

Supporting Information

Iodine (III)-Mediated Oxidative Chlorination, Bromination and Iodination of Chromone Derivatives Using Alkyl Halide as Solvent and Halogen Source

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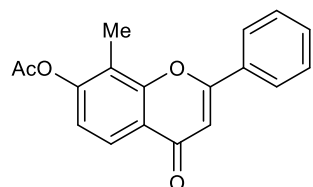
1. General Information

NMR spectra were recorded on a Bruker DRX 400 spectrometer (400 MHz for ¹H; 101 MHz for ¹³C) using CDCl₃ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.16 ppm, respectively. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in CDCl₃ (7.26 ppm for ¹H NMR) or TMS (0 ppm for ¹H NMR) and CDCl₃ (77.16 ppm for ¹³C NMR). Data are reported as follows: Chemical shift (multiplicity, coupling constants, number of protons). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity reported according to standard abbreviations. Column chromatography was performed on Aldrich® silica gel 60 (200 - 300 mesh). Thin-layer chromatography was performed with precoated TLC sheets of silica gel 60 F254 (Aldrich®). HRMS spectra were performed on Waters apparatus. Reagents and starting materials were purchased from commercial vendors and used without further purification. All organic solvents were dried over appropriate drying agents and distilled prior to use. Standard syringe techniques were used for transferring dry solvents.

2. Synthesis of protected flavones 1b-1d

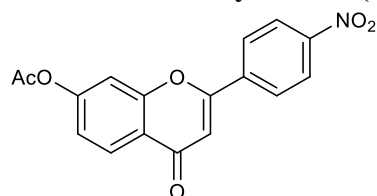
General procedure for acetylation of flavones: the mixture of flavone (1 mmol), Ac₂O (2 mL), pyridine (1 mL) was heated at 80 °C about 3 h. After completion, the mixture was evaporated by vacuum, then washed by water, dichloromethane, and submitted to column chromatography to give the *O*-acetylated product. All the *O*-acetylated flavones except the following three compounds **1b-1d** are known compound. ¹ The *O*-benzylated flavone and *O*-methylated flavone were prepared according to the literature. ²

7-acetoxy-8-methylflavone (**1b**)



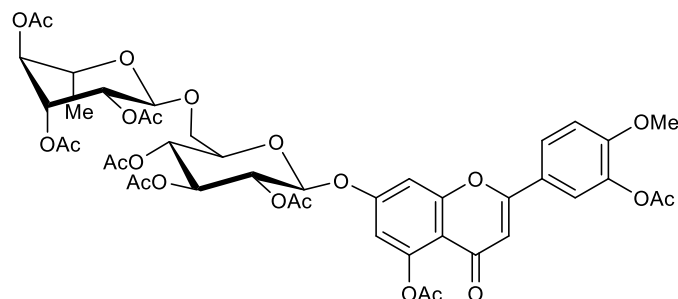
279.3 mg, 95% yield, white solid, m.p. 176-178 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.85-7.82 (m, 2H), 7.48-7.43 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.75 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 177.9, 168.8, 164.1, 156.8, 154.6, 142.6, 129.9, 128.7, 127.2, 126.3, 121.8, 119.4, 111.2, 107.0, 21.7, 21.3; HRMS (ESI) calcd for C₁₈H₁₅O₄ [(M+H)⁺]: 295.0965; Found: 295.0949.

4'-nitro-7-acetoxyflavone (**1c**)



292.5 mg, 90% yield, white solid, m.p. 248-250 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.90 (s, 1H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 177.4, 168.7, 161.0, 156.7, 155.1, 149.6, 137.5, 127.4, 127.4, 124.4, 121.8, 120.1, 111.3, 109.9, 21.3; HRMS (ESI) calcd for C₁₇H₁₂NO₆ [(M+H)⁺]: 326.0665; Found: 326.0677.

3', 4, 2'', 3'', 4'', 2''', 3''', 4'''-Oct-*O*-acetyldiosmin (**1d**)



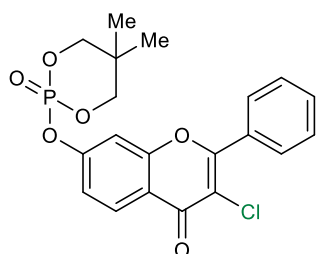
830.7 mg, 88% yield, white solid, m.p. 120-122 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.52 (s, 1H), 5.36-5.27 (m, 3H), 5.24-5.17 (m, 3H), 5.05-4.99 (m, 1H), 4.72 (d, *J* = 1.2 Hz, 1H), 3.99 (ddd, *J* = 8.0, 7.2, 2.8 Hz, 1H), 3.92 (s, 3H), 3.87-3.81 (m, 2H), 3.68 (dd, *J* = 11.8, 5.2 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.93 (s, 3H), 1.15 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.2, 170.2, 170.0, 169.9, 169.8, 169.7, 169.4, 169.2, 168.8, 161.4, 159.8, 158.2, 154.0, 150.6, 140.0, 125.4, 123.6, 121.0, 112.6, 112.5, 109.0, 107.3, 102.2, 98.0, 97.5, 73.3, 72.4, 70.8, 70.7, 69.3, 68.9, 68.6, 66.7, 66.1, 56.1, 21.1, 20.8, 20.7, 20.6, 17.3; HRMS (ESI) calcd for C₄₄H₄₉O₂₃ [(M+H)⁺]: 945.2659; Found: 945.2650.

3. Chlorination of flavone derivatives

General procedure: In a sealed tube, flavone (0.3 mmol, 1.0 equiv.), PhI (TFA)₂ (0.45 mmol, 1.5 equiv.), CHCl₃ (3.0 mL) was added and heated at 80 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture

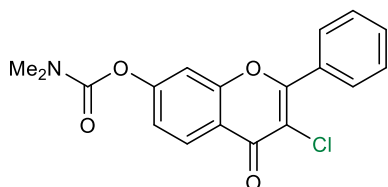
was washed by water. The organic layer was dried by anhydrous Na_2SO_4 , then it was subjected to column chromatography and the chlorinated product was obtained as pure solid. It's noteworthy that $\text{PhI}(\text{OAc})_2$ (0.9 mmol, 3.0 equiv.) instead of $\text{PhI}(\text{TFA})_2$ (0.45 mmol, 1.5 equiv.) are employed in the synthesis of compounds **2an-2as**, **2av**.

3-chloro-7-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl) oxy)-2-phenyl-4H-chromen-4-one (2aa)



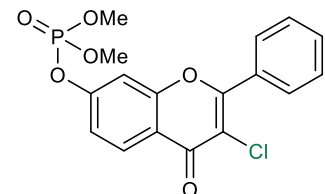
114.6 mg, 91% yield, white solid, m.p. 208-210 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, $J = 8.8, 0.8$ Hz, 1H), 7.91-7.89 (m, 2H), 7.58-7.52 (m, 4H), 7.30 (ddd, $J = 8.8, 2.4, 0.8$ Hz, 1H), 4.27 (d, $J = 11.2$ Hz, 2H), 4.05 (dd, $J = 22.8, 11.2$ Hz, 2H), 1.36 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 161.0, 156.4, 154.6 (d, $J_{\text{CP}} = 6.2$ Hz), 131.6, 131.3, 129.4, 128.6 ($\times 2$), 119.6, 118.3 (d, $J_{\text{CP}} = 6.6$ Hz), 118.2, 108.7 (d, $J_{\text{CP}} = 4.7$ Hz), 78.9 (d, $J_{\text{CP}} = 7.2$ Hz), 32.5 (d, $J_{\text{CP}} = 6.2$ Hz), 21.8, 20.3 (d, $J_{\text{CP}} = 1.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ -14.86; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{ClO}_6\text{PNa}$ [(M+Na) $^+$]: 443.0427; Found: 443.0421.

3-chloro-4-oxo-2-phenyl-4H-chromen-7-yl dimethylcarbamate (2ab)



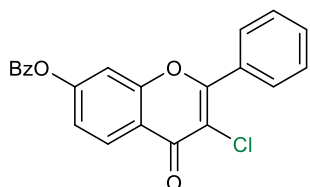
80.3 mg, 78% yield, white solid, m.p. 94-96 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.8$ Hz, 1H), 7.89-7.87 (m, 2H), 7.57-7.50 (m, 3H), 7.39 (d, $J = 2.0$ Hz, 1H), 7.22 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.12 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.6, 160.8, 156.1, 156.0, 153.6, 131.4 ($\times 2$), 129.3, 128.5, 127.5, 120.1, 119.5, 118.0, 110.7, 36.9, 36.7; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{ClNO}_4$ [(M+H) $^+$]: 344.0690; Found: 344.0715.

3-chloro-4-oxo-2-phenyl-4H-chromen-7-yl dimethyl phosphate (2ac)



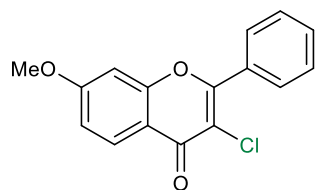
98.0 mg, 86% yield, white solid, m.p. 106-108 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.0$ Hz, 1H), 8.03-8.00 (m, 2H), 7.69-7.64 (m, 3H), 7.58 (dd, $J = 2.0, 0.8$ Hz, 1H), 7.41 (ddd, $J = 8.8, 2.0, 0.8$ Hz, 1H), 4.05 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 160.9, 156.2, 154.8 (d, $J_{\text{CP}} = 6.3$ Hz), 131.5, 131.2, 129.2, 128.5, 128.4, 119.5, 118.5 (d, $J_{\text{CP}} = 6.0$ Hz), 118.0, 108.8 (d, $J_{\text{CP}} = 4.7$ Hz), 55.4 ($\times 2$); ^{31}P NMR (162 MHz, CDCl_3) δ -4.8; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{ClO}_6\text{P}$ [(M+H) $^+$]: 381.0295; Found: 381.0294.

3-chloro-7-benzoyloxyflavone (2ad)



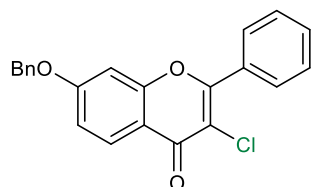
103.8 mg, 92% yield, white solid, m.p. 146-148 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 8.8$ Hz, 1H), 8.21 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.92-7.90 (m, 2H), 7.70-7.66 (m, 1H), 7.57-7.52 (m, 5H), 7.51 (d, $J = 2.0$ Hz, 1H), 7.34 (dd, $J = 8.8, 2.0$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 164.4, 160.9, 156.1, 155.3, 134.3, 131.5, 131.4, 130.4, 129.3, 128.9, 128.7, 128.5, 127.9, 120.2, 120.2, 118.2, 111.2; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{14}\text{ClO}_4$ [(M+H) $^+$]: 377.0575; Found: 377.0569.

3-chloro-7-methoxyflavone (2ae)



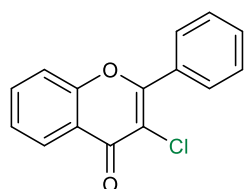
62.6 mg, 73% yield, white solid, m.p. 135-137 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.8$ Hz, 1H), 7.89-7.87 (m, 2H), 7.56-7.50 (m, 3H), 6.99 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.87 (d, $J = 2.4$ Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 164.5, 160.2, 157.4, 131.7, 131.2, 129.2, 128.5, 127.8, 117.9, 116.2, 115.3, 100.0, 56.0; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{ClO}_3$ [(M+H) $^+$]: 287.0475; Found: 287.0479.

3-chloro-7-benzyloxyflavone (2af)



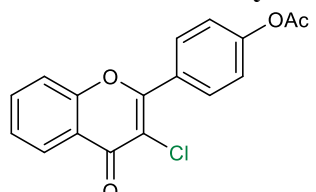
83.6 mg, 77% yield, white solid, m.p. 159-161 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.8$ Hz, 1H), 7.89-7.86 (m, 2H), 7.57-7.50 (m, 3H), 7.45-7.33 (m, 5H), 7.08 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.95 (d, $J = 2.4$ Hz, 1H), 5.15 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.4, 163.6, 160.2, 157.3, 135.6, 131.6, 131.2, 129.3, 128.9, 128.6, 128.5, 127.9, 127.6, 117.9, 116.4, 115.8, 101.1, 70.7; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{ClO}_3$ [(M+H) $^+$]: 363.0782; Found: 363.0772.

3-chloroflavone (2ag)



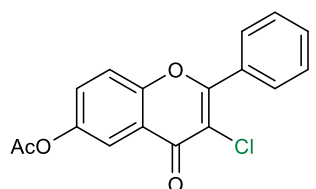
71.4 mg, 93% yield, white solid, m.p. 110-112 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.93-7.90 (m, 2H), 7.73 (ddd, $J = 8.8, 7.2, 1.6$ Hz, 1H), 7.60-7.51 (m, 4H), 7.47 (t, $J = 7.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.3, 160.8, 155.6, 134.3, 131.6, 131.4, 129.3, 128.5, 126.5, 125.8, 122.4, 118.1, 118.0; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{ClO}_2$ [(M+H) $^+$]: 257.0369; Found: 257.0380. The spectroscopic data coincide with the previous report.³

3-chloro-4'-acetoxyflavone (2ah)



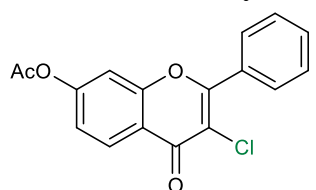
78.2 mg, 83% yield, white solid, m.p. 167-169 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.96 (d, $J = 8.8$ Hz, 2H), 7.72 (ddd, $J = 8.8, 7.2, 1.6$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.46 (tt, $J = 8.0, 0.8$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 169.1, 159.8, 155.6, 152.8, 134.4, 130.9, 129.1, 126.5, 125.9, 122.4, 121.9, 118.1, 118.0, 21.3; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{ClO}_4$ [(M+H) $^+$]: 315.0419; Found: 315.0414.

6-acetoxy-3-chloroflavone (2ai)



72.5 mg, 77% yield, white solid, m.p. 184-186 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 2.8$ Hz, 1H), 7.91-7.88 (m, 2H), 7.58-7.54 (m, 4H), 7.47 (dd, $J = 9.2, 2.8$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.7, 169.4, 161.0, 153.2, 148.0, 131.6, 131.4, 129.4, 128.7, 128.6, 123.2, 119.5, 118.4, 117.8, 21.1; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{ClO}_4$ [(M+H) $^+$]: 315.0419; Found: 315.0414.

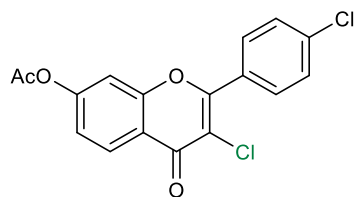
3-chloro-7-acetoxyflavone (2aj)



77.2 mg, 82% yield. White solid, m.p. 162-164 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 8.8$ Hz, 1H), 7.91-7.89 (m, 2H), 7.60-7.53 (m, 3H), 7.37 (d, $J = 2.0$ Hz, 1H), 7.21 (dd, $J = 8.8, 2.0$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3)

δ 172.6, 168.6, 161.0, 156.0, 155.0, 131.5, 131.4, 129.3, 128.6, 127.9, 120.2, 120.1, 118.2, 111.1, 21.3; HRMS (ESI) calcd for $C_{17}H_{12}ClO_4$ [(M+H)⁺]: 315.0424; Found: 315.0428.

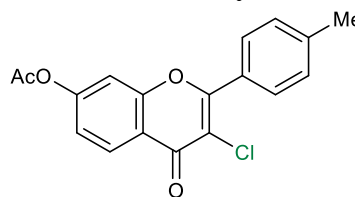
3, 4'-dichloro-7-acetoxyflavone (2ak)



89.8 mg, 86% yield, white solid, m.p. 157-159 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 168.5, 159.6, 155.9,

155.0, 137.7, 130.7, 129.7, 128.9, 127.9, 120.2, 120.0, 118.2, 111.0, 21.3; HRMS (ESI) calcd for $C_{17}H_{11}Cl_2O_4$ [(M+H)⁺]: 349.0023; Found: 349.0023.

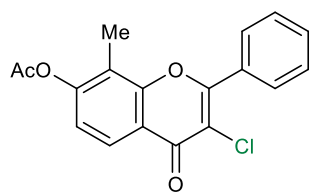
3-chloro-4'-methyl-7-acetoxyflavone (2al)



76.7 mg, 78% yield, white solid, m.p. 172-174 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6,

168.6, 161.1, 156.0, 154.9, 142.2, 129.3, 128.5, 127.9, 120.1, 120.0, 117.8, 111.0, 21.8, 21.3; HRMS (ESI) calcd for $C_{18}H_{14}ClO_4$ [(M+H)⁺]: 329.0581; Found: 329.0588.

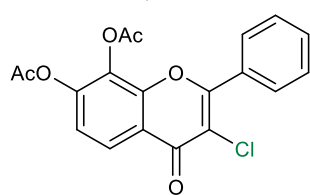
3-chloro-7-acetoxy-8-methylflavone (2am)



81.7 mg, 83% yield, white solid, m.p. 123-125 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.93-7.91 (m, 2H), 7.60-7.53 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.0,

168.6, 160.6, 154.8, 153.3, 131.6, 131.5, 129.3, 128.7, 128.7, 124.6, 120.5, 120.4, 120.2, 118.1, 20.9, 9.5; HRMS (ESI) calcd for $C_{18}H_{14}ClO_4$ [(M+H)⁺]: 329.0575; Found: 329.0588.

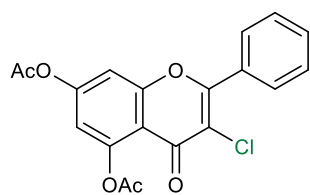
3-chloro-7, 8-di-acetoxyflavone (2an)



99.3 mg, 89% yield, white solid, m.p. 132-134 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 1H), 7.85 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.58-7.51 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 167.6, 167.3, 160.5, 148.8, 146.9, 131.6, 131.5, 131.2,

129.3, 128.6, 124.0, 121.1, 120.8, 118.4, 20.8, 20.3; HRMS (ESI) calcd for $C_{19}H_{14}ClO_6$ [(M+H)⁺]: 373.0479; Found: 373.0482.

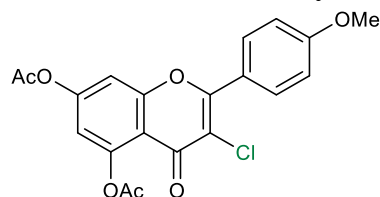
3-chloro-5, 7-di-O-acetylchrysin (2ao)



92.6 mg, 83% yield, white solid, m.p. 148-150 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.85 (m, 2H), 7.57-7.52 (m, 3H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.1, 169.6, 168.0, 160.1, 157.0, 154.4, 150.4, 131.6, 131.0, 129.3,

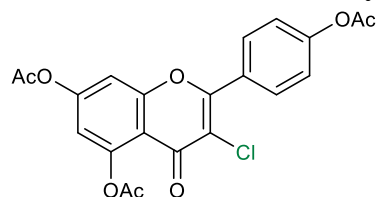
128.7, 128.6, 125.5, 118.8, 114.3, 113.6, 109.0, 21.3, 21.2; HRMS (ESI) calcd for $C_{19}H_{14}ClO_6$ [(M+H)⁺]: 373.0479; Found: 373.0482. The spectroscopic data coincide with the previous report.⁴

3-chloro-5, 7-di-*O*-acetylacacetin (2ap)



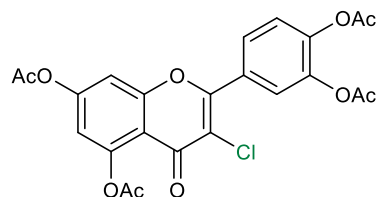
90.4 mg, 75% yield, white solid, m.p. 167-169 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.1, 169.6, 168.1, 162.1, 159.8, 156.9, 154.3, 150.4, 131.1, 123.1, 117.8, 114.2, 114.0, 113.5, 108.9, 55.6, 21.3, 21.2; HRMS (ESI) calcd for C₂₀H₁₆ClO₇ [(M+H)⁺]: 403.0579; Found: 403.0567.

3-chloro-3', 5, 7-tri-*O*-acetylapienin (2aq)



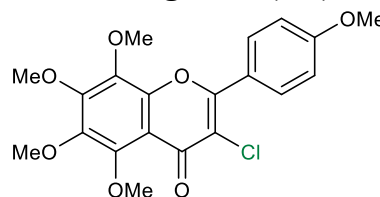
98.0 mg, 76% yield, white solid, m.p. 142-144 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 2.45 (s, 3H), 2.33 (d, *J* = 2.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 169.6, 169.1, 168.0, 159.1, 156.9, 154.5, 152.9, 150.4, 130.8, 128.5, 121.9, 118.8, 114.4, 113.6, 109.0, 21.4, 21.3, 21.2; HRMS (ESI) calcd for C₂₁H₁₆ClO₈ [(M+H)⁺]: 431.0528; Found: 431.0520.

3-chloro-3', 4', 5, 7-tetra-*O*-acetylfluteolin (2ar)



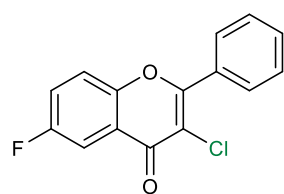
118.6 mg, 81% yield, white solid, m.p. 169-170 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 6H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 169.5, 168.1, 168.0, 167.9, 157.9, 156.8, 154.5, 150.4, 144.6, 142.1, 129.2, 127.8, 124.8, 123.8, 119.0, 114.5, 113.5, 109.0, 21.3, 21.2, 20.8, 20.7; HRMS (ESI) calcd for C₂₃H₁₈ClO₁₀ [(M+H)⁺]: 489.0588; Found: 489.0614.

3-chlorotangeretin (2as)



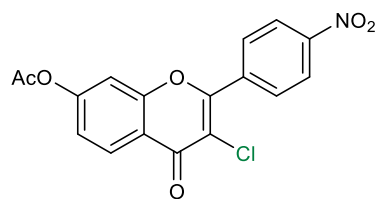
48.7 mg, 40% yield, white solid, m.p. 124-126 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.09 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H), 3.94 (s, 3H), 3.90 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 161.9, 158.4, 151.9, 148.4, 147.1, 144.6, 137.8, 131.1, 123.7, 117.3, 114.0, 113.5, 62.5, 62.2, 62.0, 61.8, 55.6; HRMS (ESI) calcd for C₂₀H₂₀ClO₇ [(M+H)⁺]: 407.0898; Found: 407.0910.

3-chloro-6-fluoroflavone (2at)



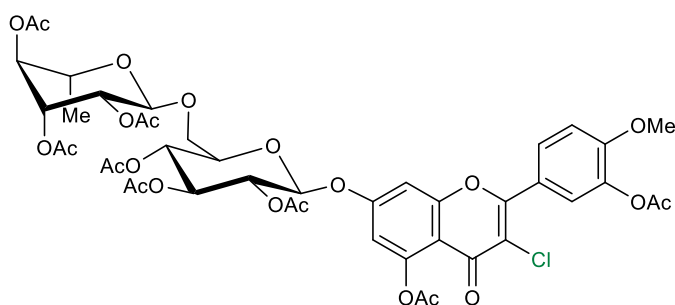
67.4 mg, 82% yield, white solid, m.p. 185-187 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.89 (m, 3H), 7.60-7.53 (m, 4H), 7.47-7.42 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 172.5 (d, *J*_{CF} = 2.5 Hz), 161.0, 159.8 (d, *J*_{CF} = 248.7 Hz), 158.6, 151.9 (d, *J*_{CF} = 1.8 Hz), 131.6, 131.3, 129.3, 128.6, 123.5 (d, *J*_{CF} = 7.8 Hz), 122.6 (d, *J*_{CF} = 25.6 Hz), 120.4 (d, *J*_{CF} = 8.3 Hz), 117.6, 111.2 (d, *J*_{CF} = 24.1 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -114.0; HRMS (ESI) calcd for C₁₅H₉ClFO₂ [(M+H)⁺]: 275.0270; Found: 275.0267.

3-chloro-4'-nitro-7-acetoxyflavone (2au)



79.7 mg, 74% yield, white solid, m.p. 206-208 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.0, 168.5, 158.3, 156.0, 155.3, 149.2, 137.1, 130.6, 128.0, 123.8, 120.6, 120.0, 119.4, 111.1, 21.3; HRMS (ESI) calcd for C₁₇H₁₁ClNO₆ [(M+H)⁺]: 360.0275; Found: 360.0281.

3-chloro-3', 4, 2'', 3'', 4'', 2''', 3''', 4'''-Oct-O-acetyldiosmin (2av)

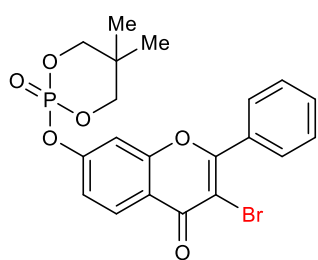


223.0 mg, 76% yield, white solid, m.p. 125-127 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 5.36-5.26 (m, 3H), 5.21-5.15 (m, 3H), 5.04-4.98 (m, 1H), 4.70 (d, *J* = 1.2 Hz, 1H), 3.98 (ddd, *J* = 8.4, 7.2, 2.8 Hz, 1H), 3.93 (s, 3H), 3.85-3.78 (m, 2H), 3.67 (dd, *J* = 12.0, 5.6 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 170.3, 170.1, 169.9, 169.7, 169.5, 169.3, 168.9, 160.2, 158.5, 157.6, 153.7, 150.9, 139.5, 128.8, 124.0, 123.4, 117.9, 111.9, 111.4, 109.9, 101.7, 98.1, 97.7, 73.7, 72.4, 70.9, 70.8, 69.3, 69.0, 68.6, 66.8, 66.1, 56.2, 21.2, 20.9, 20.8, 20.7 (×2), 17.4; HRMS (ESI) calcd for C₄₄H₄₈ClO₂₃ [(M+H)⁺]: 979.2269; Found: 979.2280.

4. Bromination of flavones

General procedure: In a sealed tube, flavone (0.3 mmol, 1 equiv.), PhI(TFA)₂ (0.45 mmol, 1.5 equiv.), CH₂Br₂ (3 mL) was added and heated at 80 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture was washed by water. The organic layer was dried by anhydrous Na₂SO₄, then it was subjected to column chromatography and the brominated product was obtained as pure solid. It's noteworthy that PhI(OAc)₂ (0.9 mmol, 3.0 equiv.) instead of PhI(TFA)₂ (0.45 mmol, 1.5 equiv.) are employed in the synthesis of compounds **2bj-2bo**.

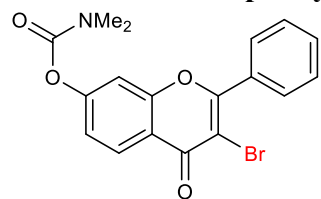
3-bromo-7-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)oxy)-2-phenyl-4H-chromen-4-one (2ba)



118.3 mg, 85% yield, white solid, m.p. 194-196 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.86-7.83 (m, 2H), 7.57-7.51 (m, 4H), 7.30 (ddd, *J* = 8.8, 2.4, 0.8 Hz, 1H), 4.27 (dd, *J* = 11.2, 2.0 Hz, 2H), 4.04 (ddt, *J* = 22.8, 11.2, 1.6 Hz, 2H), 1.36 (s, 3H), 0.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 162.3, 156.5, 154.6 (d, *J*_{CP} = 6.2 Hz), 132.6, 131.4, 129.4, 128.7 (d, *J*_{CP} = 2.6 Hz), 128.5, 119.0, 118.3 (d, *J*_{CP} = 6.8 Hz), 109.4, 108.5 (d, *J*_{CP} = 4.8 Hz), 78.9 (d, *J*_{CP} = 7.2 Hz), 32.4 (d, *J*_{CP} = 6.2 Hz), 21.8, 20.3; ³¹P NMR (162 MHz, CDCl₃) δ -14.9; HRMS (ESI) calcd for

C₂₀H₁₉BrO₆P [(M+H)⁺]: 465.0097; Found: 465.0092.

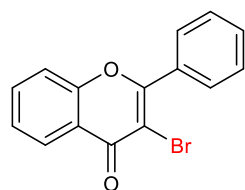
3-bromo-4-oxo-2-phenyl-4H-chromen-7-yl dimethylcarbamate (2bb)



90.5 mg, 78% yield, white solid, m.p. 103-105 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.84 (dt, *J* = 7.6, 1.6 Hz, 2H), 7.57-7.51 (m, 3H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.23 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.14 (s, 3H), 3.05 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 162.2, 156.3, 156.0, 153.6,

132.9, 131.3, 129.5, 128.5, 127.8, 120.3, 119.1, 110.7, 109.4, 37.0, 36.7; HRMS (ESI) calcd for C₁₈H₁₅BrNO₄ [(M+H)⁺]: 388.0184; Found: 388.0182.

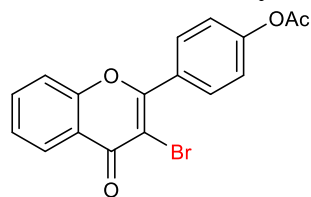
3-bromoflavone (2bc)



72.9 mg, 81% yield, white solid, m.p. 111-113 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.88-7.85 (m, 2H), 7.73 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.58-7.51 (m, 4H), 7.8 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 173.3, 162.2, 155.8, 134.3, 133.0, 131.3, 129.5, 128.5, 128.4, 126.7, 125.9, 121.9,

118.0, 109.4; HRMS (ESI) calcd for C₁₅H₁₀BrO₂ [(M+H)⁺]: 300.9864; Found: 300.9860. The spectroscopic data coincide with the previous report.⁵

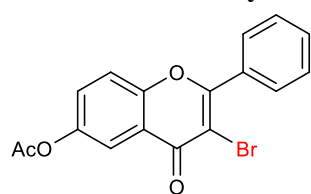
3-bromo-4'-acetoxyflavone (2bd)



70.8 mg, 66% yield, white solid, m.p. 182-184 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.54 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.32-7.26 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 2.17 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 169.1, 161.2, 155.7, 152.7, 134.4,

131.0, 130.4, 126.7, 126.0, 121.8, 121.8, 118.0, 109.4, 21.3; HRMS (ESI) calcd for C₁₇H₁₂BrO₄ [(M+H)⁺]: 358.9919; Found: 358.9926.

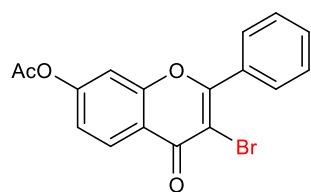
3-bromo-6-acetoxyflavone (2be)



95.5 mg, 89% yield, white solid, m.p. 187-189 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 2.8 Hz, 1H), 7.91-7.83 (m, 2H), 7.58-7.53 (m, 4H), 7.47 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 169.3, 162.3, 153.2, 148.0, 132.7, 131.4, 129.4, 128.6, 128.4, 122.5, 119.4,

118.5, 109.0, 21.1; HRMS (ESI) calcd for C₁₇H₁₂BrO₄ [(M+H)⁺]: 358.9919; Found: 358.9926.

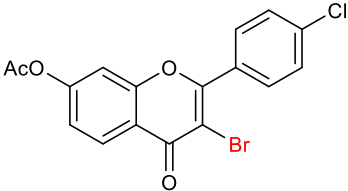
3-bromo-7-acetoxyflavone (2bf)



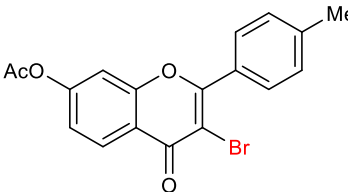
85.9 mg, 80% yield. White solid, m.p. 154-156 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.86-7.83 (m, 2H), 7.59-7.52 (m, 3H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 168.6, 162.4, 156.2, 155.0, 132.7, 131.4, 129.4,

128.5, 128.1, 120.2, 119.6, 111.0, 109.5, 21.3; HRMS (ESI) calcd for C₁₇H₁₂BrO₄ [(M+H)⁺]: 358.9919; Found: 358.9905.

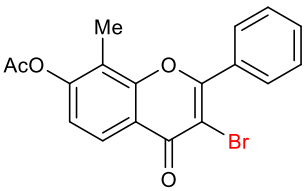
3-bromo-4'-chloro-7-acetoxyflavone (2bg)

 96.4 mg, 82% yield, white solid, m.p. 168-170 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 168.5, 161.0, 156.0, 155.0, 137.6, 131.0, 130.8, 128.8, 128.1, 120.3, 119.5, 110.9, 109.6, 21.3; HRMS (ESI) calcd for C₁₇H₁₁BrClO₄ [(M+H)⁺]: 392.9529; Found: 392.9533.

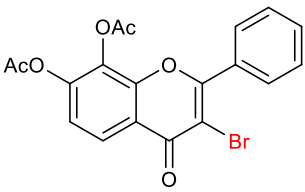
3-bromo-4'-methyl-7-acetoxyflavone (2bh)

 84.8 mg, 76% yield, white solid, m.p. 184-186 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 168.6, 162.5, 156.1, 154.9, 142.0, 129.8, 129.4, 129.2, 128.1, 120.1, 119.6, 110.9, 109.2, 21.8, 21.3; HRMS (ESI) calcd for C₁₈H₁₄BrO₄ [(M+H)⁺]: 373.0075; Found: 373.0087.

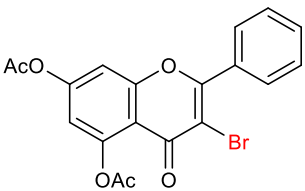
7-acetoxy-8-methylflavone (2bi)

 79.2 mg, 71% yield, white solid, m.p. 148-150 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.8 Hz, 1H), 7.87 (dt, *J* = 7.6, 1.6 Hz, 2H), 7.59-7.51 (m, 3H), 7.16 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 168.6, 162.0, 154.9, 153.3, 132.9, 131.3, 129.4, 128.5, 124.8, 124.7, 120.5, 120.1, 119.8, 119.7, 109.4, 20.9, 9.5; HRMS (ESI) calcd for C₁₈H₁₄BrO₄ [(M+H)⁺]: 373.0075; Found: 373.0087.

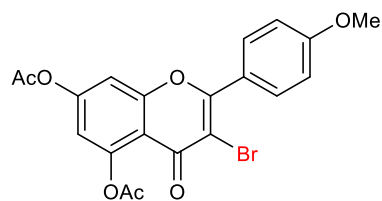
3-bromo-7, 8-diacetoxyflavone (2bj)

 89.8 mg, 72% yield, white solid, m.p. 142-143 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 1H), 7.82-7.80 (m, 2H), 7.58-7.50 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 167.6, 167.3, 161.7, 148.9, 146.9, 132.5, 131.5, 131.4, 129.4, 128.5, 124.1, 120.8, 120.5, 109.6, 20.7, 20.3; HRMS (ESI) calcd for C₁₉H₁₄BrO₆ [(M+H)⁺]: 416.9974; Found: 416.9974.

3-bromo-5, 7-di-O-acetylchrysin (2bk)

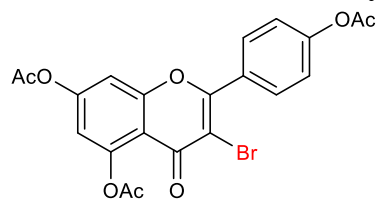
 74.8 mg, 60% yield, white solid, m.p. 151-153 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.58-7.50 (m, 3H), 7.29 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.1, 169.6, 168.0, 161.5, 157.2, 154.4, 150.4, 132.4, 131.5, 129.4, 128.5, 114.4, 113.1, 110.4, 109.0, 21.3, 21.2; HRMS (ESI) calcd for C₁₉H₁₄BrO₆ [(M+H)⁺]: 416.9968; Found: 416.9974.

3-bromo-5, 7-di-O-acetylacacetin (2bl)



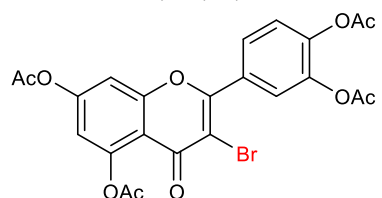
95.0 mg, 71% yield, white solid, m.p. 173-175 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 2.46 (s, 3H), 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.1, 169.5, 168.0, 162.0, 161.2, 157.0, 154.2, 150.3, 131.2, 124.4, 114.2, 113.8, 113.0, 109.5, 108.8, 55.6, 21.3, 21.2; HRMS (ESI) calcd for C₂₀H₁₆BrO₇ [(M+H)⁺]: 447.0079; Found: 447.0073.

3-bromo-4', 5, 7-tri-*O*-acetylapienin (2bm)



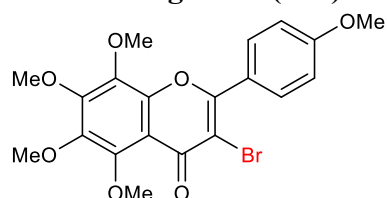
89.5 mg, 63% yield, white solid, m.p. 174-176 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 2.4 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 169.5, 169.0, 168.0, 160.5, 157.0, 154.4, 152.8, 150.3, 130.9, 129.7, 121.8, 114.4, 113.0, 110.4, 108.9, 21.3; HRMS (ESI) calcd for C₂₁H₁₆BrO₈ [(M+H)⁺]: 475.0023; Found: 475.0013.

3-bromo-3', 4', 5, 7-tetra-*O*-acetyluteolin (2bn)



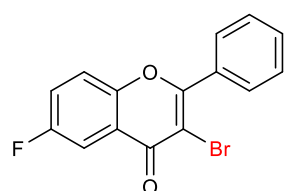
86.2 mg, 54% yield, white solid, m.p. 183-185 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 169.5, 168.0, 167.9 (×2), 159.3, 157.0, 154.5, 150.4, 144.5, 142.0, 130.5, 127.9, 125.0, 123.7, 114.5, 113.0, 110.6, 108.9, 21.3, 21.2, 20.8, 20.7; HRMS (ESI) calcd for C₂₃H₁₈BrO₁₀ [(M+H)⁺]: 533.0083; Found: 533.0106.

3-bromotangeretin (2bo)



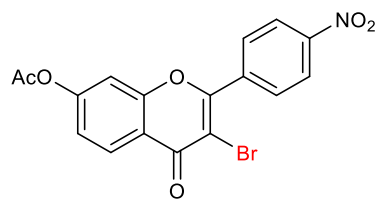
48.6 mg, 36% yield, white solid, m.p. 140-142 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 4.09 (s, 3H), 3.96 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 161.8, 159.9, 151.8, 148.4, 147.2, 144.7, 137.7, 131.3, 124.9, 113.8, 113.0, 109.2, 62.5, 62.2, 62.0, 61.8, 55.6; HRMS (ESI) calcd for C₂₀H₂₀BrO₇ [(M+H)⁺]: 451.0392; Found: 451.0425.

3-bromo-6-fluoroflavone (2bp)



62.9 mg, 66% yield, white solid, m.p. 194-196 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.85 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.59-7.51 (m, 4H), 7.44 (ddd, *J* = 9.2, 7.6, 3.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6 (d, *J*_{CF} = 2.4 Hz), 162.4, 159.9 (d, *J*_{CF} = 248.8 Hz), 152.0 (d, *J*_{CF} = 1.8 Hz), 132.7, 131.4, 129.4, 128.5, 122.9 (d, *J*_{CF} = 7.7 Hz), 122.8, 122.5, 120.2 (d, *J*_{CF} = 8.2 Hz), 111.3 (d, *J*_{CF} = 24.1 Hz), 108.8 (d, *J*_{CF} = 1.4 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -114.1; HRMS (ESI) calcd for C₁₅H₉BrFO₂ [(M+H)⁺]: 318.9764; Found: 318.9782.

3-bromo-4'-nitro-7-acetylflavone (2bq)

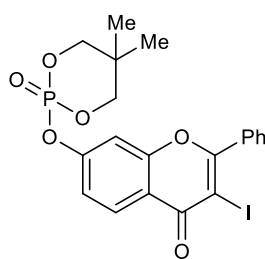


93.0 mg, 77% yield, white solid, m.p. 208-210 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 8.4 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 168.5, 159.7, 156.1, 155.3, 149.1, 138.4, 130.7, 128.2, 123.7, 120.6, 119.5, 111.0, 110.7, 21.3; HRMS (ESI) calcd for C₁₇H₁₁BrNO₆ [(M+H)⁺]: 403.9770; Found: 403.9771.

5. Iodination of flavones

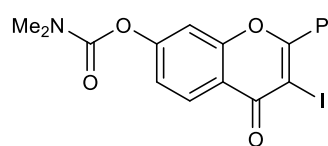
General procedure: In a sealed tube, flavone (0.3 mmol, 1 equiv.), PhI(TFA)₂ (0.6 mmol, 2.0 equiv.), CH₂I₂ (3 mL) was added and heated at 80 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture was washed by water. The organic layer was dried by anhydrous Na₂SO₄, then it was subjected to column chromatography and the iodinated product was obtained as pure solid. It's noteworthy that PhI(OAc)₂ (0.9 mmol, 3.0 equiv.) instead of PhI(TFA)₂ (0.45 mmol, 1.5 equiv.) are employed in the synthesis of compounds **2ci-2cl**.

7-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)oxy)-3-iodo-2-phenyl-4H-chromen-4-one (**2ca**)



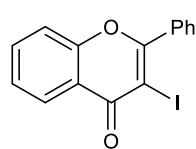
126.0 mg, 82% yield, white solid, m.p. 121-123 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.8 Hz, 1H), 7.79-7.77 (m, 2H), 7.57-7.50 (m, 4H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.28 (d, *J* = 10.8 Hz, 2H), 4.04 (dd, *J* = 22.8, 11.2 Hz, 2H), 1.36 (s, 3H), 0.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 164.9, 156.7, 154.6 (d, *J*_{CP} = 6.1 Hz), 134.8, 131.3, 129.6, 129.3, 129.0, 128.5, 128.4, 118.4 (d, *J*_{CP} = 6.6 Hz), 117.2, 108.3 (d, *J*_{CP} = 4.8 Hz), 88.5, 78.9 (d, *J*_{CP} = 7.3 Hz), 32.4 (d, *J*_{CP} = 6.3 Hz), 21.8, 20.3; ³¹P NMR (162 MHz, CDCl₃) δ -14.8; HRMS (ESI) calcd for C₂₀H₁₉IO₆P [(M+H)⁺]: 512.9958; Found: 512.9955.

3-iodo-4-oxo-2-phenyl-4H-chromen-7-yl dimethylcarbamate (**2cb**)



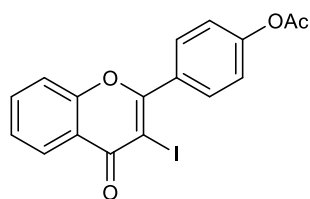
96.6 mg, 74% yield, white solid, m.p. 102-104 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.17 (dt, *J* = 8.8, 2.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.48-7.41 (m, 3H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.13 (dt, *J* = 8.8, 2.0 Hz, 1H), 3.04 (s, 3H), 2.95 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.1, 164.8, 156.4, 155.9, 153.6, 134.9, 131.2, 129.5, 128.3, 127.9, 120.3, 117.1, 110.4, 88.4, 36.9, 36.7; HRMS (ESI) calcd for C₁₈H₁₅INO₄ [(M+H)⁺]: 436.0040; Found: 436.0050.

3-iodoflavone (**2cc**)



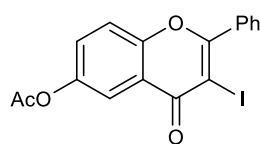
74.0 mg, 71% yield, white solid, ¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71-7.67 (m, 2H), 7.61 (ddd, *J* = 9.6, 8.0, 2.0 Hz, 1H), 7.50-7.33 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 174.6, 164.6, 155.9, 135.1, 134.3, 131.1, 129.5, 128.3, 126.7, 125.9, 120.0, 117.7, 88.4; HRMS (ESI) calcd for C₁₅H₁₀IO₂ [(M+H)⁺]: 348.9720; Found: 348.9718. The spectroscopic data coincide with the previous report.⁶

3-iodo-4'-acetoxyflavone (**2cd**)



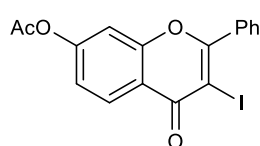
107.0 mg, 88% yield, white solid, m.p. 186-188 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.73 (ddt, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.50-7.45 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.7, 169.2, 163.8, 156.0, 152.6, 134.4, 132.6, 131.1, 126.9, 126.1, 121.7, 120.0, 117.7, 88.6, 21.4; HRMS (ESI) calcd for C₁₇H₁₂IO₄ [(M+H)⁺]: 406.9775; Found: 406.9796.

3-iodo-6-acetoxyflavone (2ce)



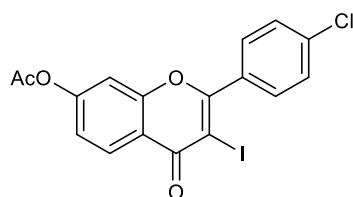
98.6 mg, 81% yield, white solid, m.p. 192-194 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 2.8 Hz, 1H), 7.78-7.73 (m, 2H), 7.57-7.50 (m, 4H), 7.46 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.1, 169.4, 164.9, 153.5, 148.1, 135.0, 131.3, 129.6, 128.7, 128.5, 120.7, 119.2, 118.8, 87.9, 21.2; HRMS (ESI) calcd for C₁₇H₁₂IO₄ [(M+H)⁺]: 406.9775; Found: 406.9755.

3-iodo-7-acetoxyflavone (2cf)



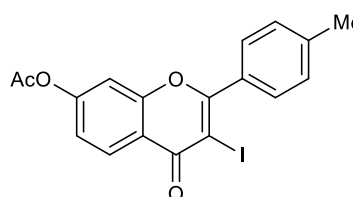
107.0 mg, 88% yield, white solid, m.p. 118-120 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 1H), 7.79-7.75 (m, 2H), 7.58-7.51 (m, 3H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.0, 168.6, 164.9, 156.4, 155.0, 134.9, 131.3, 129.5, 128.4, 128.3, 120.3, 117.8, 110.7, 88.6, 21.3; HRMS (ESI) calcd for C₁₇H₁₂IO₄ [(M+H)⁺]: 406.9775; Found: 406.9755.

3-iodo-4'-chloro-7-acetoxyflavone (2cg)



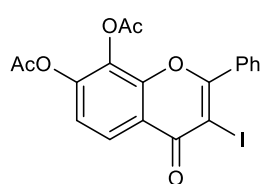
102.9 mg, 78% yield, white solid, m.p. 161-163 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.76-7.72 (m, 2H), 7.53-7.50 (m, 2H), 7.34 (t, *J* = 2.0 Hz, 1H), 7.21 (dt, *J* = 8.8, 2.0 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 168.6, 163.6, 156.3, 155.0, 137.5, 133.2, 131.0, 128.8, 128.4, 120.4, 117.7, 110.7, 88.8, 21.3; HRMS (ESI) calcd for C₁₇H₁₁ClIO₄ [(M+H)⁺]: 440.9385; Found: 440.9391.

3-iodo-4'-methyl-7-acetoxyflavone (2ch)



91.9 mg, 73% yield, white solid, m.p. 161-163 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.0, 168.6, 165.0, 156.4, 154.9, 141.8, 132.1, 129.5, 129.1, 128.3, 120.2, 117.8, 110.7, 88.2, 21.8, 21.3; HRMS (ESI) calcd for C₁₈H₁₄IO₄ [(M+H)⁺]: 420.9931; Found: 420.9917.

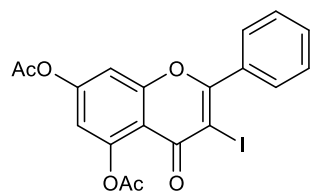
3-iodo-7, 8-diacetoxyflavone (2ci)



107.1 mg, 77% yield, white solid, m.p. 173-175 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.70-7.67 (m, 2H), 7.49-7.41 (m, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 2.27 (s, 3H), 2.23 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.6, 167.6, 167.2, 164.0, 149.1, 146.8, 134.5, 131.4, 131.2, 129.6, 128.4, 124.3, 120.8, 118.6, 88.5, 20.7, 20.3; HRMS (ESI) calcd for C₁₉H₁₄IO₆ [(M+H)⁺]: 464.9830; Found:

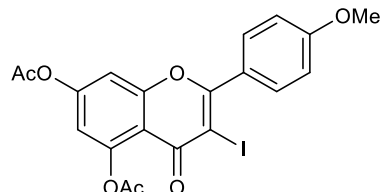
464.9843.

3-iodo-5, 7-di-*O*-acetylchrysin (2cj)



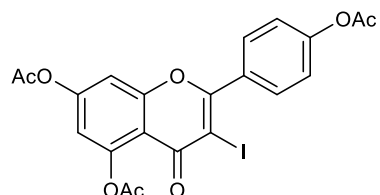
116.9 mg, 84% yield, white solid, m.p. 131-133 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.72 (m, 2H), 7.58-7.50 (m, 3H), 7.28 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 169.6, 168.0, 164.0, 157.4, 154.3, 150.2, 134.6, 131.3, 129.5, 128.5, 114.3, 111.5, 108.7, 90.0, 21.3 (×2); HRMS (ESI) calcd for C₁₉H₁₄IO₆ [(M+H)⁺]: 464.9830; Found: 464.9843.

3-iodo-5, 7-di-*O*-acetylacacetin (2ck)



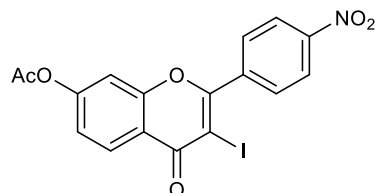
125.9 mg, 85% yield, white solid, m.p. 152-154 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 169.6, 168.0, 163.8, 161.9, 157.3, 154.2, 150.2, 131.4, 126.6, 114.2, 113.7, 111.4, 108.7, 89.2, 55.6, 21.3; HRMS (ESI) calcd for C₂₀H₁₆IO₇ [(M+H)⁺]: 494.9935; Found: 494.9959.

3-iodo-4', 5, 7-tri-*O*-acetylapienin (2cl)



117.4 mg, 75% yield, white solid, m.p. 163-165 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.27-7.25 (m, 3H), 6.91 (d, *J* = 2.0 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 169.5, 169.0, 168.0, 163.1, 157.3, 154.3, 152.7, 150.2, 131.9, 131.0, 121.7, 114.4, 111.4, 108.7, 90.1, 21.3, 21.2; HRMS (ESI) calcd for C₂₁H₁₆IO₈ [(M+H)⁺]: 522.9884; Found: 522.9902.

3-iodo-4'-nitro-7-acetoxyflavone (2cm)

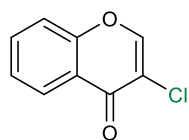


90.6 mg, 67% yield, white solid, m.p. 184-186 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 168.5, 162.3, 156.3, 155.3, 149.1, 140.6, 130.9, 128.5, 123.8, 120.7, 117.7, 110.8, 89.8, 21.3; HRMS (ESI) calcd for C₂₇H₁₁INO₆ [(M+H)⁺]: 451.9626; Found: 451.9639.

6. Chlorination of Chromones

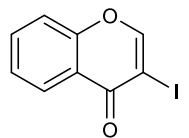
General procedure: In a sealed tube, chromone (1 mmol, 1 equiv.), PhI (TFA)₂ (3 mmol, 3 equiv.), CHCl₃ (5 mL) was added and heated at 100 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture was washed by water. The organic layer was dried by anhydrous Na₂SO₄, then it was subjected to column chromatography and the chlorinated and iodinated products were obtained as pure solid.

3-chlorochromone (4aa)



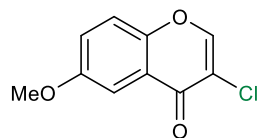
108.0 mg, 60% yield, white solid, m.p. 95-97 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.18 (s, 1H), 7.73 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.52-7.45 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 156.2, 152.3, 134.3, 126.5, 126.0, 123.5, 121.0, 118.3; HRMS (ESI) calcd for C₉H₆ClO₂ [(M+H)⁺]: 181.0056; Found: 181.0056. The spectroscopic data coincide with the previous report.⁷

3-iodochromone (4a')



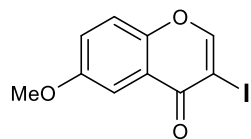
46.2 mg, 17% yield, white solid, m.p. 84-86 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 1H), 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 (ddd, *J* = 9.6, 8.0, 1.6 Hz, 1H), 7.41-7.36 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 173.5, 157.9, 156.3, 134.2, 126.7, 126.1, 121.9, 118.1, 86.9; HRMS (ESI) calcd for C₉H₆IO₂ [(M+H)⁺]: 272.9412; Found: 272.9411. The spectroscopic data coincide with the previous report.⁸

3-chloro-6-methoxychromone (4ab)



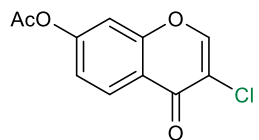
58.8 mg, 28% yield, white solid, m.p. 119-121 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 7.61 (d, *J* = 2.8 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.30 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 157.5, 152.0, 151.1, 124.6, 124.3, 120.3, 119.8, 105.2, 56.2; HRMS (ESI) calcd for C₁₀H₈ClO₃ [(M+H)⁺]: 211.0156; Found: 211.0146. The spectroscopic data coincide with the previous report.⁹

3-iodo-6-methoxychromone (4ab')



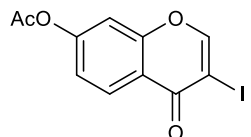
75.5 mg, 25% yield, white solid, m.p. 106-108 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 1H), 7.58 (d, *J* = 3.2 Hz, 1H), 7.41 (d, *J* = 9.2 Hz, 1H), 7.29 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 157.6, 157.5, 151.2, 124.4, 122.5, 119.6, 105.6, 86.0, 56.1; HRMS (ESI) calcd for C₁₀H₈IO₃ [(M+H)⁺]: 302.9513; Found: 302.9503. The spectroscopic data coincide with the previous report.⁸

3-chloro-7-acetoxychromone (4ac)



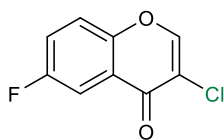
83.3 mg, 35% yield, white solid, m.p. 147-149 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 8.15 (s, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 168.5, 156.6, 154.9, 152.4, 127.8, 121.2, 121.2, 120.3, 111.2, 21.3; HRMS (ESI) calcd for C₁₁H₈ClO₄ [(M+H)⁺]: 239.0111; Found: 239.0107. The spectroscopic data coincide with the previous report.¹⁰

3-iodo-7-acetoxychromone (4ac')



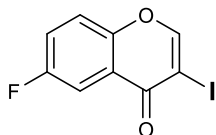
79.2 mg, 24% yield, white solid, m.p. 97-99 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 168.5, 158.0, 156.7, 154.9, 128.2, 120.4, 119.6, 111.0, 87.1, 21.3; HRMS (ESI) calcd for C₁₁H₈IO₄ [(M+H)⁺]: 330.9462; Found: 330.9464.

3-chloro-6-fluorochromone (4ad)



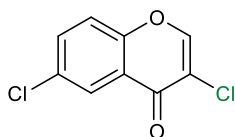
128.7 mg, 65% yield, white solid, m.p. 142-144 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.92 (dd, $J = 8.0, 3.2$ Hz, 1H), 7.52 (dd, $J = 9.2, 4.4$ Hz, 1H), 7.47-7.42 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.8, 159.9 (d, $J_{\text{CF}} = 249.3$ Hz), 152.41, 124.7 (d, $J_{\text{CF}} = 7.7$ Hz), 122.7 (d, $J_{\text{CF}} = 25.6$ Hz), 120.6 (d, $J_{\text{CF}} = 8.3$ Hz), 120.5, 111.3 (d, $J_{\text{CF}} = 24.3$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -113.7; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{ClFO}_2$ [(M+H) $^+$]: 198.9962; Found: 198.9968. The spectroscopic data coincide with the previous report.¹¹

3-iodo-6-fluorochromone (4ad')



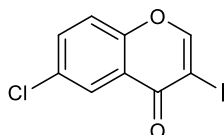
46.4 mg, 16% yield, white solid, m.p. 122-124 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.88 (dd, $J = 8.0, 2.8$ Hz, 1H), 7.50 (dd, $J = 9.2, 4.4$ Hz, 1H), 7.44 (ddd, $J = 8.8, 7.6, 3.2$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9 (d, $J_{\text{CF}} = 2.5$ Hz), 159.9 (d, $J_{\text{CF}} = 249.3$ Hz), 158.0, 152.5 (d, $J_{\text{CF}} = 1.9$ Hz), 122.9 (d, $J_{\text{CF}} = 7.7$ Hz), 122.7 (d, $J_{\text{CF}} = 25.6$ Hz), 120.4 (d, $J_{\text{CF}} = 8.3$ Hz), 111.6 (d, $J_{\text{CF}} = 24.0$ Hz), 86.1; ^{19}F NMR (377 MHz, CDCl_3) δ -113.5; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{FIO}_2$ [(M+H) $^+$]: 290.9313; Found: 290.9319. The spectroscopic data coincide with the previous report.⁸

3, 6-dichlorochromone (4ae)



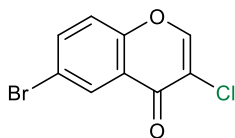
87.7 mg, 41% yield, white solid, m.p. 115-117 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 2.4$ Hz, 1H), 8.17 (s, 1H), 7.66 (dd, $J = 8.8, 2.8$ Hz, 1H), 7.47 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 154.4, 152.4, 134.6, 132.0, 125.6, 124.4, 121.0, 120.1; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{Cl}_2\text{O}_2$ [(M+H) $^+$]: 214.9661; Found: 214.9669. The spectroscopic data coincide with the previous report.¹¹

3-iodo-6-chlorochromone (4ae')



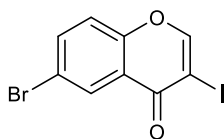
91.8 mg, 30% yield, white solid, m.p. 139-141 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.19 (d, $J = 2.8$ Hz, 1H), 7.65 (dd, $J = 8.8, 2.8$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.4, 158.0, 154.6, 134.5, 131.9, 126.0, 122.6, 119.9, 86.7; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{ClIO}_2$ [(M+H) $^+$]: 306.9017; Found: 306.9007. The spectroscopic data coincide with the previous report.⁸

3-chloro-6-bromochromone (4af)



98.0 mg, 38% yield, white solid, m.p. 136-138 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 2.4$ Hz, 1H), 8.16 (s, 1H), 7.79 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.2, 154.9, 152.4, 137.4, 128.9, 124.8, 121.2, 120.3, 119.5; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{BrClO}_2$ [(M+H) $^+$]: 258.9161; Found: 258.9164. The spectroscopic data coincide with the previous report.⁹

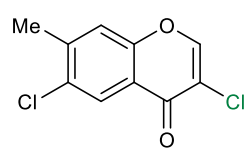
3-iodo-6-bromochromone (4af')



73.4 mg, 21% yield, white solid, m.p. 140-142 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 2.4$ Hz, 1H), 8.30 (s, 1H), 7.79 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.38 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 158.0, 155.0, 137.3, 129.2, 123.0, 120.1, 119.4, 86.7; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{BrIO}_2$ [(M+H) $^+$]: 350.8512; Found: 350.8504. The

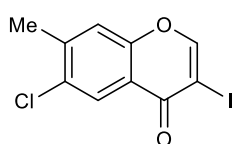
spectroscopic data coincide with the previous report.⁸

3, 6-dichloro-7-methylchromone (4ag)



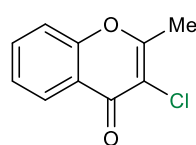
164.0 mg, 72% yield, white solid, m.p. 156-158 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 8.12 (s, 1H), 7.38 (s, 1H), 2.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.3, 154.4, 152.2, 143.9, 132.8, 125.9, 122.5, 120.9, 120.1, 21.0; HRMS (ESI) calcd for C₁₀H₇Cl₂O₂ [(M+H)⁺]: 228.9823; Found: 228.9833. The spectroscopic data coincide with the previous report.¹¹

3-iodo-6-chloro-7-methylchromone (4ag')



57.6 mg, 18% yield, white solid, m.p. 161-163 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 8.17 (s, 1H), 7.36 (s, 1H), 2.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 157.8, 154.5, 143.8, 132.7, 126.2, 120.8, 119.9, 86.6, 21.0; HRMS (ESI) calcd for C₁₀H₇ClIO₂ [(M+H)⁺]: 320.9174; Found: 320.9173. The spectroscopic data coincide with the previous report.¹²

2-methyl-3-chlorochromone (4ah)

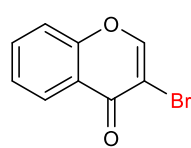


120.2 mg, 62% yield, white solid, m.p. 120-122 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.45-7.40 (m, 2H), 2.61 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 163.1, 155.3, 133.9, 126.3, 125.5, 122.6, 118.5, 117.8, 19.4; HRMS (ESI) calcd for C₁₀H₈ClO₂ [(M+H)⁺]: 195.0207; Found: 195.0206. The spectroscopic data coincide with the previous report.¹³

7. Bromination of Chromones

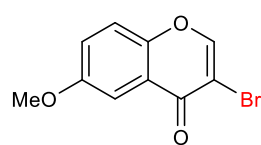
General procedure: In a sealed tube, chromone (1 mmol, 1 equiv.), PhI (TFA)₂ (1.5 mmol, 1.5 equiv.), CH₂Br₂ (5 mL) was added and heated at 100 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture was washed by water. The organic layer was dried by anhydrous Na₂SO₄, then it was subjected to column chromatography and the brominated product was obtained as pure solid.

3-bromochromone (4ba)



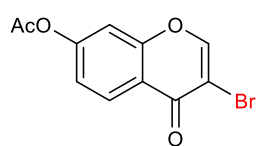
138.8 mg, 62% yield, white solid, m.p. 76-78 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (ddd, *J* = 8.0, 1.6, 0.4 Hz, 1H), 8.25 (s, 1H), 7.73 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.51-7.46 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 156.2, 154.0, 134.3, 126.6, 126.1, 123.2, 118.3, 110.8; HRMS (ESI) calcd for C₉H₆BrO₂ [(M+H)⁺]: 224.9546; Found: 224.9563. The spectroscopic data coincide with the previous report.⁷

3-bromo-6-methoxychromone (4bb)



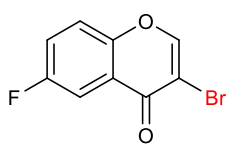
63.5 mg, 25% yield, white solid, m.p. 120-122 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 9.2 Hz, 1H), 7.24-7.19 (m, 1H), 3.84 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 157.5, 153.7, 151.1, 124.5, 124.0, 119.7, 110.0, 105.4, 56.2; HRMS (ESI) calcd for C₁₀H₈BrO₃ [(M+H)⁺]: 254.9651; Found: 254.9657. The spectroscopic data coincide with the previous report.¹¹

3-bromo-7-acetoxychromone (4bc)



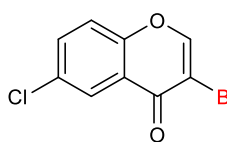
160.7 mg, 57% yield, white solid, m.p. 132-134 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.8$ Hz, 1H), 8.21 (s, 1H), 7.30 (d, $J = 2.0$ Hz, 1H), 7.19 (dd, $J = 8.8, 2.0$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.7, 168.5, 156.6, 154.9, 154.0, 128.0, 120.9, 120.3, 111.1, 111.0, 21.3; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_8\text{BrO}_4$ [(M+H) $^+$]: 282.9600; Found: 282.9595. The spectroscopic data coincide with the previous report.¹⁴

3-bromo-6-fluorochromone (4bd)



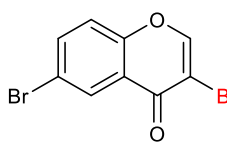
176.7 mg, 73% yield, white solid, m.p. 129-131 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.25 (s, 1H), 7.90 (dd, $J = 8.0, 3.2$ Hz, 1H), 7.52 (dd, $J = 9.2, 4.0$ Hz, 1H), 7.47-7.42 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.7, 159.9 (d, $J_{\text{CF}} = 249.4$ Hz), 154.1, 152.4, 124.4 (d, $J_{\text{CF}} = 7.6$ Hz), 122.7 (d, $J_{\text{CF}} = 25.6$ Hz), 120.5 (d, $J_{\text{CF}} = 8.3$ Hz), 111.4 (d, $J_{\text{CF}} = 24.2$ Hz), 110.2 (d, $J_{\text{CF}} = 1.5$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -113.6; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{BrFO}_2$ [(M+H) $^+$]: 242.9451; Found: 242.9447. The spectroscopic data coincide with the previous report.¹¹

3-bromo-6-chlorochromone (4be)



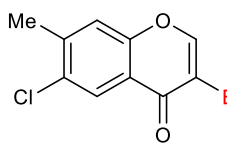
152.2 mg, 59% yield, white solid, m.p. 126-128 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 8.23-8.21 (m, 1H), 7.67-7.64 (m, 1H), 7.46 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 154.5, 154.0, 134.6, 132.0, 125.8, 124.0, 120.1, 110.7; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{BrClO}_2$ [(M+H) $^+$]: 258.9161; Found: 258.9164. The spectroscopic data coincide with the previous report.¹²

3, 6-dibromochromone (4bf)



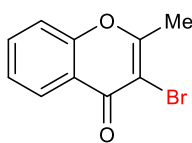
157.0 mg, 52% yield, white solid, m.p. 140-142 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 2.4$ Hz, 1H), 8.24 (s, 1H), 7.79 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.2, 154.9, 154.0, 137.3, 129.0, 124.4, 120.2, 119.5, 110.8; HRMS (ESI) calcd for $\text{C}_9\text{H}_5\text{Br}_2\text{O}_2$ [(M+H) $^+$]: 302.8651; Found: 302.8649. The spectroscopic data coincide with the previous report.¹²

3-bromo-6-chloro-7-methylchromone (4bg)



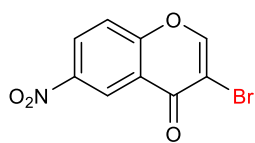
176.8 mg, 65% yield, white solid, m.p. 171-173 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 8.18 (s, 1H), 7.37 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.2, 154.4, 153.8, 143.8, 132.8, 126.0, 122.1, 120.0, 110.6, 21.0; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_7\text{BrClO}_2$ [(M+H) $^+$]: 272.9312; Found: 272.9310. The spectroscopic data coincide with the previous report.¹⁵

2-methyl-3-bromochromone (4bh)



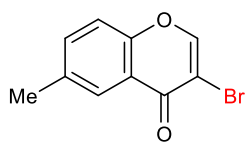
157.0 mg, 66% yield, white solid, m.p. 113-115 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.67 (ddd, $J = 8.8, 7.2, 1.6$ Hz, 1H), 7.44-7.39 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 164.1, 155.3, 133.9, 126.4, 125.6, 121.8, 117.7, 109.7, 21.8; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{BrO}_2$ [(M+H) $^+$]: 238.9702; Found: 238.9696. The spectroscopic data coincide with the previous report.¹³

3-bromo-6-nitrochromone (4bi)



96.8 mg, 36% yield, white solid, m.p. 172-174 °C, ¹H NMR (400 MHz, CDCl₃) δ 9.14 (d, *J* = 2.8 Hz, 1H), 8.55 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.31 (s, 1H), 7.68 (d, *J* = 9.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 171.1, 158.9, 154.2, 145.4, 128.6, 123.4, 123.2, 120.2, 111.7; HRMS (ESI) calcd for C₉H₅BrNO₄ [(M+H)⁺]: 269.9396; Found: 269.9385. The spectroscopic data coincide with the previous report.¹²

3-bromo-6-methylchromone (4bj)

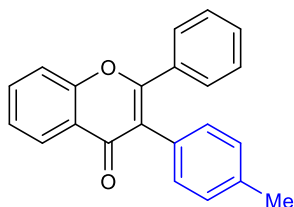


104.7 mg, 44% yield, white solid, m.p. 108-110 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H), 8.05 (s, 1H), 7.53 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 154.5, 153.9, 136.2, 135.6, 125.8, 122.9, 118.0, 110.5, 21.1; HRMS (ESI) calcd for C₁₀H₈BrO₂ [(M+H)⁺]: 238.9702; Found: 238.9702. The spectroscopic data coincide with the previous report.⁷

8. Application of 3-bromoflavone and control experiments

3-(*p*-tolyl) flavone (5a)

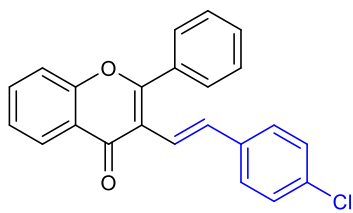
Procedure: Pd (PPh₃)₄ (12 mg, 0.01 mmol) was added to a mixture of 3-Bromo-2-phenyl chromen-4-one (100 mg, 0.33 mmol), 4-methylbenzeneboronic acid (135 mg, 0.99 mmol) and K₃PO₄ (420 mg, 1.98 mmol) in THF (5 mL). The reaction was stirred at 85 °C for 30 min and at 110 °C for 1 h. then EtOAc was added and the solid filtered off. The solvents were removed in vacuo and the mixture was purified by column chromatography to obtain the product **5a** (88.5 mg).



