Supporting Information

Synthesis of 3-Cyanomethylated Coumarins by a Visible-Light-Mediated Direct Cyanomethylation of Aryl Alkynoates

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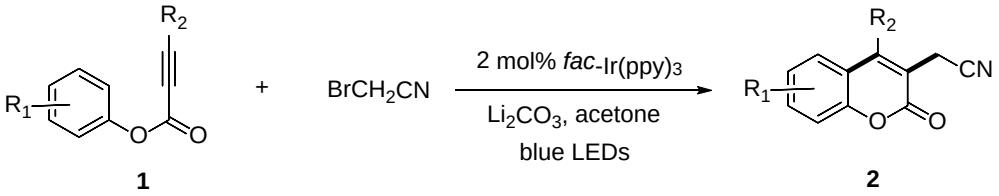
General Information.

Commercial reagents were used as received, unless otherwise stated. The purchased solvents were dried over molecular sieves and degassed by three cycles of freeze−pump−thaw before use in the reaction. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Mass spectra were obtained using electrospray ionization (ESI). Substrates **1** were synthesized according to the reported literatures.[1]

General procedure for synthesis of products 2 and 4.



Aryl alkynoate (1) (0.1 mmol), Li_2CO_3 (0.2 mmol), *fac*-Ir(ppy)$_3$ (0.002mol, 2.0 mol%) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed acetone and Bromoacetonitrile (2) (0.3 mmol) was then added to the mixture in the presence of a flow of argon. The solution was placed at a distance of about 5 cm from blue LEDs strip and irradiated for 48 h. Afterward, the crude mixture was purified by column chromatography (eluent: petroleum ether/ethyl acetate 10:1 to 4:1) to give the product 2.

*2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2a**)* White solid, 22mg, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4H), 7.43(dd, *J*= 8.4, 0.8Hz, 1H), 7.34-7.31 (m, 2H), 7.23-7.19 (m, 1H), 7.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 154.6, 153.0, 132.8, 132.5, 129.8, 129.5, 127.9, 124.7, 119.8, 117.0, 116.4, 116.2, 99.9, 17.5; HRMS (ESI) m/z calcd for $C_{17}H_{11}NO_2Na$ $[M + Na]^+$ 284.0685, found 284.0682.

*2-(7-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2b**)* Colorless solid, 19mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 3H), 7.25 (d, *J* = 7.6, 2H), 7.18 (d, *J* = 14.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H) 3.42 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 154.6, 153.1, 143.9, 133.1, 129.7, 129.4, 127.9, 127.6, 125.9, 117.4, 117.1, 116.6, 115.0, 21.7, 17.5; HRMS (ESI) m/z

calcd for $C_{18}H_{13}NO_2Na$ $[M + Na]^+$ 298.0841, found 298.0838.

*2-(7-ethyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2c**)* Colorless solid, 21mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 3H), 7.34-7.31 (m, 2H), 7.25 (s, 1H), 7.04 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.41 (s, 2H), 2.76 (q, *J*= 8.0Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 154.6, 153.3, 150.2, 133.1, 129.7, 129.4, 127.9, 127.7, 124.7, 117.6, 116.5, 115.9, 115.0, 28.9, 17.5, 15.1; HRMS (ESI) m/z calcd for $C_{19}H_{15}NO_2Na$ $[M + Na]^+$ 312.0999, found 312.0995.

*2-(7-isopropyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2d**)* White solid, 19mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.04 (dd, *J* =33.4, 8.4Hz, 2H), 3.42 (s, 2H), 3.04-2.97(m, 1H), 1.28(d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 153.8, 153.6, 152.8, 132.1, 128.7, 128.4, 126.9, 126.7, 122.3, 116.7, 115.5, 114.0, 113.5, 33.2, 22.6, 16.4; HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_2Na$ $[M + Na]^+$ 326.1155, found 326.1151.

*2-(6-(tert-butyl)-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2e**)* White solid, 21mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 3H), 7.43 (d, *J* = 4 Hz, 1H), 7.33 (d, *J* = 4 Hz, 2H) 7.27 (s, 1H), 7.01(dd, *J* = 8, 4 Hz, 1H), 3.42 (s, 2H), 1.35(s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 157.2, 154.4, 153.1, 133.1, 129.7, 129.4, 127.9, 127.4, 122.2, 117.3, 116.6, 115.1, 113.8, 35.3, 31.0, 17.4; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_2Na$ $[M + Na]^+$ 326.1155, found 326.1151.

*2-(2-oxo-4-phenyl-7-(trifluoromethyl)-2H-chromen-3-yl)acetonitrile (**2f**)* Coloress oil, 23mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.62 (m, 4H), 7.46 (d, *J* = 8 Hz,

1H), 7.36-7.32(m, 2H), 7.27-7.23(m, 1H) 3.47 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.5, 152.6, 134.03 (q, *J* = 33.8 Hz), 132.1, 130.3, 129.7, 128.8, 127.9, 124.3, 122.4(q, *J* = 274.5 Hz), 121.6 (q, *J*= 3.5 Hz), 118.6, 115.9, 114.5 (q, *J* = 3.8 Hz), 17.7; HRMS (ESI) m/z calcd for $C_{18}H_{10}F_3NO_2Na$ $[M + Na]^+$ 352.0560, found 352.0566.

2-(2-oxo-4-phenyl-7-(trifluoromethoxy)-2H-chromen-3-yl)acetonitrile ***(2g)*** Coloress oil, 23.5mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.57 (m, 3H), 7.36-7.30(m, 3H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.06 (dd, *J* = 8.0, 0.8Hz, 1H), 3.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ159.7, 153.8, 153.6, 151.6, 132.4, 130.1, 129.6, 129.5, 127.9, 120.20 (d, *J* = 258.3 Hz), 118.3, 116.9, 116.4, 116.1, 109.0, 17.5; HRMS (ESI) m/z calcd for $C_{18}H_{10}F_3NO_3Na$ $[M + Na]^+$ 368.0509, found 368.0505.

2-(2-oxo-4,7-diphenyl-2H-chromen-3-yl)acetonitrile ***(2h)*** White solid, 18mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 6H), 7.52-7.41 (m, 4H), 7.38-7.36 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H) 3.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 154.4, 153.5, 145.7, 138.8, 132.9, 129.9, 129.5, 129.2, 128.8, 128.3, 128.0, 127.3, 123.5, 118.7, 116.5, 115.8, 115.1, 17.6; HRMS (ESI) m/z calcd for $C_{23}H_{15}NO_2$ Na $[M + Na]^+$ 360.0999, found 360.0995.

2-(7-fluoro-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (***2i***) White solid, 18.7mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.57 (m, 3H), δ 7.35-7.30 (m, 2H), 7.14(dd, *J* = 8.8, 2.4 Hz, 1H), 7.08(dd, *J* = 8.8, 6.0 Hz, 1H), 6.94(td, *J* = 16.8, 8.8, 2.4Hz, 1H), 3.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 254 Hz), 160.0, 154.2 (d, *J* = 5.8 Hz), 154.0, 132.7, 130.0, 129.8 (d, *J* = 10.2 Hz), 129.6, 127.9, 116.6 (d, *J* = 2.7 Hz), 116.3, 115.1 (d, *J* = 3.1 Hz), 112.8 (d, *J* = 22.3 Hz), 104.5 (d, *J* = 25.5 Hz), 17.4;

HRMS (ESI) m/z calcd for $C_{17}H_{10}FNO_2Na$ $[M + Na]^+$ 302.0590, found 302.0588.

*2-(7-chloro-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2j**)* White solid, 23mg, 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.56 (m, 3H), 7.45(d, *J* = 10.0 Hz, 1H), 7.32-7.30 (m, 2H), 7.18(dd, *J* = 8.4, 2.0 Hz, 1H), 7.02(d, *J* = 8.0 Hz, 1H), 3.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 154.0, 153.2, 138.7, 132.5, 130.1, 129.6, 128.8, 127.8, 126.3, 118.5, 117.3, 116.3, 116.2 17.7; HRMS (ESI) m/z calcd for $C_{17}H_{10}ClNO_2Na$ $[M + Na]^+$ 318.0295, found 318.0292.

*2-(7-bromo-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2k**)* White solid, 22mg, 61% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 4H), 7.32 (td, *J* = 16.0, 8.4, 1.6 Hz,3H), 6.94 (d, *J* = 8.8 Hz, 1H), 3.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 154.0, 153.1, 132.6, 130.1, 129.6, 128.9, 128.2, 127.9, 126.6, 120.2, 118.8, 116.5, 116.1 17.7; HRMS (ESI) m/z calcd for $C_{17}H_{10}BrNO_2Na$ $[M + Na]^+$ 361.9791, found 361.9787.

*2-(2-oxo-4-(p-tolyl)-2H-chromen-3-yl)acetonitrile (**2m**)* White solid, 24mg, 80% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.2, 4.0 Hz, 3H), 7.22-7.18(m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 3.44 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 154.8, 153.0, 140.0, 132.4, 130.1, 129.9, 128.0, 127.9, 124.6, 120.0, 117.0, 116.5, 116.2, 21.4, 17.7; HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_2Na$ $[M + Na]^+$ 298.0842, found 298.0838.

*2-(4-(4-(tert-butyl)phenyl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2n**)* White solid, 22mg, 65% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.57-7.55 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.28-7.25(m, 2H), 7.22 (t, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 4.0, 1.6 Hz, 1H), 3.45 (s, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 154.8,

153.1, 153.0, 132.4, 129.8, 128.1, 127.8, 126.3, 124.6, 120.0, 117.0,116.6, 116.2, 35.0, 31.3, 17.7; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_2Na$ $[M + Na]^+$ 340.1313, found 340.1308.

*2-(4-(4-fluorophenyl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2o**)* White solid, 20mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 1H), 7.43 (dd, *J* = 8.8, 0.8 Hz 1H), 7.37 -7.30 (m, 4H), 7.25-7.22 (m, 1H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, *J* = 251.2 Hz), 160.1, 153.6, 153.0, 130.1, 130.0, 128.7(d, *J*= 4Hz), 127.7, 124.8, 119.7, 117.1, 116.9, 116.7, 116.3, 17.6; HRMS (ESI) m/z calcd for $C_{17}H_{10}FNO_2Na$ $[M + Na]^+$ 302.0592, found 302.0588.

*2-(4-(4-chlorophenyl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2p**)* White solid, 23mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 3H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 153.4, 153.0, 136.2, 132.7, 131.2, 129.9, 129.5, 127.6, 124.8, 119.5, 117.1, 116.6, 116.2, 17.5; HRMS (ESI) m/z calcd for $C_{17}H_{10}ClNO_2Na$ $[M + Na]^+$ 318.0296, found 318.0292.

*2-(4-(4-bromophenyl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2q**)* White solid, 23.5mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.59 (td, *J* = 8.8, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.25-7.21(m, 3H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 153.4, 153.0, 132.8, 132.7, 131.6, 129.6, 127.6, 124.8, 124.4, 119.4, 117.1, 116.5, 116.2, 116.2, 17.5; HRMS (ESI) m/z calcd for $C_{17}H_{10}BrNO_2Na$ $[M + Na]^+$ 361.9787, found 361.9790.

*2-(4-([1,1'-biphenyl]-4-yl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2r**)* White solid, 21mg,

59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.69-7.66 (m, 2H), 7.59 (td, *J* = 7.2, 1.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.45-7.40 (m, 4H), 7.26-7.22 (m, 1H), 7.19 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.49 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 154.4, 153.1, 142.8, 139.7, 132.6, 131.6, 129.1, 128.5, 128.2, 128.1, 128.0, 127.2, 124.7, 119.8, 117.1, 116.8, 116.4, 17.7; HRMS (ESI) m/z calcd for $C_{23}H_{15}NO_2Na$ $[M + Na]^+$ 360.0998, found 360.0995.

*2-(4-(4-methoxyphenyl)-2-oxo-2H-chromen-3-yl)acetonitrile (**2s**)* White solid, 6mg, 17% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.57 (td, *J* = 8.4, 1.2, Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29-7.26 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.14-7.11(m, 2H); 3.92 (s, 3H), 3.47 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 160.4, 154.6, 153.0, 132.4, 129.5, 128.0, 124.8, 124.6, 120.1, 117.0, 116.7, 116.3, 114.8, 55.5, 17.6; HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_3Na$ $[M + Na]^+$ 314.0790, found 314.0788.

2-(2-oxo-4-(m-tolyl)-2H-chromen-3-yl)acetonitrile (***2t***) White solid, 15mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.60-7.55 (m, 1H), 7.51-7.47(m,1H), 7.42 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.39-7.37 (m, 1H), 7.24-7.20 (m, 1H), 7.13-7.10 (m, 3H), 3.44 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ160.3, 154.8, 153.0, 139.4, 132.8, 132.4, 130.5, 129.3, 128.4, 128.0, 125.0, 124.6, 119.9, 117.0, 116.5, 116.1, 21.5, 17.6; HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_2Na$ $[M + Na]^+$ 298.0841, found 298.0838.

*2-(6,8-dimethyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**2u**)* White solid, 27mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.55 (m, 3H), 7.33-7.29 (m, 2H), 7.24(s, 1H), 6.65 (s, 1H), 3.41 (s, 2H), 2.48 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 154.9, 149.6, 140.0, 133.8, 133.4, 129.6, 129.4, 127.9, 126.1, 125.3, 119.3,

116.6, 115.7, 20.9, 17.6, 15.5; HRMS (ESI) m/z calcd for $C_{19}H_{15}NO_2Na$ $[M + Na]^+$ 312.0999, found 312.0995.

2-(6-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4a) and***

2-(8-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4a')*** Colorless solid, 22mg, 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.56 (m, 4.57H), 7.42 (d, *J* = 7.2 Hz, 0.61H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1.14H), 7.33 – 7.30 (m, 3.91H), 7.10 (t, *J* = 7.6 Hz, 0.54H), 6.90 (d, *J* = 8.4 Hz, 0.53H), 6.82(s, 1H), 3.43 (s, 1H), 3.41 (s, 2H), 2.52 (s, 1.5H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.4, 154.9, 154.6, 151.4, 151.2, 134.5, 133.8, 133.5, 133.2, 133.0, 129.8, 129.7, 129.4, 129.3, 127.9, 127.6, 126.5, 125.7, 124.1, 119.6, 119.5, 116.8, 116.5, 116.1, 115.9, 29.7, 20.9, 17.5, 15.6; HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_2Na$ $[M + Na]^+$ 298.0842, found 298.0838.

2-(6-isopropyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4b) and***

2-(8-isopropyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4b')*** Colorless solid, 24mg, 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.56 (m, 4.48H), 7.51 (d, *J* = 8.8 Hz, 0.73H), 7.45 (dd, *J* =8.4, 2.0 Hz, 1.05H), 7.37 (s, 0.55H), 7.36-7.30 (m, 3.18H), 7.16 (t, *J* = 8.0 Hz, 0.6H), 6.90 (dd, *J* = 8.0, 1.6 Hz, 0.52H), 6.86 (d, *J* = 2.0 Hz, 0.88H), 3.75-3.67(m, 0.5H), 3.43 (s, 1H), 3.42 (s, 2H), 2.87-3.80(m, 1H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.3, 155.1, 154.7, 151.3, 150.3, 145.5, 136.8, 133.3, 133.2, 133.0, 130.8, 129.8, 129.7, 129.6, 129.4, 129.3, 127.9, 125.6, 125.3, 124.4, 119.6, 119.5, 116.9, 116.5, 116.5, 116.0, 115.7, 33.6, 26.5, 23.9, 22.7, 17.6, 17.5; HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_2$ Na $[M + Na]^+$ 326.1155, found 326.1151.

2-(6-(tert-butyl)-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4c) and***

2-(8-(tert-butyl)-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4c')*** Colorless solid, 22mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.64 -7.55 (m, 5.88H), 7.37 (s, 0.69H), 7.35-7.30 (m, 3.32H), 7.12 (t, *J* = 8.0 Hz, 0.44H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.6 Hz, 0.39H), 3.43 (s, 2H), 3.42 (s, 1H), 1.55 (s, 4.5H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.8, 155.3, 154.9, 151.8, 151.1, 147.8, 138.1, 133.5, 133.0, 130.2, 130.1, 129.8, 129.6, 129.4, 128.8, 128.1, 128.0, 127.9, 126.3, 124.0, 124.0, 119.1, 116.6, 115.9, 100.0, 35.1, 34.6, 31.2, 29.9, 17.6, 17.5; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_2$ Na $[M + Na]^+$ 340.1309, found 340.1313.

2-(6-chloro -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4d) and***

2-(8-chloro -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4d')*** White solid, 22.5mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.58 (m, 5.19H), 7.52 (dd, *J* = 8.8, 2.4 Hz, 1.13H)，7.38 (d, *J* = 8.8 Hz, 1.13H), 7.39-7.30 (m, 3.03H), 7.15 (t, *J* = 8.0 Hz, 0.55H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 0.5H), 3.44 (s, 1H), 3.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 159.2, 154.3, 153.5, 151.4, 148.8, 132.8, 132.6, 132.5, 132.2, 130.2, 130.0, 129.7, 129.6, 127.9, 127.8, 127.2, 126.5, 124.7, 122.1, 121.2, 120.9, 118.5, 117.5, 117.1, 116.1, 17.6, 17.5; HRMS (ESI) m/z calcd for $C_{17}H_{10}ClNO_2Na$ $[M + Na]^+$ 318.0297, found 318.0292.

2-(6-bromo -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4e) and***

2-(8-bromo -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4e')*** White solid, 24.5mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.80 (dd, *J* = 7.6, 0.8 Hz, 0.54H), 7.68-7.58 (m, 5.36H), 7.34 – 7.30 (m, 3.92H), 7.18 (d, *J* = 2.4 Hz, 0.89H), 7.09 (t, *J* = 8.0 Hz,

0.57H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 0.52H), 3.44 (s, 1H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 159.3, 154.2, 153.4, 151.9, 149.8, 140.0, 136.0, 135.3, 132.6, 132.1, 130.2, 130.2, 130.0, 129.7, 129.6, 127.9, 127.8, 127.3, 125.2, 121.4, 121.2, 118.8, 117.5, 117.5, 117.1, 116.1, 110.7, 17.6, 17.6; HRMS (ESI) m/z calcd for $C_{17}H_{10}BrNO_2Na$ $[M + Na]^+$ 361.9790, found 361.9787.

2-(6-iodo -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile ***(4f) and*** *2-(8-iodo -2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile* ***(4f')*** White solid, 26.5mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.6, 1.6 Hz, 0.48H), 7.84 (dd, *J* = 8.8, 2.1 Hz, 0.89H), 7.67-7.58 (m, 4.15H), 7.34 (d, *J* = 2.0 Hz, 0.88H), 7.32-7.30 (m, 2.61H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.6 Hz, 0.51H), 6.96 (t, *J* = 7.6 Hz, 0.5H), 3.44 (s, 1H), 3.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 154.2, 153.3, 152.6, 152.2, 142.3, 141.1, 136.2, 132.5, 132.1, 130.2, 130.0, 129.7, 129.6, 128.3, 127.9, 127.9, 125.9, 121.8, 120.7, 119.0, 117.3, 117.1, 116.1, 87.8, 84.2, 17.6, 17.6; HRMS (ESI) m/z calcd for $C_{17}H_{10}INO_2Na$ $[M + Na]^+$ 409.9652, found 409.9648.

*2-(2-oxo-4,6-diphenyl-2H-chromen-3-yl)acetonitrile (****4g****)* ***and*** *2-(2-oxo-4,8-diphenyl-2H-chromen-3-yl)acetonitrile (****4g'****)* White solid, 18mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 2.0 Hz, 1.18H), 7.69-7.57 (m, 6.19H), 7.53-7.49 (m, 1.96H), 7.42-7.33 (m, 8.61H), 7.28 (d, *J* = 8.0 Hz, 0.55H), 7.24 (d, *J* = 2.4 Hz, 1.11H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 0.47H), 3.46 (s, 2H), 3.41 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 154.8, 154.6, 152.5, 139.3, 138.1, 135.5, 133.8, 133.2, 132.8, 131.5, 130.6, 130.0, 129.8, 129.6, 129.5, 129.0, 128.6, 128.2, 128.0, 128.0, 127.9, 127.3, 127.1, 126.1, 124.5, 120.3, 120.0, 117.5, 116.7, 116.4, 17.7, 17.6; HRMS (ESI) m/z

calcd for $C_{23}H_{15}NO_2Na$ $[M + Na]^+$ 360.0998, found 360.0995.

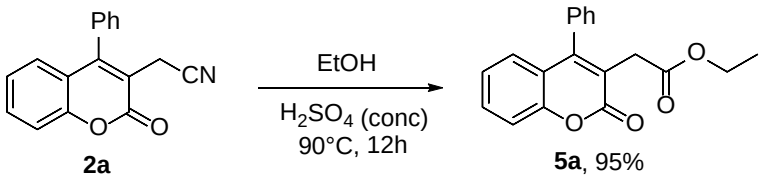
*2-(6-methoxy-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**4h**)* White solid, 19.5mg, 62% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.55 (m, 3H), 7.37-7.31 (m, 3H), 7.14 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.49 (d, *J* = 2.8 Hz, 1H), 3.67 (s, 3H), 3.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ160.4, 156.1, 154.2, 147.4, 132.9, 129.9, 129.5, 127.9, 120.2, 119.4, 118.0, 116.6, 116.4, 110.8, 55.7, 17.6; HRMS (ESI) m/z calcd for $C_{18}H_{13}NO_3Na$ $[M + Na]^+$ 314.0790, found 314.0788.

*2-(6,7-dimethyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**4i**) **and***

*2-(7,8-dimethyl-2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (**4i'**)*

^1H NMR (400 MHz, $CDCl_3$) δ7.63-7.55 (m, 4.57H), δ7.33-7.29 (m, 2.97H), 7.20 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 0.53H), 6.77 (s, 0.89H), 3.41 (s, 1H), 3.40 (s, 2H), 2.43 (s, 1.5H), 2.39 (s, 1.5H), 2.35 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 155.0, 154.6, 151.5, 151.3, 142.8, 142.5, 133.6, 133.4, 133.4, 133.2, 129.7, 129.6, 129.4, 129.3, 128.0, 127.8, 126.0, 124.8, 124.7, 117.5, 116.7 114.9, 114.5, 99.9, 20.5, 20.3, 19.3, 17.5, 17.4, 11.6; HRMS (ESI) m/z calcd for $C_{19}H_{15}O_4Na$ $[M + Na]^+$ 312.0998, found 312.0995.

General procedure for synthesis of product 5a.

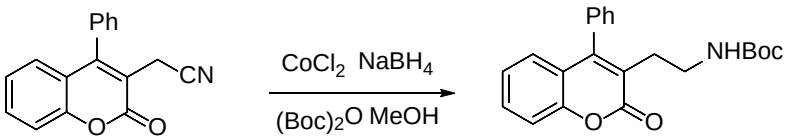


To a solution of 2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (2a, 52.2 mg, 0.2 mmol) in EtOH (2 mL) in a 25 ml two-neck flask were added H_2O (5 drops) and H_2SO_4

(conc., 0.8 mL). The reaction mixture was heated at 90 °C for 12 h. After cooling to room temperature, the reaction mixture was slowly quenched with saturated aqueous $NaHCO_3$ to pH 8 and extracted with DCM (10 mL × 3). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na2SO4, and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/ethyl acetate (4:1) to afford the pure product 5a.

*ethyl 2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetate (**5a**)* White solid, 63mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.54-7.48 (m, 4H), 7.38 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.30 - 7.26 (m, 2H), 7.17-7.13(m, 1H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.39 (s, 2H), 1.22 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 161.5, 152.9, 134.0, 131.4, 129.1, 128.9, 128.2, 127.6, 124.2, 120.5, 120.4, 116.8, 61.0, 34.4, 14.1; HRMS (ESI) m/z calcd for $C_{19}H_{16}O_4Na$ $[M + Na]^+$ 331.0943, found 331.0946.

General procedure for synthesis of product 6a.



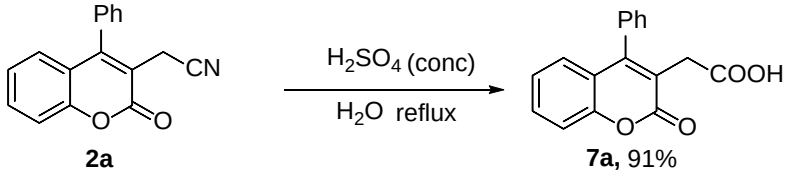
2a **6a,** 65%

To a solution of 2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (2a, 26.1 mg, 0.1 mmol), $(Boc)_2O$ (43.6 mg, 0.2 mmol) and $CoCl_2$ (26mg, 0.2mmol) in MeOH(1mL) was cooled to 0°C and was added in portions. The reaction was stirred for 7 h at room

temperatureand then quenched with water and filtered over celite (washings with DCM). The crude product was purified by column chromatography to afford the pure product 6a.

tert-butyl (2-(2-oxo-4-phenyl-2H-chromen-3-yl)ethyl)carbamate ***(6a)*** White solid, 24mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 4H), δ 7.37 (d, *J* = 8.0 Hz, 1H), δ 7.77 (s, 1H), 7.15 – 7.11 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 1H), 3.32 (q, *J* = 6.3 Hz, 0H), 3.32 (q, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.3, 155.8, 152.6, 134.3, 130.9, 128.9, 128.8, 128.3, 127.4, 124.2, 124.1,120.8, 116.6, 79.0, 39.6, 29.1, 28.3; HRMS (ESI) m/z calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1703, found 366.1700.

General procedure for synthesis of product 7a.



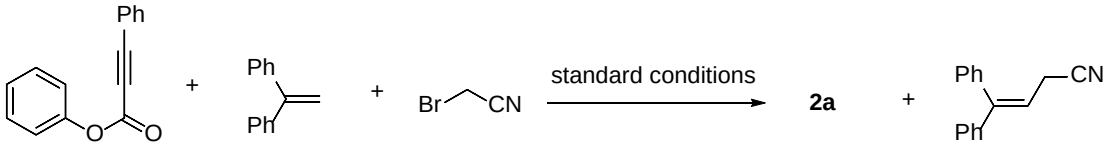
2a **7a,** 91%

A 25 ml two-neck flask was charged with 2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetonitrile (2a, 26.1 mg, 0.1 mmol) and a mixture of acetic acid, concentrated sulfuric acid and H_2O (3/3/1, 2ml), The solution was heated under reflux for 4 h. After

cooling to room temperature the mixture was diluted with water and extracted 5 times with 5 mL of CH_2Cl_2. The combined organic phases were washed with 5 mL of a saturated aqueous NaCl-solution, dried over Na_2SO4 and concentrated under reduced pressure The residue was subjected to column chromatography to afford the pure product 7a.

