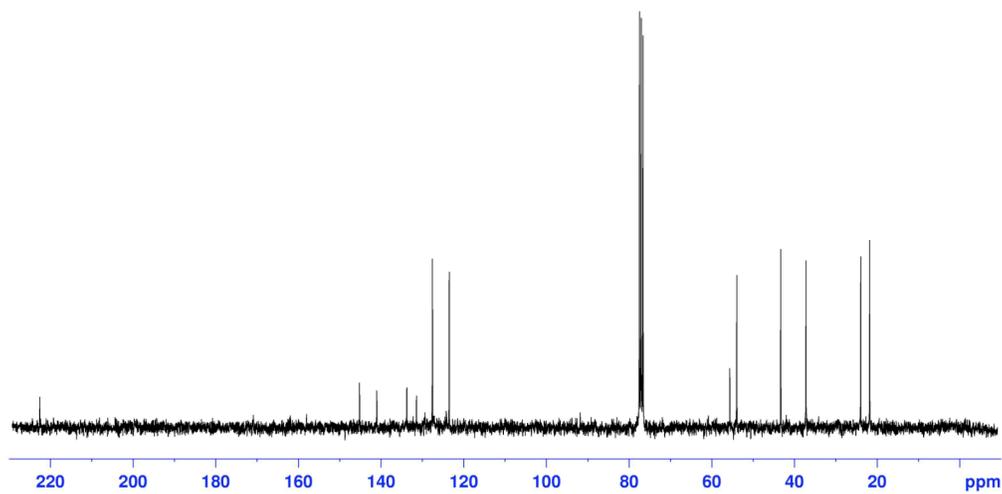
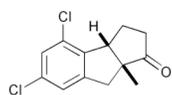
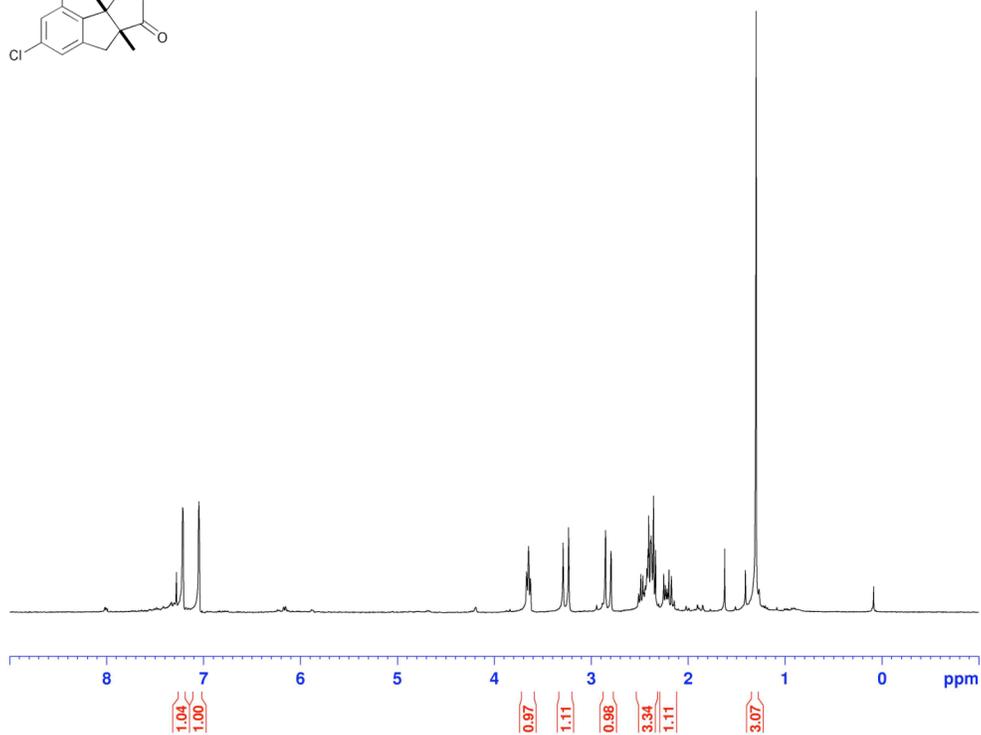
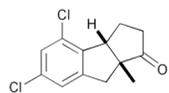
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **12**