85% yield, white solid, m.p. 148-150 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (ddt, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.43-7.38 (m, 3H), 7.35-7.31 (m, 1H), 7.28-7.24 (m, 2H), 7.11 (d, *J* = 0.8 Hz, 4H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 177.6, 161.3, 156.1, 137.3, 133.7, 133.5, 131.1, 130.0, 129.8, 129.6, 129.1, 128.1, 126.4, 125.1, 123.5, 122.9, 118.0, 21.4; HRMS (ESI) calcd for C₂₂H₁₇O₂ [(M+H)⁺]: 313.1229; Found: 313.1238. The spectroscopic data coincide with the previous report.¹⁶

(*E*)-3-(4-chlorostyryl) flavone (5b)

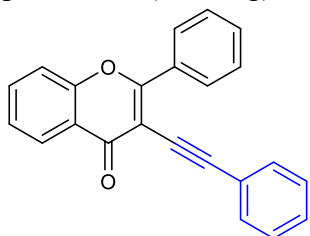
Procedure: A mixture of 3-bromoflavone (100 mg, 0.33 mmol), potassium carbonate (68 mg, 0.51 mmol), potassium chloride (25 mg, 0.34 mmol), TBAB (273 mg, 0.68 mmol), palladium (II) acetate (4 mg) and alkene (1.08 mmol) in DMF (4 mL) was heated at 110°C. After the completion of reaction, the mixture was poured into water, the mixture was extracted with EtOAc, the combined organic layers were washed with water, dried and concentrated under reduced pressure. The mixture was purified by column chromatography to provide the product **5b** (106.0 mg).



89% yield, white solid, m.p. 123-125 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.99 (d, *J* = 16.4 Hz, 1H), 7.74-7.71 (m, 2H), 7.66 (ddd, *J* = 8.0, 6.8, 1.6 Hz, 1H), 7.59-7.52 (m, 3H), 7.48-7.40 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 16.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 177.5, 163.4, 155.5, 136.8, 133.7, 133.2, 133.1, 131.0, 129.9, 128.8, 128.7, 127.7, 126.3, 125.3, 123.6, 120.9, 118.0, 117.4; HRMS (ESI) calcd for C₂₃H₁₆ClO₂ [(M+H)⁺]:359.0839; Found:359.0856. The spectroscopic data coincide with the previous report.¹⁷

3-(phenylethynyl) flavone (5c)

Procedure: A mixture of 3-bromoflavone (100 mg, 0.33 mmol), phenylacetylene (52 mg, 0.51 mmol), Pd (PPh₃)₄ (9.8 mg, 0.0085 mmol), PPh₃ (16.3 mg, 0.0084 mmol), and copper(I)iodide (0.78 mg, 0.0041 mmol) in triethylamine (2 mL) was heated at 70 °C. After completion of the starting material, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to provide the pure product **5c** (88.0 mg).



82% yield, white solid, m.p. 159-161 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.26-8.23 (m, 2H), 7.70 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.58-7.49 (m, 6H), 7.44 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.34-7.30 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 165.7, 155.6, 134.2, 132.6, 131.7, 131.7, 129.1, 128.6, 128.4, 126.3, 125.7, 123.3, 122.3, 118.1, 107.4, 97.9, 82.1; HRMS (ESI) calcd for C₂₃H₁₅O₂ [(M+H)⁺]:323.1072; Found:323.1085. The spectroscopic data coincide with the previous report.¹⁸

Control Experiments:

Synthesis of 3-iodoflavone (2cc)

Procedure: In a sealed tube, flavone (100 mg, 0.45 mmol, 1.0 equiv.), PhI(TFA)₂ (774 mg, 1.8 mmol, 4.0 equiv.), MeCN (3 mL) was added and heated at 100 °C until the starting material was consumed, which was monitored by TLC. After completion, the mixture was washed by water. The organic layer was dried by anhydrous Na₂SO₄, then it was subjected to column chromatography. The pure product was obtained in 53% yield (83.0 mg).

9. References

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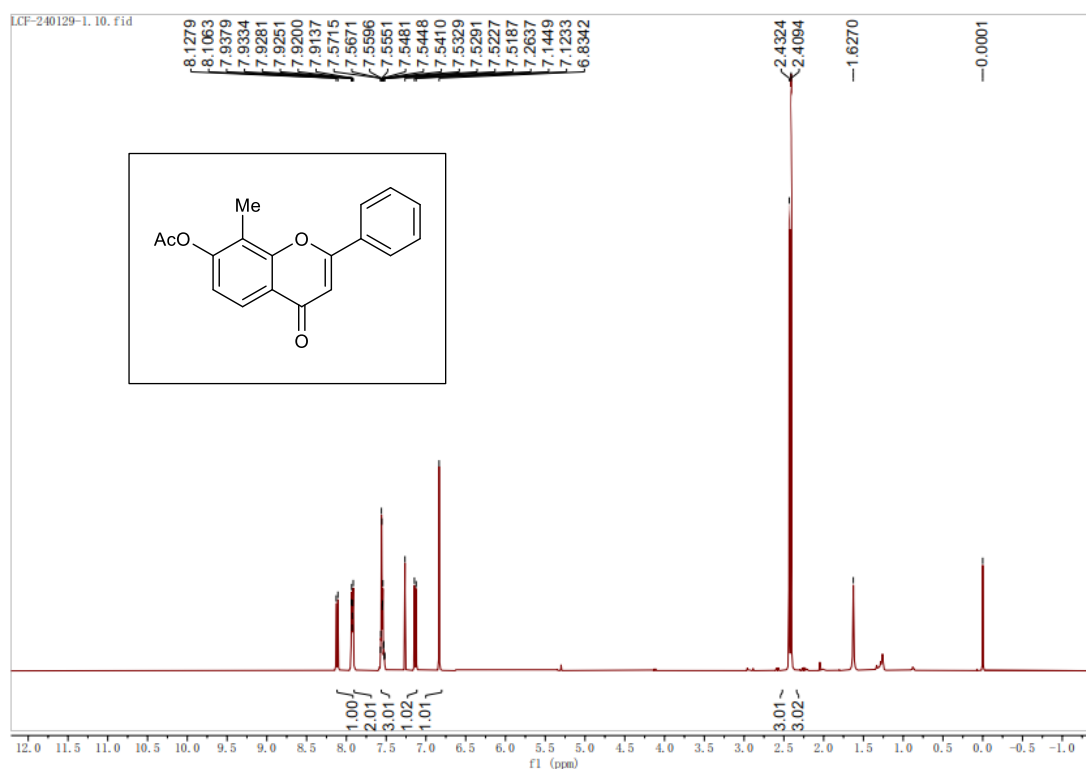
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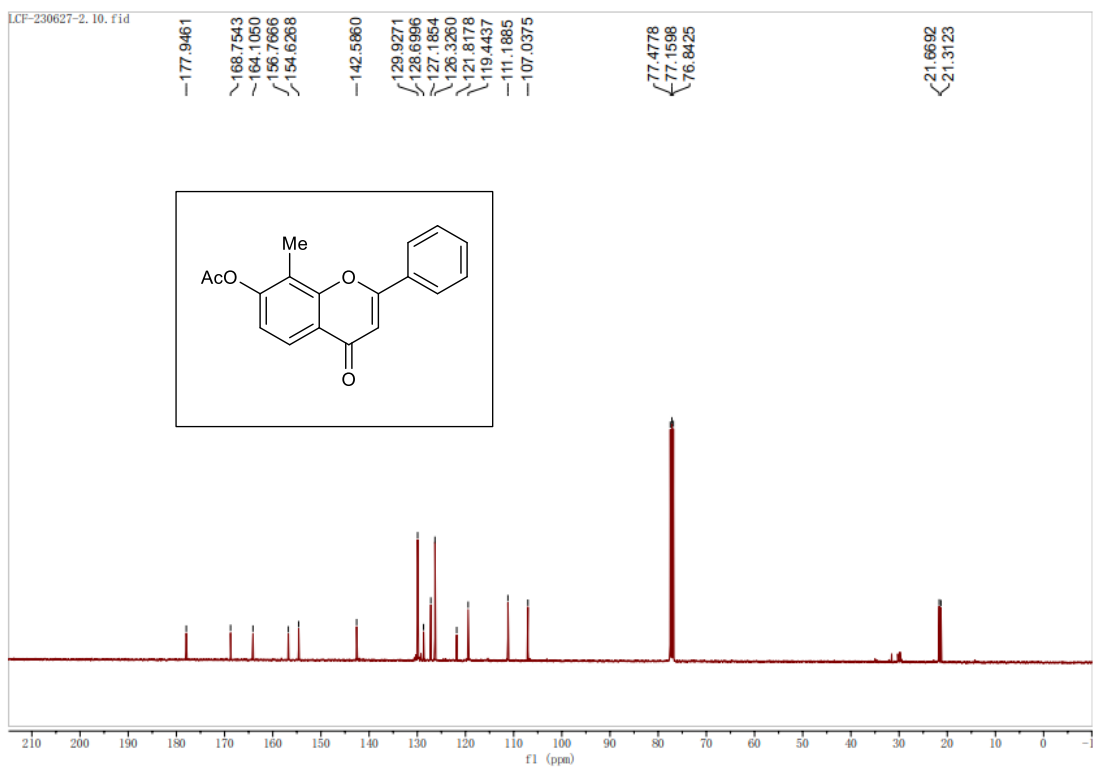
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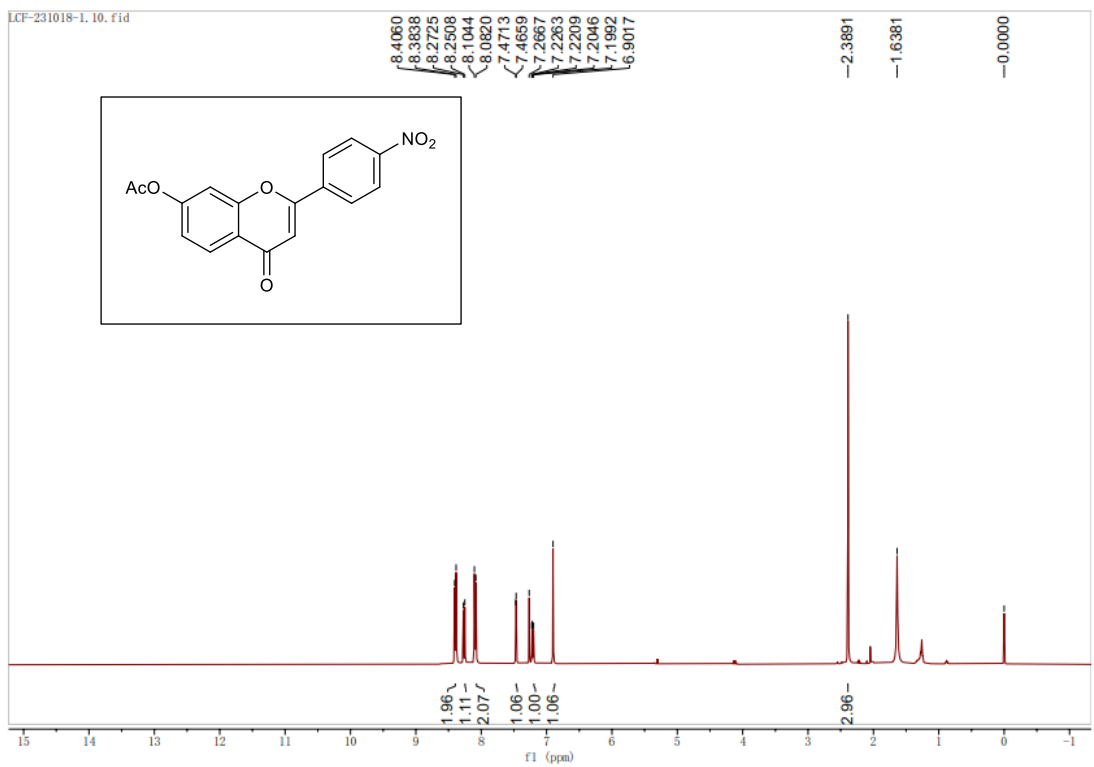
10. NMR Spectra of Products



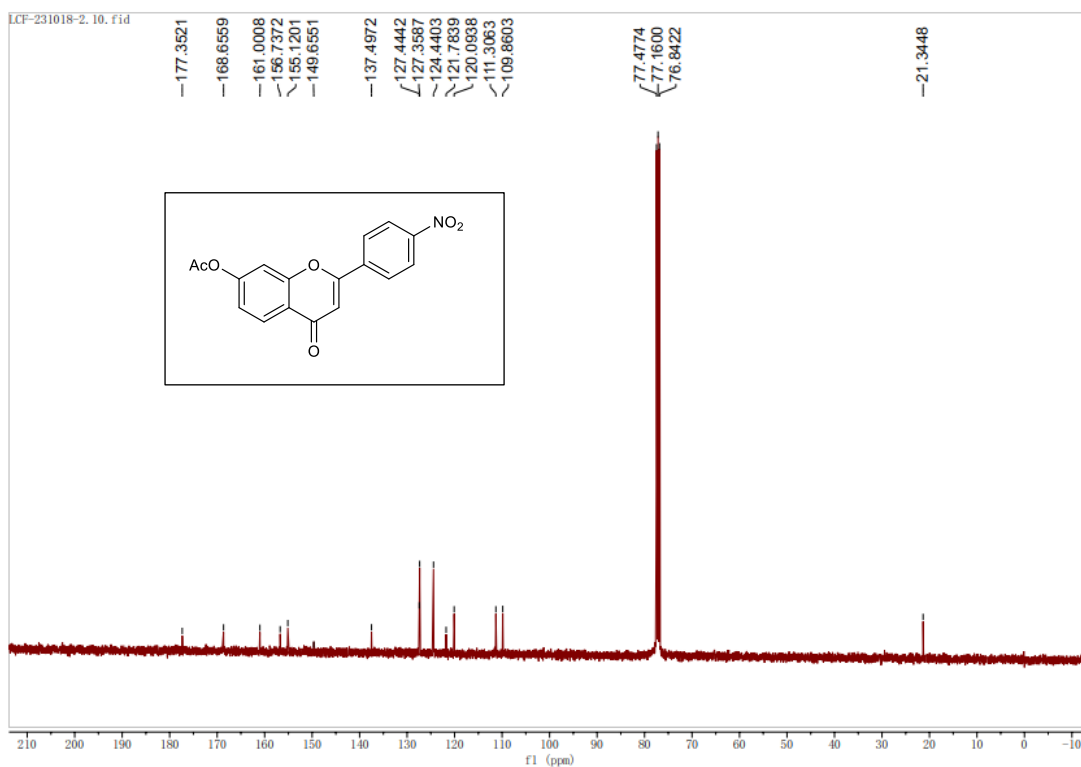
¹H NMR Spectra of compound **1b** in CDCl₃ (400 MHz)



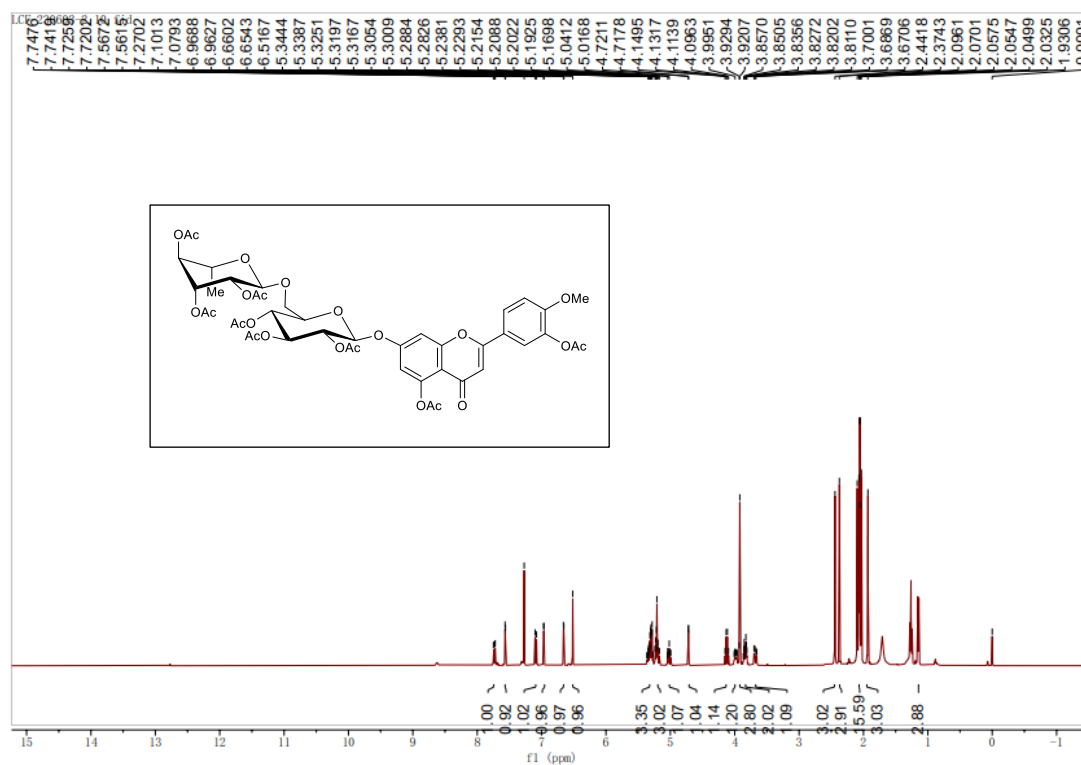
^{13}C NMR Spectra of compound **1b** in CDCl_3 (101 MHz)



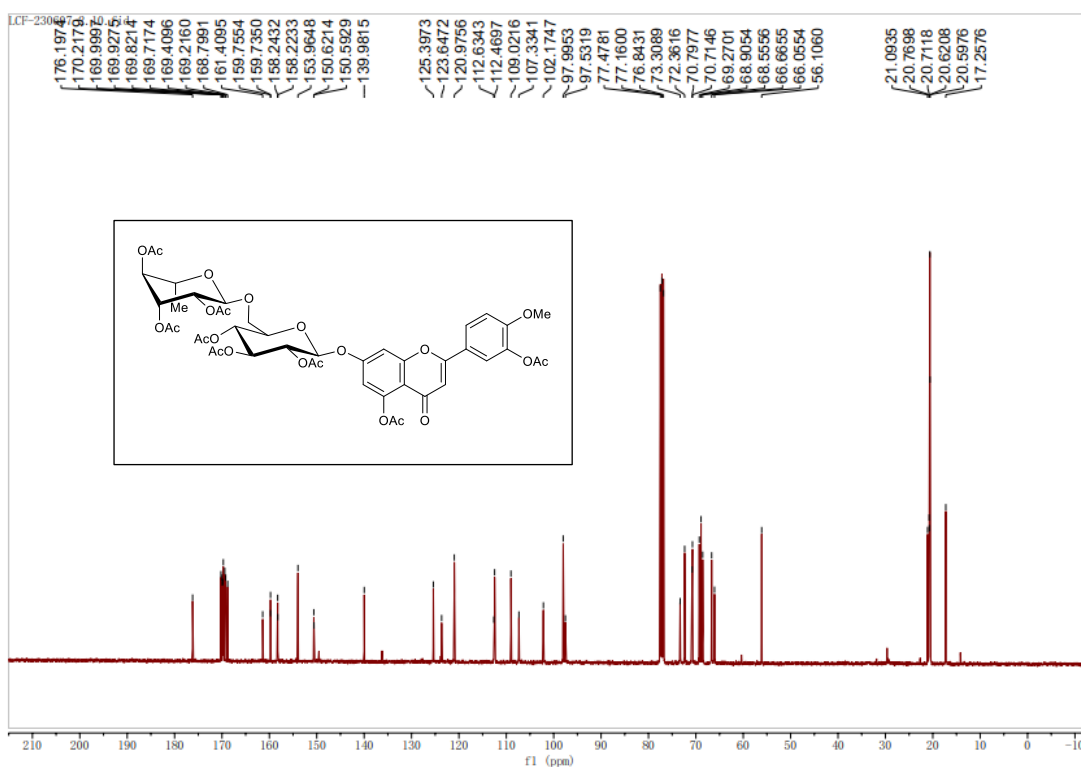
^1H NMR Spectra of compound **1c** in CDCl_3 (400 MHz)



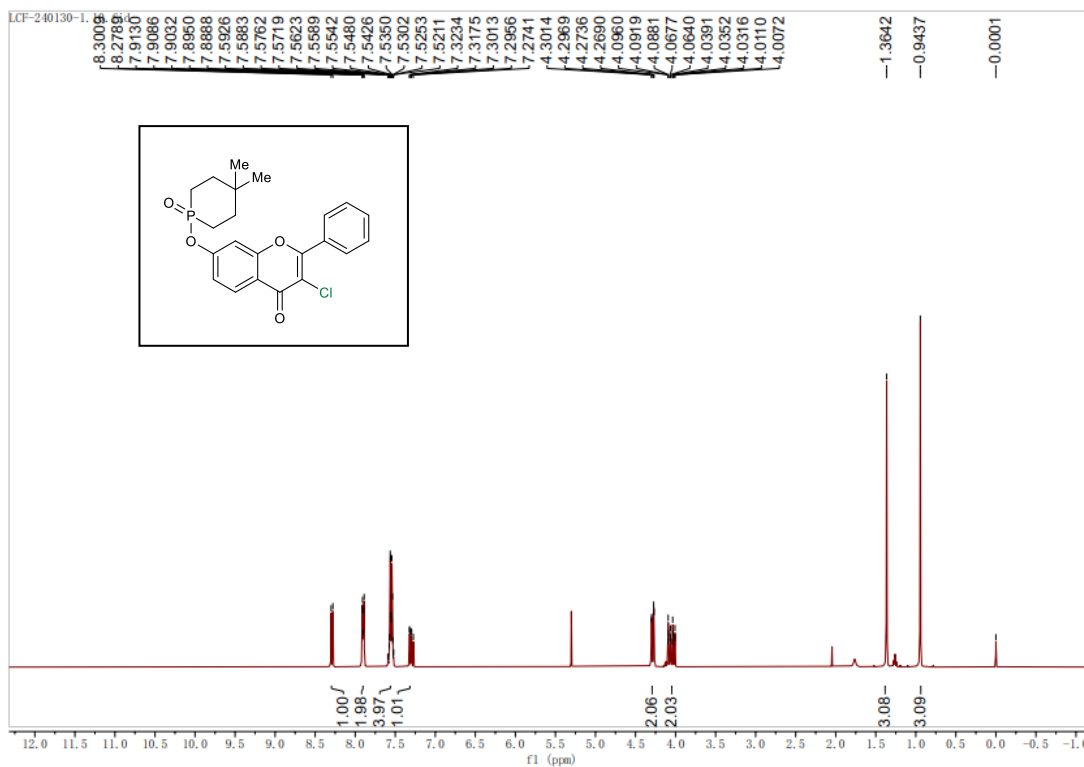
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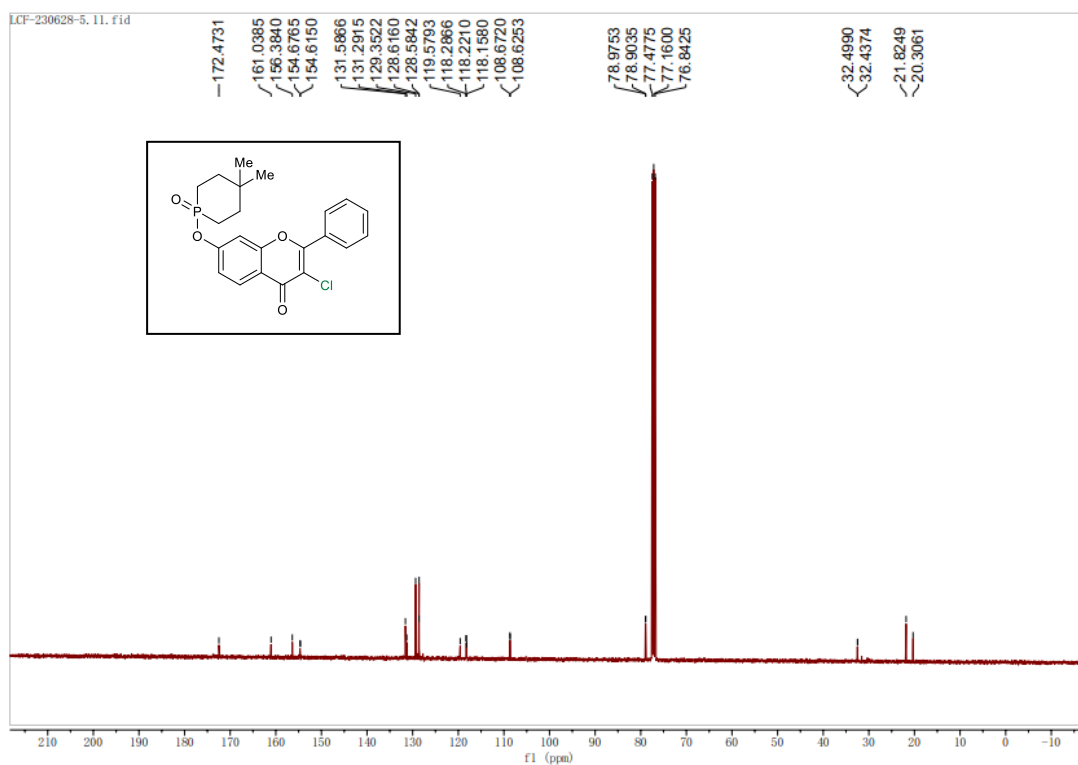
¹H NMR Spectra of compound **1d** in CDCl₃ (400 MHz)



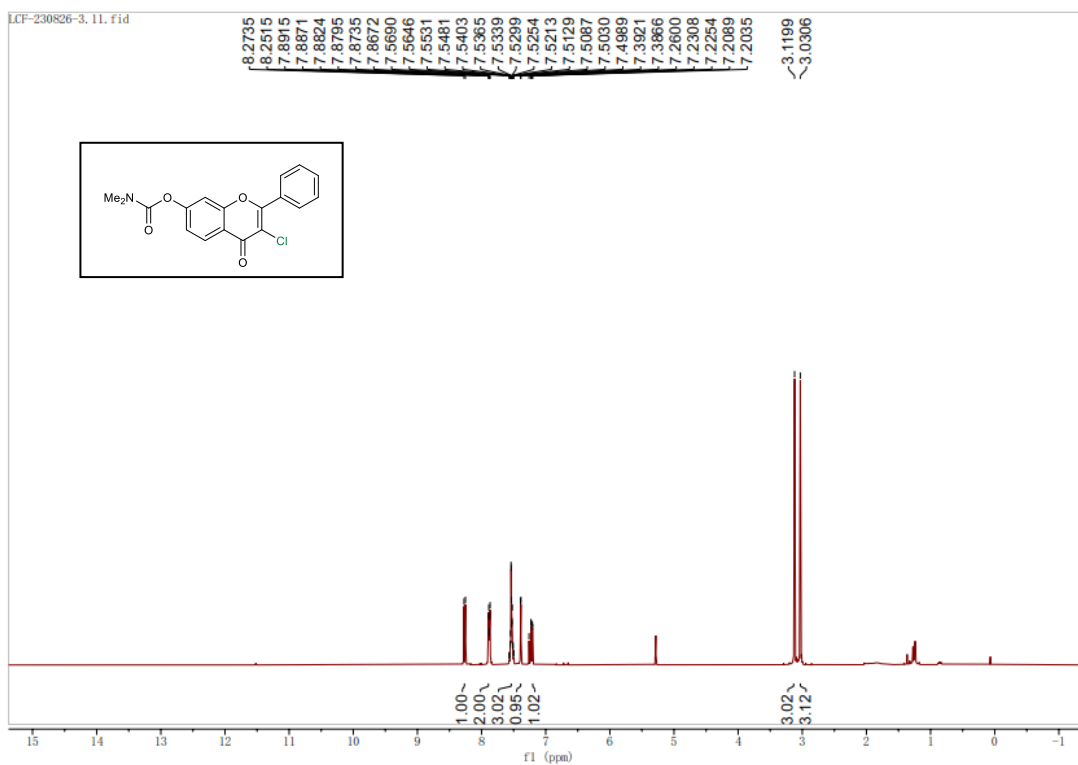
^{13}C NMR Spectra of compound **1d** in CDCl_3 (101 MHz)



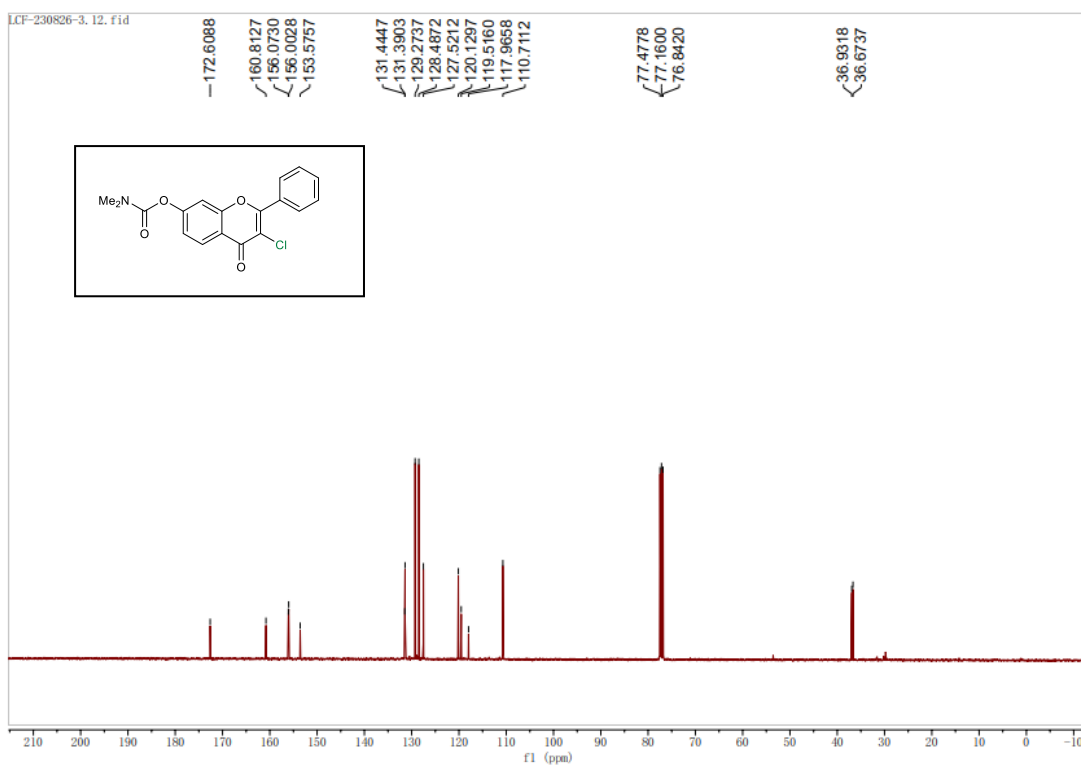
^1H NMR Spectra of compound **2aa** in CDCl_3 (400 MHz)



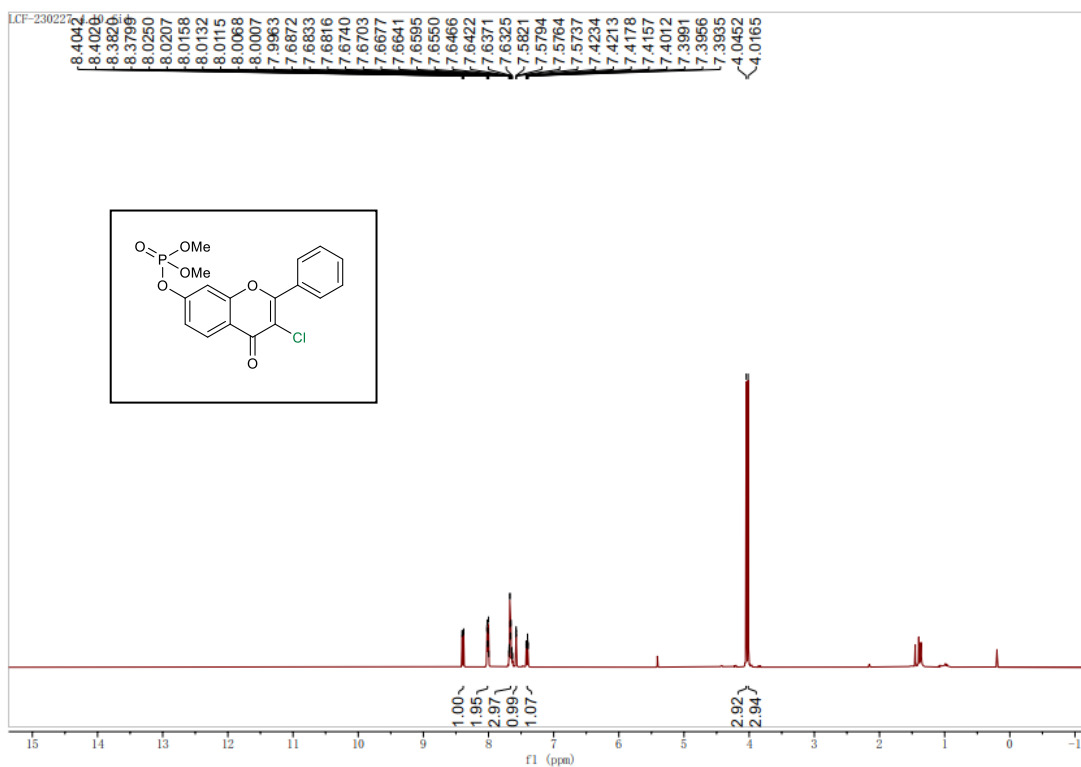
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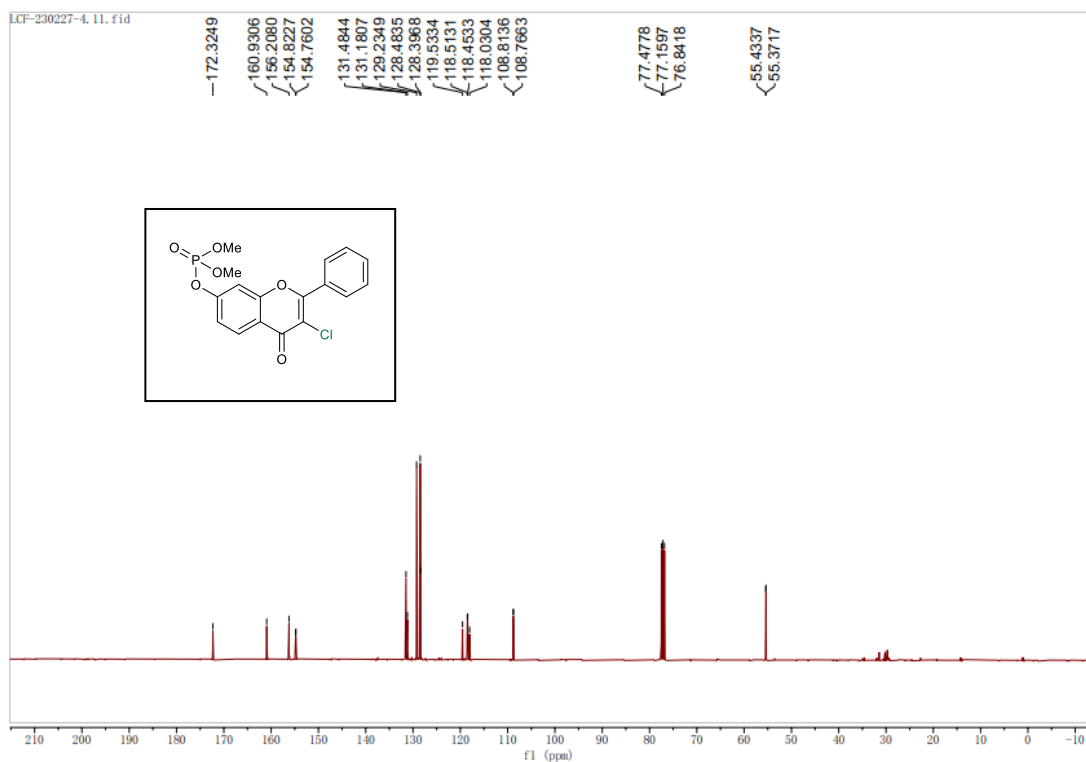
^1H NMR Spectra of compound **2ab** in CDCl_3 (400 MHz)



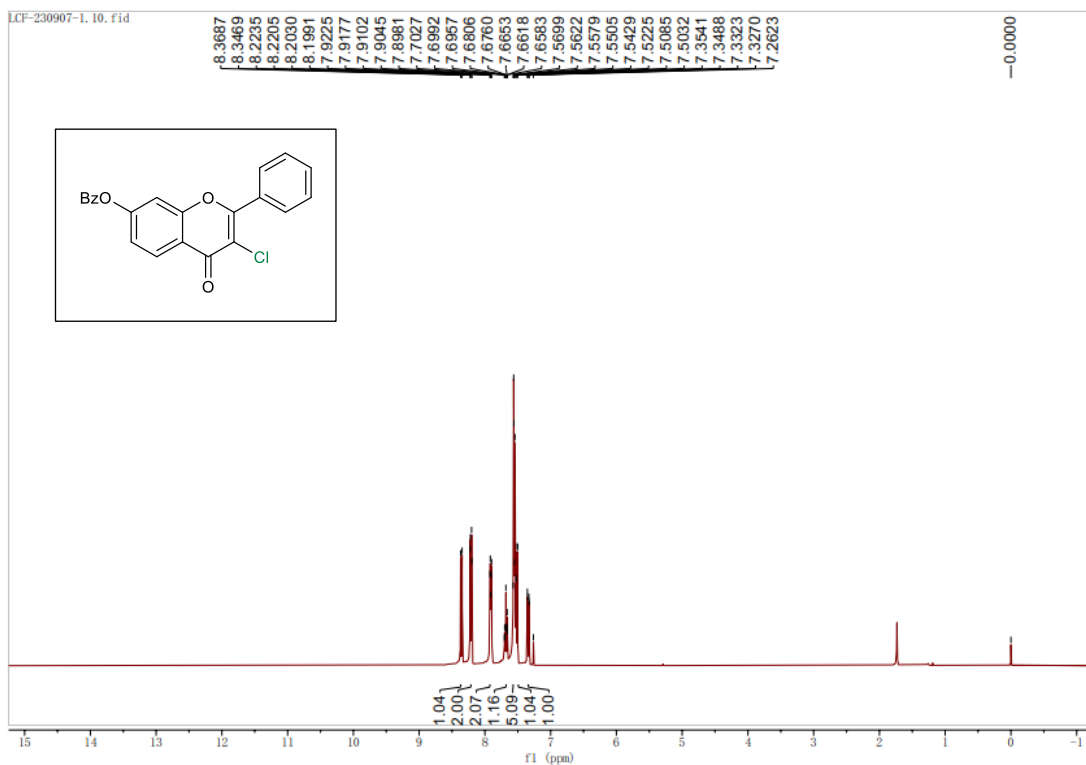
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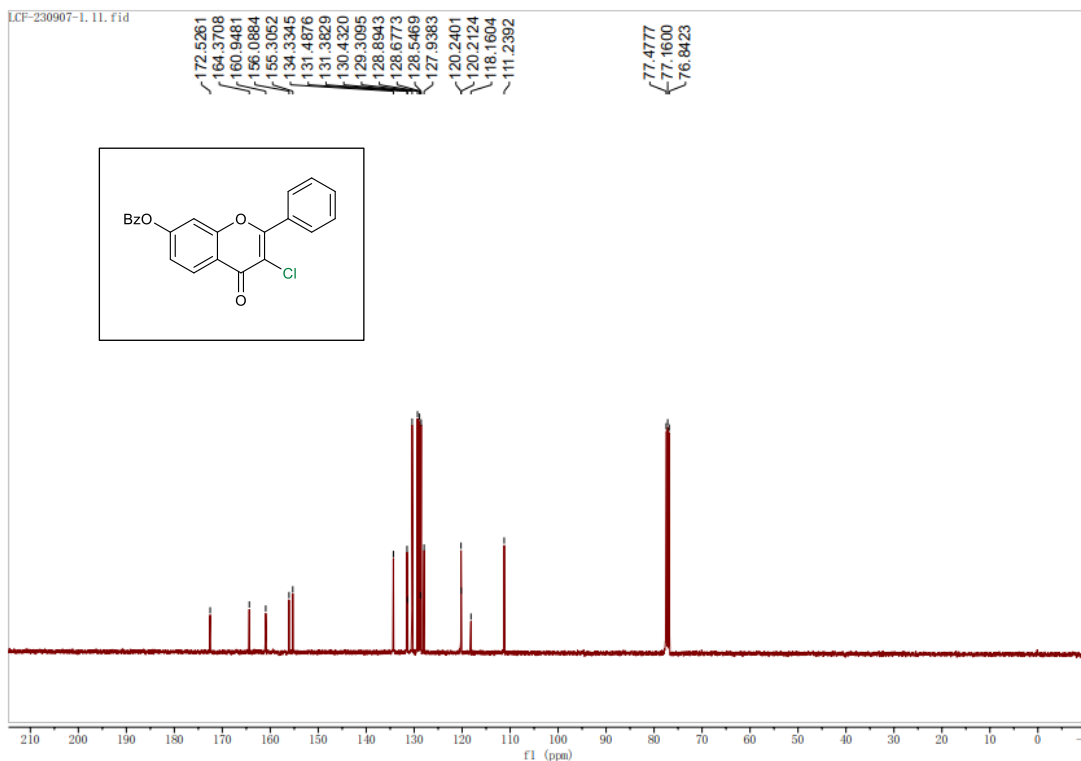
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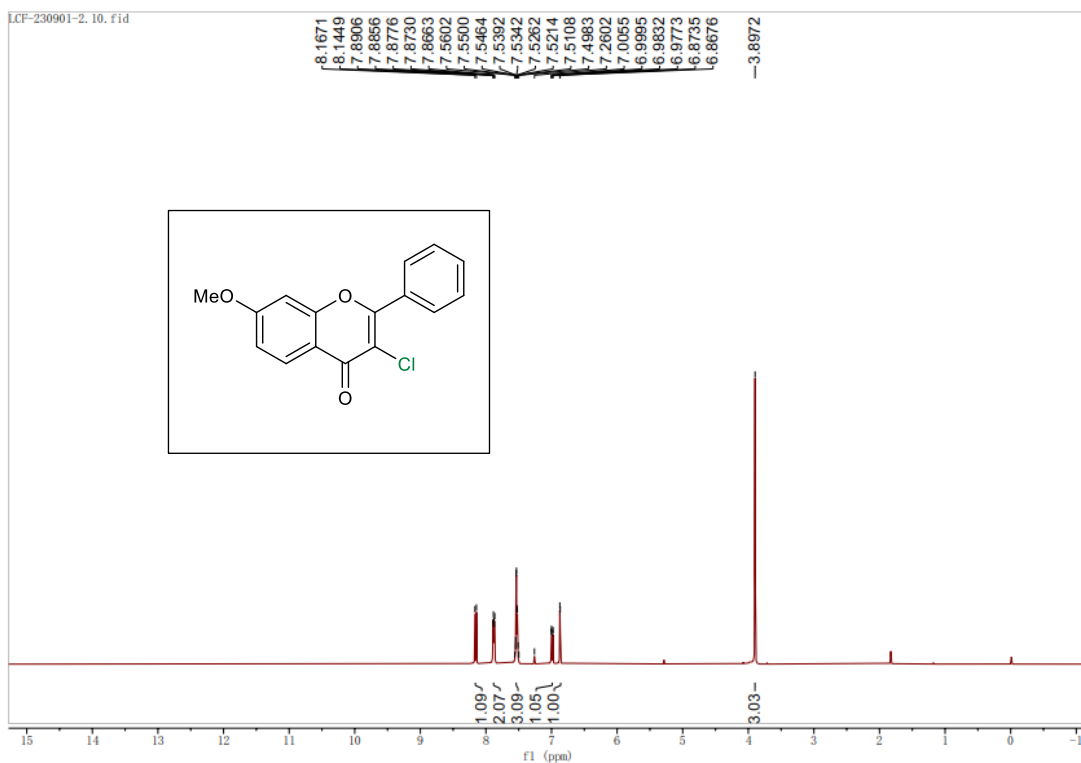
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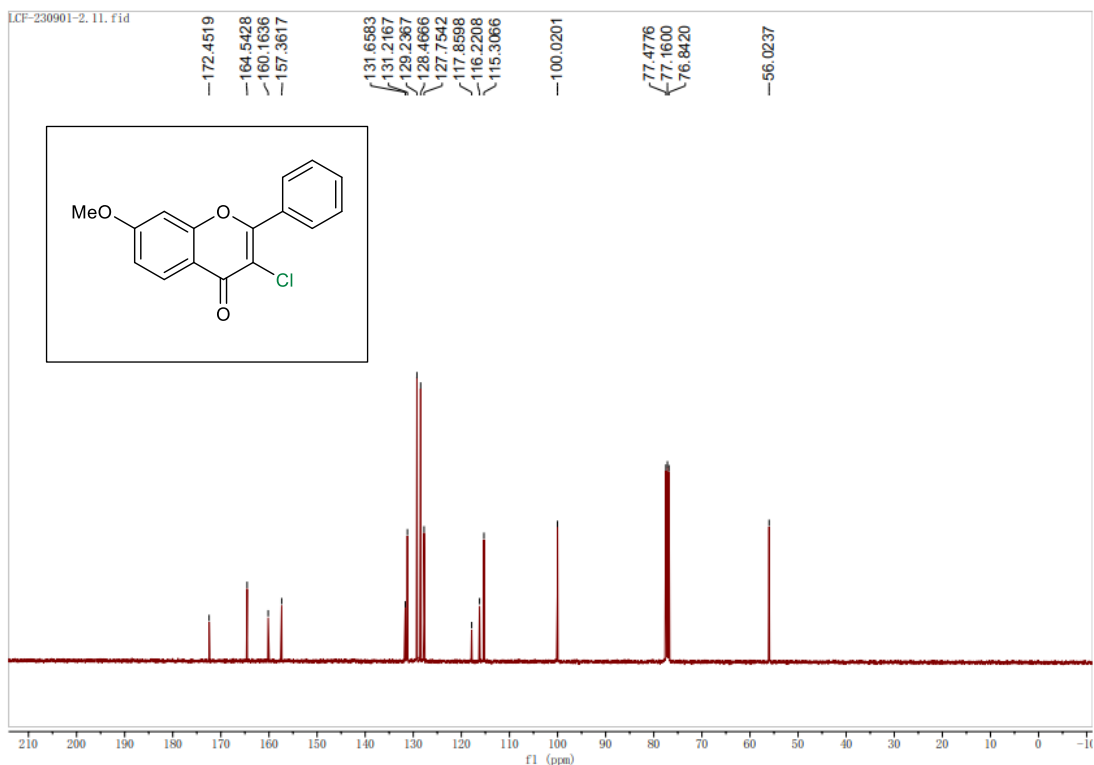
¹H NMR Spectra of compound **2ad** in CDCl₃ (400 MHz)



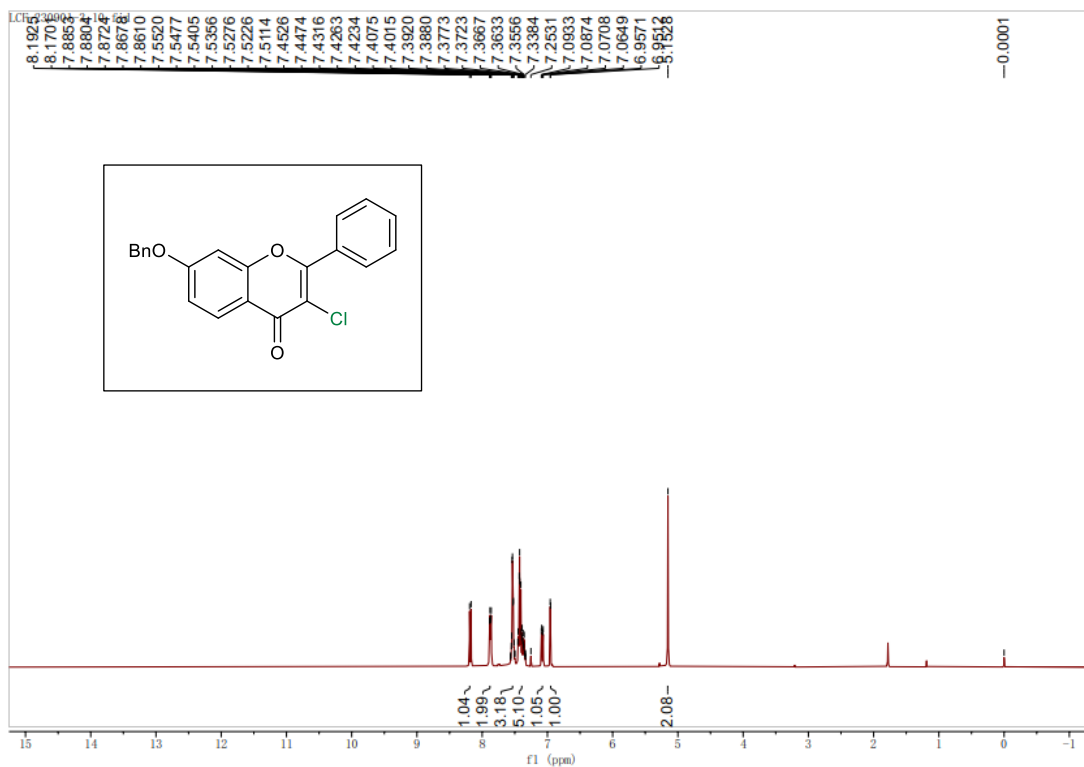
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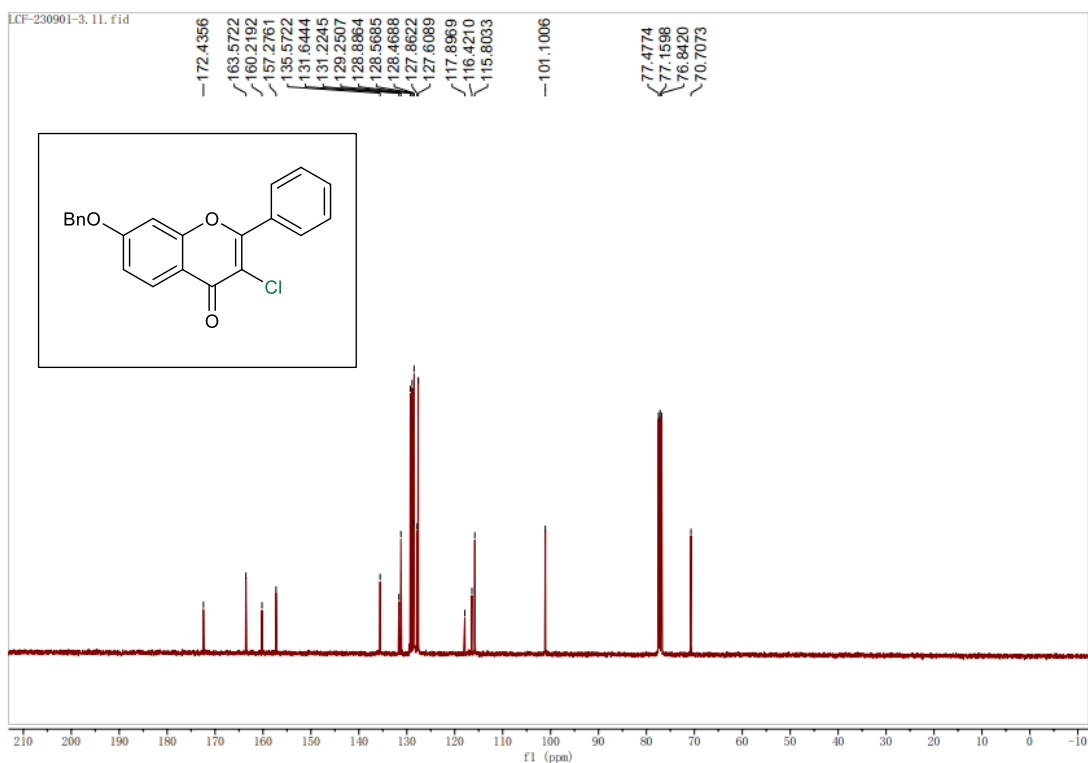
^1H NMR Spectra of compound **2ae** in CDCl_3 (400 MHz)



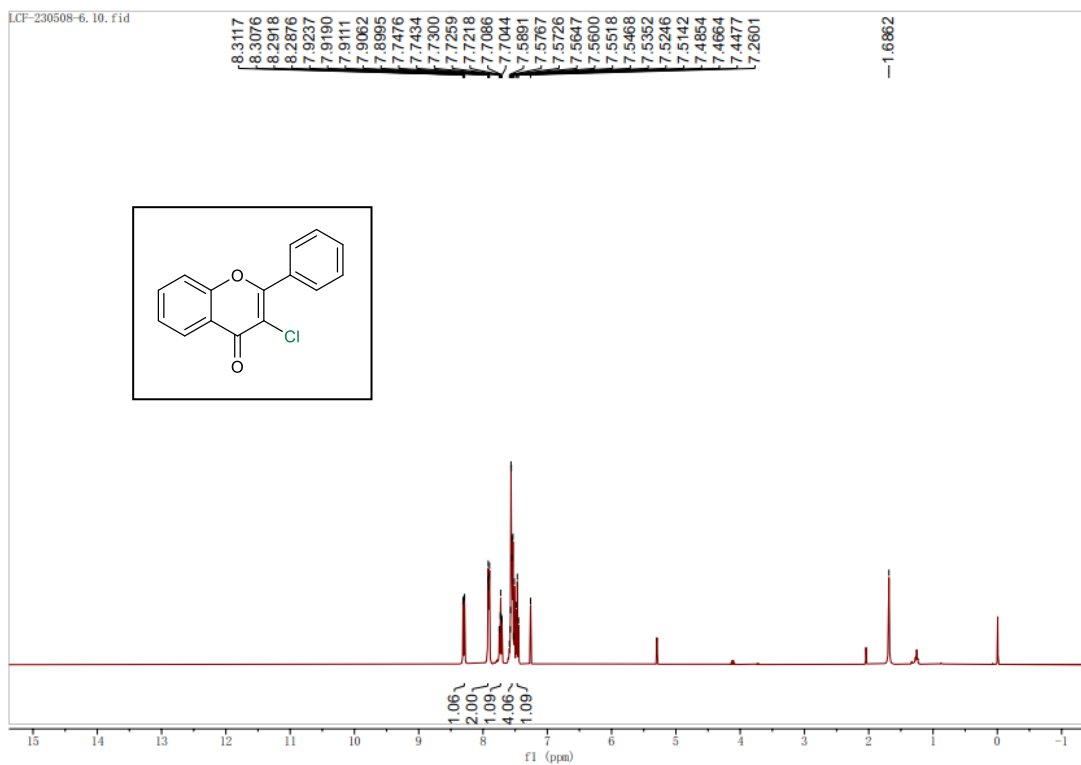
¹³C NMR Spectra of compound **2ae** in CDCl₃ (101 MHz)



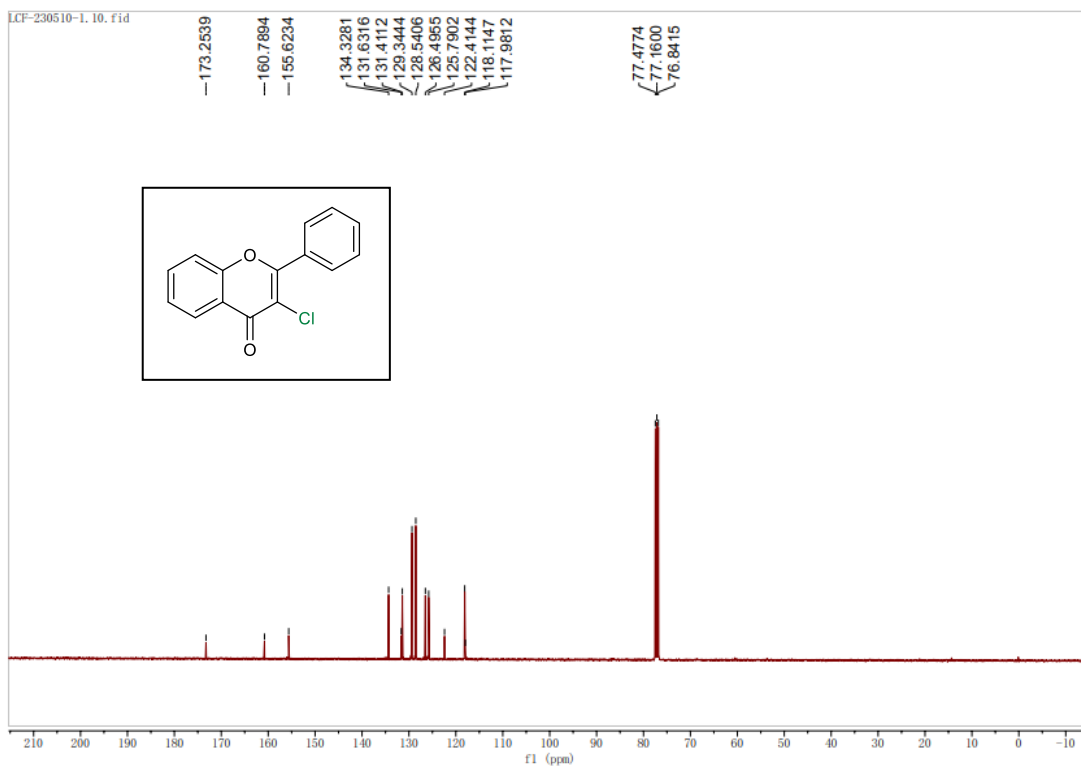
¹H NMR Spectra of compound **2af** in CDCl₃ (400 MHz)