*2-(2-oxo-4-phenyl-2H-chromen-3-yl)acetic acid (**7a**)* White solid, 25.5mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.49 (m, 4H)，7.40 (d, *J* = 8.0 Hz, 1H)，7.31-7.24 (m, 2H)，7.20-7.14 (m, 1H)，7.05 (dd, *J* = 8.0, 1.2 Hz, 1H)，3.44 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 161.7, 153.4, 152.9, 133.8, 131.6, 129.3, 129.1, 128.1, 127.6, 124.3, 120.3, 119.6, 116.8, 34.2; HRMS (ESI) m/z calcd for $C_{17}H_{13}O_4$ $[M + H]^+$ 281.0811, found 281.0808.

General procedure for synthesis of product 6b.



1a **5b** 0% **6b,** 86%

Aryl alkynoate (1) (0.1 mmol), Li_2CO_3 (0.2 mmol), *fac*-Ir(ppy)$_3$ (0.002mol, 2.0 mol%) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed acetone , Bromoacetonitrile (2)

(0.3 mmol) and 1,1-Diphenylethylene (0.4mmol) was then added to the mixture in the presence of a flow of argon. The solution was placed at a distance of about 5 cm from blue LEDs strip and irradiated for 48 h. Afterward, the crude mixture was purified by column chromatography to give the product 6b

*4,4-diphenylbut-3-enenitrile (**6b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.34 (m, 3H), 7.31-7.27 (m, 3H), 7.24-7.21(m, 2H), 7.18-7.15 (m, 2H), 6.03 (t, *J* = 7.6 Hz, 1H), 3.14 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 140.7, 137.9, 129.4, 128.8, 128.4, 128.2, 128.1, 127.5, 118.2, 115.5, 18.4;

References.

(1) C. E. Song, D. Jung, S. Y. Choung, E. J. Roh, S. Lee, *Angew. Chem. Int. Ed.*, 2004, **43**, 6183

X-ray crystallography data of 2a.

Figure S1. The x-ray single crystal structure of **2a**.

Table S2. Crystal data and structure refinement for shelxl.

X-ray crystallography data of 2a

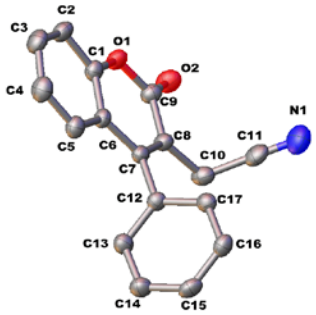


Figure S1. The x-ray single crystal structure of **2a**.

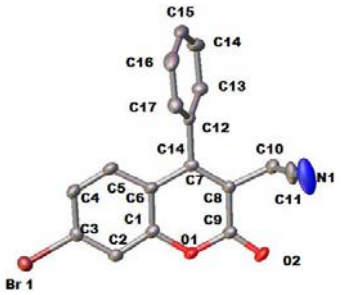
Table S1. Crystal data and structure refinement for A.

Identification code	shelxl
Empirical formula	$C_{17}H_{11}NO_2$
Formula weight	261.27
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	a = 9.812(2) Å alpha = 108.25(3) deg. b = 15.260(3) Å beta = 98.59(3) deg. c = 18.464(4) Å gamma = 92.69(3)deg.
Volume	2583.1(10) $Å^3$
Z, Calculated density	8, 1.344 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	1088
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	1.412 to 27.864 deg.
Limiting indices	-12<=h<=12, -18<=k<=20, -24<=l<=24
Reflections collected / unique	31307 / 12234 [R(int) = 0.0797]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8150
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2234 / 0 / 722
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.1133
R indices (all data)	R1 = 0.1223, wR2 = 0.1380
Extinction coefficient	0.0107(6)
Largest diff. peak and hole	0.292 and -0.256 e. $Å^{-3}$

X-ray crystallography data of 2k.

Figure S1. The x-ray single crystal structure of **2k**.

Table S2. Crystal data and structure refinement for shelxl.



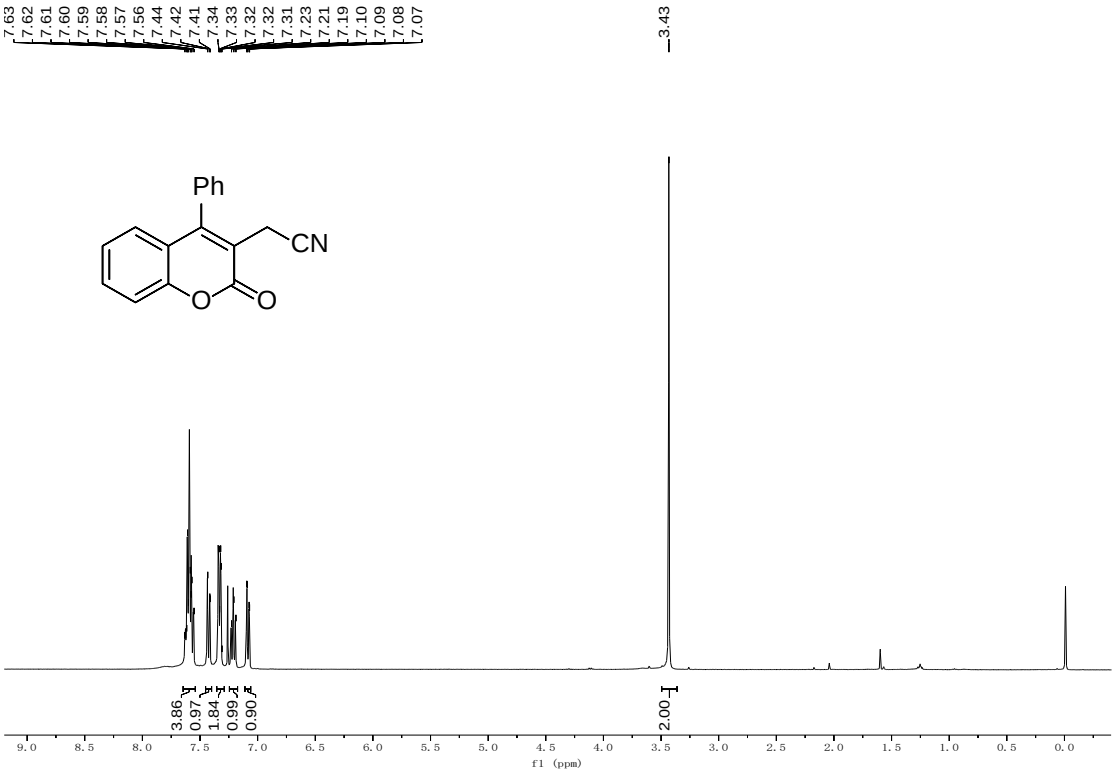
X-ray crystallography data of 2k

Figure S1. The x-ray single crystal structure of **2k**.

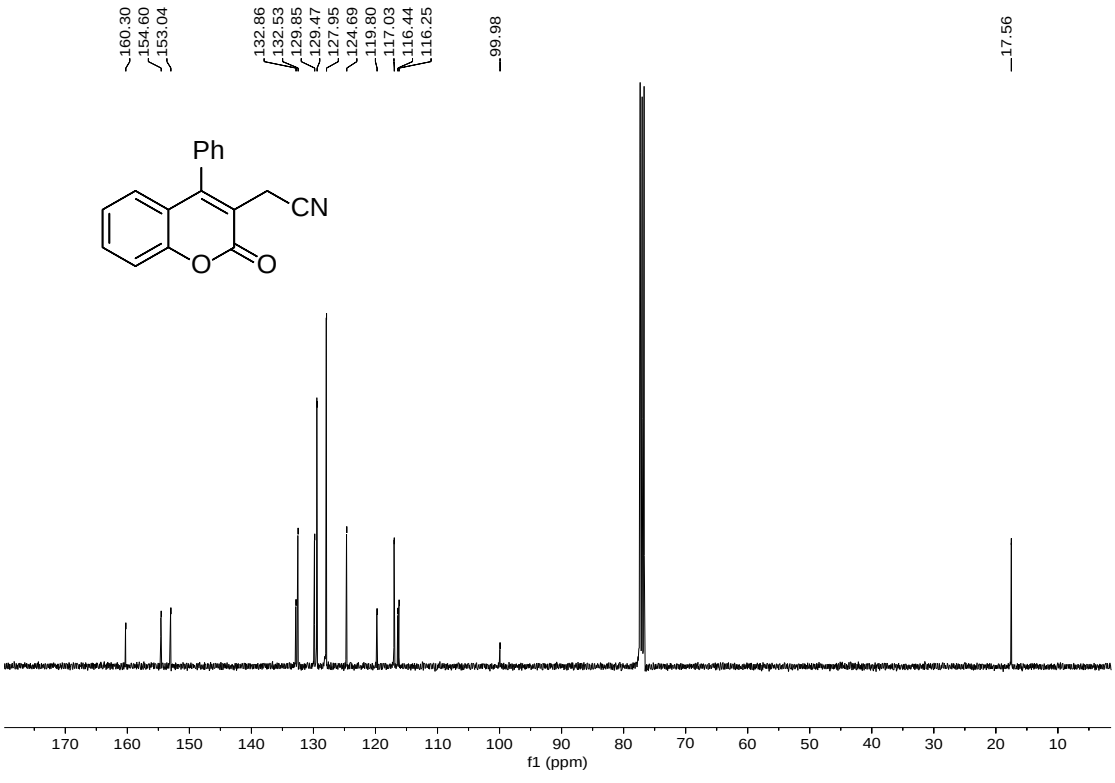
Identification code	shelxl
Empirical formula	$C_{17}H_{10}BrNO_2$
Formula weight	340.17
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.067(2) Å alpha = 90 deg. b = 9.1332(18) Å beta = 103.76(3) deg. c = 15.755(3) Å gamma = 90 deg.
Volume	1406.9(5) $Å^3$
Z	4
Calculated density	1.606 Mg/m^3
Absorption coefficient	2.924 mm^{-1}
F(000)	680
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	2.189 to 27.886 deg.
Limiting indices	-13<=h<=13, -12<=k<=11, -19<=l<=20
Reflections collected / unique	14569 / 3348 [R(int) = 0.0740]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6879
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3348 / 0 / 190
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0749
R indices (all data)	R1 = 0.0687, wR2 = 0.0824
Extinction coefficient	n/a
Largest diff. peak and hole	0.693 and -1.023 e. $Å^{-3}$

