

Eco-friendly construction of highly functionalized chromenopyridinones by an organocatalyzed solid-state melt reaction and their optical properties

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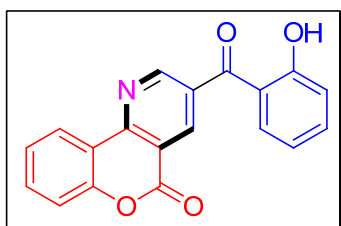
Experimental

All experiments were carried out under open air without inert gases protection. 4-hydroxycoumarin, 3-formylchromones and ammonium acetate were purchased from Sigma-Aldrich. Merck precoated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Melting points were determined with micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian-VNS or DPX (300 MHz and 600 MHz) spectrometer in CDCl_3 , $\text{DMSO}-d_6$ and pyridine- d_5 . IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High resolution mass (HRMS) were obtained with a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.

General procedure for the synthesis of chromenopyridine derivatives (4, 5 and 6):

A mixture of 4-hydroxycoumarin (1.0 mmol), ammonium acetate (2.0 mmol) and 3-formylchromone (1.0 mmol) was heated to 130 °C in the presence of L-proline (15 mol.%) for 4-5 h (TLC). After completion of the reaction (TLC), ethanol was added to the reaction mixture and the yellow solid separated was filtered and washed with ethanol. The products were finally recrystallized from hot ethanol to afford the pure product.

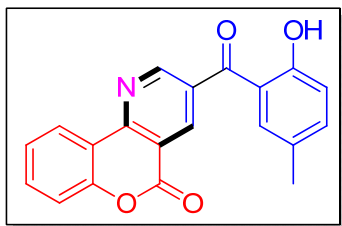
3-(2-Hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4a): The compound was



prepared according to the general procedure. Yield: 91% (289 mg); Characteristic: Yellow solid; Mp: 208-210 °C; ^1H NMR (300 MHz, CDCl_3): δ 11.71 (1H, s), 9.27 (1H, d, J = 2.1 Hz), 8.86 (1H, d, J = 2.1 Hz), 8.61 (1H, d, J = 8.1 Hz), 7.67-7.52 (3H, m), 7.46-7.39 (2H, m), 7.11 (1H, d, J = 8.4 Hz), 6.93 (1H, t, J =

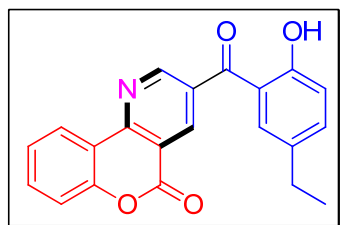
7.6 Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 197.3, 163.4, 160.3, 155.4, 153.8, 153.1, 139.0, 137.4, 133.5, 133.2, 132.6, 125.4, 125.3, 119.4, 118.9, 118.7, 118.6, 117.4, 116.5; IR (KBr): 3069, 1721, 1628, 1594, 1479, 1445 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{11}\text{NO}_4$: 317.0688, Found: 317.0686.

3-(2-Hydroxy-5-methylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4b) : The compound was prepared according to the general procedure. Yield: 92% (304 mg); Characteristic: Yellow solid; Mp: 168-170 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 10.26 (1H, s), 9.28 (1H, d,



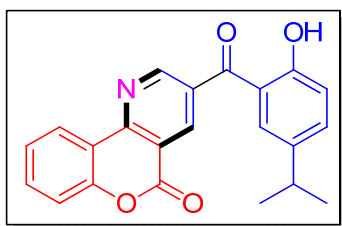
$J = 2.4$ Hz), 8.63 (1H, d, $J = 1.8$ Hz), 8.53 (1H, d, $J = 7.8$ Hz), 7.73 (1H, td, $J = 7.2, 1.2$ Hz), 7.5 (1H, d, $J = 7.2$ Hz), 7.49 (1H, t, $J = 7.2$ Hz), 7.33 (1H, dd, $J = 8.4, 1.8$ Hz), 7.29 (1H, s), 6.93 (1H, d, $J = 8.4$ Hz), 2.27 (3H, s); ^{13}C NMR (150 MHz, DMSO- d_6): δ 193.8, 160.0, 155.4, 154.7, 153.0, 152.7, 138.3, 135.1, 133.4, 133.0, 130.6, 128.4, 125.1, 124.7, 123.5, 118.6, 117.2, 116.9, 116.8, 19.8; IR: 3033, 1729, 1590, 1540, 1471, 1347, 1212 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_4$: 331.0845, Found: 331.0843.

3-(5-Ethyl-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4c): The compound



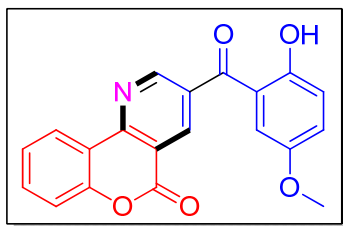
was prepared according to the general procedure. Yield: 91% (314 mg); Characteristic: Yellow solid; Mp: 143-145 $^{\circ}\text{C}$; ^1H NMR (600 MHz, DMSO- d_6): δ 10.29 (1H, s), 9.23 (1H, s), 8.60 (1H, s), 8.45 (1H, d, $J = 8.4$ Hz), 7.68 (1H, t, $J = 7.2$ Hz), 7.43 (2H, t, $J = 6.6$ Hz), 7.36 (1H, d, $J = 7.8$ Hz), 7.31 (1H, s), 6.95 (1H, d, $J = 7.8$ Hz), 2.57 (2H, q, $J = 7.8$ Hz), 1.17 (3H, t, $J = 7.8$ Hz); ^{13}C NMR (150 MHz, DMSO- d_6): δ 193.7, 159.9, 155.0, 152.9, 152.6, 134.8, 134.0, 133.9, 132.9, 129.5, 129.3, 124.9, 124.6, 123.4, 118.4, 117.2, 117.0, 116.9, 116.7, 27.0, 15.6; IR: 3047, 1732, 1597, 1545, 1463, 1349, 1212 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{21}\text{H}_{15}\text{NO}_4$: 345.1001, Found: 345.1001.

3-(2-Hydroxy-5-isopropylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4d): The



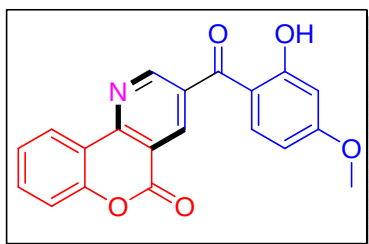
compound was prepared according to the general procedure. Yield: 90% (323 mg); Characteristic: Yellow solid; Mp: 141-143 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 11.53 (1H, s), 9.28 (1H, d, $J = 2.4$ Hz), 8.88 (1H, d, $J = 1.8$ Hz), 8.64 (1H, dd, $J = 8.4, 1.8$ Hz), 7.64 (1H, td, $J = 8.1, 1.8$ Hz), 7.47-7.40 (3H, m), 7.32 (1H, d, $J = 1.8$ Hz), 7.05 (1H, d, $J = 8.4$ Hz), 2.83 (1H, sep, $J = 7.2$ Hz), 1.18 (6H, d, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 197.2, 161.6, 160.3, 155.4, 153.8, 153.1, 139.8, 139.1, 136.1, 133.4, 129.7, 125.4, 125.3, 118.8, 118.6, 118.3, 117.4, 116.6, 33.2, 23.9; IR: 2959, 1742, 1546, 1465, 1338, 1204 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_4$: 359.1158, Found: 359.1154.

3-(2-Hydroxy-5-methoxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4e): The compound



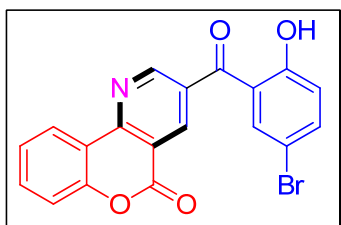
was prepared according to the general procedure. Yield: 92% (319 mg); Characteristic: Yellow solid; Mp: 188-190 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.28 (1H, s), 9.29 (1H, d, $J = 1.8$ Hz), 8.89 (1H, d, $J = 2.4$ Hz), 8.63 (1H, dd, $J = 7.8, 1.2$ Hz), 7.65 (1H, td, $J = 9.0, 1.8$ Hz), 7.44 (1H, t, $J = 7.2$ Hz), 7.41 (1H, d, $J = 8.4$ Hz), 7.20 (1H, dd, $J = 9.6, 3.0$ Hz), 7.06 (1H, d, $J = 9.0$ Hz), 6.93 (1H, d, $J = 3.0$ Hz), 3.70 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 196.8, 160.3, 157.7, 155.4, 153.9, 153.1, 151.9, 138.9, 133.5, 133.3, 125.5, 125.4, 125.3, 119.9, 118.6, 118.1, 117.4, 116.6, 114.8, 55.9; IR: 3059, 1735, 1571, 1481, 1457, 1382, 1255 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_5$: 347.0794, Found: 347.0796.

3-(2-Hydroxy-4-methoxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4f): The compound



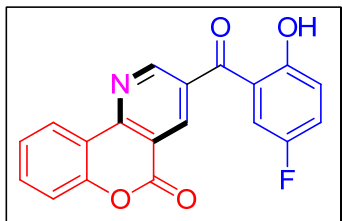
was prepared according to the general procedure. Yield: 90% (312 mg); Characteristic: Yellow solid; Mp: 206-208 °C; ^1H NMR (600 MHz, CDCl_3): δ 12.36 (1H, s), 9.24 (1H, s), 8.83 (1H, d, $J = 1.2$ Hz), 8.62 (1H, d, $J = 7.8$ Hz), 7.64 (1H, t, $J = 7.8$ Hz), 7.45-7.40 (3H, m), 6.54 (1H, d, $J = 1.2$ Hz), 6.46 (1H, dd, $J = 9.0, 1.8$ Hz), 3.88 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 195.3, 167.1, 166.6, 160.4, 155.3, 153.6, 153.1, 138.6, 134.3, 133.7, 133.3, 125.4, 125.3, 118.7, 117.4, 116.5, 112.8, 108.5, 101.4, 55.8; IR: 3077, 1748, 1597, 1507, 1369, 1286 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_5$: 347.0794, Found: 347.0795.

3-(5-Bromo-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4g): The compound



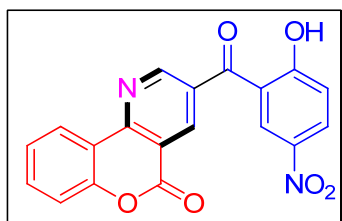
was prepared according to the general procedure. Yield: 86% (340 mg); Characteristic: Yellow solid; Mp: 221-223 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.59 (1H, s), 9.25 (1H, s), 8.87 (1H, s), 8.62 (1H, d, $J = 6.6$ Hz), 7.67-7.62 (3H, m), 7.44 (1H, t, $J = 7.8$ Hz), 7.41 (1H, d, $J = 8.4$ Hz), 7.03 (1H, d, $J = 9.0$ Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 196.4, 162.3, 160.2, 155.1, 154.2, 153.2, 140.1, 139.0, 134.3, 133.7, 132.7, 125.5, 125.3, 121.0, 119.9, 118.5, 117.5, 116.8, 110.9; IR: 3301, 1741, 1589, 1456, 1336, 1196 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{BrNO}_4$: 394.9793, Found: 394.9790.

3-(5-Fluoro-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4h): The compound



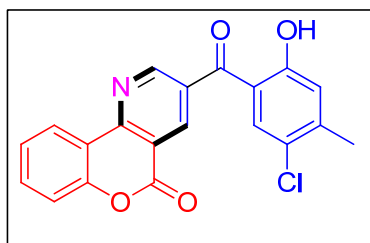
was prepared according to the general procedure. Yield: 84% (281 mg); Characteristic: Yellow solid; Mp: 224-226 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.44 (1H, s), 9.29 (1H, d, $J = 1.8$ Hz), 8.89 (1H, d, $J = 1.8$ Hz), 8.65 (1H, dd, $J = 7.8, 1.2$ Hz), 7.67 (1H, td, $J = 8.4, 1.8$ Hz), 7.47-7.42 (2H, m), 7.35-7.32 (1H, m), 7.21 (1H, dd, $J = 7.8, 2.4$ Hz), 7.11 (1H, dd, $J = 9.0, 4.2$ Hz); ^{13}C NMR (150 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$): δ 194.6 (d, $J = 2.2$ Hz), 159.7, 156.8, 155.0, 154.6 (d, $J = 239.1$ Hz), 153.4, 152.5, 138.5, 132.9, 132.2, 124.9, 124.7, 123.2 (d, $J = 23.1$ Hz), 119.7 (d, $J = 5.7$ Hz), 119.2 (d, $J = 6.9$ Hz), 118.0, 116.7, 116.4 (d, $J = 22.9$ Hz), 116.0; IR: 3064, 1738, 1628, 1471, 1341, 1209 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{FNO}_4$: 335.0594, Found: 335.0594.

3-(2-Hydroxy-5-nitrobenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4i): The compound was



prepared according to the general procedure. Yield: 75% (271 mg); Characteristic: White solid; Mp: 282-285 °C; ^1H NMR (600 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$): δ 11.96 (1H, s), 9.31 (1H, d, $J = 2.4$ Hz), 8.70 (1H, d, $J = 1.8$ Hz), 8.54 (1H, dd, $J = 7.8, 1.2$ Hz), 8.35-8.33 (2H, m), 7.71 (1H, td, $J = 8.4, 1.2$ Hz), 7.48-7.45 (2H, m), 7.22 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (150 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$): δ 191.2, 161.8, 159.8, 155.6, 153.5, 152.8, 139.8, 138.4, 133.5, 132.1, 128.8, 126.7, 125.0, 124.9, 124.7, 118.4, 117.5, 117.1, 116.8; IR: 3212, 1709, 1658, 1594, 1522, 1430, 1341, 1291 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{N}_2\text{O}_6$: 362.0539, Found: 362.0538.

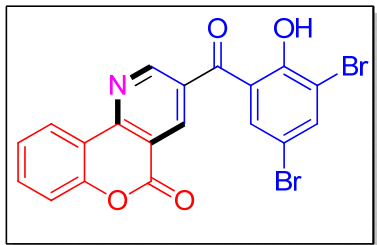
3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4j): The



compound was prepared according to the general procedure. Yield: 87% (318 mg); Characteristic: Yellow solid; Mp: 273-276 °C; ^1H NMR (600 MHz, DMSO-d_6): δ 10.62 (1H, s), 9.27 (1H, d, $J = 1.8$ Hz), 8.63 (1H, d, $J = 1.2$ Hz), 8.50 (1H, d, $J = 7.8$ Hz), 7.72 (1H, t, $J = 7.5$ Hz), 7.48-7.46 (3H, m), 6.98 (1H, s), 2.34 (3H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 191.9, 159.9, 155.5, 153.1, 152.7, 142.1, 138.3, 133.4, 132.8, 130.3, 125.1, 124.8, 123.8, 123.2, 119.4, 118.5, 117.2, 116.8, 20.0; IR: 3060, 1740, 1595, 1547, 1379, 1331 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{12}\text{ClNO}_4$:

365.0455, Found: 365.0453.

3-(3,5-Dibromo-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (4k): The

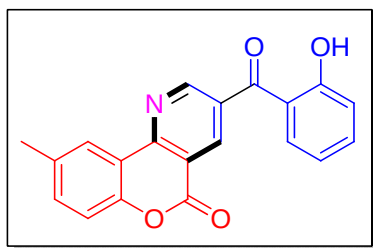


compound was prepared according to the general procedure.

Yield: 79% (375 mg); Characteristic: Yellow solid; Mp: 260-262 °C; ^1H NMR (600 MHz, DMSO- d_6): δ 10.80 (1H, s), 9.30 (1H, s), 8.64 (1H, d, J = 2.4 Hz), 8.54 (1H, d, J = 8.4 Hz), 8.08 (1H, d, J = 1.8 Hz), 7.75 (1H, t, J = 8.1 Hz),

7.64 (1H, d, J = 2.4 Hz), 7.51 (2H, d, J = 7.8 Hz); ^{13}C NMR (150 MHz, DMSO- d_6): δ 192.2, 159.9, 155.6, 153.5, 152.9, 152.8, 138.7, 138.5, 133.7, 132.3, 132.0, 127.4, 125.2, 124.9, 118.5, 117.3, 116.9, 113.8, 111.3; IR: 2920, 1744, 1584, 1423, 1324, 1225 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_9\text{Br}_2\text{NO}_4$: 472.8898, Found: 472.8899.

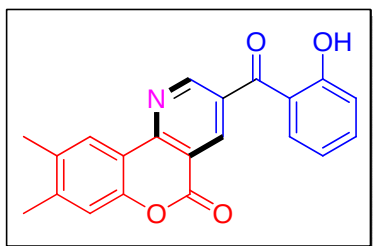
3-(2-Hydroxybenzoyl)-9-methyl-5H-chromeno[4,3-b]pyridin-5-one (5a): The compound



was prepared according to the general procedure. Yield: 91% (301 mg); Characteristic: Yellow solid; Mp: 218-220 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.7 (1H, s), 9.26 (1H, d, J = 2.4 Hz), 8.85 (1H, d, J = 2.4 Hz), 8.39 (1H, s), 7.58-7.52 (2H, m), 7.43 (1H, dd, J = 8.4, 1.8 Hz), 7.28 (1H, d, J = 8.4 Hz), 7.11

(1H, d, J = 8.4 Hz), 6.93 (1H, t, J = 7.8 Hz), 2.48 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 197.3, 163.4, 160.4, 155.3, 153.9, 151.2, 139.0, 137.4, 135.2, 134.5, 133.0, 132.6, 125.0, 119.4, 118.9, 118.6, 118.1, 117.1, 116.5, 20.9; IR: 3067, 1722, 1627, 1552, 1452, 1386, 1333, 1244 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_4$: 331.0845, Found: 331.0841.

3-(2-Hydroxybenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5b): The



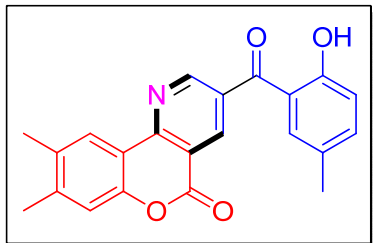
compound was prepared according to the general procedure.

Yield: 91% (314 mg); Characteristic: Yellow solid; Mp: 205-208 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.73 (1H, s), 9.25 (1H, d, J = 2.4 Hz), 8.86 (1H, d, J = 2.4 Hz), 8.33 (1H, s), 7.58-7.53 (2H, m), 7.19 (1H, s), 7.11 (1H, d, J = 8.4 Hz),

6.93 (1H, td, J = 7.8, 1.2 Hz), 2.39 (3H, s), 2.38 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 197.4, 163.4, 160.7, 155.4, 154.2, 151.5, 143.9, 139.2, 137.4, 134.3, 132.6, 125.3, 119.4,

118.9, 118.7, 117.9, 116.1, 116.0, 20.4, 19.3; IR: 2921, 1716, 1620, 1597, 1453, 1337, 1231 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{21}\text{H}_{15}\text{NO}_4$: 345.1001, Found: 345.0998.

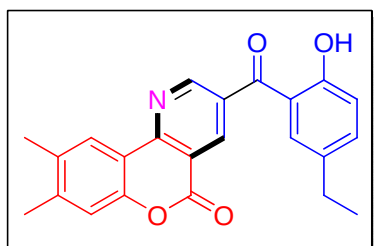
3-(2-Hydroxy-5-methylbenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5c):



The compound was prepared according to the general procedure. Yield: 93% (334 mg); Characteristic: Yellow solid; Mp: 217-219 °C; ^1H NMR (300 MHz, CDCl_3): δ 11.55 (1H, s), 9.22 (1H, d, $J = 2.1$ Hz), 8.63 (1H, d, $J = 2.1$ Hz), 8.31 (1H, s), 7.38 (1H, d, $J = 8.4$ Hz), 7.28 (1H, s), 7.17 (1H, s), 7.01 (1H, d, $J = 8.7$ Hz), 2.39 (6H, s), 2.26 (3H, s); ^{13}C NMR

(75 MHz, CDCl_3): δ 197.3, 162.3, 161.3, 155.3, 154.0, 151.4, 143.8, 139.1, 138.5, 134.2, 132.8, 132.1, 128.6, 125.2, 118.7, 118.4, 117.9, 116.2, 116.0, 20.5, 20.4, 19.3; IR: 3036, 1715, 1595, 1461, 1336, 1196 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_4$: 359.1158, Found: 359.1156.

3-(5-Ethyl-2-hydroxybenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5d): The

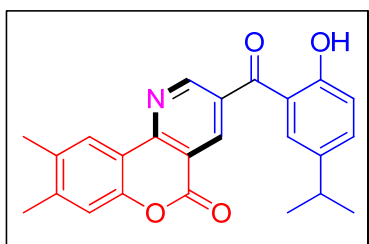


compound was prepared according to the general procedure. Yield: 92% (343 mg); Characteristic: Yellow solid; Mp: 203-204 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.57 (1H, s), 9.23 (1H, d, $J = 1.8$ Hz), 8.85 (1H, d, $J = 2.4$ Hz), 8.30 (1H, s), 7.41 (1H, dd, $J = 8.4, 1.8$ Hz), 7.30 (1H, d, $J = 1.8$ Hz), 7.16

(1H, s), 7.03 (1H, d, $J = 7.8$ Hz), 2.55 (2H, q, $J = 7.8$ Hz), 2.38 (3H, s), 2.37 (3H, s), 1.16 (3H, t, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 197.2, 161.4, 160.6, 155.2, 154.0, 151.4, 143.8, 139.2, 137.4, 135.1, 134.2, 132.8, 131.0, 125.2, 118.7, 118.4, 117.8, 116.2, 115.9, 27.8, 20.4, 19.3, 15.6; IR: 2961, 1731, 1631, 1595, 1544, 1458, 1342, 1245 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_4$: 373.1314, Found: 373.1312.

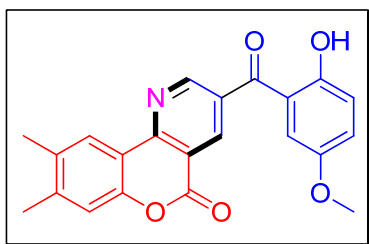
3-(2-Hydroxy-5-isopropylbenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5e):

The compound was prepared according to the general procedure. Yield: 91% (352 mg); Characteristic: Yellow solid; Mp: 167-169 °C; ^1H NMR (300 MHz, CDCl_3): δ 11.56 (1H, s), 9.23 (1H, d, $J = 2.1$ Hz), 8.86 (1H, d, $J = 2.1$ Hz), 8.32 (1H, s), 7.46 (1H, dd, $J = 8.7, 2.1$ Hz), 7.33 (1H, d, $J = 1.8$ Hz), 7.17 (1H, s), 7.05 (1H, d, $J = 8.7$ Hz), 2.83 (1H, sep, $J = 6.9$ Hz),



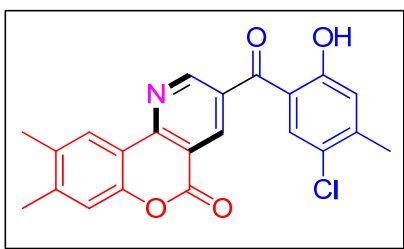
2.39 (3H, s), 2.38 (3H, s), 1.18 (6H, d, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 197.3, 161.5, 155.3, 154.1, 151.5, 143.8, 139.8, 139.3, 135.9, 134.2, 132.8, 129.8, 125.3, 118.8, 118.3, 117.9, 116.2, 33.2, 23.9, 20.4, 19.3; IR: 2961, 1727, 1633, 1594, 1543, 1458, 1343, 1248 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_4$: 387.1471, Found: 387.1472.

3-(2-Hydroxy-5-methoxybenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5f):



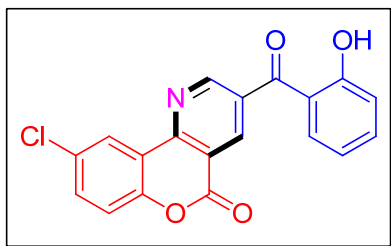
Yield: 92% (345 mg); Characteristic: Yellow solid; Mp: 224-226 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 11.29 (1H, s), 9.25 (1H, d, $J = 2.1$ Hz), 8.86 (1H, d, $J = 1.8$ Hz), 8.29 (1H, s), 7.21-7.16 (2H, m), 7.05 (1H, d, $J = 9.0$ Hz), 6.95 (1H, d, $J = 3.0$ Hz), 3.70 (3H, s), 2.38 (3H, s), 2.37 (3H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 196.9, 162.3, 160.7, 157.7, 155.3, 154.2, 151.9, 151.5, 143.9, 139.1, 134.2, 132.6, 125.3, 119.9, 118.2, 117.9, 116.1, 115.9, 114.8, 55.9, 20.4, 19.3; IR: 3058, 1720, 1599, 1553, 1471, 1353, 1211 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_5$: 375.1107, Found: 375.1104.

3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (5g):



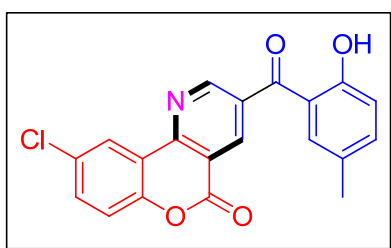
one (5g): The compound was prepared according to the general procedure. Yield: 86% (338 mg); Characteristic: Yellow solid; Mp: 282-284 $^{\circ}\text{C}$; ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 10.58 (1H, s), 9.26 (1H, d, $J = 1.8$ Hz), 8.61 (1H, d, $J = 2.4$ Hz), 8.26 (1H, s), 7.49 (1H, s), 7.30 (1H, s), 6.99 (1H, s), 2.37 (3H, s), 2.36 (3H, s), 2.35 (3H, s); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 191.9, 160.2, 155.4, 155.3, 153.3, 151.0, 143.5, 141.9, 138.4, 133.6, 132.2, 130.2, 124.6, 123.8, 123.3, 119.3, 117.5, 116.2, 115.8, 20.0, 19.7, 18.8; IR: 2923, 1734, 1627, 1586, 1457, 1331, 1209 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{22}\text{H}_{16}\text{ClNO}_4$: 393.0768, Found: 393.0768.

9-Chloro-3-(2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5h): The compound was prepared according to the general procedure. Yield: 88% (309 mg); Characteristic: Yellow solid; Mp: 237-240 $^{\circ}\text{C}$; ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 10.52 (1H, s), 9.27 (1H, d,



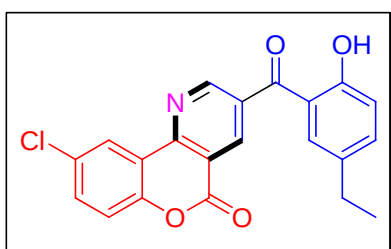
$J = 1.8$ Hz), 8.62 (1H, d, $J = 2.4$ Hz), 8.37 (1H, d, $J = 2.4$ Hz), 7.73 (1H, dd, $J = 8.4, 2.4$ Hz), 7.54-7.50 (3H, m), 7.04-7.00 (2H, m); ^{13}C NMR (150 MHz, DMSO- d_6): δ 193.6, 159.6, 156.9, 155.4, 151.8, 151.4, 138.2, 134.5, 133.5, 132.9, 130.8, 129.2, 123.7, 123.6, 120.0, 119.6, 119.4, 117.2, 116.9; IR: 3067, 1743, 1628, 1590, 1479, 1447, 1331, 1242 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{ClNO}_4$: 351.0298, Found: 351.0295.

9-Chloro-3-(2-hydroxy-5-methylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5i): The



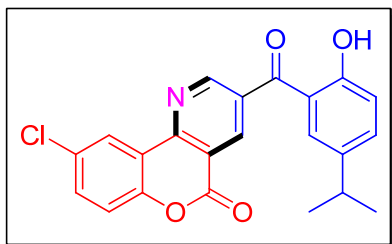
compound was prepared according to the general procedure. Yield: 88% (321 mg); Characteristic: Yellow solid; Mp: 227-229 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 11.49 (1H, s), 9.27 (1H, d, $J = 1.8$ Hz), 8.86 (1H, d, $J = 2.4$ Hz), 8.60 (1H, d, $J = 3.0$ Hz), 7.58 (1H, dd, $J = 8.4, 3.0$ Hz), 7.39 (1H, dd, $J = 7.8, 1.2$ Hz), 7.36 (1H, d, $J = 9.0$ Hz), 7.24 (1H, s), 7.02 (1H, d, $J = 9.0$ Hz), 2.26 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 197.0, 161.4, 159.8, 155.4, 152.6, 151.4, 138.9, 138.8, 134.1, 133.3, 132.0, 131.0, 128.7, 124.9, 119.9, 118.9, 118.8, 118.3, 116.8, 20.5; IR: 3059, 1744, 1618, 1473, 1339, 1201 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{12}\text{ClNO}_4$: 365.0455, Found: 365.0451.

9-Chloro-3-(5-ethyl-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5j): The



compound was prepared according to the general procedure. Yield: 85% (322 mg); Characteristic: Yellow solid; Mp: 164-165 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 11.50 (1H, s), 9.27 (1H, d, $J = 2.4$ Hz), 8.87 (1H, d, $J = 2.4$ Hz), 8.59 (1H, d, $J = 2.4$ Hz), 7.57 (1H, dd, $J = 8.4, 3.0$ Hz), 7.42 (1H, dd, $J = 9.0, 1.8$ Hz), 7.35 (1H, d, $J = 8.4$ Hz), 7.26 (1H, d, $J = 1.8$ Hz), 7.04 (1H, d, $J = 8.4$ Hz), 2.56 (2H, q, $J = 7.8$ Hz), 1.16 (3H, t, $J = 7.8$ Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 196.9, 161.6, 159.7, 155.4, 152.6, 151.4, 139.0, 137.6, 135.2, 134.0, 133.3, 130.97, 130.95, 124.9, 119.8, 118.9, 118.3, 116.8, 27.8, 15.6; IR: 3078, 1736, 1632, 1548, 1478, 1334 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{21}\text{H}_{14}\text{ClNO}_4$: 379.0611, Found: 379.0609.

9-Chloro-3-(2-hydroxy-5-isopropylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5k): The



compound was prepared according to the general procedure.

Yield: 86% (338 mg); Characteristic: Yellow solid; Mp:

132-135 °C; ¹H NMR (600 MHz, CDCl₃): δ 11.50 (1H, s),

9.28 (1H, d, *J* = 2.4 Hz), 8.88 (1H, d, *J* = 1.8 Hz), 8.60 (1H,

d, *J* = 2.4 Hz), 7.58 (1H, dd, *J* = 8.4, 2.4 Hz), 7.47 (1H, dd,

J = 8.4, 1.8 Hz), 7.36 (1H, d, *J* = 8.4 Hz), 7.29 (1H, d, *J* = 2.4 Hz), 7.05 (1H, d, *J* = 8.4 Hz),

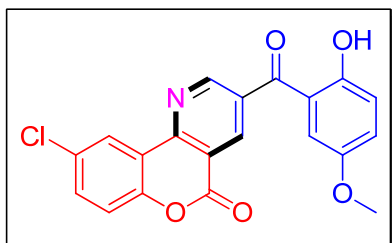
2.83 (1H, sep, *J* = 7.2 Hz), 1.18 (6H, d, *J* = 7.2 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 196.9,

161.6, 159.7, 155.4, 152.6, 151.4, 139.8, 139.1, 136.2, 134.0, 133.3, 130.9, 129.6, 124.9,

119.8, 118.9, 118.8, 118.2, 116.8, 33.1, 23.9; IR: 2964, 1732, 1614, 1542, 1342, 1199 cm⁻¹;

HRMS *m/z* (M⁺) calcd for C₂₂H₁₆ClNO₄: 393.0768, Found: 393.0765.

9-Chloro-3-(2-hydroxy-5-methoxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5l): The



compound was prepared according to the general procedure.

Yield: 90% (343 mg); Characteristic: Yellow solid; Mp:

203-205 °C; ¹H NMR (600 MHz, CDCl₃): δ 11.24 (1H, s);

9.29 (1H, s), 8.89 (1H, s), 8.58 (1H, s), 7.58 (1H, d, *J* = 7.8

Hz), 7.35 (1H, d, *J* = 7.8 Hz), 7.20 (1H, d, *J* = 9.6 Hz), 7.05

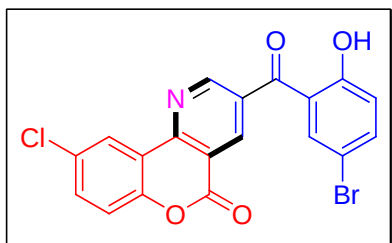
(1H, d, *J* = 9.0 Hz), 6.91 (1H, s), 3.69 (3H, s); ¹³C NMR (150 MHz, CDCl₃): δ 196.6, 159.7,

157.8, 155.4, 152.7, 151.9, 151.4, 138.9, 133.9, 133.3, 131.0, 125.5, 124.9, 119.9, 119.8,

118.9, 118.0, 116.7, 114.7, 55.9; IR: 3078, 1737, 1652, 1596, 1548, 1482, 1292 cm⁻¹; HRMS

m/z (M⁺) calcd for C₂₀H₁₂ClNO₅: 381.0404, Found: 381.0403.