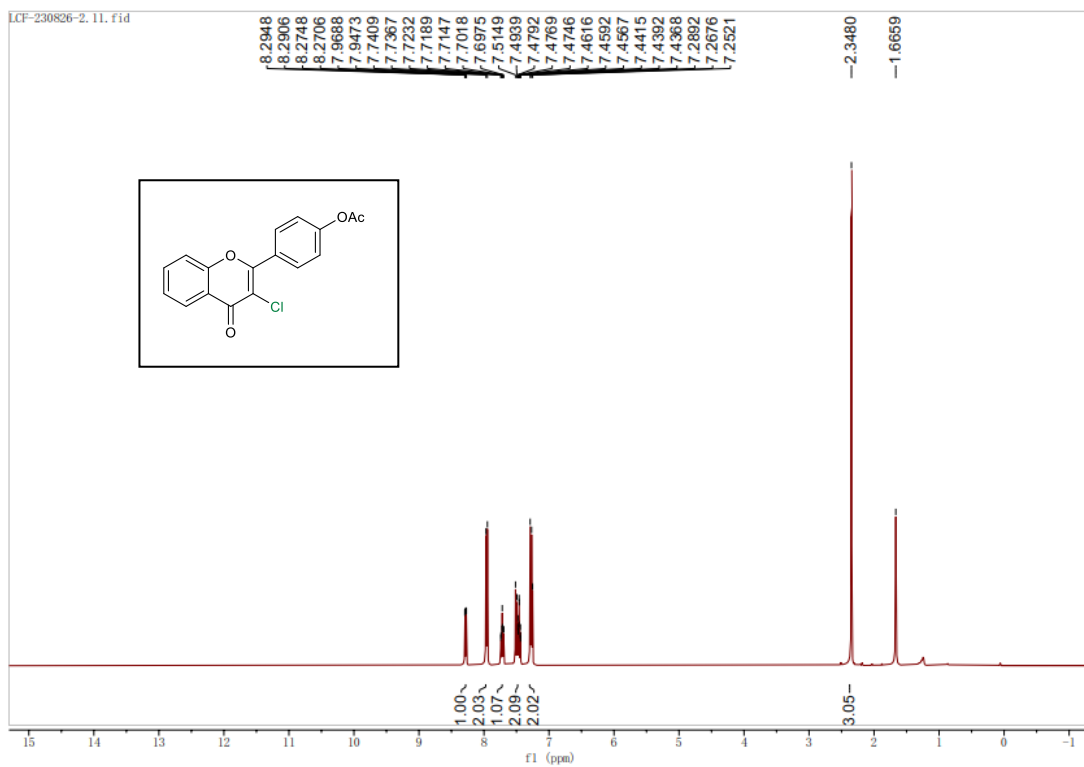
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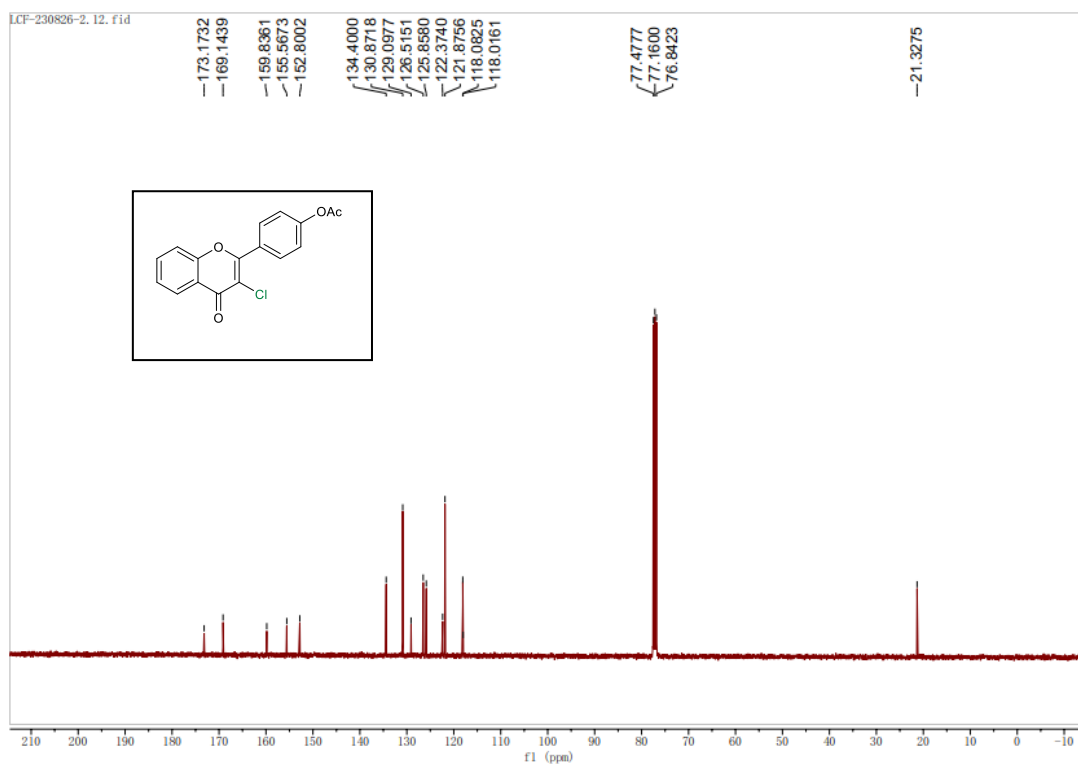
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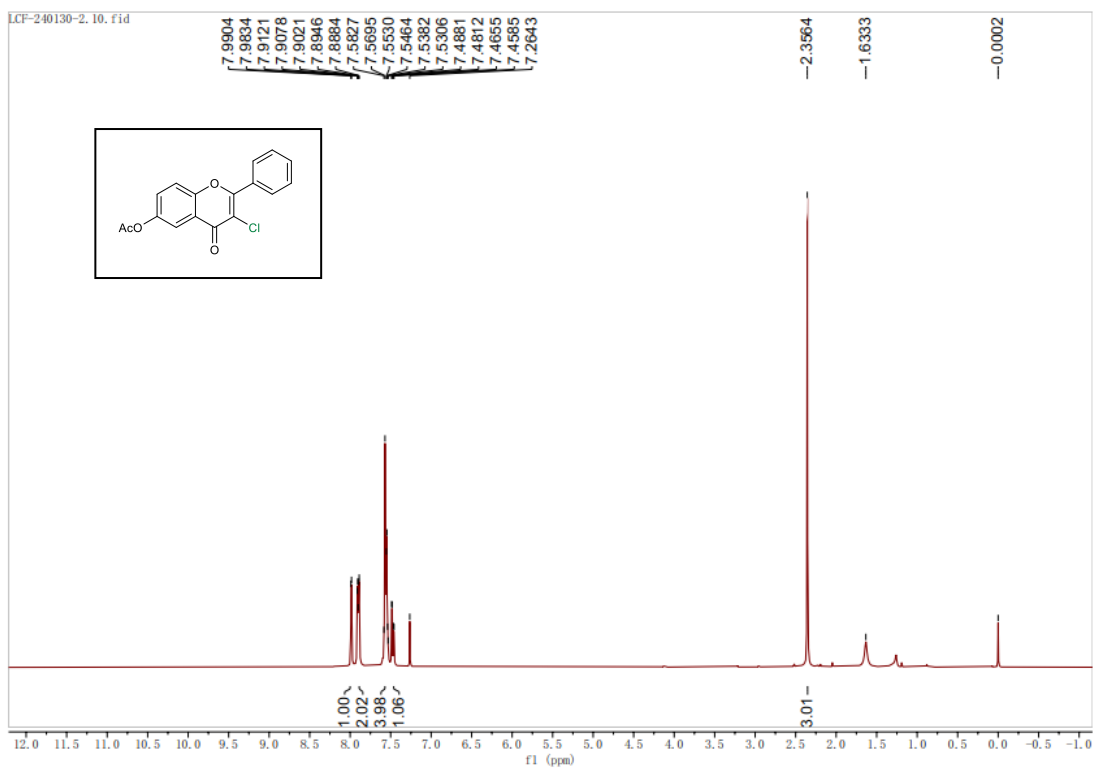
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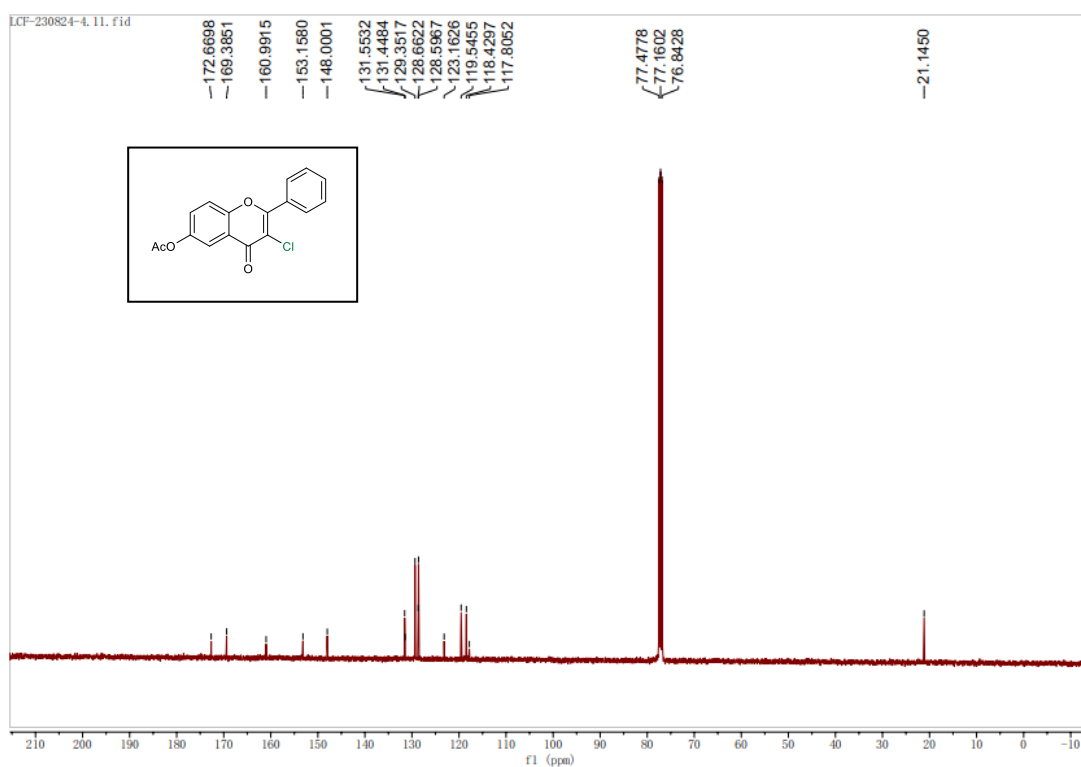
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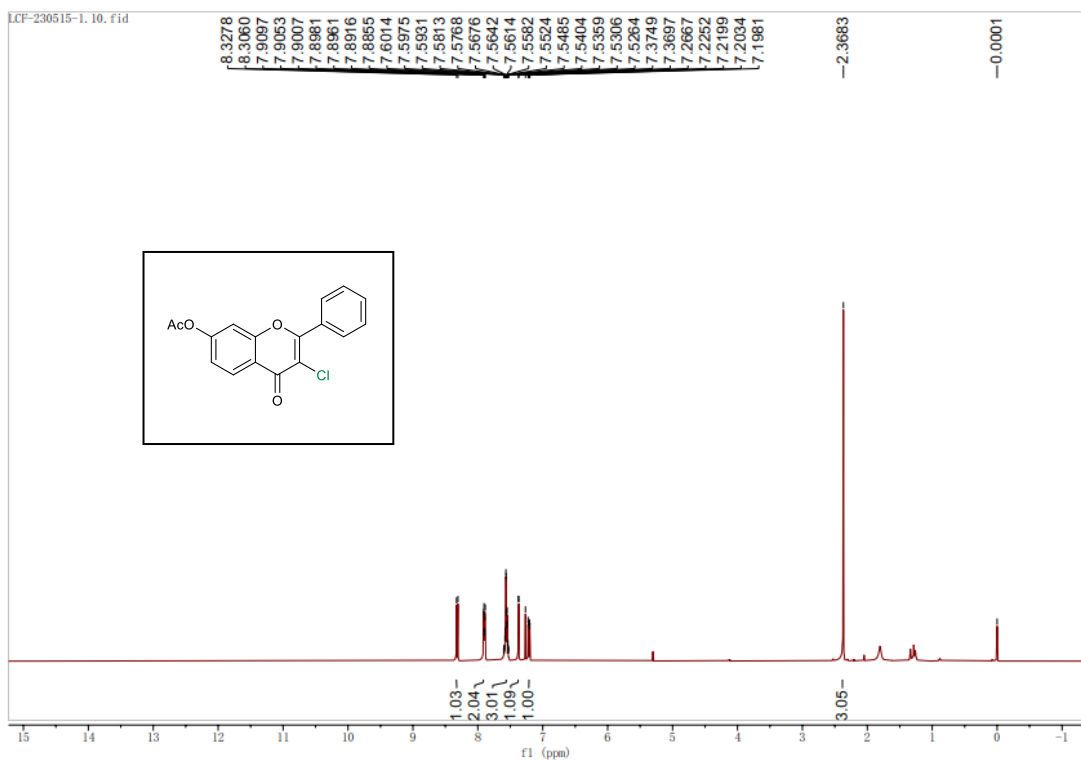
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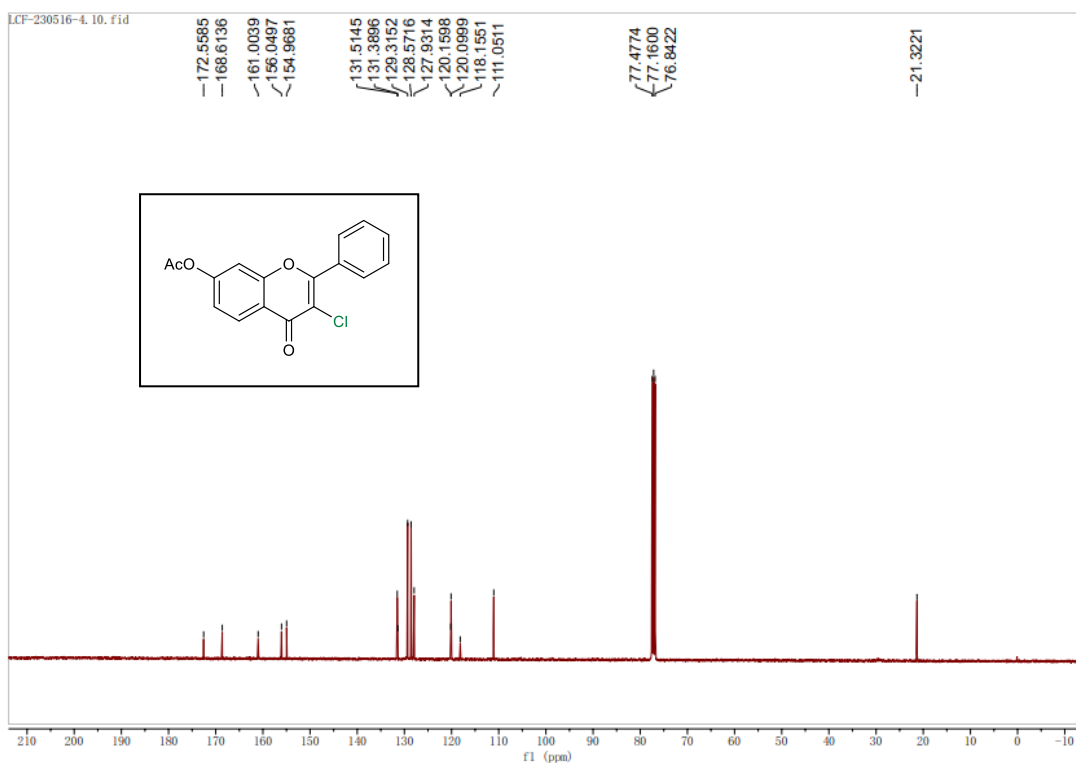
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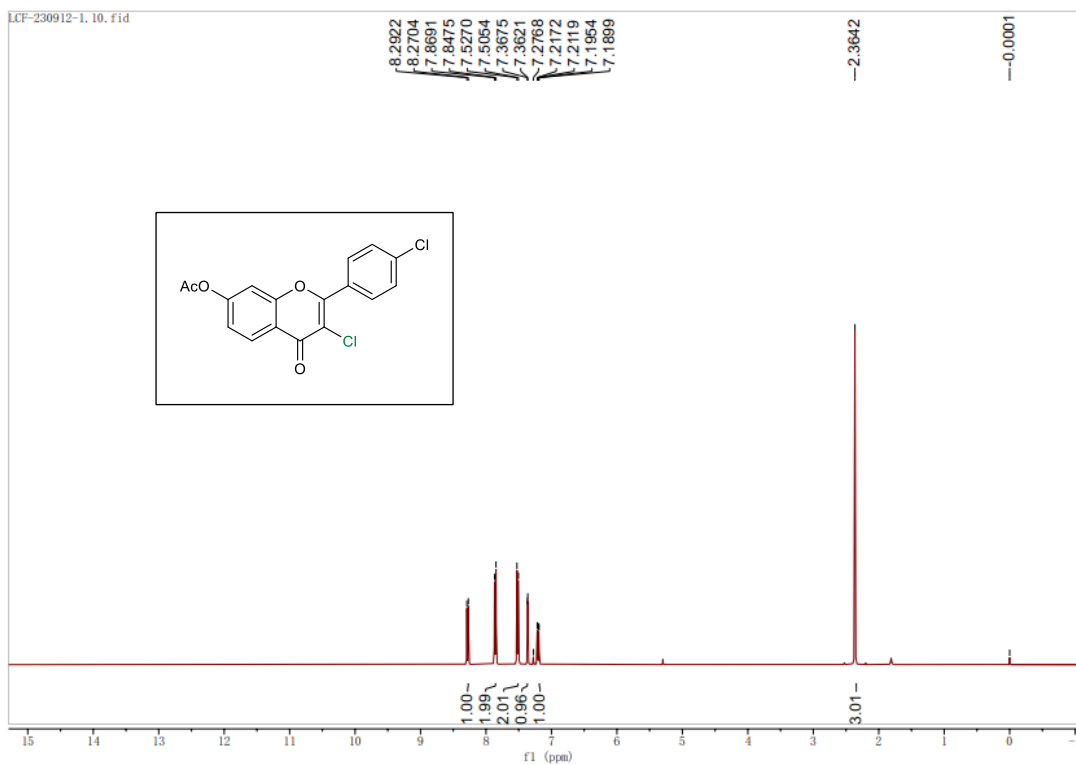
^{13}C NMR Spectra of compound **2ai** in CDCl_3 (101 MHz)



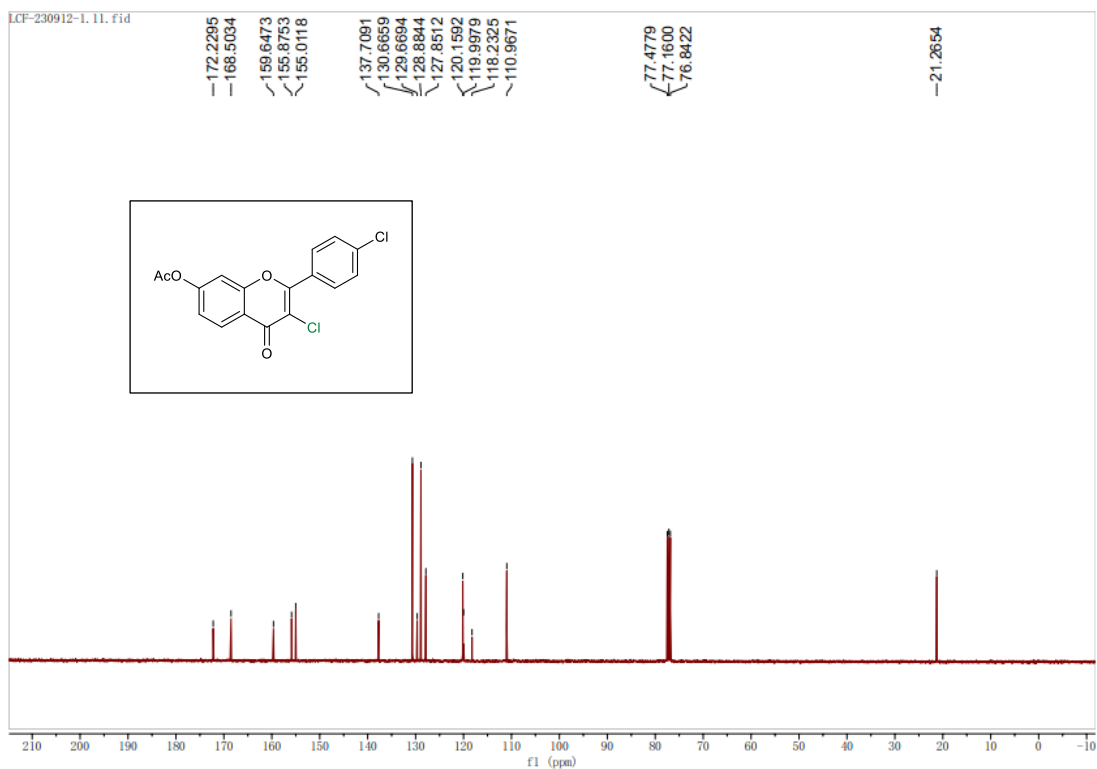
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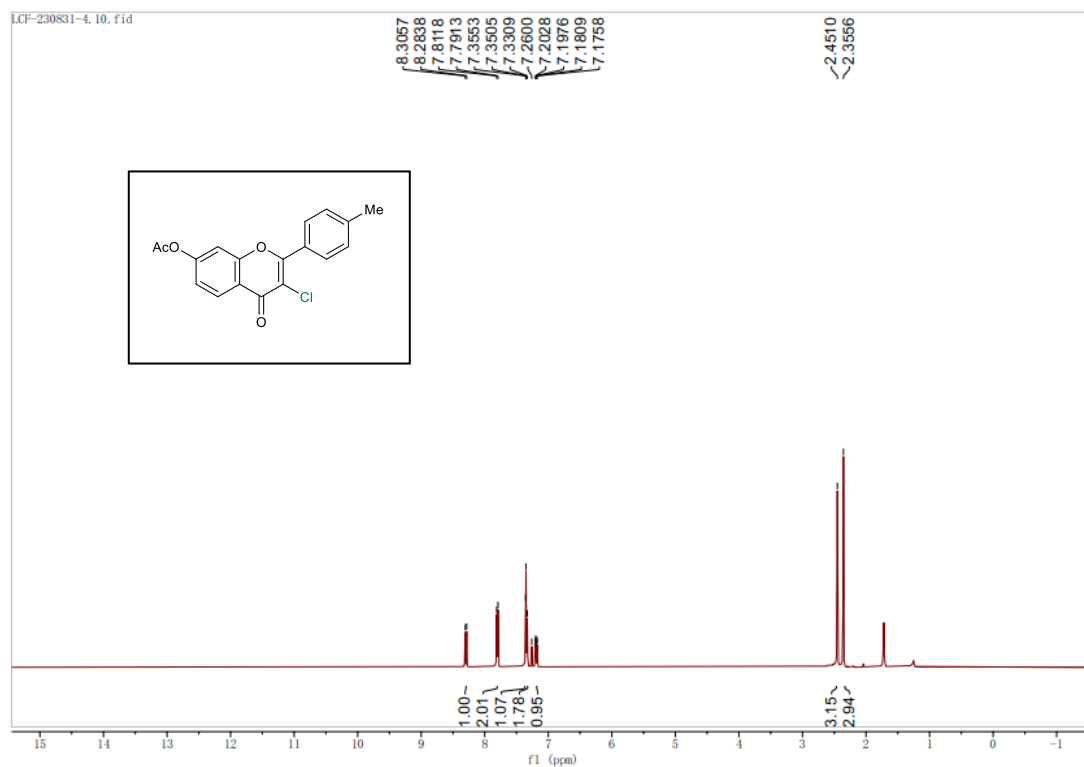
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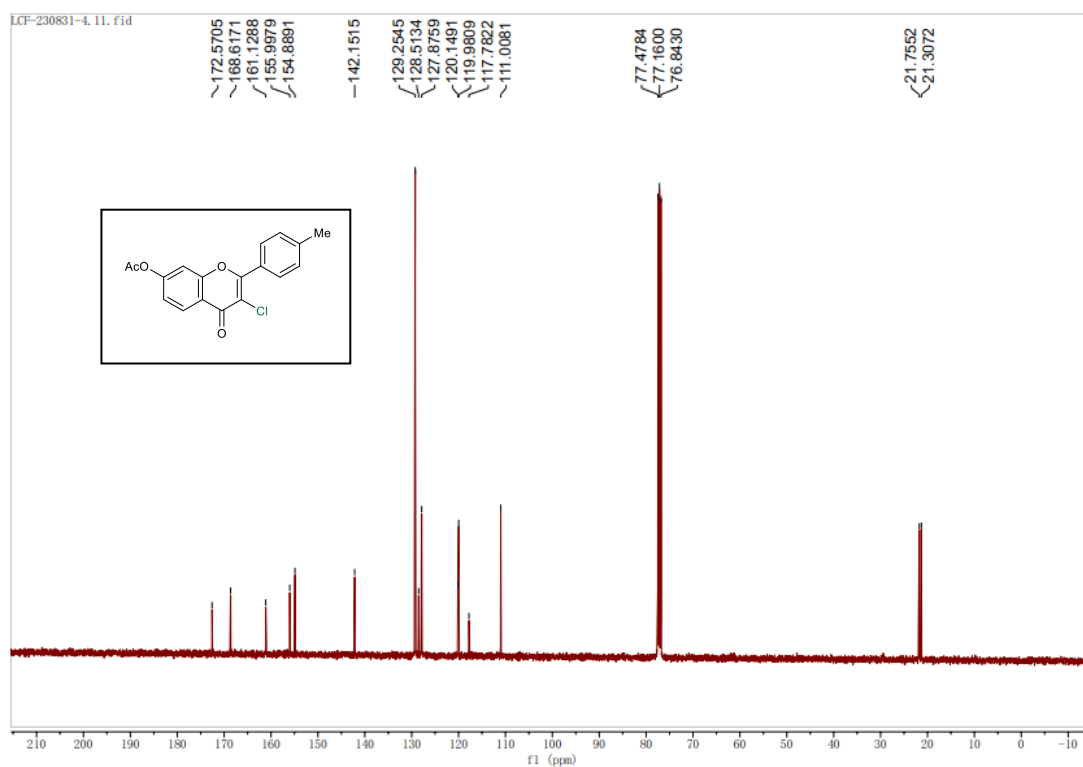
^1H NMR Spectra of compound **2ak** in CDCl_3 (400 MHz)



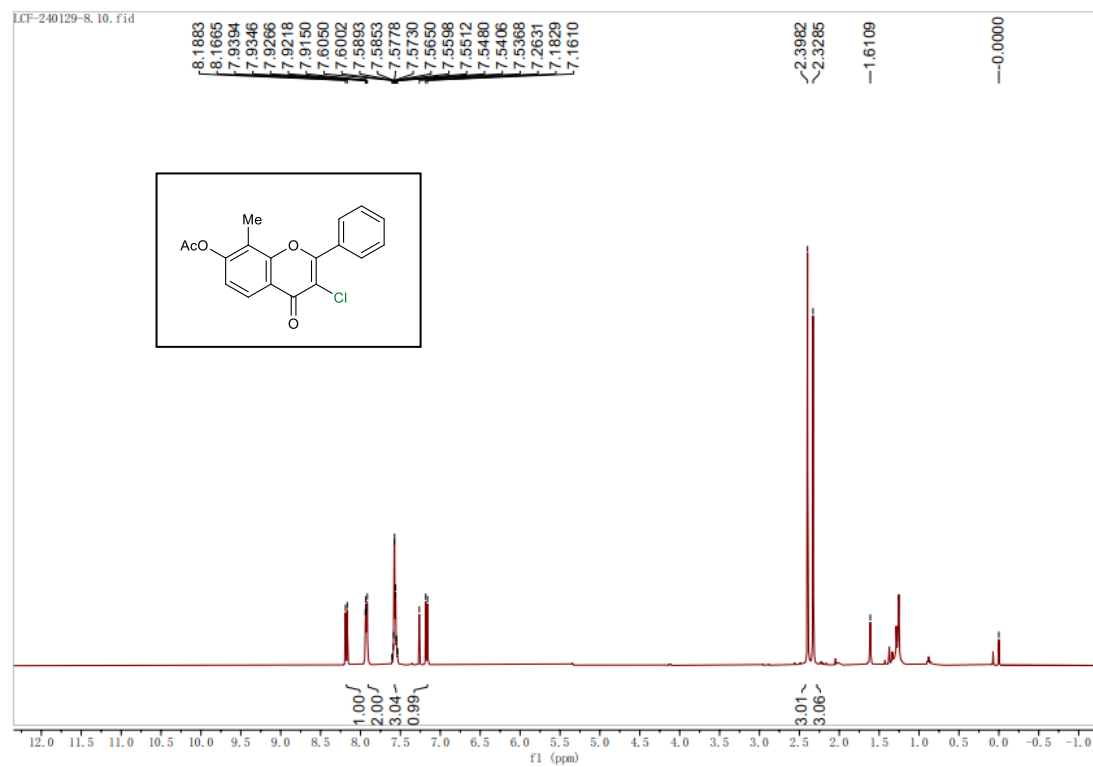
^{13}C NMR Spectra of compound **2ak** in CDCl_3 (101 MHz)



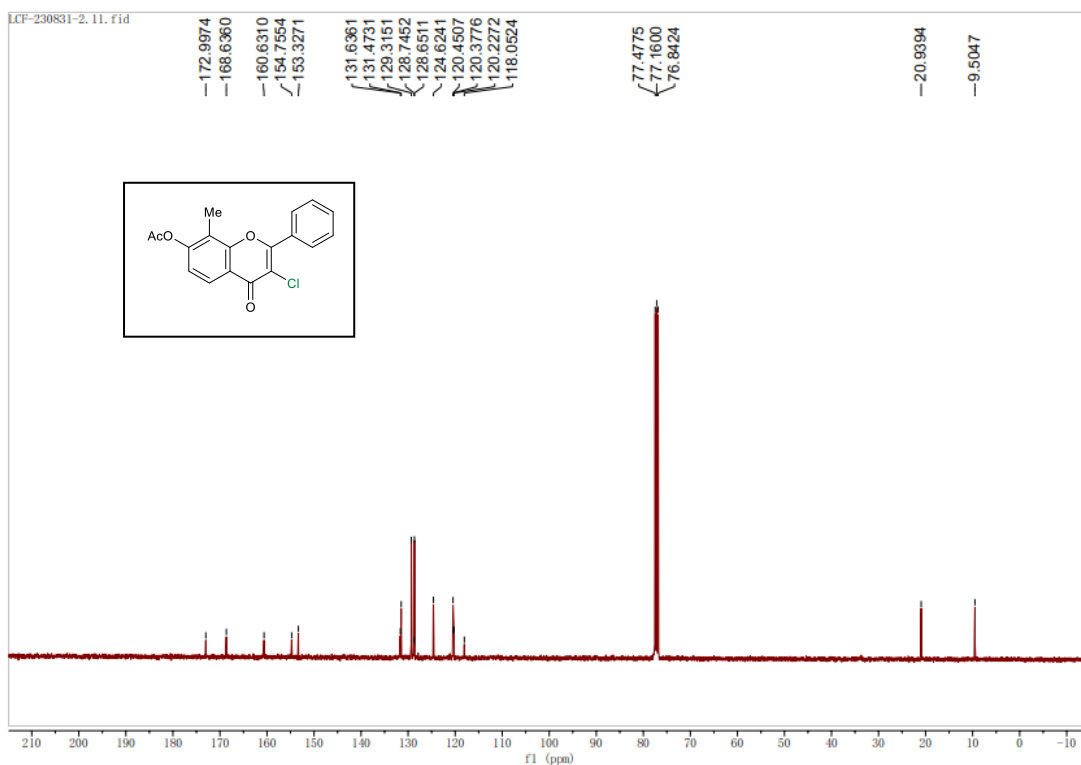
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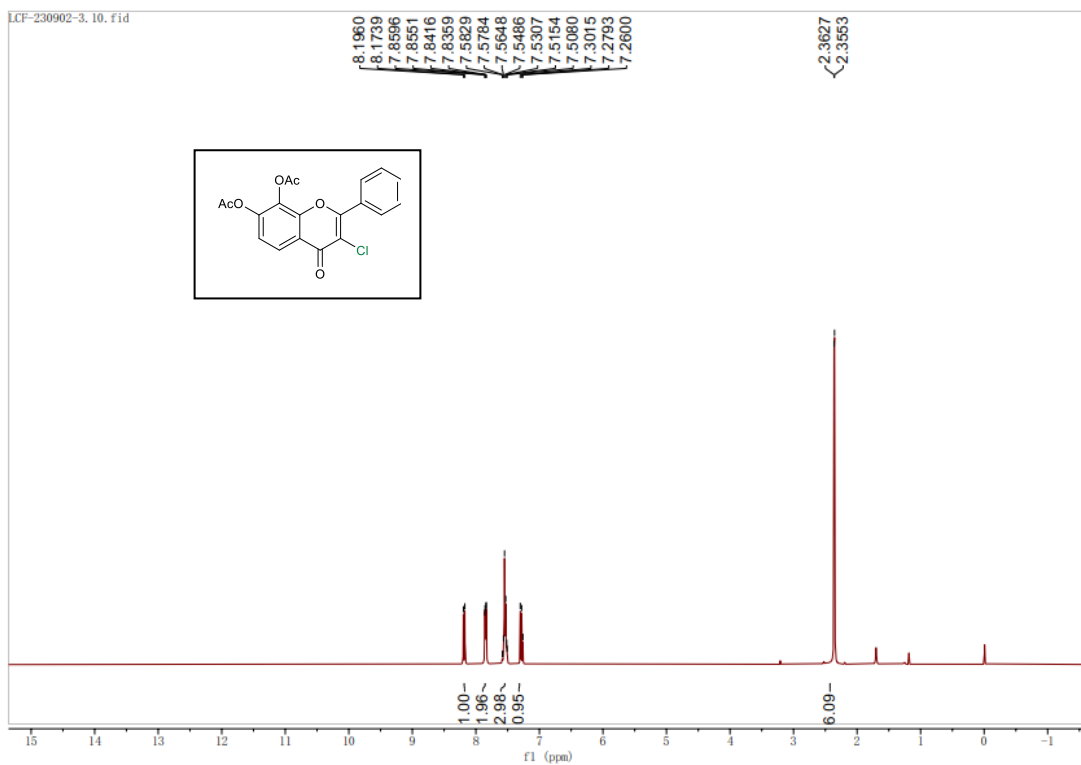
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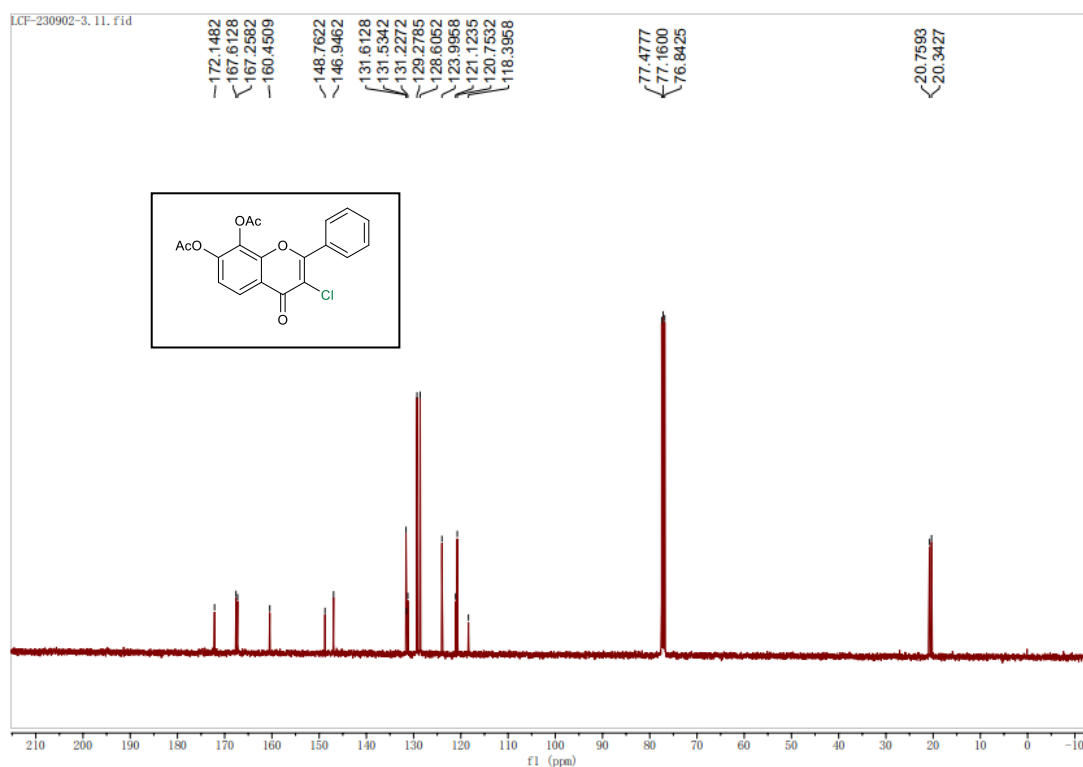
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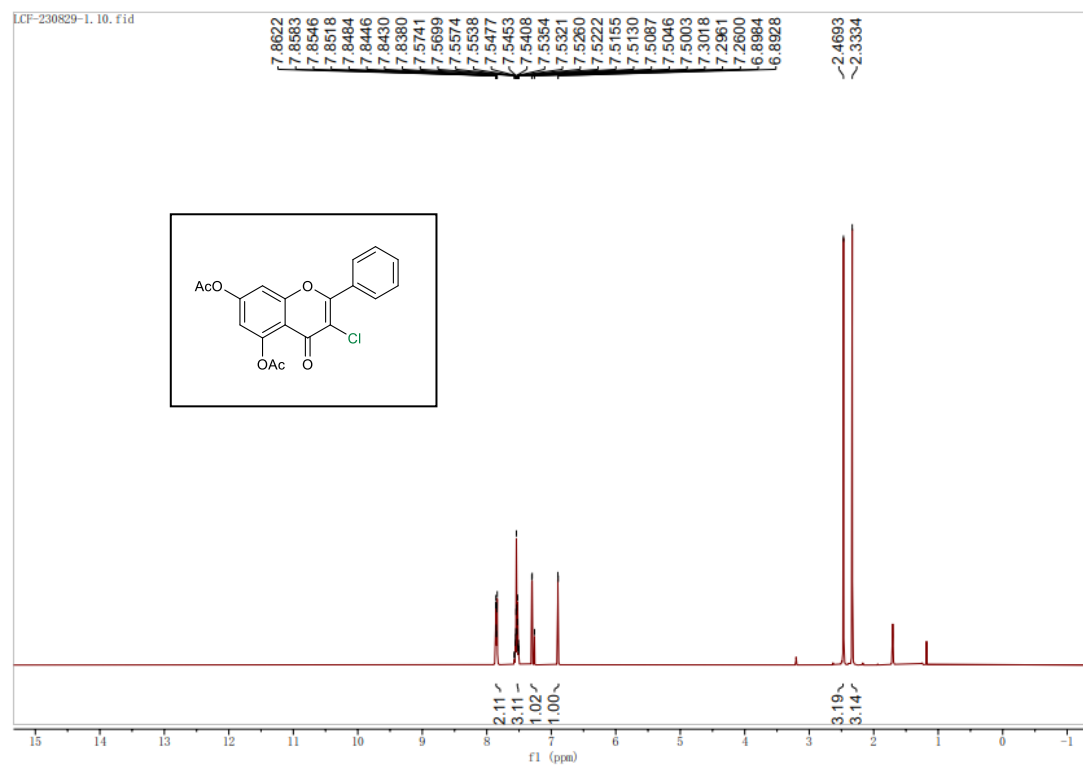
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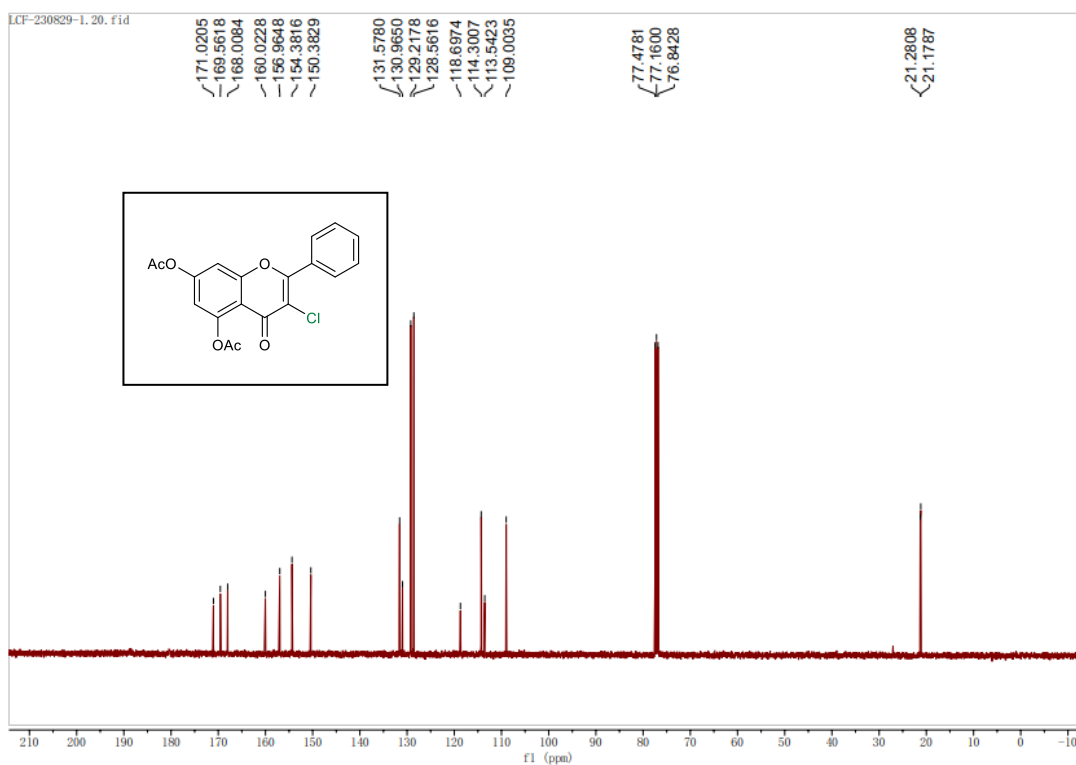
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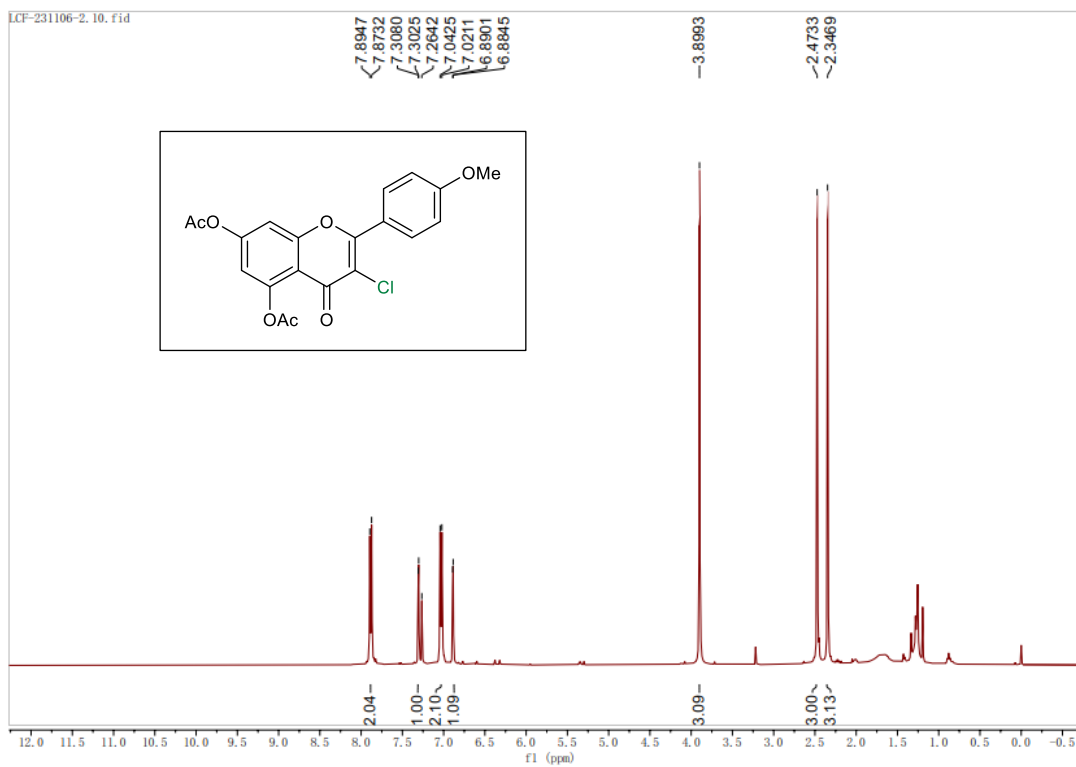
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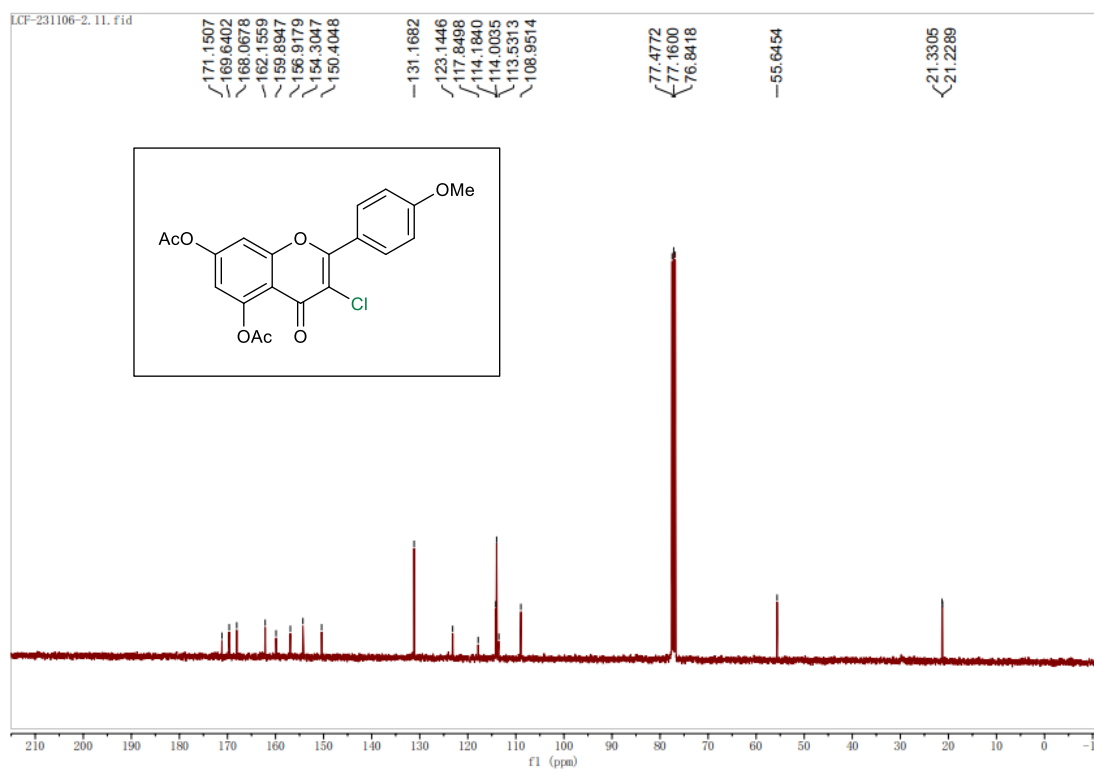
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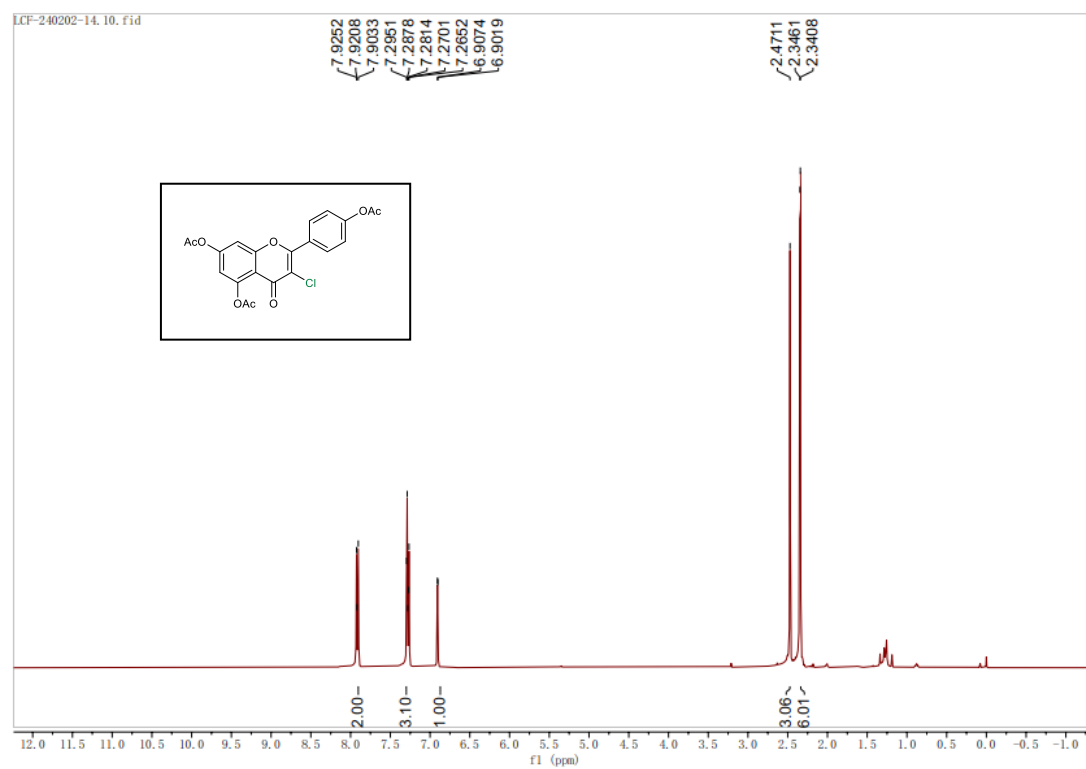
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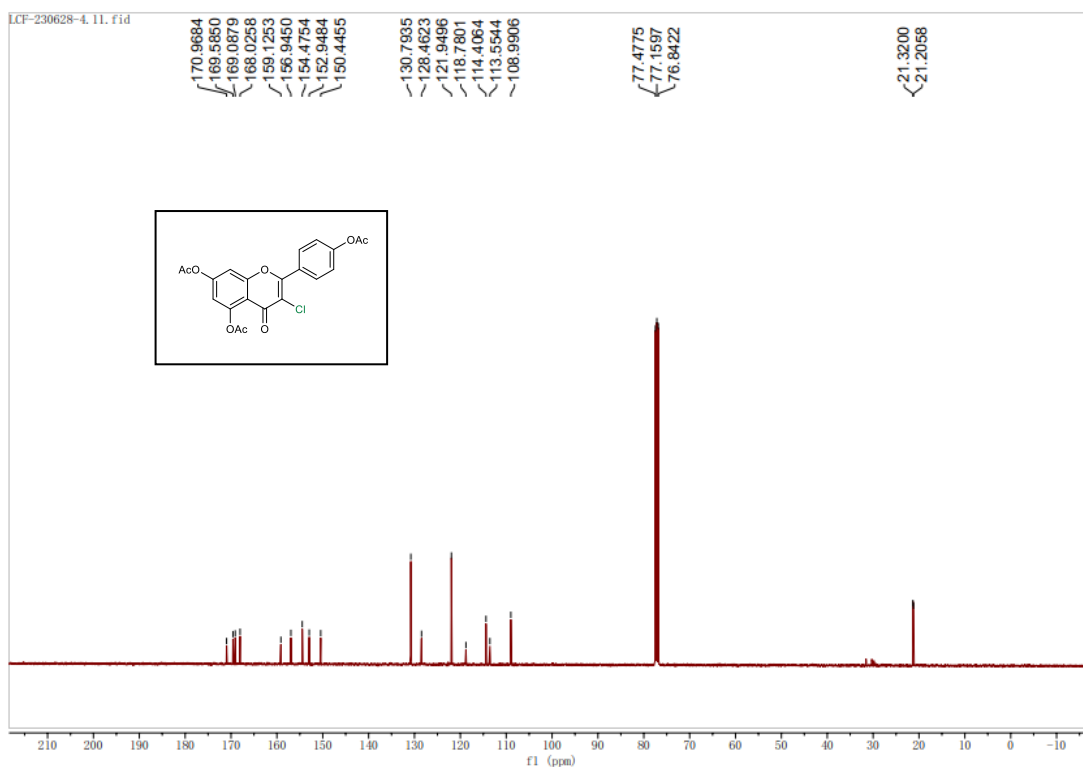
^1H NMR Spectra of compound **2ap** in CDCl_3 (400 MHz)



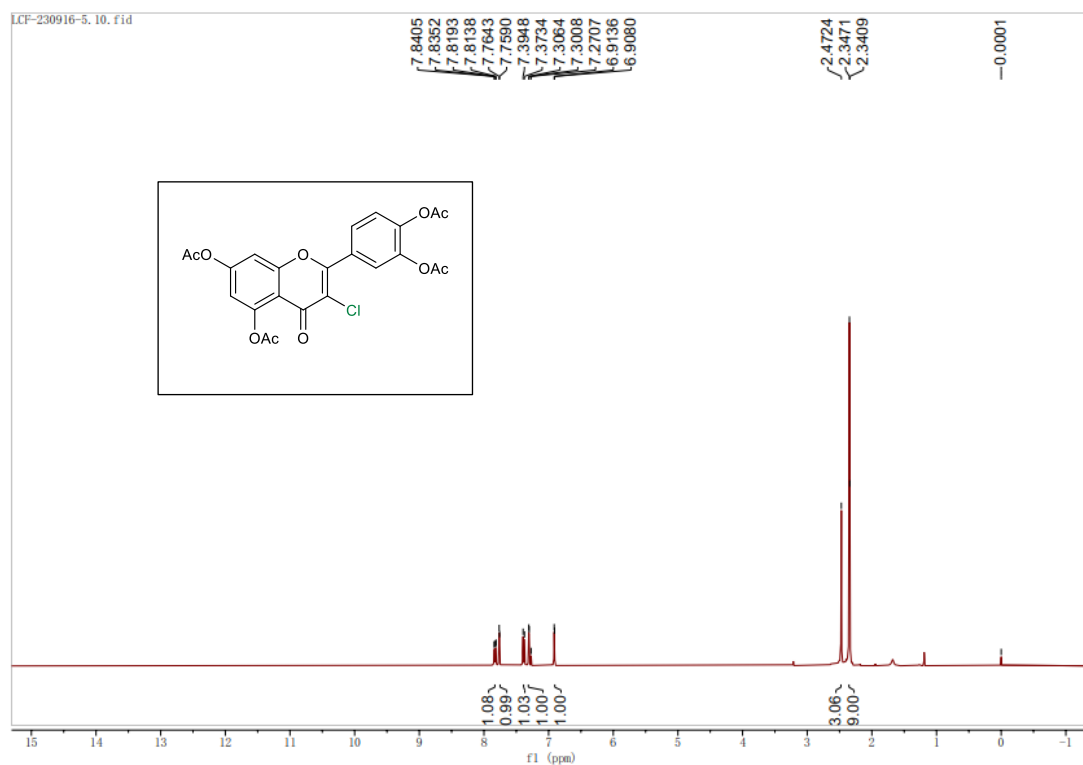
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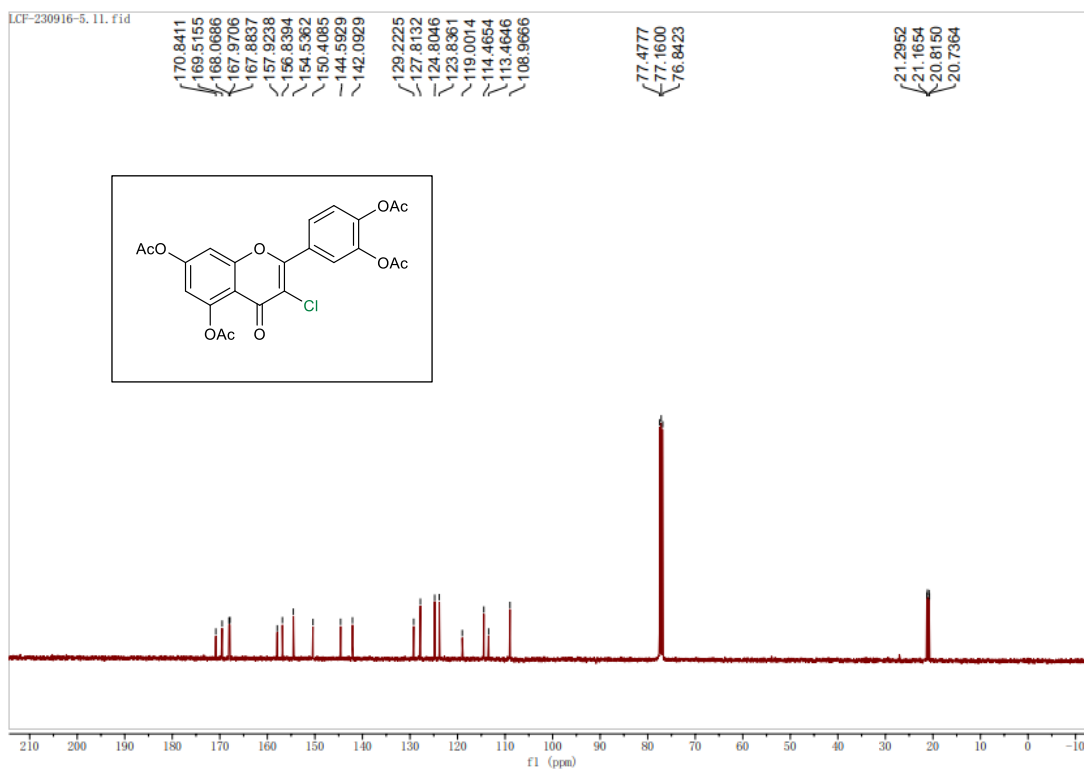
^1H NMR Spectra of compound **2aq** in CDCl_3 (400 MHz)



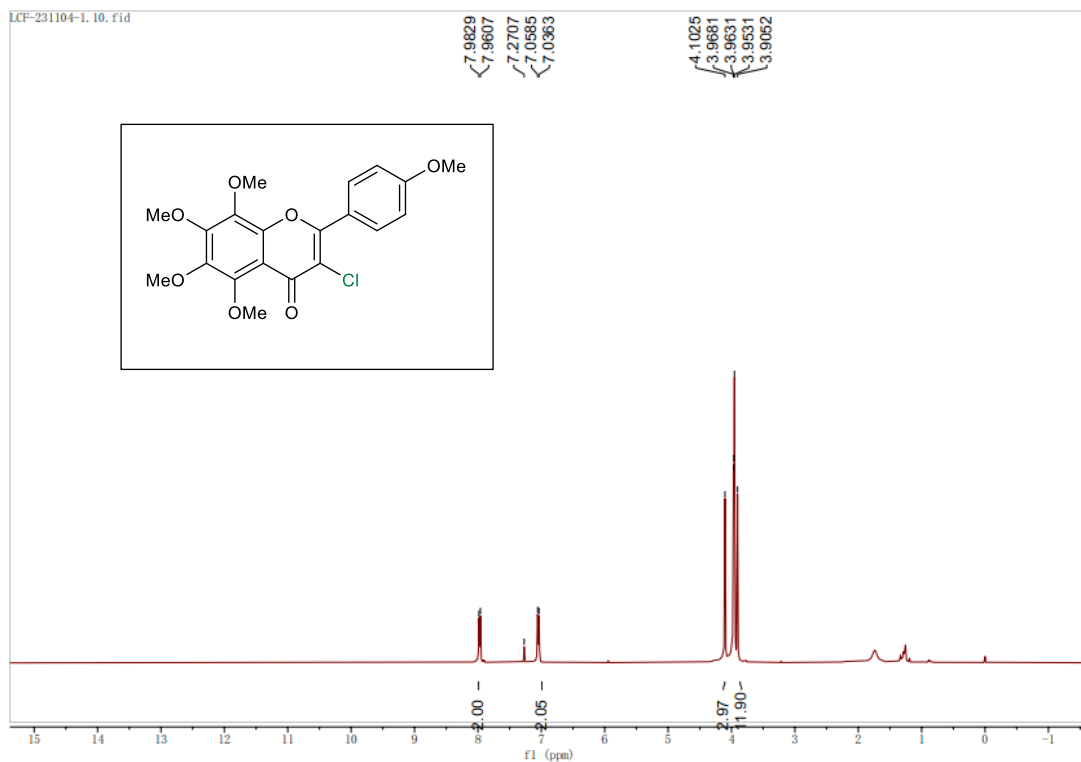
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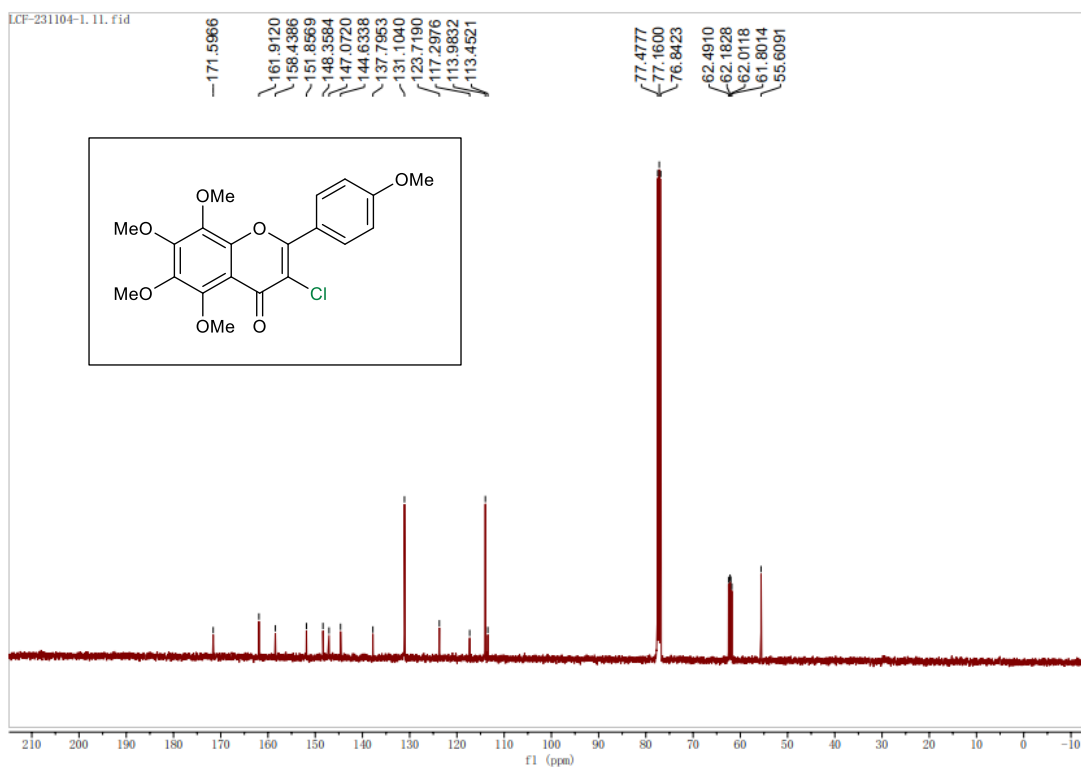
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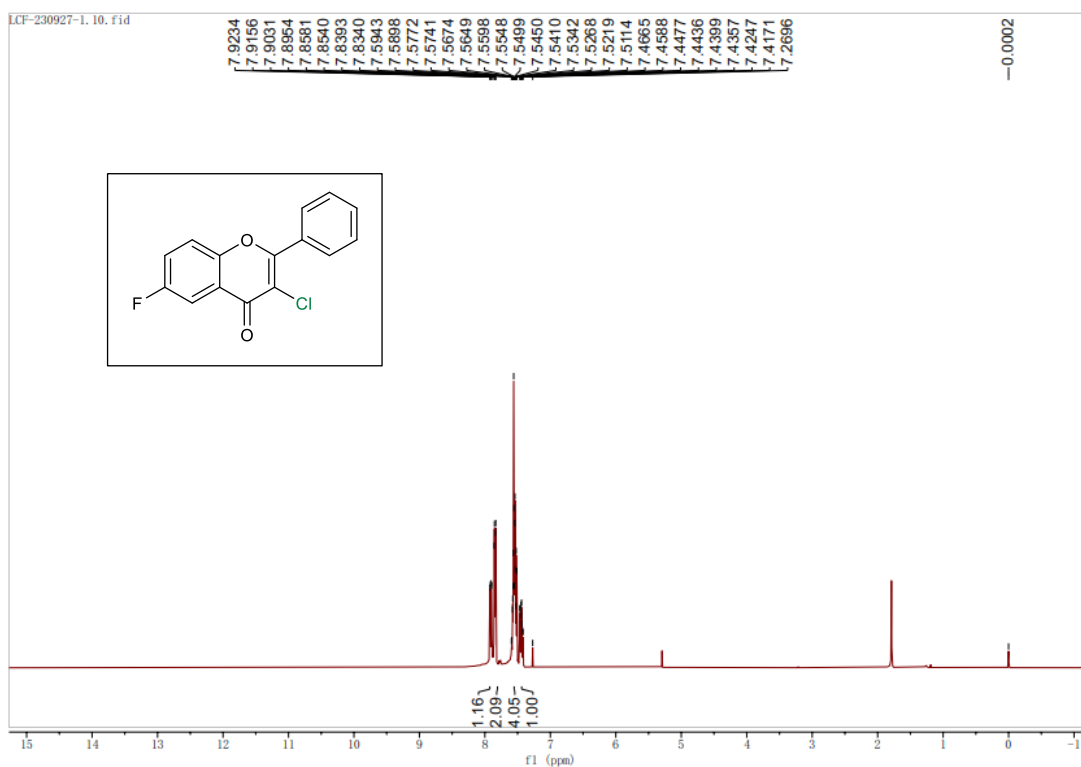
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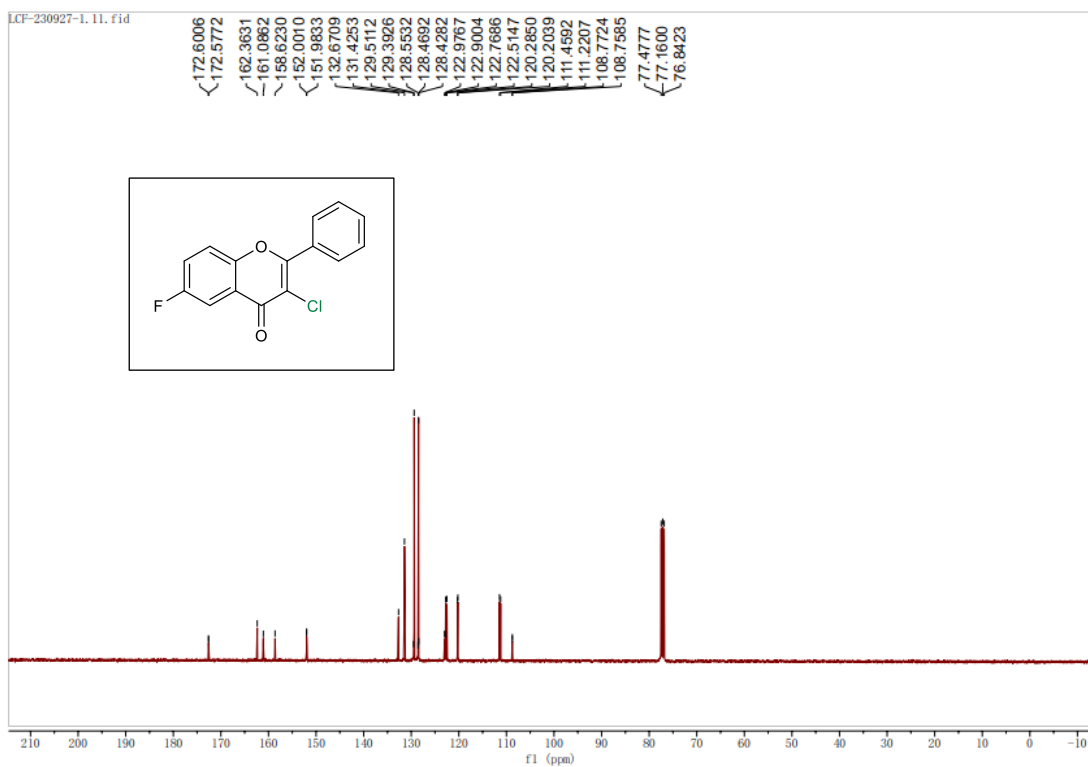
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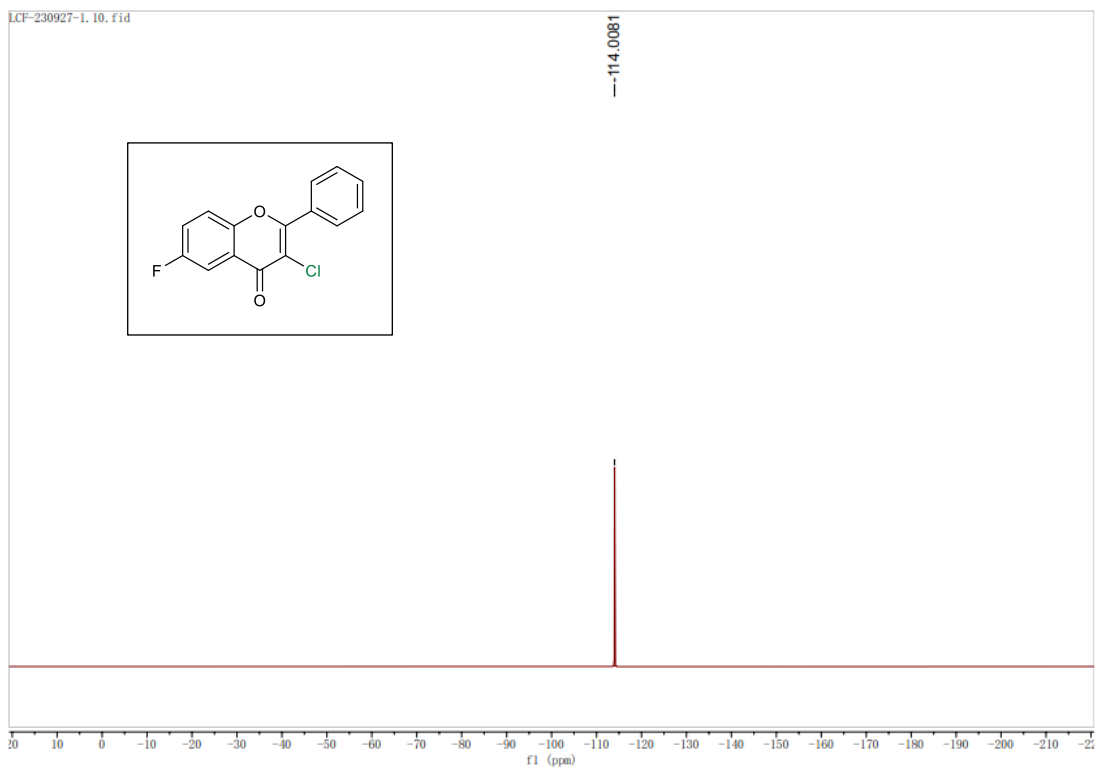
¹³C NMR Spectra of compound **2as** in CDCl₃ (101 MHz)



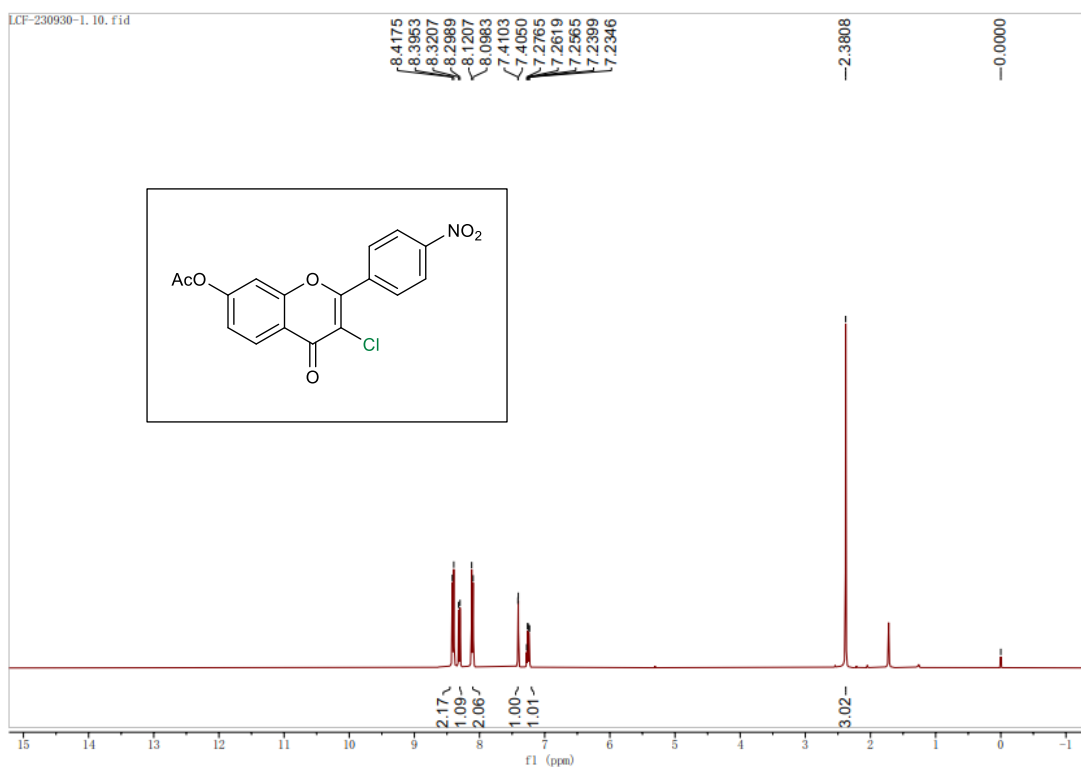
¹H NMR Spectra of compound **2at** in CDCl₃ (400 MHz)



