Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One-Pot Transition-Metal-Free Cascade Synthesis of Thieno[2,3-c]coumarins from Chromones

Yuhong Yang, Xueyu Qi, Ruiling Liu, Qian He and Chunhao Yang*
State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai, 201203, China.

* E-mail: chyang@simm.ac.cn;

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1、General Methods

Unless otherwise noted, all solvents and other reagents are commercially available and used without further purification. All reagents were weighed and handled in air at room temperature. Column chromatography was performed on silica gel (200~300 mesh). NMR spectra were recorded on Bruker AVANCE 300 NMR spectrometer or Bruker AVANCE III 400 NMR spectrometer or Bruker AVANCE III 500 NMR spectrometer or Bruker AVANCE III 600 NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), heptet (hept), multiplet (m) and broad (br). Low and high-resolution mass spectra (LRMS and HRMS) were recorded on a Finnigan/MAT-95 (EI), Finnigan LCQ/DECA and Micromass Ultra Q-TOF (ESI) spectrometer. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2、Experimental Procedures

General procedure for the synthesis of chromenones.

The chromenones were prepared by the addition of the corresponding substituted *o*-hydroxyacetophenone with N,N-dimethylformamide dimethyl acetal (DMFDMA), followed by cyclization by methylene chloride according to a reported protocol.[1]

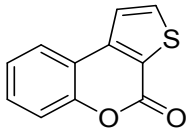
General procedure for the synthesis of thieno[2,3-c]coumarins.

To a 10 mL of round bottomed flask was added the chromenones (0.5 mmol), ethyl mercaptoacetate (**3a-r**, **3u-w**, 0.55 mmol; **3s-t** ,1.1 mmol) , and DBU (1.0 mmol) in 1,4-dioxane (3.0 mL), This mixture was heated to 60 °C with stirring for 12 h under N_2 atmosphere, after that the reaction mixture was cooled down to room temperature, washed with saturated ammonium chloride, and extracted with ethyl acetate (10 mL×3), washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give the crude product, which was further purified by silica gel chromatography using an ethyl acetate/petroleum ether gradient mixture to afford the desired product.

1. M. Khoobi, M. Alipour, S. Zarei, F. Jafarpour and A. Shafiee, *Chem. Commun.*, 2012, **48**, 2985-2987.

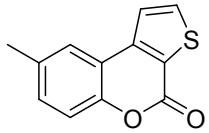
3、Analytical Characterization Data of Products

4*H*-thieno[2,3-c]chromen-4-one (3a)



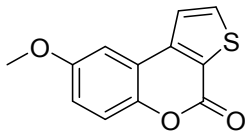
White solid (96 mg, 95 %), m. p. 135-136 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.2 Hz, 1H), 7.87–7.82 (m, 1H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.50 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38–7.33 (m, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.25, 152.64, 145.04, 136.88, 130.18, 124.60, 124.47, 123.82, 122.35, 117.58, 117.42. LRMS (ESI^{+}) found m/z 203. HRMS (ESI^{+}) calculated for $C_{11}H_7O_2S$ $[M+H]^+$ 203.0161, found: 203.0164.

8-Methyl-4*H*-thieno[2,3-c]chromen-4-one (3b)



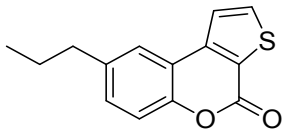
White solid (94 mg, 87 %), m. p. 211-223 ºC. ^{1} NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 5.2 Hz, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.61 (s, 1H), 7.36–7.25 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.13, 151.47, 145.76, 137.38, 134.98, 131.81, 125.16, 124.42, 122.96, 117.95, 117.78, 21.69. LRMS (ESI^{+}) found m/z 217. HRMS (ESI^{+}) calculated for $C_{12}H_9O_2S$ $[M+H]^+$ 217.0318, found: 217.0316.

8-Methoxy-4*H*-thieno[2,3-c]chromen-4-one (3c)



White solid (96 mg, 83 %), m. p. 190-191 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.26 (d, *J* = 2.9 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.06, 156.95, 147.71, 145.52, 137.37, 125.58, 123.03, 119.22, 118.54, 117.80, 107.65, 56.60. LRMS (ESI^{+}) found m/z 233. HRMS (ESI^{+}) calculated for $C_{11}H_6O_2S$ $[M+H]^+$ 233.0267, found: 233.0264.

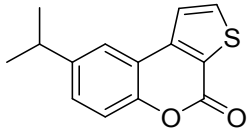
8-Propyl-4*H*-thieno[2,3-c]chromen-4-one (3d)



White solid (112 mg, 92 %), m. p. 97-100 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 5.2 Hz, 1H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.72–2.67 (m, 2H), 1.71 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR

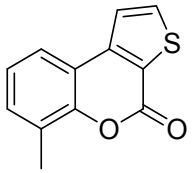
(125 MHz, Chloroform-*d*) δ 158.17, 151.66, 145.88, 139.86, 137.37, 131.24, 125.13, 123.88, 123.01, 118.01, 117.82, 38.17, 25.39, 14.43. LRMS (ESI^+) found m/z 245. HRMS (ESI^+) calculated for $C_{14}H_{13}O_2S$ $[M+H]^+$ 245.0631, found: 245.0634.

8-Isopropyl-4*H*-thieno[2,3-c]chromen-4-one (3e)



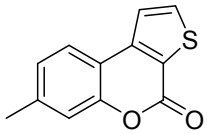
White solid (110 mg, 90 %), m. p. 150-151 ºC. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 5.2 Hz, 1H), 7.69–7.65 (m, 2H), 7.38 (s, 2H), 3.03 (hept, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.47, 150.95, 145.35, 145.24, 136.66, 128.61, 124.39, 122.31, 121.15, 117.40, 117.12, 33.79, 24.11. LRMS (ESI^+) found m/z 245. HRMS (ESI^+) calculated for $C_{14}H_{13}O_2S$ $[M+H]^+$ 245.0631, found: 245.0631.

6-Methyl-4*H*-thieno[2,3-c]chromen-4-one (3f)



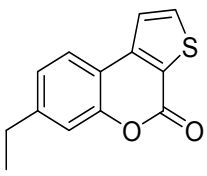
White solid (102g, 94 %), m. p. 159-161 ºC. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 5.2 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 5.2 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.33, 151.08, 145.46, 136.69, 131.55, 127.07, 124.29, 124.11, 122.52, 121.47, 117.15, 16.17. LRMS (ESI^+) found m/z 217. HRMS (ESI^+) calculated for $C_{12}H_9O_2S$ $[M+H]^+$ 217.0318, found: 217.0313.

7-Methyl-4*H*-thieno[2,3-c]chromen-4-one (3g)



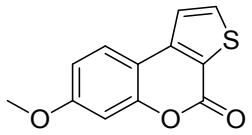
White solid (96 mg, 89 %), m. p. 145-147 ºC. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 5.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.25 (s, 1H), 7.18–7.14 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.45, 152.71, 145.22, 141.07, 136.75, 125.66, 123.63, 123.47, 122.17, 117.69, 114.96, 21.62. LRMS (ESI^+) found m/z 217. HRMS (ESI^+) calculated for $C_{12}H_9O_2S$ $[M+H]^+$ 217.0318, found: 217.0316.

7-Ethyl-4*H*-thieno[2,3-c]chromen-4-one (3h)



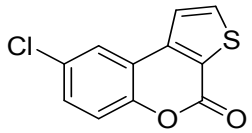
White solid (101 mg, 88 %), m. p. 108-111 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 5.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.29–7.27 (m, 1H), 7.19 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.49, 152.85, 147.41, 145.25, 136.76, 124.53, 123.68, 123.59, 122.20, 116.51, 115.15, 28.86, 15.23. LRMS (ESI$^+$) found m/z 231. HRMS (ESI$^+$) calculated for $C_{13}H_{11}O_2S$ $[M+H]^+$ 231.0474, found:231.0475.

7-Methoxy-4*H*-thieno[2,3-c]chromen-4-one (3i)



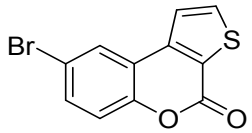
White solid (91 mg, 78 %), m. p. 140-142 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 5.2 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.00–6.88 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.32, 157.51, 154.14, 145.41, 136.93, 124.64, 121.97, 121.94, 112.53, 110.99, 101.53, 55.73. LRMS (ESI$^+$) found m/z 233. HRMS (ESI$^+$) calculated for $C_{12}H_9O_3S$ $[M+H]^+$ 233.0267, found: 233.0261.

8-Chloro-4*H*-thieno[2,3-c]chromen-4-one (3j)



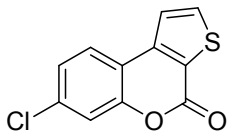
White solid (83 mg, 70 %), m. p. 237-240 ºC.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 5.2 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.45 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 156.63, 151.01, 143.75, 137.25, 130.11, 129.98, 125.18, 123.45, 122.29, 118.99, 118.54. LRMS (ESI$^+$) found m/z 237. HRMS (ESI$^+$) calculated for $C_{11}H_6ClO_2S$ $[M+H]^+$ 236.9772, found: 236.9771.

8-Bromo-4*H*-thieno[2,3-c]chromen-4-one (3k)



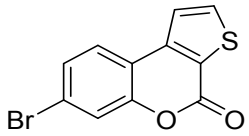
White solid (95 mg, 68 %), m. p. 230-232 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99–7.93 (m, 2H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.59 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 156.56, 151.48, 143.62, 137.26, 132.95, 126.46, 125.14, 122.27, 119.30, 119.02, 117.34. LRMS (ESI$^+$) found m/z 280. HRMS (ESI$^+$) calculated for $C_{11}H_6BrO_2S$ $[M+H]^+$ 280.9266, found: 280.9272.

7-Chloro-4*H*-thieno[2,3-c]chromen-4-one (3l)



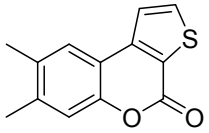
White solid (84 mg, 71 %), m. p. 183-187 ºC .^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 5.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 156.55, 152.84, 144.22, 137.29, 135.70, 125.08, 124.65, 124.25, 122.23, 117.86, 116.07. LRMS (ESI^{+}) found m/z 259. HRMS (ESI^{+}) calculated for $C_{11}H_5ClNaO_2S$ $[M+Na]^+$ 258.9591, found:258.9592.

7-Bromo-4*H*-thieno[2,3-c]chromen-4-one (3m)



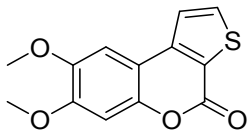
White solid (95 mg, 68 %), m. p. 170-172 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 5.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.63 (m, 2H), 7.48 (dd, *J* = 8.4, 1.7 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 156.47, 152.82, 144.26, 137.30, 127.91, 124.82, 124.43, 123.44, 122.23, 120.78, 116.44. LRMS (ESI^{+}) found m/z 281. HRMS (ESI^{+}) calculated for $C_{11}H_6BrO_2S$ $[M+H]^+$ 280.9266, found: 280.9267.

7,8-Dimethyl-4*H*-thieno[2,3-c]chromen-4-one (3n)



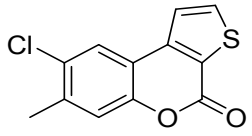
White solid (101 mg, 88 %), m. p. 198-200 ºC.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 5.2 Hz, 1H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.56 (s, 1H), 7.21 (s, 1H), 2.36 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.35, 151.72, 145.94, 140.53, 137.32, 133.94, 124.70, 124.39, 122.81, 118.70, 115.72, 20.89, 20.10. LRMS (ESI^{+}) found m/z 231. HRMS (ESI^{+}) calculated for $C_{13}H_{11}O_2S$ $[M+H]^+$ 231.0474, found: 231.0468

7,8-Dimethoxy-4*H*-thieno[2,3-c]chromen-4-one (3o)



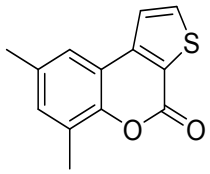
Light yellow solid (115 mg, 88 %), m. p. 255-259 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 5.1 Hz, 1H), 7.56 (d, *J* = 5.1 Hz, 1H), 7.19 (s, 1H), 6.96 (s, 1H), 3.99 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.35, 151.97, 148.63, 147.17, 146.02, 137.54, 123.11, 122.55, 110.56, 105.40, 101.43, 57.18, 57.01. LRMS (ESI^{+}) found m/z 263. HRMS (ESI^{+}) calculated for $C_{13}H_{11}O_4S$ $[M+H]^+$ 263.0373, found: 263.0372

8-Chloro-7-methyl-4*H*-thieno[2,3-c]chromen-4-one (3p)



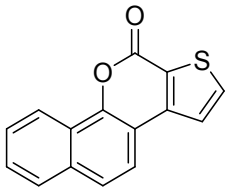
White solid (83 mg, 66 %), m. p. 125-127 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 5.2 Hz, 1H), 7.80 (s, 1H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.33 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.61, 151.66, 144.66, 139.45, 137.84, 131.05, 125.13, 124.34, 122.85, 120.17, 117.16, 21.21. LRMS (ESI^{+}) found m/z 251. HRMS (ESI^{+}) calculated for $C_{12}H_8ClO_2S$ $[M+H]^{+}$ 250.9928, found: 250.9928

6,8-Dimethyl-4*H*-thieno[2,3-c]chromen-4-one (3q)



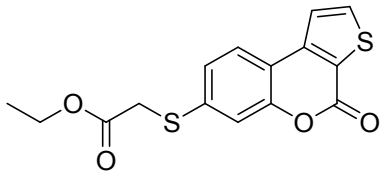
White solid (100 mg, 87 %), m. p. 127-128 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 5.2 Hz, 1H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.45 (s, 1H), 7.16 (s, 1H), 2.48 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.23, 149.92, 146.17, 137.21, 134.39, 133.33, 127.34, 124.97, 123.16, 122.06, 117.54, 21.61, 16.76. LRMS (ESI^{+}) found m/z 231. HRMS (ESI^{+}) calculated for $C_{13}H_{11}O_2S$ $[M+H]^{+}$ 231.0474, found: 231.0480

11*H*-benzo[*h*]thieno[2,3-c]chromen-11-one (3r)



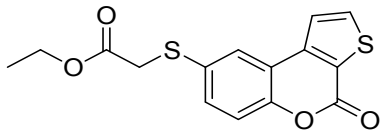
White solid (112 mg, 89 %), m. p. 215-218 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57–8.53 (m, 1H), 7.93 (d, *J* = 5.1 Hz, 1H), 7.86–7.82 (m, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 5.1 Hz, 1H), 7.60 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.92, 149.47, 146.50, 137.70, 134.69, 128.55, 128.49, 127.90, 125.38, 124.72, 124.33, 123.27, 123.00, 120.98, 113.33. LRMS (ESI^{+}) found m/z 253. HRMS (ESI^{+}) calculated for $C_{15}H_9O_2S$ $[M+H]^{+}$ 253.0318, found: 253.0317

Ethyl 2-((4-oxo-4*H*-thieno[2,3-c]chromen-7-yl)thio)acetate (3s)



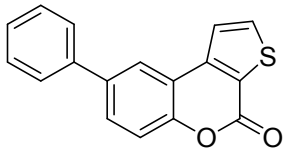
Light yellow solid (98 mg, 61 %), m. p. 99-102 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 169.01, 156.87, 152.82, 144.63, 138.77, 137.12, 124.56, 124.08, 123.97, 122.21, 116.53, 115.62, 61.97, 35.65 , 14.14 . LRMS (ESI^{+}) found m/z 321. HRMS (ESI^{+}) calculated for $C_{15}H_{13}O_4S_2$ $[M+H]^{+}$ 321.0250, found: 321.0255

Ethyl 2-((4-oxo-4*H*-thieno[2,3-c]chromen-8-yl)thio)acetate (3t)



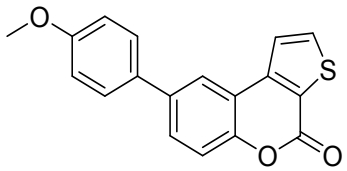
Light yellow solid (96 mg, 60 %), m. p. 100-102 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.2 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 169.00, 156.86, 152.81, 144.62, 138.77, 137.12, 124.55, 124.08, 123.97, 122.21, 116.52, 115.61, 61.97, 35.64, 14.14. LRMS (ESI^{+}) found m/z 321. HRMS (ESI^{+}) calculated for $C_{15}H_{13}O_4S_2$ $[M+H]^{+}$ 321.0250, found: 321.0255

8-Phenyl-4*H*-thieno[2,3-c]chromen-4-one (3u)



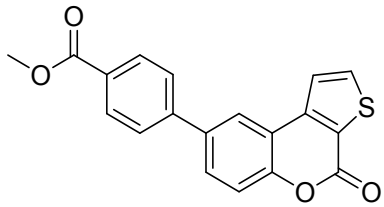
White solid (126 mg, 91 %), m. p. 195-198 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.95 (d, *J* = 5.2 Hz, 1H), 7.74–7.70 (m, 2H), 7.66–7.61 (m, 2H), 7.55–7.47 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.89, 152.77, 145.70, 140.52, 138.73, 137.67, 129.86, 129.72, 128.48, 127.90, 125.44, 123.05, 122.88, 118.65, 118.34. LRMS (ESI^{+}) found m/z 279. HRMS (ESI^{+}) calculated for $C_{17}H_{11}O_2S$ $[M+H]^{+}$ 279.0474, found: 279.0478

8-(4-Methoxyphenyl)-4*H*-thieno[2,3-c]chromen-4-one (3v)



White solid (142 mg, 92 %), m. p. 226-228 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98–7.93 (m, 2H), 7.71 (d, *J* = 5.2 Hz, 1H), 7.67 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.21, 157.96, 152.38, 145.77, 138.37, 137.60, 133.01, 129.50, 128.94, 125.39, 123.05, 122.31, 118.57, 118.30, 115.15, 56.13. LRMS (ESI^{+}) found m/z 309. HRMS (ESI^{+}) calculated for $C_{18}H_{13}O_3S$ $[M+H]^{+}$ 309.0580, found: 309.0586

Methyl 4-(4-oxo-4*H*-thieno[2,3-c]chromen-yl)benzoate (3w)