NMR Spectra

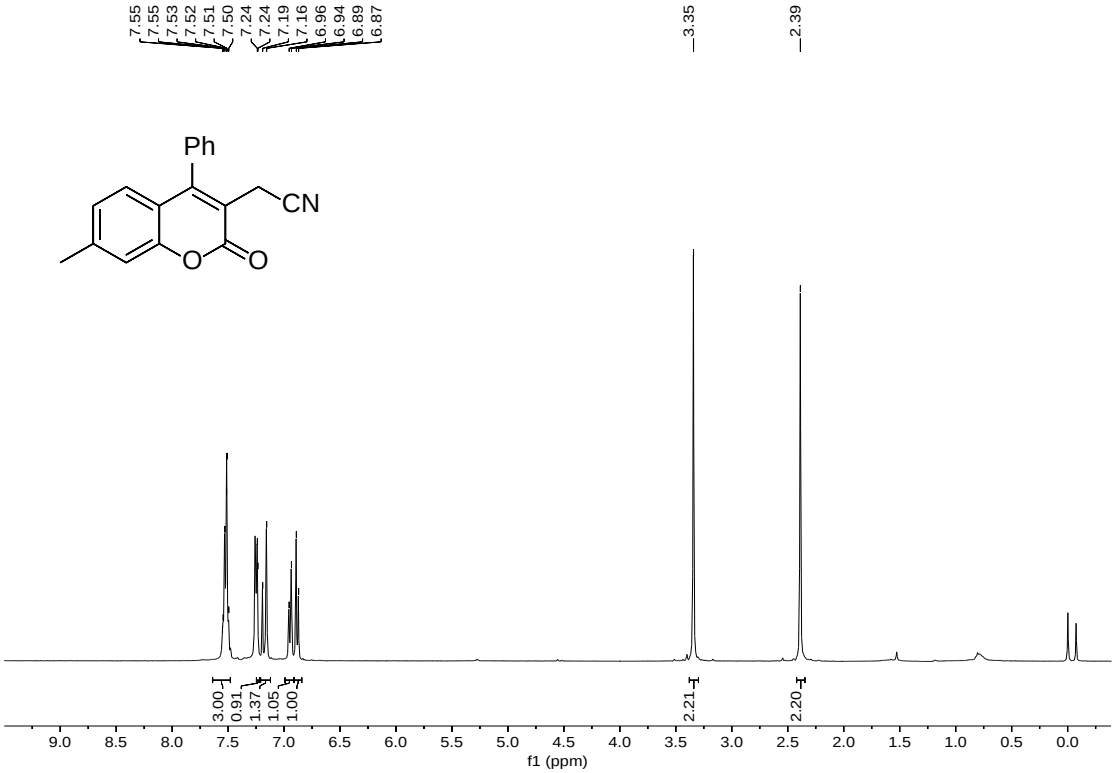
[1] H NMR Spectrum of **2a**



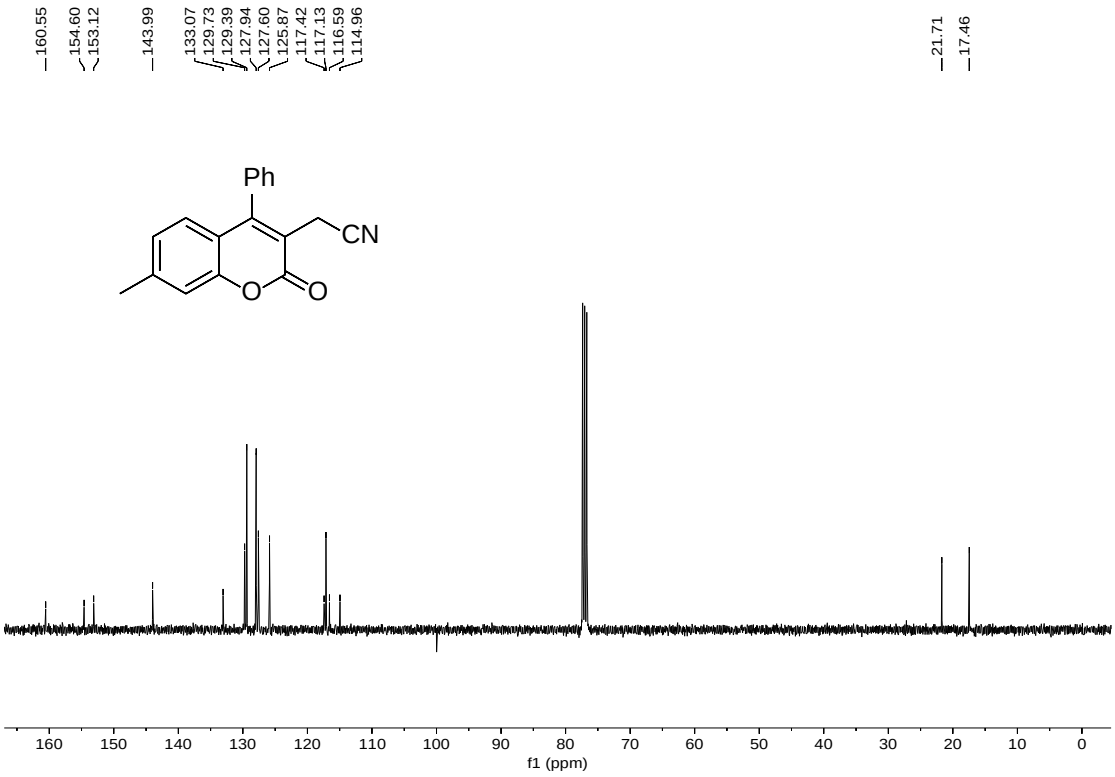
[13] C NMR Spectrum of **2a**



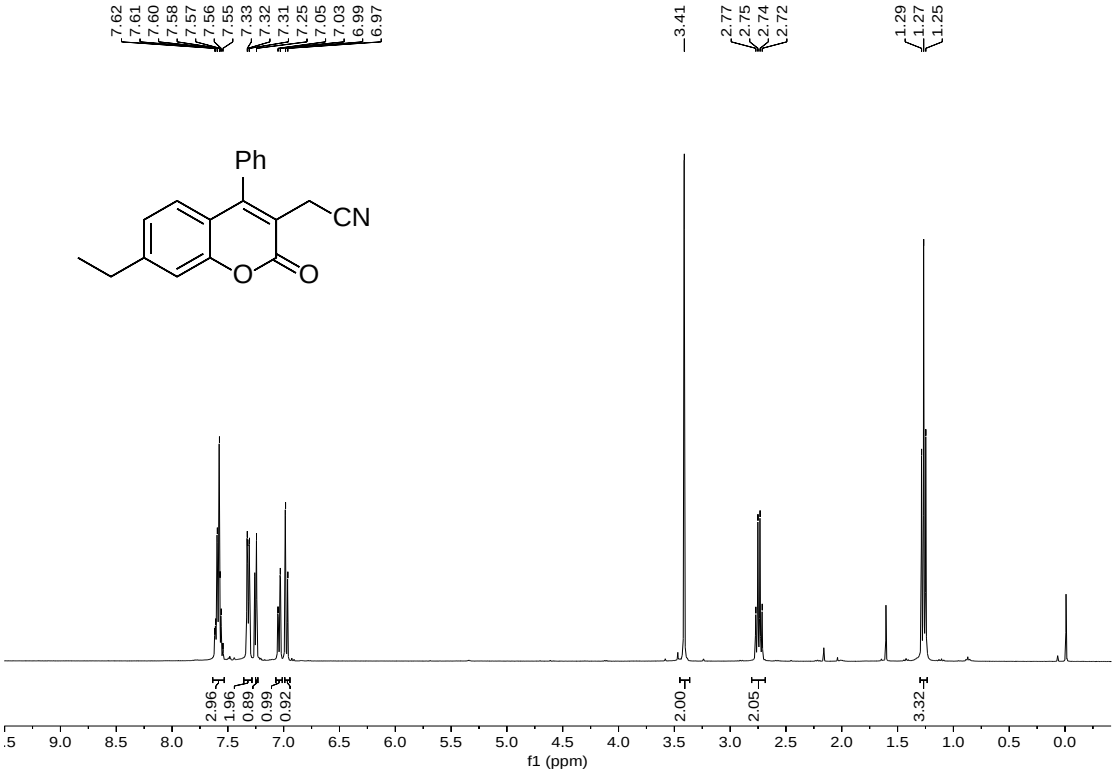
[1] H NMR Spectrum of **2b**



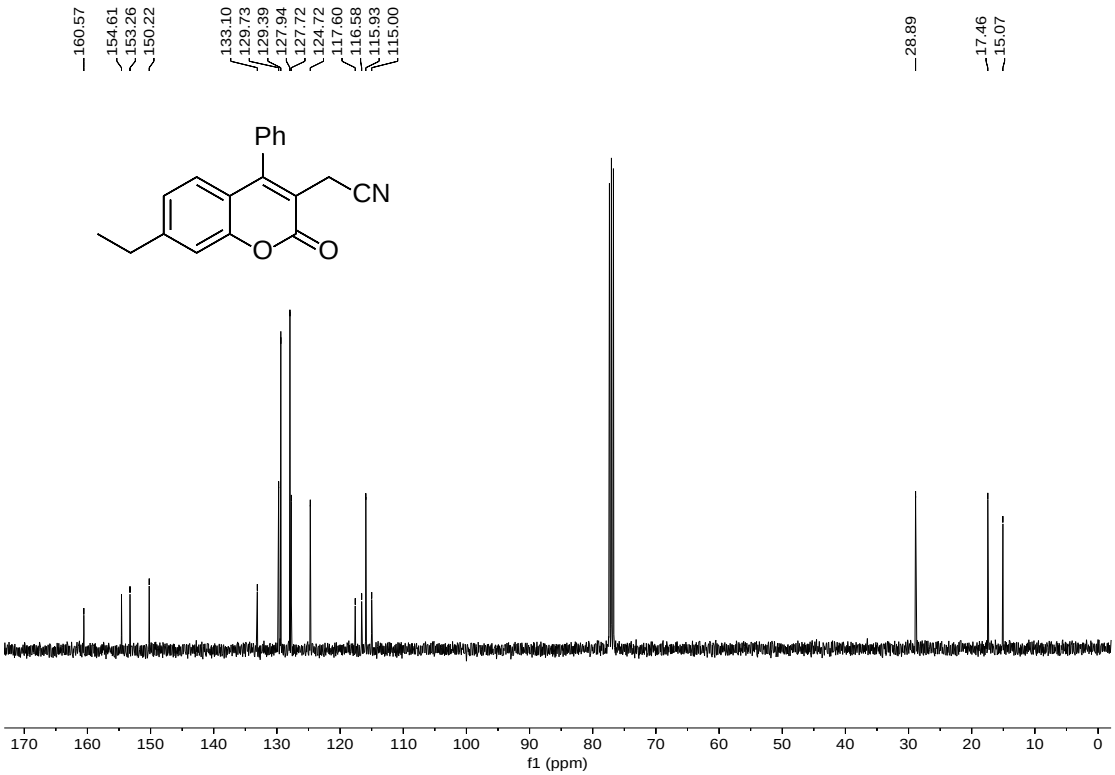
[13] C NMR Spectrum of **2b**



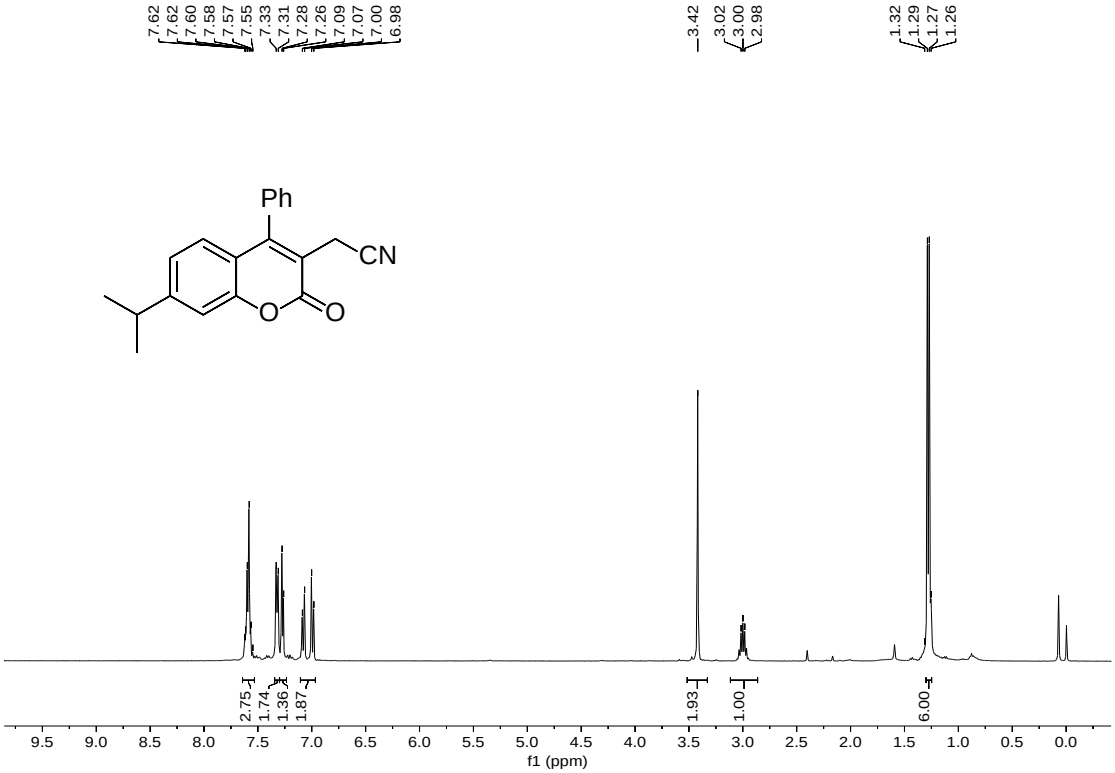
[1] H NMR Spectrum of **2c**



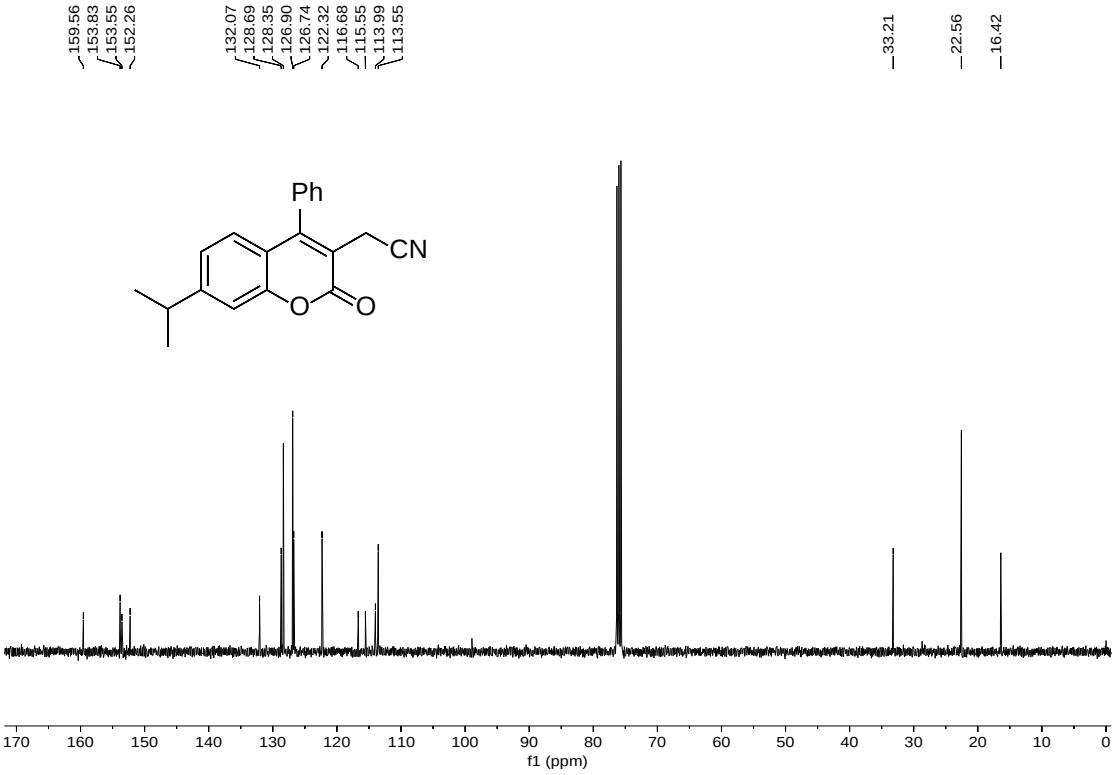
[13] C NMR Spectrum of **2c**



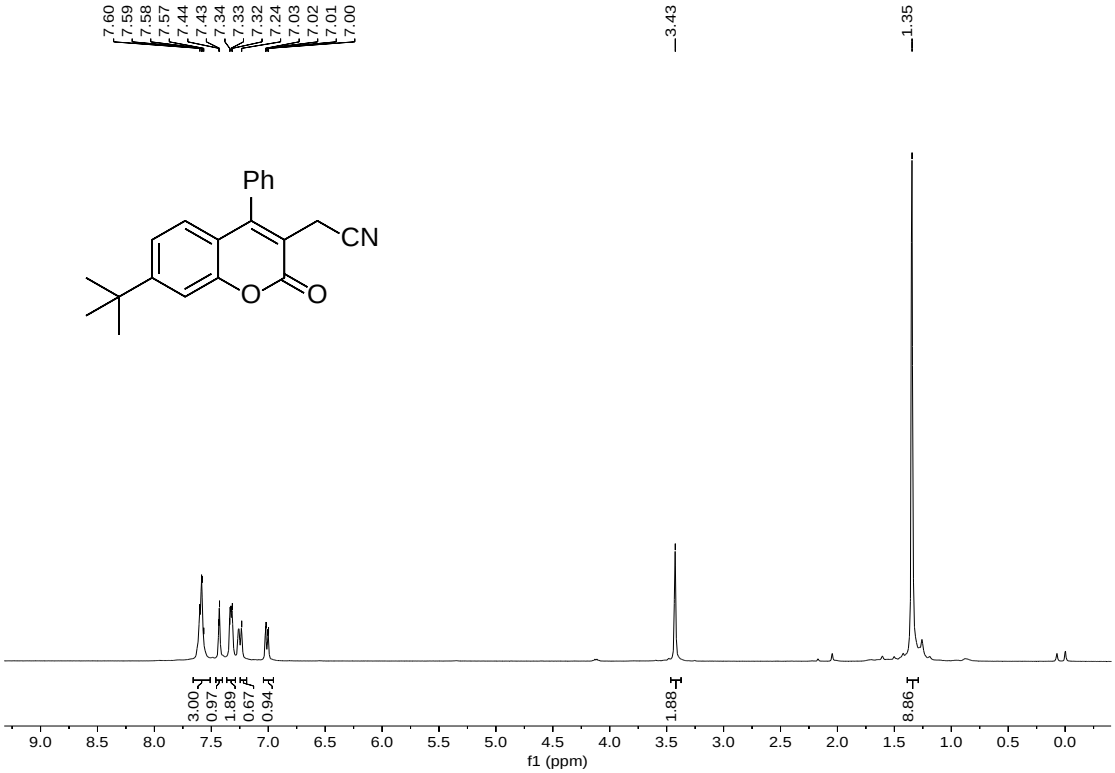
[1] H NMR Spectrum of **2d**



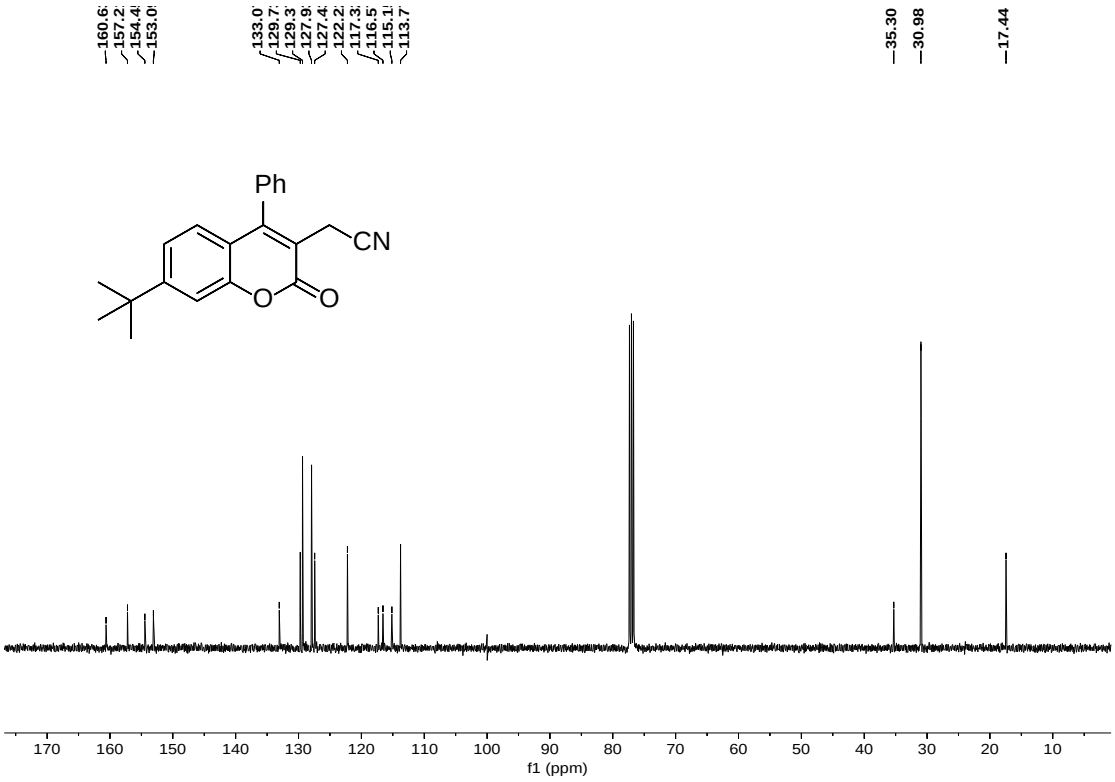
[13] C NMR Spectrum of **2d**



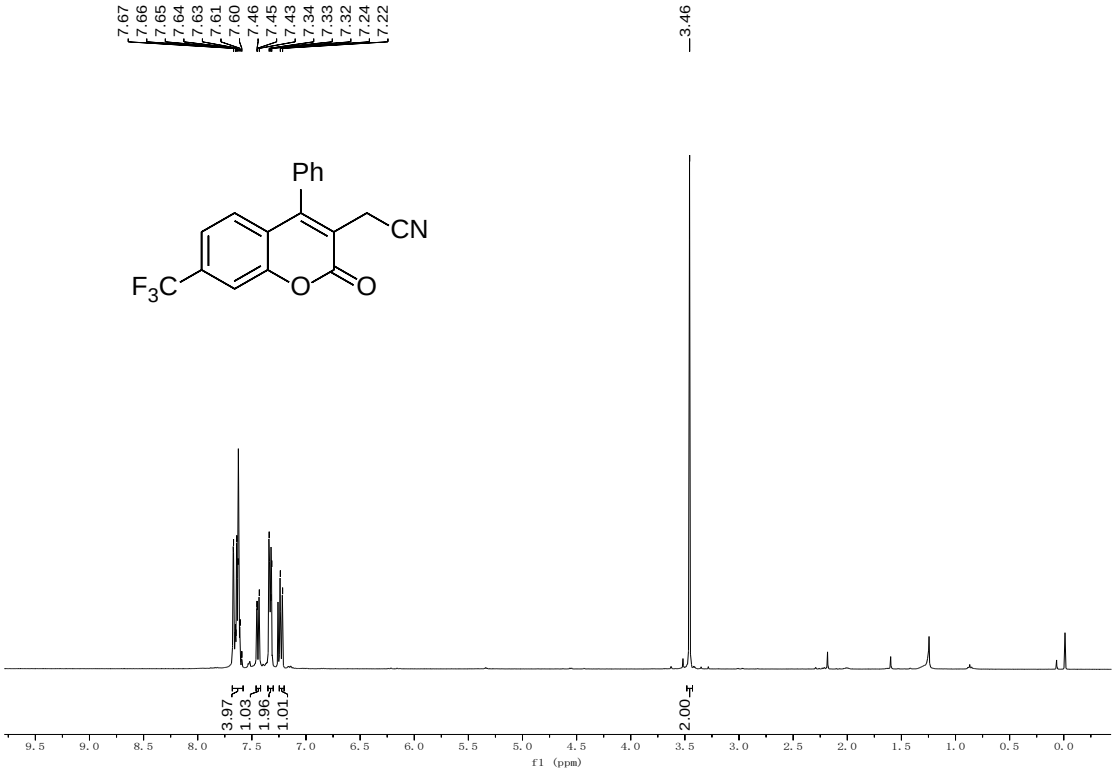
[1] H NMR Spectrum of **2e**



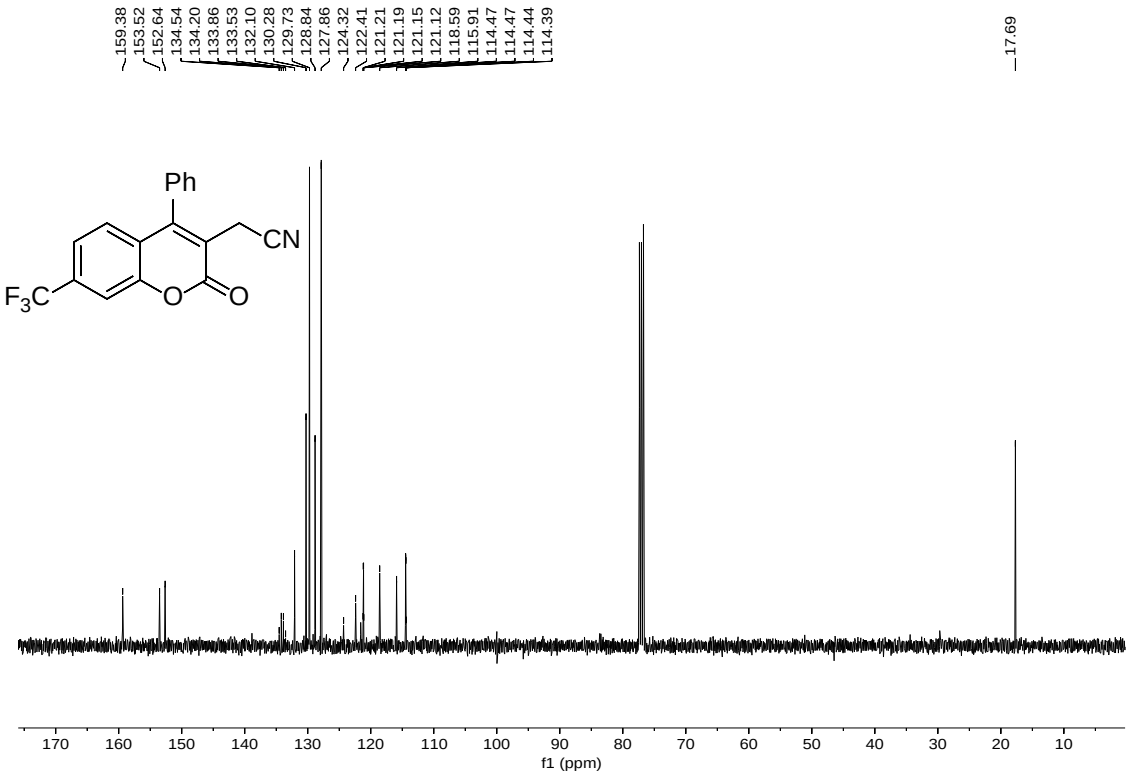
[13] C NMR Spectrum of **2e**



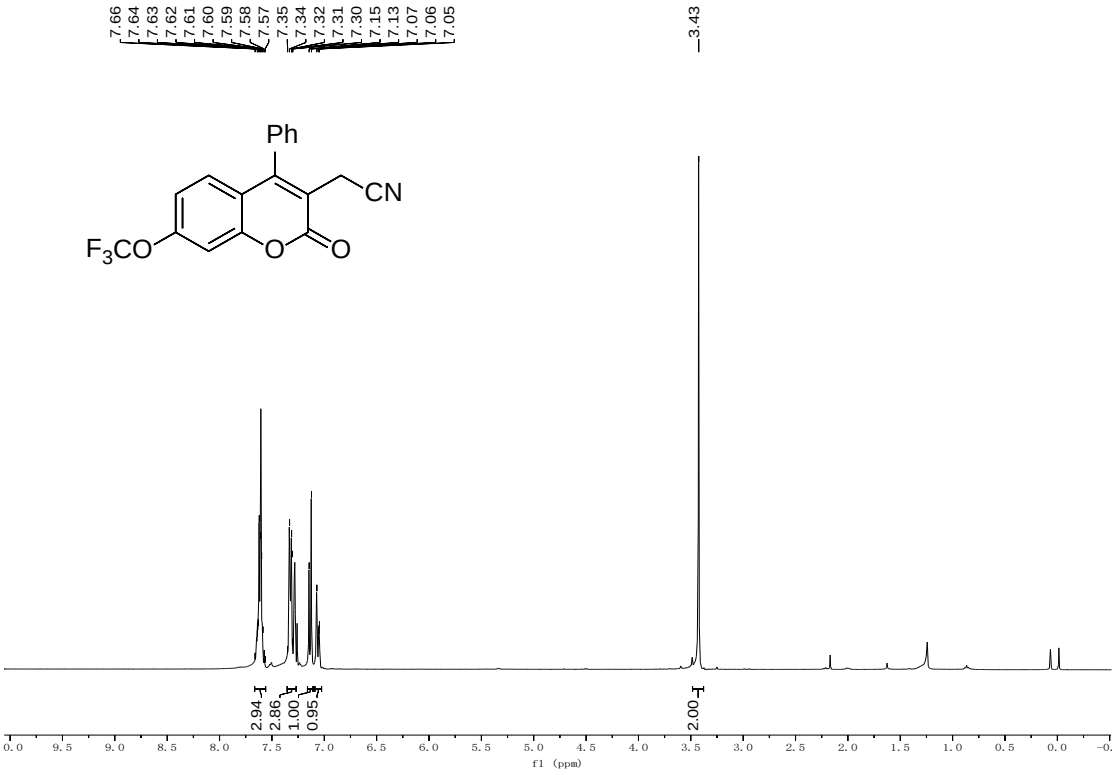
[1] H NMR Spectrum of **2f**