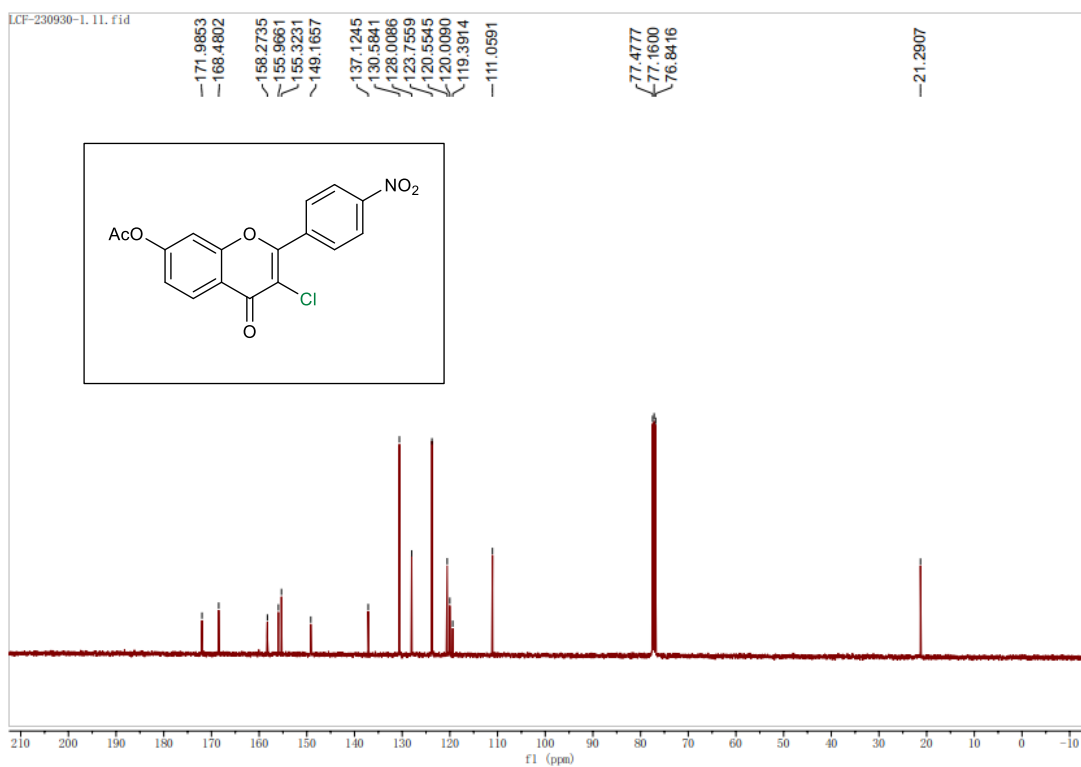
^{13}C NMR Spectra of compound **2at** in CDCl_3 (101 MHz)



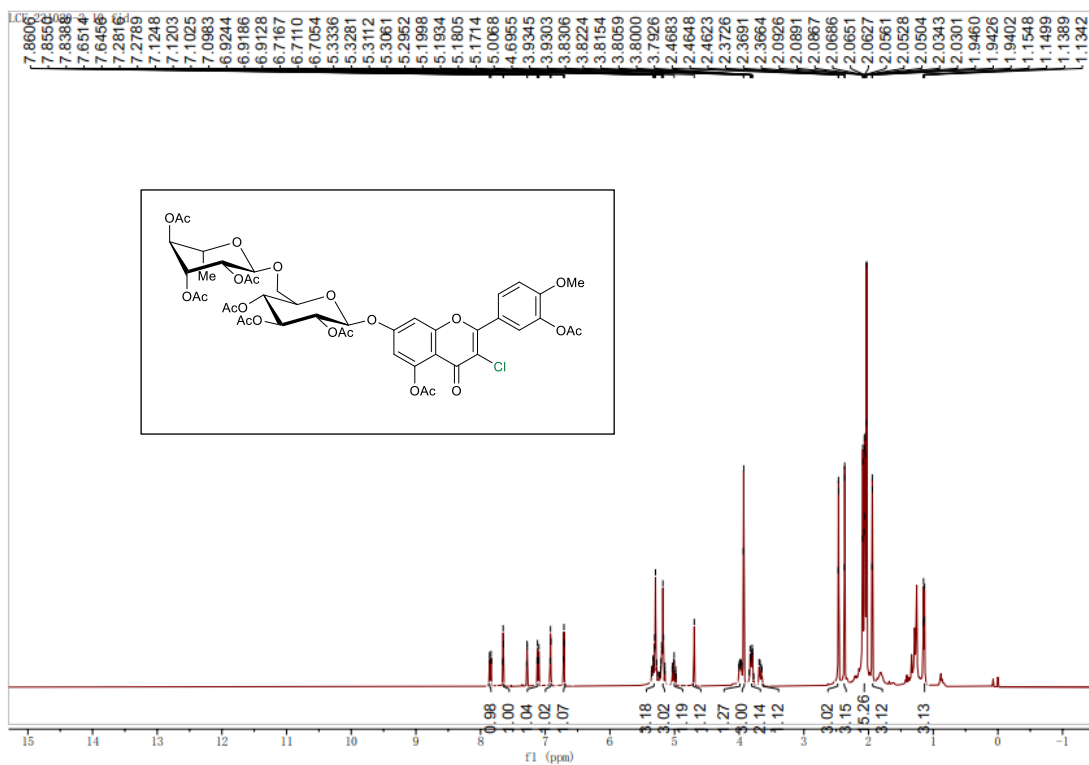
^{19}F NMR Spectra of compound **2at** in CDCl_3 (377 MHz)



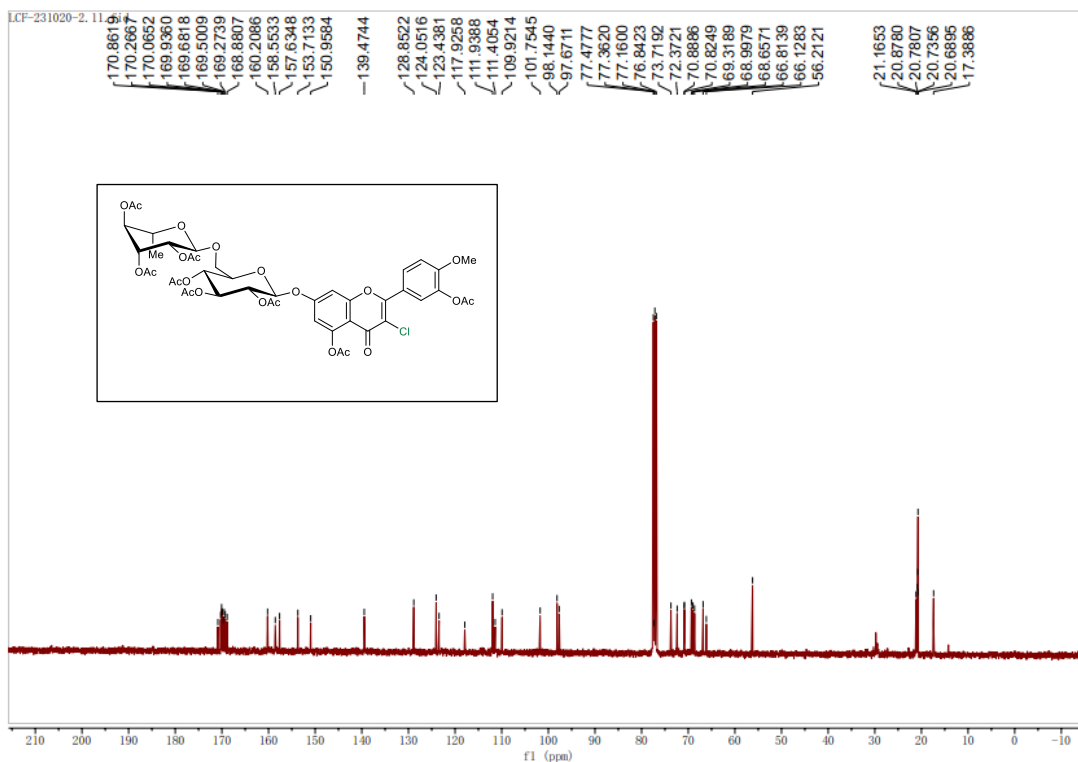
¹H NMR Spectra of compound **2au** in CDCl₃ (400 MHz)



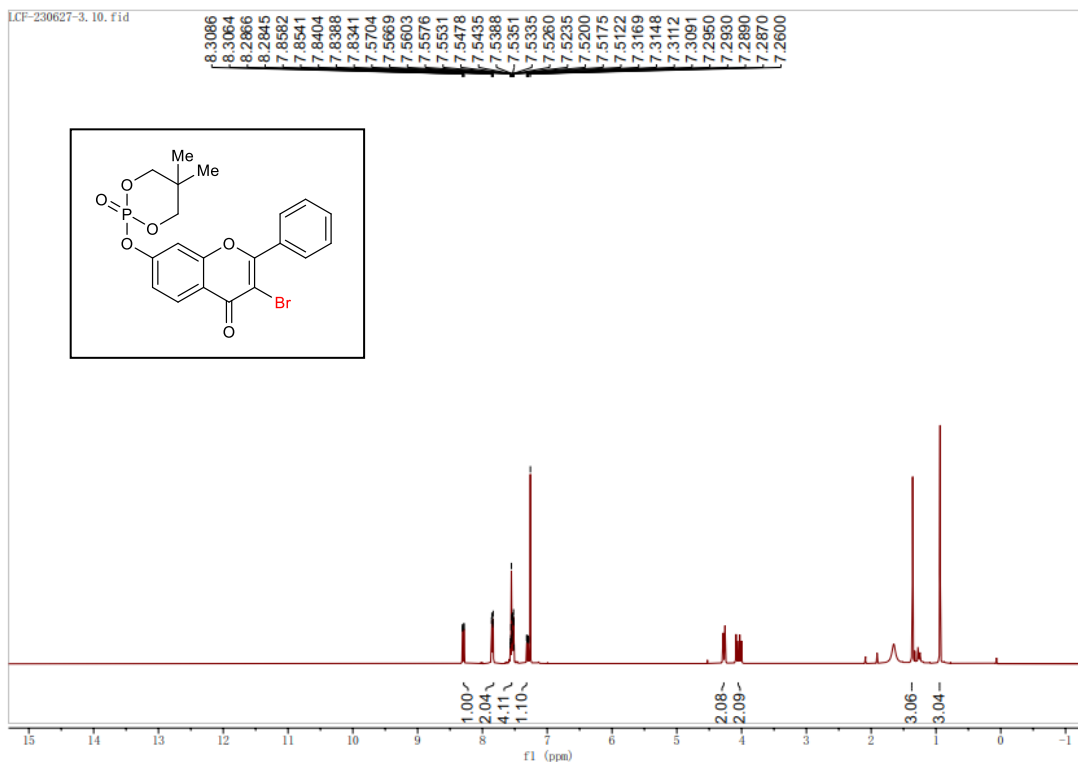
¹³C NMR Spectra of compound **2au** in CDCl₃ (101 MHz)



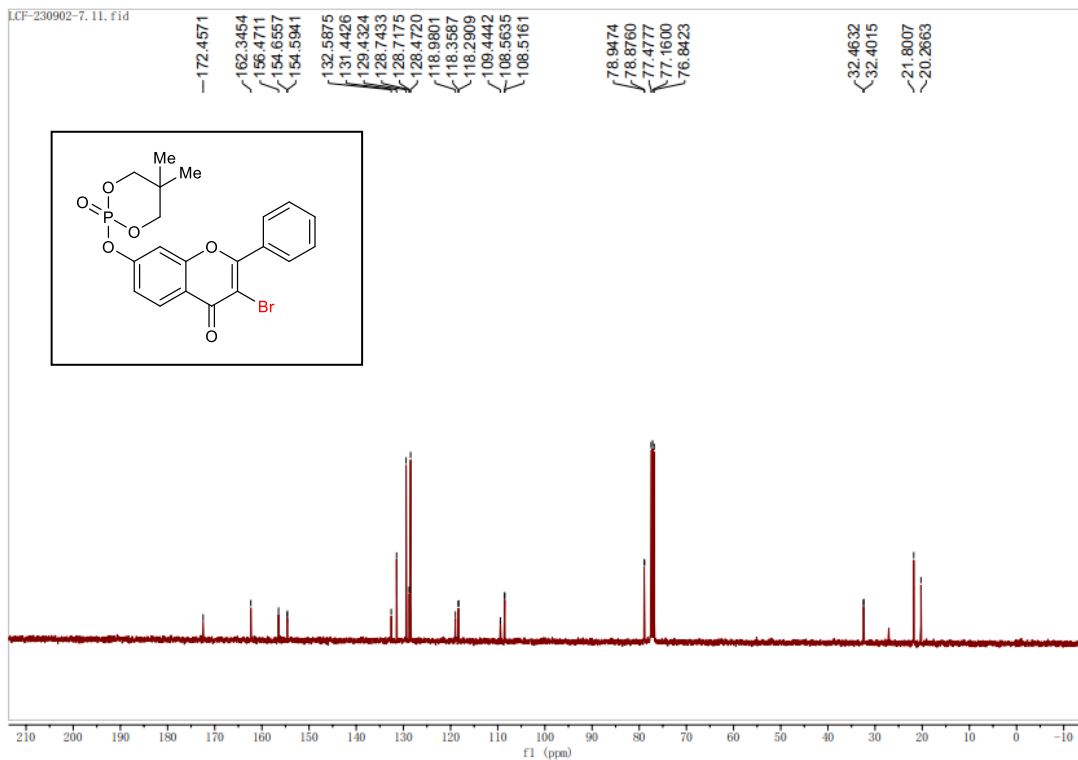
¹H NMR Spectra of compound **2av** in CDCl₃ (400 MHz)



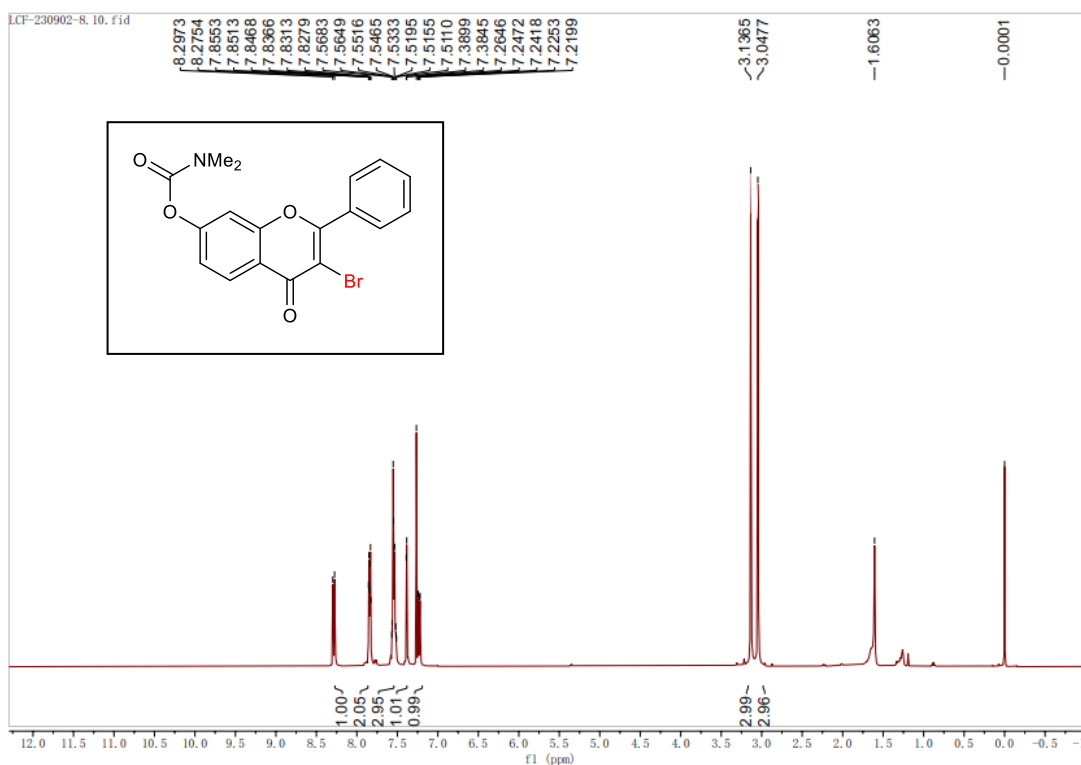
¹³C NMR Spectra of compound **2av** in CDCl₃ (101 MHz)



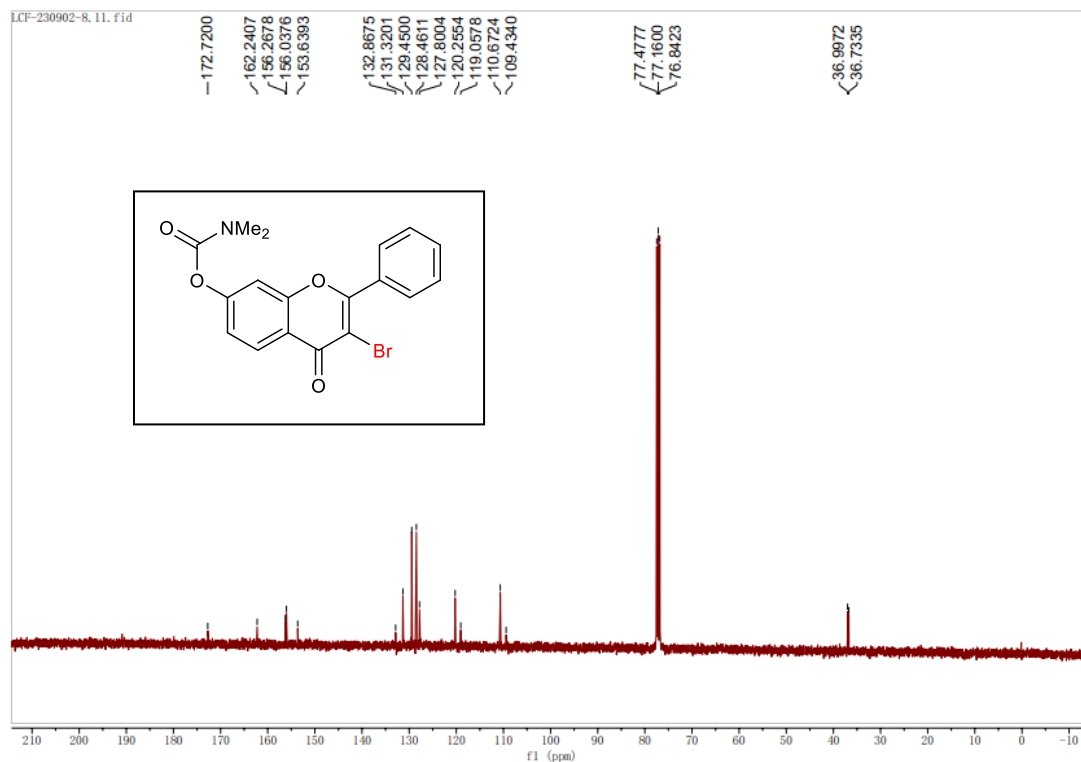
^1H NMR Spectra of compound **2ba** in CDCl_3 (400 MHz)



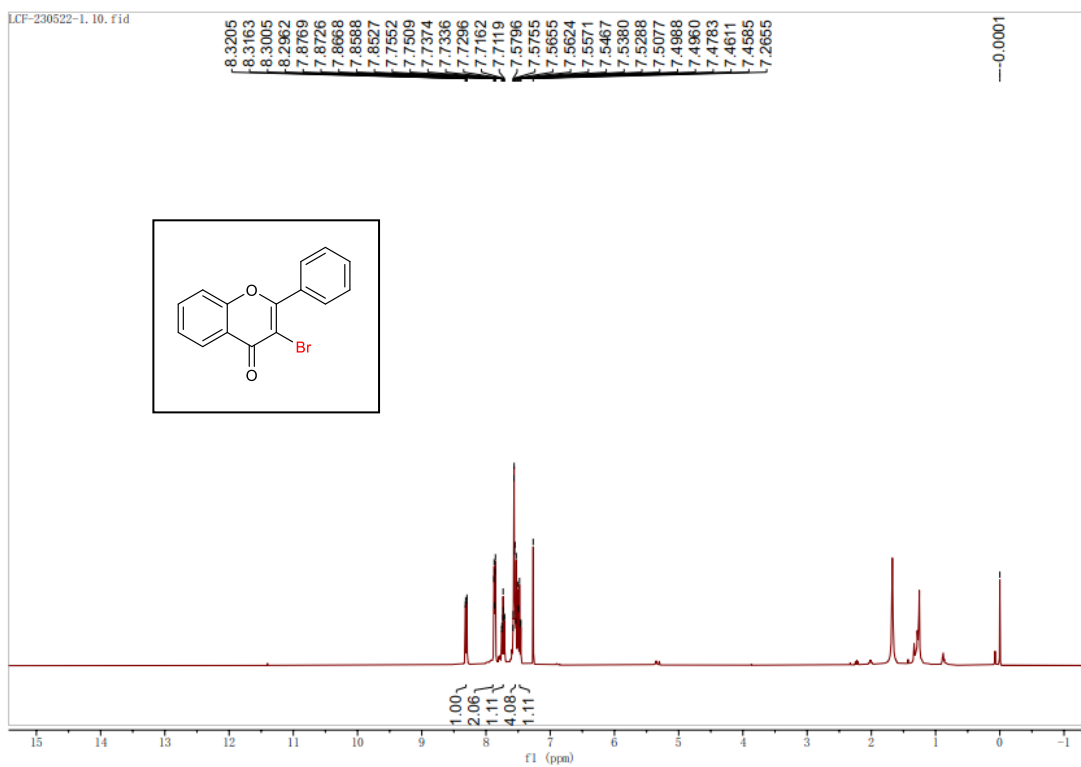
^{13}C NMR Spectra of compound **2ba** in CDCl_3 (101 MHz)



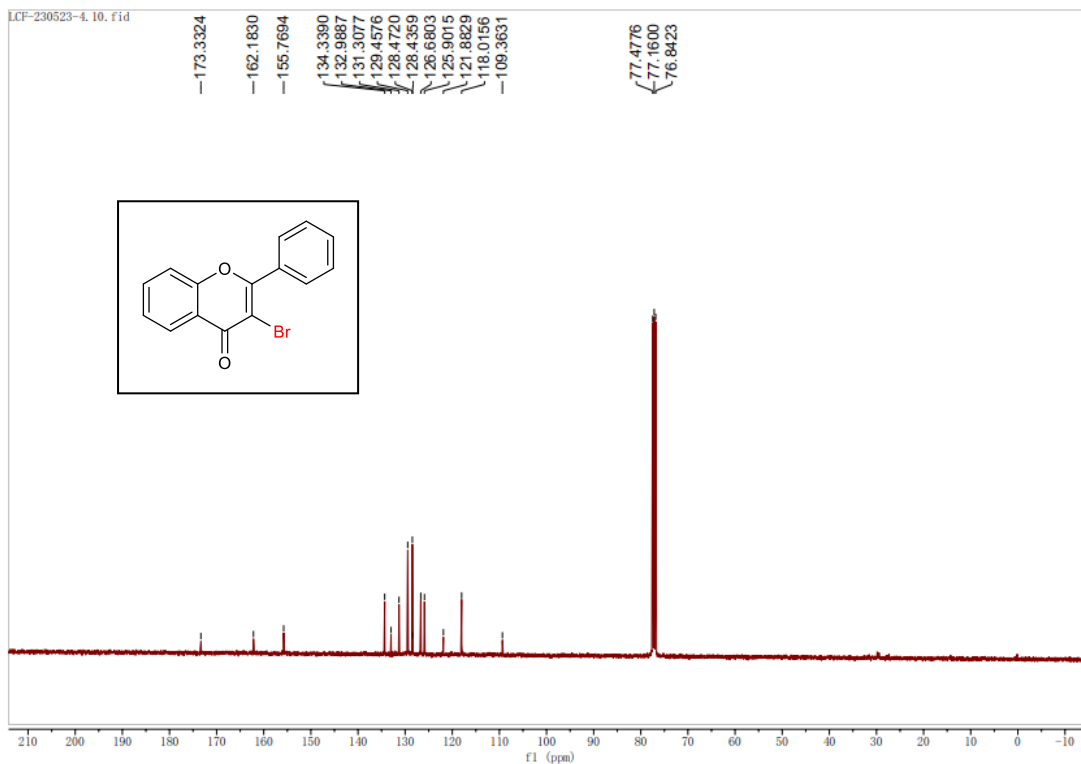
¹H NMR Spectra of compound **2bb** in CDCl₃ (400 MHz)



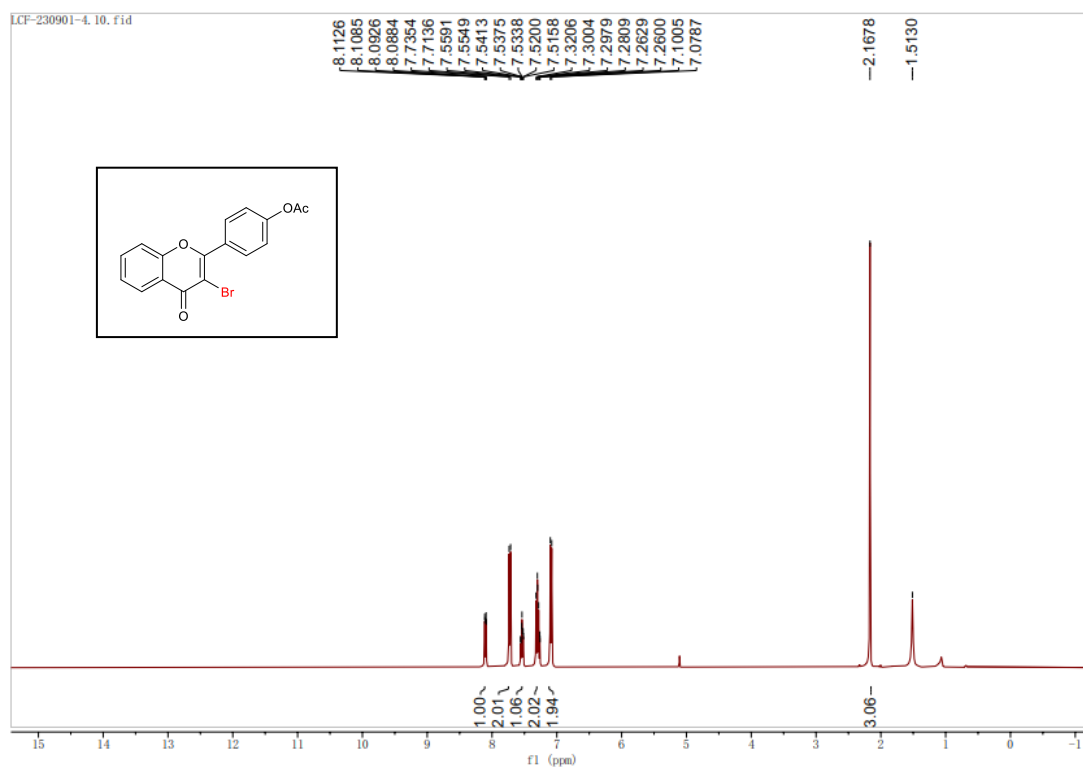
¹³C NMR Spectra of compound **2bb** in CDCl₃ (101 MHz)



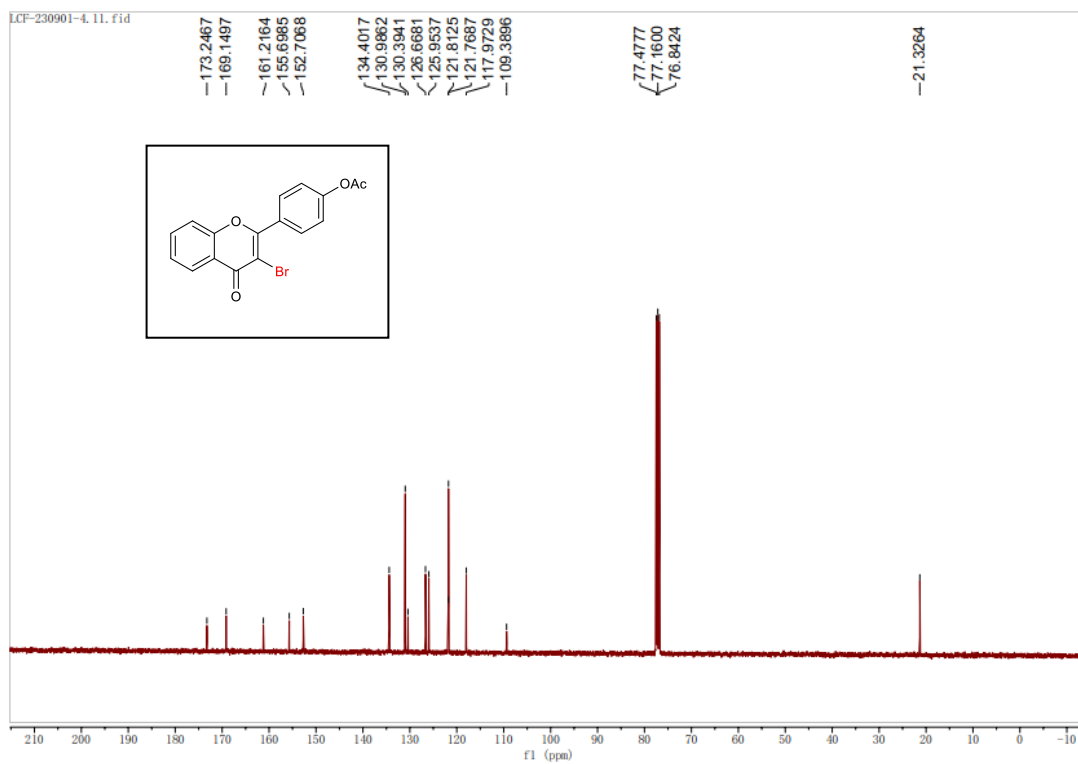
^1H NMR Spectra of compound **2bc** in CDCl_3 (400 MHz)



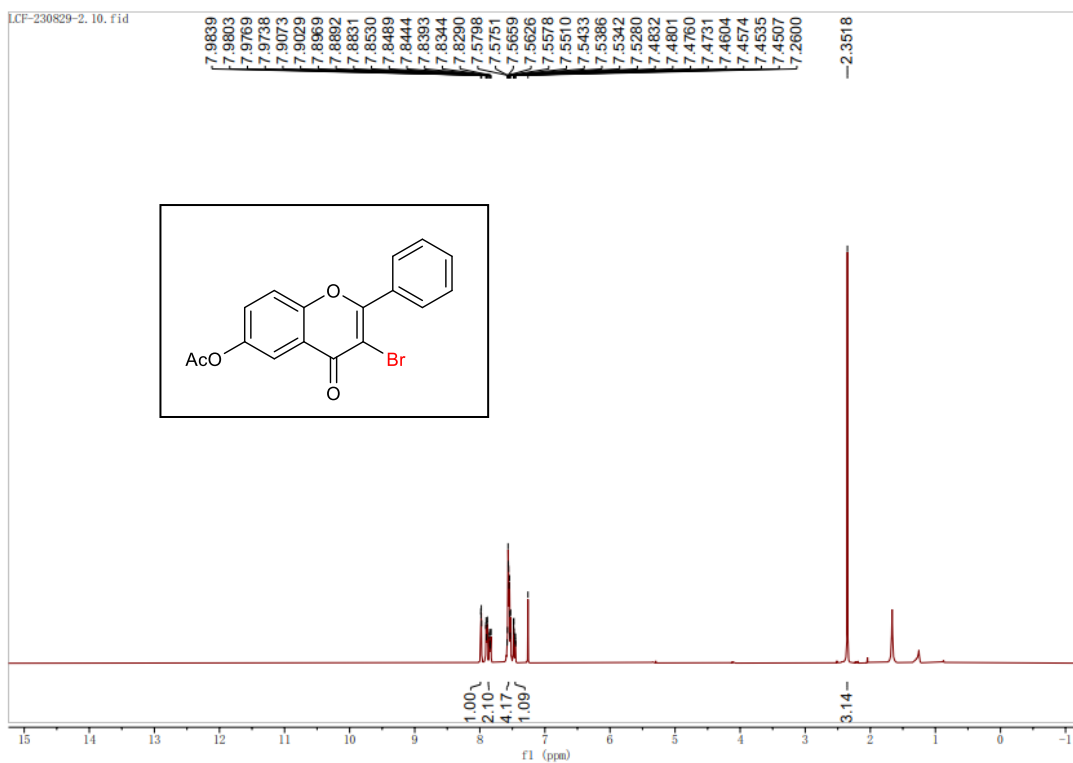
^{13}C NMR Spectra of compound **2bc** in CDCl_3 (101 MHz)

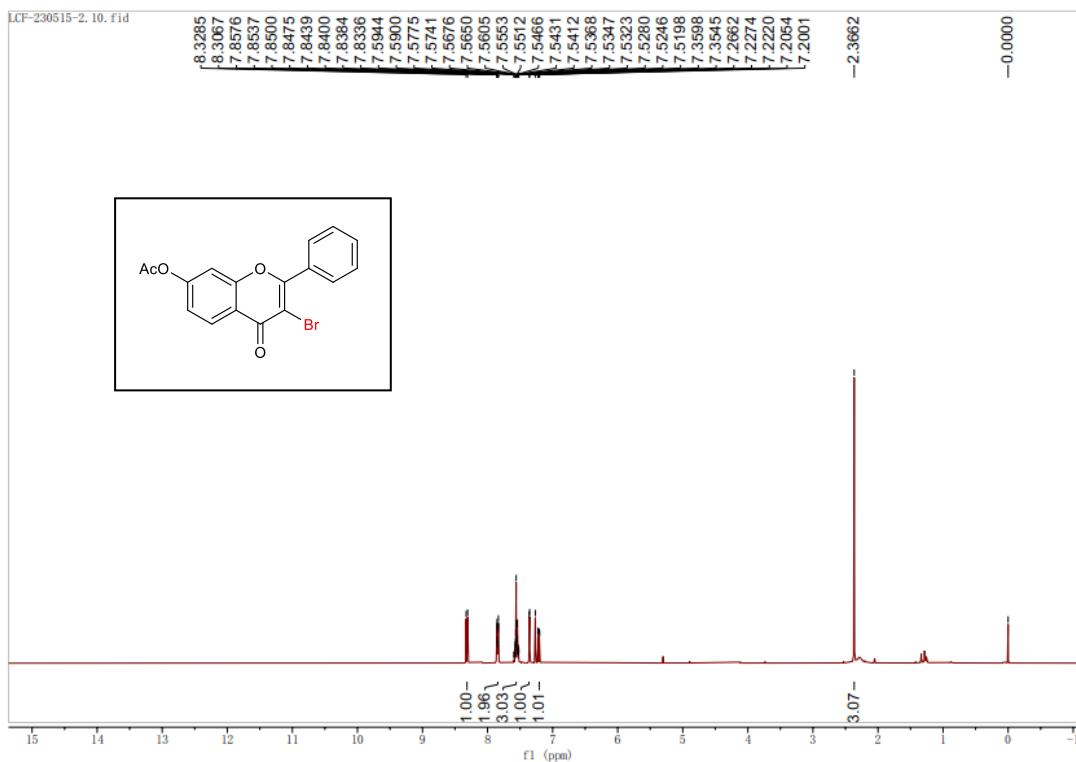


^1H NMR Spectra of compound **2bd** in CDCl_3 (400 MHz)

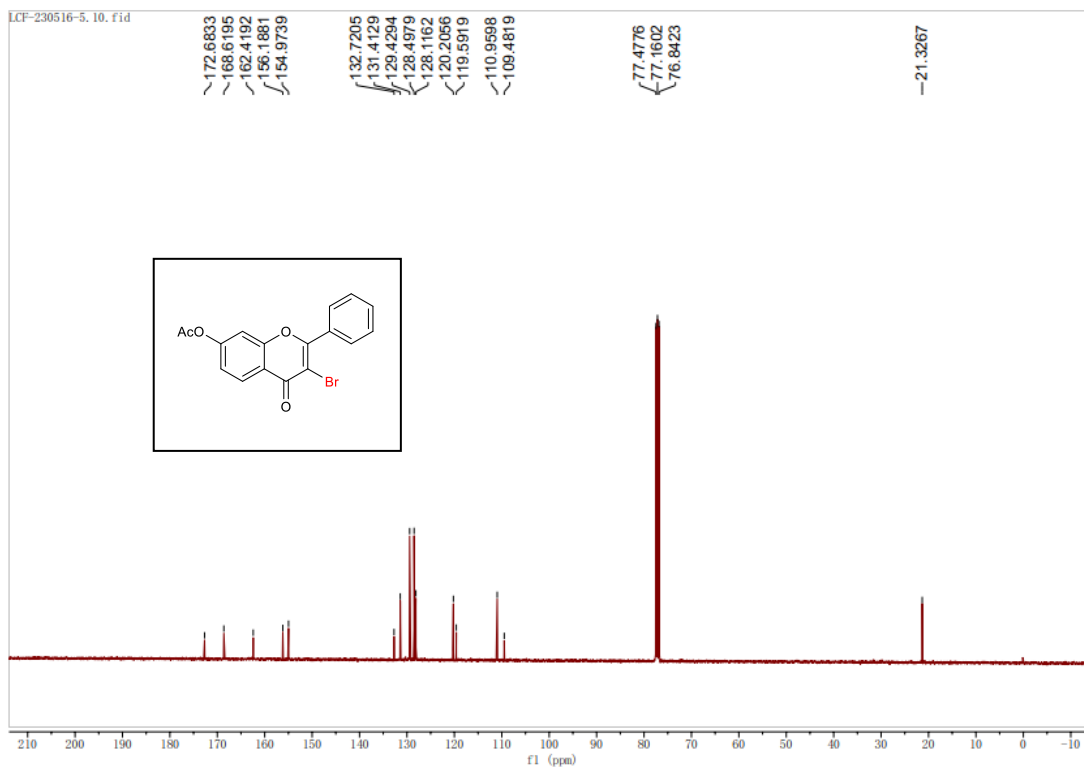


^{13}C NMR Spectra of compound **2bd** in CDCl_3 (101 MHz)

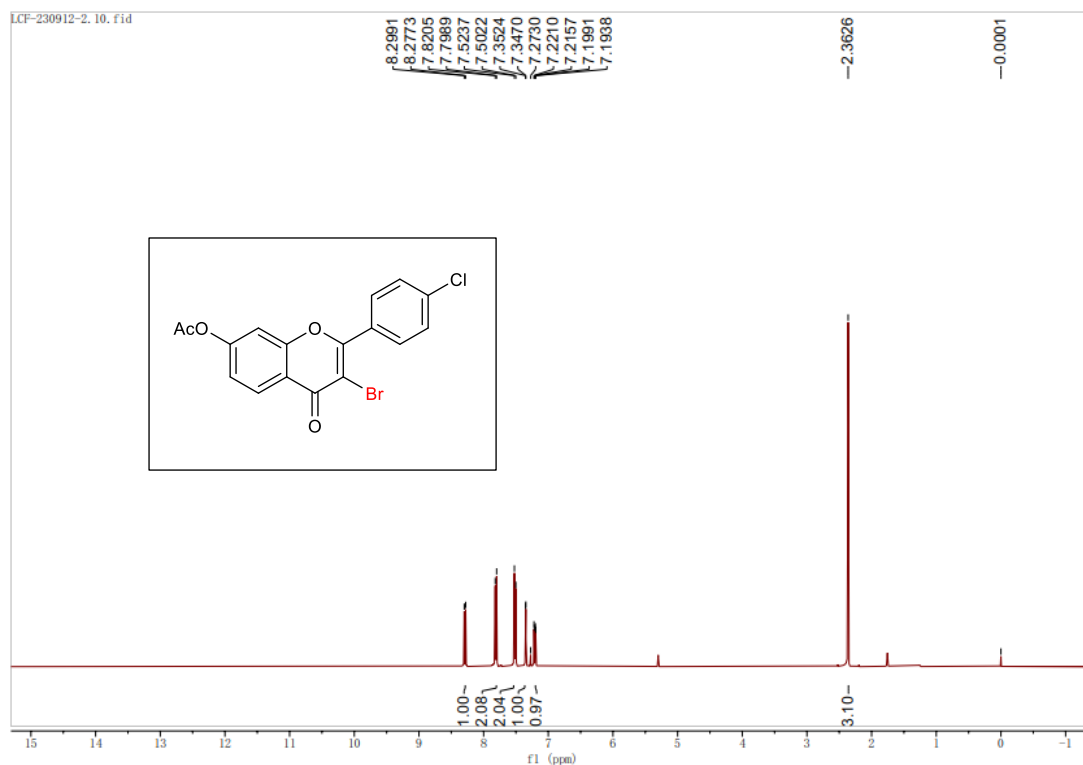




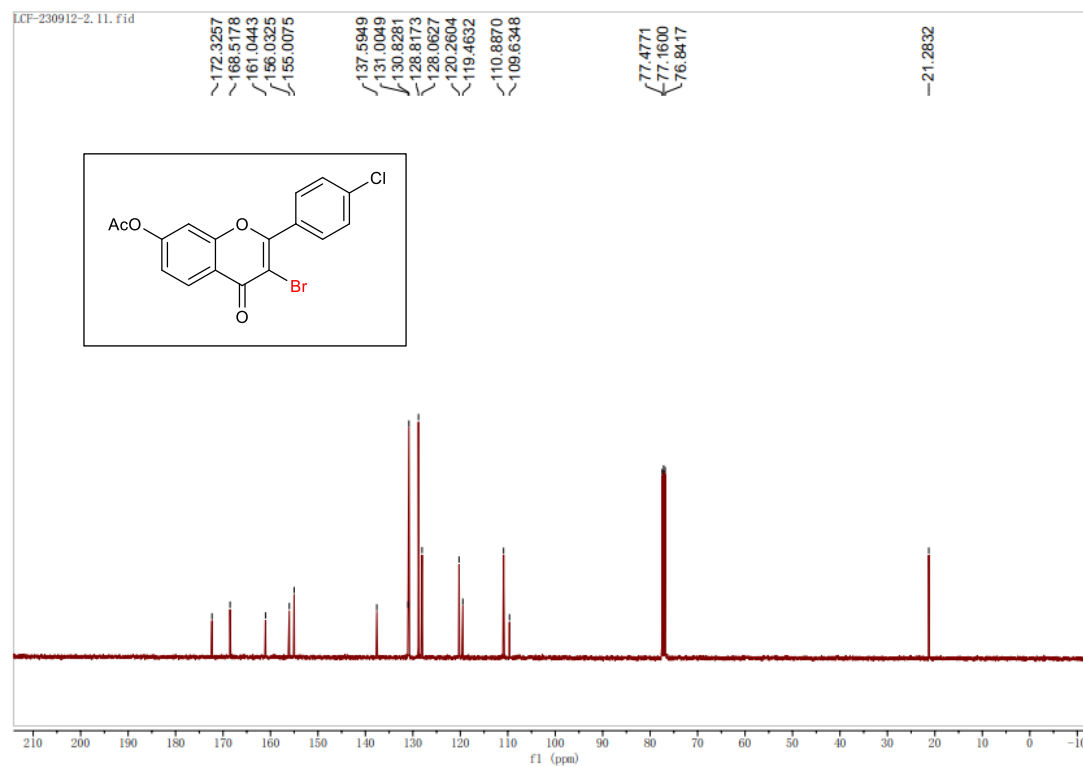
^1H NMR Spectra of compound **2bf** in CDCl_3 (400 MHz)



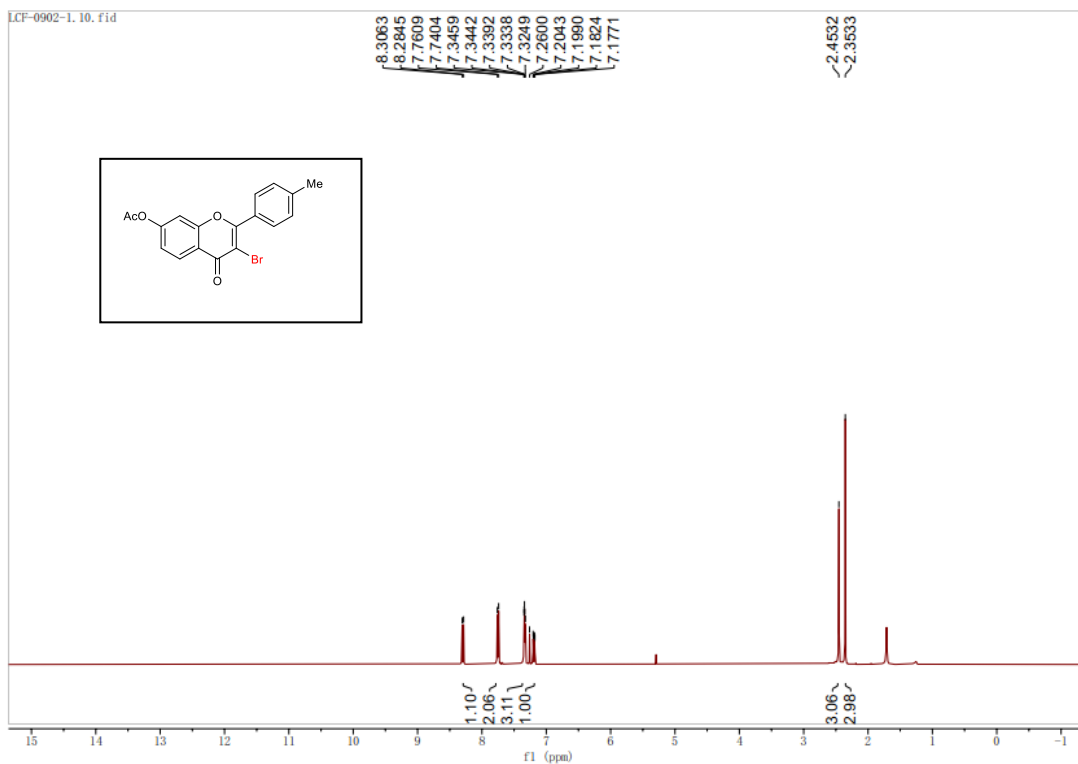
^{13}C NMR Spectra of compound **2bf** in CDCl_3 (101 MHz)



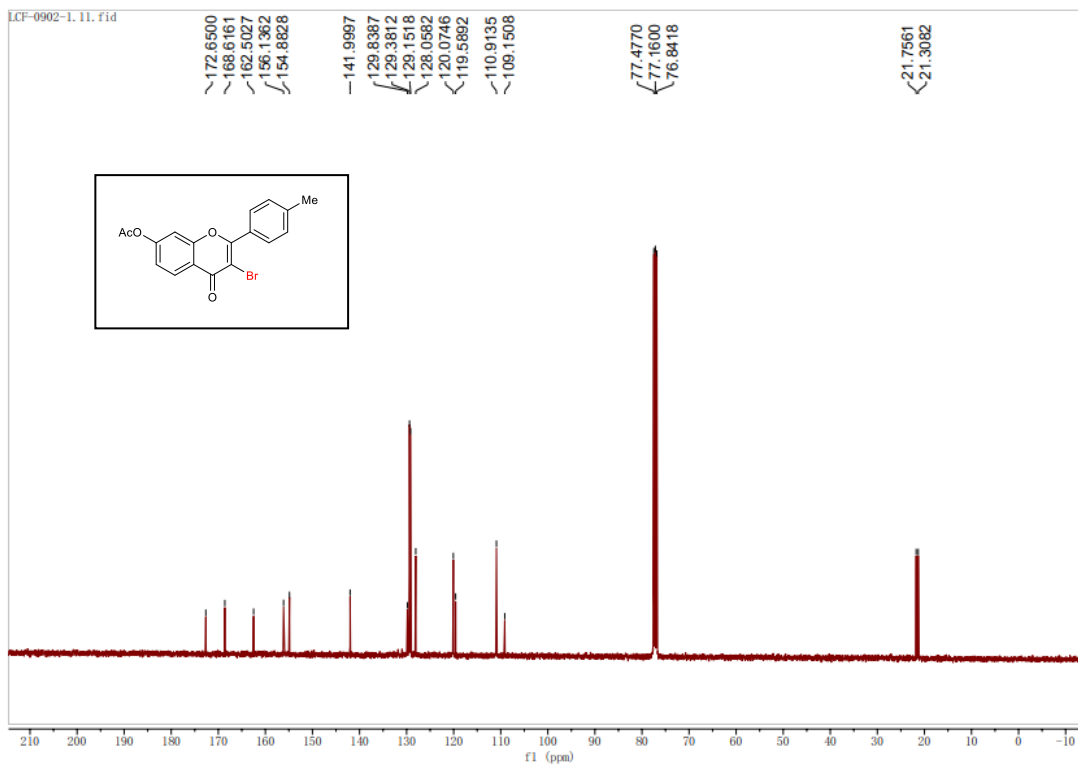
^1H NMR Spectra of compound **2bg** in CDCl_3 (400 MHz)



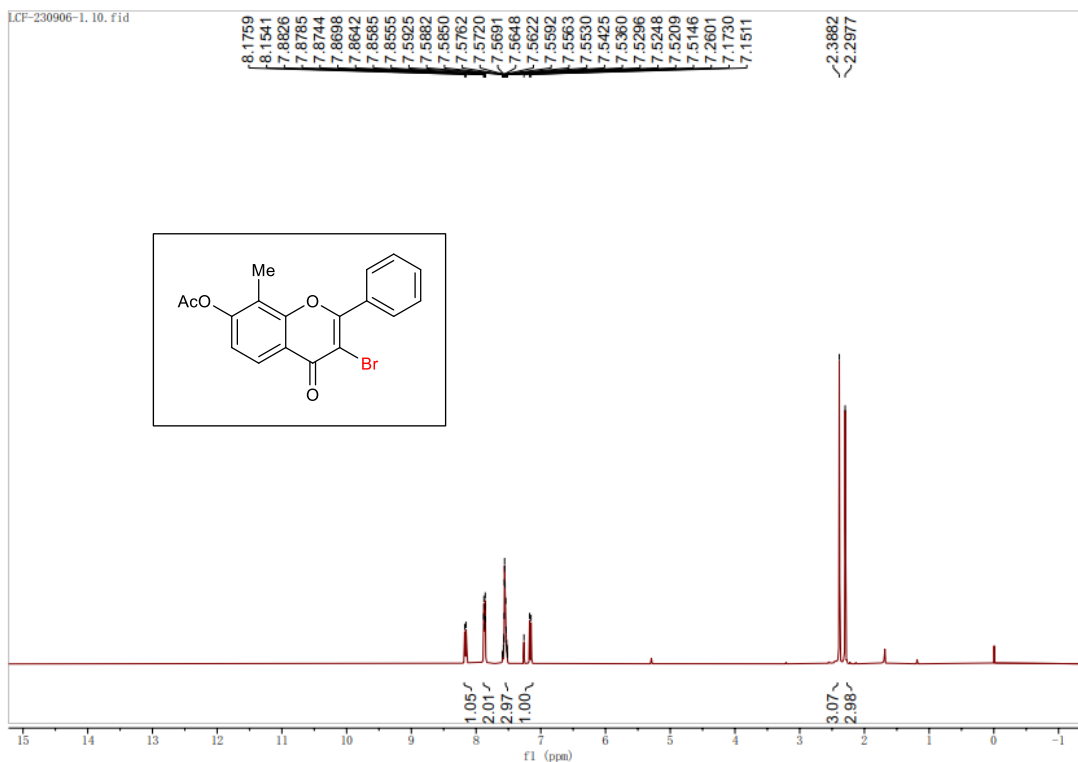
^{13}C NMR Spectra of compound **2bg** in CDCl_3 (101 MHz)



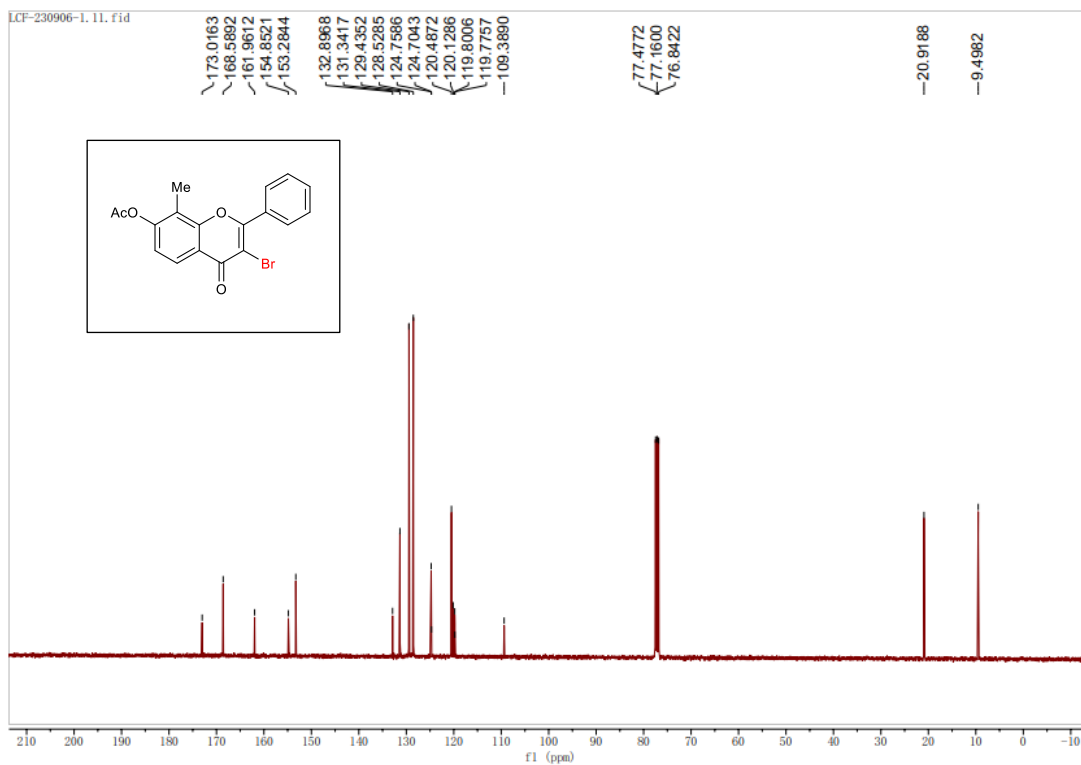
^1H NMR Spectra of compound **2bh** in CDCl_3 (400 MHz)



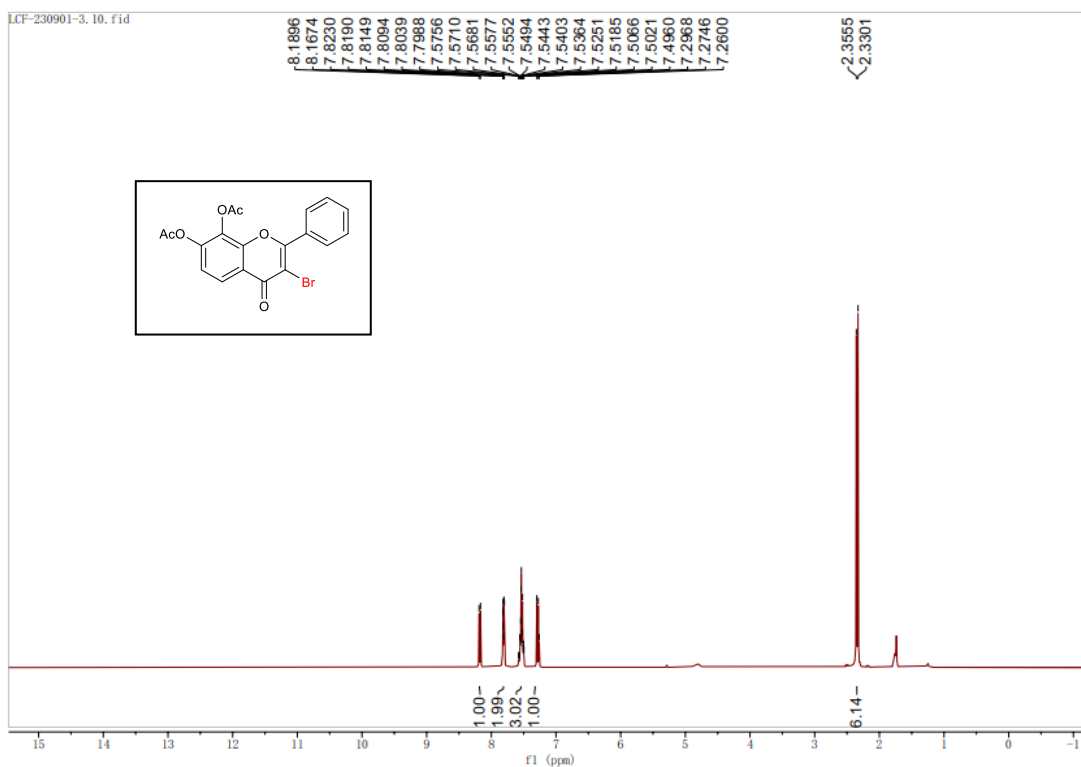
^{13}C NMR Spectra of compound **2bh** in CDCl_3 (101 MHz)



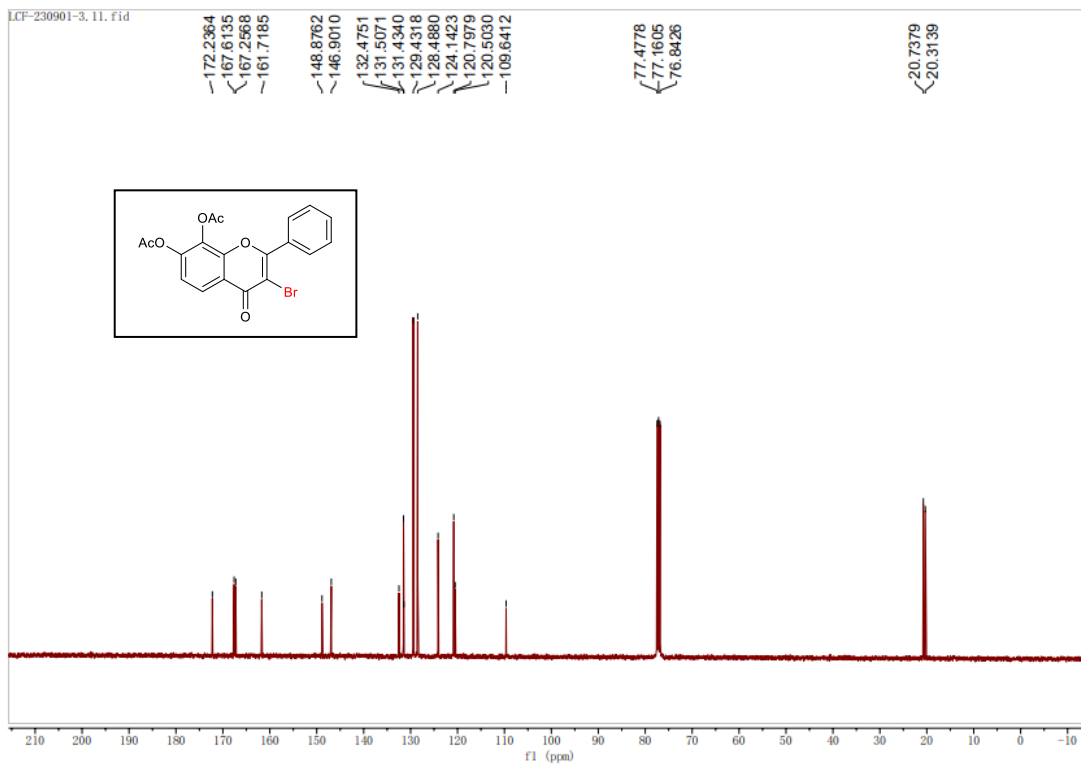
^1H NMR Spectra of compound **2bi** in CDCl_3 (400 MHz)



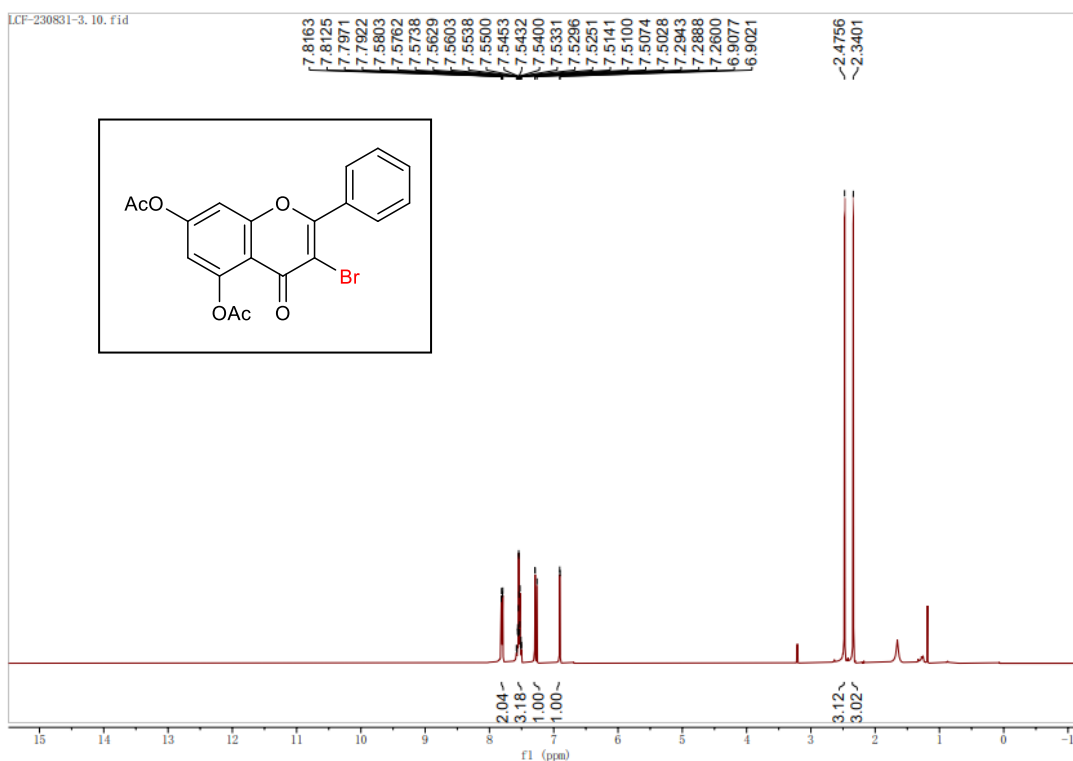
^{13}C NMR Spectra of compound **2bi** in CDCl_3 (101 MHz)



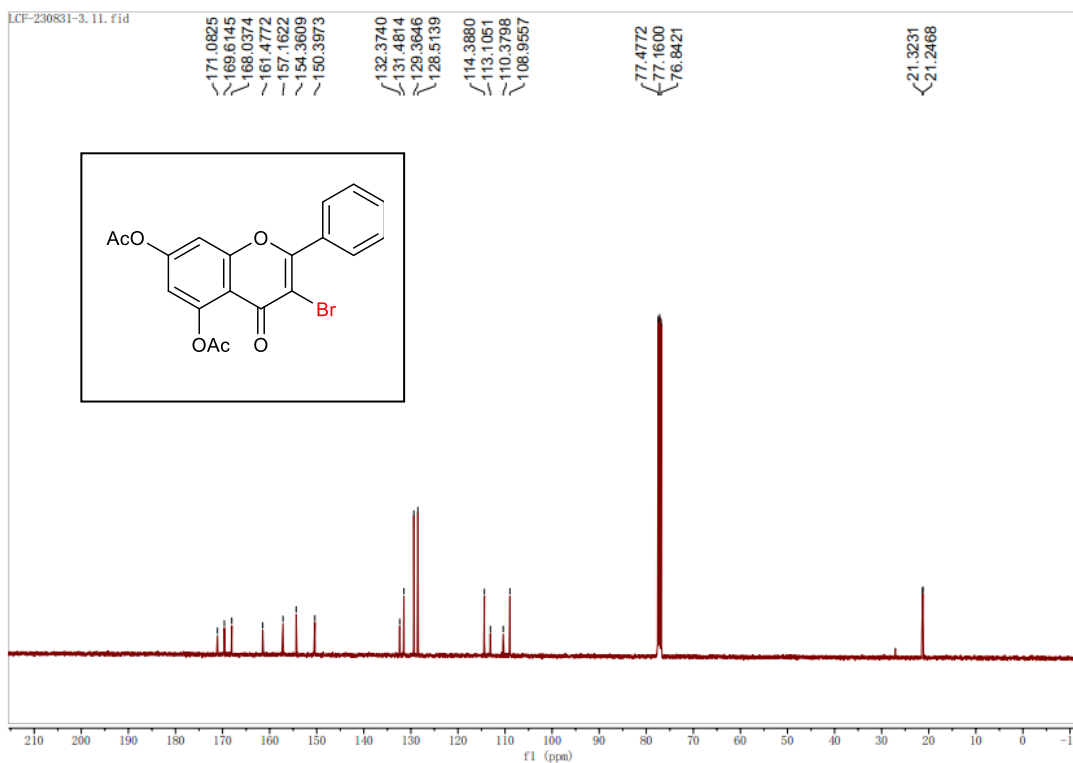
^1H NMR Spectra of compound **2bj** in CDCl_3 (400 MHz)



