

## Supporting Information

### Gold(I)-Catalyzed Intramolecular Hydroarylation and the Subsequent Ring Enlargement of Methylene cyclopropanes to Cyclobutenes

Wei Fang,<sup>a</sup> Xiang-Ying Tang,<sup>b</sup> and Min Shi<sup>ab\*</sup>

<sup>a</sup>Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237 China.

<sup>b</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China.

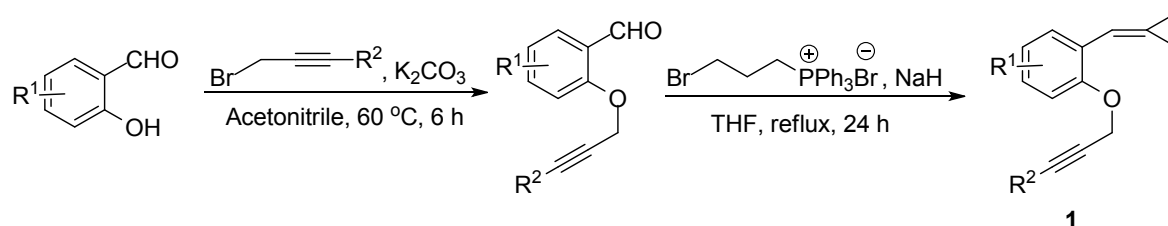
[mshi@mail.sioc.ac.cn](mailto:mshi@mail.sioc.ac.cn). Fax 86-21-64166128

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**1. General Remarks.** MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected.  $^1\text{H}$  NMR spectra were recorded for solution in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard.  $J$ -values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

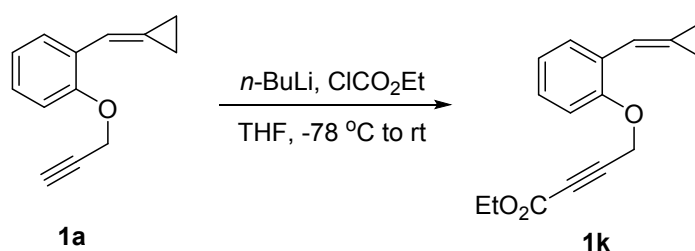
## 2. General procedure for the synthesis of methylenecyclopropanes **1a-j**.



Salicylaldehyde (10.0 mmol, 1.0 equiv) was suspended in acetonitrile (40 mL), followed by addition of  $K_2CO_3$  (20.0 mmol, 2.0 equiv). The suspension was stirred for 10 min, and then propargyl bromide (1.5 equiv) was added via a syringe at 60 °C. The reaction mixture was stirred for 6 hours at 60 °C, whereupon a brown mixture was obtained. The crude product was collected by filtration, then purified by silica gel chromatography (PE:EA = 25:1) to get the *o*-(propargyloxy)-benzaldehyde in over 90% yield.<sup>[1]</sup>

To a suspension of sodium hydride (15.0 mmol, 3.0 equiv) in THF (30 mL) was added (3-bromo-propyl)-triphenylphosphonium bromide (7.5 mmol, 1.5 equiv) and the mixture was stirred for 12 hours under reflux, then a solution of aldehyde (5.0 mmol, 1.0 equiv) in THF (20 mL) was added to the mixture and stirred for another 12 hours. The reaction was quenched with water and extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous  $Na_2SO_4$ , then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (PE) to give methylenecyclopropane **1a-h** in about 35% yield.<sup>[2]</sup>

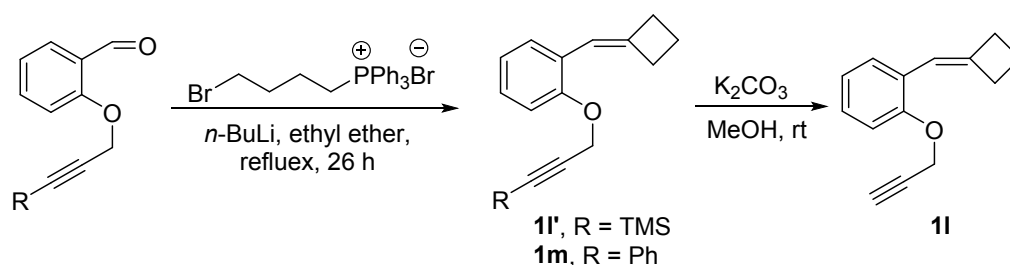
## 3. General procedure for the synthesis of methylenecyclopropanes **1k**.



To a solution of methylenecyclopropane **1a** (1.8 mmol, 1.0 equiv) in THF (20 mL) was added *n*-butyllithium (1.98 mmol, 1.1 equiv) via a syringe at -78 °C. The reaction mixtures were stirred

at that temperature for 2 hours. Then, ethyl chloroformate (1.98 mmol, 1.1 equiv) was added to the mixture and the reaction vessel was naturally warmed to room temperature. The reaction mixture was stirred at room temperature for another 12 hours. After that, the resulting mixture was quenched with water (10 mL) and extracted with ethyl acetate (25 mL) three times. The organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (PE:EA = 10:1) to give methylenecyclobutane **1k** in 22% yield.

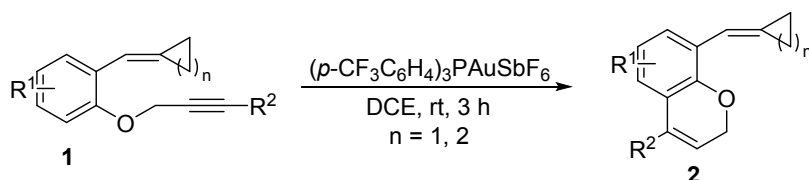
#### 4. General procedure for the synthesis of methylenecyclobutane **1i**.



To a suspension of (4-bromo-butyl)-triphenylphosphonium bromide (10 mmol, 1.0 equiv) in ethyl ether (50 mL) was added *n*-butyllithium (11 mmol, 1.1 equiv) and the mixture was stirred for 24 hours under reflux, then *n*-butyllithium (11 mmol, 1.1 equiv) was added to the mixture and stirred for another 1 hour then a solution of aldehyde (10 mmol, 1.0 equiv) in ethyl ether (20 mL) was added to the mixture and stirred for another 1 hour. The reaction was quenched with water and extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (PE) to give methylenecyclobutanes **1i'** and **1i** in 32% and 36% yield, respectively.<sup>[3]</sup>

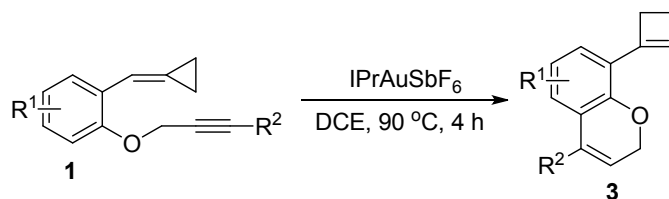
methylenecyclobutane **1i'** (3.2 mmol, 1.0 equiv) was suspended in methanol (10 mL), followed by addition of  $\text{K}_2\text{CO}_3$  (6.4 mmol, 2.0 equiv). The suspension was stirred for 2 hours at room temperature. The reaction was extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (PE) to give methylenecyclobutane **1i** in 92% yield.

#### 5. General procedure for the synthesis of **2**.



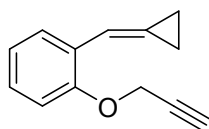
To a flame-dried flask were added the methylenecyclopropane (or methylenecyclobutane) (0.2 mmol, 1.0 equiv) and the  $(p\text{-CF}_3\text{C}_6\text{H}_4)_3\text{PAuSbF}_6$  (0.005 mmol, 0.025 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 3 hours at room temperature. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature, the crude product was purified by silica gel chromatography (PE) to get the desired product **2**.

### 6. General procedure for the synthesis of **3**.



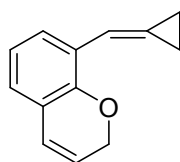
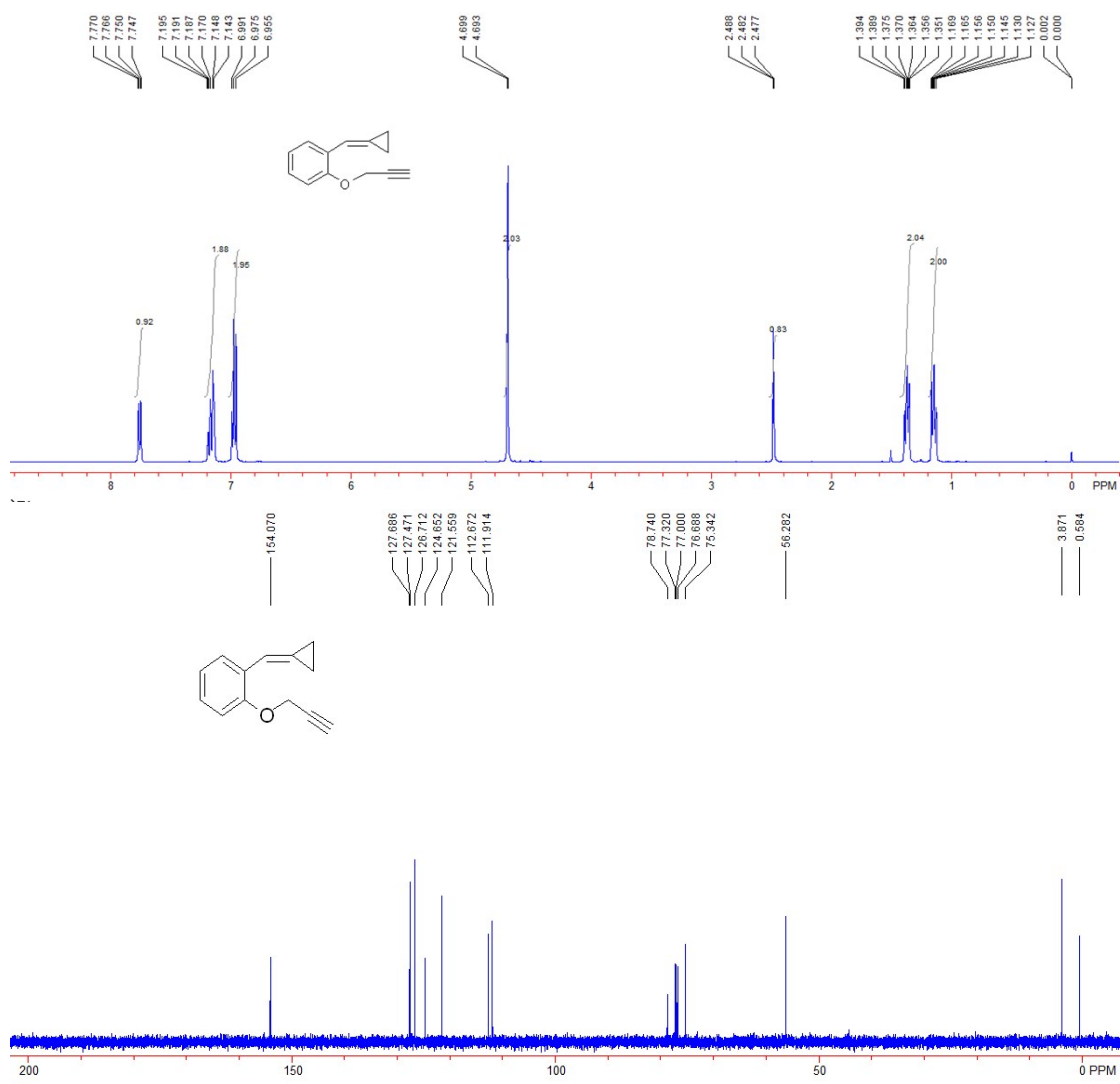
To a flame-dried flask were added the methylenecyclopropane (0.2 mmol, 1.0 equiv) and the  $\text{IPrAuSbF}_6$  (0.005 mmol, 0.025 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 4 hours at 90 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum pump at low temperature, the crude product was purified by silica gel chromatography (PE) to get the desired product **3**.

### 7. Characterization and spectra charts



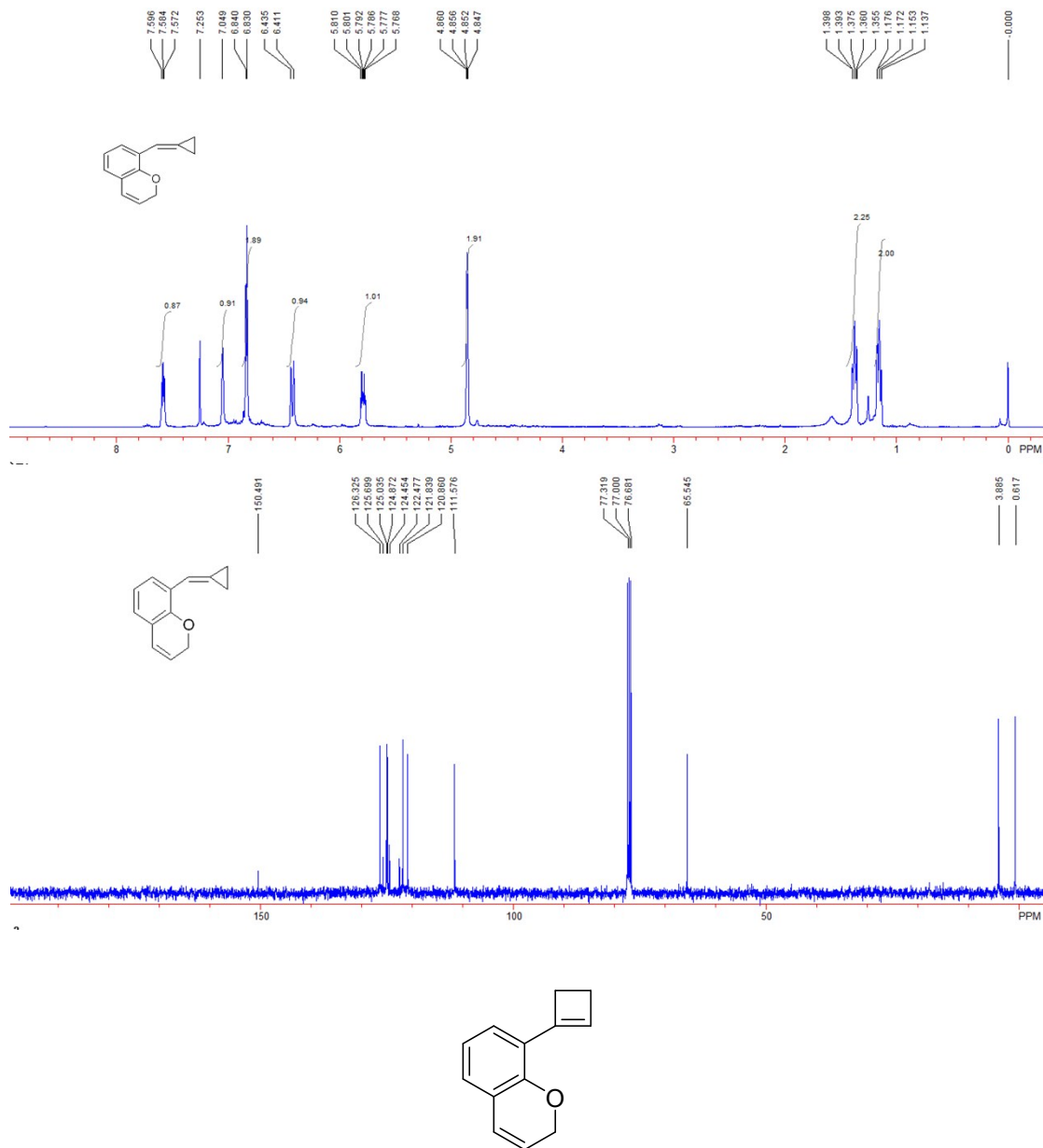
Compound **1a**. 662 mg, yield: 36%; colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.13-1.17 (m, 2H,  $\text{CH}_2$ ), 1.35-1.39 (m, 2H,  $\text{CH}_2$ ), 2.48 (t,  $J = 2.4$  Hz, 1H, CH), 4.69 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.96-6.99 (m, 2H, =CH, Ar), 7.14-7.20 (m, 2H, Ar), 7.76 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 1H,

Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 56.3, 75.3, 78.7, 111.9, 112.7, 121.6, 124.7, 126.7, 127.5, 127.9, 154.1. IR (neat)  $\nu$  3291, 3043, 2975, 2926, 2122, 1632, 1488, 1454, 1372, 1291, 1113, 1024, 975, 848, 748  $\text{cm}^{-1}$ . MS (%)  $m/e$  184 ( $\text{M}^+$ , 2.05), 155 (2.93), 145 (100.00), 127 (9.41), 115 (52.65), 91 (25.02), 77 (8.85), 63 (8.26), 51 (9.43). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}$ : 184.0888, found: 184.0883.

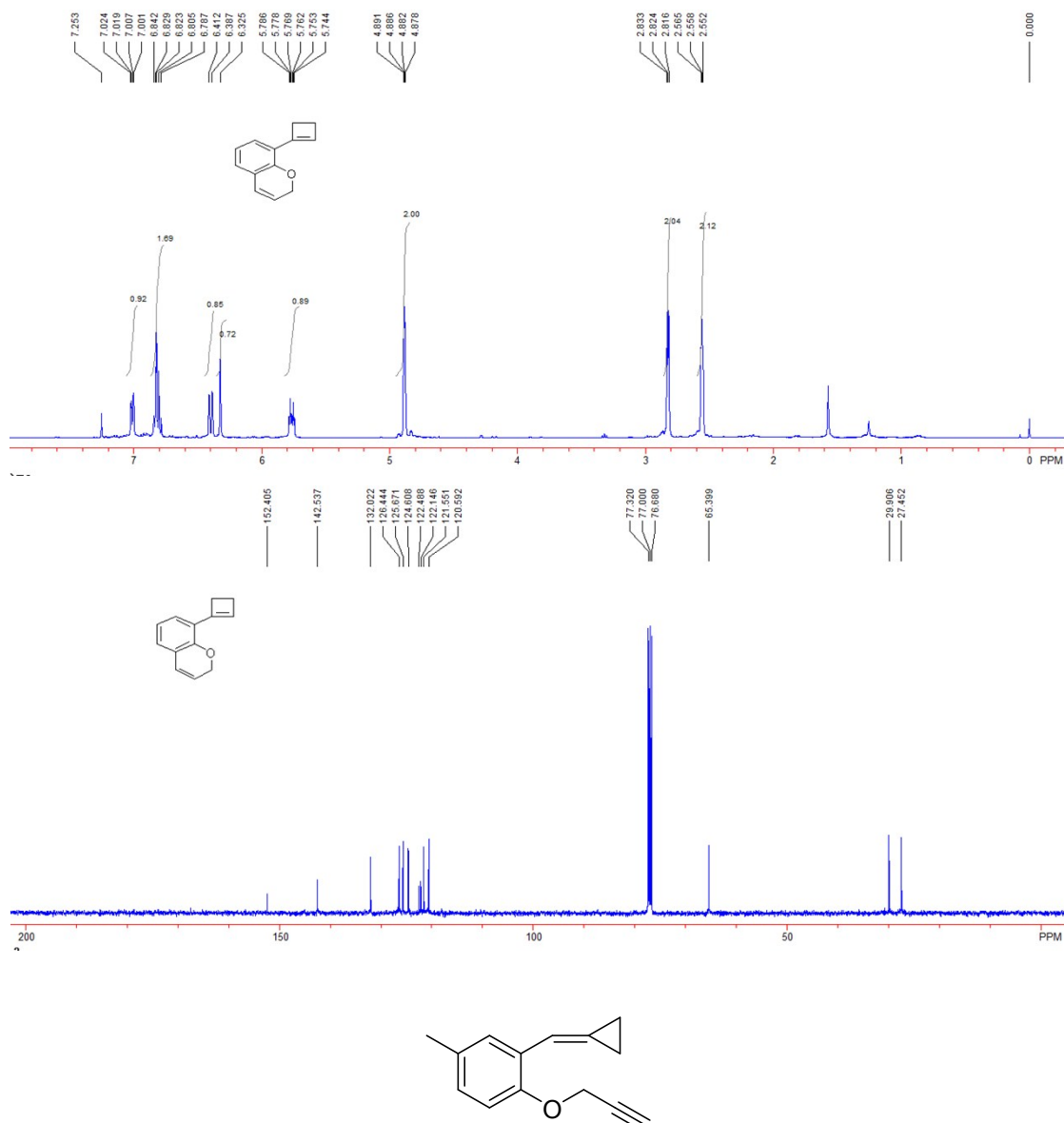


Compound **2a**. 32 mg, yield: 86%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.14-1.18 (m, 2H,  $\text{CH}_2$ ), 1.36-1.40 (m, 2H,  $\text{CH}_2$ ), 4.85 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.79 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.42 (d,  $J = 9.6$  Hz, 1H, =CH), 6.83-6.84 (m, 2H, Ar), 7.05 (s, 1H, =CH), 7.58 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 4.8$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 65.5, 111.6, 120.9, 121.8, 122.5, 124.5, 124.9, 125.0, 125.7, 126.3, 150.5. IR (neat)  $\nu$  3291, 3046, 2972, 2846, 2123, 1784, 1638, 1581, 1460, 1323, 1237, 1199, 1086, 975, 745  $\text{cm}^{-1}$ . MS (%)  $m/e$  184 ( $\text{M}^+$ , 84.89), 183 (100.00), 169 (34.64), 155 (37.71), 141 (35.89), 128 (37.02), 115 (56.60),

91 (24.40), 51 (16.02). HRMS (EI) calcd. for C<sub>13</sub>H<sub>12</sub>O: 184.0888, found: 184.0886.

