Supporting Information

Iron-catalyzed oxidative bis-arylation of indolin-2-one for direct construction of quaternary carbons

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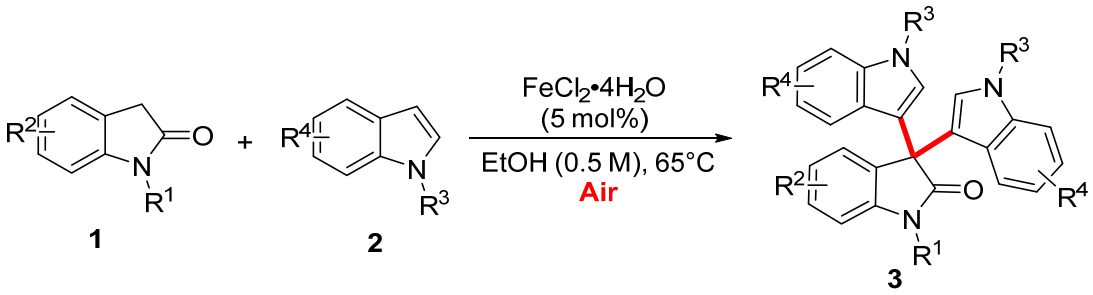
1. General information

All chemicals were purchased from commercial suppliers and were used without further purification. Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-*d*$_6$ as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource.

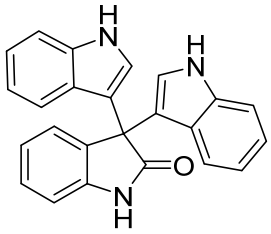
2. General Procedure

General procedure for the synthesis of compounds 3.



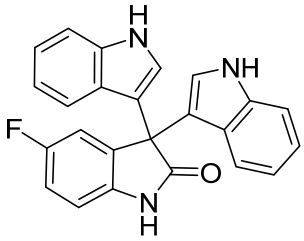
In a 10-mL reaction vial, equipped with a magnetic stirring bar, indolin-2-ones (0.5 mmol, 1.0 equiv), indoles (1.05 mmol, 2.1 equiv) and $FeCl_2{\cdot}4H_2O$ (5 mol%, 9.9 mg) were added to ethanol (1.0 mL). Then the vial was placed in a pre-heated metal block at 65 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, cold water (15 mL) was added. The mixture was extracted with ethyl acetate (3×15 mL). The organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum/ethyl acetate (4/1) as eluent to afford the pure product.

3. Characterization data of compounds 3a-3ah



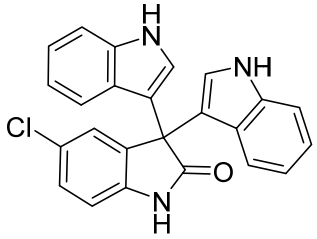
Trisindoline (3a)[1]

The title compound was obtained as a white solid. Mp 277-280°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.79 (t, 2H, ArH, *J* = 7.2 Hz), 6.86 (d, 2H, NH, *J* = 2.0 Hz), 6.91 (t, 1H, ArH, *J* = 7.6 Hz), 7.00 (t, 3H, ArH, *J* = 8.0 Hz), 7.18-7.27 (m, 4H, ArH), 7.35 (d, 2H, ArH, *J* = 8.0 Hz), 10.58 (s, 1H, NH), 10.92 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.0, 110.0, 112.1, 114.8, 118.7, 121.2, 121.4, 121.9, 124.7, 125.4, 126.2, 128.3, 135.1, 137.4, 141.8, 179.2.



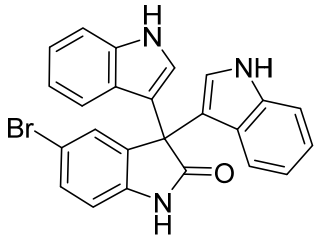
5'-Fluoro-[3,3':3',3''-terindolin]-2'-one (3b)[1]

The title compound was obtained as a light gray solid. Mp 300-301°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.84 (t, 2H, ArH, *J* = 7.4 Hz), 6.92 (d, 2H, ArH, *J* = 2.0 Hz), 6.99-7.11 (m, 5H, ArH), 7.25 (d, 2H, ArH, *J* = 8.0 Hz), 7.38 (d, 2H, ArH, *J* = 8.4 Hz), 10.67 (s, 1H, NH), 11.03 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.6, 110.8, 112.2, 113.0, 114.1, 114.8, 118.9, 121.1, 121.5, 124.9, 126.0, 136.8, 137.4, 138.0, 158.3 (d, $^{1}J_{CF}$ = 235.4 Hz, C-F), 179.2.



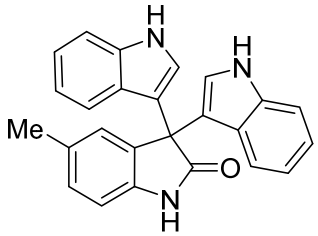
5-Chloro-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3c)[1]

The title compound was obtained as a grey solid. Mp 290-292°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.82 (t, 2H, ArH), 6.88-6.89 (m, 2H, ArH), 7.00-7.05 (m, 3H, ArH), 7.21 (d, 3H, ArH, J = 8.0 Hz), 7.28-7.31 (m, 1H, ArH), 7.37 (d, 2H, ArH, J = 8.0 Hz), 10.77 (s, 1H, NH), 11.03 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 53.3, 111.6, 112.2, 114.0, 118.9, 121.0, 121.6, 124.9, 125.2, 125.9, 126.0, 128.3, 137.1, 137.4, 140.8, 178.9.



5'-Bromo-[3,3':3',3''-terindolin]-2'-one (3d)[1]

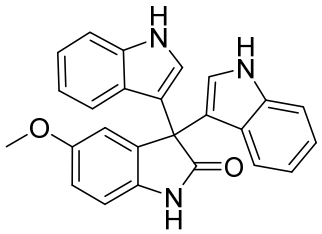
The title compound was obtained as a yellow solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.82 (t, 2H, ArH, J = 7.2 Hz), 6.87 (d, 2H, ArH, J = 2.0 Hz), 7.03 (t, 2H, ArH, J = 7.4 Hz), 7.12-7.24 (m, 3H, ArH), 7.23 (d, 2H, ArH, J = 8.0 Hz), 7.36 (d, 2H, ArH, J = 8.0 Hz), 10.77 (s, 1H, NH), 11.03 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 52.8, 112.2, 112.8, 114.0, 118.8, 120.8, 121.1, 121.5, 124.6, 124.8, 126.0, 127.2, 134.3, 137.4, 143.5, 179.0.



5'-Methyl-[3,3':3',3''-terindolin]-2'-one (3e)[2]

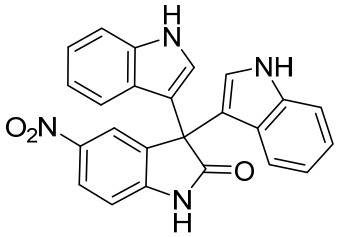
The title compound was obtained as a white solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 2.19 (s, 3H, CH_3), 6.80-6.88 (m, 5H, ArH), 7.01 (s, 4H, ArH), 7.24 (d, 2H, ArH, J = 7.4 Hz), 7.35 (d, 2H, ArH, J = 7.7 Hz), 10.49 (s, 1H, NH), 10.94 (s, 2H,

NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 21.3, 53.1, 109.8, 112.0, 114.9, 118.7, 121.3, 121.4, 124.8, 125.9, 126.2, 128.6, 130.6, 135.1, 137.4, 139.4, 179.2.



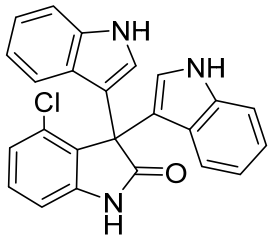
5'-Methoxy-[3,3':3',3''-terindolin]-2'-one (3f)[2]

The title compound was obtained as a brown solid. Mp 280-281°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 3.61 (s, 1H, CH_3), 6.83-6.79 (m, 4H, ArH), 6.92-6.88 (m, 3H, ArH), 7.02 (t, 2H, ArH, *J* = 7.4 Hz), 7.24 (d, 2H, ArH, *J* = 8.0 Hz), 7.36 (t, 2H, ArH, *J* = 8.0Hz), 10.45 (s, 1H, NH), 10.97 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.0, 55.3, 109.8, 111.6, 112.0, 112.1, 114.2, 118.2, 120.7, 120.9, 124.3, 125.7, 134.7, 135.9, 136.9, 154.6, 178.6.



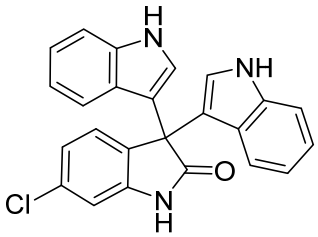
5'-Nitro-[3,3':3',3''-terindolin]-2'-one (3g)[2]

The title compound was obtained as a yellow solid. Mp > 300°C. 1H NMR (400MHz, DMSO-d6): δ 6.86 (t, 2H, ArH, *J* = 7.4 Hz), 6.99 (d, 2H, ArH, *J* = 1.8 Hz), 7.06 (t, 2H, ArH, *J* = 7.4 Hz), 7.23 (t, 3H, ArH, *J* = 8.6 Hz), 7.40 (d, 2H, ArH, *J* = 8.0 Hz), 8.00 (d, 1H, ArH, *J* = 1.3 Hz), 8.26 (d-d, 1H, ArH, J_1 = 8.6 Hz, J_2 = 1.6 Hz), 11.12 (s, 2H, NH), 11.37 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.0, 110.4, 113.3, 119.1, 120.6, 120.8, 121.7, 125.1, 125.9, 126.0, 137.5, 142.7, 148.3, 179.4.



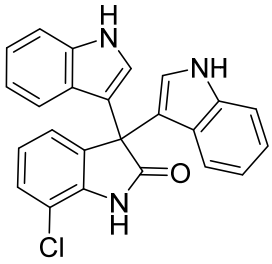
4'-Chloro-[3,3':3',3''-terindolin]-2'-one (3h)

The title compound was obtained as a pink solid. Mp 286-288°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.86 (t, 2H, ArH, *J* = 7.4 Hz), 6.93 (d, 3H, ArH, *J* = 7.2 Hz), 7.01 (d, 1H, ArH, *J* = 7.6 Hz), 7.05 (t, 2H, ArH, *J* = 7.4 Hz), 7.26 (d, 2H, ArH, *J* = 8.0 Hz), 7.31 (d, 1H, ArH, *J* = 8.0 Hz), 7.39 (d, 2H, ArH, *J* = 8.0 Hz), 10.81 (s, 1H, NH), 11.02 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.9, 109.1, 111.1, 112.1, 118.8, 121.4, 123.3, 125.9, 126.3, 130.4, 131.5, 137.2, 144.2, 178.5. HRMS (ESI) m/z calcd for $C_{24}H_{16}ClN_3NaO$ ([M+Na]$^+$): 420.0874; found: 420.0872.



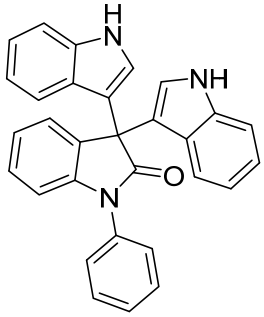
6'-Chloro-[3,3':3',3''-terindolin]-2'-one (3i)[3]

The title compound was obtained as a light pink solid. Mp 205-206°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.82 (t, 2H, ArH, *J* = 7.4 Hz), 6.88 (d, 2H, ArH, *J* = 2.4 Hz), 6.97-7.05 (m, 4H, ArH), 7.21-7.25 (t, 3H, ArH, *J* = 8.0 Hz), 7.37 (d, 2H, ArH, *J* = 8.0 Hz), 10.78 (s, 1H, NH), 11.01 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.8, 110.1, 112.2, 114.2, 118.9, 121.1, 121.5, 1217, 124.9, 126.0, 126.8, 132.5, 133.9, 137.4, 143.3, 179.1.



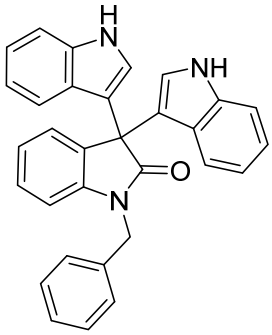
7'-Chloro-[3,3':3',3''-terindolin]-2'-one (3j)[2]

The title compound was obtained as a light brown solid. Mp 288-289°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.82-6.86 (m, 4H, ArH), 6.95-7.03 (m, 3H, ArH), 7.18-7.22 (m, 3H, ArH), 7.31 (d, 2H, ArH, *J* = 7.8 Hz), 7.37 (d, 2H, ArH, *J* = 7.4 Hz), 11.03 (s, 2H, NH), 11.06 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 53.9, 112.2, 114.1, 114.3, 118.9, 121.1, 121.5, 123.3, 124.0, 124.9, 126.0, 128.3, 136.7, 137.4, 139.5, 179.0.



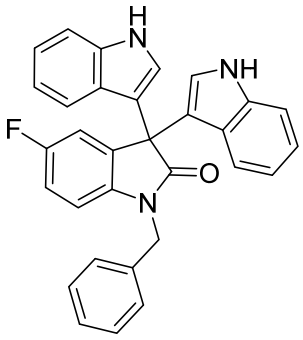
1'-Phenyl-[3,3':3',3''-terindolin]-2'-one (3k)

The title compound was obtained as a yellow solid. Mp >300°C . ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.83 (t, 2H, ArH, *J* = 7.5 Hz), 6.92 (d, 2H, ArH, *J* = 7.9 Hz), 6.97 (d, 2H, ArH, *J* = 7.9 Hz), 7.02-7.09 (m, 3H, ArH), 7.27-7.30 (m, 3H, ArH), 7.39 (d, 3H, ArH, *J* = 8.2 Hz), 7.46 (d, 1H, ArH, *J* = 7.2 Hz), 7.49 (d, 2H, ArH, *J* = 7.6 Hz), 7.59 (t, 2H, ArH, *J* = 7.2 Hz), 11.07 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.4, 109.1, 111.7, 113.9, 118.5, 120.5, 121.1, 122.9, 124.6, 125.2, 125.6, 126.6, 128.0, 128.1, 129.7, 133.6, 134.5, 137.0, 142.2, 176.4. HRMS (ESI) m/z calcd for $C_{30}H_{22}N_3O$ ([M+H]$^+$): 440.1757; found: 440.1763.



1'-Benzyl-[3,3':3',3''-terindolin]-2'-one (3l)[4]

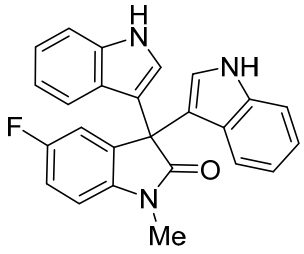
The title compound was obtained as a white solid. Mp 276-277℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 5.02 (s, 2H, CH_2), 6.75 (t, 2H, ArH, J = 7.6 Hz), 6.89 (d, 2H, ArH, J = 2.4 Hz), 6.96-7.03 (m, 3H, ArH), 7.10 (d, 1H, ArH, J = 7.6 Hz), 7.15 (d, 2H, ArH, J = 8.0 Hz), 7.22-7.32 (m, 5H, ArH), 7.37 (d, 4H, ArH, J = 8.0 Hz), 11.01 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 43.5, 52.8, 109.8, 112.1, 114.5, 118.7, 121.3, 121.5, 122.8, 124.8, 125.3, 126.1, 128.0, 128.1, 128.4, 129.0, 134.3, 137.0, 137.4, 142.2, 177.6.



1-Benzyl-5-fluoro-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3m)

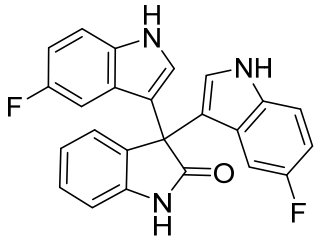
The title compound was obtained as a light yellow solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 5.03 (s, 2H, CH_2), 6.77 (t, 2H, ArH, J = 7.4 Hz), 6.93 (s, 2H, ArH), 7.04 (t, 2H, ArH, J = 7.4 Hz), 7.12 (d, 5H, ArH, J = 7.6 Hz), 7.31-7.39 (m, 7H, ArH), 11.07 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 43.6, 53.2, 110.7, 112.2, 112.8, 113.1, 113.8, 114.8, 118.9, 121.1, 121.6, 125.0, 125.9, 128.1, 129.1, 136.1, 136.8, 137.4, 138.4, 158.8 (d, $^{1}J_{CF}$ = 236.5 Hz, C-F), 177.4. HRMS (ESI) m/z calcd

for $C_{31}H_{22}FN_3NaO$ ($[M+Na]^+$): 494.1639; found: 494.1636.



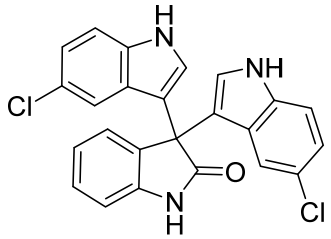
5-Fluoro-1-methyl-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3n)

The title compound was obtained as a light yellow solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 3.26 (s, 3H, CH_3), 6.81 (t, 2H, ArH, *J* = 7.2 Hz), 6.89 (s, 2H, ArH), 7.03 (t, 2H, ArH, *J* = 7.2 Hz), 7.09-7.20 (m, 5H, ArH), 7.36 (d, 2H, ArH, *J* = 8.0 Hz), 11.04 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 26.9, 53.0, 110.1, 112.2, 112.9, 112.9, 113.9, 114.8, 118.9, 121.0, 121.5, 125.0, 125.9, 135.9, 135.9, 137.4, 139.5, 158.8 (d, $^1J_{CF}$ = 236.0 Hz, C-F), 177.2. HRMS (ESI) m/z calcd for $C_{25}H_{19}FN_3O$ ($[M+H]^+$): 396.1507; found: 396.1501.



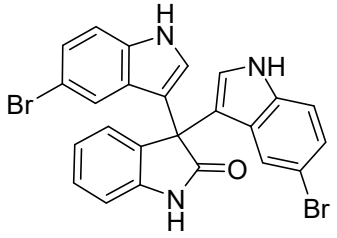
5,5''-Difluoro-[3,3':3',3''-terindolin]-2'-one (3o)[5]

The title compound was isolated as a light brown solid. Mp 154-156°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.88-6.94 (m, 4H, ArH), 6.96-7.00 (m, 3H, ArH), 7.05 (d, 1H, ArH, *J* = 8.0 Hz), 7.24-7.29 (m, 2H, ArH), 7.38-7.42 (m, 2H, ArH), 10.73 (s, 1H, NH), 11.16 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.2, 105.0, 105.2, 109.2, 109.5, 109.8, 112.6, 112.7, 114.2, 114.2, 121.8, 124.9, 125.7, 125.8, 126.3, 128.1, 133.6, 133.8, 141.2, 155.1, 157.4, 178.6.



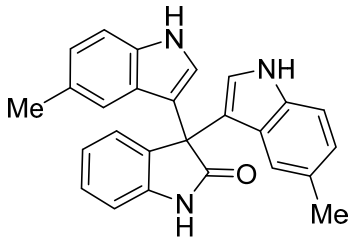
5,5''-Dichloro-[3,3':3',3''-terindolin]-2'-one (3p)[5]

The title compound was isolated as a light white solid. Mp >300℃. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.95 (d, 2H, ArH, *J* = 4.0 Hz), 6.97-7.04 (m, 3H, ArH), 7.06 (d, 1H, ArH, *J* = 4.0 Hz), 7.19-7.23 (m, 3H, ArH), 7.27 (t, 1H, ArH, *J* = 8.0 Hz), 7.41 (d, 2H, ArH, *J* = 8.0 Hz), 10.75 (s, 1H, NH), 11.24 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.6, 110.3, 113.8, 114.4, 120.1, 121.6, 122.3, 123.5, 125.4, 126.6, 127.1, 128.7, 134.1, 135.9, 141.7, 178.9.



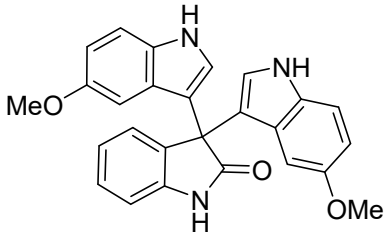
5,5-Dibromo-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3q)[1]

The title compound was obtained as a light red solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.92 (s, 2H, ArH), 6.98-7.04 (m, 2H, ArH), 7.16 (d, 3H, ArH, *J* = 6.8 Hz), 7.28 (t, 1H, ArH, *J* = 6.4 Hz), 7.36 (s, 1H, ArH), 10.76 (s, 1H, NH), 11.26 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.6, 110.3, 111.6, 114.3, 114.3, 122.3, 123.1, 124.1, 125.3, 126.5, 127.7, 128.8, 134.1, 136.2, 141.7, 178.9.



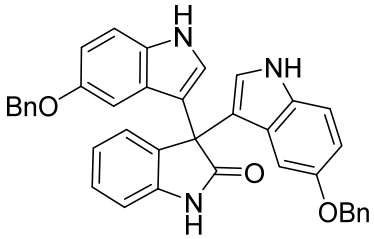
5,5''-Dimethyl-[3,3':3',3''-terindolin]-2'-one (3r)[5]

The title compound was isolated as a brown and white solid. Mp >300℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 2.21 (s, 6H, CH), 6.79 (s, 2H, ArH), 6.84-7.00 (m, 4H, ArH), 7.05 (s, 2H, ArH), 7.18-7.26 (m, 4H, ArH), 10.58 (s, 1H, NH), 10.80 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 179.4, 141.8, 135.8, 135.1, 128.3, 126.8, 126.4, 125.4, 125.0, 123.1, 121.9, 120.9, 114.3, 111.8, 109.9, 53.1, 22.0.



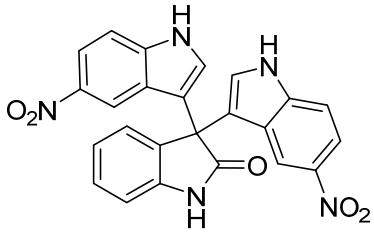
5,5''-Dimethoxy-[3,3':3',3''-terindolin]-2'-one (3s)[1]

The title compound was obtained as a brown solid. Mp 189-190℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.53 (s, 6H, CH_3), 6.70-6.72 (m, 4H, ArH), 6.87 (d, 2H, ArH, J = 2.4 Hz), 6.94 (t, 1H, ArH, J = 7.4 Hz), 7.01 (d, 1H, ArH, J = 7.6 Hz), 7.21-7.28 (m, 4H, ArH), 10.62 (s, 1H, NH), 10.81 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 53.0, 55.6, 103.8, 109.9, 110.9, 112.6, 114.1, 122.0, 125.5, 125.7, 126.6, 128.3, 132.7, 135.0, 141.9, 152.9, 179.3.



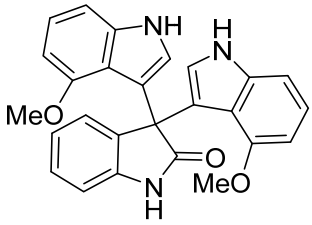
5,5''-Bis(benzyloxy)-[3,3':3',3''-terindolin]-2'-one (3t)[6]

The title compound was isolated as a white solid. Mp 197-198℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 4.78-4.86 (m, 4H, CH), 6.76-6.78 (m, 4H, ArH), 6.85-6.89 (m, 3H, ArH), 6.99 (d, 1H, ArH, J = 8.0 Hz), 7.04 (d, 1H, ArH, J = 4.0 Hz), 7.20-7.36 (m, 13H, ArH), 10.59 (s, 1H, NH), 10.83 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 52.9, 70.2, 105.4, 110.0, 111.8, 112.6, 114.2, 121.9, 125.4, 125.5, 126.6, 128.1, 128.2, 128.8, 132.8, 135.0, 138.0, 141.7, 151.8, 179.1.



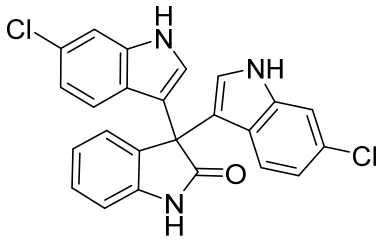
5,5''-Dinitro-[3,3':3',3''-terindolin]-2'-one (3u)[1]

The title compound was obtained as a yellow solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d6): δ 7.03 (t, 1H, ArH, *J* = 6.7 Hz), 7.10 (d, 1H, ArH, *J* = 7.2Hz), 7.23-7.34 (m, 4H, ArH), 7.59 (d, 2H, ArH, *J* = 8.8Hz), 7.98 (d, 2H, ArH, *J* = 8.2Hz), 8.27 (s, 2H, ArH), 11.01 (s, 1H, NH), 11.85 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 52.6, 110.7, 113.0, 117.2, 118.0, 122.7, 125.1, 125.4, 128.8, 129.2, 133.4, 140.7, 141.7, 178.5.



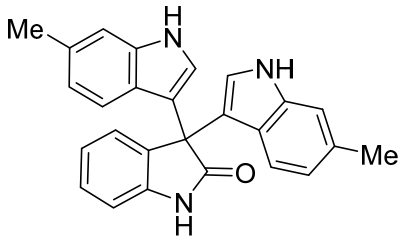
4,4''-Dimethoxy-[3,3':3',3''-terindolin]-2'-one (3v)[7]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1 as a white solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 3.20 (s, 3H, CH), 3.55 (s, 3H, CH), 6.16 - 6.26 (m, 1H, ArH), 6.50 - 6.73 (m, 3H, ArH), 6.81-7.01 (m, 7H, ArH), 7.49 (d, 1H, ArH, *J* = 7.5 Hz), 10.37 (s, 1H, NH), 10.73 (s, 1H, NH), 10.95 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 54.6, 99.5, 100.9, 105.1, 105.5, 108.7, 115.3, 121.0, 121.7, 123.2, 125.1, 126.5, 138.8, 139.5, 142.7, 153.7, 181.9.



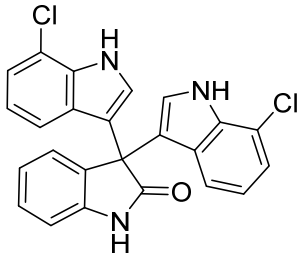
6,6''-Dichloro-[3,3':3',3''-terindolin]-2'-one (3w)[8]

The title compound was obtained as a gray solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.83 (d, 2H, ArH, J = 8.2 Hz), 6.90-7.00 (m, 4H, ArH), 7.18 (d, 2H, ArH, J = 8.4 Hz), 7.21-7.26 (m, 2H, ArH), 7.40 (s, 2H, ArH), 10.66 (s, 1H, NH), 11.12 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 52.7, 110.3, 111.7, 115.0, 119.2, 122.1, 122.4, 124.9, 125.3, 125.8, 126.3, 128.6, 134.5, 137.8, 141.7, 178.8.



6,6''-Dimethyl-[3,3':3',3''-terindolin]-2'-one (3x)[6]

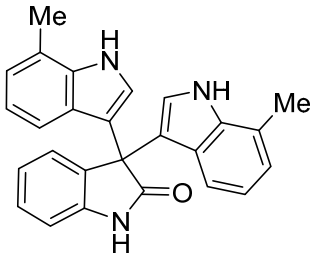
The title compound was obtained as a pink solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 2.32 (s, 6H, CH), 6.61 (dd, 2H, ArH, J_1 = 0.8 Hz, J_2 = 8.2 Hz), 6.74 (d, 2H, ArH, J = 2.4 Hz), 6.90 (t, 1H, ArH, J = 7.5 Hz), 6.96 (d, 1H, ArH, J = 7.6 Hz), 7.07 - 7.12 (m, 4H, ArH), 7.19-7.22 (m, 2H, ArH), 10.54 (s, 1H, NH), 10.76 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 21.7, 110.0, 111.8, 114.7, 120.5, 121.0, 121.8, 123.9, 124.2, 125.3, 128.2, 130.4, 135.2, 137.8, 141.8, 179.2.



7,7''-Dichloro-[3,3':3',3''-terindolin]-2'-one (3y)

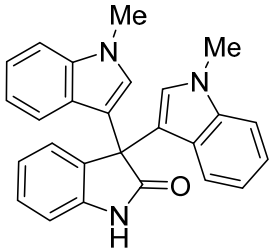
The title compound was isolated as a brown solid. Mp 184-186°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.86 (t, 2H, ArH, J = 8.0 Hz), 6.93 (d, 2H, ArH, J = 4.0 Hz), 6.97 (d, 1H, ArH, J = 8.0 Hz), 7.05 (d, 1H, ArH, J = 8.0 Hz), 7.14 (d, 2H, ArH, J = 8.0 Hz), 7.24-7.29 (m, 4H, ArH), 10.75 (s, 1H, NH), 11.44 (s, 2H, NH). ^{13}C NMR (100MHz,

DMSO-d_6): δ 52.9, 110.4, 116.0, 116.5, 120.0, 120.3, 121.2, 122.2, 125.4, 125.9, 128.1, 128.7, 134.2, 134.3, 141.8, 178.7. HRMS (ESI) m/z calcd for $C_{24}H_{15}Cl_2N_3NaO$ ($[M+Na]^+$): 454.0484; found: 454.0479.



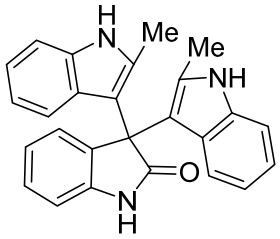
7,7''-Dimethyl-[3,3':3',3''-terindolin]-2'-one (3z)[6]

The title compound was obtained as a brown solid. Mp 228-230°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 2.44 (s, 6H, CH), 6.72 (t, 2H, ArH, J = 7.4 Hz), 6.82 (d, 4H, ArH, J = 8.8 Hz), 6.91 (t, 1H, ArH, J = 7.4 Hz), 6.99 (d, 1H, ArH, J = 7.6 Hz), 7.09 (d, 2H, ArH, J = 8.0 Hz), 7.19 - 7.24 (m, 2H, ArH), 10.60 (s, 1H, NH), 10.93 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 17.3, 26.8, 53.2, 110.0, 115.3, 118.9, 119.0, 121.1, 121.9, 124.5, 125.4, 125.9, 128.3, 135.2, 136.9, 141.8, 179.3.



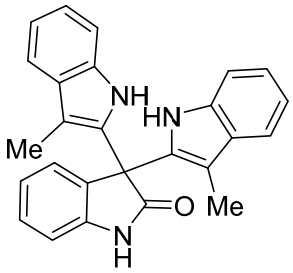
1,1''-Dimethyl-[3,3':3',3''-terindolin]-2'-one (3aa)[9]

The title compound was obtained as a white solid. Mp > 300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.68 (s, 6H, CH_3), 6.83 (t, 2H, ArH, J = 7.6 Hz), 6.88 (s, 2H, ArH), 6.92 (t, 1H, ArH, J = 7.6 Hz), 6.99 (d, 1H, ArH, J = 7.6 Hz), 7.07 (t, 2H, ArH, J = 7.6 Hz), 7.20-7.25 (m, 4H, ArH), 7.36 (d, 2H, ArH, J = 8.8 Hz), 10.63 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 32.3, 52.4, 109.6, 109.7, 113.4, 118.4, 120.9, 121.1, 121.5, 124.9, 126.0, 127.9, 128.4, 134.5, 137.3, 141.2, 178.5.