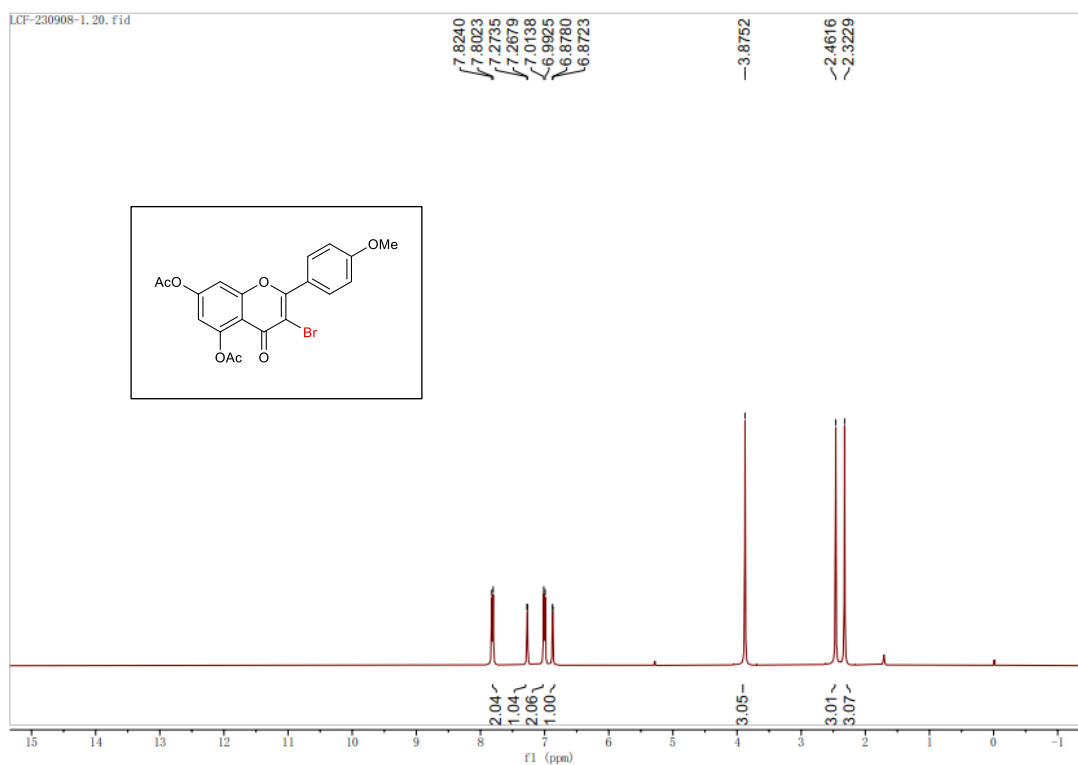
^{13}C NMR Spectra of compound **2bj** in CDCl_3 (101 MHz)



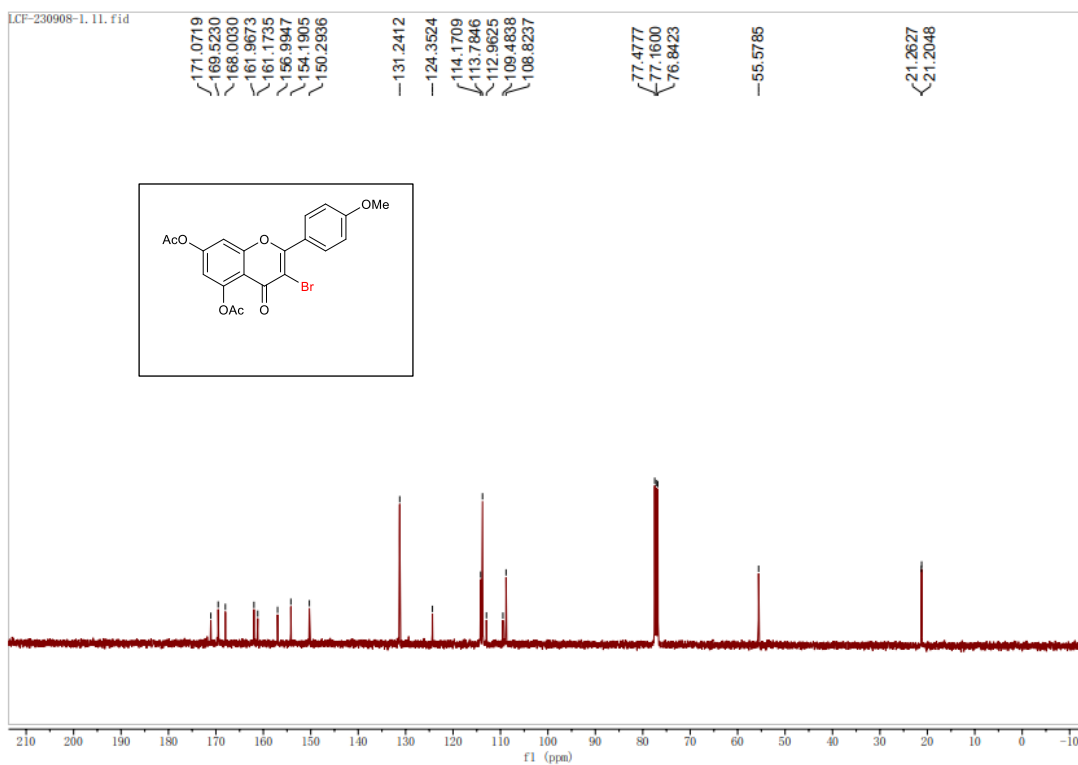
^1H NMR Spectra of compound **2bk** in CDCl_3 (400 MHz)



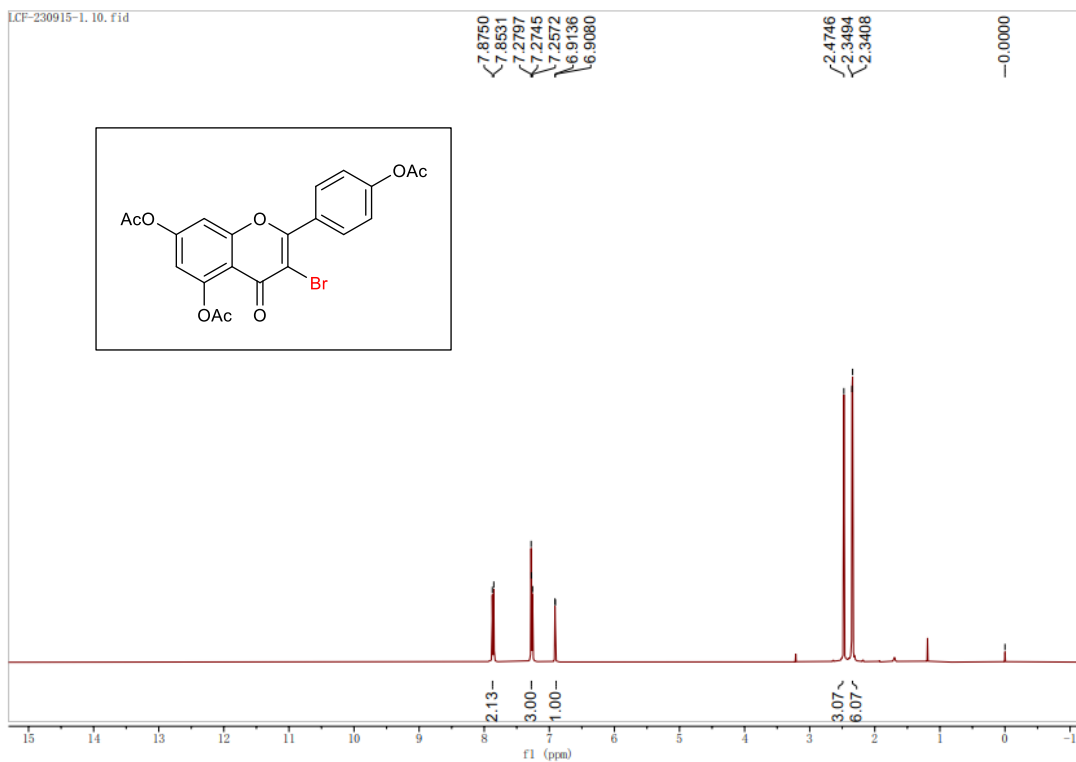
^{13}C NMR Spectra of compound **2bk** in CDCl_3 (101 MHz)



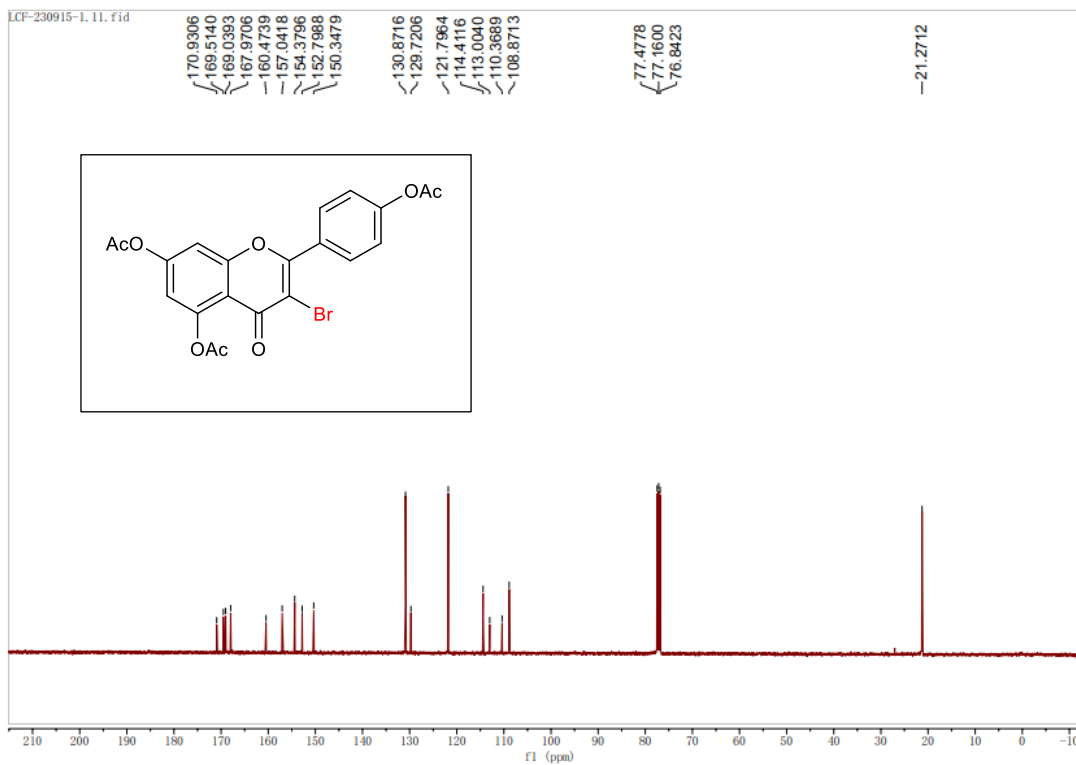
¹H NMR Spectra of compound **2b1** in CDCl₃ (400 MHz)



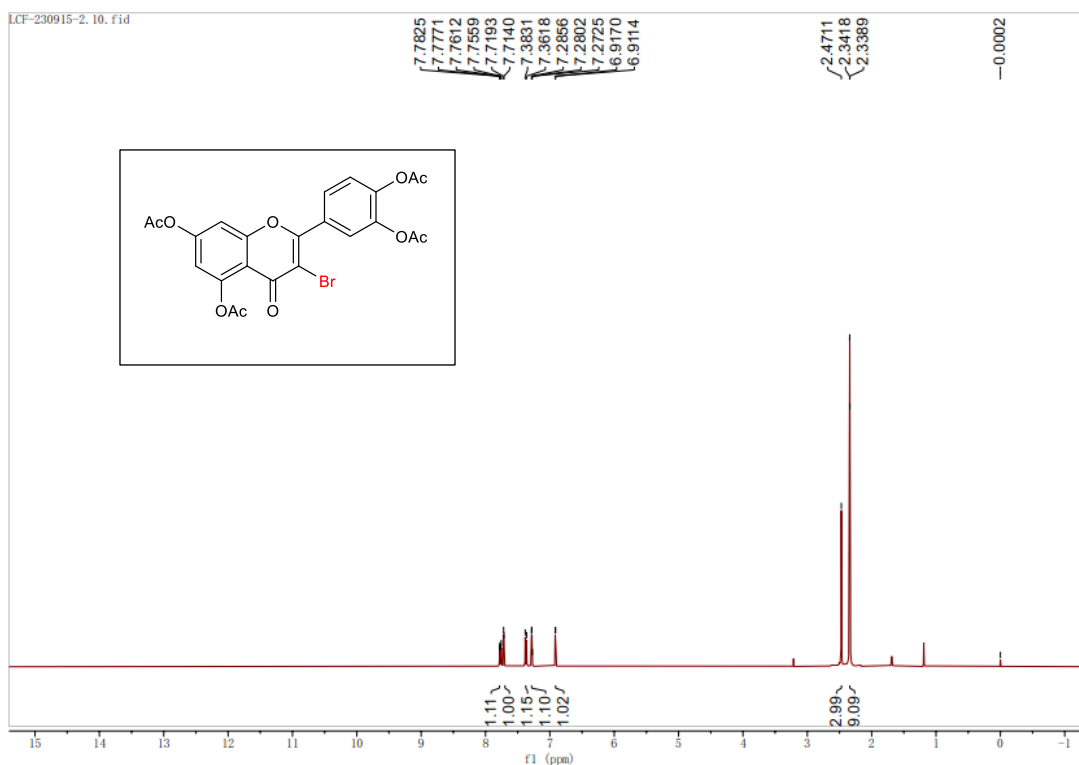
¹³C NMR Spectra of compound **2b1** in CDCl₃ (101 MHz)



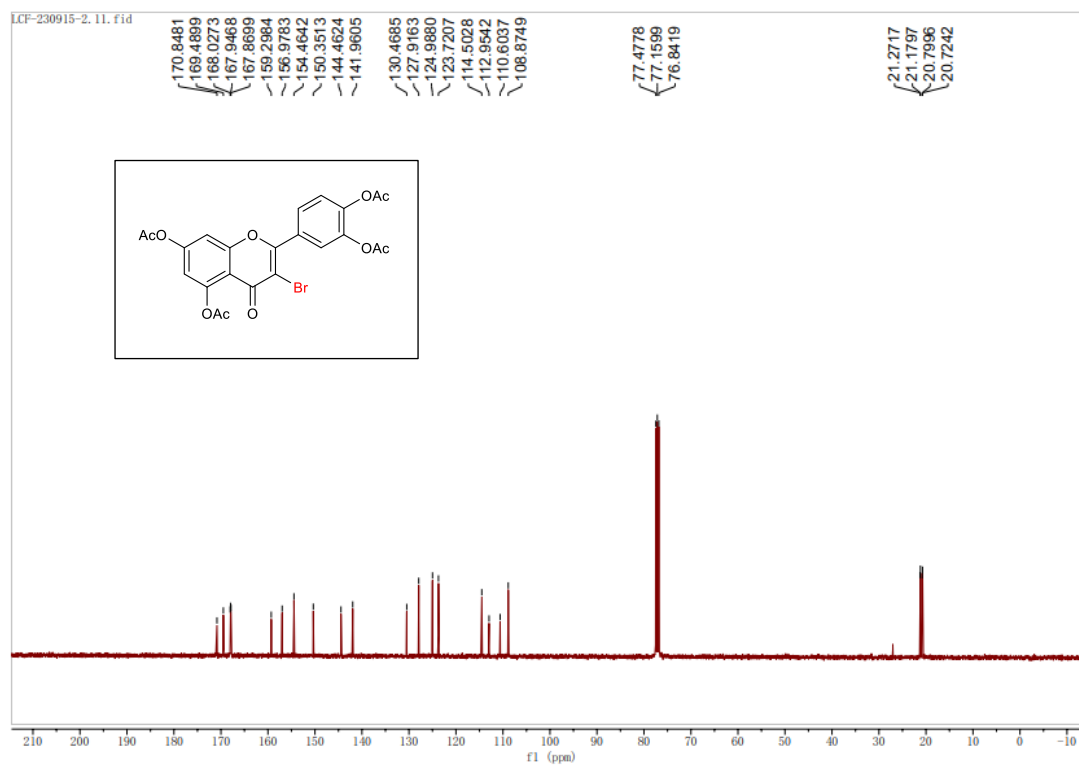
^1H NMR Spectra of compound **2bm** in CDCl_3 (400 MHz)



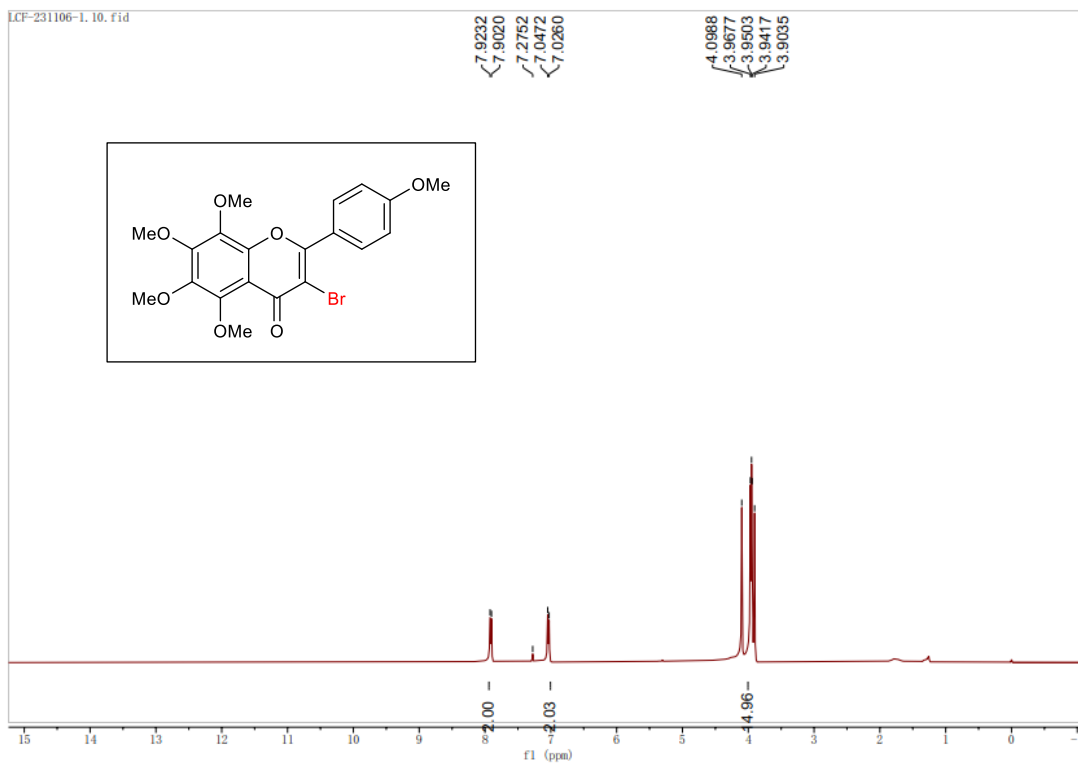
^{13}C NMR Spectra of compound **2bm** in CDCl_3 (101 MHz)



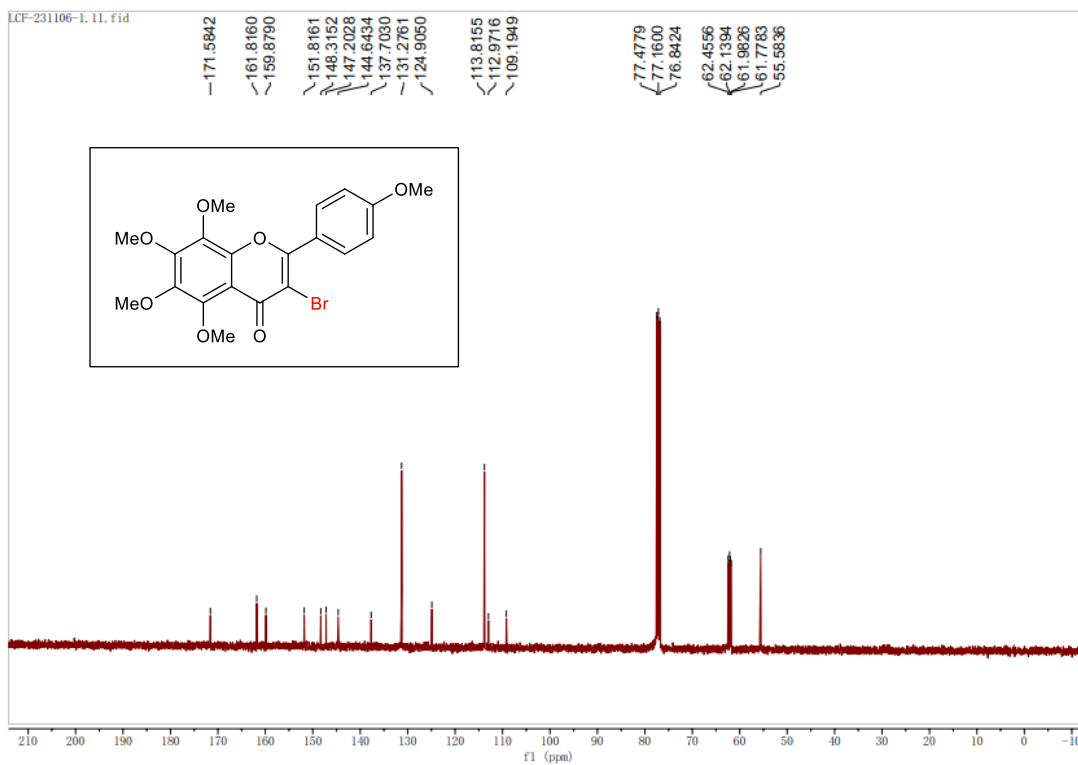
¹H NMR Spectra of compound **2bn** in CDCl₃ (400 MHz)



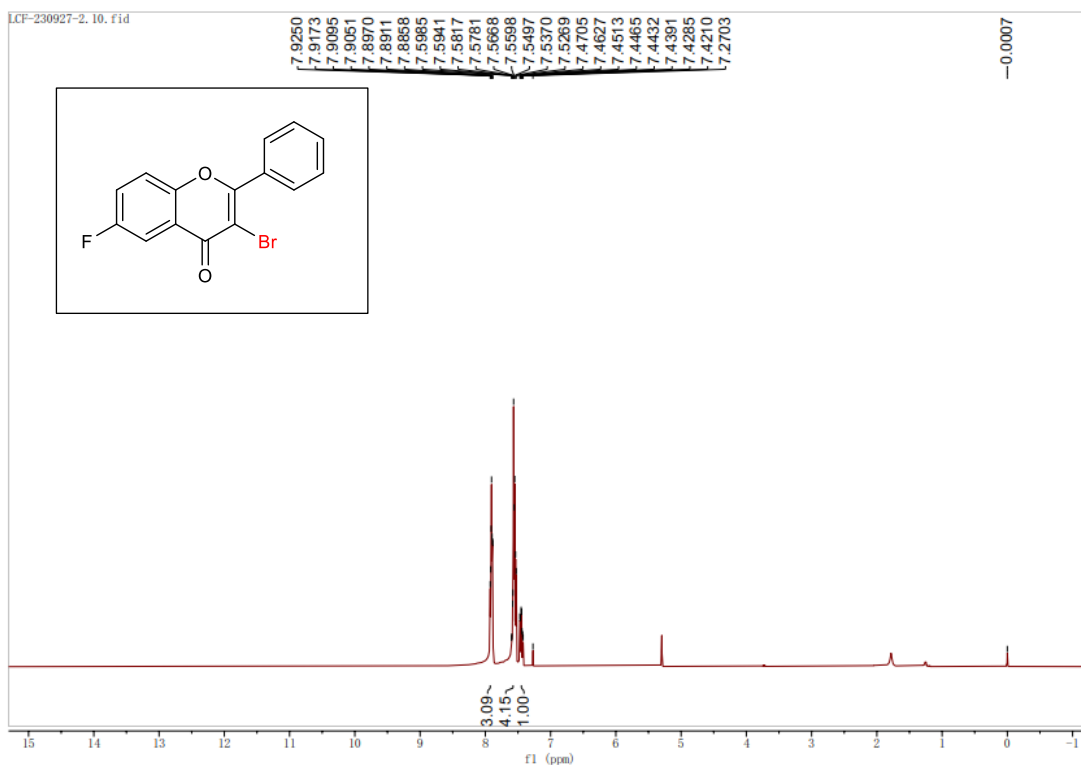
¹³C NMR Spectra of compound **2bn** in CDCl₃ (101 MHz)



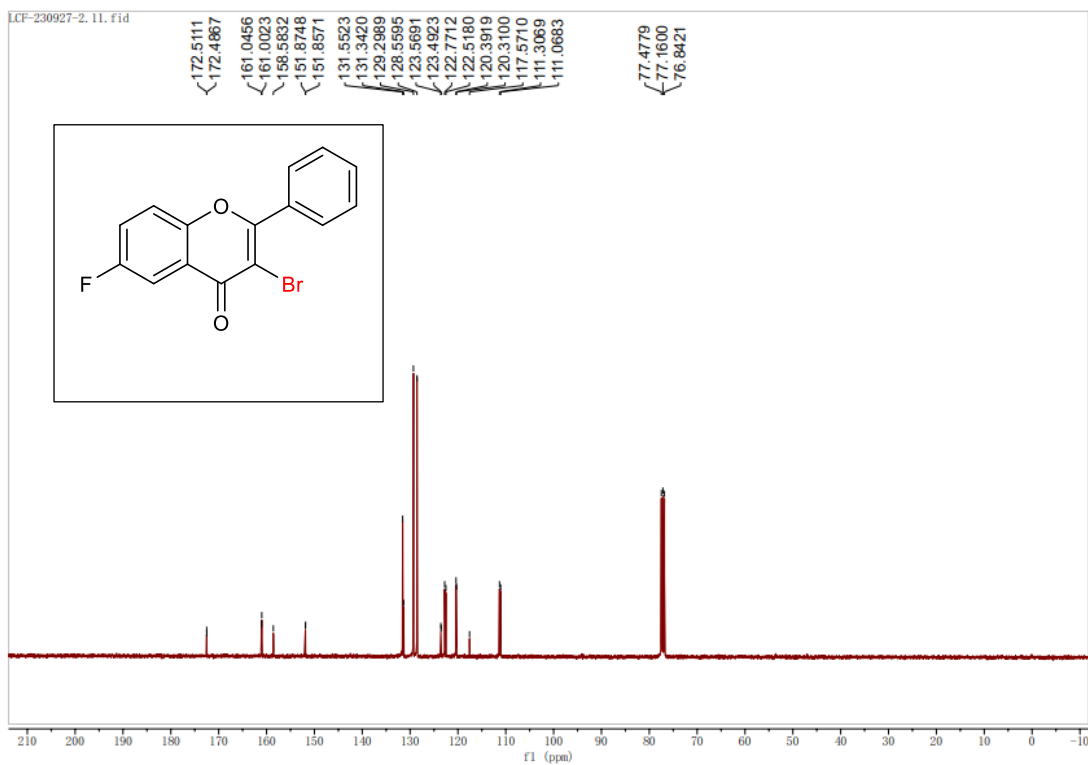
¹H NMR Spectra of compound **2bo** in CDCl₃ (400 MHz)



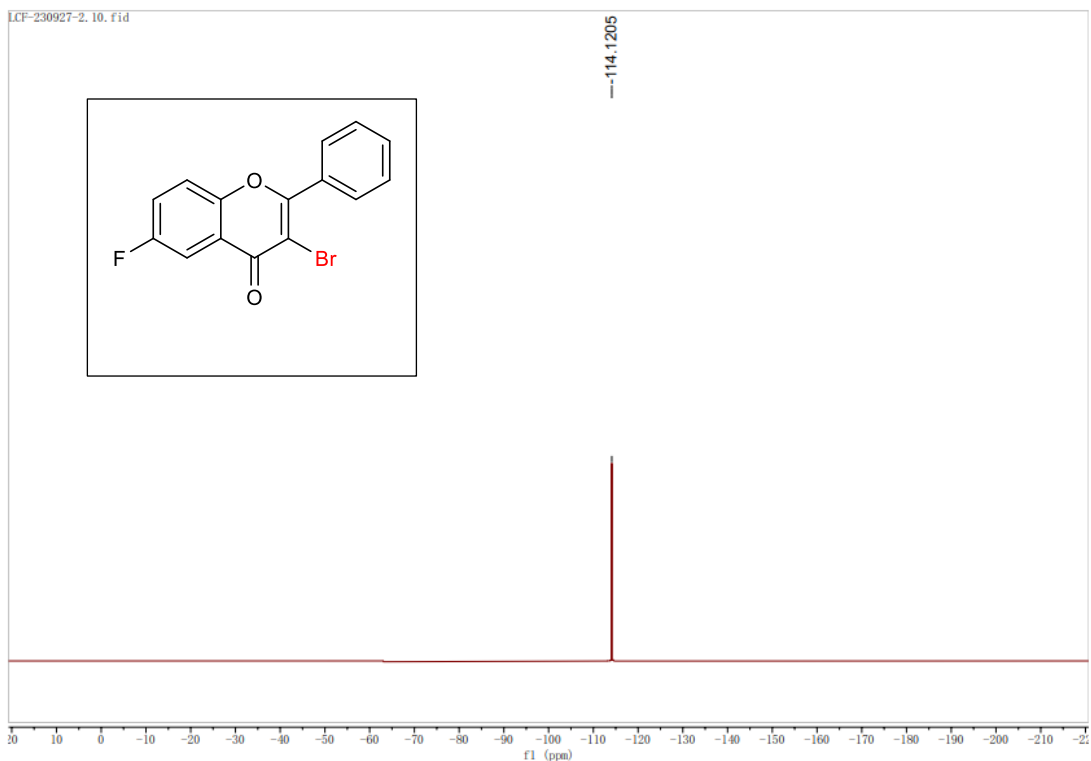
¹³C NMR Spectra of compound **2bo** in CDCl₃ (101 MHz)



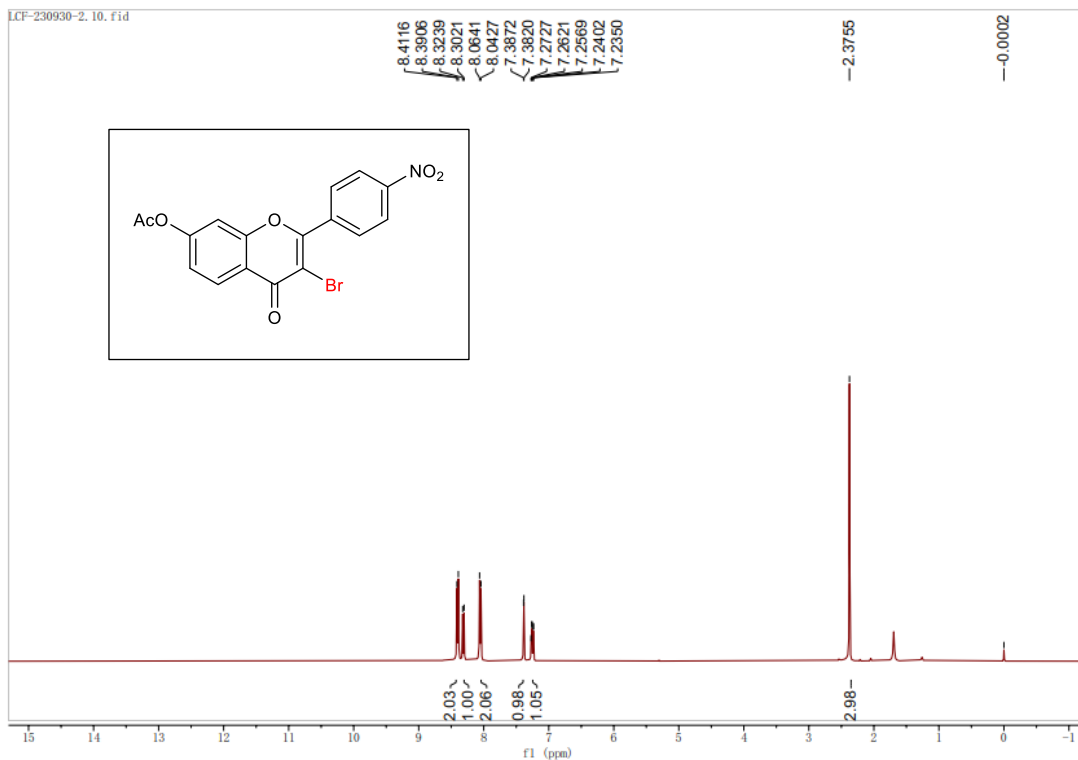
¹H NMR Spectra of compound **2bp** in CDCl₃ (400 MHz)



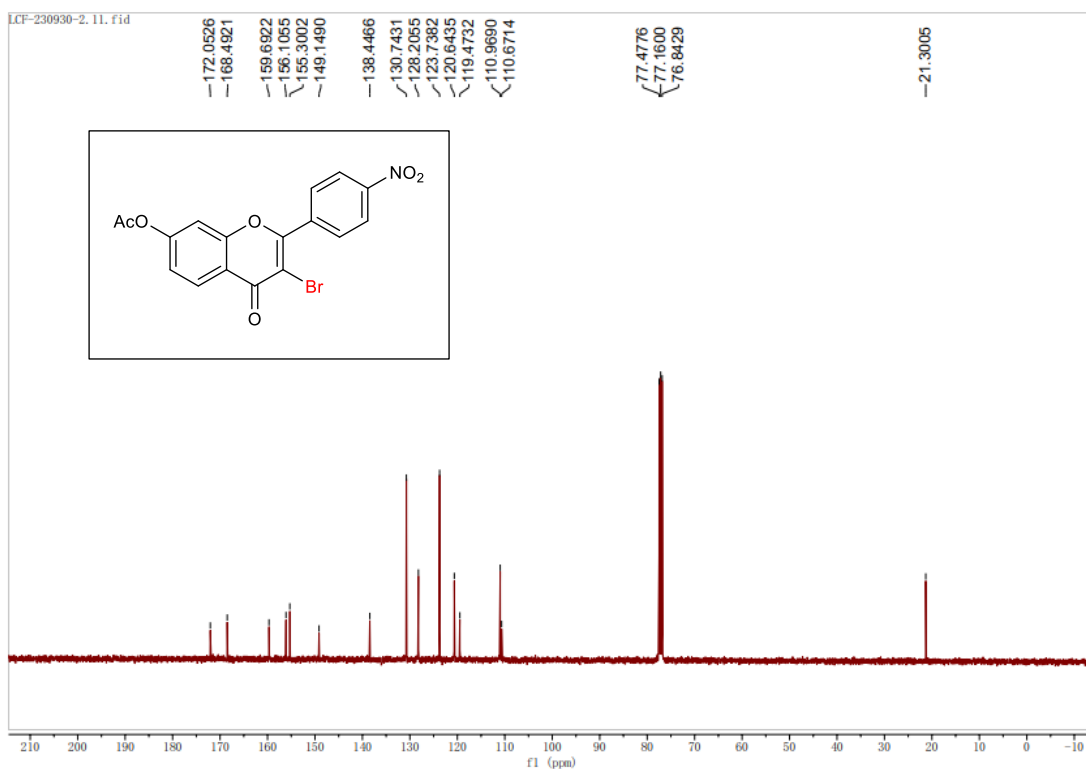
¹³C NMR Spectra of compound **2bp** in CDCl₃ (101 MHz)



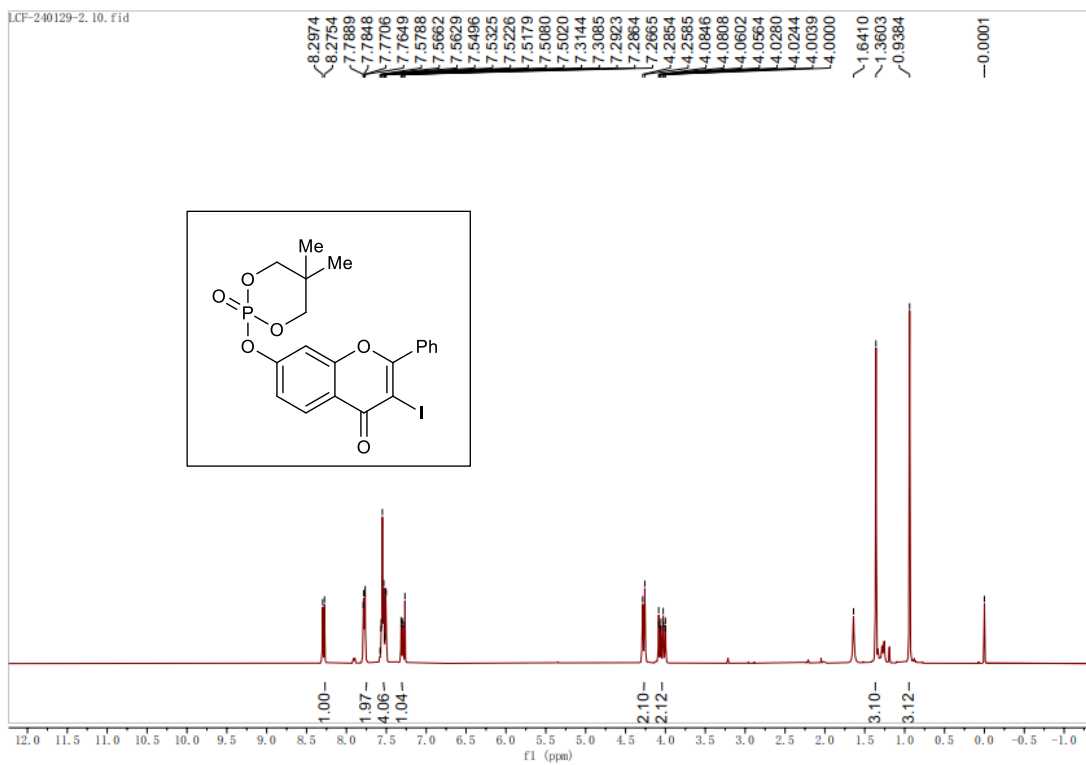
^{19}F NMR Spectra of compound **2bp** in CDCl_3 (377 MHz)



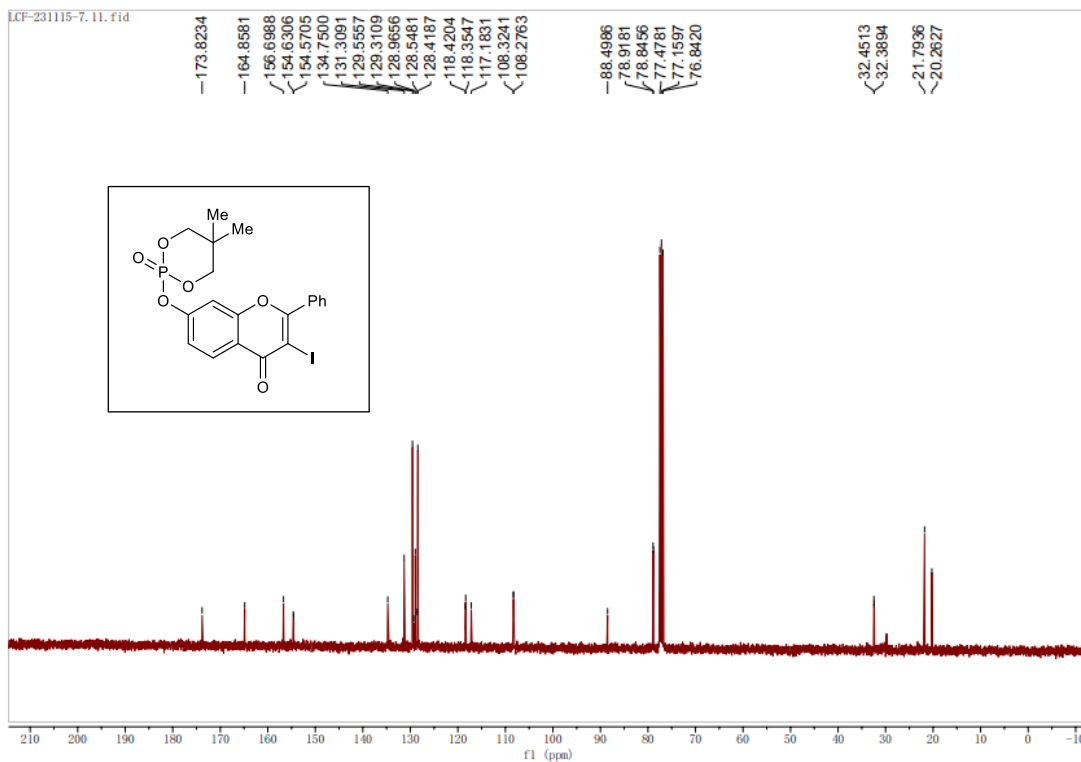
^1H NMR Spectra of compound **2bq** in CDCl_3 (400 MHz)



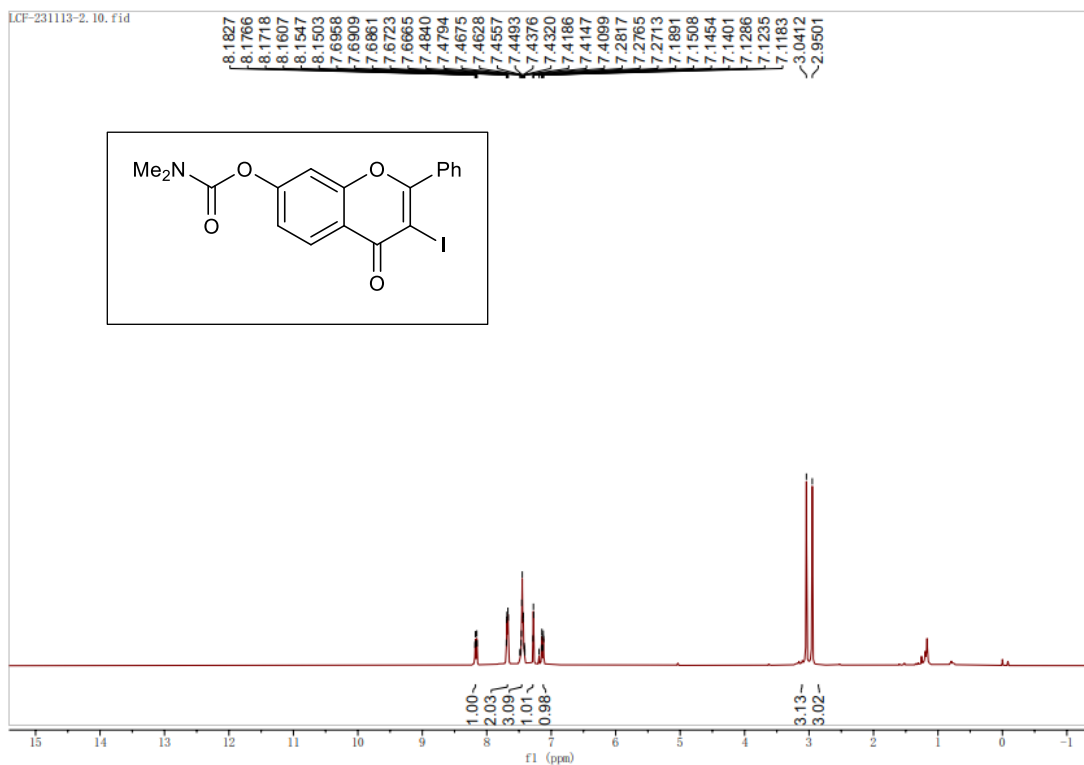
^{13}C NMR Spectra of compound **2bq** in CDCl_3 (101 MHz)



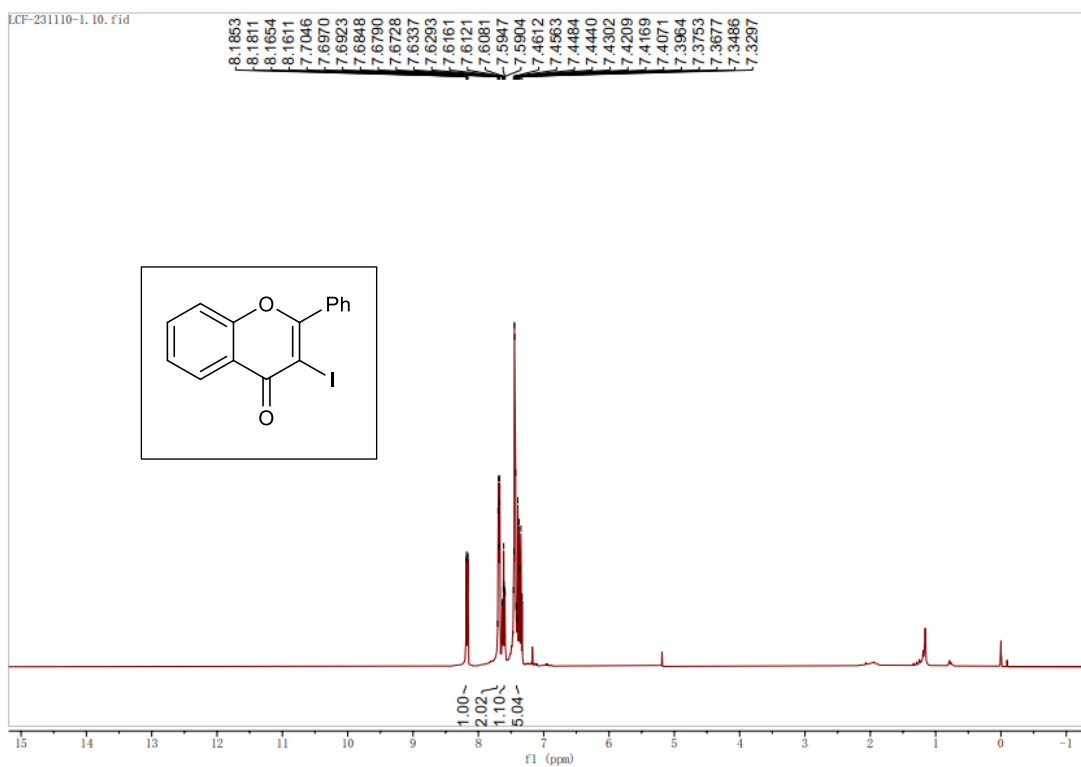
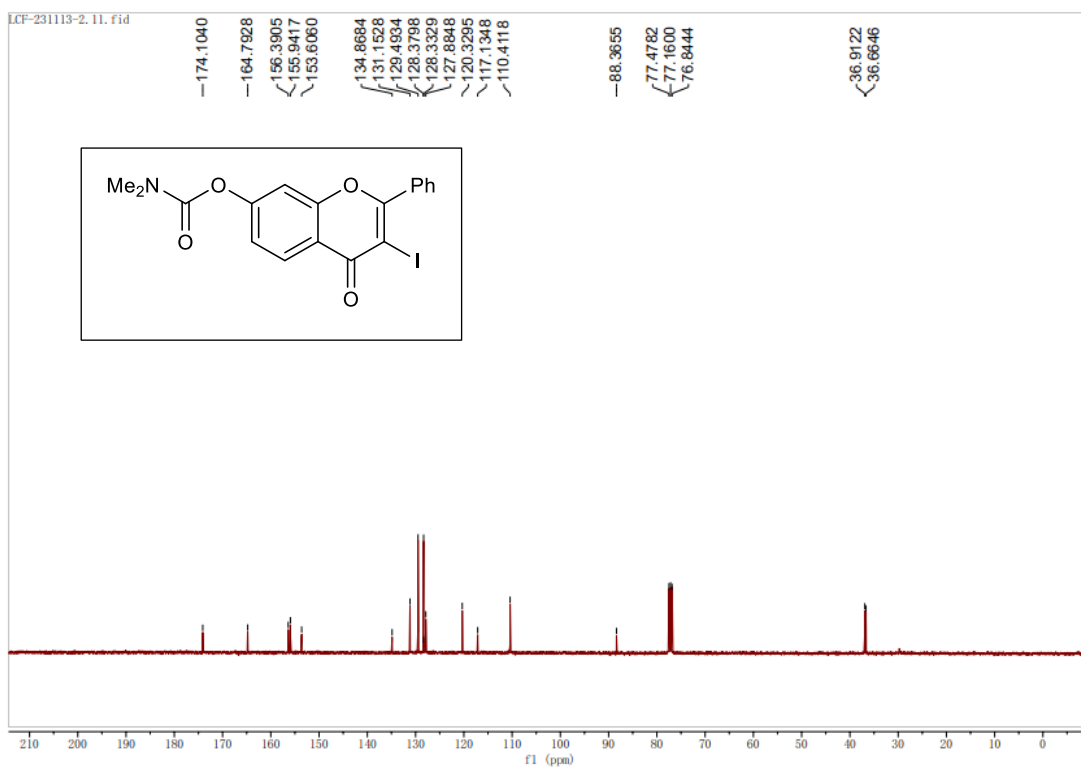
^1H NMR Spectra of compound **2ca** in CDCl_3 (400 MHz)

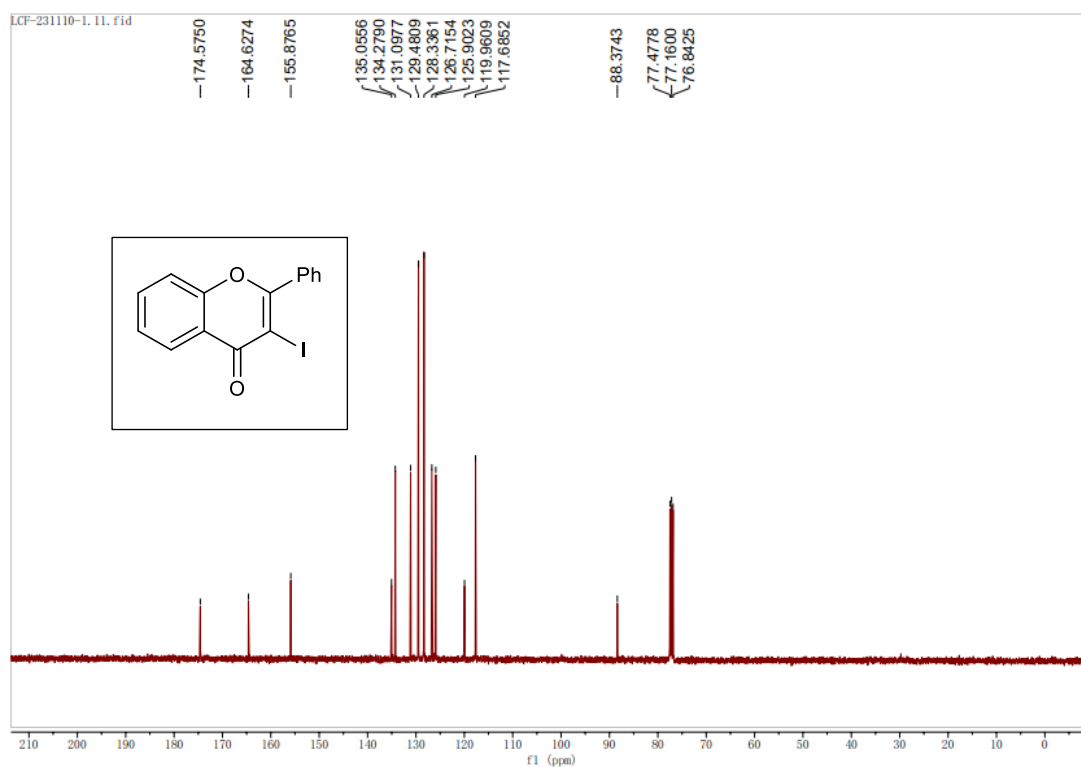


^{13}C NMR Spectra of compound **2ca** in CDCl_3 (101 MHz)

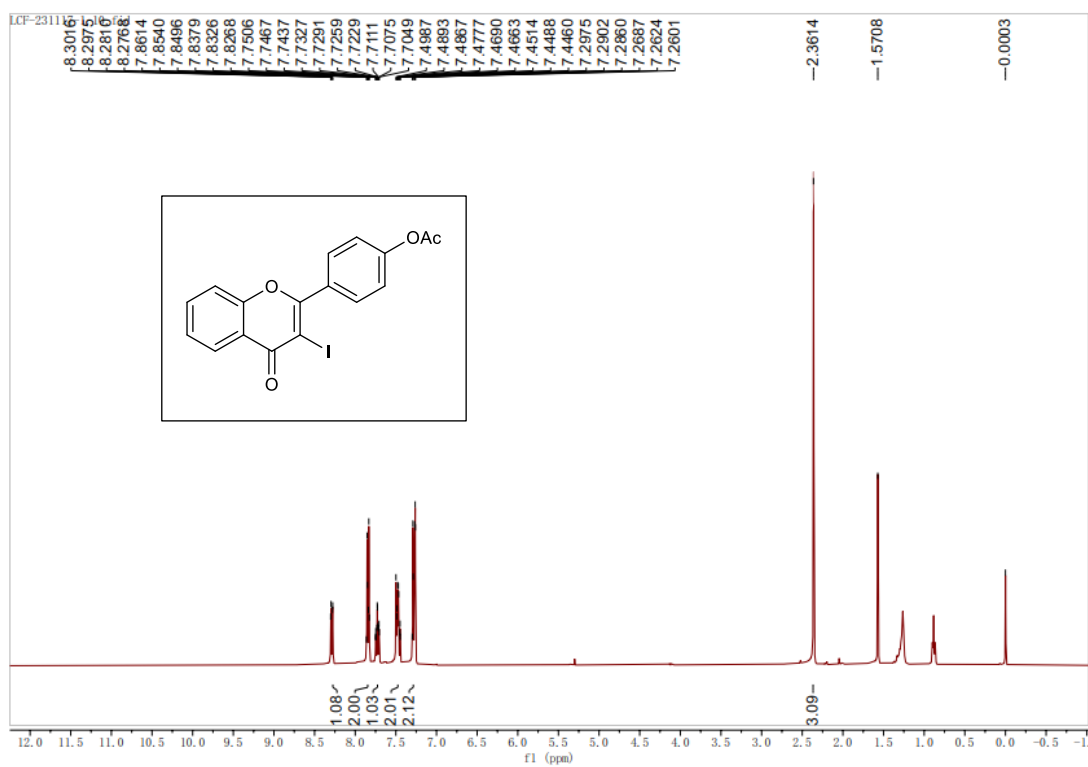


^1H NMR Spectra of compound **2cb** in CDCl_3 (400 MHz)

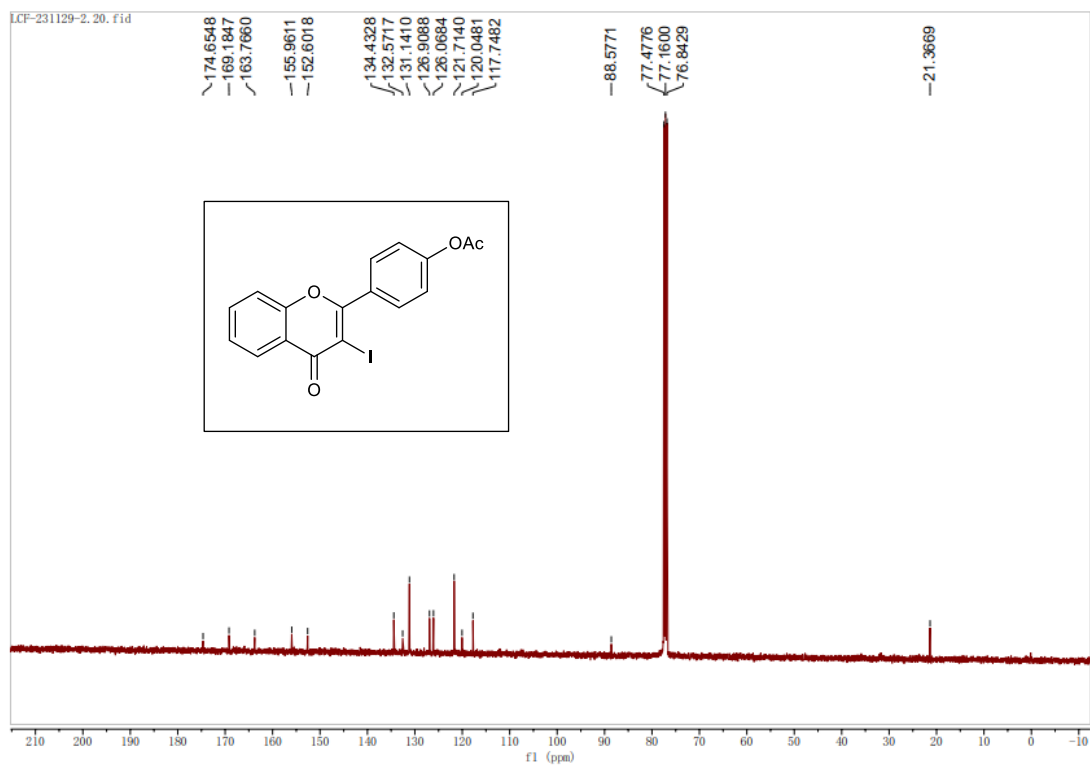




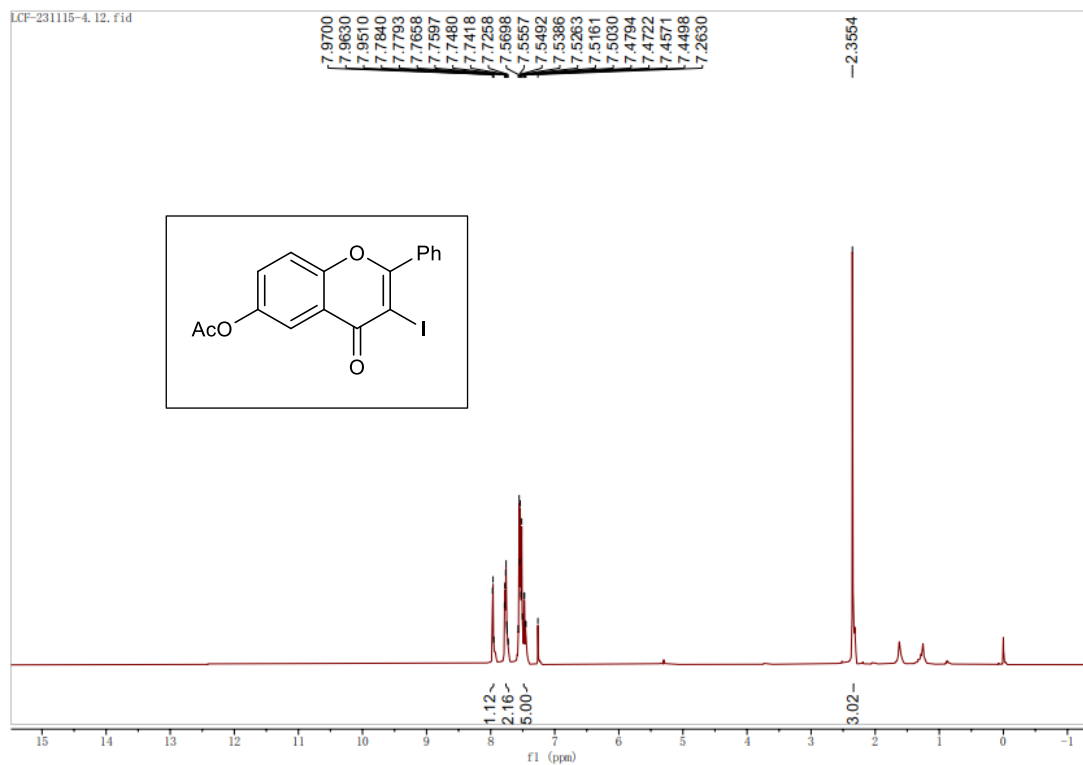
^{13}C NMR Spectra of compound **2cc** in CDCl_3 (101 MHz)



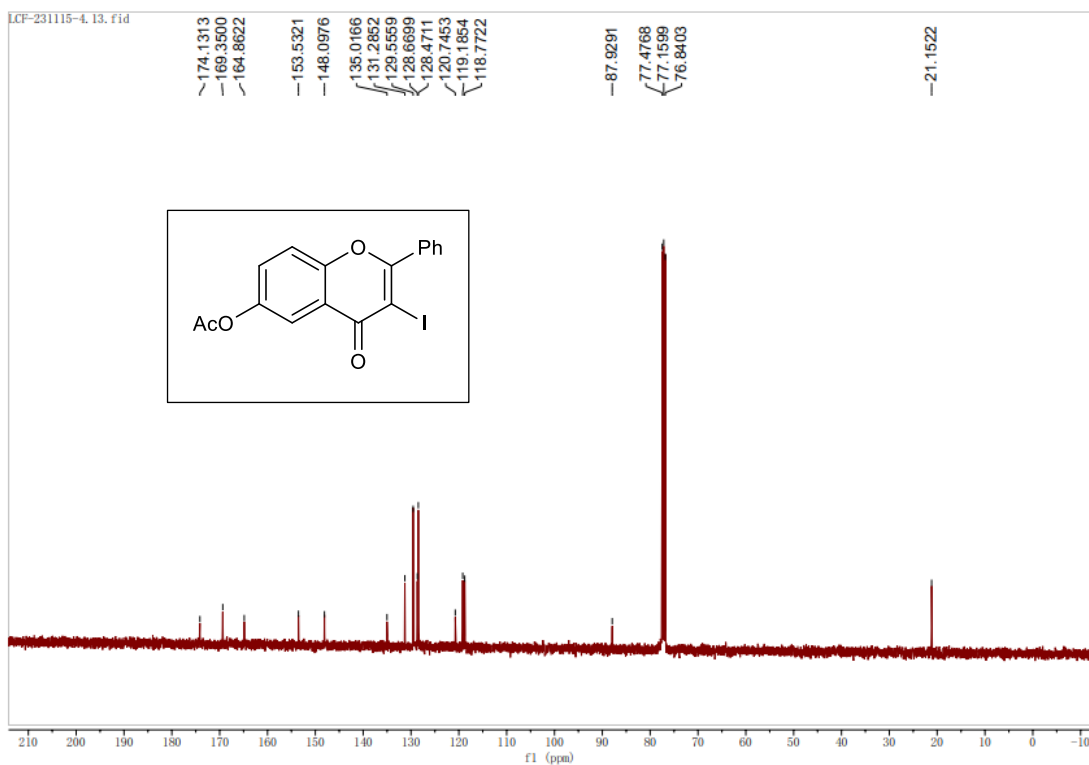
^1H NMR Spectra of compound **2cd** in CDCl_3 (400 MHz)



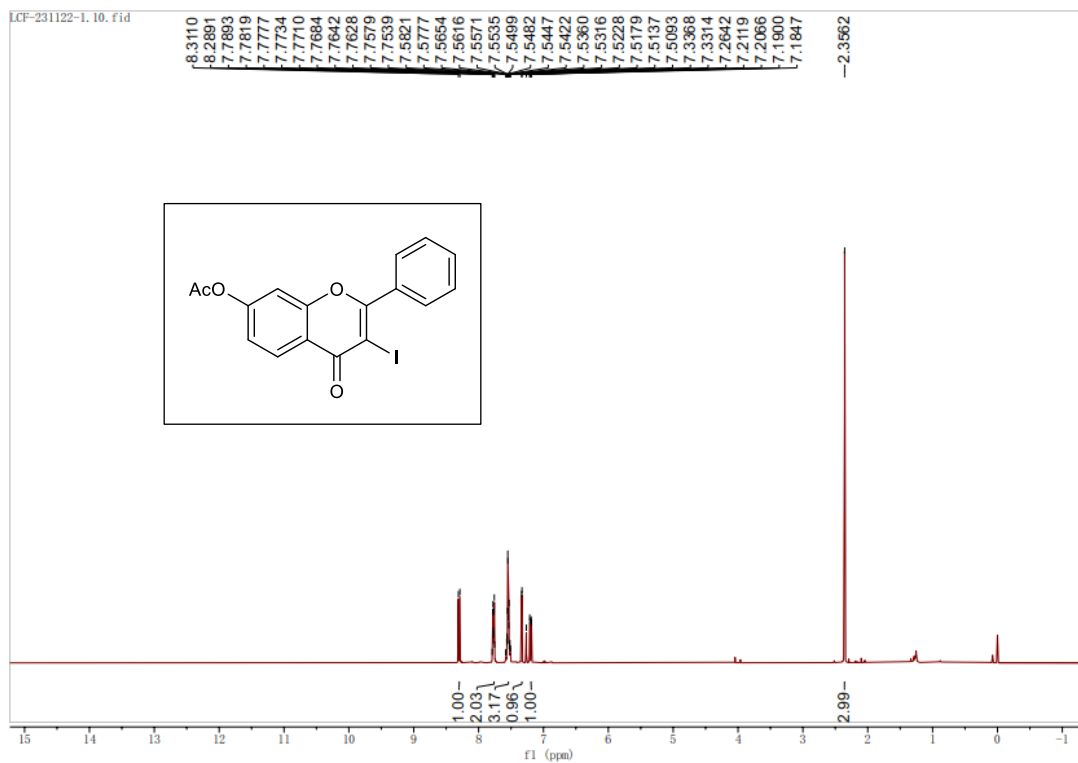
^{13}C NMR Spectra of compound **2cd** in CDCl_3 (101 MHz)



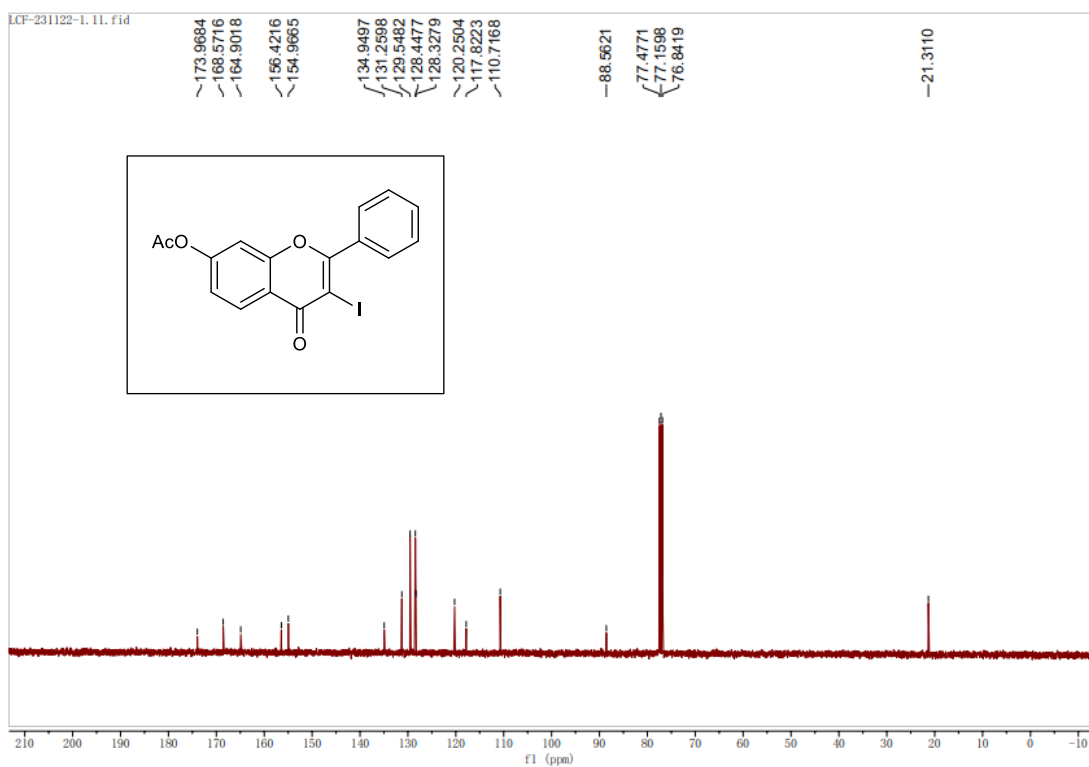
^1H NMR Spectra of compound **2ce** in CDCl_3 (400 MHz)



