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SUPPORTING INFORMATION

Indium(III)-catalyzed efficient synthesis of 3-aryldiazonoindolin-2-ones and fluorescent metal sensing studies

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1. General information

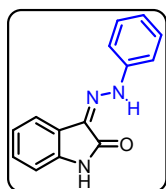
All experiments were carried out under nitrogen atmosphere. Merck, pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined using micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. Starting diazo compounds **1a-1q** were prepared according to the reported procedures.¹ Hydrazines **2a-2m**, and all other chemicals were purchased from Sigma-Aldrich, TCI Chemicals, or Alfa Aesar. ¹H NMR and ¹³C NMR spectra were recorded on VNS (600 and 150 MHz) spectrometers, respectively at the core research support center for natural products and medical materials of Yeungnam University. The chemical shifts were described in parts per million (δ) relative to TMS (0 ppm) as the internal standard or relative to the resonance of the residual protonated solvent (¹H NMR: CDCl₃, δ = 7.24 ppm or DMSO-*d*₆, δ = 2.5 ppm) and (¹³C NMR: CDCl₃, δ = 77.0 ppm or DMSO-*d*₆, δ = 39.5 ppm). The following abbreviations were used to describe signal patterns where appropriate: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), and multiplet (m). The coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a PerkinElmer FT-IR spectrometer Spectrum Two™. Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected. The high-resolution mass spectra (HRMS) were analyzed using Thermo Fisher Q exactive orbitrap mass spectrometer.

2. General procedure for the synthesis of 3-arylhydrazonoindolin-2-ones (**3** or **4**)

To a mixture of 3-diazoindoles (**1**, 0.5 mmol) and hydrazine (**2**, 0.55 mmol) in 5 mL fluorobenzene, 5 mol% of In(OTf)₃ was added and the reaction mixture was stirred at 60 °C temperature for 6 h under N₂ atmosphere. After completion of the reaction as indicated by TLC, the reaction mixture was evaporated to remove solvents in a rotary evaporator under reduced pressure and the residue so obtained was purified by silica gel column chromatography using n-hexane/ethyl acetate as eluent to afford the desired products **3** or **4**.

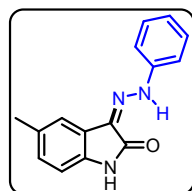
3. Characterization data of synthesized compounds

3-(2-Phenylhydrazineylidene)indolin-2-one (3a).



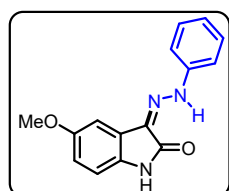
Yield 93% (110 mg) as a yellowish solid; mp 205-207 °C; IR (ATR) 3134, 3050, 2930, 1677, 1590, 1557, 1493, 1463, 1350, 1290, 1246, 1170, 1101, 990 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.75 (s, 1H), 11.02 (s, 1H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.23 (t, $J = 8.5$ Hz, 1H), 7.06-7.02 (m, 2H), 6.92 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.1, 142.4, 142.4, 139.7, 129.4, 128.4, 127.6, 122.8, 121.8, 121.1, 118.5, 114.0, 110.4; HRMS ESI m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}$: 238.0975; Found: 238.0973.

5-Methyl-3-(2-phenylhydrazineylidene)indolin-2-one (3b).



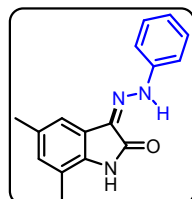
Yield 85% (106 mg) as a yellowish solid: mp 141-143 °C; IR (ATR) 3154, 3051, 1739, 1681, 1554, 1320, 1234, 1207, 1167, 1051 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.72 (s, 1H), 10.90 (s, 1H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.38-7.35 (m, 3H), 7.05-7.02 (m, 2H), 6.80 (d, $J = 7.8$ Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.3, 142.5, 137.6, 130.7, 129.4, 129.0, 127.8, 122.7, 121.2, 119.0, 114.0, 110.2, 20.69. HRMS m/z (MH^+) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$: 252.1131; Found: 252.1130.

5-Methoxy-3-(2-phenylhydrazineylidene)indolin-2-one (3c).



Yield 86% (114 mg) as a yellowish solid: mp 199-201 °C; IR (ATR) 3318, 3047, 1740, 1677, 1594, 1322, 1239, 1177, 1100 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.78 (s, 1H), 10.83 (s, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.7$ Hz, 2H), 7.13 (s, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.83 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.9, 155.5, 142.9, 134.0, 129.9, 128.5, 123.4, 122.4, 115.2, 114.6, 111.7, 104.3, 56.0. HRMS m/z (MH^+) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_2$: 268.1081; Found: 268.1080.

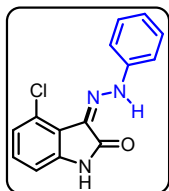
5,7-Dimethyl-3-(2-phenylhydrazineylidene)indolin-2-one (3d).



Yield 89% (118 mg) as a yellowish solid: mp 179-181 °C; IR (ATR) 3119, 2971, 1736, 1675, 1546, 1458, 1230, 1165, 1189 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.74 (s, 1H), 10.95 (s, 1H), 7.40 (d, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.19 (s, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.86 (s, 1H), 2.27 (s, 3H),

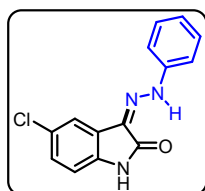
2.19 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.7, 142.6, 136.3, 130.7, 130.4, 130.4, 129.4, 128.2, 122.7, 120.8, 119.5, 116.5, 113.9, 20.6, 15.9. HRMS m/z (MH^+) calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$: 266.1288; Found: 266.1284.

4-Chloro-3-(2-phenylhydrazineylidene)indolin-2-one (3e).



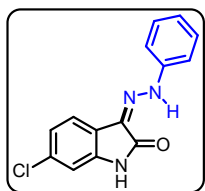
Yield 87% (118 mg) as a yellowish solid: mp 123-125 °C; IR (ATR) 3167, 2923, 1739, 1618, 1595, 1546, 1228, 1175 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.78 (s, 1H), 11.41 (s, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 1H), 7.09-7.06 (m, 2H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 162.6, 142.4, 141.0, 129.5, 129.1, 126.3, 125.4, 123.3, 122.9, 117.8, 114.3, 109.1. HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{ClN}_3\text{O}$: 272.0585; Found: 272.0581.

5-Chloro-3-(2-phenylhydrazineylidene)indolin-2-one (3f).



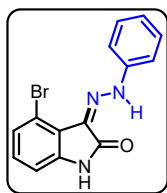
Yield 84% (114 mg) as a yellowish solid: mp 137-139 °C; IR (ATR) 3130, 2926, 1740, 1670, 1440, 1235, 1204 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.74 (s, 1H), 11.12 (s, 1H), 7.56 (s, 1H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.38 (t, $J = 8.4$ Hz, 2H), 7.26 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.07 (t, $J = 6.6$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 162.9, 142.2, 138.3, 129.4, 127.7, 126.4, 126.1, 123.3, 122.9, 118.1, 114.4, 111.9, 109.5. HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{ClN}_3\text{O}$: 272.0585; Found: 272.0583.

6-Chloro-3-(2-phenylhydrazineylidene)indolin-2-one (3g).



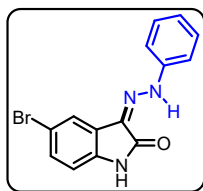
Yield 89% (121 mg) as a yellowish solid: mp 167-169 °C; IR (ATR) 3151, 2920, 1742, 1682, 1620, 1556, 1441, 1171 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.715 (s, 1H), 11.15 (s, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.07-7.04 (m, 2H), 6.94 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.0, 142.3, 140.8, 132.3, 129.4, 126.6, 123.2, 121.6, 120.1, 119.8, 114.3, 110.4; HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{ClN}_3\text{O}$: 272.0585; Found: 272.0581.

4-Bromo-3-(2-phenylhydrazineylidene)indolin-2-one (3h).



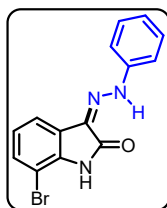
Yield 88% (139 mg) as a yellowish solid: mp 151-153 °C; IR (ATR) 2968, 2922, 1738, 1550, 1438, 1365, 1217, 1229 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.95 (s, 1H), 11.23 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 2H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 7.08 (t, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 162.6, 142.5, 141.1, 129.5, 129.2, 126.4, 126.0, 123.3, 119.4, 114.3, 113.2, 109.6, 109.5; HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{BrN}_3\text{O}$: 316.0080. Found: 316.0080.

5-Bromo-3-(2-phenylhydrazineylidene)indolin-2-one (3i).



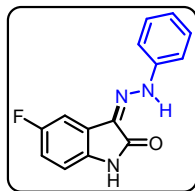
Yield 85% (134 mg) as a yellowish solid: mp 181-183 °C; IR (ATR) 3015, 2917, 1740, 6178, 1514, 1463, 1370, 1217, 1169 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.73 (s, 1H), 11.12 (s, 1H), 7.67 (d, $J = 1.8$ Hz, 1H), 7.48-7.46 (m, 2H), 7.39-7.35 (m, 3H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 162.7, 142.2, 138.6, 130.4, 129.4, 126.3, 123.4, 123.3, 120.9, 114.4, 113.7, 112.3. HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{BrN}_3\text{O}$: 316.0080; Found: 316.0080.

7-Bromo-3-(2-phenylhydrazineylidene)indolin-2-one (3j).



Yield 87% (137 mg) as a yellowish solid: mp 143-145 °C; IR (ATR) 3036, 2968, 1738, 1681, 1556, 1434, 1365, 1217 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.78 (s, 1H), 11.31 (s, 1H), 7.56 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.43 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.091 (t, $J = 1.2$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.0, 142.2, 138.5, 130.7, 129.4, 127.0, 123.4, 123.3, 123.2, 117.5, 114.4, 102.9. HRMS m/z (MH^+) calcd for $\text{C}_{14}\text{H}_{11}\text{BrN}_3\text{O}$: 316.0080; Found: 316.0077.

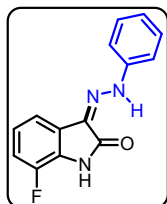
5-Fluoro-3-(2-phenylhydrazineylidene)indolin-2-one (3k).



Yield 87% (111 mg) as a yellowish solid: mp 131-131 °C; IR (ATR) 3069, 2940, 1785, 1632, 1580, 1469, 1341, 1276, 1122, 1031 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.78 (s, 1H), 11.02 (s, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.39-7.35 (m, 3H), 7.07-7.04 (m, 2H), 6.9-6.89 (m, 1H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.3, 158.1 (d, $J_{\text{C-F}} = 235.05$ Hz), 142.3, 135.9, 129.4, 127.16 (d, $J_{\text{C-F}} = 3.3$ Hz),

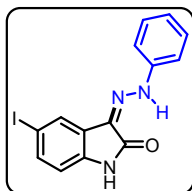
123.3, 122.4 (d, $J_{C-F} = 9.15$ Hz), 114.5 (d, $J_{C-F} = 24.0$ Hz), 114.3, 111.3 (d, $J_{C-F} = 8.4$ Hz), 105.5 (d, $J_{C-F} = 25.35$ Hz). HRMS m/z (MH^+) calcd for $C_{14}H_{11}FN_3O$: 256.0881; Found: 256.0877.

7-Fluoro-3-(2-phenylhydrazineylidene)indolin-2-one (3l).



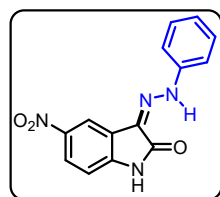
Yield 81% (104 mg) as a yellowish solid: mp 124-126 °C; IR (ATR) 3062, 2920, 1685, 1553, 1460, 1214, 1341, 1171, 1027 cm^{-1} ; 1H NMR (600 MHz, $DMSO-d_6$) δ 12.79 (s, 1H), 11.52 (s, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.40-7.37 (m, 3H), 7.14 (t, $J = 7.8$ Hz, 1H), 7.08-7.03 (m, 2H); ^{13}C NMR (150 MHz, $DMSO-d_6$) δ 162.9, 146.8 (d, $J_{C-F} = 240.9$ Hz), 142.2, 129.4, 126.8 (d, $J_{C-F} = 4.5$ Hz), 126.8 (d, $J_{C-F} = 4.5$ Hz), 126.4 (d, $J_{C-F} = 13.8$ Hz), 124.2 (d, $J_{C-F} = 4.95$ Hz), 122.6 (d, $J_{C-F} = 6.0$ Hz), 114.9 (d, $J_{C-F} = 17.2$ Hz), 114.6 (d, $J_{C-F} = 1.5$ Hz), 114.4. HRMS m/z (MH^+) calcd for $C_{14}H_{11}FN_3O$: 256.0881; Found: 256.0878.

5-Iodo-3-(2-phenylhydrazineylidene)indolin-2-one (3m).



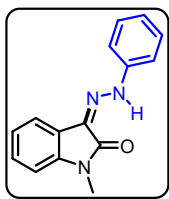
Yield 88% (159 mg) as a yellowish solid: mp 119-121 °C; IR (ATR) 3023, 2917, 1742, 1672, 1550, 1450, 1231, 1217 cm^{-1} ; 1H NMR (600 MHz, $DMSO-d_6$) δ 12.72 (s, 1H), 11.11 (s, 1H), 7.83 (s, 1H), 7.54 - 7.53 (m, 1H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (150 MHz, $DMSO-d_6$) δ 162.5, 142.3, 139.1, 136.3, 129.4, 129.0, 126.5, 127.0, 123.7, 123.3, 114.4, 112.8, 84.8. HRMS m/z (MH^+) calcd for $C_{14}H_{11}IN_3O$: 363.9941; Found: 363.9939.

5-Nitro-3-(2-phenylhydrazineylidene)indolin-2-one (3n).



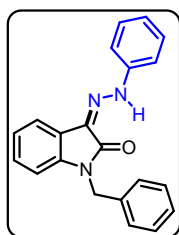
Yield 80% (112 mg) as a yellowish solid: mp 210-212 °C; IR (ATR) 3327, 3067, 1755, 1667, 1455, 1372, 1239, 1045, 900 cm^{-1} ; 1H NMR (600 MHz, $DMSO-d_6$) δ 12.69 (s, 1H), 11.62 (s, 1H), 8.26 (d, $J = 2.3$ Hz, 1H), 8.12 (dd, $J = 8.0, 2.3$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.38 (t, $J = 7.8$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (150 MHz, $DMSO-d_6$) δ 163.7, 145.1, 142.8, 142.5, 129.9, 126.0, 124.7, 124.3, 122.3, 115.3, 113.9, 110.9. HRMS m/z (MNa^+) calcd for $C_{14}H_{10}N_4O_3Na$: 305.0645; Found: 305.0641.

1-Methyl-3-(2-phenylhydrazineylidene)indolin-2-one (3o).



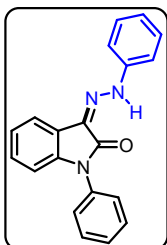
Yield 81% (102 mg) as a yellowish solid: mp 105-107 °C; IR (ATR) 3225, 3061, 1742, 1669, 1466, 1557, 1373, 1230, 1217, 1095, 1041 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.65 (s, 1H), 7.53 (d, $J = 7.2$ Hz, 1H), 7.40-7.34 (m, 4H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.08 (t, $J = 7.8$ Hz, 1H), 7.05 - 7.02 (m, 2H), 3.21 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 161.1, 142.4, 141.0, 129.9, 128.3, 126.8, 122.9, 122.2, 120.3, 118.2, 114.1, 110.0, 25.3. HRMS m/z (MH^+) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$: 252.1131; Found: 252.1129.

1-Benzyl-3-(2-phenylhydrazineylidene)indolin-2-one (3p).



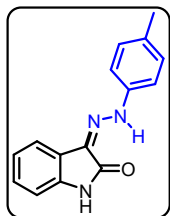
Yield 84% (137 mg) as a yellowish solid: mp 110-112 °C; IR (ATR) 3160, 3030, 1662, 1590, 1561, 1516, 1466, 1360, 1299, 1246, 1160, 1100, 1078, 1050 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 12.8 (s, 1H), 7.66 (d, $J = 7.38$ Hz, 1H), 7.39-7.35 (m, 4H), 7.32-7.31 (m, 4H), 7.28-7.26 (m, 1H), 7.17 (t, $J = 7.08$ Hz, 1H), 7.09-7.04 (m, 2H), 6.78 (d, $J = 7.8$ Hz, 1H), 4.99 (s, 2H). ^{13}C ^{13}C NMR (150 MHz, CDCl_3) δ 162.2, 142.6, 140.1, 135.8, 129.4, 128.9, 127.9, 127.7, 127.3, 126.7, 123.3, 122.6, 121.4, 118.9, 114.4, 109.3, 43.23. HRMS m/z (MH^+) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}$: 328.1444; Found: 328.1443.

1-Phenyl-3-(2-phenylhydrazineylidene)indolin-2-one (3q).



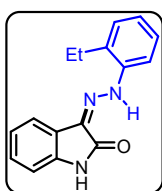
Yield 85% (133 mg) as a yellowish solid: mp 145-147 °C; IR (ATR) 3209, 3032, 1739, 1685, 1595, 1459, 1370, 1167, 1148 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 12.89 (s, 1H), 7.72 (d, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.46 (d, $J = 7.5$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.36-7.35 (m, 4H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.02 - 7.04 (m, 1H), 6.90 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR 150 MHz, CDCl_3) δ 161.6, 161.6, 142.5, 140.7, 133.7, 129.6, 129.5, 128.1, 127.9, 126.5, 126.4, 123.4, 123.1, 121.4, 119.0, 114.4, 109.7. HRMS m/z (MH^+) calcd for $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$: 314.1288; Found: 314.1285.

3-(2-(*p*-Tolyl)hydrazineylidene)indolin-2-one (4a).



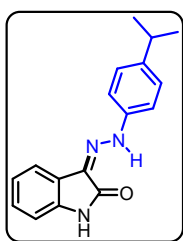
Yield 81% (101 mg) as a yellowish solid: mp 157-159 °C; IR (ATR) 3167, 3032, 1739, 1685, 1559, 1444, 1230, 1204 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.75 (s, 1H), 10.98 (s, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.2, 140.2, 139.5, 132.0, 129.9, 128.2, 127.0, 121.2, 114.0, 20.3. HRMS m/z (MH^+) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$: 252.1131; Found: 252.1128.

3-(2-(2-Ethylphenyl)hydrazineylidene)indolin-2-one (4b).



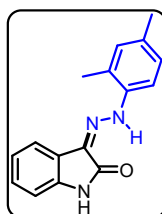
Yield 88% (117 mg) as a yellowish solid: mp 135-137 °C; IR (ATR) 3029, 12974, 11737, 1614, 1461, 1365, 1228, 1216 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 13.08 (s, 1H), 11.07 (s, 1H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.28-7.24 (m, 2H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 2.63-2.61 (m, 2H), 1.25 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.5, 139.7, 139.6, 128.9, 128.4, 128.4, 128.4, 127.2, 122.8, 121.9, 120.9, 118.6, 112.6, 110.6, 23.1, 13.5; HRMS m/z (MH^+) calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$: 267.1361; Found: 267.1363.

3-(2-(4-Isopropylphenyl)hydrazineylidene)indolin-2-one (4c).



Yield 87% (121 mg) as a yellowish solid: mp 133-135 °C IR (ATR) 2974, 2971, 1737, 1675, 1551, 1462, 1372, 1218, 1204, 1167 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.76 (s, 1H), 10.99 (s, 1H), 7.53 (d, $J = 7.2$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.24-7.21 (m, 3H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 2.86-2.83(m, 1H), 1.19, (s, 3H), 1.18 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 163.2, 143.2, 140.4, 139.5, 128.2, 127.2, 127.0, 121.7, 121.2, 118.4, 114.1, 110.4, 32.8, 23.9. HRMS m/z (MH^+) calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}_2$: 280.1444; Found: 280.1444.

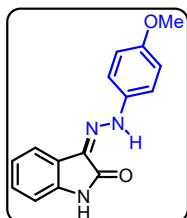
3-(2-(4-Methoxyphenyl)hydrazineylidene)indolin-2-one (4d).



Yield 82% (108 mg) as a yellowish solid: mp 121-123 °C; IR (ATR) 2923, 2856, 1736, 1672, 1547, 1466, 1463, 1227, 1205 cm^{-1} ; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.93 (s, 1H), 11.06 (s, 1H), 7.57-7.54 (m, 2H), 7.25-7.22 (m, 1H), 7.08-7.02 (m, 3H), 6.93 (d, $J = 7.8$ Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (150 MHz,

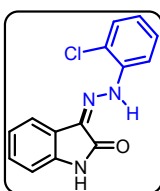
DMSO-*d*₆) δ 163.5, 139.5, 138.0, 131.6, 131.3, 131.2, 128.2, 127.8, 127.7, 122.3, 121.8, 121.0, 118.5, 112.2, 110.5, 104.8, 20.3, 16.2. HRMS *m/z* (MH⁺) calcd for C₁₆H₁₆N₃O: 266.1288; Found: 266.1284.

3-(2-(4-Methoxyphenyl)hydrazineylidene)indolin-2-one (4e).



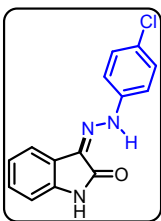
Yield 80% (106 mg) as a yellowish solid: mp 170-17 °C; IR (ATR) 3026, 2860, 1739, 1685, 1595, 1554, 1445, 1232, 1206, 1168 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.77 (s, 1H), 10.95 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.1, 155.5, 139.3, 136.1, 127.9, 126.3, 121.7, 121.3, 118.2, 115.4, 114.8, 110.3, 55.3. HRMS *m/z* (MH⁺) calcd for C₁₅H₁₄N₃O₂: 268.1080; Found: 268.1077.

3-(2-(2-Chlorophenyl)hydrazineylidene)indolin-2-one (4f).



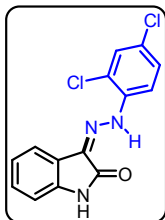
Yield 84% (113 mg) as a yellowish solid: mp 121-123 °C; IR (ATR) 3128, 2890, 1740, 1680, 1590, 1429, 1089 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.09 (s, 1H), 11.15 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.2 (t, *J* = 7.8 Hz, 1H), 7.08-7.03 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.3, 140.4, 138.7, 130.4, 129.5, 129.3, 128.5, 123.2, 122.0, 120.5, 119.2, 118.1, 114.1, 110.7. HRMS *m/z* (MH⁺) calcd for C₁₄H₁₁NCION₃O: 272.0585; Found: 272.0584.

3-(2-(4-Chlorophenyl)hydrazineylidene)indolin-2-one (4g).



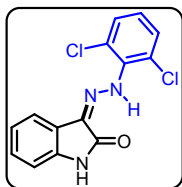
Yield 85% (115 mg) as a yellowish solid: mp 171-173 °C; IR (ATR) 2975, 2923, 1737, 1685, 1559, 1449, 1365, 1229, 1217, 1159, 1084 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.69 (s, 1H), 11.01 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 6.0 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 6.0 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.5, 142.1, 140.5, 129.7, 129.2, 128.8, 126.8, 122.3, 121.5, 119.2, 116.1, 111.0. HRMS *m/z* (MH⁺) calcd for C₁₄H₁₁ClN₃O: 272.0585; Found: 272.0585.

3-(2-(2,4-Dichlorophenyl)hydrazineylidene)indolin-2-one (4h).



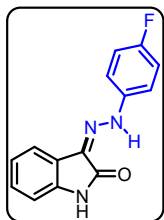
Yield 87% (133 mg) as a yellowish solid: mp 151-153 °C; IR (ATR) 3167, 3016, 1738, 1691, 1450, 1418, 1227, 1216, 1205 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.05 (s, 1H), 11.16 (s, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.3, 140.6, 138.0, 131.0, 129.6, 128.8, 128.6, 125.9, 122.1, 120.3, 119.3, 118.6, 115.1, 113.5, 110.8, 109.5. HRMS *m/z* (MH⁺) calcd for C₁₄H₁₀Cl₂N₃O: 306.0195; 306.0195.

3-(2-(2,6-Dichlorophenyl)hydrazineylidene)indolin-2-one (4i).



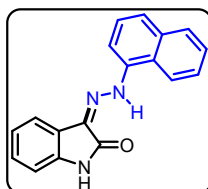
Yield 88% (134 mg) as a yellowish solid: mp 161-163 °C; IR (ATR) 3067, 2853, 1739, 1694, 1455, 1427, 1240, 1200 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.68 (s, 1H), 11.13 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.0, 140.3, 135.8, 130.1, 129.7, 129.3, 125.8, 125.6, 123.0, 120.6, 118.9, 110.7. HRMS *m/z* (MH⁺) calcd for C₁₄H₁₀Cl₂N₃O: 306.0195; Found: 306.0191.

3-(2-(4-Fluorophenyl)hydrazineylidene)indolin-2-one (4j).



Yield 82% (103 mg) as a yellowish solid: mp 133-135 °C; IR (ATR) 3029, 2923, 1738, 1675, 1553, 1494, 1461, 1365, 1204, 1167, 1097 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.72 (s, 1H), 11.00 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.47-4.44 (m, 2H), 7.24 -7.18 (m, 3H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 163.0, 158.9, 157.3, 139.7, 139.2, 139.1, 128.4, 127.6, 121.7, 121.1, 118.5, 116.1, 115.9, 115.6, 115.5, 110.4,. HRMS *m/z* (MH⁺) calcd for C₁₄H₁₁FN₃O: 256.0881; Found: 256.0877.

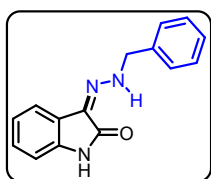
3-(2-(Naphthalen-1-yl)hydrazineylidene)indolin-2-one (4k).