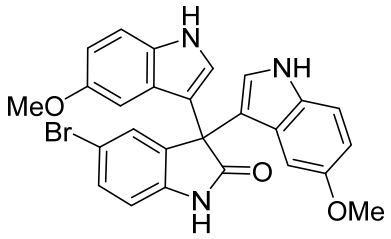
2,2''-Dimethyl-[3,3':3',3''-terindolin]-2'-one (3ab)[1]

The title compound was obtained as a pink solid. Mp 286-287℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.94 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 6.47 (d, 1H, ArH, J = 8.0 Hz), 6.60 (d, 1H, ArH, J = 7.6 Hz), 6.64 (d, 1H, ArH, J = 7.6 Hz), 6.71 (d, 1H, ArH, J = 8.0 Hz), 6.84-6.91 (m, 3H, ArH), 6.95 (d, 1H, ArH, J = 8.0 Hz), 7.16 (d, 1H, ArH, J = 7.2 Hz), 7.20-7.23 (m, 3H, ArH), 10.53 (s, 1H, NH), 10.86 (d, 2H, NH, J = 11.6 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 13.5, 13.7, 52.9, 109.8, 110.8, 110.9, 118.4, 118.4, 119.8, 119.8, 120.1, 120.2, 121.7, 125.9, 127.5, 128.2, 128.3, 132.5, 134.4, 135.4, 135.5, 136.1, 141.7, 179.8.



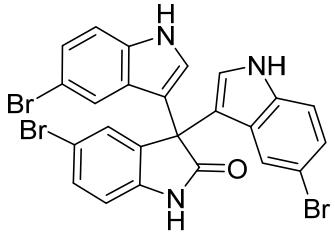
3,3''-Dimethyl-[2,3':3',2''-terindolin]-2'-one (3ac)[10]

The title compound was obtained as a light white solid. Mp >300℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.92 (s, 6H, CH), 6.94 - 7.05 (m, 6H, ArH), 7.25 - 7.42 (m, 6H, ArH), 10.48 (s, 2H, NH), 10.83 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 9.4, 55.1, 107.8, 110.5, 111.9, 118.3, 118.8, 121.4, 122.8, 126.1, 129.2, 129.6, 131.7, 132.2, 135.8, 142.0, 176.4.



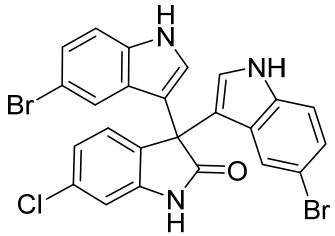
5-Bromo-5,5-dimethoxy-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3ad)[9]

The title compound was obtained as a light yellow solid, Mp 289-291°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.54 (s, 6H, CH_3), 6.67 (s, 2H, ArH), 6.72 (d, 2H, ArH, J = 8.8 Hz), 6.87 (d, 2H, ArH, J = 4.0 Hz), 7.14-7.16 (m, 3H, ArH), 7.27 (d, 2H, ArH, J = 8.8 Hz), 10.77 (s, 1H, NH), 10.87 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 52.7, 55.6, 103.6, 110.9, 112.6, 112.7, 113.4, 120.7, 124.7, 125.7, 126.4, 127.2, 132.7, 134.2, 143.6, 152.9, 179.0.



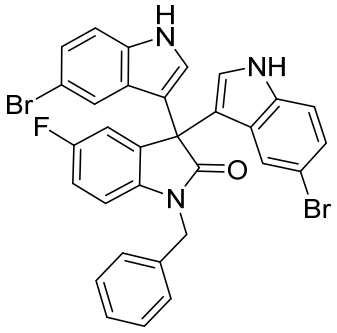
5,5',5''-Tribromo-[3,3':3',3''-terindolin]-2'-one (3ae)[11]

The title compound was obtained as a pink solid. Mp > 300°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.96 (s, 2H, ArH), 7.01 (d, 1H, ArH, J = 8.4 Hz), 7.17 (s, 1H, ArH), 7.19 (s, 1H, ArH), 7.26 (s, 1H, ArH), 7.35 (s, 2H, ArH), 7.38 (s, 1H, ArH), 7.40 (s, 1H, ArH), 7.47 (d, 1H, ArH, J = 8.0 Hz), 10.91 (s, 1H, NH), 11.29 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 52.9, 111.7, 112.4, 113.5, 114.0, 114.5, 122.9, 124.3, 126.7, 127.5, 128.0, 131.6, 136.2, 136.4, 141.1, 178.5.



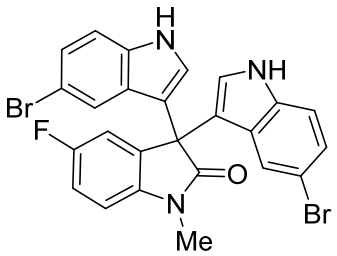
5,5-Dibromo-6-chloro-1H,1H-[3,3:3,3-terindol]-2(1H)-one (3af)

The title compound was obtained as a yellow solid. Mp 288-290°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 6.94 (s, 2H, ArH), 7.05 (s, 2H, ArH), 7.17 (d, 3H, ArH, *J* = 7.2 Hz), 7.36 (s, 4H, ArH), 10.91 (s, 1H, NH), 11.29 (s, 2H, NH). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 51.8, 109.9, 111.1, 113.9, 121.6, 122.4, 123.7, 126.0, 126.3, 127.1, 132.4, 132.4, 135.7, 142.6, 178.3. HRMS (ESI) m/z calcd for $C_{24}H_{14}Br_2ClN_3NaO$ ([M+Na]$^+$): 575.9084; found: 575.9081.



1'-Benzyl-5,5''-dibromo-5'-fluoro-[3,3':3',3''-terindolin]-2'-one (3ag)

The title compound was obtained as a yellow solid. Mp >300°C. ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ 5.02 (s, 2H, CH_2), 7.02-7.18 (m, 9H, ArH), 7.27-7.44 (m, 7H, ArH), 11.33 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 43.7, 52.7, 111.1, 112.9, 113.4, 114.0, 115.1, 120.0, 121.8, 123.7, 126.8, 126.9, 127.9, 128.1, 129.2, 134.9, 136.0, 136.8, 138.4, 158.9 (d, $^{1}J_{CF}$ = 237.7 Hz, C-F), 177.0. HRMS (ESI) m/z calcd for $C_{31}H_{20}Br_2FN_3NaO$ ([M+Na]$^+$): 649.9849; found: 649.9849.



5,5''-Dibromo-5'-fluoro-1'-methyl-[3,3':3',3''-terindolin]-2'-one (3ah)

The title compound was obtained as a white solid. Mp >300°C. ^{1}H NMR (400MHz,

DMSO-*d*$_6$): δ 3.28 (s, 3H, CH_3), 7.00-7.38 (m, 11H, ArH), 11.32 (s, 2H, NH). ^{13}C NMR (100MHz, DMSO-*d*$_6$): δ 27.0, 52.6, 110.4, 111.7, 113.4, 114.4, 115.3, 123.0, 124.3, 126.6, 127.5, 134.8, 134.9, 136.2, 139.3, 158.9 (d, $^1J_{CF}$ = 236.9 Hz, C-F), 176.8. HRMS (ESI) m/z calcd for $C_{25}H_{16}Br_2FN_3NaO$ ($[M+Na]^+$): 573.9536; found: 573.9531.

4. References

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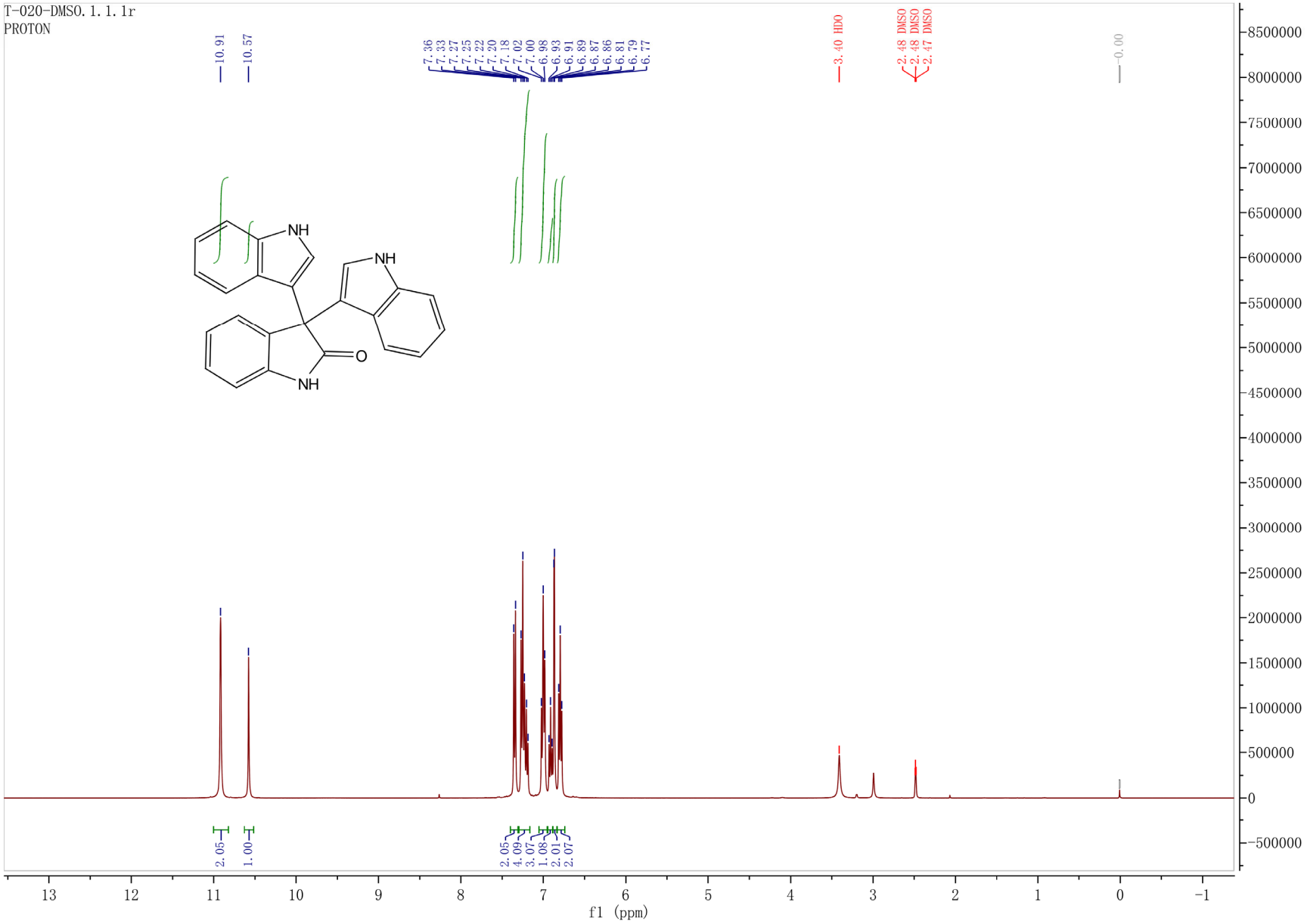
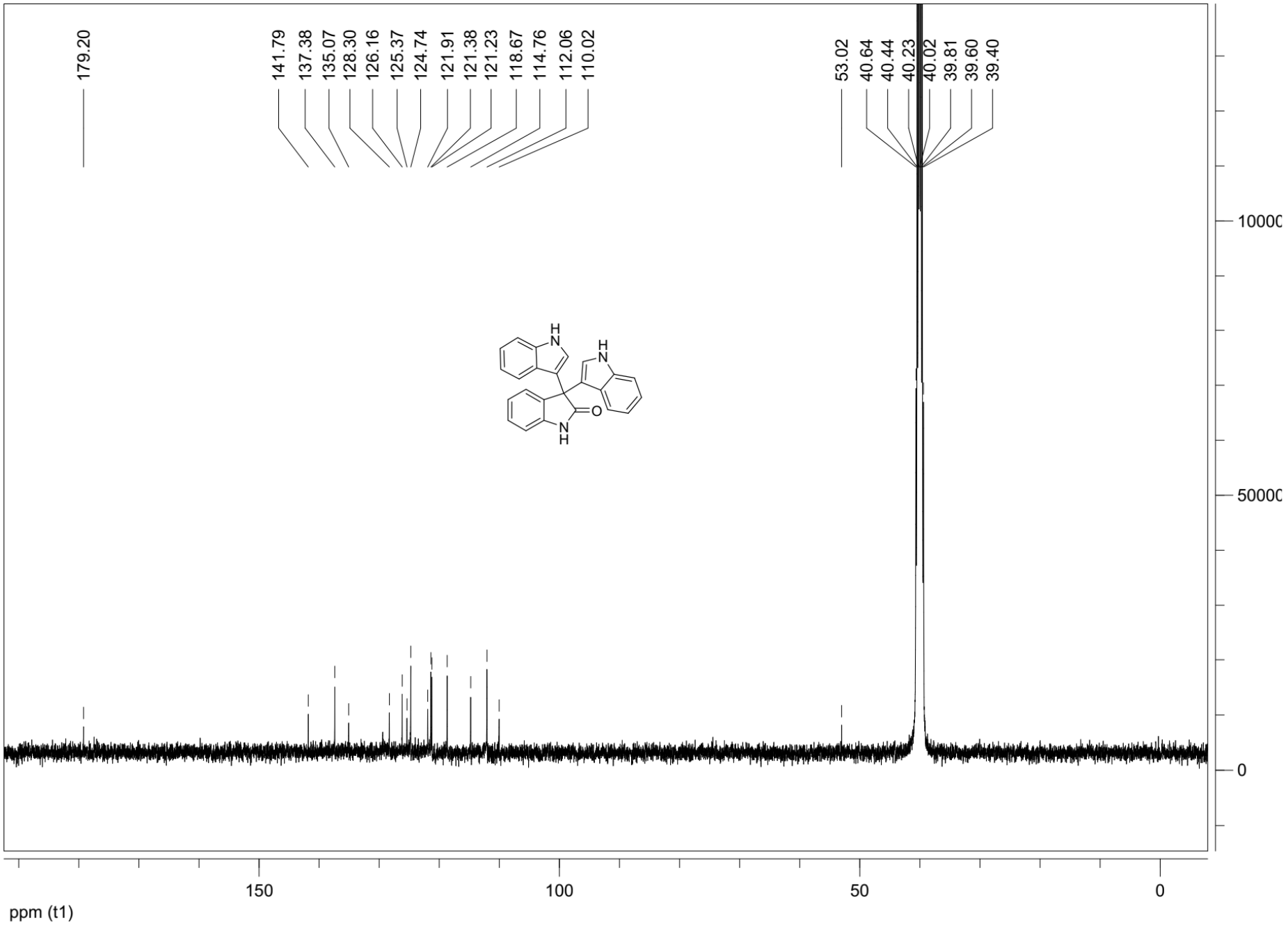
5. Spectroscopic data for compounds 3a-3ah

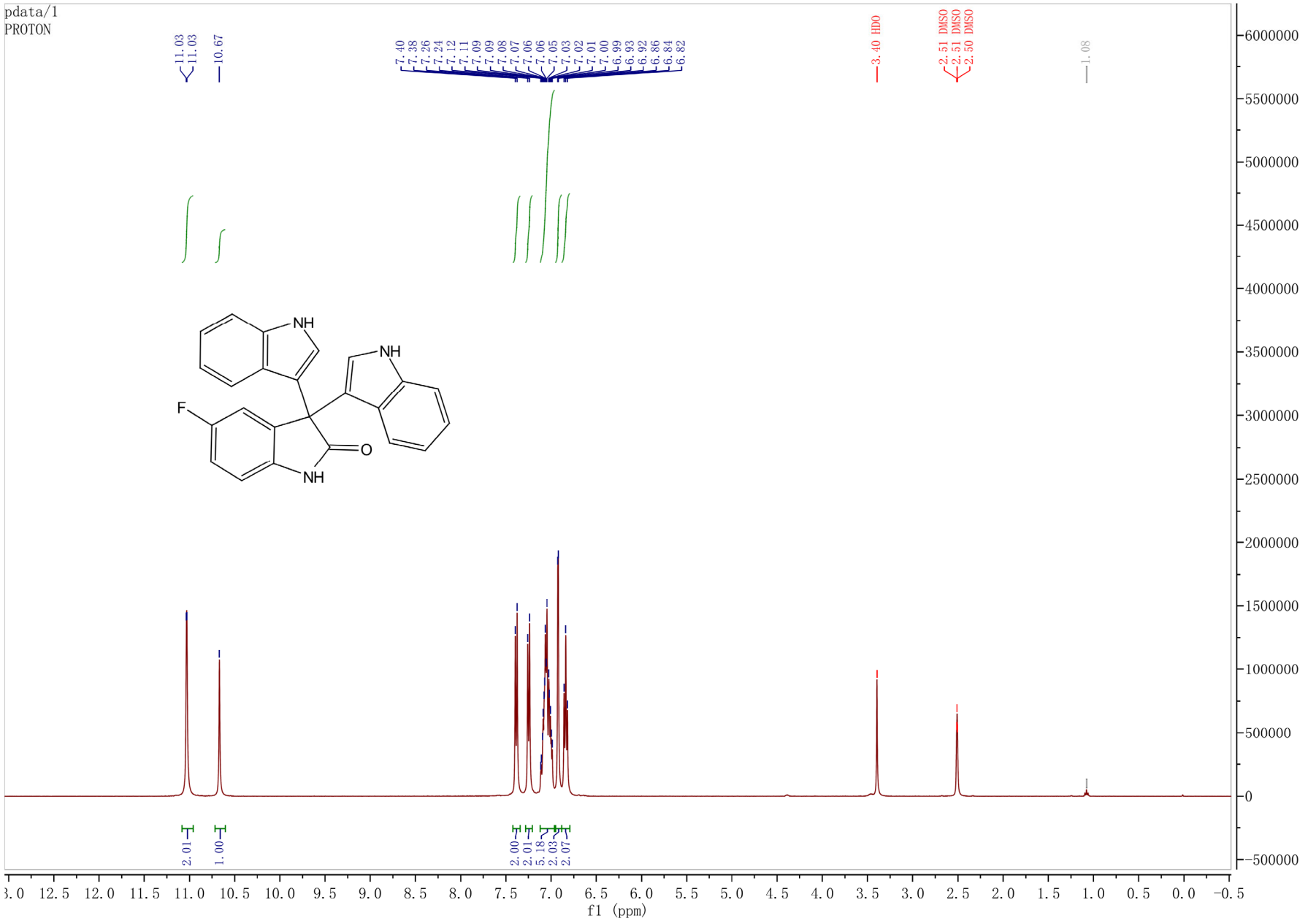
^{1}H NMR spectrum of Compound 3a (DMSO-d_6, 400 MHz)



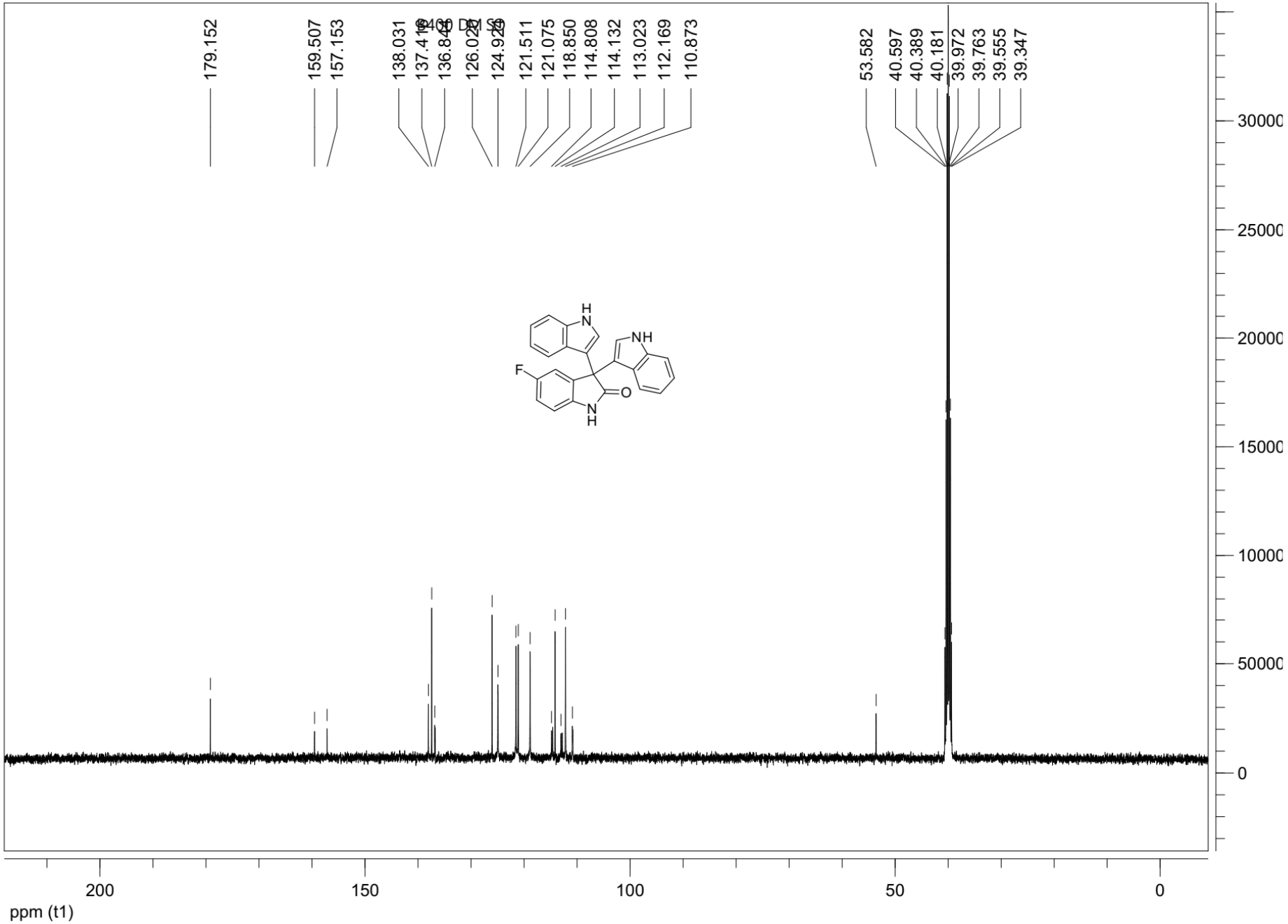
^{13}C NMR spectrum of Compound 3a (DMSO-d_6, 100 MHz)



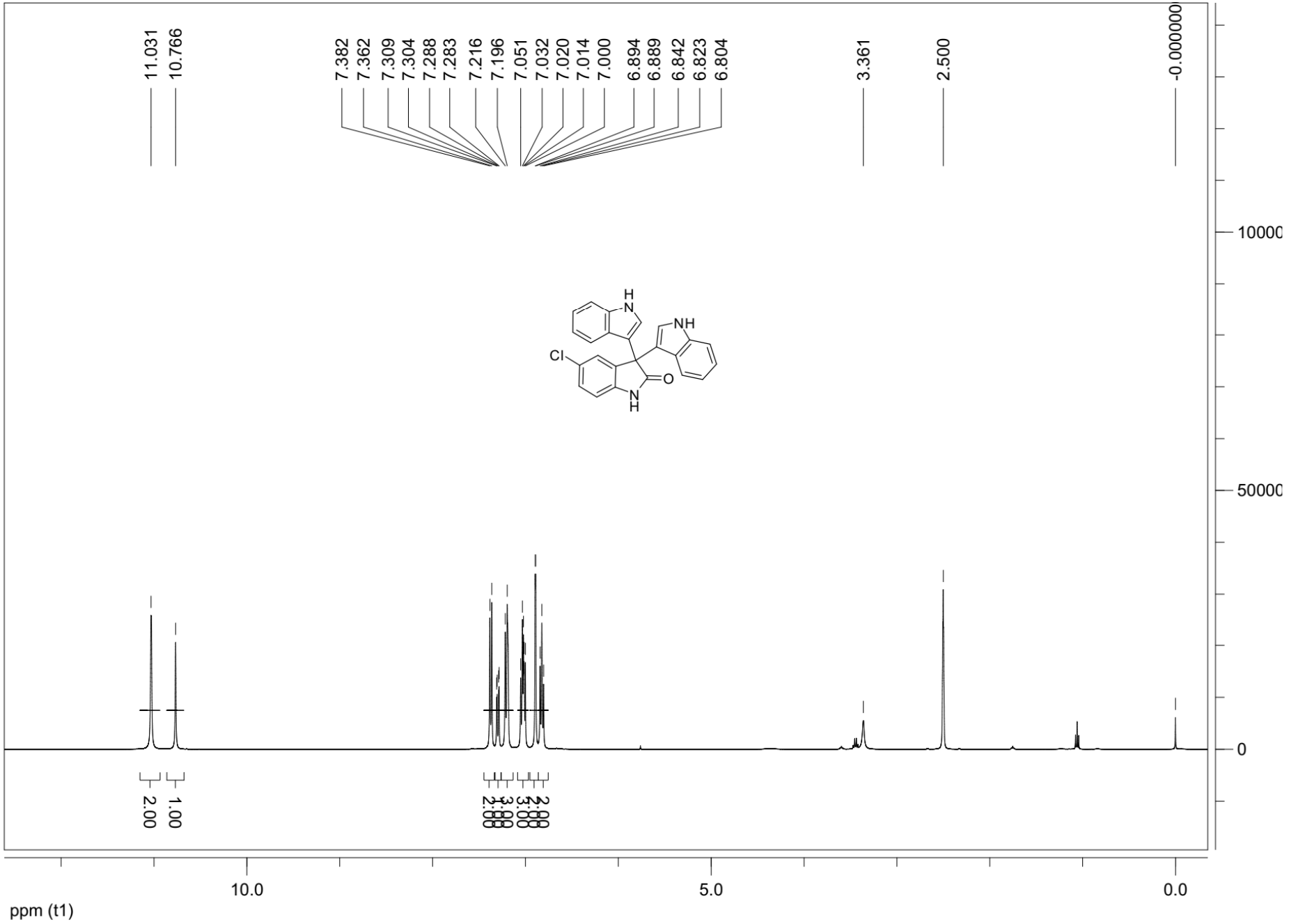
^{1}H NMR spectrum of Compound 3b (DMSO-d_6, 400 MHz)



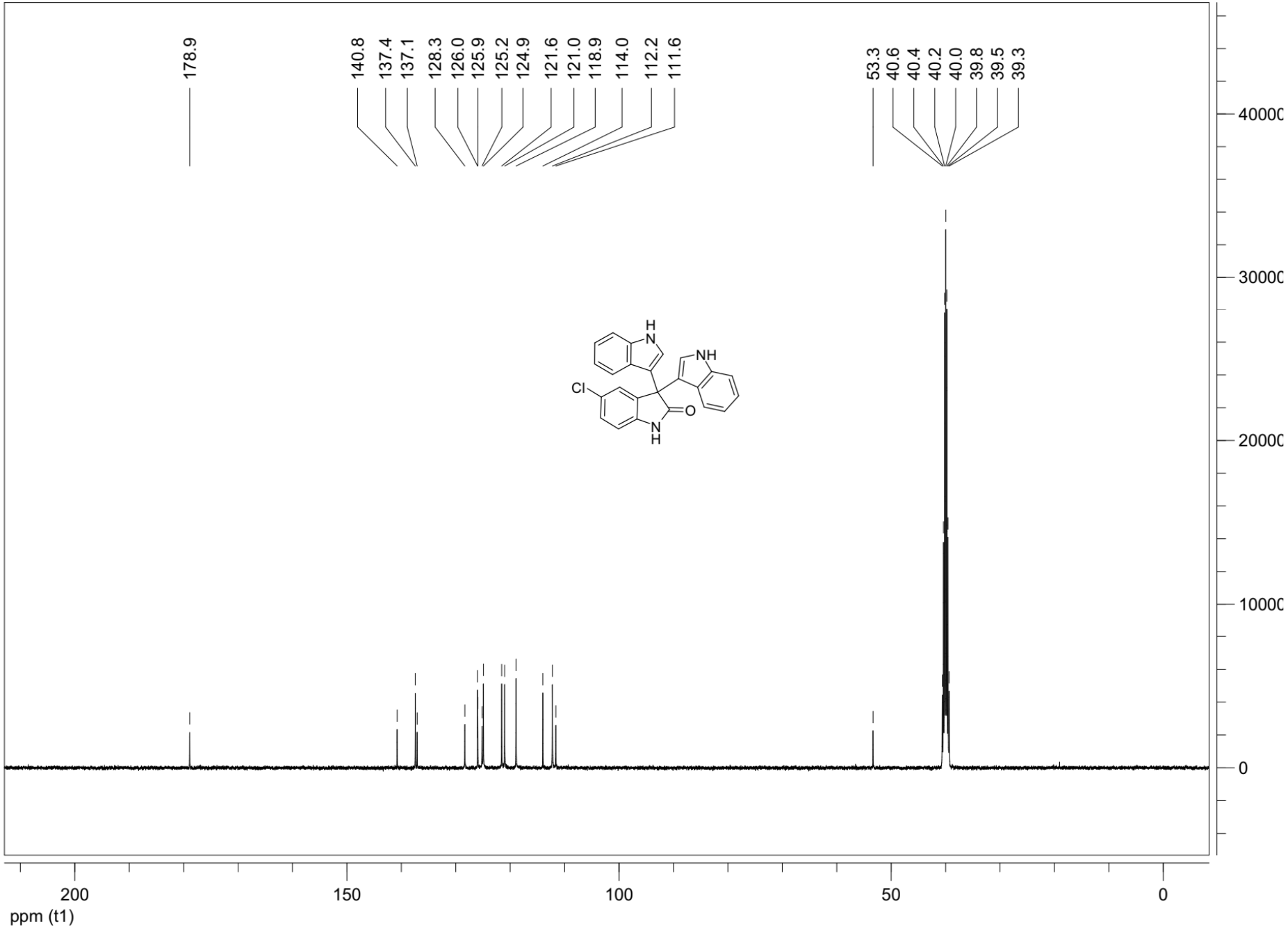
^{13}C NMR spectrum of Compound 3b (DMSO-d_6, 100 MHz)