3-(5-Bromo-2-hydroxybenzoyl)-9-chloro-5H-chromeno[4,3-b]pyridin-5-one (5m): The



compound was prepared according to the general procedure.

Yield: 82% (353 mg); Characteristic: Yellow solid; Mp:

170-172 °C; ¹H NMR (600 MHz, CDCl₃): δ 11.57 (1H, s),

9.26 (1H, d, *J* = 2.4 Hz), 8.87 (1H, d, *J* = 2.4 Hz), 8.60 (1H,

d, *J* = 2.4 Hz), 7.64 (1H, dd, *J* = 9.6, 2.4 Hz), 7.60-7.58 (2H,

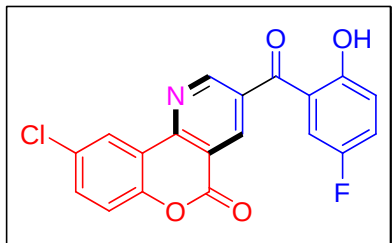
m), 7.36 (1H, d, *J* = 9.0 Hz), 7.03 (1H, d, *J* = 8.4 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 196.2,

162.3, 159.6, 155.2, 153.1, 151.5, 140.3, 139.0, 134.3, 133.5, 133.3, 131.1, 125.0, 121.1,

119.9, 119.7, 118.9, 116.9, 111.0; IR: 3072, 1741, 1644, 1597, 1457, 1332, 1298 cm⁻¹;

HRMS m/z (M^+) calcd for $C_{19}H_9BrClNO_4$: 428.9403, Found: 428.9404.

9-Chloro-3-(5-fluoro-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5n): The



compound was prepared according to the general procedure.

Yield: 80% (295 mg); Characteristic: Yellow solid; Mp:

188-190 °C; 1H NMR (600 MHz, $CDCl_3$): δ 11.40 (1H, s),

9.29 (1H, d, $J = 1.2$ Hz), 8.87 (1H, d, $J = 1.2$ Hz), 8.61 (1H,

d, $J = 1.8$ Hz), 7.59 (1H, dd, $J = 9.0, 1.8$ Hz), 7.37 (1H, d, J

= 9.0 Hz), 7.34 (1H, td, $J = 9.0, 1.8$ Hz), 7.18 (1H, dd, $J = 8.4, 2.4$ Hz), 7.11 (1H, dd, $J = 9.0,$

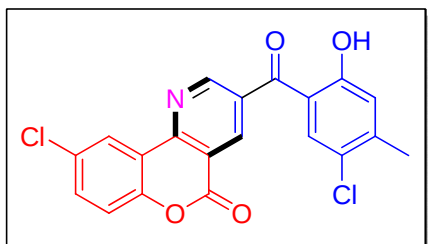
4.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.3, 159.6, 155.3, 154.8 (d, $J = 239.1$ Hz), 153.0,

151.5, 138.9, 133.5, 133.3, 131.1, 125.5, 125.3, 125.1, 120.6 (d, $J = 8.1$ Hz), 119.7, 118.9,

117.9, 117.1 (d, $J = 24.1$ Hz), 116.8; IR: 3078, 1732, 1590, 1545, 1474, 1388, 1253 cm^{-1} ;

HRMS m/z (M^+) calcd for $C_{19}H_9ClFNO_4$: 369.0204, Found: 369.0202.

9-Chloro-3-(5-chloro-2-hydroxy-4-methylbenzoyl)-5H-chromeno[4,3-b]pyridin-5-one



(5o): The compound was prepared according to the

general procedure. Yield: 82% (328 mg); Characteristic:

Yellow solid; Mp: 244-246 °C; 1H NMR (600 MHz,

$DMSO-d_6$): δ 10.63 (1H, s), 9.24 (1H, d, $J = 1.8$ Hz),

8.60 (1H, d, $J = 2.4$ Hz), 8.35 (1H, d, $J = 3.0$ Hz), 7.71

(1H, dd, $J = 8.4, 1.8$ Hz), 7.49 (1H, d, $J = 8.4$ Hz), 7.46 (1H, s), 6.96 (1H, s), 2.33 (3H, s); ^{13}C

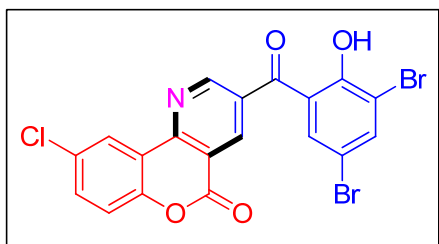
NMR (150 MHz, $DMSO-d_6$): δ 191.7, 159.5, 155.6, 155.4, 151.9, 151.3, 142.2, 138.2, 133.3,

132.9, 130.3, 129.2, 123.8, 123.7, 123.0, 119.9, 119.4, 119.3, 117.1, 20.0; IR: 3068, 1735,

1626, 1595, 1549, 1450, 1337, 1213 cm^{-1} ; HRMS m/z (M^+) calcd for $C_{20}H_{11}Cl_2NO_4$:

399.0065, Found: 399.0066.

9-Chloro-3-(3,5-dibromo-2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5p):



The compound was prepared according to the general

procedure. Yield: 78% (397 mg); Characteristic: Yellow

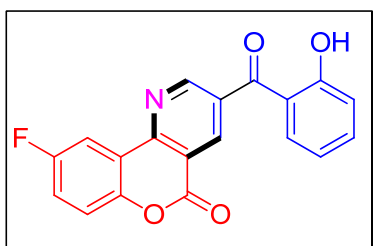
solid; Mp: 296-298 °C; 1H NMR (600 MHz, $CDCl_3$ +

$DMSO-d_6$): δ 10.82 (1H, s), 9.30 (1H, d, $J = 1.2$ Hz),

8.67 (1H, d, $J = 1.2$ Hz), 8.47 (1H, d, $J = 2.4$ Hz), 8.06

(1H, t, $J = 1.2$ Hz), 7.77 (1H, dd, $J = 8.4, 1.8$ Hz), 7.62 (1H, d, $J = 1.2$ Hz), 7.56 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (150 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$): δ 192.1, 159.5, 155.6, 152.9, 152.3, 151.5, 138.8, 138.5, 133.1, 132.6, 132.3, 129.3, 127.2, 123.8, 120.0, 119.4, 117.3, 113.8, 111.3; IR: 3060, 1744, 1623, 1551, 1422, 1328, 1224 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_8\text{Br}_2\text{ClNO}_4$: 506.8509, Found: 506.8507.

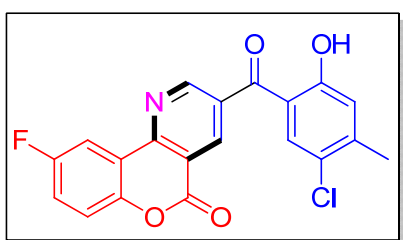
9-Fluoro-3-(2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5q): The compound



was prepared according to the general procedure. Yield: 85% (285 mg); Characteristic: Yellow solid; Mp: 206-208 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 11.68 (1H, s), 9.29 (1H, d, $J = 1.8$ Hz), 8.88 (1H, d, $J = 1.8$ Hz), 8.29 (1H, dd, $J = 8.4, 3.0$ Hz), 7.58 (1H, t, $J = 7.8$ Hz), 7.51 (1H, d, $J = 8.4$ Hz), 7.41-

7.31 (2H, m), 7.11 (1H, d, $J = 7.8$ Hz), 6.94 (1H, t, $J = 7.5$ Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 197.1, 163.4, 160.4, 159.9 (d, $J = 178.2$ Hz), 155.4, 153.0, 149.2, 139.0, 137.6, 133.8, 132.6, 120.8 (d, $J = 24.1$ Hz), 119.9 (d, $J = 9.3$ Hz), 119.5, 119.1 (d, $J = 8.1$ Hz), 119.0, 118.6, 116.6, 111.1 (d, $J = 25.3$ Hz); IR: 3081, 1736, 1622, 1588, 1466, 1381, 1239 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{FNO}_4$: 335.0594, Found: 335.0591.

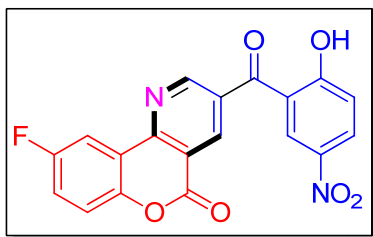
3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-9-fluoro-5H-chromeno[4,3-b]pyridin-5-one



(5r): The compound was prepared according to the general procedure. Yield: 83% (318 mg); Characteristic: Yellow solid; Mp: 248-250 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 11.56 (1H, s), 9.26 (1H, d, $J = 2.4$ Hz), 8.86 (1H, d, $J = 2.4$ Hz), 8.29 (1H, dd, $J = 8.4, 3.0$ Hz), 7.43 (1H, s), 7.42-7.36

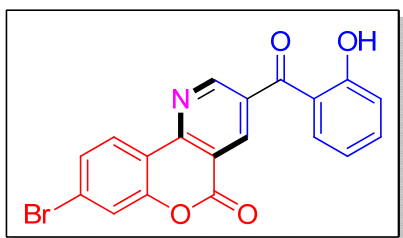
(2H, m), 7.01 (1H, s), 2.42 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 195.8, 161.8, 160.4, 159.3 (d, $J = 162$ Hz), 155.1, 153.2, 149.2, 147.3, 138.9, 133.5, 131.7, 124.9, 120.9 (d, $J = 21.7$ Hz), 119.9, 119.1 (d, $J = 7.9$ Hz), 117.6, 116.9, 111.1 (d, $J = 25.3$ Hz), 21.0; IR: 3056, 1752, 1634, 1607, 1568, 1475, 1344, 1260 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{20}\text{H}_{11}\text{ClFNO}_4$: 383.0361, Found: 383.0359.

9-Fluoro-3-(2-hydroxy-5-nitrobenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5s): The compound was prepared according to the general procedure. Yield: 81% (308 mg);



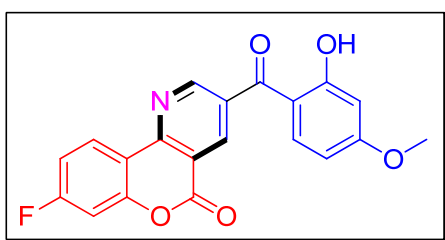
Characteristic: White solid; Mp: >300 °C; ^1H NMR (600 MHz, DMSO- d_6): δ 11.97 (1H, s), 9.32 (1H, d, J = 2.4 Hz), 8.67 (1H, d, J = 2.4 Hz), 8.38-8.37 (2H, m), 8.17 (1H, dd, J = 9.0, 3.0 Hz), 7.63-7.56 (2H, m), 7.20-7.18 (1H, m); ^{13}C NMR (150 MHz, DMSO- d_6): δ 191.3, 161.9, 159.7, 158.7 (d, J = 240.3 Hz), 155.5, 152.7, 149.2, 139.8, 138.2, 132.7, 129.0, 126.9, 124.7, 120.8 (d, J = 24.1 Hz), 119.8 (d, J = 8.1 Hz), 119.5 (d, J = 7.9 Hz), 117.6, 117.3, 110.1 (d, J = 24.1 Hz); IR: 3236, 1711, 1660, 1592, 1525, 1464, 1342, 1262 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_9\text{FN}_2\text{O}_6$: 380.0445, Found: 380.0442.

8-Bromo-3-(2-hydroxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5t): The compound



was prepared according to the general procedure. Yield: 88% (348 mg); Characteristic: Yellow solid; Mp: 225-227 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.68 (1H, s), 9.27 (1H, d, J = 2.4 Hz), 8.85 (1H, d, J = 1.8 Hz), 8.48 (1H, d, J = 7.8 Hz), 7.59-7.56 (3H, m), 7.51 (1H, dd, J = 7.8, 1.2 Hz), 7.12 (1H, d, J = 9.0 Hz), 6.94 (1H, t, J = 7.5 Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 197.1, 163.4, 159.7, 155.6, 153.2, 153.1, 139.0, 137.5, 133.6, 132.5, 128.8, 127.4, 126.6, 120.7, 119.5, 119.0, 118.6, 117.7, 116.4; IR: 3058, 1739, 1620, 1584, 1347, 1224 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{19}\text{H}_{10}\text{BrNO}_4$: 394.9793, Found: 394.9795.

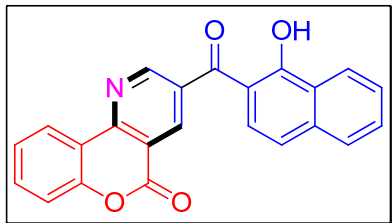
8-Fluoro-3-(2-hydroxy-4-methoxybenzoyl)-5H-chromeno[4,3-b]pyridin-5-one (5u): The



compound was prepared according to the general procedure. Yield: 88% (321 mg); Characteristic: Yellow solid; Mp: 218-220 °C; ^1H NMR (600 MHz, CDCl_3): δ 11.26 (1H, s), 9.28 (1H, d, J = 1.8 Hz), 8.88 (1H, d, J = 1.8 Hz), 8.64 (1H, dd, J = 9.0, 6.6 Hz), 7.21 (1H, dd, J = 8.4, 2.4 Hz), 7.17 (1H, td, J = 9.0, 3.0 Hz), 7.13 (1H, dd, J = 9.0, 2.4 Hz), 7.06 (1H, d, J = 9.6 Hz), 6.92 (1H, d, J = 3.0 Hz), 3.70 (3H, s); ^{13}C NMR (150 MHz, CDCl_3): δ 196.7, 165.6 (d, J = 254.1 Hz), 160.0, 157.8, 155.5, 154.1 (d, J = 12.6 Hz), 153.3, 151.9, 139.1, 133.2, 127.5 (d, J = 9.1 Hz), 125.4, 119.9, 118.1, 115.8, 115.3, 114.8, 113.4 (d, J = 22.9 Hz), 104.9 (d, J = 25.3 Hz), 55.9; IR: 3079, 1743, 1595, 1488, 1460, 1346, 1242 cm^{-1} ; HRMS m/z (M^+)

calcd for C₂₀H₁₂FNO₅: 365.0700, Found: 365.0702.

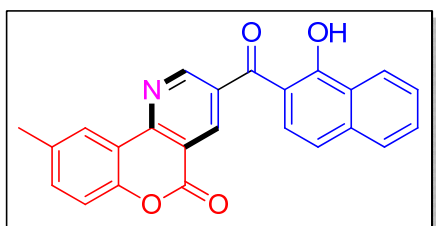
3-(1-Hydroxy-2-naphthoyl)-5H-chromeno[4,3-b]pyridin-5-one (6a): The compound was



prepared according to the general procedure. Yield: 88% (323 mg); Characteristic: Yellow solid; Mp: 238-240 °C; ¹H NMR (300 MHz, DMSO-d₆): δ 12.89 (1H, s), 9.37 (1H, d, *J* = 2.1 Hz), 8.76 (1H, d, *J* = 2.1 Hz), 8.58 (1H, dd, *J* = 8.1, 1.2 Hz), 8.41 (1H, d, *J* = 8.1 Hz), 7.97 (1H, d, *J* = 8.1 Hz),

7.79-7.73 (2H, m), 7.66 (1H, t, *J* = 7.2 Hz), 7.58-7.47 (4H, m); ¹³C NMR (150 MHz, DMSO-d₆): δ 196.5, 160.5, 159.9, 155.2, 152.8, 152.7, 138.4, 136.9, 133.4, 133.3, 130.5, 127.8, 126.6, 126.5, 125.2, 124.7, 124.5, 123.6, 119.0, 118.6, 117.3, 116.8, 114.1; IR: 3049, 1735, 1555, 1444, 1344, 1163 cm⁻¹; HRMS *m/z* (M⁺) calcd for C₂₃H₁₃NO₄: 367.0845, Found: 367.0847.

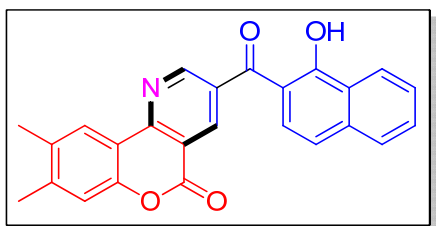
3-(1-Hydroxy-2-naphthoyl)-9-methyl-5H-chromeno[4,3-b]pyridin-5-one (6b): The



compound was prepared according to the general procedure. Yield: 90% (343 mg); Characteristic: Yellow solid; Mp: 225-227 °C; ¹H NMR (600 MHz, DMSO-d₆): δ 12.88 (1H, s), 9.34 (1H, d, *J* = 1.8 Hz), 8.73 (1H, d, *J* = 1.8 Hz), 8.40 (1H, d, *J* = 7.8 Hz), 8.34 (1H, s), 7.96 (1H,

d, *J* = 8.4 Hz), 7.76 (1H, t, *J* = 7.2 Hz), 7.65 (1H, t, *J* = 7.8 Hz), 7.55 (2H, t, *J* = 9.0 Hz), 7.48 (1H, d, *J* = 9.0 Hz), 7.40 (1H, d, *J* = 8.4 Hz), 2.46 (3H, s); ¹³C NMR (150 MHz, DMSO-d₆): δ 196.4, 160.5, 160.0, 155.1, 152.7, 150.8, 138.4, 136.9, 134.5, 134.2, 133.2, 130.5, 127.8, 126.5, 124.5, 124.4, 123.6, 119.0, 118.1, 117.0, 116.6, 114.1, 20.4; IR: 2924, 1737, 1592, 1456, 1386, 1346, 1237 cm⁻¹; HRMS *m/z* (M⁺) calcd for C₂₄H₁₅NO₄: 381.1001, Found: 381.1003.

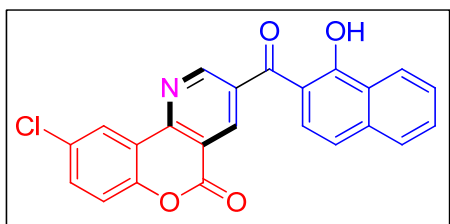
3-(1-Hydroxy-2-naphthoyl)-8,9-dimethyl-5H-chromeno[4,3-b]pyridin-5-one (6c): The



compound was prepared according to the general procedure. Yield: 90% (355 mg); Characteristic: Yellow solid; Mp: 288-290 °C; ¹H NMR (600 MHz, DMSO-d₆): δ 12.87 (1H, s), 9.33 (1H, d, *J* = 1.8 Hz), 8.73 (1H, s),

8.41 (1H, d, $J = 8.4$ Hz), 8.31 (1H, s), 7.97 (1H, d, $J = 7.8$ Hz), 7.77 (1H, t, $J = 7.2$ Hz), 7.66 (1H, t, $J = 8.4$ Hz), 7.57 (1H, d, $J = 9.0$ Hz), 7.49 (1H, d, $J = 8.4$ Hz), 7.34 (1H, s), 2.38 (3H, s), 2.37 (3H, s); ^{13}C NMR (150 MHz, DMSO- d_6 + Pyridine- d_5): δ 197.7, 161.2, 156.0, 154.3, 152.2, 144.1, 139.5, 138.2, 134.5, 133.6, 131.4, 128.5, 127.2, 127.1, 125.9, 125.8, 124.9, 119.6, 118.3, 117.2, 117.0, 114.1, 20.4, 19.5; IR: 2918, 1733, 1579, 1459, 1414, 1377, 1332, 1240 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{25}\text{H}_{17}\text{NO}_4$: 395.1158, Found: 395.1155.

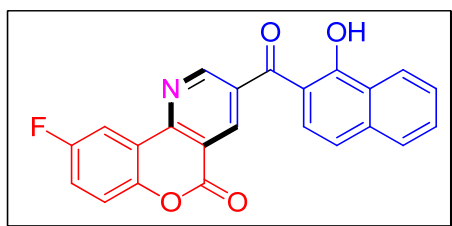
9-Chloro-3-(1-hydroxy-2-naphthoyl)-5H-chromeno[4,3-b]pyridin-5-one (6d): The



compound was prepared according to the general procedure. Yield: 85% (341 mg); Characteristic: Yellow solid; Mp: 237-239 $^{\circ}\text{C}$; ^1H NMR (600 MHz, DMSO- d_6): δ 12.87 (1H, s), 9.36 (1H, d, $J = 2.4$ Hz), 8.76 (1H, d, $J = 1.8$ Hz), 8.45 (1H, d, $J = 1.8$ Hz), 8.39 (1H, d, J

$= 7.8$ Hz), 7.95 (1H, d, $J = 7.8$ Hz), 7.79-7.74 (2H, m), 7.65 (1H, t, $J = 7.8$ Hz), 7.57 (1H, d, $J = 9.0$ Hz), 7.53 (1H, d, $J = 9.0$ Hz), 7.47 (1H, d, $J = 9.0$ Hz); ^{13}C NMR (150 MHz, DMSO- d_6): δ 196.4, 160.6, 159.6, 155.2, 151.6, 151.4, 138.3, 136.9, 133.9, 132.9, 130.6, 129.3, 127.9, 126.6, 126.5, 124.5, 123.7, 120.1, 119.5, 119.1, 117.2, 114.1; IR: 3075, 1743, 1596, 1566, 1454, 1388, 1343, 1242 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{23}\text{H}_{12}\text{ClNO}_4$: 401.0455, Found: 401.0452.

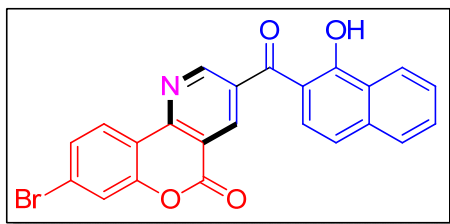
9-Fluoro-3-(1-hydroxy-2-naphthoyl)-5H-chromeno[4,3-b]pyridin-5-one (6e): The



compound was prepared according to the general procedure. Yield: 83% (320 mg); Characteristic: Yellow solid; Mp: 260-262 $^{\circ}\text{C}$; ^1H NMR (600 MHz, DMSO- d_6): δ 12.86 (1H, s), 9.38 (1H, d, $J = 1.8$ Hz), 8.77 (1H, d, $J = 2.4$ Hz), 8.41 (1H, d, $J = 8.4$ Hz), 8.25

(1H, dd, $J = 8.4, 2.4$ Hz), 7.96 (1H, d, $J = 7.8$ Hz), 7.76 (1H, t, $J = 7.8$ Hz), 7.66-7.62 (3H, m), 7.55 (1H, d, $J = 9.0$ Hz), 7.47 (1H, d, $J = 9.0$ Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 196.6, 164.7, 160.1, 159.6 ($J = 242.5$ Hz), 155.5, 152.8, 149.2, 138.9, 137.7, 134.2, 131.2, 127.6, 126.5, 125.7, 125.2, 124.7, 120.8 ($J = 24.1$ Hz), 119.1 ($J = 9.3$ Hz), 119.0, 116.7, 112.2, 111.1 ($J = 25.3$ Hz); IR: 3084, 1742, 1596, 1562, 1499, 1462, 1389, 1341, 1255 cm^{-1} ; HRMS m/z (M^+) calcd for $\text{C}_{23}\text{H}_{12}\text{FNO}_4$: 385.0750, Found: 385.0748.

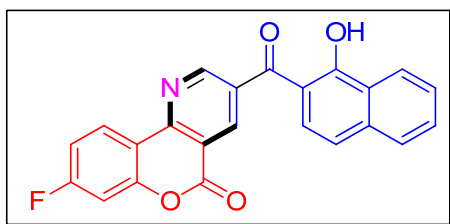
8-Bromo-3-(1-hydroxy-2-naphthoyl)-5H-chromeno[4,3-b]pyridin-5-one (6f): The



compound was prepared according to the general procedure. Yield: 82% (366 mg); Characteristic: Yellow solid; Mp: 240-242 °C; ¹H NMR (600 MHz, DMSO-d₆): δ 12.87 (1H, s), 9.37 (1H, d, *J* = 2.4 Hz), 8.76 (1H, d, *J* = 1.8 Hz), 8.48 (1H, d, *J* = 8.4 Hz), 8.42

(1H, d, *J* = 8.4 Hz), 7.97 (1H, d, *J* = 8.4 Hz), 7.88 (1H, d, *J* = 1.8 Hz), 7.77 (1H, t, *J* = 8.4 Hz), 7.72 (1H, dd, *J* = 8.4, 1.8 Hz), 7.66 (1H, t, *J* = 8.4 Hz), 7.55 (1H, d, *J* = 9.0 Hz), 7.48 (1H, d, *J* = 9.0 Hz); ¹³C NMR (150 MHz, DMSO-d₆): δ 196.4, 160.6, 159.6, 155.2, 153.1, 152.1, 138.3, 136.9, 133.7, 130.5, 128.3, 127.8, 126.6, 126.5, 126.3, 125.9, 124.6, 123.6, 120.2, 118.9, 118.0, 117.0, 114.2; IR: 3060, 1746, 1585, 1457, 1388, 1236 cm⁻¹; HRMS *m/z* (*M*⁺) calcd for C₂₃H₁₂BrNO₄: 444.9950, Found: 444.9952.

8-Fluoro-3-(1-hydroxy-2-naphthoyl)-5H-chromeno[4,3-b]pyridin-5-one (6g): The

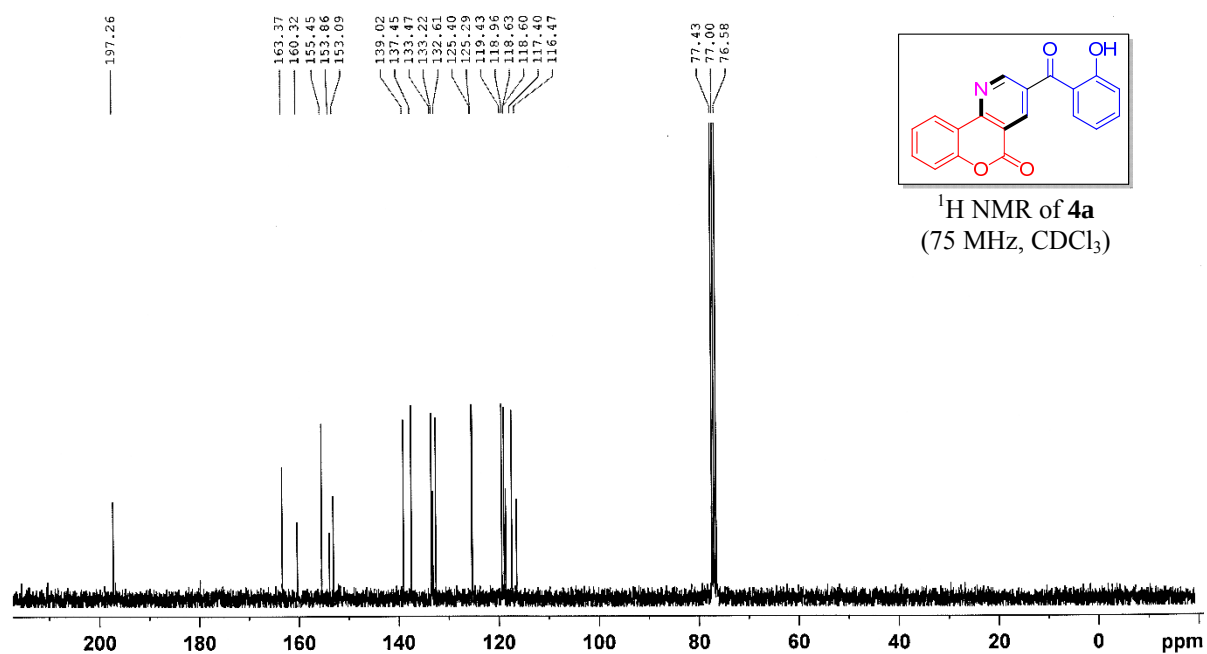
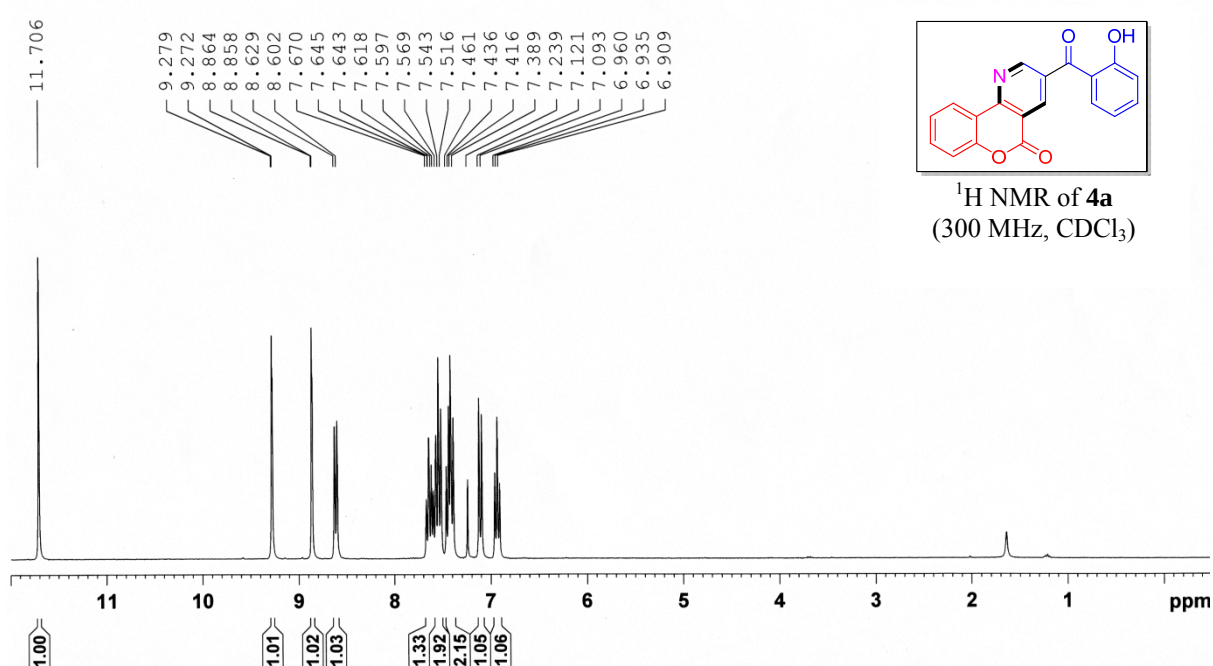