Yield 83% (119 mg) as a yellowish solid: mp 125-127 °C; IR (ATR) 3023, 2971, 1738, 1675, 1559, 1365, 1216, 1199 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.79 (s, 1H), 11.23 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82

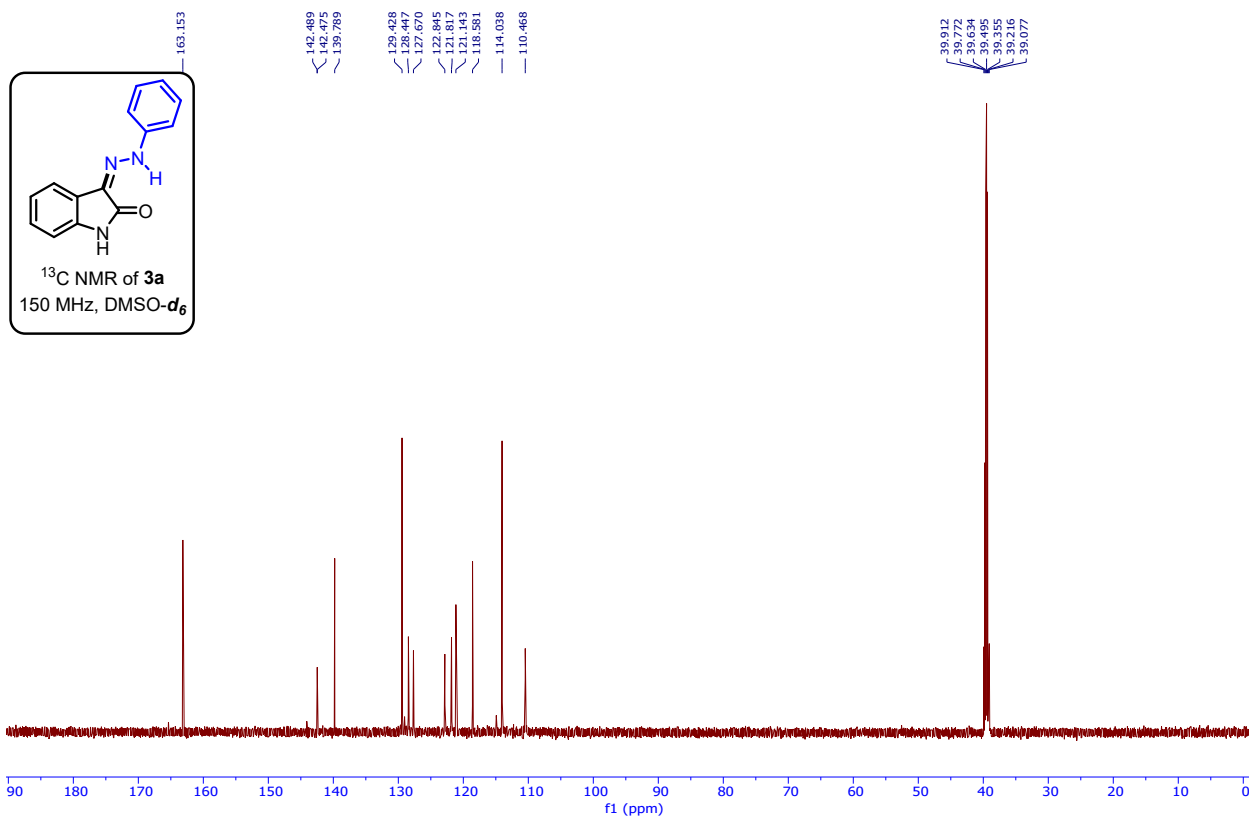
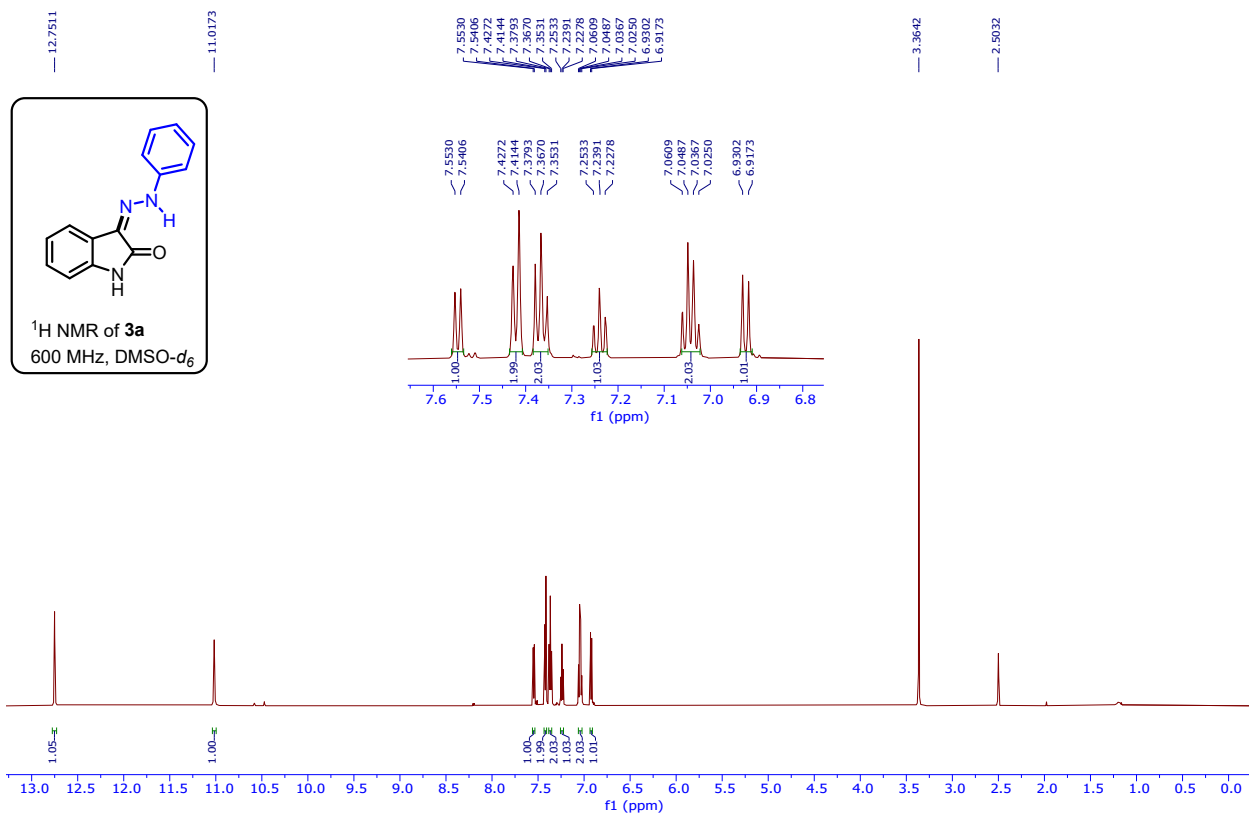
(d, $J = 7.8$ Hz, 1H), 7.68-7.62 (m, 3H), 7.60-7.55 (m, 2H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 163.8, 140.0, 137.08, 133.7, 129.8, 128.9, 128.7, 126.5, 126.4, 126.4, 122.5, 122.1, 121.5, 120.8, 118.9, 118.9, 110.7, 108.3. HRMS m/z (M^+) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}$: 288.1131; Found: 288.1131.

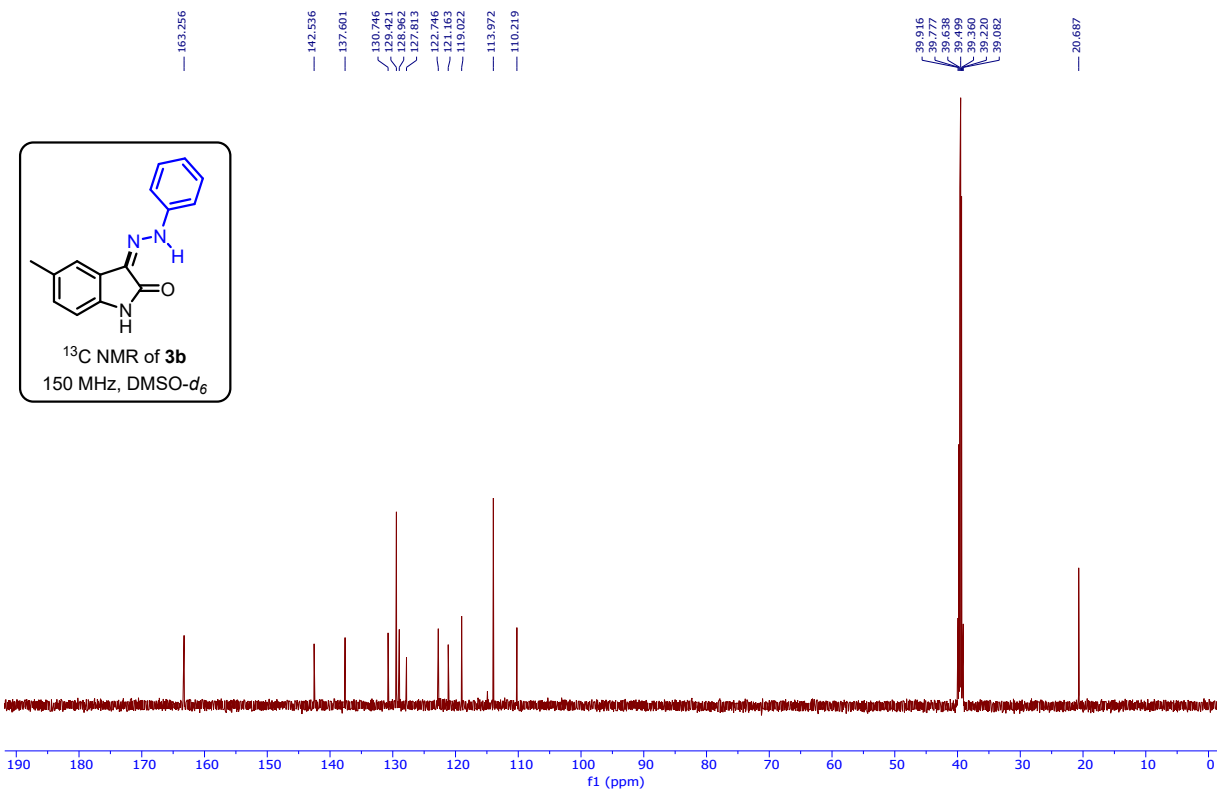
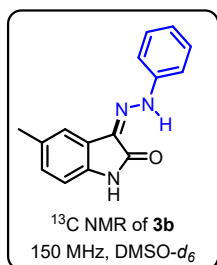
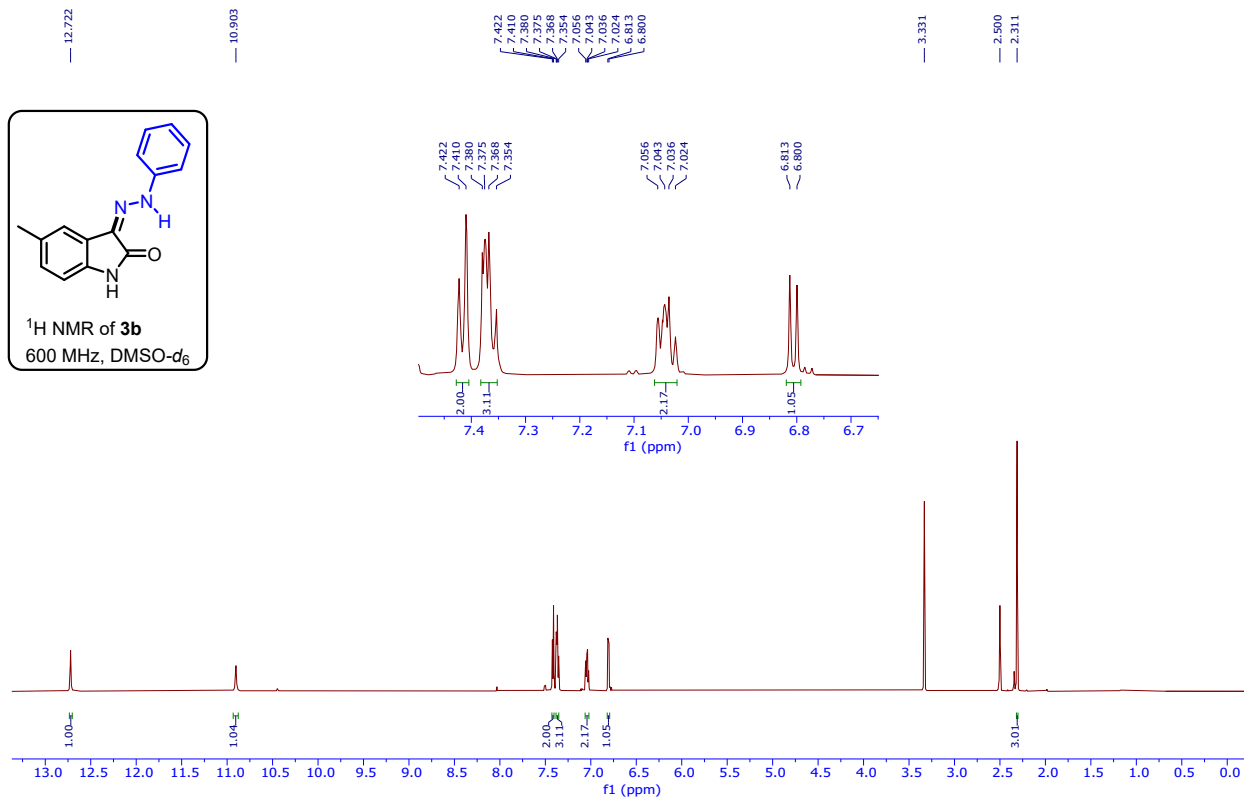
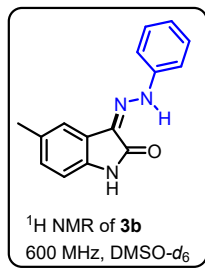
3-(2-Benzylhydrazineylidene)indolin-2-one (4l).

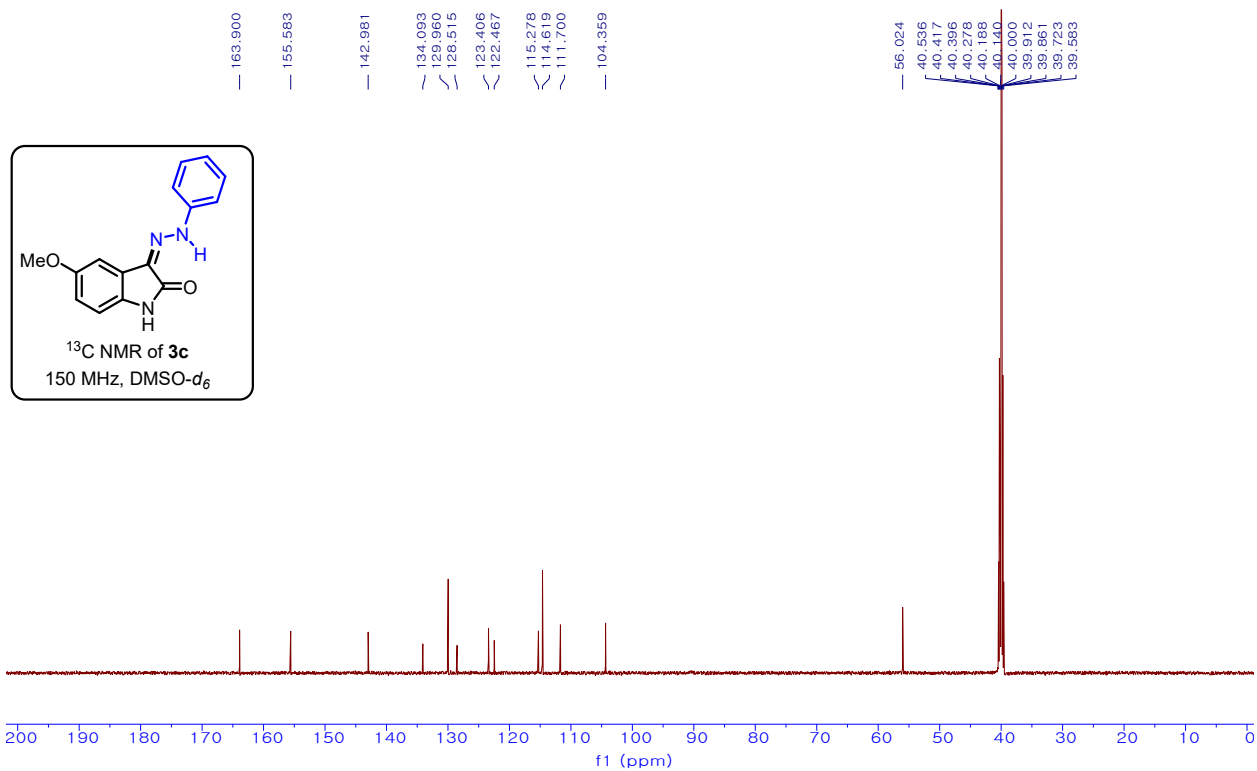
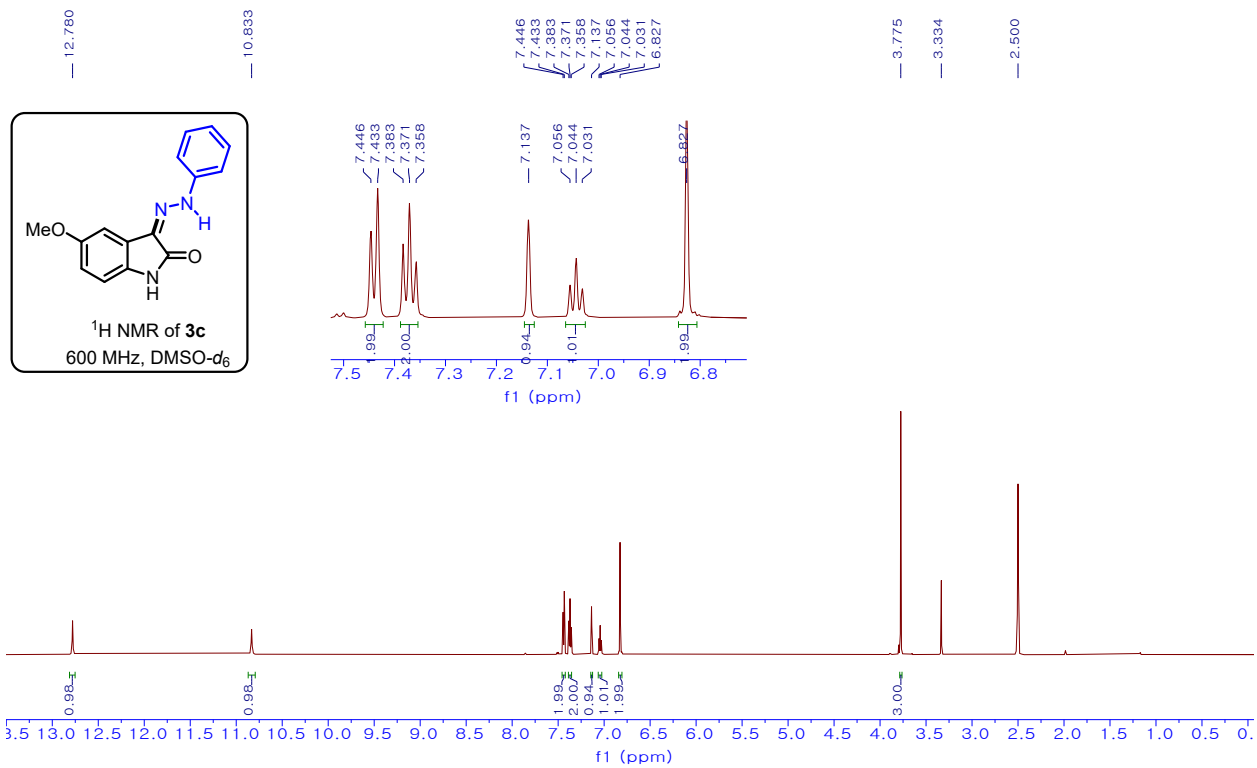


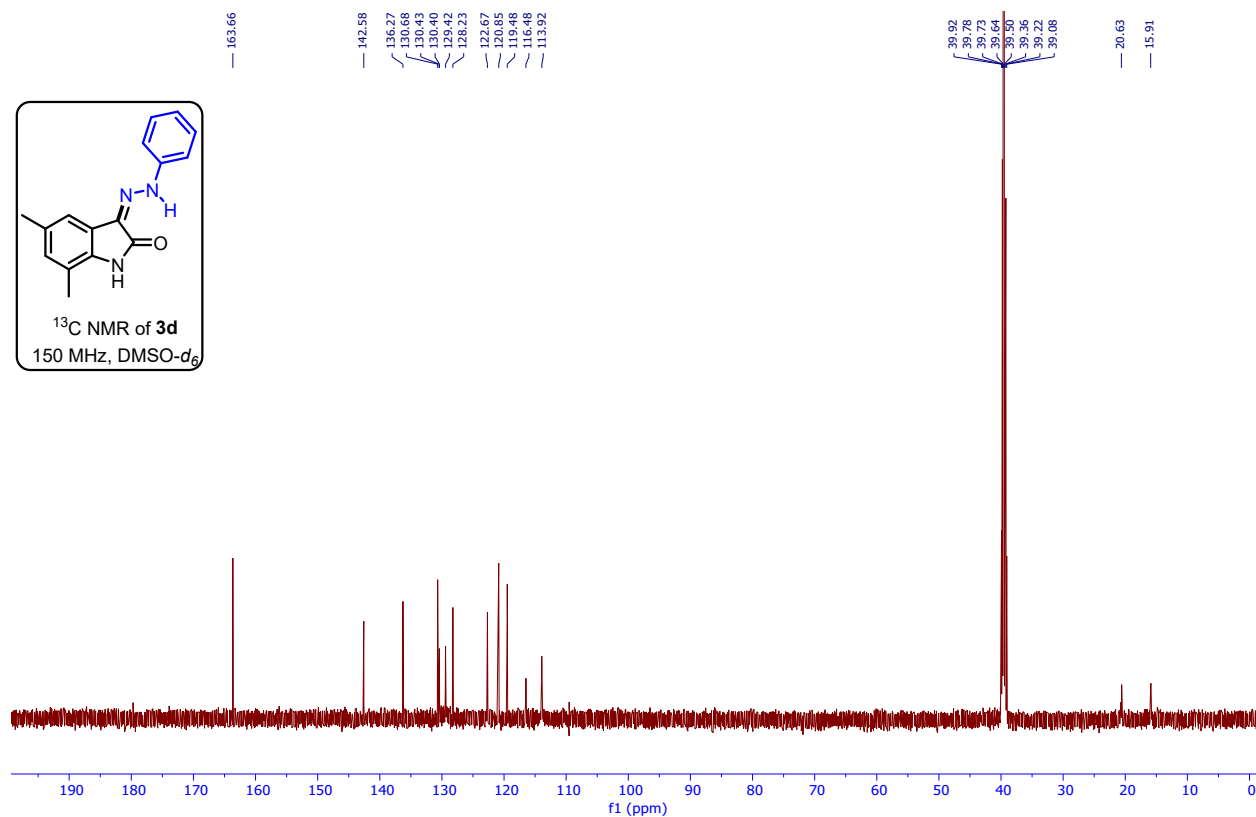
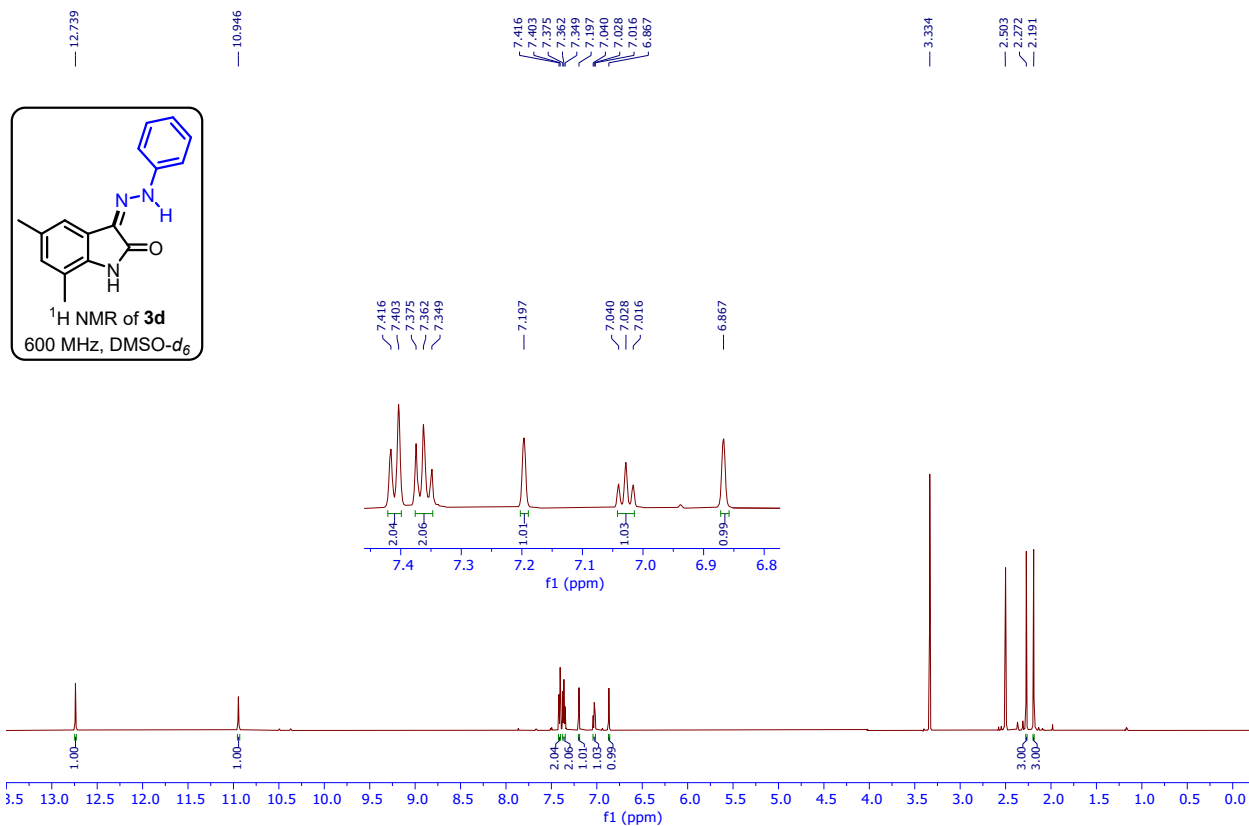
Yield 85% (106 mg) as a yellowish solid: mp 119-121 °C; IR (ATR) 3032, 2968, 1736, 1681, 1617, 1540, 1466, 1204, 1030 cm^{-1} ; ^1H NMR (600 MHz, DMSO- d_6) δ 11.30 (s, 1H), 10.75 (s, 1H), 7.367-7.34 (m, 5H), 7.29-7.28 (m, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 6.96 (t, $J = 6.06$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 4.74 (s, $J = 4.8$ Hz, 2H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 162.9, 138.7, 138.4, 128.5, 128.4, 127.7, 127.5, 127.3, 126.9, 125.02, 121.9, 121.3, 117.4, 110.0, 54.7. HRMS m/z (MH^+) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$: 252.1131; Found: 252.1127.

