Coumarin-3-formylpyrazoles as 3-Carbon Synthons in Cyclocondensation for the Synthesis of Spiro-fused Pentacyclic Spirooxindoles

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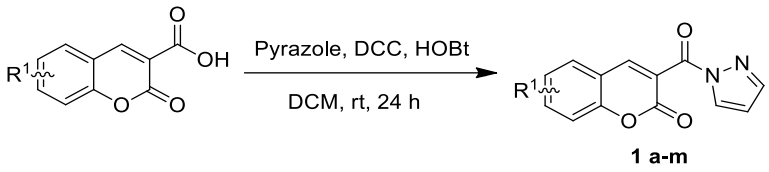
1. General experimental information.

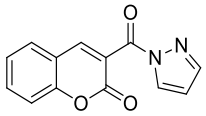
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.23 ppm, DMSO-d_6 at 39.51 ppm). Melting points were recorded on a melting point apparatus.

2. General procedure for the synthesis of 1.

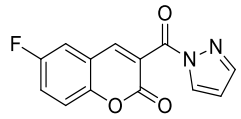


1 a-m

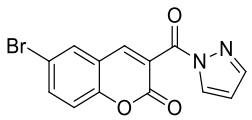
To a suspension of the 2-oxo-2*H*-chromene-3-carboxylic acid (5.0 mmol), HOBt (1.01 g, 7.5 mmol) and pyrazole (0.51 g, 7.5 mmol) in CH_2Cl_2 (20 mL) was added DCC (1.03 g, 5.0 mmol) at 0 ^{o}C and stirred for 15 min. The reaction mixture was warmed to room temperature and stirred for 24-72 h. Upon completion, the mixture was filtered through celite, and washed with CH_2Cl_2 (approximately 10 mL) and concentrated *in vacuo*. The desired products were recrystallised from absolute ethanol to give compounds **1a-m** as a solid.



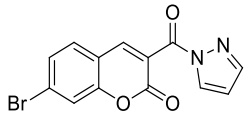
3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1a). White solid; 744.1 mg, 62% yield; m.p. 168.5-169.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.9 Hz, 1H), 8.18 (s, 1H), 7.75 (s, 1H), 7.69 – 7.58 (m, 2H), 7.42 – 7.32 (m, 2H), 6.54 (dd, *J* = 2.9, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 157.6, 154.9, 146.0, 145.3, 134.1, 129.5, 129.4, 125.2, 122.3, 117.9, 117.3, 110.8; HRMS (ESI) calcd. for $C_{13}H_8N_2NaO_3$ $[M + Na]^+$ 263.0433, found: 263.0427.



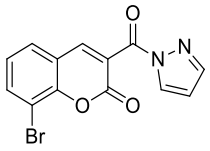
6-fluoro-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1b). White solid; 283.6 mg, 22% yield; m.p. 214.2-215.0 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.9 Hz, 1H), 8.10 (s, 1H), 7.75 (d, *J* = 0.9 Hz, 1H), 7.46 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.56 (dd, *J* = 2.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 159.1 (d, *J* = 245.9 Hz), 157.2, 151.0, 145.4, 144.6 (d, *J* = 2.9 Hz), 129.4, 123.6, 121.6 (d, *J* = 24.5 Hz), 118.9 (d, *J* = 8.3 Hz), 118.5 (d, *J* = 9.2 Hz), 114.5 (d, *J* = 24.0 Hz), 111.0; HRMS (ESI) calcd. for $C_{13}H_7FN_2NaO_3$ $[M + Na]^+$ 281.0333, found: 281.0326.



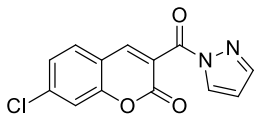
6-bromo-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1c). White solid; 380.0 mg, 24% yield; m.p. 212.7-214.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 1H), 8.07 (s, 1H), 7.76 – 7.69 (m, 3H), 7.32 – 7.27 (m, 1H), 6.55 (dd, *J* = 2.9, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 156.9, 153.6, 145.4, 144.4, 136.7, 131.5, 129.4, 123.4, 119.8, 119.0, 117.8, 111.0; HRMS (ESI) calcd. for $C_{13}H_7BrN_2NaO_3$ $[M + Na]^+$ 340.9532, found: 340.9529.



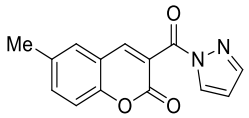
7-bromo-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1d). White solid; 396.3 mg, 25% yield; m.p. 200.1-201.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 1H), 8.13 (s, 1H), 7.75 (s, 1H), 7.58 (s, 1H), 7.53 – 7.41 (m, 2H), 6.55 (dd, *J* = 2.9, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 156.6, 154.8, 145.1, 145.1, 130.1, 129.2, 128.6, 128.3, 122.2, 120.4, 116.6, 110.8; HRMS (ESI) calcd. for $C_{13}H_7BrN_2NaO_3$ [M + Na]$^+$ 340.9532, found: 340.9547.



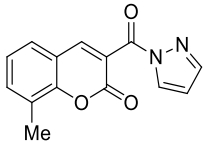
8-bromo-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1e). White solid; 301.0 mg, 19% yield; m.p. 196.9-197.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 1H), 8.13 (s, 1H), 7.87 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.76 (s, 1H), 7.61 – 7.51 (m, 1H), 7.25 (d, *J* = 5.8 Hz, 1H), 6.56 (dd, *J* = 2.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 156.6, 151.6, 145.4, 145.3, 137.4, 129.4, 128.6, 125.8, 123.2, 119.2, 111.0, 110.8; HRMS (ESI) calcd. for $C_{13}H_7BrN_2NaO_3$ [M + Na]$^+$ 340.9532, found: 340.9522.



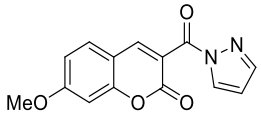
7-chloro-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1f). White solid; 301.1 mg, 22% yield; m.p. 213.1-214.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 1H), 8.14 (s, 1H), 7.75 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.55 (dd, *J* = 2.9, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 156.8, 155.1, 145.3, 145.1, 140.3, 130.2, 129.4, 125.9, 122.2, 117.6, 116.5, 110.9; HRMS (ESI) calcd. for $C_{13}H_7ClN_2NaO_3$ [M + Na]$^+$ 297.0037, found: 297.0048.



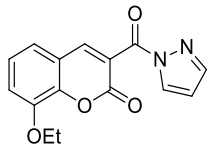
6-methyl-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1g). White solid; 825.7 mg, 65% yield; m.p. 172.1-173.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9, 1H), 8.12 (s, 1H), 7.74 (d, *J* = 1.7, 1H), 7.45 (dd, *J* = 8.6, 1.7, 1H,), 7.38 (s, 1H), 7.28 (d, *J* = 8.6, 1H), 6.54 (dd, *J* = 2.9, 1.5, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 157.8, 153.1, 146.2, 145.2, 135.2, 135.1, 129.4, 129.1, 122.0, 117.6, 116.9, 110.7, 20.9; HRMS (ESI) calcd. for $C_{14}H_{10}N_2NaO_3$ [M + Na]$^+$ 277.0584, found: 277.0572.



8-methyl-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1h): White solid; 558.6 mg, 44% yield; m.p. 165.3-167.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.9 Hz, 1H), 8.21 (s, 1H), 7.80 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 6.58 (dd, *J* = 2.9, 1.4 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 157.7, 153.2, 146.5, 145.1, 135.4, 129.4, 127.2, 126.8, 124.8, 121.9, 117.6, 110.7, 15.6; HRMS (ESI) calcd. for $C_{14}H_{10}N_2NaO_3$ [M + Na]$^+$ 277.0584, found: 277.0576.

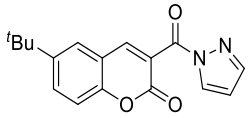


7-methoxy-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1i). White solid; 891.1 mg, 66% yield; m.p. 164.9-166.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 1H), 8.20 (s, 1H), 7.75 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.53 (dd, *J* = 2.9, 1.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.0, 157.9, 157.2, 147.1, 144.9, 130.8, 129.6, 117.8, 113.8, 111.6, 110.5, 100.9, 56.2; HRMS (ESI) calcd. for $C_{14}H_{10}N_2NaO_4$ [M + Na]$^+$ 293.0533, found: 293.0528.

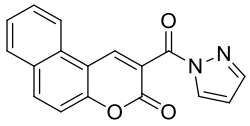


8-ethoxy-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1j). White solid; 894.1 mg, 63% yield; m.p. 185.0-186.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.9 Hz, 1H), 8.13 (s, 1H), 7.76 – 7.68 (m, 1H), 7.26 –

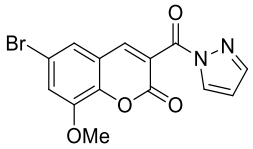
7.20 (m, 1H), 7.19 – 7.10 (m, 2H), 6.52 (dd, *J* = 2.9, 1.4 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 157.3, 146.8, 146.2, 145.1, 144.8, 129.6, 125.0, 122.4, 120.6, 118.6, 117.1, 110.8, 65.4, 14.9; HRMS (ESI) calcd. for $C_{15}H_{12}N_2NaO_4$ [M + Na]$^+$ 307.0689, found: 307.0688.



6-(*tert*-butyl)-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1k). White solid; 591.6 mg, 40% yield; m.p. 162.0-163.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.9 Hz, 1H), 8.19 (s, 1H), 7.75 (s, 1H), 7.69 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 6.54 (dd, *J* = 2.9, 1.5 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 157.9, 152.9, 148.5, 146.7, 145.2, 132.0, 129.5, 125.7, 121.8, 117.3, 116.8, 110.7, 34.8, 31.5; HRMS (ESI) calcd. for $C_{17}H_{16}N_2NaO_3$ [M + Na]$^+$ 319.1053, found: 319.1044.

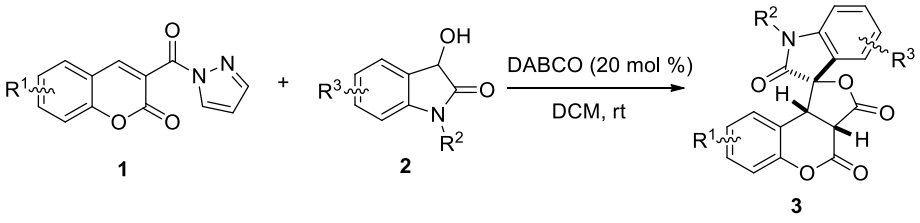


2-(1*H*-pyrazole-1-carbonyl)-3*H*-benzo[*f*]chromen-3-one (1l). Yellow solid; 376.8 mg, 26% yield; m.p. 174.6-176.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.41 (d, *J* = 2.5 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 1H), 7.77 – 7.68 (m, 1H), 7.65 – 7.57 (m, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 6.57 (dd, *J* = 2.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 157.6, 155.5, 145.2, 142.4, 135.8, 130.5, 129.5, 129.4, 129.2, 126.8, 121.6, 120.6, 117.0, 112.4, 110.8; HRMS (ESI) calcd. for $C_{17}H_{10}N_2NaO_3$ [M + Na]$^+$ 313.0584, found: 313.0584.

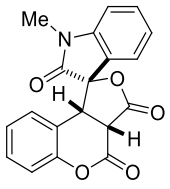


6-bromo-8-methoxy-3-(1*H*-pyrazole-1-carbonyl)-2*H*-chromen-2-one (1m). White solid; 365.1 mg, 21% yield; m.p. 226.4-228.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.9 Hz, 1H), 8.03 (s, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.26 (s, 1H), 6.54 (dd, *J* = 2.9, 1.4 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 156.5, 148.2, 145.4, 144.6, 143.7, 129.4, 123.7, 122.6, 119.5, 118.8, 117.5, 111.0, 56.9; HRMS (ESI) calcd. for $C_{14}H_9N_2NaO_4$ [M + Na]$^+$ 370.9638, found: 370.9625.

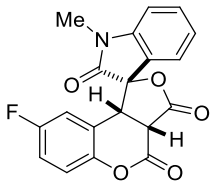
3. General experimental procedures for synthesis of compounds 3.



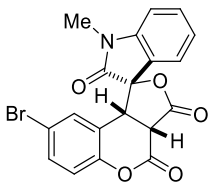
In an ordinary glass tube equipped with a magnetic stirring bar, coumarin-3-formylpyrazoles **1** (0.1 mmol, 1.0 equiv.), 3-hydroxyoxindoles **2** (0.12 mmol, 1.2 equiv.) and DABCO (20 mol %, 0.02 mmol) were placed in 0.5 mL of DCM at room temperature, and the mixture was stirred at this temperature until the reaction completed (monitored by TLC). Then, the resulting mixture was purified by column chromatography (dichloromethane/ethyl acetate = 100/1 to 20/1) to give the desired product **3**. The diastereomeric ratio (dr) was determined by ^{1}H NMR.



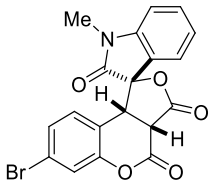
1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3a). White solid; 33.3 mg, 99% yield; > 20:1 dr; m.p. 267.8-269.5 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (dd, J = 7.5, 1.3 Hz, 1H), 7.55 (td, J = 7.8, 1.3 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.13 – 7.03 (m, 2H), 6.93 (td, J = 7.6, 1.2 Hz, 1H), 6.30 (dd, J = 7.6, 1.6 Hz, 1H), 4.67 (s, 2H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 168.9, 158.5, 150.8, 144.4, 132.21, 130.2, 127.2, 125.5, 124.5, 124.0, 123.1, 117.1, 114.4, 109.8, 85.4, 43.2, 42.7, 25.9; HRMS (ESI) calcd. for $C_{19}H_{13}NNaO_5$ [M + Na]$^+$ 358.0691, found: 358.0691. The ee of compound **3a** was determined by HPLC analysis using a Chiralpak AD-H column (60/40 hexane/EtOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 11.8 min, t_{minor} = 10.3 min).



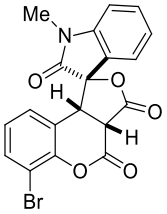
8-fluoro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3b). White solid; 27.2 mg, 77% yield; > 20:1 dr; m.p. 274.1-276.0 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.4 Hz, 1H), 7.57 (dd, J = 8.3, 7.2 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.10 (d, J = 7.7 Hz, 1H), 6.20 – 5.92 (m, 1H), 4.84 – 4.56 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.6, 158.2, 157.9 (d, J = 240.3 Hz), 147.2 (d, J = 2.3 Hz), 144.3, 132.3, 125.6, 124.1, 122.6, 118.9 (d, J = 8.7 Hz), 117.0 (d, J = 23.4 Hz), 116.1 (d, J = 8.2 Hz), 113.3 (d, J = 24.2 Hz), 109.8, 85.2, 43.1, 42.2, 26.0; HRMS (ESI) calcd. for $C_{19}H_{12}FNNaO_5$ [M + Na]$^+$ 376.0592, found: 376.0578.



8-bromo-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3c). White solid; 34.6 mg, 84% yield; > 20:1 dr; m.p. 289.2-291.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.2 Hz, 1H), 7.64 – 7.46 (m, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.11 (dd, J = 8.3, 5.3 Hz, 2H), 6.37 (d, J = 2.4 Hz, 1H), 4.68 (s, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.5, 158.0, 150.2, 144.3, 132.9, 132.3, 129.6, 125.6, 124.1, 122.6, 119.3, 117.0, 115.6, 109.8, 85.2, 42.8, 42.3, 26.0; HRMS (ESI) calcd. for $C_{19}H_{12}BrNNaO_5$ [M + Na]$^+$: 435.9791, found: 435.9782.

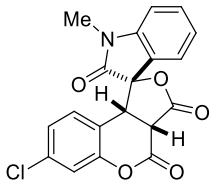


7-bromo-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3d). White solid; 33.4 mg, 81% yield; > 20:1 dr; m.p. 256.6-257.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.1 Hz, 1H), 7.55 (td, J = 7.8, 1.3 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.38 – 7.25 (m, 1H), 7.17 (dd, J = 8.2, 2.0 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.25 (d, J = 8.2 Hz, 1H), 4.67 (s, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.5, 158.1, 151.5, 144.4, 132.3, 128.9, 127.4, 125.6, 124.1, 122.8, 122.1, 120.0, 114.1, 109.9, 85.1, 42.6, 42.5, 26.0; HRMS (ESI) calcd. for $C_{19}H_{12}BrNNaO_5$ [M + Na]$^+$ 435.9791, found: 435.9793.

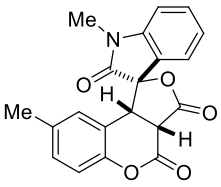


6-bromo-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3e). White solid; 40.0 mg, 97% yield; > 20:1 dr; m.p. 267.9-269.4 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.89 (t, J = 7.7 Hz, 1H), 6.30 (d, J = 7.3 Hz, 1H), 4.84 – 4.62 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.5, 158.0, 147.6, 144.4, 133.6, 132.3, 126.7, 125.6, 125.5, 124.1, 122.9, 116.7, 109.9, 109.7, 85.3, 43.1, 42.8, 26.0; HRMS

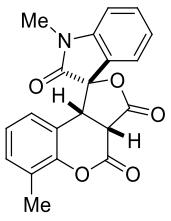
(ESI) calcd. for $C_{19}H_{12}BrNNaO_5$ $[M + Na]^+$ 435.9791, found: 435.9786.



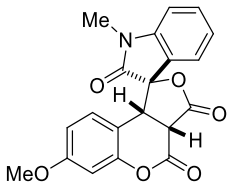
7-chloro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3f). White solid; 29.5 mg, 80% yield; > 20:1 dr; m.p. 296.6-297.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.3 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.13 – 6.99 (m, 2H), 6.31 (d, J = 8.3 Hz, 1H), 4.87 – 4.54 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.6, 158.1, 151.5, 144.4, 134.0, 132.3, 128.7, 125.5, 124.6, 124.1, 122.8, 117.2, 113.7, 109.9, 85.2, 42.5, 42.5, 26.0; HRMS (ESI) calcd. for $C_{19}H_{12}ClNNaO_5$ $[M + Na]^+$ 392.0296, found: 392.0297.



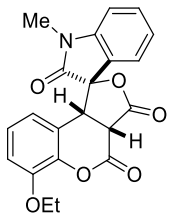
1',8-dimethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3g). White solid; 34.3 mg, 98% yield; > 20:1 dr; m.p. 253.4-254.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.4 Hz, 1H), 7.56 (td, J = 7.8, 1.3 Hz, 1H), 7.40 – 7.23 (m, 1H), 7.20 – 7.04 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.05 (d, J = 2.2 Hz, 1H), 4.66 – 4.56 (m, 2H), 2.79 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.8, 158.5, 148.7, 144.4, 133.4, 132.1, 130.5, 127.2, 125.3, 123.9, 123.1, 116.7, 114.0, 109.6, 85.3, 43.2, 42.6, 25.9, 20.0; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_5$ $[M + Na]^+$ 372.0842, found: 372.0842.



1',6-dimethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3h). White solid; 33.8 mg, 97% yield; > 20:1 dr; m.p. 276.9-278.3 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, J = 7.4 Hz, 1H), 7.64 – 7.47 (m, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.12 (d, J = 7.6 Hz, 1H), 4.73 – 4.54 (m, 2H), 2.80 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.9, 158.5, 149.1, 144.4, 132.1, 131.3, 125.5, 125.4, 124.7, 123.9, 123.8, 123.2, 114.1, 109.7, 85.4, 43.1, 42.6, 25.9, 15.5; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_5$ $[M + Na]^+$ 372.0842, found: 372.0835.

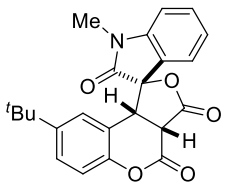


7-methoxy-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3i). White solid; 36.1 mg, 99% yield; > 20:1 dr; m.p. 265.1-266.7 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.84 (d, J = 6.9 Hz, 1H), 7.53 (td, J = 7.8, 1.1 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 2.5 Hz, 1H), 6.53 (dd, J = 8.5, 2.5 Hz, 1H), 6.20 (d, J = 8.5 Hz, 1H), 4.68 – 4.54 (m, 2H), 3.70 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.4, 168.9, 160.4, 158.6, 151.8, 144.4, 132.2, 128.0, 125.5, 124.0, 123.2, 111.0, 109.8, 106.0, 102.2, 85.4, 55.6, 42.7, 42.7, 26.0; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_6$ $[M + Na]^+$ 388.0792, found: 388.0787.

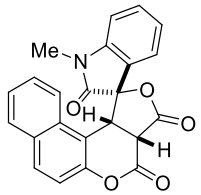


6-ethoxy-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3j). White solid; 36.8 mg, 97% yield; > 20:1 dr; m.p. 233.3-234.7 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.85 (t, J = 7.9 Hz, 1H), 5.82 (d, J = 7.6 Hz, 1H), 4.71 – 4.57 (m, 2H), 4.11 – 3.96 (q, J = 7.0 Hz, 2H), 2.82 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.9, 158.4, 146.2, 144.5, 140.0, 132.2, 125.4, 124.4, 124.0, 123.3, 118.1, 115.1, 113.6, 109.8, 85.3, 64.1, 43.2, 42.5, 26.0, 14.6; HRMS (ESI) calcd. for $C_{21}H_{17}NNaO_6$ [M +

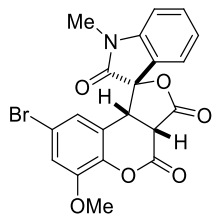
Na]$^+$ 402.0948, found: 402.0929.



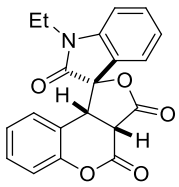
8-(*tert*-butyl)-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)trione (3k). White solid; 27.4 mg, 70% yield; > 20:1 dr; m.p. 255.6-257.2 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.13 (d, *J* = 2.2 Hz, 1H), 4.65 – 4.55 (m, 2H), 2.71 (s, 3H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 169.0, 158.5, 148.4, 146.7, 144.3, 132.0, 126.8, 125.5, 124.0, 123.3, 116.4, 113.6, 109.6, 85.6, 44.0, 42.4, 33.7, 30.7, 25.7; HRMS (ESI) calcd. for $C_{23}H_{21}NNaO_5$ [M + Na]$^+$ 414.1312, found: 414.1325.



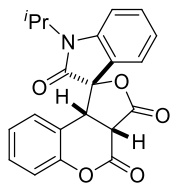
1'-methylspiro[benzo[*f*]furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,11c*H*)-trione (3l). Yellow solid; 33.1 mg, 86% yield; > 20:1 dr; m.p. 268.3-270.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.09 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.1 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.99 (d, *J* = 3.9 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 4.74 (d, *J* = 10.5 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 169.0, 158.9, 149.4, 144.1, 132.0, 131.0, 130.5, 130.3, 128.5, 126.4, 125.5, 125.1, 124.1, 123.8, 122.5, 117.5, 109.8, 108.0, 86.0, 43.3, 40.7, 25.8; HRMS (ESI) calcd. for $C_{23}H_{15}NNaO_5$ [M + Na]$^+$ 408.0842, found: 408.0848.



8-bromo-6-methoxy-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3m). White solid; 34.0 mg, 77% yield; > 20:1 dr; m.p. 236.9-238.7 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.57 (td, *J* = 7.8, 1.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 2.2 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 2.0 Hz, 1H), 4.74 – 4.57 (m, 2H), 3.83 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 168.4, 157.7, 147.8, 144.4, 139.4, 132.3, 125.5, 124.0, 122.8, 120.4, 116.9, 115.8, 115.6, 109.7, 85.1, 56.4, 42.8, 42.2, 26.0; HRMS (ESI) calcd. for $C_{20}H_{14}BrNNaO_6$ [M + Na]$^+$ 465.9902, found: 465.9880.

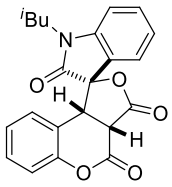


1'-ethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3n). White solid; 33.9 mg, 97% yield; > 20:1 dr; m.p. 229.1-231.0 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.53 (td, *J* = 7.8, 1.2 Hz, 1H), 7.38 – 7.26 (m, 2H), 7.16 – 7.06 (m, 2H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 6.32 – 6.20 (m, 1H), 4.79 – 4.48 (m, 2H), 3.52 – 3.40 (m, 1H), 3.32 – 3.21 (m, 1H), 0.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 168.9, 158.4, 150.9, 143.2, 132.1, 130.1, 127.3, 125.6, 124.4, 123.8, 123.2, 116.9, 114.3, 109.7, 85.3, 43.7, 42.6, 34.0, 11.6; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_5$ [M + Na]$^+$ 372.0842, found: 372.0834.

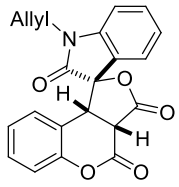


1'-isopropylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3o). White solid; 34.8 mg, 96% yield; > 20:1 dr; m.p. 338.6-340.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.85 (d, *J* = 6.6 Hz, 1H), 7.50 (dd, *J* = 12.3, 4.5 Hz, 1H), 7.37 - 7.24 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 6.5 Hz, 1H), 4.61 (q, *J* = 11.0 Hz, 2H), 4.12 - 3.93 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.9, 158.3, 150.9, 143.1, 132.0, 130.0, 127.2, 125.7, 124.3, 123.6, 123.4, 116.9, 114.4,

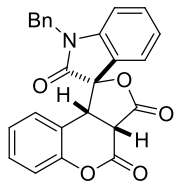
110.5, 85.2, 44.0, 43.9, 42.5, 18.5, 17.9; HRMS (ESI) calcd. for $C_{21}H_{17}NNaO_5$ [M + Na]$^+$ 386.0999, found: 386.0985.



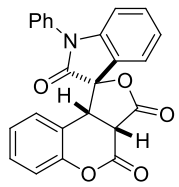
1'-isobutylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3p). White solid; 33.2 mg, 88% yield; > 20:1 dr; m.p. 261.4-263.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 (d, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.30 (t, J = 7.7 Hz, 2H), 7.13 - 7.05 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.37 (d, J = 7.7 Hz, 1H), 4.75 – 4.62 (m, 2H), 3.26 (dd, J = 13.9, 7.8 Hz, 1H), 3.13 (dd, J = 13.9, 6.6 Hz, 1H), 1.49 (dt, J = 13.6, 6.7 Hz, 1H), 0.58 (d, J = 6.7 Hz, 3H), 0.25 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.7, 168.9, 158.5, 151.0, 144.4, 132.1, 130.2, 127.6, 125.6, 124.6, 123.7, 123.0, 117.0, 114.4, 110.2, 85.2, 46.8, 43.1, 42.7, 26.5, 19.8, 18.9; HRMS (ESI) calcd. for $C_{22}H_{19}NNaO_5$ [M + Na]$^+$ 400.1155, found: 400.1148.



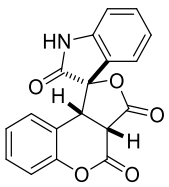
1'-allylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3q). White solid; 31.4 mg, 87% yield; > 20:1 dr; m.p. 252.2-253.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (d, J = 6.7 Hz, 1H), 7.51 (td, J = 7.8, 1.2 Hz, 1H), 7.32 (ddd, J = 10.9, 4.7, 2.0 Hz, 2H), 7.14 – 7.04 (m, 1H), 6.95 (ddd, J = 8.7, 5.3, 1.5 Hz, 2H), 6.34 (dd, J = 7.6, 1.4 Hz, 1H), 5.32 – 5.21 (m, 1H), 4.83 – 4.75 (m, 1H), 4.75 – 4.60 (m, 2H), 4.40 (dd, J = 17.0, 1.2 Hz, 1H), 4.18 – 4.04 (m, 1H), 3.91 (dd, J = 17.0, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.9, 158.5, 151.0, 143.5, 132.1, 130.4, 130.2, 127.5, 125.7, 124.5, 124.0, 123.0, 117.1, 116.3, 114.4, 110.3, 85.4, 43.4, 42.7, 41.4; HRMS (ESI) calcd. for $C_{21}H_{15}NNaO_5$ [M + Na]$^+$ 384.0842, found: 384.0831.



1'-benzylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3r). White solid; 36.2 mg, 88% yield; > 20:1 dr; m.p. 188.7-190.2 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.91 (d, J = 7.1 Hz, 1H), 7.44 (dd, J = 15.0, 7.1 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 – 7.03 (m, 4H), 6.97 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.51 (d, J = 7.0 Hz, 2H), 6.37 (d, J = 6.7 Hz, 1H), 4.93 – 4.66 (m, 3H), 4.45 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.6, 168.8, 158.6, 151.0, 143.5, 134.8, 132.1, 130.4, 128.6, 127.8, 127.3, 126.4, 125.8, 124.8, 124.1, 123.0, 117.2, 114.3, 110.3, 85.3, 43.1, 42.8, 42.8; HRMS (ESI) calcd for $C_{25}H_{17}NNaO_5$ [M + Na]$^+$ 434.0999, found: 434.1009.

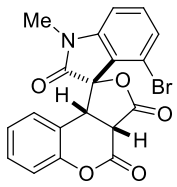


1'-phenylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3s). White solid; 34.6 mg, 87% yield; > 20:1 dr; m.p. 270.1-271.7 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.97 (dd, J = 7.4, 1.4 Hz, 1H), 7.55 – 7.34 (m, 6H), 7.15 (dd, J = 8.3, 1.2 Hz, 1H), 7.02 (td, J = 7.4, 1.4 Hz, 1H), 6.76 – 6.66 (m, 3H), 6.36 (dd, J = 7.7, 1.6 Hz, 1H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 168.9, 158.3, 150.9, 143.9, 132.4, 132.2, 130.3, 129.8, 128.8, 127.3, 126.0, 125.9, 124.7, 124.5, 123.1, 117.2, 114.4, 109.9, 85.6, 44.4, 42.6; HRMS (ESI) calcd. for $C_{24}H_{15}NNaO_5$ [M + Na]$^+$ 420.0842; found: 420.0826.

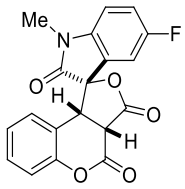


spiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3t). White solid; 29.6 mg, 92% yield; > 20:1 dr; m.p. 247.1-248.1 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.66 (s, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.44 (td, J = 7.7, 1.2 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.15 – 7.05 (m, 1H), 7.03 – 6.93 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.36 (dd, J = 7.6, 1.4 Hz, 1H), 4.64 (s,

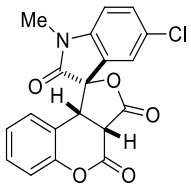
2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.0, 168.8, 158.4, 150.9, 143.0, 132.0, 130.0, 127.4, 125.8, 124.5, 123.6, 123.3, 116.9, 114.7, 110.7, 85.7, 43.1, 42.6; HRMS (ESI) calcd. for $C_{18}H_{11}NNaO_5$ [M + Na]$^+$ 344.0529, found: 344.0527.



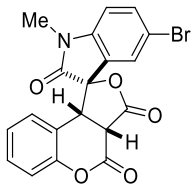
4'-bromo-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3u). White solid; 30.1 mg, 73% yield; > 20:1 dr; m.p. 288.1-290.0 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.58 – 7.44 (m, 2H), 7.36 (td, *J* = 7.9, 7.3, 1.6 Hz, 1H), 7.19 – 7.07 (m, 2H), 7.00 (td, *J* = 7.5, 1.2 Hz, 1H), 6.39 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.5, 168.3, 158.0, 150.7, 146.4, 134.2, 130.5, 127.7, 127.4, 124.8, 120.3, 119.2, 117.2, 113.8, 109.6, 85.9, 41.7, 40.2, 26.1; HRMS (ESI) calcd. for $C_{19}H_{12}BrNNaO_5$ [M + Na]$^+$ 435.9812, found: 435.9797.



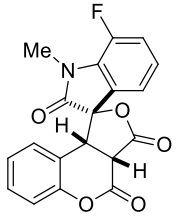
5'-fluoro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3v): white solid; 31.0 mg, 88% yield; > 20:1 dr; m.p. 206.4-208.2 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.84 (dd, *J* = 7.9, 2.7 Hz, 1H), 7.42 (td, *J* = 9.3, 2.7 Hz, 1H), 7.32 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.17 – 7.06 (m, 2H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.40 (d, *J* = 6.3 Hz, 1H), 4.70 (s, 2H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.6, 150.1 (d, *J* = 237.8 Hz), 157.9, 150.8, 140.6 (d, *J* = 1.7 Hz), 130.2, 127.4, 124.8 (d, *J* = 8.6 Hz), 124.5, 118.5 (d, *J* = 23.5 Hz), 117.0, 114.2, 113.6 (d, *J* = 25.9 Hz), 111.1 (d, *J* = 8.1 Hz), 85.2, 43.1, 42.5, 26.1; HRMS (ESI) calcd. for $C_{19}H_{12}FNNaO_5$ [M + Na]$^+$ 376.0592, found: 376.0596.



5'-chloro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3w). White solid; 31.7 mg, 86% yield; > 20:1 dr; m.p. 261.5-262.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (d, *J* = 1.9 Hz, 1H), 7.62 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 – 7.04 (m, 2H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 6.9 Hz, 1H), 4.89 – 4.34 (m, 2H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 168.5, 158.4, 150.7, 143.2, 131.9, 130.2, 128.0, 127.3, 125.8, 125.1, 124.5, 117.0, 114.2, 111.4, 85.0, 43.0, 42.5, 26.0; HRMS (ESI) calcd. for $C_{19}H_{12}ClNNaO_5$ [M + Na]$^+$ 392.0296, found: 392.0301.

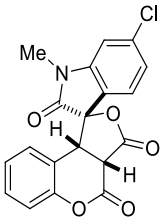


5'-bromo-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3x). White solid; 36.7 mg, 89% yield; > 20:1 dr; m.p. 265.9-267.8 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 10.4, 8.5 Hz, 2H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 6.5 Hz, 1H), 4.78 – 4.63 (m, 2H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.9, 168.6, 158.4, 150.8, 143.7, 134.8, 130.2, 128.5, 127.3, 125.5, 124.6, 117.0, 115.6, 114.2, 111.9, 84.9, 43.0, 42.5, 26.1; HRMS (ESI) calcd. for $C_{19}H_{12}BrNNaO_5$ [M + Na]$^+$ 435.9791, found: 435.9771.

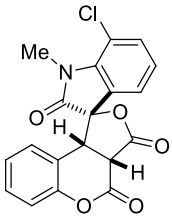


7'-fluoro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3y). White solid; 33.2 mg, 94% yield; > 20:1 dr; m.p. 277.2-278.5 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.75 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.52 – 7.40 (m, 1H), 7.40 – 7.29 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.35 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.82 – 4.45 (m, 2H), 2.94 (d, *J* = 2.7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.6, 158.4, 150.8, 147.0 (d, *J* = 244.0

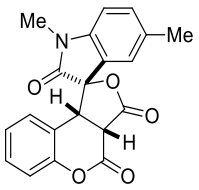
Hz), 130.6 (d, *J* = 8.9 Hz), 130.3, 127.2, 126.1 (d, *J* = 3.1 Hz), 125.3 (d, *J* = 6.4), 124.6, 121.9 (d, *J* = 3.1 Hz), 120.1 (d, *J* = 19.0 Hz), 117.1, 114.1, 85.1, 43.5, 42.6, 28.3 (d, *J* = 5.4 Hz); HRMS (ESI) calcd. for $C_{19}H_{12}FNNaO_5$ [M + Na]$^+$ 376.0592, found: 376.0578.



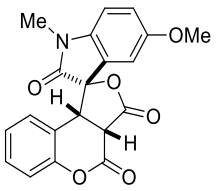
6'-chloro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*, 9b*H*)-trione (3z). White solid; 23.6 mg 64% yield; > 20:1 dr; m.p. 248.5-249.9 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.28 (m, 2H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.15 – 7.03 (m, 1H), 7.03 – 6.89 (m, 1H), 6.50 – 6.31 (m, 1H), 4.68 (s, 2H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.4, 168.7, 158.5, 150.8, 145.9, 136.7, 130.2, 127.3, 127.1, 124.6, 123.8, 122.0, 117.1, 114.2, 110.5, 84.9, 43.0, 42.6, 26.2; HRMS (ESI) calcd. for $C_{19}H_{12}ClNNaO_5$ [M + Na]$^+$ 392.0302, found: 392.0302.



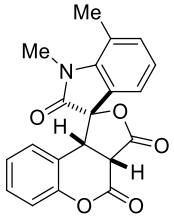
7'-chloro-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3a'). White solid; 31.7 mg, 86% yield; > 20:1 dr; m.p. 260.0-261.6 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.57 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.75 – 4.54 (m, 2H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 168.6, 158.4, 150.8, 139.9, 134.0, 130.3, 127.2, 126.3, 125.4, 124.7, 124.6, 117.1, 115.3, 114.1, 84.6, 43.5, 42.6, 29.2; HRMS (ESI) calcd. for $C_{19}H_{12}ClNNaO_5$ [M + Na]$^+$ 392.0319, found: 392.0302.



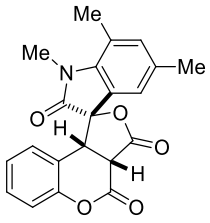
1',5'-dimethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3b'). White solid; 30.0 mg, 86% yield; > 20:1 dr; m.p. 247.1-248.5 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.69 (s, 1H), 7.36 – 7.26 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 2H), 6.33 (d, *J* = 7.5 Hz, 1H), 4.65 (s, 2H), 2.76 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 168.8, 158.4, 150.8, 142.0, 133.2, 132.2, 130.0, 127.3, 126.0, 124.4, 123.1, 117.0, 114.4, 109.5, 85.5, 43.1, 42.6, 25.9, 20.7; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_5$ [M + Na]$^+$ 372.0842, found: 372.0856.



