

Supporting Information

A new [4+1]/[4+2]bicycliaztion strategy for accessing functionalized indeno[1,2-*b*]pyran-2-ones

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Experimental

General Information

^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $\text{DMSO-}d_6$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI-TOF or ESI-TOF) was determined by using microTOF-Q II HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

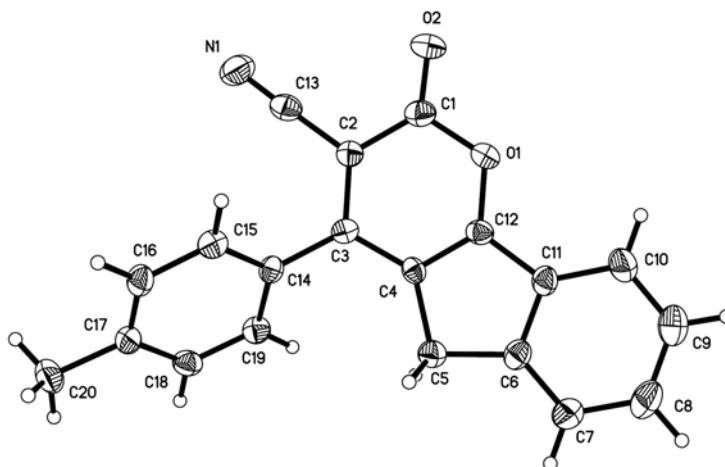
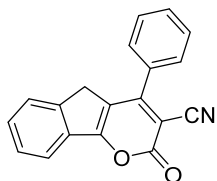


Fig 1, X-Ray Structure of **3g**

Experimental Section

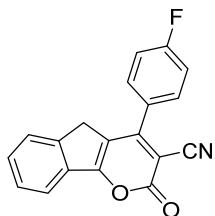
Example for the synthesis of **3a**: 2-Oxo-4-phenyl-2,5-dihydroindeno[1,2-*b*]pyran-3-carbonitrile

Phthalaldehyde **1a** (1.0 mmol) was introduced in a 50-mL round flask, 2-(1-phenylethylidene) malononitrile (**2a**, 1.0 mmol), Et₃N (1.0 mmol), and DMF (8.0 mL) were then successively added and stirred at room temperature for 12 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with cold water (20 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95% EtOH to afford the desired pure indeno[1,2-*b*]pyrans **3a** as a yellow solid



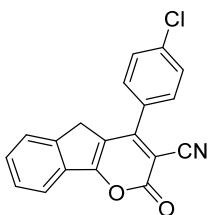
Yellow solid; mp 231- 232 °C; IR (KBr, ν , cm^{-1}) 3079, 2214, 1627, 1608, 1560, 1493, 1398, 1223, 1093, 827; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 7.86 (d, J = 7.6 Hz, 1H, ArH), 7.80-7.76 (m, 2H, ArH), 7.70 (d, J = 7.2 Hz, 1H, ArH), 7.65 (dd, J_1 = 7.6, J_2 = 3.6 Hz, 3H, ArH), 7.58 (q, J = 8.0 Hz, 2H, ArH), 3.80 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 163.6, 162.0, 159.7, 145.5, 133.2, 133.0, 131.2, 131.0, 128.9, 128.3, 128.0, 125.7, 120.8, 118.2, 115.6, 93.3, 33.0; HRMS (ESI) m/z calc. for C₁₉H₁₂NO₂, 286.0868 [M+H]⁺; found 286.0875.

4-(4-Fluorophenyl)-2-oxo-2,5-dihydroindeno[1,2-*b*]pyran-3-carbonitrile (**3b**)



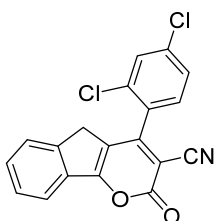
Yellow solid; mp 237-239 °C; IR (KBr, ν , cm^{-1}) 3070, 2215, 1718, 1655, 1598, 1561, 1492, 1384, 1234, 1154, 847; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 7.91-7.84 (m, 3H, ArH), 7.71 (d, J = 7.2 Hz, 1H, ArH), 7.65-7.54 (m, 2H, ArH), 7.50 (t, J = 8.8 Hz, 2H, ArH), 3.80 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 163.6 (J_{CF} = 248.4 Hz), 163.6, 161.0, 159.6, 145.5, 133.2, 131.1 (J_{CF} = 8.9 Hz), 131.1, 129.4 (J_{CF} = 3.2 Hz), 128.0, 125.7, 120.9, 118.2, 116.1 (J_{CF} = 21.9 Hz), 115.6, 93.4, 32.9; HRMS (ESI) m/z calc. for C₁₉H₁₁FNO₂, 304.0774 [M+H]⁺; found 304.0787.

4-(4-Chlorophenyl)-2-oxo-2,5-dihydroindeno[1,2-*b*]pyran-3-carbonitrile (**3c**)



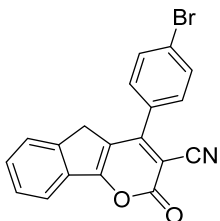
Yellow solid; mp 254-255 °C; IR (KBr, ν , cm^{-1}) 3090, 2215, 1717, 1615, 1590, 1561, 1497, 1460, 1385, 1203, 1155, 839; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 7.87 (d, $J = 7.2$ Hz, 1H, ArH), 7.81 (d, $J = 8.4$, 2H, ArH), 7.76-7.68 (m, 3H, ArH), 7.65-7.53 (m, 2H, ArH), 3.78 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$); δ , ppm) 163.7, 160.8, 159.6, 145.5, 136.1, 133.2, 131.8, 131.1, 130.2, 129.1, 128.1, 125.7, 120.9, 118.1, 115.5, 93.4, 32.8; HRMS (ESI) m/z calc. for $\text{C}_{19}\text{H}_{10}\text{ClNNO}_2$, 342.0298 $[\text{M} + \text{Na}]^+$; found 342.0296.

4-(2,4-Dichlorophenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (**3d**)



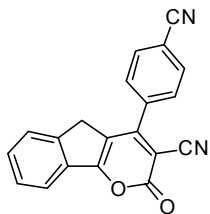
Yellow solid; mp 287-289 °C; IR (KBr, ν , cm^{-1}) 3049, 2224, 1717, 1621, 1569, 1543, 1477, 1377, 1282, 1104, 828; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 8.01 (s, 1H, ArH), 7.89 (d, $J = 7.2$ Hz, 1H, ArH), 7.75 (d, $J = 8.8$ Hz, 1H, ArH), 7.69 (d, $J = 8.8$ Hz, 2H, ArH), 7.65-7.56 (m, 2H, ArH), 3.63 (d, $J = 8.4$ Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$); δ , ppm) 164.4, 159.0, 159.0, 145.4, 136.2, 133.1, 131.6, 131.5, 131.0, 129.8, 128.3, 128.2, 125.9, 121.1, 118.5, 114.6, 112.7, 95.2, 32.3; HRMS (ESI) m/z calc. for $\text{C}_{19}\text{H}_{10}\text{Cl}_2\text{NO}_2$, 354.0089 $[\text{M} + \text{H}]^+$; found 354.0073.

4-(4-Bromophenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (**3e**)



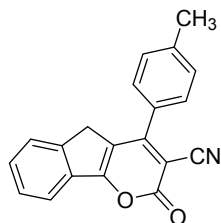
Yellow solid; mp 259 - 260 °C; IR (KBr, ν , cm^{-1}) 2918, 2217, 1775, 1718, 1609, 1561, 1460, 1383, 1204, 1156, 828; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 7.87 (d, $J = 8.4$ Hz, 3H, ArH), 7.71 (dd, $J_1 = 12.8$, $J_2 = 8.0$ Hz, 3H, ArH), 7.63-7.55 (m, 2H, ArH), 3.78 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm) 163.7, 160.9, 159.6, 145.5, 133.2, 132.1, 131.7, 131.2, 130.4, 128.1, 125.7, 125.0, 120.9, 118.1, 115.5, 93.3, 32.8; HRMS (ESI) m/z calc. for $\text{C}_{19}\text{H}_{10}\text{BrNNO}_2$, 385.9793 $[\text{M} + \text{Na}]^+$; found 385.9767.

4-(4-Cyanophenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (**3f**)



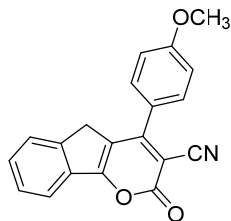
Yellow solid; mp > 300 °C; IR (KBr, ν , cm^{-1}) 2946, 2224, 2214, 1636, 1614, 1588, 1562, 1490, 1355, 1231, 1156, 844, 772; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm) 8.19 (s, 1H, ArH), 8.09 (d, $J = 8.0$ Hz, 2H, ArH), 7.88 (d, $J = 8.0$ Hz, 2H, ArH), 7.63 (d, $J = 6.8$ Hz, 1H, ArH), 7.57-7.47 (m, 2H, ArH), 3.66 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm) 169.4, 165.6, 162.2, 158.1, 146.6, 140.0, 133.2, 131.0, 129.8, 128.1, 126.0, 122.6, 122.5, 118.8, 117.1, 113.1, 34.1.; HRMS (ESI) m/z calc. for $\text{C}_{20}\text{H}_{11}\text{N}_2\text{O}_2$, 311.0821 $[\text{M}+\text{H}]^+$; found 311.0835.

2-Oxo-4-(*p*-tolyl)-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (**3g**)



Yellow solid; mp 261-262 °C; IR (KBr, ν , cm^{-1}) 3047, 2211, 1718, 1655, 1638, 1613, 1560, 1493, 1382, 1187, 1069, 837, 762; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm) 7.85 (d, $J = 6.8$ Hz, 1H, ArH), 7.72-7.66 (m, 3H, ArH), 7.63-7.53 (m, 2H, ArH), 7.45 (d, $J = 8.0$ Hz, 2H, ArH), 3.80 (s, 2H, CH_2), 2.44 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm) 163.4, 162.1, 159.8, 145.5, 141.5, 133.3, 131.0, 130.2, 129.5, 128.4, 128.0, 125.7, 120.8, 118.2, 115.8, 92.9, 33.1, 21.0; HRMS (ESI) m/z calc. for $\text{C}_{20}\text{H}_{14}\text{NO}_2$, 300.1025 $[\text{M}+\text{H}]^+$; found 300.1035.

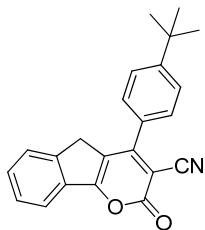
4-(4-Methoxyphenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (**3h**)



Yellow solid; mp 263-264 °C; IR (KBr, ν , cm^{-1}) 2933, 2216, 1708, 1603, 1565, 1496, 1384, 1260, 1183, 1154, 840, 763, 726; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm) 7.85 (d, $J = 6.8$ Hz, 1H, ArH), 7.79 (d, $J = 8.8$ Hz, 2H, ArH), 7.70 (d, $J = 7.3$ Hz, 1H, ArH), 7.63 – 7.54 (m, 2H, ArH), 7.19 (d, $J = 8.8$ Hz, 2H, ArH), 3.89 (s, 3H, OCH_3), 3.84 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm) 163.3, 161.7, 160.2, 159.9, 145.4, 133.3, 130.9, 130.5, 128.0, 125.6, 125.0, 120.8, 118.2, 116.0, 114.4, 92.3, 55.5, 33.2; HRMS (ESI) m/z calc. for $\text{C}_{20}\text{H}_{14}\text{NO}_3$,

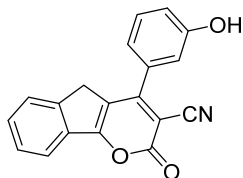
316.0974 [M+H]⁺; found 316.0946.

4-(4-(tert-Butyl)phenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (3i)



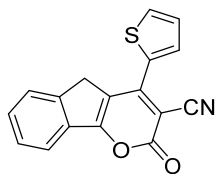
Yellow solid; mp 259-260 °C; IR (KBr, ν , cm^{-1}) 3056, 2959, 2223, 1724, 1611, 1588, 1572, 1491, 1462, 1379, 1199, 835, 770; ¹H NMR(400 MHz, DMSO-*d*₆; δ , ppm) 7.85 (d, J = 7.2 Hz, 1H, ArH), 7.75 (d, J = 8.4 Hz, 2H, ArH), 7.71-7.66 (m, 3H, ArH), 7.63-7.54 (m, 2H, ArH), 3.83 (s, 2H, CH₂), 1.36 (s, 9H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 163.9, 162.4, 160.3, 154.7, 146.1, 133.7, 131.5, 130.7, 128.8, 128.5, 126.3, 126.2, 121.3, 118.8, 116.4, 93.3, 35.3, 33.7, 31.4.; HRMS (ESI) m/z calc. for C₂₃H₂₀NO₂, 342.1494 [M+H]⁺; found 342.1486.

4-(3-Hydroxyphenyl)-2-oxo-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (3j)



Yellow solid; mp 247-248 °C; IR (KBr, ν , cm^{-1}) 3048, 2225, 1726, 1699, 1561, 1494, 1386, 1198, 1150, 765, 730, 611; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 10.05 (s, 1H, OH), 7.80 (d, J = 7.6 Hz, 1H, ArH), 7.68 (d, J = 7.2 Hz, 1H, ArH), 7.62-7.49 (m, 2H, ArH), 7.43 (t, J = 8.0 Hz, 1H, ArH), 7.14 (d, J = 7.6 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.02 (dd, J_1 = 8.0, J_2 = 1.6 Hz, 1H, ArH), 3.71 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 163.5, 162.0, 159.7, 157.6, 145.3, 134.1, 133.2, 130.9, 130.1, 127.9, 125.6, 120.7, 118.7, 118.1, 118.0, 115.5, 114.8, 93.0, 33.0; HRMS (ESI) m/z calc. for C₁₉H₁₂NO₃, 302.0817 [M+H]⁺; found 302.0814.

2-Oxo-4-(thiophen-2-yl)-2,5-dihydroindeno[1,2-b]pyran-3-carbonitrile (3k)

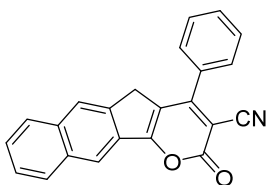


Yellow solid; mp 235-236 °C; IR (KBr, ν , cm^{-1}) 3068, 2220, 1728, 1559, 1479, 1422, 1151, 785, 764, 726; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 8.23 (s, 1H, ArH), 8.13 (s, 1H, ArH), 7.82 (d, J = 6.4 Hz, 1H, ArH), 7.74 (d,

$J = 6.4$ Hz, 1H, ArH), 7.61-7.56 (m, 2H, ArH), 7.44 (s, 1H, ArH), 4.05 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 163.4, 159.9, 153.0, 145.0, 134.3, 134.0, 133.3, 133.1, 131.1, 128.8, 128.0, 125.5, 121.8, 120.7, 116.7, 89.9, 34.5; HRMS (ESI) m/z calc. for C₁₇H₁₀NO₂S, 292.0426 [M+H]⁺; found 292.0436.

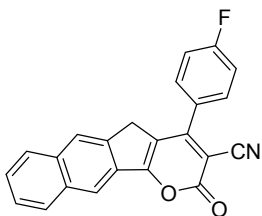
Example for the synthesis of **3I**: *2-Oxo-4-phenyl-2,5-dihydro benzo[5,6]indeno[1,2-b]pyran-3-carbonitrile*

Naphthalene-2,3-dicarbaldehyde **1b** (1.0 mmol) was introduced in a 50-mL round flask, 2-(1-phenylethylidene) malononitrile (**2a**, 1.0 mmol), Et₃N (1.0 mmol), and DMF (8.0 mL) were then successively added and stirred at 0 °C for 24 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with cold water (20 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95% EtOH to afford the desired pure indeno[1,2-*b*]pyrans **3I** as a yellow solid



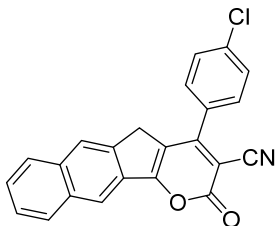
Yellow solid; mp 247-248 °C; IR (KBr, ν , cm⁻¹) 3054, 2223, 1731, 1573, 1496, 1440, 1329, 1145, 875, 748; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 8.45 (s, 1H, ArH), 8.21-8.10 (m, 2H, ArH), 8.01 (d, $J = 7.6$ Hz, 1H, ArH), 7.83-7.78 (m, 2H, ArH), 7.69-7.66 (m, 3H, ArH), 7.62 (d, $J = 2.0$ Hz, 1H, ArH), 7.59 (d, $J = 6.8$ Hz, 1H, ArH), 3.87 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 162.9, 162.0, 159.5, 139.6, 134.0, 133.0, 132.1, 131.5, 131.2, 129.1, 128.9, 128.2, 127.9, 127.8, 126.4, 124.0, 120.6, 119.3, 115.6, 94.4, 32.1; HRMS (ESI) m/z calc. for C₂₃H₁₄NO₂Na, 358.0844[M+Na]⁺; found 358.0840.