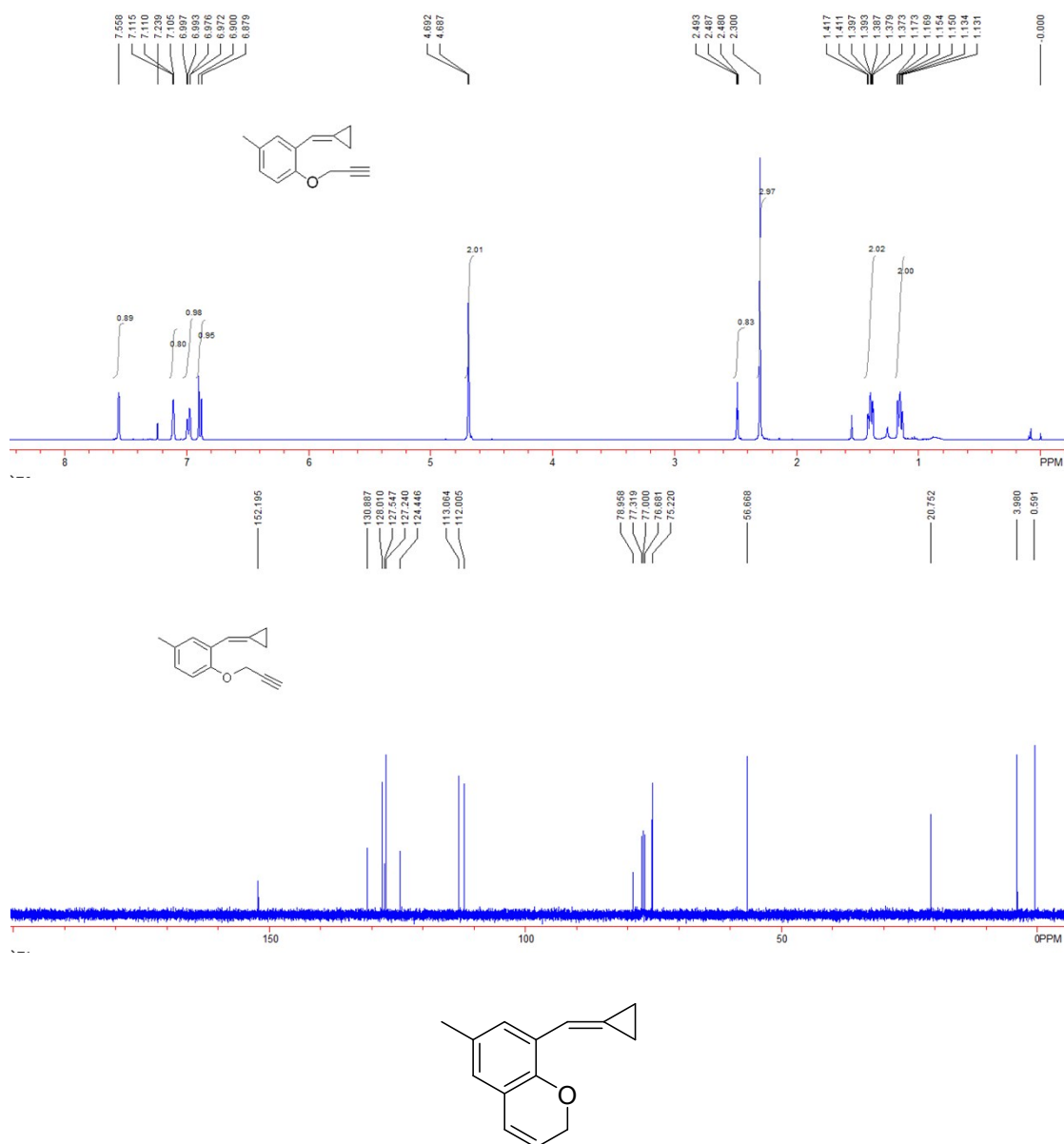


Compound **3a**. 35 mg, yield: 94%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.55-2.57 (m, 2H, CH<sub>2</sub>), 2.82-2.83 (m, 2H, CH<sub>2</sub>), 4.88 (dd, *J*<sub>1</sub> = 3.6 Hz, *J*<sub>2</sub> = 2.0 Hz, 2H, CH<sub>2</sub>), 5.76 (dt, *J*<sub>1</sub> = 10.0 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H, =CH), 6.32 (s, 1H, =CH), 6.40 (d, *J* = 10.0 Hz, 1H, =CH), 6.79-6.84 (m, 2H, Ar), 7.01 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 27.5, 29.9, 65.4, 120.6, 121.6, 122.1, 122.5, 124.6, 125.7, 126.4, 132.0, 142.5, 152.4. IR (neat) ν 3048, 2919, 2849, 1639, 1594, 1460, 1392, 1235, 1215, 1079, 1017, 927, 805, 750, 698 cm<sup>-1</sup>. MS (%) *m/e* 184 (M<sup>+</sup>, 100.00), 169 (42.04), 155 (56.12), 141 (30.97), 128 (47.38), 115 (50.82), 102 (15.29), 91 (23.72), 51 (22.85). HRMS (EI) calcd. for C<sub>13</sub>H<sub>12</sub>O: 184.0888, found: 184.0892.

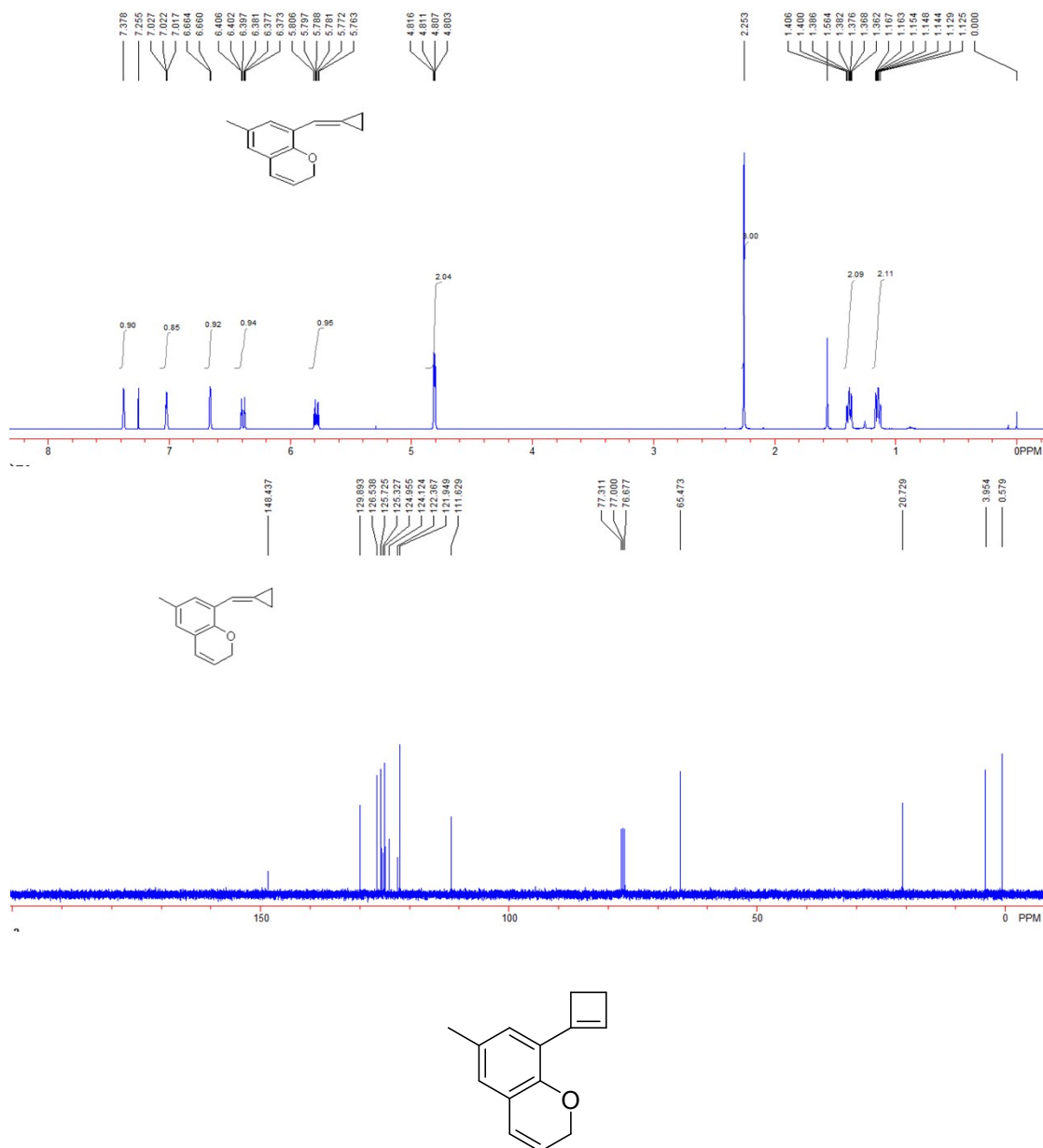


Compound **1b**. 1.215 g, yield: 64%; white solid. MP: 48-49 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.13-1.17 (m, 2H,  $\text{CH}_2$ ), 1.37-1.42 (m, 2H,  $\text{CH}_2$ ), 2.30 (s, 1H,  $\text{CH}_3$ ), 2.49 (t,  $J = 2.4$  Hz, 1H, CH), 4.69 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.89 (d,  $J = 8.4$  Hz, 1H, Ar), 6.98 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 2.0$  Hz, 1H, Ar), 7.11 (dd,  $J_1 = 2.0$  Hz,  $J_2 = 2.0$  Hz, 1H, Ar), 7.56 (s 1H, =CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 4.0, 20.8, 56.7, 75.2, 79.0, 112.0, 113.1, 124.4, 127.2, 127.5, 128.0, 130.9, 152.2. IR (neat)  $\nu$  3287, 2953, 2856, 2121, 1731, 1607, 1587, 1495, 1455, 1376, 1260, 1163, 1070, 923, 802  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 4.41), 183 (8.10), 159 (100.00), 143 (13.65), 131 (21.09), 115 (45.50), 91 (36.26), 77 (17.61), 51 (10.04). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}$ : 198.1045, found: 198.1046.

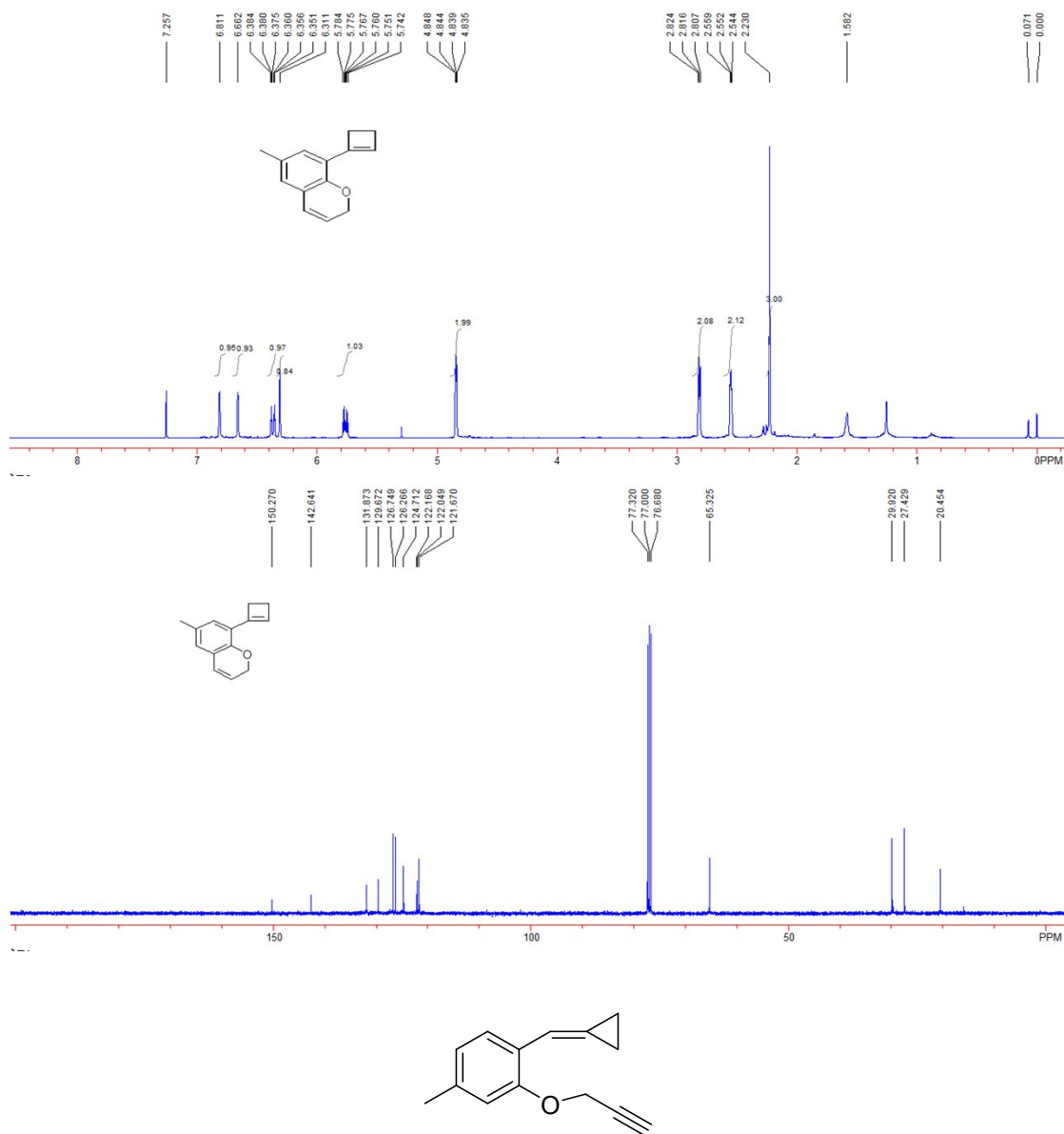




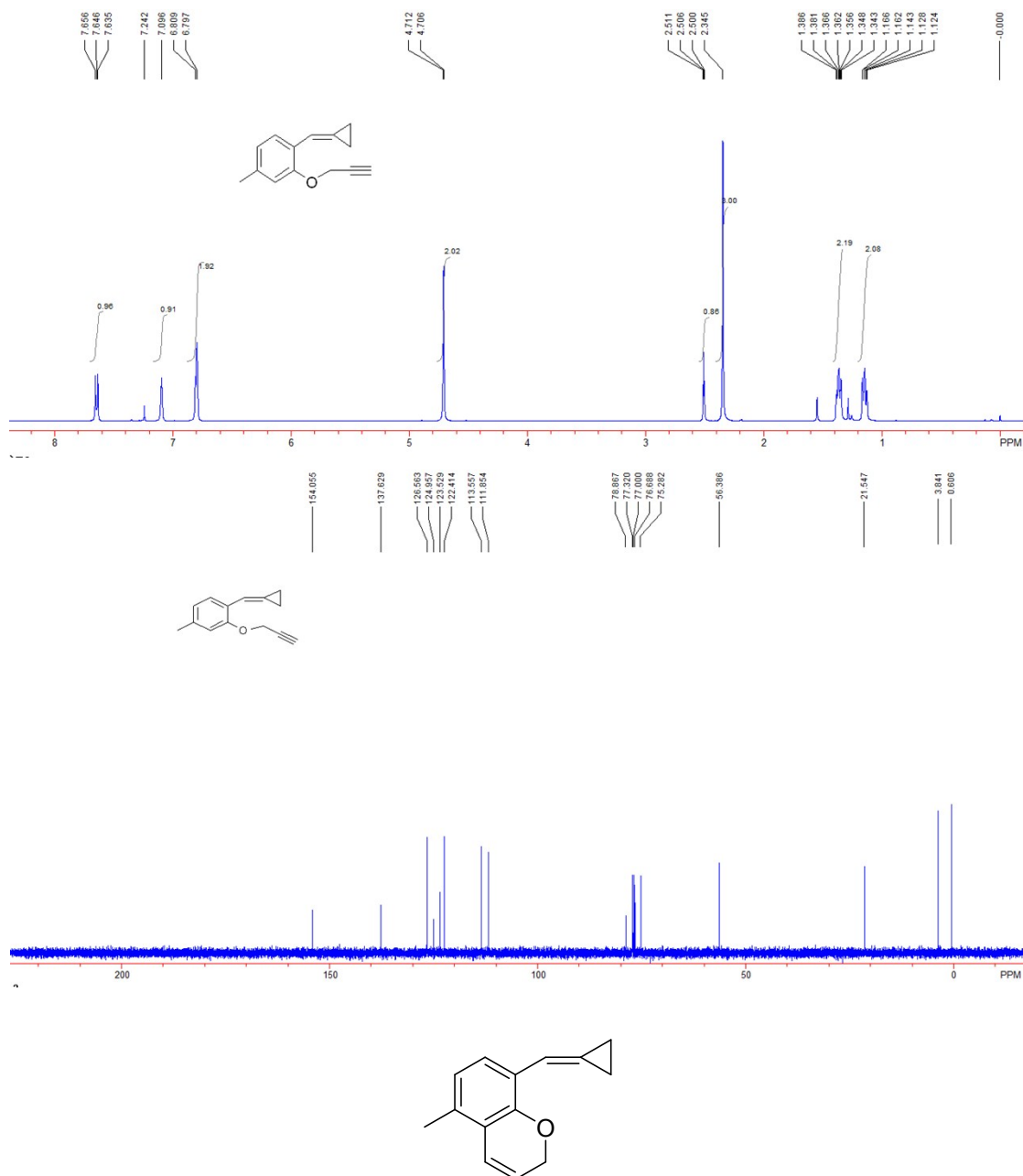
Compound **2b**. 31 mg, yield: 78%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.13-1.17 (m, 2H,  $\text{CH}_2$ ), 1.36-1.41 (m, 2H,  $\text{CH}_2$ ), 2.25 (s, 3H,  $\text{CH}_3$ ), 4.81 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.78 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H), 6.39 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 2.0$  Hz, 1H), 6.66 (d,  $J = 2.0$  Hz, 1H), 7.02 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.38 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 4.0, 20.7, 65.5, 111.6, 121.9, 122.4, 124.1, 125.0, 125.3, 125.7, 126.5, 129.9, 148.4. IR (neat)  $\nu$  3045, 2973, 2826, 1638, 1468, 1425, 1240, 1209, 1154, 1037, 1024, 937, 860, 773, 694  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 76.49), 183 (100.00), 169 (17.35), 155 (32.75), 153 (36.67), 128 (46.89), 115 (53.56), 91 (31.28), 77 (27.44). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1040.



