

## Ligand- and Brønsted Acid/Base-Switchable Reaction Pathways in Gold(I)-Catalyzed Cycloisomerizations of Allenic Acids

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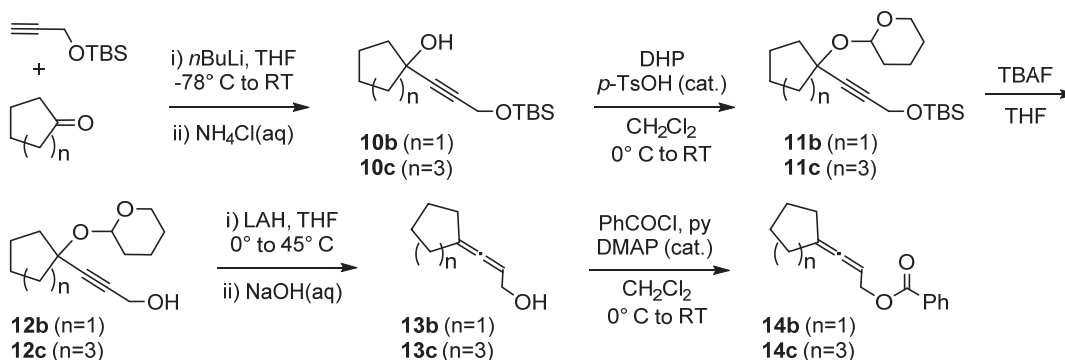
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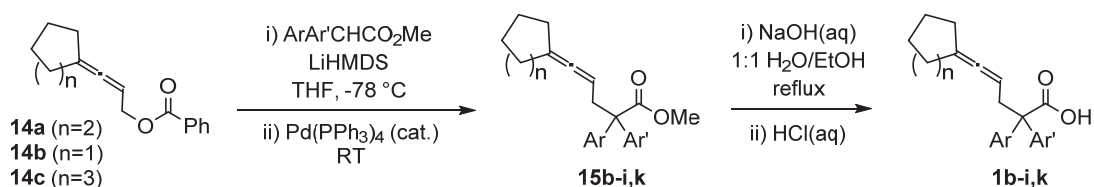
## SYNTHESIS OF ALLENOIC ACID SUBSTRATES (1a-k)

Substrates **1a** and **1j** were synthesized by literature procedures.<sup>1</sup> Substrates **1b** and **1c** were synthesized by a modified procedure starting from the corresponding cycloalkanones (Schemes S1 and S2).<sup>2</sup> Substrates **1d-i** and **1k** were synthesized according to Scheme S2,<sup>2,3</sup> starting from allenic esters **14a**<sup>1a</sup> or **14b**. Pd(PPh<sub>3</sub>)<sub>4</sub> (min. 99.5%, min. 9% wt/wt Pd) was purchased from Chem-Impex International, Inc.

**Scheme S1.** Synthesis of precursors to allenic acid substrates.



**Scheme S2.** Synthesis of allenic acid substrates.



**1-(3-((*tert*-Butyldimethylsilyloxy)prop-1-yn-1-yl)cyclopentanol (10b).** To a well-dried two neck round-bottom flask equipped with a septum and nitrogen balloon, 70 mL dry THF and *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (5.0 g, 29 mmol) were added. The reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , and then 11.7 mL of *n*BuLi (2.5 M in hexanes; 29 mmol)

was added slowly over 5 min via syringe. The reaction mixture was stirred for 10 min at  $-78\text{ }^{\circ}\text{C}$ . Cyclopentanone (2.60 mL, 29.4 mmol) was then slowly added to the reaction mixture over 2 min. The reaction mixture was stirred for 30 min at  $-78\text{ }^{\circ}\text{C}$  and then for an additional 50 min at  $25\text{ }^{\circ}\text{C}$ . The reaction mixture was quenched with 0.5 M aqueous  $\text{NH}_4\text{Cl}$  and then extracted twice with 100 mL of diethyl ether. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to obtain a viscous oil, which was purified by flash column chromatography on silica.  $R_f$  0.45 (1:9 diethyl ether/hexanes); colorless oil, yield 7.0 g (94%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.35 (s, 2H), 2.04 (br. s, 1H, OH), 1.89-1.82 (m, 2H), 1.72-1.59 (m, 2H), 1.58-1.46 (m, 4H), 0.90 (s, 9H), 0.12 (s, 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  88.6, 81.9, 74.6, 51.9, 42.4, 26.0, 23.5,  $-4.9$  ppm. IR (neat):  $\nu$  3274, 2359, 1104, 1070  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si} + \text{H}]^+$ ) calcd 255.1780, found  $m/z$  255.1784.

**1-(3-((*tert*-Butyldimethylsilyloxy)prop-1-yn-1-yl)cycloheptanol (10c).** To a well-dried two neck round-bottom flask equipped with a septum and nitrogen balloon, 50 mL dry THF and *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (5.0 g, 29 mmol) were added. The reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , and then 11.7 mL of *n*BuLi (2.5 M in hexanes; 29 mmol) was added slowly over 5 min via syringe. The reaction mixture was stirred for 45 min at  $-78\text{ }^{\circ}\text{C}$ . Cycloheptanone (3.50 mL, 29.7 mmol) was then slowly added to the reaction mixture over 2 min. The reaction mixture was stirred for 1 h at  $-78\text{ }^{\circ}\text{C}$  and then for an additional 2 h at  $25\text{ }^{\circ}\text{C}$ . The reaction mixture was quenched with 0.5 M aqueous  $\text{NH}_4\text{Cl}$  and then extracted twice with 100 mL of diethyl ether. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to obtain a viscous oil. After further drying under high vacuum, an analytically pure white solid was obtained. White solid, m.p. 62-63  $^{\circ}\text{C}$ , yield 7.40 g (89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.35 (s, 2H), 2.01 (d,  $J = 8.0$  Hz, 1H), 1.98 (d,  $J = 8.0$  Hz, 1H), 1.85-1.77 (m, 3H), 1.67-1.49 (m, 7H), 0.91 (s, 9H), 0.12 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  89.7, 82.1, 71.8, 51.9, 43.2, 28.3, 25.9, 22.3,  $-4.9$ . IR (neat):  $\nu$  3272, 2358, 1101, 1071  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si} + \text{H}]^+$ ) calcd 283.2093, found  $m/z$  283.2101.

***tert*-Butyldimethyl[3-(1-((tetrahydro-2*H*-pyran-2-yl)oxy)cyclopentyl)prop-2-yn-1-yl]oxy]silane (11b).** To a solution of **10b** (3.17 g, 12.4 mmol) in 5 mL of dry dichloromethane was added  $\text{TsOH}\cdot\text{H}_2\text{O}$  (12 mg, 0.063 mmol), and the reaction mixture was stirred for 10 min at 0

°C. 3,4-Dihydro-2*H*-pyran (8.8 mL, 96 mmol) was then added, and the reaction mixture was stirred for 12 h at 25 °C. The reaction mixture was quenched with 5 mL of NEt<sub>3</sub> and then stirred for an additional 20 min at 25 °C. The solvent was evaporated to obtain a viscous yellow oil. The crude material was dissolved in 200 mL of diethyl ether and then washed sequentially with 0.5 M NaHCO<sub>3</sub>, 0.05 M cold HCl, and water. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was again removed, and the crude product was purified by flash chromatography on silica. *R*<sub>f</sub> 0.55 (1:19 diethyl ether/hexanes); viscous yellow oil, yield 3.37 g (80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.04 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.35 (s, 2H), 3.94-3.89 (m, 1H), 3.53-3.47 (m, 1H), 2.24-2.18 (m, 1H), 2.00-1.47 (m, 13H), 0.91 (s, 9H), 0.12 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 96.7, 86.6, 83.3, 81.0, 63.6, 52.0, 41.4, 40.0, 32.1, 25.9, 25.6, 23.4, 23.0, 20.5, 18.4, -4.9. IR (neat): ν 3276, 2368, 1111, 1070 cm<sup>-1</sup>. HRMS (ESI-orbitrap, [C<sub>19</sub>H<sub>34</sub>O<sub>3</sub>Si + H]<sup>+</sup>) calcd 339.2355, found *m/z* 339.2361.

***tert*-Butyldimethyl[(3-(1-((tetrahydro-2*H*-pyran-2-yl)oxy)cycloheptyl)prop-2-yn-1-yl)oxy]silane (11c).** This compound was synthesized from **10c** (10.0 g, 35.4 mmol) by the same procedure used to prepare **11b**. *R*<sub>f</sub> 0.67 (1:19 diethyl ether/hexanes); viscous yellow oil, yield 9.34 g (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.05 (dd, *J* = 6.4, 3.6 Hz, 1H), 4.36 (s, 2H), 3.96-3.91 (m, 1H), 3.50-3.46 (m, 1H), 2.02-1.95 (m, 3H), 1.89-1.82 (m, 2H), 1.71-1.45 (m, 13H), 0.90 (s, 9H), 0.12 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 96.0, 87.4, 83.8, 78.4, 63.7, 51.9, 42.2, 40.8, 32.4, 28.8, 25.9, 25.6, 22.2, 22.0, 20.7, 18.3, -4.9. IR (neat): ν 3277, 2357, 1101, 1076 cm<sup>-1</sup>. HRMS (ESI-orbitrap, [C<sub>21</sub>H<sub>38</sub>O<sub>3</sub>Si + H]<sup>+</sup>) calcd 367.2668, found *m/z* 367.2667.

**3-[1-((Tetrahydro-2*H*-pyran-2-yl)oxy)cyclopentyl]prop-2-yn-1-ol (12b).** To a solution of **11b** (3.94 g, 11.6 mmol) in 50 mL of THF was added [*n*Bu<sub>4</sub>N]F (3.34 g, 12.8 mmol), and the reaction mixture was stirred for 12 h at 25 °C. After complete consumption of the starting material as monitored by TLC, the reaction mixture was diluted with 100 mL of ethyl acetate and then washed thoroughly with water. The organic layer was separated and dried over anhydrous sodium sulfate. The crude material was purified by column chromatography on silica. *R*<sub>f</sub> 0.48 (1:4 acetone/hexanes); viscous yellow oil, yield 1.8 g (69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.05 (dd, *J* = 4.8, 3.2 Hz, 1H), 2.28 (d, *J* = 6.4 Hz, 2H), 3.95-3.89 (m, 1H), 3.54-3.49 (m, 1H), 2.37-2.30 (m, 1H), 2.22-2.15 (m, 1H), 2.01-1.88 (m, 2H), 1.85-1.75 (m, 4H), 1.74-1.64 (m, 3H), 1.58-1.48 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 96.3, 87.4, 83.0, 80.7, 63.3, 51.2,

41.2, 40.3, 32.0, 25.5, 23.4, 23.0, 20.1. IR (neat):  $\nu$  3312, 3257, 2359, 1103, 1066  $\text{cm}^{-1}$ . HRMS (ESI,  $[\text{C}_{13}\text{H}_{20}\text{O}_3 + \text{Na}]^+$ ) calcd 247.1310, found  $m/z$  247.1313.

**3-[1-((Tetrahydro-2H-pyran-2-yl)oxy)cycloheptyl]prop-2-yn-1-ol (12c).** This compound was synthesized from **11c** (11.6 g, 31.7 mmol) by the same procedure used to prepare **12b**.  $R_f$  0.50 (1:4 acetone/hexanes); viscous yellow oil, yield 6.0 g (75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.08 (dd,  $J = 5.2, 3.6$  Hz, 1H), 4.30 (s, 2H), 3.98-3.92 (m, 1H), 3.53-3.47 (m, 1H), 2.11 (br. s, 1H, OH), 2.06-1.95 (m, 2H), 1.96 (d,  $J = 7.6$  Hz, 1H), 1.90-1.79 (m, 2H), 1.72-1.57 (m, 3H), 1.56-1.46 (m, 10H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  95.7, 88.6, 83.5, 78.1, 63.3, 51.3, 42.0, 41.2, 32.3, 28.7, 28.2, 25.6, 22.3, 22.1, 19.3. IR (neat):  $\nu$  3311, 3258, 2358, 1101, 1066  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{15}\text{H}_{24}\text{O}_3 + \text{Na}]^+$ ) calcd 275.1623, found  $m/z$  275.1630.

**3-Cyclopentylideneprop-2-en-1-ol (13b).** A well-dried 500 mL two-neck round bottom flask was fitted with a condenser topped with a nitrogen balloon, and 200 mL of dry THF was added by syringe. The flask contents were cooled to 0 °C under inert atmosphere, and  $\text{LiAlH}_4$  (2.33 g, 61.6 mmol) was added under nitrogen counterflow. The slurry was stirred for 5 min, and then a solution of **12b** (6.9 g, 31 mmol) in 20 mL of dry THF was added dropwise via syringe. The reaction mixture was allowed to warm to 25 °C and then heated at reflux for 45 min. The mixture was then cooled to 0 °C, and the unreacted  $\text{LiAlH}_4$  was quenched with 5.0 *M* NaOH. The quenched mixture was stirred for 30 min at 25 °C and then diluted with 200 mL of diethyl ether and filtered through celite. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to obtain analytically pure material as a colorless oil.  $R_f$  0.38 (1:4 acetone/hexanes); colorless oil, yield 2.8 g (73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.33-5.26 (m, 1H), 4.08 (d,  $J = 5.2$  Hz, 2H), 2.40-2.36 (m, 4H), 1.71-1.65 (m, 4H), 1.55 (br s, 1H, OH).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  196.4, 107.1, 92.7, 61.3, 31.7, 27.4. IR (neat)  $\nu$  3311 (m), 1961 (w), 1901 (w)  $\text{cm}^{-1}$ . HRMS (ESI,  $[\text{C}_8\text{H}_{12}\text{O} + \text{H}]^+$ ) calcd 125.0966, found  $m/z$  125.0954.

**3-Cycloheptylideneprop-2-en-1-ol (13c).** This compound was synthesized from **12c** (4.0 g, 16 mmol) by the same procedure used to prepare **13b**.  $R_f$  0.39 (1:4 acetone/hexanes); colorless oil, yield 1.8 g (75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.20-5.16 (m, 1H), 4.06 (t,  $J = 6.0$  Hz, 2H), 2.27-2.24 (m, 4H), 1.65-1.51 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.7, 108.0, 89.7, 61.2, 32.6, 29.4, 28.6. HRMS (ESI-orbitrap,  $[\text{C}_{10}\text{H}_{16}\text{O} + \text{Na}]^+$ ) calcd 175.1099, found  $m/z$  175.1101.

**3-Cyclopentylideneallyl benzoate (14b).** This compound was prepared by a modification of literature procedures used to prepare **14a**.<sup>1a</sup> Under dry conditions, a solution of allenol **13b** (1.90 g, 15.2 mmol) in 50 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was placed in a two-necked round bottom flask. The solution was cooled to 0 °C, and pyridine (1.4 mL, 17 mmol) and a catalytic amount of DMAP (186 mg, 1.52 mmol) were added followed by slow syringe addition of benzoyl chloride (2.6 mL, 22 mmol). The reaction mixture was then warmed to RT and stirred for an additional 12 h. After complete consumption of starting material as monitored by TLC, the solvent was evaporated under reduced pressure. The resulting oily residue was dissolved in 50.0 mL CH<sub>2</sub>Cl<sub>2</sub> and then sequentially washed with cold 0.5 M HCl (2 x 50 mL) and saturated aqueous NaHCO<sub>3</sub>. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to obtain a pale yellow viscous oil, which was purified by flash column chromatography on silica. *R*<sub>f</sub> 0.52 (8:92 diethyl ether/hexanes); yellow oil, yield 3.13 g (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.08-8.05 (m, 2H), 7.57-7.53 (m, 1H), 7.35 (dt, *J* = 7.6, 1.6 Hz, 2H), 5.35-5.28 (m, 1H), 4.79 (d, *J* = 6.8 Hz, 2H), 2.40-2.36 (m, 4H), 1.67-1.61 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 198.8, 166.5, 133.0, 130.1, 129.7, 128.4, 106.1, 87.4, 63.8, 31.3, 27.1. IR (neat): ν 2958 (m), 2867 (m), 1972 (w), 1715 (s), 1450 (m) cm<sup>-1</sup>. HRMS (ESI-orbitrap, [C<sub>15</sub>H<sub>16</sub>O<sub>2</sub> + H]<sup>+</sup>) calcd 229.1229, found *m/z* 229.1222.

**3-Cycloheptylideneallyl benzoate (14c).** This compound was prepared from **13c** (1.30 g, 8.51 mmol) by the same procedure used to synthesize **14b**. The compound was highly unstable over silica and was used immediately after moderate purification. *R*<sub>f</sub> 0.56 (8:92 diethyl ether/hexanes); colorless oil, yield 1.95 g (89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.08-8.06 (m, 2H), 7.55-7.53 (m, 1H), 7.43 (dt, *J* = 8.0, 1.6 Hz, 2H), 5.24-5.19 (m, 1H), 4.77 (d, *J* = 6.4 Hz, 2H), 2.29-2.24 (m, 4H), 1.63-1.57 (m, 4H), 1.54-1.49 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 203.3, 166.5, 132.9, 130.6, 129.8, 128.4, 106.9, 84.7, 63.9, 32.3, 29.4, 28.4. IR (neat): ν 3068 (w), 2923 (m), 2850 (m), 1960 (w), 1717 (s), 1601 (w), 1584 (w), 1451 (m). HRMS (ESI-orbitrap, [C<sub>17</sub>H<sub>20</sub>O<sub>2</sub> + H]<sup>+</sup>) calcd 257.1542, found *m/z* 257.1551.

**General procedure for the synthesis of 2,2-diaryl allene methyl esters (15b-i,k).** A modification of literature procedures was used.<sup>1a,4</sup> Into an oven-dried 100 mL, two-neck round bottom flask containing the corresponding methyl diarylacetate<sup>56</sup> (1.0 equiv relative to **14**) was added 50.0 mL of dry THF via vacuum distillation. The reaction mixture was cooled to -78 °C, and lithium hexamethyldisilazide (1.18 g, 7.08 mmol) was added under argon counterflow. The

reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  under argon for approximately 2 h. Meanwhile, 100 mL of dry THF was distilled under vacuum into another oven-dried 250 mL two-neck round bottom flask, and a solution of **14** (3.0-5.0 mmol) in dry THF was added via syringe followed by addition of  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%). This mixture was stirred at room temperature for 2 h, then cooled to  $-78\text{ }^{\circ}\text{C}$  and transferred via cannula into the vessel containing the cold ( $-78\text{ }^{\circ}\text{C}$ ) solution of lithiated methyldiaryl acetate. The resulting mixture was allowed to warm slowly to room temperature and stirred for 12 h. The mixture was then diluted with 100 mL of ethyl acetate and sequentially washed with 0.5 M  $\text{NaHCO}_3$  and water. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to obtain the crude product, which was purified by flash column chromatography on silica.

**Methyl-5-cyclopentylidene-2,2-diphenylpent-4-enoate (15b).** Because of inseparable impurities, compound was used as obtained for the next step without further purification. Viscous oil, yield 1.12 g (82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34-7.23 (m, 10H), 7.87-7.79 (m, 1H), 3.70 (s, 3H), 3.10 (d,  $J = 7.2$  Hz, 2H), 2.15-2.11 (m, 4H), 1.59-1.54 (m, 4H).

**Methyl-5-cycloheptylidene-2,2-diphenylpent-4-enoate (15c).**  $R_f$  0.55 (1:9 acetone/hexanes); yellow viscous oil, yield 0.95 g (89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32-7.22 (m, 10H), 4.75-4.69 (m, 1H), 3.70 (s, 3H), 3.10 (d,  $J = 7.2$  Hz, 2H), 2.12-1.99 (m, 4H), 1.55-1.46 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 174.7, 142.6, 129.2, 127.9, 126.8, 103.8, 84.3, 60.7, 52.5, 39.6, 32.2, 29.4, 28.5. HRMS (ESI-orbitrap,  $[\text{C}_{25}\text{H}_{28}\text{O}_2 + \text{H}]^+$ ) calcd 361.2167, found  $m/z$  361.2165.

**Methyl-2,2-bis(4-chlorophenyl)-5-cyclohexylidenepent-4-enoate (15d).**  $R_f$  0.59 (1:9 acetone/hexanes); yellow viscous oil, yield 1.20 g (78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28-7.24 (m, 4H), 7.21-7.18 (m, 4H), 4.68-4.63 (m, 1H), 3.70 (s, 3H), 3.03 (d,  $J = 7.2$  Hz, 2H), 1.88-1.87 (m, 4H), 1.53-1.44 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.8, 173.9, 140.8, 133.1, 130.6, 128.2, 102.3, 83.83, 59.9, 52.7, 39.5, 31.2, 27.4, 26.1. HRMS (ESI,  $[\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{O}_2 + \text{H}]^+$ ) calcd 415.1232, found  $m/z$  415.1228.

**Methyl-2,2-bis(4-chlorophenyl)-5-cyclopentylidenepent-4-enoate (15e).**  $R_f$  0.56 (1:9 acetone/hexanes); yellow viscous oil, yield 1.10 g (79%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27-7.23 (m, 4H), 7.19-7.15 (m, 4H), 4.79-4.72 (m, 1H), 3.68 (s, 3H), 3.01 (d,  $J = 7.6$  Hz, 2H), 2.15-2.08 (m, 4H), 1.58-1.55 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.6, 173.9, 140.8, 133.1,

130.5, 128.2, 103.7, 86.5, 59.8, 52.7, 39.2, 31.0, 27.1. HRMS (ESI,  $[C_{23}H_{22}Cl_2O_2 + Na]^+$ ) calcd 423.0895, found  $m/z$  423.0889.

**Methyl-5-cyclohexylidene-2,2-bis(2,3-dihydrobenzofuran-5-yl)pent-4-enoate (15f).**  $R_f$  0.49 (3:7 ethyl acetate/hexanes); yellow viscous oil, yield 1.75 g (82%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.12-7.11 (m, 2H), 7.01 (dd,  $J = 8.8, 1.6$  Hz, 2H), 6.69 (d,  $J = 8.4$  Hz, 2H), 4.71-4.67 (m, 1H), 4.55 (t,  $J = 8.8$  Hz, 4H), 3.69 (s, 3H), 3.16 (t,  $J = 8.8$  Hz, 4H), 3.02 (d,  $J = 7.6$  Hz, 2H), 1.94-1.92 (m, 4H), 1.55-1.44 (m, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  200.5, 175.4, 158.9, 135.1, 129.0, 126.5, 125.8, 108.5, 101.8, 84.9, 71.5, 59.7, 52.4, 40.2, 31.3, 30.0, 27.5, 26.3. HRMS (ESI,  $[C_{28}H_{30}O_4 + Na]^+$ ) calcd 453.2042, found  $m/z$  453.2036.

**Methyl-5-cyclopentylidene-2,2-bis(2,3-dihydrobenzofuran-5-yl)pent-4-enoate (15g).**  $R_f$  0.45 (3:7 ethyl acetate/hexanes); yellow viscous oil, yield 1.12 g (79%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.12-7.11 (m, 2H), 7.01 (dd,  $J = 8.4, 1.6$  Hz, 2H), 6.69 (d,  $J = 8.4$  Hz, 2H), 4.84-4.78 (m, 1H), 4.56 (t,  $J = 8.8$  Hz, 4H), 3.69 (s, 3H), 3.17 (t,  $J = 8.8$  Hz, 4H), 3.02 (d,  $J = 7.6$  Hz, 2H), 2.20-2.16 (m, 4H), 1.61-1.57 (m, 4H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  199.3, 175.4, 158.9, 135.1, 128.9, 126.5, 125.8, 108.4, 103.1, 87.5, 71.5, 59.7, 52.4, 39.8, 30.9, 30.0, 27.1. HRMS (ESI,  $[C_{27}H_{28}O_4 + Na]^+$ ) calcd 439.1885, found  $m/z$  439.1880.

**Methyl-9-(3-cyclohexylideneallyl)-9H-xanthene-9-carboxylate (15h).**  $R_f$  0.48 (1:9 acetone/hexanes); yellow viscous oil, yield 1.20 g (87%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.24-7.20 (m, 2H), 7.16 (dd,  $J = 7.6, 1.2$  Hz, 2H), 7.07-7.01 (m, 4H), 4.41-4.36 (m, 1H), 3.59 (s, 3H), 2.95 (d,  $J = 7.6$  Hz, 2H), 1.61-1.53 (m, 4H), and 1.36-1.27 (m, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  201.2, 174.5, 150.8, 134.0, 133.8, 128.6, 127.3, 123.2, 121.4, 116.7, 101.9, 82.5, 52.9, 50.5, 42.1, 31.1, 27.3, 26.1. HRMS (ESI,  $[C_{24}H_{24}O_3 + Na]^+$ ) calcd 383.1623, found  $m/z$  383.1622.

**Methyl-9-(3-cyclopentylideneallyl)-9H-xanthene-9-carboxylate (15i).**  $R_f$  0.46 (1:9 acetone/hexanes); yellow viscous oil, yield 1.20 g (89%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.24-7.16 (m, 4H), 7.06-7.01 (m, 4H), 4.61-4.53 (m, 1H), 3.58 (s, 3H), 2.99 (d,  $J = 6.8$  Hz, 2H), 1.92-1.83 (m, 2H), 1.71-1.62 (m, 2H), 1.45-1.41 (m, 4H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  199.7, 174.4, 150.8, 134.0, 133.8, 128.6, 127.2, 123.3, 121.5, 116.7, 103.8, 85.3, 52.9, 50.2, 41.0, 30.7, 26.9. HRMS (ESI,  $[C_{23}H_{22}O_3 + Na]^+$ ) calcd 369.1467, found  $m/z$  369.1464.

**Methyl-5-cyclohexylidene-2-(3-methoxyphenyl)-2-phenylpent-4-enoate (15k).** Due to inseparable impurities, the compound was only moderately purified by flash column



chromatography and was used as such for the next step.  $R_f$  0.55 (3:7 diethyl ether/hexanes); yellow viscous oil, yield 1.12 g (70%; per  $^1\text{H}$  NMR).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33-7.18 (m, 6H), 6.86-6.75 (m, 3H), 4.74-4.68 (m, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.11-3.01 (m, 2H), 1.88-1.86 (m, 4H), 1.51-1.41 (m, 6H).

**2-(3-Methoxyphenyl)-2-phenylacetic acid (16).** This compound was prepared according to the literature procedure via the corresponding diaryl acetonitrile.<sup>6a,6b</sup> Full characterization data of **16** have not been previously reported.  $R_f$  0.39 (4:19 diethyl ether/hexanes); colorless oil, yield 1.98 g (93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.1 (br. s, 1H, COOH), 7.34-7.23 (m, 6H), 6.92 (dd,  $J = 7.6, 0.8$  Hz, 1H), 6.88 (t,  $J = 2.0$  Hz, 1H), 6.82 (ddd,  $J = 8.0, 2.8, 0.8$  Hz, 1H), 5.02 (s, 1H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  177.8, 159.9, 139.5, 137.9, 129.8, 129.5, 128.8, 127.7, 121.2, 114.8, 112.9, 57.0, 55.4. IR (neat):  $\nu$  3045, 2955  $\text{cm}^{-1}$ . HRMS (ESI,  $[\text{C}_{15}\text{H}_{14}\text{O}_3 + \text{Na}]^+$ ) calcd 265.0841, found  $m/z$  265.0844.

**Methyl-2-(3-methoxyphenyl)-2-phenylacetate (17).** The compound was prepared from **16** via Fischer esterification. Analytical data were in agreement with the literature.<sup>6c,7</sup>

**General procedure for synthesis of allenic acid substrates (1b-i,k).** Into a 100 mL two-neck round bottom flask fitted with a condenser was added a solution of allene ester **15** (2.1 – 2.9 mmol) in 30 mL of ethanol. Aqueous 2.0 M NaOH (30 mL) was added, and the reaction mixture was heated at reflux for 12 h. The reaction mixture was then cooled to 25 °C and diluted with 20 mL of water. This mixture was washed with 50 mL of hexanes. The aqueous layer was separated and washed twice more with 10 mL portions of hexanes. The aqueous layer was neutralized with 0.5 M HCl to obtain a turbid solution containing the desired compound. The aqueous layer was extracted twice with  $\text{CH}_2\text{Cl}_2$  (15 mL). The organic layer was separated and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to obtain the crude product, which was purified by flash column chromatography on silica.

**5-Cyclopentylidene-2,2-diphenylpent-4-enoic acid (1b).**<sup>3</sup>  $R_f$  0.35 (1:4 ethyl acetate/hexanes); white crystalline solid, m.p. 153-154 °C (reported<sup>1b</sup> 129-132 °C), yield 0.80 g (89%). Spectroscopic data were in agreement with the literature.<sup>1b</sup>

**5-Cycloheptylidene-2,2-diphenylpent-4-enoic acid (1c).**  $R_f$  0.55 (1:4 ethyl acetate/hexanes); white crystalline solid, m.p. 68-69 °C, yield 0.78 g (81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.1 (br s, 1H, COOH), 7.34-7.23 (m, 10H), 4.74-4.69 (m, 1H), 3.08 (d,  $J = 7.6$  Hz, 2H), 2.09-1.95 (m, 4H), 1.51-1.43 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.1, 179.3,

142.1, 129.4, 129.2, 128.0, 127.1, 104.0, 84.0, 60.6, 39.4, 32.1, 29.5, 28.5. IR (neat):  $\nu$  2919 (m), 2952 (m), 1960 (w), 1759 (s), 1689 (s), 1495 (m)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{24}\text{H}_{26}\text{O}_2 + \text{Na}]^+$ ) calcd 369.1830, found  $m/z$  369.1820.

**2,2-Bis(4-chlorophenyl)-5-cyclohexylidenepent-4-enoic acid (1d).**  $R_f$  0.57 (1:4 ethyl acetate/hexanes); white crystalline solid, m.p. 157-158  $^\circ\text{C}$ , yield 0.80 g (87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.4 (br. s, 1H, COOH), 7.27-7.20 (m, 8H), 4.67-4.63 (m, 1H), 3.00 (d,  $J = 7.2$  Hz, 2H), 1.90-1.78 (m, 4H), 1.46-1.39 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.0, 179.1, 140.2, 133.4, 130.7, 128.3, 102.6, 83.6, 59.8, 39.3, 31.1, 27.3, 26.1. IR (neat):  $\nu$  3062 (br), 2918 (m), 2851 (w), 1965 (w), 1690 (s), 1490 (s)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{23}\text{H}_{22}\text{Cl}_2\text{O}_2 + \text{Na}]^+$ ) calcd 423.0894, found  $m/z$  423.0896.

**2,2-Bis(4-chlorophenyl)-5-cyclopentylidenepent-4-enoic acid (1e).**<sup>3</sup>  $R_f$  0.53 (1:4 ethyl acetate/hexanes); white crystalline solid, m.p. 122-124  $^\circ\text{C}$  (decomp), yield 0.80 g (88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.1 (br. s, 1H, COOH), 7.27-7.19 (m, 8H), 4.79-4.73 (m, 1H), 3.00 (d,  $J = 7.2$  Hz, 2H), 2.12-2.05 (m, 4H), 1.57-1.51 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.8, 178.8, 140.2, 133.4, 130.7, 128.3, 103.9, 86.3, 59.7, 39.1, 30.9, 27.0. IR (neat):  $\nu$  3060 (br), 2917 (m), 2853 (w), 1962 (w), 1691 (s), 1491 (s)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{O}_2 + \text{Na}]^+$ ) calcd 409.0738, found  $m/z$  409.0738.

**5-Cyclohexylidene-2,2-bis(2,3-dihydrobenzofuran-5-yl)pent-4-enoic acid (1f).**  $R_f$  0.33 (3:2 ethyl acetate/hexanes); viscous yellow oil, yield 0.70 g (66%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.5 (br. s, 1H, COOH), 7.21-7.05 (m, 4H), 6.71-6.66 (m, 2H), 4.73-4.68 (m, 1H), 4.59-4.51 (m, 4H), 3.23-3.13 (m, 4H), 3.03-2.88 (m, 2H), 1.97-1.89 (m, 4H), 1.52-1.41 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.7, 159.1, 134.5, 129.1, 126.6, 125.9, 108.5, 102.0, 84.6, 71.5, 59.5, 40.1, 31.3, 30.0, 27.5, 26.3. IR (neat):  $\nu$  3033 (br), 2919 (m), 2855 (w), 1969 (w), 1699 (s), 1491 (s)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{27}\text{H}_{28}\text{O}_4 + \text{Na}]^+$ ) calcd 439.1885, found  $m/z$  439.1883.

**5-Cyclopentylidene-2,2-bis(2,3-dihydrobenzofuran-5-yl)pent-4-enoic acid (1g).**  $R_f$  0.36 (3:2 ethyl acetate/hexanes); viscous yellow oil, yield 0.55 g (65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.2 (br. s, 1H, COOH), 7.16-7.12 (m, 2H), 7.06 (dt,  $J = 8.4, 2.0$  Hz, 2H), 6.70 (d,  $J = 8.8$  Hz, 2H), 4.84-4.79 (m, 1H), 4.56 (t,  $J = 8.8$  Hz, 4H), 3.17 (t,  $J = 8.8$  Hz, 4H), 3.02 (d,  $J = 7.2$  Hz, 2H), 2.16 (sextet,  $J = 3.2$  Hz, 4H), 1.61-1.56 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.5, 159.1, 134.5, 129.1, 126.6, 126.0, 126.0, 108.5, 103.3, 87.3, 71.5, 59.5, 39.7, 30.9, 30.0,

27.1. IR (neat):  $\nu$  2959 (br), 2921 (m), 2856 (w), 1968 (w), 1697 (s), 1490 (s)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{26}\text{H}_{26}\text{O}_4 + \text{Na}]^+$ ) calcd 425.1729, found  $m/z$  425.1730.

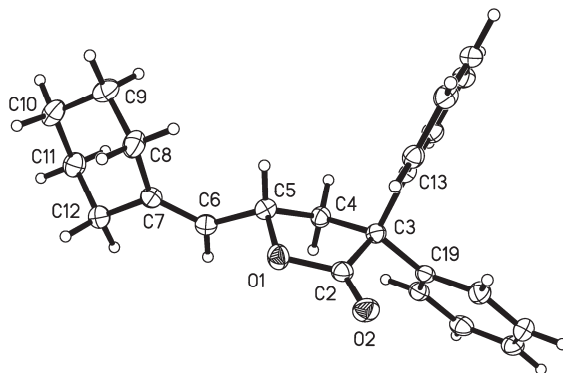
**9-(3-Cyclohexylideneallyl)-9H-xanthene-9-carboxylic acid (1h).**<sup>3</sup>  $R_f$  0.53 (1:4 ethyl acetate/hexanes); white solid, m.p. 64-65 °C, yield 0.80 g (80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.2 (br s, 1H, COOH), 7.24-7.20 (m, 4H), 7.06-7.00 (m, 4H), 4.43-4.39 (m, 1H), 2.92 (d,  $J = 6.8$  Hz, 2H), 1.61-1.49 (m, 4H), 1.38-1.24 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.2, 179.0, 150.9, 128.9, 127.6, 123.3, 120.8, 116.8, 102.1, 82.5, 50.2, 40.8, 31.0, 27.2, 26.1. IR (neat):  $\nu$  3055 (br), 2971(m), 2919 (m), 2865 (w), 1965 (w), 1901(w) 1698 (s), 1481 (m)  $\text{cm}^{-1}$ . HRMS (ESI-orbitrap,  $[\text{C}_{23}\text{H}_{22}\text{O}_3 + \text{Na}]^+$ ) calcd 369.1467, found  $m/z$  369.1465.

**9-(3-Cyclopentylideneallyl)-9H-xanthene-9-carboxylic acid (1i).**<sup>3</sup>  $R_f$  0.55 (1:4 ethyl acetate/hexanes); white solid, m.p. 62-63 °C, yield 0.55 g (76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.8 (br. s, 1H, COOH), 7.27-7.21 (m, 4H), 7.07-7.03 (m, 4H), 4.61-4.54 (m, 1H), 2.99 (d,  $J = 6.8$  Hz, 2H), 1.88-1.82 (m, 2H), 1.63-1.57 (m, 2H), 1.45-1.40 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.8, 178.5, 150.9, 129.0, 127.4, 123.3, 120.7, 116.8, 104.1, 85.2, 49.9, 39.5, 30.7, 26.9. IR (neat):  $\nu$  3053 (br), 2970 (m), 2921 (m), 2866 (w), 1961 (w), 1901 (w) 1696 (s), 1480 (m)  $\text{cm}^{-1}$ . HRMS (ESI,  $[\text{C}_{22}\text{H}_{20}\text{O}_3 + \text{Na}]^+$ ) calcd 355.1310, found  $m/z$  355.1313.

**5-Cyclohexylidene-2-(3-methoxyphenyl)-2-phenylpent-4-enoic acid (1k).**  $R_f$  0.41 (1:4 ethyl acetate/hexanes); white solid, m.p. 134-135 °C, yield 0.78 g (84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.7 (br. s, 1H, COOH), 7.32-7.18 (m, 6H), 6.90 (ddd,  $J = 8.4, 2.4$  Hz, 1H), 6.86 (t,  $J = 2.0$  Hz, 1H), 6.77 (ddd,  $J = 8.4, 2.4, 0.8$  Hz, 1H), 4.73-4.69 (m, 1H), 3.72 (s, 3H), 3.11-3.01 (m, 2H), 1.89-1.81 (m, 4H), 1.49-1.39 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.8, 179.3, 159.3, 143.7, 141.9, 129.3, 128.9, 127.9, 127.1, 121.8, 115.9, 112.0, 102.1, 84.3, 60.6, 55.3, 39.5, 31.2, 27.4, 26.2. IR (neat):  $\nu$  2918 (br), 2589 (w), 1699 (s), 1750 (s), 1612 (m)  $\text{cm}^{-1}$ . HRMS (ESI,  $[\text{C}_{24}\text{H}_{26}\text{O}_3 + \text{H}]^+$ ) calcd 363.1960, found  $m/z$  363.1956.

## X-RAY CRYSTALLOGRAPHIC DATA AND PROCEDURES

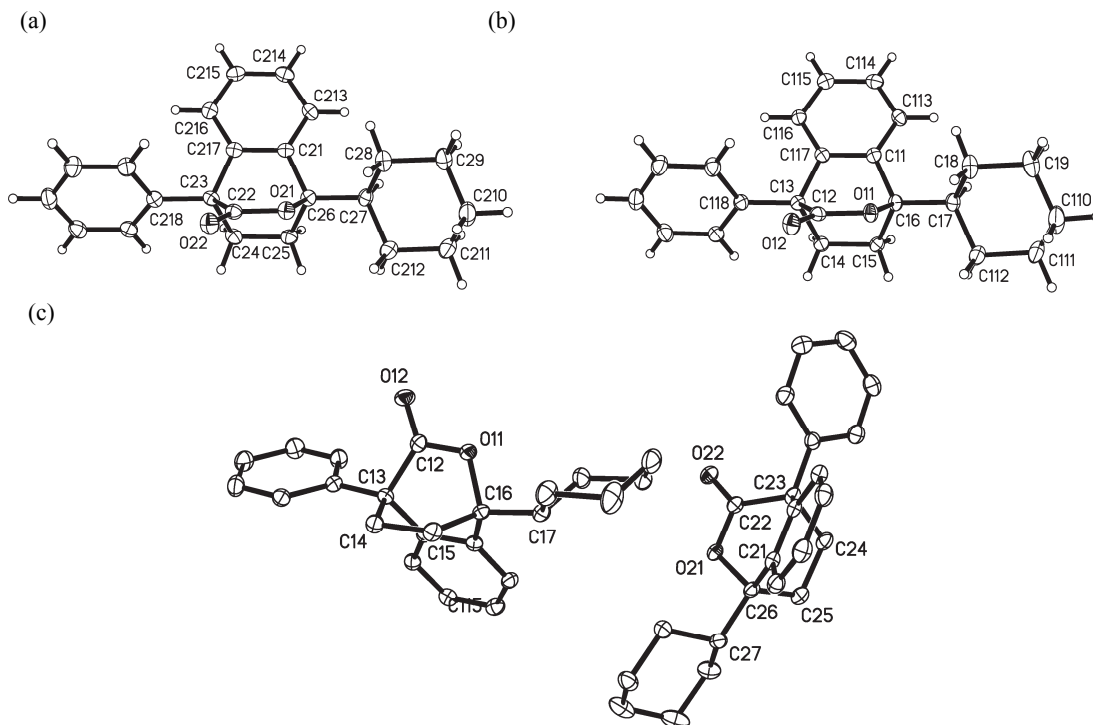
**General Considerations.** X-ray diffraction data were collected on Bruker single crystal diffractometers equipped with CCD detectors (APEX or APEX II) using a combination of  $\phi$  and  $\omega$  scans. Unit cell determination and data collection utilized the Bruker SMART<sup>8</sup> and APEX2<sup>9</sup> software packages. Data integration employed SAINT.<sup>10</sup> Multiscan absorption corrections were implemented using SADABS.<sup>11</sup> Structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software suite.<sup>12</sup> Non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions (riding model) with isotropic  $U$  fixed at 1.5 times the  $U_{\text{eq}}$  of the attached atom for  $-\text{CH}_3$  groups and 1.2 times the  $U_{\text{eq}}$  of the attached atom for other hydrogen atoms. CCDC 997310-997312 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure S1.** X-ray structure of **2a**, with displacement ellipsoids drawn at the 50% probability level

**X-ray Crystallographic Analysis of 2a.** Colorless blocks were obtained by slow diffusion of pentane into a  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  (98:2) solution of **2a**. A sample measuring 0.40 x 0.25 x 0.25 mm was placed on the goniometer of an APEX II DUO diffractometer, and reflection data were collected using radiation from a Cu  $\text{I}\mu\text{S}$  microfocus X-ray source ( $\lambda=1.54178 \text{ \AA}$ ). The sample was cooled to 125(1) K during data collection using an Oxford Cryostream liquid nitrogen cooling device.  $\text{C}_{23}\text{H}_{24}\text{O}_2$ ,  $M_r = 332.42 \text{ g mol}^{-1}$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.2882(1)$ ,

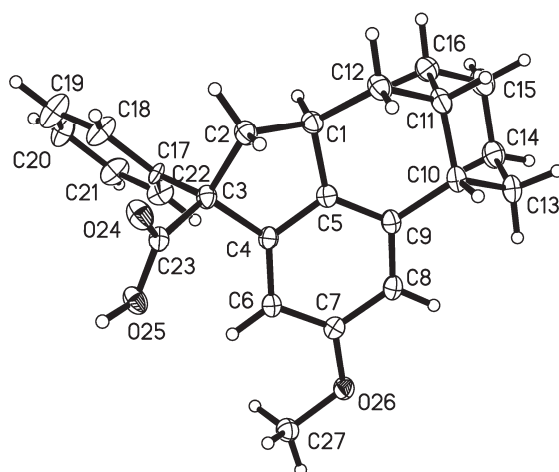
$b = 10.0834(1)$ ,  $c = 17.6278(2)$  Å,  $\beta = 100.1728(4)^\circ$ ,  $V = 1799.96(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $Z' = 1$ ,  $\rho_{\text{calcd}} = 1.227$  g cm<sup>-3</sup>,  $\mu = 0.598$  mm<sup>-1</sup>,  $T = 125(2)$  K,  $2\theta_{\text{max}} = 133.19^\circ$ , 26227 total reflections, 3169 independent ( $R_{\text{int}} = 0.024$ ), 3122 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0345,  $wR2$  (all data) = 0.0844, largest difference peak (hole) 0.284 (-0.203) e Å<sup>-3</sup>. CCDC 997310.