2-Oxo-4-fluorophenyl-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3- carbonitrile (3m)



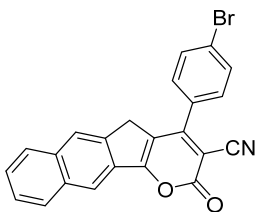
Yellow solid; mp 292-293 °C; IR (KBr, ν , cm⁻¹) 3063, 2223, 1729, 1573, 1493, 1417, 1227, 1160, 1101, 851; ¹H NMR (400 MHz, DMSO-*d*₆; δ , ppm) 8.45 (s, 1H, ArH), 8.19-8.12 (m, 2H, ArH), 8.02 (d, $J = 7.6$ Hz, 1H, ArH), 7.93-7.86 (m, 2H, ArH), 7.64-7.60 (m, 2H, ArH), 7.53 (t, $J = 8.8$ Hz, 2H, ArH), 3.88 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ , ppm) 164.6 ($J_{CF} = 220.0$ Hz), 162.9, 161.4, 159.5, 139.3, 134.0, 131.5, 131.1, 131.0, 129.1, 127.9 ($J_{CF} = 8.9$ Hz), 127.0, 126.5, 124.0 ($J_{CF} = 2.3$ Hz), 121.2, 120.6, 119.4, 116.1 ($J_{CF} = 21.8$ Hz), 115.5, 112.6, 94.6, 32.4; HRMS (ESI) m/z calc. for C₂₃H₁₂FNO₂Na, 376.0750 [M+Na]⁺; found 376.0752.

2-Oxo-4-chlorophenyl-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3- carbonitrile (**3n**)



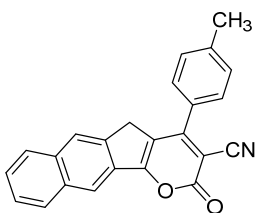
Yellow solid; mp 254-256 °C; IR (KBr, ν , cm^{-1}) 3083, 2221, 1716, 1634, 1455, 1397, 1065, 875, 765; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 8.42 (s, 1H, ArH), 8.19-8.09 (m, 2H, ArH), 8.00 (d, $J = 8.0$ Hz, 1H, ArH), 7.83 (d, $J = 8.0$ Hz, 2H ArH), 7.76 (d, $J = 7.6$ Hz, 2H, ArH), 7.64-7.58 (m, 2H, ArH), 3.83 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm) 163.1, 160.8, 159.4, 147.7, 139.7, 136.3, 134.1, 132.2, 131.8, 131.5, 130.3, 129.2, 128.0, 126.5, 124.1, 120.7, 119.4, 115.5, 112.7, 94.6, 32.1; HRMS (ESI) m/z calc. for $\text{C}_{23}\text{H}_{12}\text{ClNO}_2\text{Na}$, 392.0454 $[\text{M}+\text{Na}]^+$; found 392.0454.

2-Oxo-4- bromophenyl-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3- carbonitrile (**3o**)



Yellow solid; mp 269-270 °C; IR (KBr, ν , cm^{-1}) 3057, 2220, 1743, 1687, 1507, 1401, 1169, 889, 787; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 8.42 (s, 1H, ArH), 8.18-8.09 (m, 2H, ArH), 8.00 (d, $J = 8.0$ Hz, 1H, ArH), 7.89 (d, $J = 8.4$ Hz, 2H ArH), 7.75 (d, $J = 8.4$ Hz, 2H, ArH), 7.67-7.55 (m, 2H, ArH), 3.82 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm) 163.0, 160.8, 159.3, 139.6, 134.0, 132.1, 132.1, 132.0, 131.4, 130.3, 129.1, 127.9, 127.9, 126.4, 125.0, 124.0, 120.6, 119.1, 115.3, 94.4, 32.0; HRMS (ESI) m/z calc. for $\text{C}_{23}\text{H}_{12}\text{BrNO}_2\text{Na}$, 435.9944 $[\text{M}+\text{Na}]^+$; found 435.9949.

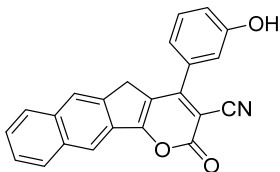
2-Oxo- *p*-tolyl -2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3- carbonitrile (**3p**)



Yellow solid; mp 232-234 °C; IR (KBr, ν , cm^{-1}) 3012, 2222, 1714, 1615, 1498, 1432, 1289, 876, 799; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 8.42 (s, 1H, ArH), 8.13 (t, $J = 8.8$ Hz, 2H, ArH), 8.00 (d, $J = 7.7$ Hz, 1H, ArH), 7.70 (d, $J = 8.0$ Hz, 2H, ArH), 7.64-7.57 (m, 2H, ArH), 7.48 (d, $J = 8.0$ Hz, 2H, ArH), 3.86 (s, 2H, CH_2), 2.45 (s,

3H, CH₃); ¹³C NMR (100 MHz, DMSO-*d*₆; δ, ppm) 162.7, 162.0, 159.6, 141.4, 139.6, 134.0, 132.1, 131.5, 130.1, 129.5, 129.0, 128.3, 127.9, 127.8, 126.4, 123.9, 120.5, 119.3, 115.6, 94.2, 32.2, 21.0; HRMS (ESI) *m/z* calc. for C₂₄H₁₅NO₂Na, 372.1000 [M+Na]⁺; found 372.0998.

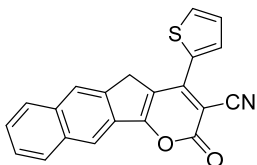
2-oxo-3-hydroxyphenyl-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3-carbonitrile (3q)



Yellow solid; mp 298-299 °C; IR (KBr, ν, cm⁻¹) 3412, 2220, 1768, 1621, 1497, 1354, 1187, 885;

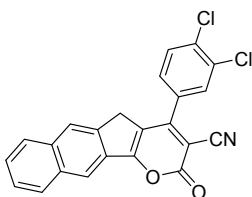
¹H NMR (400 MHz, DMSO-*d*₆; δ, ppm) 10.03 (s, 1H, OH), 8.35 (s, 1H, ArH), 8.14-8.06 (m, 2H, ArH), 7.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.59 (t, *J* = 8.0 Hz, 2H, ArH), 7.46 (t, *J* = 7.6 Hz, 1H, ArH), 7.16 (d, *J* = 7.2 Hz, 1H, ArH), 7.12 (s, 1H, ArH), 7.05 (d, *J* = 8.0 Hz, 1H, ArH), 3.77 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ, ppm) 162.9, 162.0, 159.6, 157.6, 139.6, 134.2, 134.0, 132.1, 131.6, 130.3, 129.1, 128.0, 127.8, 124.0, 120.5, 119.3, 118.1, 115.5, 114.8, 94.2, 32.3; HRMS (ESI) *m/z* calc. for C₂₃H₁₃NNaO₃, 374.0793 [M+Na]⁺; found 374.0779.

2-Oxo-(thiophen-2-yl)-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3-carbonitrile (3r)



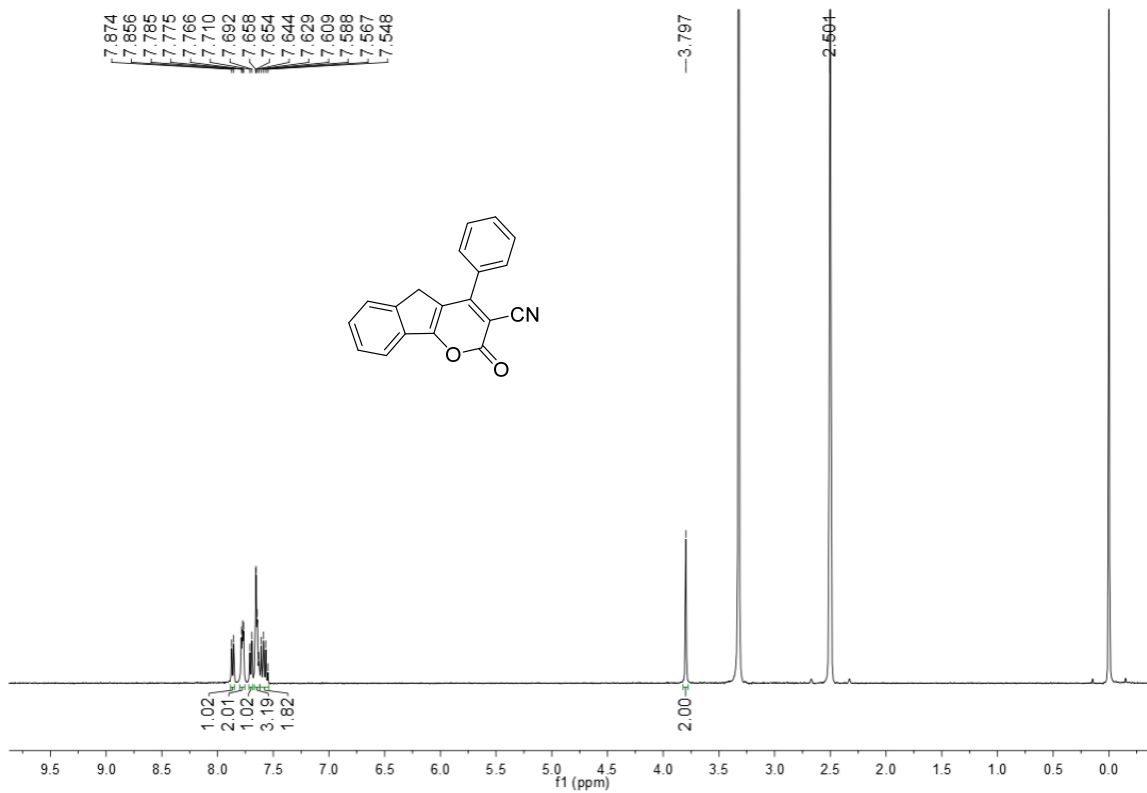
Yellow solid; mp 243-244 °C; IR (KBr, ν, cm⁻¹) 3012, 2220, 1768, 1621, 1497, 1354, 1187, 885; ¹H NMR (400 MHz, DMSO-*d*₆; δ, ppm) 8.39 (s, 1H, ArH), 8.27 (s, 1H, ArH), 8.13 (d, *J* = 9.8 Hz, 3H, ArH), 8.01 (d, *J* = 8.4 Hz, 1H, ArH), 7.66 – 7.54 (m, 3H, ArH), 7.46 (s, 1H, ArH), 4.10 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆; δ, ppm) 163.6, 162.9, 159.8, 139.3, 134.1, 133.3, 132.2, 131.5, 129.8, 129.1, 128.8, 128.8, 128.0, 127.0, 126.5, 120.6, 118.0, 115.2, 105.7, 91.0, 31.6; HRMS (ESI) *m/z* calc. for C₂₁H₁₂NO₂S 342.0583 [M+H]⁺; found 342.0589.

2-Oxo-3,4-dichlorophenyl-2,5-dihydrobenzo[5,6]indeno[1,2-b]pyran-3-carbonitrile (3s)

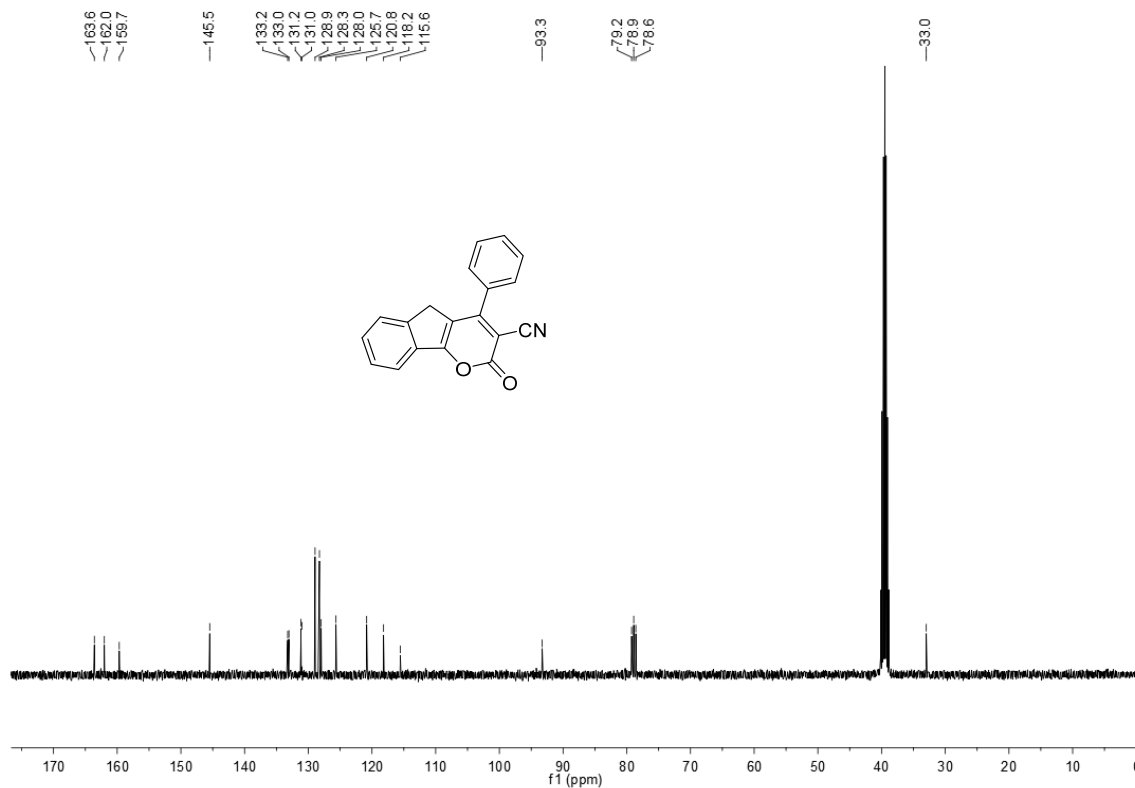


Yellow solid; mp 295-297 °C; IR (KBr, ν , cm^{-1}) 3051, 2220, 1768, 1621, 1497, 1354, 1187, 885; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm) 8.48 (s, 1H, ArH), 8.15 (t, $J = 8.0$ Hz, 3H, ArH), 8.03 (d, $J = 7.2$ Hz, 1H, ArH), 7.97 (d, $J = 8.4$ Hz, 1H, ArH), 7.80 (d, $J = 9.2$ Hz, 1H, ArH), 7.66 – 7.60 (m, 2H, ArH), 3.90 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm) 163.3, 159.4, 159.2, 139.6, 134.2, 134.1, 133.4, 132.1, 132.0, 131.4, 131.4, 130.1, 129.2, 128.6, 128.0, 128.0, 126.5, 124.1, 120.8, 119.2, 115.2, 95.0, 31.9; HRMS (ESI) m/z calc. for $\text{C}_{23}\text{H}_{12}\text{Cl}_2\text{NO}_2$, 404.0240 $[\text{M}+\text{H}]^+$; found 404.0249.