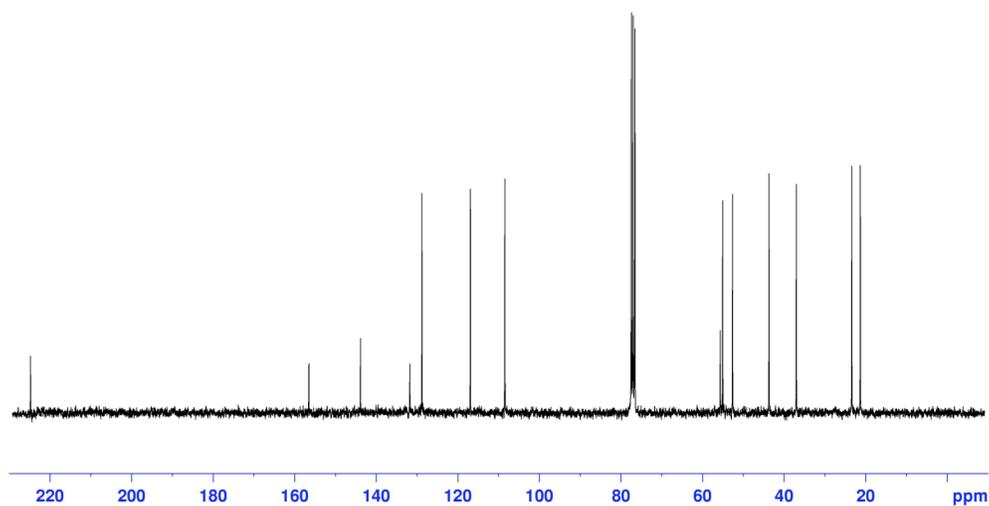
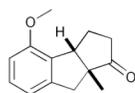
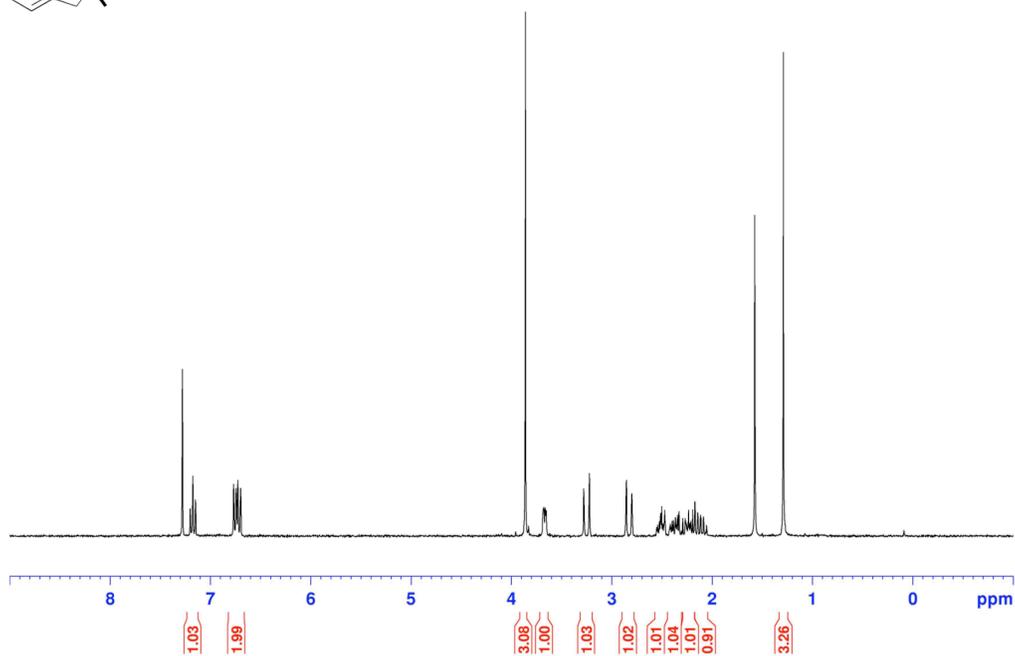
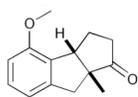
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **13**