**Figure S2.** Views of the X-ray structure of **4a**, showing the two crystallographically independent molecules (a,b) and the asymmetric unit (c). Displacement ellipsoids are drawn at the 50% probability level

**X-ray Crystallographic Analysis of 4a.** Colorless needles were obtained by slow diffusion of pentane into a CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O solution (98:2) of **4a**. A sample measuring 0.24 x 0.07 x 0.02 mm was placed on the goniometer of an APEX II DUO diffractometer, and reflection data were collected using graphite-monochromated radiation from a Mo sealed-tube X-ray source ( $\lambda=0.71073$  Å) equipped with a MonoCap waveguide collimator. The sample was cooled to 125(1) K during data collection using an Oxford Cryostream liquid nitrogen cooling device. By analyzing reflection data with CELL\_NOW<sup>13</sup> and TWINABS,<sup>14</sup> the crystal was modeled as a two-component nonmerohedral twin. Final refinement was performed on both twin components

using data in HKLF5 format. The refined proportion of twin components was 0.477(1):0.523(1), with a twin law corresponding to a 180 degree rotation about reciprocal axis 0.031 1.000 -0.005 and real axis 0.003 1.000 0.000. The asymmetric unit contains two crystallographically independent molecules.  $C_{23}H_{24}O_2$ ,  $M_r = 332.42 \text{ g mol}^{-1}$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.1469(5)$ ,  $b = 15.303(1)$ ,  $c = 16.4534(10) \text{ \AA}$ ,  $\alpha = 73.1224(1)$ ,  $\beta = 89.797(1)$ ,  $\gamma = 88.864(1)^\circ$ ,  $V = 1799.96(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $Z' = 2$ ,  $\rho_{\text{calcd}} = 1.282 \text{ g cm}^{-3}$ ,  $\mu = 0.080 \text{ mm}^{-1}$ ,  $T = 125(2) \text{ K}$ ,  $2\theta_{\text{max}} = 61.02^\circ$ , 22822 total reflections, 10426 independent ( $R_{\text{int}} = 0.086$ ), 9443 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0626,  $wR2$  (all data) = 0.1600, largest difference peak (hole) 0.382 (-0.335)  $e \text{ \AA}^{-3}$ . CCDC 997311.



**Figure S3.** X-ray structure of **9**, with displacement ellipsoids drawn at the 50% probability level. Only the major orientation of the disordered phenyl group (C17-C21) is shown.

**X-ray Crystallographic Analysis of 9.** Colorless plates were obtained by slow diffusion of pentane into a  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  (9:1) solution of **9**. A sample measuring 0.52 x 0.40 x 0.02 mm was placed on the goniometer of a SMART APEX diffractometer, and reflection data were collected using graphite-monochromated radiation from a Mo sealed-tube X-ray source ( $\lambda=0.71073 \text{ \AA}$ ) equipped with a MonoCap waveguide collimator. The sample was cooled to 100(1) K during data collection using an Oxford Cryostream liquid nitrogen cooling device. The phenyl group showed slight rotational disorder, which was treated with a two-part disorder model. The occupancies for atoms C17 – C22 refined to 0.60(2) and 0.40(2) for the two phenyl ring orientations indicated by unprimed and primed atoms, respectively. Restraints on the positional

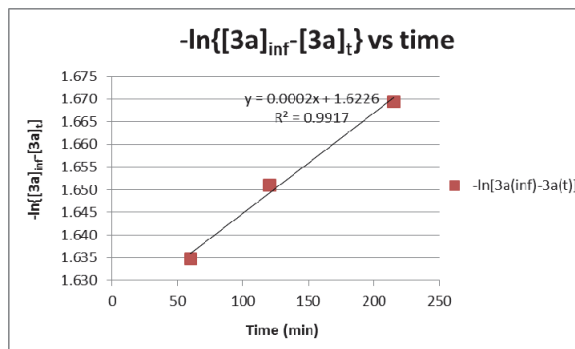
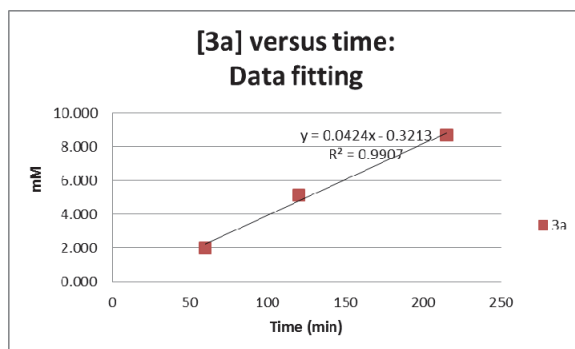
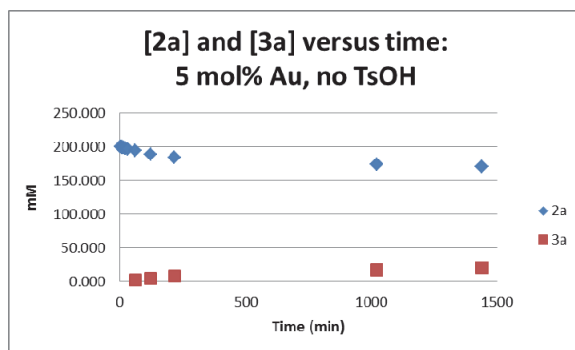
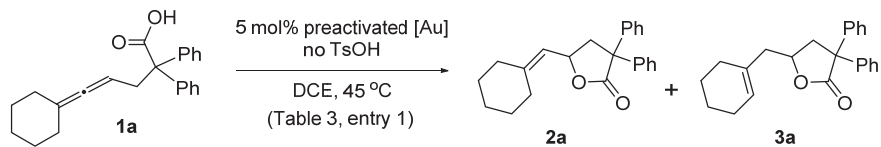
and displacement parameters of the disordered atoms were required. The COOH hydrogen bonded to O25 was located on a difference map, and its position was allowed to refine freely. C<sub>24</sub>H<sub>26</sub>O<sub>3</sub>,  $M_r = 362.45 \text{ g mol}^{-1}$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.7954(4)$ ,  $b = 9.8427(4)$ ,  $c = 11.0909(5) \text{ \AA}$ ,  $\alpha = 78.548(2)$ ,  $\beta = 77.234(2)$ ,  $\gamma = 64.389(2)^\circ$ ,  $V = 933.94(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $Z' = 1$ ,  $\rho_{\text{calcd}} = 1.289 \text{ g cm}^{-3}$ ,  $\mu = 0.083 \text{ mm}^{-1}$ ,  $T = 100(2) \text{ K}$ ,  $2\theta_{\text{max}} = 50.5^\circ$ , 17614 total reflections, 4626 independent ( $R_{\text{int}} = 0.015$ ), 4139 observed [ $I > 2\sigma(I)$ ]. Final  $R1$  [ $I > 2\sigma(I)$ ] = 0.0431,  $wR2$  (all data) = 0.1243, largest difference peak (hole) 0.422 (-0.182) e  $\text{\AA}^{-3}$ . CCDC 997312.

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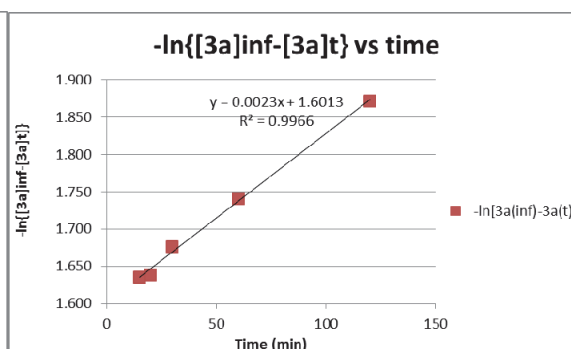
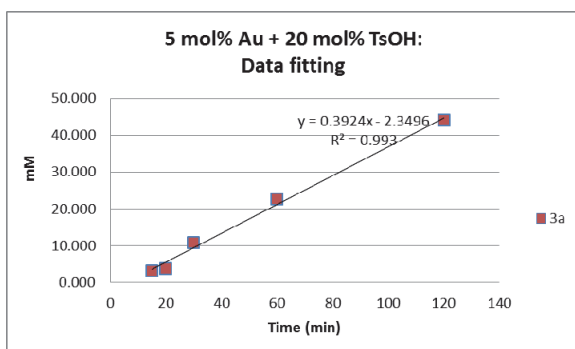
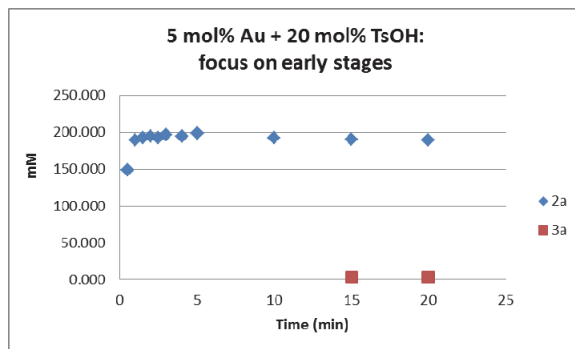
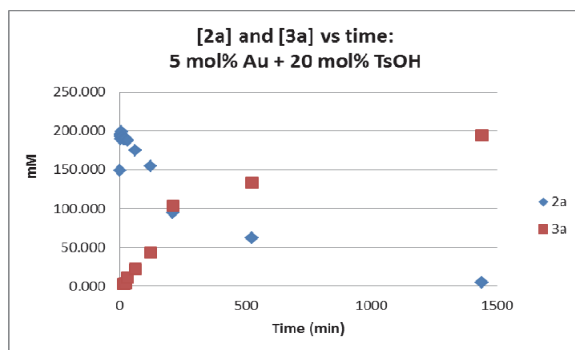
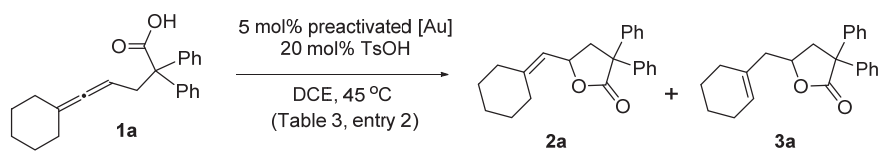


## KINETIC PLOTS



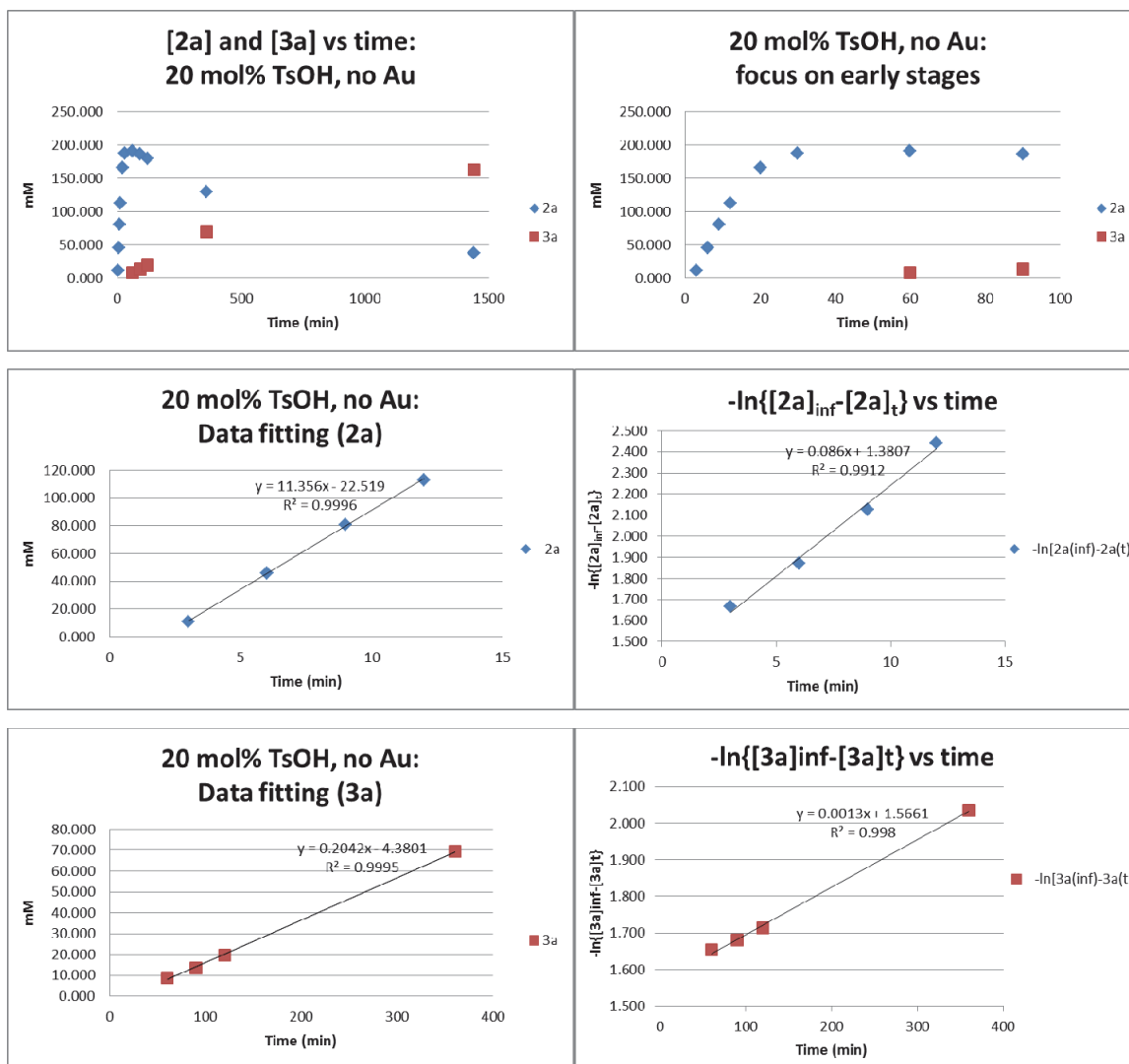
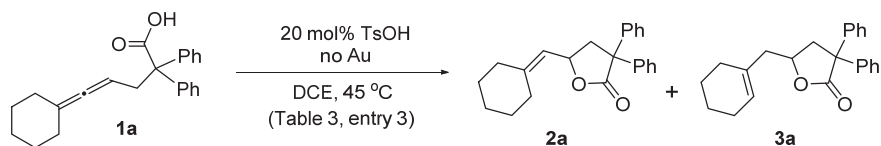
Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

$$k_{\text{obs}} = 2(2) \times 10^{-4} \text{ min}^{-1}$$



Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

$$k_{\text{obs}} = 2.3(2) \times 10^{-3} \text{ min}^{-1}$$

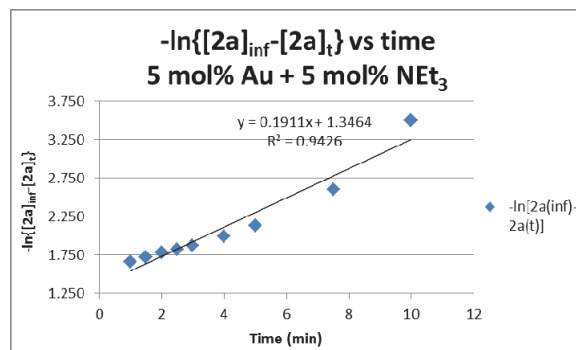
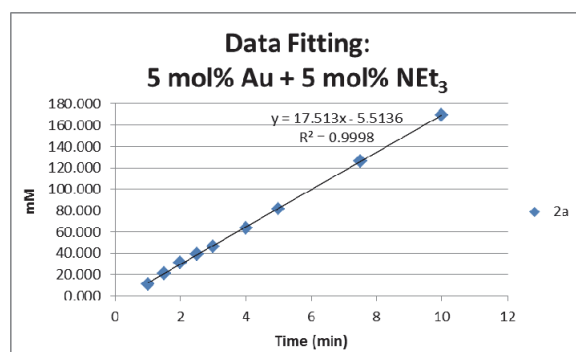
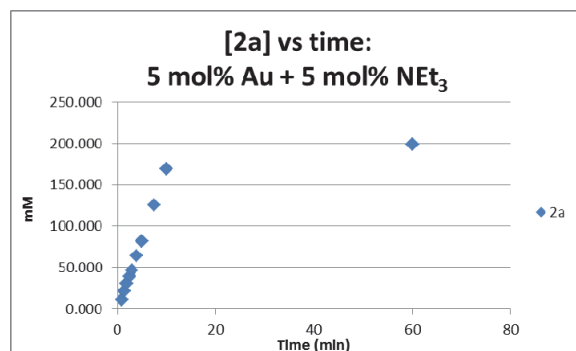
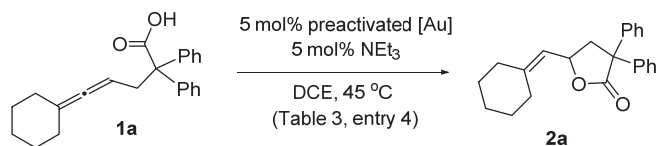


Pseudo zero-order rate constant for **2a** formation (incorporates concentrations of catalyst and

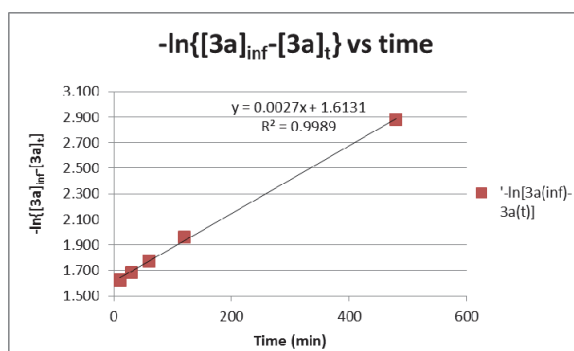
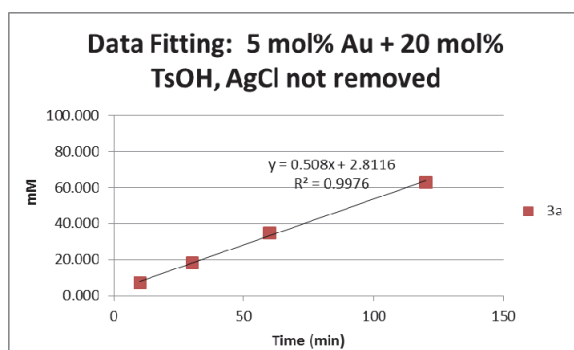
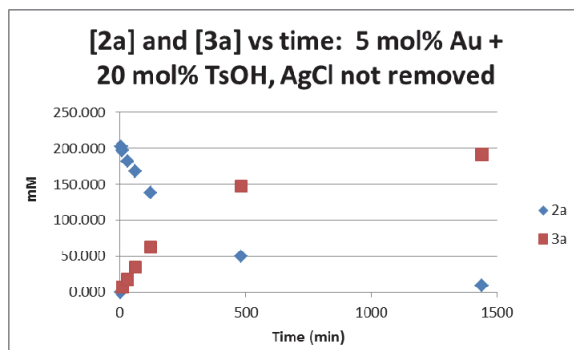
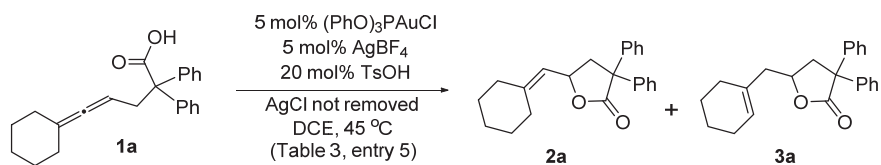
$$\mathbf{1a): } k_{\text{obs}} = 11.4(7) \text{ mM min}^{-1}$$

Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

$$k_{\text{obs}} = 1.18(5) \times 10^{-3} \text{ min}^{-1}$$

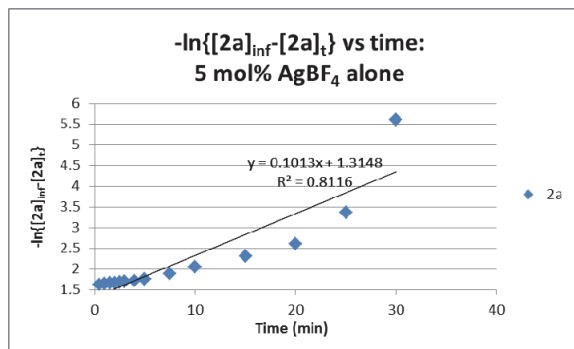
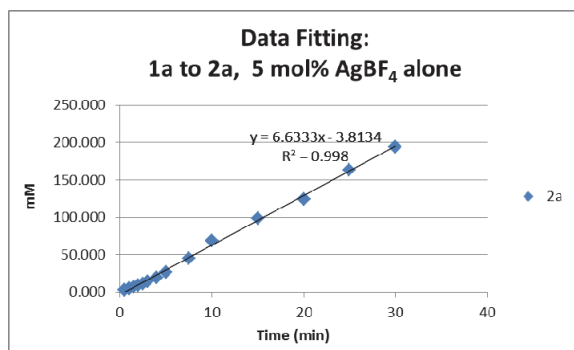
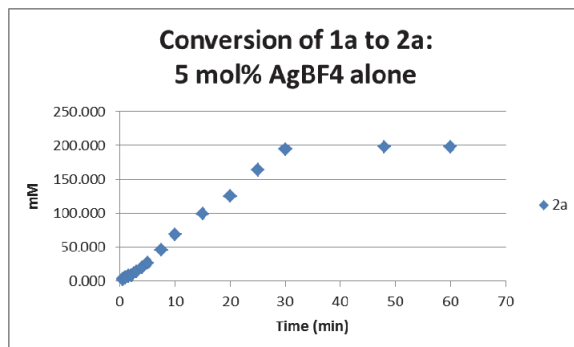
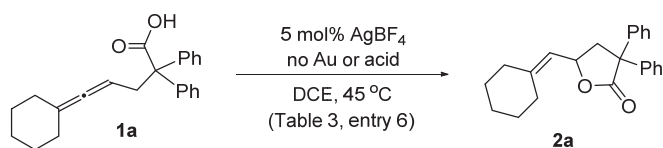


Pseudo zero-order rate constant for **2a** formation (incorporates concentrations of catalyst and **1a**):  $k_{obs} = 17.5(2) \text{ mM min}^{-1}$

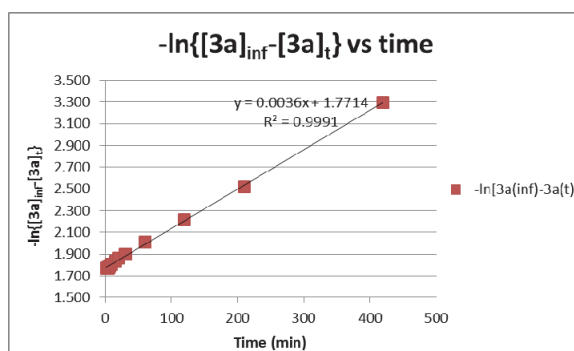
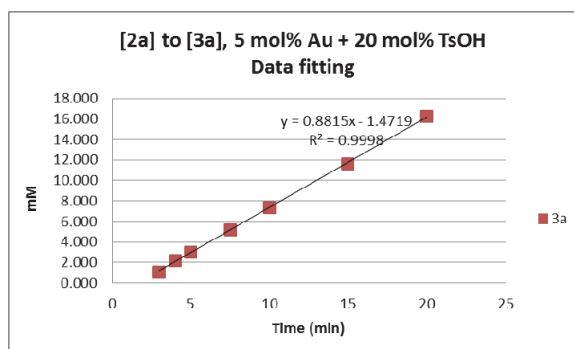
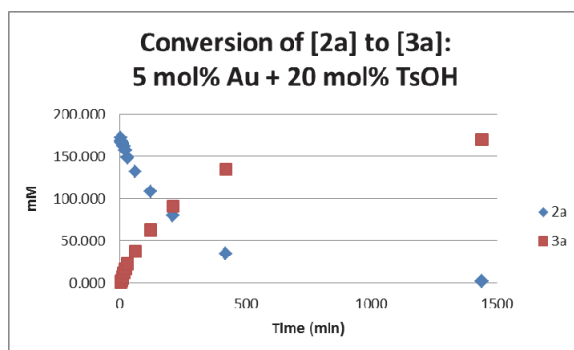
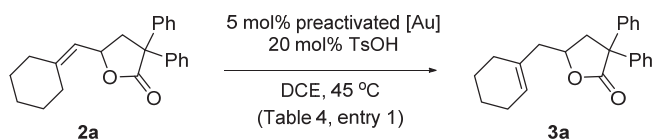


Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

$$k_{obs} = 2.7(2) \times 10^{-3} \text{ min}^{-1}$$

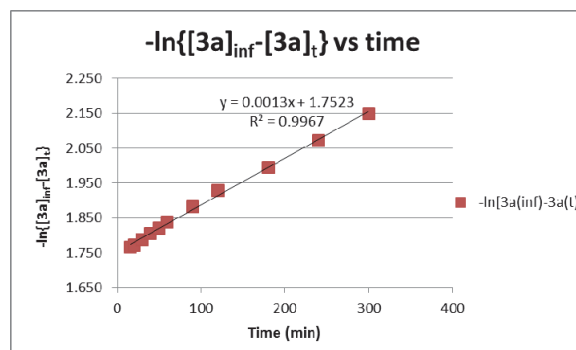
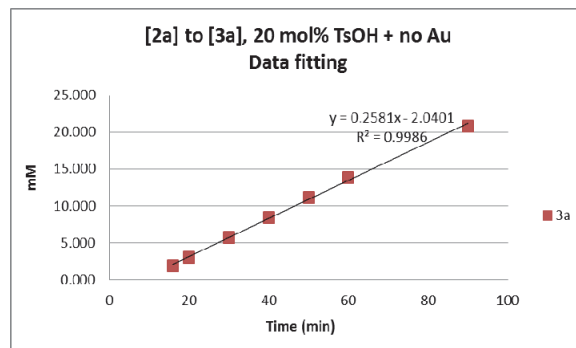
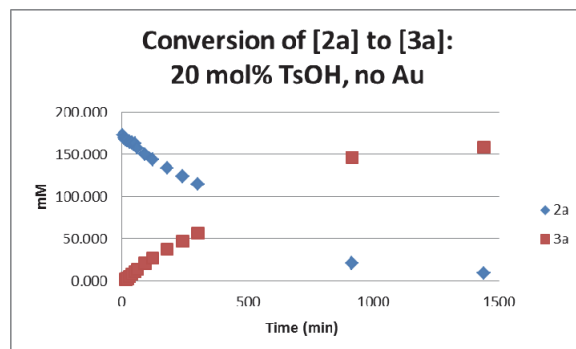
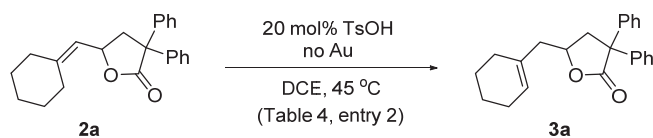


Pseudo zero-order rate constant for **2a** formation (incorporates concentrations of catalyst and **1a**):  $k_{obs} = 6.6(2) \text{ mM min}^{-1}$



Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

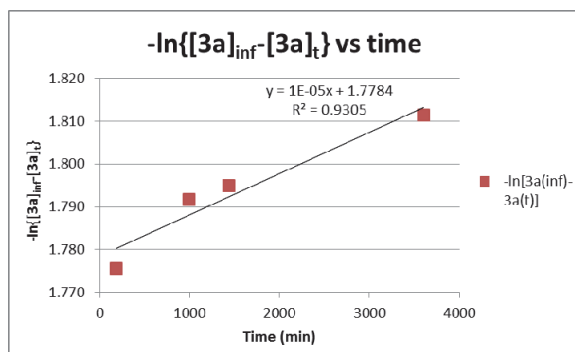
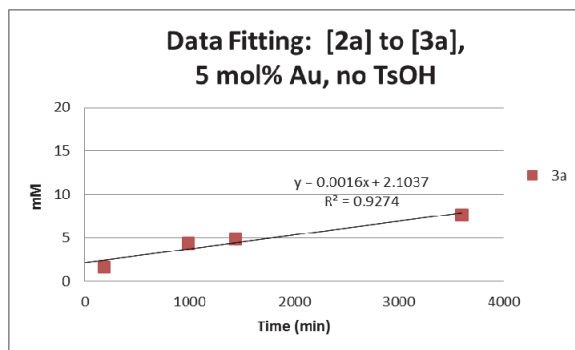
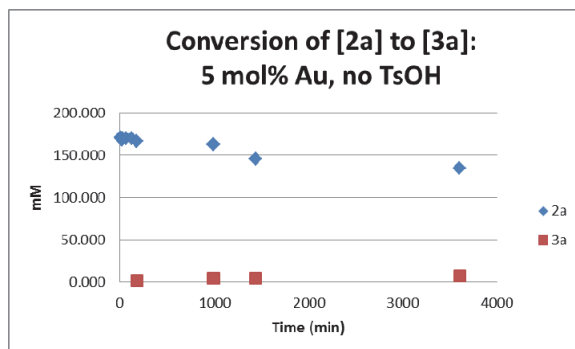
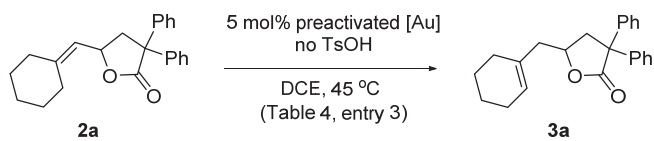
$$k_{obs} = 3.63(8) \times 10^{-3} \text{ min}^{-1}$$



Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

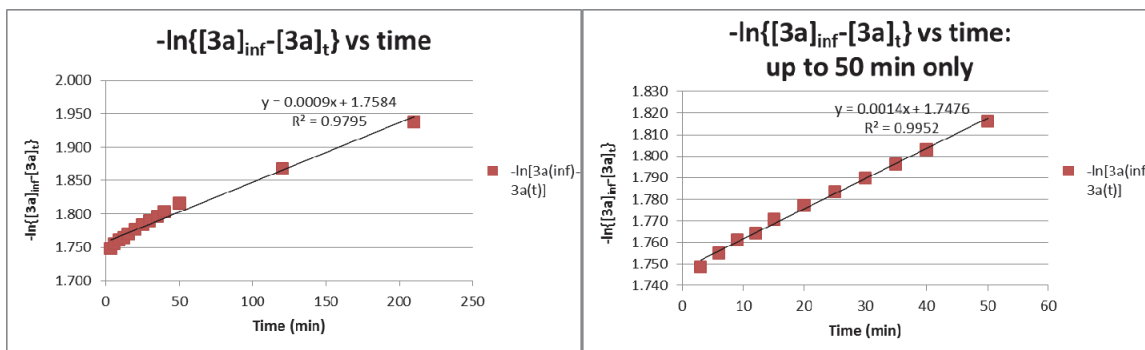
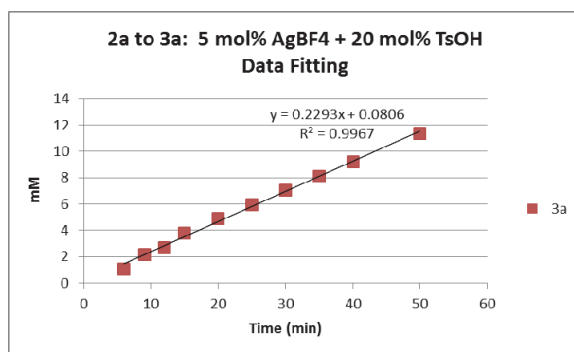
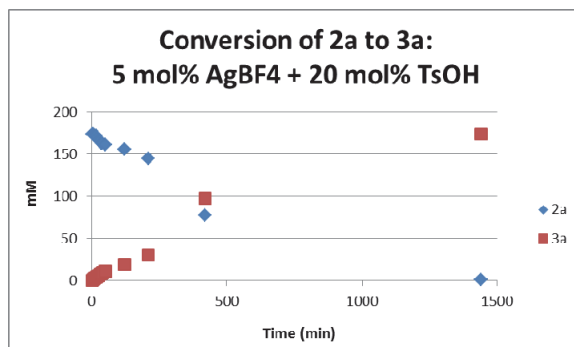
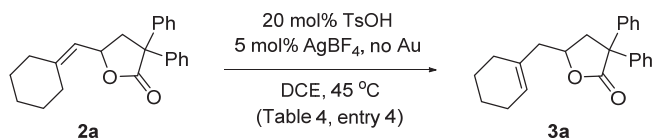
$$k_{obs} = 1.34(6) \times 10^{-3} \text{ min}^{-1}$$





Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

$$k_{obs} = 1.0(8) \times 10^{-5} \text{ min}^{-1}$$

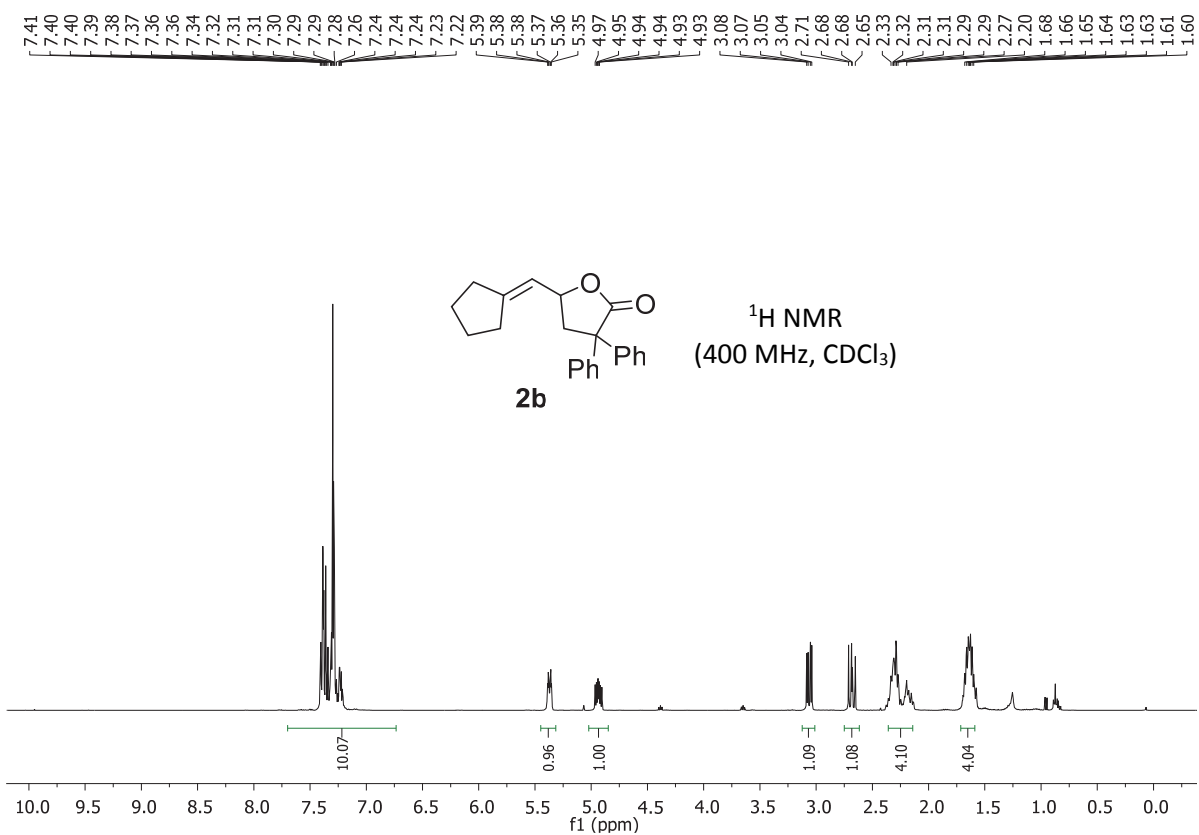
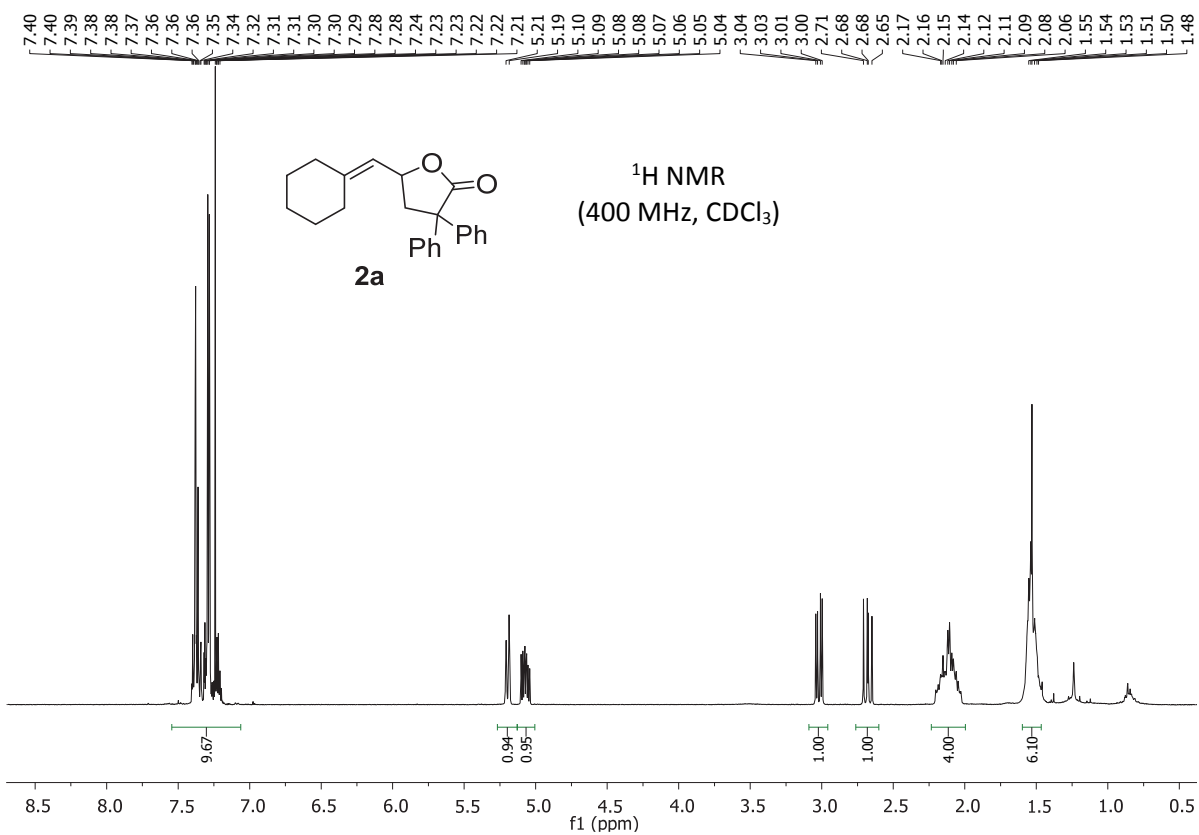


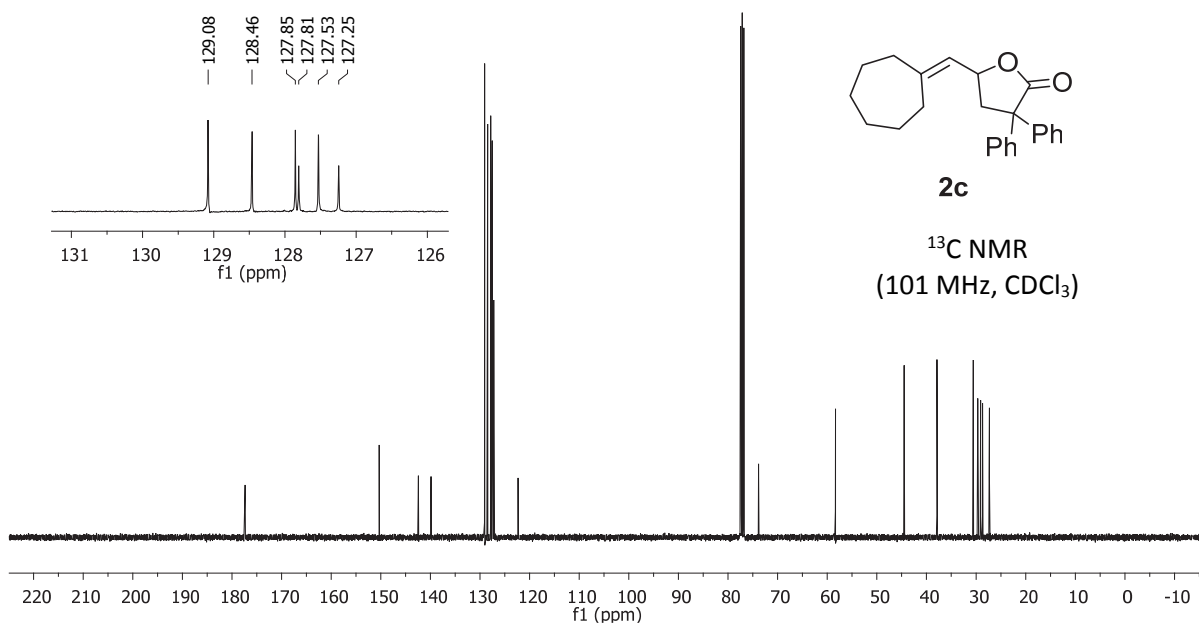
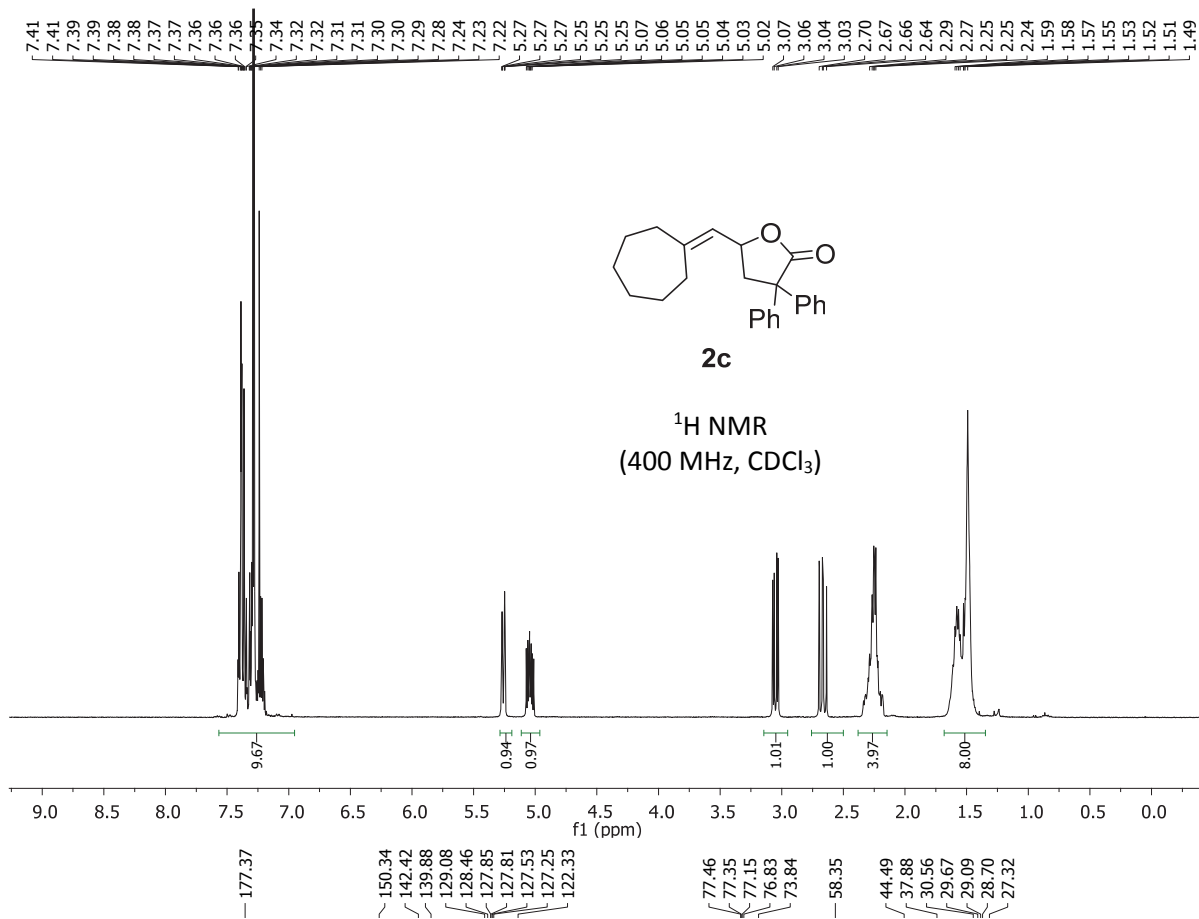
(note: the left plot suggests a change in the catalyst after 50 min)

