

Sulfonamide and Tertiary Amine as Nucleophiles in Pd(II)-Catalyzed Diamination of Alkynes: Synthesis of Tetracyclic Indolobenzothiazine S,S-dioxides

Tu M. Ha, Bo Yao, Qian Wang, Jieping Zhu*

Laboratory of Synthesis and Natural Products, Institute of Chemical Sciences and Engineering, Ecole Polytechnique
Fédérale de Lausanne, EPFL-SB-ISIC-LSPN, BCH 5304, 1015 Lausanne, Switzerland

Supporting Information

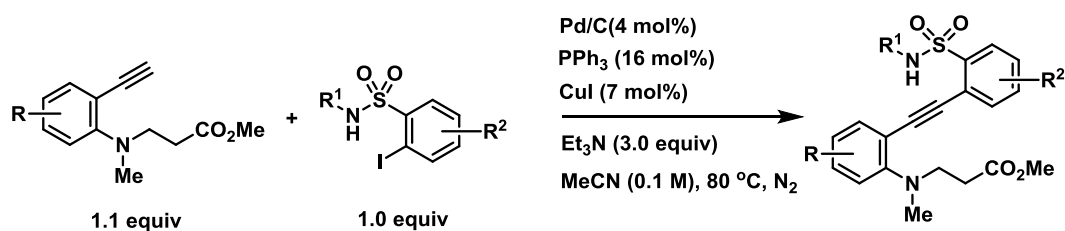
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General Information

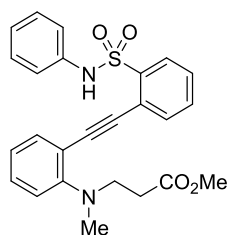
All reactions were carried out in oven dried glasswares. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used directly unless stated otherwise. CH₃CN, toluene, and DMF were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 30 ppm, Karl-Fischer titration). DMSO was bought from Fischer Bioreagent (anhydrous, >99.7% pure) and used directly as the solvent for the coupling reaction. Chromatographic purification was conducted with technical grade solvents and silica gel 40-63 μ m. TLC was performed on Merck silica gel 60 F₂₅₄ TLC aluminium plates and visualized with UV light (254 nm), permanganate stain, CAN stain or anisaldehyde stain. Melting points were measured on a Stuart SMP30 melting point apparatus using open glass capillaries (uncorrected). ¹H NMR spectra were recorded on a 400 MHz spectrometer and a 600 MHz spectrometer in CDCl₃ or DMSO-*d*₆ (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, or the internal DMSO signal at 2.50 ppm as standard). ¹³C NMR spectra were recorded with ¹H-decoupling on a 101 MHz spectrometer and a 125 MHz spectrometer in CDCl₃ or DMSO-*d*₆ (all signals are reported in ppm with the internal chloroform signal at 77.2 ppm, or the internal DMSO signal at 39.5 ppm as standard). Infrared spectra are recorded on a FT/IR-4100 spectrometer with MIRacle ATR and a diamond/ZnSe crystal plate and were reported as cm⁻¹ (w = weak, m = medium, s = strong). Low resolution mass spectrometric measurements were performed on UPLC/MS System. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL.

Preparation of Starting Materials



To a solution of 2-iodobenzensulfonamide (5) (0.4 mmol) in 4.0 mL ACN were added Pd/C 10% (17.10 mg, 4 mol%), Ph_3P (17.10 mg, 16 mol%), CuI (54.4 mg, 7 mol%) and triethylamine (0.16 mL, 1.2 mmol), successively, under argon. After being stirred for 30 min, *o*-alkynylaniline 4 (0.44 mmol) was added and the reaction mixture was heated with stirring at 80 °C for 1.5 – 2.0 hours. The reaction mixture was cooled down, filtered through a short bed of celite and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give compound 2.

Methyl 3-((2-((2-(*N*-benzylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2a)



Yield: 144.0 mg (80%), yellow solid; 80 – 81 °C;

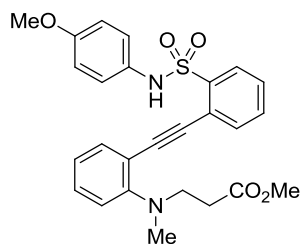
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.69 (s, 1H), 8.00 (dd, J = 8.0, 1.3 Hz, 1H), 7.62 (ddd, J = 9.1, 7.6, 1.5 Hz, 2H), 7.46 (td, J = 7.6, 1.3 Hz, 1H), 7.41 (ddd, J = 8.2, 7.3, 1.6 Hz, 1H), 7.35 (td, J = 7.7, 1.3 Hz, 1H), 7.23 (dd, J = 8.2, 1.1 Hz, 1H), 7.17 (td, J = 7.5, 1.1 Hz, 1H), 7.15 – 7.09 (m, 4H), 7.02 – 6.87 (m, 1H), 3.60 (t, J = 7.5 Hz, 2H), 3.52 (s, 3H), 2.84 (s, 3H), 2.52 (t, J = 7.5 Hz, 2H);

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 153.6, 140.2, 136.7, 133.8, 133.8, 132.2, 130.4, 129.9, 129.1, 128.3, 125.2, 124.5, 122.0, 121.3, 120.9, 118.9, 96.0, 90.5, 52.1, 51.6, 43.4, 31.0.

ATR-IR ν 3119 (w), 3078 (w), 2948 (w), 2859 (w), 1724 (s), 1598 (w), 1490 (m), 1345 (m), 1336 (m), 1160 (s), 1040 (m), 928 (w);

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+$ $[\text{M}+\text{H}]^+$ 449.1530; found 449.1538.

Methyl 3-((2-((2-(*N*-(4-methoxyphenyl)sulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2b)



Yield: 162.4 mg (85%), yellow oil;

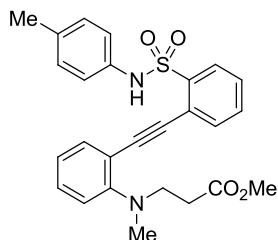
¹H NMR (400 MHz, CDCl₃) δ 9.53 (s, 1H), 7.92 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.39 (td, *J* = 7.8, 1.6 Hz, 1H), 7.33 (td, *J* = 7.7, 1.3 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.68 (s, 3H), 3.53 – 3.49 (m, 5H), 2.79 (s, 3H), 2.49 (t, *J* = 7.7 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.4, 157.7, 153.5, 140.3, 133.7, 132.0, 130.3, 129.8, 129.1, 128.3, 125.5, 125.4, 124.6, 121.4, 120.8, 119.3, 114.3, 96.1, 90.3, 55.3, 51.9, 51.6, 44.1, 31.1;

ATR-IR ν 3066 (w), 2952 (w), 2951 (w), 2840 (w), 2839 (w), 2215 (w), 1736 (m), 1510 (m), 1337 (m), 1250 (m), 1164 (s), 1035 (w), 1034 (w), 763 (m);

HRMS (ESI) calcd for C₂₆H₂₇N₂O₅S⁺ [M+H]⁺ 479.1635; found 479.1646.

Methyl 3-(methyl(2-((2-(*N*-(*p*-tolyl)sulfamoyl)phenyl)ethynyl)phenyl)amino)propanoate (2c)



Yield: 147.8 mg (80%), yellow oil;

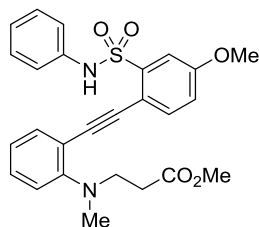
¹H NMR (400 MHz, CDCl₃) δ 9.57 (s, 1H), 7.97 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.3 Hz, 1H), 7.42-7.37 (m, 1H), 7.34 (td, *J* = 7.7, 1.3 Hz, 1H), 7.22 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.16 (td, *J* = 7.5, 1.1 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.57 (d, *J* = 7.6 Hz, 2H), 3.52 (s, 3H), 2.83 (s, 3H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 153.7, 140.4, 135.2, 134.0, 133.9, 133.8, 132.2, 130.5, 130.0, 129.8, 128.4, 124.6, 122.8, 121.5, 121.0, 119.2, 96.1, 90.6, 52.2, 51.7, 43.7, 31.1, 20.9.

ATR-IR ν 3065 (w), 3060 (w), 3059 (w), 3058 (w), 2950 (w), 2858 (w), 2857 (w), 2856 (w), 2214 (w), 2213 (w), 1732 (m), 1510 (m), 1437 (m), 1337 (m), 1161 (s);

HRMS (ESI) calcd for $C_{26}H_{27}N_2O_4S^+$ $[M+H]^+$ 463.1686; found 463.1693.

Methyl 3-((2-((2-(N-benzylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2d)



Yield: 78.5 mg (41%), brown oil;

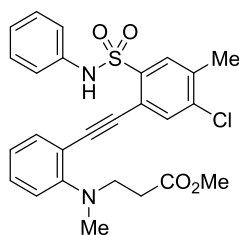
1H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.60 (dd, J = 7.7, 1.6 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.54 (d, J = 2.7 Hz, 1H), 7.39 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 7.24 (dd, J = 8.2, 1.1 Hz, 1H), 7.21 – 7.13 (m, 5H), 7.07 – 7.02 (m, 1H), 6.99 (dd, J = 8.5, 2.7 Hz, 1H), 3.83 (s, 3H), 3.61 (d, J = 7.6 Hz, 2H), 3.55 (s, 3H), 2.85 (s, 3H), 2.53 (t, J = 7.6 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 159.4, 153.3, 141.9, 136.7, 135.3, 133.5, 130.0, 129.3, 125.4, 124.7, 122.5, 121.5, 119.7, 118.7, 114.9, 112.8, 94.4, 90.6, 55.9, 52.2, 51.7, 43.6, 31.1.

ATR-IR ν 3232 (w), 3223 (w), 3067 (w), 3057 (w), 3056 (w), 2952 (w), 2853 (w), 1734 (m), 1600 (m), 1495 (m), 1228 (m), 1160 (s);

HRMS (ESI) calcd for $C_{26}H_{27}N_2O_5S^+$ $[M+H]^+$ 479.1635; found 479.1634.

Methyl 3-((2-((5-chloro-4-methyl-2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2e)



Yield: 105.2 mg (53%), yellow oil;

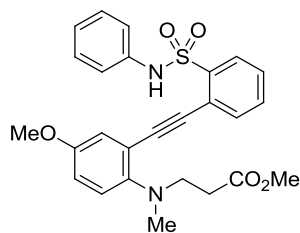
1H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.85 (s, 1H), 7.61 – 7.58 (m, 2H), 7.44 – 7.38 (m, 1H), 7.24 – 7.13 (m, 6H), 7.06 – 7.02 (m, 1H), 3.58 (t, J = 7.8 Hz, 2H), 3.52 (s, 3H), 2.83 (s, 3H), 2.51 (t, J = 7.7 Hz, 2H), 2.36 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 153.7, 138.7, 138.5, 137.3, 136.6, 133.9, 133.9, 132.2, 130.7, 129.4, 125.5, 124.8, 122.4, 121.6, 119.7, 118.9, 96.3, 89.5, 52.3, 51.8, 43.6, 31.1, 20.2;

ATR-IR ν 3070 (w), 3069 (w), 2951 (w), 2854 (w), 1735 (m), 1596 (w), 1493 (m), 1472 (m), 1344 (w), 1162 (s), 954 (m);

HRMS (ESI) calcd for C₂₆H₂₆ClN₂O₄S⁺ [M+H]⁺ 497.1296; found 497.1299.

Methyl 3-((4-methoxy-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)-propanoate (2f)



Yield: 95.7 mg (50%), light yellow oil;

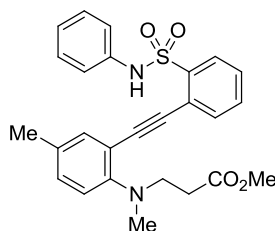
¹H NMR (400 MHz, CDCl₃) δ 10.06 (s, 1H), 7.98 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 (td, *J* = 7.7, 1.3 Hz, 1H), 7.21 – 7.09 (m, 6H), 7.04 – 6.99 (m, 1H), 6.97 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.85 (s, 3H), 3.53 (s, 3H), 3.44 (t, *J* = 7.8 Hz, 2H), 2.75 (s, 3H), 2.51 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 156.5, 140.4, 136.7, 133.7, 132.1, 129.9, 129.1, 128.41, 128.37, 125.3, 123.0, 122.5, 120.8, 120.7, 117.4, 116.8, 95.7, 90.0, 55.6, 52.8, 51.6, 44.5, 31.0;

ATR-IR ν 3073 (w), 2987 (m), 2970 (m), 2901 (m), 2213 (w), 2212 (w), 1735 (m), 1600 (w), 1599 (w), 1496 (m), 1343 (m), 1342 (m), 1225 (m), 1224 (m), 1165 (s), 1065 (m), 1037 (m), 919 (w), 760 (m), 730 (m);

HRMS (ESI) calcd for C₂₆H₂₇N₂O₅S⁺ [M+H]⁺ 479.1635; found 479.1639.

Methyl 3-(methyl(4-methyl-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)amino)propanoate (2g)



Yield: 97.9 mg (53%), light yellow solid; mp: 86 – 88 °C;

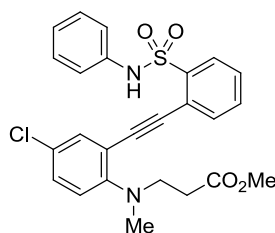
¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 1H), 7.99 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.69 – 7.56 (m, 1H), 7.46-7.42 (m, 2H), 7.34 (td, *J* = 7.8, 1.3 Hz, 1H), 7.21 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.18 – 7.08 (m, 5H), 7.00 (m, 1H), 3.53-3.49 (m, 5H), 2.80 (s, 3H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.35 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 151.1, 140.2, 136.7, 134.5, 134.0, 133.7, 132.1, 131.2, 129.9, 129.1, 128.2, 125.1, 122.2, 121.4, 121.0, 119.1, 96.1, 90.0, 52.4, 51.6, 43.8, 30.9, 20.6;

ATR-IR ν 3073 (w), 3041 (w), 3027 (w), 2951 (w), 2921 (w), 2920 (w), 2880 (w), 2207 (w), 1736 (m), 1599 (w), 1496 (m), 1346 (m), 1165 (s), 759 (w);

HRMS (ESI) calcd for C₂₆H₂₇N₂O₄S⁺ [M+H]⁺ 463.1686; found 463.1689.

Methyl 3-((4-chloro-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2h)



Yield: 133.3 mg (69%), light yellow solid; mp: 110 – 112 °C;

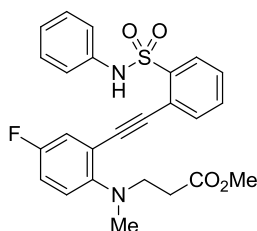
¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 1H), 8.01 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.17 – 7.09 (m, 5H), 7.05 – 6.97 (m, 1H), 3.61 (d, *J* = 7.5 Hz, 2H), 3.53 (s, 3H), 2.84 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.4, 152.1, 140.3, 136.5, 134.0, 133.2, 132.3, 130.3, 130.0, 129.2 (2C), 128.7, 125.2, 122.5, 121.8, 120.4, 120.3, 94.3, 91.4, 52.0, 51.7, 43.3, 30.9;

ATR-IR ν 3127 (w), 3117 (w), 3072 (w), 3030 (w), 3029 (w), 2951 (w), 2845 (w), 2219 (w), 2211 (w), 1732 (m), 1597 (w), 1489 (m), 1345 (m), 1162 (s), 911 (m), 756 (m), 730 (s), 695 (m);

HRMS (ESI) calcd for C₂₅H₂₄ClN₂O₄S⁺ [M+H]⁺ 483.1140; found 483.1146.

Methyl 3-((4-fluoro-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (2i)



Yield: 123.1 mg (66%), white solid; mp: 110 – 111 °C;

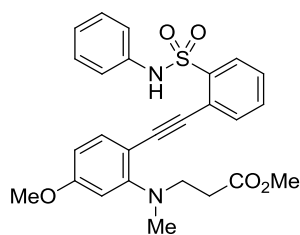
¹H NMR (400 MHz, CDCl₃) δ 9.70 (s, 1H), 7.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37 (td, *J* = 7.7, 1.4 Hz, 1H), 7.31 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.17 – 7.07 (m, 4H), 7.12 – 7.08 (m, 1H), 7.05 – 6.99 (m, 1H), 3.53 (s, 3H), 3.53 – 3.50 (m, 2H), 2.79 (s, 3H), 2.52 (t, *J* = 7.6 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.4, 159.2 (d, *J* = 244.7 Hz), 149.7, 140.4, 136.6, 133.9, 132.2, 129.9, 129.2, 128.7, 125.3, 123.2 (d, *J* = 9.2 Hz), 122.2, 121.0 (d, *J* = 10.0 Hz), 120.3, 119.8 (d, *J* = 23.6 Hz), 117.4 (d, *J* = 22.2 Hz), 94.4, 91.0, 52.5, 51.6, 44.1, 30.9;

ATR-IR ν 3115 (w), 3075 (w), 2952 (w), 2886 (w), 2885 (w), 2208 (w), 1734 (m), 1494 (m), 1345 (m), 1202 (m), 1164 (s), 921 (w), 759 (m);

HRMS (ESI) calcd for C₂₅H₂₄FN₂O₄S⁺ [M+H]⁺ 467.1435; found 467.1438.

Methyl 3-((5-methoxy-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)-propanoate (2j)



Yield: 151.6 mg (79%), yellow solid; mp: 115 – 117 °C;

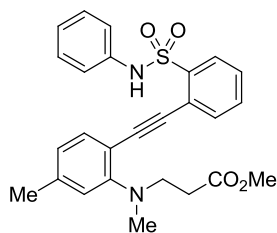
¹H NMR (400 MHz, CDCl₃) δ 9.50 (s, 1H), 7.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.31 (td, *J* = 7.6, 1.3 Hz, 1H), 7.12 (d, *J* = 4.3 Hz, 4H), 7.02 – 6.97 (m, 1H), 6.73 – 6.71 (m, 1H), 6.69 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.86 (s, 3H), 3.61 (t, *J* = 7.6 Hz, 2H), 3.54 (s, 3H), 2.85 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 161.4, 155.2, 139.6, 136.7, 135.0, 133.3, 132.2, 129.8, 129.1, 127.7, 125.0, 121.7, 121.3, 110.7, 109.3, 107.7, 96.4, 89.5, 55.5, 51.9, 51.6, 43.0, 30.9;

ATR-IR ν 2987 (w), 2971 (m), 2901 (w), 2209 (w), 1734 (m), 1600 (m), 1496 (m), 1345 (m), 1298 (m), 1232 (s), 1163 (s), 1079 (m), 1065 (m), 1039 (m), 915 (w), 759 (m), 730 (w), 696 (w);

HRMS (ESI) calcd for C₂₆H₂₇N₂O₅S⁺ [M+H]⁺ 479.1635; found 479.1645.

Methyl 3-(methyl(5-methyl-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)amino)propanoate (2k)



Yield: 138.0 mg (75%), white solid; mp: 80 – 81 °C;

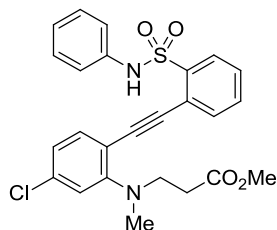
¹H NMR (400 MHz, CDCl₃) δ 9.68 (s, 1H), 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.45 (td, *J* = 7.6, 1.4 Hz, 1H), 7.32 (td, *J* = 7.8, 1.3 Hz, 1H), 7.16 – 7.09 (m, 4H), 7.03 – 6.94 (m, 3H), 3.58 (t, *J* = 7.7 Hz, 2H), 3.53 (s, 3H), 2.83 (s, 3H), 2.54 (t, *J* = 7.7 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 153.5, 141.0, 140.0, 136.7, 133.6, 133.5, 132.1, 129.8, 129.1, 128.0, 125.4, 125.0, 122.0, 121.9, 121.1, 115.9, 96.2, 89.9, 52.1, 51.6, 43.4, 30.9, 21.8;

ATR-IR ν 3070 (w), 3063 (w), 2950 (w), 2845 (w), 2211 (w), 1734 (m), 1601 (w), 1495 (m), 1467 (w), 1436 (w), 1346 (m), 1164 (s), 916 (w), 758 (m), 730 (w), 730 (w), 696 (w);

HRMS (ESI) calcd for C₂₆H₂₇N₂O₄S⁺ [M+H]⁺ 463.1686; found 463.1695.

Methyl 3-((5-chloro-2-((2-(N-phenylsulfamoyl)phenyl)ethynyl)phenyl)(methylamino)propanoate (21)



Yield: 142.7 mg (74%), yellow oil;

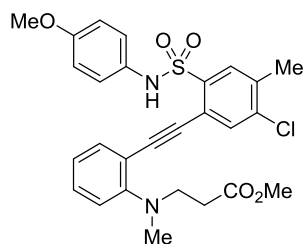
¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 1H), 8.00 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 (td, *J* = 7.7, 1.3 Hz, 1H), 7.18 – 7.07 (m, 6H), 7.03 – 6.97 (m, 1H), 3.68 (t, *J* = 7.5 Hz, 2H), 3.54 (s, 3H), 2.88 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.3, 154.5, 140.0, 136.5, 136.1, 134.7, 133.8, 132.3, 129.9, 129.1, 128.4, 125.1, 124.1, 121.5, 121.3, 120.6, 116.3, 95.0, 91.3, 51.7, 42.5, 30.9;

ATR-IR ν 3074 (w), 2951 (w), 2861 (w), 2844 (w), 2843 (w), 2814 (w), 2813 (w), 2211 (w), 1732 (m), 1582 (w), 1492 (m), 1401 (w), 1346 (m), 1162 (s), 1125 (w), 911 (m), 756 (m), 729 (s), 694 (m);

HRMS (ESI) calcd for C₂₅H₂₄ClN₂O₄S⁺ [M+H]⁺ 483.1140; found 483.1136.

Methyl 3-((2-((5-chloro-2-(N-(4-methoxyphenyl)sulfamoyl)-4-methylphenyl)ethynyl)phenyl)(methyl)-amino)propanoate (**2m**)



Yield: 116.0 mg (55%), yellow oil;

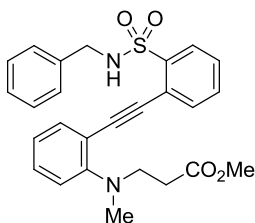
¹H NMR (400 MHz, CDCl₃) δ 9.56 (s, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.60 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.24 – 7.15 (m, 2H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H), 3.53 (s, 3H), 3.49 (t, *J* = 7.7 Hz, 2H), 2.77 (s, 3H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 158.0, 153.8, 138.7, 138.5, 137.3, 133.8, 133.8, 132.1, 130.7, 129.0, 125.9, 124.9, 121.7, 119.7, 119.3, 114.5, 96.4, 89.4, 55.5, 52.1, 51.8, 44.4, 31.3, 20.2;

ATR-IR ν 3000 (w), 2952 (w), 2836 (w), 1734 (m), 1644 (s), 1525 (s), 1512 (s), 1458 (m), 1247 (s), 1208 (m);

HRMS (ESI) calcd for C₂₇H₂₈ClN₂O₅S⁺ [M+H]⁺ 527.1402; found 527.1400.

Methyl 3-((2-((2-(N-benzylsulfamoyl)phenyl)ethynyl)phenyl)(methyl)amino)propanoate (**2n**)



Yield: 164.8 mg (89%), brown oil;

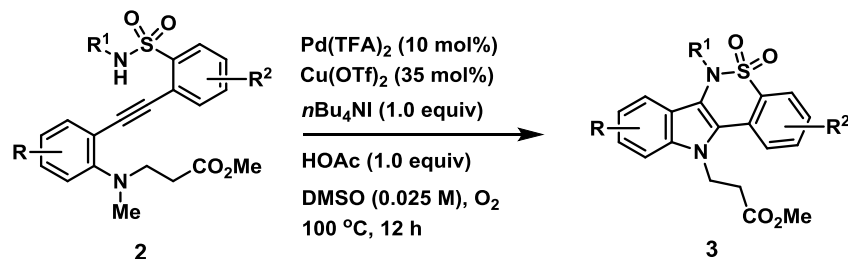
¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 6.3 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.10 (dt, *J* = 15.4, 6.0 Hz, 4H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.03 (d, *J* = 6.3 Hz, 2H), 3.52 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.5, 153.5, 140.5, 136.2, 133.7, 133.6, 132.0, 130.1, 129.6, 128.41, 128.37 (2C), 127.6, 123.7, 120.7, 120.6, 118.2, 95.8, 89.9, 51.5, 51.4, 47.2, 42.0, 30.7;

ATR-IR ν 3065 (w), 2950 (w), 2925 (w), 2854 (w), 2213 (w), 1732 (m), 1492 (w), 1466 (w), 1455 (w), 1437 (m), 1331 (m), 1161 (s), 1066 (m), 761 (s), 701 (m);

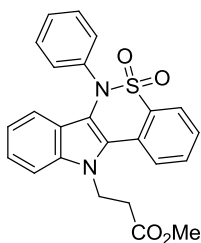
HRMS (ESI) calcd for $C_{26}H_{27}N_2O_4S^+$ $[M+H]^+$ 463.1686; found 463.1694.

Pd(II)-Catalyzed Intramolecular Diamination of Alkynes



A 5-mL-Vial was charged with **2** (0.1 mmol), $Pd(TFA)_2$ (10 mol%), $Cu(OTf)_2$ (35 mol%), nBu_4NI (1.0 equiv), acetic acid (1.0 equiv) together with 4 mL dry DMSO and heated at $100\text{ }^\circ\text{C}$ under oxygen (1 atm) for 12 hours. The reaction mixture was quenched with ice and the aqueous phase was extracted with DCM (3 x 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 , filtered and concentrated in *vacuo*. Then the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give compound **3**.

Methyl3-(5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-*b*]indol-11(6H)-yl)propanoate (**3a**)



Yield: 32.4 mg (75%), yellow solid; mp: $230 - 232\text{ }^\circ\text{C}$;

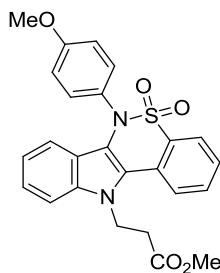
1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.77 (t, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.37 – 7.22 (m, 4H), 7.19 (dd, $J = 7.1, 1.9$ Hz, 2H), 7.07 (t, $J = 7.9$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 4.86 (t, $J = 7.8$, 2H), 3.68 (s, 3H), 2.89 (t, $J = 7.8$ Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 138.5, 138.0, 132.7, 132.4, 129.0, 127.7, 127.4, 127.0, 126.1, 125.6, 125.4, 125.0, 123.6, 121.5, 121.2, 120.5, 119.6, 110.2, 52.1, 41.5, 34.3;

ATR-IR ν 2951 (w), 2924 (w), 2853 (w), 1734 (m), 1593 (w), 1488 (w), 1459 (w), 1350 (s), 1177 (s);

HRMS (ESI) calcd for $C_{24}H_{21}N_2O_4S^+$ $[M+H]^+$ 433.1217; found 433.1231.

Methyl 3-(6-(4-methoxyphenyl)-5,5-dioxidobenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3b)



Yield: 18.5 mg (41%), yellow solid; mp: 186 – 187 °C;

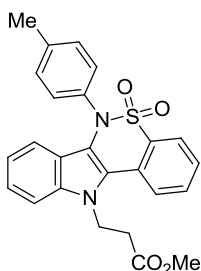
¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.76 (td, *J* = 7.8, 1.4 Hz, 1H), 7.53 (td, *J* = 7.6, 1.0 Hz, 1H), 7.45 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.32 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.16 – 7.07 (m, 3H), 7.04 (ddd, *J* = 7.9, 6.9, 0.9 Hz, 1H), 4.85 (t, *J* = 7.8, 2H), 3.76 (s, 3H), 3.67 (s, 3H), 2.88 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 171.0, 158.8, 138.0, 132.6, 132.0, 131.4, 127.6, 127.0, 125.4, 125.1, 125.0, 123.5, 121.5, 121.1, 121.1, 119.6, 114.2, 110.2, 55.4, 52.1, 41.5, 34.3;

ATR-IR ν 2987 (w), 2968 (w), 2956 (w), 2902 (w), 1734 (m), 1507 (m), 1507 (m), 1462 (w), 1348 (s), 1251 (m), 1207 (w), 1174 (s), 1032 (w), 746 (m), 735 (m);

HRMS (ESI) calcd for C₂₅H₂₃N₂O₅S⁺ [M+H]⁺ 463.1322; found 463.1333.

Methyl 3-(5,5-dioxido-6-(p-tolyl)benzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)propanoate (3c)



Yield: 31.2 mg (70%), dark brown solid; mp: 192 – 194 °C;

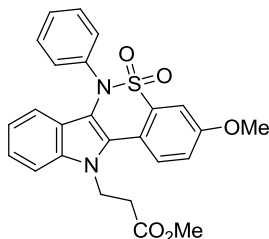
¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.76 (td, *J* = 7.8, 1.4 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.48 – 7.43 (m, 1H), 7.32 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.17 – 6.99 (m, 6H), 4.85 (t, *J* = 7.8 Hz, 2H), 3.67 (s, 3H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 171.2, 138.1, 137.6, 136.1, 132.8, 132.4, 129.8, 127.8, 127.2, 126.2, 125.6, 125.5, 125.1, 123.7, 121.7, 121.3, 121.0, 119.8, 110.3, 52.3, 41.7, 34.5, 21.2;

ATR-IR ν 2985 (w), 2945 (w), 1738 (s), 1373 (m), 1236 (s), 1045 (s);

HRMS (ESI) calcd for $C_{25}H_{23}N_2O_4S^+$ $[M+H]^+$ 447.1373; found 447.1378.

Methyl 3-(3-methoxy-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (**3d**)



Yield: 34.6 mg (74%), yellow solid; mp: 111 – 112 °C;

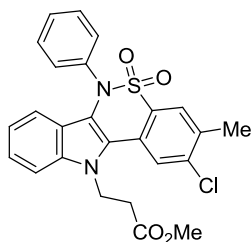
1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 2.7 Hz, 1H), 7.44 (dt, J = 8.4, 0.9 Hz, 1H), 7.32 – 7.24 (m, 5H), 7.21 – 7.16 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.03 (ddd, J = 7.9, 6.9, 0.9 Hz, 1H), 4.83 (t, J = 7.8 Hz, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 2.89 (t, J = 7.8 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 159.3, 138.8, 137.6, 134.1, 129.1, 127.5, 126.2, 126.2, 125.4, 124.5, 121.9, 121.2, 120.3, 119.7, 119.3, 118.6, 110.1, 109.3, 56.0, 52.3, 41.6, 34.5;

ATR-IR ν 2955 (w), 2930 (w), 1732 (m), 1605 (w), 1503 (w), 1457 (w), 1348 (s), 1167 (s), 1028 (m), 745 (s), 696 (s);

HRMS (ESI) calcd for $C_{25}H_{22}N_2O_5SNa^+$ $[M+Na]^+$ 485.1142; found 485.1134.

Methyl 3-(2-chloro-3-methyl-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)propanoate (**3e**)



Yield: 34.6 mg (72%), yellow solid; mp: 137 – 138 °C;

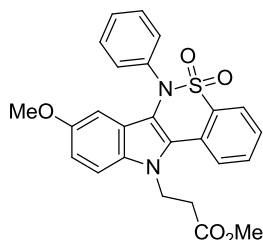
1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.83 (s, 1H), 7.46 (dd, J = 8.5, 0.9 Hz, 1H), 7.36 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 7.10 – 7.02 (m, 2H), 4.84 (t, J = 7.7, 2H), 3.68 (s, 3H), 2.88 (t, J = 7.7, 2H), 2.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.3, 138.6, 138.1, 136.5, 130.6, 129.2, 127.6, 127.6, 126.2, 126.1, 125.3, 124.8, 124.1, 121.6, 121.5, 121.0, 119.7, 110.4, 52.3, 41.6, 34.5, 20.2;

ATR-IR ν 2966 (w), 2920 (w), 1734 (m), 1595 (w), 1558 (w), 1489 (w), 1458 (w), 1349 (s), 1170 (s), 1081 (m), 745 (m);

HRMS (ESI) calcd for $C_{25}H_{21}ClN_2O_4SNa^+$ $[M+Na]^+$ 503.0803; found 503.0802.

Methyl 3-(8-methoxy-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3f)



Yield: 35.1 mg (76%), yellow solid; mp: 225 – 226 °C;

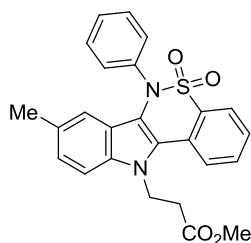
1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.9, 1.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.11 (dd, J = 7.2, 1.8 Hz, 2H), 6.89 (dd, J = 8.9, 2.5 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 4.74 (t, J = 7.8, 2H), 3.60 (s, 3H), 3.57 (s, 3H), 2.79 (t, J = 7.8 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 155.0, 138.6, 133.4, 132.8, 132.5, 129.1, 127.8, 127.4, 127.2, 126.4, 126.1, 125.6, 123.7, 122.2, 120.2, 115.7, 111.4, 100.7, 55.8, 52.3, 41.8, 34.5;

ATR-IR ν 2951 (w), 2924 (w), 2853 (w), 1721 (m), 1496 (m), 1489 (m), 1457 (m), 1346 (s), 1327 (m), 1249 (m), 1210 (m), 1168 (s), 1051 (m), 1021 (m), 803 (m), 761 (m), 737 (m), 698 (m);

HRMS (ESI) calcd for $C_{25}H_{23}N_2O_5S^+$ $[M+H]^+$ 463.1322; found 463.1324.

Methyl 3-(8-methyl-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3g)



Yield: 32.7 mg (73%), yellow solid; mp: 150 – 151 °C;

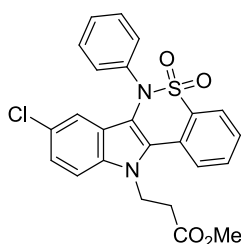
1H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.8, 1.3 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.57 – 7.48 (m, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.18 – 7.13 (m, 3H), 6.88 (s, 1H), 4.82 (t, J = 7.8, 2H), 3.67 (s, 3H), 2.87 (t, J = 7.8 Hz, 2H), 2.30 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 138.6, 136.4, 132.7, 132.3, 130.8, 129.0, 127.6, 127.3, 127.1, 126.8, 126.0, 125.9, 125.5, 123.6, 121.8, 120.0, 119.0, 109.9, 52.1, 41.5, 34.3, 21.3.

ATR-IR ν 2952 (w), 2923 (w), 2855 (w), 1736 (m), 1736 (m), 1593 (w), 1489 (m), 1459 (w), 1436 (w), 1353 (s), 1317 (m), 1247 (w), 1237 (w), 1205 (m), 1176 (s), 1138 (w), 737 (m);

HRMS (ESI) calcd for C₂₅H₂₃N₂O₄S⁺ [M+H]⁺ 447.1373; found 447.1371.

Methyl 3-(8-chloro-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3h)



Yield: 24.7 mg (53%), yellow solid; mp: 179 – 180 °C;

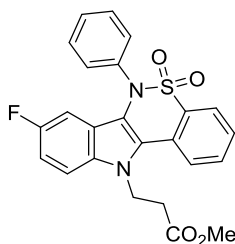
¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.76 (td, *J* = 7.6, 1.3 Hz, 1H), 7.55 (td, *J* = 7.6, 1.0 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.18 – 7.11 (m, 2H), 7.05 (d, *J* = 2.0 Hz, 1H), 4.82 (t, *J* = 7.8, 2H), 3.68 (s, 3H), 2.86 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 171.0, 138.4, 136.3, 132.9, 132.8, 129.3, 128.4, 127.8, 127.1, 127.1, 126.7, 126.1, 125.7, 125.5, 123.9, 122.7, 119.8, 118.9, 111.6, 52.4, 41.7, 34.4;

ATR-IR ν 3067 (w), 3066 (w), 2952 (w), 2926 (w), 2853 (w), 1734 (m), 1488 (m), 1456 (m), 1352 (s), 1302 (m), 1266 (w), 1204 (m), 1174 (s), 736 (s), 694 (m);

HRMS (ESI) calcd for C₂₄H₂₀ClN₂O₄S⁺ [M+H]⁺ 467.0827; found 467.0816.

Methyl 3-(8-fluoro-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3i)



Yield: 28.1 mg (62%), yellow solid; mp: 217 – 219 °C;

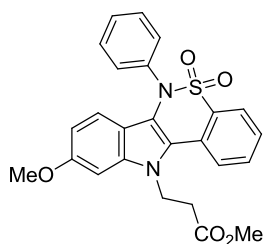
¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.78 (td, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.40 (dd, *J* = 9.1, 4.0 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.16 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.06 (td, *J* = 9.0, 2.5 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.84 (t, *J* = 7.8, 2H), 3.67 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 171.0, 158.3 (d, *J* = 238.8 Hz), 138.4, 134.6, 132.9, 132.8, 129.3, 128.3, 127.7, 127.3, 126.8, 126.1, 125.6, 123.8, 122.1 (d, *J* = 10.3 Hz), 120.4 (d, *J* = 5.0 Hz), 113.8 (d, *J* = 26.6 Hz), 111.5 (d, *J* = 9.5 Hz), 104.7 (d, *J* = 24.7 Hz), 52.3, 41.8, 34.5;

ATR-IR ν 3059 (w), 2947 (w), 2929 (w), 2849 (w), 1732 (m), 1490 (m), 1350 (s), 1327 (m), 1243 (m), 1178 (s), 1169 (s), 1158 (s), 1158 (s), 805 (m), 758 (s), 735 (s), 695 (m);

HRMS (ESI) calcd for C₂₄H₂₀FN₂O₄S⁺ [M+H]⁺ 451.1122; found 451.1117.

Methyl 3-(9-methoxy-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3j)



Yield: 36.0 mg (78%), yellow solid; mp: 133 – 134 °C;

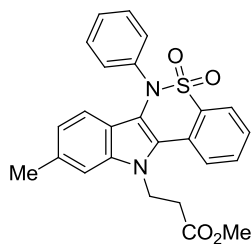
¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.83 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 (td, *J* = 7.7, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.19 – 7.16 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 2.1 Hz, 1H), 6.68 (dd, *J* = 8.8, 2.1 Hz, 1H), 4.80 (t, *J* = 7.8, 2H), 3.86 (s, 3H), 3.68 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 158.7, 139.3, 138.4, 132.6, 131.5, 129.0, 127.4, 127.2, 127.0, 126.1, 125.3, 124.4, 123.0, 120.9, 120.4, 115.7, 111.1, 93.7, 55.7, 52.1, 41.5, 34.1;

ATR-IR ν 2987 (w), 2953 (w), 2908 (w), 2902 (w), 1735 (m), 1735 (m), 1622 (w), 1593 (m), 1489 (m), 1351 (s), 1252 (m), 1222 (m), 1177 (s), 1028 (w), 759 (w), 736 (w);

HRMS (ESI) calcd for C₂₅H₂₃N₂O₅S⁺ [M+H]⁺ 463.1322; found 463.1305.

Methyl 3-(9-methyl-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3k)



Yield: 37.5 mg (80%), yellow solid; mp: 173 – 174 °C;

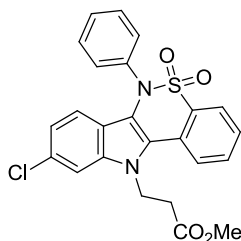
¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.75 (td, *J* = 7.8, 1.4 Hz, 1H), 7.51 (td, *J* = 7.7, 1.1 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.20 – 7.15 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.86 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.82 (t, *J* = 7.8, 2H), 3.69 (s, 3H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.48 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 138.5, 138.5, 135.3, 132.6, 132.0, 129.0, 127.4, 127.3, 127.1, 126.0, 125.3, 125.0, 123.4, 123.0, 120.6, 119.4, 119.2, 110.1, 52.1, 41.4, 34.3, 22.1;

ATR-IR ν 2984 (w), 2952 (w), 2921 (w), 2920 (w), 1735 (m), 1593 (w), 1489 (m), 1458 (w), 1349 (s), 1199 (w), 1177 (s), 758 (w), 736 (m);

HRMS (ESI) calcd for C₂₅H₂₃N₂O₄S⁺ [M+H]⁺ 447.1373; found 447.1384.

Methyl 3-(9-chloro-5,5-dioxido-6-phenylbenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)-propanoate (3I)



Yield: 22.8 mg (49%), white solid; mp: 191 – 192 °C;

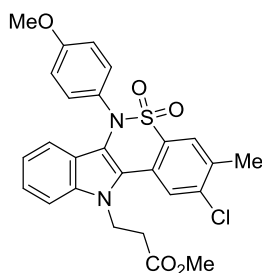
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 7.32 – 7.26 (m, 3H), 7.20 – 7.14 (m, 2H), 7.03 – 6.94 (m, 2H), 4.82 (t, *J* = 7.8, 2H), 3.69 (s, 3H), 2.89 (t, *J* = 7.8 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 170.9, 138.4 (2C), 132.9, 132.5, 131.2, 129.2, 128.2, 127.7, 126.8, 126.3, 126.2, 125.6, 123.7, 122.2, 120.6, 120.1, 110.5 (2C), 52.4, 41.8, 34.4;

ATR-IR ν 2996 (w), 2995 (w), 2987 (w), 2979 (w), 2972 (w), 2954 (w), 1736 (m), 1489 (w), 1355 (s), 1205 (w), 1204 (w), 1177 (s), 1138 (w), 763 (w), 737 (m), 695 (w);

HRMS (ESI) calcd for C₂₄H₂₀ClN₂O₄S⁺ [M+H]⁺ 467.0827; found 467.0829.

Methyl 3-(2-chloro-6-(4-methoxyphenyl)-3-methyl-5,5-dioxidobenzo[5,6][1,2]thiazino[4,3-b]indol-11(6H)-yl)propanoate (3m)



Yield: 22.4 mg (44%), yellow solid; mp: 165 – 166 °C;

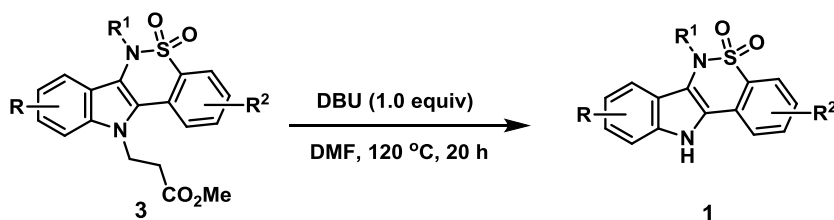
¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.75 (d, J = 0.8 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.24 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.08 – 6.93 (m, 4H), 6.73 (d, J = 9.0 Hz, 2H), 4.75 (t, J = 7.6 Hz, 2H), 3.69 (s, 3H), 3.61 (s, 3H), 2.79 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 159.1, 139.3, 138.1, 136.4, 131.4, 130.3, 127.7, 127.6, 126.1, 125.3, 124.4, 124.1, 121.6, 121.6, 121.4, 119.8, 114.4, 110.4, 55.6, 52.3, 41.6, 34.5, 20.2;

ATR-IR ν 2987 (w), 2969 (w), 2922 (w), 2909 (w), 2902 (w), 1736 (m), 1507 (s), 1460 (w), 1348 (s), 1251 (s);

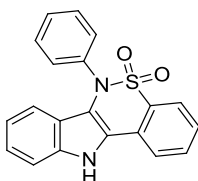
HRMS (ESI) calcd for C₂₆H₂₄ClN₂O₅S⁺ [M+H]⁺ 511.1089; found 511.1076.

N-Deprotection Reactions to Form NH-Indoles



General Procedure: A 5-mL-Vial was charged with **3** (0.05 mmol), DBU (1.0 equiv) and DMF (2.5 mL) and was flushed by N₂ for 5 minutes. The reaction mixture was then heated at 120 °C under nitrogen atmosphere for 20 h. The solvent was evaporated directly, then the crude product was purified by flash column chromatography on silica gel to give compound **1**.

6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1a)



Yield: 16.1 mg (93%), white solid; mp: 273 – 275 °C;

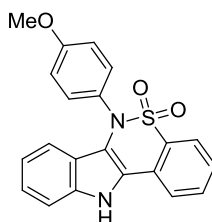
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.25 (s, 1H), 8.15 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.91 (td, *J* = 7.7, 1.3 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.63 (td, *J* = 7.7, 1.1 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.25 (ddd, *J* = 8.2, 6.1, 2.1 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.01 – 6.91 (m, 2H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 138.8, 135.8, 133.4, 130.8, 129.2, 128.5, 127.7, 126.8, 126.4, 124.22, 124.15, 124.0, 123.7, 120.5, 120.3, 117.9, 117.8, 112.4;

ATR-IR ν 3332 (w), 2987 (m), 2974 (m), 2901 (w), 2892 (w), 2884 (w), 1593 (w), 1487 (w), 1335 (m), 1153 (s), 1074 (s), 1068 (s), 1053 (s), 741 (s), 732 (m), 693 (m);

HRMS (ESI) calcd for C₂₀H₁₅N₂O₂S⁺ [M+H]⁺ 347.0849; found 347.0848.

