

Supporting Information
for
***Copper-Cascade Catalysis: Synthesis of
3-Functionalized Indoles***

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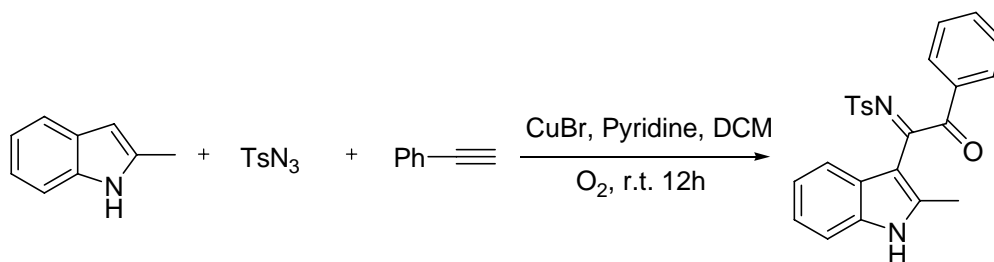
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General Considerations

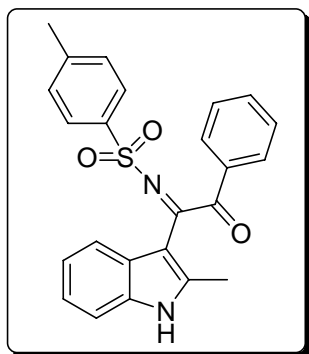
Infrared spectras were obtained on a FTIR spectrometer. ^1H NMR spectras were recorded on 500 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in CDCl_3 or 2.5 in $\text{DMSO-}d_6$. The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants were reported in Hertz (Hz). ^{13}C NMR were recorded on 125 MHz spectrometer, referred to the internal solvent signals (77.0 ppm for CDCl_3 or 40.0 ppm for $\text{DMSO-}d_6$). MS and HRMS were obtained using ESI ionization. Melting points were measured with micro melting point apparatus. Sulfonyl azides were prepared according the published methods.^{1,2}

General Procedure for the synthesis of 4



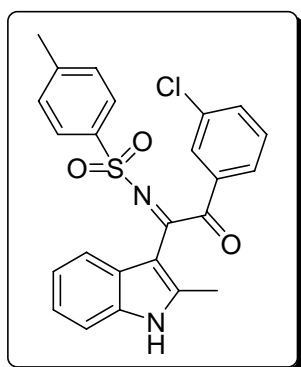
To a solution of 2-methyl indole (0.5 mmol), sulfonyl azide (1 mmol) and CuBr (0.05 mmol) in DCM (0.8 mL) in Schlenk tube was added the mixture of alkynes (1 mmol) and pyridine (1 mmol) in DCM (0.8 mL) slowly via syringe. The reaction mixture was stirred at room temperature for 12 h under oxygen. The solution was diluted by DCM (3 mL) and quenched by a mixture of 1N HCl and saturated NH_4Cl . The aqueous layer was extracted by DCM and the combined organic layer was washed with NH_4Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel to give corresponding products. All the compounds were further recrystallized from EA.

Characterization Data for 4



4-methyl-N-(1-(2-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4a)

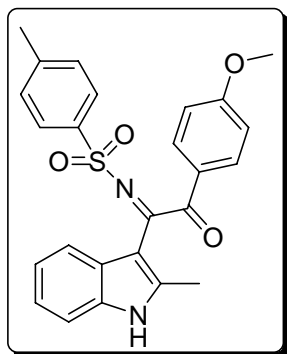
Yellow solid; mp. 227-228 °C; ¹H NMR (DMSO-*d*₆) δ 12.66 (s, 1H), 7.92-7.90 (m, 3H), 7.73-7.70 (m, 3H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.43-7.39 (m, 3H), 7.22-7.13 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 197.0, 170.7, 150.5, 143.8, 138.6, 136.1, 135.1, 135.0, 130.2, 129.8, 129.0, 127.1, 126.6, 124.0, 123.4, 121.7, 112.6, 107.9, 21.5, 15.9 ppm; IR (KBr) ν 3270, 3062, 2924, 1675, 1522, 1457, 1284, 1146, 1083, 817, 771, 673 cm⁻¹; MS (ESI) *m/z* 439.2 ([M+Na]⁺); HRMS (ESI) calcd for C₂₄H₂₀N₂O₃S ([M+Na]⁺), 439.1087; found, 439.1079.



N-(2-(3-chlorophenyl)-1-(2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4b)

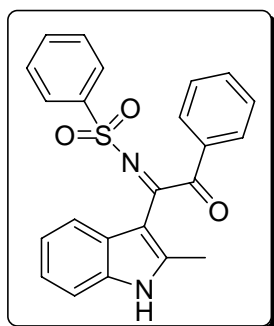
Yellow solid; mp. 211-212 °C; ¹H NMR (CDCl₃) δ 9.83 (s, 1H), 7.95-7.90 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 4H), 7.11-7.09 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 196.0, 170.0, 149.6, 143.8, 137.7, 136.4, 135.4, 135.3, 134.2, 130.4, 129.6, 128.3,

127.3, 127.1, 126.4, 123.9, 123.5, 122.0, 111.7, 108.6, 21.5, 16.0 ppm; IR (KBr) ν 3277, 3063, 2924, 1684, 1515, 1457, 1257, 1146, 1083, 822, 785, 752 cm^{-1} ; MS (ESI) m/z 450.9 ($[\text{M}+\text{Na}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{ClN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 473.0697; found, 473.0685.



***N*-(2-(4-methoxyphenyl)-1-(2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4c)**

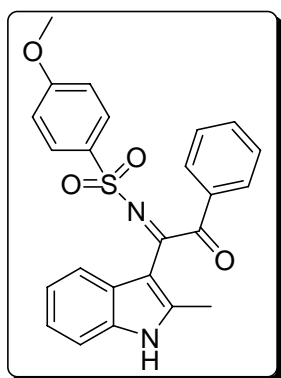
Yellow oil; ^1H NMR (CDCl_3) δ 9.93 (s, 1H), 8.01 (b, 1H), 7.85-7.82 (m, 4H), 7.24-7.18 (m, 3H), 7.09-7.05 (m, 2H), 6.71 (d, $J=8.5$ Hz, 2H), 3.67 (s, 3H), 2.36 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 195.1, 171.3, 164.4, 149.6, 143.4, 138.2, 135.4, 131.4, 129.4, 128.1, 127.1, 126.6, 123.6, 123.2, 122.1, 114.2, 111.7, 108.8, 55.4, 21.5, 15.6 ppm; IR (KBr) ν 3283, 3053, 2932, 2841, 1671, 1597, 1513, 1457, 1260, 1147, 1084, 820, 787, 673, 556 cm^{-1} ; MS (ESI) m/z 445.1 ($[\text{M}-\text{H}]^-$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$), 447.1373; found, 447.1367.



***N*-(1-(2-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4d)**

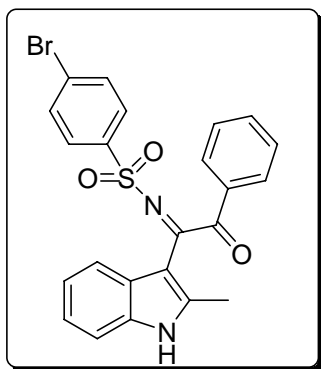
Yellow solid; mp. 119-120 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 9.89 (s, 1H), 7.97-7.88 (m, 5H),

7.51 (t, $J = 7.0$ Hz, 1H), 7.45-7.42 (m, 3H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.22-7.20 (m, 1H), 7.09-7.07 (m, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 196.9, 171.4, 149.8, 140.9, 135.4, 134.8, 134.4, 132.7, 128.9, 128.8, 127.0, 126.5, 123.8, 123.4, 122.1, 111.7, 108.8, 15.8 ppm; IR (KBr) ν 3273, 3058, 2973, 2927, 1679, 1525, 1458, 1285, 1257, 1236, 1147, 1082, 813, 774, 752, 687, 555 cm^{-1} ; MS (ESI) m/z 403.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 425.0930; found, 425.0915.



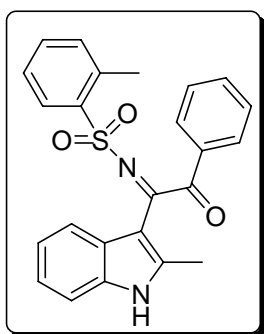
4-methoxy-*N*-(1-(2-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4e)

Yellow solid; mp. 242-243 °C; ^1H NMR ($\text{DMSO}-d_6$) δ 12.6 (s, 1H), 7.90-7.89 (m, 3H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.72 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.16-7.11 (m, 3H), 3.83 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ 197.1, 170.3, 163.1, 150.2, 136.1, 135.1, 135.0, 133.0, 129.8, 129.3, 129.0, 126.7, 124.0, 123.4, 121.6, 114.9, 112.5, 107.8, 56.2, 15.8 ppm; IR (KBr) ν 3257, 2928, 2840, 1675, 1595, 1458, 1287, 1260, 1144, 1085, 813, 770, 561 cm^{-1} ; MS (ESI) m/z 433.2 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ ($[\text{M}+\text{Na}]^+$), 455.1036; found, 455.1032.



4-bromo-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4f)

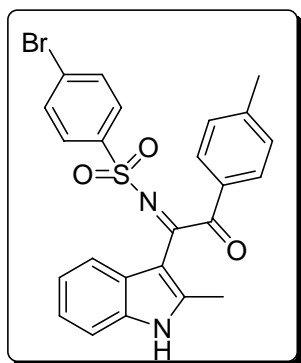
Yellow solid; mp. 227-228 °C; ^1H NMR (CDCl_3) δ 9.86 (s, 1H), 7.99 (b, 1H), 7.89 (d, $J = 6.0$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 2H), 7.22-7.20 (m, 1H), 7.12-7.10 (m, 2H), 2.21 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 196.8, 171.6, 150.2, 139.9, 135.4, 134.7, 134.5, 132.1, 129.0, 128.9, 128.6, 127.7, 126.4, 124.0, 123.6, 122.1, 111.7, 109.0, 15.9 ppm; IR (KBr) ν 3274, 3059, 2970, 1678, 1456, 1258, 1145, 1081, 814, 775, 752, 554 cm^{-1} ; MS (ESI) m/z 481.1 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 503.0035; found, 503.0024.



2-methyl-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4g)

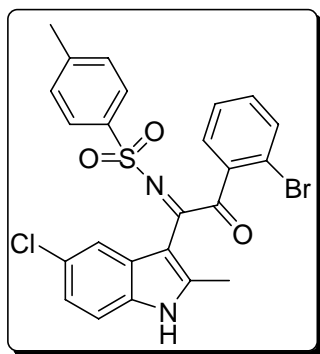
Pale yellow solid; mp. 204-205 °C; ^1H NMR ($\text{DMSO-}d_6$) δ 12.70 (s, 1H), 7.88 (m, 3H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.58-7.52 (m, 3H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.16-7.14 (m, 1H), 2.75 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO-}d_6$) δ 196.5, 171.3, 150.6, 139.8, 137.6,

136.1, 135.0, 134.9, 133.4, 132.8, 129.7, 129.1, 128.0, 126.7, 126.6, 124.1, 123.4, 121.4, 112.6, 108.1, 20.4, 15.9 ppm; IR (KBr) ν 3339, 3060, 2928, 1679, 1524, 1457, 1305, 1260, 1153, 1127, 1062, 813, 760, 690, 548 cm^{-1} ; MS (ESI) m/z 417.2 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 439.1087; found, 439.1078.



4-bromo-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-p-tolyloethylidene)benzenesulfonamide (4h)

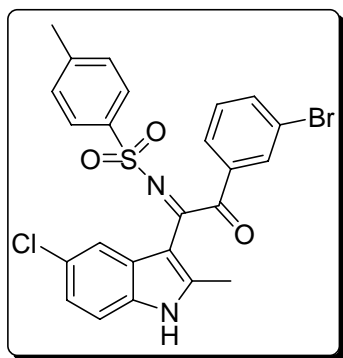
Yellow solid; mp. 216-217 °C; ^1H NMR (CDCl_3) δ 9.90 (s, 1H), 7.98 (b, 1H), 7.79-7.76 (m, 4H), 7.58-7.56 (m, 2H), 7.20-7.18 (m, 1H), 7.12-7.06 (m, 4H), 2.23 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 196.2, 171.8, 150.2, 145.9, 140.1, 135.4, 132.3, 132.1, 129.7, 129.0, 128.6, 127.6, 126.5, 123.9, 123.5, 122.1, 111.8, 109.0, 21.7, 15.8 ppm; IR (KBr) ν 3272, 3059, 2924, 1674, 1603, 1518, 1454, 1311, 1266, 1144, 1082, 1008, 805, 745, 632, 539 cm^{-1} ; MS (ESI) m/z 493.3 ($[\text{M}-\text{H}]^-$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 517.0192; found, 517.0180.



N-(2-(2-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide

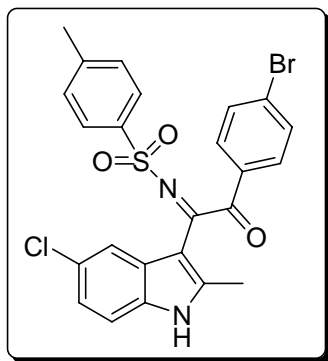
ethylbenzenesulfonamide (4i)

Yellow solid; mp. 244-245 °C; ^1H NMR (DMSO- d_6) δ 12.80 (s, 1H), 7.90-7.88 (m, 3H), 7.71 (d, $J=7.5$ Hz, 2H), 7.62-7.54 (m, 2H), 7.43 (t, $J = 8.0$ Hz, 3H), 7.24 (d, $J = 8.5$ Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 195.0, 169.9, 151.3, 144.1, 138.1, 136.3, 136.2, 135.9, 134.7, 134.5, 132.9, 130.2, 128.9, 128.0, 127.9, 127.2, 124.0, 122.1, 120.1, 114.1, 107.6, 21.5, 15.7 ppm; IR (KBr) ν 3292, 2923, 2853, 1581, 1524, 1459, 1287, 1146, 1084, 810, 773, 544 cm^{-1} ; MS (ESI) m/z 529.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{BrClN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 550.9802; found, 550.9798.



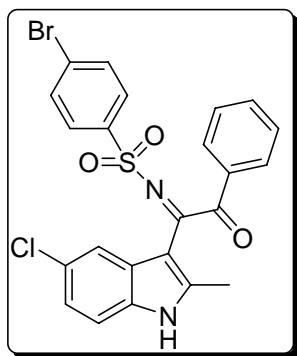
***N*-(2-(3-bromophenyl)-1-(5-chloro-2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4j)**

Yellow oil; ^1H NMR (CDCl_3) δ 10.03 (s, 1H), 8.03-7.99 (m, 2H), 7.79-7.78 (m, 3H), 7.59-7.57 (m, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.08-7.06 (m, 1H), 2.40 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 195.4, 169.7, 150.4, 144.1, 137.3, 137.2, 136.3, 133.7, 131.2, 130.6, 129.7, 129.3, 127.6, 127.1, 124.3, 123.5, 122.0, 112.7, 108.2, 21.6, 15.7 ppm; IR (KBr) ν 3279, 3063, 2923, 2852, 1689, 1523, 1456, 1350, 1288, 1229, 1148, 1084, 824, 787, 545 cm^{-1} ; MS (ESI) m/z 528.8 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{BrClN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 550.9802; found, 550.9798.



***N*-(2-(4-bromophenyl)-1-(5-chloro-2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4k)**

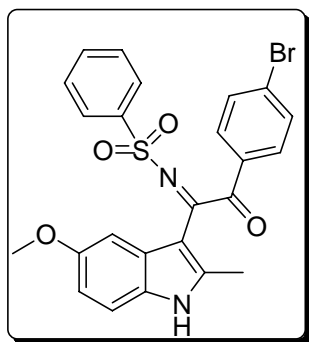
Yellow oil; ^1H NMR (CDCl_3) δ 9.84 (s, 1H), 8.02 (br, 1H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.5$ Hz, 1H), 7.09 (m, 1H), 2.41 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 195.7, 170.0, 149.8, 144.1, 137.3, 133.6, 133.5, 132.4, 130.2, 130.1, 129.7, 129.3, 127.6, 127.2, 124.3, 122.0, 112.5, 108.2, 21.6, 15.7 ppm; IR (KBr) ν 3275, 2982, 2926, 1732, 1713, 1684, 1584, 1457, 1288, 1244, 1149, 1084, 807, 545 cm^{-1} ; MS (ESI) m/z 528.9 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{BrClN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 550.9802; found, 550.9798.



4-bromo-*N*-(1-(5-chloro-2-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4l)

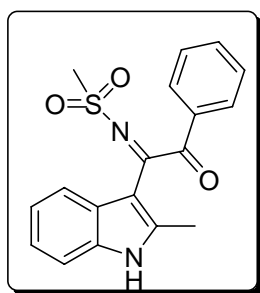
Orange solid; mp. 220-221 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 9.65 (s, 1H), 8.05 (b, 1H), 7.87 (d, $J = 7.5$ Hz, 2H), 7.80-7.78 (m, 2H), 7.63-7.61 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.16-7.09 (m, 2H), 2.20 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 196.3, 171.4, 150.3, 139.6, 134.7, 134.5, 133.6, 132.3, 129.5, 129.1, 128.9, 128.8, 128.1, 127.6, 124.4, 122.1, 112.5, 108.6, 15.7 ppm; IR (KBr) ν 3282, 3093, 2925, 1677, 1577,

1454, 1350, 1307, 1232, 1147, 1083, 815, 778, 740 cm^{-1} ; MS (ESI) m/z 513.5 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{BrClN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 536.9646; found, 536.9653.



***N*-(2-(4-bromophenyl)-1-(5-methoxy-2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)benzenesulfonamide (4m)**

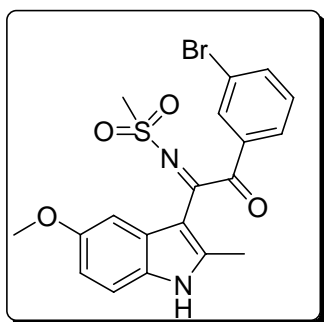
Yellow solid; mp. 165-166 °C; ^1H NMR (CDCl_3) δ 9.65 (s, 1H), 7.94 (d, $J=7.0$ Hz, 2H), 7.79 (d, $J=8.0$ Hz, 2H), 7.54-7.45 (m, 6H), 7.09 (d, $J=8.5$ Hz, 1H), 6.74-6.72 (m, 1H), 3.65 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 195.7, 170.2, 156.7, 149.3, 141.1, 133.6, 132.8, 132.4, 130.3, 129.9, 129.9, 128.9, 127.5, 127.0, 113.4, 112.3, 108.8, 104.8, 55.4, 15.8 cm^{-1} ; IR (KBr) ν 3378, 2925, 1680, 1586, 1461, 1303, 1281, 1149, 1084, 815, 554 cm^{-1} ; MS (ESI) m/z 511.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{O}_4\text{S}$ ($[\text{M}+\text{Na}]^+$), 533.0141; found, 533.0127.



***N*-(1-(2-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)methanesulfonamide (4n)**

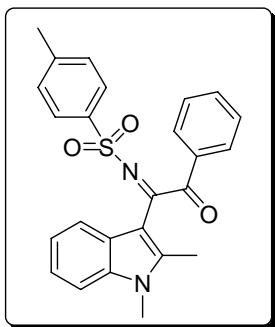
Yellow solid; mp. 191-192 °C; ^1H NMR (CDCl_3) δ 9.94 (s, 1H), 8.10 (b, 1H), 7.87 (d, $J=8.0$ Hz, 2H), 7.42 (t, $J=7.5$ Hz, 1H), 7.29-7.26 (m, 3H), 7.15-7.14 (m, 2H), 3.17

(s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 196.5, 172.5, 149.8, 135.5, 134.7, 134.5, 128.9, 126.5, 123.9, 123.4, 122.1, 111.8, 108.6, 42.7, 15.6 ppm; IR (KBr) ν 3361, 3057, 2975, 1675, 1527, 1458, 1291, 1127, 966, 817, 749, 517 cm^{-1} ; MS (ESI) m/z 339.0 ($[\text{M}-\text{H}]^-$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 363.0774; found, 363.0775.



***N*-(2-(3-bromophenyl)-1-(5-methoxy-2-methyl-1*H*-indol-3-yl)-2-oxoethylidene)methanesulfonamide (4o)**

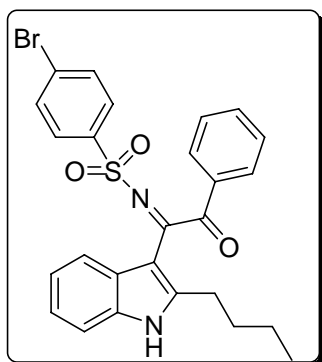
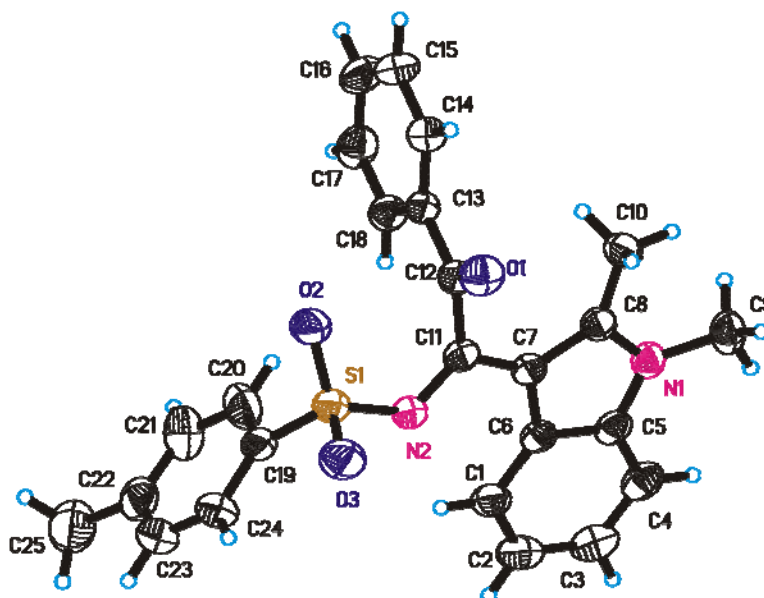
Orange solid; mp. 213-214 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 12.57 (s, 1H), 8.02 (s, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 7.5$ Hz, 1H), 7.55-7.34 (m, 3H), 6.88-6.86 (m, 1H), 3.73 (s, 3H), 3.18 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ 195.6, 170.1, 156.5, 150.1, 137.6, 136.9, 132.1, 130.7, 130.6, 128.6, 127.5, 123.0, 113.3, 112.5, 107.3, 105.0, 55.7, 42.8, 16.0 ppm; IR (KBr) ν 3308, 2928, 1675, 1592, 1468, 1282, 1121, 965, 832, 543 cm^{-1} ; MS (ESI) m/z 449.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2\text{O}_4\text{S}$ ($[\text{M}+\text{Na}]^+$), 470.9985; found, 470.9973.



***N*-(1-(1,2-dimethyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)-4-methylbenzenesul**

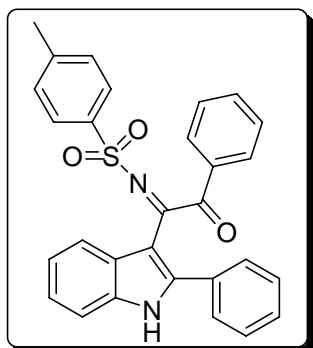
fonamide (4p)

Pale yellow solid; mp. 225-226 °C; ^1H NMR (CDCl_3) δ 8.00 (d, $J=7.0$ Hz, 2H), 7.96-7.95 (b, 1H), 7.83 (d, $J=8.5$ Hz, 2H), 7.57 (t, $J=7.5$ Hz, 1H), 7.45 (t, $J=8.0$ Hz, 2H), 7.26-7.12 (m, 5H), 3.59 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 197.3, 170.5, 148.9, 143.2, 138.2, 137.3, 135.2, 134.1, 129.4, 129.0, 128.9, 127.4, 125.9, 123.5, 123.4, 122.1, 109.7, 108.5, 30.2, 21.5, 13.6 cm^{-1} ; IR (KBr) ν 3449, 3060, 2925, 1679, 1504, 1469, 1410, 1302, 1150, 1082, 819, 739, 673, 561, 540 cm^{-1} ; MS (ESI) m/z 430.9 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 453.1243; found, 453.1233.



4-bromo-*N*-(1-(2-butyl-1*H*-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4q)

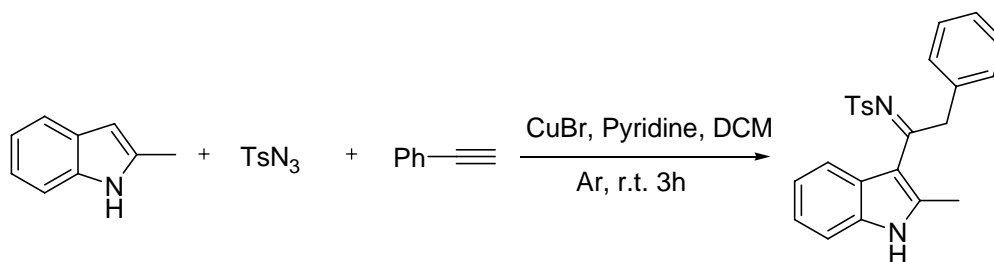
Orange oil; ^1H NMR (DMSO- d_6) δ 12.73 (s, 1H), 7.91 (d, J =7.0 Hz, 2H), 7.85-7.83 (m, 2H), 7.75-7.58 (m, 6H), 7.42 (d, J =7.5 Hz, 1H), 7.19 (t, J =7.0 Hz, 1H), 7.10-7.09 (m, 1H), 2.81 (br, 2H), 1.45-1.30 (m, 2H), 1.13 (br, 2H), 0.73 (t, J =7.5Hz, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 196.6, 171.0, 155.4, 140.7, 136.4, 135.2, 134.9, 132.9, 129.8, 129.1, 129.0, 127.3, 126.3, 124.0, 123.4, 121.2, 122.9, 107.2, 31.2, 29.0, 22.5, 13.9 cm^{-1} ; IR (KBr) ν 3283, 3089, 2957, 2923, 2852, 1678, 1517, 1451, 1148, 1082, 813, 773, 546 cm^{-1} ; MS (ESI) m/z 522.8 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 545.0505; found, 545.0509.



4-methyl-N-(2-oxo-2-phenyl-1-(2-phenyl-1H-indol-3-yl)ethylidene)benzenesulfonamide (4r)

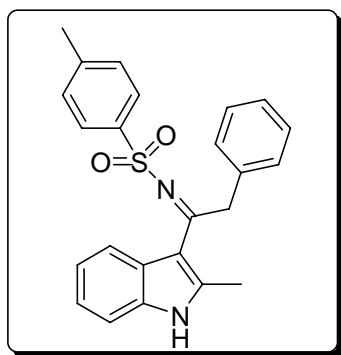
Pale yellow solid; mp. 245-246 $^{\circ}\text{C}$; ^1H NMR (DMSO- d_6) δ 12.79 (s, 1H), 8.20 (d, J =7.5 Hz, 1H), 7.70 (d, J =8.5 Hz, 2H), 7.56-7.54 (m, 1H), 7.46-7.42 (m, 3H), 7.35-7.26 (m, 7H), 7.13 (t, J =7.5 Hz, 2H), 7.00 (d, J =7.5 Hz, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 194.8, 171.3, 151.4, 143.8, 138.3, 136.5, 135.0, 134.1, 130.9, 130.1, 129.8, 128.8, 128.5, 127.6, 127.2, 126.6, 124.7, 123.8, 122.7, 112.8, 108.9, 21.4 ppm; IR (KBr) ν 3392, 3263, 3062, 2924, 1677, 1516, 1449, 1432, 1153, 1084, 757, 667, 552, 534 cm^{-1} ; MS (ESI) m/z 478.9 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 501.1243; found, 501.1255.

General Procedure for the synthesis of 5 and 6



To a solution of 2-methyl indole (0.5 mmol), sulfonyl azide (1 mmol) and CuBr (0.05 mmol) in DCM (0.8 mL) in Schlenk tube was added the mixture of alkynes (1 mmol) and pyridine (1 mmol) in DCM (0.8 mL) slowly via syringe. The reaction mixture was stirred at room temperature for 3 h under argon. The solution was diluted by DCM (3 mL) and quenched by a mixture of 1N HCl and saturated NH₄Cl under argon atmosphere. The aqueous layer was extracted by DCM and the combined organic layer was washed with saturated NH₄Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel to give corresponding products. All the compounds were further recrystallized from EA.

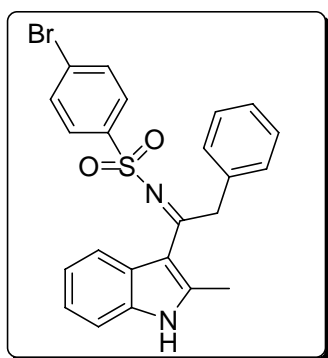
Characterization Data for 5 and 6



4-methyl-N-(1-(2-methyl-1H-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5a)

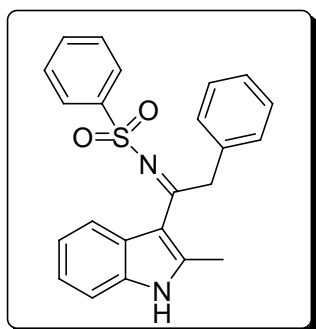
Pale yellow solid; mp. 208-209 °C; ¹H NMR (DMSO-*d*₆) δ 12.21 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz,

1H), 7.25-7.20 (m, 4H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 4.84 (s, 2H), 2.50 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 176.7, 147.9, 143.0, 140.5, 136.5, 135.7, 129.9, 128.9, 128.5, 127.0, 126.7, 126.6, 123.0, 122.5, 121.8, 112.3, 112.1, 40.9, 21.5, 16.5 ppm; IR (KBr) ν 3278, 3056, 2921, 1518, 1461, 1250, 1136, 1076, 1003, 778, 742, 543 cm^{-1} ; MS (ESI) m/z 403.2 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 425.1294; found, 425.1285.



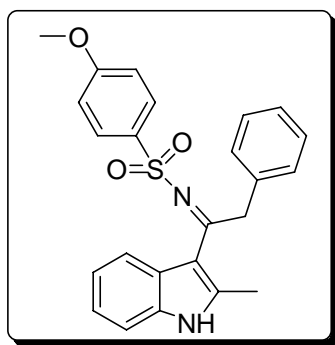
4-bromo-*N*-(1-(2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5b)

Pale yellow solid; mp. 198-199 °C; ^1H NMR (DMSO- d_6) δ 12.31 (s, 1H), 7.90 (m, 3H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.25 (t, $J = 7.0$ Hz, 2H), 7.21-7.13 (m, 4H), 7.06 (t, $J = 7.5$ Hz, 1H), 4.84 (s, 2H), 2.51 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 177.2, 148.7, 142.6, 136.3, 135.8, 132.6, 128.9, 128.8, 128.5, 126.9, 126.7, 126.6, 123.2, 122.8, 121.8, 112.4, 112.2, 41.1, 16.6 ppm; IR (KBr) ν 3297, 3060, 3027, 1578, 1460, 1270, 1141, 1082, 1009, 790, 744, 539 cm^{-1} ; MS (ESI) m/z 466.9 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{BrN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 489.0243; found, 489.0237.



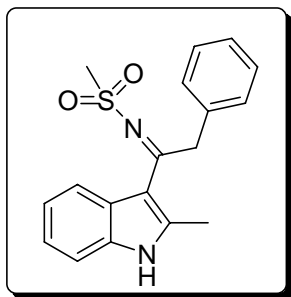
***N*-(1-(2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5c)**

Pale yellow solid; mp. 175-176 °C; ¹H NMR (DMSO-*d*₆) δ 12.24 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.67-7.60 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 4H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 4.86 (s, 2H), 2.50 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 176.9, 148.2, 143.3, 136.5, 135.7, 132.8, 129.6, 128.9, 128.6, 127.0, 126.7, 126.6, 123.1, 122.6, 121.8, 112.4, 112.1, 41.1, 16.5 ppm; IR (KBr) ν 3318, 3059, 1526, 1486, 1459, 1282, 1257, 1141, 1081, 789, 750, 585, 529 cm⁻¹; MS (ESI) *m/z* 389.0 ([*M*+*H*]⁺); HRMS (ESI) calcd for C₂₃H₂₀N₂O₂S ([*M*+*Na*]⁺), 411.1138; found, 411.1131.



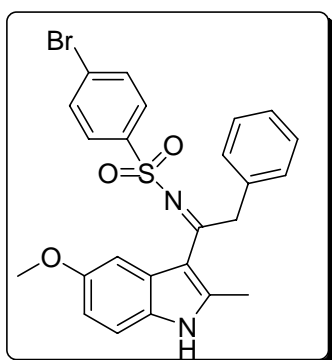
4-methoxy-*N*-(1-(2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5d)

Pale yellow solid; mp. 201-202 °C; ¹H NMR (DMSO-*d*₆) δ 12.19 (s, 1H), 7.92-7.87 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.21-7.10 (m, 6H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.83 (s, 2H), 3.84 (s, 3H), 2.50 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 176.4, 162.5, 137.7, 136.5, 135.7, 135.2, 128.9, 128.5, 127.0, 126.7, 123.0, 122.5, 121.9, 114.7, 112.3, 112.0, 56.1, 40.7, 16.4 ppm; IR (KBr) ν 3281, 3063, 2967, 1596, 1582, 1515, 1498, 1460, 1258, 1139, 1082, 809, 778, 548 cm⁻¹; MS (ESI) *m/z* 419.0 ([*M*+*H*]⁺); HRMS (ESI) calcd for C₂₄H₂₂N₂O₃S ([*M*+*Na*]⁺), 441.1243; found, 441.1232.