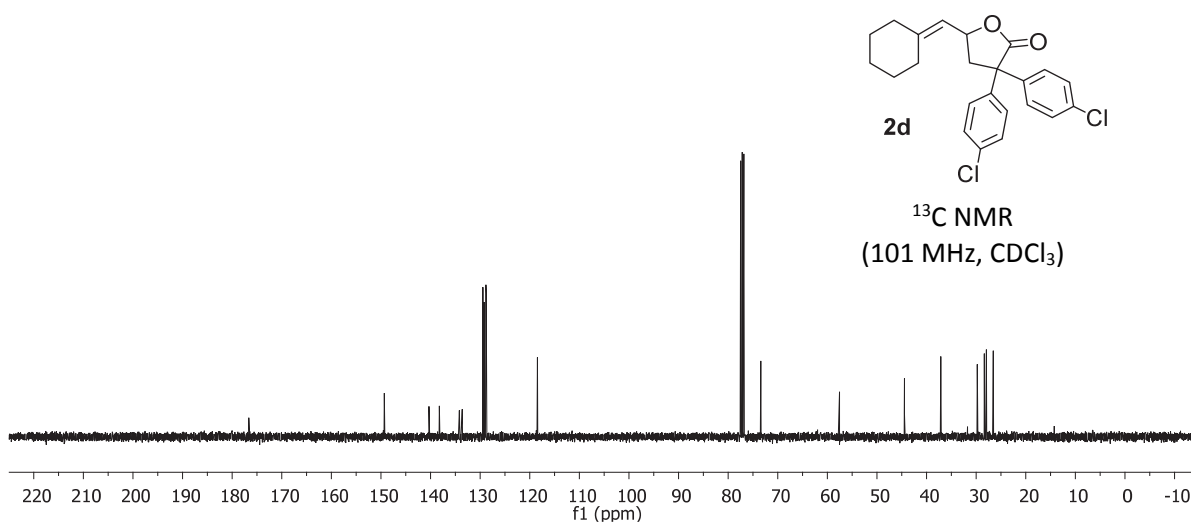
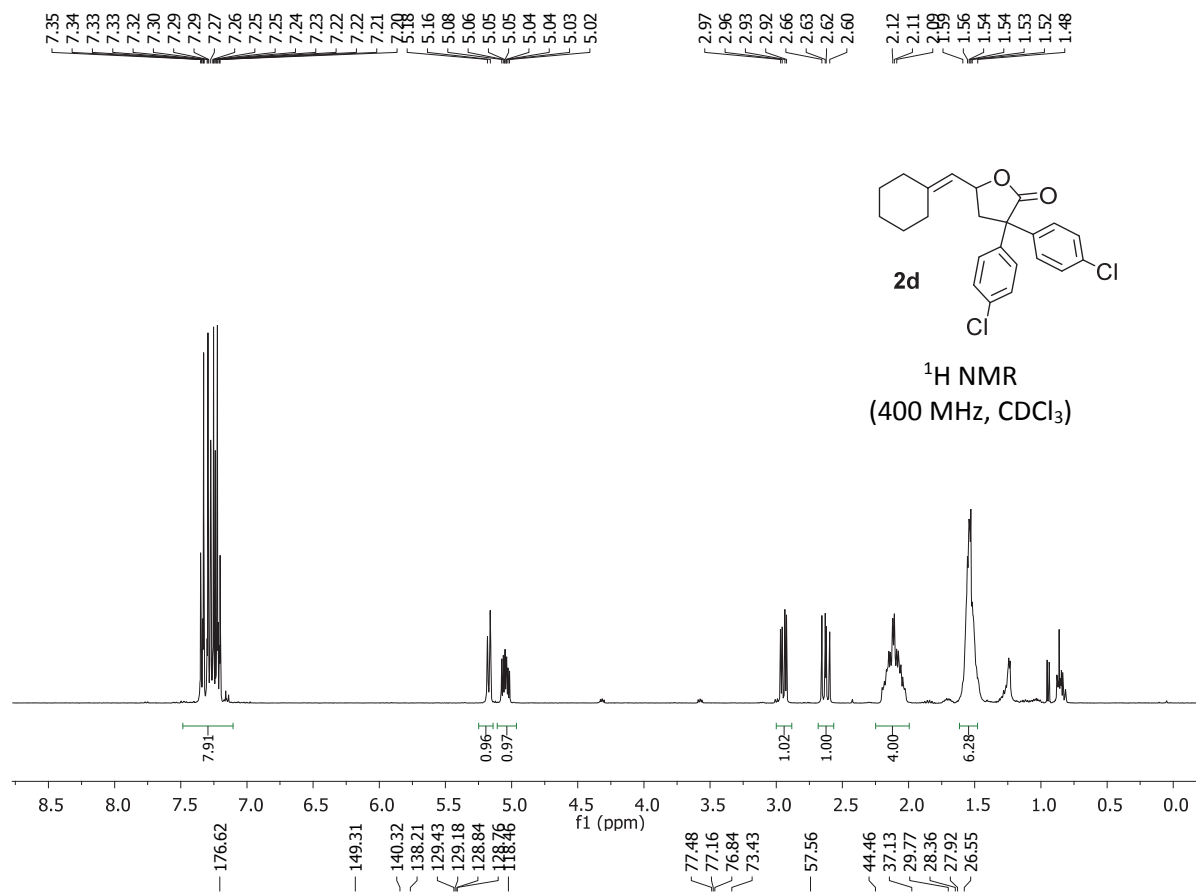
Pseudo first-order rate constant for **3a** formation (incorporates catalyst concentration):

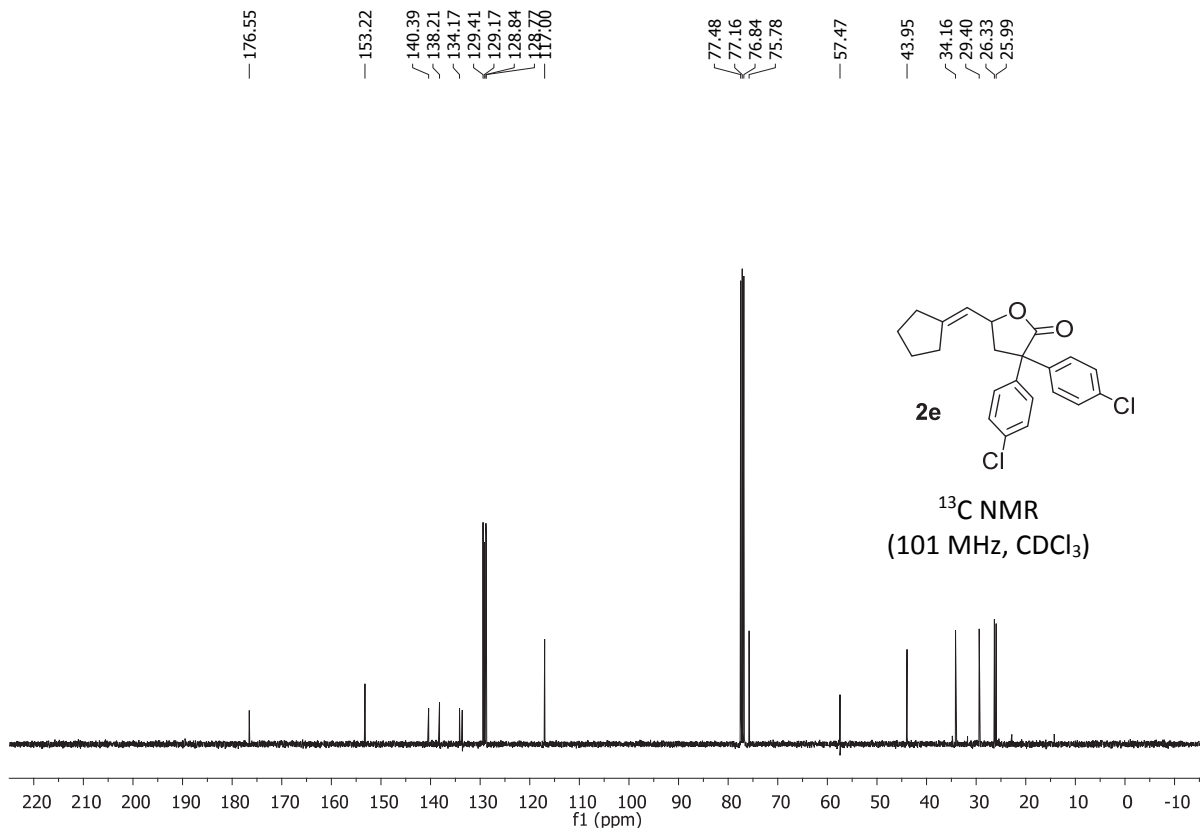
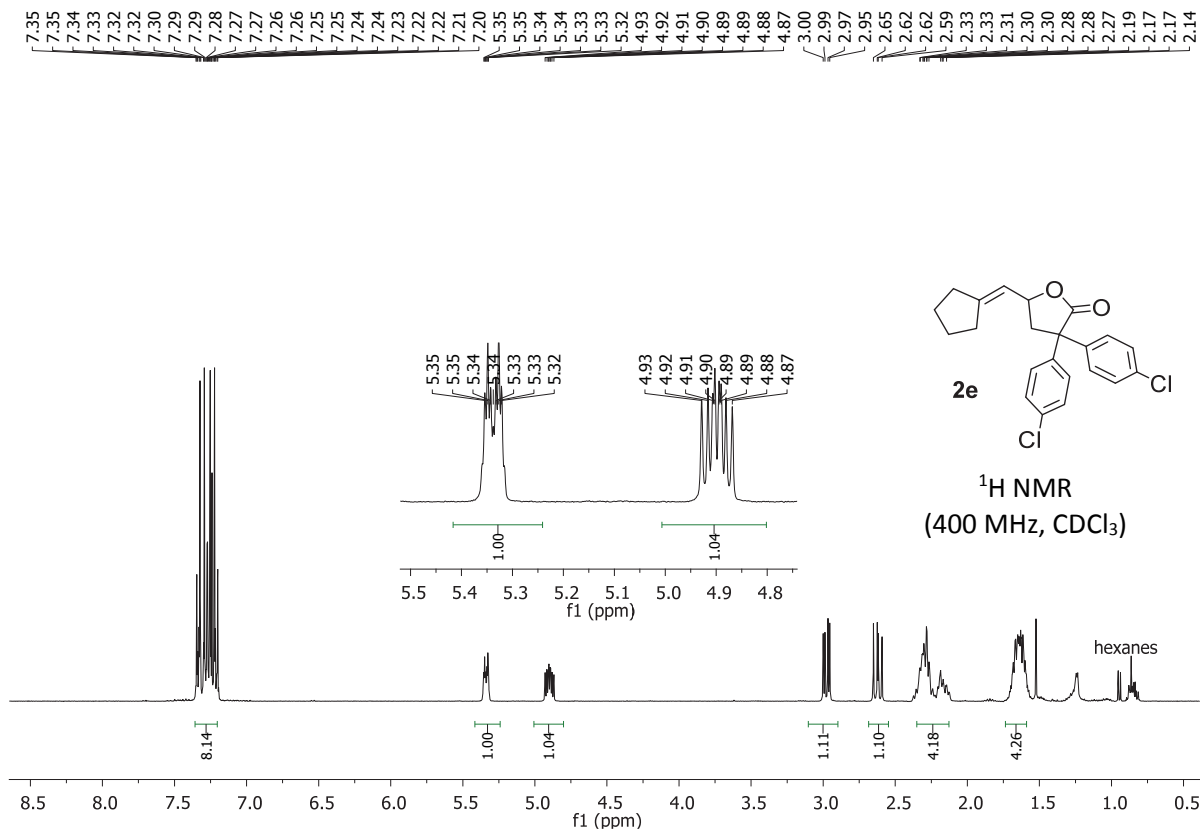
$$k_{\text{obs}} = 1.37(6) \times 10^{-3} \text{ min}^{-1}$$

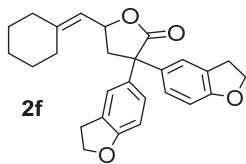
# <sup>1</sup>H AND <sup>13</sup>C NMR SPECTRA



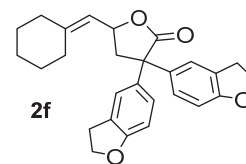
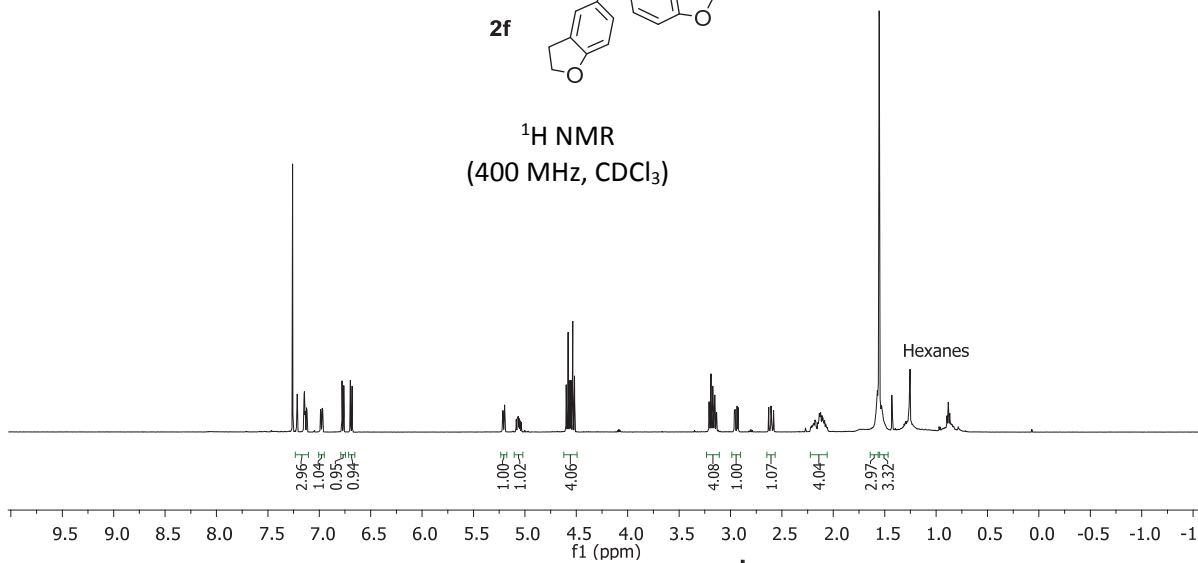




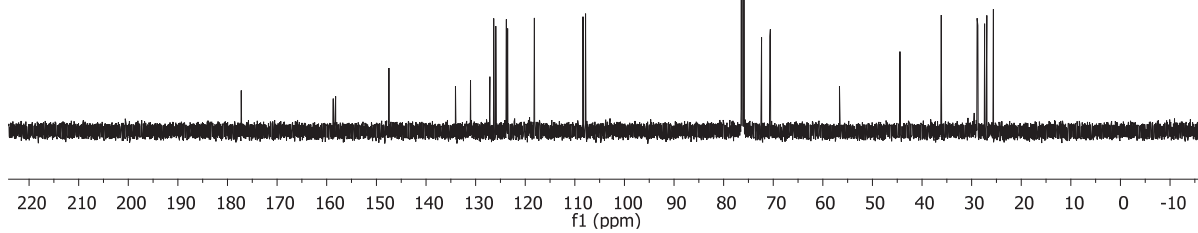


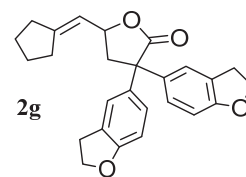


<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

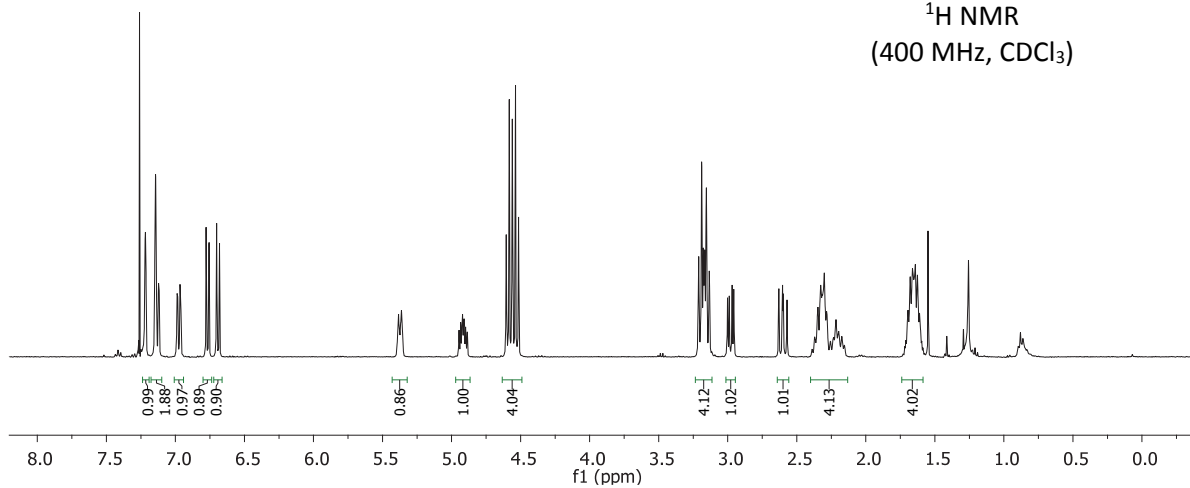


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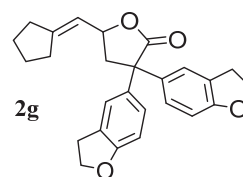




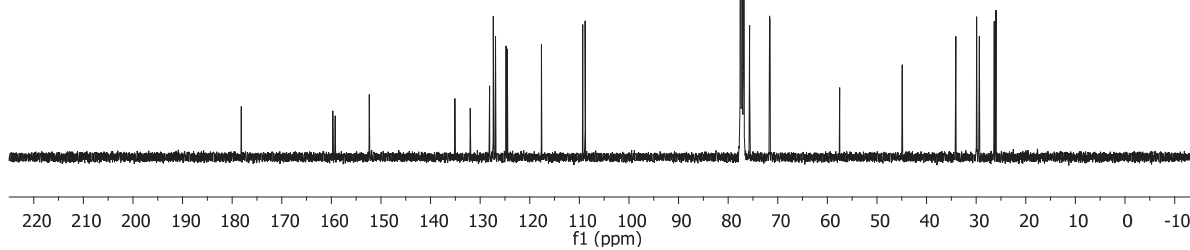
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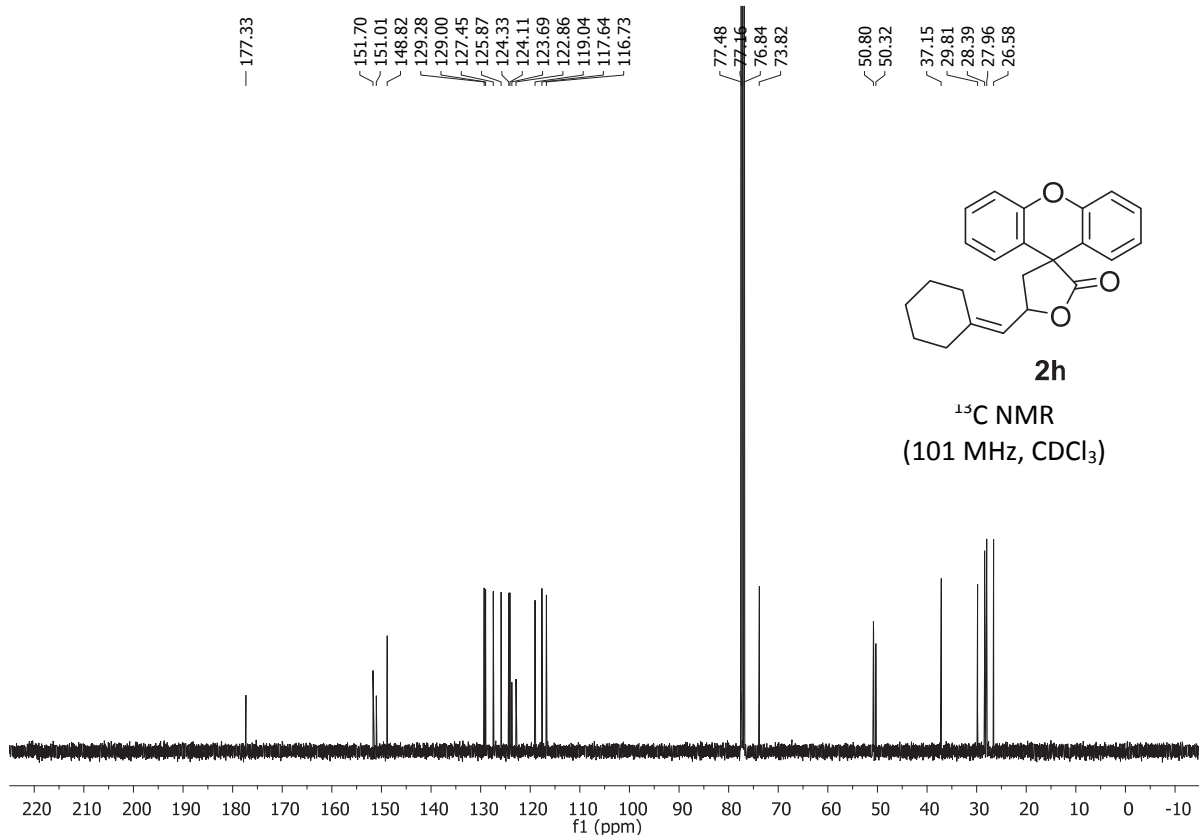
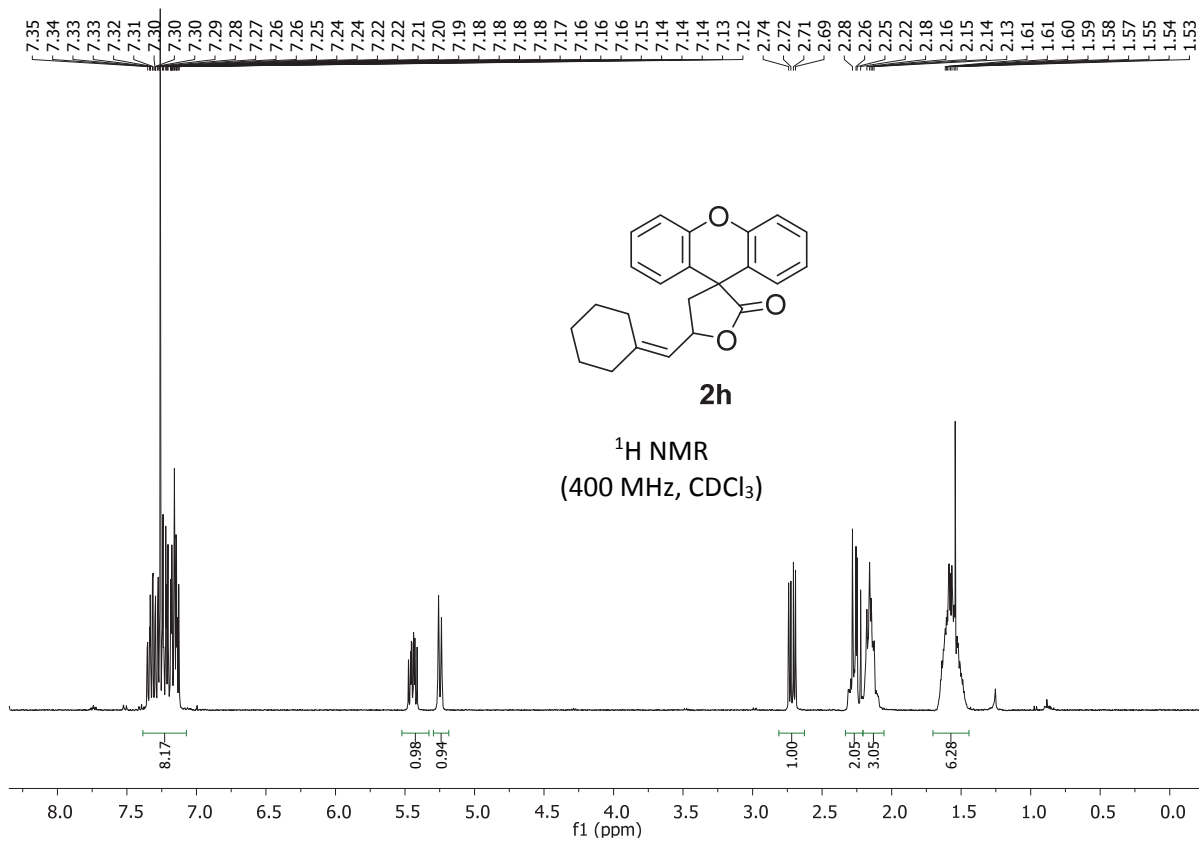
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159.22  
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124.53  
117.64  
109.34  
108.84  
77.48  
77.16  
76.84  
75.69  
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29.92  
29.89  
29.37  
26.37  
26.02

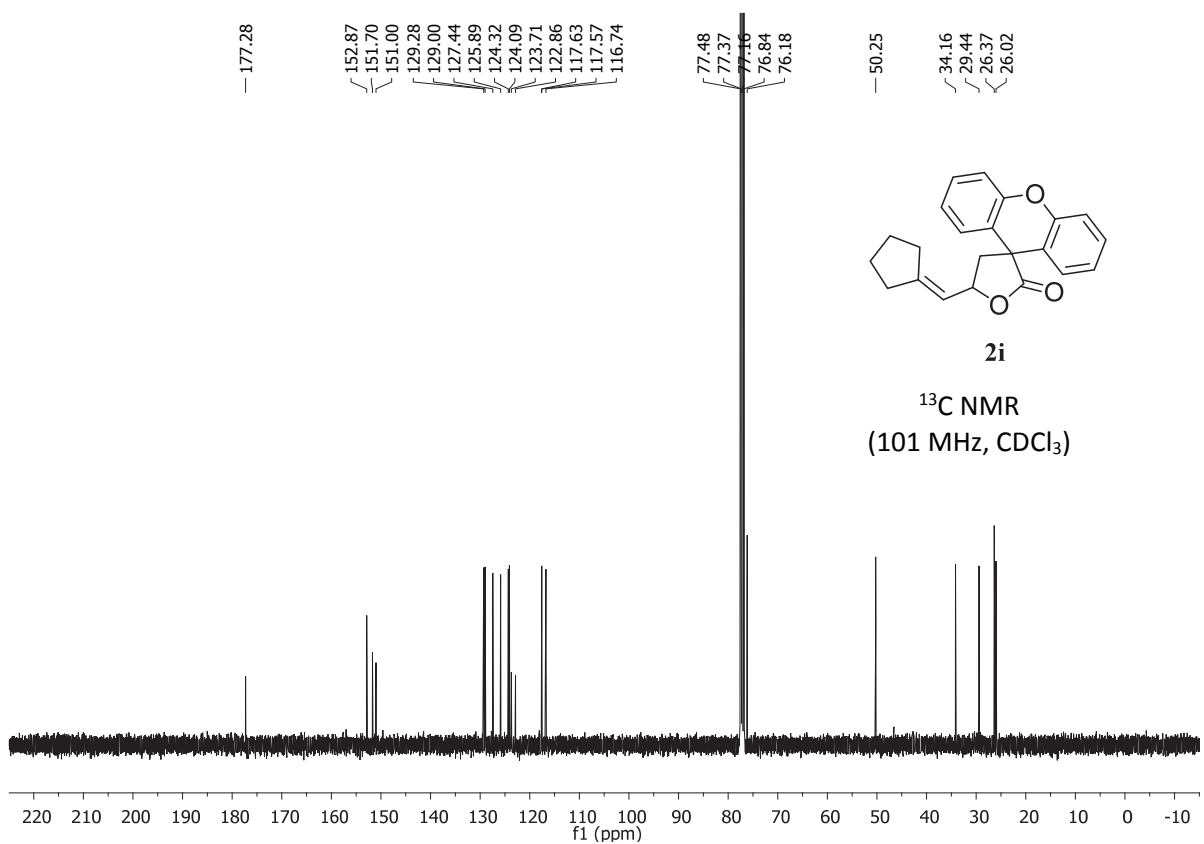
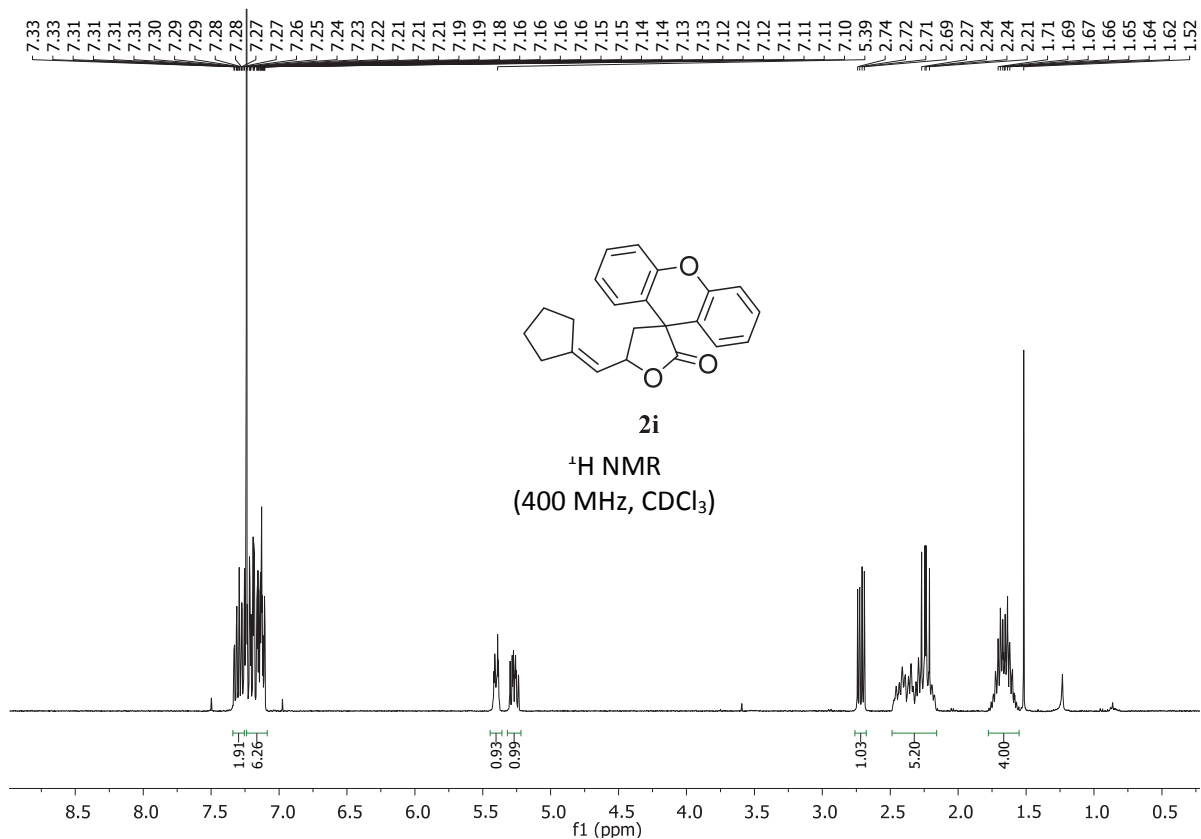


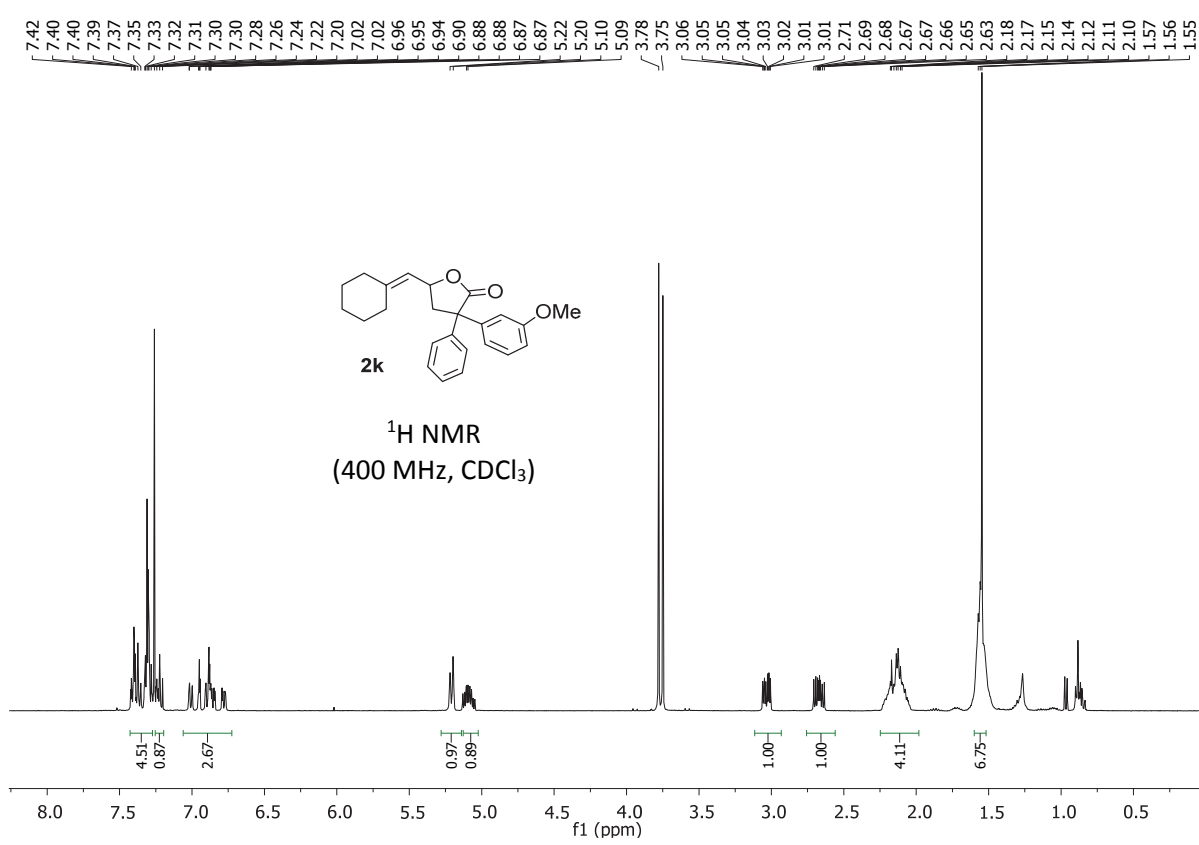
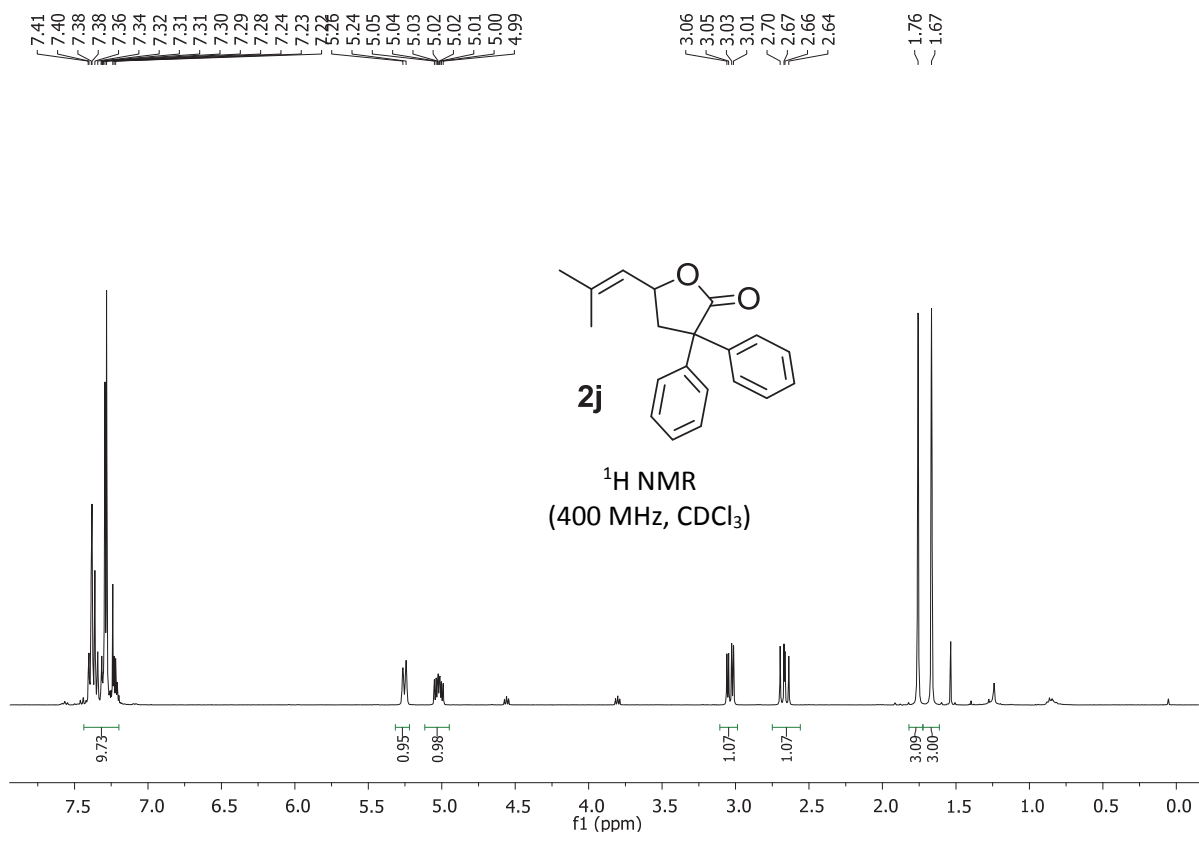
<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)

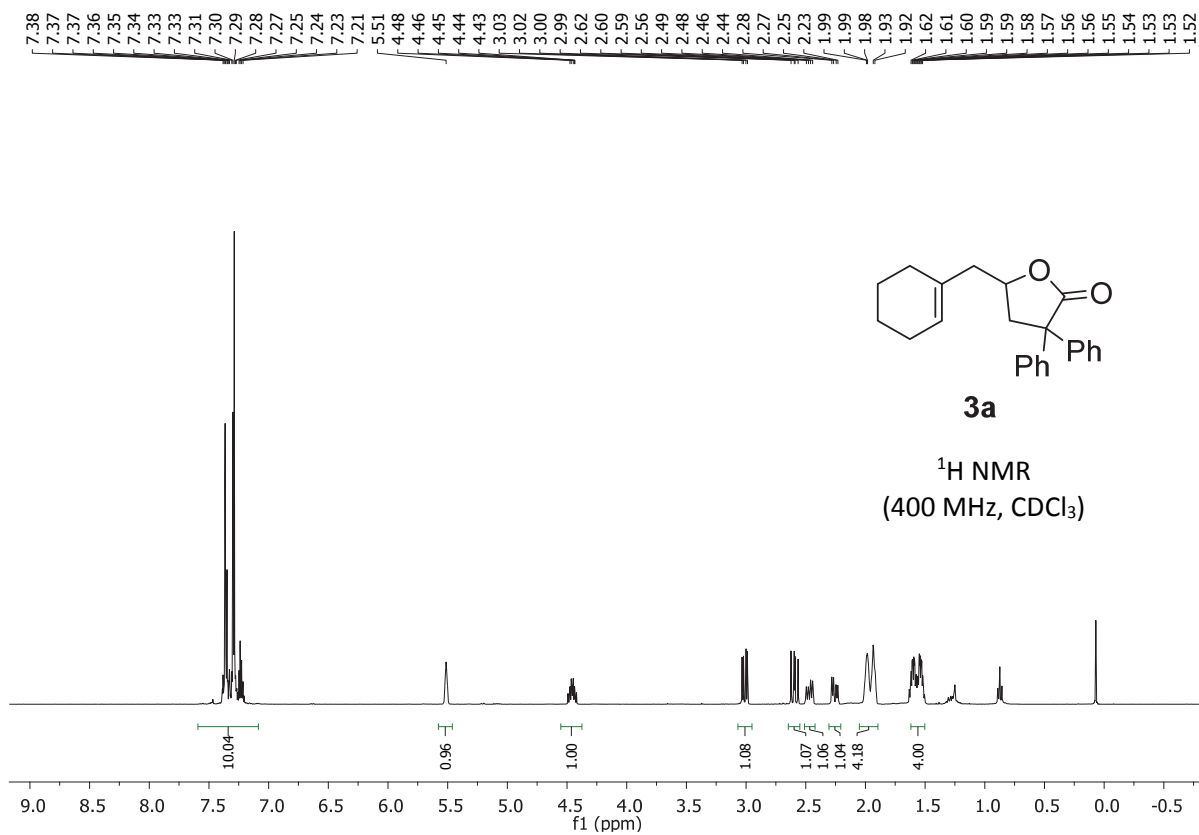
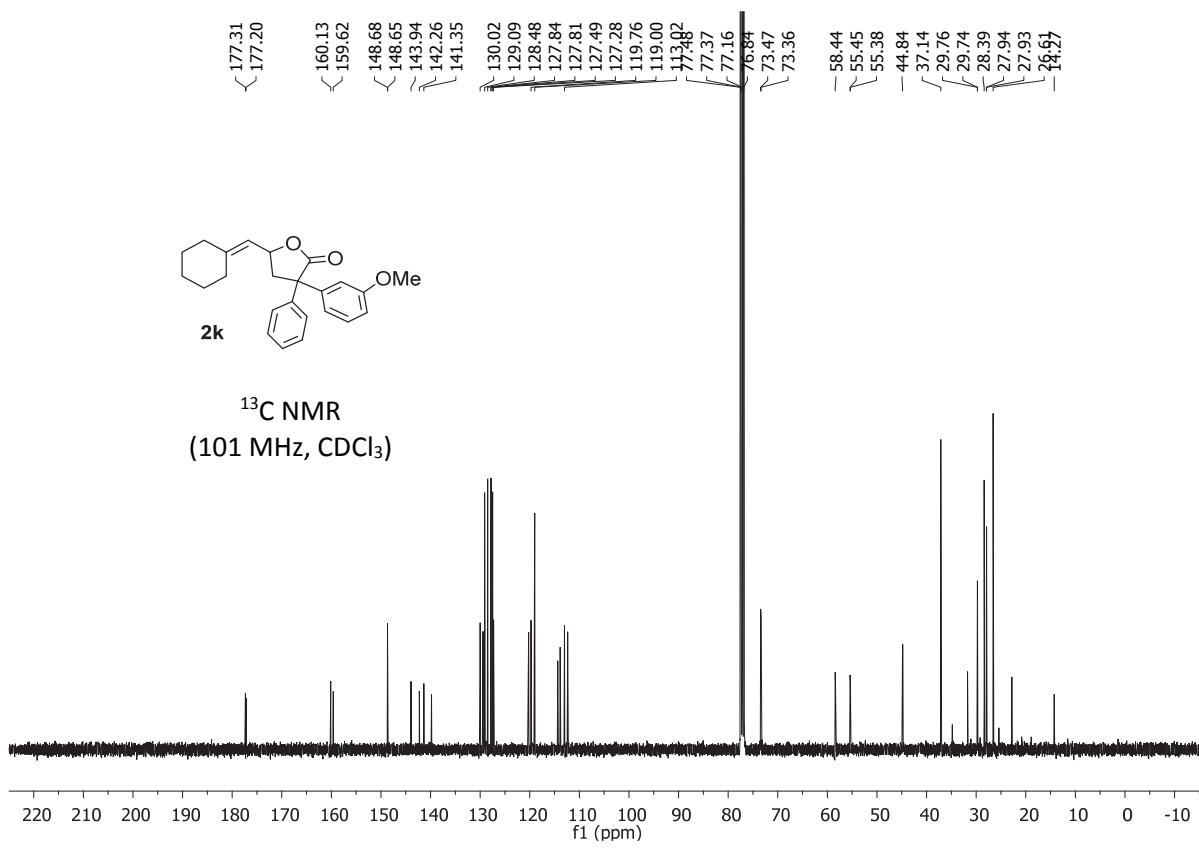