6-(4-methoxyphenyl)-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-*b*]indole 5,5-dioxide (**1b**)



Yield: 15.6 mg (84%), light yellow solid; mp: 242 – 244 °C;

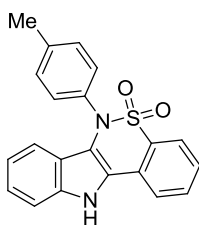
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.21 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.24 (ddd, *J* = 8.4, 6.2, 1.9 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 158.6, 135.8, 133.3, 131.6, 130.6, 128.4, 127.9, 126.8, 124.1, 124.0, 123.8, 123.6, 120.6, 120.2, 118.5, 118.0, 114.4, 112.4, 55.3;

ATR-IR ν 3346 (w), 3345 (w), 3340 (w), 2957 (w), 2925 (w), 2925 (w), 2925 (w), 2853 (w), 1505 (s), 1337 (s), 1337 (s), 1301 (m), 1248 (s), 1160 (s), 1032 (m), 739 (s);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₃S⁺ [M+H]⁺ 377.0954; found 377.0952.

6-(*p*-tolyl)-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-*b*]indole 5,5-dioxide (**1c**)



Yield: 15.1 mg (84%), white solid; mp: 303 – 305 °C;

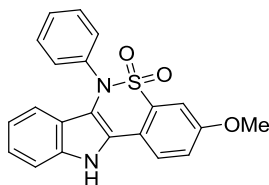
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.21 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.96 (m, 4H), 2.27 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 137.3, 136.3, 135.8, 133.3, 130.7, 129.7, 128.4, 126.8, 126.2, 124.1, 124.04, 123.97, 123.6, 120.6, 120.2, 118.0, 117.9, 112.4, 20.6;

ATR-IR ν 3344 (w), 2959 (w), 2958 (w), 2922 (w), 2853 (w), 1592 (w), 1506 (w), 1442 (w), 1332 (s), 1155 (s), 741 (s), 728 (s);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₂S⁺ [M+H]⁺ 361.1005; found 361.1010.

3-methoxy-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1d)



Yield: 17.4 mg (93%), yellow solid; mp: 290 – 291 °C;

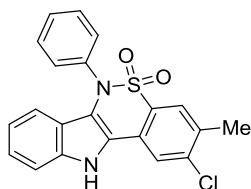
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.14 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.40 – 7.26 (m, 4H), 7.21 (ddd, *J* = 8.2, 4.6, 3.6 Hz, 1H), 7.12 – 7.09 (m, 2H), 6.98 – 6.92 (m, 2H), 3.88 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.2, 139.0, 135.4, 132.2, 129.2, 127.6, 126.3, 125.5, 124.7, 123.5, 120.8, 120.2, 120.1, 119.6, 117.4, 116.0, 112.2, 108.0, 55.9;

ATR-IR ν 3345 (w), 2956 (w), 2926 (w), 2925 (w), 2854 (w), 2853 (w), 1734 (w), 1717 (w), 1595 (w), 1457 (m), 1342 (s), 1237 (m), 1154 (s), 758 (s), 747 (s);

HRMS (ESI) calcd for C₂₁H₁₆N₂NaO₃S⁺ [M+Na]⁺ 399.0774; found 399.0768.

2-Chloro-3-methyl-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1e)



Yield: 16.4 mg (83%), yellow solid; mp: 280 – 281 °C;

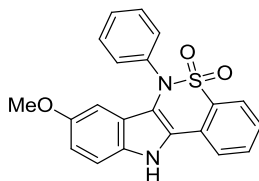
¹H NMR (400 MHz, DMSO-*d*₆): δ 12.23 (s, 1H), 8.26 (s, 1H), 7.88 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.25 (ddd, *J* = 8.3, 5.8, 2.5 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.02 – 6.93 (m, 2H), 2.46 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.2 (2C), 138.9, 136.9, 136.2, 129.7, 128.3, 127.0, 126.9, 126.6, 124.8, 124.3, 123.8, 120.9, 120.9, 118.7, 118.4, 113.0, 20.0;

ATR-IR ν 3363 (w), 2923 (w), 2853 (w), 1595 (w), 1488 (m), 1488 (m), 1455 (w), 1355 (m), 1329 (s), 1320 (s), 1263 (m), 1152 (s), 942 (m), 868 (m), 741 (s);

HRMS (ESI) calcd for C₂₁H₁₅ClN₂NaO₂S⁺ [M+Na]⁺ 417.0435; found 417.0441.

8-methoxy-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1f)



Yield: 17.5 mg (94%), yellow solid; mp: 271 – 273 °C;

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.13 (s, 1H), 8.12 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.91 (td, *J* = 7.6, 1.7 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.46 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.41 – 7.27 (m, 3H), 7.14 (dd, *J* = 7.6, 2.4 Hz, 2H), 6.92 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 3.59 (s, 3H);

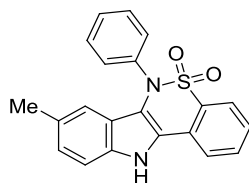
¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.8, 138.7, 133.3, 131.0, 130.8, 129.2, 128.3, 127.6, 126.9, 126.3, 124.8, 124.0, 123.5, 120.9, 117.5, 114.5, 113.4, 99.0, 55.2;

ATR-IR ν 3335 (w), 2954 (w), 2922 (w), 2853 (w), 1492 (w), 1454 (w), 1341 (s), 1261 (m), 1168 (m), 1154 (s), 1028 (m), 768 (m), 732 (m), 622 (m);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₃S⁺ [M+H]⁺ 377.0954; found 377.0956

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8-methyl-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1g)



Yield: 15.7 mg (87%), yellow solid; mp: 275 – 277 °C;

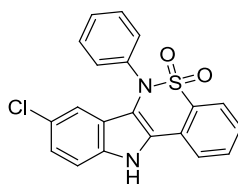
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.13 (s, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.23 (m, 3H), 7.10 – 7.06 (m, 3H), 6.76 (s, 1H), 2.24 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.0, 134.3, 133.4, 130.7, 129.2, 129.1, 128.4, 127.6, 127.0, 126.2, 125.9, 124.5, 124.1, 123.6, 120.9, 117.3, 117.1, 112.2, 21.1;

ATR-IR ν 3335 (m), 2957 (w), 2920 (w), 2853 (w), 1593 (m), 1493 (m), 1342 (s), 1149 (s), 766 (s), 735 (s);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₂S⁺ [M+H]⁺ 361.1005; found 361.1010.

8-chloro-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1h)



Yield: 17.1 mg (90%), light yellow solid; mp: 279 – 281 °C;

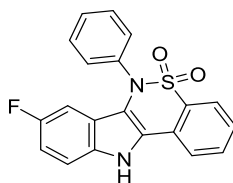
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.52 (s, 1H), 8.15 (d, *J* = 7.7, 1H), 7.93 (td, *J* = 7.7, 1.3 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.66 (td, *J* = 7.7, 1.1 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.26 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.92 (d, *J* = 2.1 Hz, 1H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 138.6, 134.2, 133.6, 131.1, 129.4, 129.0, 127.9, 126.4, 126.4, 125.8, 124.7, 124.2, 124.1, 123.9, 121.5, 117.2, 116.7, 114.3;

ATR-IR ν 3326 (w), 2923 (w), 2853 (w), 1594 (w), 1487 (w), 1487 (w), 1471 (w), 1471 (w), 1455 (w), 1455 (w), 1329 (s), 1292 (s), 1154 (s), 762 (s), 745 (m), 696 (m);

HRMS (ESI) calcd for C₂₀H₁₄ClN₂O₂S⁺ [M+H]⁺ 381.0459; found 381.0461.

8-fluoro-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1i)



Yield: 17.0 mg (93%), yellow solid; mp: 245- 247 °C;

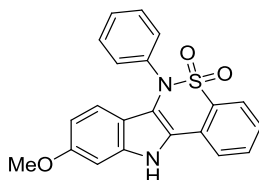
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.41 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.93 (td, *J* = 7.7, 1.3 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.56 (dd, *J* = 8.9, 4.4 Hz, 1H), 7.43 – 7.25 (m, 3H), 7.17 – 6.98 (m, 3H), 6.65 (dd, *J* = 9.2, 2.5 Hz, 1H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.0 (d, *J* = 235.1 Hz), 138.6, 133.5 (2C), 132.5, 131.0, 129.3, 128.9, 127.9, 126.5, 126.4, 126.1, 124.0 (d, *J* = 23.8 Hz), 120.7 (d, *J* = 10.5 Hz), 117.8 (d, *J* = 4.9 Hz), 114.0 (d, *J* = 9.7 Hz), 112.7 (d, *J* = 26.3 Hz), 102.4 (d, *J* = 24.6 Hz);

ATR-IR ν 3409 (w), 2958 (w), 2922 (w), 2874 (w), 2873 (w), 2854 (w), 1490 (m), 1344 (s), 1304 (m), 1254 (m), 1169 (s), 1151 (s), 946 (m), 756 (s), 693 (s);

HRMS (ESI) calcd for C₂₀H₁₄FN₂O₂S⁺ [M+H]⁺ 365.0755; found 365.0738.

9-methoxy-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1j)



Yield: 16.3 mg (87%), yellow solid; mp: 253 – 255 °C;

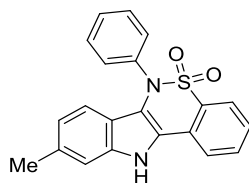
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.05 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.37-7.30 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.6, 138.7, 137.1, 133.3, 129.9, 129.2, 127.7 (2C), 127.0, 126.4, 123.9, 123.1, 122.9, 118.7, 118.2, 114.8, 110.9, 94.9, 55.3;

ATR-IR ν 3359 (w), 2957 (w), 2924 (w), 2924 (w), 2904 (w), 1594 (m), 1359 (m), 1326 (s), 1326 (s), 1274 (s), 1149 (s), 1025 (m), 815 (m), 752 (s), 742 (m);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₂S⁺ [M+H]⁺ 377.0954; found 377.0961.

9-methyl-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (1k)



Yield: 16.5 mg (92%), yellow solid; mp: 289 – 291 °C;

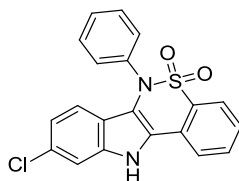
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.08 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.30 (m, 4H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.83 – 6.79 (m, 2H), 2.41 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 138.8, 136.3, 133.8, 133.3, 130.5, 129.2, 128.1, 127.6, 127.0, 126.3, 123.9, 123.6, 123.4, 122.1, 118.5, 117.9, 117.6, 112.0, 21.5;

ATR-IR ν 3358 (w), 2957 (w), 2922 (w), 2854 (w), 1592 (m), 1336 (s), 1155 (s), 807 (m), 757 (s), 732 (m), 692 (s);

HRMS (ESI) calcd for C₂₁H₁₇N₂O₂S⁺ [M+H]⁺ 361.1005; found 361.1012.

9-chloro-6-phenyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (**1l**)



Yield: 16.7 mg (88%), yellow solid; mp: 238 – 239 °C;

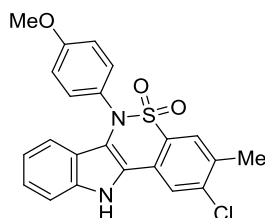
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.45 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.11 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.01 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H);

¹³C NMR (101 MHz, DMSO-*d*₆) 138.6, 136.1, 133.5, 130.8, 129.3, 128.9, 128.8, 127.9, 126.42, 126.38, 125.2, 124.0, 123.8, 120.8, 119.33, 119.27, 117.8, 112.0;

ATR-IR ν 3344 (w), 2955 (m), 2921 (s), 2853 (m), 1724 (w), 1609 (m), 1596 (m), 1454 (m), 1341 (s), 1158 (s), 1056 (s);

HRMS (ESI) calcd for C₂₀H₁₃ClN₂NaO₂S⁺ [M+Na]⁺ 403.0278; found 403.0283.

2-Chloro-6-(4-methoxyphenyl)-3-methyl-6,11-dihydrobenzo[5,6][1,2]thiazino[4,3-b]indole 5,5-dioxide (**1m**)



Yield: 18.6 mg (88%), yellow solid; mp: 295 – 296 °C;

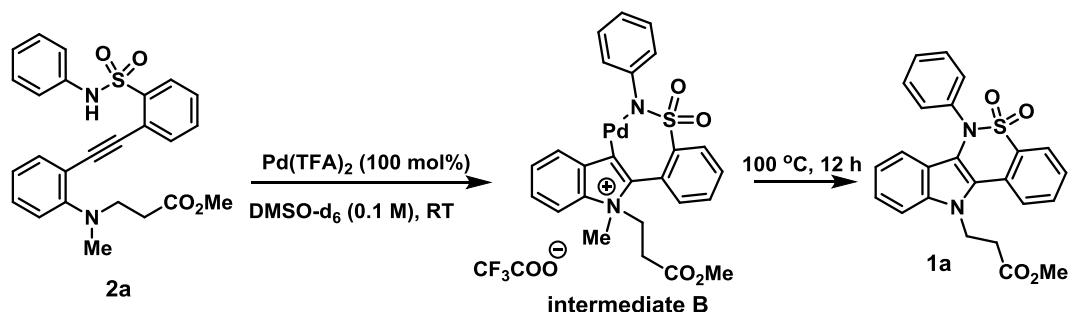
¹H NMR (400 MHz, DMSO-*d*₆) δ 12.16 (s, 1H), 8.26 (s, 1H), 7.86 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.24 (ddd, *J* = 8.4, 6.4, 2.2 Hz, 1H), 7.11 – 6.95 (m, 4H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.72 (s, 3H), 2.46 (s, 3H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 158.7, 138.3, 136.3, 135.8, 131.5, 129.1, 128.0, 126.4, 126.1, 124.3, 123.7, 122.8, 120.4, 120.3, 118.9, 118.0, 114.4, 112.4, 55.3, 19.5;

ATR-IR ν 3319 (w), 3314 (w), 2954 (w), 2929 (w), 2928 (w), 2853 (w), 2836 (w), 1605 (w), 1508 (s), 1460 (m), 1460 (m), 1443 (w), 1319 (s), 1250 (s), 1146 (s), 1035 (s), 748 (s);

HRMS (ESI) calcd for C₂₂H₁₇ClN₂NaO₃S⁺ [M+Na]⁺ 447.0541; found 447.0539.

Mechanistic Study



In the glovebox, a NMR tube was charged with **2a** (0.1 mmol), Pd(TFA)₂ (100 mol%) together with 1 mL DMSO-*d*₆ and then sonicated at room temperature. The reaction was monitored by NMR. The starting material was totally consumed after 45 minutes; intermediate B was observed and characterized by NMR, HRMS. The reaction mixture was further heated to 100 °C overnight, then quenched with ice and the aqueous phase was extracted with DCM (3 x 10 mL). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated in *vacuo*. Then the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give compound **1a**.

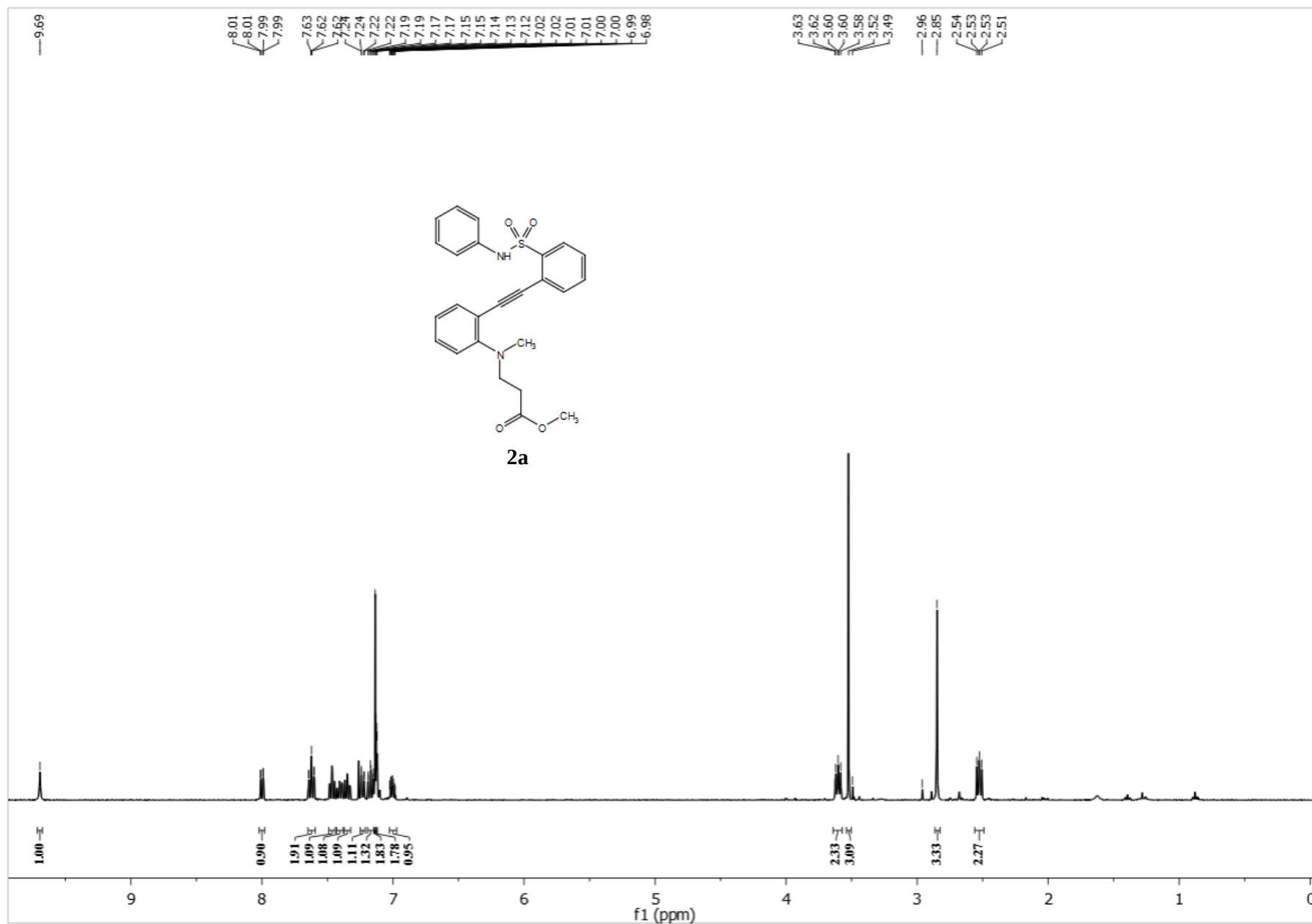
¹H NMR (400 MHz, DMSO-*d*₆) δ 8.23 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.89 - 7.86 (m, 2H), 7.82 - 7.78 (m, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.49 - 7.46

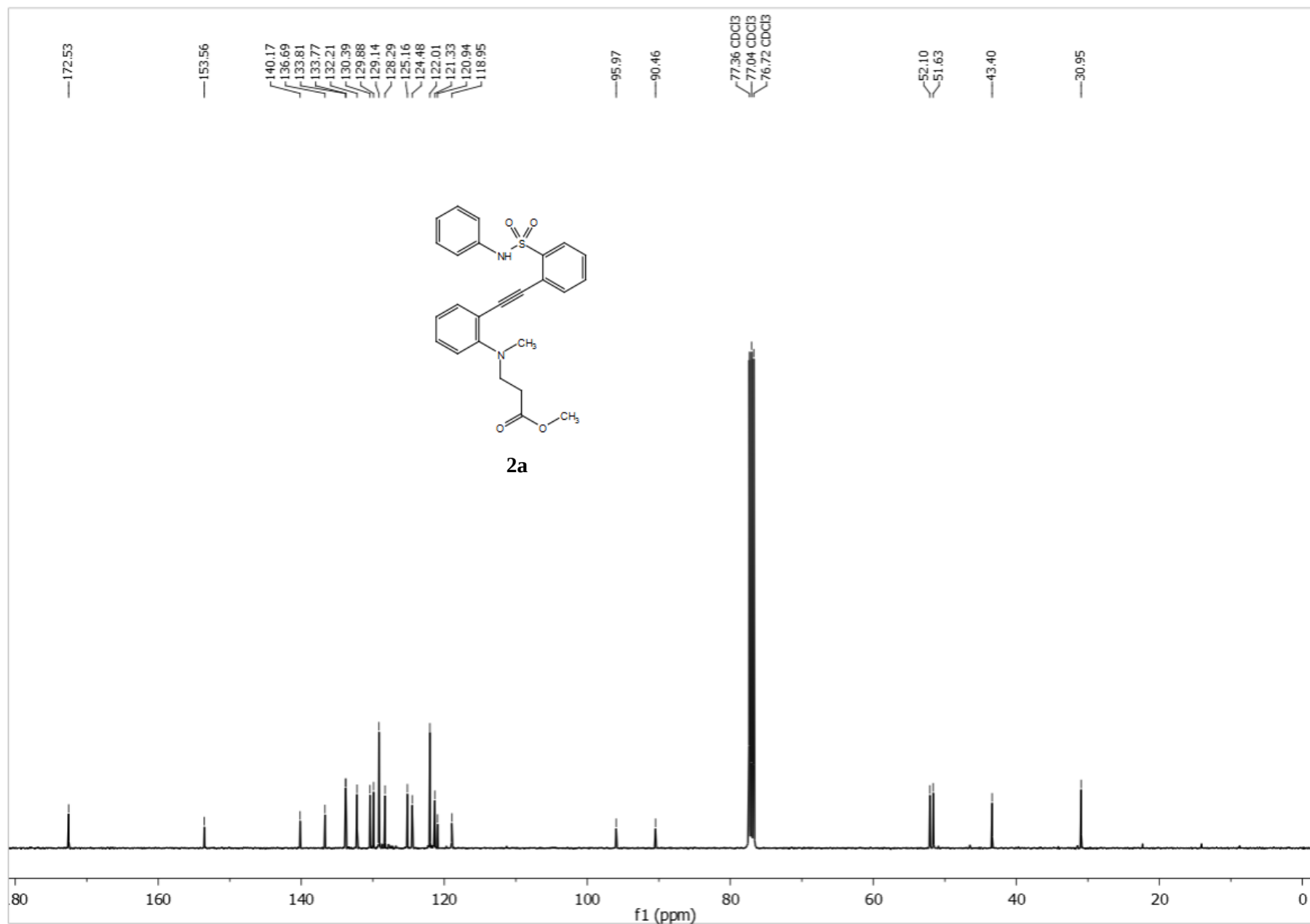
(m, 2H), 7.18 (t, $J = 7.7$ Hz, 2H), 7.00 (t, $J = 7.4$ Hz, 1H), 4.68 (t, $J = 9.0$ Hz, 2H), 3.51 (s, 3H), 3.48 (s, 3H), 2.83 (m, 1H), 1.99 – 1.80 (m, 1H).

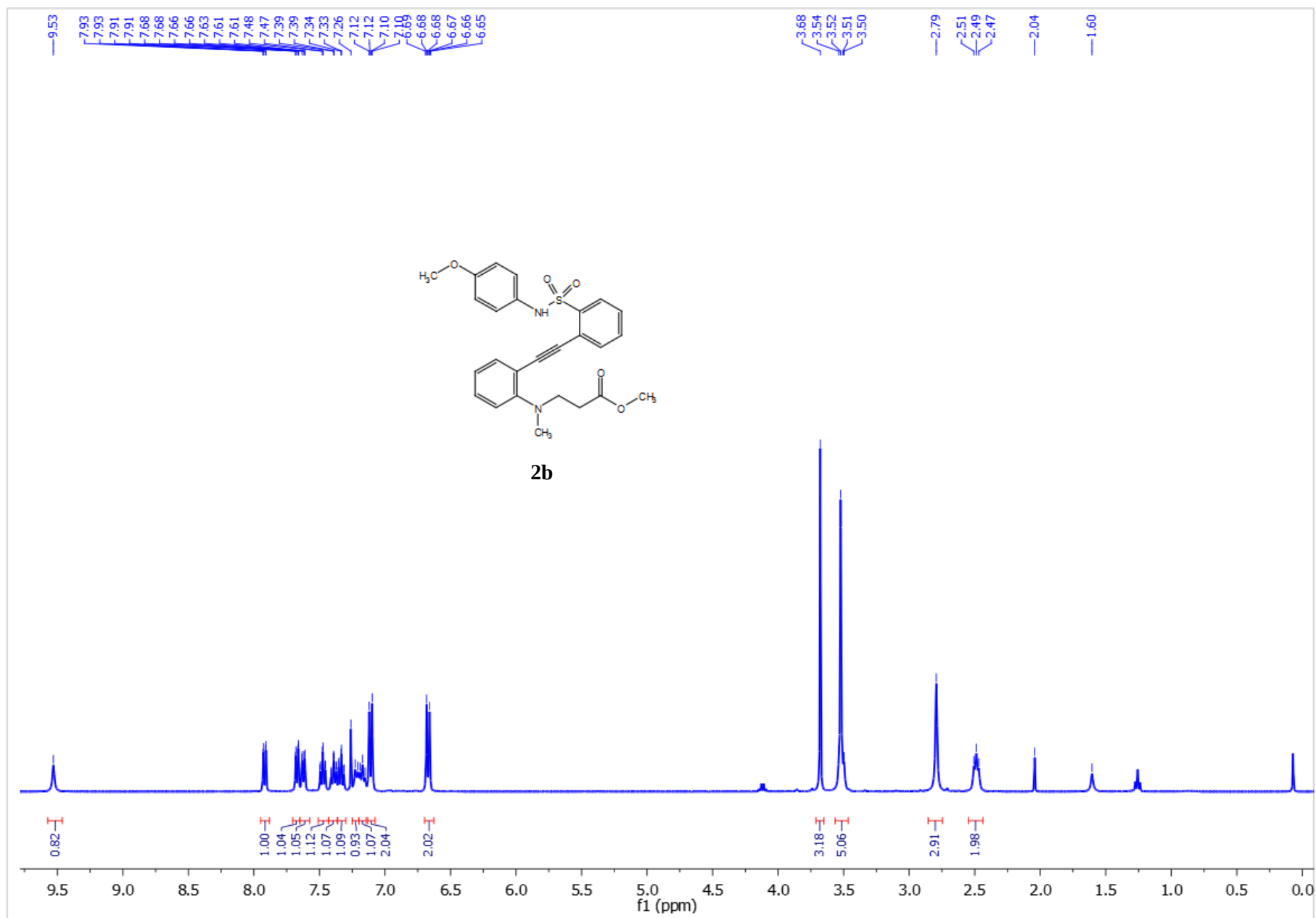
^{13}C NMR (101 MHz, DMSO- d_6) δ 170.2, 146.5, 145.0, 138.8 (2C), 137.1, 132.9, 131.8, 130.8, 130.2, 130.1, 129.2, 128.9, 128.5, 128.1 (3C), 128.0, 126.5, 123.5, 117.7, 59.8, 52.3, 50.9, 27.6;

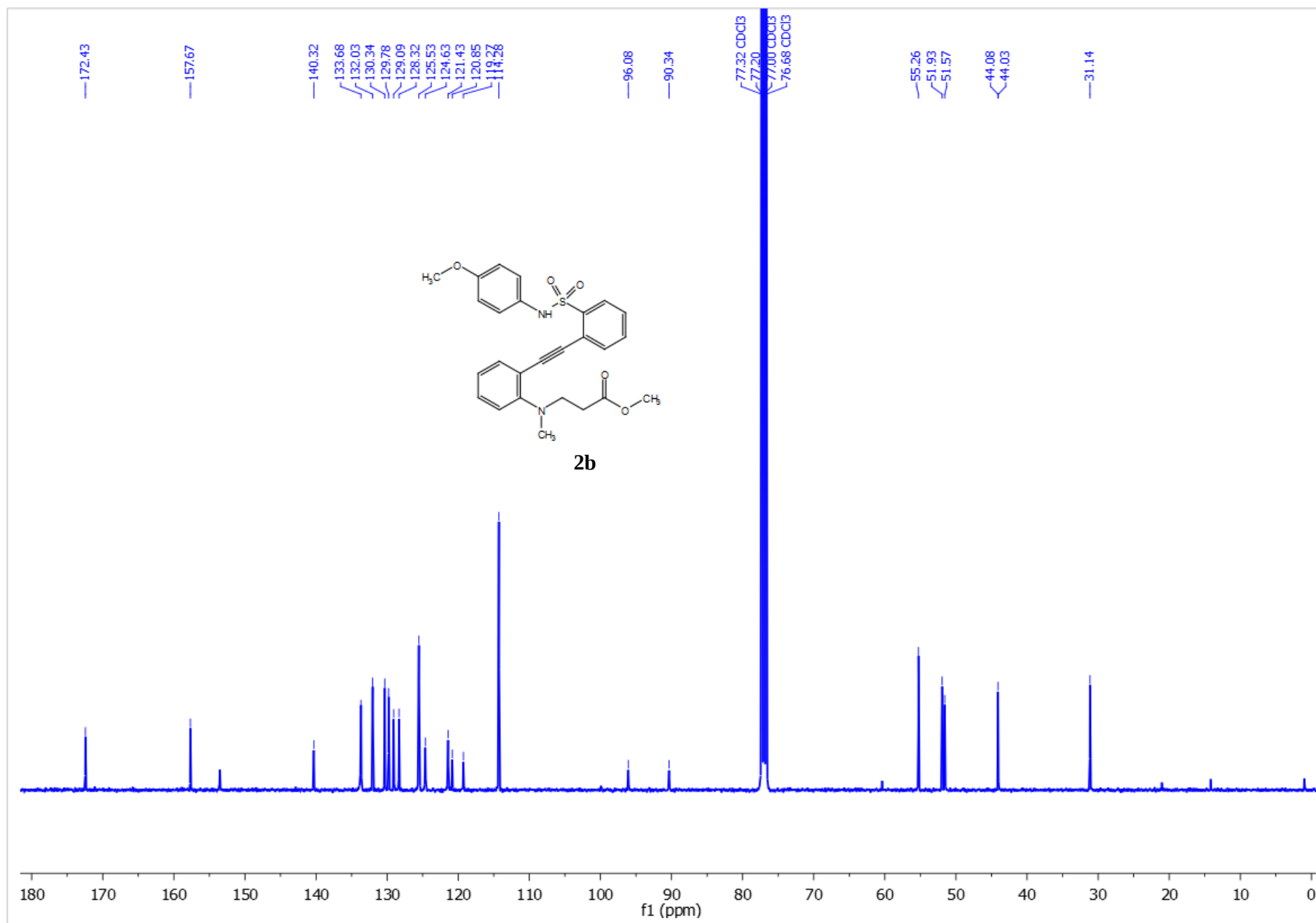
HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_4\text{PdS}^+ [\text{M}-\text{CF}_3\text{COO}^-]$ 553.0413; found 553.0432.