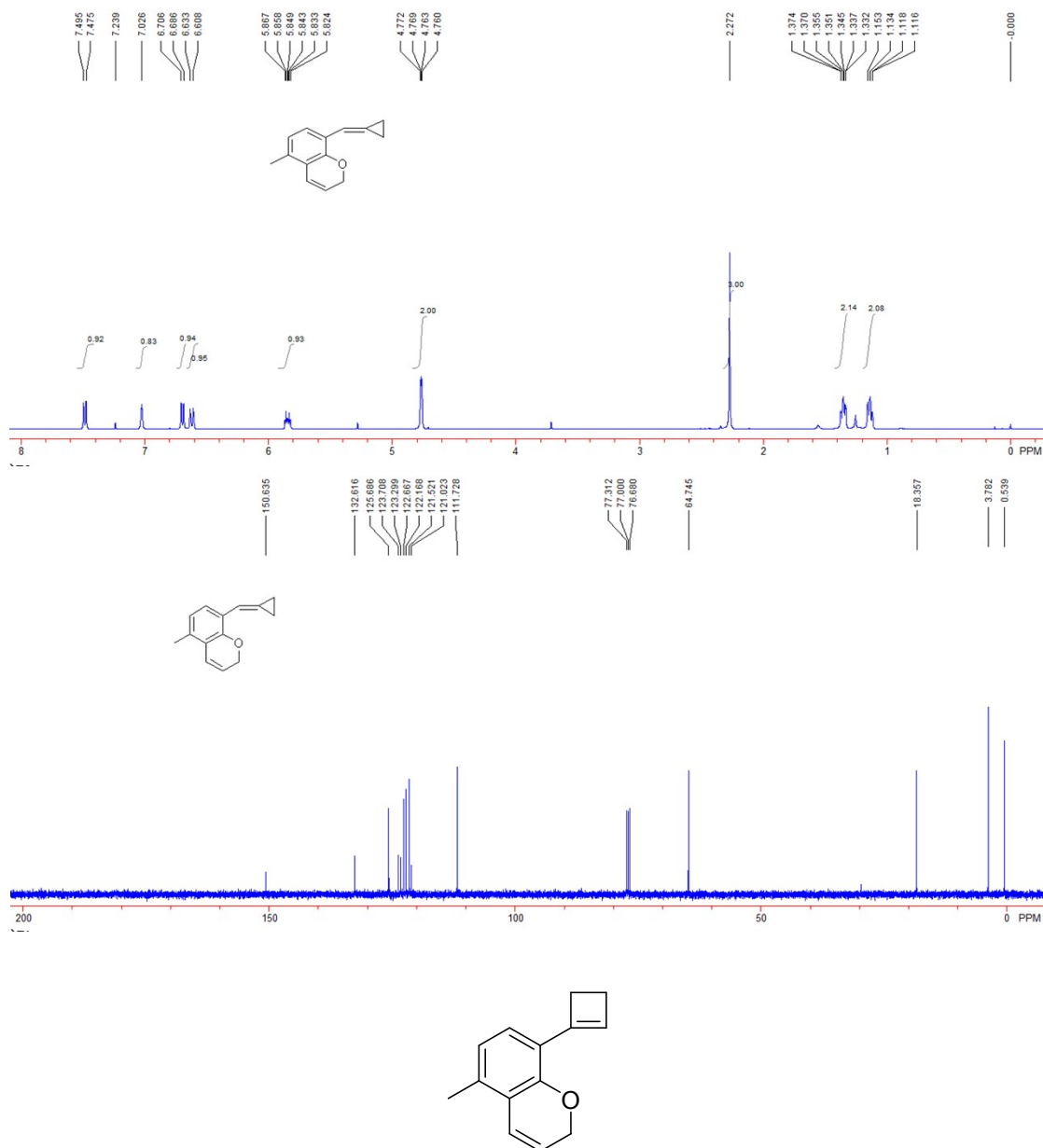
Compound **3b**. 18 mg, yield: 45%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.23 (s, 3H,  $\text{CH}_3$ ), 2.54-2.56 (m, 2H,  $\text{CH}_2$ ), 2.81-2.82 (m, 2H,  $\text{CH}_2$ ), 4.84 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.6$  Hz, 2H,  $\text{CH}_2$ ), 5.76 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.31 (s, 1H, =CH), 6.37 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 1.6$  Hz, 1H, =CH), 6.66 (s, 1H, Ar), 6.81 (s, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  20.5, 27.4, 29.9, 65.3, 121.7, 122.0, 122.2, 124.7, 126.3, 126.7, 129.7, 131.9, 142.6, 150.3. IR (neat)  $\nu$  2915, 2833, 1713, 1675, 1583, 1469, 1379, 1238, 1217, 1132, 1035, 914, 861, 752, 694  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 100.00), 183 (77.19), 155 (43.30), 128 (41.48), 115 (44.44), 91 (26.40), 77 (24.78), 63 (16.42), 51 (15.88). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1049.



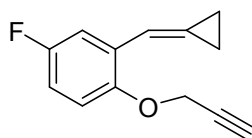
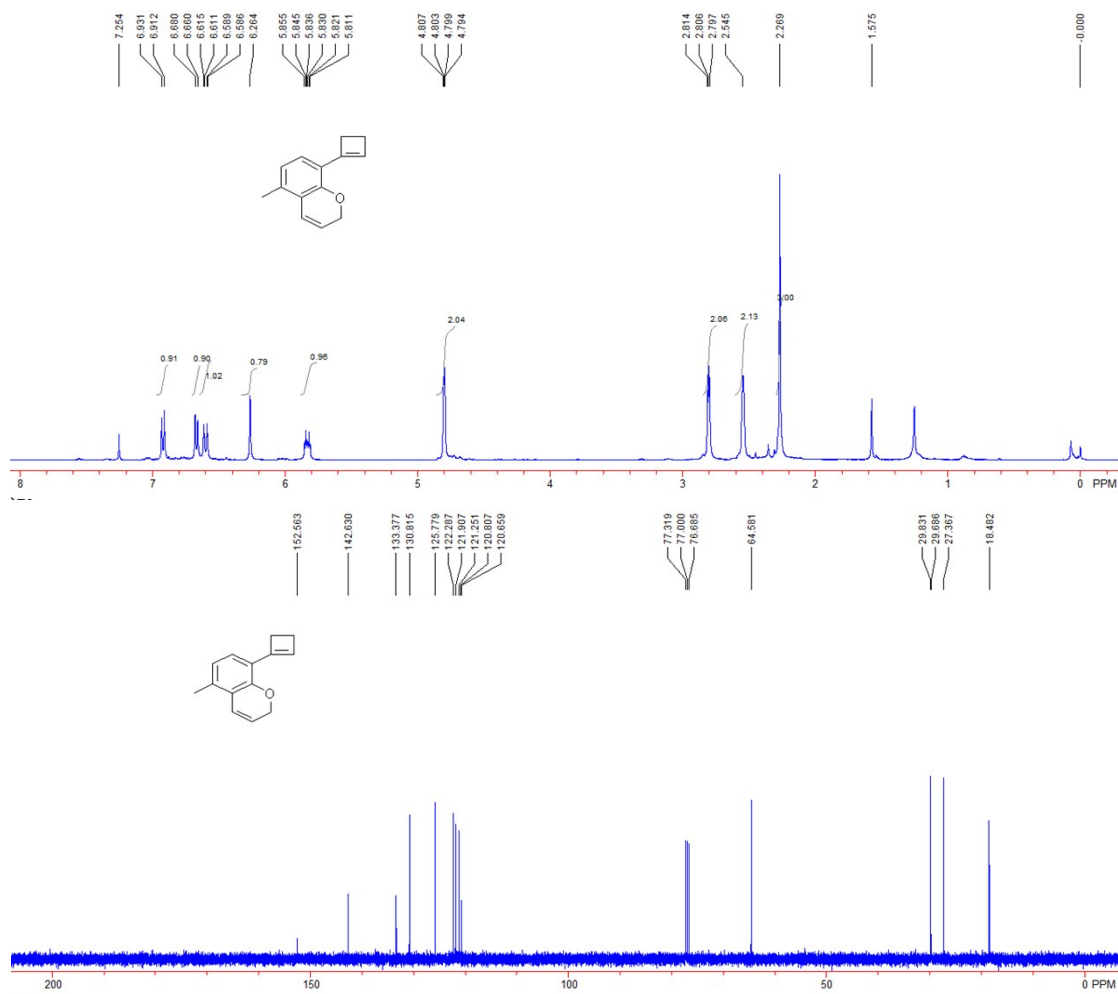
Compound **1c**. 426 mg, yield: 21%; white solid. MP: 63-64 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.13-1.17 (m, 2H,  $\text{CH}_2$ ), 1.34-1.39 (m, 2H,  $\text{CH}_2$ ), 2.35 (s, 3H,  $\text{CH}_3$ ), 2.51 (t,  $J = 2.4$  Hz, 1H, CH), 4.71 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.80 (d,  $J = 4.4$  Hz, 2H, Ar), 7.1 (s, 1H, =CH), 7.65 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 4.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 21.5, 56.4, 75.3, 78.9, 111.9, 113.6, 122.4, 123.5, 125.0, 126.6, 137.6, 154.1. IR (neat)  $\nu$  3286, 2920, 2864, 2122, 1777, 1735, 1611, 1504, 1452, 1364, 1287, 1191, 1080, 971, 815  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 4.48), 183 (8.33), 159 (100.00), 143 (13.57), 128 (21.70), 115 (45.61), 91 (35.15), 77 (17.66), 51 (9.68). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1040.



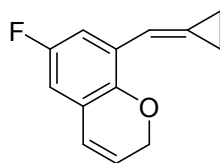
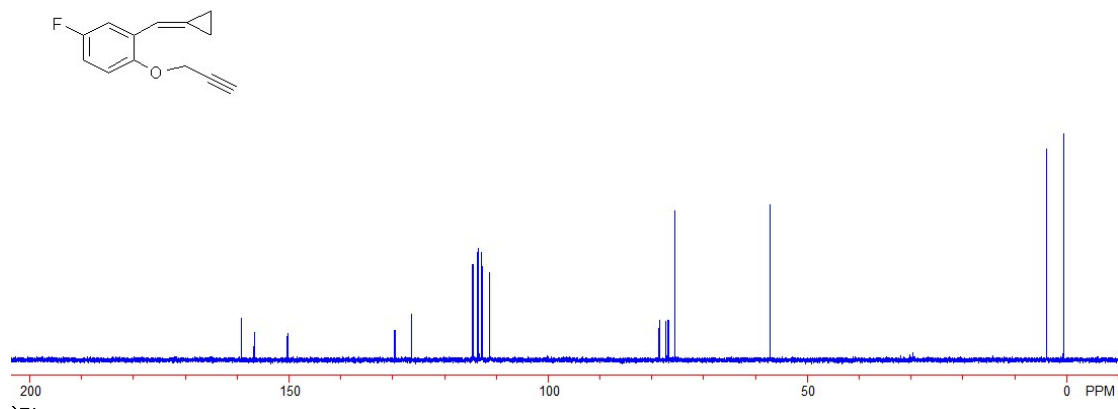
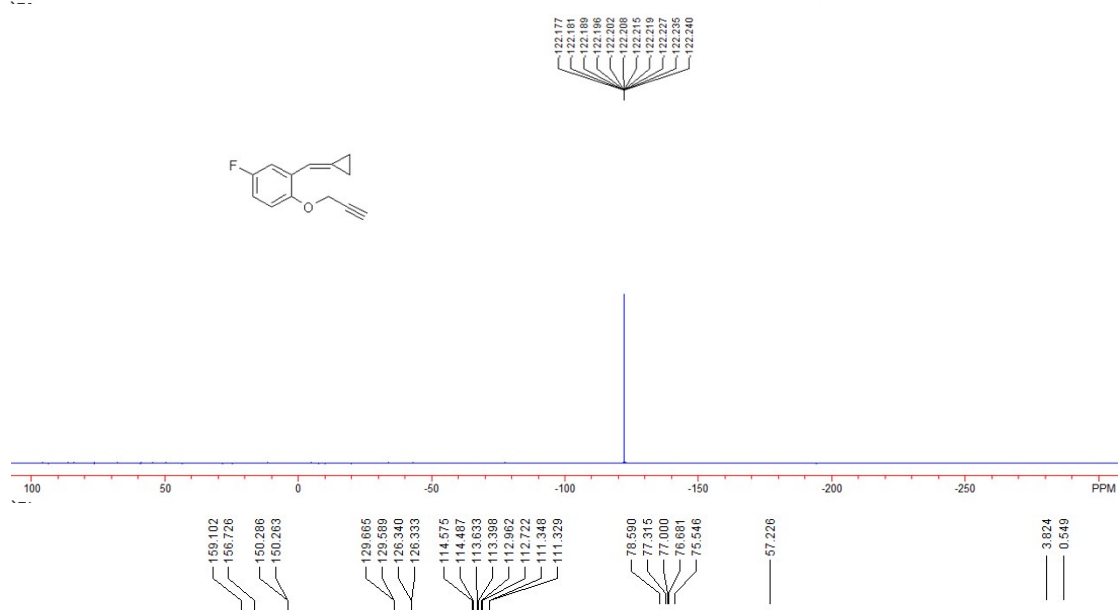
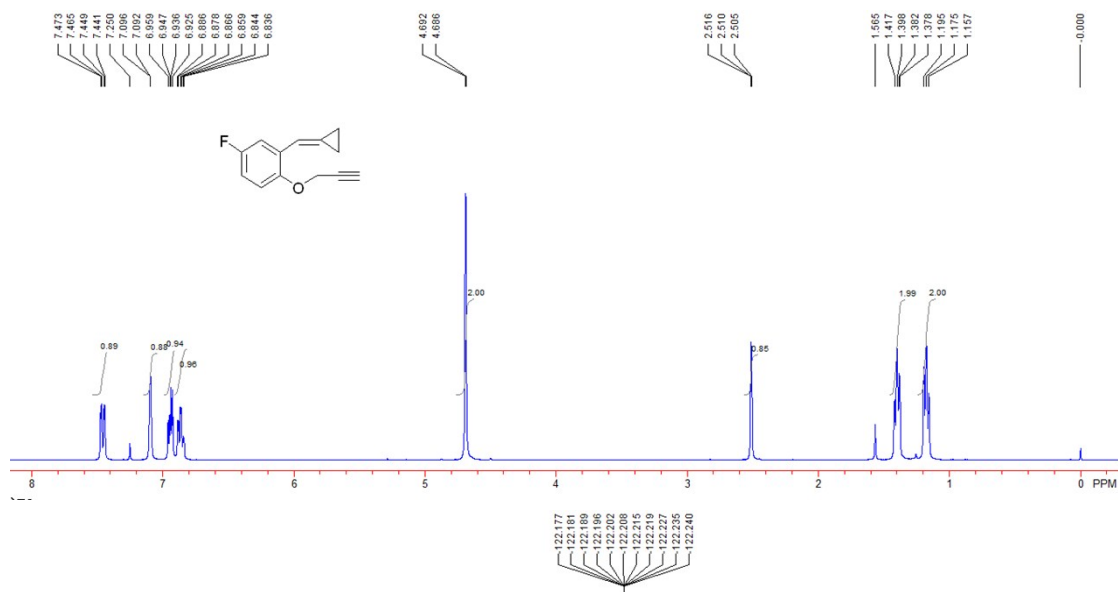
Compound **2c**. 29 mg, yield: 73%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.12-1.15 (m, 2H,  $\text{CH}_2$ ), 1.33-1.37 (m, 2H,  $\text{CH}_2$ ), 2.27 (s, 3H,  $\text{CH}_3$ ), 4.76 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 5.84 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.62 (d,  $J = 10.0$  Hz, 1H, =CH), 6.70 (d,  $J = 8.0$  Hz, 1H, Ar), 7.03 (s, 1H, =CH), 7.49 (d,  $J = 8.0$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.5, 3.8, 18.4, 64.7, 111.7, 121.0, 121.5, 122.2, 122.7, 123.3, 123.7, 125.7, 132.6, 150.6. IR (neat)  $\nu$  3046, 2972, 2853, 1782, 1595, 1488, 1459, 1255, 1203, 1088, 1021, 941, 827, 732, 693  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 44.83), 183 (100.00), 153 (27.02), 128 (26.20), 115 (30.45), 91 (21.90), 77 (15.28), 63 (8.19), 51 (9.17). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1040.



Compound **3c**. 25 mg, yield: 63%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.27 (s, 3H,  $\text{CH}_3$ ), 2.55 (s, 2H,  $\text{CH}_2$ ), 2.80-2.81 (m, 2H,  $\text{CH}_2$ ), 4.80 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.83 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.27 (s, 1H, =CH), 6.60 (dd,  $J_1 = 10.0$  Hz,  $J_2 = 2.0$  Hz, 1H, =CH), 6.67 (d,  $J = 8.0$  Hz, 1H, Ar), 6.92 (d,  $J = 8.0$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  18.5, 27.4, 29.8, 64.6, 120.7, 120.8, 121.3, 121.9, 122.3, 125.8, 130.8, 133.4, 142.6, 152.6. IR (neat)  $\nu$  2976, 2917, 2834, 1780, 1705, 1642, 1952, 1454, 1381, 1213, 1087, 1046, 879, 748, 697 $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 100.00), 183 (79.41), 155 (48.78), 128 (40.68), 115 (40.74), 91 (20.32), 77 (18.41), 63 (12.31), 51 (11.99). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1047.

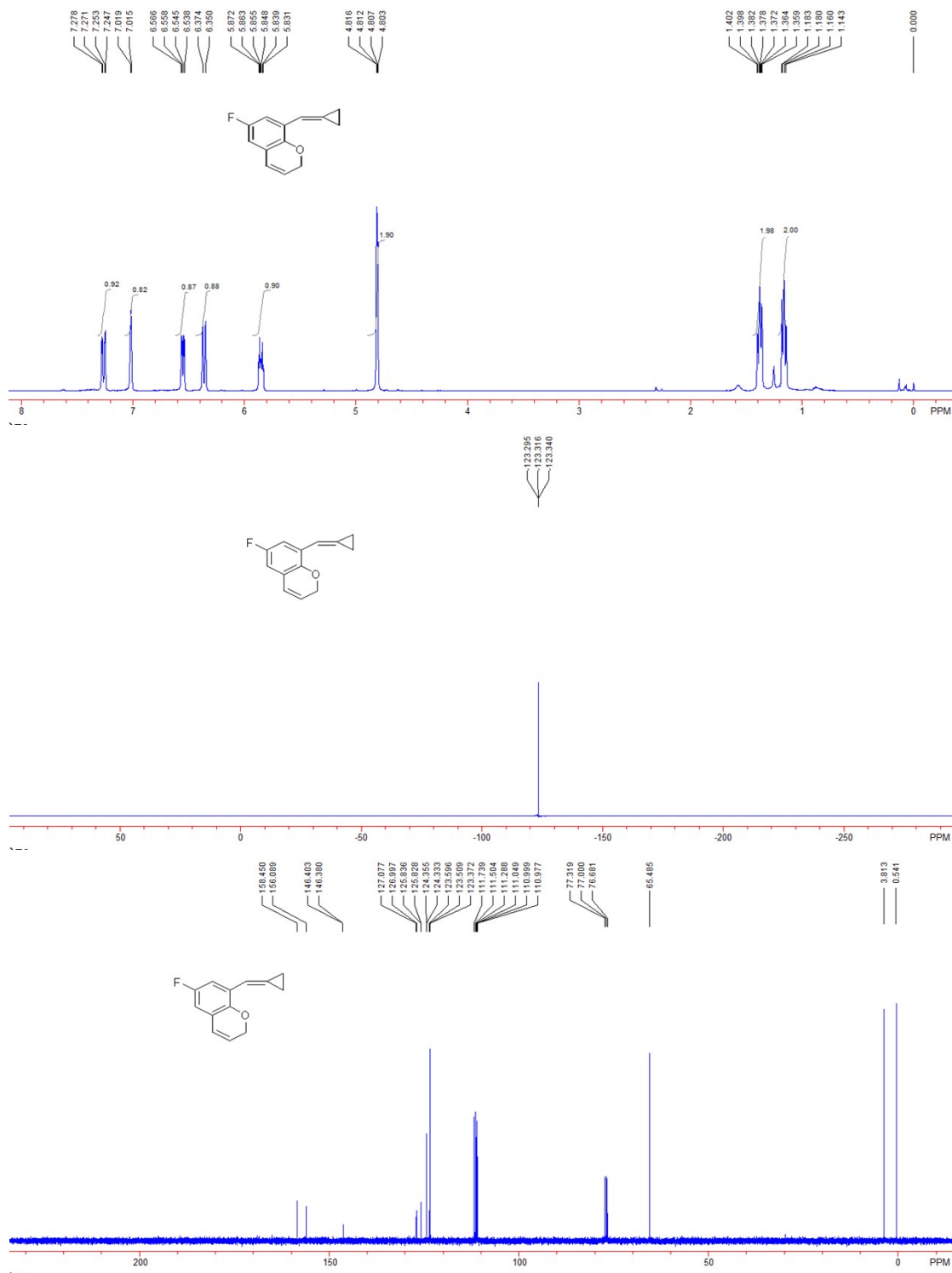


Compound **1d**. 495mg, yield: 26%; white solid. MP: 43-45 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.16-1.20 (m, 2H,  $\text{CH}_2$ ), 1.38-1.42 (m, 2H,  $\text{CH}_2$ ), 2.51 (t,  $J = 2.4$  Hz, 1H, CH), 4.69 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.84-6.89 (m, 1H), 6.94 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 4.8$  Hz, 1H), 7.09 (s 1H), 7.46 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.8, 57.2, 75.6, 78.6, 111.3 (d,  $J_{\text{C-F}} = 1.9$  Hz), 112.8 (d,  $J_{\text{C-F}} = 24.0$  Hz), 113.5 (d,  $J_{\text{C-F}} = 23.5$  Hz), 114.5 (d,  $J_{\text{C-F}} = 8.8$  Hz), 126.3 (d,  $J_{\text{C-F}} = 0.7$  Hz), 129.6 (d,  $J_{\text{C-F}} = 7.6$  Hz), 150.3 (d,  $J_{\text{C-F}} = 2.3$  Hz), 157.9 (d,  $J_{\text{C-F}} = 237.6$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ):  $\delta$  -122.24 ~ -122.17 (m, 1F). IR (neat)  $\nu$  3296, 3077, 2921, 2871, 2123, 1769, 1732, 1611, 1491, 1372, 1237, 1182, 1066, 987, 805  $\text{cm}^{-1}$ . MS (%)  $m/e$  202 ( $\text{M}^+$ , 2.68), 163 (100.00), 147 (10.13), 133 (41.85), 115 (47.97), 109 (25.59), 75 (9.72), 57 (9.90), 51 (5.98). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OF}$ : 202.0794, found: 202.0791.