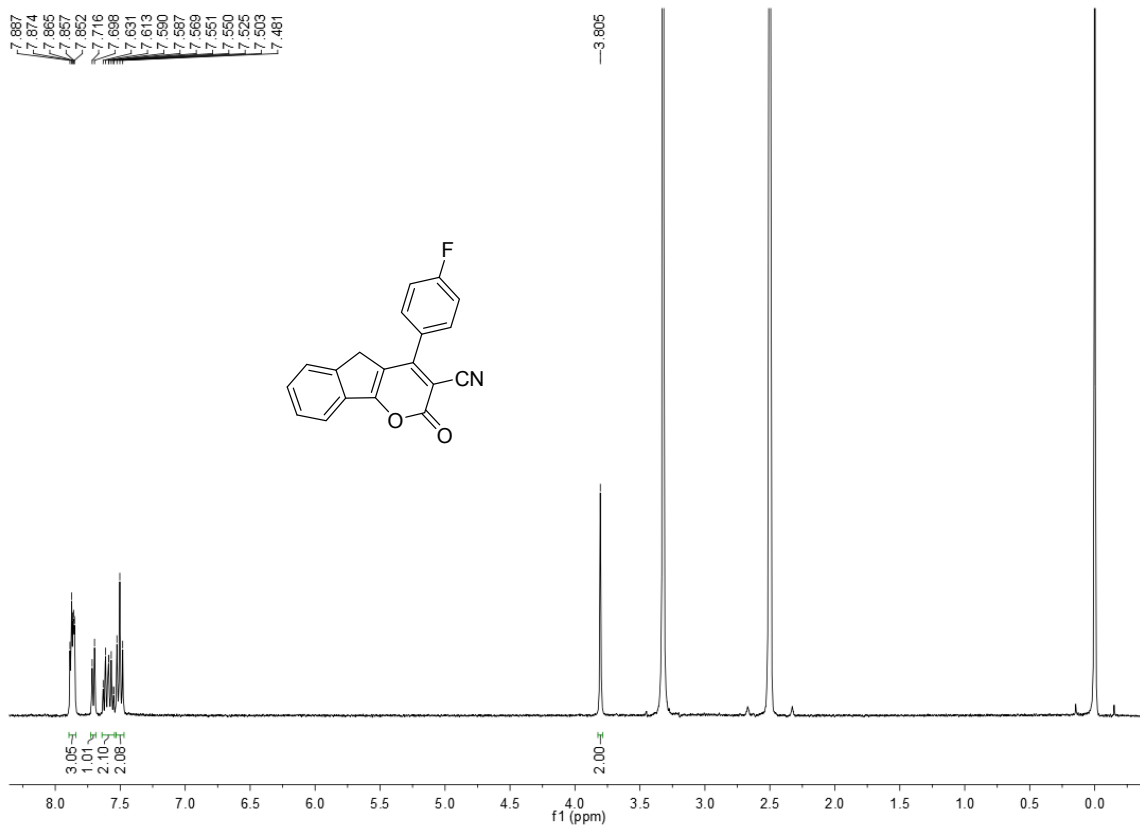
Copies of ^1H NMR and ^{13}C NMR of Compounds 3