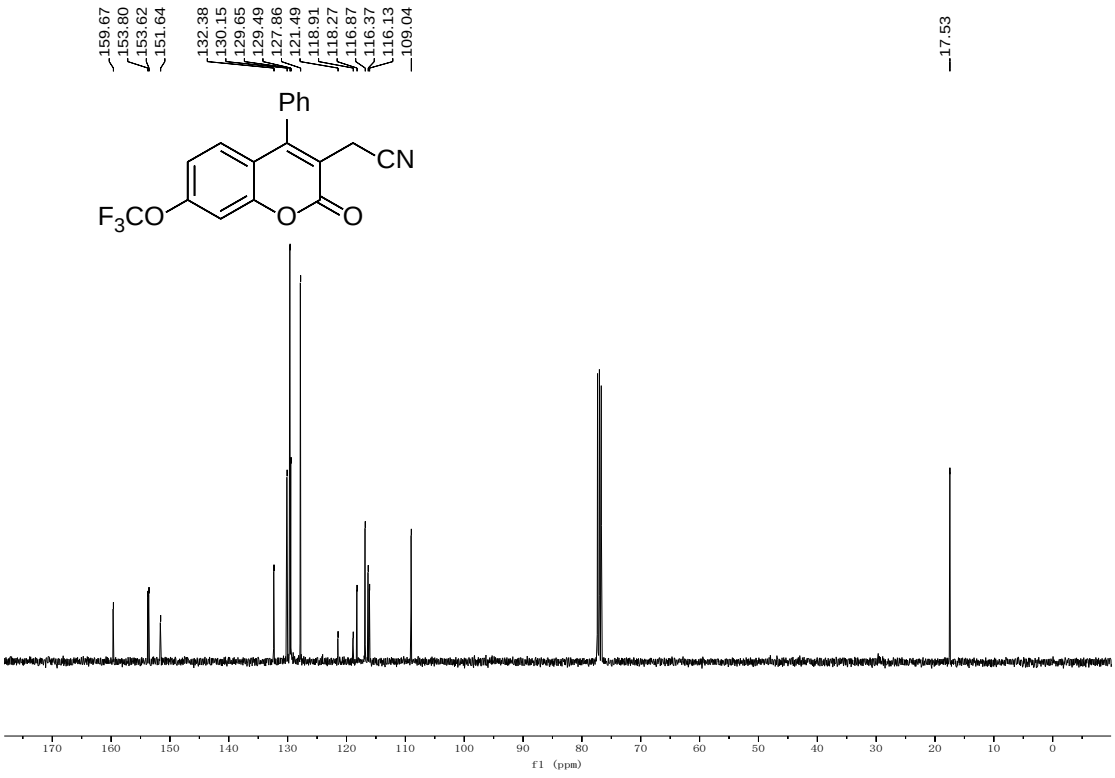
[13] C NMR Spectrum of **2f**



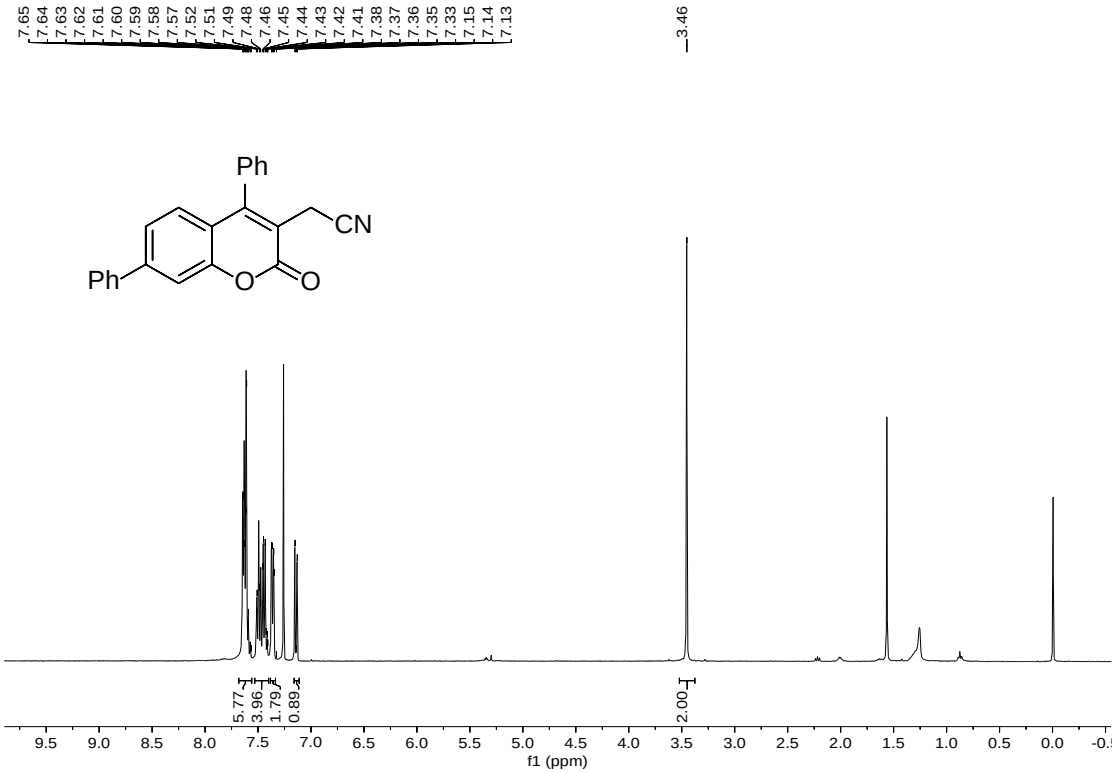
^{1}H NMR Spectrum of **2g**



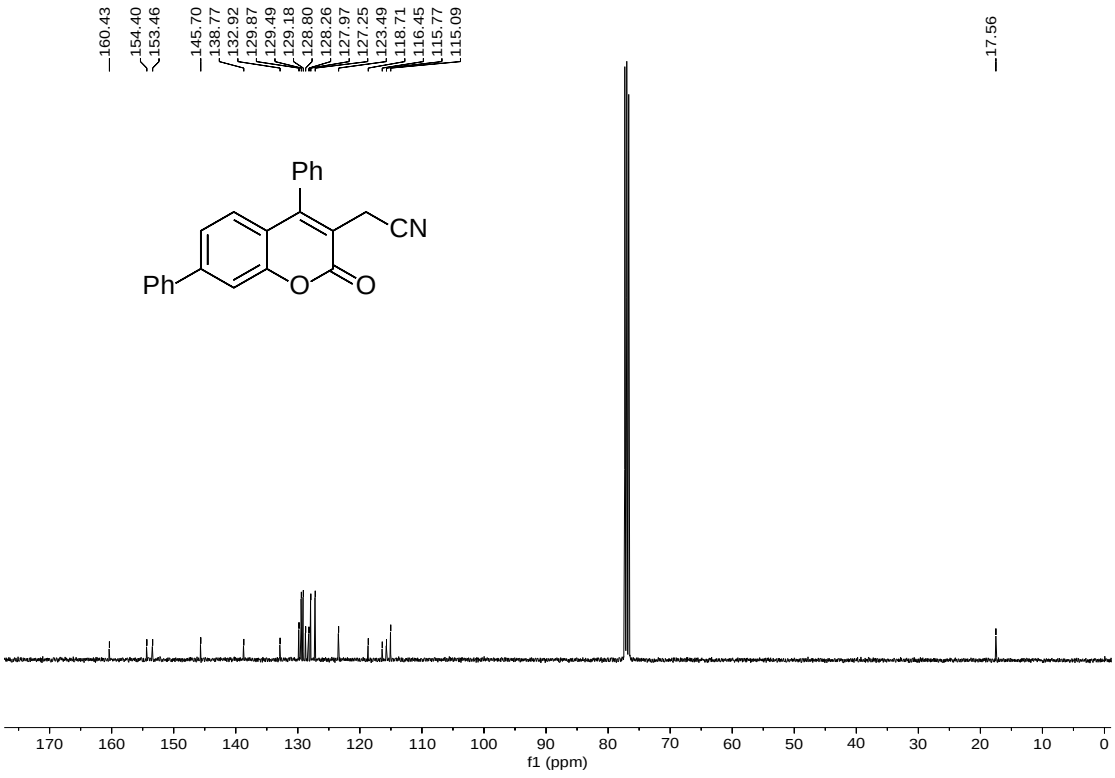
^{13}C NMR Spectrum of **2g**



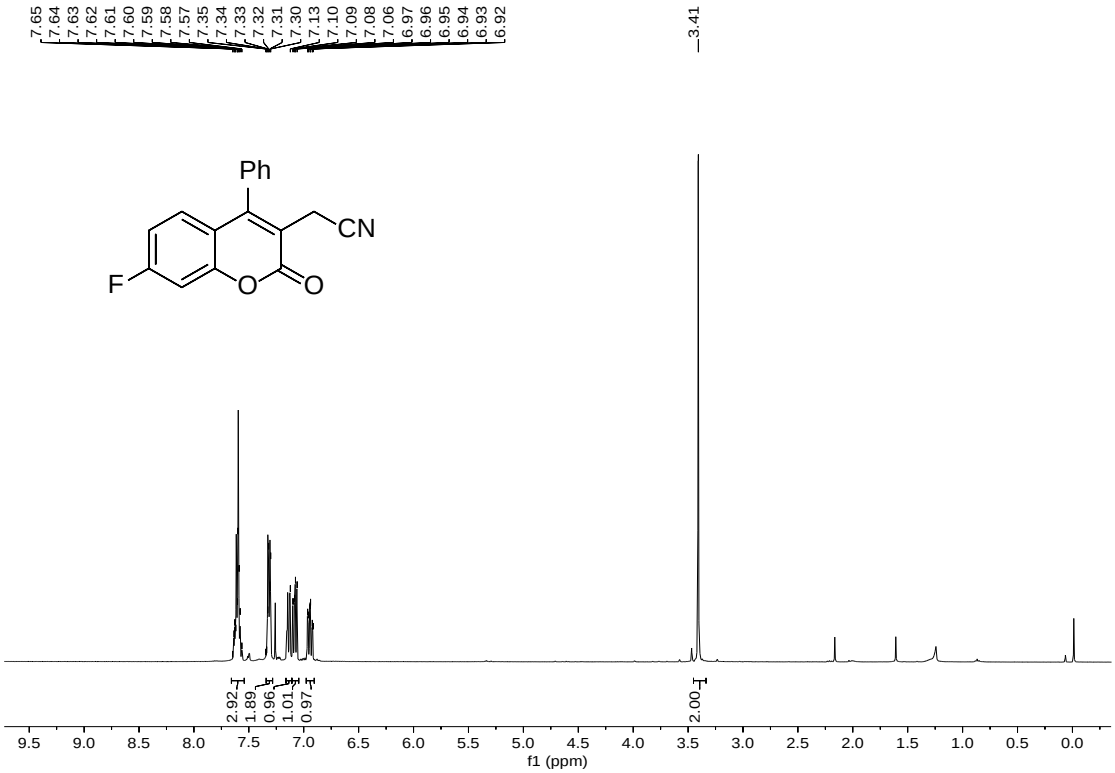
[1] H NMR Spectrum of **2h**



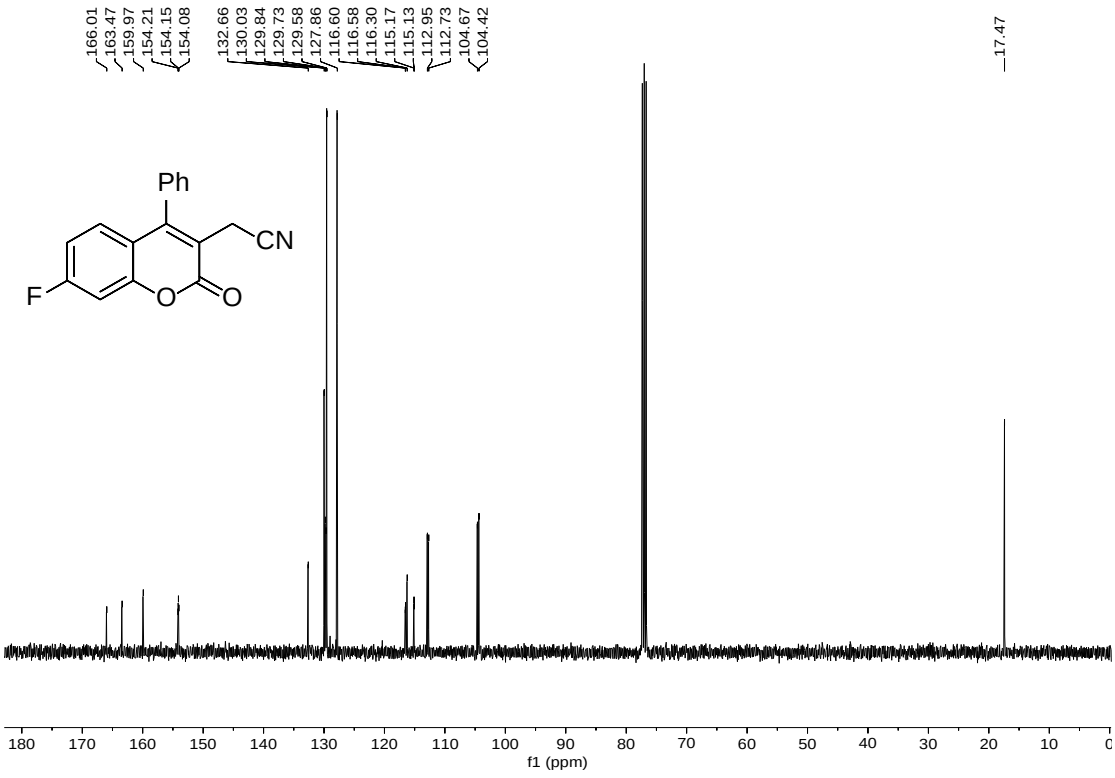
[13] C NMR Spectrum of **2h**



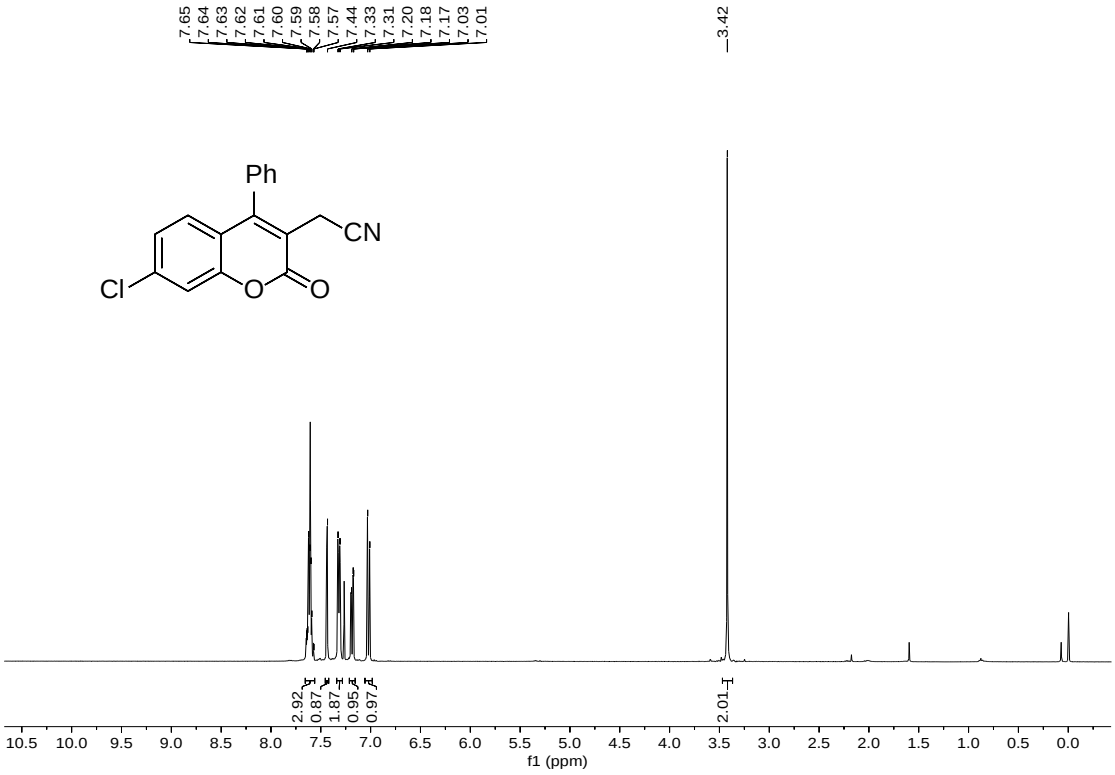
^{1}H NMR Spectrum of **2i**



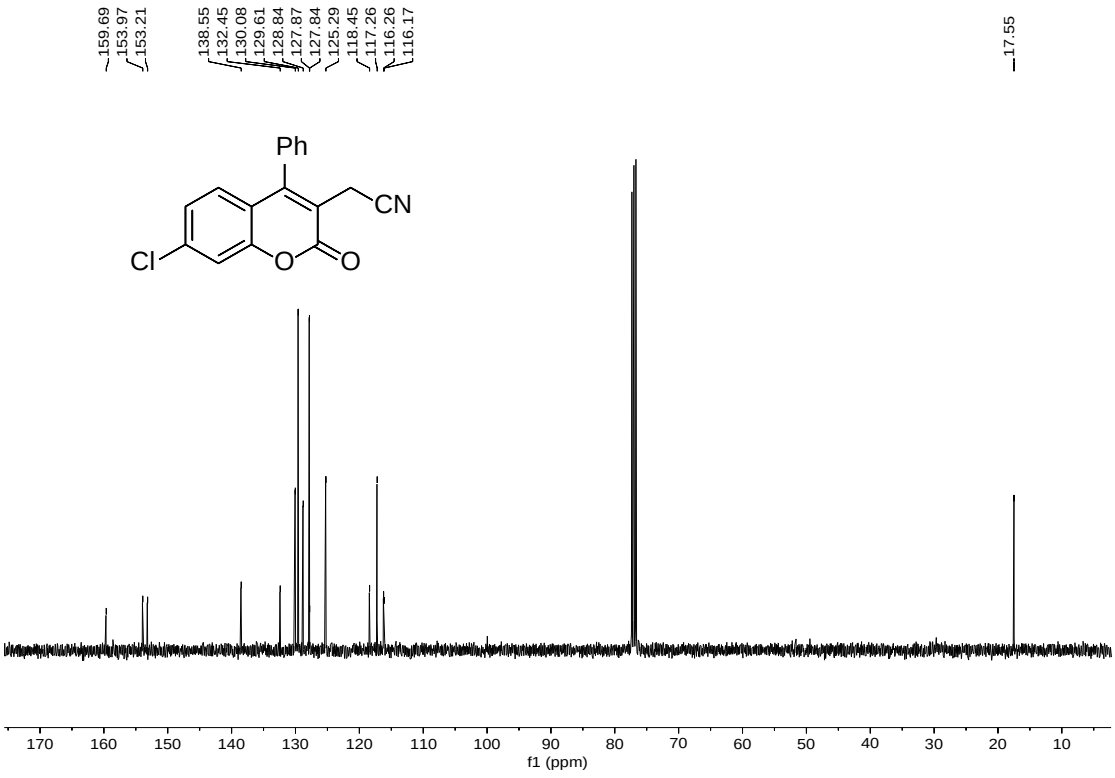
^{13}C NMR Spectrum of **2i**



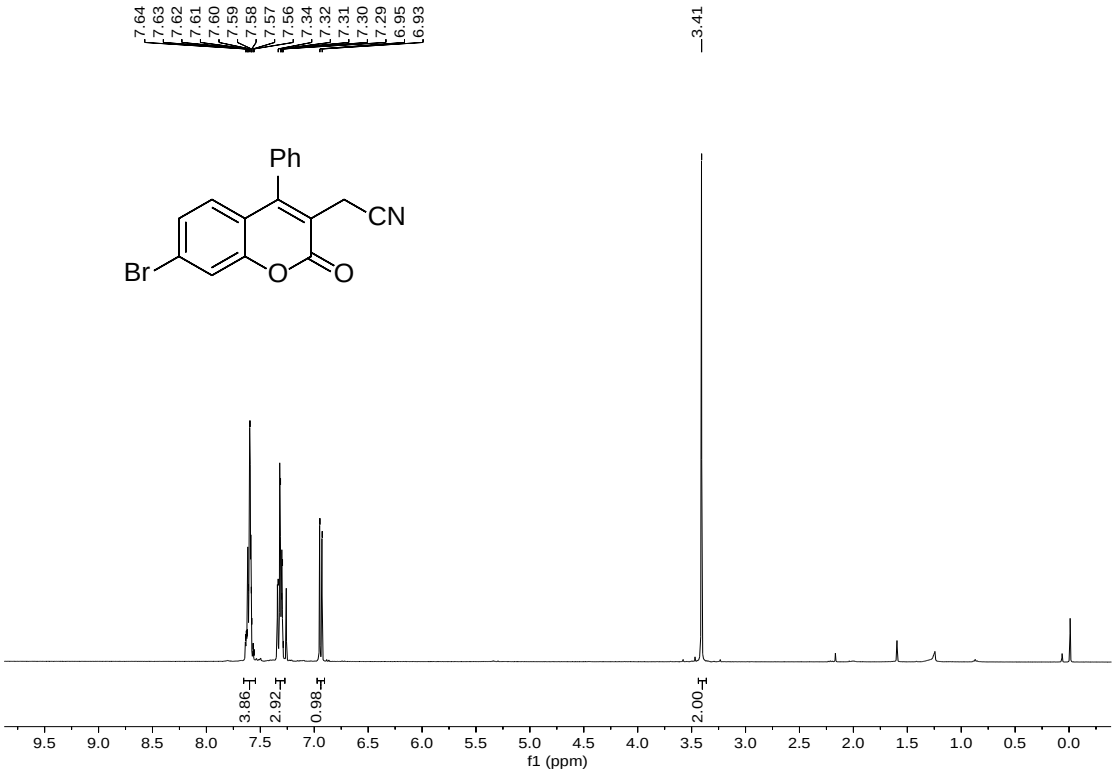
[1] H NMR Spectrum of **2j**



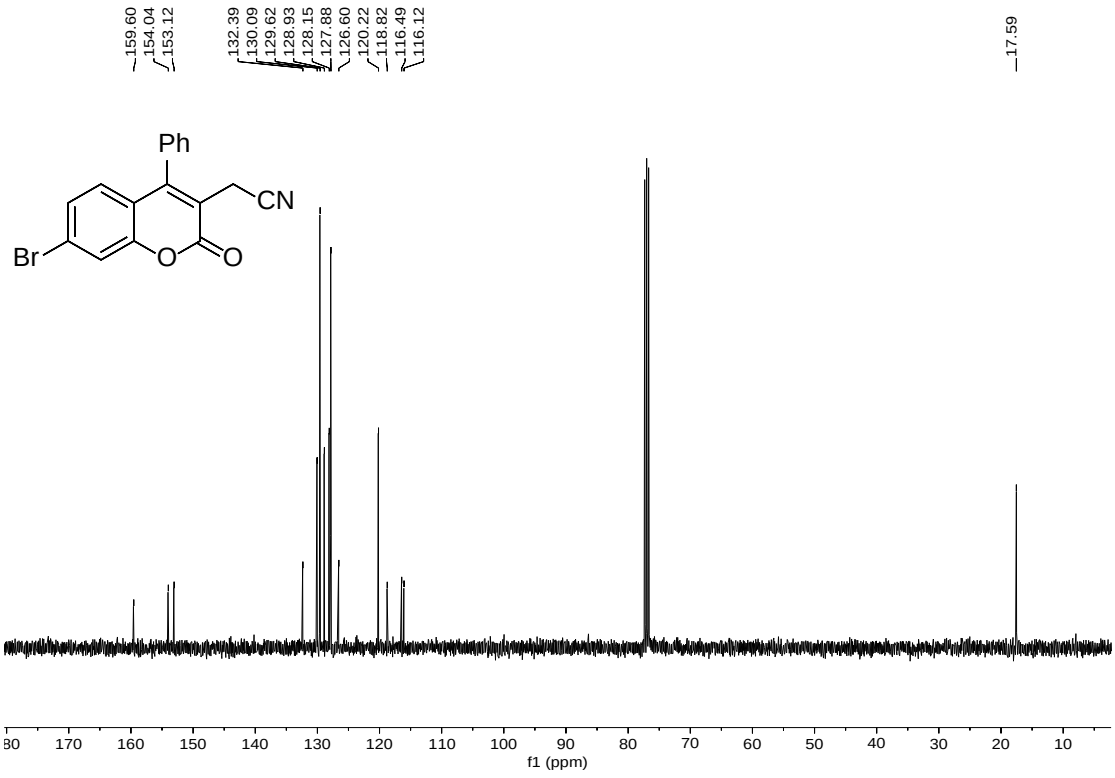
[13] C NMR Spectrum of **2j**



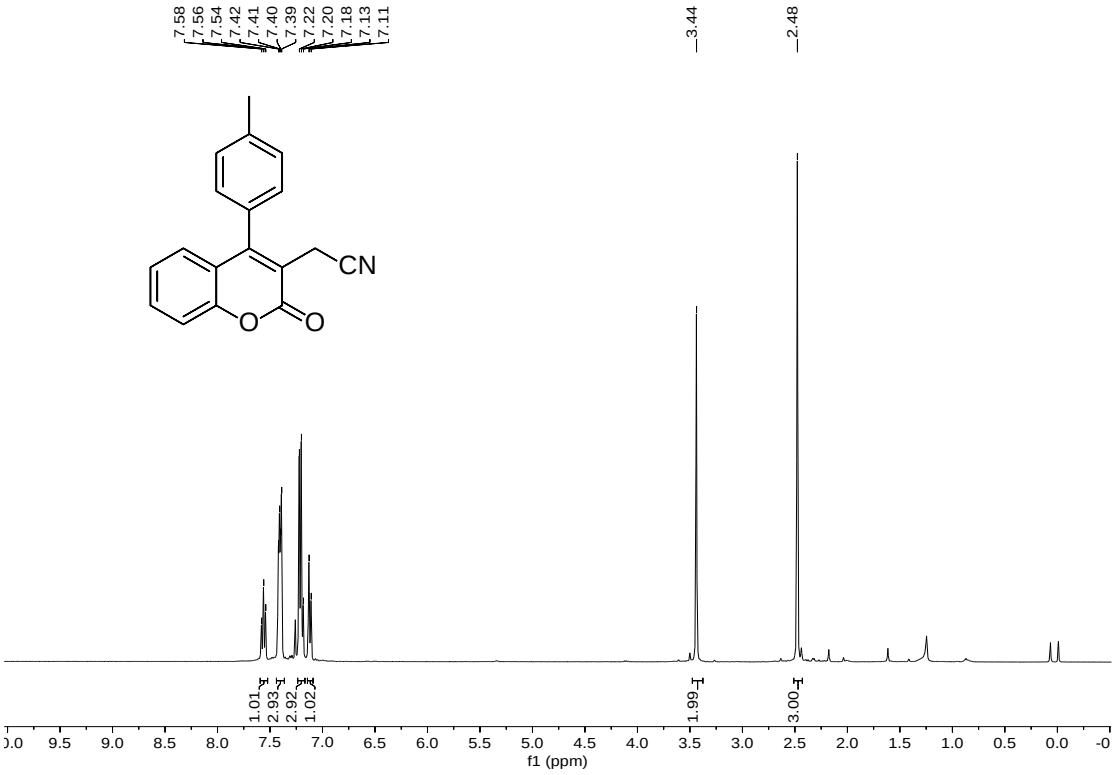
[1] H NMR Spectrum of **2k**



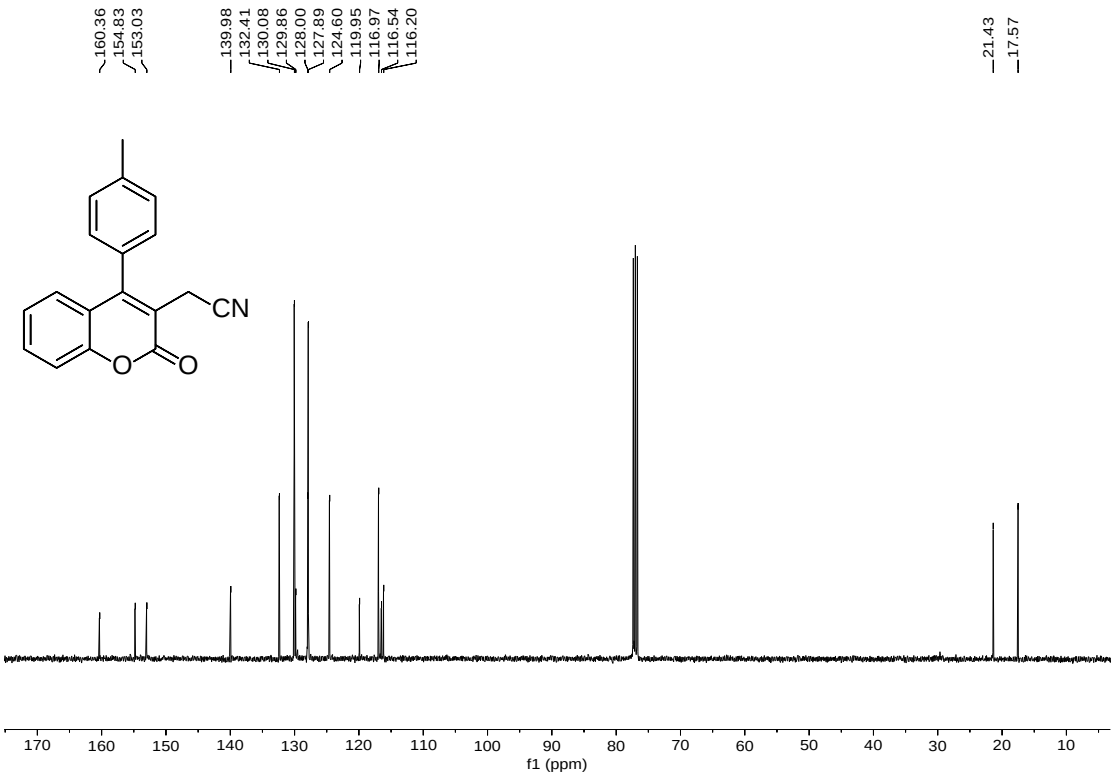
[13] C NMR Spectrum of **2k**