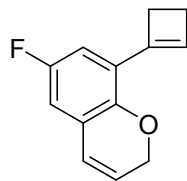


Compound **2d**. 33 mg, yield: 80%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.14-1.18 (m, 2H, CH<sub>2</sub>), 1.36-1.40 (m, 2H, CH<sub>2</sub>), 4.81 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H, CH<sub>2</sub>), 5.85 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.36 (d,  $J = 9.6$  Hz, 1H, =CH), 6.55 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.8$  Hz,

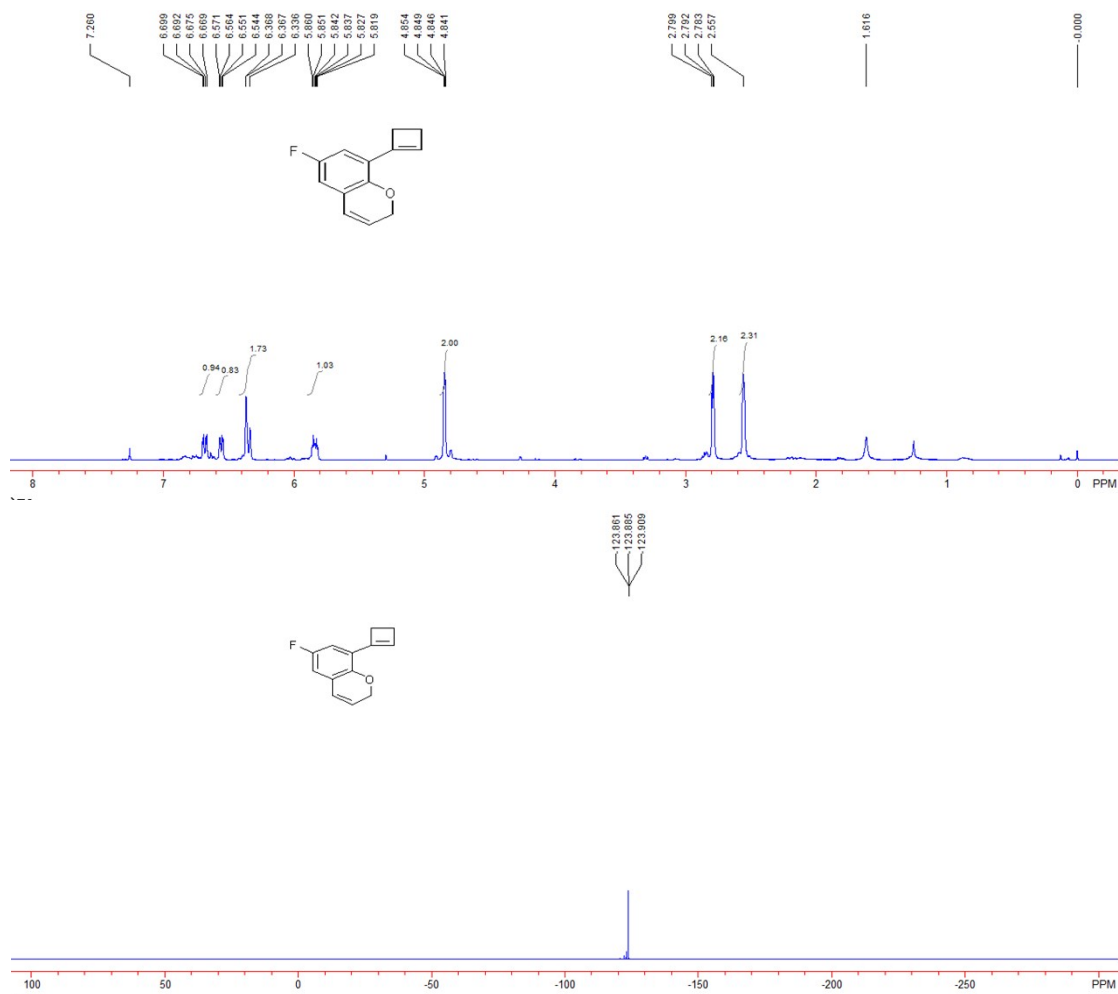
1H, Ar), 7.02 (d,  $J = 1.6$  Hz, 1H, =CH), 7.26 (dd,  $J_1 = 9.6$  Hz,  $J_2 = 2.8$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  0.5, 3.8, 65.5, 111.0 (d,  $J_{\text{C-F}} = 2.2$  Hz), 111.2 (d,  $J_{\text{C-F}} = 23.9$  Hz), 111.6 (d,  $J_{\text{C-F}} = 23.5$  Hz), 123.4, 123.5 (d,  $J_{\text{C-F}} = 8.7$  Hz), 124.4 (d,  $J_{\text{C-F}} = 2.2$  Hz), 125.8 (d,  $J_{\text{C-F}} = 0.8$  Hz), 127.0 (d,  $J_{\text{C-F}} = 8.0$  Hz), 146.4 (d,  $J_{\text{C-F}} = 2.3$  Hz), 157.3 (d,  $J_{\text{C-F}} = 236.1$  Hz).  $^{19}\text{F}$  NMR (376 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>):  $\delta$  -123.34 ~ -123.29 (m). IR (neat)  $\nu$  3050, 2975, 2845, 1594, 1465, 1446, 1301, 1209, 1196, 1129, 1039, 997, 861, 775, 692 cm<sup>-1</sup>. MS (%)  $m/e$  202 (M<sup>+</sup>, 100.00), 201 (99.36), 187 (40.34), 173 (36.62), 159 (39.49), 146 (40.31), 133 (68.39), 115 (17.54), 51 (13.69). HRMS (EI) calcd. for C<sub>13</sub>H<sub>11</sub>OF: 202.0794, found: 202.0792.

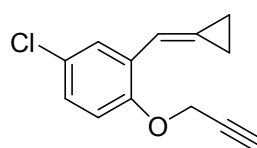
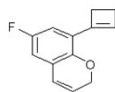
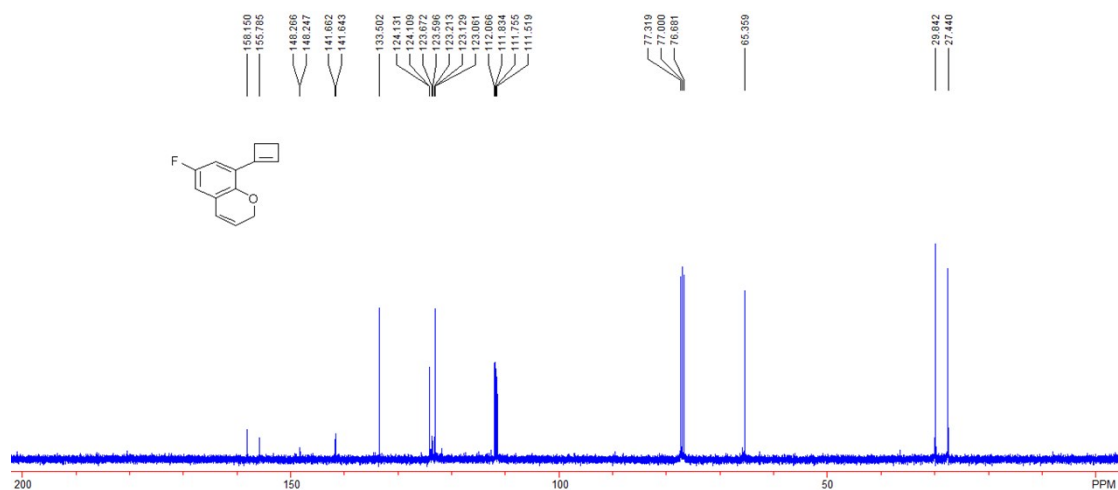




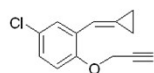
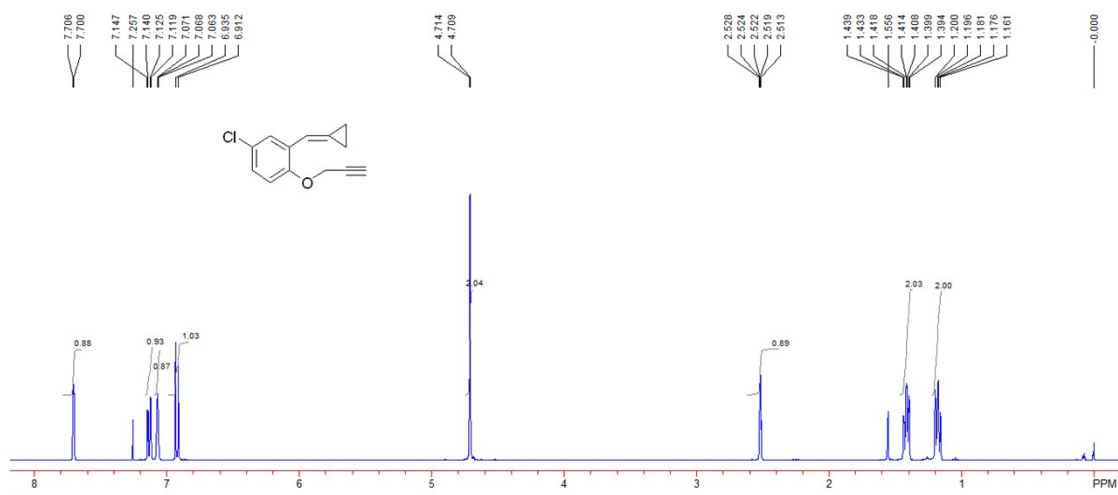


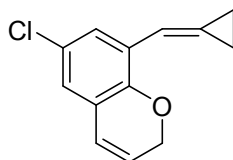
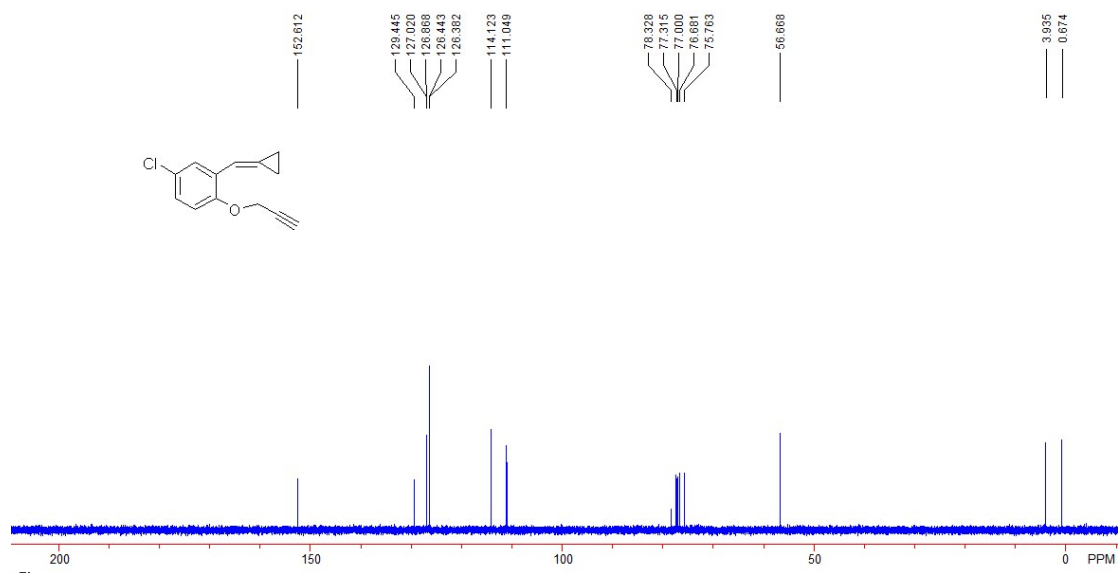
Compound **3d**. 17 mg, yield: 41%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.56 (s, 2H,  $\text{CH}_2$ ), 2.78-2.80 (m, 2H,  $\text{CH}_2$ ), 4.85 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.84 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.34-6.37 (m, 2H, =CH, Ar), 6.56 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.8$  Hz, 1H, Ar), 6.68 (dd,  $J_1 = 9.6$  Hz,  $J_2 = 2.8$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  27.4, 29.8, 65.4, 111.6 (d,  $J_{\text{C-F}} = 23.6$  Hz), 112.0 (d,  $J_{\text{C-F}} = 23.6$  Hz), 123.1, 123.2 (d,  $J_{\text{C-F}} = 8.4$  Hz), 123.6 (d,  $J_{\text{C-F}} = 7.2$  Hz), 124.1 (d,  $J_{\text{C-F}} = 2.2$  Hz), 133.5, 141.6 (d,  $J_{\text{C-F}} = 1.9$  Hz), 148.3 (d,  $J_{\text{C-F}} = 1.9$  Hz), 157.0 (d,  $J_{\text{C-F}} = 236.5$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ):  $\delta$  -123.91 ~ -123.86 (m, 1F). IR (neat)  $\nu$  2916, 2833, 1713, 1675, 1588, 1467, 1446, 1314, 1204, 1155, 1035, 978, 854, 750, 693  $\text{cm}^{-1}$ . MS (%)  $m/e$  202 ( $\text{M}^+$ , 100.00), 187 (43.38), 173 (47.66), 159 (32.14), 146 (38.14), 133 (43.72), 101 (11.79), 75 (14.08), 51 (11.38). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OF}$ : 202.0794, found: 202.0795.



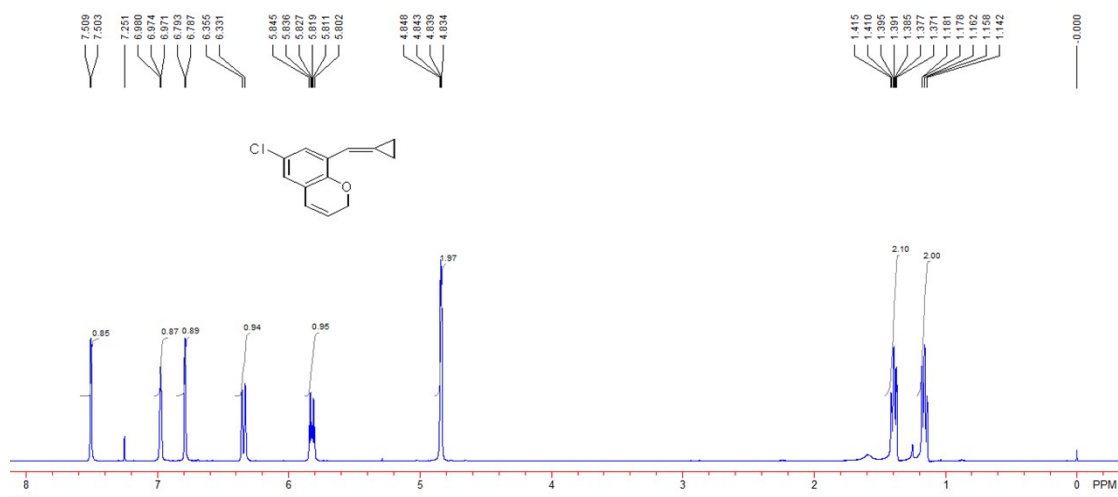


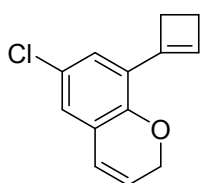
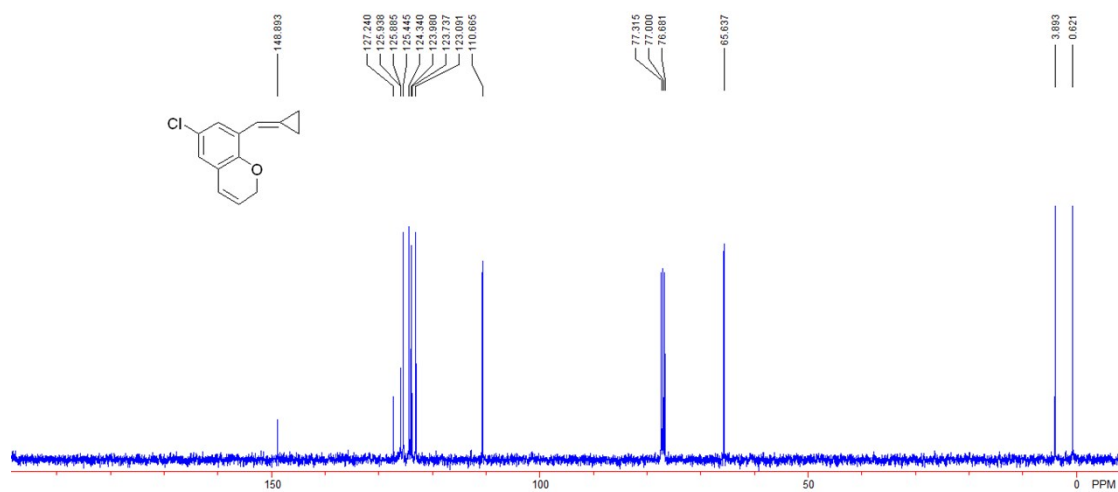
Compound **1e**. 1.015 g, yield: 47%; white solid. MP: 77-79 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.16-1.20 (m, 2H,  $\text{CH}_2$ ), 1.39-1.44 (m, 2H,  $\text{CH}_2$ ), 2.52 (t,  $J = 2.4$  Hz, 1H, CH), 4.71 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.92 (d,  $J = 8.8$  Hz, 1H, Ar), 7.07 (s, 1H, =CH), 7.13 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H, Ar), 7.70 (d,  $J = 2.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.7, 3.9, 56.7, 75.8, 78.3, 111.0, 114.1, 126.4, 126.5, 126.9, 127.0, 129.4, 152.6. IR (neat)  $\nu$  3293, 3076, 2954, 2924, 2123, 1770, 1716, 1592, 1482, 1452, 1223, 1123, 1021, 801, 733  $\text{cm}^{-1}$ . MS (%)  $m/e$  218 ( $\text{M}^+$ , 2.80), 183 (23.42), 179 (84.28), 155 (10.00), 144 (24.61), 115 (100.00), 89 (18.95), 75 (15.53), 51 (9.33). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OCl}$ : 218.0498, found: 218.0499.



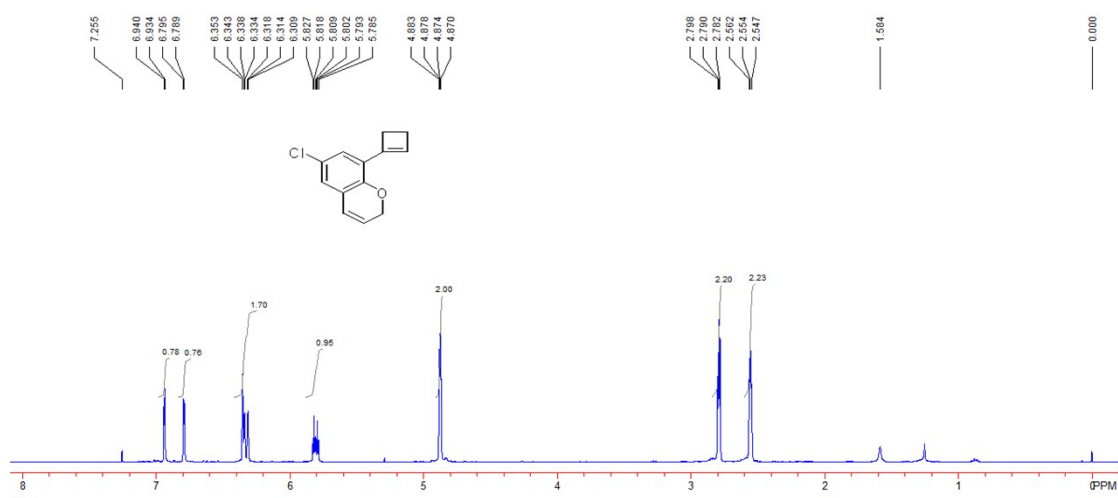


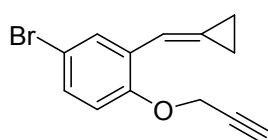
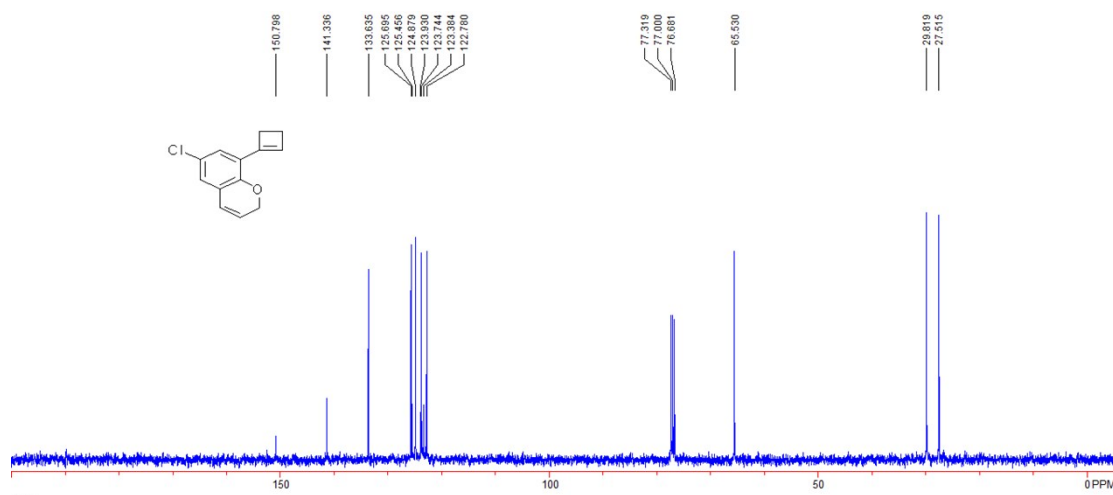
Compound **2e**. 42 mg, yield: 95%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.14-1.18 (m, 2H, CH<sub>2</sub>), 1.37-1.42 (m, 2H, CH<sub>2</sub>), 4.84 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H, CH<sub>2</sub>), 5.82 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.34 (d,  $J = 9.6$  Hz, 1H, =CH), 6.79 (d,  $J = 2.4$  Hz, 2H, Ar), 6.97 (t,  $J = 2.0$  Hz, 1H, =CH), 7.51 (d,  $J = 2.4$  Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 0.6, 3.9, 65.6, 111.7, 123.1, 123.7, 124.0, 124.3, 125.4, 125.9, 126.0, 127.2, 148.9. IR (neat)  $\nu$  3051, 2974, 2850, 2005, 1778, 1733, 1576, 1463, 1422, 1328, 1200, 1023, 990, 867, 736 cm<sup>-1</sup>. MS (%)  $m/e$  218 (M<sup>+</sup>, 10.17), 183 (100.00), 153 (24.09), 128 (13.86), 115 (18.62), 102 (4.23), 91 (7.34), 77 (9.48), 51 (7.61). HRMS (EI) calcd. for C<sub>13</sub>H<sub>11</sub>OCl: 218.0498, found: 218.0496.