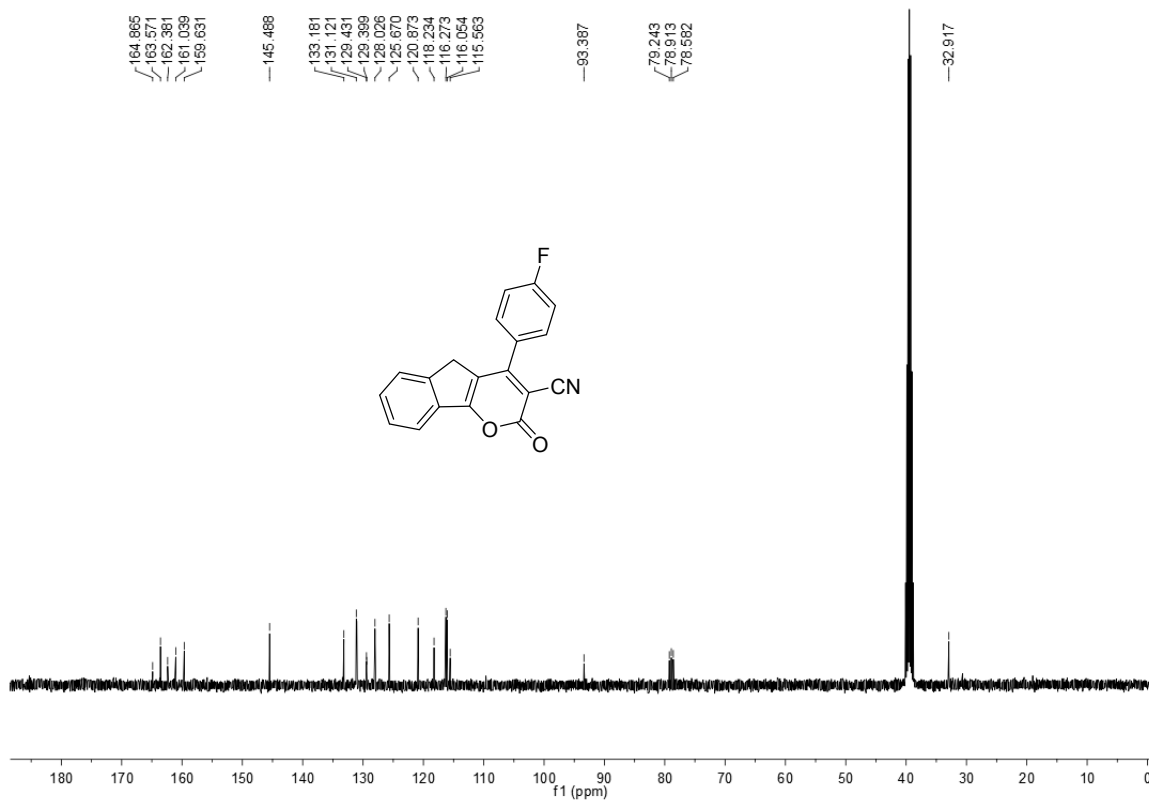
^1H NMR Spectrum of Compound 3a



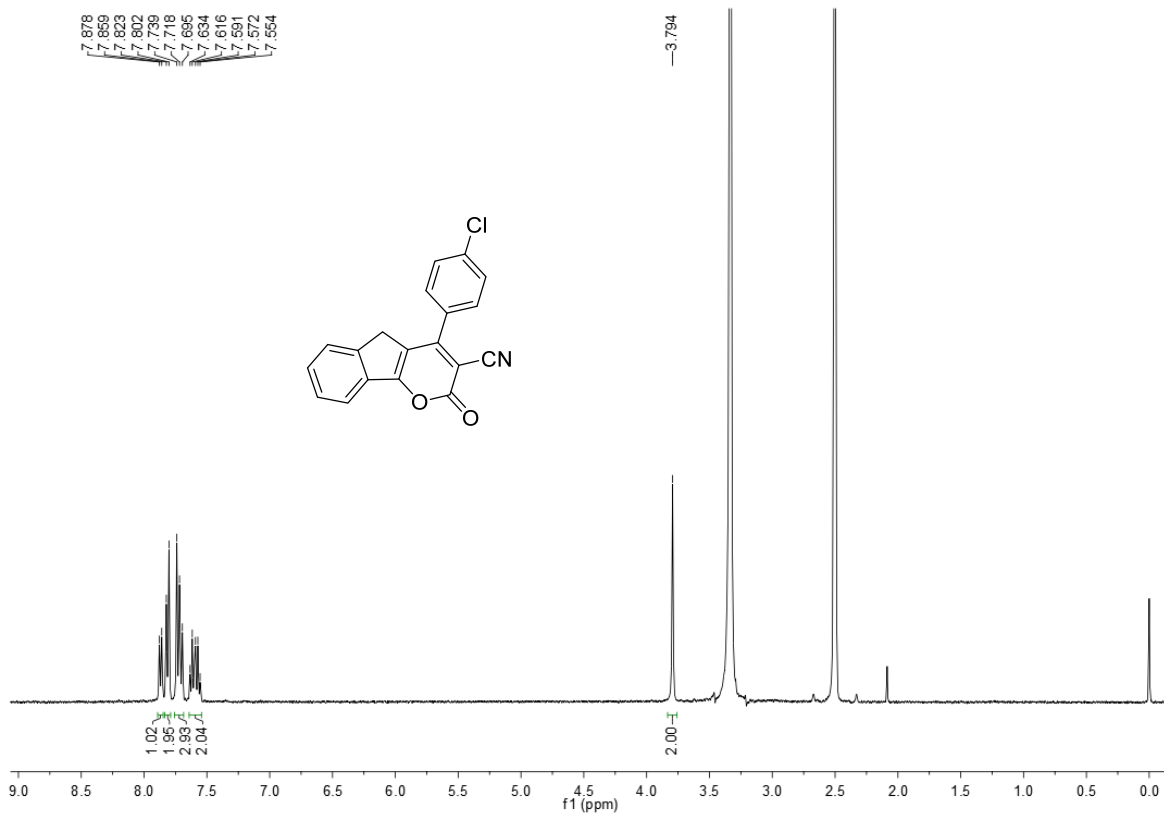
^{13}C NMR Spectrum of Compound 3a



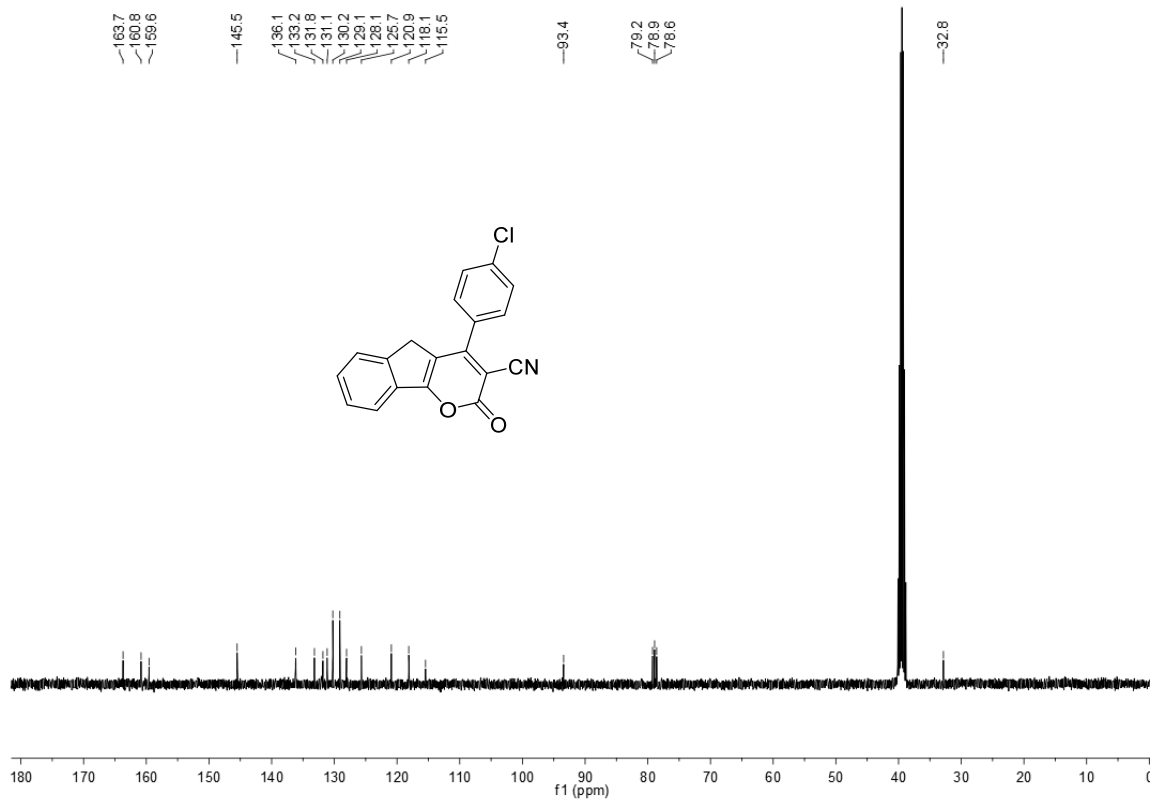
¹H NMR Spectrum of Compound 3b



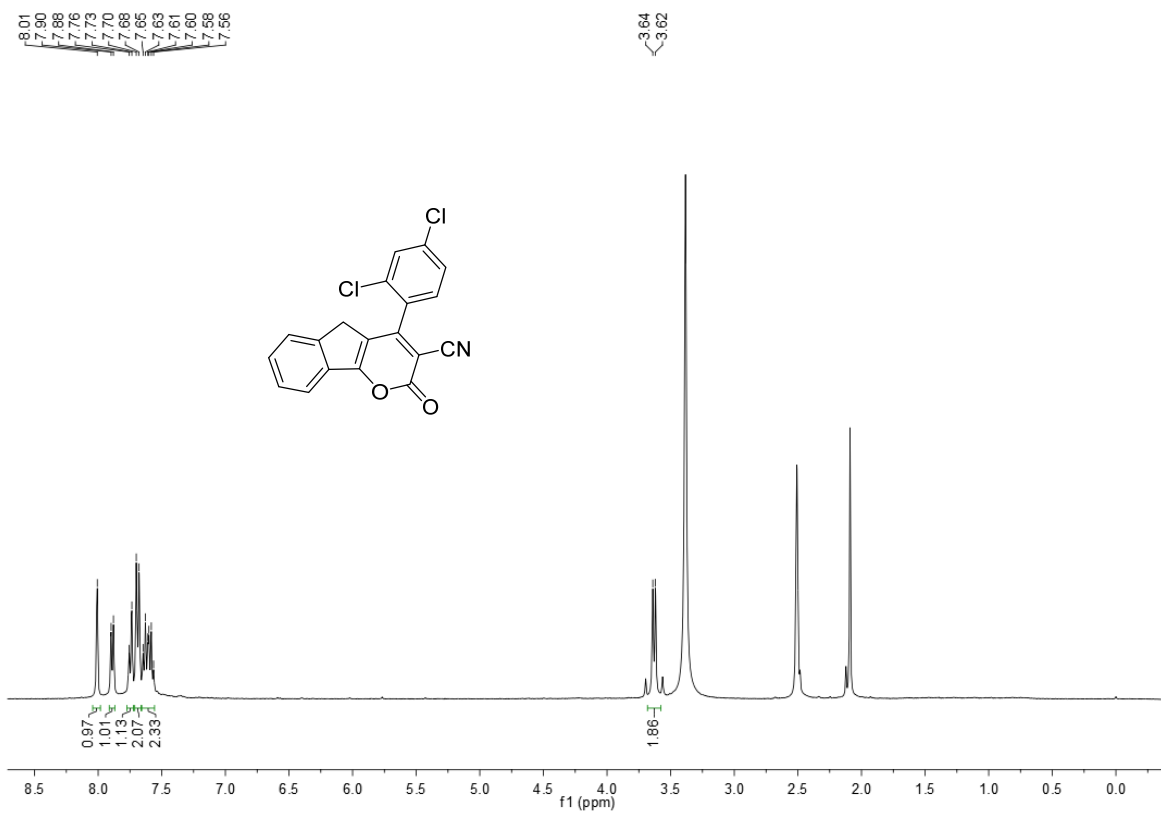
¹³C NMR Spectrum of Compound 3b



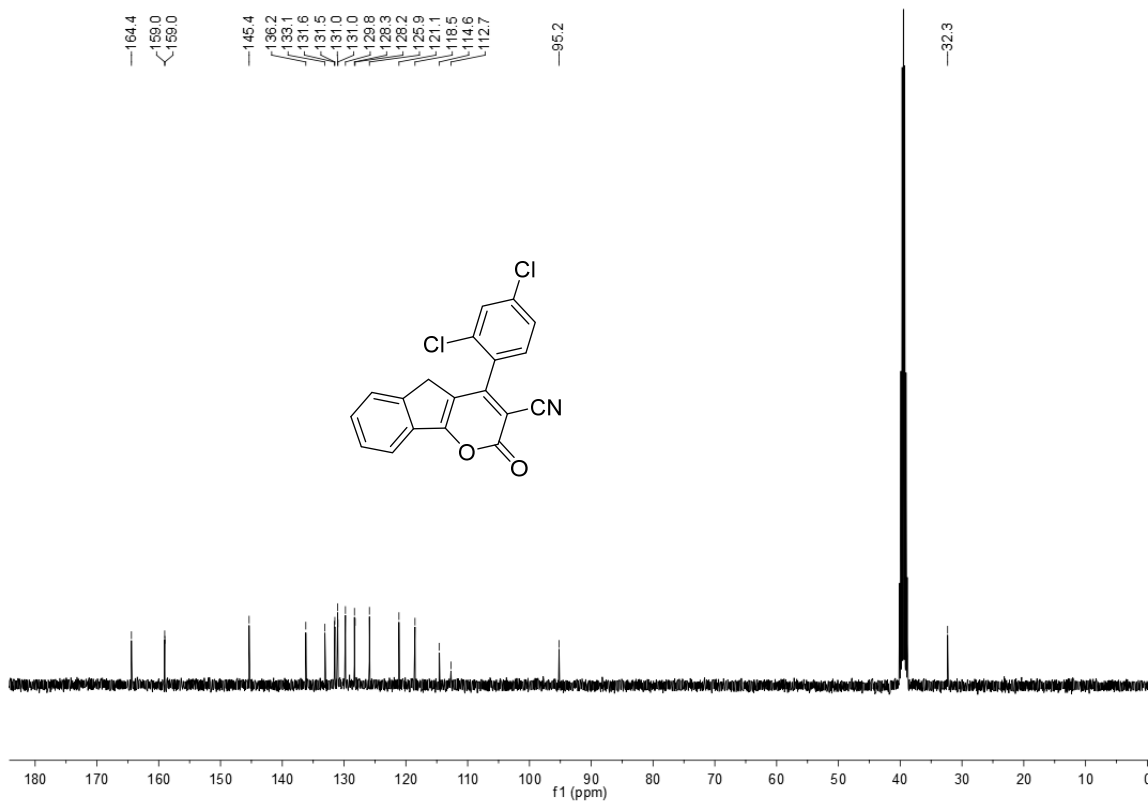
¹H NMR Spectrum of Compound 3c



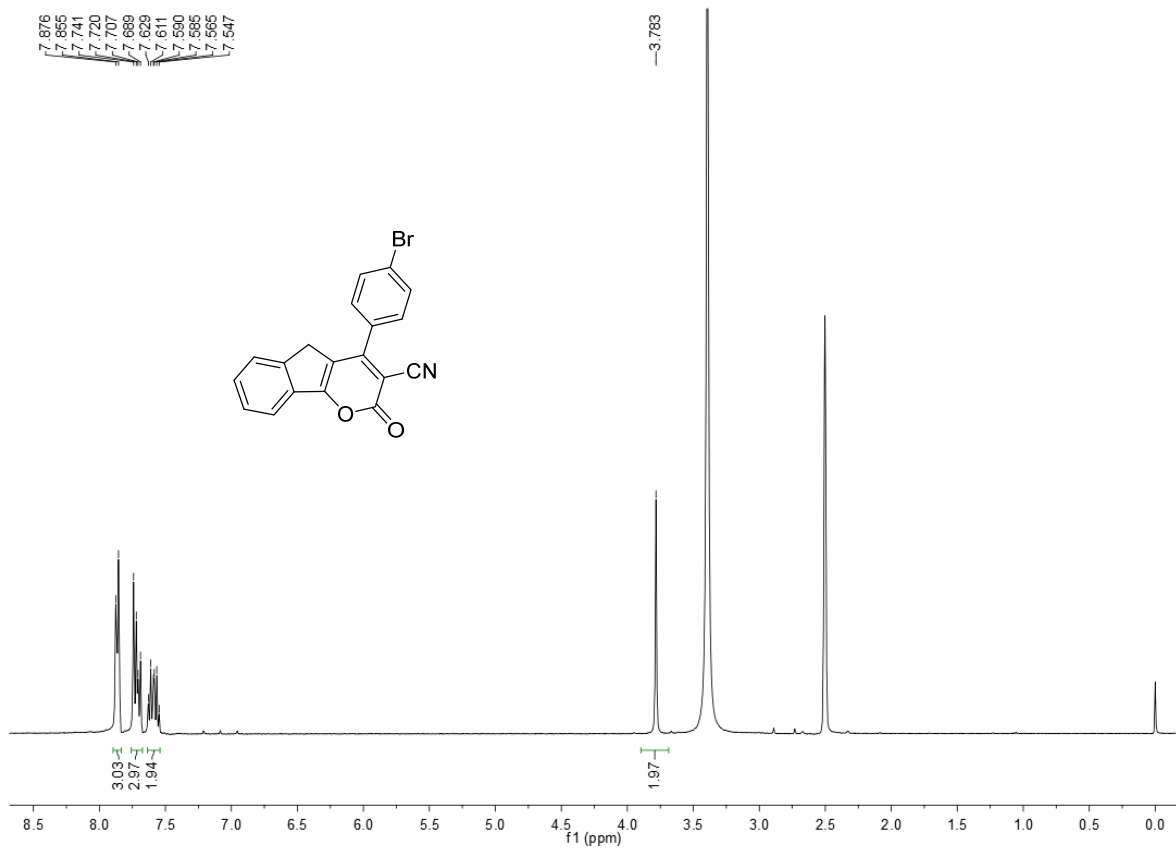
¹³C NMR Spectrum of Compound 3c



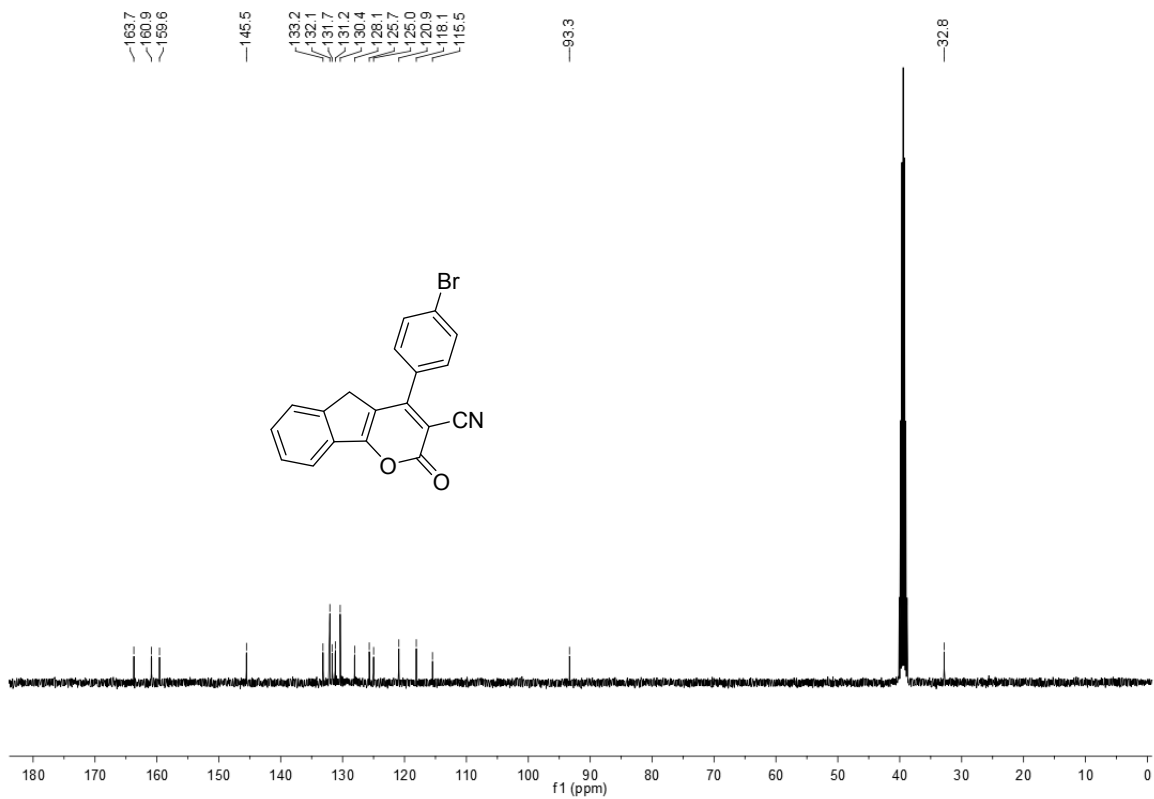
¹H NMR Spectrum of Compound 3d