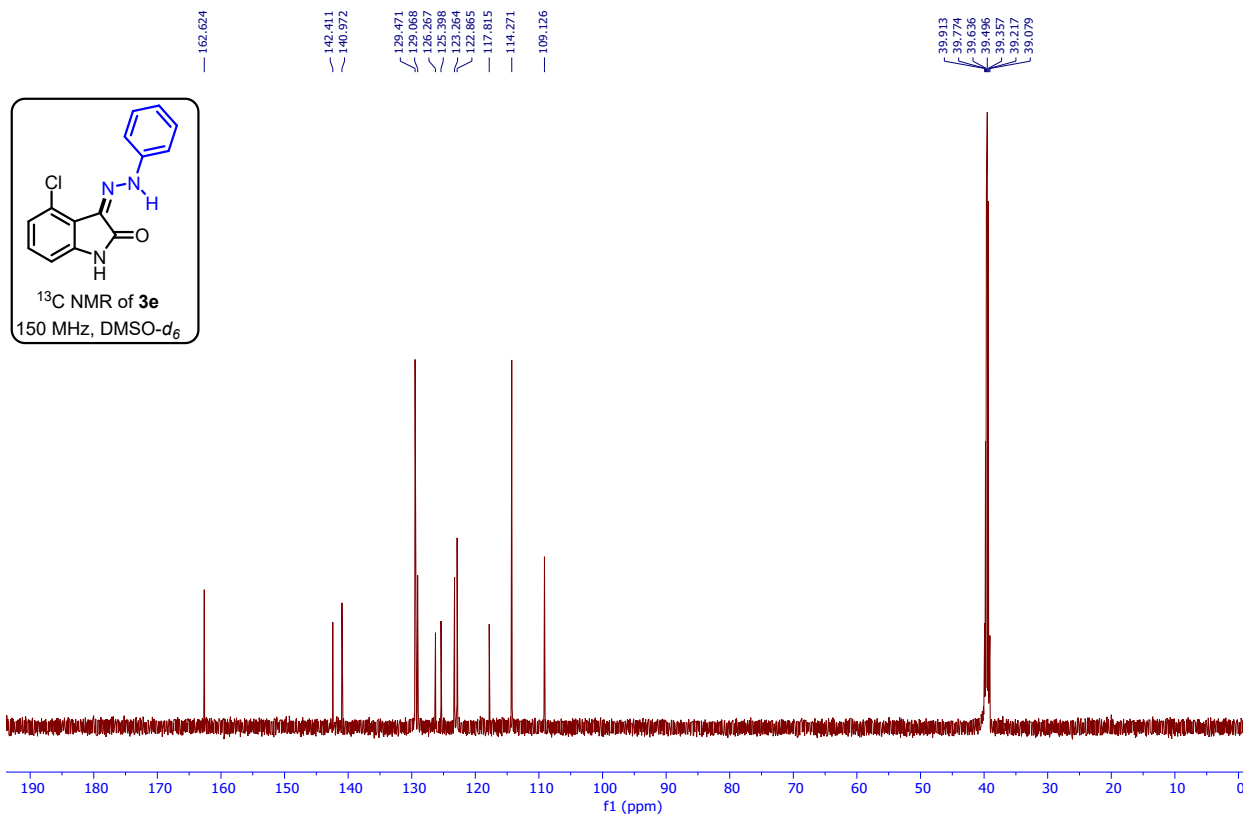
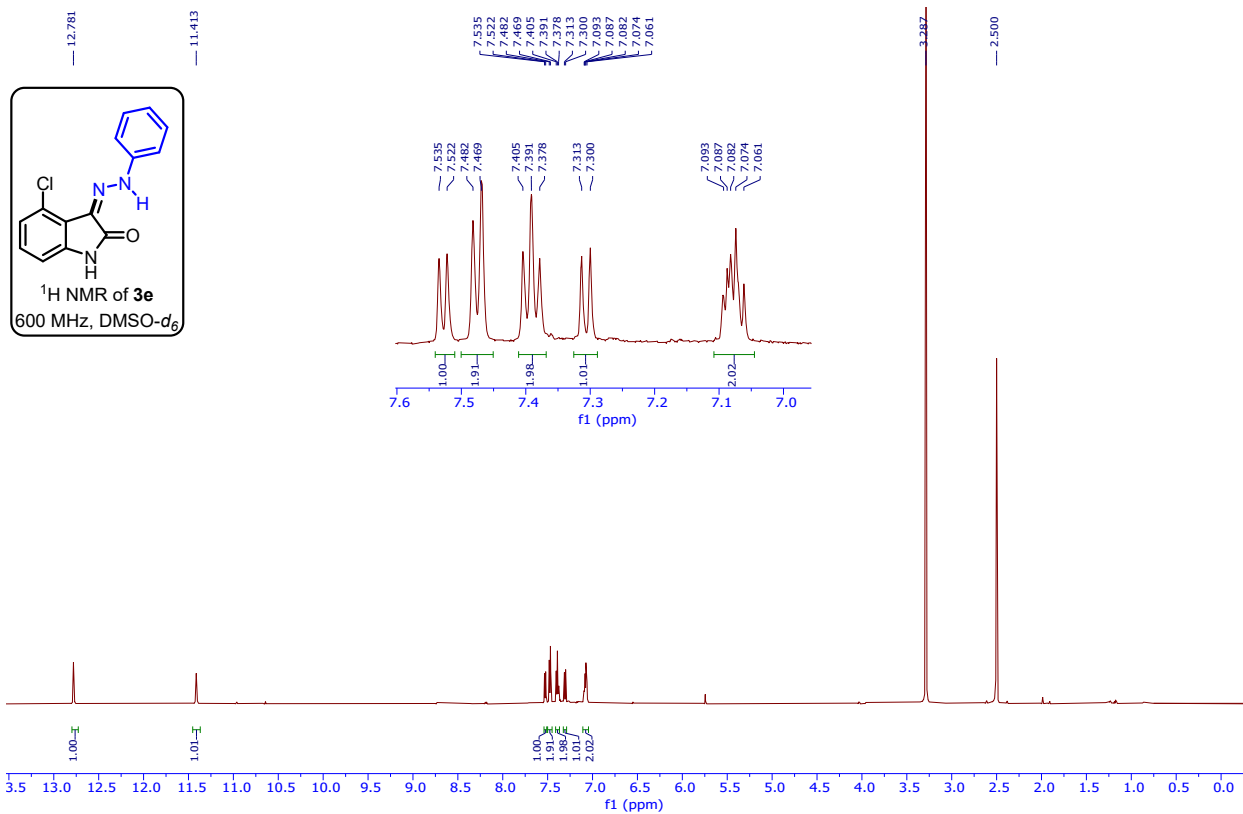
4. ^1H NMR and ^{13}C NMR spectra of synthesized compounds

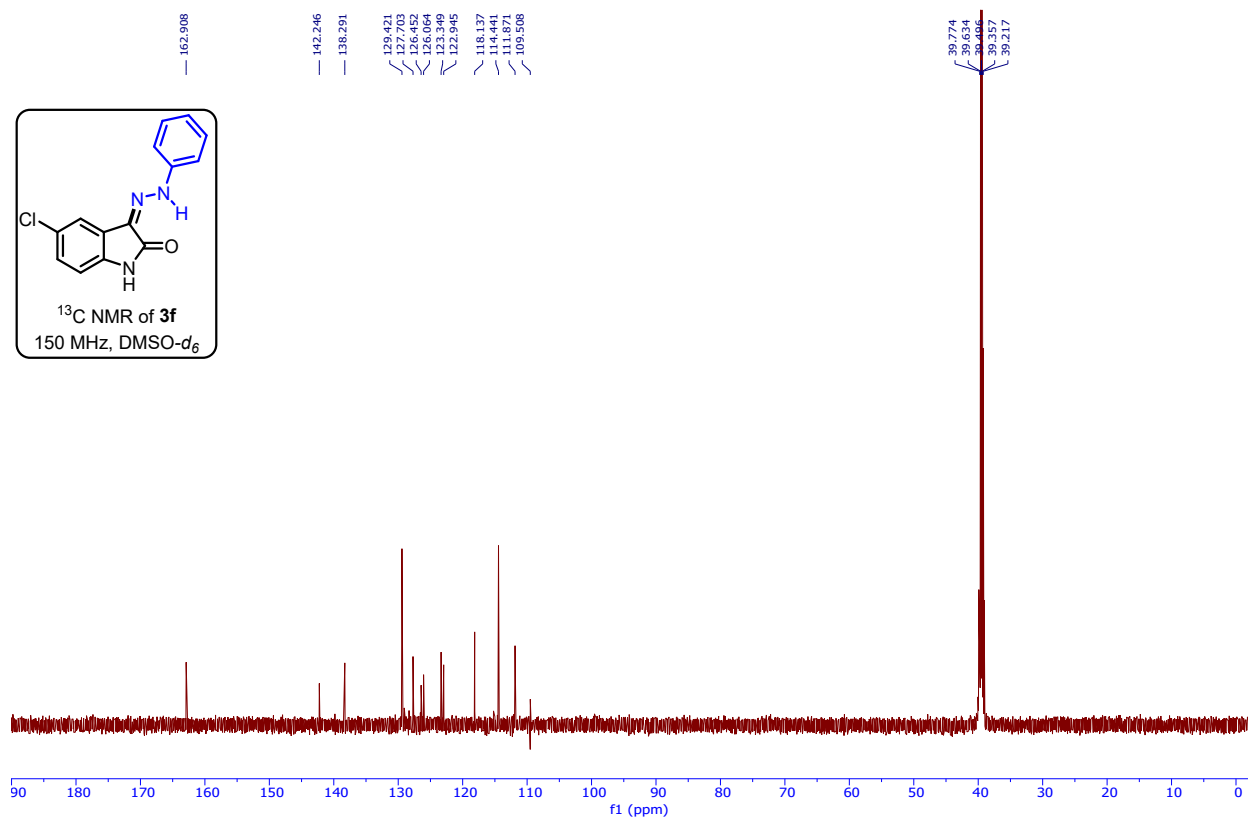
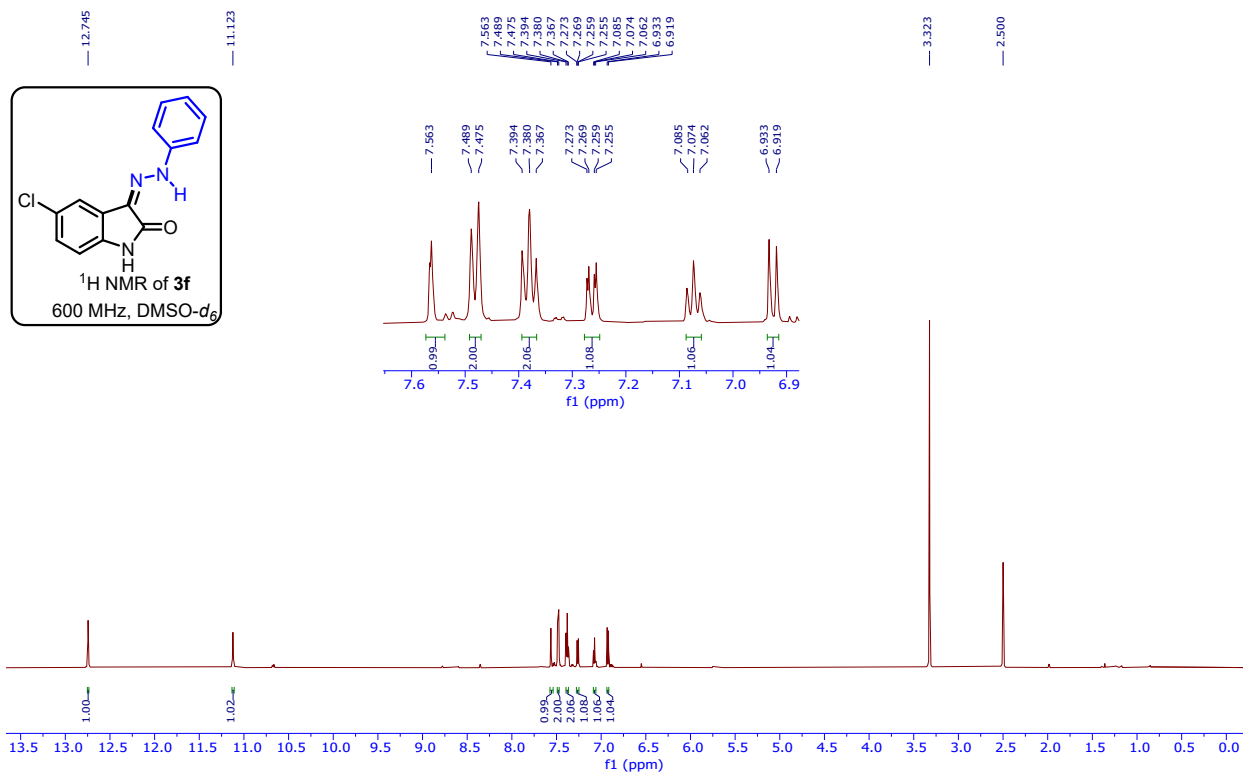


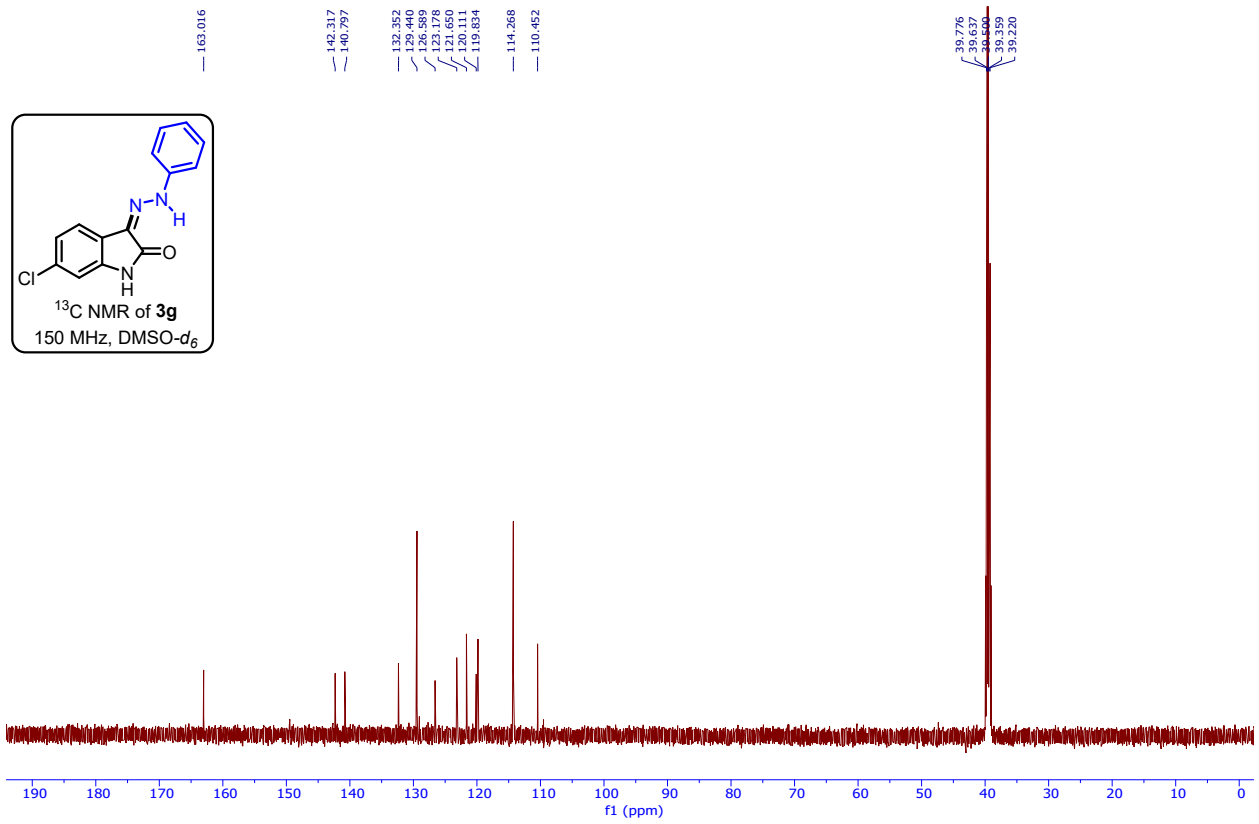
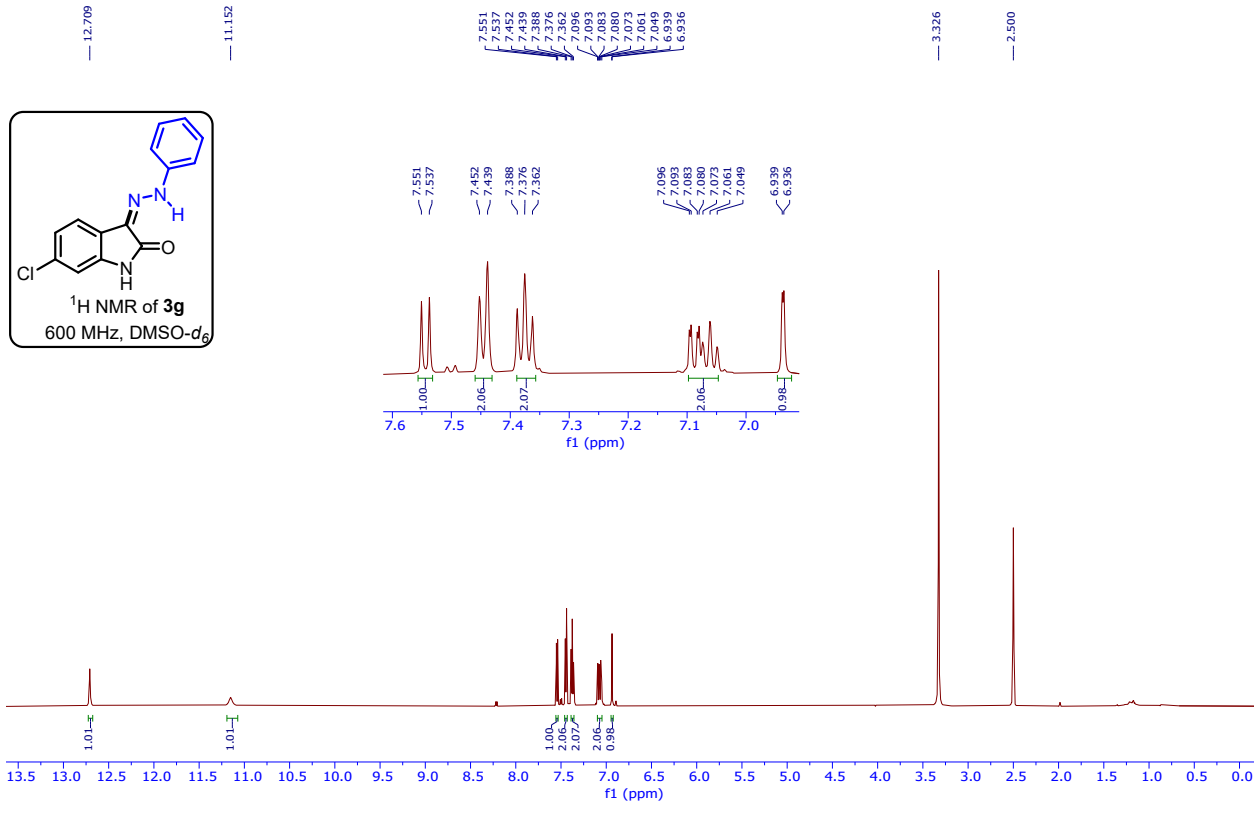


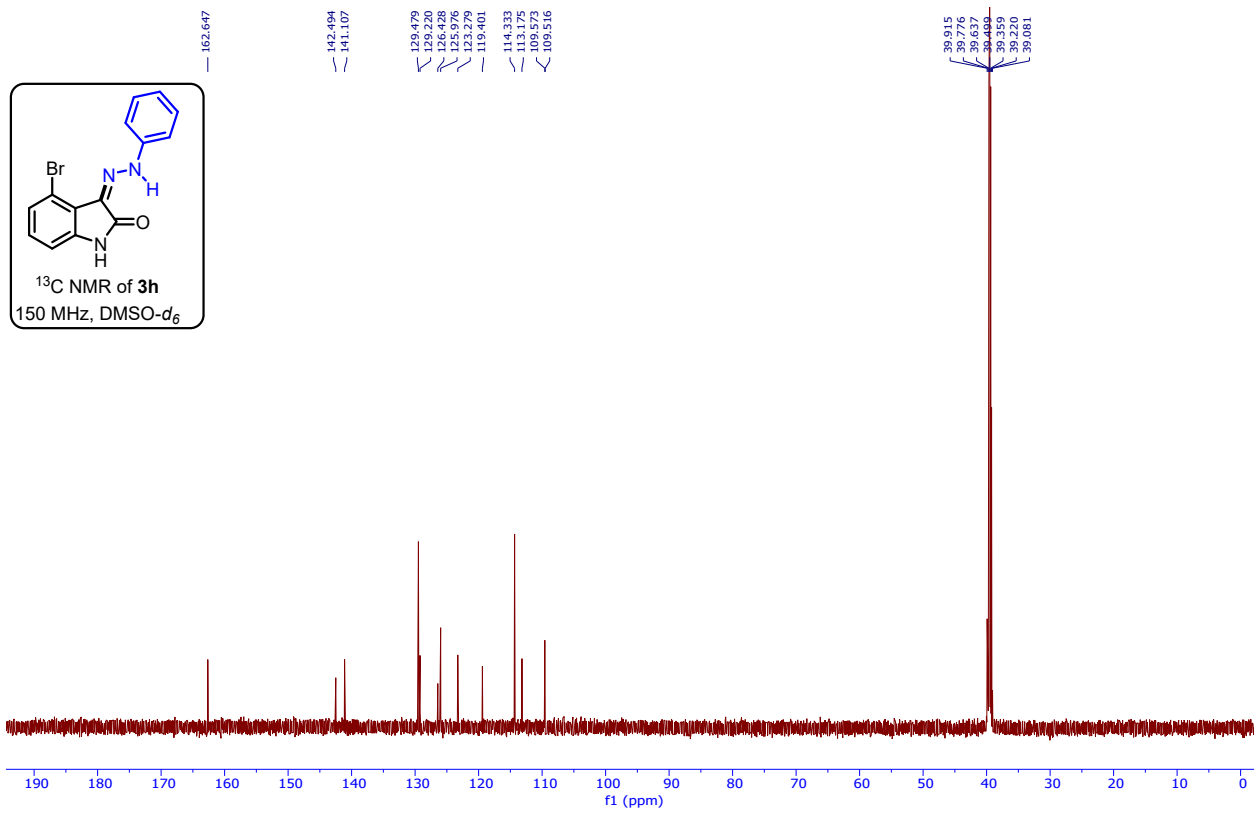
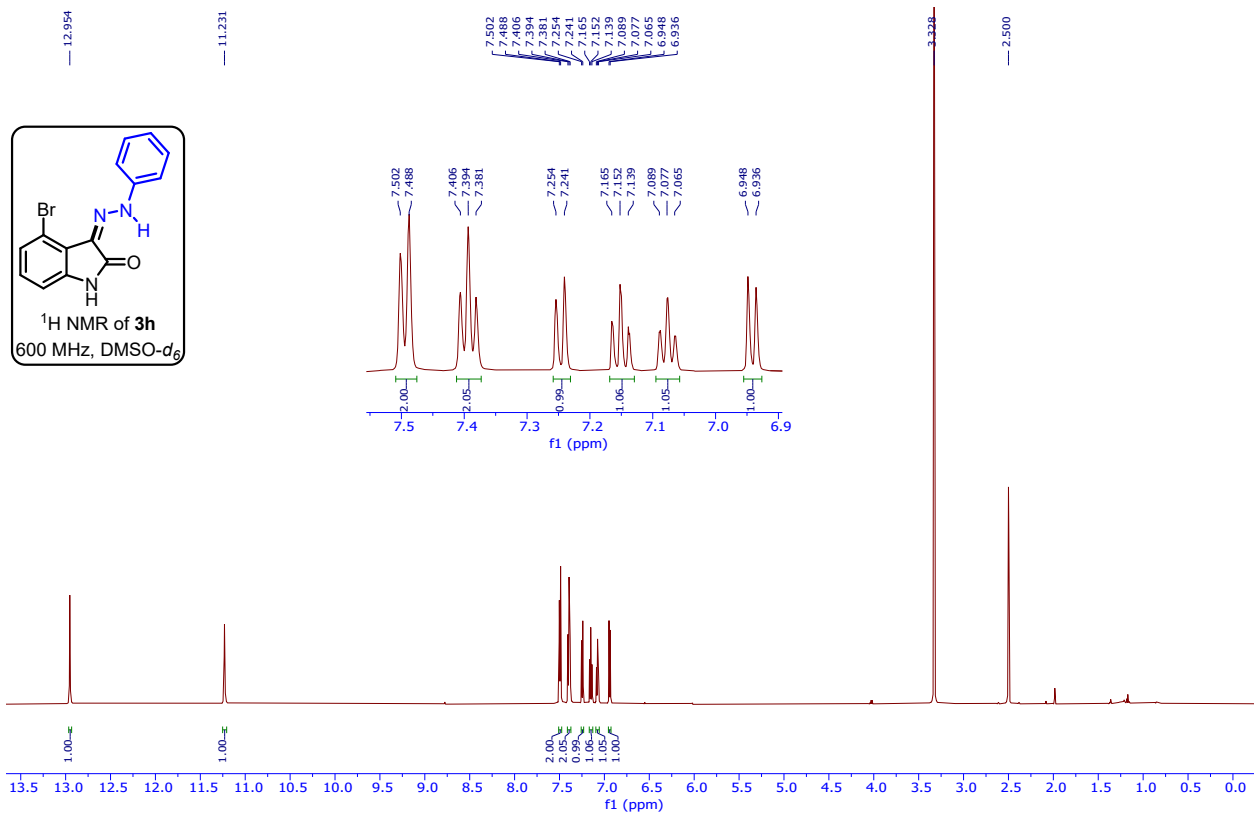


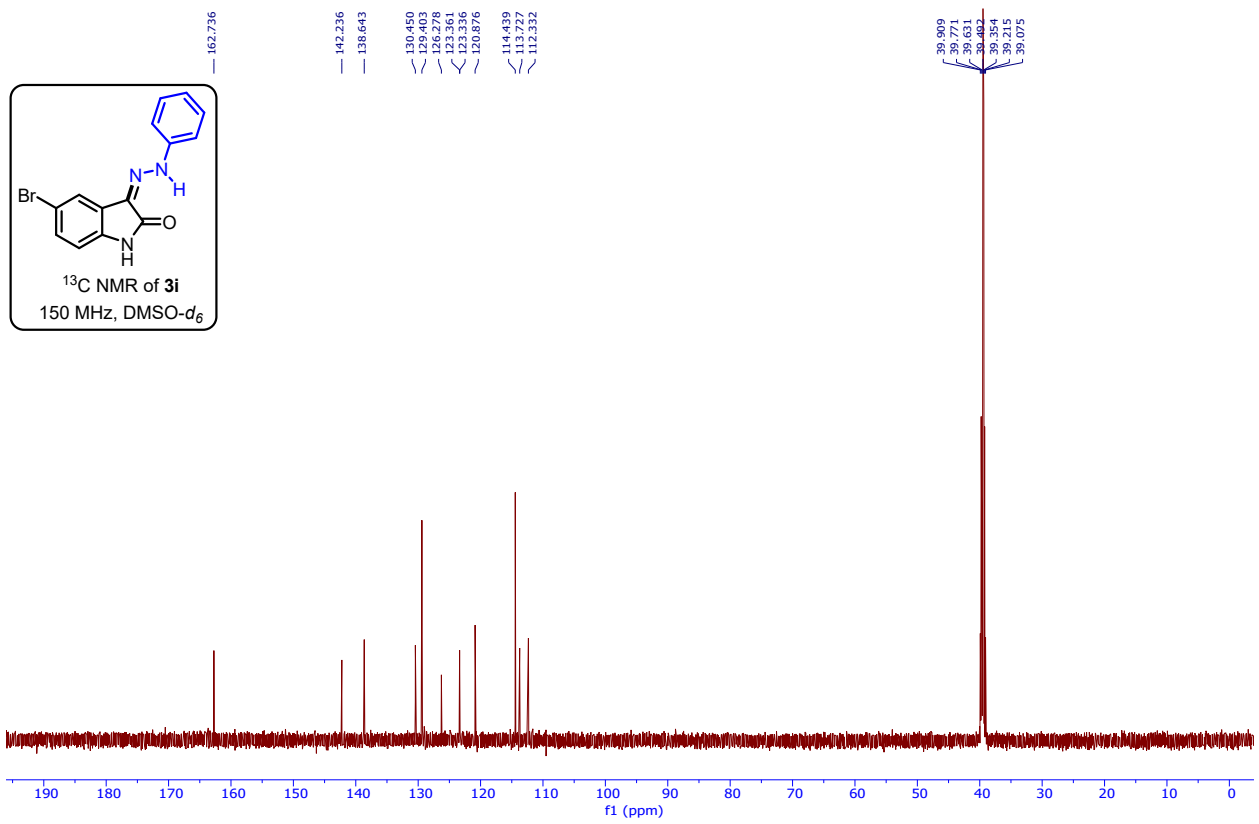
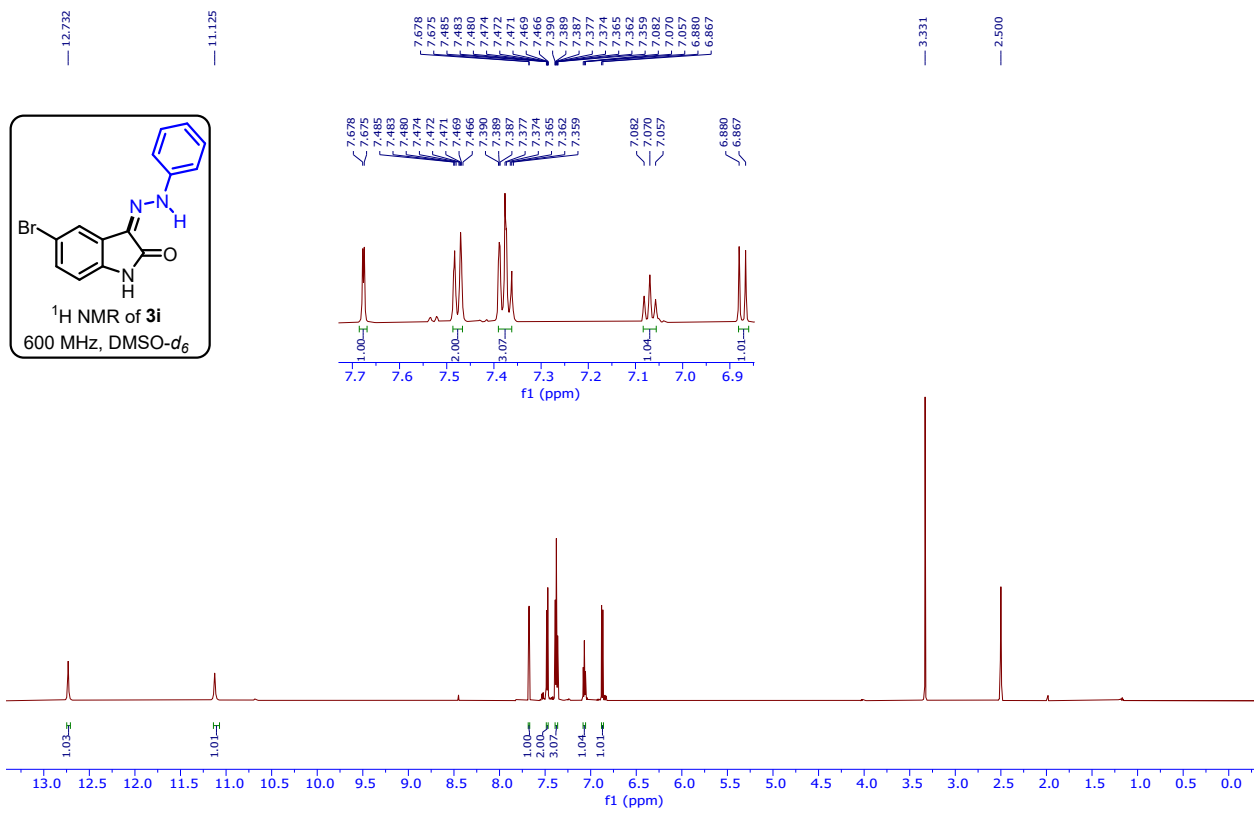