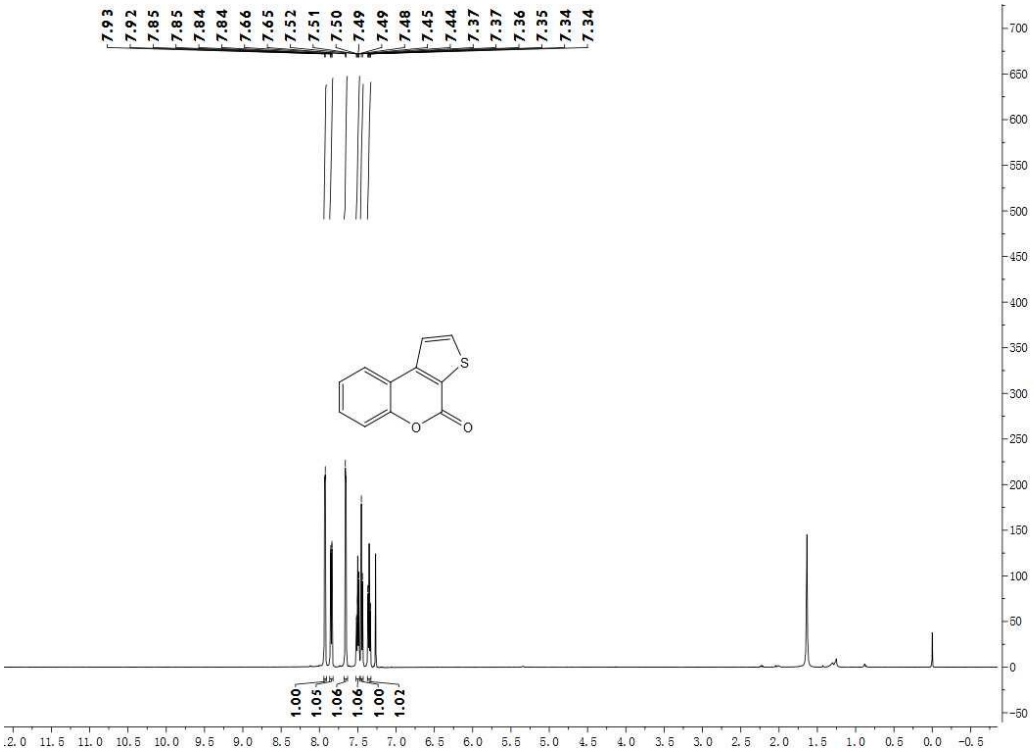


White solid (151 mg, 90 %), m. p. 242-245 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (d, *J* =

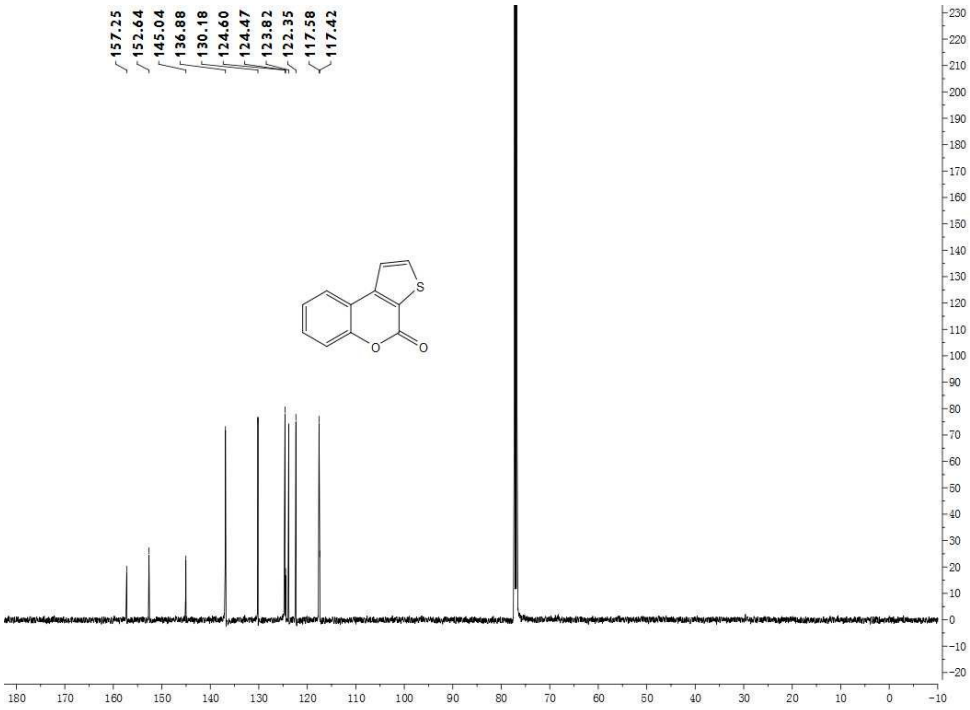
8.3 Hz, 2H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.98 (d, *J* = 5.2 Hz, 1H), 7.77–7.73 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 167.50, 157.69, 153.25, 145.44, 144.84, 137.83, 137.46, 131.02, 130.10, 129.87, 127.81, 125.59, 123.13, 123.05, 118.89, 118.52, 52.96. LRMS (ESI$^+$) found m/z 337. HRMS (ESI$^+$) calculated for $C_{19}H_{13}O_4S$ $[M+H]^+$ 337.0529, found:337.0537.