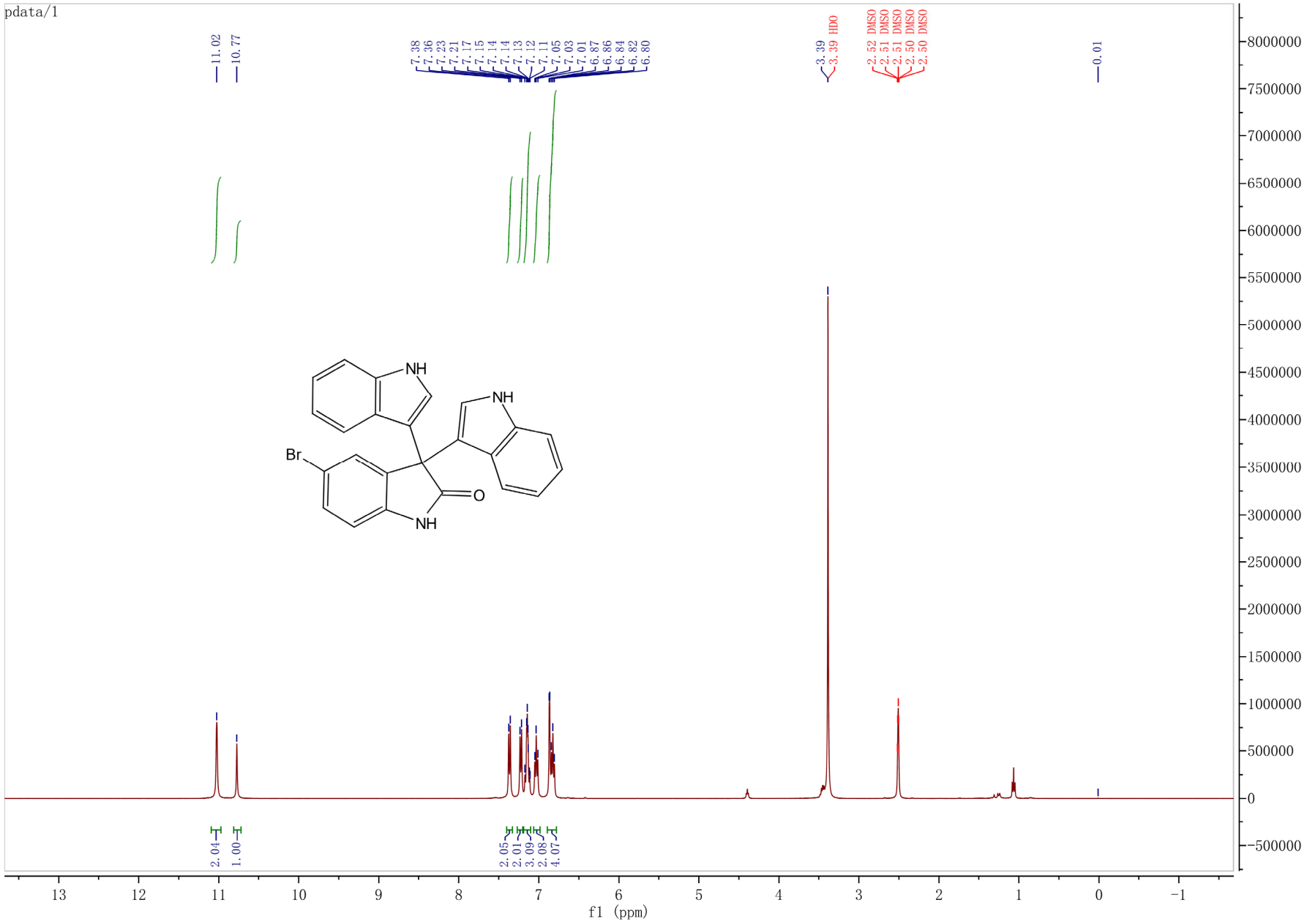
^{1}H NMR spectrum of Compound 3c (DMSO-d_6, 400 MHz)



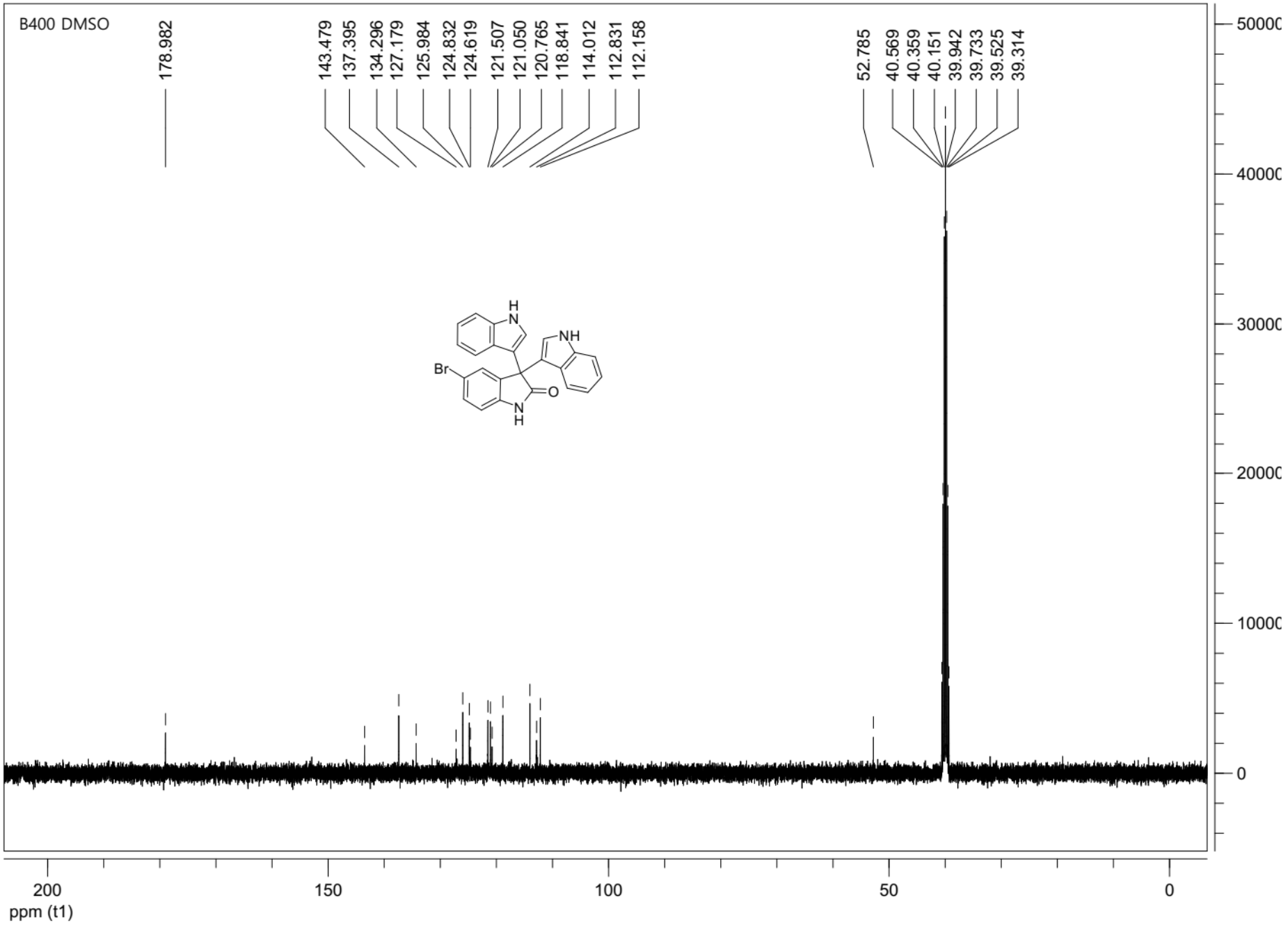
^{13}C NMR spectrum of Compound 3c (DMSO-d_6, 100 MHz)



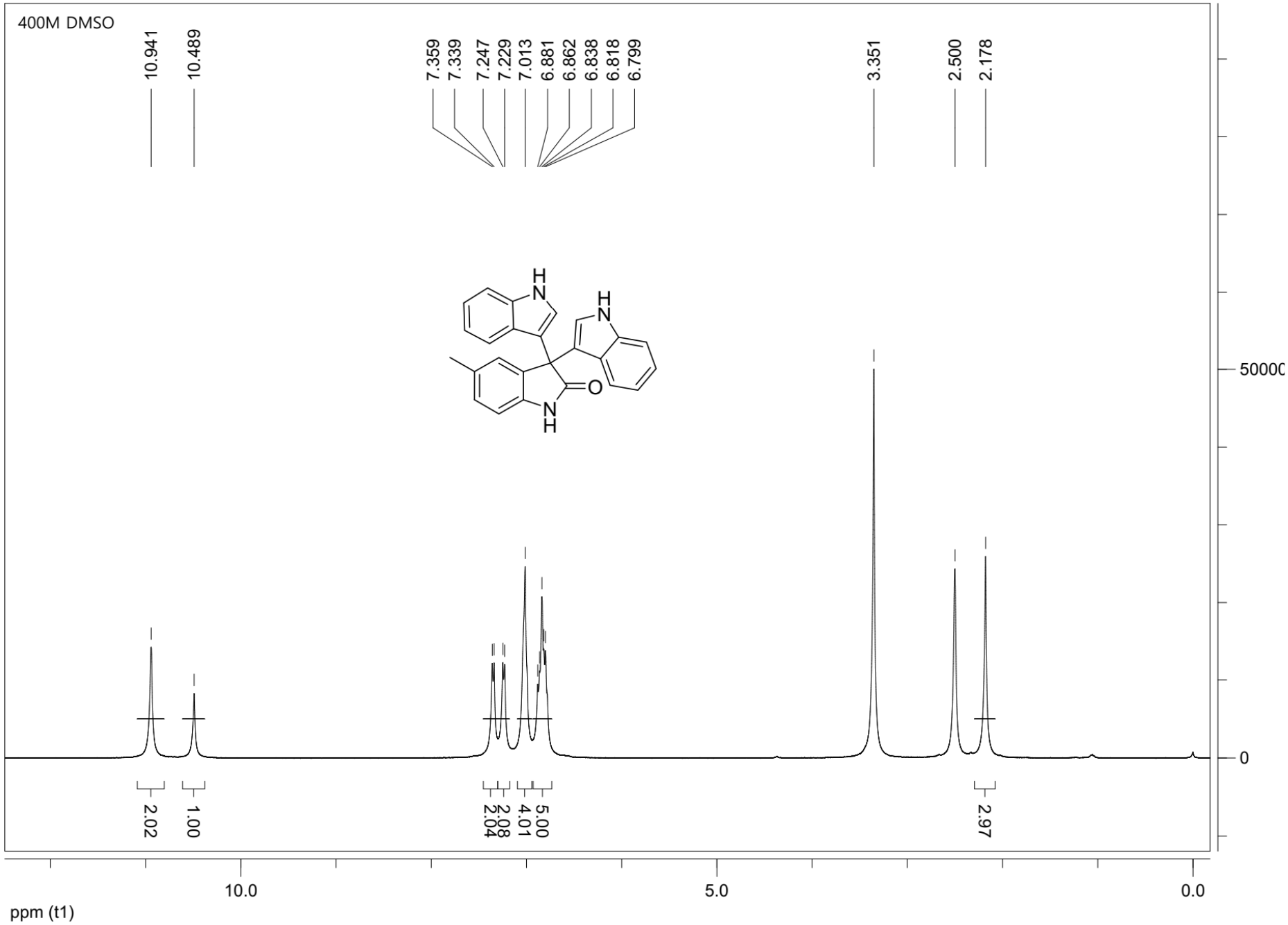
^{1}H NMR spectrum of Compound 3d (DMSO-d_6, 400 MHz)



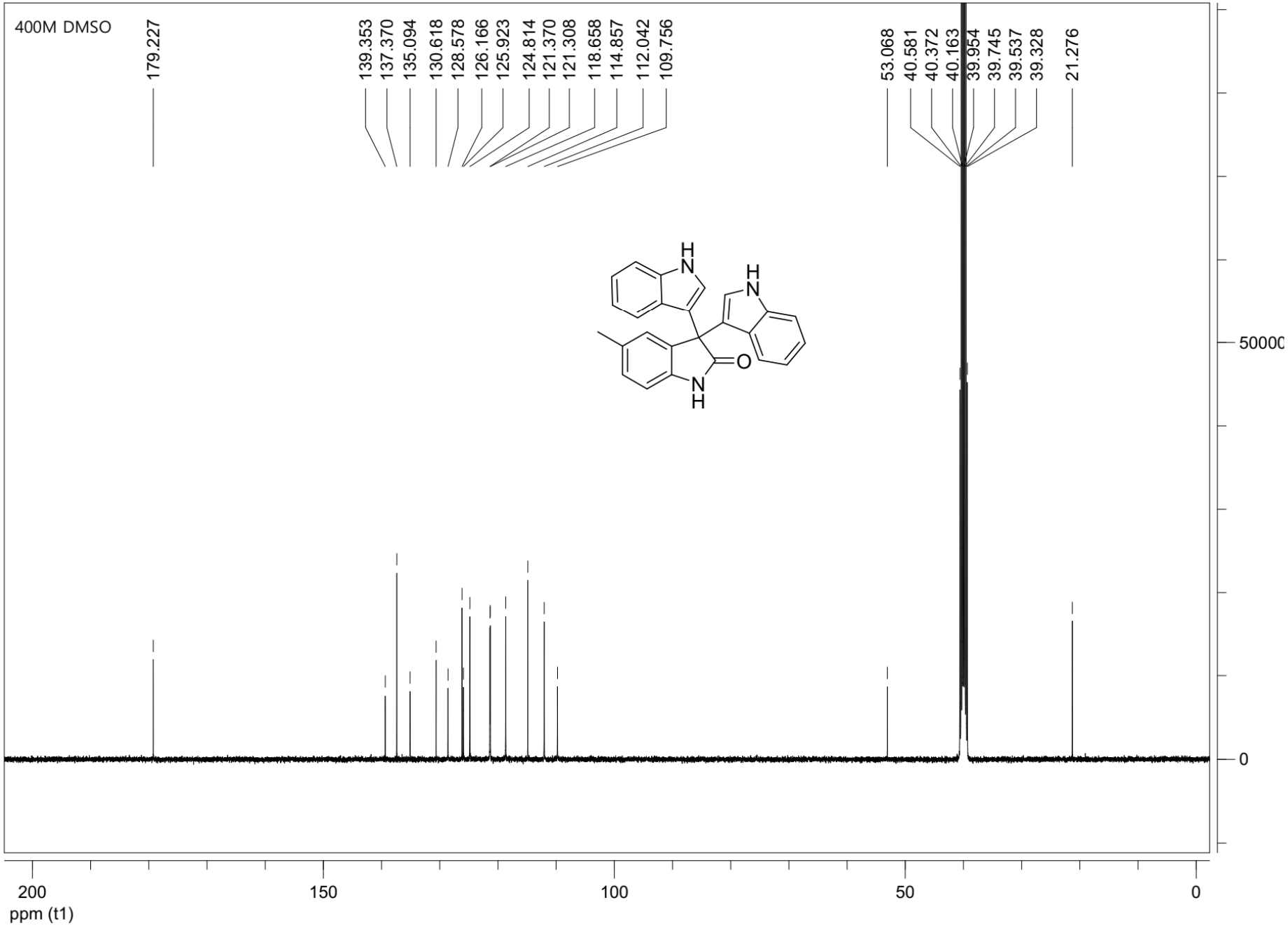
^{13}C NMR spectrum of Compound 3d (DMSO-d_6, 100 MHz)



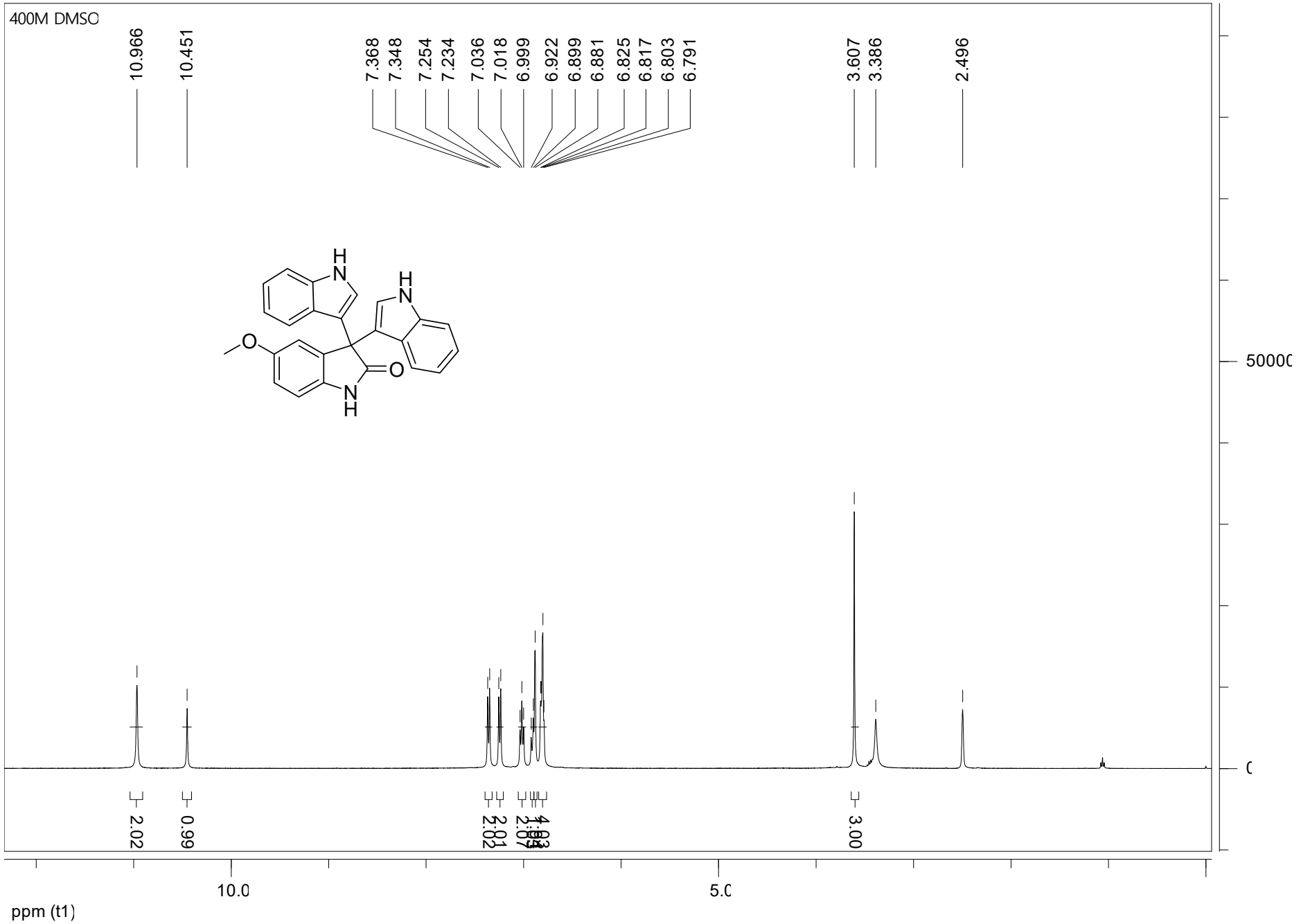
^{1}H NMR spectrum of Compound 3e (DMSO-d_6, 400 MHz)



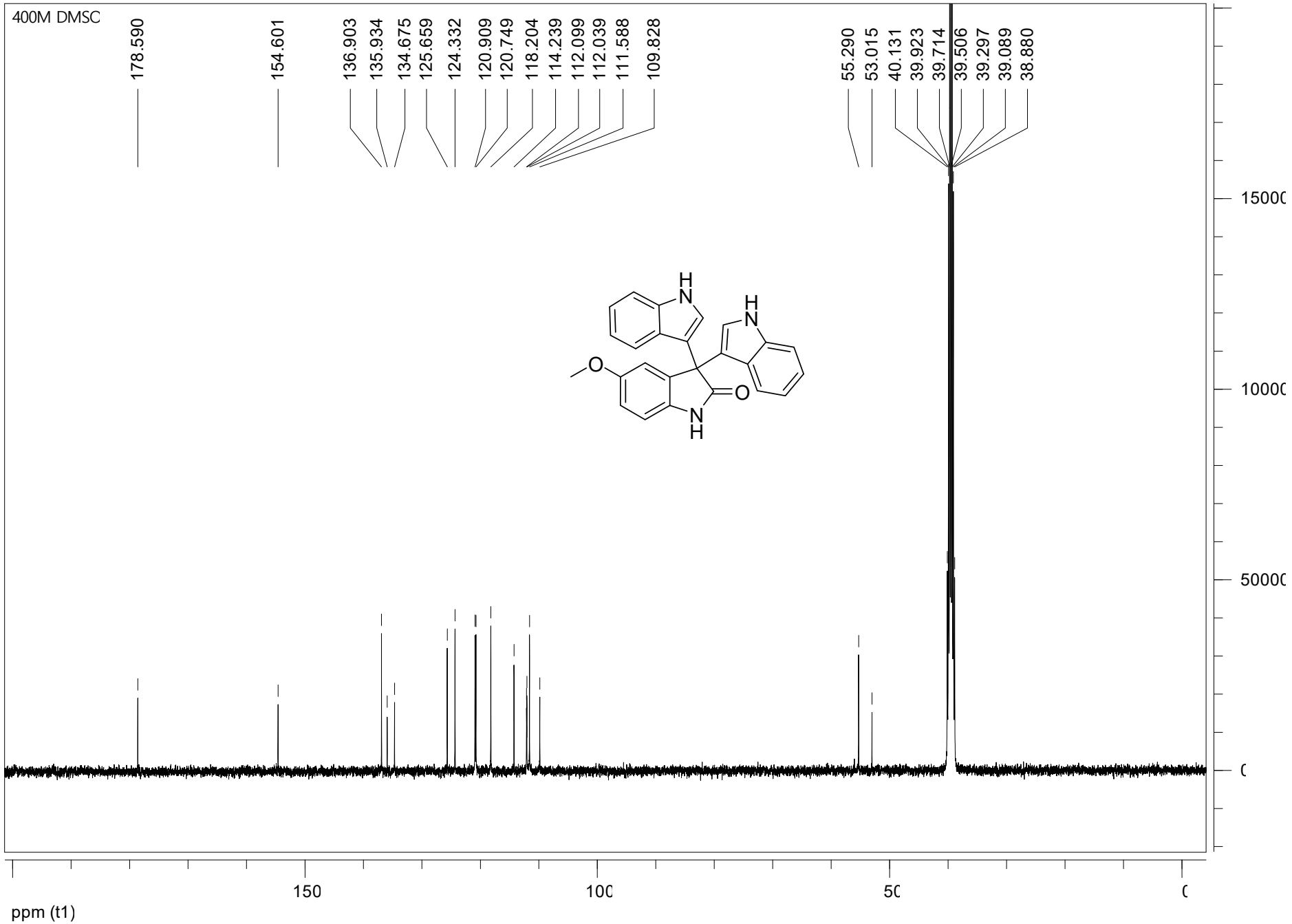
^{13}C NMR spectrum of Compound 3e (DMSO-d_6, 100 MHz)



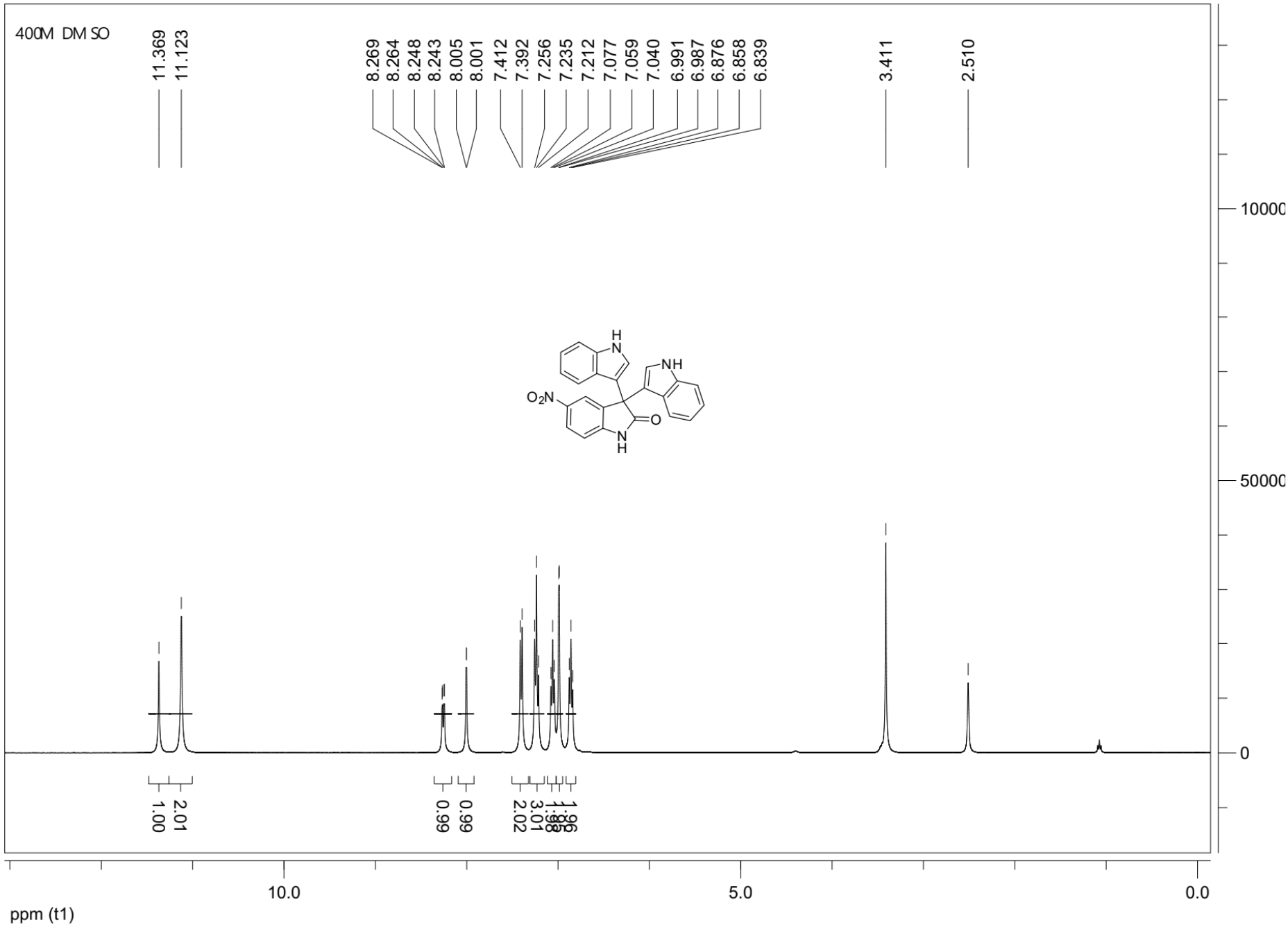
^{1}H NMR spectrum of Compound 3f (DMSO-d_6, 400 MHz)



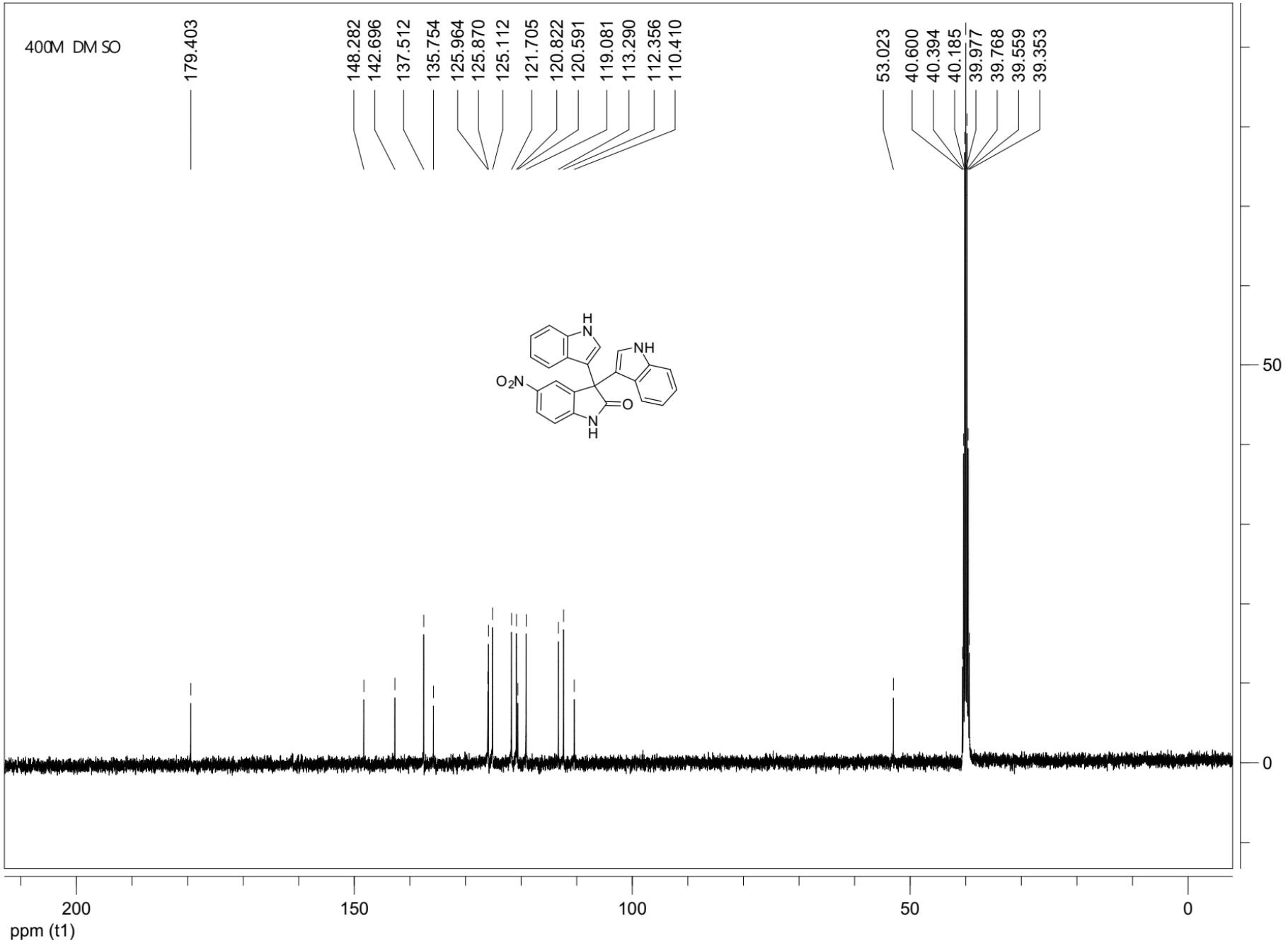
^{13}C NMR spectrum of Compound 3f (DMSO-d_6, 100 MHz)



