

**Visible Light-Induced Radical Cascade Acylmethylation/Cyclization
of 2-(Allyloxy)arylaldehydes with α -Bromo ketones: Access to Cyclic
1,5-Diketones Containing Chroman-4-one Skeletons**

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1. Experimental section

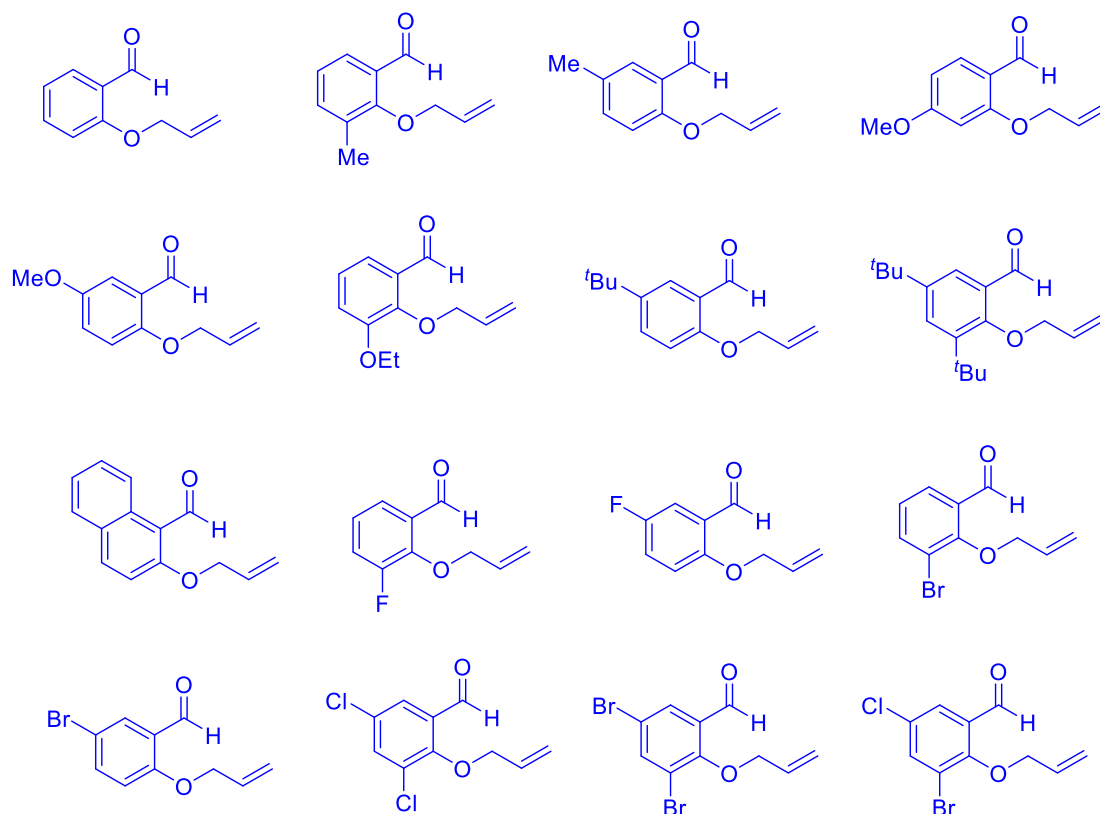
All chemicals were purchased from the Wencai New Material Technology and Merck in high purity and were used directly without any purification. Solvents were freshly distilled prior to use. All reactions were carried out under air atmosphere unless noted. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer in CDCl_3 solution. High-resolution mass (HRMS) spectra were measured with a VG Auto Spec-3000 spectrometer. Melting points (mp) were determined with a digital electrothermal apparatus without further correction. TLC analyses were performed on commercial glass plates bearing a 0.25mm layer of Merck silica gel 60 F254. Silica gel (200-300 mesh) was used for column chromatography.

2. Preparation of starting materials

2-allyloxyarylaldehyde derivatives were prepared according to the reported methods^[1]



To a 50 mL round-bottomed flask with a stir bar was added 2-hydroxyarylaldehyde (5 mmol), DMF (15 mL), then was added potassium carbonate (5.5 mmol), followed by the dropwise addition of allyl bromide (5.5 mmol). The reaction mixture was then stirred for 12 h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over Mg₂SO₄, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired 2-(allyloxy)arylaldehydes.



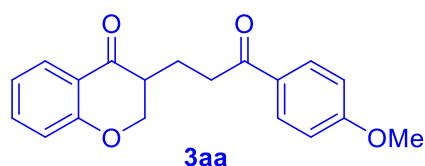
3. General procedure and spectral data of products



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (1.0 equiv., 0.2 mmol), **2a** (1.5 equiv., 0.3 mmol), 4CzIPN (0.05 equiv., 0.01 mmol), TIPA (2.0 equiv., 0.4 mmol) and 2.0 mL DMSO/H₂O (v/v=5:1). The reaction mixture was then stirred under the irradiation with

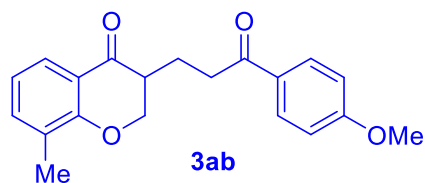
9W blue LEDs for 12 h under Ar atmosphere. Upon completion, quench the reaction with saturated NaCl (10 mL), and the mixture was extracted with dichloromethane (3×15 mL). The combined organic layer was washed three times with H₂O (3×10 mL), dried over anhydrous MgSO₄, and concentrated in vacuo. The crude product was purified by SiO₂ column chromatography to afford the desired products.

3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3aa)^[2]



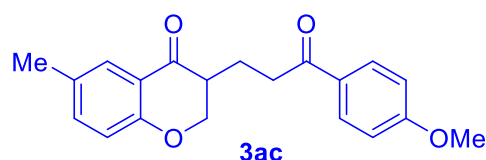
Yellow liquid, yield: 78% (48 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.45 (t, *J* = 8.5 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 14.1, 8.9 Hz, 3H), 4.57 (dd, *J* = 11.4, 4.5 Hz, 1H), 4.32 (dd, *J* = 11.4, 8.9 Hz, 1H), 3.86 (s, 3H), 3.15 (t, *J* = 8.6 Hz, 2H), 2.83-2.77 (m, 1H), 2.23-2.16 (m, 1H), 2.05-1.98 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 194.7, 163.7, 161.6, 136.0, 130.5, 130.0, 127.5, 121.5, 120.7, 117.9, 113.9, 71.1, 55.6, 45.3, 35.7, 21.5.

3-(3-(4-methoxyphenyl)-3-oxopropyl)-8-methylchroman-4-one (3ab)



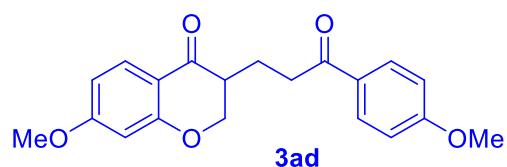
Yellow liquid, yield: 63% (41 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 6.91 (dd, *J* = 14.5, 8.1 Hz, 3H), 4.59 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.33 (dd, *J* = 11.3, 9.0 Hz, 1H), 3.86 (s, 3H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.79-2.74 (m, 1H), 2.22 (s, 3H), 2.20-2.17 (m, 1H), 2.04-1.98 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.1, 195.0, 163.7, 159.9, 136.8, 130.5, 130.0, 127.1, 125.0, 120.9, 120.3, 113.9, 71.0, 55.6, 45.1, 35.7, 21.6, 15.6. HRMS (ESI) [M+H]⁺ Calcd For C₂₀H₂₁O₄: 325.1434, Found: 325.1440.

3-(3-(4-methoxyphenyl)-3-oxopropyl)-6-methylchroman-4-one (3ac)



Yellow liquid, yield: 66% (43 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 1.5 Hz, 1H), 7.27 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.52 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.28 (dd, *J* = 11.3, 8.8 Hz, 1H), 3.85 (s, 3H), 3.18-3.09 (m, 2H), 2.78-2.73 (m, 1H), 2.29 (s, 3H), 2.21-2.14 (m, 1H), 2.03-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0, 194.9, 163.6, 159.6, 137.0, 130.9, 130.4, 130.0, 127.0, 120.2, 117.6, 113.8, 71.1, 55.5, 45.3, 35.7, 21.6, 20.5. HRMS (ESI) [M+H]⁺ Calcd For C₂₀H₂₁O₄: 325.1434, Found: 325.1438.

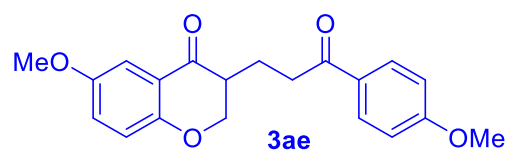
6-methoxy-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ad)



Yellow solid, yield: 68% (46 mg), Mp: 71-73 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 9.6 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.56 (dd, *J* = 8.8, 3.3 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 4.53 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.29 (dd, *J* = 11.0, 8.9 Hz, 1H), 3.79 (t, *J* = 36.0 Hz, 6H), 3.15-3.11 (m, 2H), 2.74-2.68 (m, 1H), 2.20-2.12 (m, 1H), 2.02-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.1, 193.3, 166.0, 163.6, 130.4, 130.0, 129.1, 114.5, 113.8, 110.1,

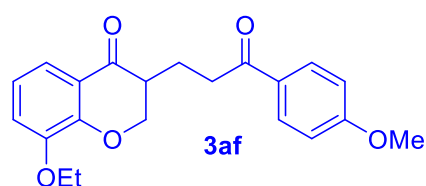
100.7, 71.4, 55.7, 55.6, 44.9, 35.8, 21.7, 5.3. HRMS (ESI) $[M+H]^+$ Calcd For $C_{20}H_{21}O_4$: 325.1434, Found: 325.1441.

6-methoxy-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ae)



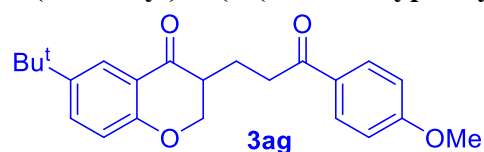
Yellow solid, yield: 68% (46 mg), Mp: 82-84 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, $J = 8.9$ Hz, 2H), 7.30 (d, $J = 3.2$ Hz, 1H), 7.07 (dd, $J = 9.0, 3.2$ Hz, 1H), 6.90 (dd, $J = 18.3, 8.9$ Hz, 3H), 4.51 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.27 (dd, $J = 11.4, 8.8$ Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.17-3.09 (m, 2H), 2.79-2.73 (m, 1H), 2.22-2.15 (m, 1H), 2.04-1.97 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 194.7, 163.7, 156.3, 154.2, 130.4, 130.0, 125.2, 120.4, 119.1, 113.9, 107.8, 71.2, 55.9, 55.6, 45.2, 35.7, 21.6. HRMS (ESI) $[M+H]^+$ Calcd For $C_{20}H_{21}O_5$: 341.1384, Found: 341.1388.

8-ethoxy-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3af)



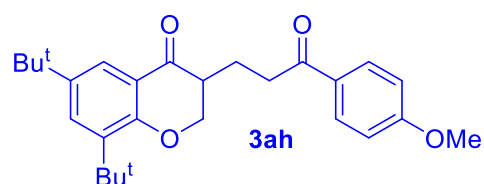
Yellow solid, yield: 63% (44 mg), Mp: 109-111 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.7$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 7.9$ Hz, 1H), 6.93-6.90 (m, 3H), 4.64 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.40 (dd, $J = 11.3, 8.9$ Hz, 1H), 4.09 (q, $J = 7.0$ Hz, 2H), 3.85 (s, 3H), 3.13 (t, $J = 7.2$ Hz, 2H), 2.81-2.76 (m, 1H), 2.23-2.15 (m, 1H), 2.05-1.98 (m, 1H), 1.47 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 194.6, 163.6, 151.8, 148.2, 130.4, 130.0, 121.3, 120.9, 118.5, 118.1, 113.8, 71.5, 64.9, 55.6, 45.1, 35.6, 21.5, 14.8. HRMS (ESI) $[M+H]^+$ Calcd For $C_{21}H_{23}O_5$: 355.1540, Found: 355.1545.

6-(tert-butyl)-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ag)



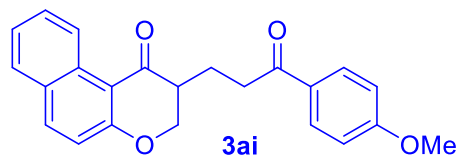
Yellow liquid, yield: 75% (55 mg). 1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 2.5$ Hz, 1H), 7.52 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.91 (dd, $J = 12.9, 8.8$ Hz, 3H), 4.53 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.29 (dd, $J = 11.3, 8.8$ Hz, 1H), 3.86 (s, 3H), 3.18-3.10 (m, 2H), 2.80-2.74 (m, 1H), 2.22-2.15 (m, 1H), 2.05-1.98 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 195.0, 163.7, 159.6, 144.4, 133.7, 130.5, 130.0, 123.3, 119.9, 117.5, 113.9, 71.1, 55.6, 45.4, 35.7, 34.4, 31.4, 21.7. HRMS (ESI) $[M+H]^+$ Calcd For $C_{23}H_{27}O_4$: 367.1904, Found: 367.1908.

6,8-di-tert-butyl-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ah)



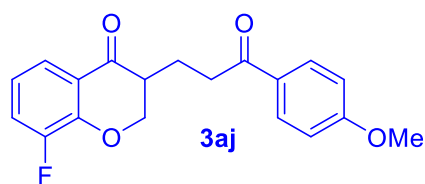
Yellow solid, yield: 64% (43 mg), Mp: 110-112 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.9$ Hz, 2H), 7.80 (d, $J = 2.5$ Hz, 1H), 7.53 (d, $J = 2.5$ Hz, 1H), 6.93 (d, $J = 8.9$ Hz, 2H), 4.57 (dd, $J = 11.3, 4.5$ Hz, 1H), 4.31 (dd, $J = 11.3, 8.9$ Hz, 1H), 3.87 (s, 3H), 3.21-3.14 (m, 2H), 2.80-2.75 (m, 1H), 2.22-2.15 (m, 1H), 2.08-2.01 (m, 1H), 1.39 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 195.6, 163.7, 158.8, 143.4, 138.4, 130.7, 130.5, 131.1, 121.4, 120.7, 113.9, 70.6, 55.6, 45.2, 35.8, 35.2, 34.6, 31.5, 29.8, 21.7. HRMS (ESI) $[M+H]^+$ Calcd For $C_{27}H_{35}O_4$: 423.2530, Found: 423.2537.

2-(3-(4-methoxyphenyl)-3-oxopropyl)-2,3-dihydro-1H-benzo[f]chromen-1-one (3ai)



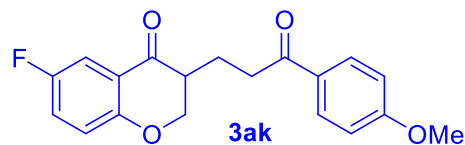
Yellow solid, yield: 43% (31 mg), Mp: 94-95 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.46 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.66 (dd, *J* = 11.3, 4.5 Hz, 1H), 4.43 (dd, *J* = 11.3, 8.5 Hz, 1H), 3.86 (s, 3H), 3.21-3.13 (m, 2H), 2.88-2.83 (m, 1H), 2.29-2.22 (m, 1H), 2.10-2.04 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.1, 195.9, 163.7, 163.5, 137.4, 131.9, 130.5, 130.1, 129.7, 129.4, 128.6, 125.9, 124.9, 118.8, 113.9, 112.0, 71.1, 55.6, 46.0, 35.9, 22.1. HRMS (ESI) [M+H]⁺ Calcd For C₂₃H₂₁O₄: 361.1434, Found: 361.1440.

8-fluoro-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3aj)



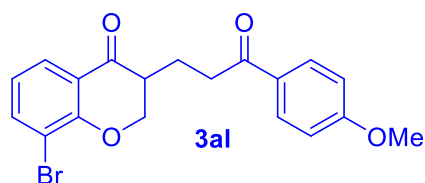
Yellow solid, yield: 61% (40 mg), Mp: 108-110 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.28-7.24 (m, 1H), 6.96-6.91 (m, 3H), 4.66 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.40 (dd, *J* = 11.4, 9.0 Hz, 1H), 3.86 (s, 3H), 3.18-3.09 (m, 2H), 2.88-2.82 (m, 1H), 2.24-2.17 (m, 1H), 2.05-1.98 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.8, 193.6 (d, *J*_{CF} = 3.0 Hz), 163.7, 152.7, 150.7, 150.0 (d, *J*_{CF} = 11.6 Hz), 130.4 (d, *J*_{CF} = 60.2 Hz), 122.7, 122.5 (d, *J*_{CF} = 3.9 Hz), 121.8, (d, *J*_{CF} = 17.6 Hz), 120.8 (d, *J*_{CF} = 6.4 Hz), 113.9, 71.8, 55.6, 45.3, 35.5, 21.4. ¹⁹F NMR (471 MHz, CDCl₃) δ = -135.5. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₈FO₄: 329.1184, Found: 329.1189.

6-fluoro-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ak)



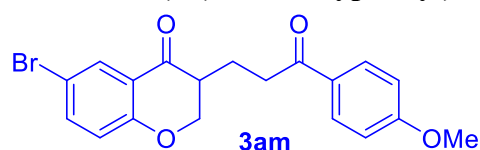
Yellow solid, yield: 62% (40 mg), Mp: 94-96 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.52 (dd, *J* = 8.3, 3.2 Hz, 1H), 7.20-7.16 (m, 1H), 6.95-6.92 (m, 3H), 4.55 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.30 (dd, *J* = 11.5, 9.0 Hz, 1H), 3.86 (s, 3H), 3.19-3.08 (m, 2H), 2.82-2.76 (m, 1H), 2.22-2.15 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.9, 193.7 (d, *J*_{CF} = 1.5 Hz), 163.7, 158.4, 157.9 (d, *J*_{CF} = 1.5 Hz), 156.4, 130.5, 130.0, 123.6 (d, *J*_{CF} = 24.6 Hz), 121.1 (d, *J*_{CF} = 6.3 Hz), 119.5 (d, *J*_{CF} = 7.3 Hz), 113.9, 112.4 (d, *J*_{CF} = 23.3 Hz), 71.3, 55.6, 35.6, 21.4. ¹⁹F NMR (471 MHz, CDCl₃) δ = -121.5. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₈FO₄: 329.1184, Found: 329.1191.

8-bromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3al)



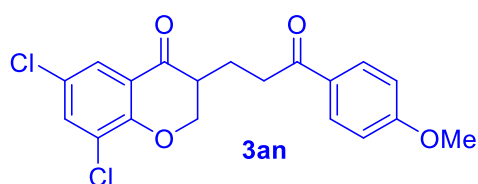
Yellow solid, yield: 62% (55 mg), Mp: 82-84 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.93-6.88 (m, 3H), 4.68 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.41 (dd, *J* = 11.5, 9.2 Hz, 1H), 3.85 (s, 3H), 3.15-3.12 (m, 2H), 2.86-2.81 (m, 1H), 2.24-2.16 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 193.7, 163.7, 157.9, 139.2, 130.4, 129.9, 126.8, 122.2, 121.9, 113.9, 111.5, 71.6, 55.6, 44.8, 35.5, 21.2. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₈BrO₄: 389.0383, Found: 389.03839.

6-bromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3am)



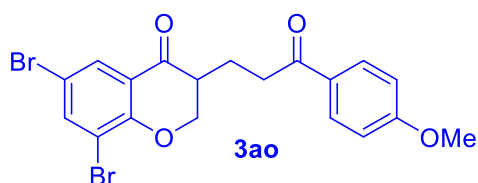
Yellow solid, yield: 49% (38 mg), Mp: 86-88 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 2.4 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.53 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.57 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.31 (dd, *J* = 11.4, 9.0 Hz, 1H), 3.86 (s, 3H), 3.19-3.08 (m, 2H), 2.82-2.77 (m, 1H), 2.21-2.14 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.8, 193.4, 163.7, 160.5, 138.6, 130.5, 129.9, 129.94, 121.90, 120.0, 114.2, 113.9, 71.2, 55.7, 45.0, 35.5, 21.4. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₈BrO₄: 389.0383, Found: 389.0387.

6,8-dichloro-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3an)



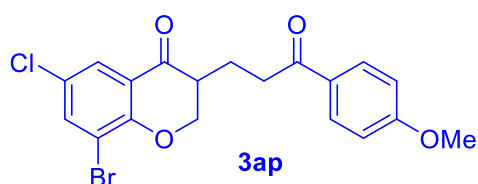
Yellow solid, yield: 42% (32 mg), Mp: 111-113 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.68 (dd, *J* = 11.6, 4.5 Hz, 1H), 4.41 (dd, *J* = 11.3, 9.4 Hz, 1H), 3.86 (s, 3H), 3.17-3.09 (m, 2H), 2.87-2.82 (m, 1H), 2.23-2.15 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.6, 192.6, 163.8, 155.8, 135.5, 130.4, 129.9, 126.7, 125.5, 123.8, 122.2, 113.9, 71.8, 55.6, 44.8, 35.4, 21.2. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₇Cl₂O₄: 379.0498, Found: 379.0506.

6,8-dibromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ao)



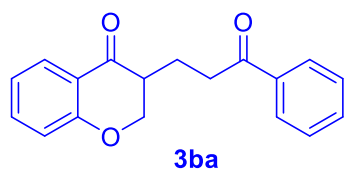
Yellow solid, yield: 37% (35 mg), Mp: 113-115 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.95-7.92 (m, 3H), 7.82 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.68 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.42-4.38 (m, 1H), 3.86 (s, 3H), 3.17-3.09 (m, 2H), 2.87-2.81 (m, 1H), 2.22-2.15 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.5, 192.4, 163.6, 156.9, 140.9, 130.3, 129.7, 129.2, 122.4, 113.9, 113.8, 112.6, 71.6, 55.5, 44.5, 35.2, 21.0. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₇Br₂O₄: 466.9488, Found: 466.9493.

8-bromo-6-chloro-3-(3-(4-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ap)



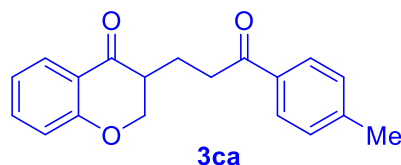
Yellow solid, yield: 51% (43 mg), Mp: 99-101 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 2.6 Hz, 1H), 7.69 (d, *J* = 2.6 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.68 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.40 (dd, *J* = 11.6, 9.2 Hz, 1H), 3.86 (s, 3H), 3.15-3.11 (m, 2H), 2.87-2.81 (m, 1H), 2.23-2.15 (m, 1H), 2.04-1.97 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 197.6, 192.6, 163.8, 156.7, 138.7, 130.4, 129.9, 127.2, 126.3, 122.1, 113.9, 112.4, 71.8, 55.6, 44.7, 35.4, 21.1. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₁₇BrClO₄: 422.9993, Found: 422.9998.

3-(3-oxo-3-phenylpropyl)chroman-4-one (3ba)^[2]



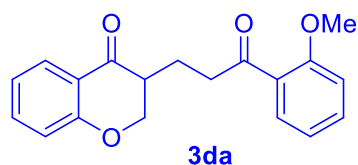
Yellow liquid, yield: 80% (45 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.97 (dd, $J = 8.3, 1.1$ Hz, 2H), 7.88 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.48-7.44 (m, 3H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.32 (dd, $J = 11.4, 8.9$ Hz, 1H), 3.21 (t, $J = 7.6$ Hz, 2H), 2.83-2.78 (m, 1H), 2.25-2.17 (m, 1H), 2.06-1.99 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.4, 194.6, 161.6, 136.9, 136.0, 133.3, 128.7, 128.2, 127.4, 121.5, 120.6, 117.9, 71.1, 45.2, 36.1, 21.3.

3-(3-oxo-3-(p-tolyl)propyl)chroman-4-one (3ca)^[2]



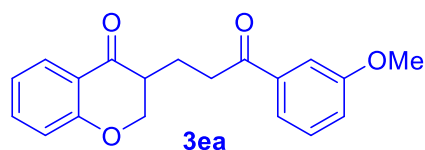
Yellow solid, yield: 77% (46 mg), Mp: 84-86 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.87 (dd, $J = 8.0, 1.0$ Hz, 3H), 7.45 (t, $J = 8.5$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 4.56 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.31 (dd, $J = 11.4, 9.0$ Hz, 1H), 3.17 (t, $J = 7.4$ Hz, 2H), 2.82-2.77 (m, 1H), 2.39 (s, 3H), 2.23-2.16 (m, 1H), 2.04-1.97 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.0, 194.5, 161.6, 144.0, 135.9, 134.5, 129.4, 128.3, 127.4, 121.5, 120.7, 117.9, 71.1, 45.3, 35.9, 21.7, 21.4.

3-(3-(2-methoxyphenyl)-3-oxopropyl)chroman-4-one (3da)



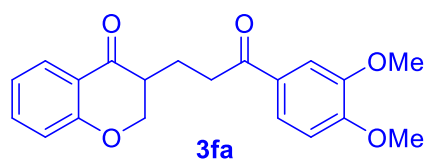
Yellow liquid, yield: 60% (37 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.88 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.68 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.47-7.42 (m, 2H), 7.00-6.97 (m, 2H), 6.94 (dd, $J = 8.3, 3.0$ Hz, 2H), 4.56 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.30 (dd, $J = 11.4, 8.7$ Hz, 1H), 3.86 (s, 3H), 3.17 (t, $J = 7.3$ Hz, 2H), 2.80-2.74 (m, 1H), 2.26-2.19 (m, 1H), 1.99-1.91 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.6, 194.5, 161.6, 158.7, 135.8, 133.6, 130.4, 128.2, 127.4, 121.4, 120.8, 120.7, 117.8, 111.7, 71.0, 55.6, 45.4, 41.2, 21.4. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{19}\text{H}_{19}\text{O}_4$: 311.1278, Found: 311.1282.

3-(3-(3-methoxyphenyl)-3-oxopropyl)chroman-4-one (3ea)



Yellow solid, yield: 64% (40 mg), Mp: 65-67 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.88 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.55 (d, $J = 7.7$ Hz, 1H), 7.49-7.44 (m, 2H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.10 (dd, $J = 8.2, 3.4$ Hz, 1H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 4.56 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.31 (dd, $J = 11.4, 9.0$ Hz, 1H), 3.84 (s, 3H), 3.19 (t, $J = 7.2$ Hz, 2H), 2.82-2.80 (m, 1H), 2.21-2.17 (m, 1H), 2.04-2.01 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.2, 194.5, 161.6, 160.0, 138.2, 136.0, 129.7, 127.4, 121.5, 120.8, 120.6, 119.8, 117.9, 112.4, 71.1, 55.6, 45.2, 36.2, 21.4. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{19}\text{H}_{19}\text{O}_4$: 311.1278, Found: 311.1285.

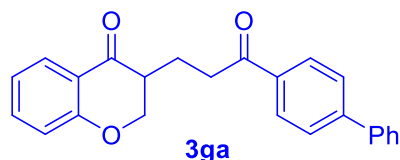
3-(3-(3,4-dimethoxyphenyl)-3-oxopropyl)chroman-4-one (3fa)



Yellow solid, yield: 75% (51 mg), Mp: 111-113 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.60 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.51 (d, $J = 1.9$ Hz, 1H), 7.44 (t, $J = 8.6$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 4.55 (dd, $J = 11.4, 4.6$ Hz, 1H), 4.29 (dd, $J = 11.4, 9.1$ Hz, 1H), 3.91 (d, $J = 3.9$ Hz, 6H), 3.15-3.12 (m, 2H), 2.81-2.78 (m, 1H), 2.28-2.14 (m, 1H),

2.03-2.00 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.0, 194.5, 161.6, 153.4, 149.1, 135.9, 130.1, 127.4, 122.8, 121.4, 120.6, 117.8, 110.3, 110.2, 71.0, 56.12, 55.06, 45.2, 35.6, 21.6. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{20}\text{H}_{21}\text{O}_5$: 341.1384, Found: 341.1388.

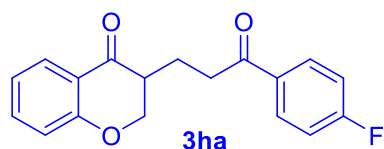
3-(3-([1,1'-biphenyl]-4-yl)-3-oxopropyl)chroman-4-one (3ga)



Yellow solid, yield: 68% (49 mg), Mp: 116-118 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.90 (dd, $J = 7.9$, 1.7 Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 7.7$ Hz, 2H), 7.47 (t, $J = 7.5$ Hz, 3H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.03 (t, $J = 15.0$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 4.59 (dd, $J = 11.4$, 4.5 Hz, 1H),

4.34 (dd, $J = 11.4$, 8.9 Hz, 1H), 3.24 (t, $J = 7.0$ Hz, 2H), 2.85-2.80 (m, 1H), 2.28-2.20 (m, 1H), 2.09-2.06 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.0, 194.6, 161.6, 145.9, 140.0, 136.0, 135.6, 129.1, 128.8, 128.3, 127.5, 127.4, 121.5, 120.7, 117.9, 71.1, 45.2, 36.1, 21.4. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{24}\text{H}_{21}\text{O}_3$: 357.1485, Found: 357.1491.

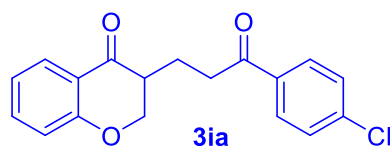
3-(3-(4-fluorophenyl)-3-oxopropyl)chroman-4-one (3ha)^[2]



Yellow liquid, yield: 70% (42 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.99 (dd, $J = 8.8$, 5.4 Hz, 2H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.46 (t, $J = 8.6$ Hz, 1H), 7.12 (t, $J = 8.6$ Hz, 2H), 7.02-6.94 (m, 2H), 4.56 (dd, $J = 11.4$, 4.5 Hz, 1H), 4.31 (dd, $J = 11.4$, 8.9 Hz, 1H), 3.18 (t, $J = 7.3$ Hz, 2H), 2.83-2.74 (m, 1H), 2.22-2.15 (m, 1H), 2.05-1.98

(m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.8, 194.6, 165.9 (d, $J_{\text{CF}} = 254.5$ Hz), 161.6, 136.1, 133.3 (d, $J_{\text{CF}} = 3.0$ Hz), 130.9 (d, $J_{\text{CF}} = 9.5$ Hz), 127.4, 121.6, 120.6, 117.9, 115.9 (d, $J_{\text{CF}} = 21.8$ Hz), 71.1, 45.2, 36.0, 21.4. ^{19}F NMR (471 MHz, CDCl_3) $\delta = -105.1$.

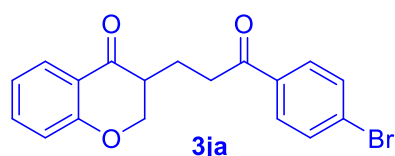
3-(3-(4-chlorophenyl)-3-oxopropyl)chroman-4-one (3ia)



Yellow liquid, yield: 52% (33 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (dd, $J = 16.5$, 8.2 Hz, 3H), 7.44 (dd, $J = 16.3$, 8.8 Hz, 3H), 7.03-6.95 (m, 2H), 4.56 (dd, $J = 11.4$, 4.5 Hz, 1H), 4.31 (dd, $J = 11.4$, 9.0 Hz, 1H), 3.17 (t, $J = 7.2$ Hz, 2H), 2.82-2.76 (m, 1H),

2.22-2.15 (m, 1H), 2.05-1.98 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.2, 194.6, 161.6, 139.7, 136.1, 135.2, 129.6, 129.1, 127.5, 121.6, 120.6, 117.9, 71.1, 45.1, 36.1, 21.4. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{18}\text{H}_{16}\text{ClO}_3$: 315.0782, Found: 315.0786.