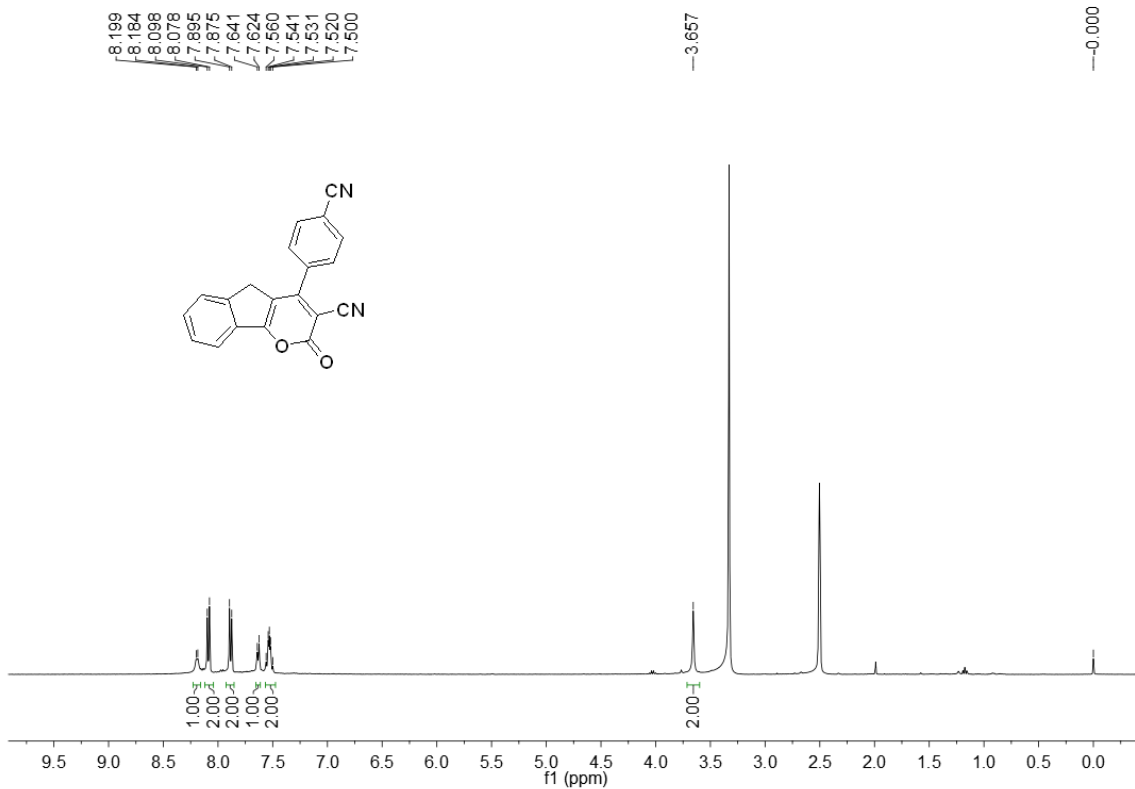
¹³C NMR Spectrum of Compound 3d



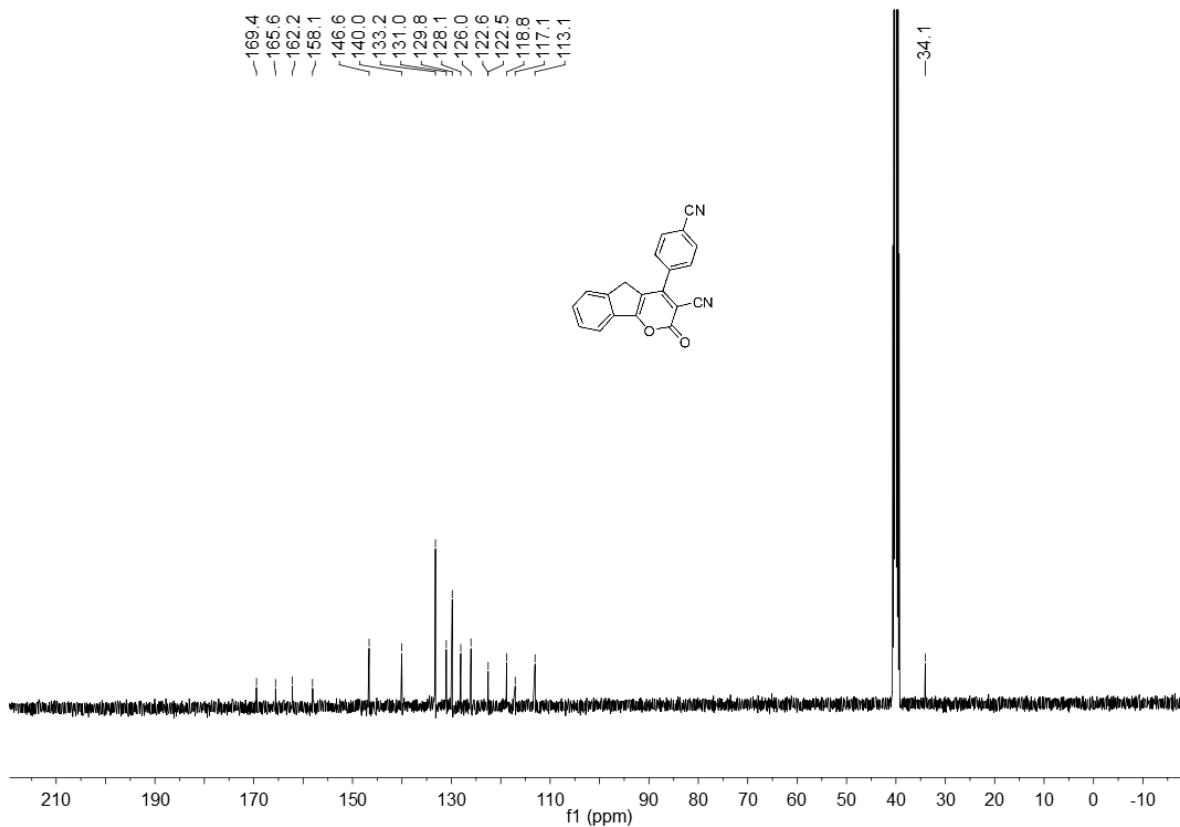
¹H NMR Spectrum of Compound 3e



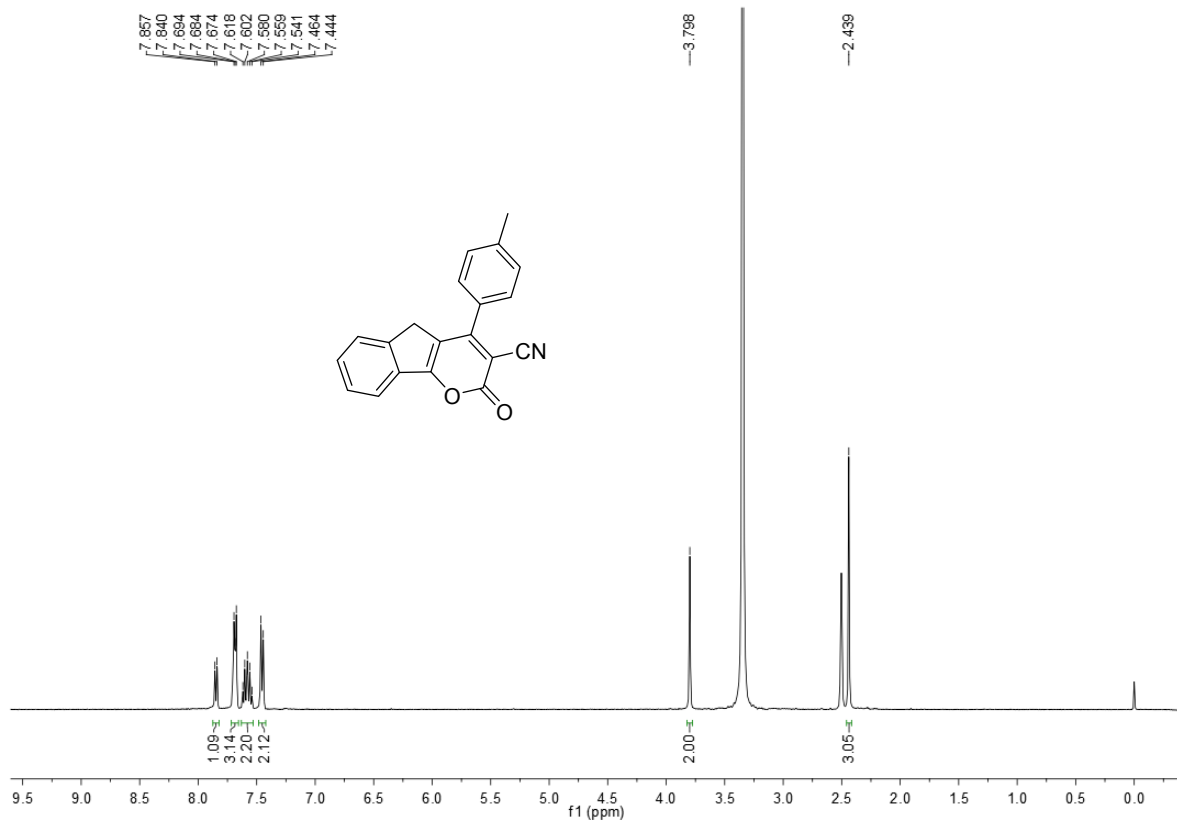
¹³C NMR Spectrum of Compound 3e



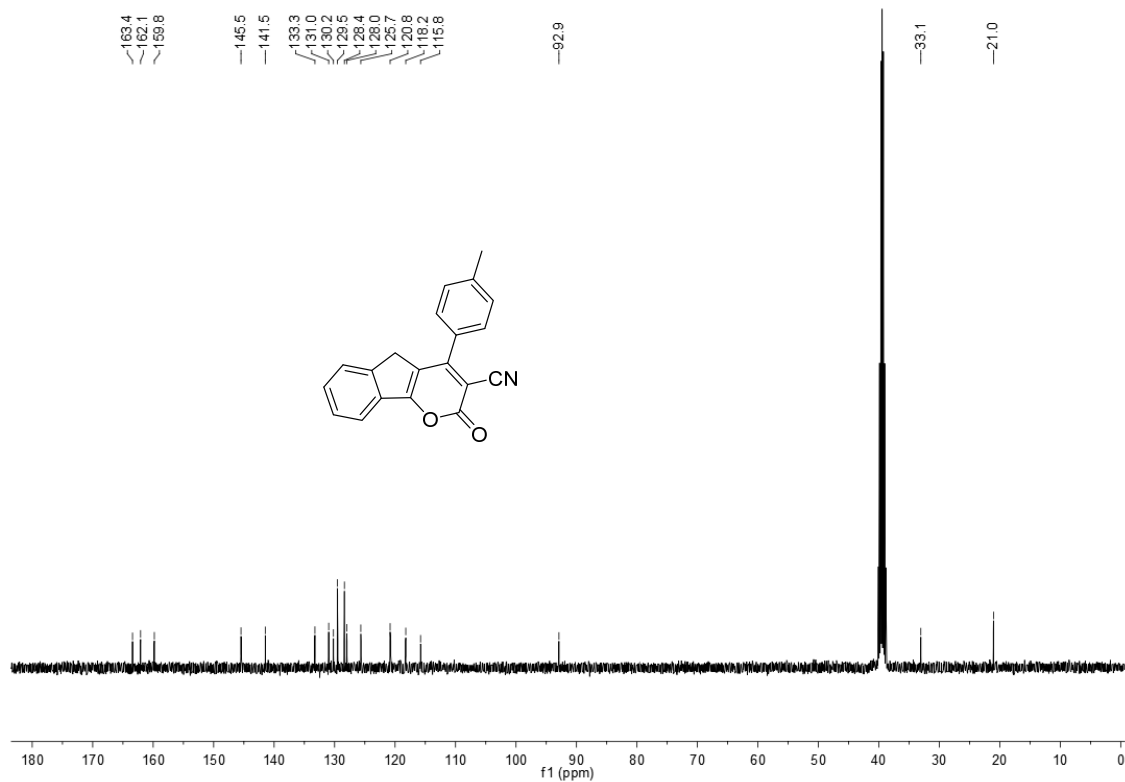
¹H NMR Spectrum of Compound 3f



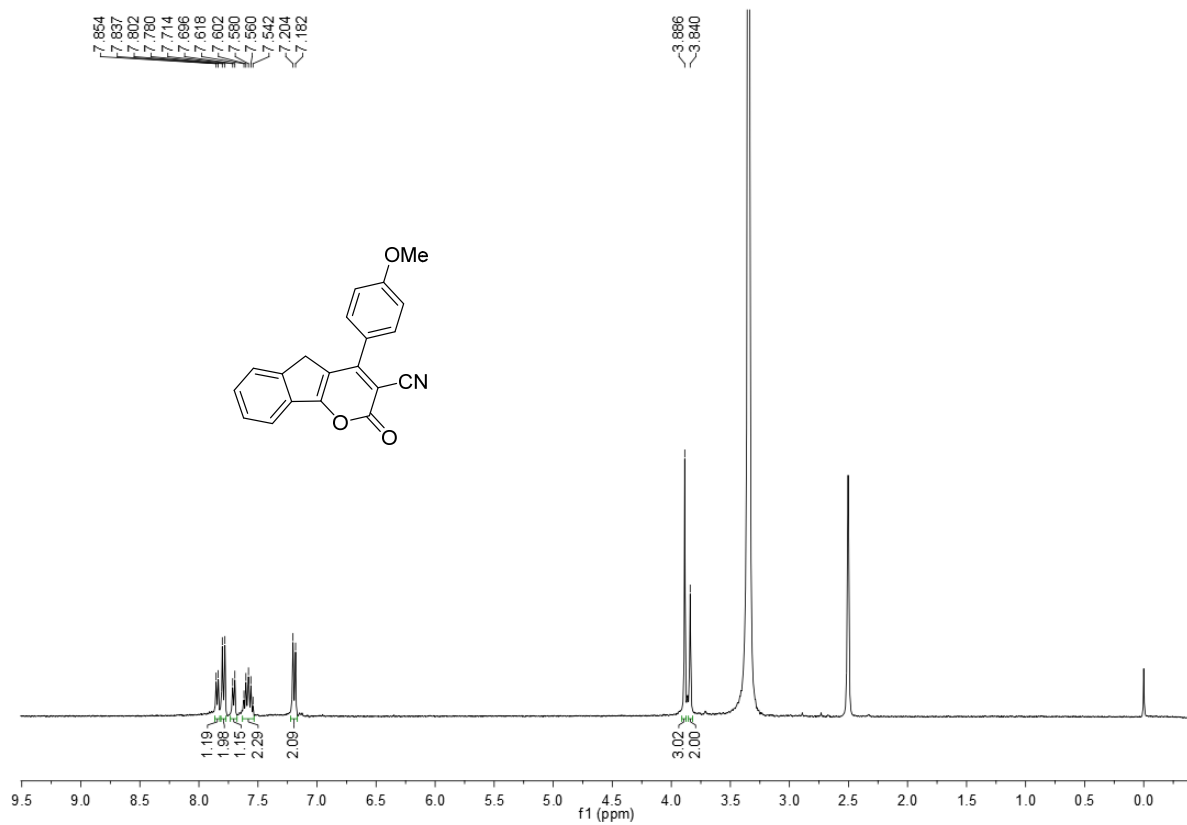
¹³C NMR Spectrum of Compound 3f



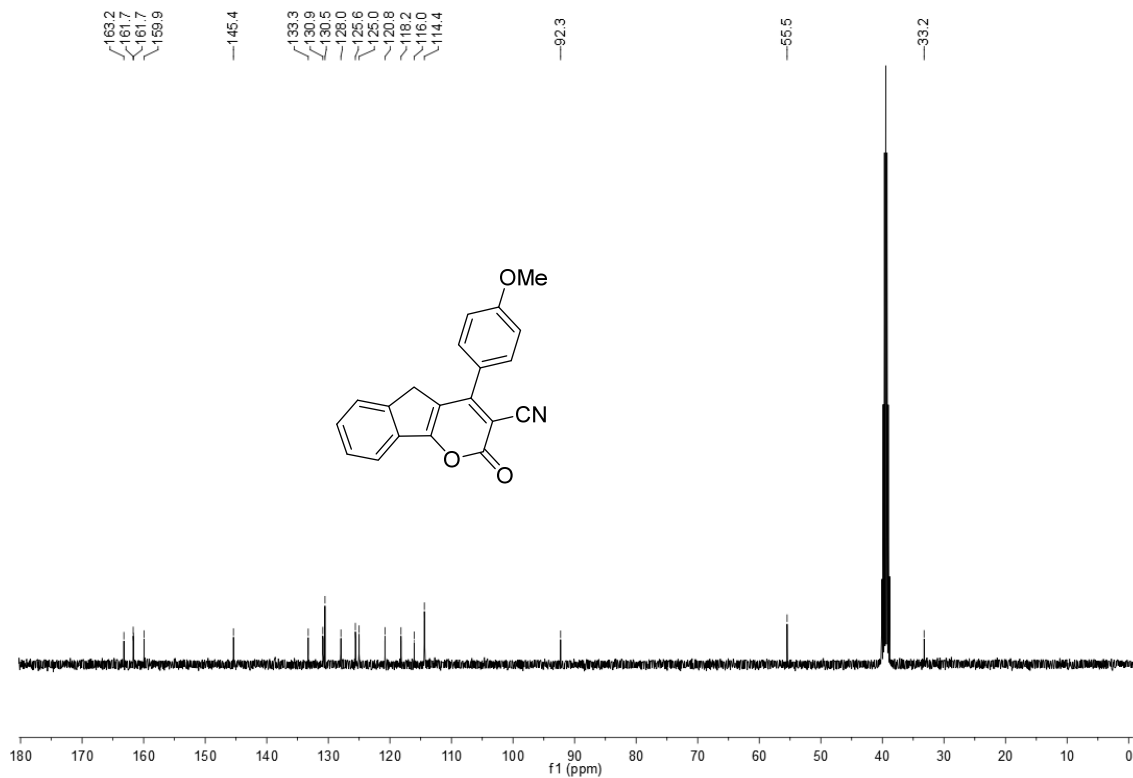
¹H NMR Spectrum of Compound 3g



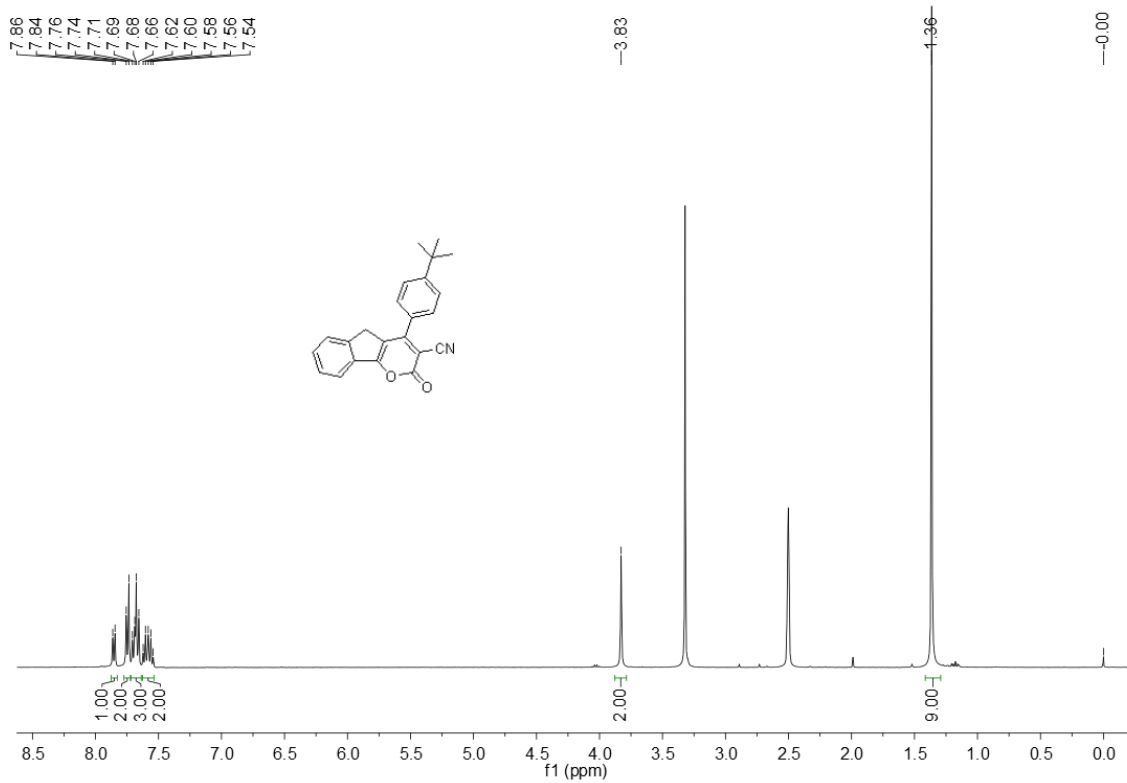