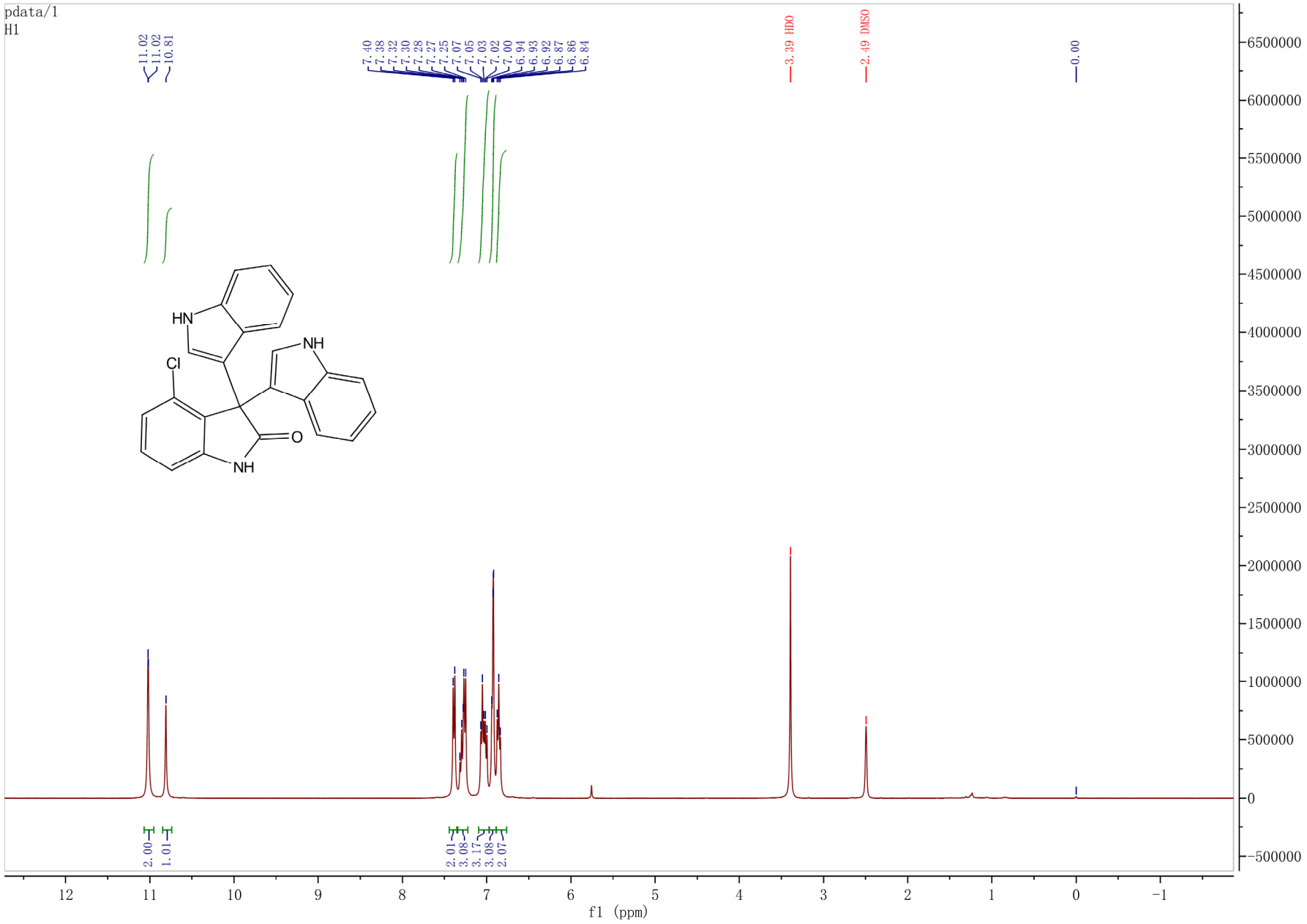
^{1}H NMR spectrum of Compound 3g (DMSO-d_6, 400 MHz)



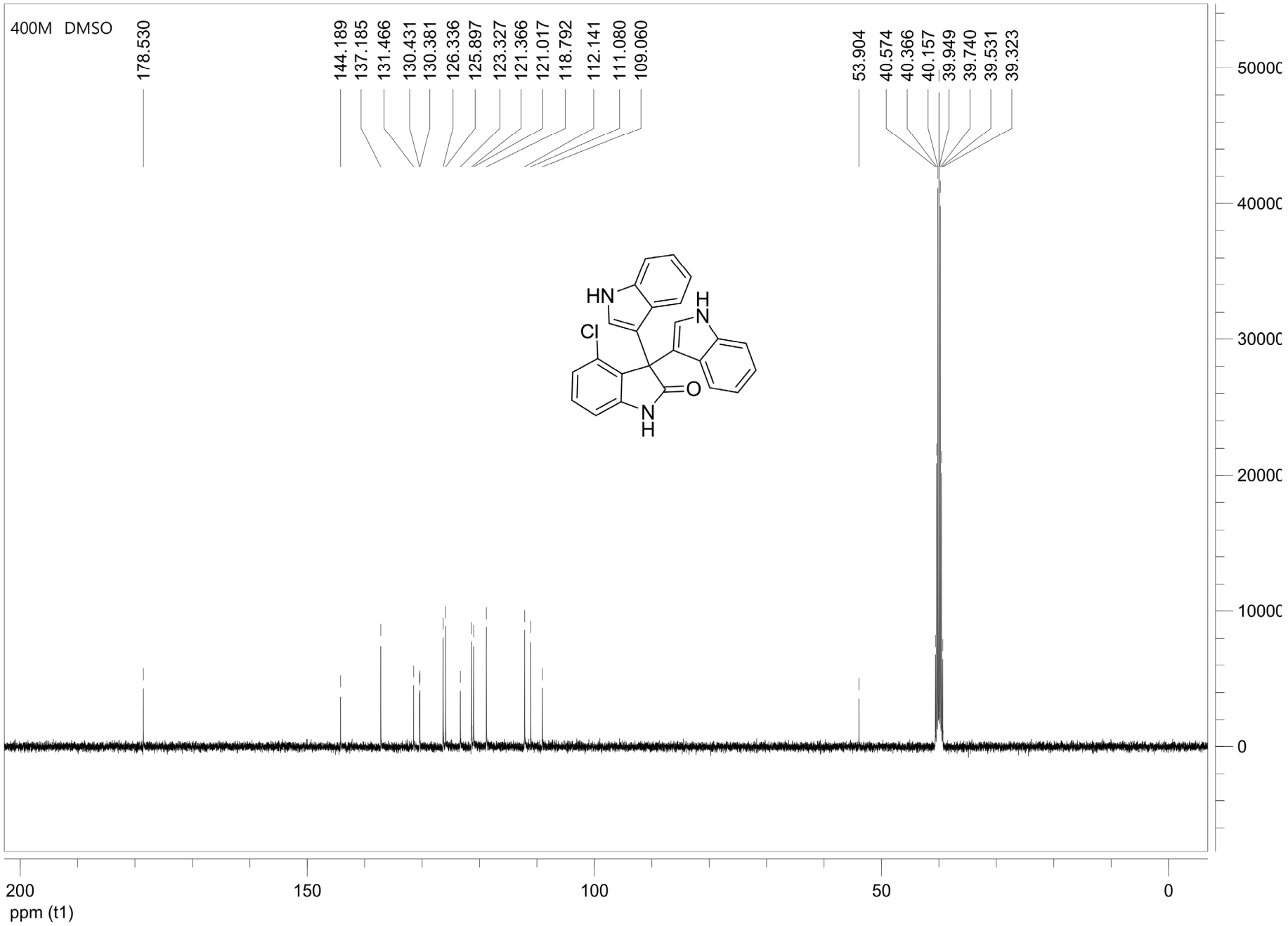
^{13}C NMR spectrum of Compound 3g (DMSO-d_6, 100 MHz)



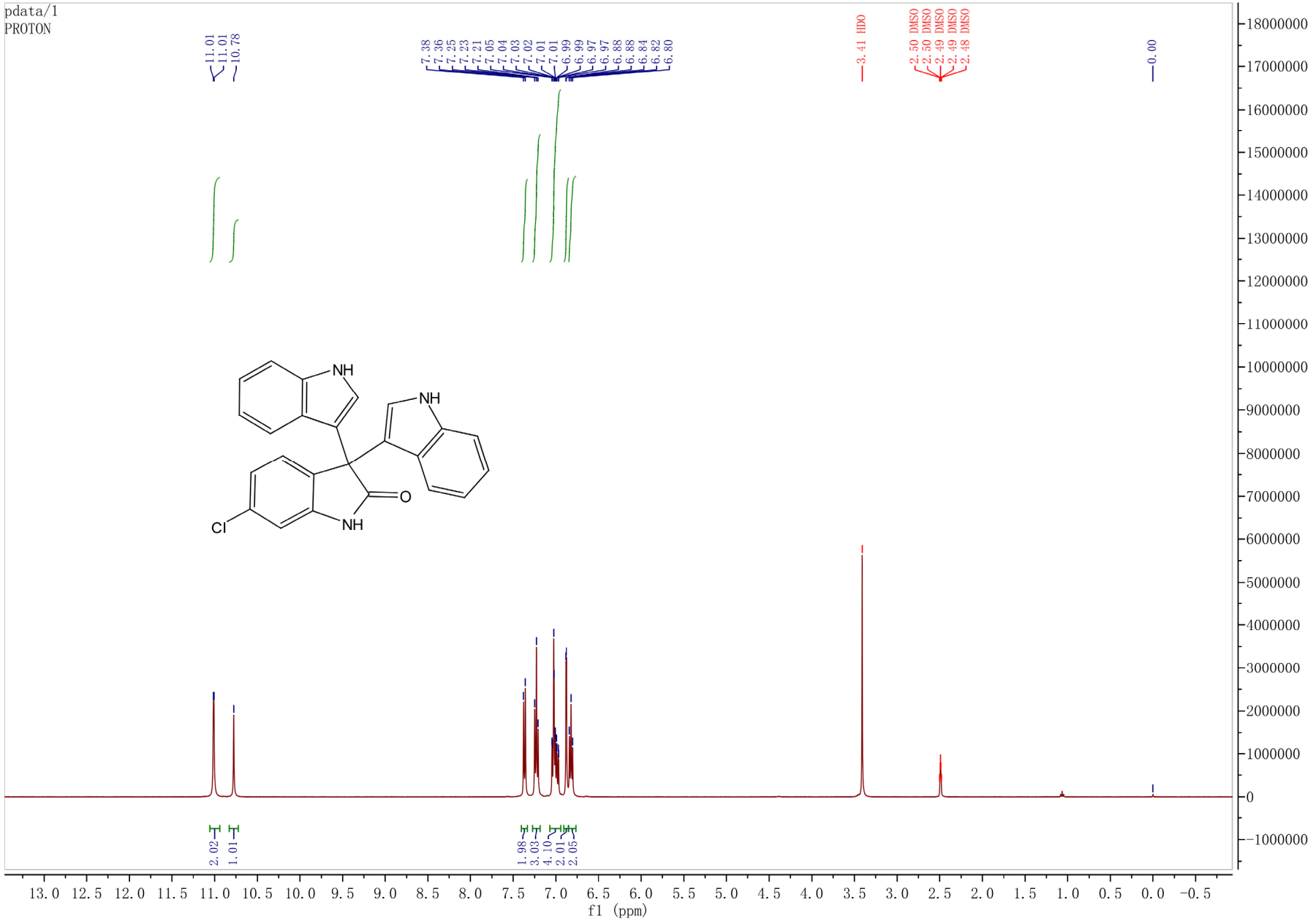
^{1}H NMR spectrum of Compound 3h (DMSO-d_6, 400 MHz)



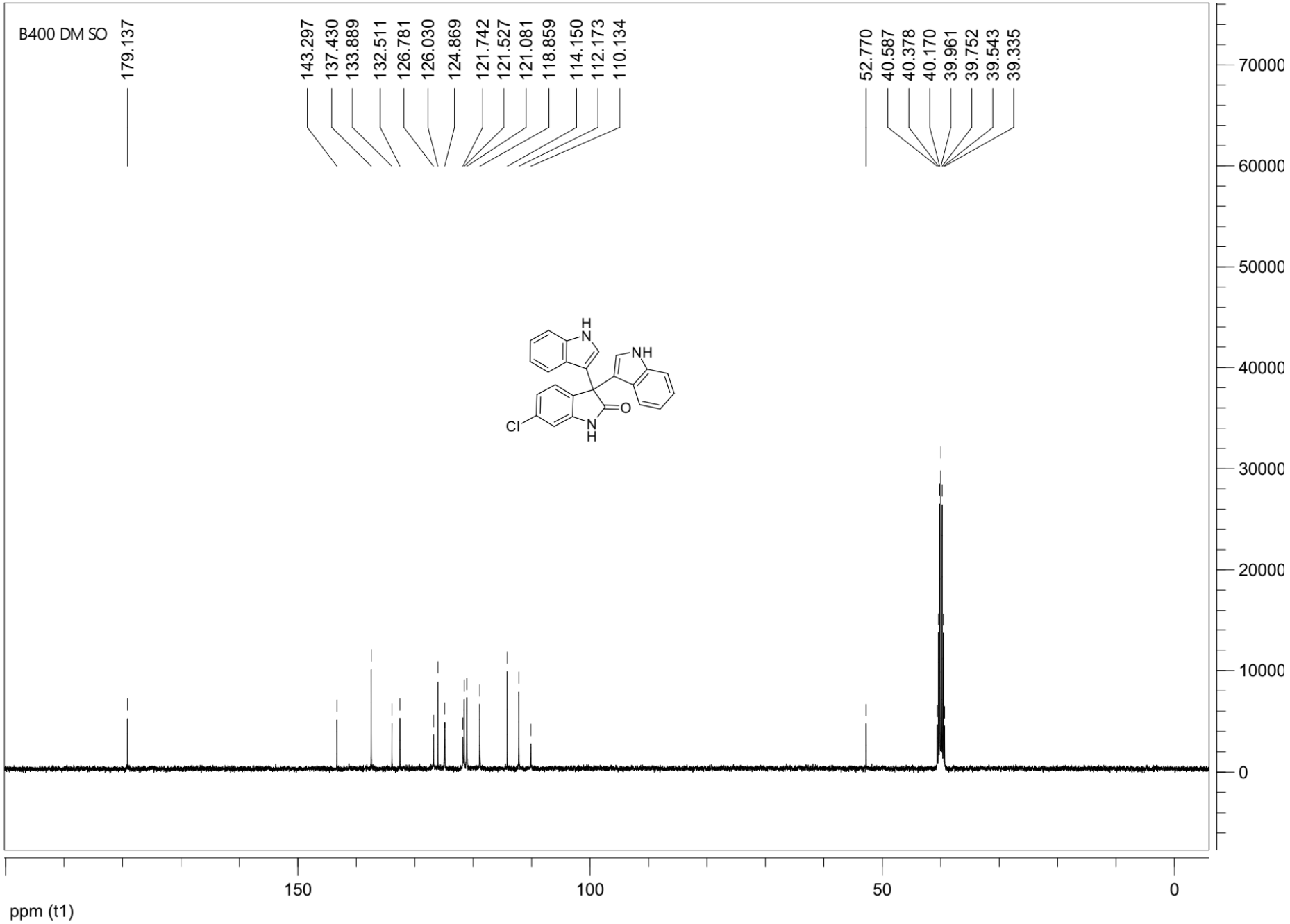
^{13}C NMR spectrum of Compound 3h (DMSO-d_6, 100 MHz)



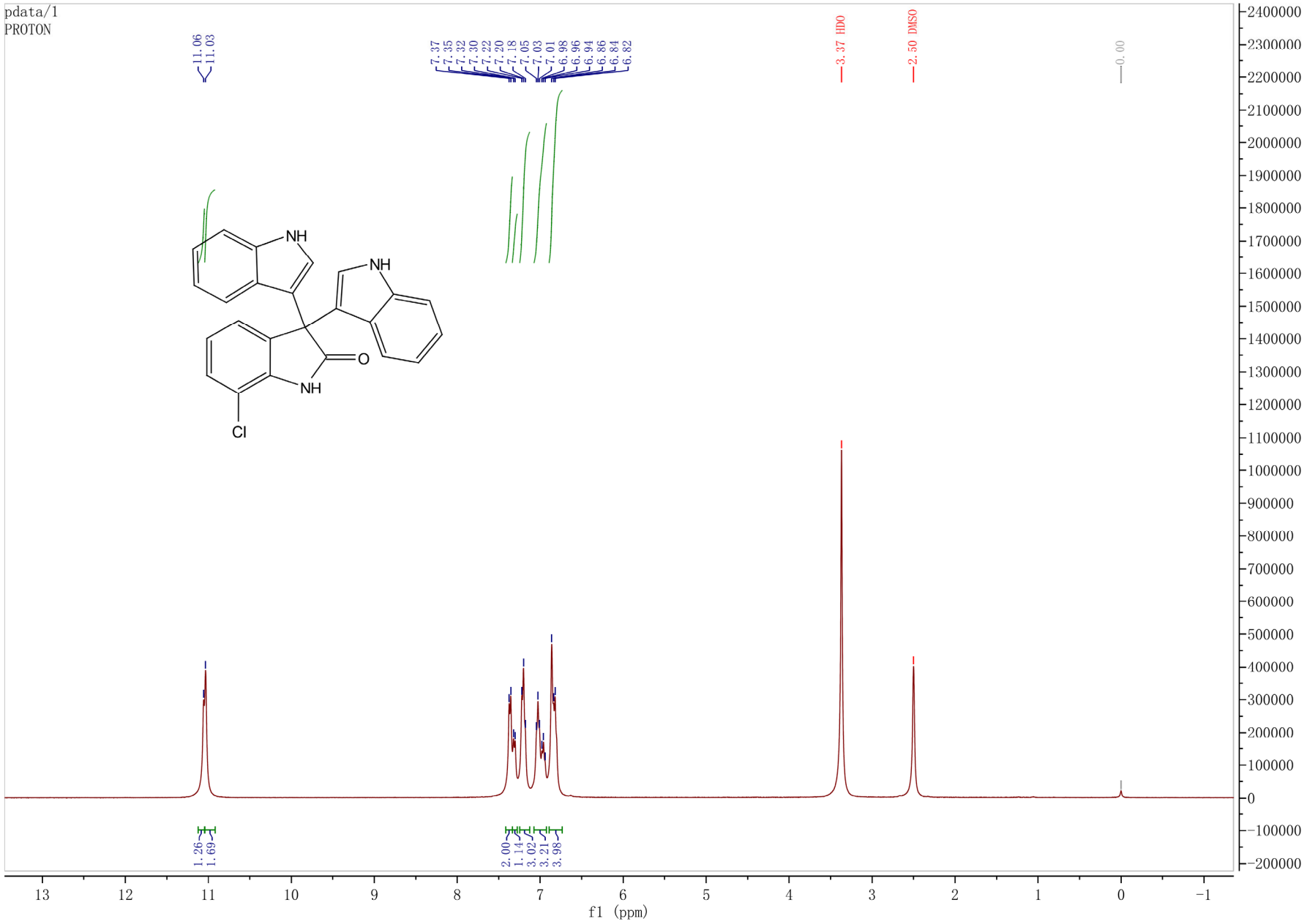
^{1}H NMR spectrum of Compound 3i (DMSO-d_6, 400 MHz)



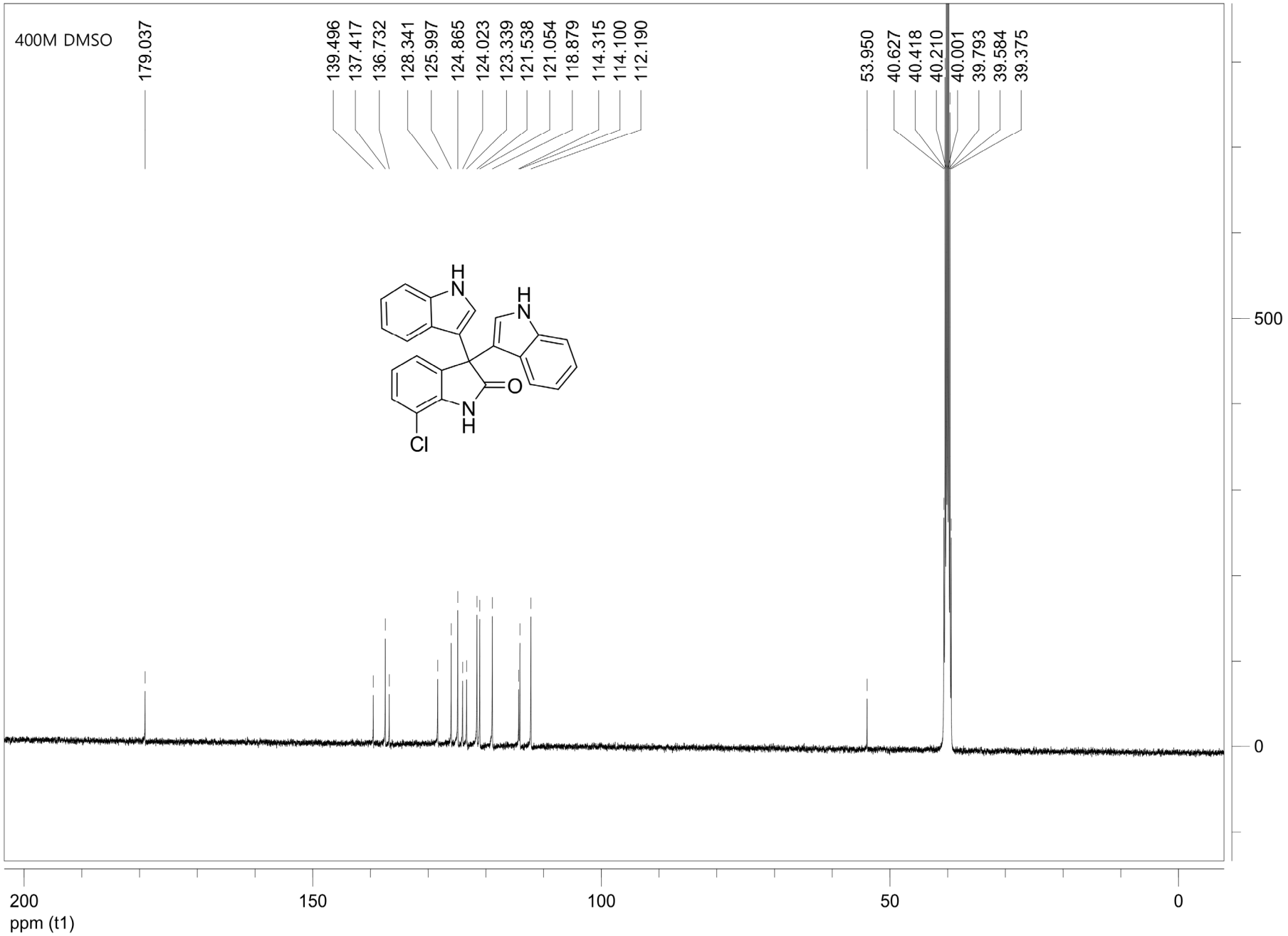
^{13}C NMR spectrum of Compound 3i (DMSO-d_6, 100 MHz)



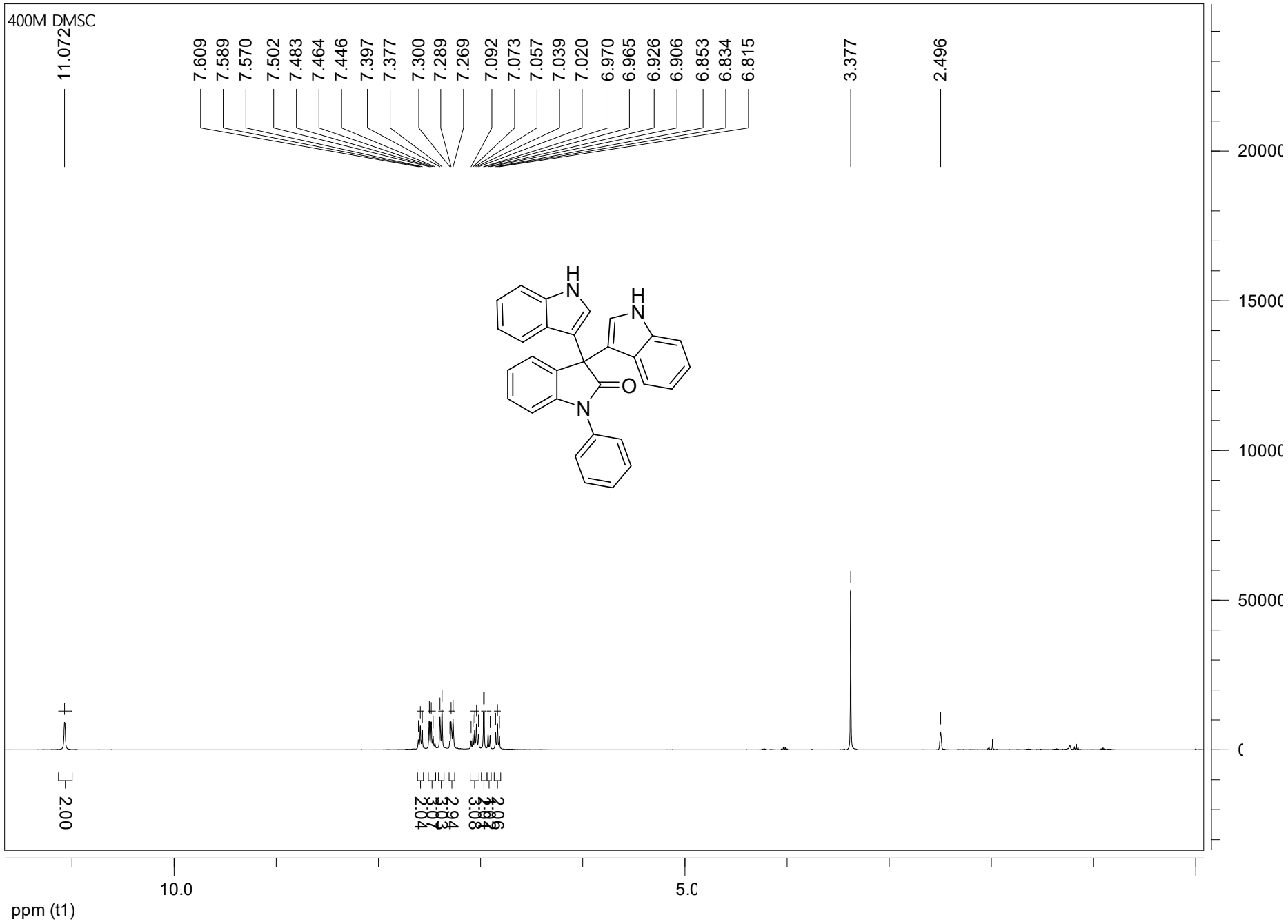
^{1}H NMR spectrum of Compound 3j (DMSO-d_6, 400 MHz)



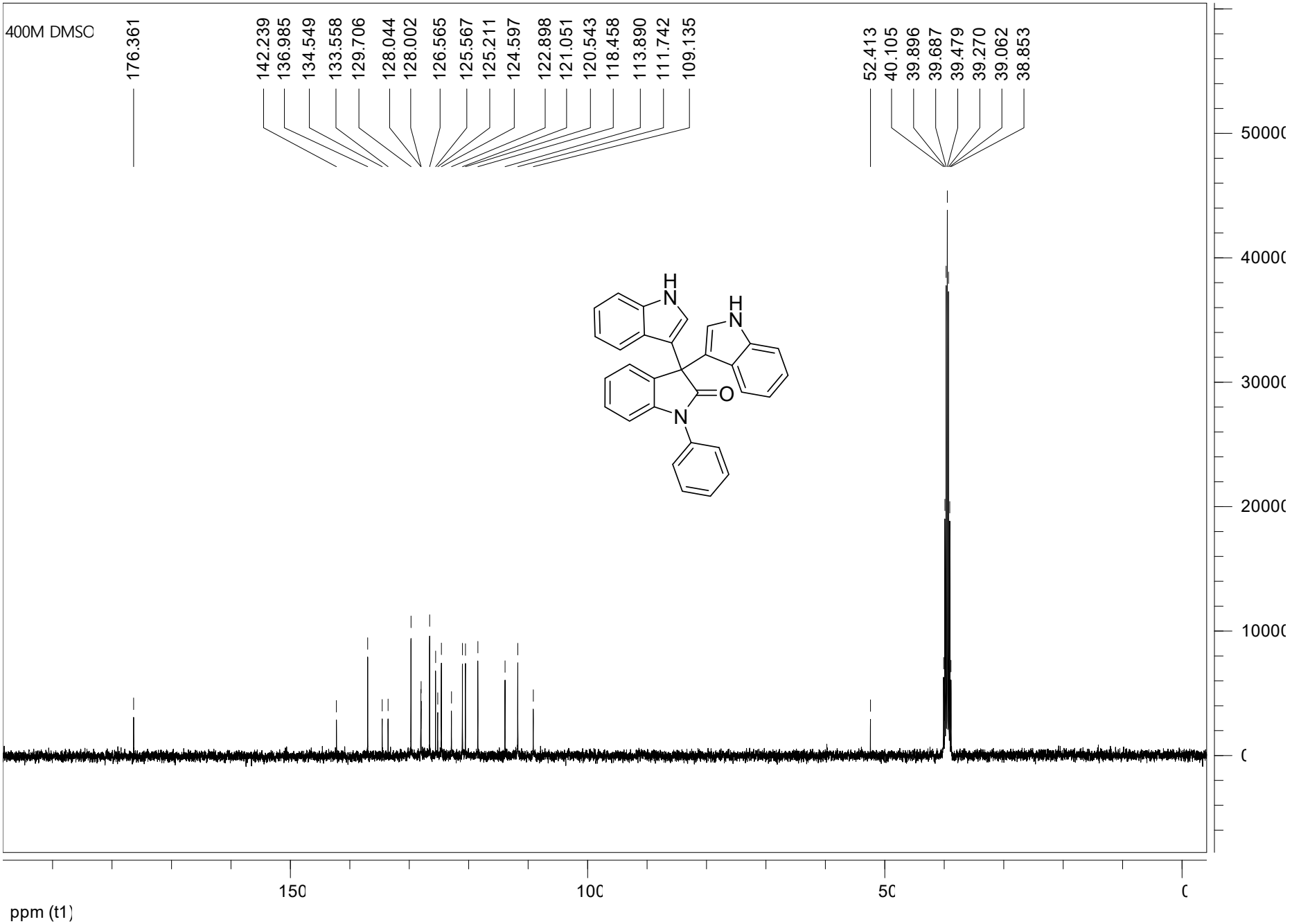
^{13}C NMR spectrum of Compound 3j (DMSO-d_6, 100 MHz)