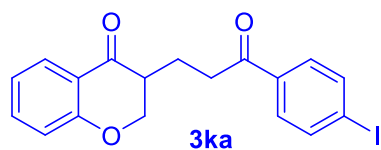
4-(3-(4-bromophenyl)-3-oxopropyl)chroman-4-one (3ja)



Yellow solid, yield: 42% (30 mg), Mp: 58-59 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.87 (dd, $J = 7.9$, 1.7 Hz, 1H), 7.83 (d, $J = 8.6$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 7.48-7.45 (m, 1H), 7.01 (t, $J = 7.9$ Hz, 1H), 6.95 (d, $J = 8.3$ Hz, 1H), 4.56 (dd, $J = 11.4$, 4.5 Hz, 1H), 4.31 (dd, $J = 11.4$, 8.9 Hz, 1H), 3.17 (t, $J = 7.2$ Hz, 2H),

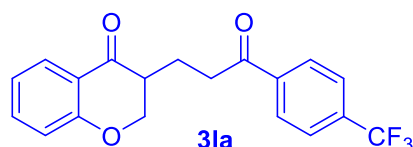
2.85-2.74 (m, 1H), 2.22-2.15 (m, 1H), 2.05-1.98 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.4, 194.6, 161.6, 136.1, 135.6, 132.1, 129.7, 128.5, 127.4, 121.8, 120.6, 117.9, 71.1, 45.1, 36.1, 21.3. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{18}\text{H}_{16}\text{BrO}_3$: 359.0277, Found: 359.0283.

3-(3-(4-iodophenyl)-3-oxopropyl)chroman-4-one (3ka)



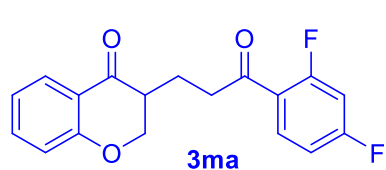
Yellow liquid, yield: 38% (31 mg), $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.87 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.46 (t, $J = 17.0$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 8.2$ Hz, 1H), 4.56 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.31 (dd, $J = 11.4, 8.9$ Hz, 1H), 3.16 (t, $J = 7.2$ Hz, 2H), 2.81-2.79 (m, 1H), 2.22-2.14 (m, 1H), 2.04-1.97 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.7, 194.6, 161.6, 138.1, 136.1, 129.6, 128.7, 128.2, 127.5, 121.6, 120.6, 117.9, 71.1, 45.1, 36.0, 21.3. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{18}\text{H}_{16}\text{IO}_3$: 407.0139, Found: 407.0145.

3-(3-oxo-3-(4-(trifluoromethyl)phenyl)propyl)chroman-4-one (3la)^[2]



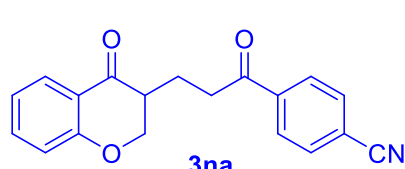
Yellow solid, yield: 40% (28 mg), Mp: 127-129 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.07 (d, $J = 8.1$ Hz, 2H), 7.88 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.47 (t, $J = 8.6$ Hz, 1H), 7.02 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.33 (dd, $J = 11.4, 8.9$ Hz, 1H), 3.24 (t, $J = 7.2$ Hz, 2H), 2.81-2.78 (m, 1H), 2.25-2.17 (m, 1H), 2.08-2.01 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.5, 194.6, 161.6, 139.1, 136.1, 128.6 (d, $J_{\text{CF}} = 8.3$ Hz), 127.5, 125.9 (dq, $J_{\text{CF}} = 11.2$ Hz), 121.6, 120.6, 117.9, 71.1, 45.1, 36.4, 32.9, 21.3. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -63.1$.

3-(3-(2,4-difluorophenyl)-3-oxopropyl)chroman-4-one (3ma)



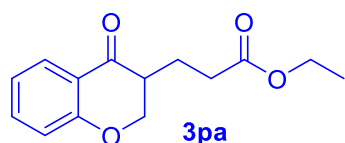
Yellow liquid, yield: 43% (28 mg), $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.93 – 7.90 (m, 1H), 7.87 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.46 (t, $J = 8.6$ Hz, 1H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.97-6.93 (m, 2H), 6.88-6.86 (m, 1H), 4.56 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.31 (dd, $J = 11.4, 8.8$ Hz, 1H), 3.18-3.15 (m, 2H), 2.81-2.76 (m, 1H), 2.26-2.19 (m, 1H), 2.01-1.94 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 196.0$ (d, $J_{\text{CF}} = 4.7$ Hz), 194.4, 167.0 (d, $J_{\text{CF}} = 12.3$ Hz), 165.0 (d, $J_{\text{CF}} = 12.3$ Hz), 164.0 (d, $J_{\text{CF}} = 12.6$ Hz), 161.9 (d, $J_{\text{CF}} = 12.6$ Hz), 161.6, 136.0, 132.8 (dd, $J_{\text{CF}} = 14.9$ Hz), 127.5, 122.2 (dd, $J_{\text{CF}} = 16.8$ Hz), 121.5, 120.7, 117.8, 112.4 (dd, $J_{\text{CF}} = 24.9$ Hz), 105.1 (dd, $J_{\text{CF}} = 53.3$ Hz), 71.0, 45.1, 40.8 (d, $J_{\text{CF}} = 7.6$ Hz), 21.0 (d, $J_{\text{CF}} = 2.5$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -101.7, -104.1$. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_3$: 317.0984, Found: 317.0989.

4-(3-(4-oxochroman-3-yl)propanoyl)benzotrile (3na)



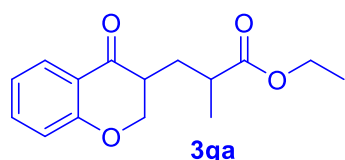
Yellow solid, yield: 33% (20 mg), Mp: 104-106 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.3$ Hz, 2H), 7.88 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.48 (t, $J = 8.5$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 11.4, 4.5$ Hz, 1H), 4.33 (dd, $J = 11.4, 8.8$ Hz, 1H), 3.23 (t, $J = 7.1$ Hz, 2H), 2.80-2.78 (m, 1H), 2.24-2.16 (m, 1H), 2.08-2.01 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.1, 194.6, 161.6, 139.8, 136.2, 132.7, 128.6, 127.5, 121.7, 120.6, 118.0, 117.9, 116.6, 71.1, 45.0, 36.5, 21.3. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{19}\text{H}_{16}\text{NO}_3$: 306.1125, Found: 306.1129.

ethyl 3-(4-oxochroman-3-yl)propanoate (3pa)



Yellow liquid, yield: 74% (37 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.87 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.47-7.44 (m, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 8.3$ Hz, 1H), 4.52 (dd, $J = 11.5, 4.5$ Hz, 1H), 4.26 (dd, $J = 11.4, 8.9$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.76-2.71 (m, 1H), 2.49 (t, $J = 7.5$ Hz, 2H), 2.20-2.13 (m, 1H), 1.86-1.79 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.0, 173.0, 161.5, 136.0, 127.5, 121.6, 120.6, 117.8, 70.7, 60.7, 45.2, 31.8, 22.1, 14.3.

ethyl 2-methyl-3-(4-oxochroman-3-yl)propanoate (3qa)

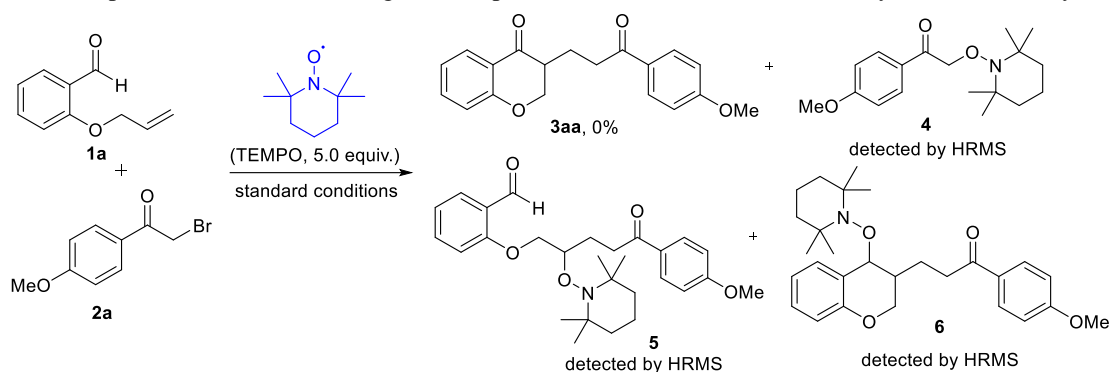


Yellow liquid, yield: 62% (32 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.88 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.48-7.44 (m, 1H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 1H), 4.49 (dd, $J = 11.4, 4.6$ Hz, 1H), 4.23 (dd, $J = 11.4, 9.4$ Hz, 1H), 4.18-4.12 (m, 2H), 2.77-2.66 (m, 2H), 1.98-1.93 (m, 1H), 1.79-1.73 (m, 1H), 1.25 (t, $J = 14.2$ Hz, 3H), 1.21 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.3, 176.3, 161.6, 136.0, 127.6, 121.5, 120.7, 117.8, 71.0, 60.7, 44.3, 38.0, 30.3, 18.1, 14.4.

4. Evidence for a radical pathway

Catalytic reaction interfered with a radical quencher:

An 25 mL oven-dried Schlenk tube was equipped with a stirring bar, 2-(allyloxy)benzaldehyde **1a** (0.2 mmol, 1.0 equiv.), α -bromo ketone **2a** (0.3 mmol, 1.5 equiv.), 4CzIPN (0.01 mmol, 5 mol%), TIPA (0.4 mmol, 2.0 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 5.0 equiv.). The mixture was degassed by using standard Schlenk techniques with an oil pump and DMSO/ H_2O (v:v = 5:1, 2 mL) were injected into the reaction tube. The solution was placed in a distance of 3 cm from 9 W blue LEDs at room temperature for 12 h under argon atmosphere. The solution was used directly for HRMS analysis.



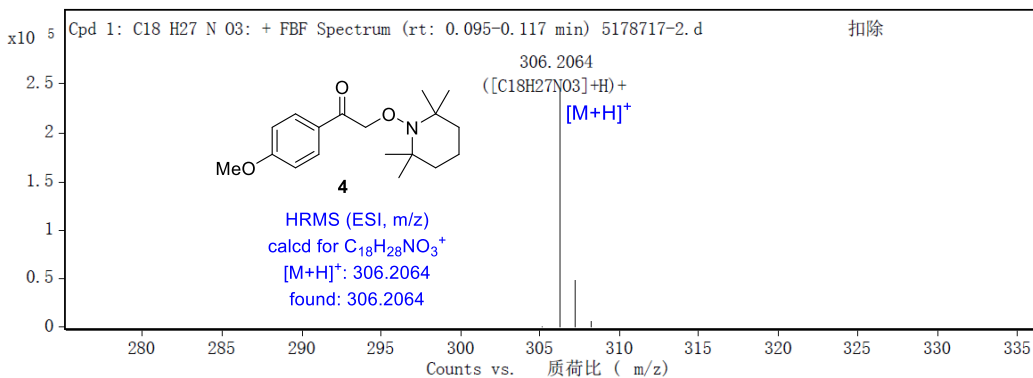
定性化合物报告

数据文件	5178717-2.d	样品名称	5178717-2
样品类型	Sample	位置	P1-C4
仪器名称	Instrument 1	用户名称	
采集方法	POS-1MIN-350-550.m	采集时间	2023-05-23 18:55:02
IRM 校正状态	成功	数据方法	ZNZ-2022.m
注释			
设备类型	QuadrupoleTimeOfFlight	Sample Group	
Info.		Stream Name	LC 1
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)		

化合物列表

化合物标签	RT	质量数	丰度	分子式	目标质量	误差 (ppm)
Cpd 1: C18 H27 N O3	0.075	305.199	244962	C18 H27 N O3	305.1991	-0.15
Cpd 2: C28 H37 N O5	0.086	467.2669	2804	C28 H37 N O5	467.2672	-0.65
Cpd 3: C28 H37 N O4	0.532	451.2693	172	C28 H37 N O4	451.2723	-6.65

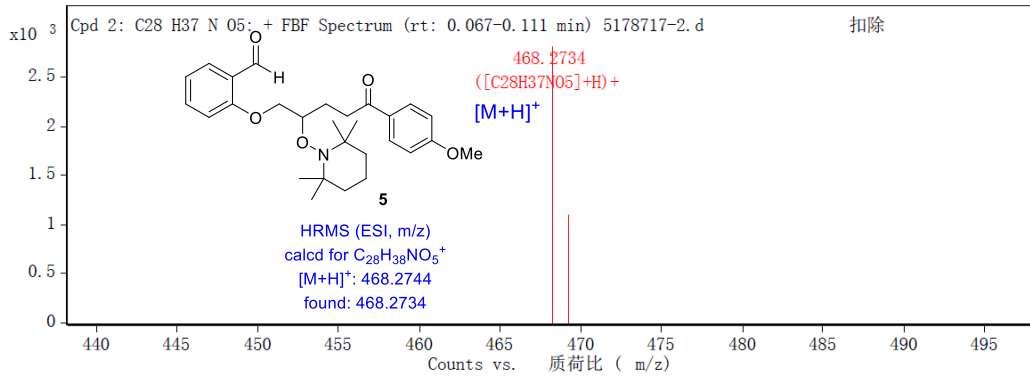
MS 缩放的质谱图



MS 质谱图峰列表

m/z	z	丰度	分子式	离子
305.1904	1	179.2	C18H27NO3	M ⁺
306.2064	1	244961.66	C18H27NO3	(M+H) ⁺
307.2095	1	48945.75	C18H27NO3	(M+H) ⁺
308.2118	1	5769.73	C18H27NO3	(M+H) ⁺

MS 缩放的质谱图



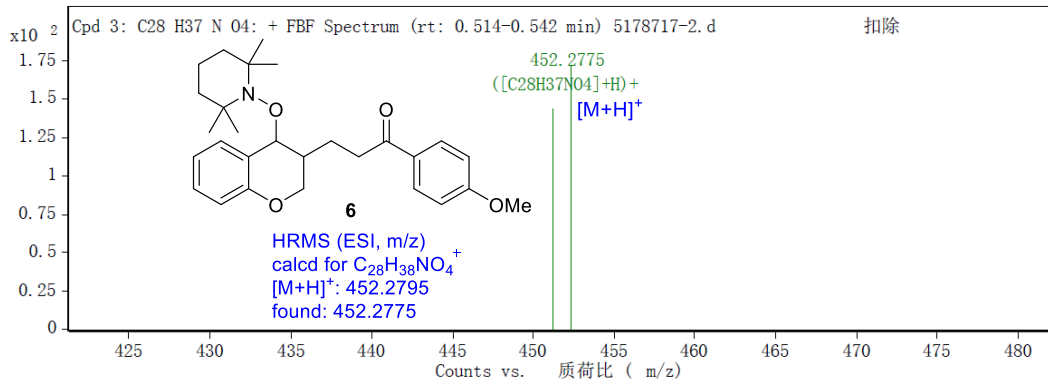
MS 质谱图峰列表

m/z	z	丰度	分子式	离子
468.2734	1	2804.14	C28H37NO5	(M+H)+
469.2794	1	1099.64	C28H37NO5	(M+H)+

MS 缩放的质谱图



定性化合物报告



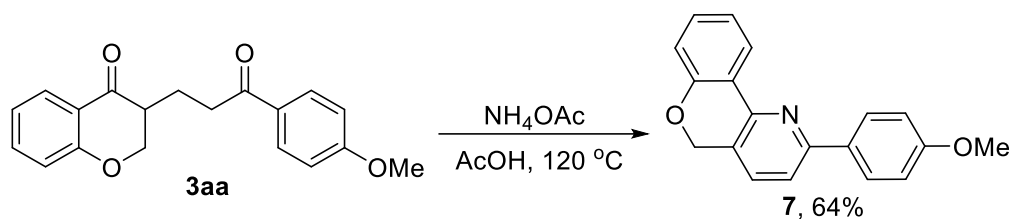
MS 质谱图峰列表

m/z	z	丰度	分子式	离子
451.2676	1	143.58	C28H37NO4	M+
452.2775	1	171.54	C28H37NO4	(M+H)+

--- 报告结束 ---

5. Follow-up chemistry

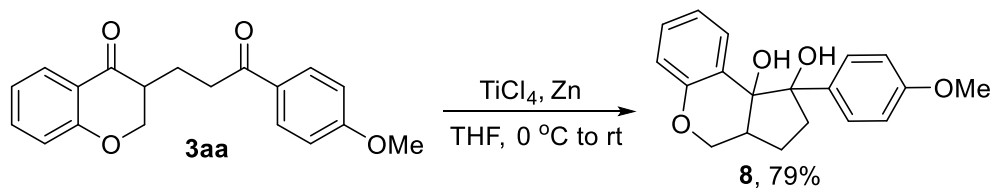
(a) 2-(4-methoxyphenyl)-5H-chromeno[4,3-b]pyridine (7)



According to the procedure reported by C. Che^[3] et al. To a solution of compound **3aa** (62 mg, 0.20 mmol) in AcOH (1.0 ml), followed by NH_4OAc (124 mg, 8.0 mmol). The mixture was stirred at $120\text{ }^\circ\text{C}$ and refluxed for 3 h. The reaction was quenched with saturated Na_2CO_3 solution. The mixture was extracted three times with EtOAc . The combined organic phases were dried over MgSO_4 , concentrated in vacuo and the residue was purified by silica gel flash chromatography (PE/EA = 4:1) to give product **7**.

Compound (**7**): Yellow oil, yield: 64% (37 mg). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.41 (dd, $J = 7.7, 1.7$ Hz, 1H), 8.09 (d, $J = 8.9$ Hz, 2H), 7.56 (t, $J = 7.9$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.34-7.31 (m, 1H), 7.14-7.11 (m, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.98 (d, $J = 8.1$ Hz, 1H), 5.24 (s, 2H), 3.88 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.7, 156.63, 156.57, 148.2, 132.9, 132.0, 131.3, 128.3, 125.0, 123.8, 123.6, 122.4, 118.3, 117.0, 114.2, 68.0, 55.5. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{19}\text{H}_{16}\text{NO}_2$: 290.1176, Found: 290.1184.

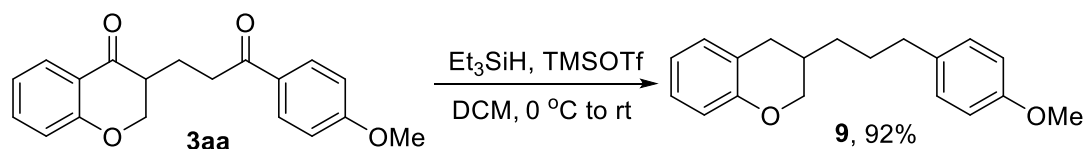
(b) 1-(4-methoxyphenyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene-1,9b(1H)-diol (8)



According to the procedure reported by R. Guo^[4] et al. Rigorously deoxygenated THF (4.0 mL) was added to a mixture of compound **3aa** (62 mg, 0.20 mmol) and Zn dust (36 mg, 0.6 mmol) under Ar atmosphere at $0\text{ }^\circ\text{C}$. A solution of TiCl_4 (57 mg, 0.3 mmol) in THF (2 mL) was then added. The mixture was stirred for 1 h at $0\text{ }^\circ\text{C}$ and then allowed to stand 12 h at room temperature. The reaction was quenched with saturated NaHCO_3 solution and extracted three times with EtOAc . The combined organic phases were dried over MgSO_4 , concentrated in vacuo and the residue was purified by silica gel flash chromatography (PE/EA = 20:1) to give product **8**.

Compound (**8**): Colorless oil, yield: 79% (49 mg). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 (d, $J = 8.6$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.07 (t, $J = 8.3$ Hz, 1H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.64 (t, $J = 7.8$ Hz, 1H), 4.55 (dd, $J = 10.1, 5.0$ Hz, 1H), 3.85 (s, 3H), 3.82 (s, 1H), 3.23 – 3.17 (m, 1H), 3.08 – 3.01 (m, 1H), 2.55 (dd, $J = 15.8, 9.4$ Hz, 1H), 2.23 – 2.18 (m, 1H), 1.52 – 1.44 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.9, 154.6, 135.4, 131.5, 131.2, 129.2, 128.8, 126.7, 120.1, 119.9, 117.1, 114.1, 72.7, 55.4, 43.6, 38.9, 25.8. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{19}\text{H}_{21}\text{O}_4$: 313.1434, Found: 313.1441.

3-(3-(4-methoxyphenyl)propyl)chromane (9)

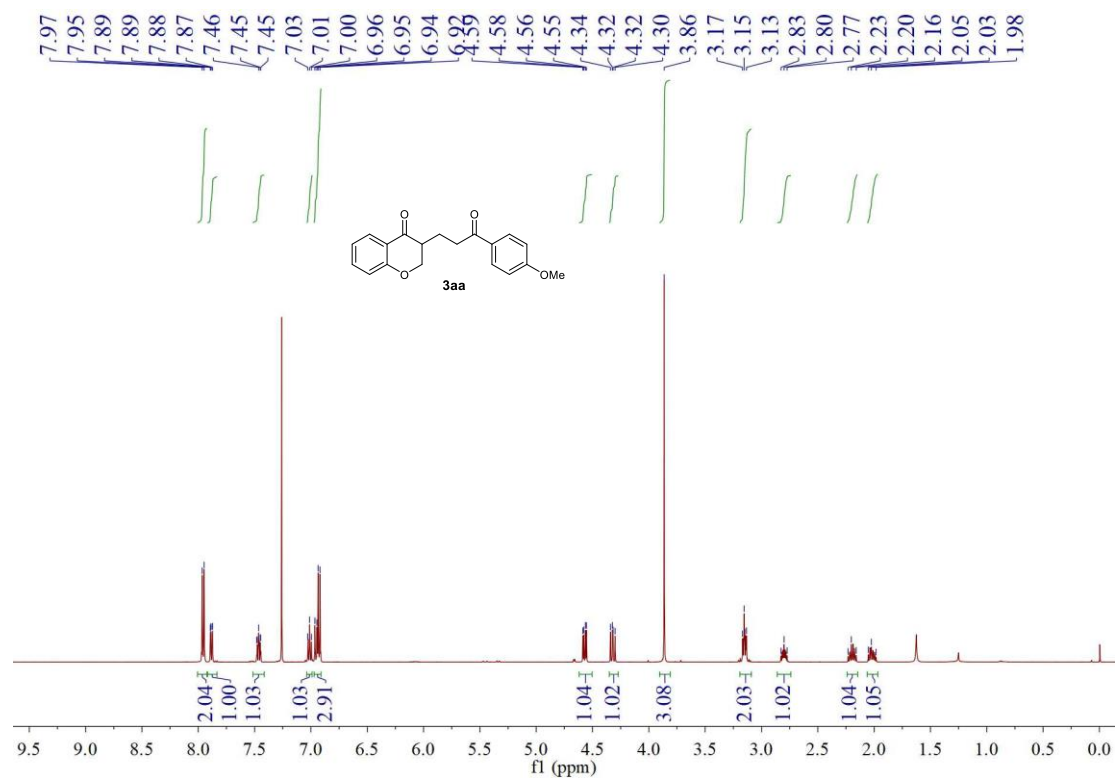


According to the procedure reported by R. Guo^[4] et al. To a solution of compound **3aa** (62 mg, 0.20 mmol) in CH₂Cl₂ (0.8 ml) was added Et₃SiH (116 mg, 1.0 mmol), followed by TMSOTf (0.9 mg, 0.004 mmol) at 0 °C. The mixture was stirred at 0 °C for 4 h and then allowed to stand 12 h at room temperature. The reaction was quenched with saturated NaHCO₃ solution. The mixture was extracted three times with CH₂Cl₂. The combined organic phases were dried over MgSO₄, concentrated in vacuo and the residue was purified by silica gel flash chromatography (PE/EA = 20:1) to give product **9**.

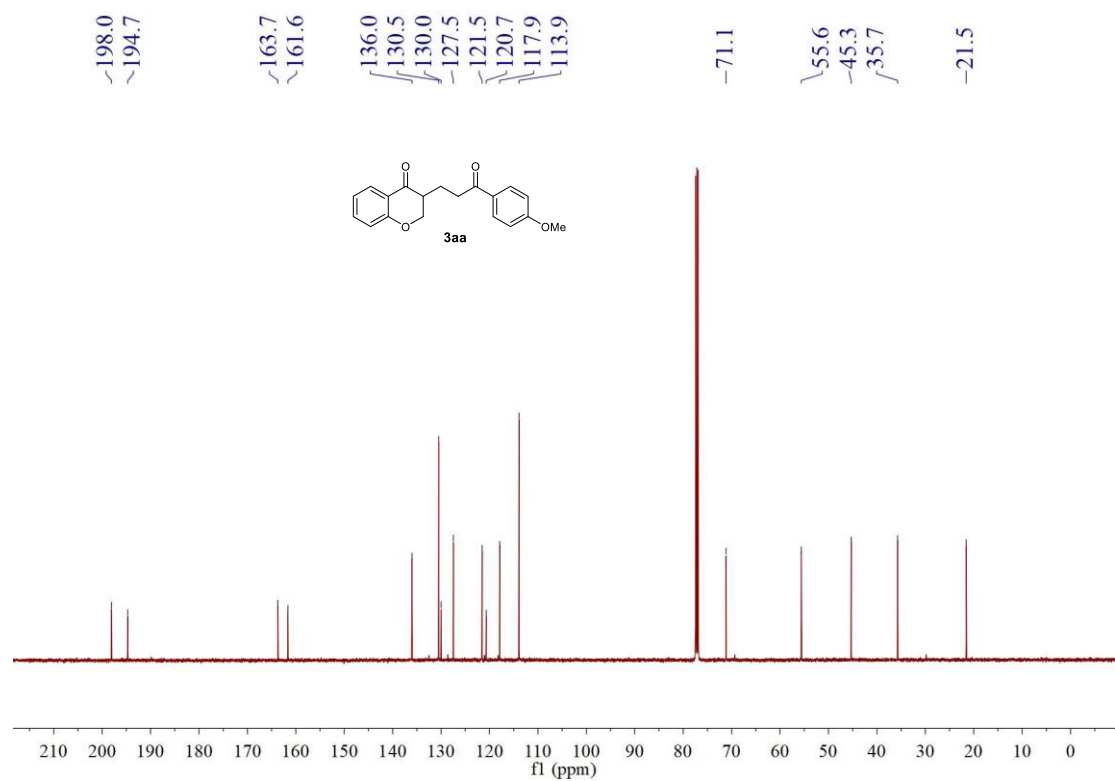
Compound (**9**): Colorless oil, yield: 92% (52 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.13-7.08 (m, 3H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 15.1 Hz, 3H), 6.81 (d, *J* = 8.2 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 3H), 3.74 (t, *J* = 19.9 Hz, 1H), 2.87 (dd, *J* = 16.1, 4.4 Hz, 1H), 2.61 (t, *J* = 8.9 Hz, 2H), 2.47 (dd, *J* = 16.1, 9.7 Hz, 1H), 2.07-2.02 (m, 1H), 1.77-1.69 (m, 2H), 1.47-1.40 (m, 1H), 1.38-1.32 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 157.9, 154.8, 134.4, 130.0, 129.4, 127.3, 121.9, 120.3, 116.5, 113.9, 70.7, 55.4, 35.2, 32.2, 31.7, 31.5, 29.0. HRMS (ESI) [M+H]⁺ Calcd For C₁₉H₂₃O₂: 283.1693, Found: 283.1699.