4、Copies of ^{1}H NMR and ^{13}C NMR Spectra for the Products

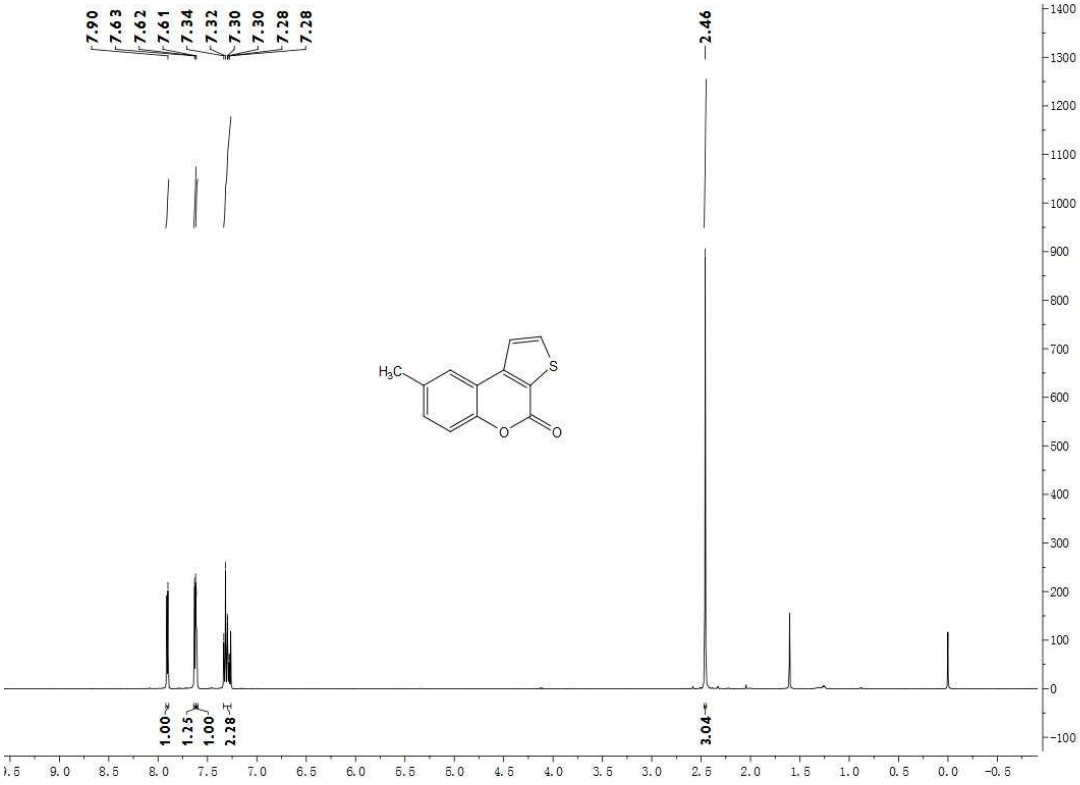
^{1}H NMR spectrum of **3a**



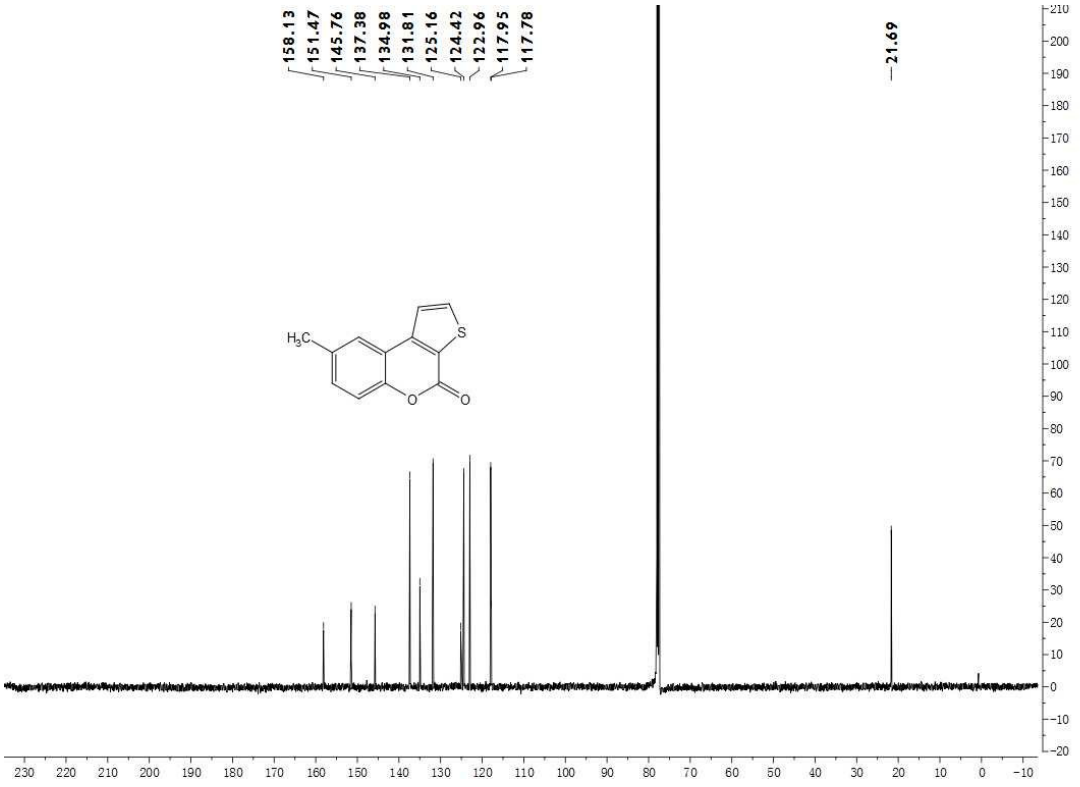
^{13}C NMR spectrum of **3a**



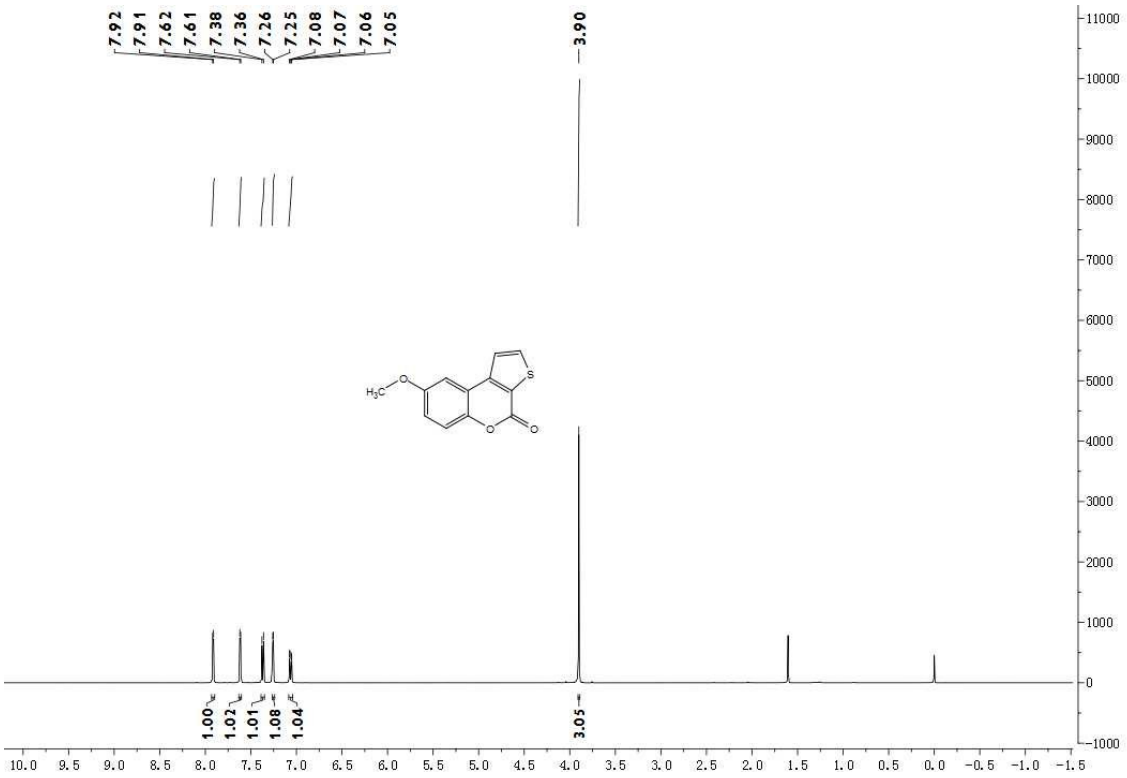
^{1}H NMR spectrum of **3b**



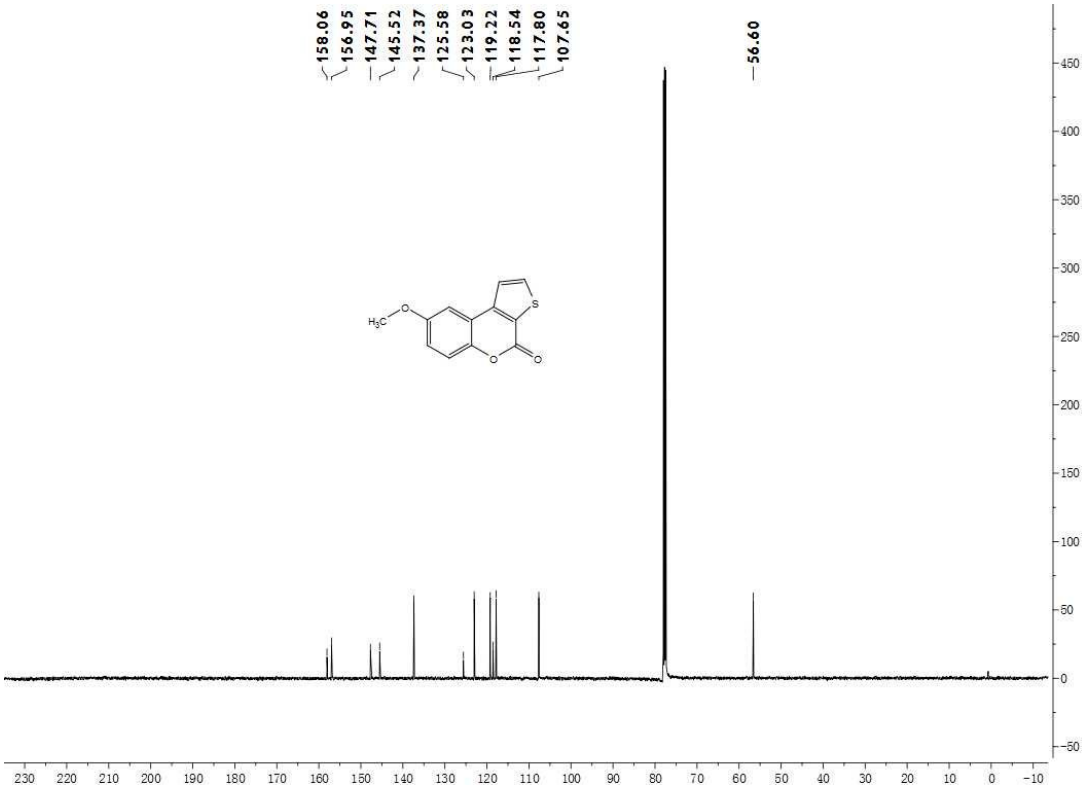
^{13}C NMR spectrum of **3b**



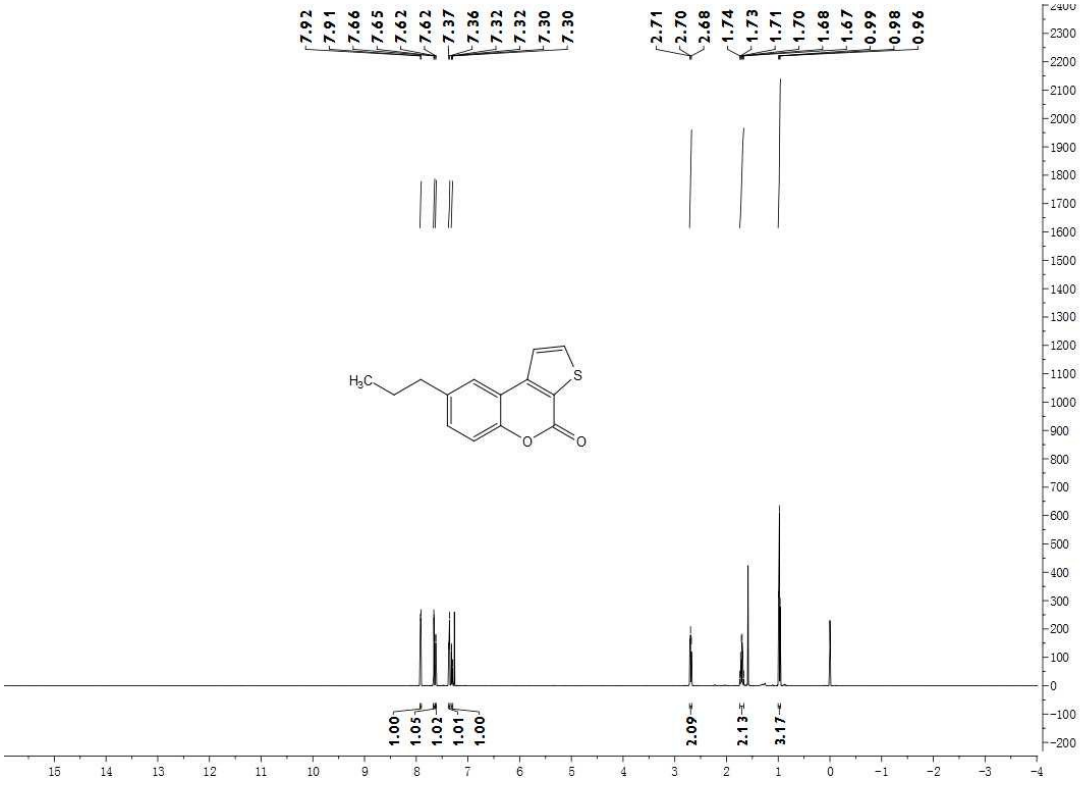
^{1}H NMR spectrum of **3c**



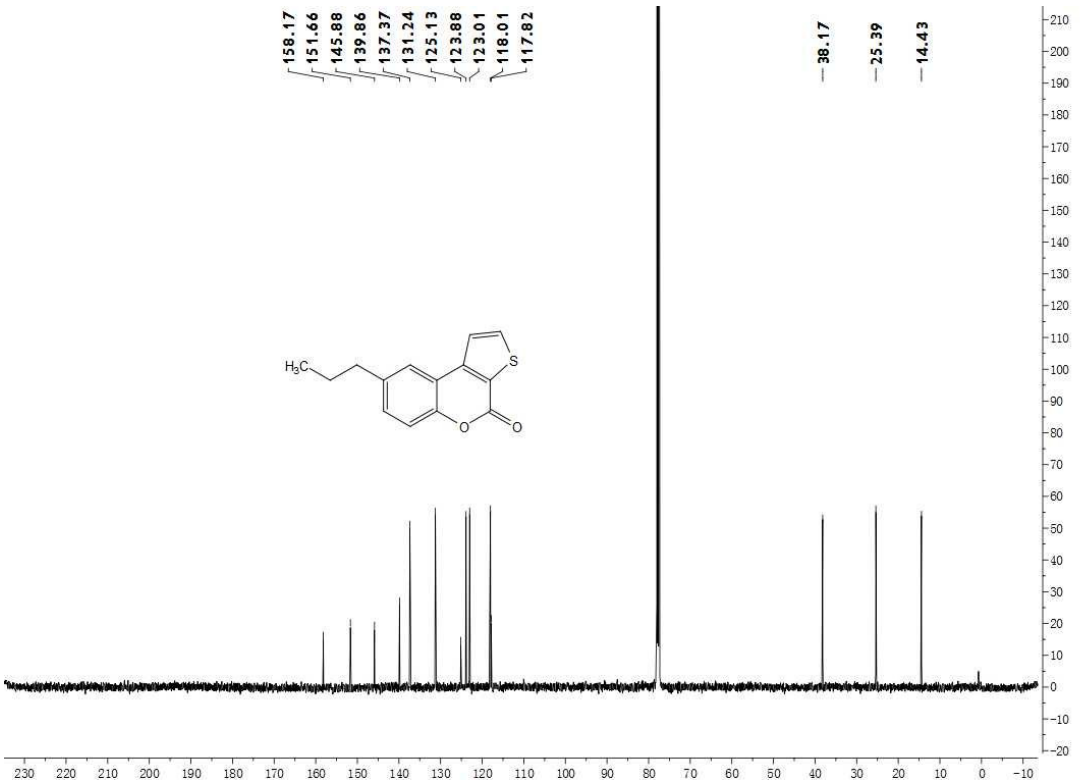
^{13}C NMR spectrum of **3c**



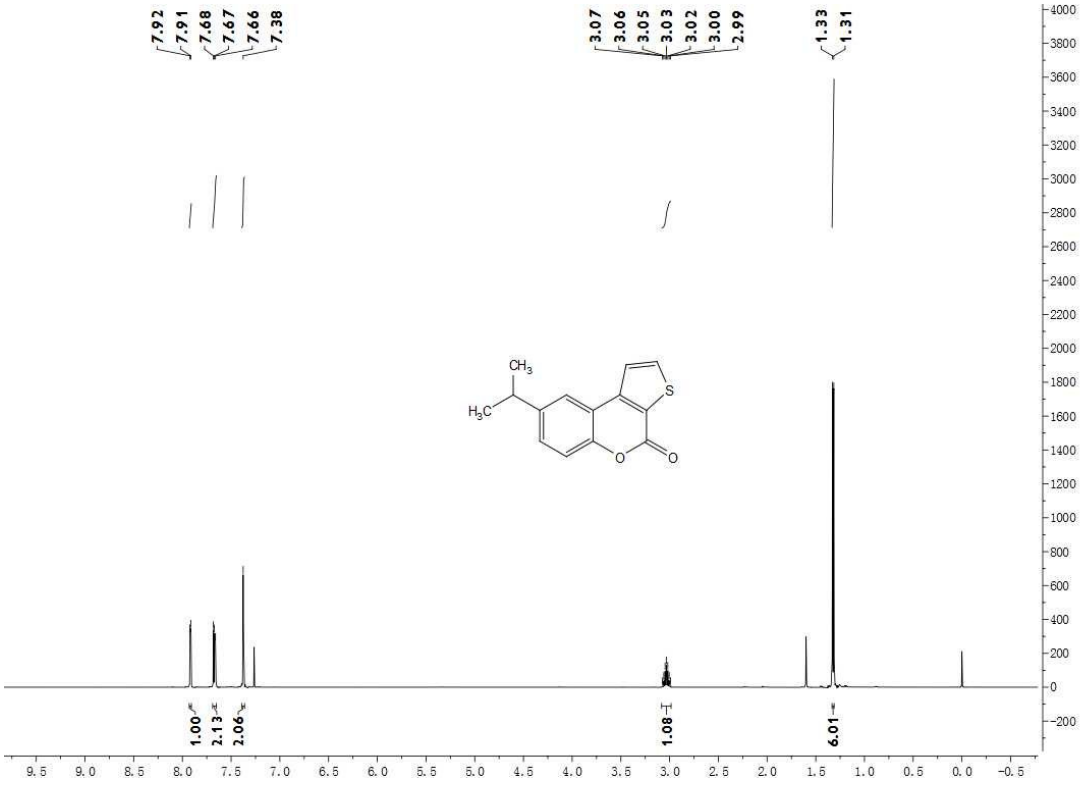
^{1}H NMR spectrum of **3d**



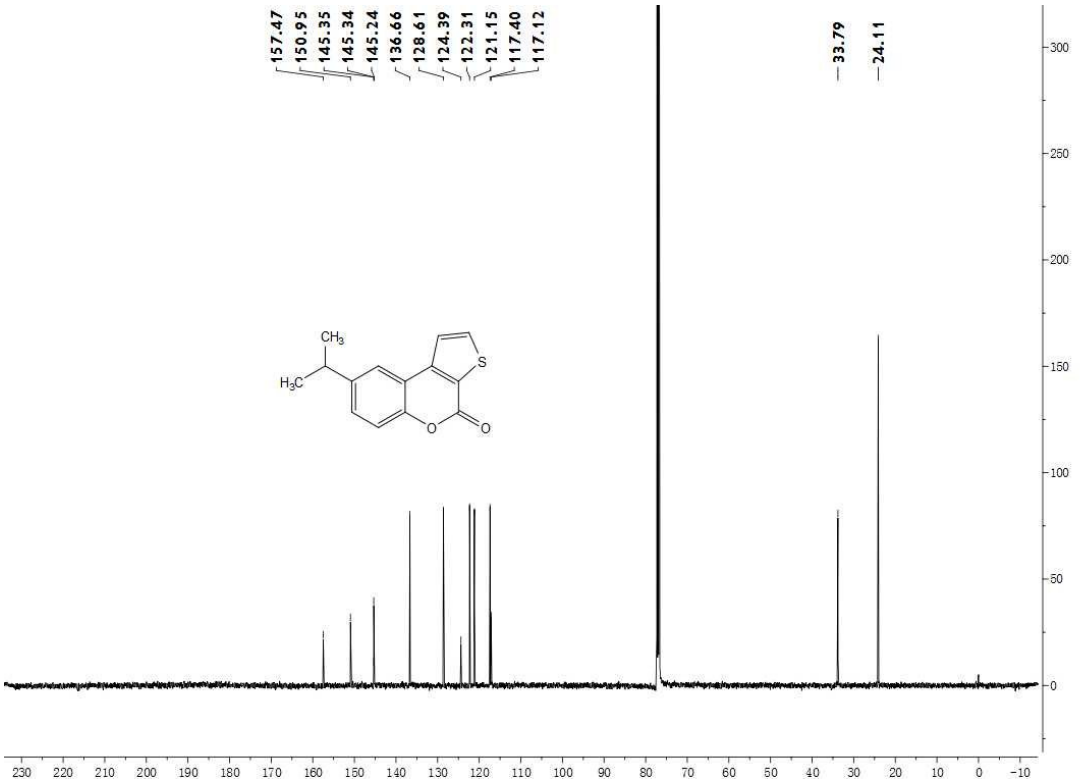
^{13}C NMR spectrum of **3d**