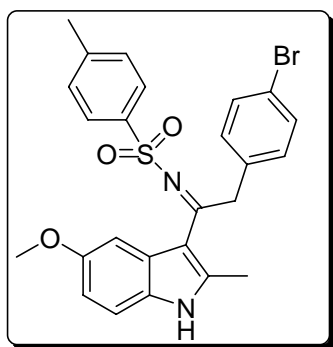
***N*-(1-(2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)methanesulfonamide (5e)**

Pale yellow solid; mp. 205-206 °C; ¹H NMR (DMSO-*d*₆) δ 12.14 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.37-7.36 (m, 1H), 7.26-7.22 (m, 4H), 7.18-7.13 (m, 3H), 4.76 (s, 2H), 3.25 (s, 3H), 2.58 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 176.5, 147.2, 136.5, 135.7, 128.8, 128.7, 127.0, 126.7, 122.9, 122.4, 122.0, 112.0, 111.8, 43.9, 41.3, 16.5 ppm; IR (KBr) ν 3263, 3029, 2936, 1541, 1520, 1462, 1269, 1104, 810, 743, 501 cm⁻¹; MS (ESI) *m/z* 327.1 ([*M*+*H*]⁺); HRMS (ESI) calcd for C₁₈H₁₈N₂O₂S ([*M*+*Na*]⁺), 349.0981; found, 349.0973.



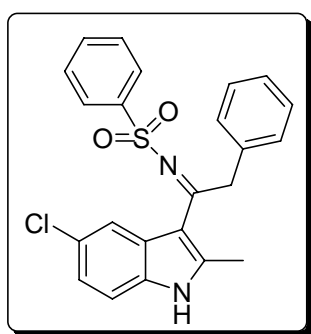
4-bromo-*N*-(1-(5-methoxy-2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5f)

Pale yellow solid; mp. 215-216 °C; ¹H NMR (DMSO-*d*₆) δ 12.18 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.32-7.28 (m, 3H), 7.24-7.20 (m, 4H), 6.74 (d, *J* = 7.5 Hz, 1H), 4.82 (s, 2H), 3.42 (s, 3H), 2.47 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 176.5, 156.0, 148.6, 142.9, 136.3, 132.6, 130.3, 129.0, 128.8, 128.5, 127.9, 126.8, 126.5, 112.8, 112.4, 104.4, 55.1, 41.3, 16.5 ppm; IR (KBr) ν 3281, 3088, 2951, 1534, 1472, 1303, 1280, 1138, 1080, 827, 773, 539 cm⁻¹; MS (ESI) *m/z* 495.2 ([*M*-*H*]); HRMS (ESI) calcd for C₂₄H₂₁BrN₂O₃S ([*M*+*Na*]⁺), 519.0348; found, 519.0340.



***N*-(2-(4-bromophenyl)-1-(5-methoxy-2-methyl-1*H*-indol-3-yl)ethylidene)-4-methylbenzenesulfonamide (5g)**

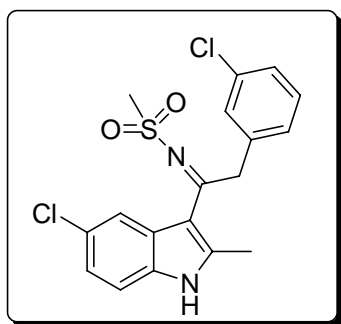
Pale yellow solid; mp. 204-205 °C; ^1H NMR (DMSO- d_6) δ 12.14 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 1.5 Hz, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.74 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 4.77 (s, 2H), 3.41 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 175.3, 156.0, 148.1, 143.0, 140.7, 136.0, 131.8, 130.7, 130.3, 129.9, 127.9, 126.7, 119.9, 112.7, 112.7, 112.1, 104.4, 55.1, 40.5, 21.4, 16.5 ppm; IR (KBr) ν 3290, 2957, 1592, 1513, 1473, 1279, 1142, 1075, 828, 768, 542 cm^{-1} ; MS (ESI) m/z 509.3 ($[\text{M}-\text{H}]^-$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 533.0505; found, 533.0489.



***N*-(1-(5-chloro-2-methyl-1*H*-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5h)**

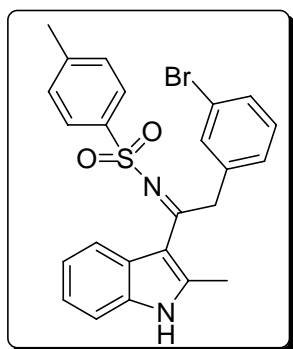
Pale yellow solid; mp. 177-178 °C; ^1H NMR (DMSO- d_6) δ 12.36 (s, 1H), 7.99 (d, J = 7.0 Hz, 2H), 7.89 (d, J = 2.0 Hz, 1H), 7.71-7.63 (m, 3H), 7.34 (d, J = 9.0 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.23-7.18 (m, 3H), 7.15 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H),

4.83 (s, 2H), 2.48 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 176.5, 149.2, 143.1, 136.2, 134.2, 133.0, 129.6, 129.0, 128.5, 128.3, 127.3, 126.8, 126.6, 123.1, 121.6, 113.5, 111.9, 41.1, 16.2 ppm; IR (KBr) ν 3309, 3063, 3027, 1578, 1521, 1458, 1356, 1284, 1143, 1082, 793, 751, 727, 589, 533 cm^{-1} ; MS (ESI) m/z 422.7 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 445.0748; found, 445.0746.



***N*-(1-(5-chloro-2-methyl-1*H*-indol-3-yl)-2-(3-chlorophenyl)ethylidene)methanesulfonamide (5i)**

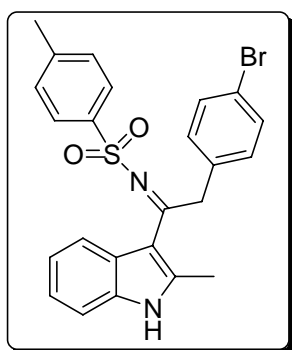
Pale yellow solid; mp. 188-189 °C; ^1H NMR (DMSO- d_6) δ 12.36 (s, 1H), 8.08 (s, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.32-7.24 (m, 3H), 7.20-7.16 (m, 2H), 4.75 (s, 2H), 3.28 (s, 3H), 2.57 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 175.5, 148.6, 138.8, 134.2, 133.5, 130.8, 128.4, 128.1, 127.3, 127.2, 126.9, 123.0, 121.3, 113.6, 111.2, 43.8, 40.7, 16.5 ppm; IR (KBr) ν 3246, 1531, 1476, 1462, 1440, 1271, 1115, 1004, 959, 815, 497 cm^{-1} ; MS (ESI) m/z 417.6 ($[\text{M}+\text{Na}]^+$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 417.0202; found, 417.0209.



***N*-(2-(3-bromophenyl)-1-(2-methyl-1*H*-indol-3-yl)ethylidene)-4-methylbenzenesulfonamide**

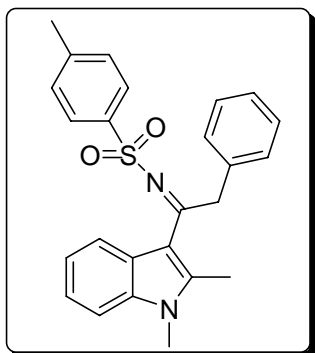
fonamide (5j)

Pale yellow solid; mp. 204-205 °C; ^1H NMR (DMSO- d_6) δ 12.31 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.39-7.35 (m, 5H), 7.24-7.21 (m, 2H), 7.15 (t, J = 8.0 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 4.84 (s, 2H), 2.52 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 175.8, 148.4, 143.2, 140.3, 139.2, 135.8, 131.1, 131.1, 130.0, 129.7, 127.6, 126.9, 126.8, 123.2, 122.8, 122.2, 121.8, 112.2, 112.2, 21.5, 16.6 ppm; IR (KBr) ν 3293, 3060, 2978, 2920, 1584, 1516, 1459, 1257, 1138, 1077, 1004, 778, 742, 544 cm^{-1} ; MS (ESI) m/z 481.2 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 503.0399; found, 503.0398.



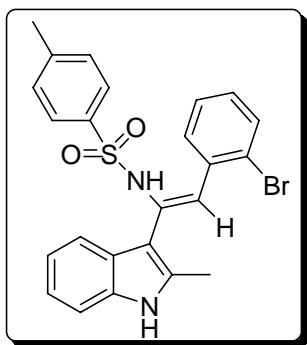
N-(2-(4-bromophenyl)-1-(2-methyl-1*H*-indol-3-yl)ethylidene)-4-methylbenzenesulfonamide (5k)

Pale yellow solid; mp. 211-212 °C; ^1H NMR (DMSO- d_6) δ 12.27 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.5 Hz, 1H), 7.15-7.12 (m, 3H), 7.05 (t, J = 7.5 Hz, 1H), 4.79 (s, 2H), 2.50 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 176.1, 148.2, 143.1, 140.4, 135.9, 135.7, 131.8, 130.7, 129.9, 126.9, 126.7, 123.1, 122.6, 121.8, 119.9, 112.2, 21.5, 16.5 ppm; IR (KBr) ν 3360, 3264, 3065, 2920, 1518, 1460, 1305, 1261, 1157, 1138, 1077, 1007, 814, 777, 540 cm^{-1} ; MS (ESI) m/z 481.2 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 503.0399; found, 503.0398.



***N*-(1-(1,2-dimethyl-1*H*-indol-3-yl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5l)**

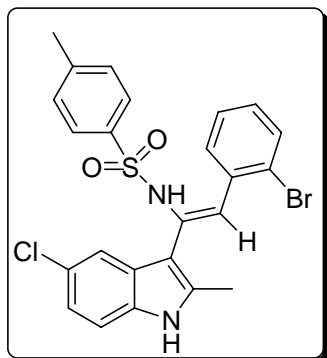
Orange solid; mp. 171-172 °C; ¹H NMR (DMSO-*d*₆) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23-7.07 (m, 7H), 4.90 (s, 2H), 3.67 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 176.9, 148.1, 143.1, 140.4, 137.4, 136.6, 130.0, 128.9, 128.6, 126.7, 126.0, 122.9, 122.8, 121.4, 112.2, 111.1, 41.4, 30.5, 21.4, 14.0 ppm; IR (KBr) ν 3449, 3030, 2924, 1513, 1470, 1410, 1379, 1144, 1085, 738, 542 cm⁻¹; MS (ESI) *m/z* 417.7 ([*M*+*H*]⁺); HRMS (ESI) calcd for C₂₅H₂₄N₂O₂S ([*M*+*Na*]⁺), 439.1451; found, 439.1442.



***(Z)*-*N*-(2-(2-bromophenyl)-1-(2-methyl-1*H*-indol-3-yl)vinyl)-4-methylbenzenesulfonamide (6a)**

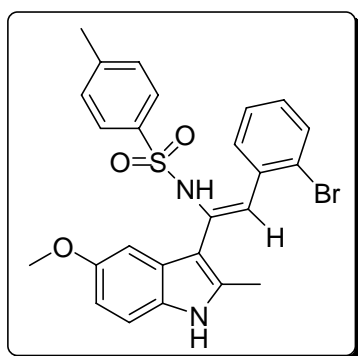
Pale yellow solid; mp. 173-174 °C; ¹H NMR (DMSO-*d*₆) δ 11.00 (s, 1H), 9.68 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.88-6.82 (m, 2H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.53-6.52 (m, 1H), 6.32 (s, 1H), 2.39 (s, 3H), 1.78 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆) δ 143.4, 137.9, 137.8, 136.0, 135.6, 133.0, 132.6, 129.9, 129.7, 127.8, 127.7, 127.4, 127.2, 123.7, 120.9, 119.4, 118.9, 115.8, 111.0, 106.6, 21.5,

12.3 ppm; IR (KBr) ν 3334, 3215, 3057, 2919, 2851, 1628, 1459, 1418, 1291, 1157, 1061, 745, 706, 699, 549 cm^{-1} ; MS (ESI) m/z 481.4 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 503.0399; found, 503.0398.



(Z)-N-(2-(2-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide (6b)

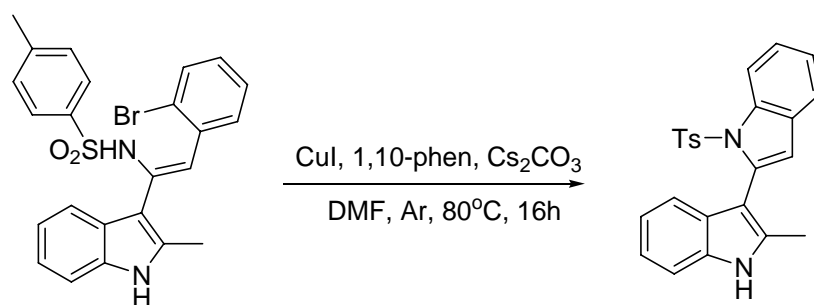
Pale yellow solid; mp. 208-209 °C; ^1H NMR ($\text{DMSO}-d_6$) δ 11.19 (s, 1H), 9.74 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 1H), 6.95-6.89 (m, 2H), 6.82 (t, $J = 7.5$ Hz, 1H), 6.77 (m, 1H), 6.51 (t, $J = 7.5$ Hz, 1H), 6.42 (s, 1H), 2.39 (s, 3H), 1.79 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ 143.6, 138.0, 137.6, 137.5, 134.0, 132.6, 132.3, 130.0, 129.7, 129.0, 128.1, 127.4, 127.3, 124.1, 123.7, 120.8, 117.9, 116.7, 112.4, 106.4, 21.5, 12.3 ppm; IR (KBr) ν 3314, 3220, 2920, 1630, 1467, 1441, 1301, 1155, 1072, 803, 753, 708, 684 cm^{-1} ; MS (ESI) m/z 515.1 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{BrClN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 537.0010; found, 537.0018.



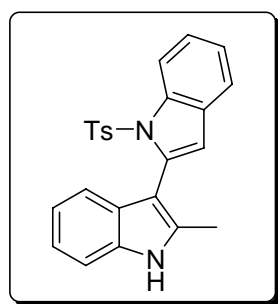
(Z)-N-(2-(2-bromophenyl)-1-(5-methoxy-2-methyl-1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide (6c)

Pale yellow solid; mp. 155-156 °C; ^1H NMR (DMSO- d_6) δ 10.88 (s, 1H), 9.65 (s, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.48-7.46 (m, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 1H), 6.88-6.85 (m, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.59-6.57 (m, 1H), 6.55-6.53 (m, 1H), 6.33 (t, J = 2.5 Hz, 1H), 6.29 (s, 1H), 3.54 (s, 3H), 2.38 (s, 3H), 1.93 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 153.7, 143.4, 138.0, 137.6, 137.0, 133.1, 132.5, 130.4, 129.9, 128.0, 127.8, 127.4, 127.2, 123.6, 115.3, 111.5, 110.6, 106.4, 100.8, 55.3, 21.4, 12.6 ppm; IR (KBr) ν 3394, 3328, 3228, 2924, 1625, 1484, 1451, 1163, 1063, 806, 675, 550 cm^{-1} ; MS (ESI) m/z 511.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 533.0505; found, 533.0508.

General Procedure for the synthesis of 7.

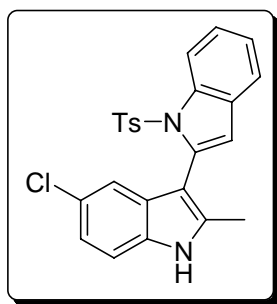


To a mixture of **6a** (0.3 mmol), CuI (0.03 mmol, 0.1 equiv), 1,10-phenanthroline (0.06 mmol, 0.2 equiv), and Cs_2CO_3 (0.6 mmol, 2.0 equiv) was added DMF (4 mL). The reaction mixture was heated at 80 °C for 16 h under argon. The reaction was diluted with EA and washed with H_2O and saturated NaCl solution. The organic layer was dried over MgSO_4 , and concentrated in vacuo. The residue was purified by column chromatography on silica gel.



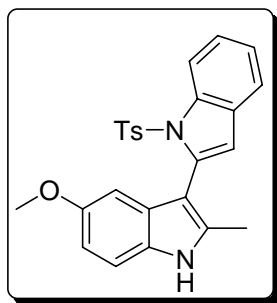
2'-methyl-1-tosyl-2,3'-bi(1H-indole) (7a)

Pale yellow solid; mp. 91-92°C. ^1H NMR (CDCl_3) δ 8.38 (d, $J=8.5$ Hz, 1H), 8.15 (s, 1H), 7.47 (d, $J=7.5$ Hz, 1H), 7.35 (t, $J=7.5$, 1H), 7.31-7.26 (m, 2H), 7.17 (d, $J=8.5$ Hz, 2H), 7.14-7.11 (m, 2H), 6.99 (t, $J=7.5$, 1H), 6.86 (d, $J=8.0$ Hz, 2H), 6.57 (s, 1H), 2.39 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 144.2, 138.0, 136.7, 134.9, 134.7, 130.8, 129.3, 129.1, 126.8, 124.1, 123.8, 121.3, 120.2, 120.0, 118.7, 116.3, 113.3, 110.3, 104.8, 21.4, 13.1 ppm; IR (KBr) ν 3402, 3056, 2922, 2854, 1598, 1456, 1367, 1172, 1090, 1055, 747, 675, 578 cm^{-1} ; MS (ESI) m/z 401.3 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 423.1138; found, 423.1134.



5'-chloro-2'-methyl-1-tosyl-2,3'-bi(1'*H*-indole) (7b)

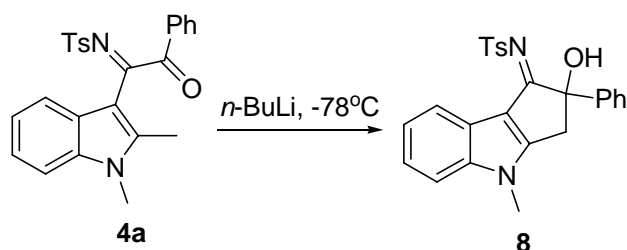
Pale yellow solid; mp. 205-206°C. ^1H NMR (CDCl_3) δ 8.40 (dd, $J_2=0.5$ Hz, $J_2=8.5$ Hz, 1H), 8.23 (s, 1H), 7.51 (d, $J=7.5$ Hz, 1H), 7.35 (m, 1H), 7.32-7.31 (m, 1H), 7.19 (d, $J=8.5$ Hz, 1H), 7.07 (d, $J=8.0$ Hz, 2H), 7.05-7.03 (m, 1H), 6.86 (d, $J=7.5$, 2H), 6.73 (d, $J=2.0$ Hz, 1H), 6.57 (s, 1H), 2.42 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 144.6, 138.6, 138.1, 135.0, 133.6, 132.9, 130.4, 130.3, 129.1, 126.7, 125.8, 124.4, 123.9, 121.4, 120.4, 117.9, 116.2, 113.5, 111.2, 104.3, 21.5, 13.2 ppm; IR (KBr) ν 3404, 3057, 2922, 1597, 1467, 1452, 1364, 1224, 1173, 812, 733 cm^{-1} ; MS (ESI) m/z 435.0 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{ClN}_2\text{O}_2\text{S}$ ($[\text{M}+\text{Na}]^+$), 457.0748; found, 457.0759.



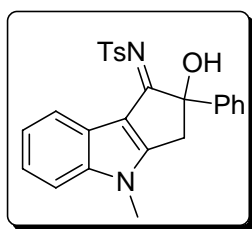
5'-methoxy-2'-methyl-1-tosyl-2,3'-bi(1'*H*-indole) (**7c**)

Yellow oil; ^1H NMR (CDCl_3) δ 8.40 (d, $J=8.05$ Hz, 1H), 8.08 (s, 1H), 7.51 (d, $J=7.5$ Hz, 1H), 7.38-7.35 (m, 1H), 7.31-7.29 (m, 1H), 7.19-7.15 (m, 3H), 6.86 (d, $J=8.0$ Hz, 2H), 6.77-6.75 (m, 1H), 6.57 (s, 1H), 6.04 (d, $J=2.0$ Hz, 1H), 3.65 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 154.4, 144.2, 138.0, 137.6, 135.2, 134.7, 130.6, 129.9, 129.5, 129.0, 126.9, 124.2, 123.7, 120.2, 116.2, 113.0, 111.2, 111.0, 104.5, 100.3, 55.5, 21.3, 13.1 ppm; IR (KBr) ν 3409, 1633, 1485, 1453, 1254, 1175, 909, 812, 799, 676 cm^{-1} ; MS (ESI) m/z 431.1 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 453.1243; found, 453.1252.

General procedure for the synthesis of **8**

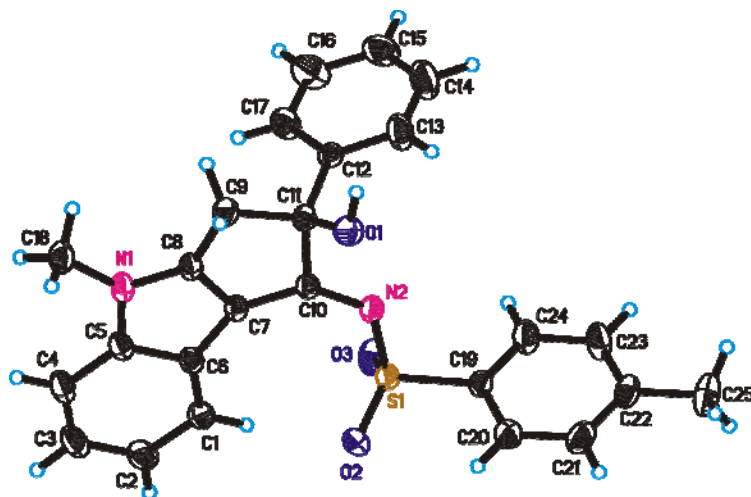


To a solution of **4a** (0.25 mmol) in dry THF was slowly added *n*-BuLi in hexane (120 μL , 0.3 mmol) at -78°C under Ar. And the reaction mixture was stirred at this temperature for 2h, then warmed to room temperature for 1h. The solution was diluted with DCM (3 mL) and quenched by saturated NH_4Cl under argon atmosphere. The aqueous layer was extracted by DCM and the combined organic layer was washed with saturated NH_4Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel and further recrystallized from EA.



***N*-(2-hydroxy-4-methyl-2-phenyl-2,3-dihydrocyclopenta[*b*]indol-1(4*H*)-ylidene)-4-methylbenzenesulfonamide (8)**

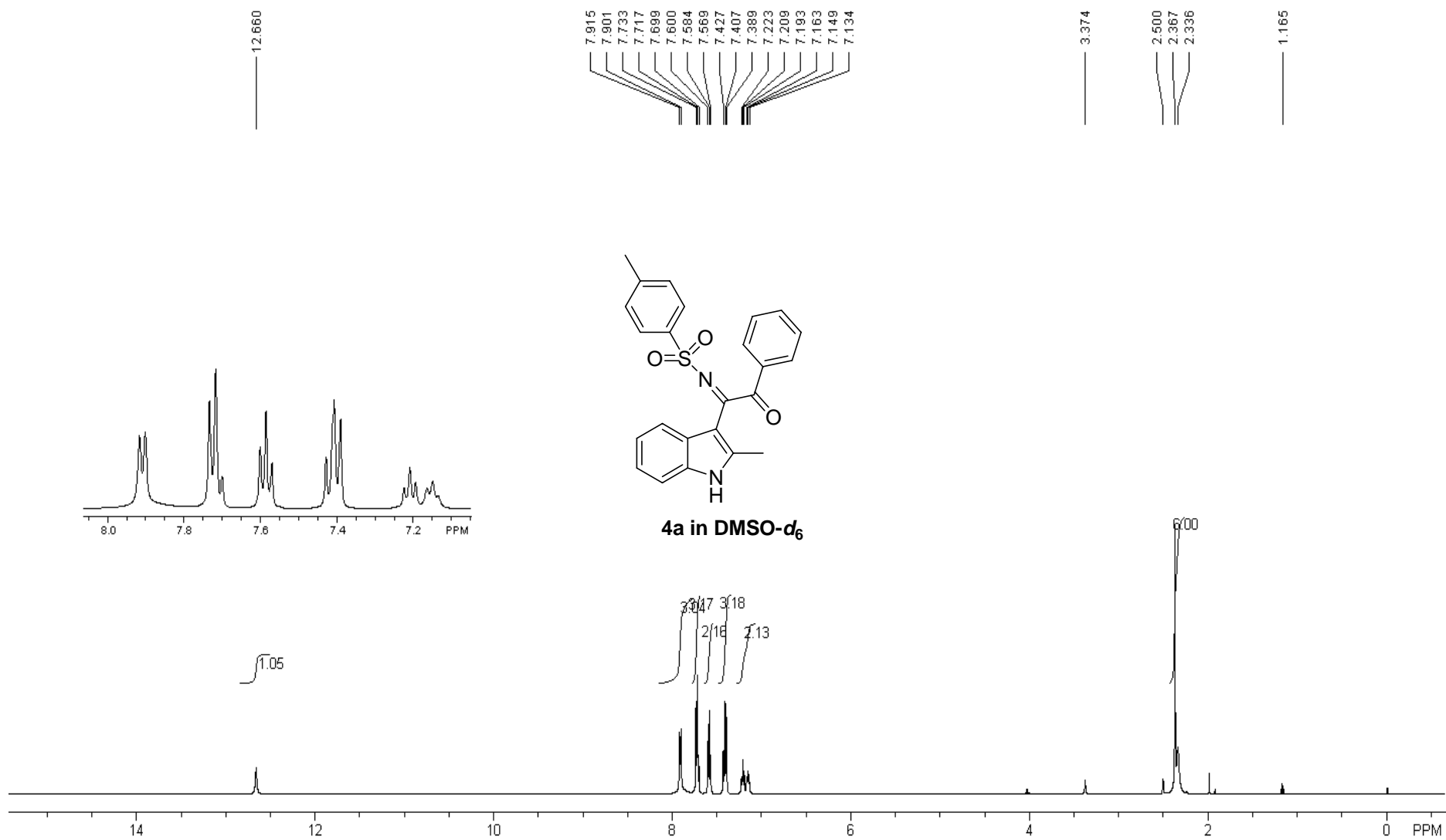
Yellow solid; mp. 219-220 °C; ^1H NMR (DMSO- d_6) δ 8.49 (d, $J = 7.5$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$, 1H), 7.42-7.24 (m, 9H), 6.47 (s, 1H), 3.85 (s, 3H), 3.64 (d, $J = 18.5$, 1H), 3.48 (d, $J = 18.0$ Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (DMSO- d_6) δ 177.2, 166.9, 145.4, 144.2, 142.5, 140.9, 129.6, 128.4, 127.6, 126.5, 125.5, 124.4, 123.3, 122.9, 113.7, 111.7, 88.3, 40.8, 31.9, 21.4 ppm; IR (KBr) ν 3543, 3453, 3058, 2950, 1597, 1526, 1451, 1412, 1282, 1147, 1084, 856, 824, 754, 576 cm^{-1} ; MS (ESI) m/z 431.4 ($[\text{M}+\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{Na}]^+$), 453.1243; found, 453.1232.

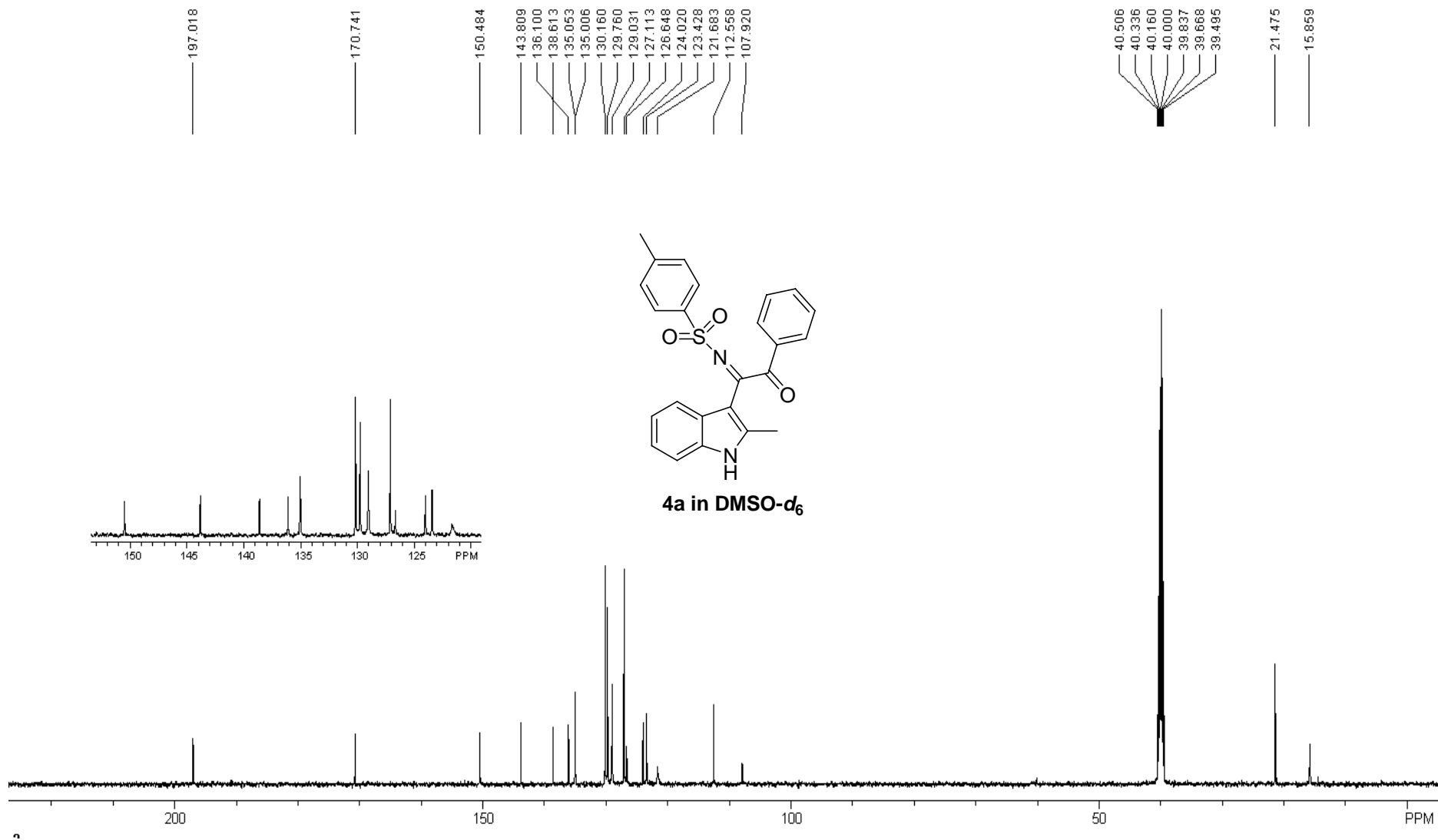


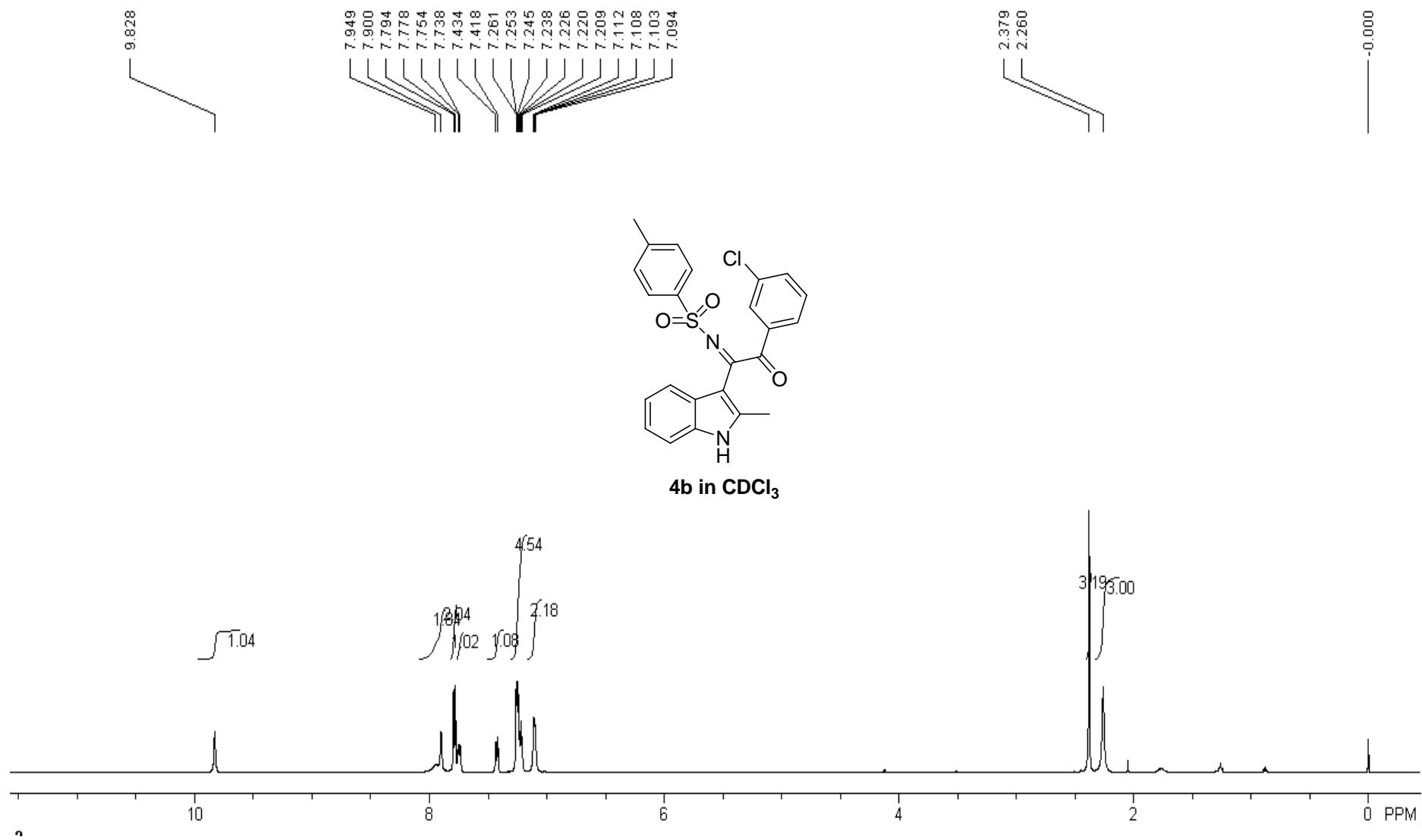
References and Notes

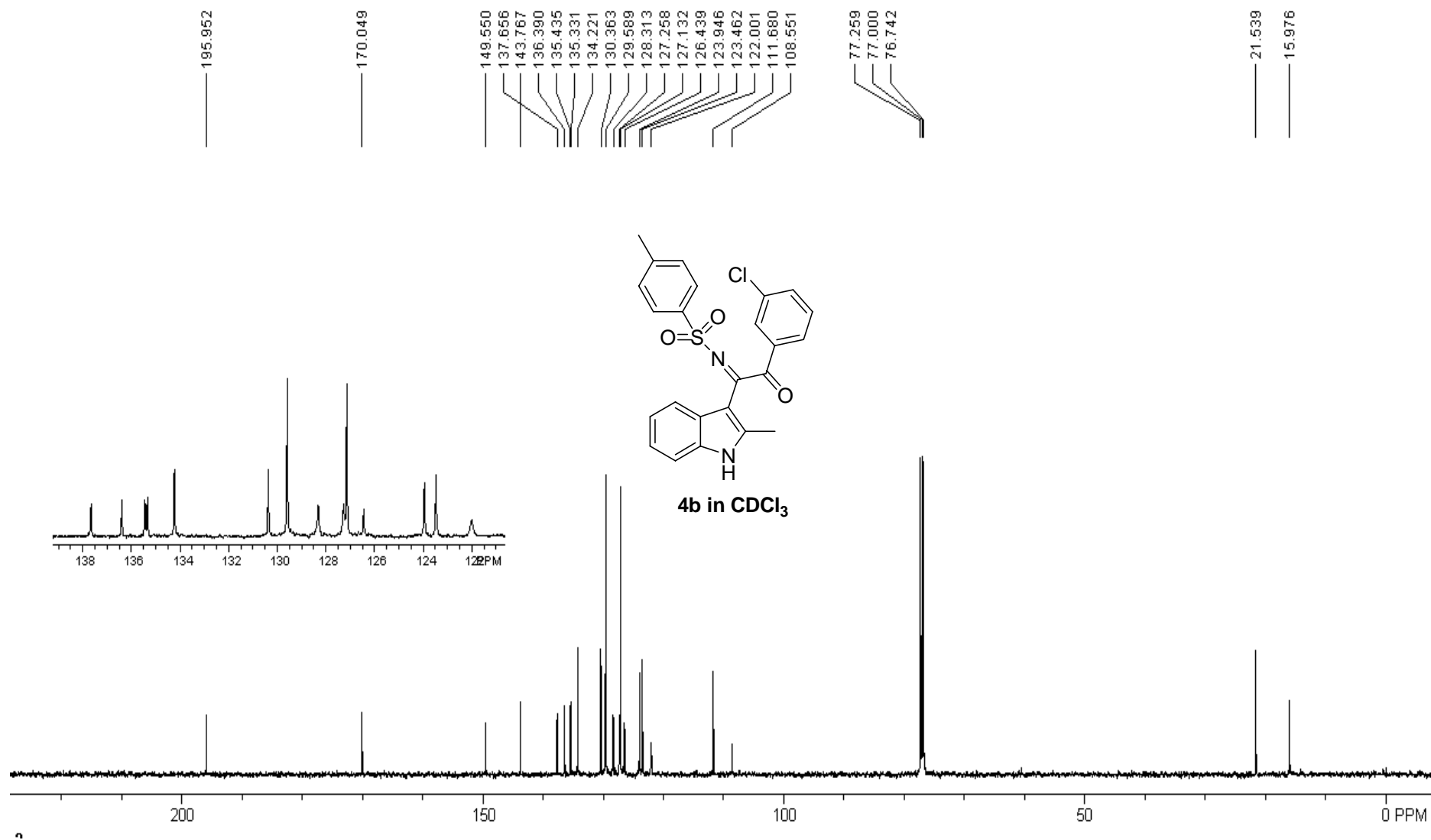
1. (a) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.*; **1990**; 55, 1959-1964. (b) Hazen, G. G.; Bollinger, F. W.; Roberts, F. E.; Russ, W. K.; Seman, J. J.; Staskiewicz, S. *Org. Synth.* **1998**, *Coll. Vol. 9*, 400; **1996**, *Vol. 73*, 144.