6. Copies of ^1H NMR and ^{13}C NMR spectra

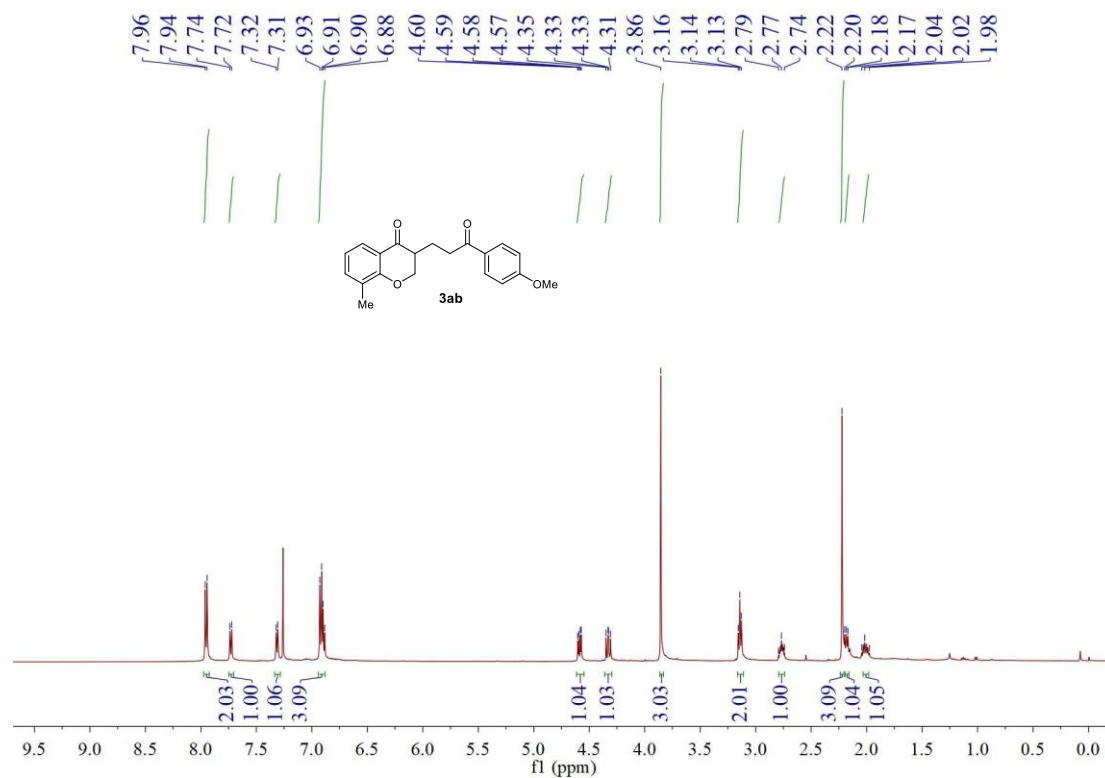
^1H NMR of **3aa** in CDCl_3



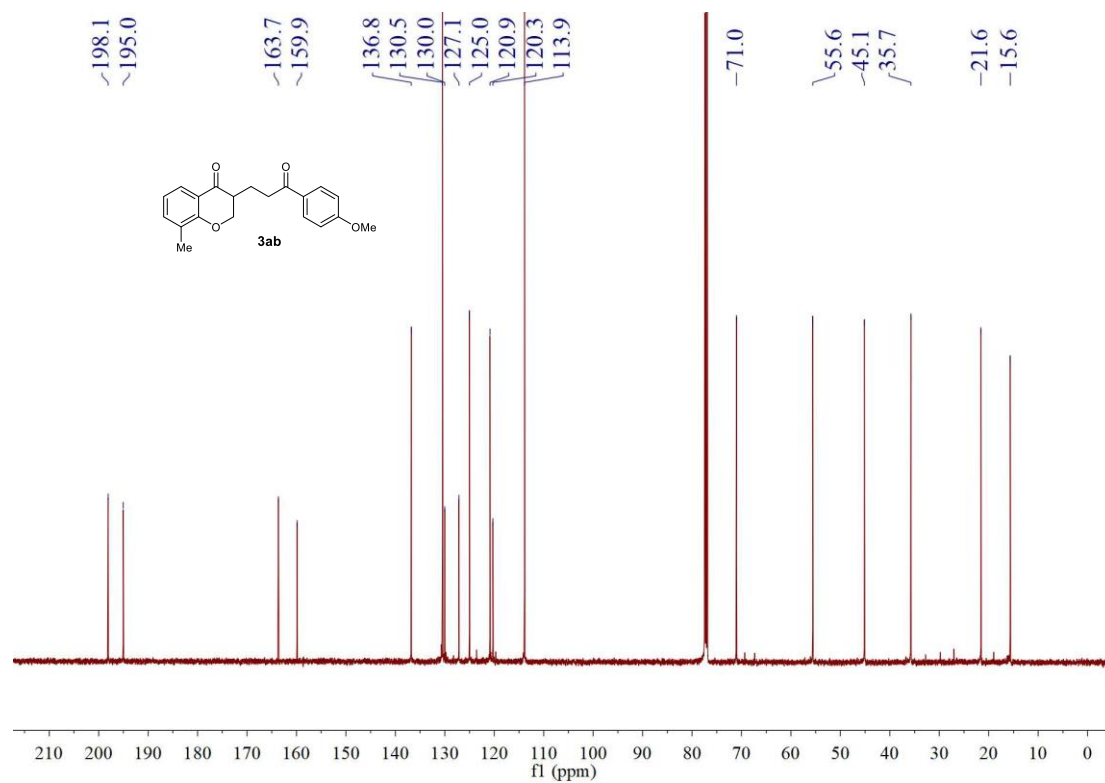
^{13}C NMR of **3aa** in CDCl_3



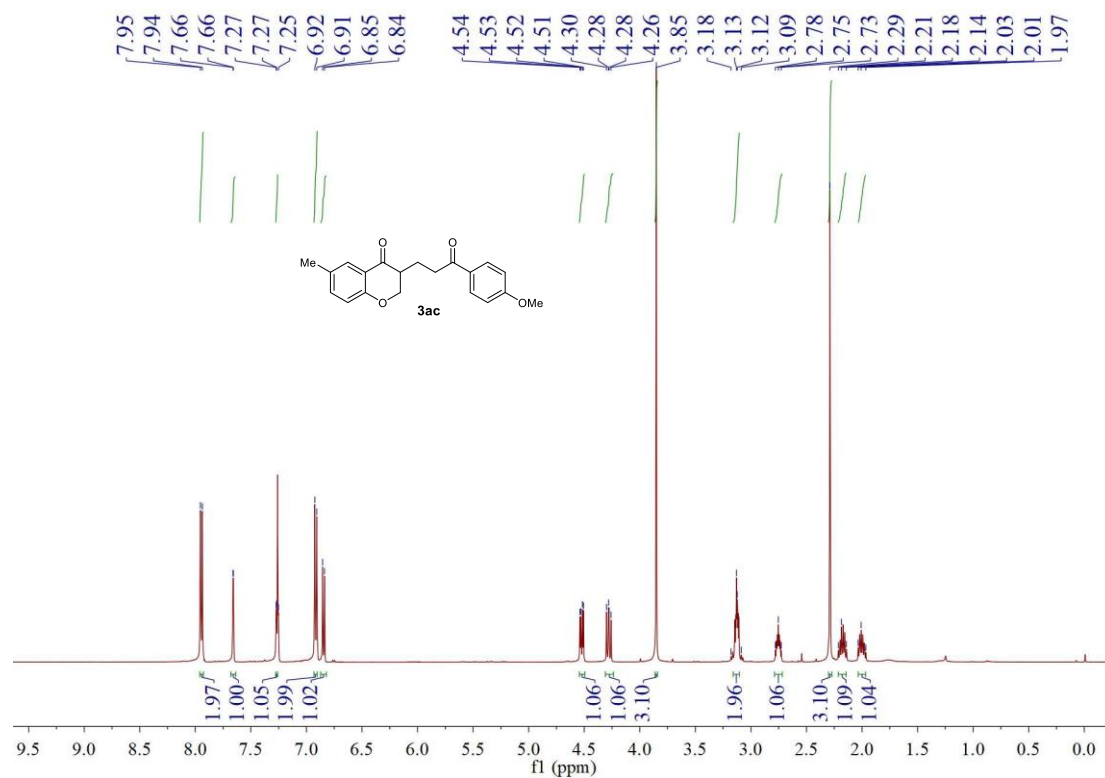
¹H NMR of **3ab** in CDCl₃



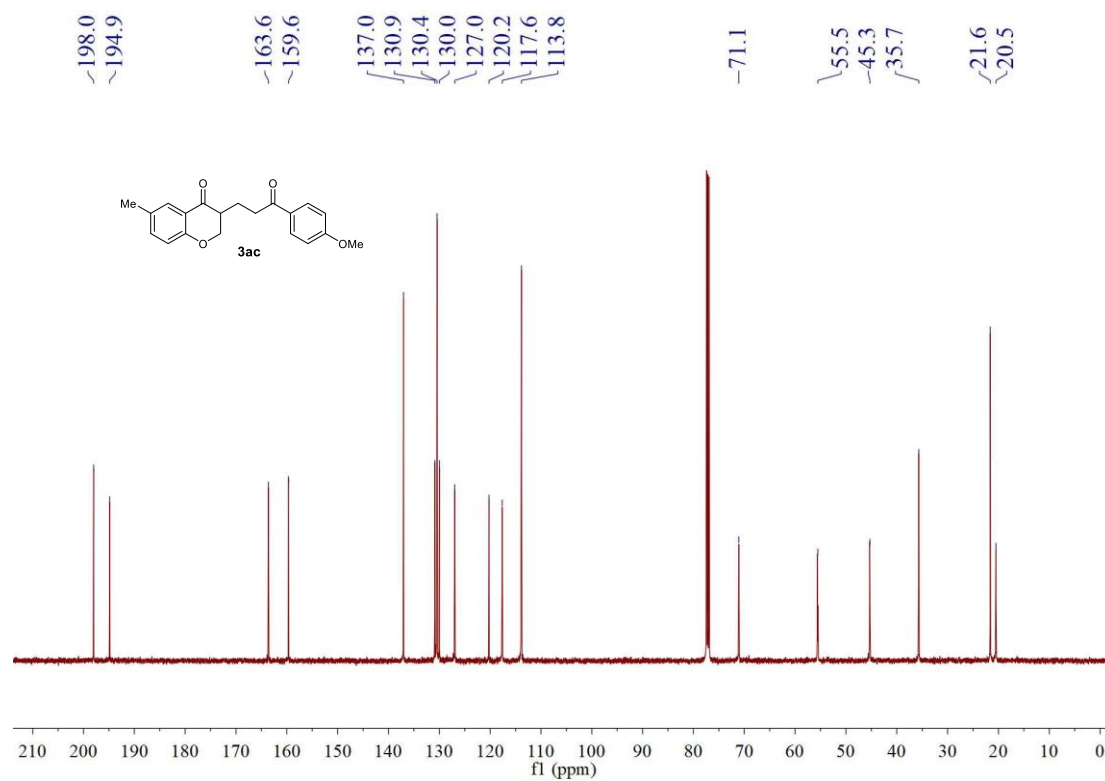
¹³C NMR of **3ab** in CDCl₃



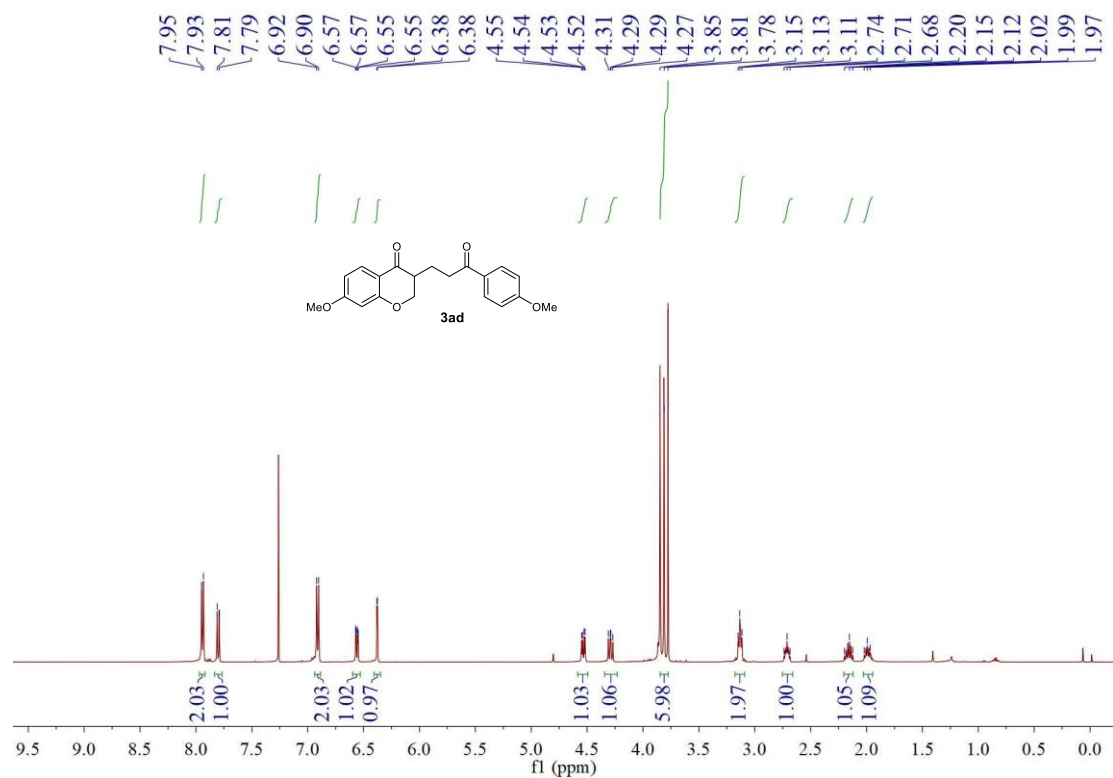
^1H NMR of **3ac** in CDCl_3



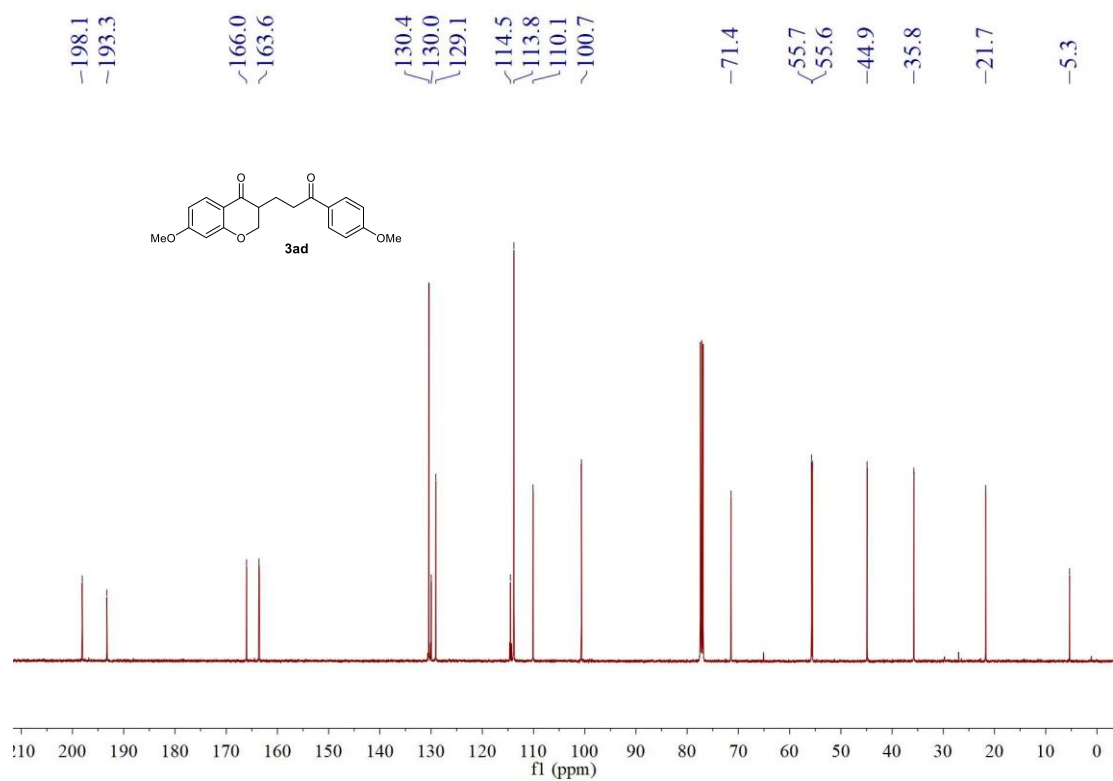
^{13}C NMR of **3ac** in CDCl_3



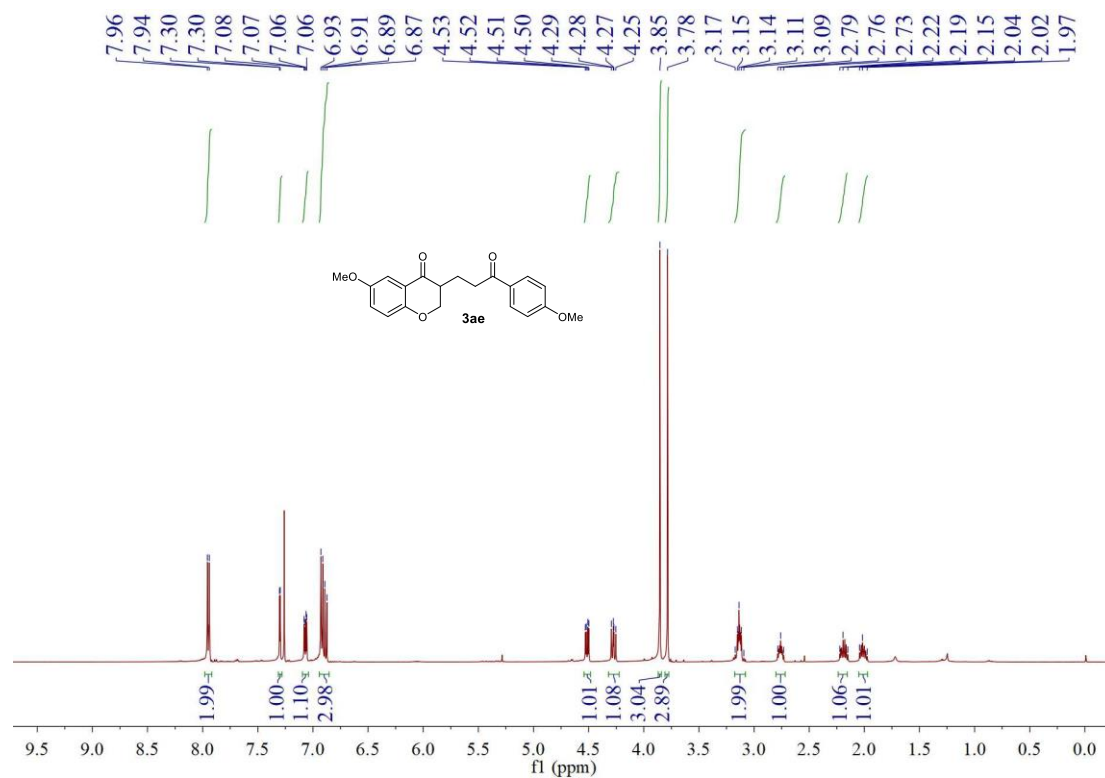
¹H NMR of **3ad** in CDCl₃



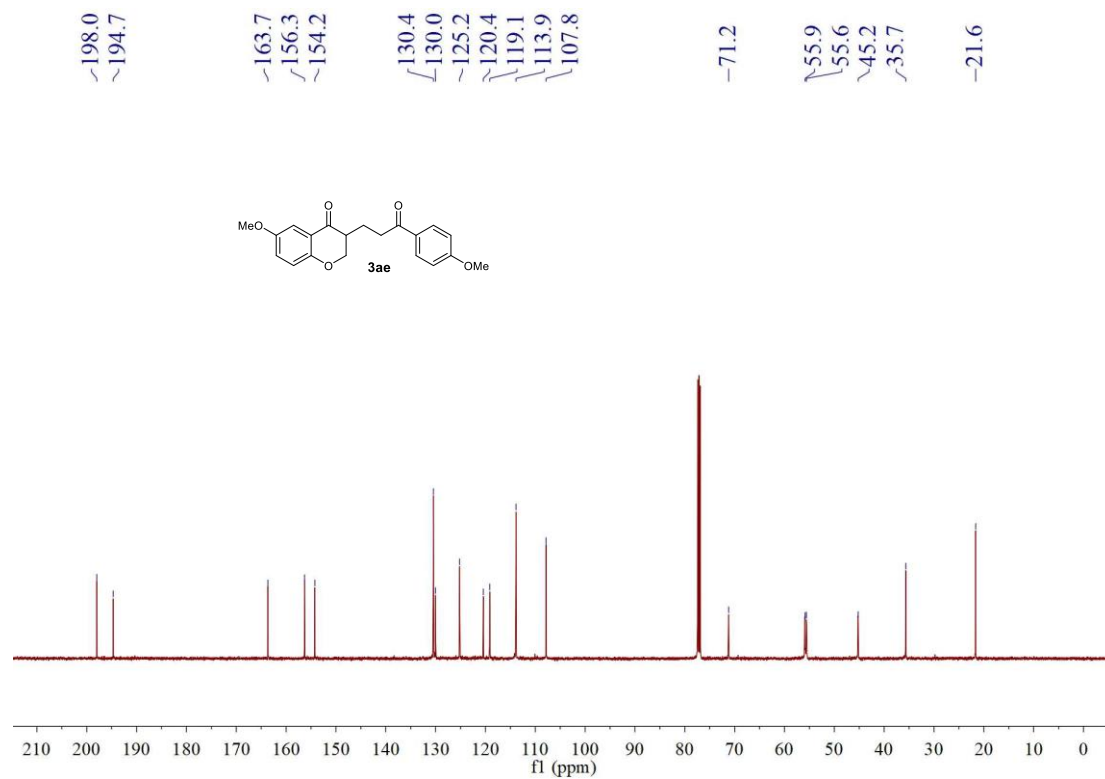
¹³C NMR of **3ad** in CDCl₃



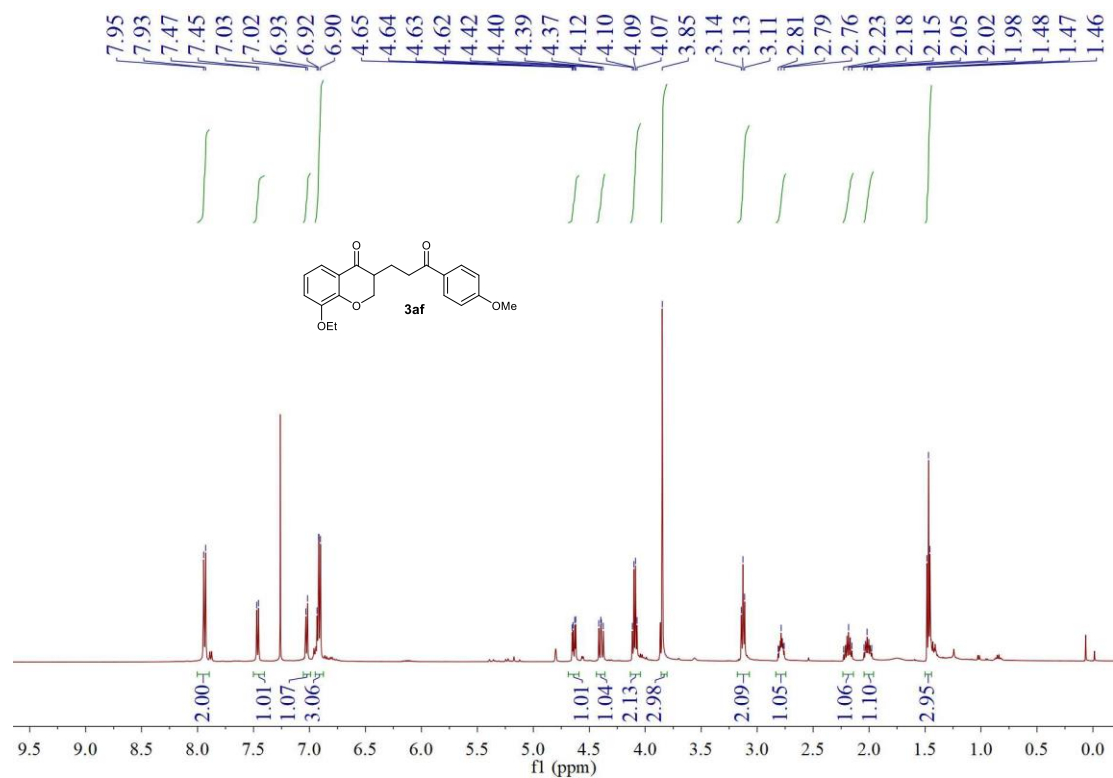
¹H NMR of **3ae** in CDCl₃



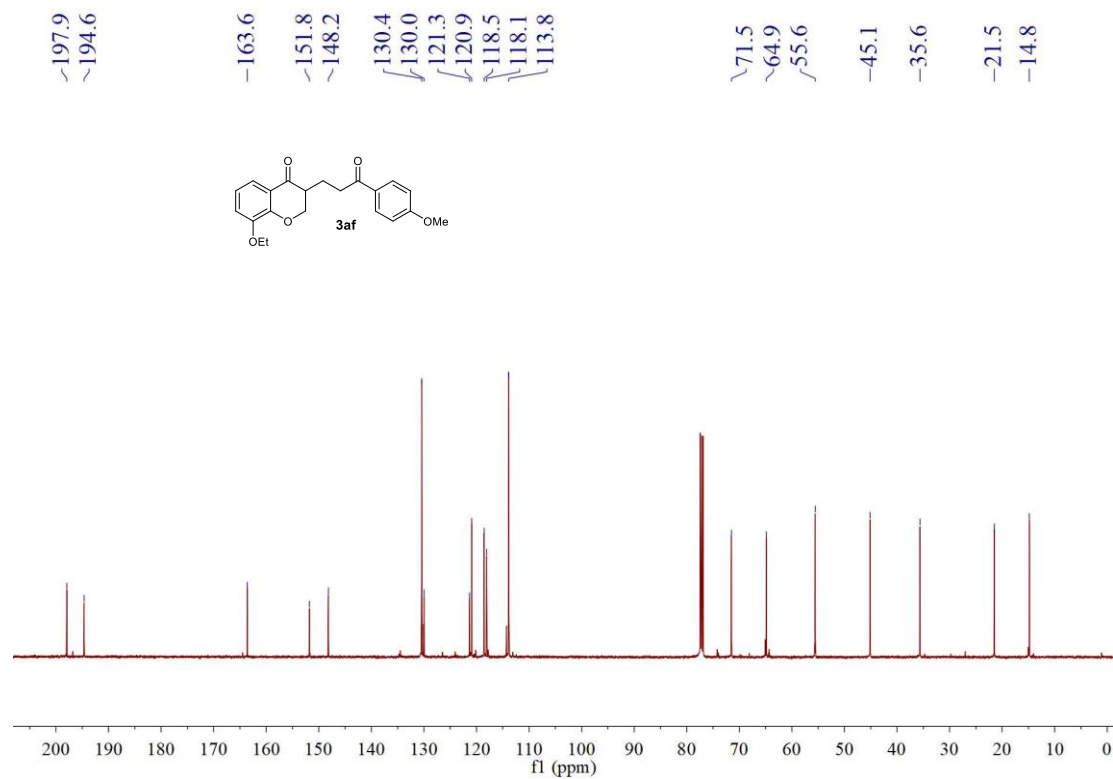
¹³C NMR of **3ae** in CDCl₃



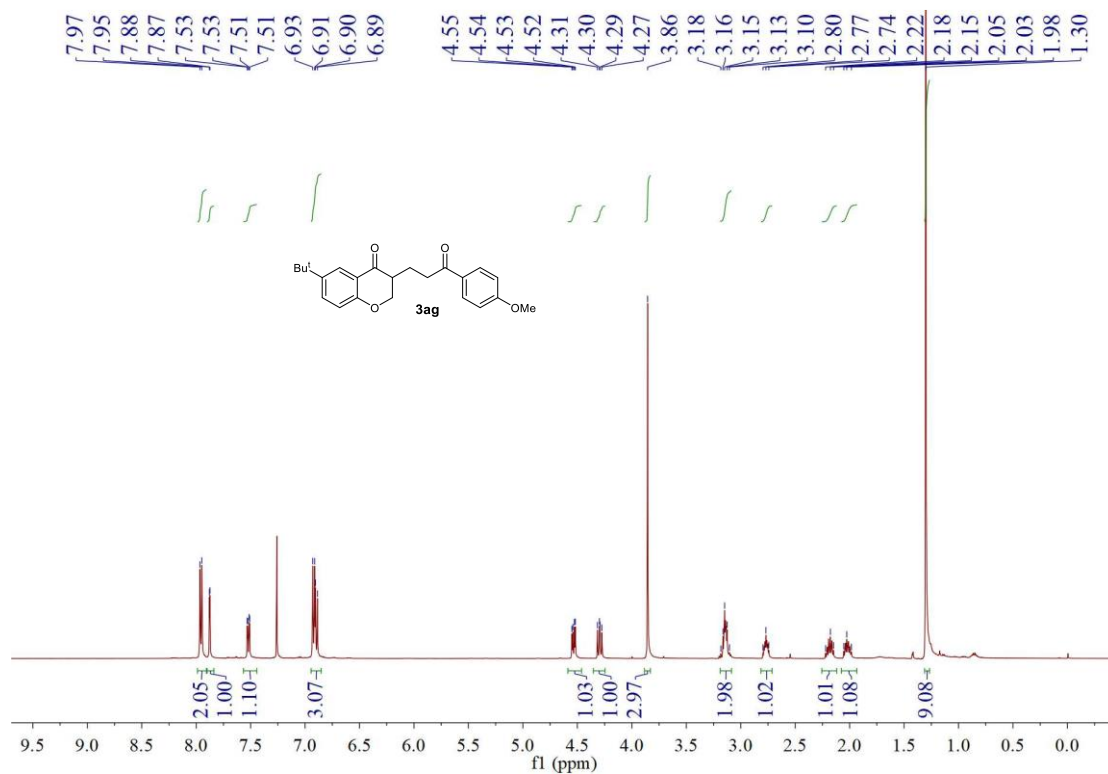
¹H NMR of **3af** in CDCl₃



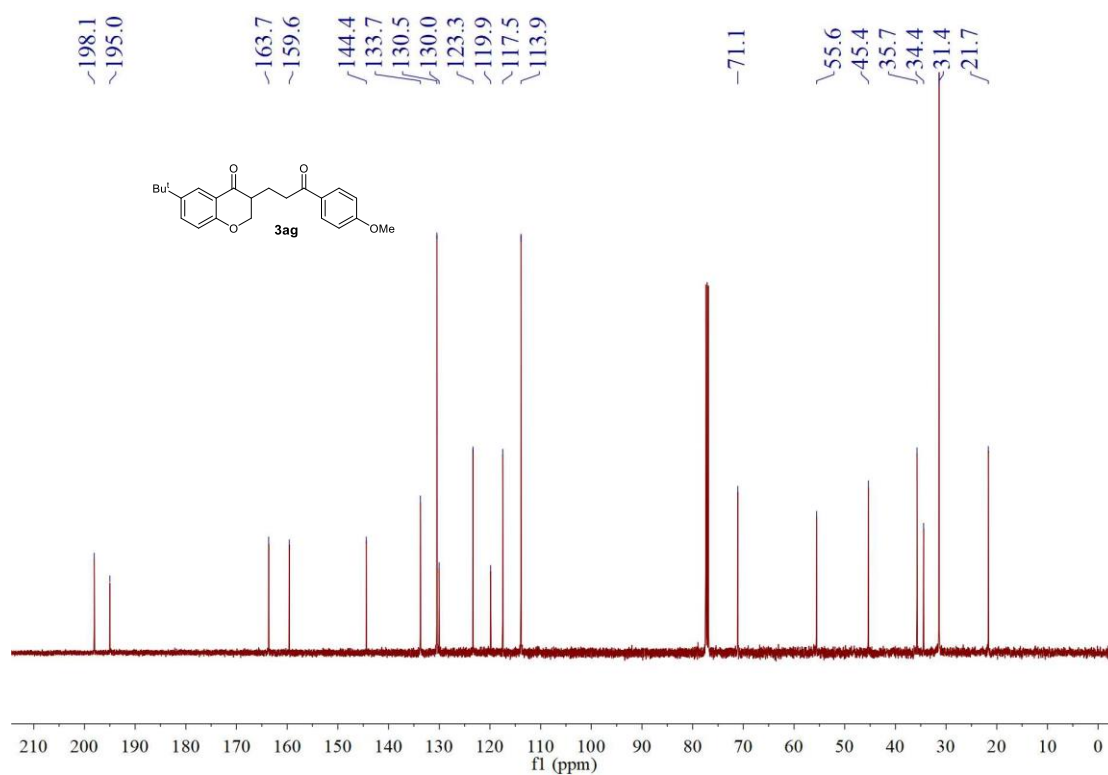
¹³C NMR of **3af** in CDCl₃



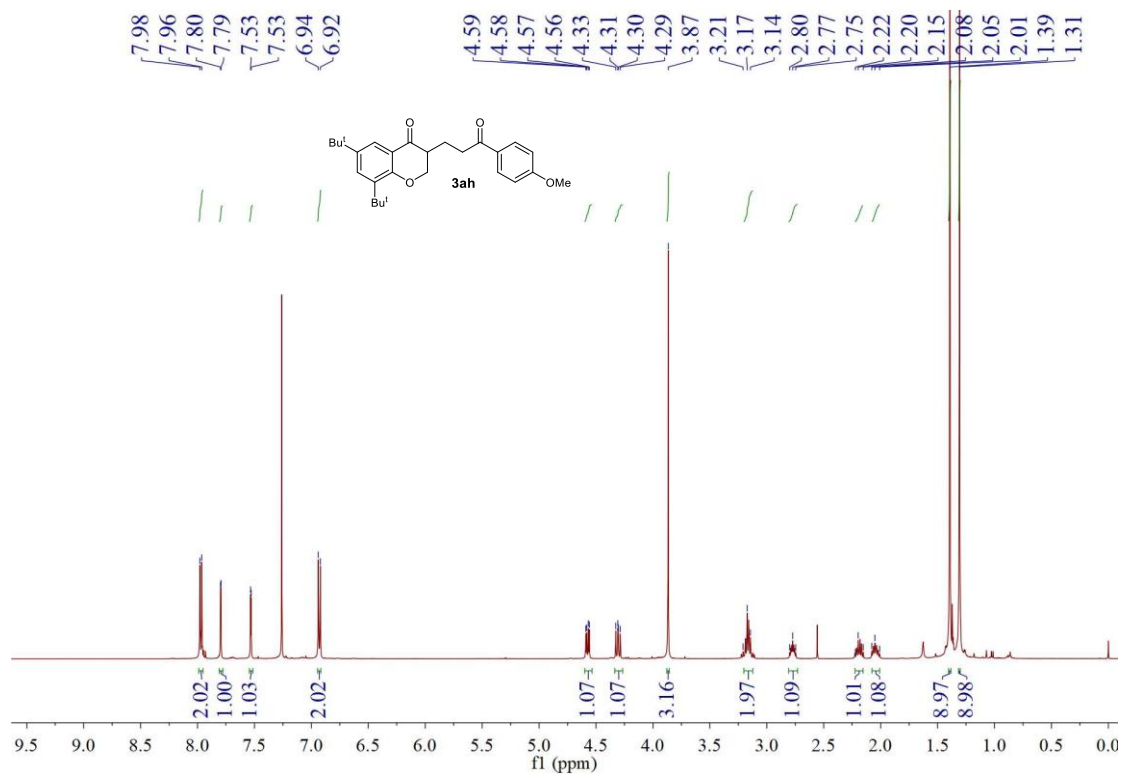