5'-methoxy-1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3c'). White solid; 34.4 mg, 94% yield; > 20:1 dr; m.p. 236.7-238.5 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.59 (d, *J* = 2.5 Hz, 1H), 7.31 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.03 – 6.87 (m, 2H), 6.35 (d, *J* = 6.3 Hz, 1H), 4.87 – 4.31 (m, 2H), 3.82 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.9, 168.8, 158.5, 156.5, 150.8, 137.5, 130.1, 127.4, 124.4, 124.3, 117.0, 116.7, 114.5, 112.2, 110.4, 85.6, 55.7, 43.1, 42.6, 25.9; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_6$ [M + Na]$^+$ 388.0792, found: 388.0786.



1',7'-dimethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3d'). White solid; 32.5 mg, 93 % yield; >20:1 dr; m.p. 262.4-264.3 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.71 (d, *J* = 6.6 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.36 – 6.26 (m, 1H), 4.89 – 4.48 (m, 2H), 3.04 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 168.9, 158.6, 150.8, 142.1, 135.6, 130.1, 127.3, 124.5, 123.9, 123.8, 123.3, 121.1, 117.0, 114.5, 84.9, 43.3, 42.8, 28.9, 18.1; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_5$ [M + Na]$^+$ 372.0842, found: 372.0842.



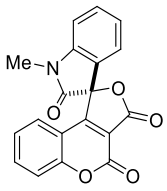
1',5',7'-trimethylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4(3a*H*,9b*H*)-trione (3e'). White solid; 31.3 mg, 86% yield; > 20:1 dr; m.p. 243.6-245.5 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.53 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.15 – 7.02 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 6.7 Hz, 1H), 4.62 (q, *J* = 11.0 Hz, 2H), 3.01 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 168.8, 158.5, 150.8, 139.6, 135.9, 133.0, 130.1, 127.4, 124.4, 123.8, 123.8, 120.8, 116.9, 114.5, 85.0, 43.3, 42.7, 28.8, 20.4, 17.9; HRMS (ESI) calcd. for $C_{21}H_{17}NNaO_5$ [M+Na]$^+$ 386.0999, found: 386.0988.

4. Procedure for the gram-scale experiment.

In a round bottomed flask equipped with a magnetic stirring bar, coumarin-3-formylpyrazole **1a** (0.96 g, 4.0 mmol), 3-hydroxyoxindole **2a** (0.78 g, 4.8 mmol) and DABCO (20 mol %, 0.8 mmol) were placed in 20 mL of DCM at room temperature, and the reaction mixture was stirred at this temperature until the reaction completed (monitored by TLC). Then, the resulting mixture was concentrated and the residue was purified by column chromatography (dichloromethane/ethyl acetate = 50/1) on silica gel to afford the corresponding product **3a** as a white solid; 1.322 g, 99% yield.

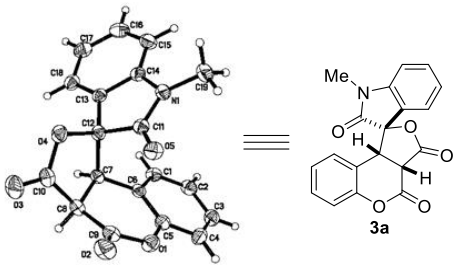
5. Synthesis of compound 4.

To a solution of compound **3a** (33.5 mg, 0.1 mmol) in 2.0 mL DCM was added DDQ (33.9 mg, 0.15 mmol). Then the mixture was stirred at room temperature for 4 h. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (dichloromethane/ethyl acetate = 100/1) to afford the corresponding product **4** with 98% yield.



1'-methylspiro[furo[3,4-*c*]chromene-1,3'-indoline]-2',3,4-trione (4). White solid; 32.6 mg, 98% yield; m.p. 323.9-325.0 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 – 7.74 (m, 1H), 7.62 (dd, *J* = 8.7, 6.4 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.2, 165.0, 164.4, 155.8, 153.6, 144.1, 136.4, 132.9, 126.1, 126.0, 124.4, 124.2, 122.1, 117.9, 112.9, 112.8, 111.1, 82.6, 27.4; HRMS (ESI) calcd. for $C_{19}H_{11}NNaO_5$ [M + Na]$^+$ 356.0529, found: 356.0517.

6. X-ray crystal structure of compound 3a.

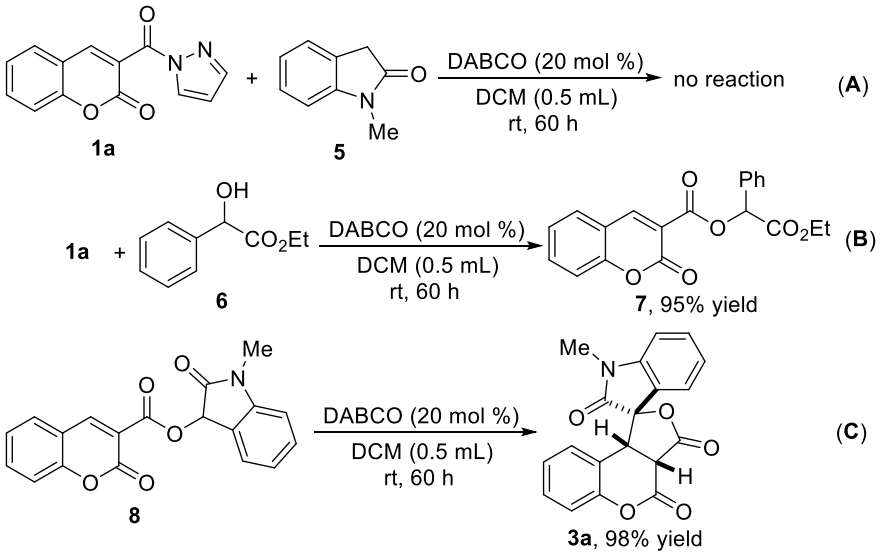


Crystal data and structure refinement for **3a** (CCDC 1941065)**.**

Identification code	**3a**
Empirical formula	$C_{19}H_{13}NO_5$
Formula weight	335.30
Temperature/K	293(2)

Crystal system	orthorhombic
Space group	Pbca
a/Å	13.9043(5)
b/Å	10.8551(4)
c/Å	20.2244(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3052.52(19)
Z	8
ρ_{calc}g/cm^3	1.459
μ/mm^{-1}	0.894
F(000)	1392.0
Crystal size/mm^3	0.19 × 0.13 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.744 to 134.128
Index ranges	-13 ≤ h ≤ 16, -7 ≤ k ≤ 12, -24 ≤ l ≤ 21
Reflections collected	7243
Independent reflections	2722 [R_{int} = 0.0372, R_{sigma} = 0.0412]
Data/restraints/parameters	2722/0/228
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.17/-0.24

7. Control experiments (The Scheme 6 and Fig. 3 in manuscript).



Scheme 6 Control experiments

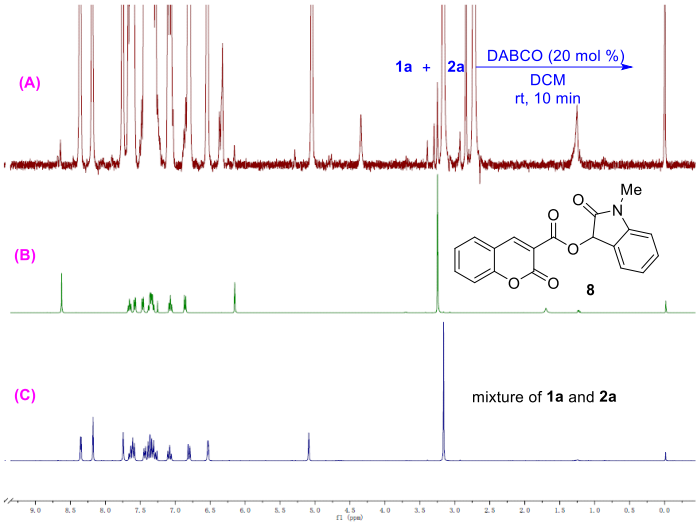
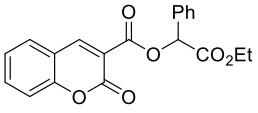


Fig.3 Tracking and monitoring to the reaction of **1a** and **2a**. (A) The reaction of **1a** and **2a** under the standard conditions for 10 mins. (B) The ^{1}H NMR spectra of compound **8**. (C) The ^{1}H NMR spectra of compounds **1a** and **2a**.

Synthesis of compound 7.

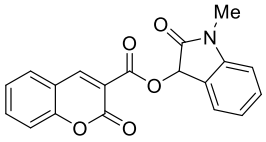
In an ordinary vial equipped with a magnetic stirring bar, compound **1a** (0.1 mmol), compound **6** (0.12 mmol) and DABCO (20 mol %, 0.02 mmol) were placed in 0.5 mL of DCM at room temperature for 60 h. Then, the mixture was by column chromatography (petroleum ether/ethyl acetate = 5:1) to give compound **7**.



2-ethoxy-2-oxo-1-phenylethyl 2-oxo-2H-chromene-3-carboxylate (**7**): White solid; 27.2 mg, 95%. yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.68 – 7.53 (m, 4H), 7.44 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 6.13 (s, 1H), 4.30 – 4.20 (m, 1H), 4.18 – 4.09 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 162.1, 156.5, 155.5, 149.7, 135.0, 133.6, 129.9, 129.5, 129.0, 127.8, 125.1, 117.9, 117.2, 117.0, 75.5, 62.1, 14.2. HRMS (ESI) calcd. for $C_{20}H_{16}NaO_6$ [M + Na]+ 375.0839, found: 375.0824.

Synthesis of compound 8.

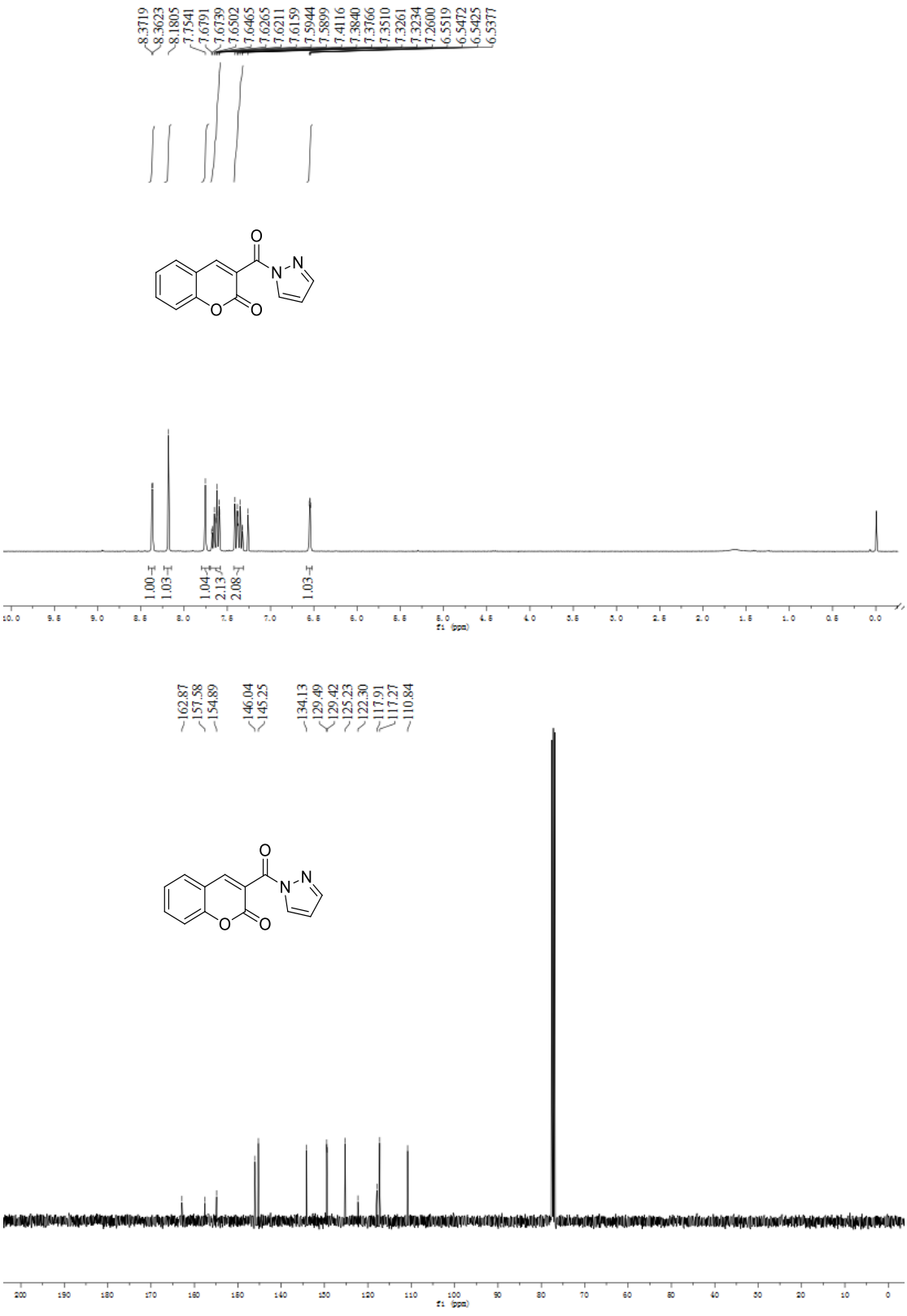
To a 10 mL round bottomed flask was added 2-oxo-2*H*-chromene-3-carboxylic acids (1.0 mmol), HOBt (1.2. mmol), 3-hydroxy-1-methylindolin-2-one (1.05 mmol) and CH_2Cl_2 (5 mL). The mixture was added DCC (1.2 mmol) at 0 °C and stirred for 15 min. Then, the reaction system was warmed to room temperature and stirred for 24 h. Upon completion, the mixture was filtered through celite, and washed with CH_2Cl_2 and concentrated in vacuo. The desired product was recrystallised from absolute ethanol.



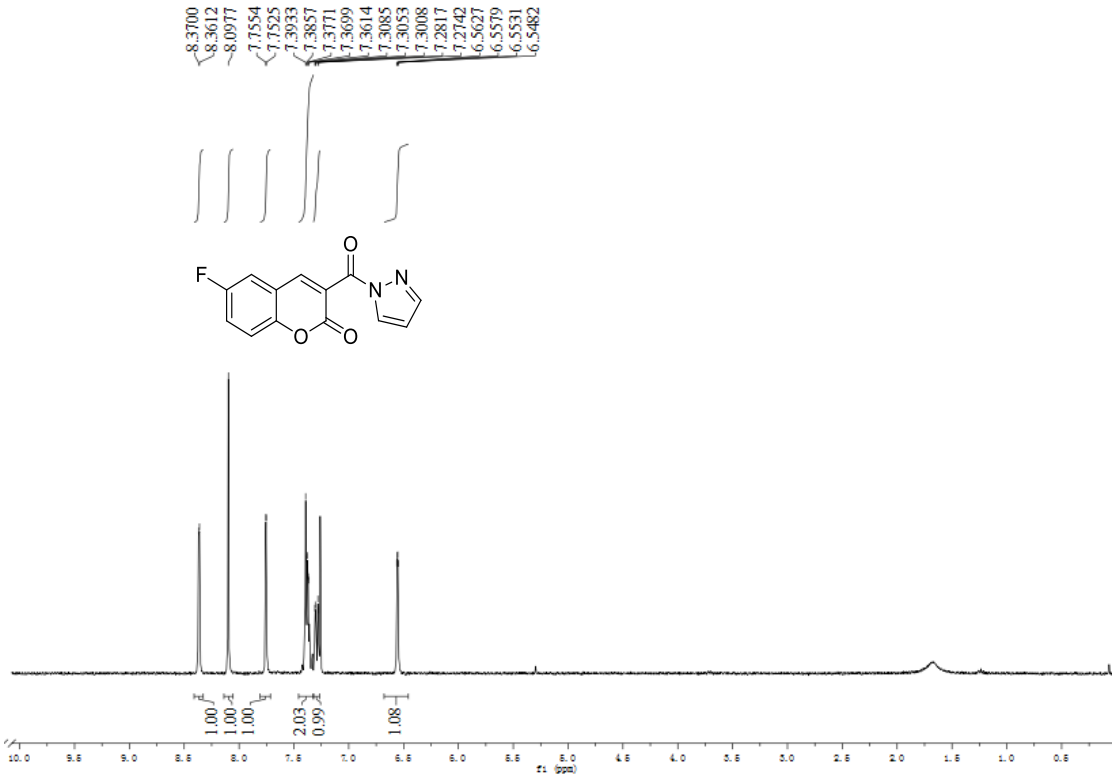
1-methyl-2-oxoindolin-3-yl 2-oxo-2*H*-chromene-3-carboxylate (8). White solid, 48.7 mg, 15% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.64 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.26 (m, 3H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.14 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 161.9, 156.5, 155.5, 150.2, 144.8, 135.1, 130.8, 130.0, 126.2, 125.2, 124.0, 123.5, 117.9, 117.1, 116.7, 108.8, 71.0, 26.7; HRMS (ESI) calcd. for $C_{19}H_{13}NNaO_5$ [M + Na]$^{+}$ 358.0686, found: 358.0683.

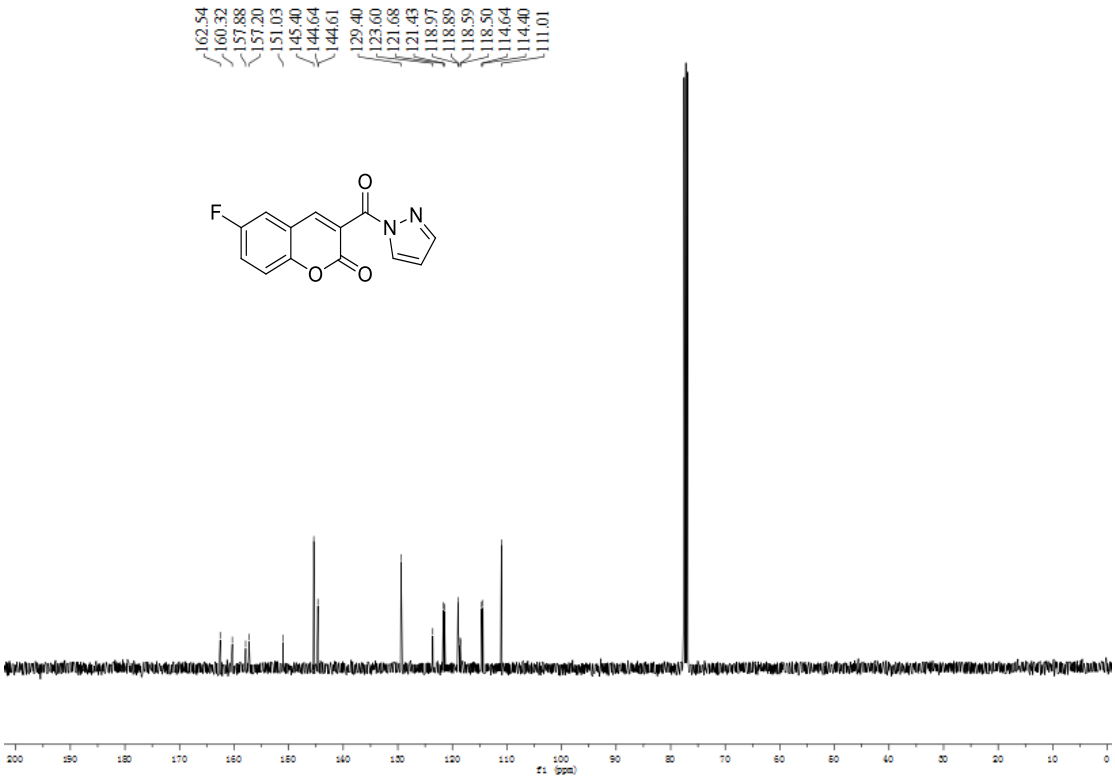
8. ^{1}H and ^{13}C NMR spectra for compounds 1, 3 and 4.