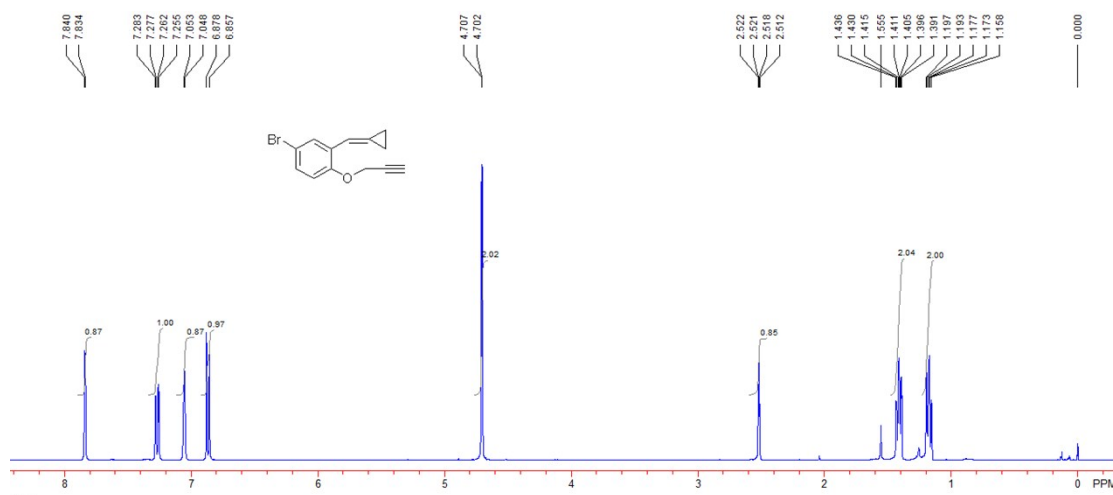


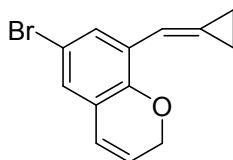
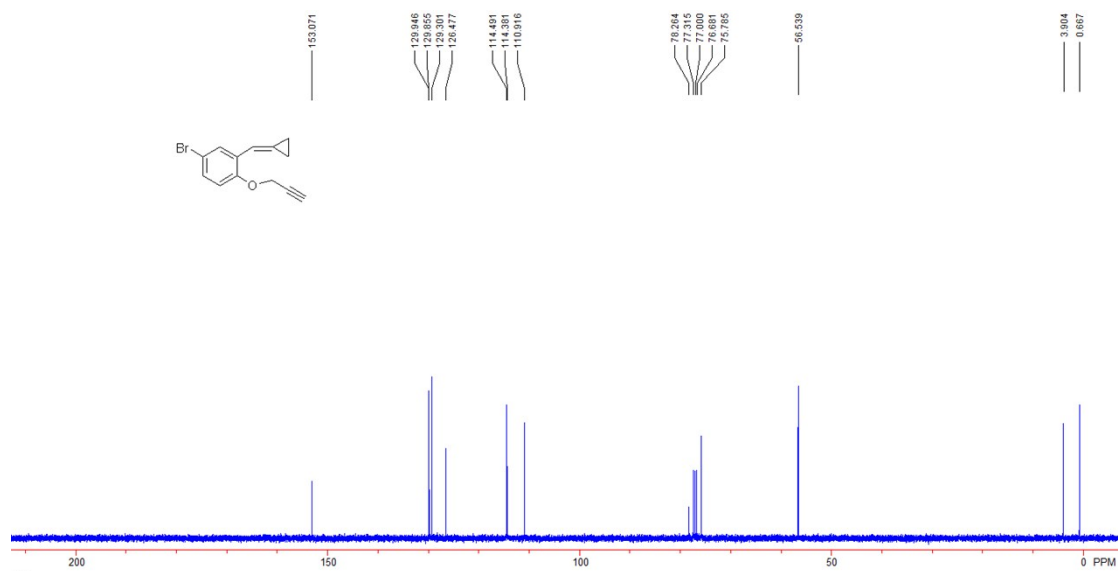
Compound **3e**. 28 mg, yield: 64%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.55-2.56 (m, 2H,  $\text{CH}_2$ ), 2.78-2.80 (m, 2H,  $\text{CH}_2$ ), 4.88 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.80 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.33 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 2.0$  Hz, 1H, =CH), 6.35 (s, 1H, =CH), 6.79 (d,  $J = 2.4$  Hz, 1H, Ar), 6.94 (d,  $J = 2.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  27.5, 29.8, 65.5, 122.8, 123.4, 123.7, 123.9, 124.9, 125.5, 125.7, 133.6, 141.3, 150.8. IR (neat)  $\nu$  3051, 2914, 2832, 1733, 1678, 1567, 1465, 1449, 1306, 1252, 1212, 1137, 1034, 915, 863, 747  $\text{cm}^{-1}$ . MS (%)  $m/e$  218 ( $\text{M}^+$ , 84.62), 183 (100.00), 155 (81.27), 128 (42.57), 115 (38.45), 102 (16.57), 91 (17.82), 76 (42.16), 51 (35.02). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OCl}$ : 218.0498, found: 218.0493.



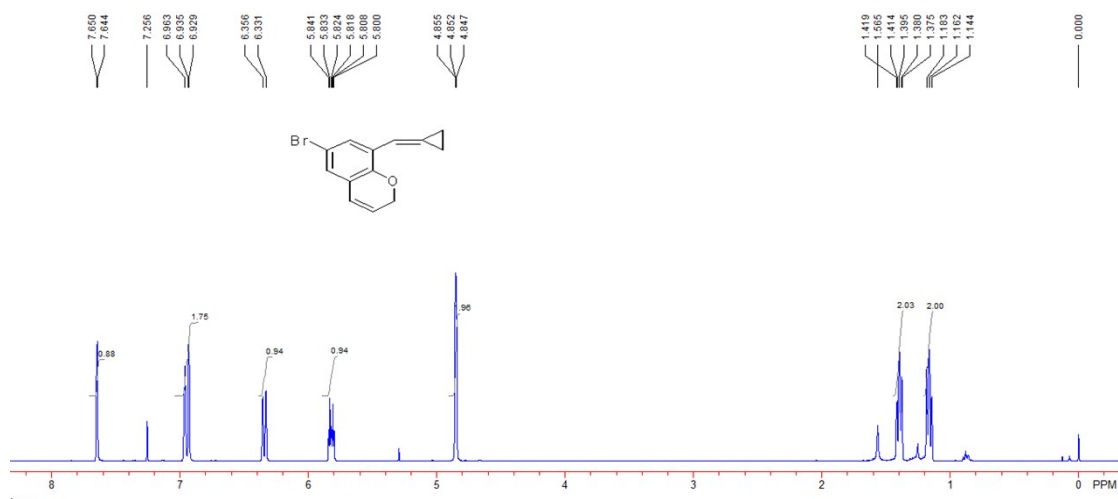


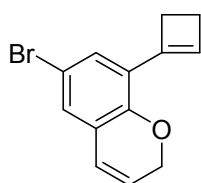
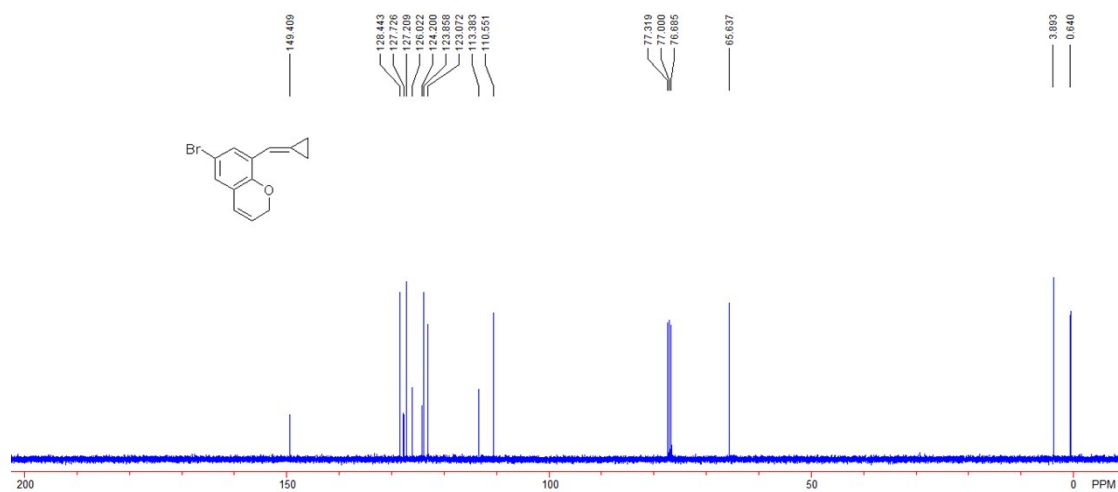
Compound **1f**. 857 mg, yield: 35%; white solid. MP: 91-92 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.16-1.20 (m, 2H, CH<sub>2</sub>), 1.40-1.44 (m, 2H, CH<sub>2</sub>), 2.52 (t, *J* = 2.0 Hz, 1H, CH), 4.70 (d, *J* = 2.0 Hz, 2H, CH<sub>2</sub>), 6.87 (d, *J* = 8.4 Hz, 1H, Ar), 7.05 (d, *J* = 2.0 Hz, 1H, =CH), 7.27 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, Ar), 7.84 (d, *J* = 2.4 Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) 0.7, 3.9, 56.5, 75.8, 78.3, 110.9, 114.4, 114.5, 126.5, 129.3, 129.9, 130.0, 153.1. IR (neat) ν 3292, 3075, 2953, 2868, 2122, 1769, 1734, 1589, 1481, 1373, 1222, 1114, 1021, 926, 801 cm<sup>-1</sup>. MS (%) *m/e* 262 (M<sup>+</sup>, 1.93), 223 (45.97), 183 (17.12), 168 (27.21), 155 (11.12), 144 (46.22), 115 (100.00), 89 (17.12), 51 (9.52). HRMS (EI) calcd. for C<sub>13</sub>H<sub>11</sub>OBr: 261.9993, found: 261.9999.



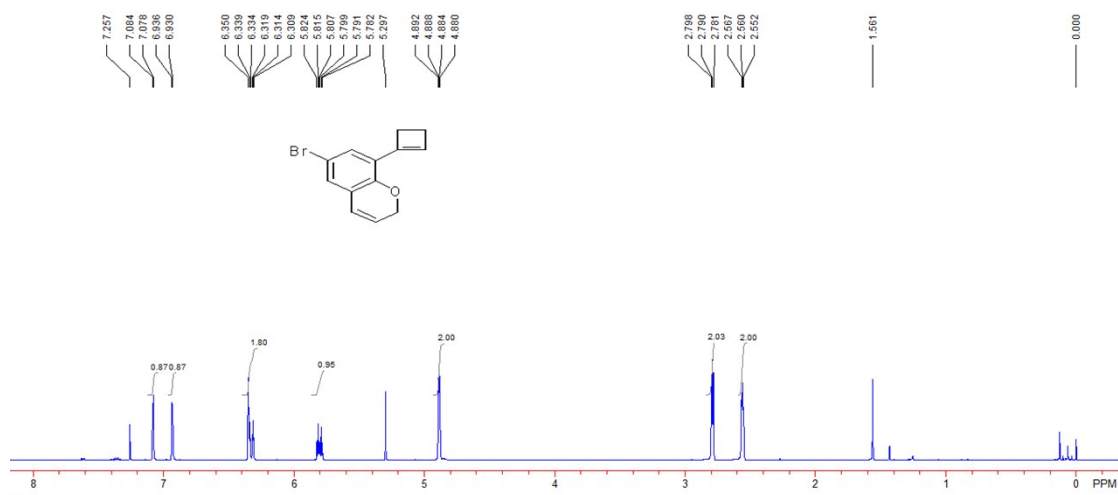


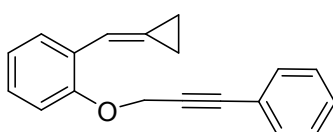
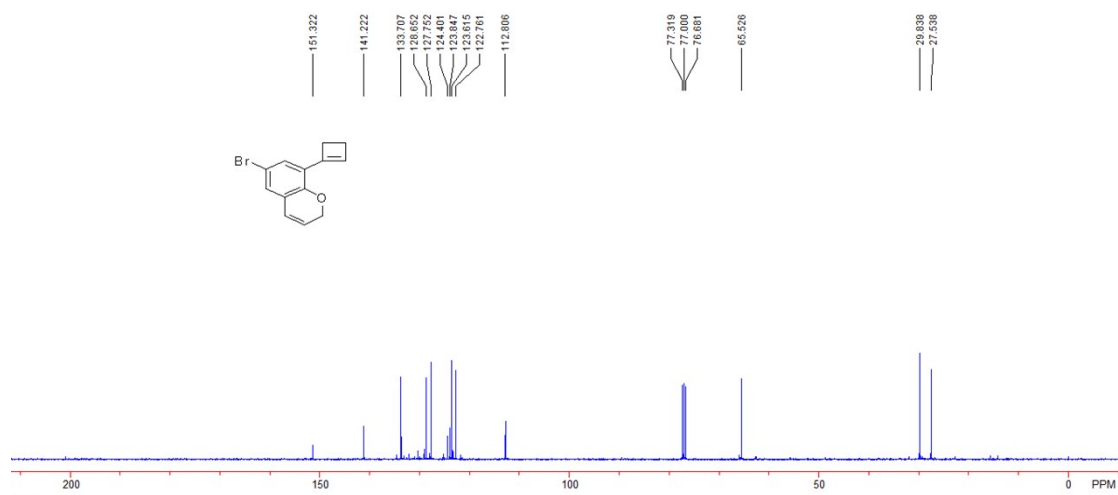
Compound **2f**. 34 mg, yield: 64%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.14-1.18 (m, 2H,  $\text{CH}_2$ ), 1.38-1.42 (m, 2H,  $\text{CH}_2$ ), 4.84-4.85 (m, 2H,  $\text{CH}_2$ ), 5.82 (dt,  $J_1 = 9.6$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.34 (d,  $J = 9.6$  Hz, 1H, =CH), 6.93-6.96 (m, 2H, =CH, Ar), 7.65 (d,  $J = 2.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 65.6, 110.6, 113.4, 123.1, 123.9, 124.2, 126.0, 127.2, 127.7, 128.4, 149.4. IR (neat)  $\nu$  2922, 2850, 1780, 1640, 1570, 1463, 1449, 1421, 1254, 1201, 1070, 935, 840, 769, 694  $\text{cm}^{-1}$ . MS (%)  $m/e$  262 ( $\text{M}^+$ , 8.42), 183 (100.00), 153 (27.53), 128 (20.86), 115 (22.92), 102 (5.52), 91 (17.80), 77 (16.03), 51 (10.50). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OBr}$ : 221.9993, found: 261.9991.



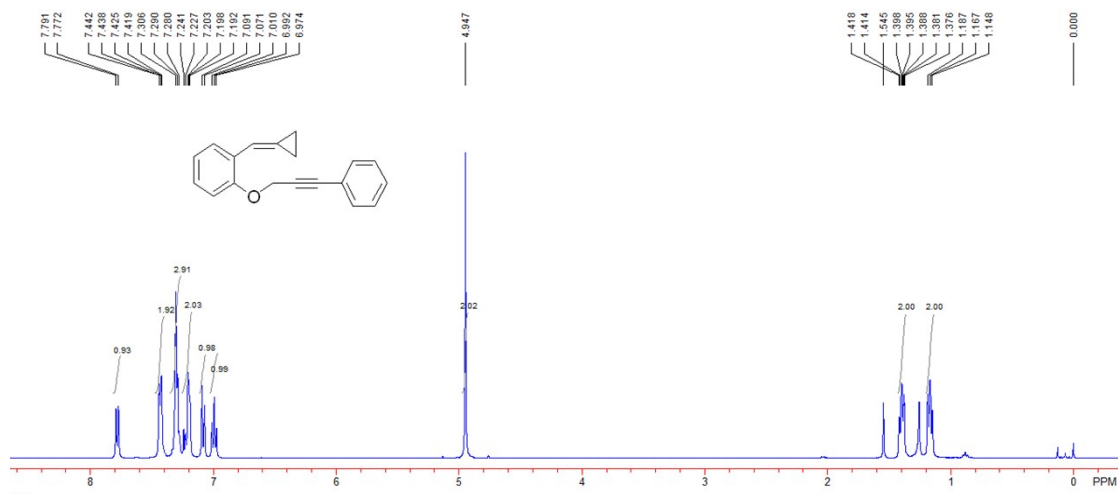


Compound **3f**. 34 mg, yield: 64%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.55-2.57 (m, 2H, CH<sub>2</sub>), 2.78-2.80 (m, 2H, CH<sub>2</sub>), 4.89 (dd, *J*<sub>1</sub> = 3.6 Hz, *J*<sub>2</sub> = 2.0 Hz, 2H, CH<sub>2</sub>), 5.80 (dt, *J*<sub>1</sub> = 10.0 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H, =CH), 6.32 (dt, *J*<sub>1</sub> = 10.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H, =CH), 6.35 (s, 1H, =CH), 6.93 (d, *J* = 2.4 Hz, 1H, Ar), 7.08 (d, *J* = 2.4 Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 27.5, 29.8, 65.5, 112.8, 122.8, 123.6, 123.8, 124.4, 127.8, 128.7, 133.7, 141.2, 151.3. IR (neat) ν 2954, 2925, 2853, 1713, 1587, 1443, 1381, 1211, 1111, 1073, 995, 908, 883, 732, 637 cm<sup>-1</sup>. MS (%) *m/e* 262 (M<sup>+</sup>, 44.32), 183 (100.00), 155 (89.61), 128 (53.10), 115 (46.63), 102 (19.59), 91 (22.32), 77 (38.56), 51 (33.08). HRMS (EI) calcd. for C<sub>13</sub>H<sub>11</sub>OBr: 261.9993, found: 291.9990.