— 177.29

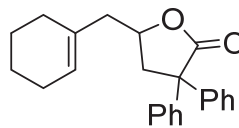
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125.18

77.48  
77.16  
76.84  
76.16

— 58.18

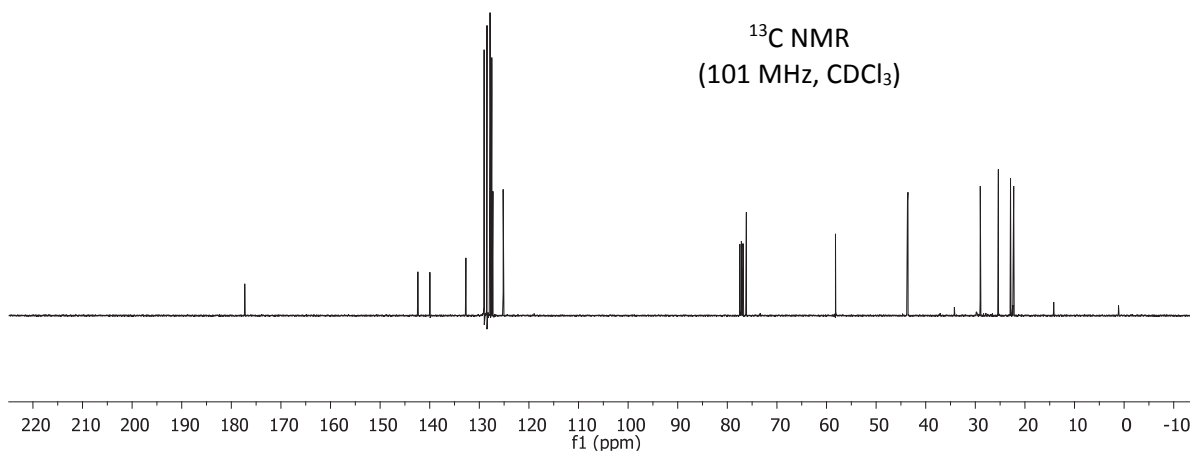
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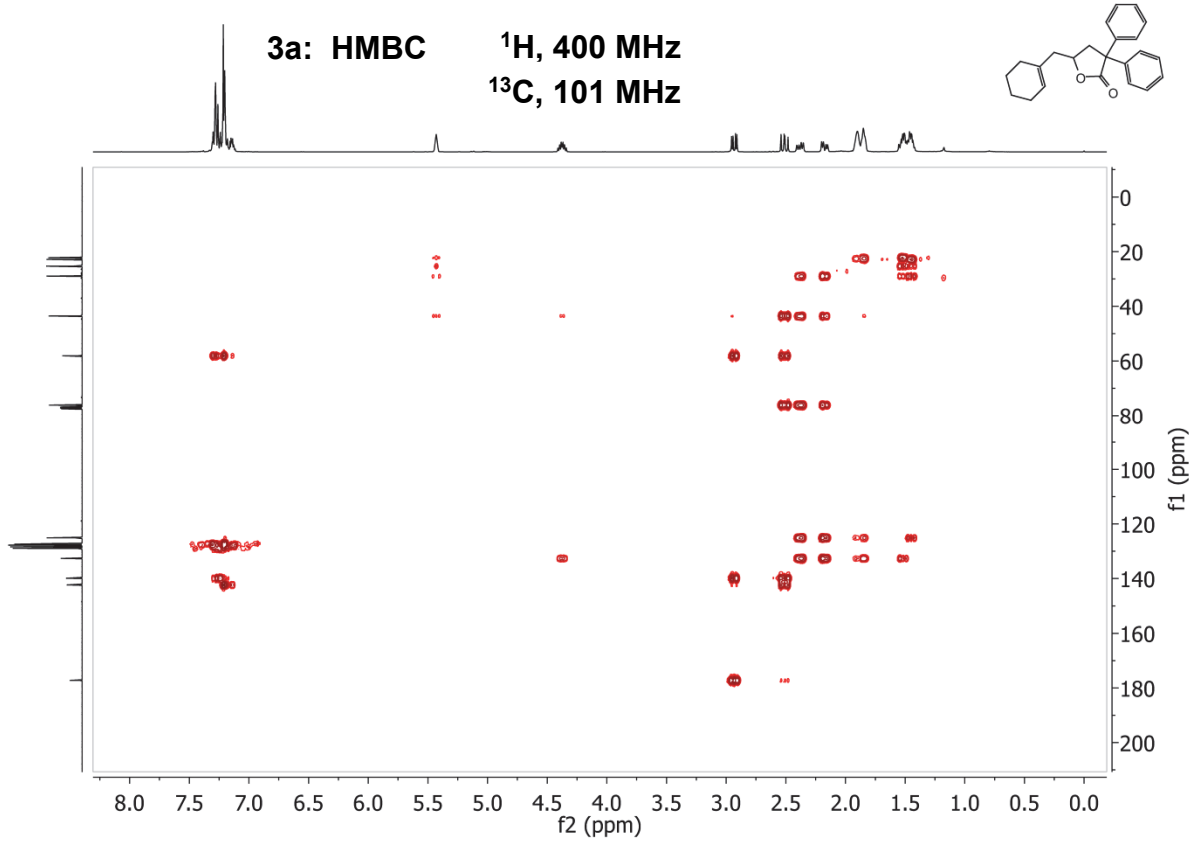
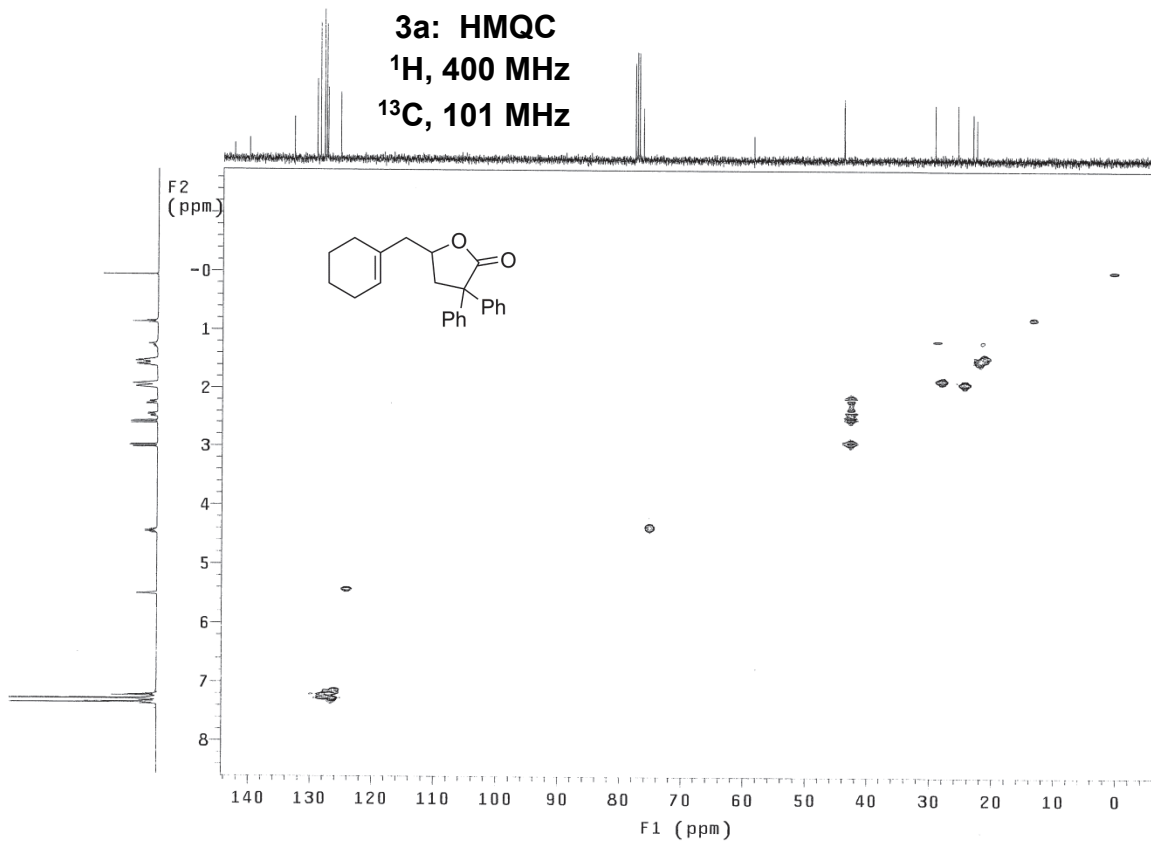
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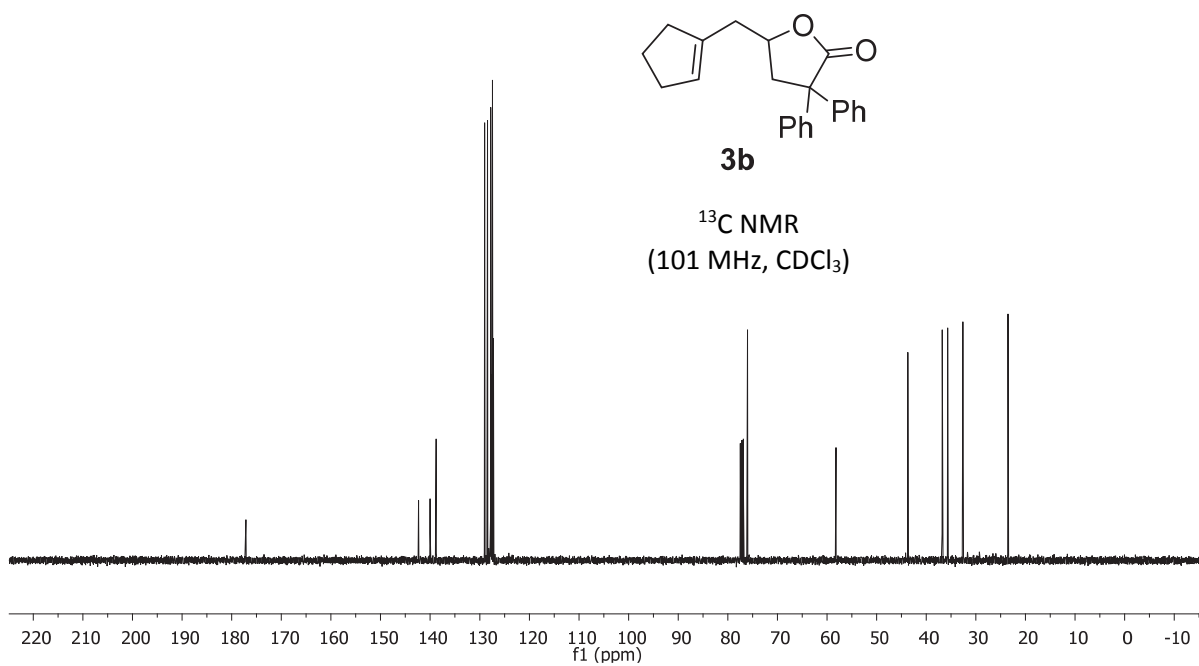
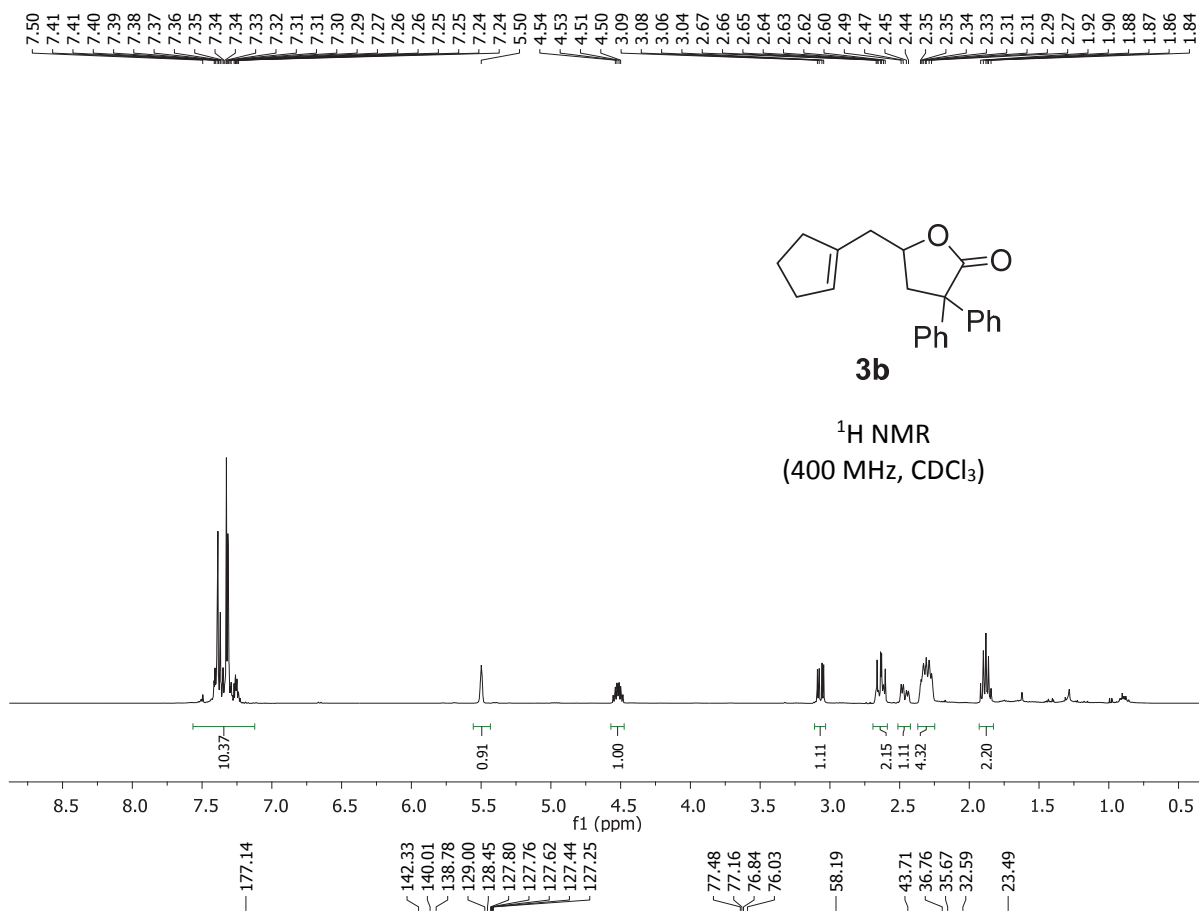


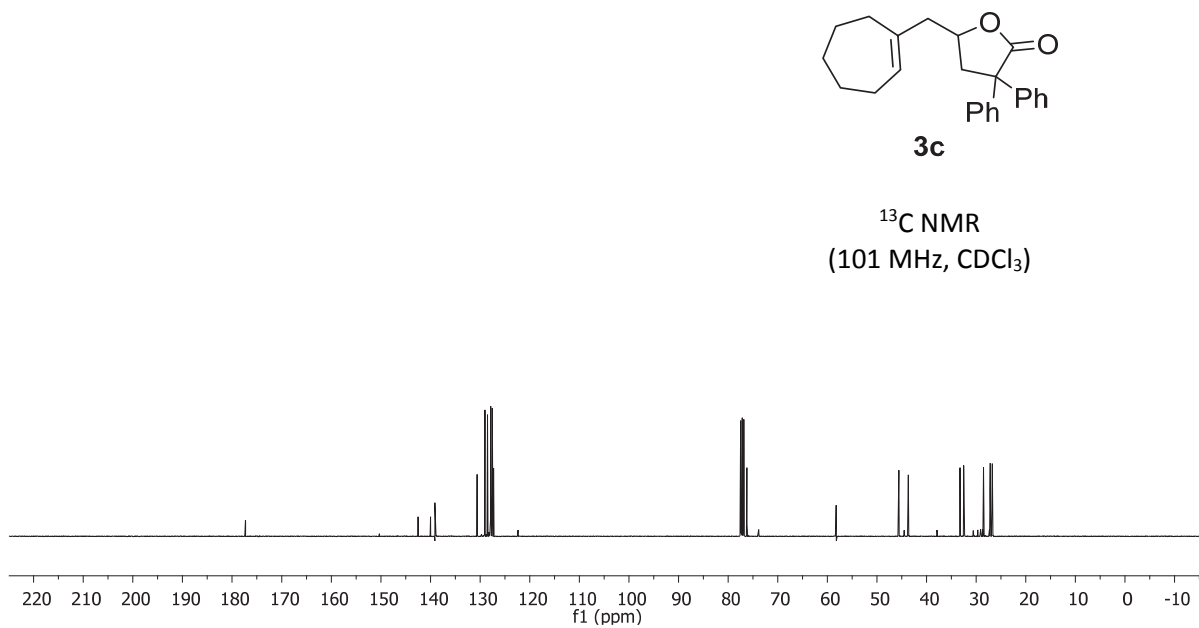
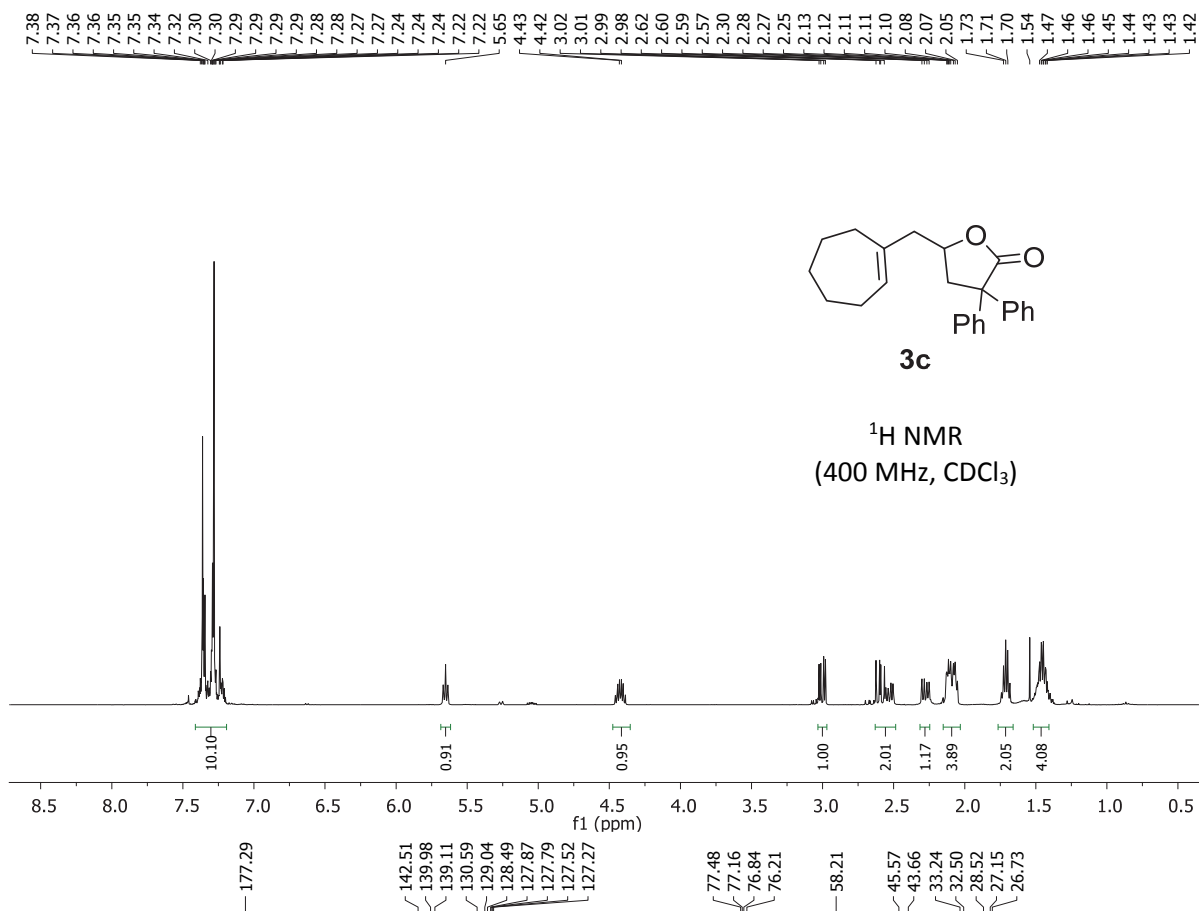
**3a**

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

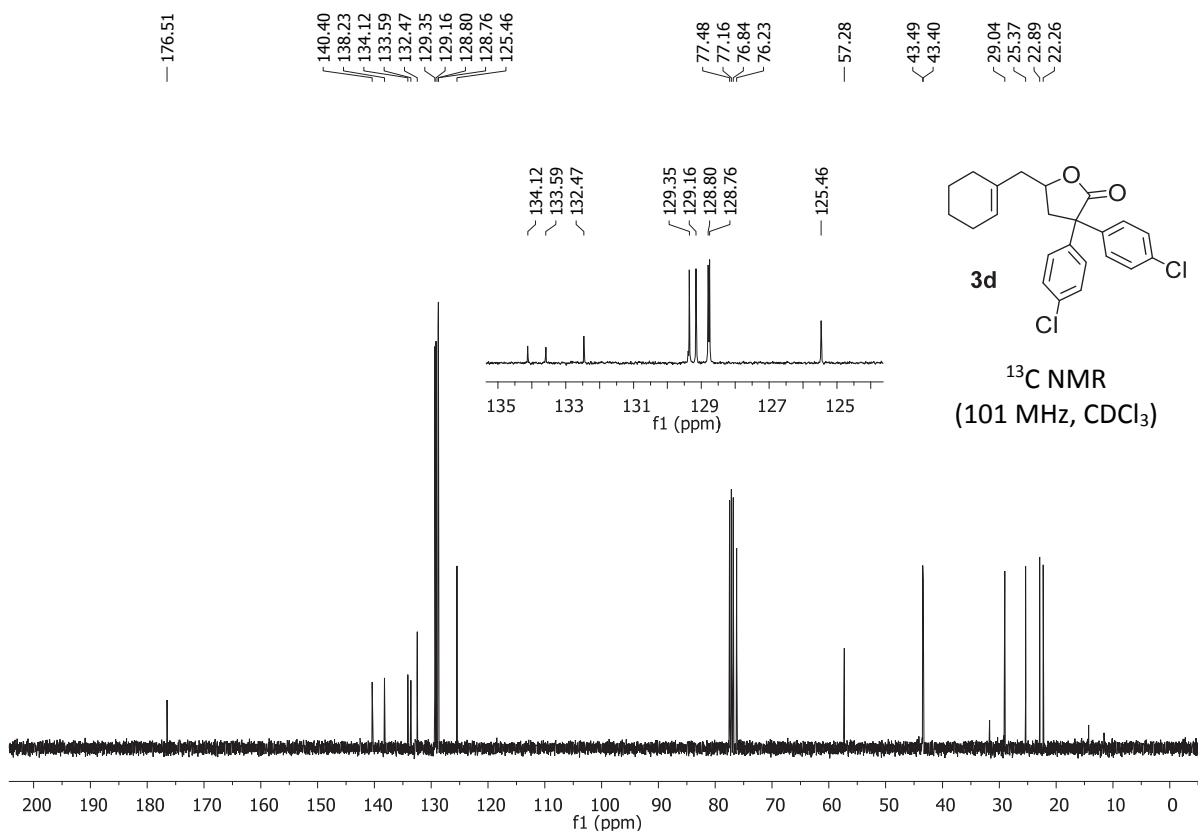
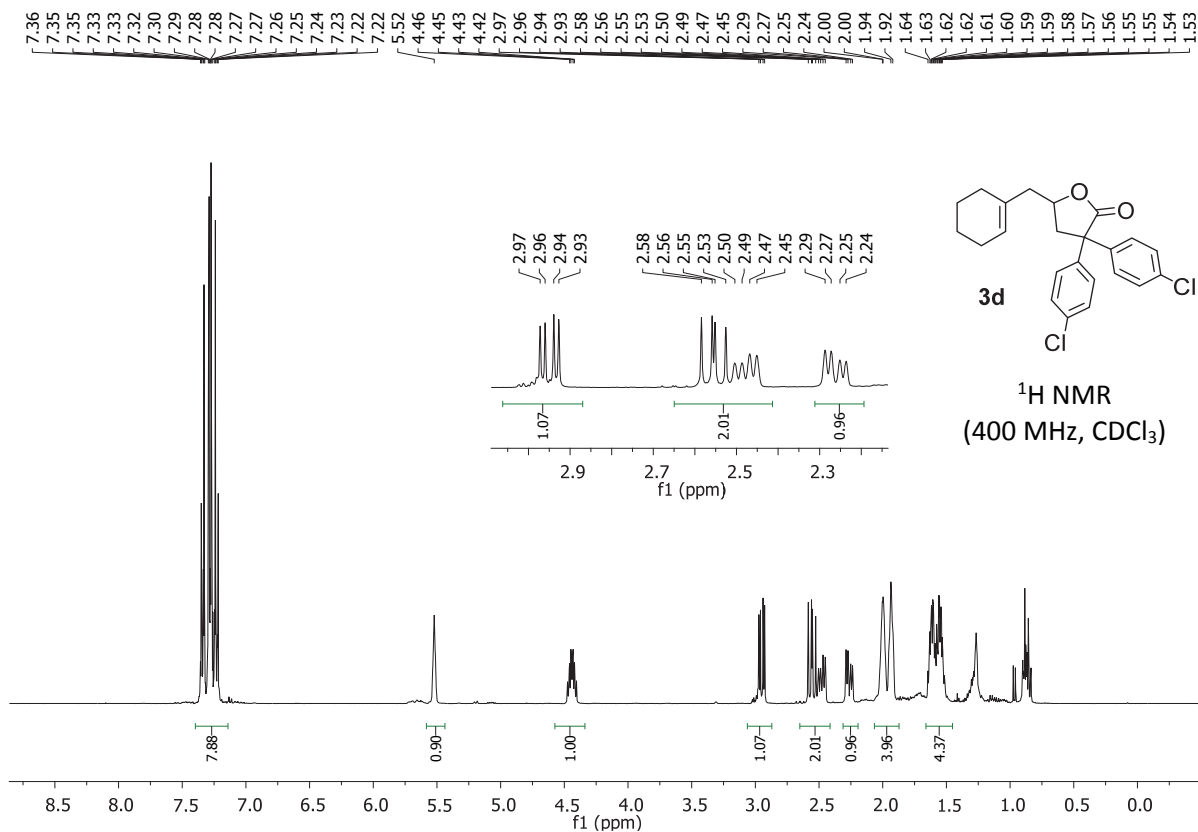


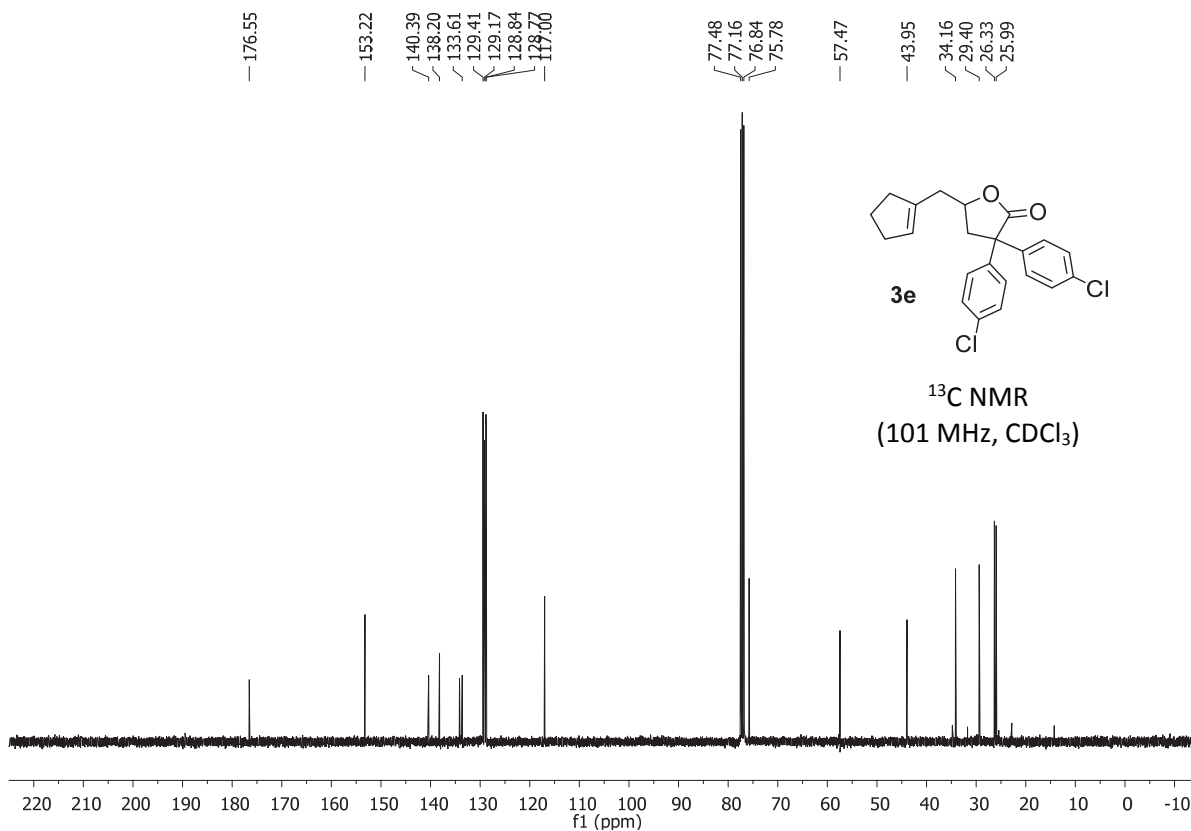
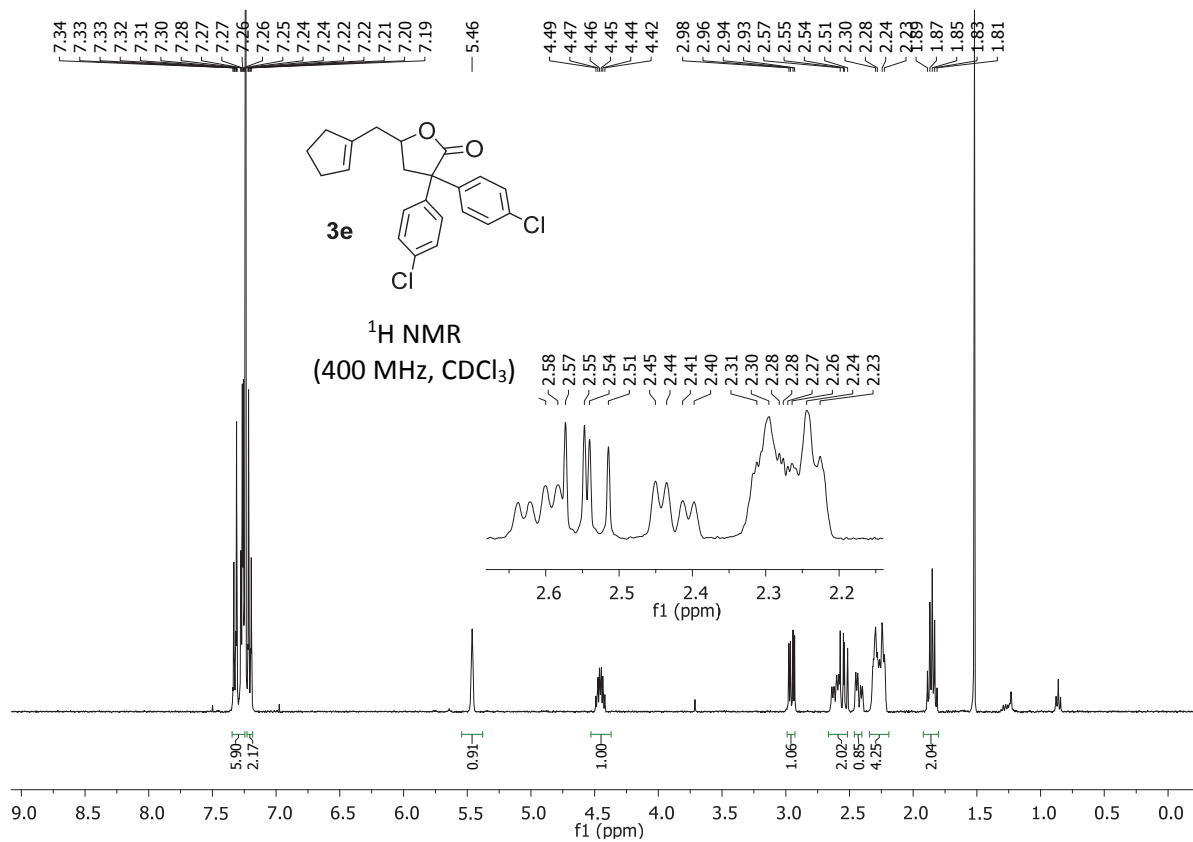


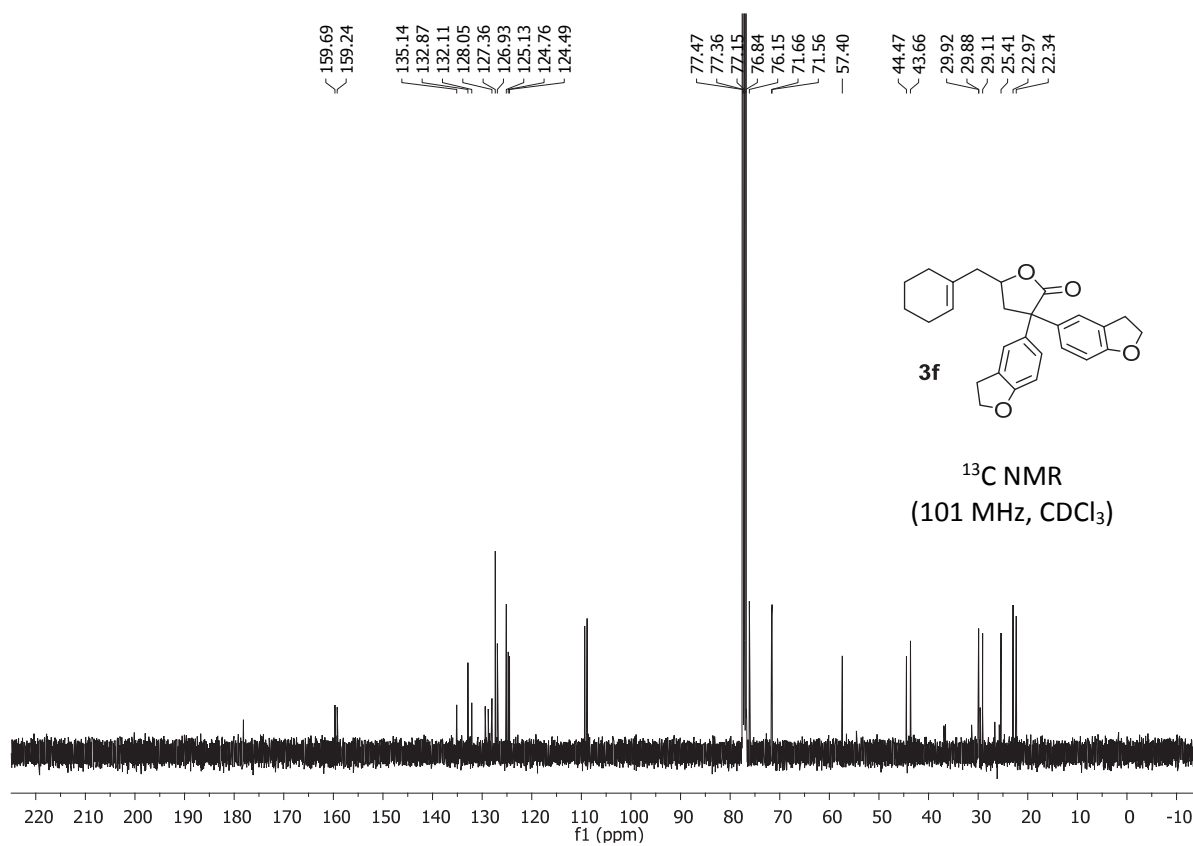
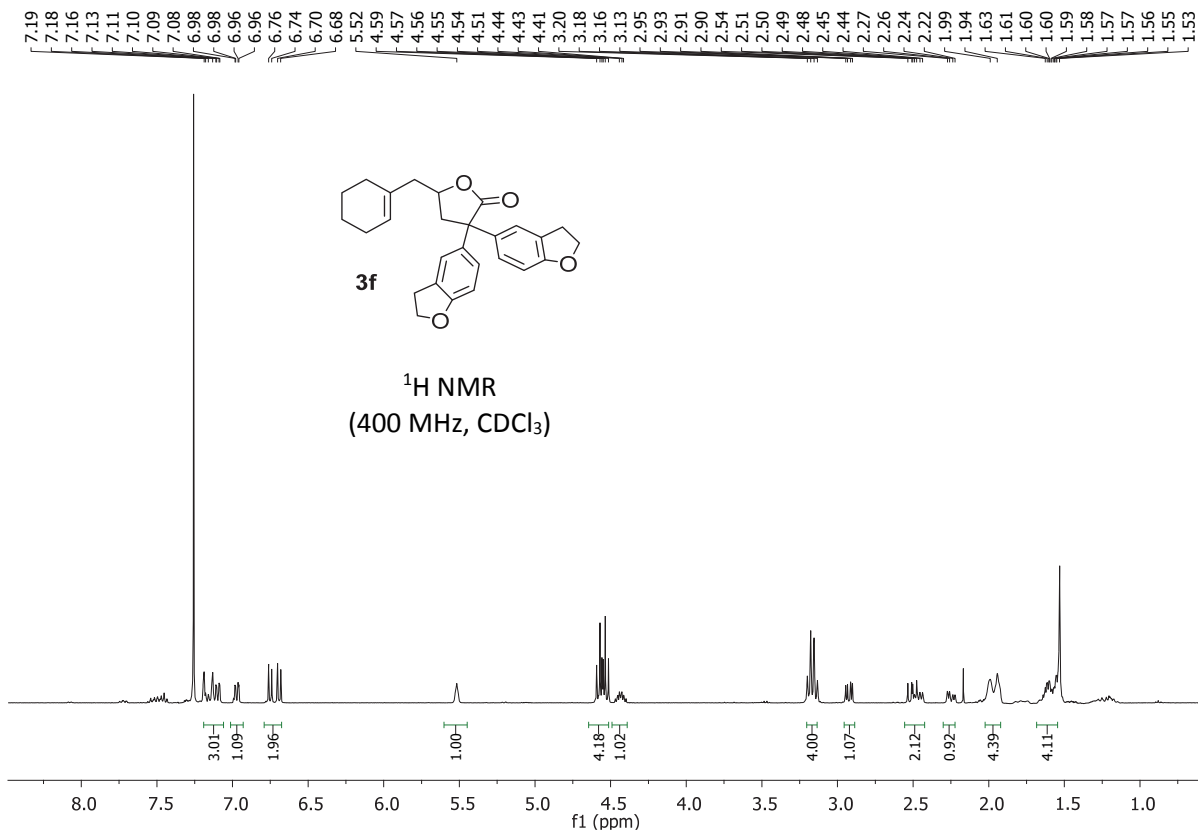


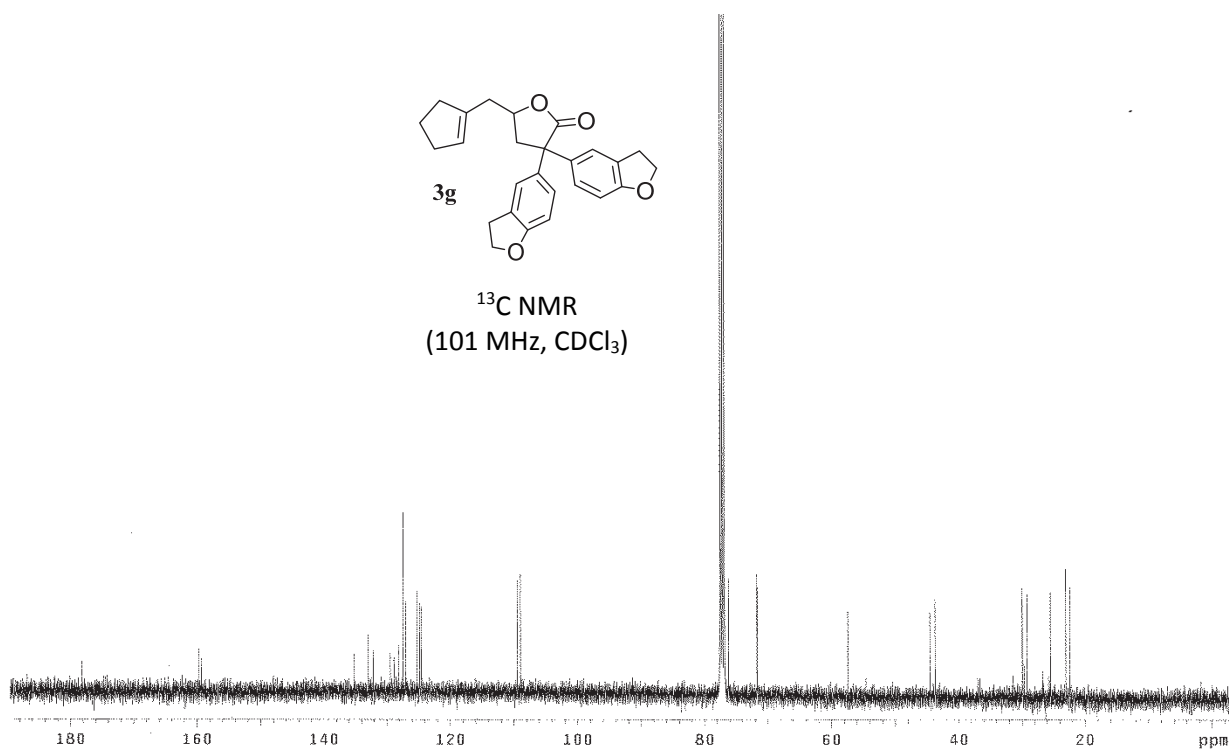
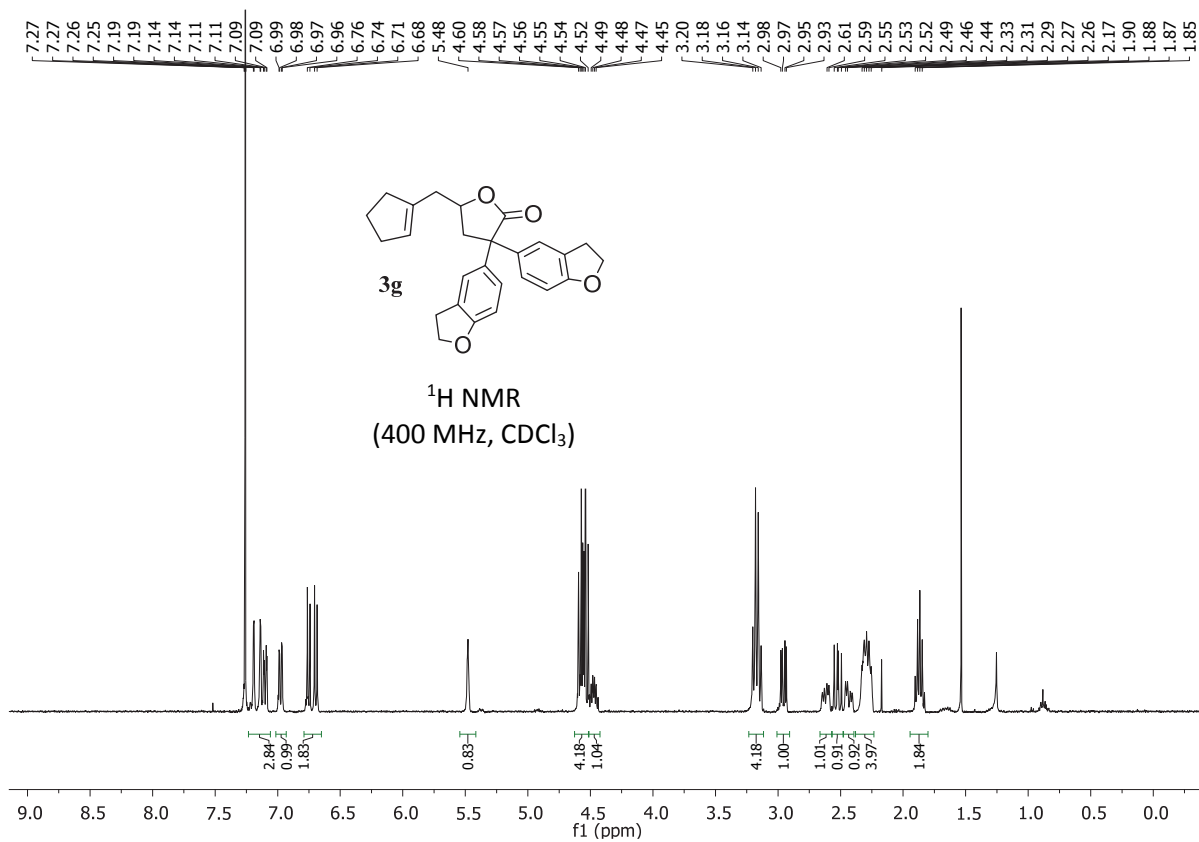