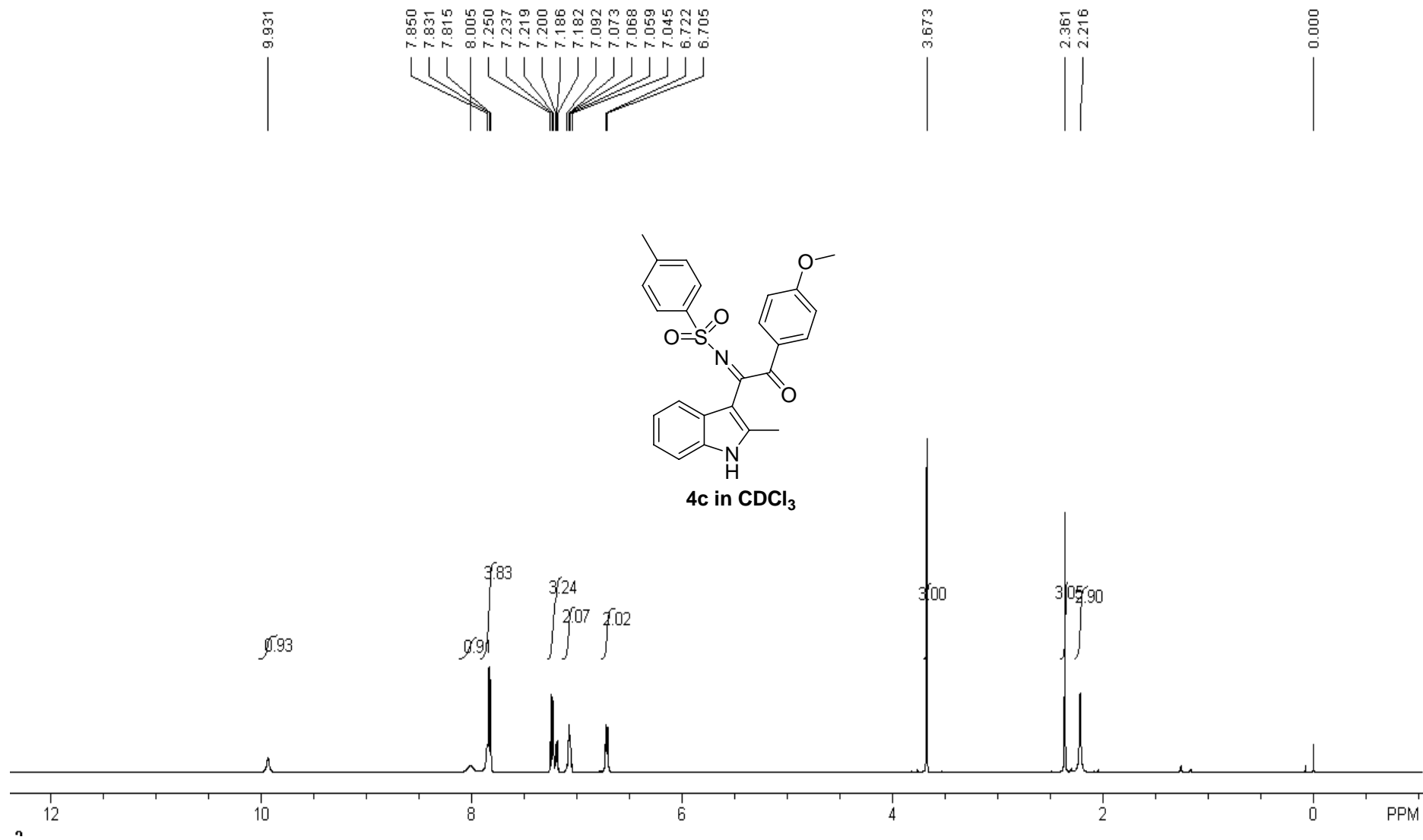
2. Caution: Although the mixture of sulfonyl azides is the safest of a group of diazo compounds, one should keep in mind the inherent instability, shock sensitivity, and explosive power of azides. All users should exercise appropriate caution.