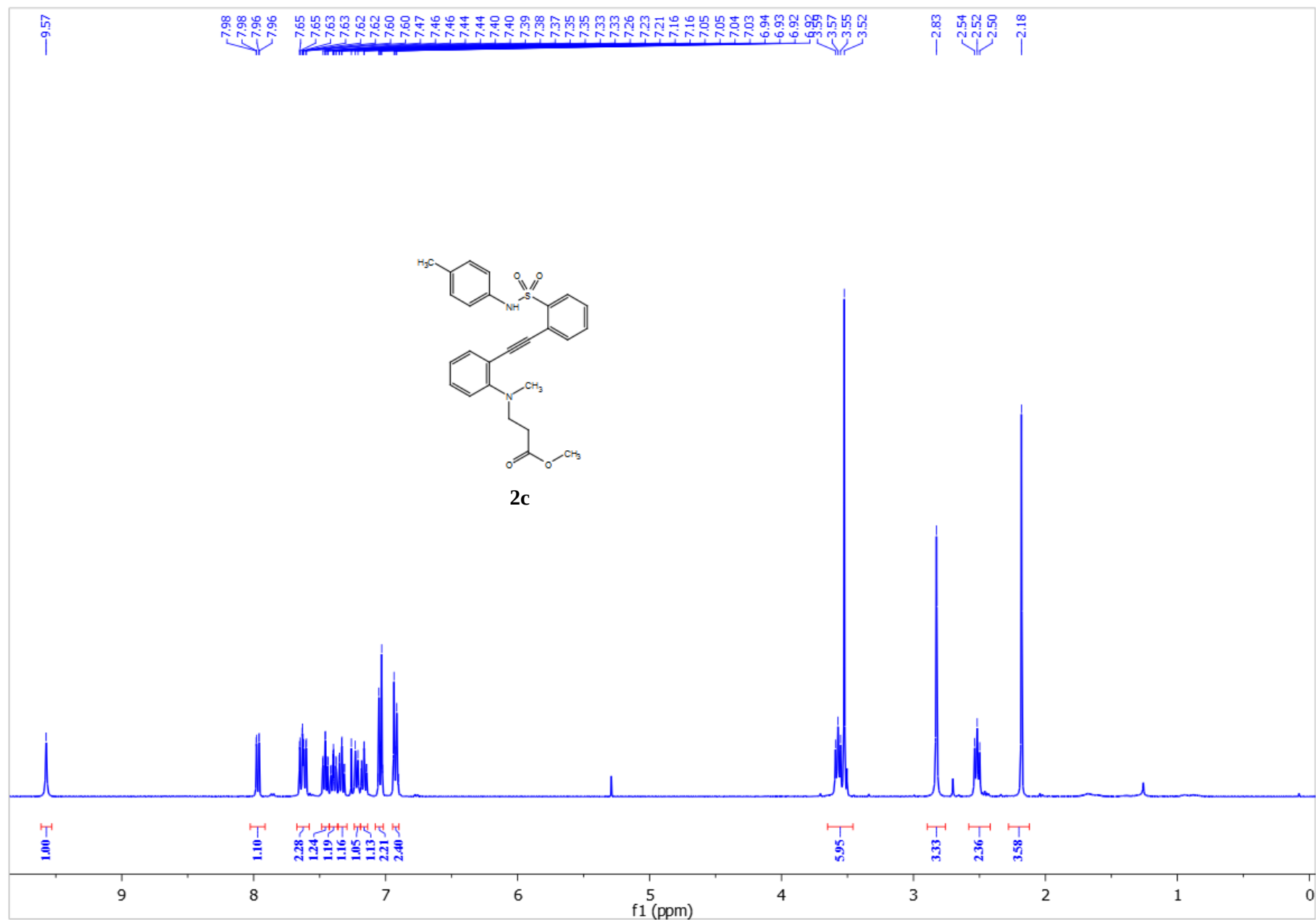
Copies of ^1H and ^{13}C NMR Spectra



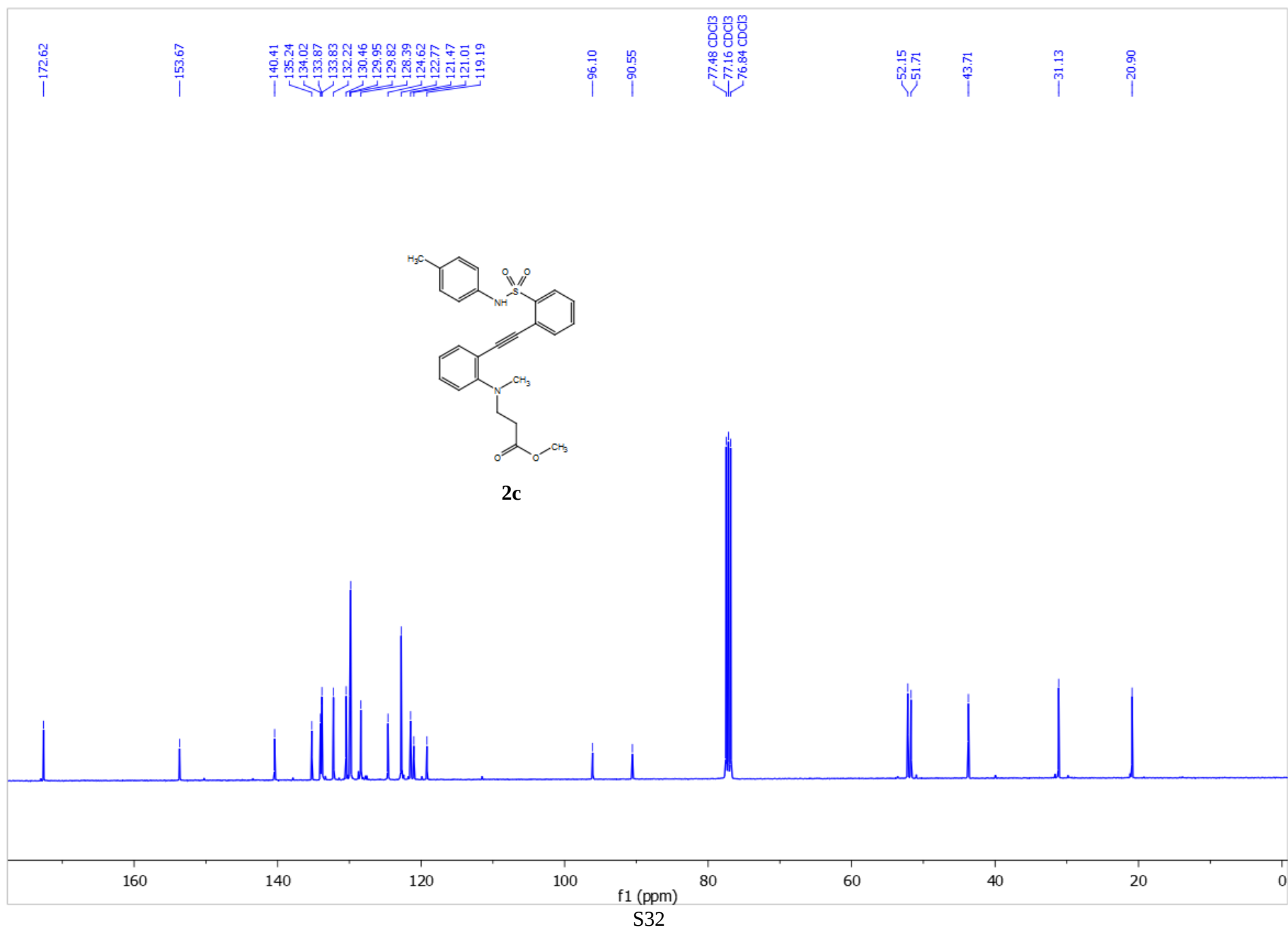


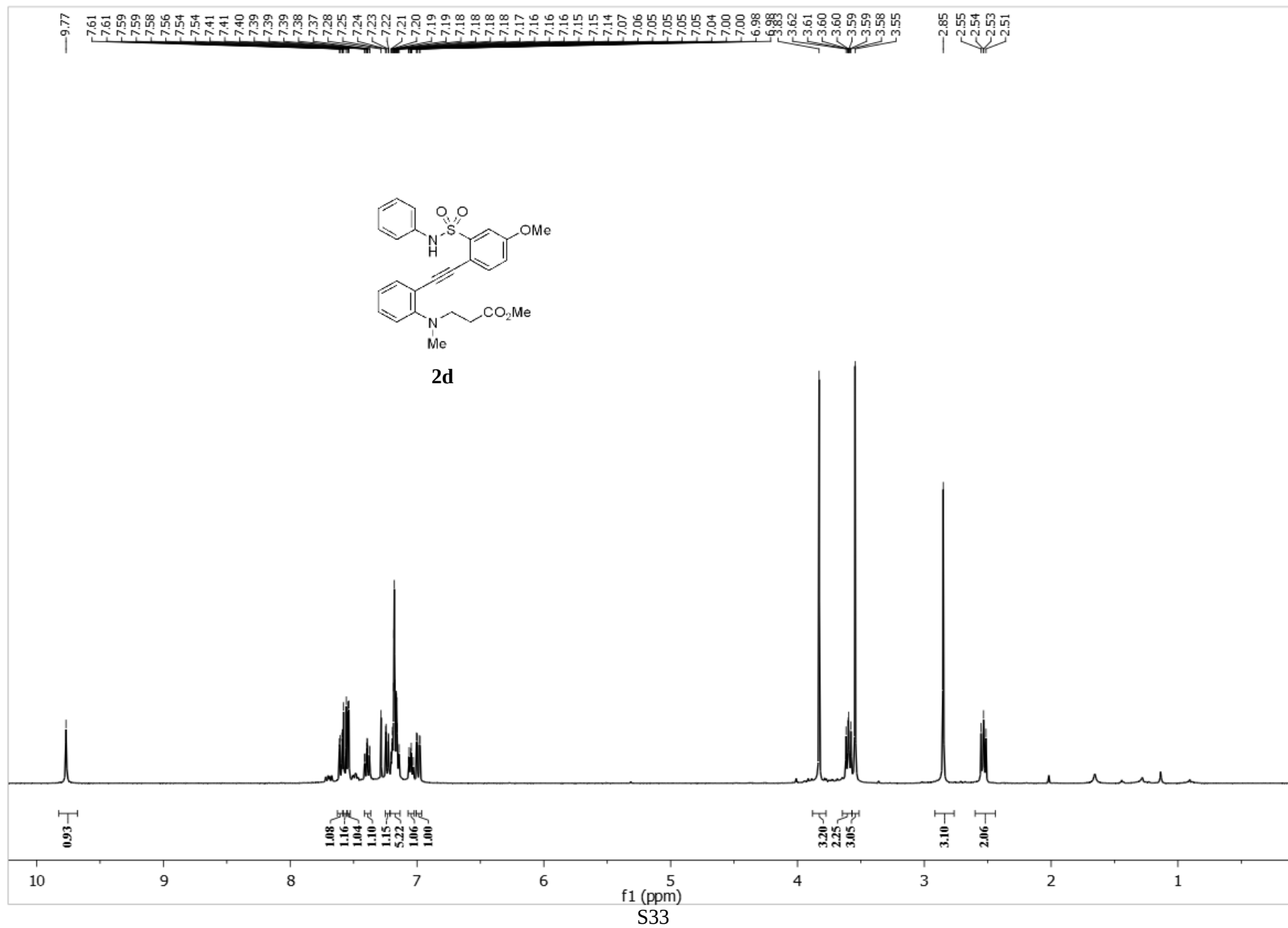


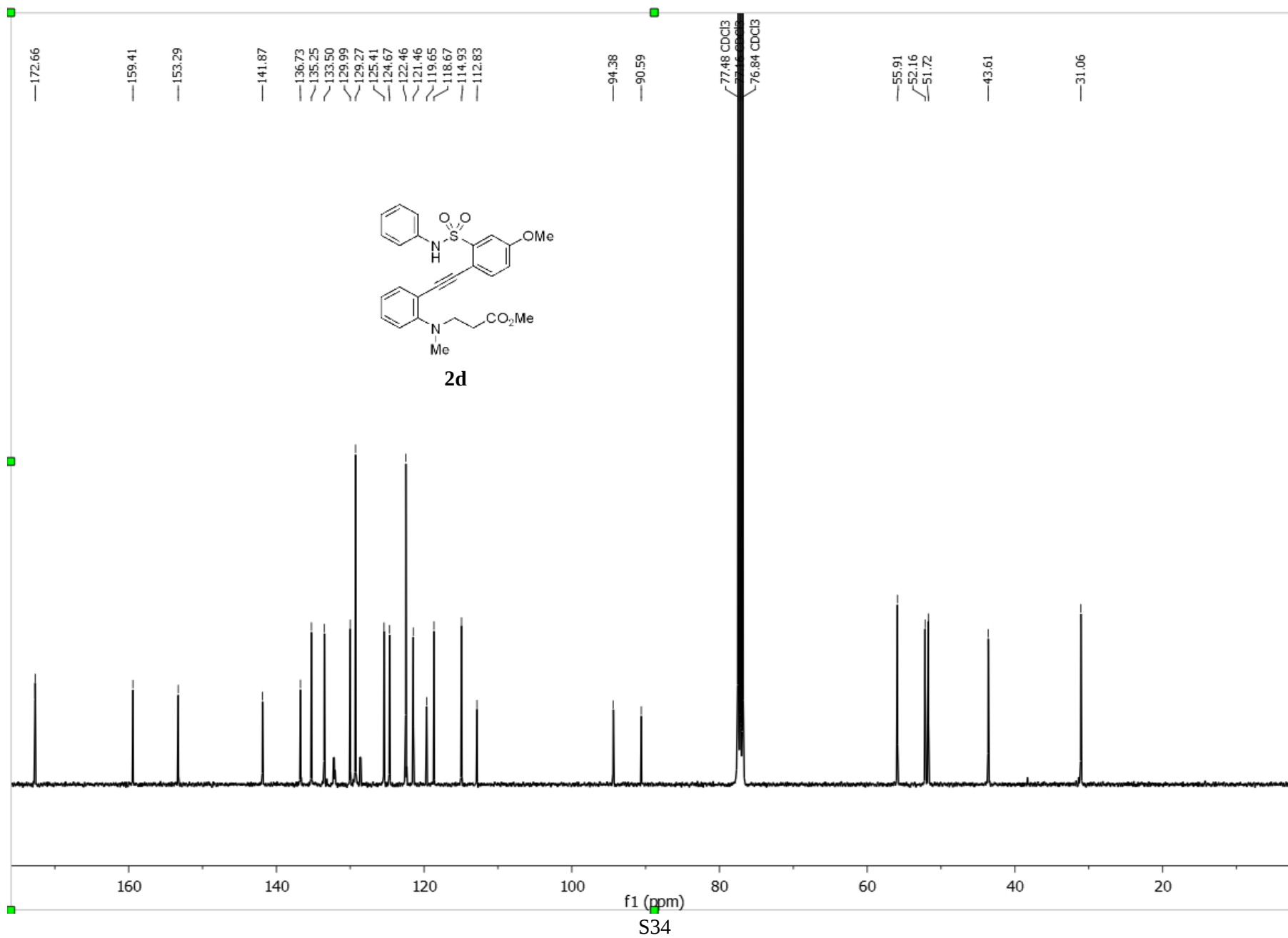


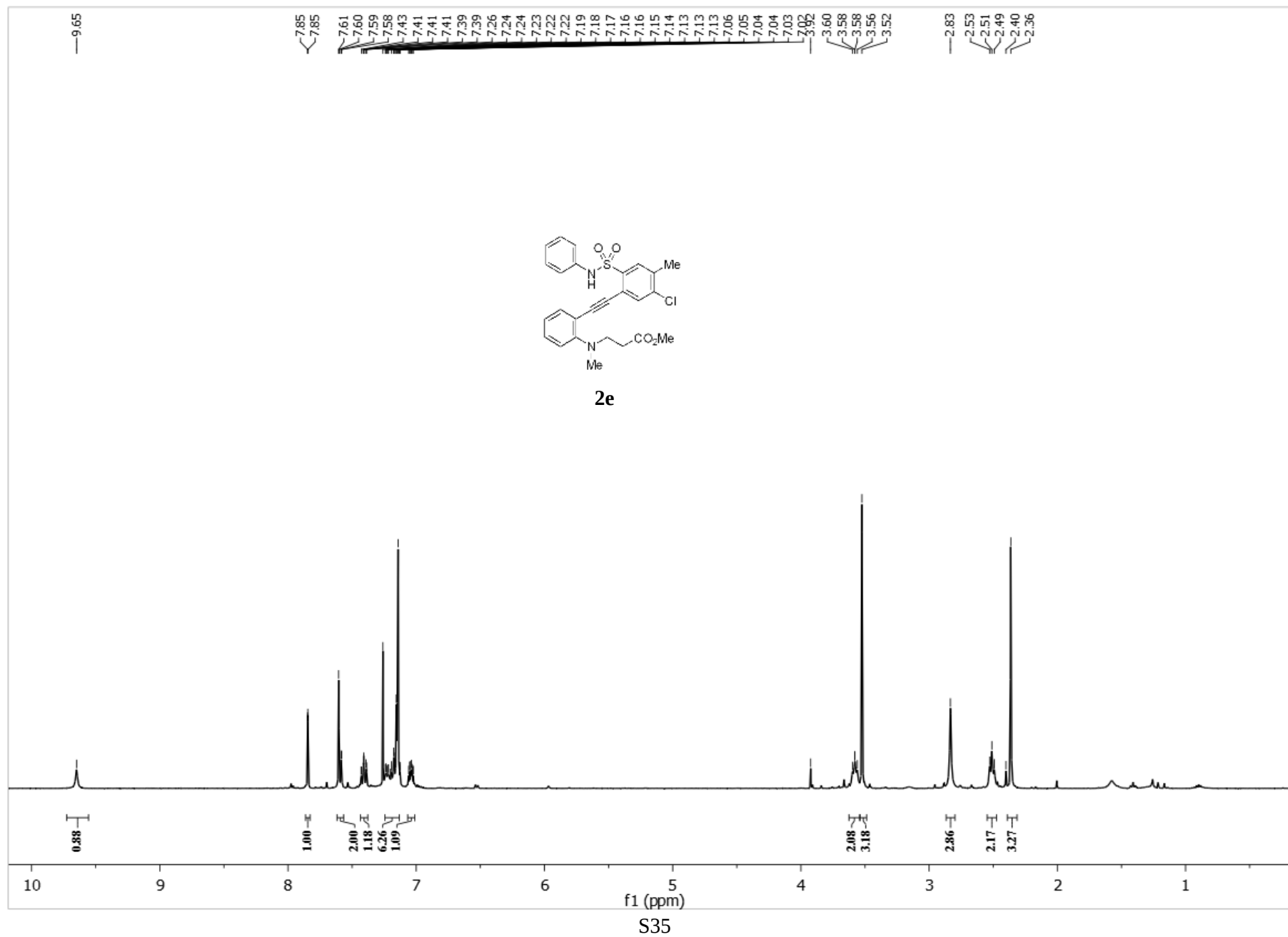


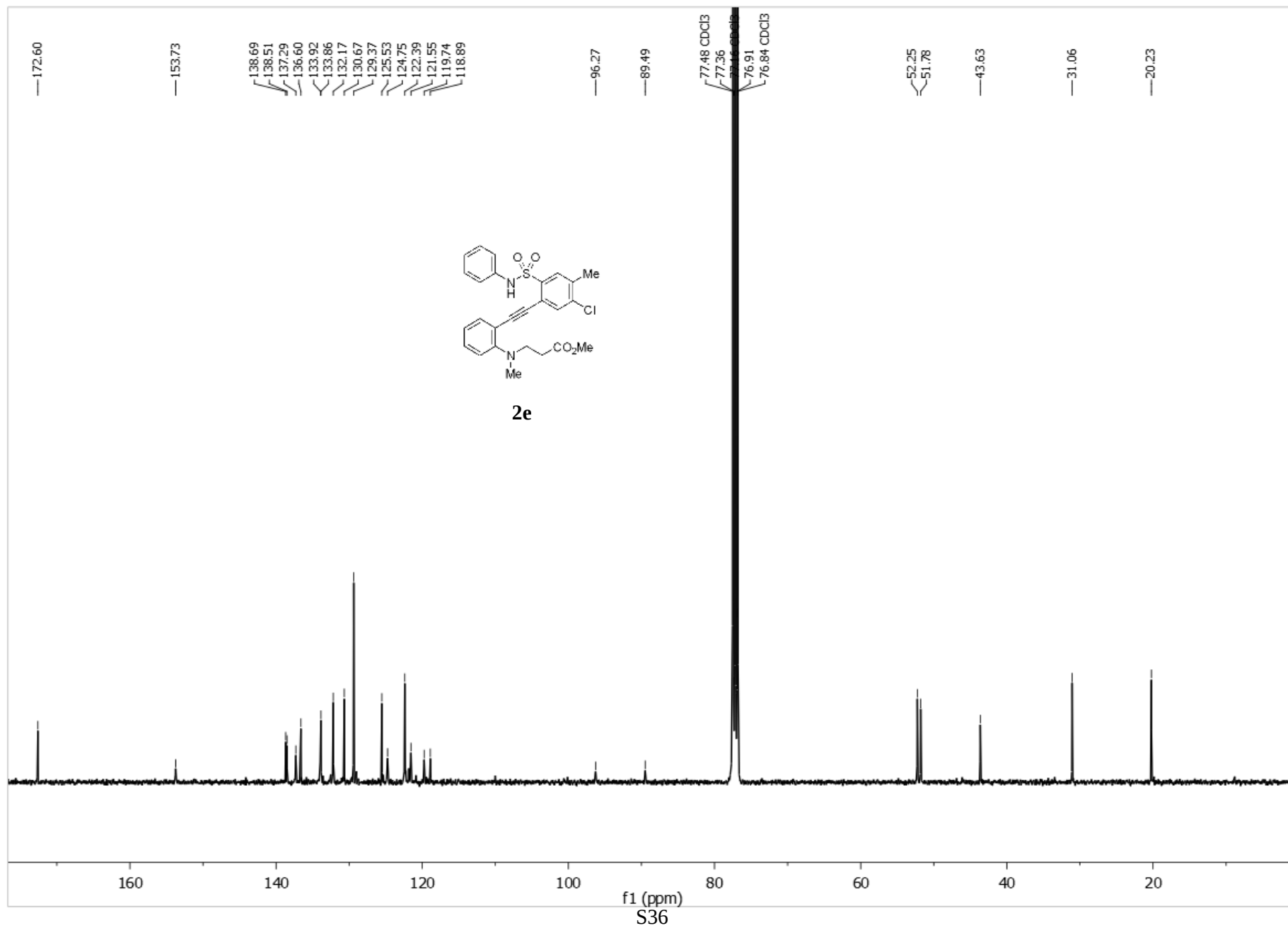
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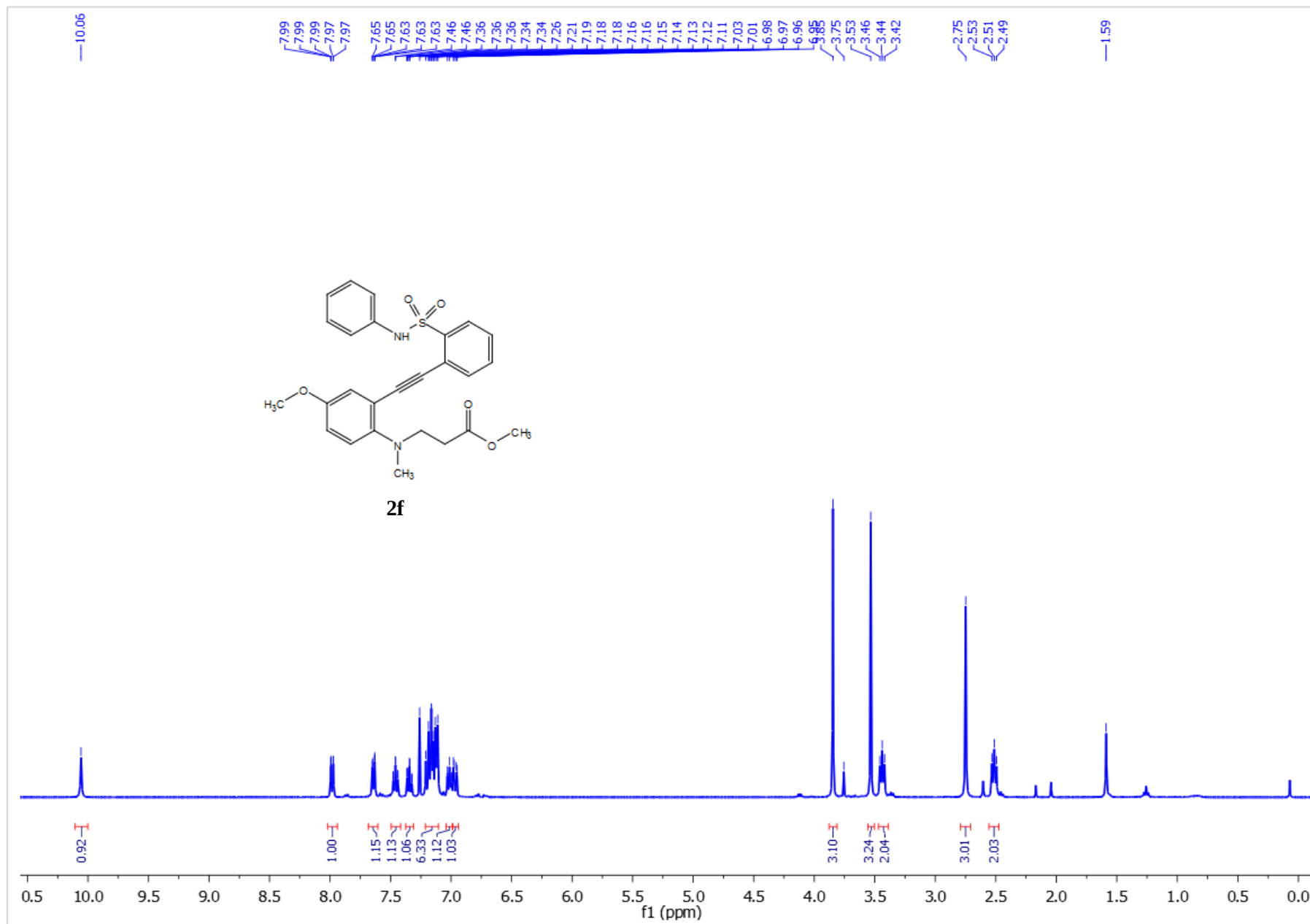