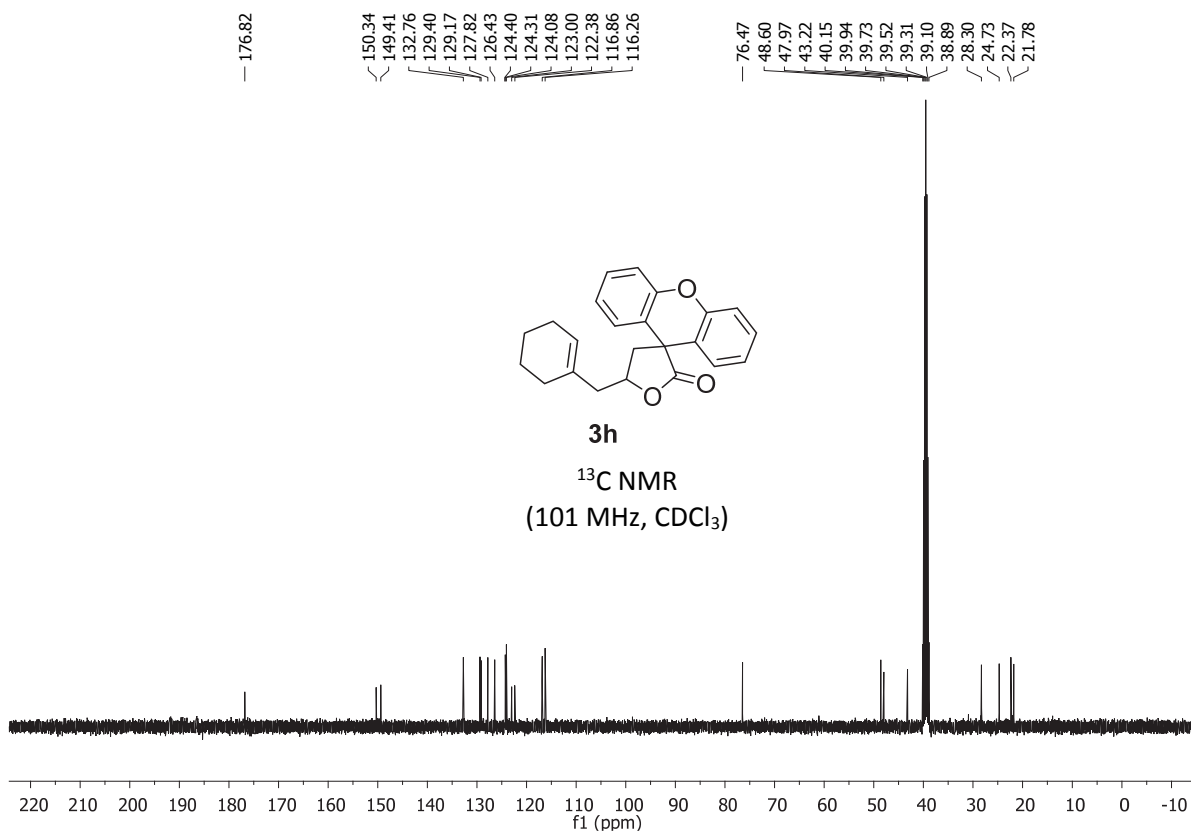
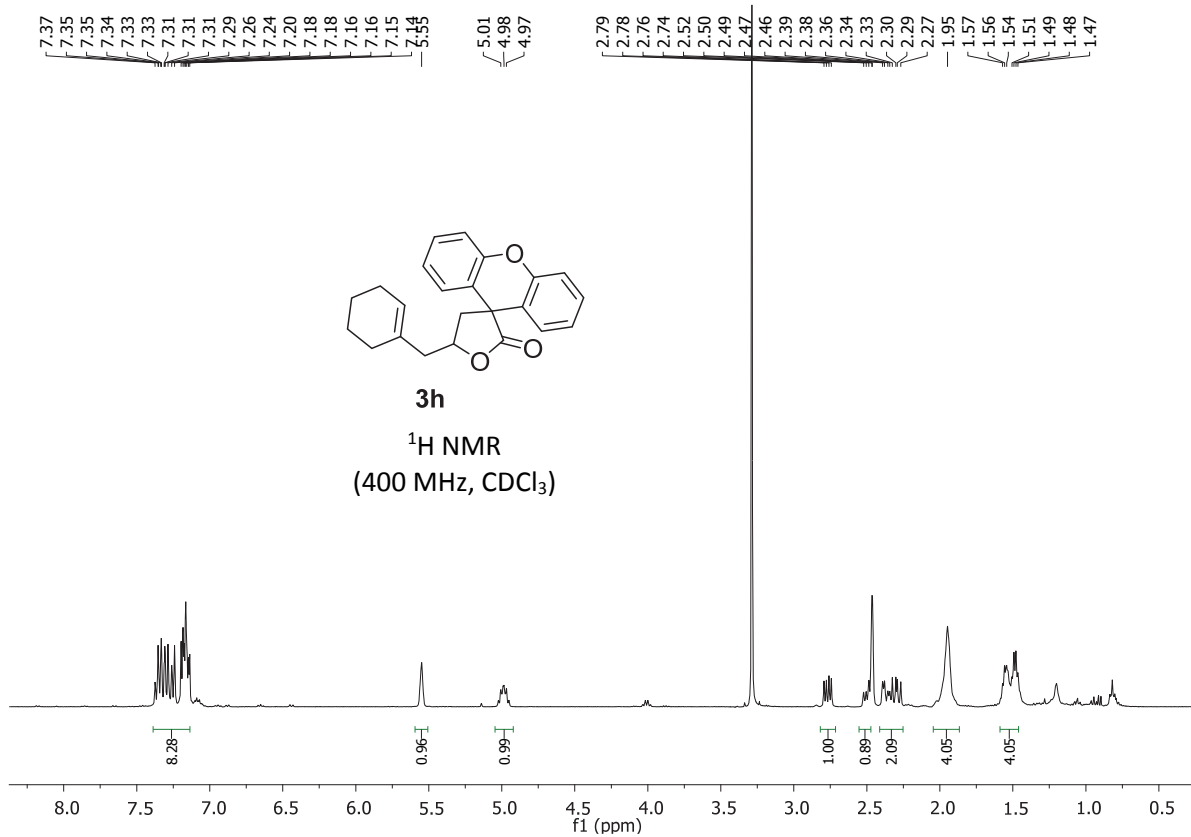


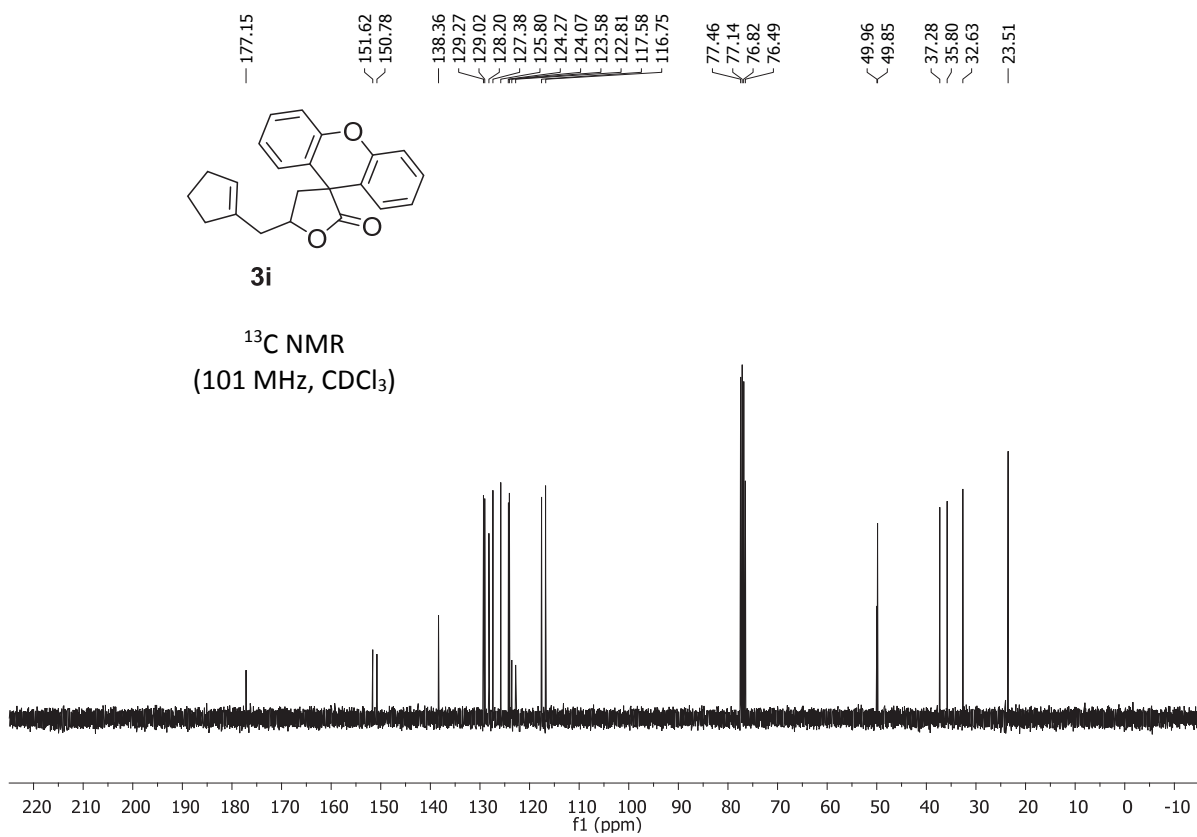
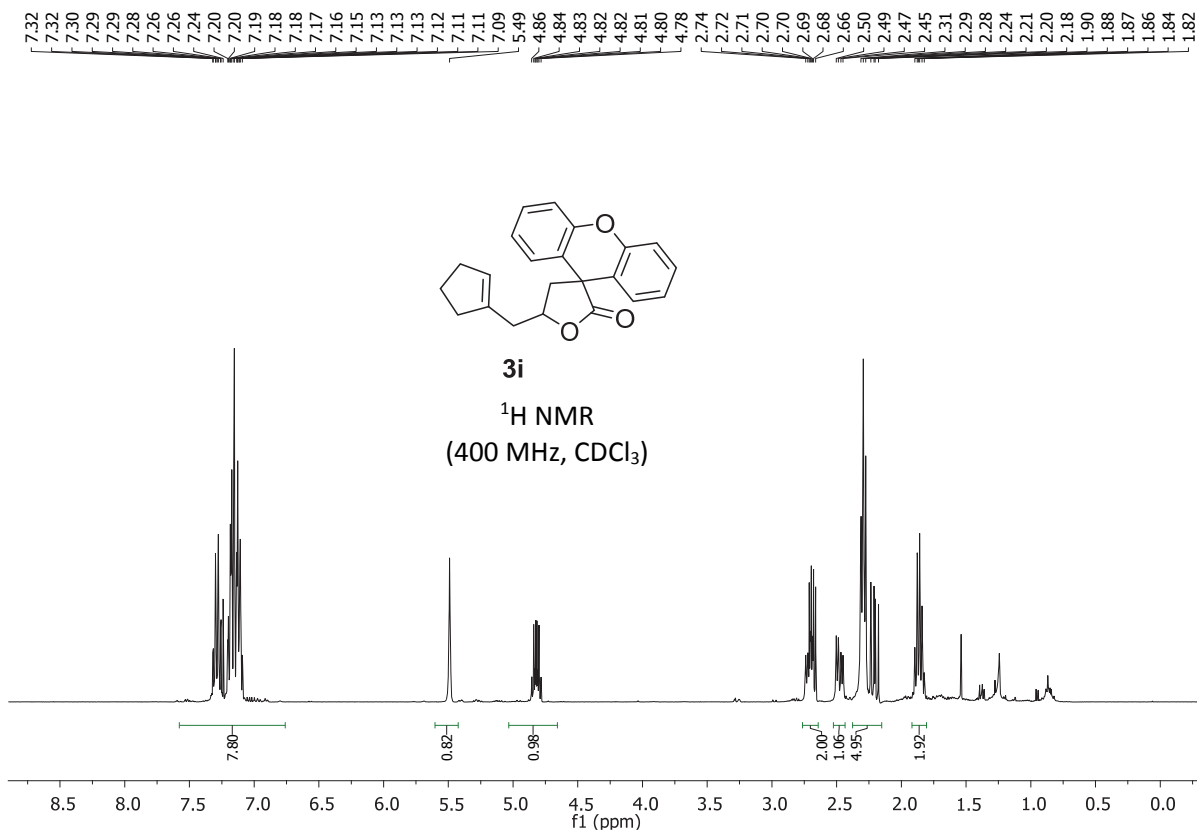


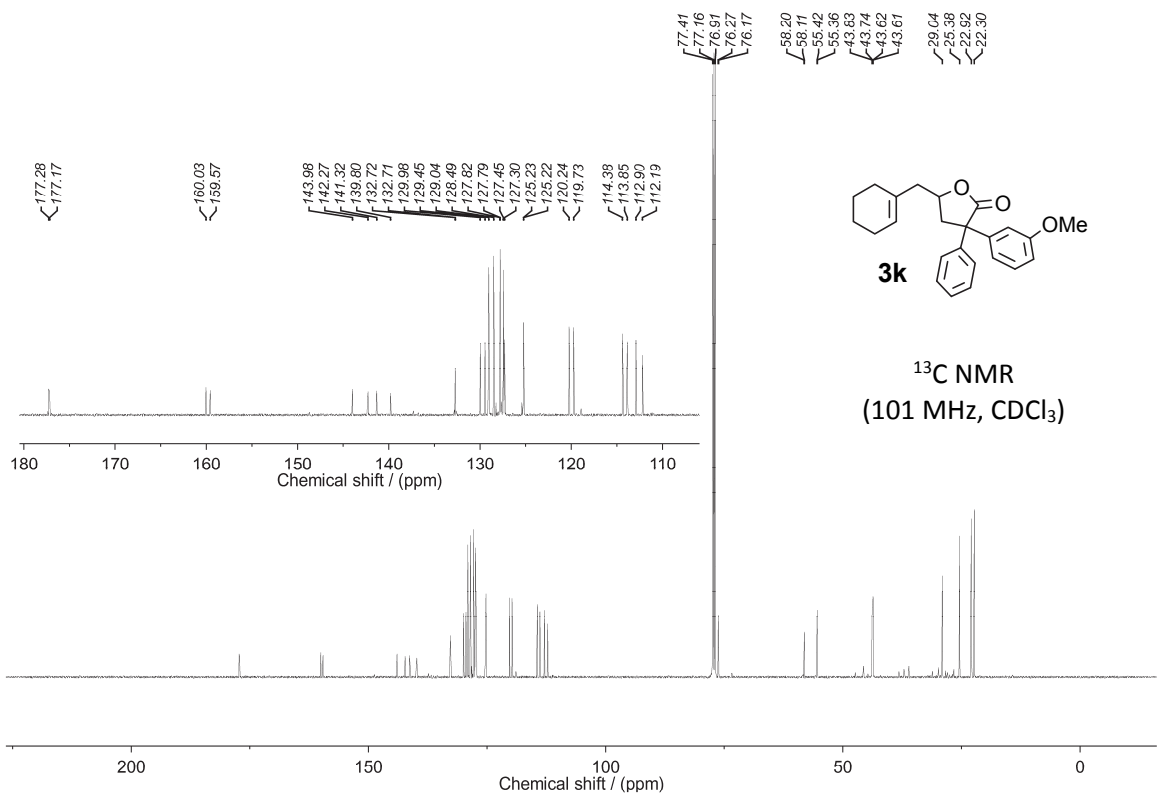
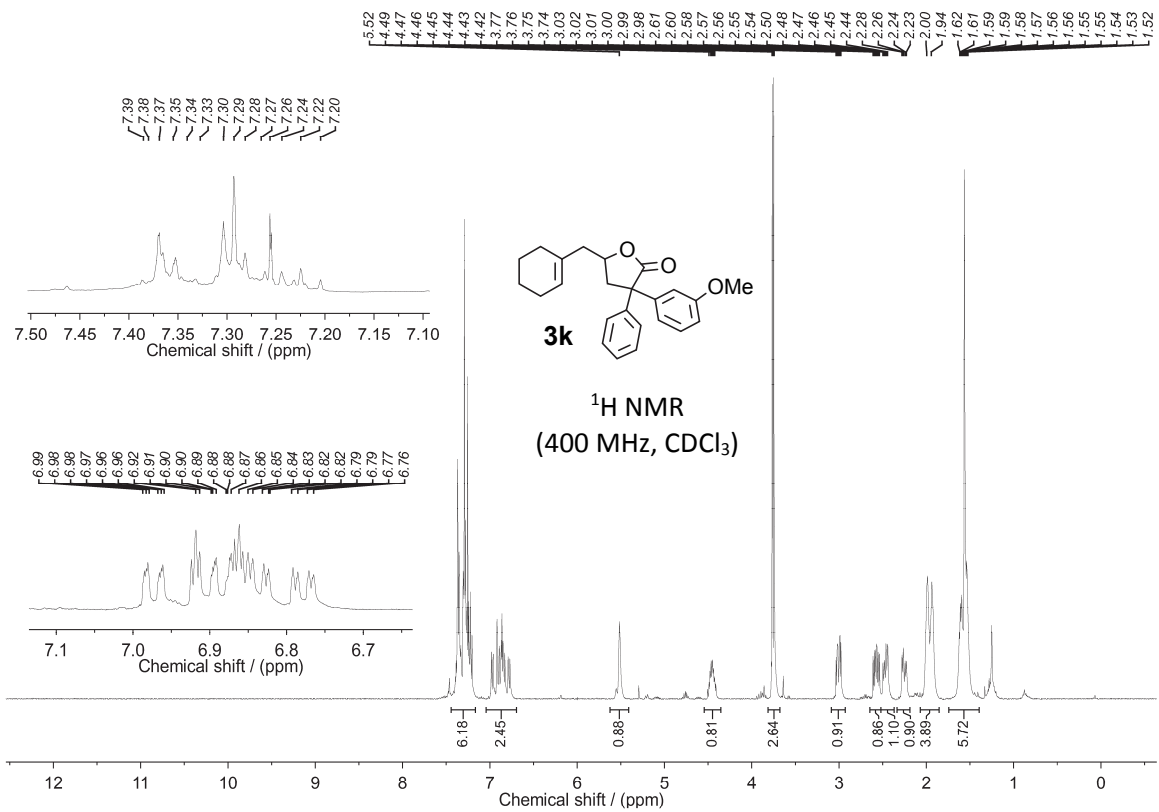


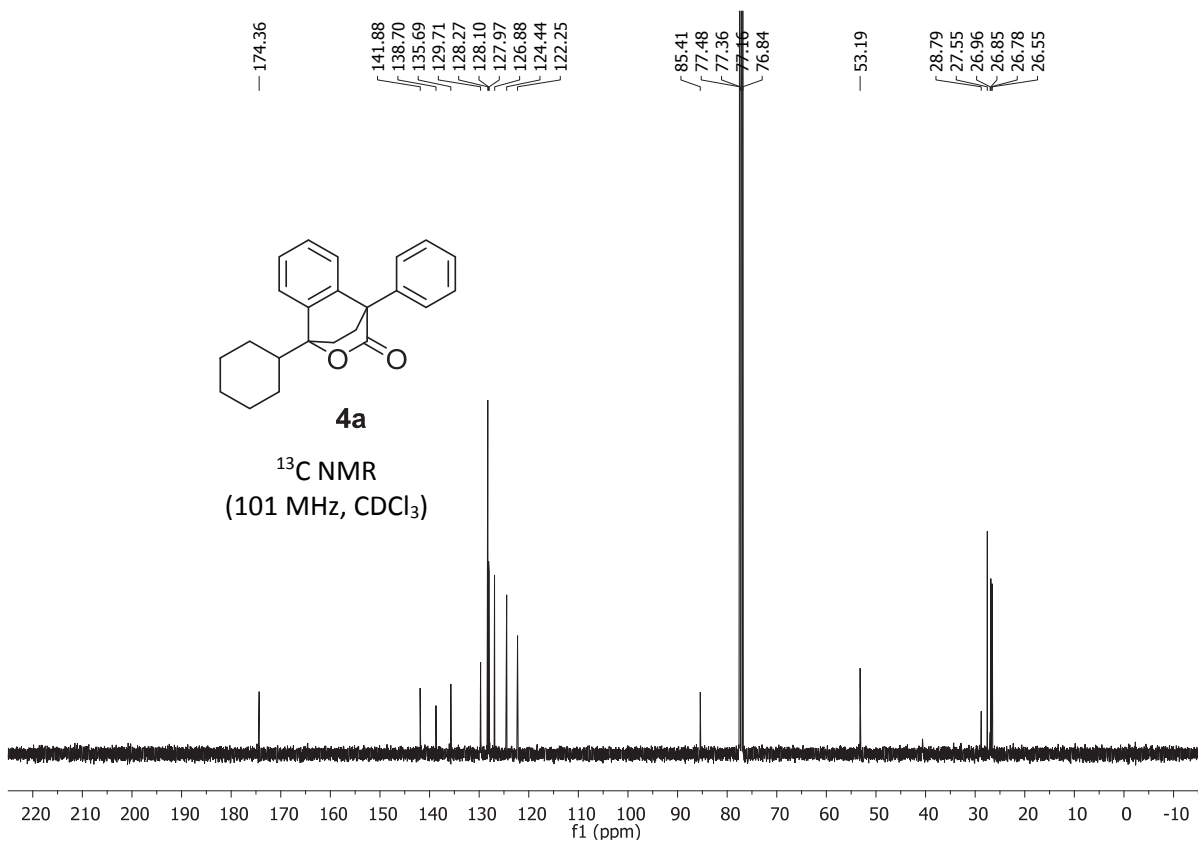
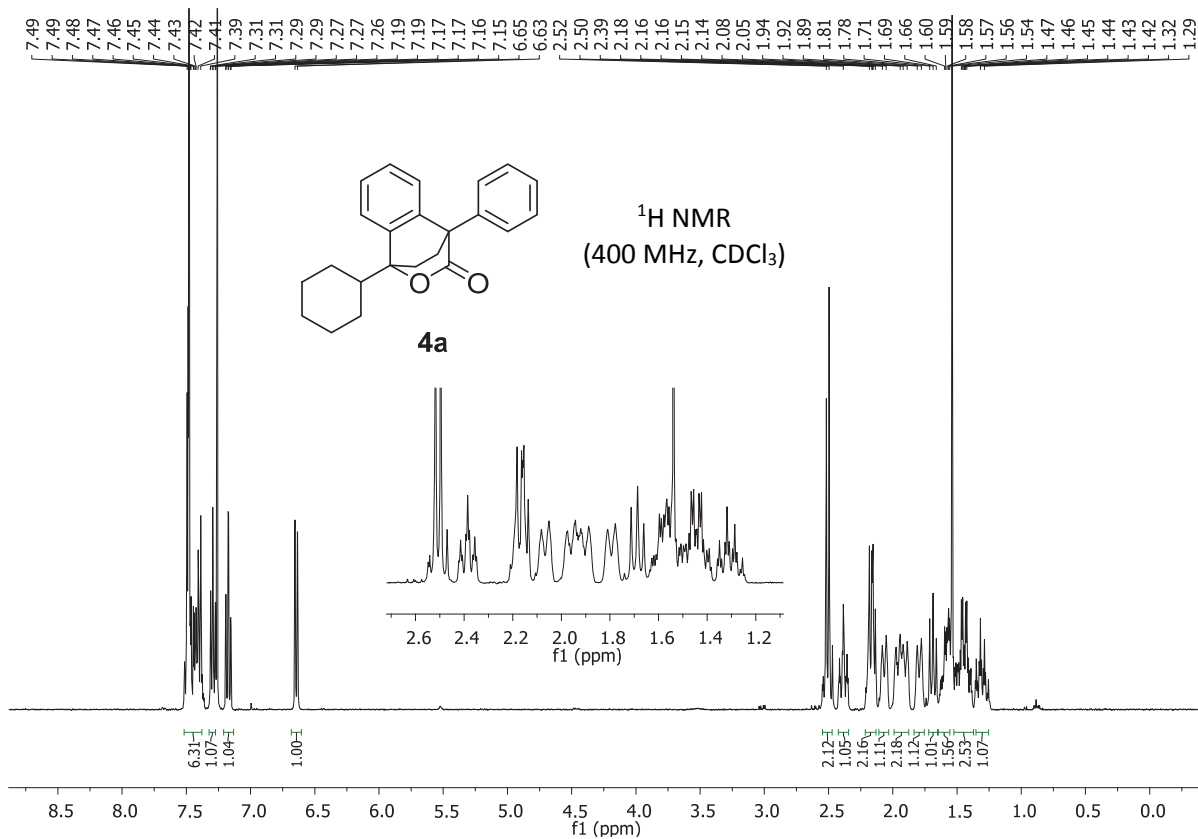




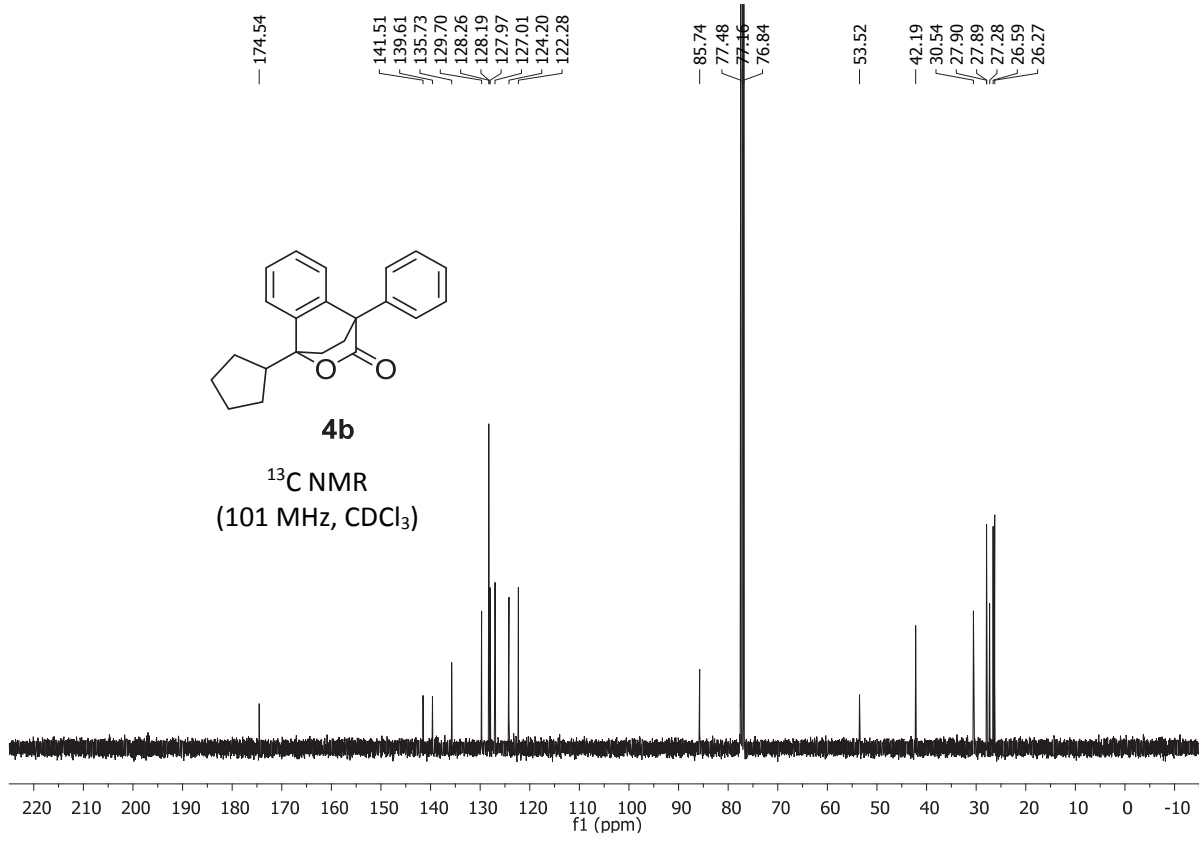
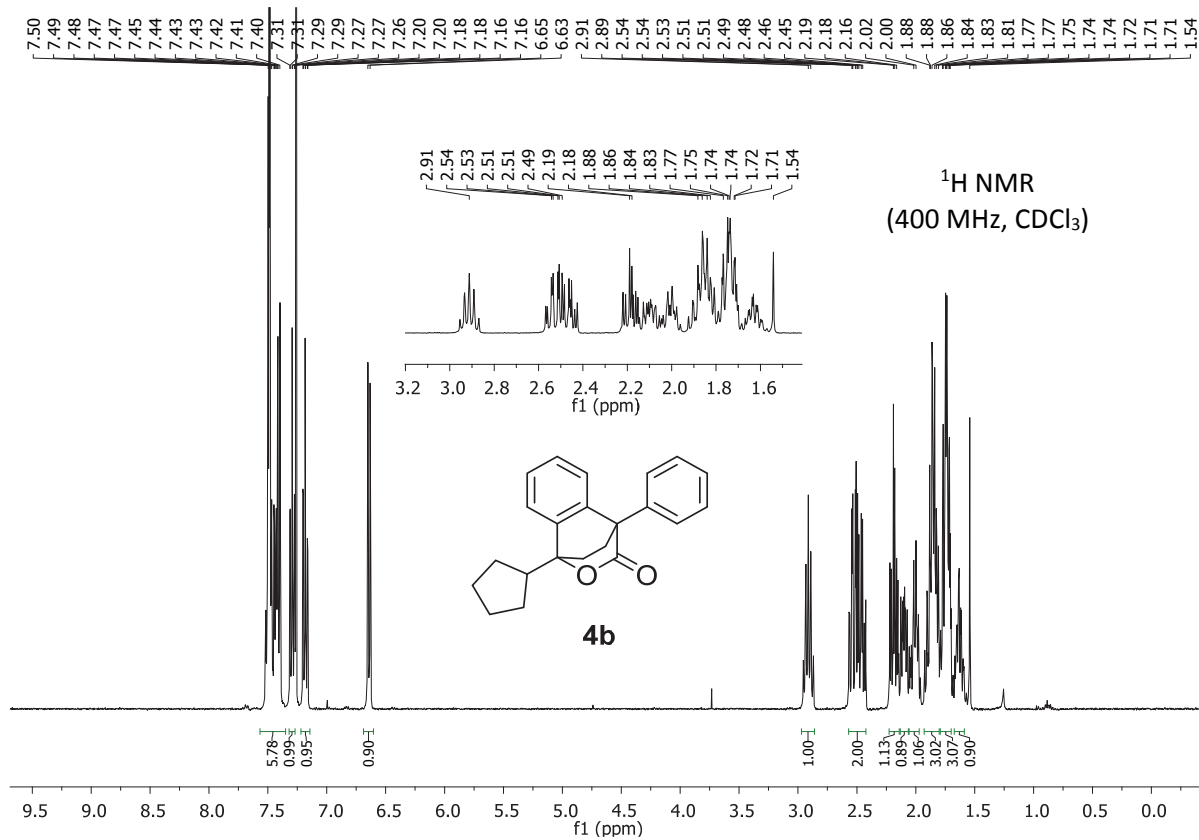


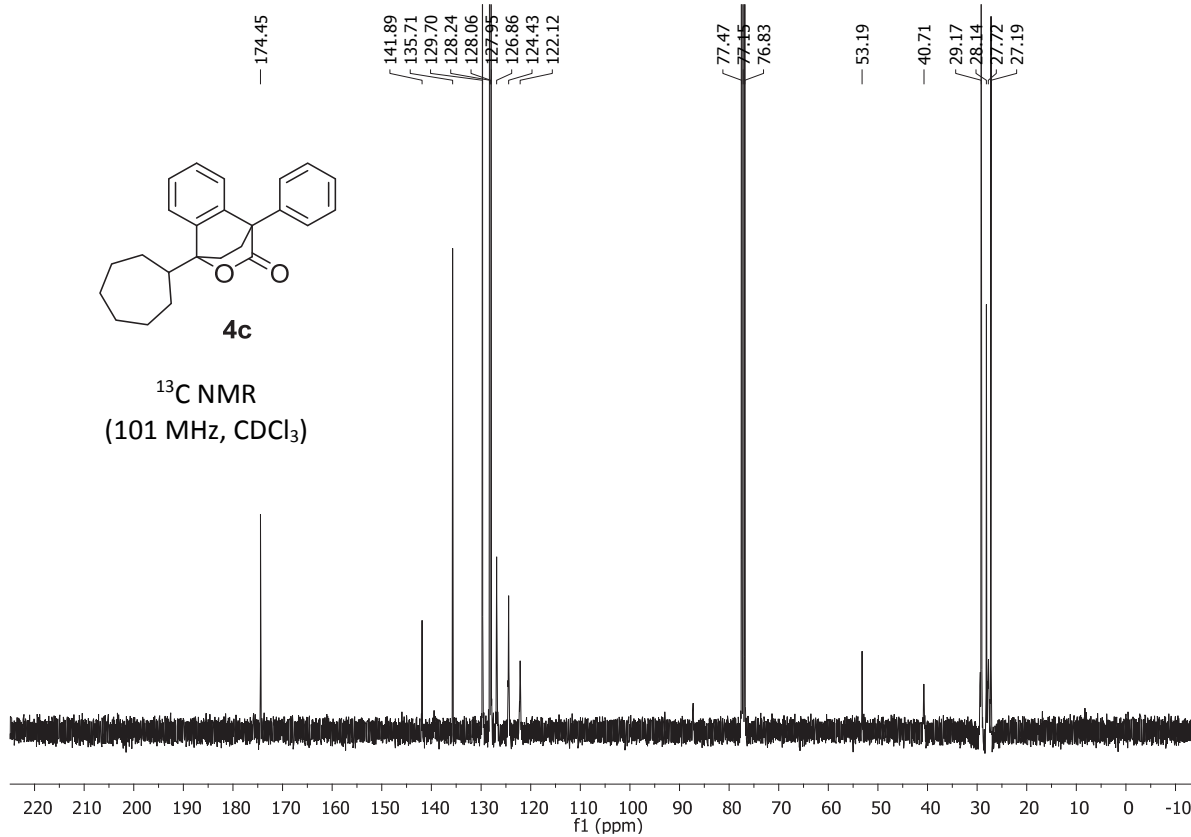
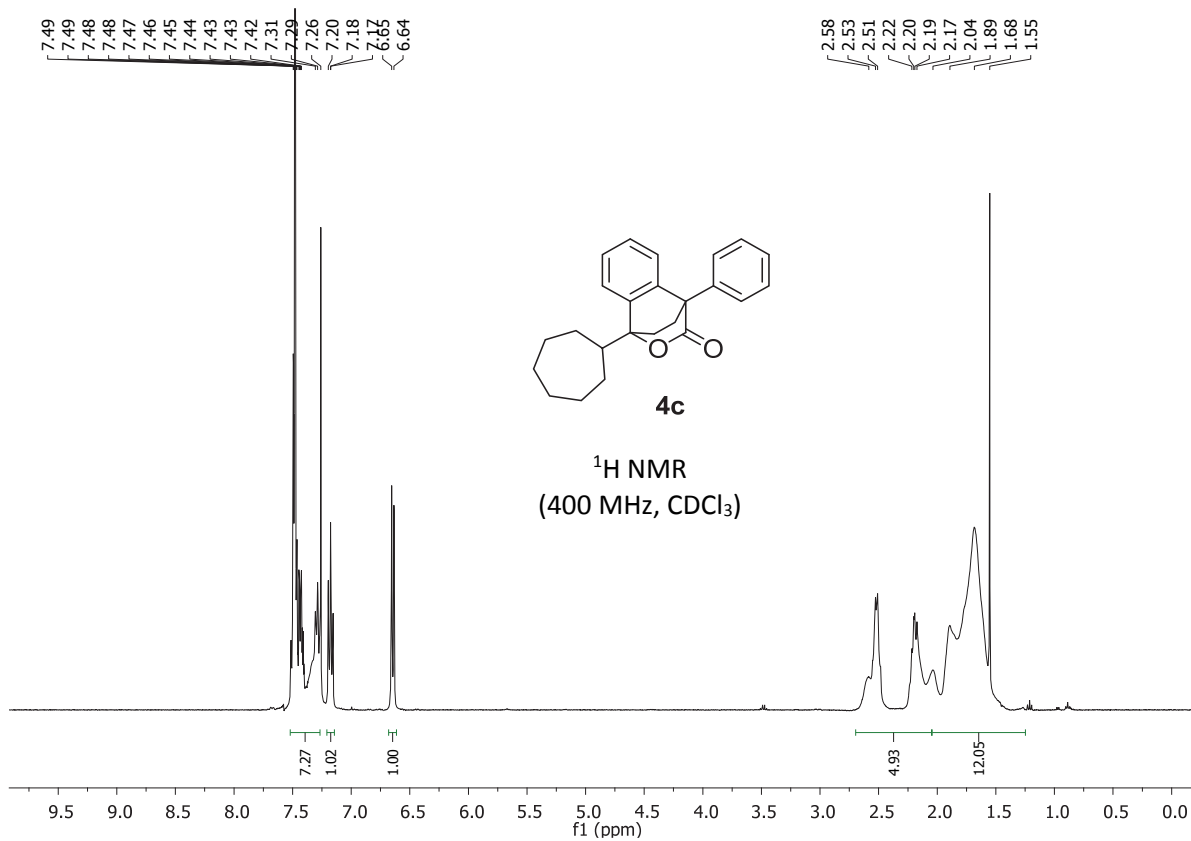


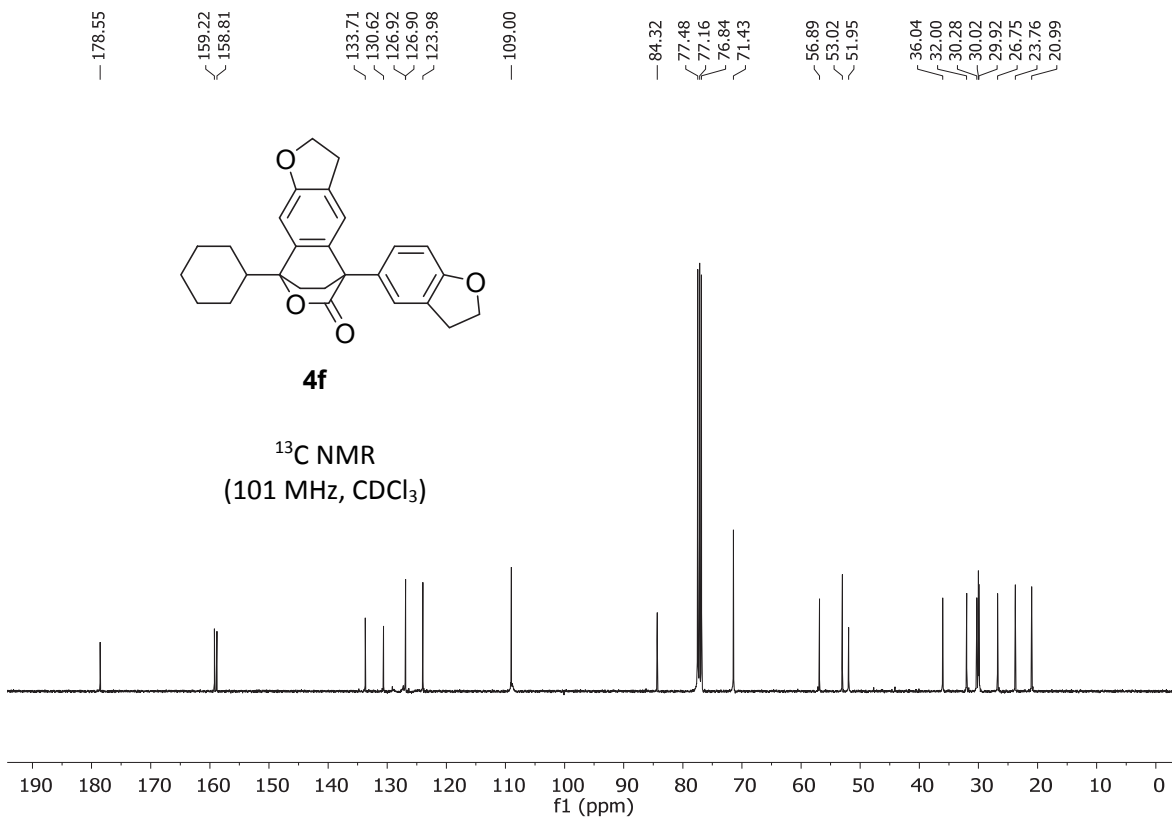
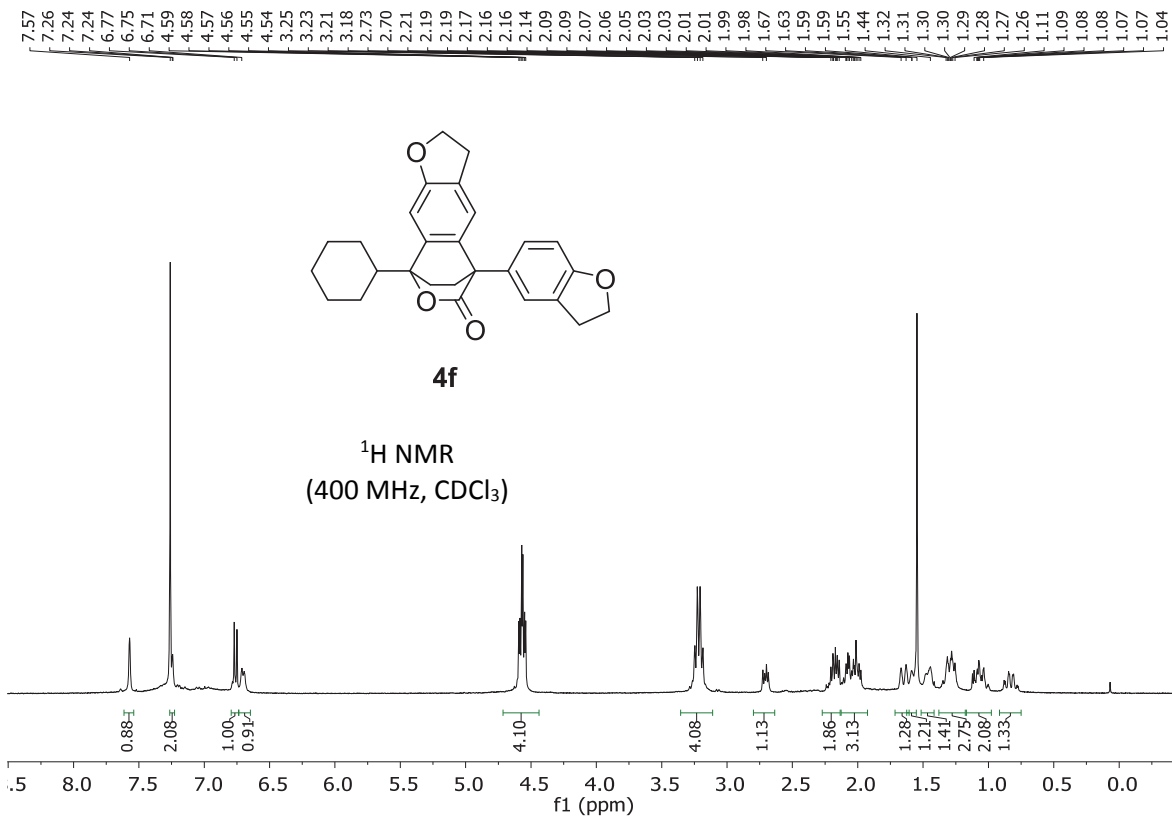