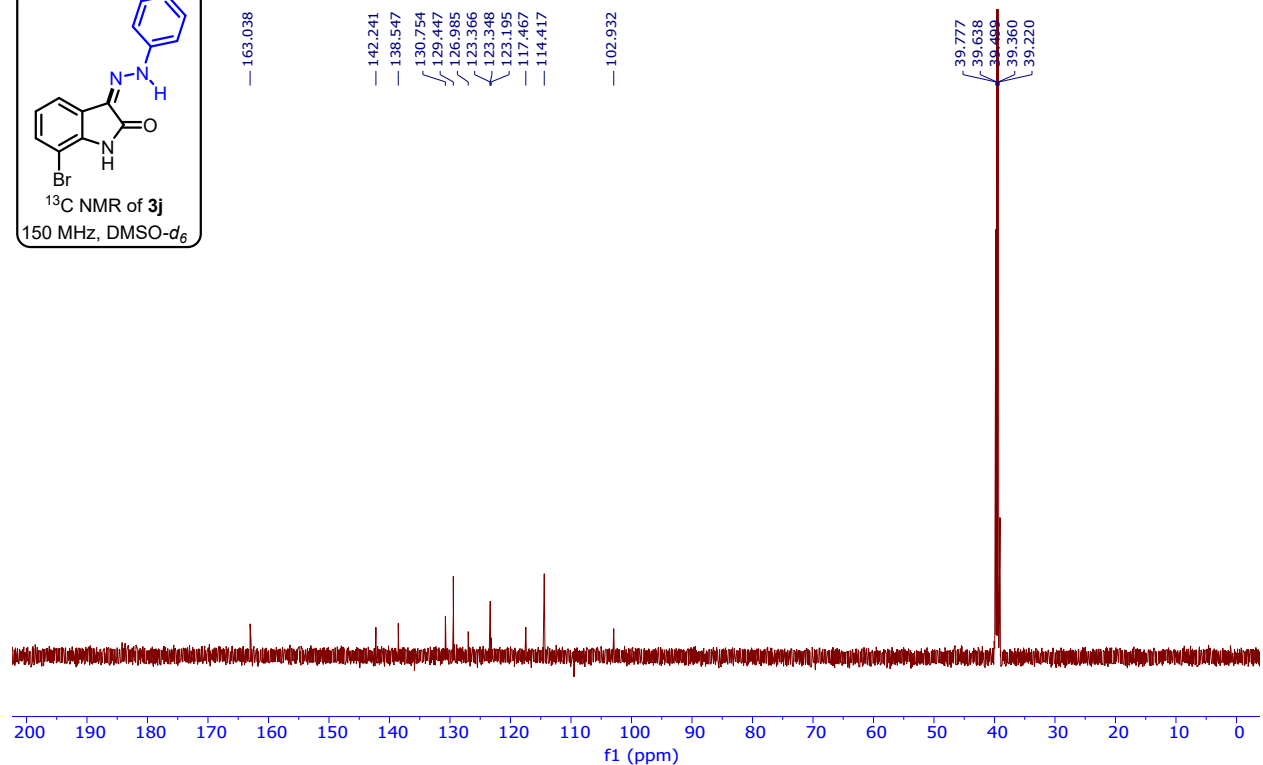
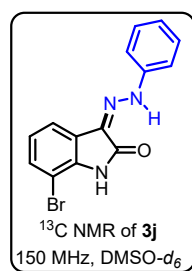
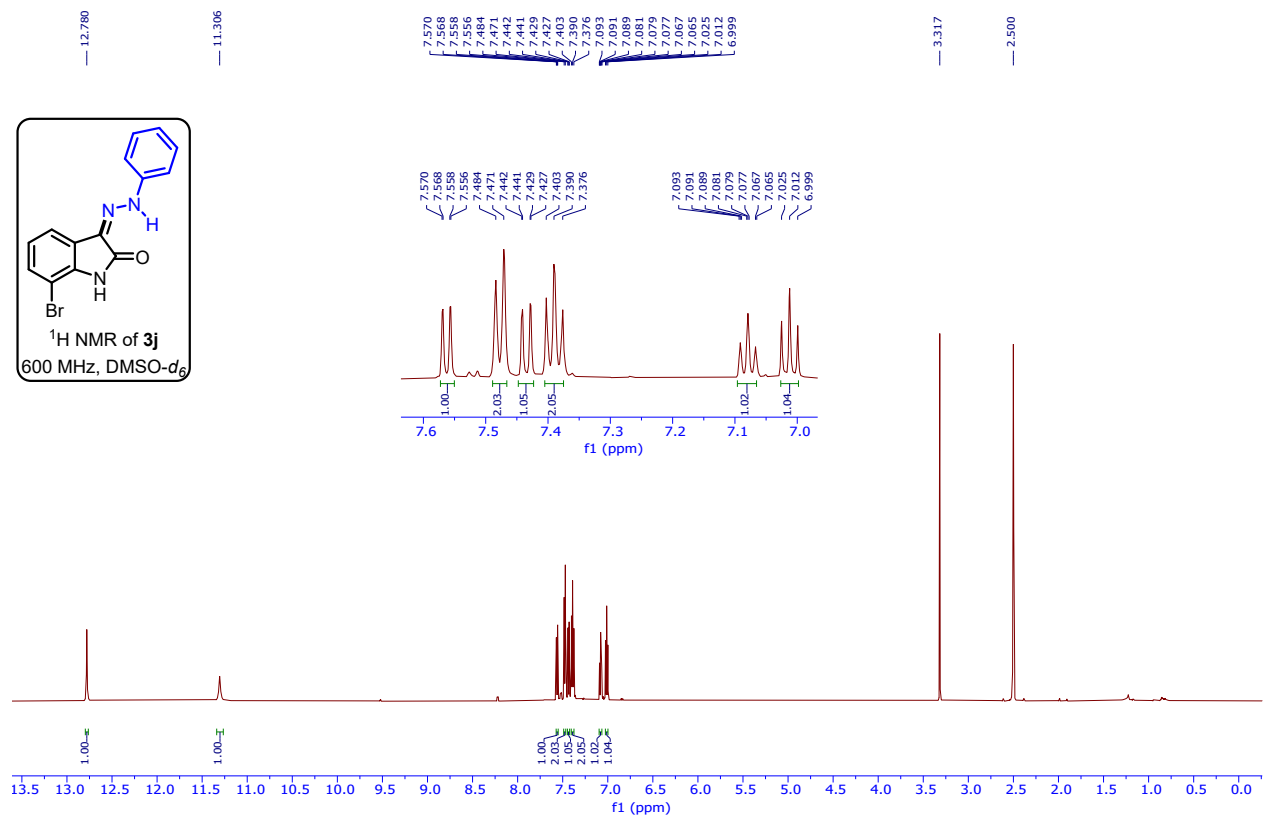
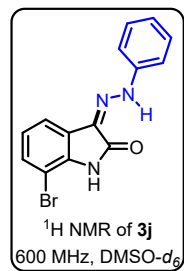


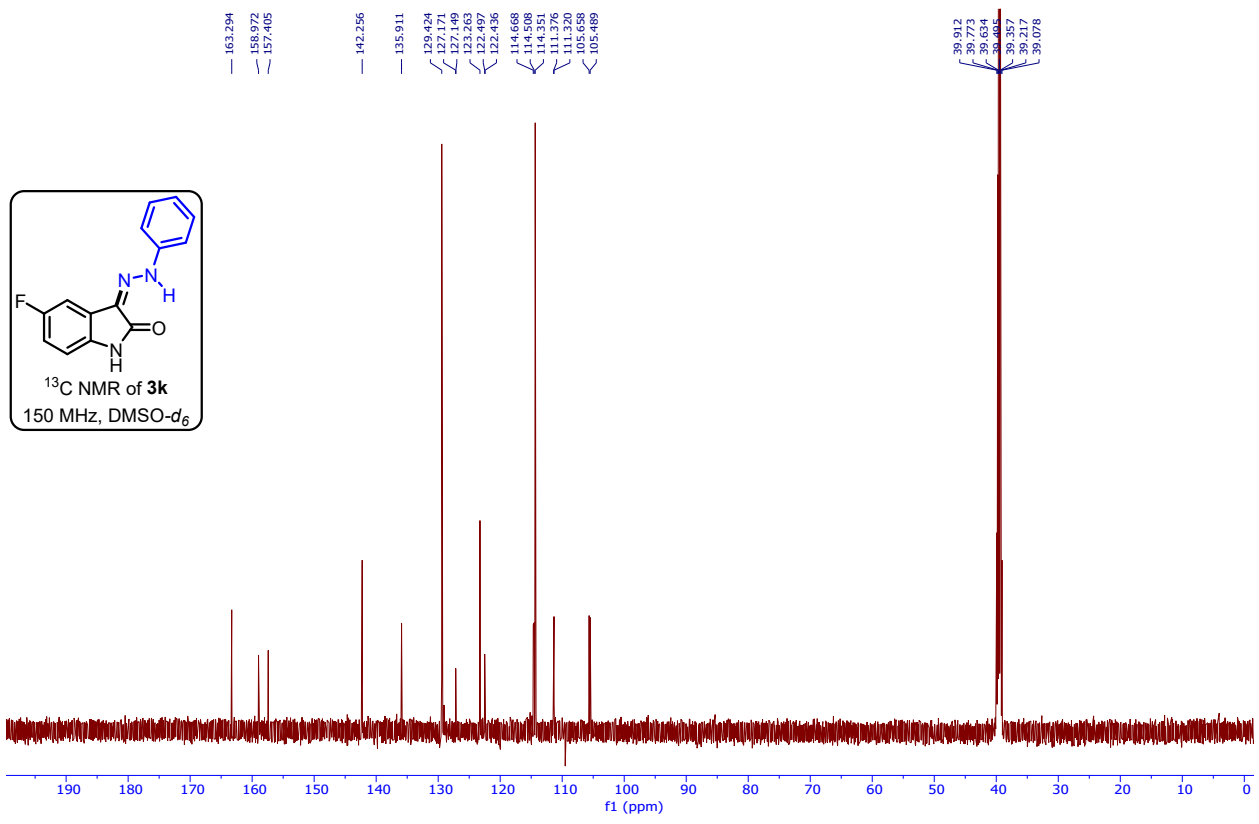
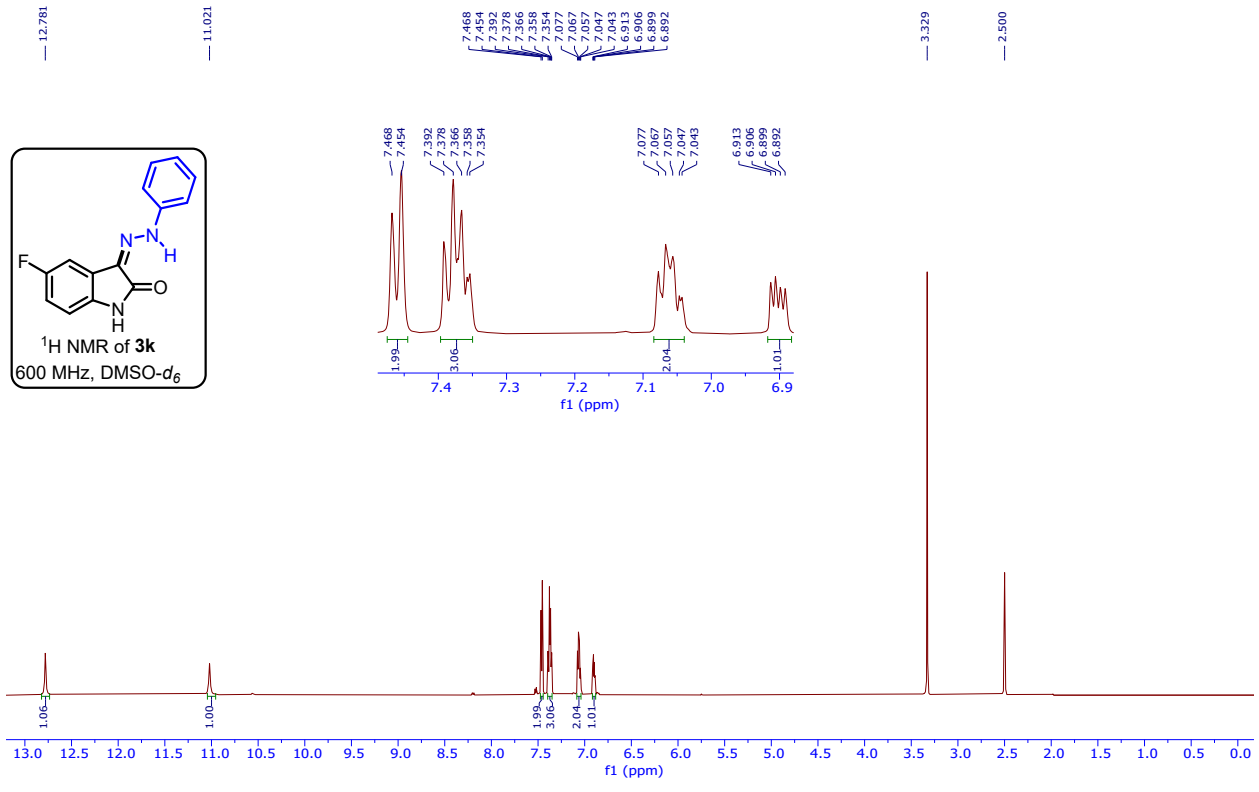


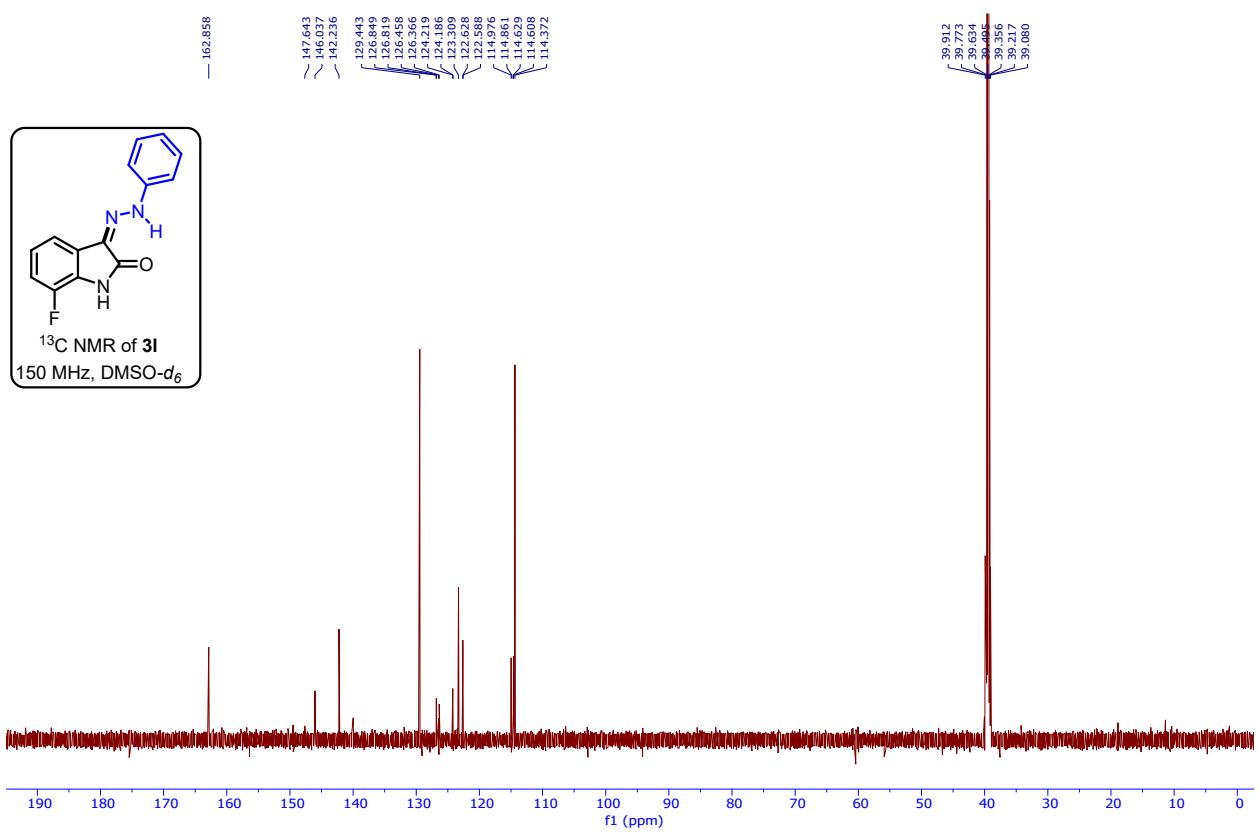
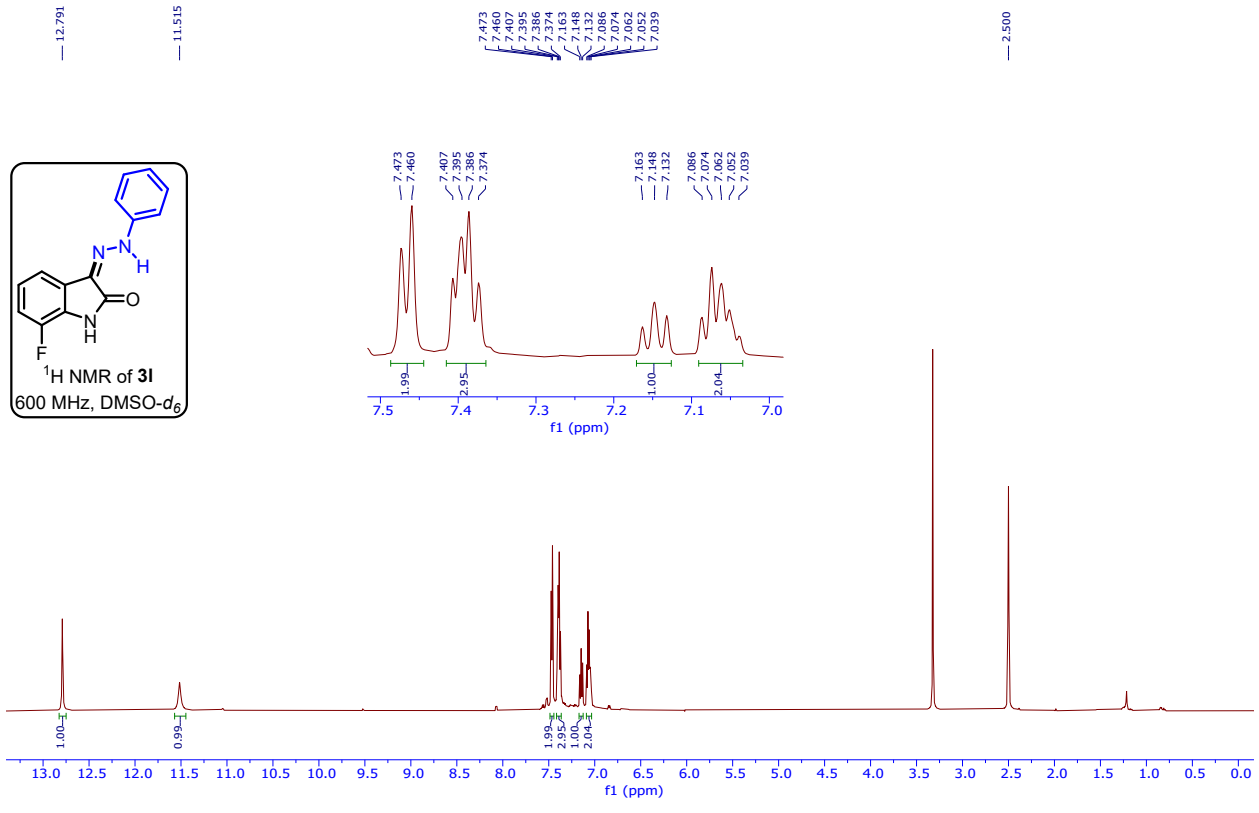


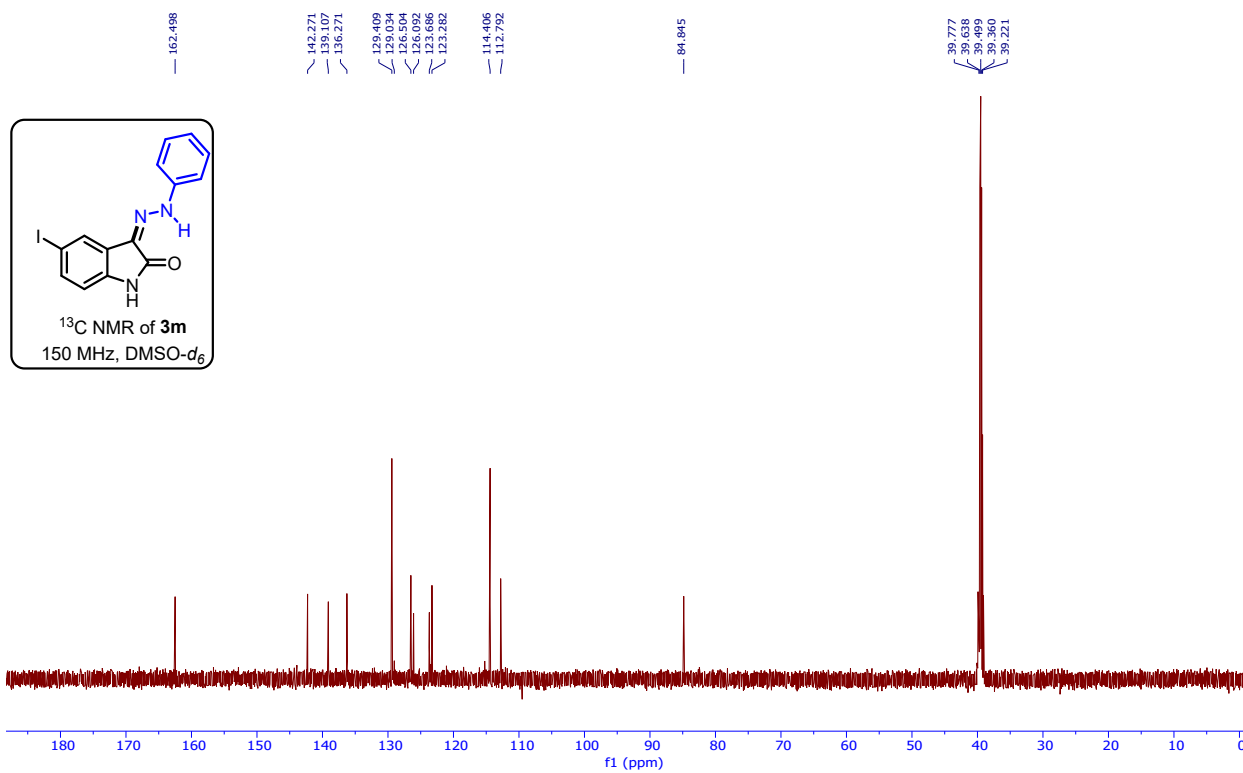
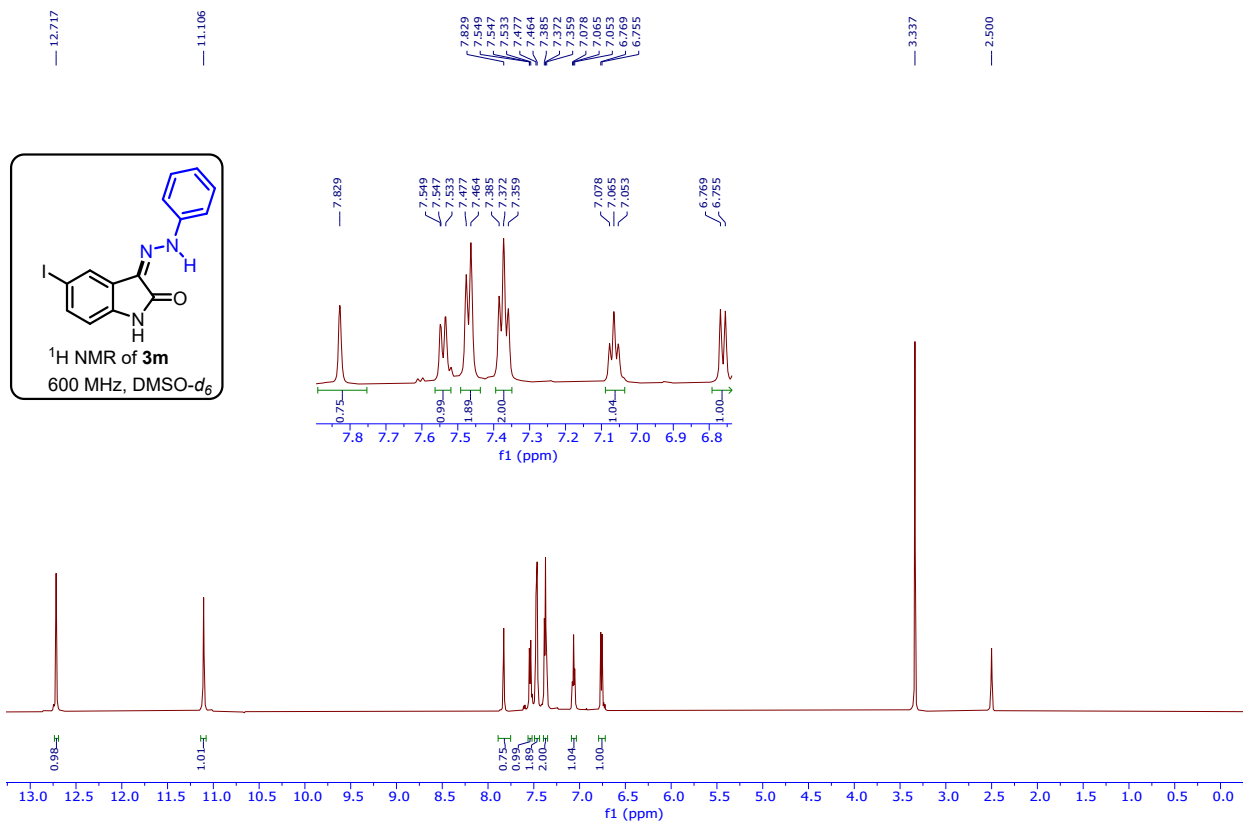