¹³C NMR Spectrum of Compound 3g



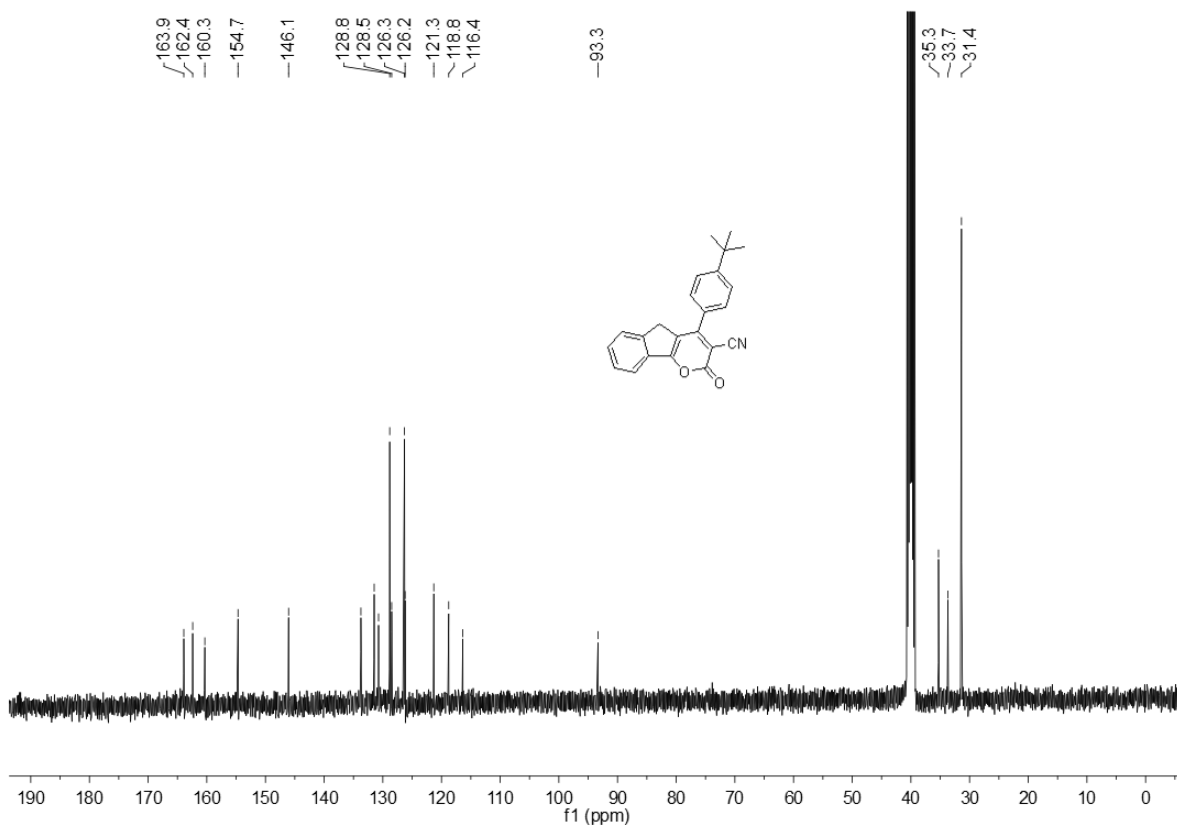
¹H NMR Spectrum of Compound 3h



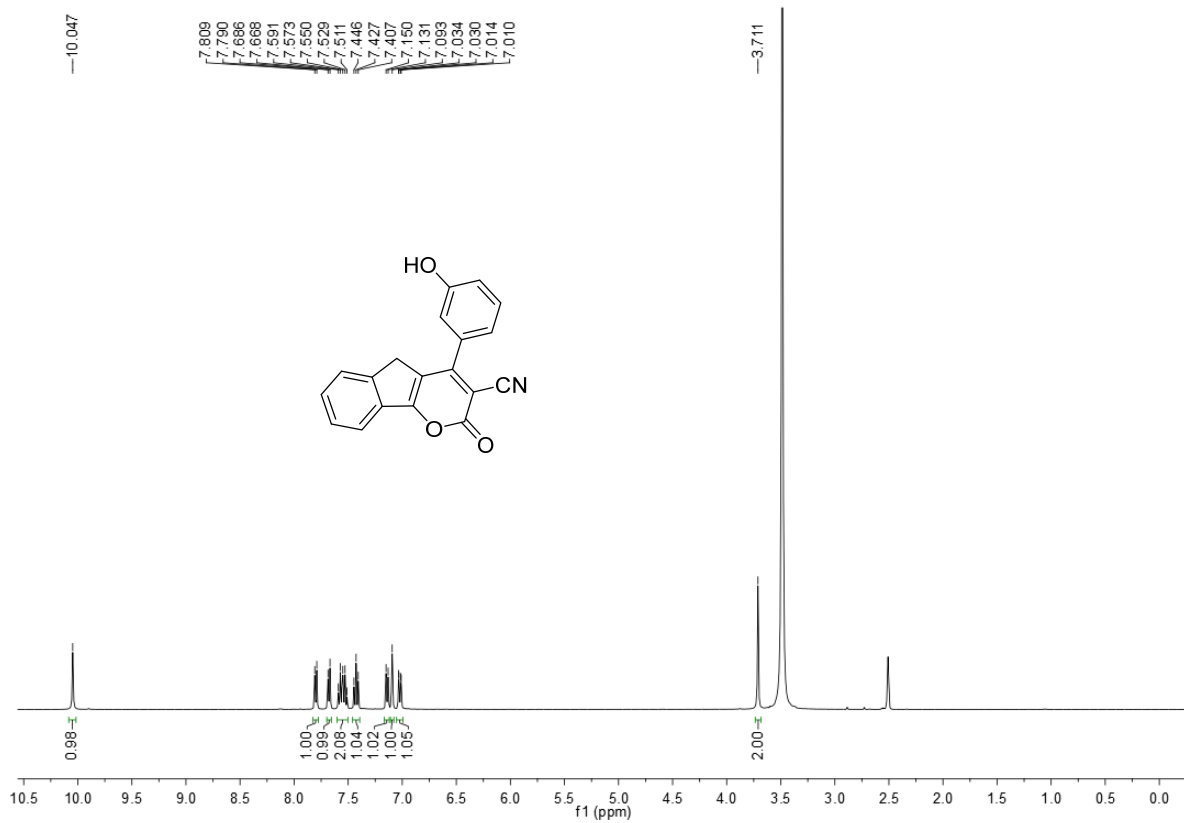
¹³C NMR Spectrum of Compound 3h



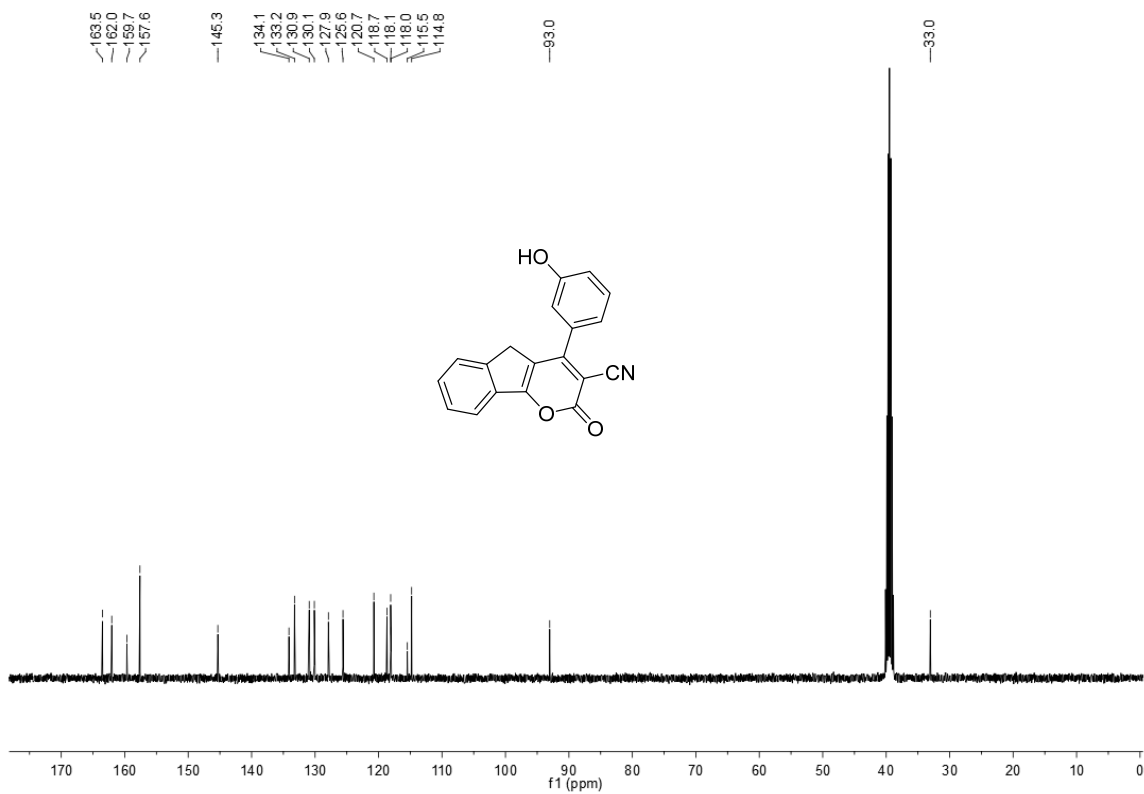
¹H NMR Spectrum of Compound 3i



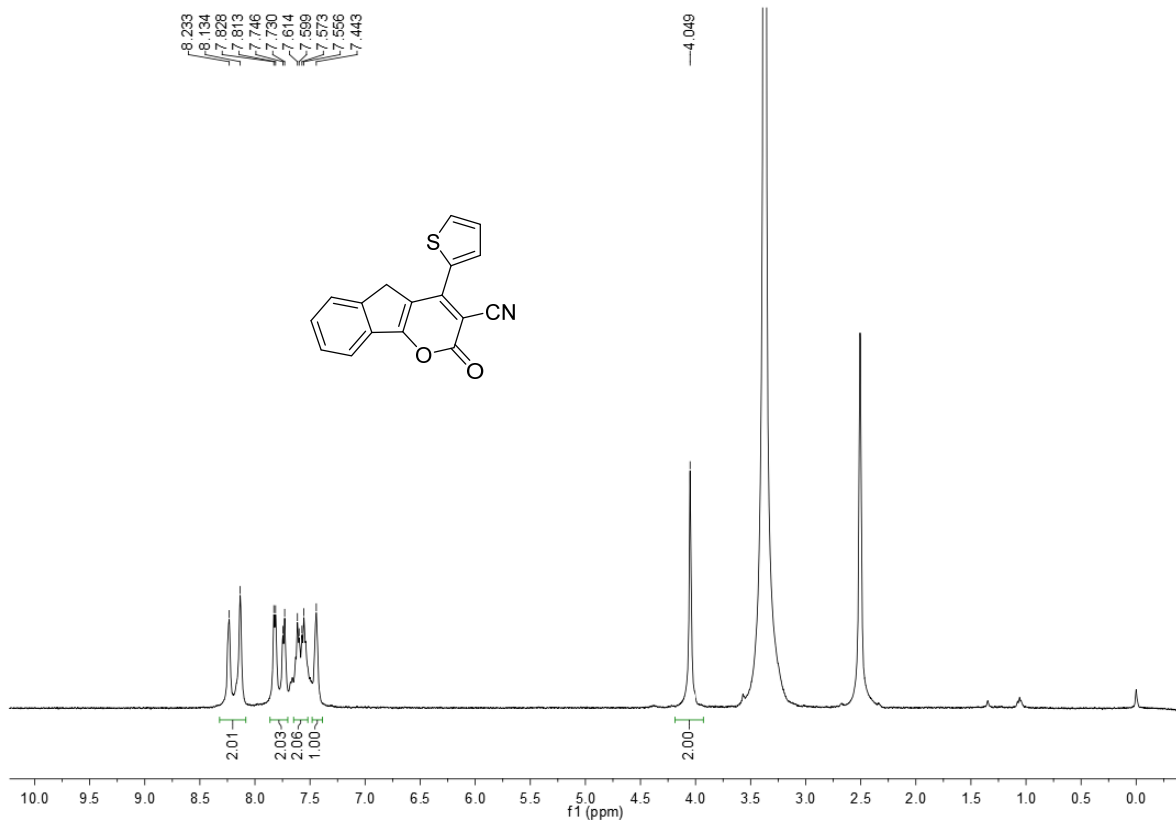
¹³C NMR Spectrum of Compound 3i



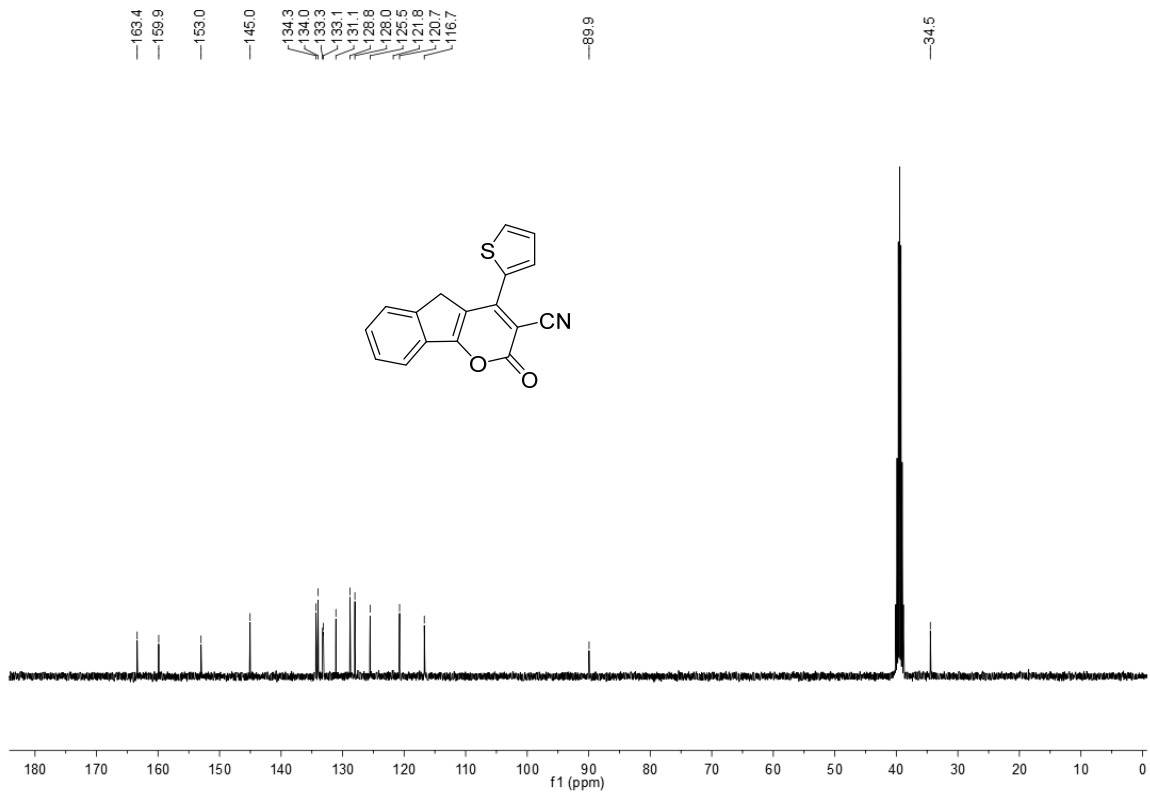
¹H NMR Spectrum of Compound 3j



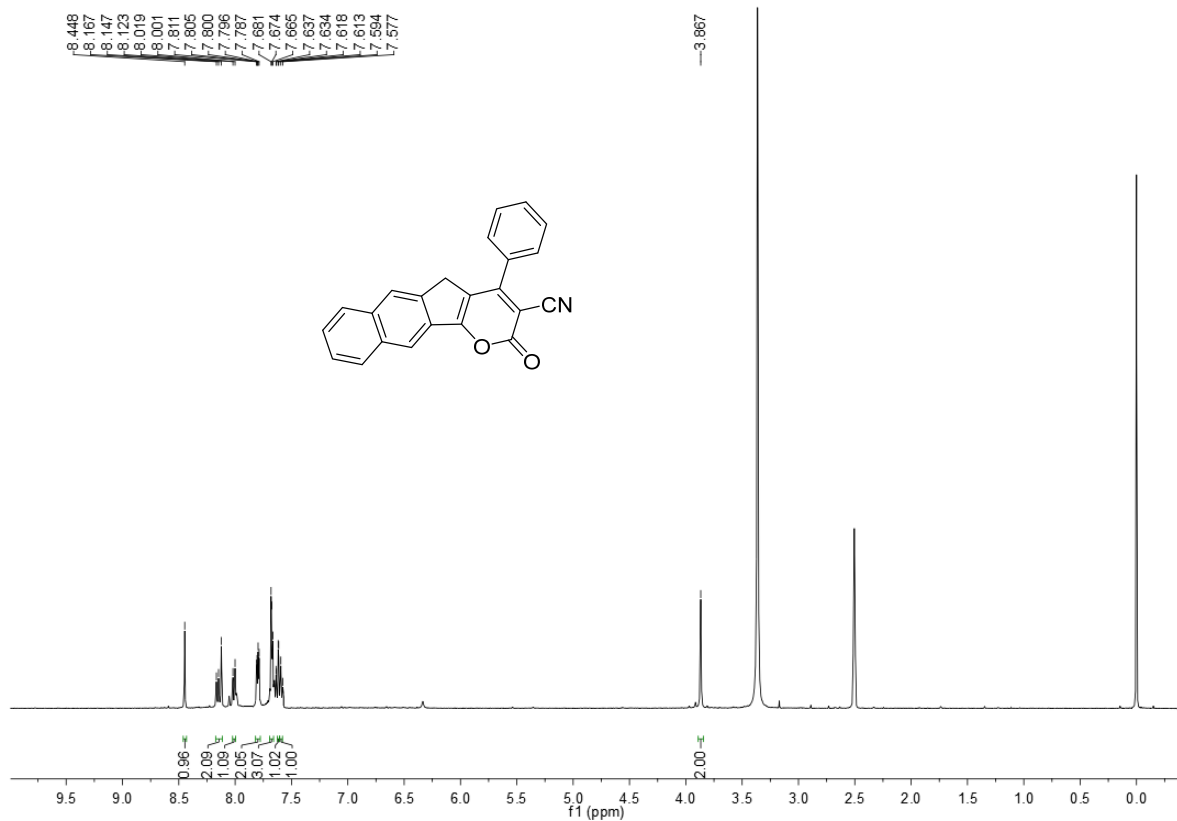
¹³C NMR Spectrum of Compound 3j



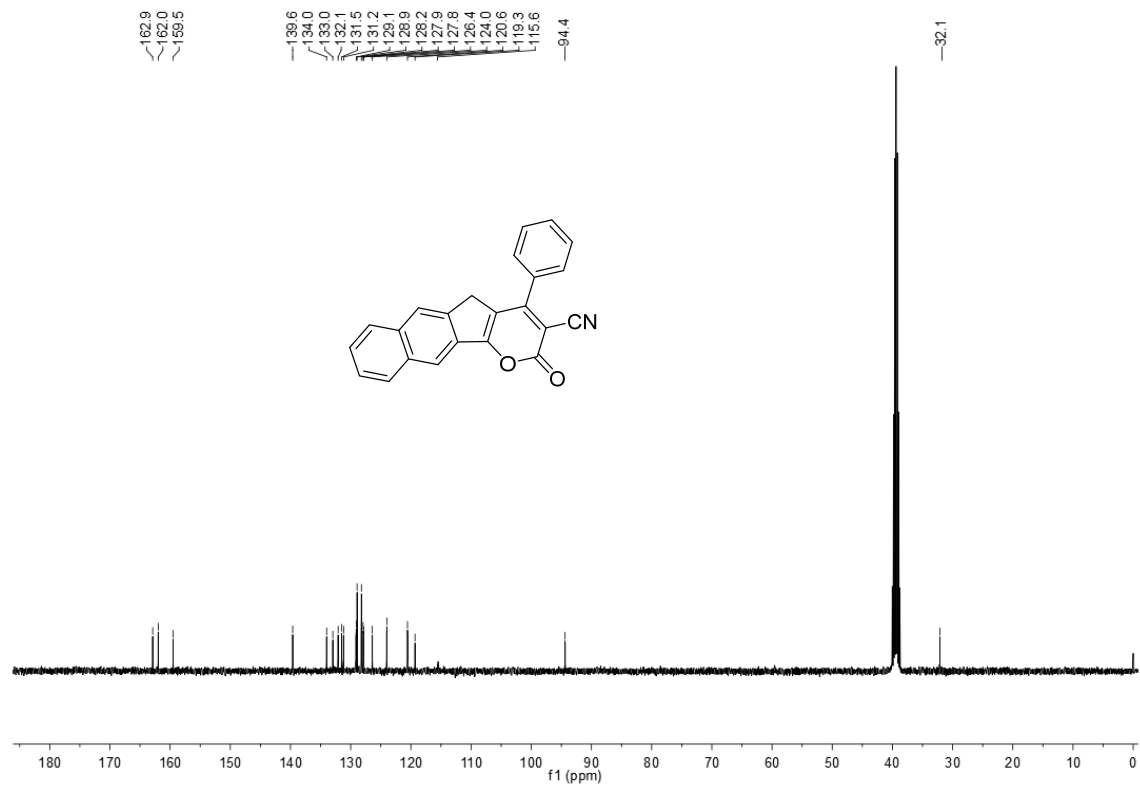