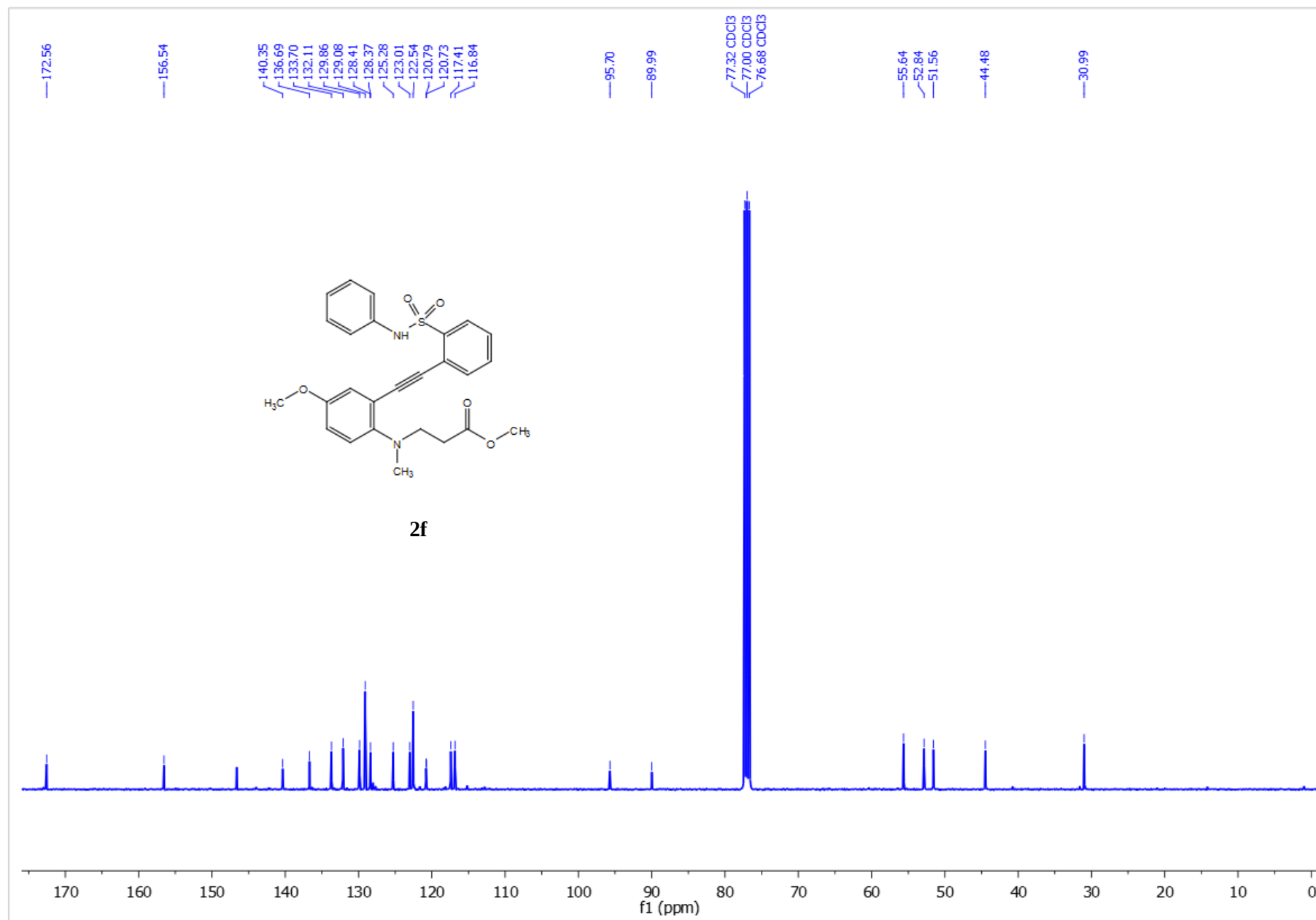


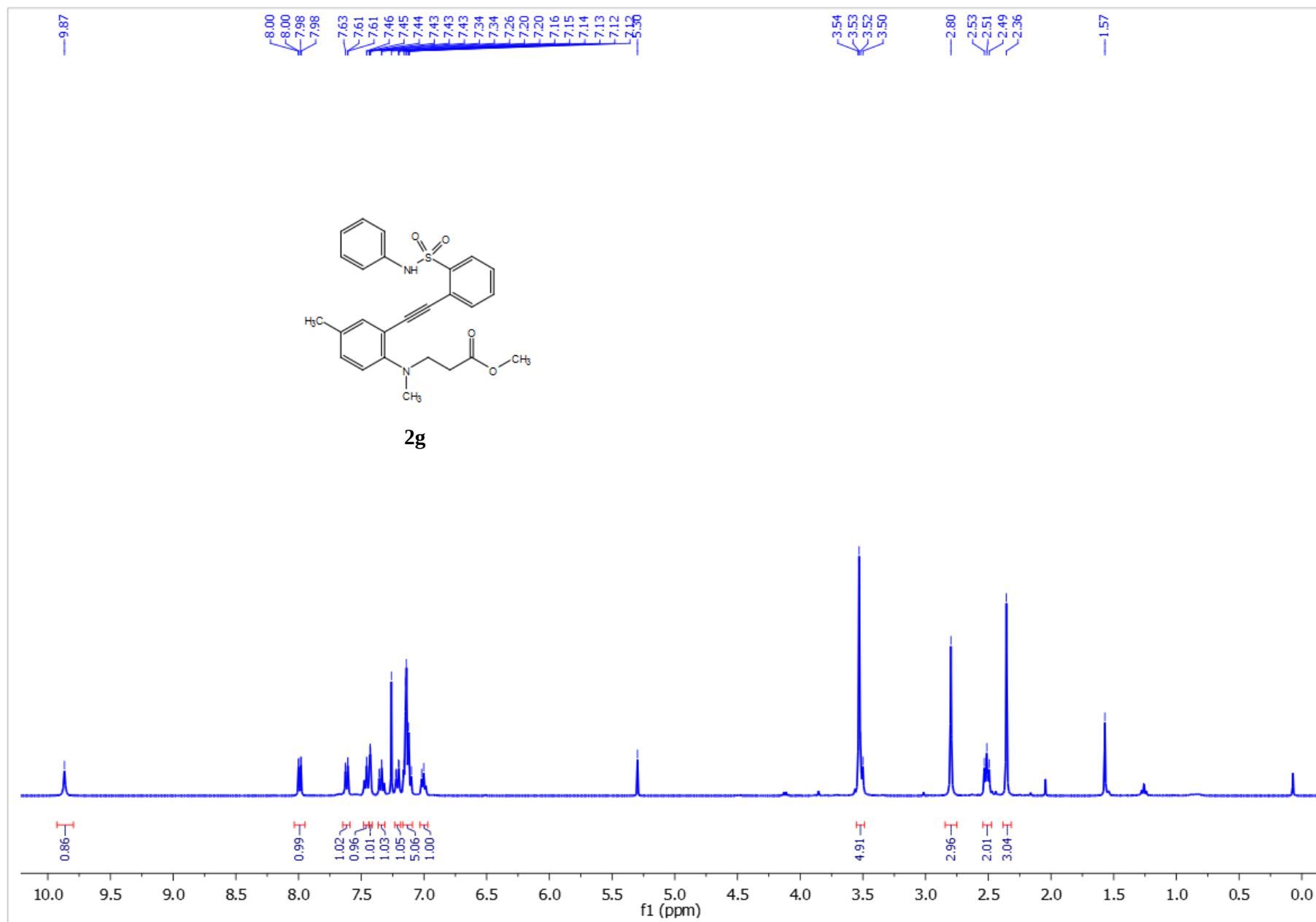


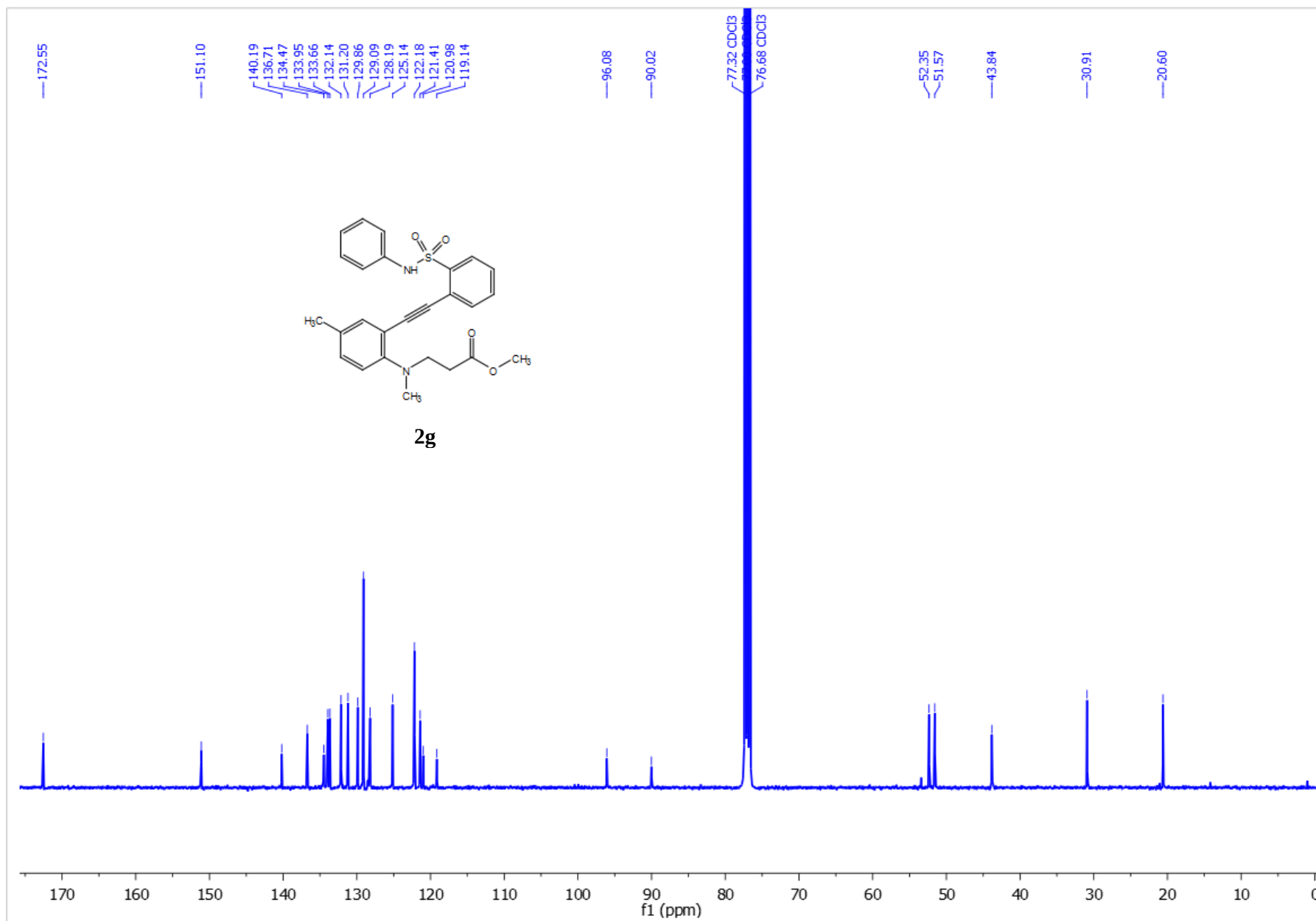


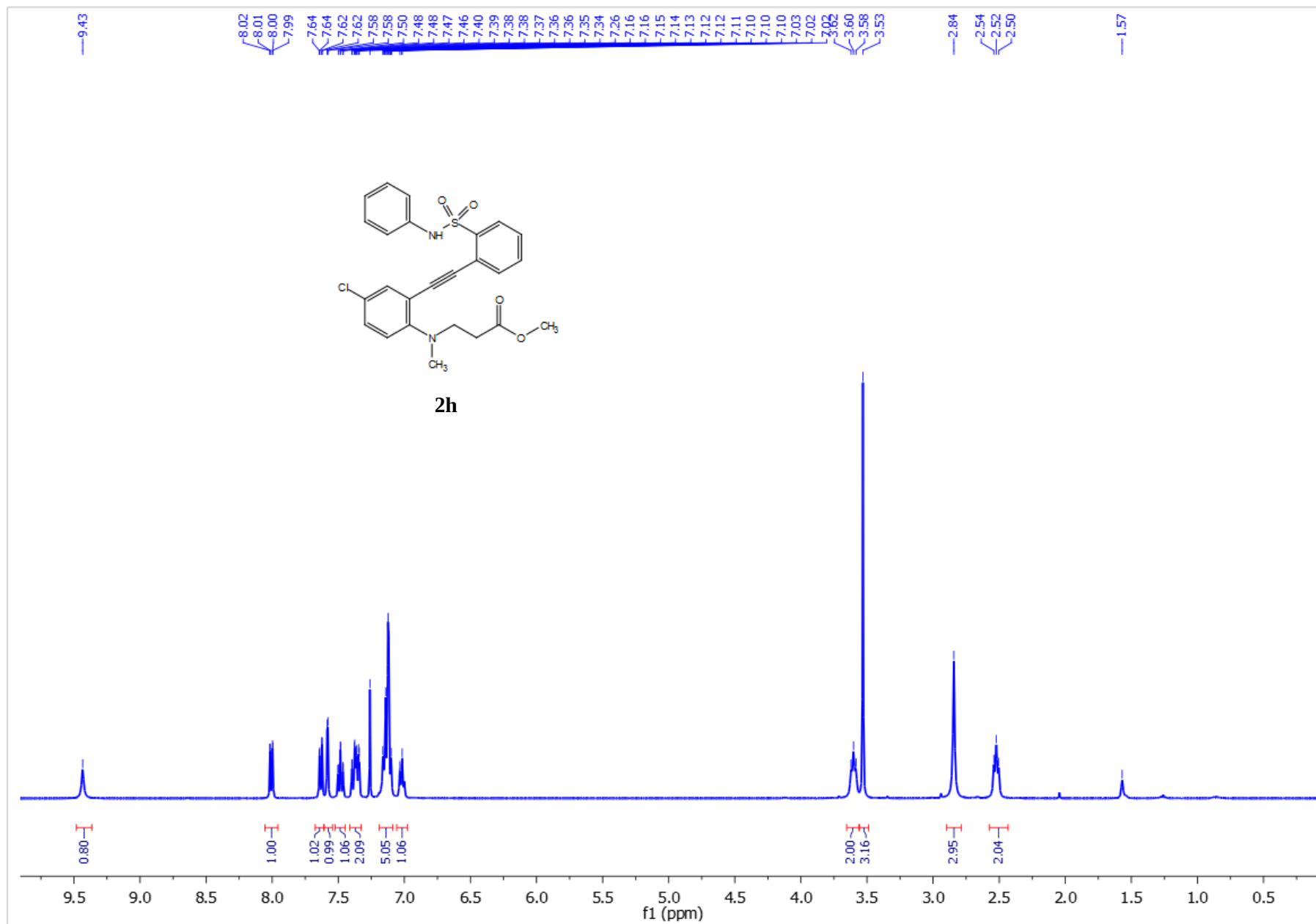


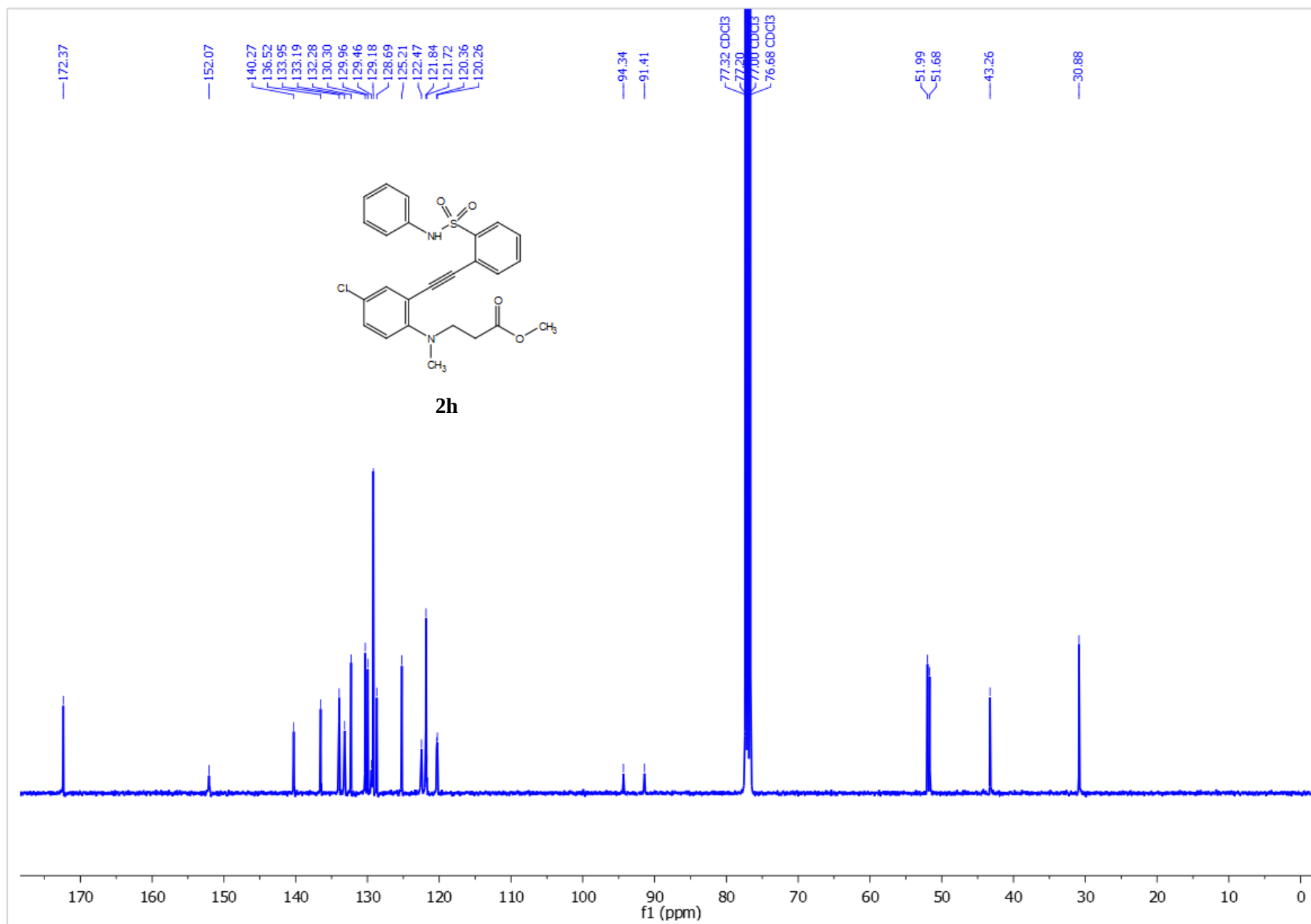


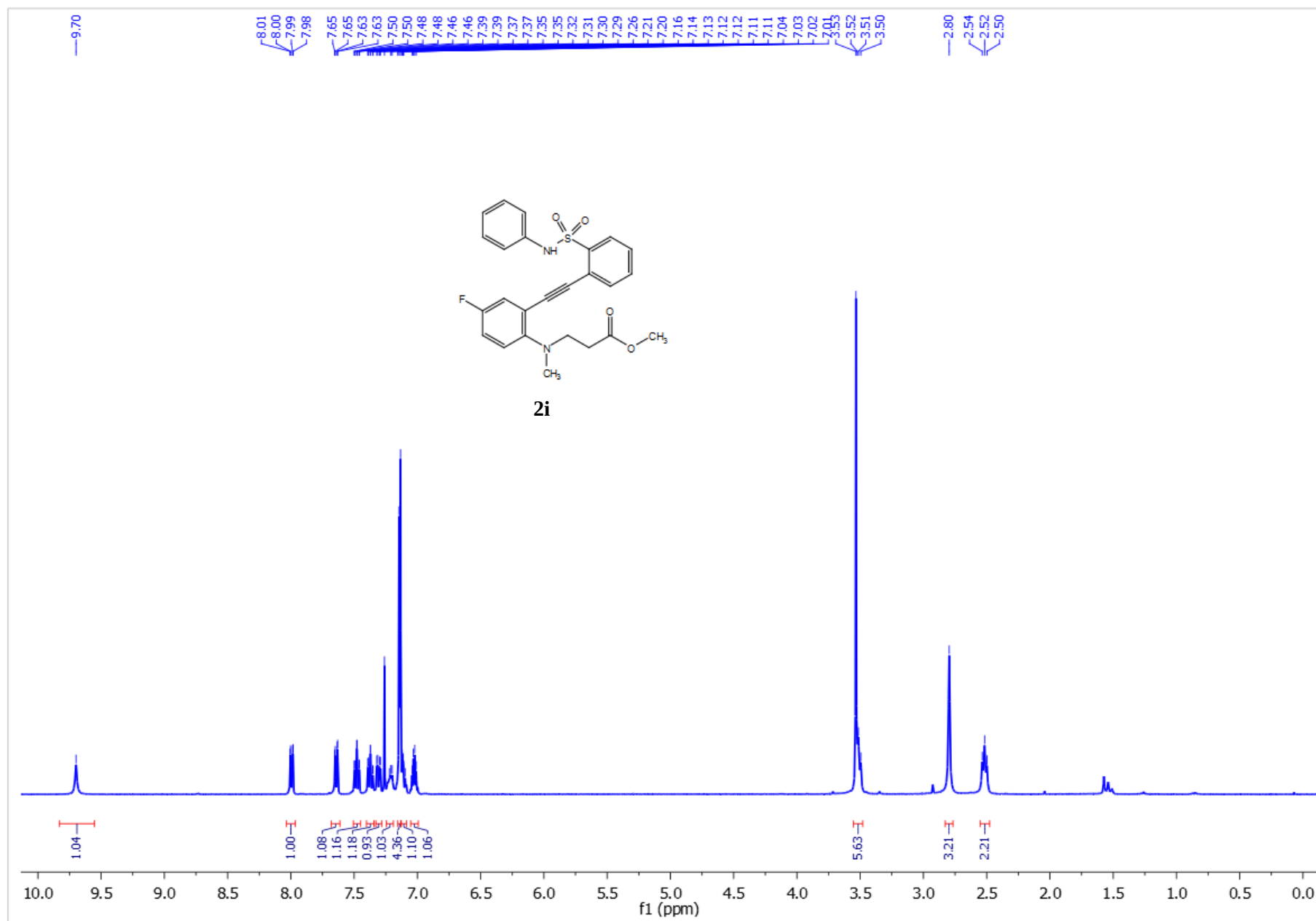


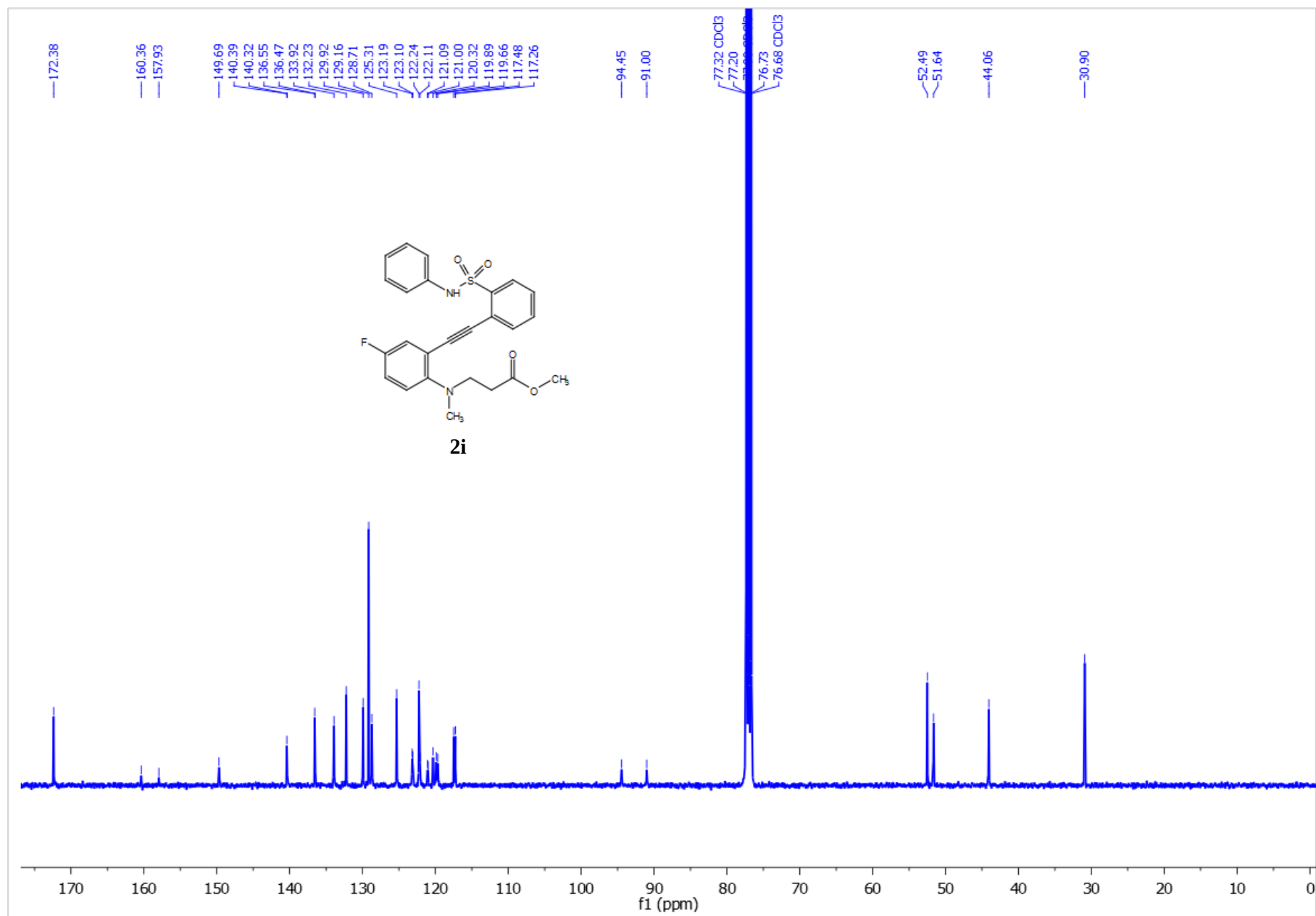


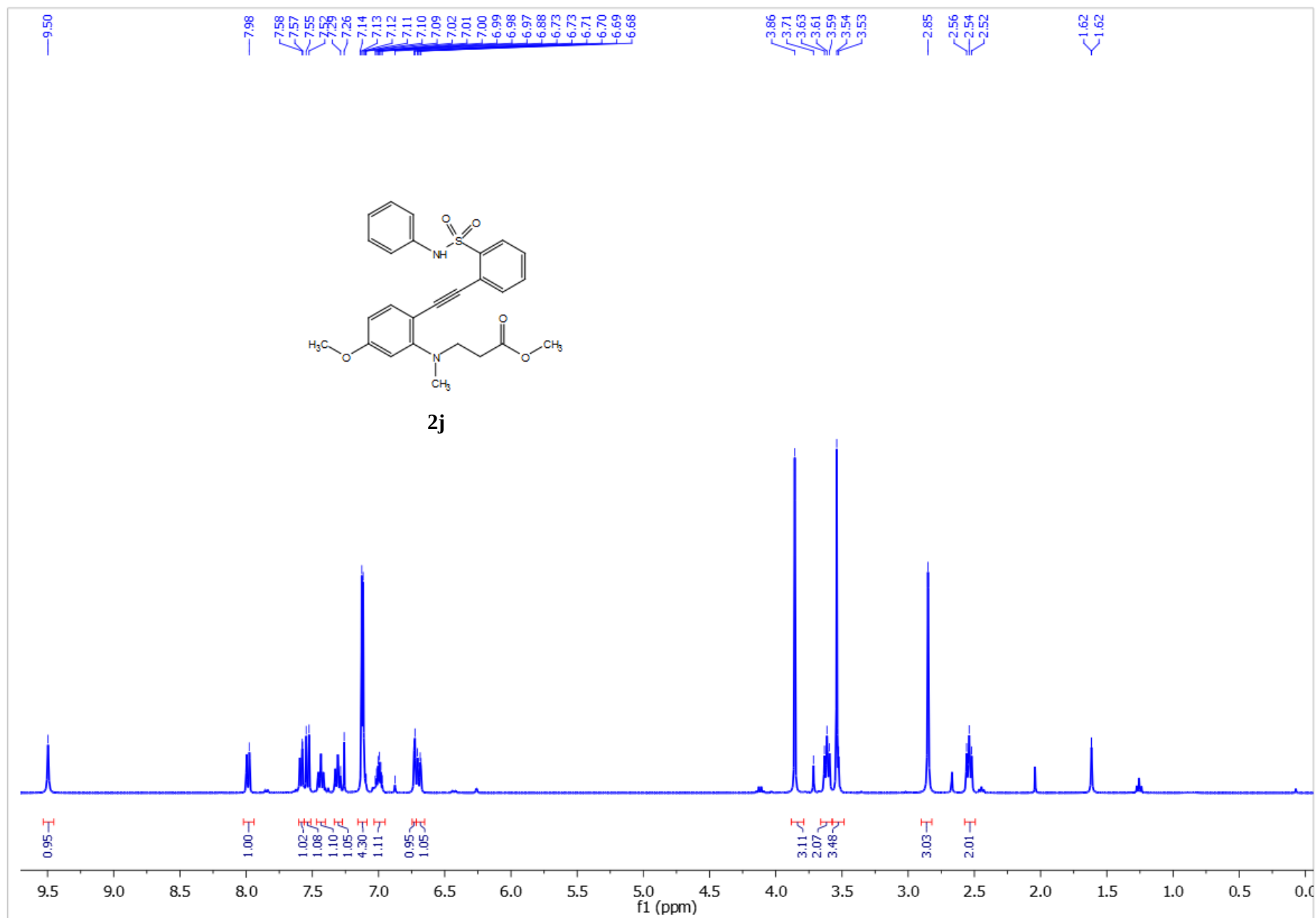


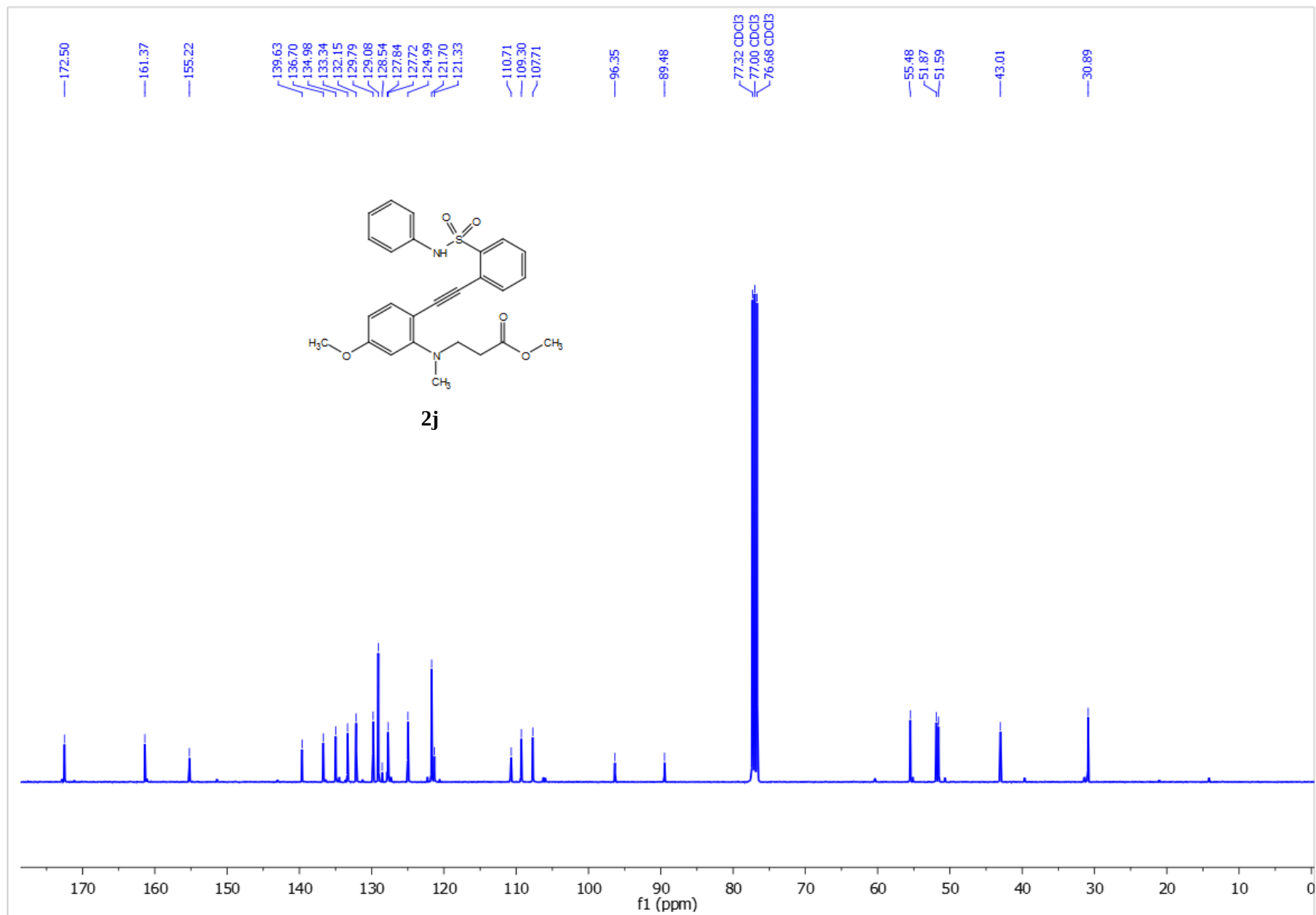


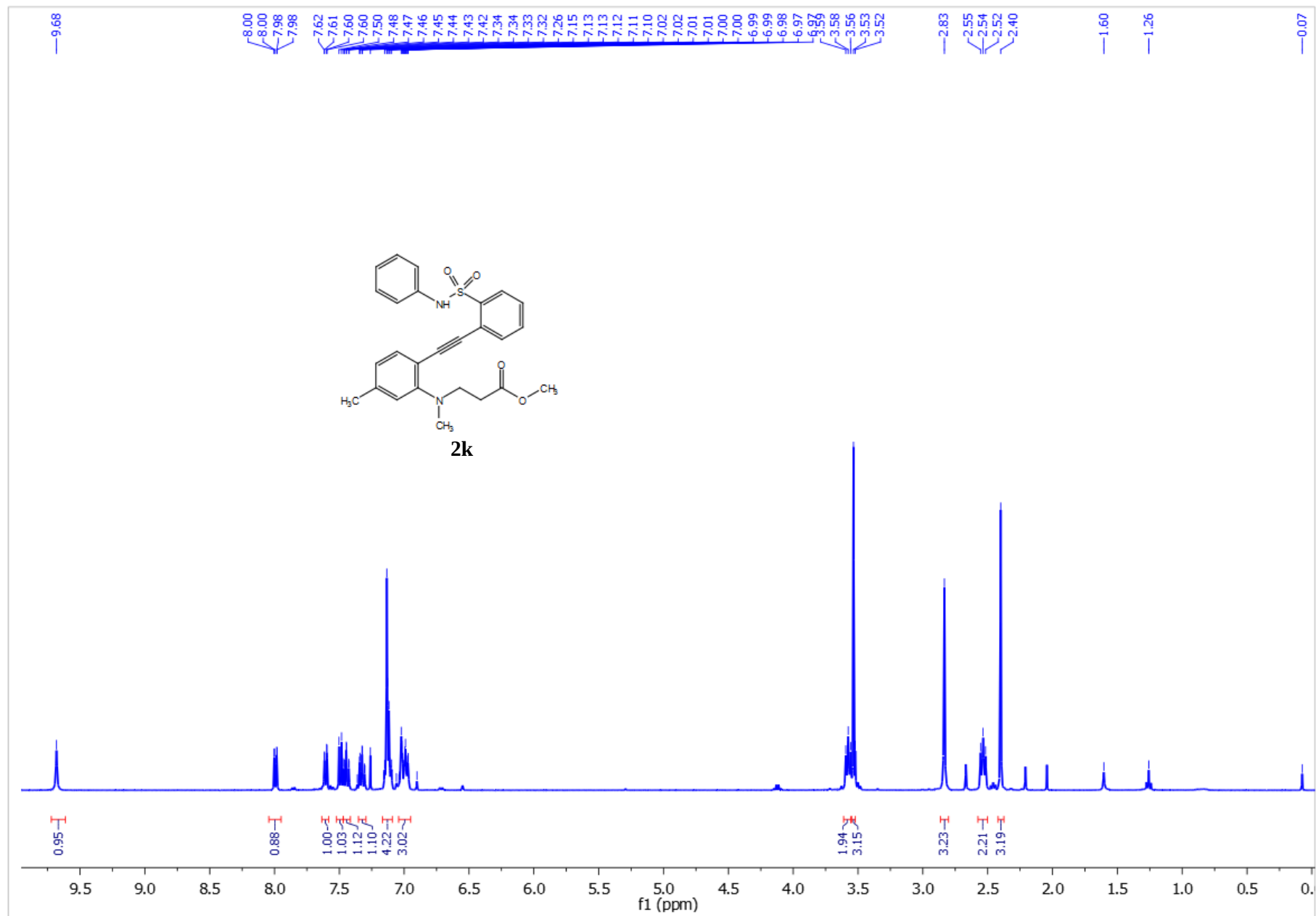


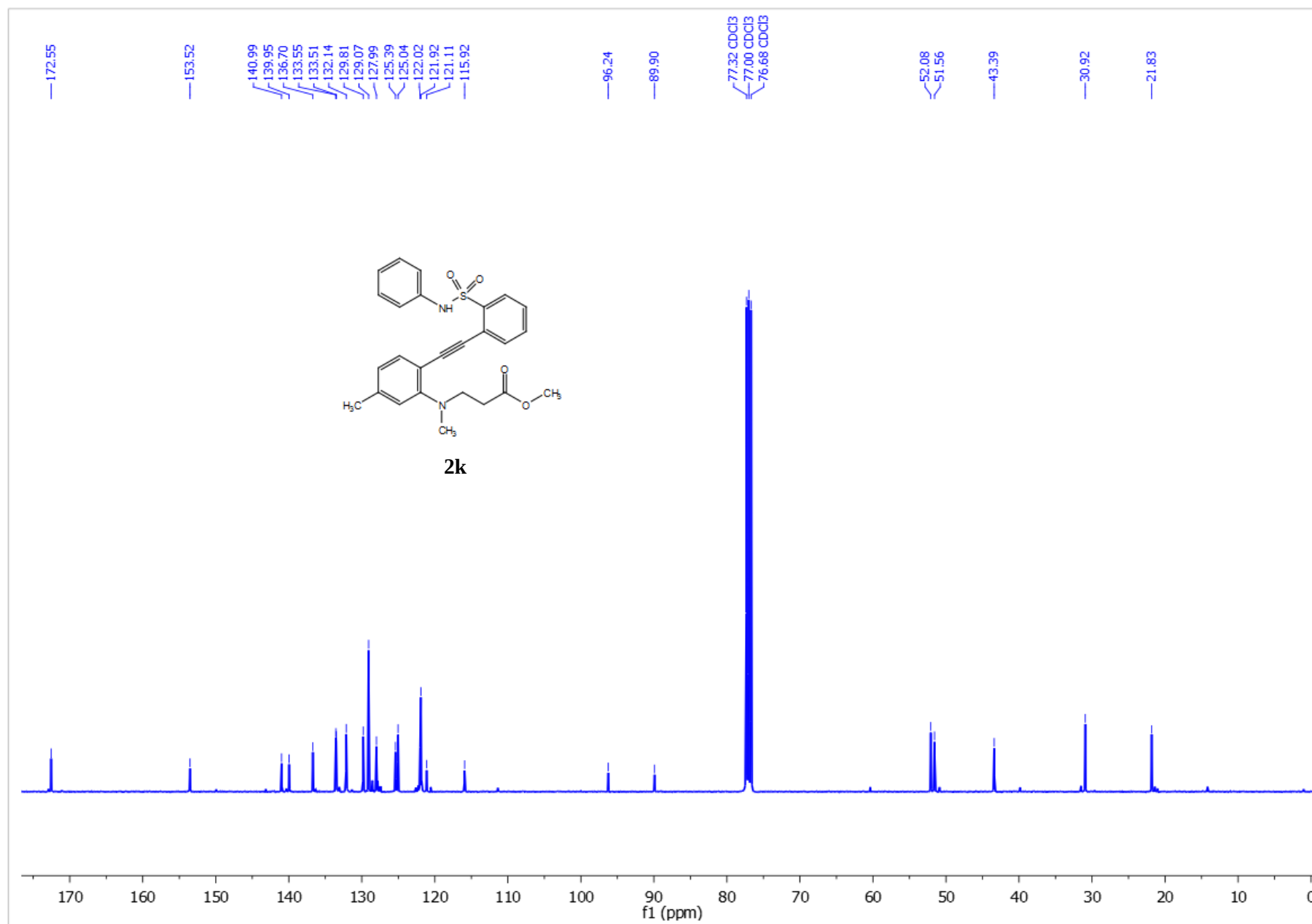


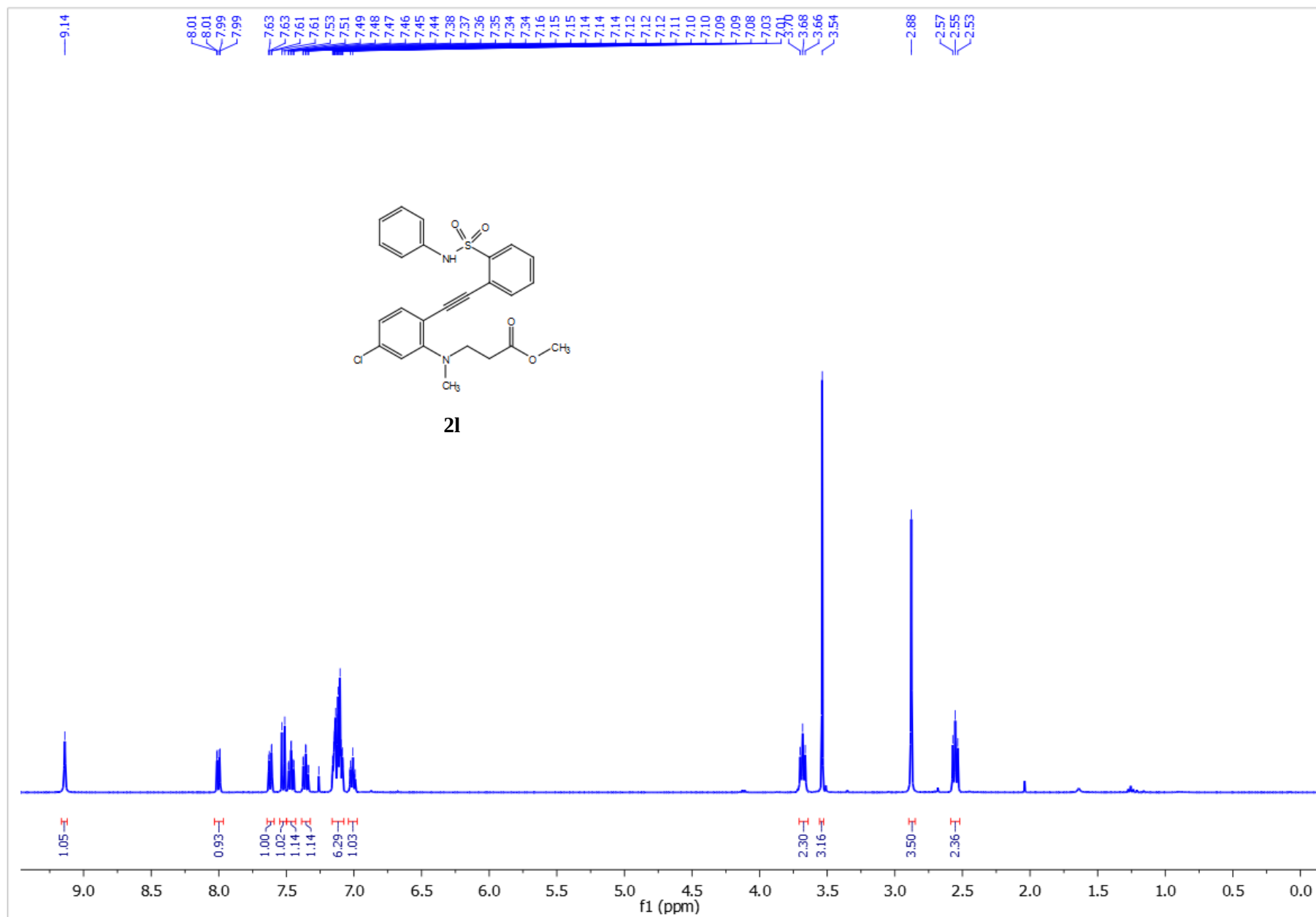


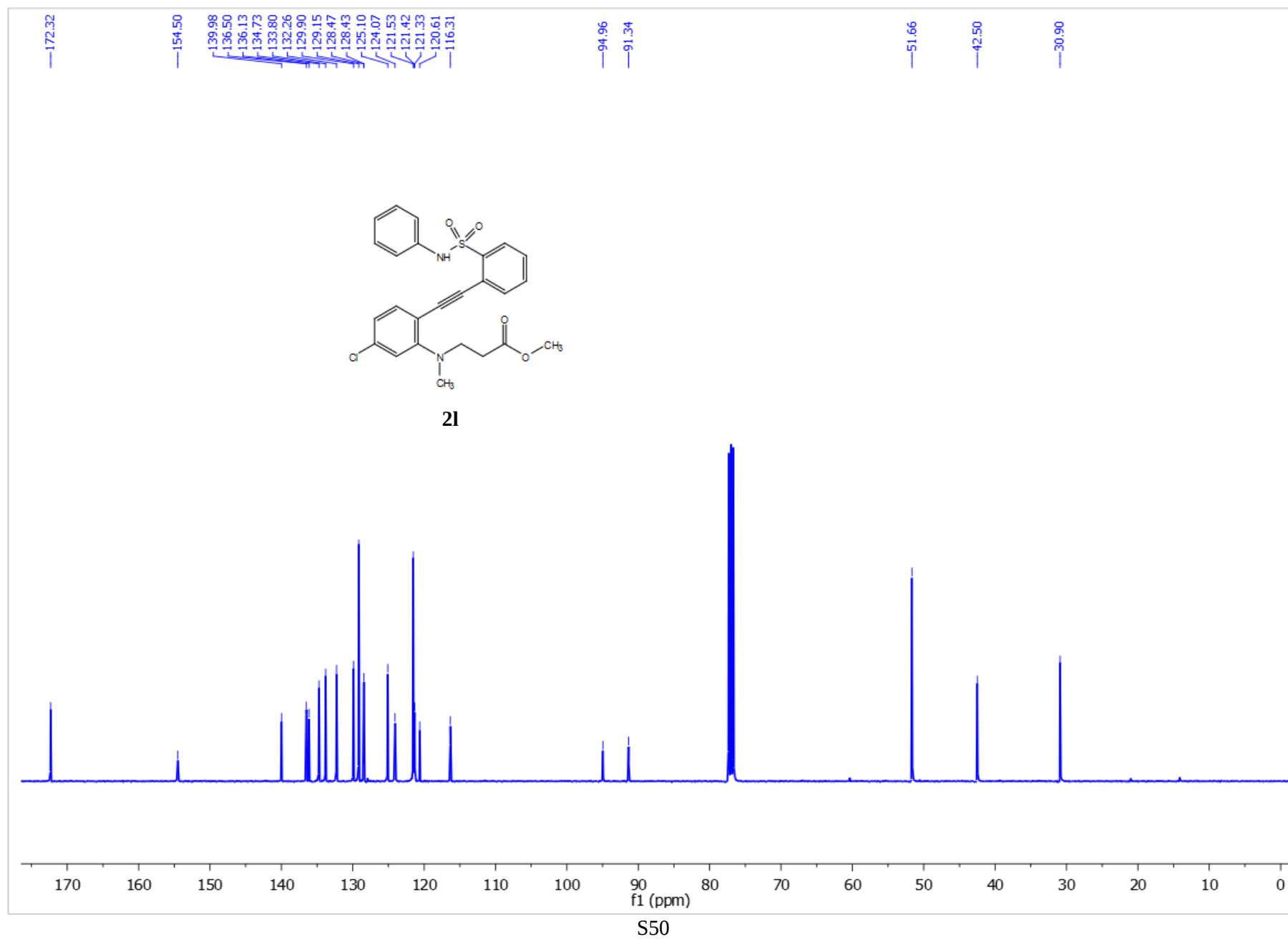


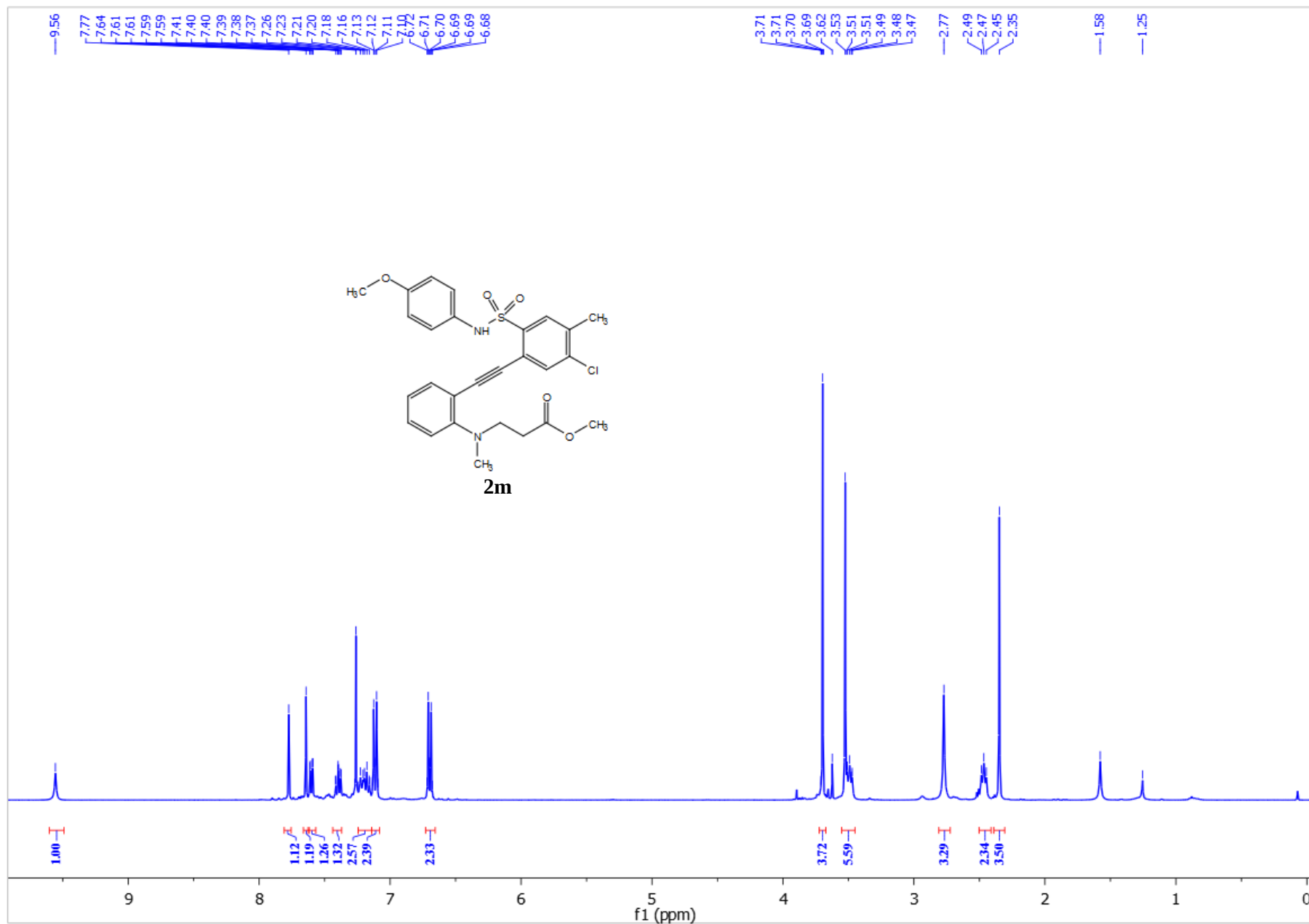




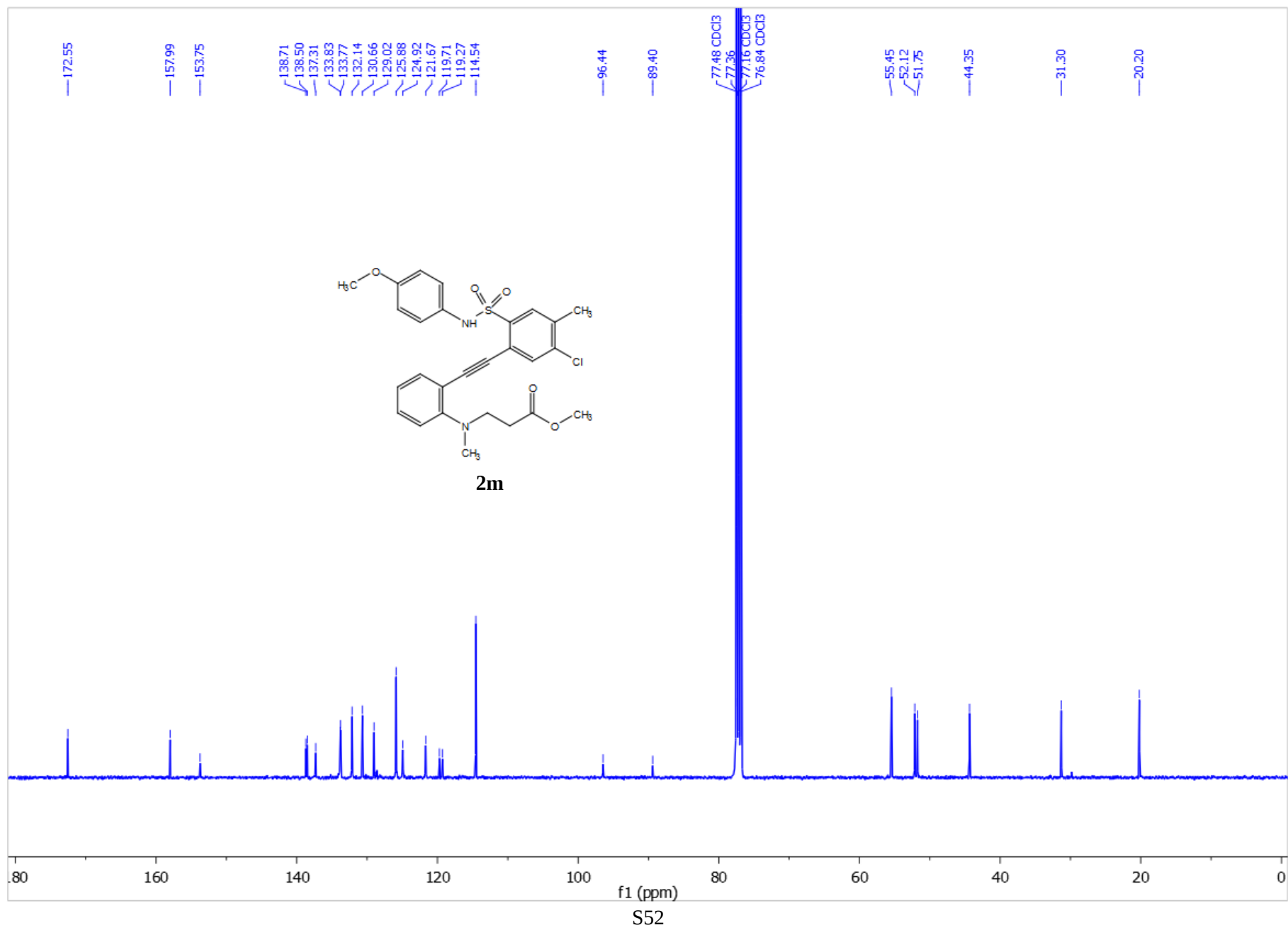


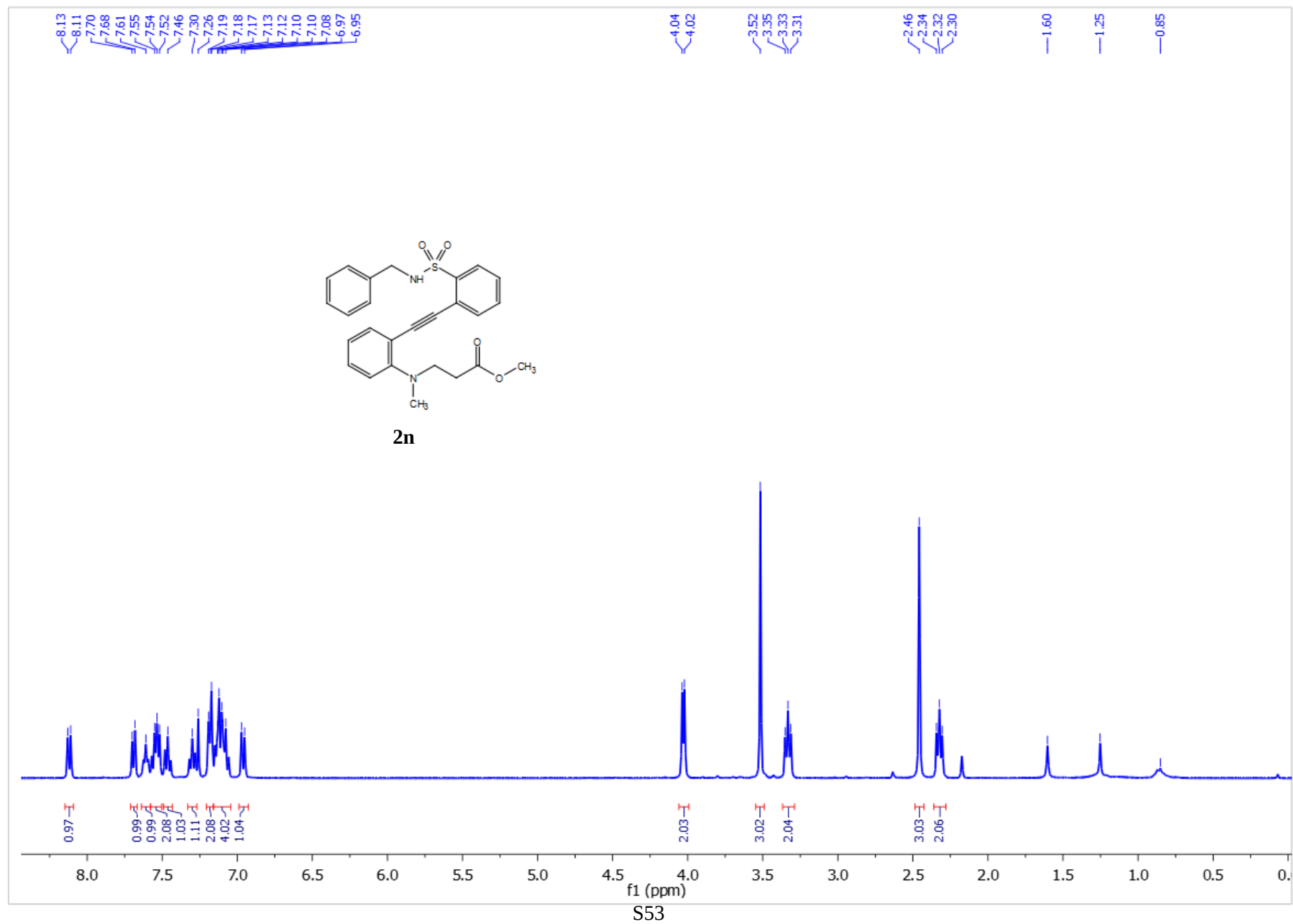


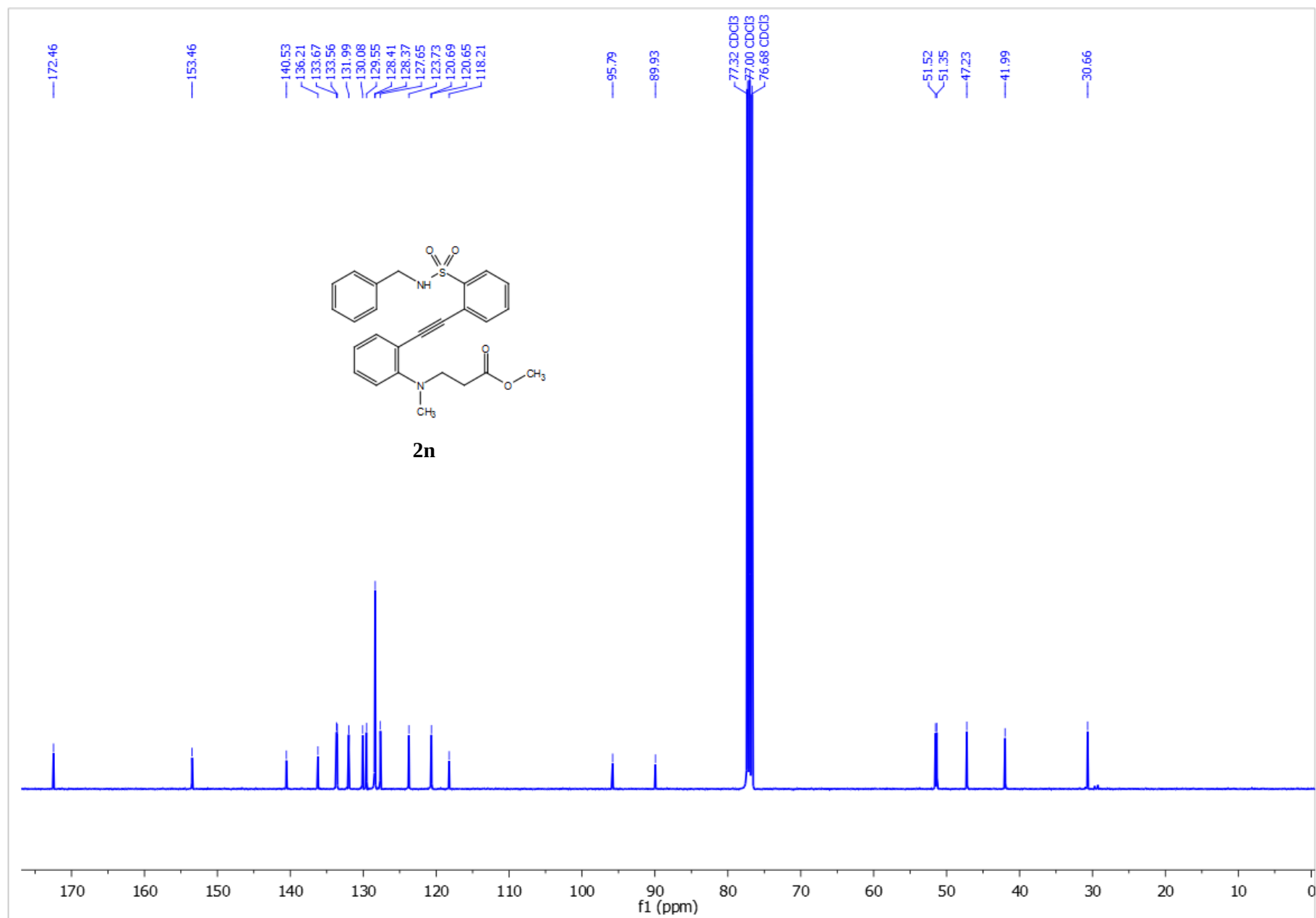


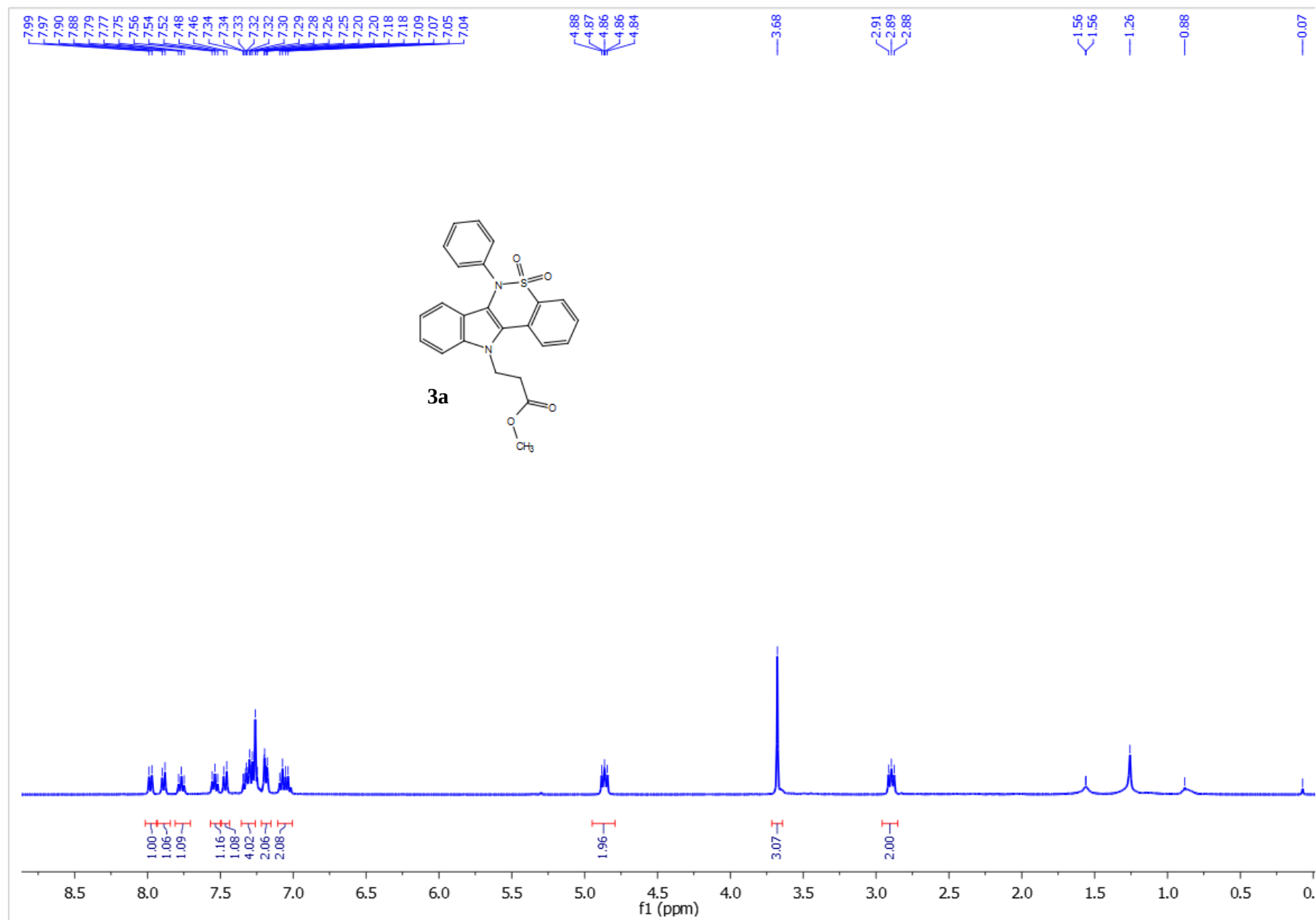


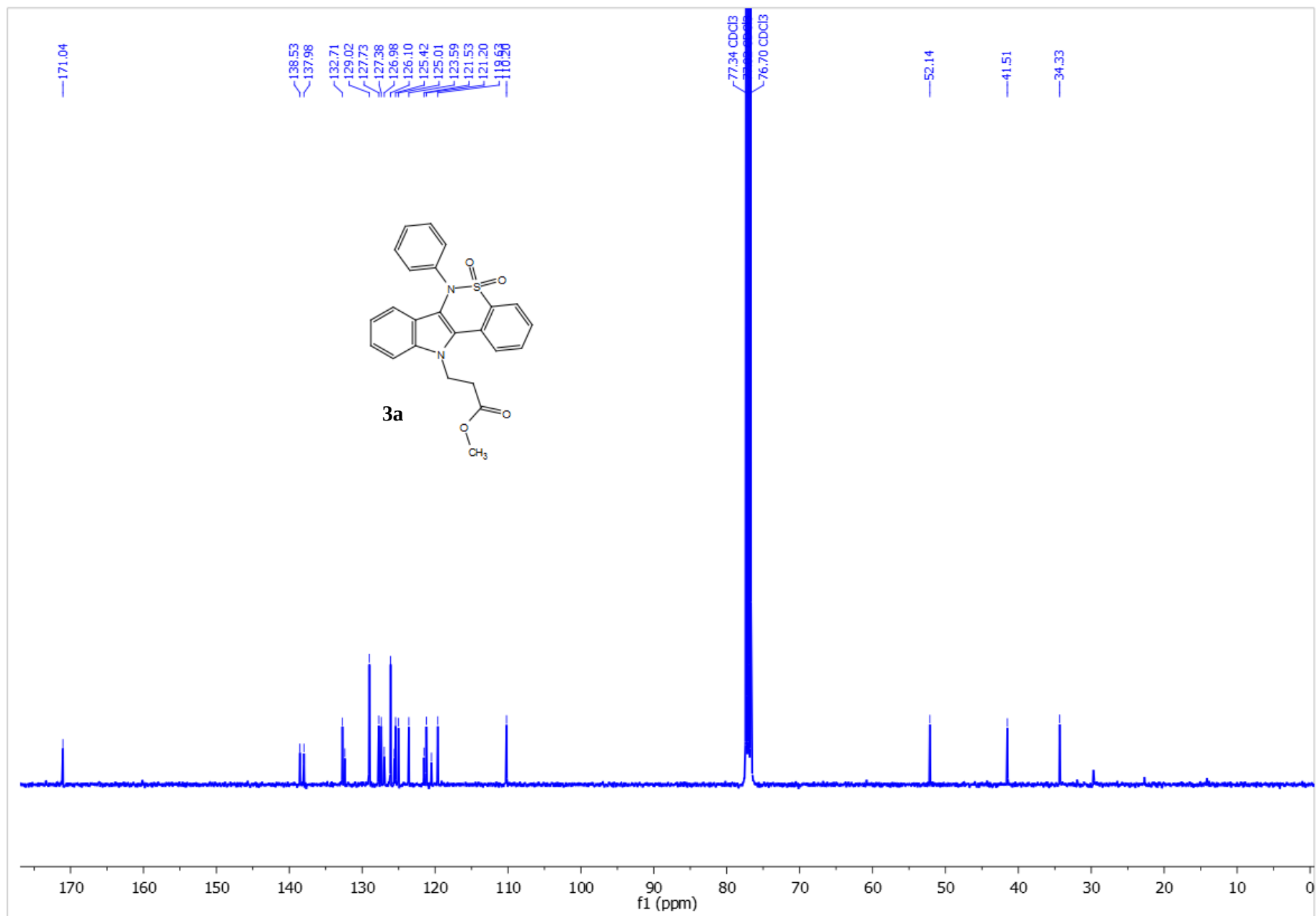
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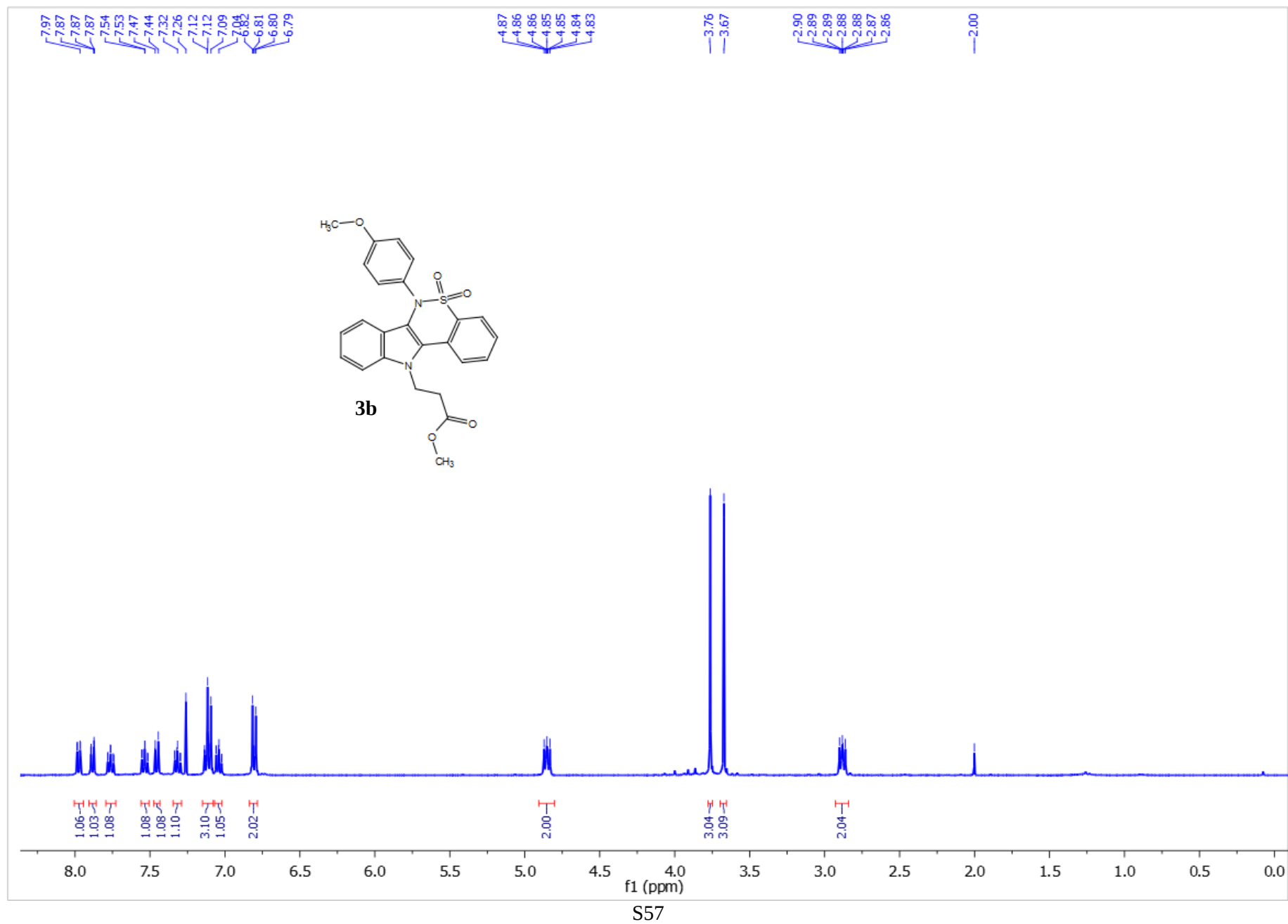