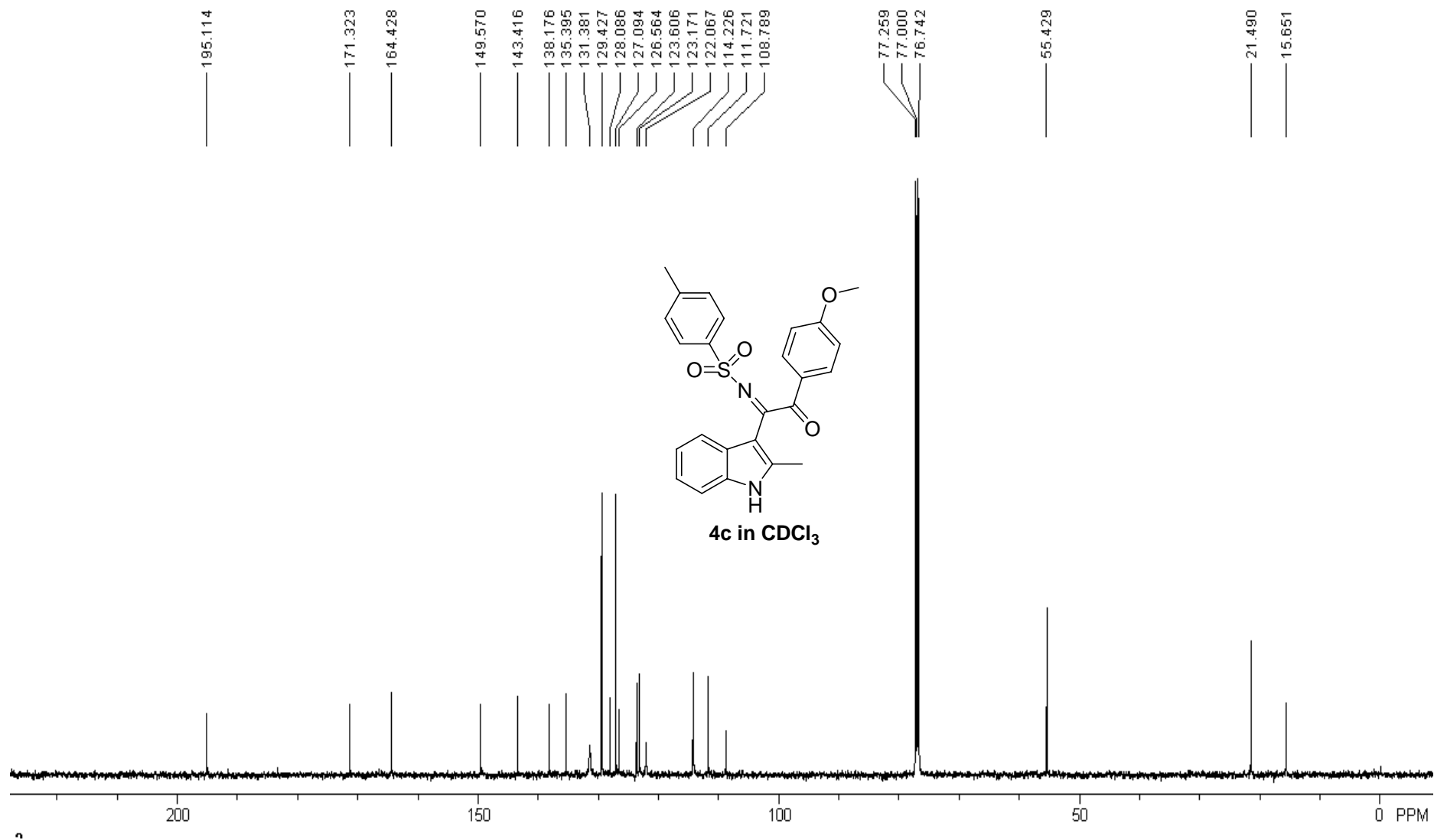


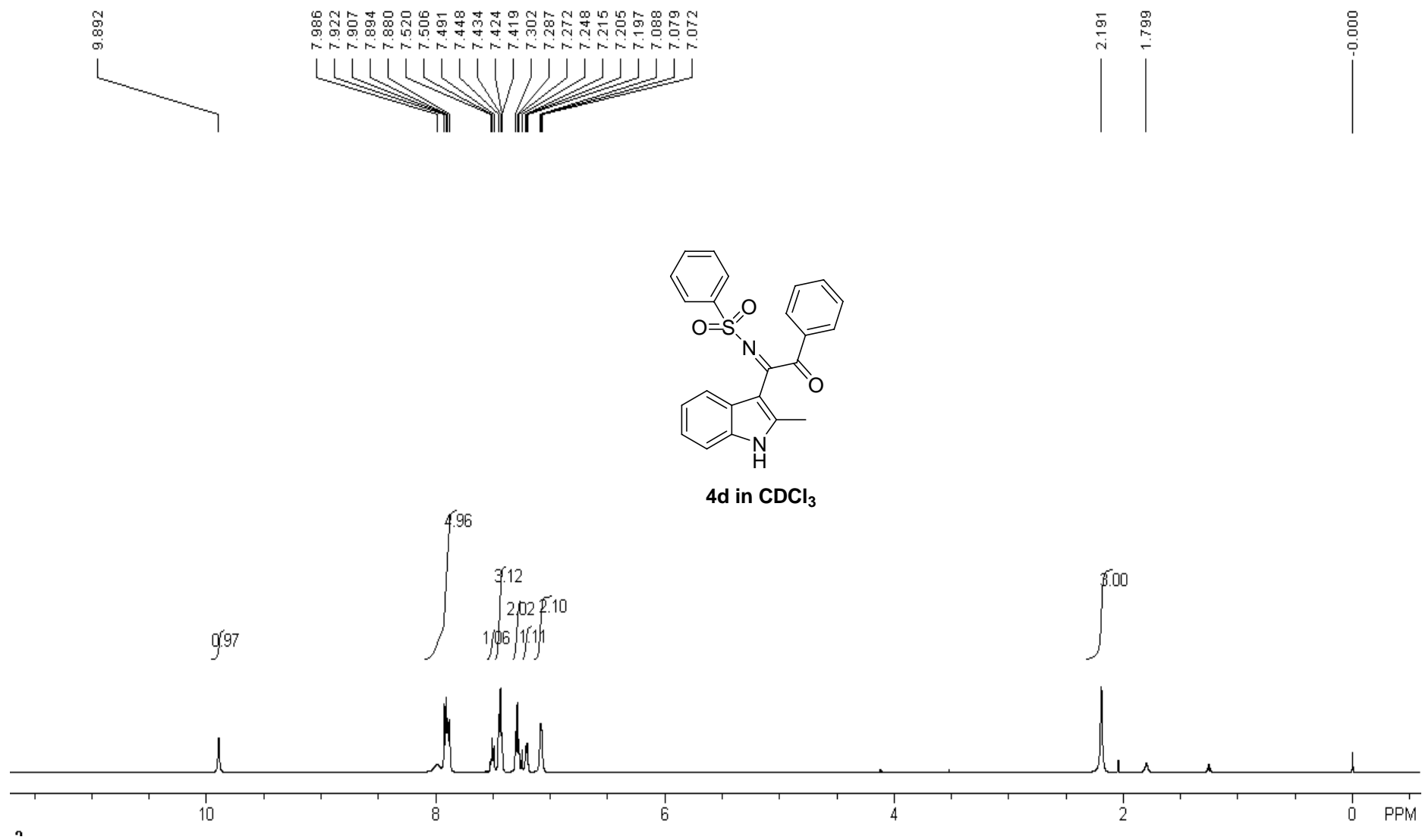


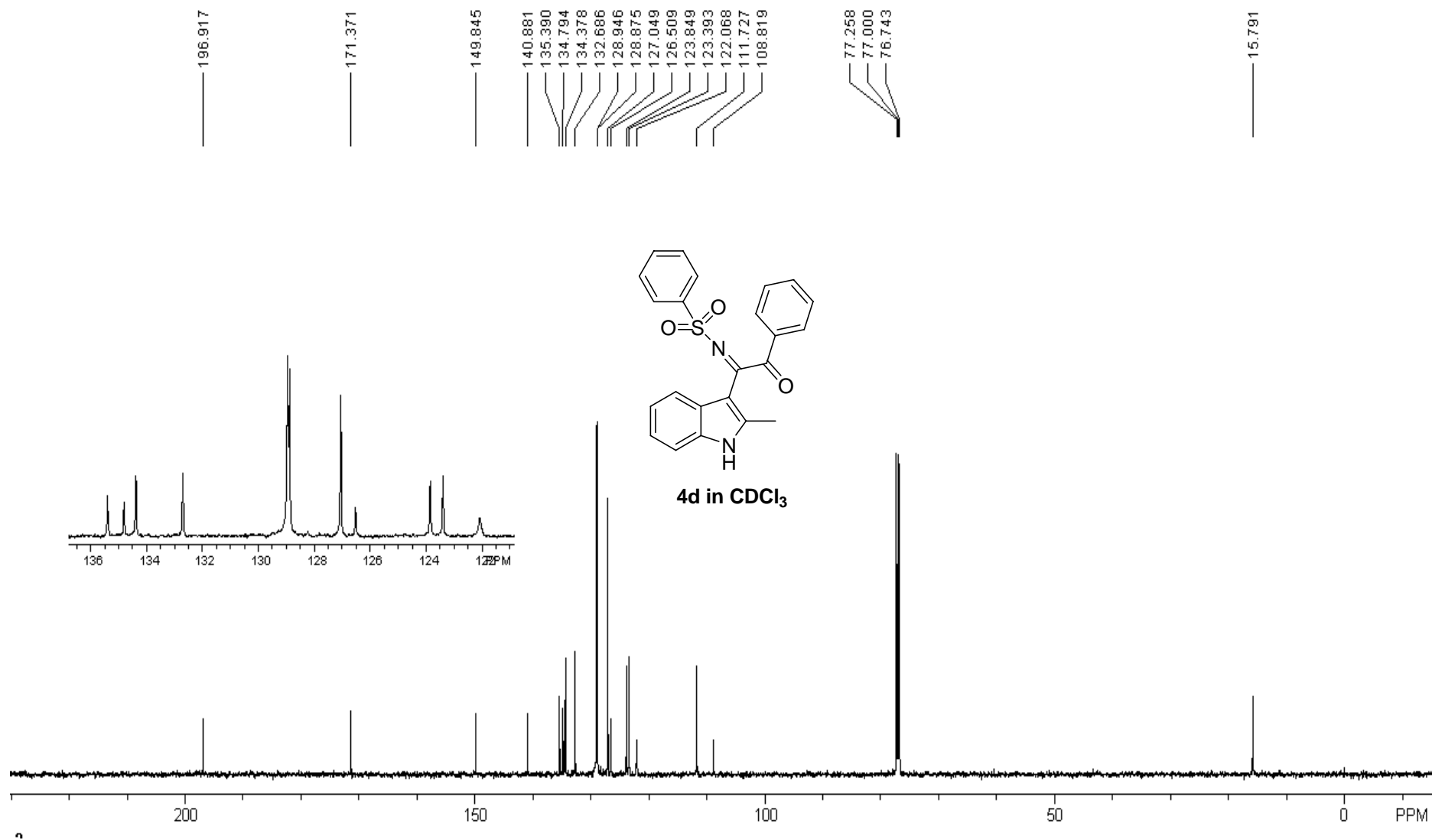


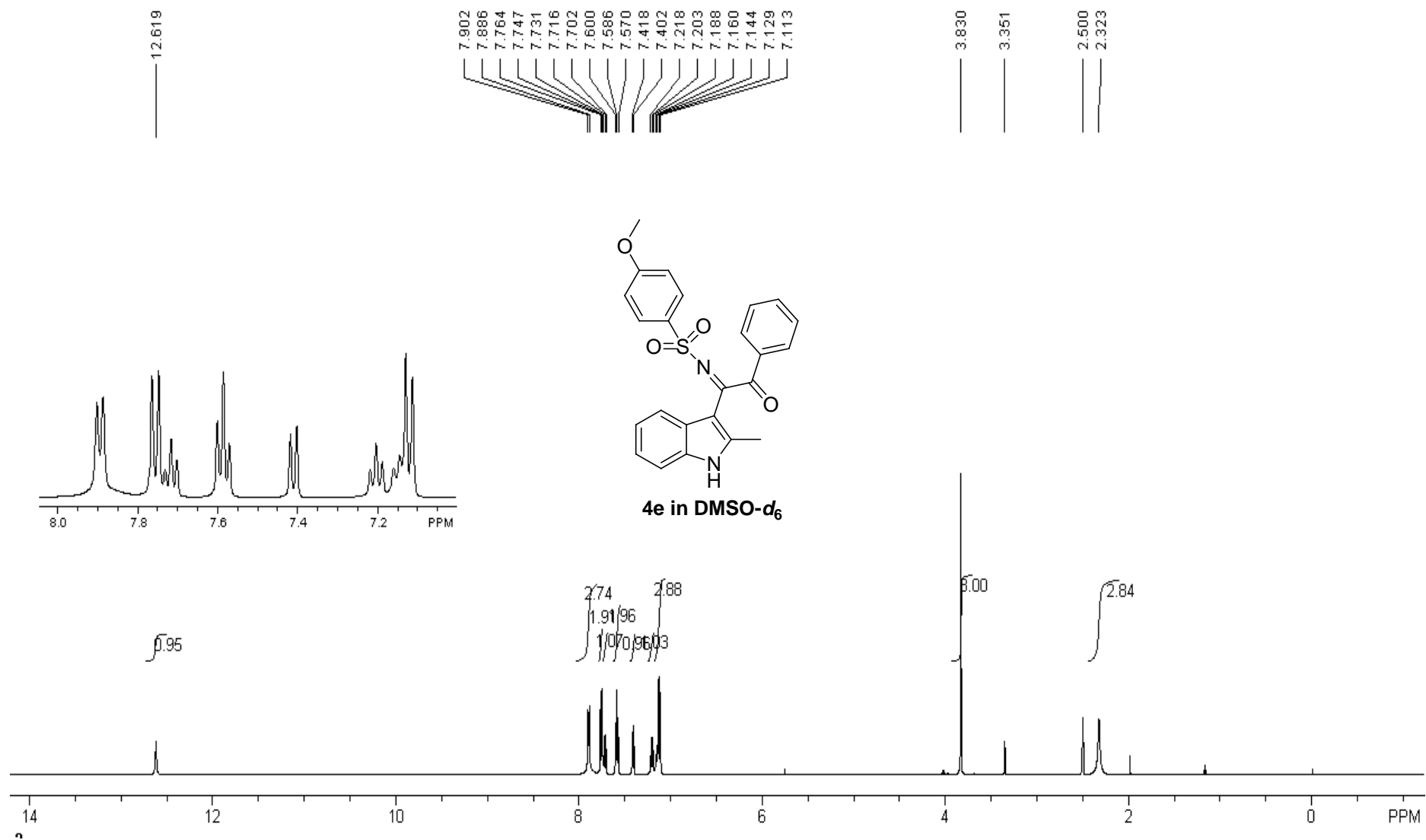


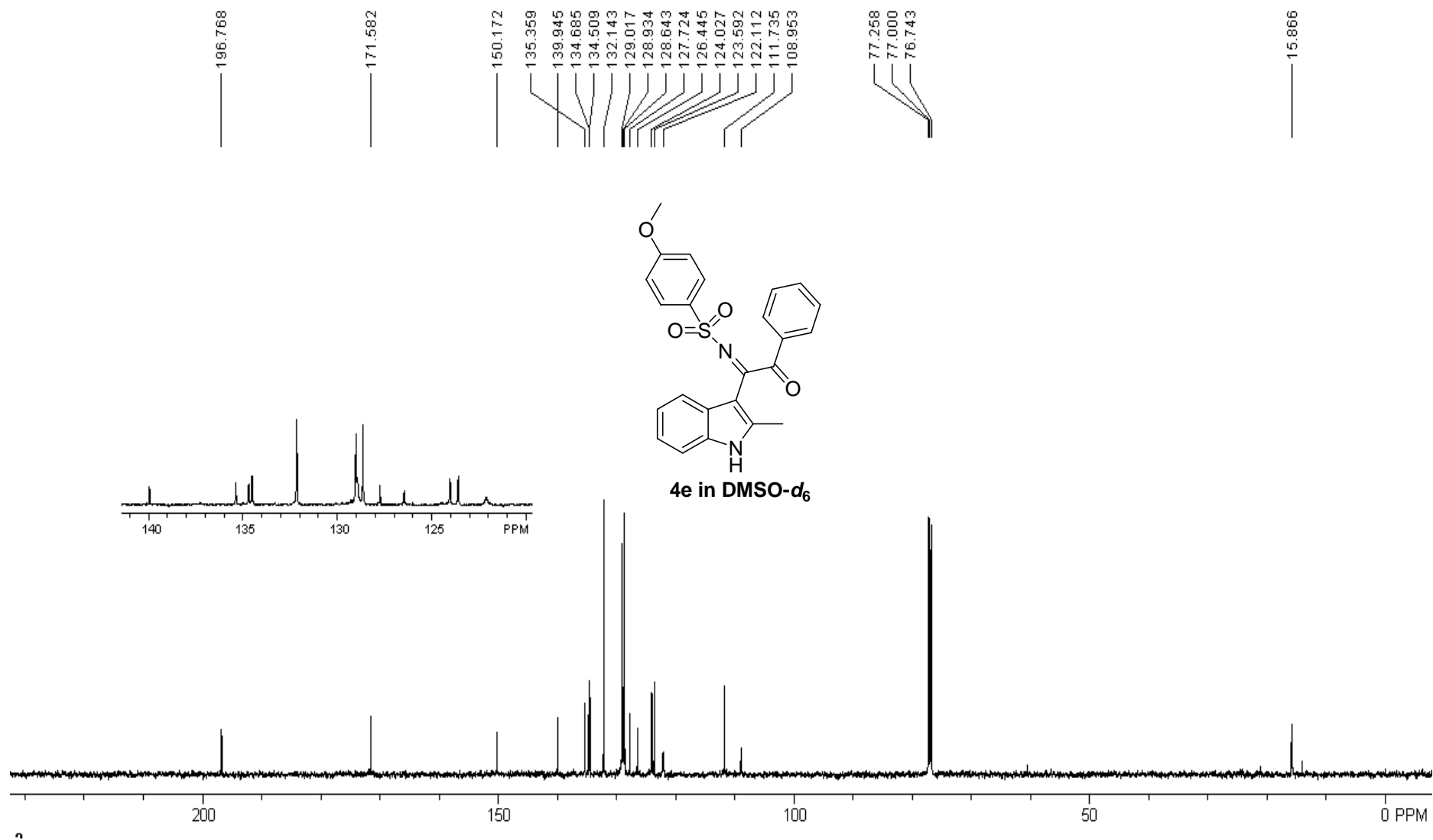


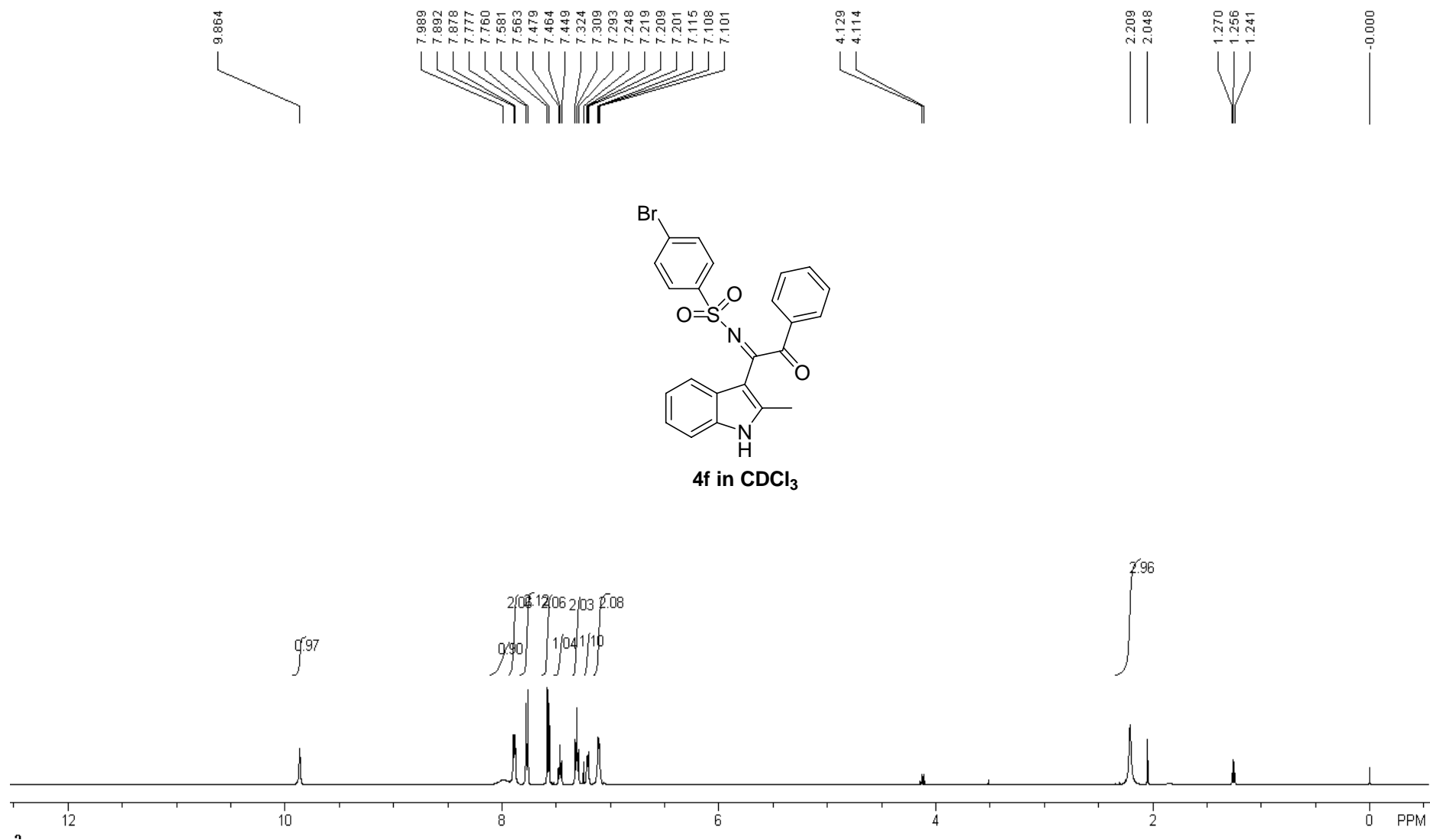


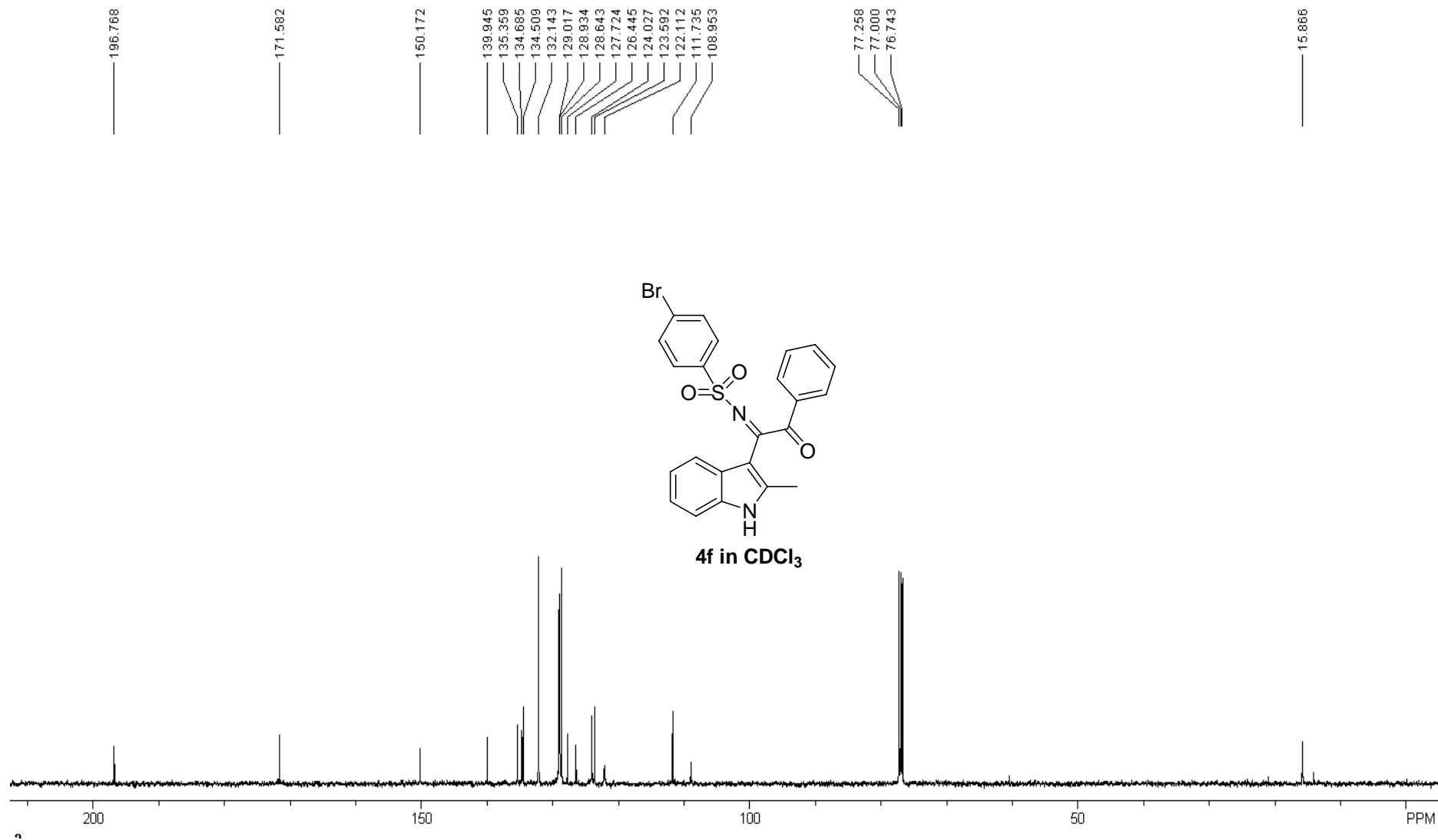


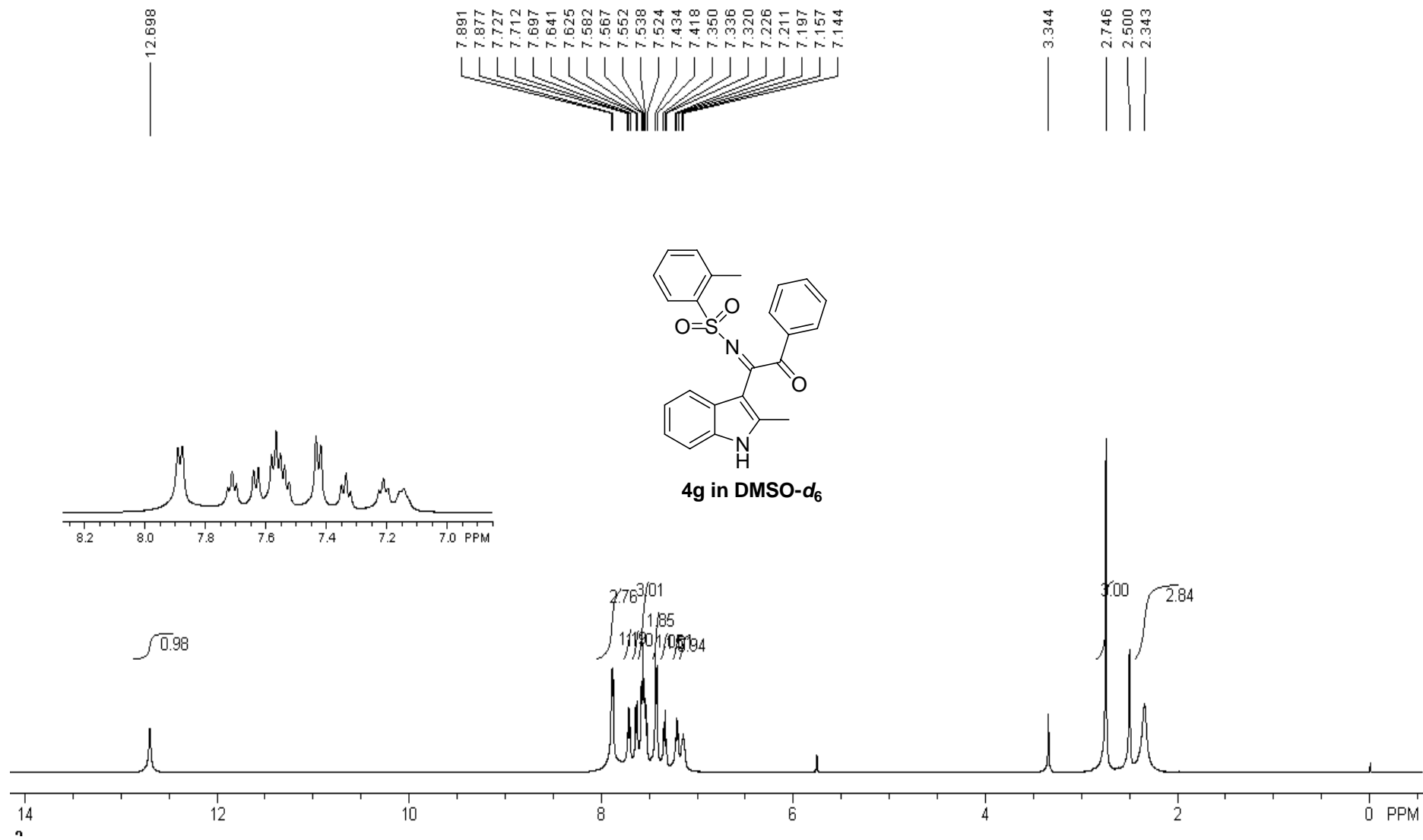


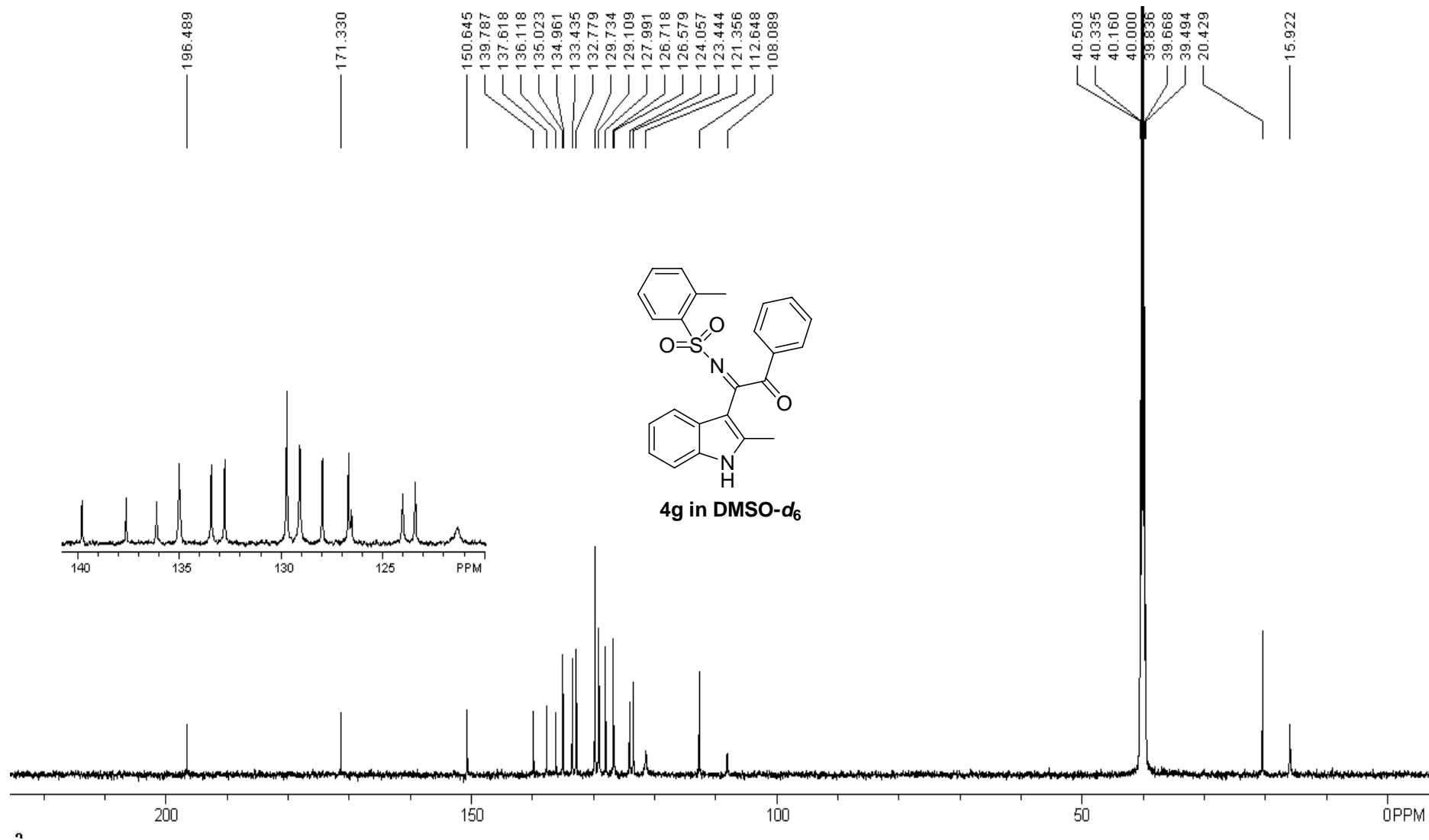


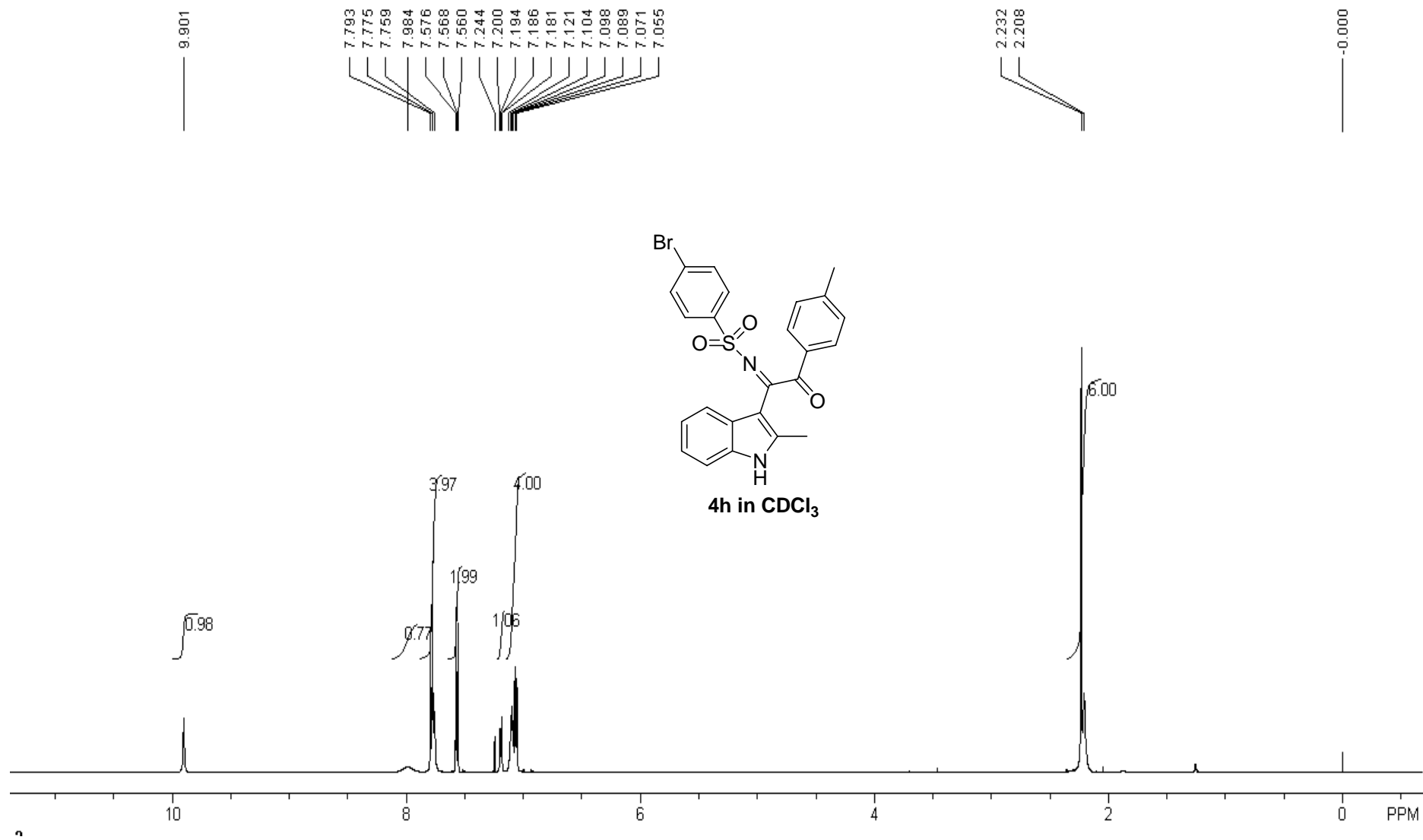