¹H NMR of **3ag** in CDCl₃



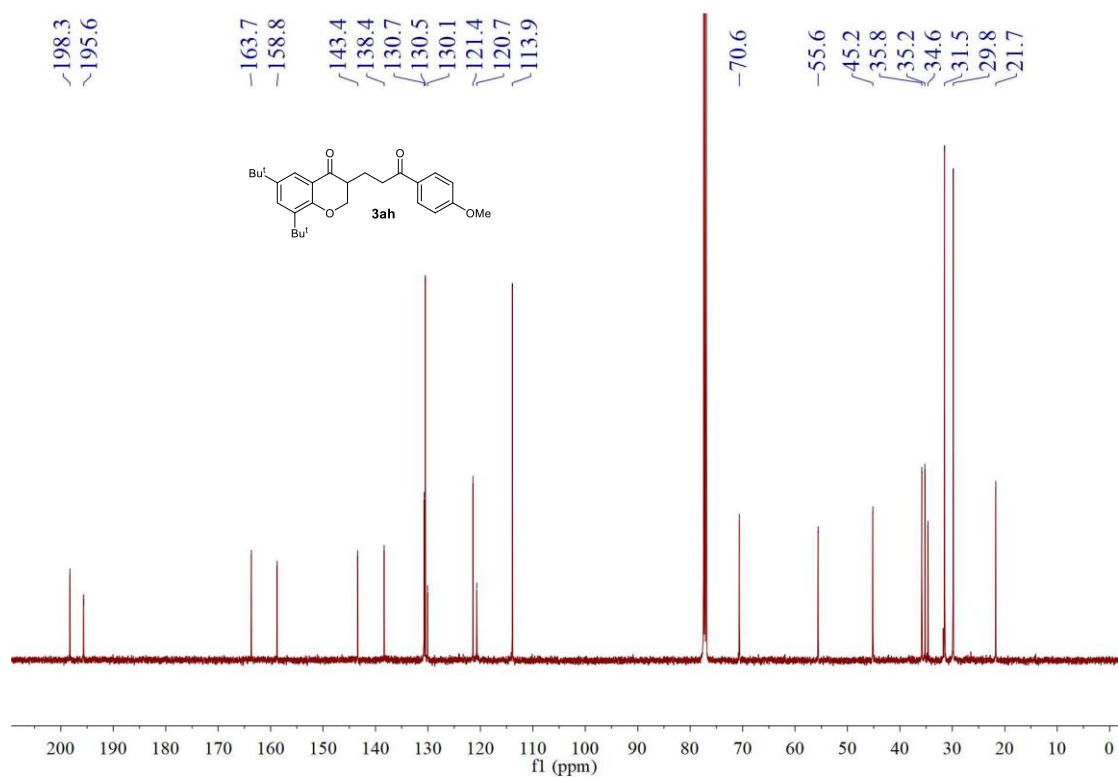
¹³C NMR of **3ag** in CDCl₃



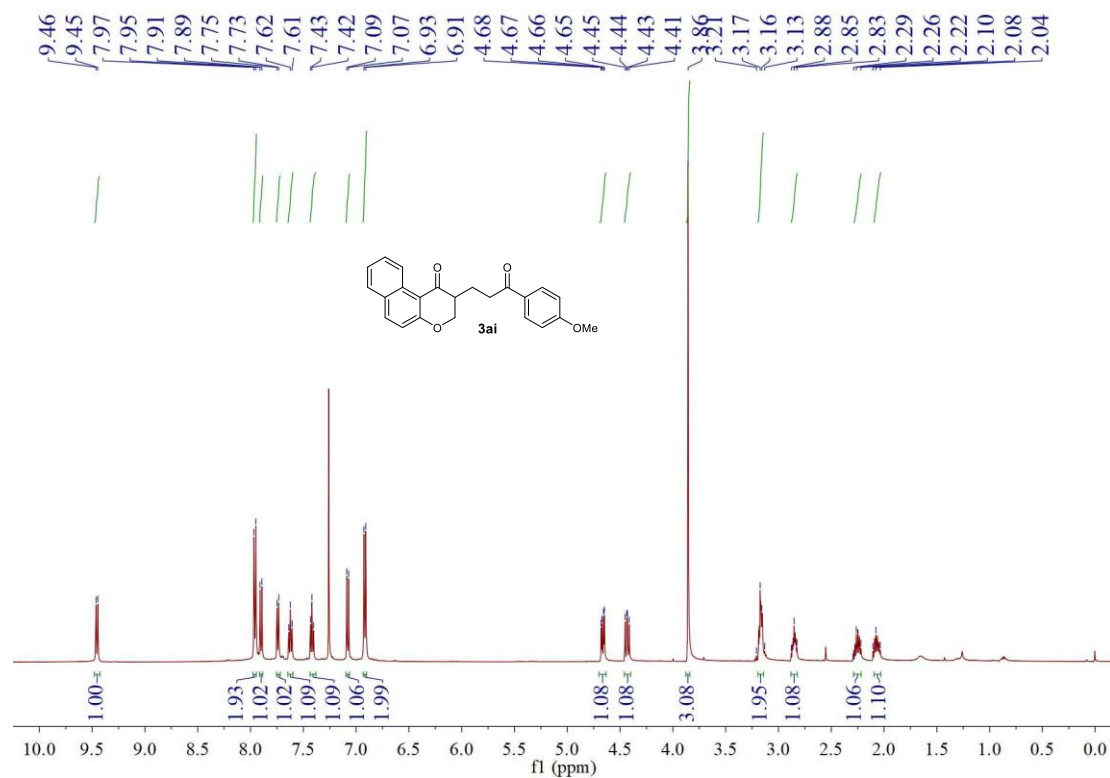
¹H NMR of **3ah** in CDCl₃



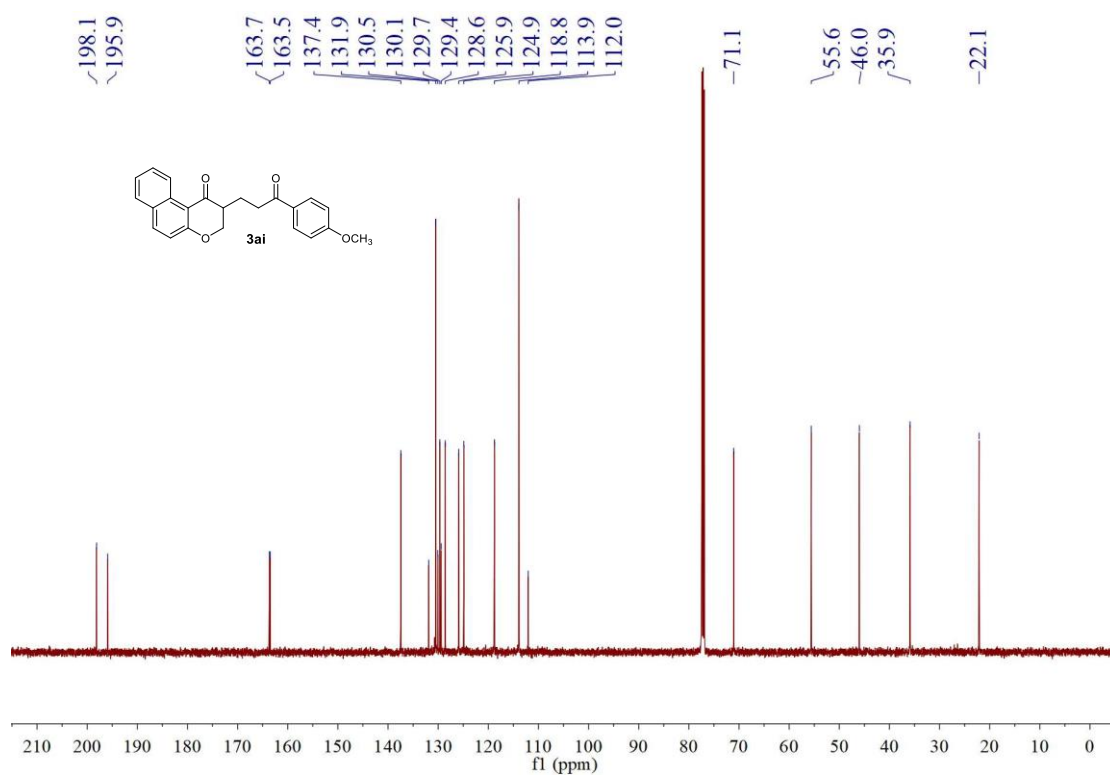
¹³C NMR of **3ah** in CDCl₃



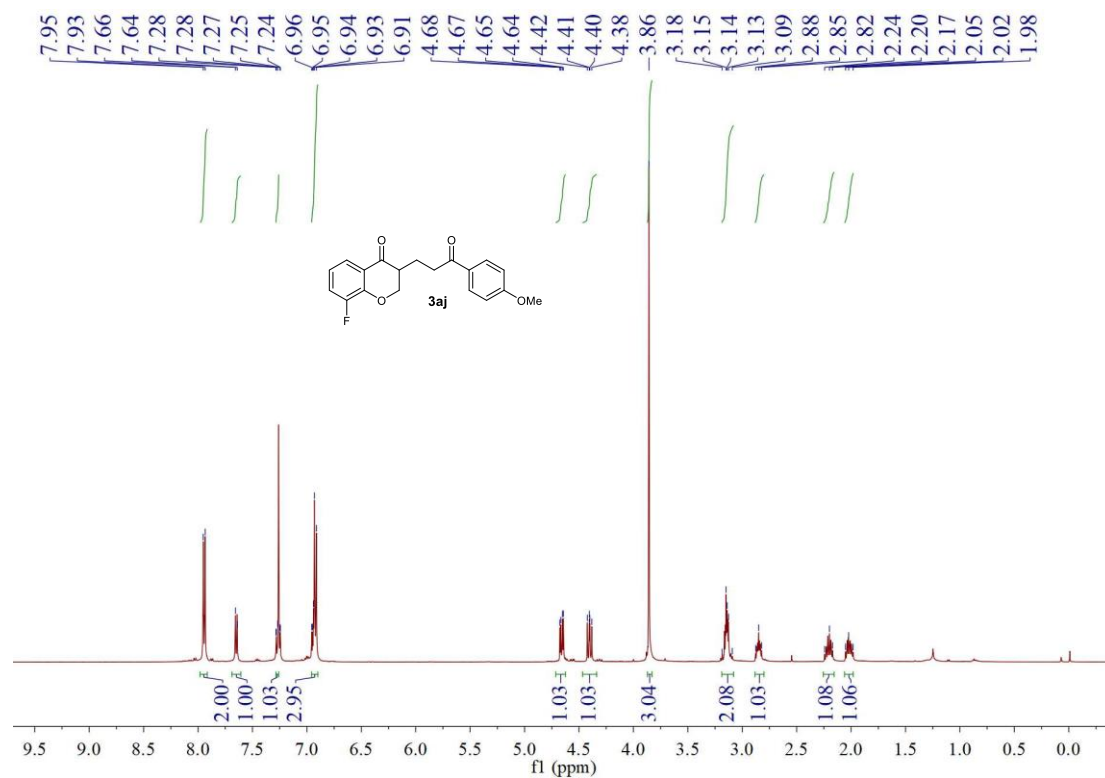
¹H NMR of **3ai** in CDCl₃



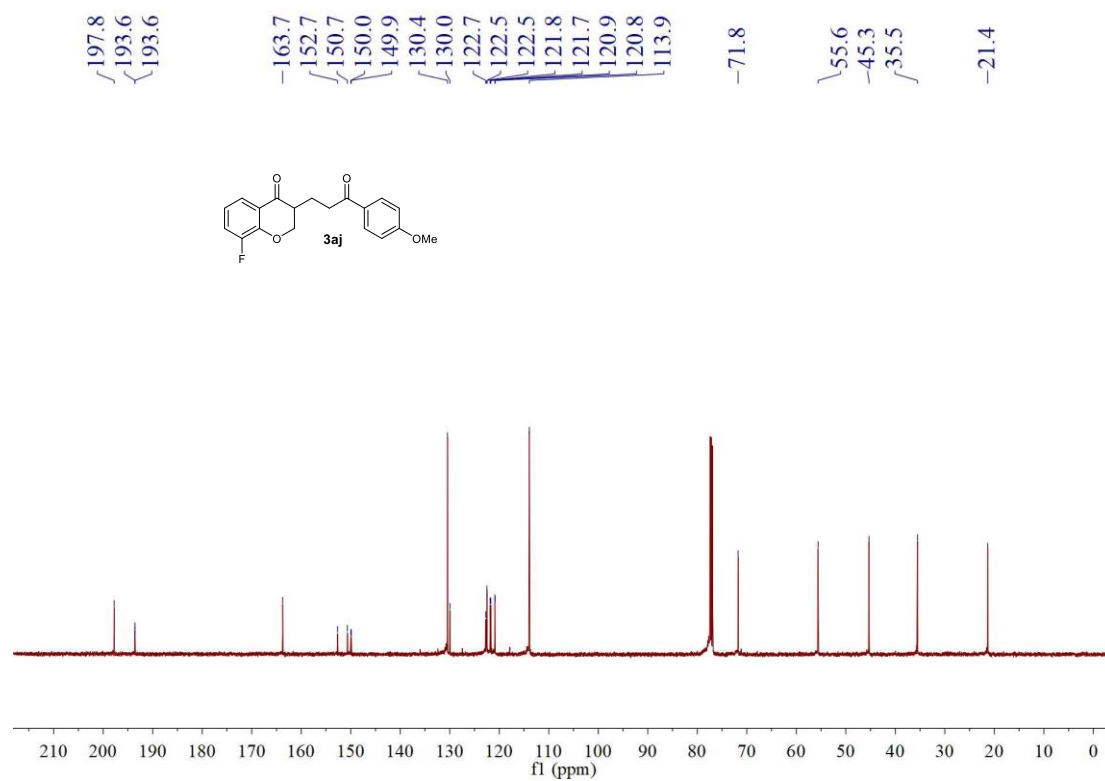
¹³C NMR of **3ai** in CDCl₃



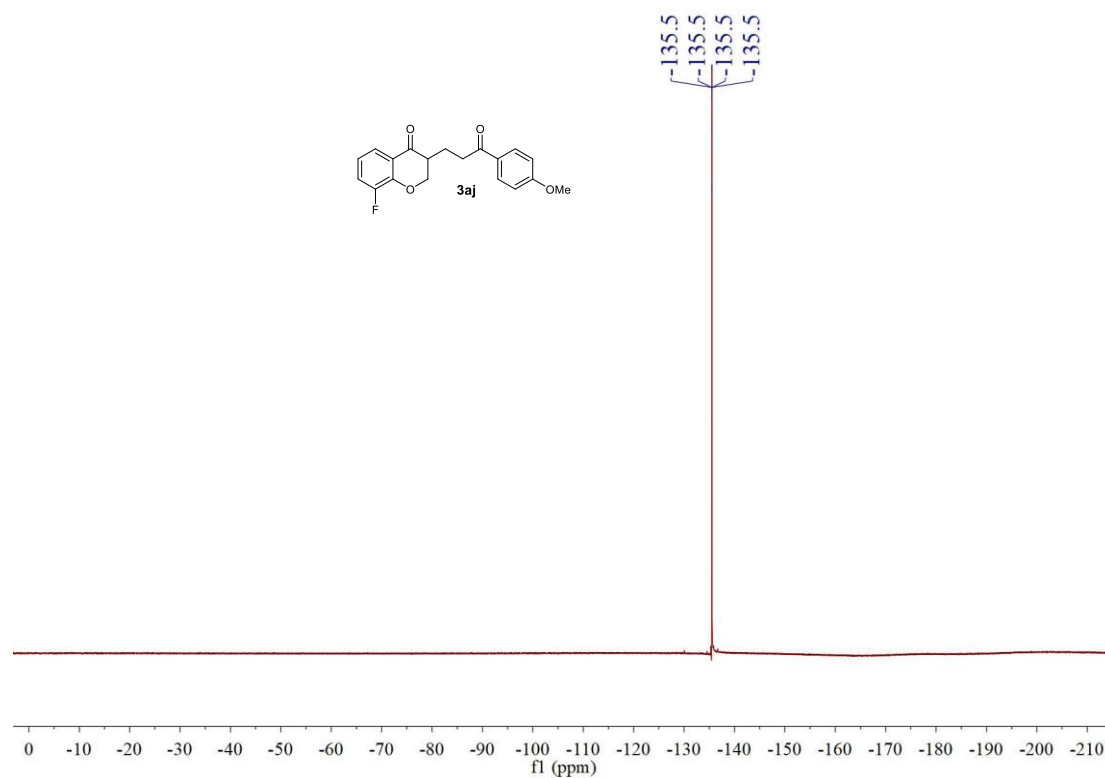
¹H NMR of **3aj** in CDCl₃



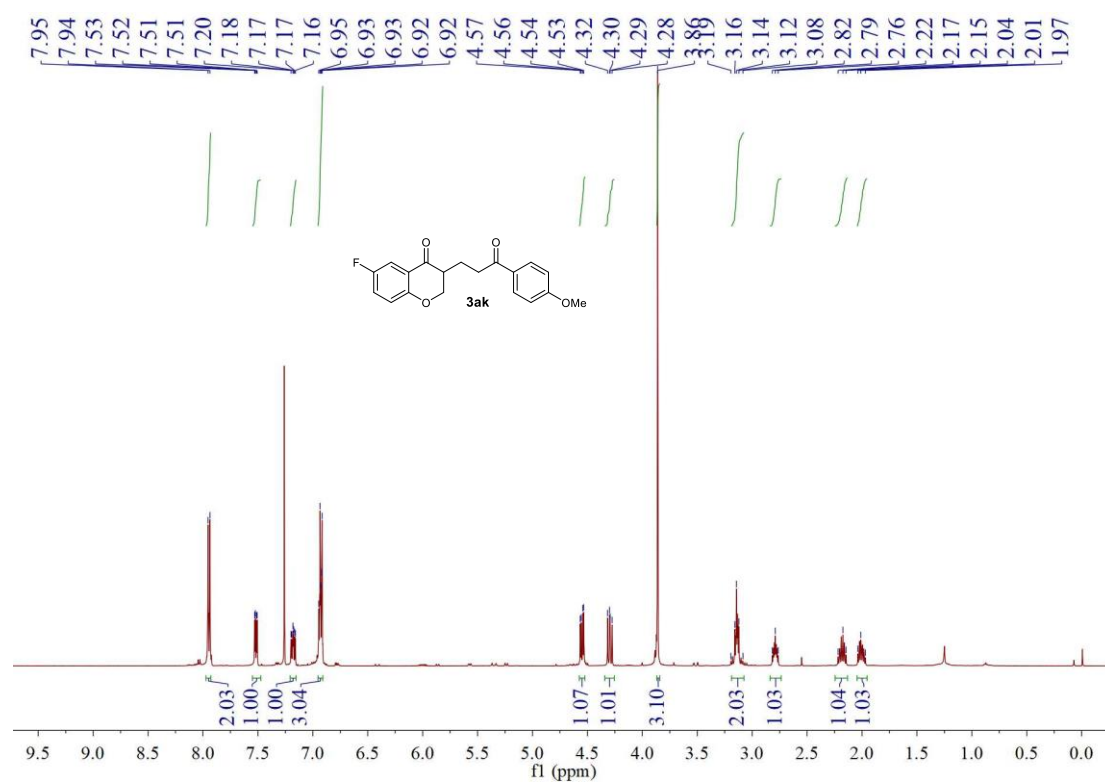
¹³C NMR of **3aj** in CDCl₃



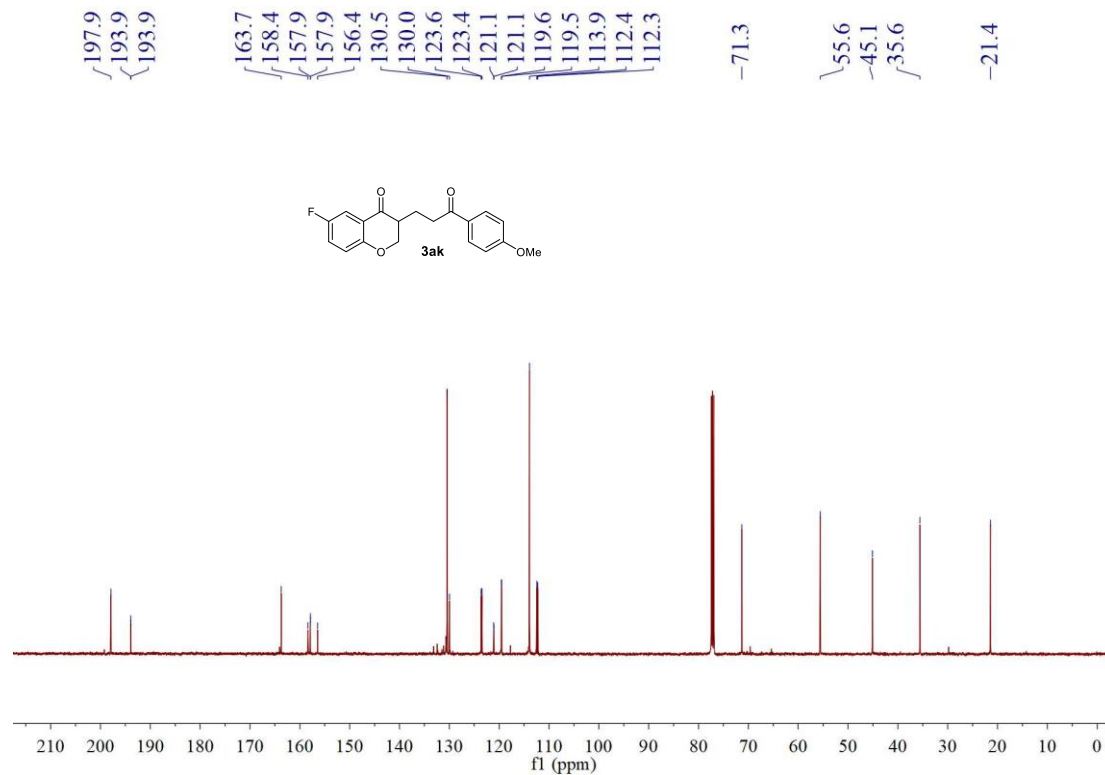
^{19}F NMR of **3aj** in CDCl_3



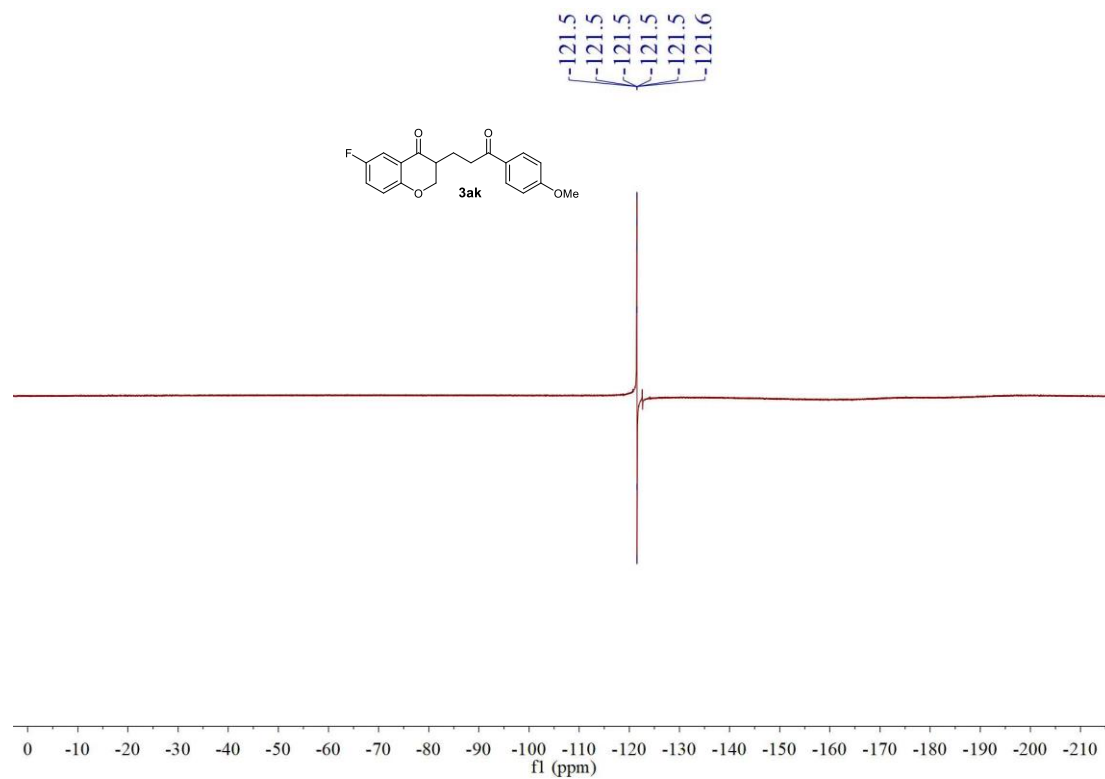
^1H NMR of **3ak** in CDCl_3



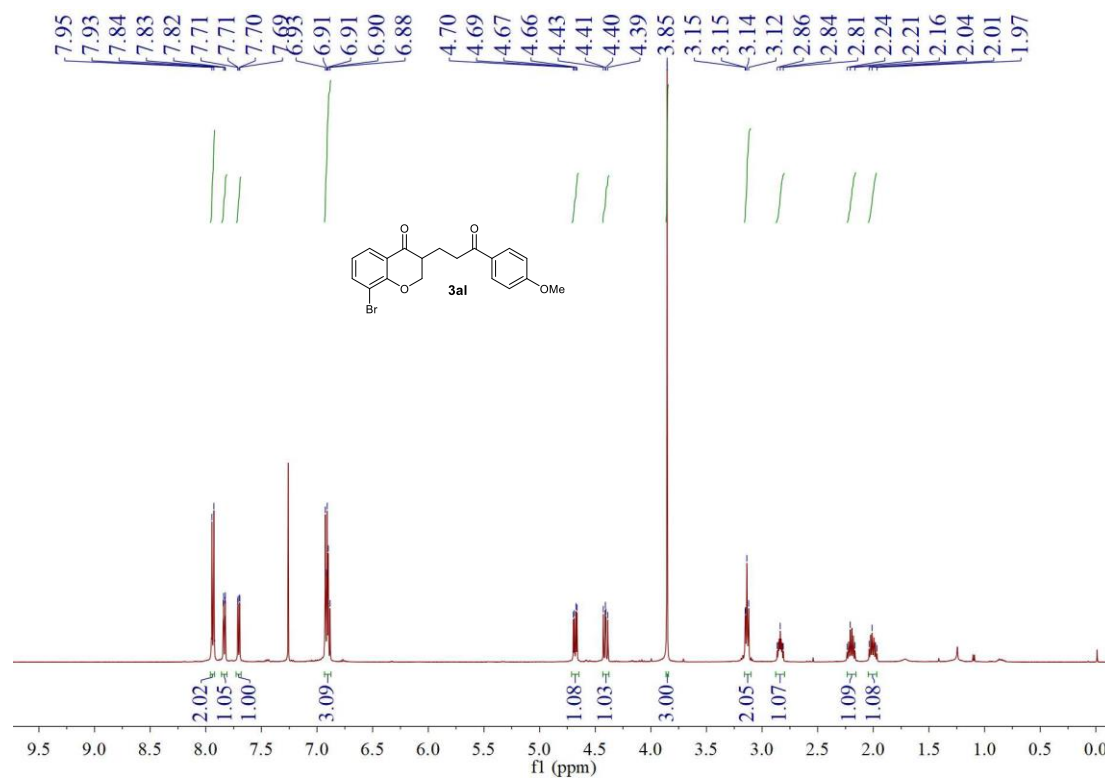
¹³C NMR of **3ak** in CDCl₃



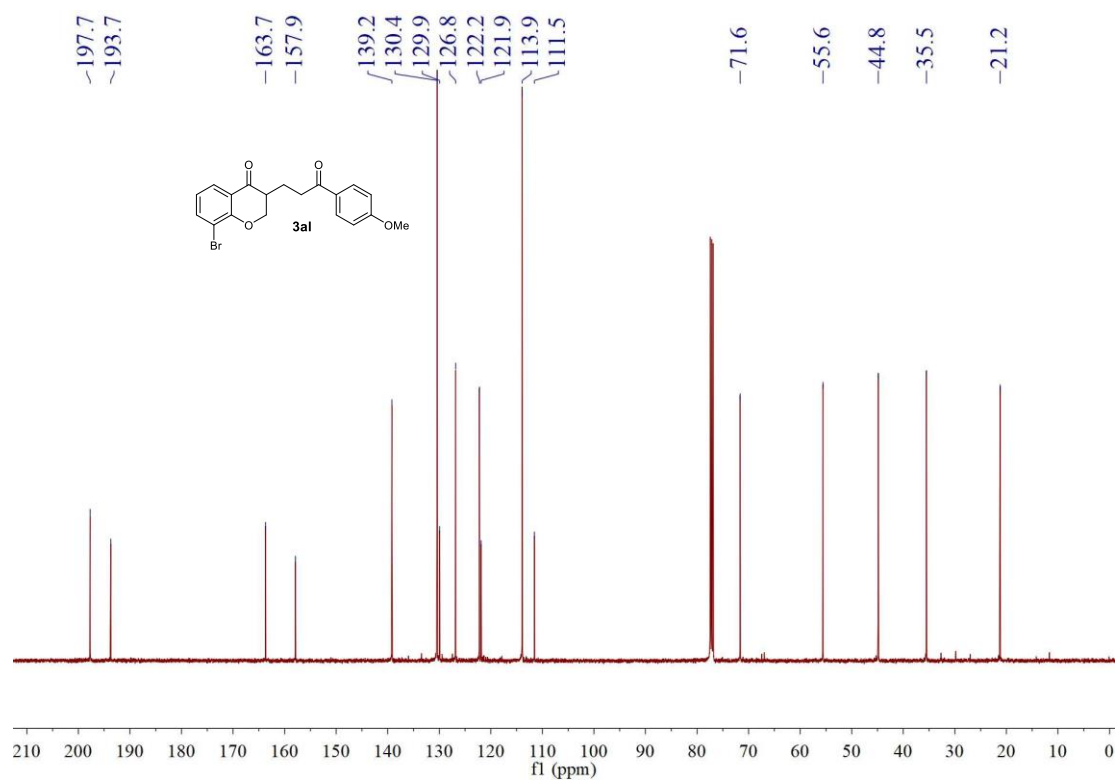
¹⁹F NMR of **3ak** in CDCl₃



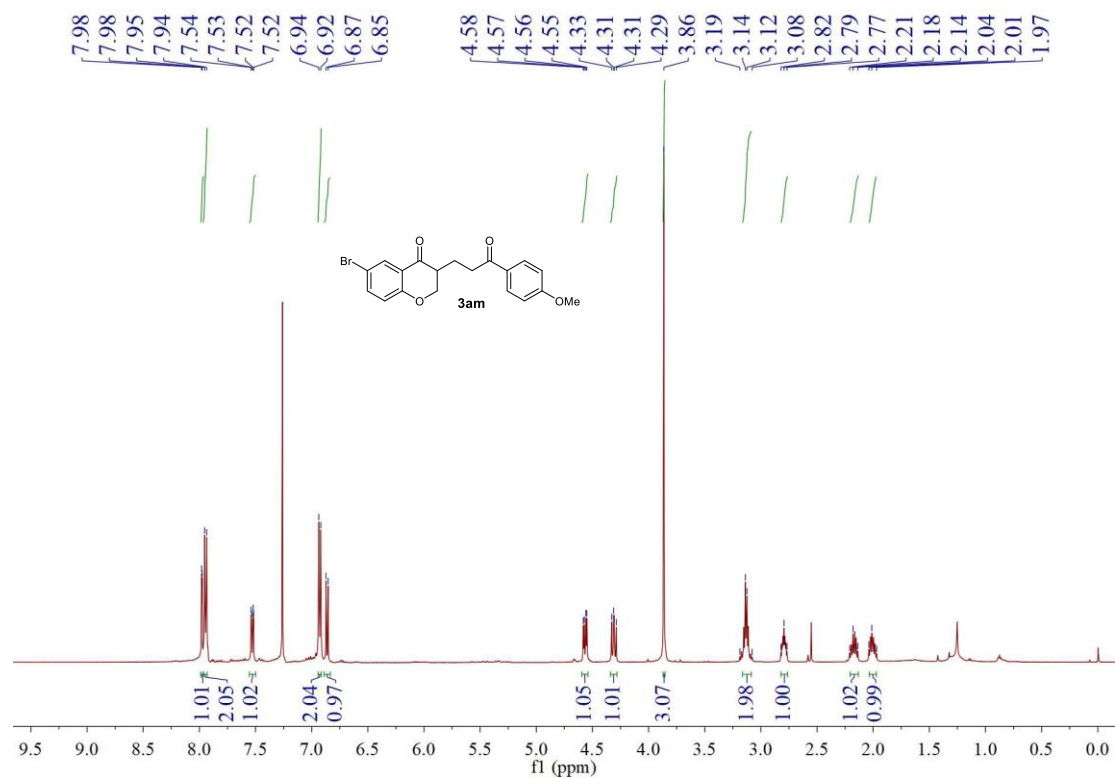
¹H NMR of **3al** in CDCl₃



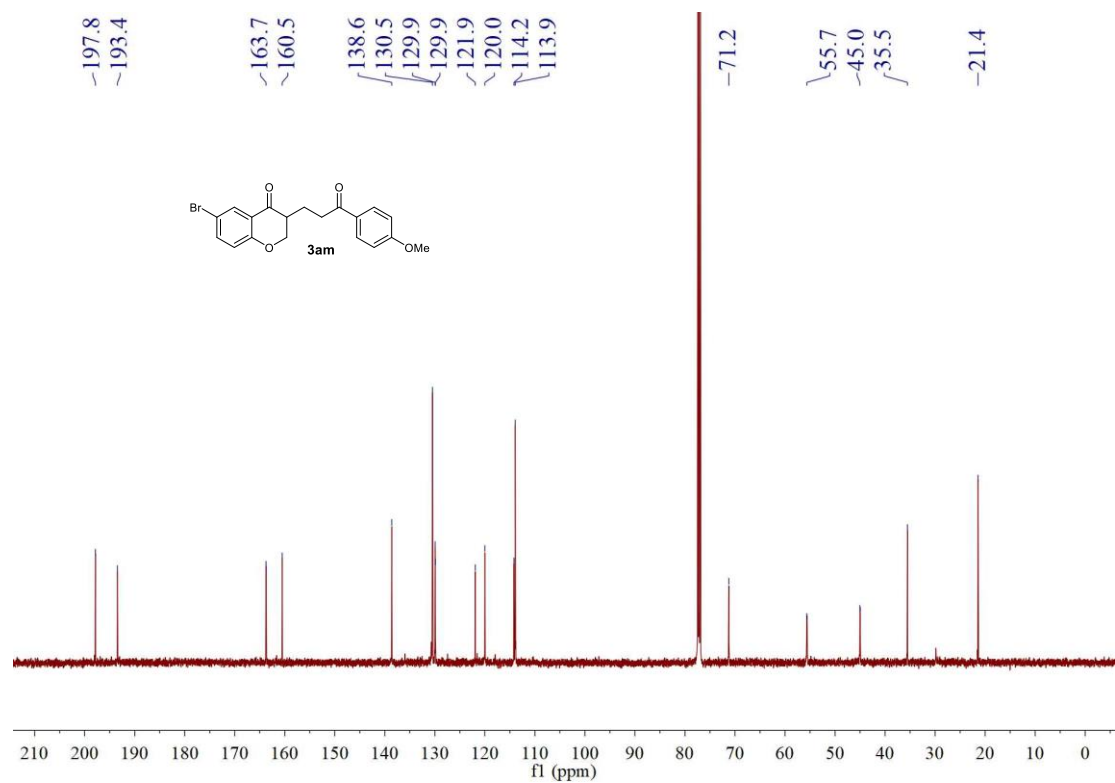