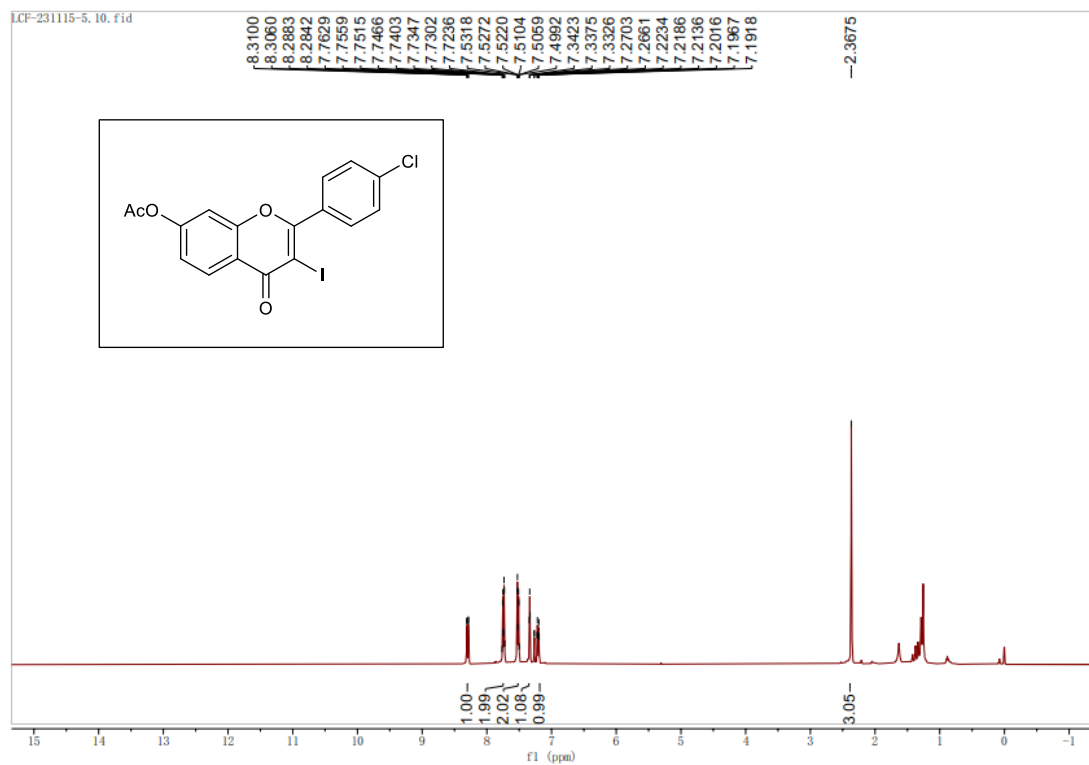
^{13}C NMR Spectra of compound **2ce** in CDCl_3 (101 MHz)



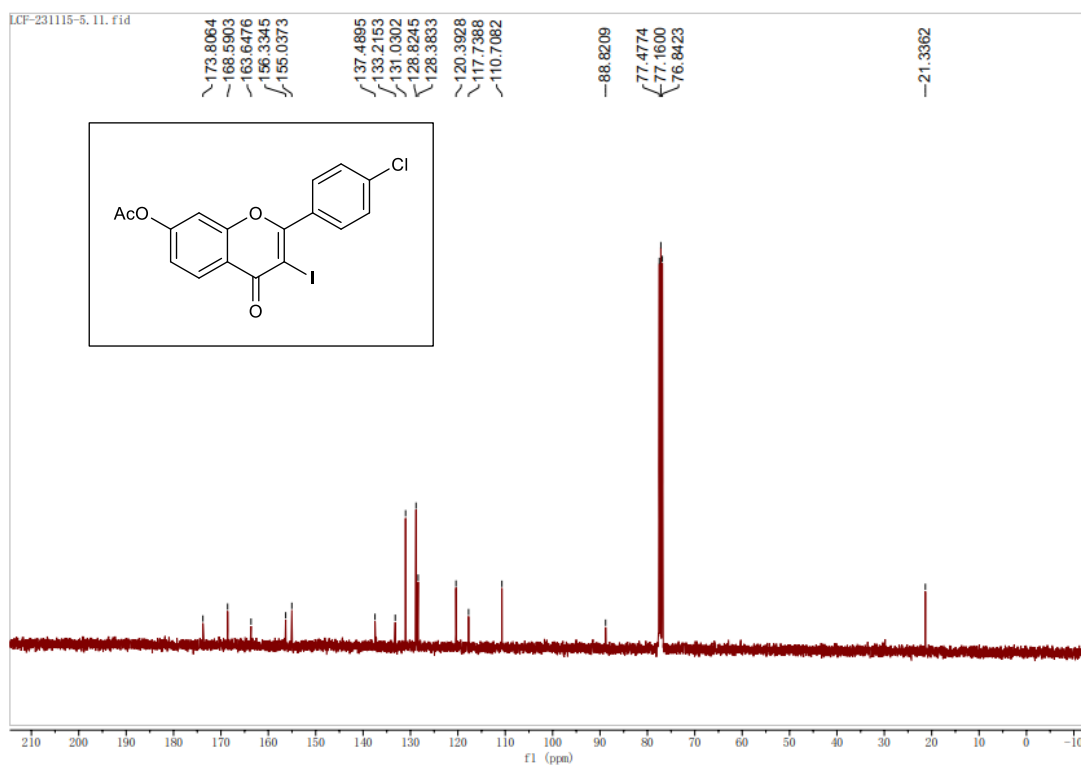
^1H NMR Spectra of compound **2cf** in CDCl_3 (400 MHz)



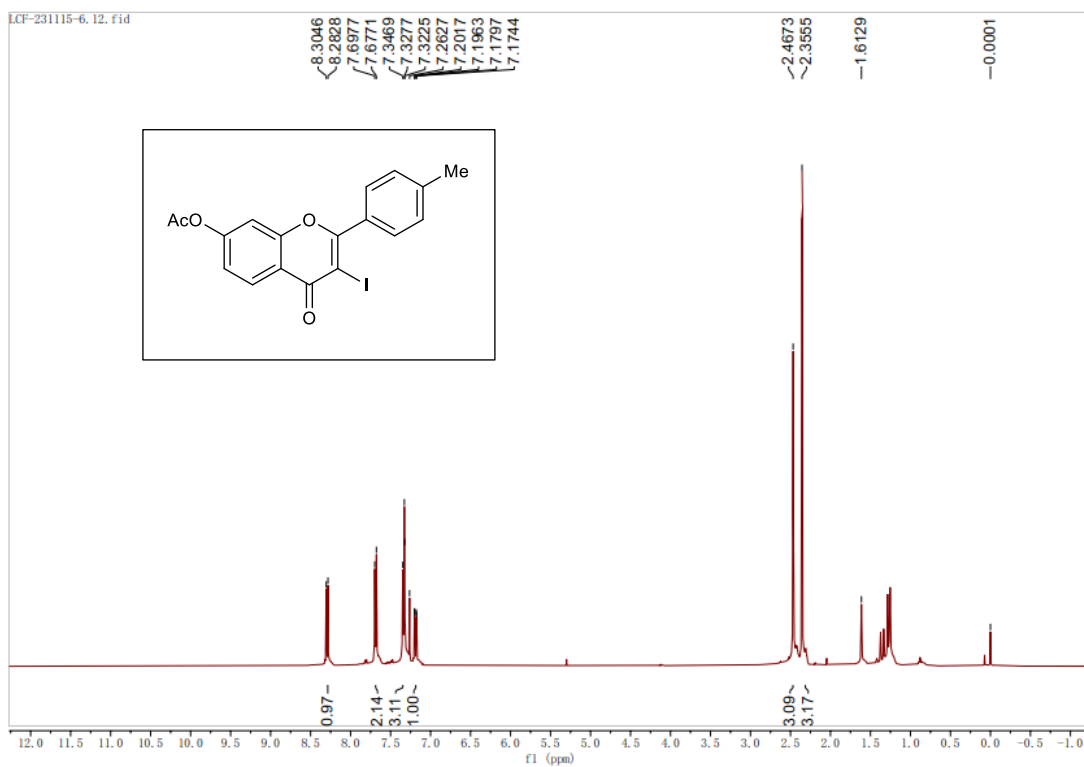
^{13}C NMR Spectra of compound **2cf** in CDCl_3 (101 MHz)



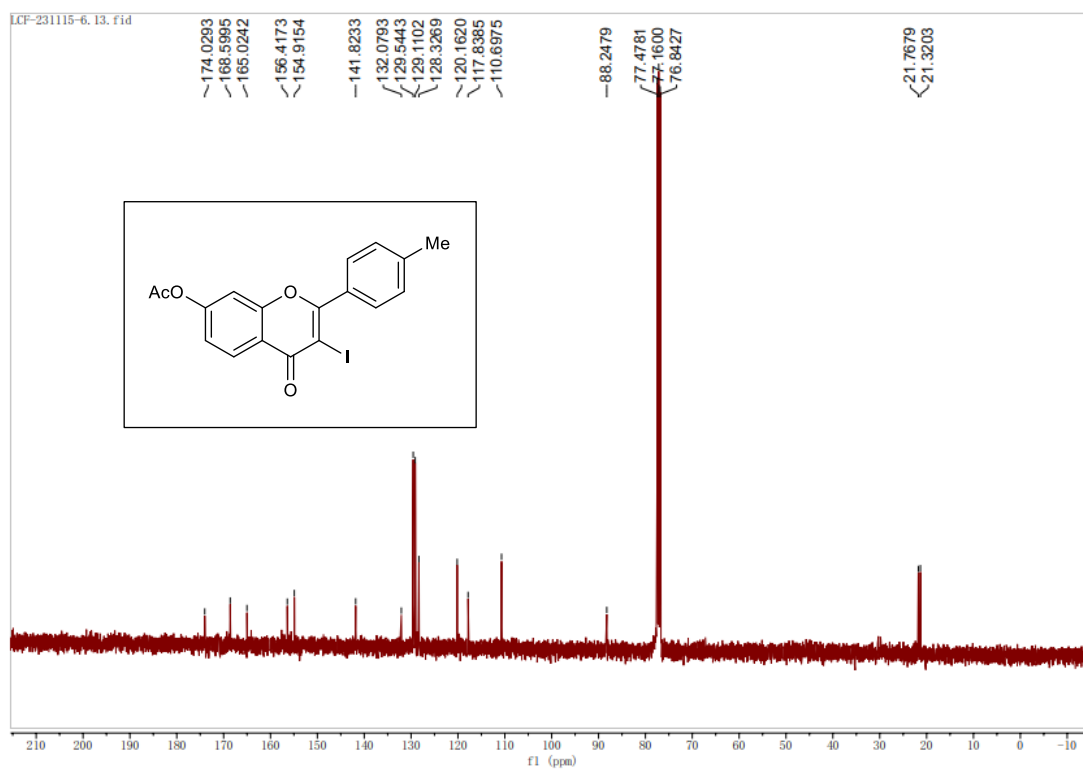
^1H NMR Spectra of compound **2cg** in CDCl_3 (400 MHz)



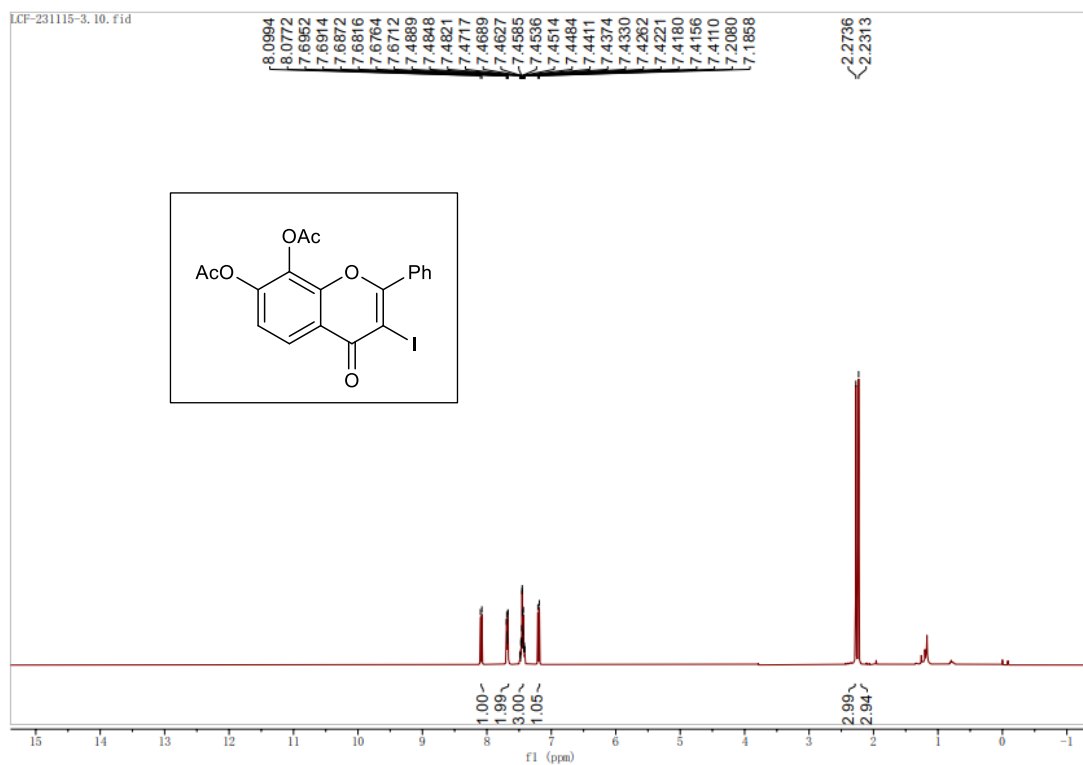
^{13}C NMR Spectra of compound **2cg** in CDCl_3 (101 MHz)



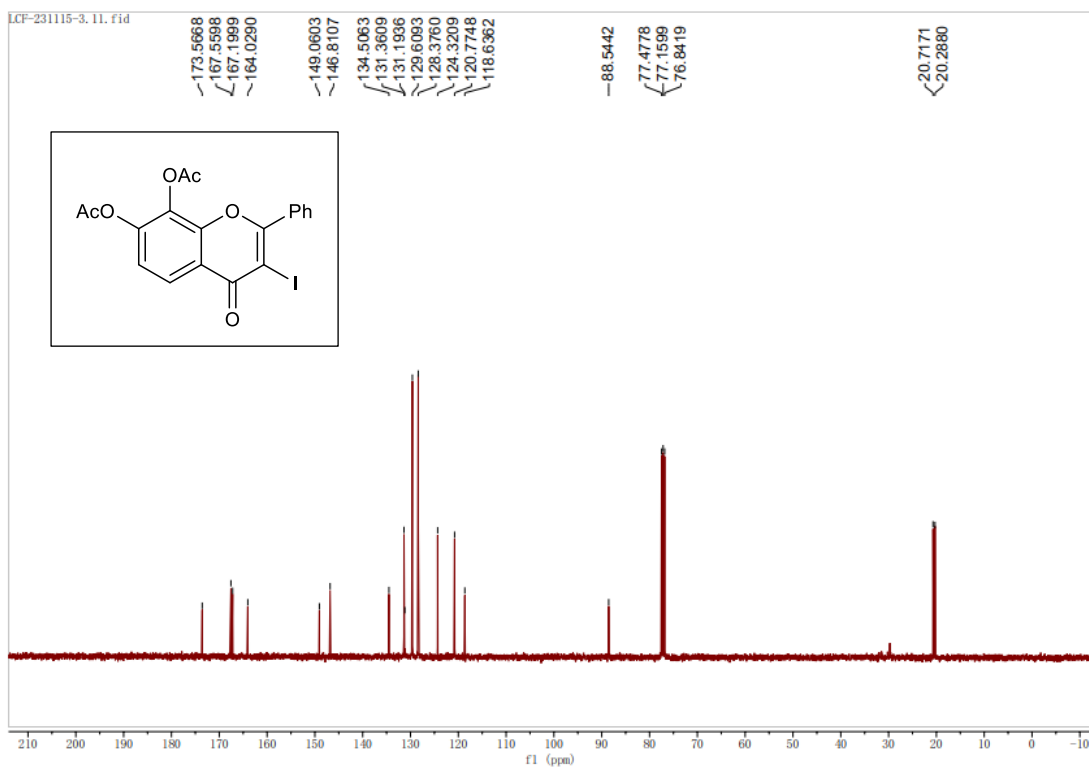
^1H NMR Spectra of compound **2ch** in CDCl_3 (400 MHz)



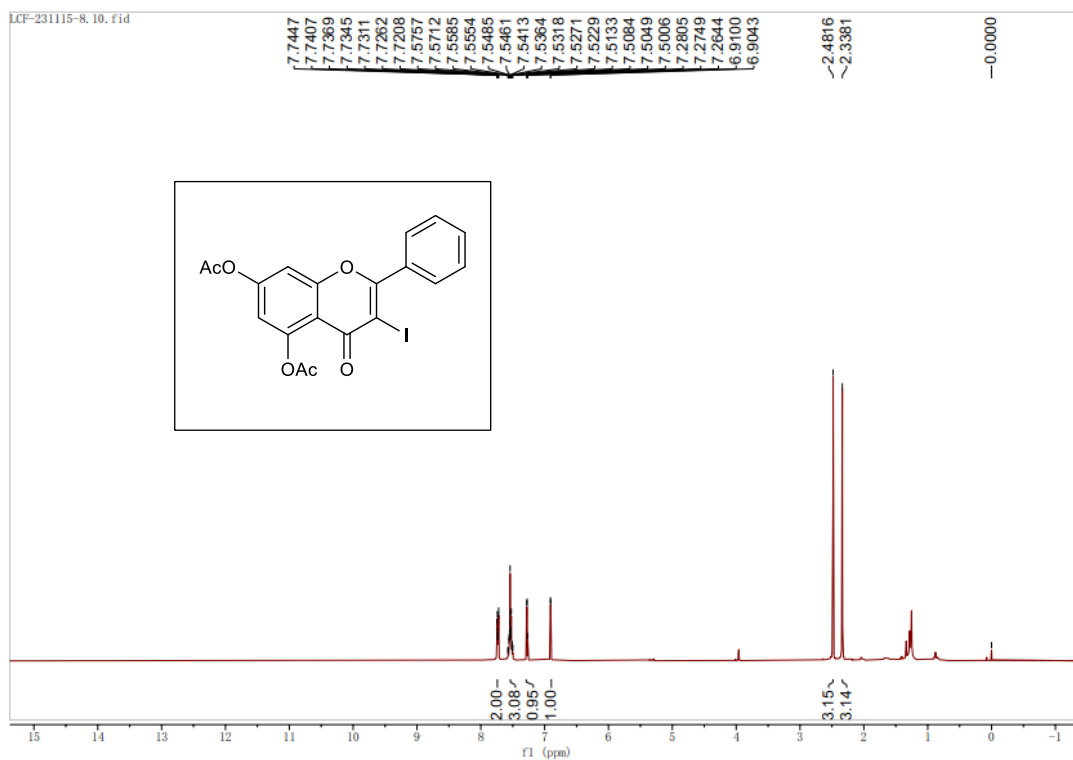
^{13}C NMR Spectra of compound **2ch** in CDCl_3 (101 MHz)



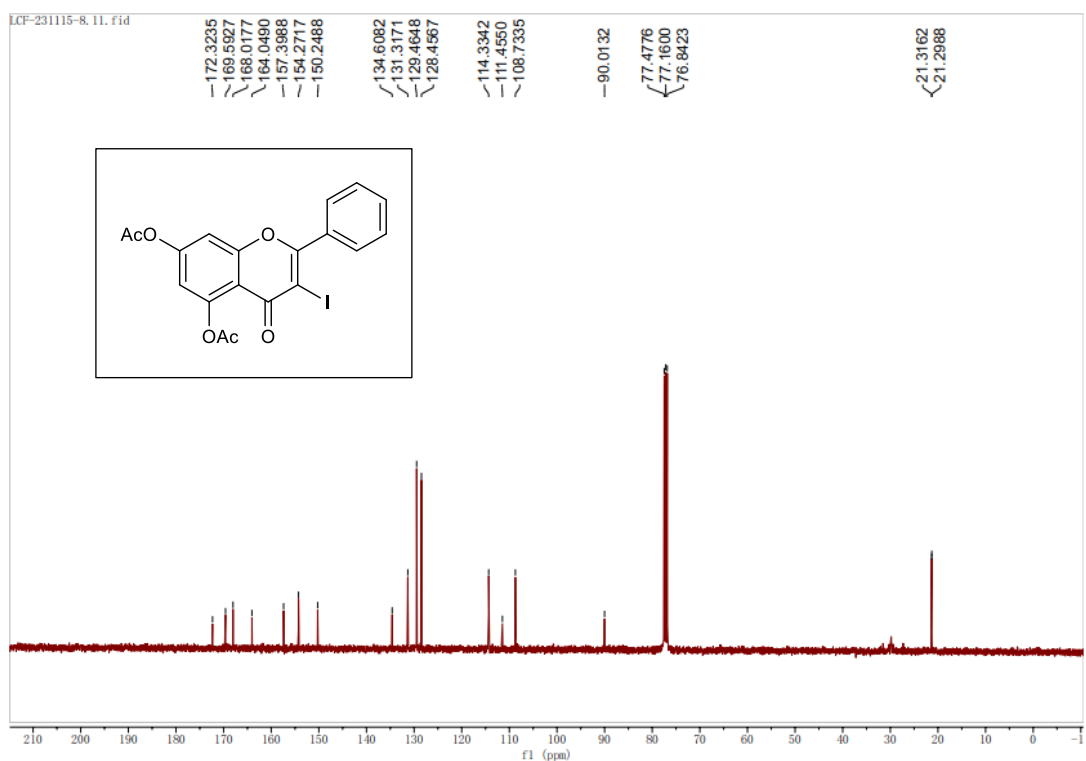
^1H NMR Spectra of compound **2ci** in CDCl_3 (400 MHz)



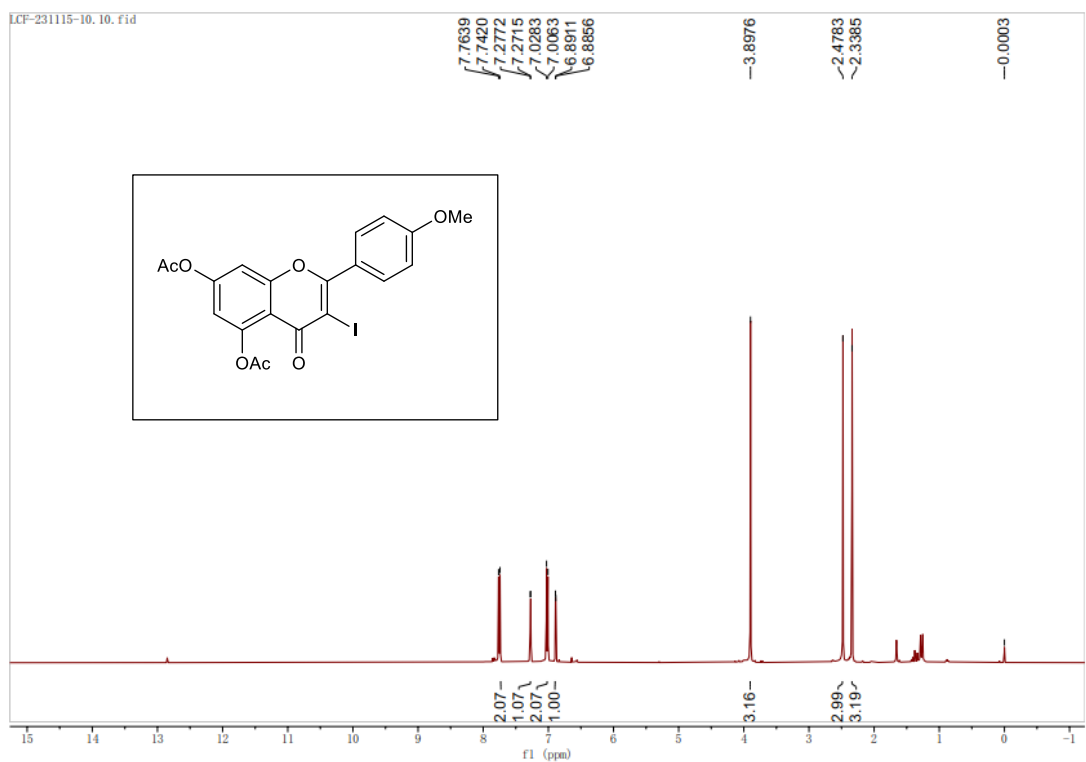
¹³C NMR Spectra of compound **2ci** in CDCl₃ (101 MHz)



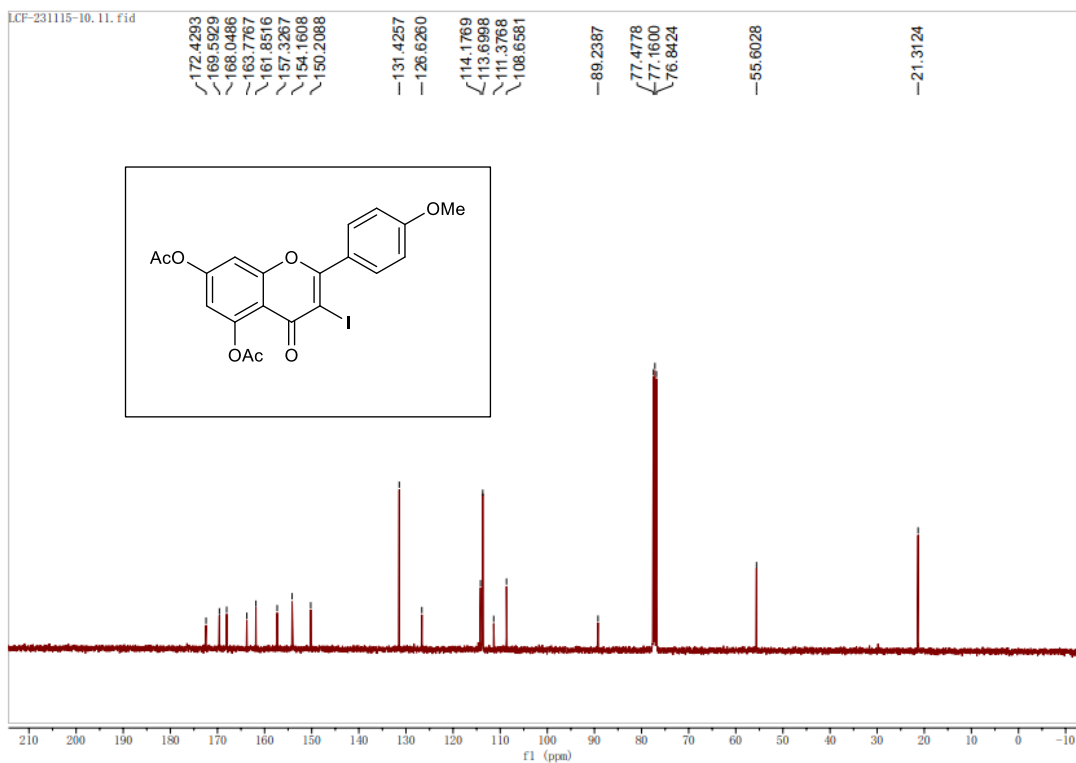
¹H NMR Spectra of compound **2cj** in CDCl₃ (400 MHz)



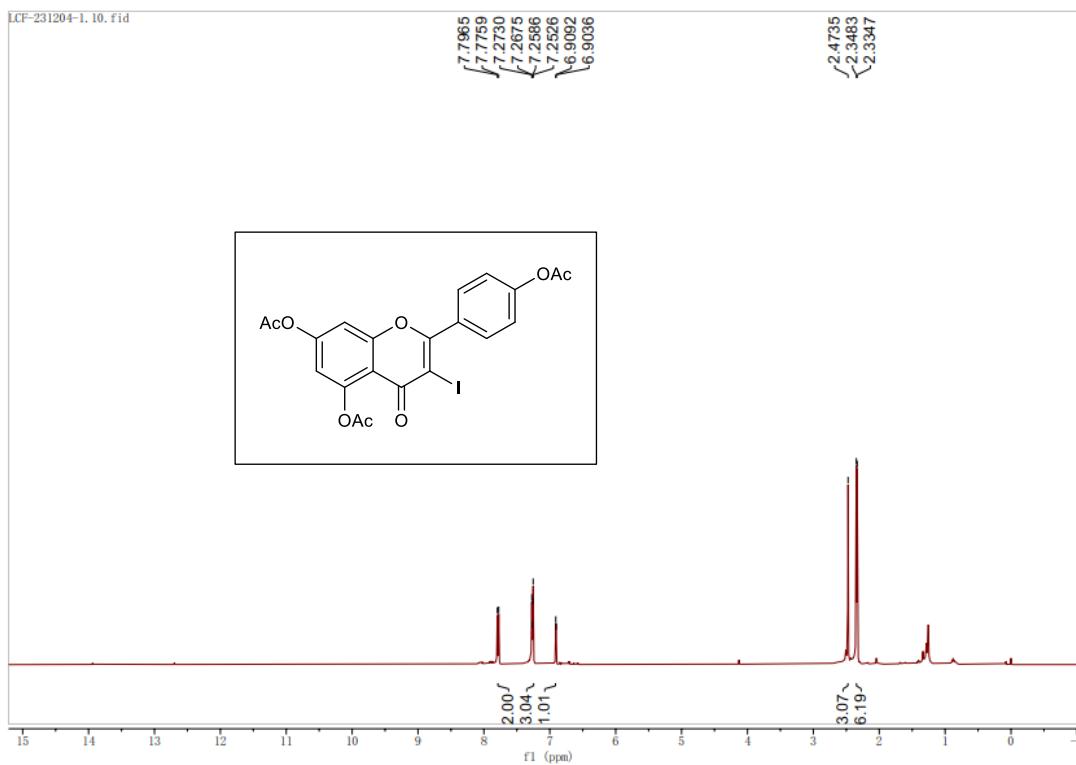
^{13}C NMR Spectra of compound **2cj** in CDCl_3 (101 MHz)



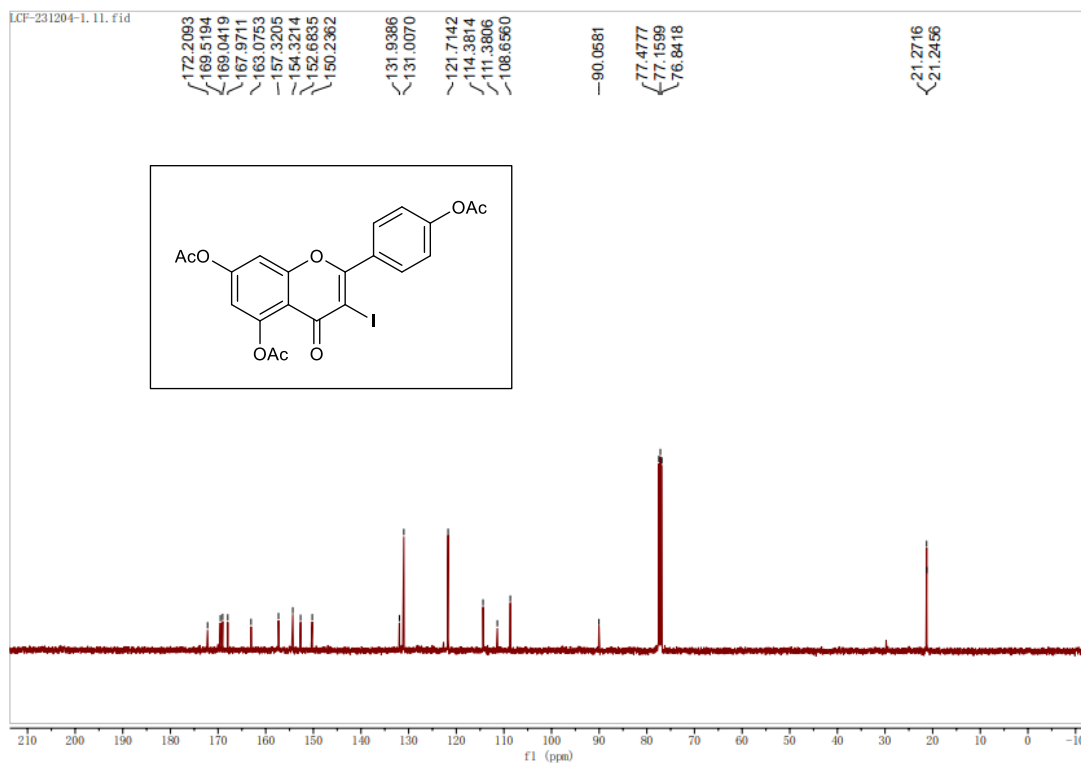
^1H NMR Spectra of compound **2ck** in CDCl_3 (400 MHz)



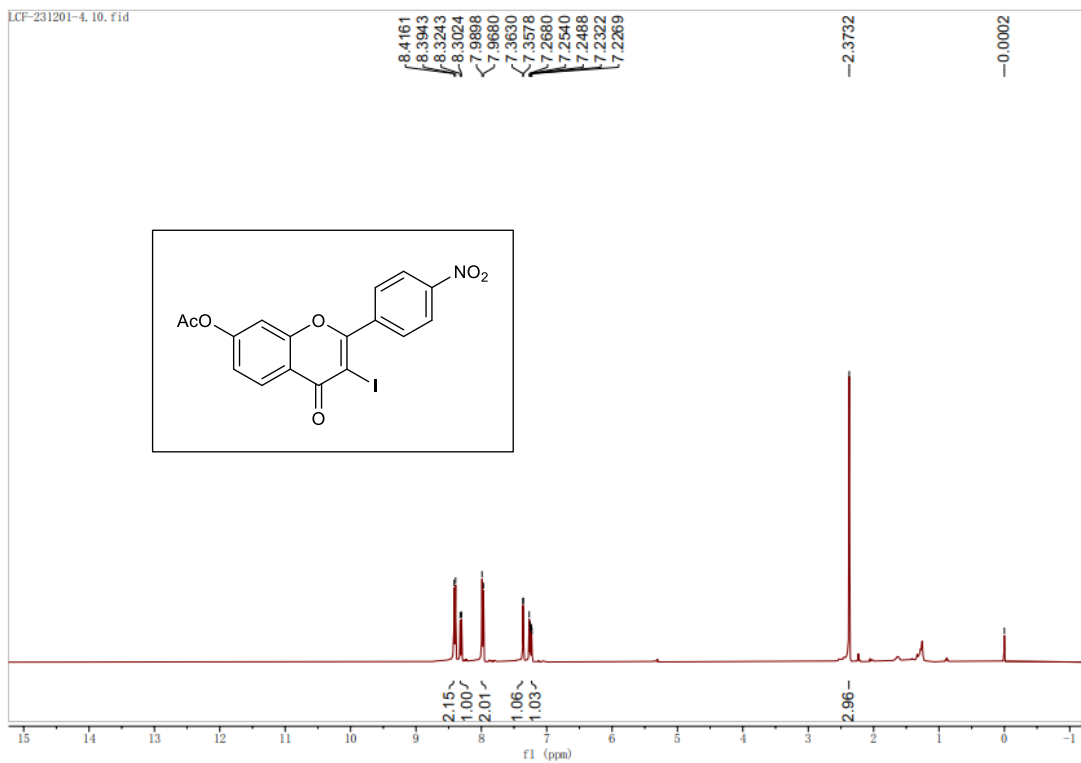
^{13}C NMR Spectra of compound **2ck** in CDCl_3 (101 MHz)



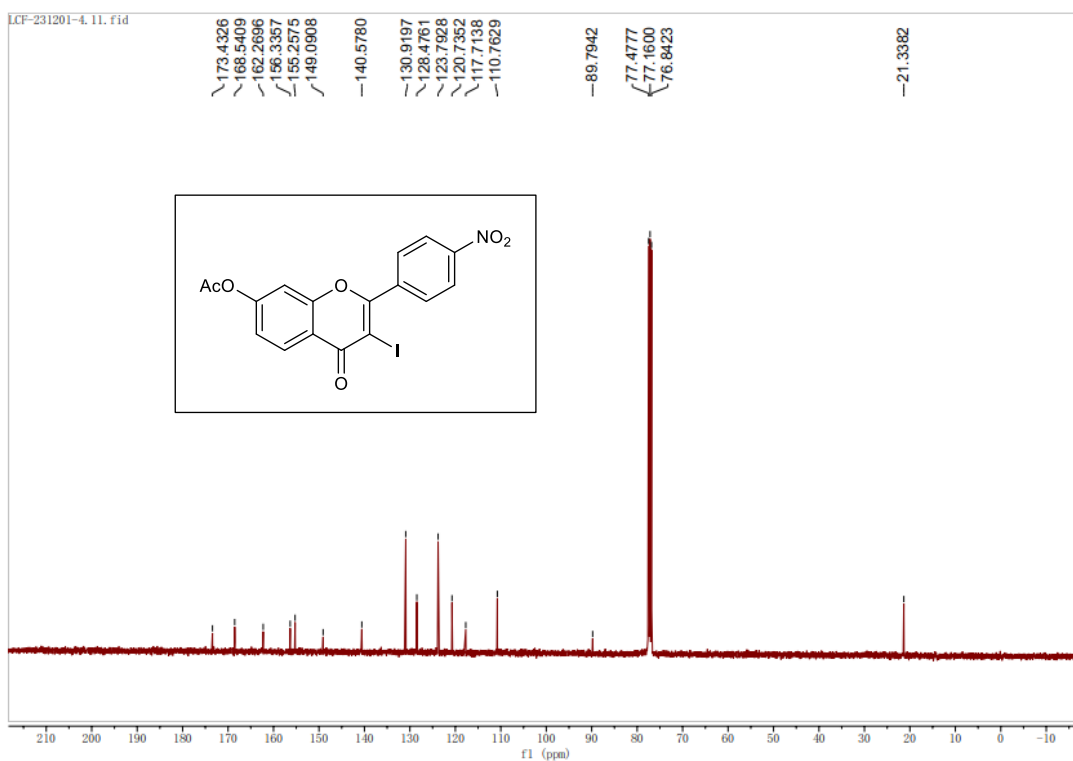
^1H NMR Spectra of compound **2cl** in CDCl_3 (400 MHz)



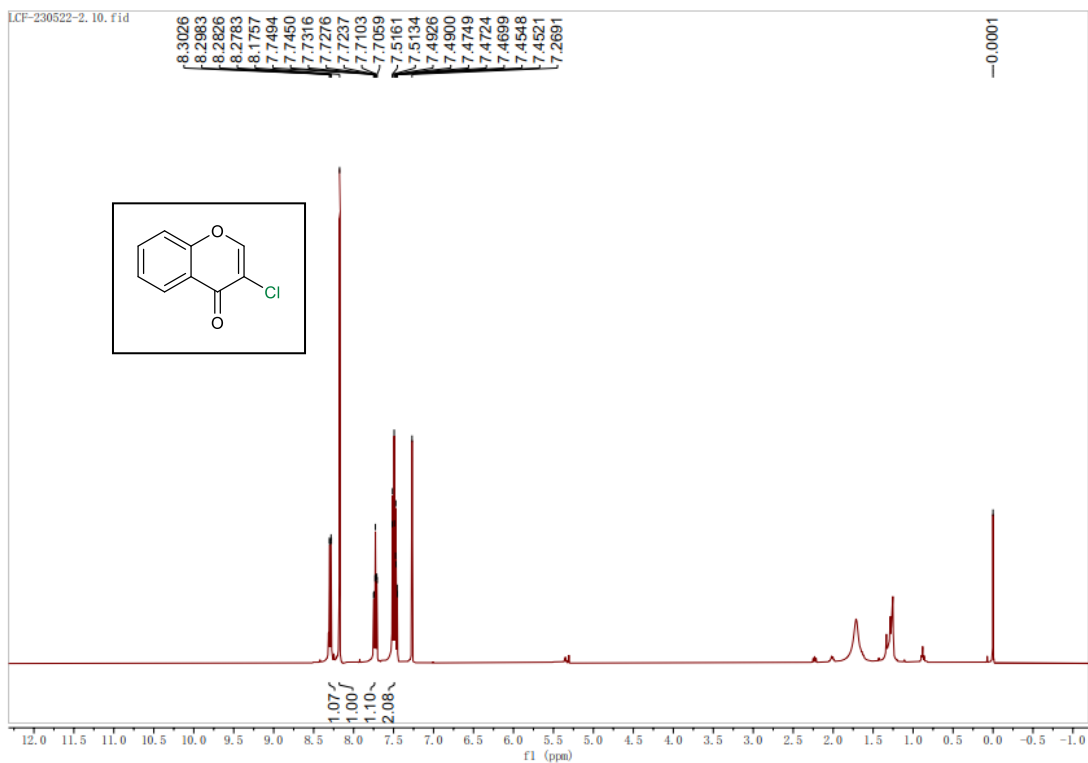
^{13}C NMR Spectra of compound **2cl** in CDCl_3 (101 MHz)



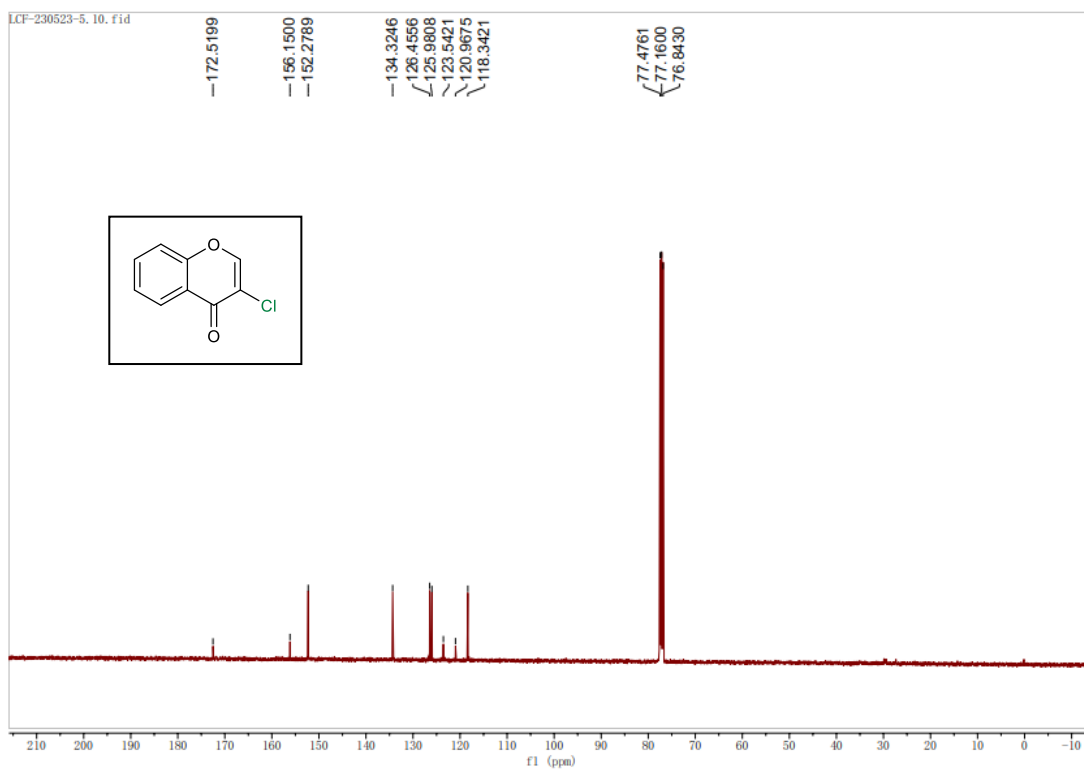
^1H NMR Spectra of compound **2cm** in CDCl_3 (400 MHz)



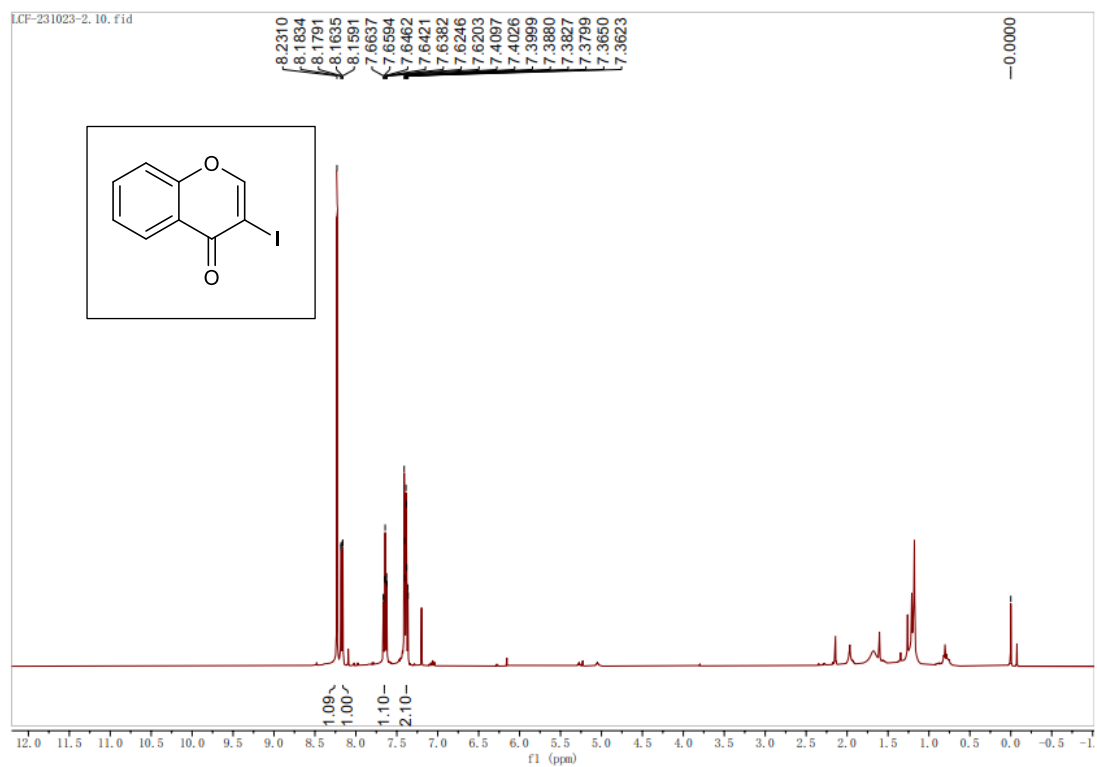
^{13}C NMR Spectra of compound **2cm** in CDCl_3 (101 MHz)



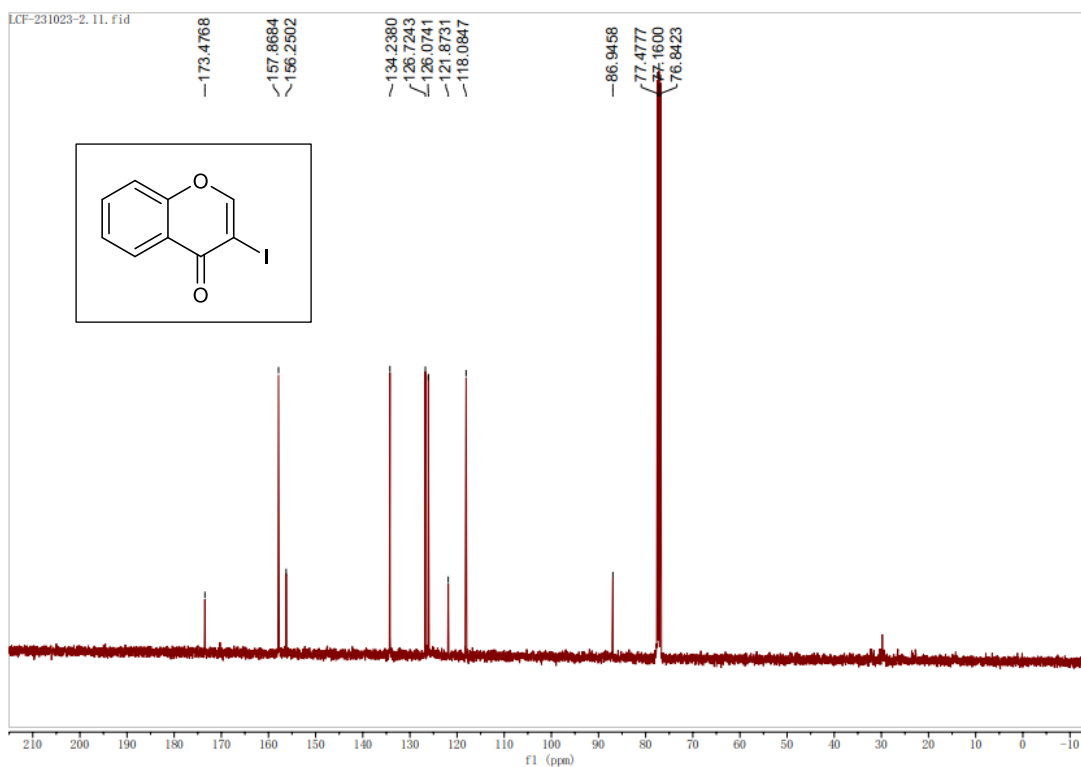
^1H NMR Spectra of compound **4aa** in CDCl_3 (400 MHz)



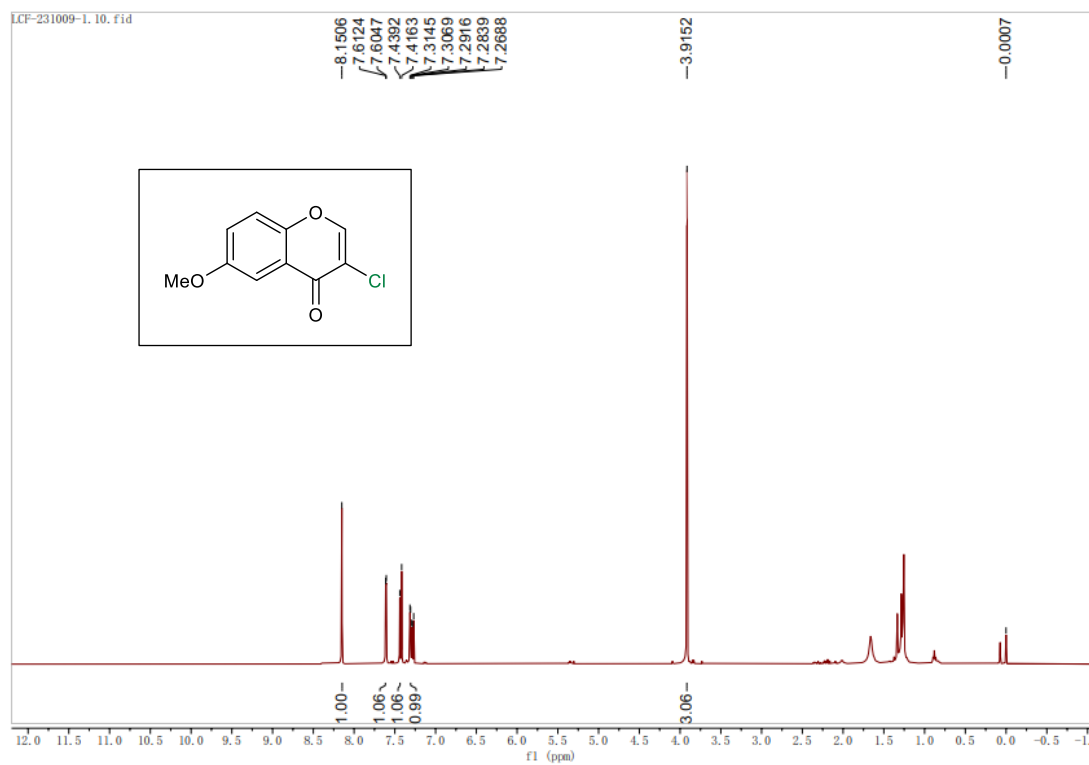
^{13}C NMR Spectra of compound **4aa** in CDCl_3 (101 MHz)



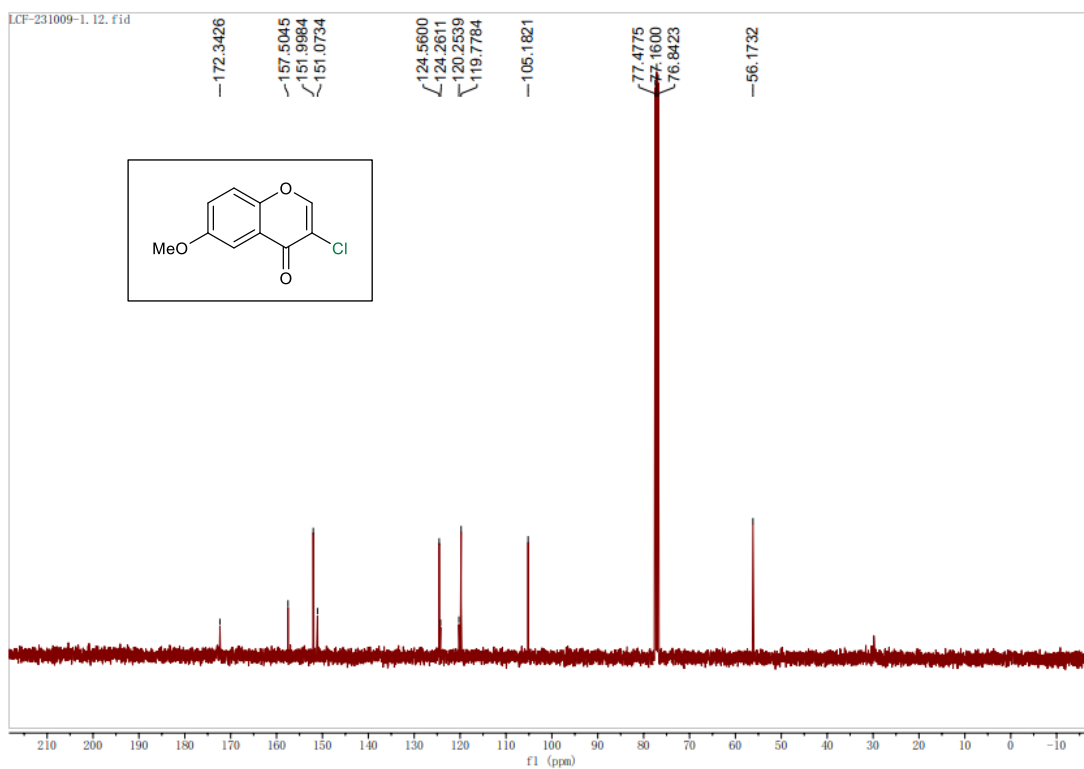
^1H NMR Spectra of compound **4aa'** in CDCl_3 (400 MHz)



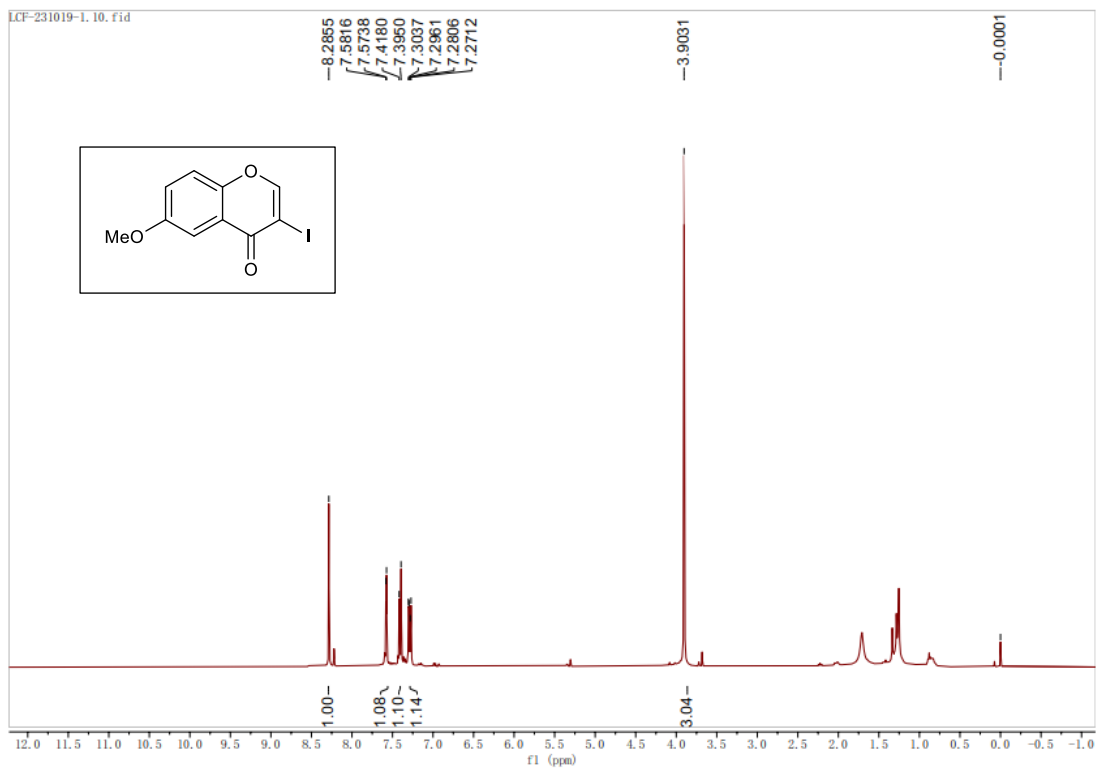
^{13}C NMR Spectra of compound **4aa'** in CDCl_3 (101 MHz)



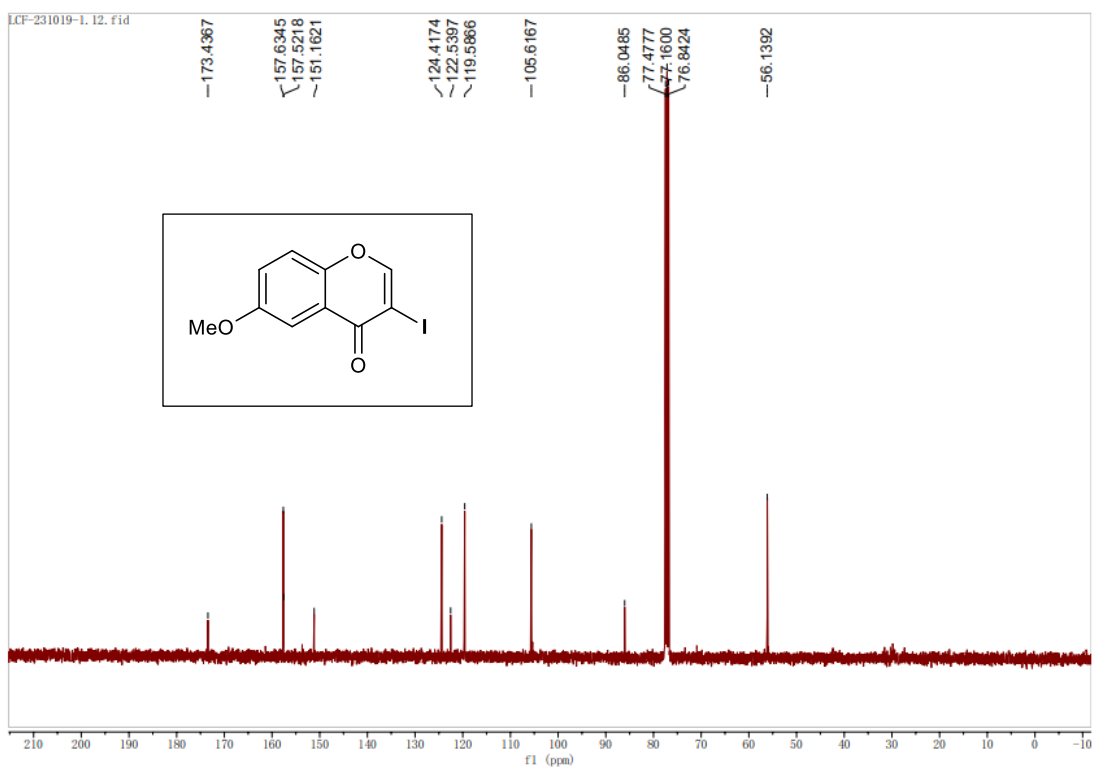
^1H NMR Spectra of compound **4ab** in CDCl_3 (400 MHz)



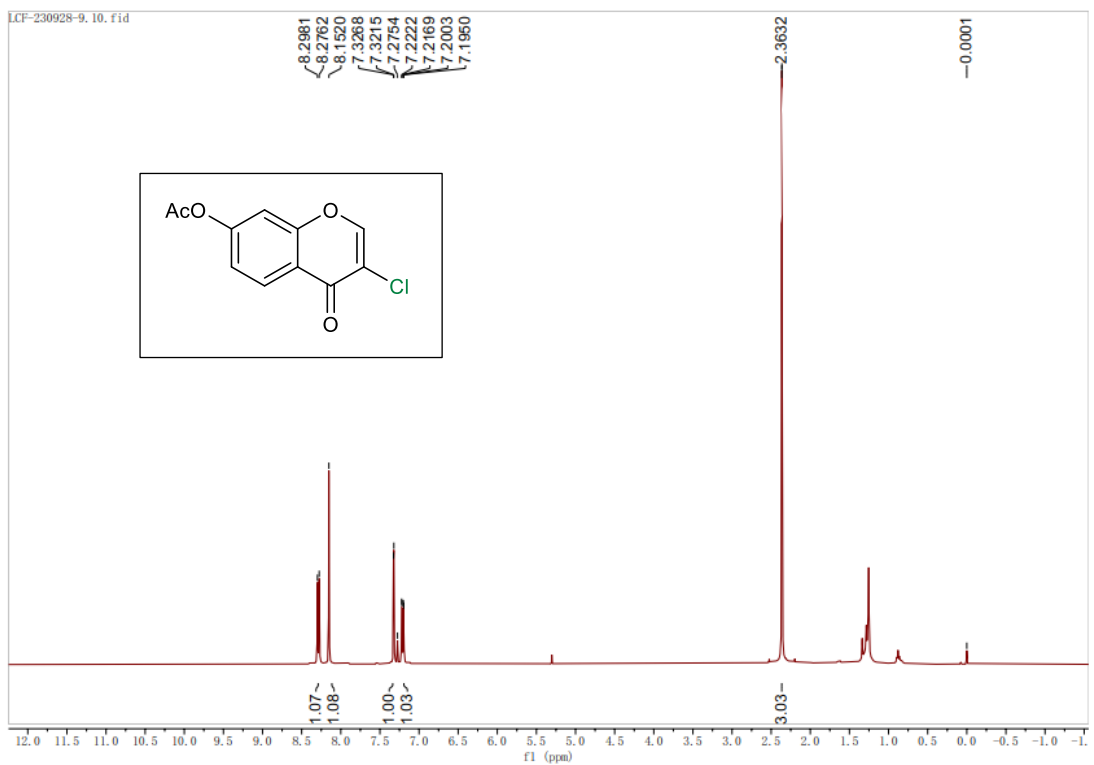
^{13}C NMR Spectra of compound **4ab** in CDCl_3 (101 MHz)



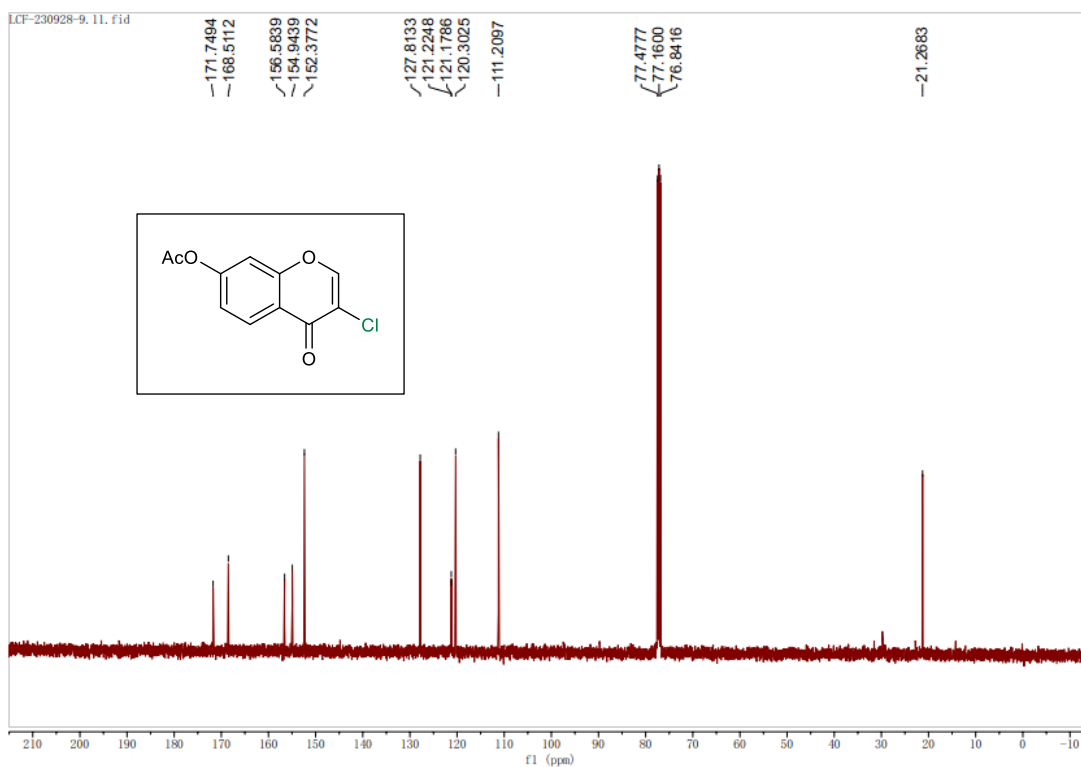
^1H NMR Spectra of compound **4ab'** in CDCl_3 (400 MHz)