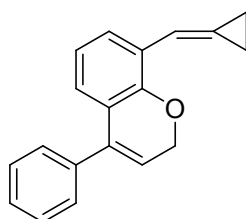
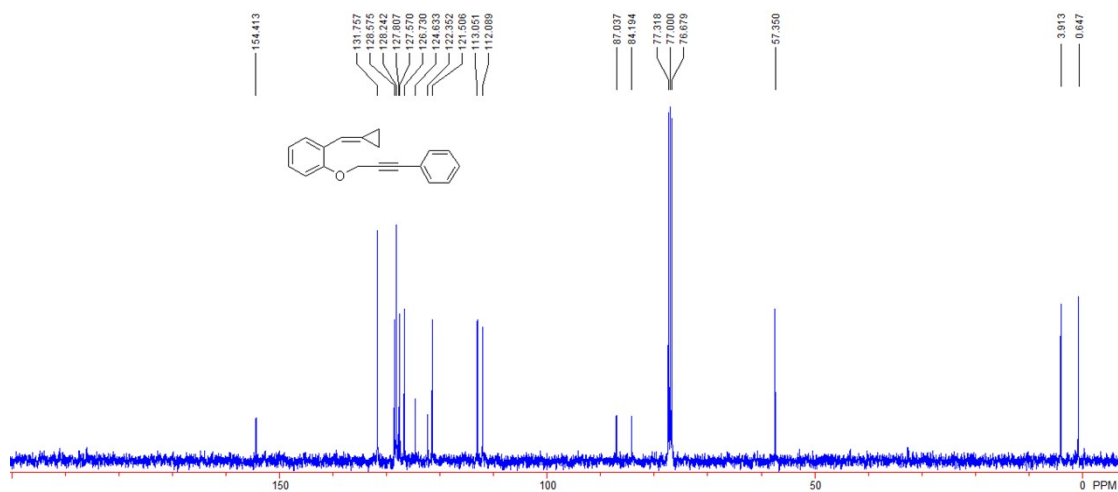




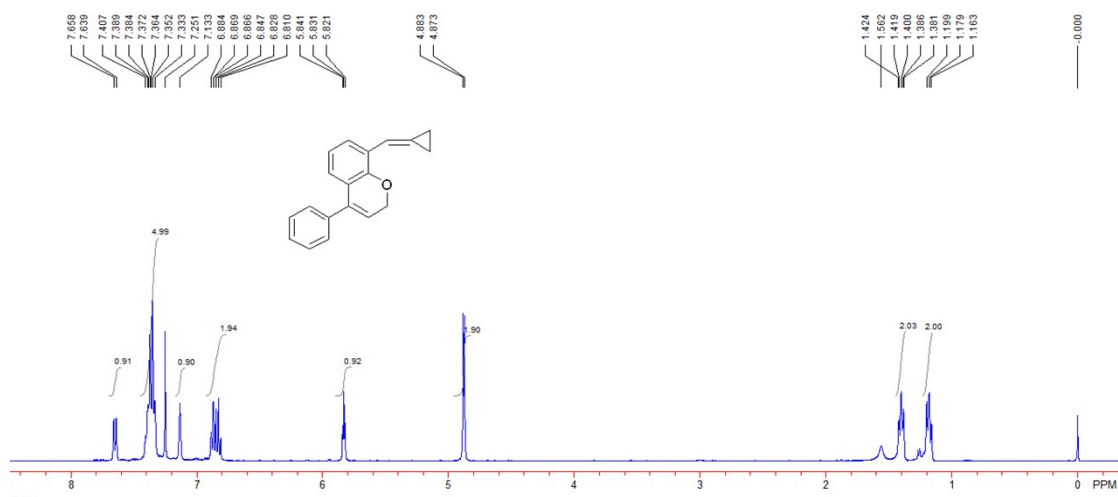
Compound **1g**. 1.208 g, yield: 43%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 1.15-1.19 (m, 2H, CH<sub>2</sub>), 1.38-1.42 (m, 2H, CH<sub>2</sub>), 4.95 (s, 2H, CH<sub>2</sub>), 7.00 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H, Ar), 7.08 (d, *J* = 8.0 Hz, 1H, Ar), 7.09-7.20 (m, 2H, =CH, Ar), 7.28-7.31 (m, 3H, Ar), 7.43 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 2.4 Hz, 2H, Ar), 7.78 (d, *J* = 7.6 Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 0.6, 3.9, 57.4, 84.2, 87.0, 112.1, 113.1, 121.5, 122.4, 124.6, 126.7, 127.6, 127.8, 128.2, 128.6, 131.8, 154.4. IR (neat) ν 3062, 2921, 2856, 2238, 1773, 1744, 1597, 1488, 1370, 1261, 1221, 1188, 1017, 908, 751 cm<sup>-1</sup>. MS (%) *m/e* 260 (M<sup>+</sup>, 100.00), 245 (9.54), 231 (17.09), 165 (8.76), 153 (10.29), 131 (33.01), 115 (17.35), 91 (9.03), 51 (5.37). HRMS (EI) calcd. for C<sub>19</sub>H<sub>16</sub>O: 260.1021, found: 260.1023.

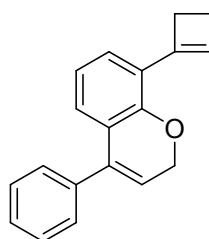
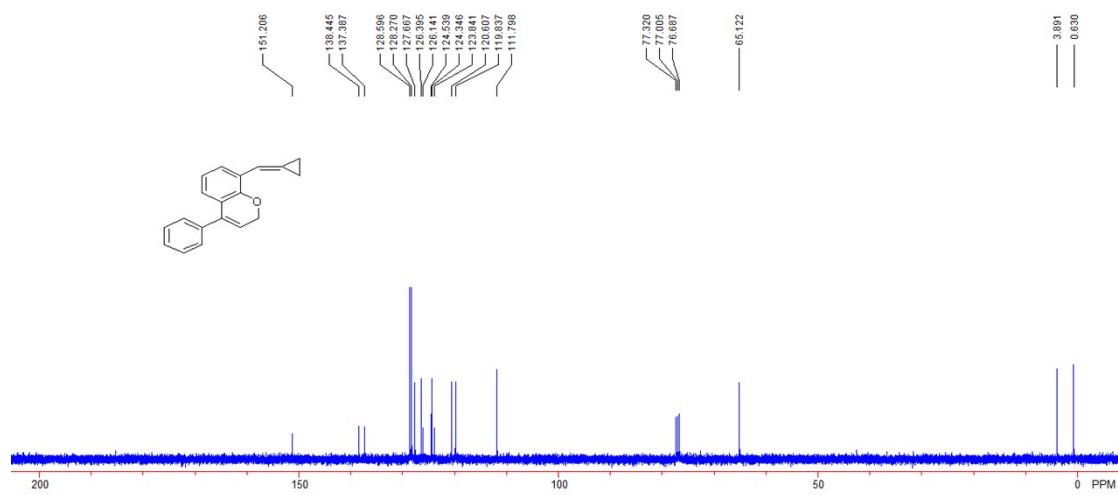




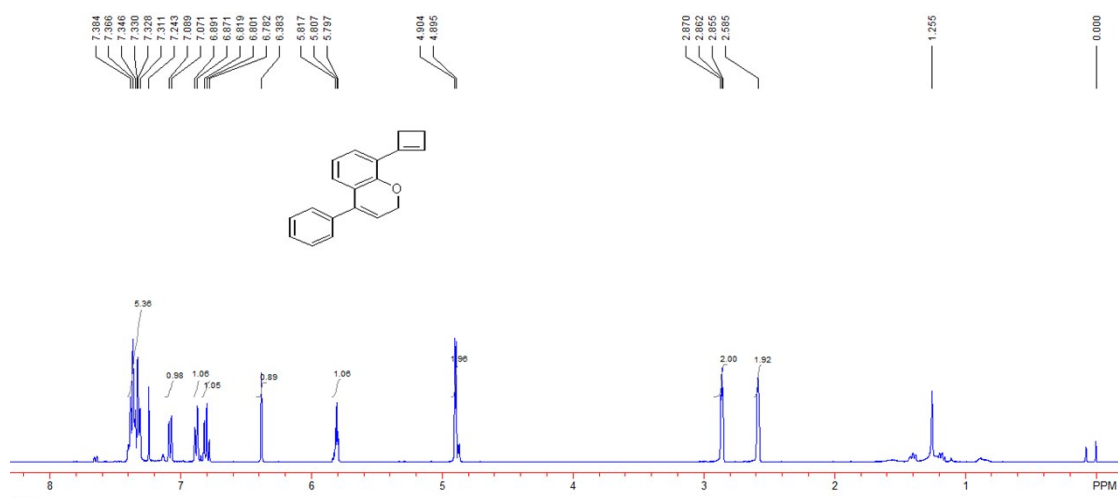


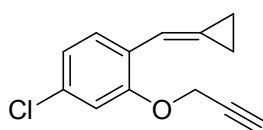
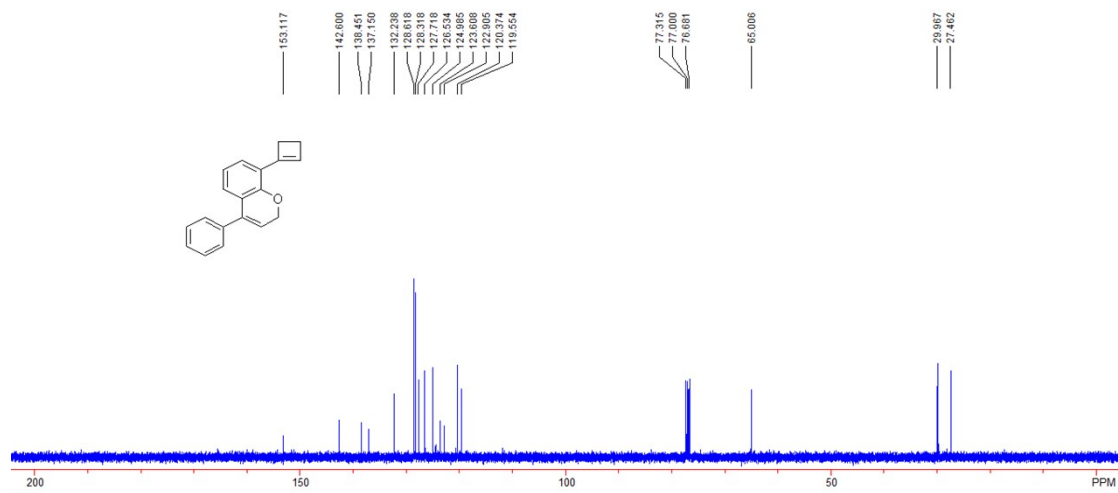
Compound **2g**. 44 mg, yield: 83%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.16-1.20 (m, 2H,  $\text{CH}_2$ ), 1.38-1.42 (m, 2H,  $\text{CH}_2$ ), 4.88 (d,  $J = 4.0$  Hz, 2H,  $\text{CH}_2$ ), 5.82 (t,  $J = 4.0$  Hz, 1H, =CH), 6.81-6.88 (m, 2H, Ar), 7.13 (s, 1H, =CH), 7.33-7.41 (m, 5H, Ar), 7.65 (d,  $J = 7.2$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 65.1, 111.8, 119.8, 120.6, 123.8, 124.3, 124.5, 126.1, 126.4, 127.7, 128.3, 128.6, 137.4, 138.4, 151.2. IR (neat)  $\nu$  3051, 2973, 2918, 1837, 1777, 1634, 1589, 1493, 1460, 1354, 1259, 1186, 1020, 820, 761  $\text{cm}^{-1}$ . MS (%)  $m/e$  260 ( $\text{M}^+$ , 100.00), 245 (29.69), 215 (31.71), 202 (29.46), 183 (20.39), 145 (30.79), 128 (18.41), 115 (49.74), 63 (8.44). HRMS (EI) calcd. for  $\text{C}_{19}\text{H}_{16}\text{O}$ : 260.1201, found: 260.1202.



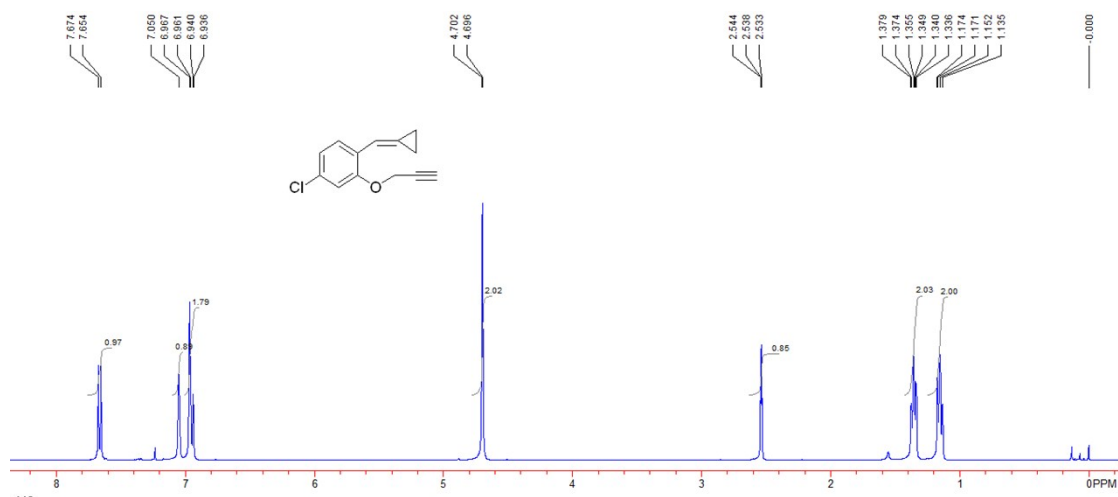


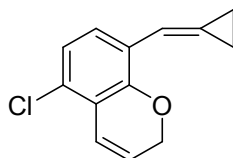
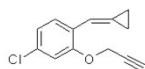
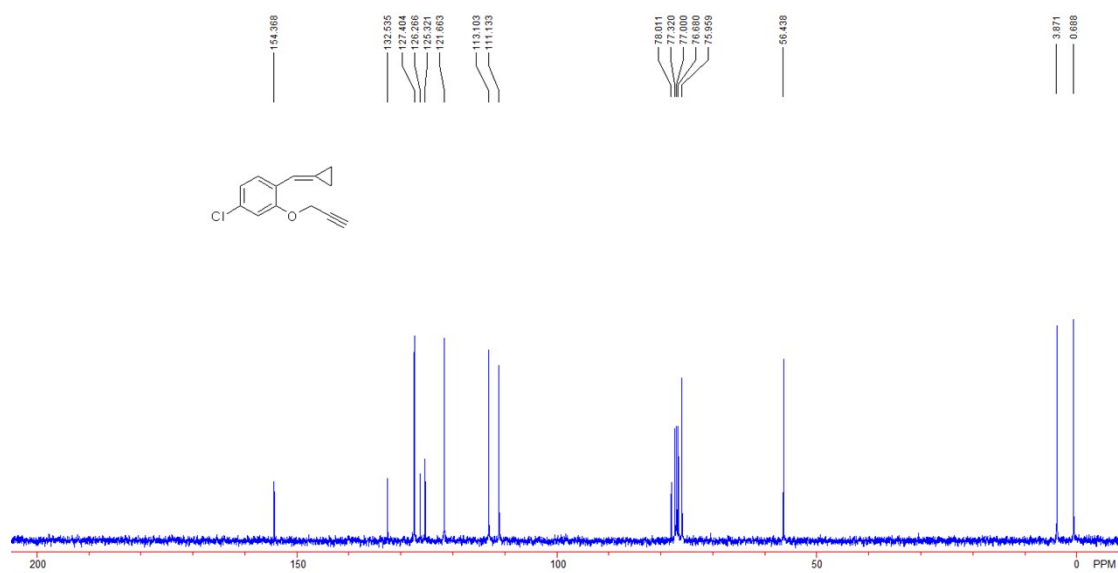
Compound **3g**. 40 mg, yield: 76%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.59 (br s, 2H, CH<sub>2</sub>), 2.86-2.87 (m, 2H, CH<sub>2</sub>), 4.89 (dd, *J*<sub>1</sub> = 10.0 Hz, *J*<sub>2</sub> = 4.0 Hz, 2H, CH<sub>2</sub>), 5.81 (t, *J* = 4.0 Hz, 1H, =CH), 6.38 (s, 1H, =CH), 6.78-6.82 (m, 1H, Ar), 6.88 (d, *J* = 8.0 Hz, 1H, Ar), 7.08 (d, *J* = 8.0 Hz, 1H, Ar), 7.31-7.33 (m, 2H, Ar), 7.35-7.38 (m, 3H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 27.5, 30.0, 65.0, 119.6, 120.4, 122.9, 123.6, 125.0, 126.5, 127.7, 128.3, 128.6, 132.2, 137.2, 138.5, 142.6, 153.1. IR (neat) ν 3054, 2915, 2834, 1635, 1600, 1461, 1444, 1351, 1227, 1110, 1087, 956, 851, 754, 652 cm<sup>-1</sup>. MS (%) *m/e* 260 (M<sup>+</sup>, 100.00), 245 (30.35), 215 (19.29), 183 (9.42), 152 (9.75), 128 (8.36), 115 (23.76), 77 (8.27), 51 (4.61). HRMS (EI) calcd. for C<sub>19</sub>H<sub>16</sub>O: 260. 1201, found: 260. 1198.



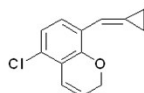
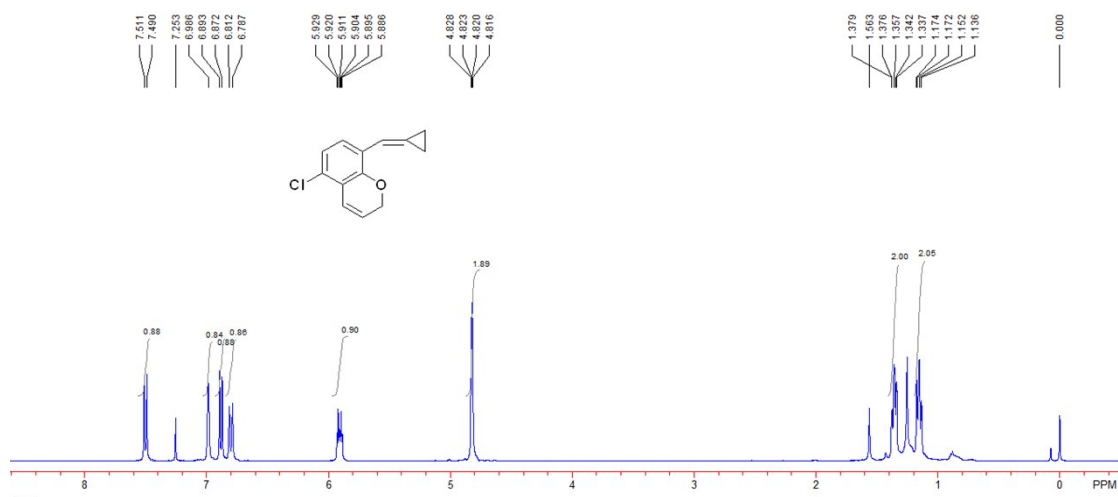


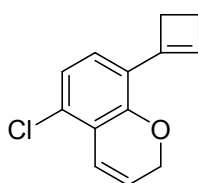
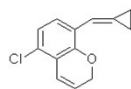
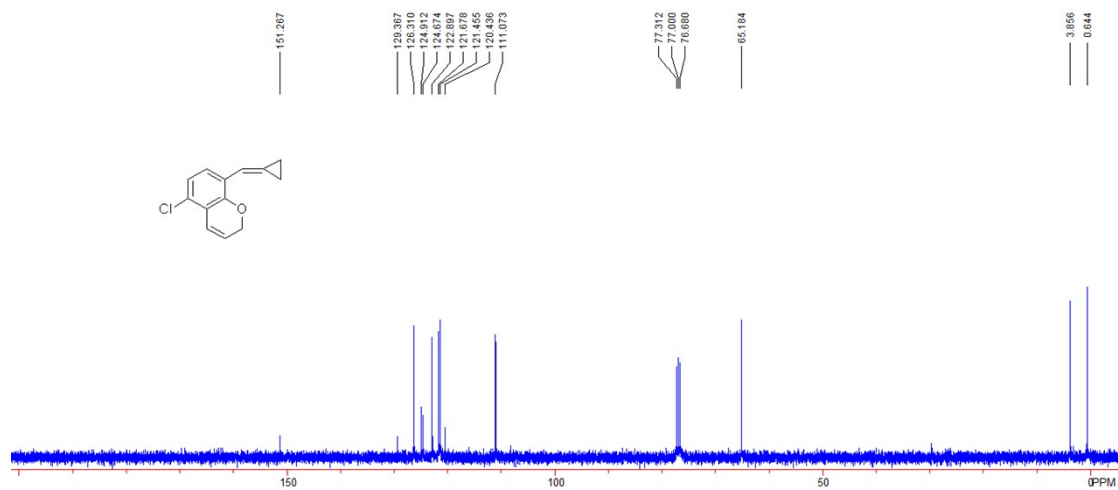
Compound **1h**. 448 mg, yield: 21%; white solid. MP: 72-75 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.14-1.17 (m, 2H,  $\text{CH}_2$ ), 1.34-1.38 (m, 2H,  $\text{CH}_2$ ), 2.54 (t,  $J = 2.4$  Hz, 1H, CH), 4.70 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 6.94-6.97 (m, 2H, Ar), 7.05 (s, 1H, =CH), 7.66 (d,  $J = 8.0$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.7, 3.9, 56.4, 76.0, 78.0, 111.1, 113.1, 121.7, 125.3, 126.3, 127.4, 132.5, 154.4. IR (neat)  $\nu$  3296, 2923, 2853, 2123, 1739, 1591, 1486, 1455, 1376, 1242, 1171, 1096, 1020, 931, 872  $\text{cm}^{-1}$ . MS (%)  $m/e$  218 ( $\text{M}^+$ , 2.56), 183 (20.49), 179 (74.67), 155 (8.26), 144 (21.27), 115 (100.00), 89 (16.21), 75 (14.83), 51 (9.37). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OCl}$ : 218.0498, found: 218.0506.