¹H NMR Spectrum of Compound 3k



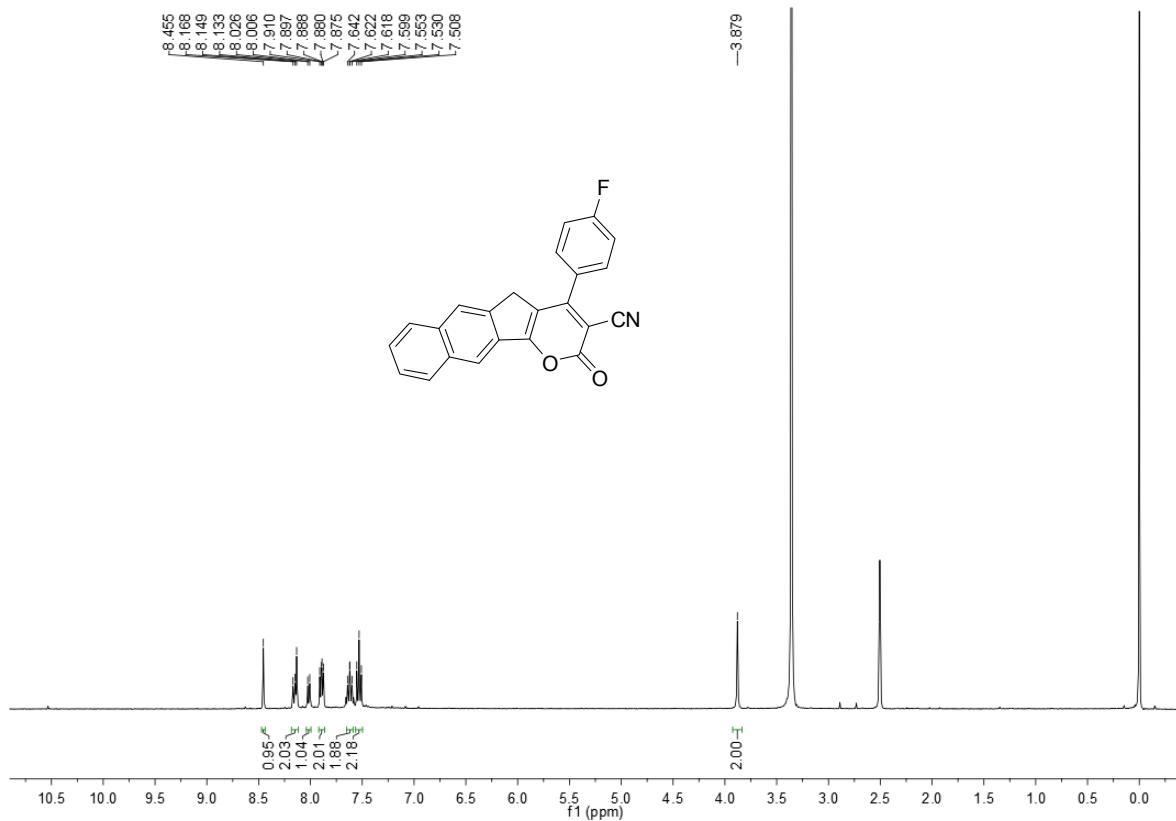
¹³C NMR Spectrum of Compound 3k



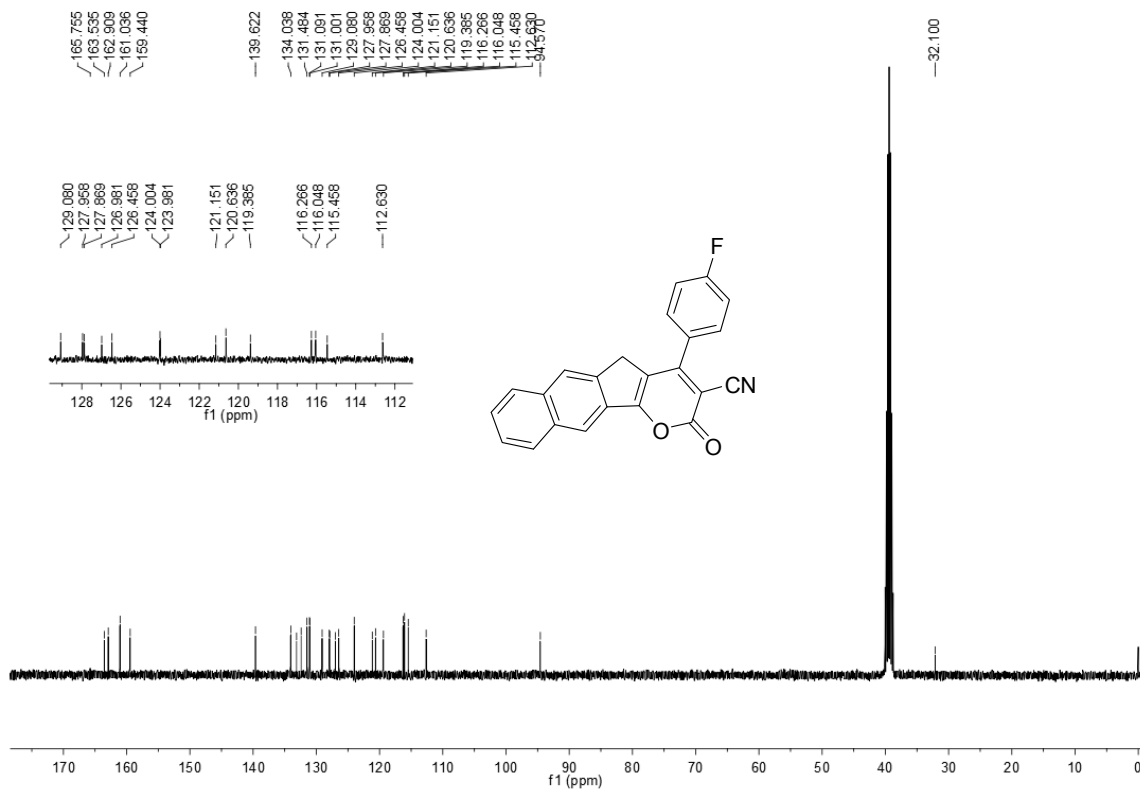
¹H NMR Spectrum of Compound 3l



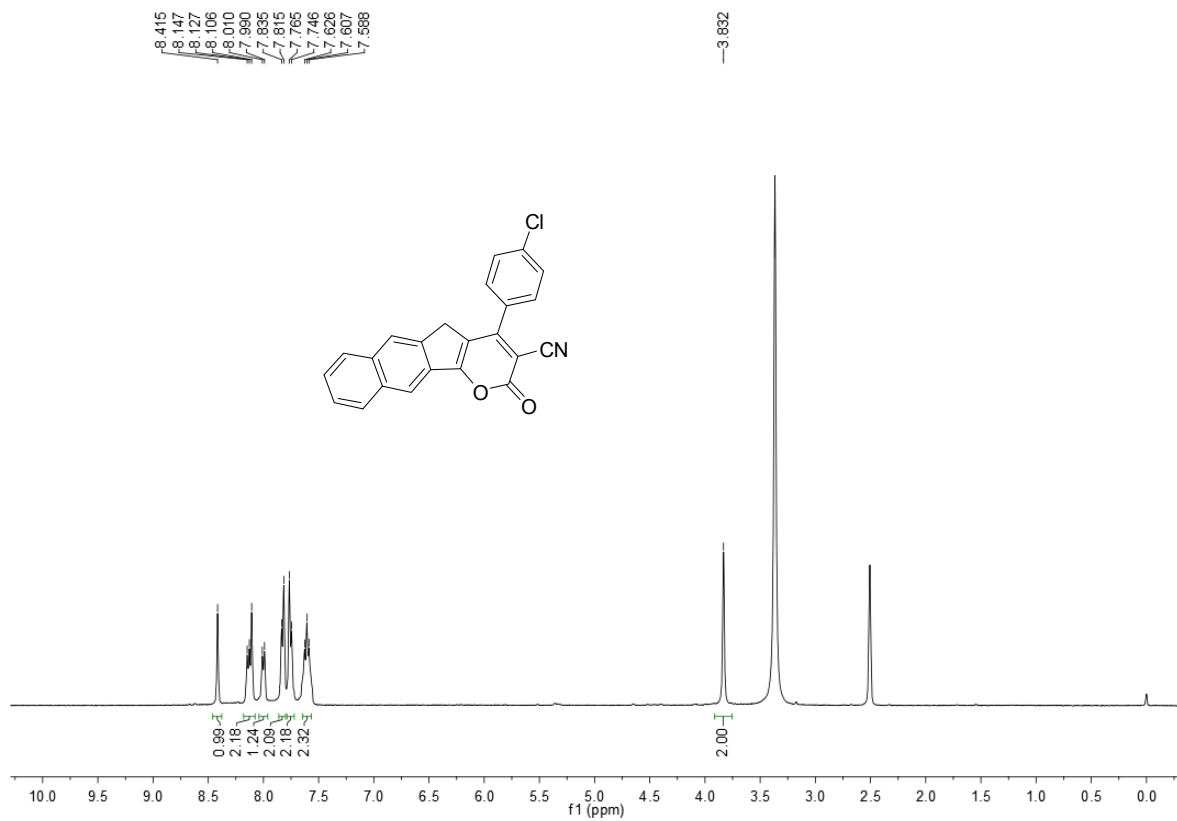
¹³C NMR Spectrum of Compound 3l



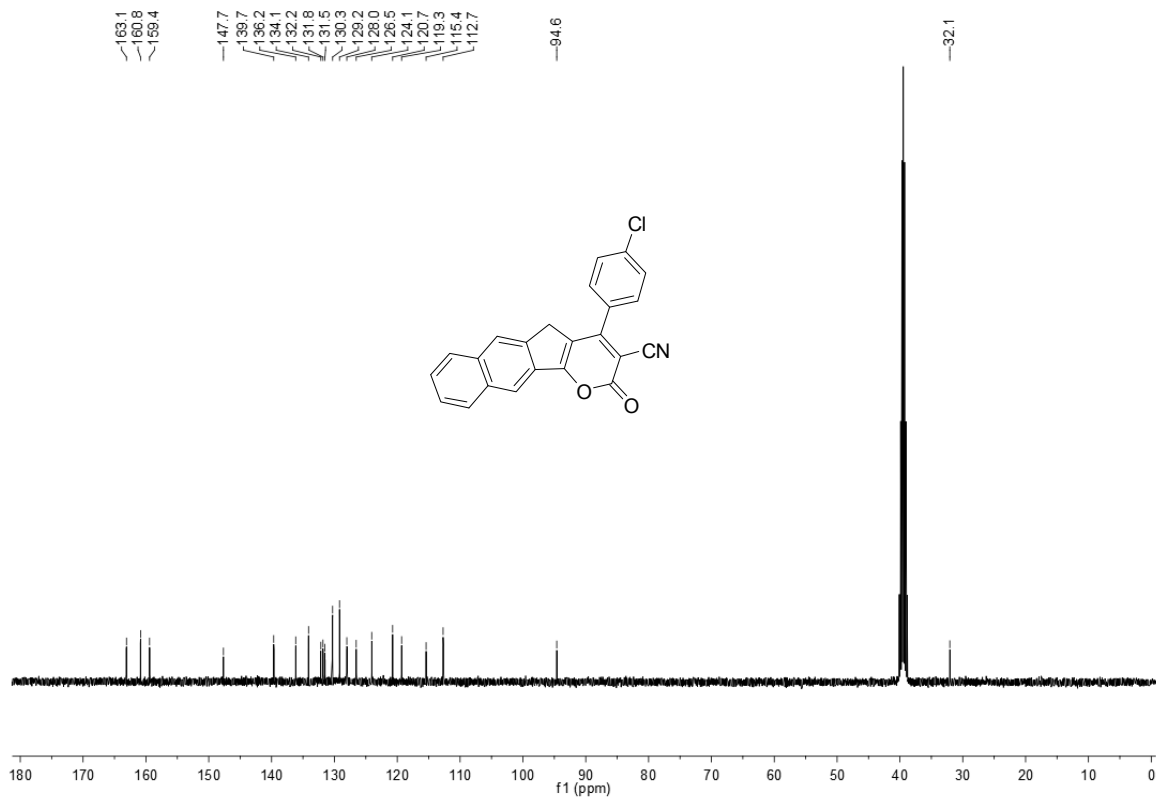
¹H NMR Spectrum of Compound 3m



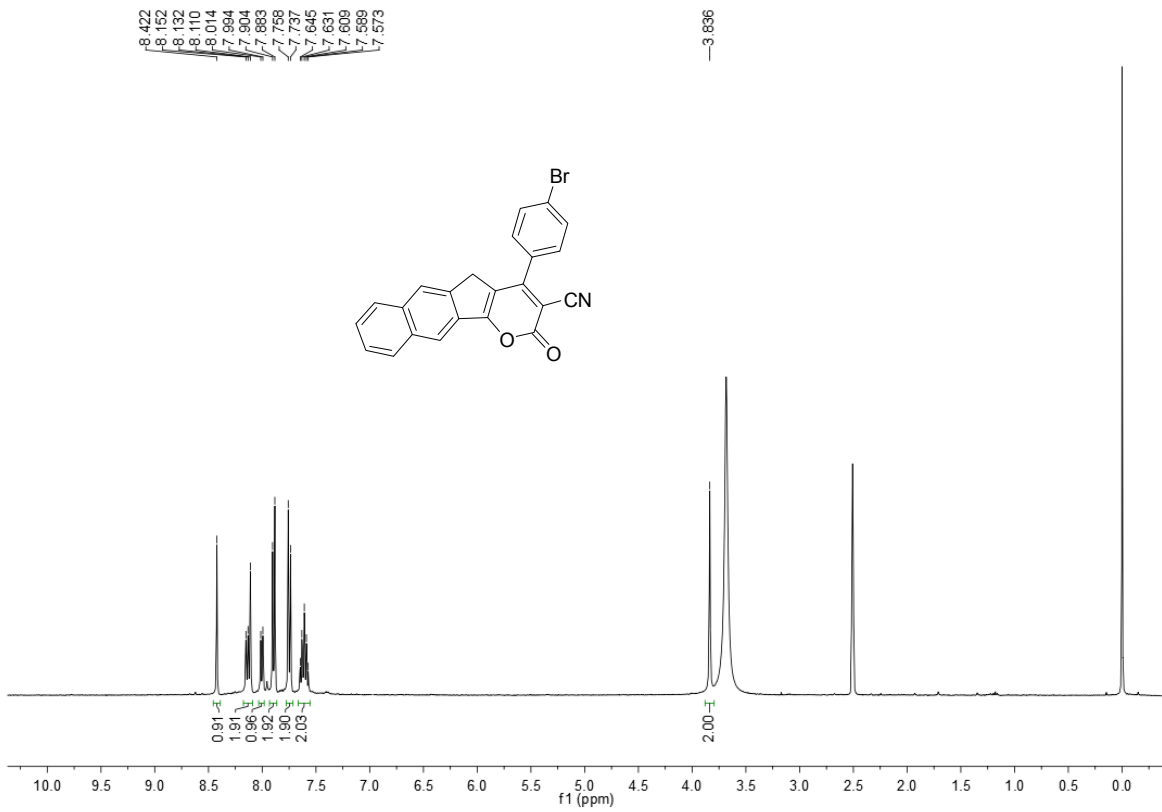
¹³C NMR Spectrum of Compound 3m



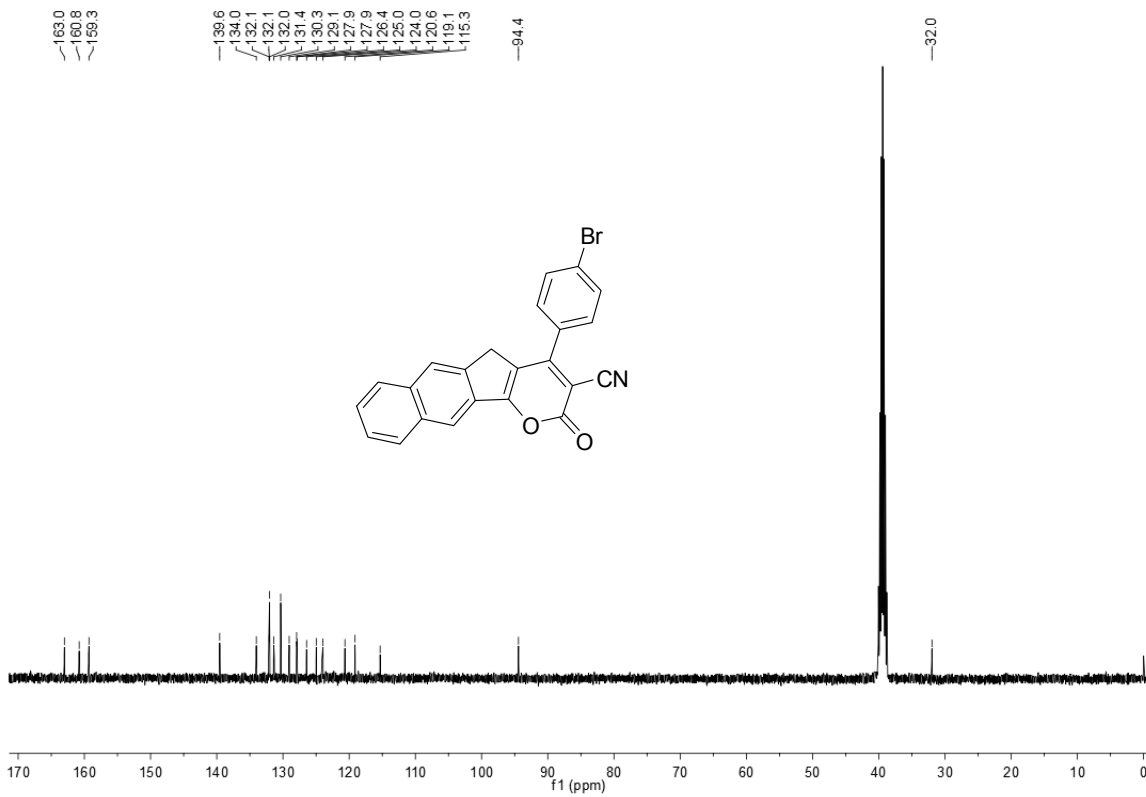
¹H NMR Spectrum of Compound 3n



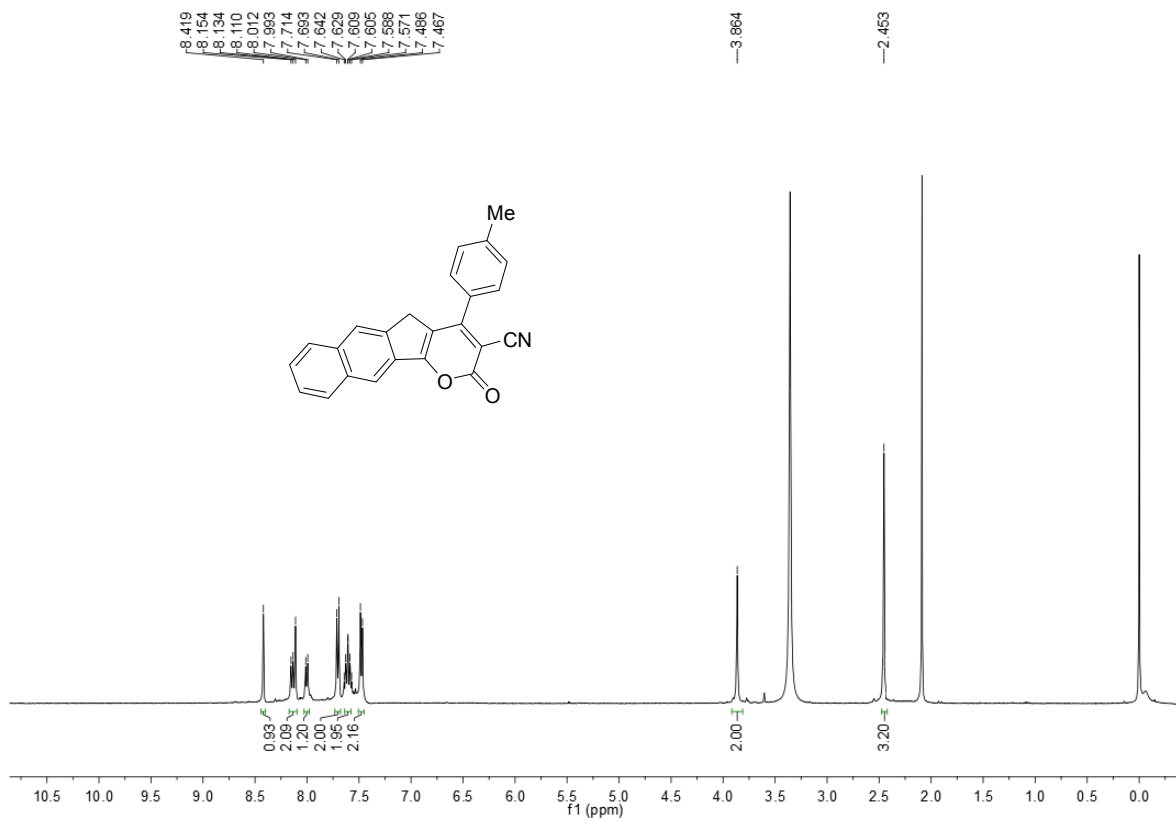