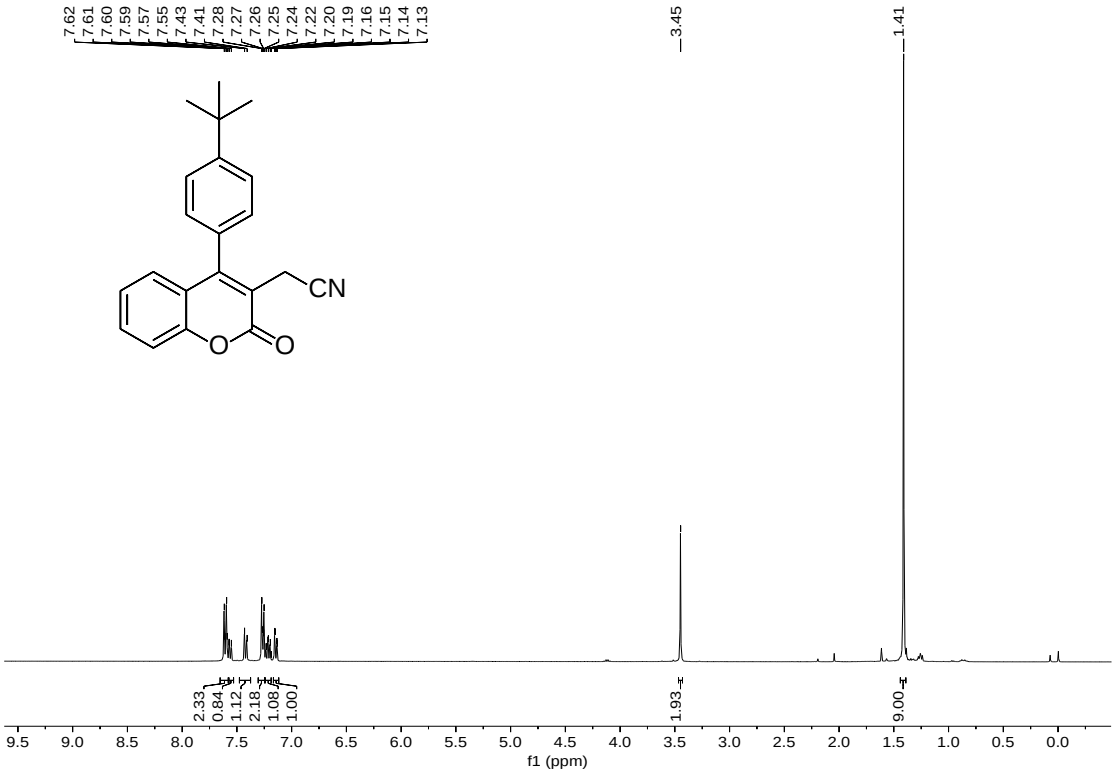
^{1} H NMR Spectrum of **2m**



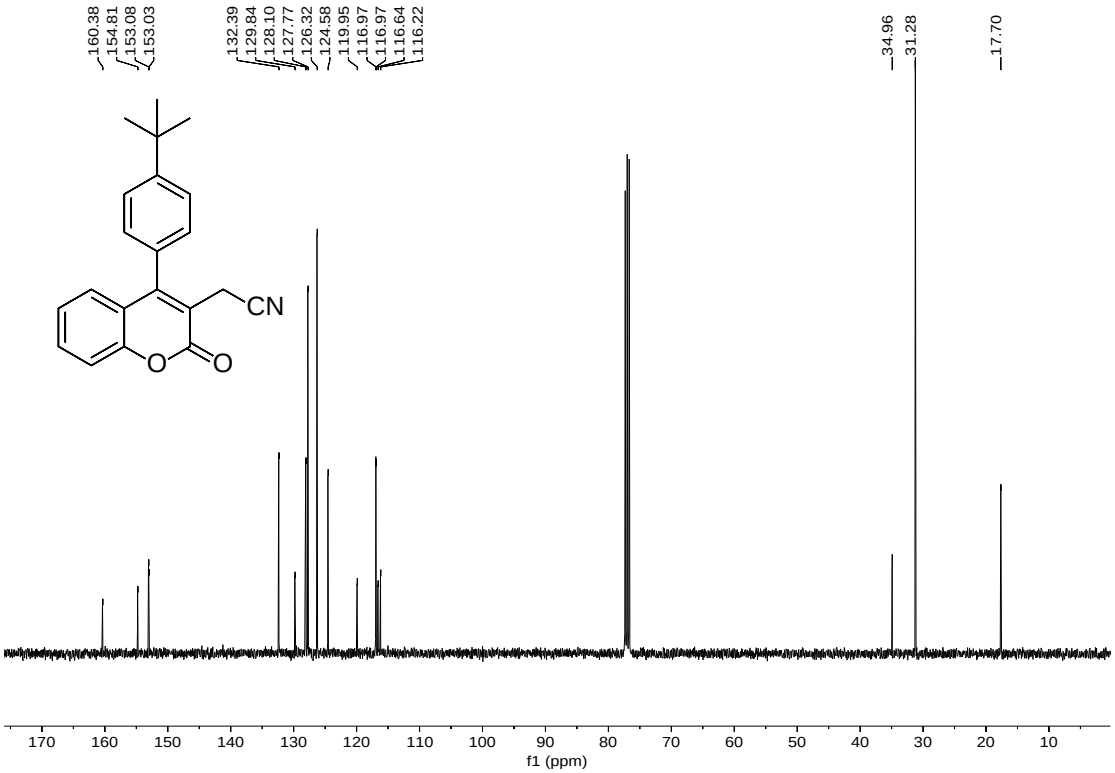
^{13} C NMR Spectrum of **2m**



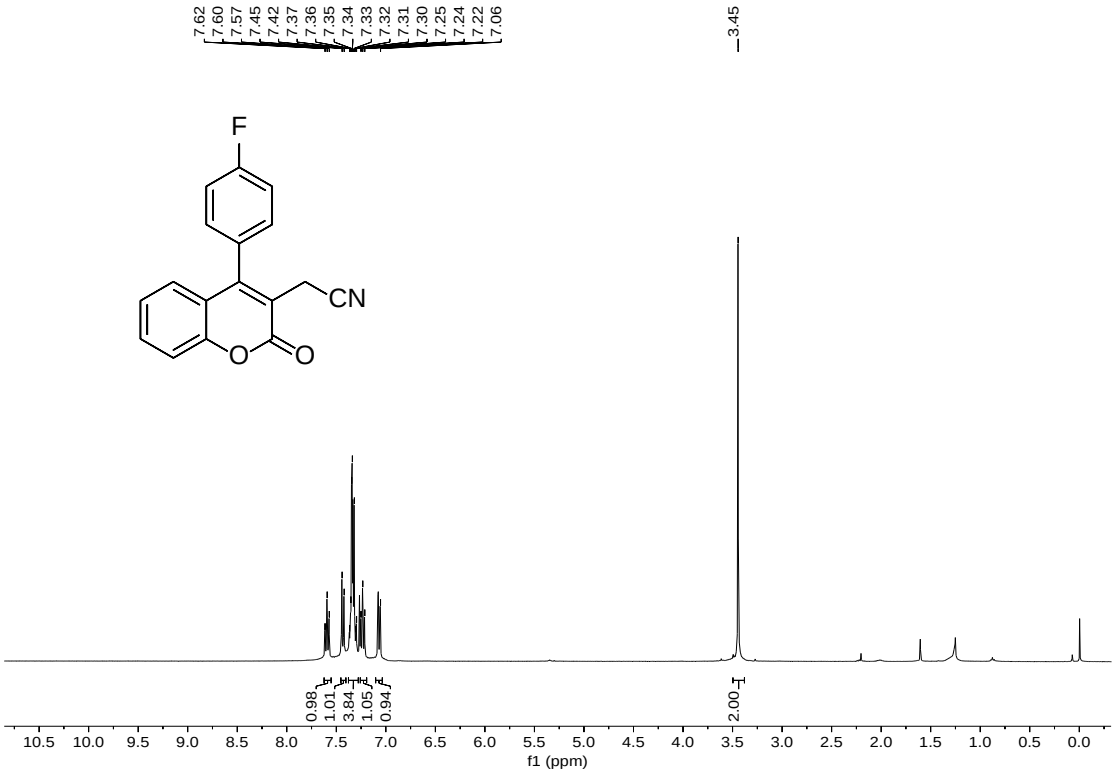
[1] H NMR Spectrum of **2n**



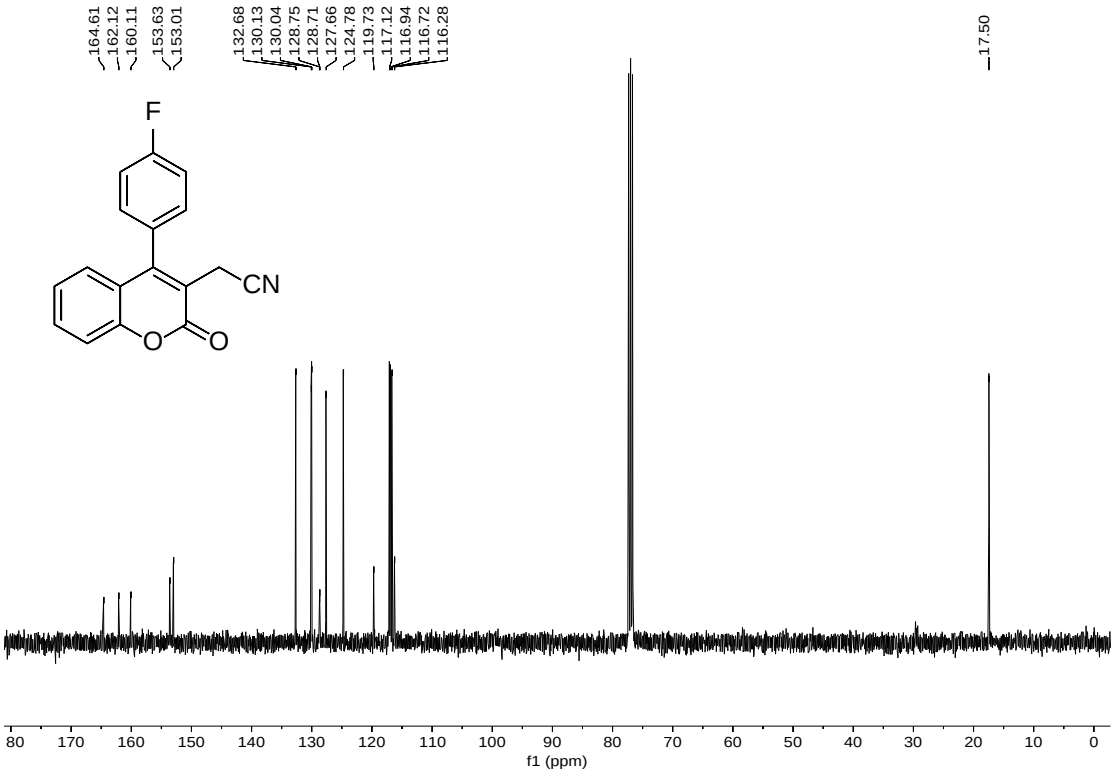
[13] C NMR Spectrum of **2n**



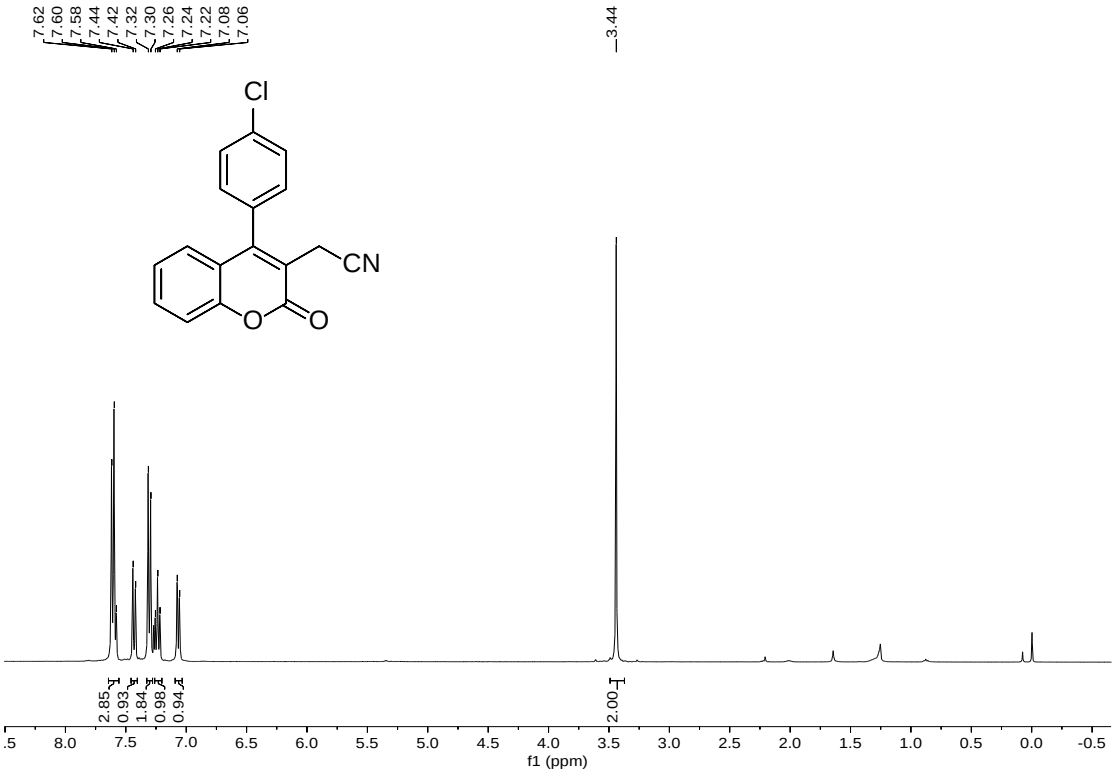
[1] H NMR Spectrum of **2o**



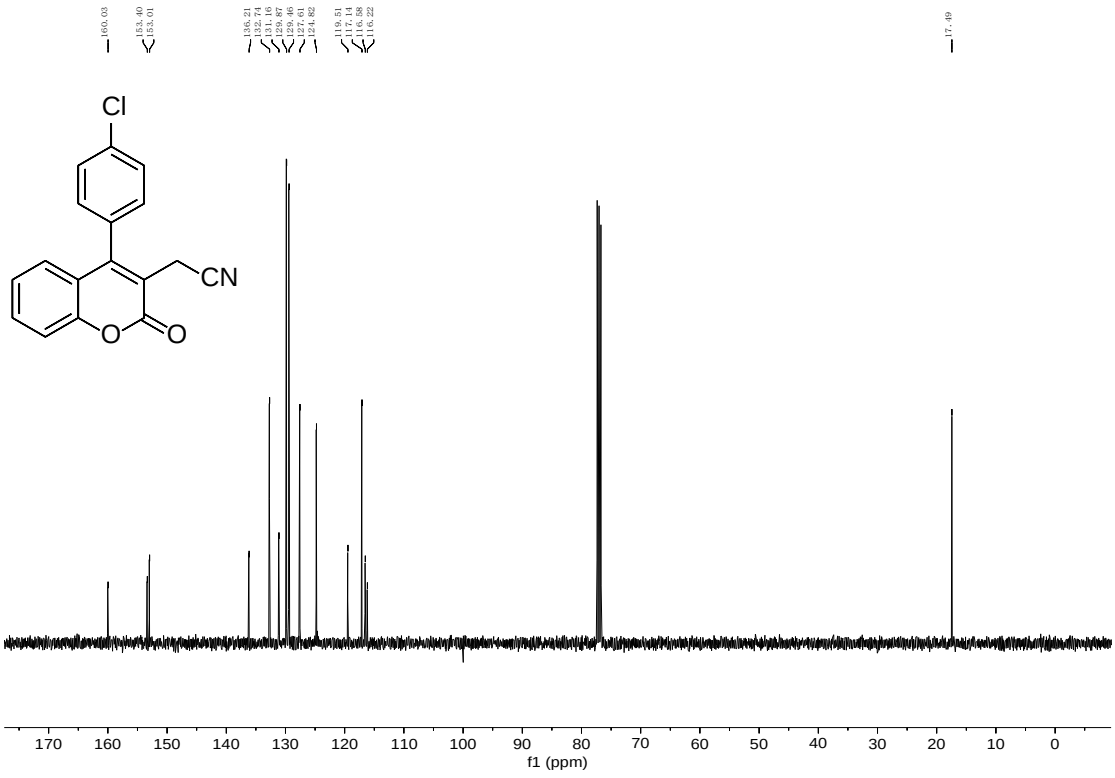
[13] C NMR Spectrum of **2o**



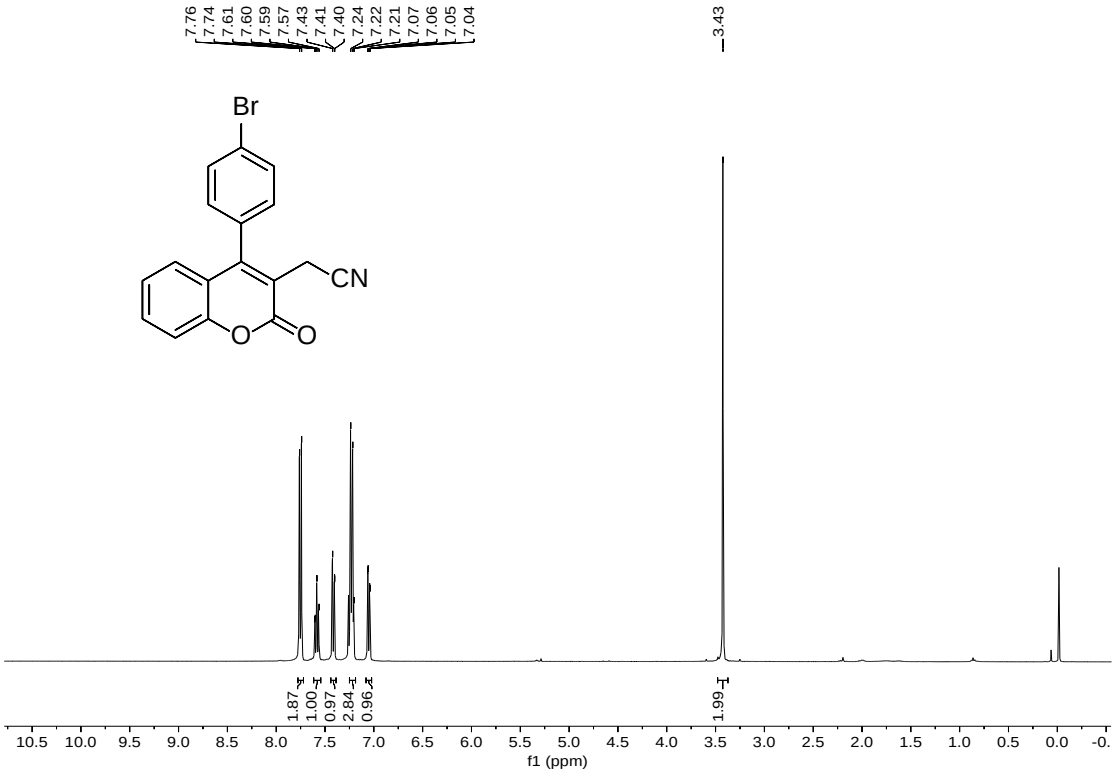
^{1}H NMR Spectrum of **2p**



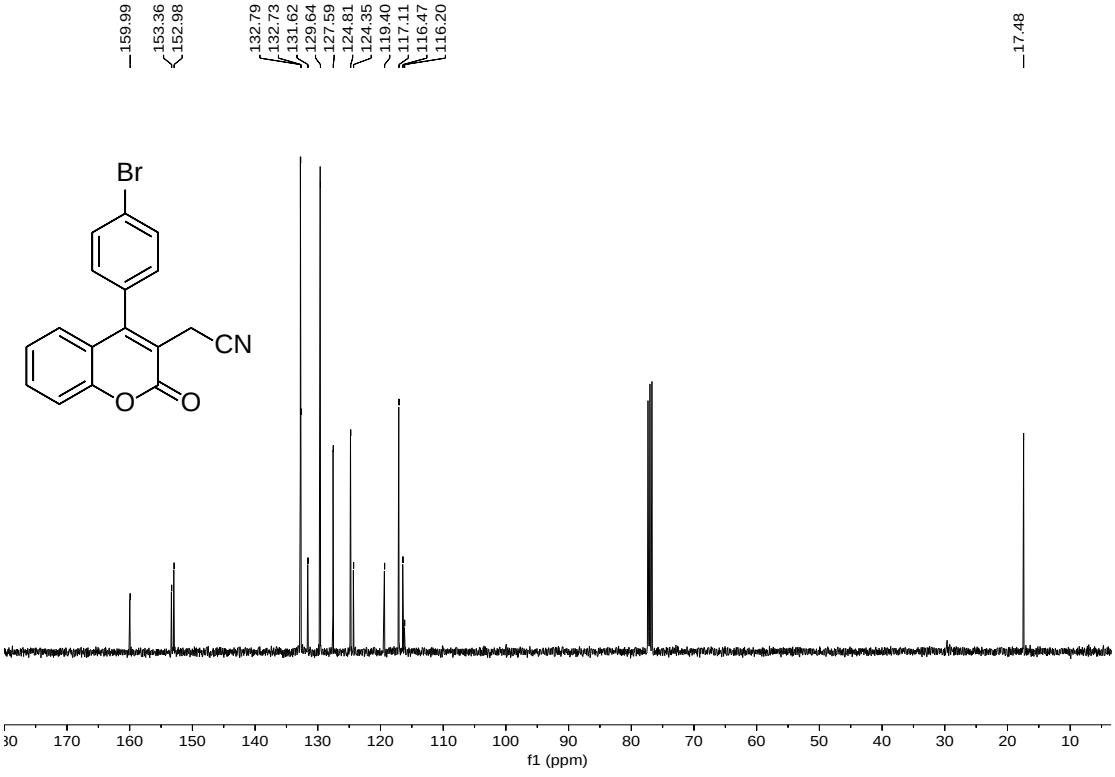
^{13}C NMR Spectrum of **2p**



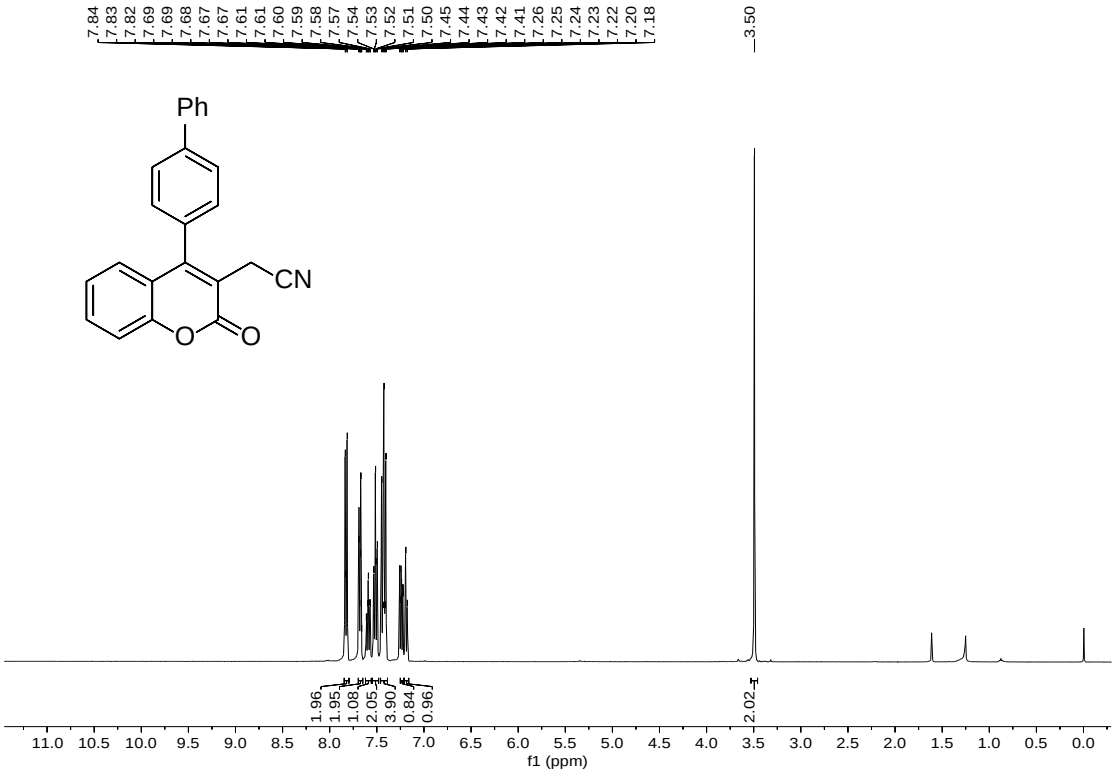
[1] H NMR Spectrum of **2q**



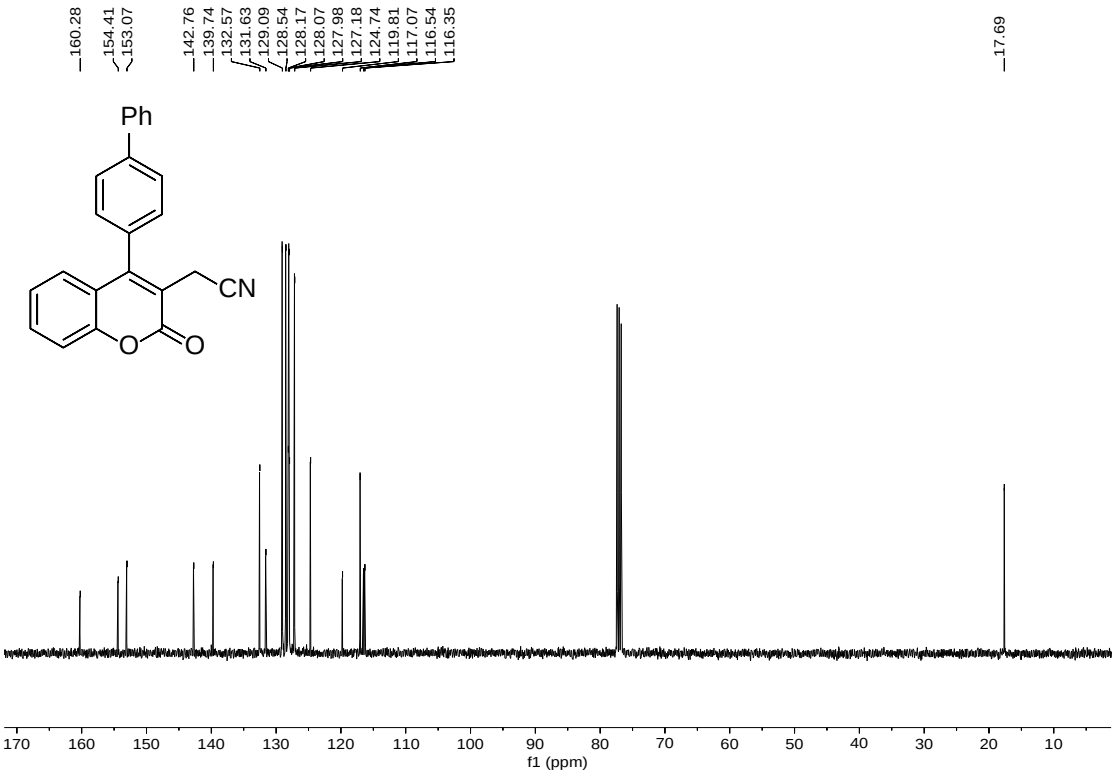
[13] C NMR Spectrum of **2q**



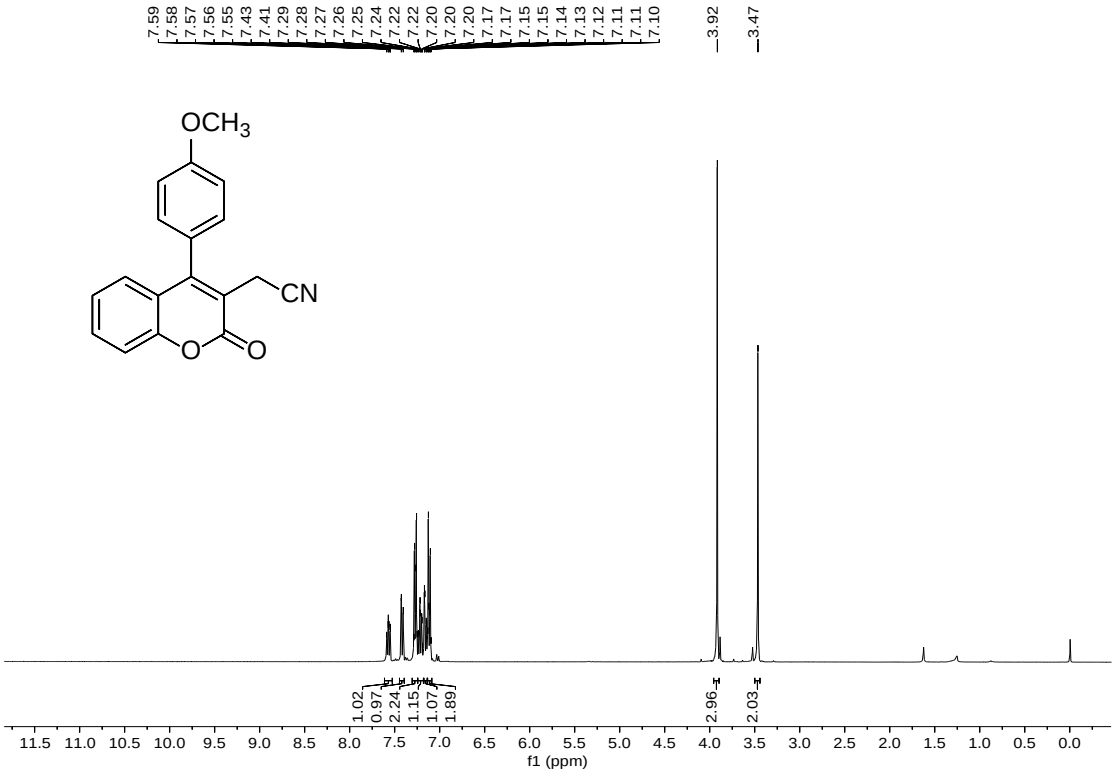
^{1}H NMR Spectrum of **2r**