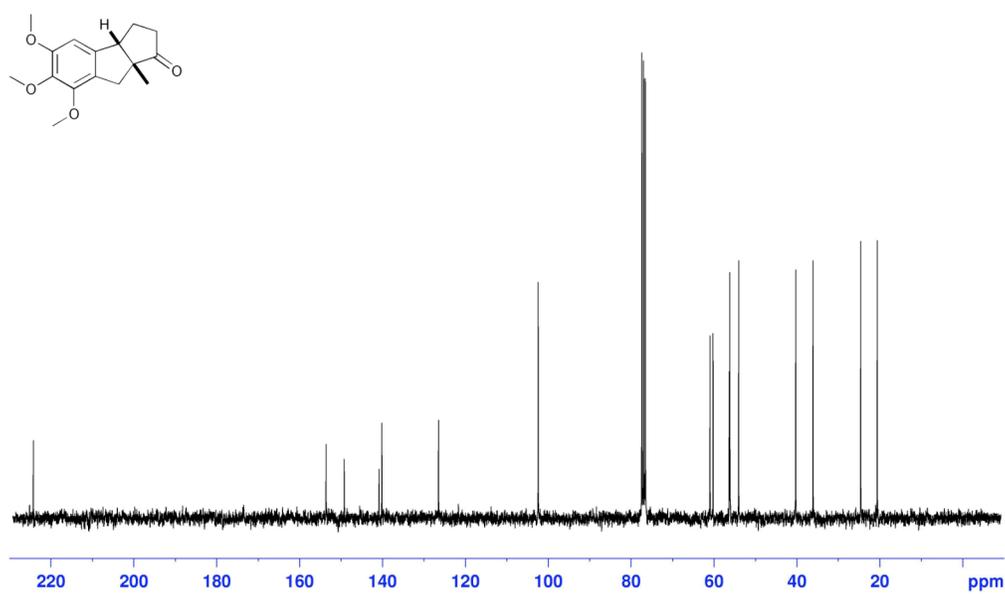
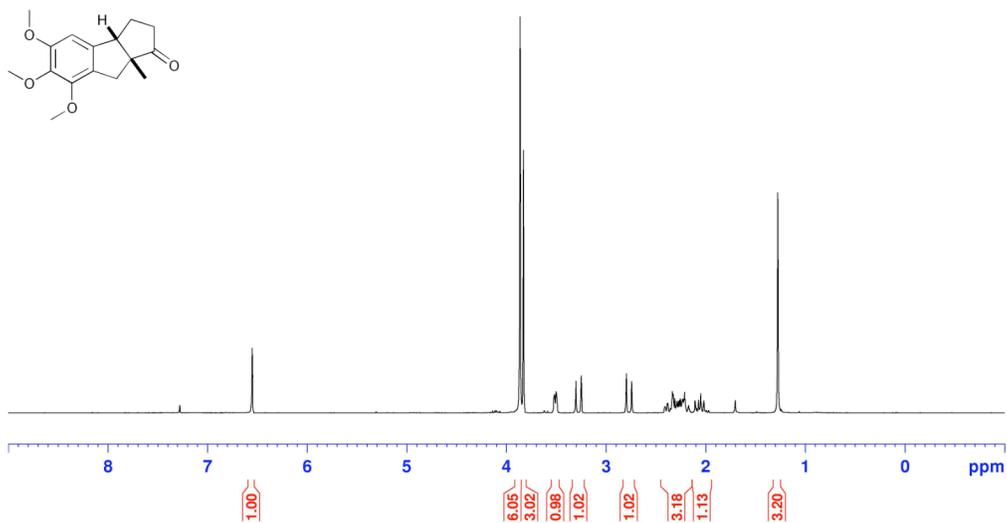
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **14**