^{1}H and ^{13}C NMR of **1a**

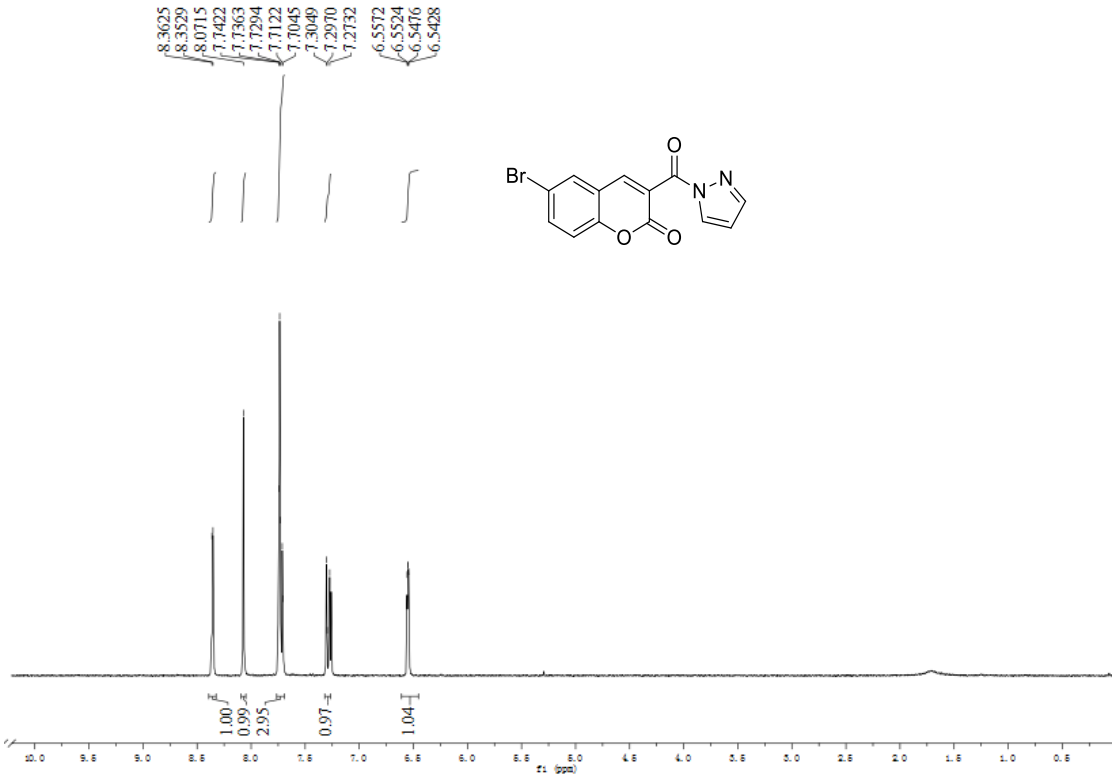


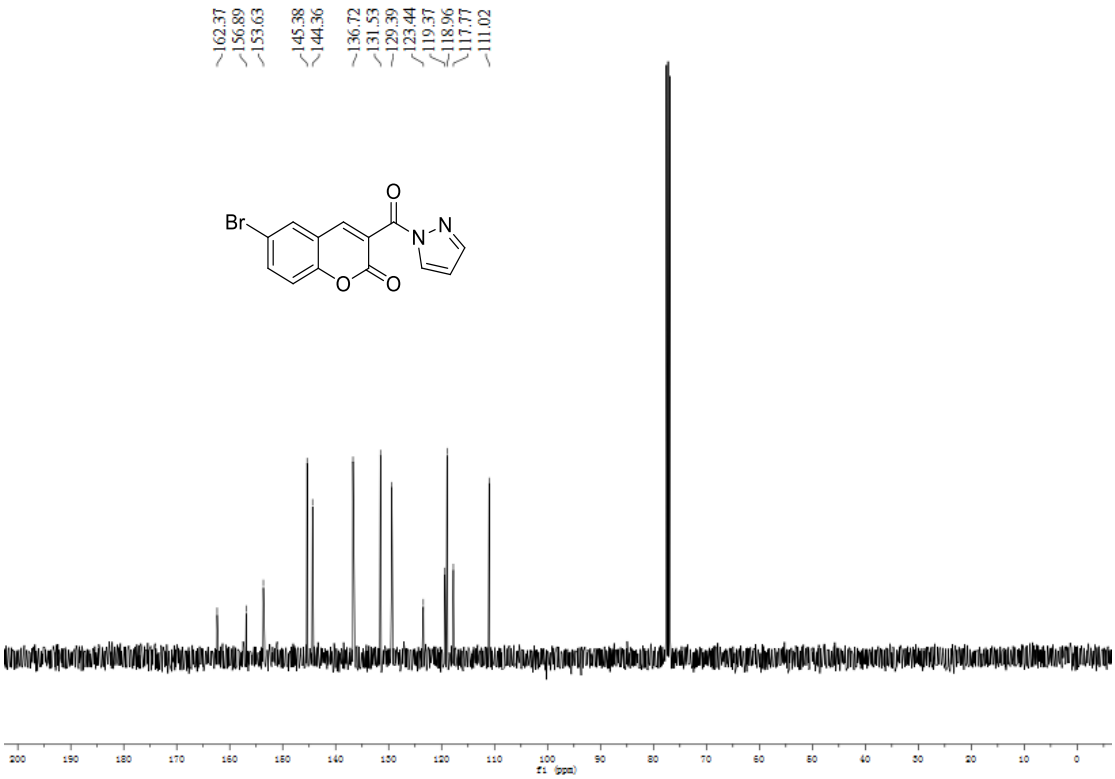
^{1}H and ^{13}C NMR of **1b**



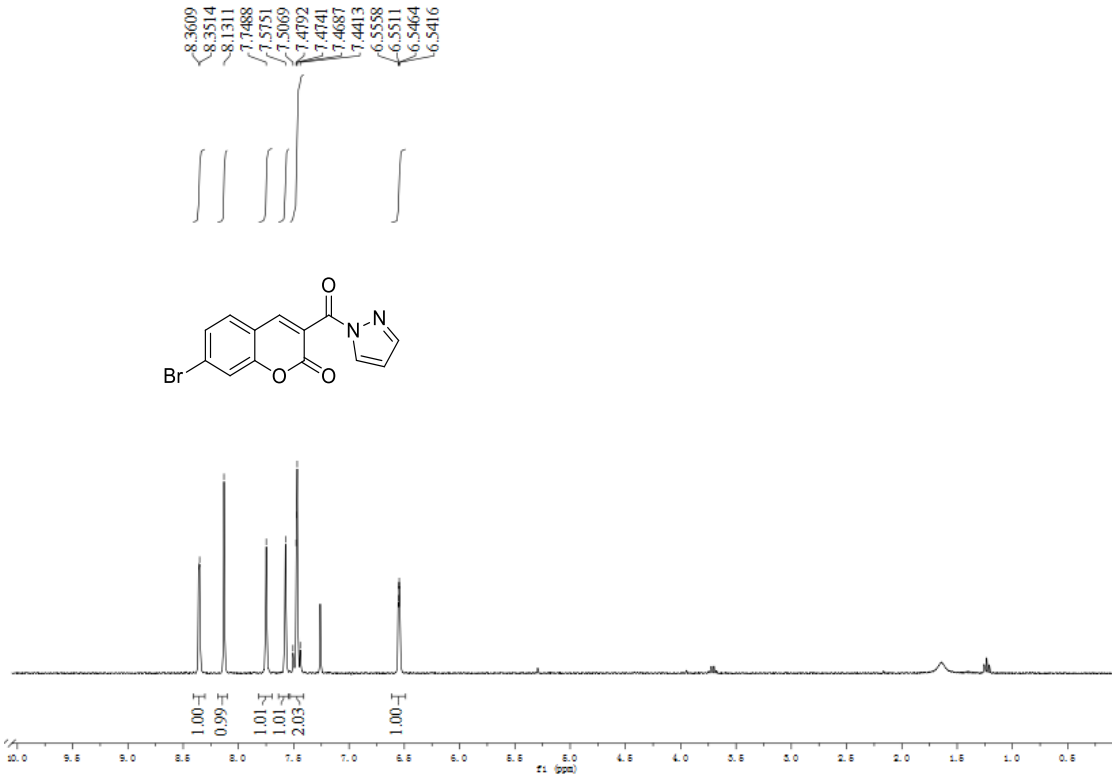


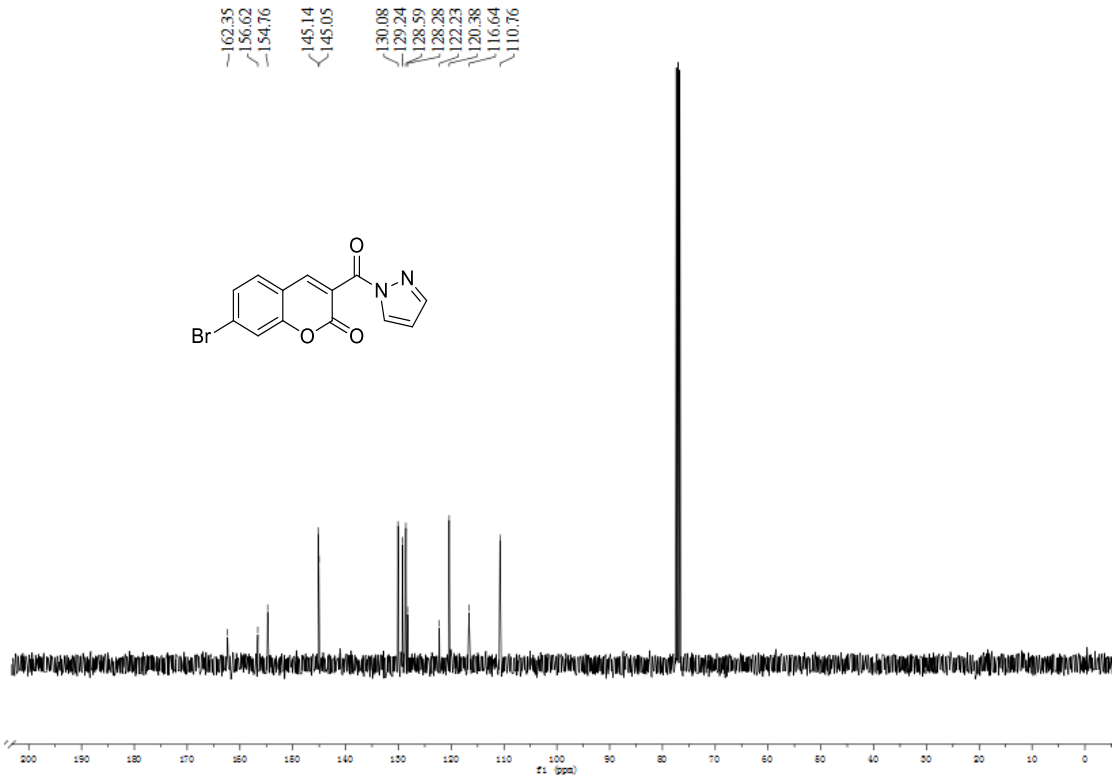
^{1}H and ^{13}C NMR of **1c**



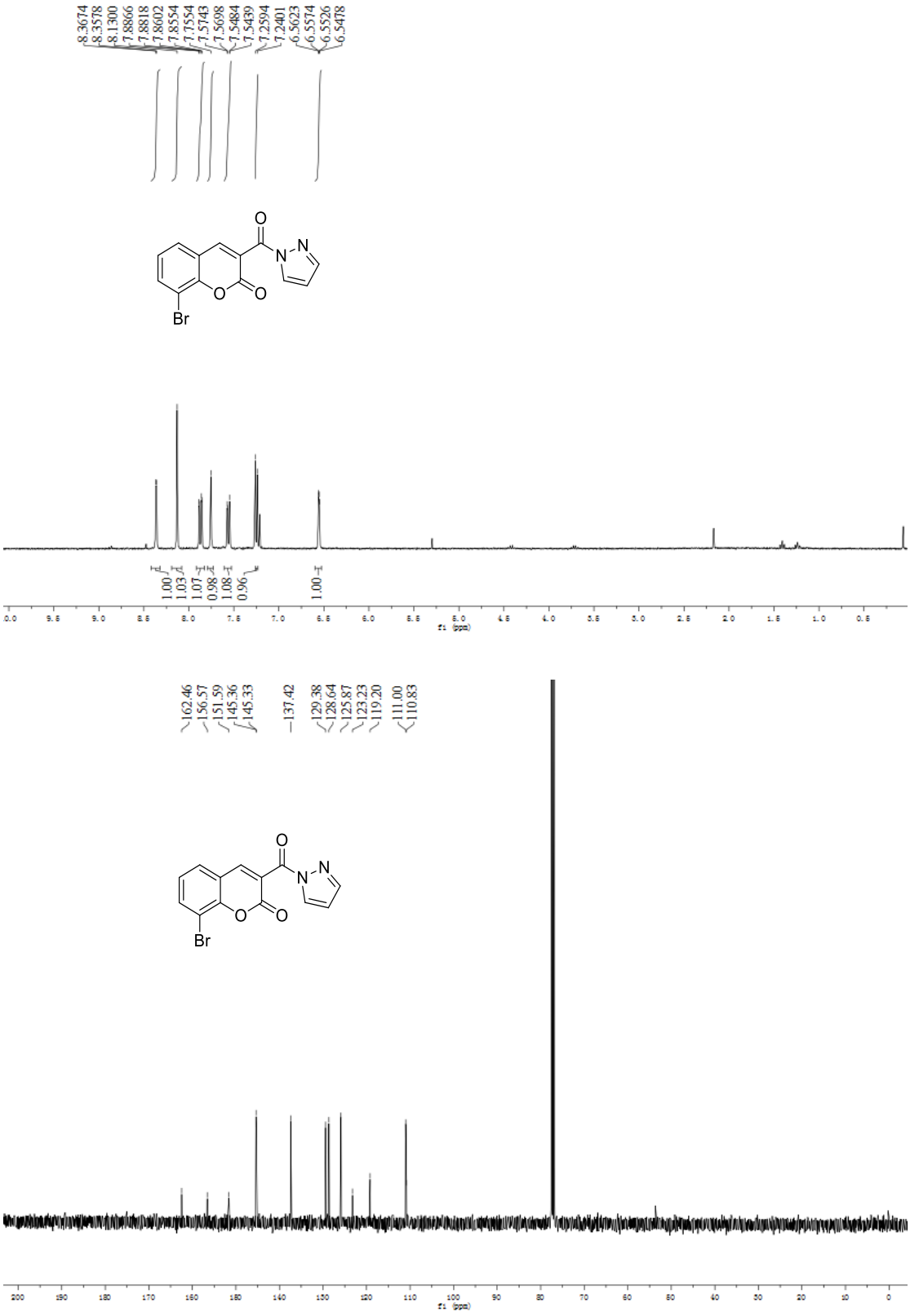


^{1}H and ^{13}C NMR of **1d**

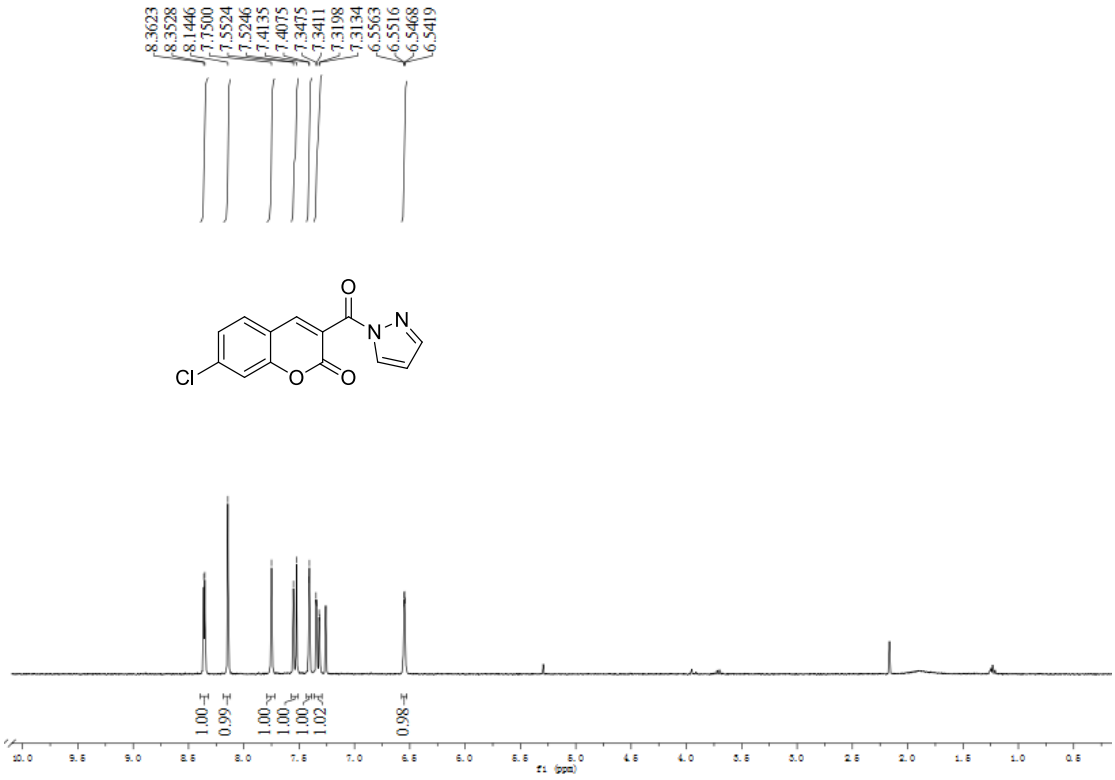


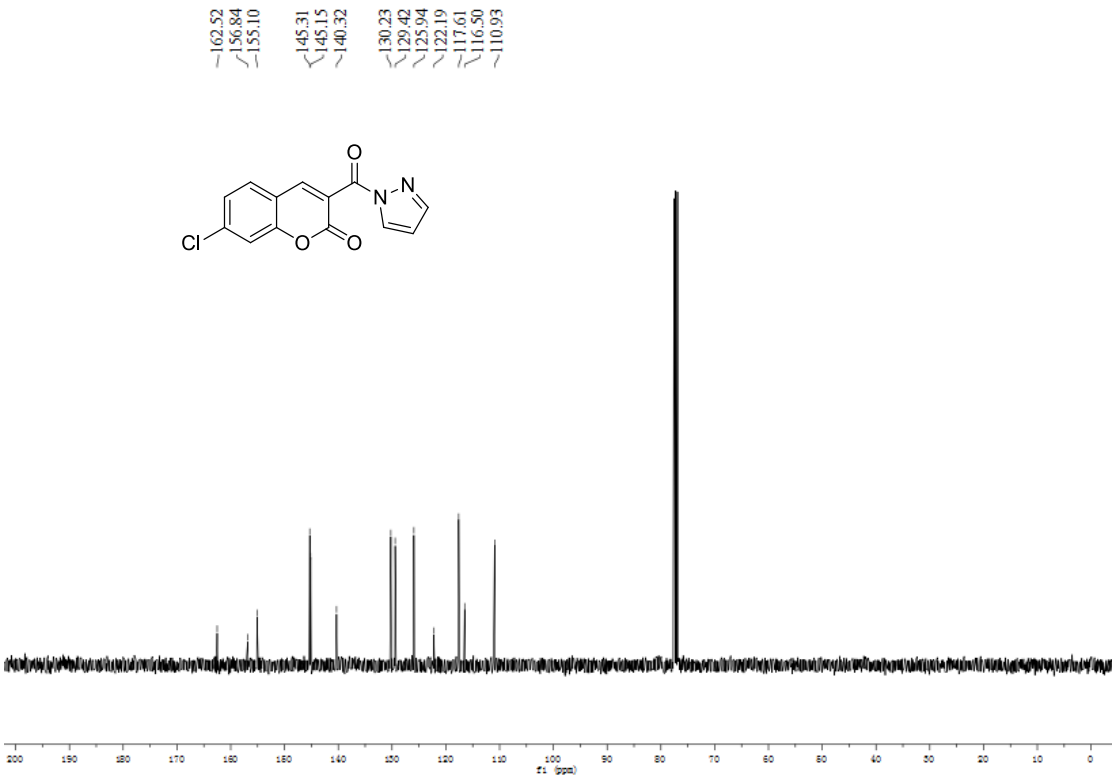


^{1}H and ^{13}C NMR of **1e**

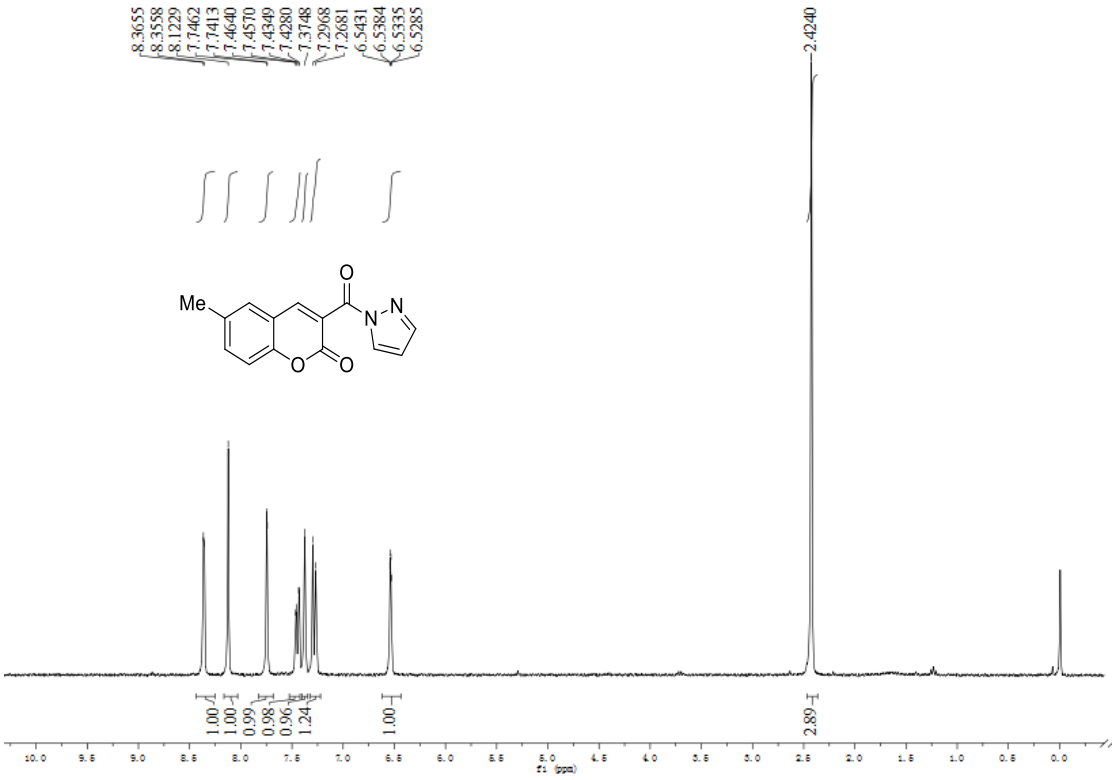


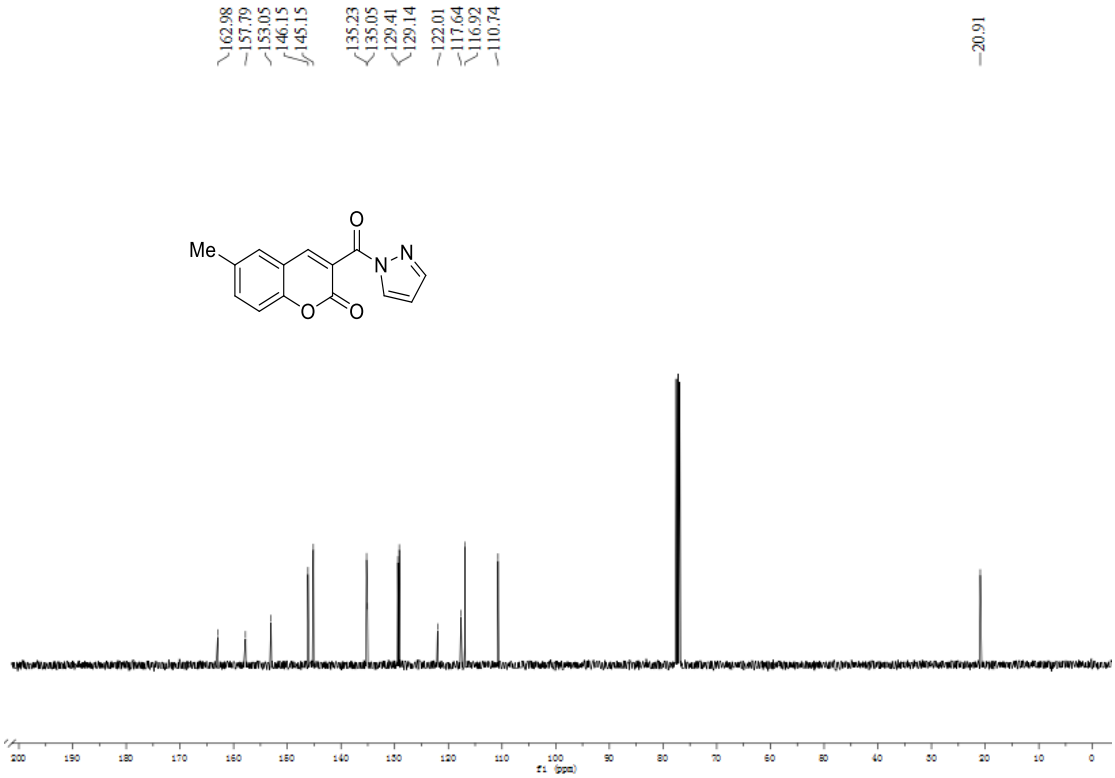
^{1}H and ^{13}C NMR of **1f**



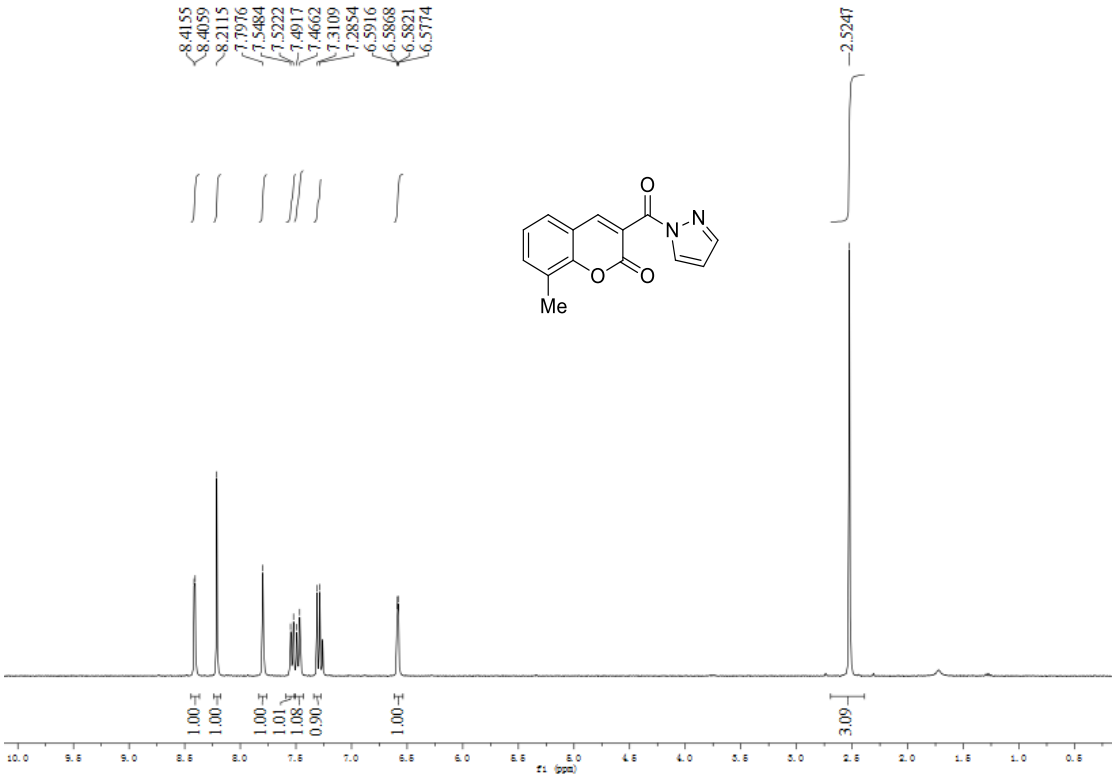


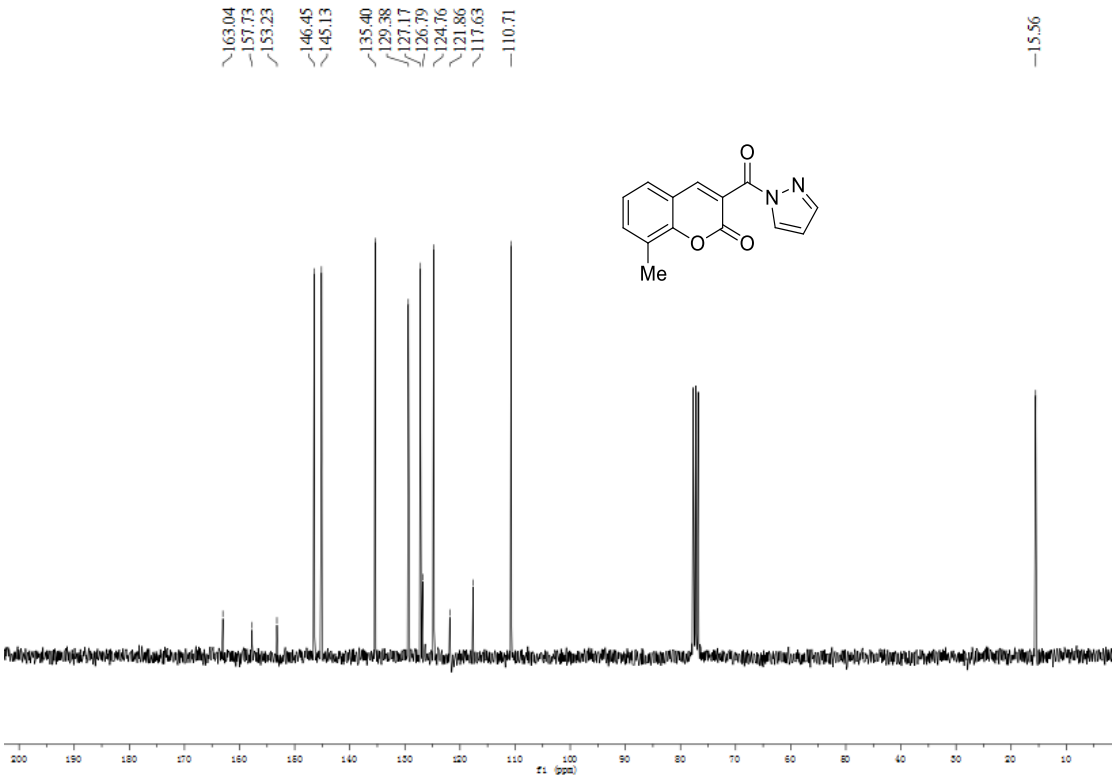
^{1}H and ^{13}C NMR of **1g**



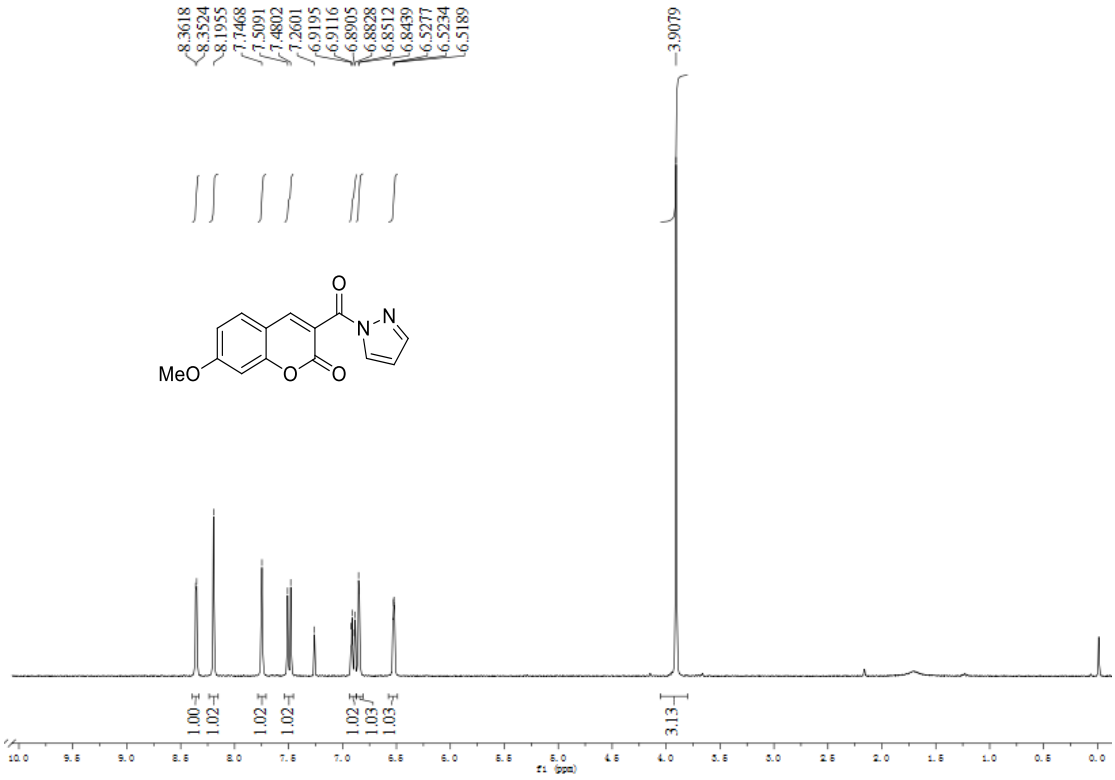


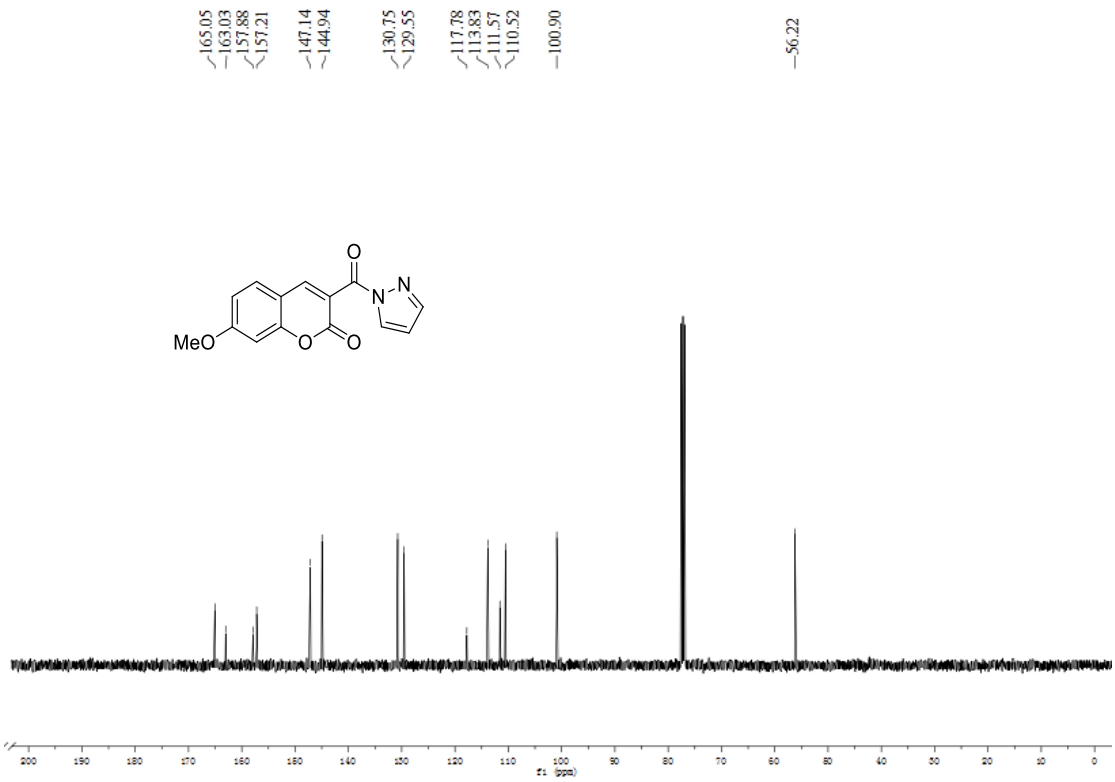
^{1}H and ^{13}C NMR of **1h**



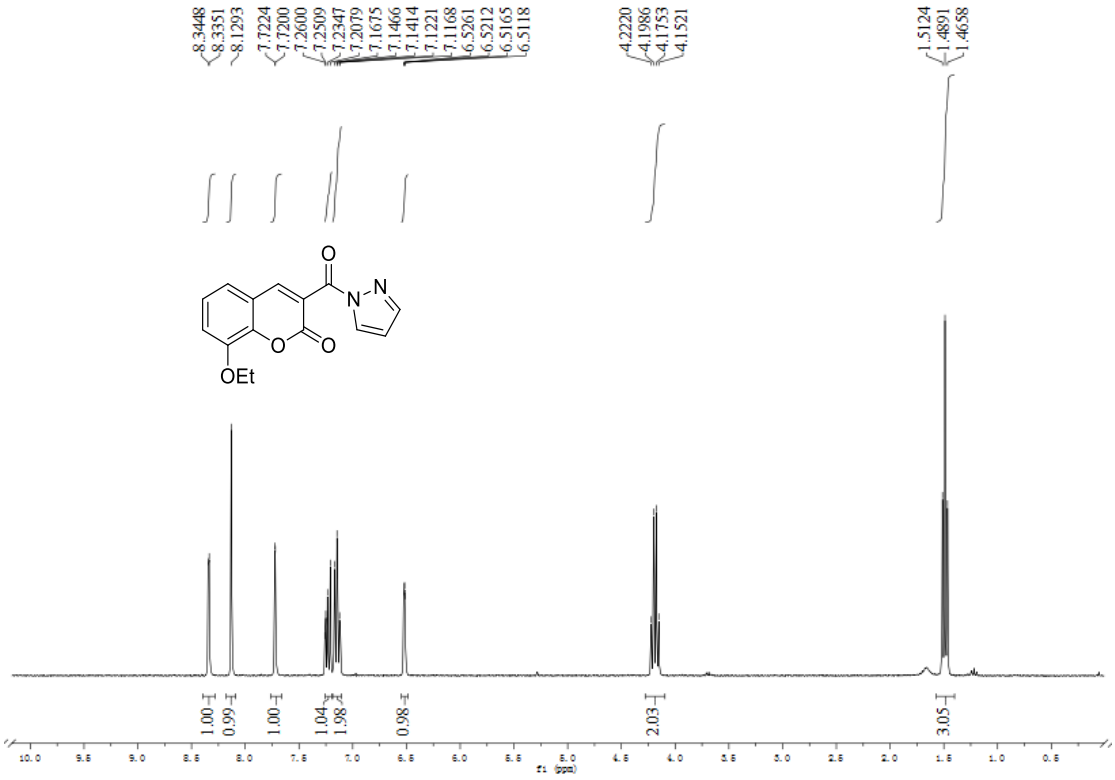


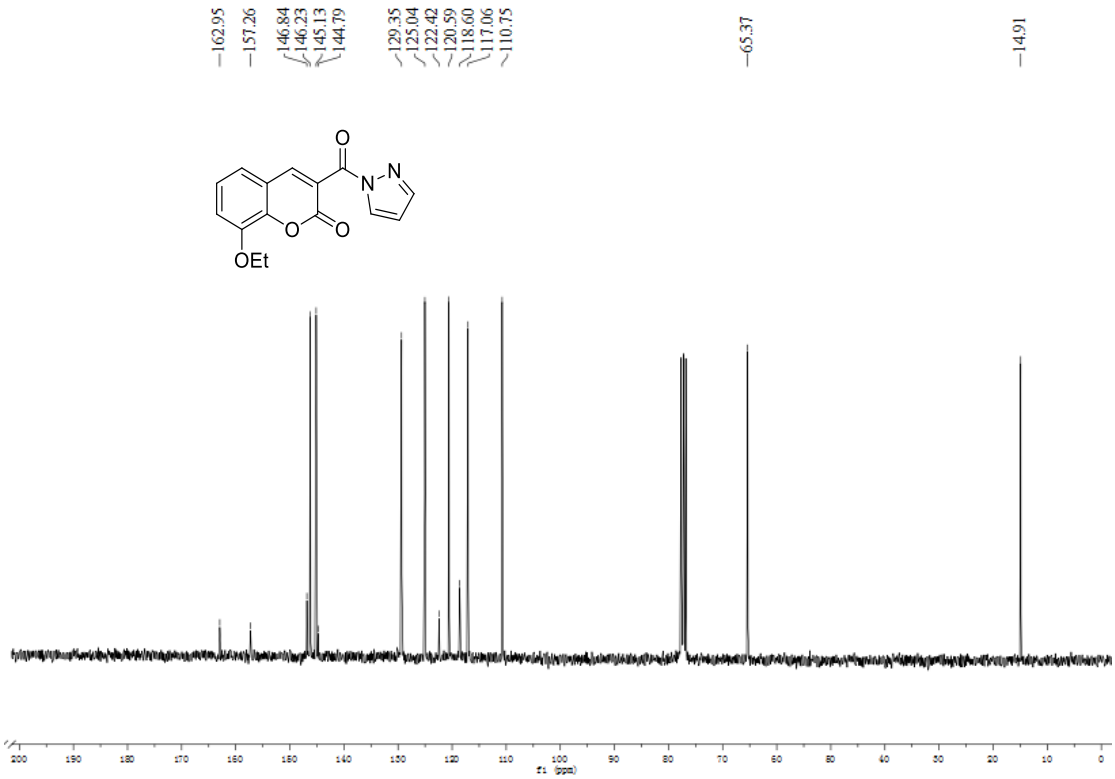
^{1}H and ^{13}C NMR of **1i**



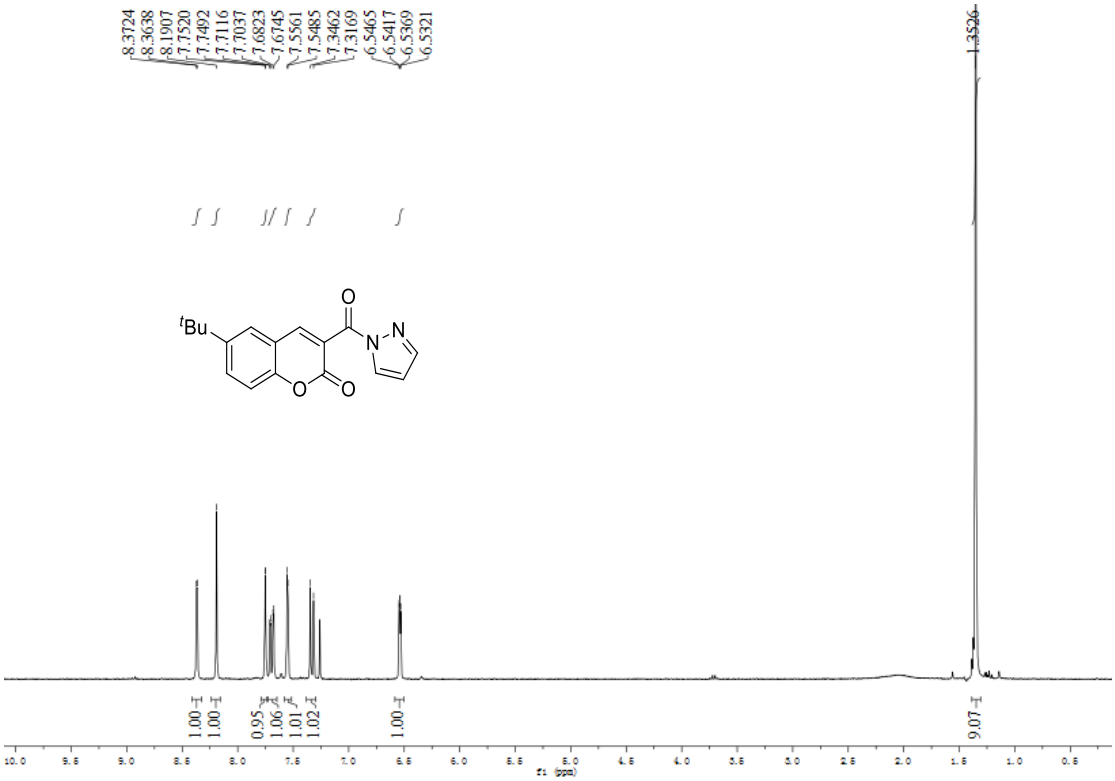