¹³C NMR of **3al** in CDCl₃



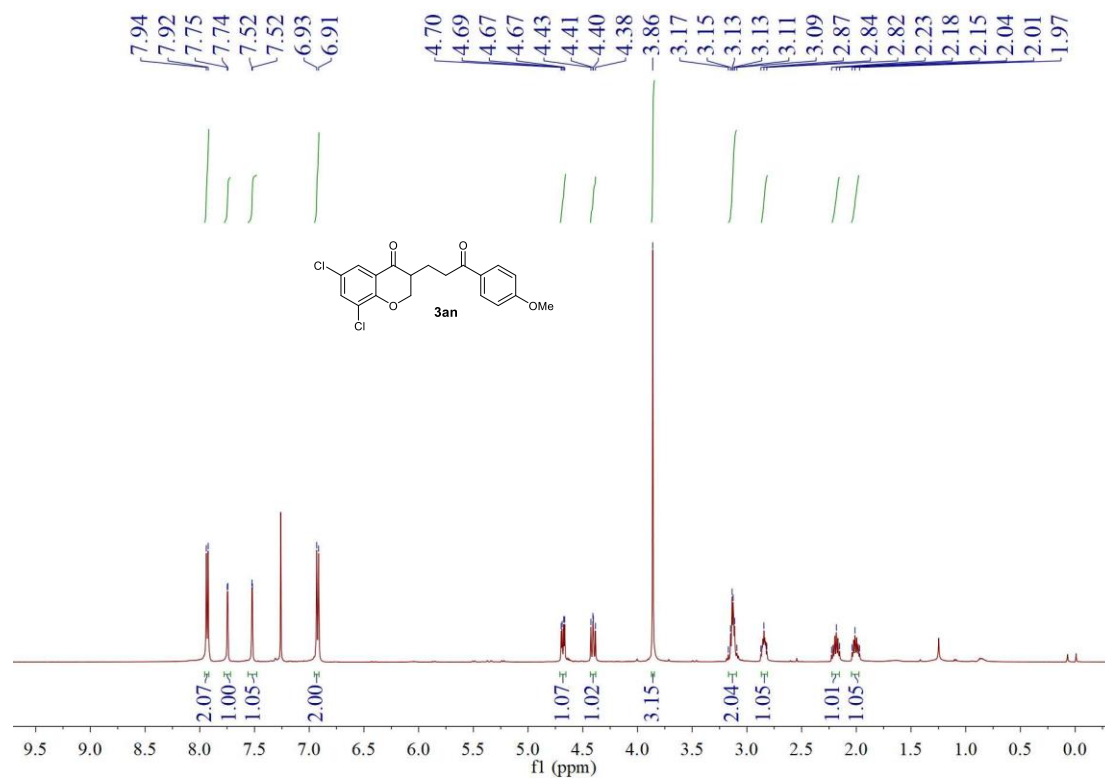
¹H NMR of **3am** in CDCl₃



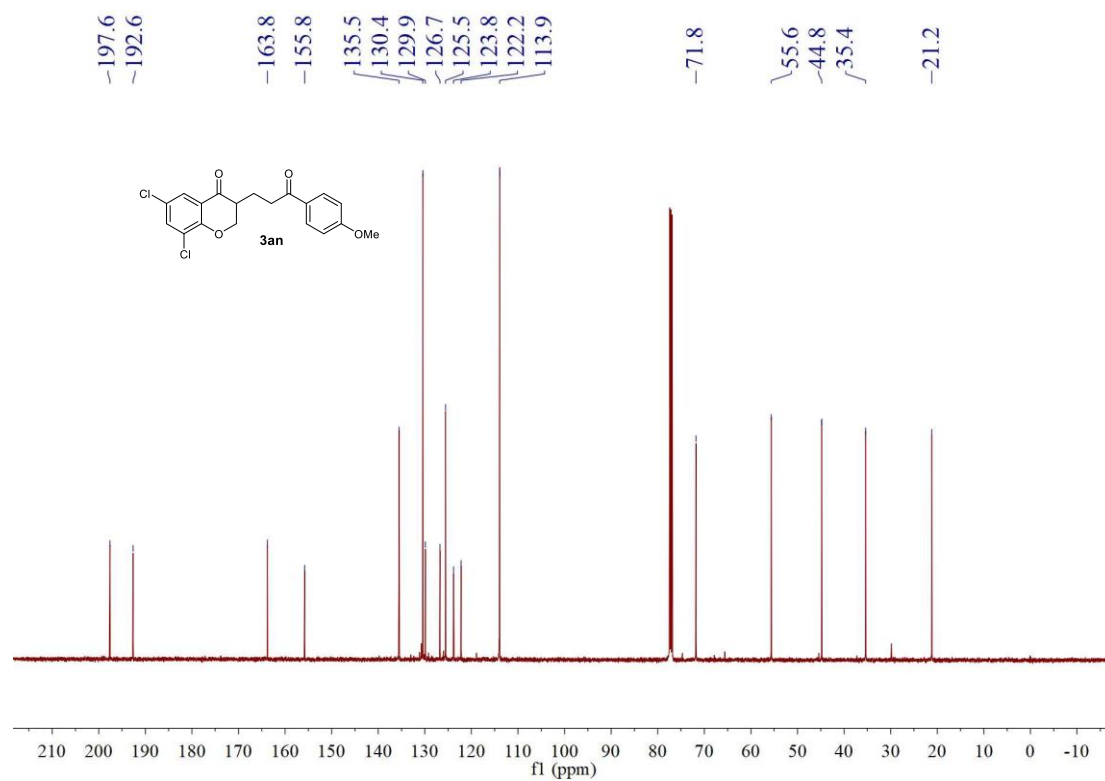
¹³C NMR of **3am** in CDCl₃



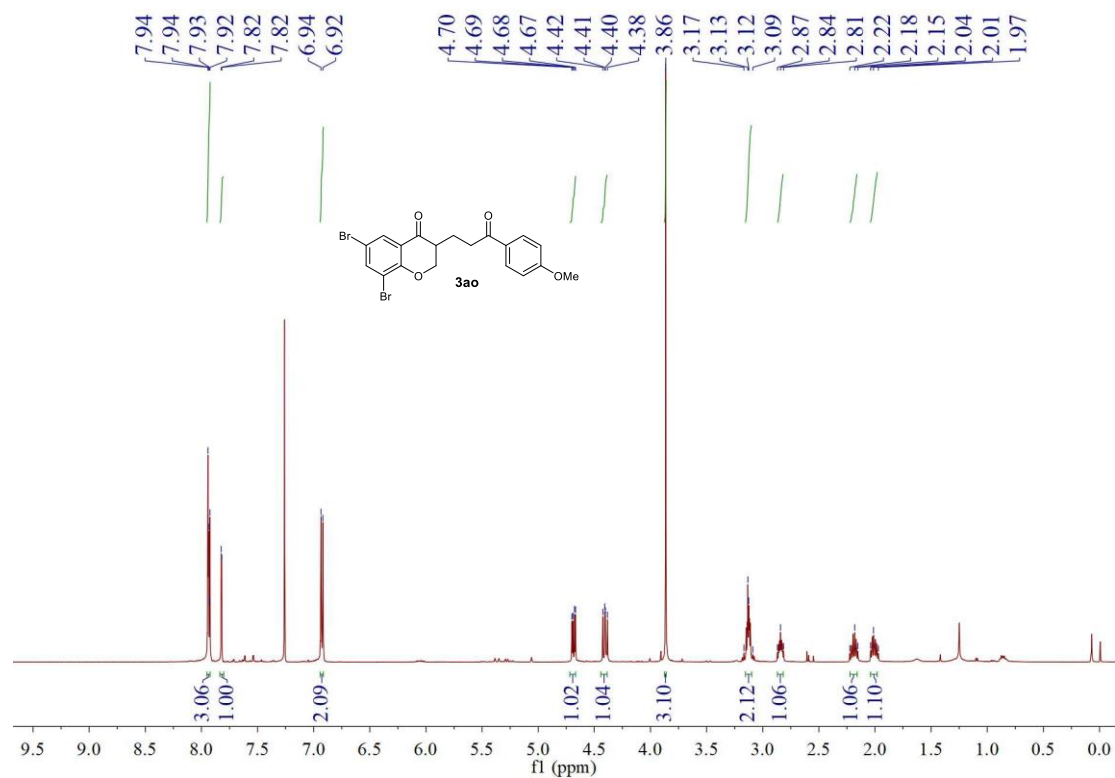
^1H NMR of **3an** in CDCl_3



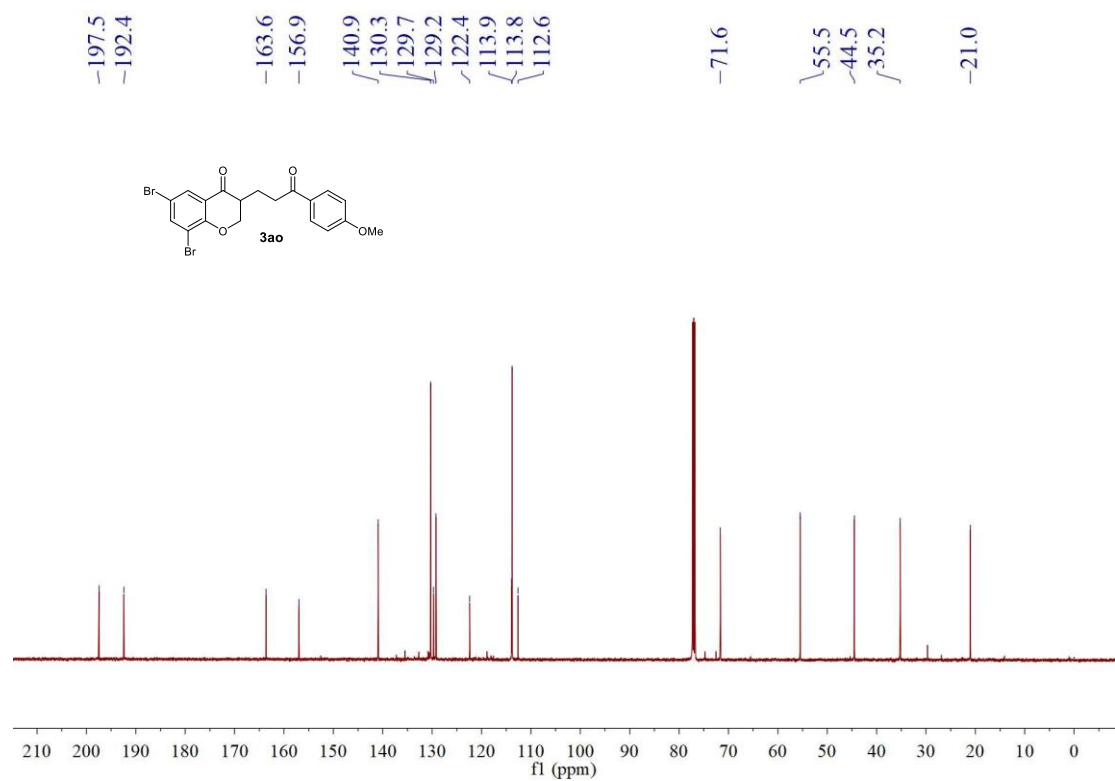
^{13}C NMR of **3an** in CDCl_3



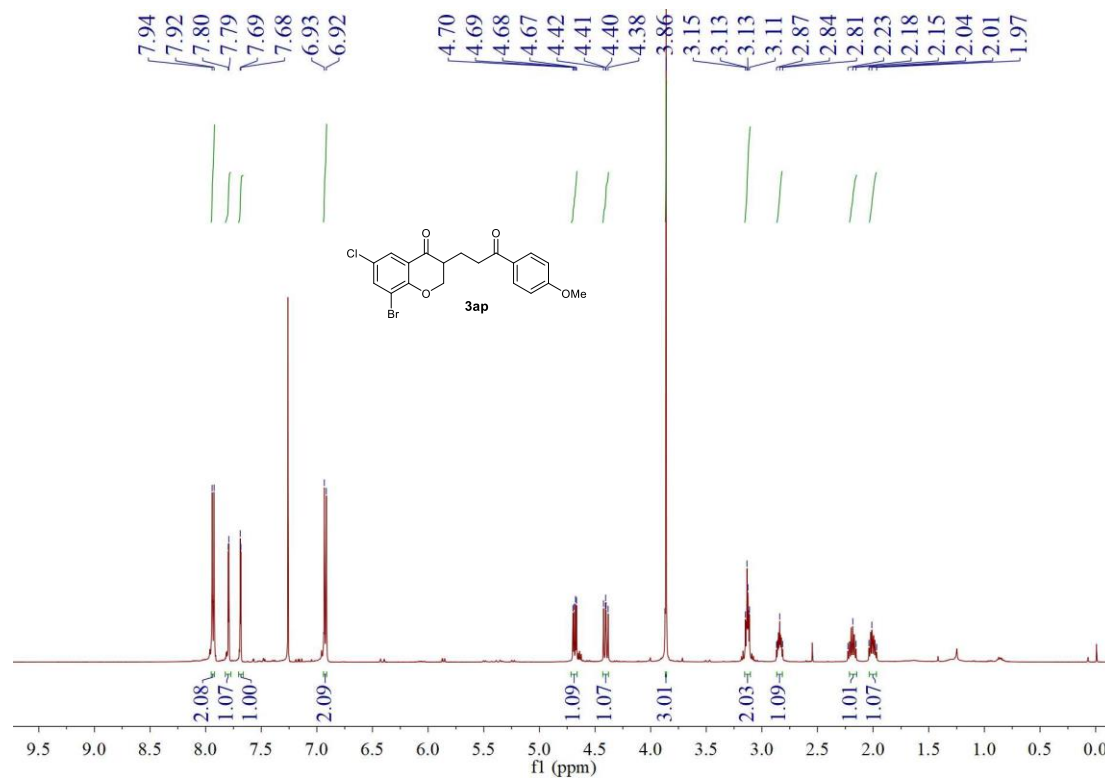
¹H NMR of **3ao** in CDCl₃



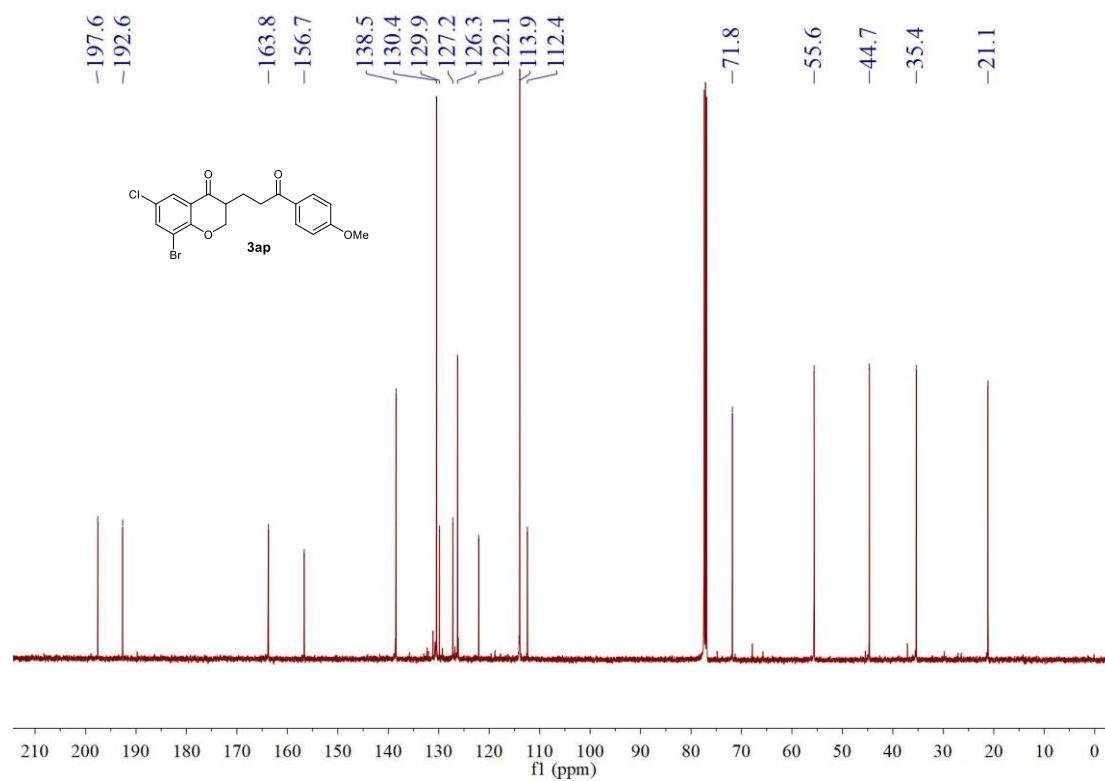
¹³C NMR of **3ao** in CDCl₃



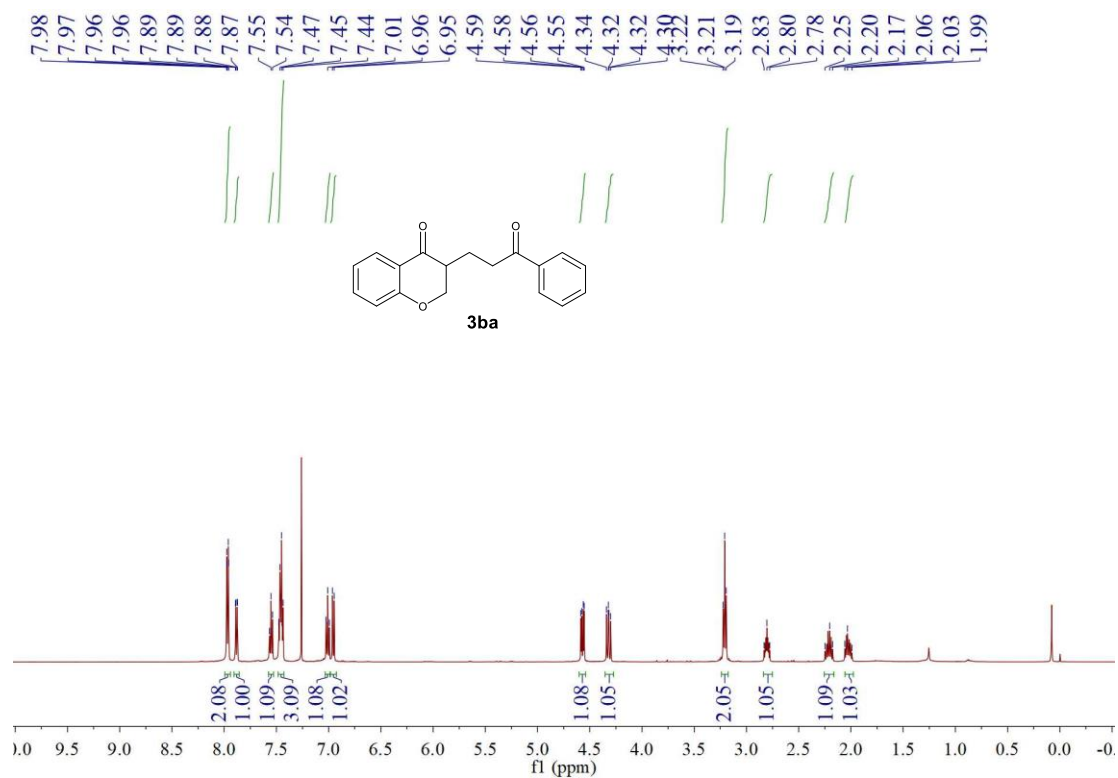
^1H NMR of **3ap** in CDCl_3



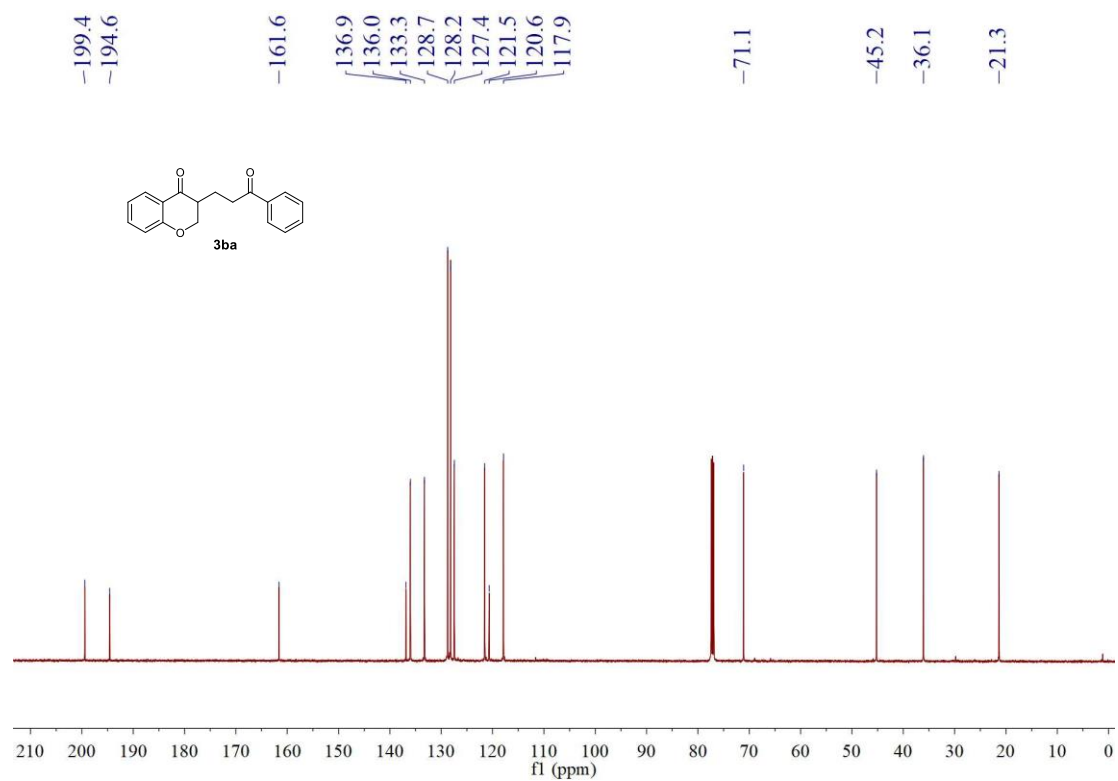
^{13}C NMR of **3ap** in CDCl_3



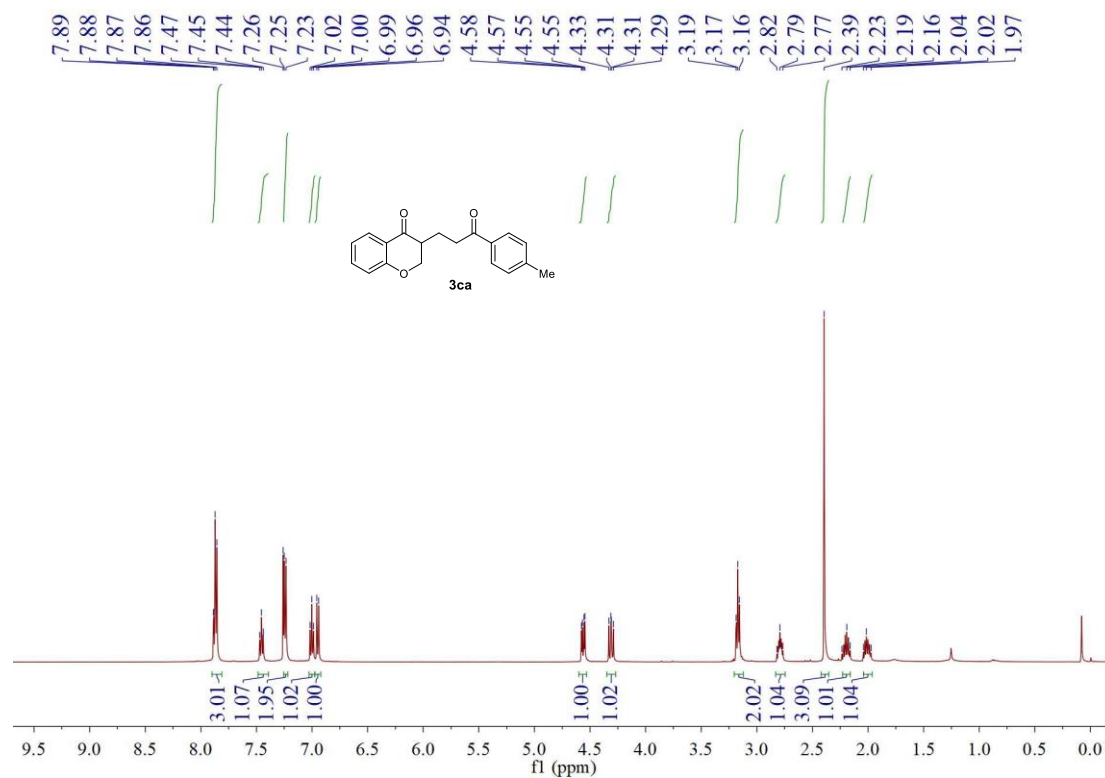
¹H NMR of **3ba** in CDCl₃



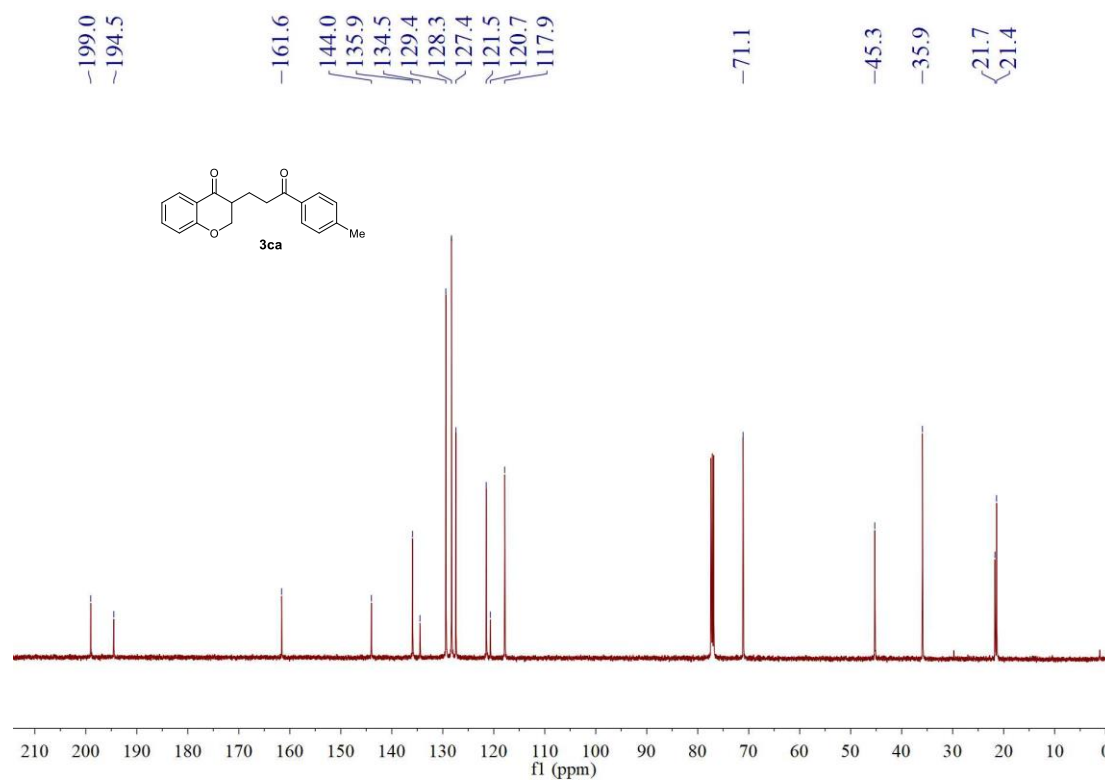
¹³C NMR of **3ba** in CDCl₃



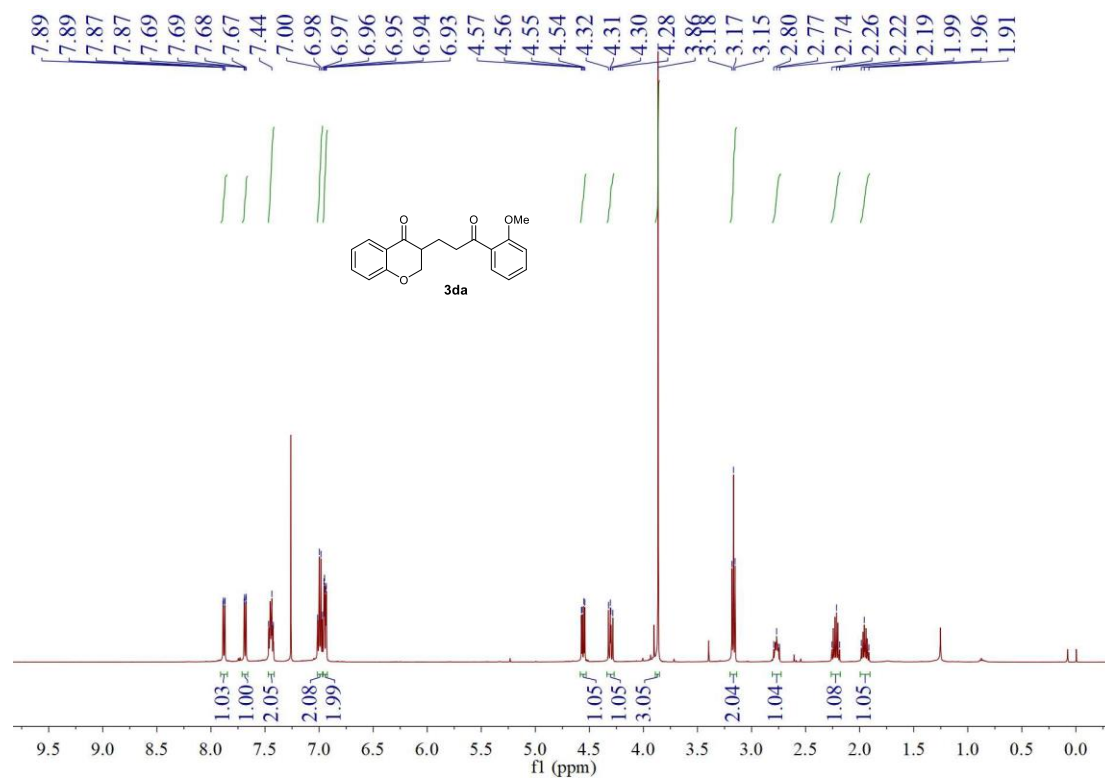
¹H NMR of **3ca** in CDCl₃



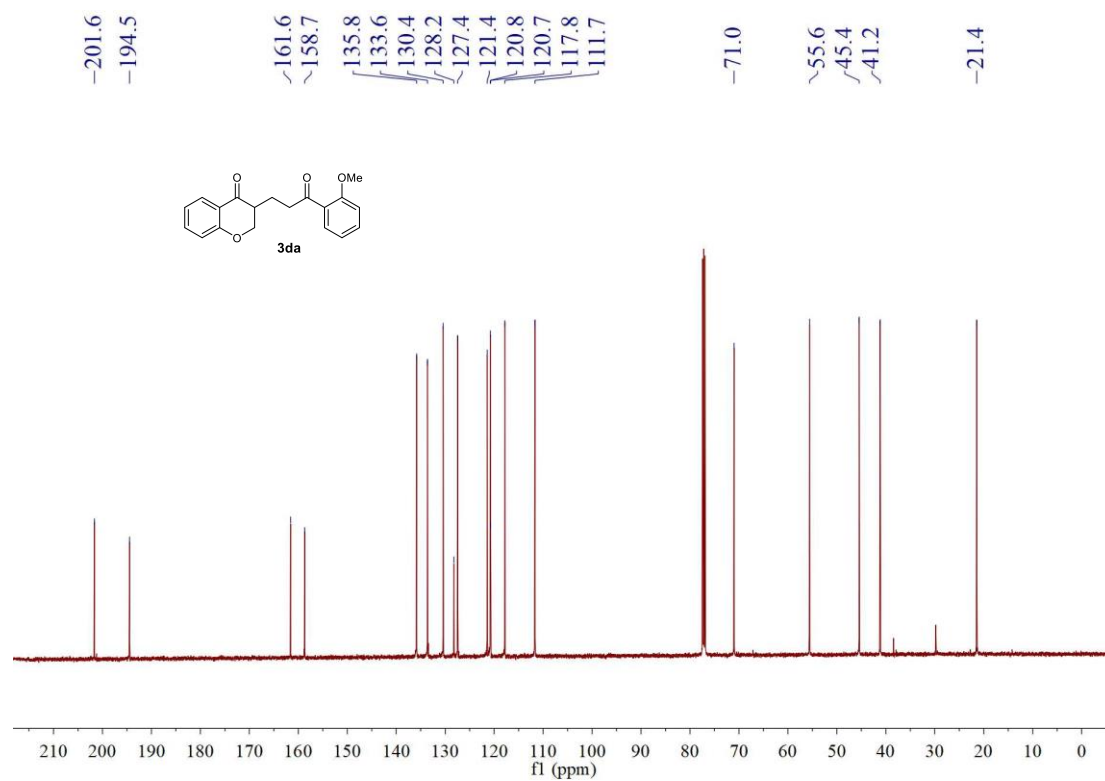
¹³C NMR of **3ca** in CDCl₃



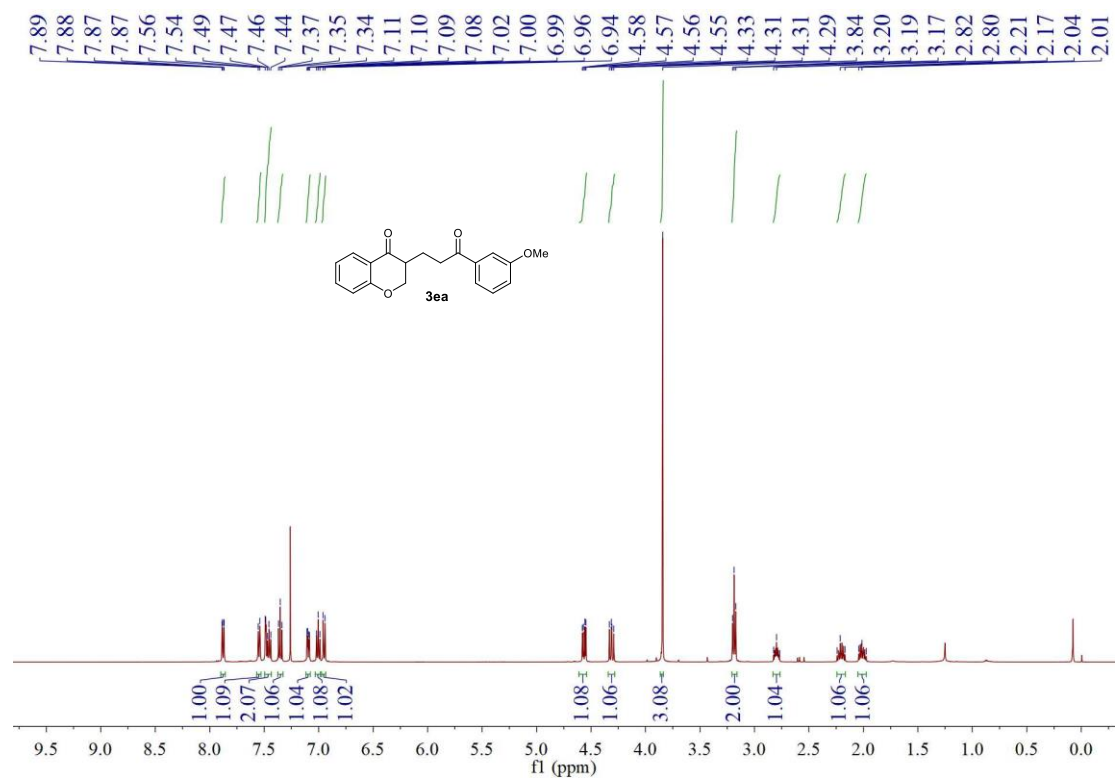