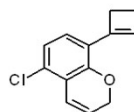
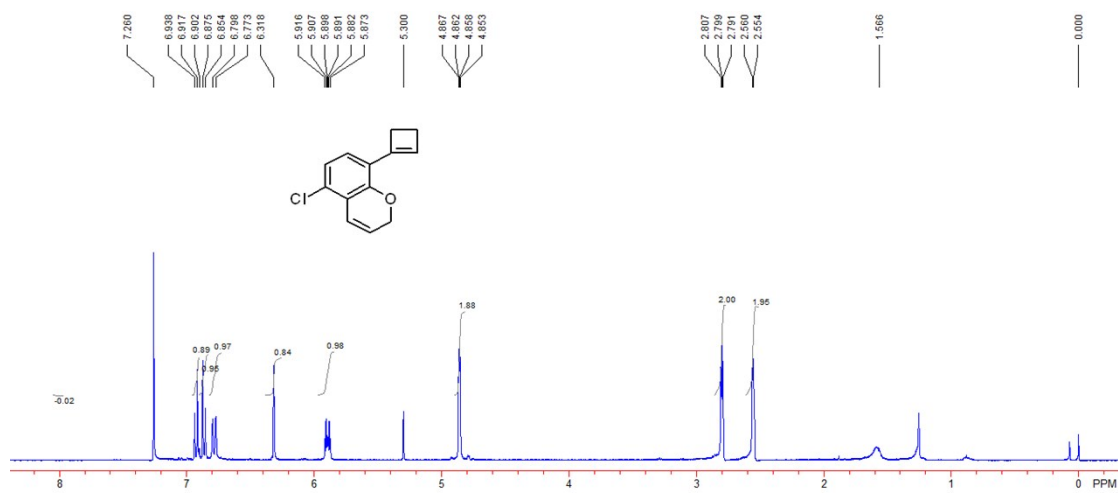


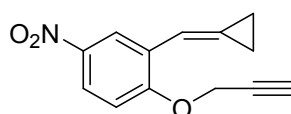
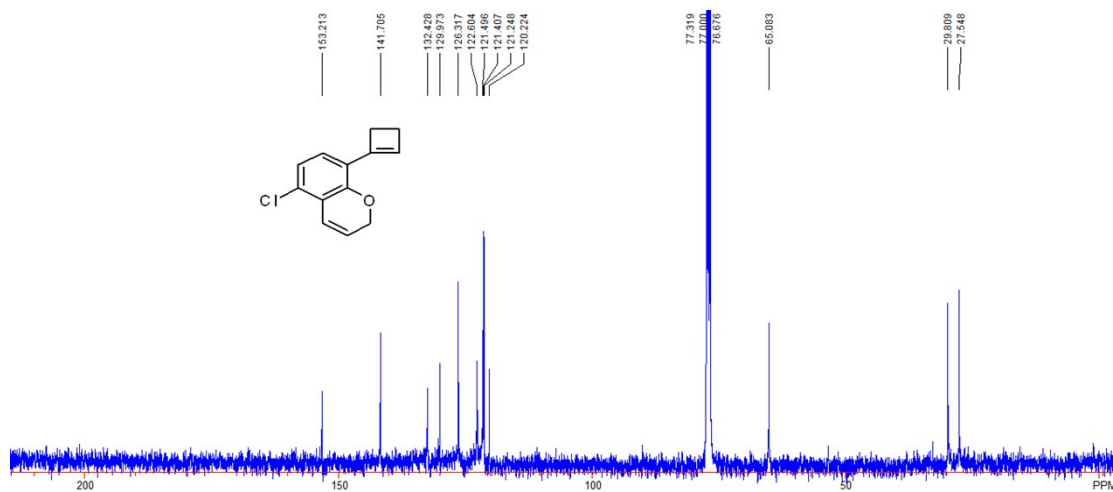
Compound **2h**. 27 mg, yield: 61%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.14-1.18 (m, 2H,  $\text{CH}_2$ ), 1.34-1.38 (m, 2H,  $\text{CH}_2$ ), 4.82 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.6$  Hz, 2H,  $\text{CH}_2$ ), 5.91 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H,  $=\text{CH}$ ), 6.80 (d,  $J = 10.0$  Hz, 1H,  $=\text{CH}$ ), 6.88 (d,  $J = 8.4$  Hz, 1H, Ar), 6.99 (s, 1H,  $=\text{CH}$ ), 7.50 (d,  $J = 8.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 65.2, 111.1, 120.4, 121.5, 121.7, 122.9, 124.7, 124.9, 126.3, 129.4, 151.3. IR (neat)  $\nu$  2974, 2839, 1777, 1574, 1466, 1434, 1428, 1382, 1325, 1206, 1149, 1048, 936, 871, 786, 693  $\text{cm}^{-1}$ . MS (%)  $m/e$  218 ( $\text{M}^+$ , 12.96), 183 (100.00), 155 (14.02), 153 (27.29), 128 (15.48), 115 (17.10), 91 (7.33), 77 (11.47), 63 (9.38). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OCl}$ : 218.0498, found: 218.0501.



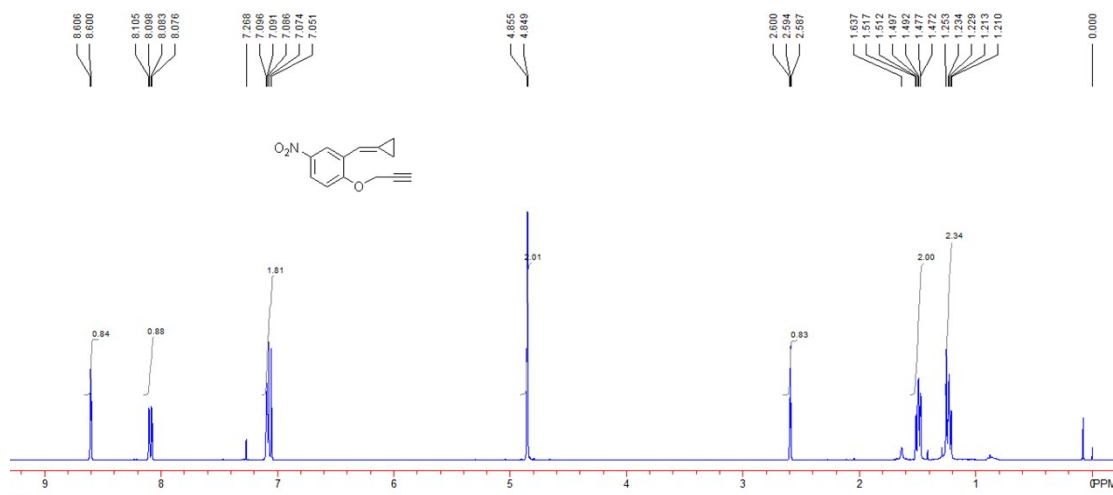


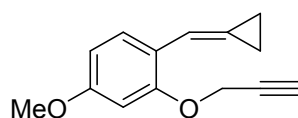
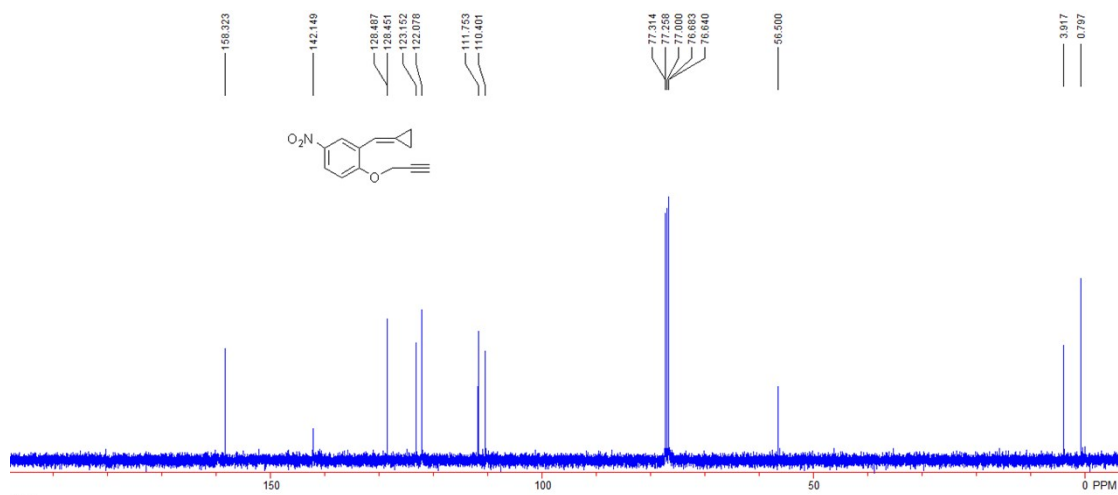
Compound **3h**. 20 mg, yield: 46%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.55-2.56 (m, 2H,  $\text{CH}_2$ ), 2.79-2.81 (m, 2H,  $\text{CH}_2$ ), 4.86 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.89 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.32 (s, 1H, =CH), 6.79 (d,  $J = 10.0$  Hz, 1H, =CH), 6.86 (d,  $J = 8.0$  Hz, 1H, Ar), 6.93 (d,  $J = 8.0$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  27.5, 29.8, 65.1, 120.2, 121.2, 121.4, 121.5, 122.6, 126.3, 130.0, 132.4, 141.7, 153.2. IR (neat)  $\nu$  2920, 2850, 1707, 1673, 1578, 1464, 1426, 1359, 1218, 1149, 1047, 959, 847, 959, 847, 810, 730  $\text{cm}^{-1}$ . MS (%)  $m/e$  218 ( $\text{M}^+$ , 1.90), 183 (15.13), 179 (58.47), 155 (6.15), 144 (17.03), 115 (100.00), 89 (15.73), 75 (13.85), 51 (7.83). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{OCl}$ : 218.0498, found: 218.0501.



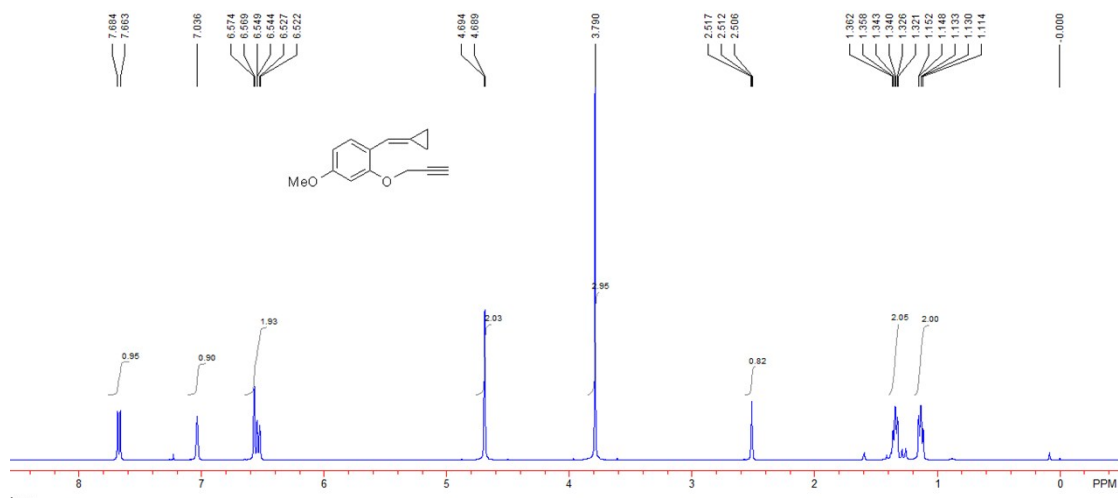


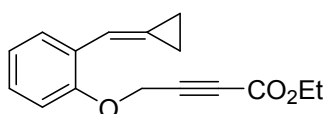
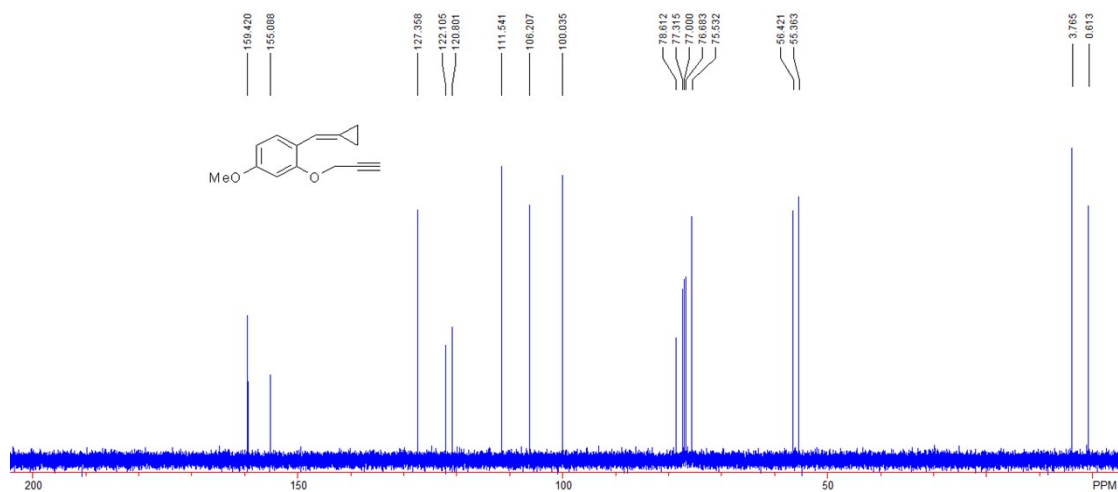
Compound **1i**. 290 mg, yield: 29%; yellow solid. MP: 112-114 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.21-1.25 (m, 2H,  $\text{CH}_2$ ), 1.47-1.52 (m, 2H,  $\text{CH}_2$ ), 2.59 (t,  $J = 2.4$  Hz, 1H, CH), 4.85 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2$ ), 7.06 (d,  $J = 9.2$  Hz, 1H, Ar), 7.09 (t,  $J = 2.0$  Hz, 1H, =CH), 8.09 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.8$  Hz, 1H, Ar), 8.60 (d,  $J = 2.8$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.8, 3.9, 56.5, 76.6, 77.2, 110.4, 111.8, 122.1, 123.2, 128.4, 128.5, 142.2, 158.3. IR (neat)  $\nu$  3285, 3106, 22919, 2135, 1735, 1610, 1578, 1505, 1484, 1335, 1249, 1147, 938, 831, 746  $\text{cm}^{-1}$ . MS (%)  $m/e$  229 ( $\text{M}^+$ , 2.66), 212 (7.70), 190 (29.43), 168 (14.62), 155 (6.62), 144 (32.23), 115 (100.00), 89 (20.81), 77 (11.05). HRMS (EI) calcd. for  $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}$ : 229.0739, found: 229.0736.



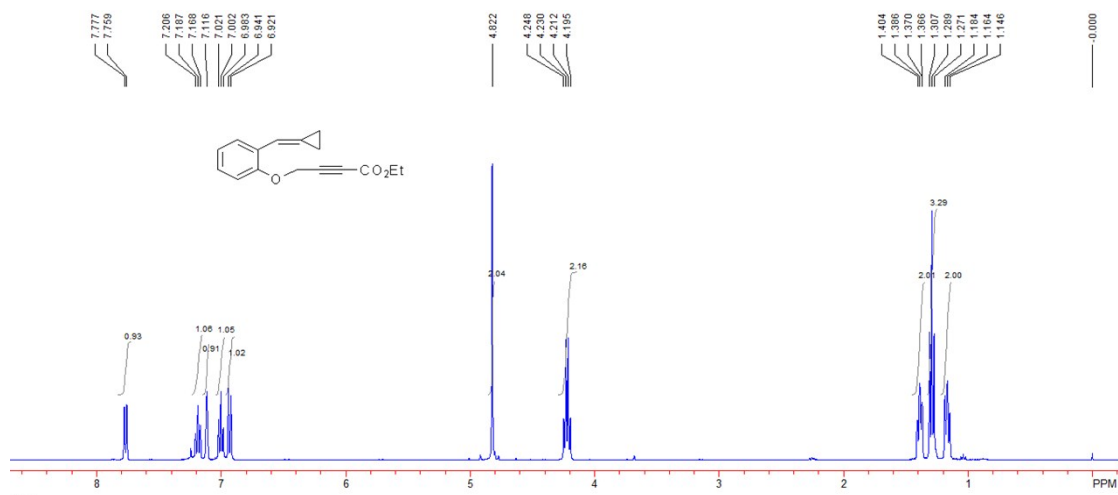


Compound **1j**. 851 mg, yield: 43%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.11-1.15 (m, 2H,  $\text{CH}_2$ ), 1.32-1.36 (m, 2H,  $\text{CH}_2$ ), 2.51 (t,  $J = 2.0$  Hz, 1H, CH), 3.79 (s, 1H,  $\text{CH}_3$ ), 4.69 (d,  $J = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 6.52-6.57 (m, 2H, Ar), 7.04 (s, 1H, =CH), 7.67 (d,  $J = 8.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.8, 55.4, 56.4, 75.5, 78.6, 100.0, 106.2, 111.5, 120.8, 122.1, 127.4, 155.1, 159.4. IR (neat)  $\nu$  3287, 2995, 2970 2836, 2121, 1781, 1607, 1503, 1444, 1256, 1160, 1027, 974, 827, 763  $\text{cm}^{-1}$ . MS (%)  $m/e$  214 ( $\text{M}^+$ , 10.24), 183 (3.96), 175 (100.00), 159 (17.78), 147 (20.52), 132 (20.63), 115 (60.94), 103 (24.14), 77 (26.11). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : 214.0994, found: 214.0985.

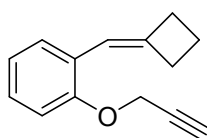
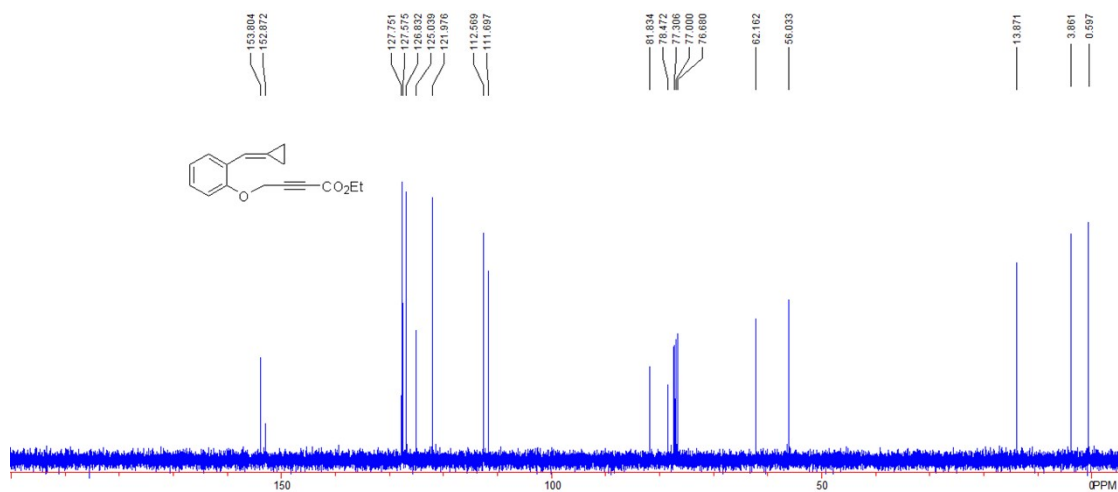




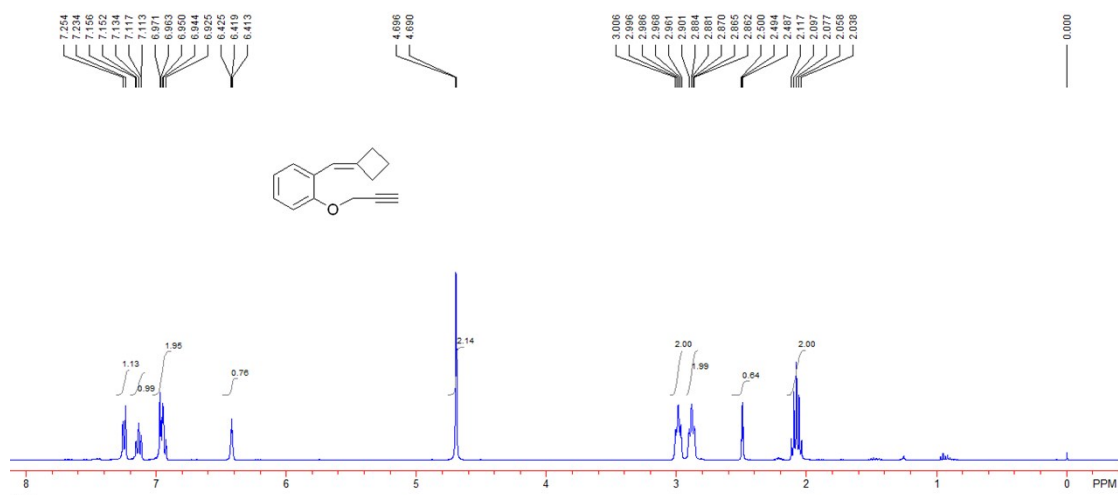
Compound **1k**. 103 mg, yield: 22%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.15-1.19 (m, 2H,  $\text{CH}_2$ ), 1.29 (t,  $J = 6.8$  Hz, 3H,  $\text{CH}_3$ ), 1.37-1.41 (m, 2H,  $\text{CH}_2$ ), 4.20-4.25 (m, 2H,  $\text{CH}_2$ ), 4.82 (s, 2H,  $\text{CH}_2$ ), 6.93 (d,  $J = 8.4$  Hz, 2H, Ar), 7.00 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 7.6$  Hz, 1H, Ar), 7.12 (s, 1H, =CH), 7.19 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 7.6$  Hz, 1H, Ar), 7.77 (d,  $J = 7.6$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS)  $\delta$  0.6, 3.9, 13.9, 56.0, 62.2, 78.5, 81.8, 111.7, 112.6, 122.0, 125.0, 126.8, 127.6, 127.8, 152.9, 153.8. IR (neat)  $\nu$  2977, 2920, 2866, 2242, 1713, 1598, 1489, 1366, 1247, 1115, 1072, 1021, 976, 802, 749  $\text{cm}^{-1}$ . MS (%)  $m/e$  256 ( $\text{M}^+$ , 37.51), 211 (10.64), 183 (100.00), 165 (25.66), 153 (27.24), 128 (23.99), 115 (39.30), 91 (12.72), 77 (18.08). HRMS (EI) calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_3$ : 256.1099, found: 256.1102.