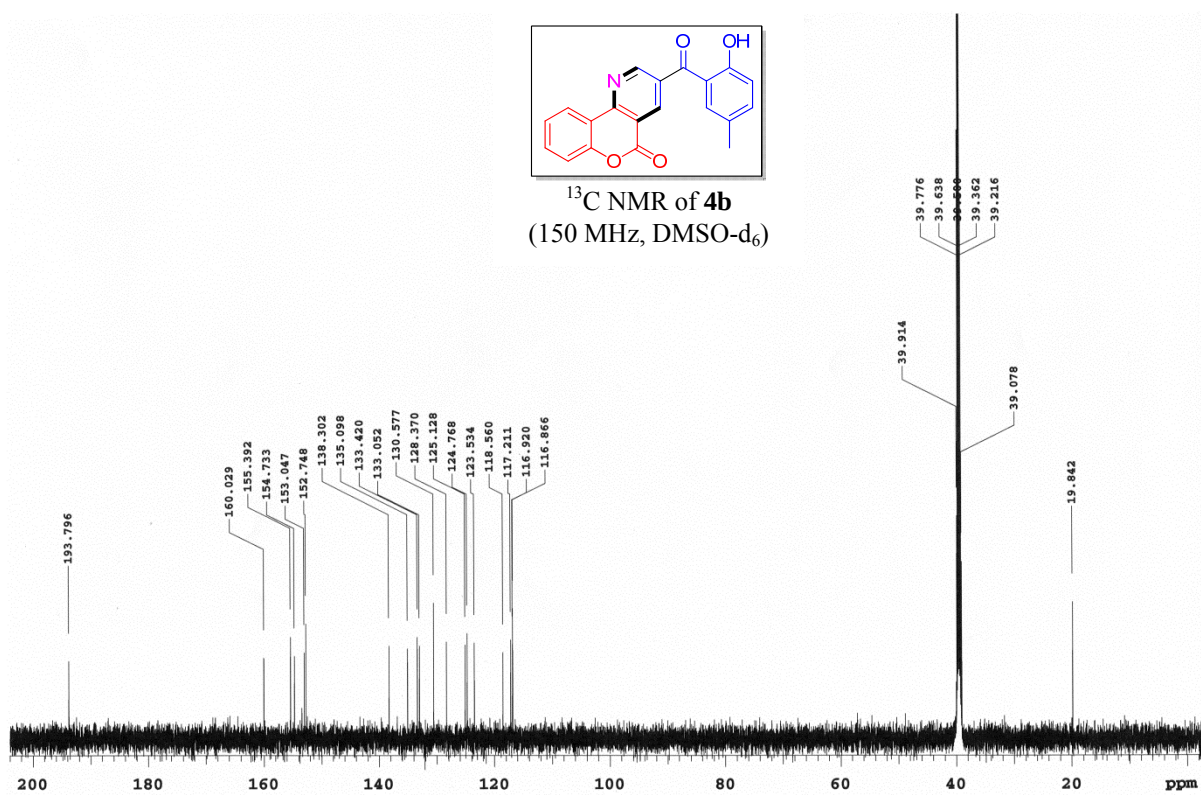
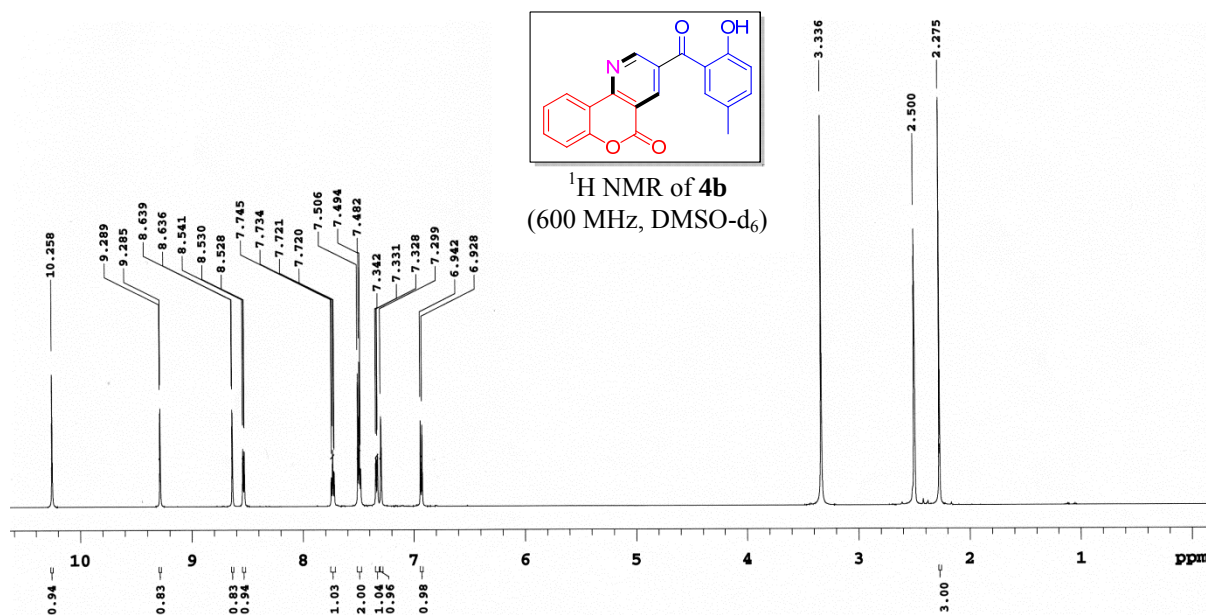
compound was prepared according to the general procedure. Yield: 81% (312 mg); Characteristic: Yellow solid; Mp: 236-238 °C; ¹H NMR (600 MHz, DMSO-d₆): δ 12.87 (1H, s), 9.36 (1H, d, *J* = 1.8 Hz), 8.76 (1H, d, *J* = 1.2 Hz), 8.62 (1H, dd, *J* = 8.4, 6.0

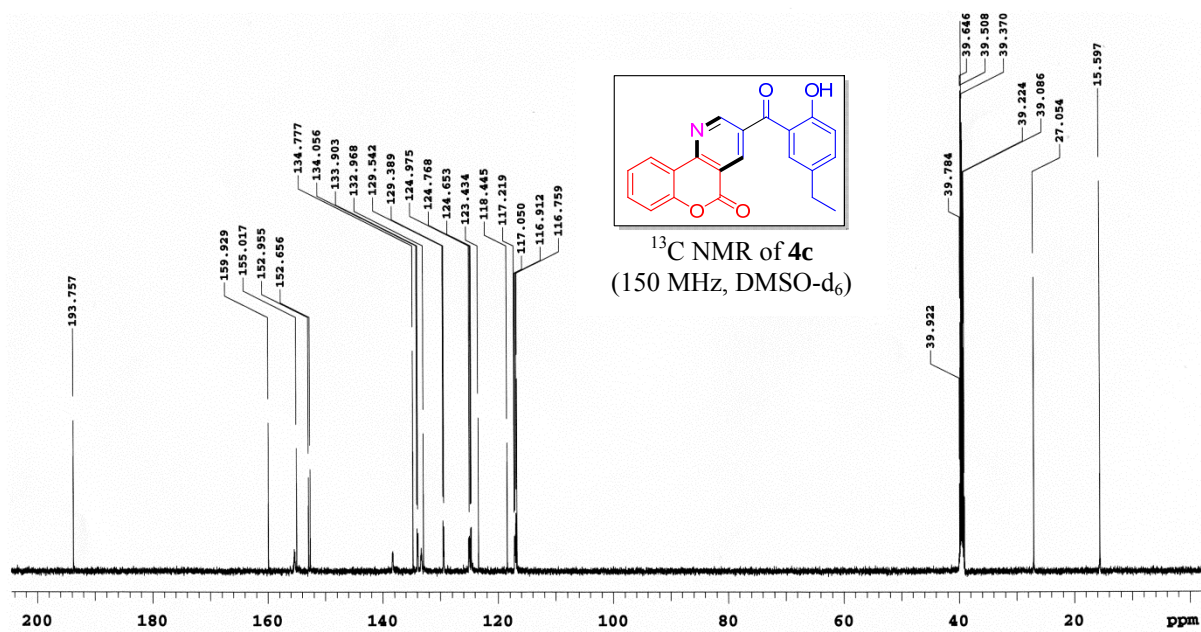
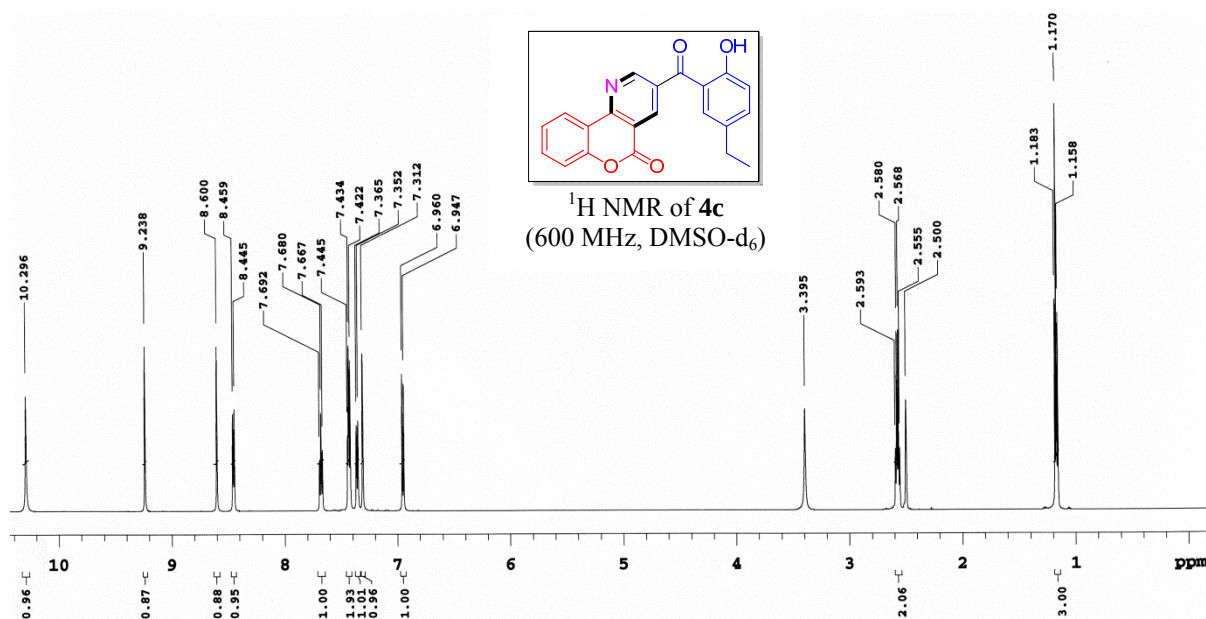
Hz), 8.41 (1H, d, *J* = 8.4 Hz), 7.97 (1H, d, *J* = 8.4 Hz), 7.77 (1H, t, *J* = 7.5 Hz), 7.66 (1H, t, *J* = 7.8 Hz), 7.56 (2H, d, *J* = 8.4 Hz), 7.49 (1H, d, *J* = 8.4 Hz), 7.41 (1H, td, *J* = 8.4, 2.4 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 196.6, 166.4, 164.6, 160.1, 155.6, 153.6 (*J* = 164.4 Hz), 139.1, 137.6, 133.6, 131.1, 127.6, 127.5 (*J* = 10.3 Hz), 126.5, 125.7, 125.2, 124.7, 119.0, 115.8, 115.3, 113.4 (*J* = 21.9 Hz), 112.2, 104.9 (*J* = 26.4 Hz); IR: 3056, 1746, 1618, 1584, 1459, 1388, 1247 cm⁻¹; HRMS *m/z* (*M*⁺) calcd for C₂₃H₁₂FNO₄: 385.0750, Found: 385.0748.

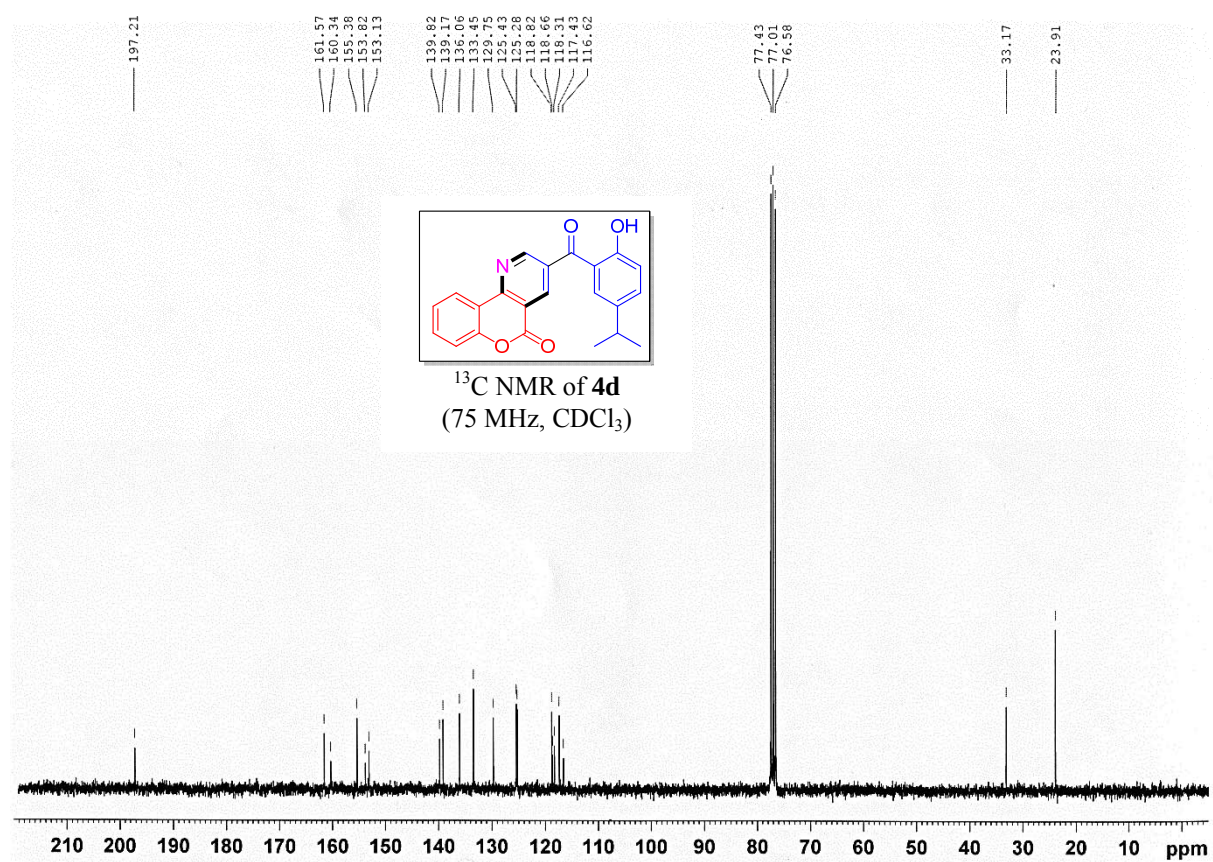
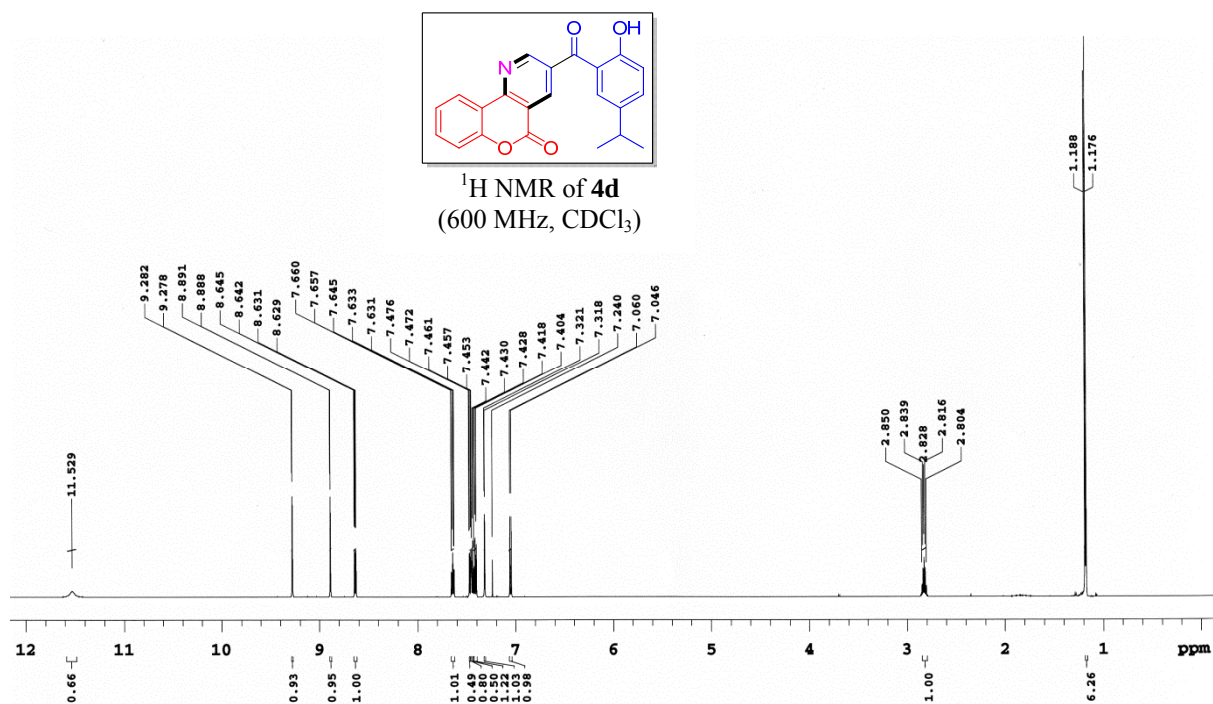
Optical Measurements

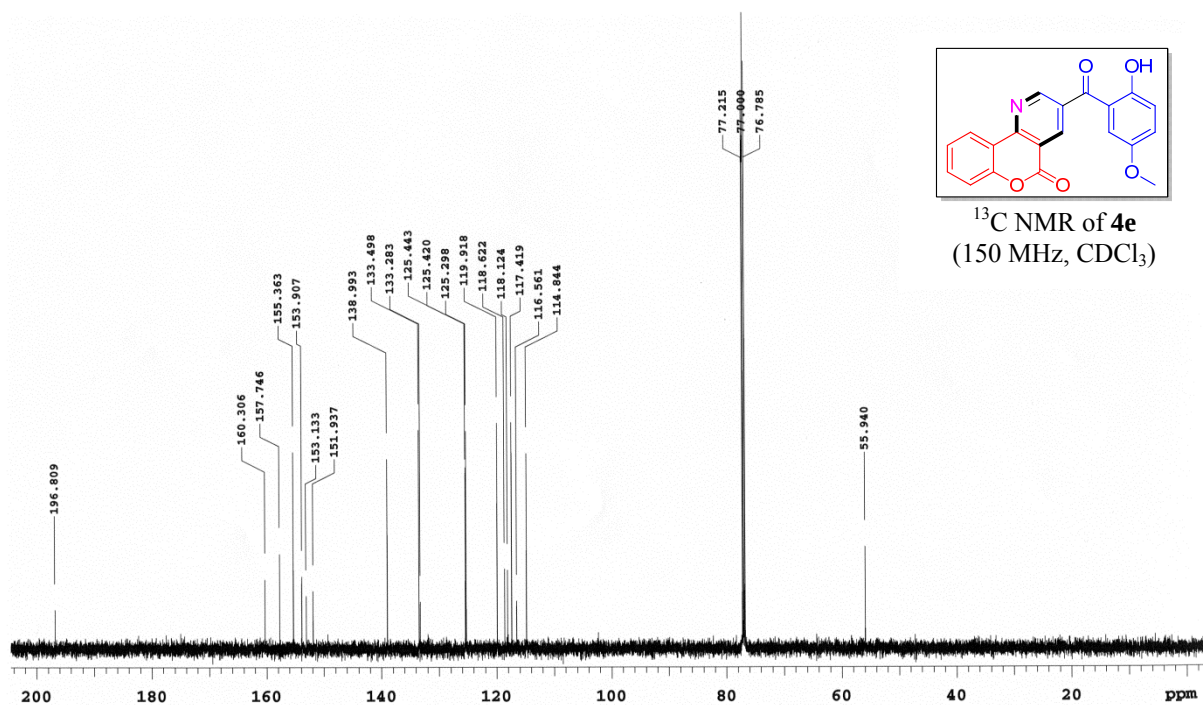
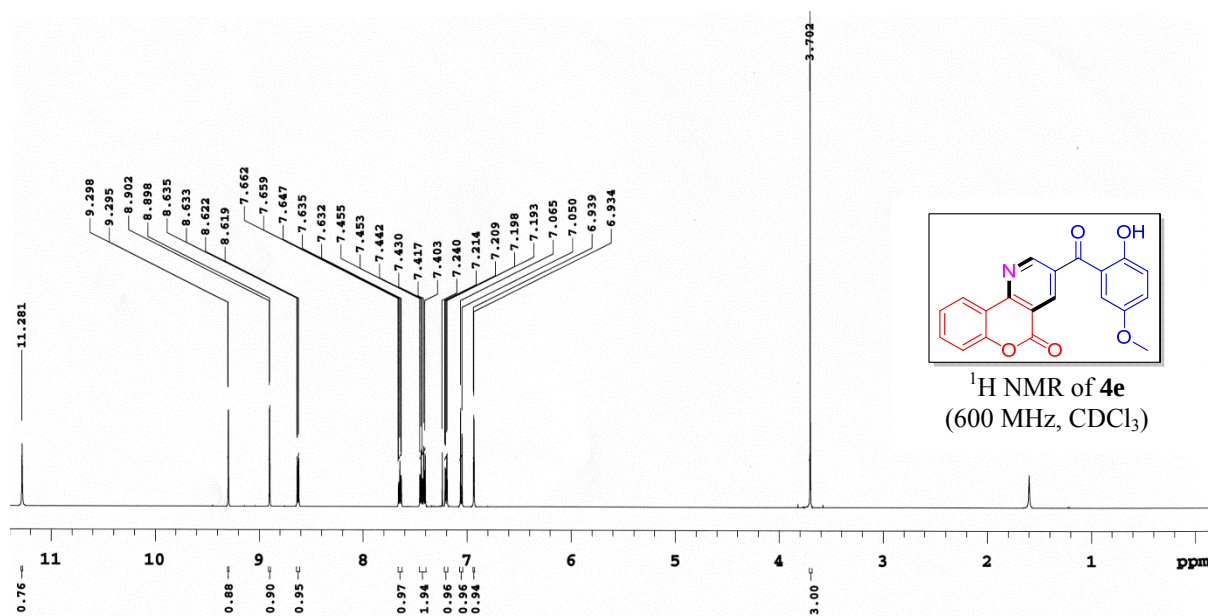
1mM solutions of the synthesized compounds (**5a**, **6a**, **6b**, **6c**, **6d** and **6f**) in MeOH, DMSO, CH₂Cl₂, and dioxane were used to assay the optical properties. OPTIZEN 3220UV UV-Visible spectrophotometer and Hitachi-7000 F fluorescence spectrometer were used for acquiring the absorption and emission spectral data using Quartz cell (10 mm). All solutions were prepared in spectroscopic grade solvents without further purification. For acquiring emission spectral data, excitation wavelengths were 335 nm for compound **6b** and 390 nm for compounds **5a**, **6a**, **6c**, **6d** and **6f**, respectively.

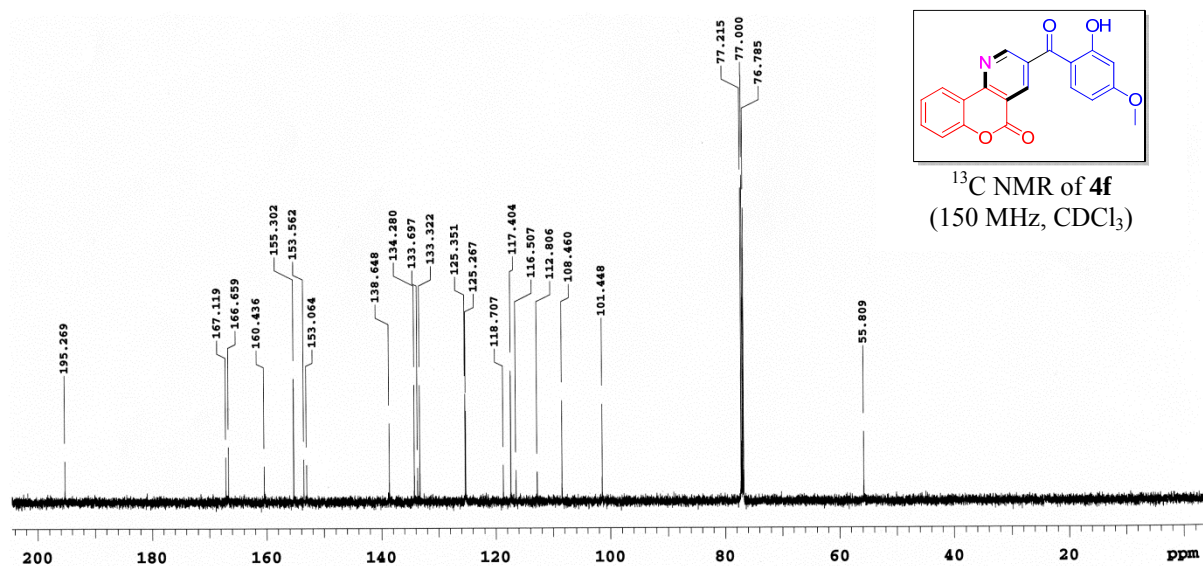
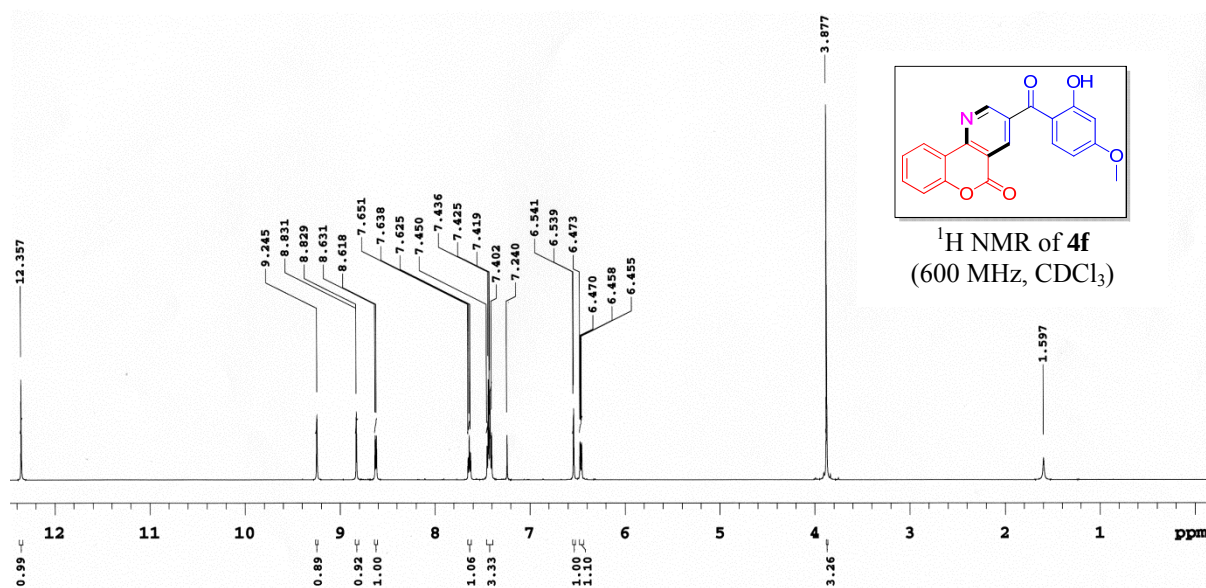


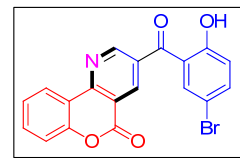
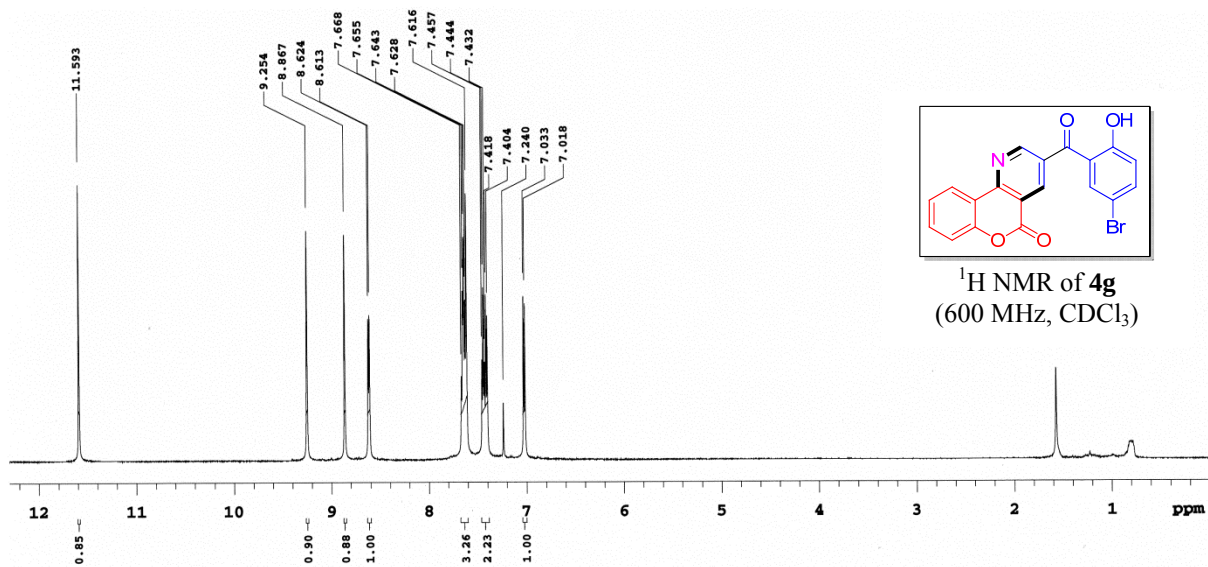




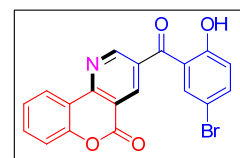
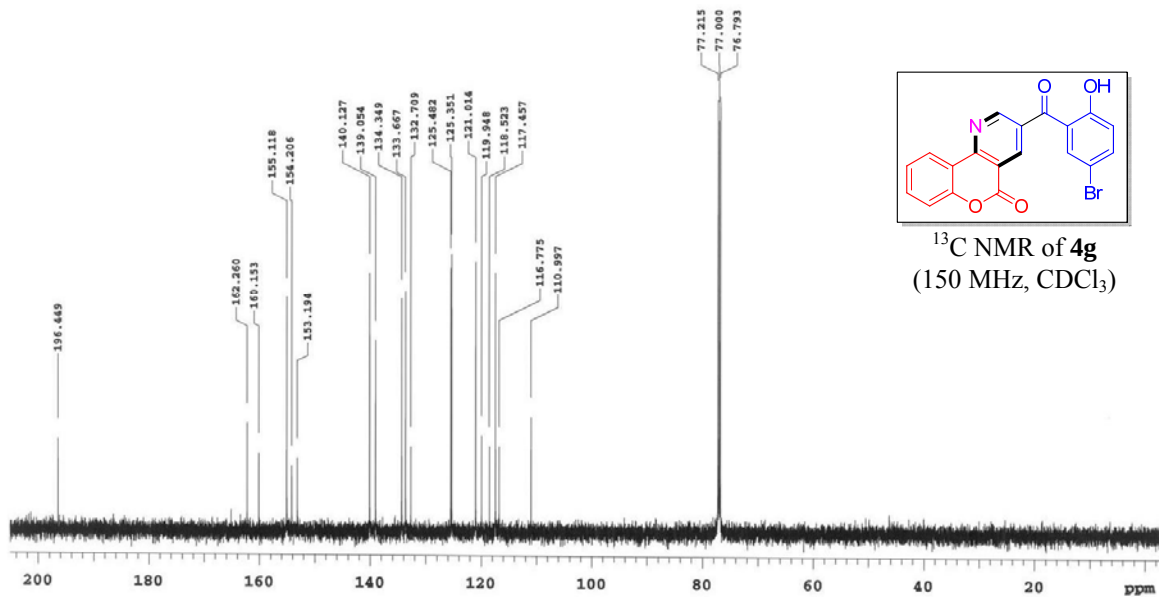




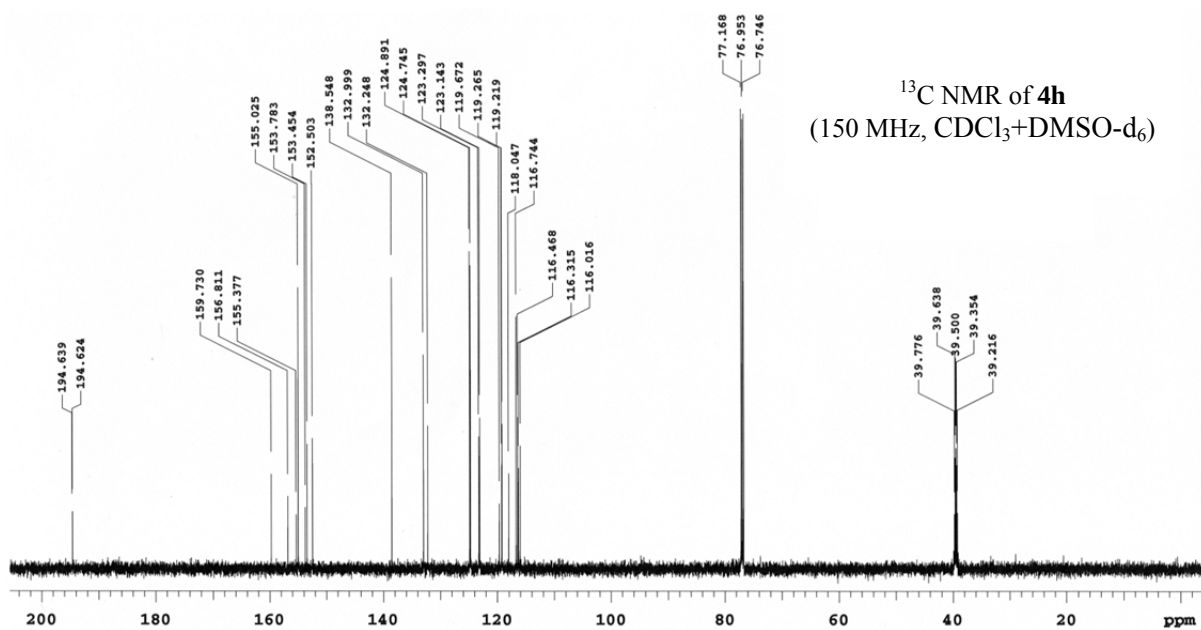
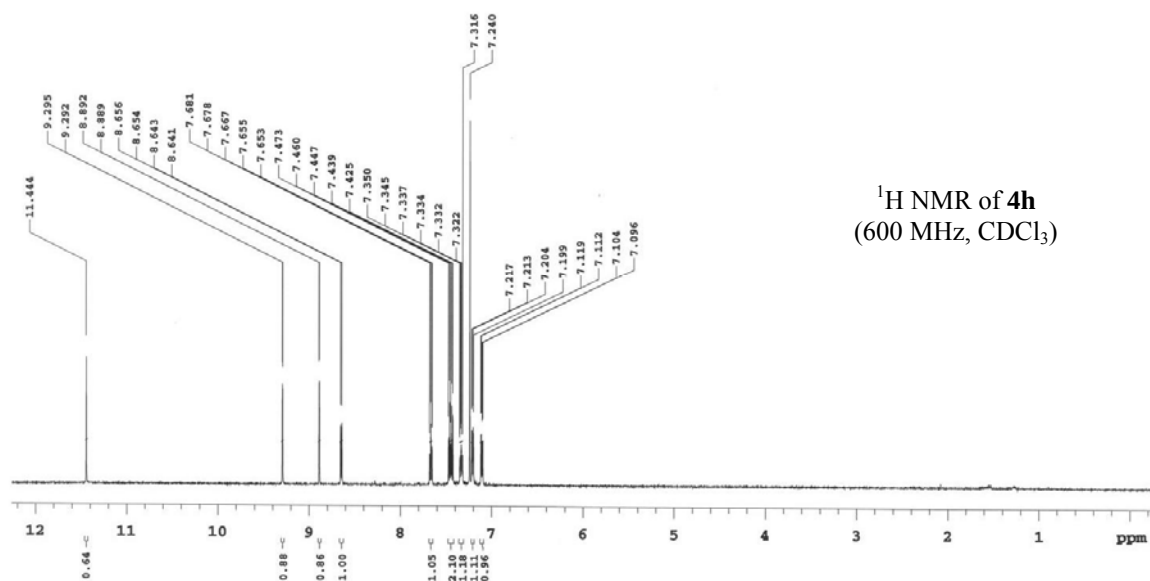