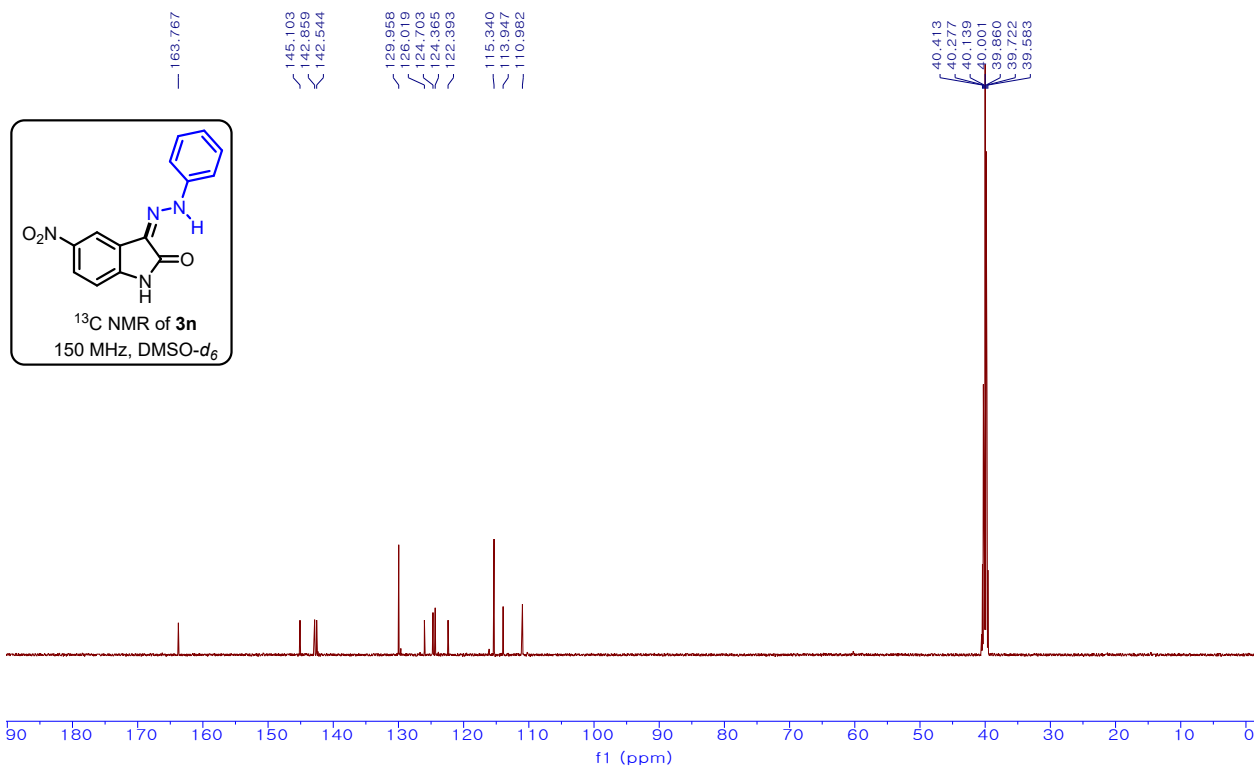
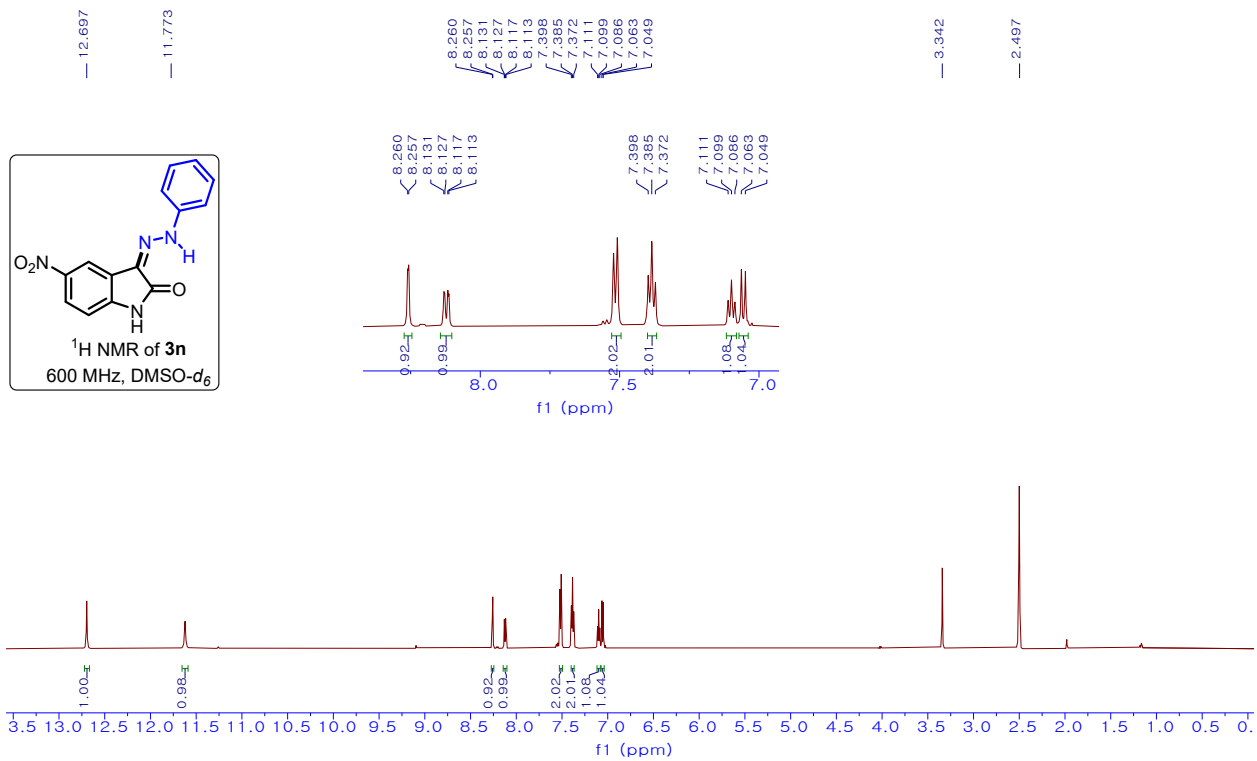


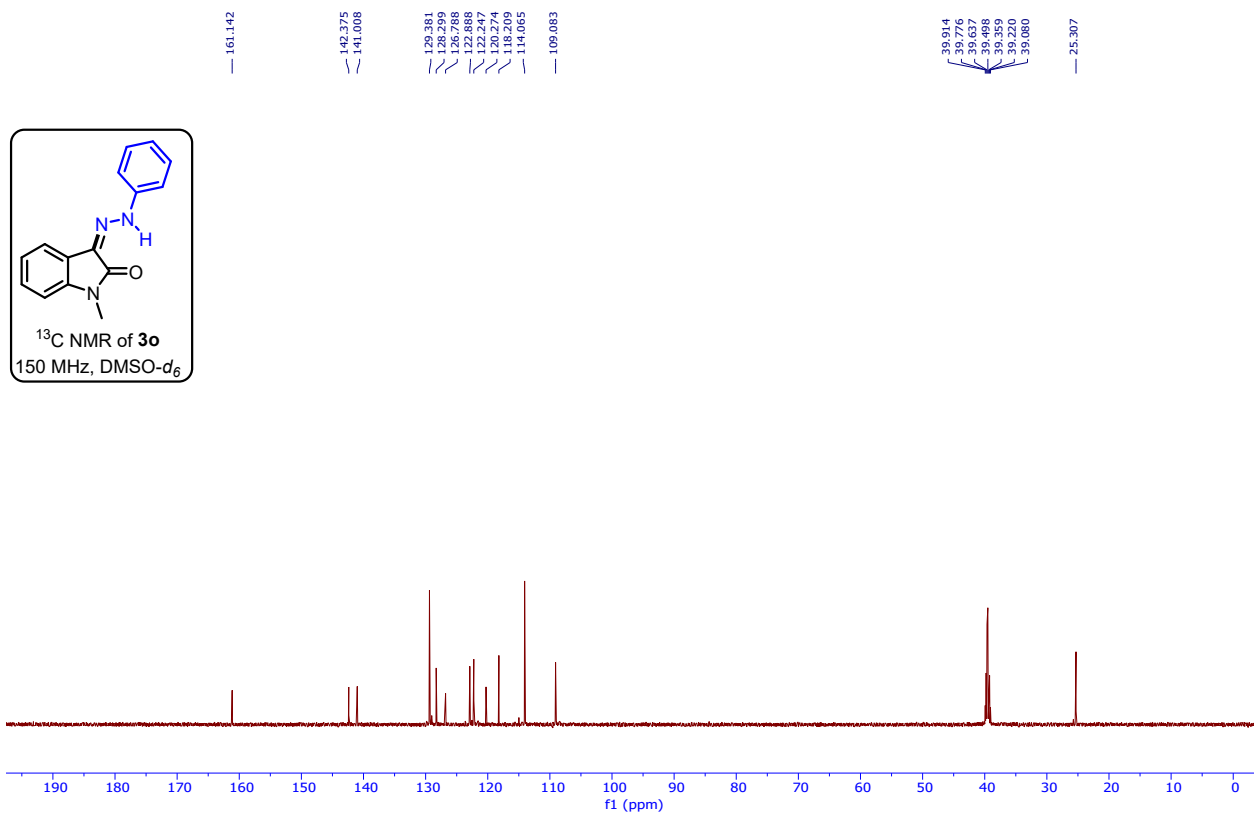
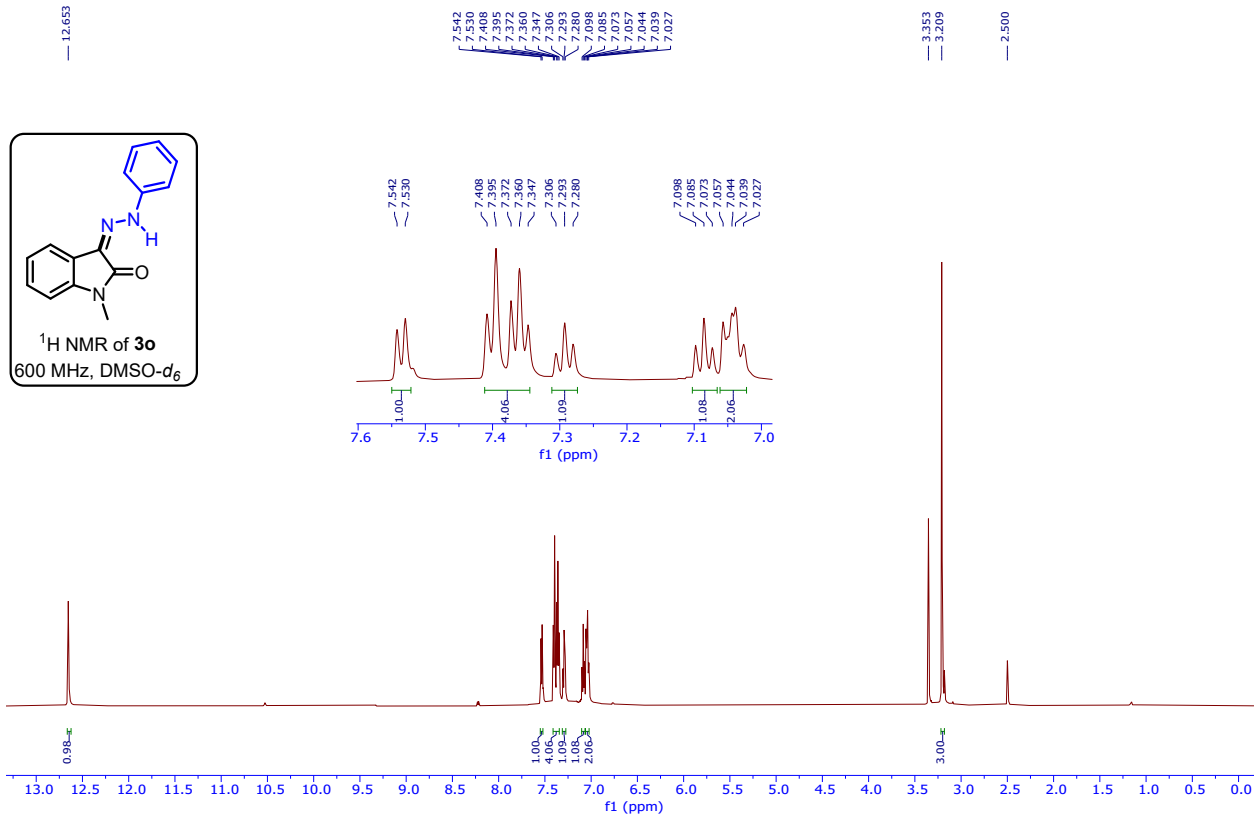


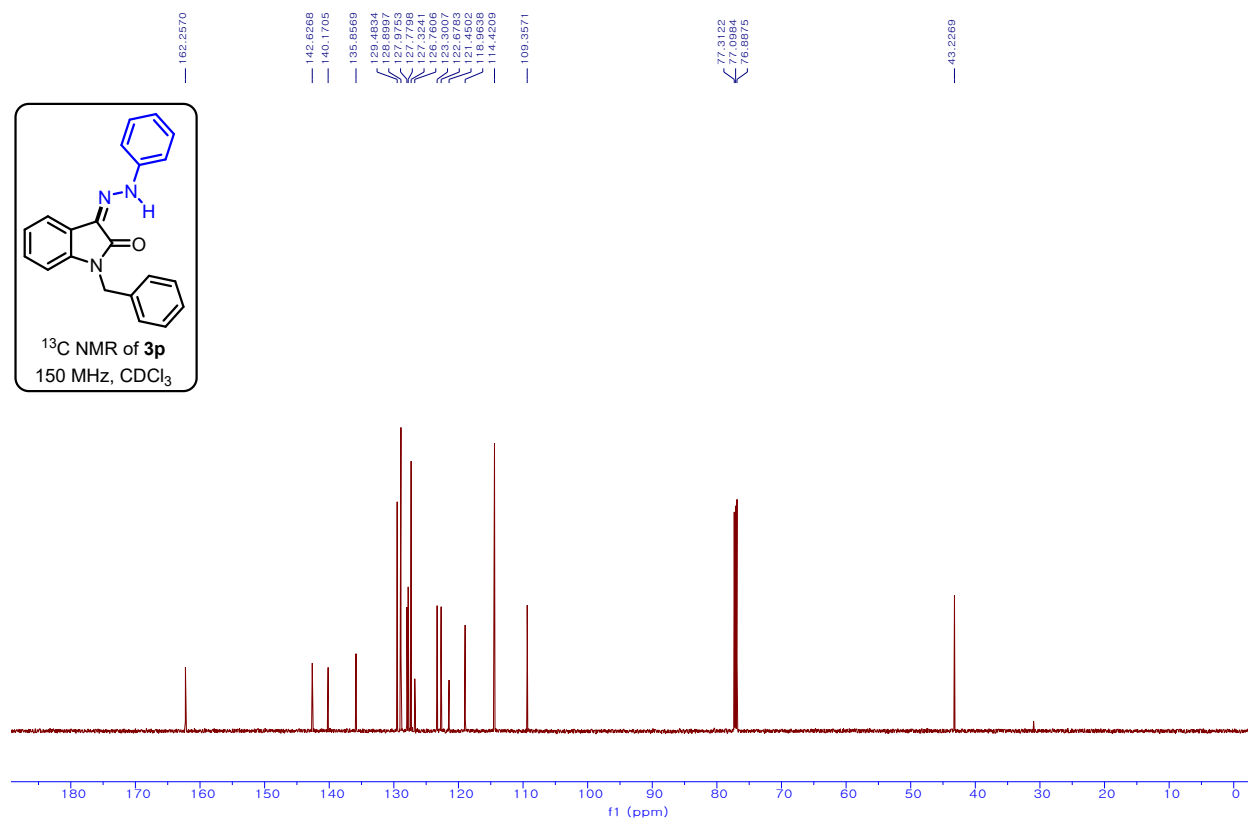
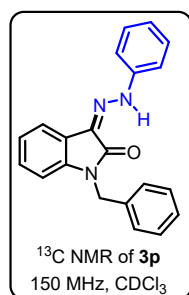
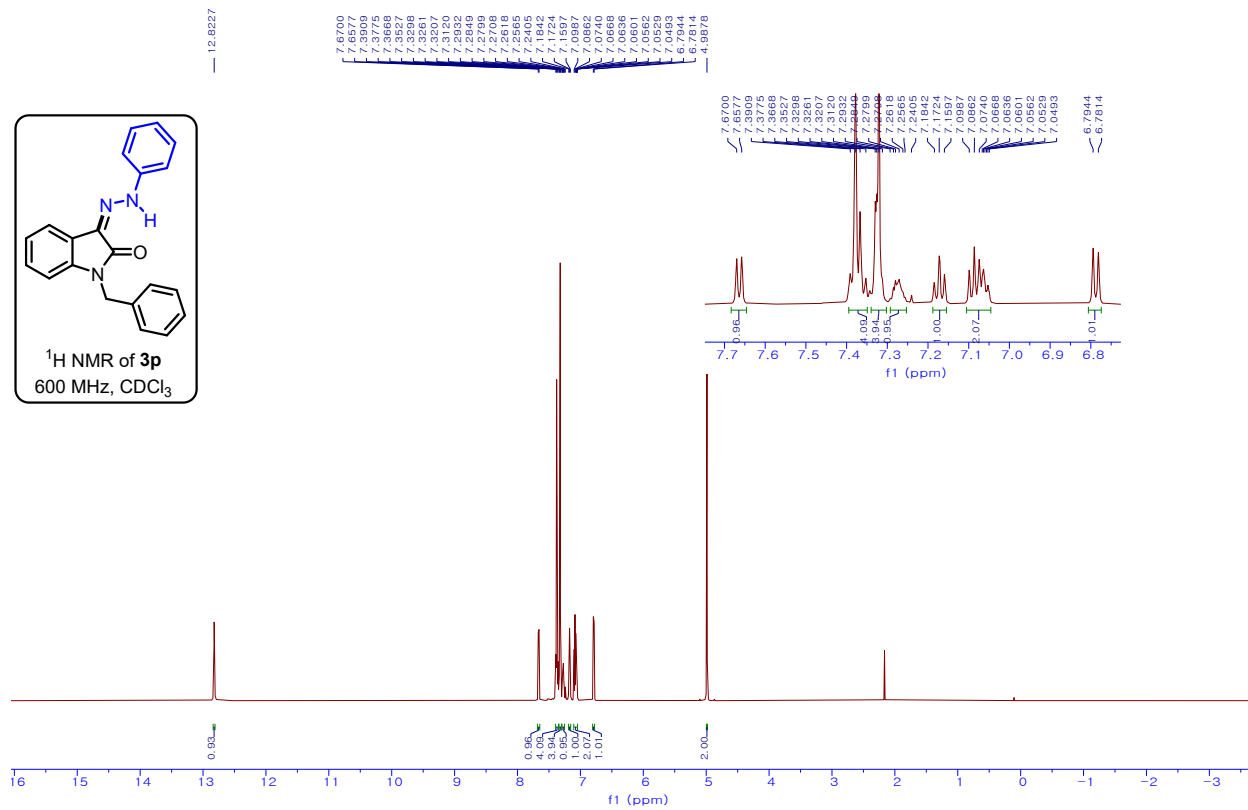
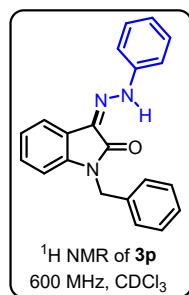


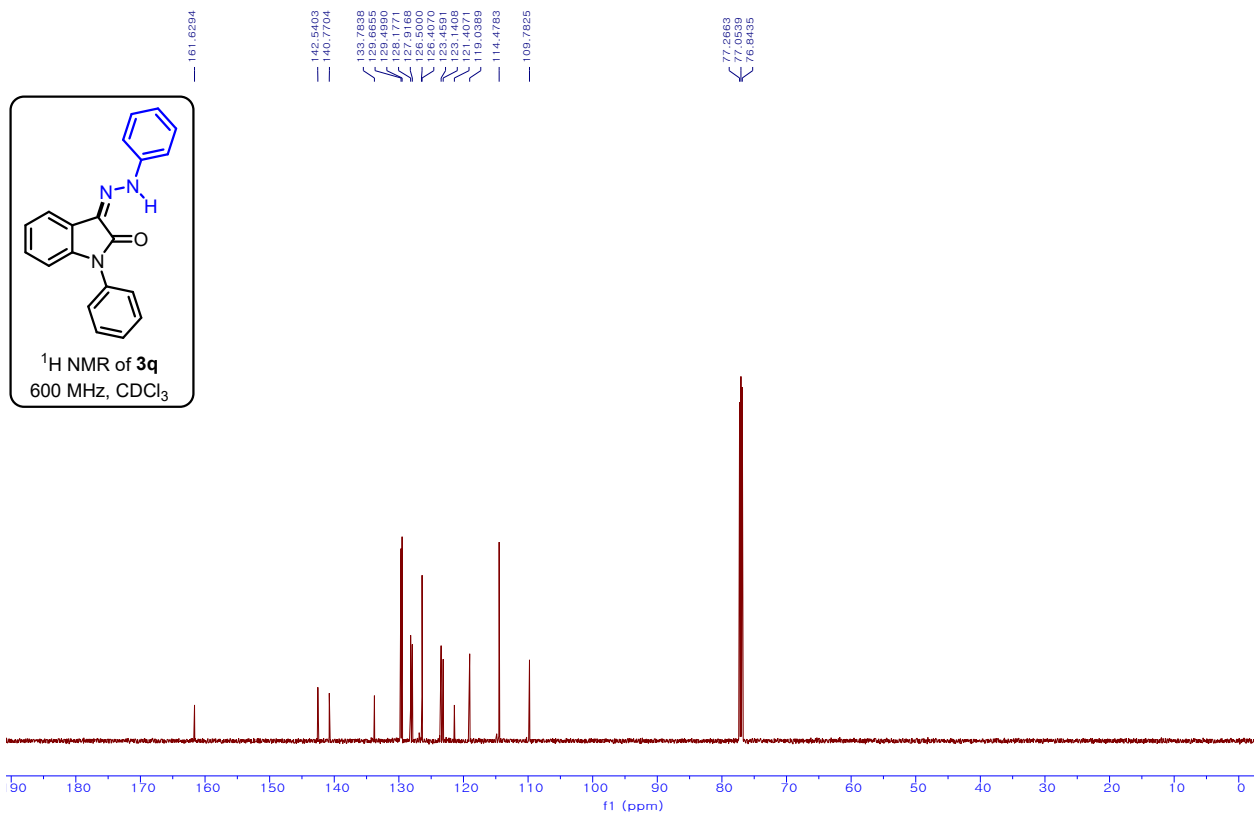
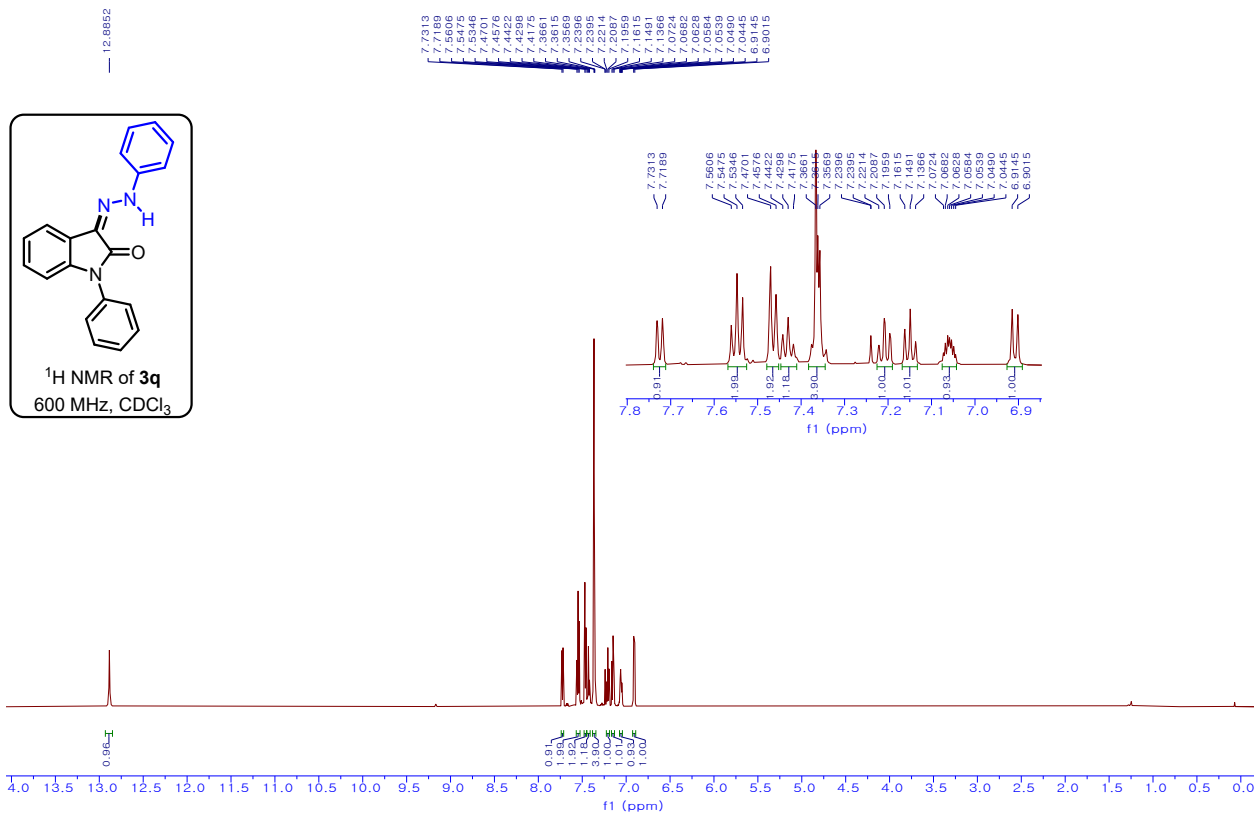