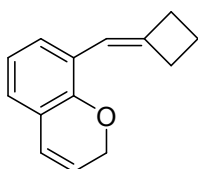
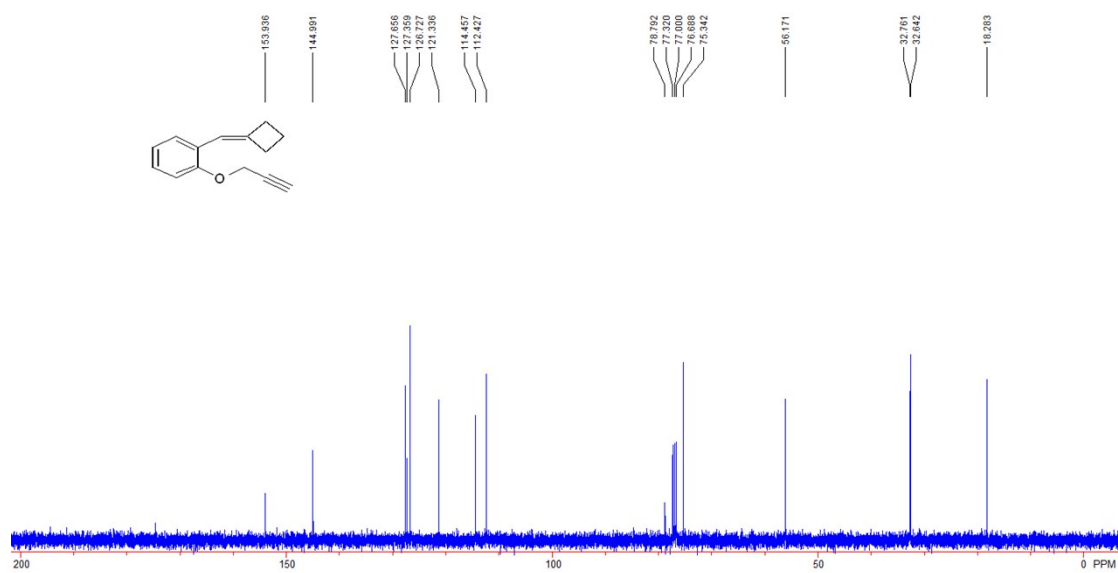




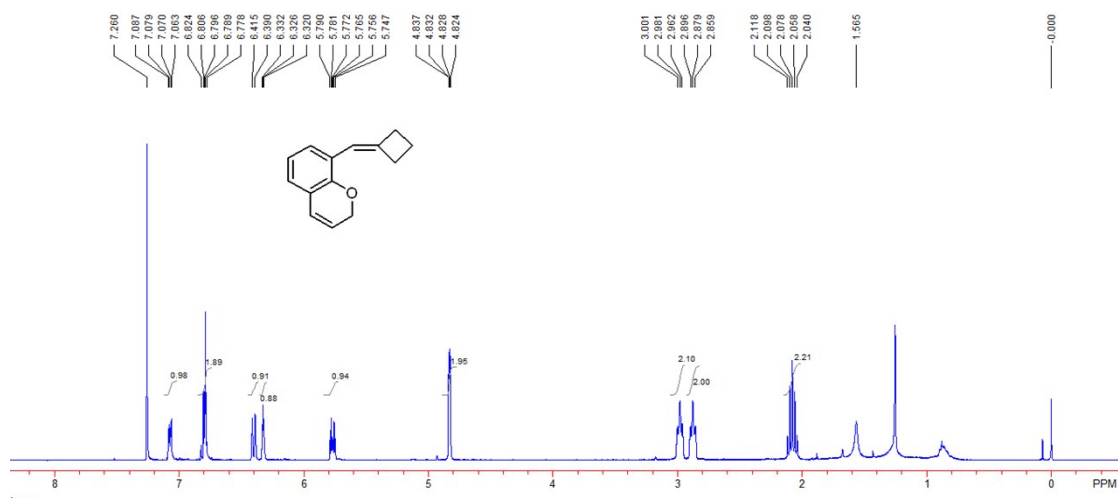


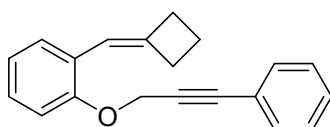
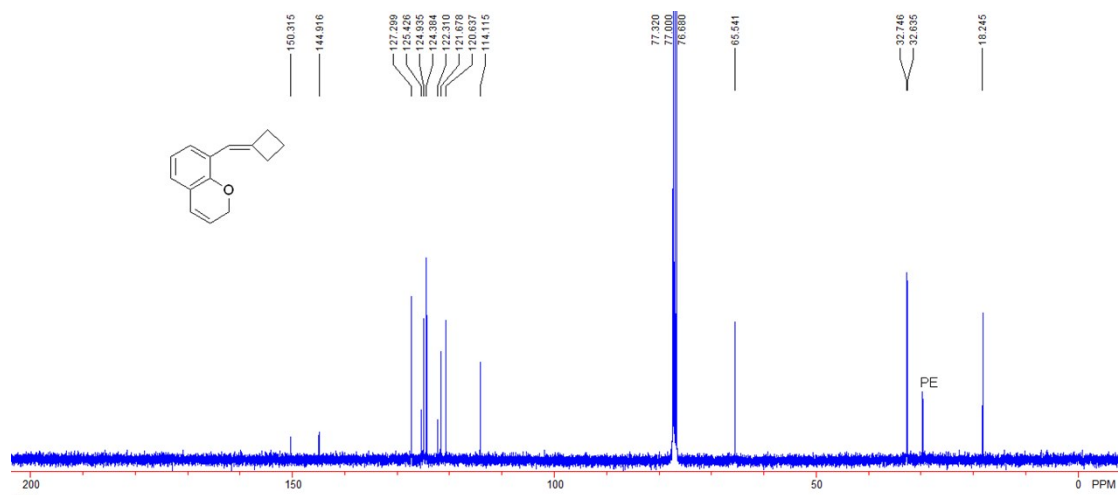
Compound **11**. 560 mg, yield: 92%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.04-2.12 (m, 2H, CH<sub>2</sub>), 2.49 (t, *J* = 2.4 Hz, 1H, CH), 2.86-2.90 (m, 2H, CH<sub>2</sub>), 2.96-3.01 (m, 2H, CH<sub>2</sub>), 4.69 (d, *J* = 2.4 Hz, 2H, CH<sub>2</sub>), 6.42 (t, *J* = 2.4 Hz, 1H, =CH), 6.93-6.97 (m, 2H, Ar), 7.11-7.16 (m, 1H, Ar), 7.24 (d, *J* = 8.0 Hz, 1H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 18.3, 32.6, 32.8, 56.2, 75.3, 78.8, 112.4, 114.5, 121.3, 126.7, 127.4, 127.7, 145.0, 153.9. IR (neat) ν 3289, 2952, 2912, 2122, 1739, 1671, 1597, 1486, 1261, 1191, 1116, 1024, 925, 871, 747 cm<sup>-1</sup>. MS (%) *m/e* 198 (M<sup>+</sup>, 31.67), 183 (11.04), 159 (42.34), 143 (16.52), 131 (100.00), 115 (32.69), 91 (34.47), 77 (46.65), 51 (15.03). HRMS (EI) calcd. for C<sub>14</sub>H<sub>14</sub>O: 198.1045, found: 198.1039.



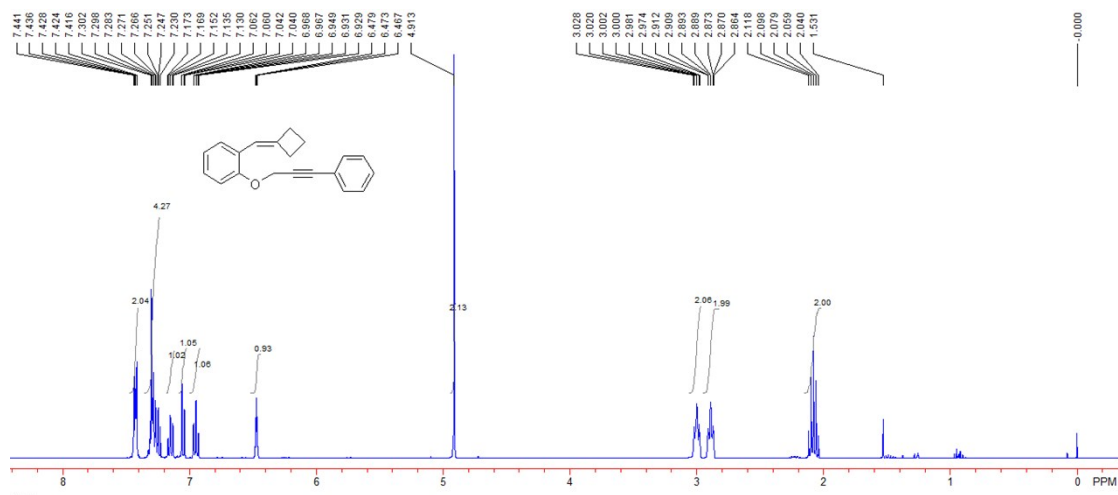


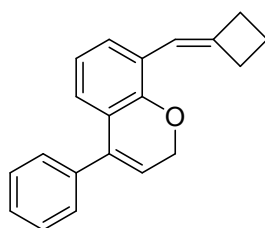
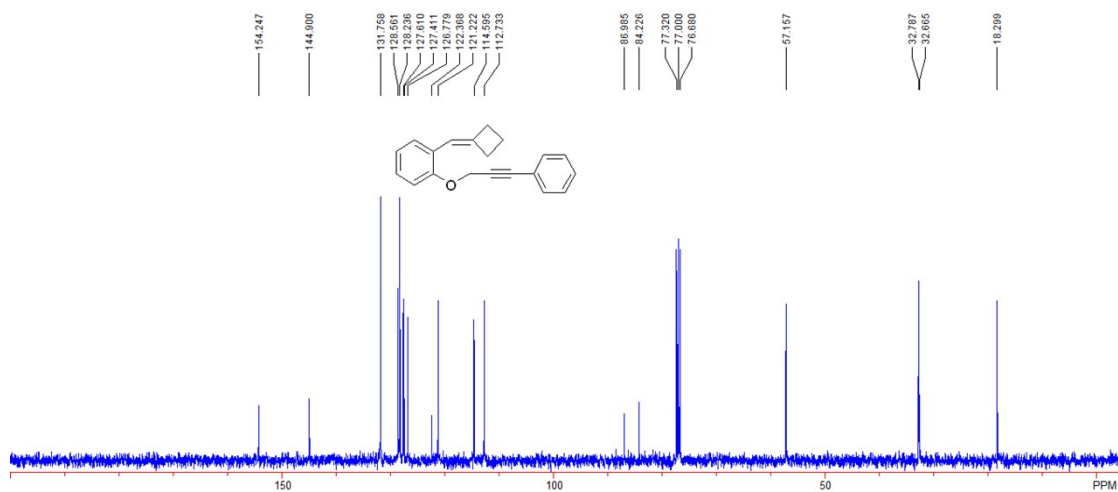
Compound **2i**. 13 mg, yield: 33%; colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS) 2.04-2.12 (m, 2H,  $\text{CH}_2$ ), 2.88 (t,  $J = 7.6$  Hz, 2H, CH), 2.98 (t,  $J = 7.6$  Hz, 2H, CH), 4.83 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 2.0$  Hz, 2H,  $\text{CH}_2$ ), 5.77 (dt,  $J_1 = 10.0$  Hz,  $J_2 = 3.6$  Hz, 1H, =CH), 6.33 (t,  $J = 2.4$  Hz, 1H, =CH), 6.40 (d,  $J = 10.0$  Hz, 1H, =CH), 6.78-6.82 (m, 2H, Ar), 7.07 (dd,  $J_1 = 6.4$  Hz,  $J_2 = 2.4$  Hz, 1H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS) 18.2, 32.6, 32.7, 65.5, 114.1, 120.6, 121.7, 122.3, 124.4, 124.9, 125.4, 127.3, 144.9, 150.3. IR (neat) 3050, 2952, 2924, 2852, 1671, 1639, 1460, 1441, 1260, 1234, 1083, 1028, 953, 849, 747, 692  $\text{cm}^{-1}$ . MS (%)  $m/e$  198 ( $\text{M}^+$ , 100.00), 183 (31.33), 169 (68.07), 155 (32.41), 141 (64.35), 128 (30.11), 115 (73.21), 91 (16.72), 51 (1.95). HRMS (EI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found: 198.1042.



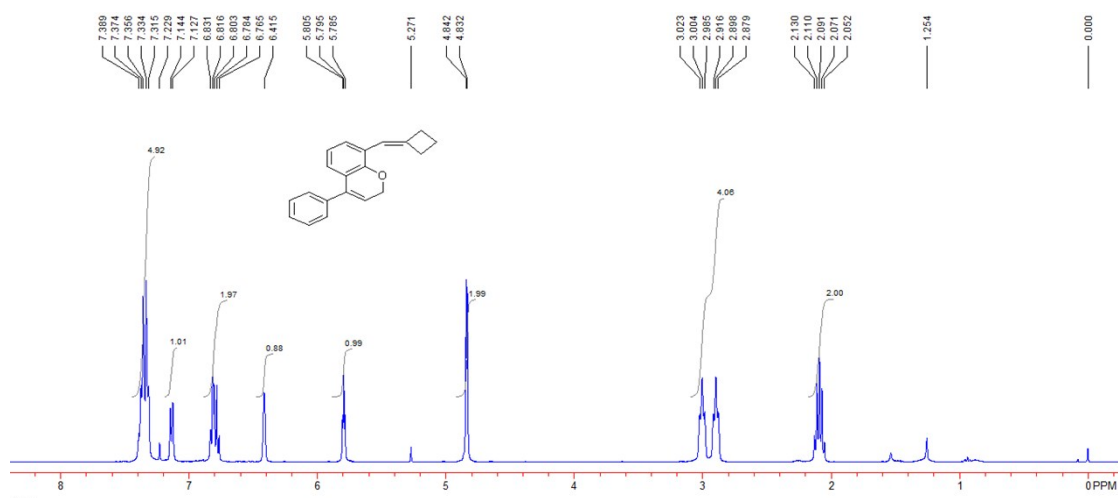


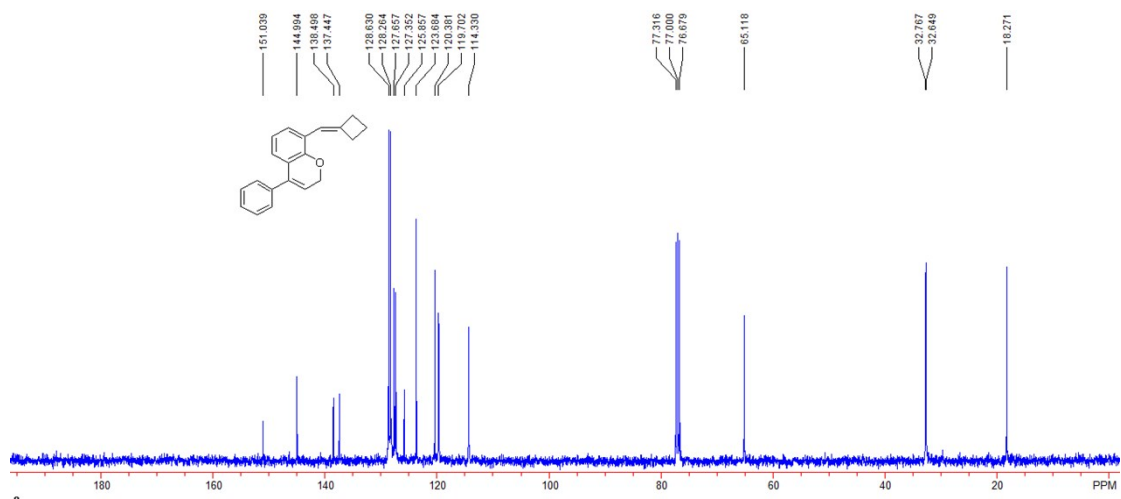
Compound **1m**. 986 mg, yield: 36%; colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS) δ 2.04-2.12 (m, 2H, CH<sub>2</sub>), 2.86-2.91 (m, 2H, CH<sub>2</sub>), 2.97-3.03 (m, 2H, CH<sub>2</sub>), 4.91 (s, 2H, CH<sub>2</sub>), 6.47 (t, *J* = 2.4 Hz, 1H, =CH), 6.93-6.97 (m, 1H, Ar), 7.04-7.06 (m, 1H, Ar), 7.13-7.17 (m, 1H, Ar), 7.25-7.30 (m, 4H, Ar), 7.42-7.44 (m, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 18.3, 32.7, 32.8, 57.2, 84.2, 87.0, 112.7, 114.6, 121.2, 122.4, 126.8, 127.4, 127.6, 128.2, 128.6, 131.8, 144.9, 154.2. IR (neat) ν 3056, 2950, 2856, 2238, 1671, 1596, 1485, 1453, 1373, 1216, 1116, 1030, 999, 871, 747 cm<sup>-1</sup>. MS (%) *m/e* 274 (M<sup>+</sup>, 12.90), 245 (12.83), 215 (3.26), 183 (3.84), 159 (7.38), 131 (28.09), 115 (100.00), 91 (9.27), 77 (11.33). HRMS (EI) calcd. for C<sub>20</sub>H<sub>18</sub>O: 274.1358, found: 274.1345.





Compound **2m**. 44 mg, yield: 80%; white solid. MP: 95-97 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS) 2.05-2.13 (m, 2H,  $\text{CH}_2$ ), 2.90 (t,  $J = 7.6$  Hz, 2H, CH), 3.00 (t,  $J = 7.6$  Hz, 2H, CH), 4.84 (d,  $J = 4.0$  Hz, 2H,  $\text{CH}_2$ ), 5.79 (t,  $J = 4.0$  Hz, 1H, =CH), 6.41 (s, 1H, =CH), 6.77-6.83 (m, 2H, Ar), 7.13 (d,  $J = 6.8$  Hz, 1H, Ar), 7.32-7.39 (m, 5H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, TMS) 18.3, 32.7, 32.8, 65.1, 114.3, 119.7, 120.4, 123.7, 125.9, 127.4, 127.7, 128.3, 128.6, 137.5, 138.5, 145.0, 151.0. IR (neat) 3059, 2951, 2901, 2829, 1671, 1586, 1458, 1438, 1293, 1220, 1187, 1096, 907, 810, 731  $\text{cm}^{-1}$ . MS (%)  $m/e$  274 ( $\text{M}^+$ , 100.00), 245 (26.06), 215 (14.24), 189 (7.13), 165 (5.14), 131 (7.42), 115 (19.49), 91 (5.71), 77 (3.68). HRMS (EI) calcd. for  $\text{C}_{20}\text{H}_{18}\text{O}$ : 274.1358, found: 274.1352.





## 7. References

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