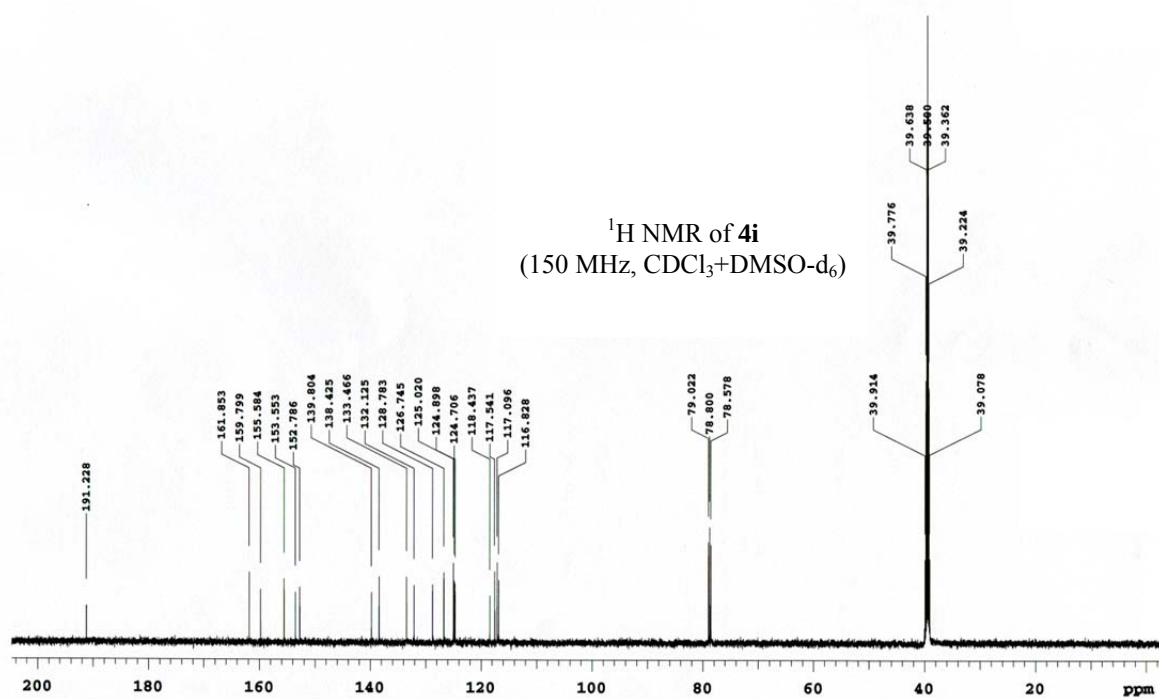
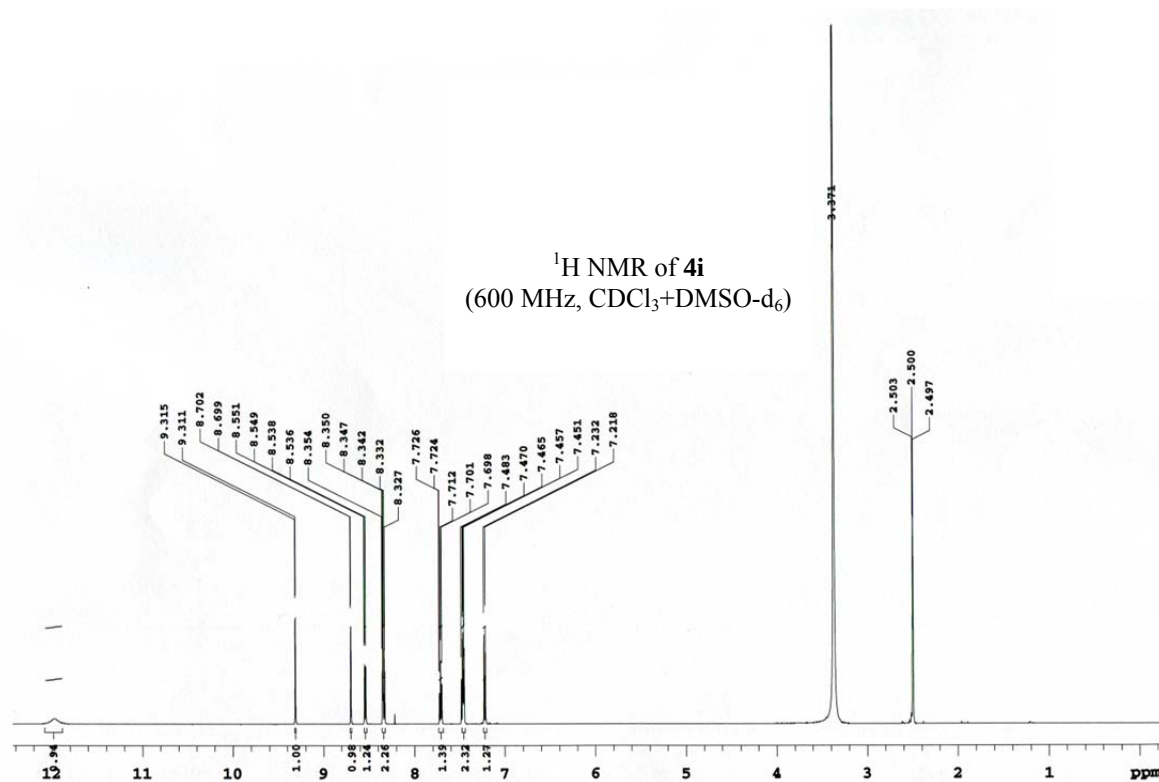


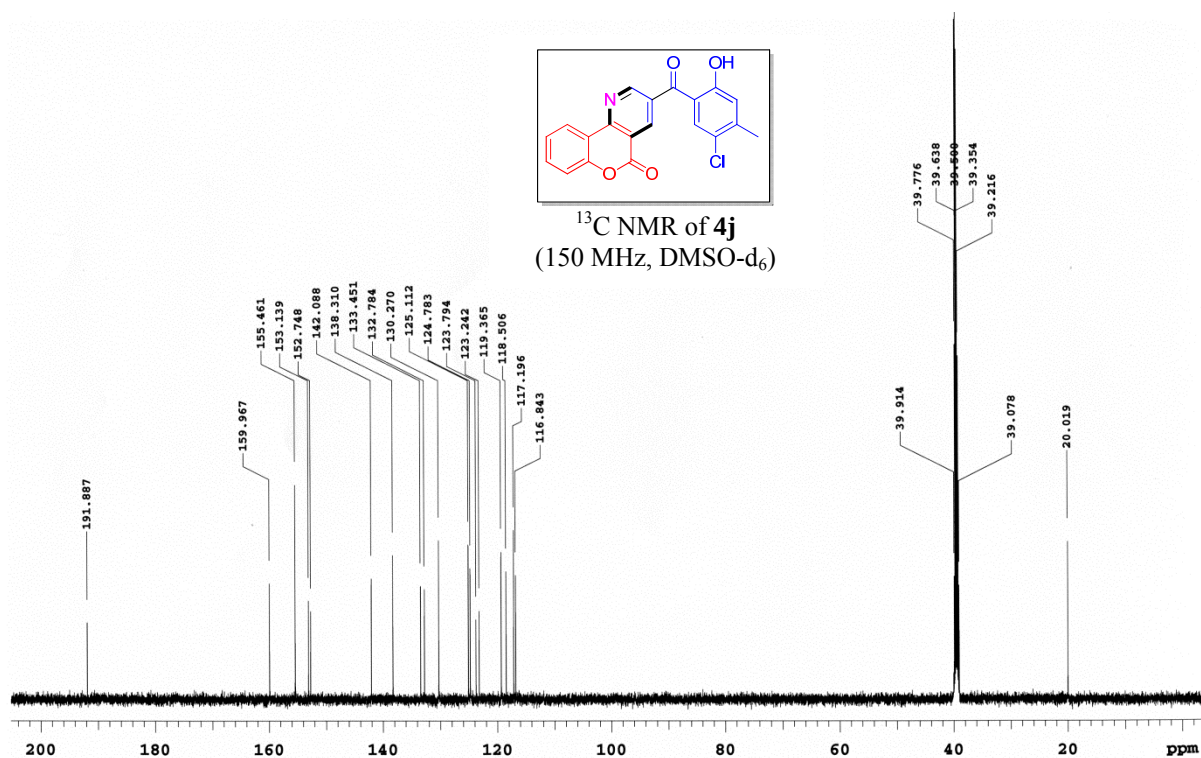
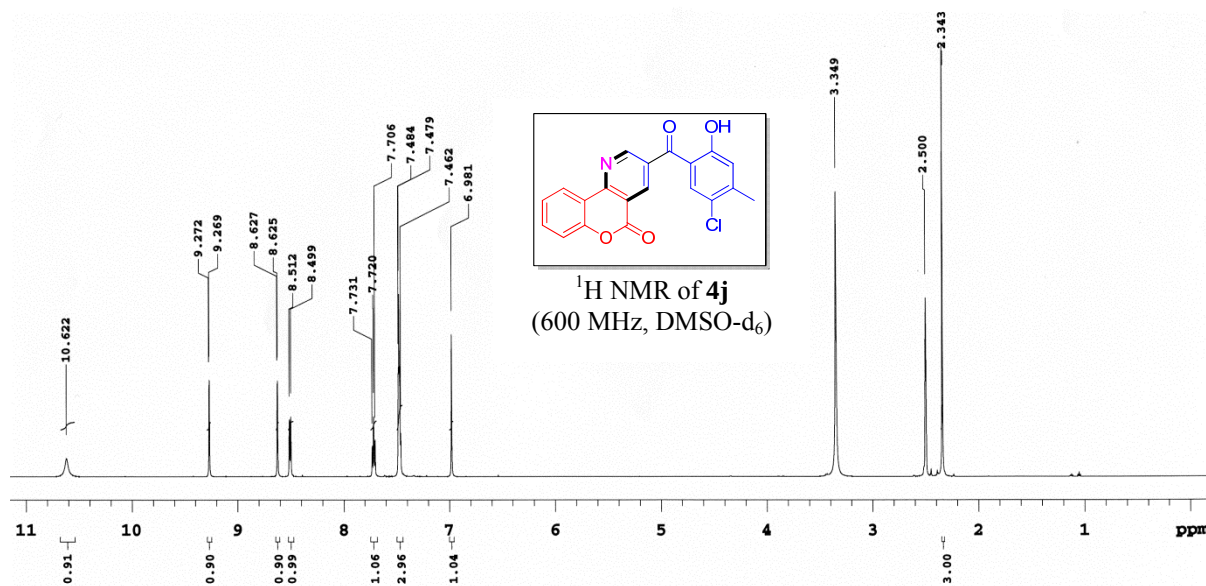
¹H NMR of 4g
(600 MHz, CDCl₃)

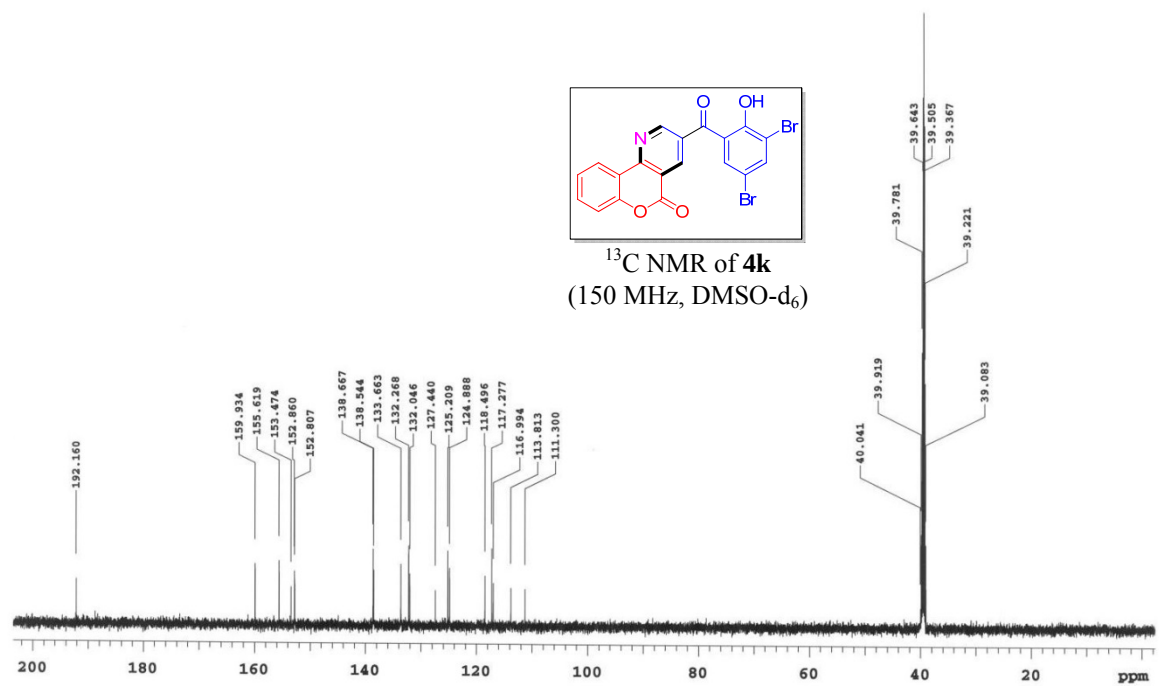
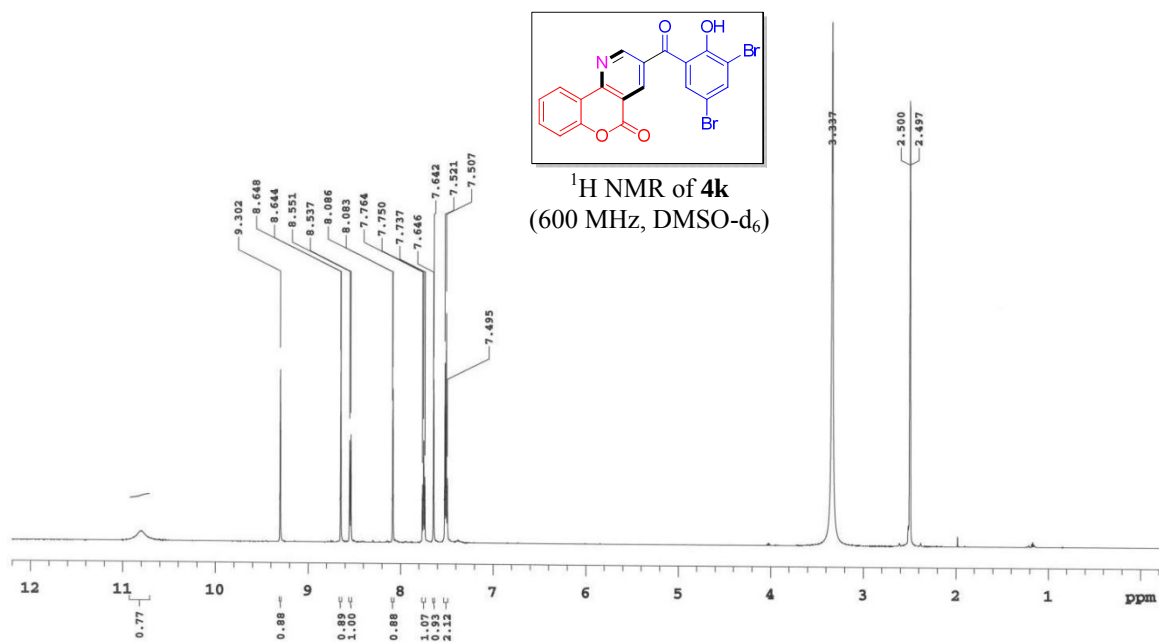


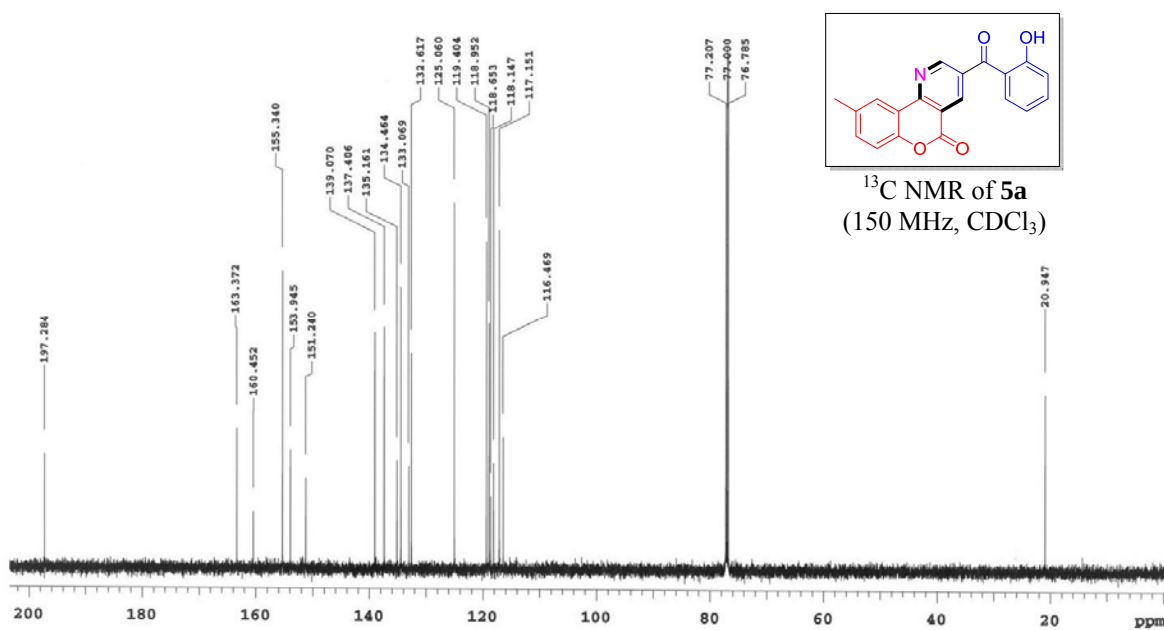
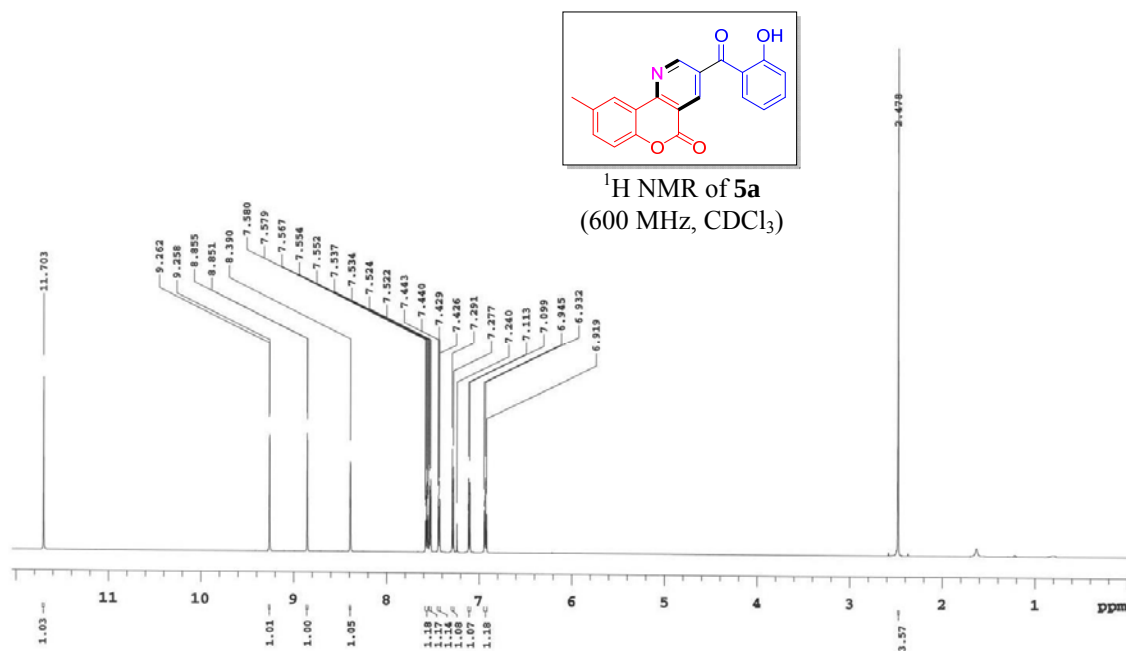
¹³C NMR of 4g
(150 MHz, CDCl₃)

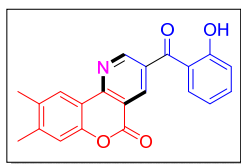




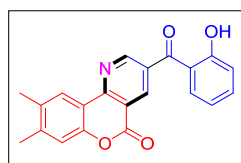
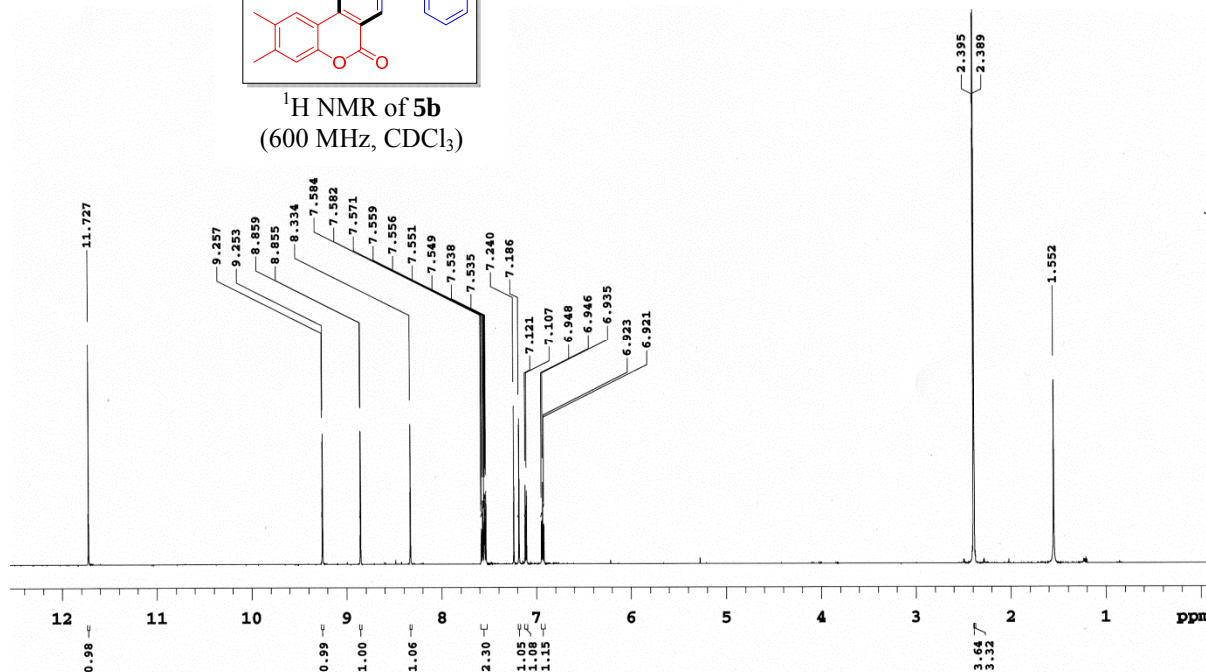




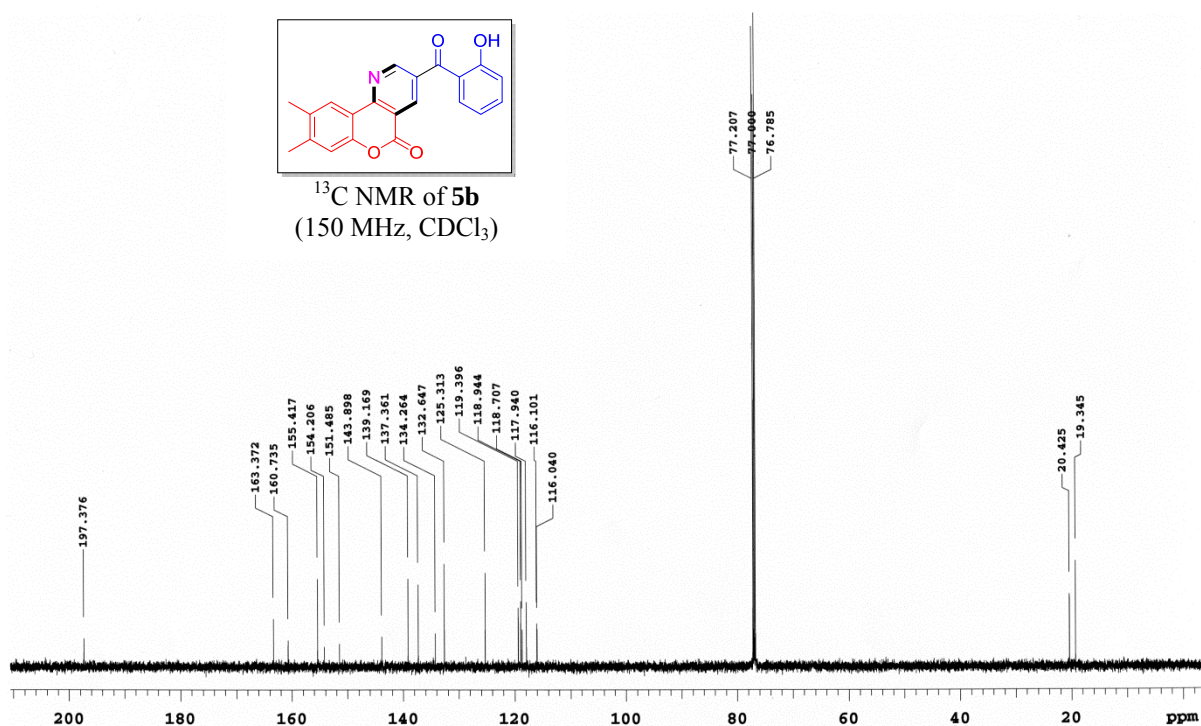


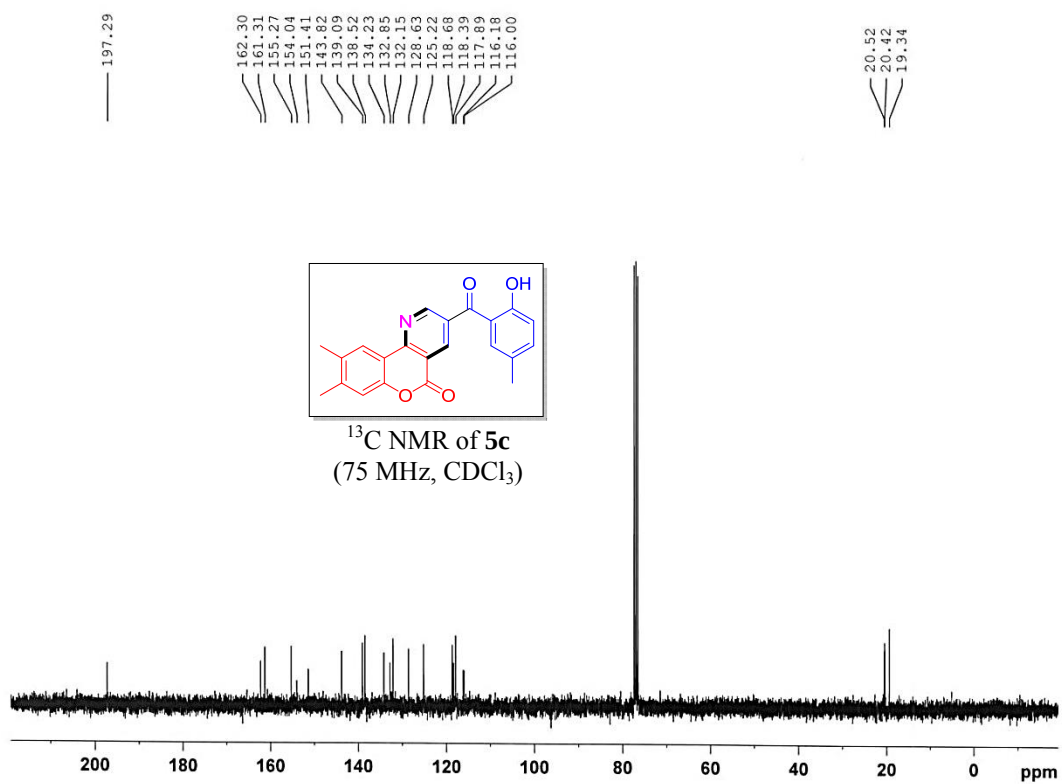
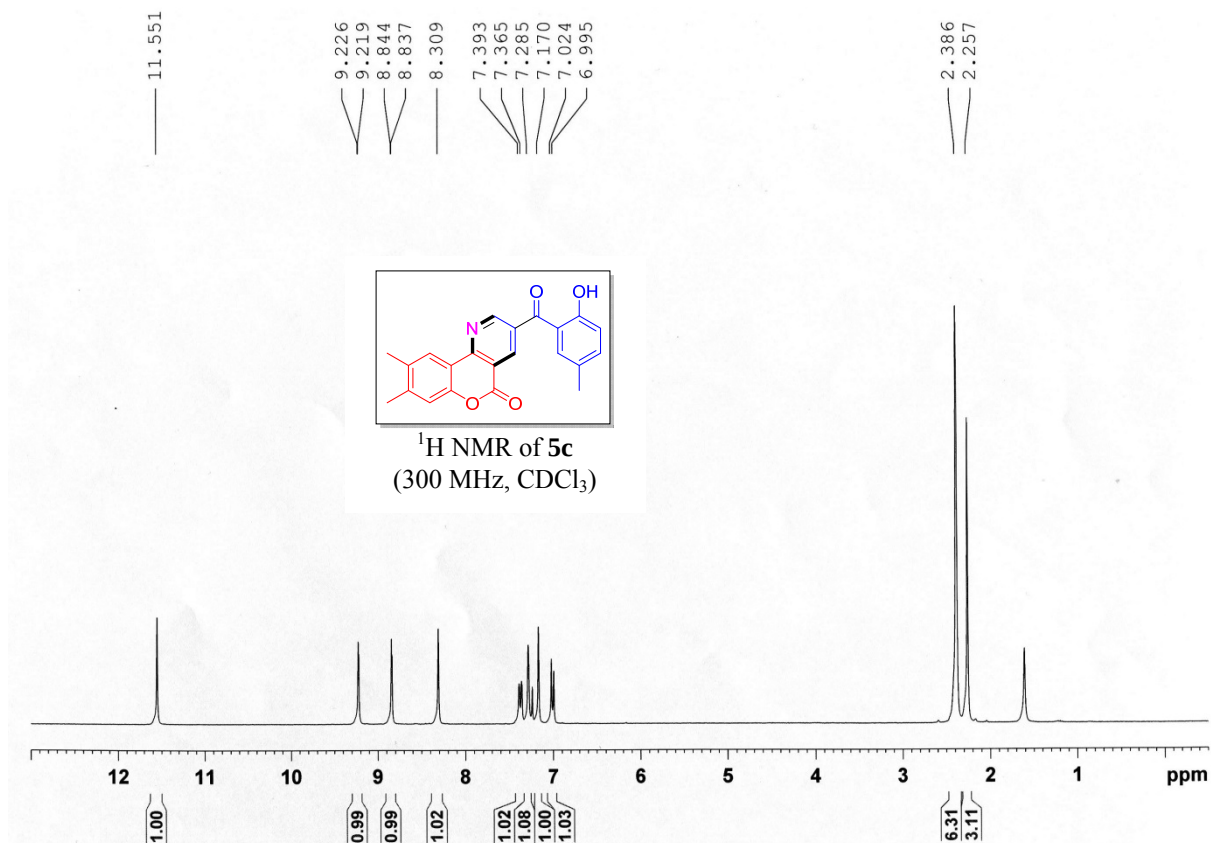