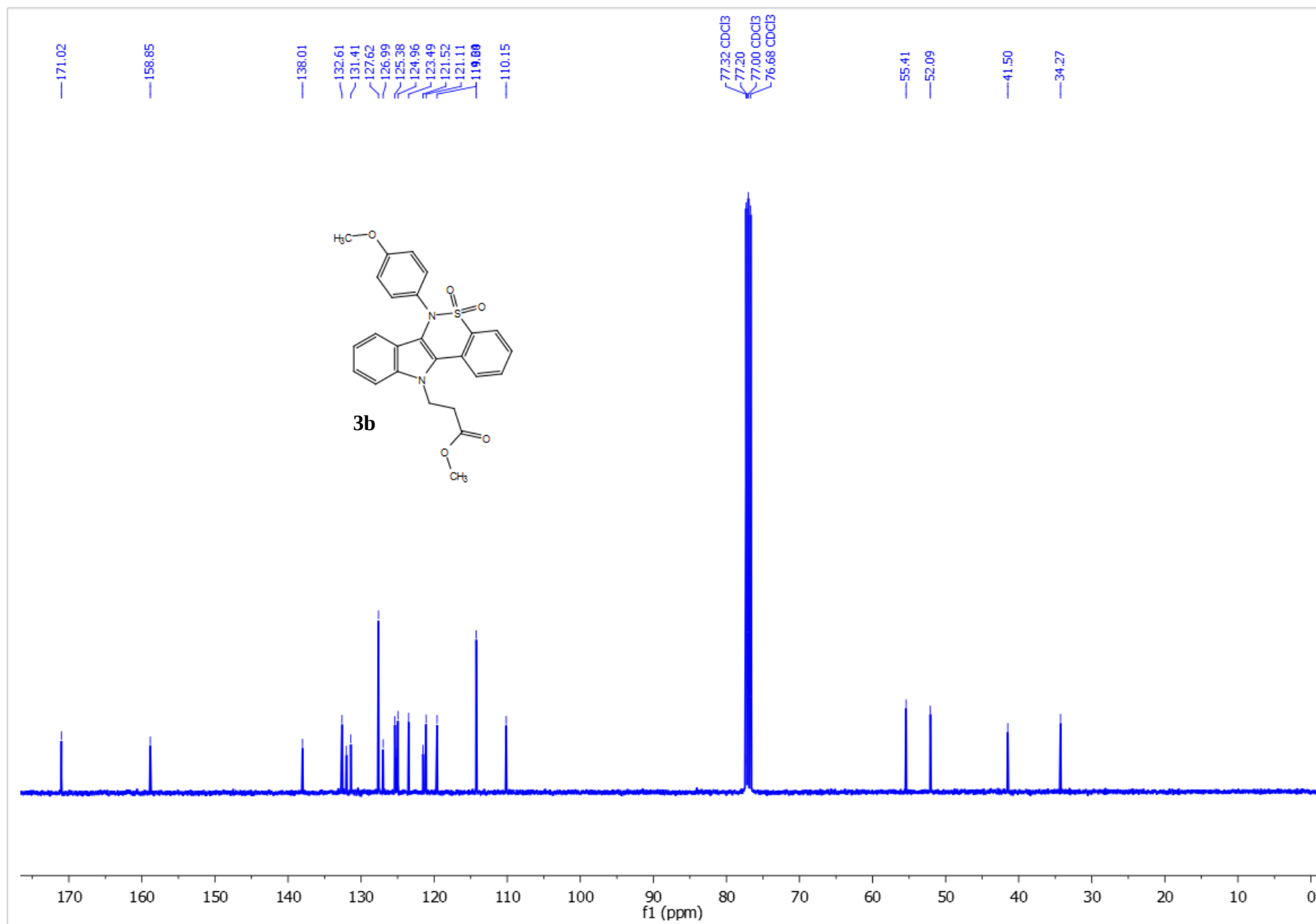


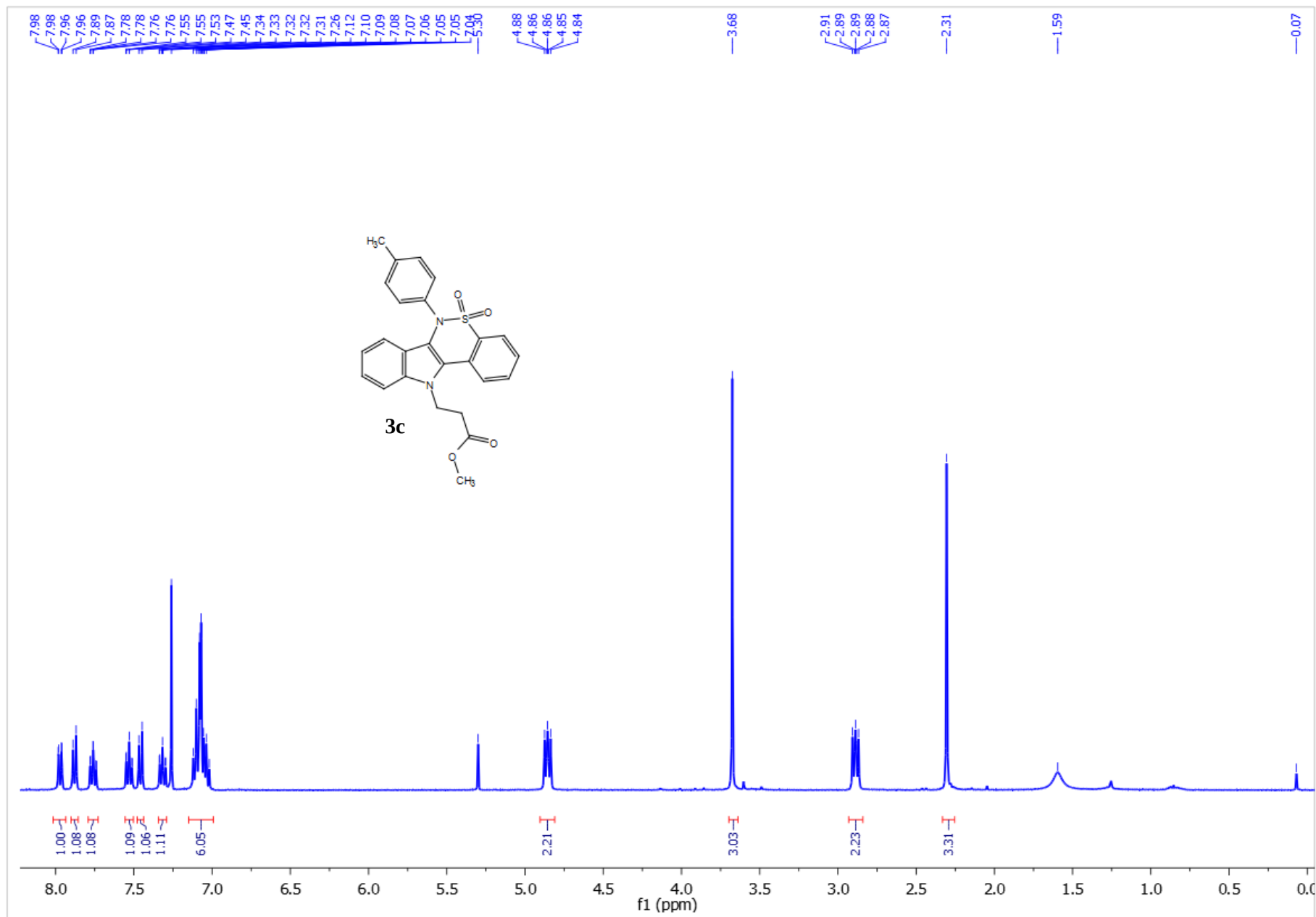


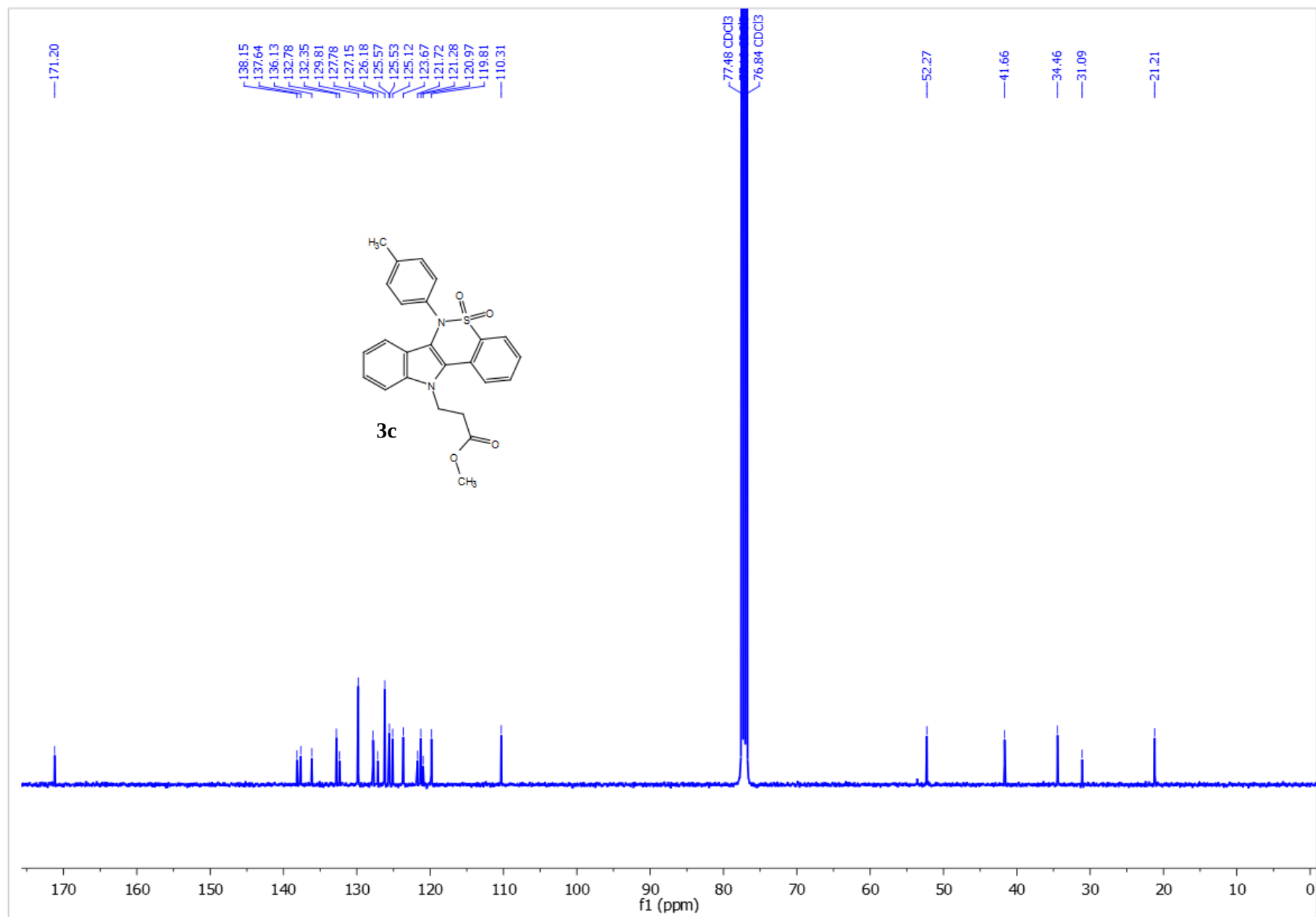




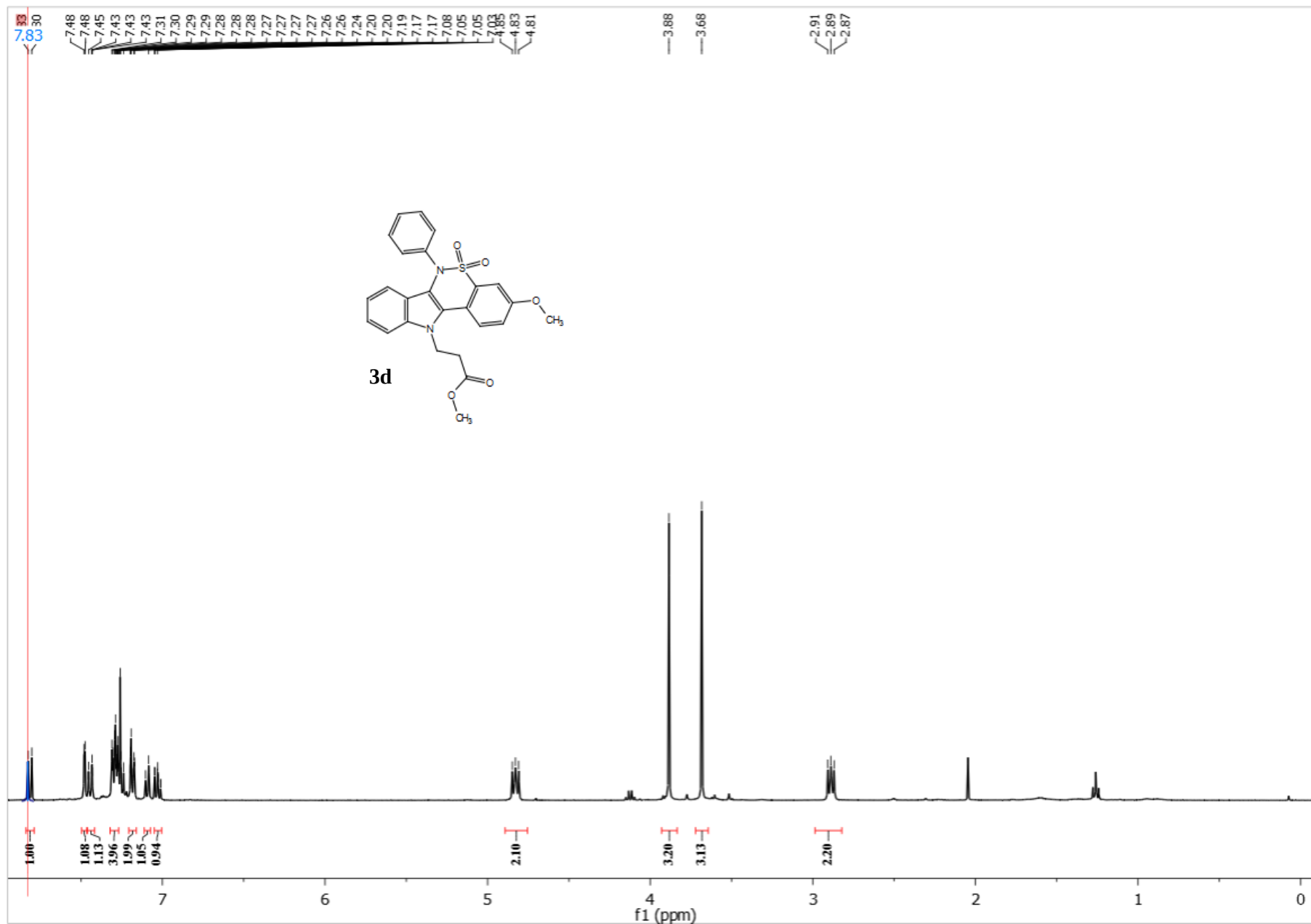


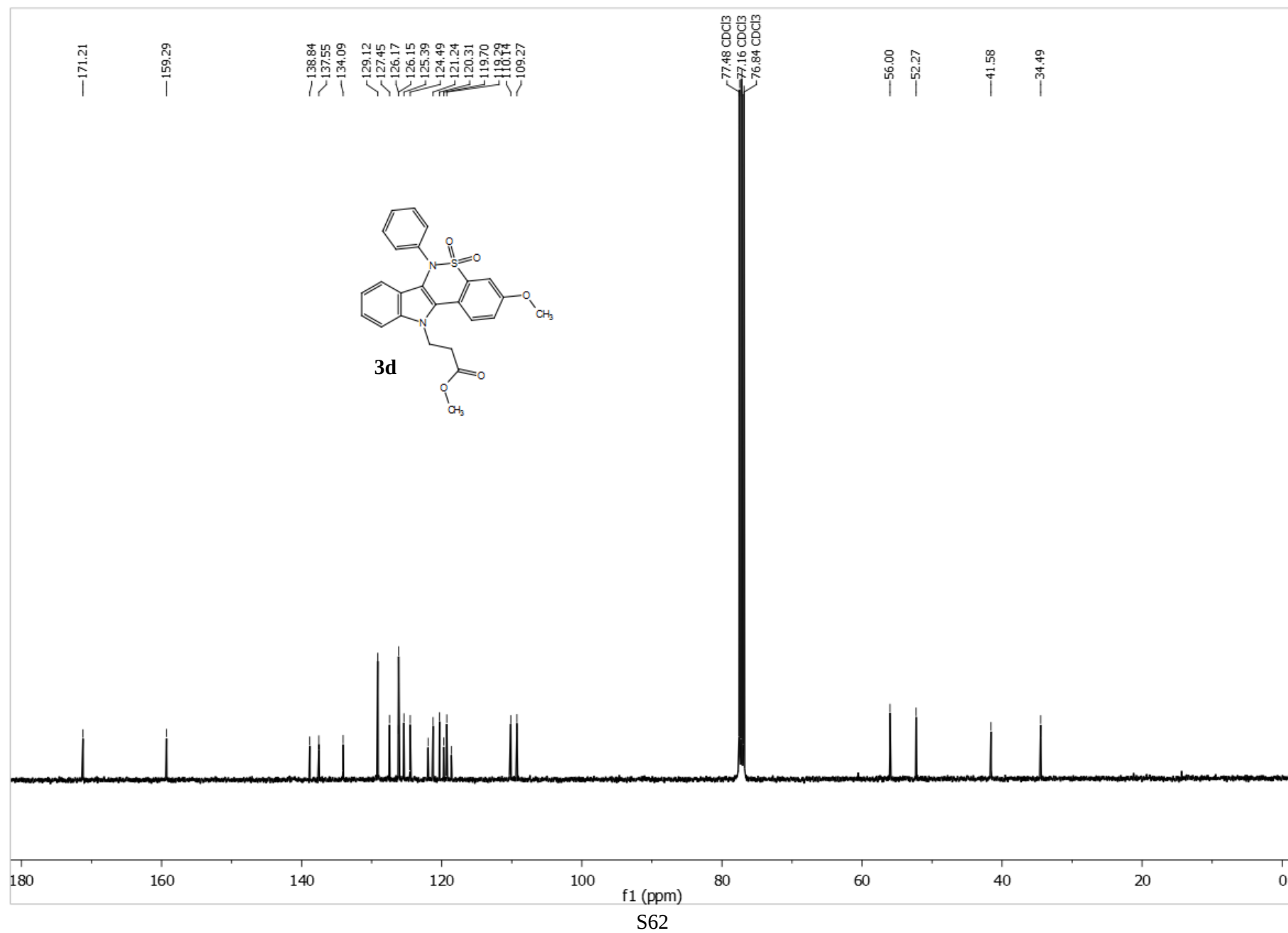


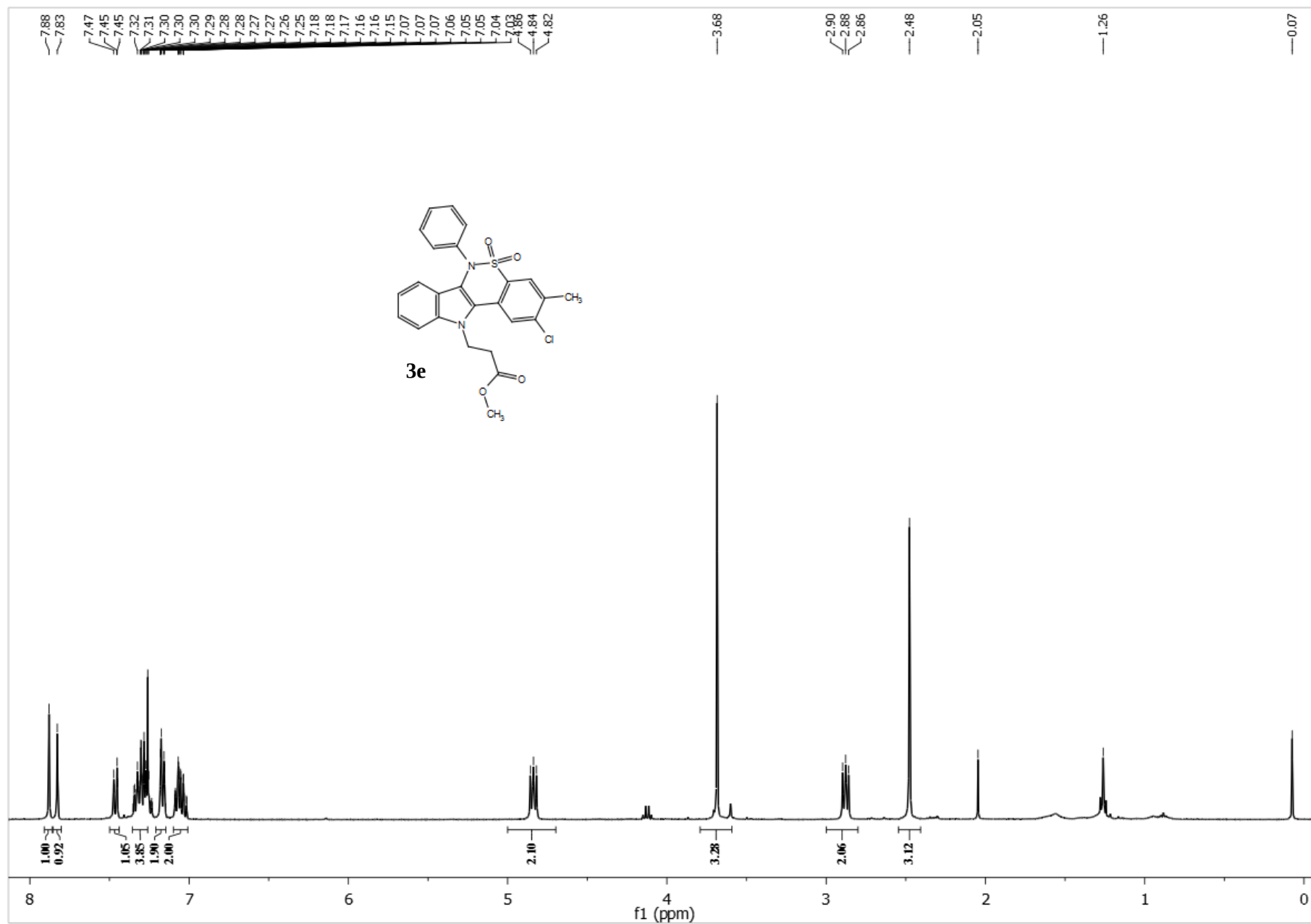




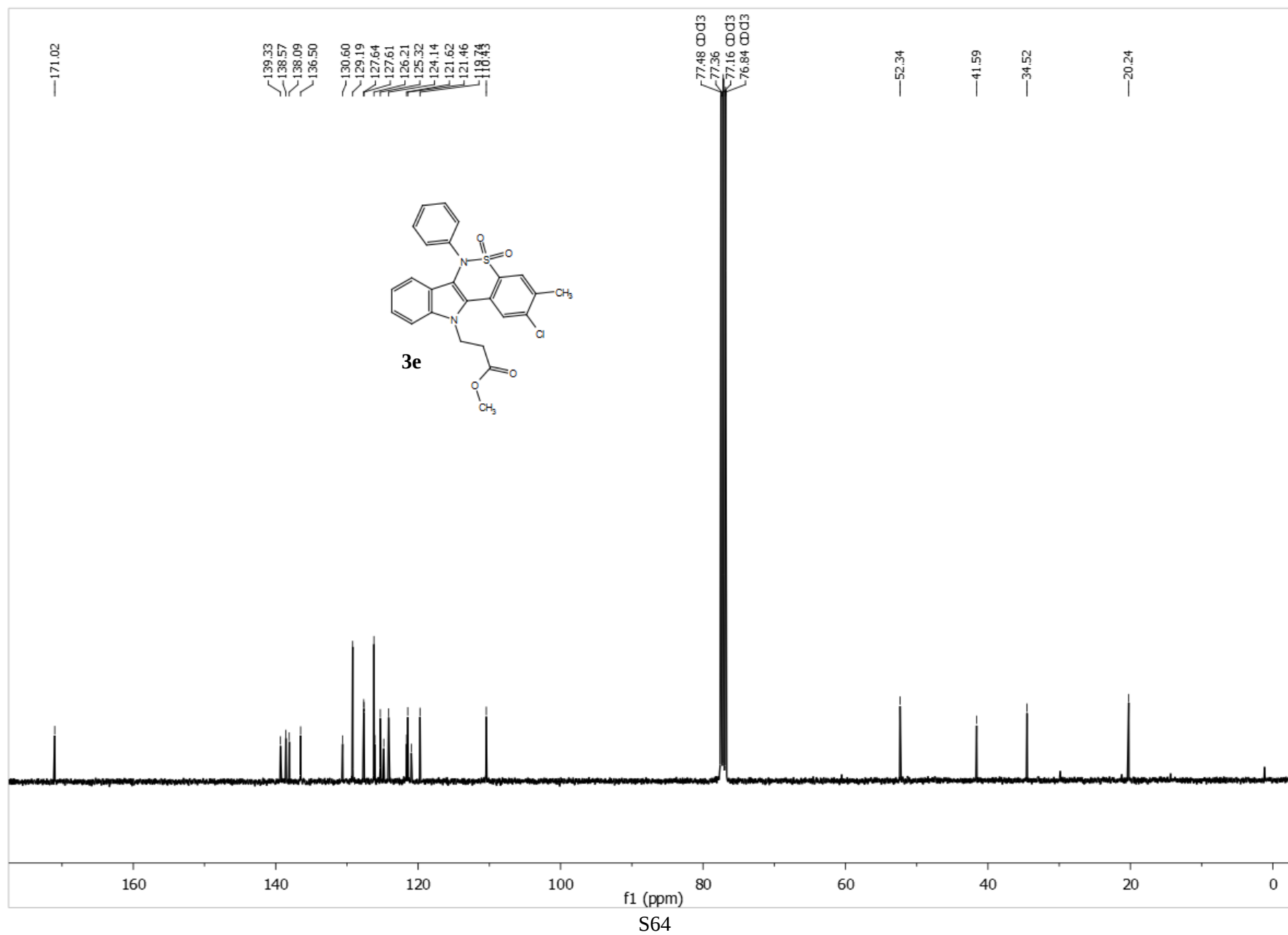
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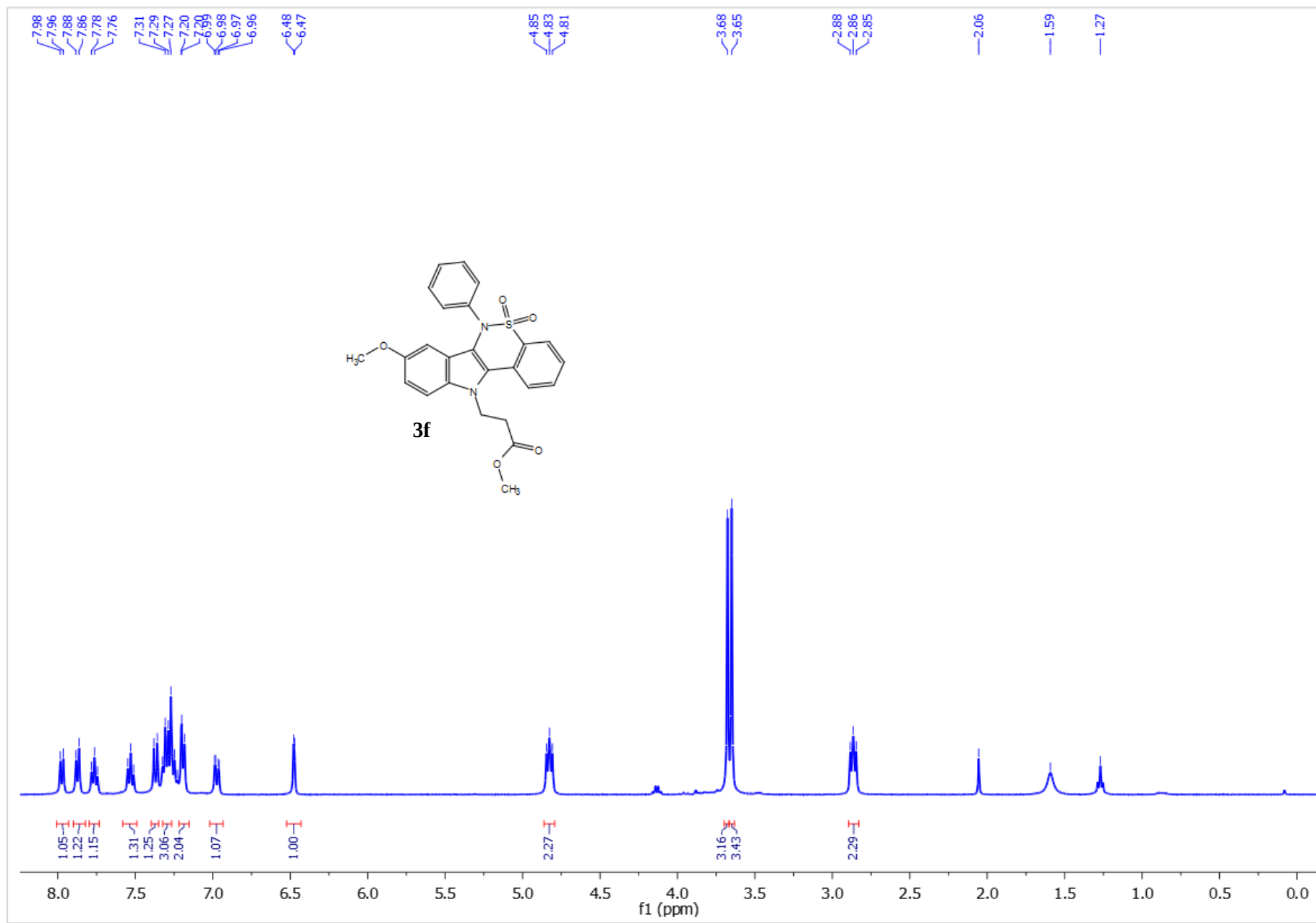




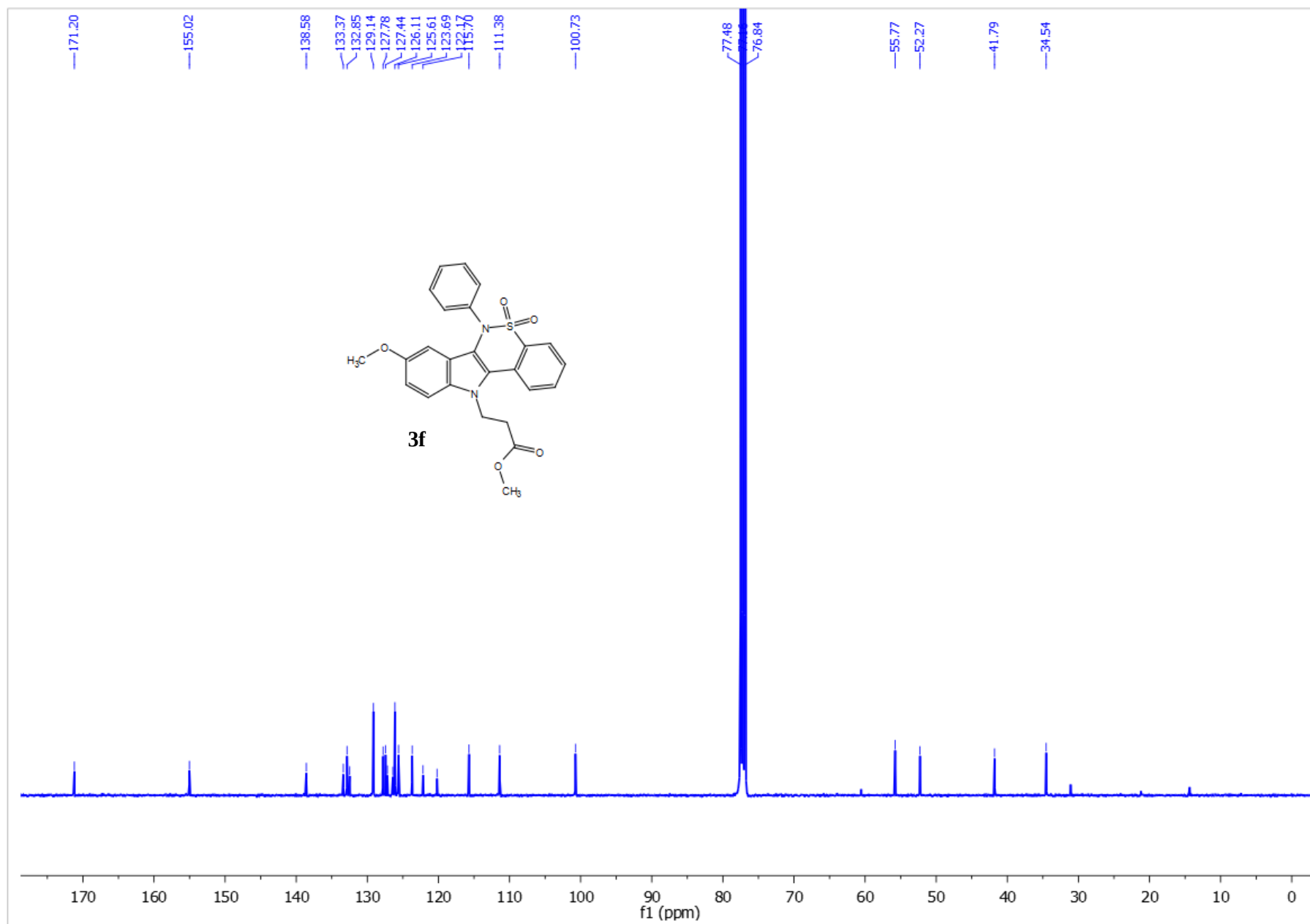


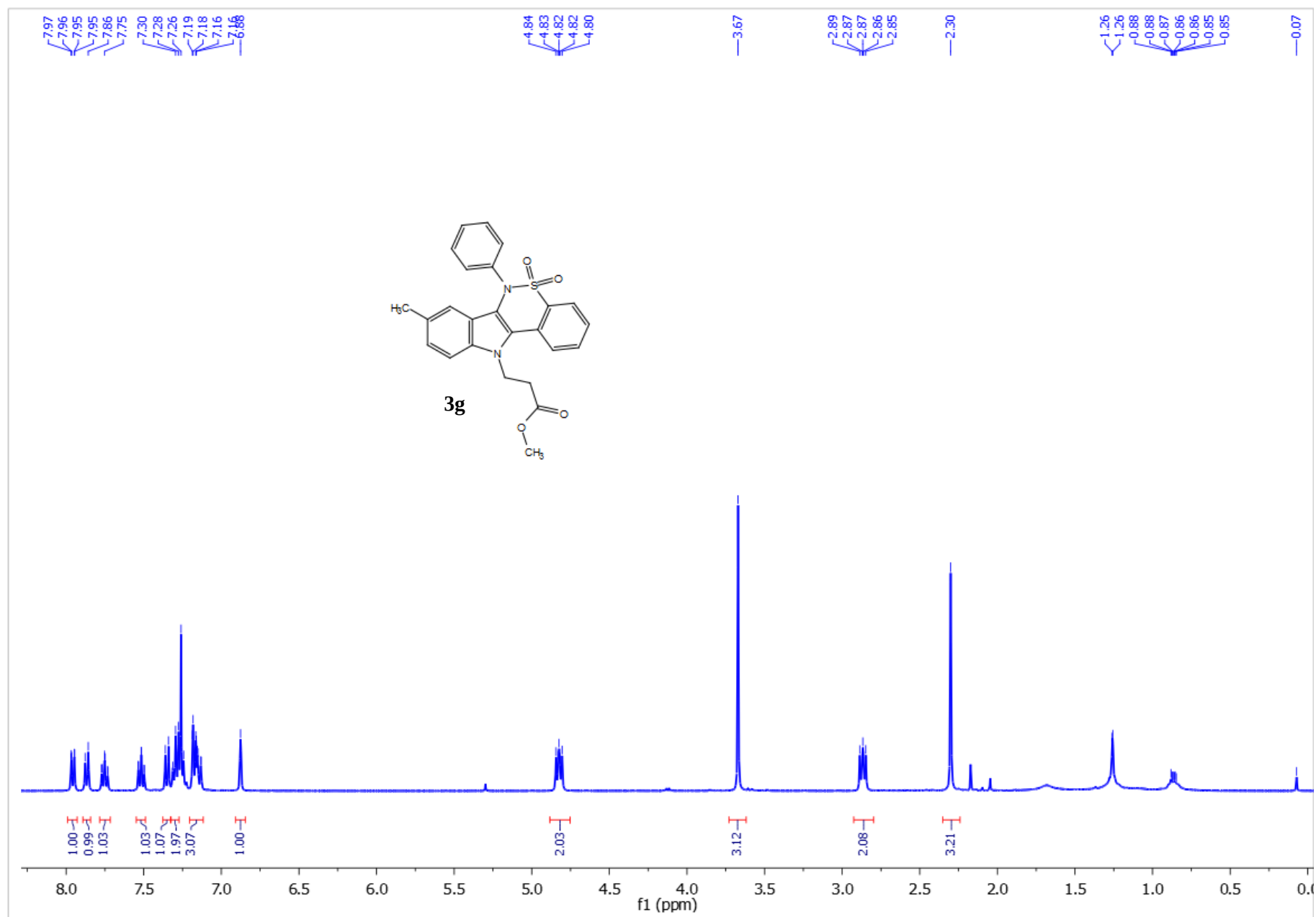
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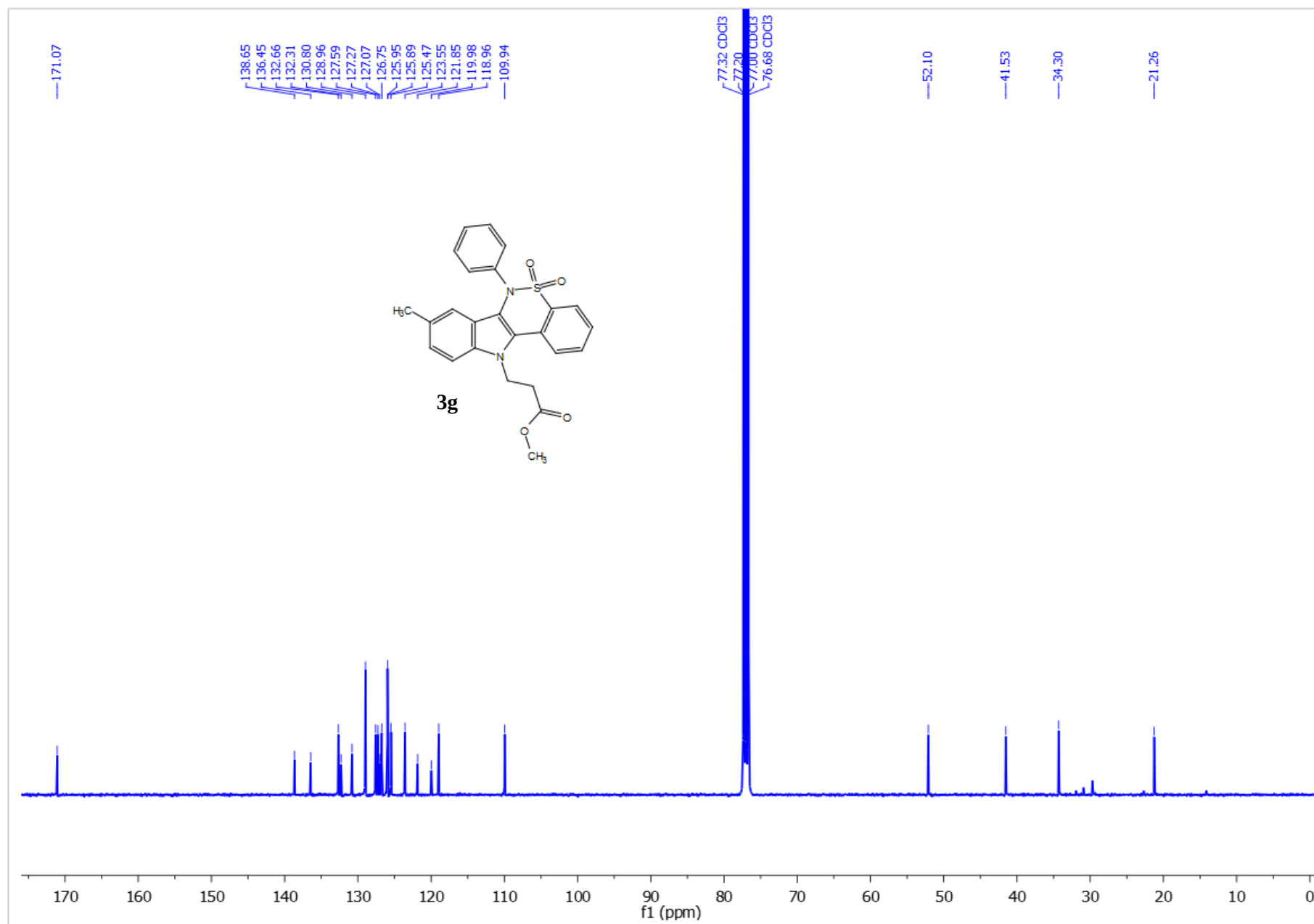