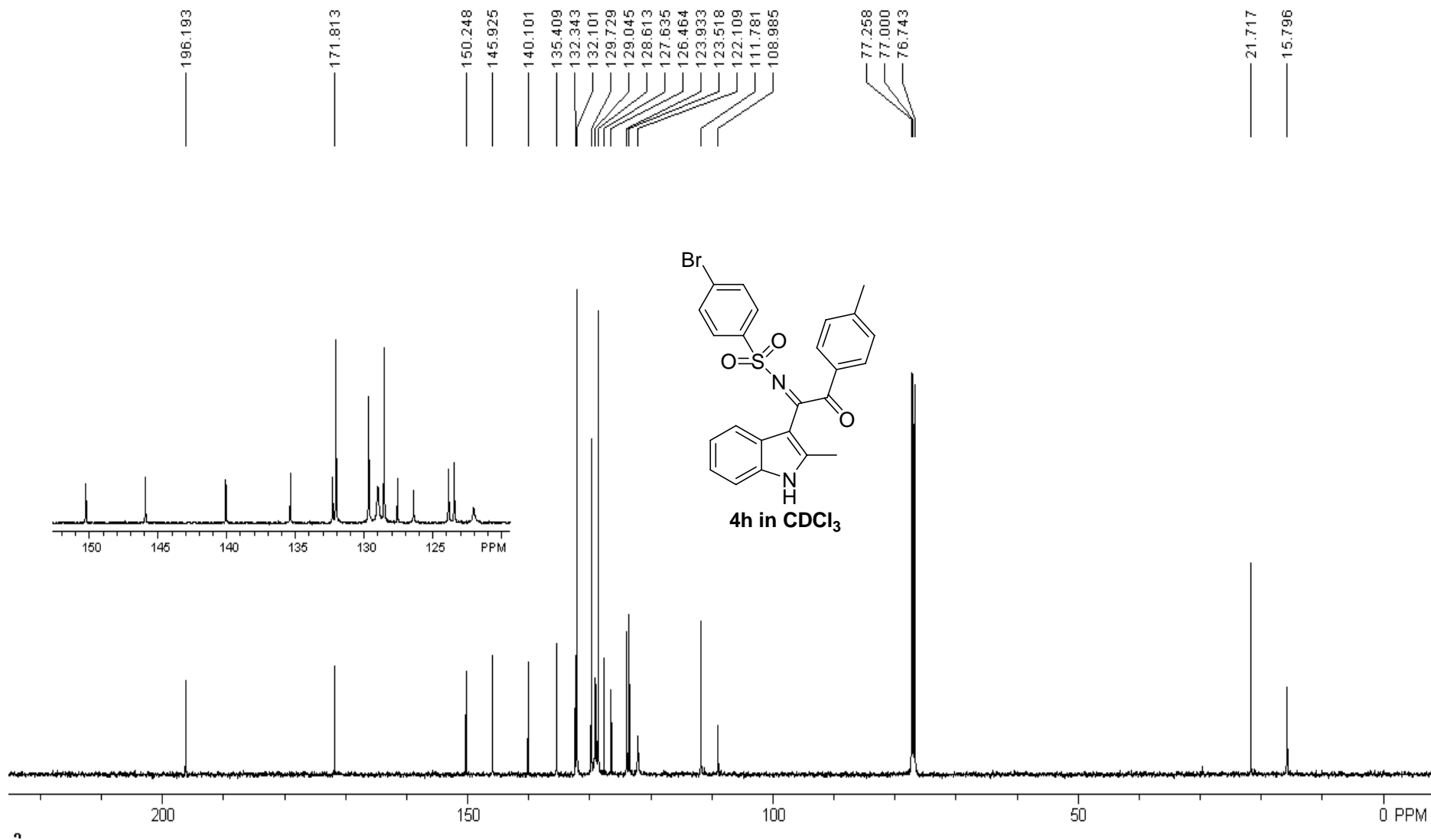


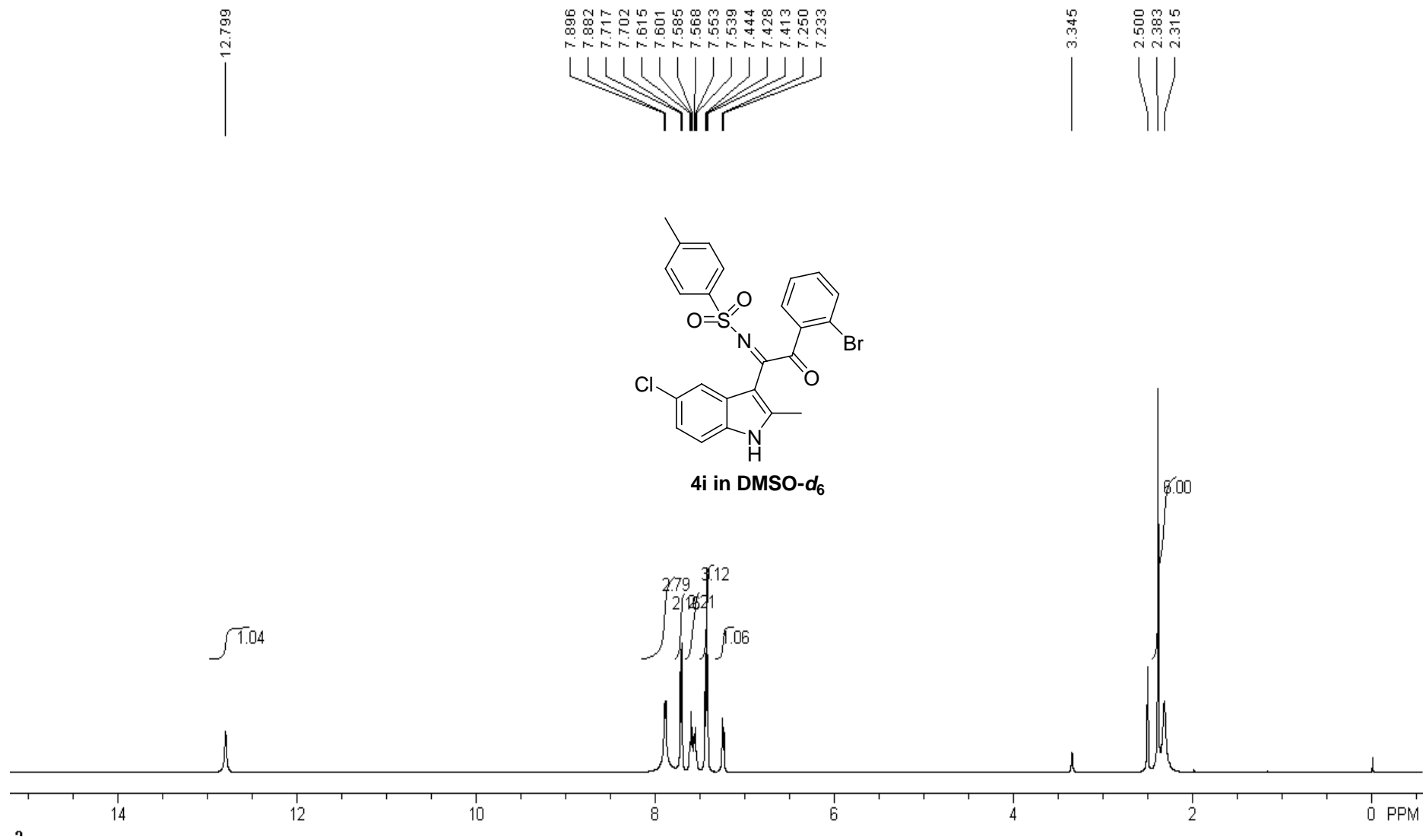


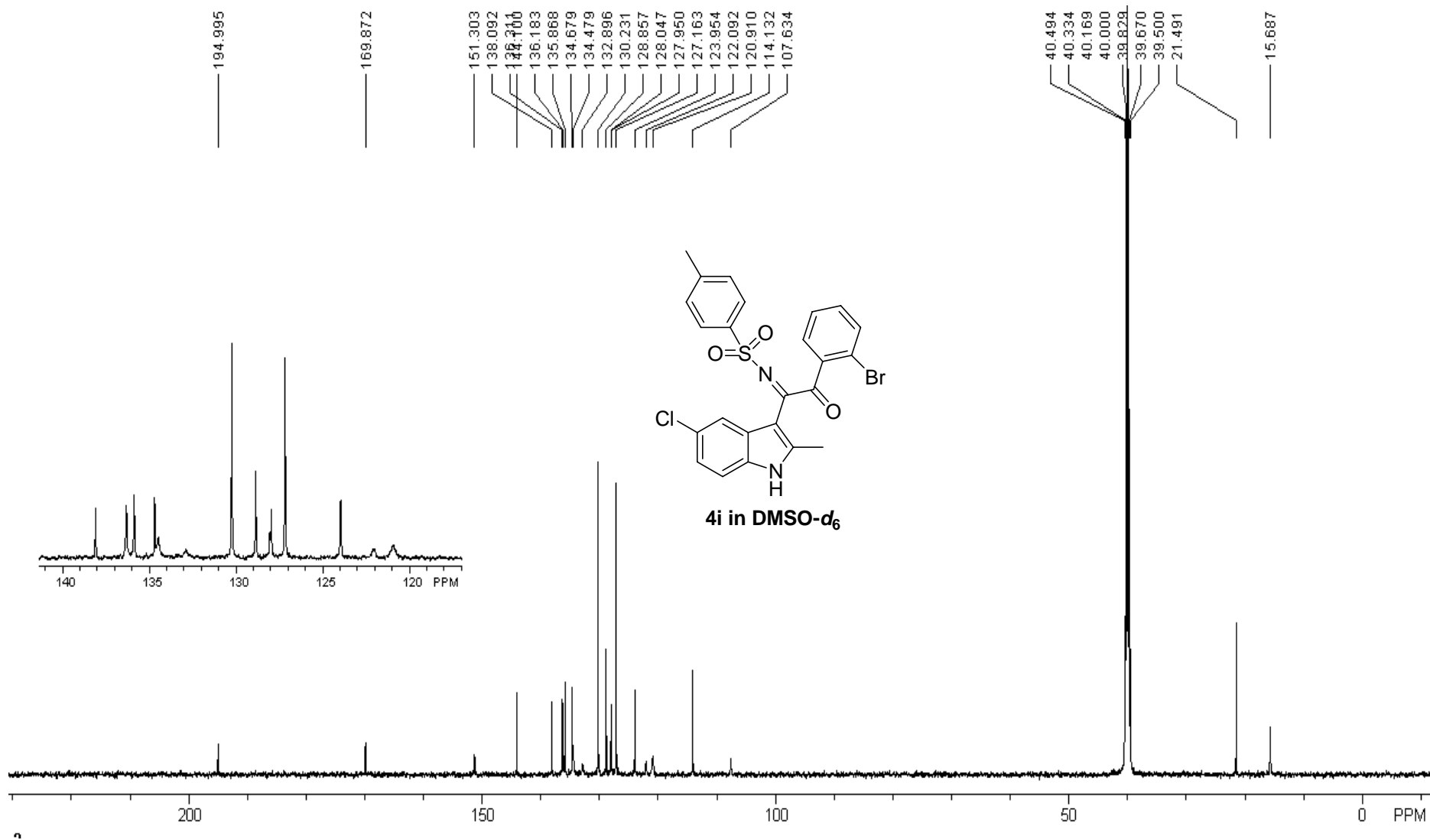


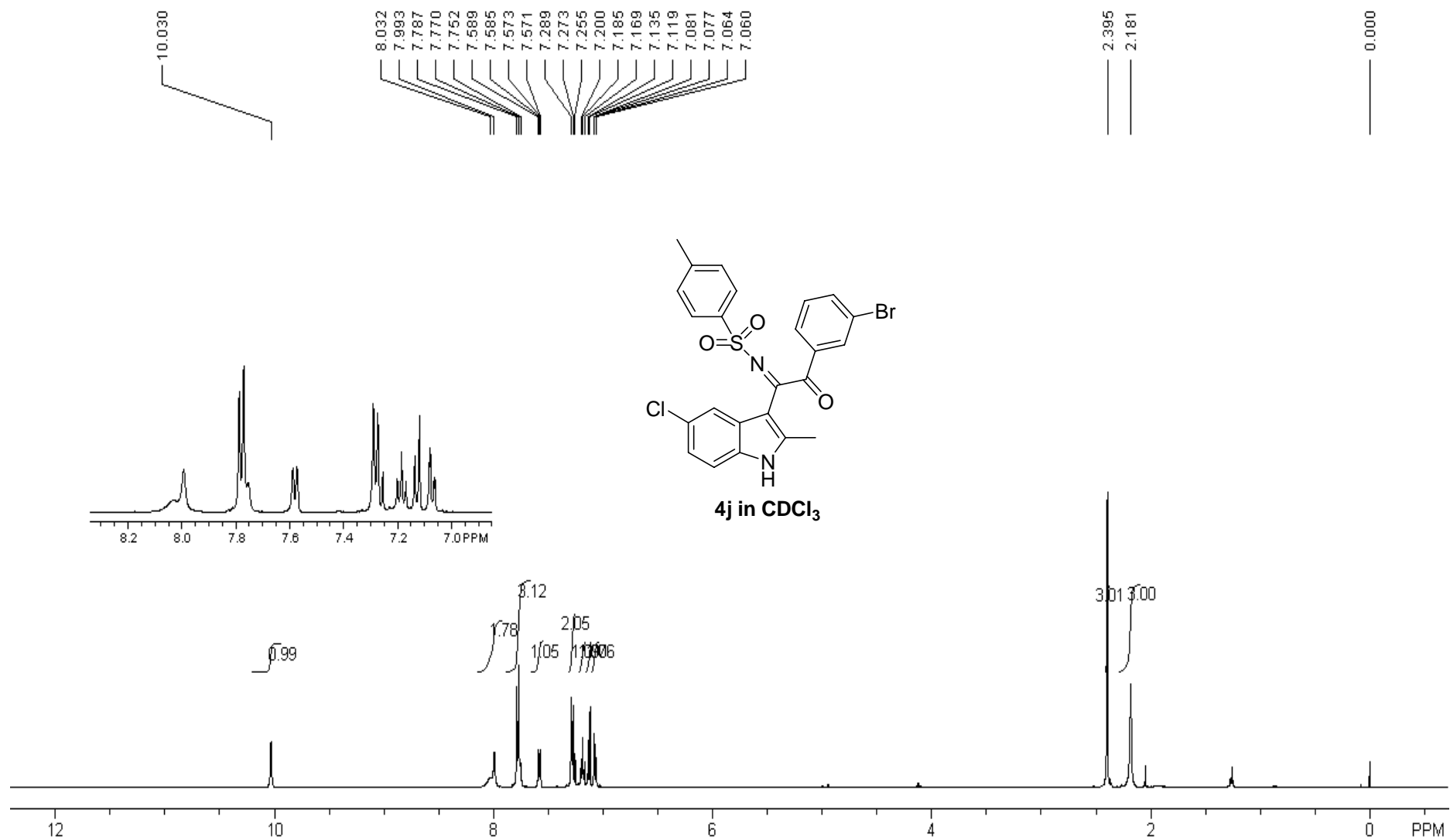


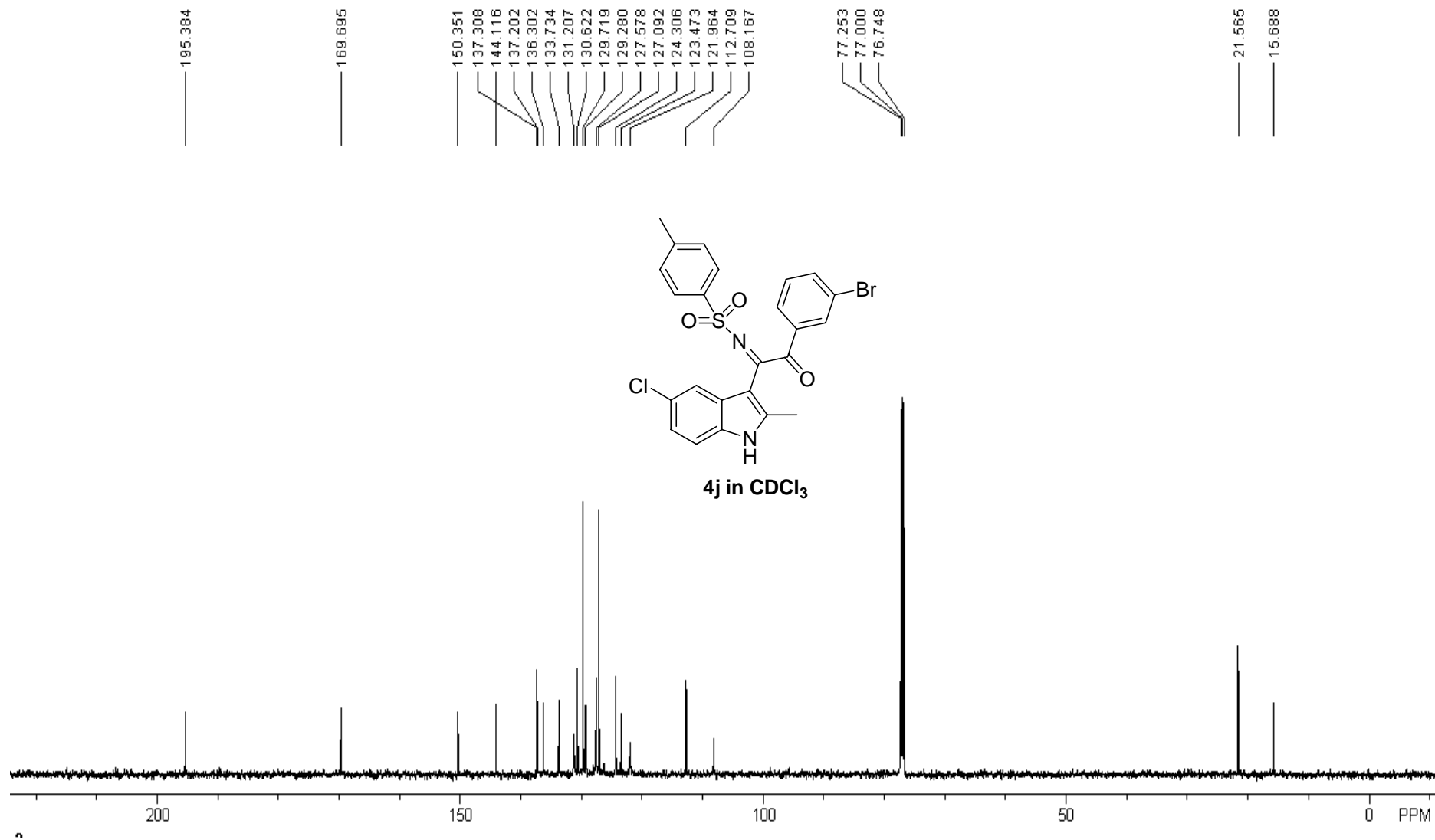


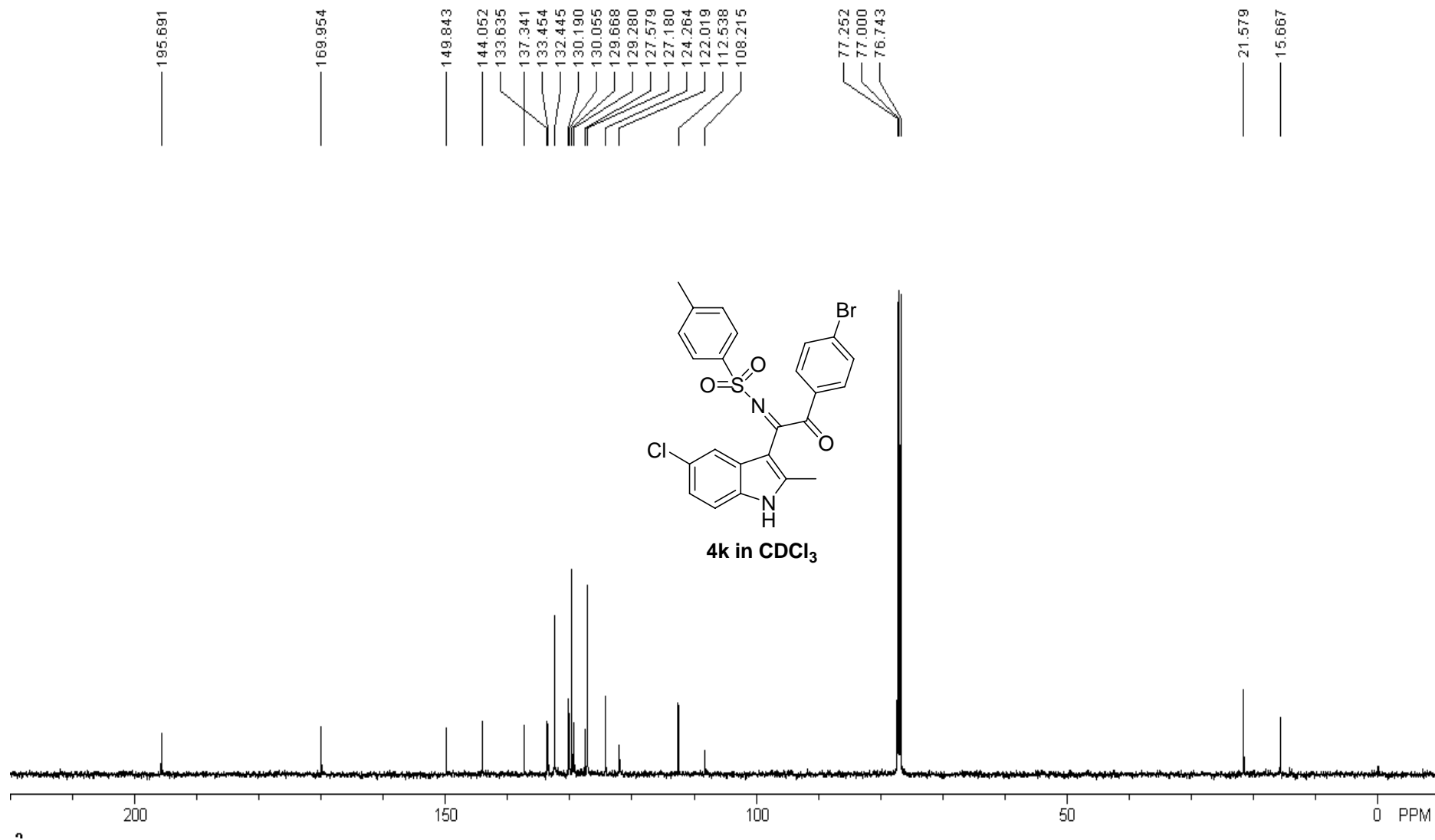


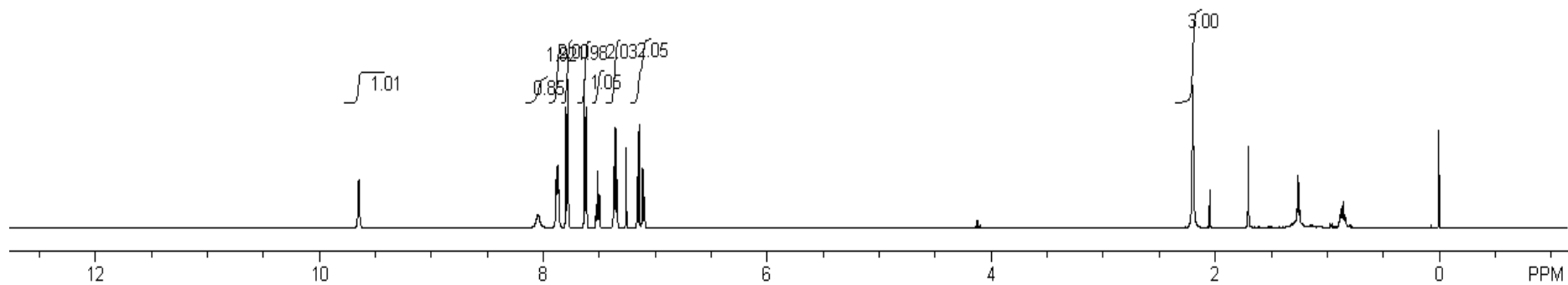
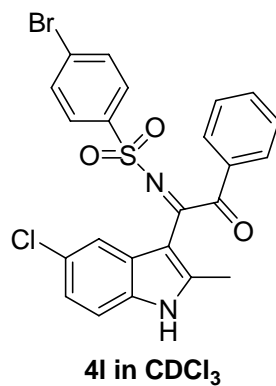
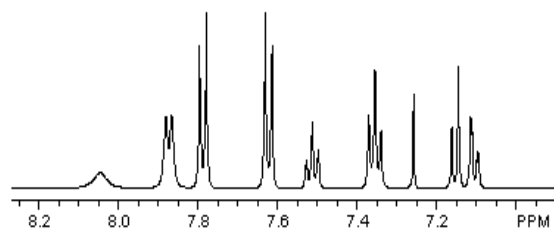
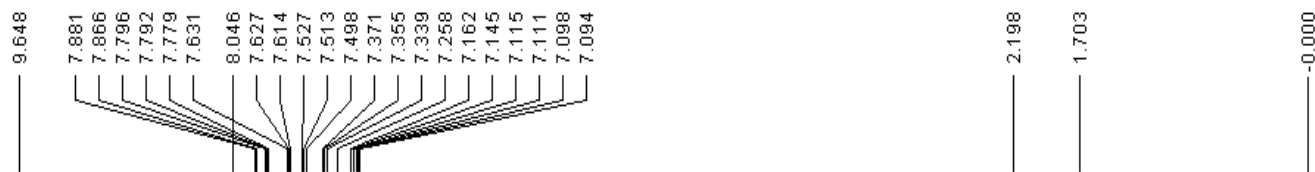