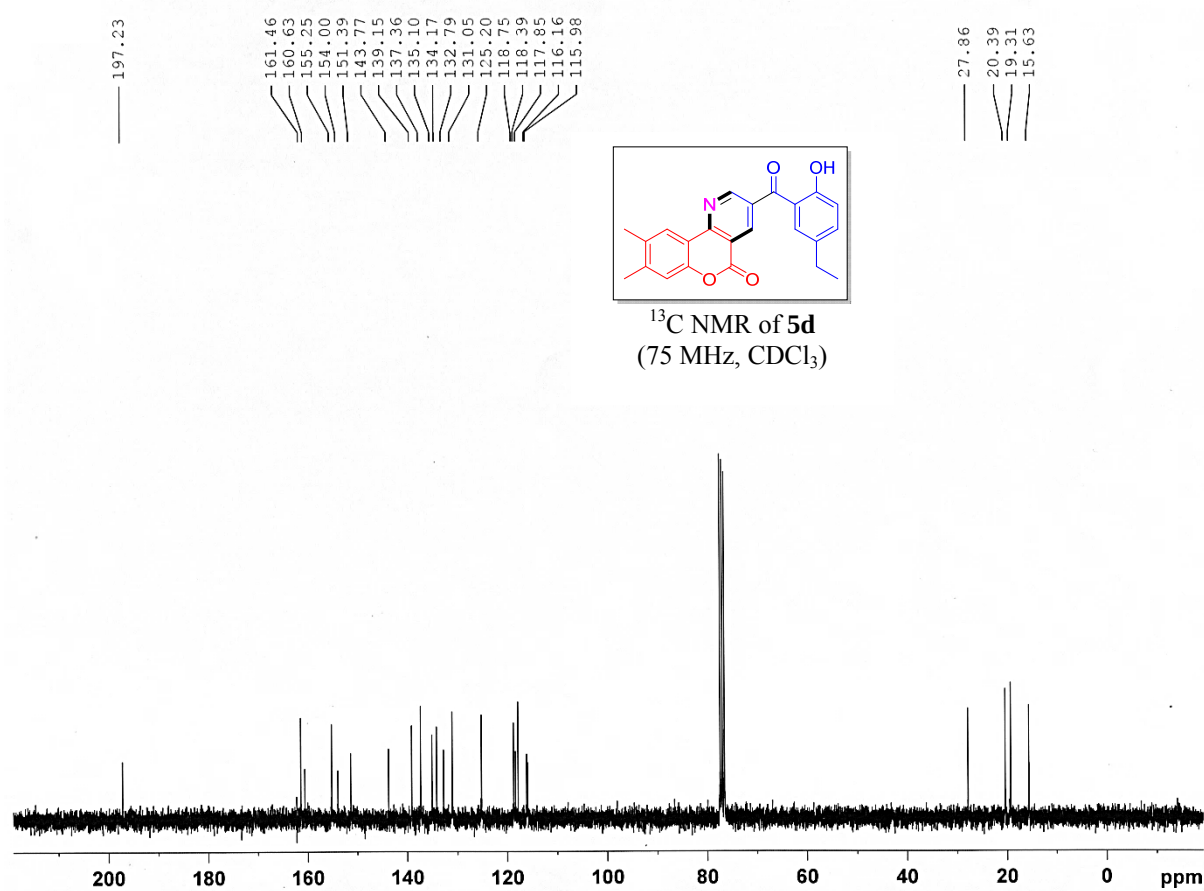
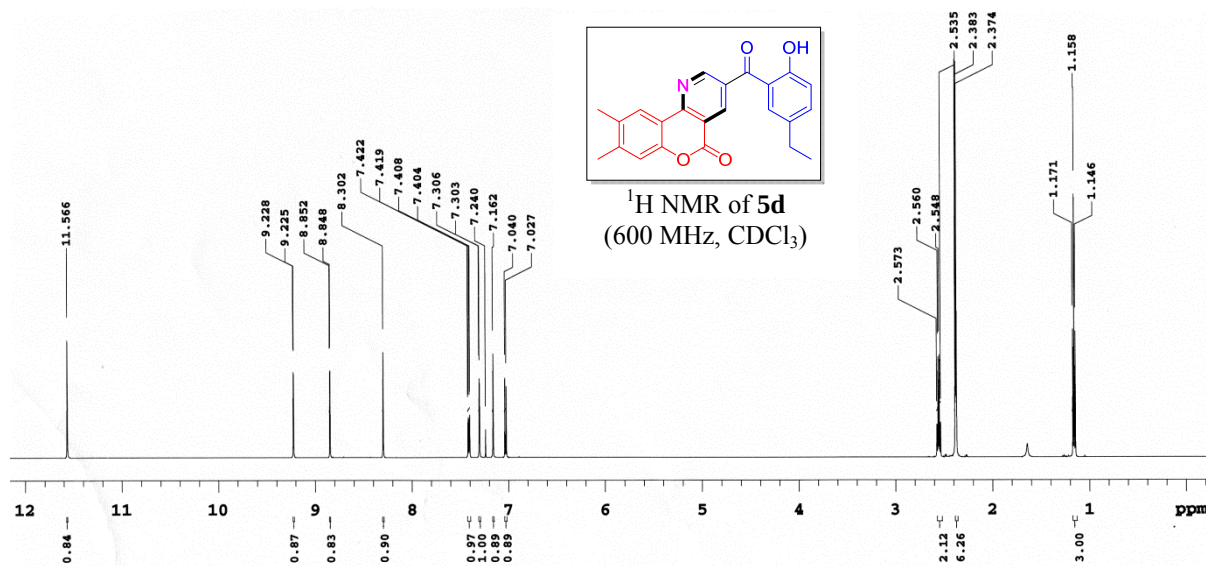
¹H NMR of **5b**
(600 MHz, CDCl₃)

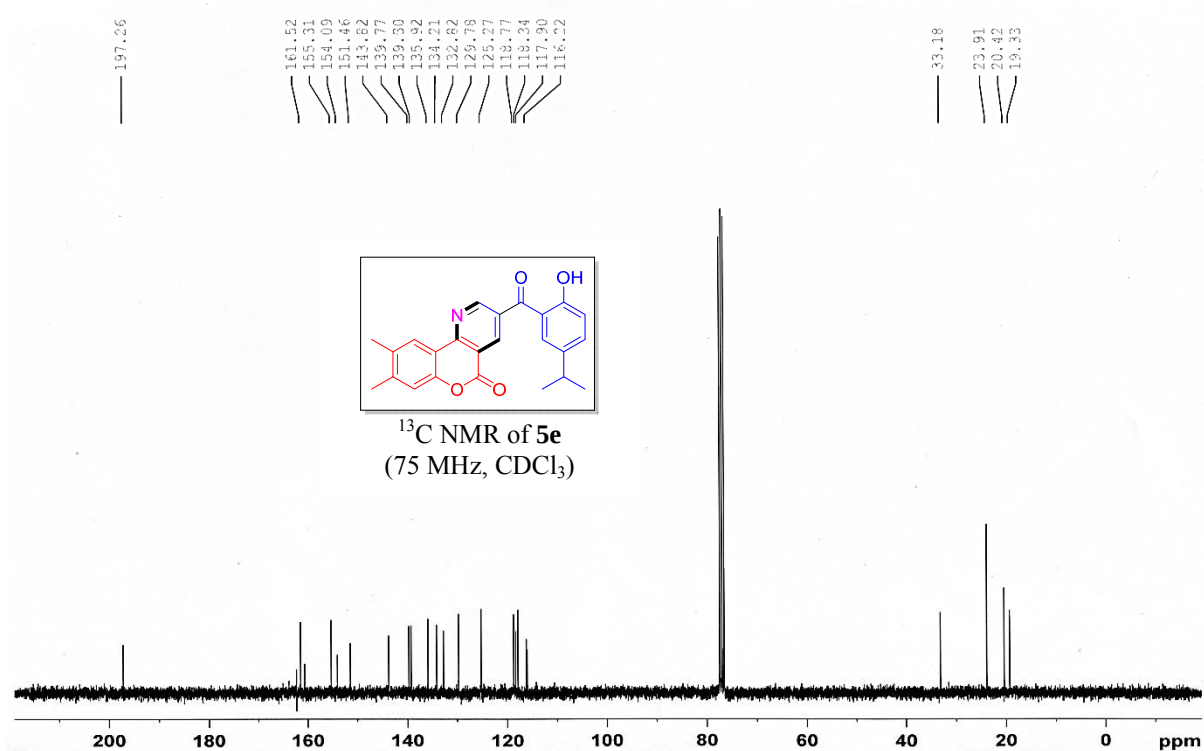
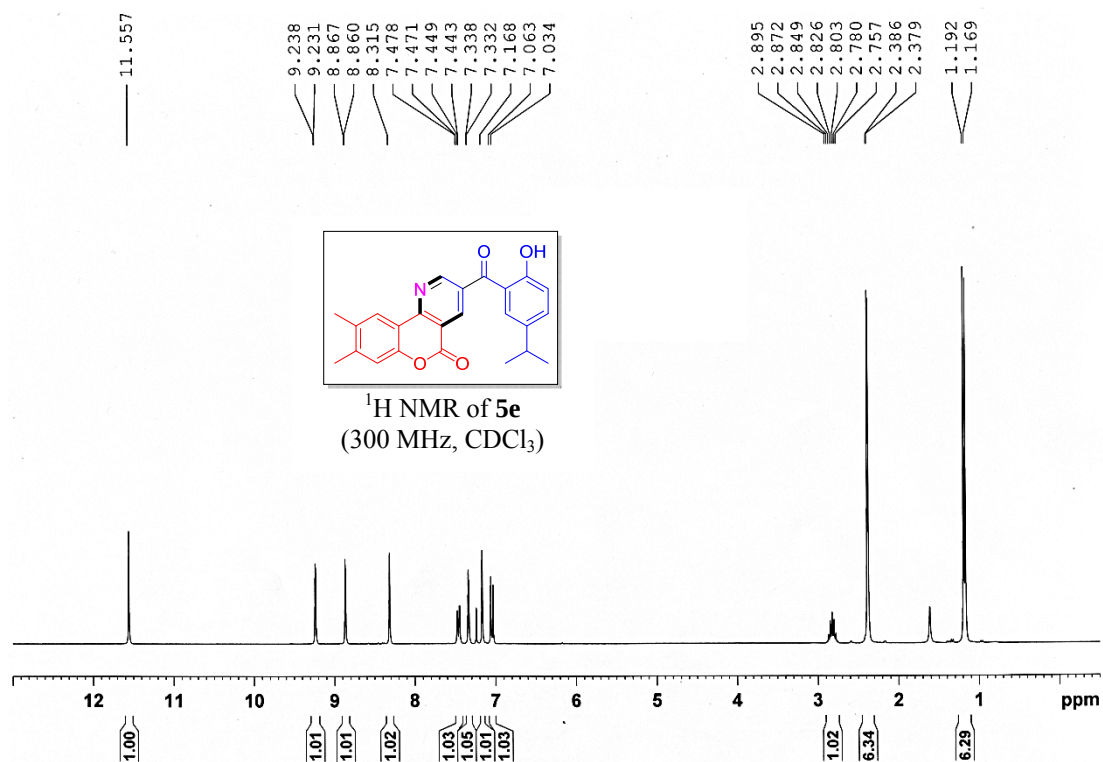


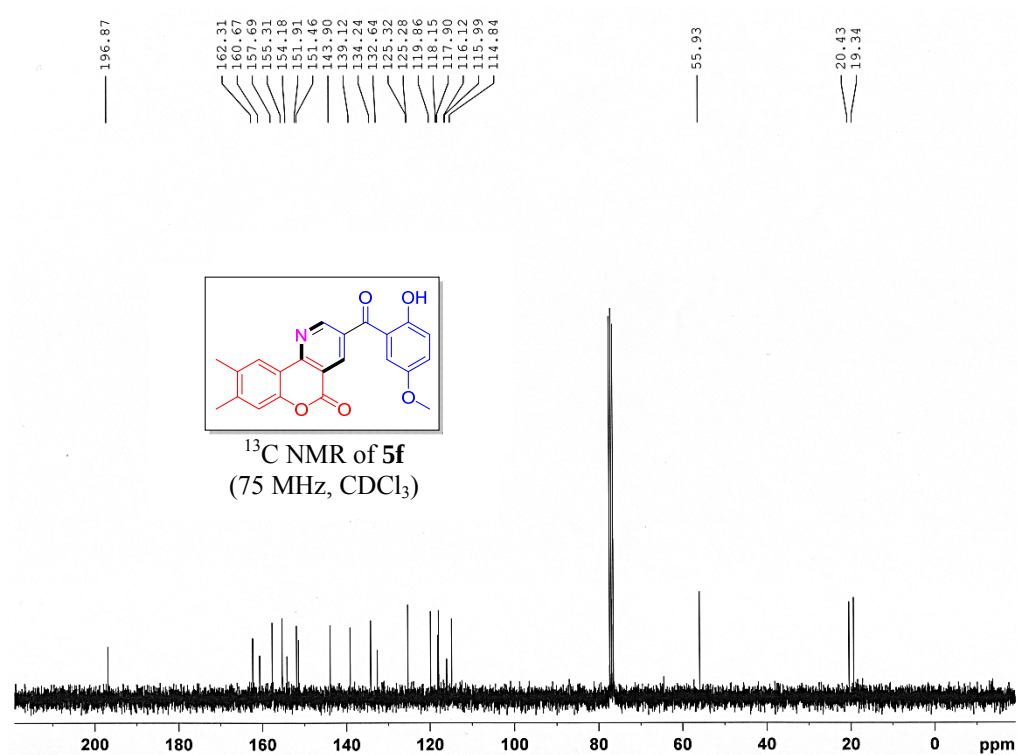
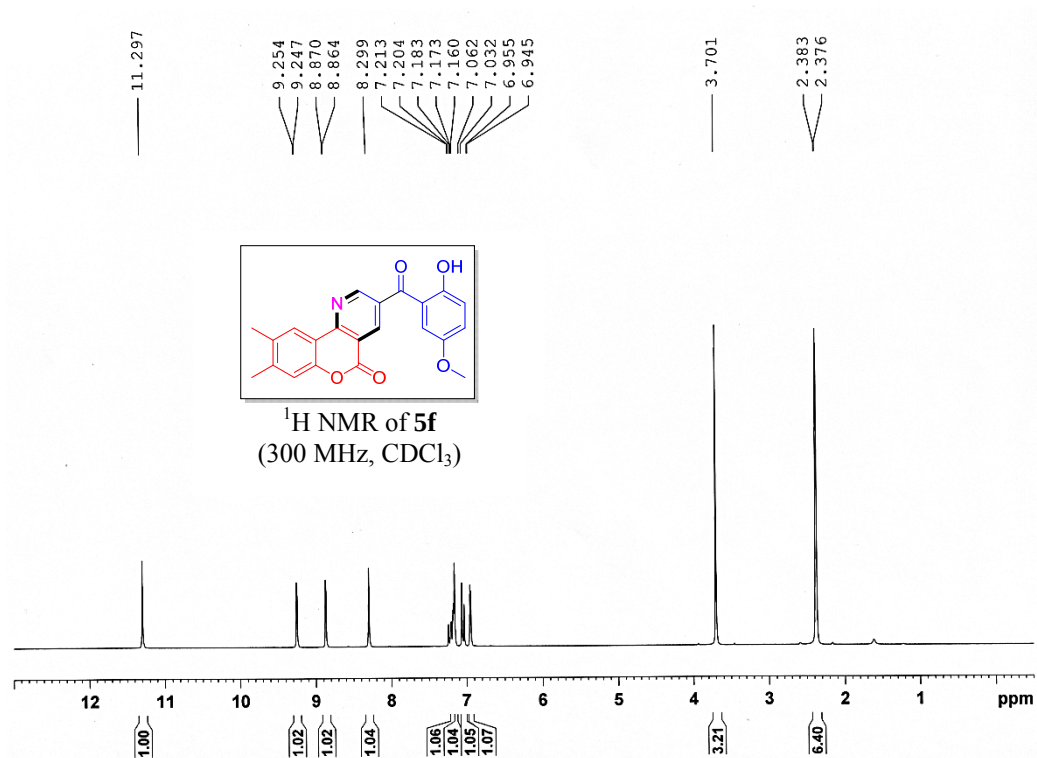
¹³C NMR of **5b**
(150 MHz, CDCl₃)

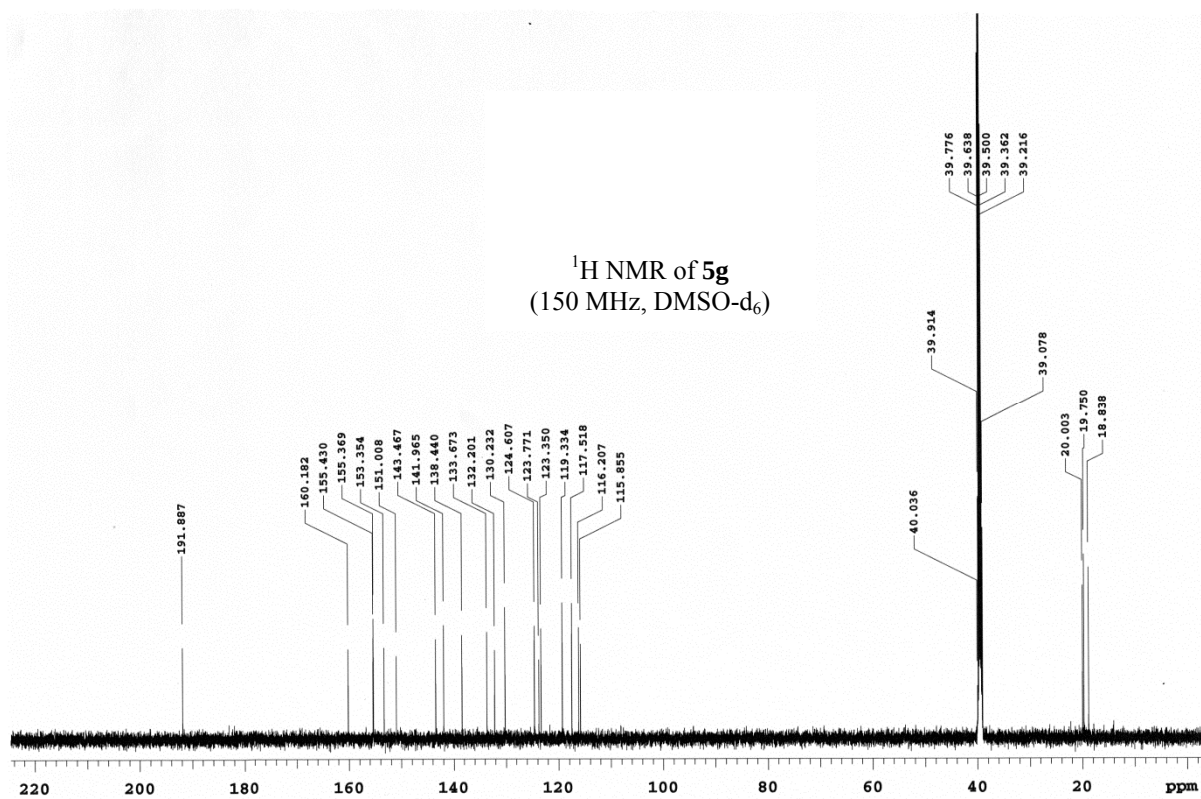
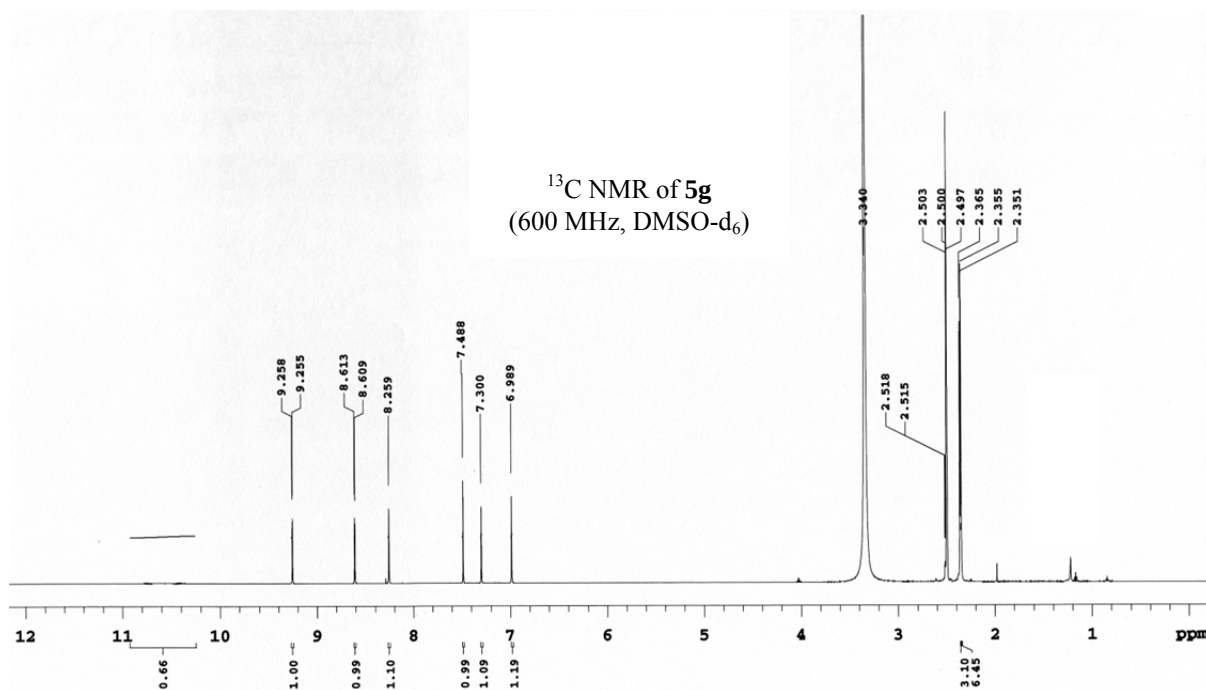


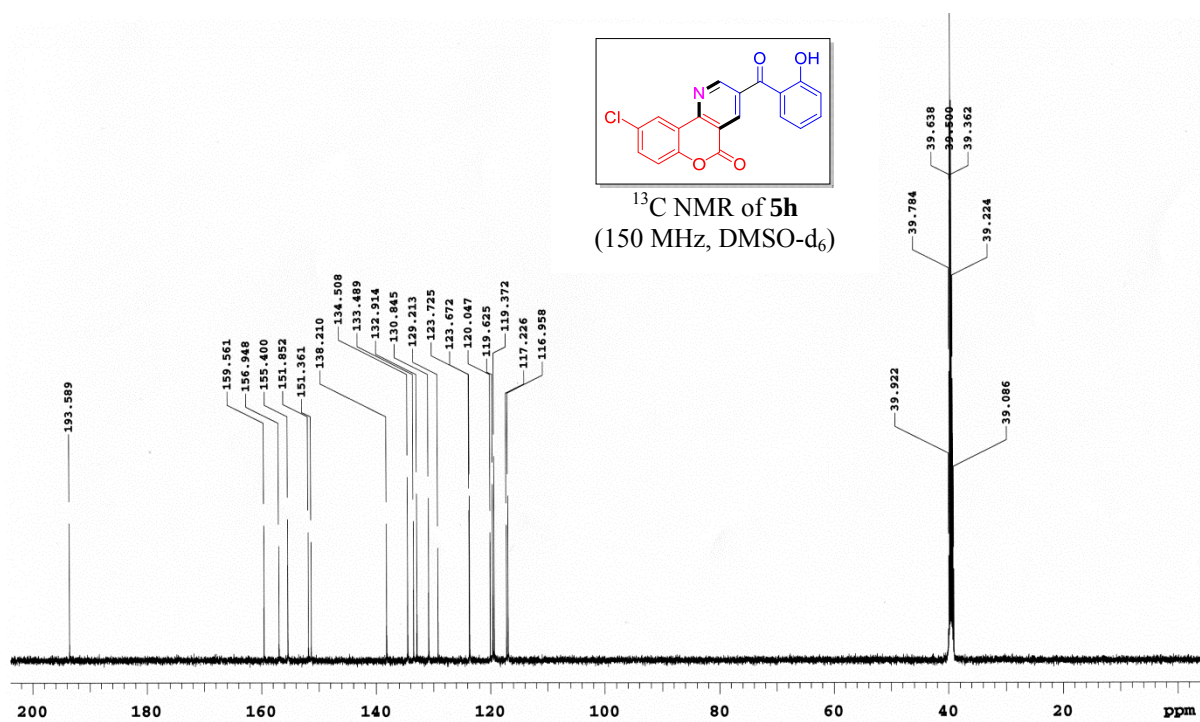
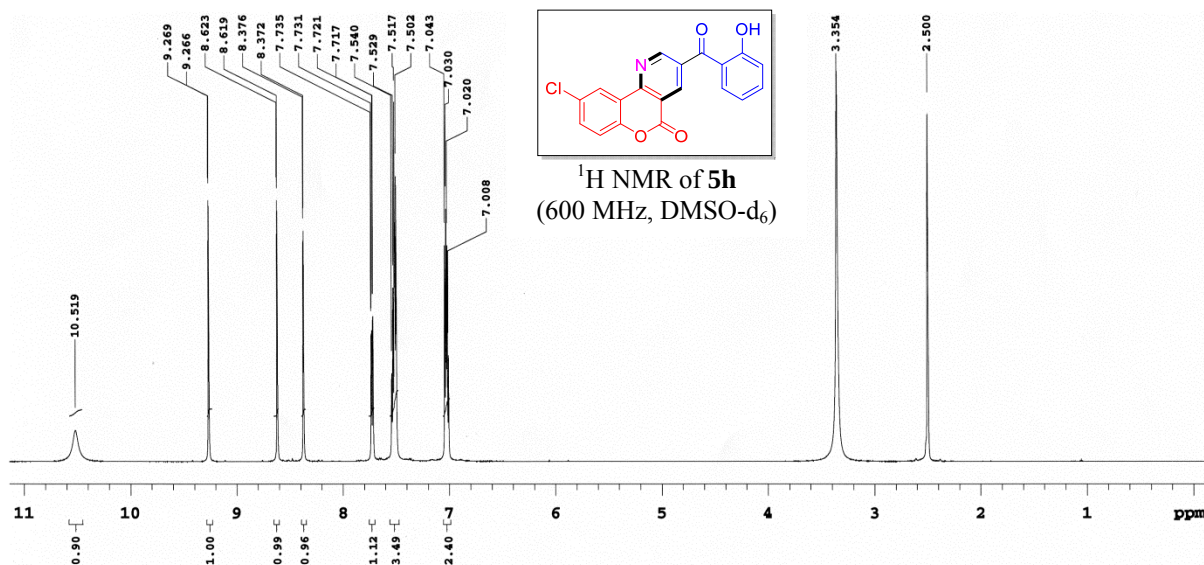


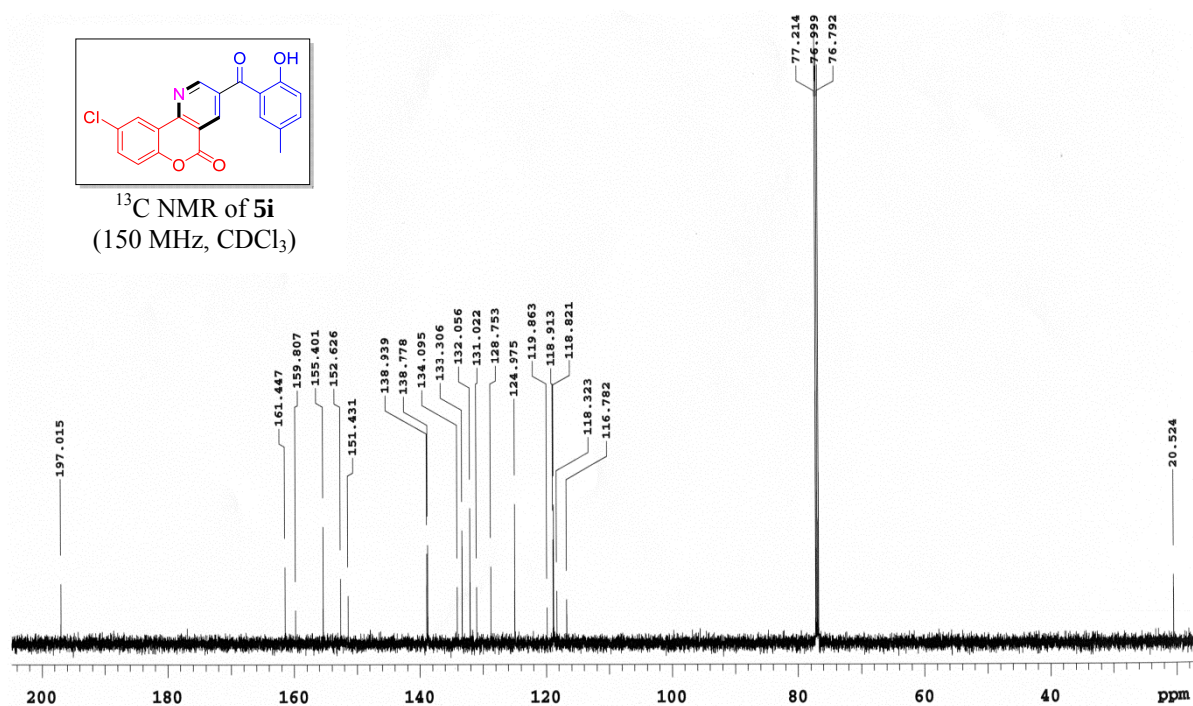
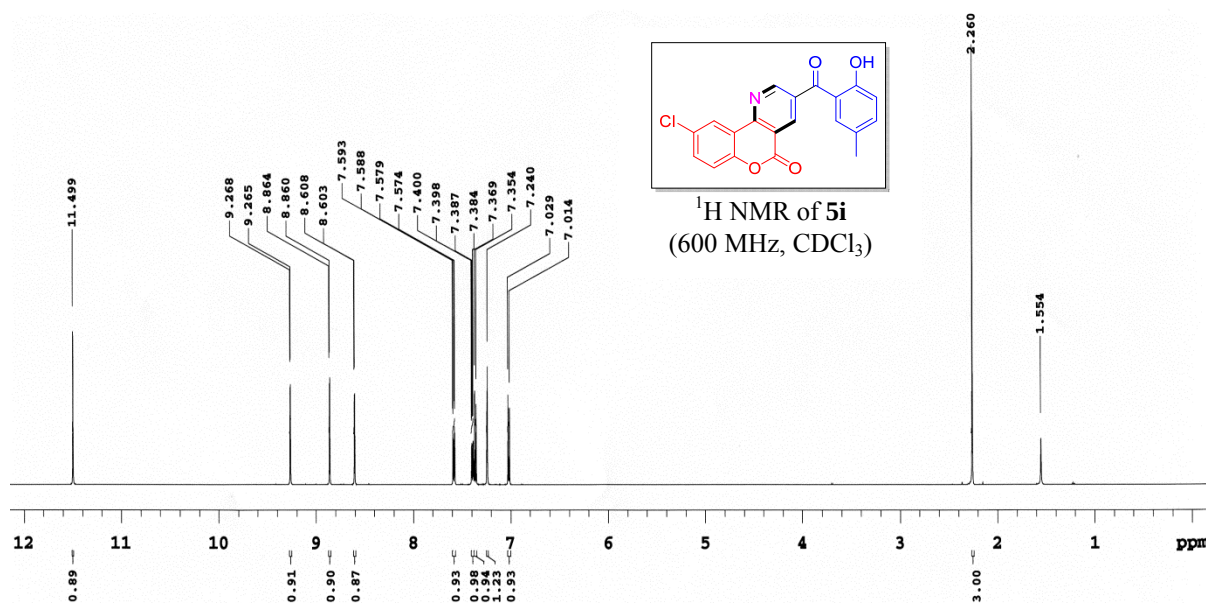