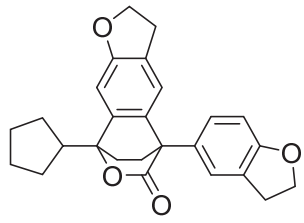






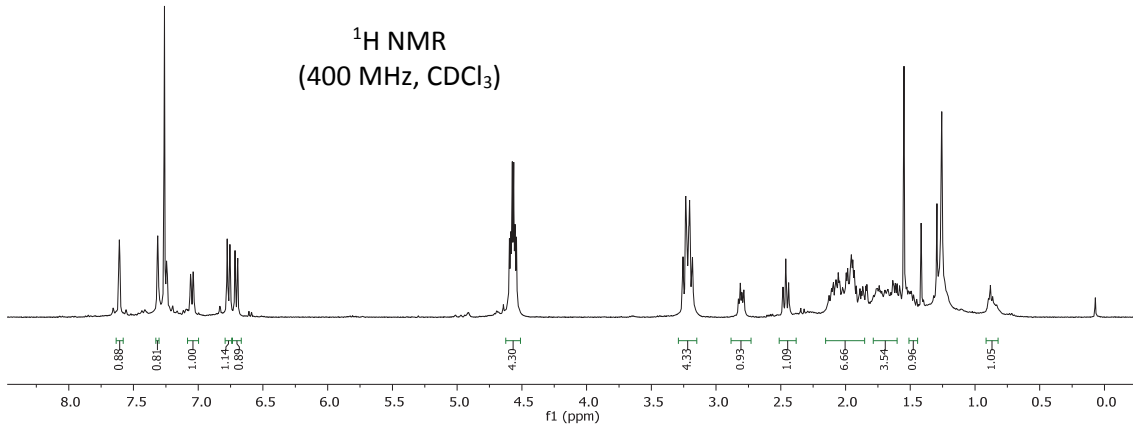


7.61  
7.61  
7.31  
7.26  
7.24  
7.06  
7.05  
7.04  
6.78  
6.72  
6.70  
4.60  
4.59  
4.57  
4.56  
4.55  
4.54  
4.54  
3.26  
3.23  
3.23  
3.21  
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2.79  
2.46  
2.46  
2.44  
2.41  
2.11  
2.10  
2.09  
2.08  
2.07  
2.07  
2.06  
2.06  
2.04  
2.02  
2.02  
2.00  
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0.88

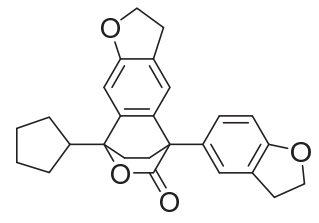


**4g**

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

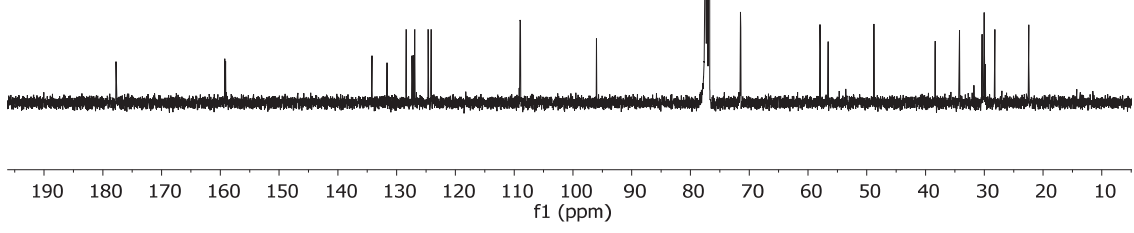


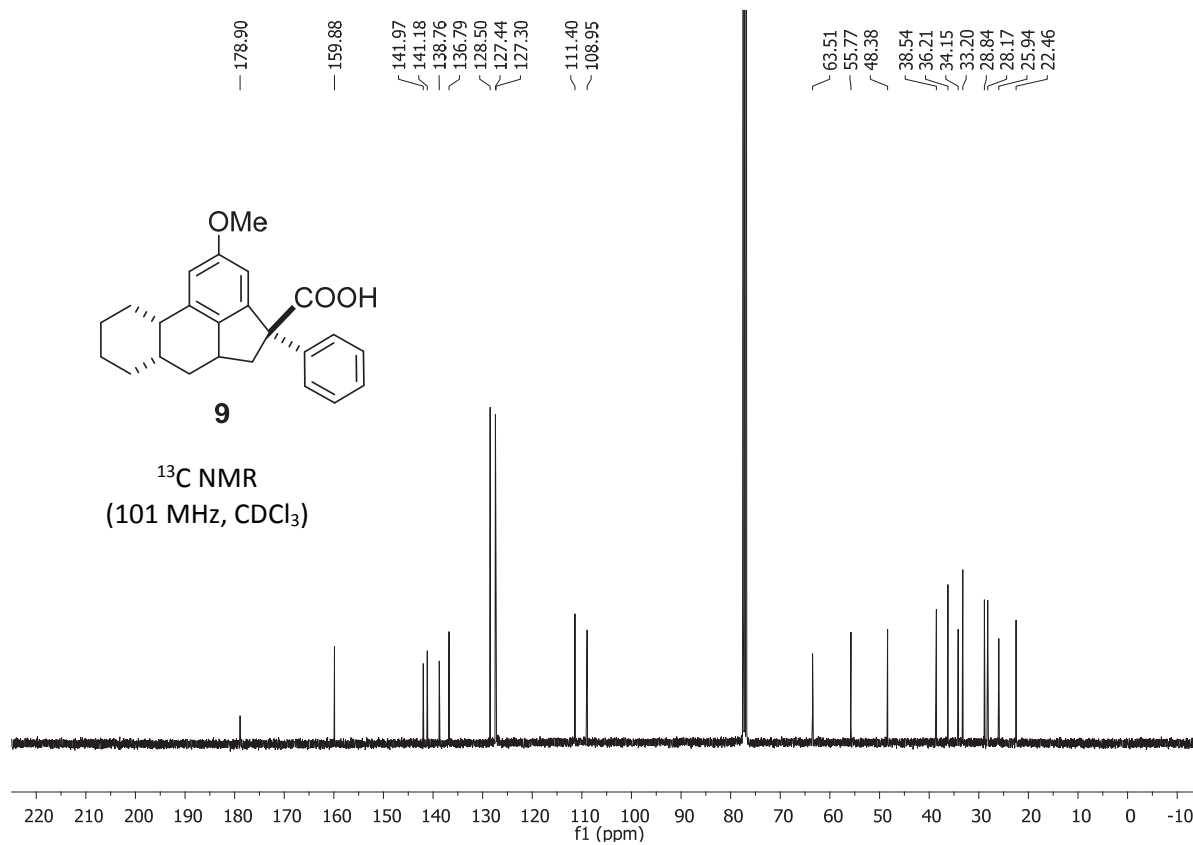
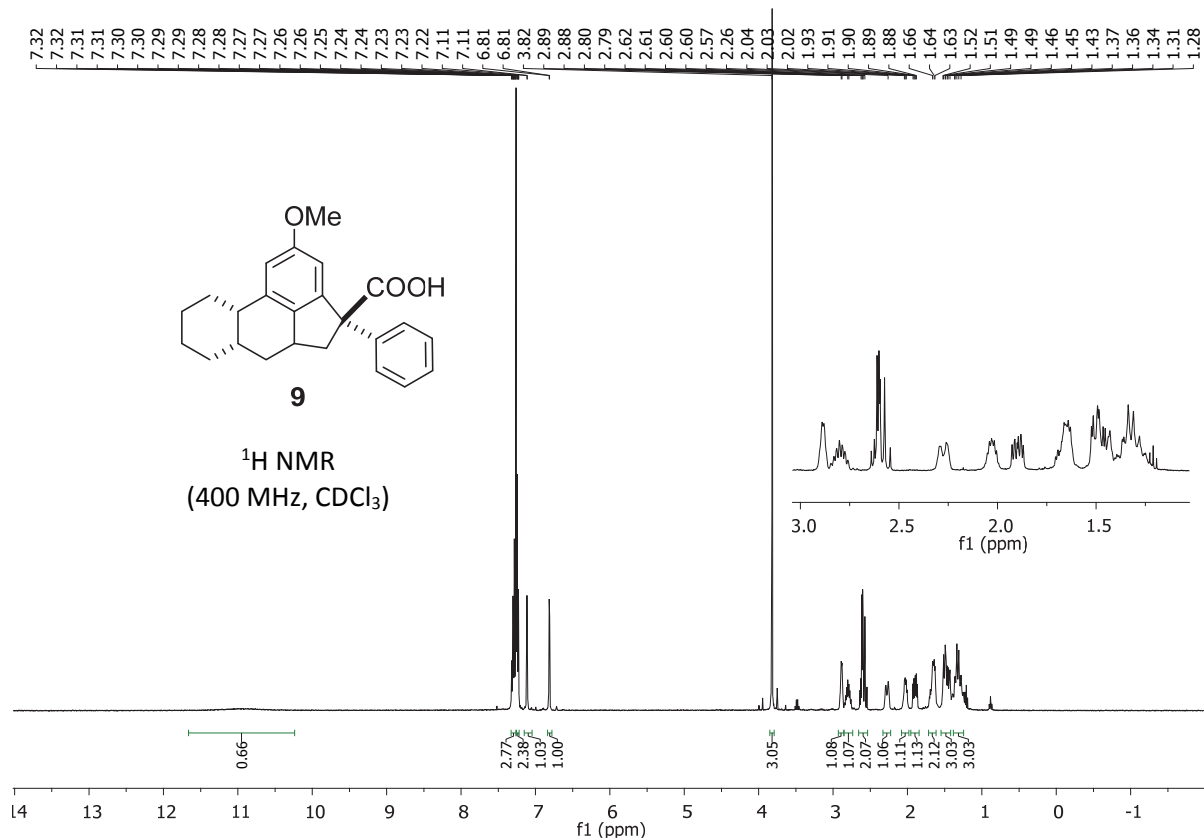
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 ~ 159.25  
 ~ 159.11  
 134.20  
 131.64  
 128.35  
 127.38  
 127.18  
 126.92  
 124.65  
 124.13  
 ~ 109.01  
 ~ 108.91  
 — 95.99  
 77.48  
 77.36  
 77.16  
 76.84  
 71.50  
 ~ 57.95  
 ~ 56.58  
 — 48.77  
 ~ 38.37  
 ~ 34.22  
 ~ 30.39  
 ~ 30.04  
 ~ 29.96  
 ~ 28.21  
 ~ 22.43



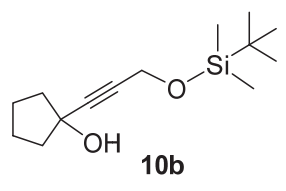
**4g**

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

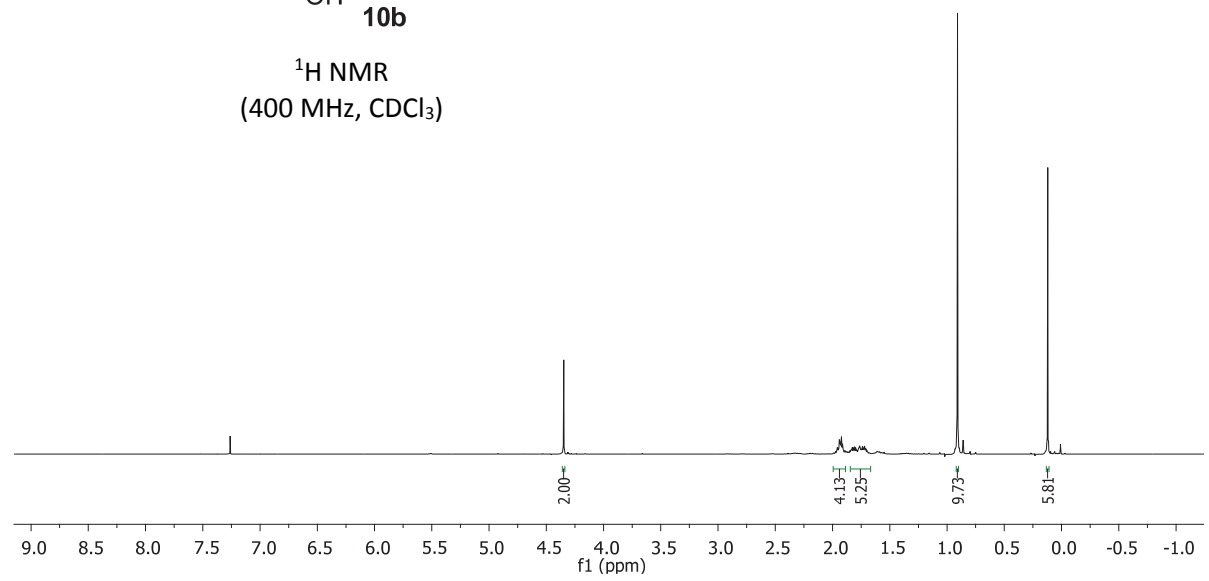




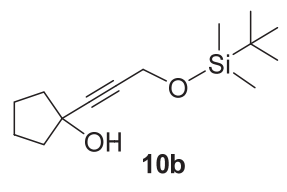
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1.95  
1.94  
1.93  
1.93  
1.93  
1.92  
1.91  
1.90  
1.89  
1.88  
1.88  
1.87  
1.86  
1.85  
1.85  
1.84  
1.83  
1.82  
1.81  
1.81  
1.80  
1.80  
1.79  
1.79  
1.77  
1.77  
1.76  
1.75  
1.75  
1.74  
1.74  
1.74  
1.73  
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1.61  
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0.91  
0.90  
0.12



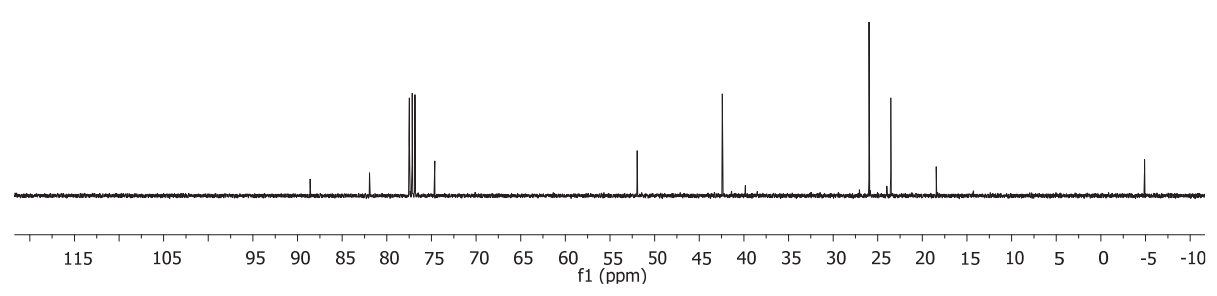
<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

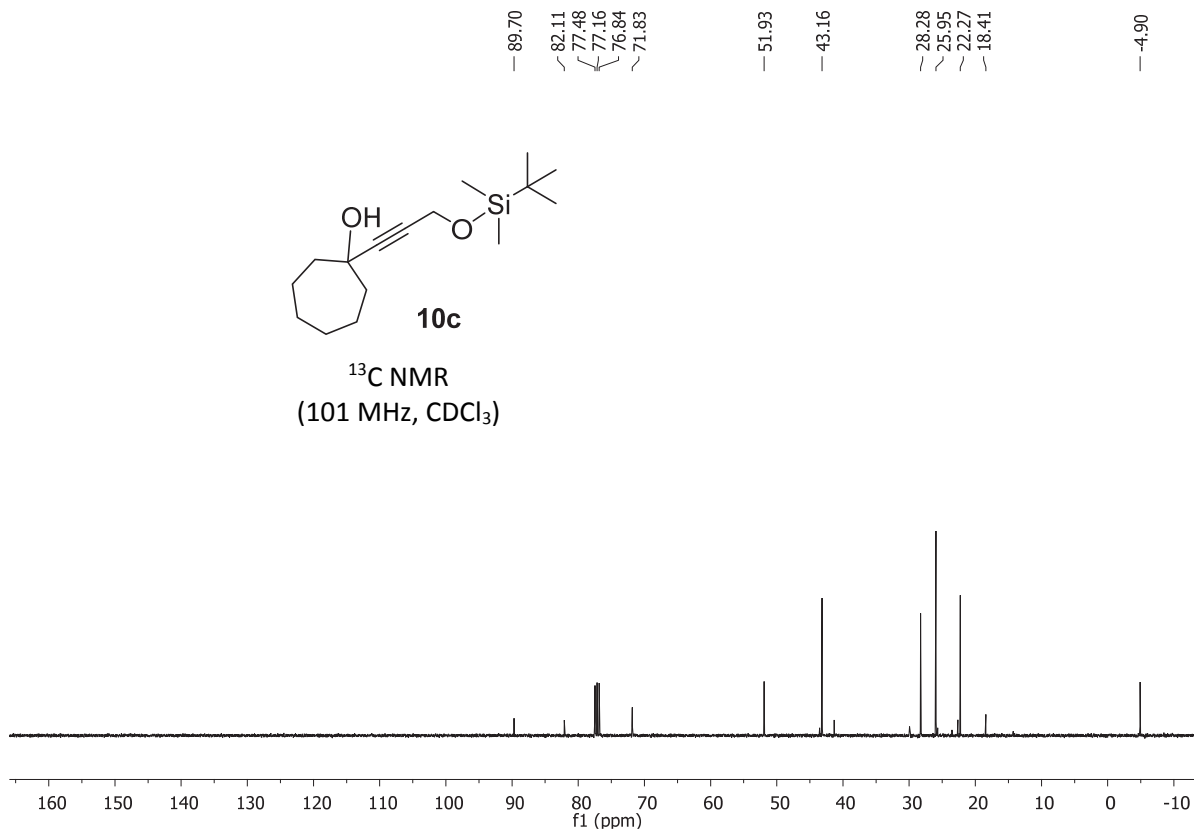
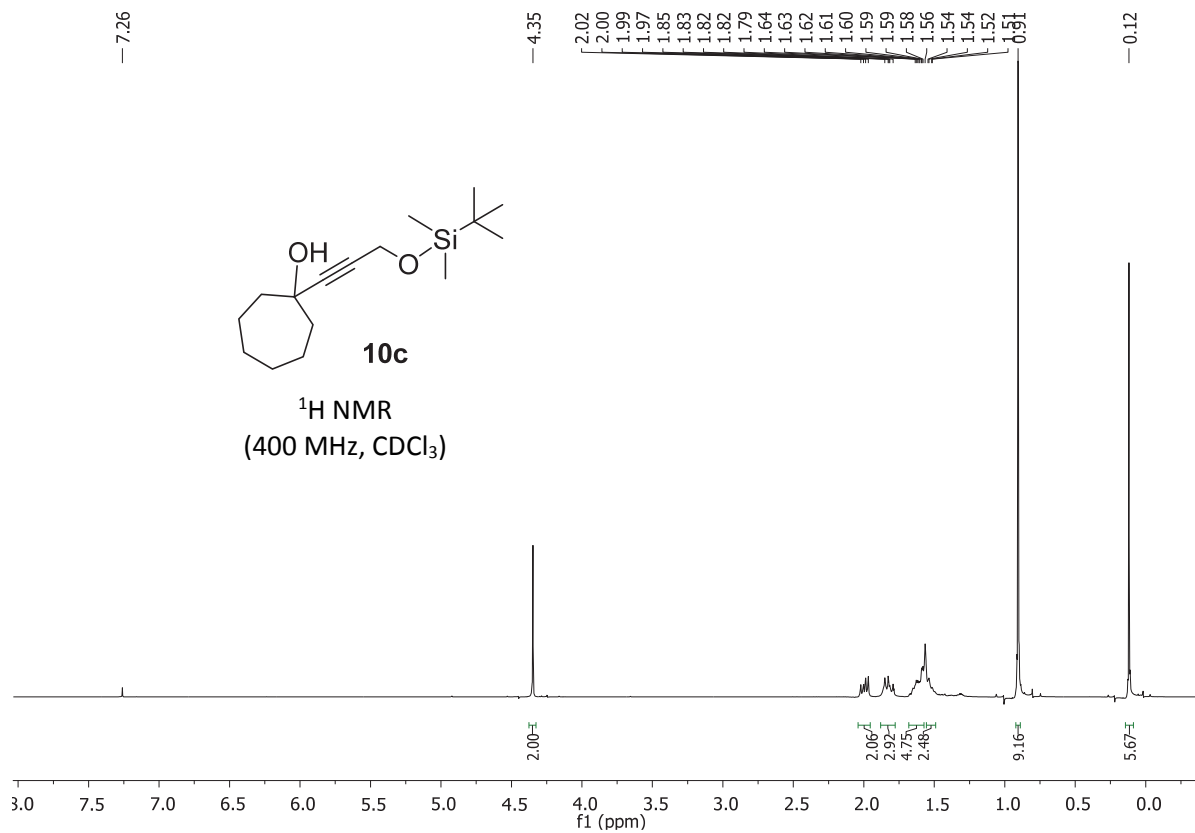


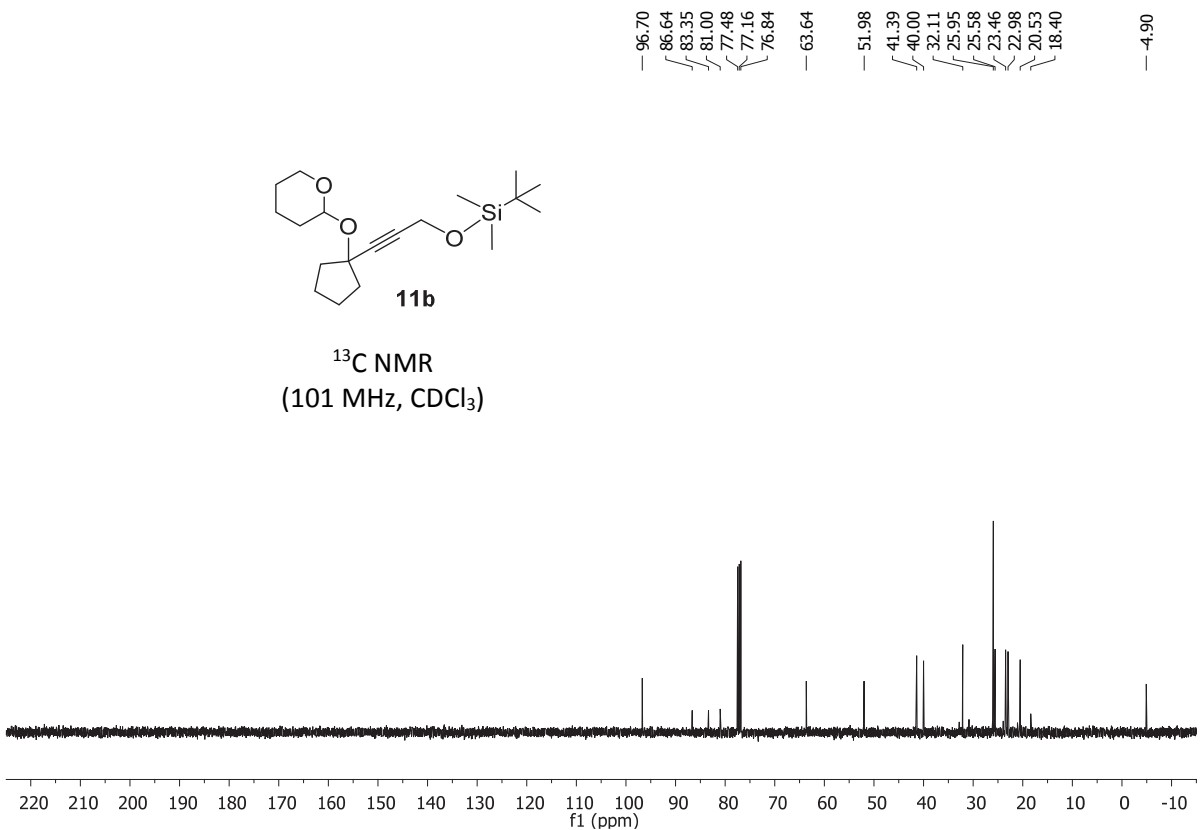
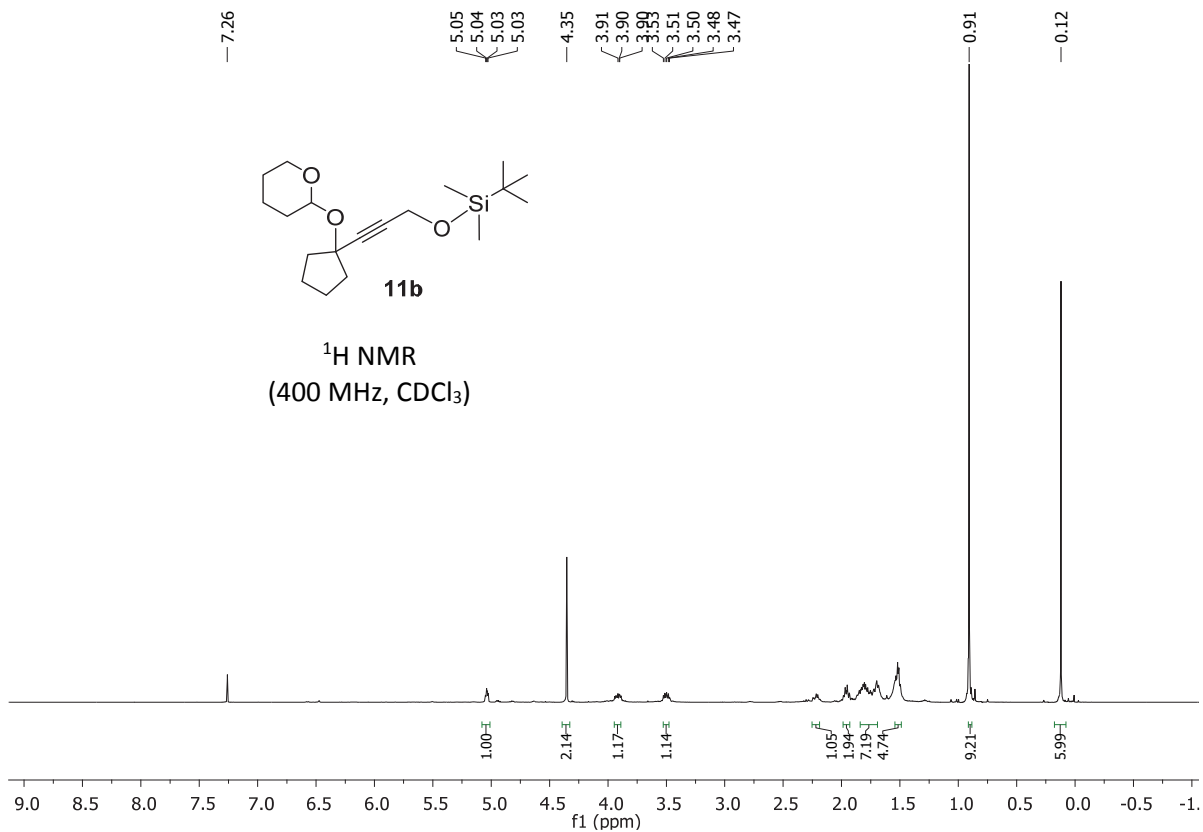
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81.95  
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77.16  
76.84  
74.63  
51.95  
42.40  
25.98  
23.54  
18.44  
-4.90



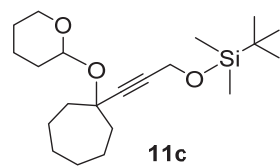
<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)



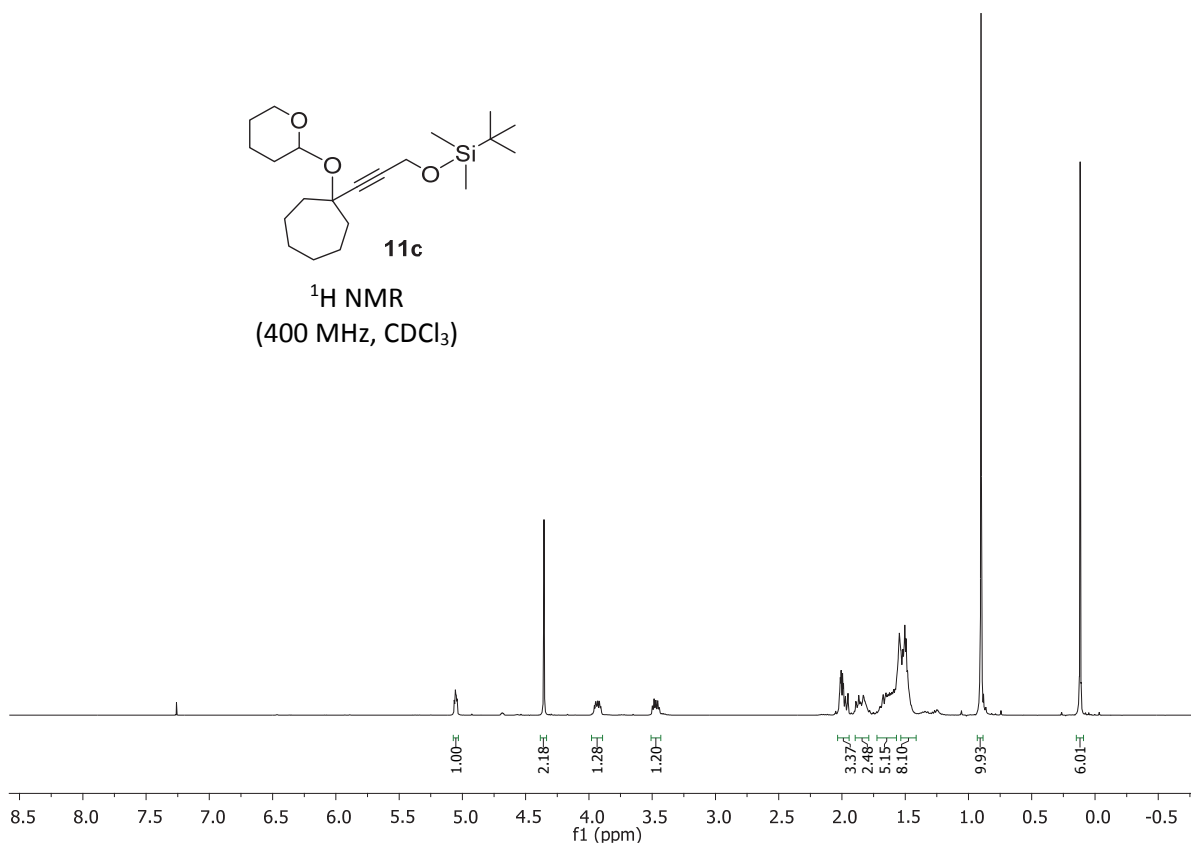




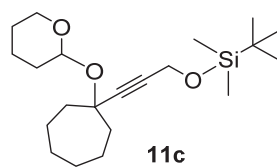




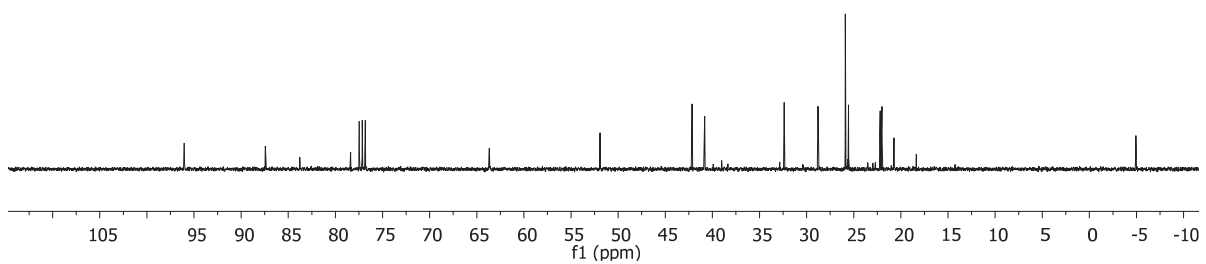
<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

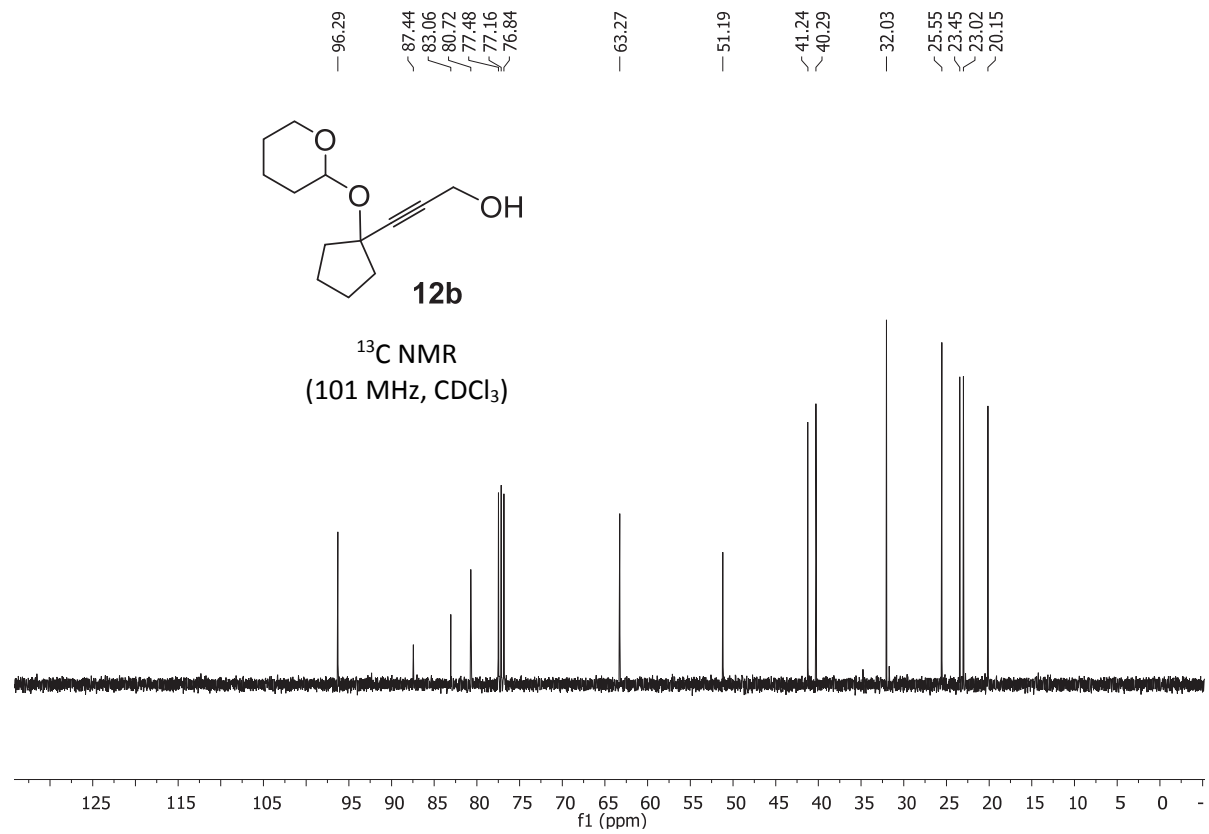
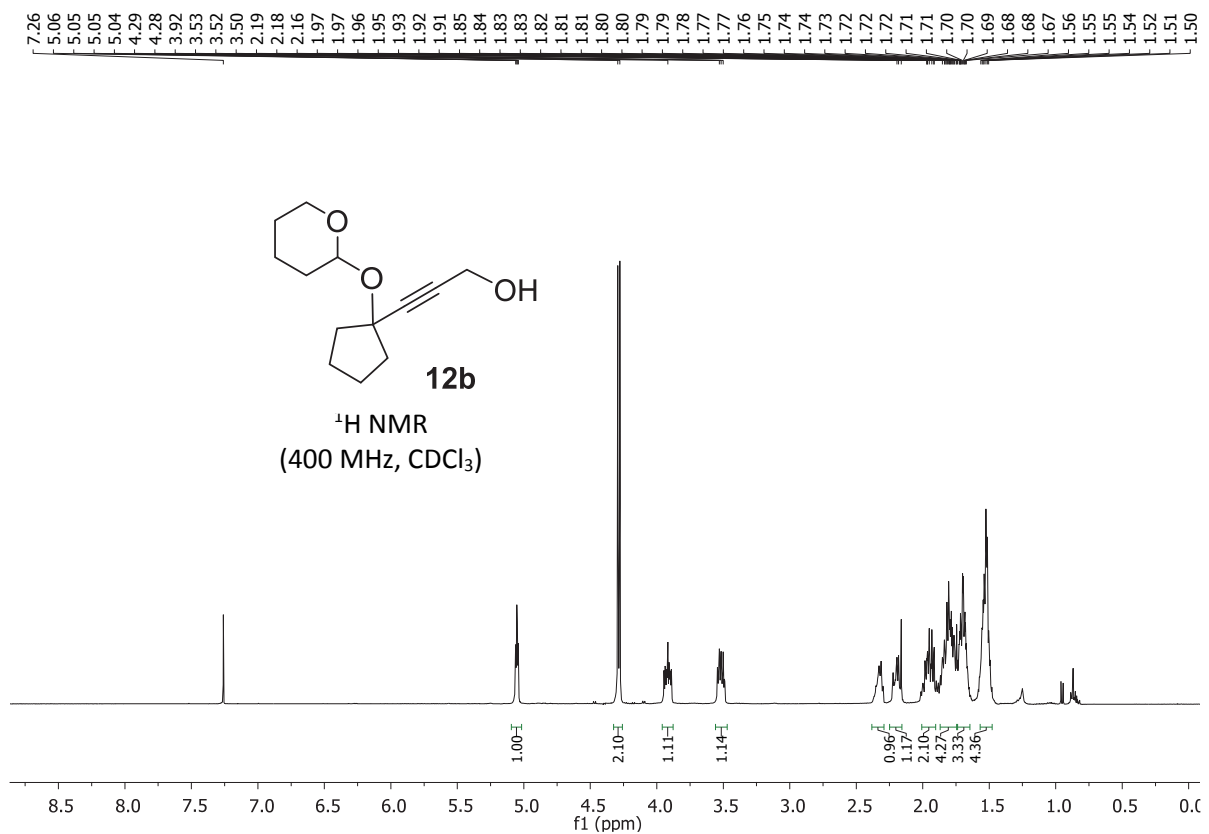


— 96.04 — 87.43 — 83.78 — 78.39 — 77.47 — 77.15 — 76.83 — 63.67 — 51.92 — 42.16 — 40.82 — 32.37 — 28.79 — 25.89 — 25.55 — 22.20 — 22.02 — 20.74 — 18.35 — -4.94

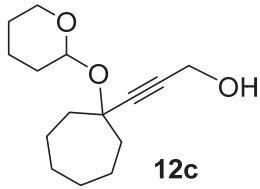


<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)

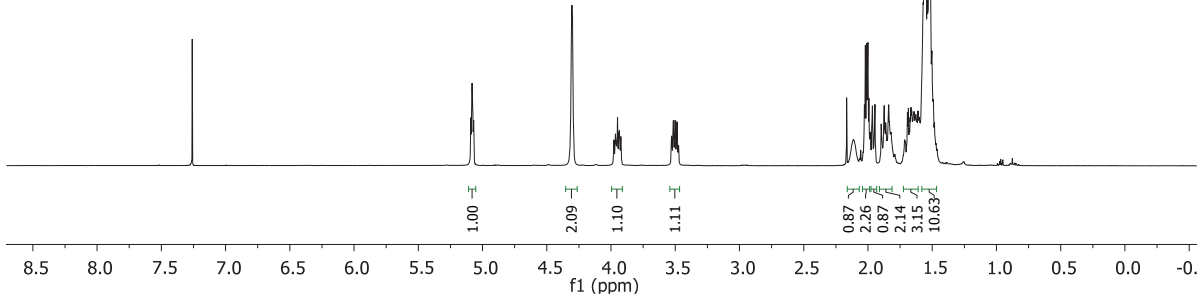




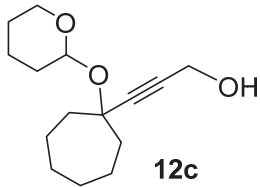
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5.08  
5.07  
4.30  
3.98  
3.97  
3.95  
3.94  
3.93  
3.92  
3.53  
3.51  
3.50  
3.49  
2.11  
2.03  
2.02  
2.01  
2.00  
1.99  
1.98  
1.98  
1.97  
1.95  
1.90  
1.87  
1.87  
1.86  
1.85  
1.84  
1.82  
1.71  
1.69  
1.68  
1.67  
1.67  
1.66  
1.66  
1.65  
1.65  
1.64  
1.63  
1.62  
1.61  
1.60  
1.57  
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1.53  
1.52  
1.51  
1.50  
1.49  
1.48



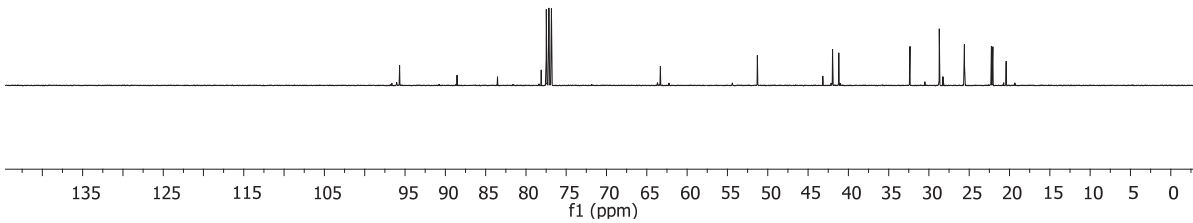
<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)



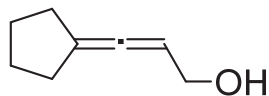
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88.55  
83.52  
78.11  
77.48  
77.16  
76.84  
63.33  
51.29  
43.16  
41.96  
41.19  
32.35  
28.71  
28.25  
25.60  
22.28  
22.25  
22.06  
20.41



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

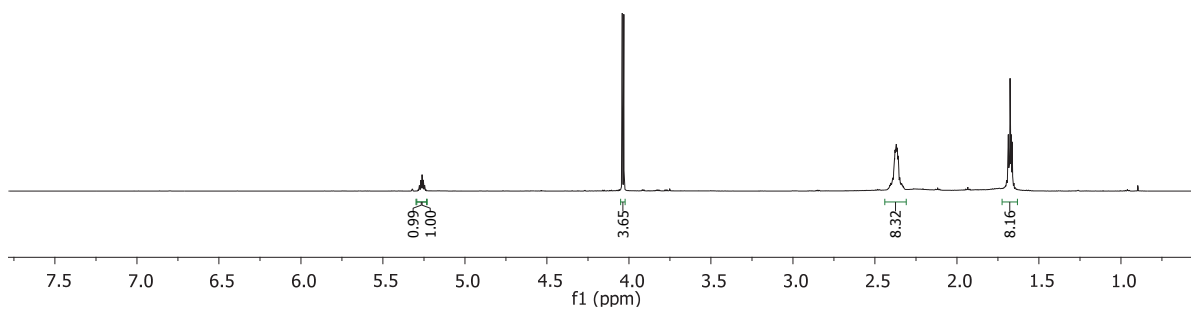


5.32 5.32 5.28 5.28 5.27 5.27 5.26 5.26 5.25 5.25 5.25 5.24 4.04 4.03 2.39 2.39 2.38 2.38 2.38 2.38 2.37 2.37 2.37 2.36 2.36 2.36 2.35 2.35 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.66