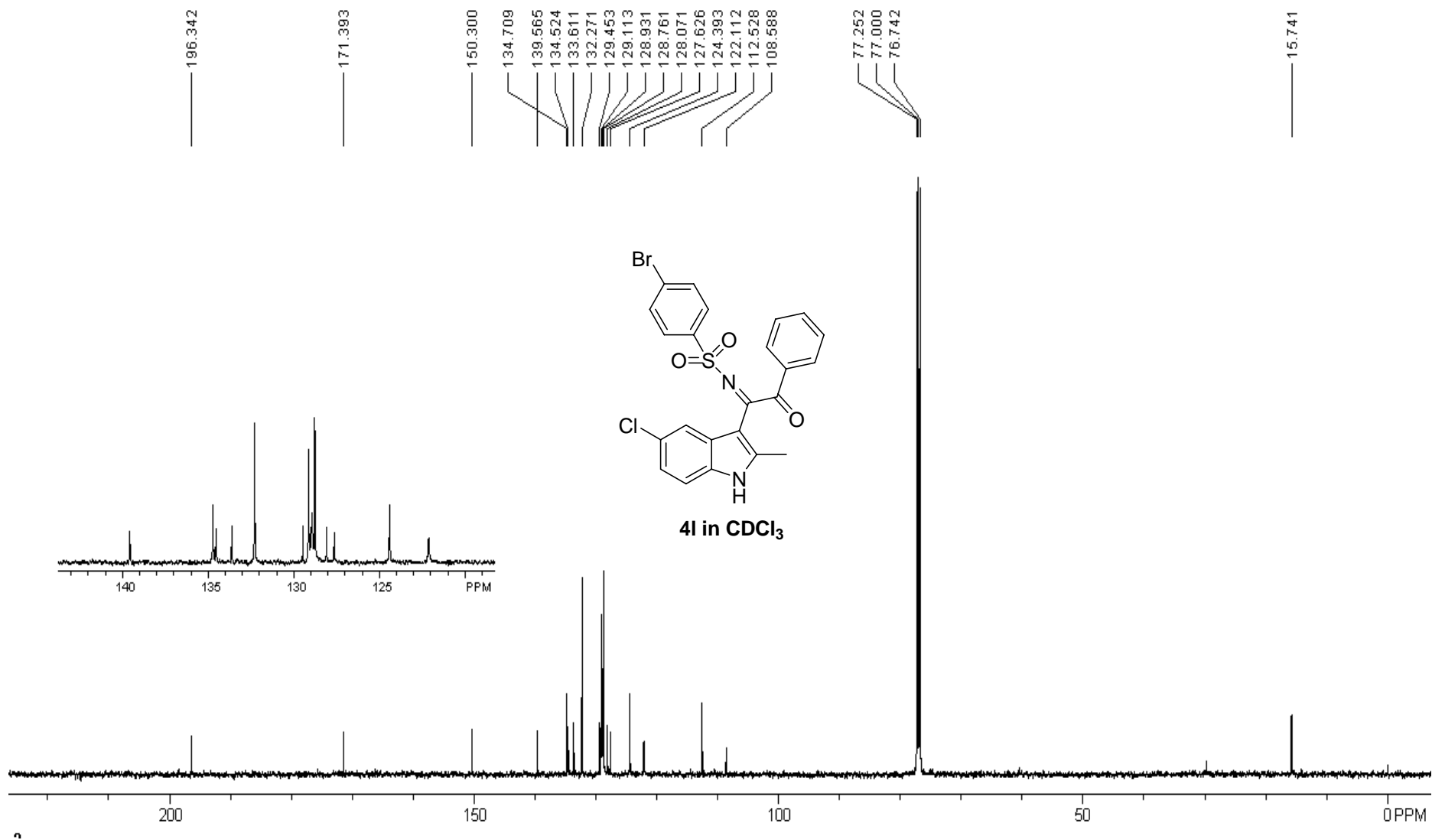


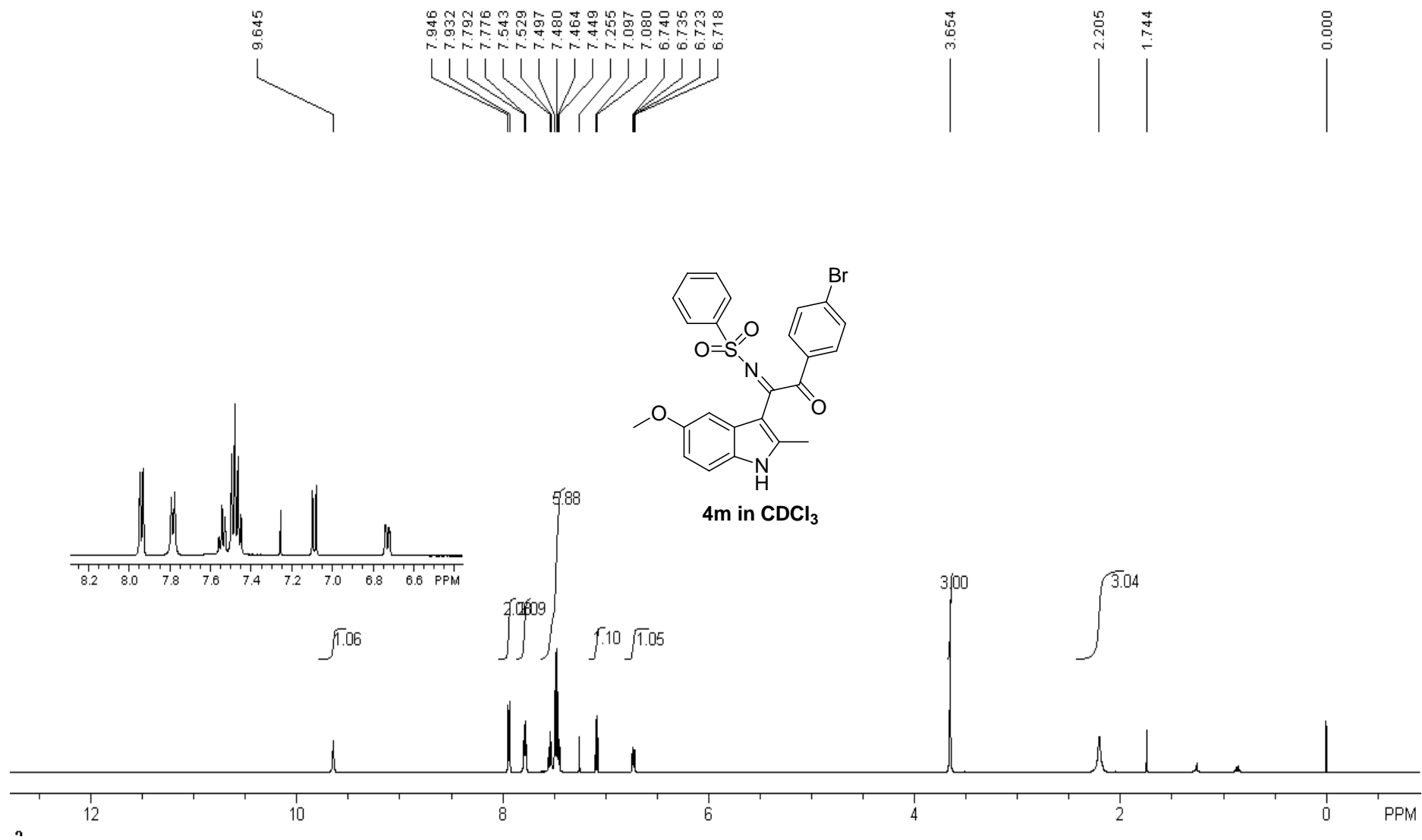


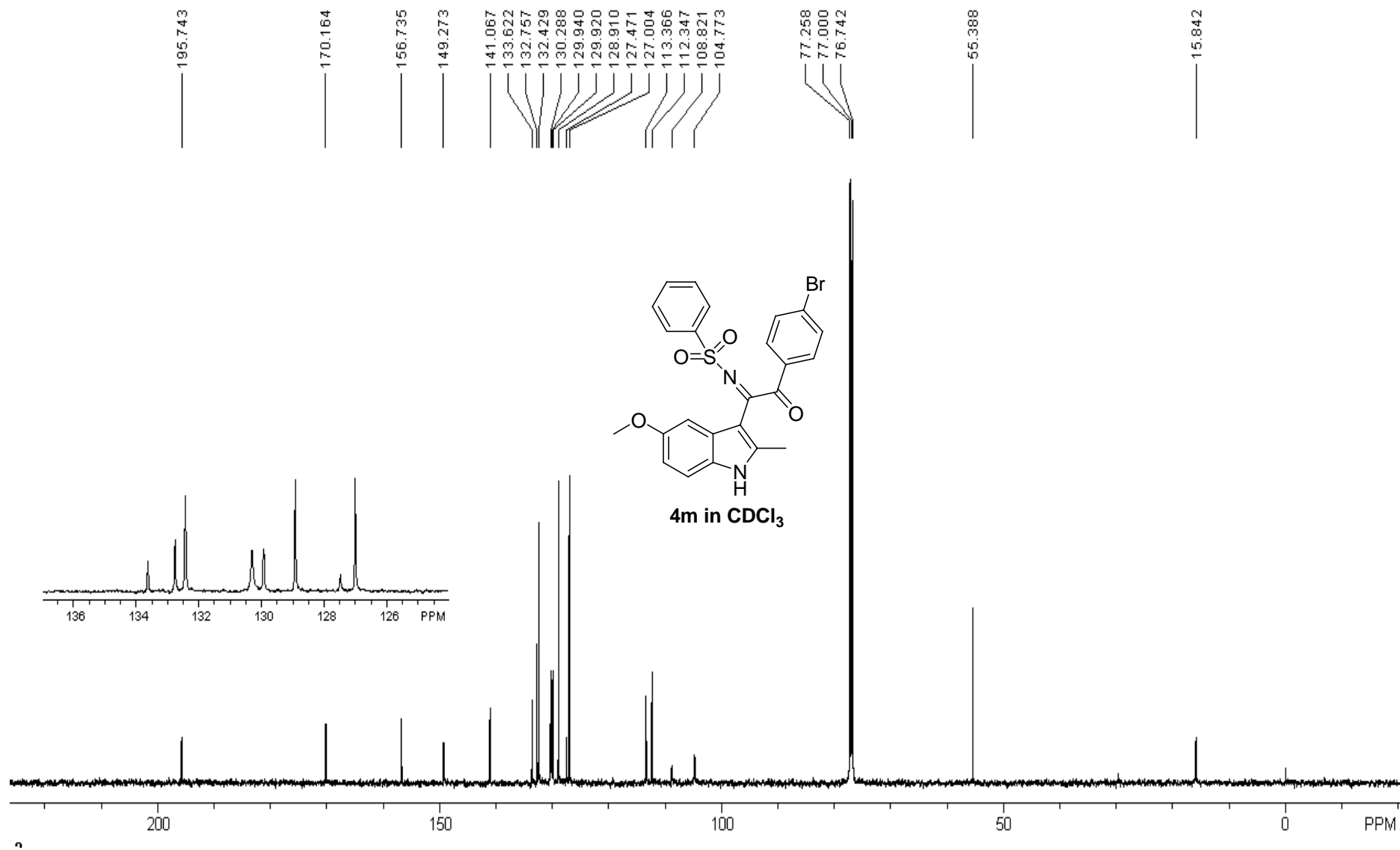


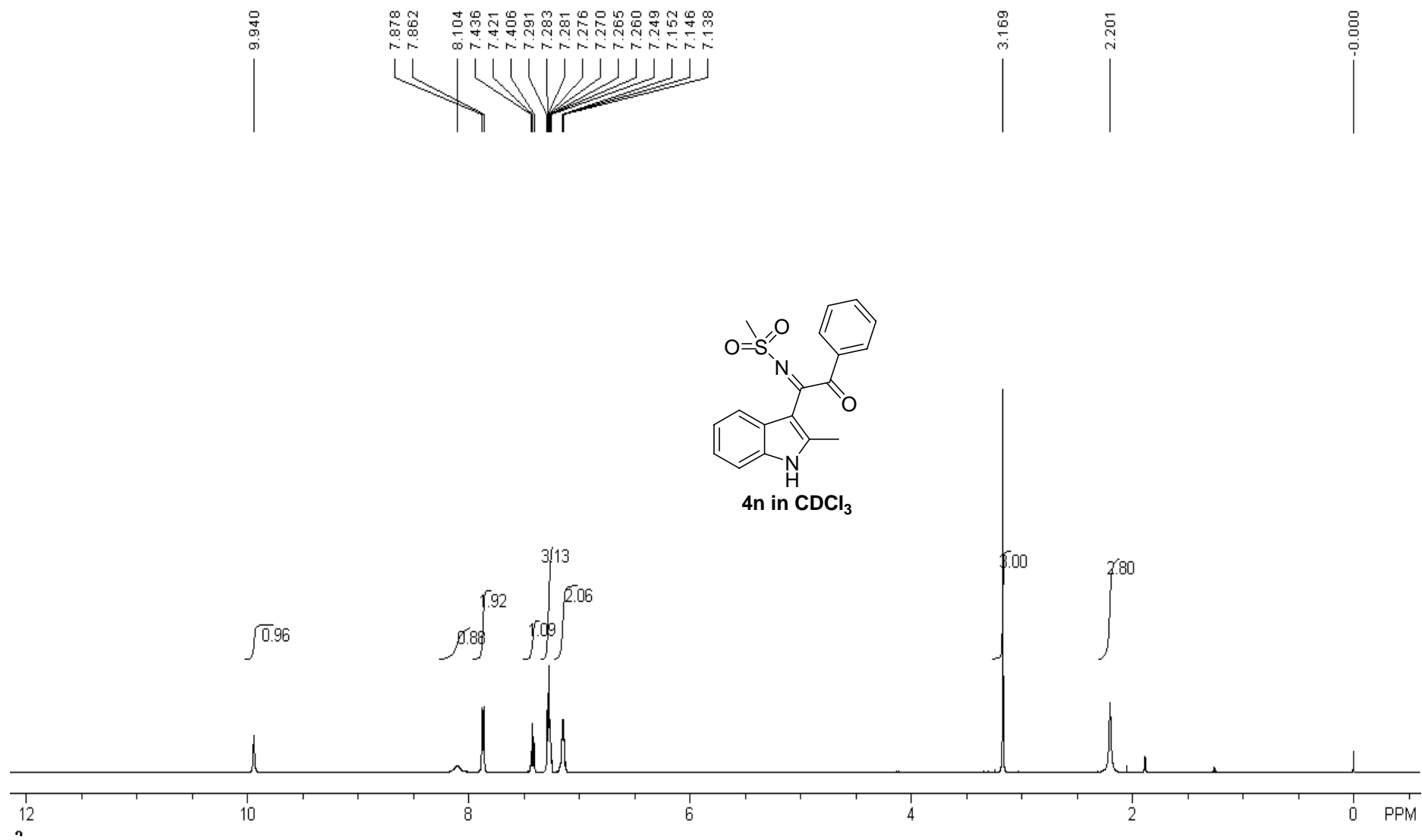


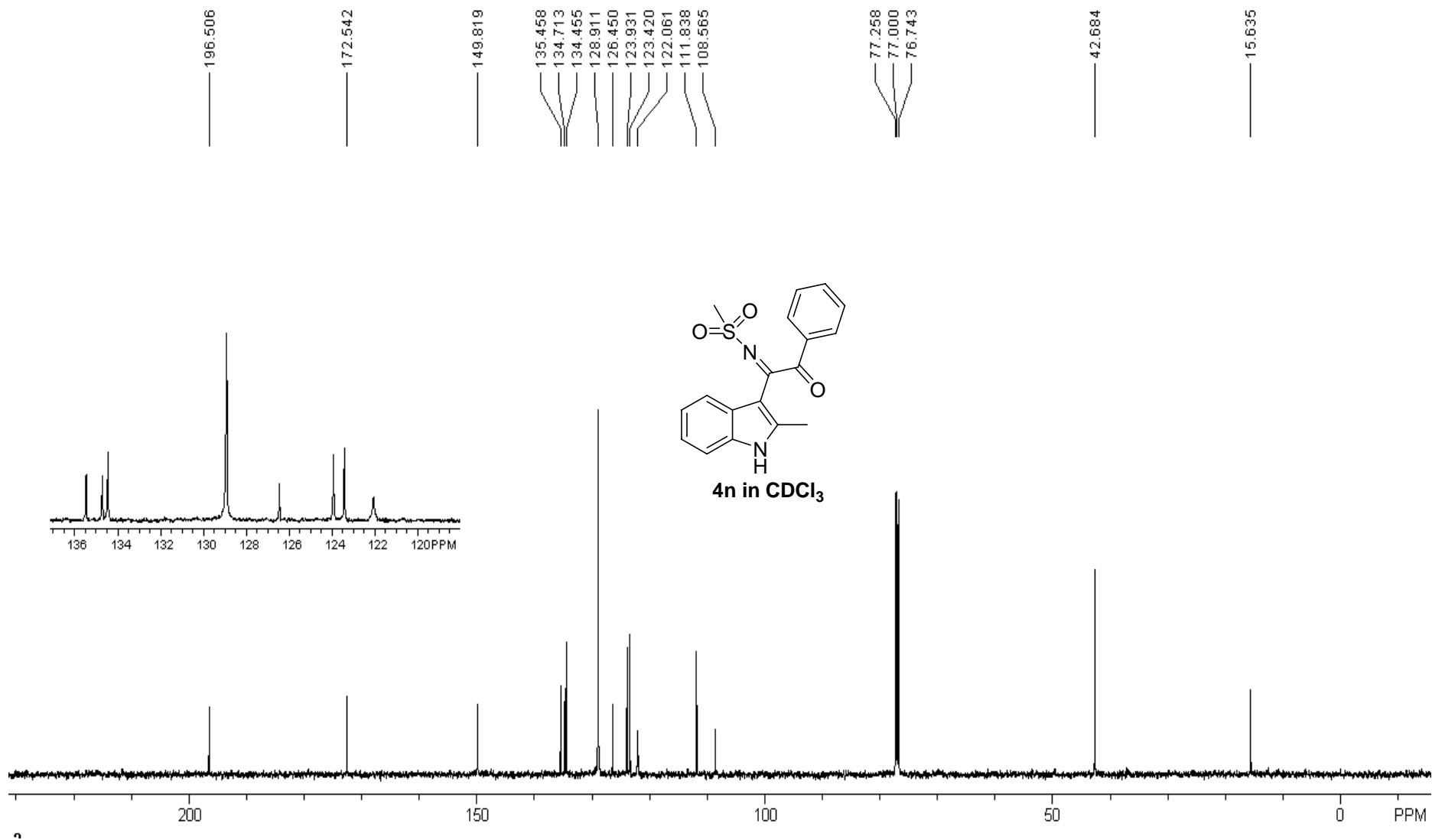


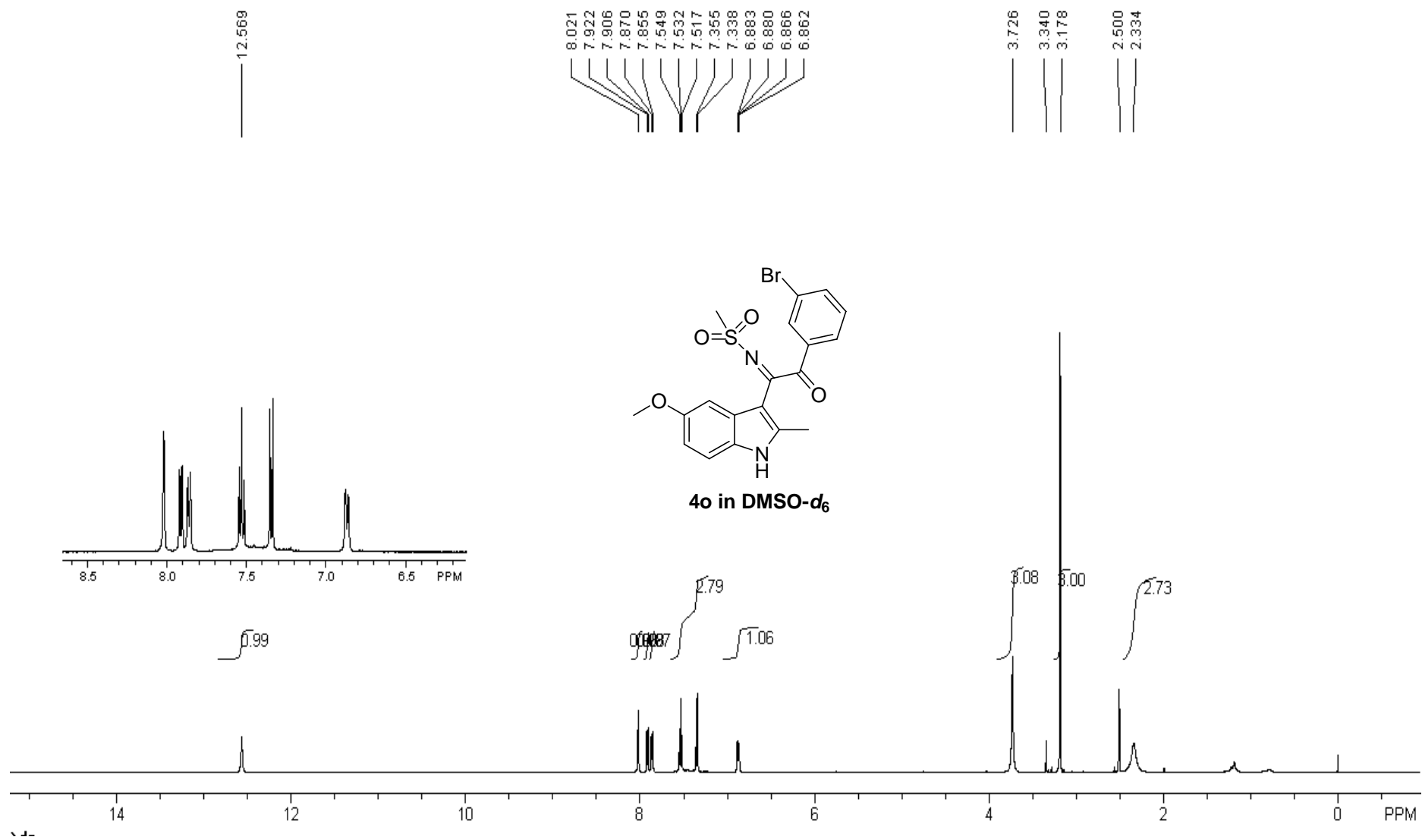


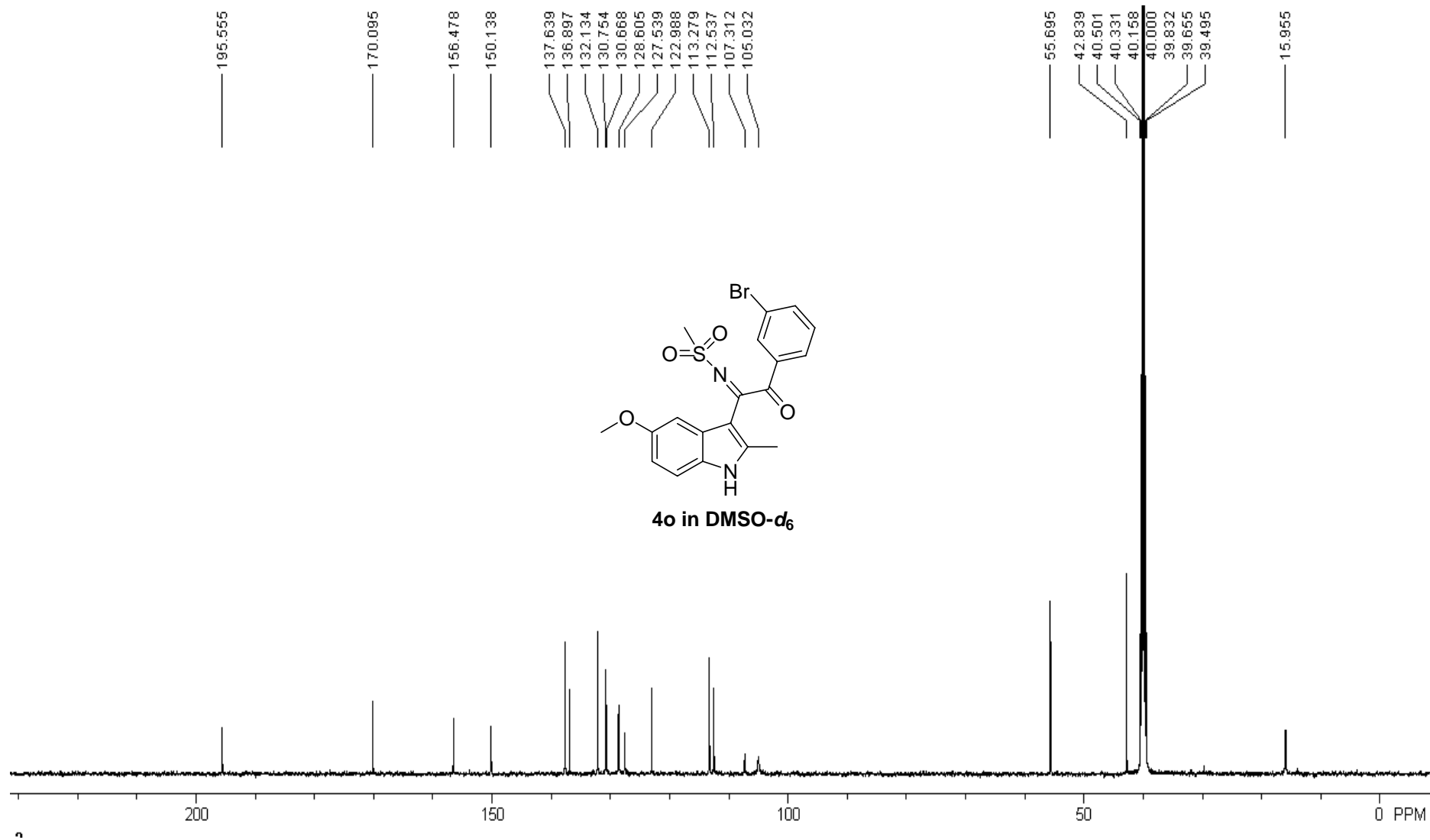


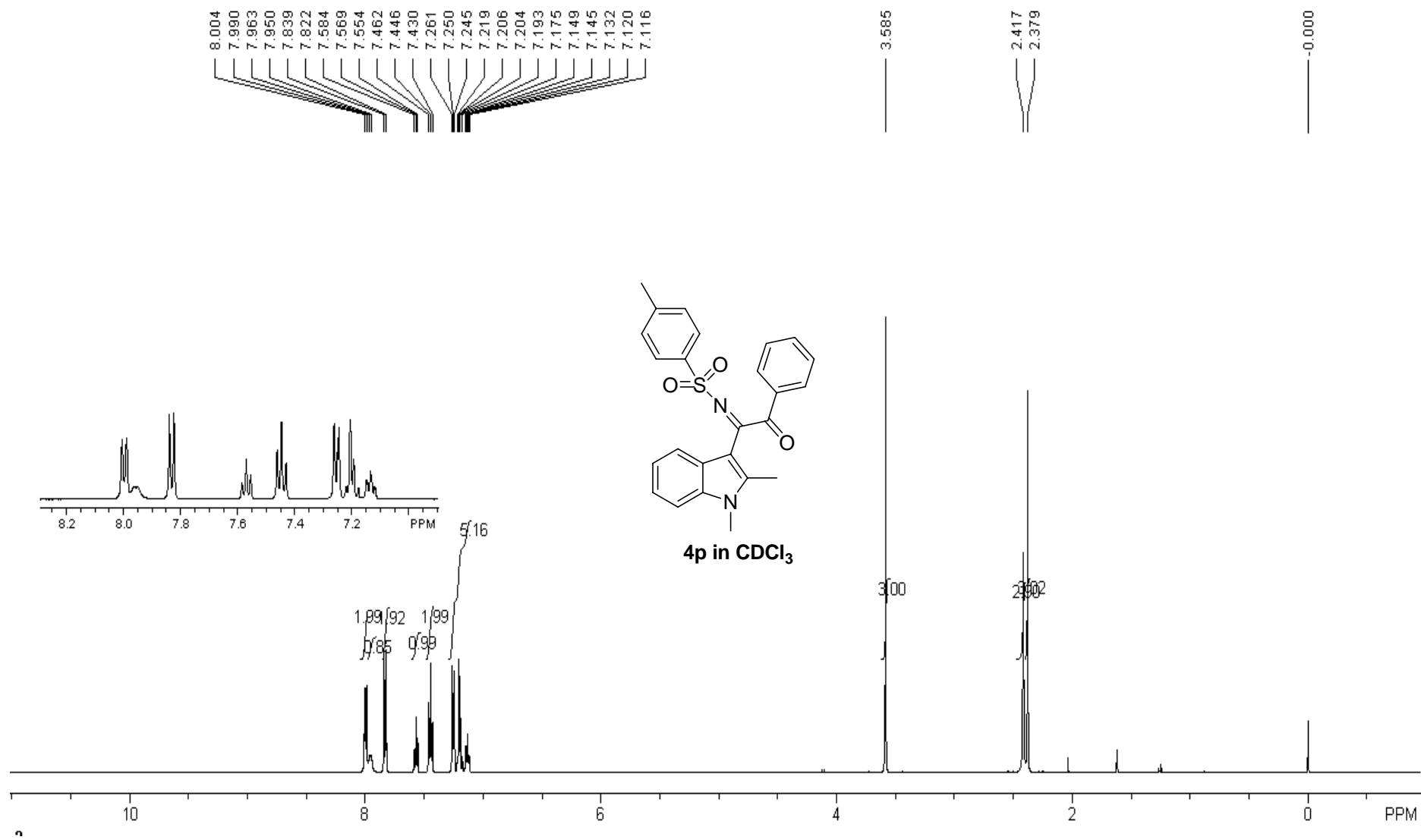


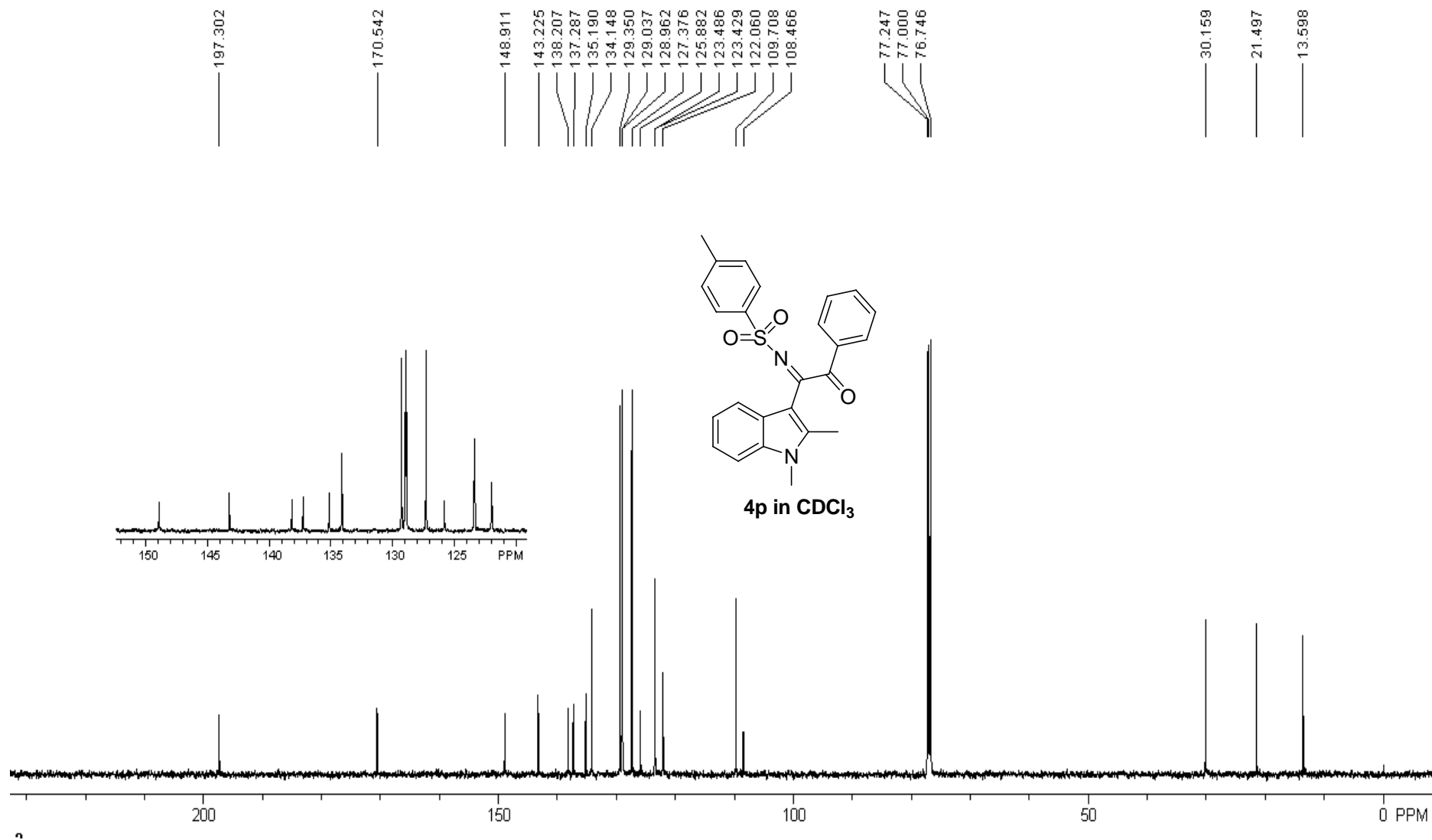


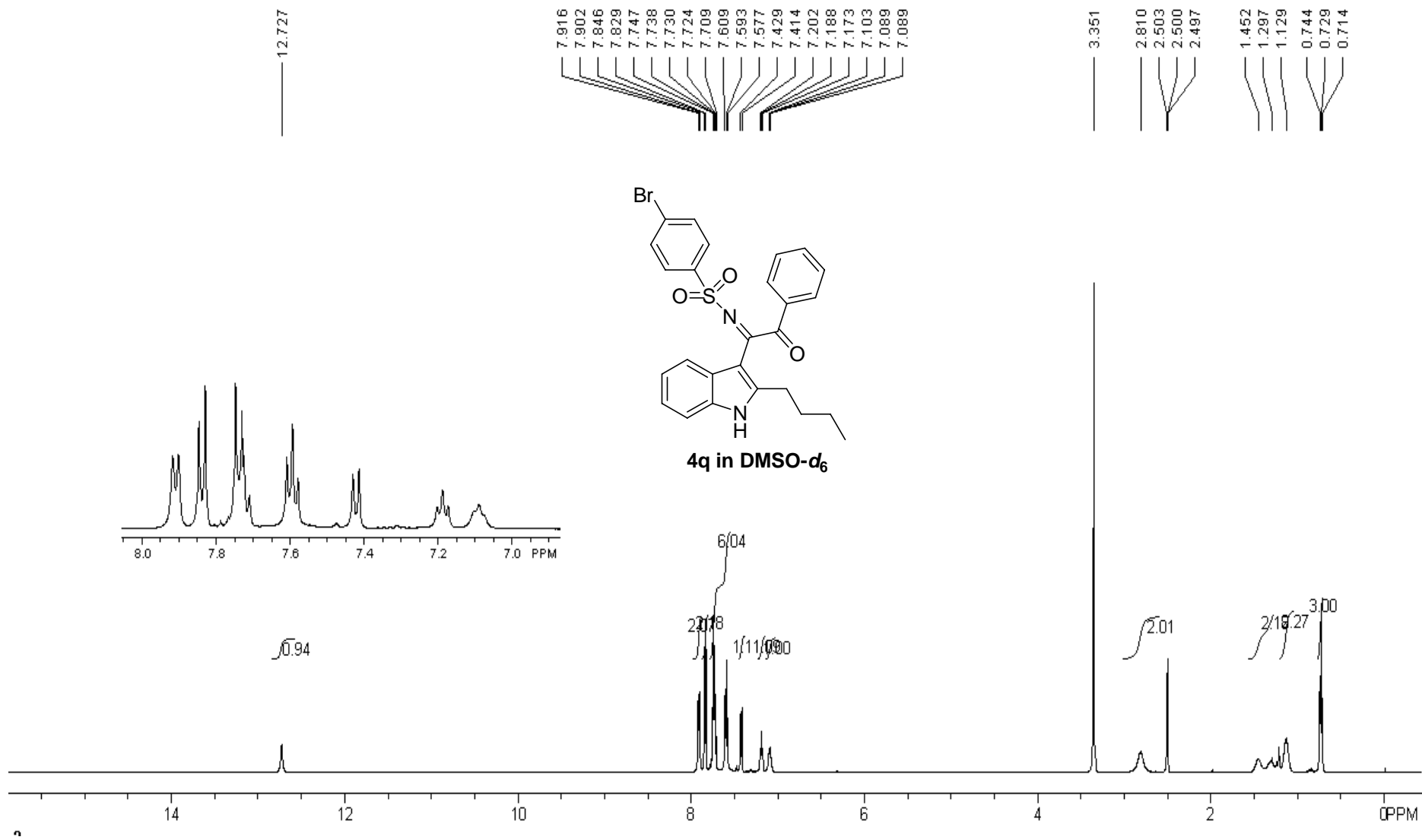


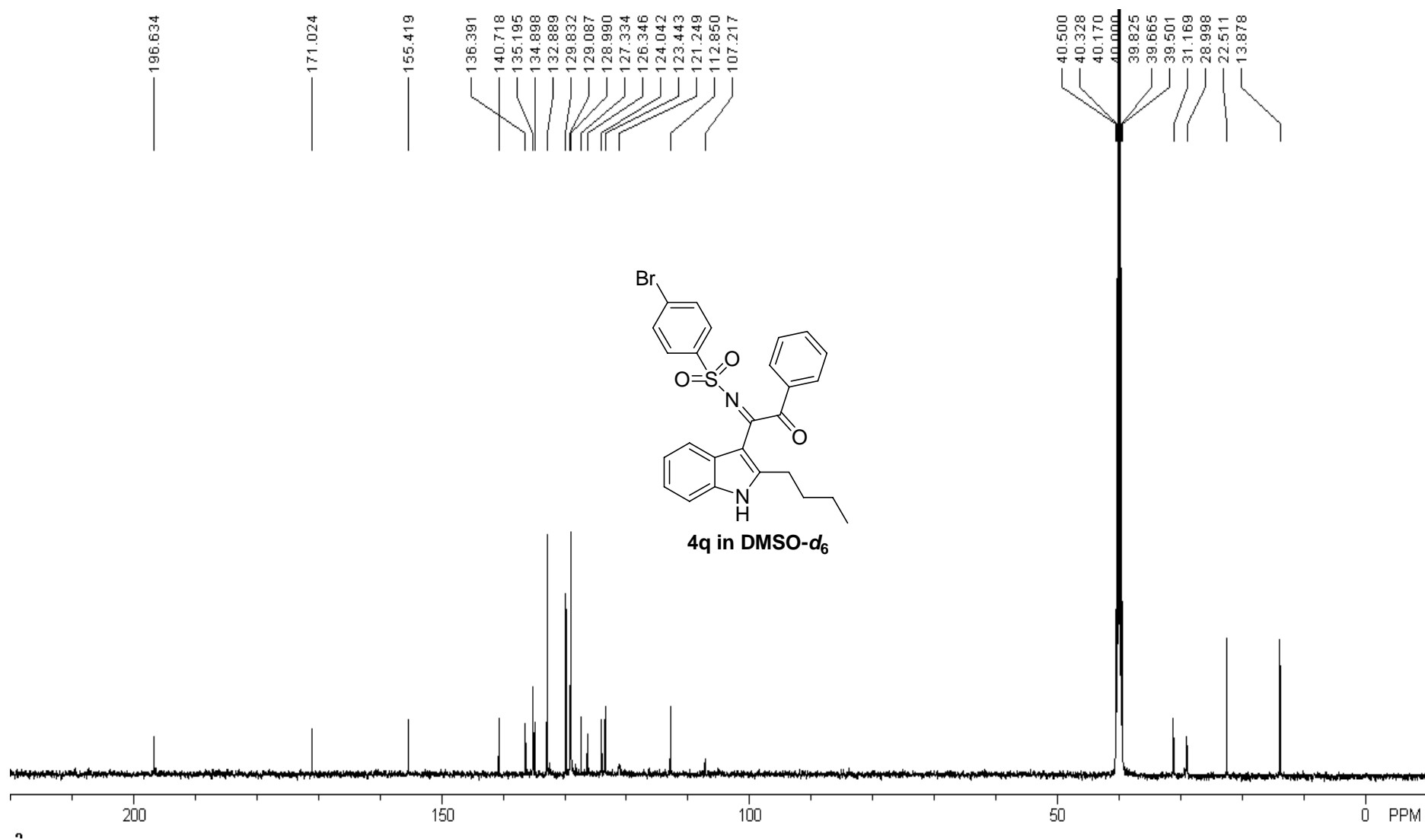


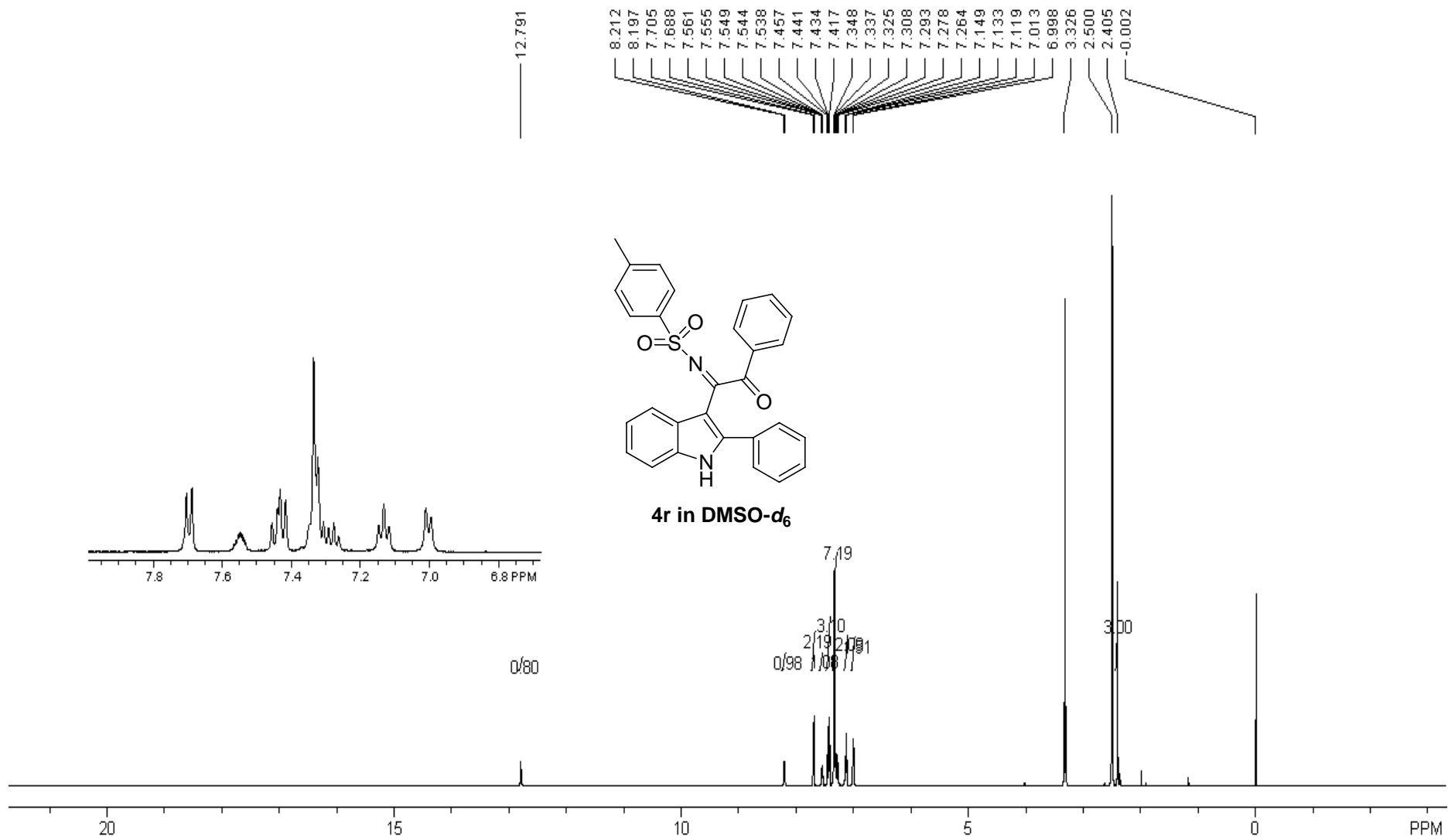


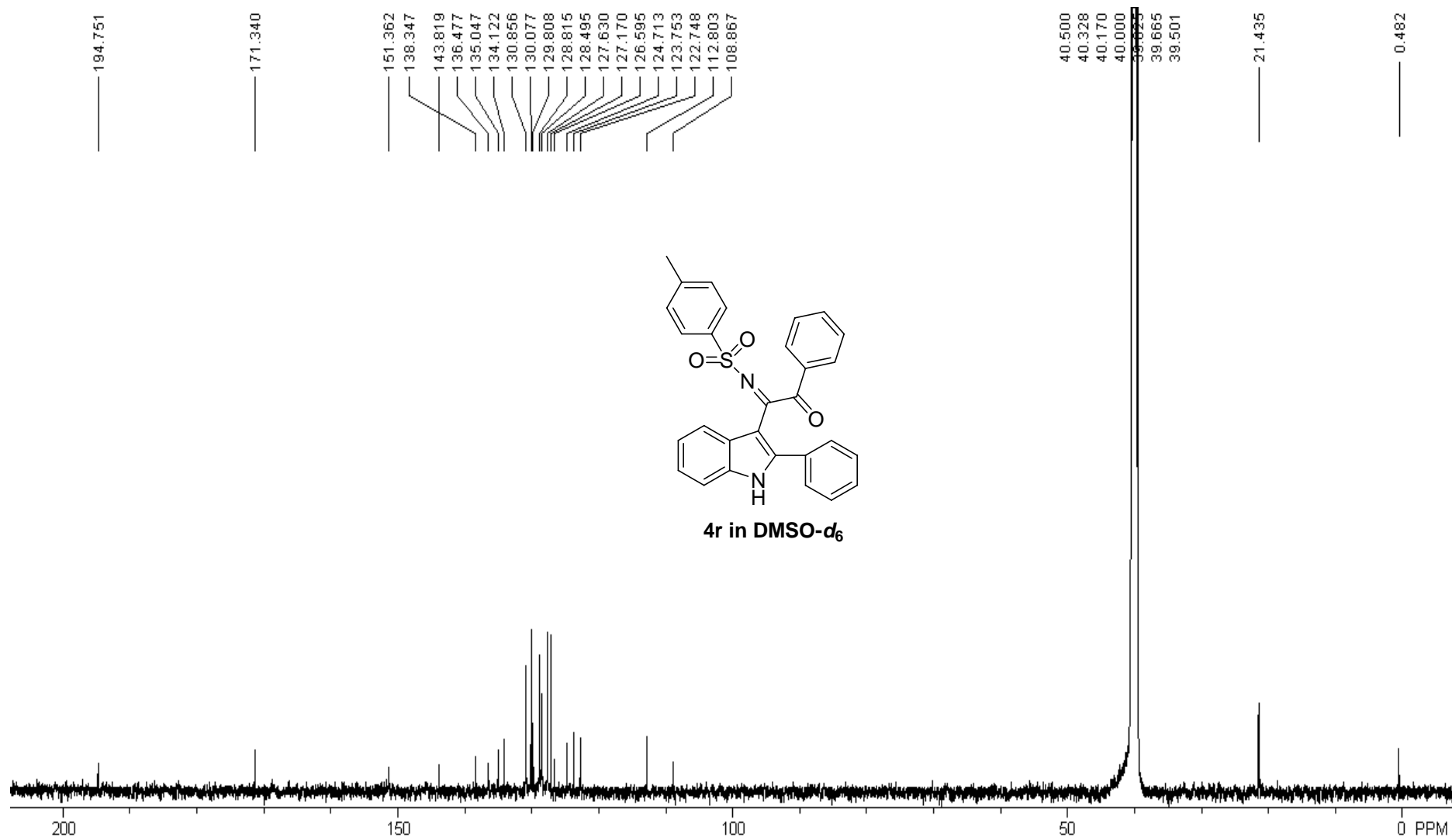


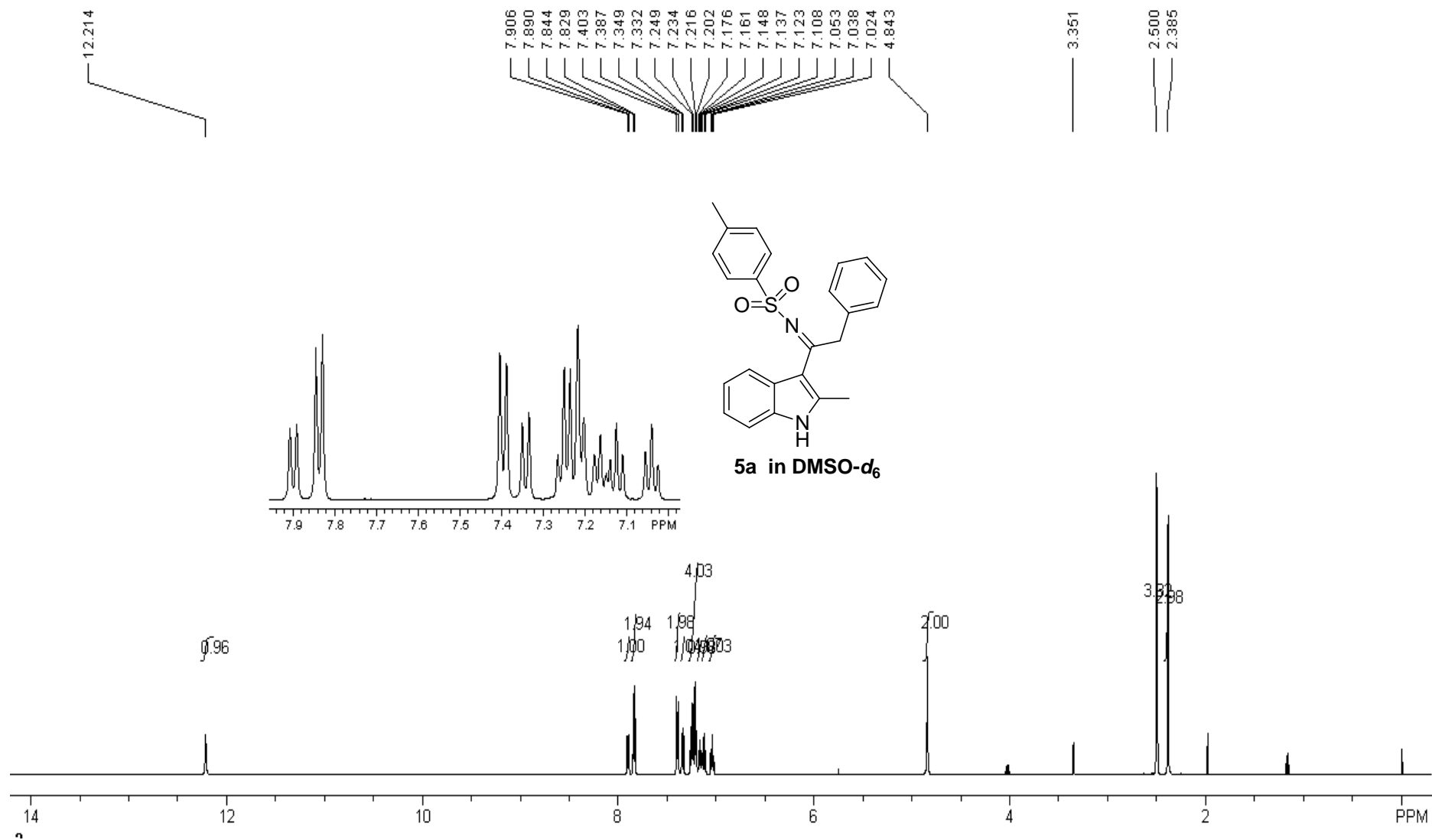