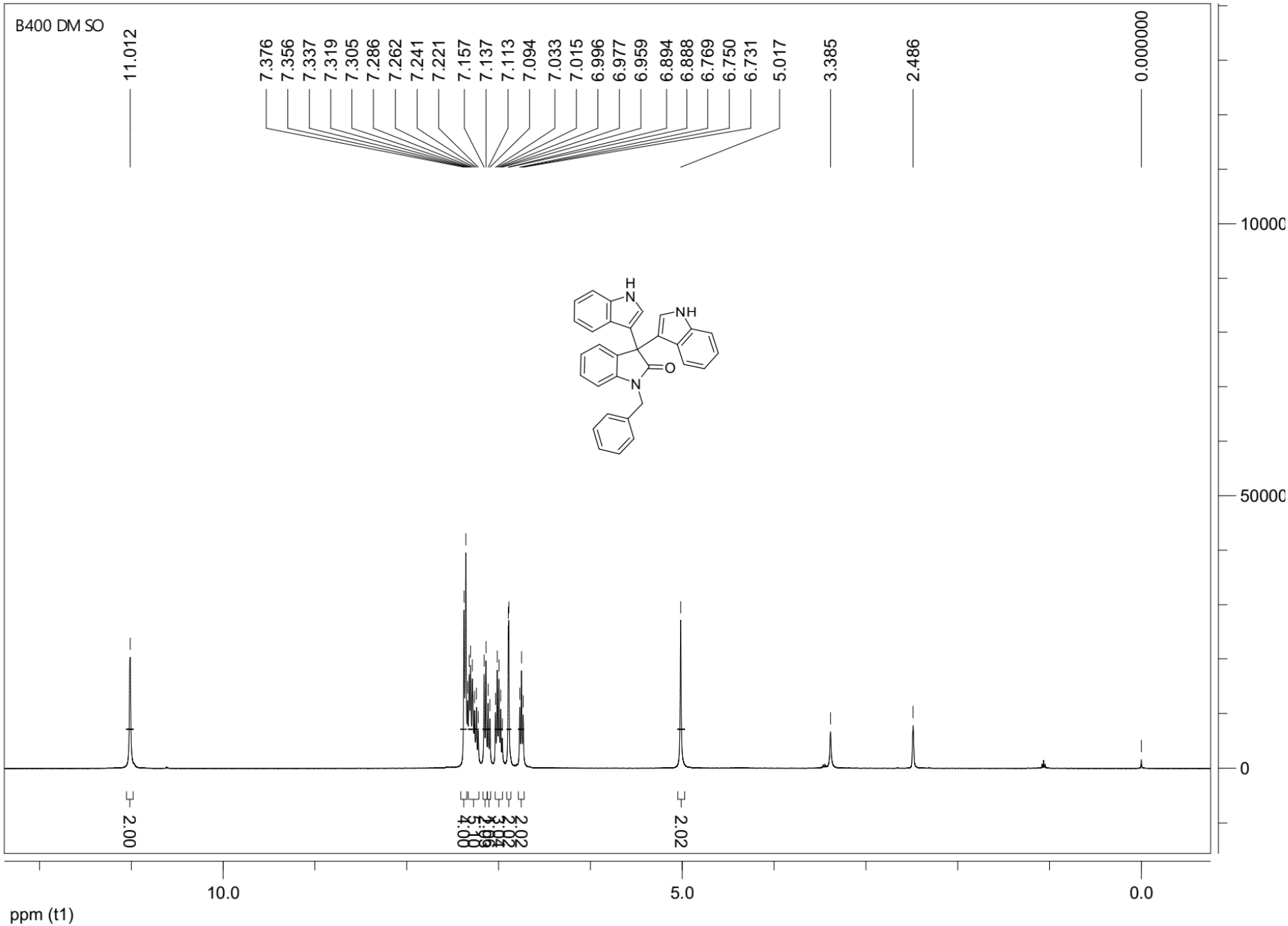
^{1}H NMR spectrum of Compound 3k (DMSO-d_6, 400 MHz)



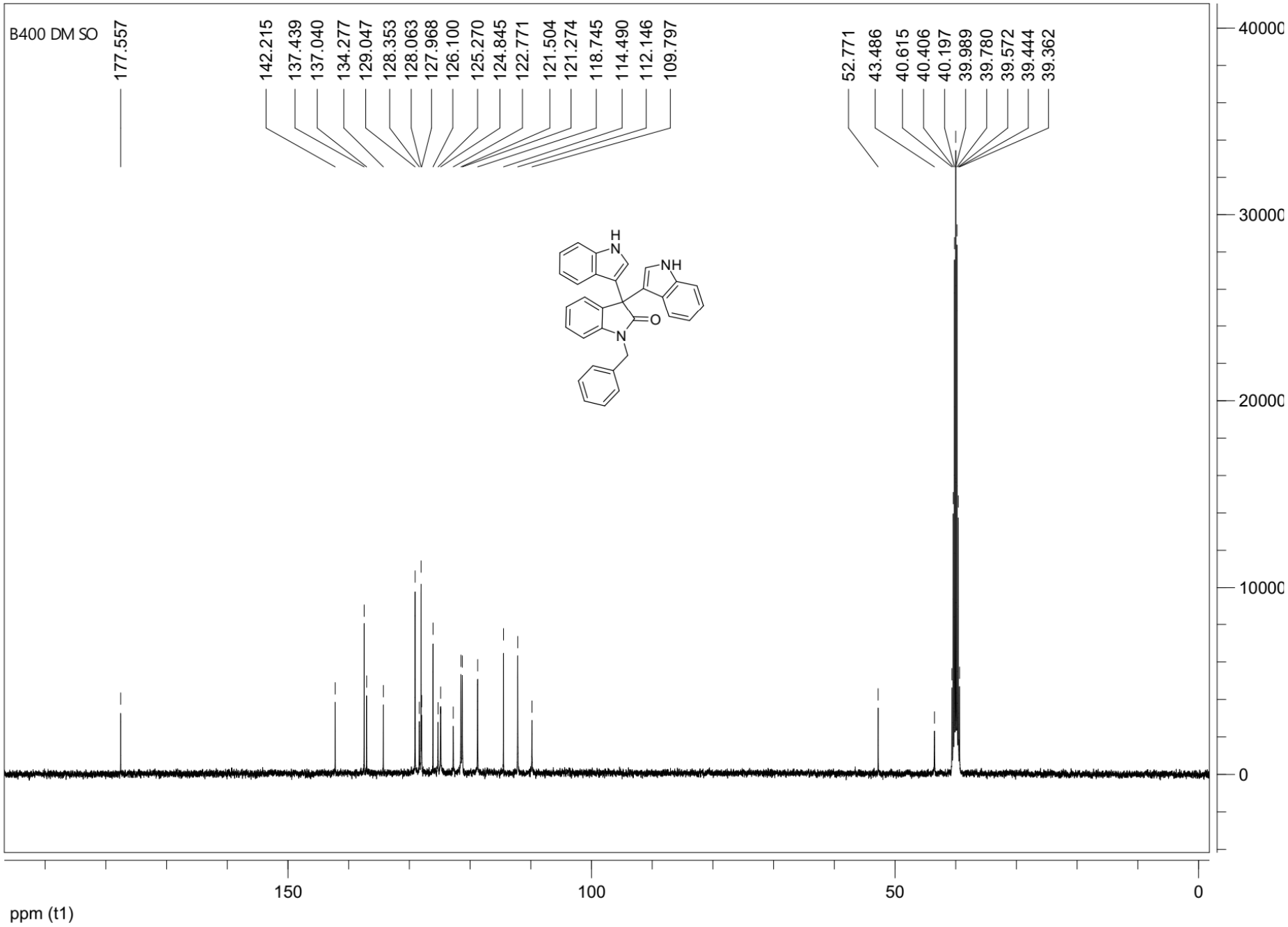
^{13}C NMR spectrum of Compound 3k (DMSO-d_6, 100 MHz)



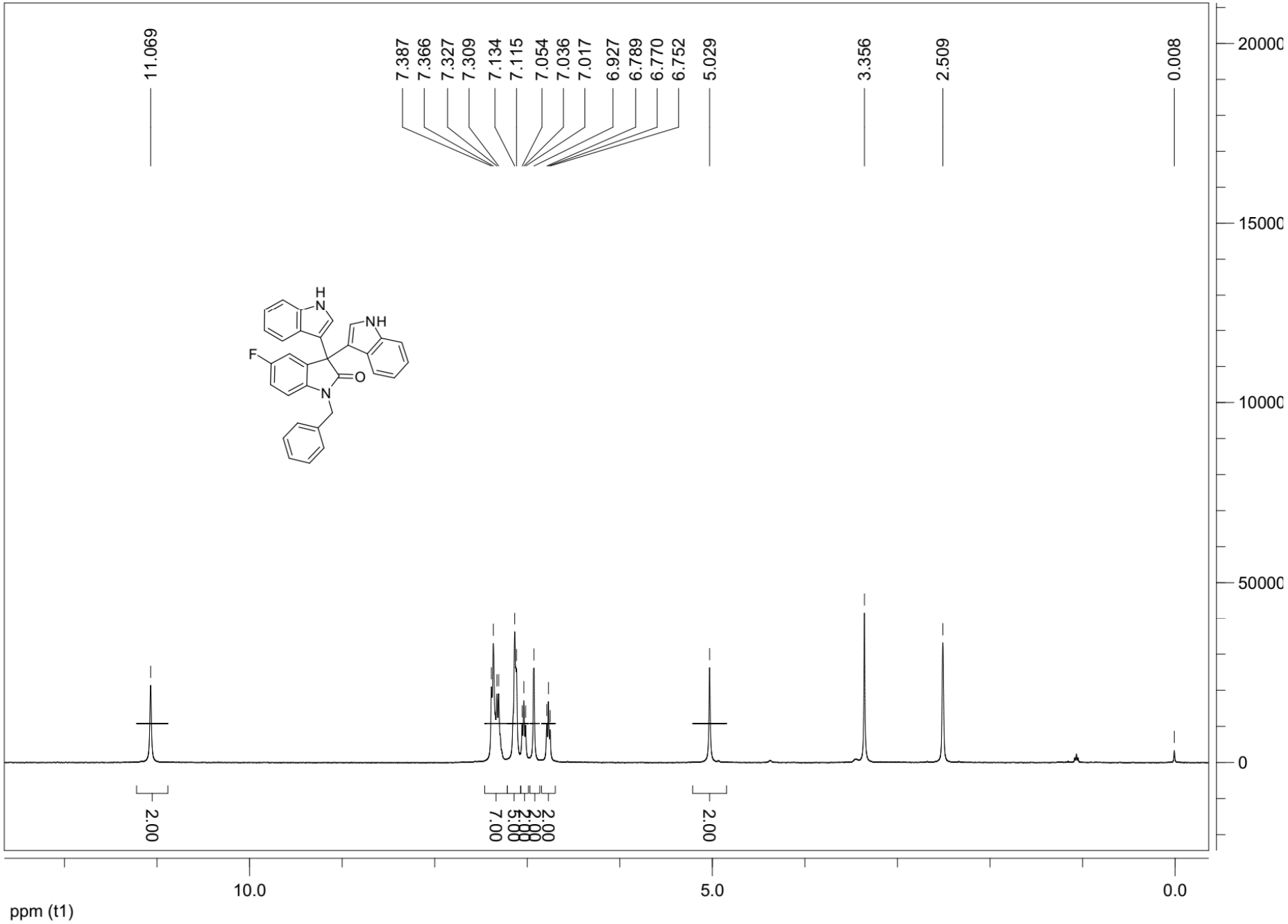
^{1}H NMR spectrum of Compound 3l (DMSO-d_6, 400 MHz)



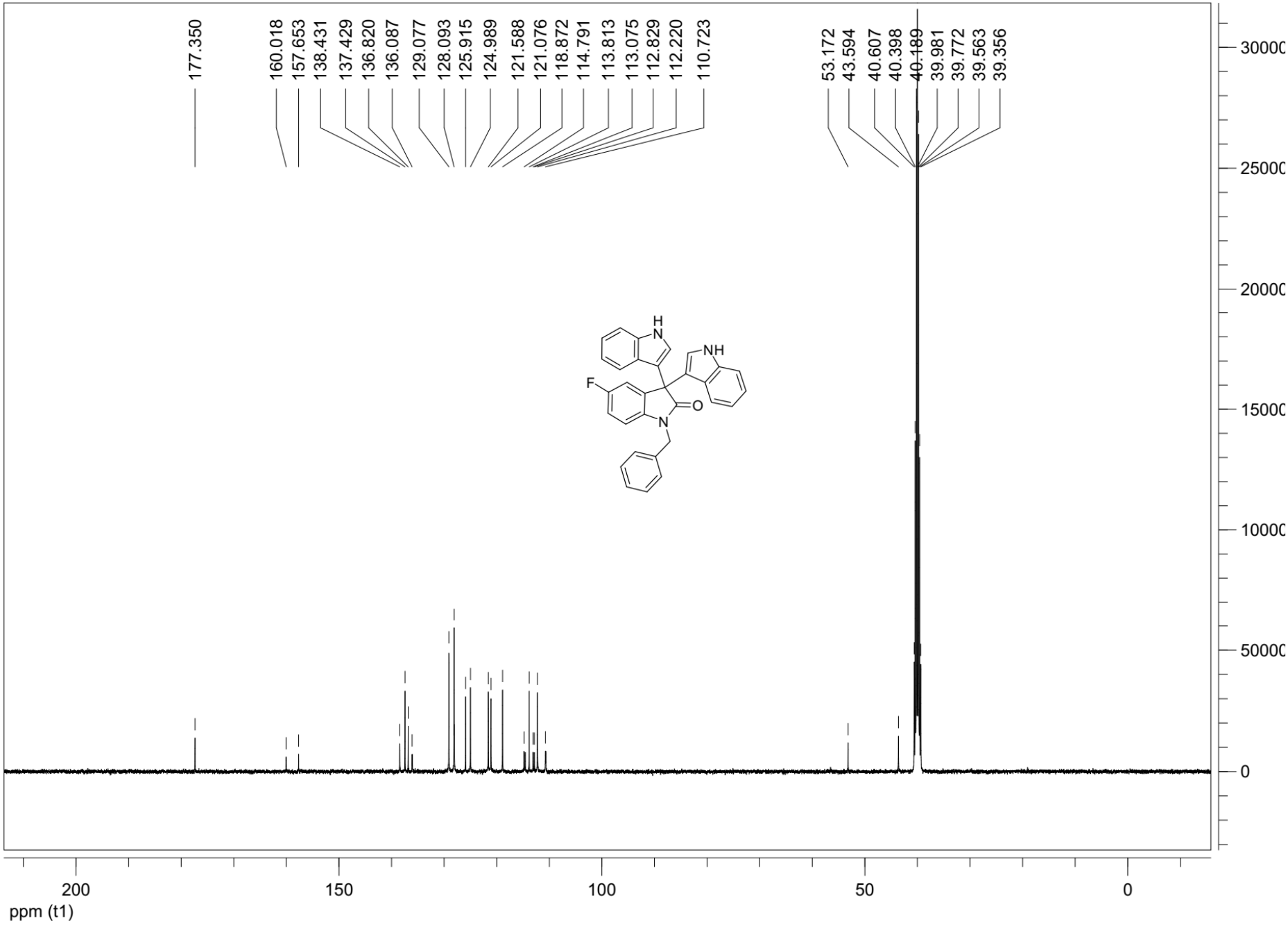
^{13}C NMR spectrum of Compound 3l (DMSO-d_6, 100 MHz)



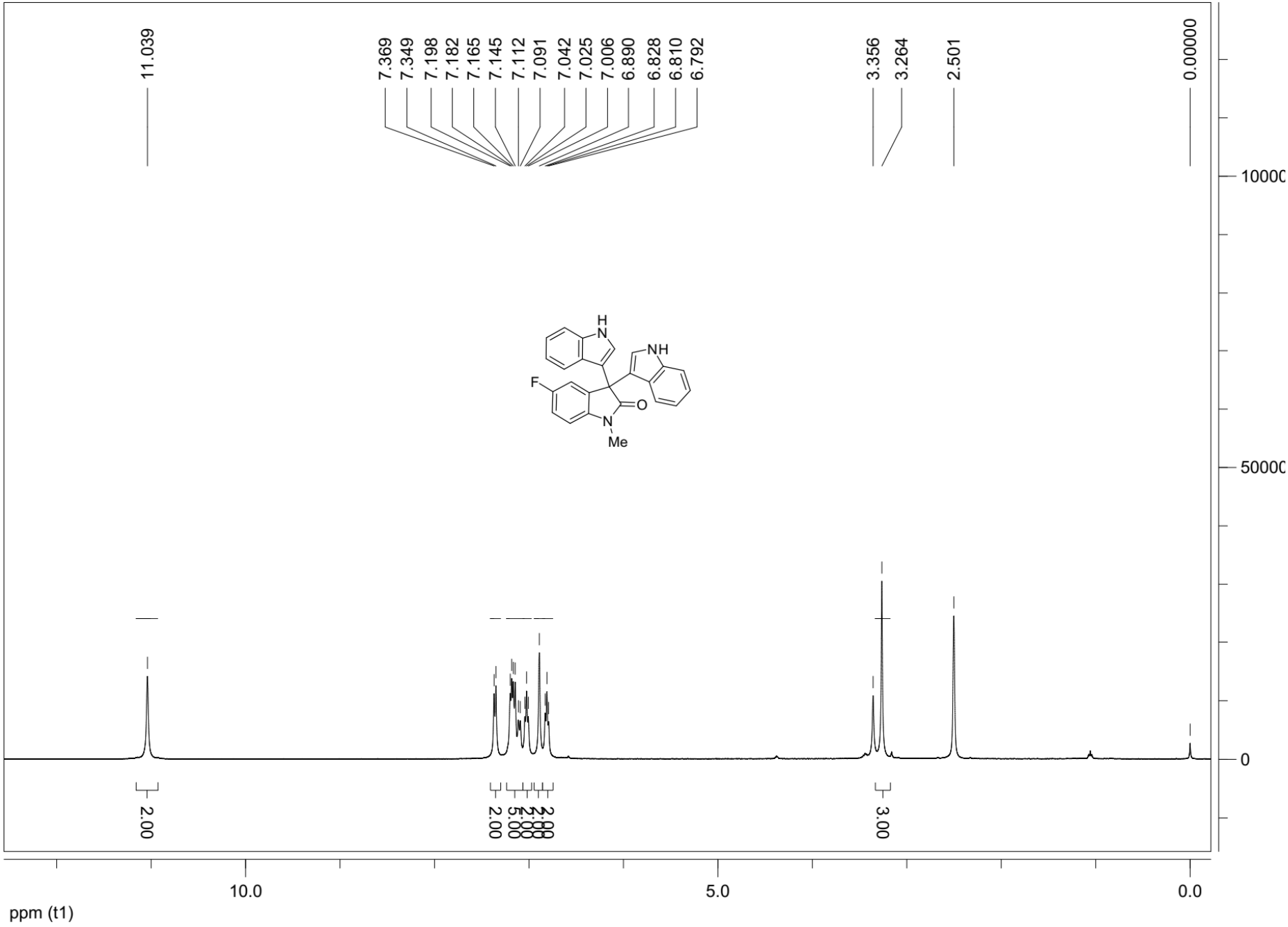
^{1}H NMR spectrum of Compound 3m (DMSO-d_6, 400 MHz)



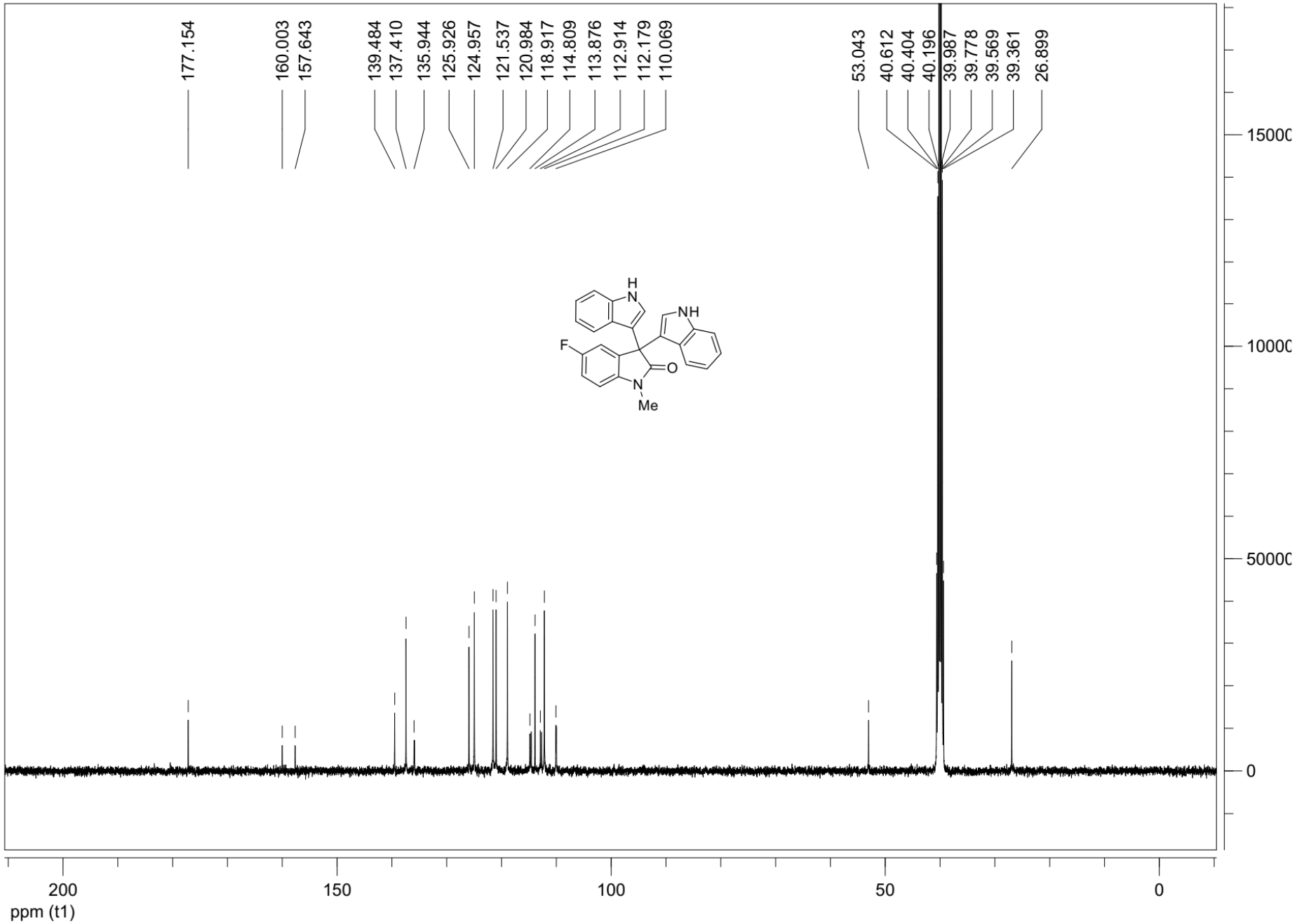
^{13}C NMR spectrum of Compound 3m (DMSO-d_6, 100 MHz)



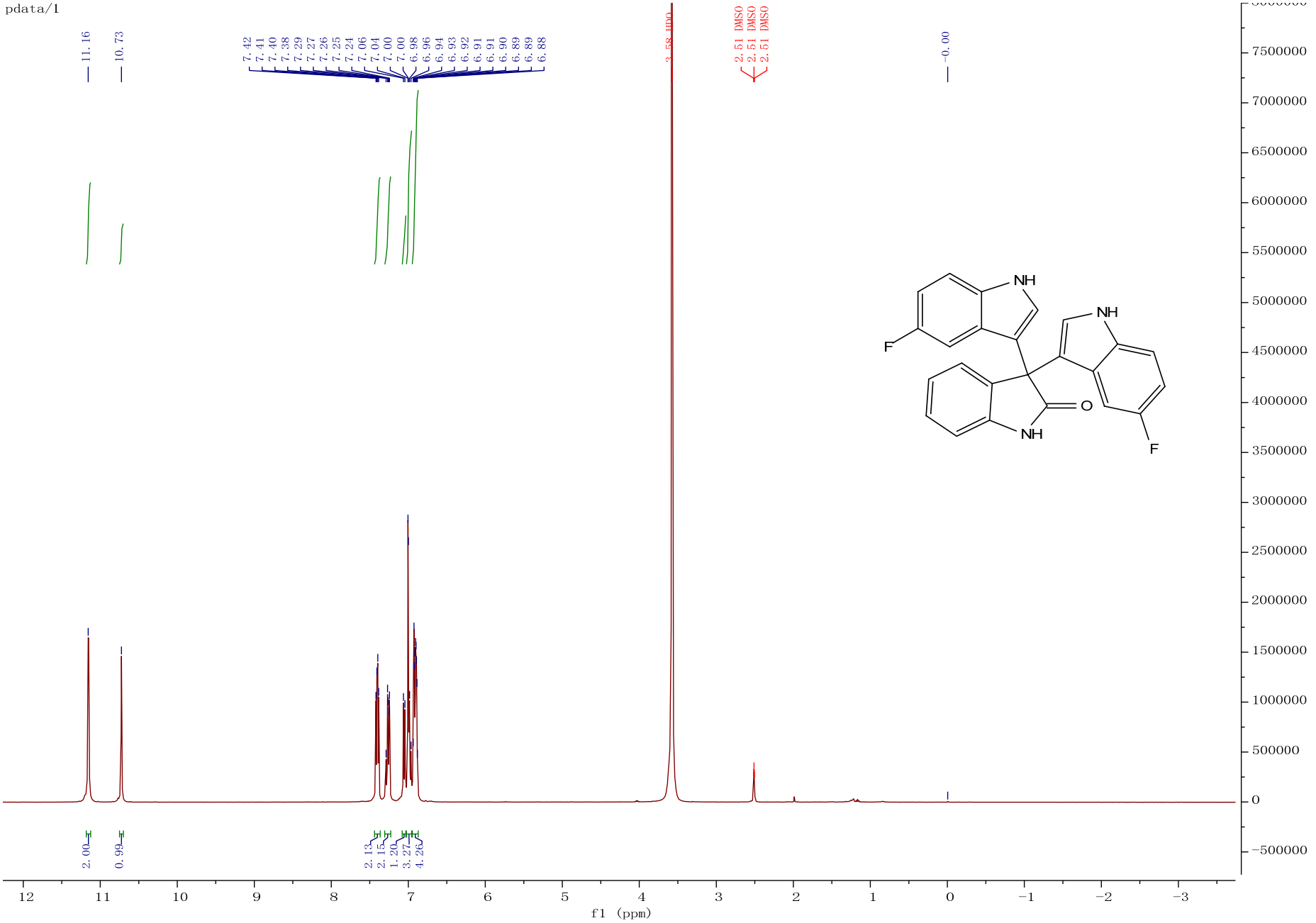
^{1}H NMR spectrum of Compound 3n (DMSO-d_6, 400 MHz)



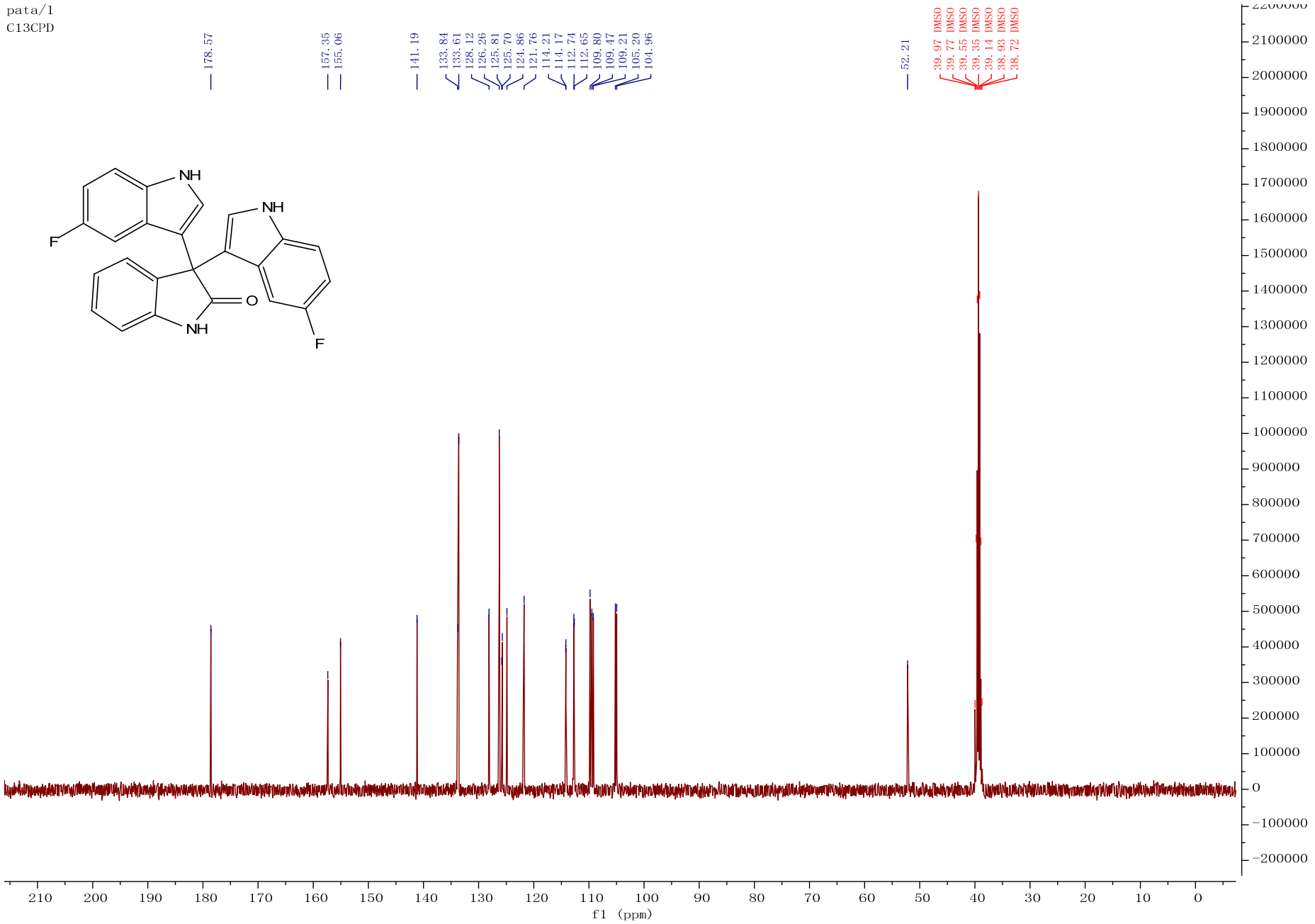
^{13}C NMR spectrum of Compound 3n (DMSO-d_6, 100 MHz)