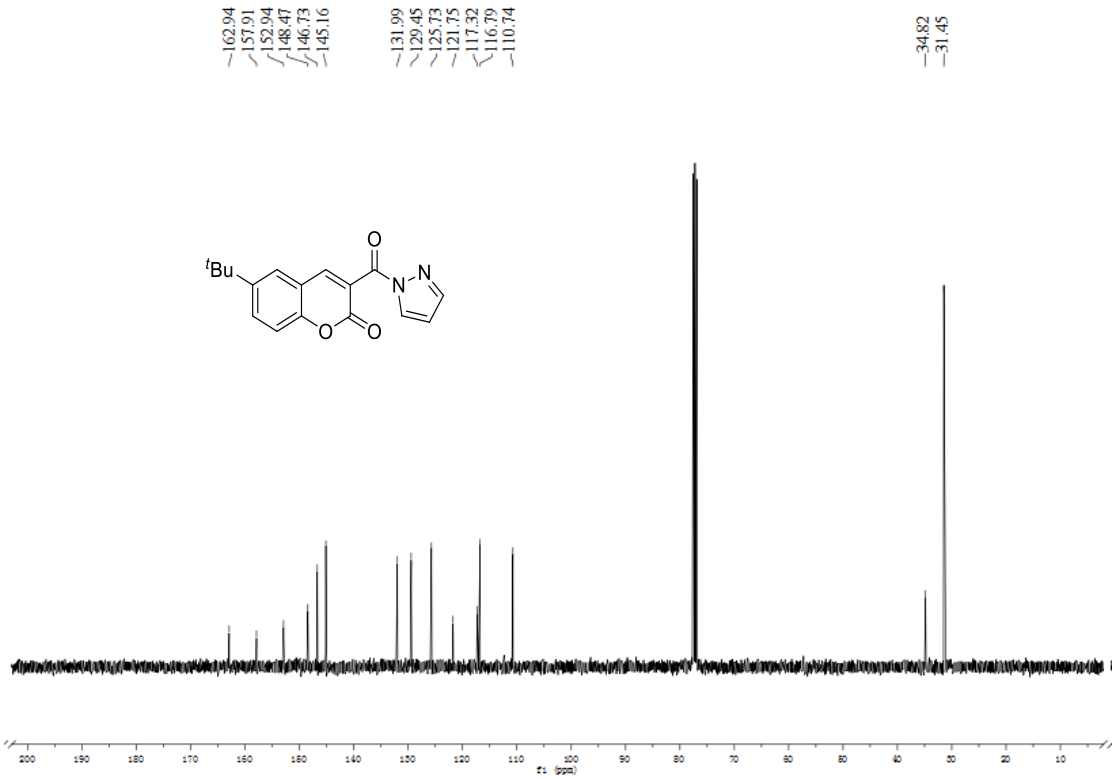
^{1}H and ^{13}C NMR of **1j**



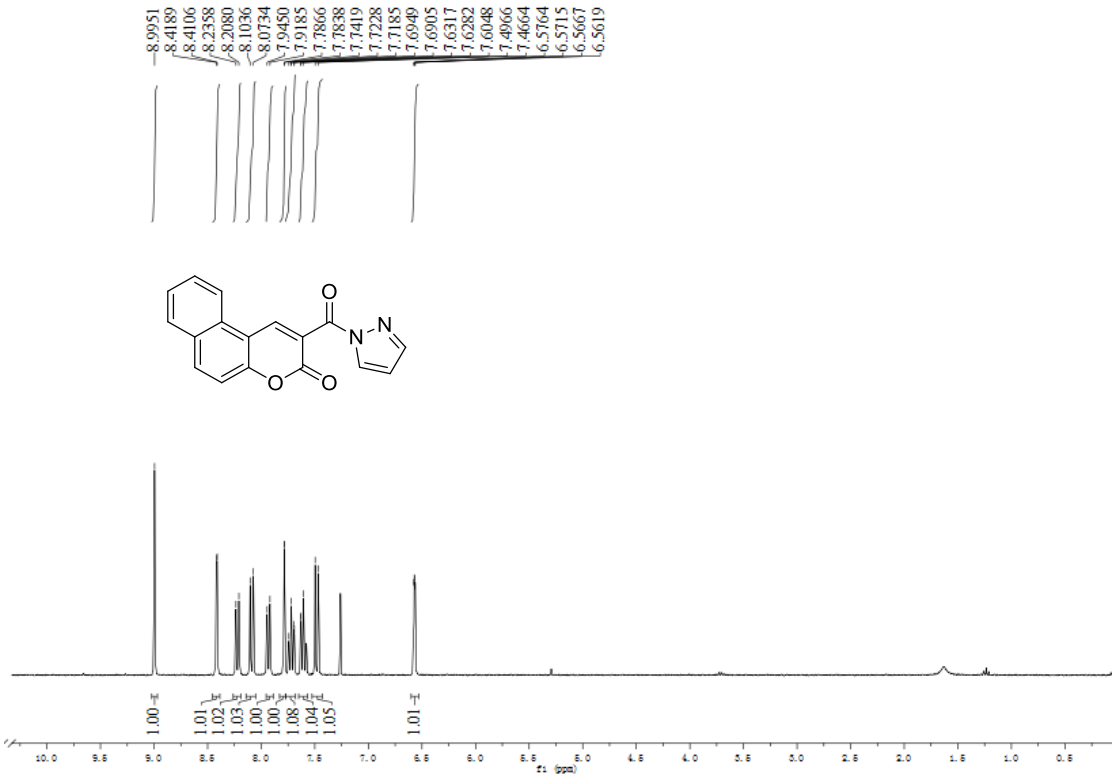


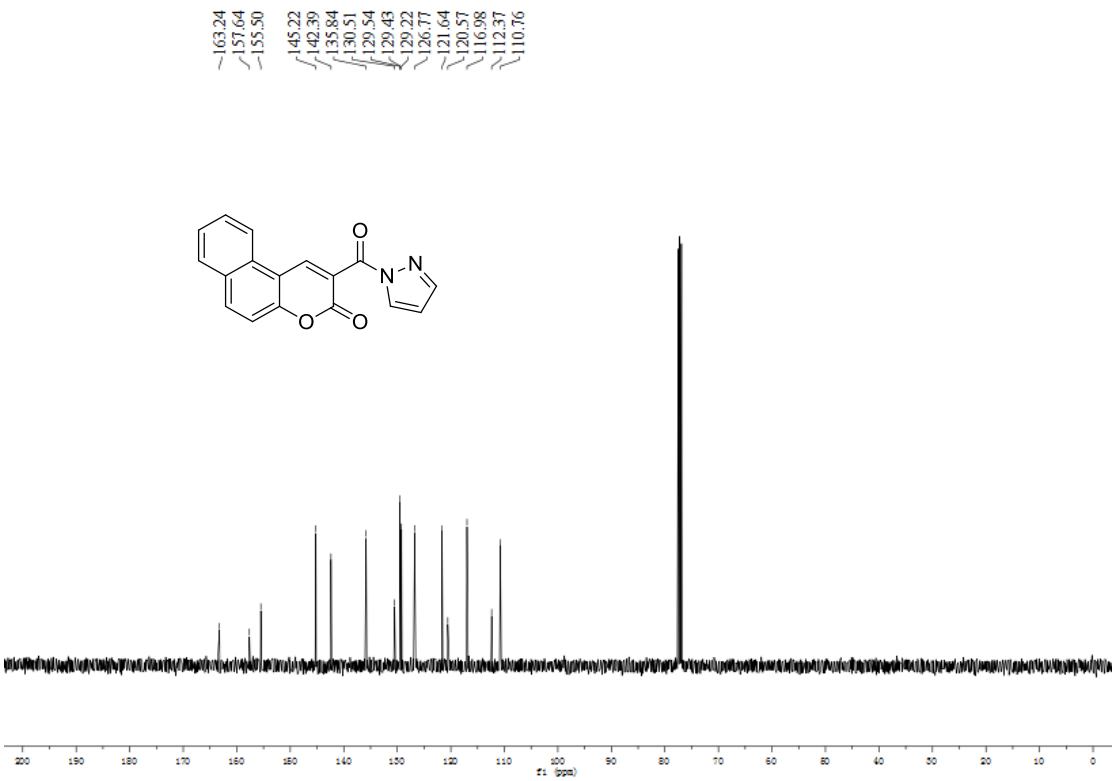
^{1}H and ^{13}C NMR of **1k**



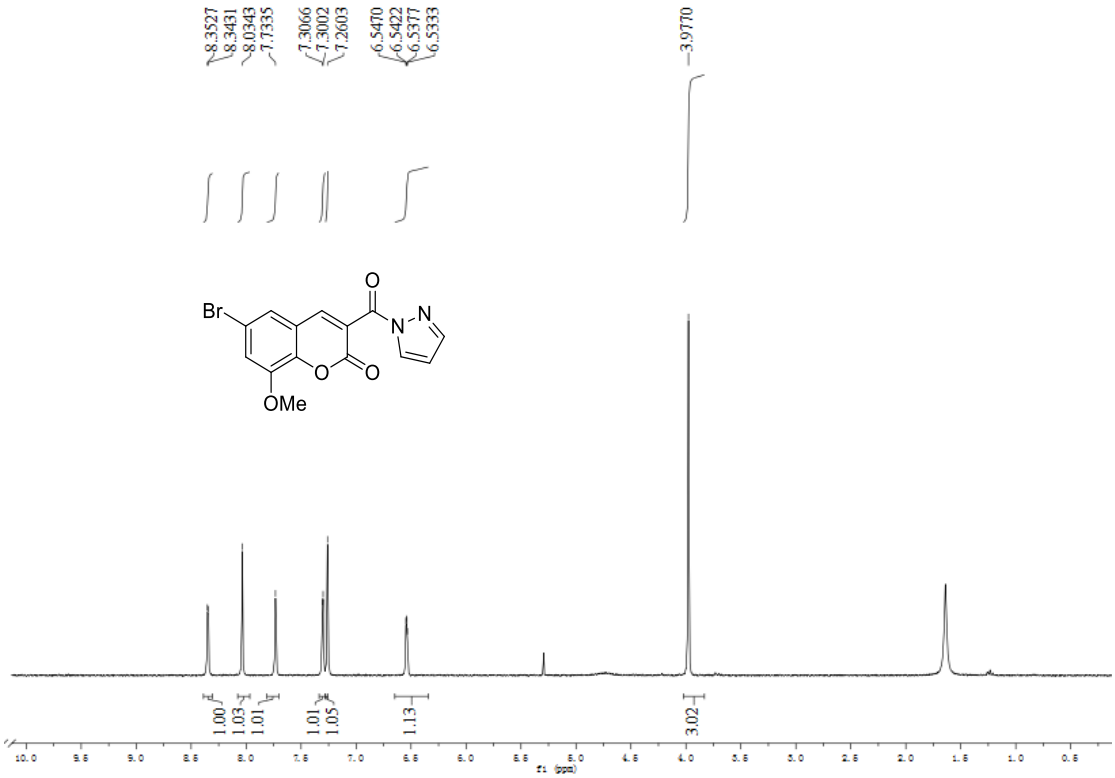


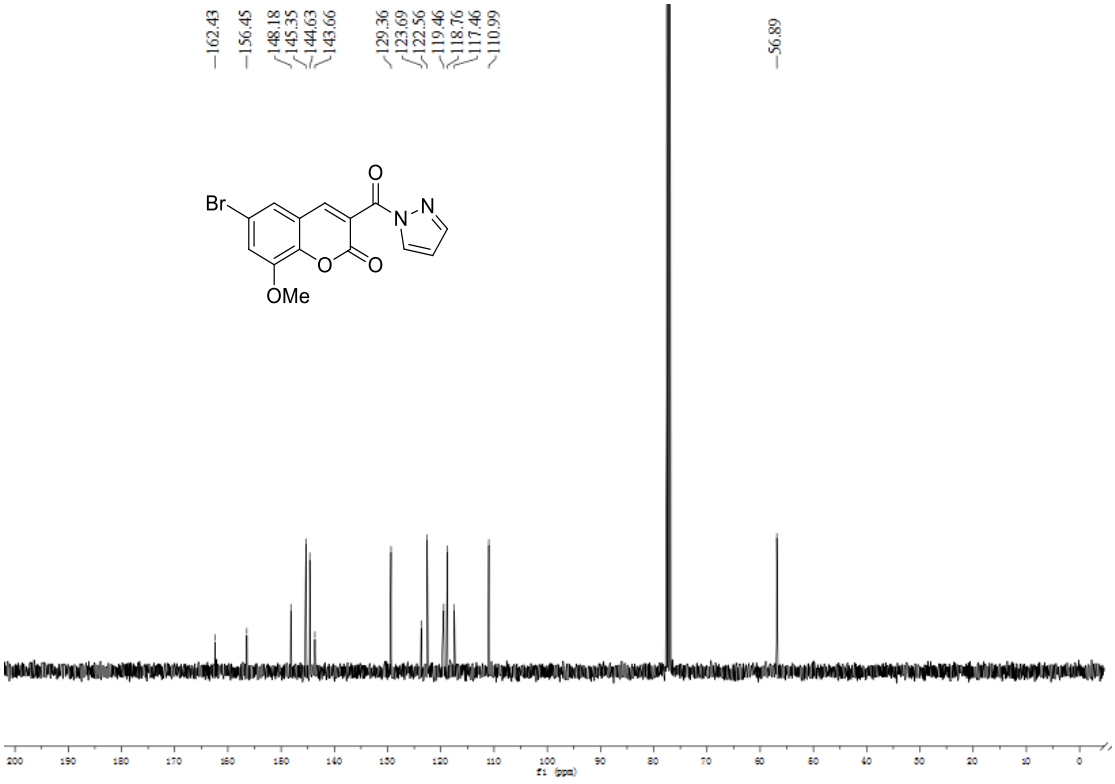
^{1}H and ^{13}C NMR of **1l**



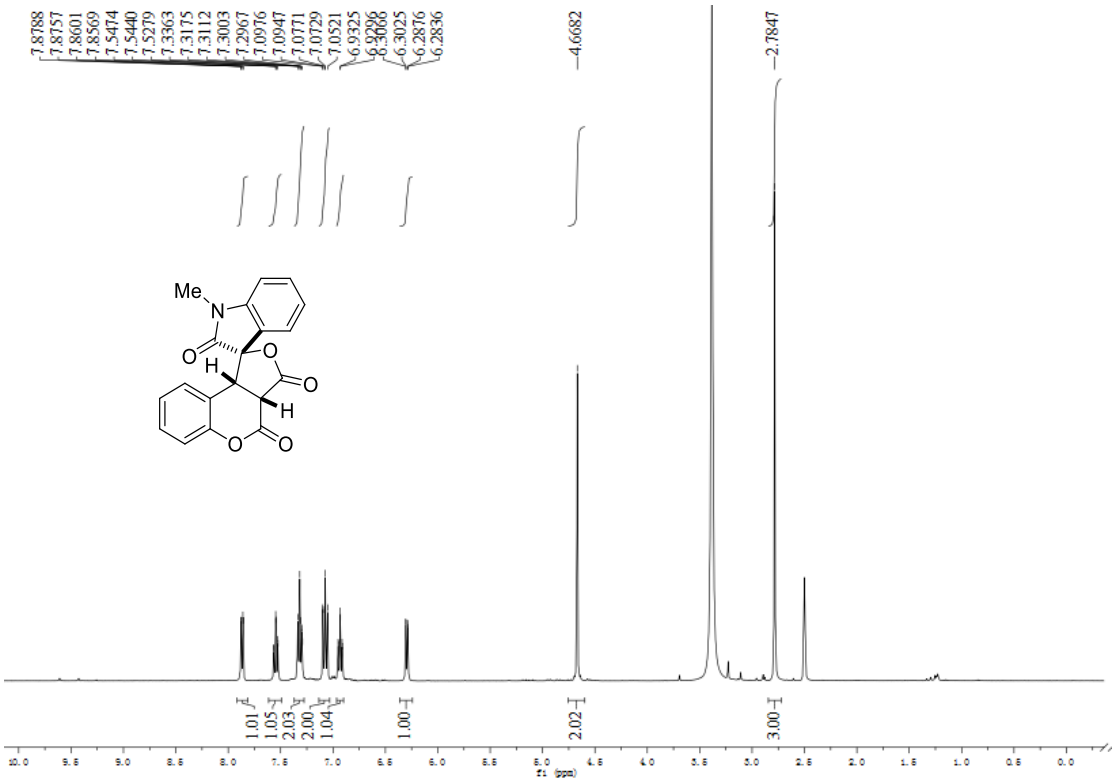


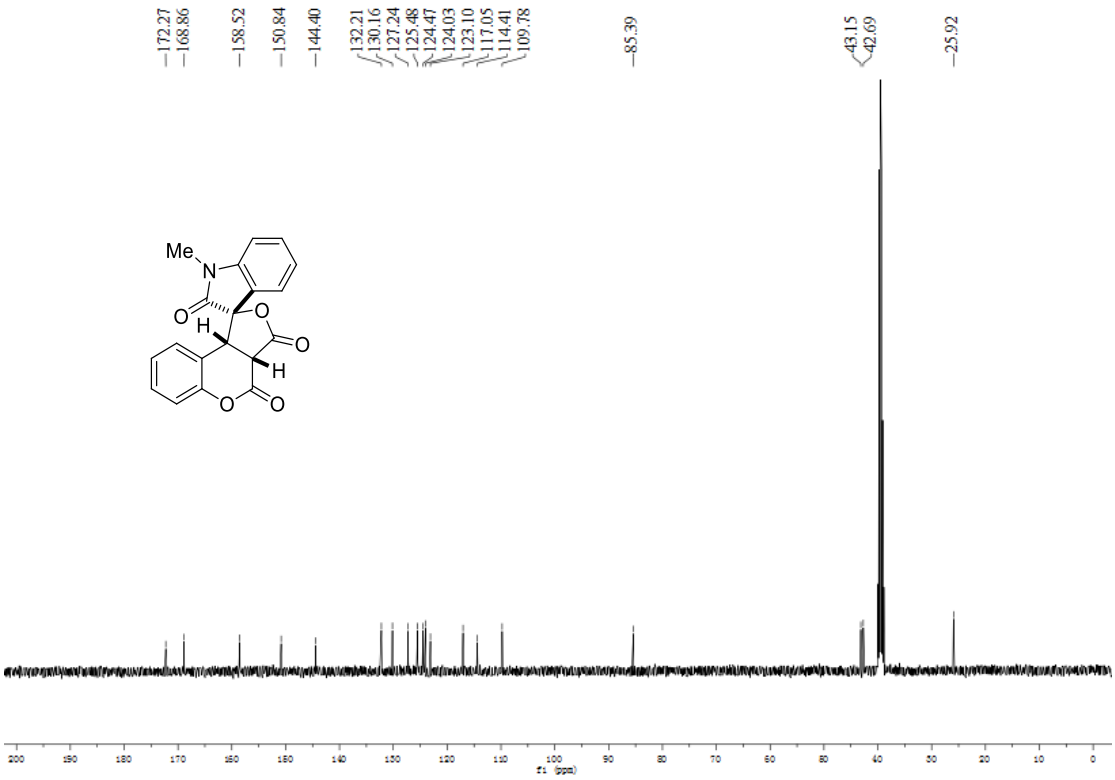
^{1}H and ^{13}C NMR of **1m**



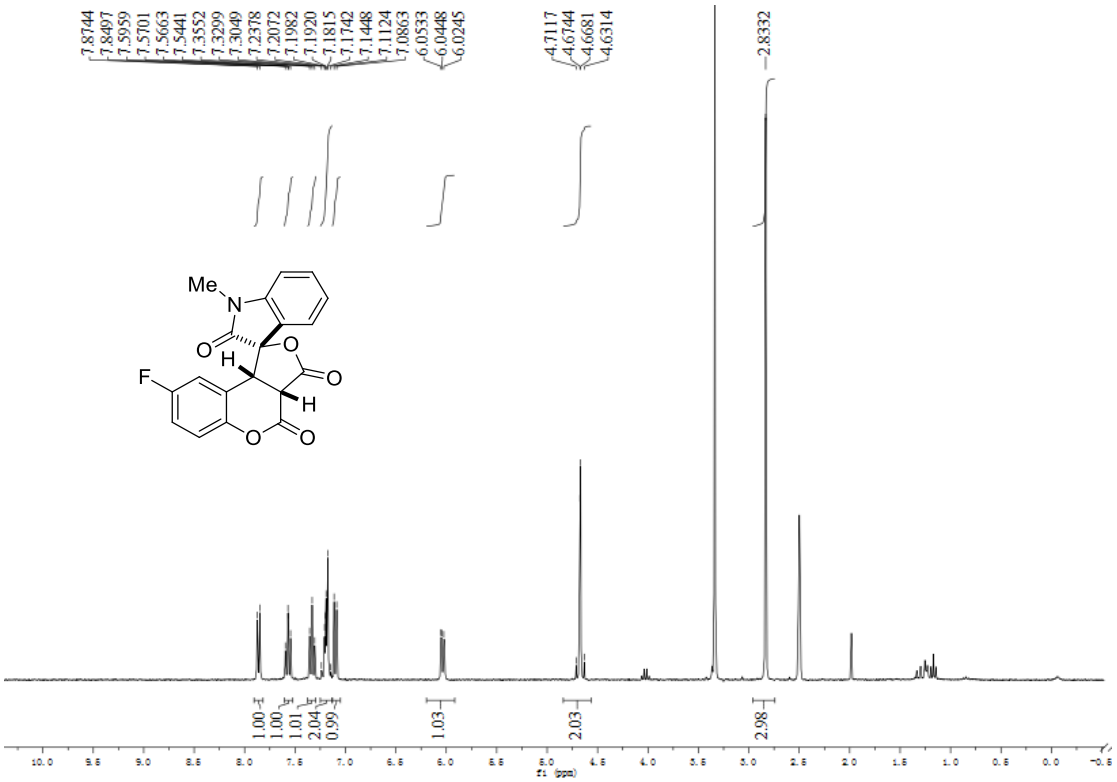


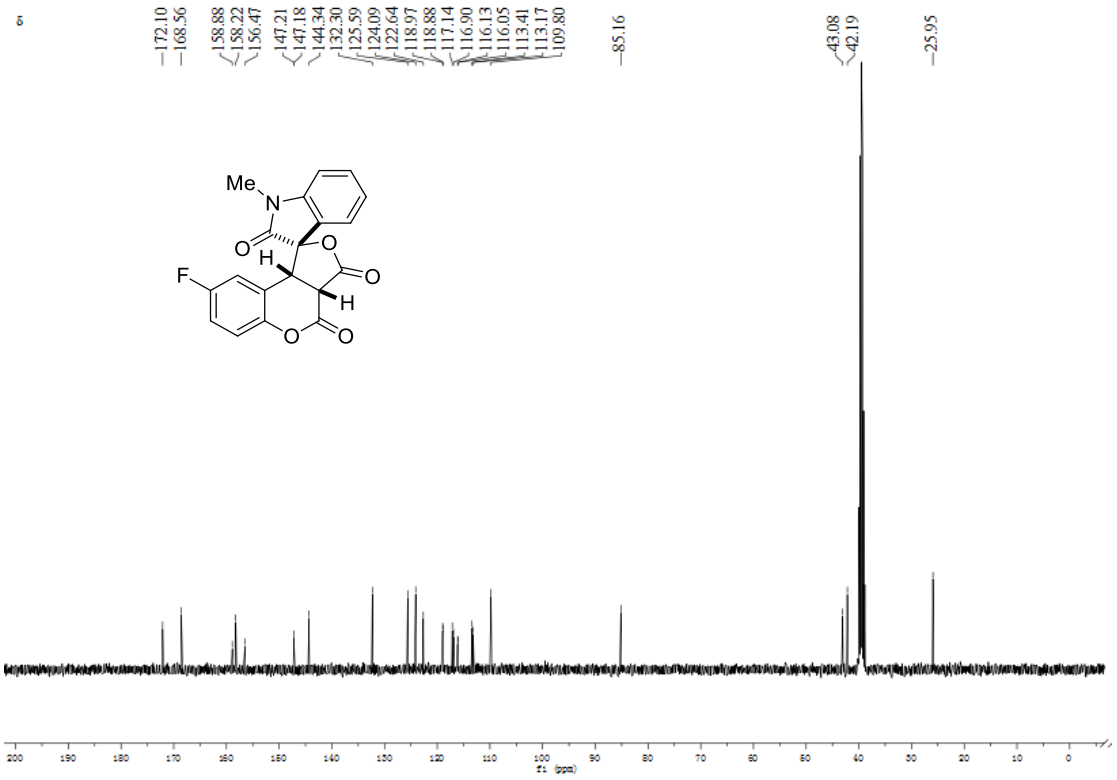
^{1}H and ^{13}C NMR of **3a**



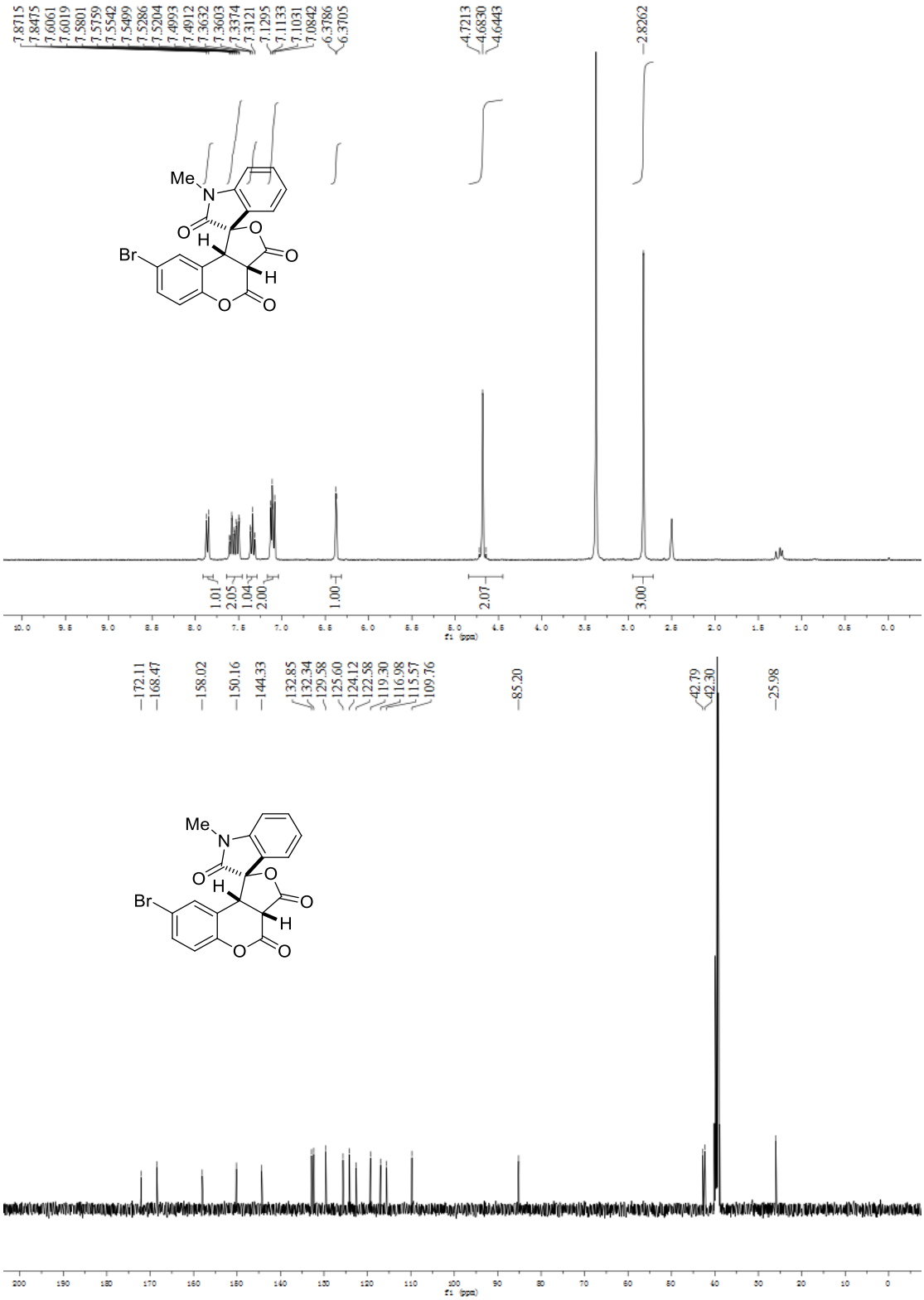


^{1}H and ^{13}C NMR of **3b**

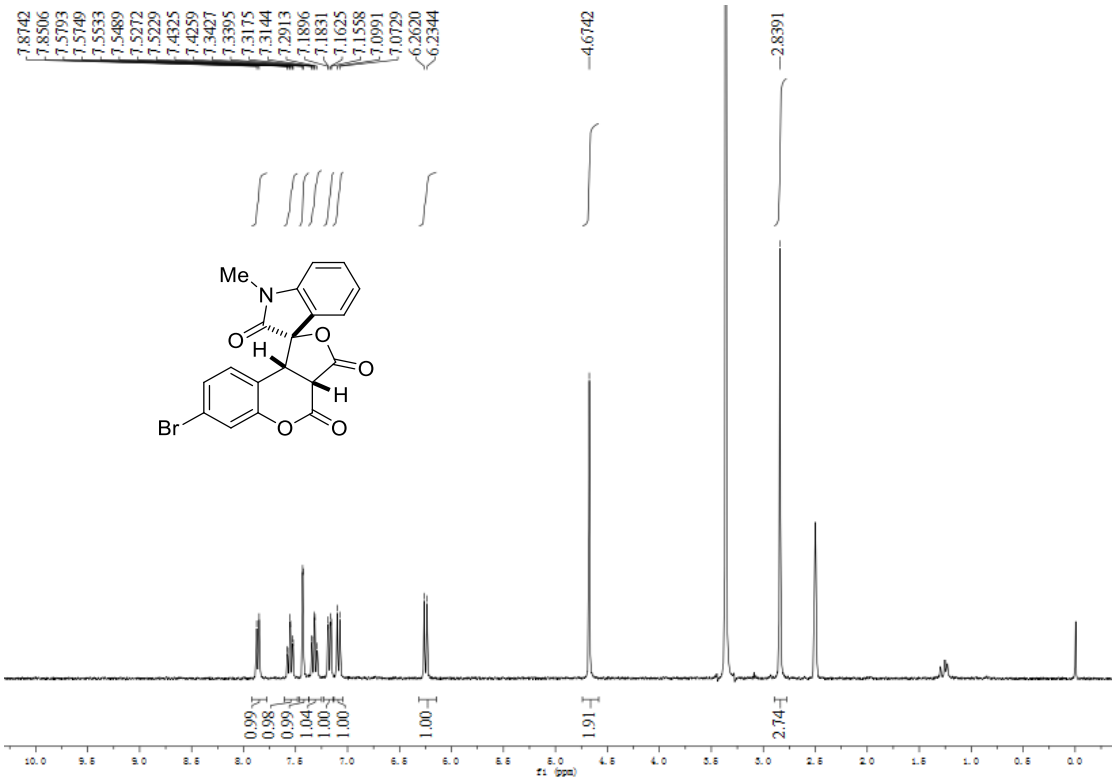


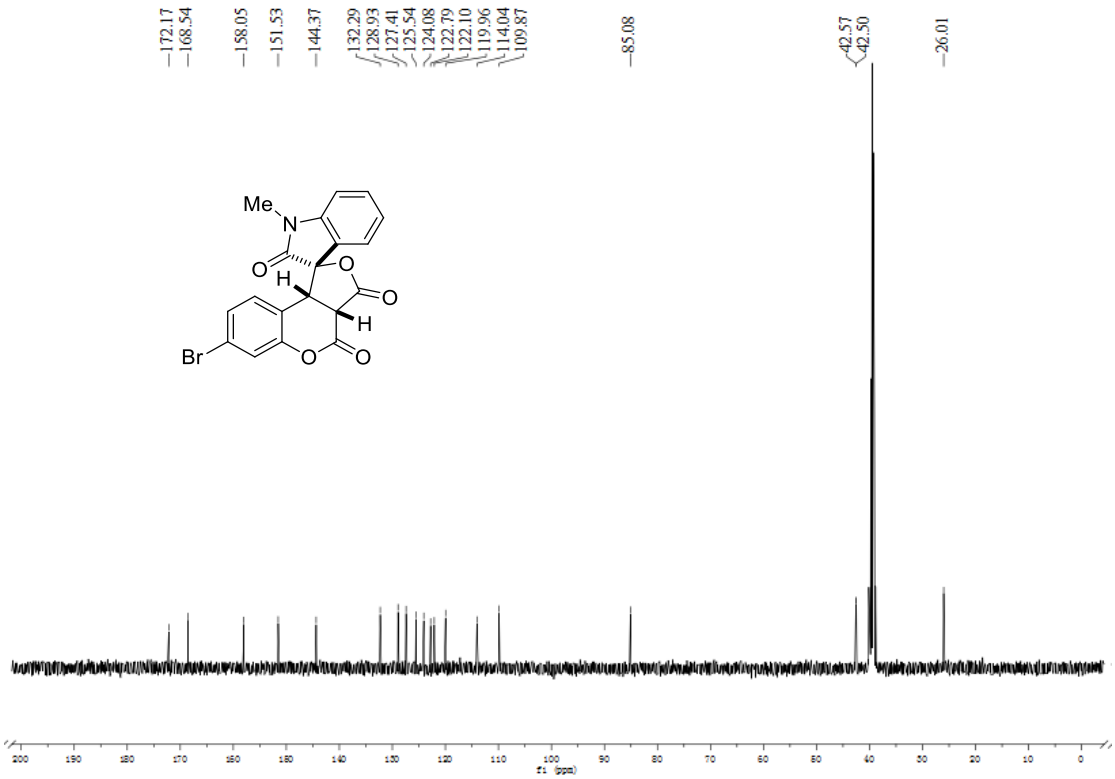


^{1}H and ^{13}C NMR of **3c**

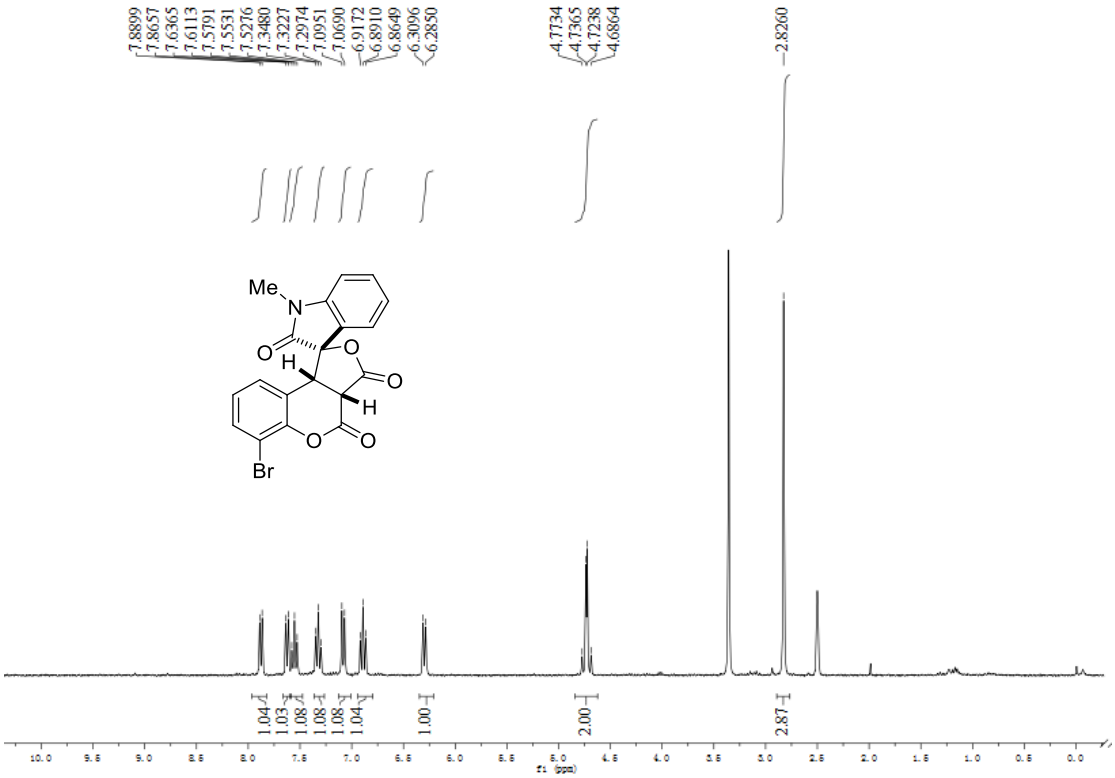


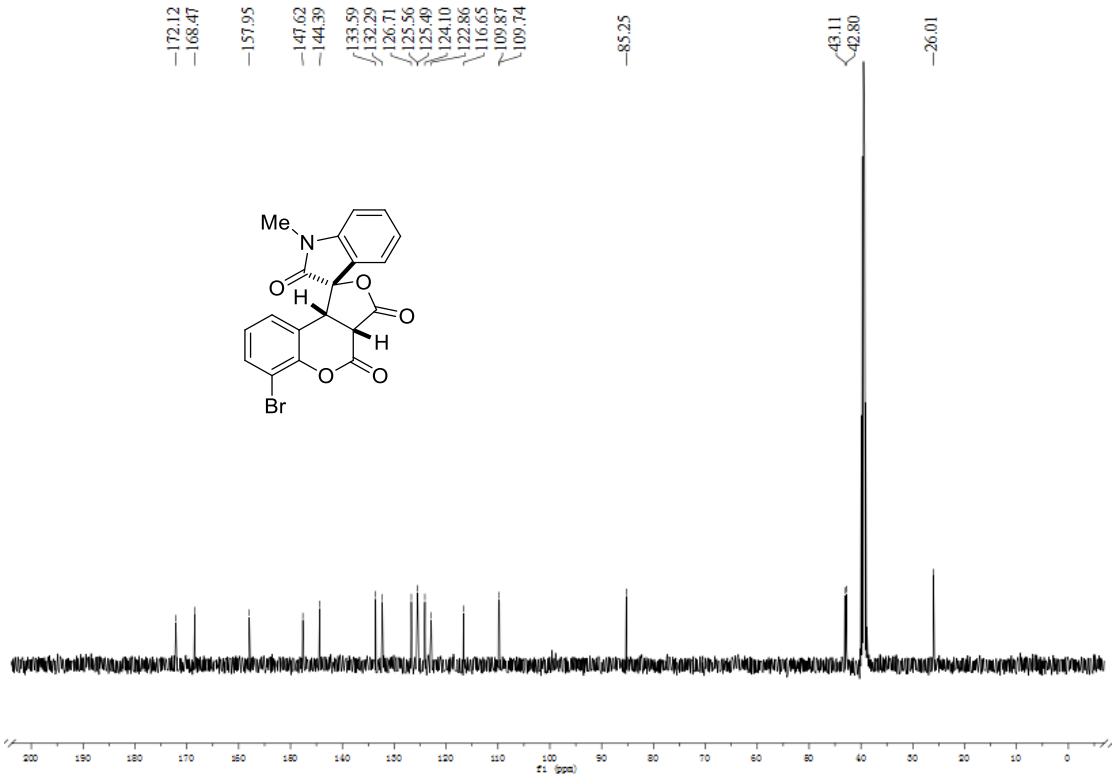
^{1}H and ^{13}C NMR of **3d**



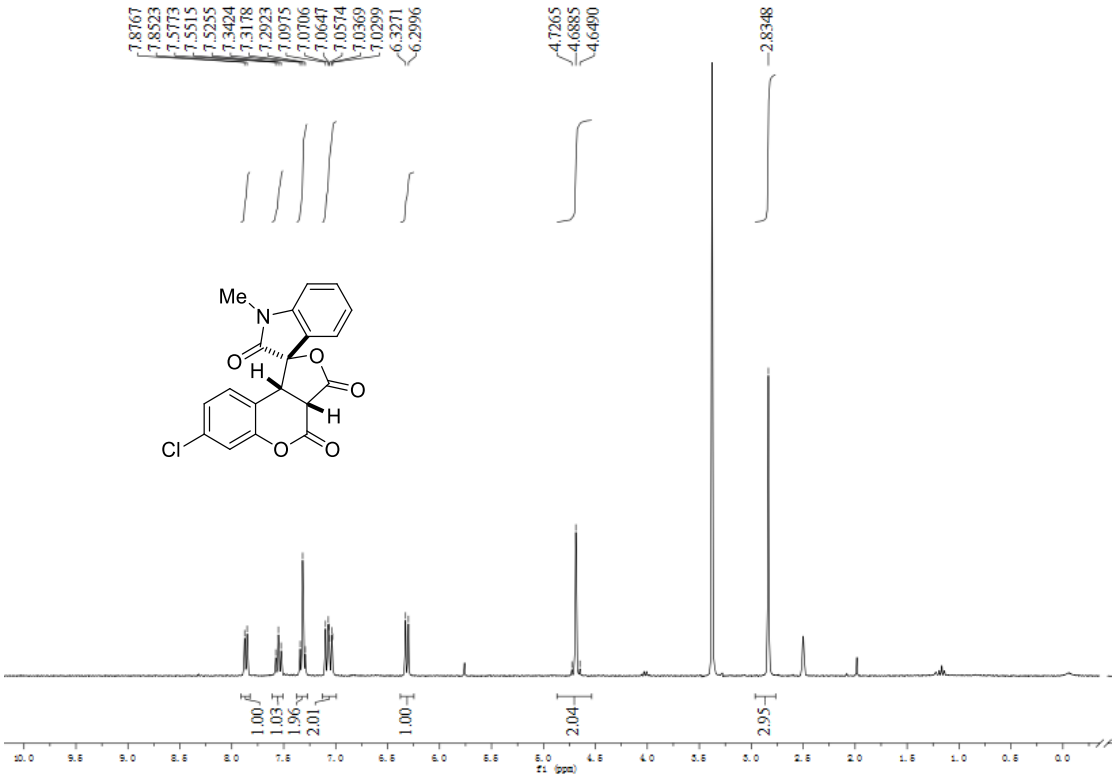


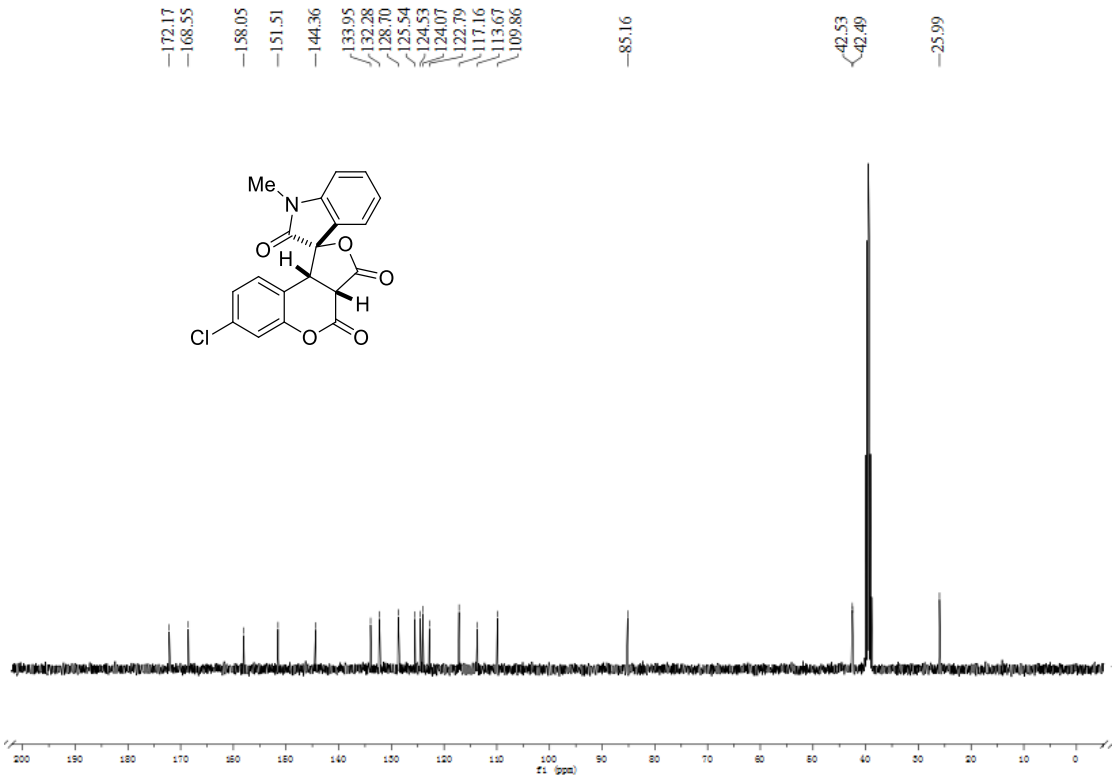