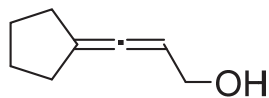


**13b**

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

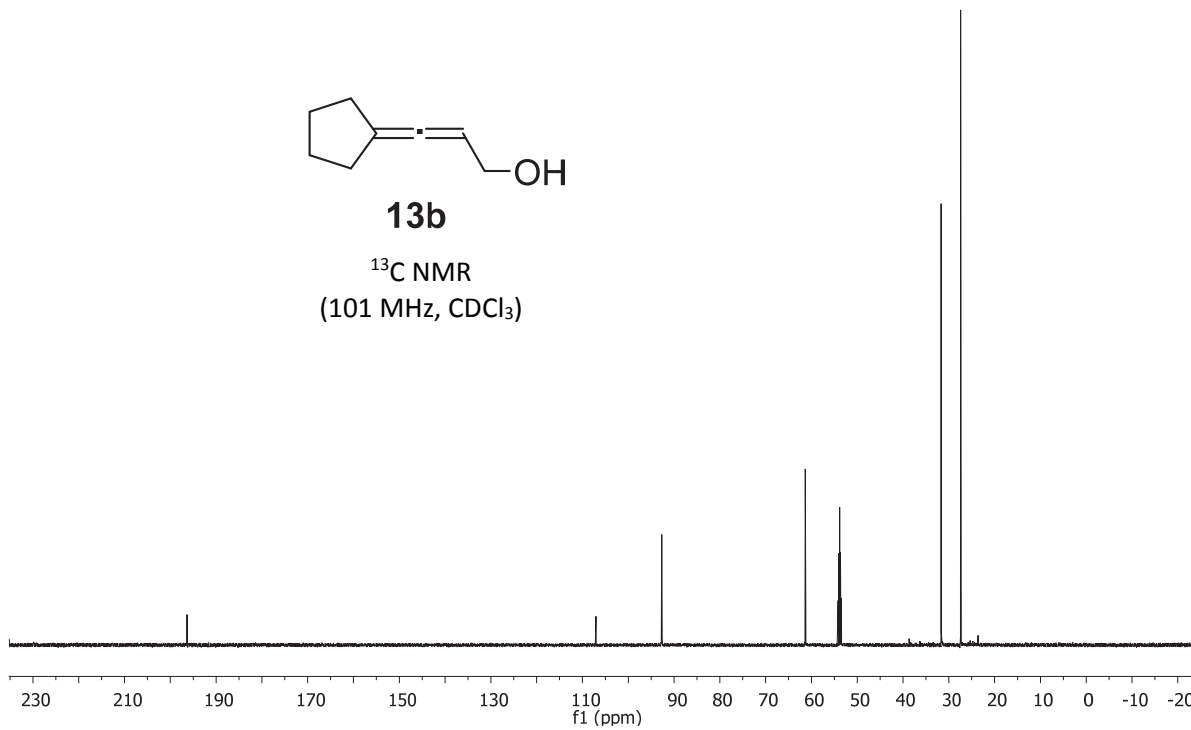


196.34 107.06 92.70 61.34 54.20 54.02 53.84 53.66 53.48 31.68 27.42



**13b**

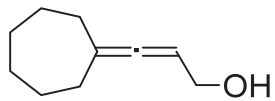
<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)



— 7.26

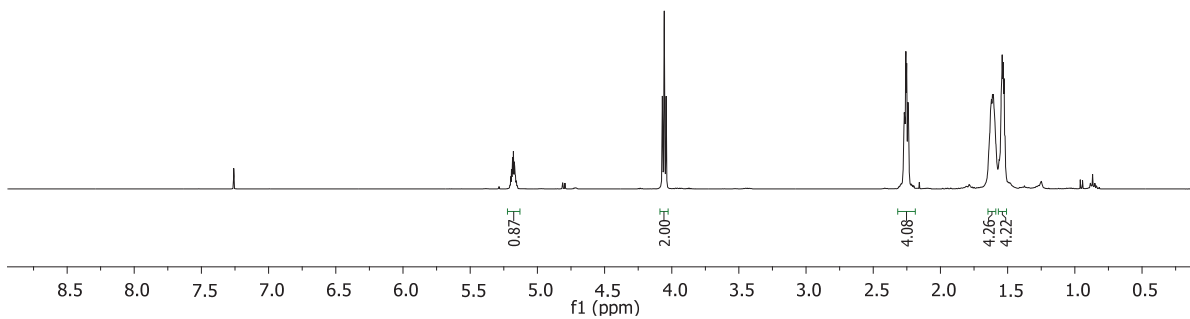
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5.19  
5.19  
5.18  
5.18  
5.17  
5.17  
5.16  
5.16  
4.07  
4.06  
4.04

2.27  
2.26  
2.26  
2.25  
2.24  
2.24  
2.24  
2.24  
1.62  
1.62  
1.61  
1.61  
1.60  
1.56  
1.55  
1.54  
1.53  
1.53  
1.53



**13c**

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



— 200.69

— 107.99

— 89.71

77.48

77.16

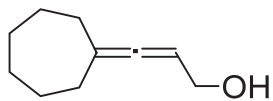
76.84

— 61.24

32.59

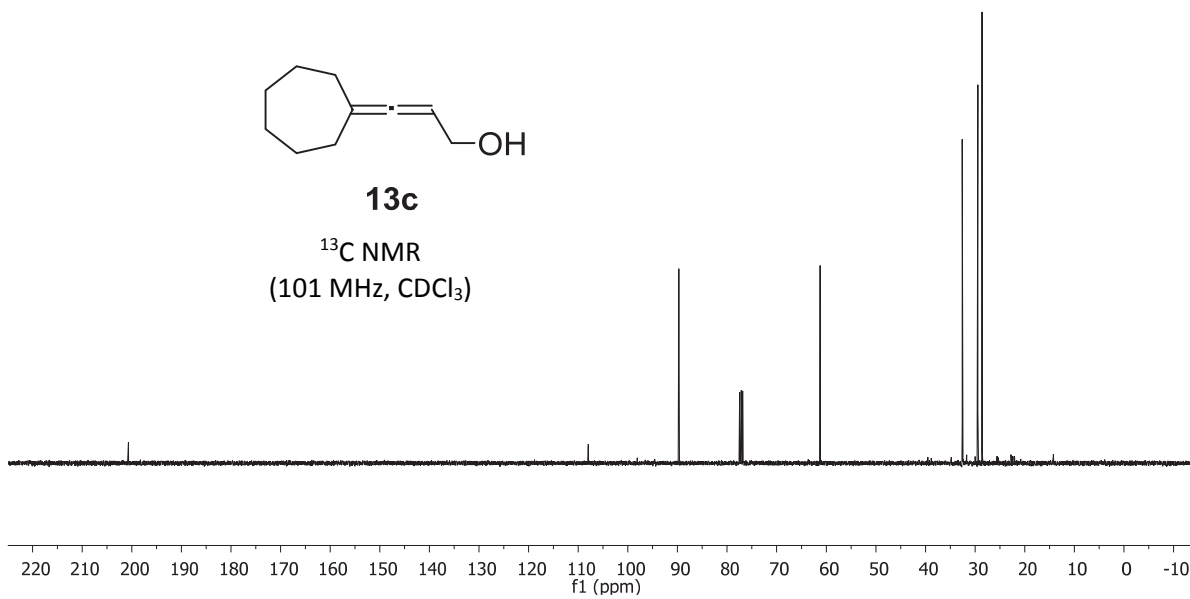
29.44

28.59



**13c**

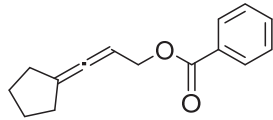
<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)



8.07  
8.06  
8.05  
8.05  
7.57  
7.55  
7.54  
7.46  
7.44  
7.42  
7.26

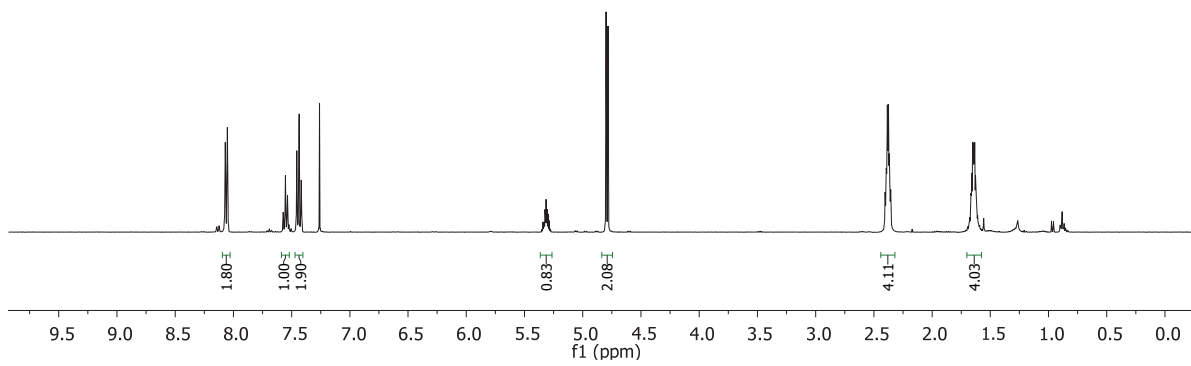
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5.30  
5.30  
5.29  
4.80  
4.78

2.40  
2.39  
2.38  
2.37  
2.37  
2.36  
1.67  
1.66  
1.65  
1.65  
1.64  
1.63  
1.62



**14b**

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



198.78

166.49

132.96

130.59

129.74

128.42

106.14

87.39

77.48

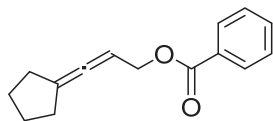
77.16

76.84

63.86

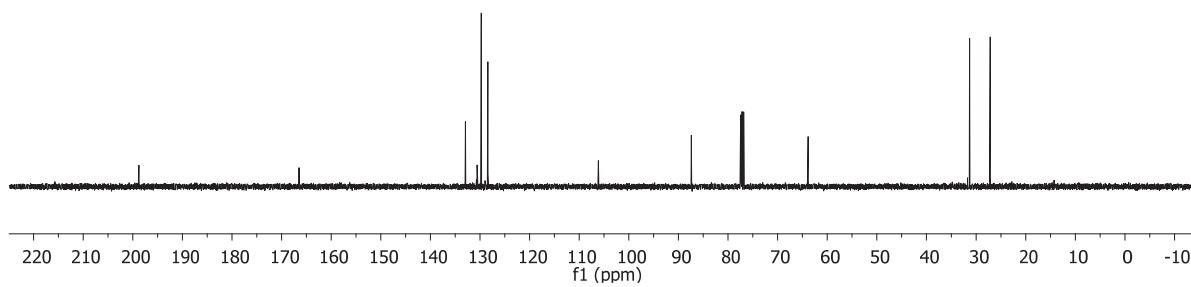
31.31

27.15

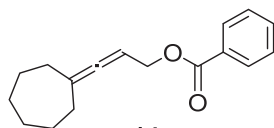


**14b**

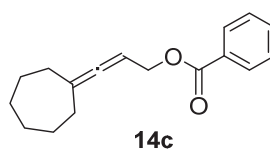
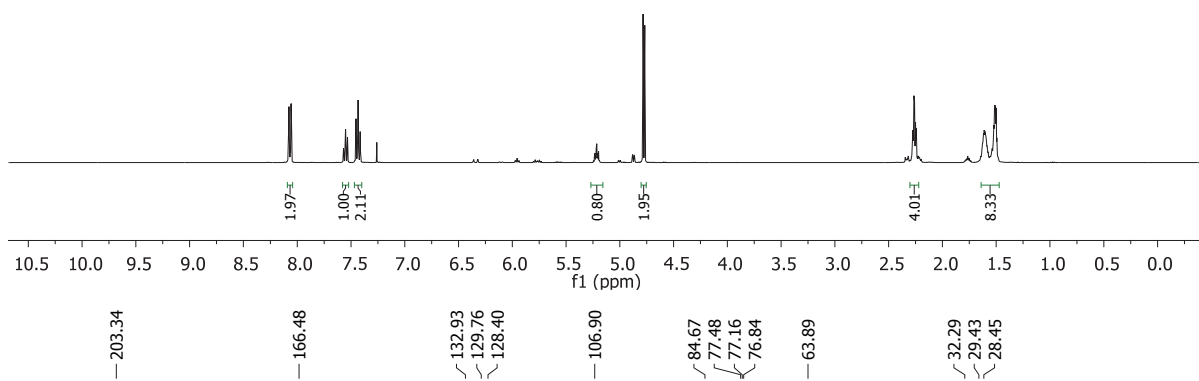
<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)



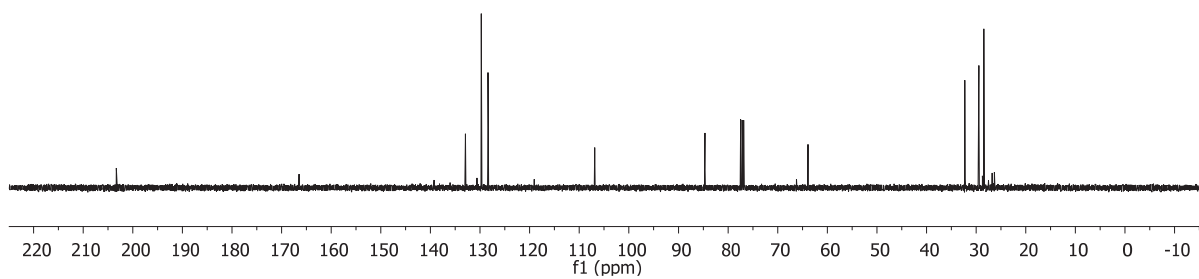
8.08  
8.08  
8.07  
8.06  
8.06  
8.06  
7.57  
7.56  
7.55  
7.55  
7.54  
7.53  
7.53  
7.46  
7.45  
7.45  
7.44  
7.43  
7.42  
7.42  
7.41  
5.23  
5.22  
5.21  
5.21  
5.20  
5.20  
4.78  
4.77  
2.28  
2.28  
2.28  
2.27  
2.27  
2.26  
2.25  
2.25  
2.24  
2.24  
1.63  
1.62  
1.62  
1.61  
1.61  
1.60  
1.60  
1.59  
1.59  
1.59  
1.58  
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1.53  
1.53  
1.52  
1.52  
1.51  
1.51  
1.49

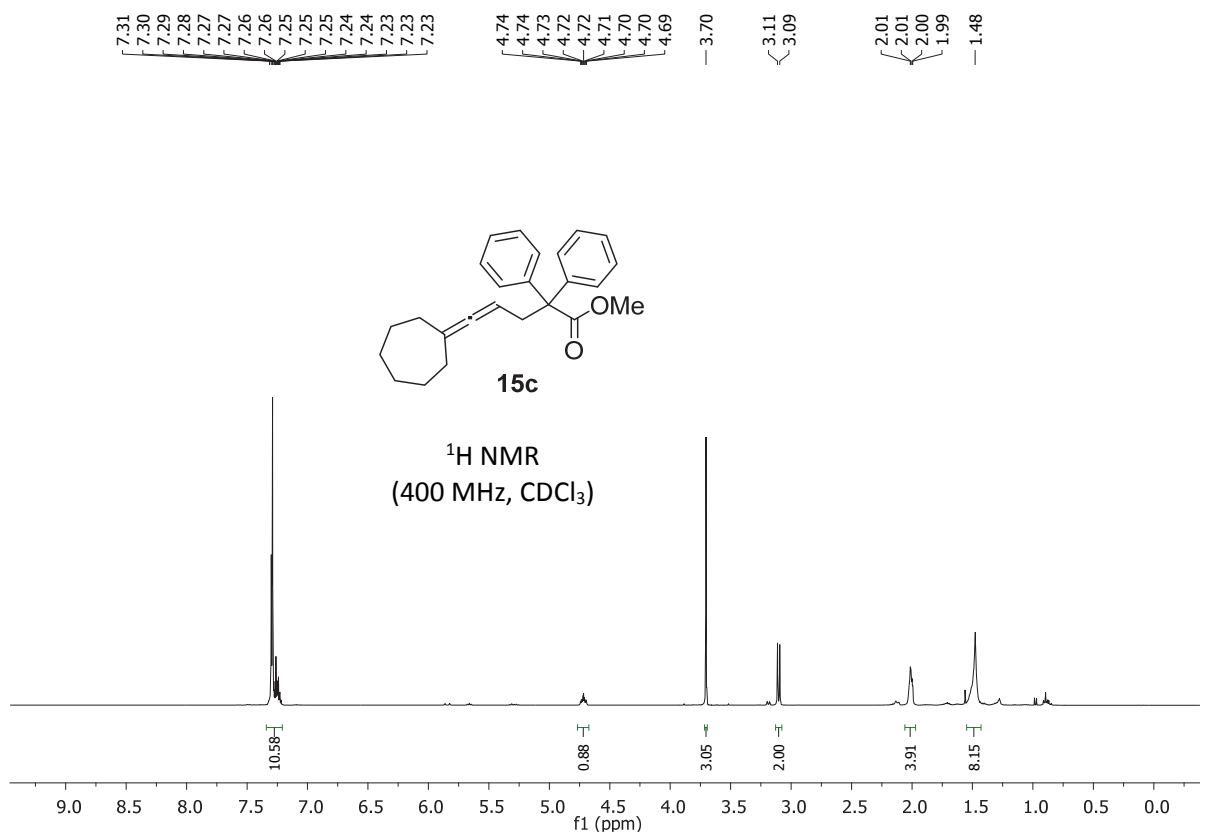
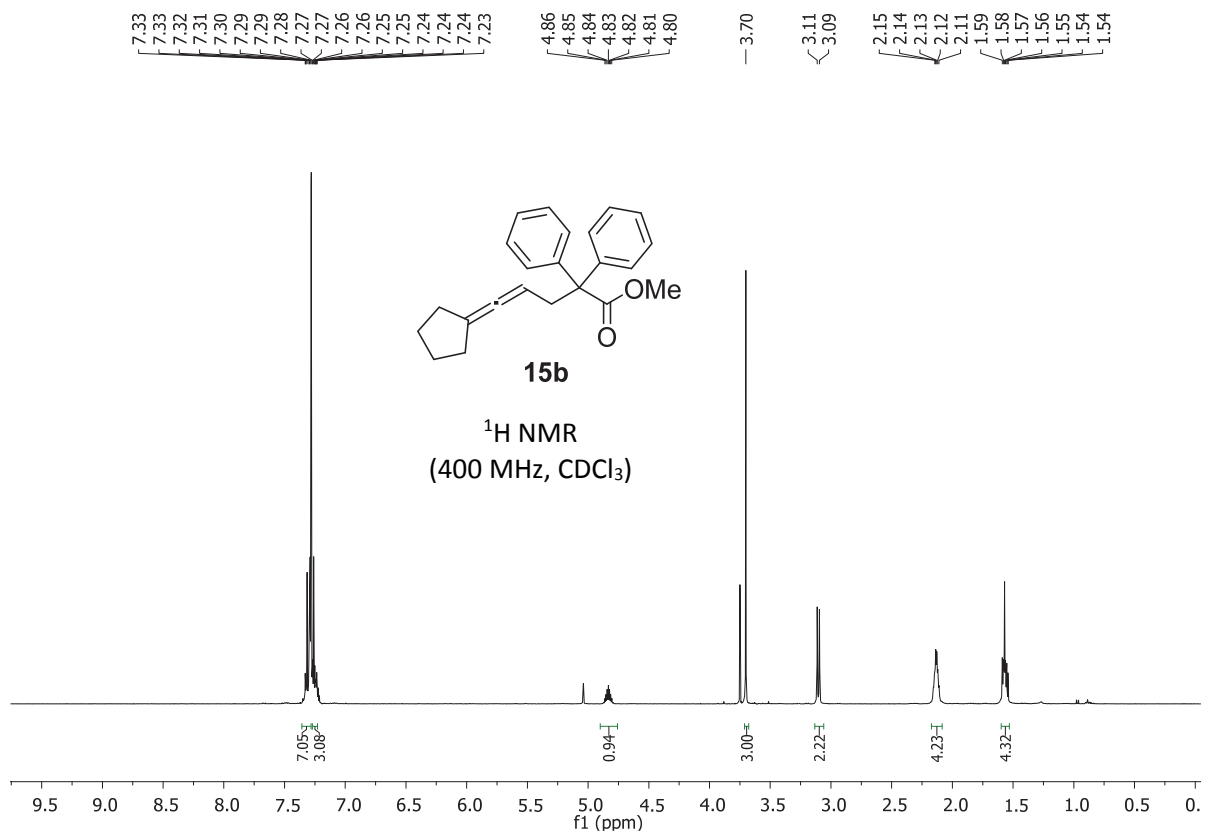


<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)



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







— 203.92

— 174.75

— 142.63

129.25

129.11

127.90

126.85

— 103.85

84.28

77.48

77.16

76.84

— 60.72

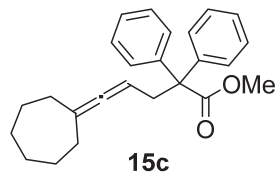
— 52.48

39.59

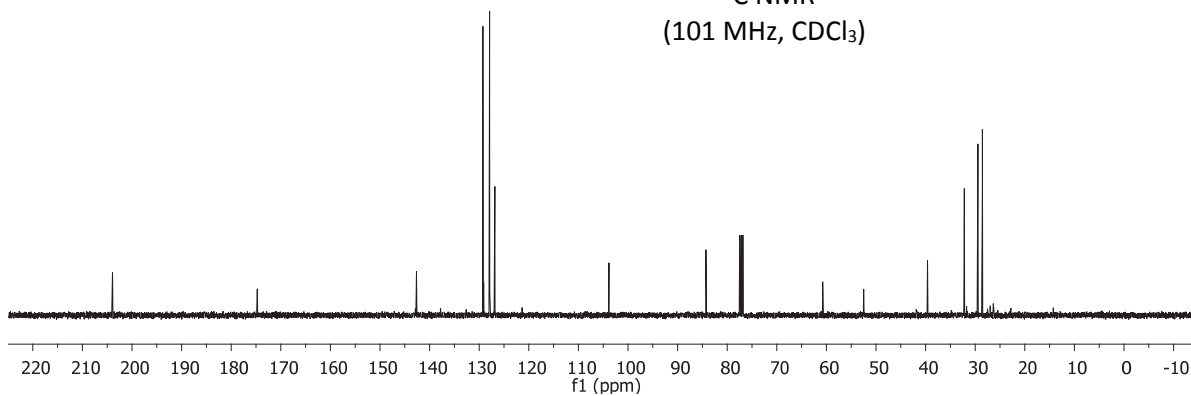
32.17

29.46

28.55



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



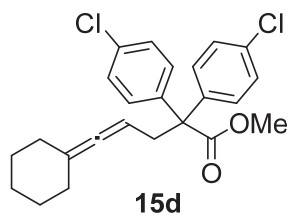
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7.25  
7.24  
7.23  
7.19  
7.18  
7.18  
7.17  
7.16

4.66  
4.66  
4.65  
4.64  
4.64  
4.63  
4.63  
4.62

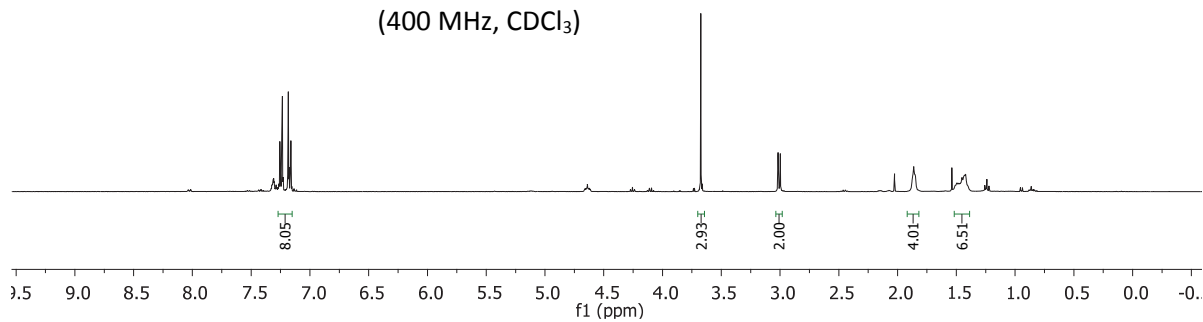
— 3.67

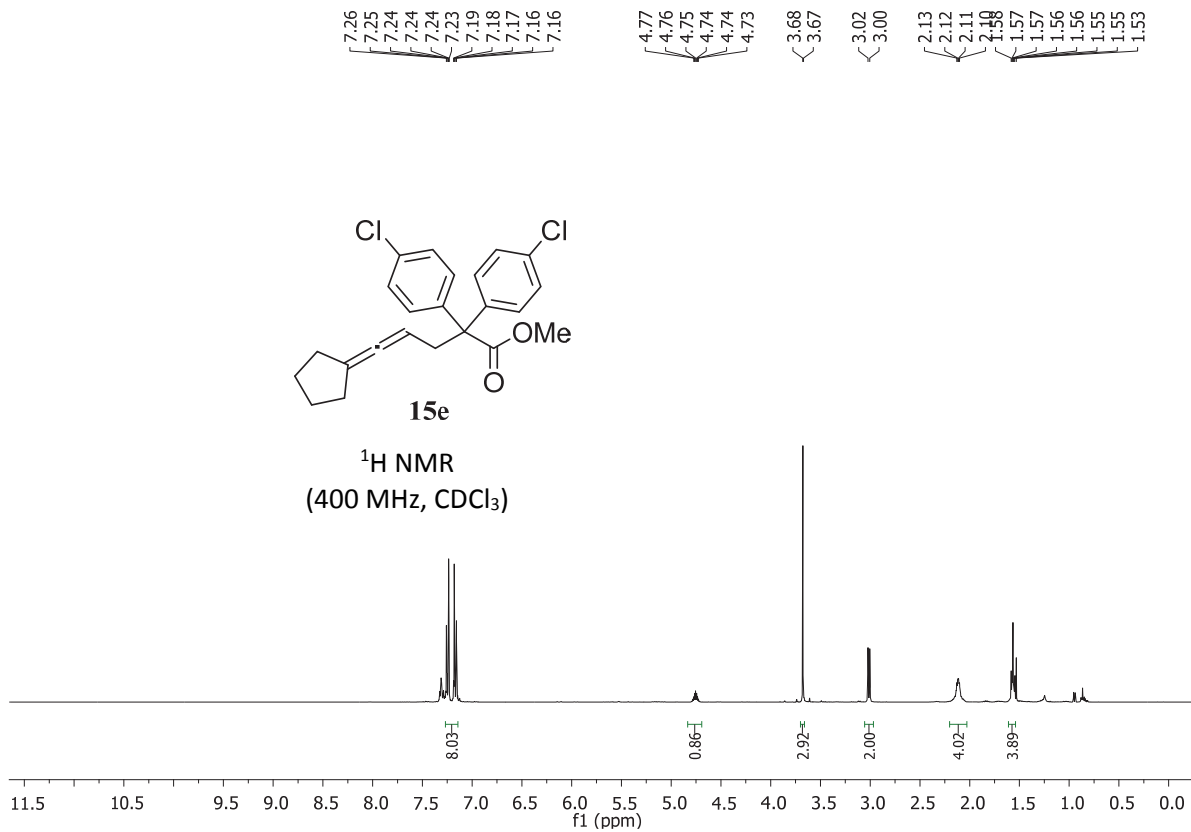
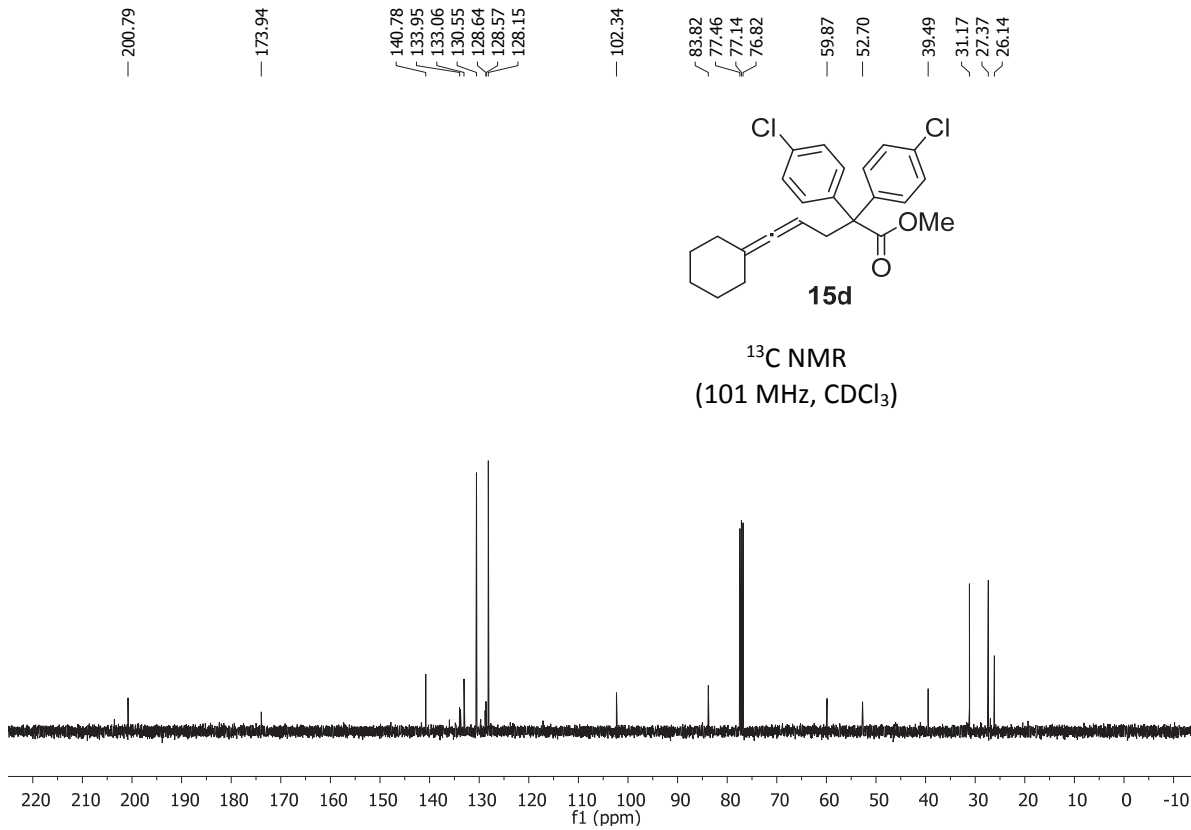
3.02  
3.00

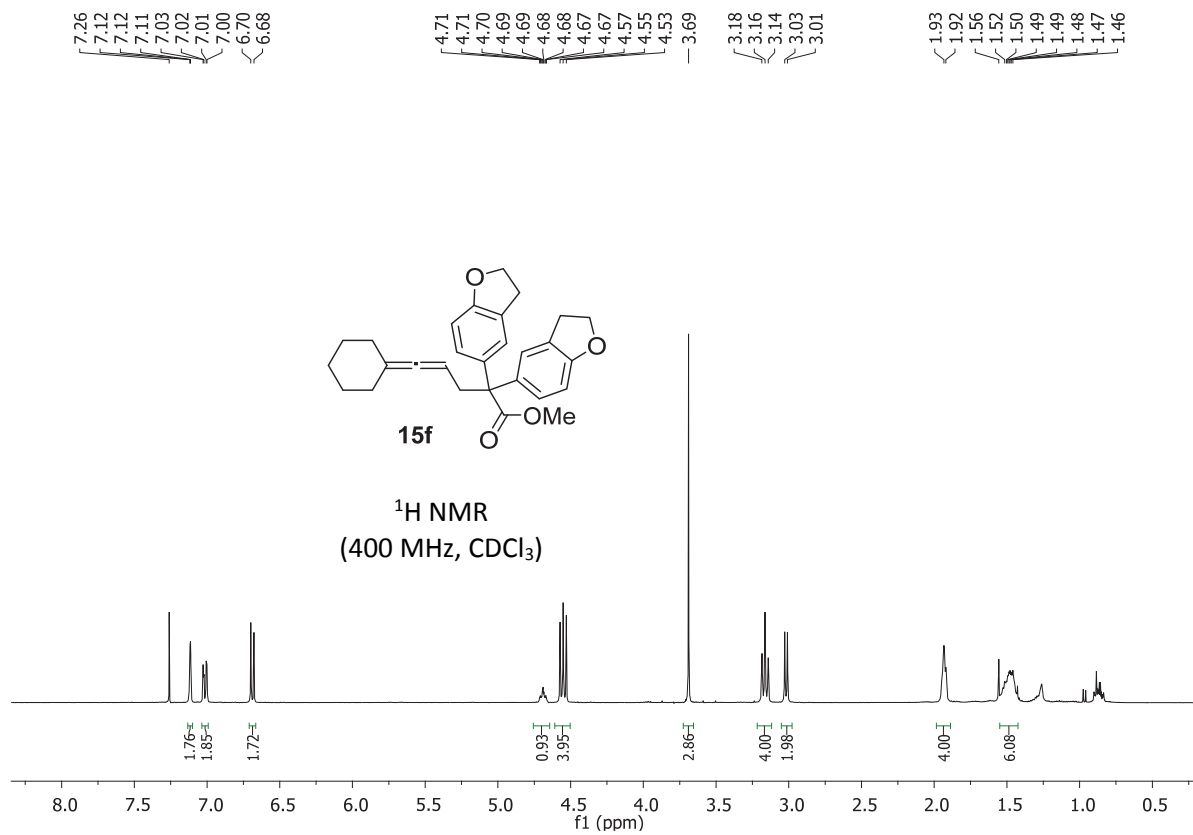
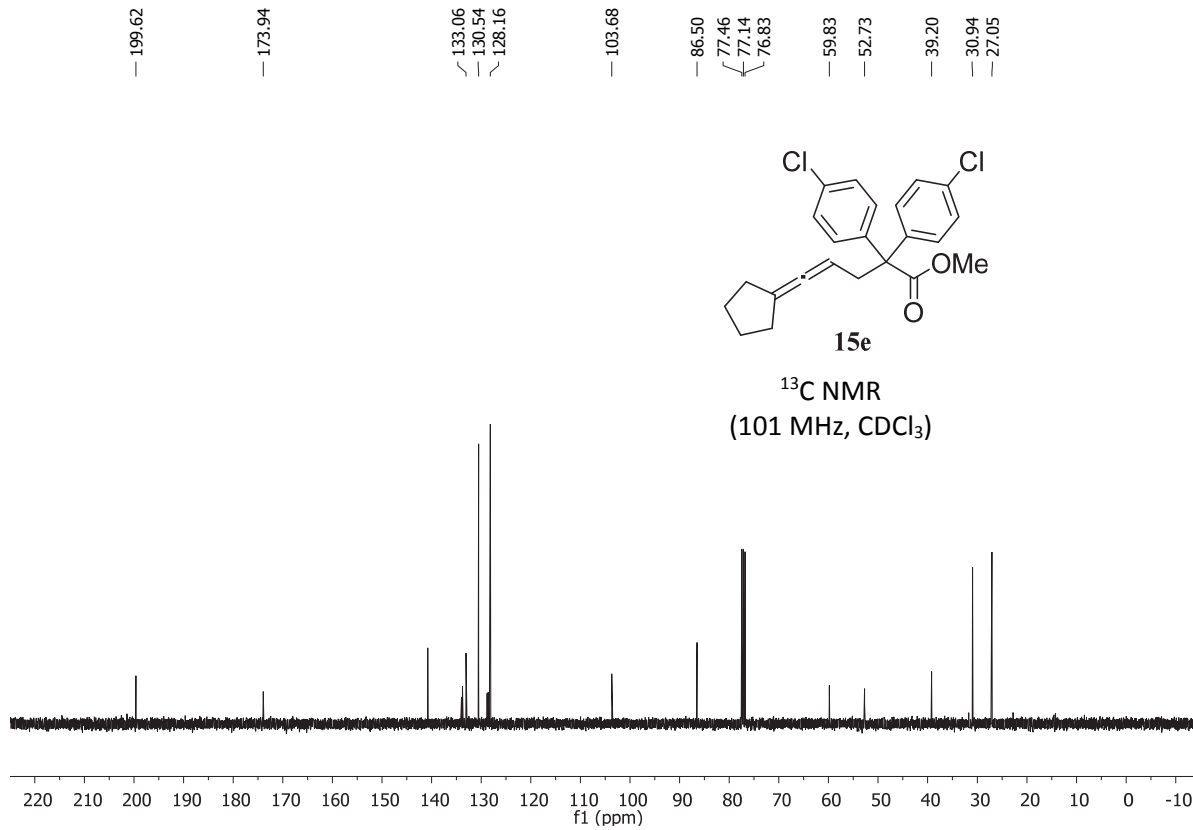
1.86  
1.86  
1.85  
1.54  
1.49  
1.48  
1.47  
1.45  
1.43  
1.42

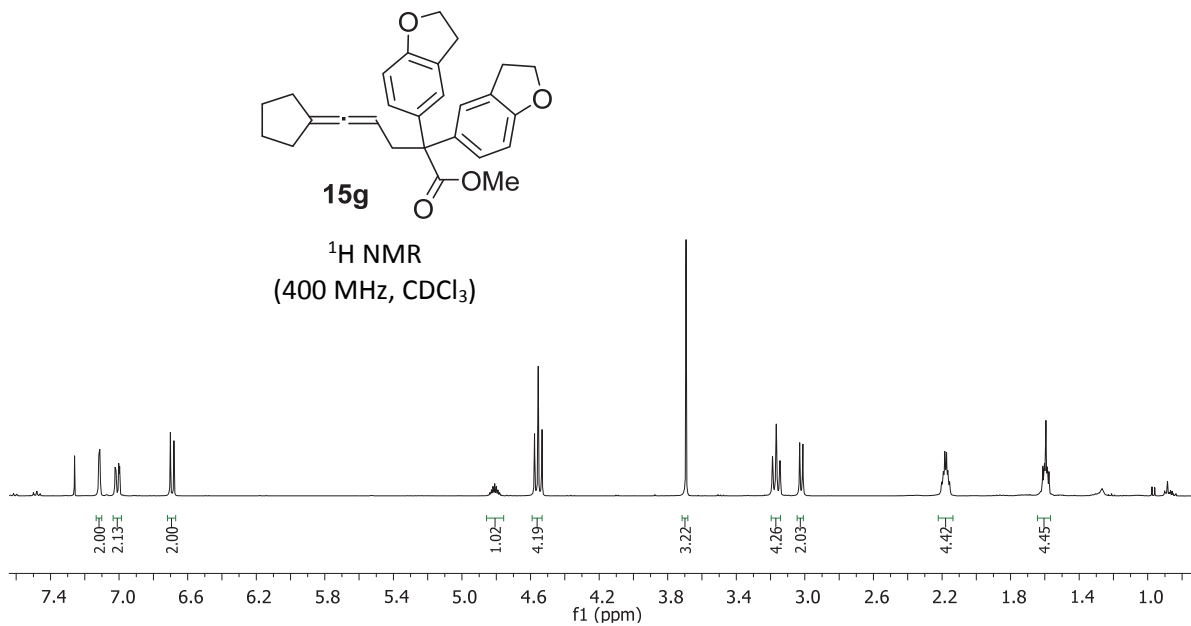
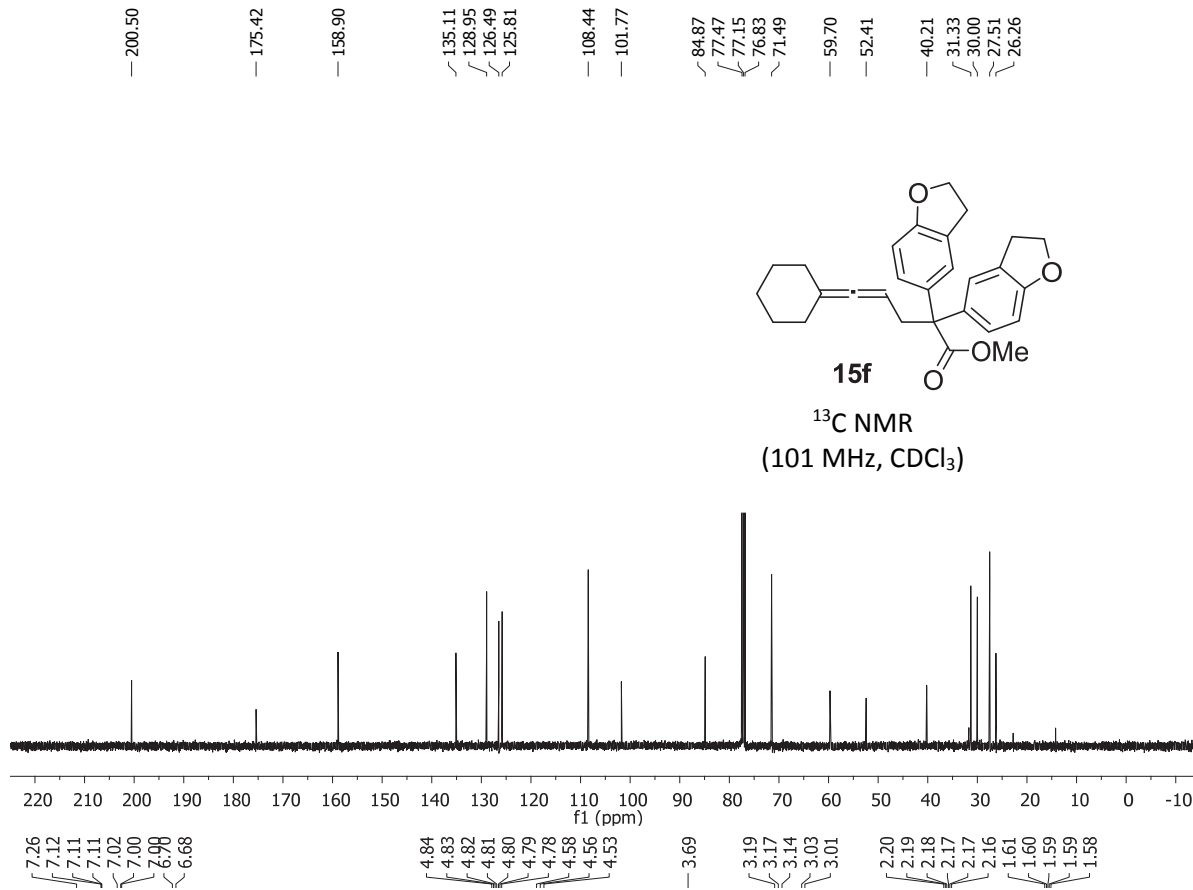