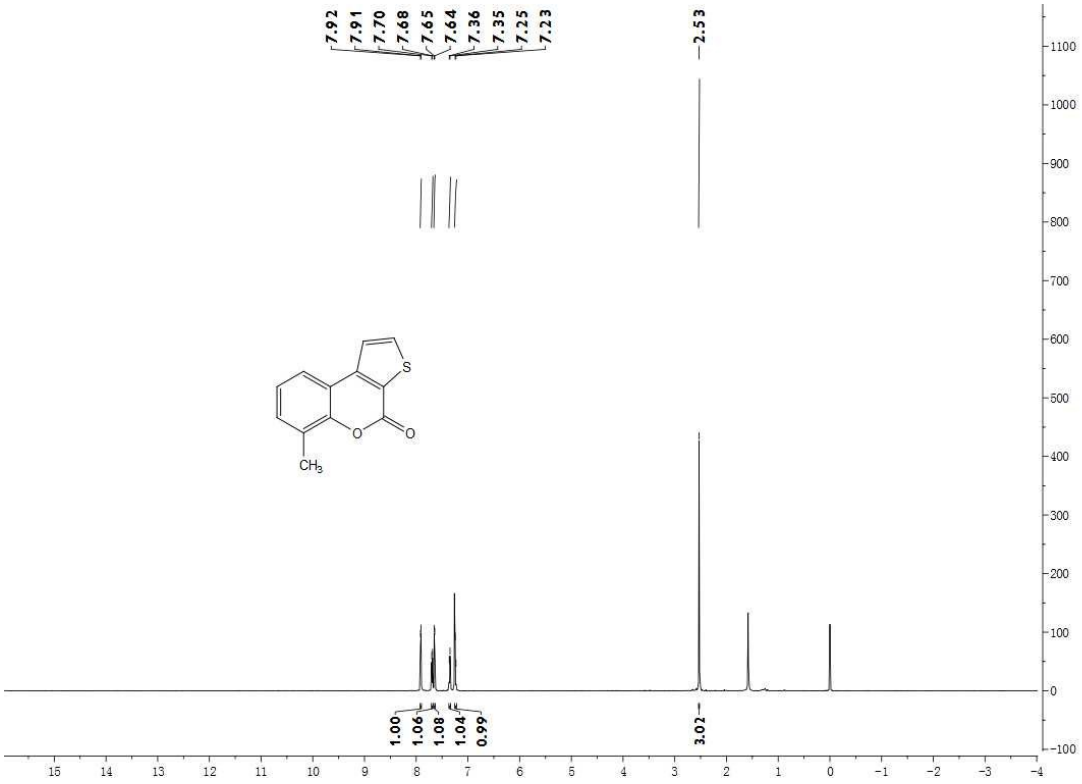
^{1}H NMR spectrum of **3e**



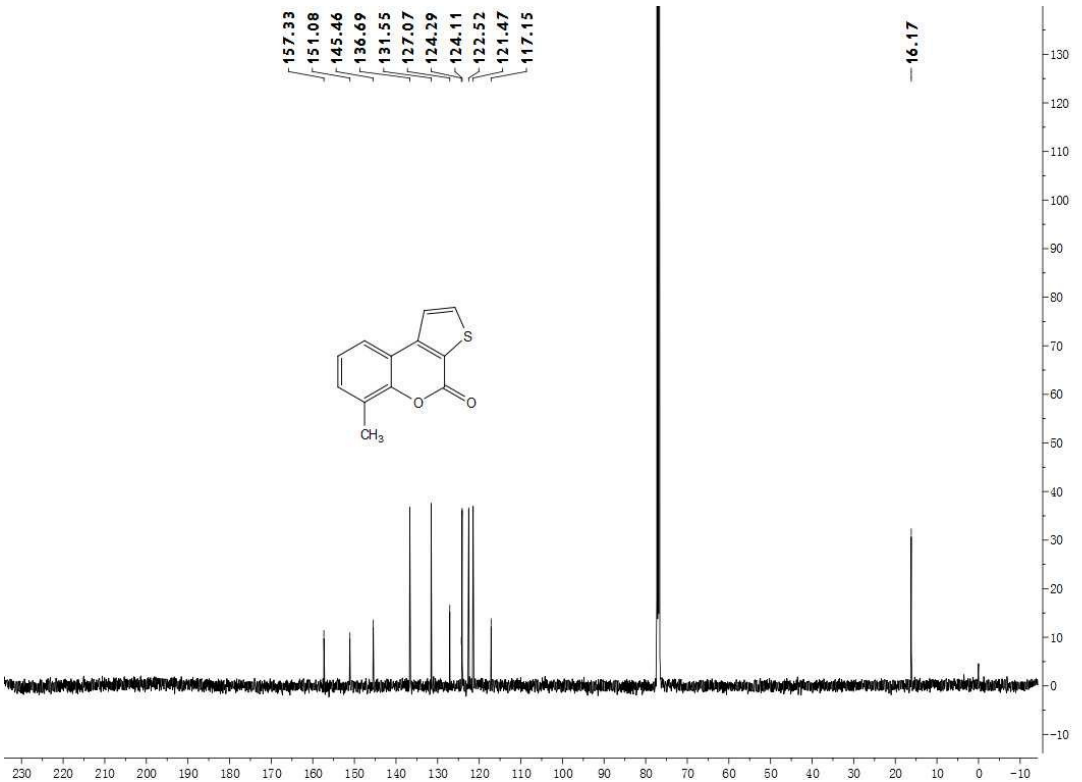
^{13}C NMR spectrum of **3e**



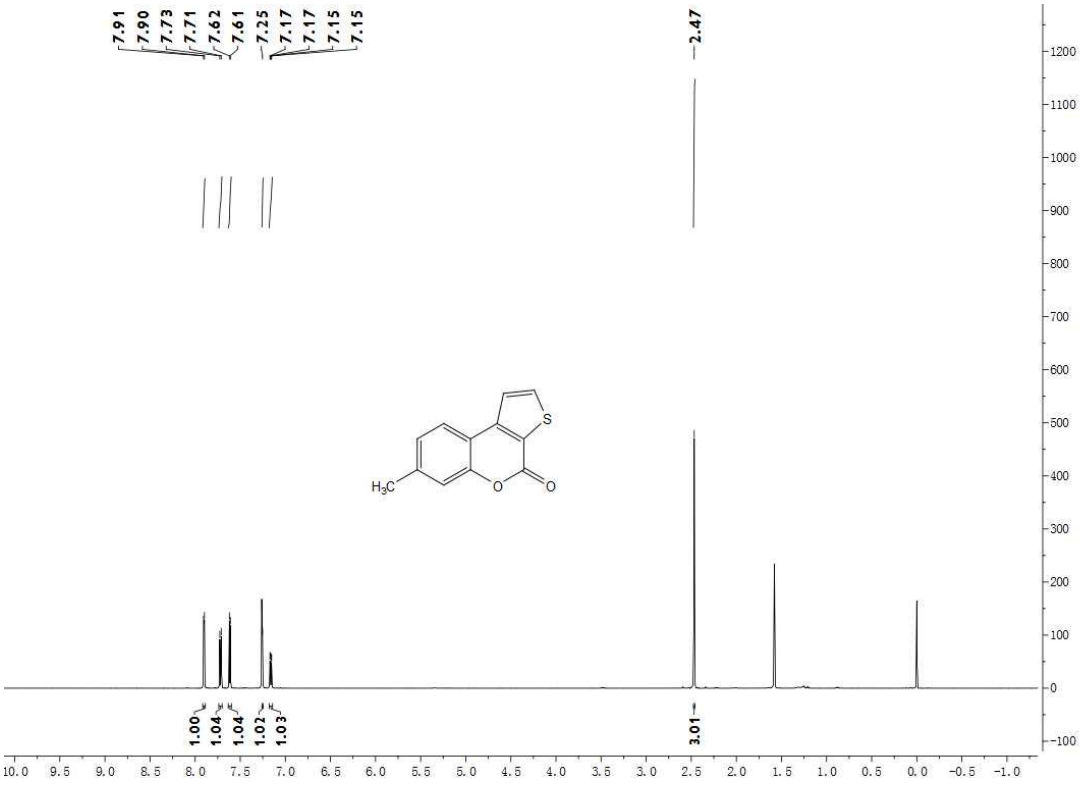
^{1}H NMR spectrum of **3f**



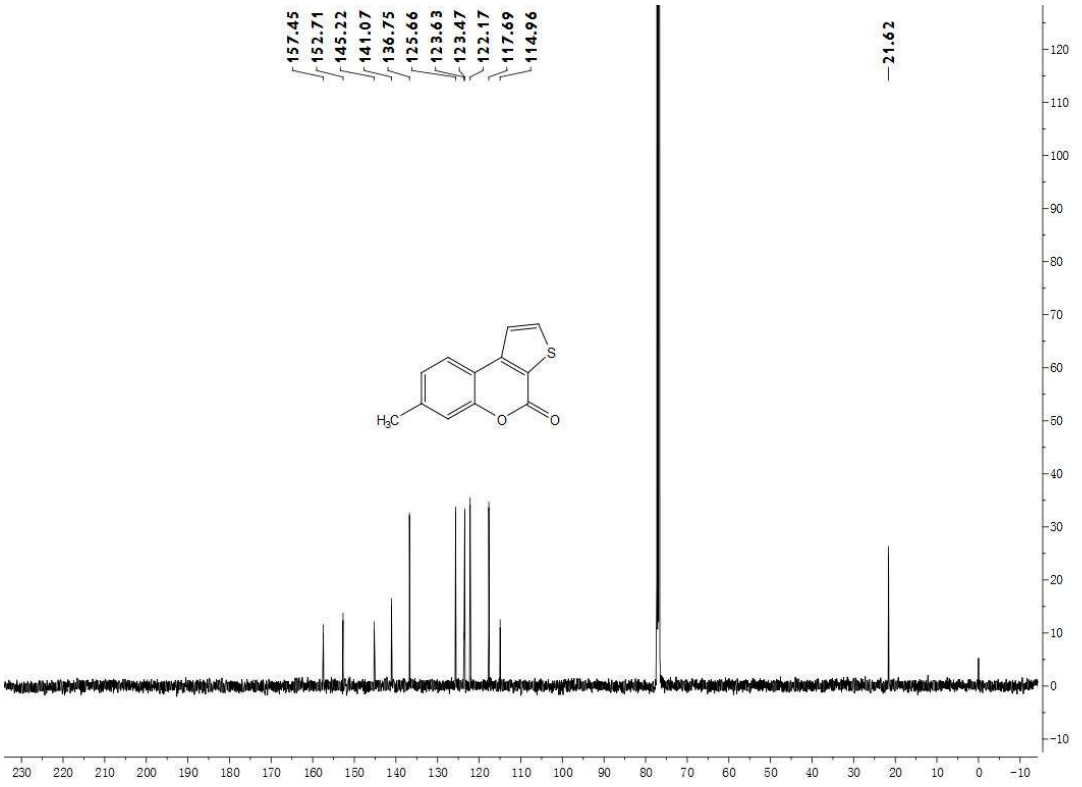
^{13}C NMR spectrum of **3f**



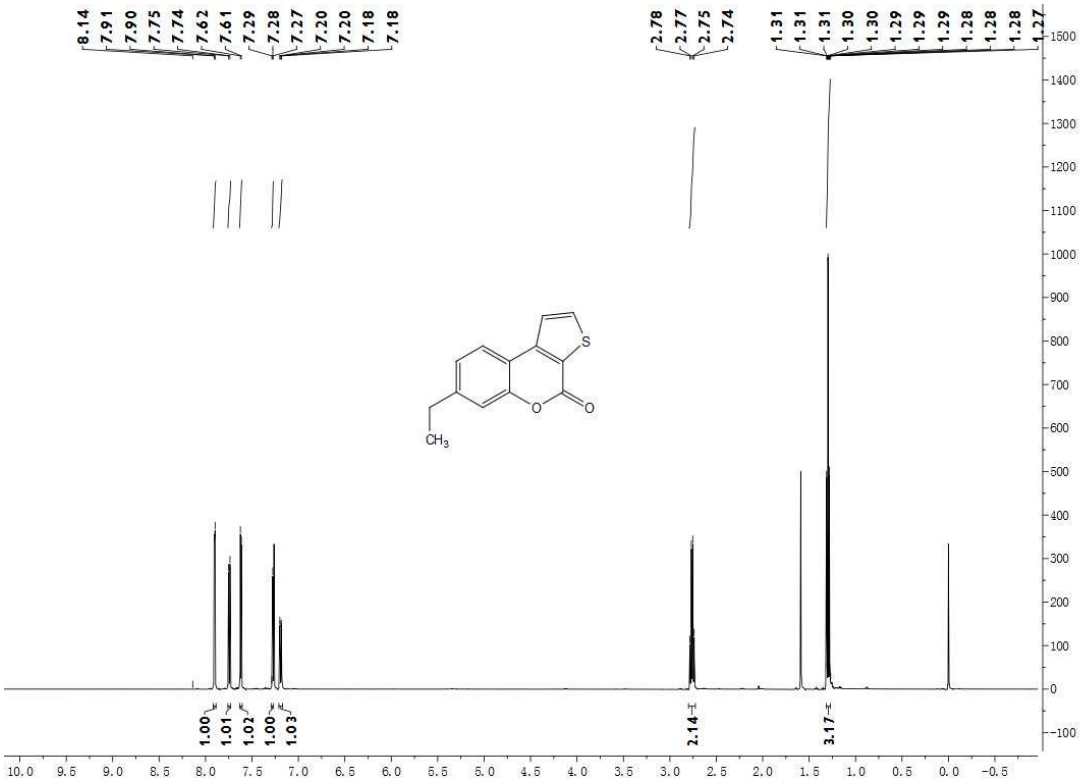
^{1}H NMR spectrum of **3g**



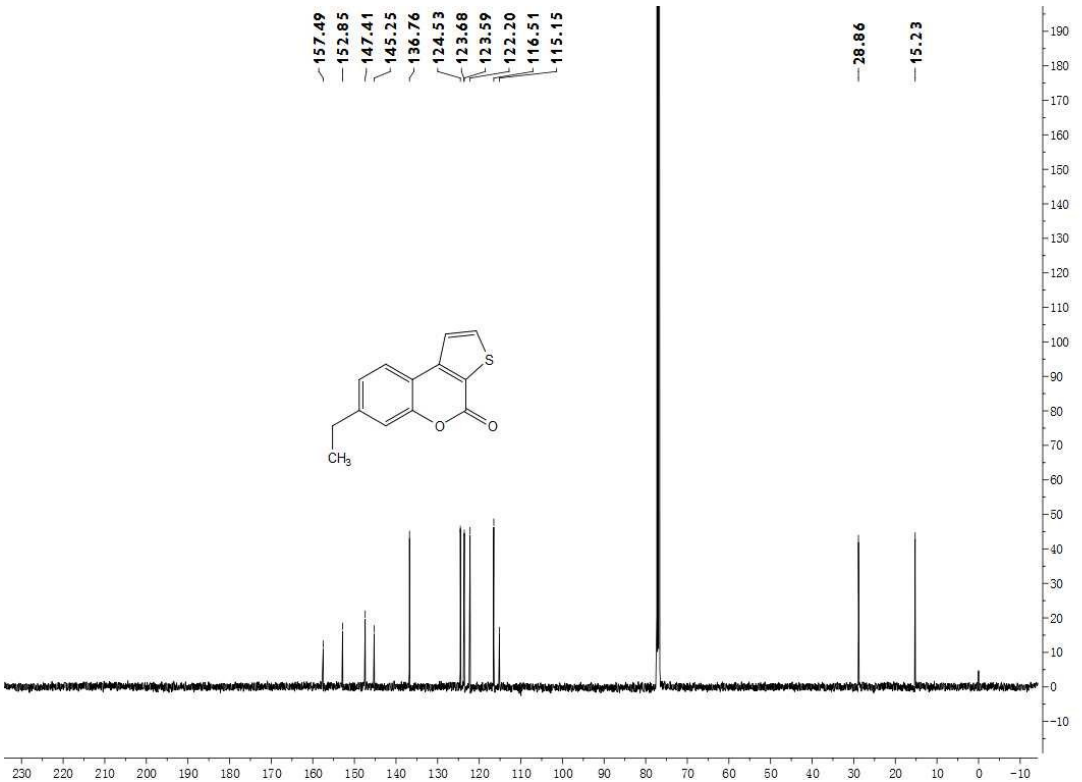
^{13}C NMR spectrum of **3g**



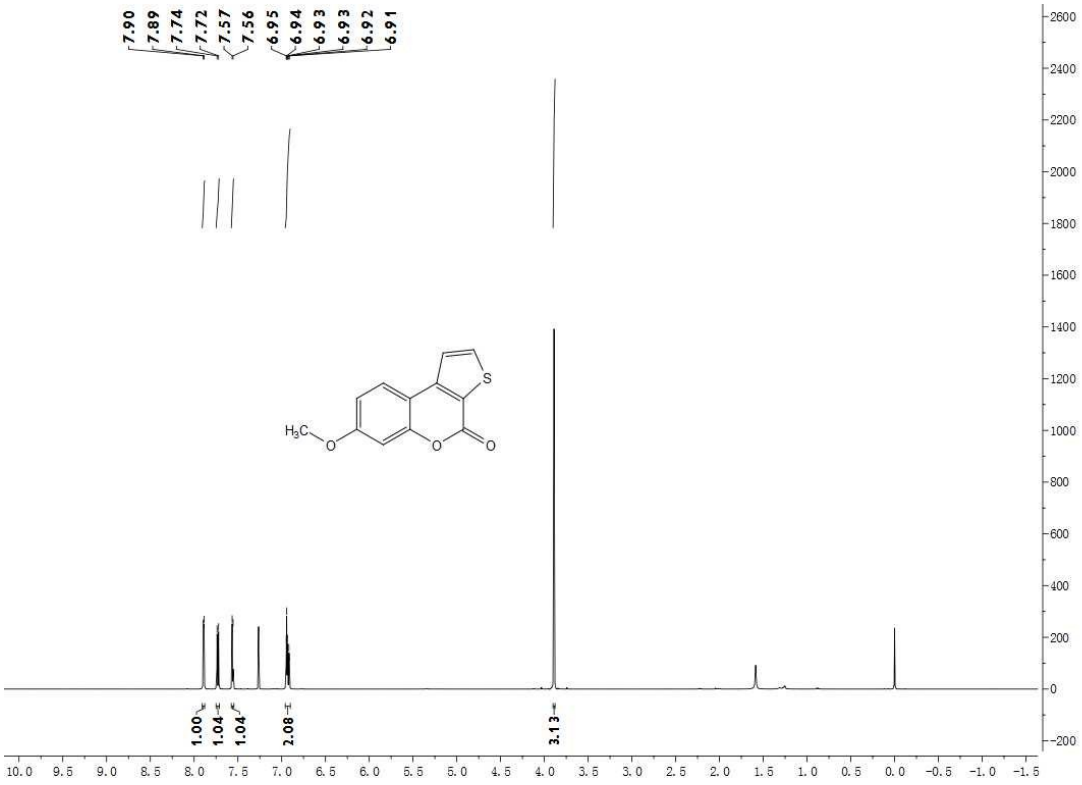
^{1}H NMR spectrum of **3h**



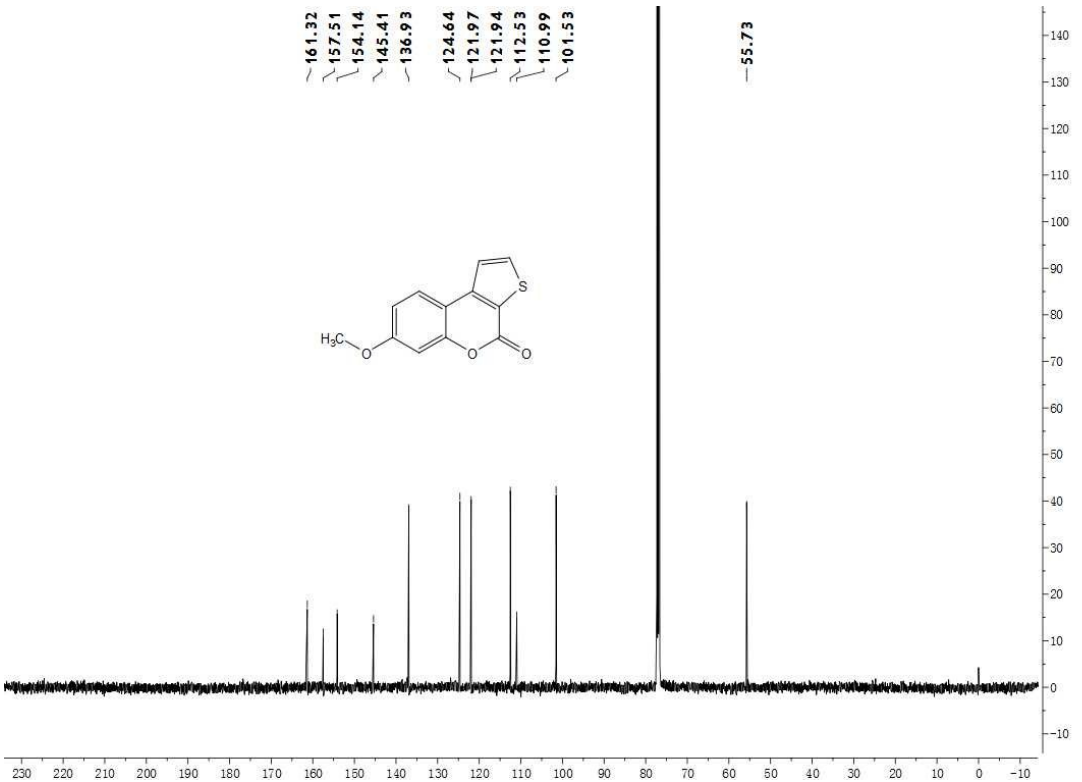
^{13}C NMR spectrum of **3h**



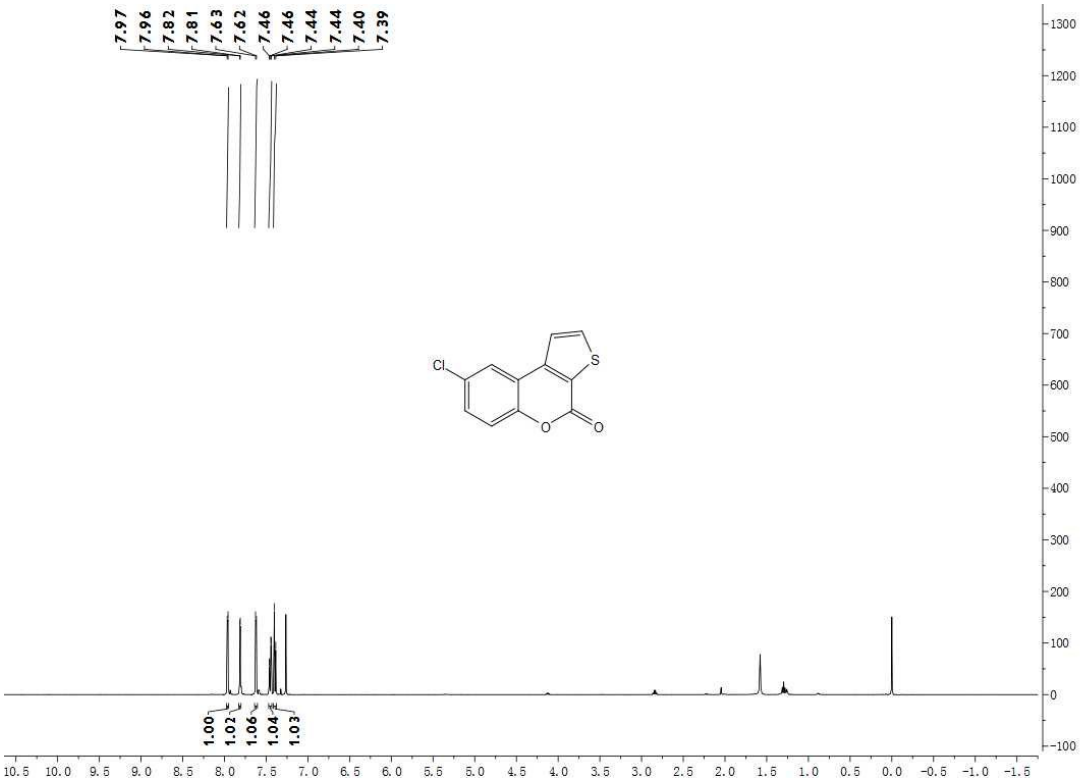