$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **15**

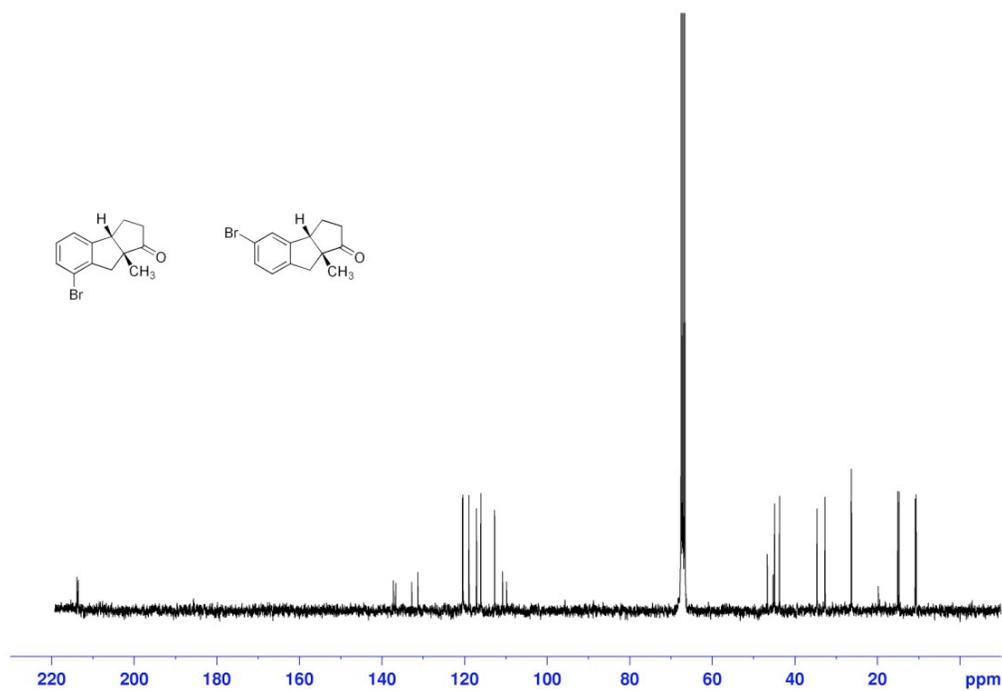
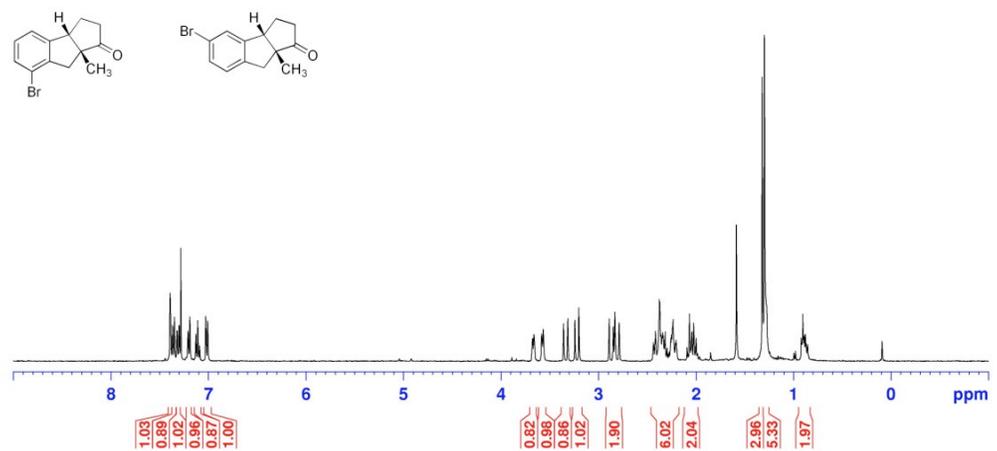
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **16**