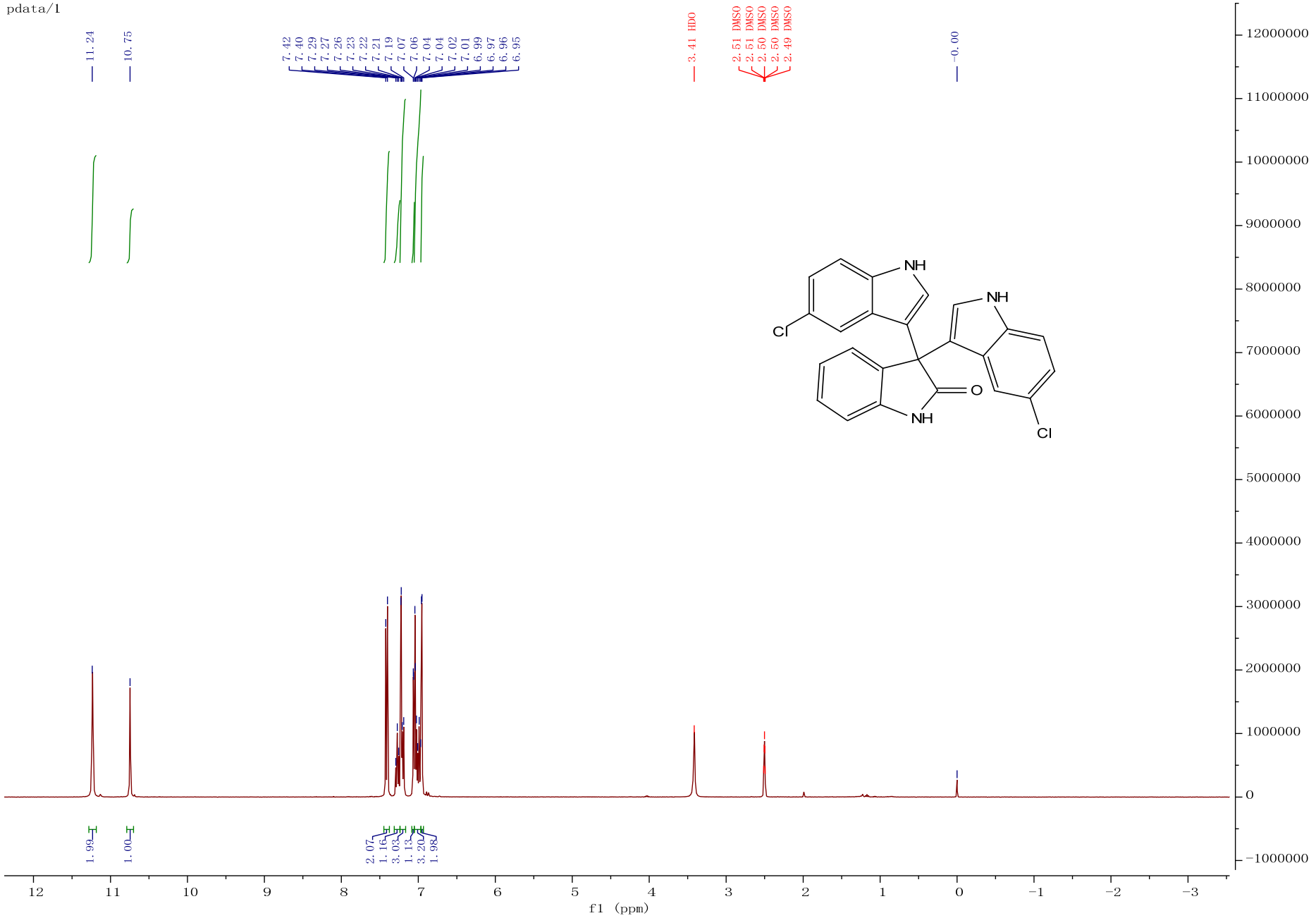
^{1}H NMR spectrum of Compound 3o (DMSO-d_6, 400 MHz)



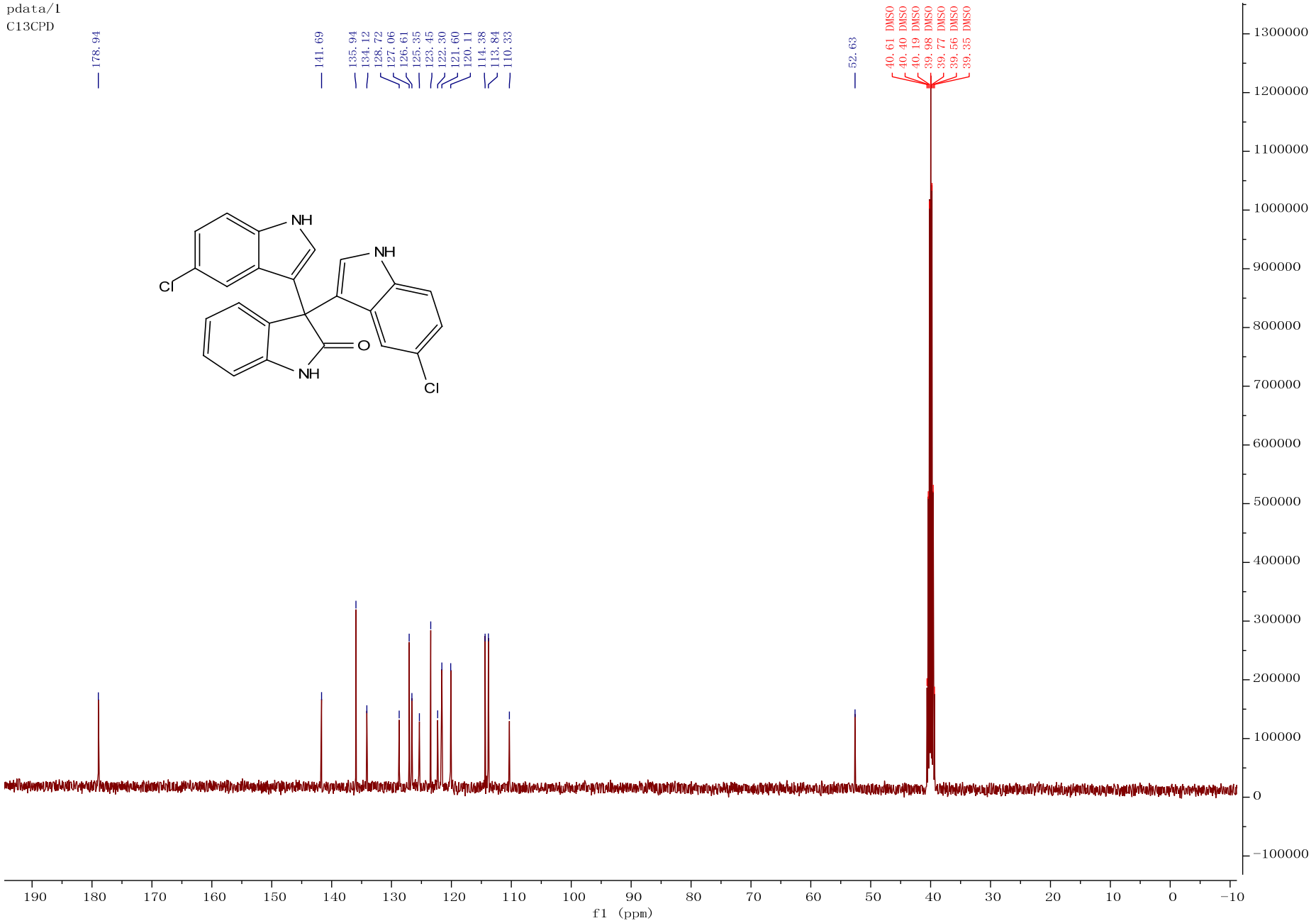
^{13}C NMR spectrum of Compound 3o (DMSO-d_6, 100 MHz)



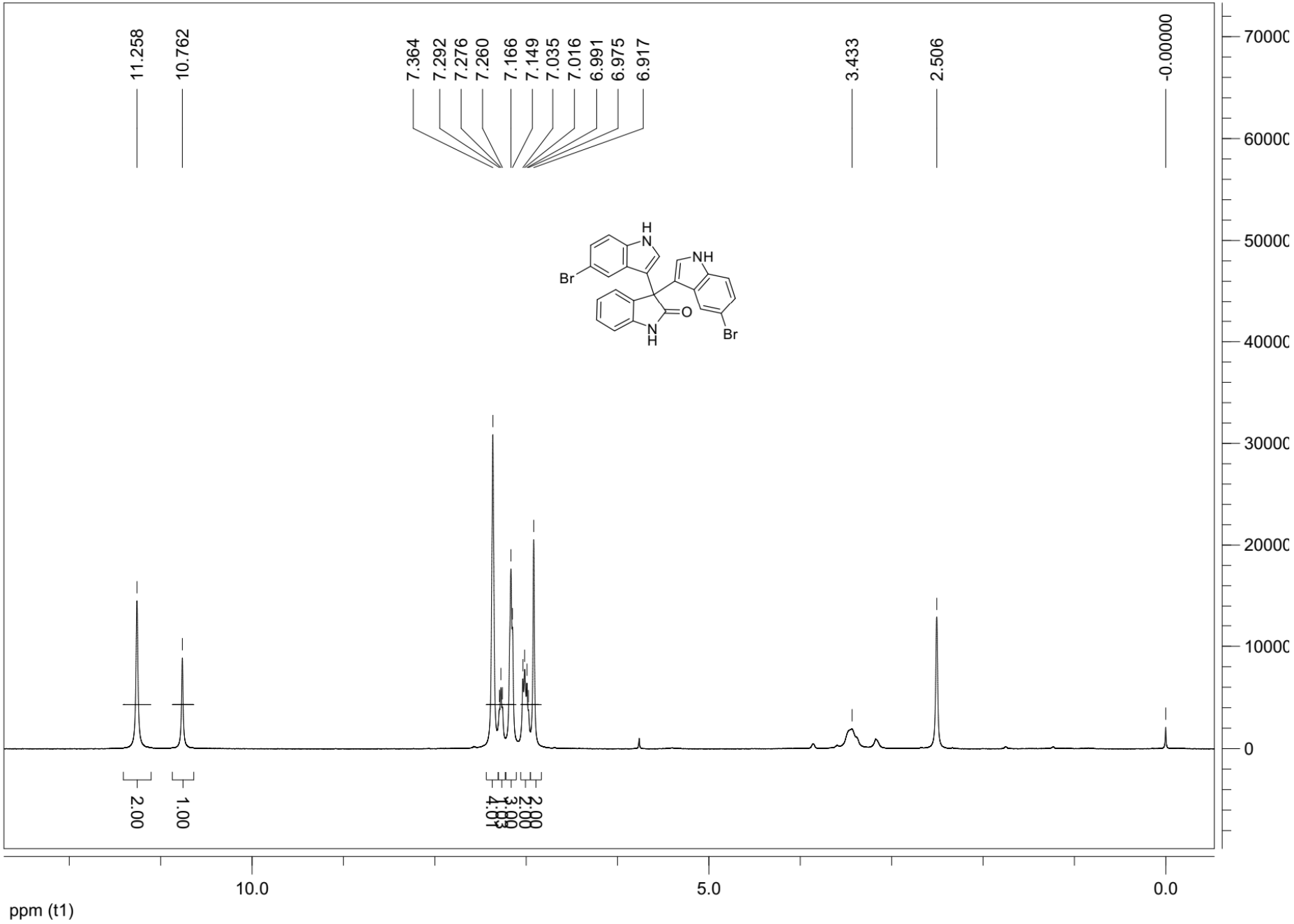
^{1}H NMR spectrum of Compound 3p (DMSO-d_6, 400 MHz)



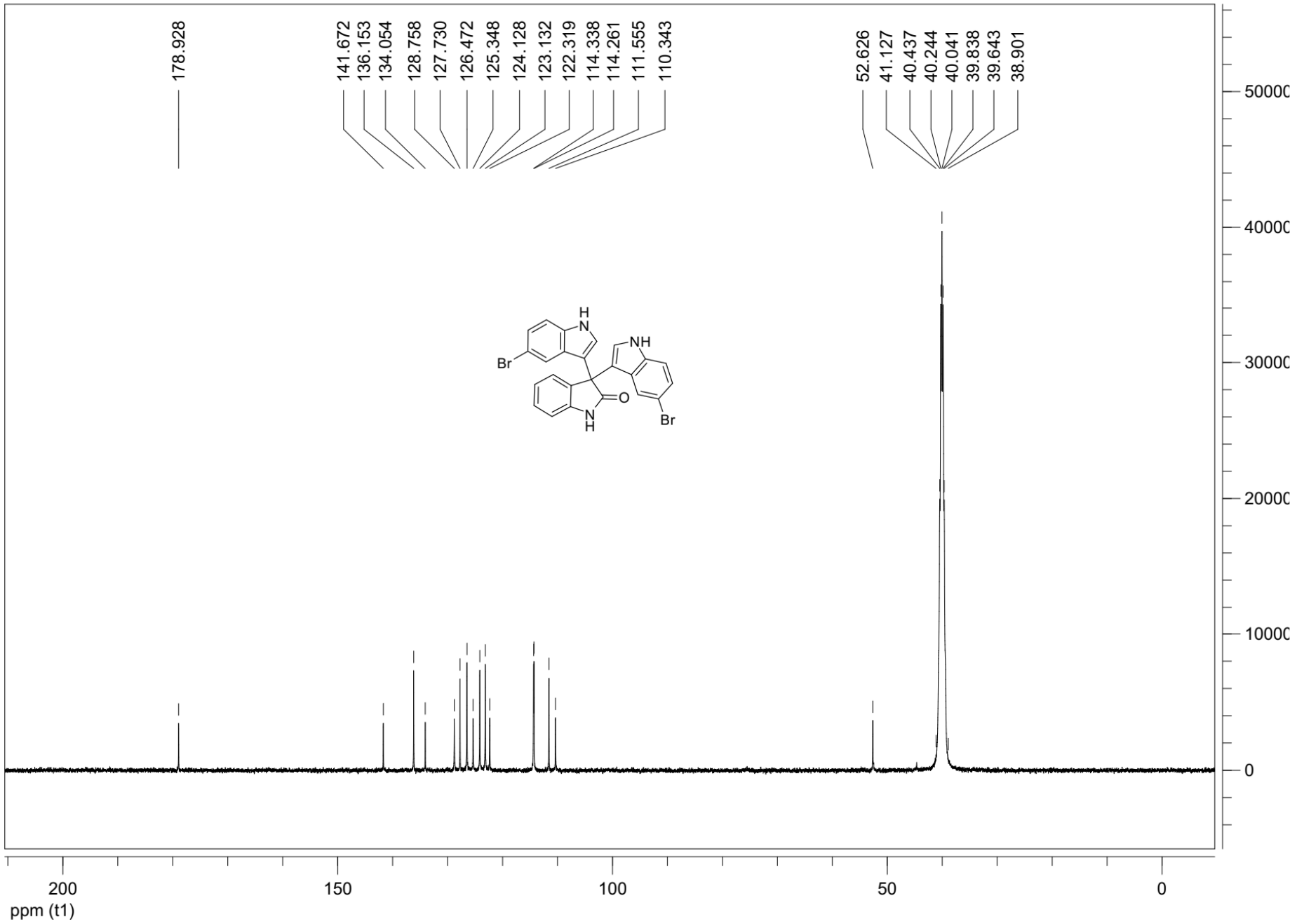
^{13}C NMR spectrum of Compound 3p (DMSO-d_6, 100 MHz)



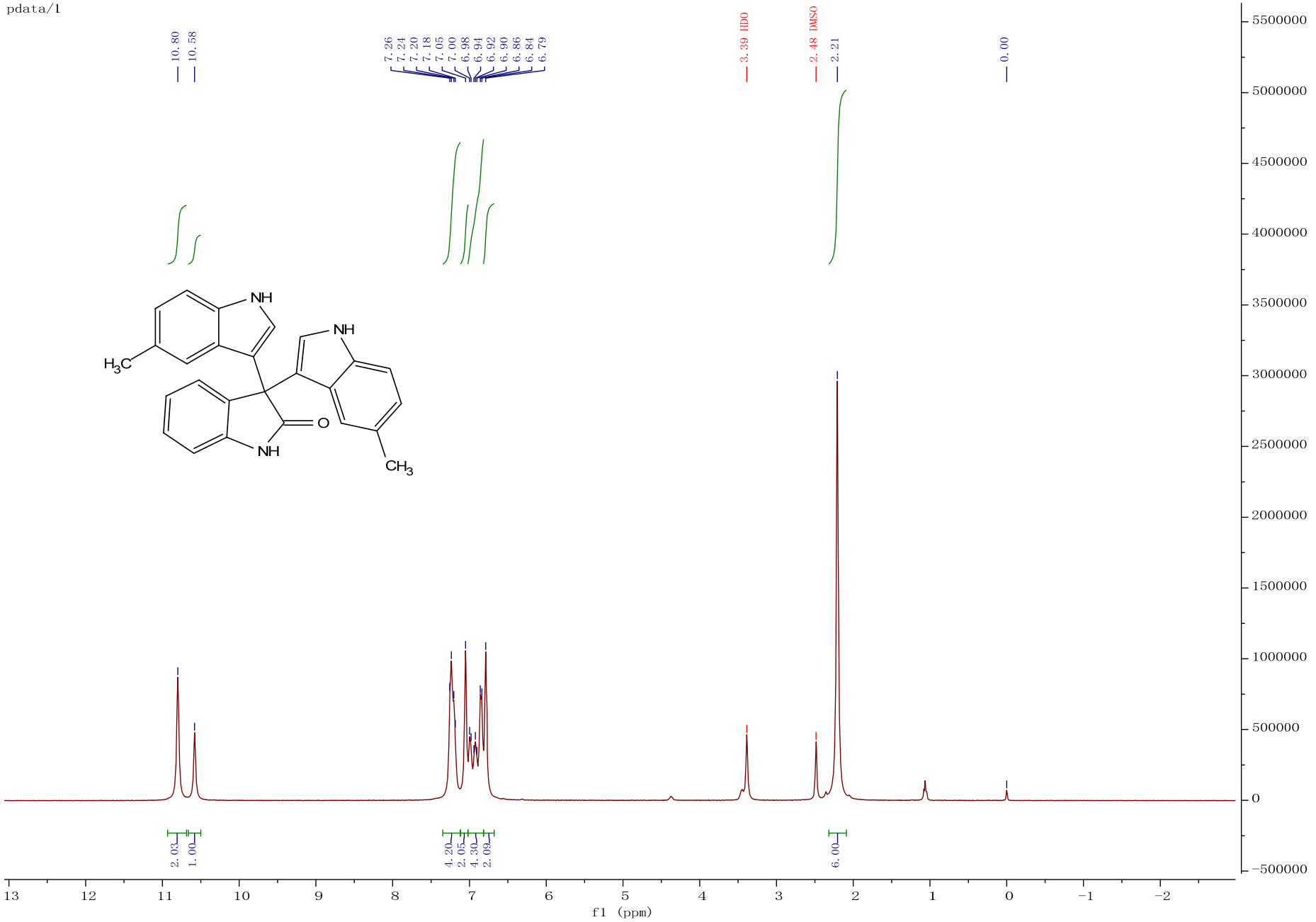
^{1}H NMR spectrum of Compound 3q (DMSO-d_6, 400 MHz)



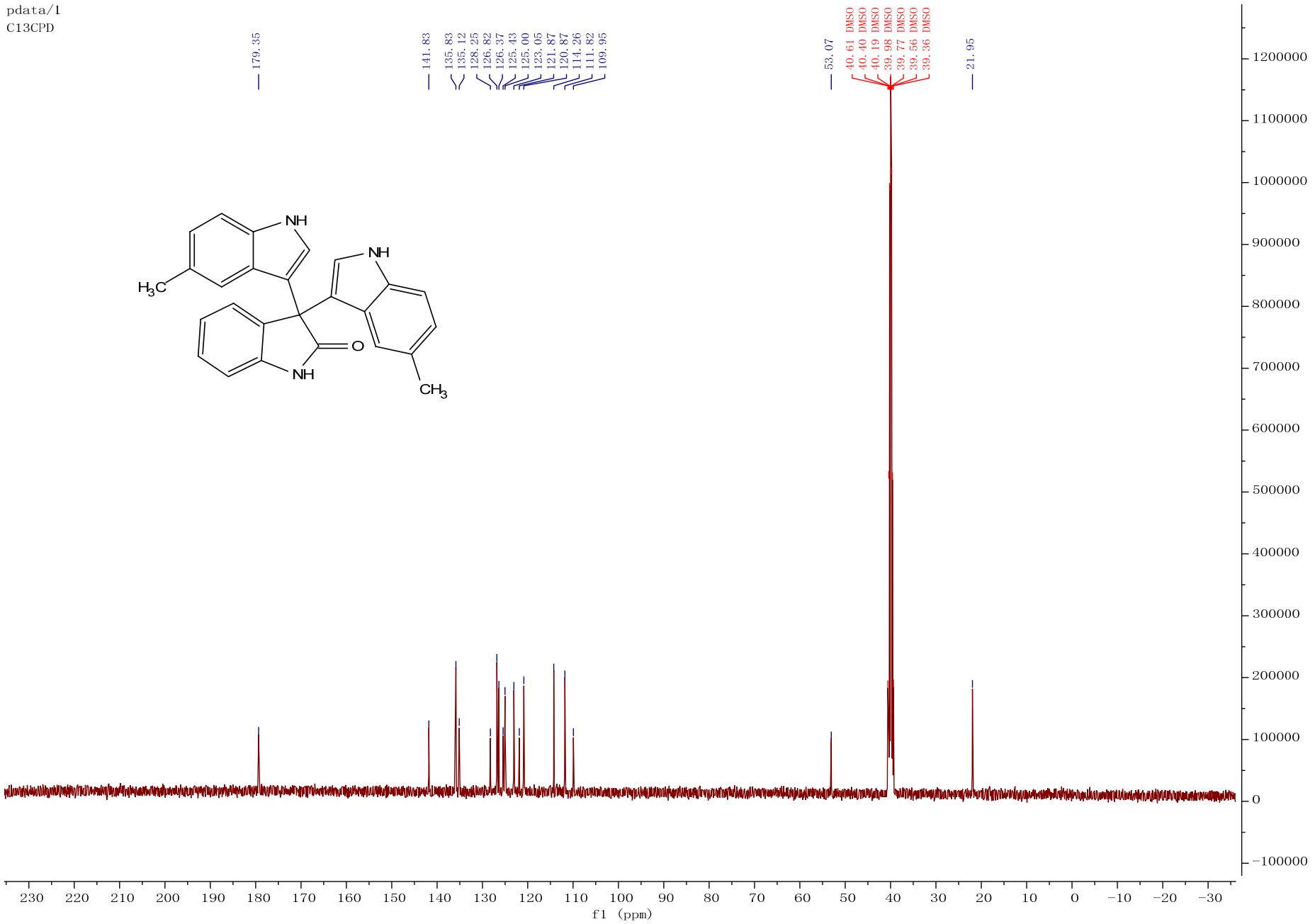
^{13}C NMR spectrum of Compound 3q (DMSO-d_6, 100 MHz)



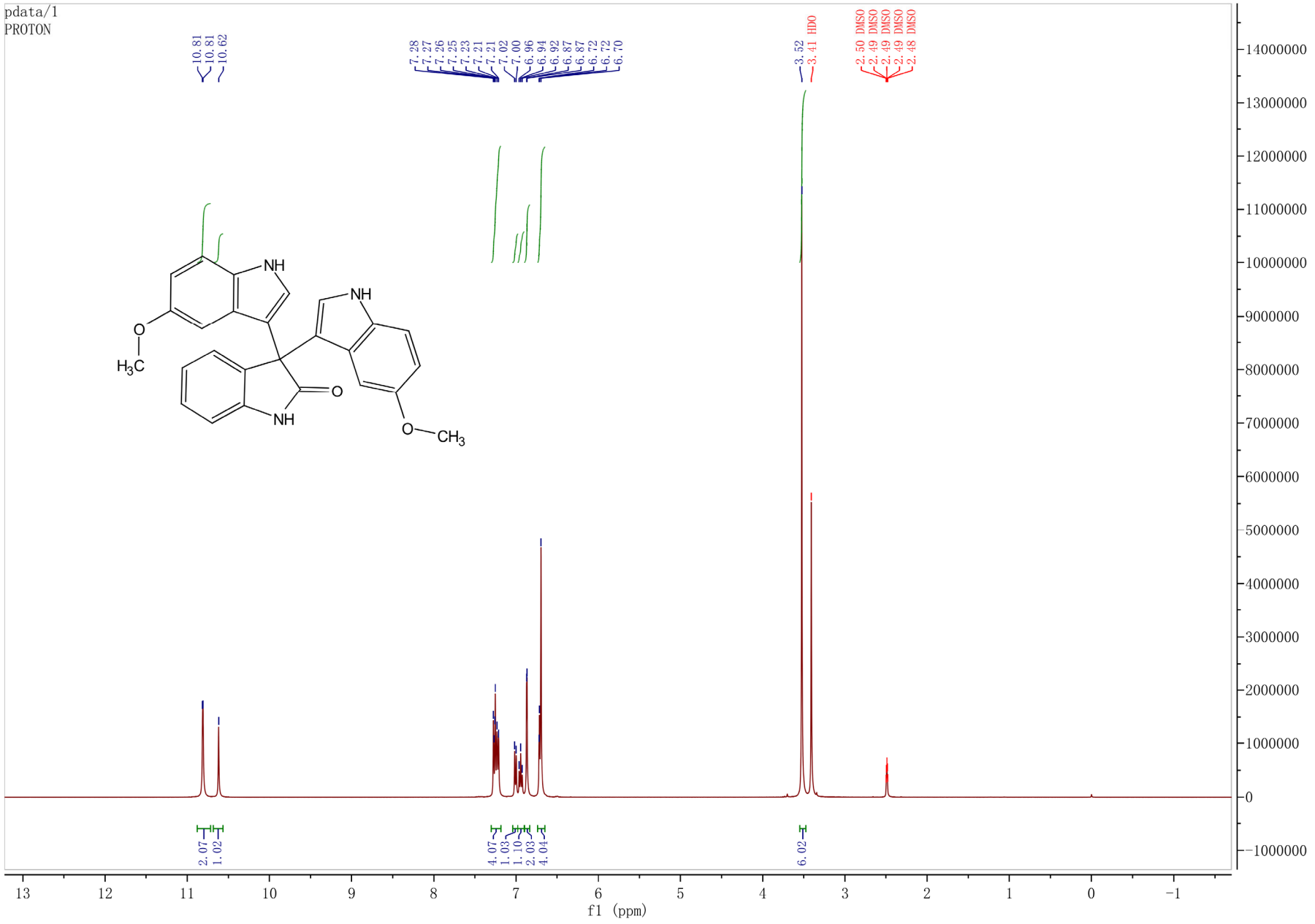
^{1}H NMR spectrum of Compound 3r (DMSO-d_6, 400 MHz)



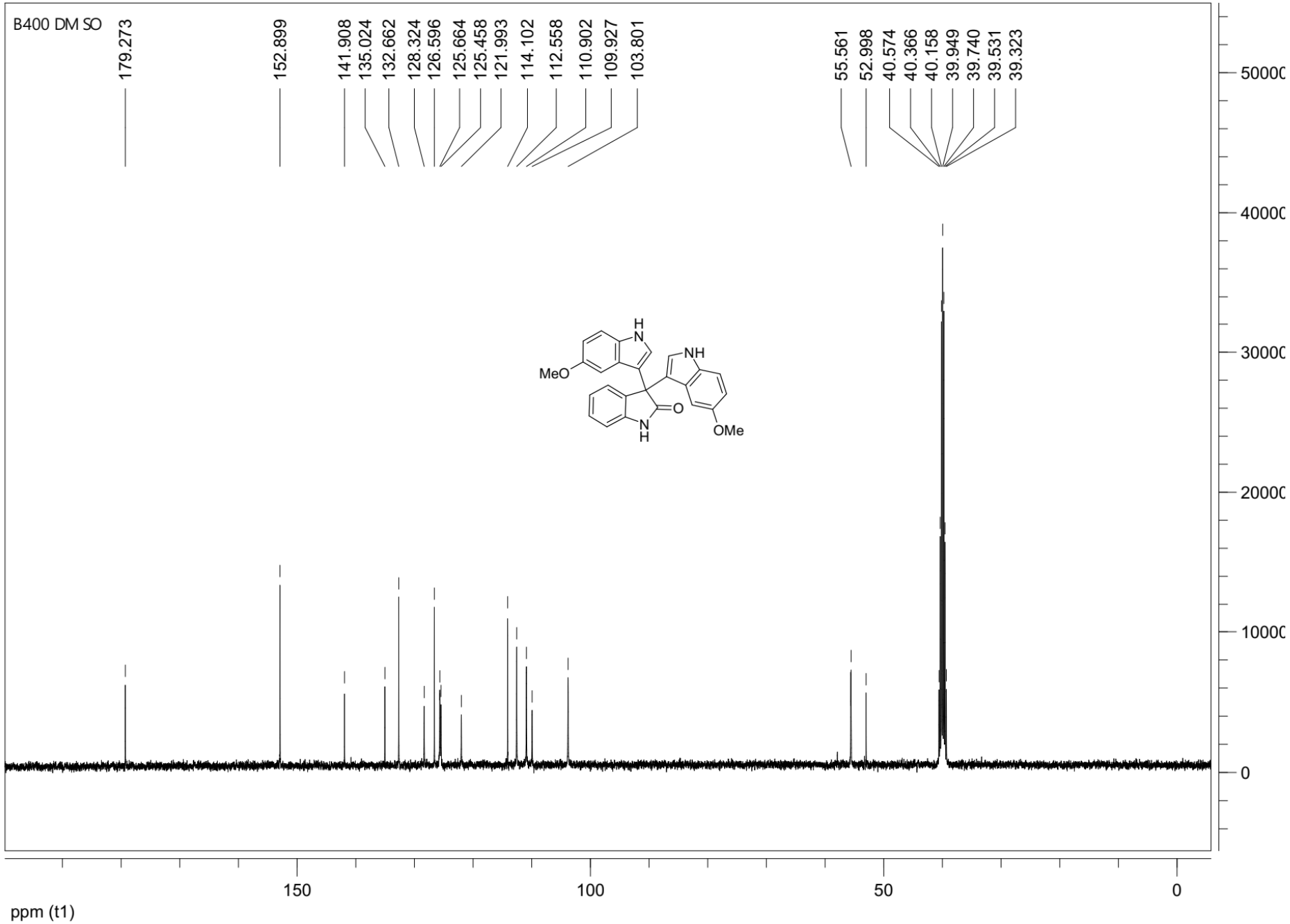
^{13}C NMR spectrum of Compound 3r (DMSO-d_6, 100 MHz)