^{1}H NMR spectrum of **3i**



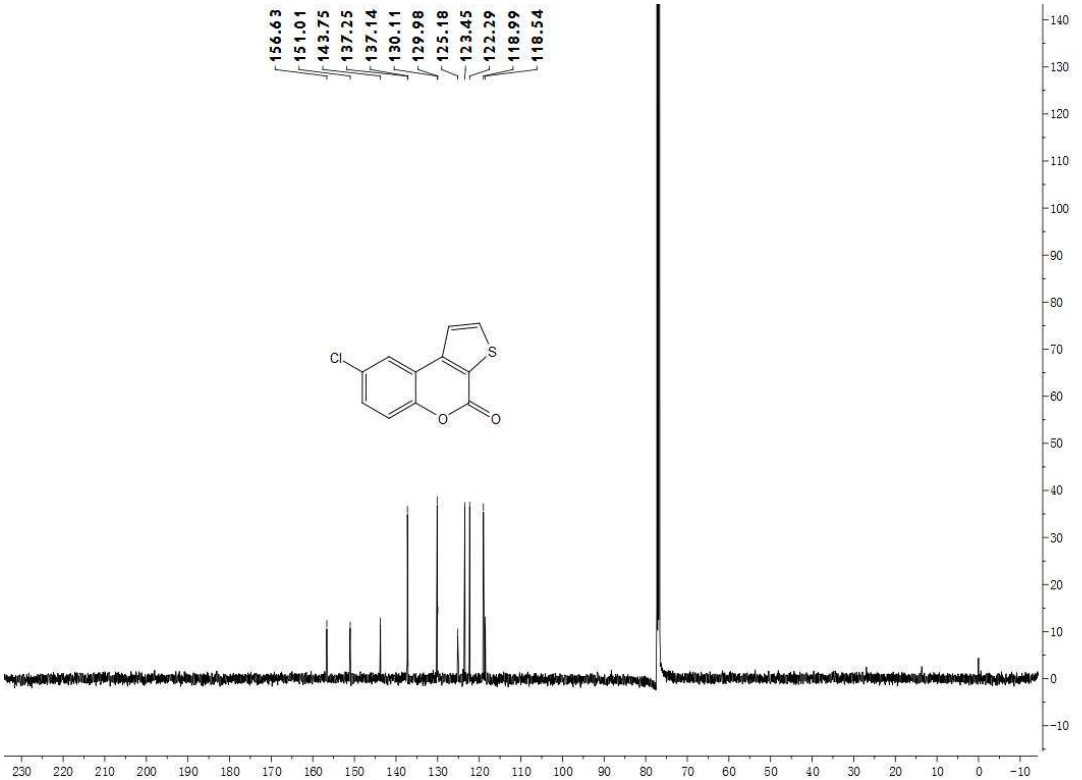
^{13}C NMR spectrum of **3i**



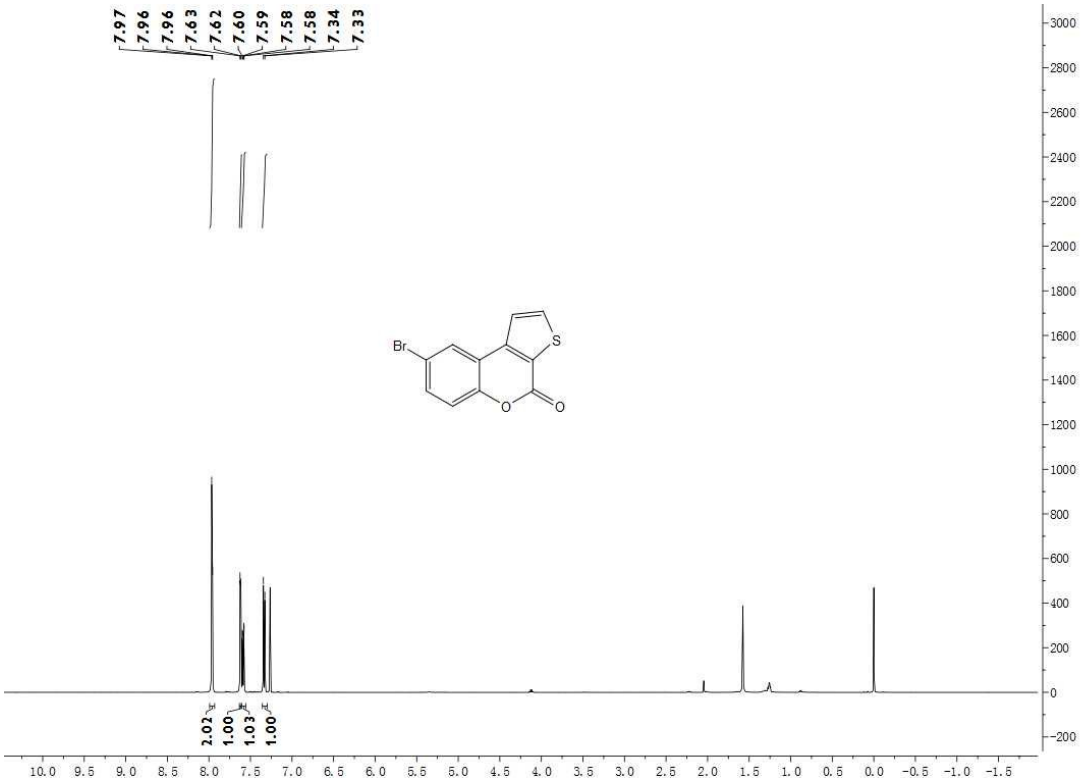
^{1}H NMR spectrum of **3j**



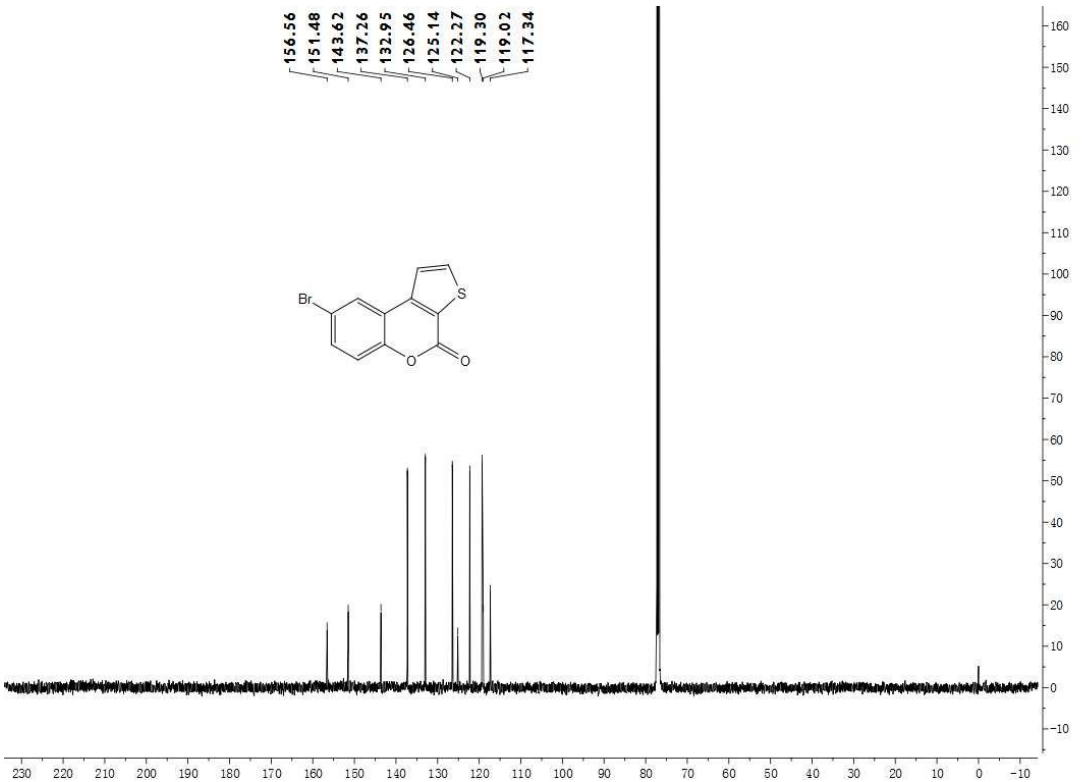
^{13}C NMR spectrum of **3j**



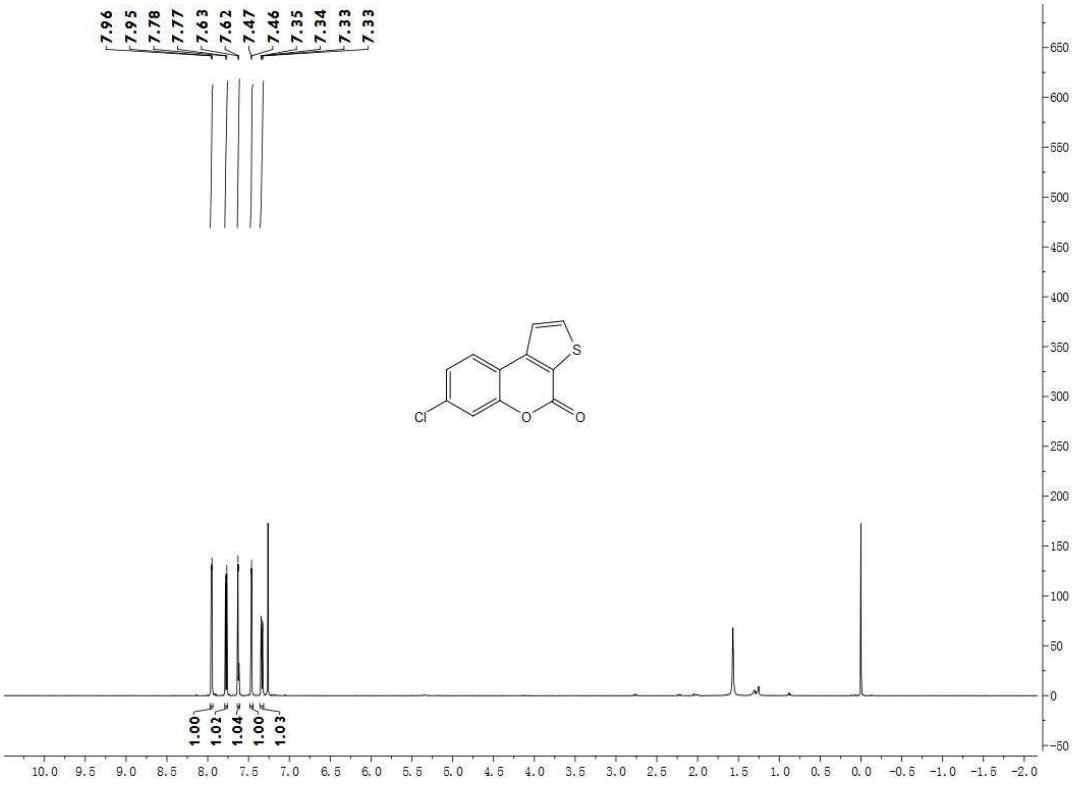
^{1}H NMR spectrum of **3k**



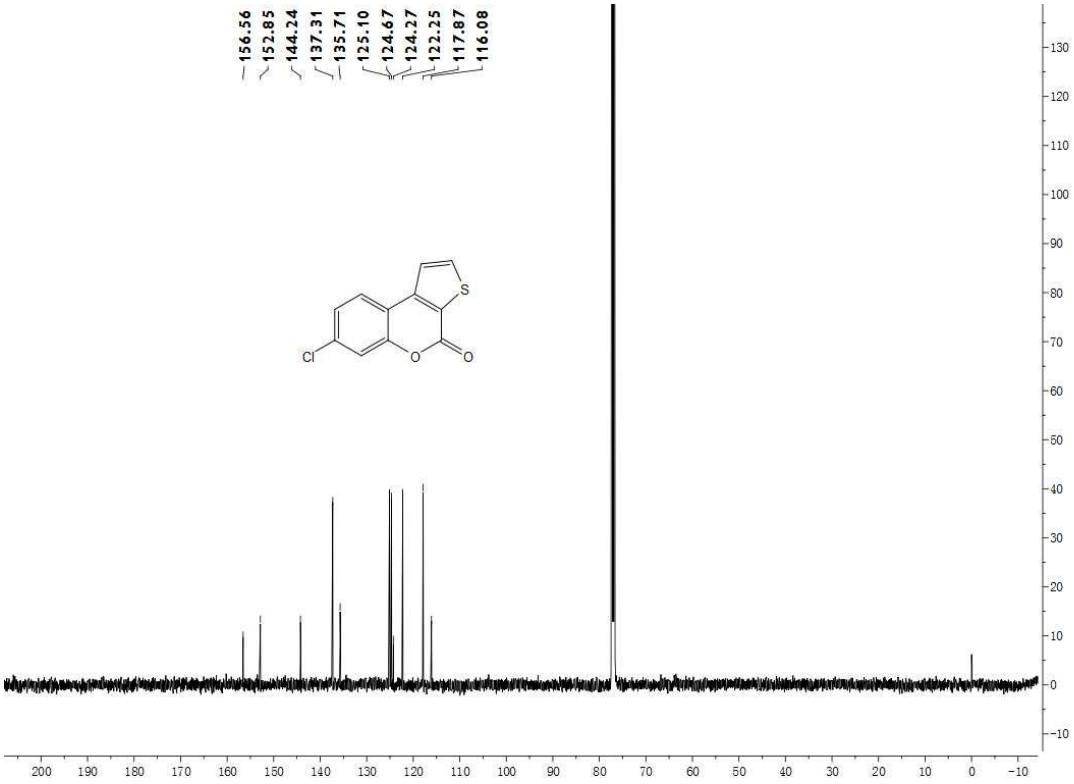
^{13}C NMR spectrum of **3k**



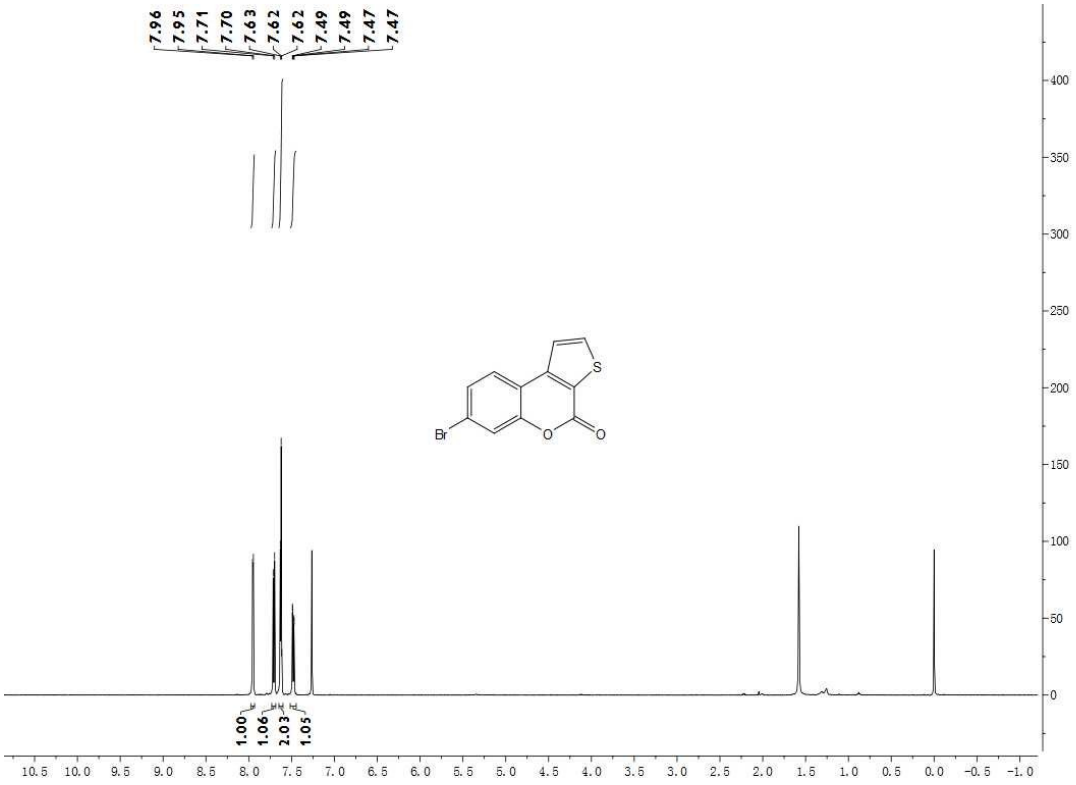
^{1}H NMR spectrum of **3l**



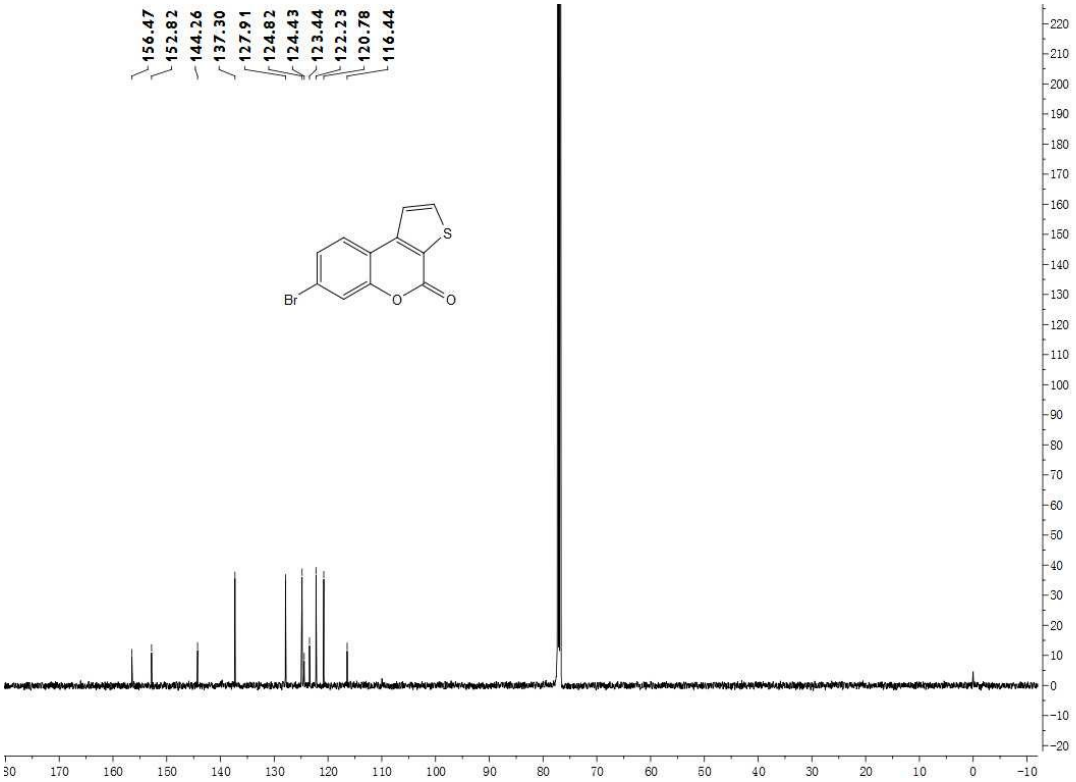
^{13}C NMR spectrum of **3l**



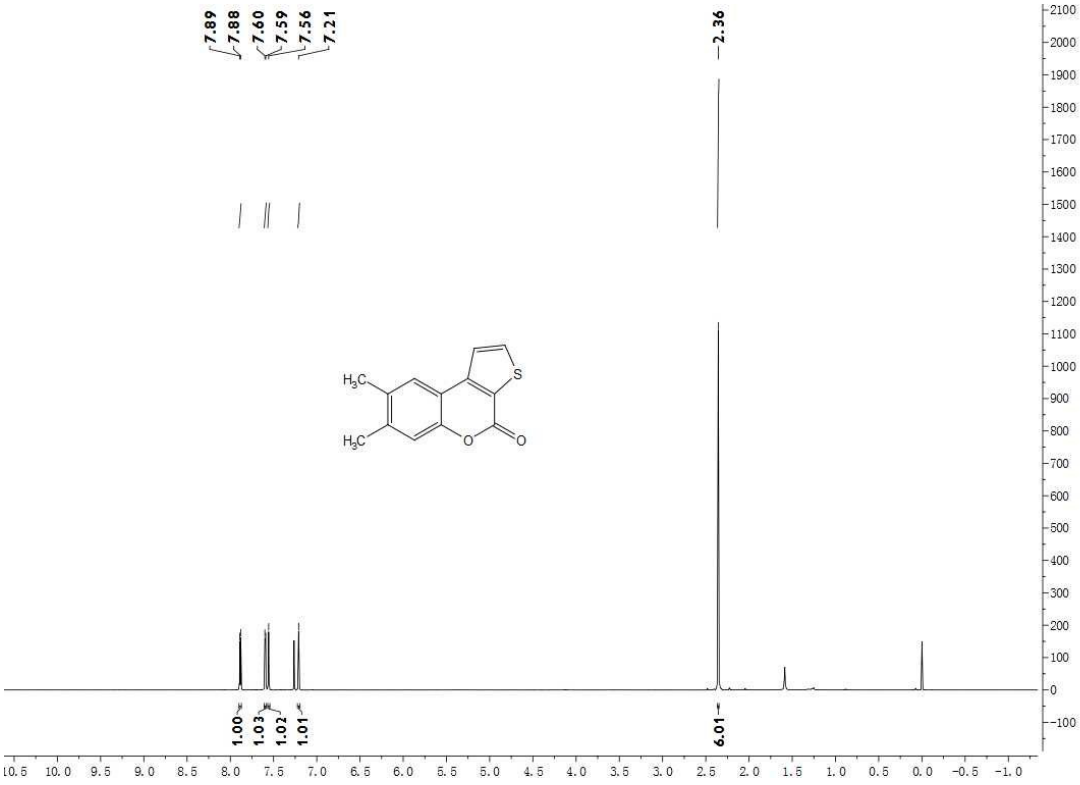
^{1}H NMR spectrum of **3m**



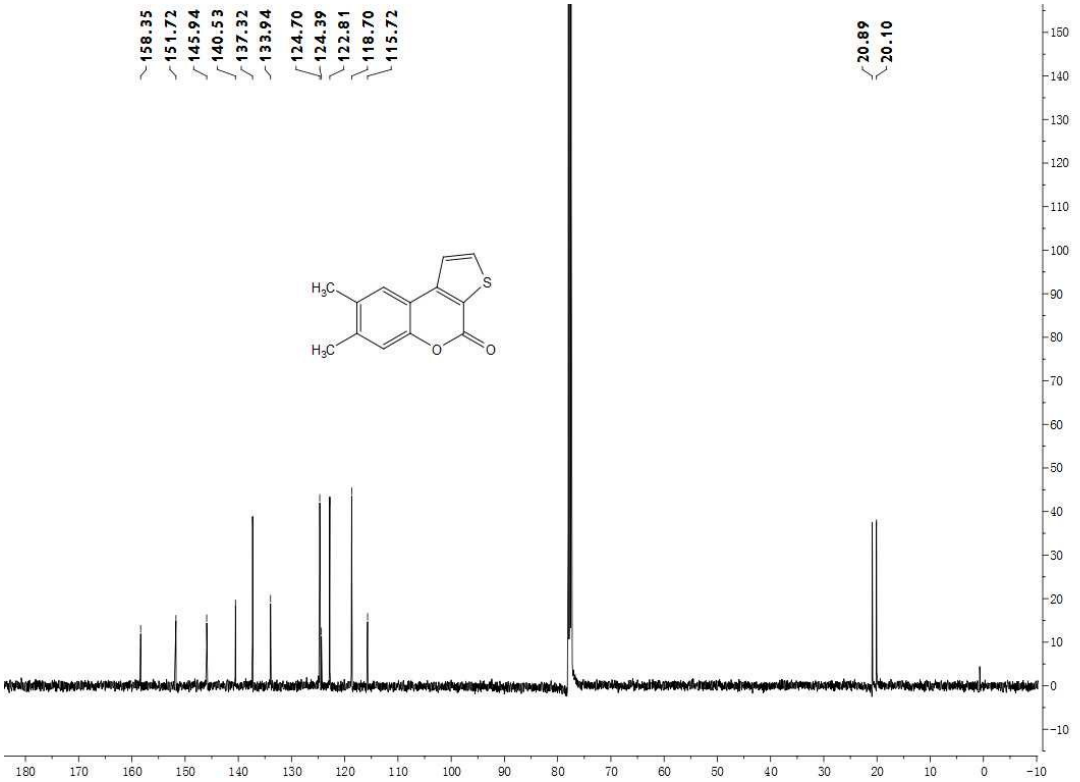