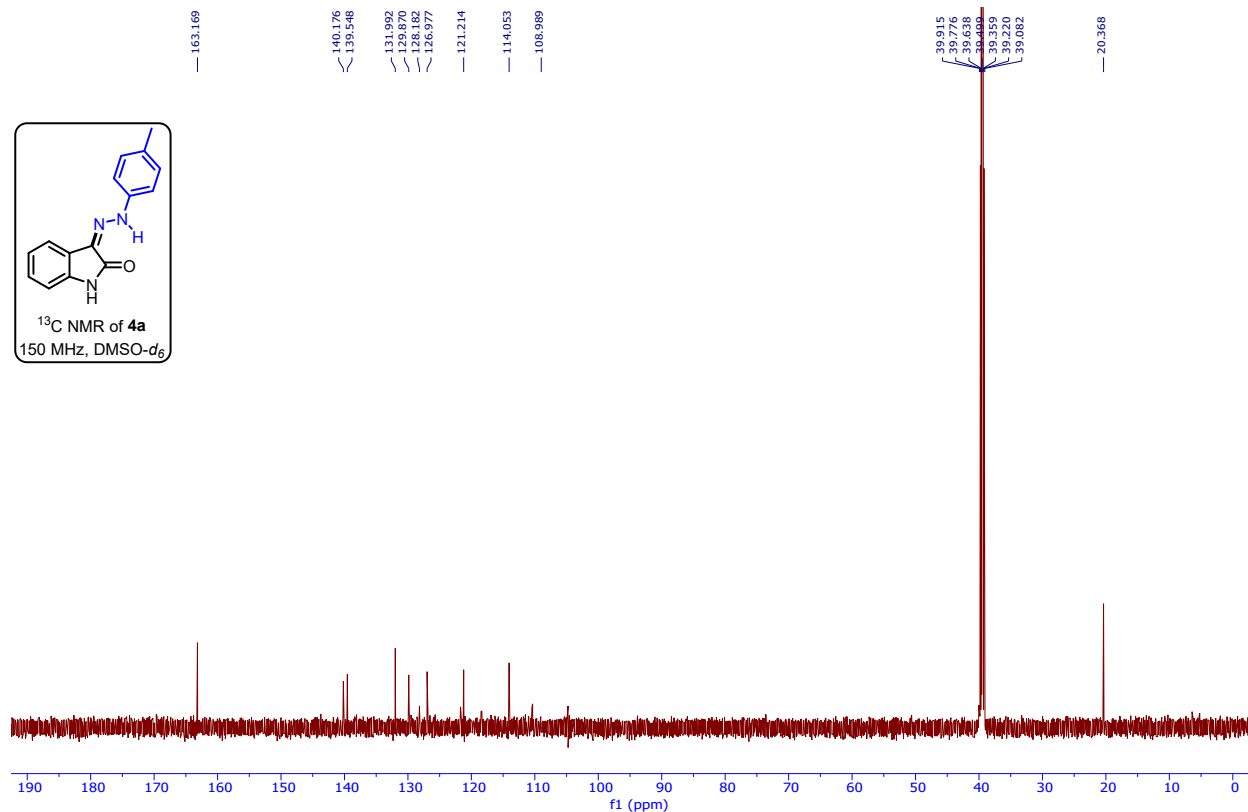
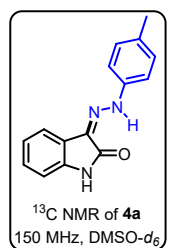
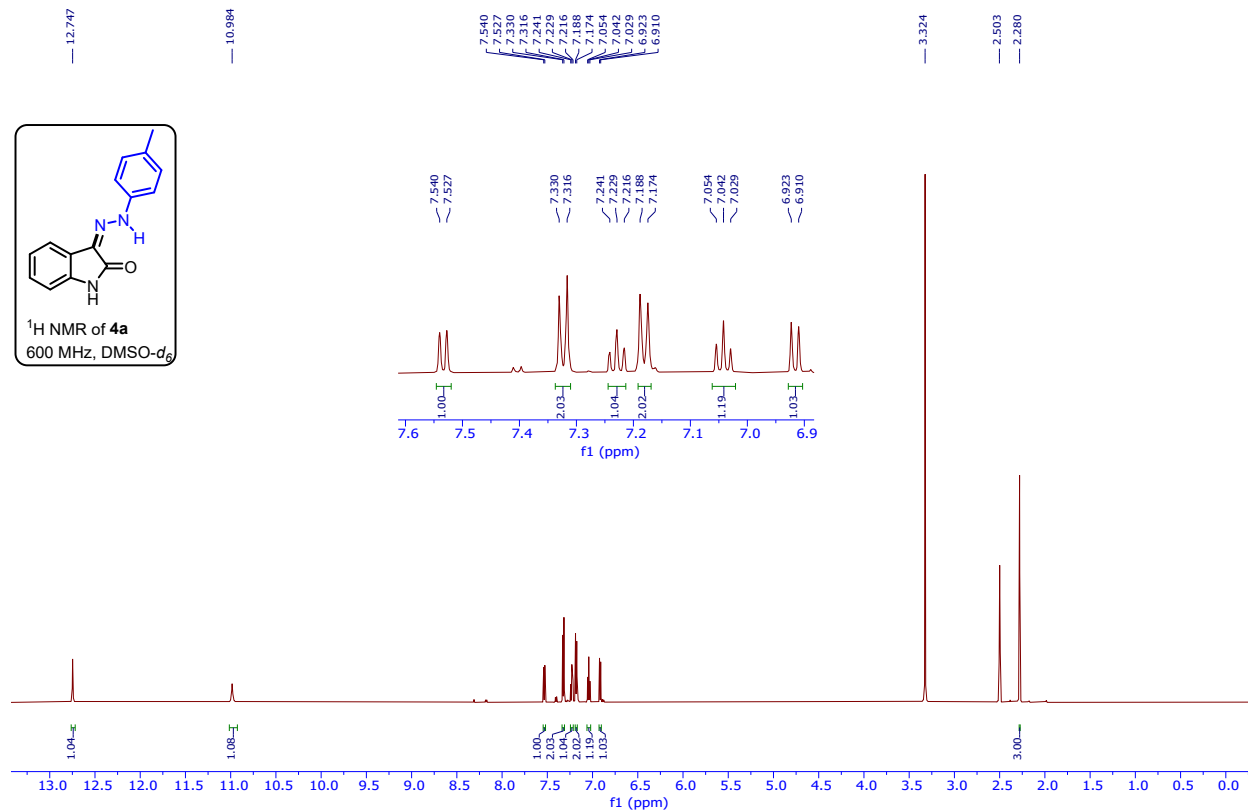
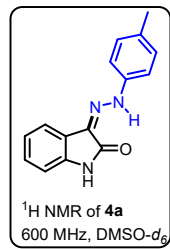


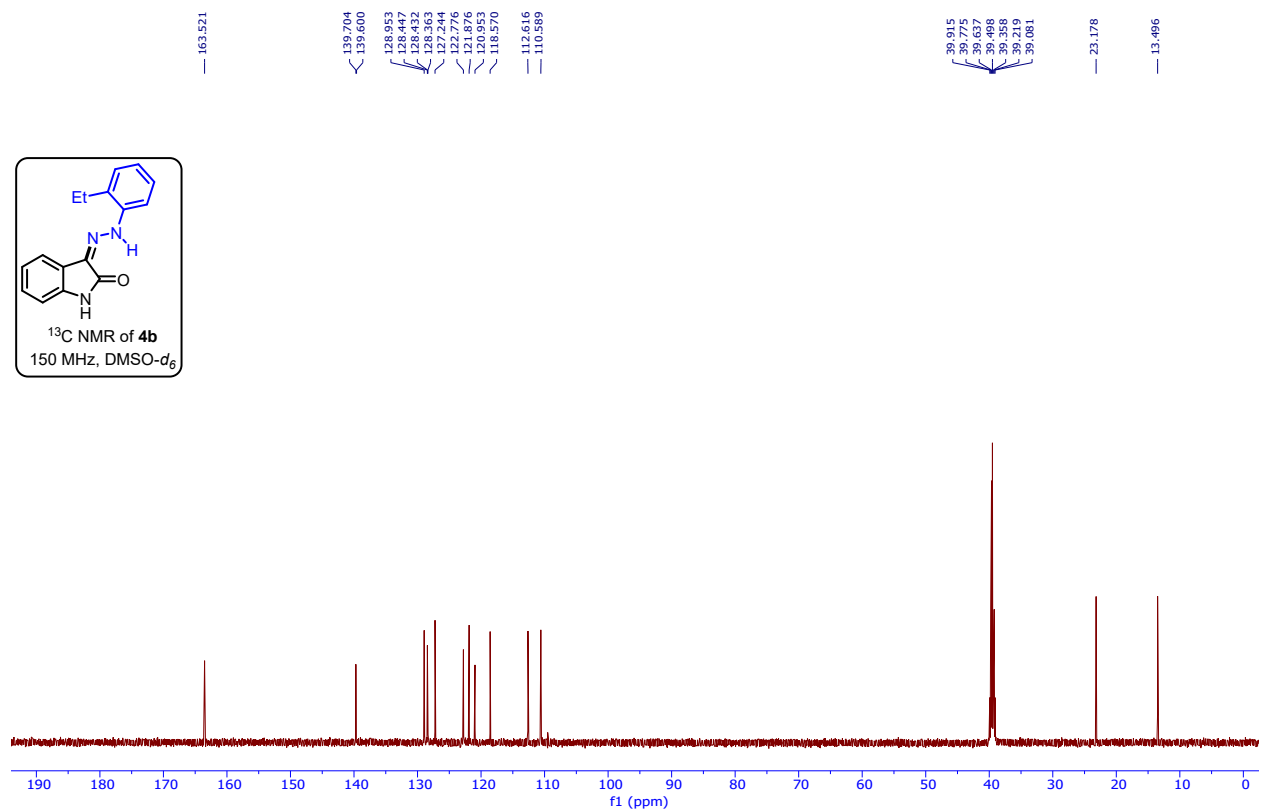
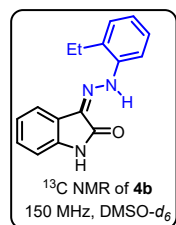
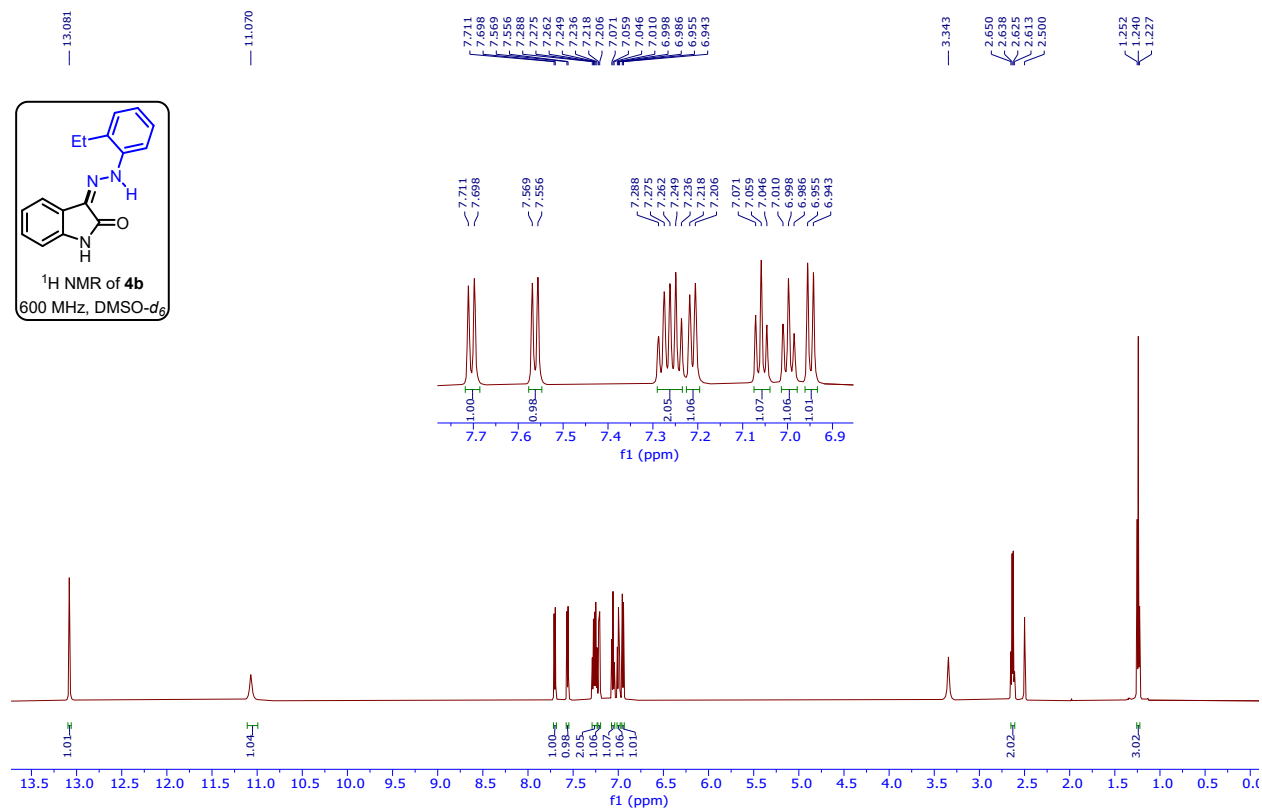
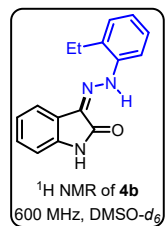


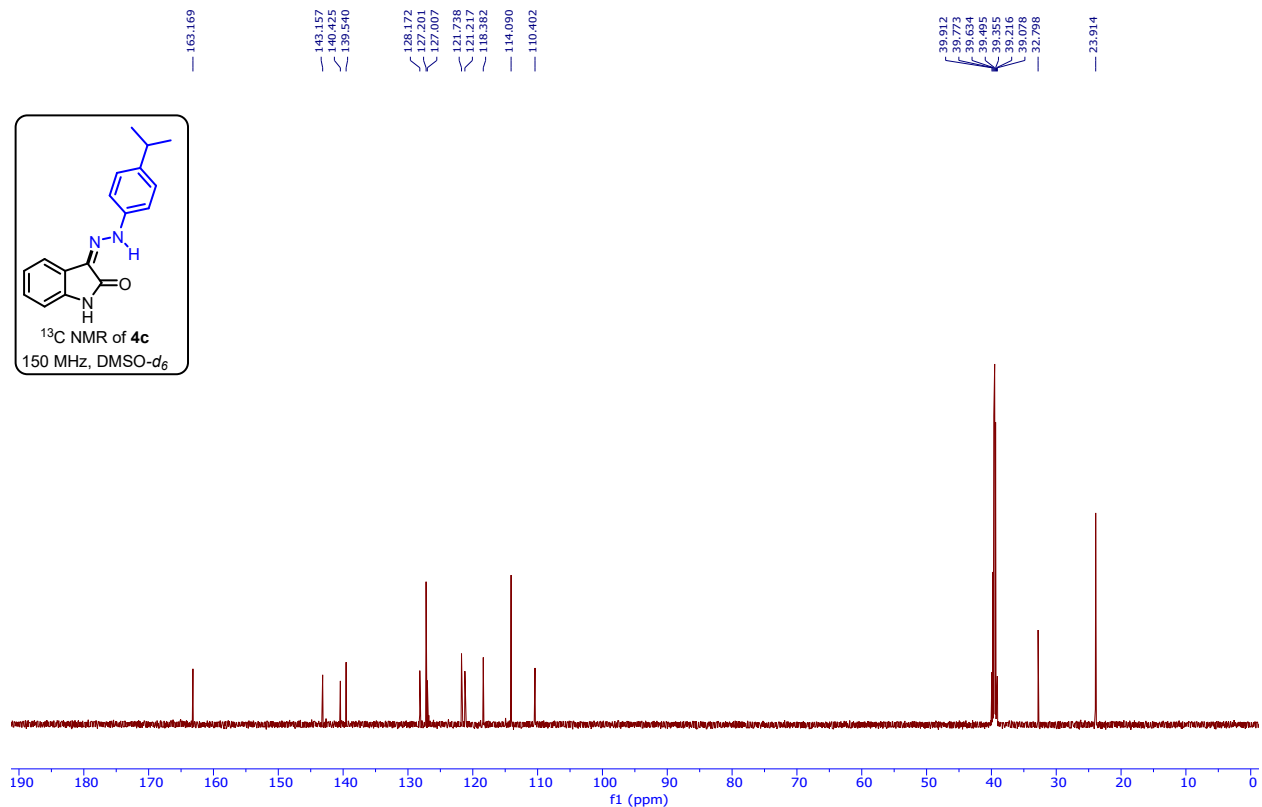
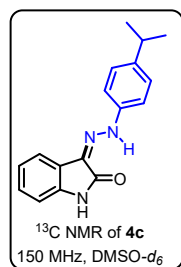
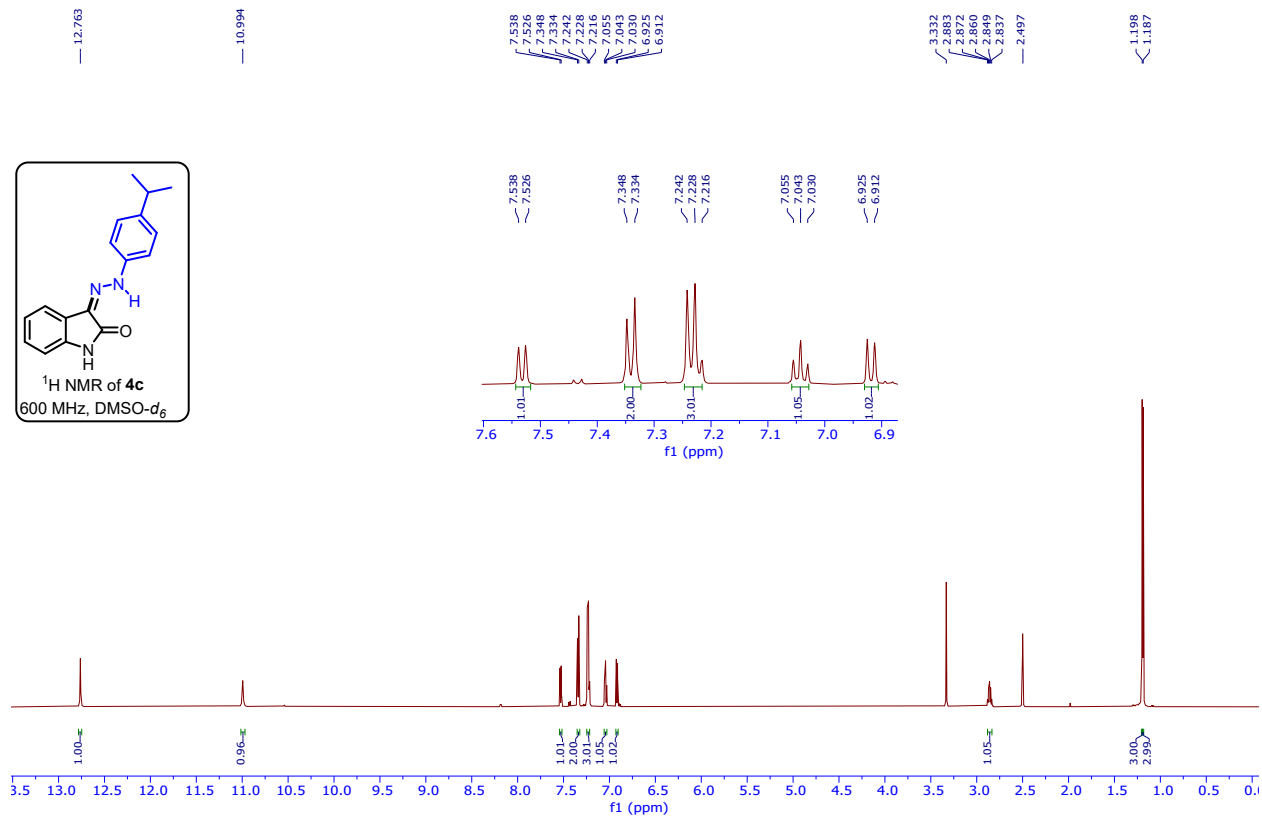
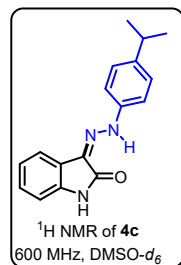


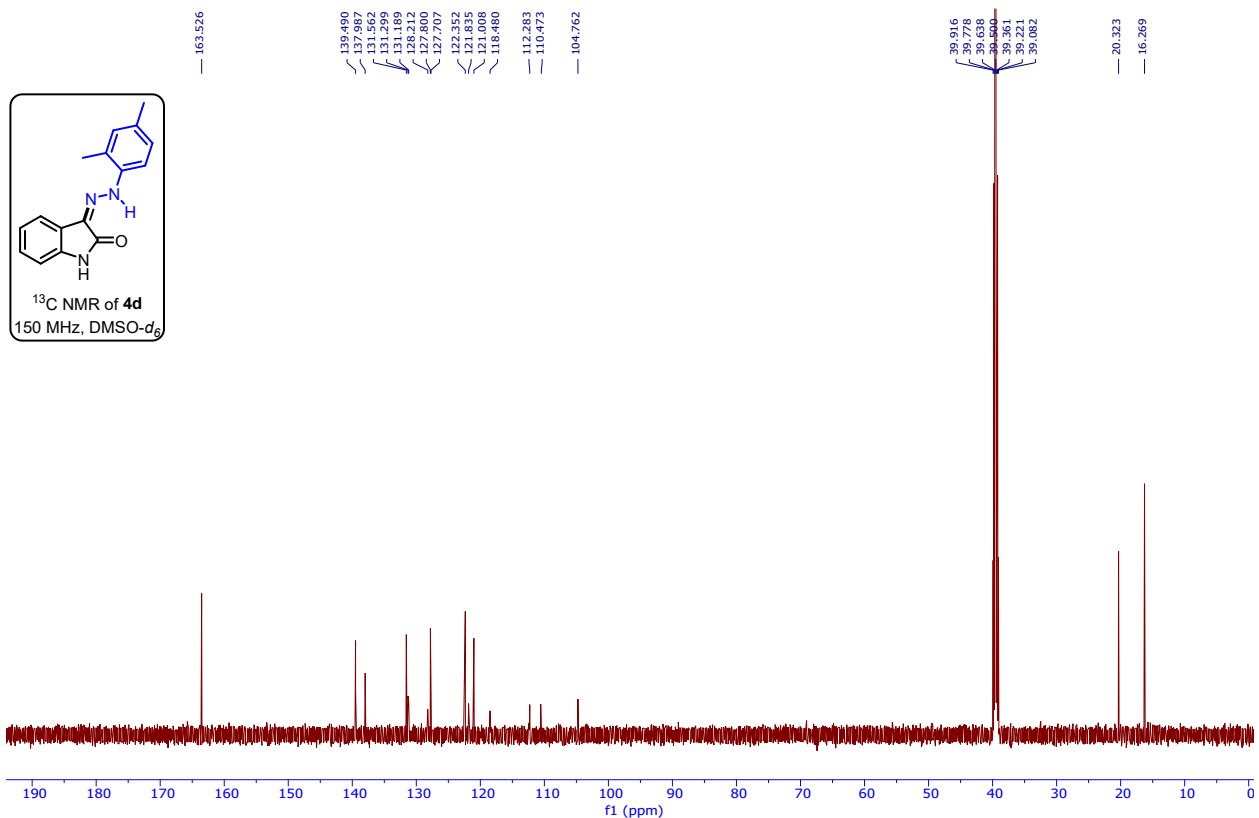
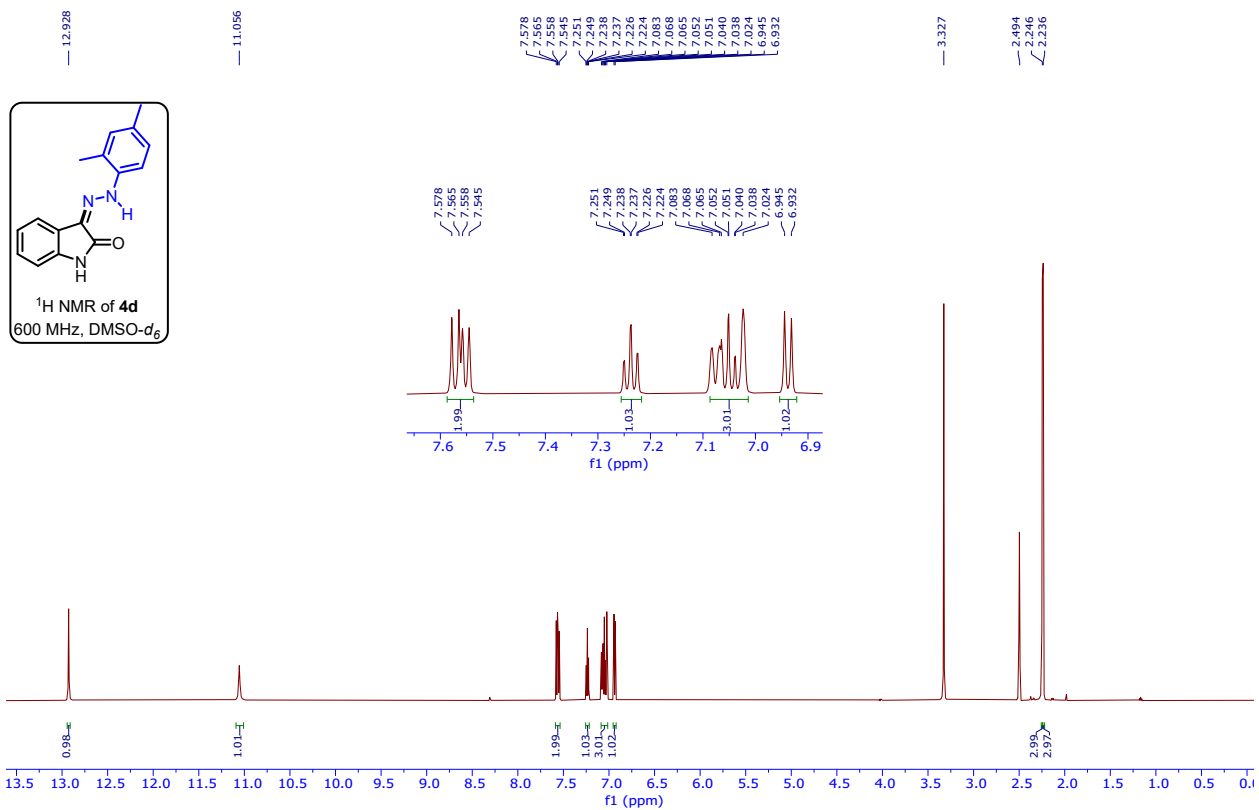