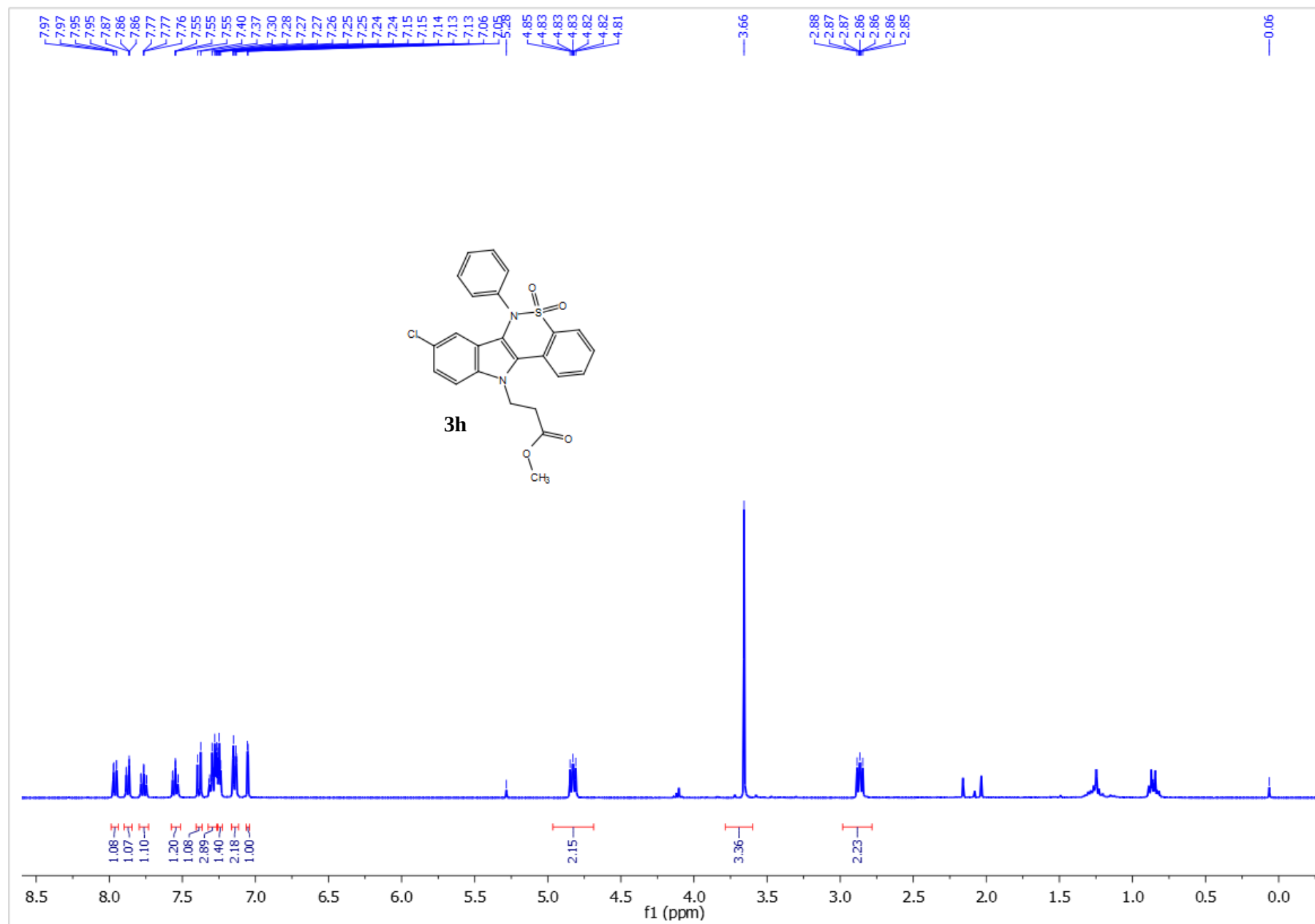


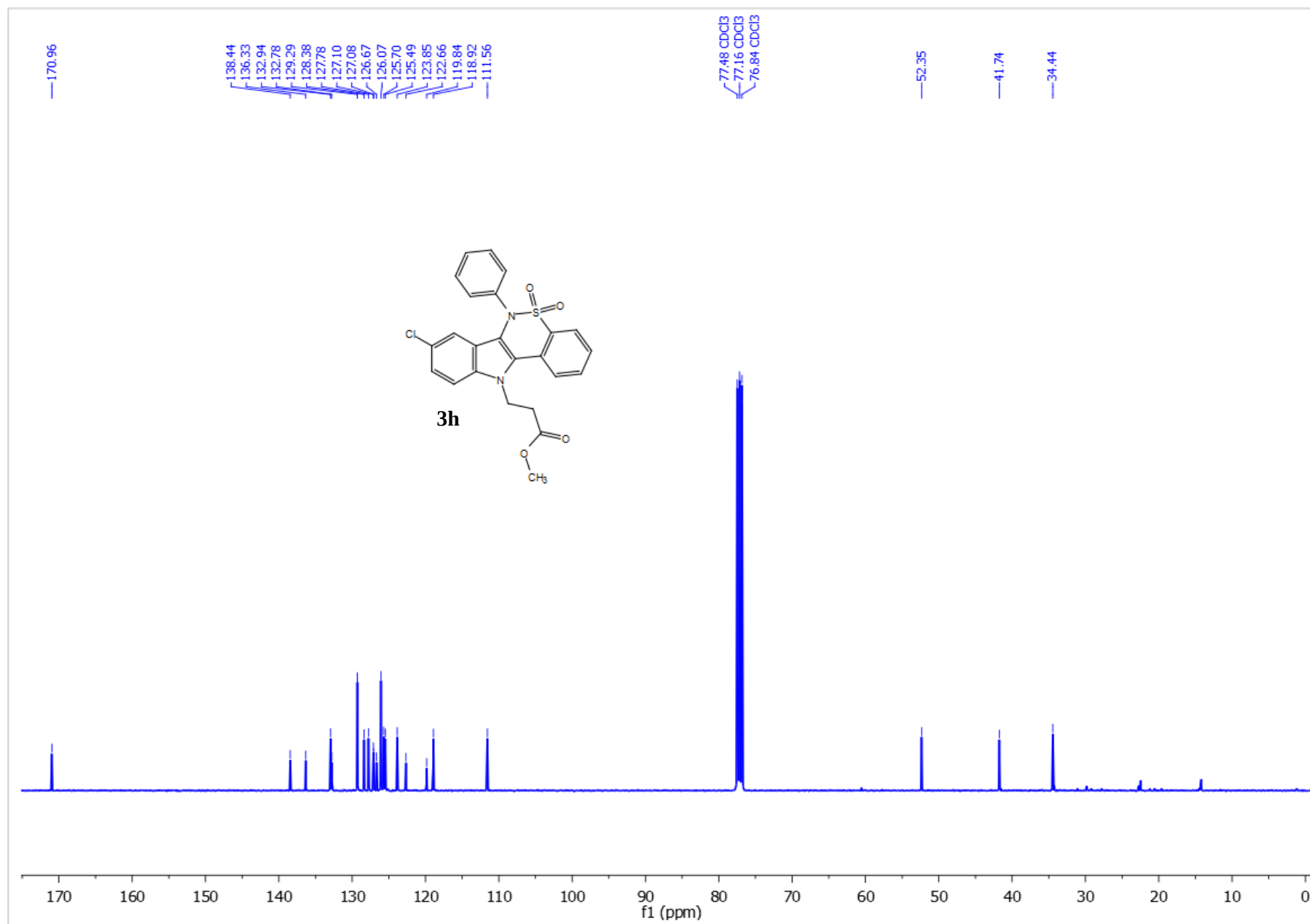
S65

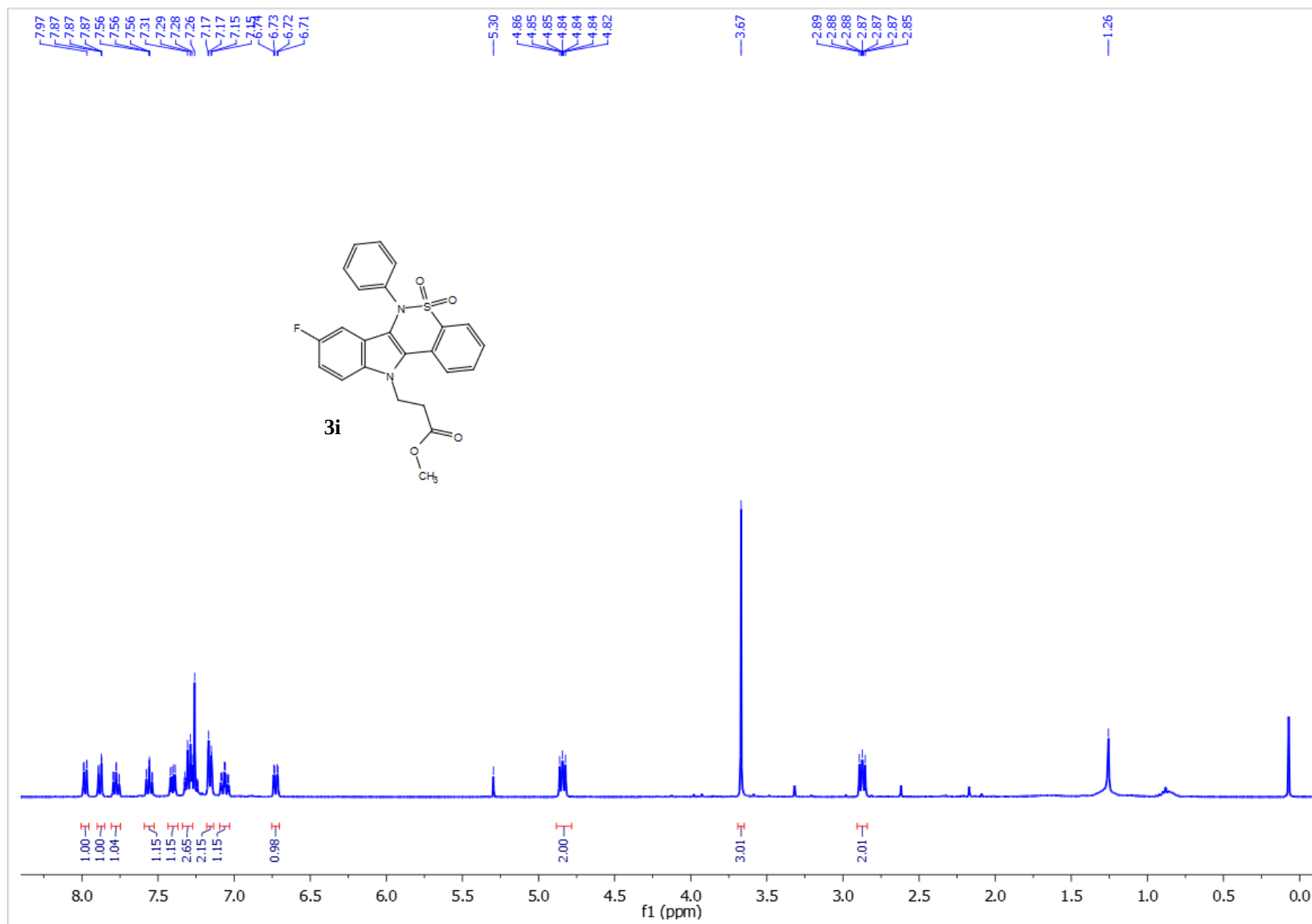


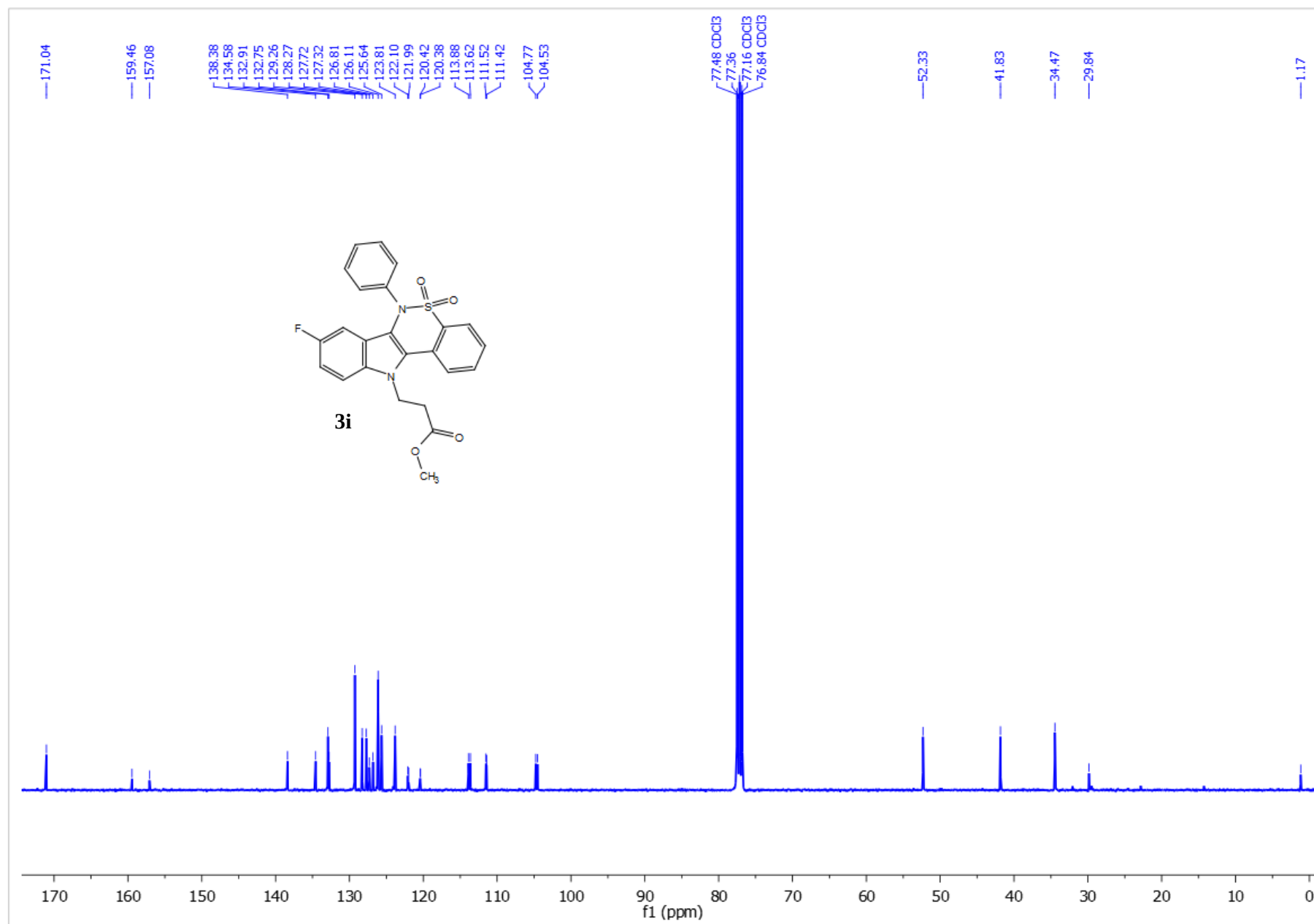


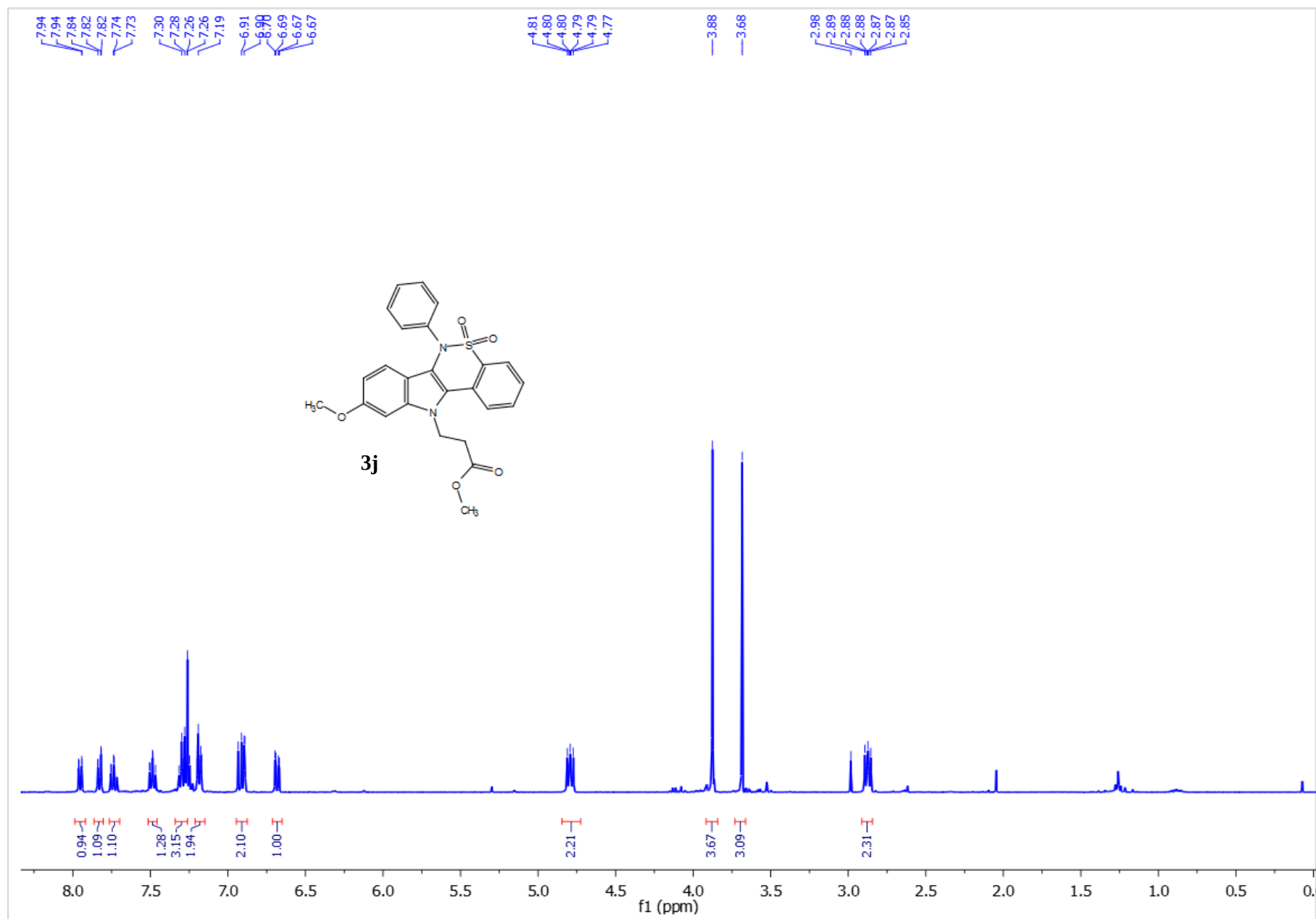


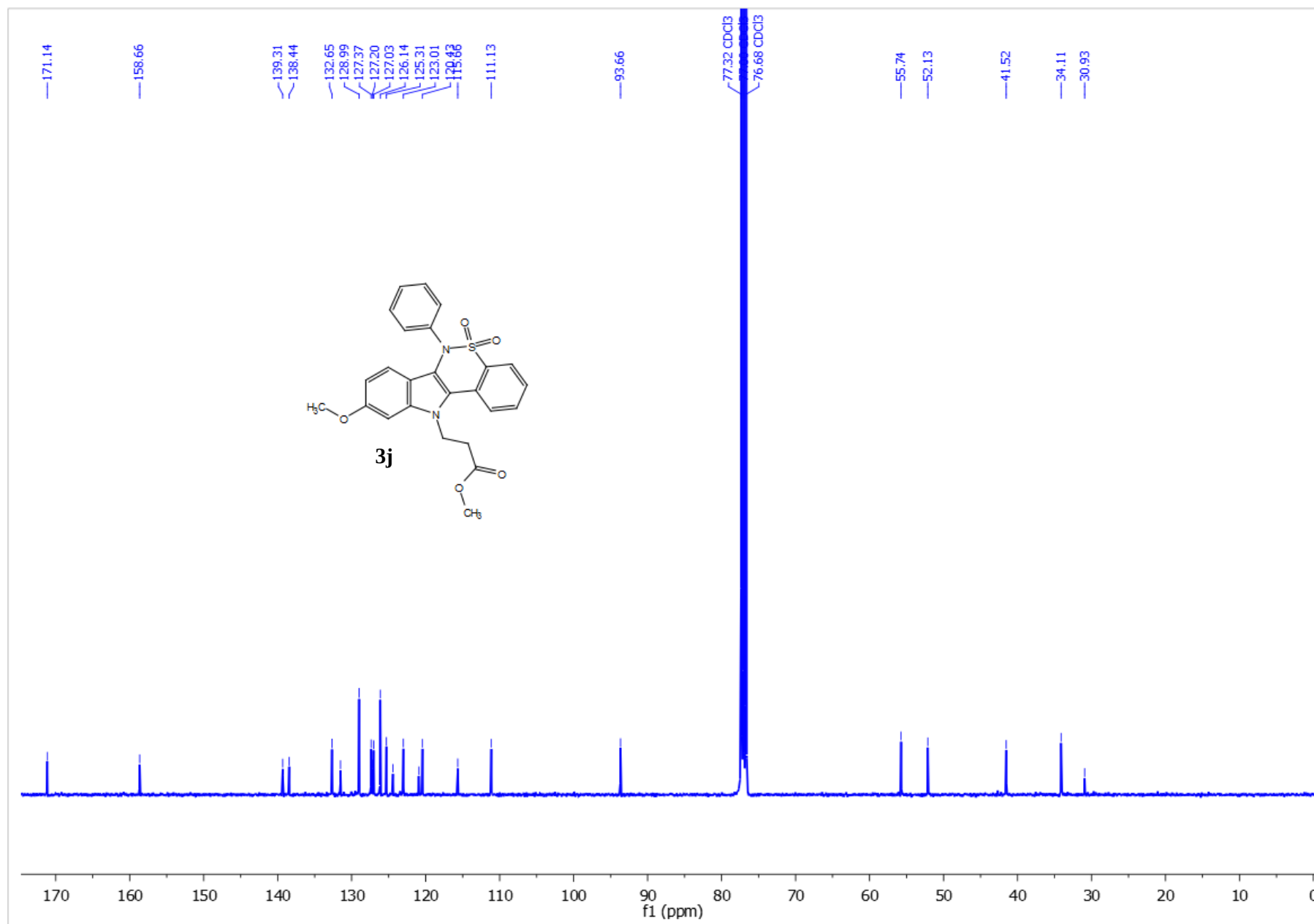


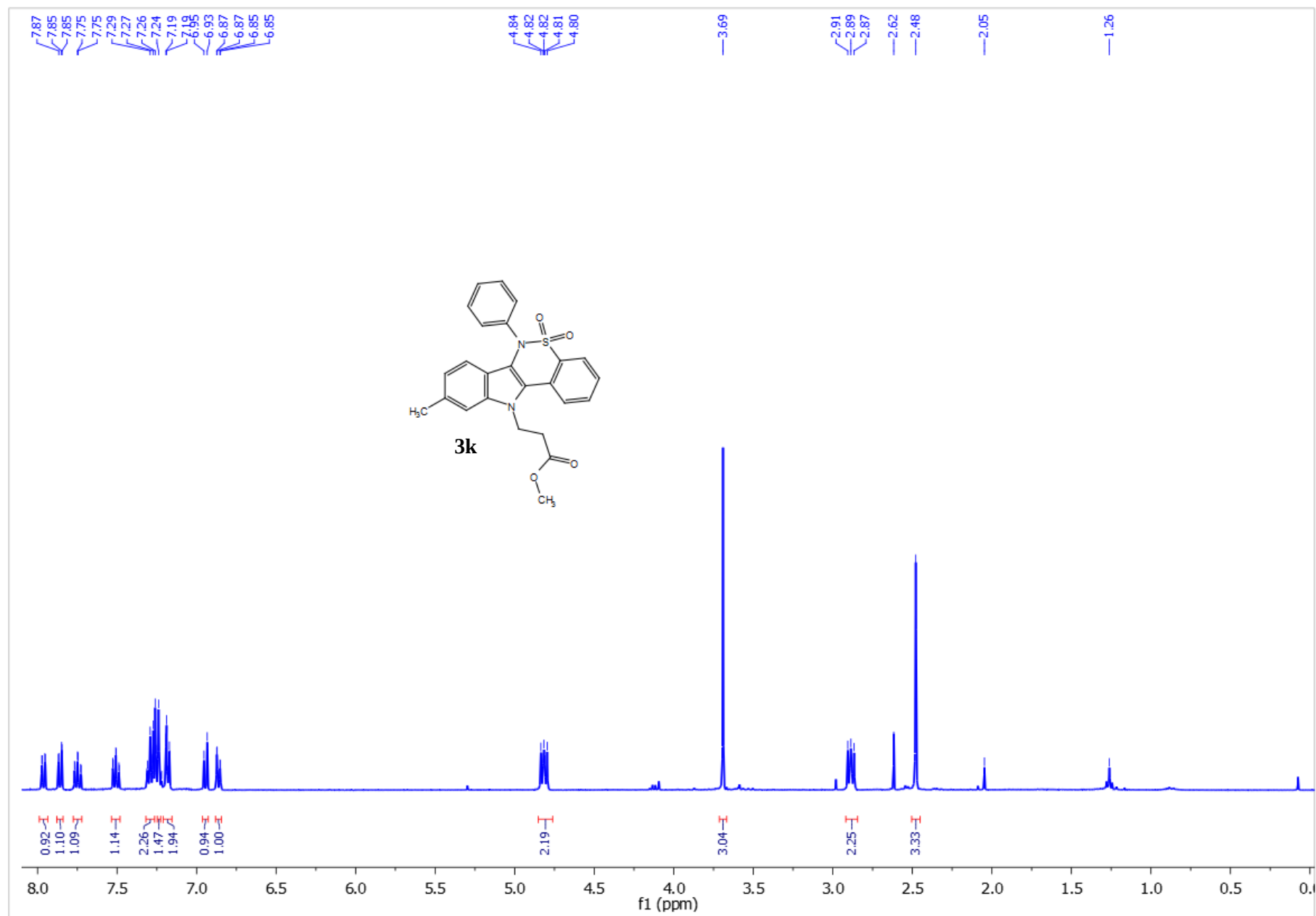


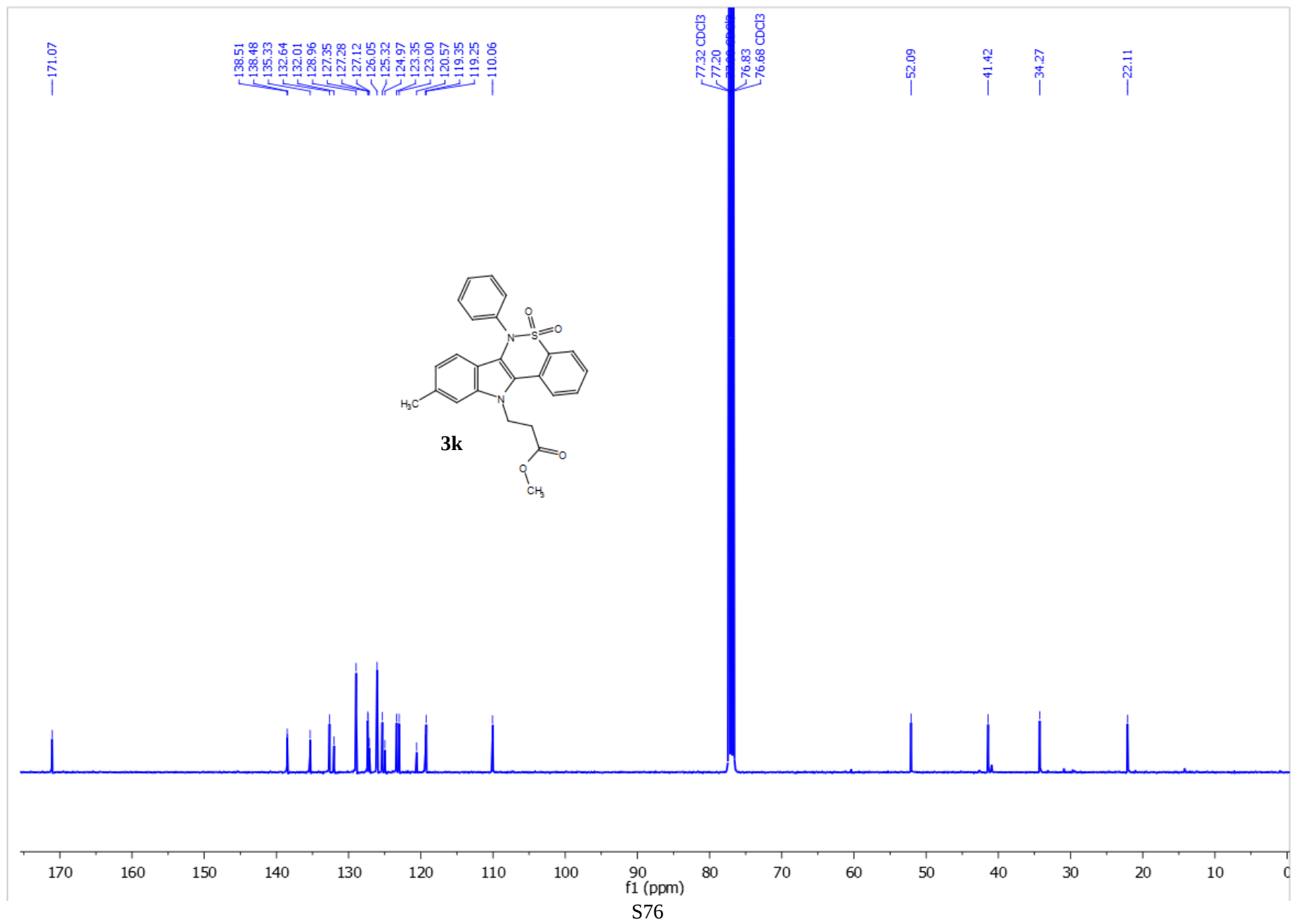


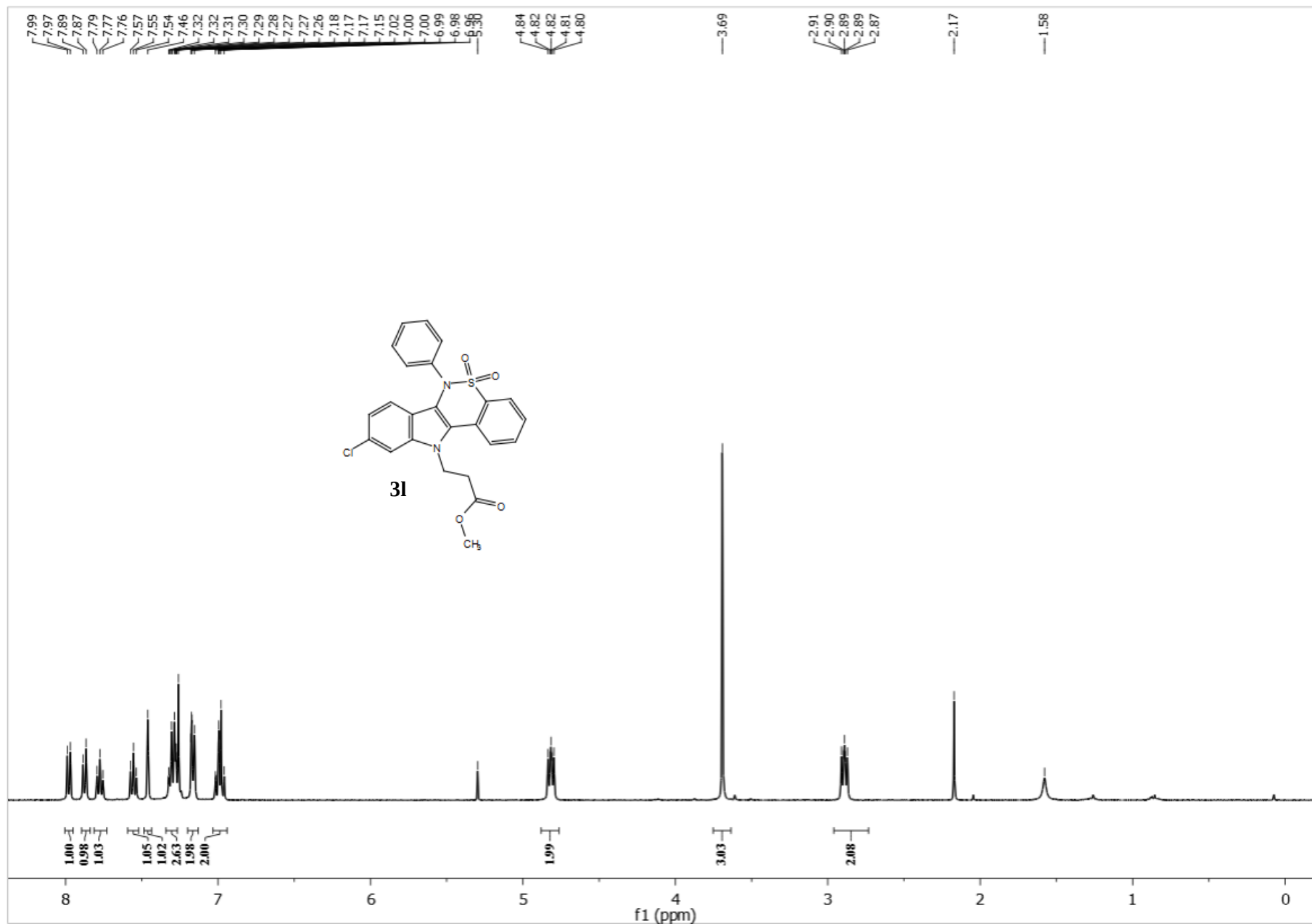


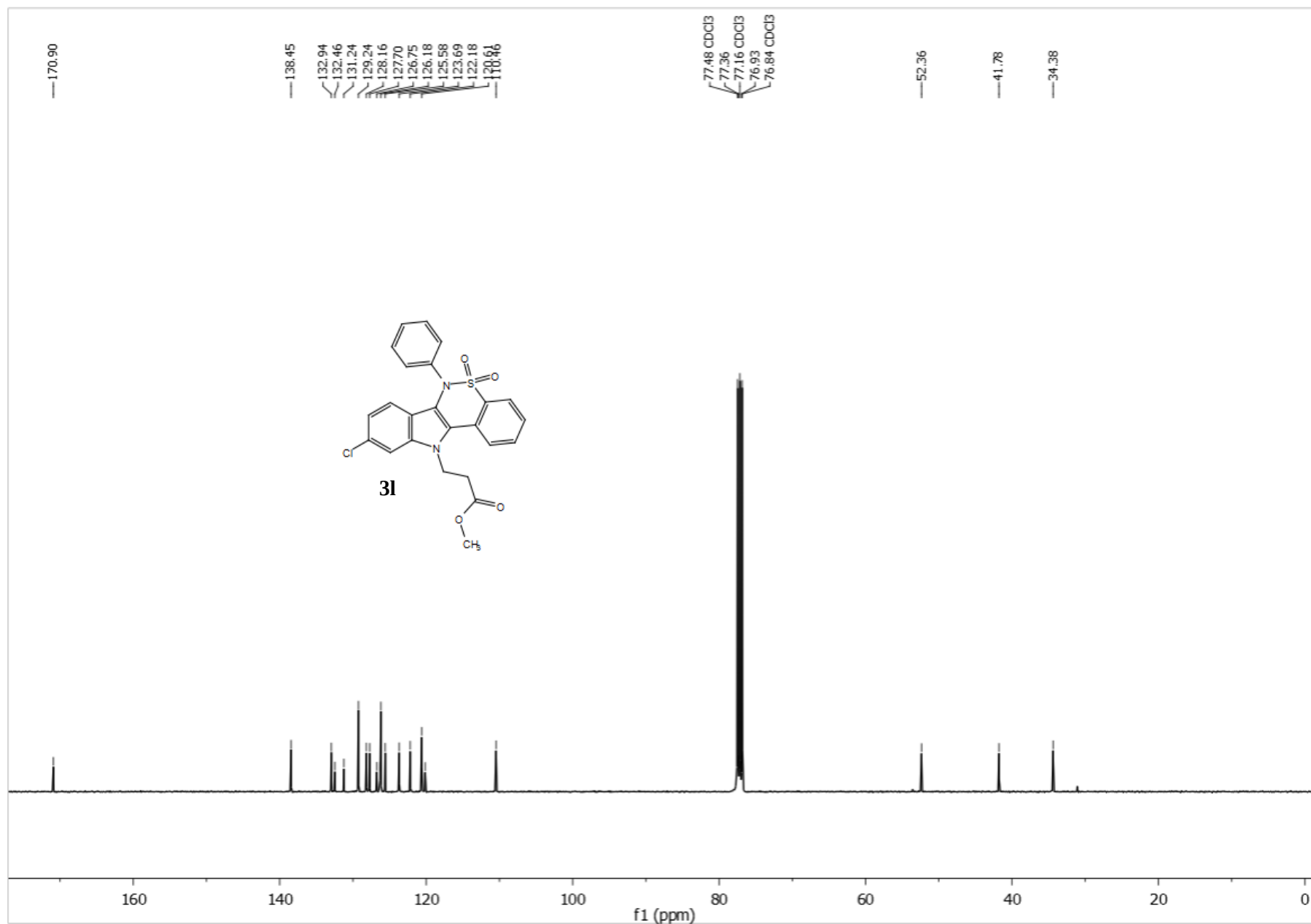


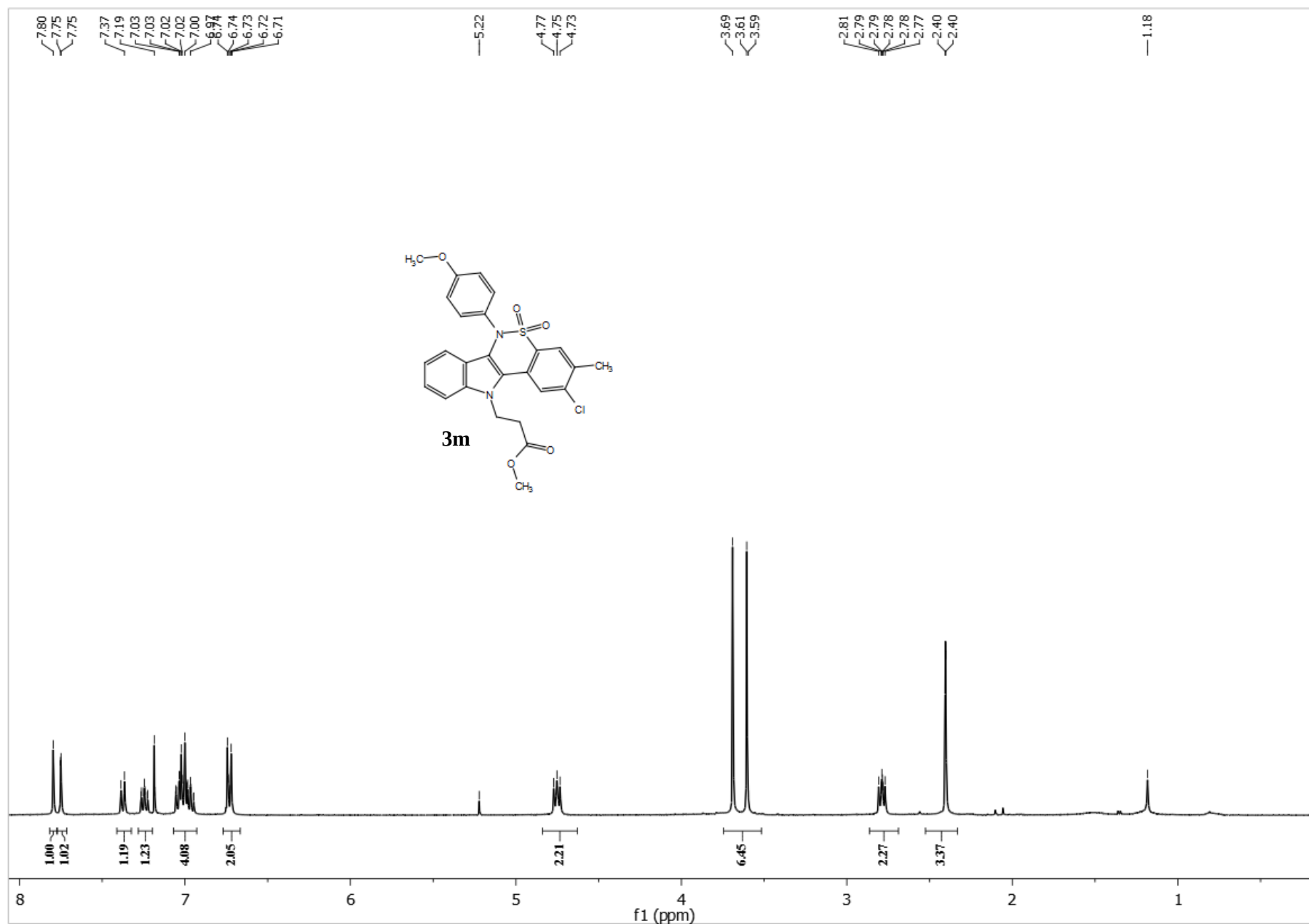


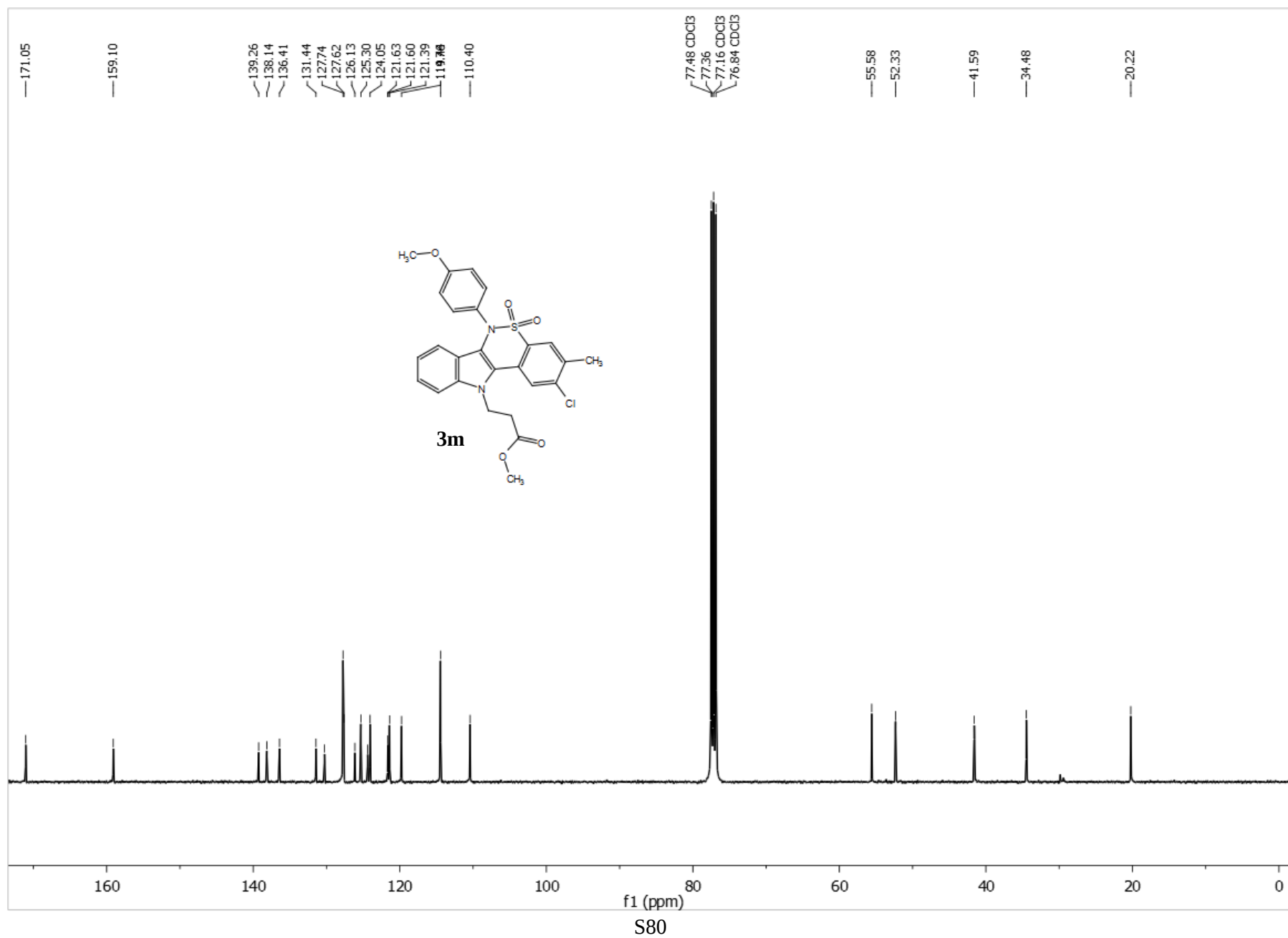


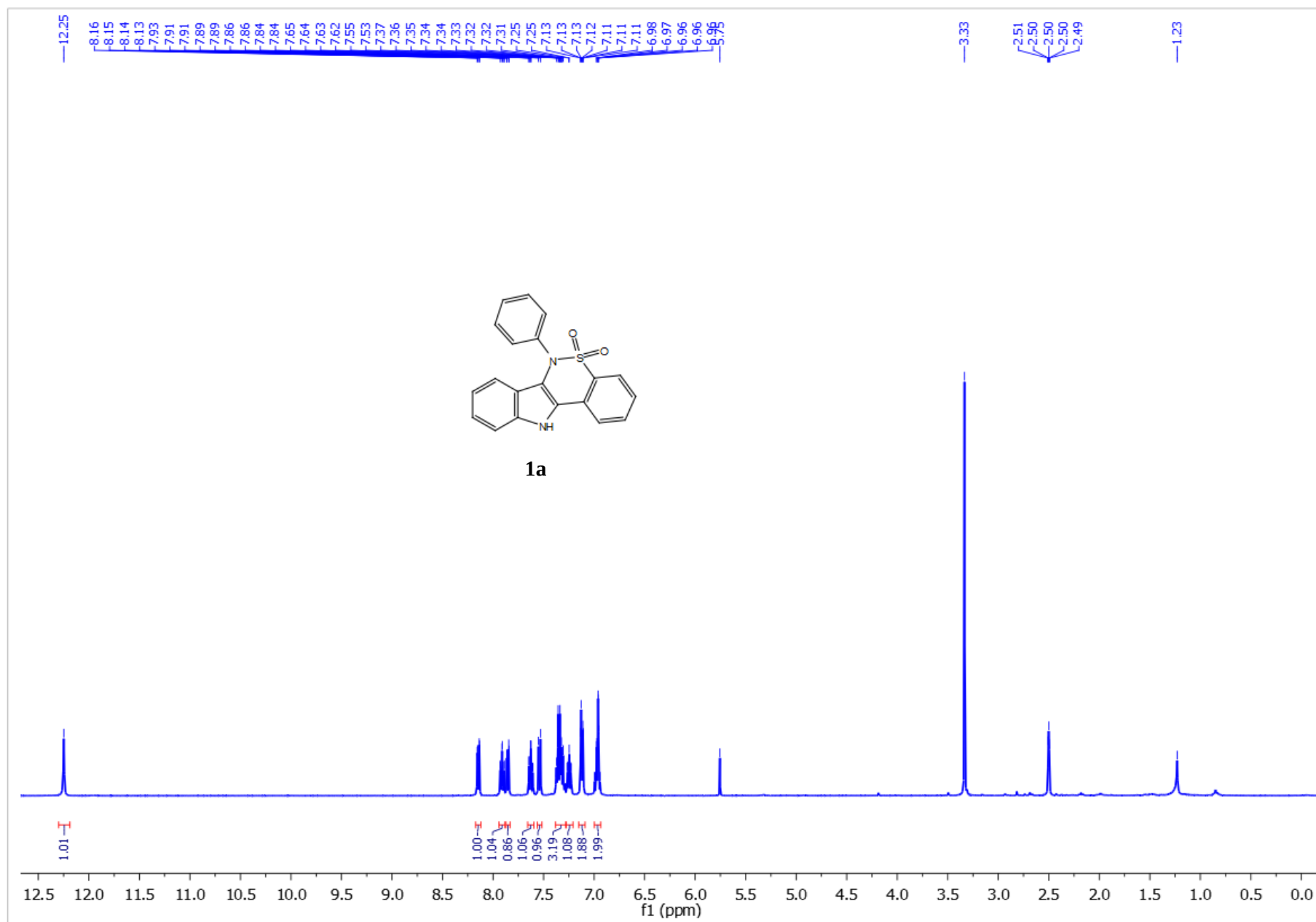