¹H NMR of **3da** in CDCl₃



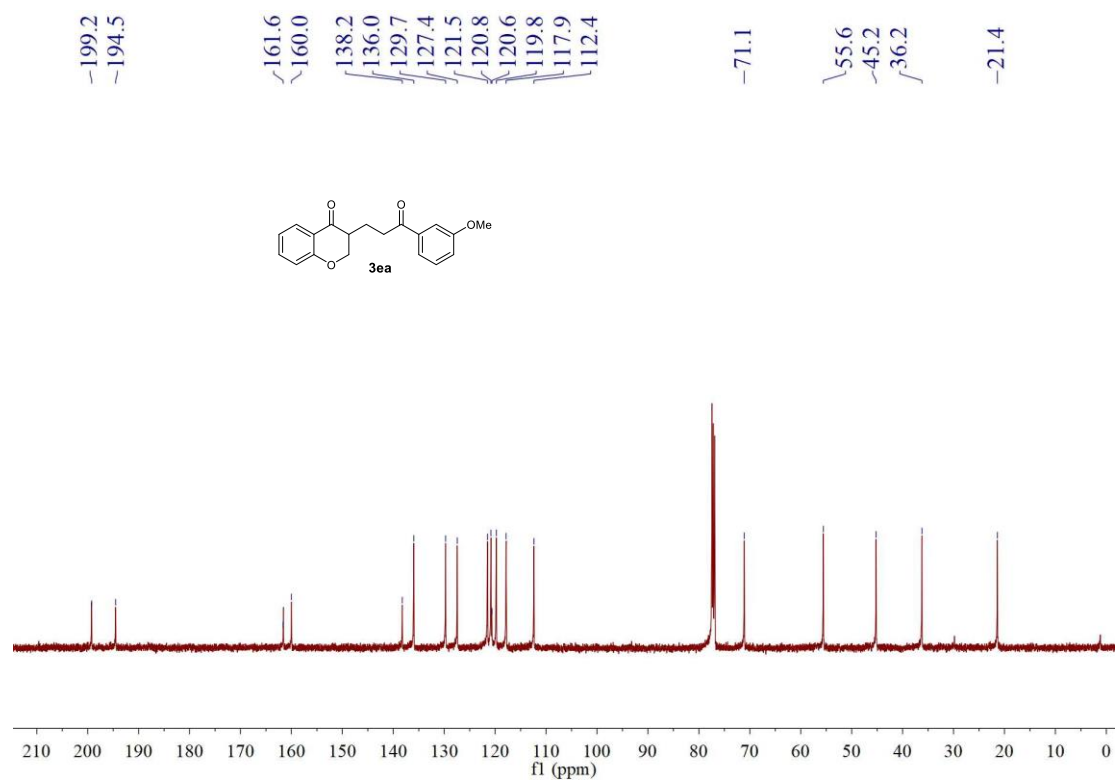
¹³C NMR of **3da** in CDCl₃



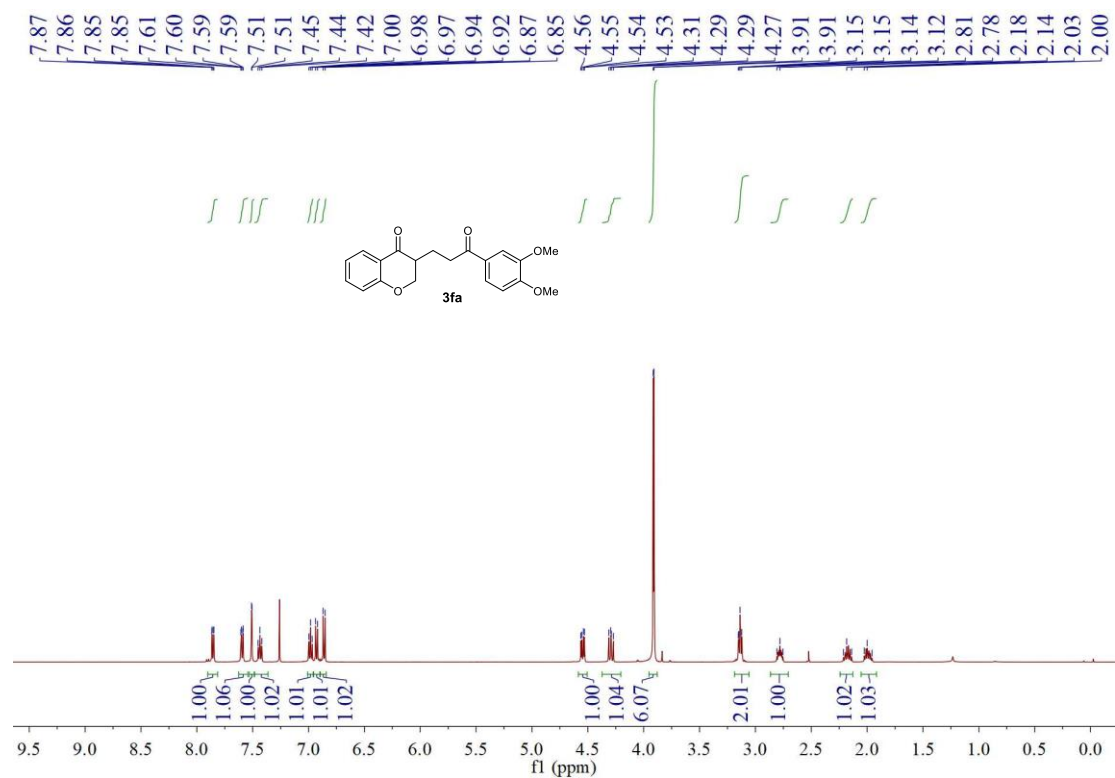
¹H NMR of **3ea** in CDCl₃



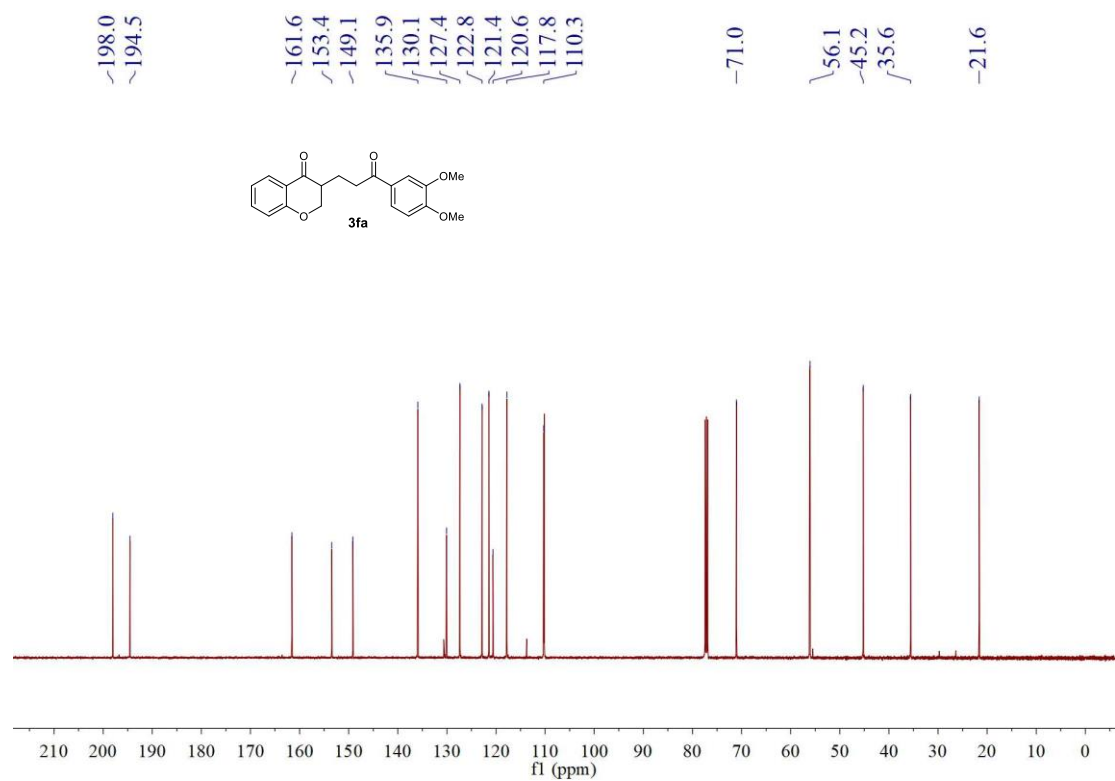
¹³C NMR of **3ea** in CDCl₃



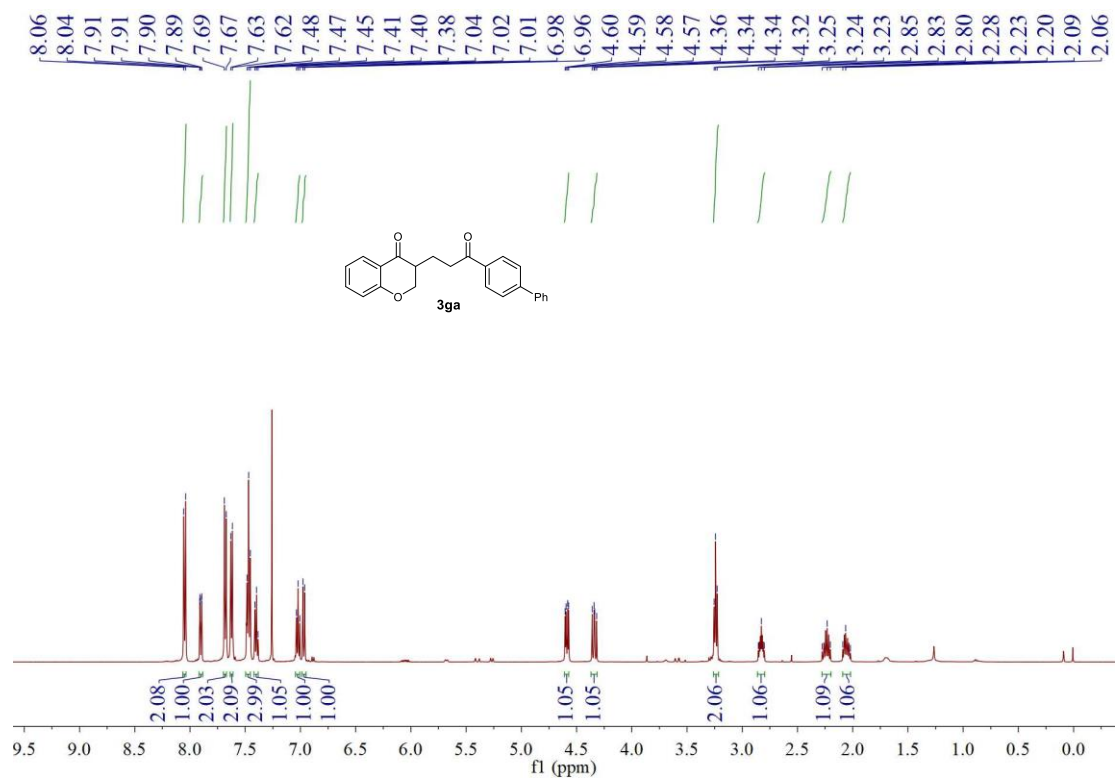
¹H NMR of **3fa** in CDCl₃



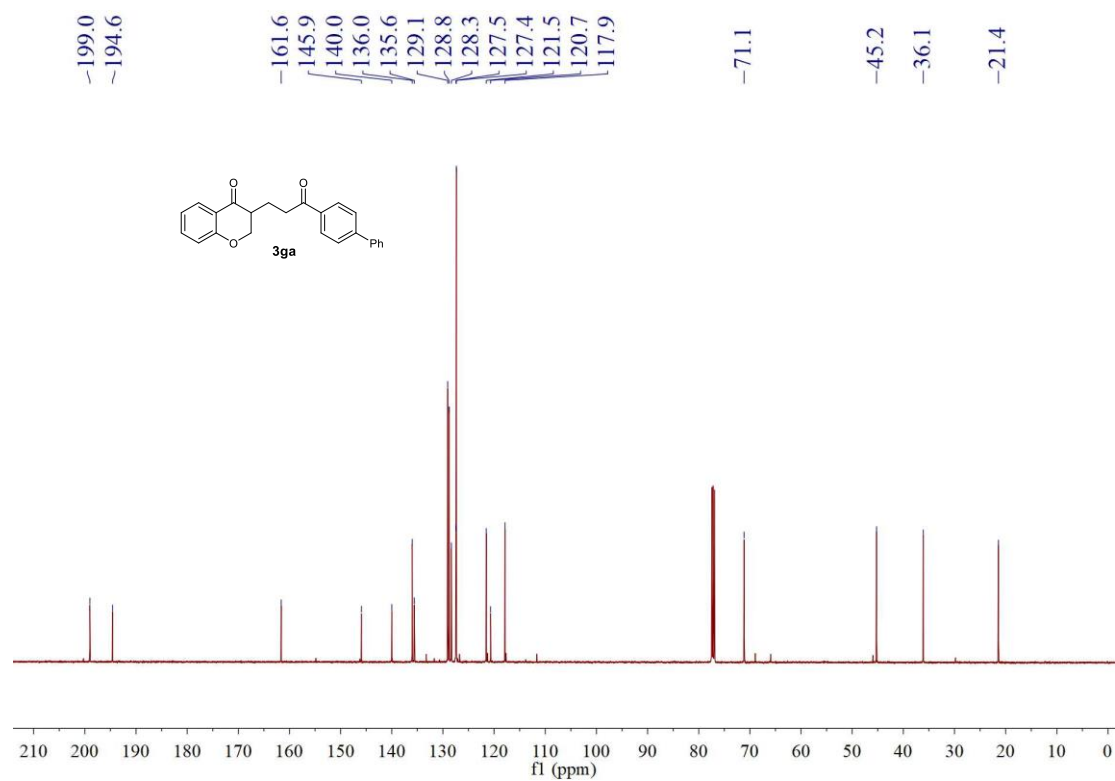
¹³C NMR of **3fa** in CDCl₃



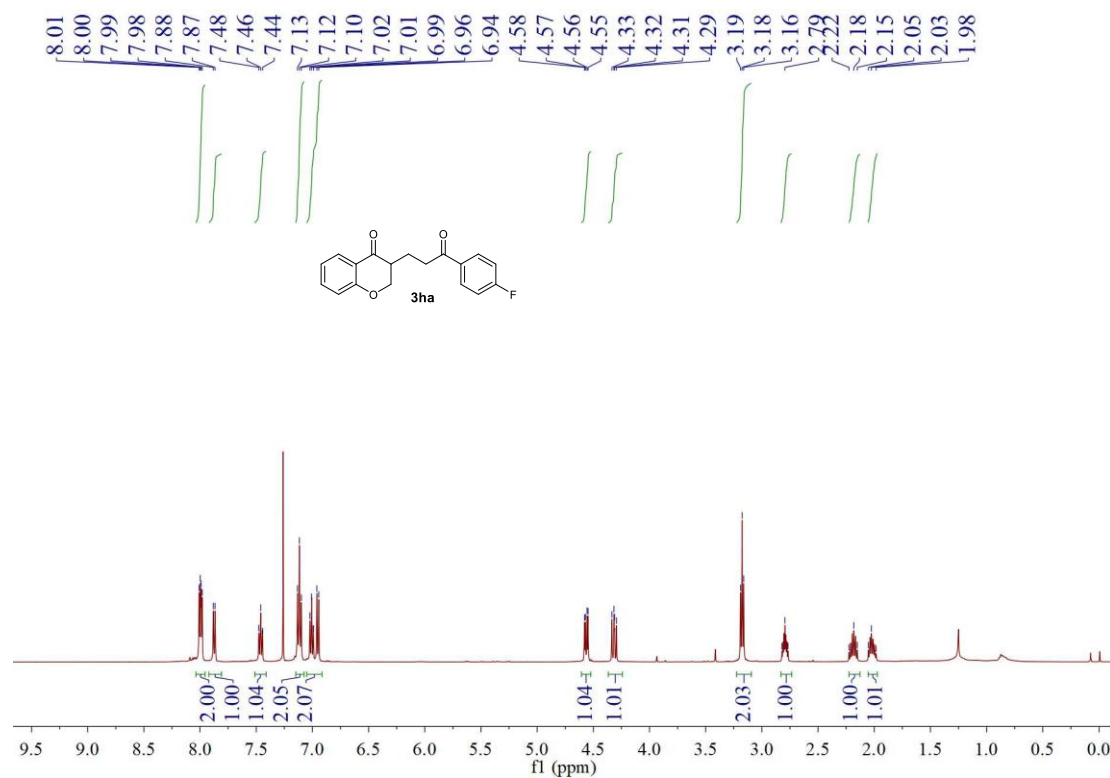
¹H NMR of **3ga** in CDCl₃



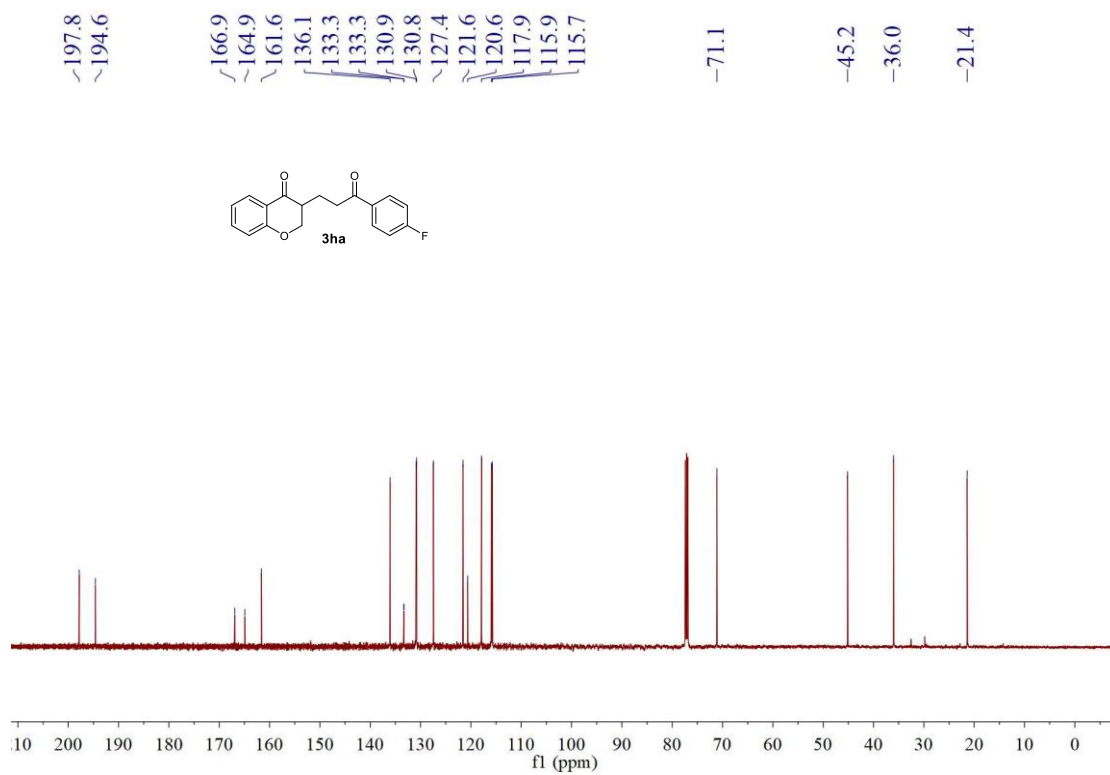
¹³C NMR of **3ga** in CDCl₃



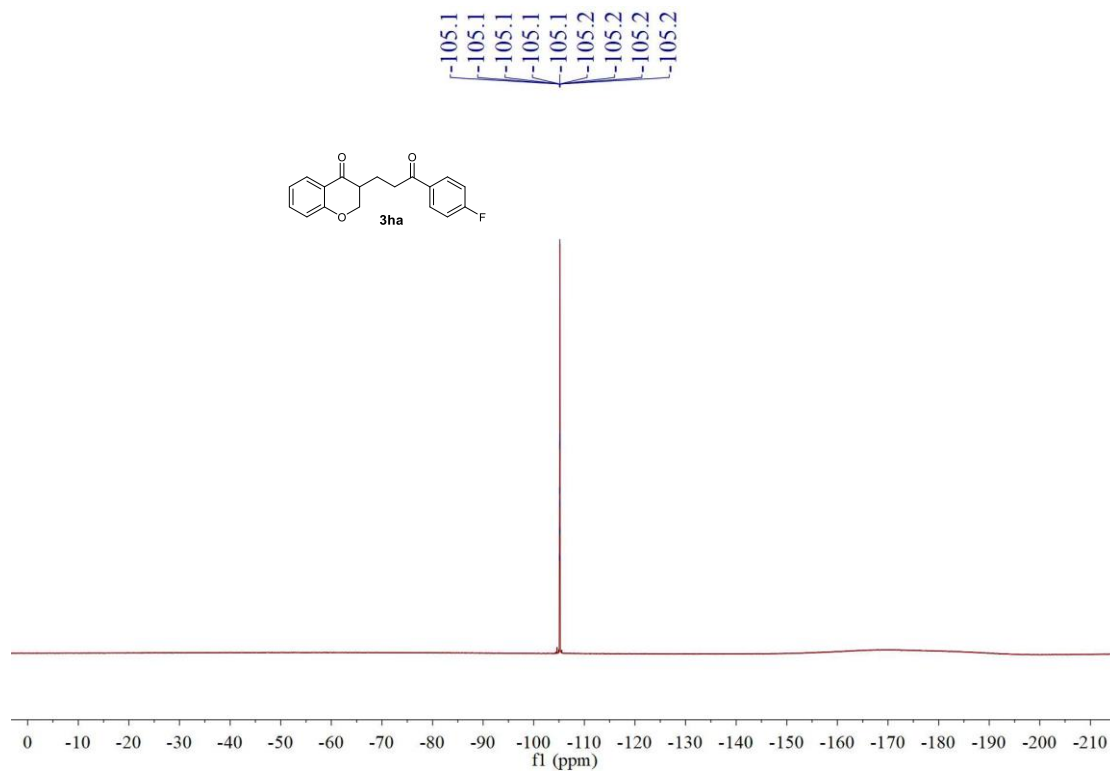
¹H NMR of **3ha** in CDCl₃



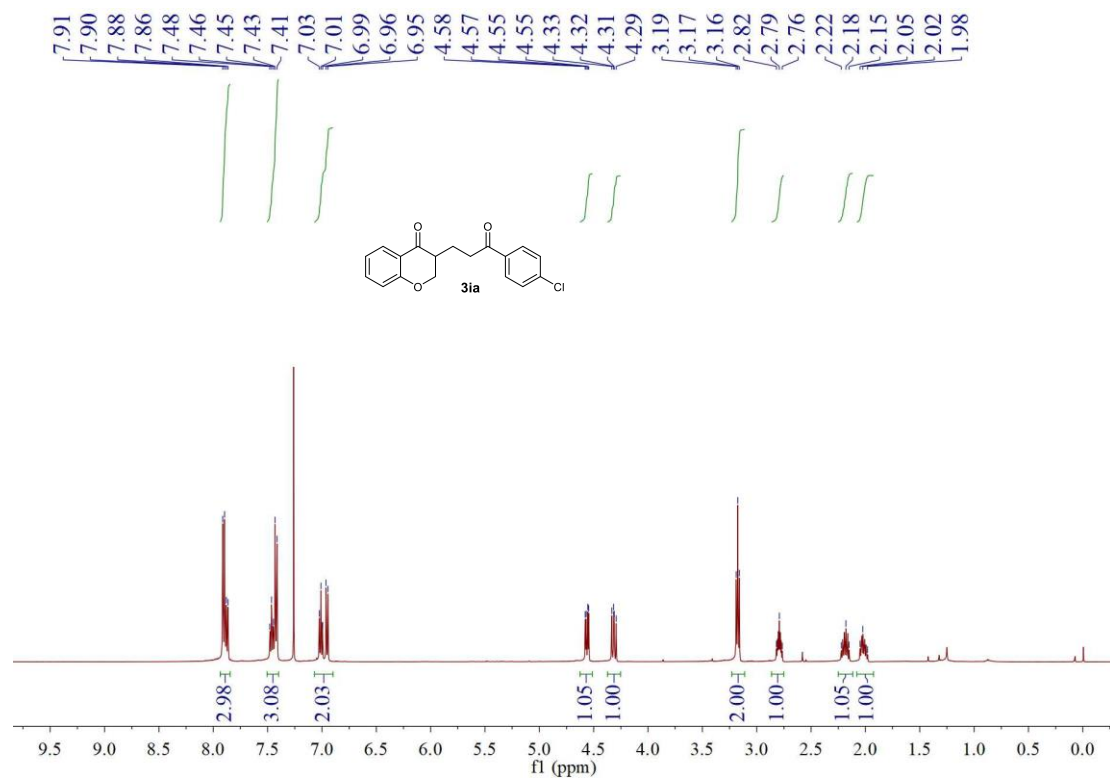
¹³C NMR of **3ha** in CDCl₃



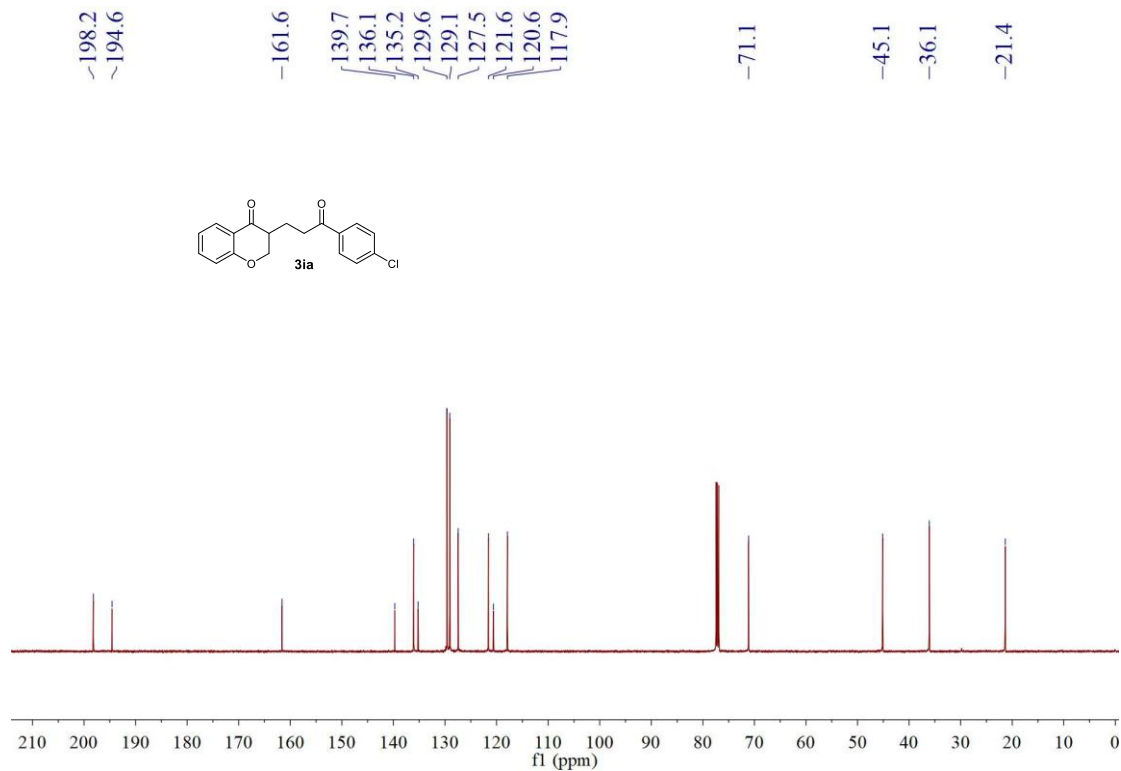
^{19}F NMR of **3ha** in CDCl_3



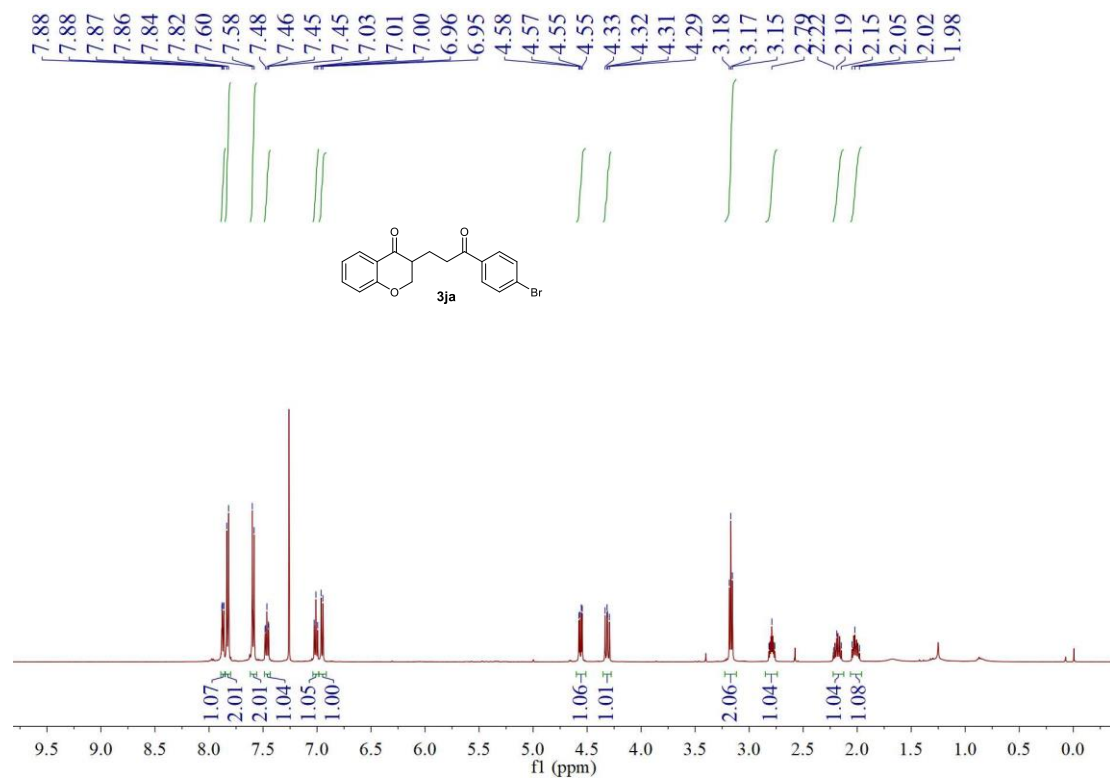
^1H NMR of **3ia** in CDCl_3



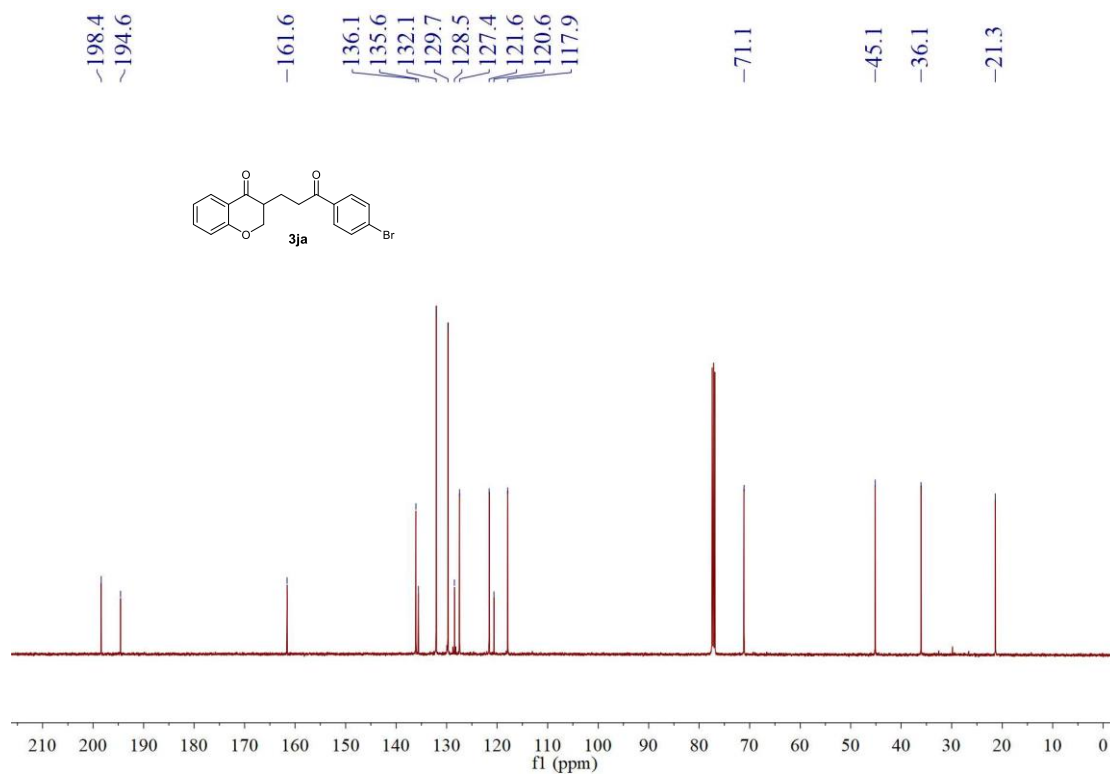
¹³C NMR of **3ia** in CDCl₃



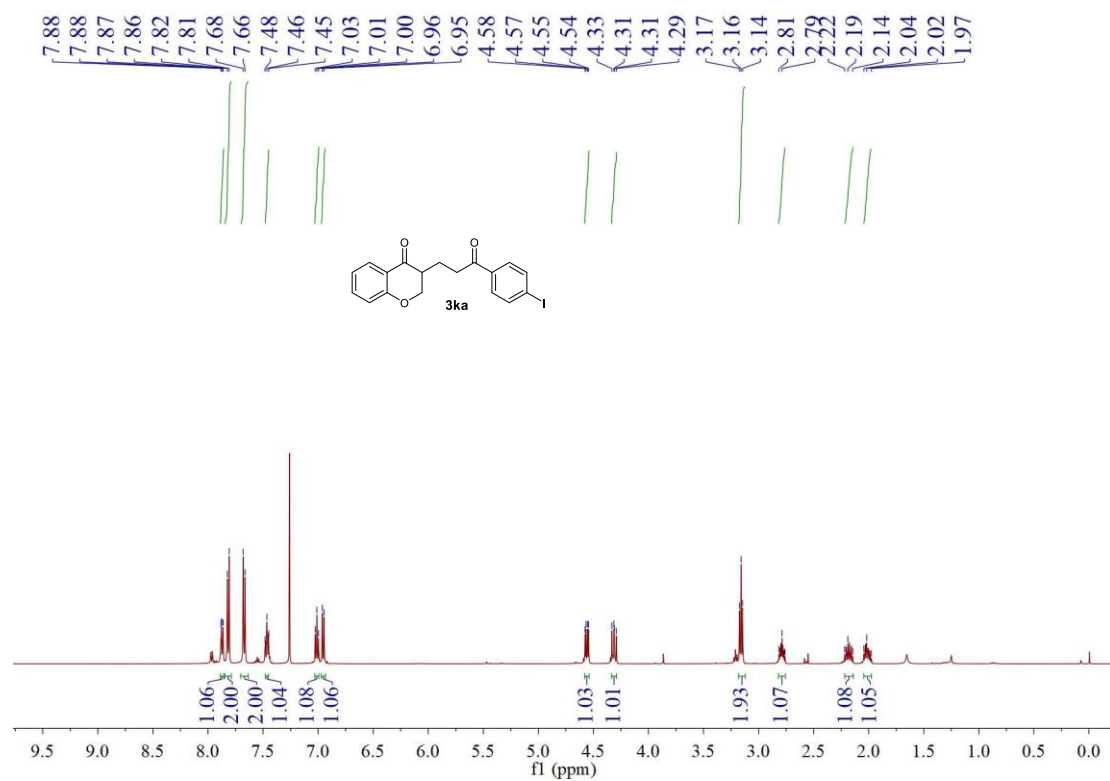
¹H NMR of **3ja** in CDCl₃