^{13}C NMR spectrum of **3m**



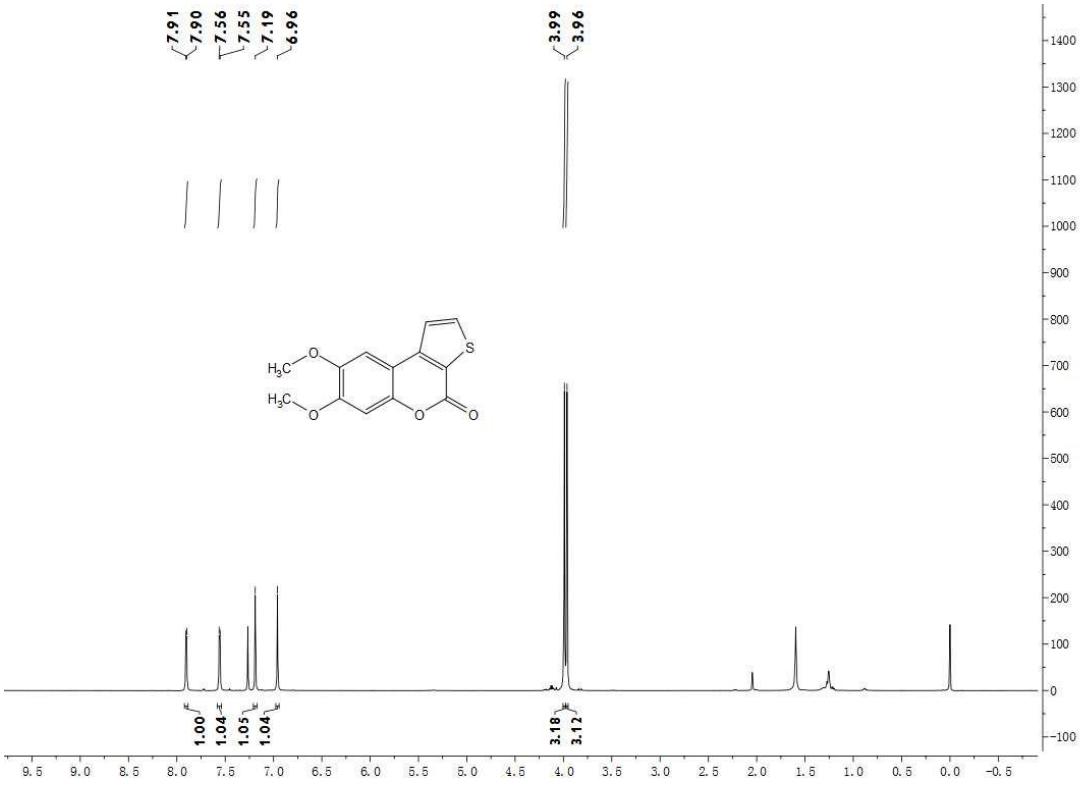
^{1}H NMR spectrum of **3n**



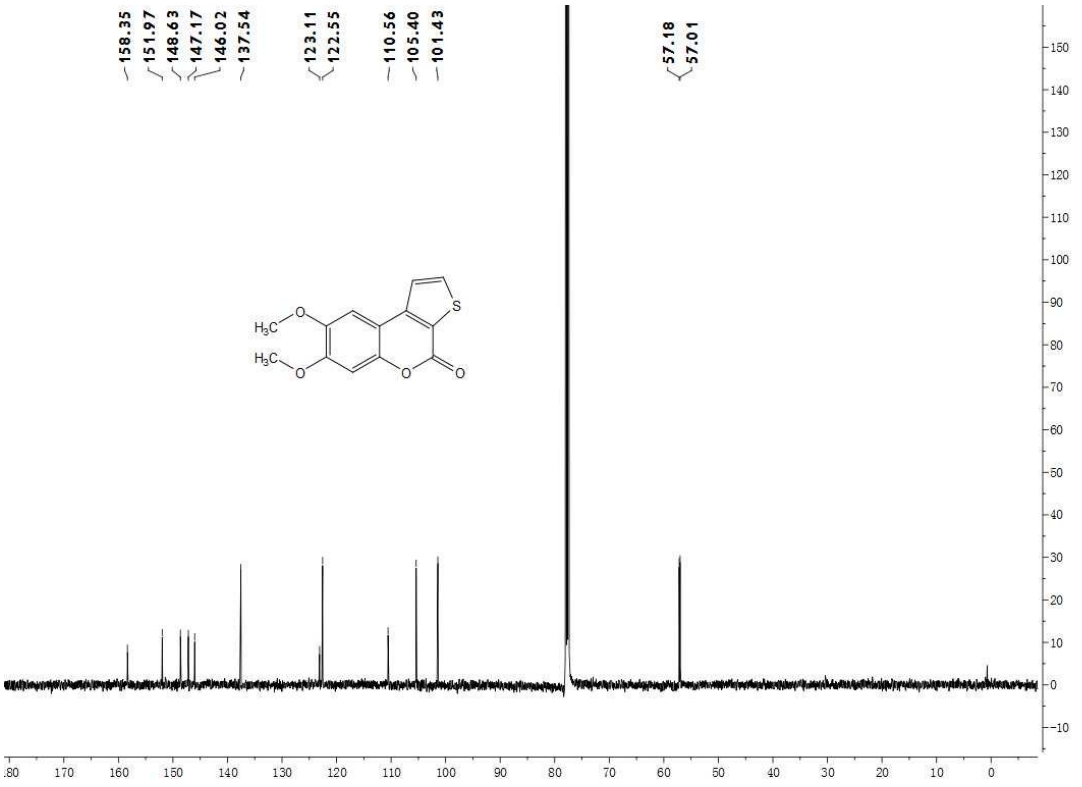
^{13}C NMR spectrum of **3n**



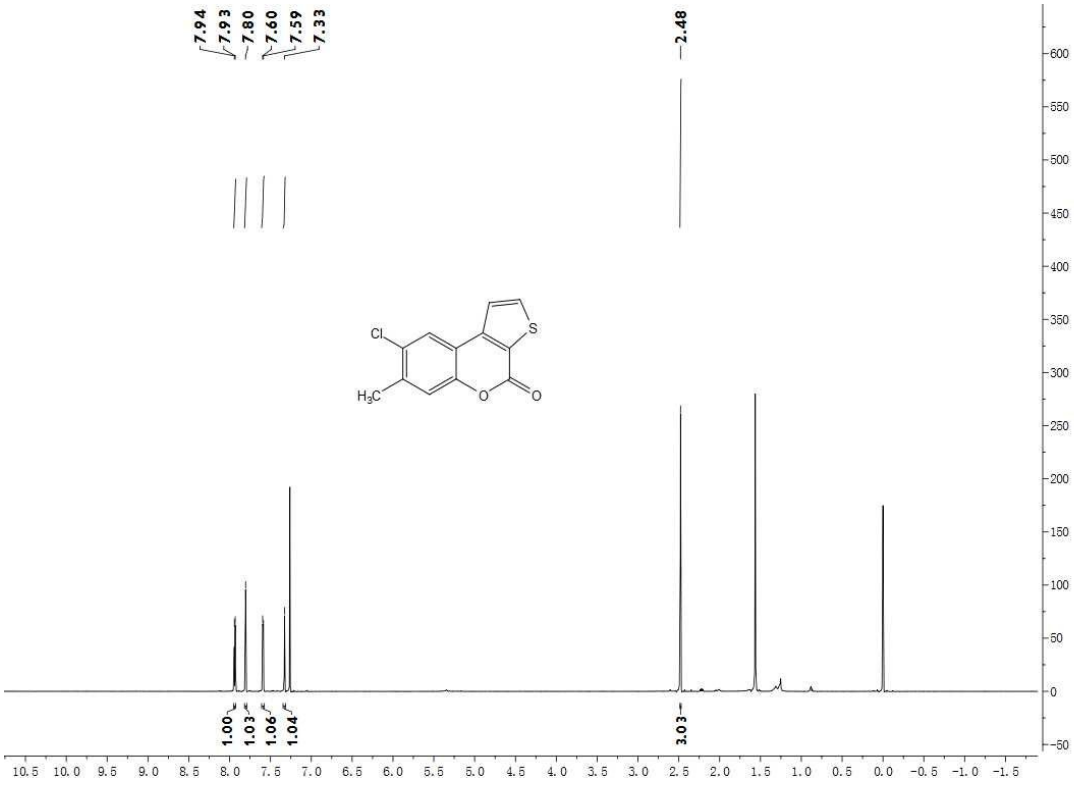
^{1}H NMR spectrum of **3o**



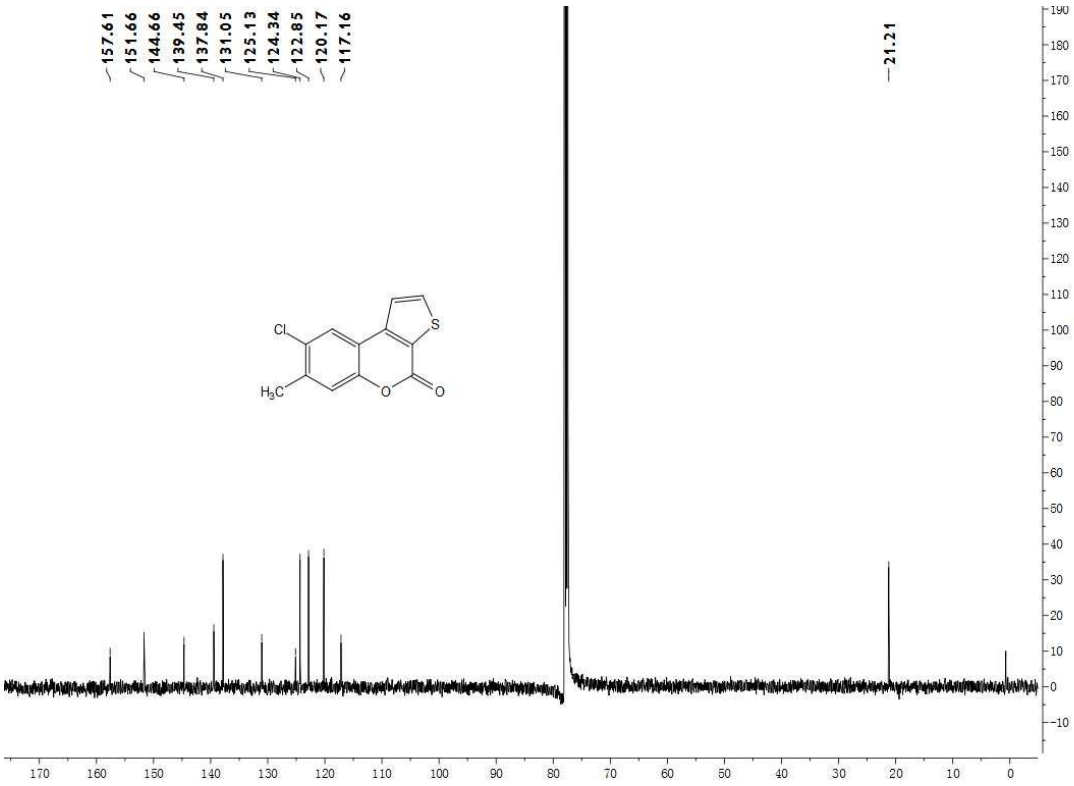
^{13}C NMR spectrum of **3o**



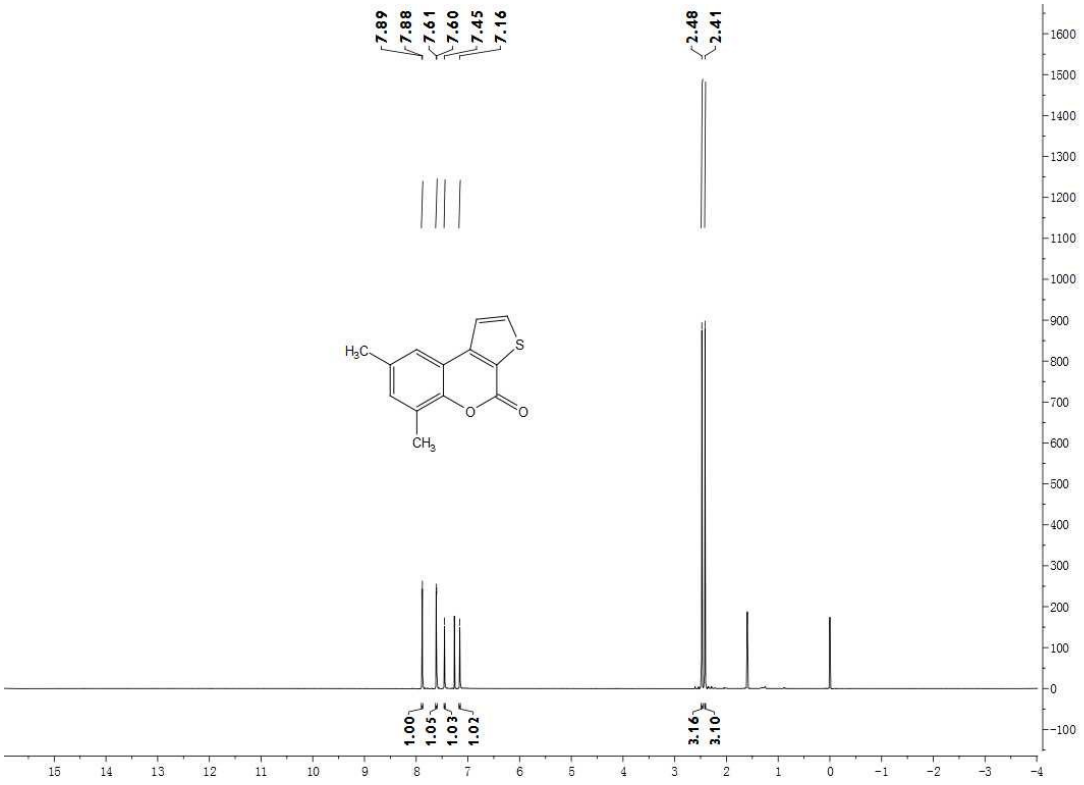
^{1}H NMR spectrum of **3p**



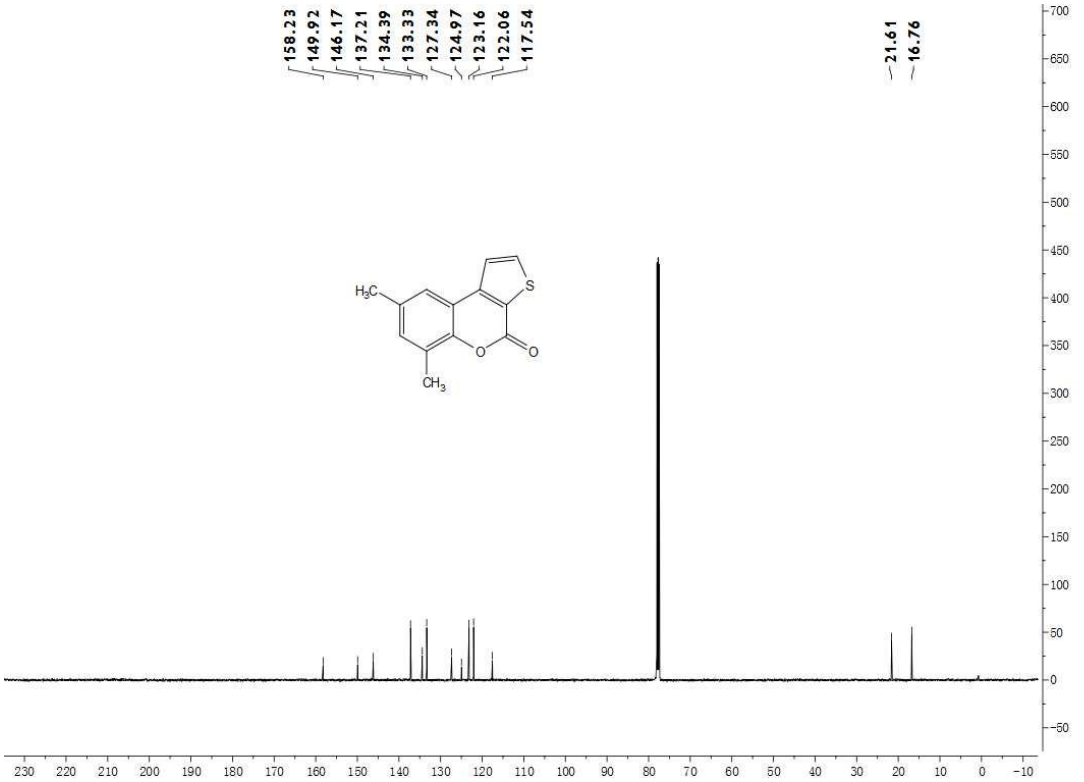
^{13}C NMR spectrum of **3p**



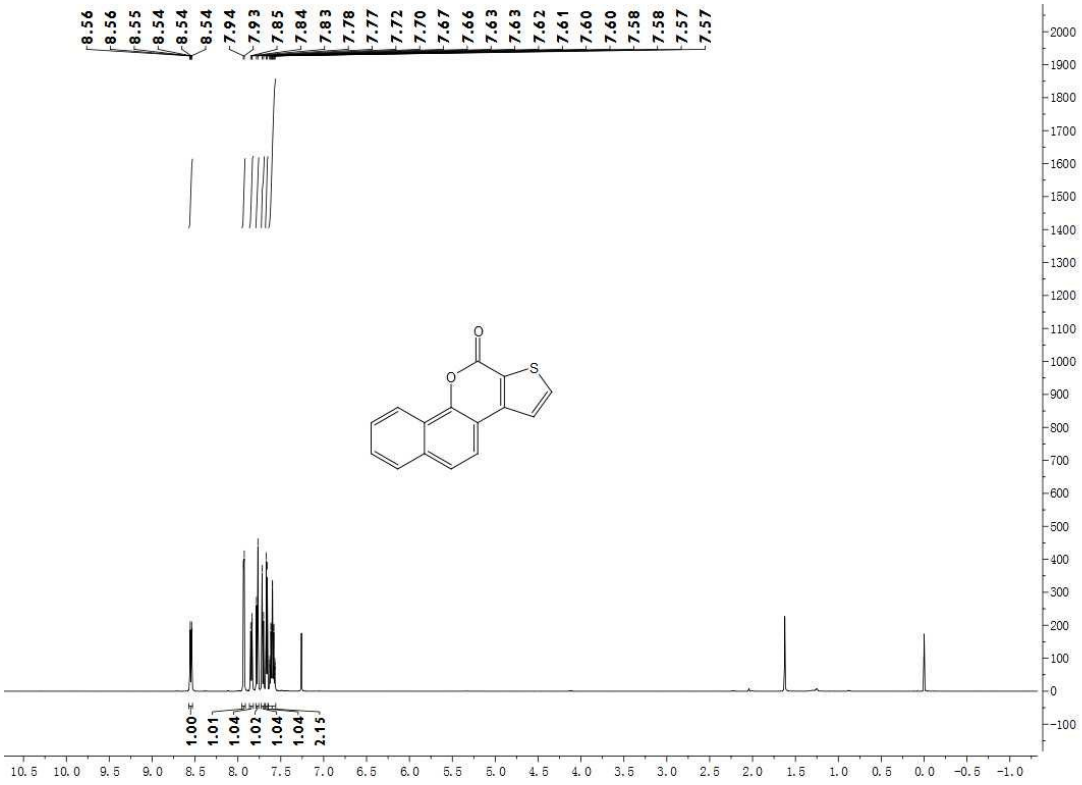
^{1}H NMR spectrum of **3q**



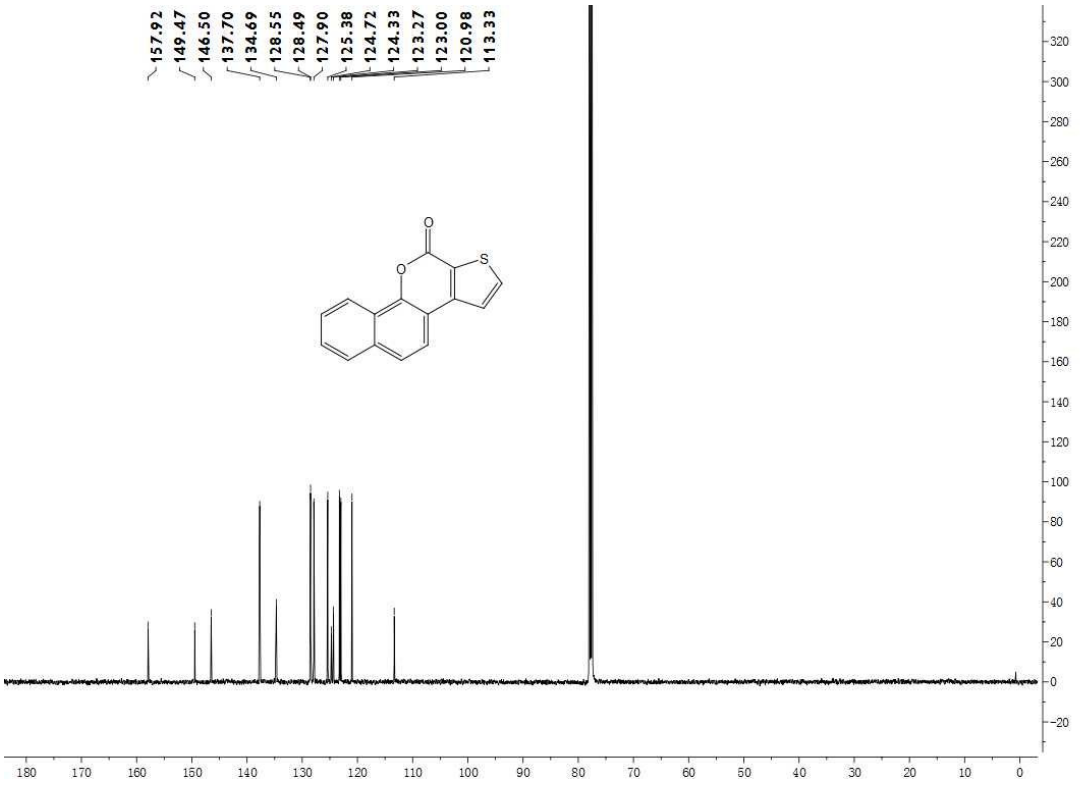
^{13}C NMR spectrum of **3q**



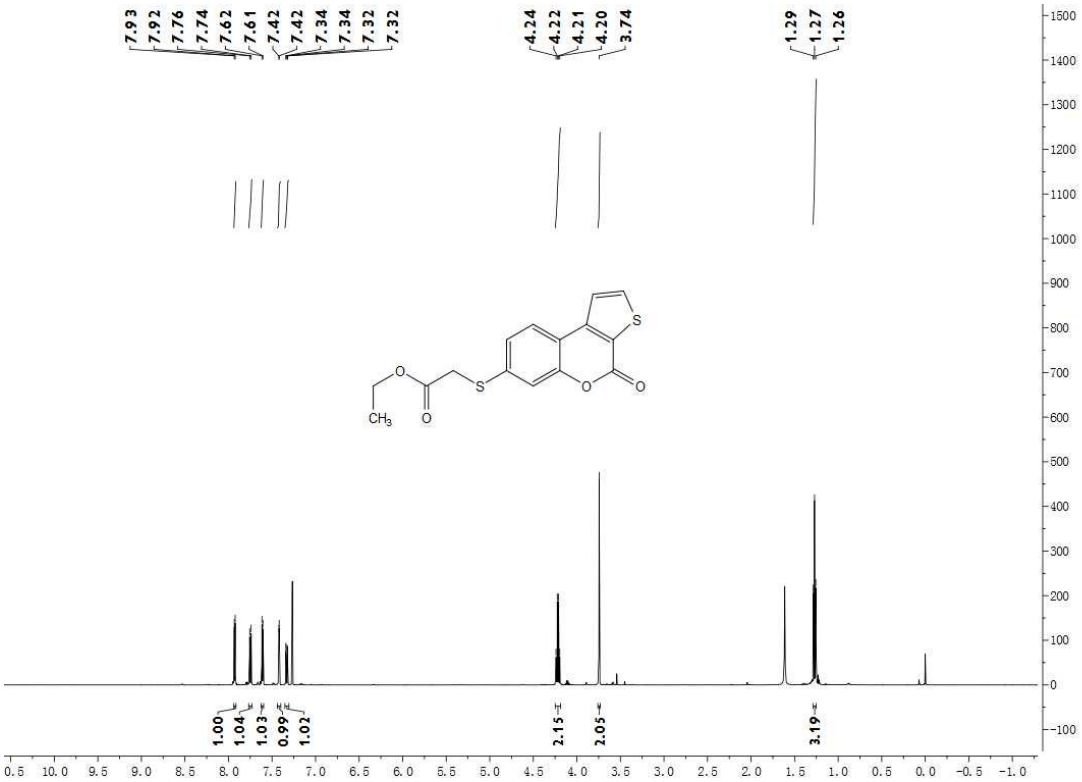