^{1}H and ^{13}C NMR of **3e**



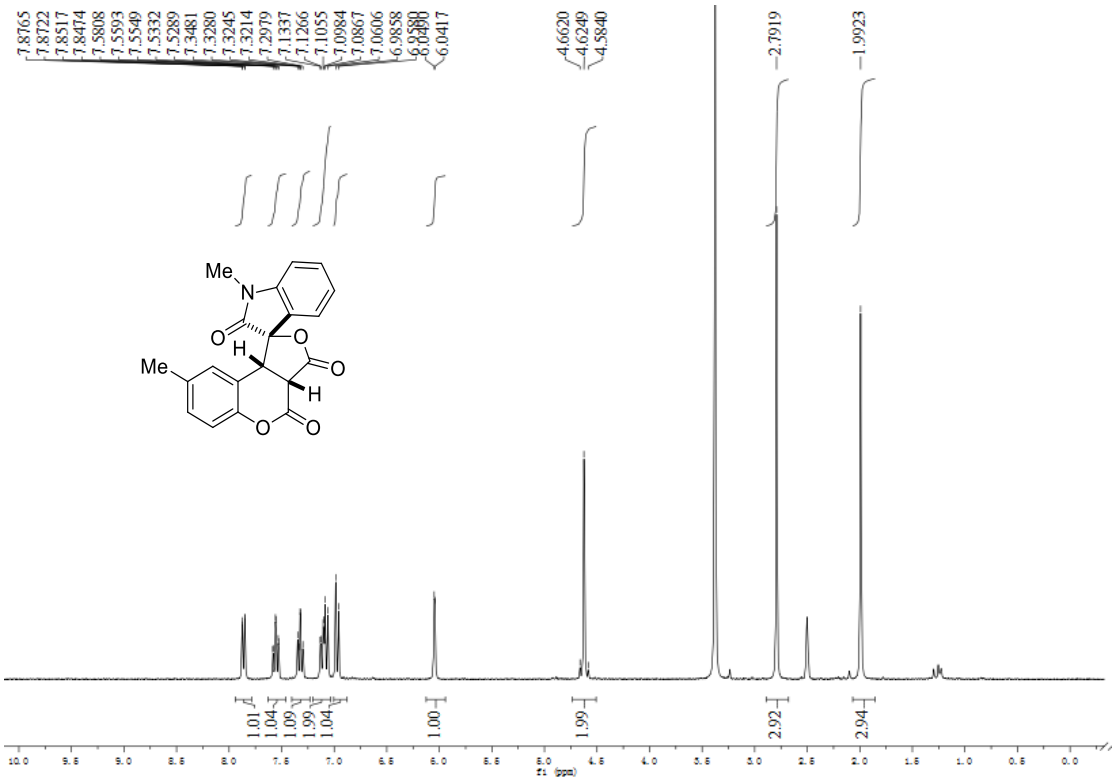


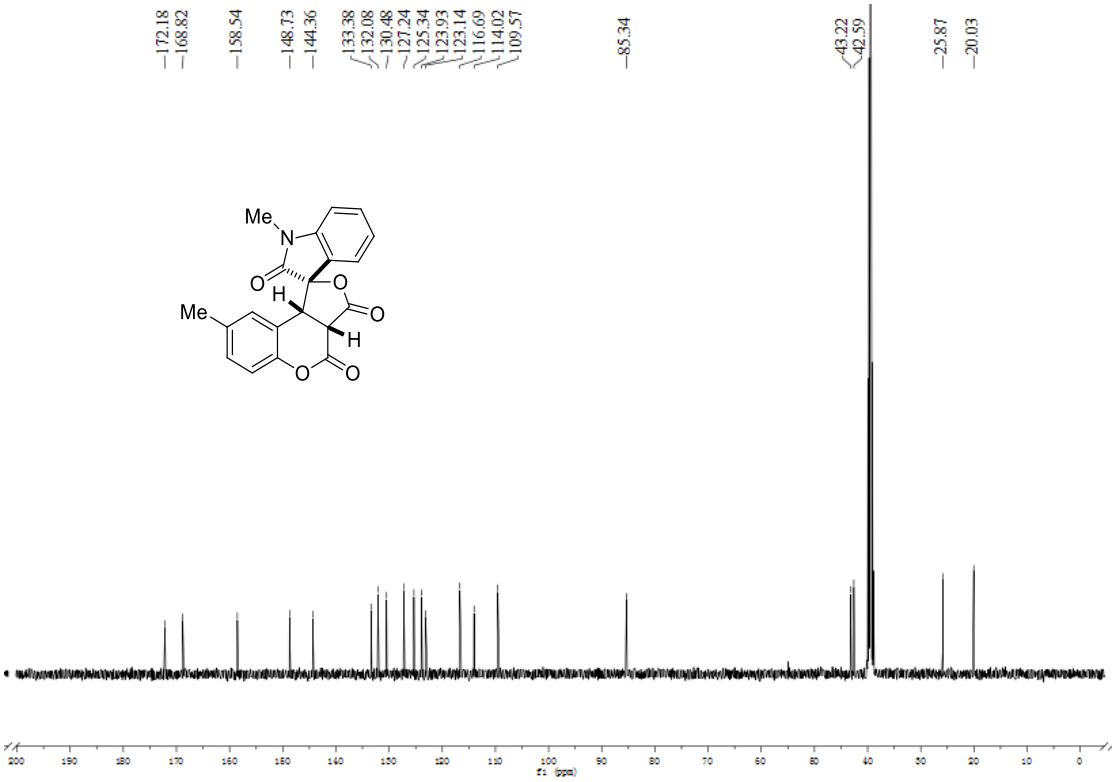
^{1}H and ^{13}C NMR of **3f**



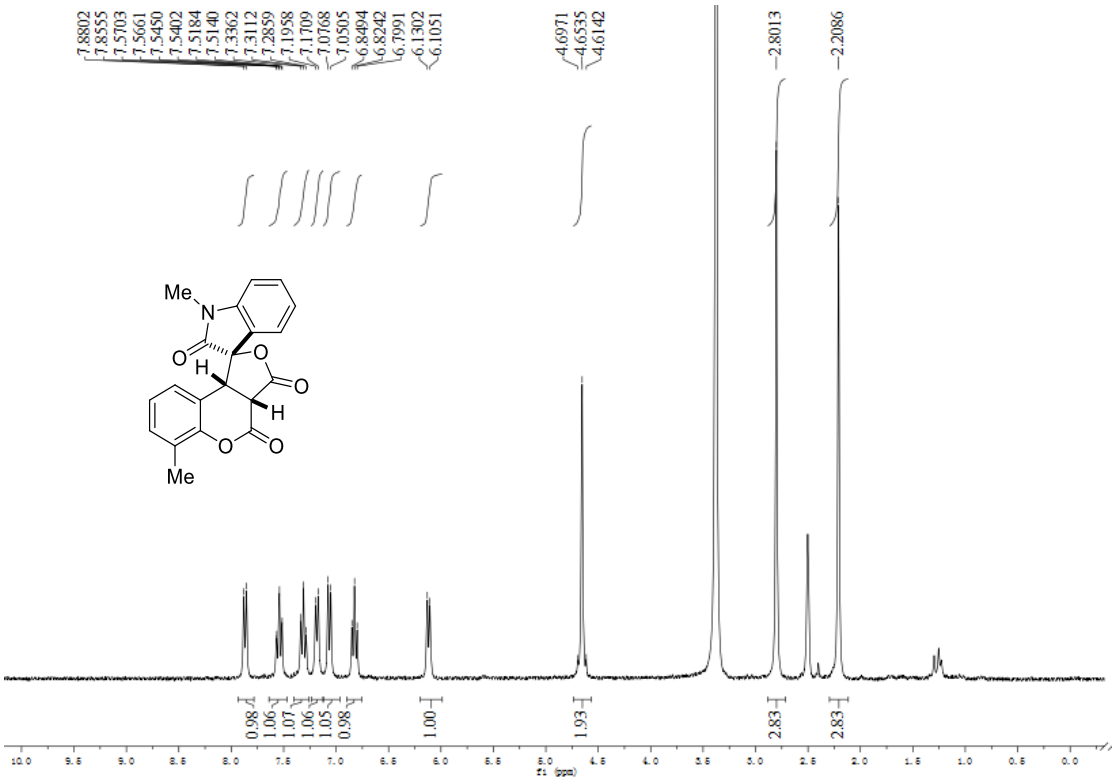


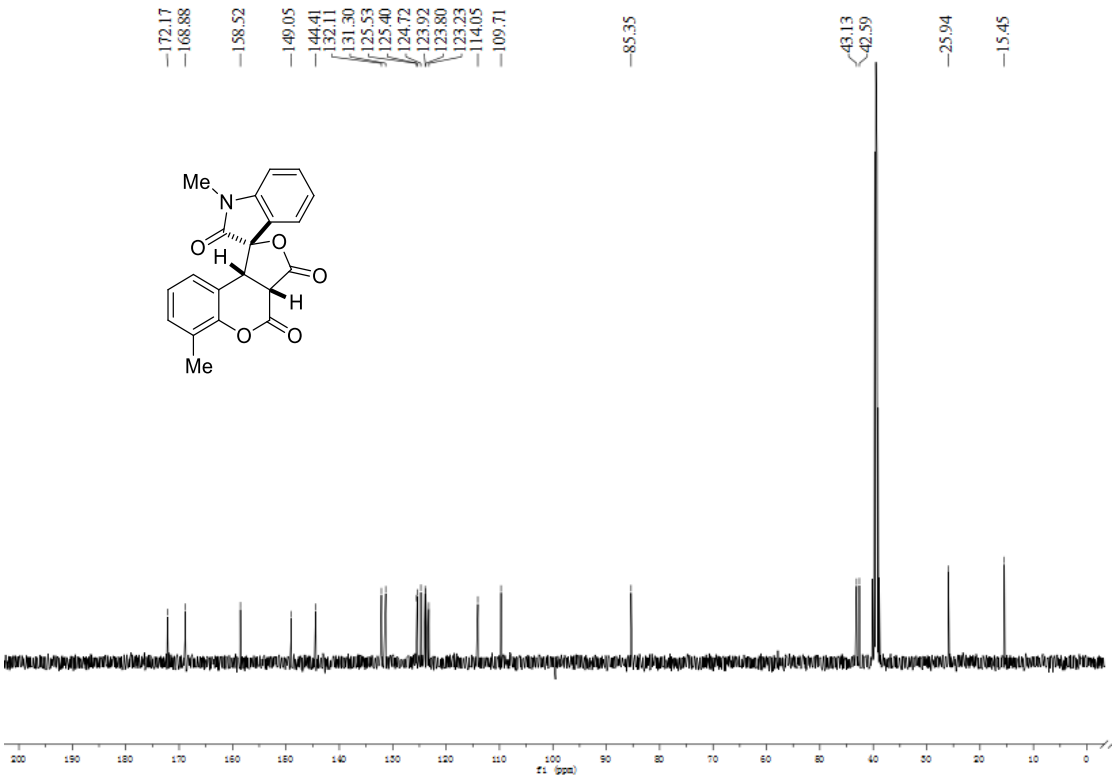
^{1}H and ^{13}C NMR of **3g**



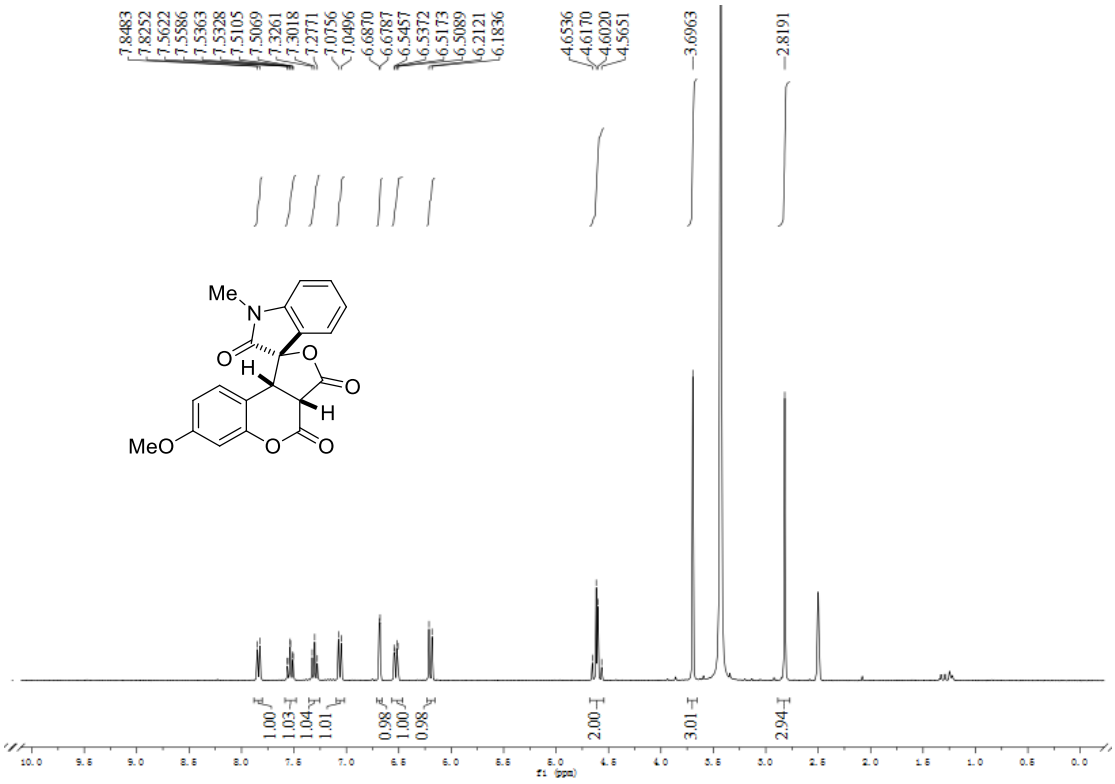


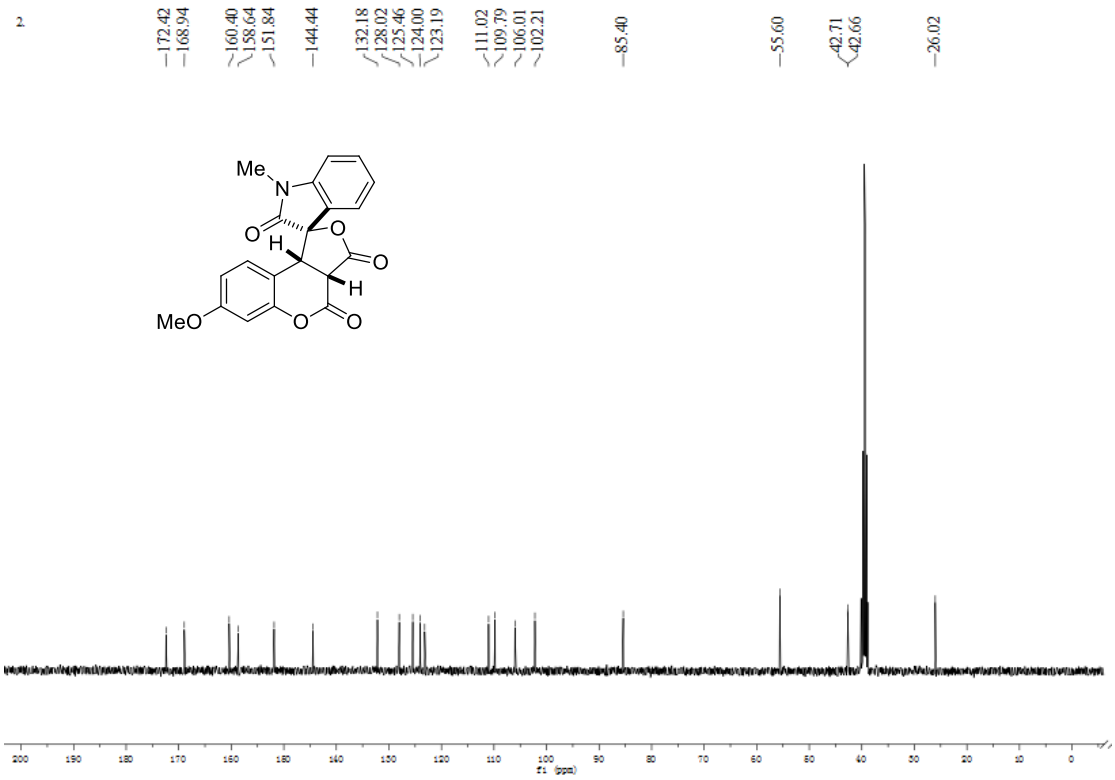
^{1}H and ^{13}C NMR of **3h**



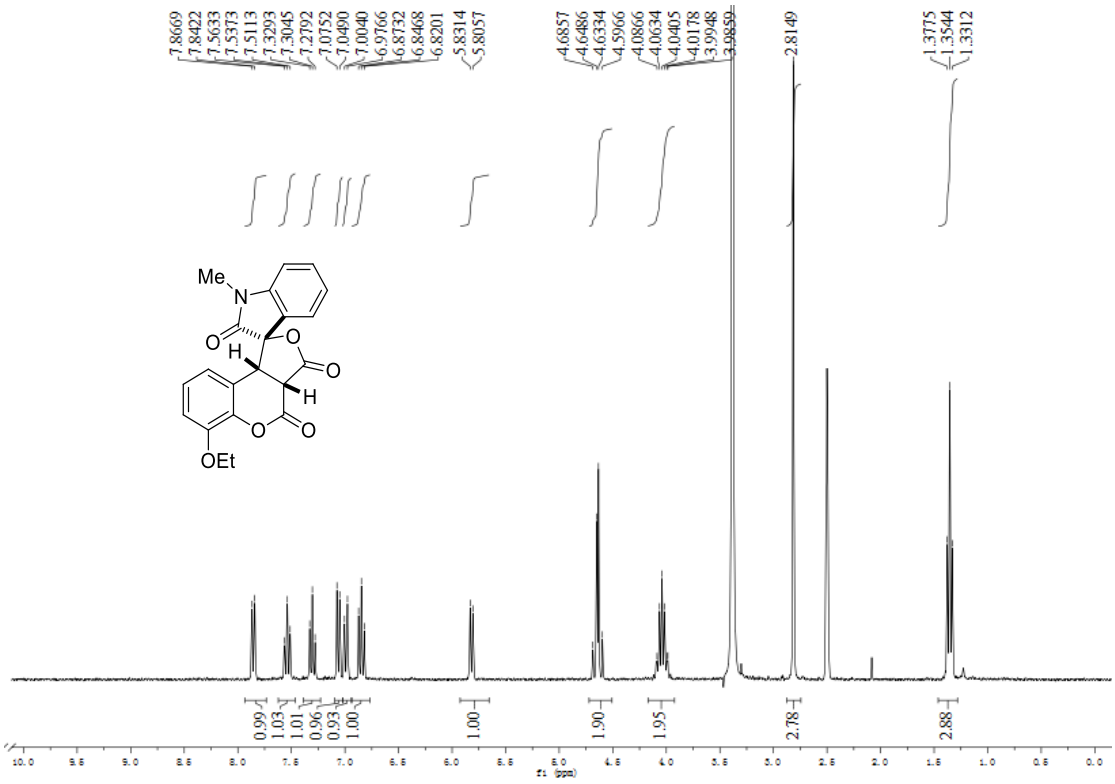


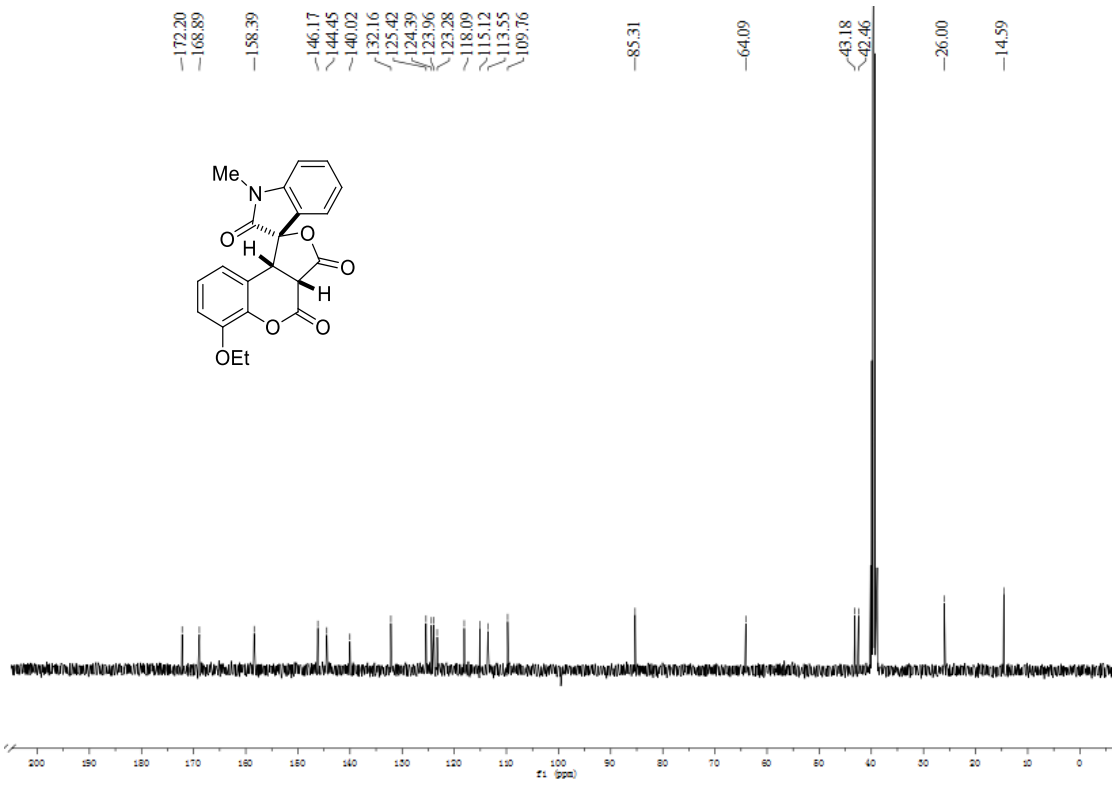
^{1}H and ^{13}C NMR of **3i**



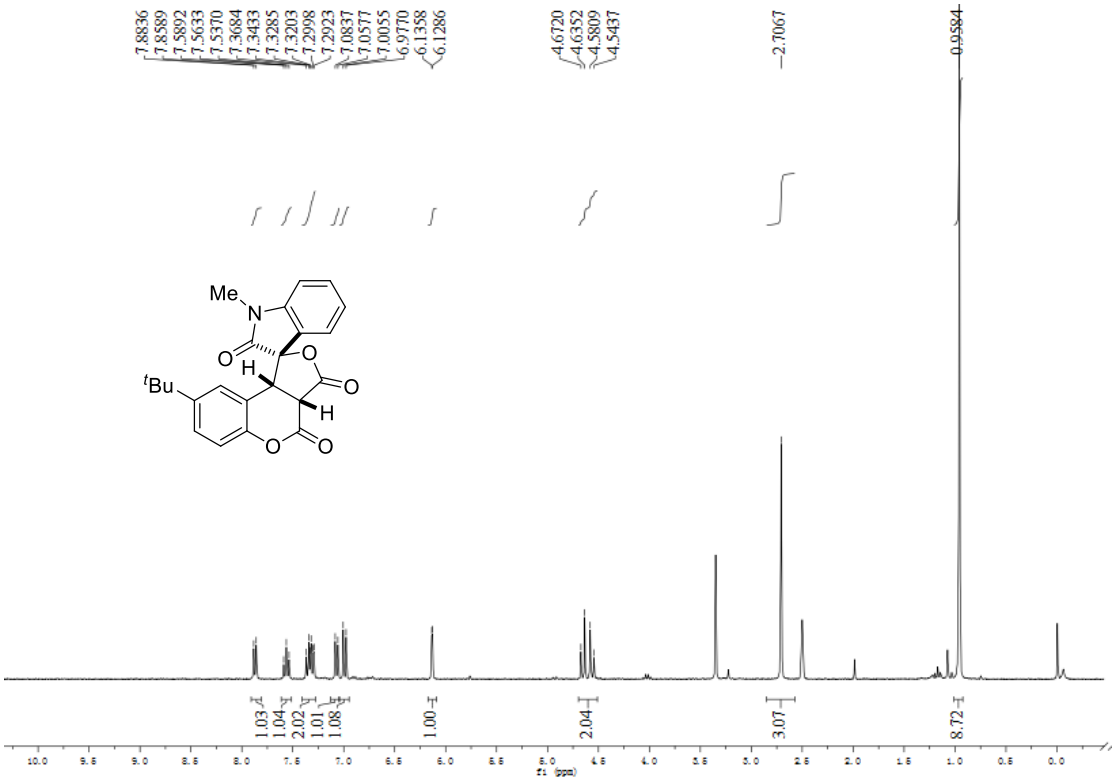


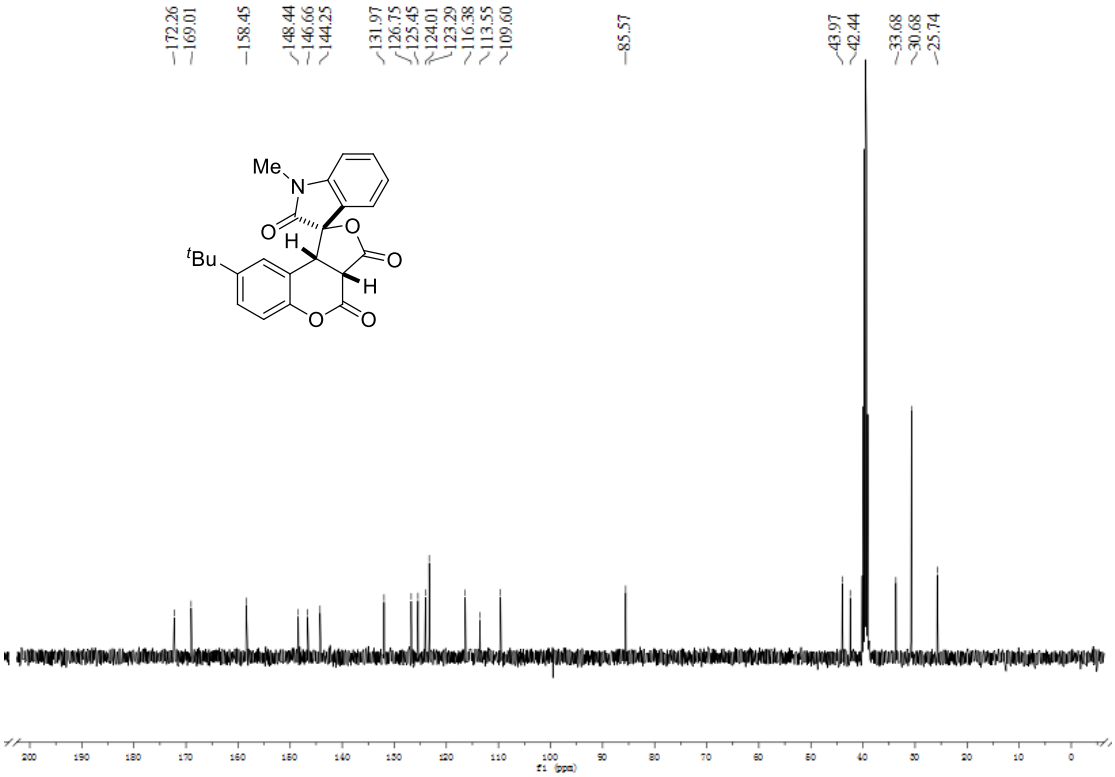
^{1}H and ^{13}C NMR of **3j**



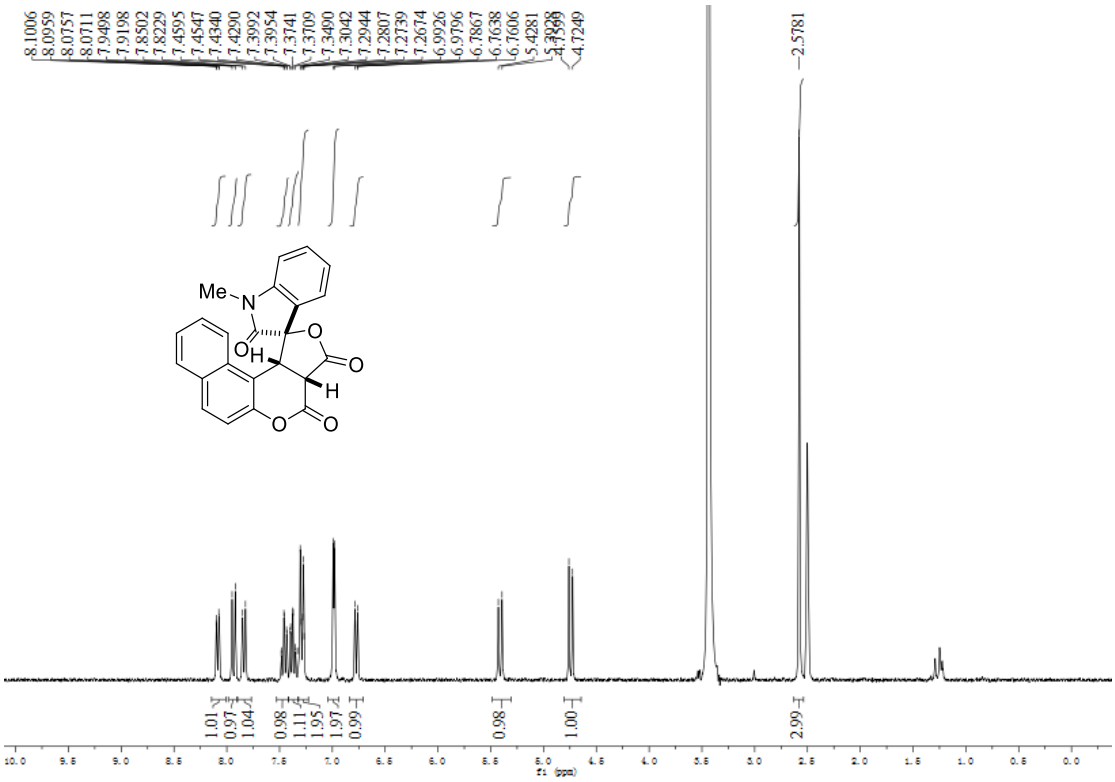


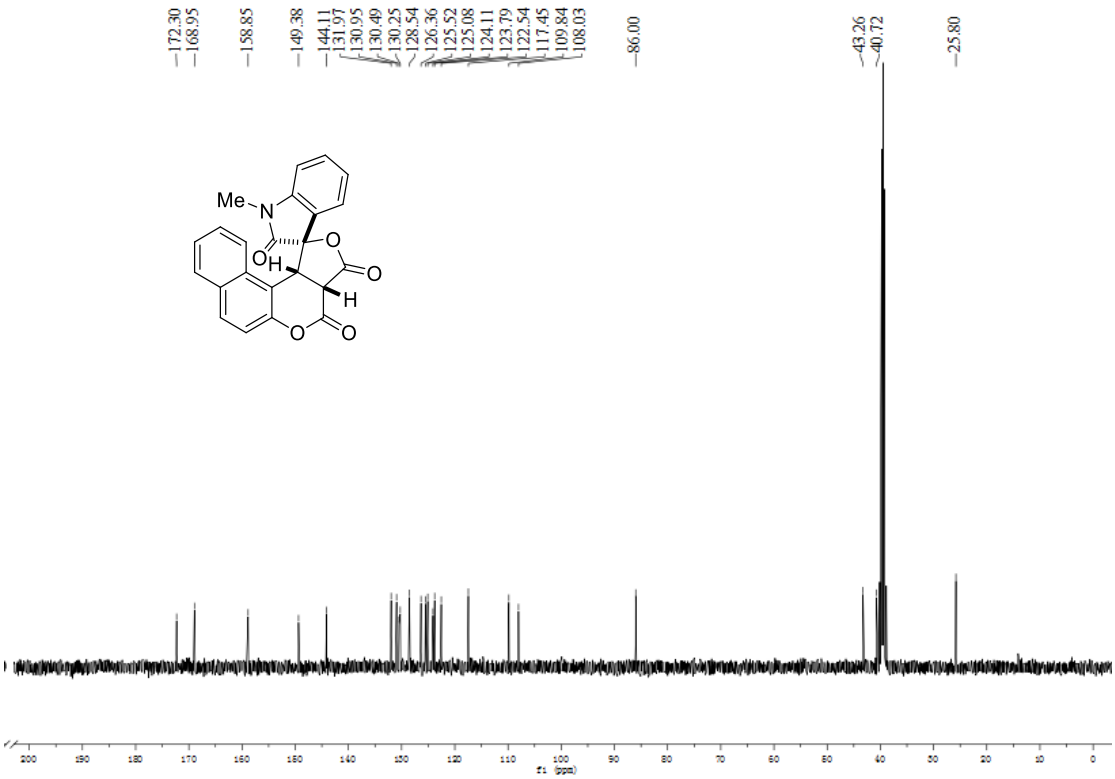
^{1}H and ^{13}C NMR of **3k**



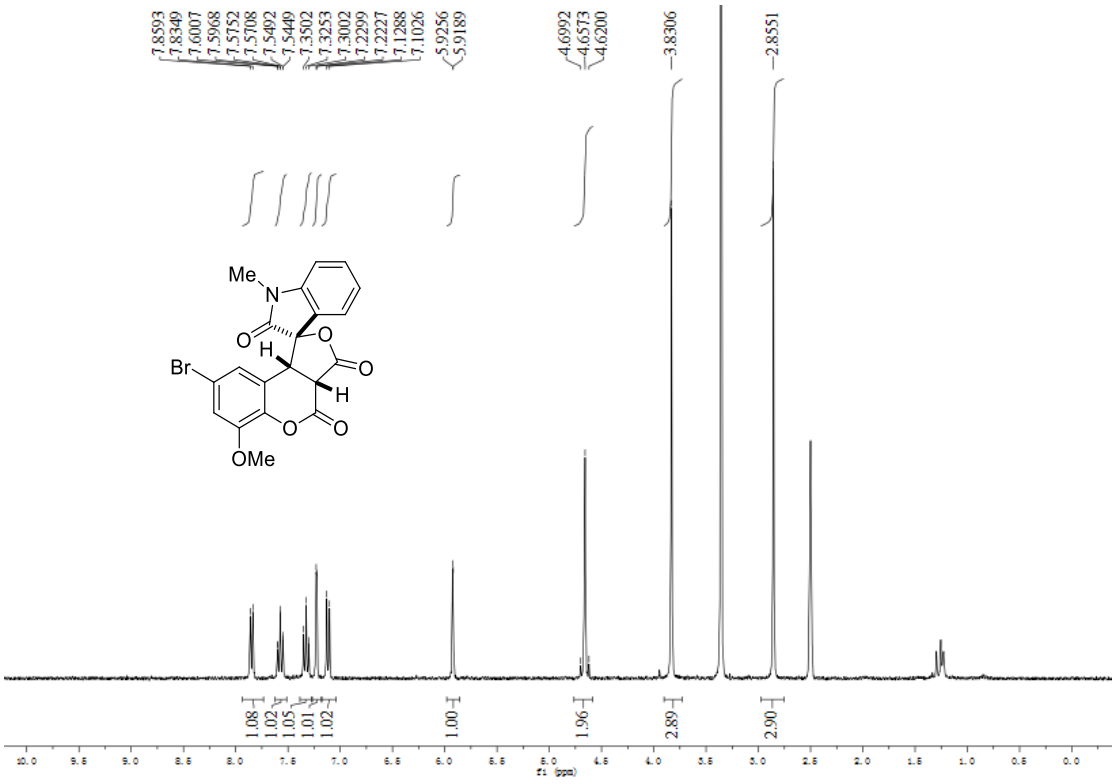


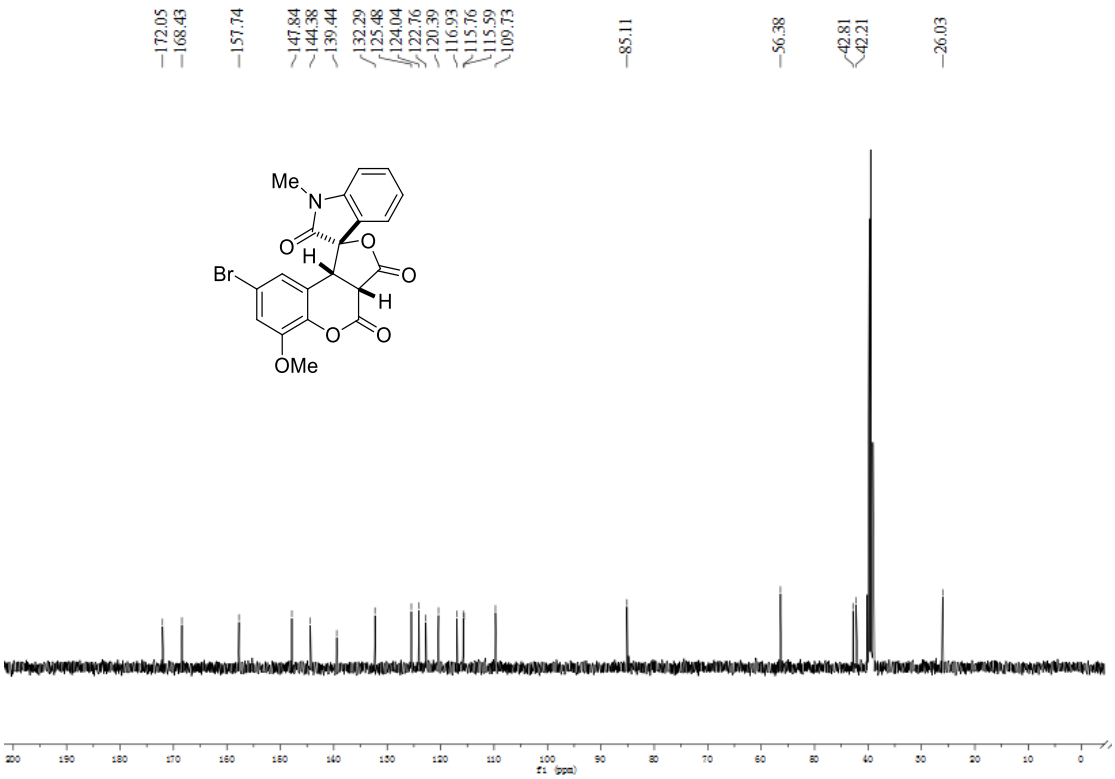
^{1}H and ^{13}C NMR of **3l**



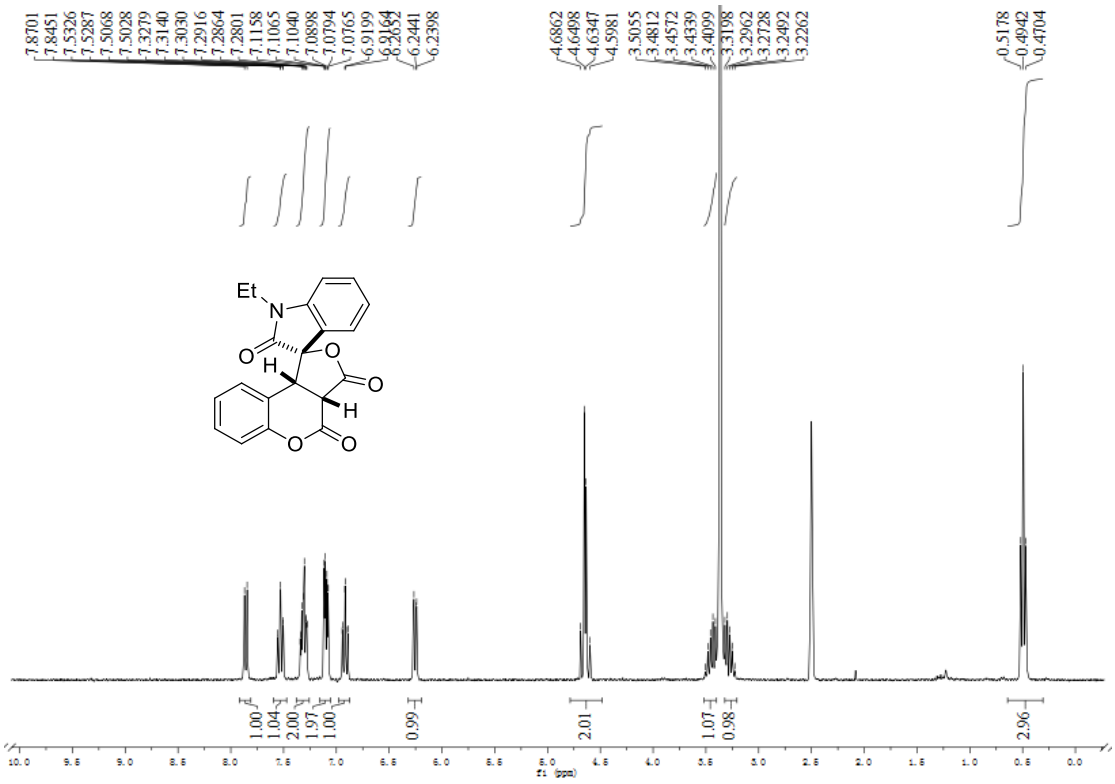


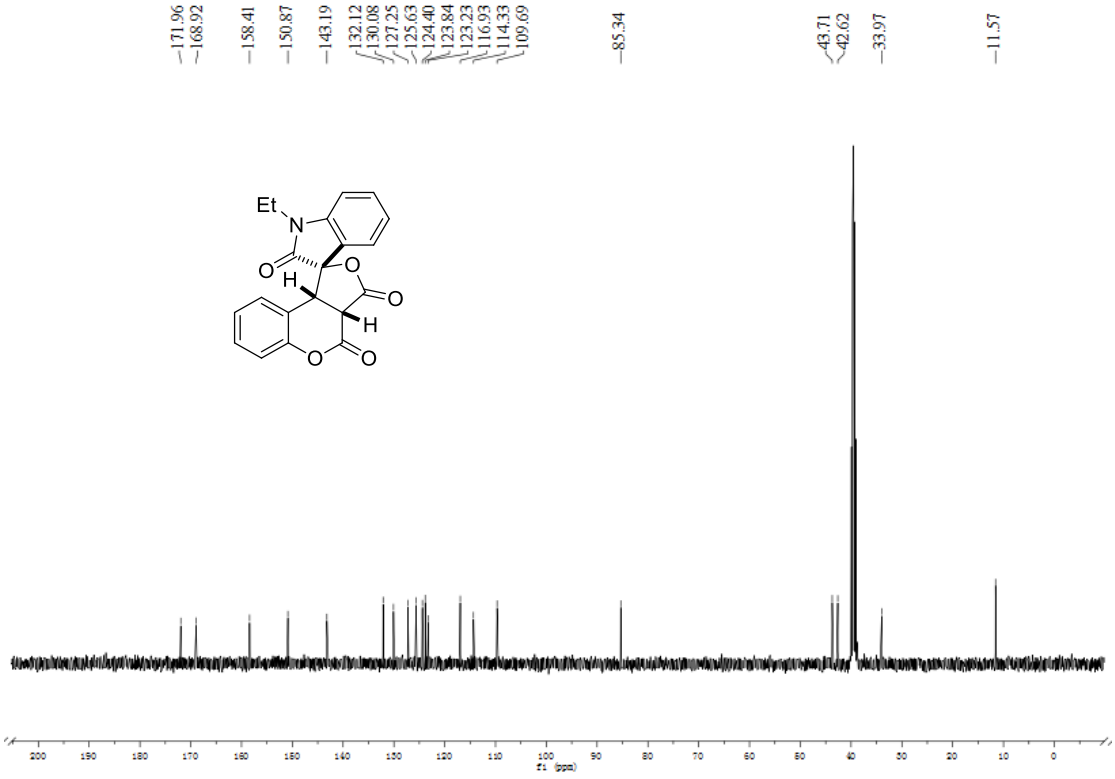
^{1}H and ^{13}C NMR of **3m**