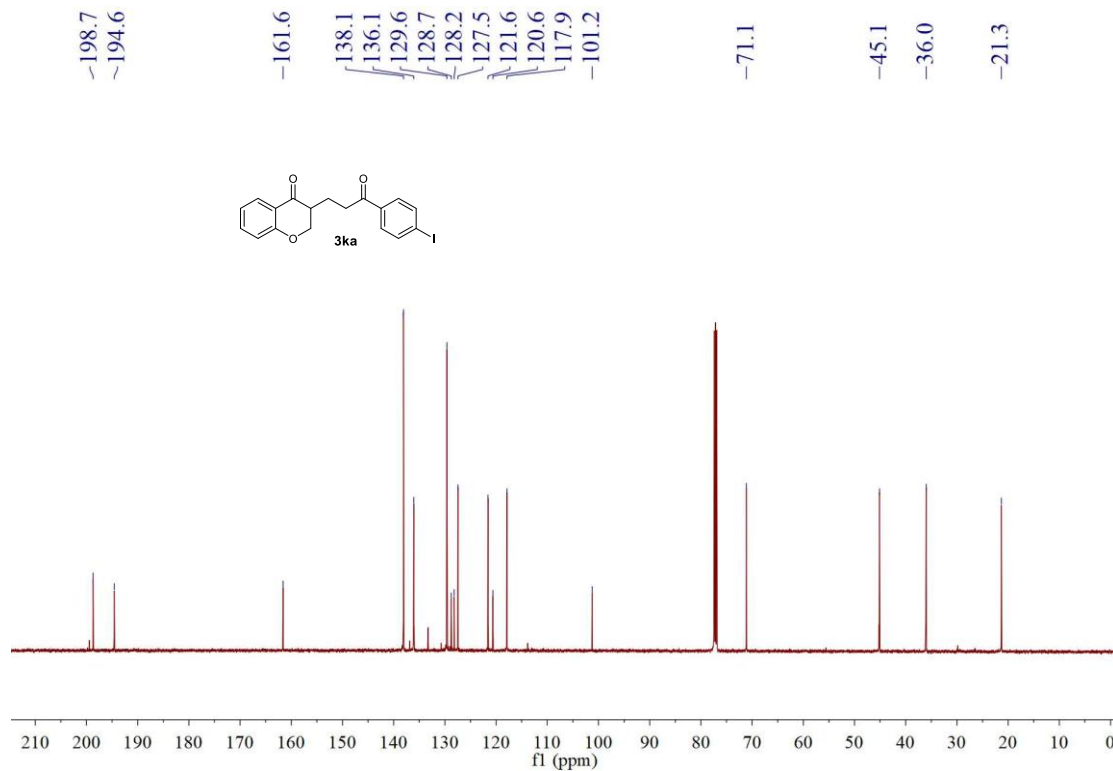
^{13}C NMR of **3ja** in CDCl_3



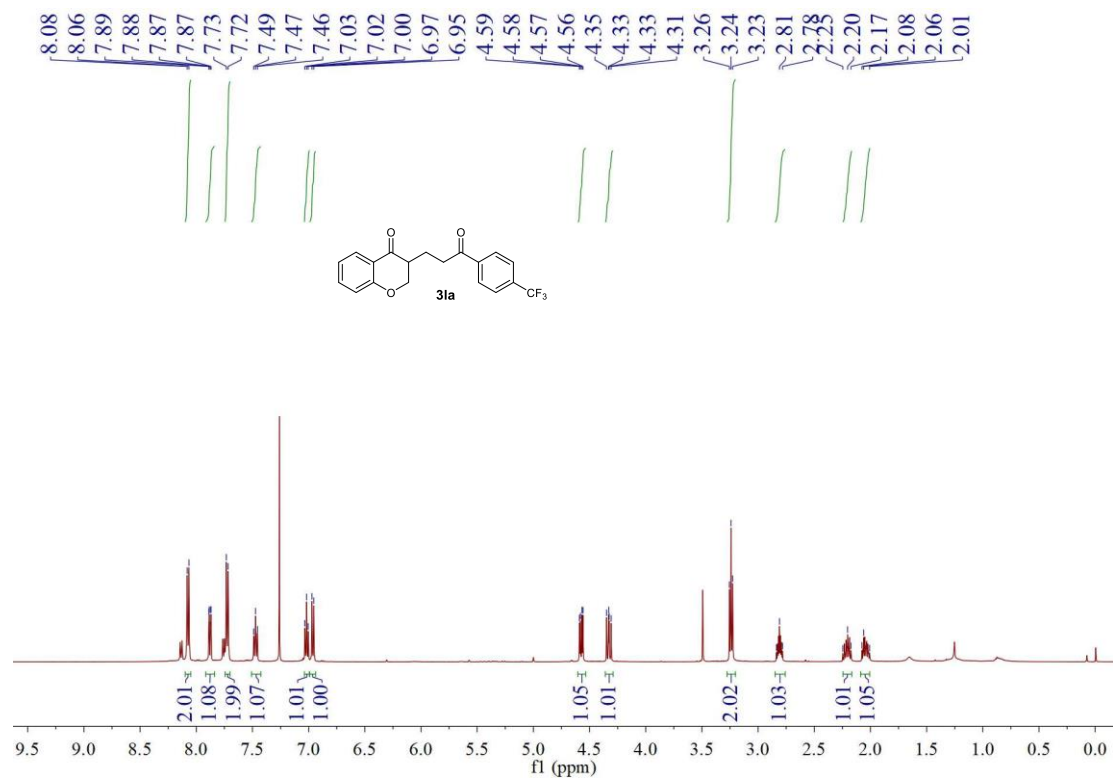
^1H NMR of **3ka** in CDCl_3



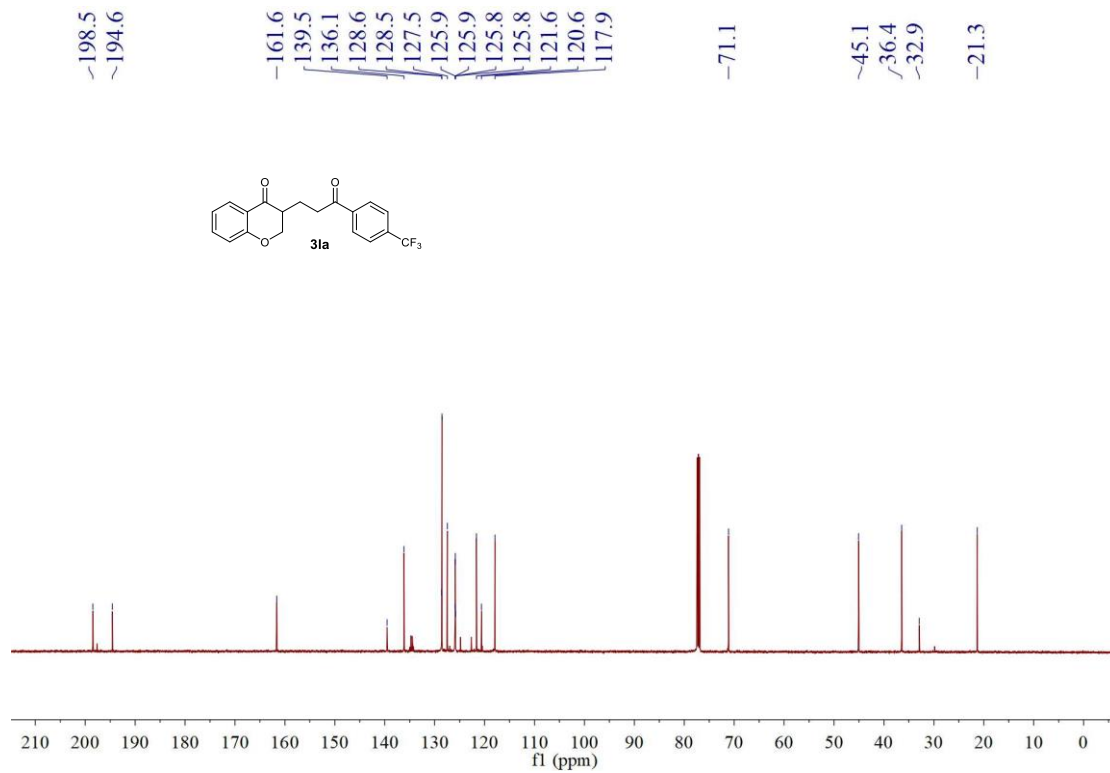
¹³C NMR of **3ka** in CDCl₃



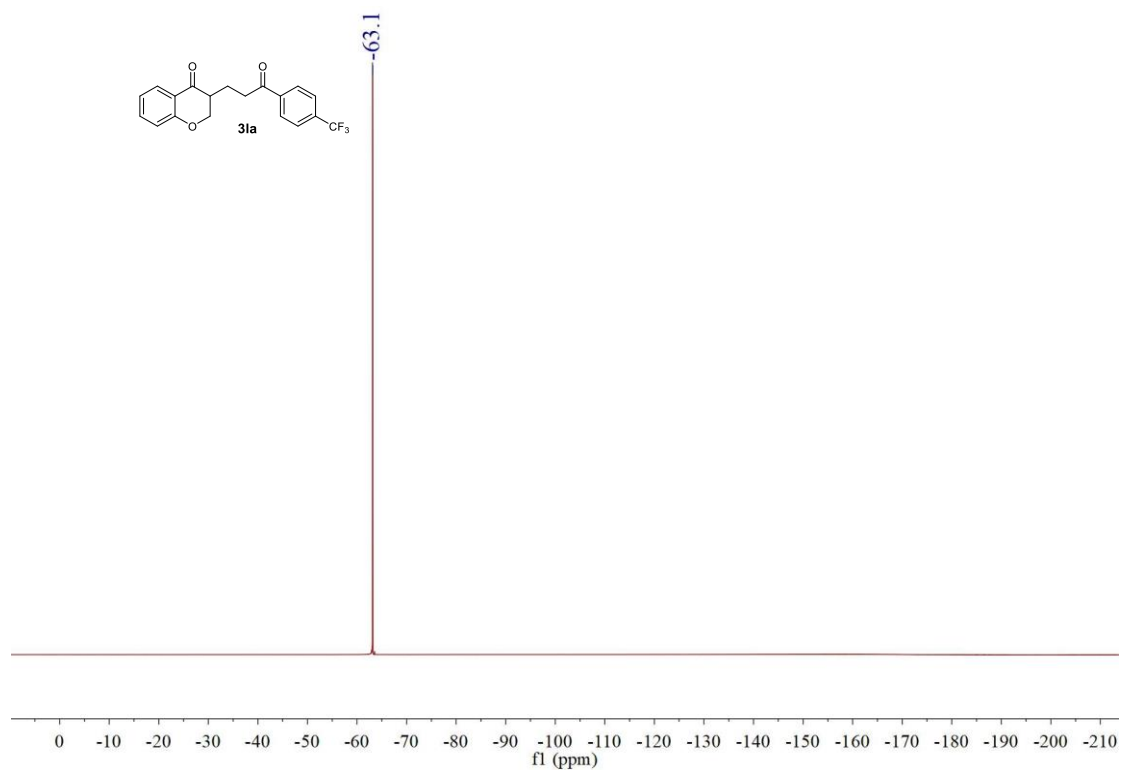
¹H NMR of **3la** in CDCl₃



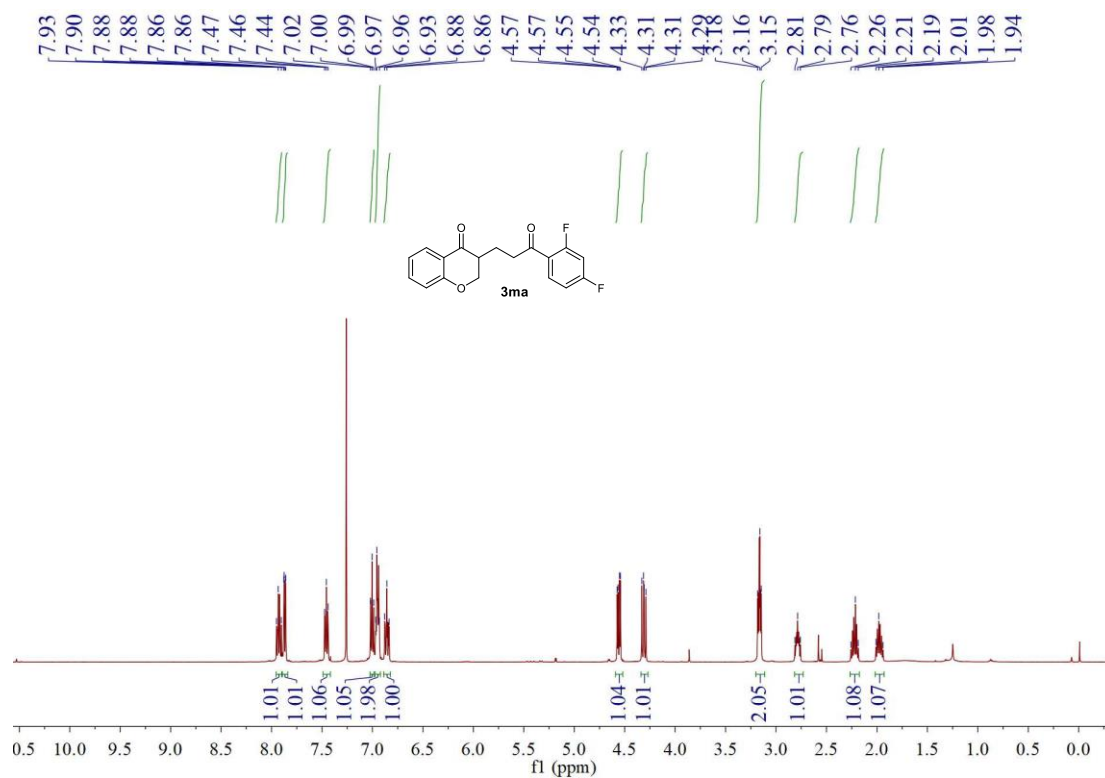
¹³C NMR of **3la** in CDCl₃



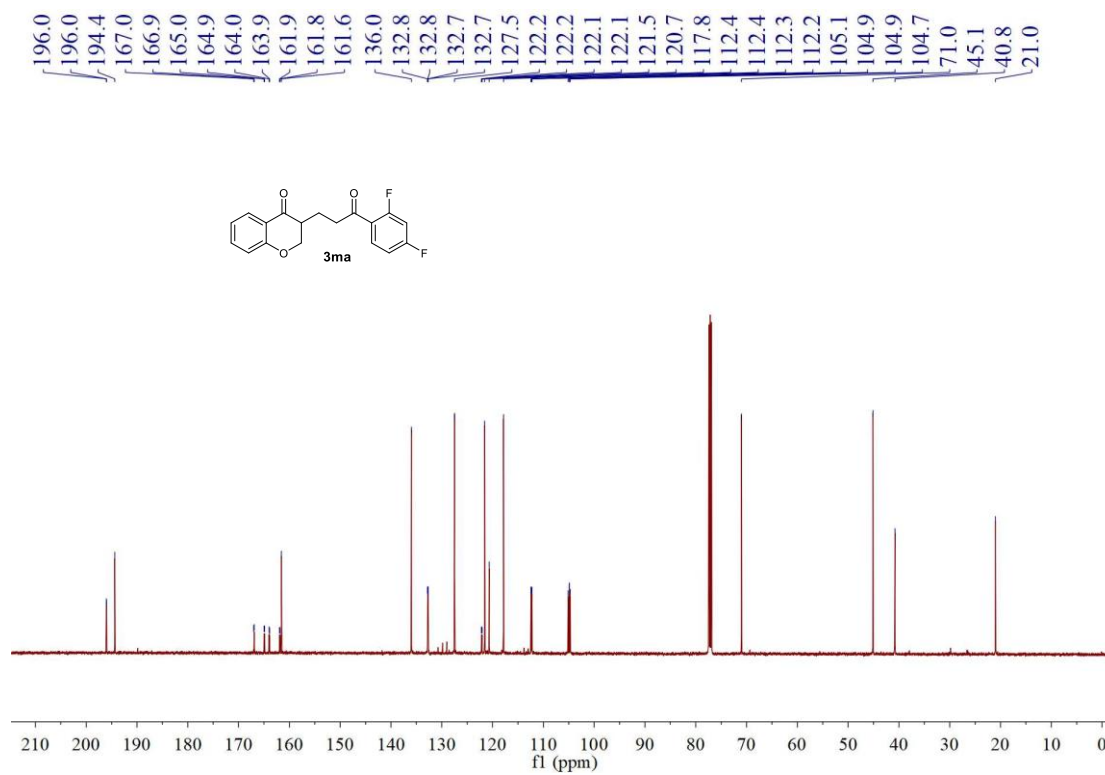
¹⁹F NMR of **3la** in CDCl₃



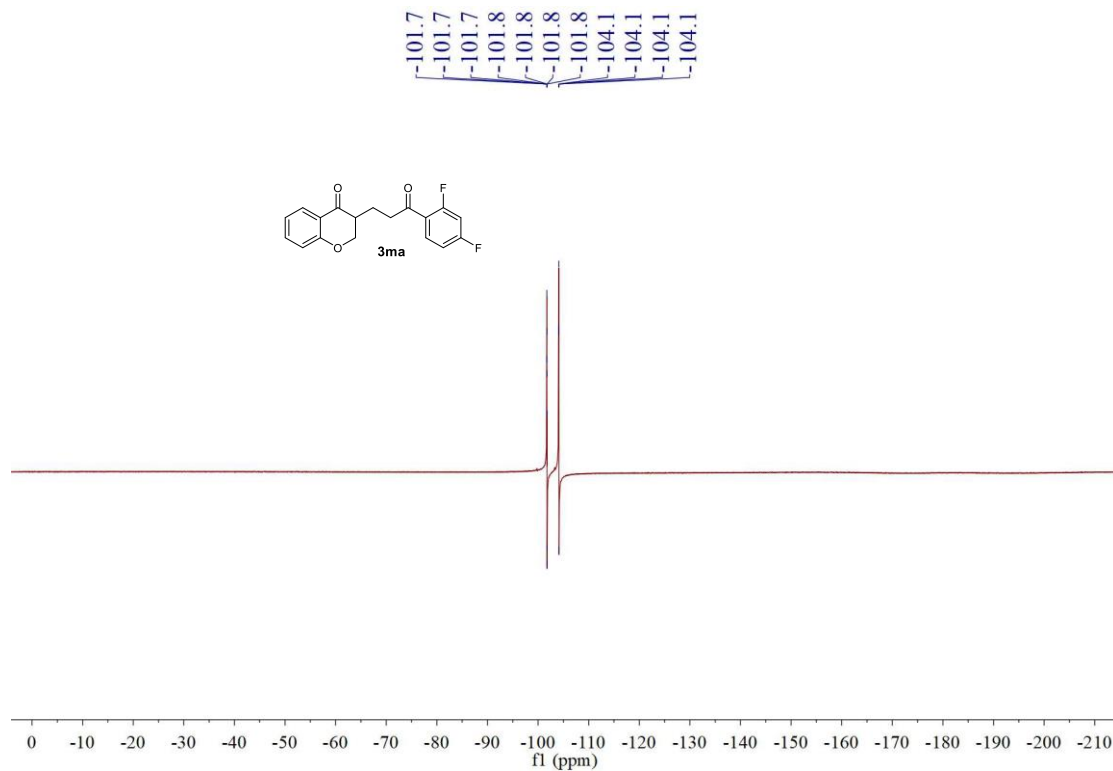
¹H NMR of **3ma** in CDCl₃



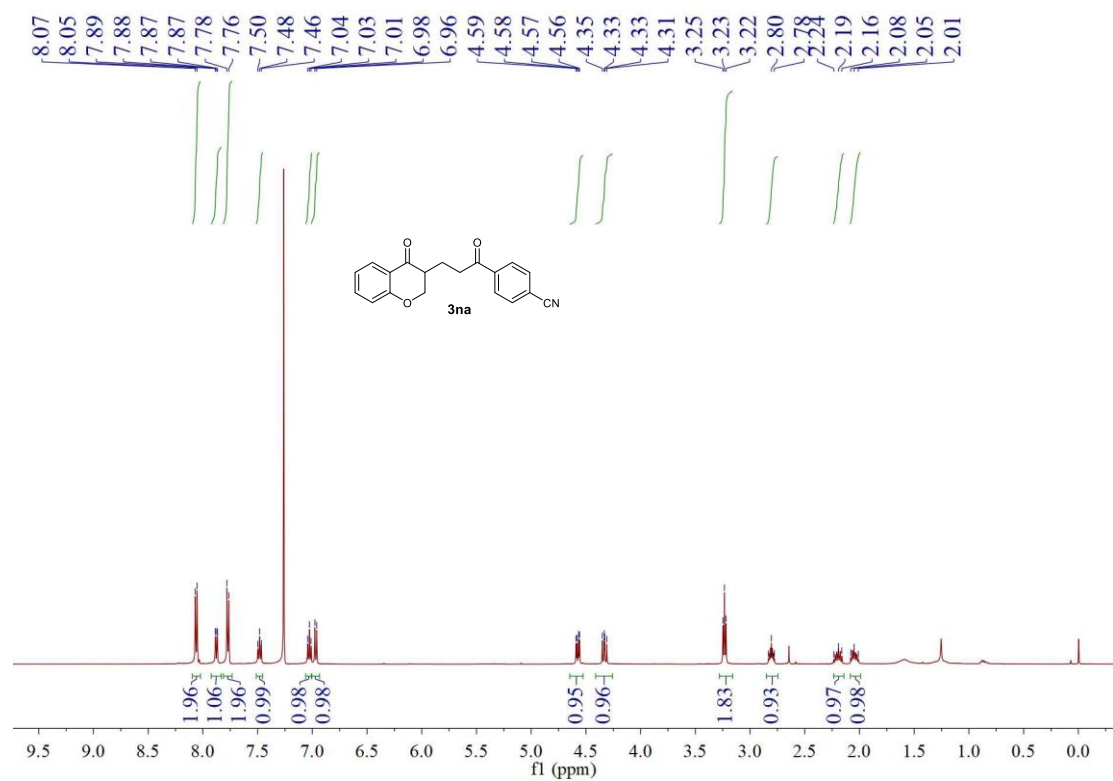
¹³C NMR of **3ma** in CDCl₃



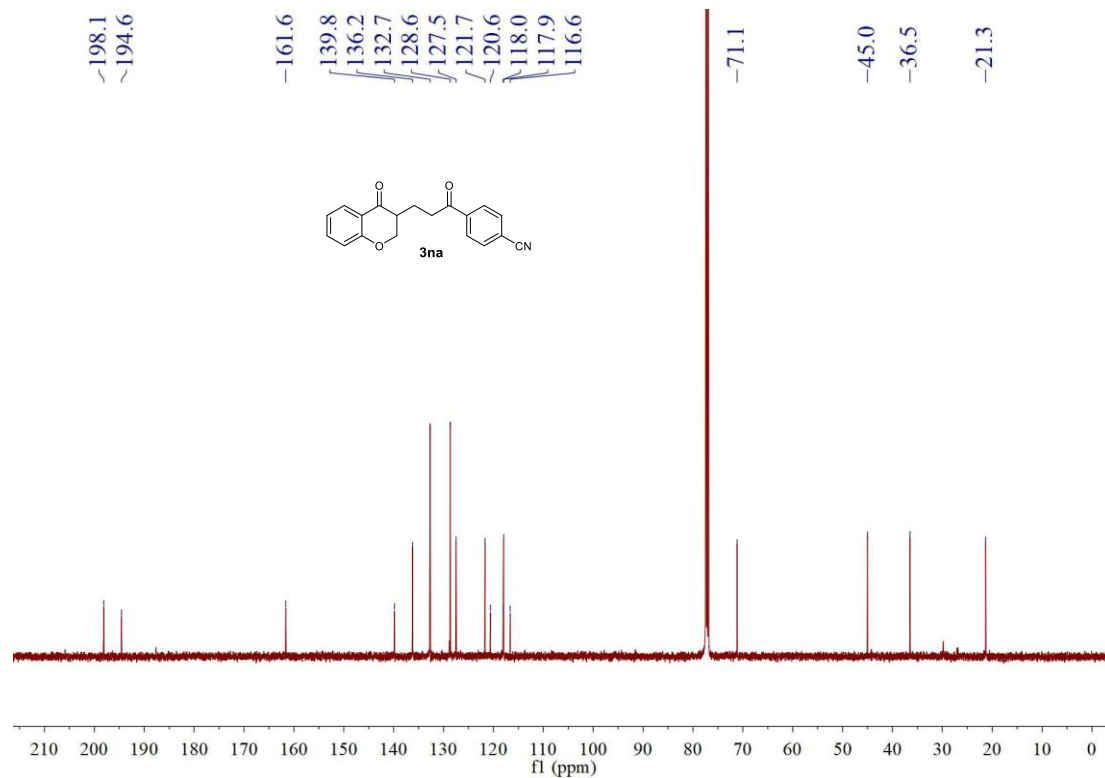
^{19}F NMR of **3ma** in CDCl_3



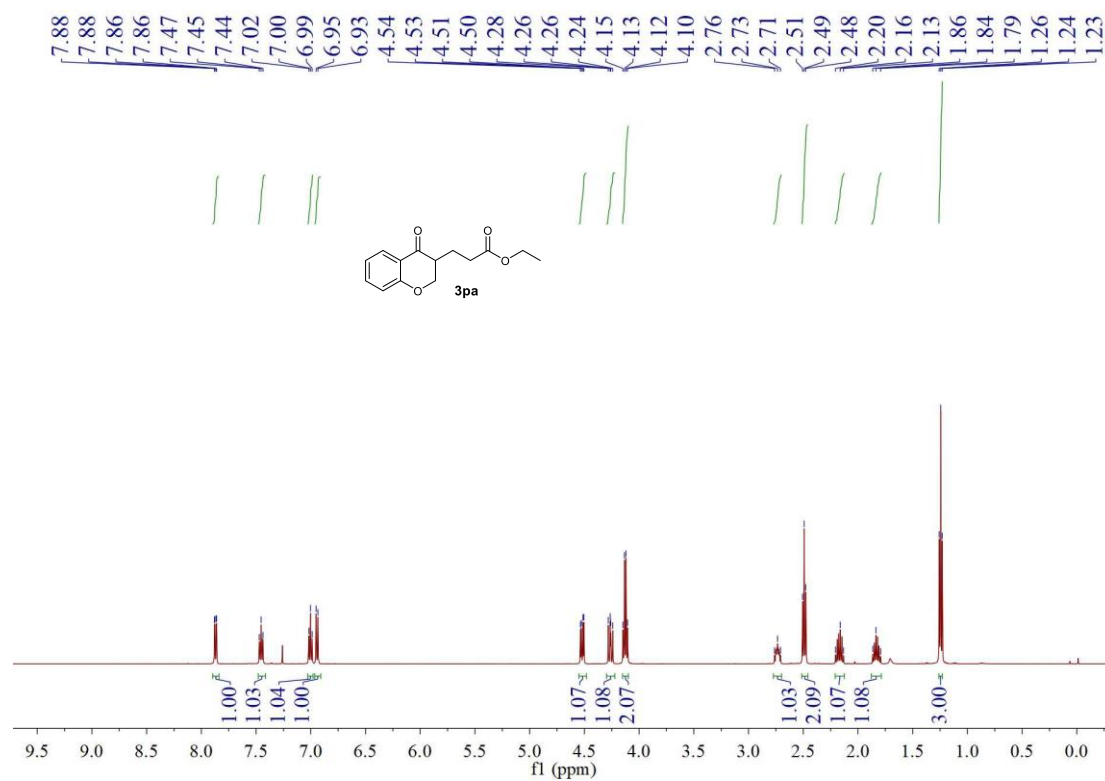
^1H NMR of **3na** in CDCl_3



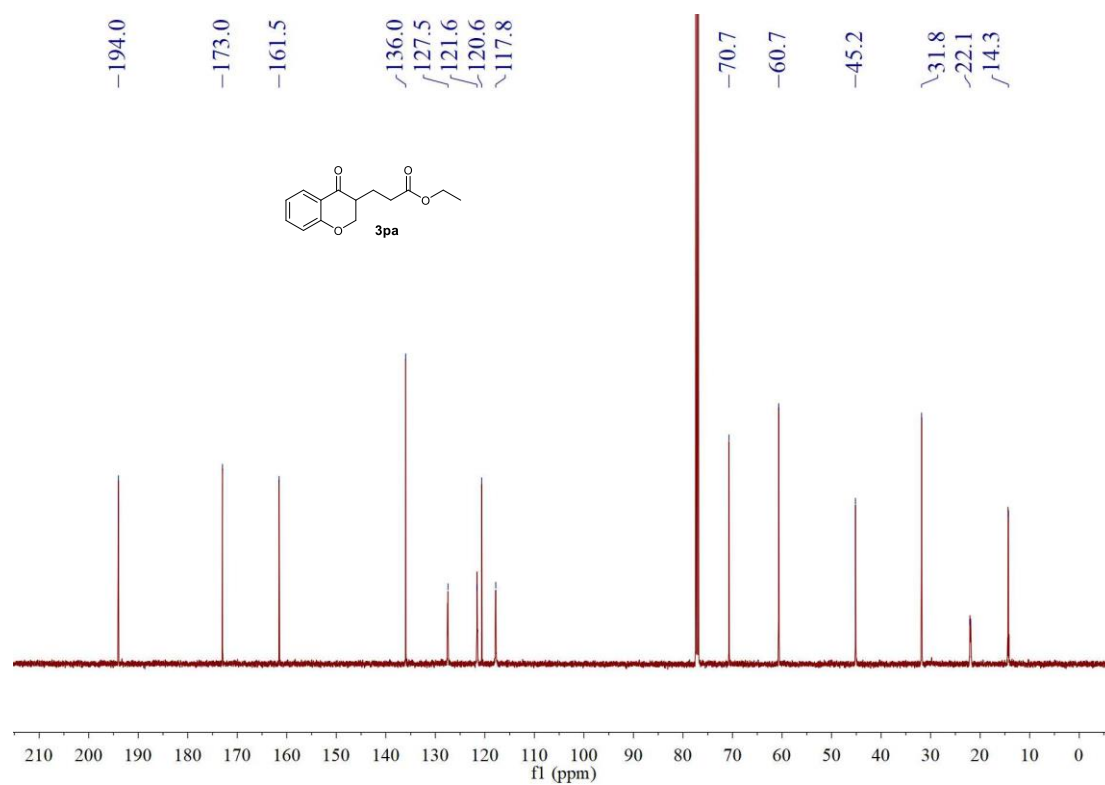
¹³C NMR of **3na** in CDCl₃



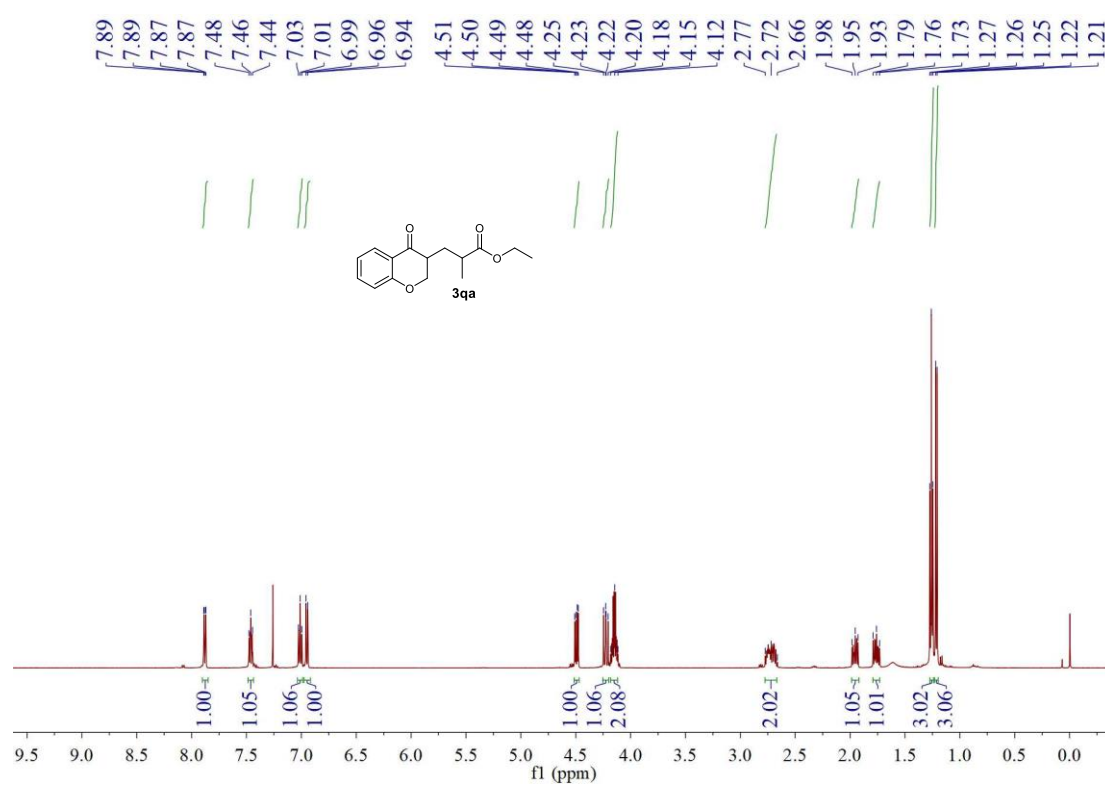
¹H NMR of **3pa** in CDCl₃



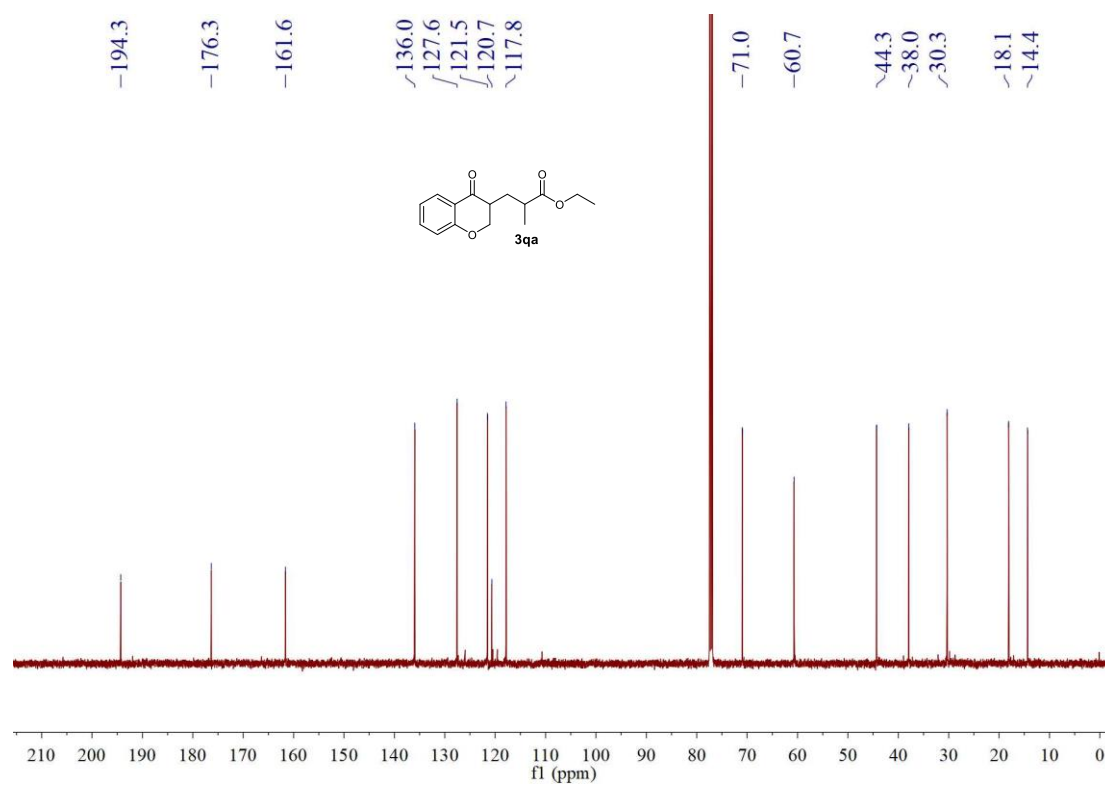
¹³C NMR of **3pa** in CDCl₃