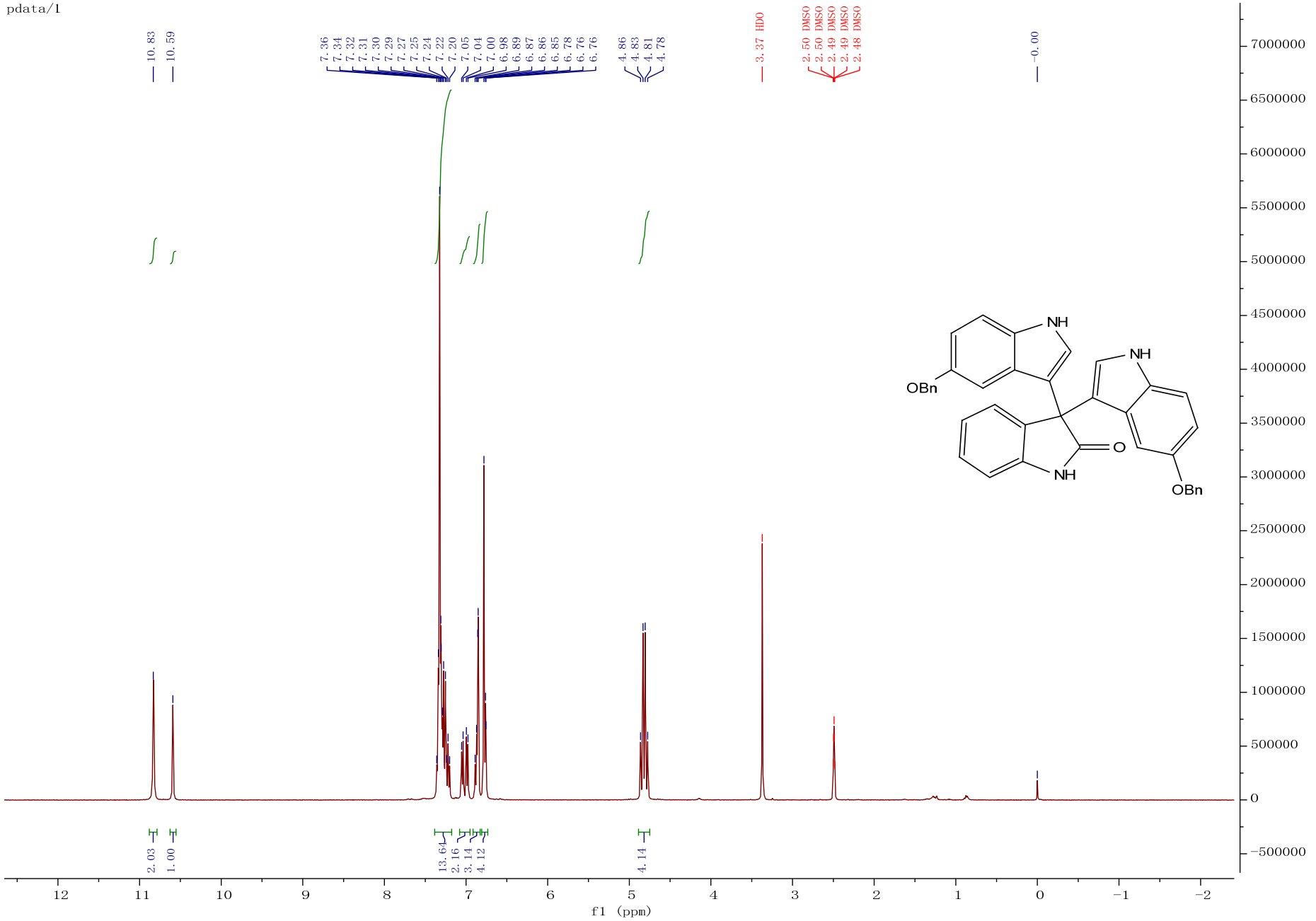
^{1}H NMR spectrum of Compound 3s (DMSO-d_6, 400 MHz)



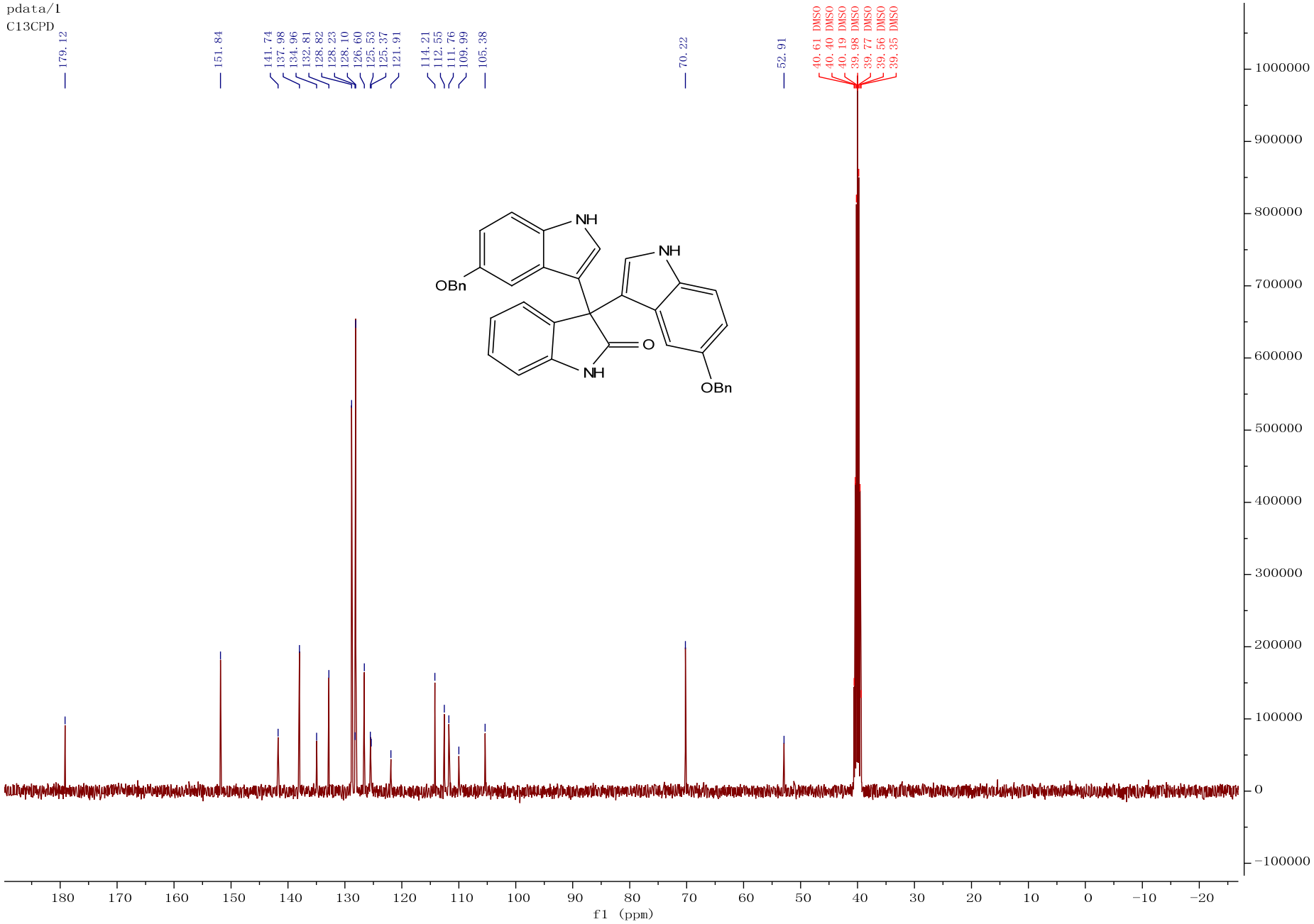
^{13}C NMR spectrum of Compound 3s (DMSO-d_6, 100 MHz)



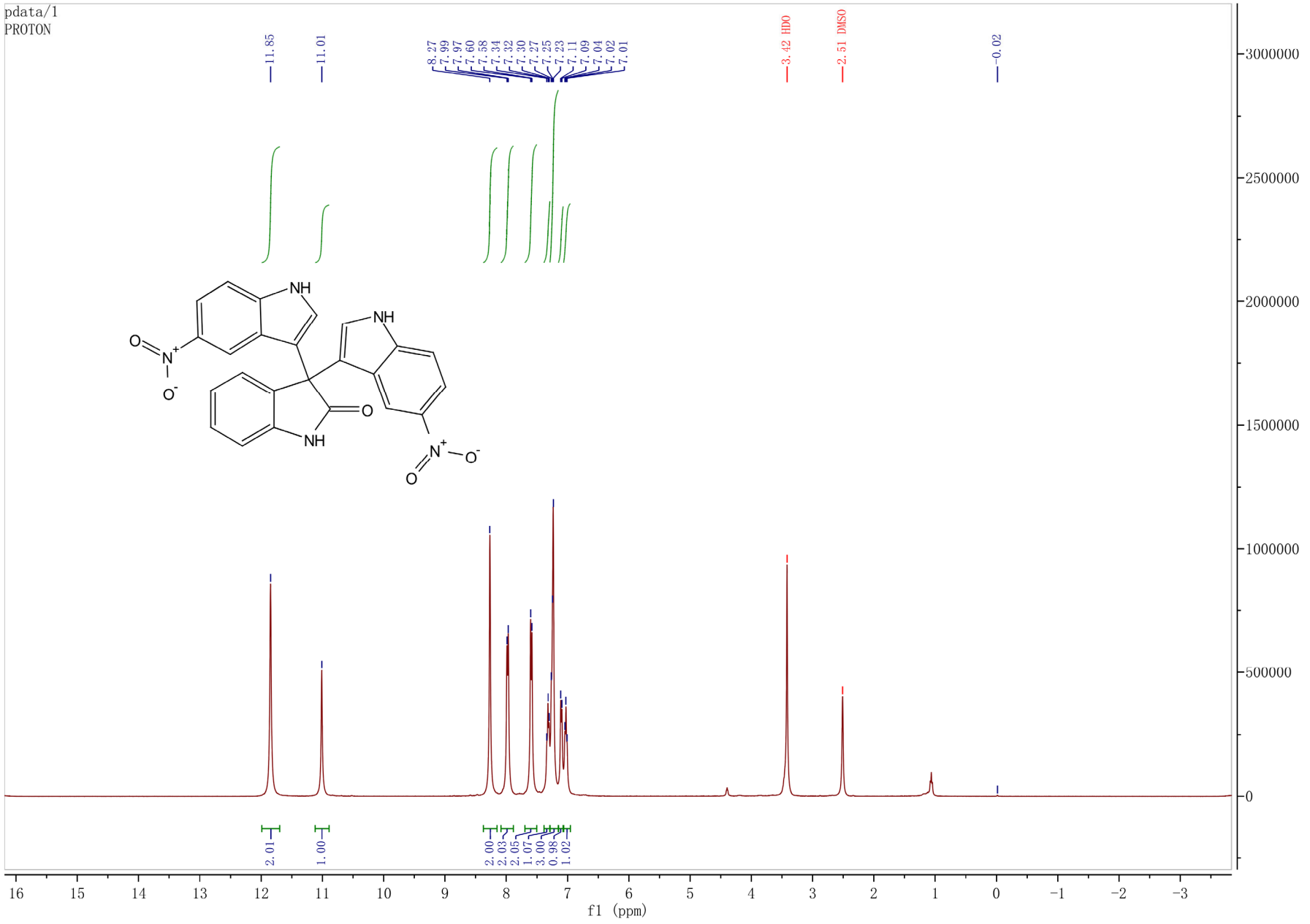
^{1}H NMR spectrum of Compound 3t (DMSO-d_6, 400 MHz)



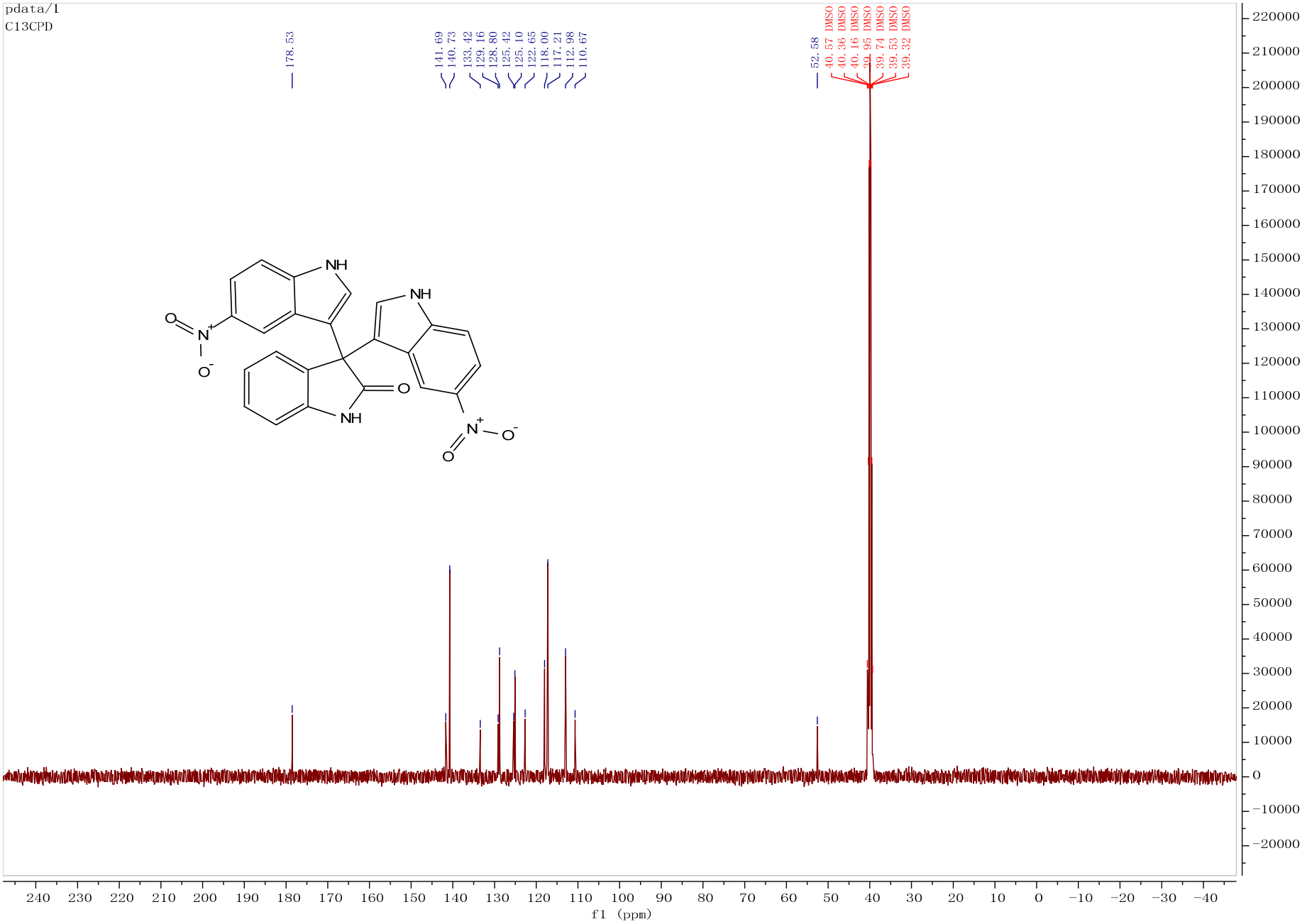
^{13}C NMR spectrum of Compound 3t (DMSO-d_6, 100 MHz)



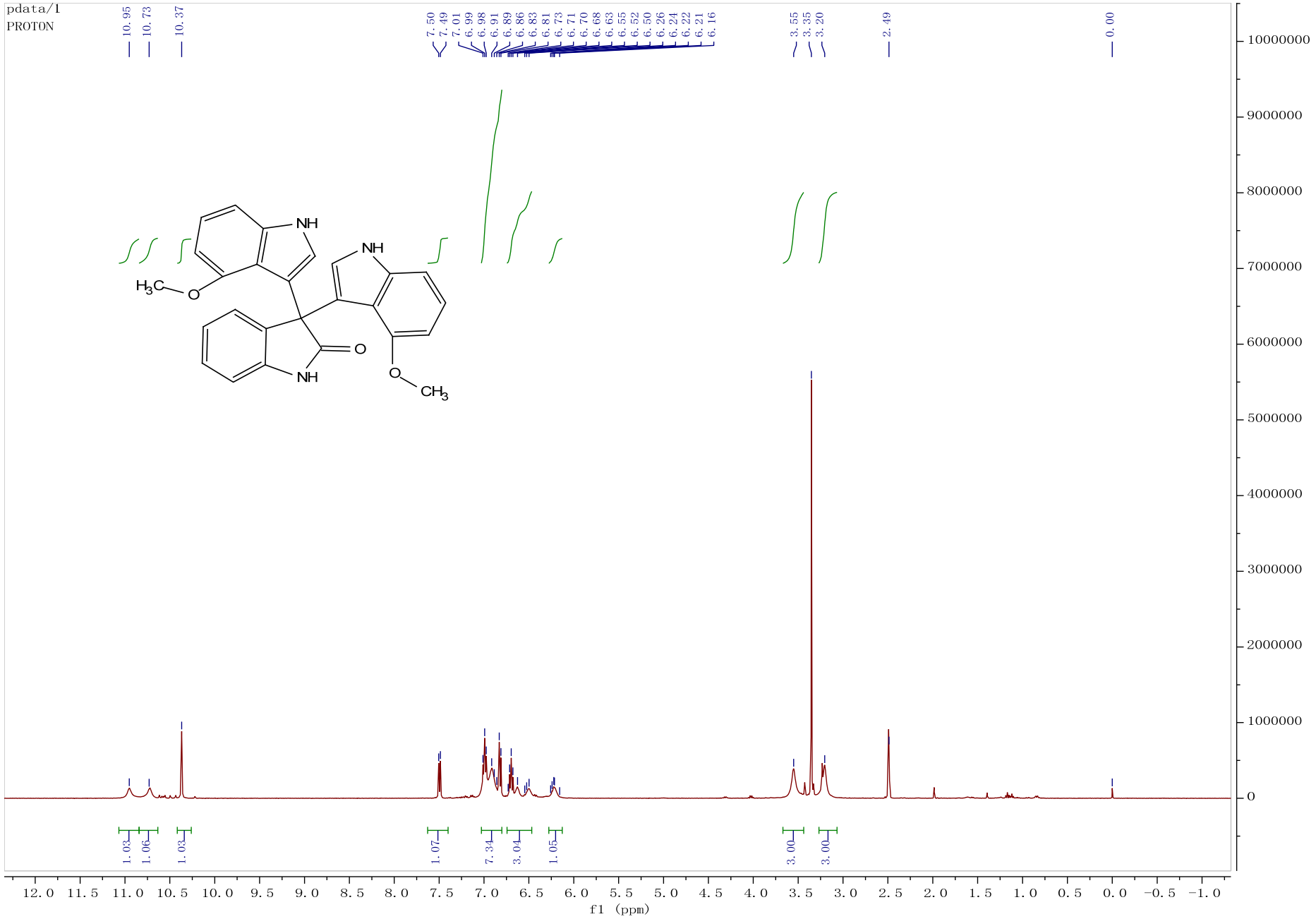
^{1}H NMR spectrum of Compound 3u (DMSO-d_6, 400 MHz)



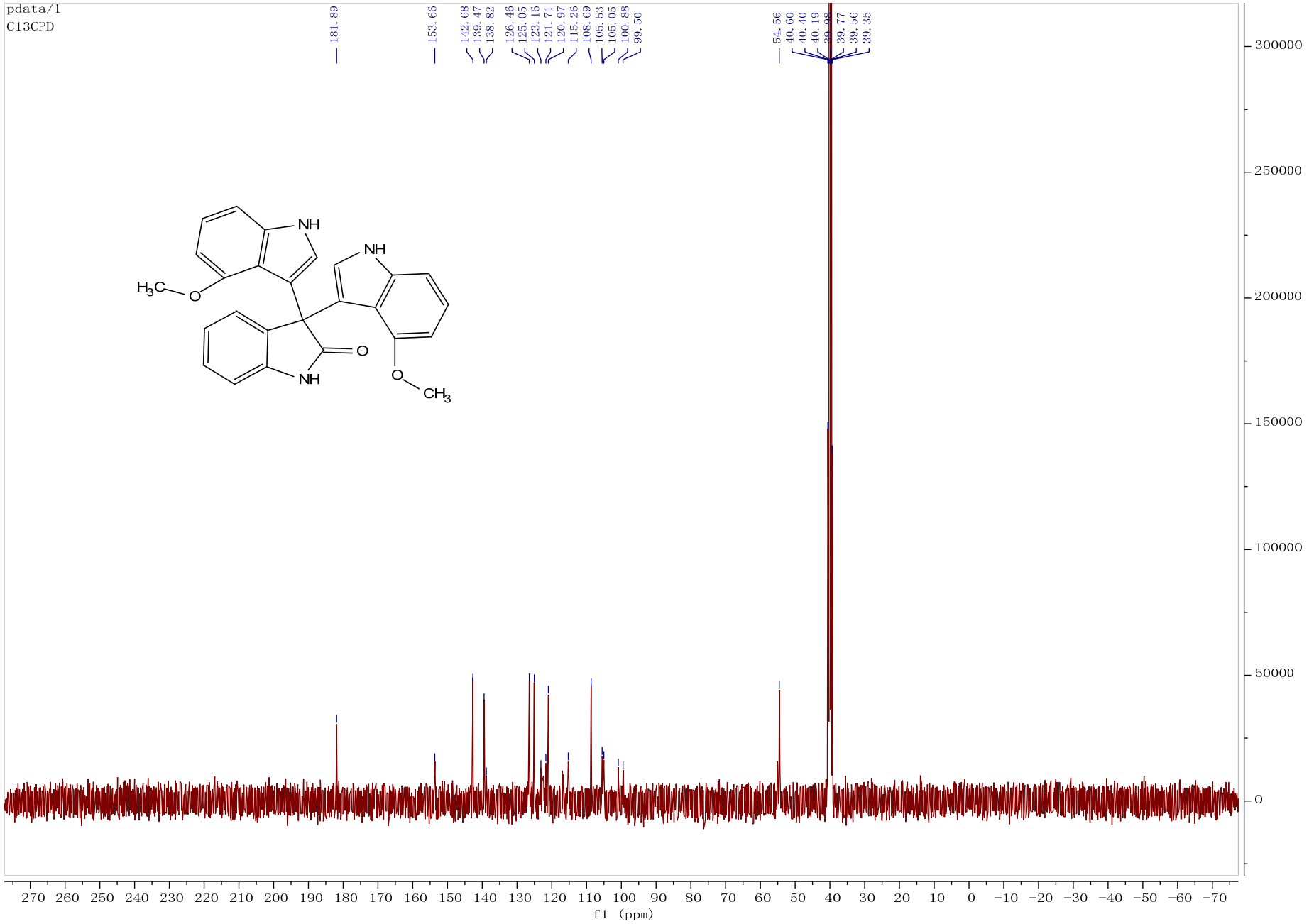
^{13}C NMR spectrum of Compound 3u (DMSO-d_6, 100 MHz)



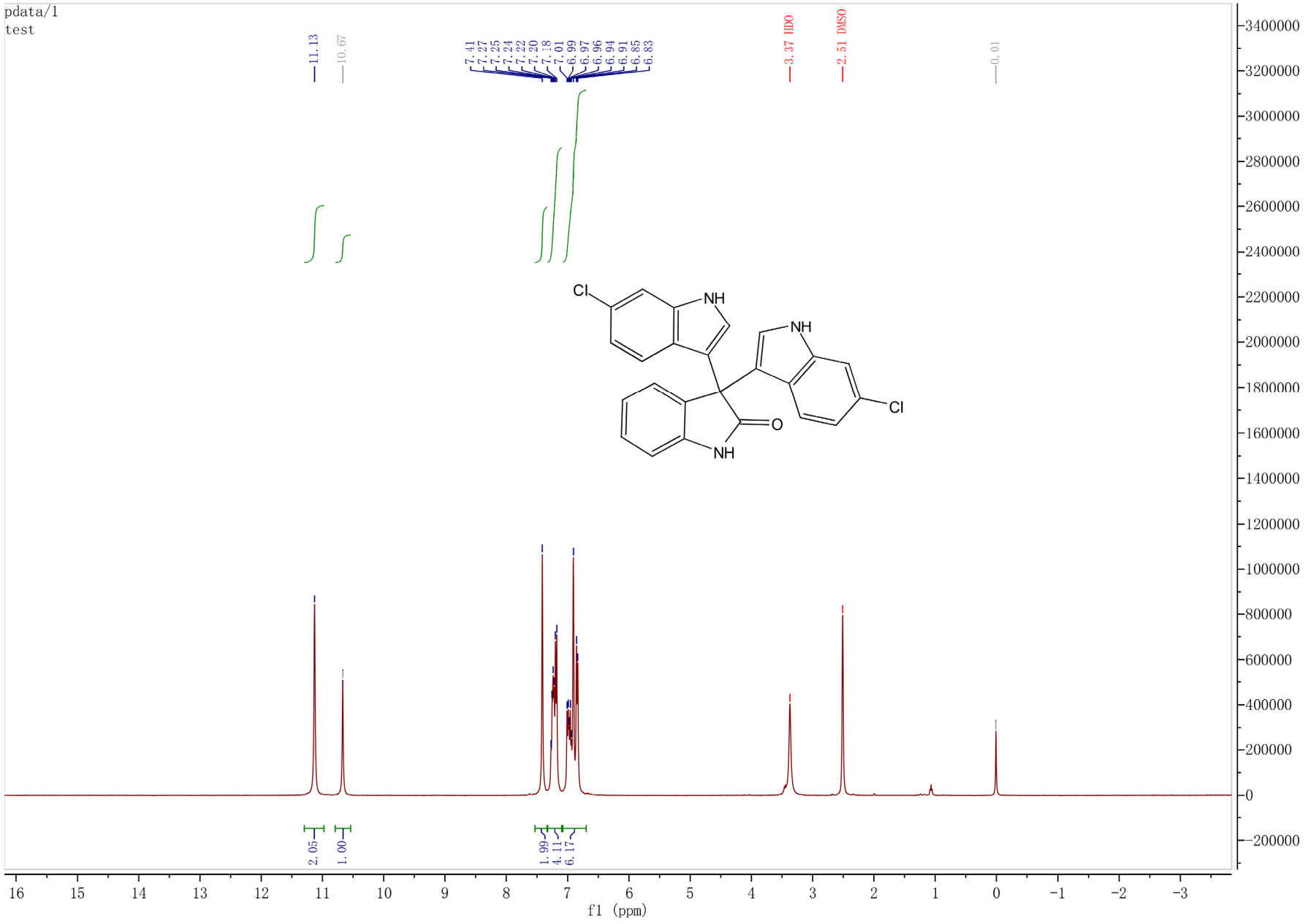
^{1}H NMR spectrum of Compound 3v (DMSO-d_6, 400 MHz)



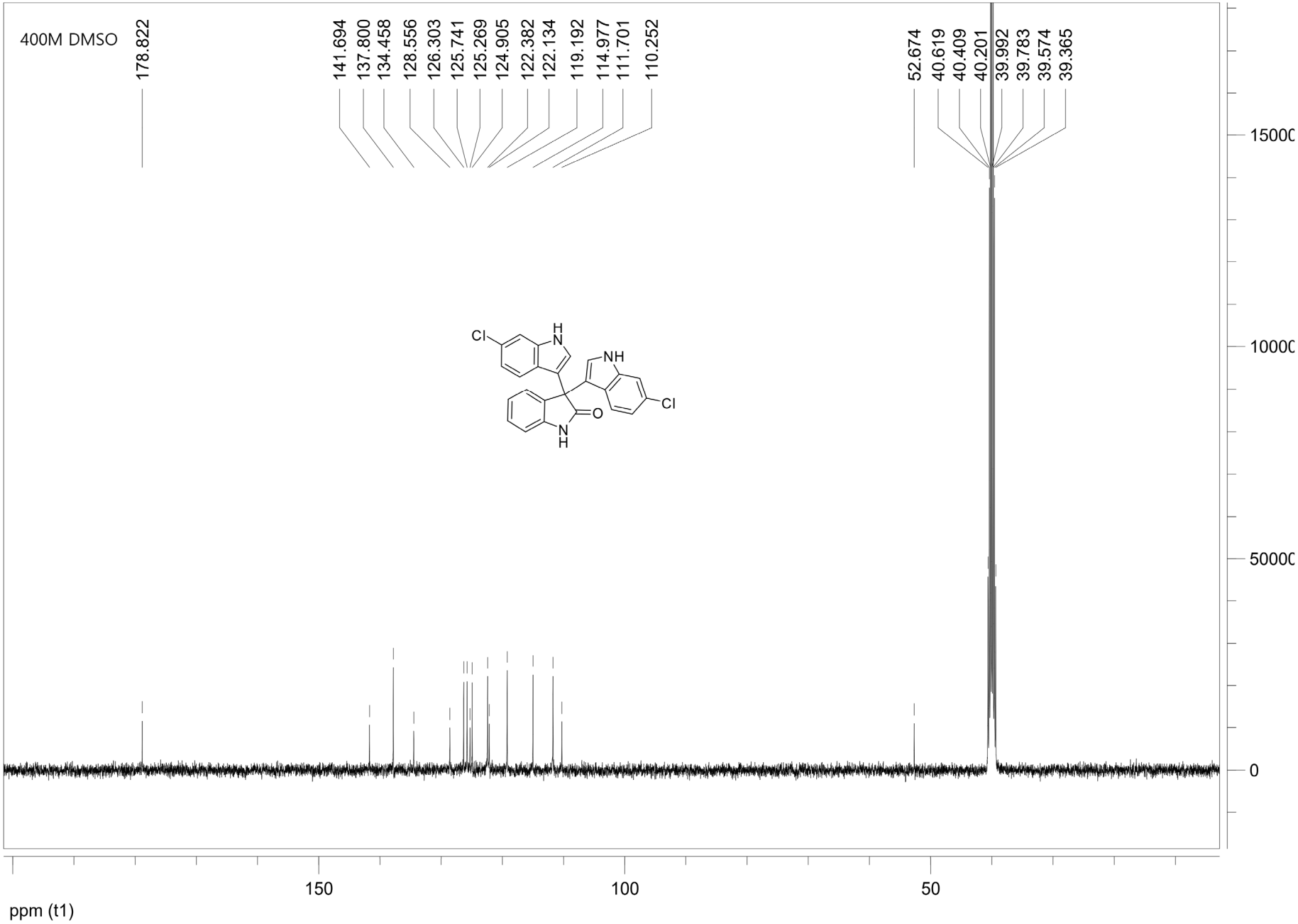
^{13}C NMR spectrum of Compound 3v (DMSO-d_6, 100 MHz)