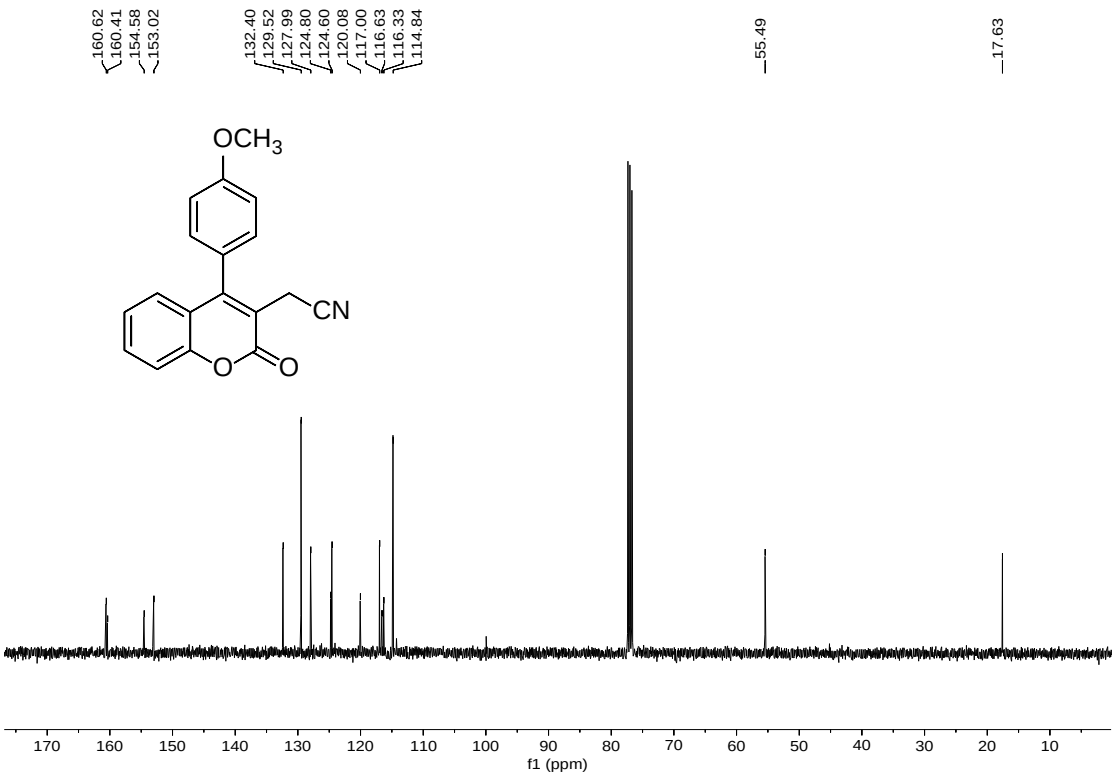
^{13}C NMR Spectrum of **2r**



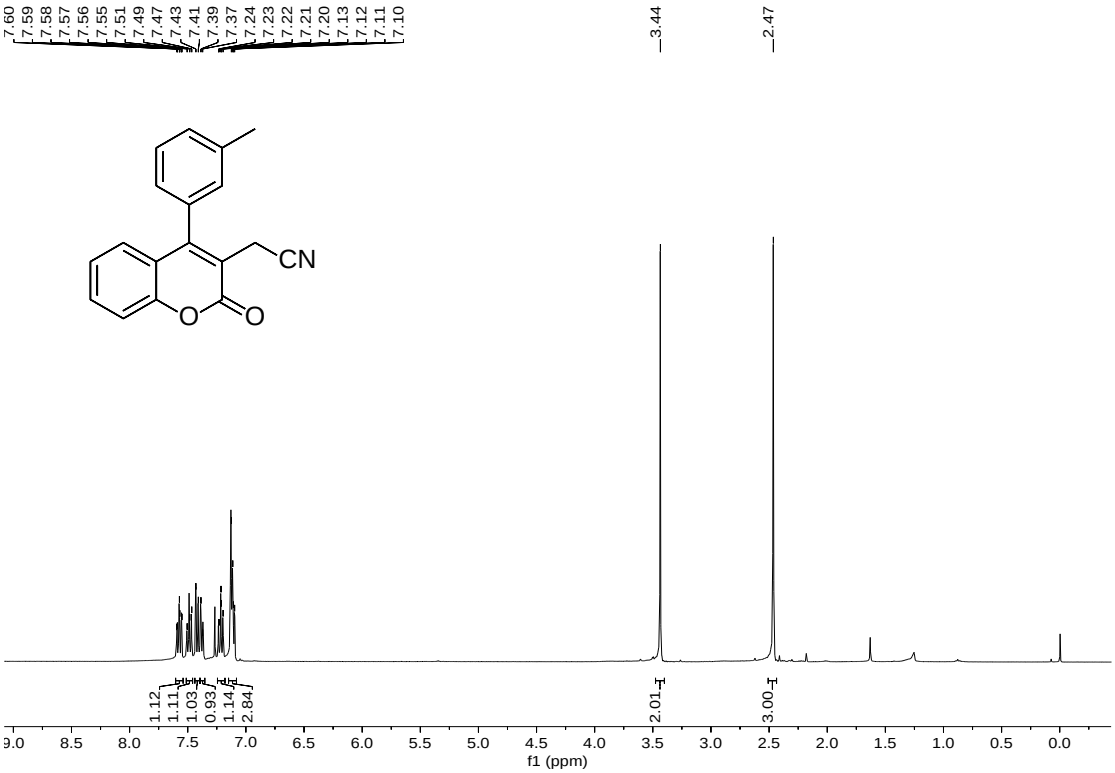
[1] H NMR Spectrum of **2s**



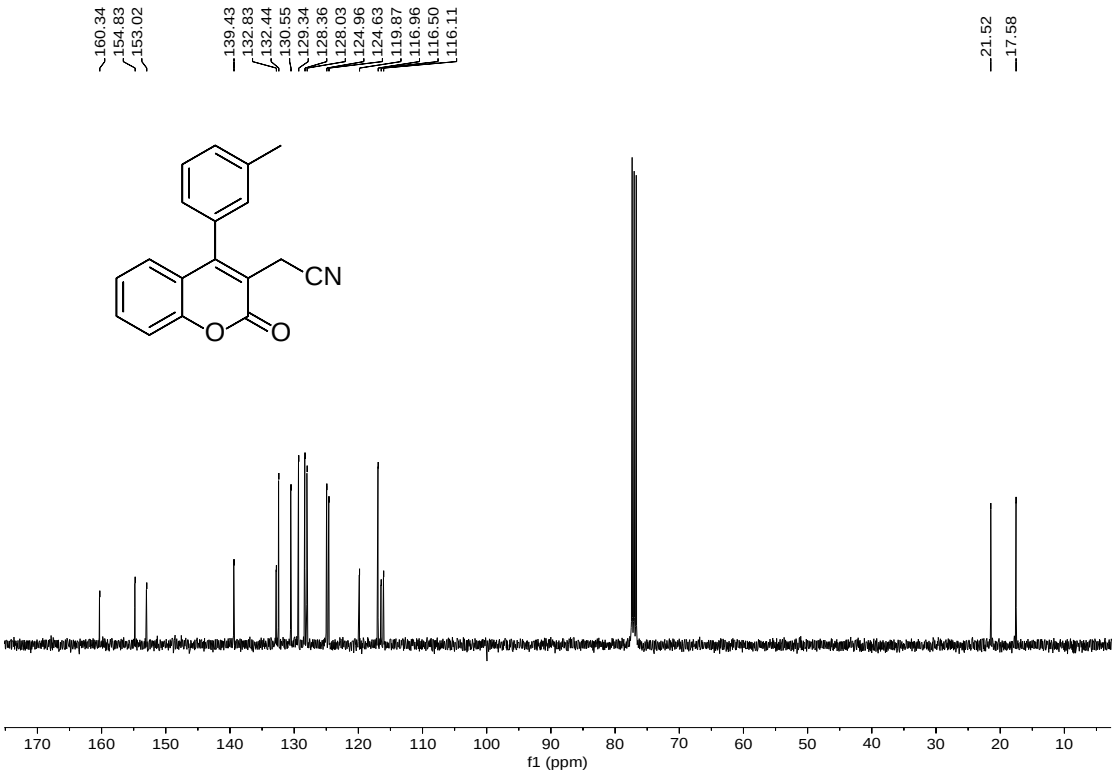
[13] C NMR Spectrum of **2s**



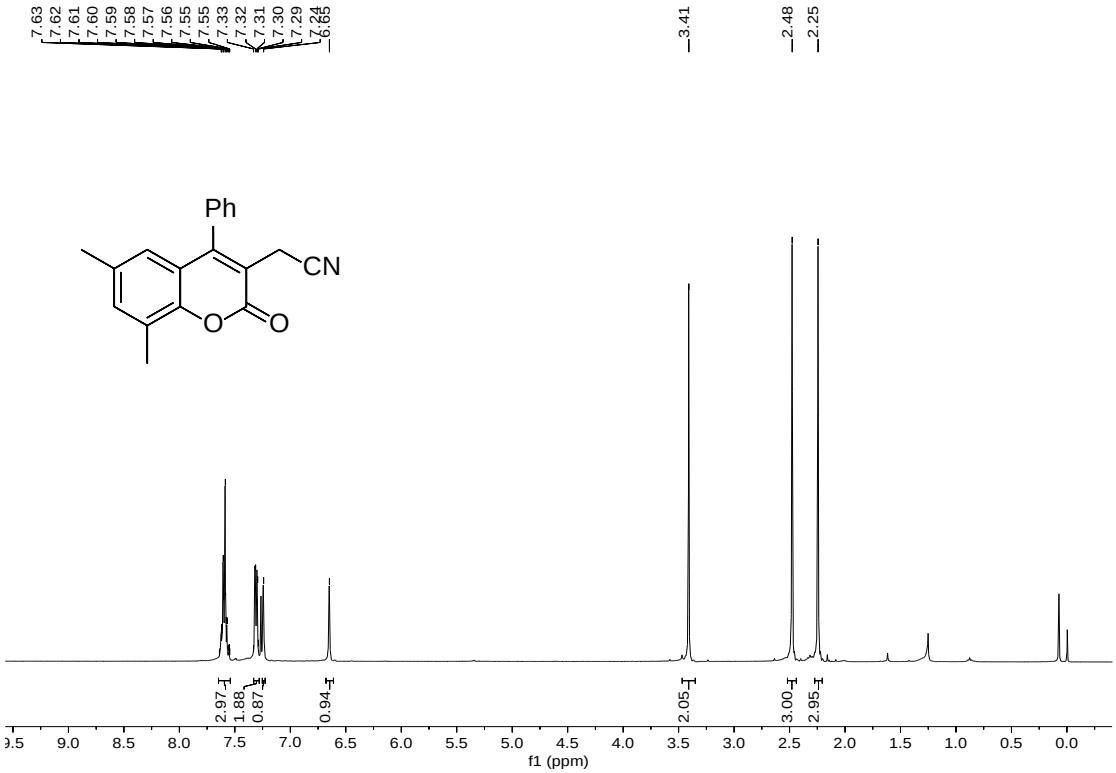
^{1} H NMR Spectrum of **2t**



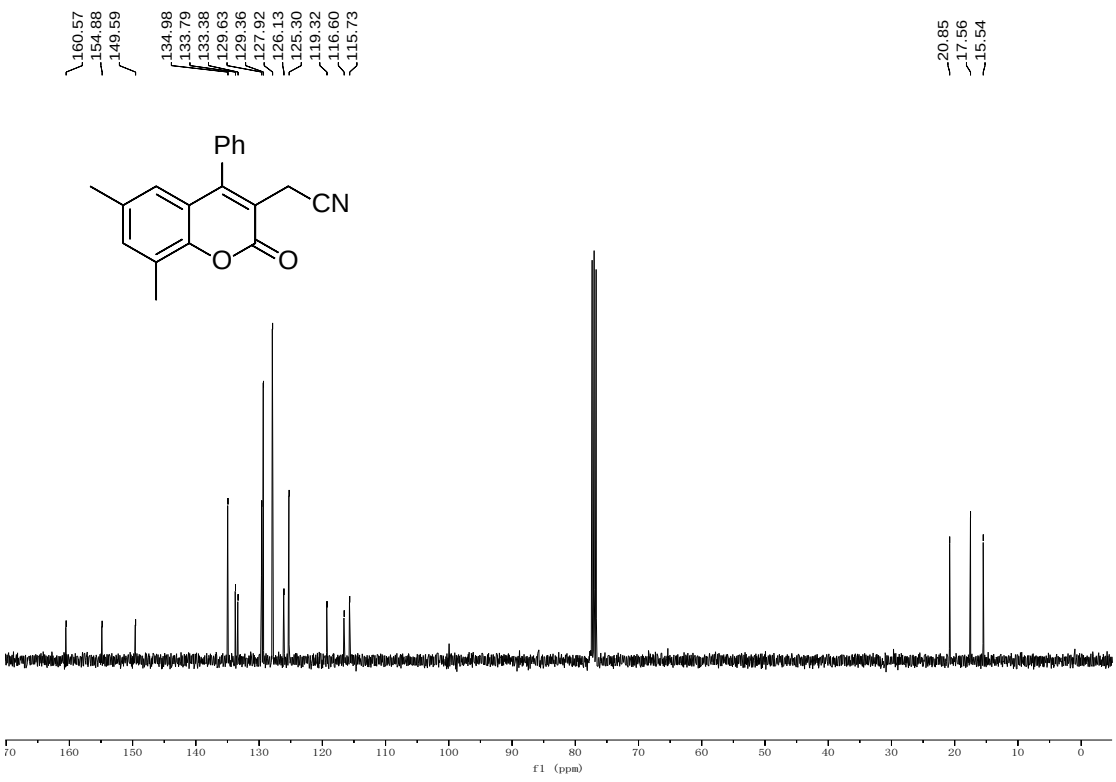
^{13} C NMR Spectrum of **2t**



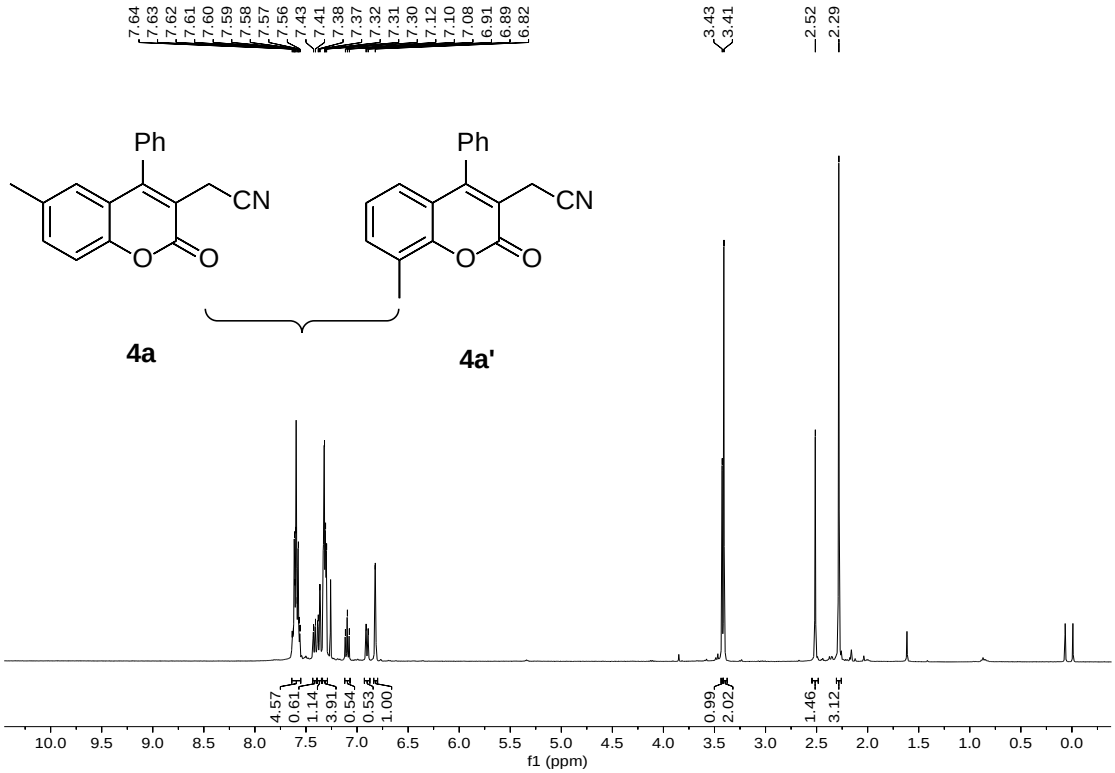
[1] H NMR Spectrum of **2u**



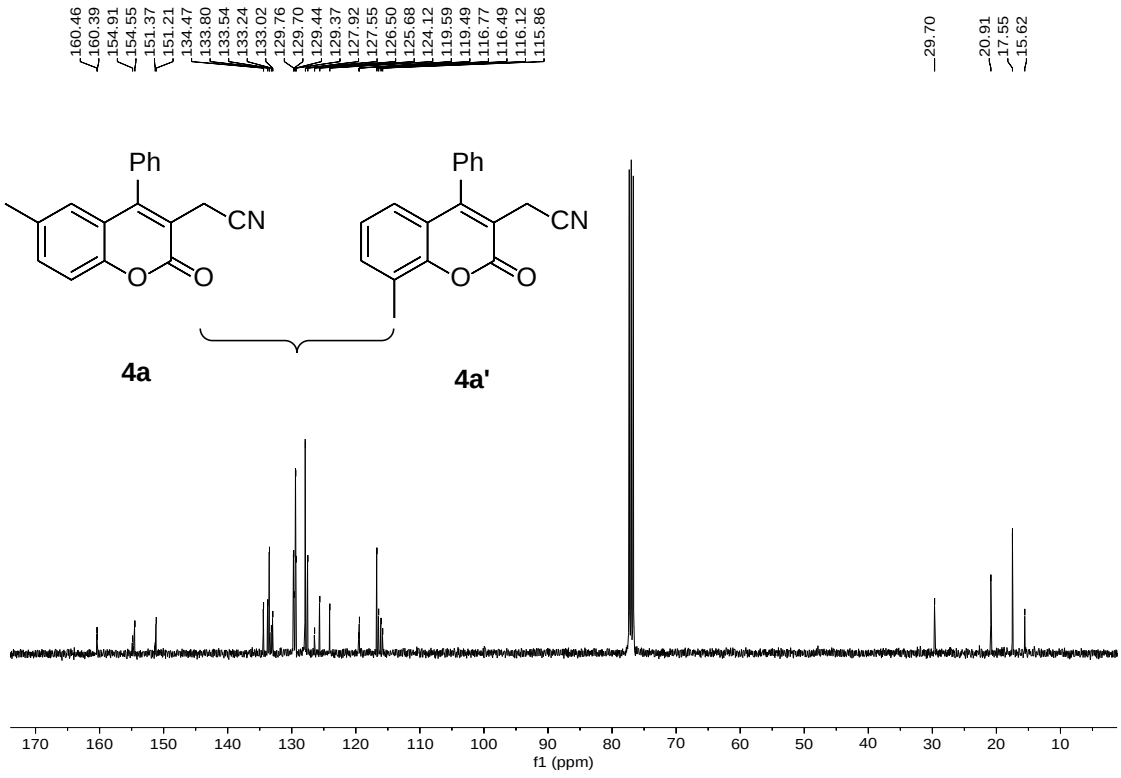
[13] C NMR Spectrum of **2u**



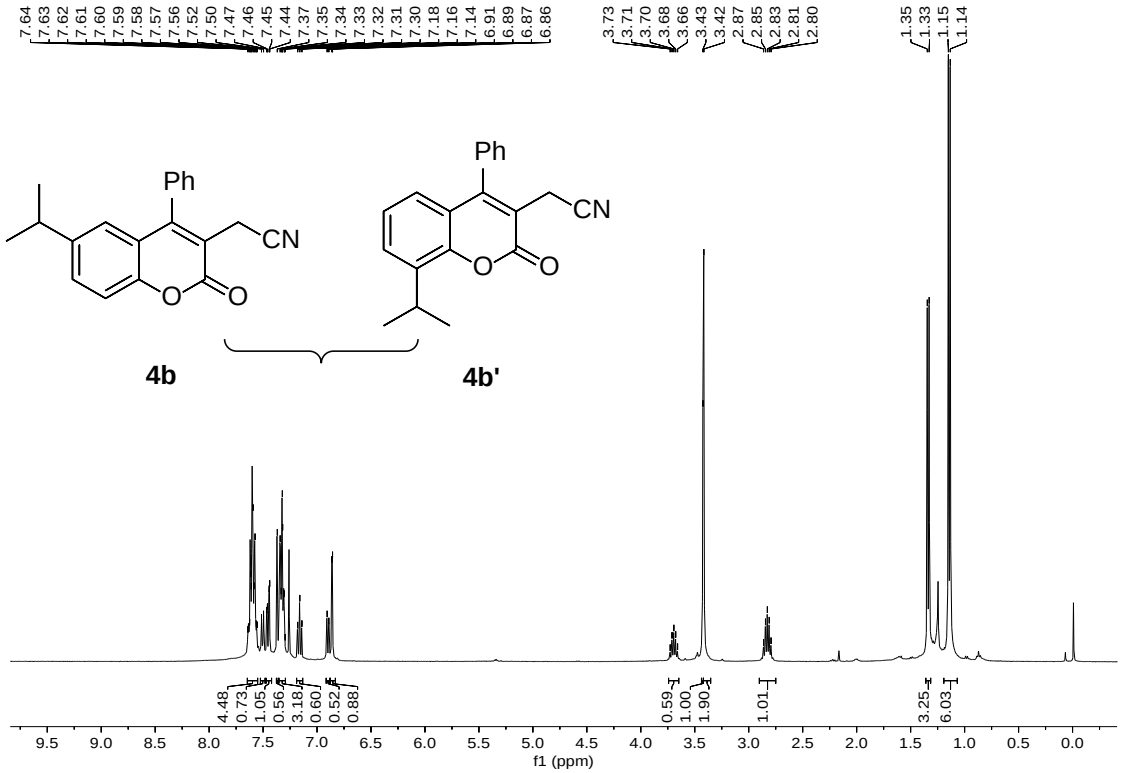
[1] H NMR Spectrum of **4a and 4a'**



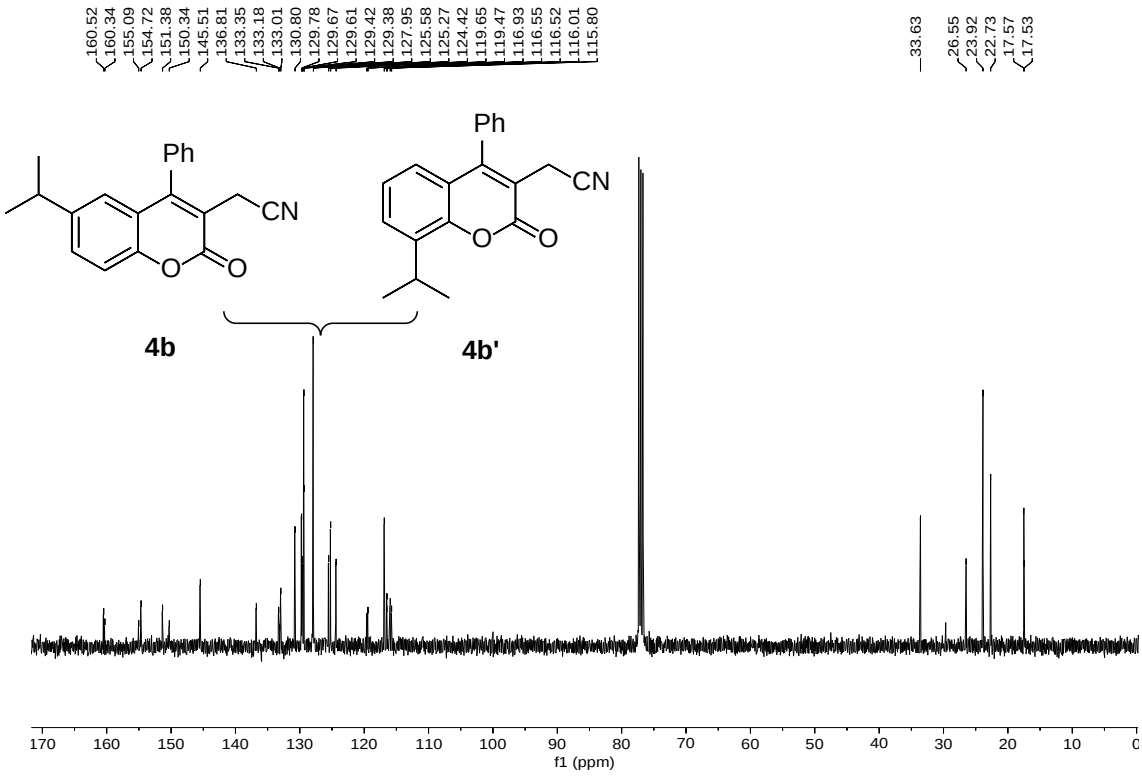
[13] C NMR Spectrum of **4a and 4a'**



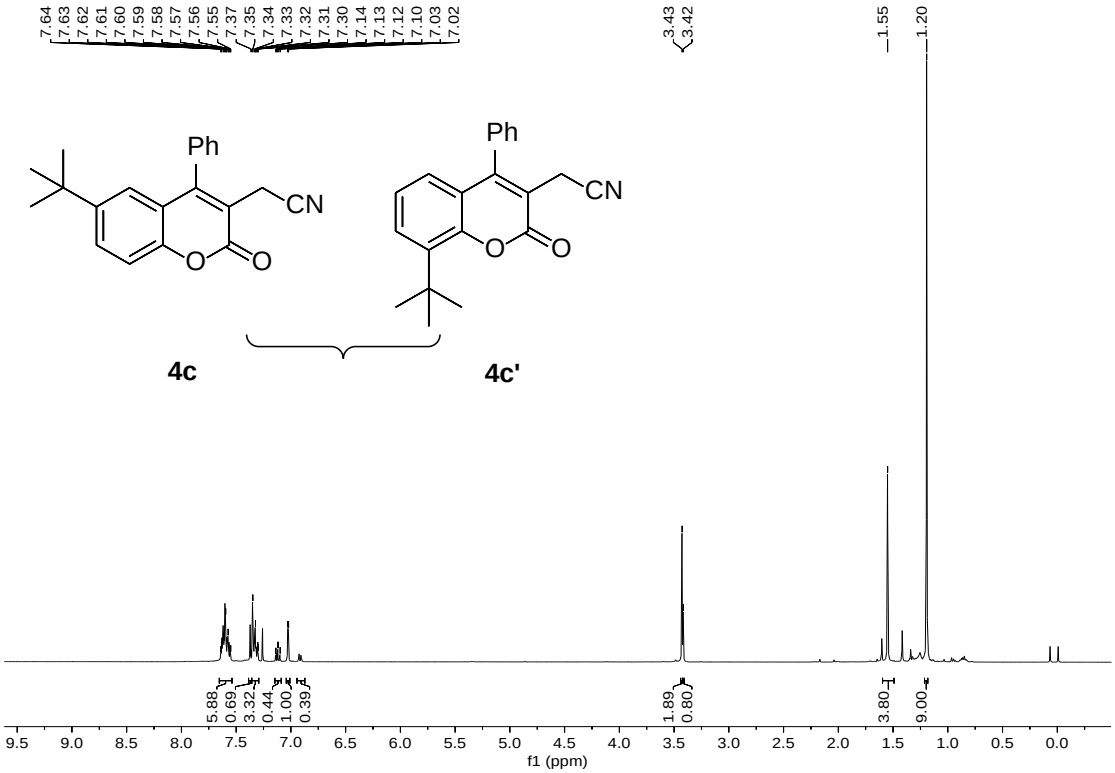
[1] H NMR Spectrum of **4b and 4b'**



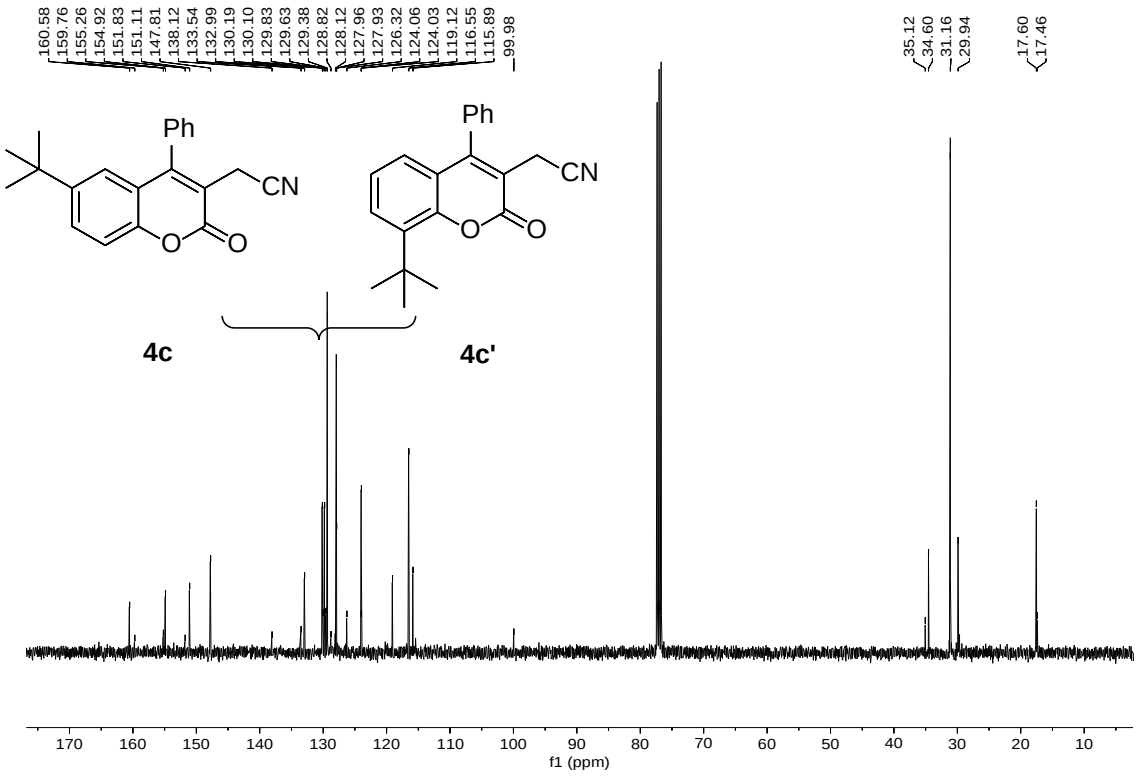