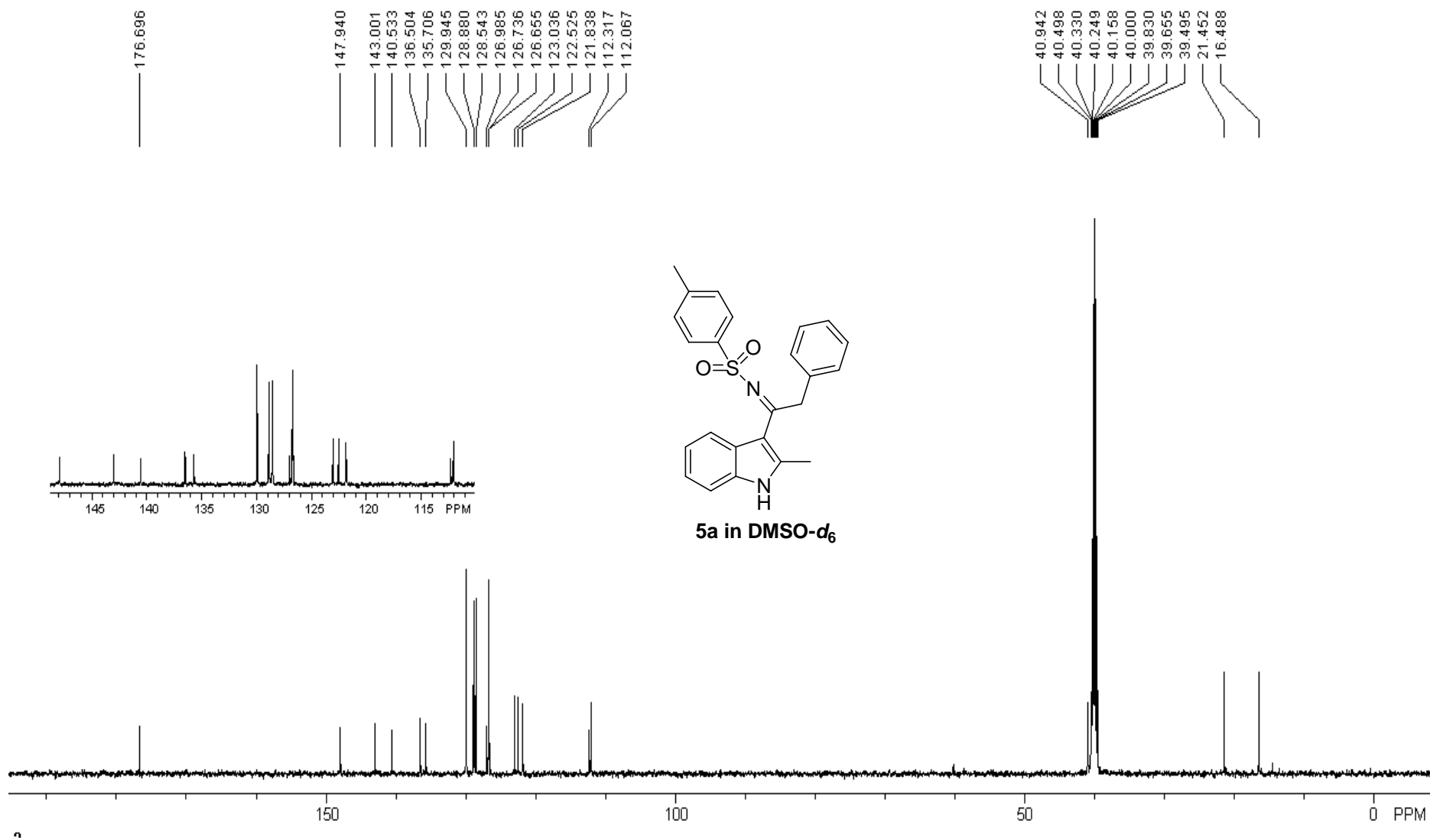


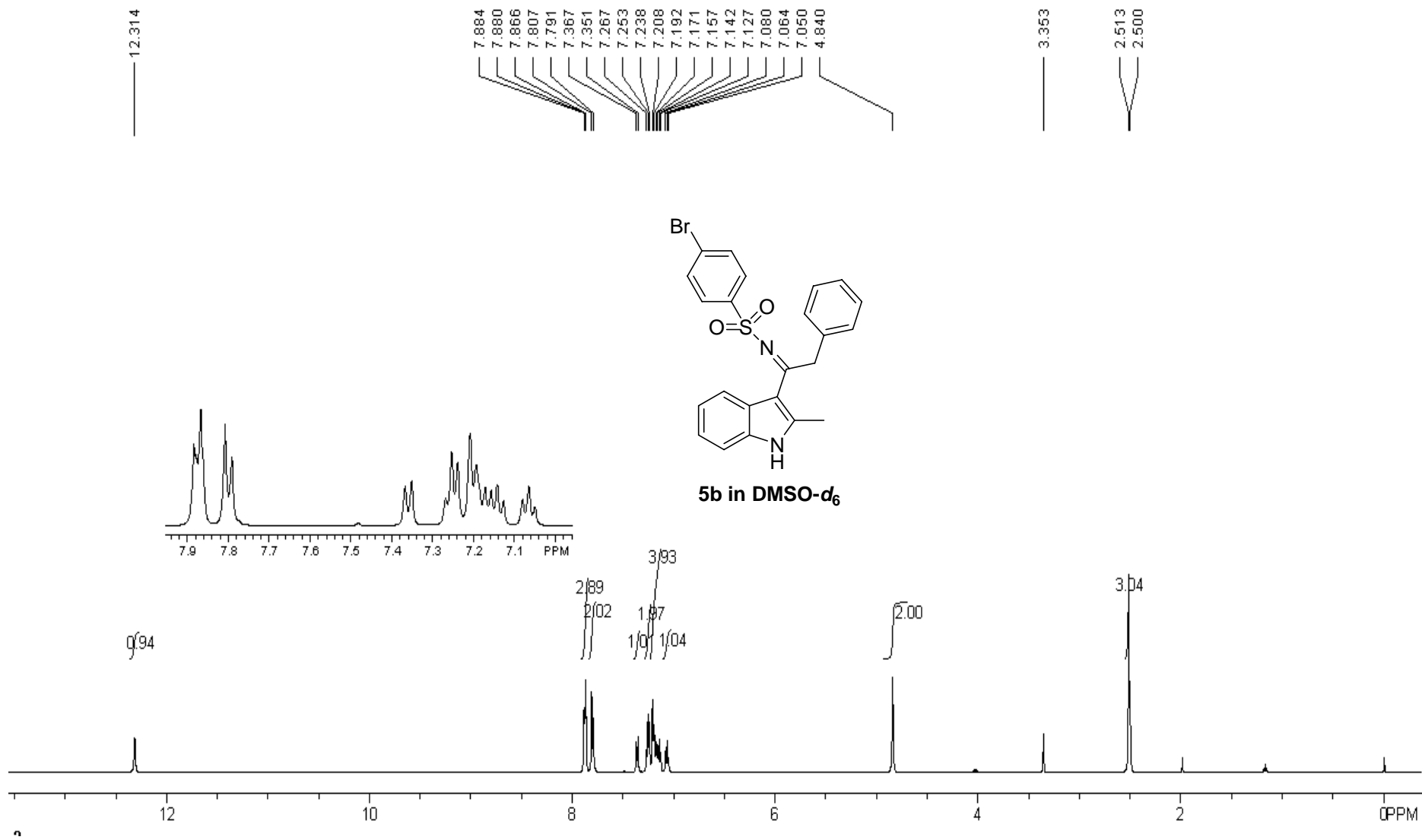


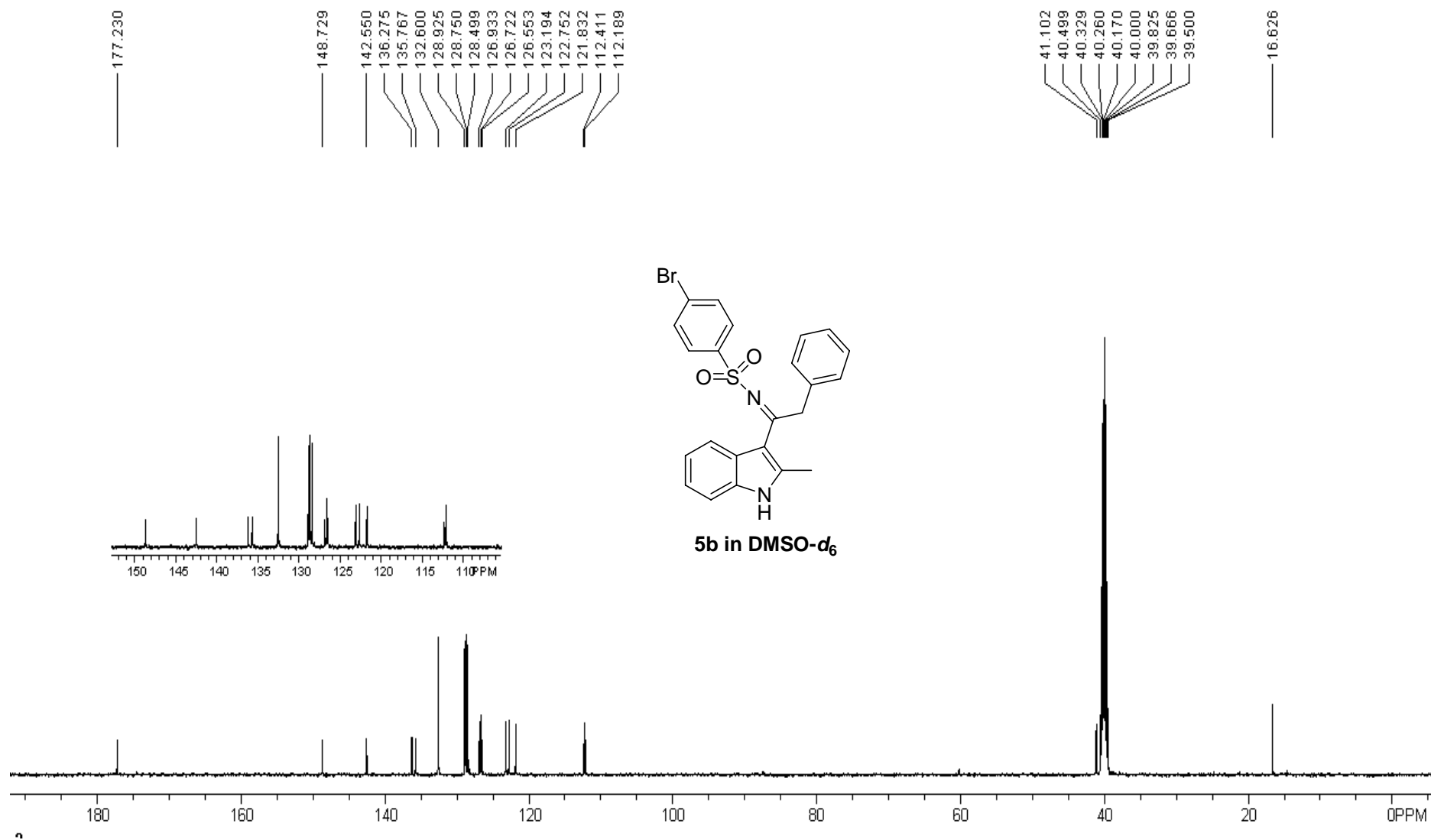


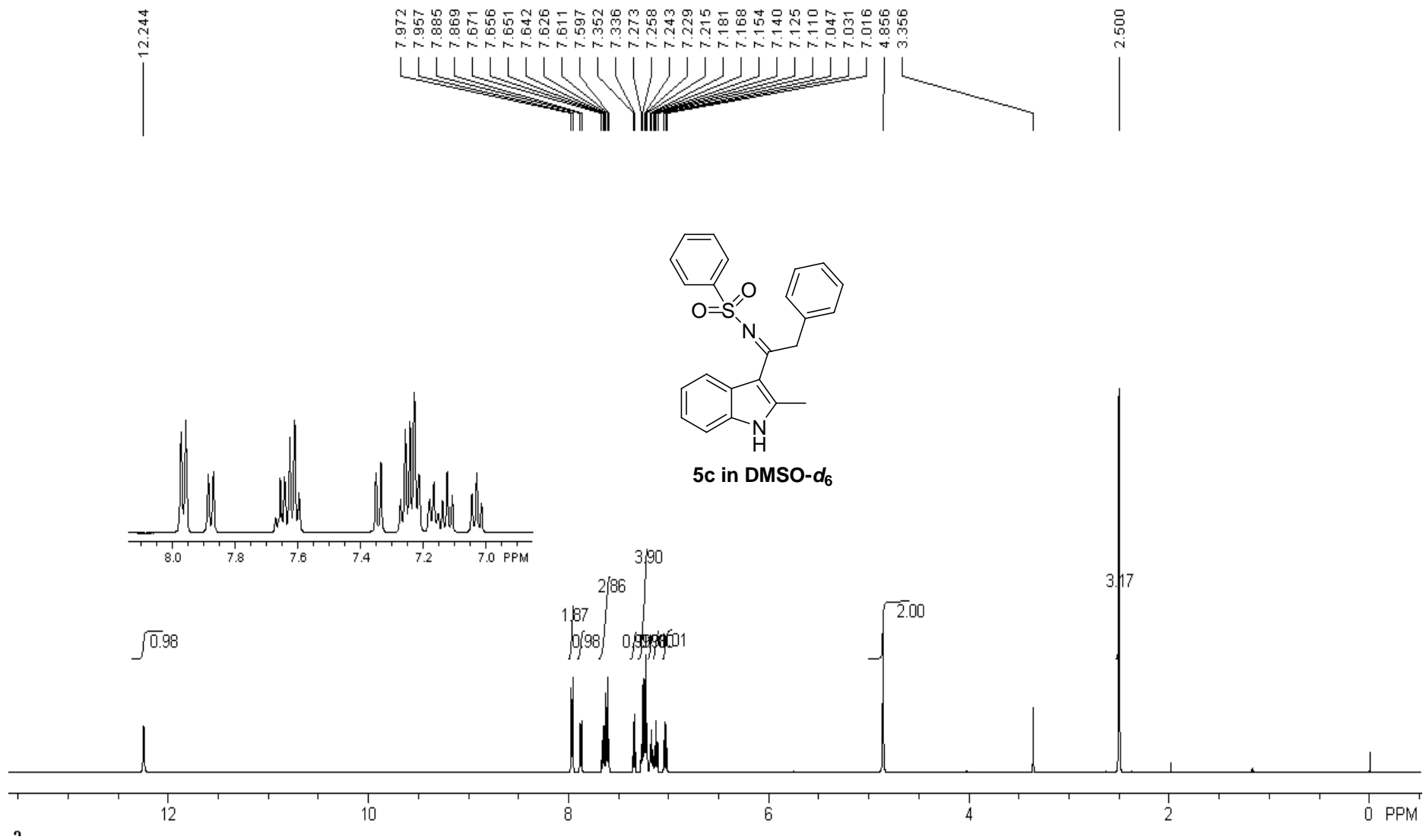


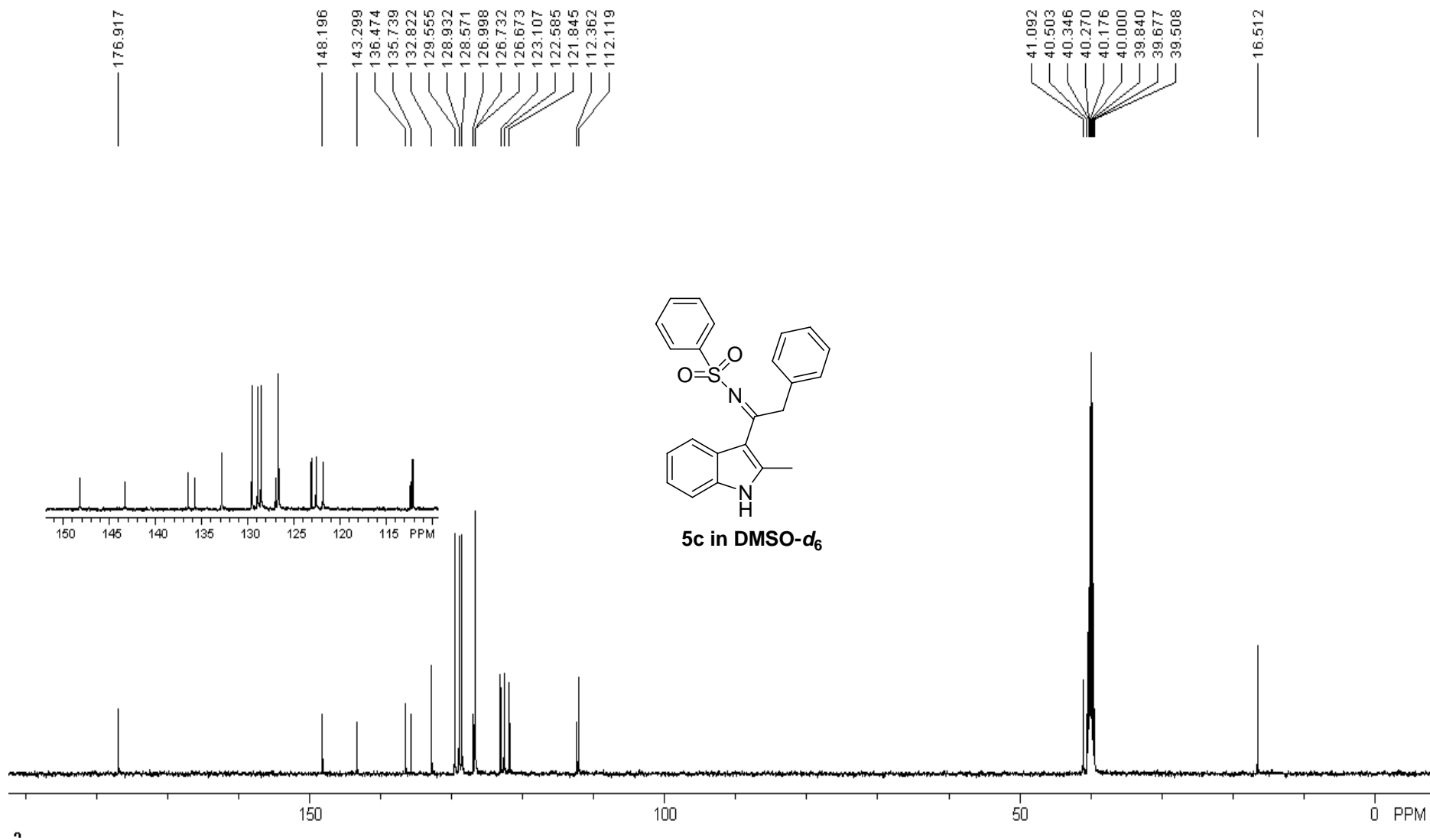


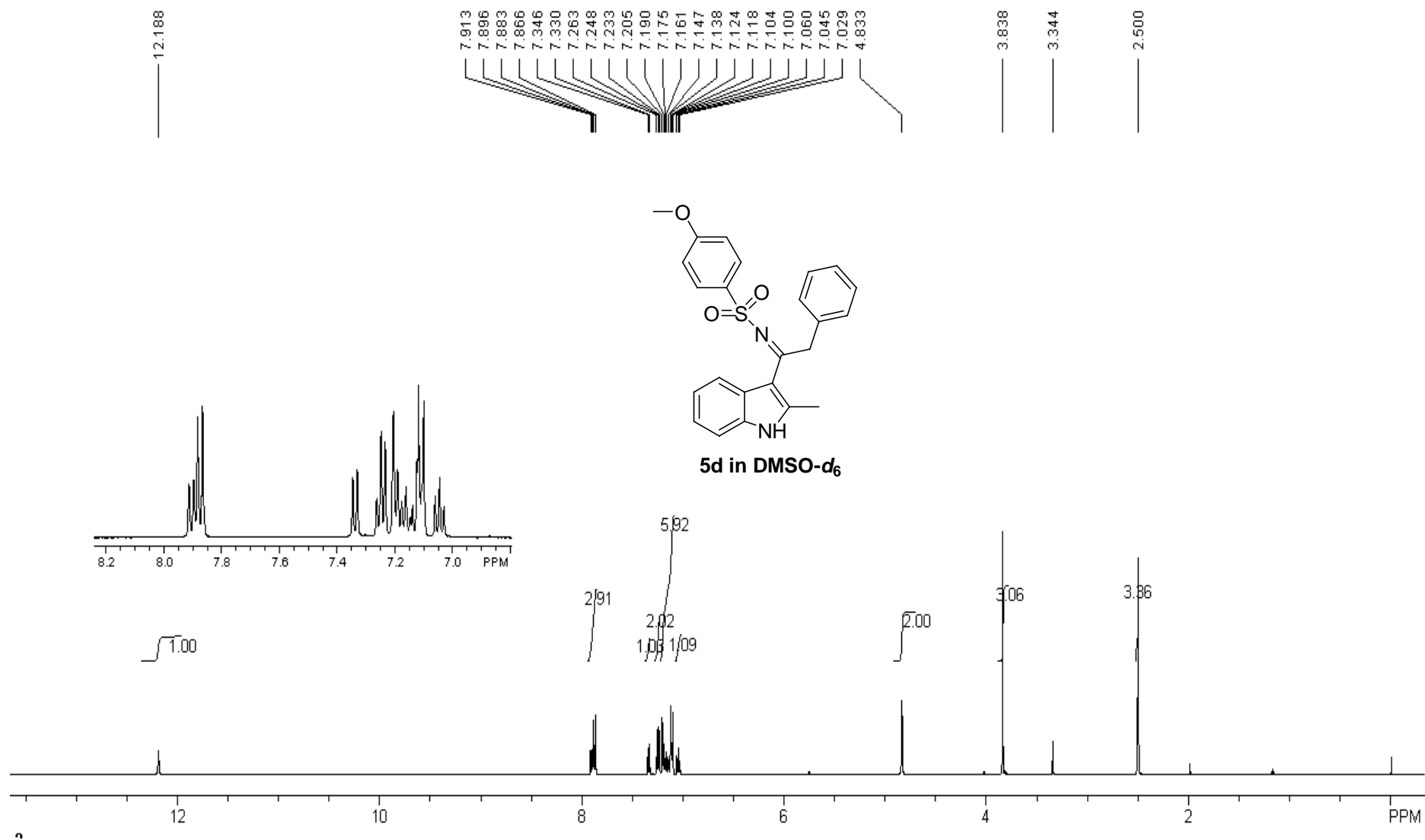


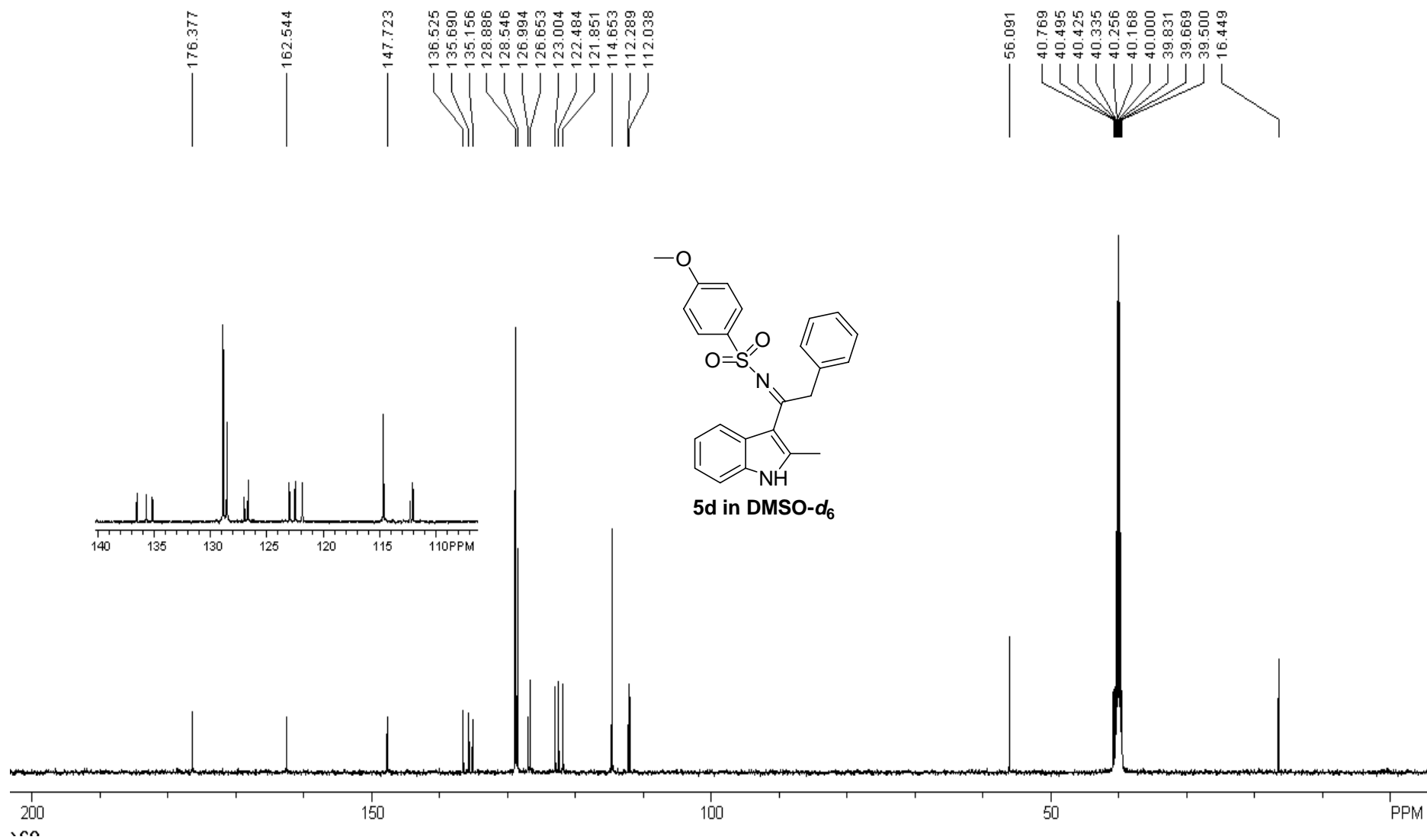


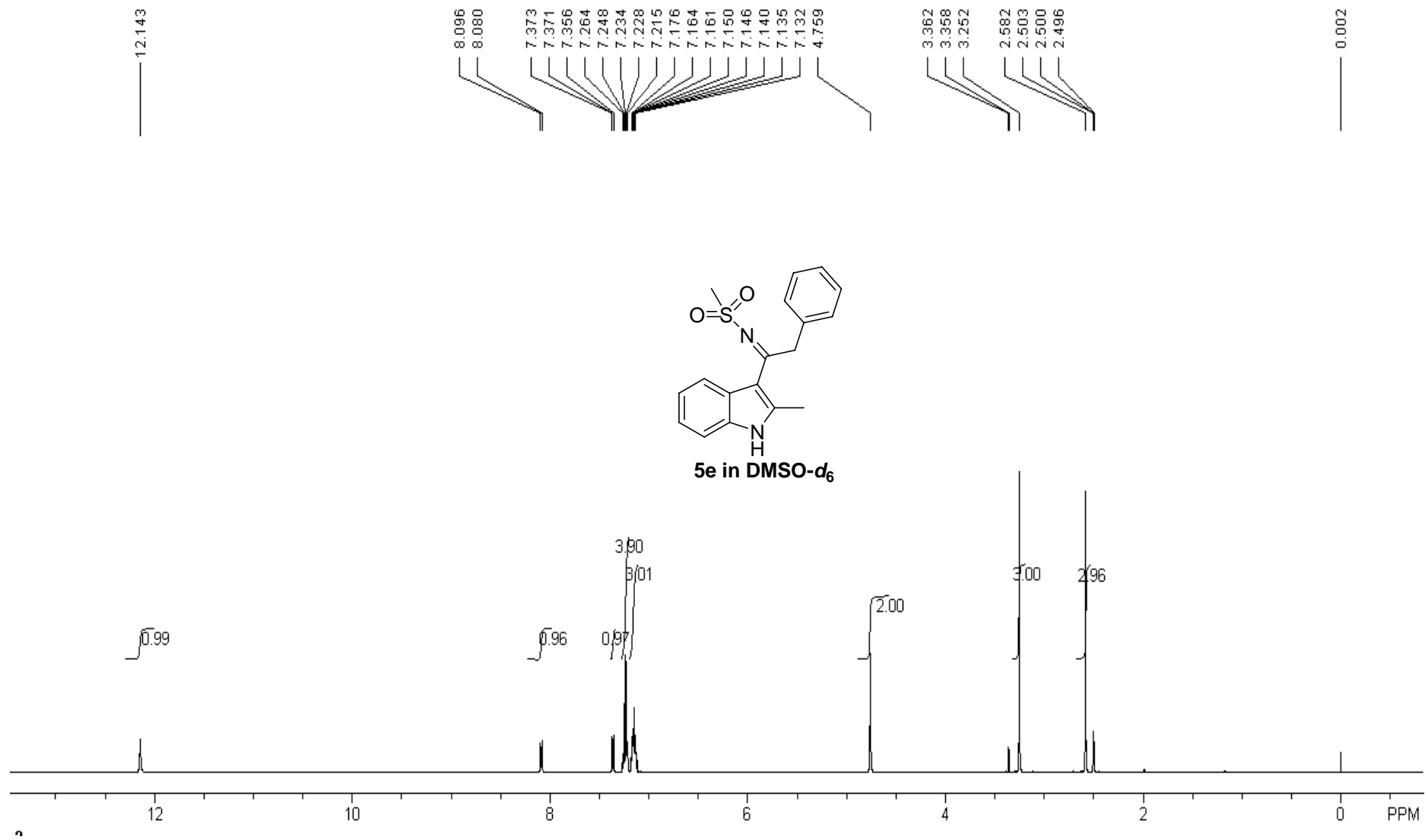


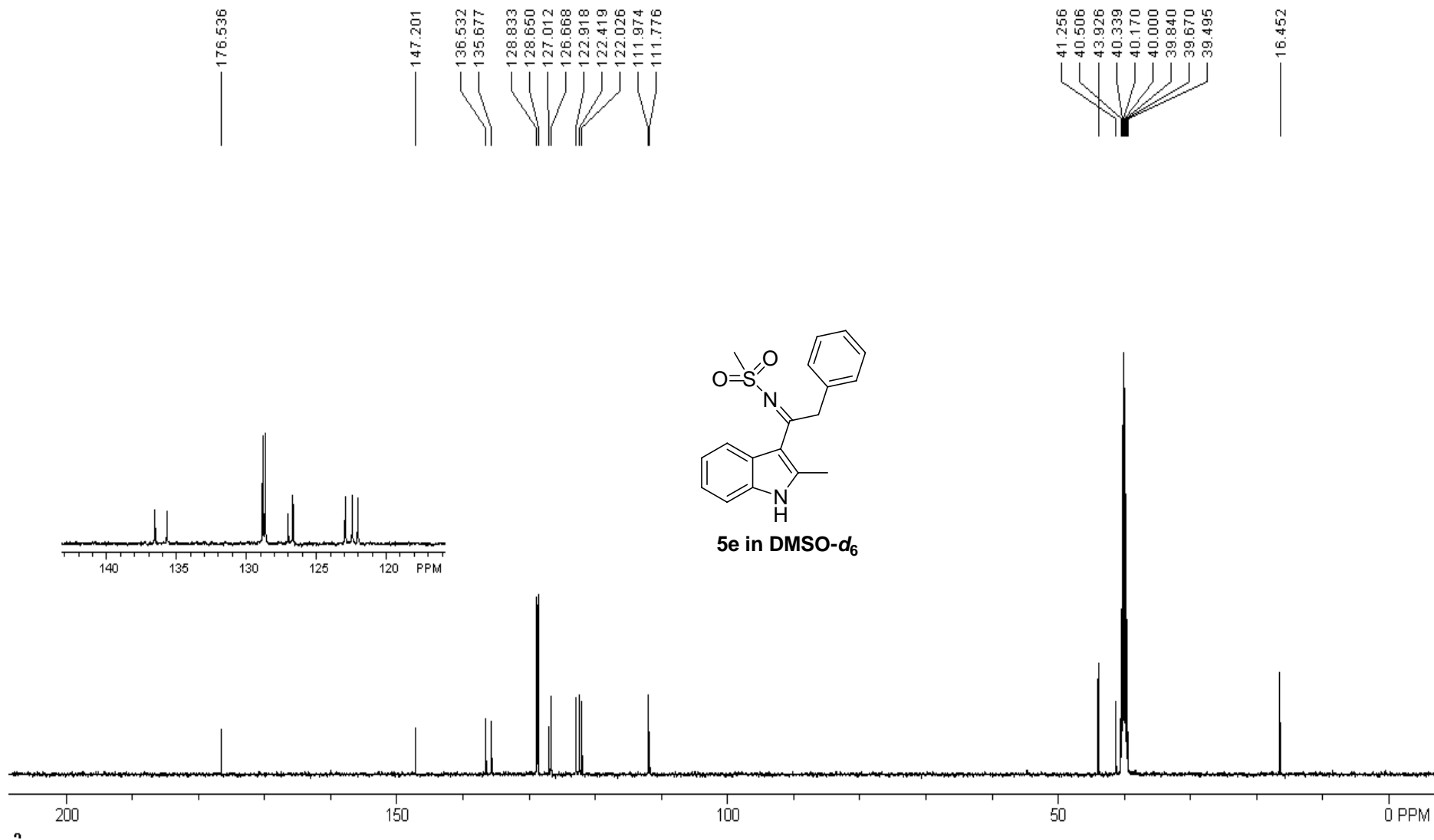


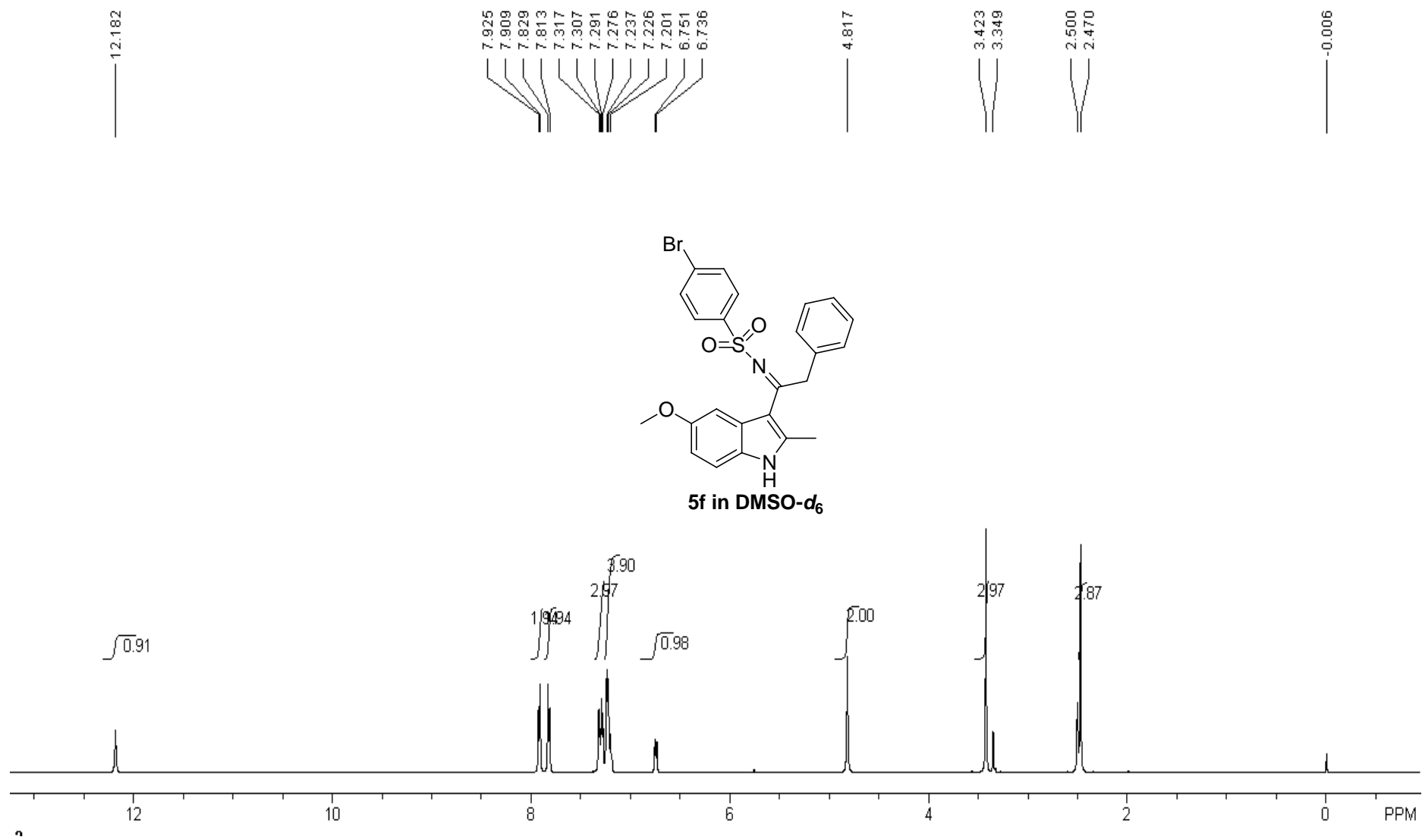


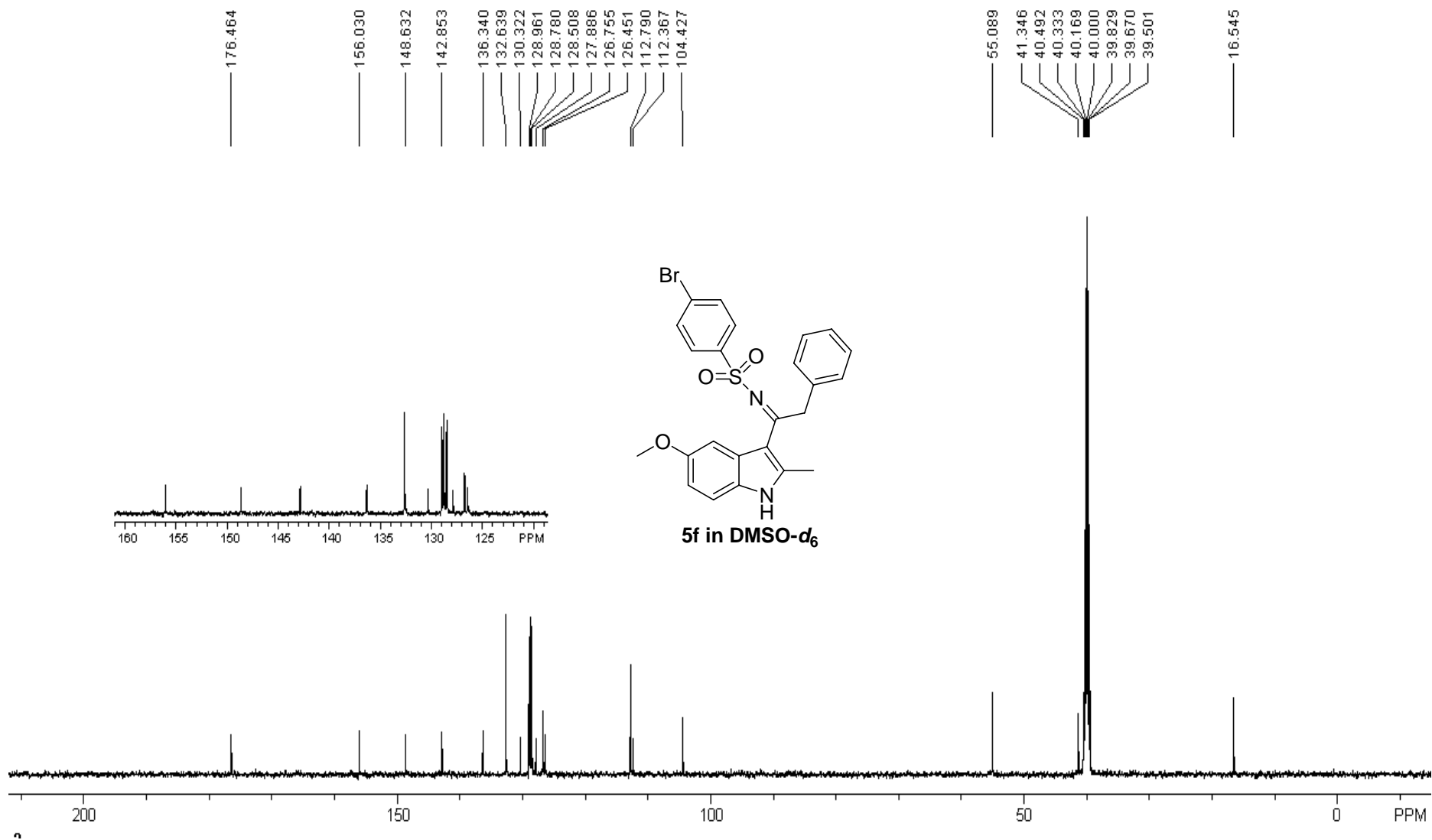


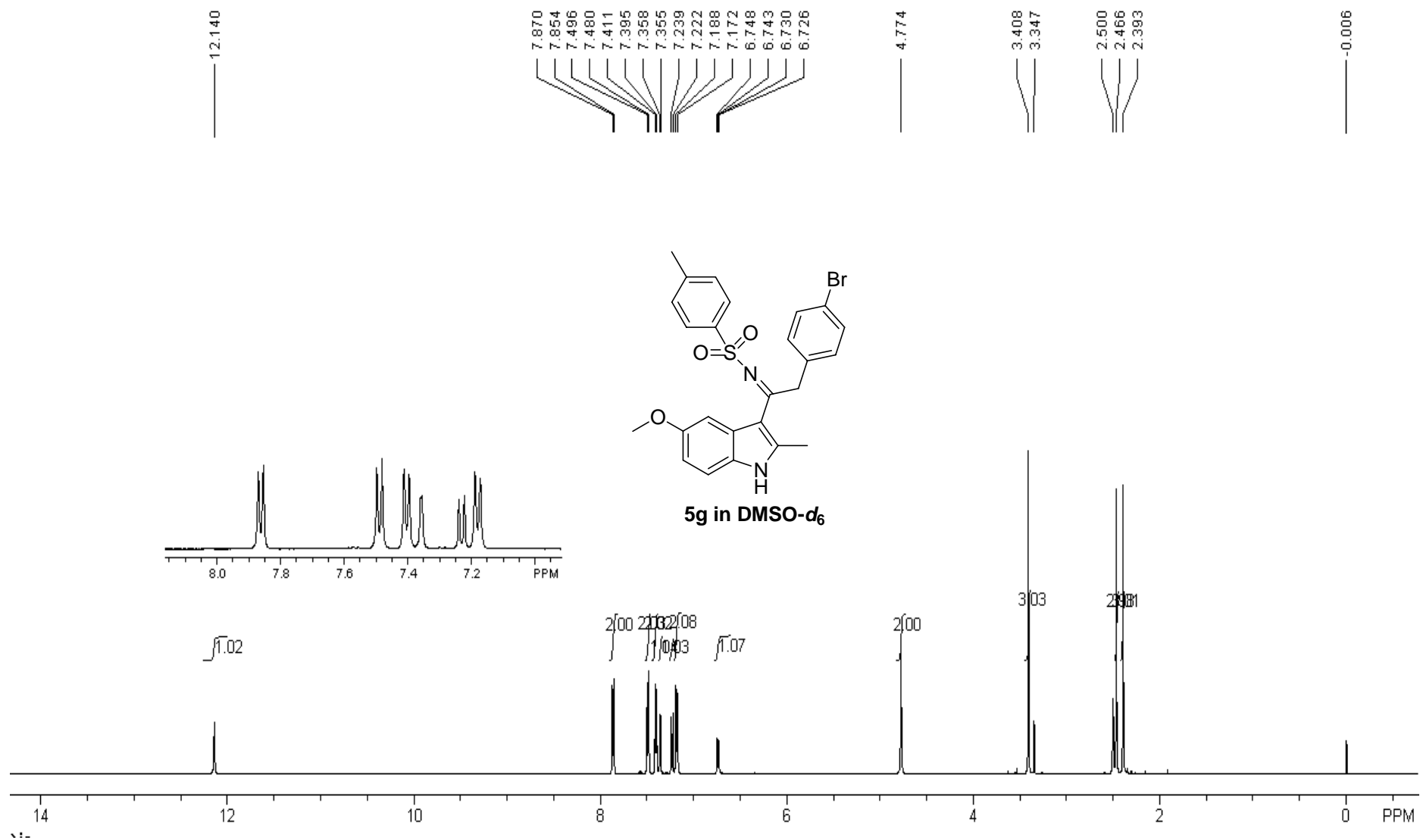


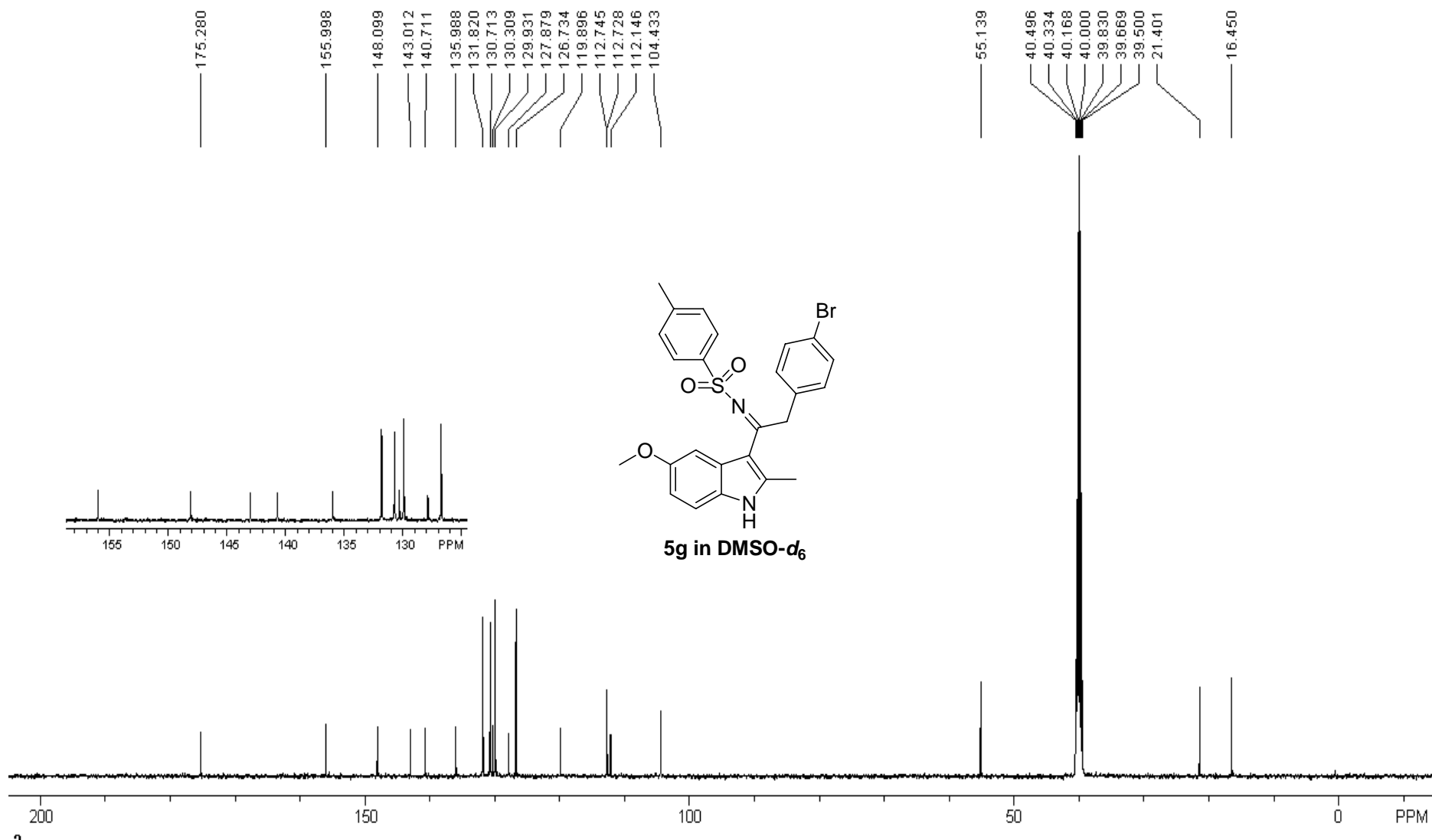