¹³C NMR Spectrum of Compound 3n



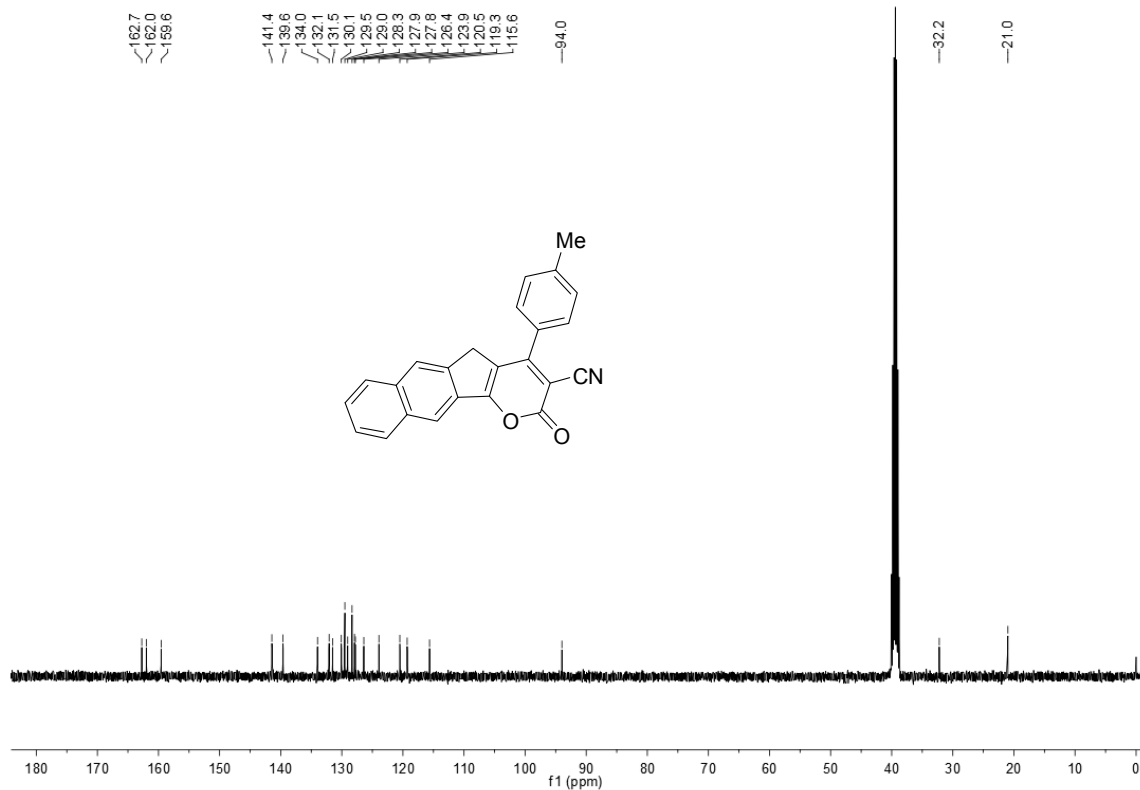
¹H NMR Spectrum of Compound 3o



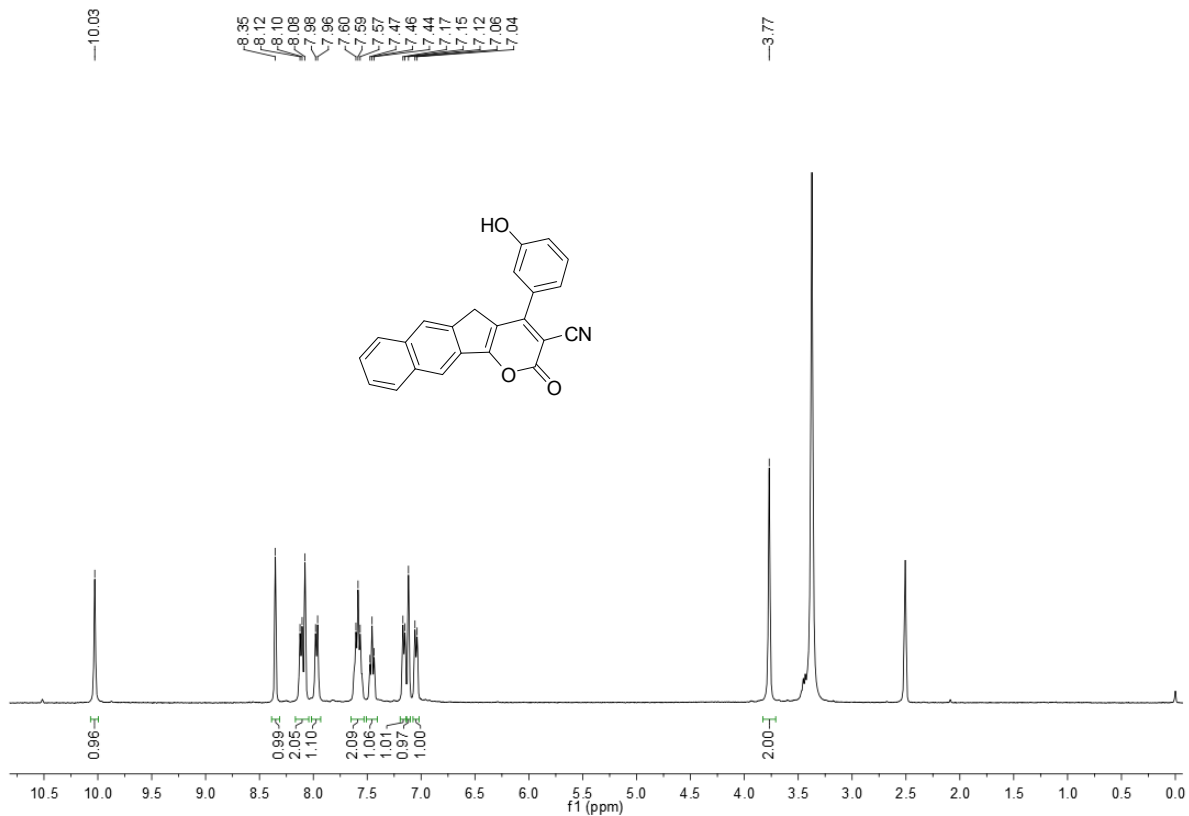
¹³C NMR Spectrum of Compound 3o



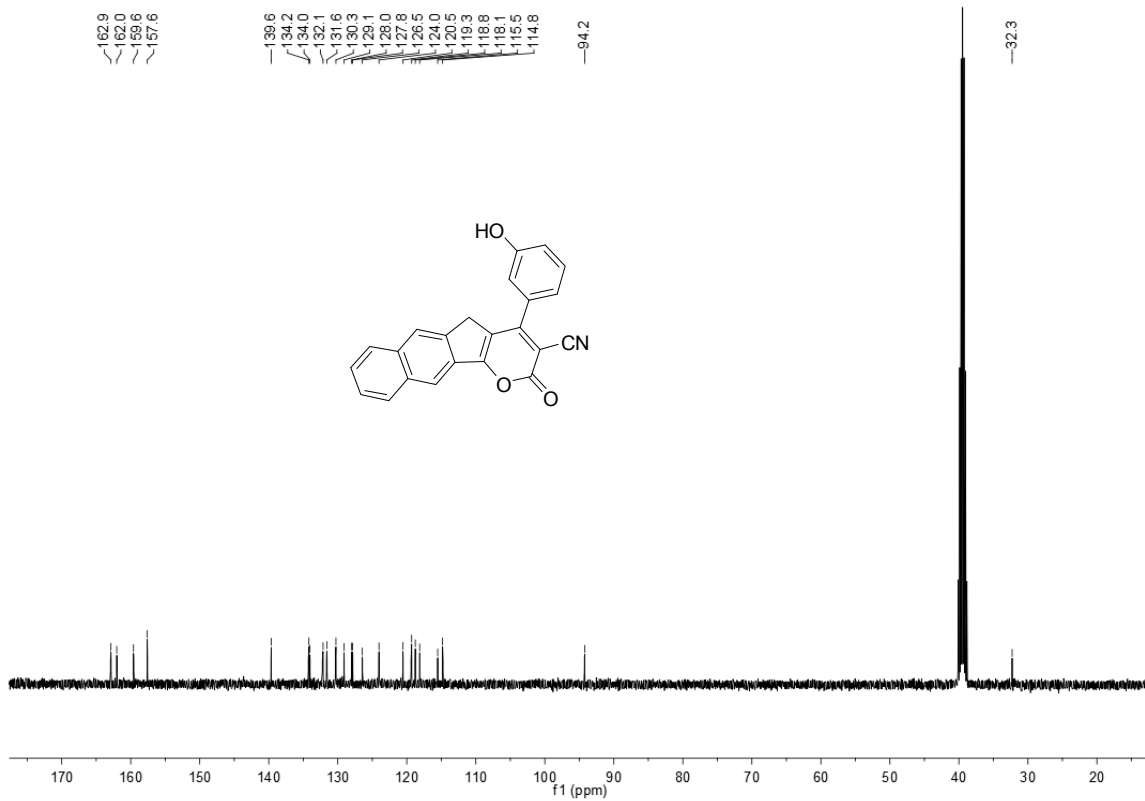
¹H NMR Spectrum of Compound 3p



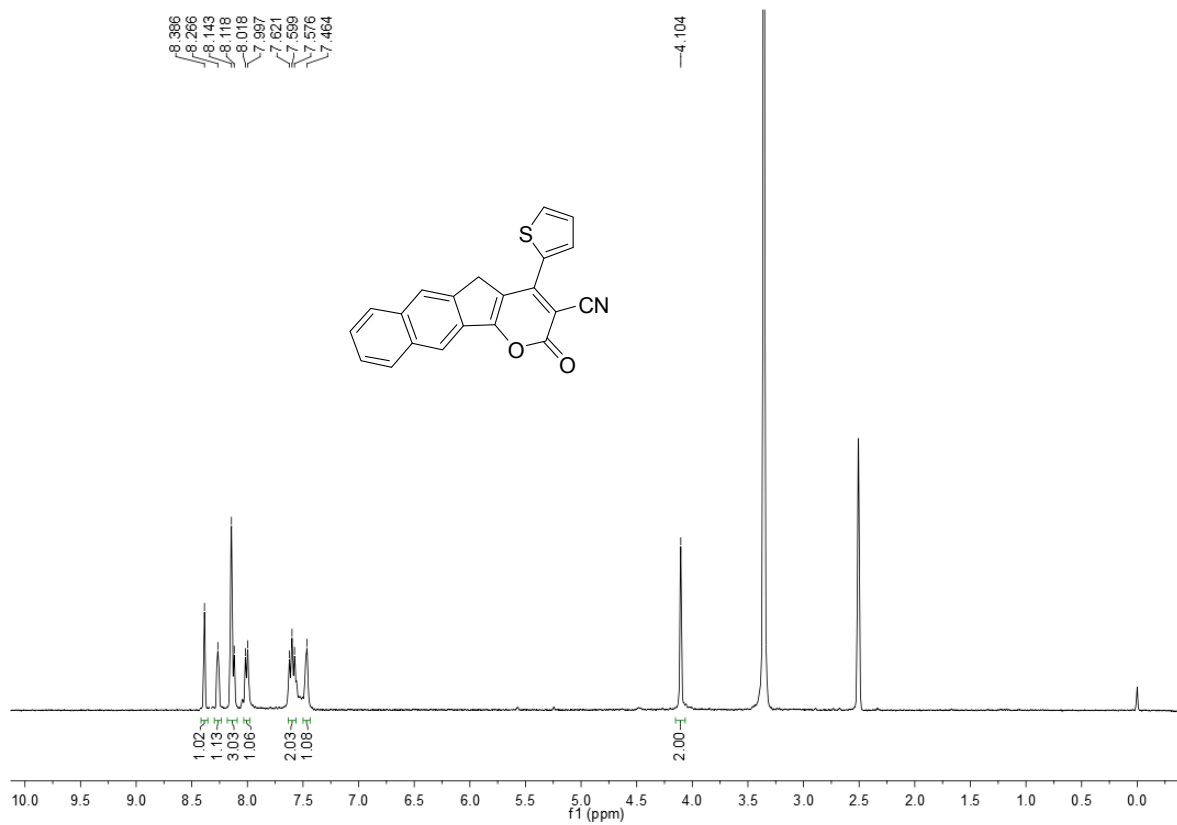
¹³C NMR Spectrum of Compound 3p



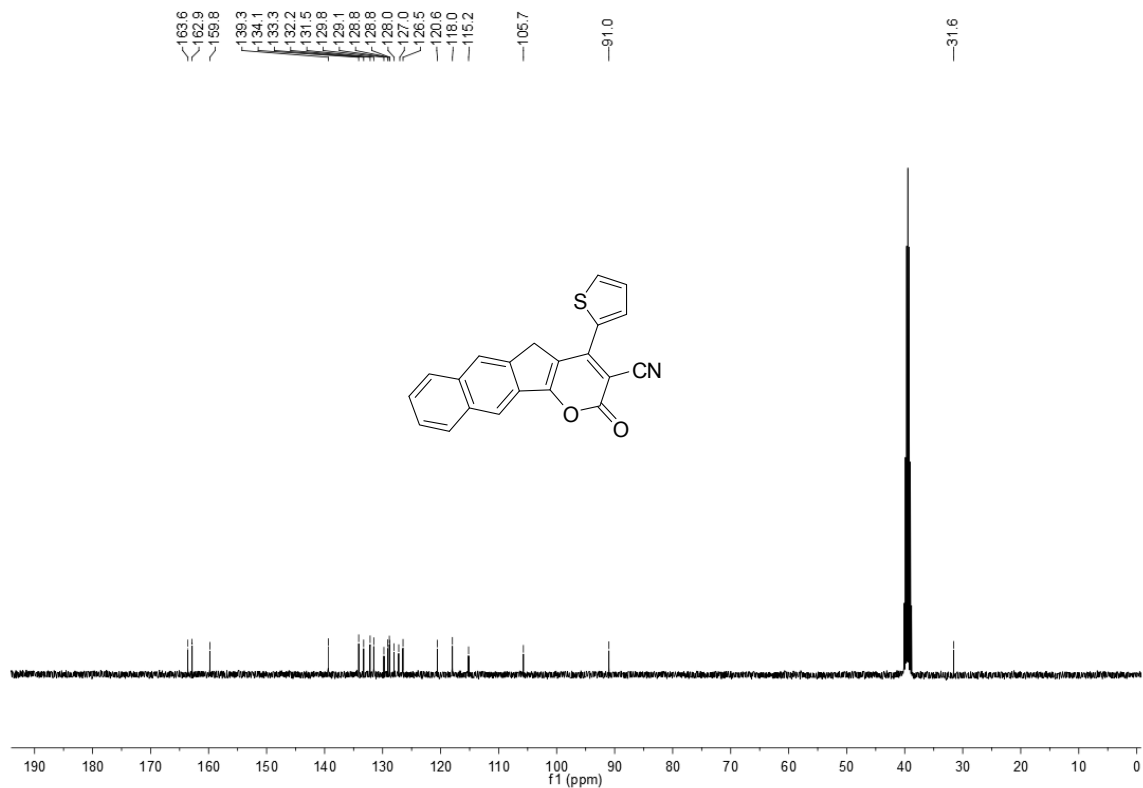
¹H NMR Spectrum of Compound 3q



¹³C NMR Spectrum of Compound 3q



¹H NMR Spectrum of Compound 3r



¹³C NMR Spectrum of Compound 3r