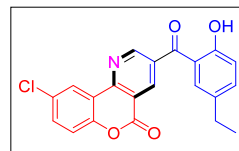




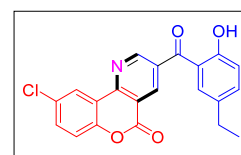
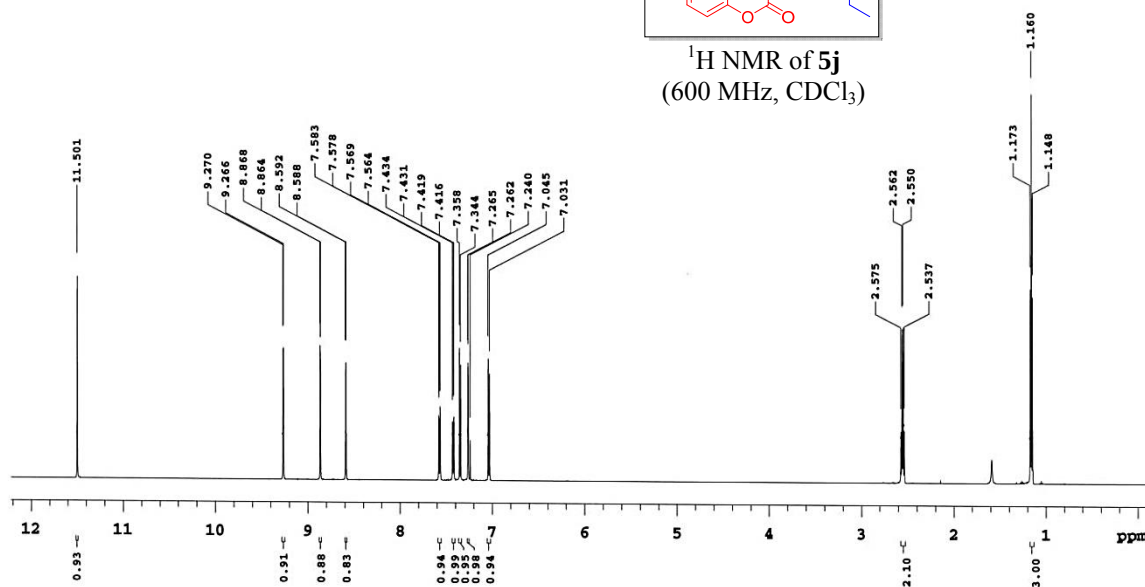




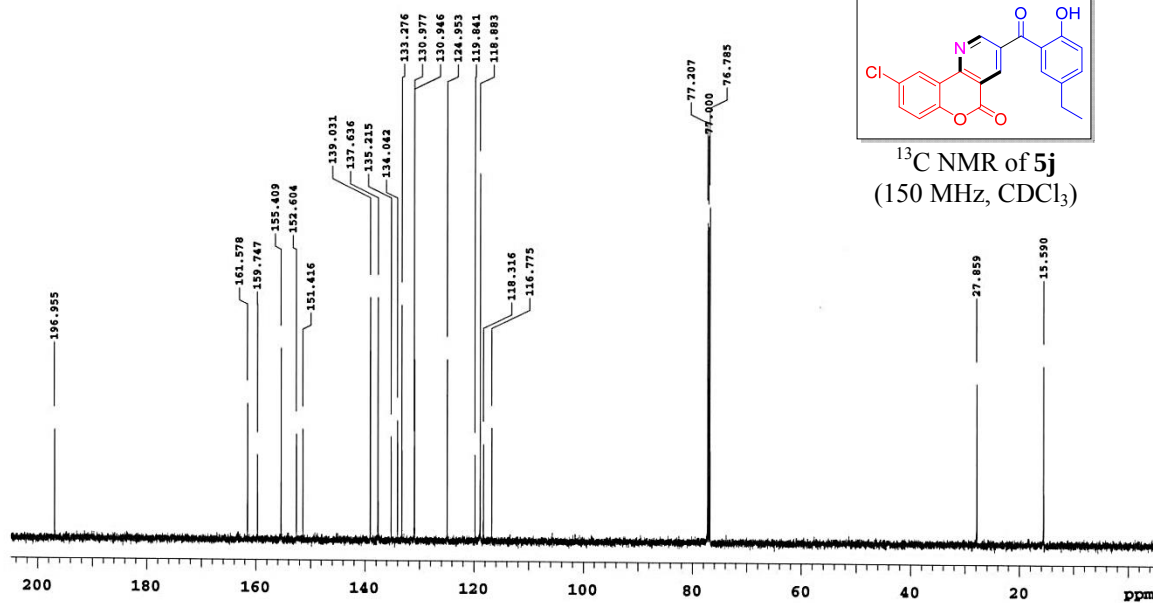


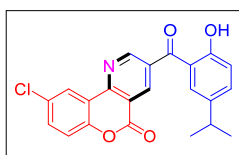


¹H NMR of **5j**
(600 MHz, CDCl₃)

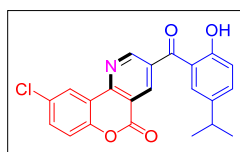
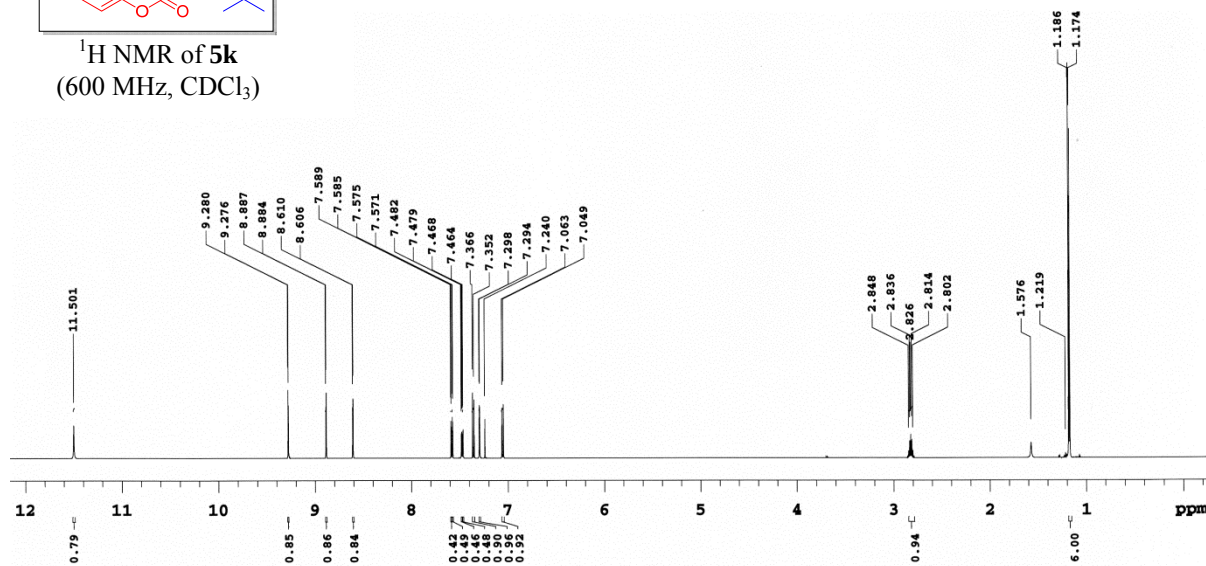


¹³C NMR of **5j**
(150 MHz, CDCl₃)

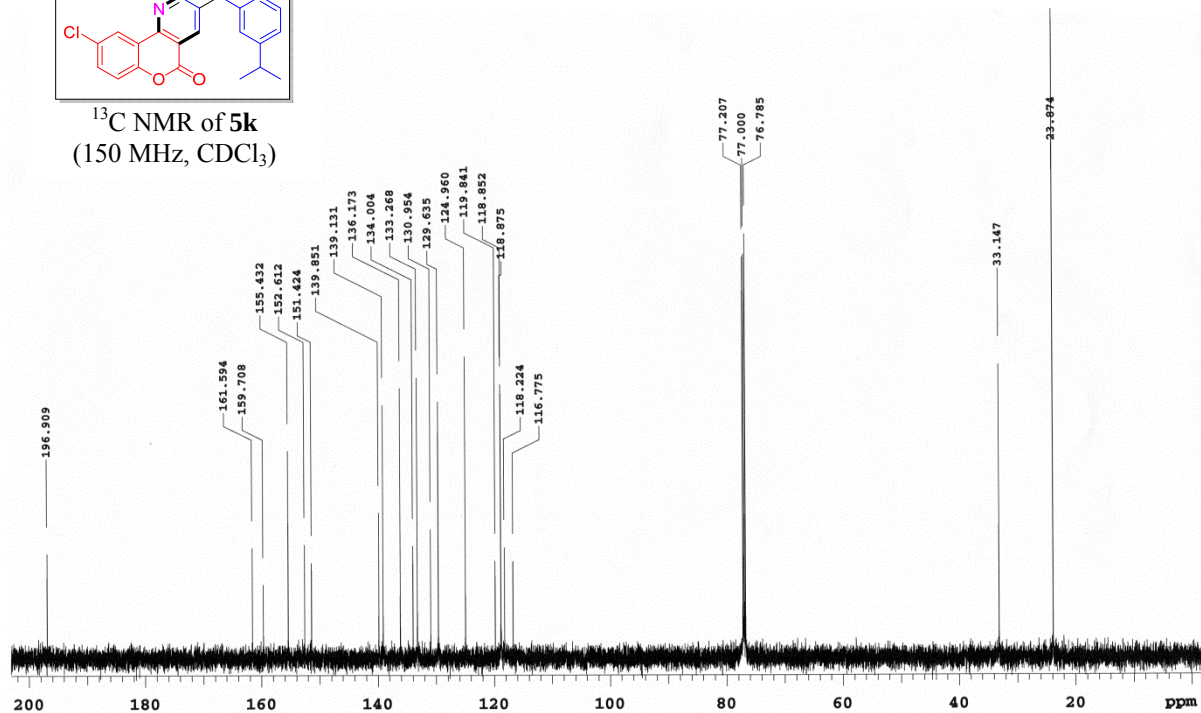


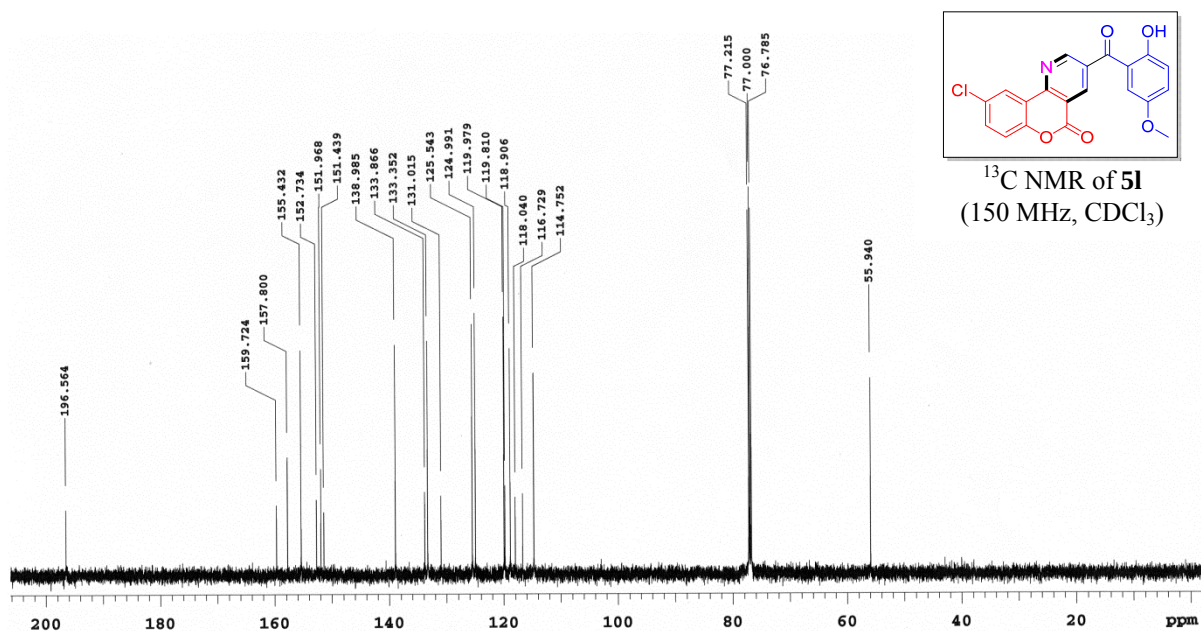
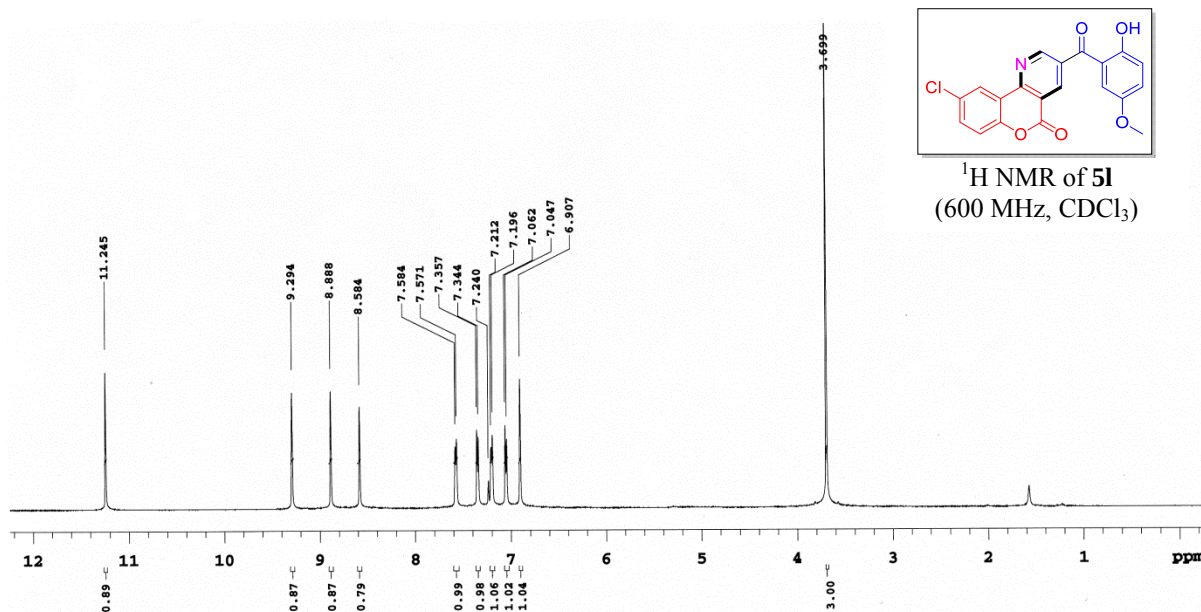


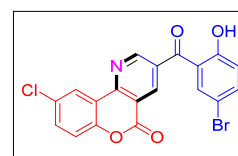
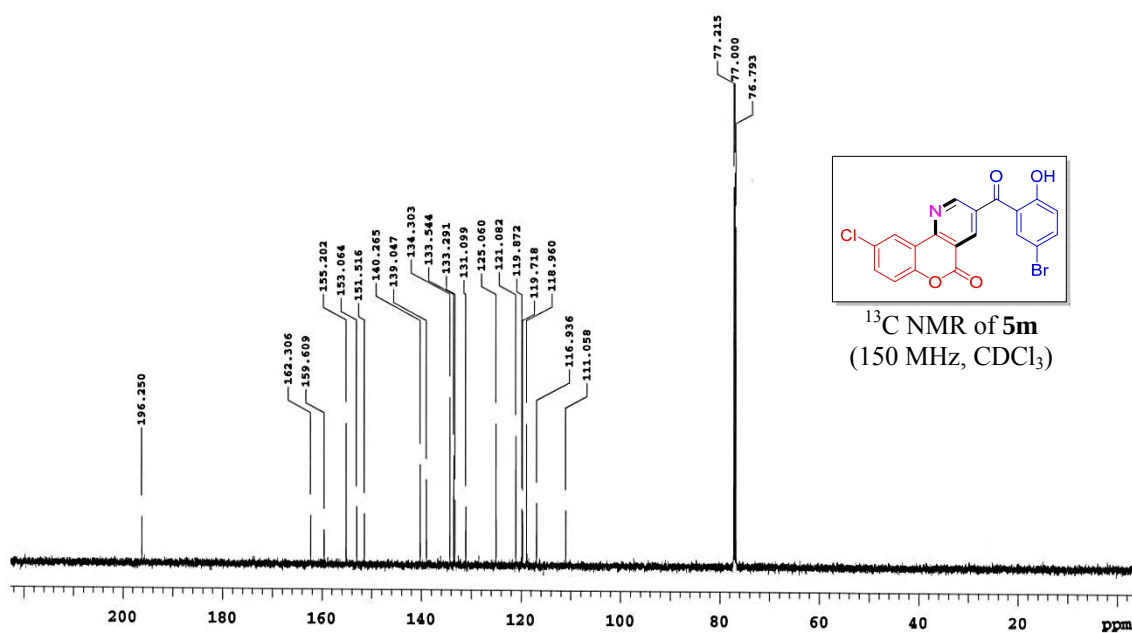
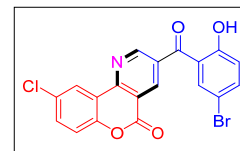
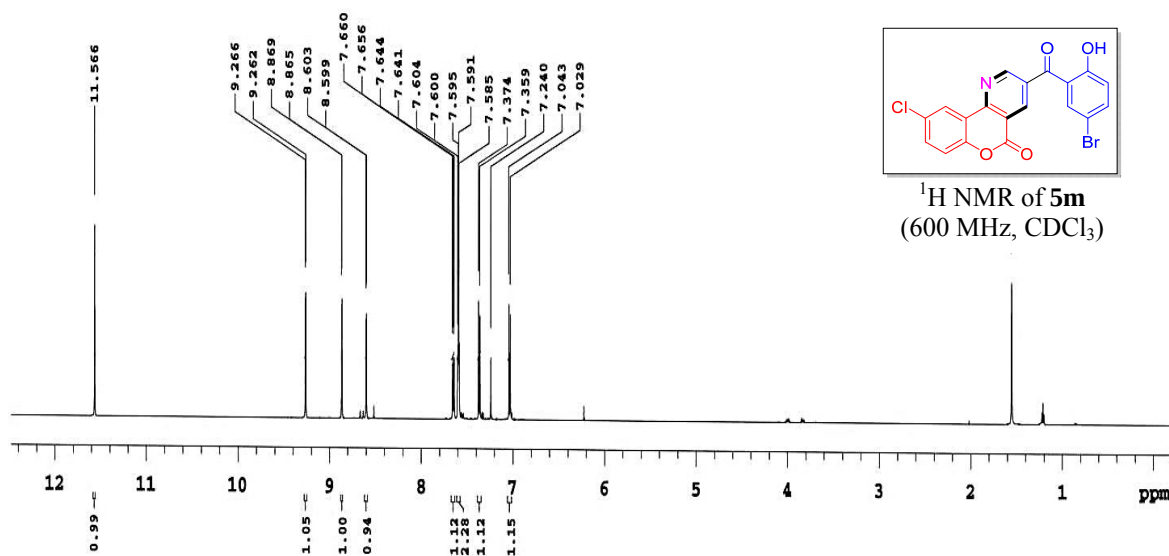
¹H NMR of **5k**
(600 MHz, CDCl₃)

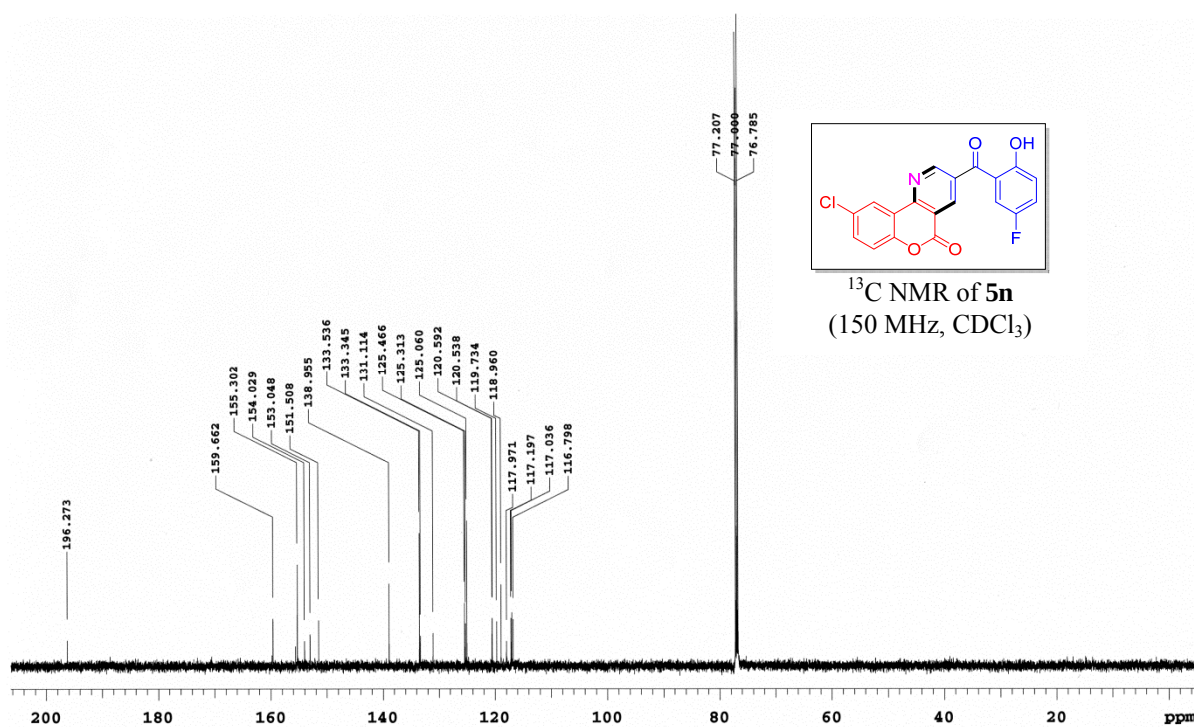
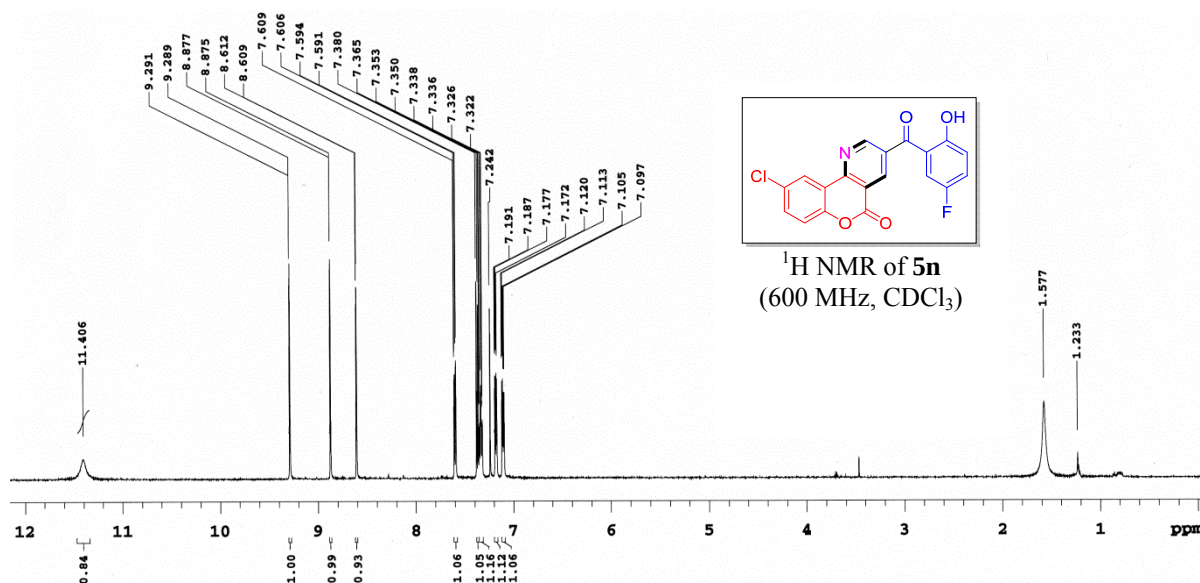


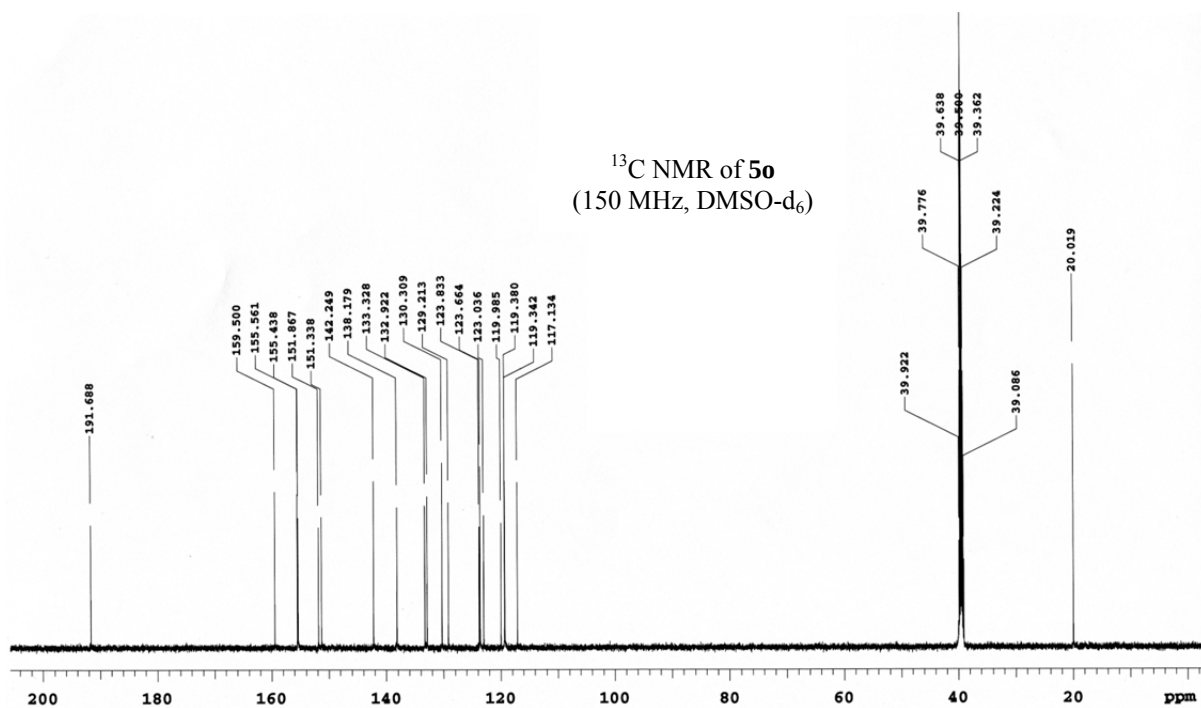
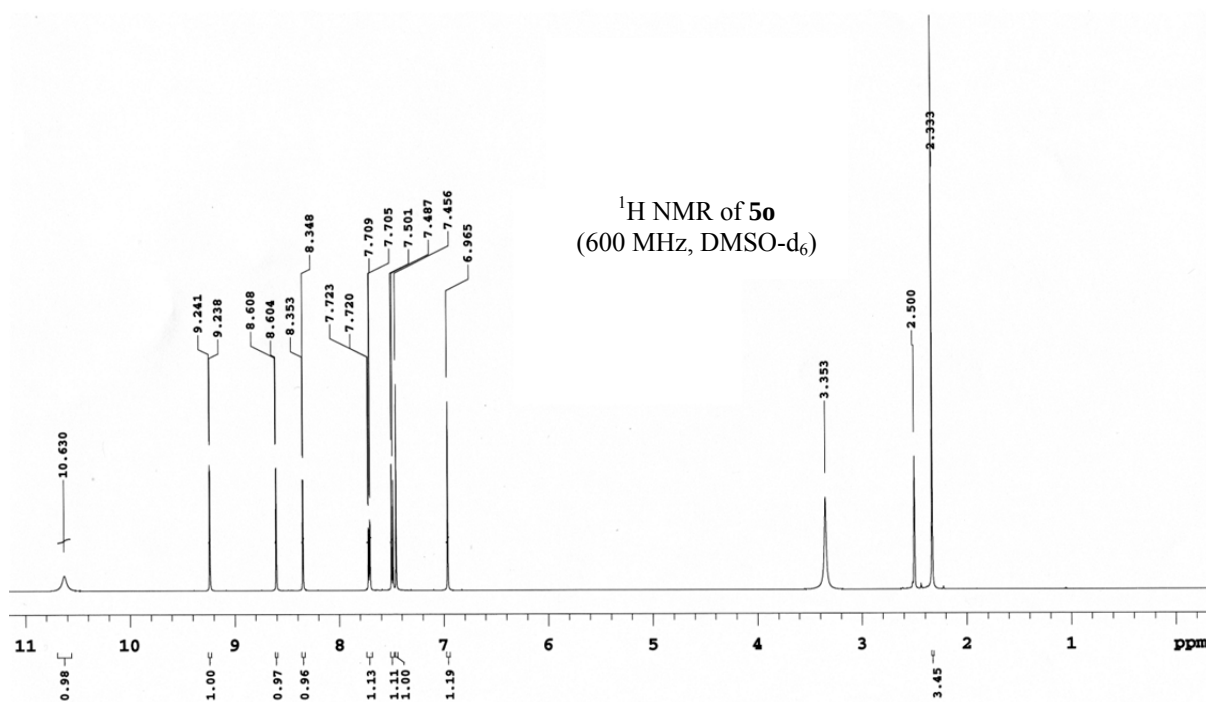
¹³C NMR of **5k**
(150 MHz, CDCl₃)

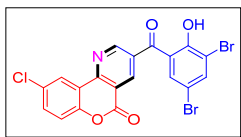




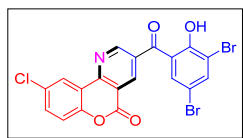
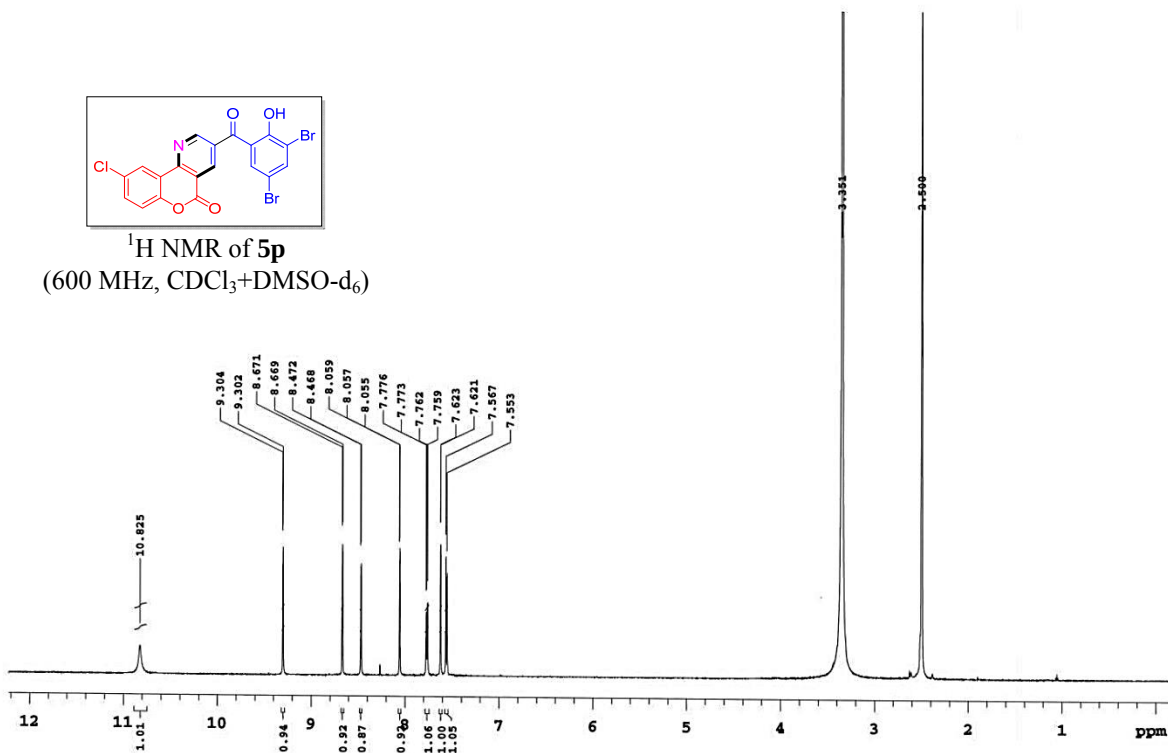