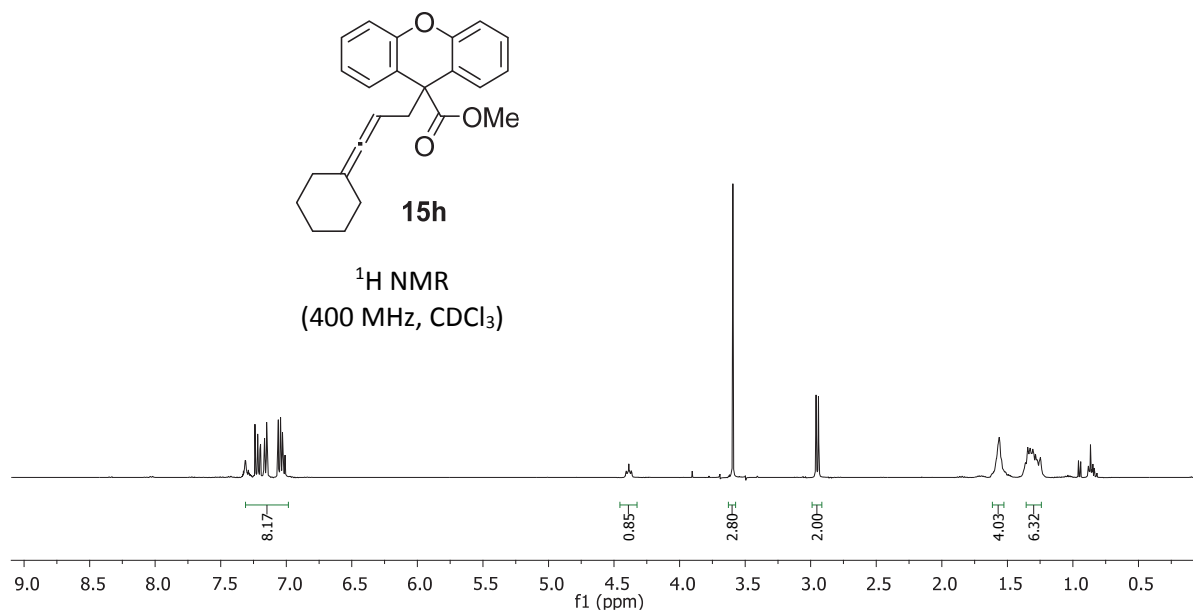
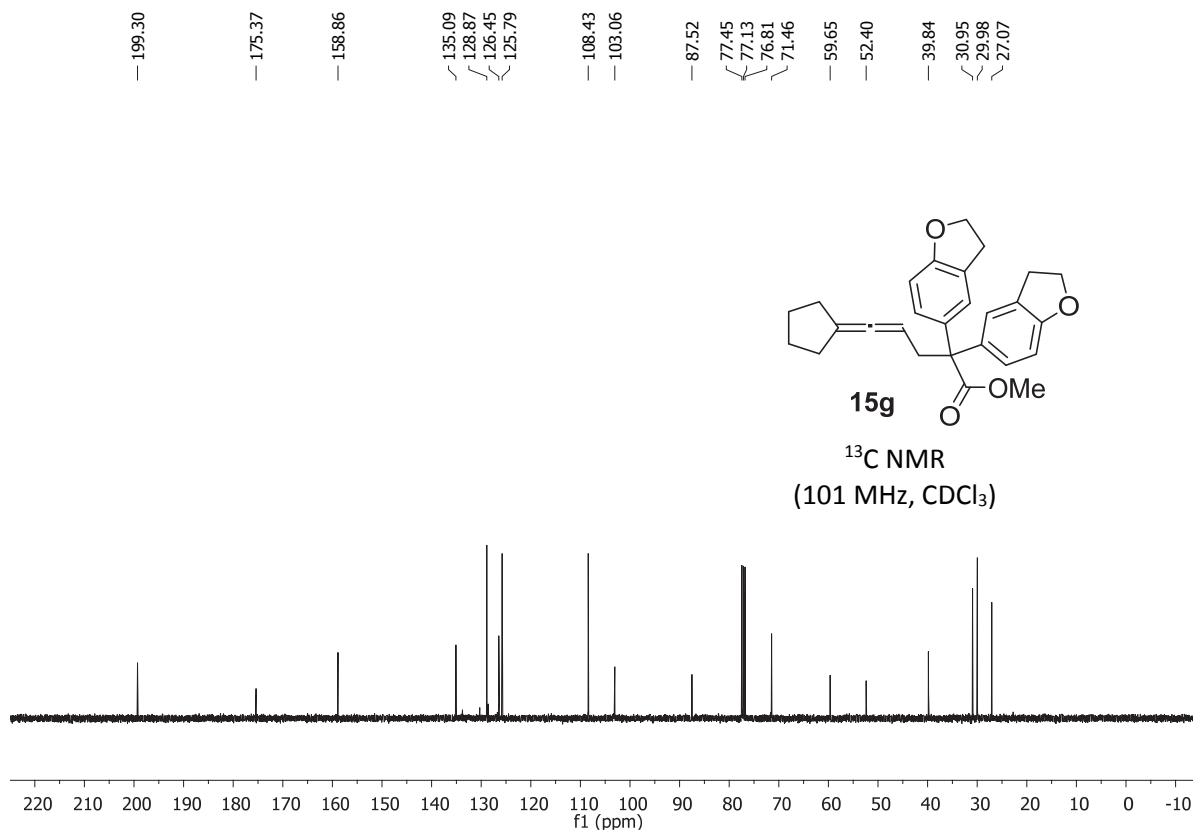
<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

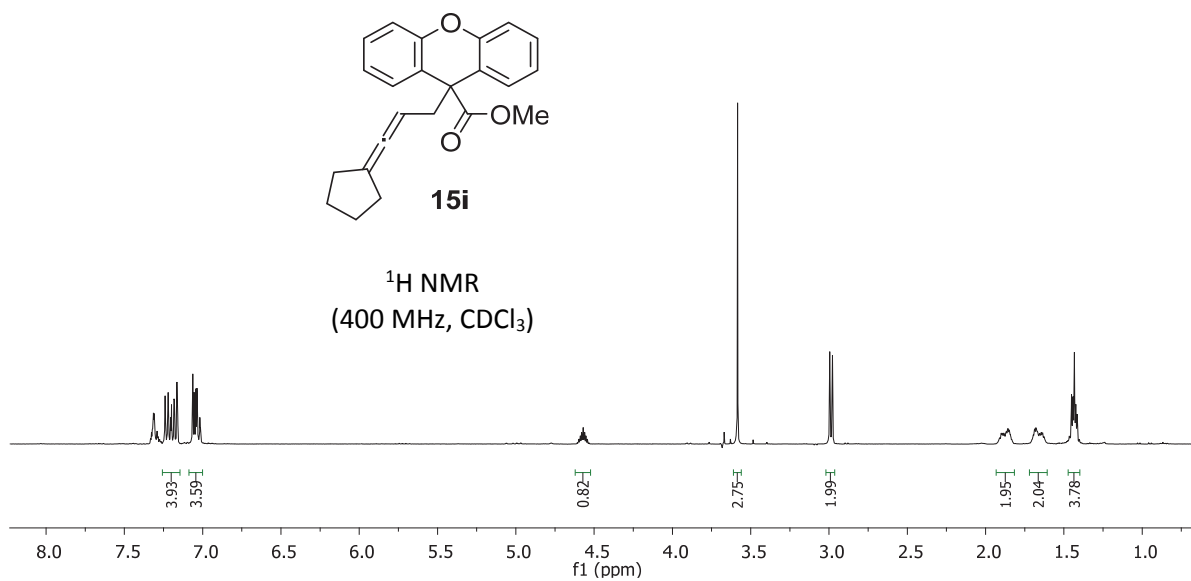
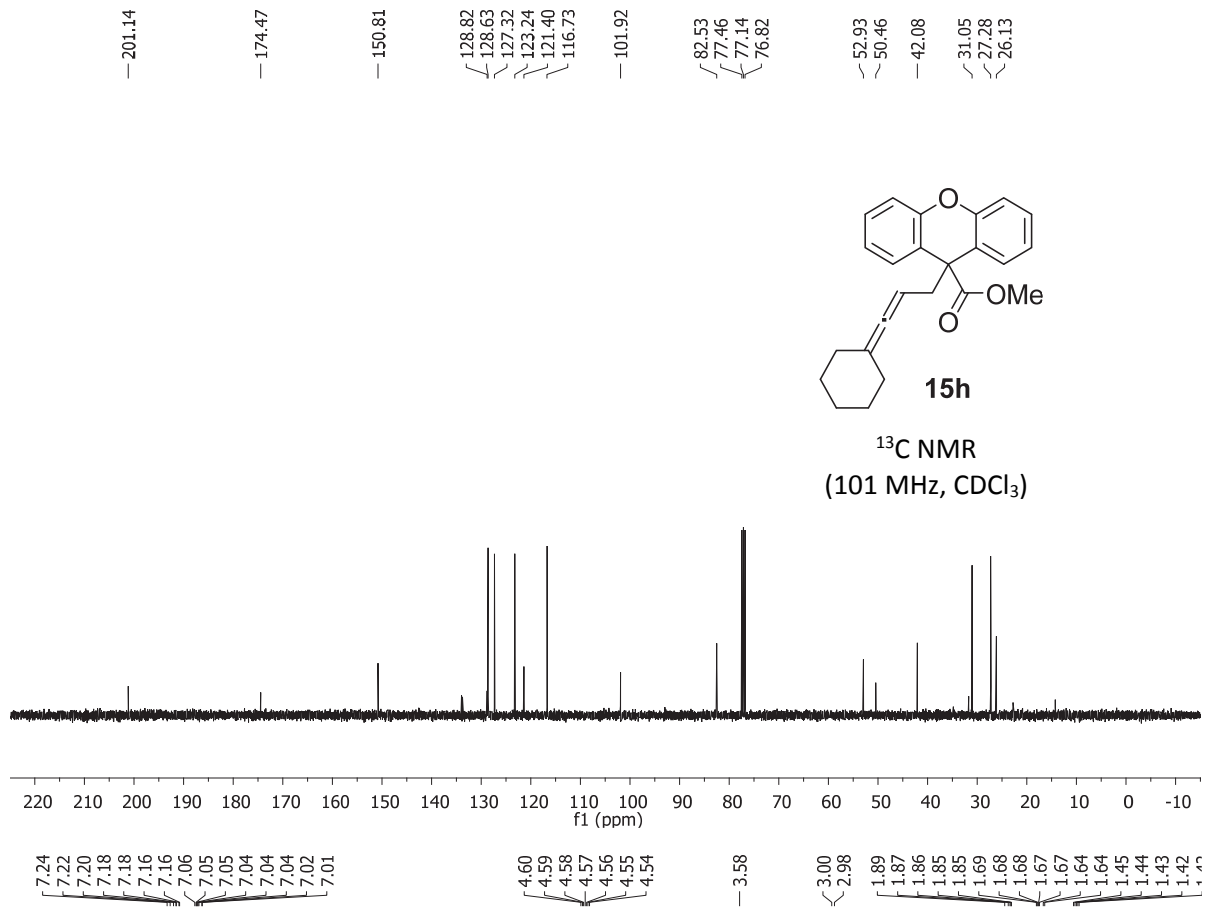




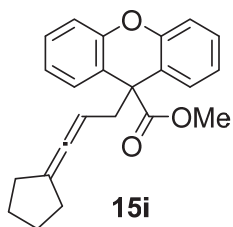




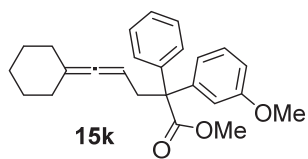
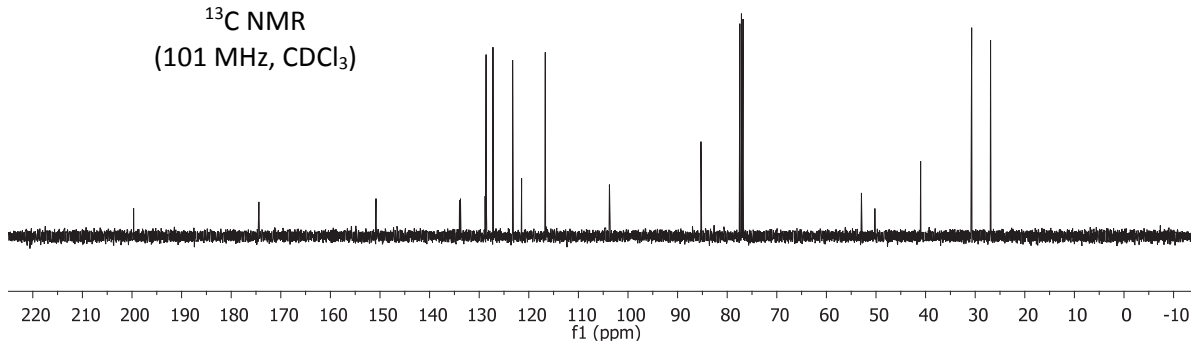




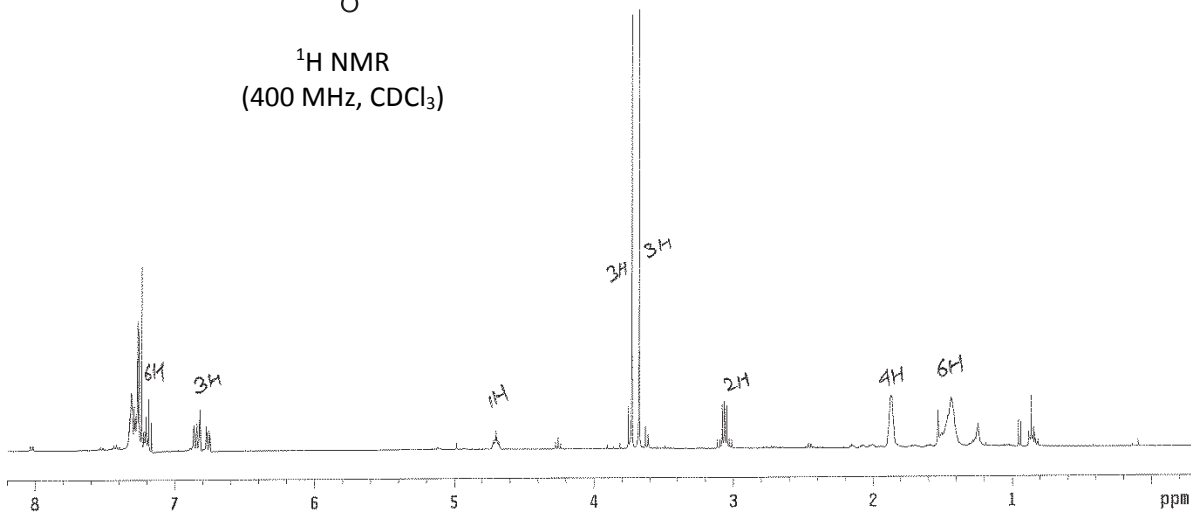
— 199.68 — 174.41 — 150.82 — 133.95 — 133.76 — 128.82 — 128.62 — 128.57 — 127.22 — 123.25 — 121.47 — 116.68 — 103.76 — 85.28 — 77.46 — 77.14 — 76.82 — 52.94 — 41.01 — 30.73 — 26.92

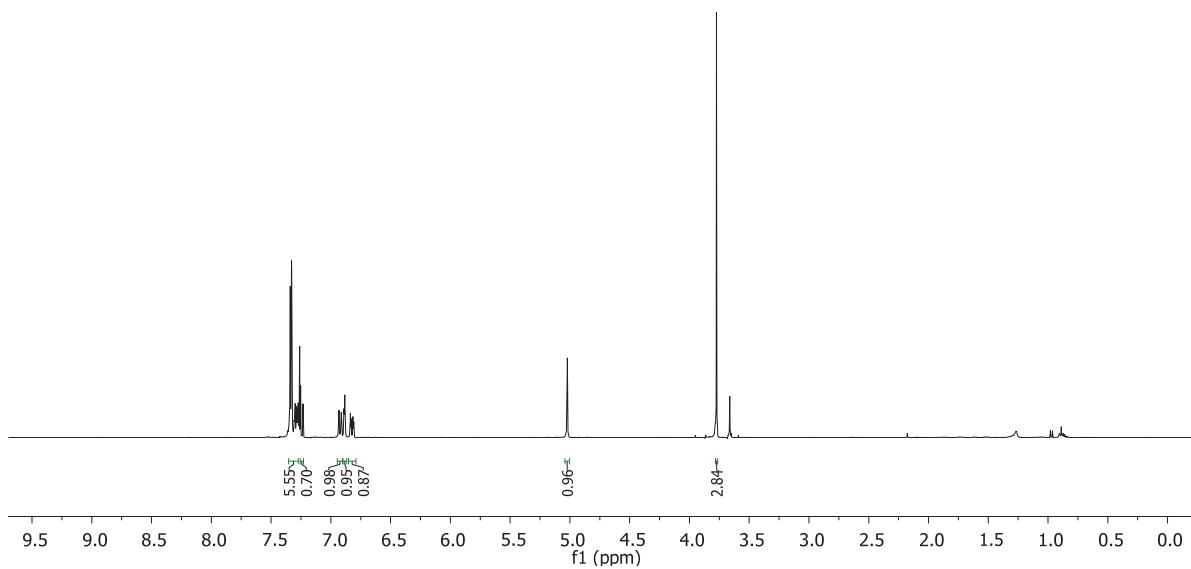


<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)

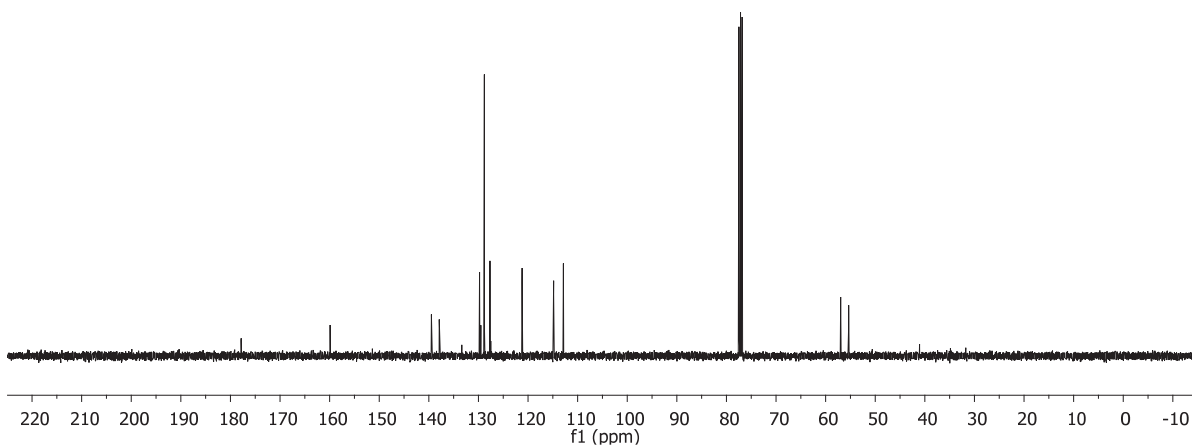


<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

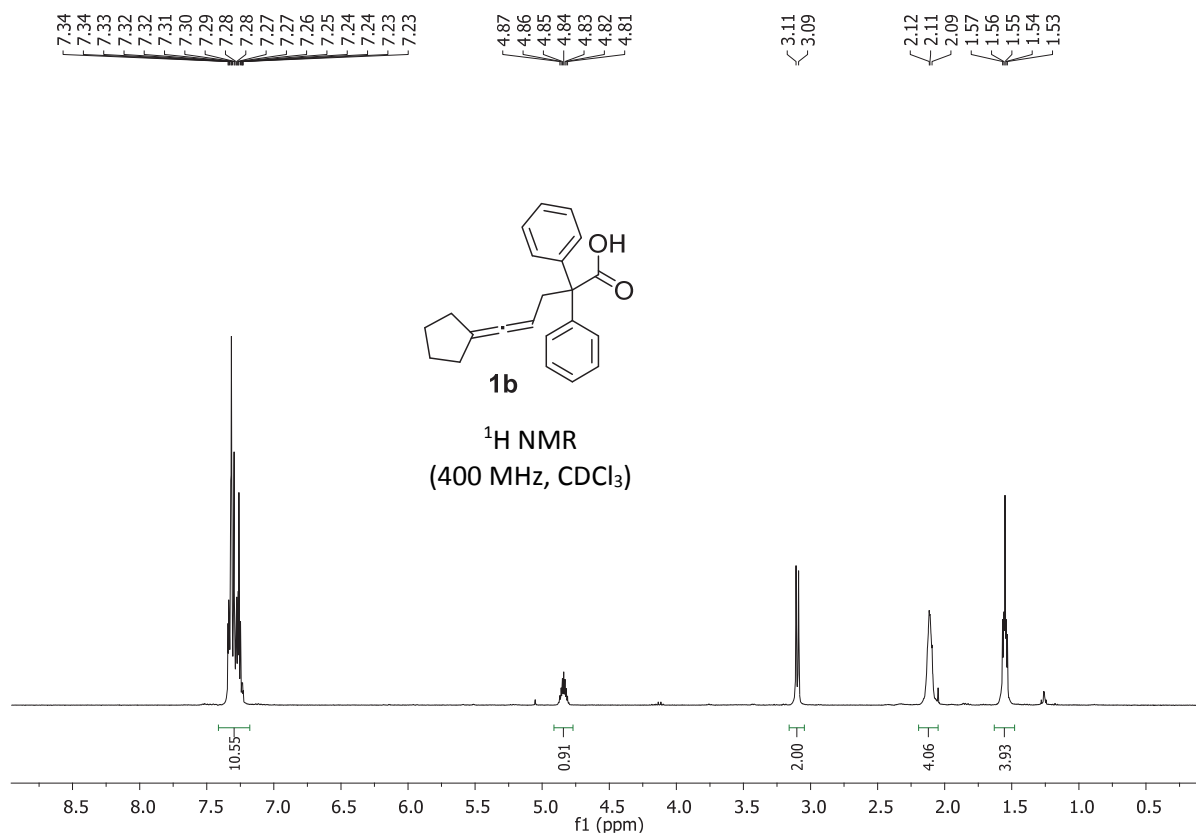




177.83  
 159.90  
 139.47  
 137.89  
 129.78  
 129.52  
 128.80  
 127.67  
 127.51  
 121.19  
 114.84  
 112.87  
 56.97  
 55.37







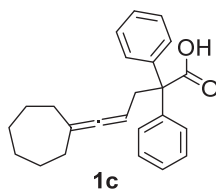
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7.32  
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7.25  
7.25  
7.24  
7.24  
7.23  
7.23

4.72  
4.71  
4.71  
4.70  
4.69  
4.68  
4.67  
4.67

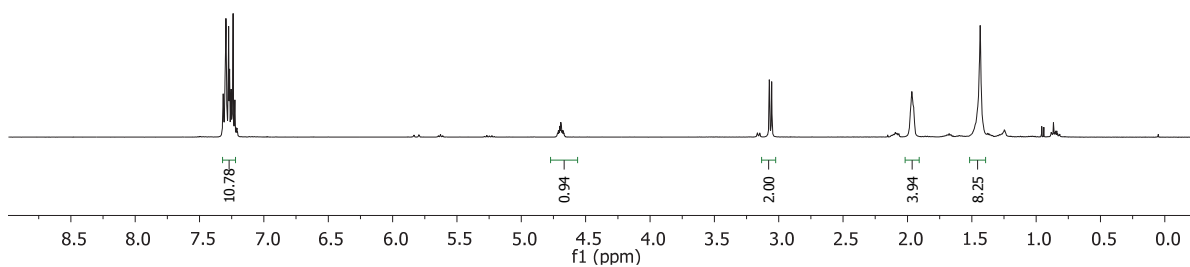
3.07  
3.05

1.97  
1.95

1.43



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



204.03

179.28

142.08

129.34

129.23

127.97

127.07

104.02

84.04

77.46

77.15

76.83

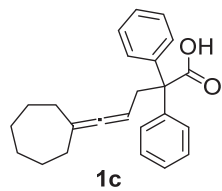
60.56

39.39

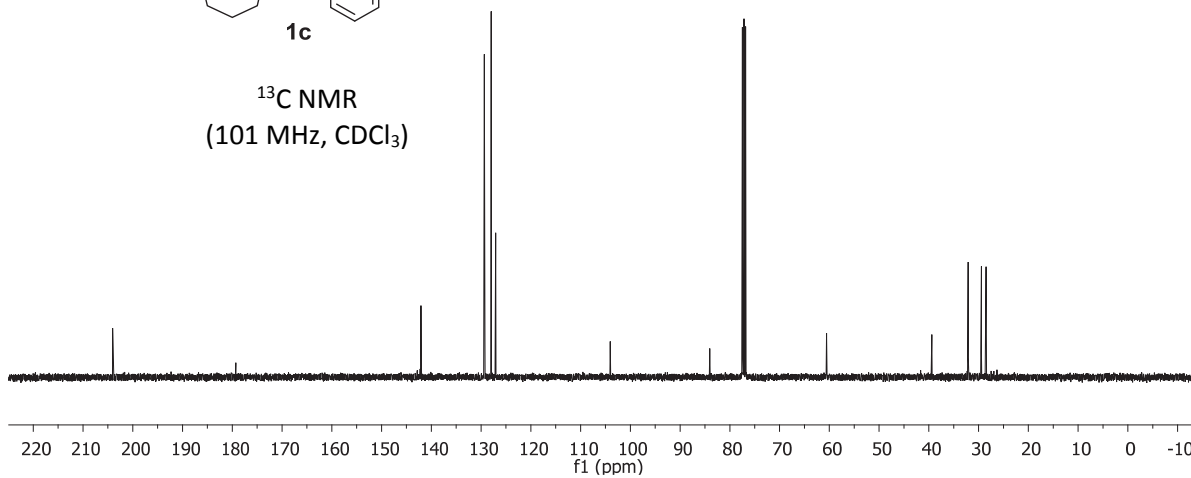
32.10

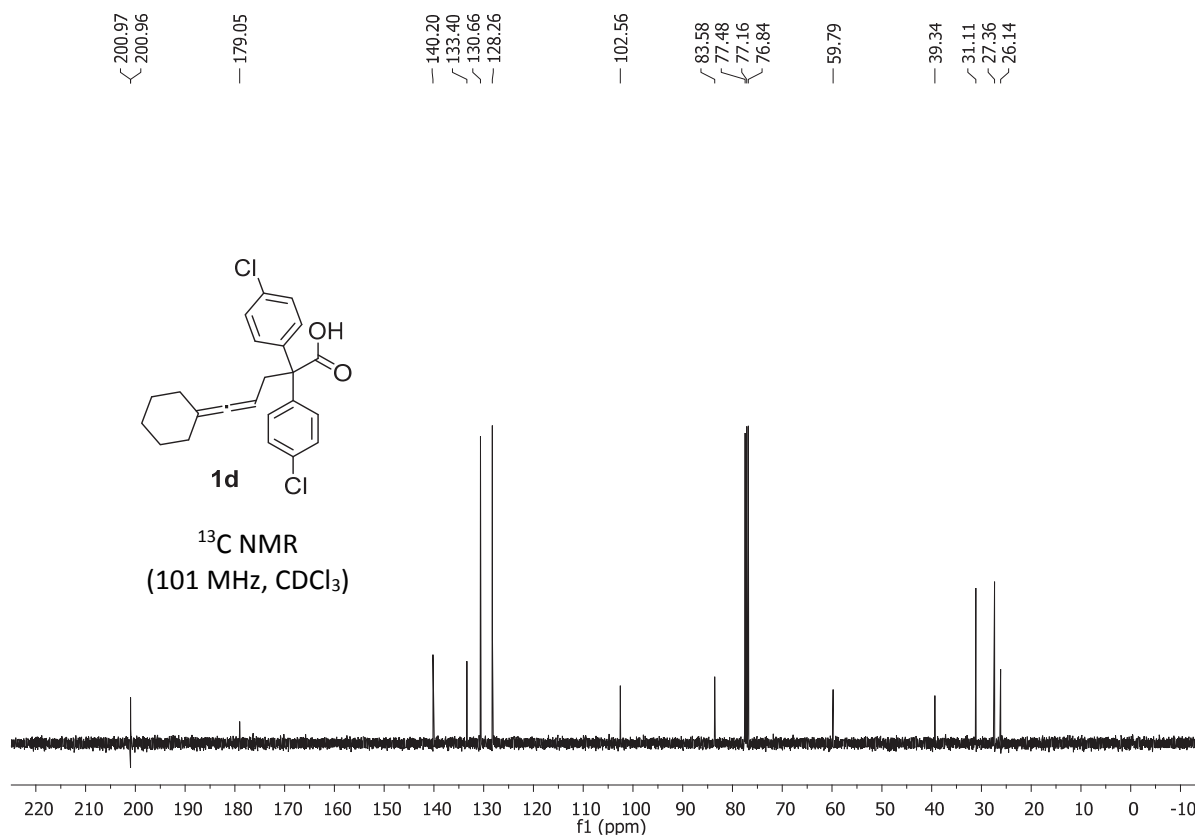
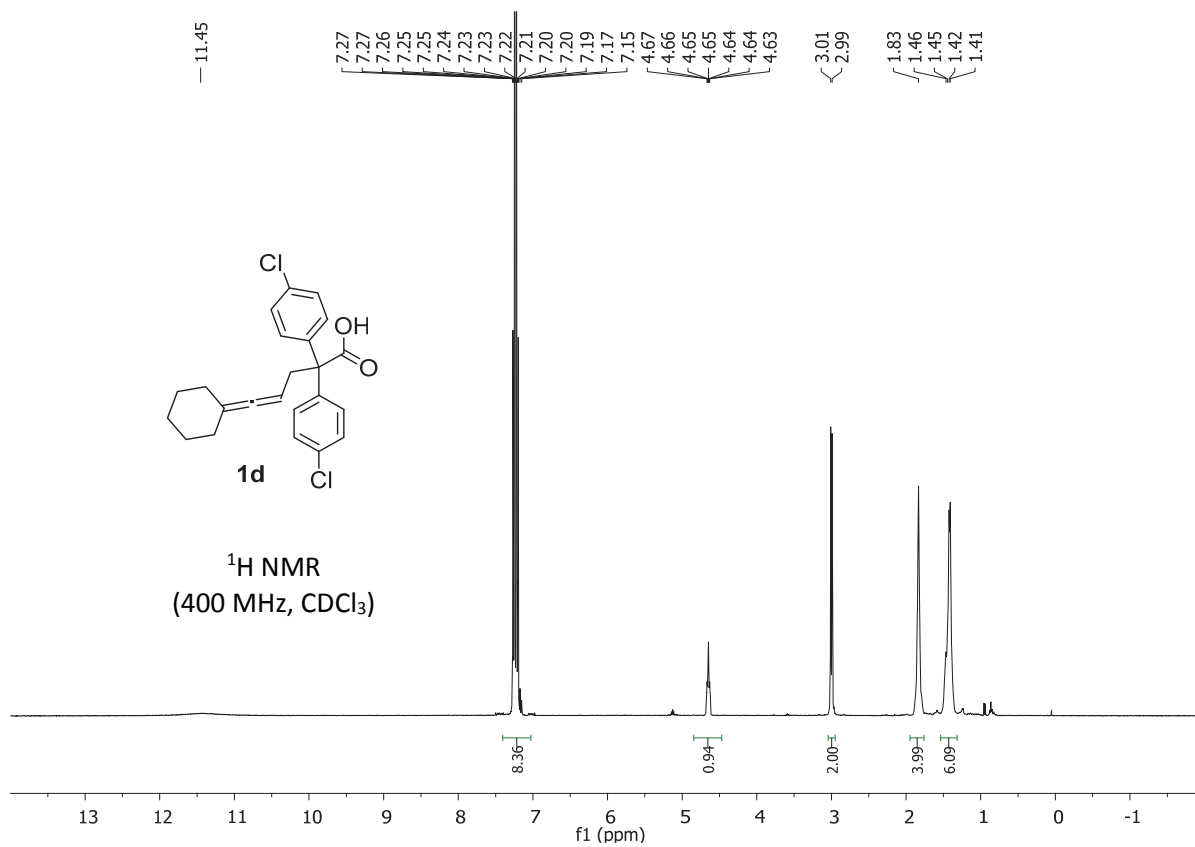
29.45

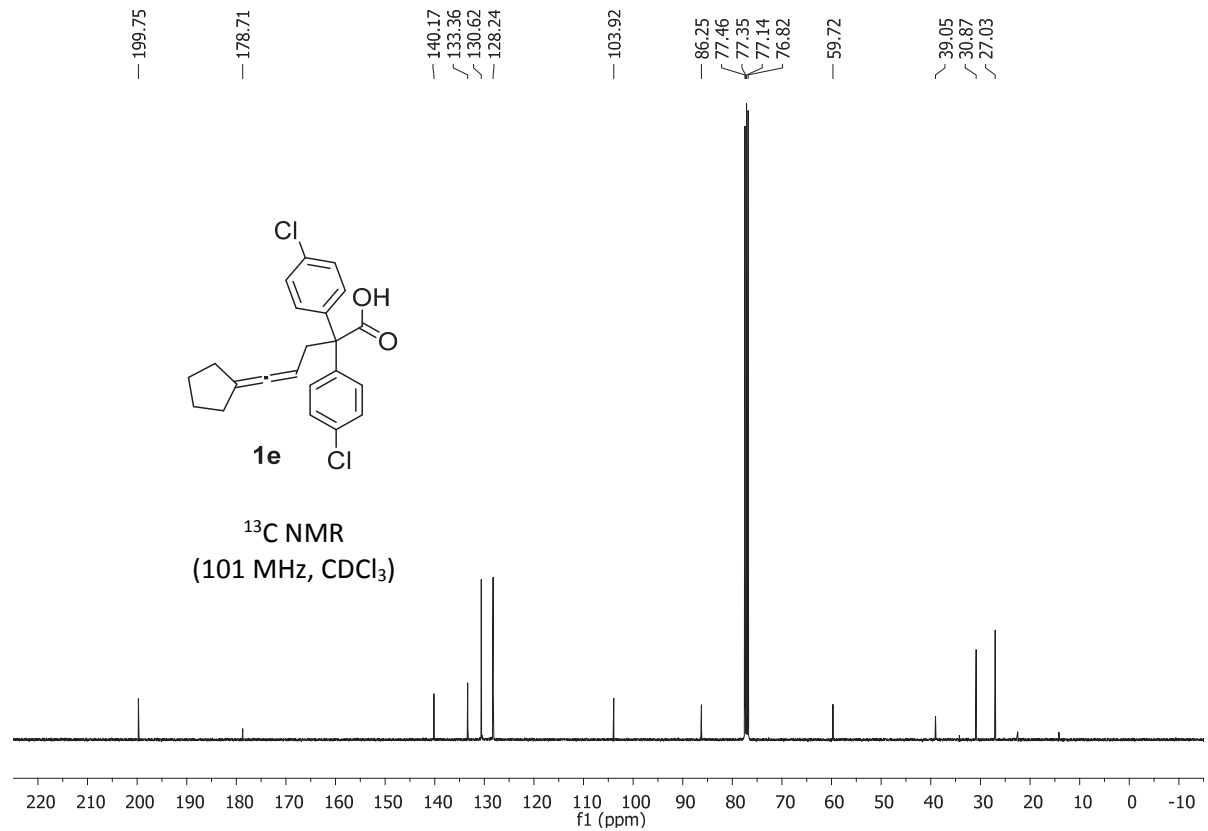
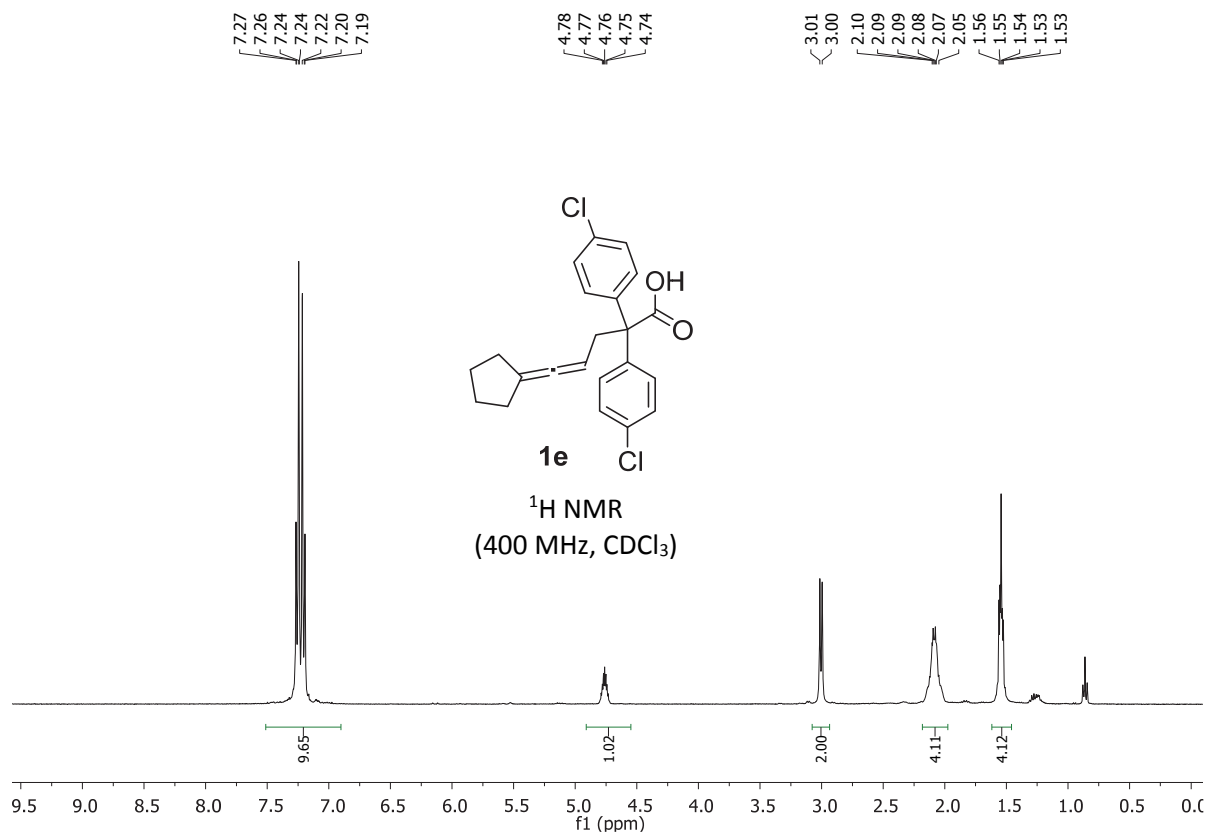
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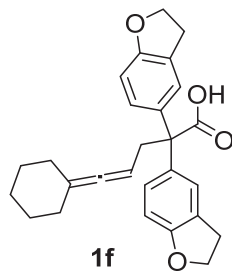


<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)

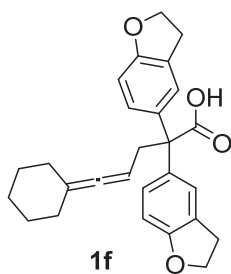
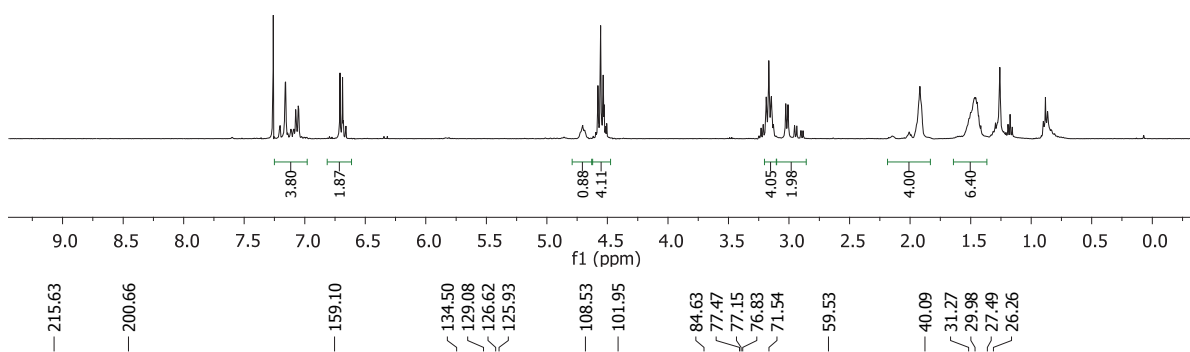




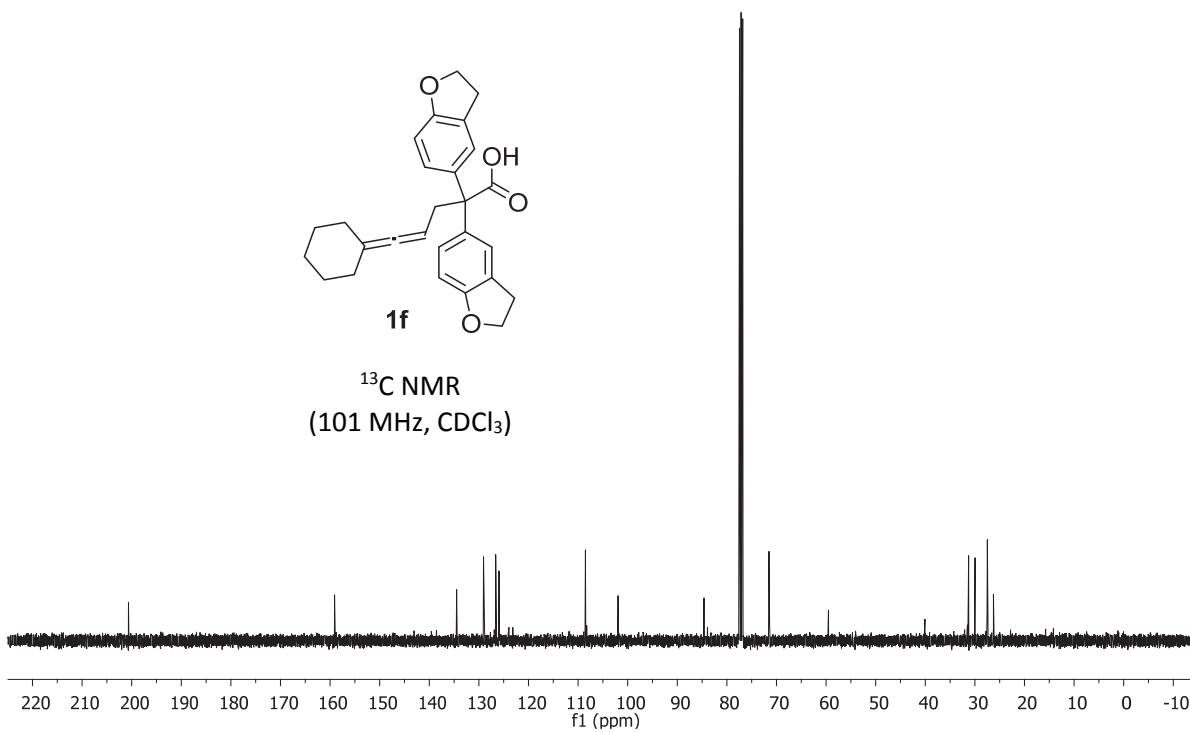


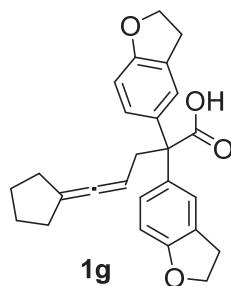


<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

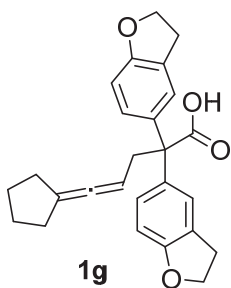
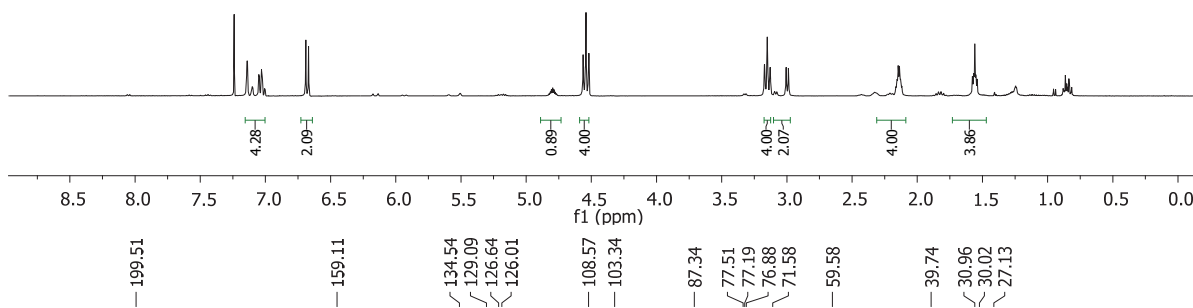


<sup>13</sup>C NMR  
(101 MHz, CDCl<sub>3</sub>)





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



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