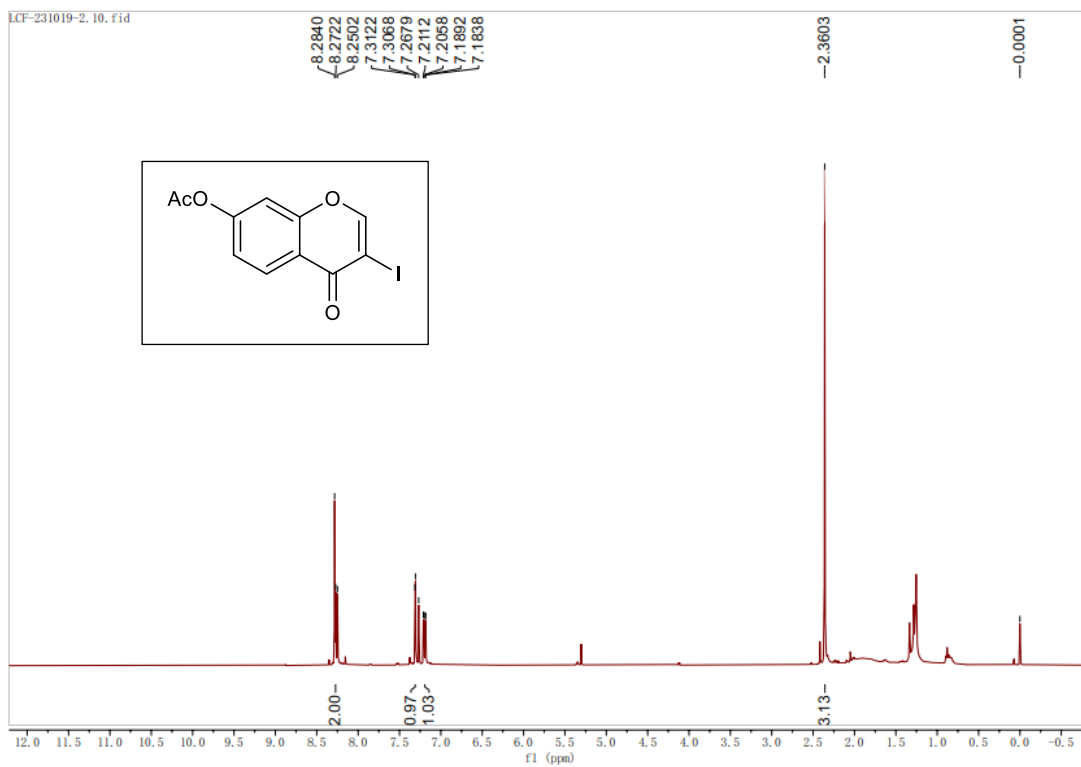
^{13}C NMR Spectra of compound **4ab'** in CDCl_3 (101 MHz)



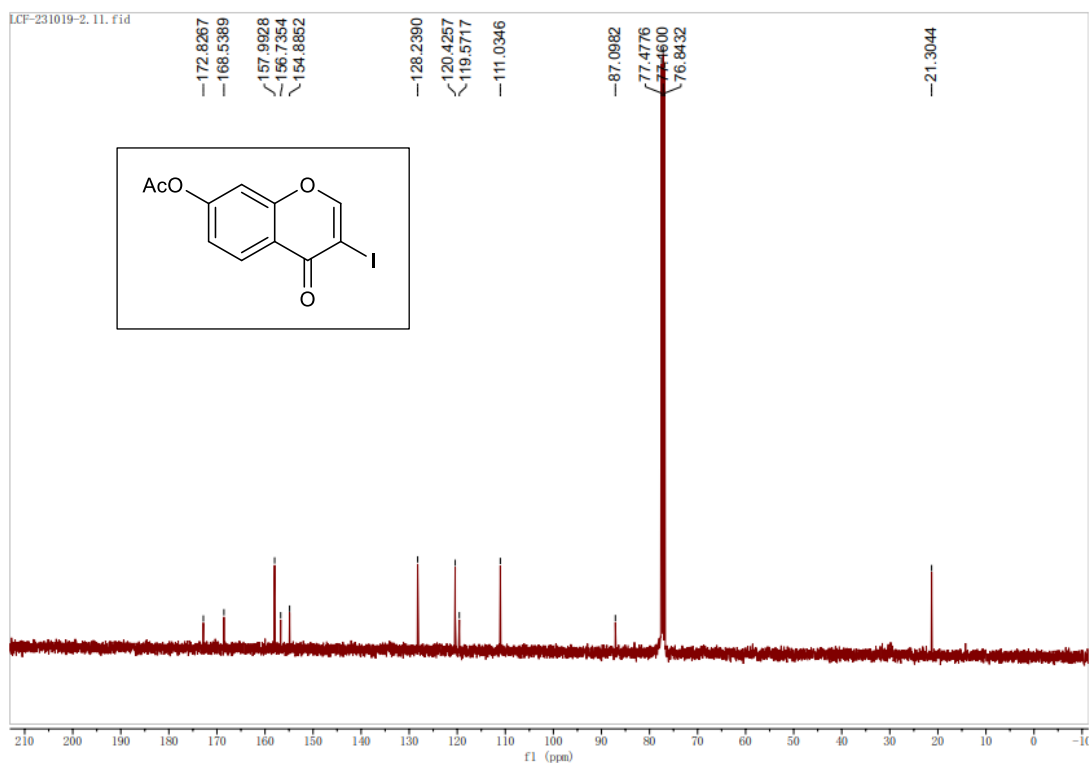
^1H NMR Spectra of compound **4ac** in CDCl_3 (400 MHz)



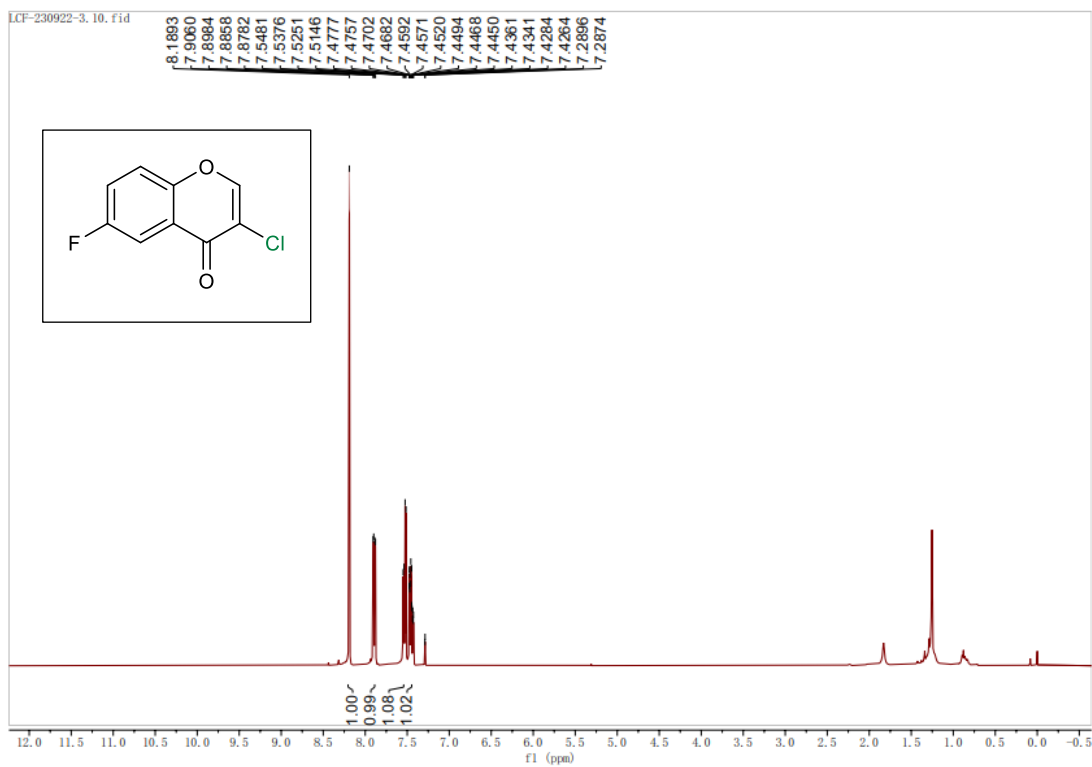
^{13}C NMR Spectra of compound **4ac** in CDCl_3 (101 MHz)



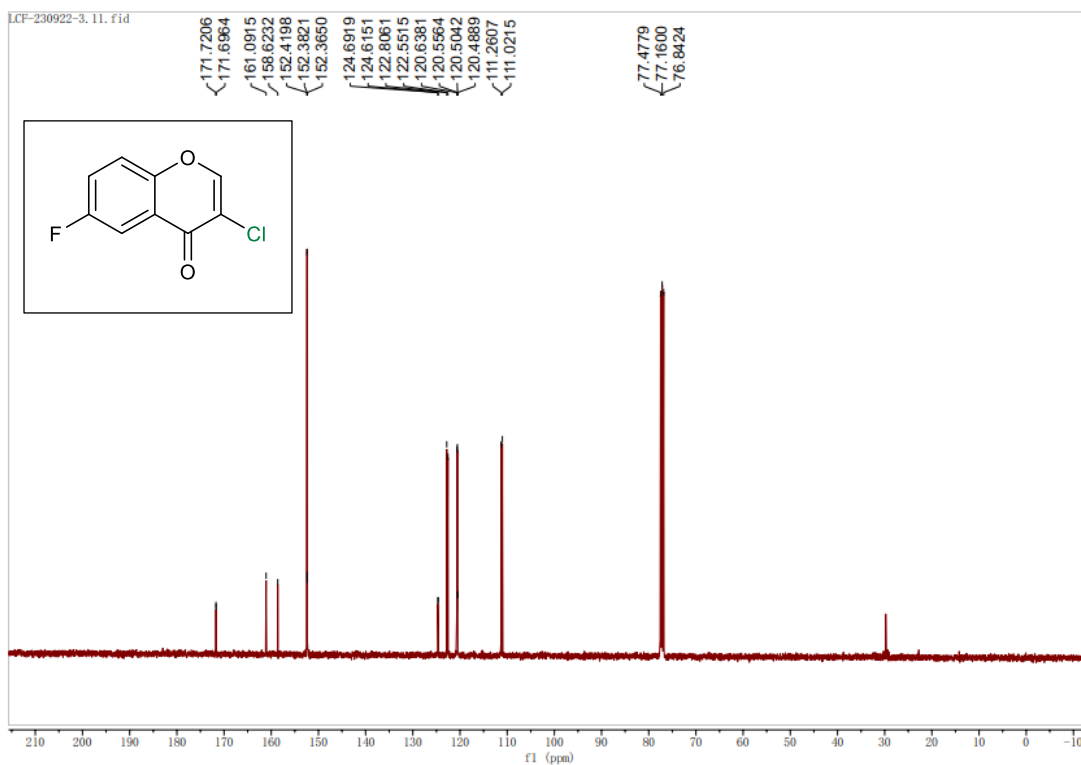
^1H NMR Spectra of compound **4ac'** in CDCl_3 (400 MHz)



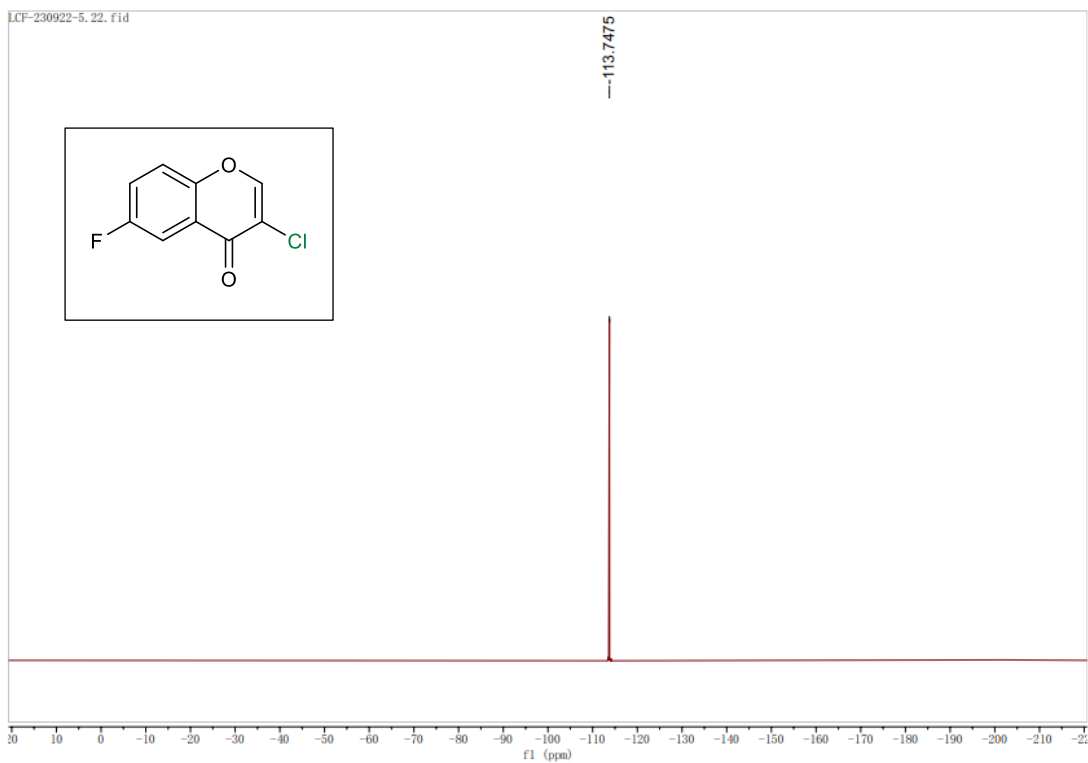
^{13}C NMR Spectra of compound **4ac'** in CDCl_3 (101 MHz)



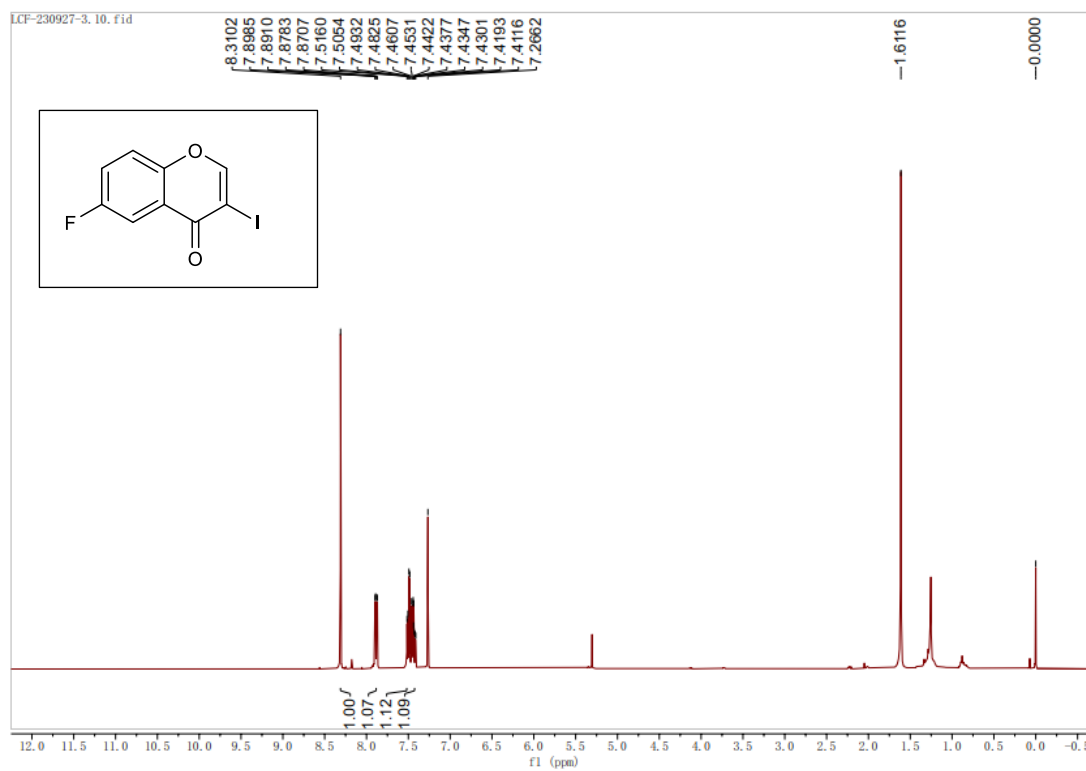
^1H NMR Spectra of compound **4ad** in CDCl_3 (400 MHz)



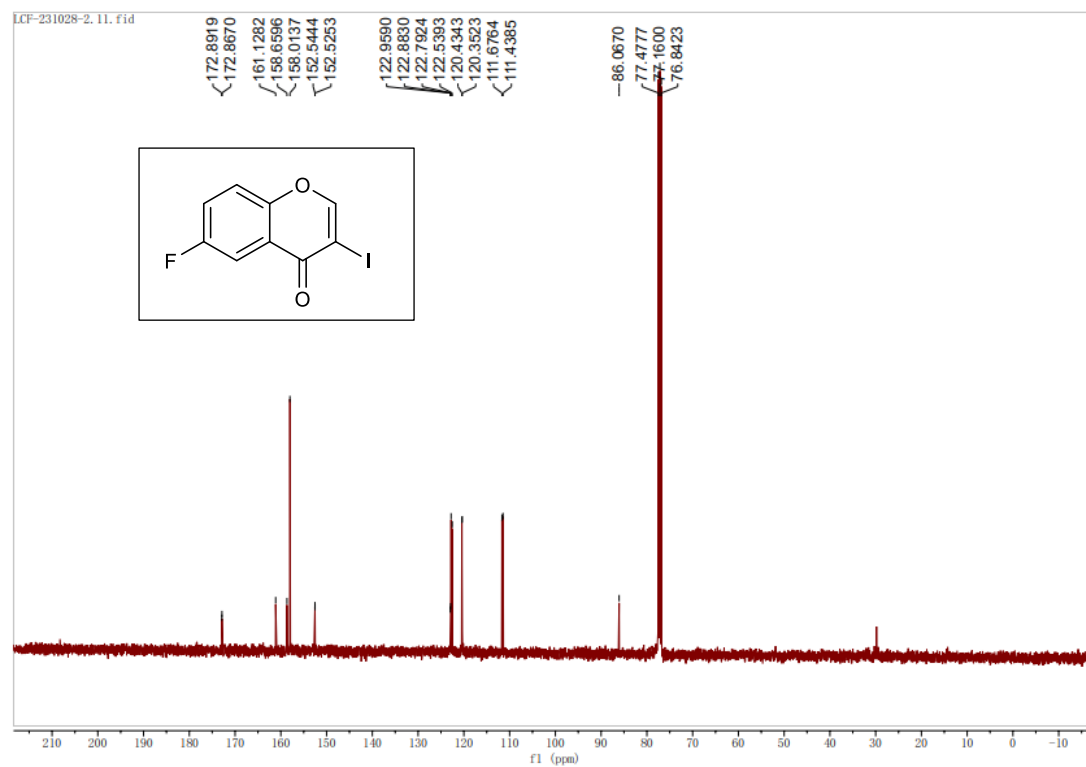
^{13}C NMR Spectra of compound **4ad** in CDCl_3 (101 MHz)



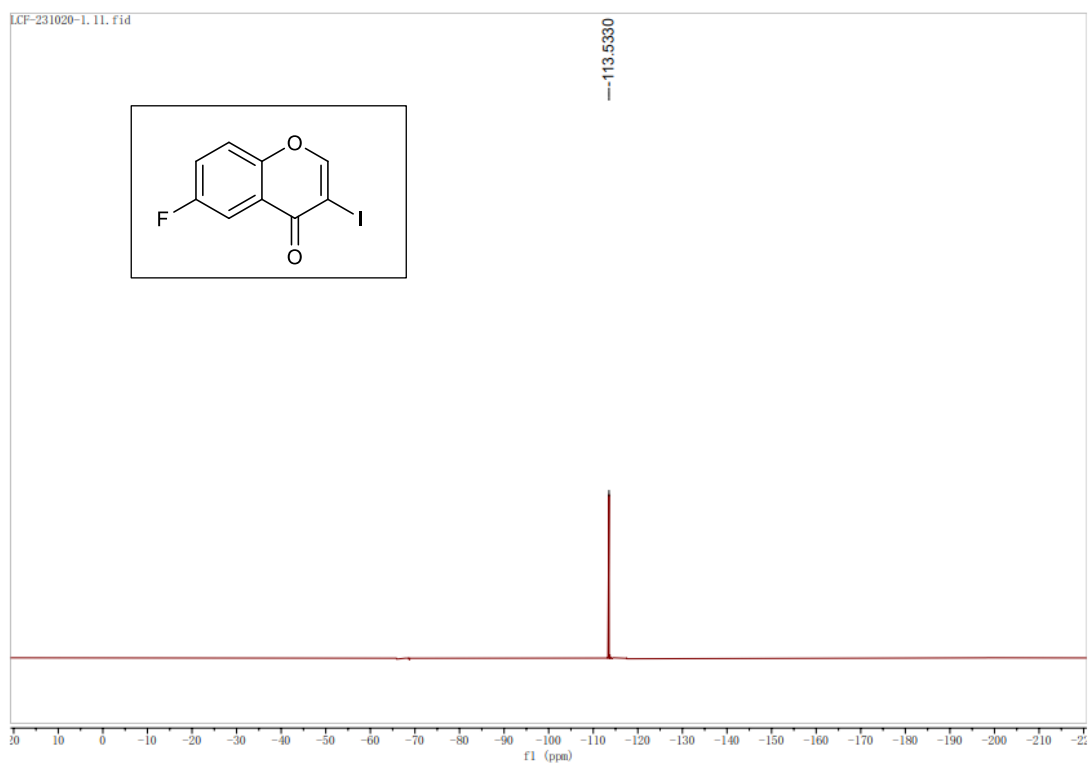
^{19}F NMR Spectra of compound **4ad** in CDCl_3 (377 MHz)



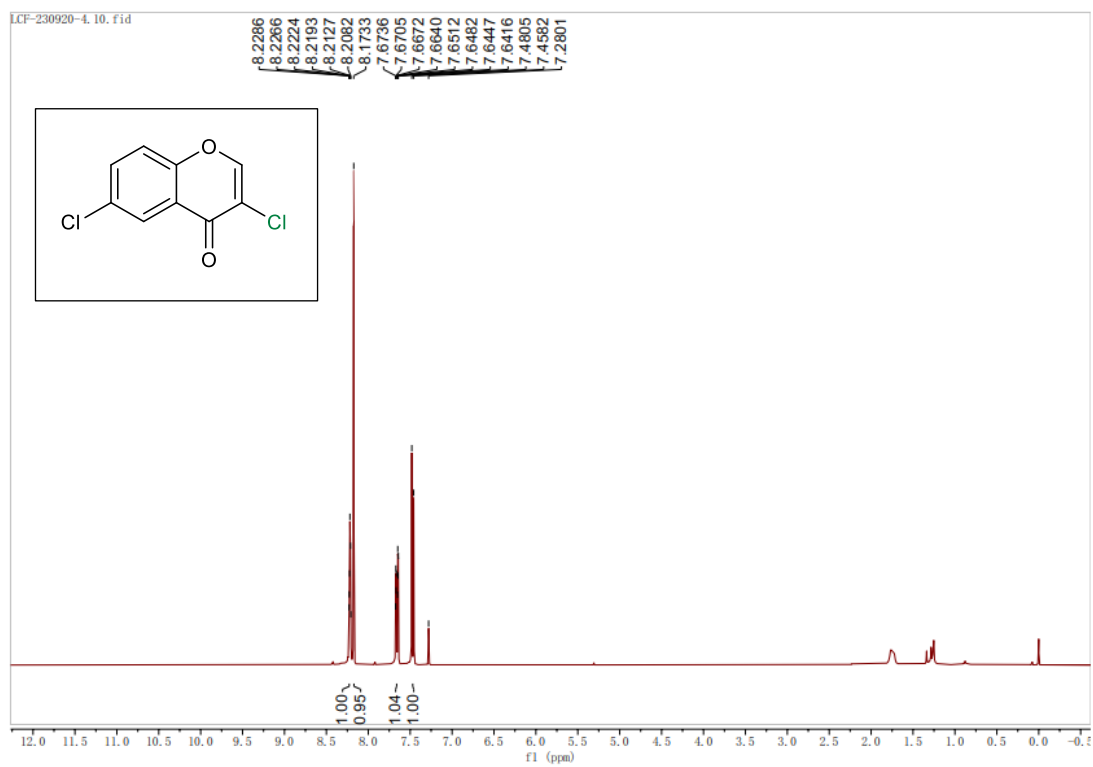
^1H NMR Spectra of compound **4ad'** in CDCl_3 (400 MHz)



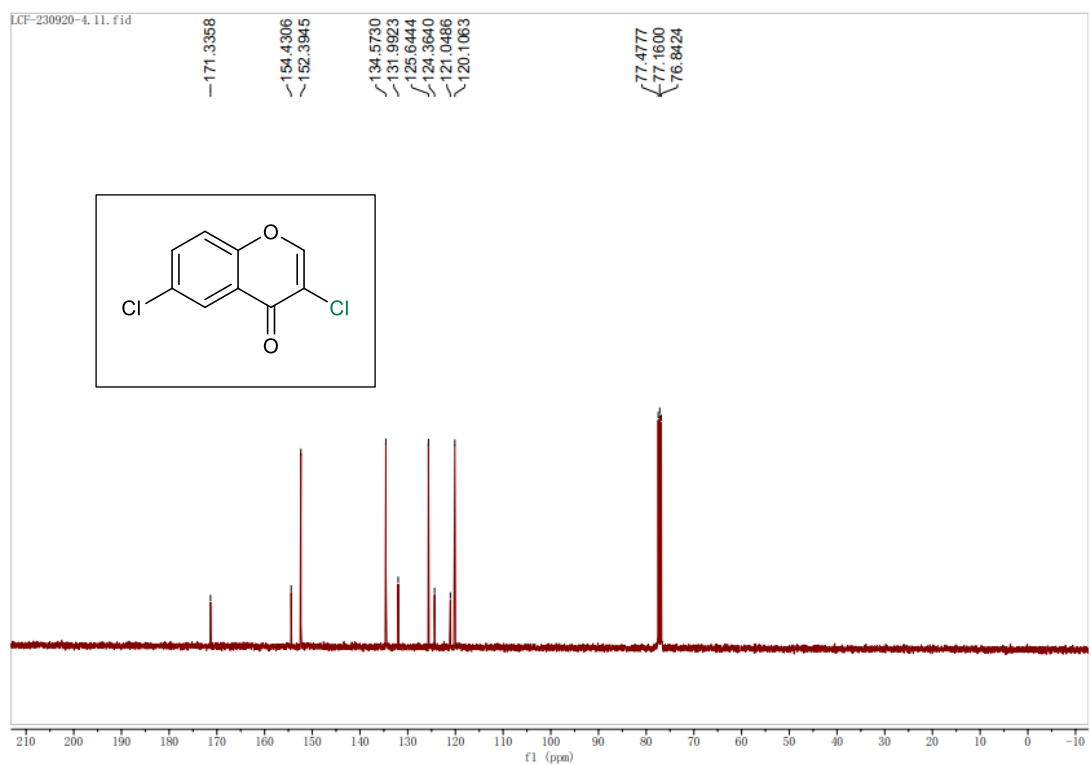
^{13}C NMR Spectra of compound **4ad'** in CDCl_3 (101 MHz)



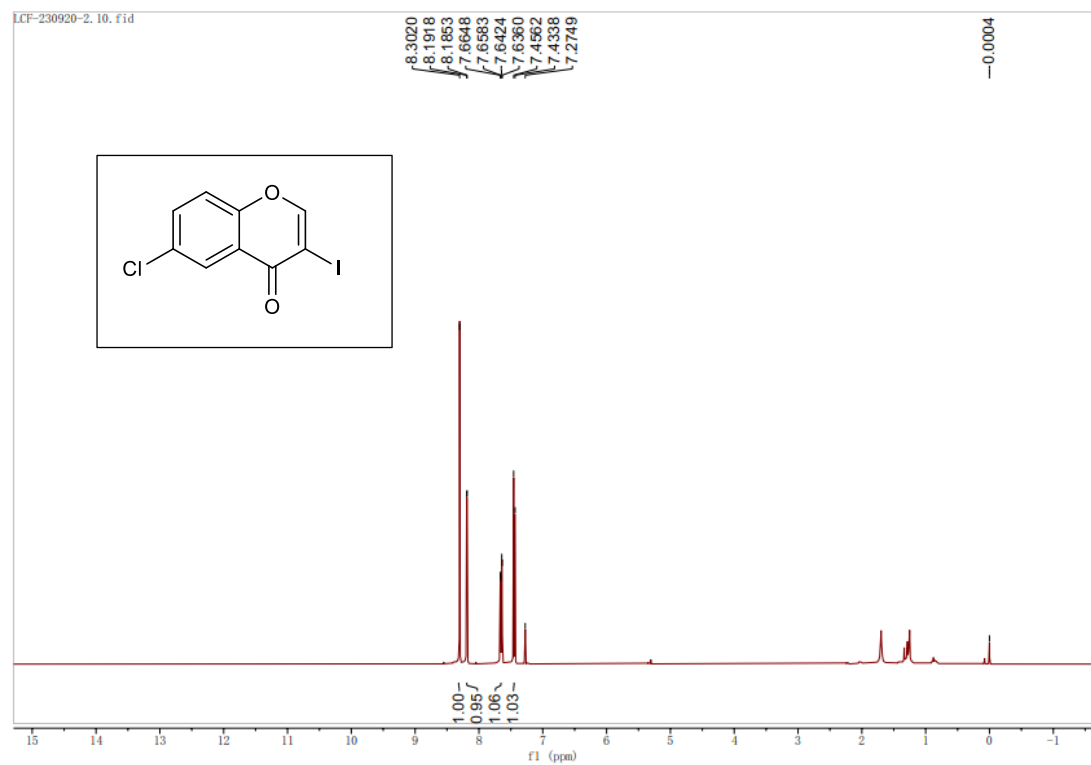
^{19}F NMR Spectra of compound **4ad'** in CDCl_3 (377 MHz)



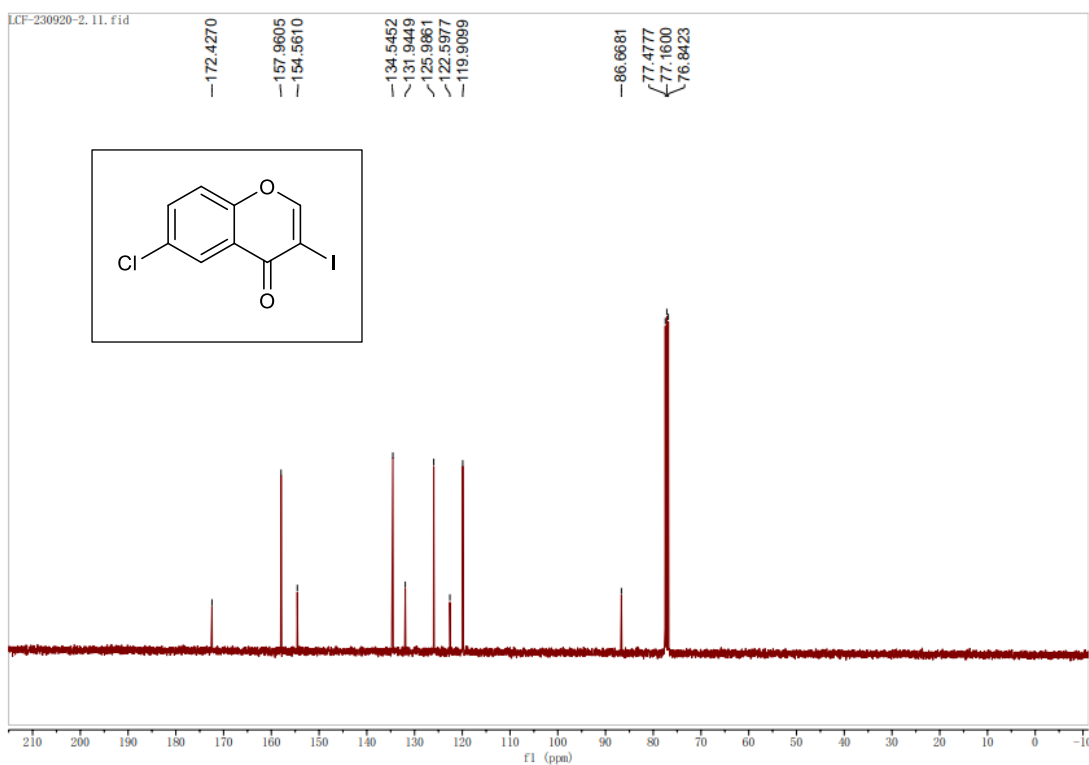
^1H NMR Spectra of compound **4ae** in CDCl_3 (400 MHz)



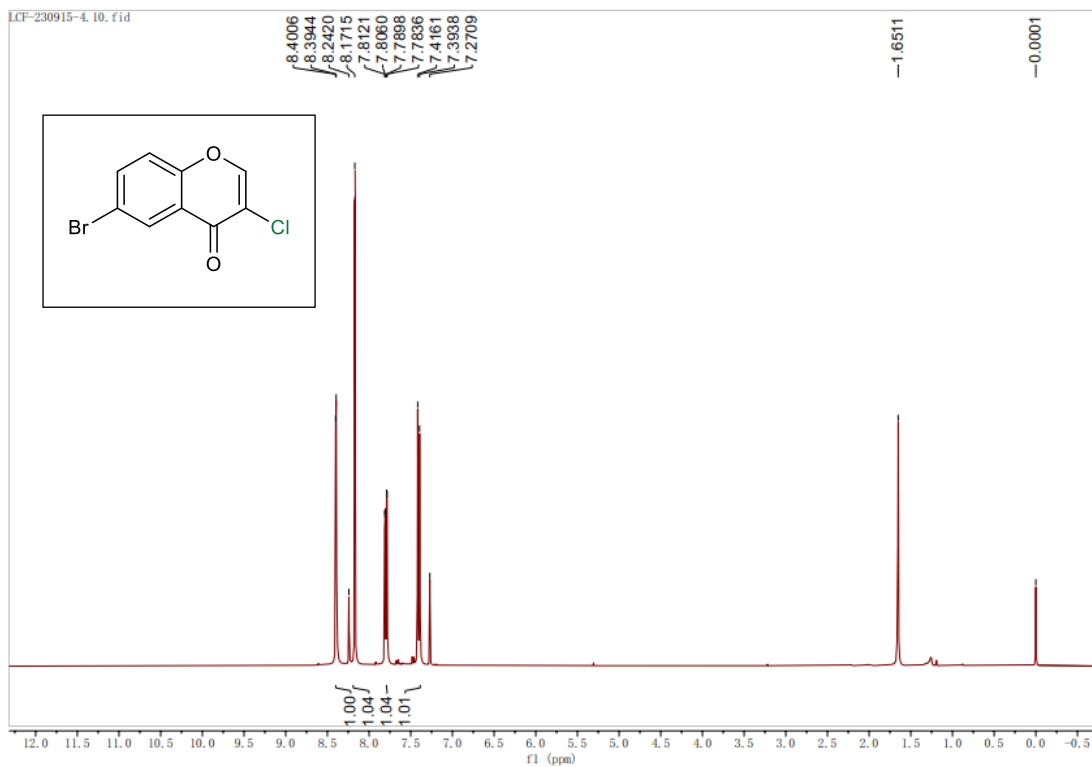
^{13}C NMR Spectra of compound **4ae** in CDCl_3 (101 MHz)



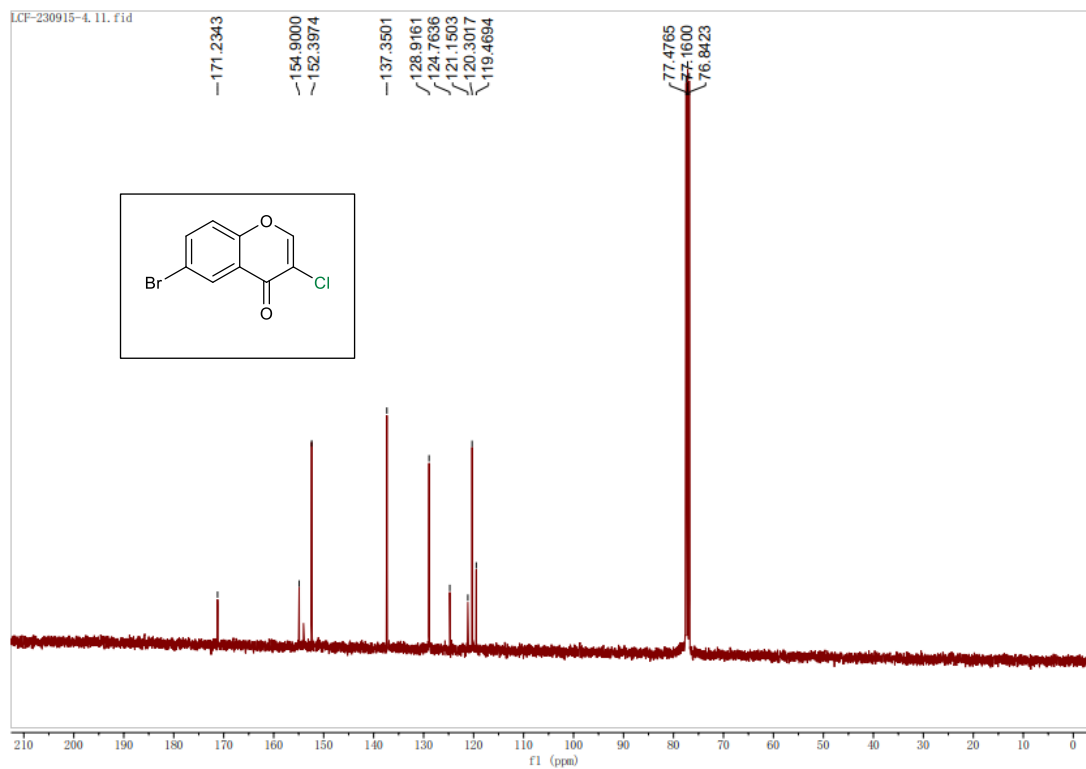
^1H NMR Spectra of compound **4ae'** in CDCl_3 (400 MHz)



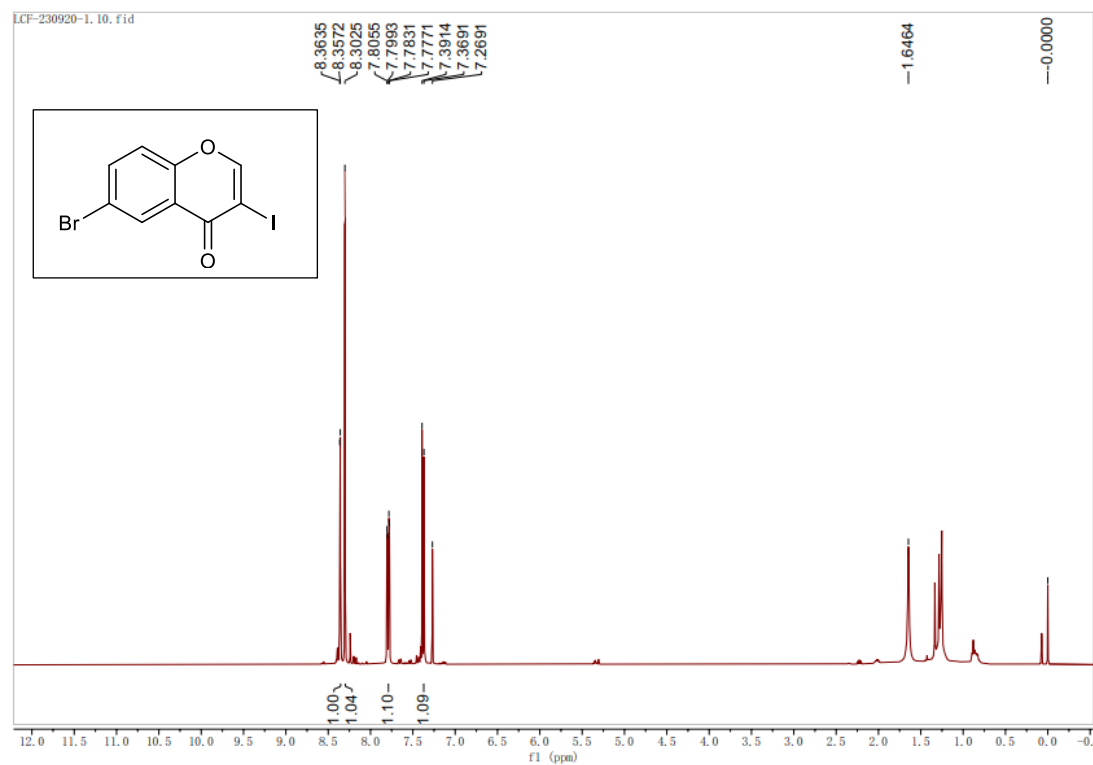
^{13}C NMR Spectra of compound **4ae'** in CDCl_3 (101 MHz)



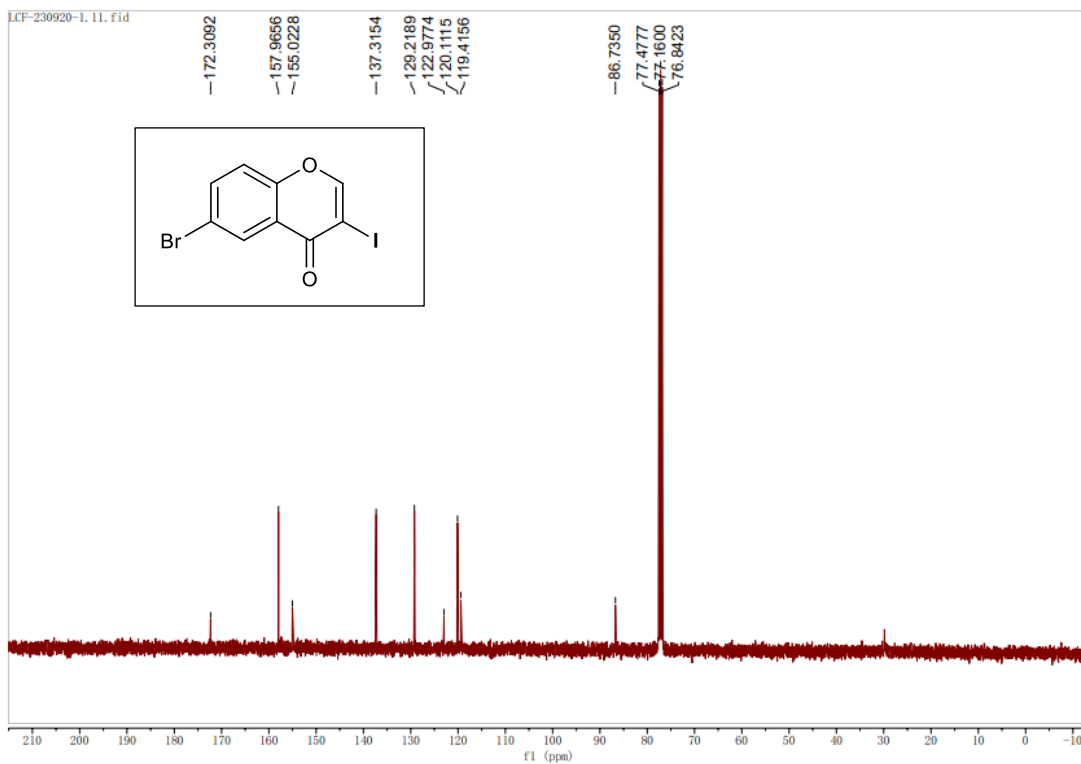
^1H NMR Spectra of compound **4af** in CDCl_3 (400 MHz)



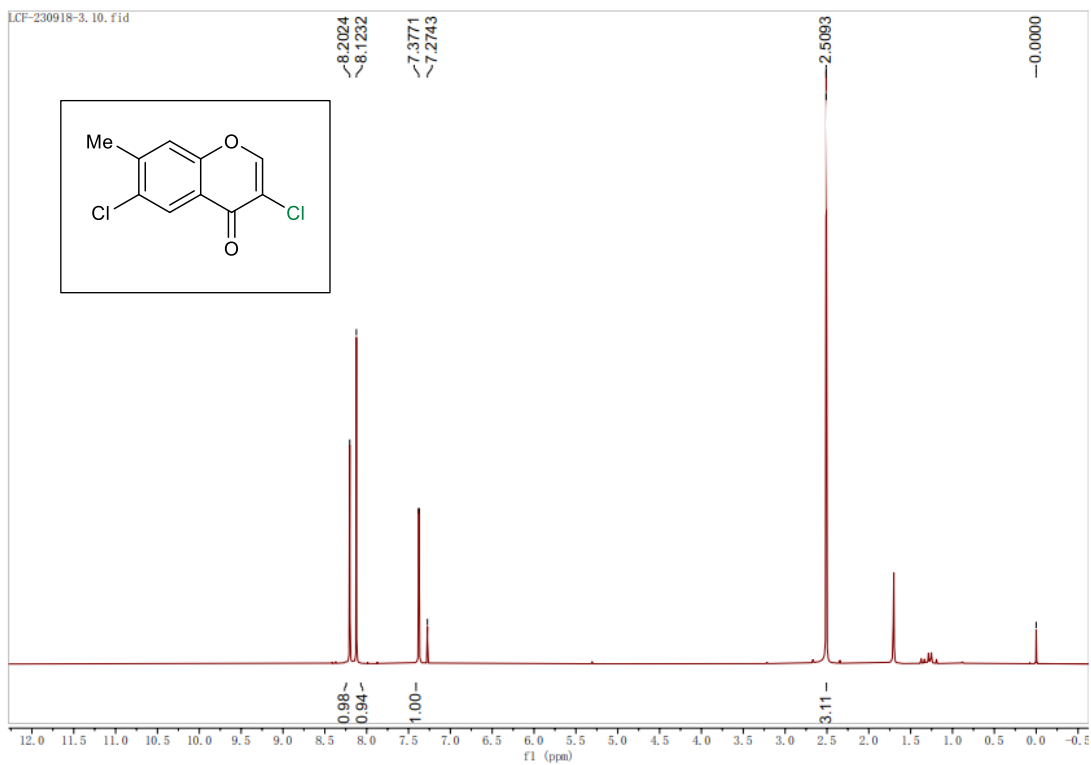
^{13}C NMR Spectra of compound **4af** in CDCl_3 (101 MHz)



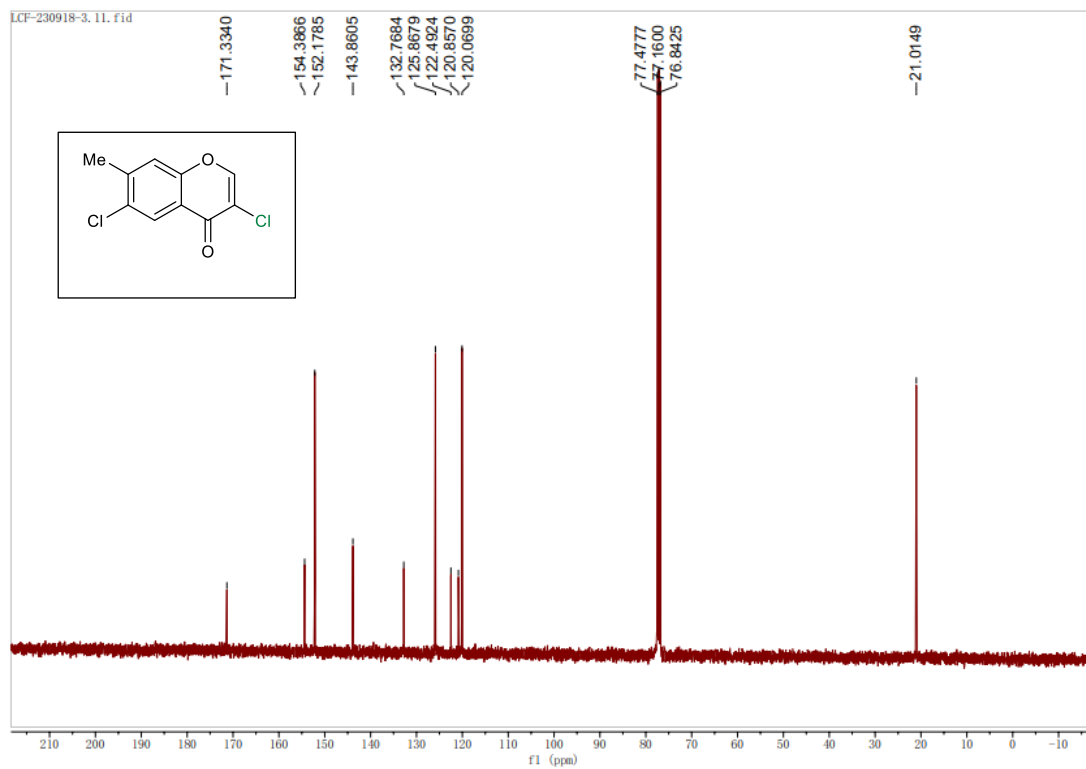
^1H NMR Spectra of compound **4af'** in CDCl_3 (400 MHz)



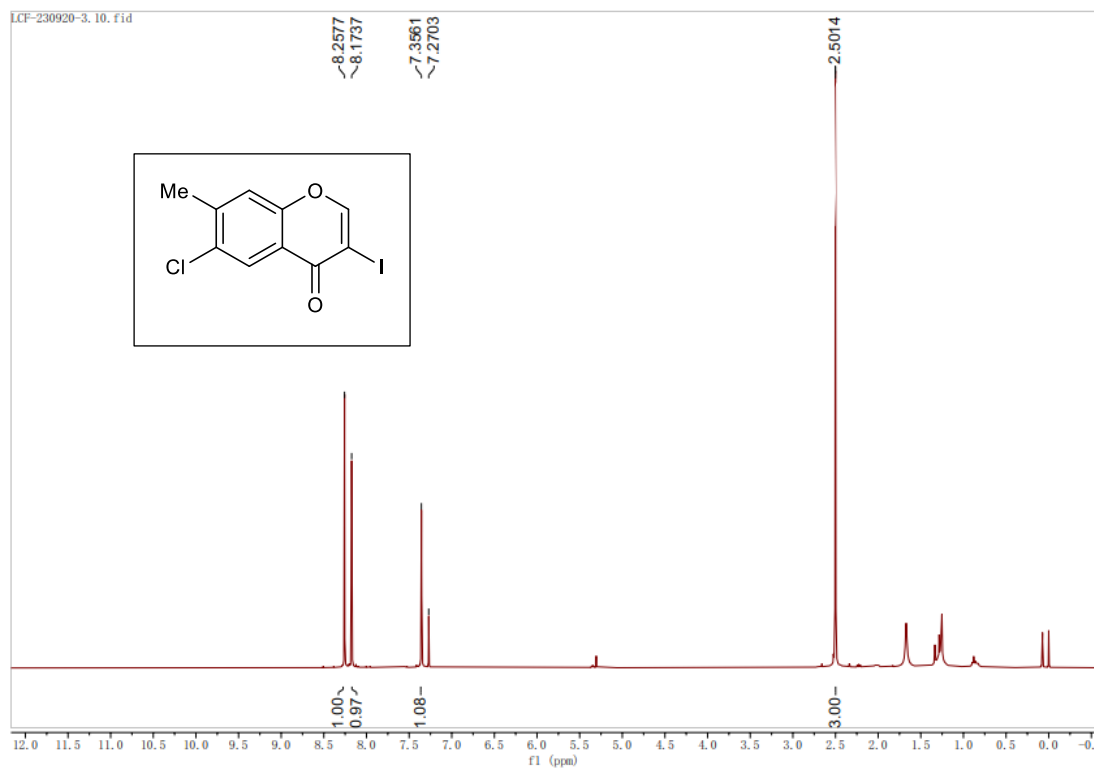
^{13}C NMR Spectra of compound **4af'** in CDCl_3 (101 MHz)



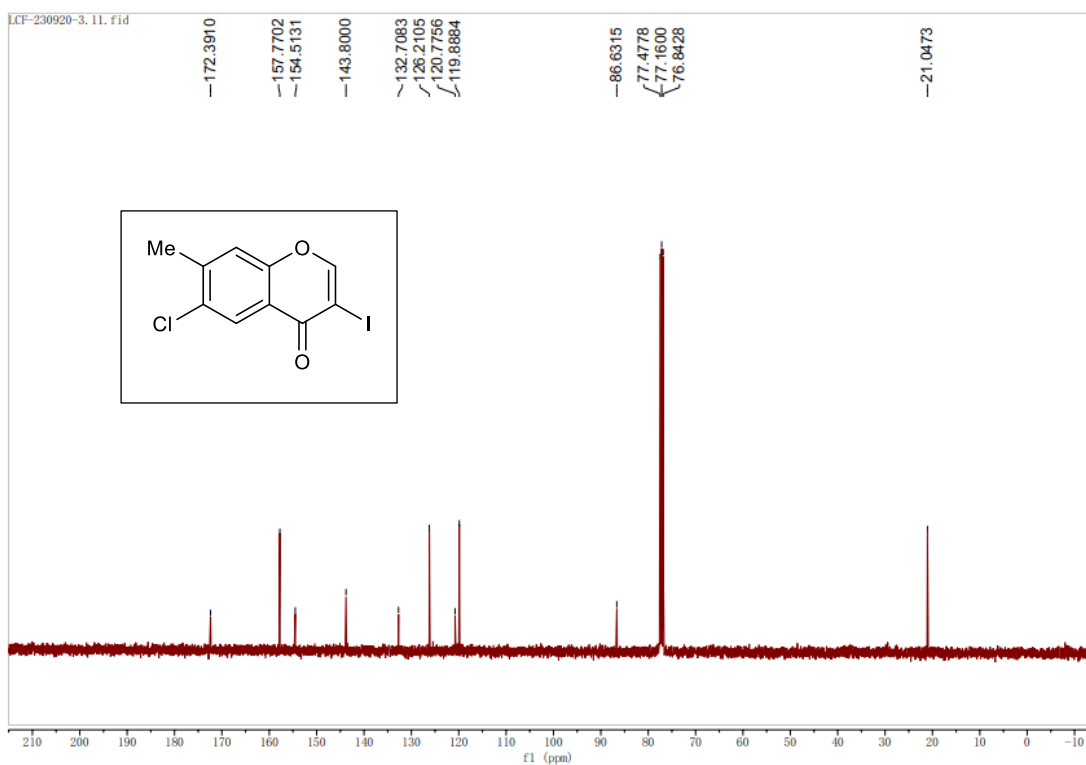
^1H NMR Spectra of compound **4ag** in CDCl_3 (400 MHz)



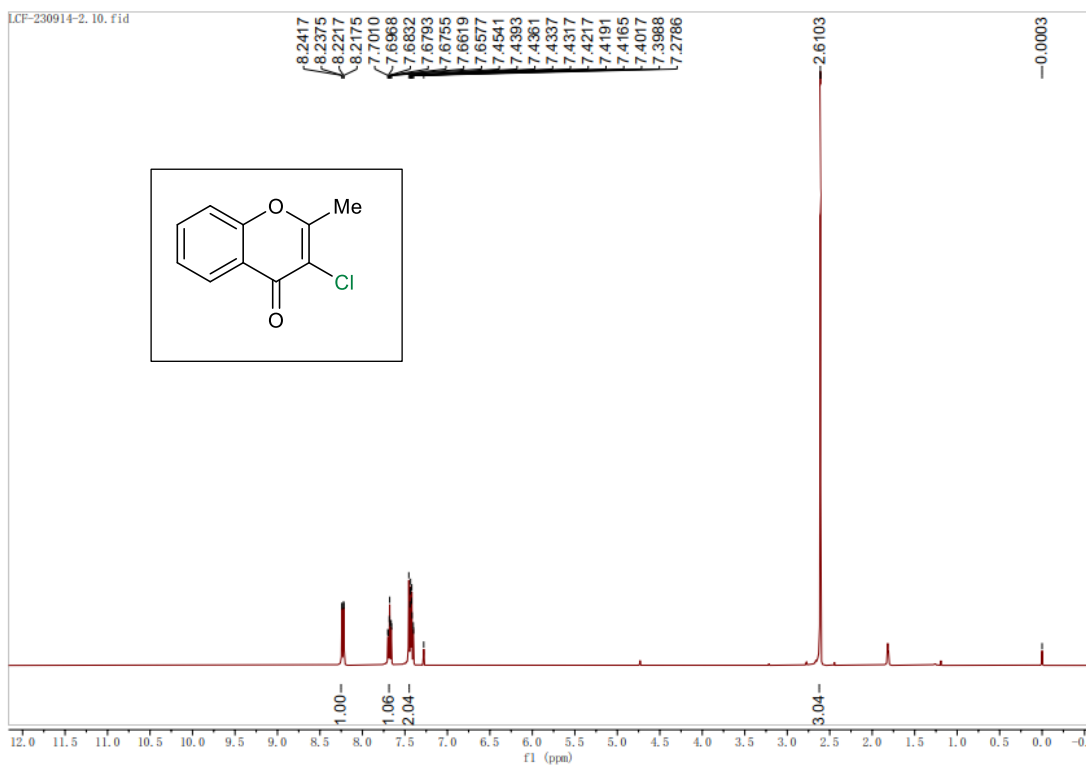
^{13}C NMR Spectra of compound **4ag** in CDCl_3 (101 MHz)



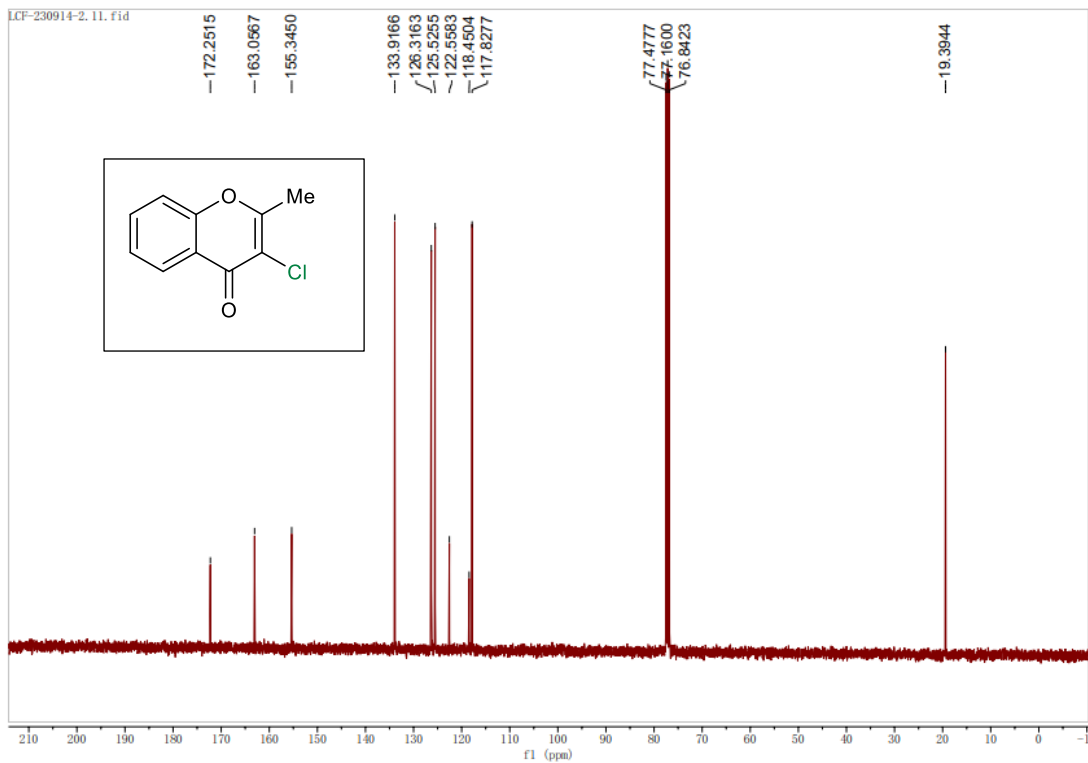
^1H NMR Spectra of compound **4ag'** in CDCl_3 (400 MHz)



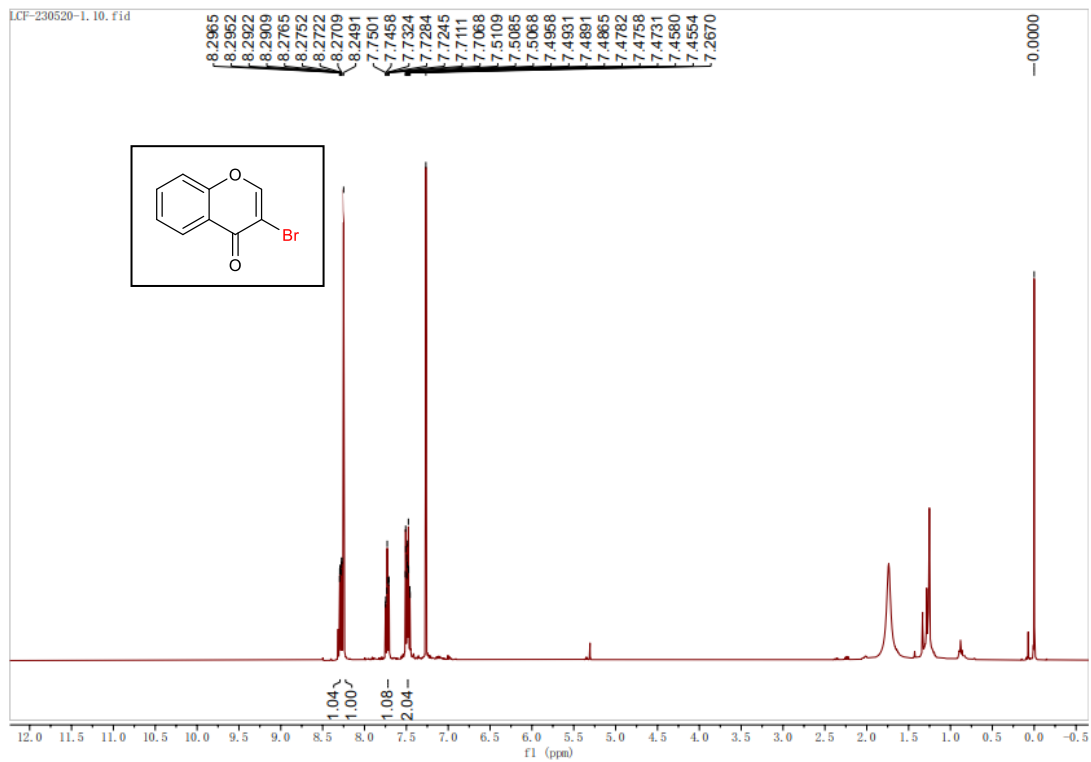
^{13}C NMR Spectra of compound **4ag'** in CDCl_3 (101 MHz)



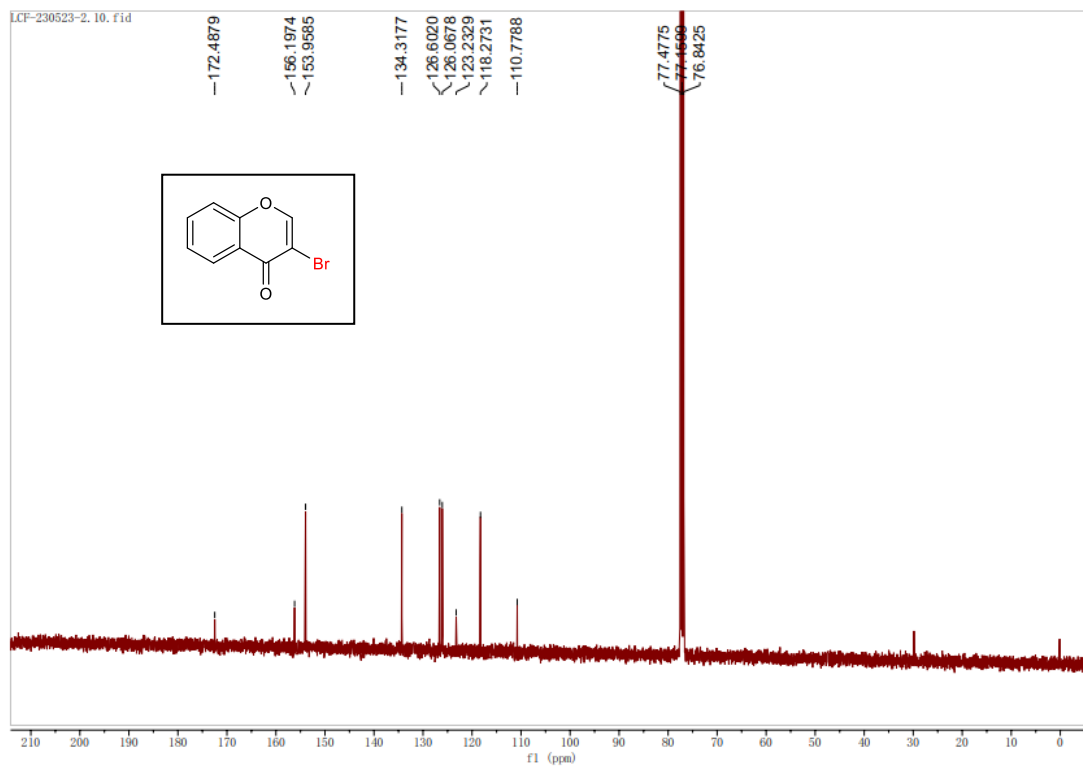
^1H NMR Spectra of compound **4ah** in CDCl_3 (400 MHz)



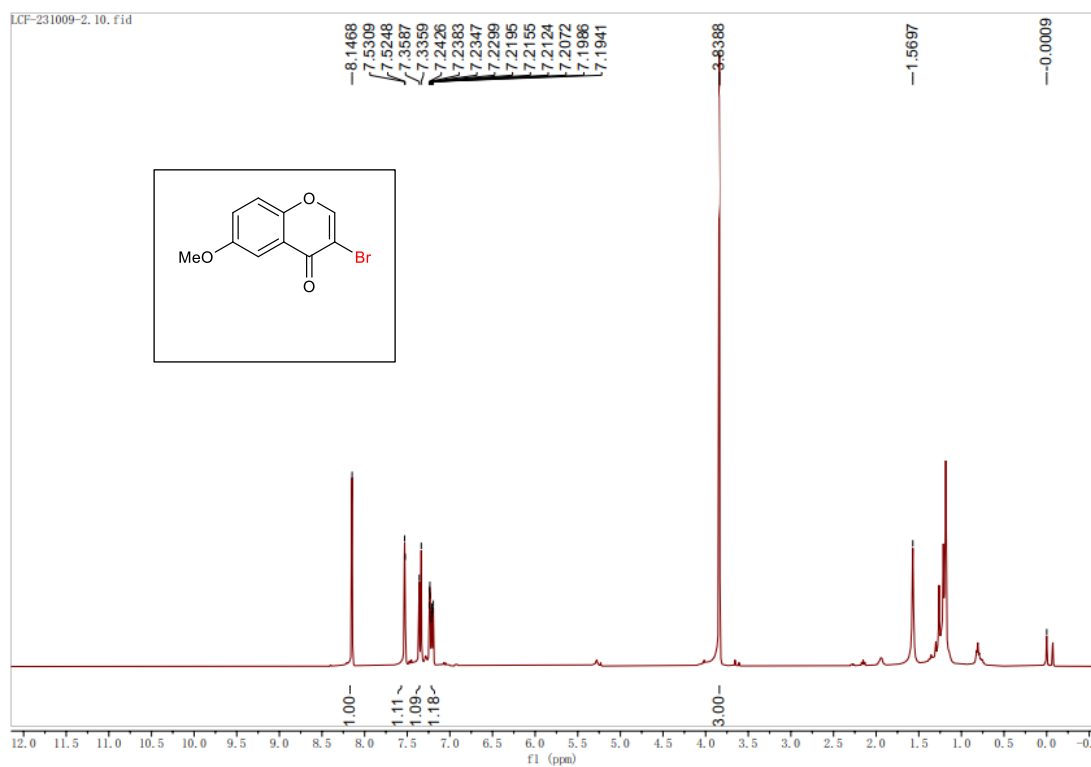
^{13}C NMR Spectra of compound **4ah** in CDCl_3 (101 MHz)