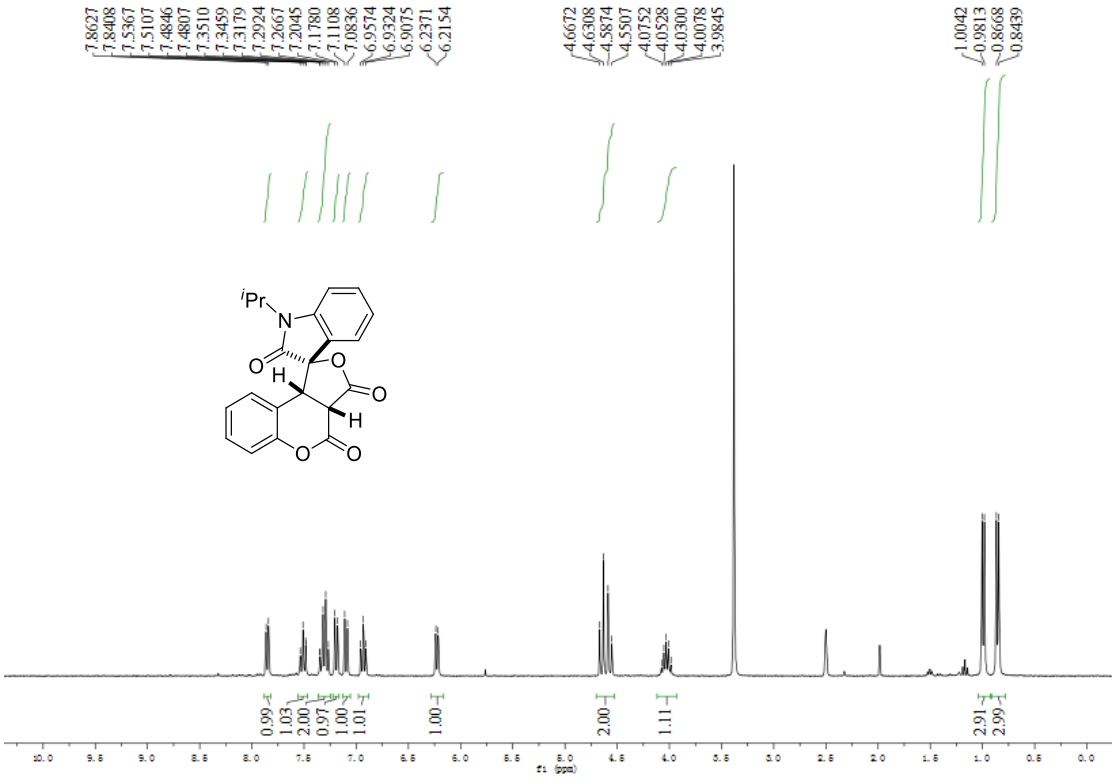


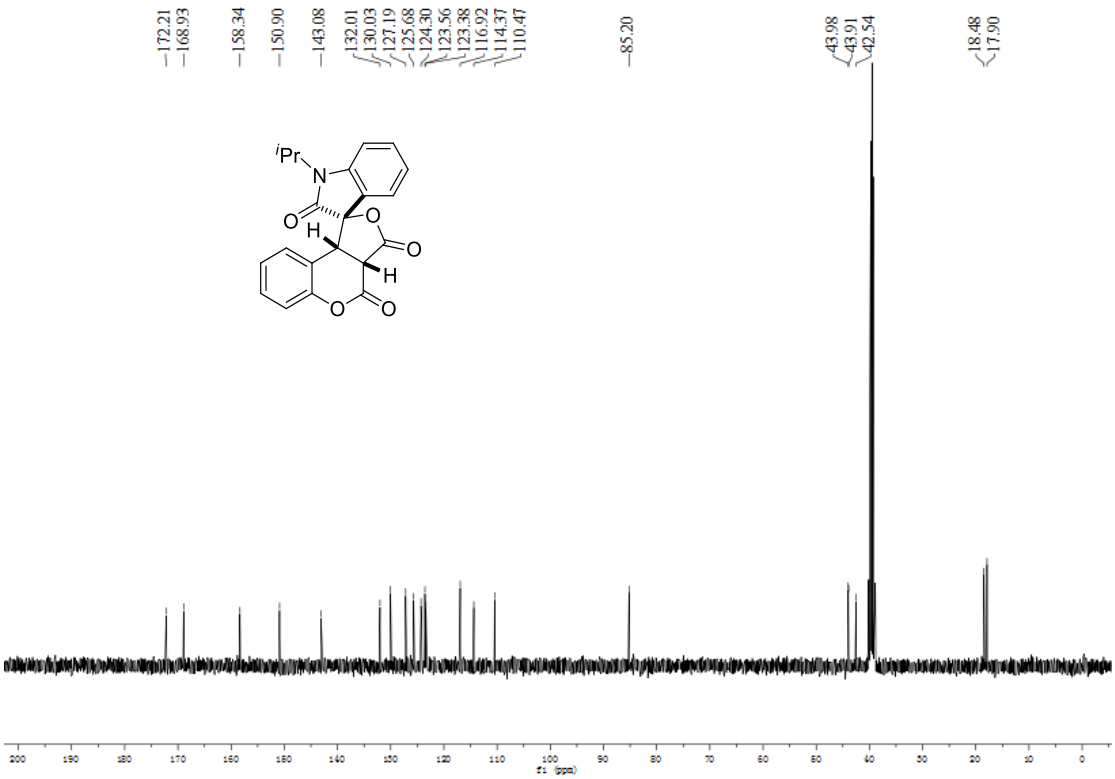
^{1}H and ^{13}C NMR of **3n**



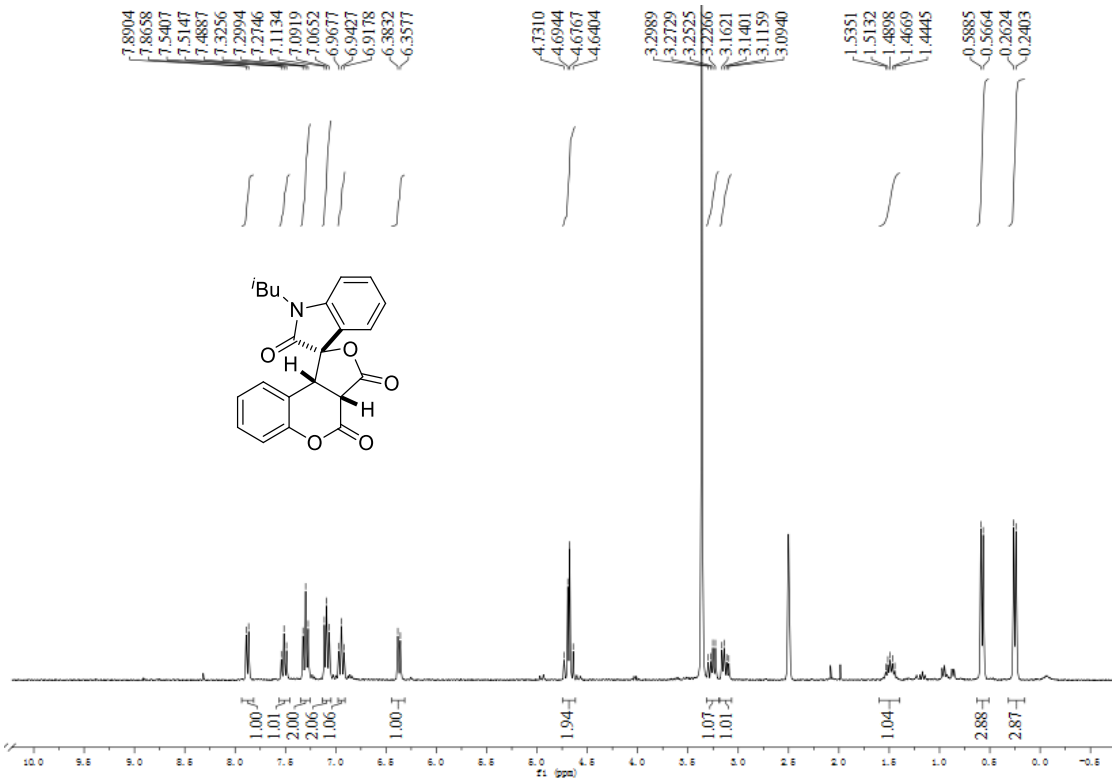


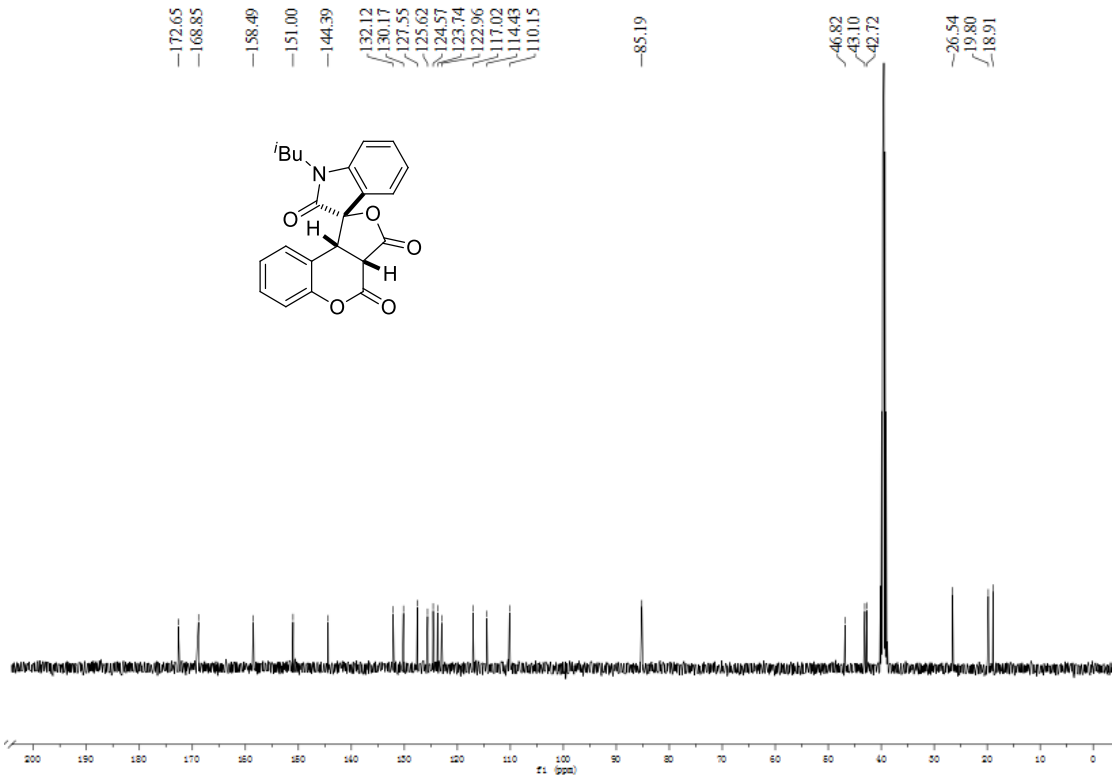
^{1}H and ^{13}C NMR of **3o**



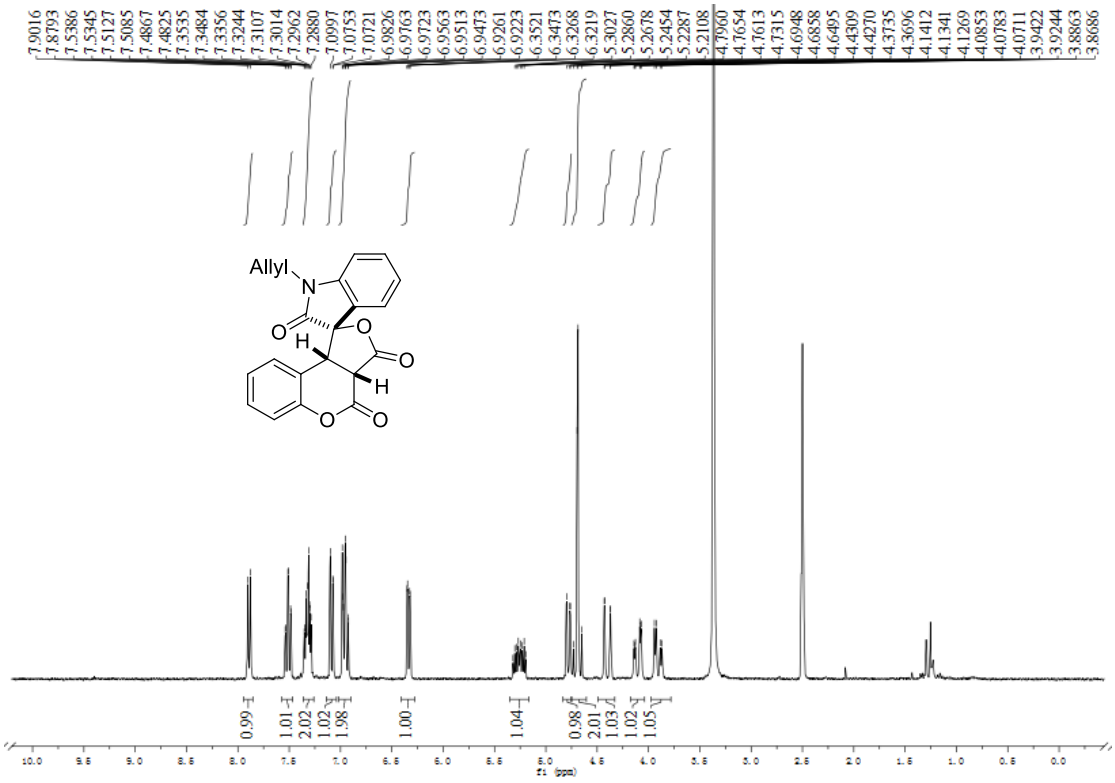


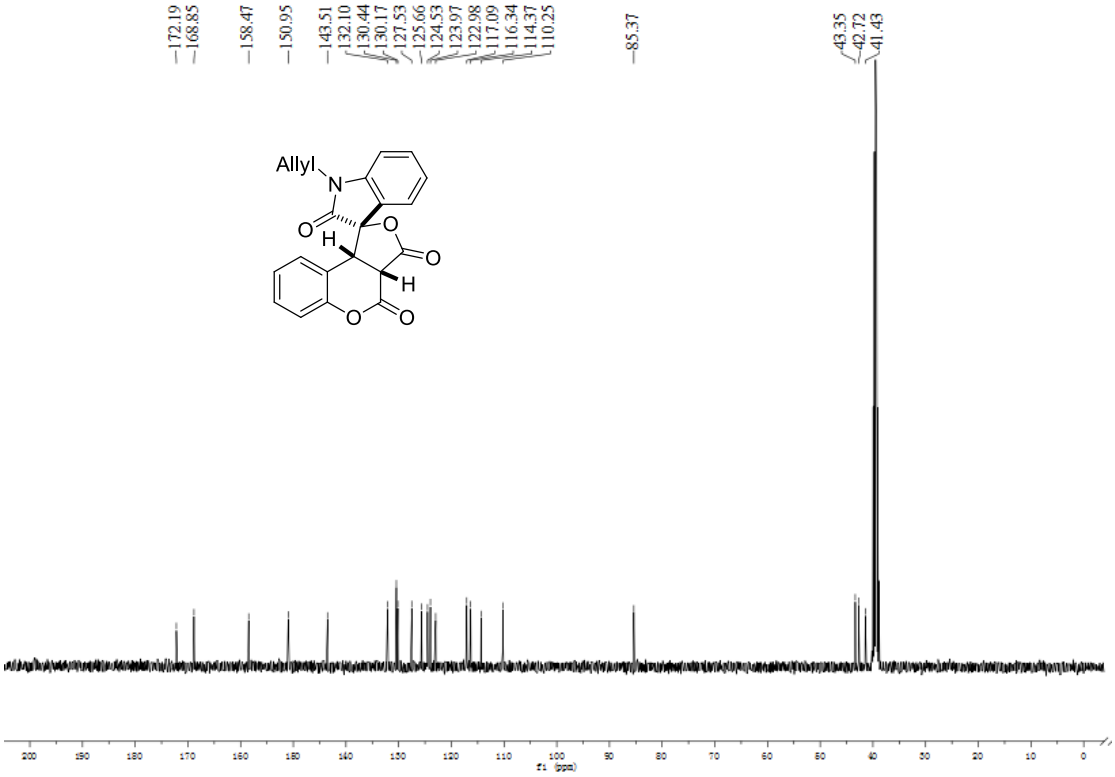
^{1}H and ^{13}C NMR of **3p**



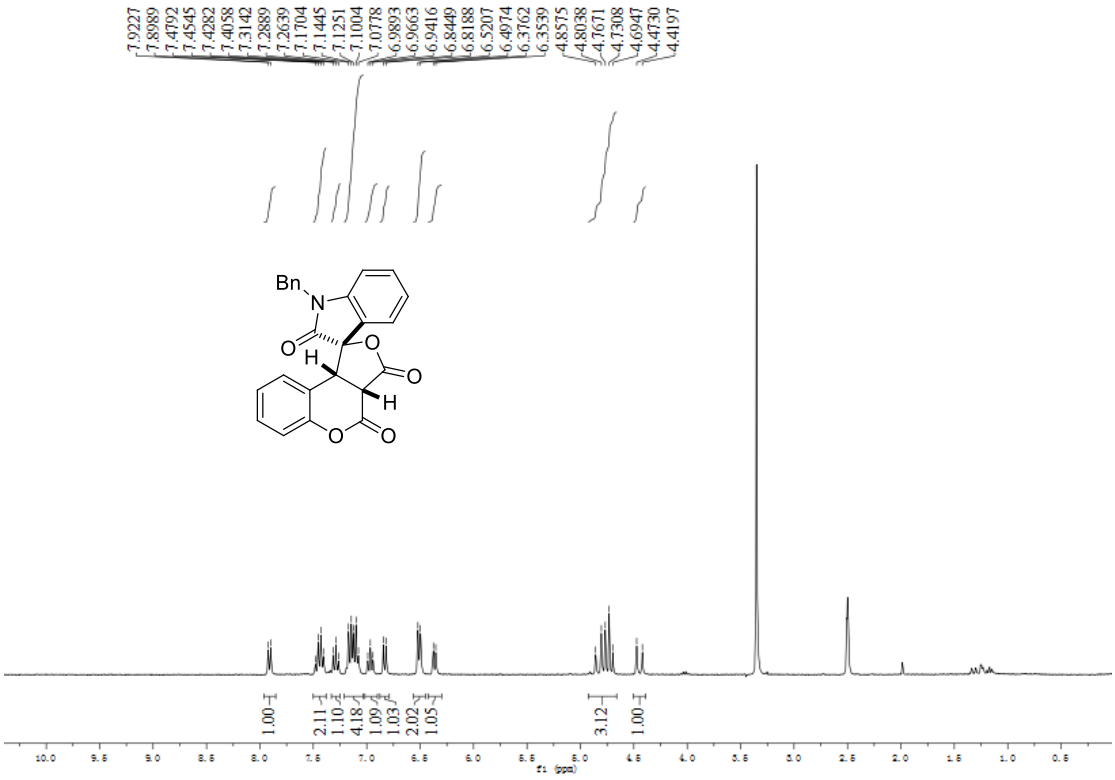


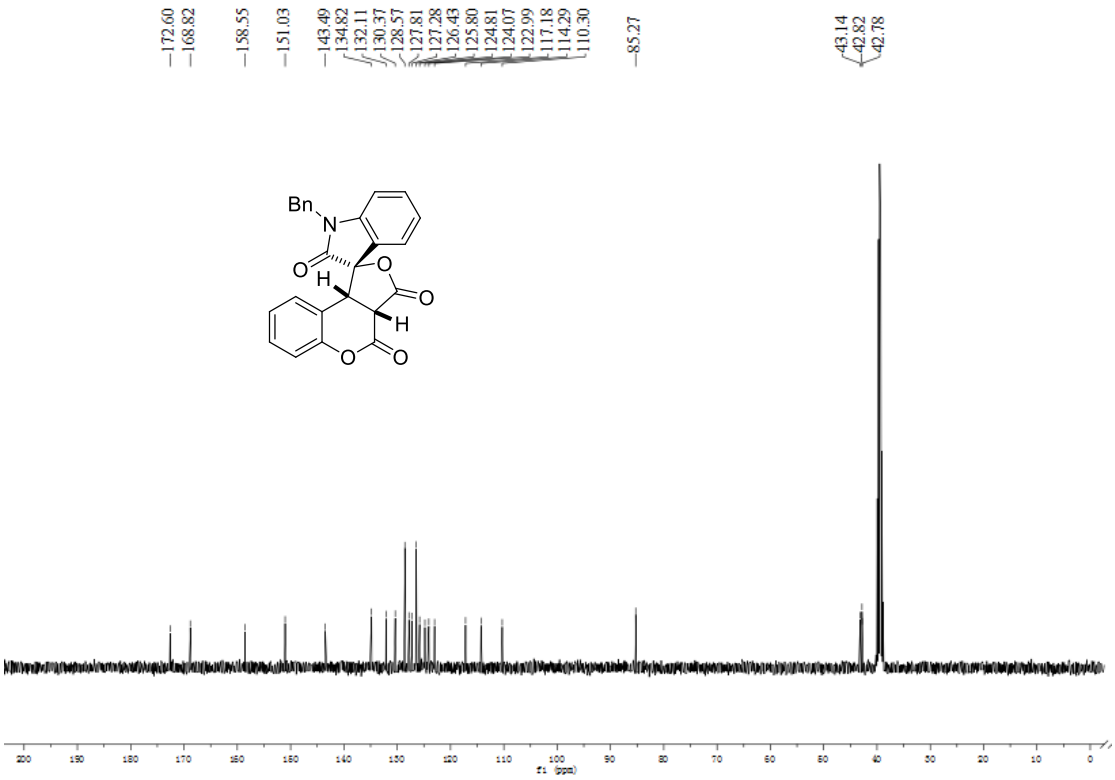
^{1}H and ^{13}C NMR of **3q**



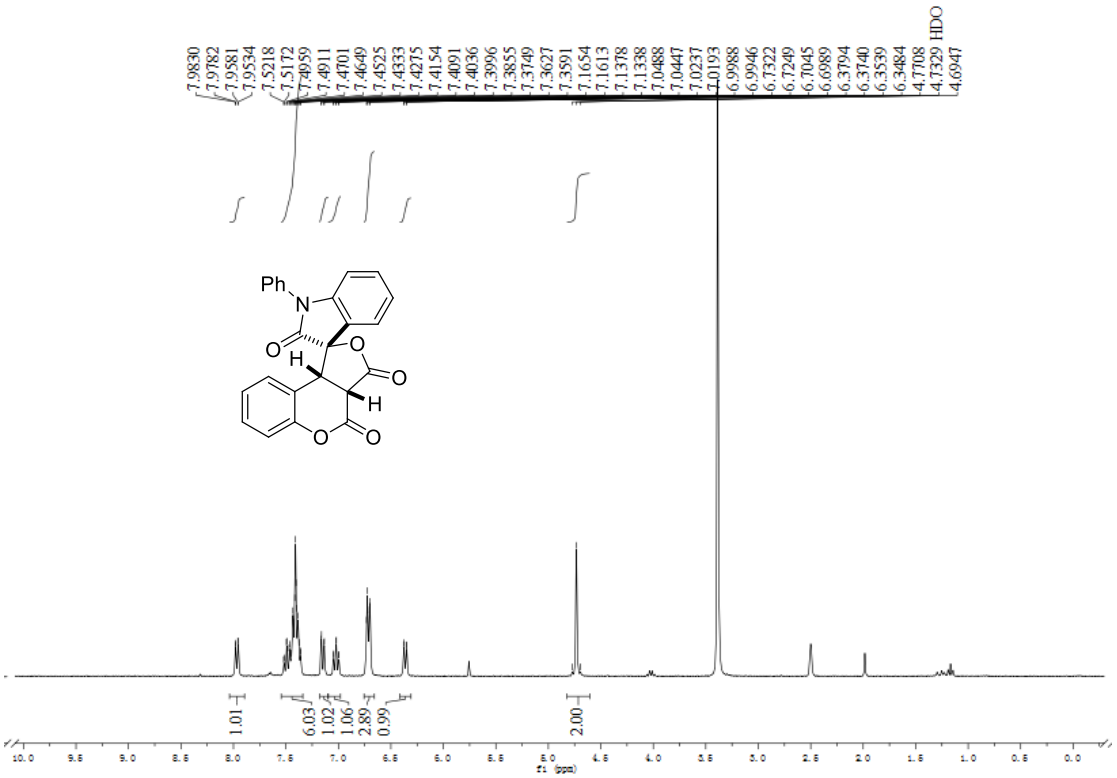


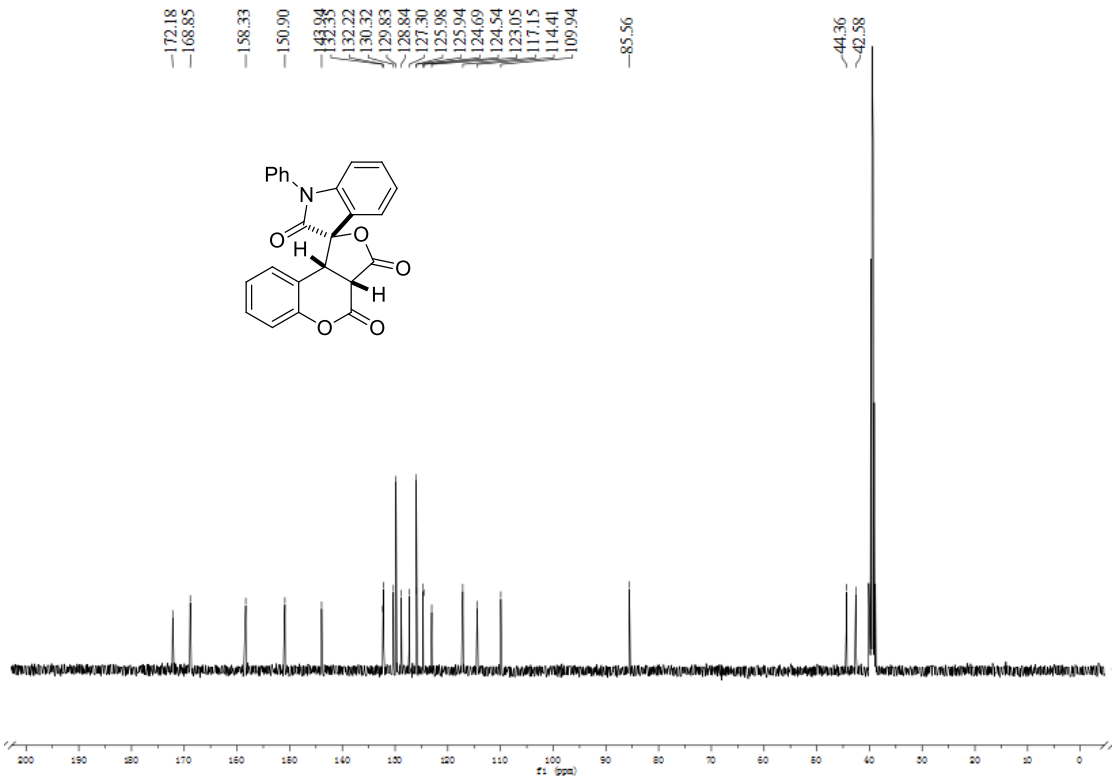
^{1}H and ^{13}C NMR of **3r**



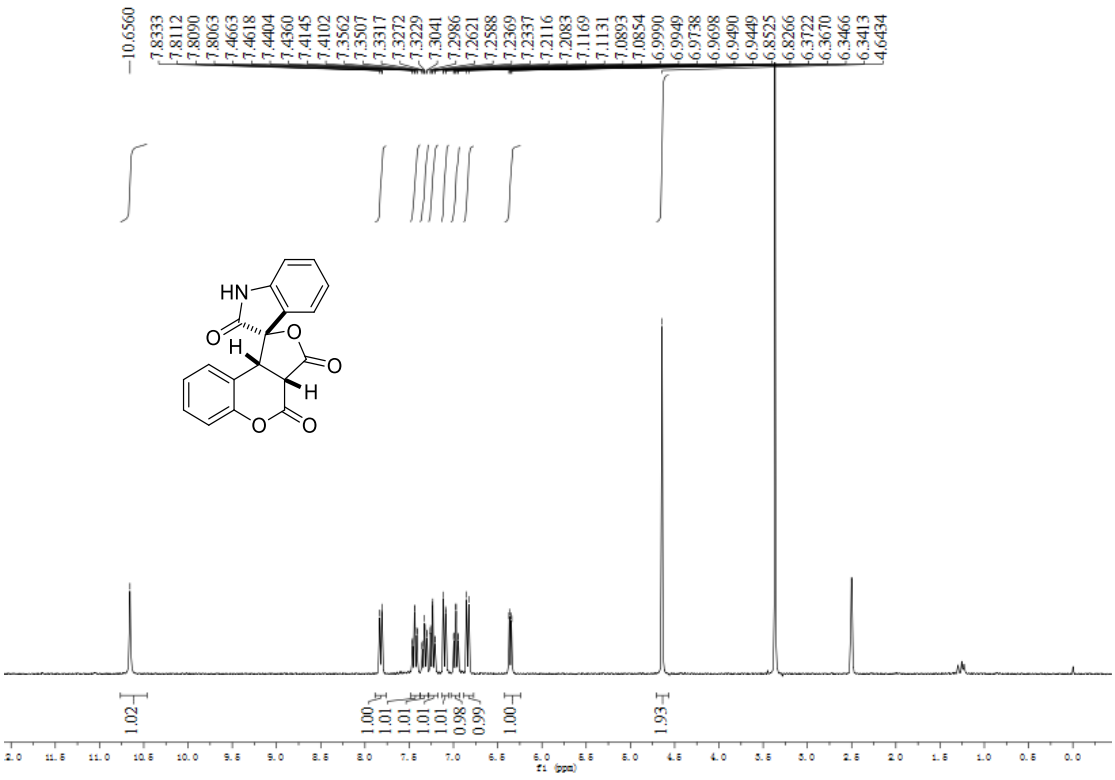


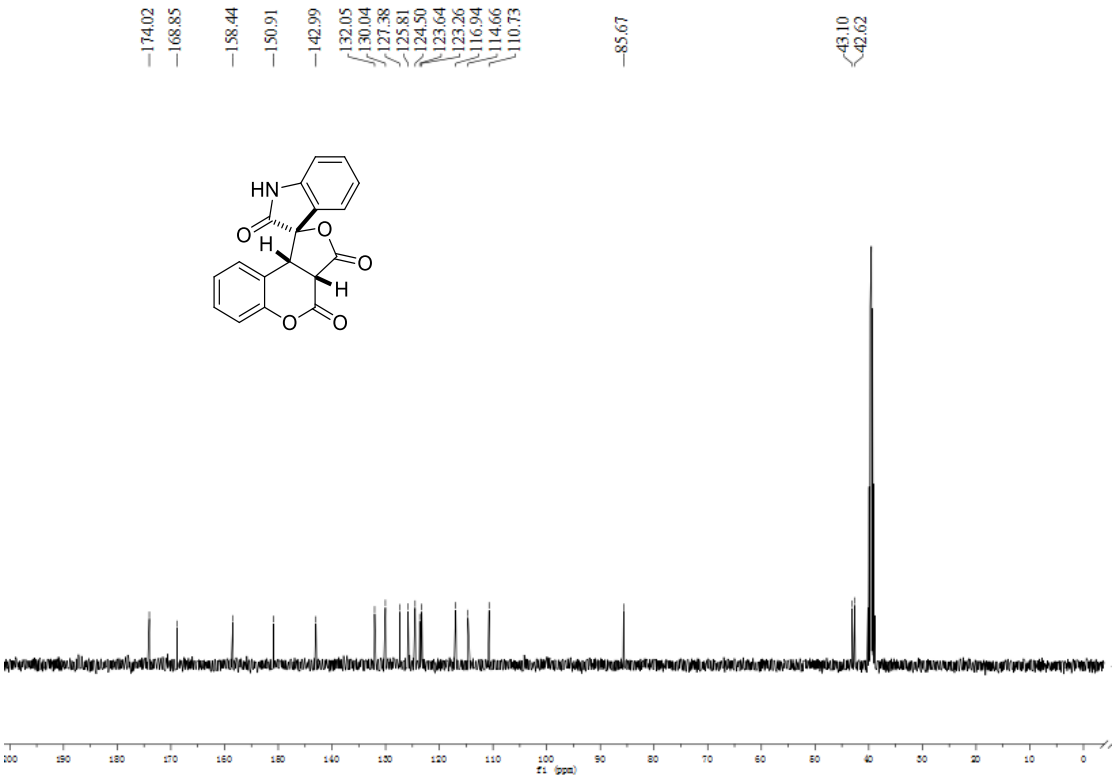
^{1}H and ^{13}C NMR of **3s**



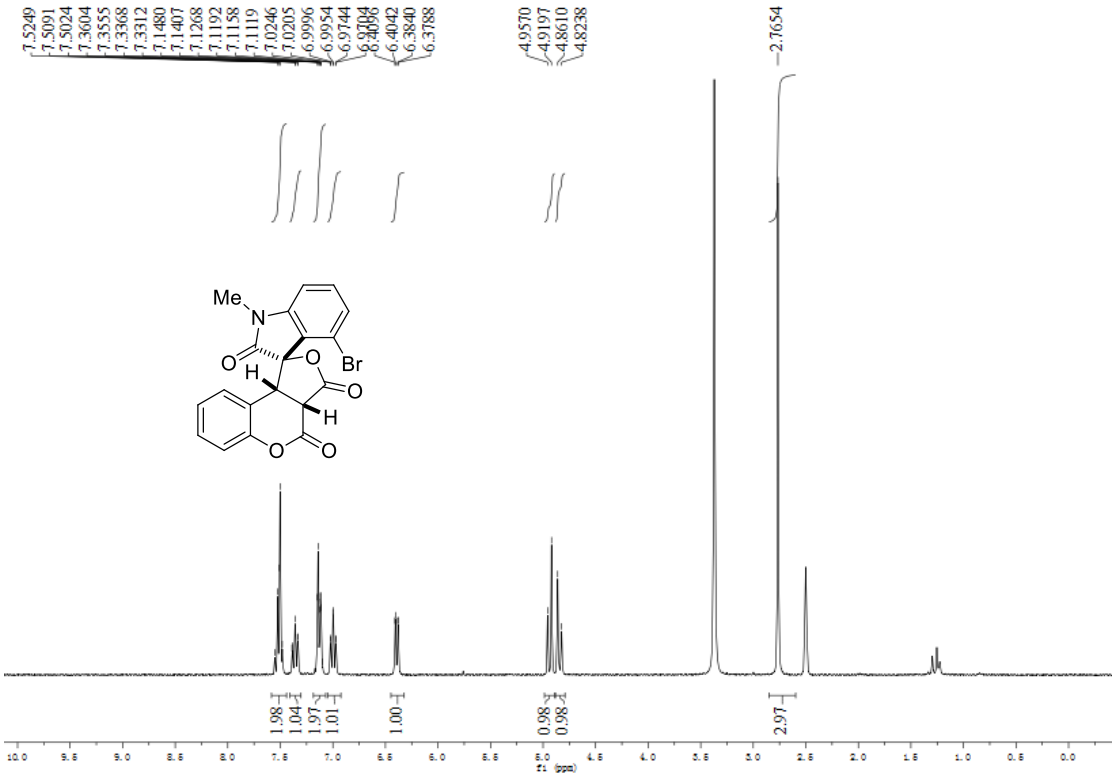


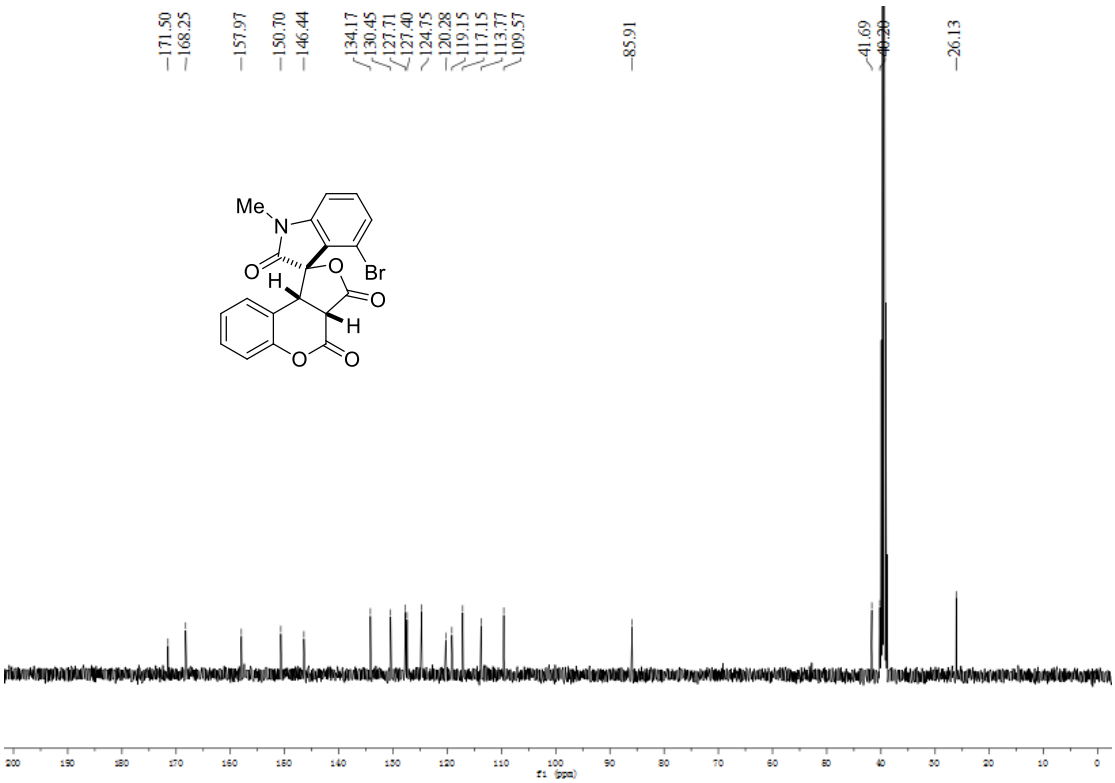
^{1}H and ^{13}C NMR of **3t**



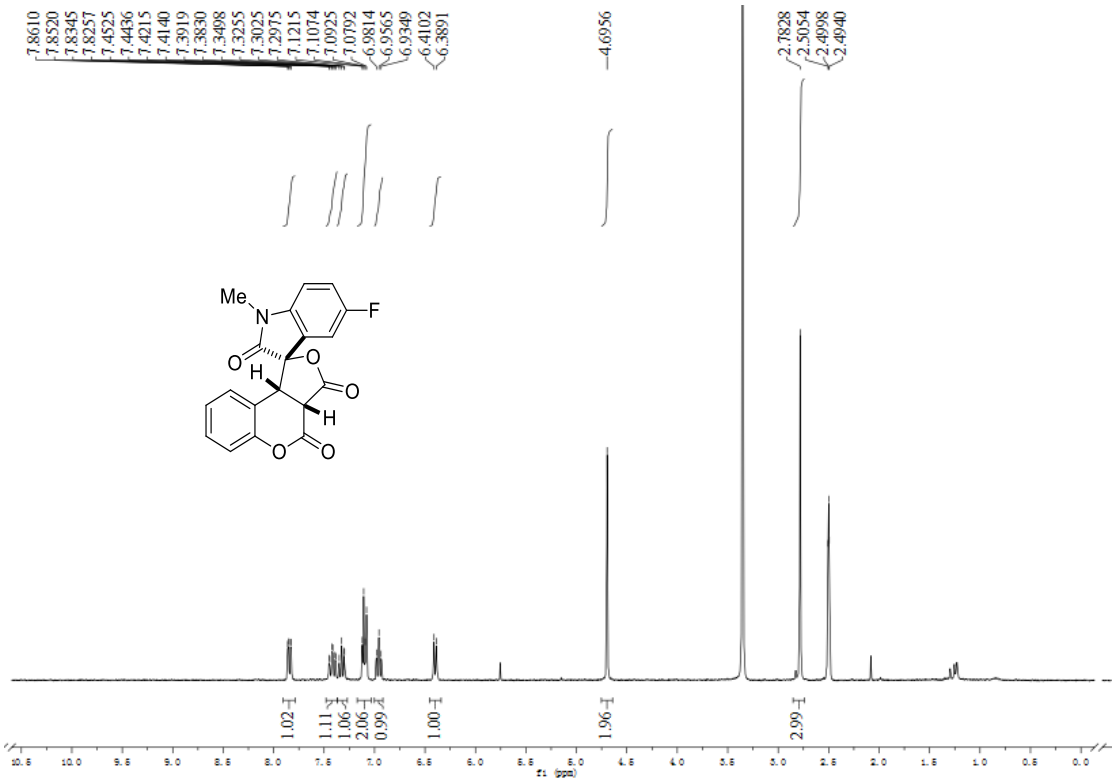


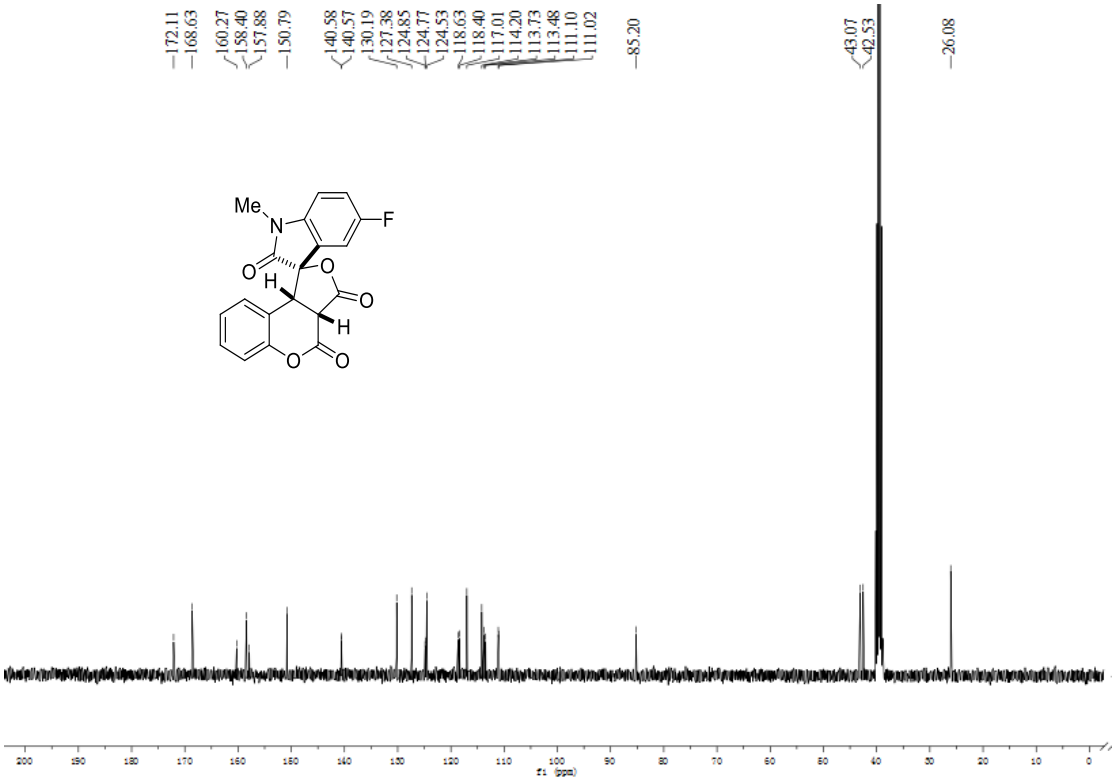
^{1}H and ^{13}C NMR of **3u**