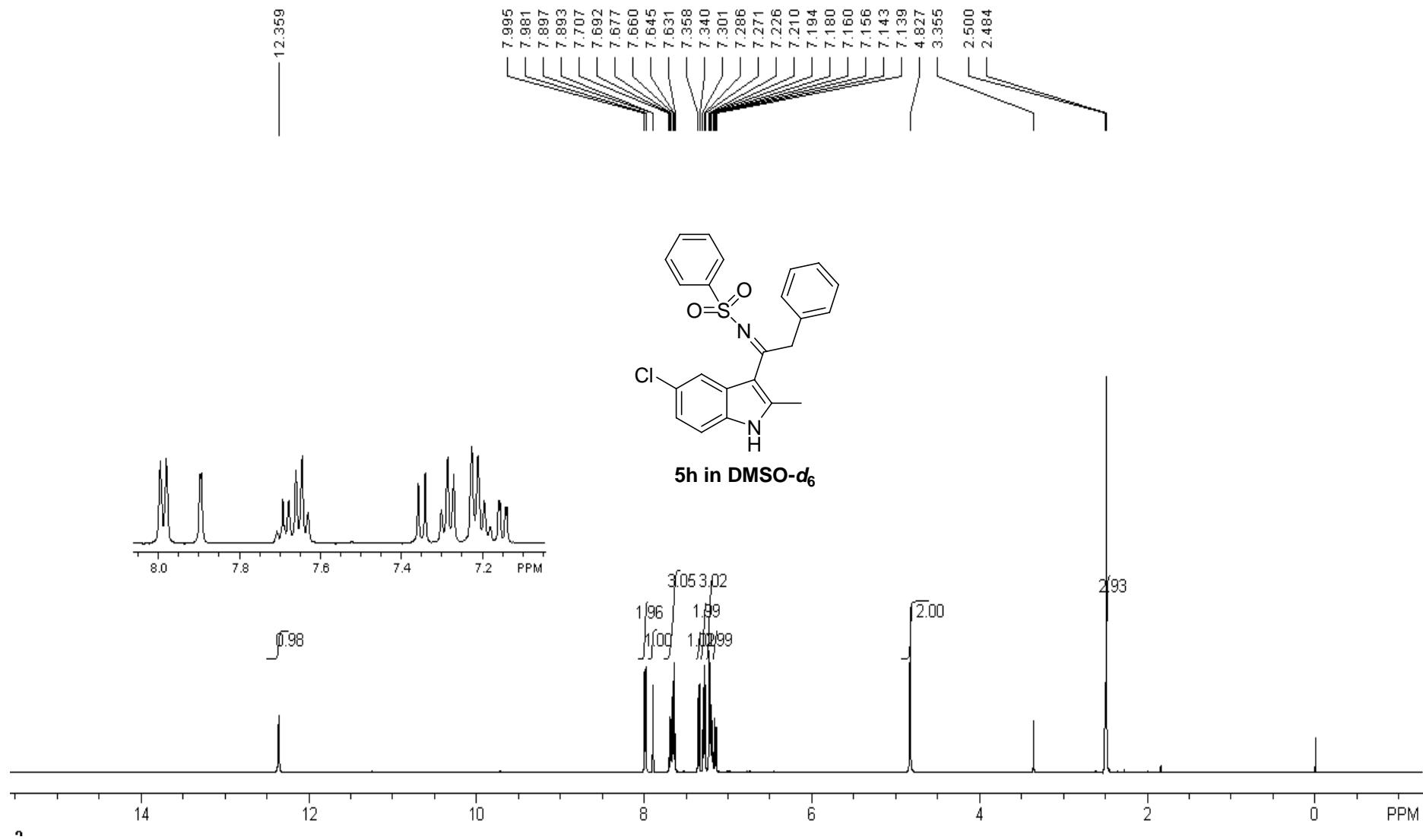


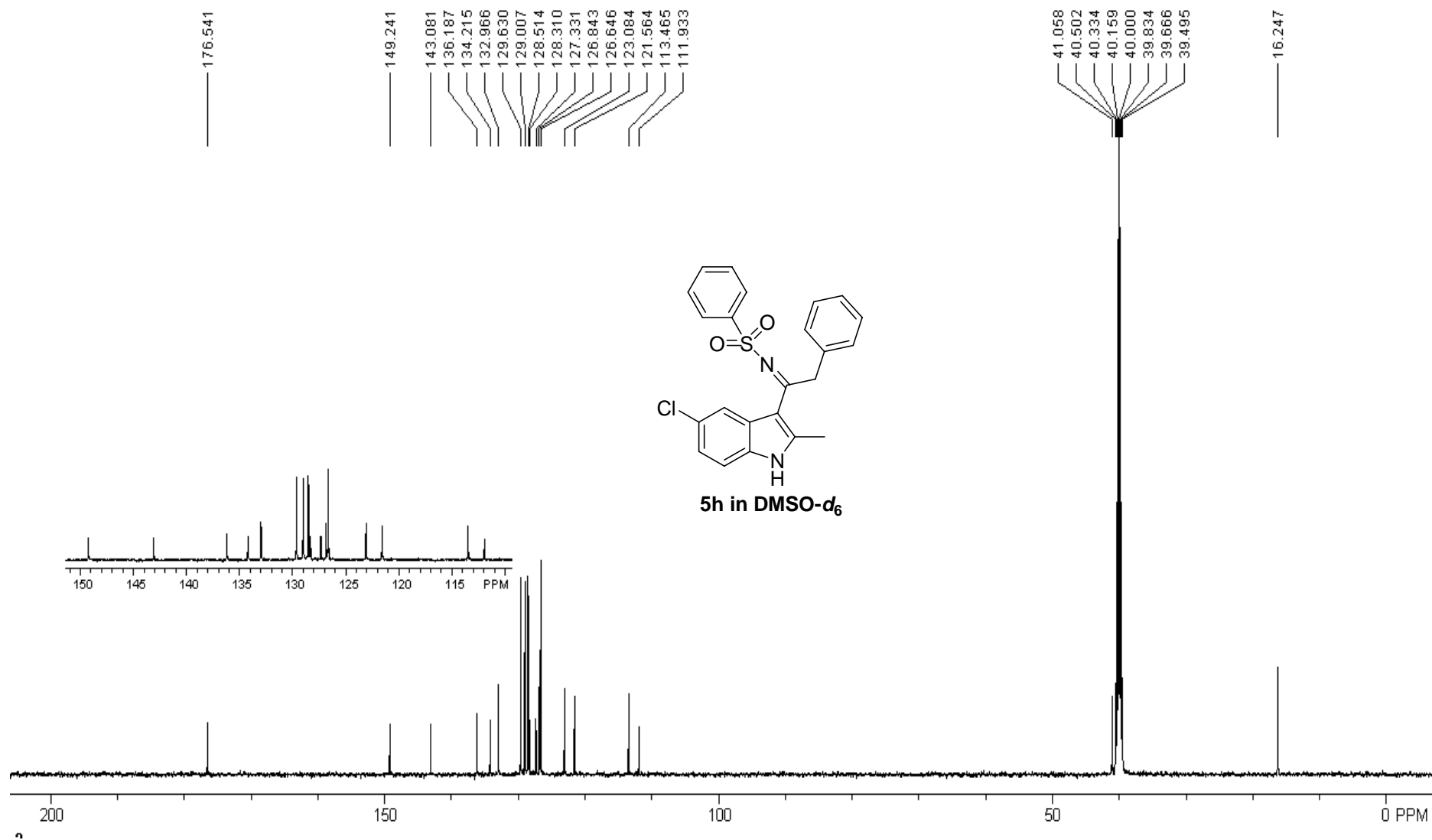




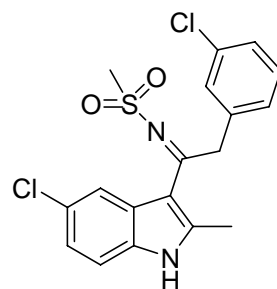
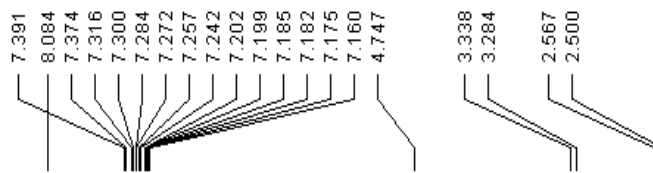




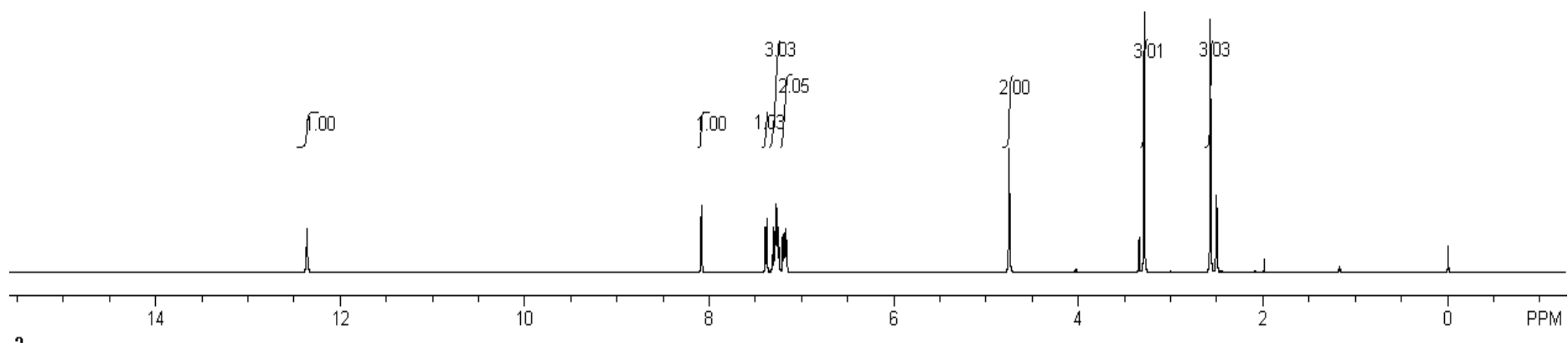


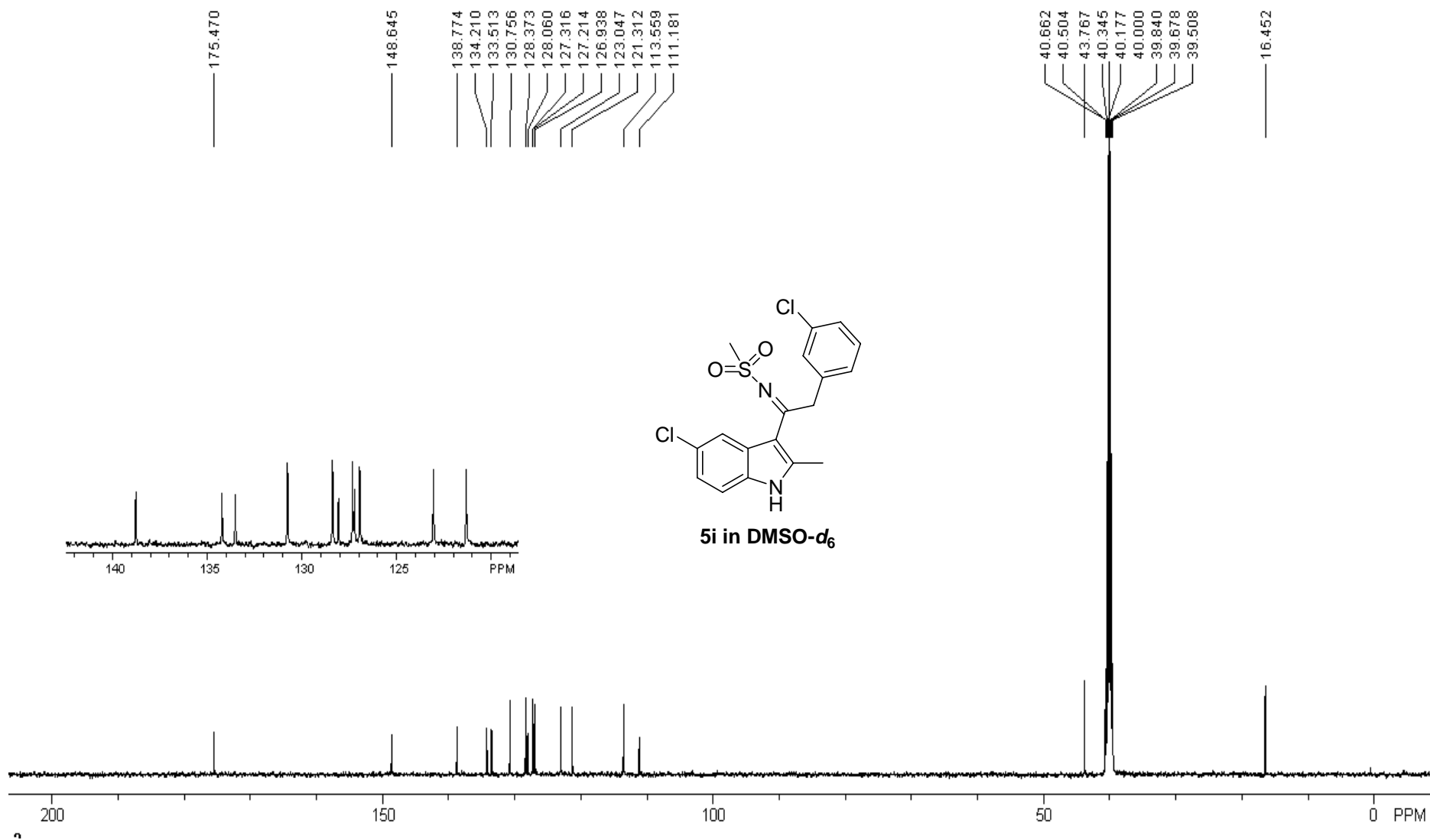


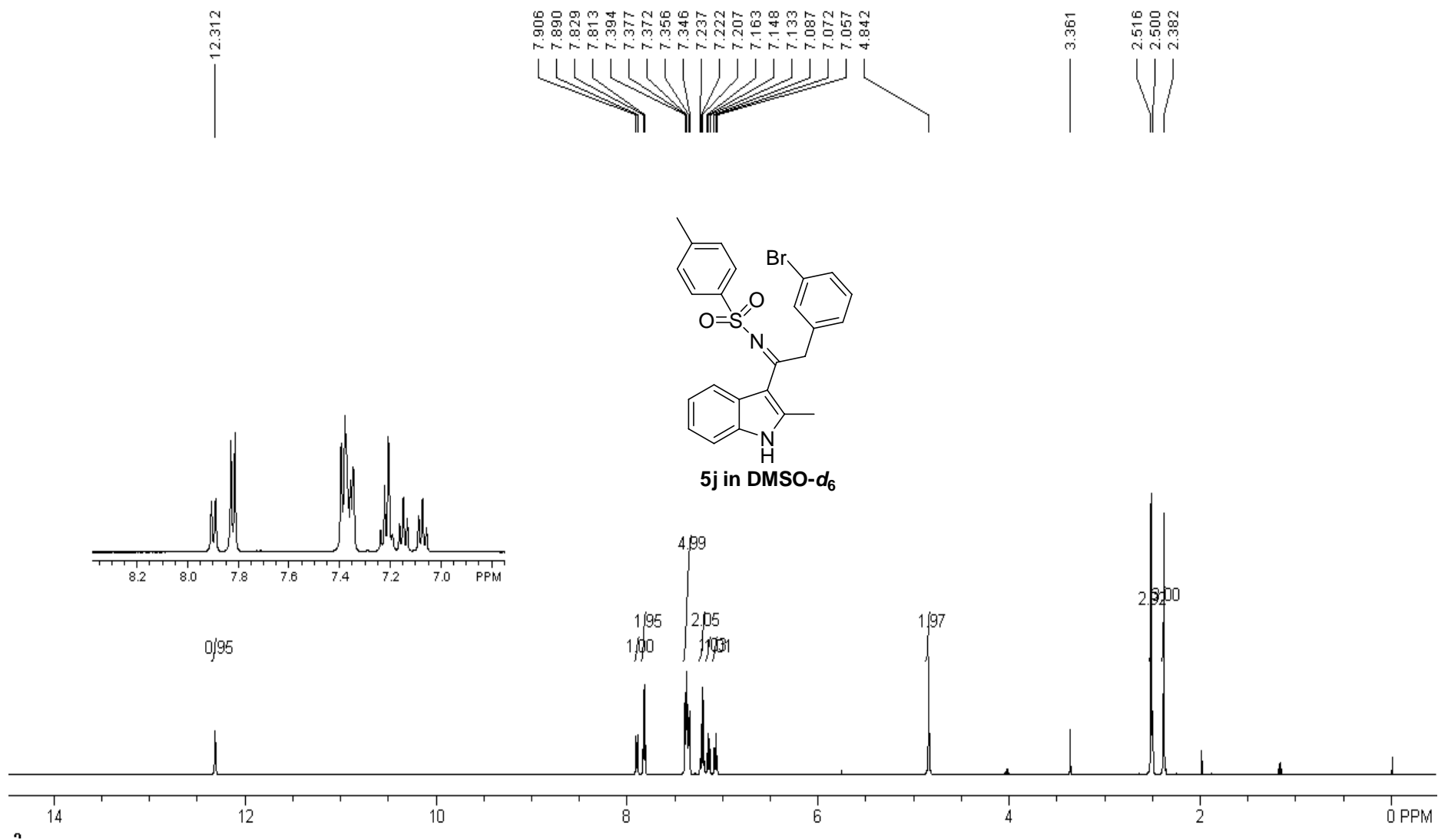
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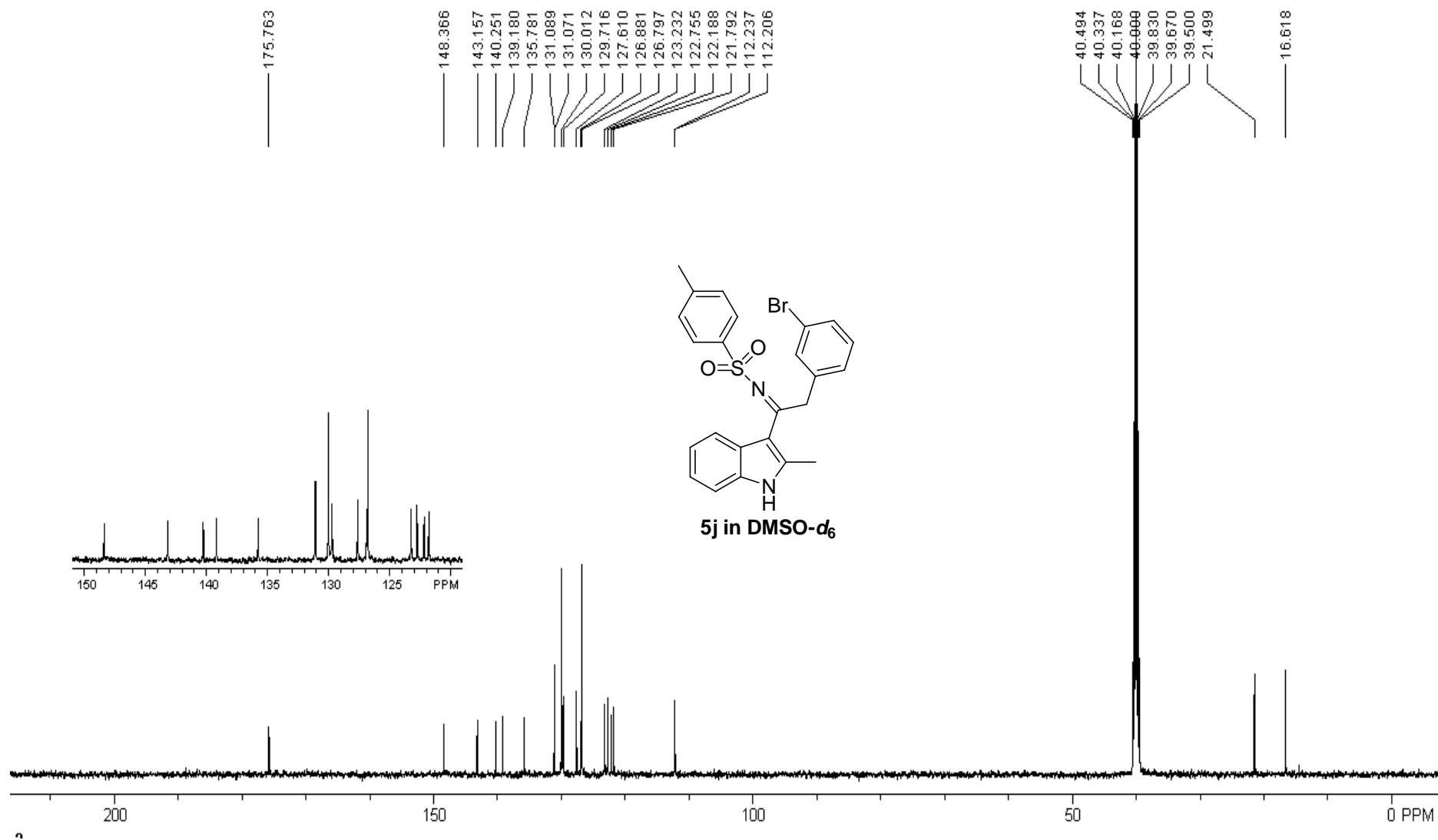


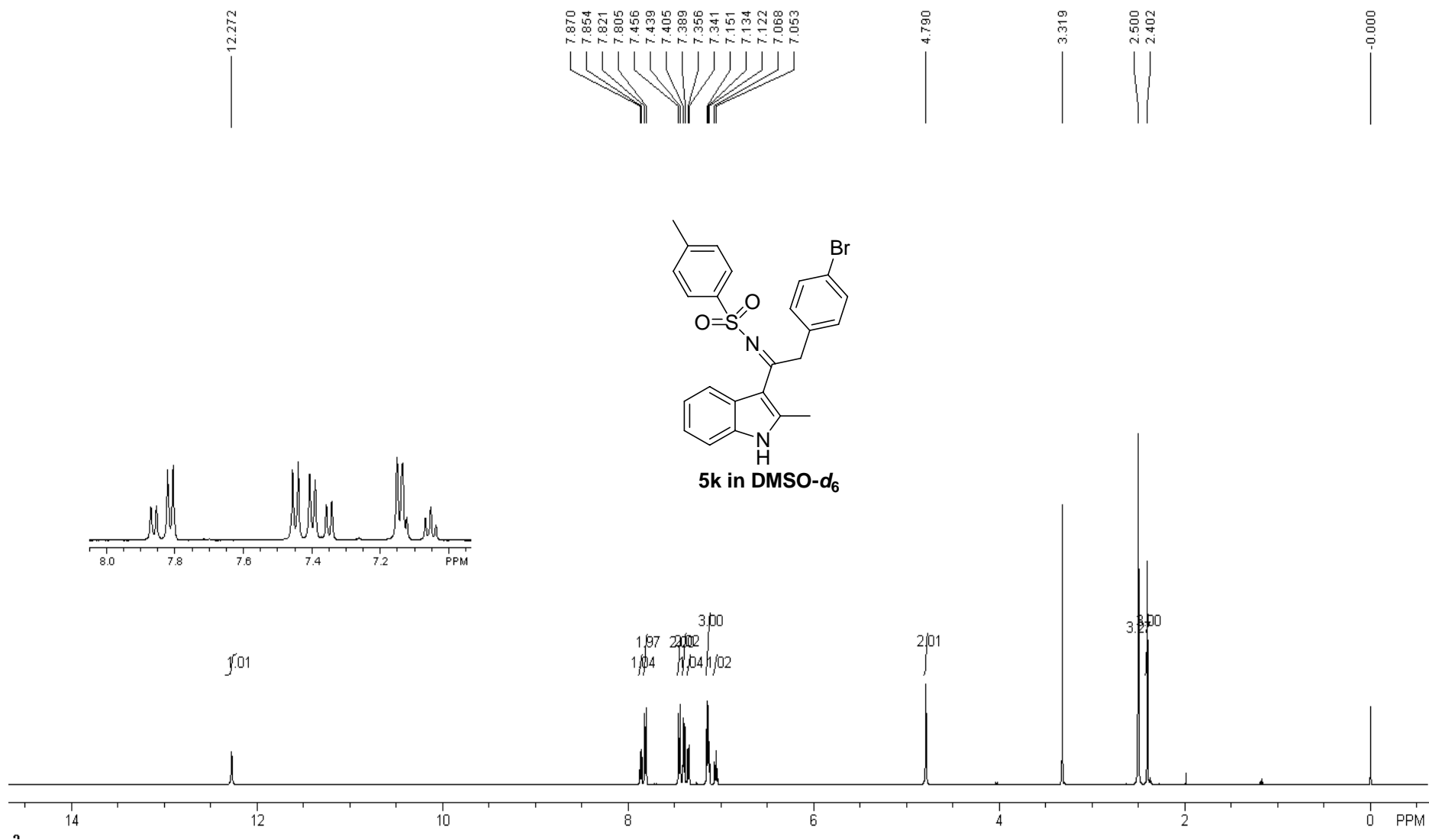
5i in DMSO-*d*₆

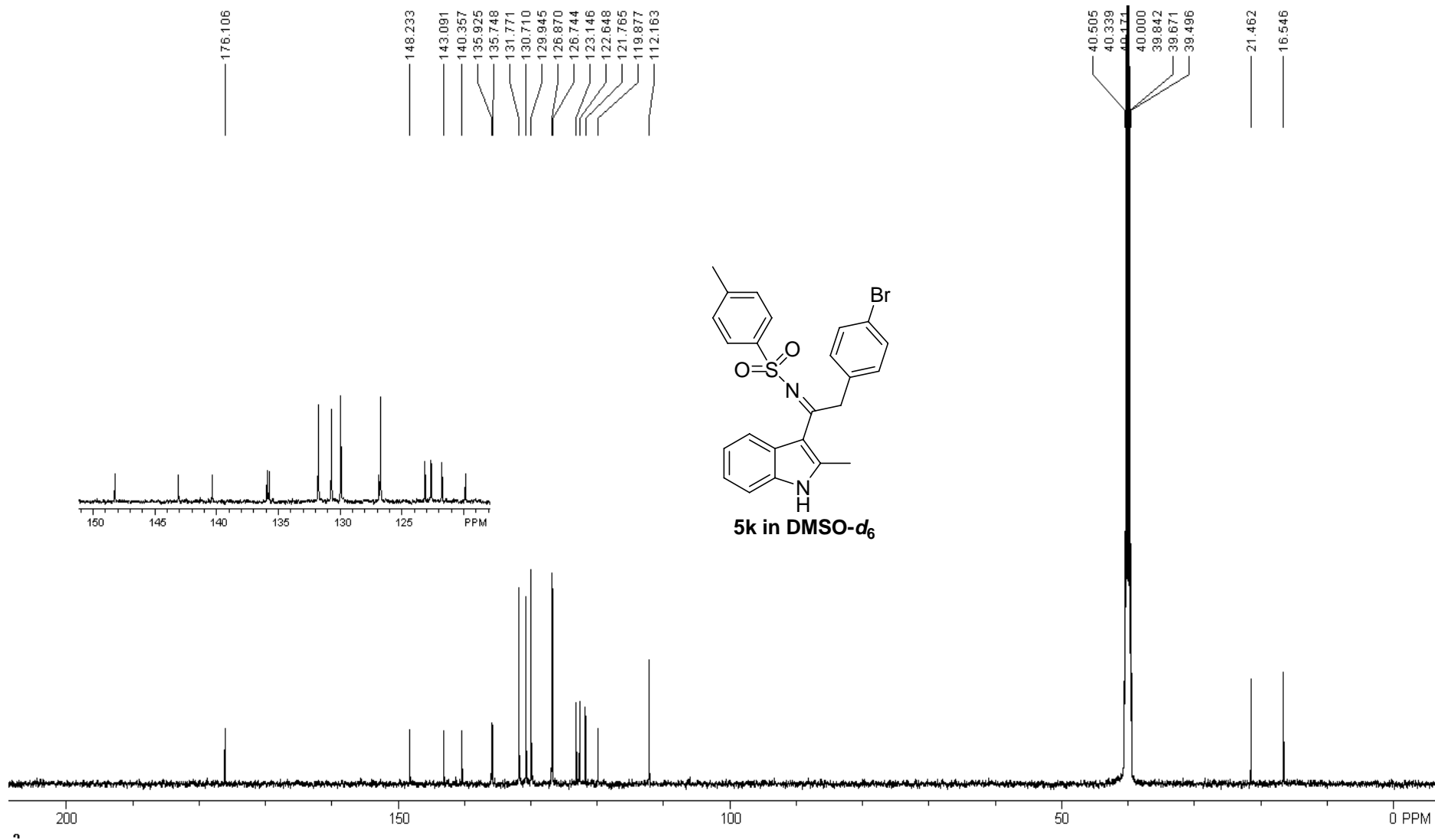


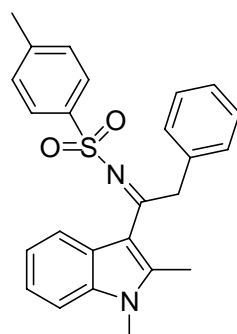
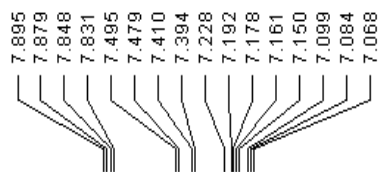












5l in DMSO-*d*₆