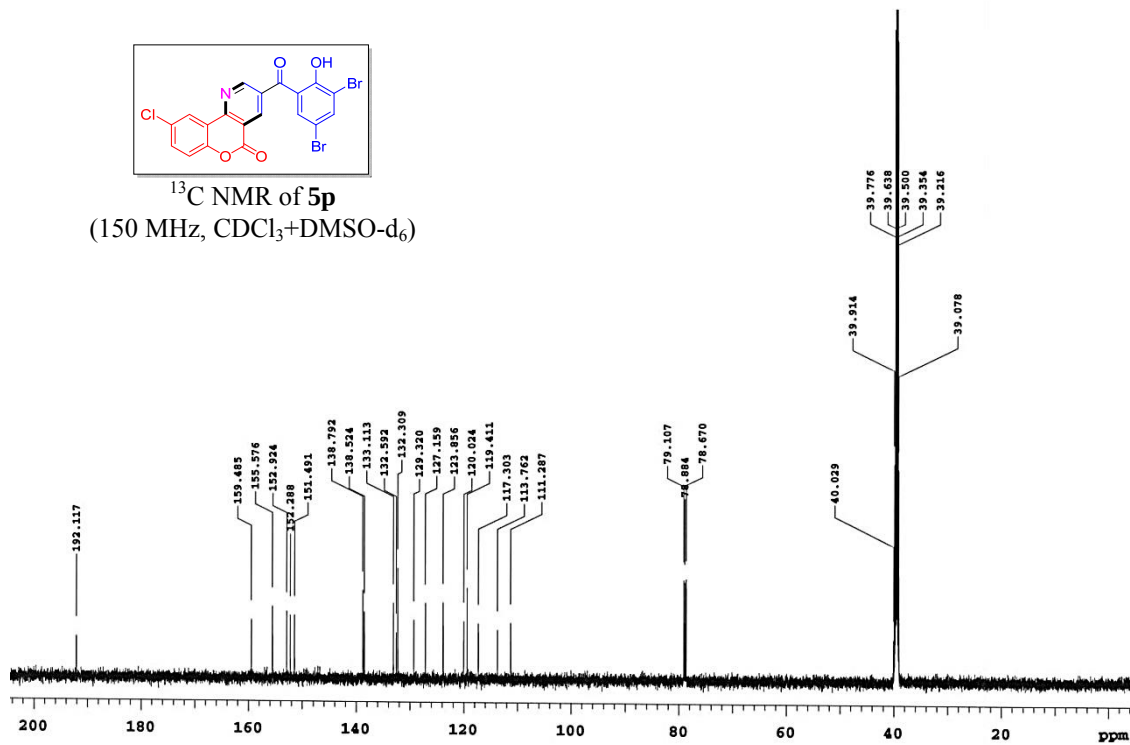


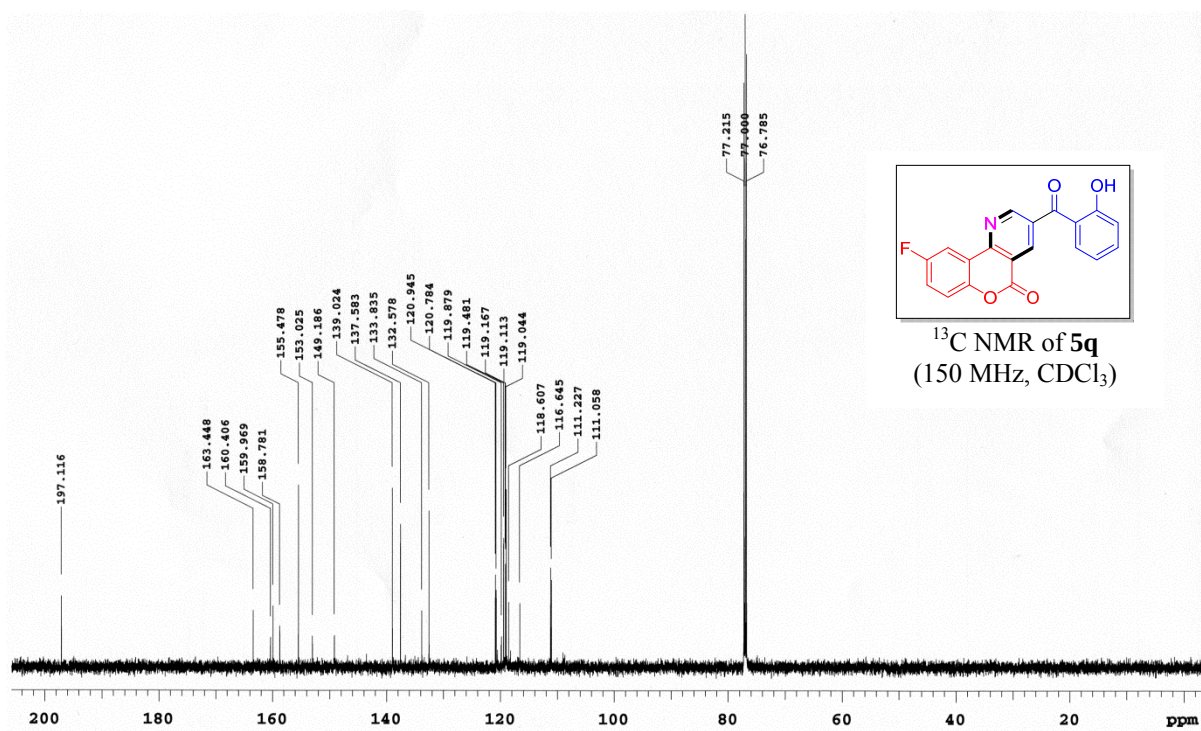
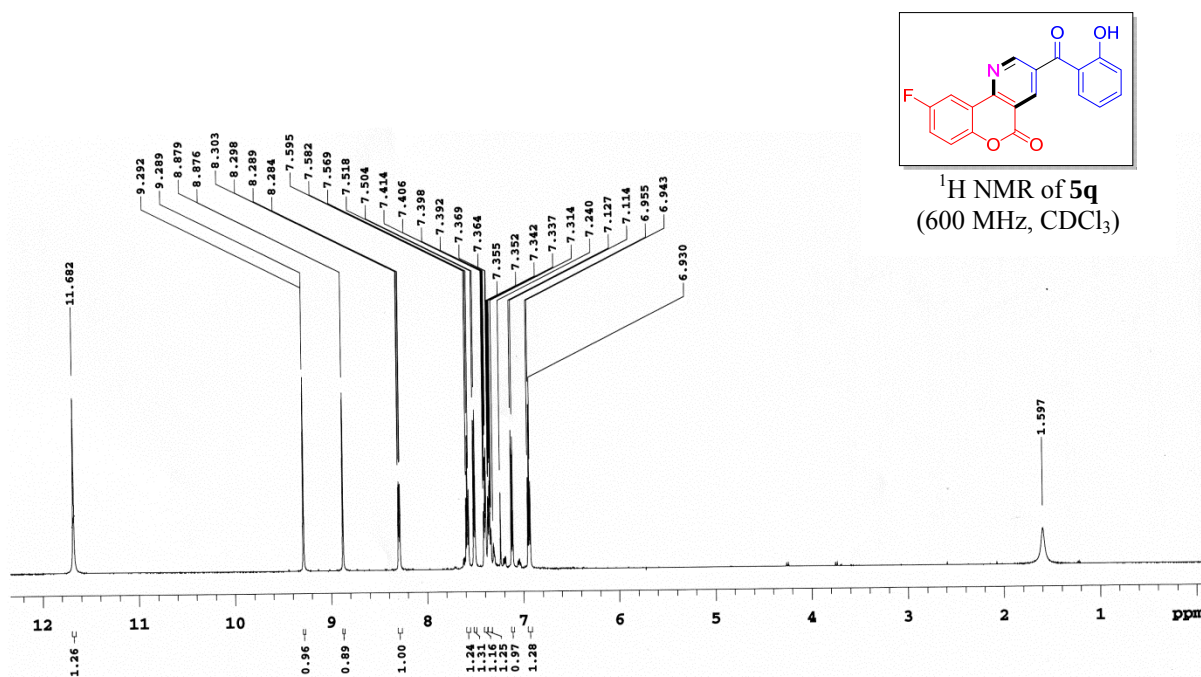


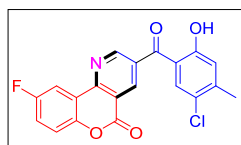
^1H NMR of **5p**
(600 MHz, CDCl_3 +DMSO- d_6)



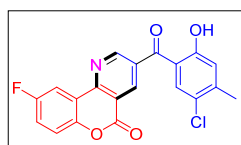
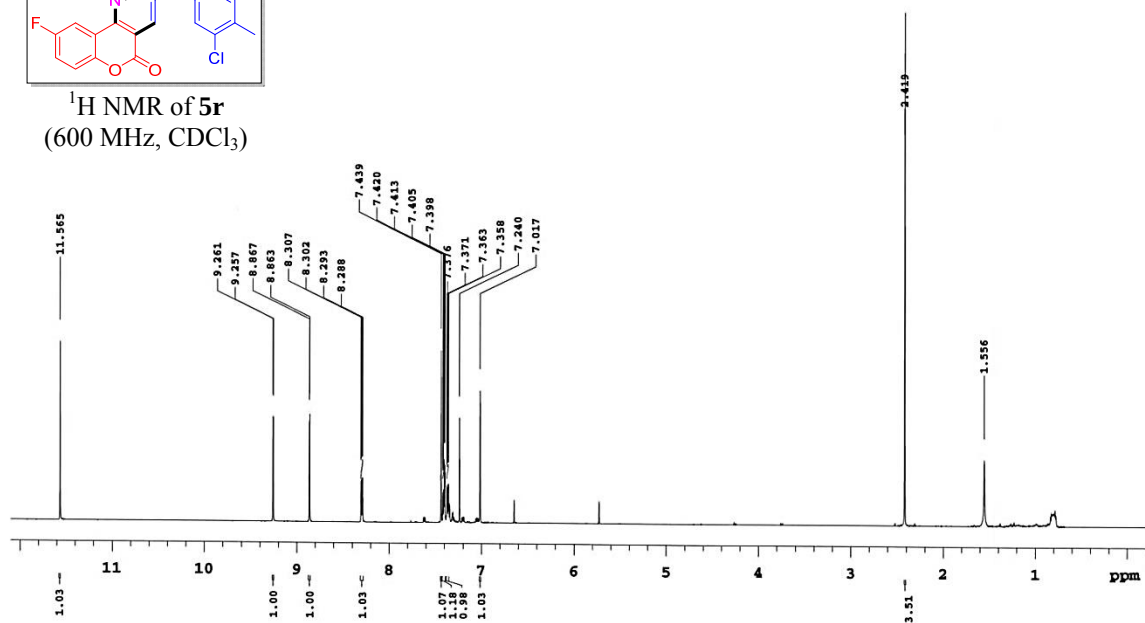
^{13}C NMR of **5p**
(150 MHz, CDCl_3 +DMSO- d_6)



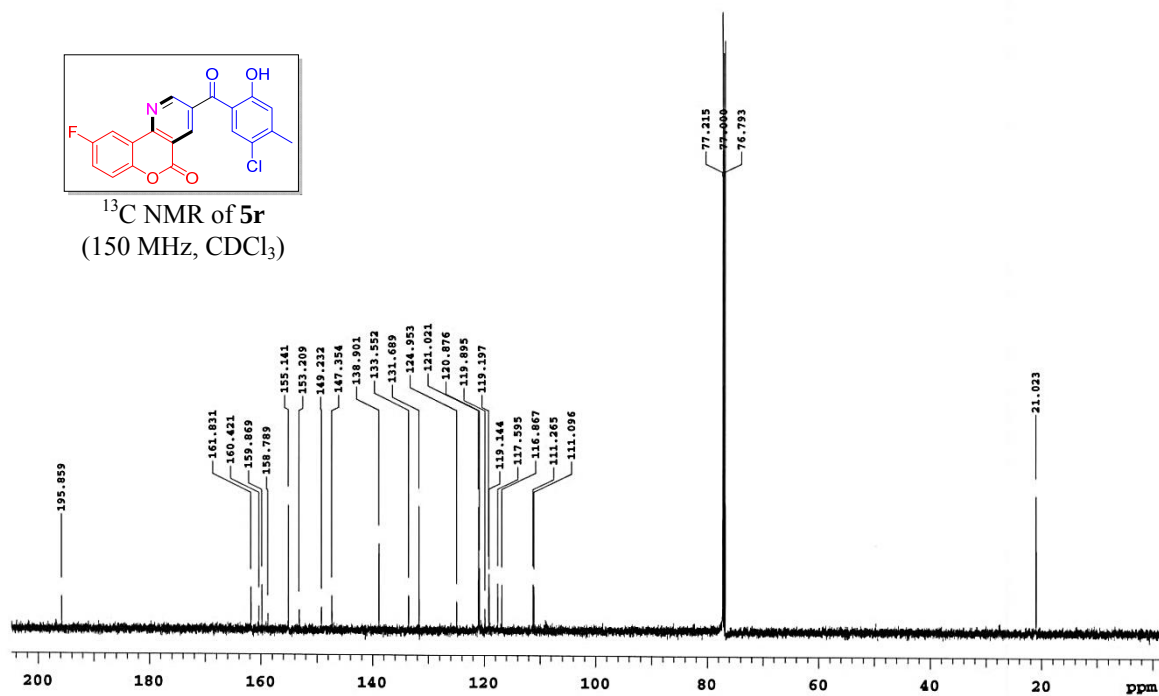


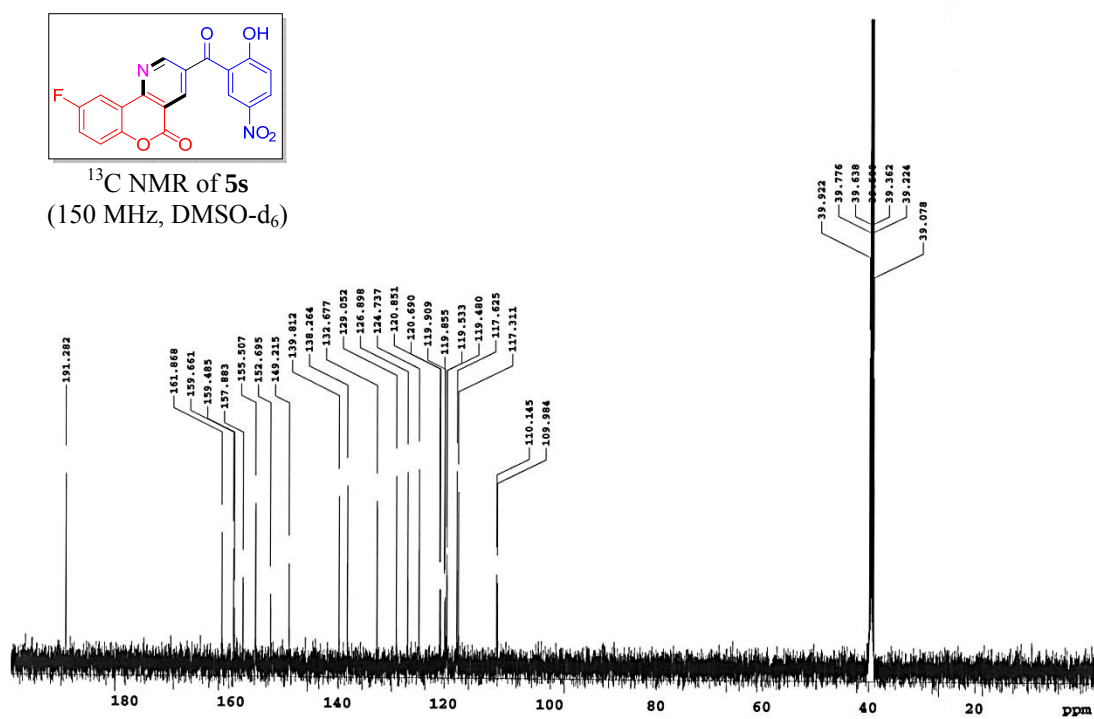
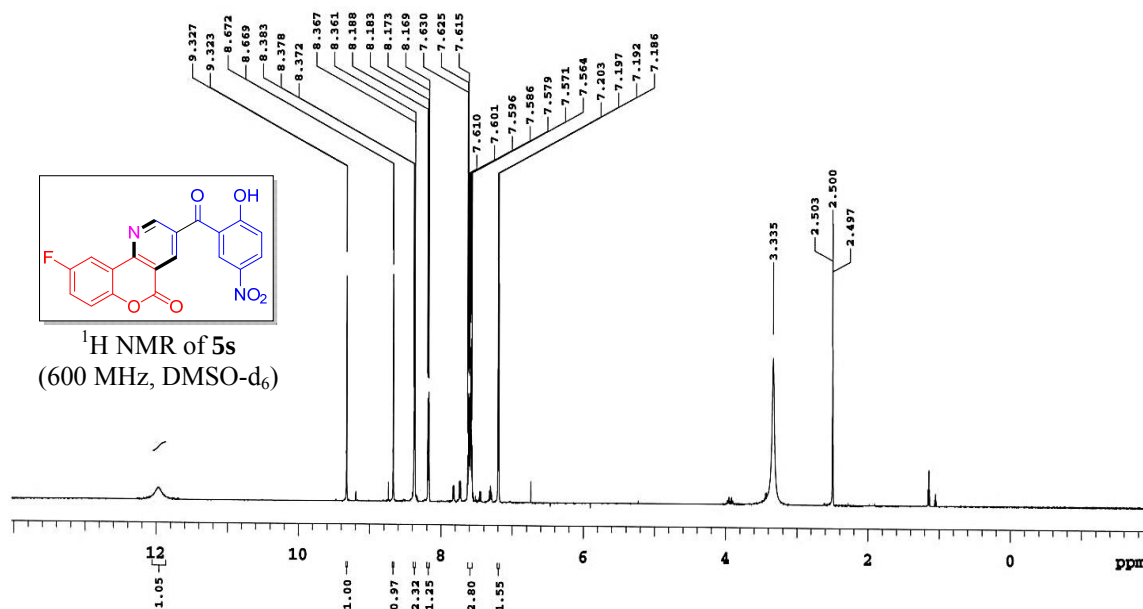


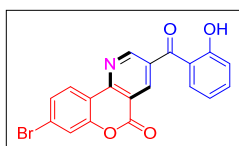
^1H NMR of **5r**
(600 MHz, CDCl_3)



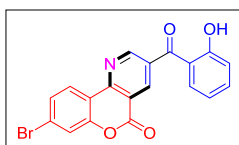
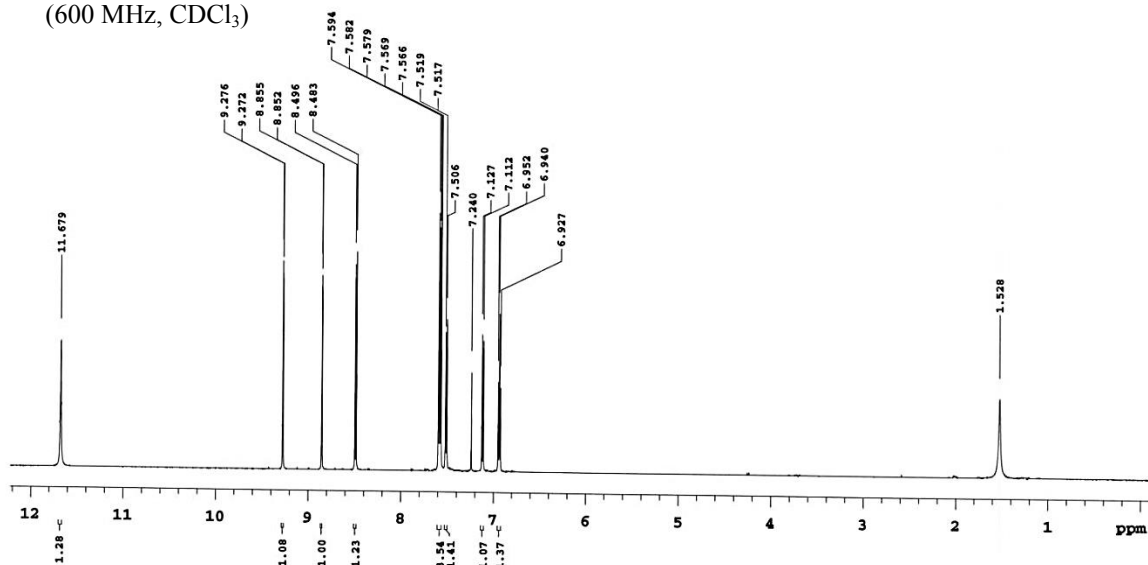
^{13}C NMR of **5r**
(150 MHz, CDCl_3)



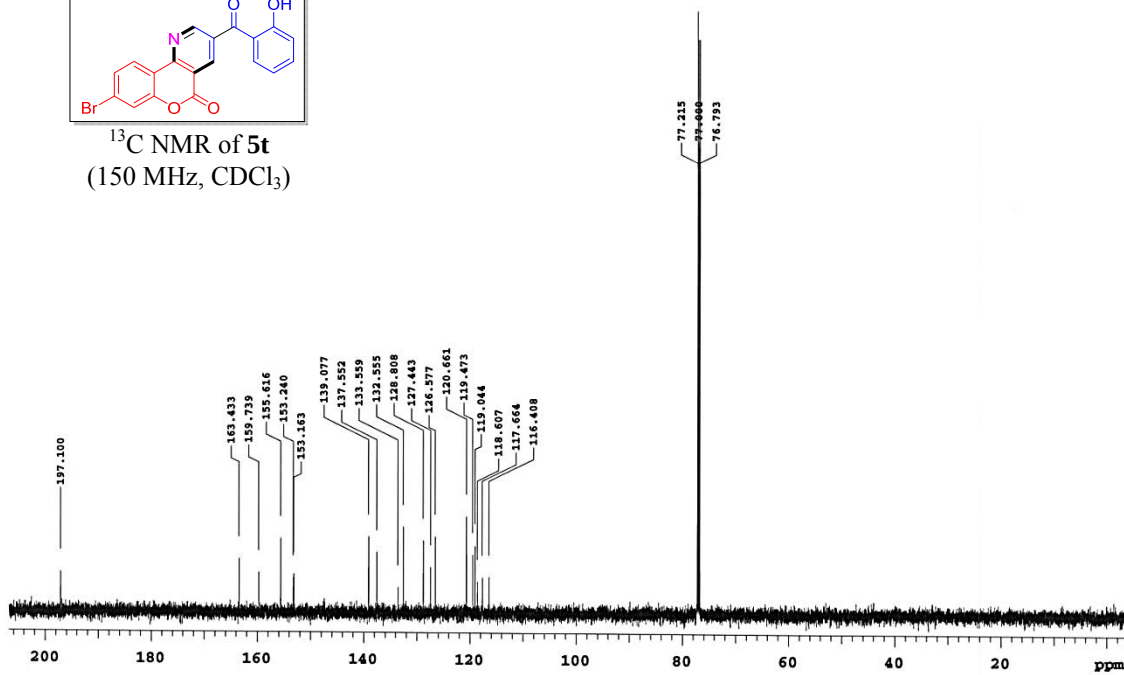


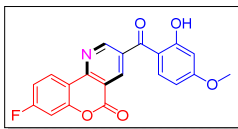


¹H NMR of **5t**
(600 MHz, CDCl₃)

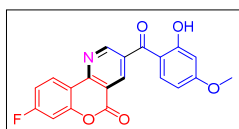
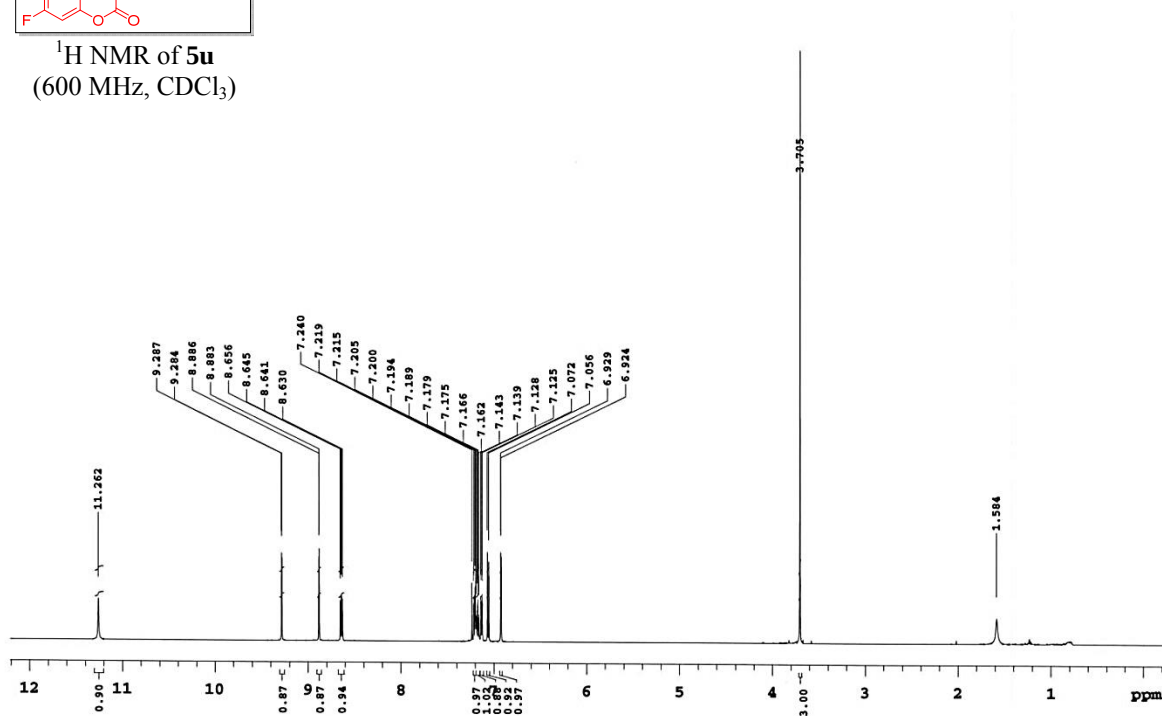


¹³C NMR of **5t**
(150 MHz, CDCl₃)

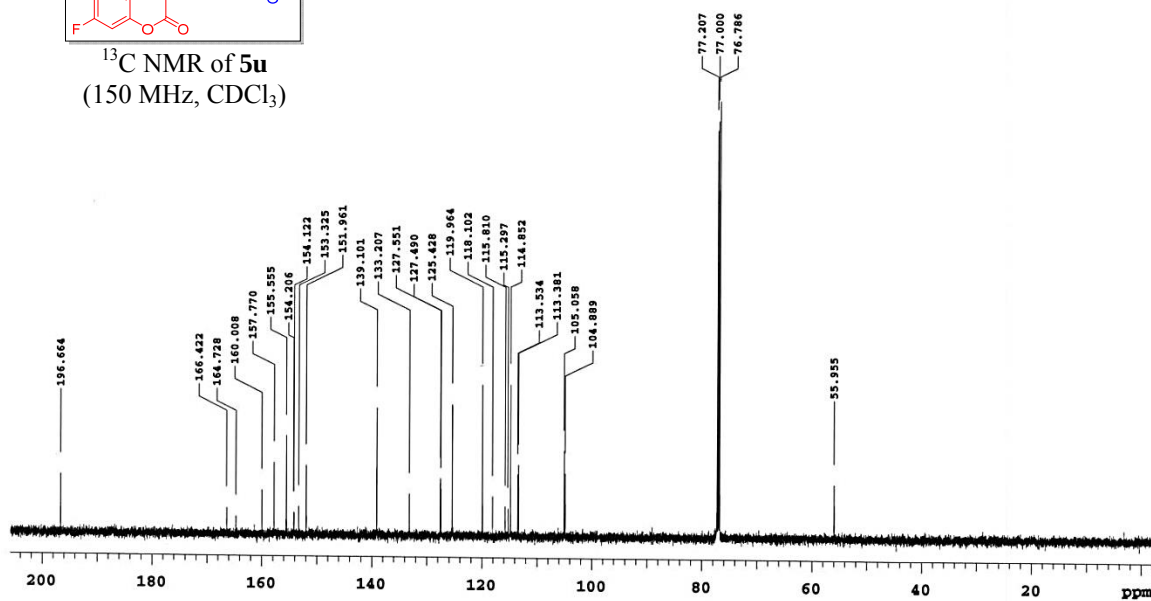


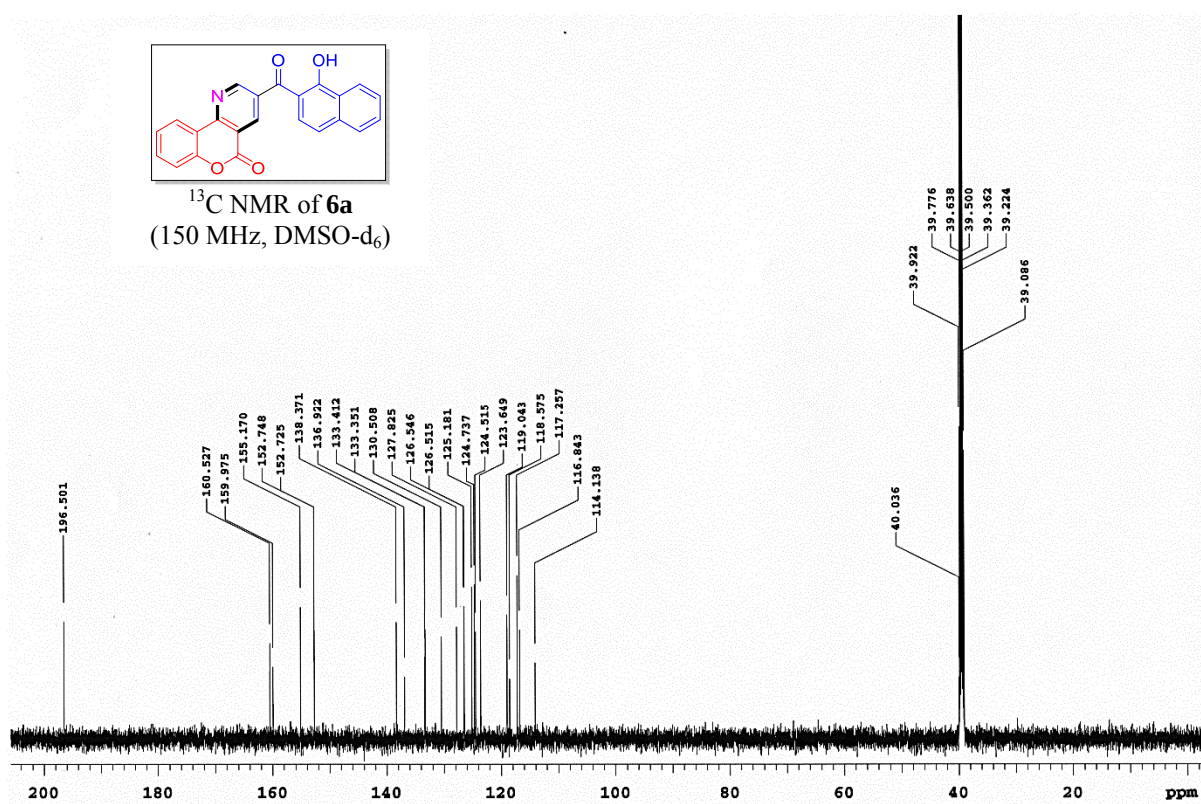
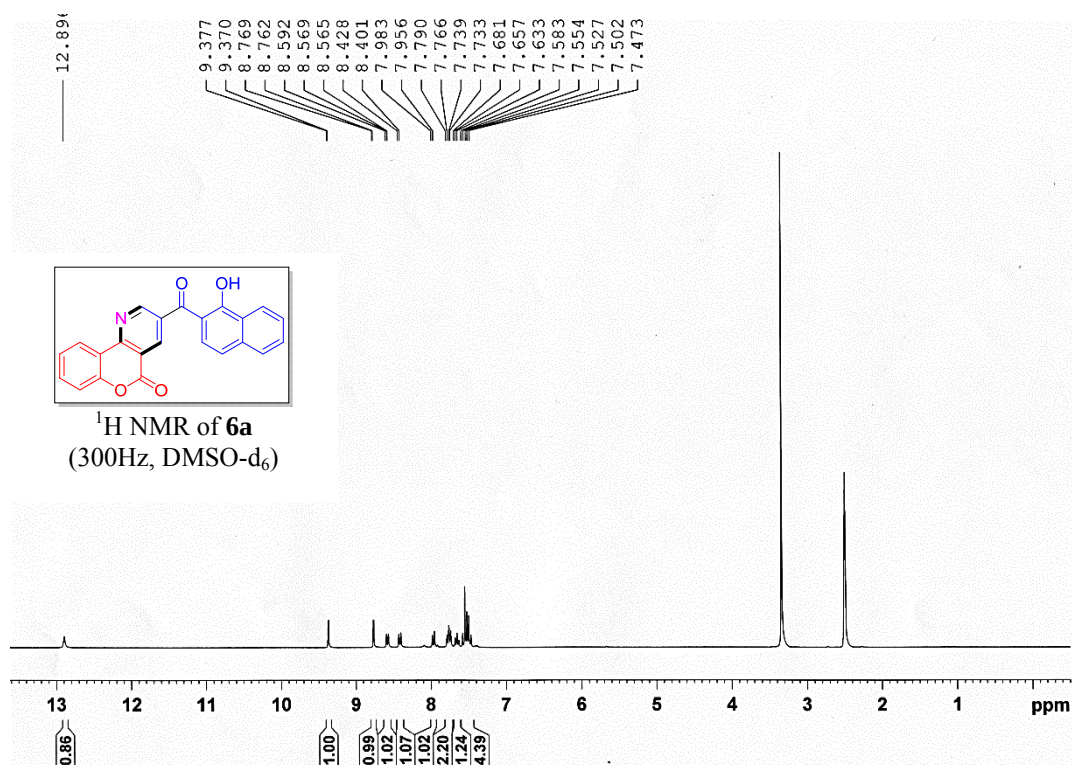