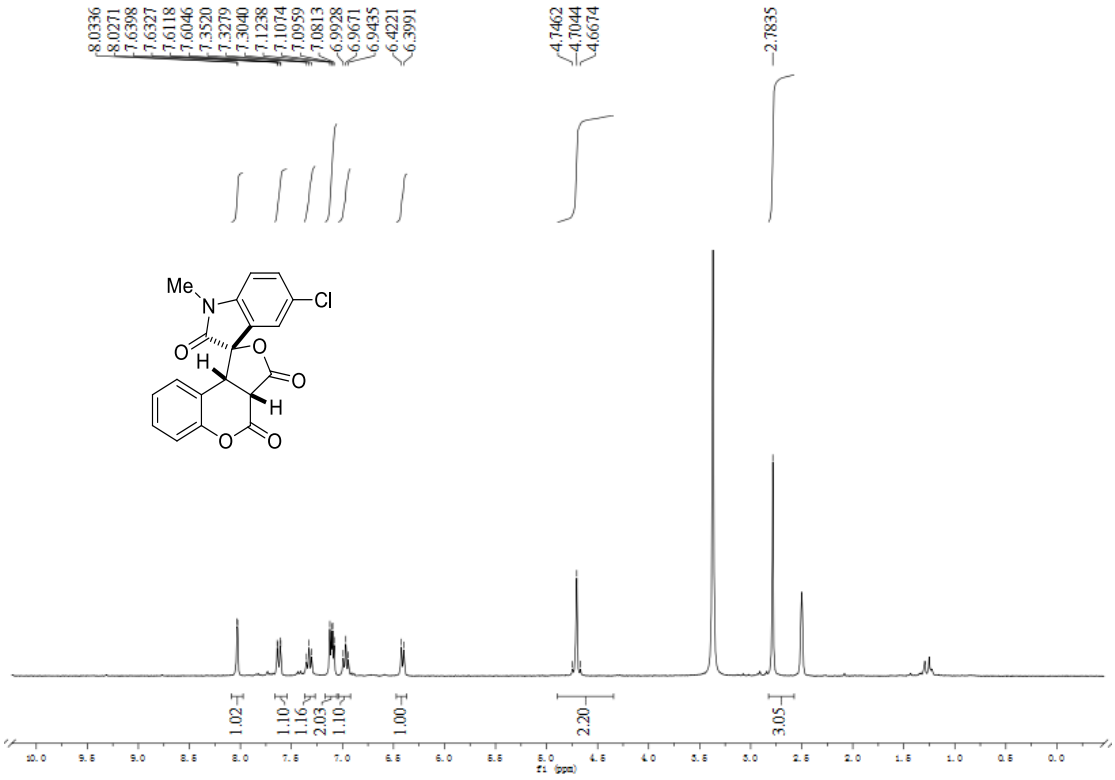


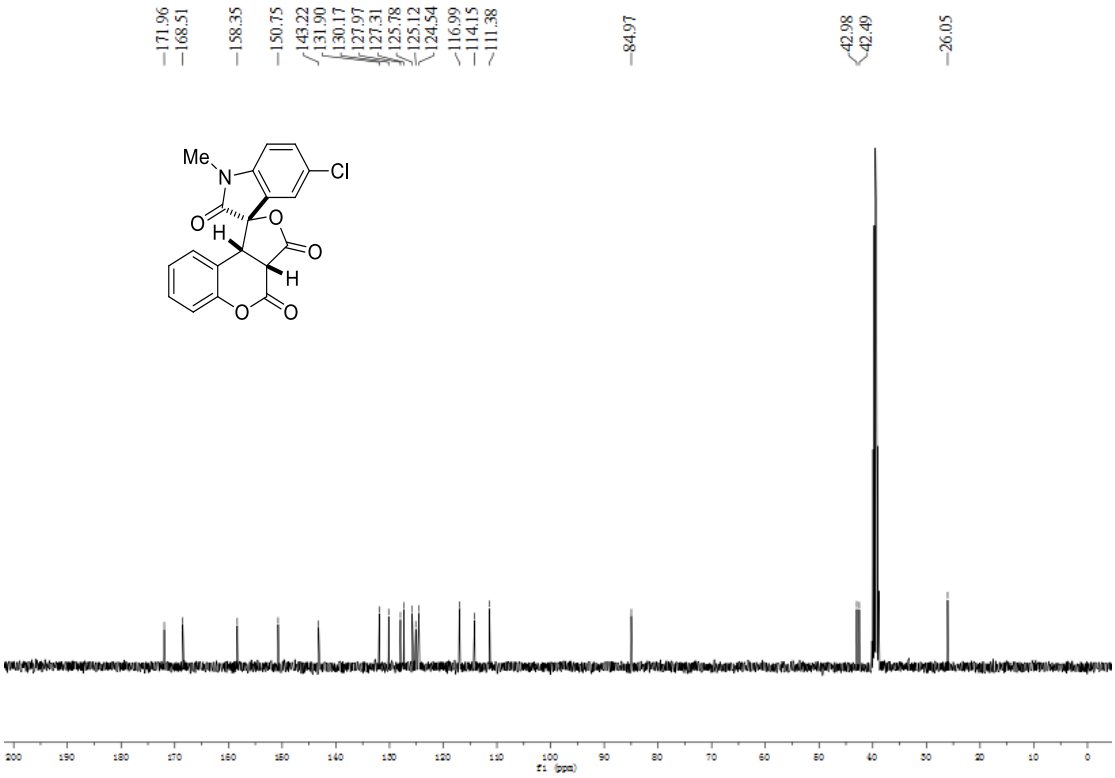
^{1}H and ^{13}C NMR of **3v**



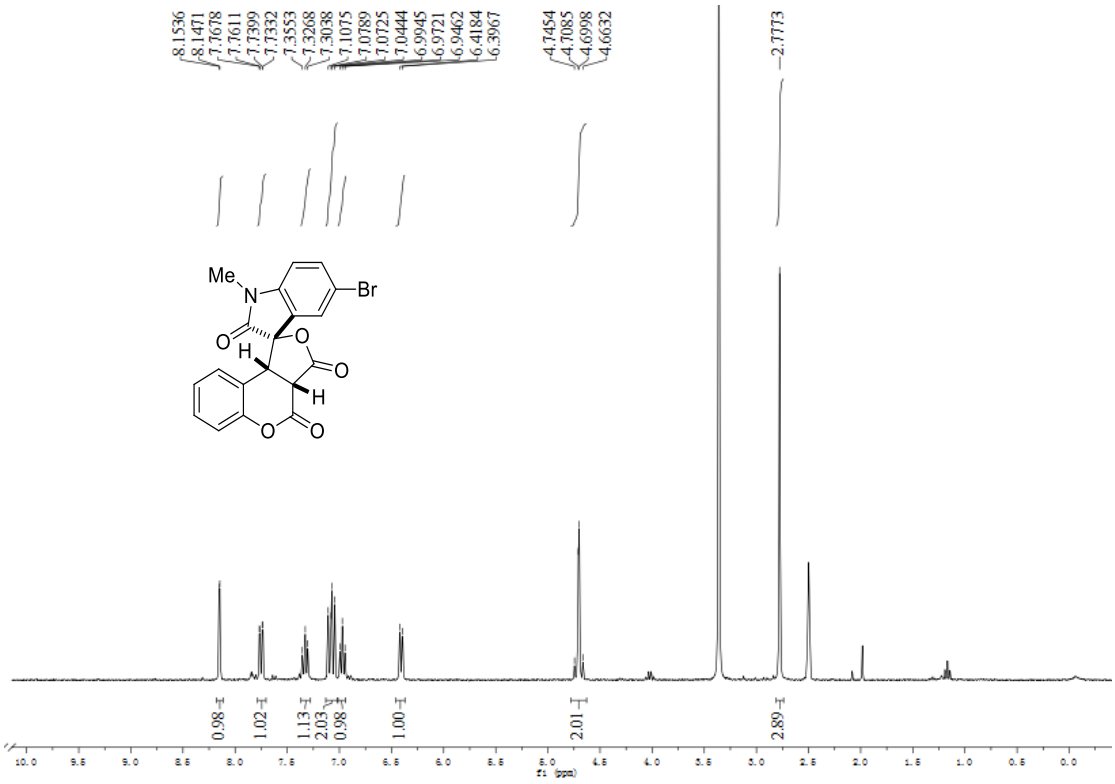


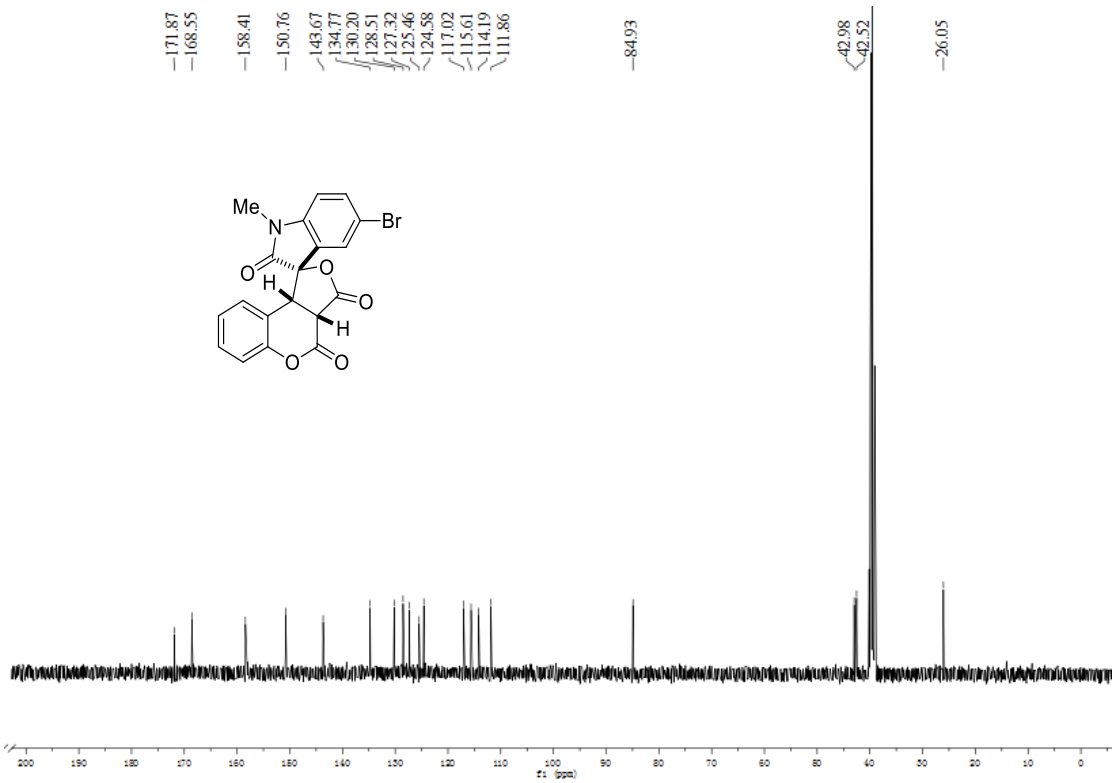
^{1}H and ^{13}C NMR of **3w**



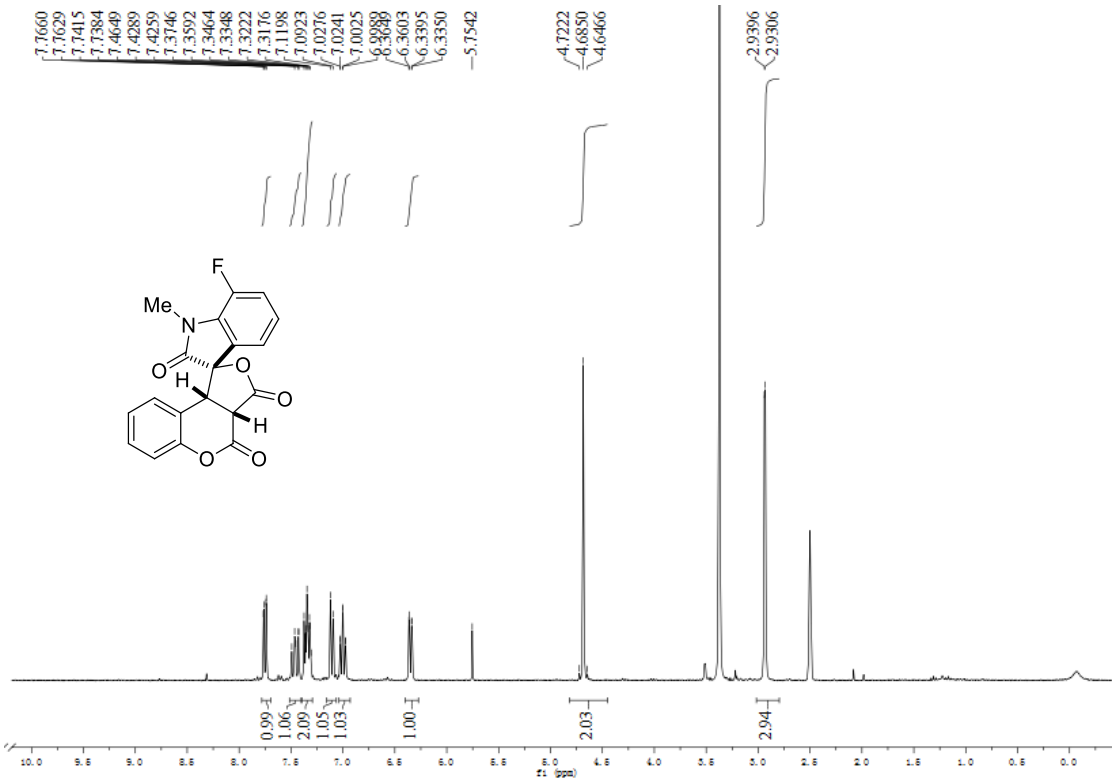


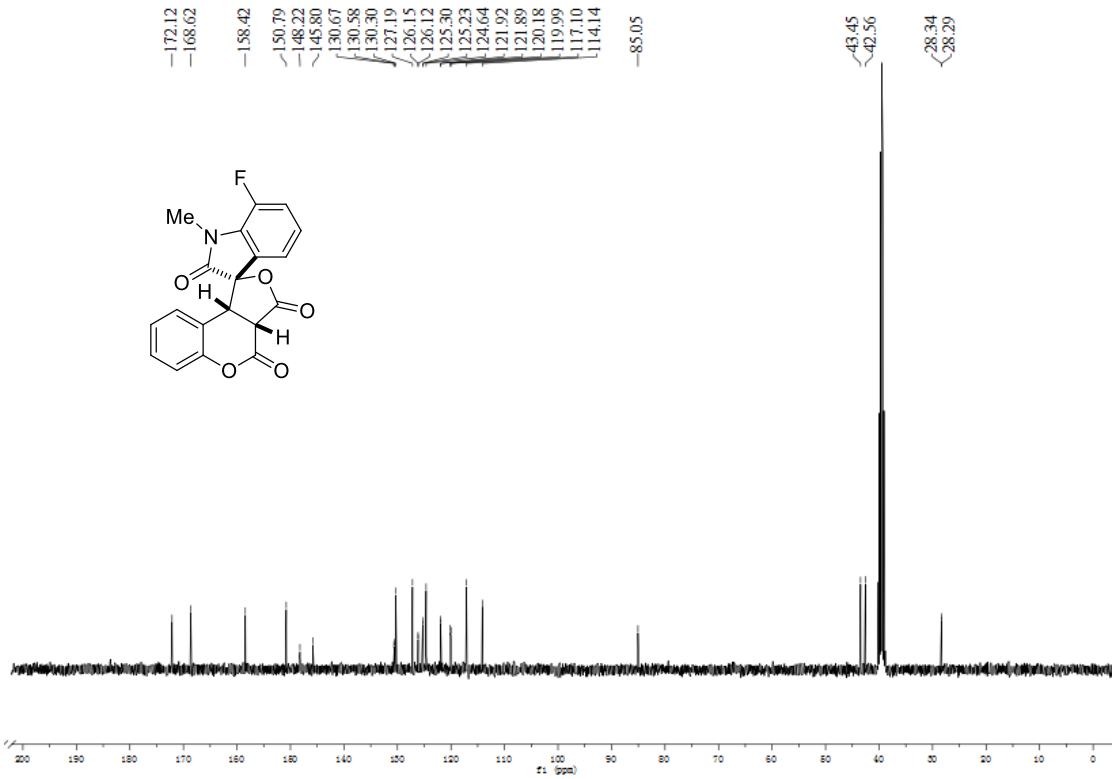
^{1}H and ^{13}C NMR of **3x**



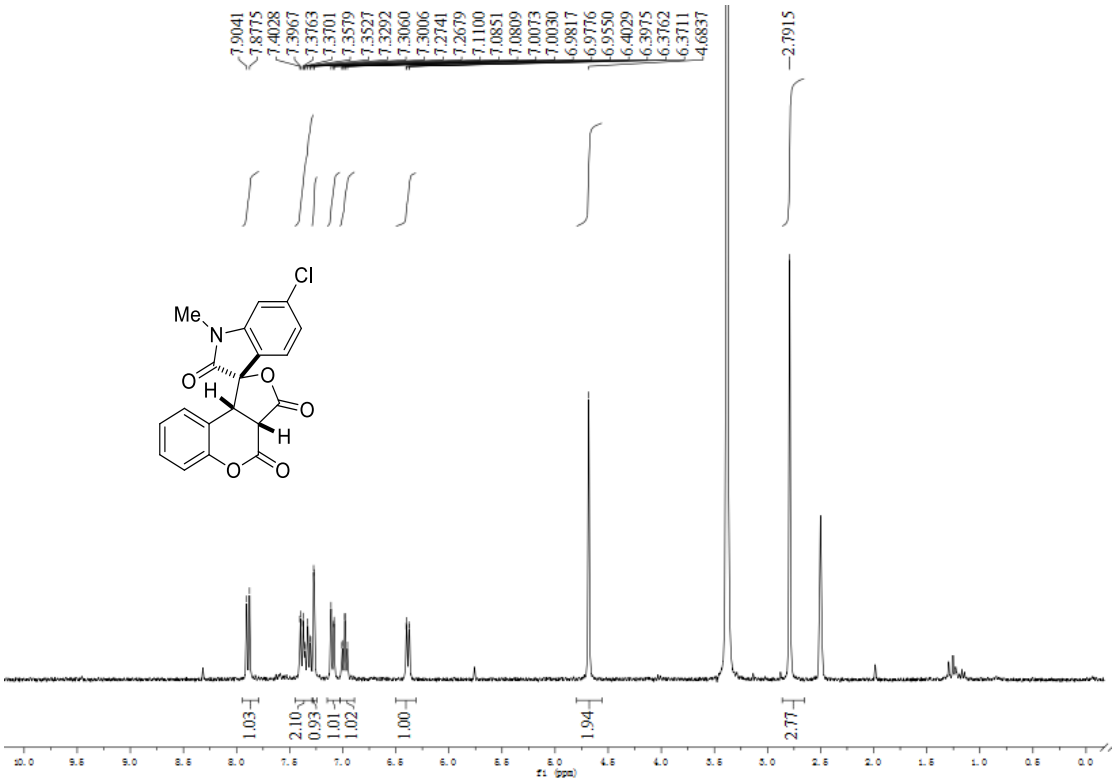


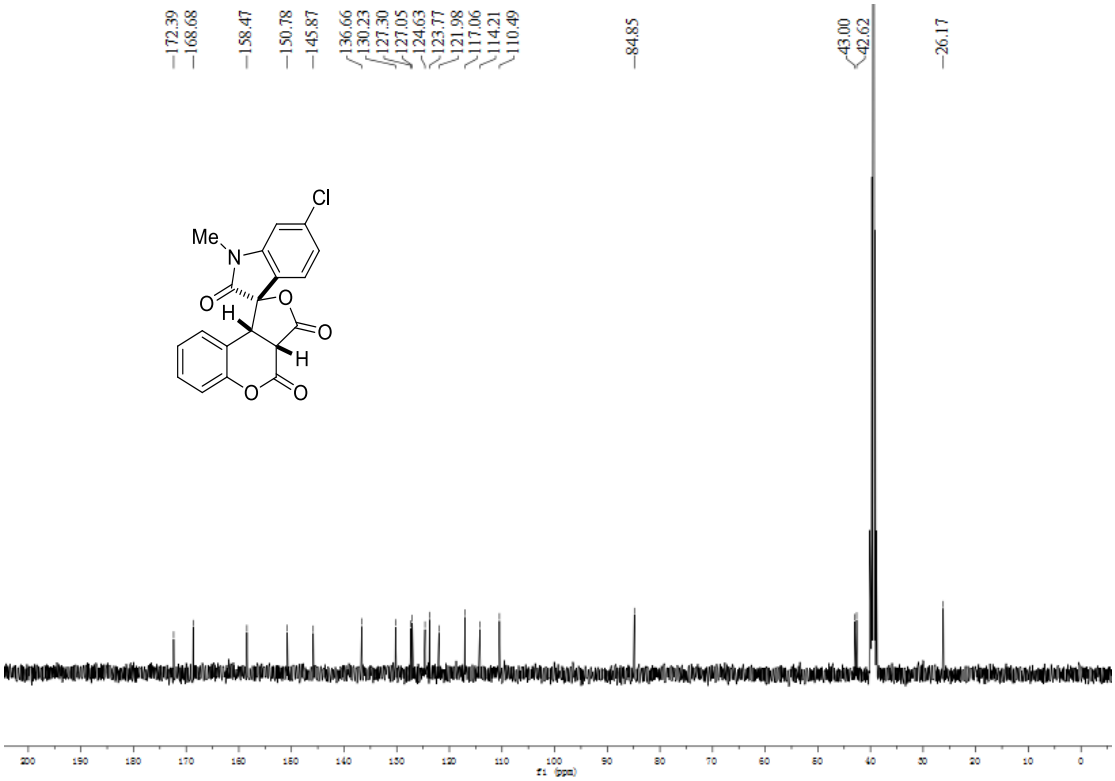
^{1}H and ^{13}C NMR of **3y**



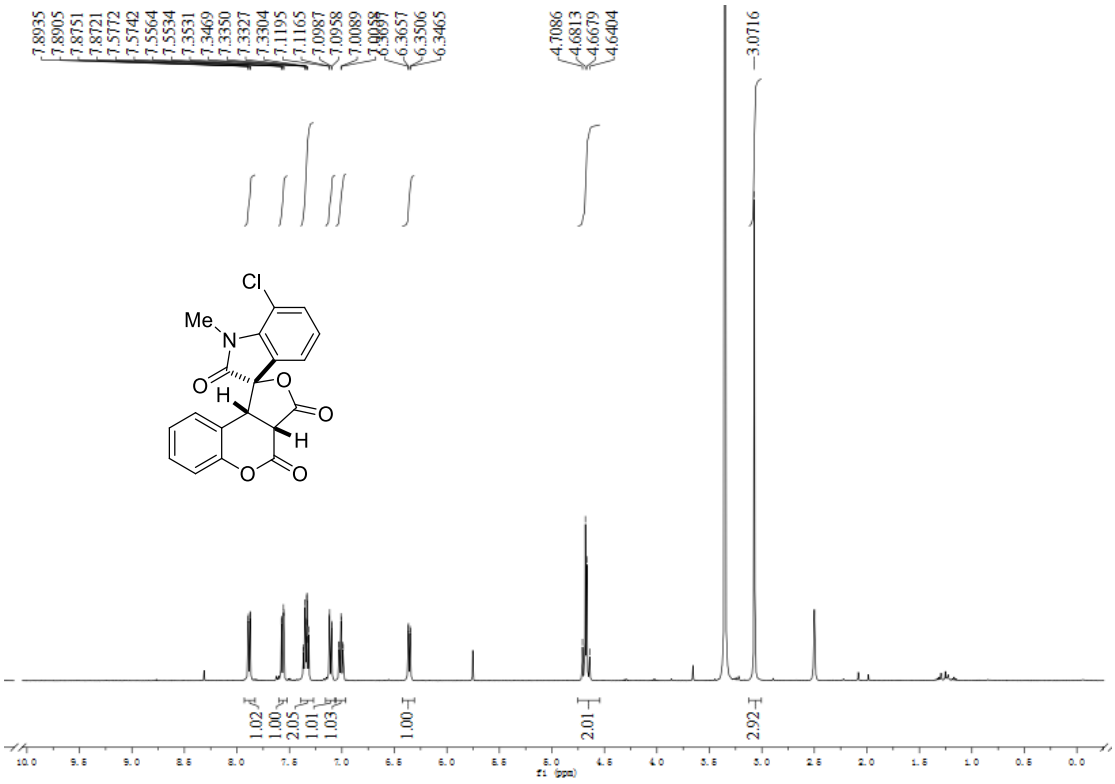


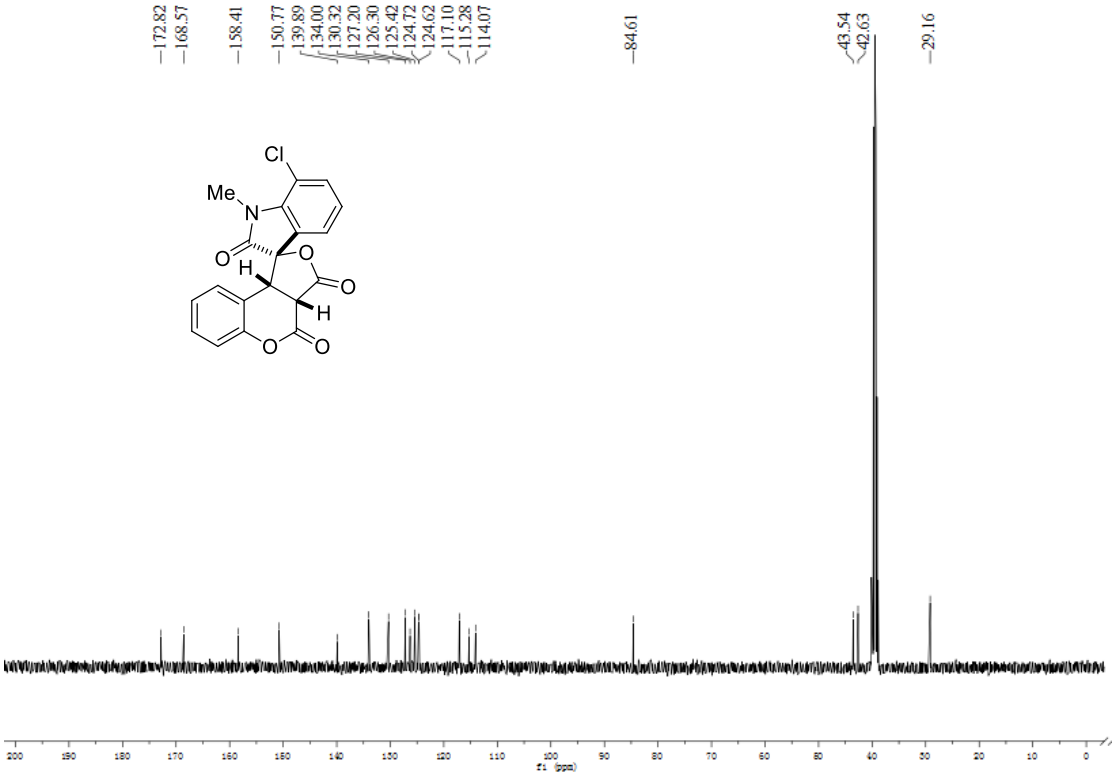
^{1}H and ^{13}C NMR of **3z**



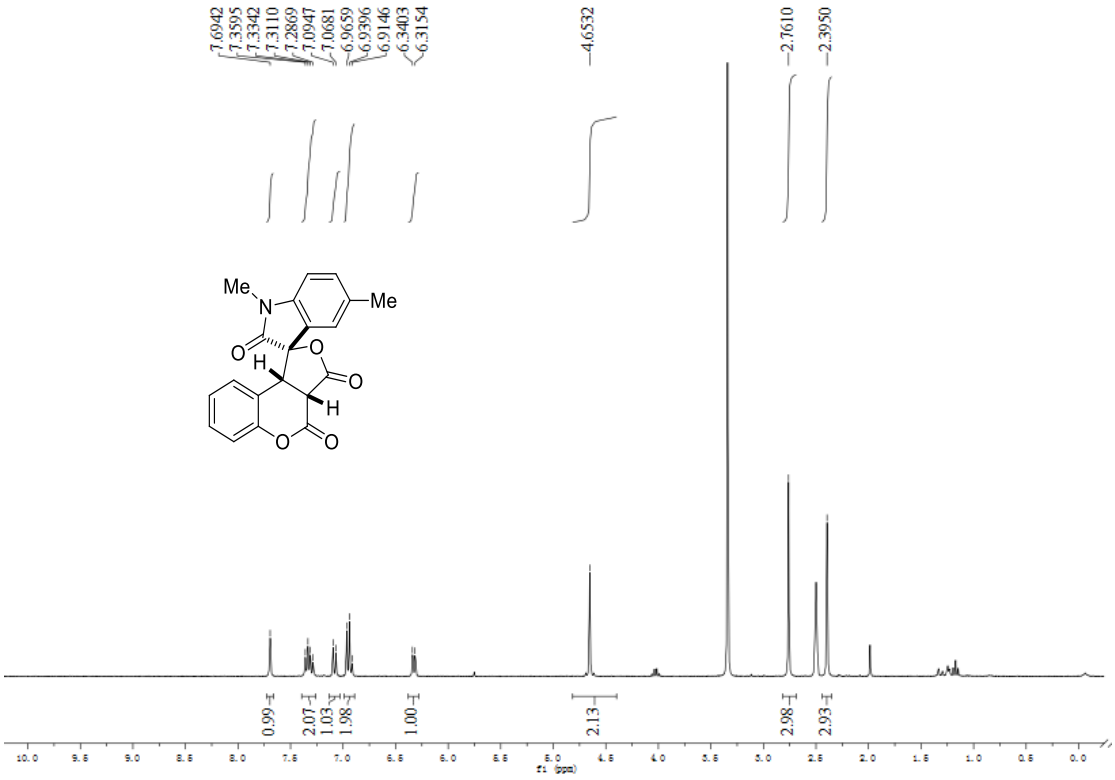


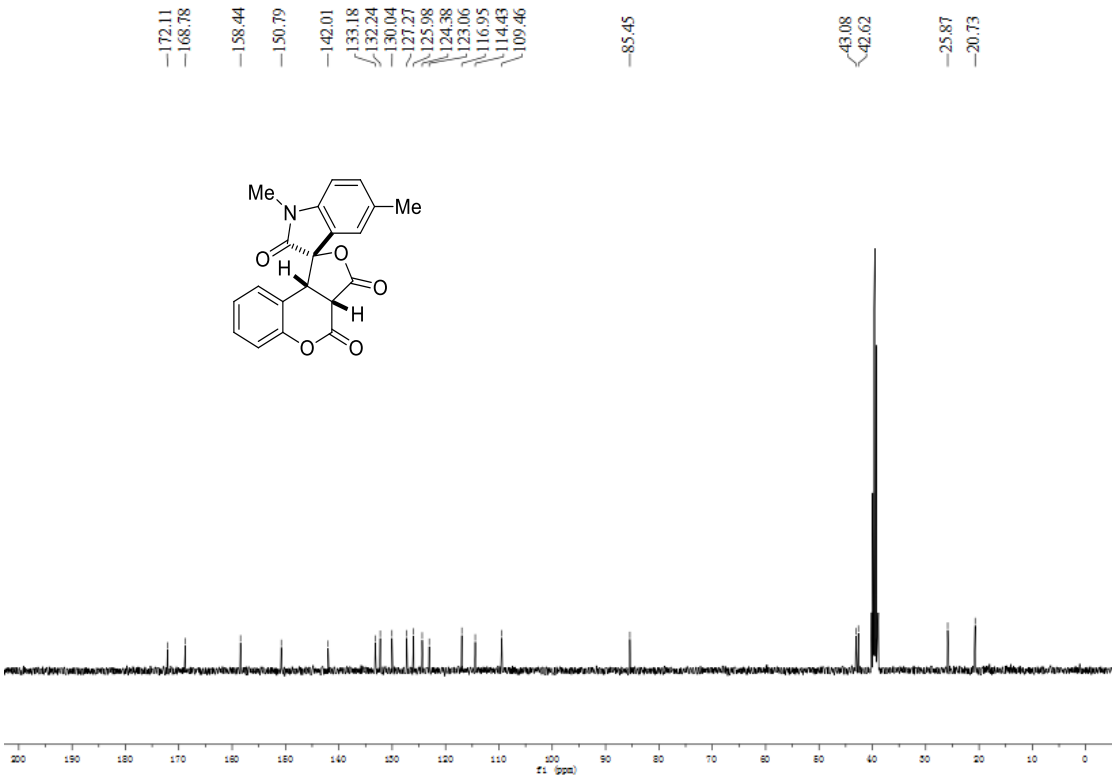
^{1}H and ^{13}C NMR of **3a'**



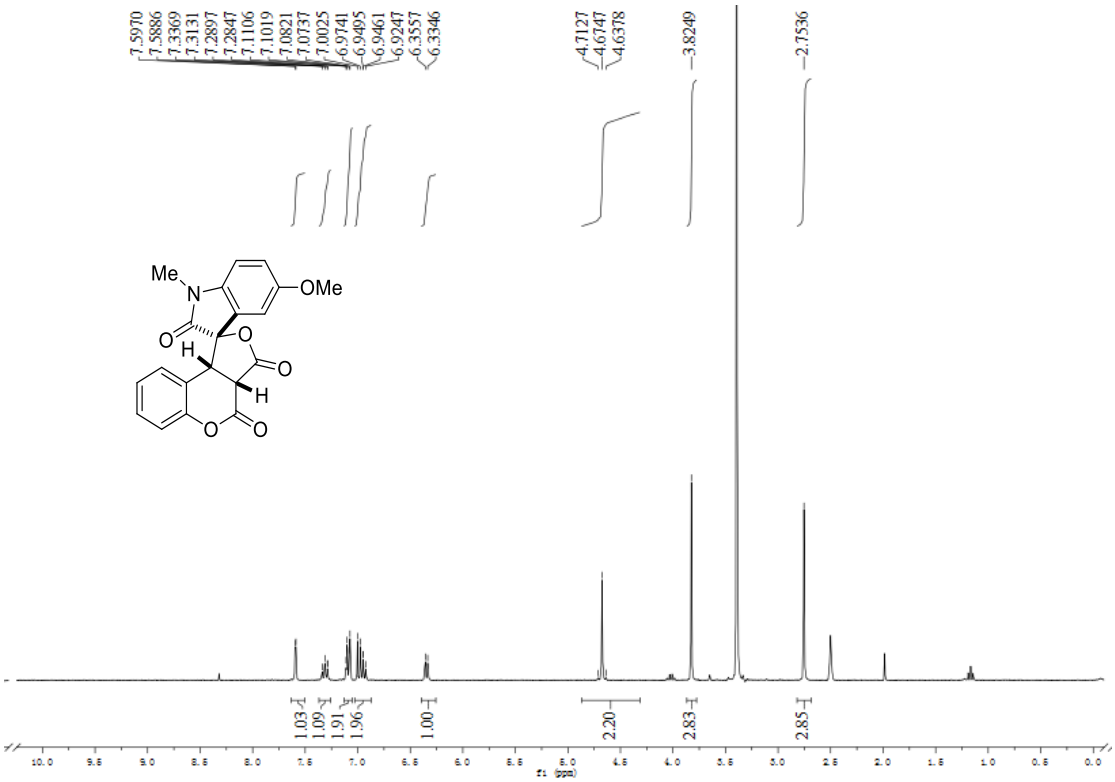


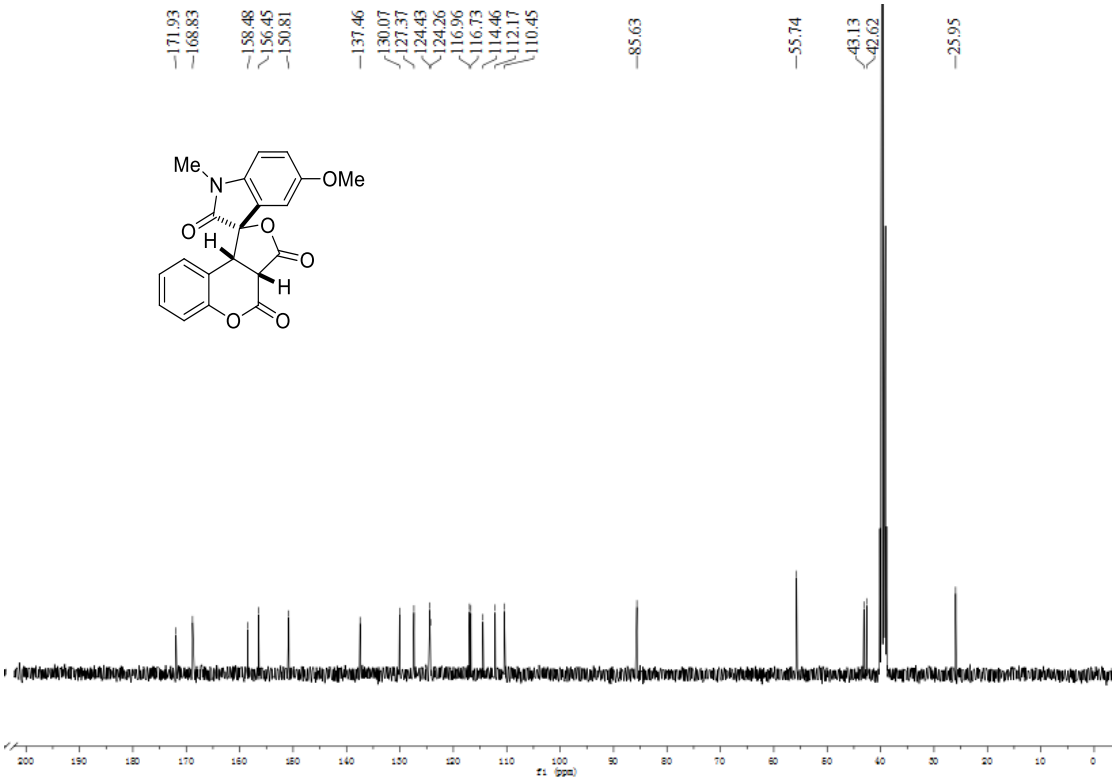
^{1}H and ^{13}C NMR of **3b'**



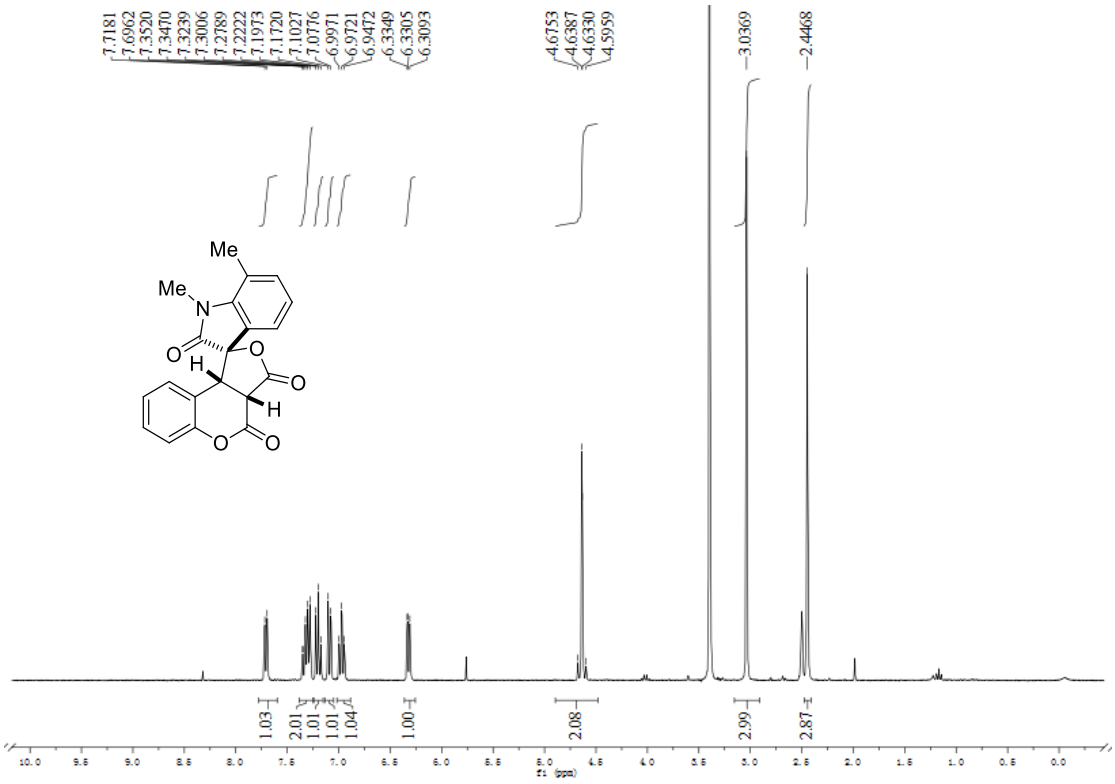


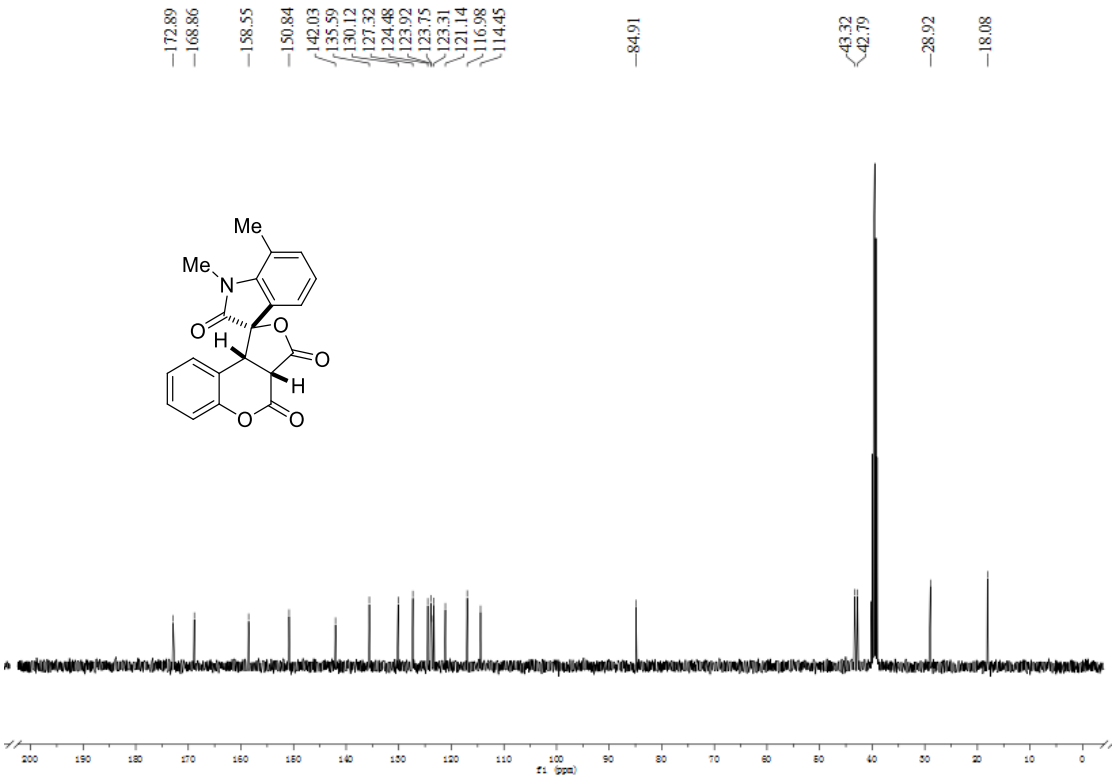
^{1}H and ^{13}C NMR of **3c'**



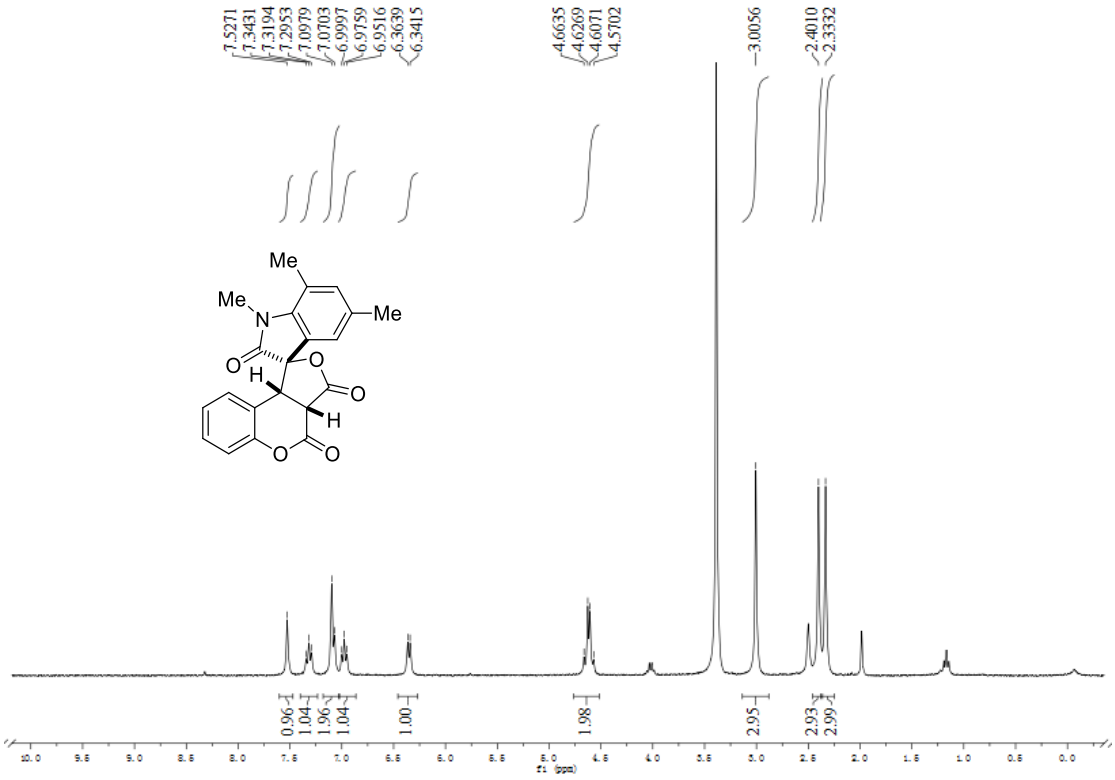