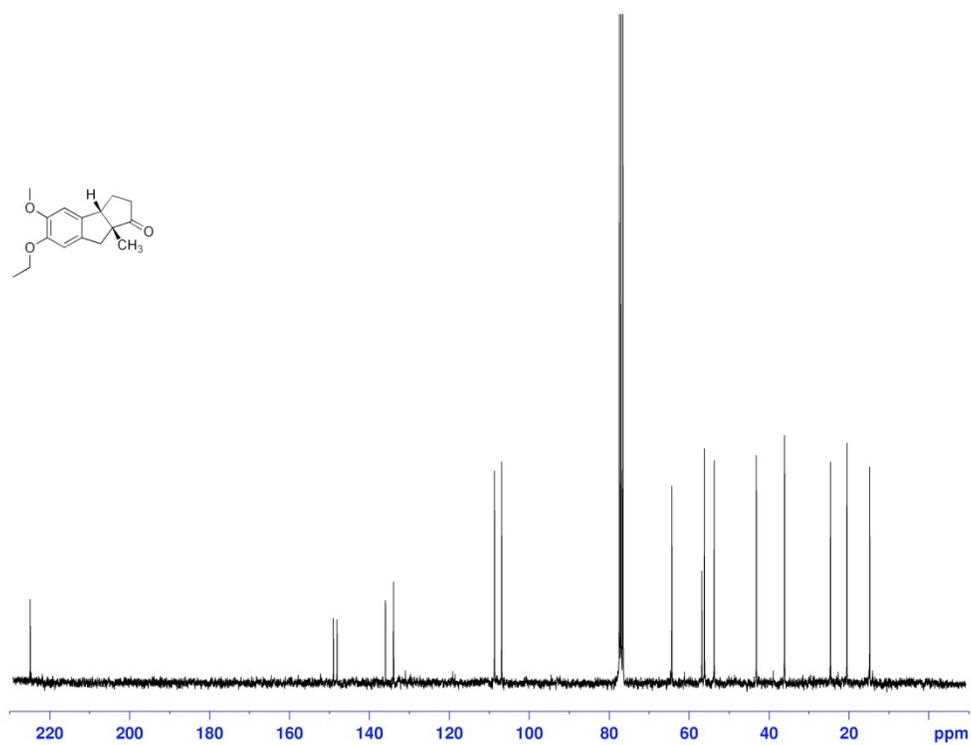
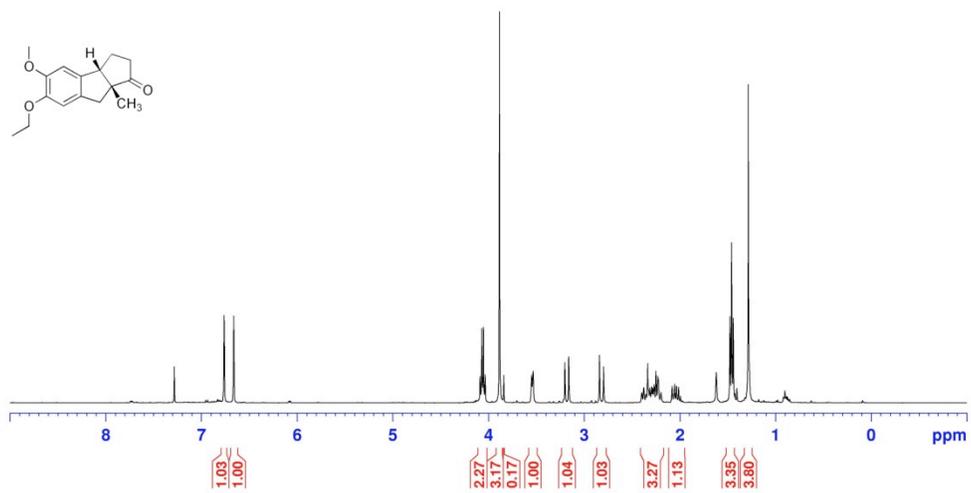
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **17**