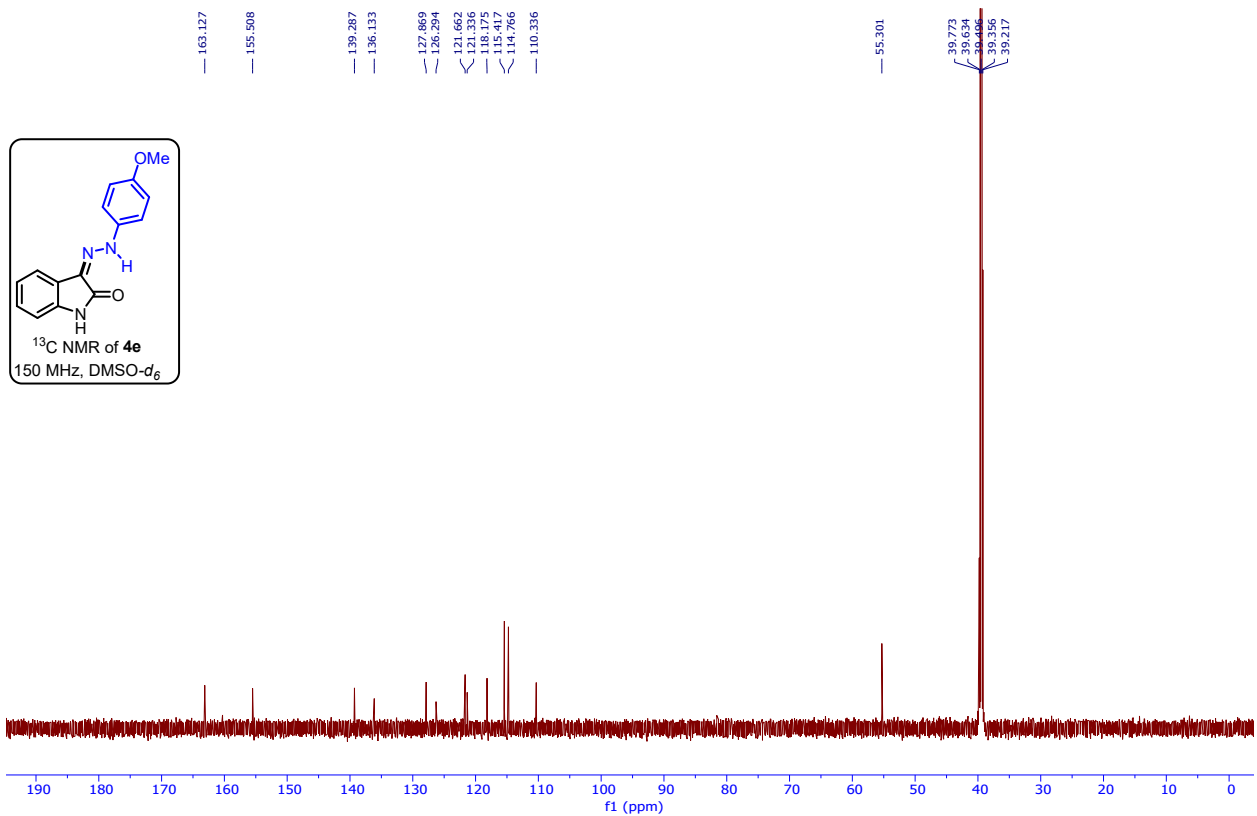
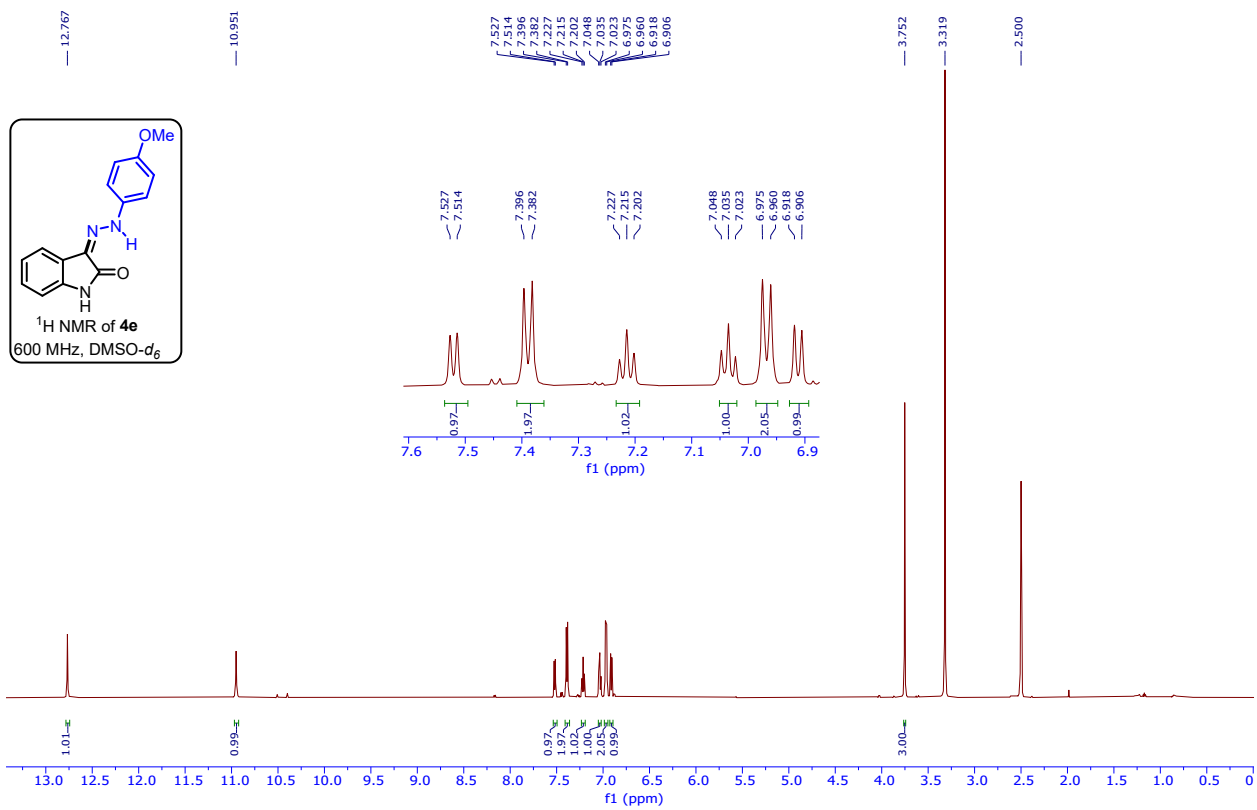


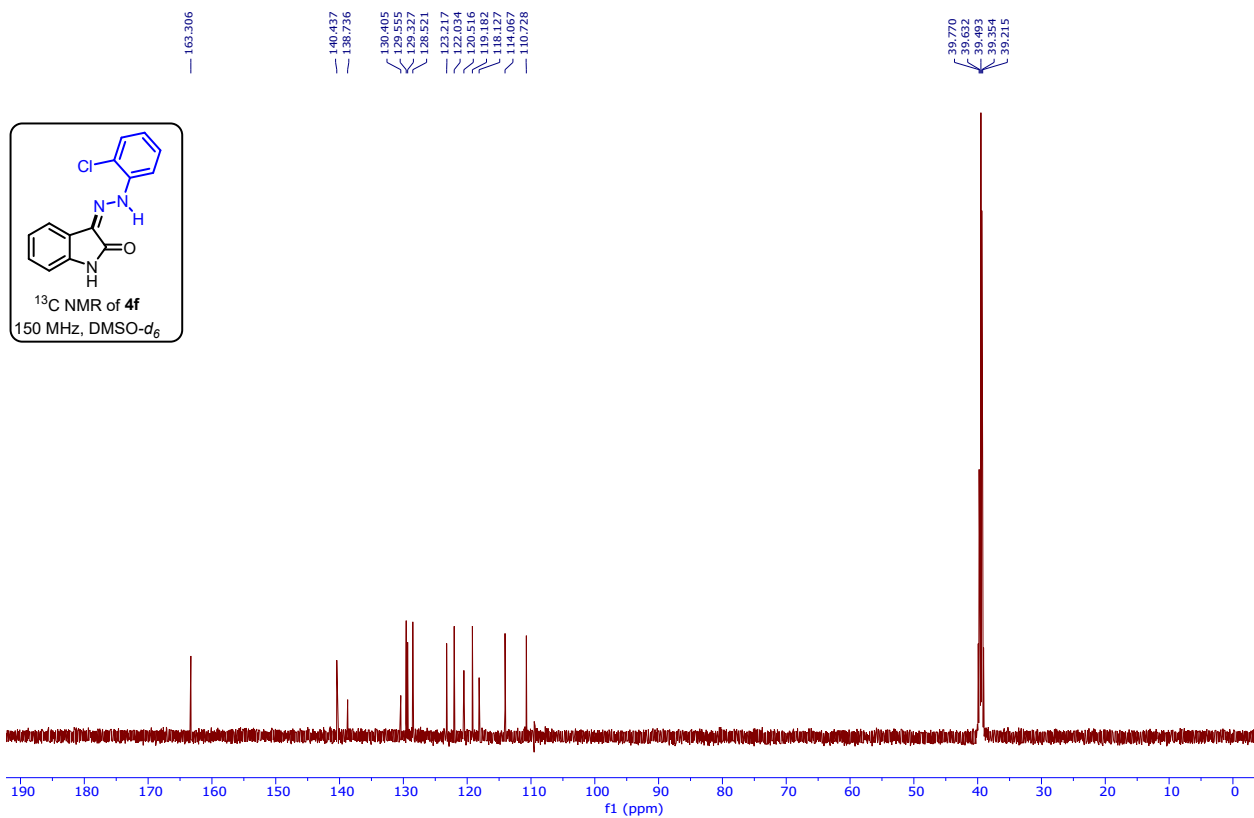
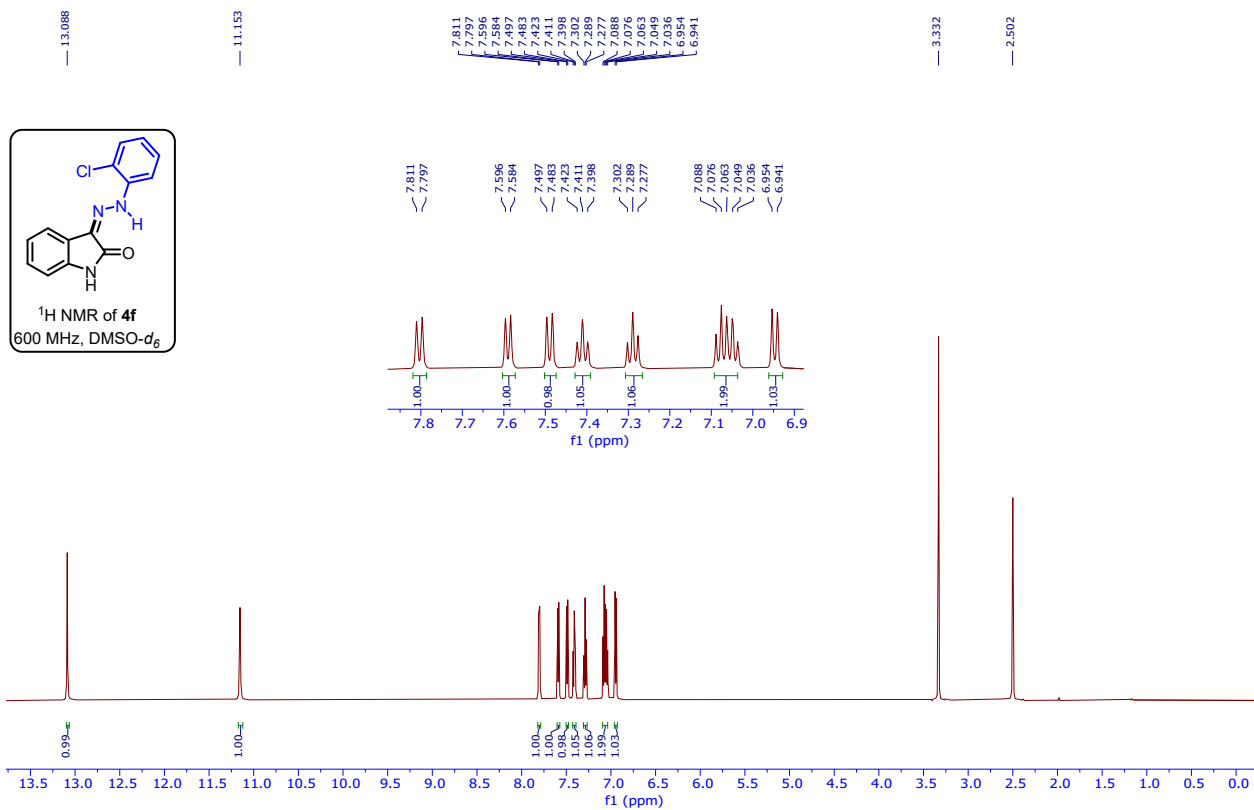


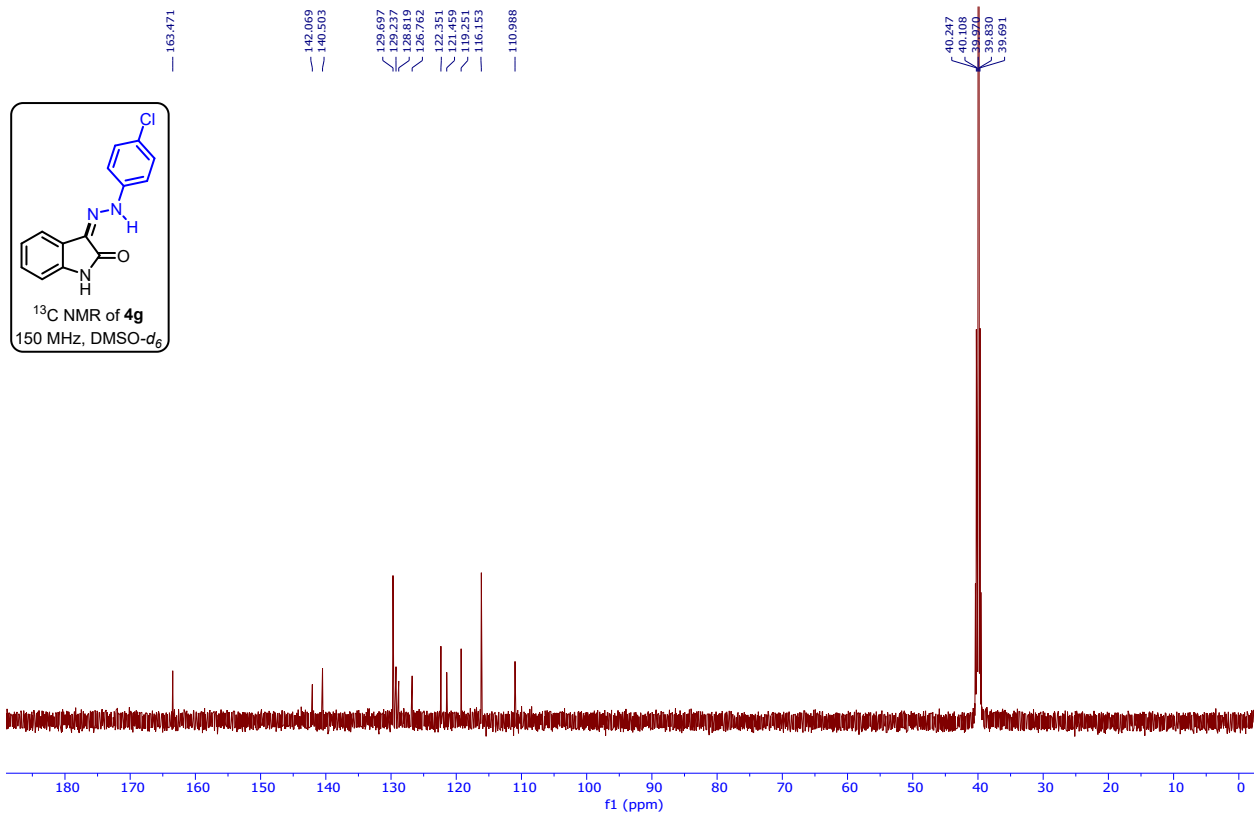
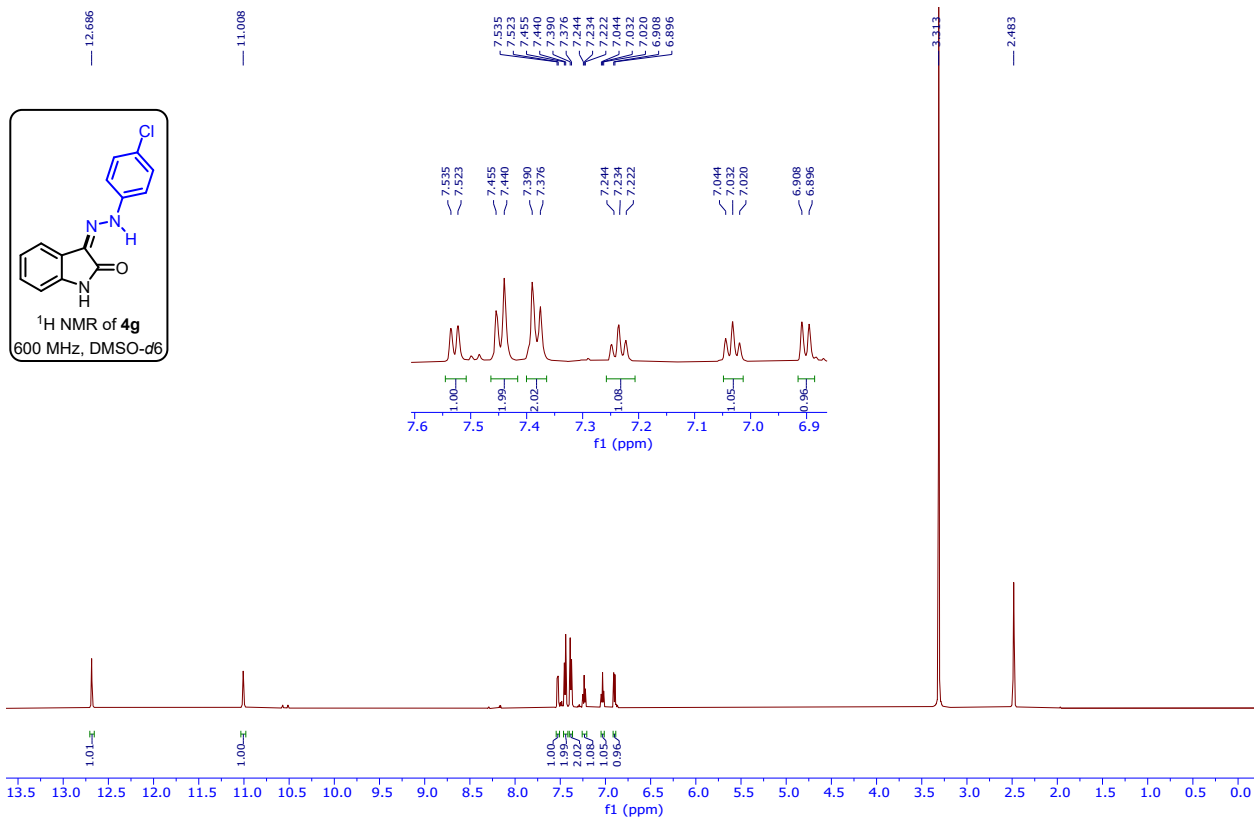


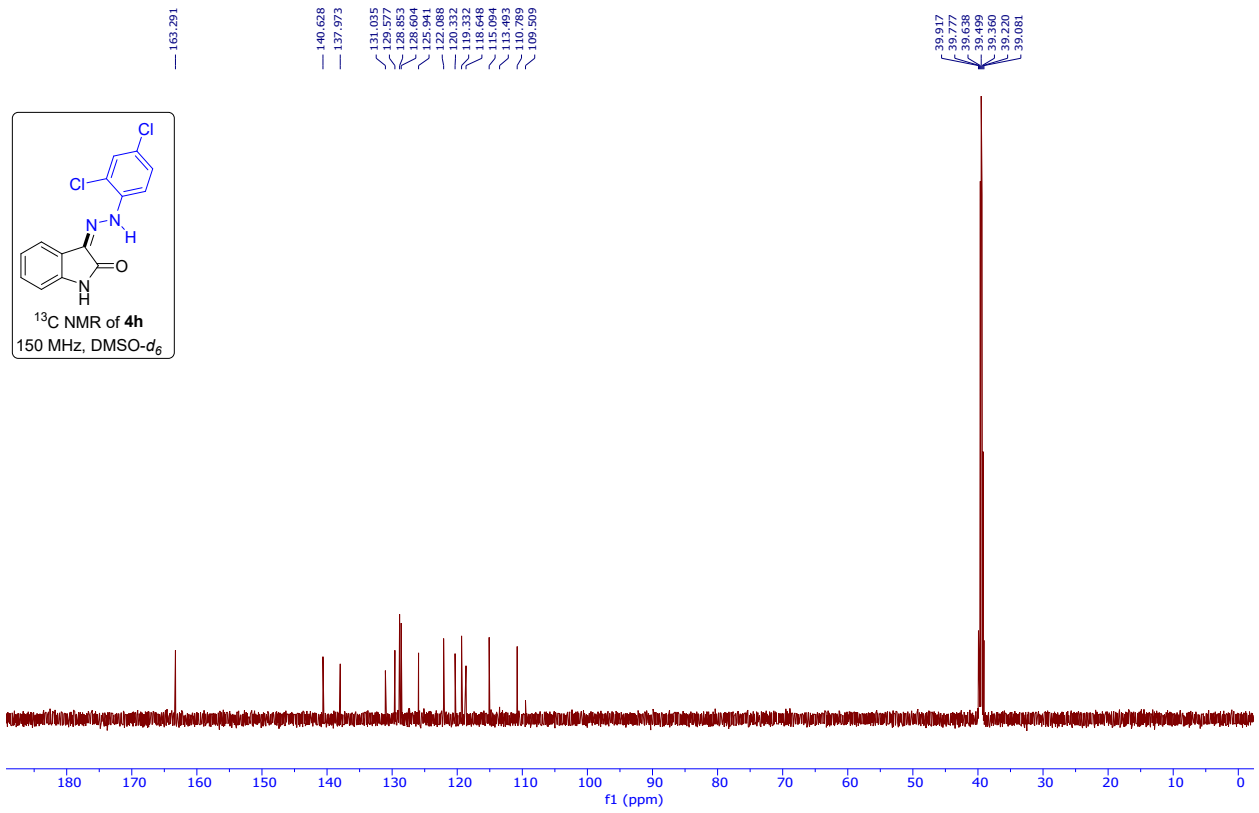
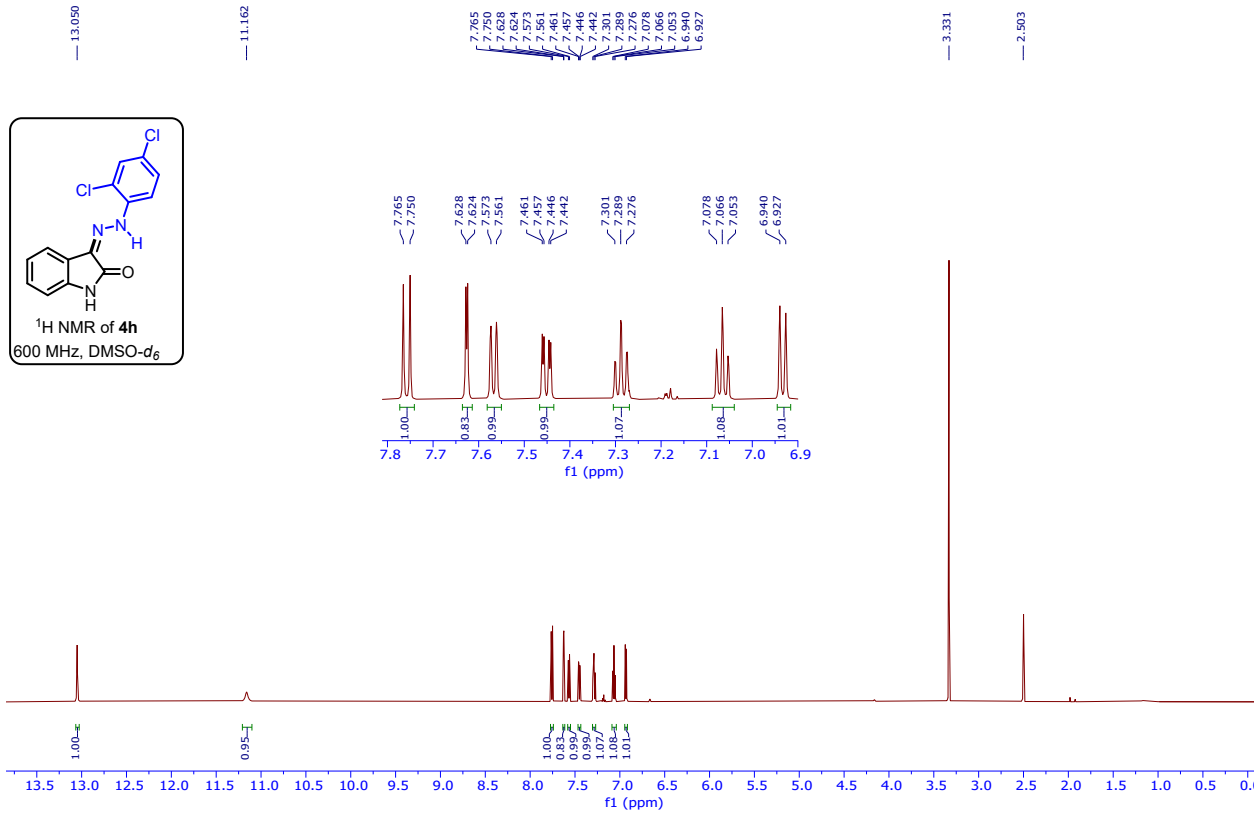


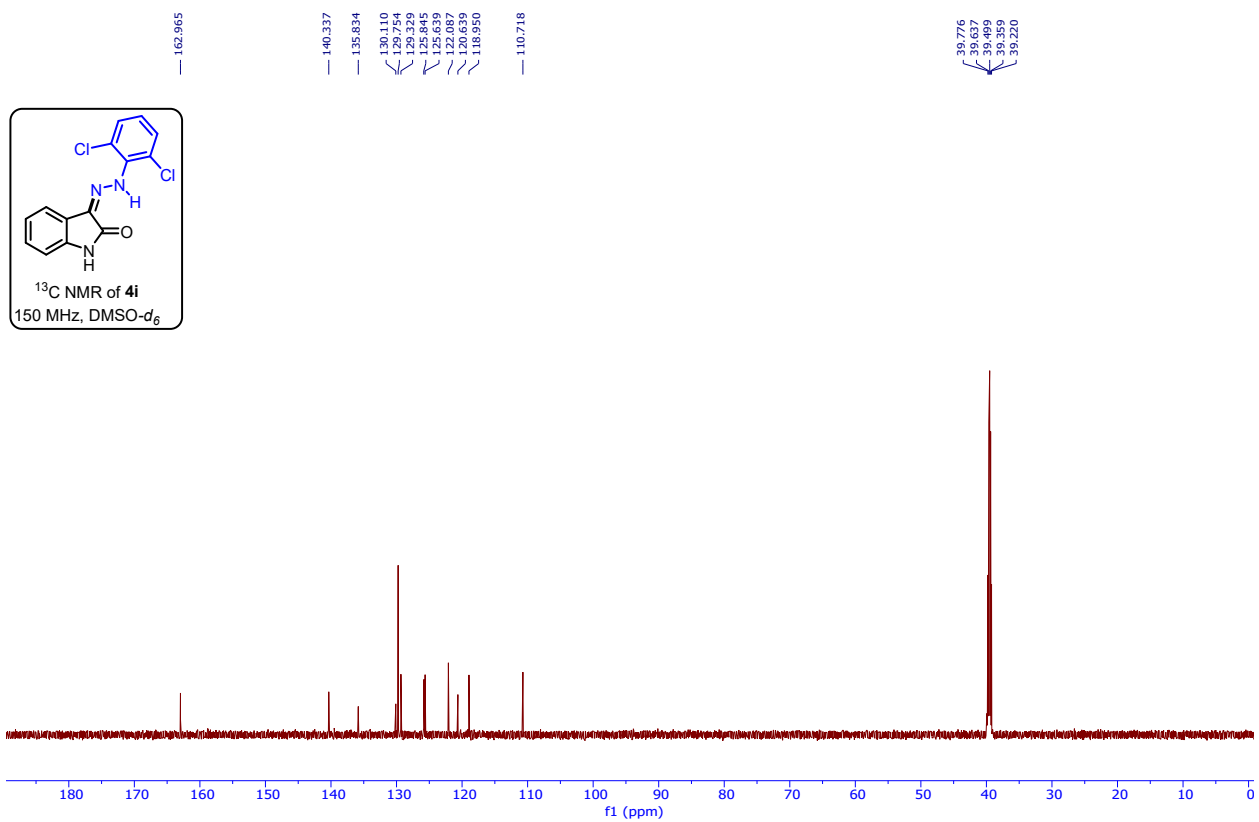
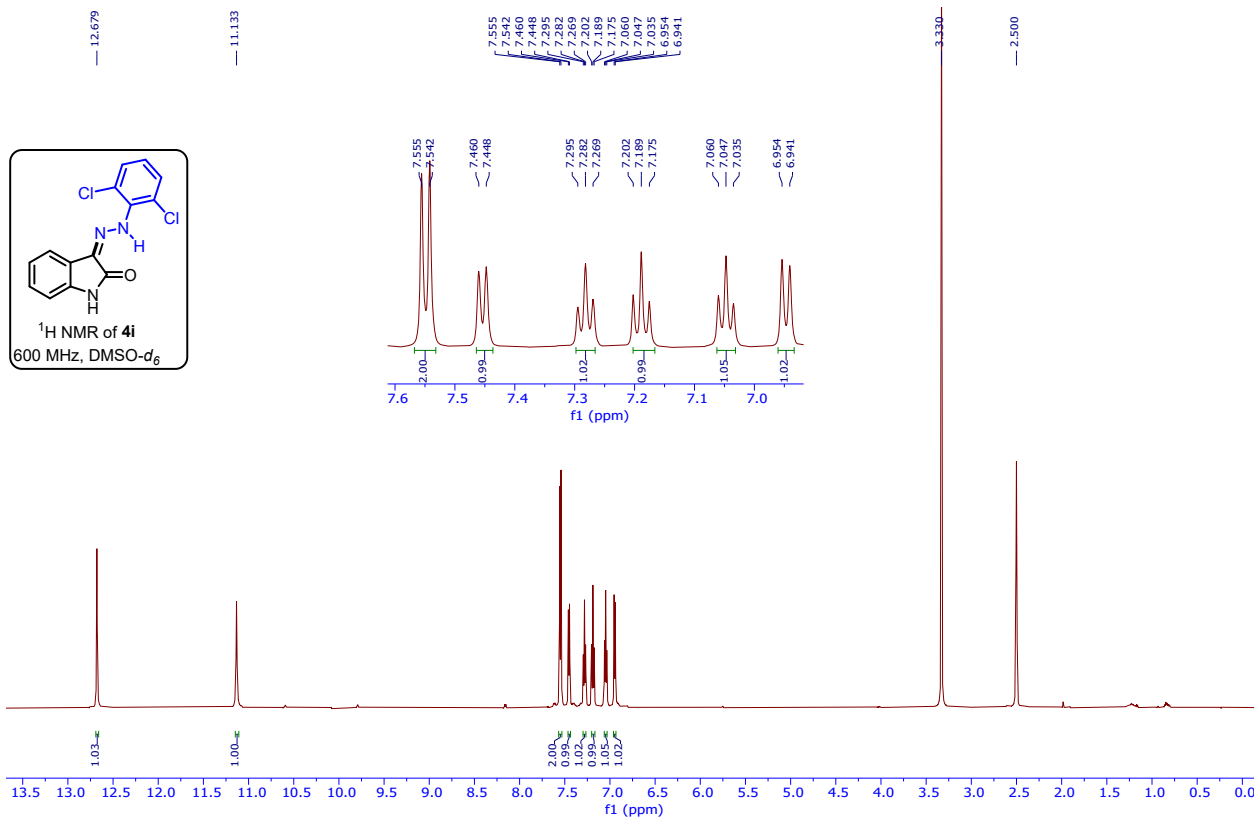