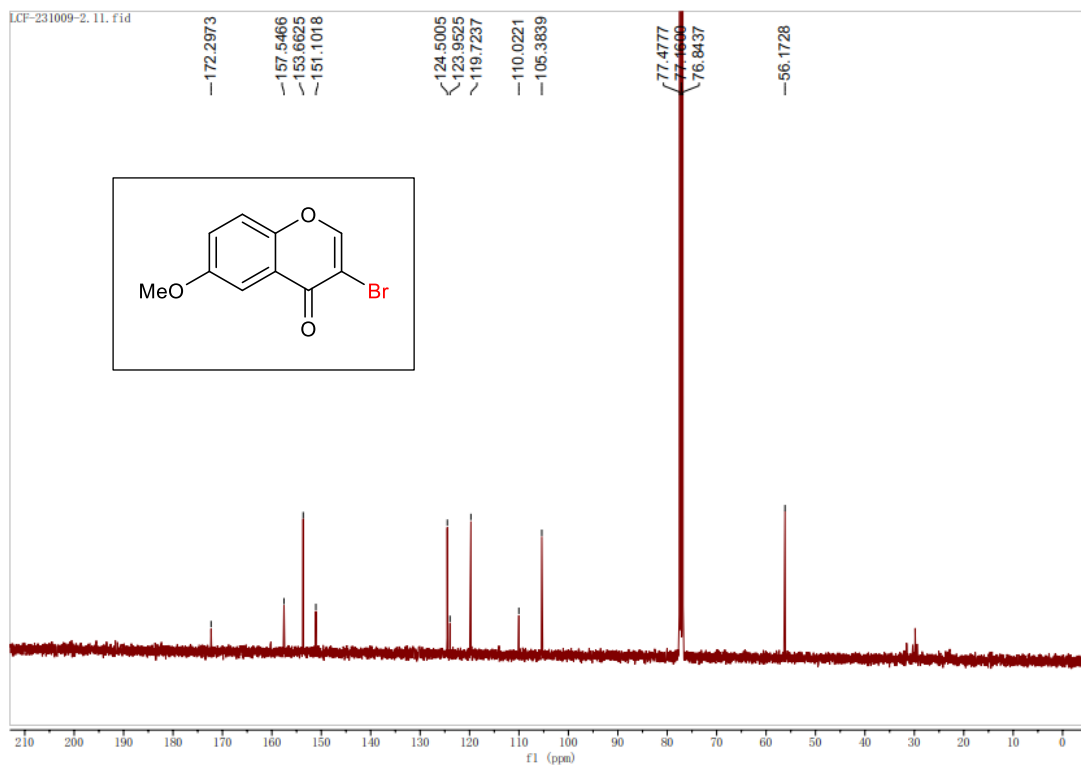
^1H NMR Spectra of compound **4ba** in CDCl_3 (400 MHz)



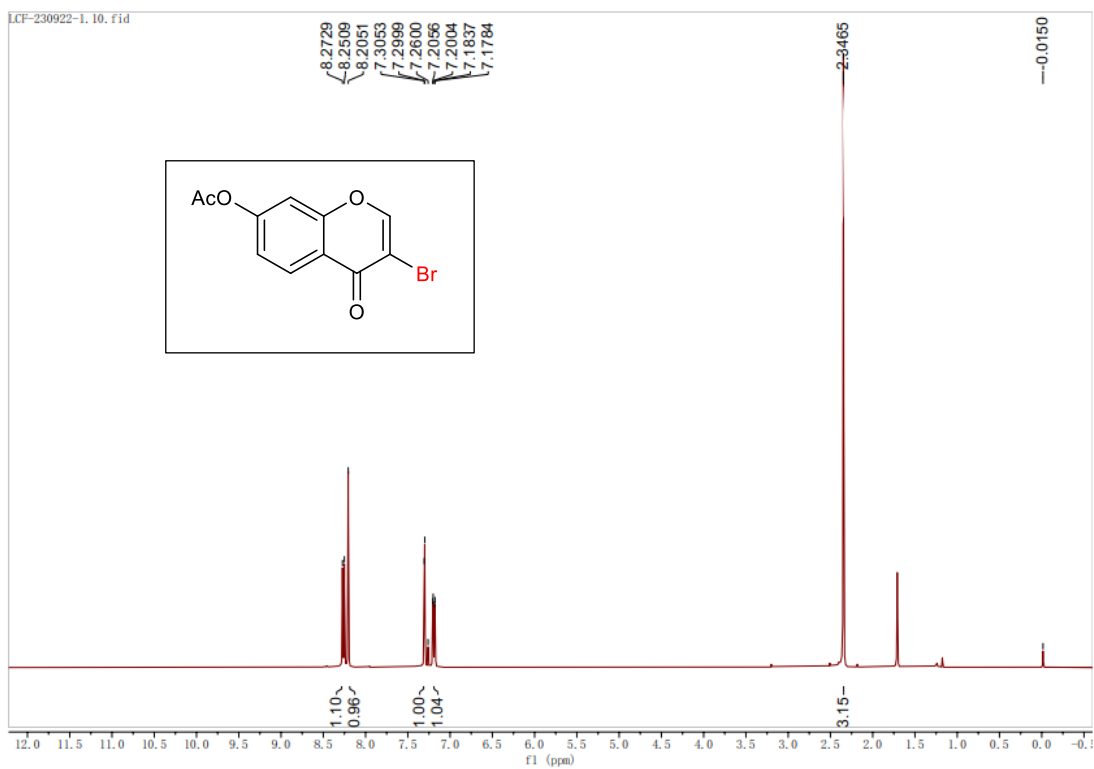
^{13}C NMR Spectra of compound **4ba** in CDCl_3 (101 MHz)



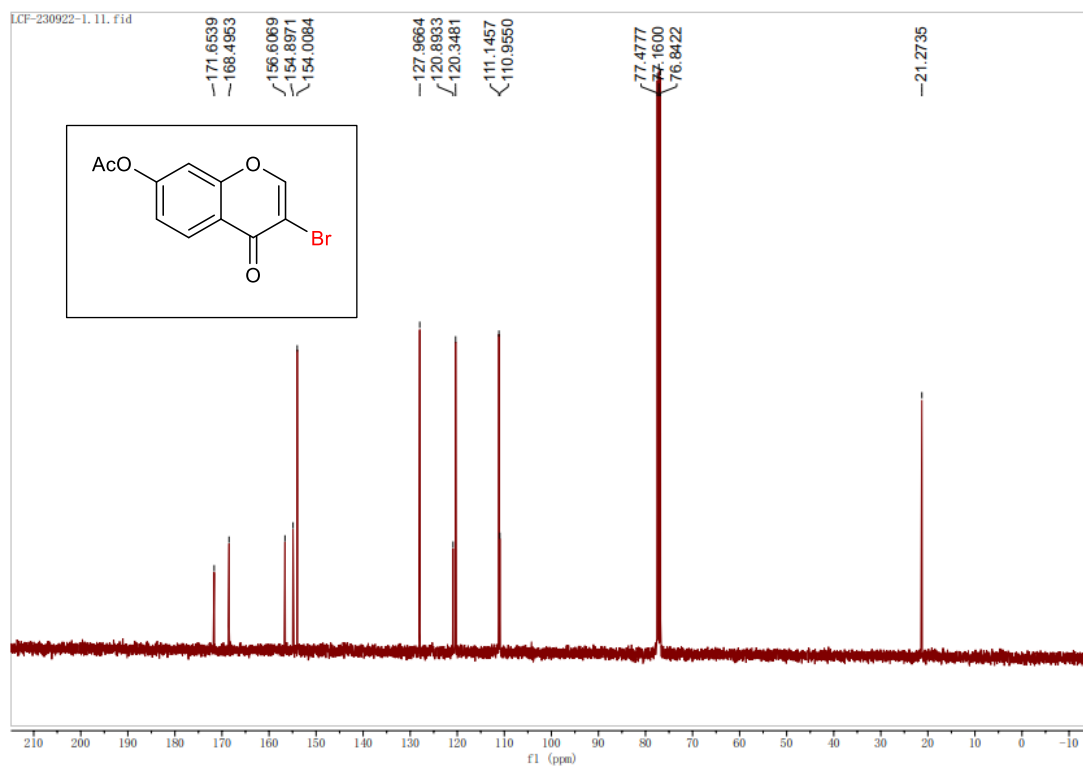
^1H NMR Spectra of compound **4bb** in CDCl_3 (400 MHz)



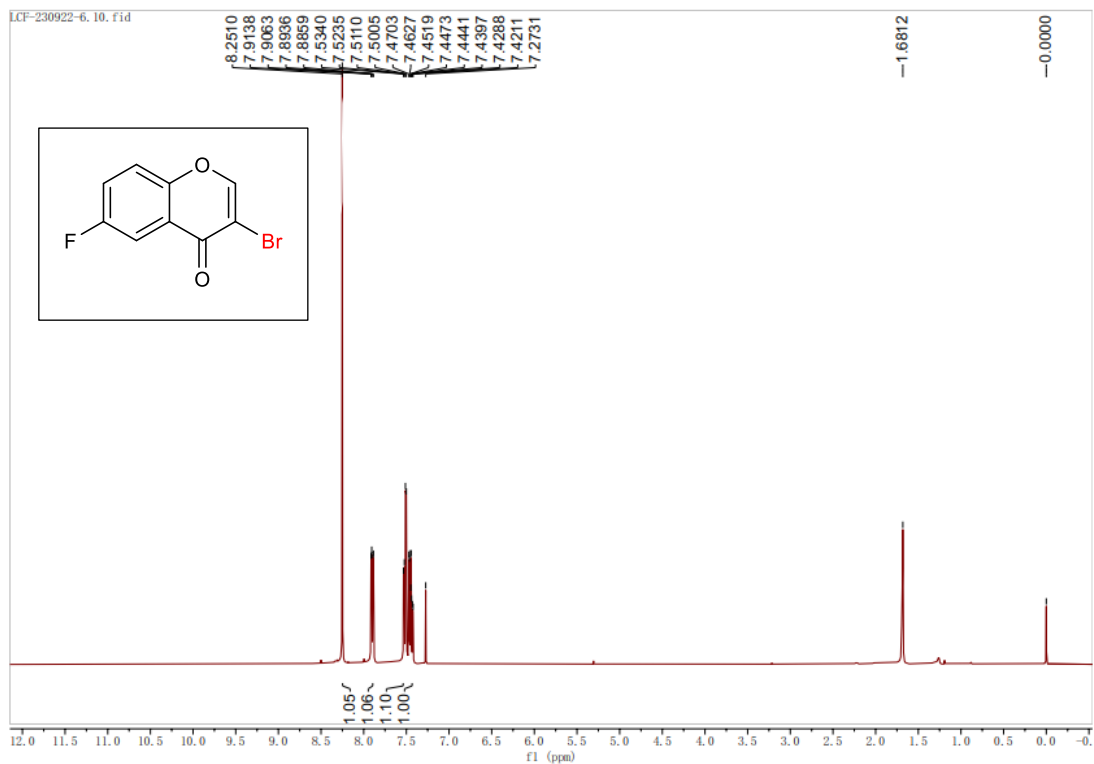
^{13}C NMR Spectra of compound **4bb** in CDCl_3 (101 MHz)



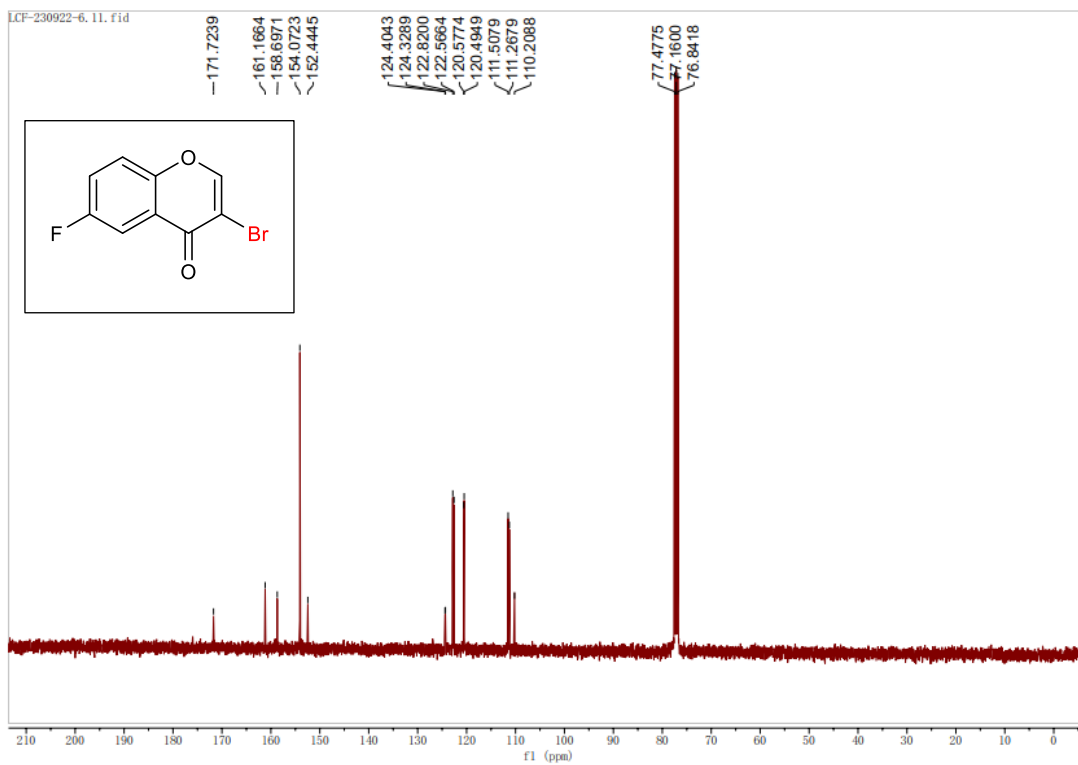
^1H NMR Spectra of compound **4bc** in CDCl_3 (400 MHz)



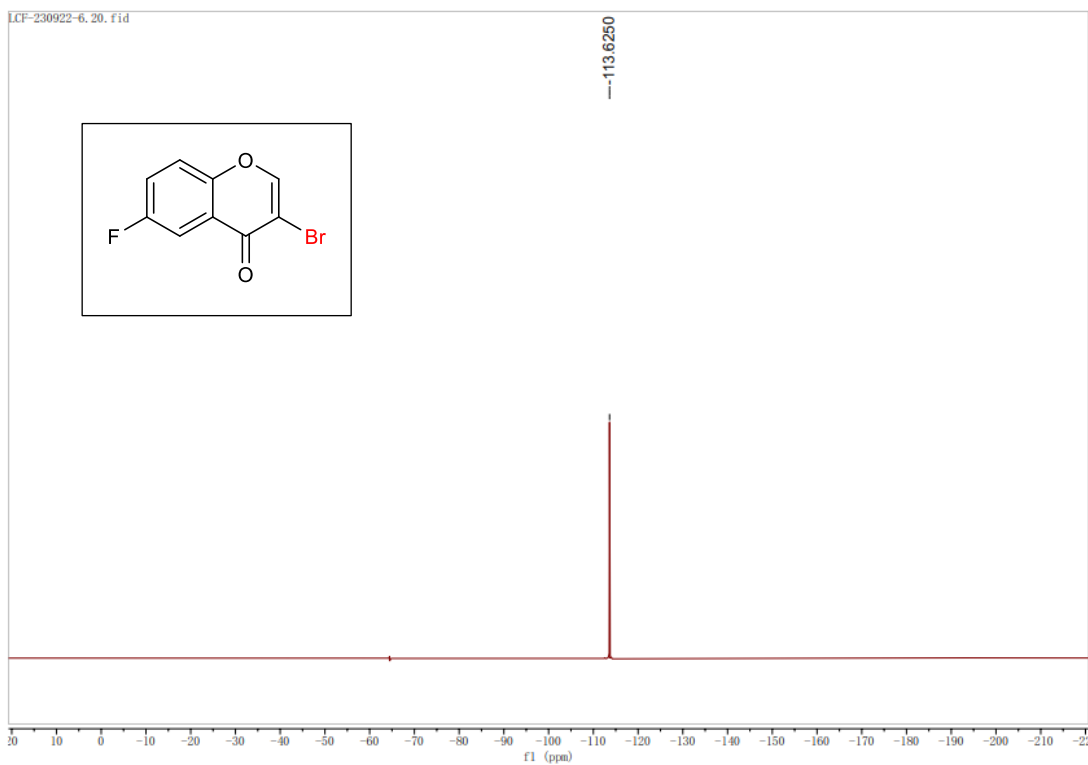
^{13}C NMR Spectra of compound **4bc** in CDCl_3 (101 MHz)



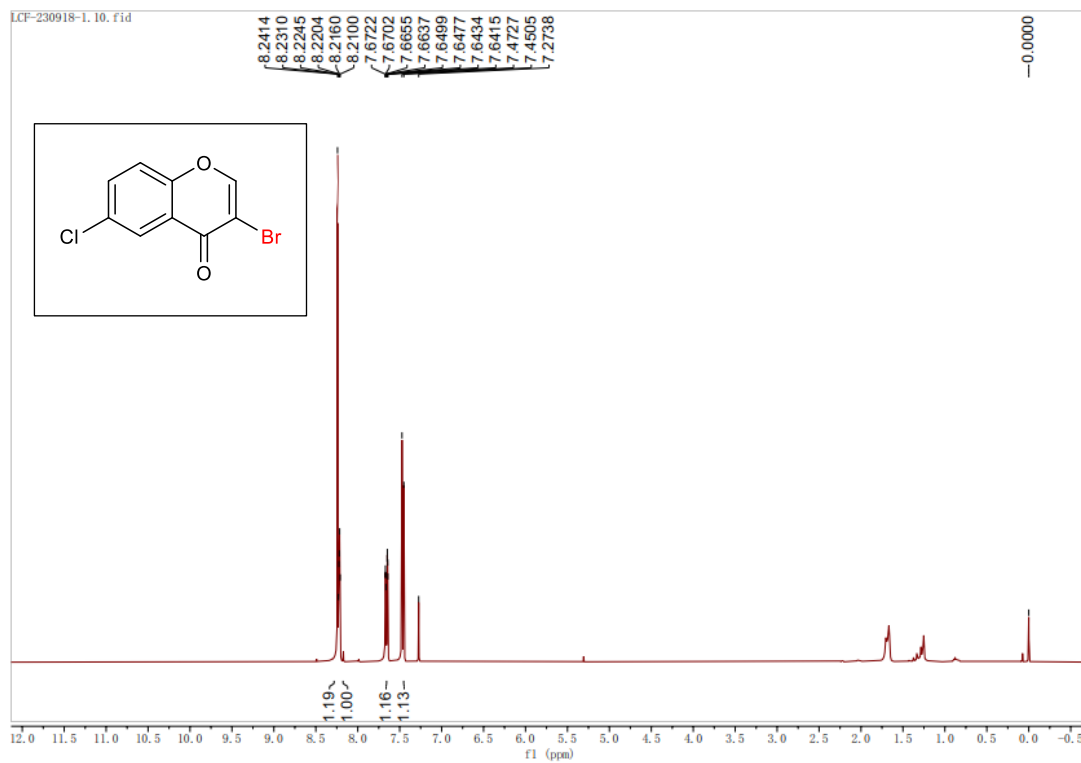
^1H NMR Spectra of compound **4bd** in CDCl_3 (400 MHz)



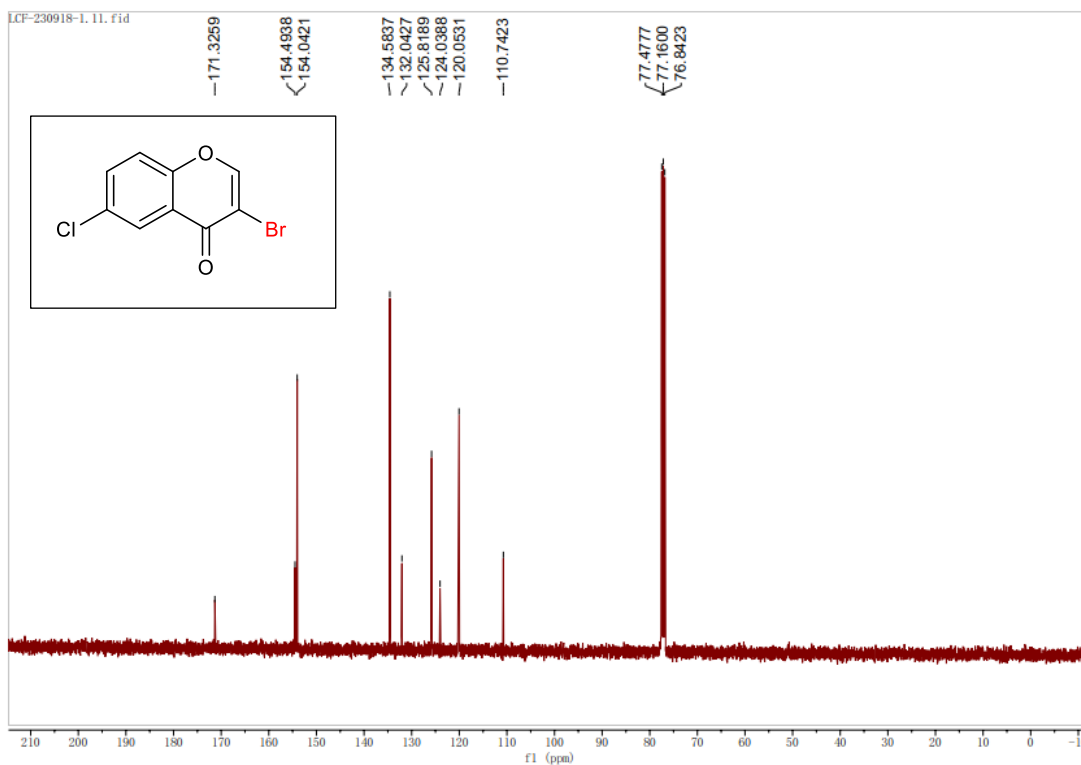
^{13}C NMR Spectra of compound **4bd** in CDCl_3 (101 MHz)



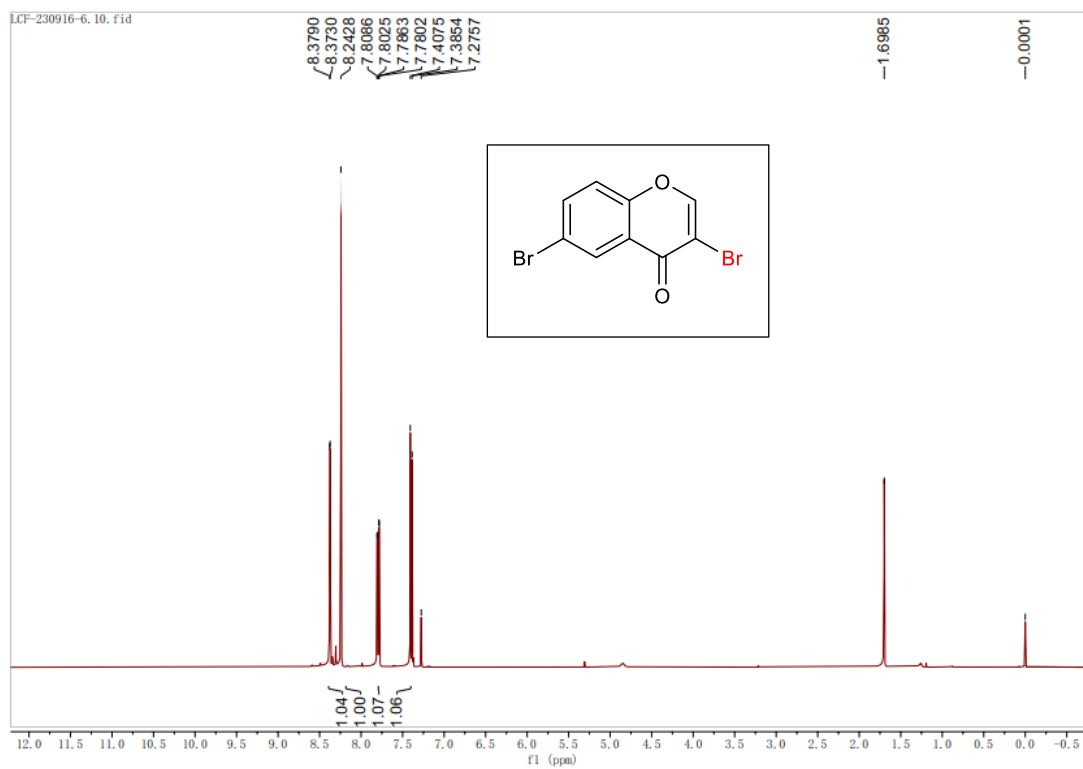
^{19}F NMR Spectra of compound **4bd** in CDCl_3 (377 MHz)



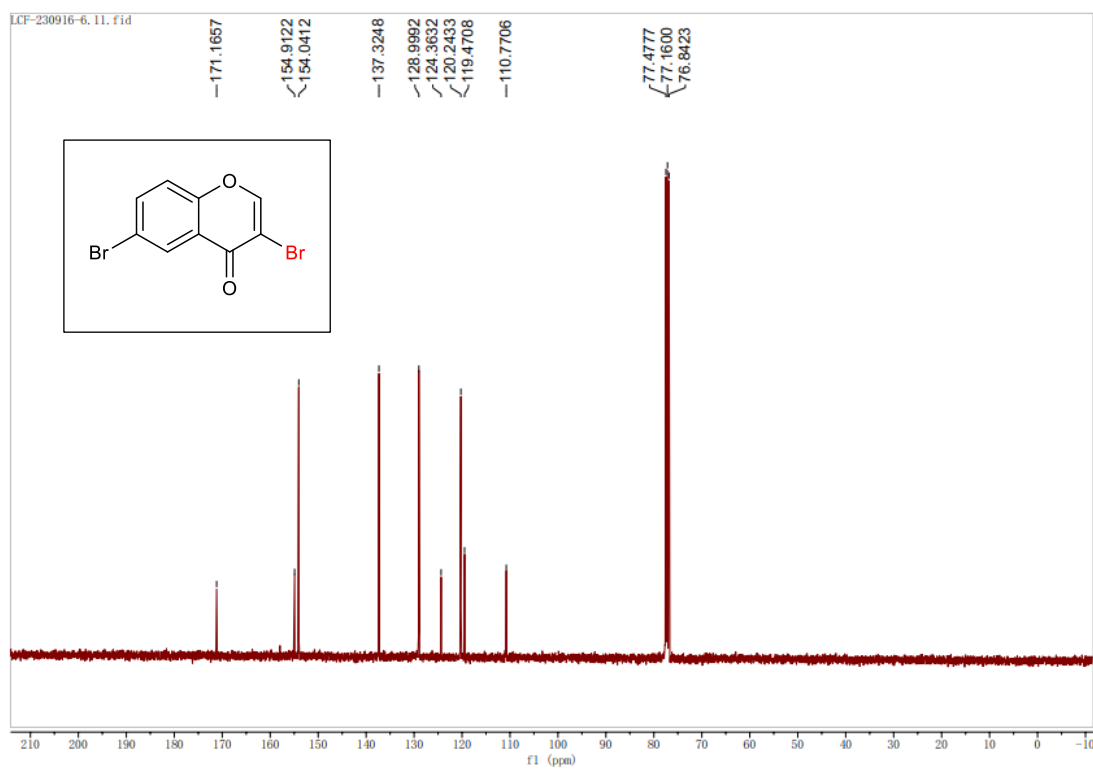
^1H NMR Spectra of compound **4be** in CDCl_3 (400 MHz)



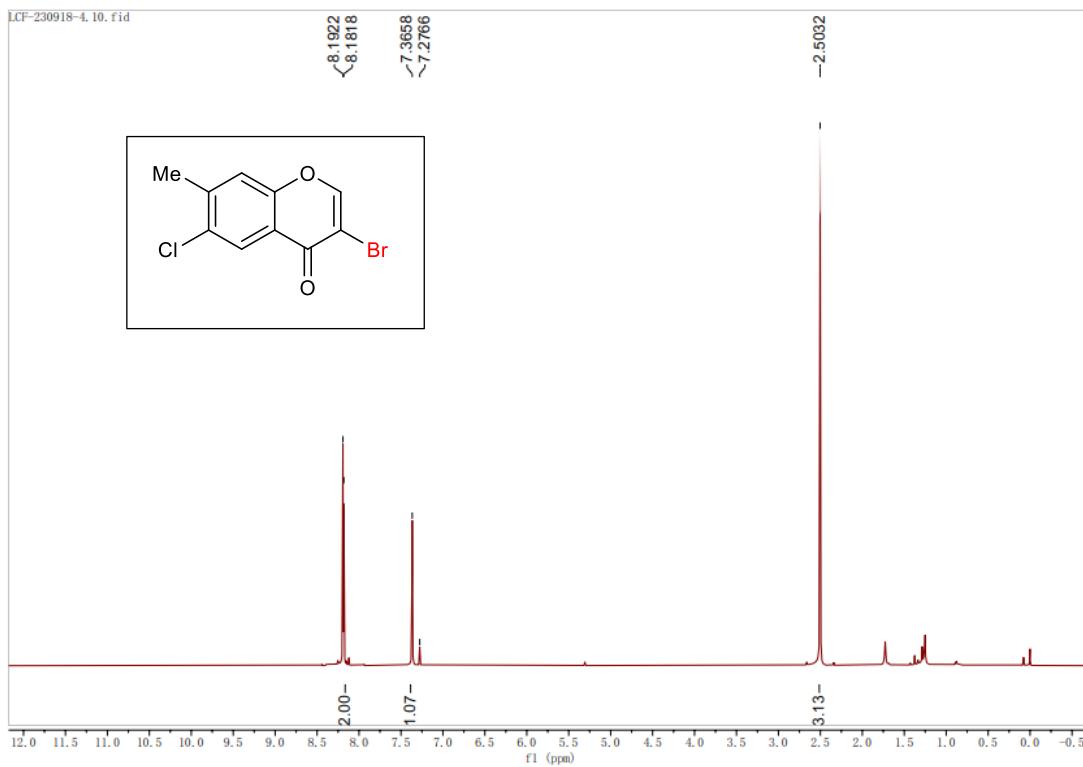
^{13}C NMR Spectra of compound **4be** in CDCl_3 (101 MHz)



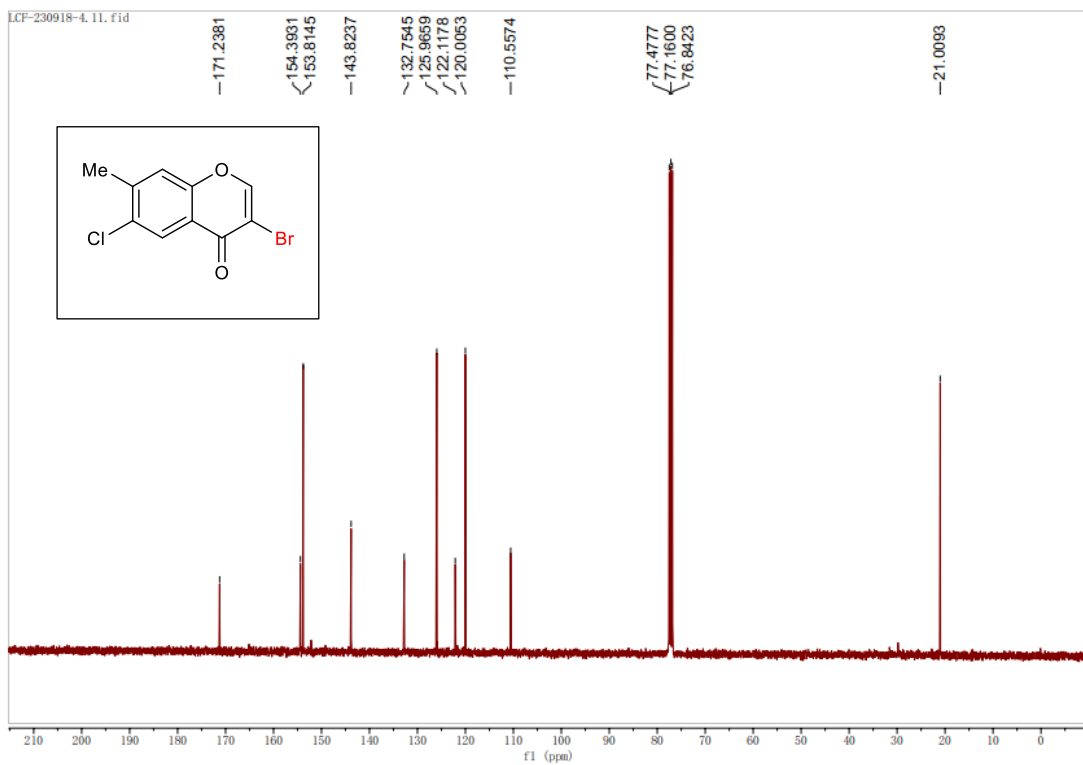
^1H NMR Spectra of compound **4bf** in CDCl_3 (400 MHz)



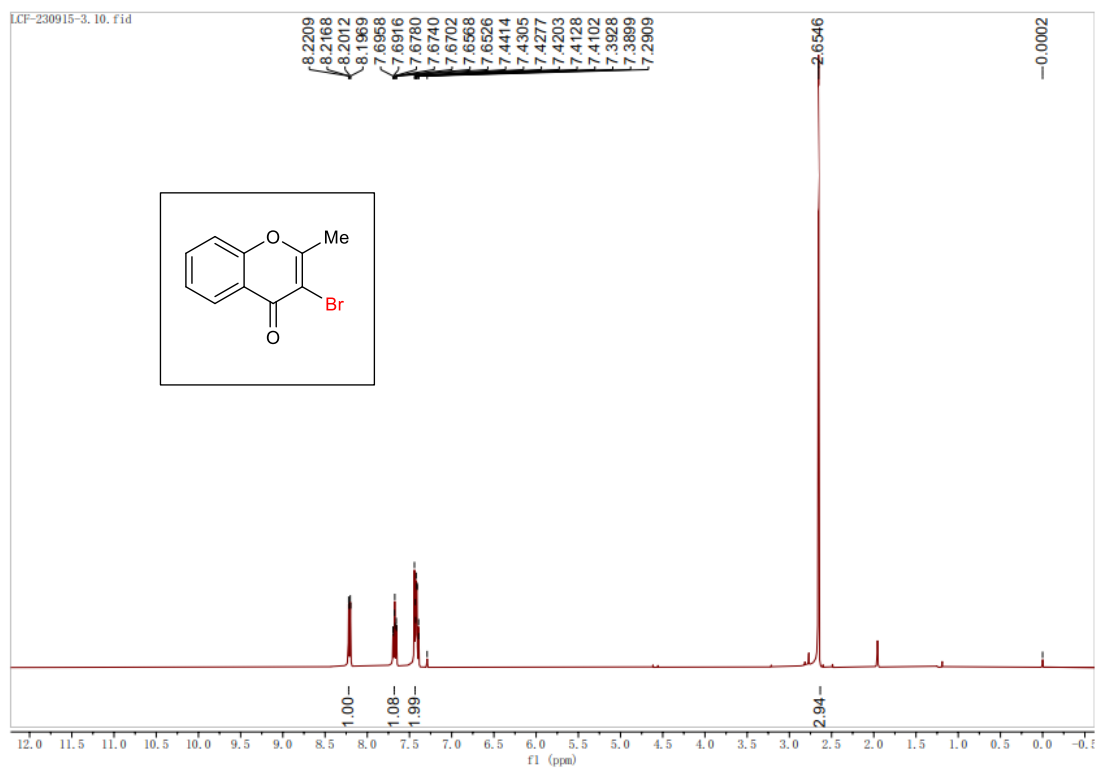
^{13}C NMR Spectra of compound **4bf** in CDCl_3 (101 MHz)



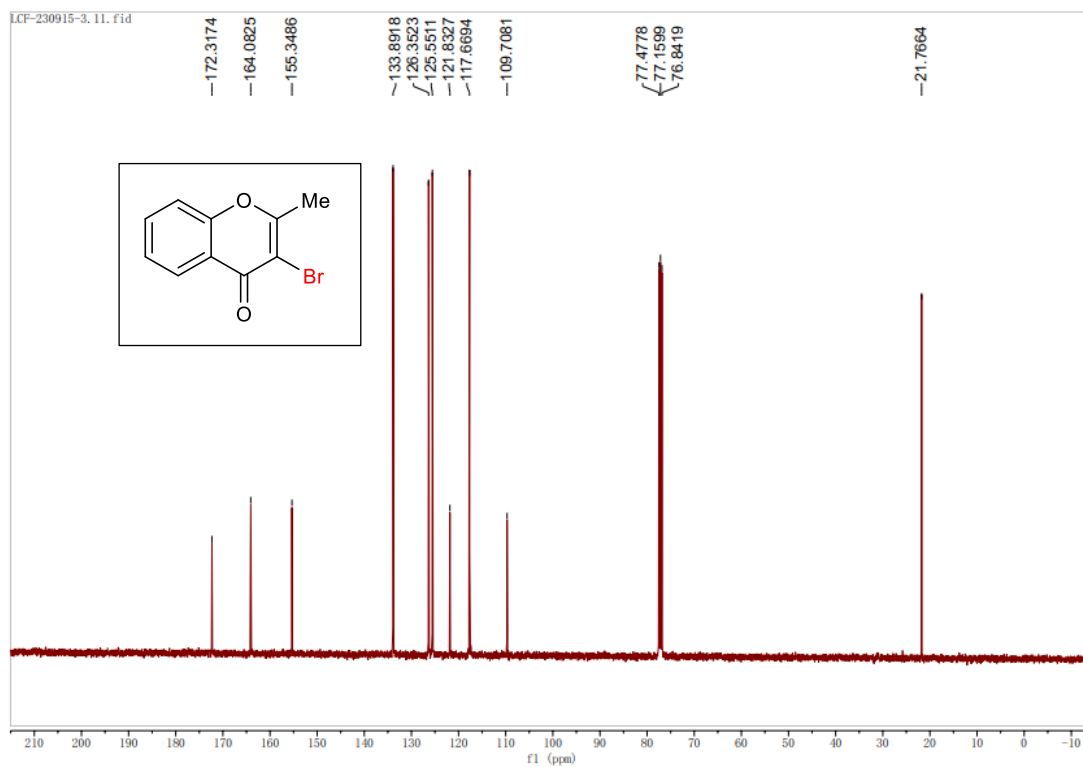
¹H NMR Spectra of compound **4bg** in CDCl₃ (400 MHz)



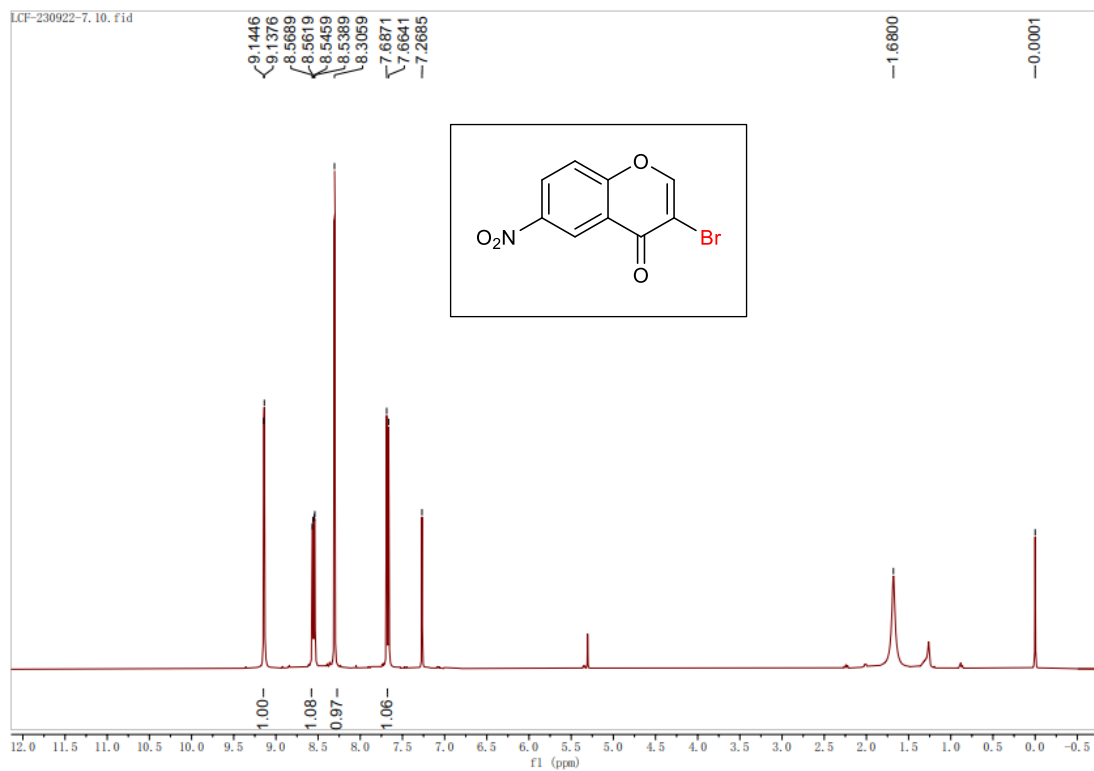
¹³C NMR Spectra of compound **4bg** in CDCl₃ (101 MHz)



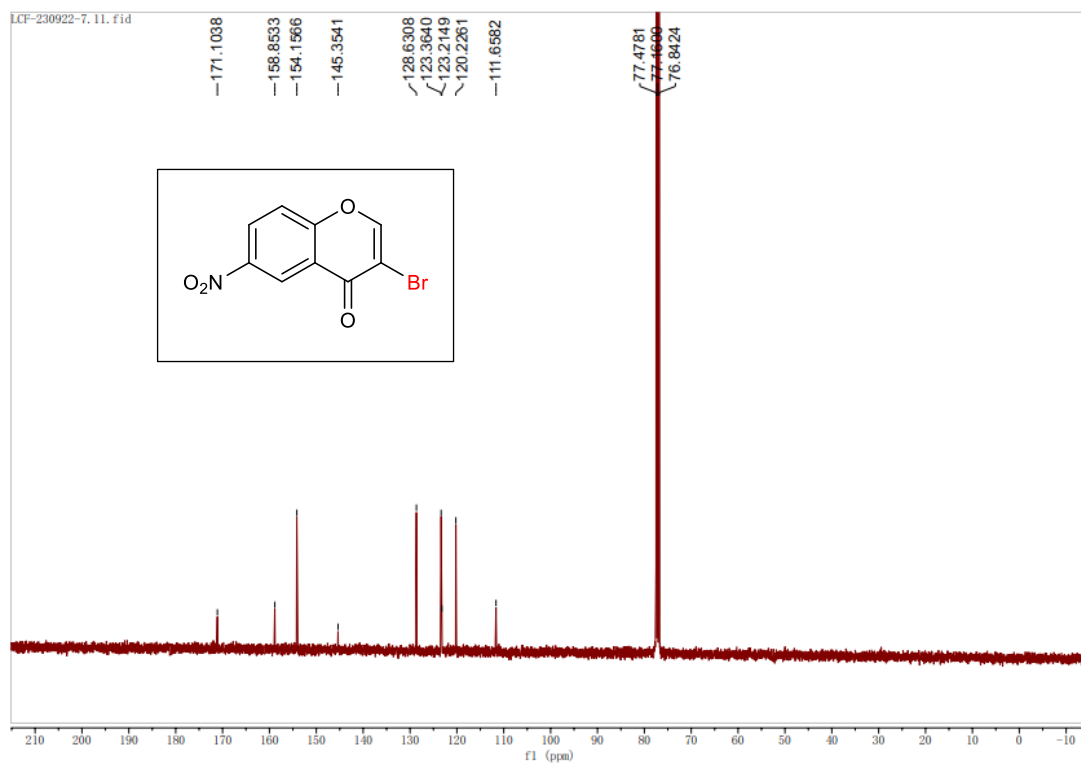
¹H NMR Spectra of compound **4bh** in CDCl₃ (400 MHz)



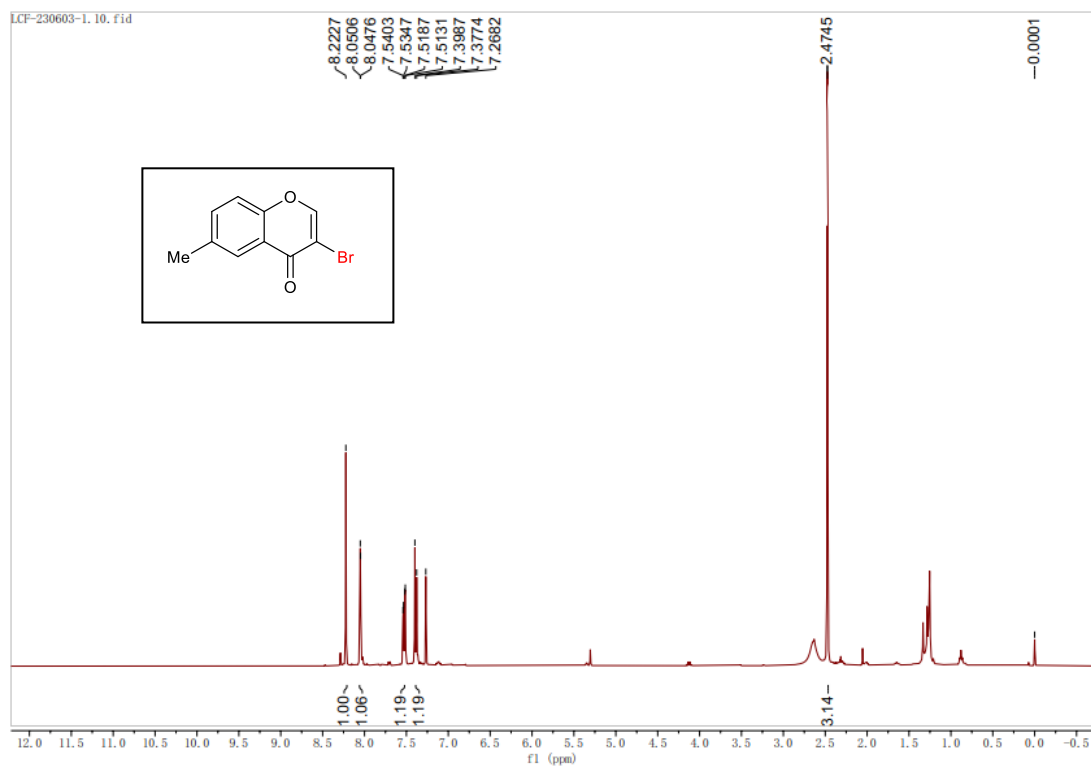
¹³C NMR Spectra of compound **4bh** in CDCl₃ (101 MHz)



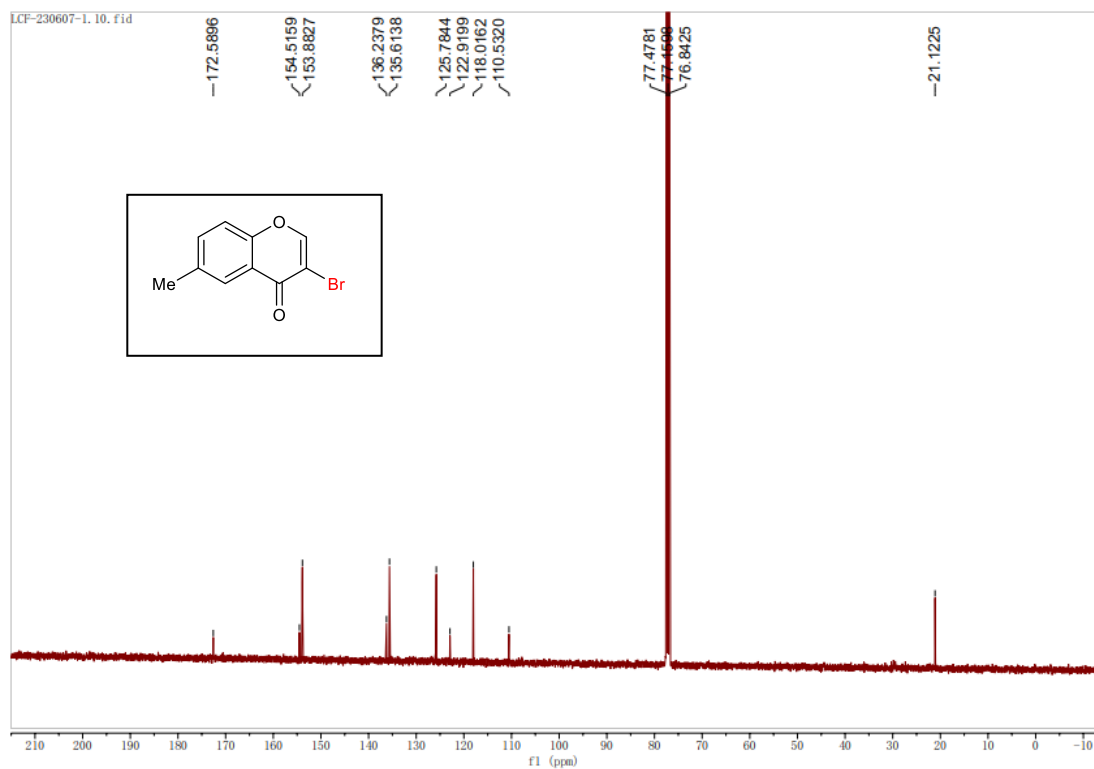
^1H NMR Spectra of compound **4bi** in CDCl_3 (400 MHz)



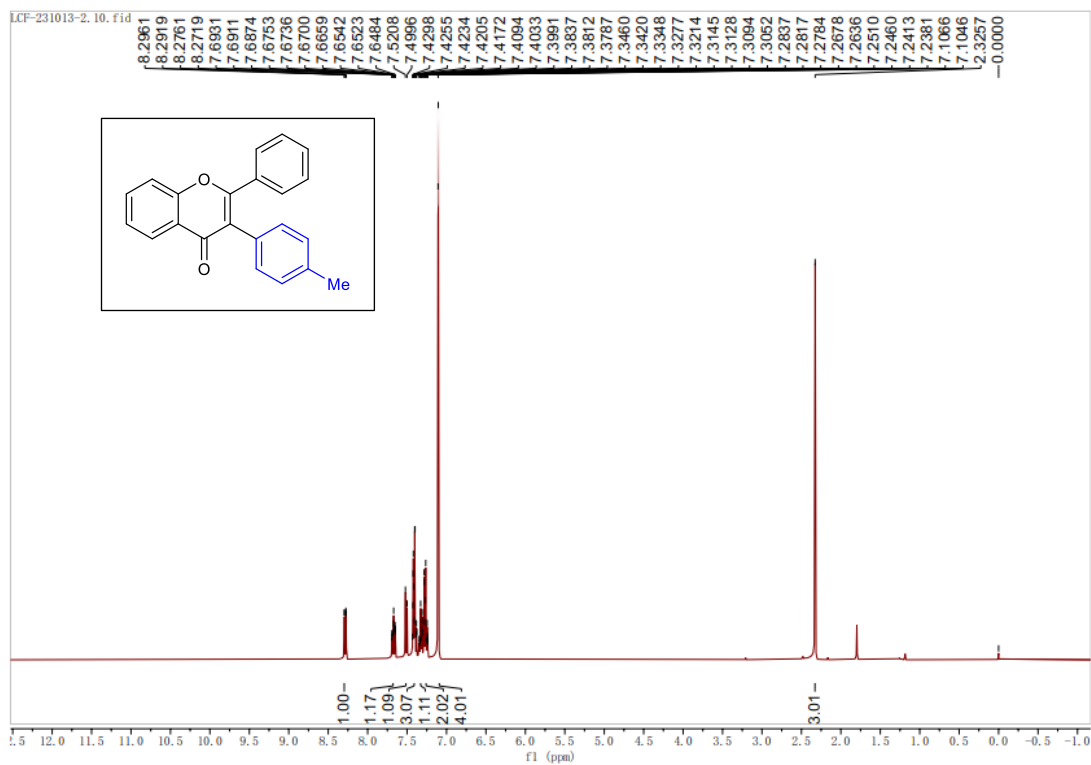
^{13}C NMR Spectra of compound **4bi** in CDCl_3 (101 MHz)



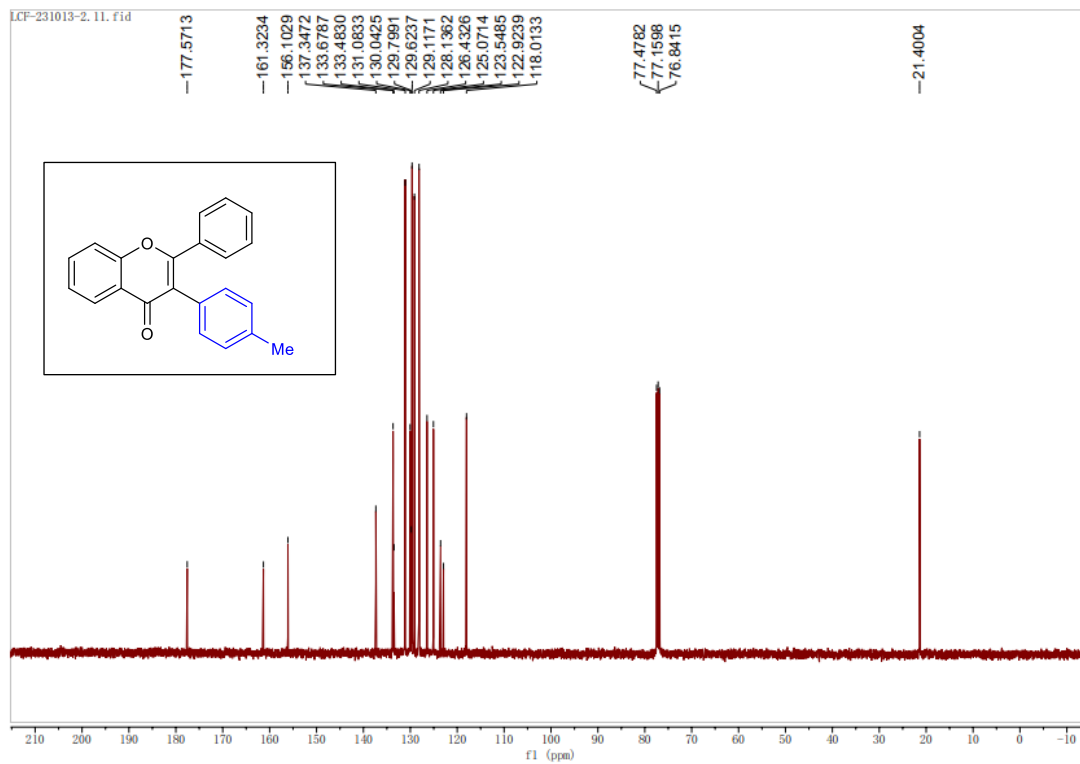
¹H NMR Spectra of compound **4bj** in CDCl₃ (400 MHz)



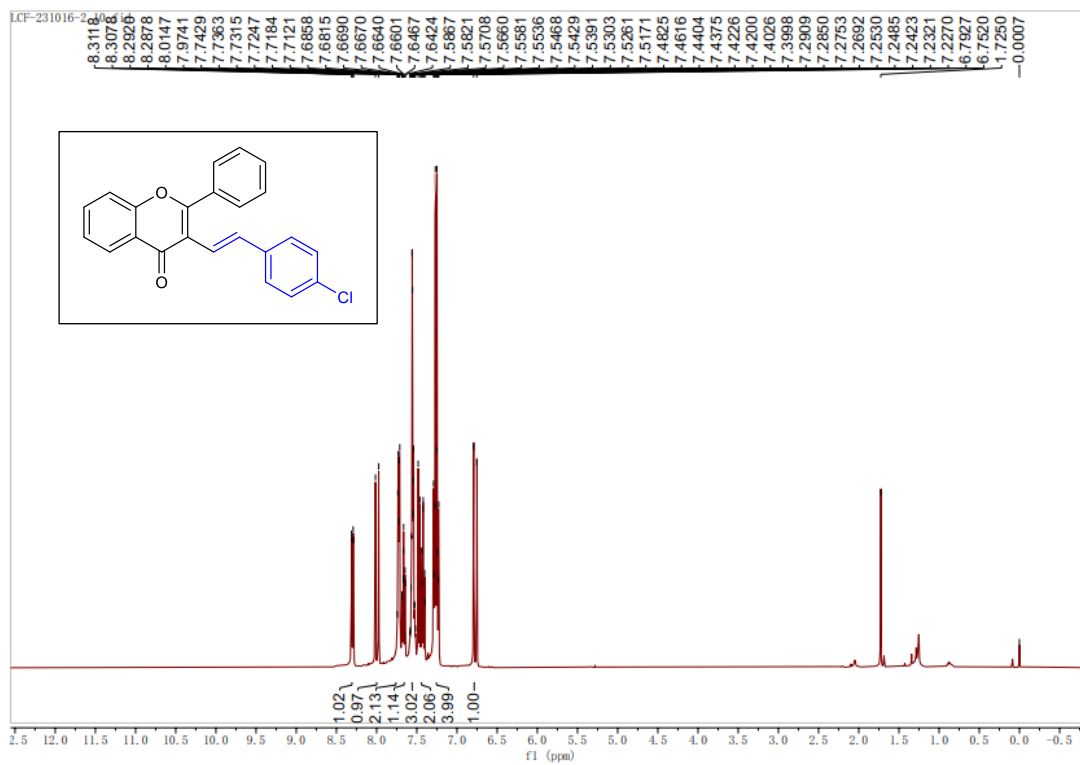
¹³C NMR Spectra of compound **4bj** in CDCl₃ (101 MHz)



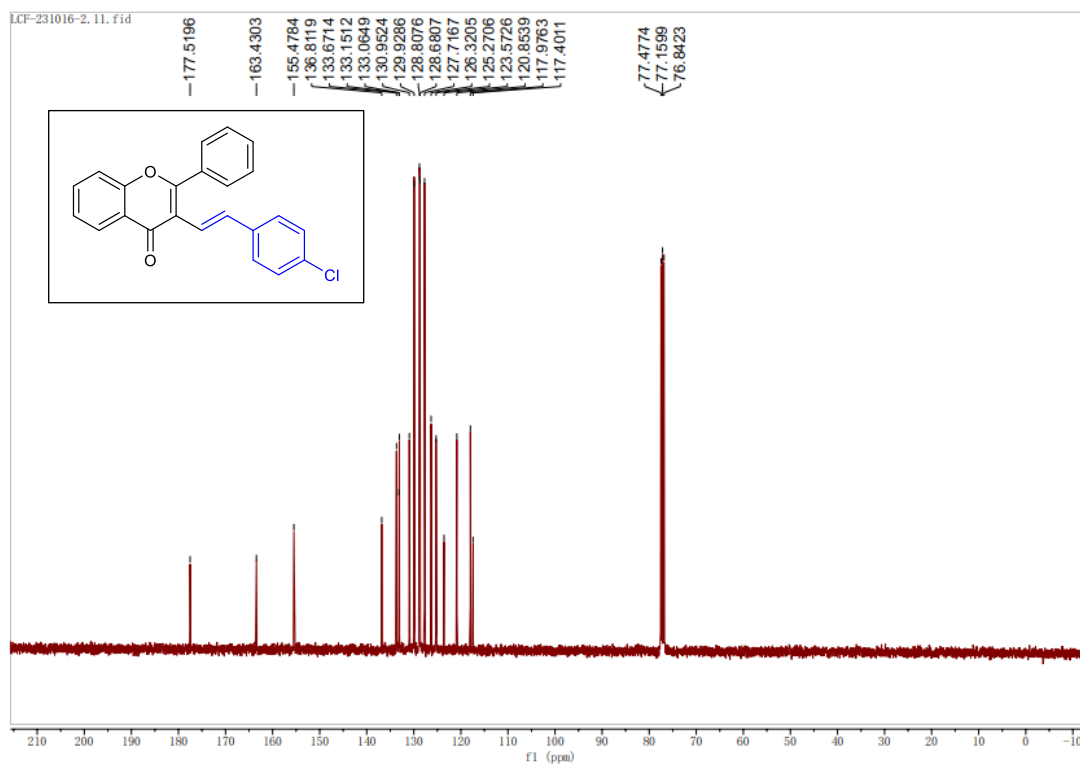
^1H NMR Spectra of compound **5a** in CDCl_3 (400 MHz)



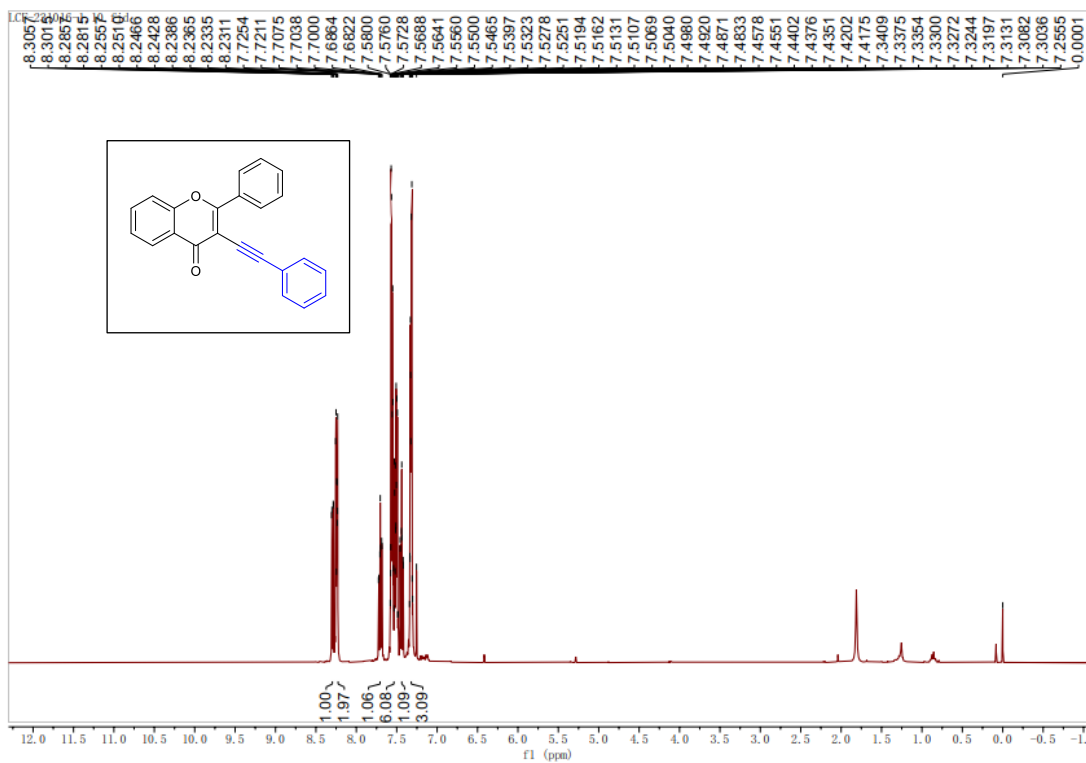
^{13}C NMR Spectra of compound **5a** in CDCl_3 (101 MHz)



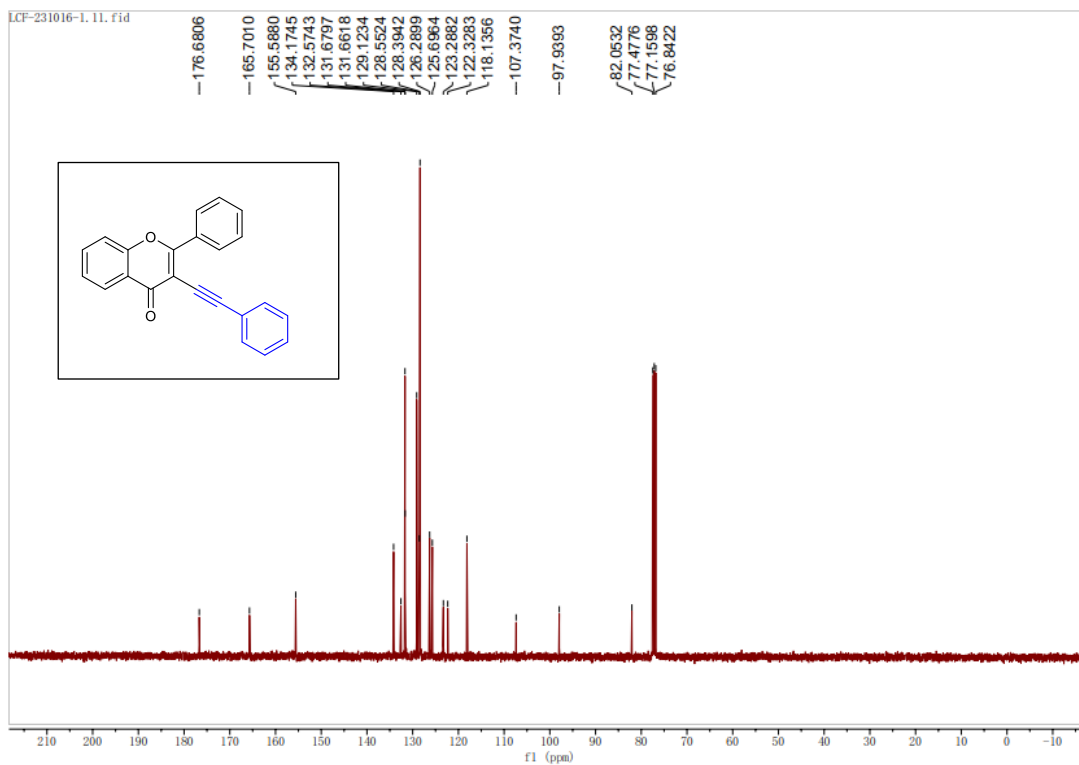
^1H NMR Spectra of compound **5b** in CDCl_3 (400 MHz)



^{13}C NMR Spectra of compound **5b** in CDCl_3 (101 MHz)



¹H NMR Spectra of compound **5c** in CDCl₃ (400 MHz)



¹³C NMR Spectra of compound **5c** in CDCl₃ (101 MHz)