[13] C NMR Spectrum of **4b and 4b'**



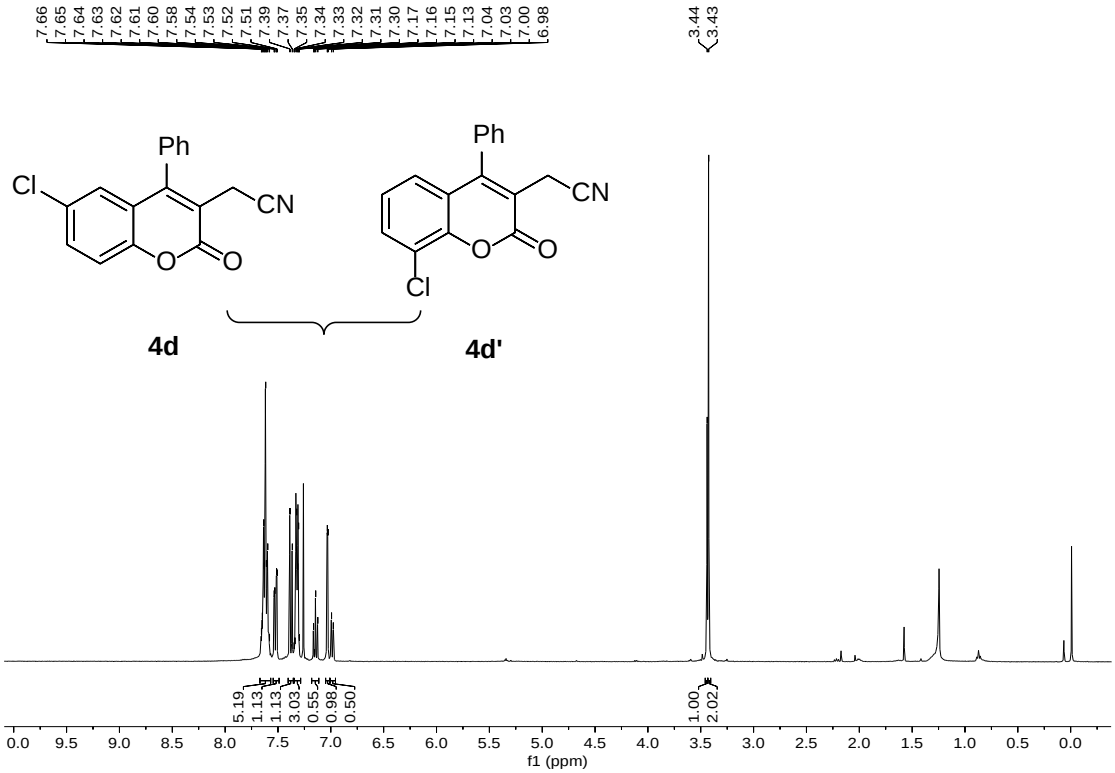
^{1}H NMR Spectrum of **4c and 4c'**



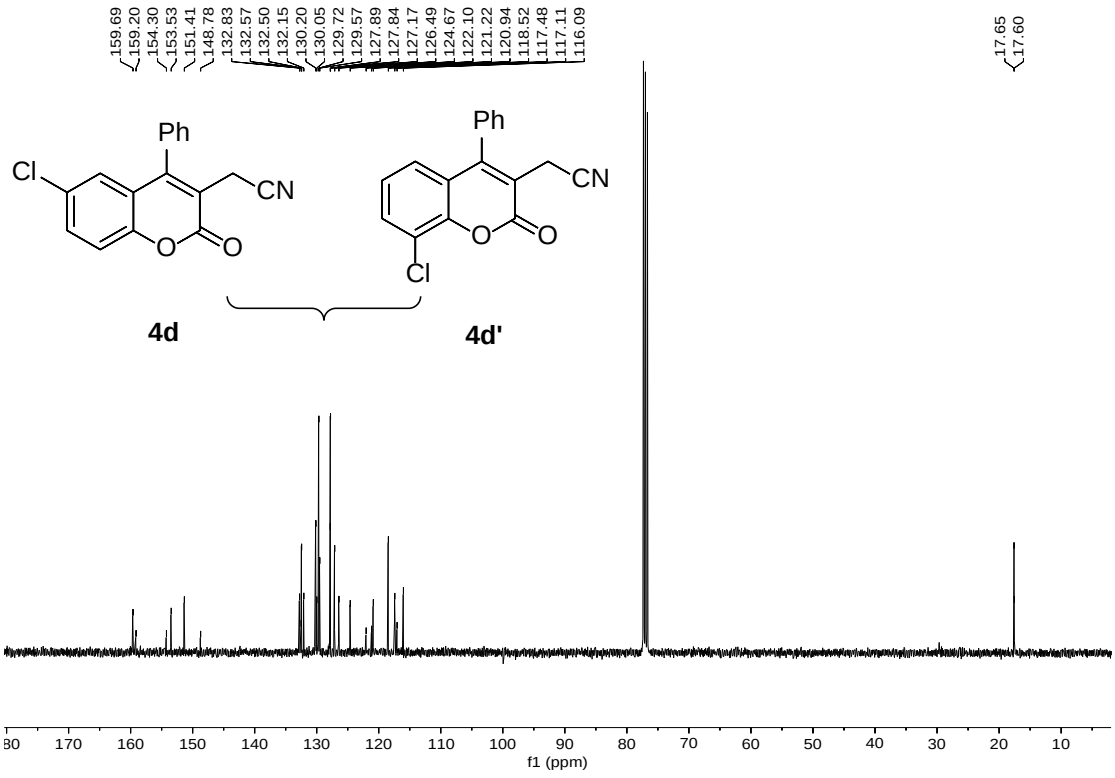
^{13}C NMR Spectrum of **4c and 4c'**



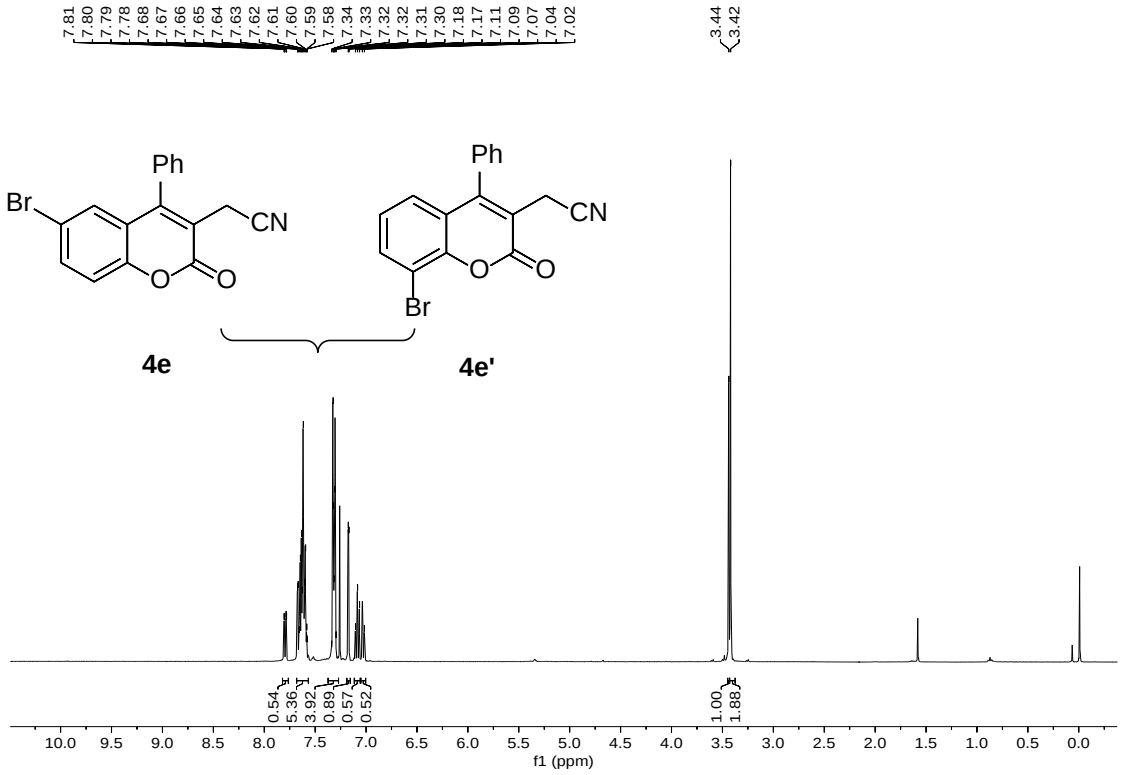
^{1} H NMR Spectrum of **4d and 4d'**



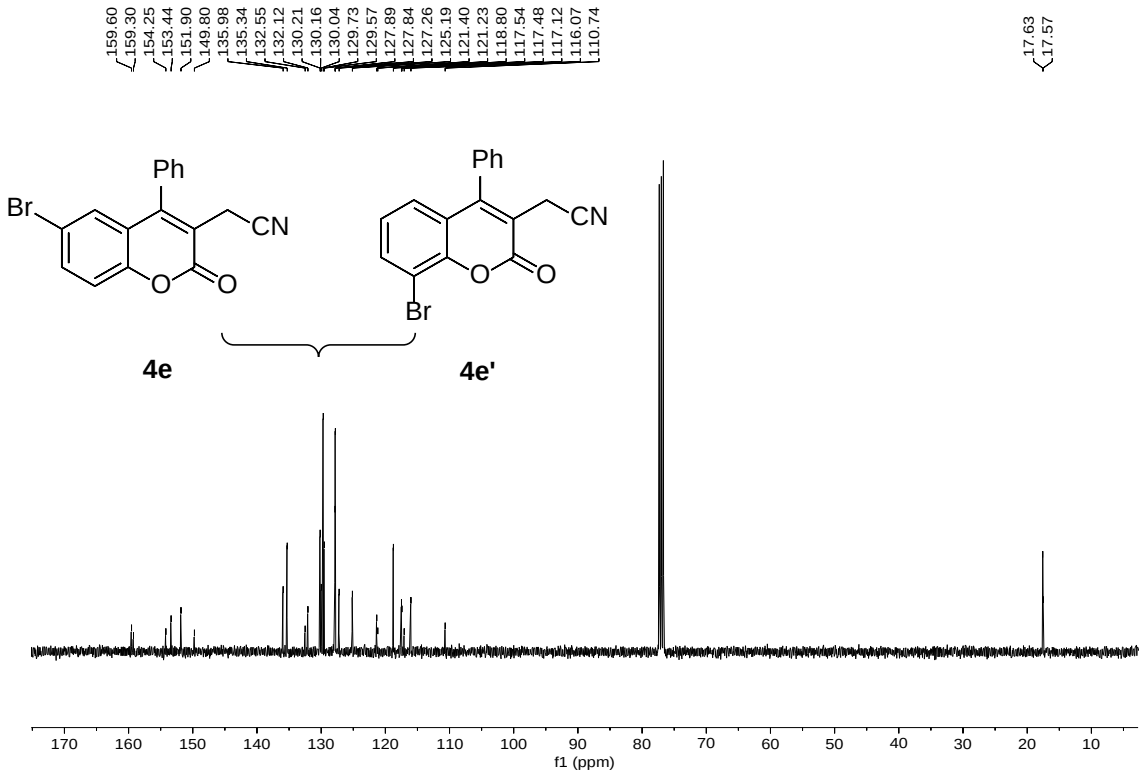
^{13} C NMR Spectrum of **4d and 4d'**



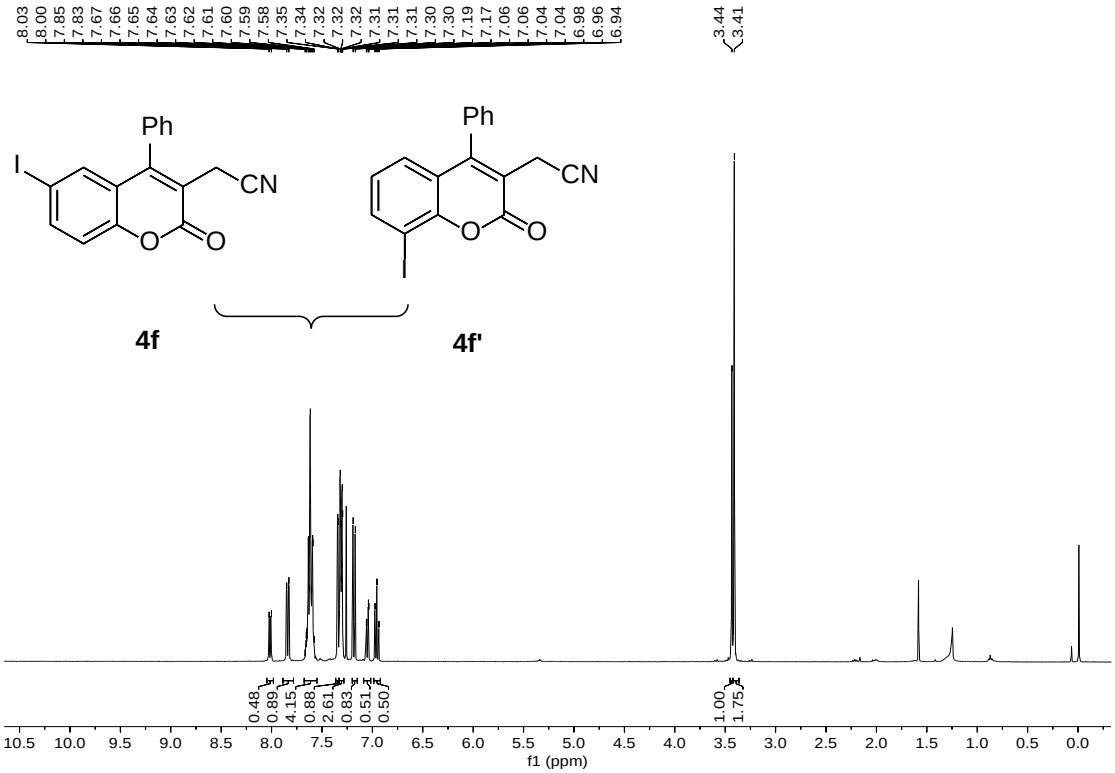
[1] H NMR Spectrum of **4e and 4e'**



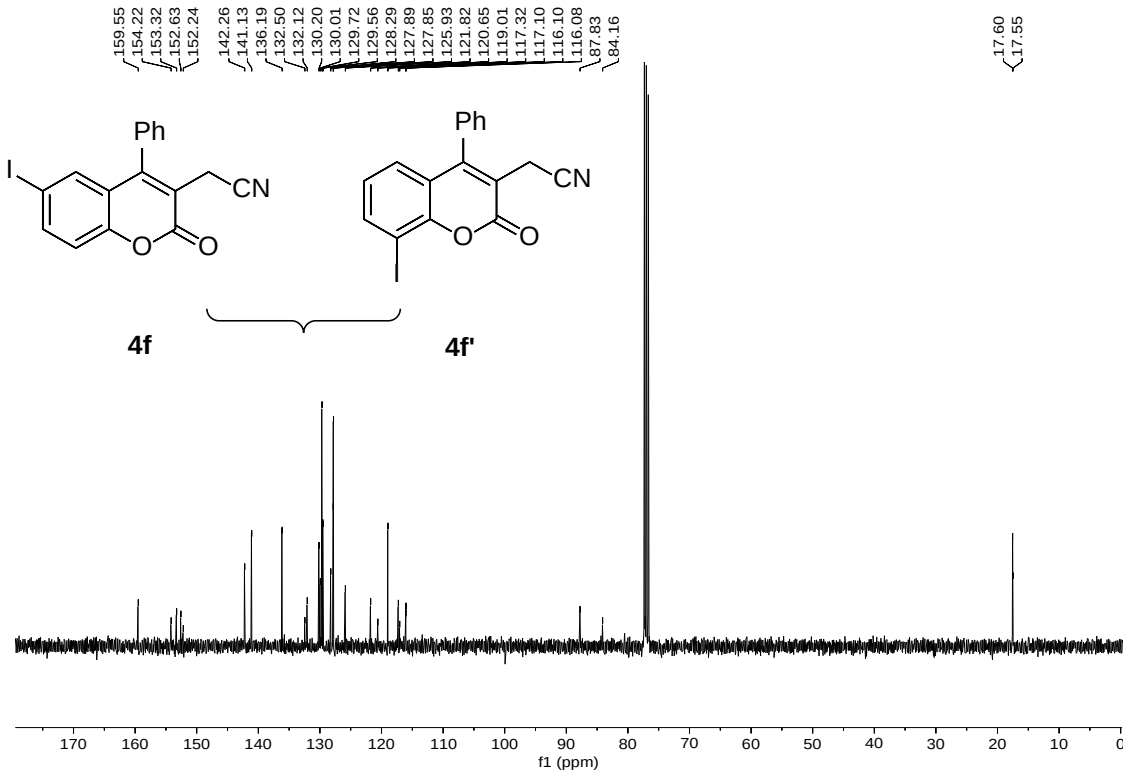
[13] C NMR Spectrum of **4e and 4e'**



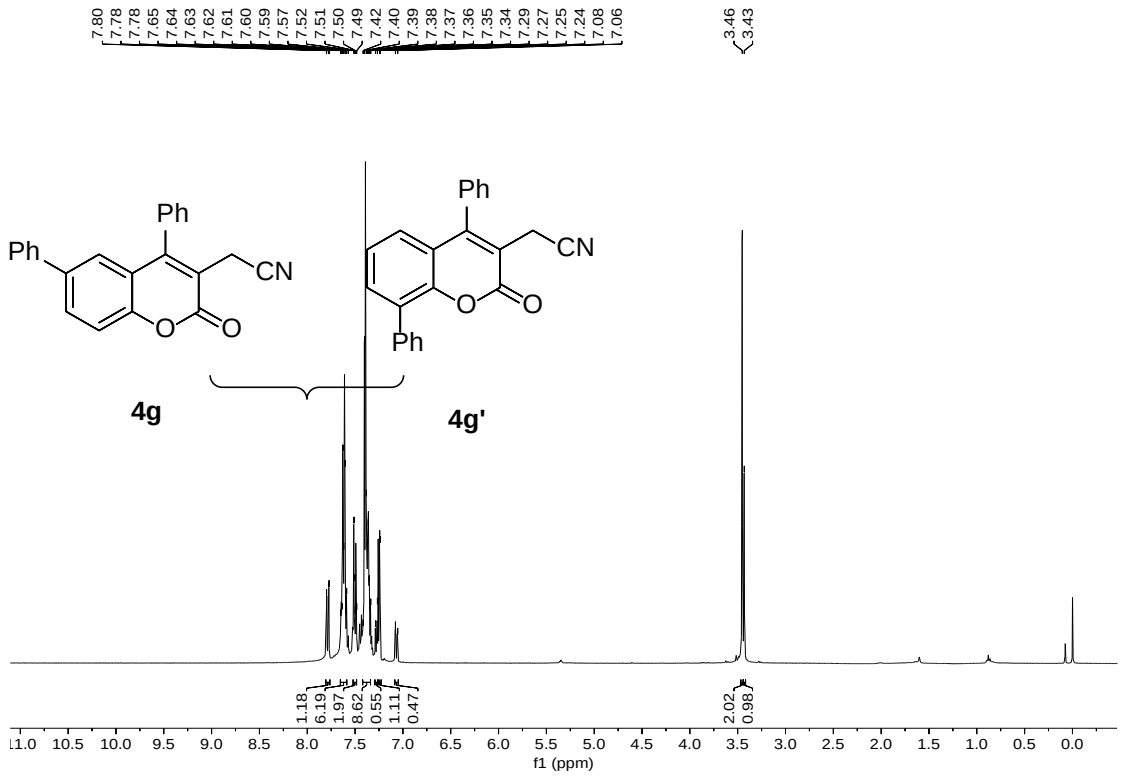
^{1} H NMR Spectrum of **4f and 4f'**



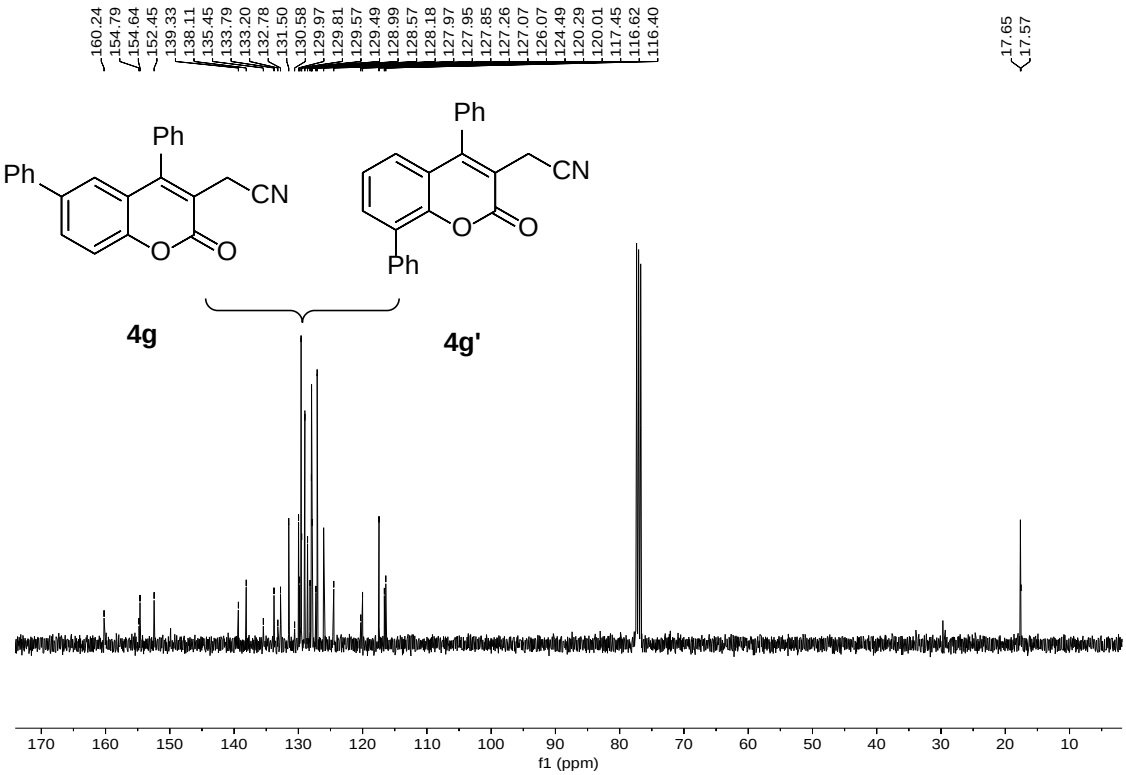
^{13} C NMR Spectrum of **4f and 4f'**



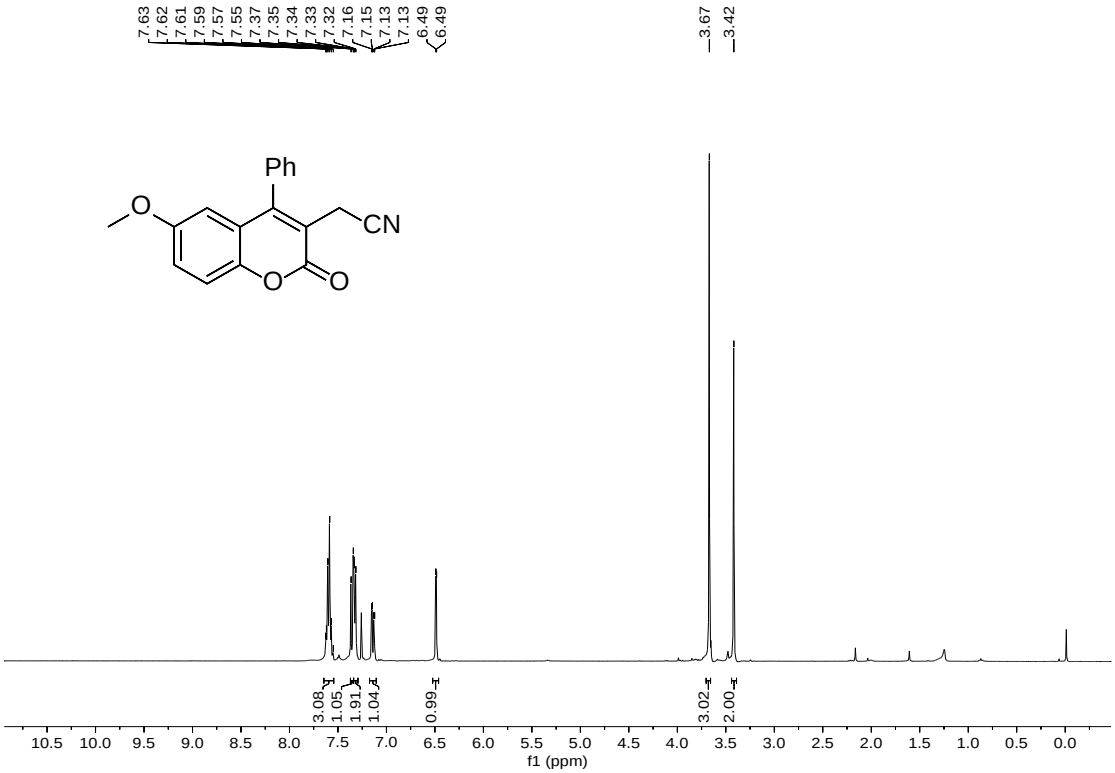
[1] H NMR Spectrum of **4g and 4g'**



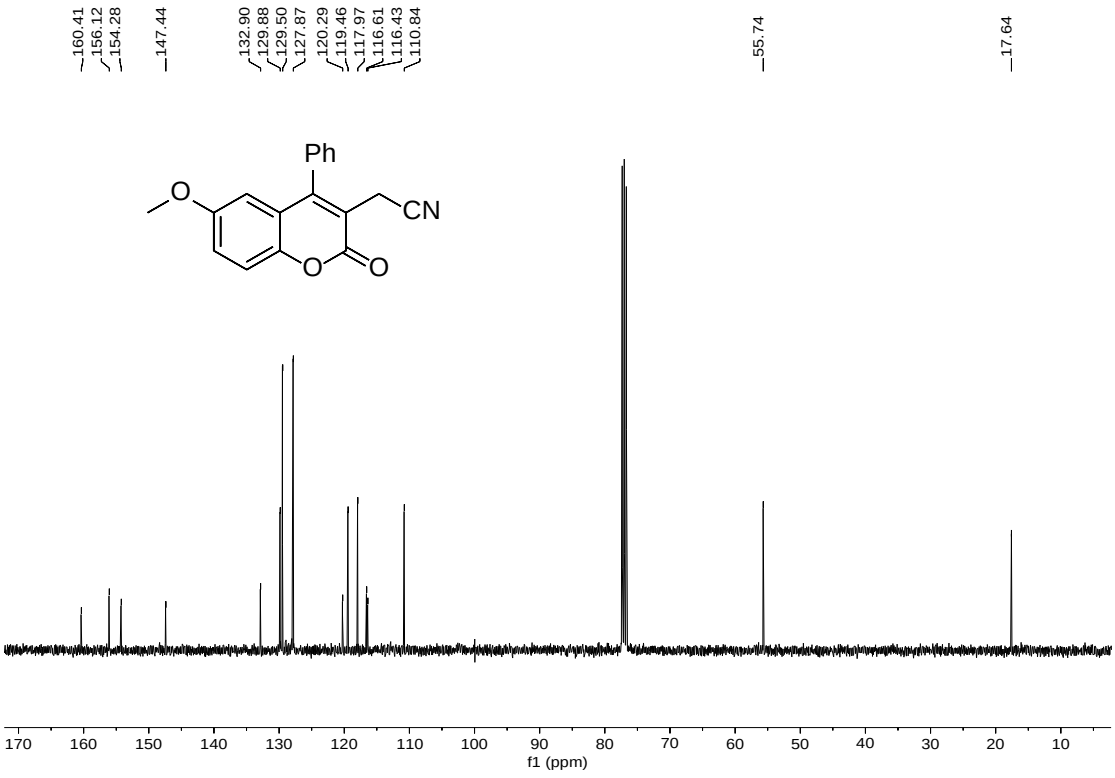