^1H NMR of **5u**
(600 MHz, CDCl_3)

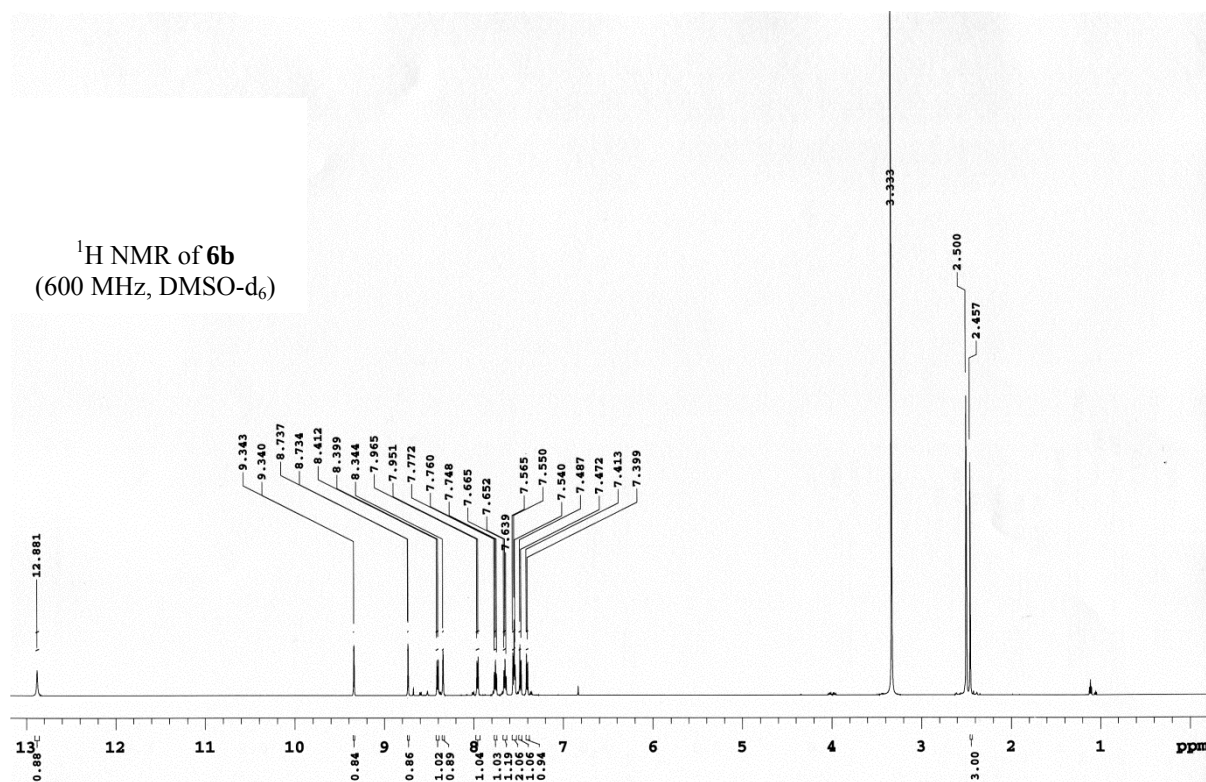


^{13}C NMR of **5u**
(150 MHz, CDCl_3)

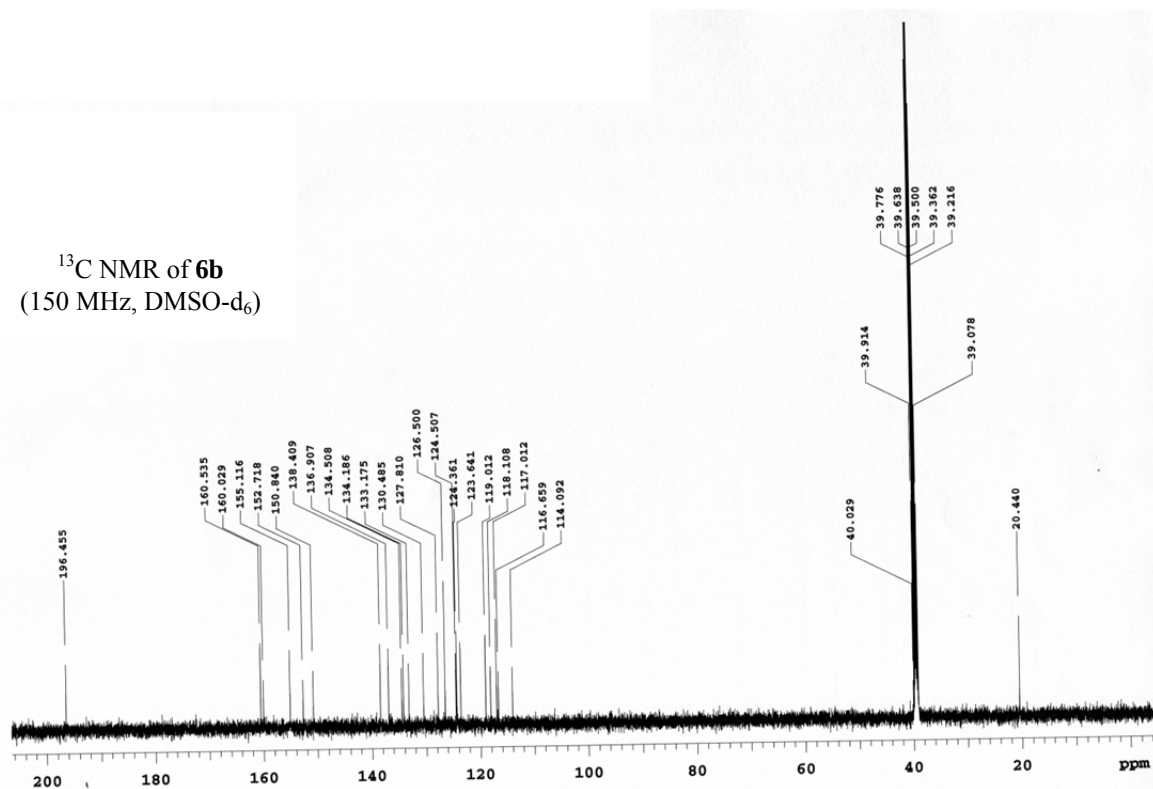


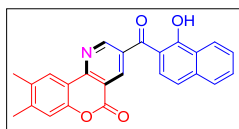


^1H NMR of **6b**
(600 MHz, DMSO- d_6)

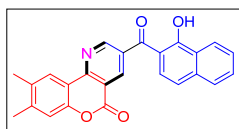
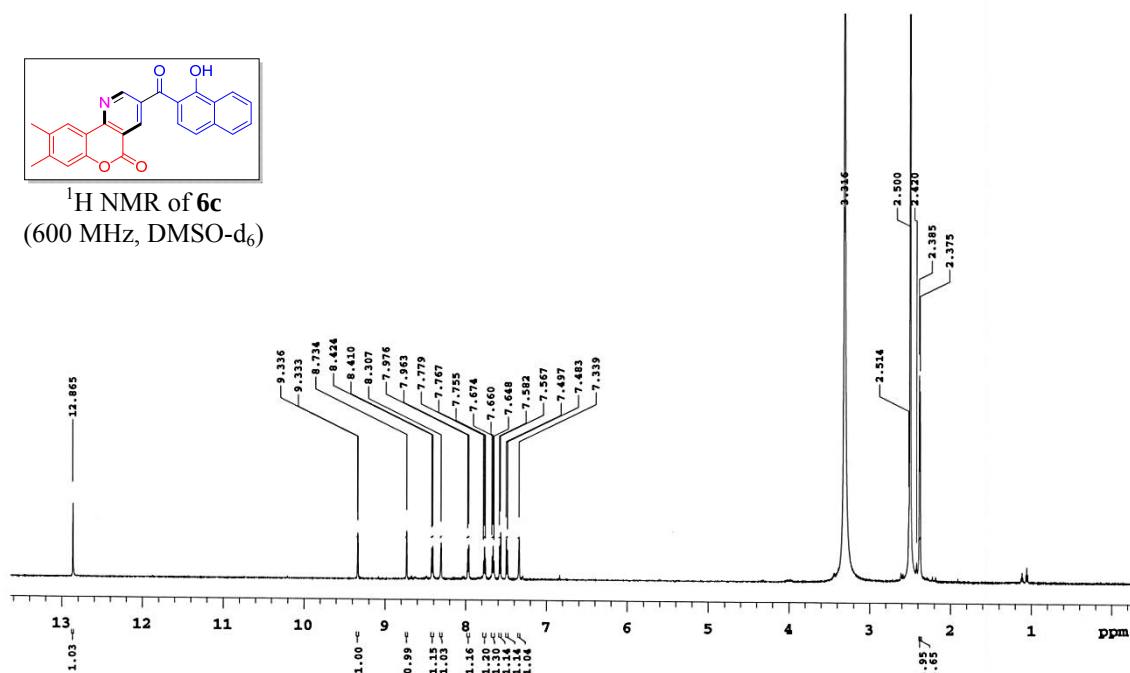


^{13}C NMR of **6b**
(150 MHz, DMSO- d_6)

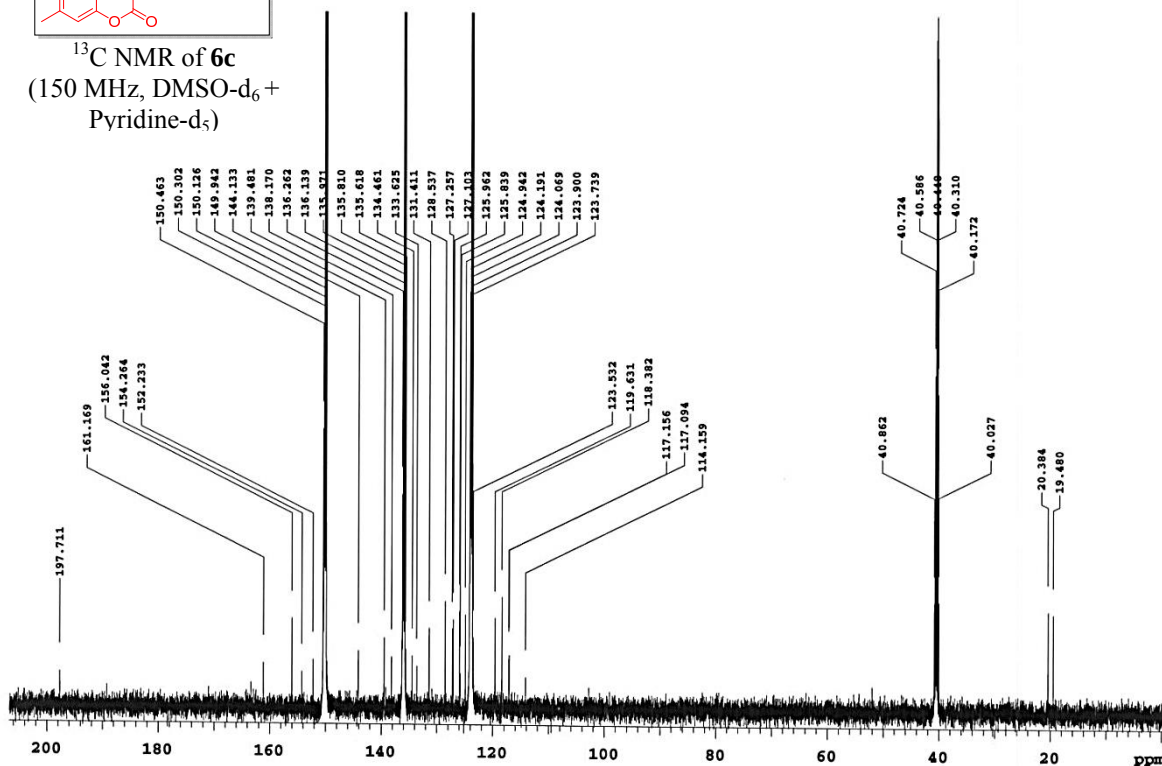


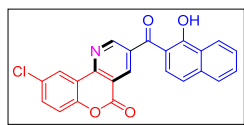


¹H NMR of **6c**
(600 MHz, DMSO-d₆)

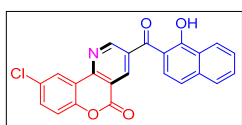
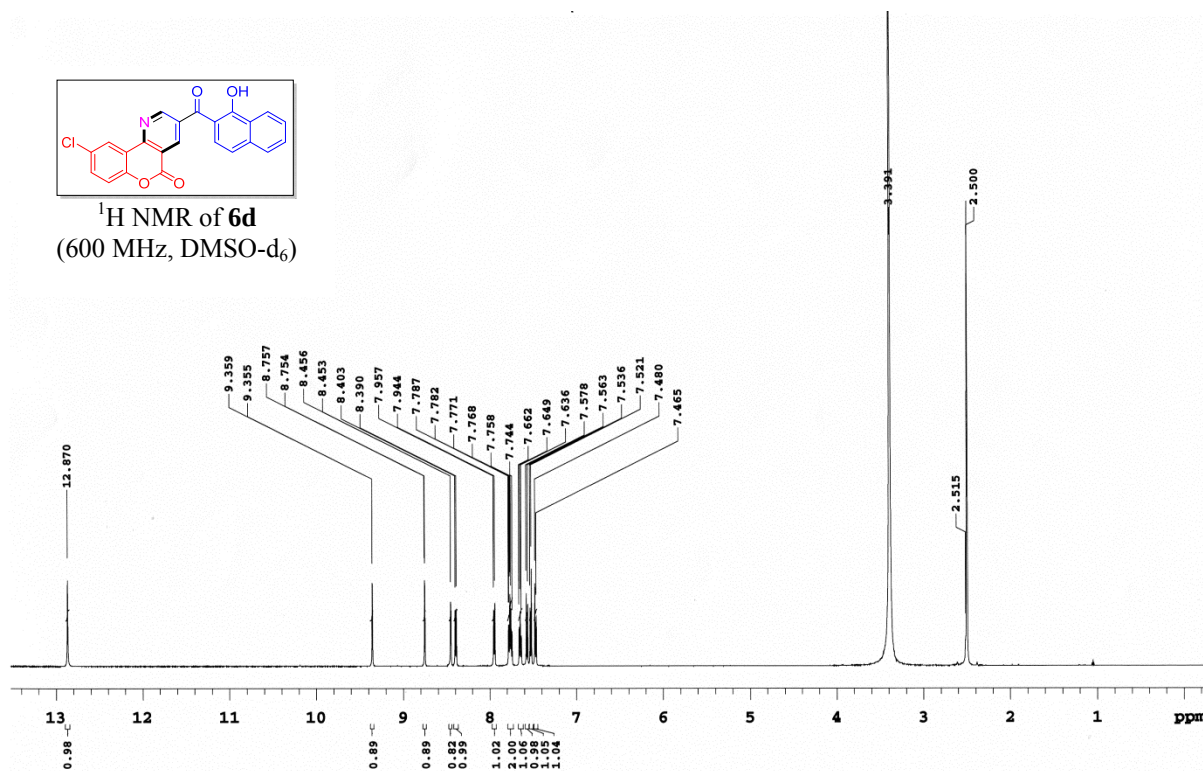


¹³C NMR of **6c**
(150 MHz, DMSO-d₆ +
Pyridine-d₅)

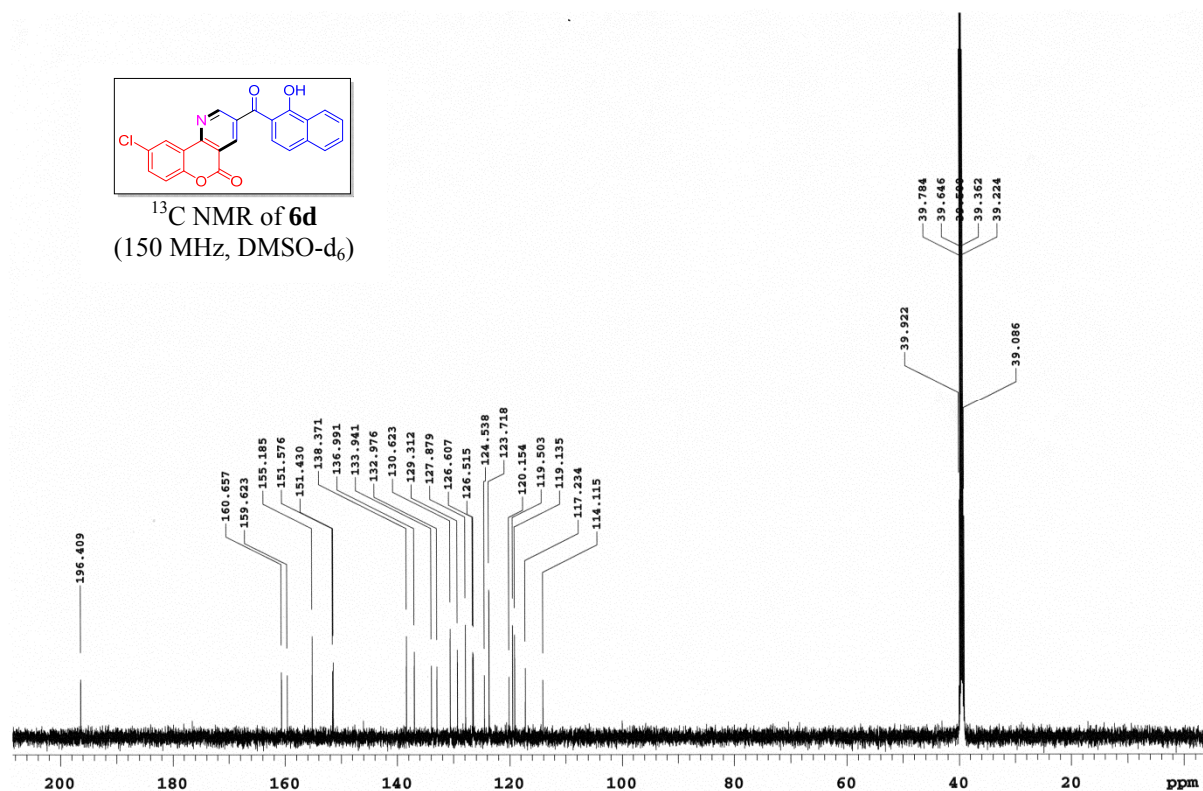


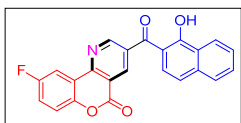


^1H NMR of **6d**
(600 MHz, DMSO- d_6)

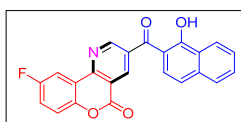
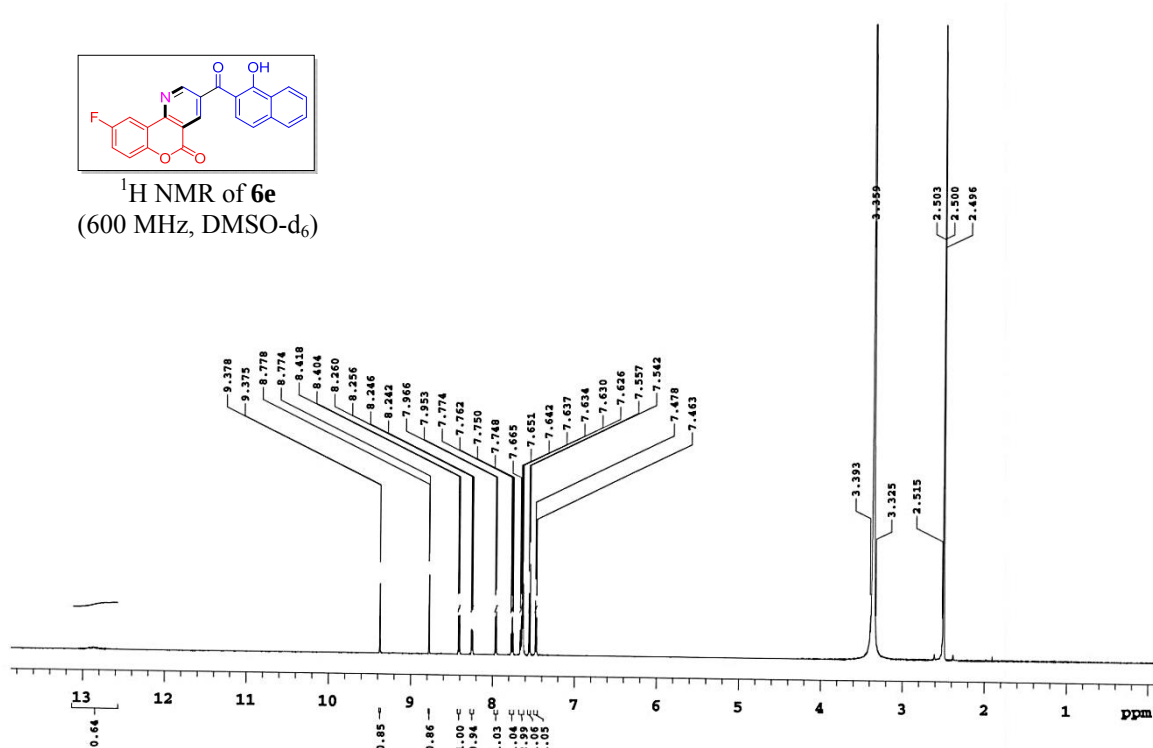


^{13}C NMR of **6d**
(150 MHz, DMSO- d_6)

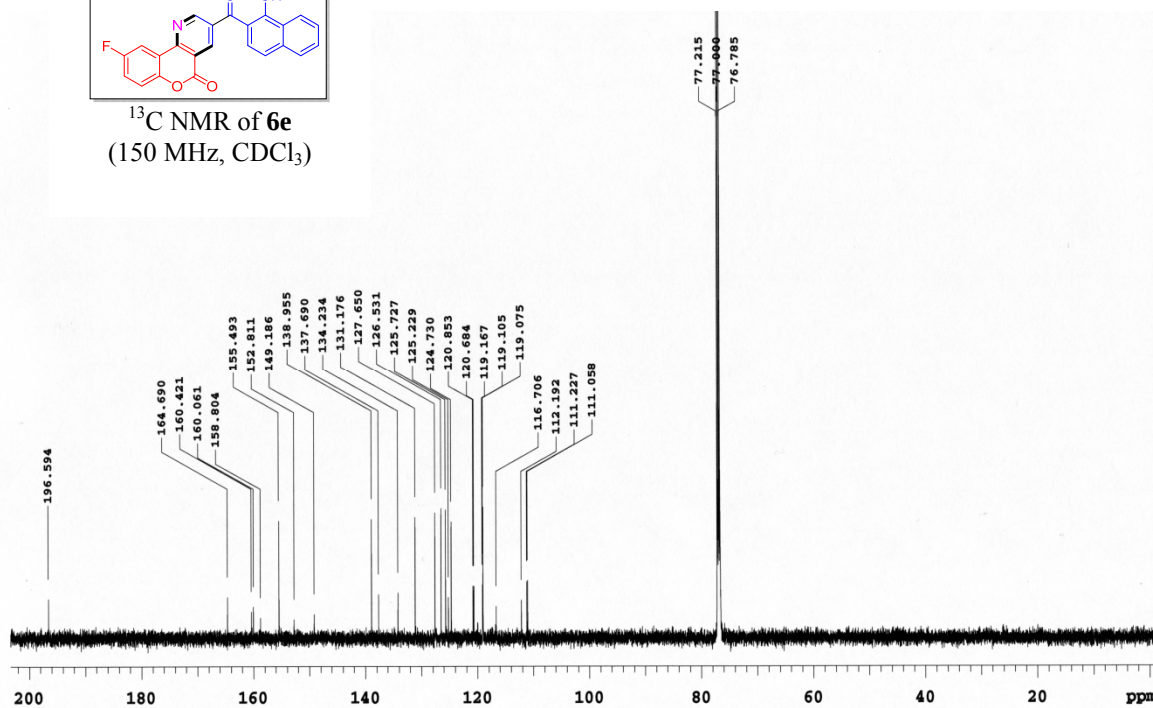


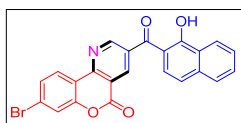


^1H NMR of **6e**
(600 MHz, DMSO- d_6)

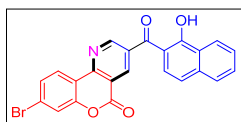
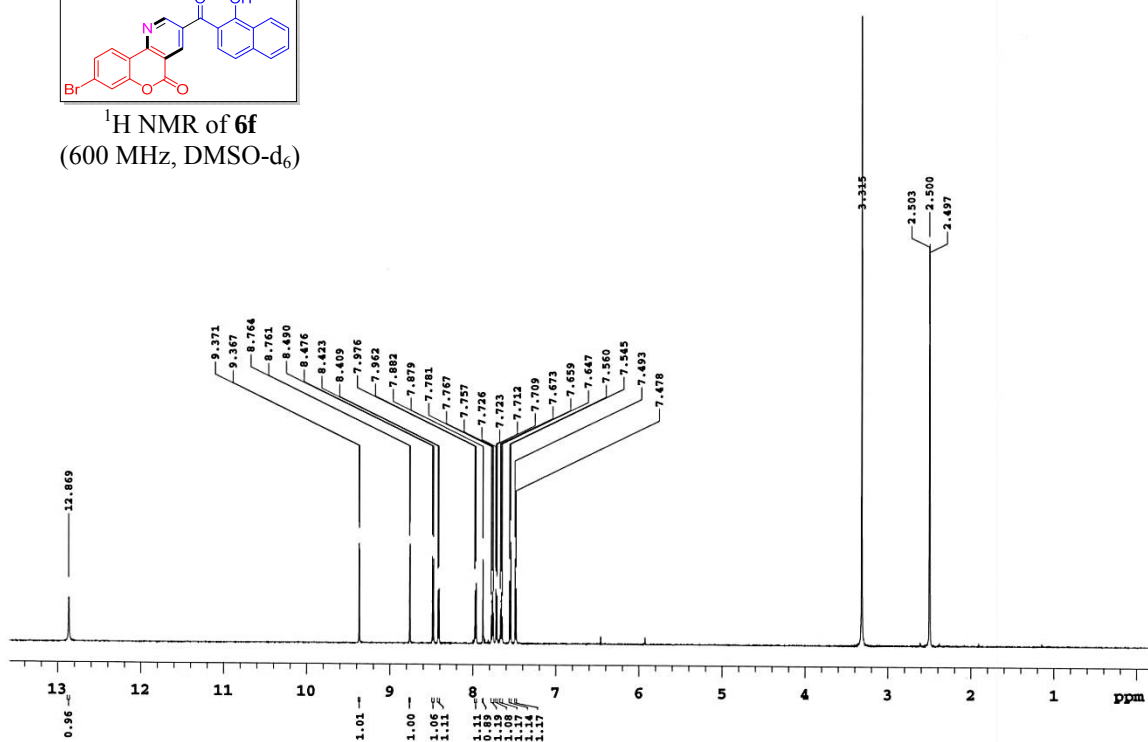


^{13}C NMR of **6e**
(150 MHz, CDCl_3)

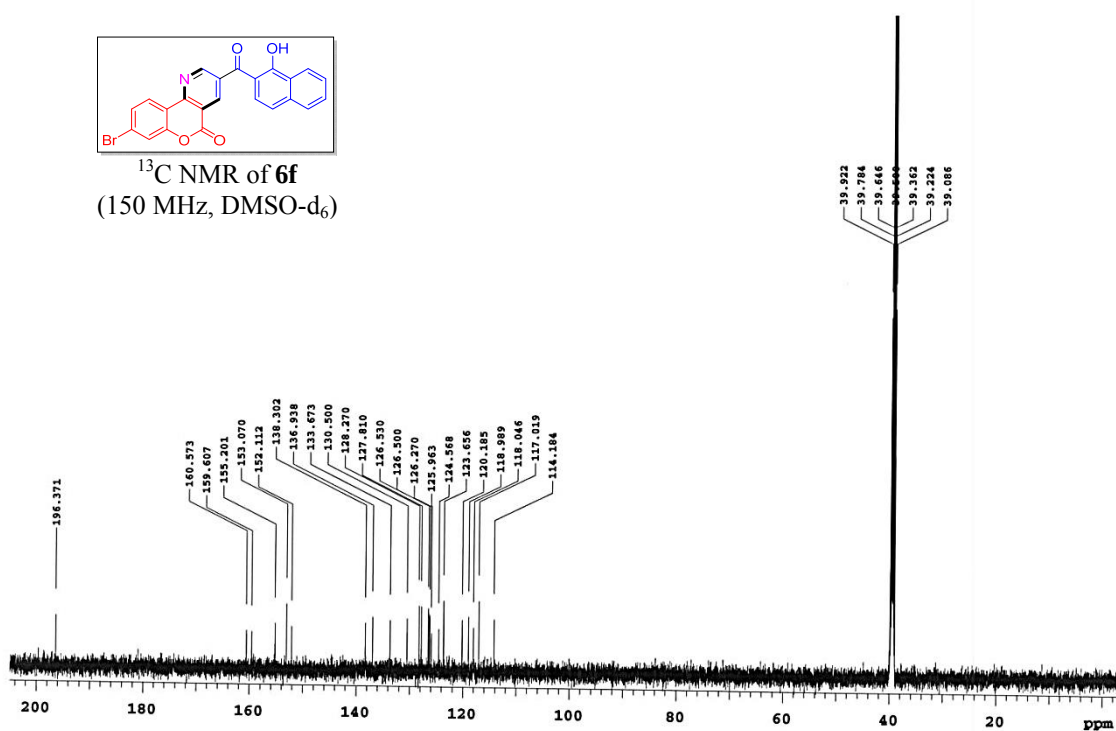


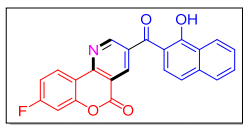


¹H NMR of **6f**
(600 MHz, DMSO-d₆)

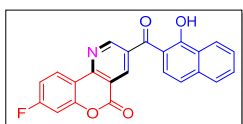
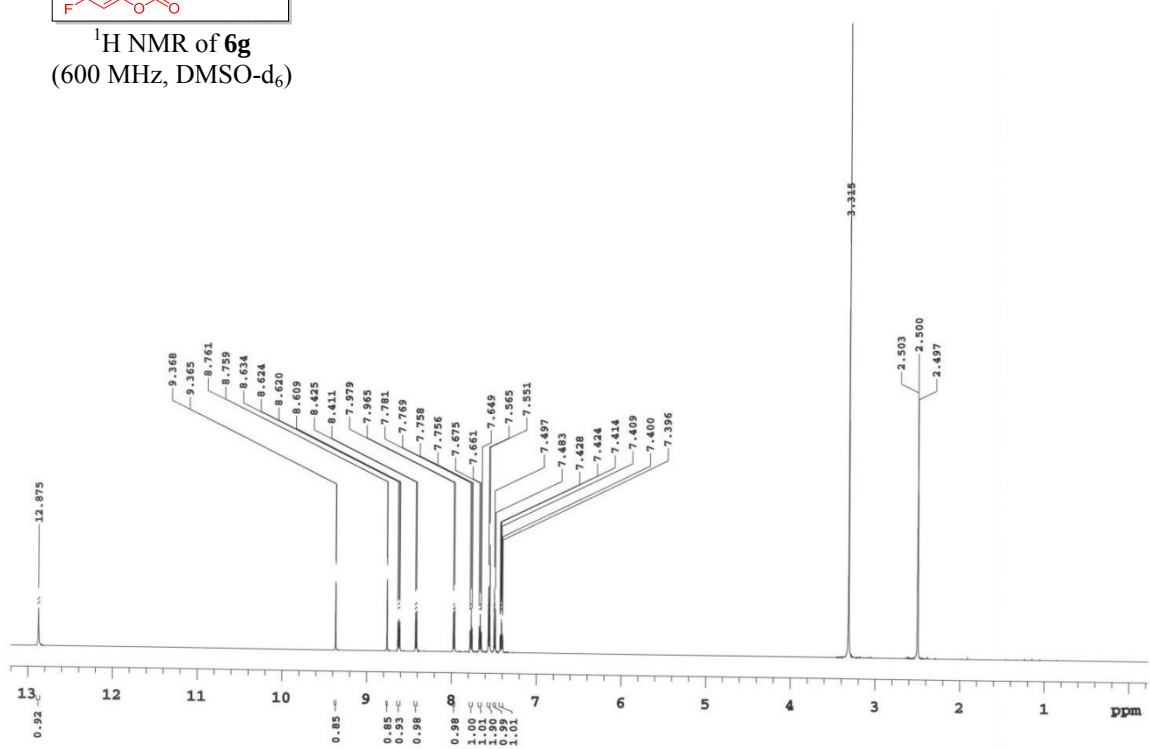


¹³C NMR of **6f**
(150 MHz, DMSO-d₆)





^1H NMR of **6g**
(600 MHz, DMSO- d_6)



^{13}C NMR of **6g**
(150 MHz, CDCl_3)