^{1}H NMR spectrum of **3r**



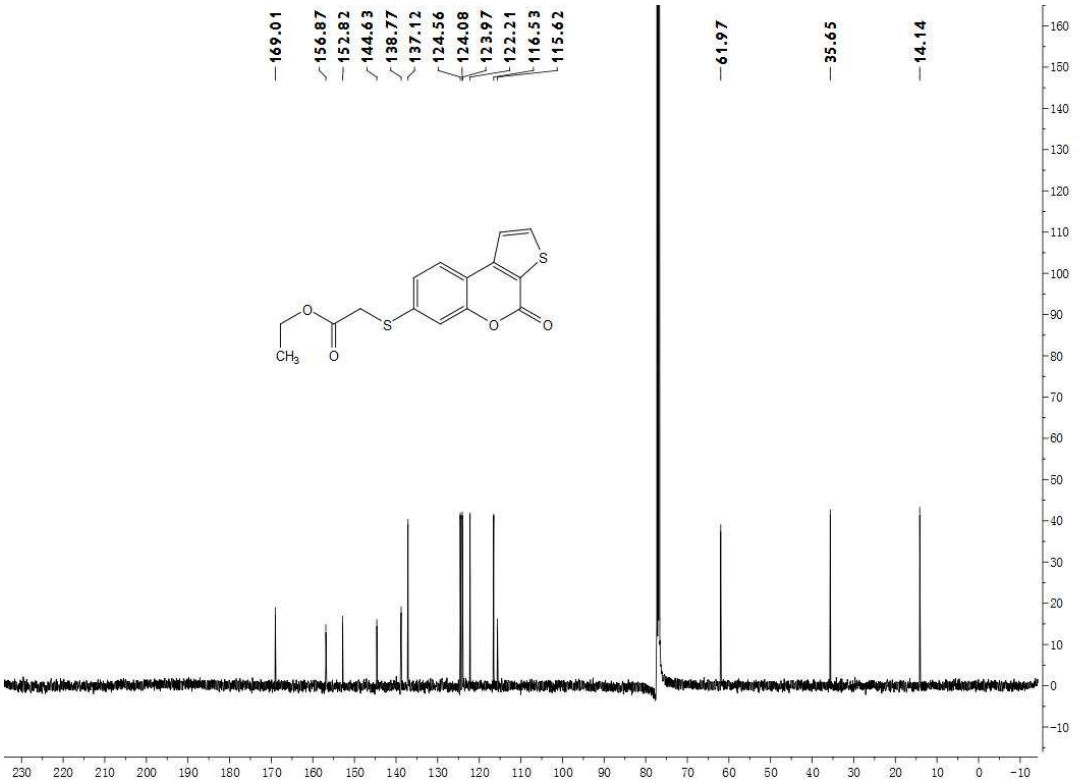
^{13}C NMR spectrum of **3r**



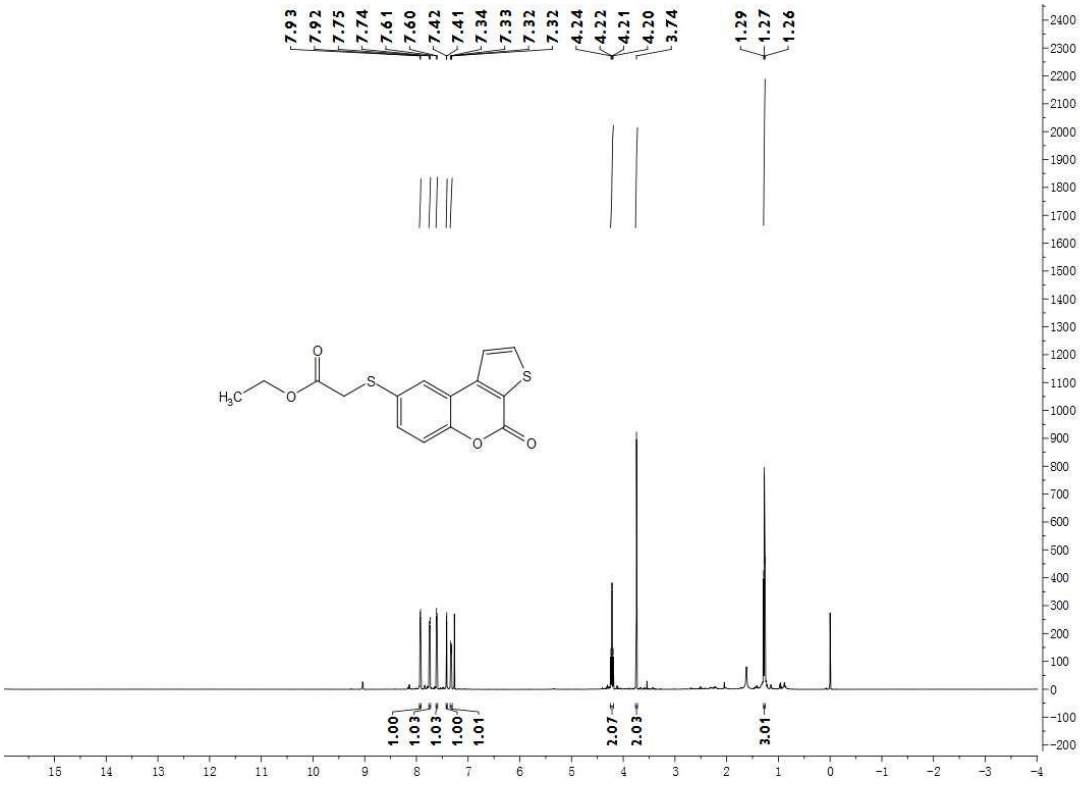
^{1}H NMR spectrum of **3s**



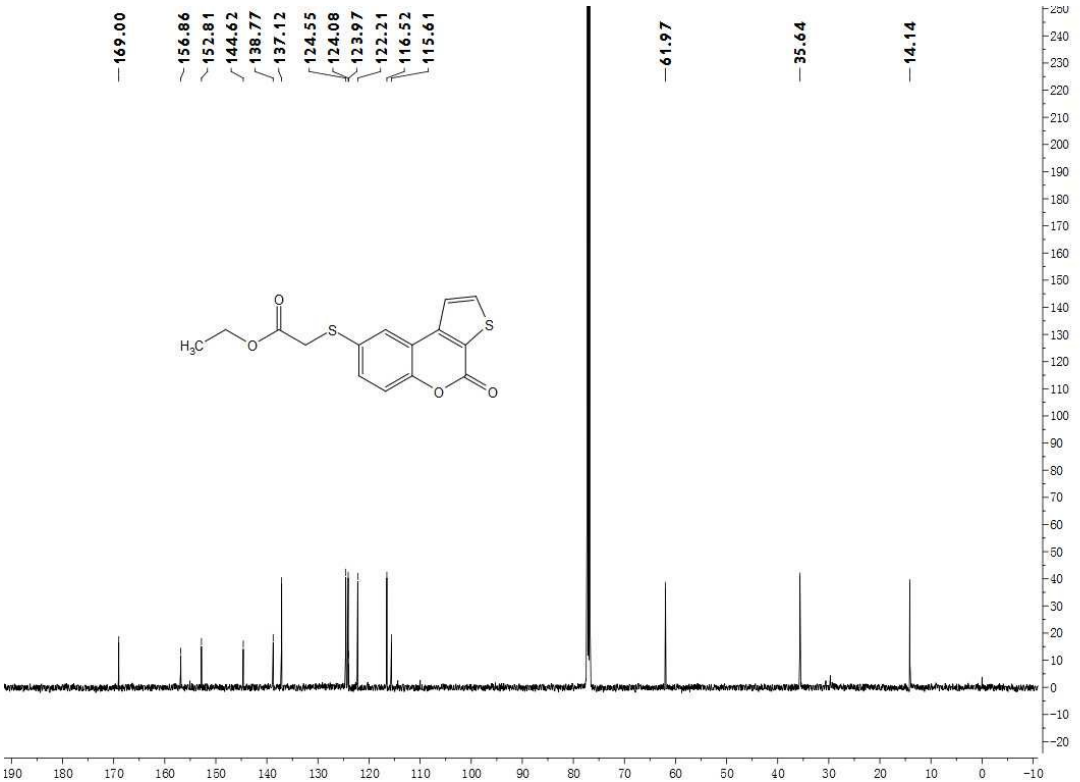
^{13}C NMR spectrum of **3s**



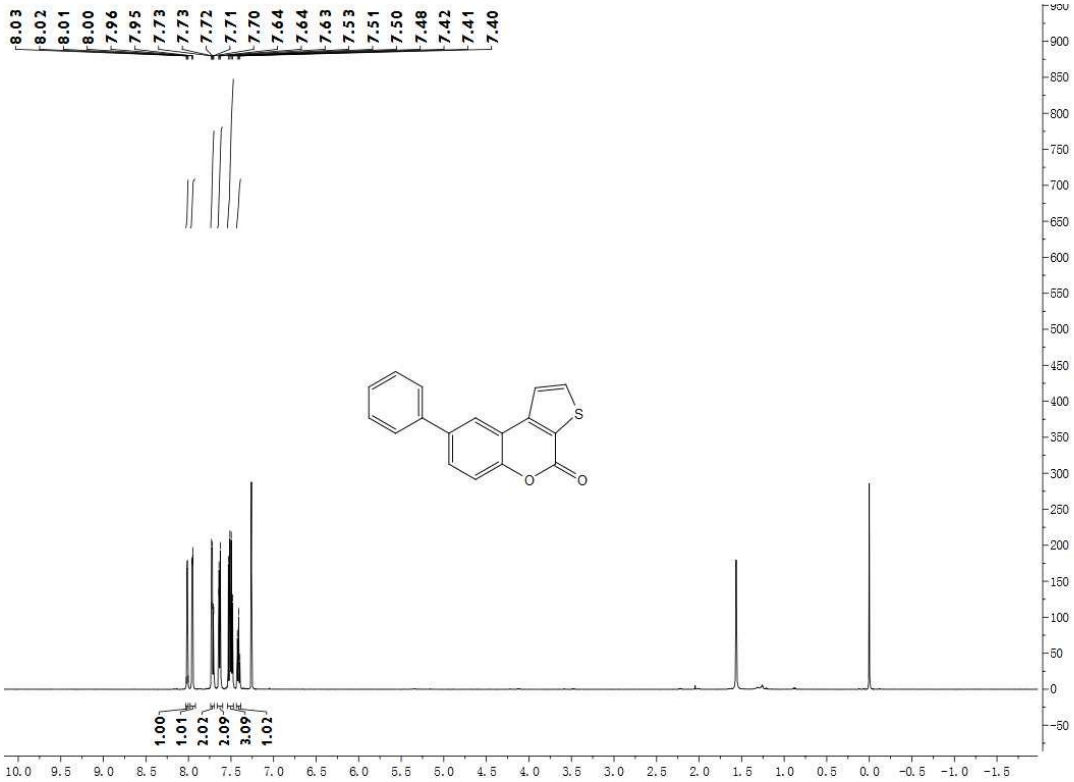
^{1}H NMR spectrum of **3t**



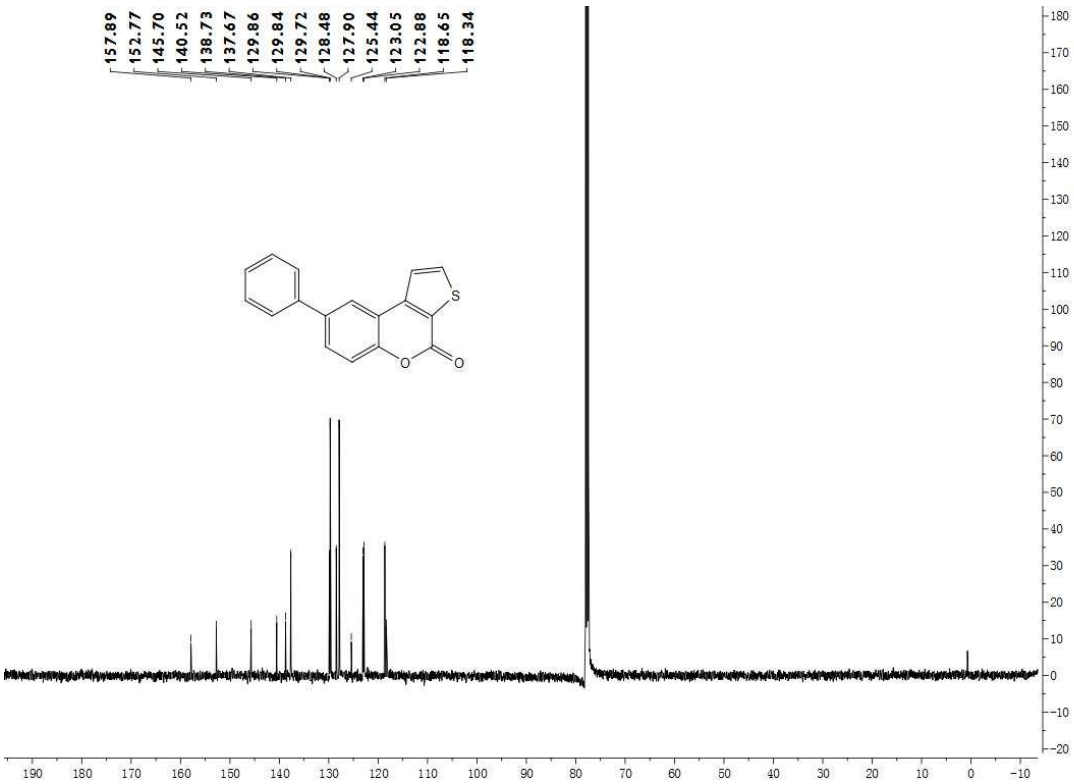
^{13}C NMR spectrum of **3t**



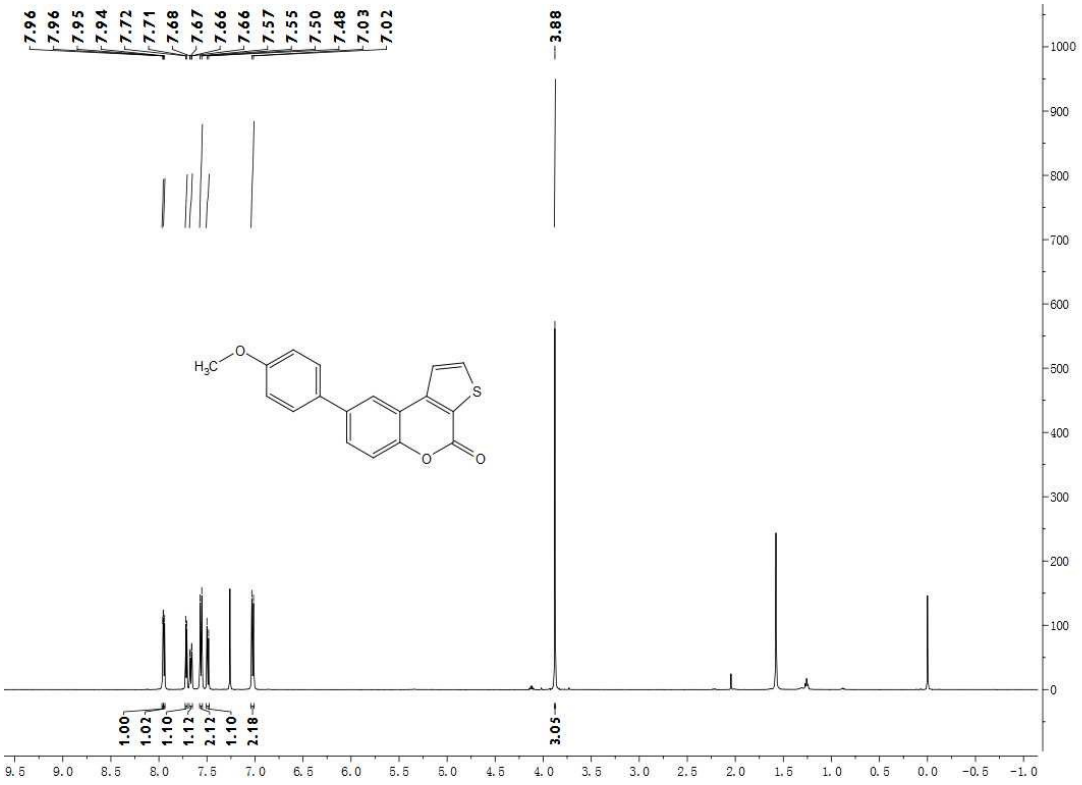
^{1}H NMR spectrum of **3u**



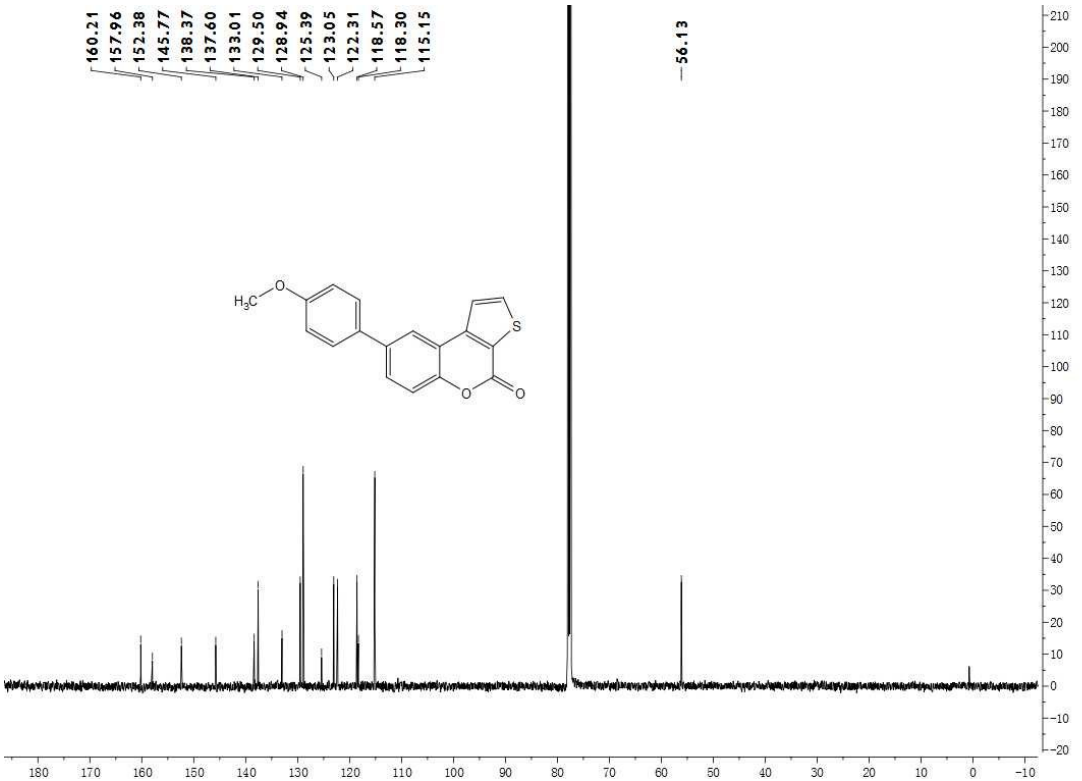
^{13}C NMR spectrum of **3u**



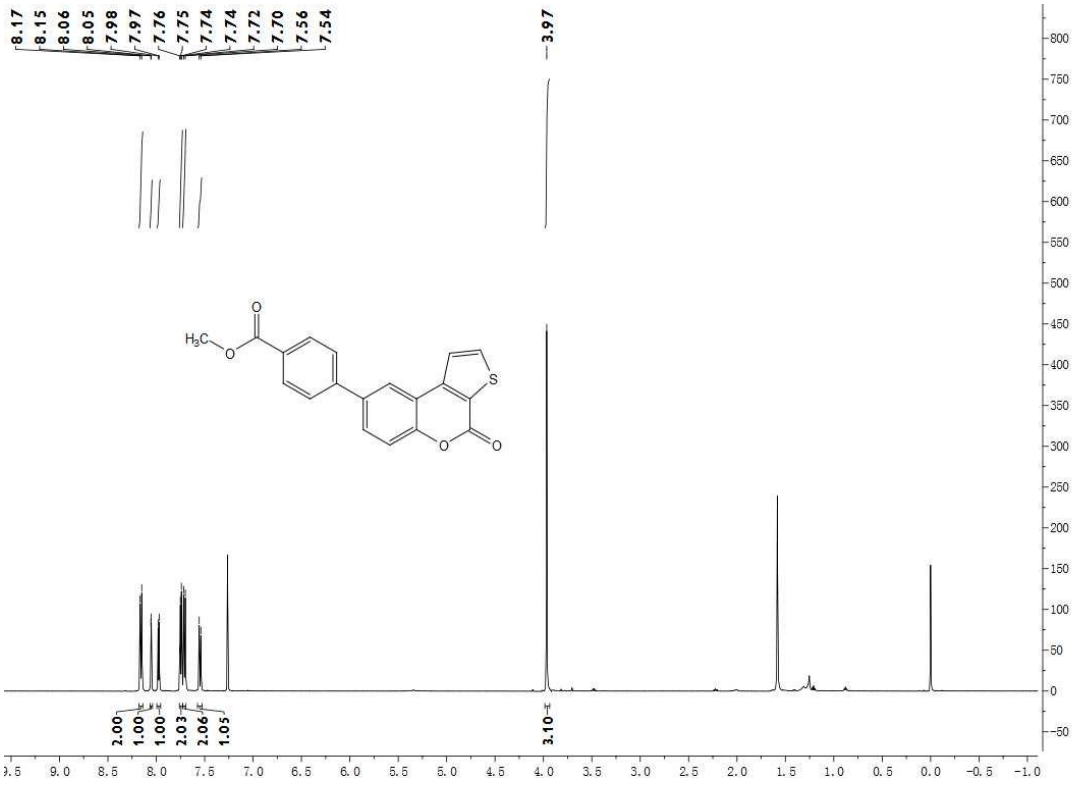
^{1}H NMR spectrum of **3v**