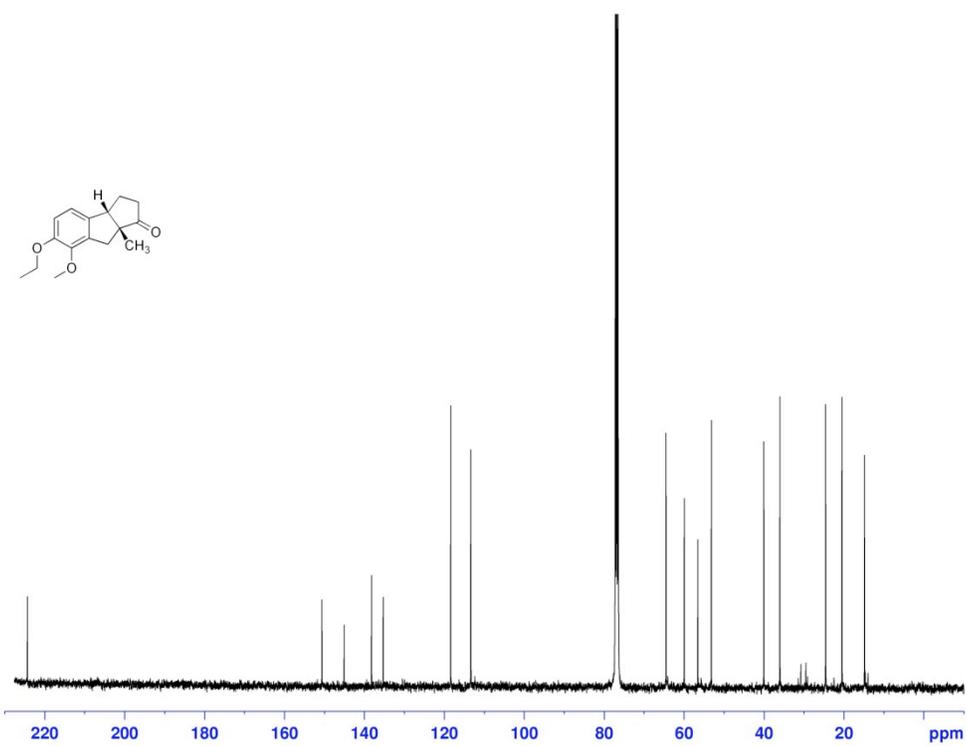
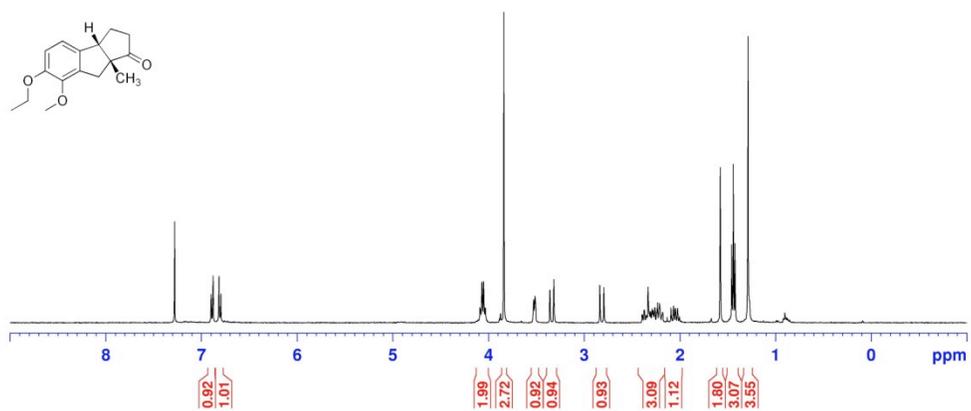
$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **18**

$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **19**

$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compounds **22** and **23** (mixture)



$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **24**

$^1\text{H}$  and  $^{13}\text{C}$ -NMR data for compound **25**

### References

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- <sup>1</sup> Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
  - <sup>2</sup> Shi, M.; Liu, L-P; Tang, J. *J. Am. Chem. Soc.* **2006**, *128*, 7430.
  - <sup>3</sup> Aggarwal, V.; Grainger, R.; Gültekin, Z; Adams, H.; Spargo, P. *J. Org. Chem.* **1995**, *60*, 4962.
  - <sup>4</sup> Cohen, T.; Brockunier, L.; *Tetrahedron*, **1989**, *45*, 2917