[13] C NMR Spectrum of **4g and 4g'**



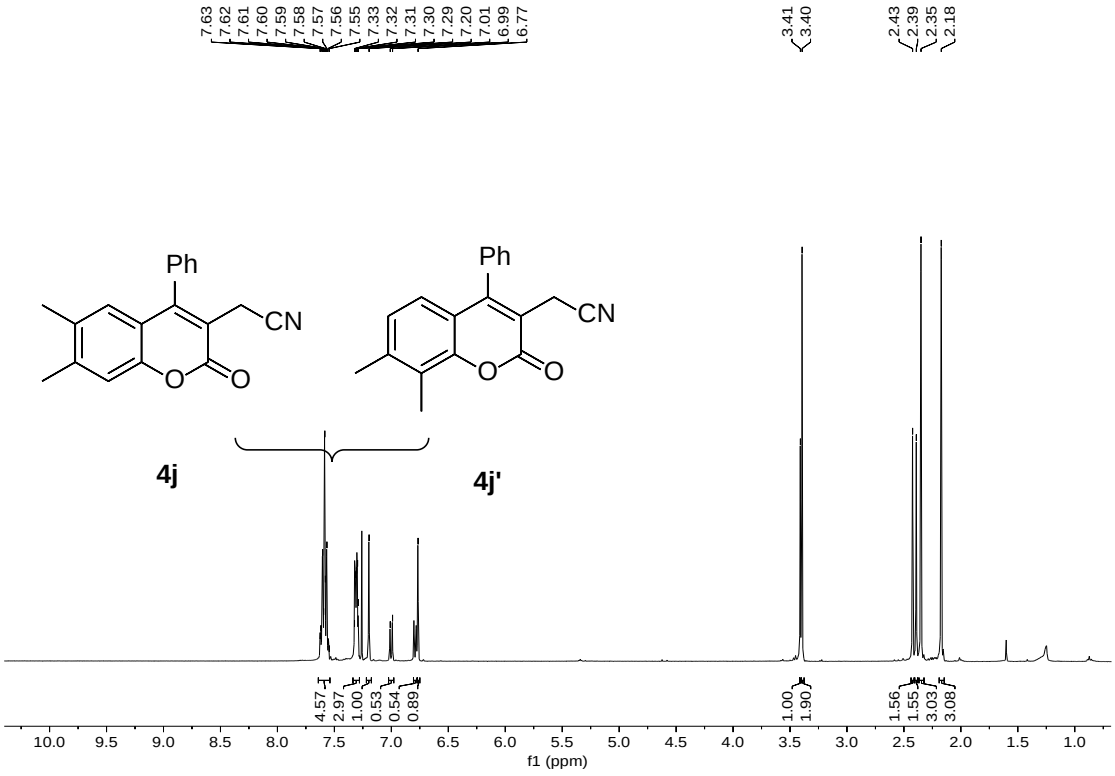
[1] H NMR Spectrum of **4h**



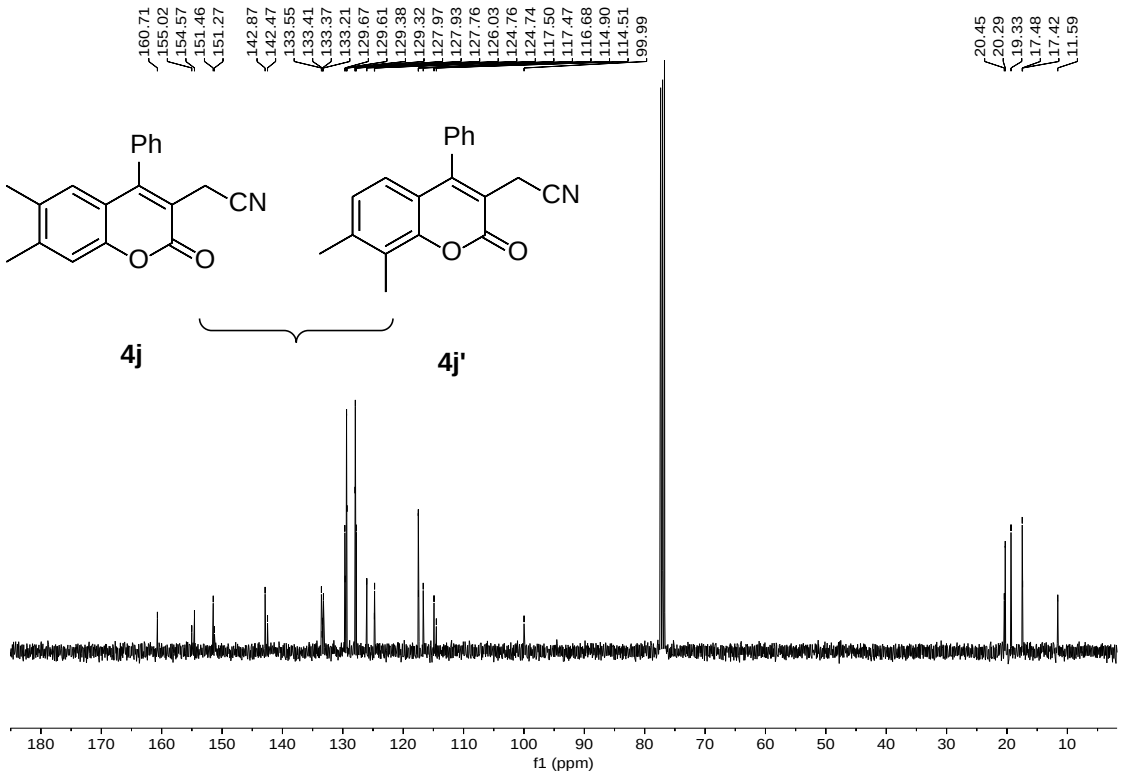
[13] C NMR Spectrum of **4h**



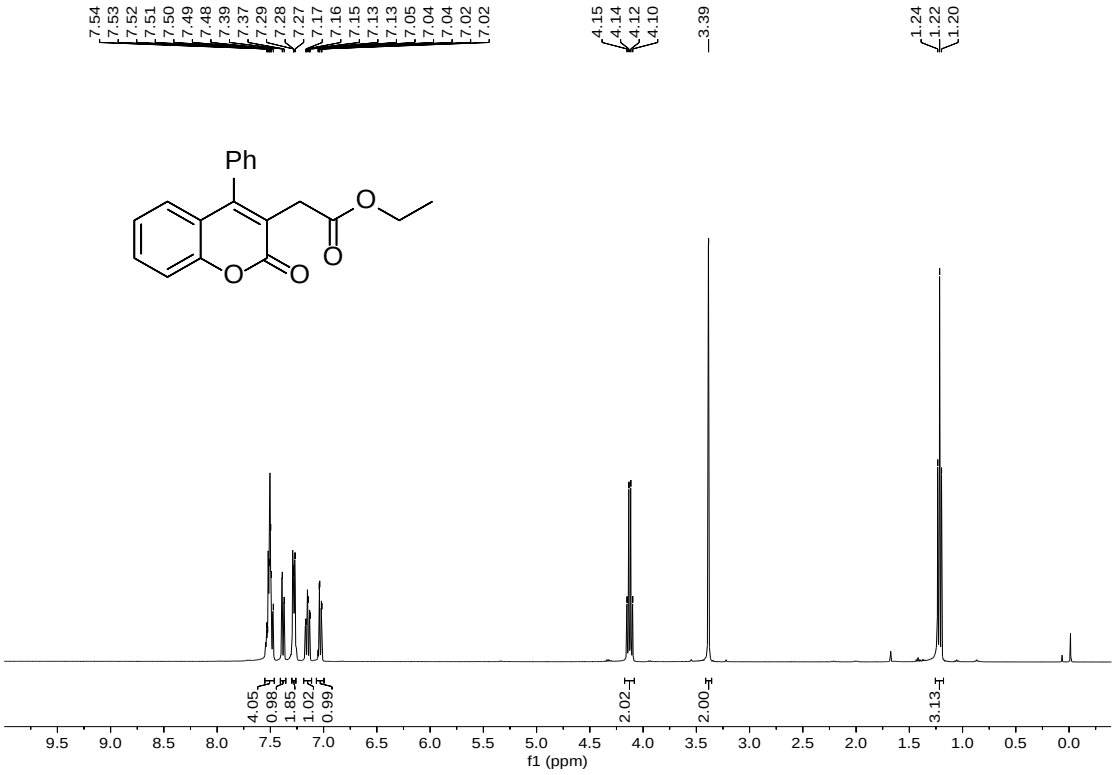
[1] H NMR Spectrum of **4i and 4i'**



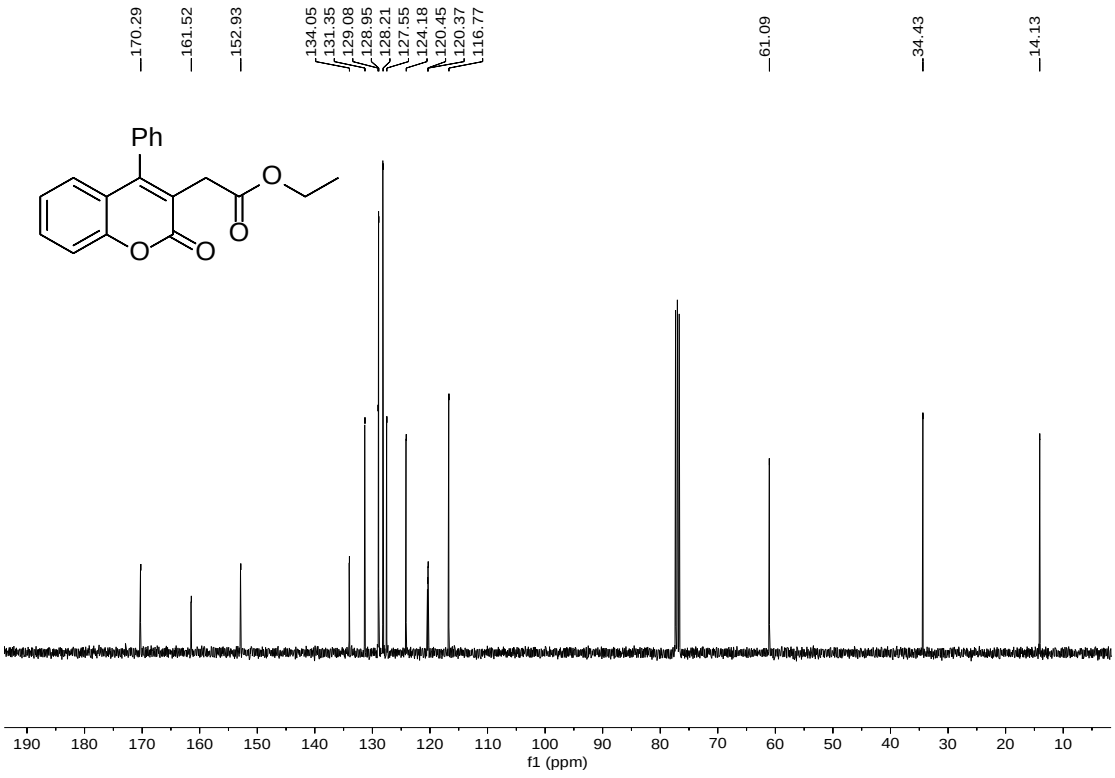
[13] C NMR Spectrum of **4i and 4i'**



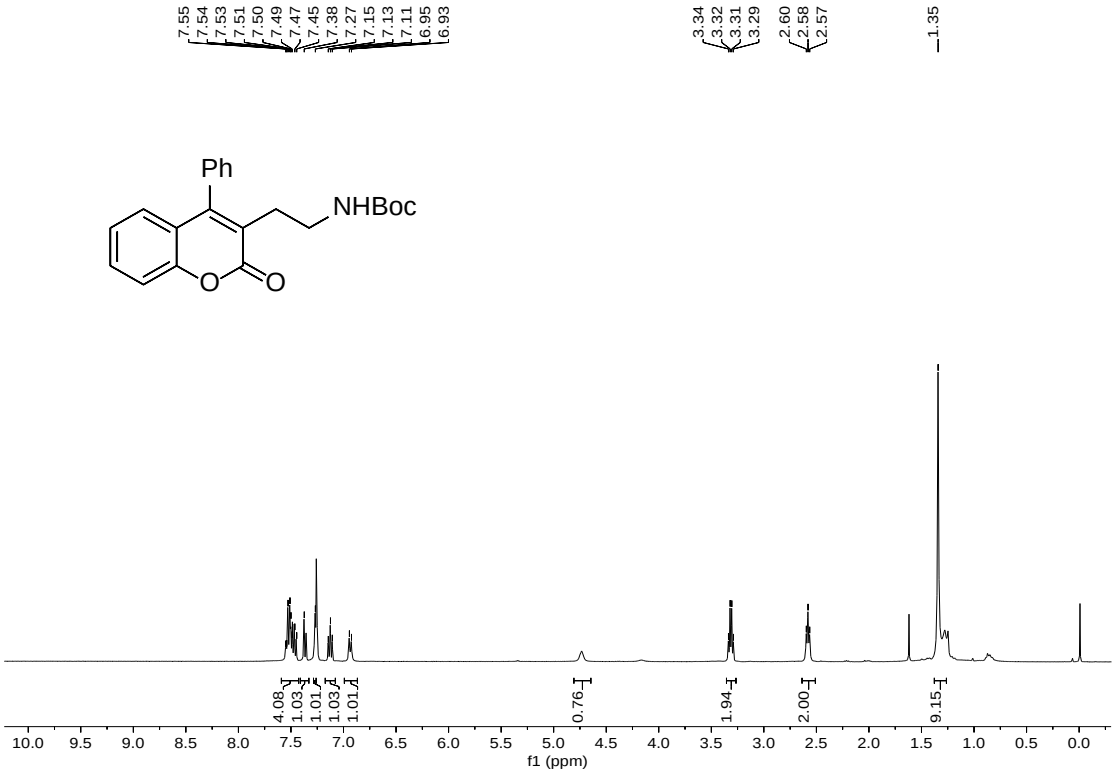
^{1}H NMR Spectrum of **5a**



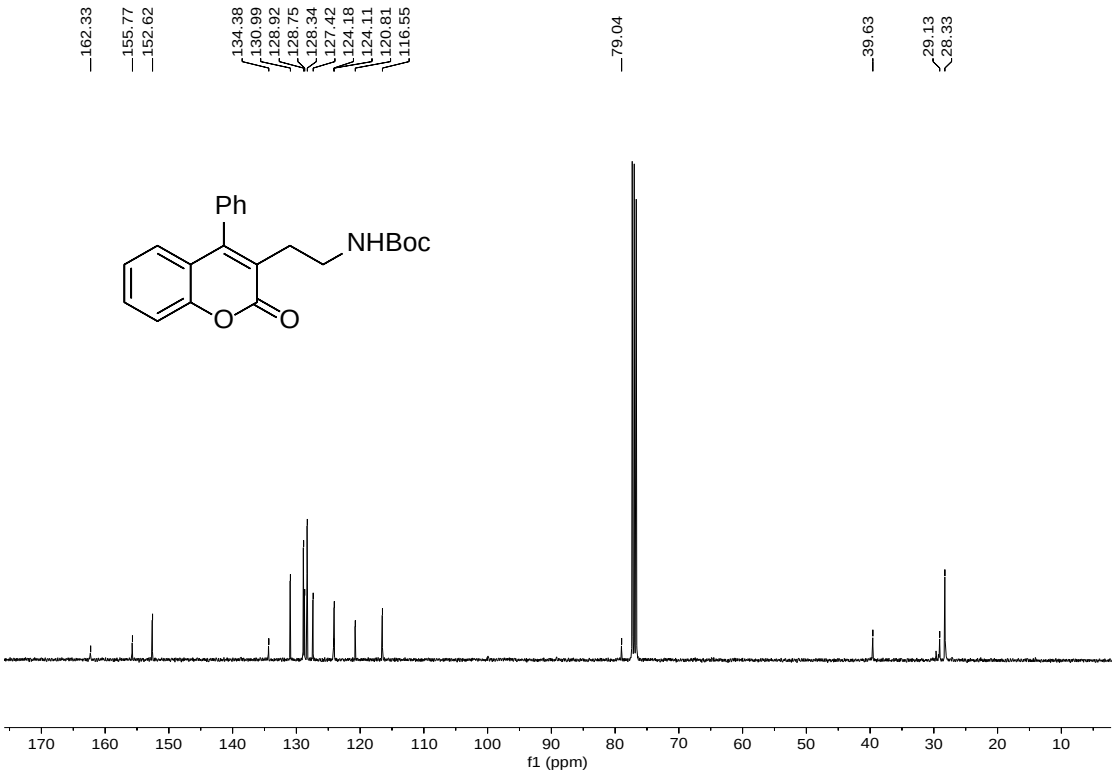
^{13}C NMR Spectrum of **5a**



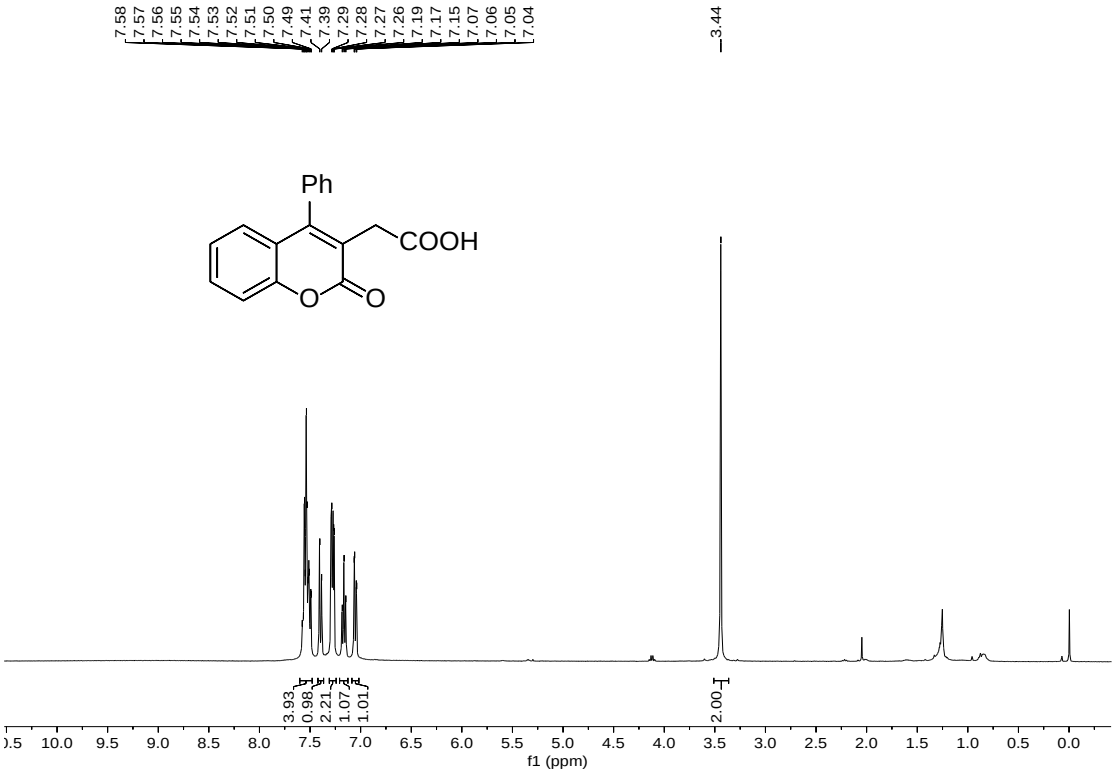
[1] H NMR Spectrum of **6a**



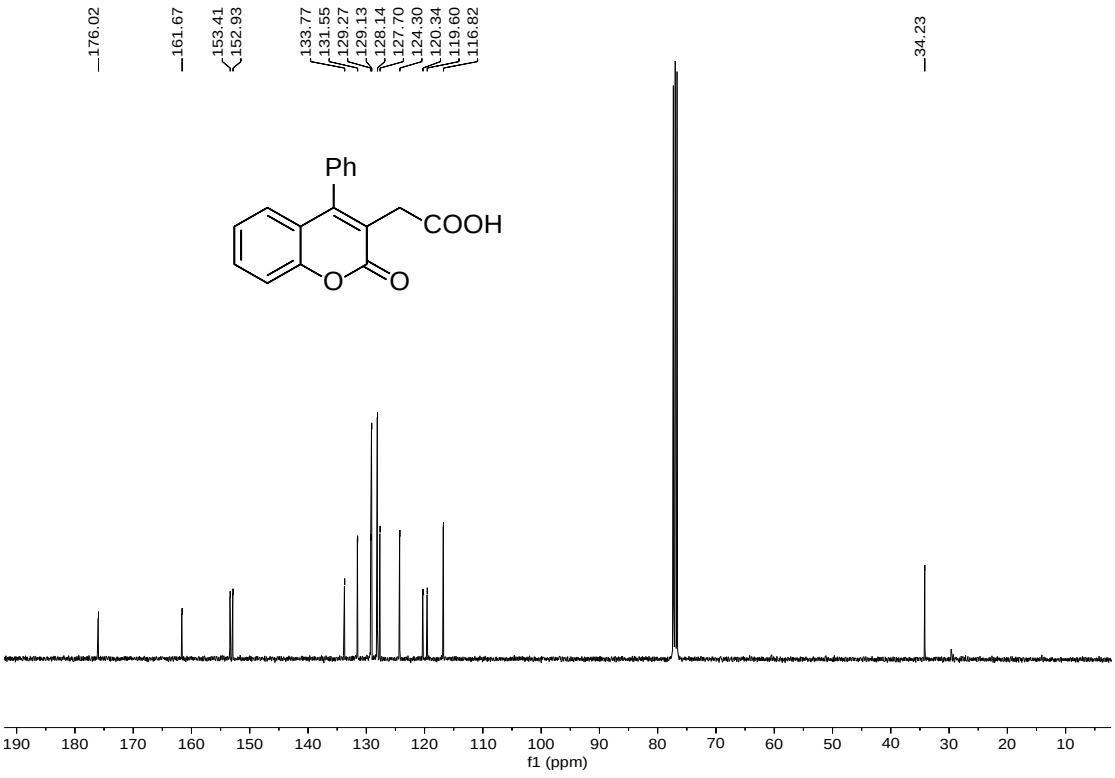
[13] C NMR Spectrum of **6a**



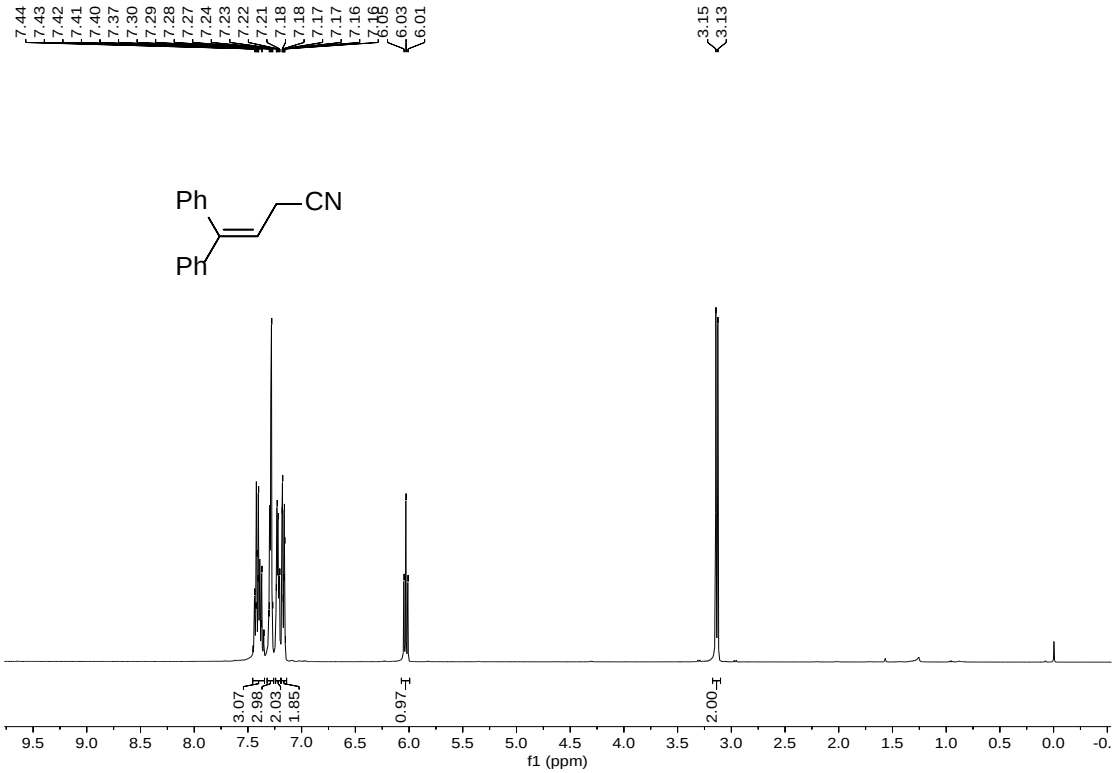
[1] H NMR Spectrum of **7a**



[13] C NMR Spectrum of **7a**



[1] H NMR Spectrum of **6b**



[13] C NMR Spectrum of **6b**