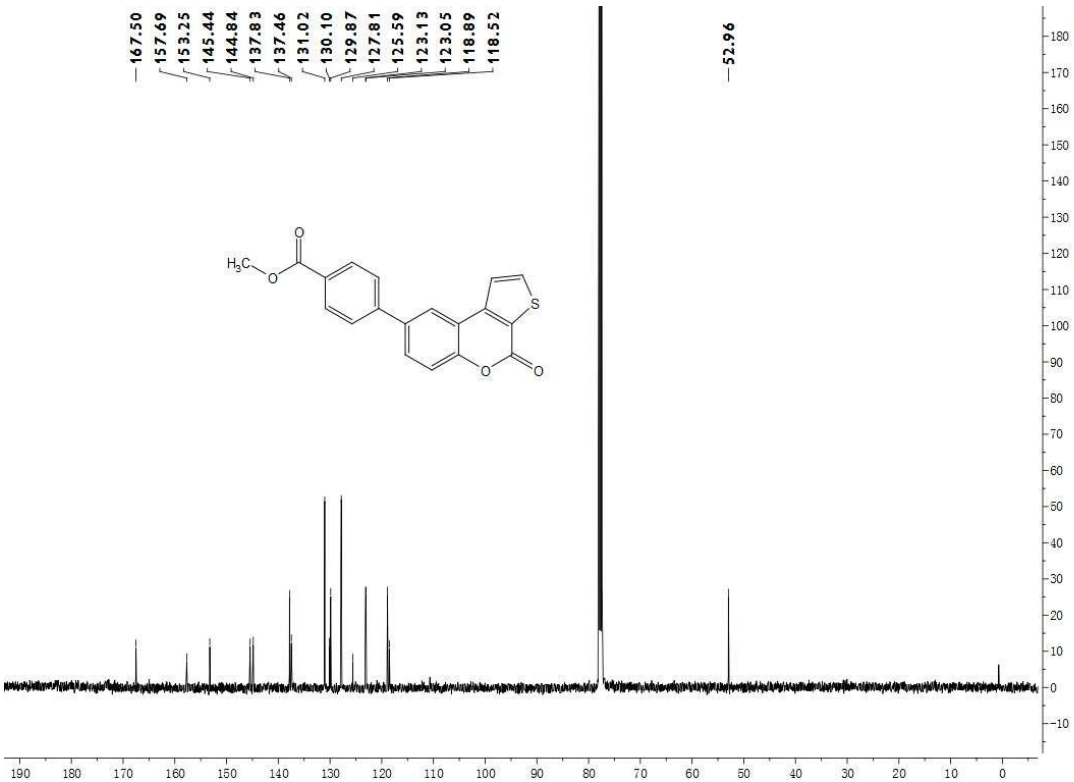
^{13}C NMR spectrum of **3v**



^{1}H NMR spectrum of **3w**



^{13}C NMR spectrum of **3w**



5、 X-ray Crystallography of 4*H*-thieno[2,3-c]chromen-4-one 3a

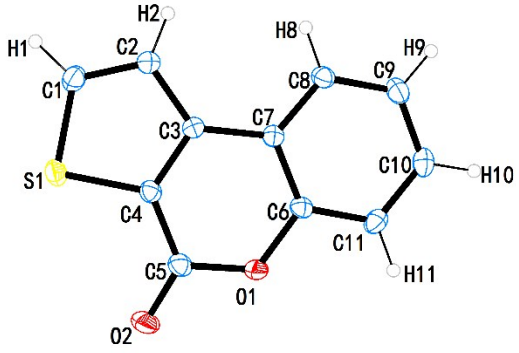


Table 1. Crystal data and structure refinement for **3a**.

CCDC number:	1498043
Empirical formula:	$C_{11}H_6O_2S$
Formula weight:	202.22
Temperature:	296 K
Wavelength:	0.71073Å
Crystal system:	Orthorhombic
Unit cell dimensions:	
	a = 12.1145 (11) Å
	b = 8.2023 (8) Å
	c = 18.5724 (16) Å
Volume:	1772.3 (3) $Å^3$
Z	8
Density (calculated):	1.516 Mg m^{-3}
Absorption coefficient:	m = 0.33 mm^{-1}
F(000)	832