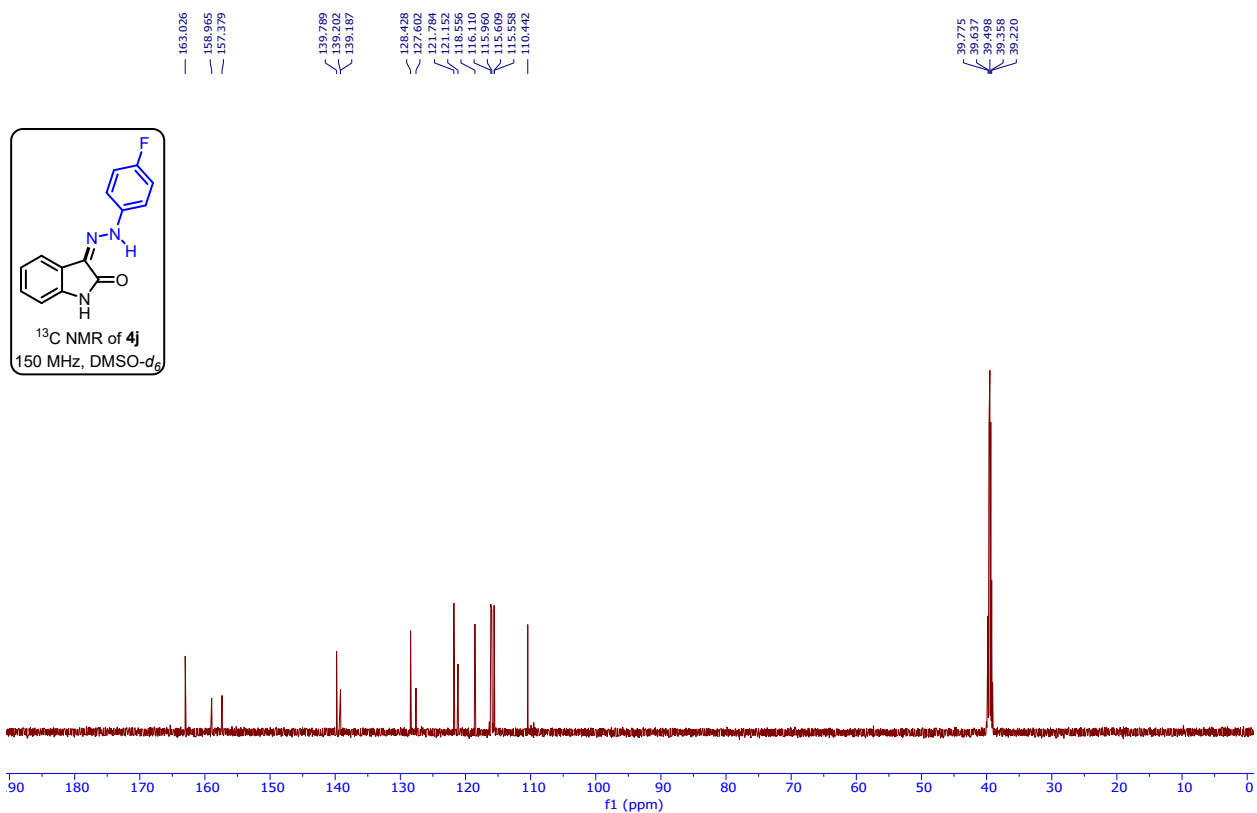
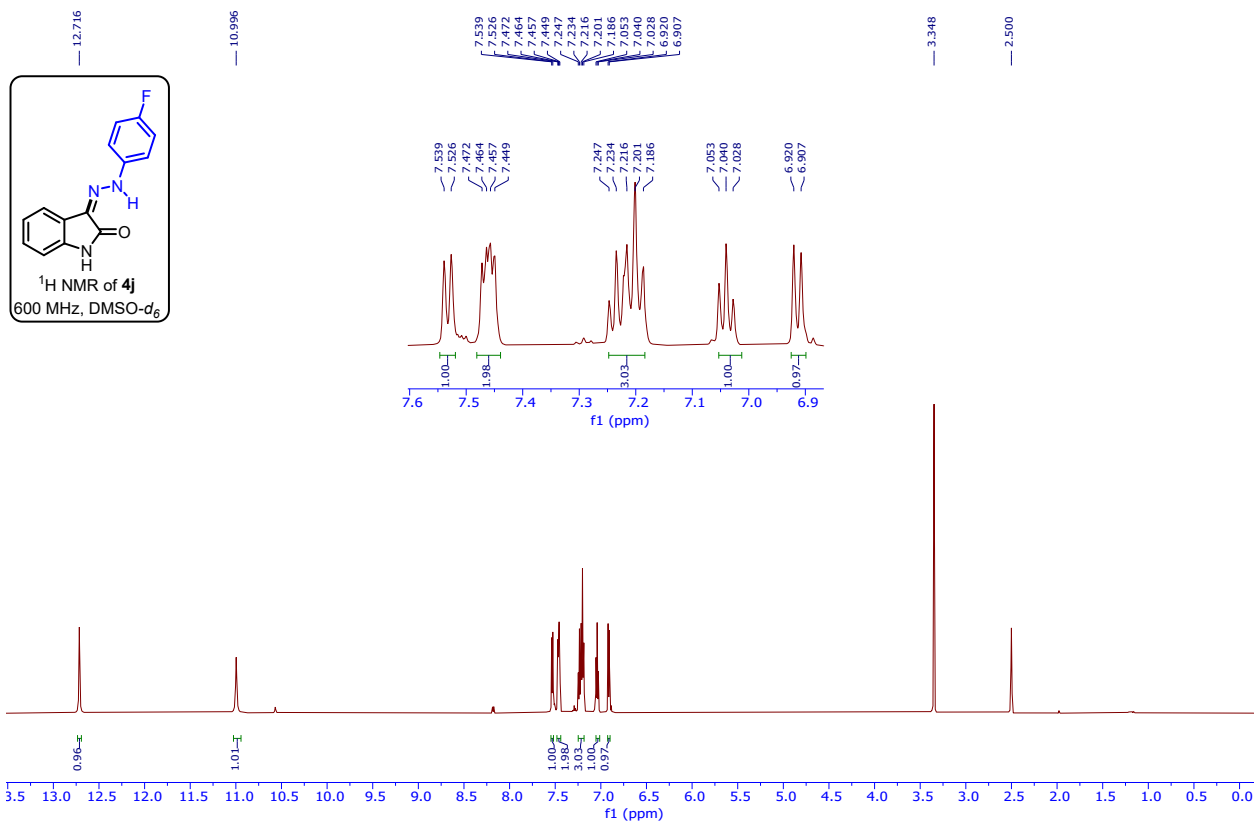


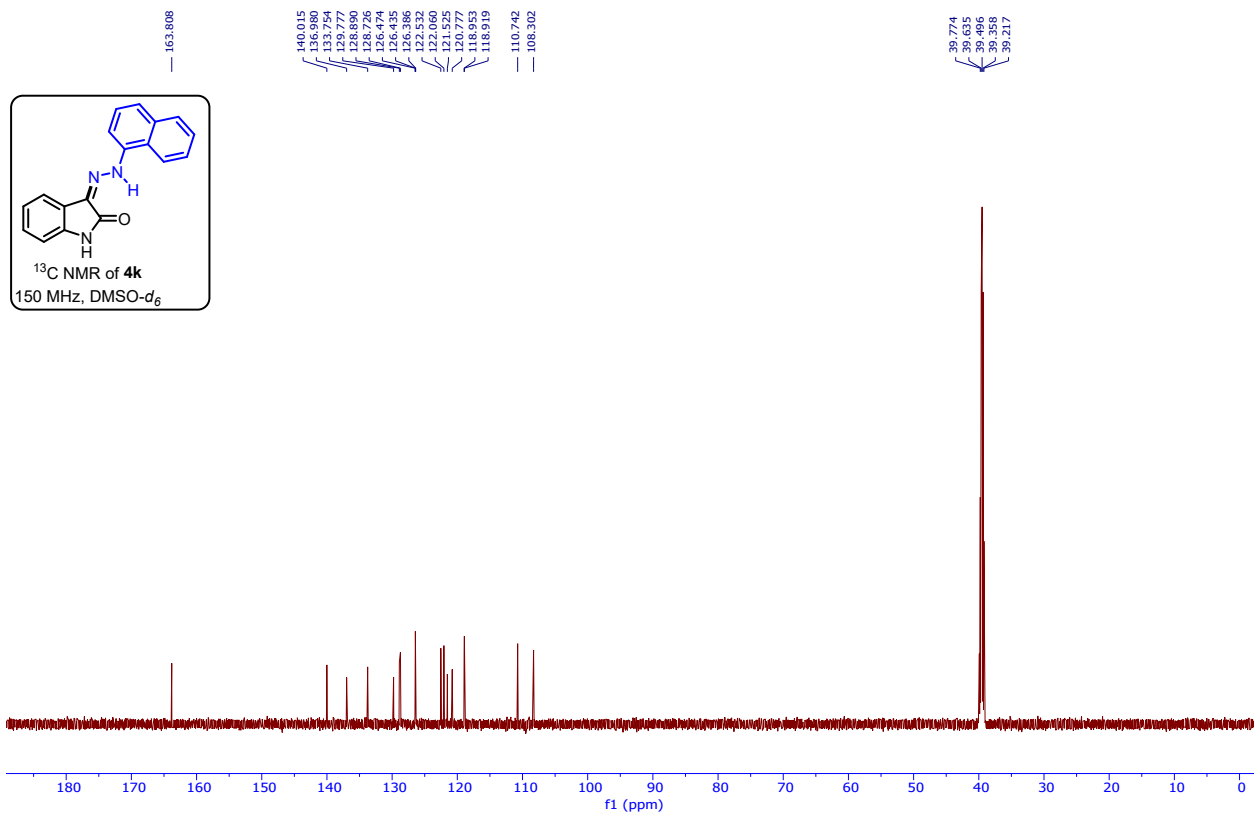
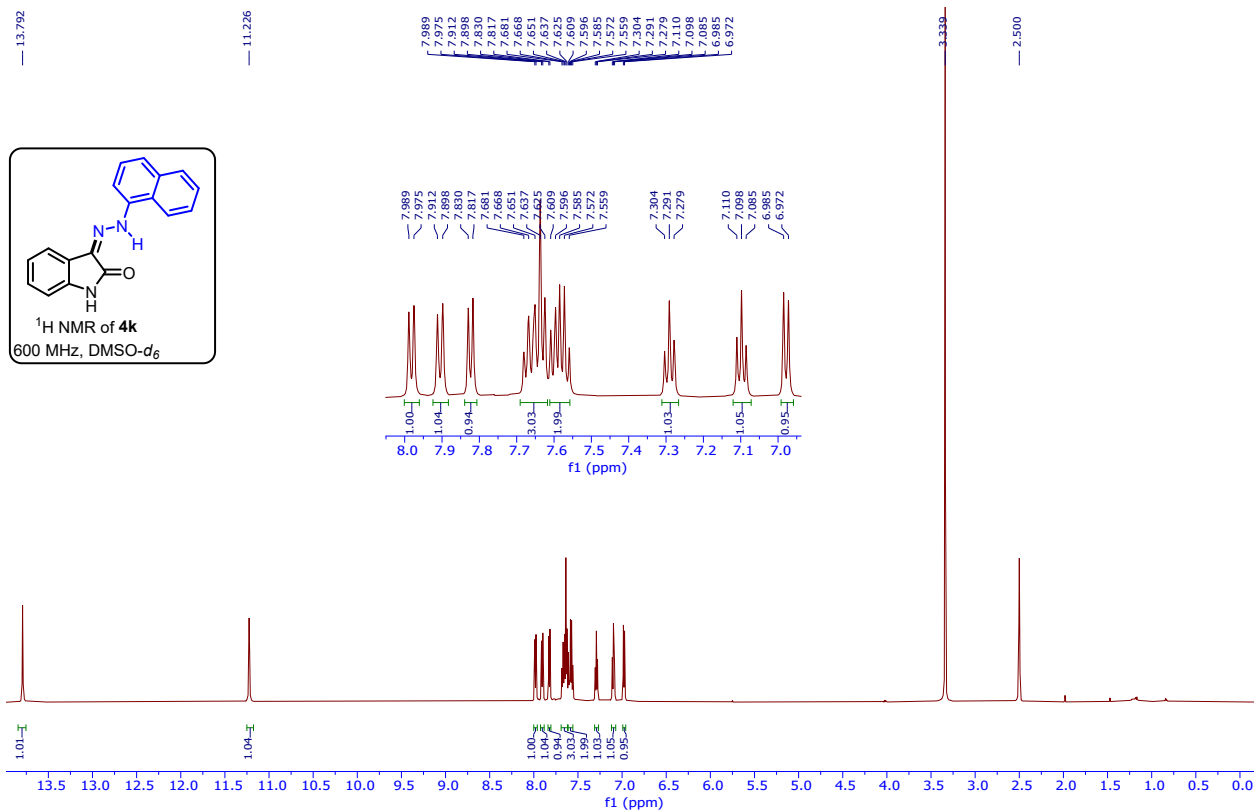


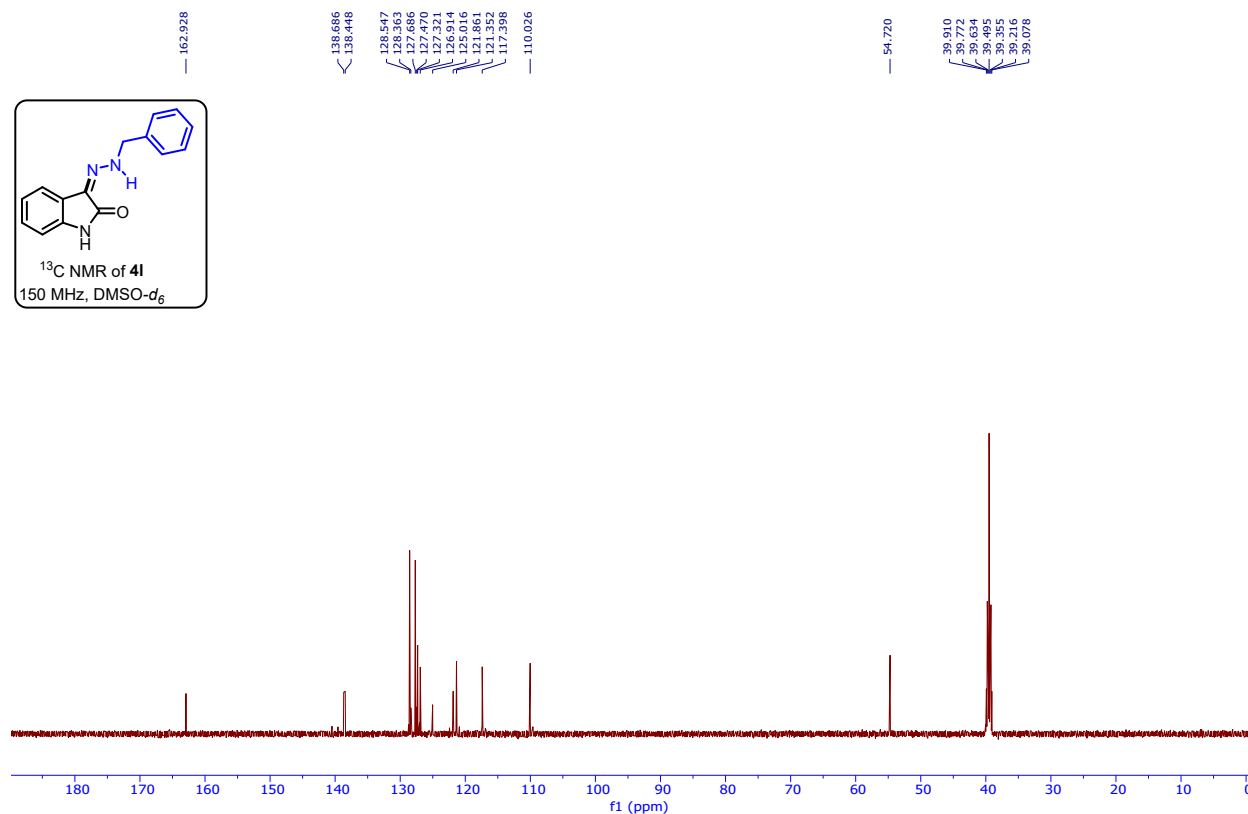
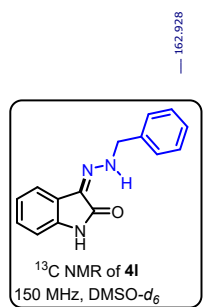
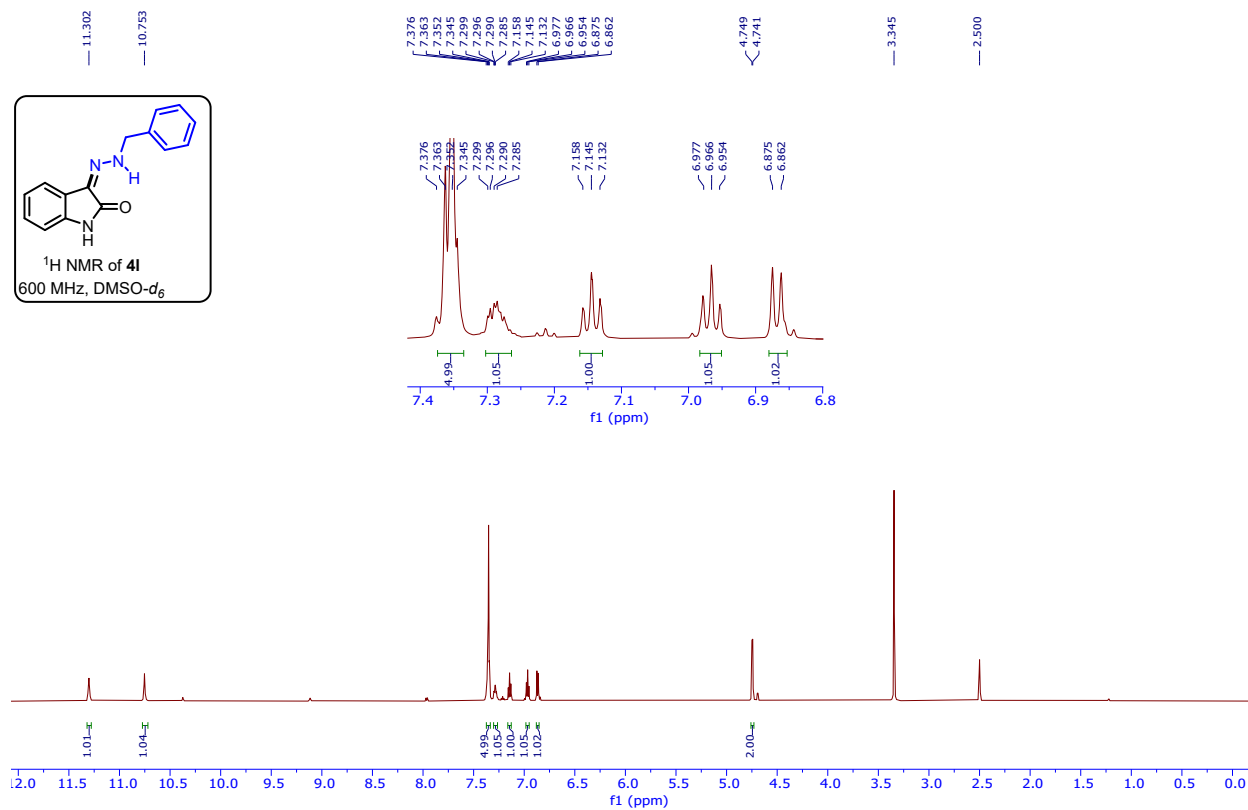
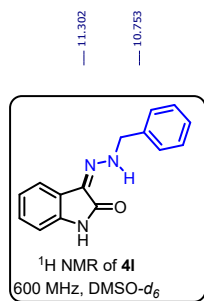












5. Chemosensor study

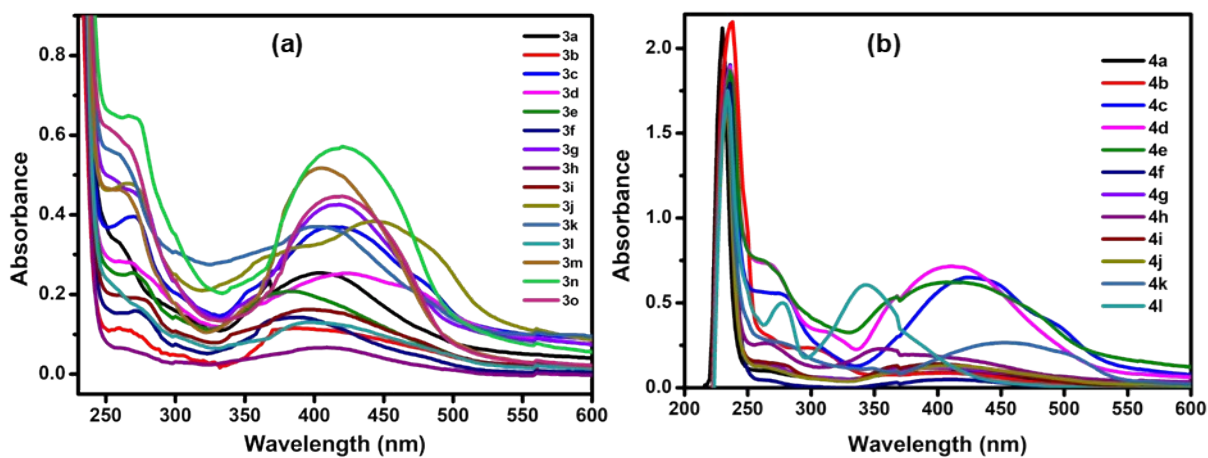


Fig. S1 UV-Visible spectral properties of (a) 3a-3o and (b) 4a-4l.

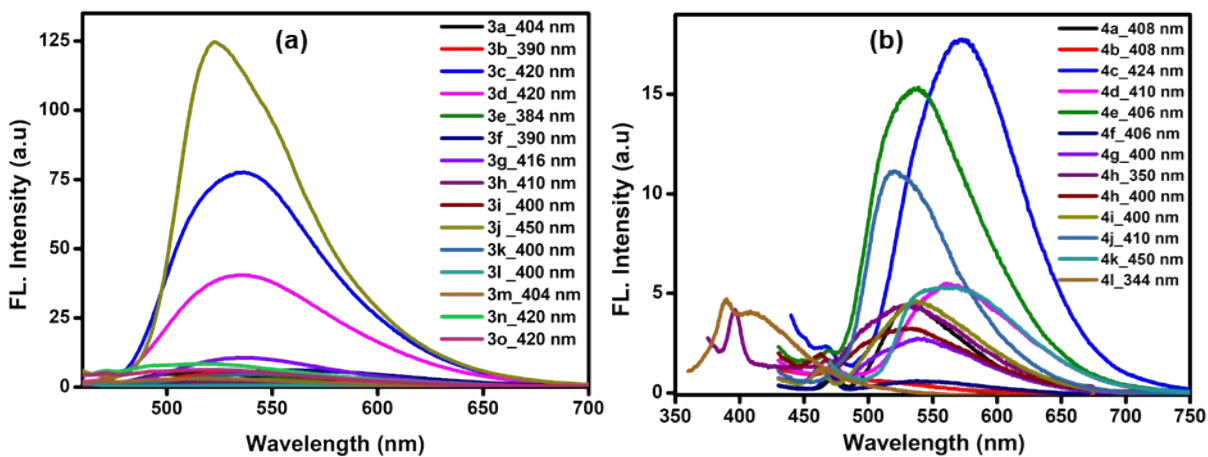


Fig. S2 Fluorescence spectral properties of (a) 3a-3o and (b) 4a-4l.

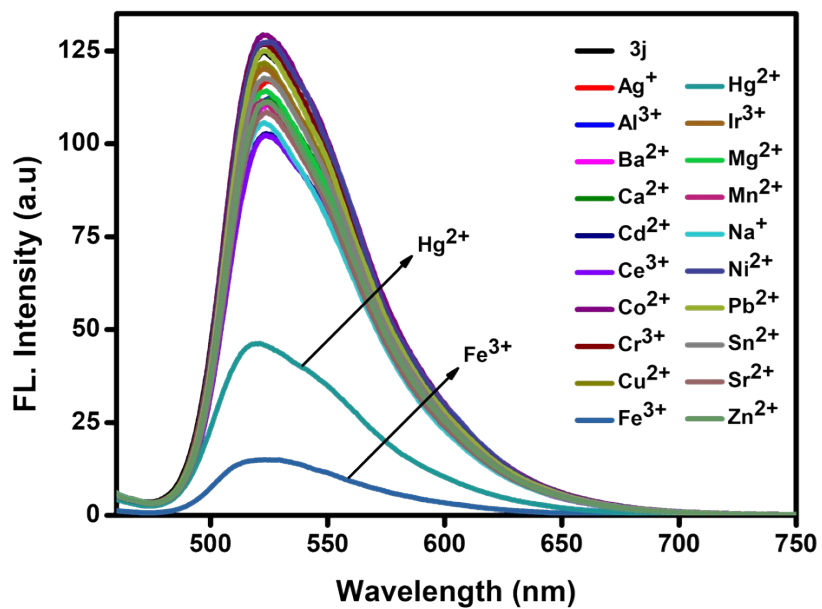


Fig. S3 Fluorescence spectra of **3j** with the addition of various metal ions (50 μ M).

6. References

- (a) S. Muthusamy, C. Gunanathan and M. Nethaji, *J. Org. Chem.*, 2004, **69**, 5631.
 (b) C. Marti and E. M. Carreira, *J. Am. Chem. Soc.*, 2005, **127**, 11505.