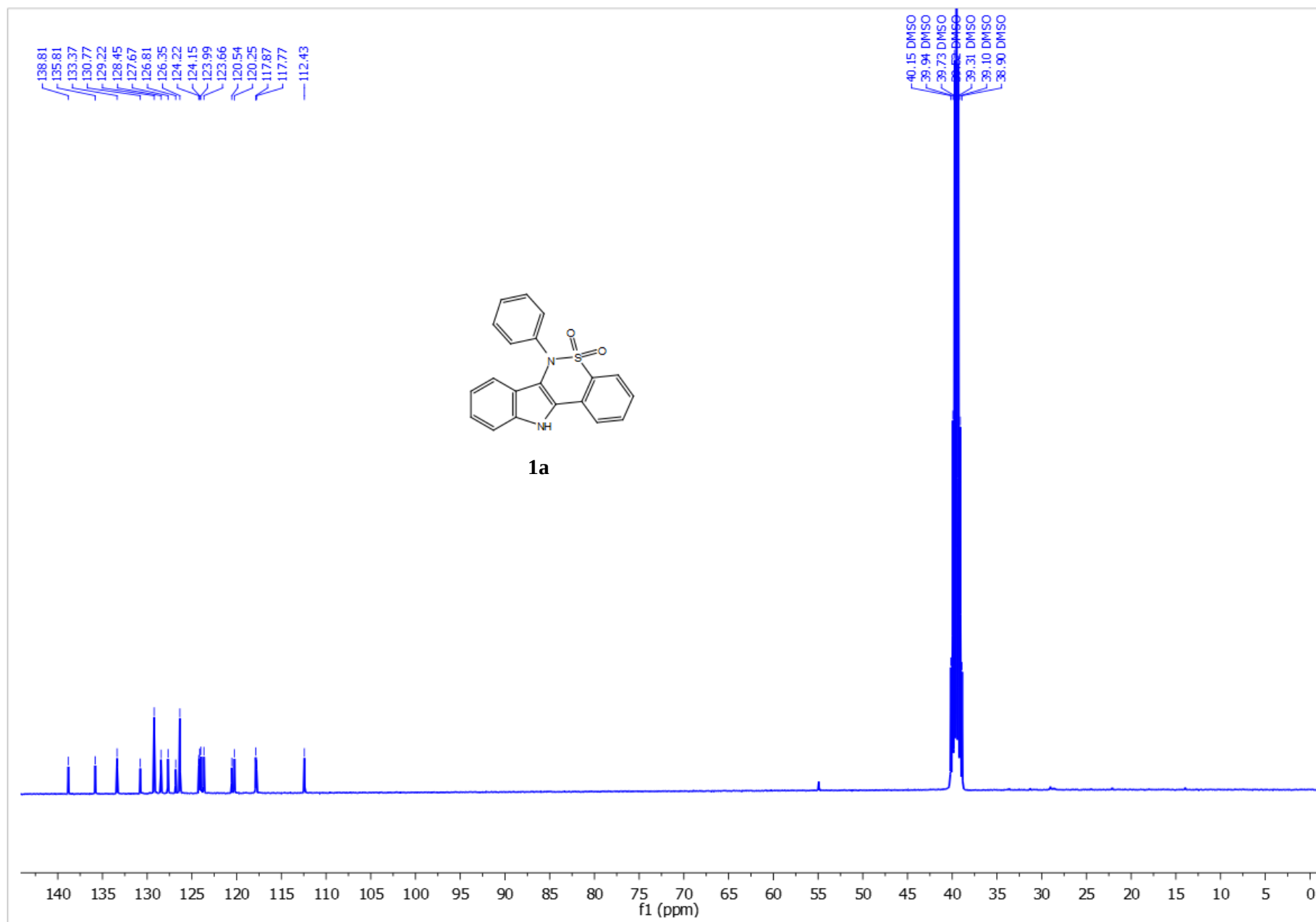


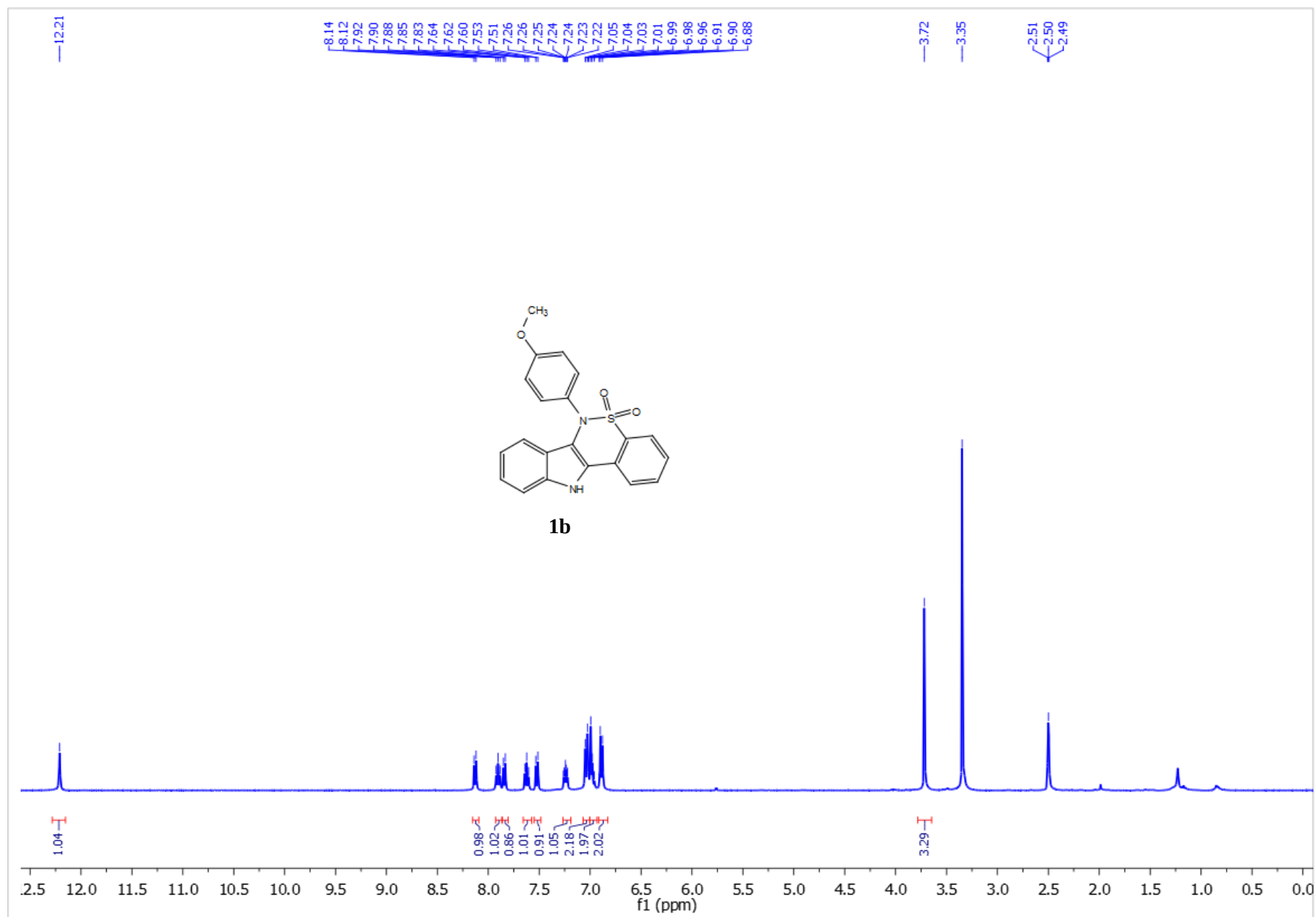


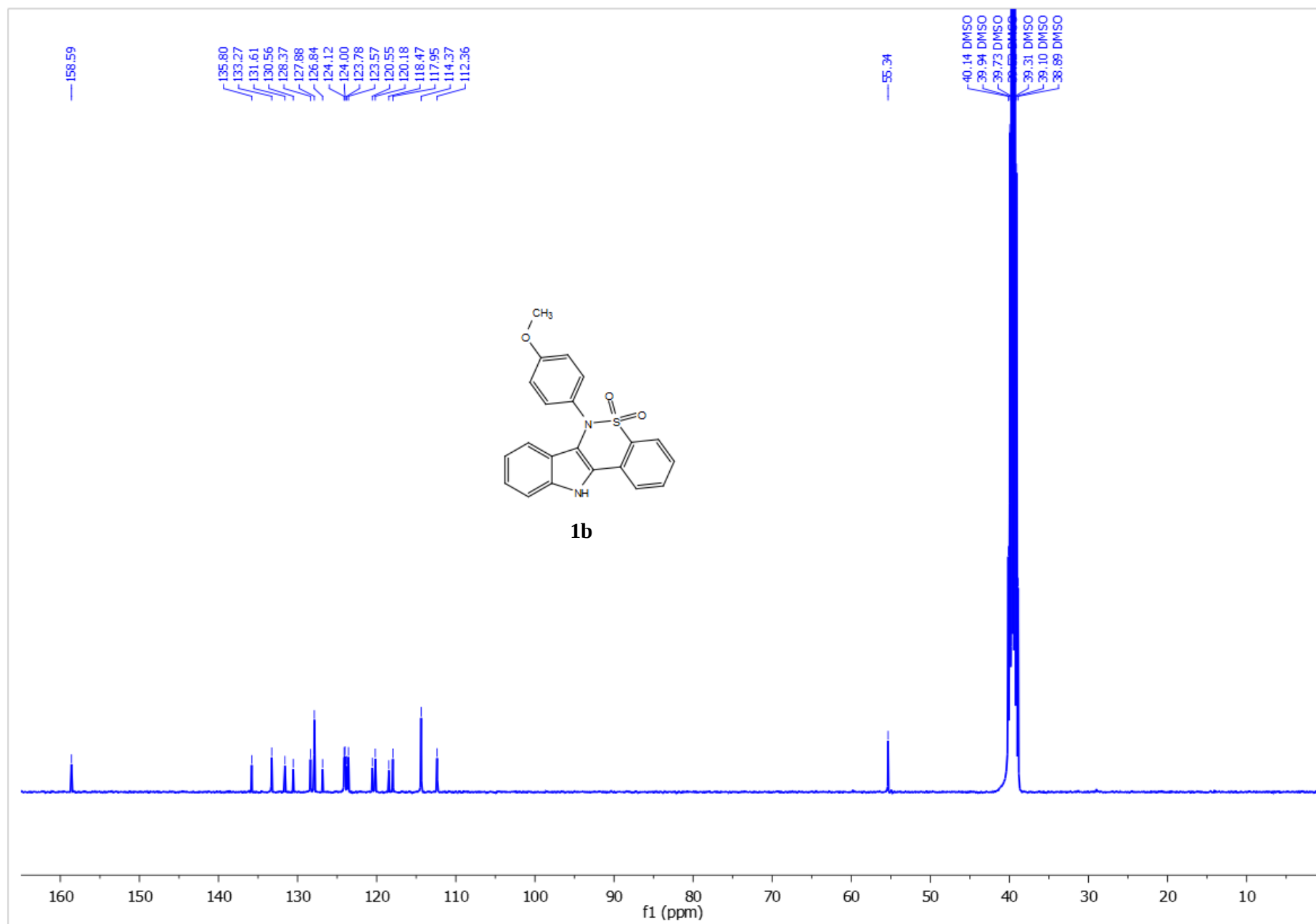


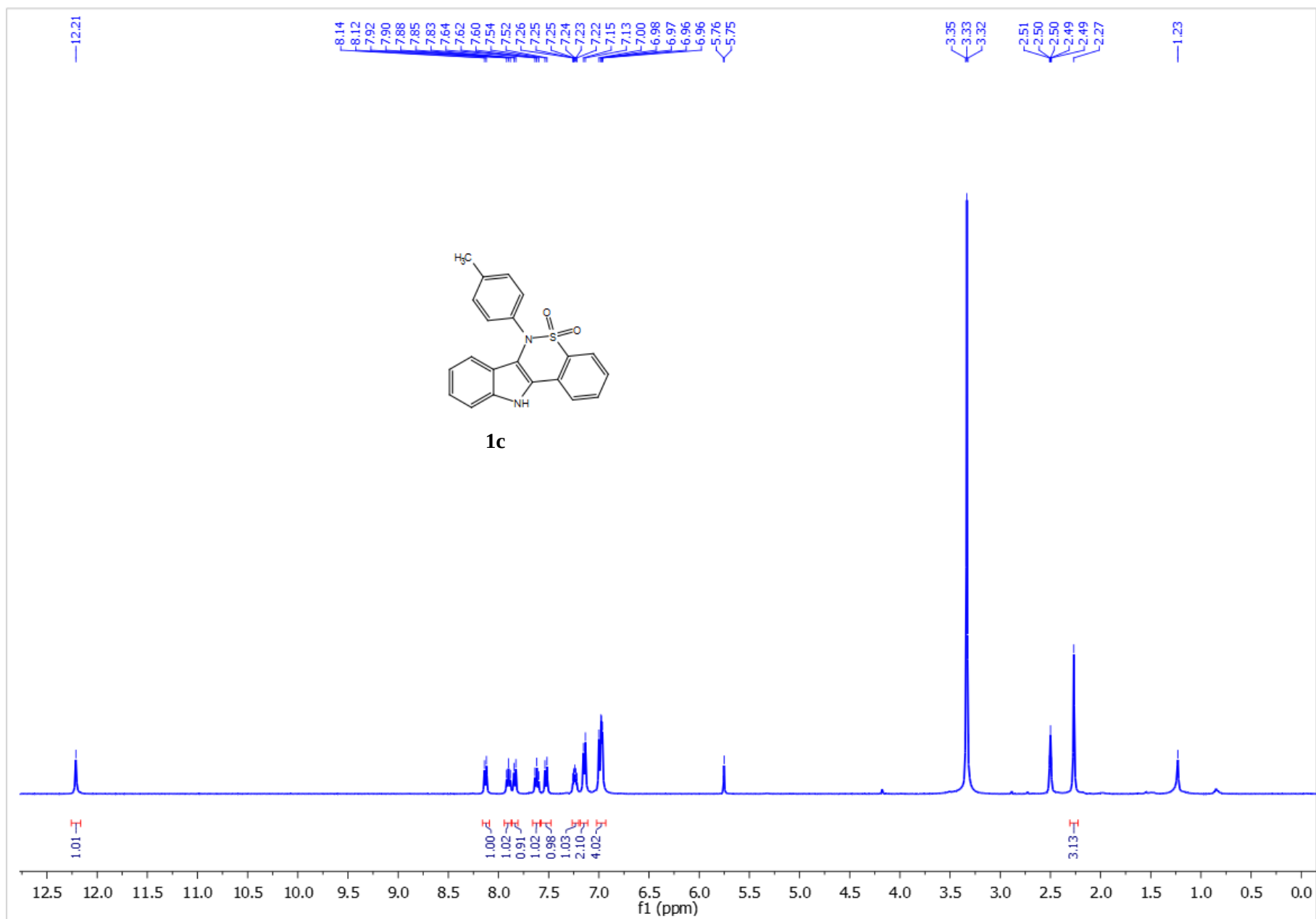


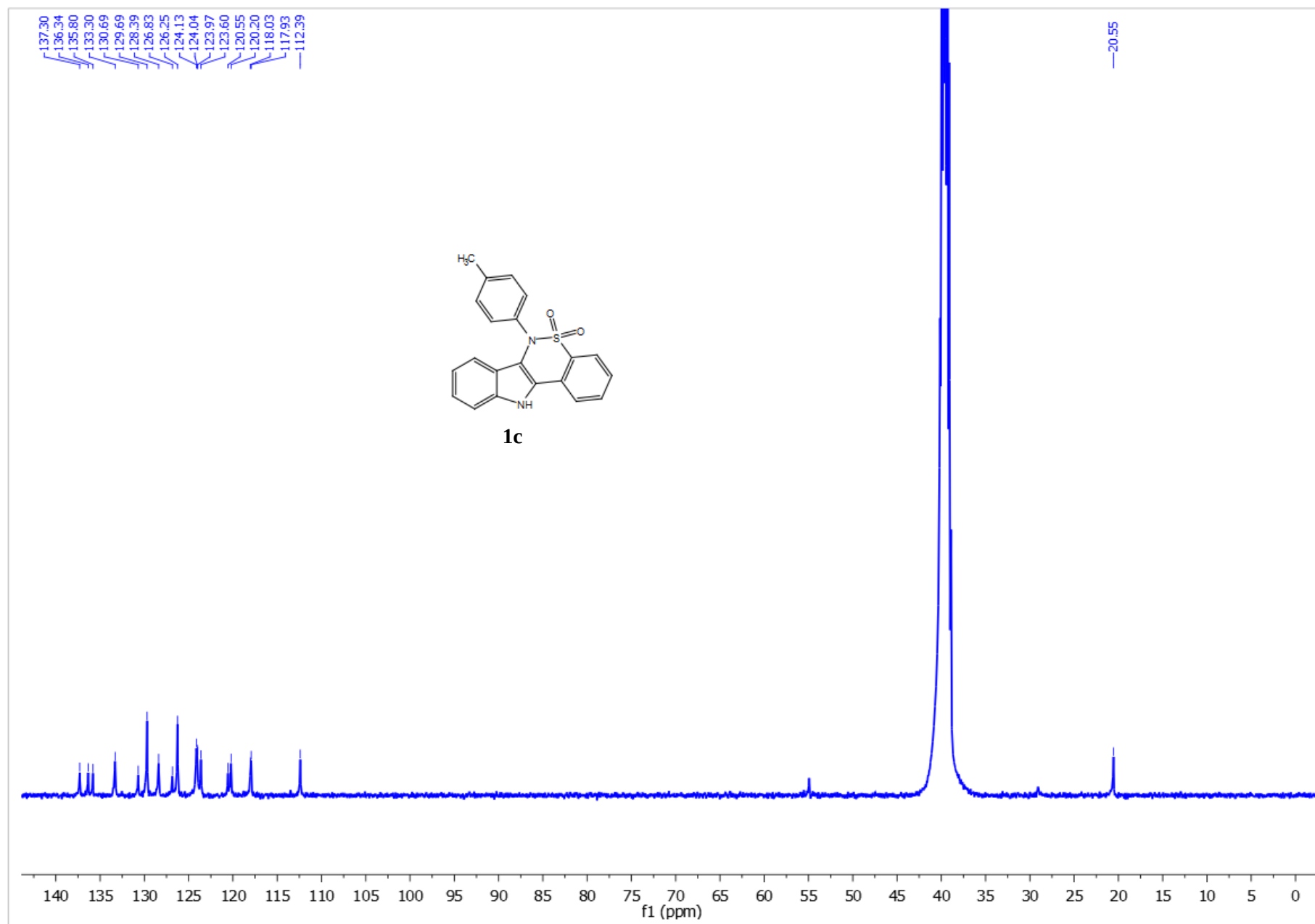


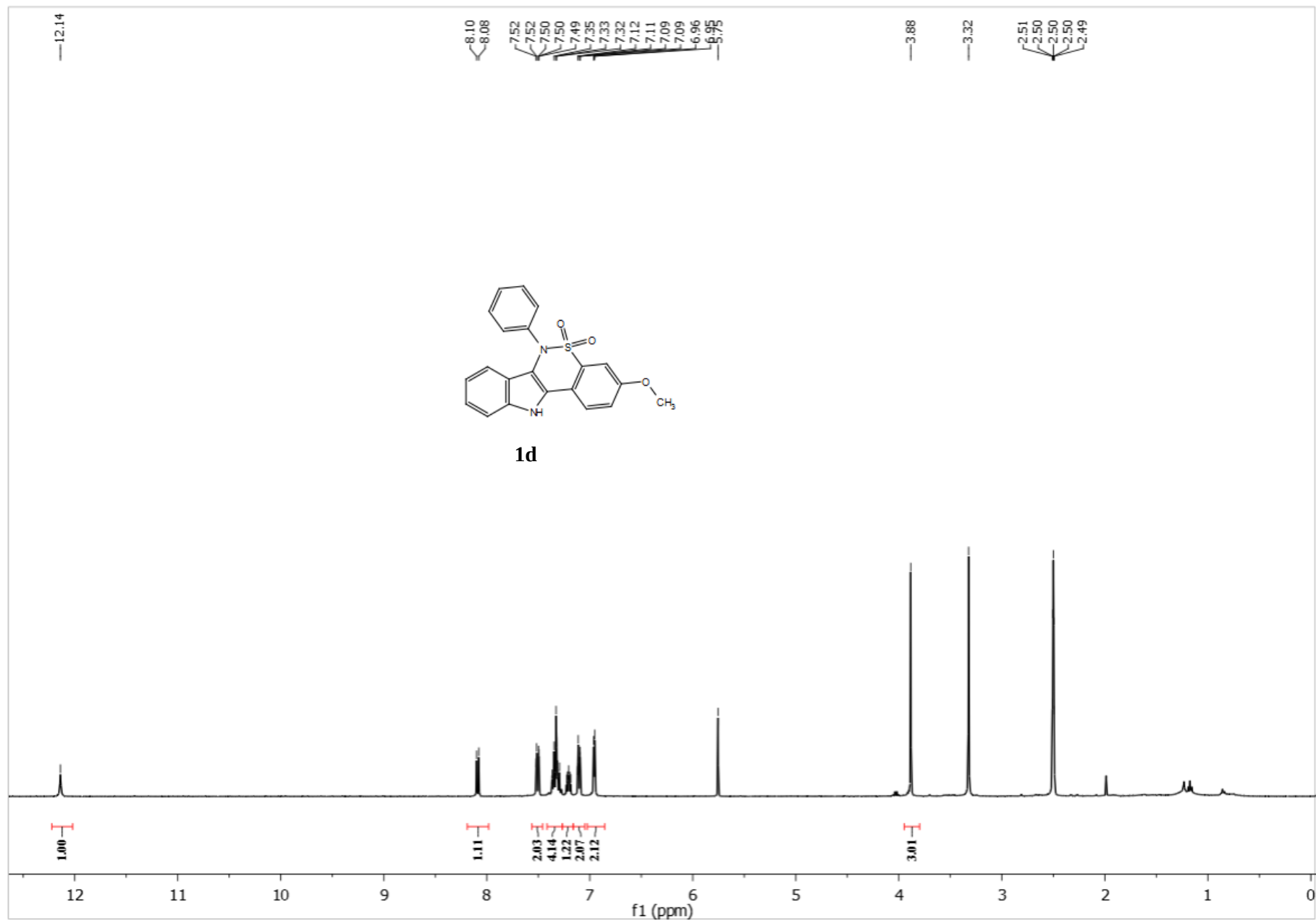


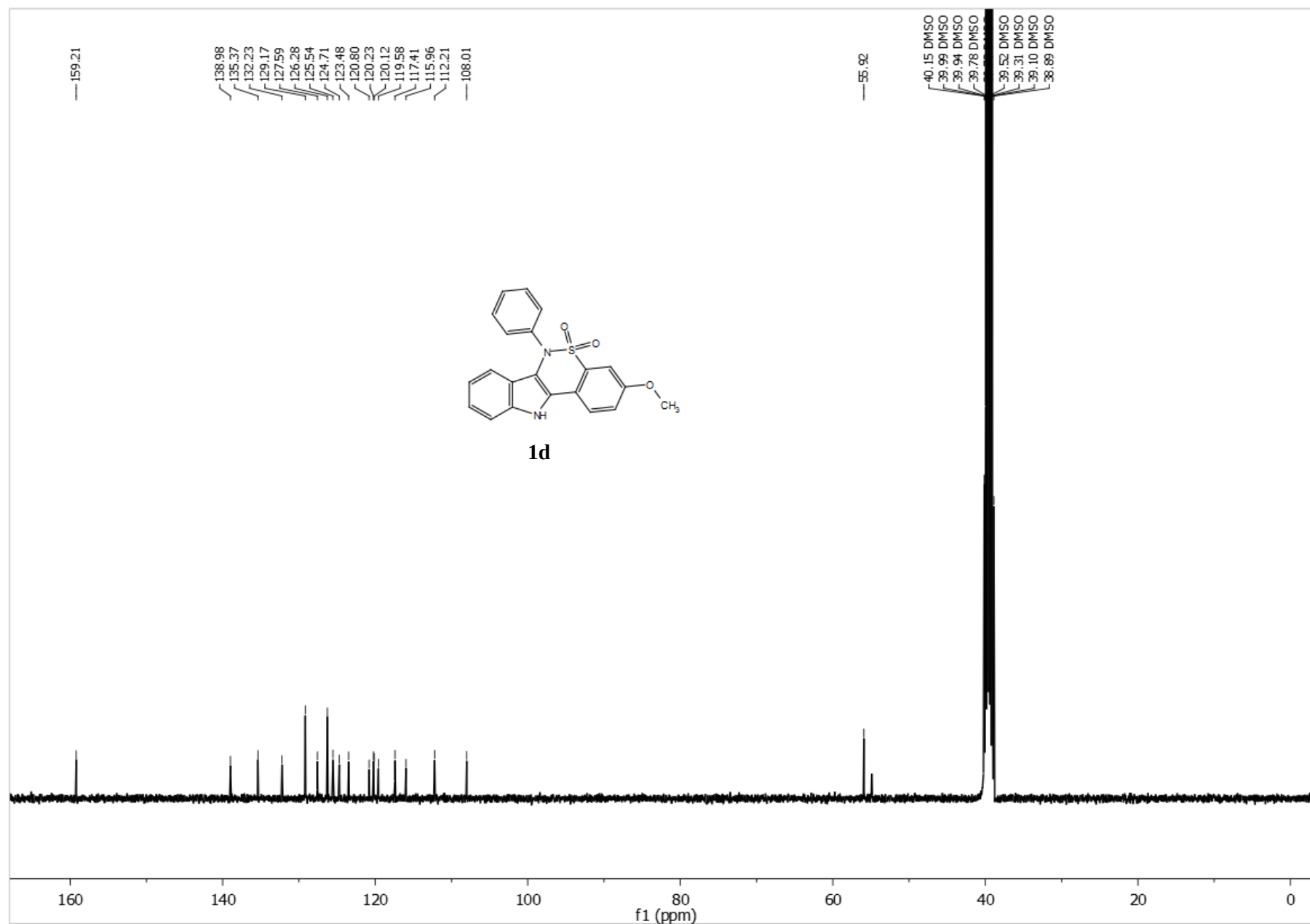


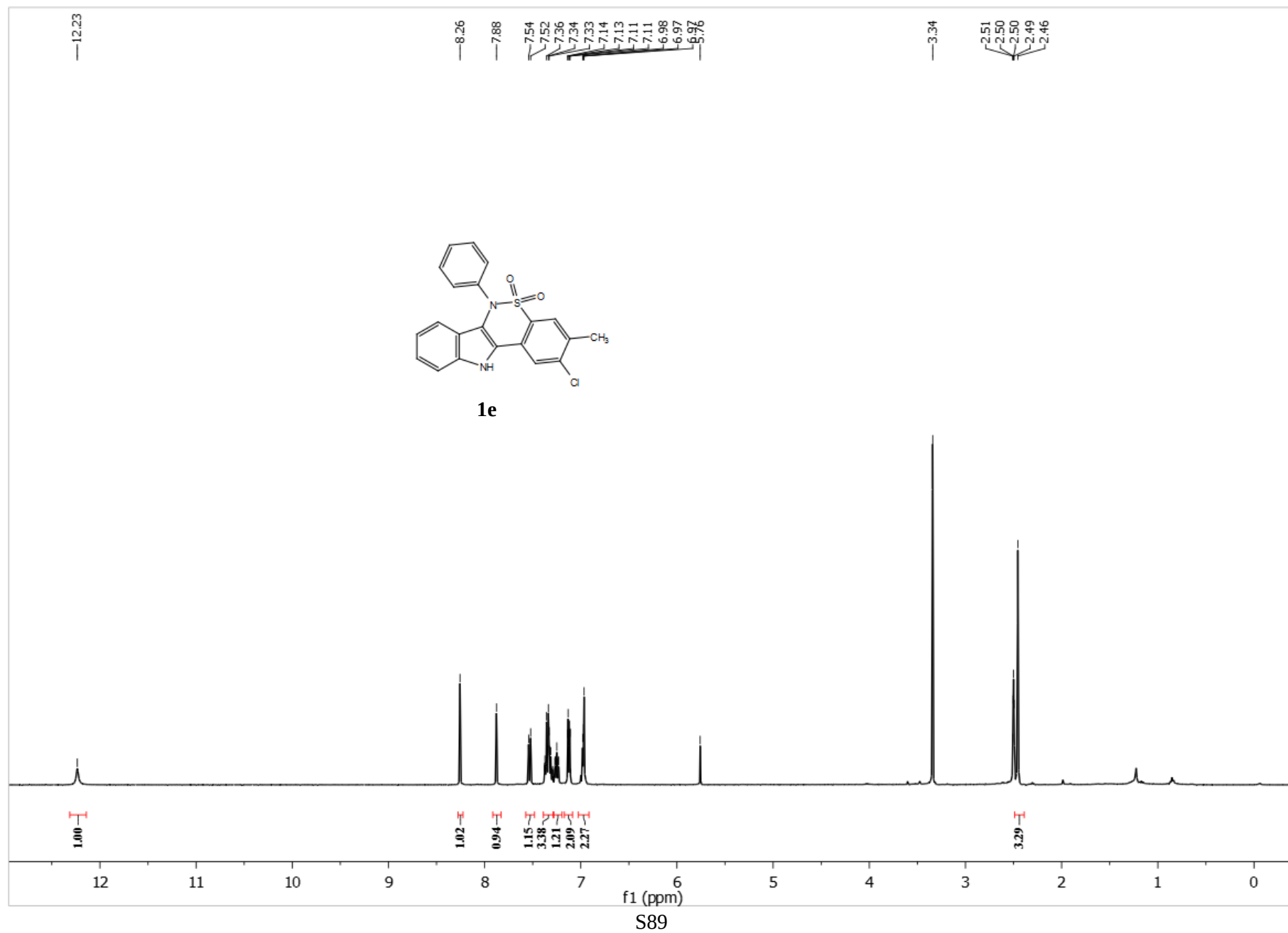


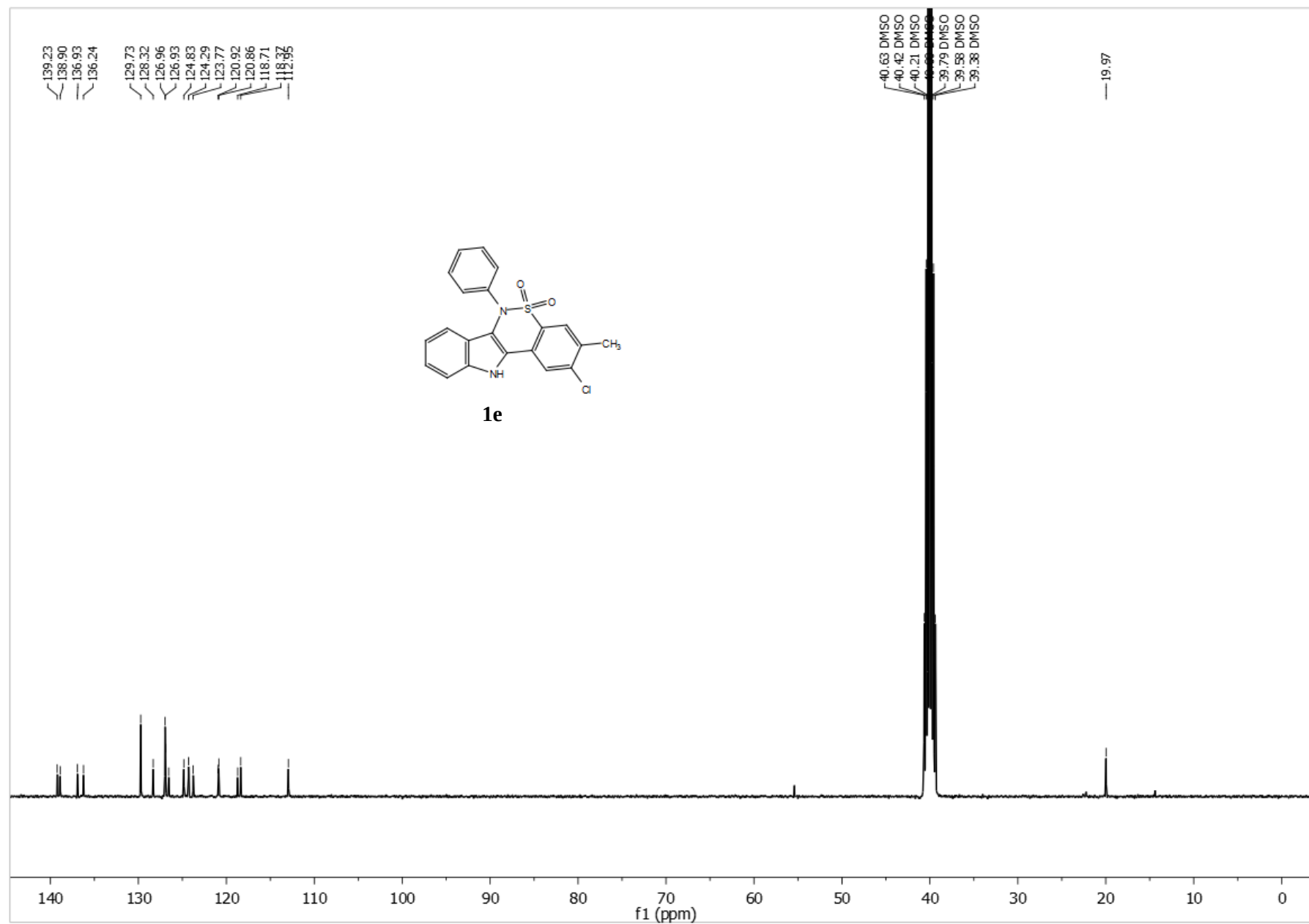


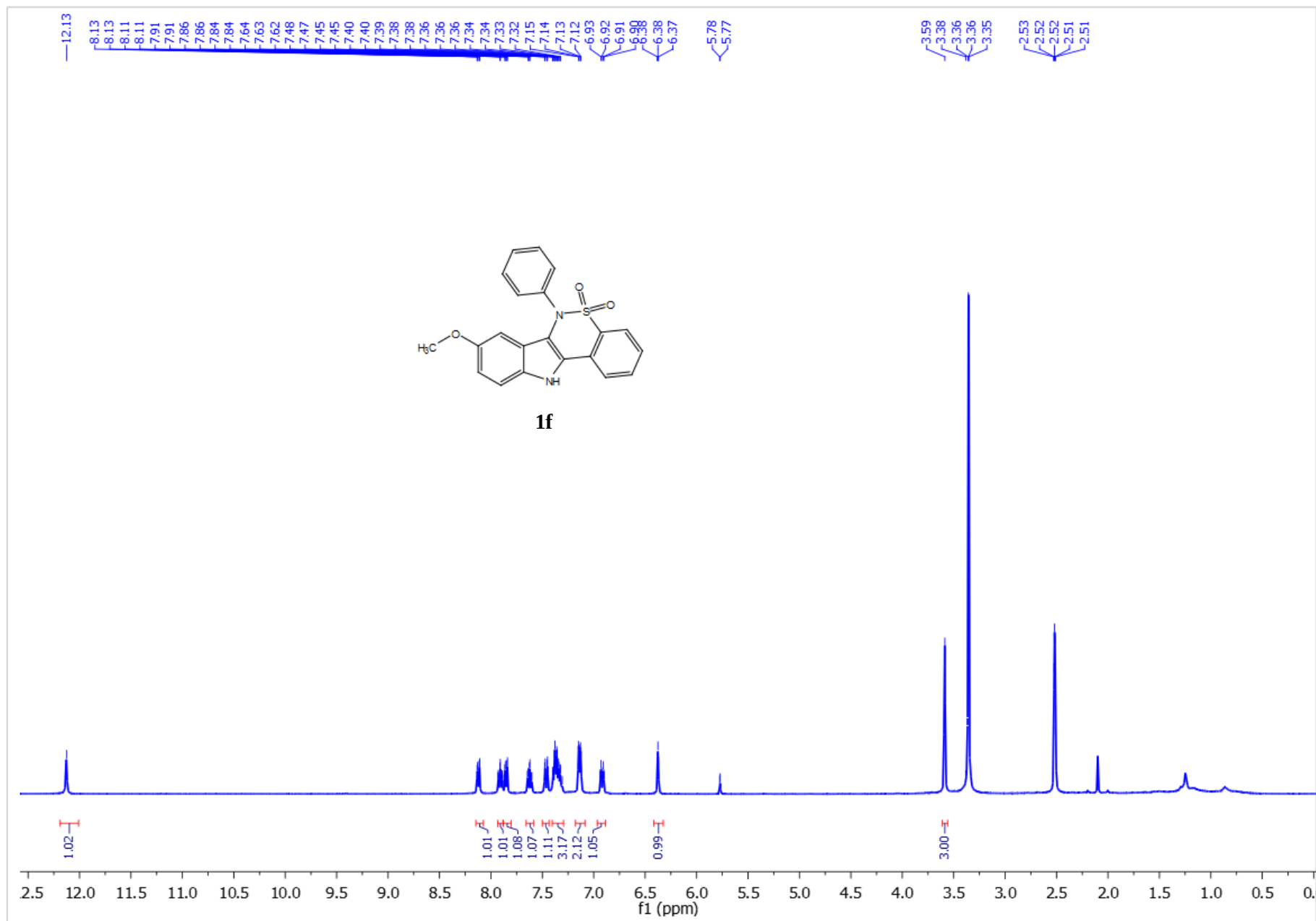




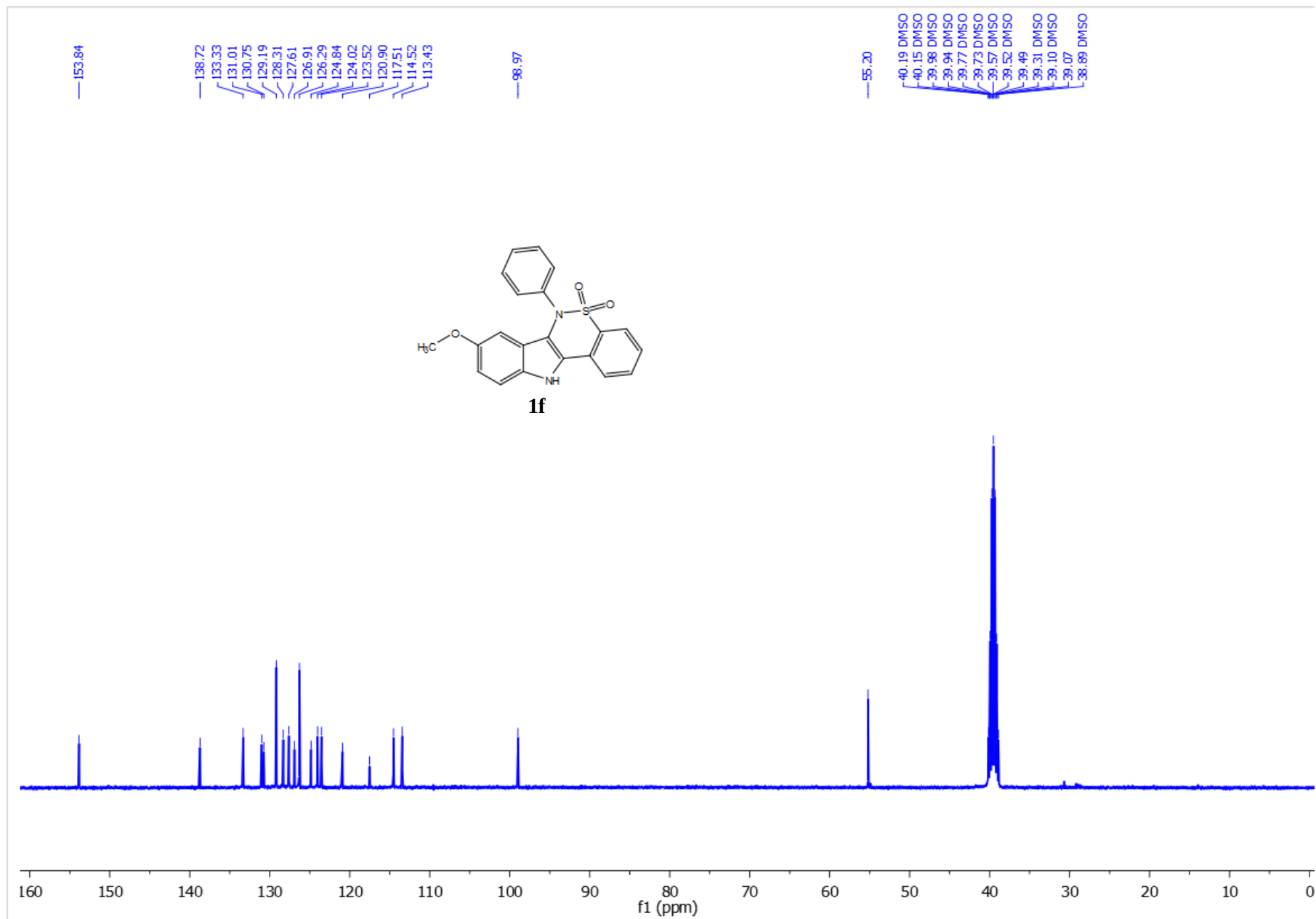


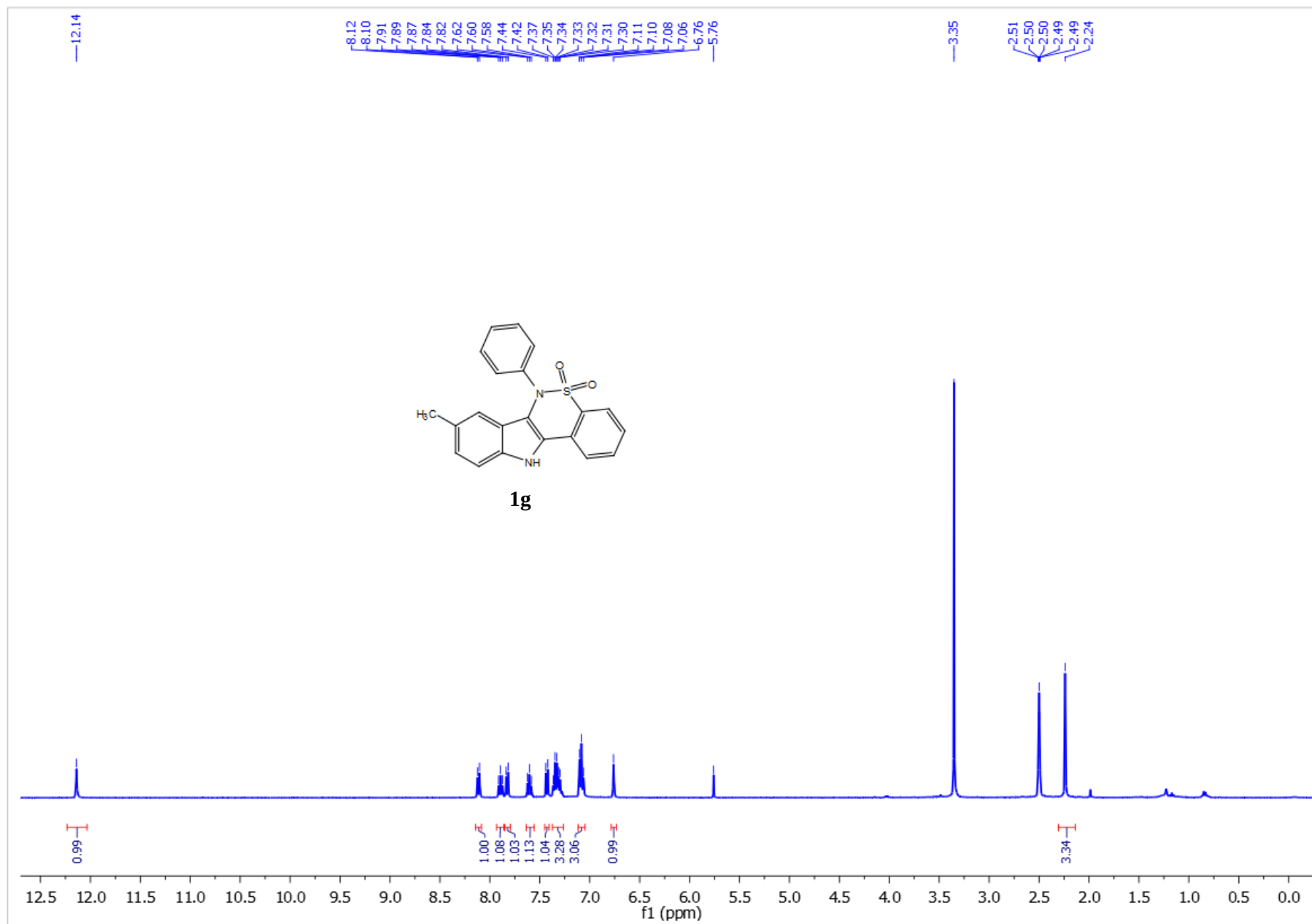


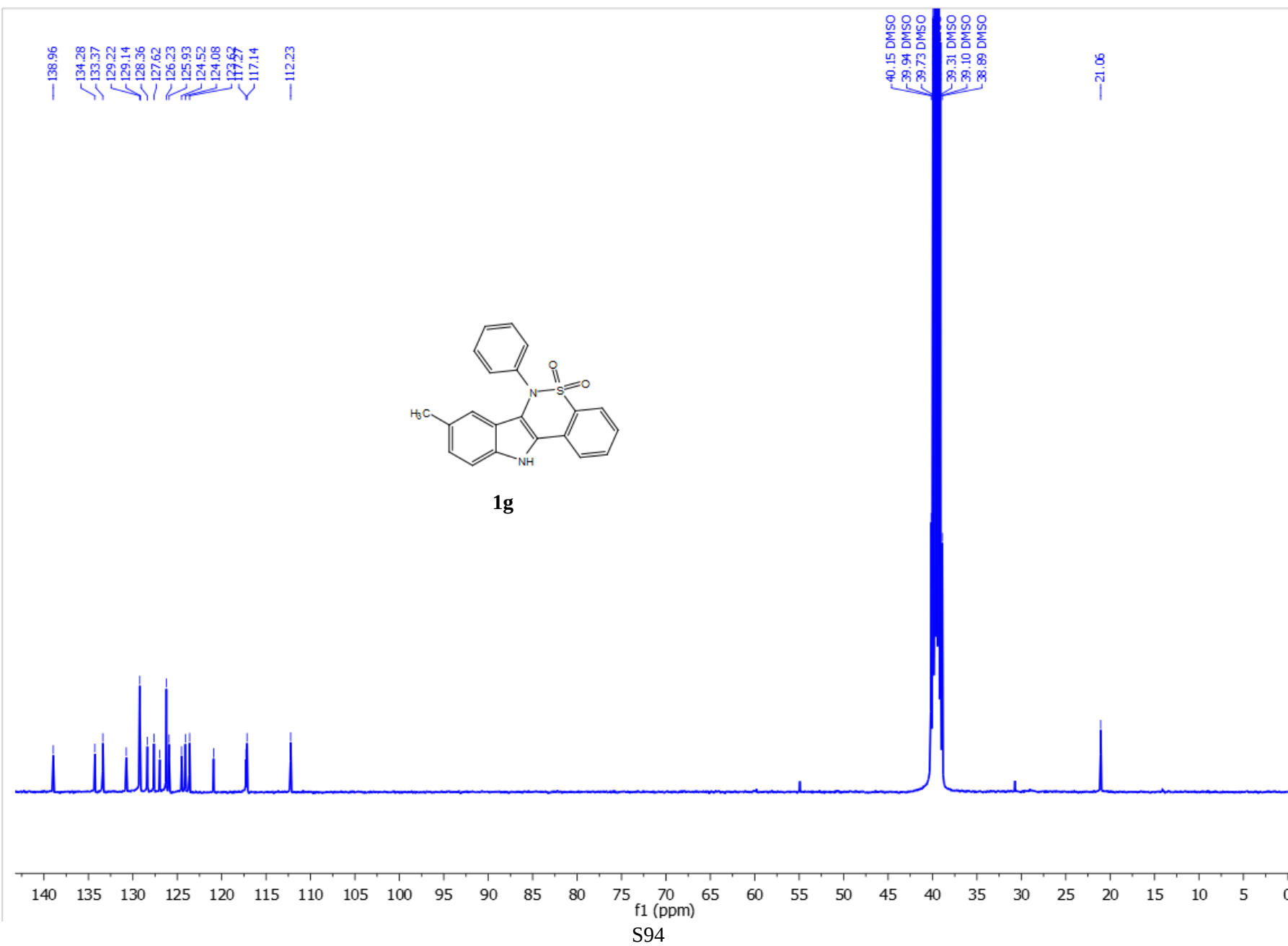