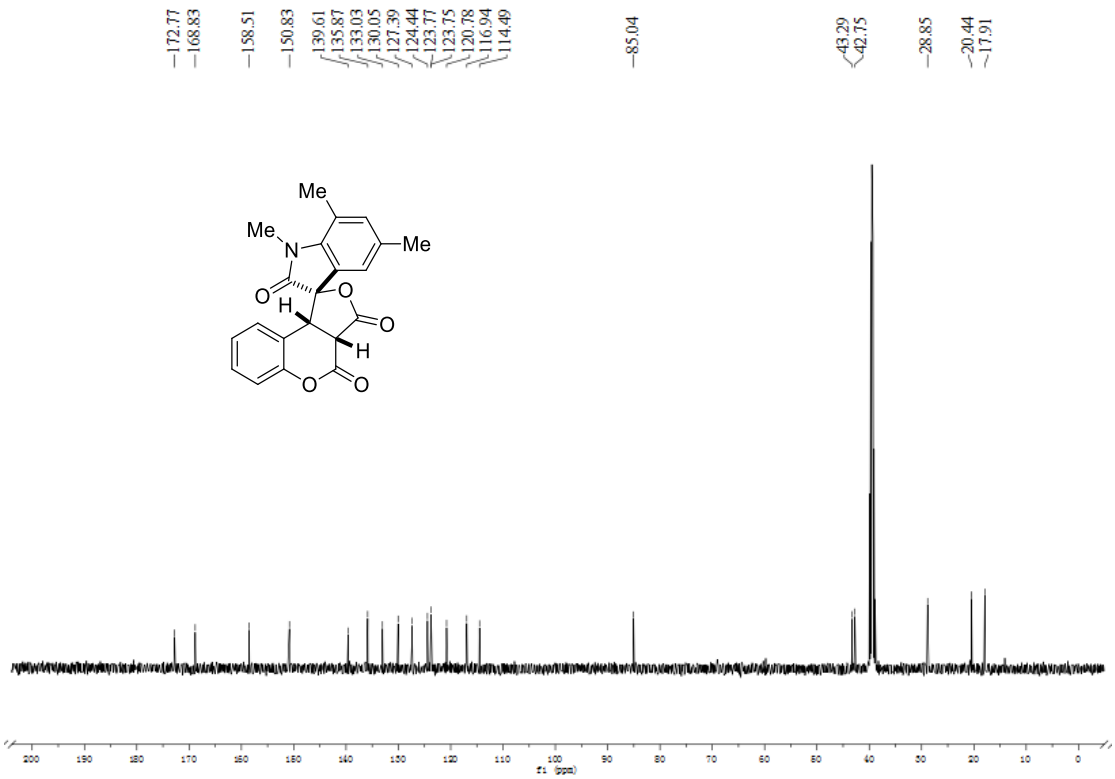
^{1}H and ^{13}C NMR of **3d'**



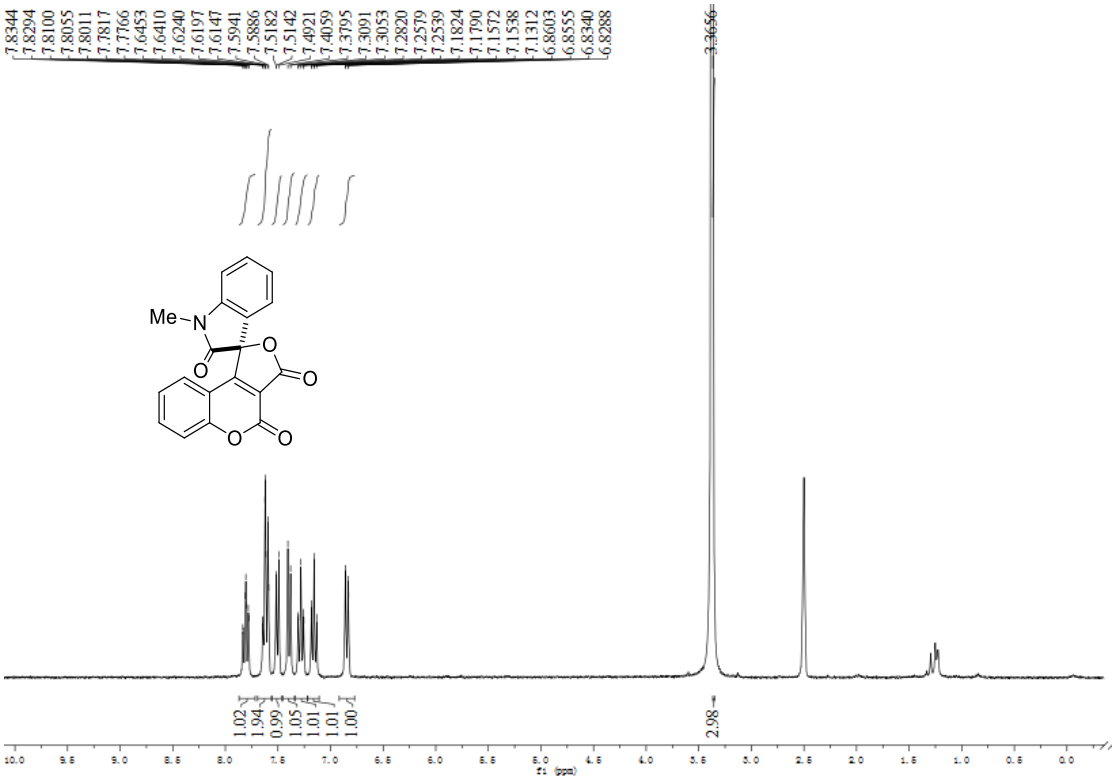


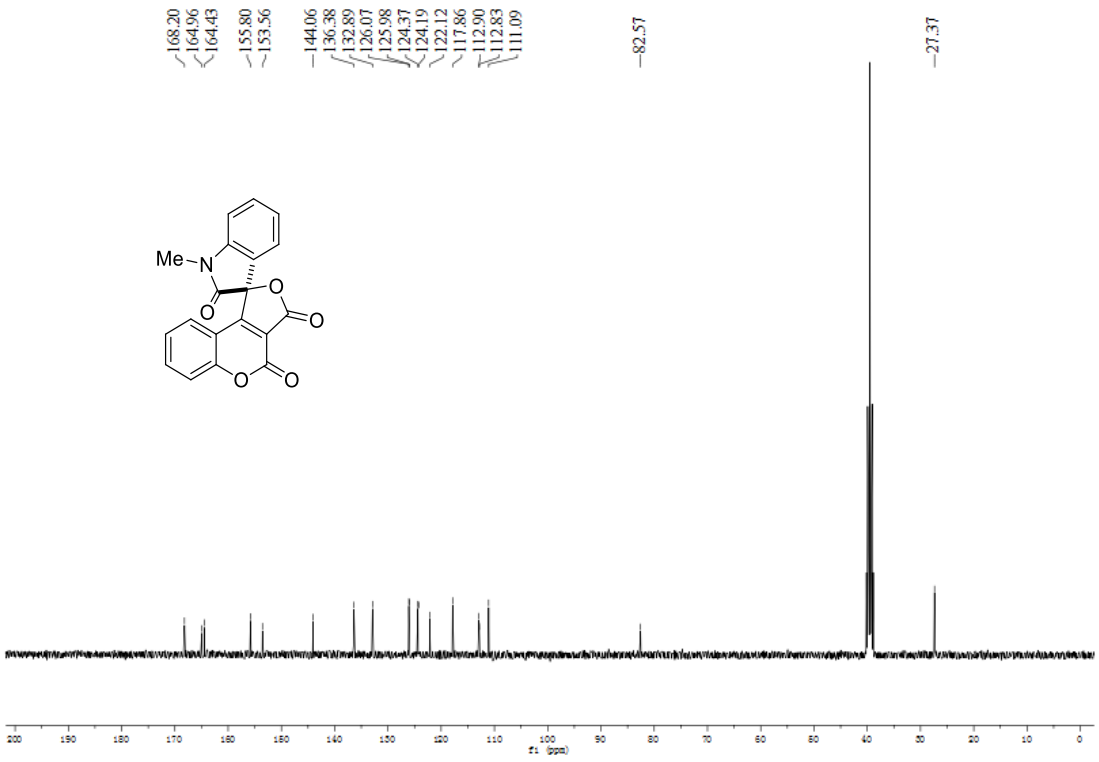
^{1}H and ^{13}C NMR of **3e'**



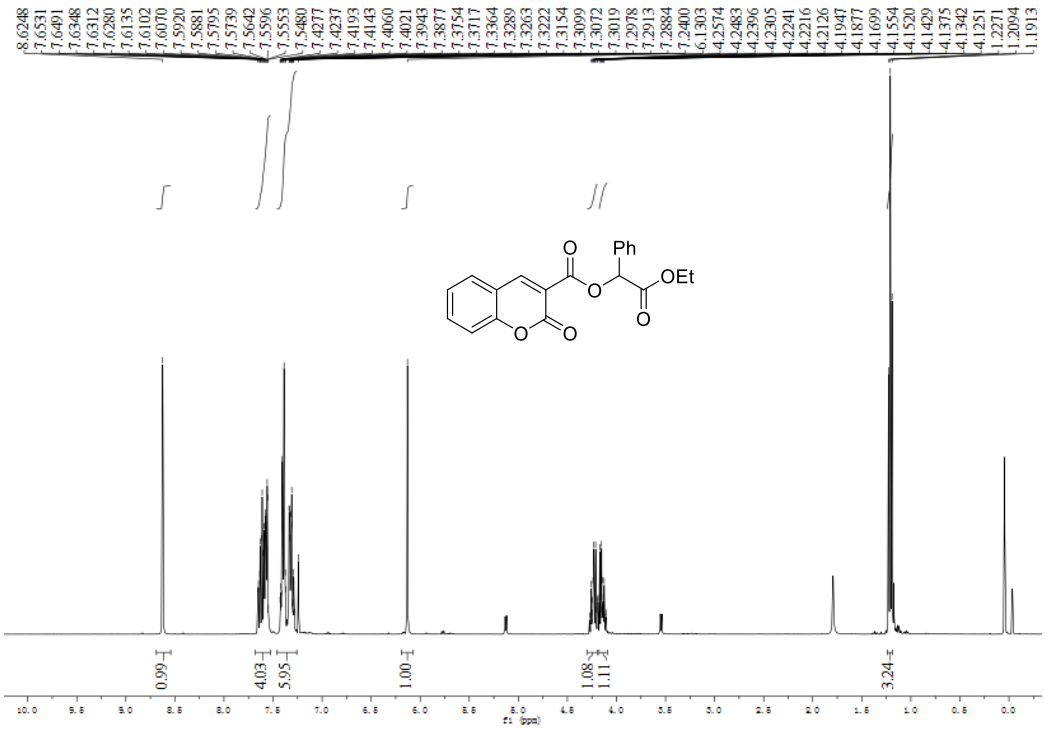


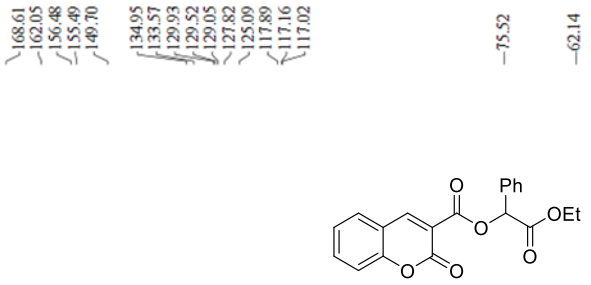
^{1}H and ^{13}C NMR of **4**

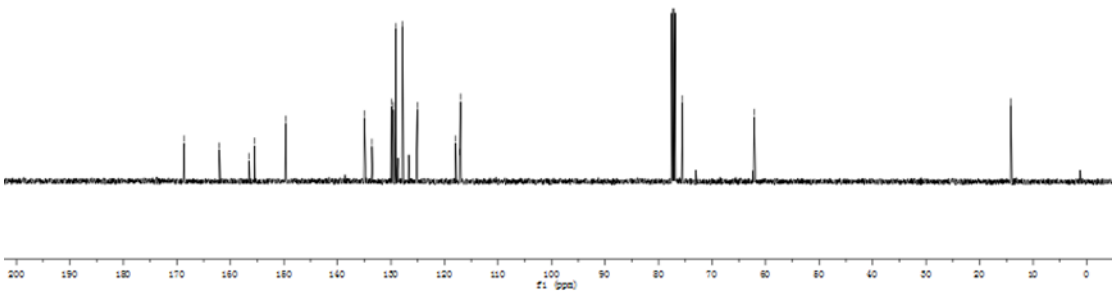




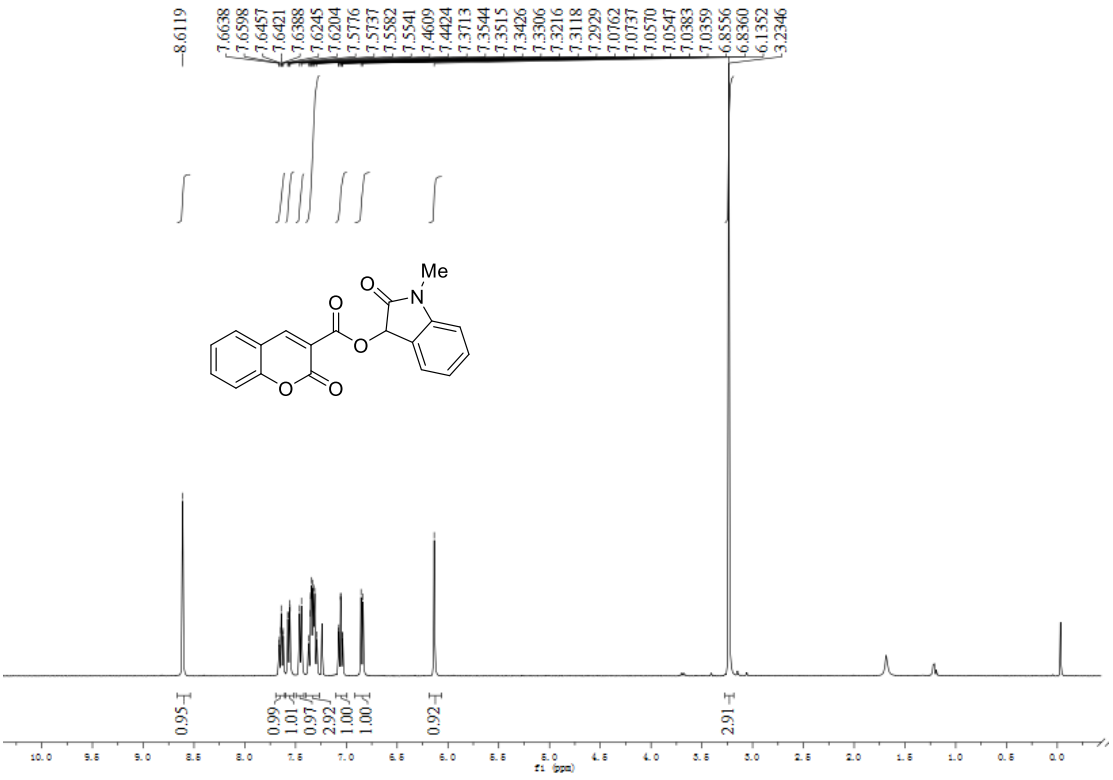
^{1}H and ^{13}C NMR of **7**

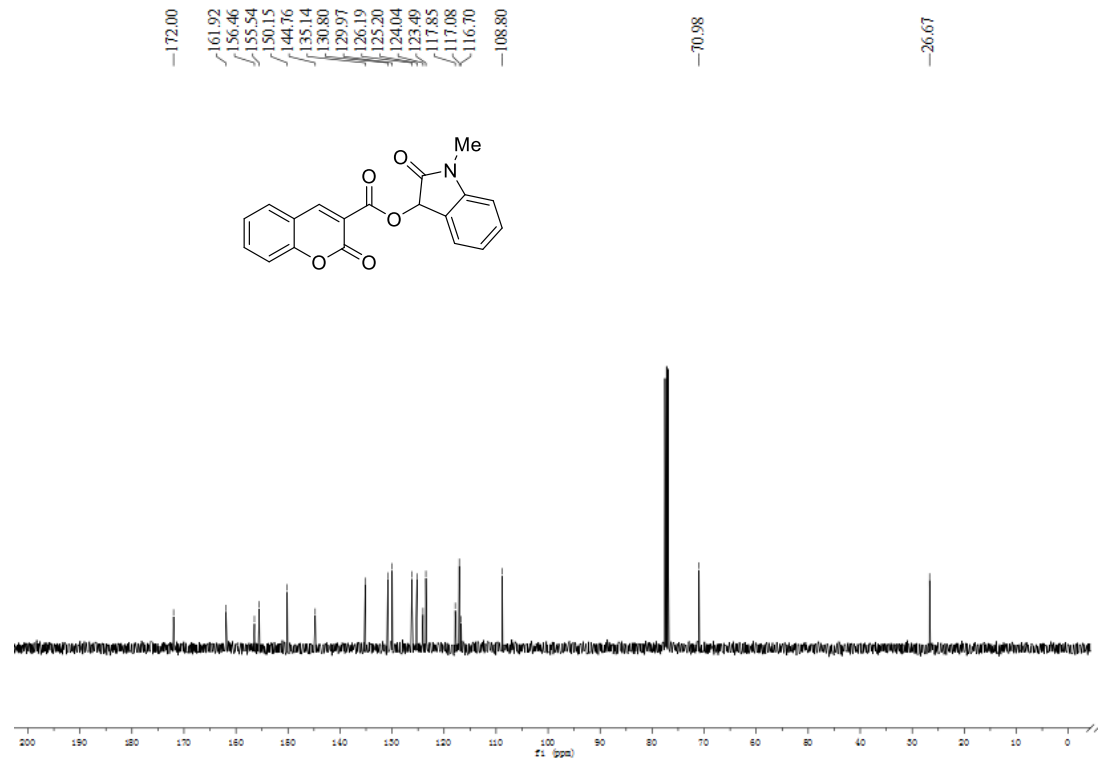




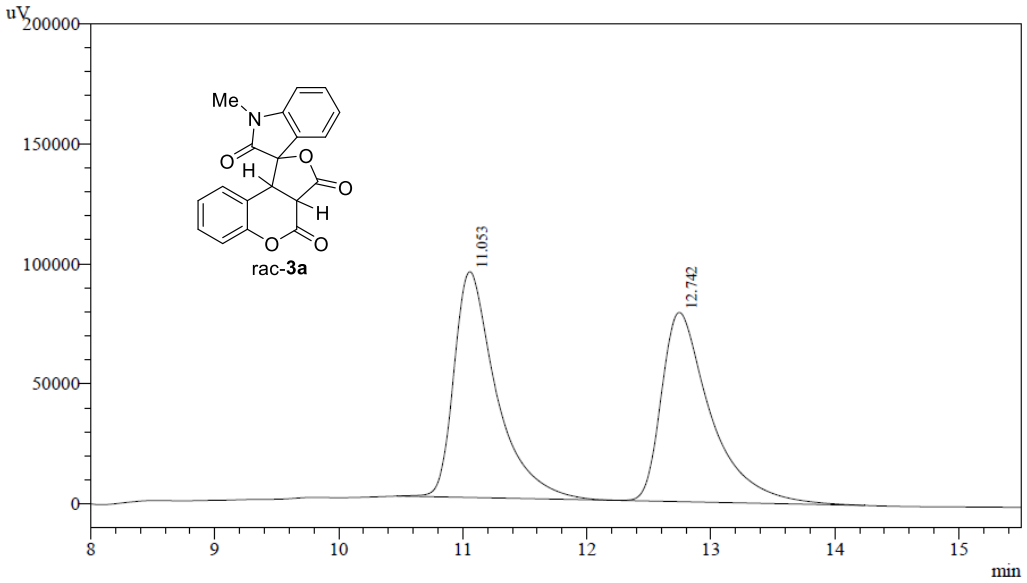


^{1}H and ^{13}C NMR of **8**





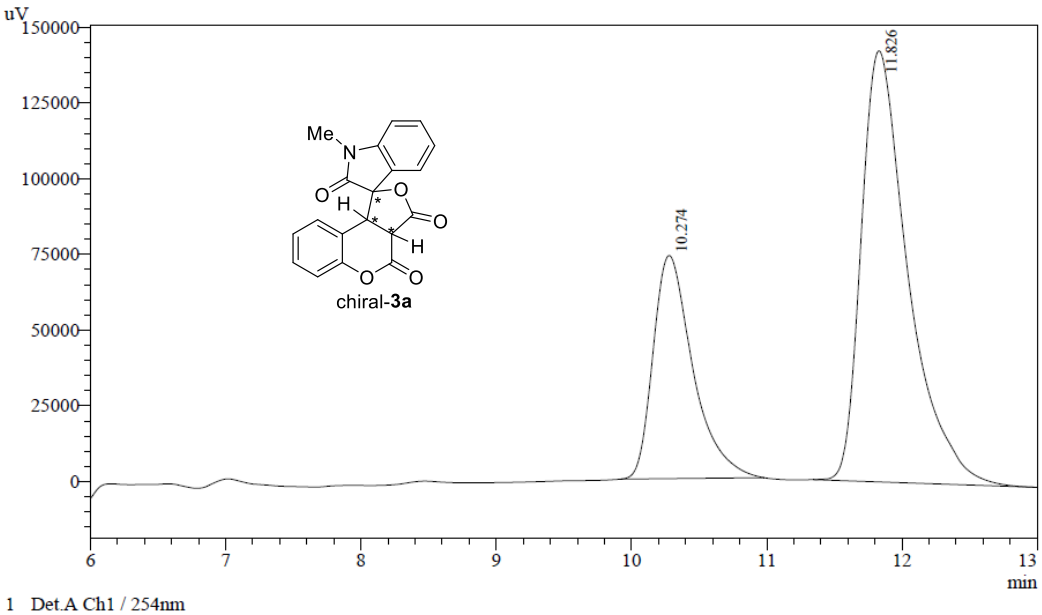
HPLC of **3a** with Catalyst **B**



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.053	2233081	94013	50.595	54.408
2	12.742	2180519	78779	49.405	45.592
Total		4413600	172792	100.000	100.000



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.274	1505970	73659	30.516	34.102
2	11.826	3428979	142340	69.484	65.898
Total		4934948	215999	100.000	100.000