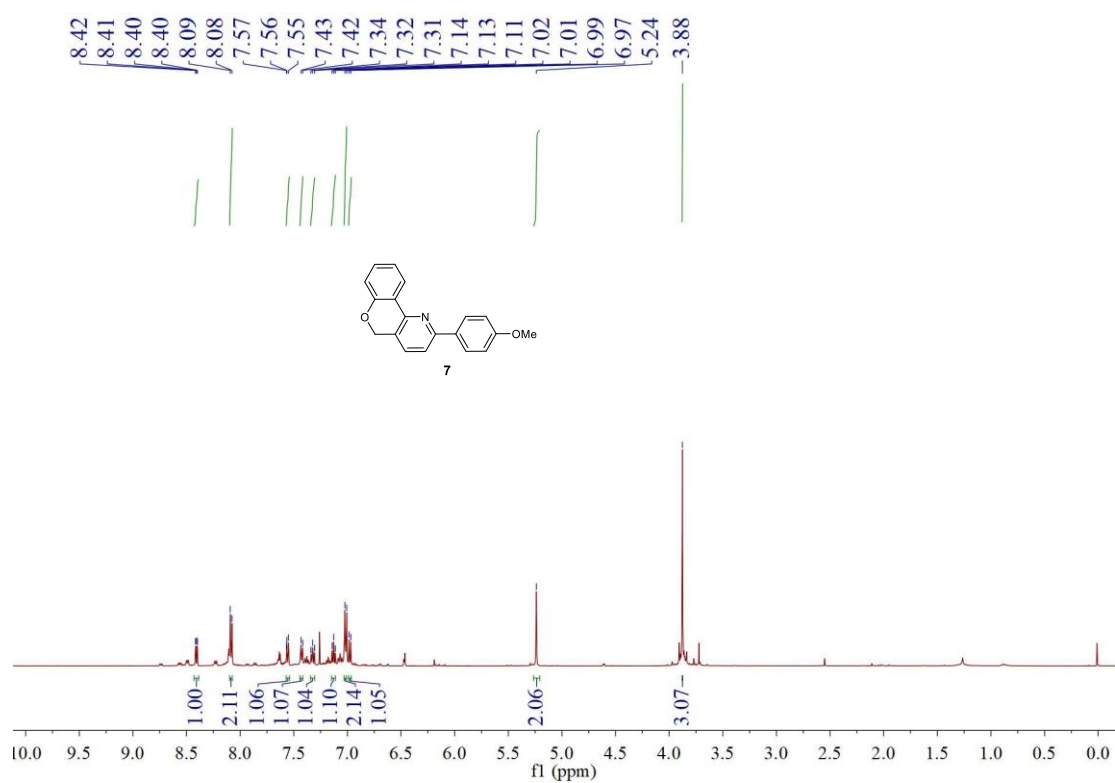
¹H NMR of **3qa** in CDCl₃



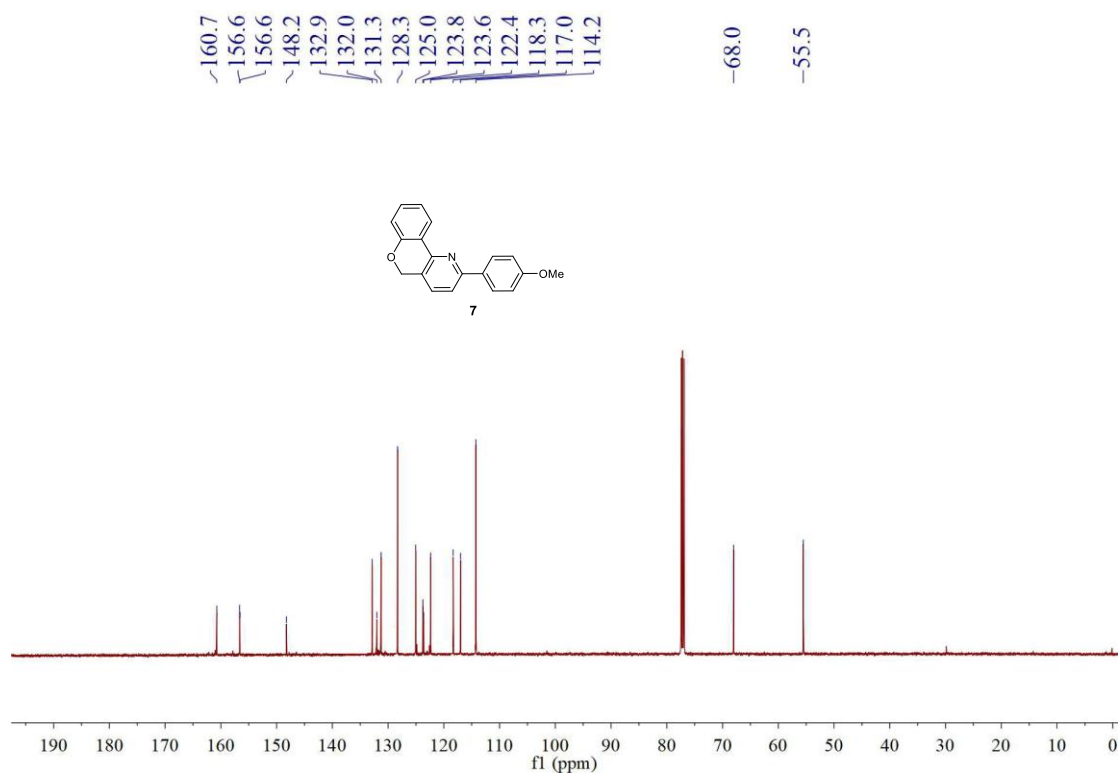
¹³C NMR of **3qa** in CDCl₃



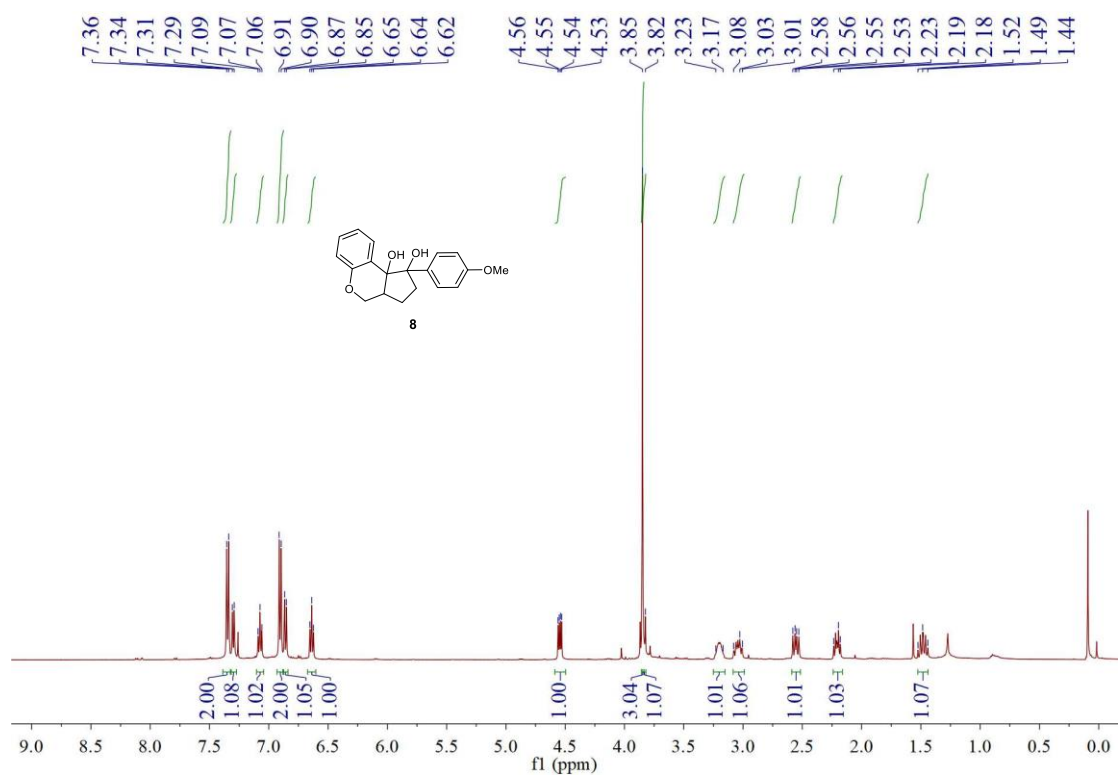
¹H NMR of **7** in CDCl₃



^{13}C NMR of **7** in CDCl_3

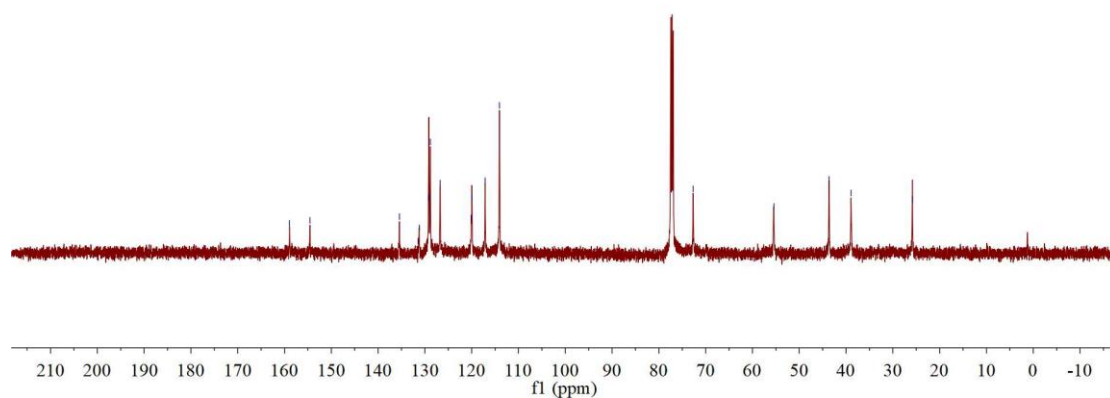
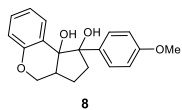


^1H NMR of **8** in CDCl_3



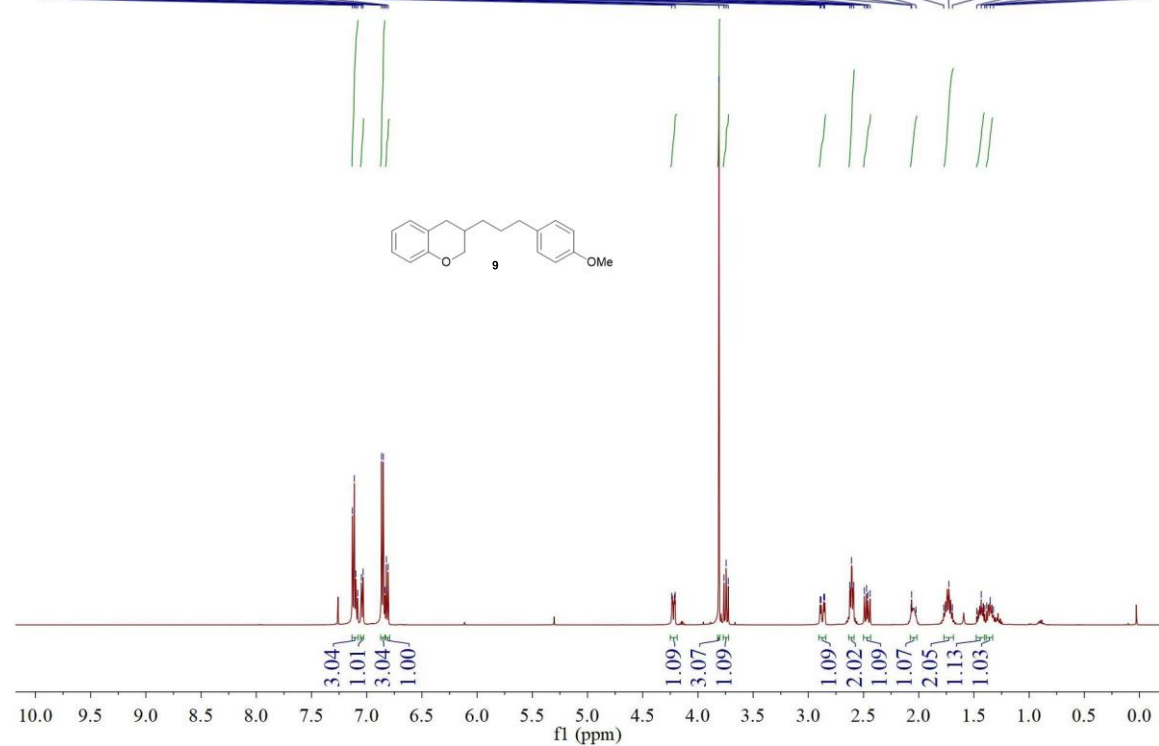
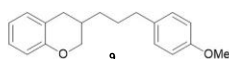
¹³C NMR of **8** in CDCl₃

~158.9
~154.6
135.4
131.5
131.2
129.2
128.8
126.7
120.1
119.9
117.1
114.1
-72.7
-55.4
-43.6
-38.9
-25.8

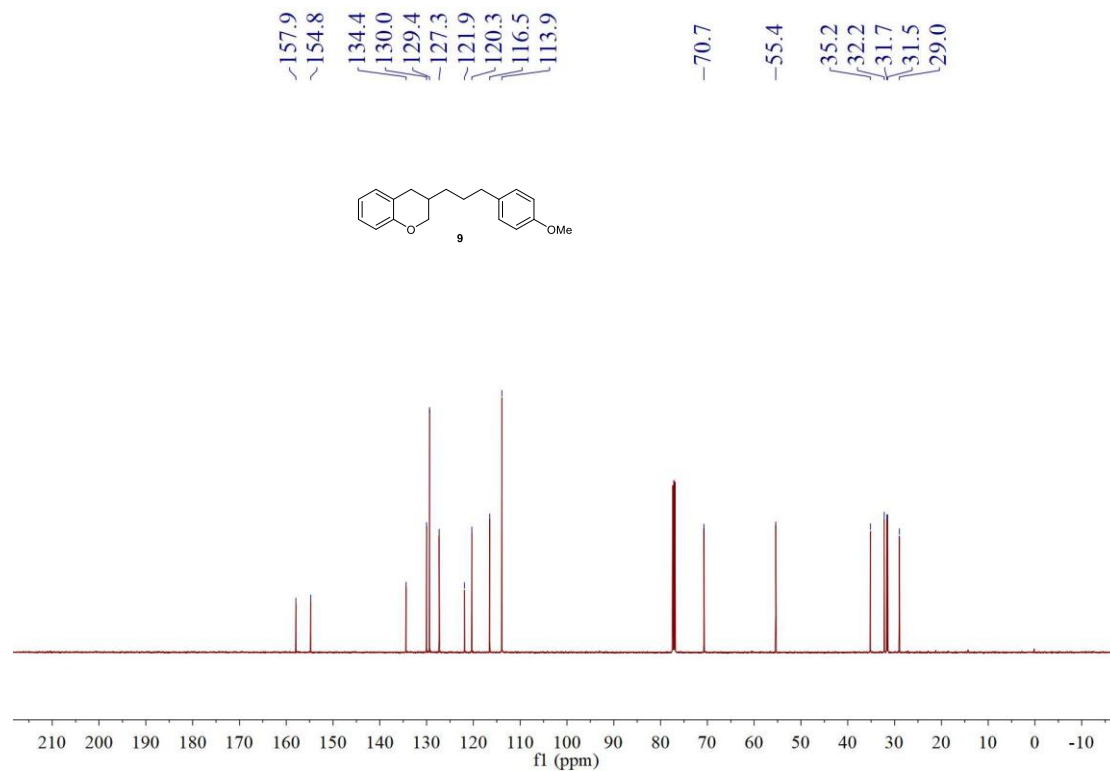


¹H NMR of **9** in CDCl₃

7.13
7.11
7.10
7.08
7.05
7.03
6.87
6.85
6.84
6.82
6.81
4.24
4.21
3.81
3.76
3.74
3.72
2.89
2.88
2.86
2.85
2.62
2.61
2.59
2.49
2.47
2.46
2.44
2.07
2.06
2.02
1.77
1.73
1.69
1.47
1.43
1.40
1.38
1.35
1.32



^{13}C NMR of **9** in CDCl_3



7. References

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