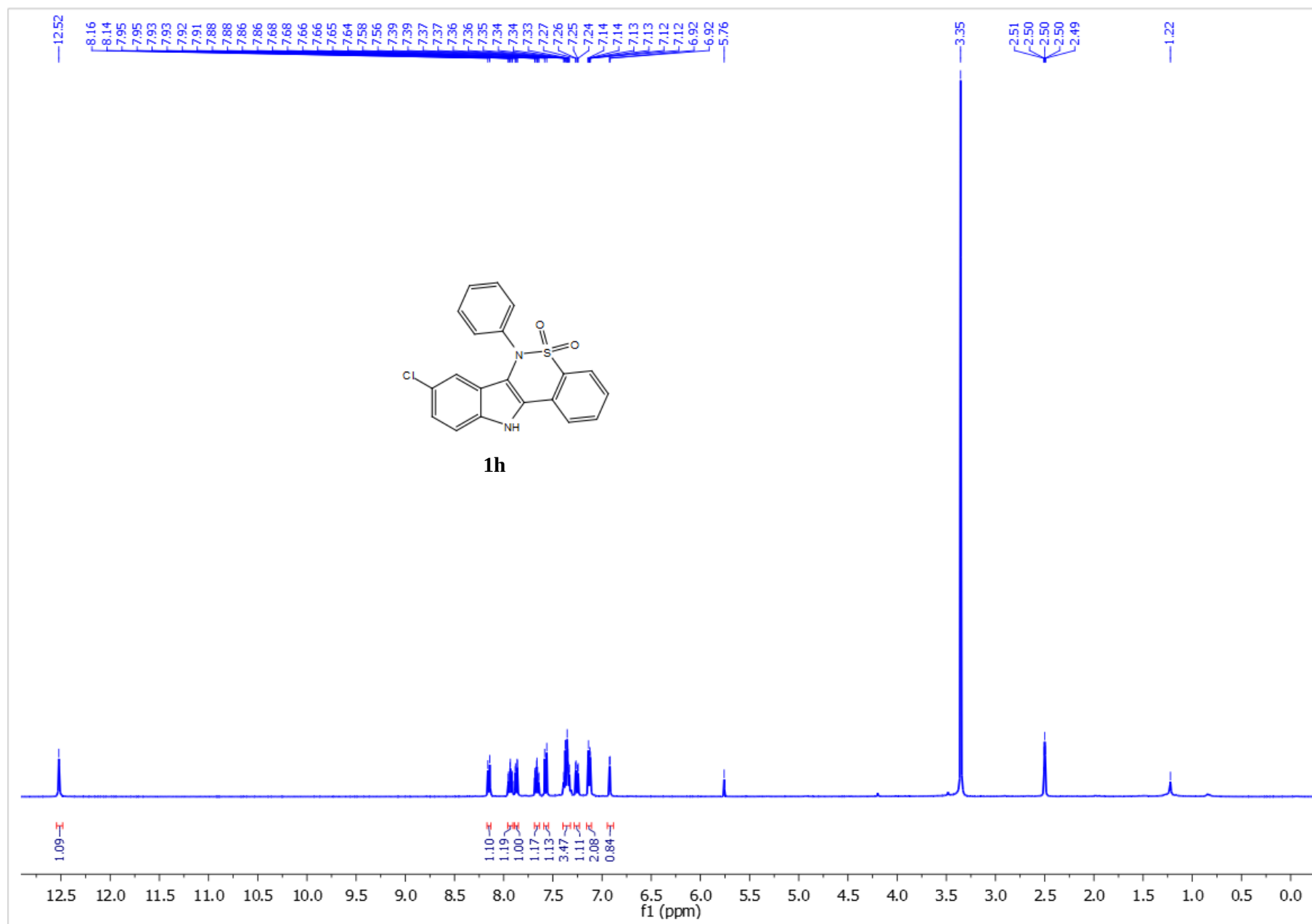


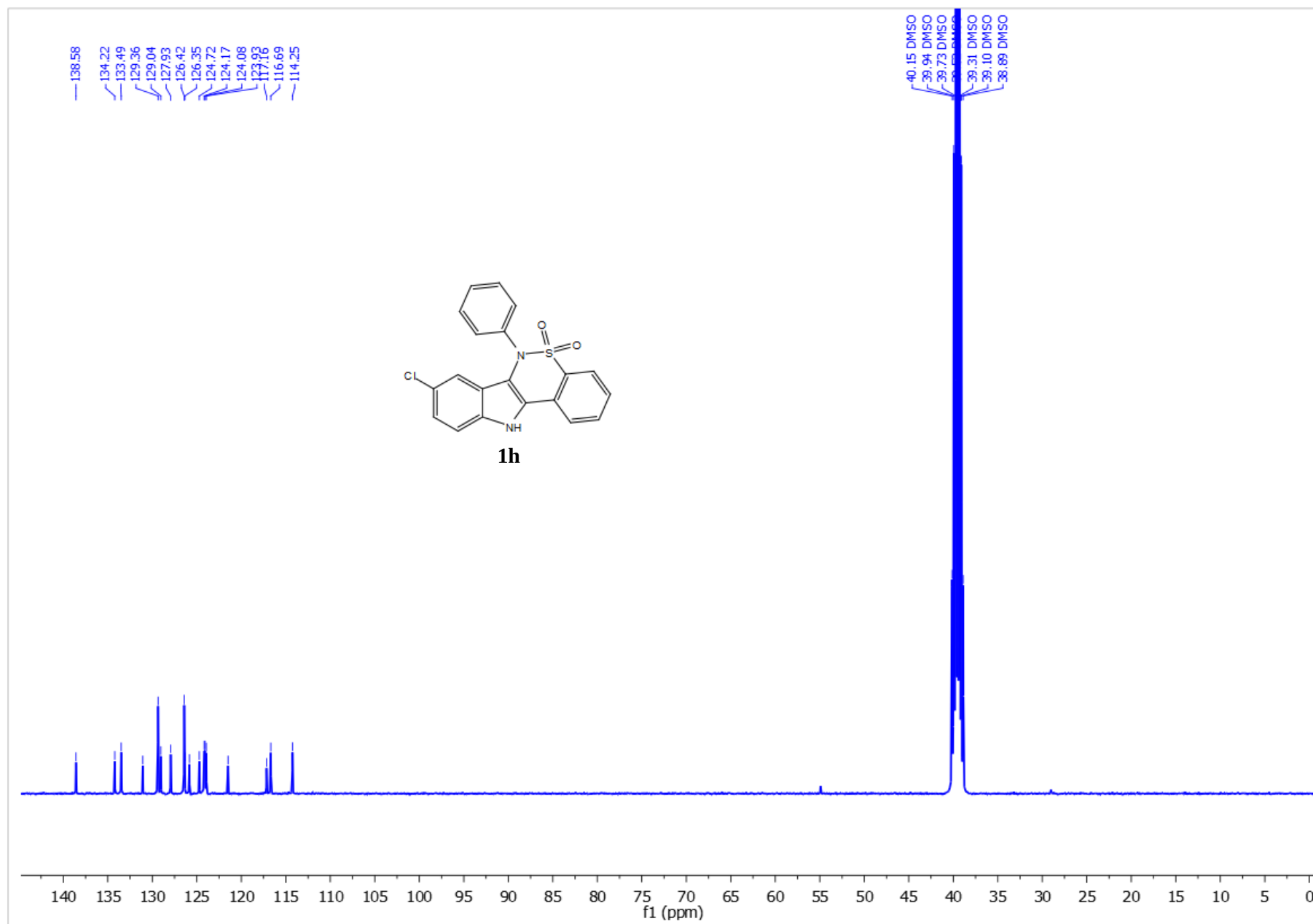
S91

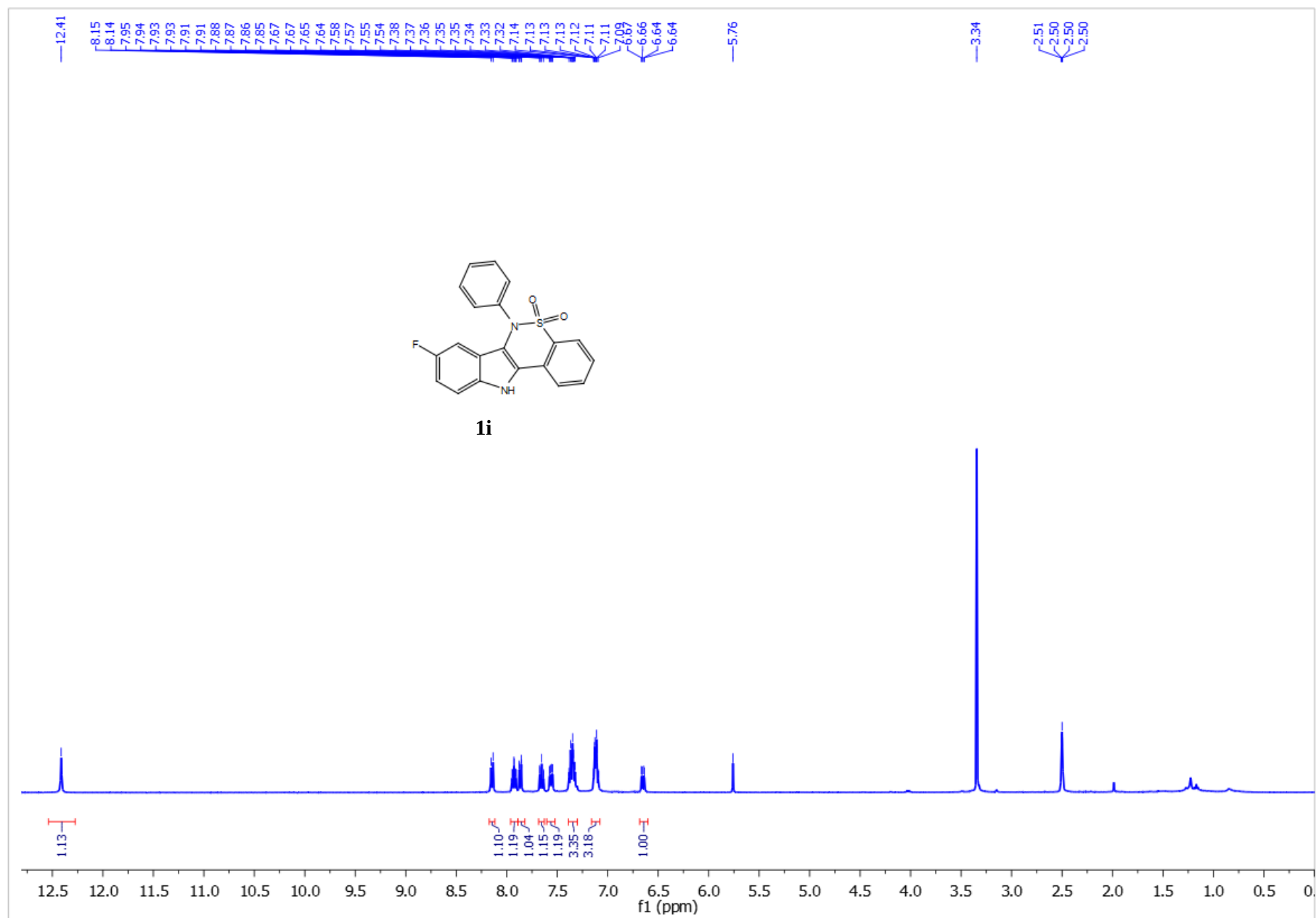


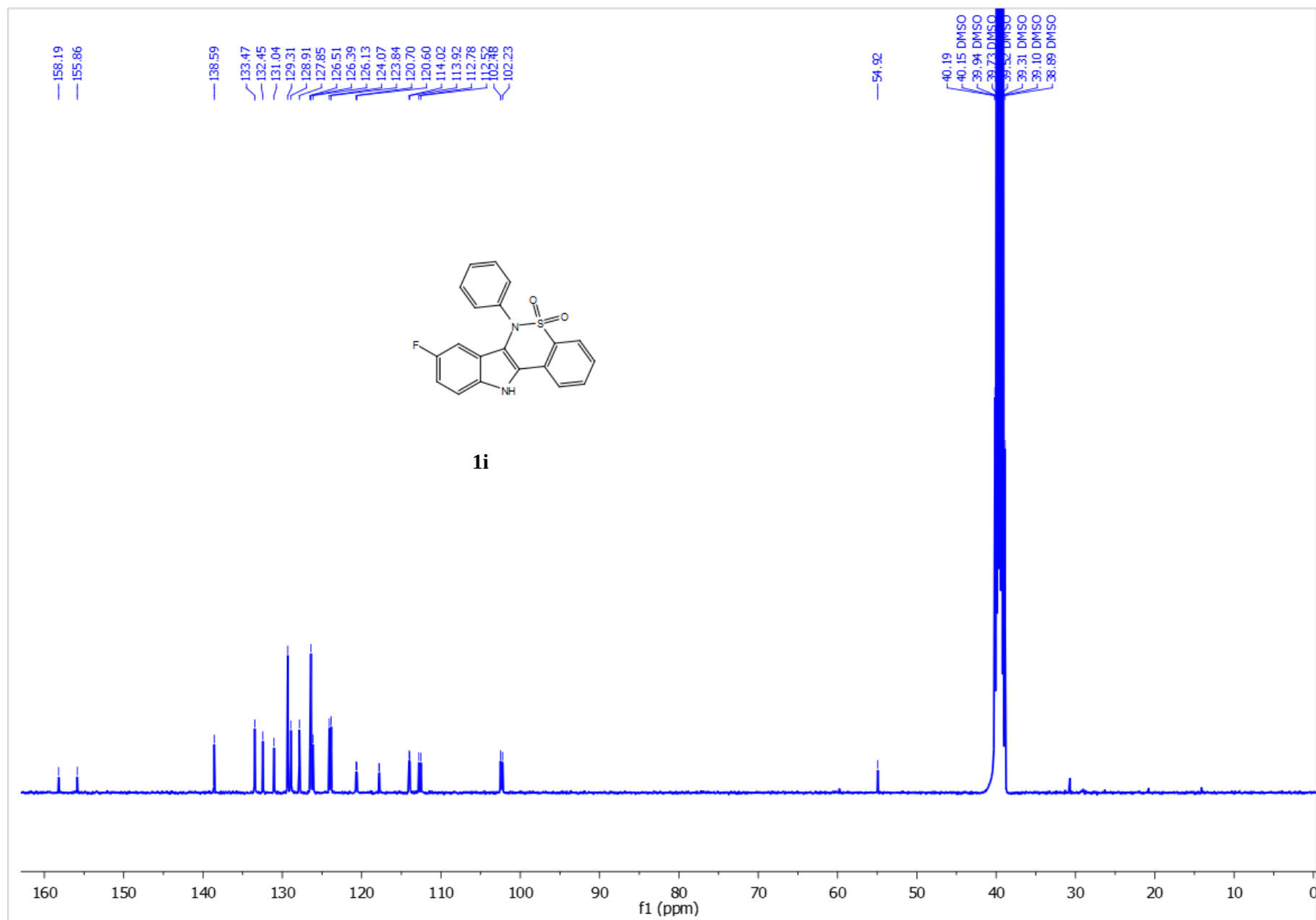




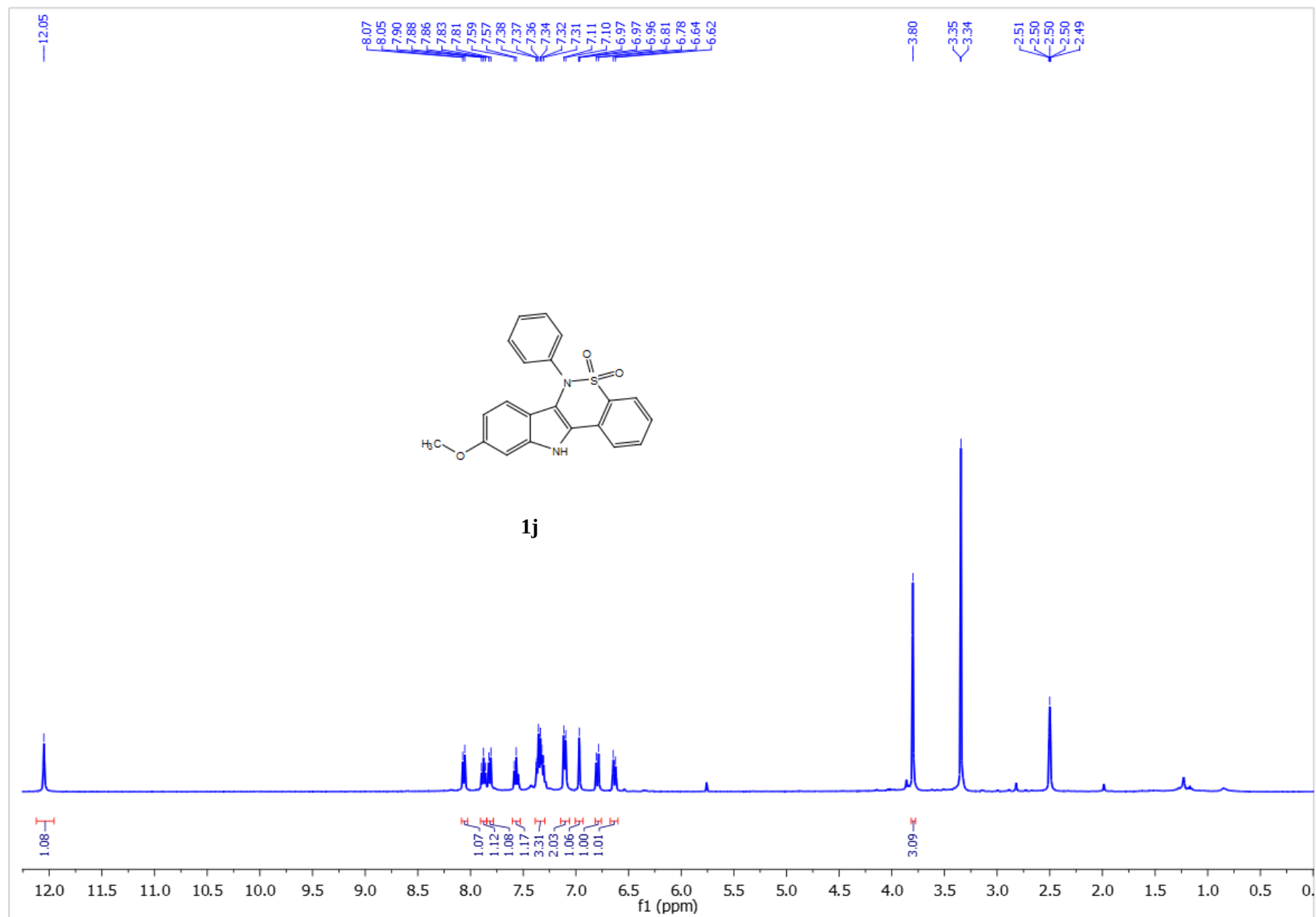


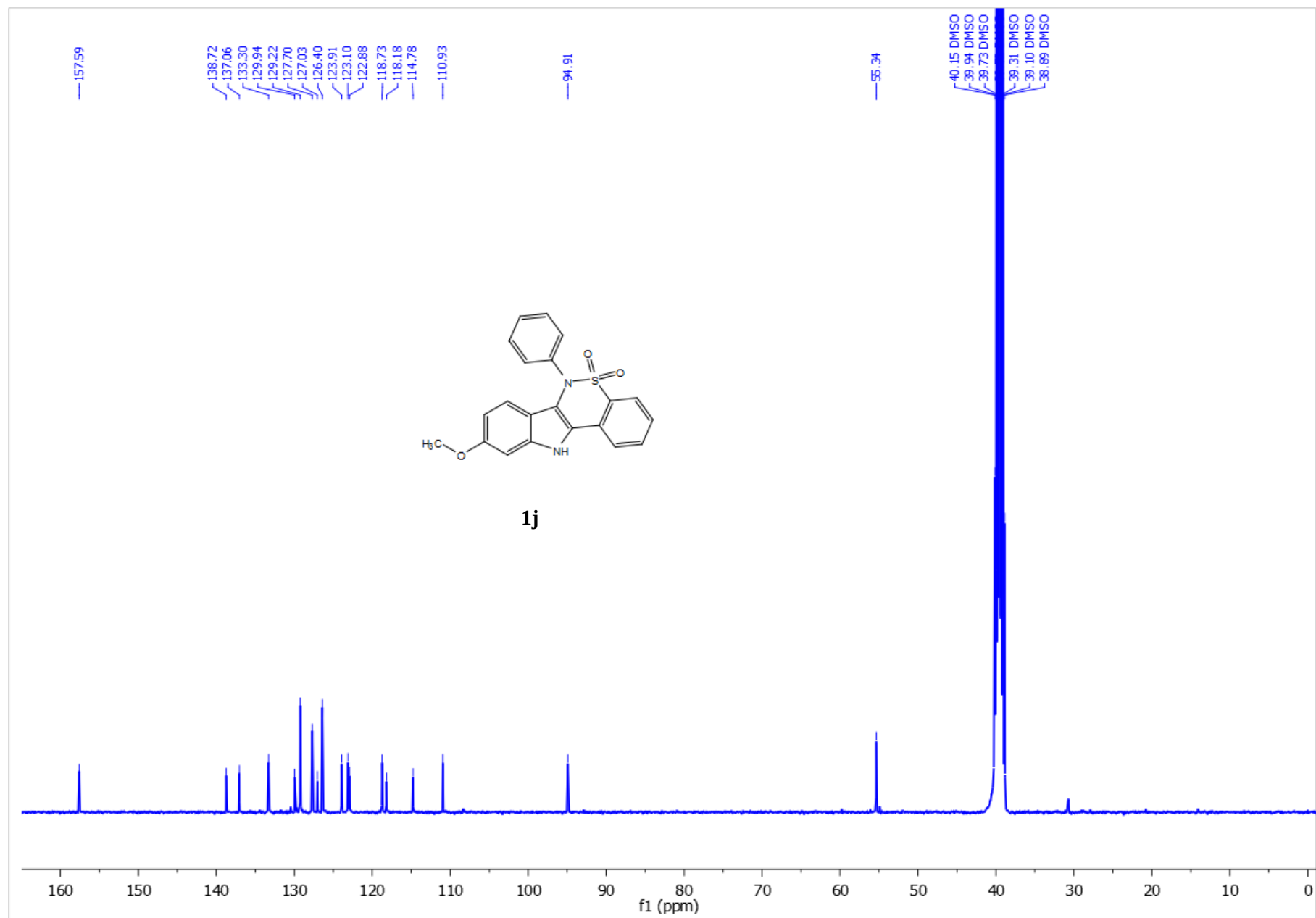




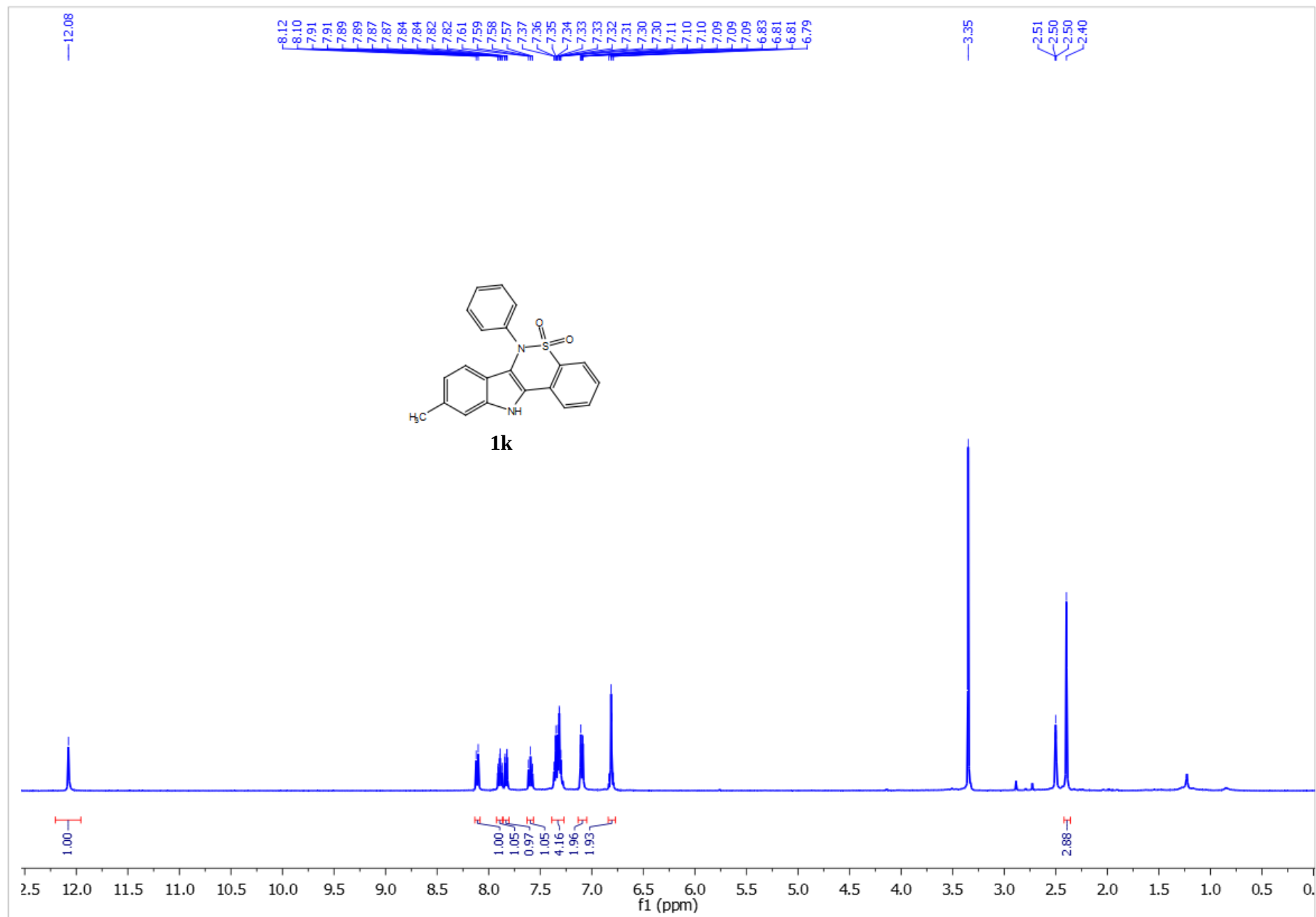


S98

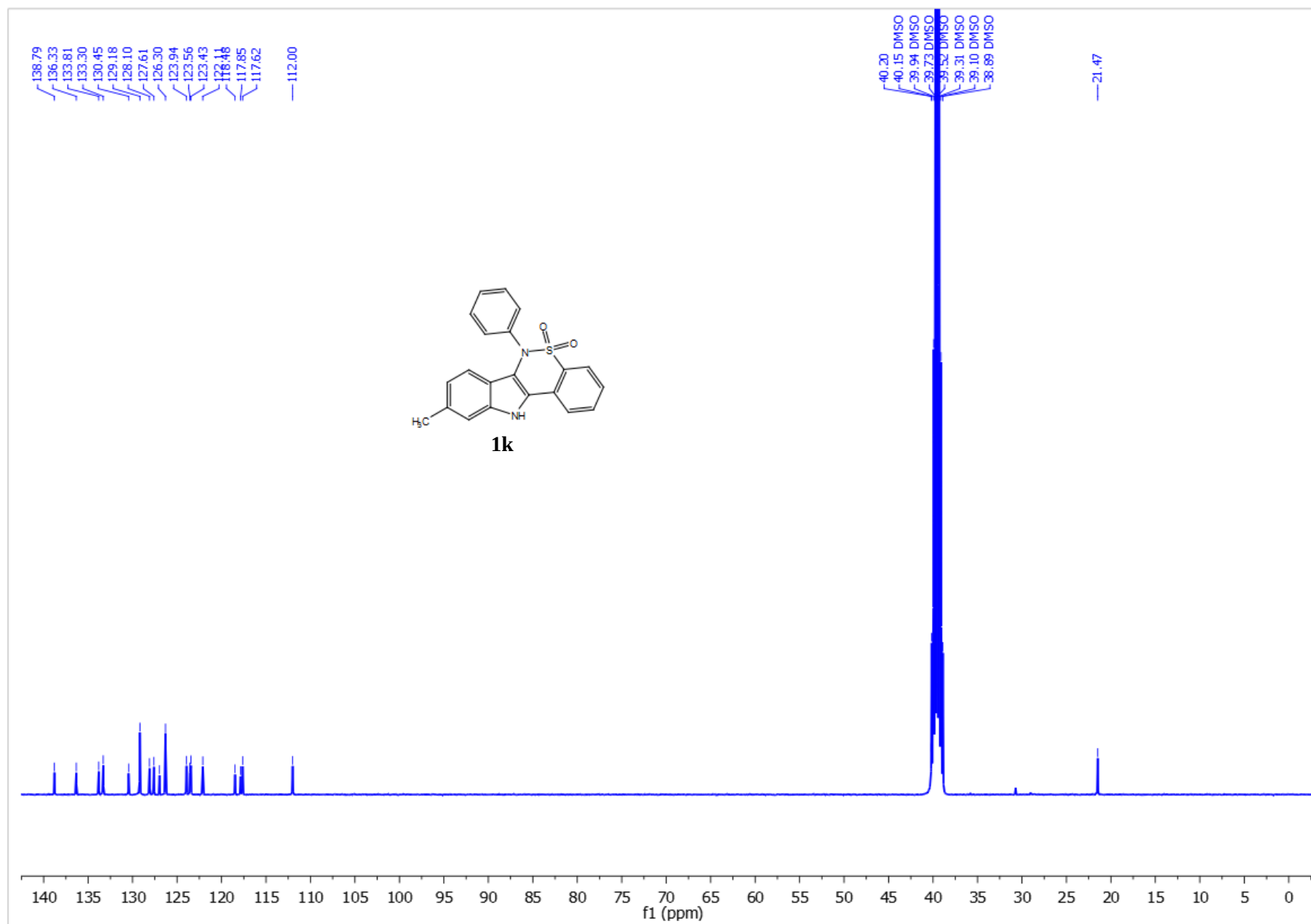


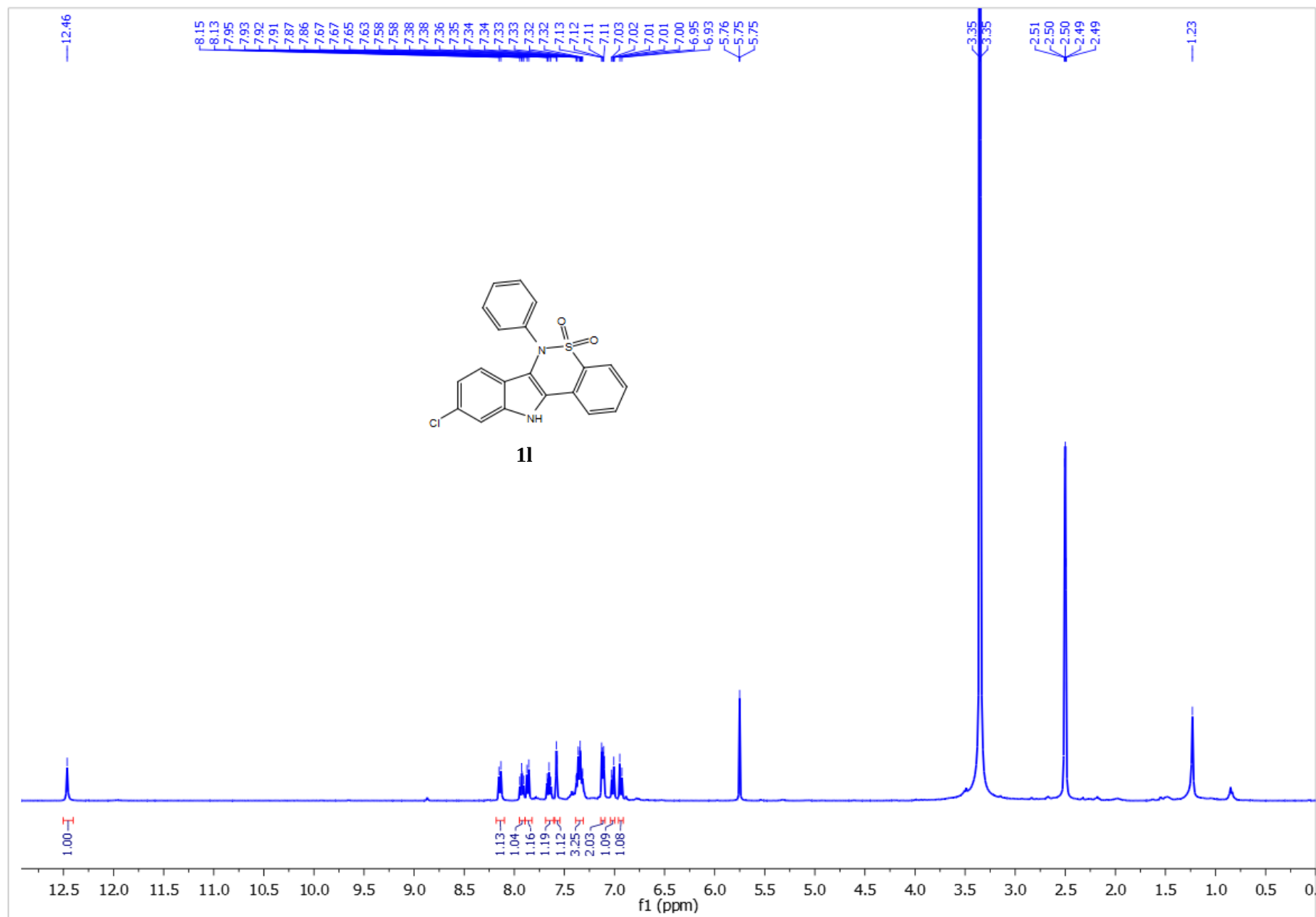


S100

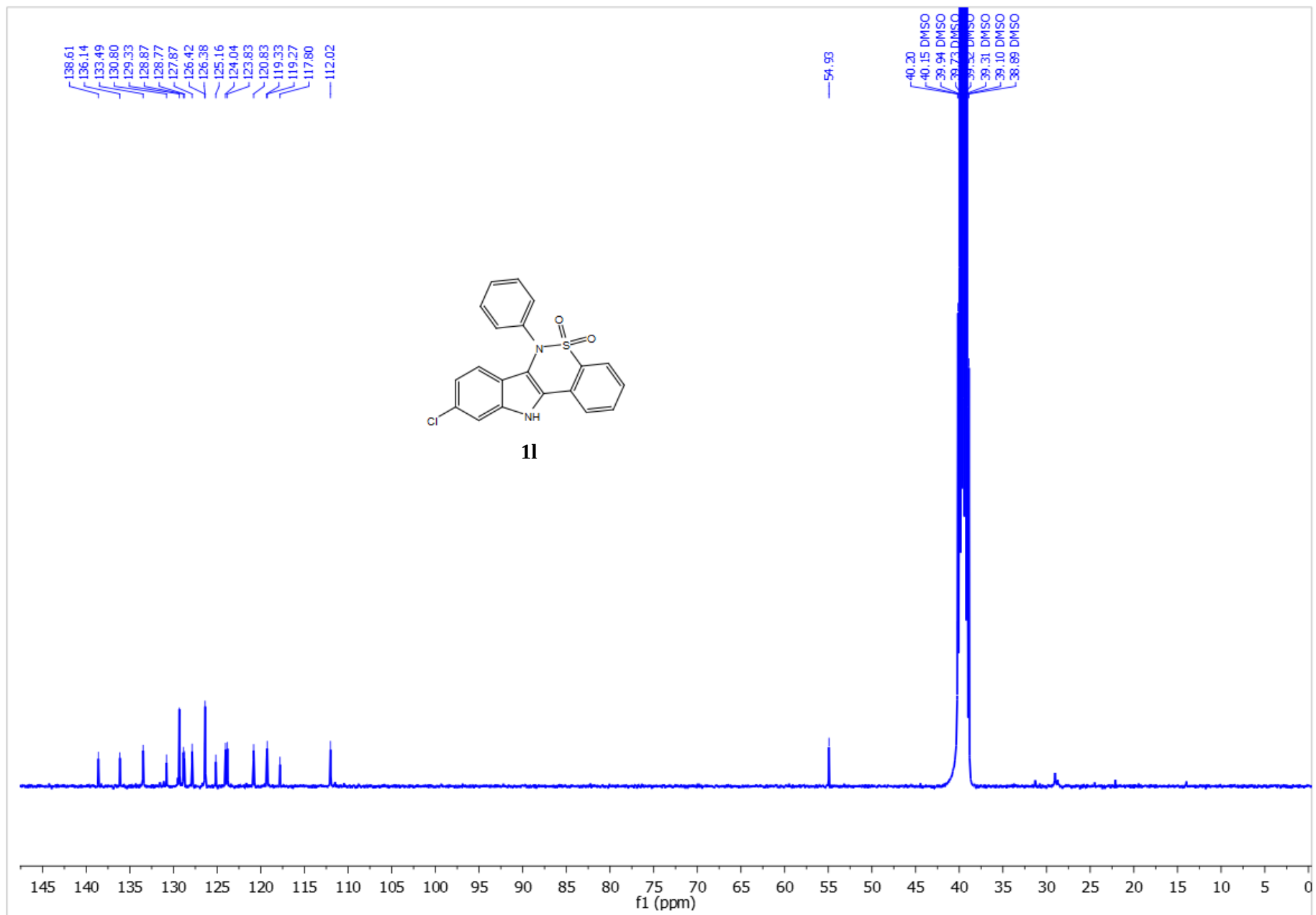


S101

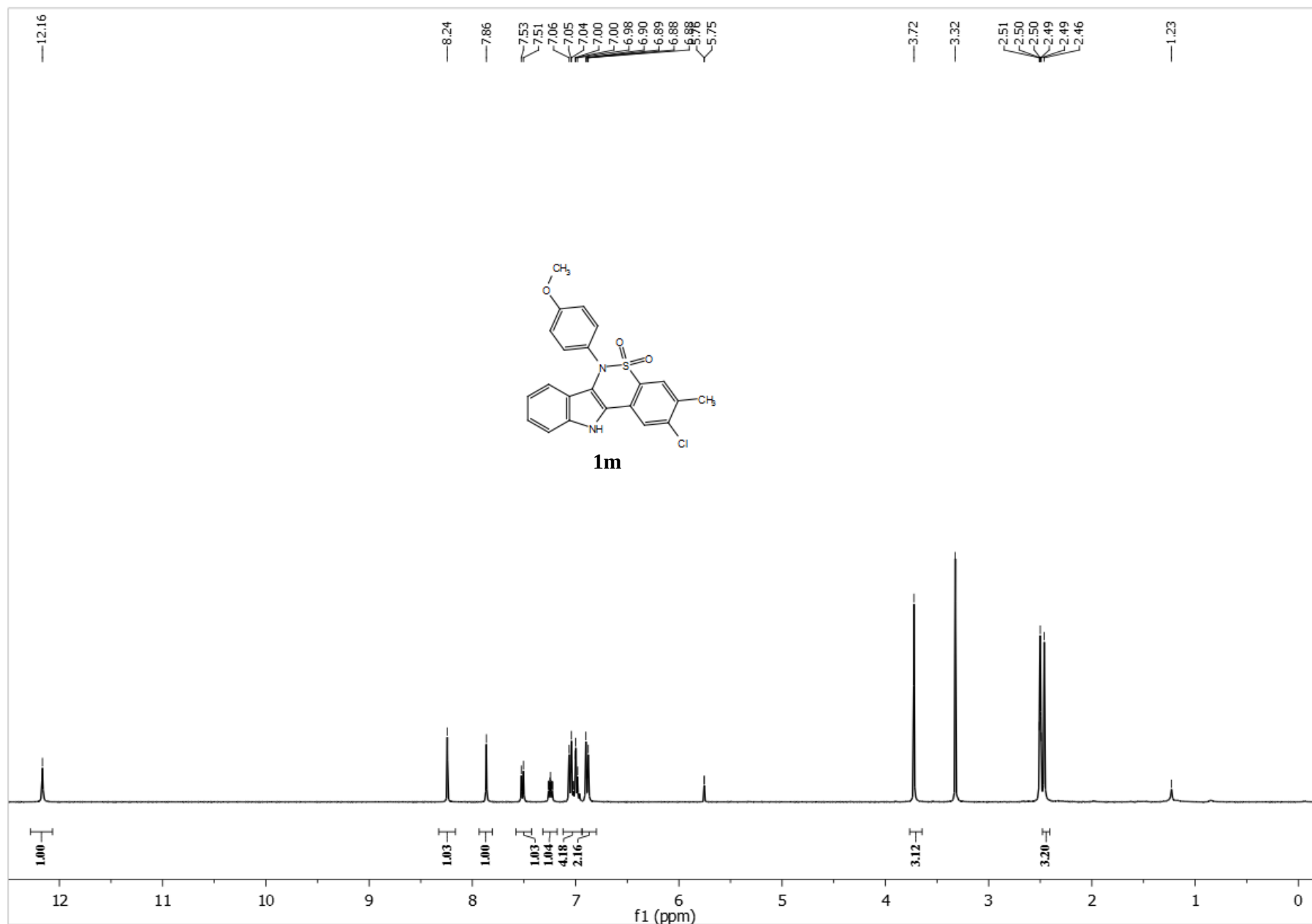




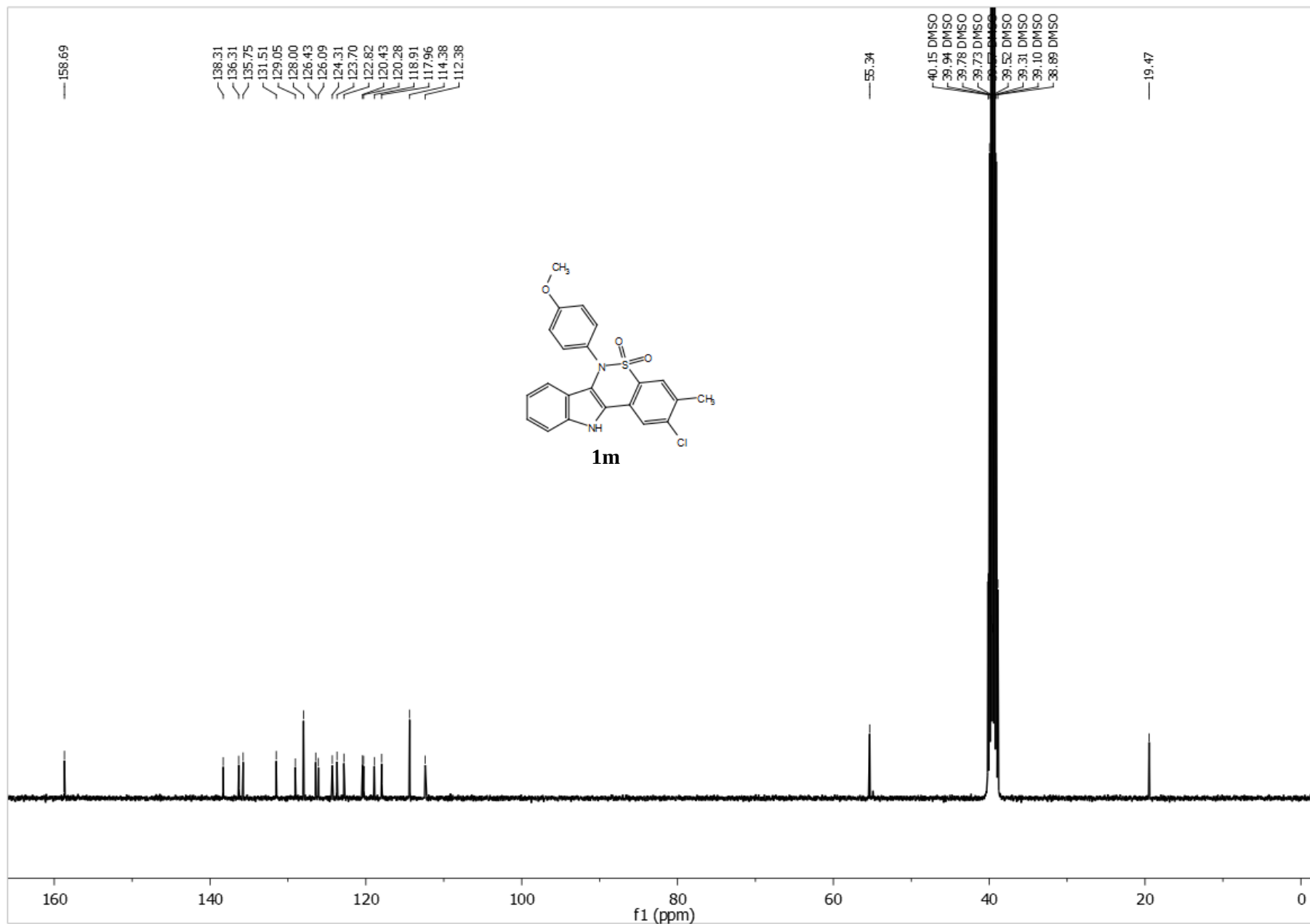
S103



S104



S105



S106