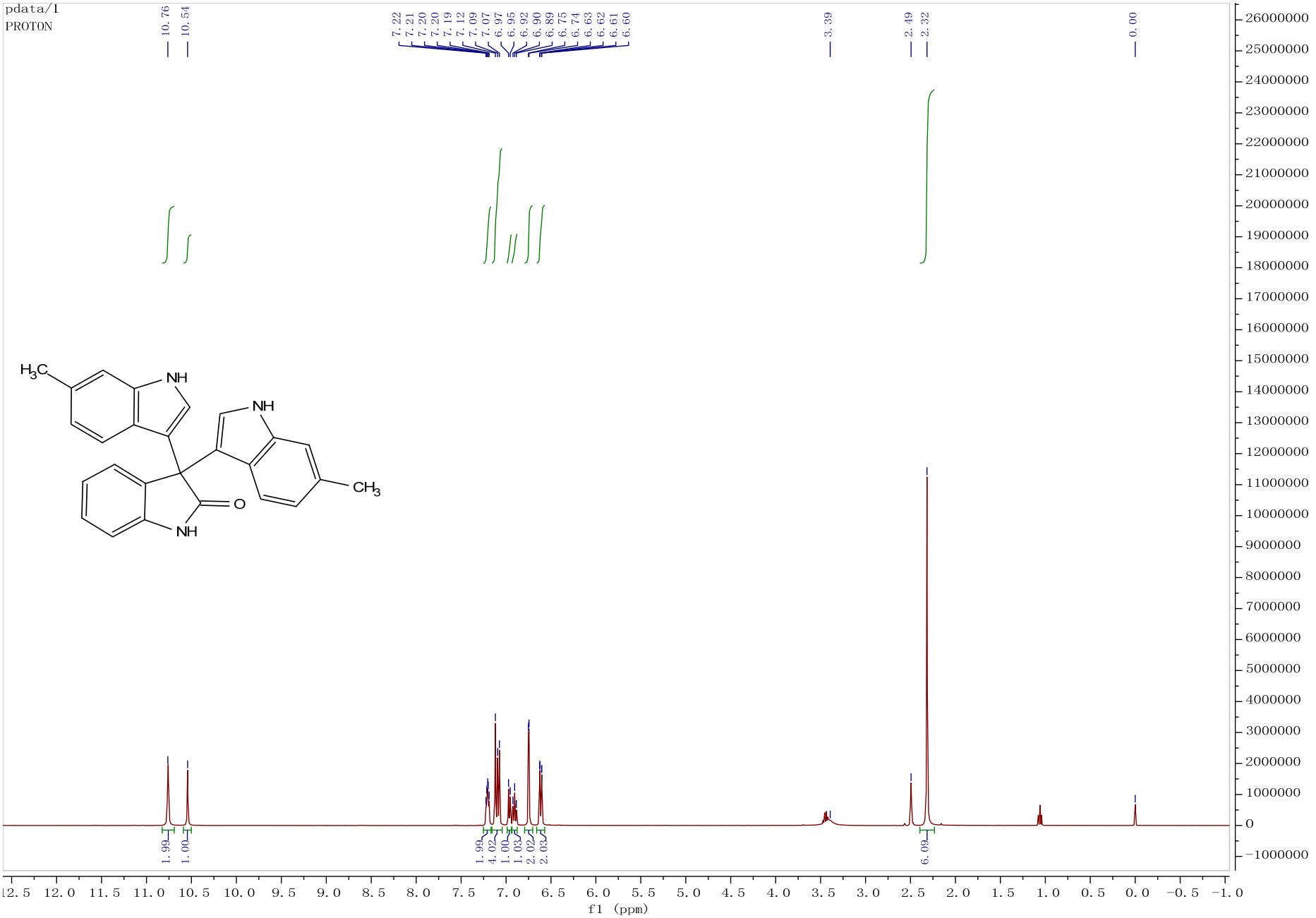
^{1}H NMR spectrum of Compound 3w (DMSO-d_6, 400 MHz)



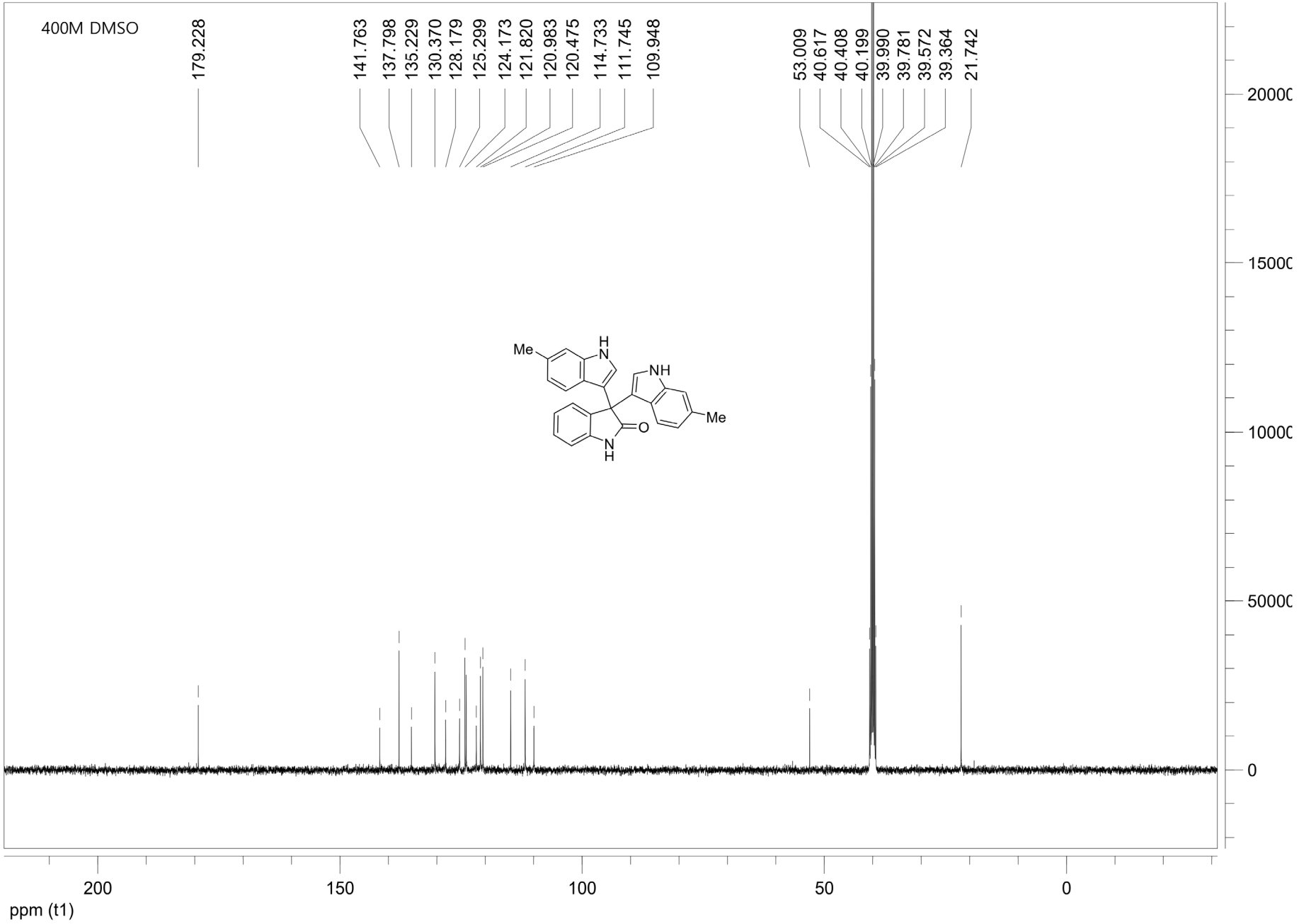
^{13}C NMR spectrum of Compound 3w (DMSO-d_6, 100 MHz)



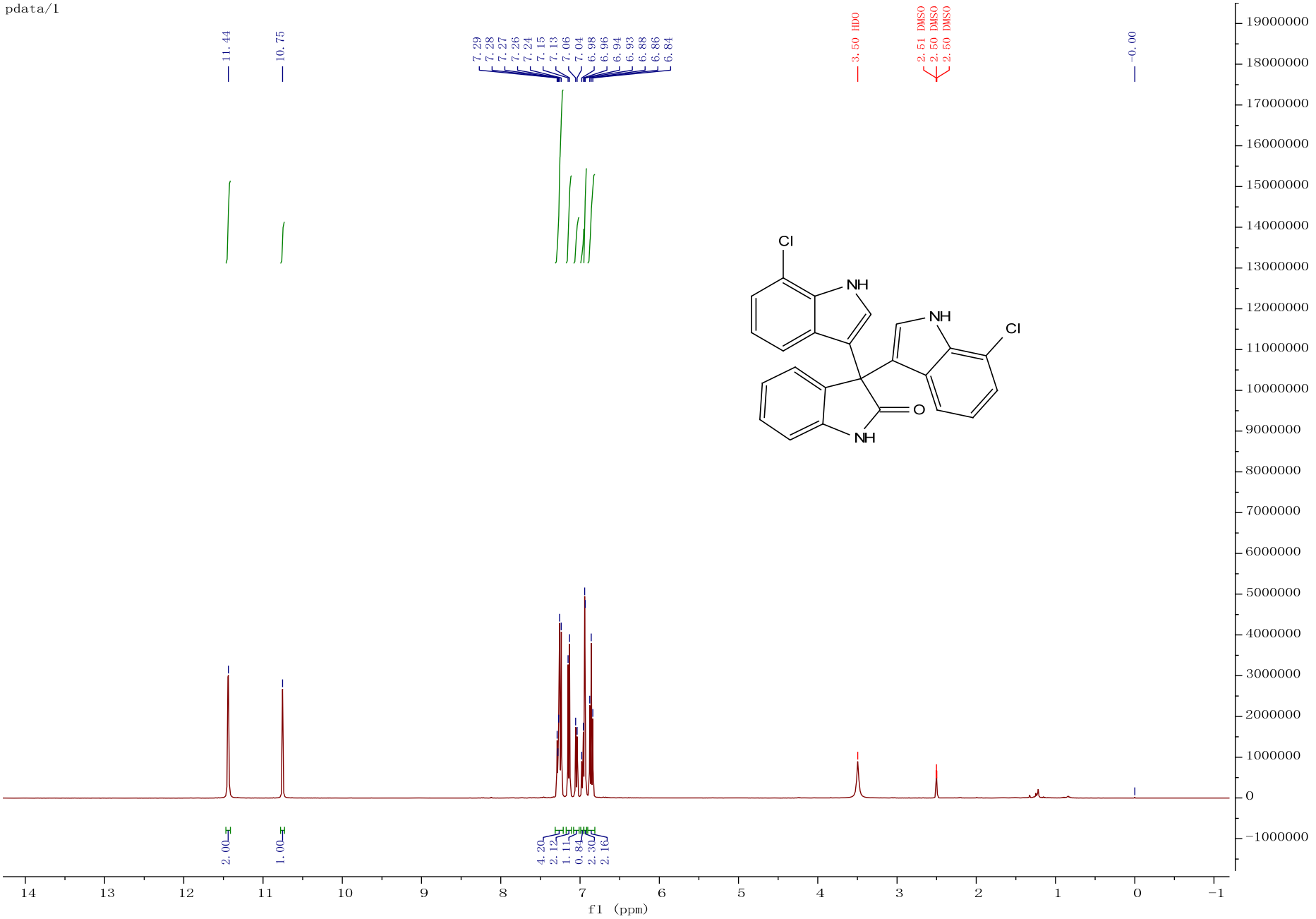
^{1}H NMR spectrum of Compound 3x (DMSO-d_6, 400 MHz)



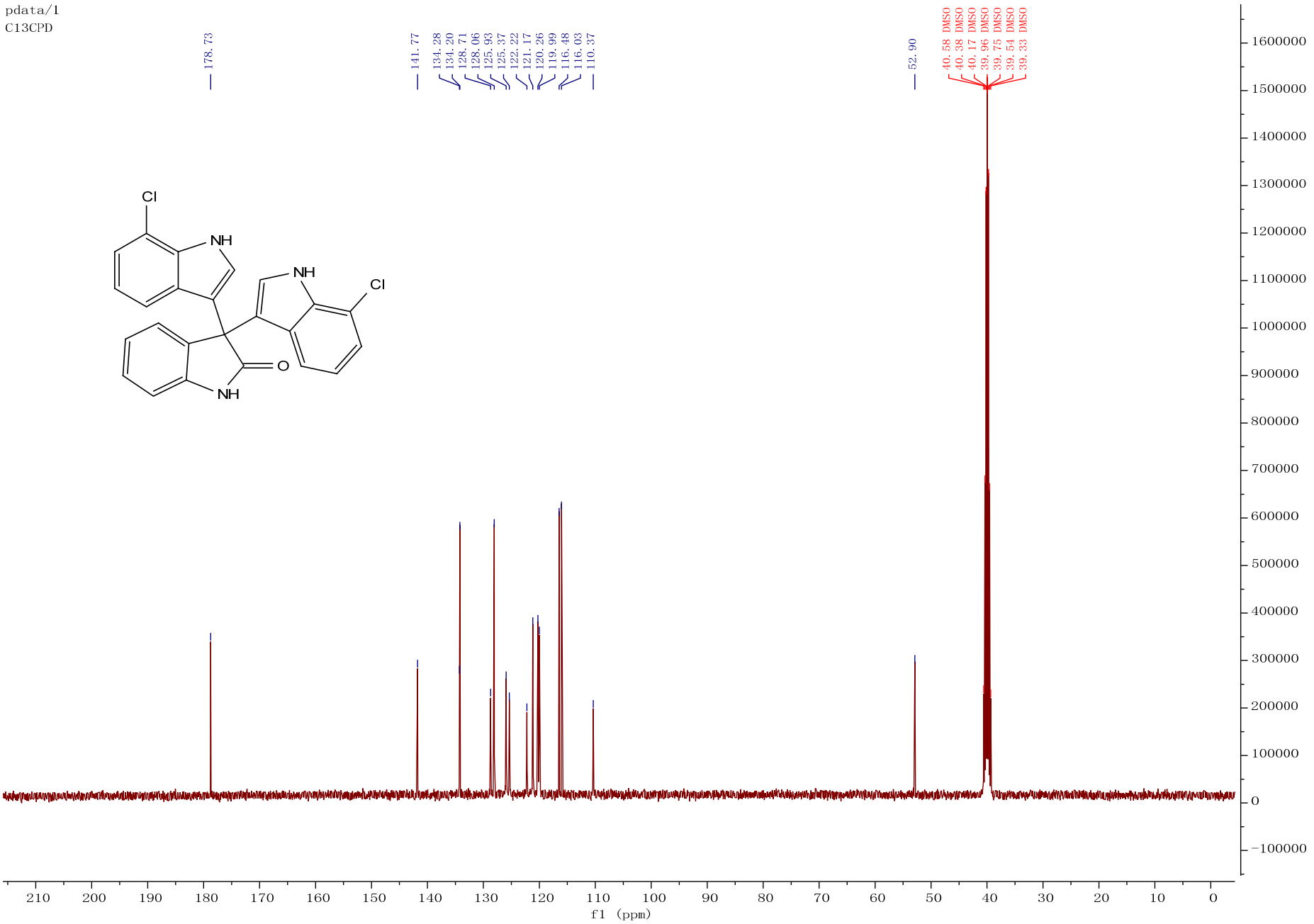
^{13}C NMR spectrum of Compound 3x (DMSO-d_6, 100 MHz)



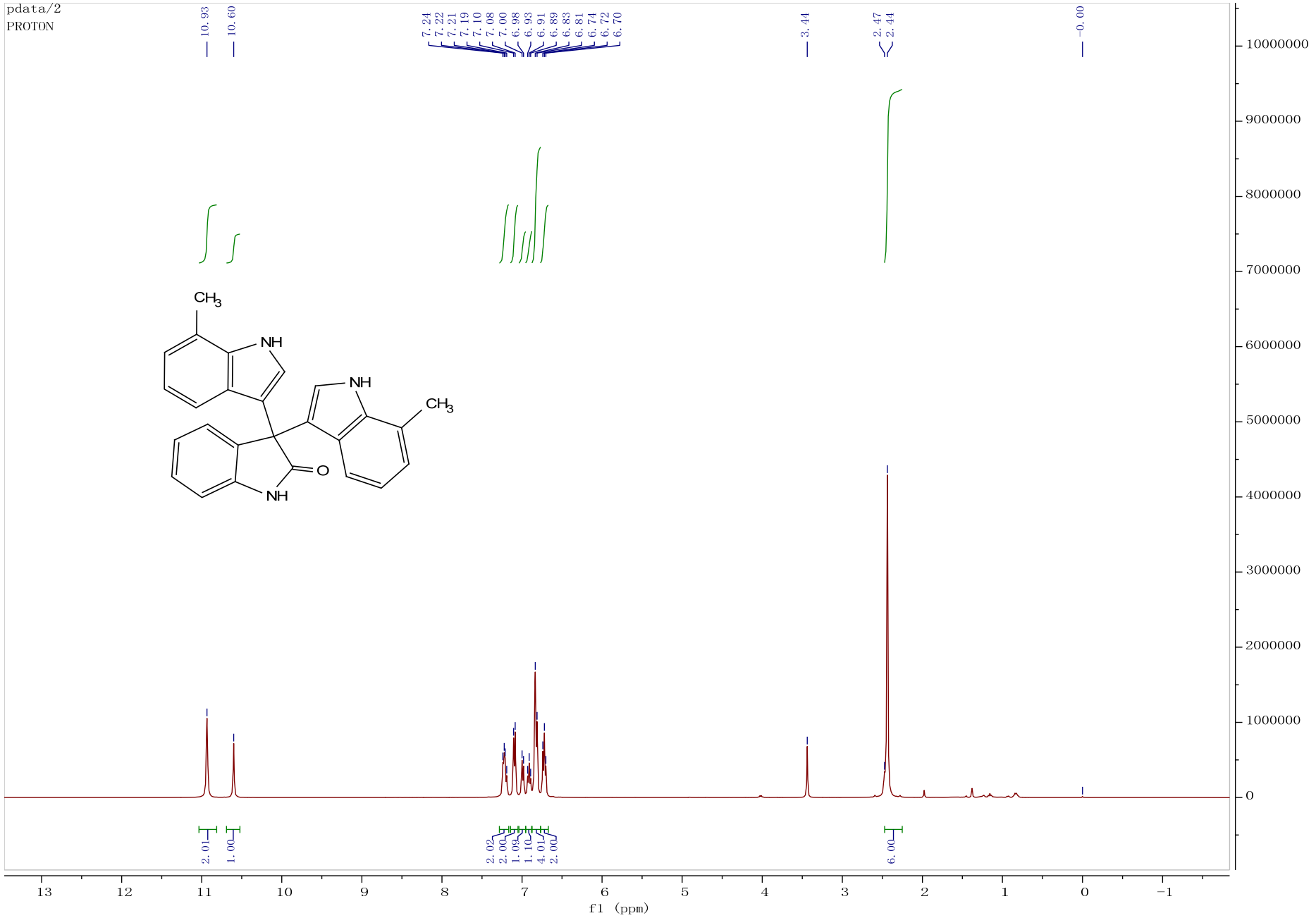
^{1}H NMR spectrum of Compound 3y (DMSO-d_6, 400 MHz)



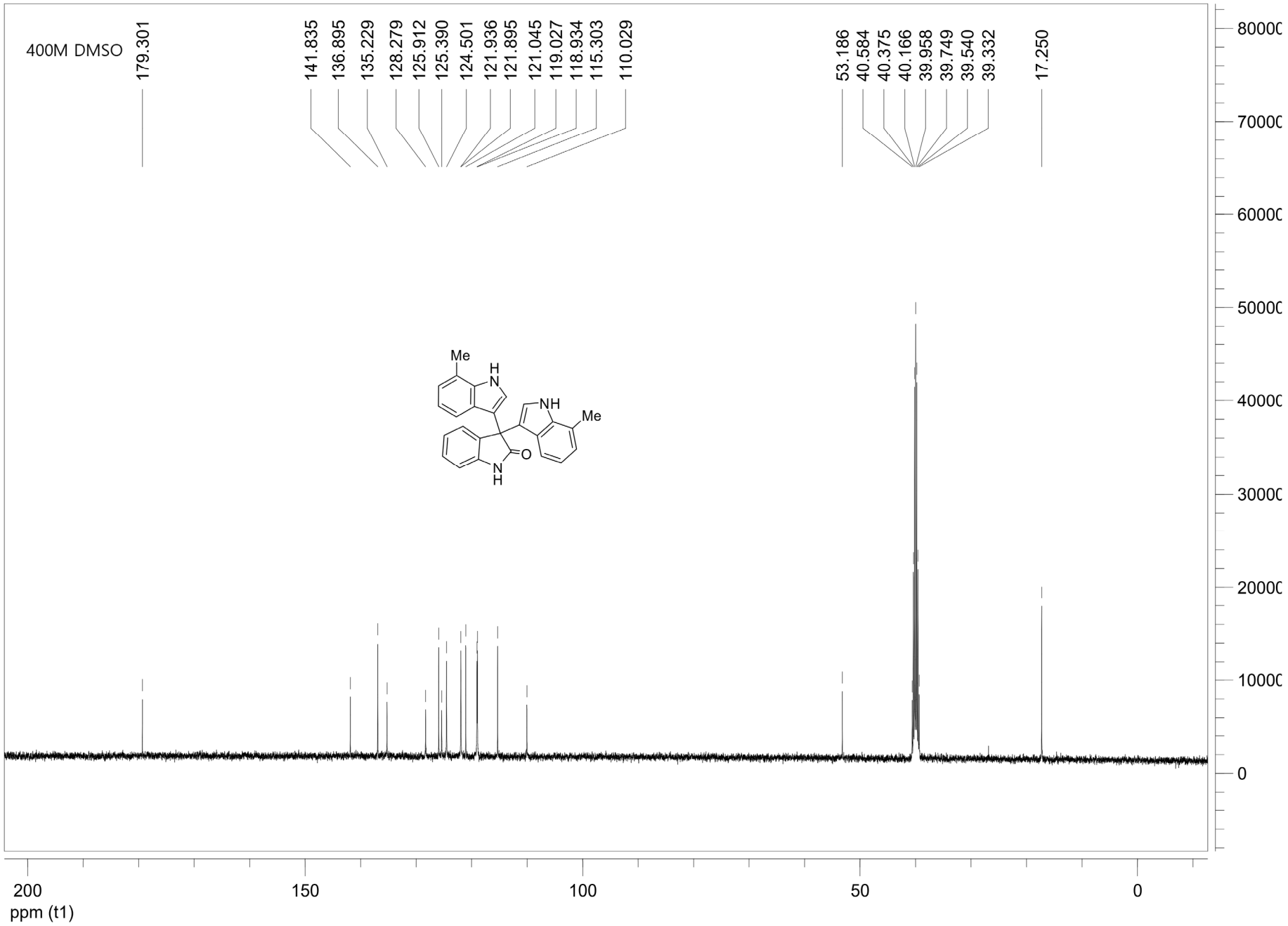
^{13}C NMR spectrum of Compound 3y (DMSO-d_6, 100 MHz)



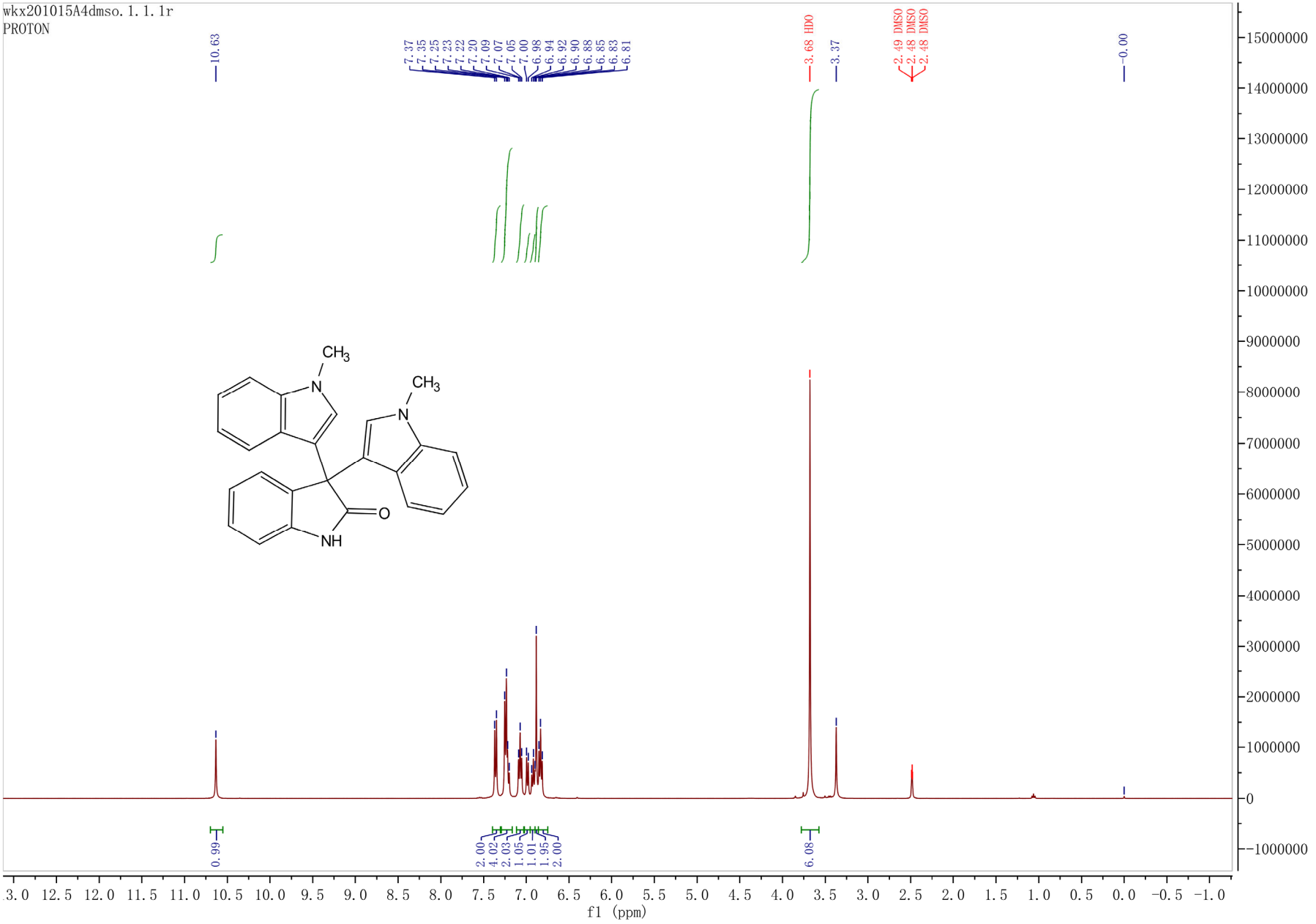
^{1}H NMR spectrum of Compound 3z (DMSO-d_6, 400 MHz)



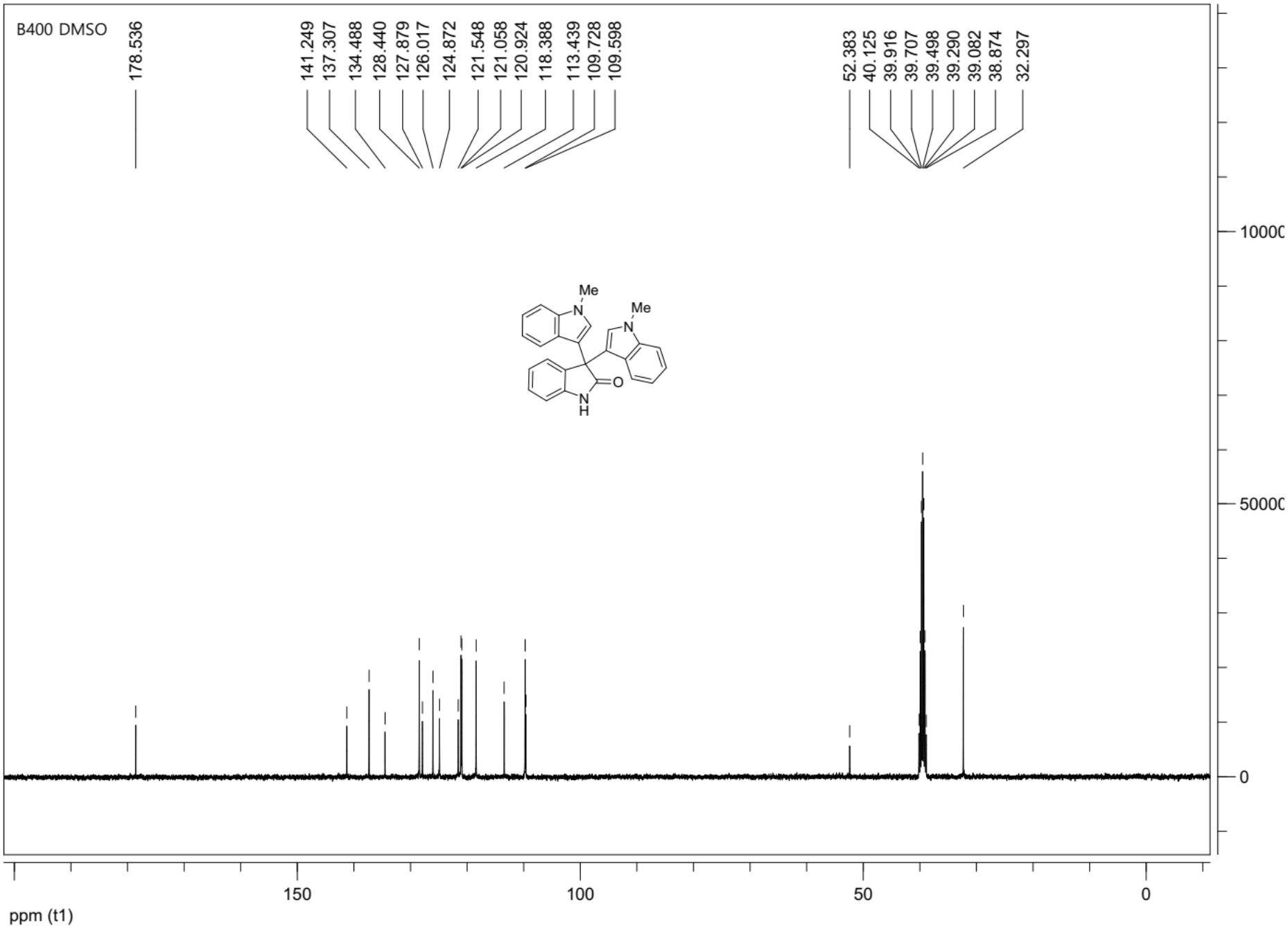
^{13}C NMR spectrum of Compound 3z (DMSO-d_6, 100 MHz)



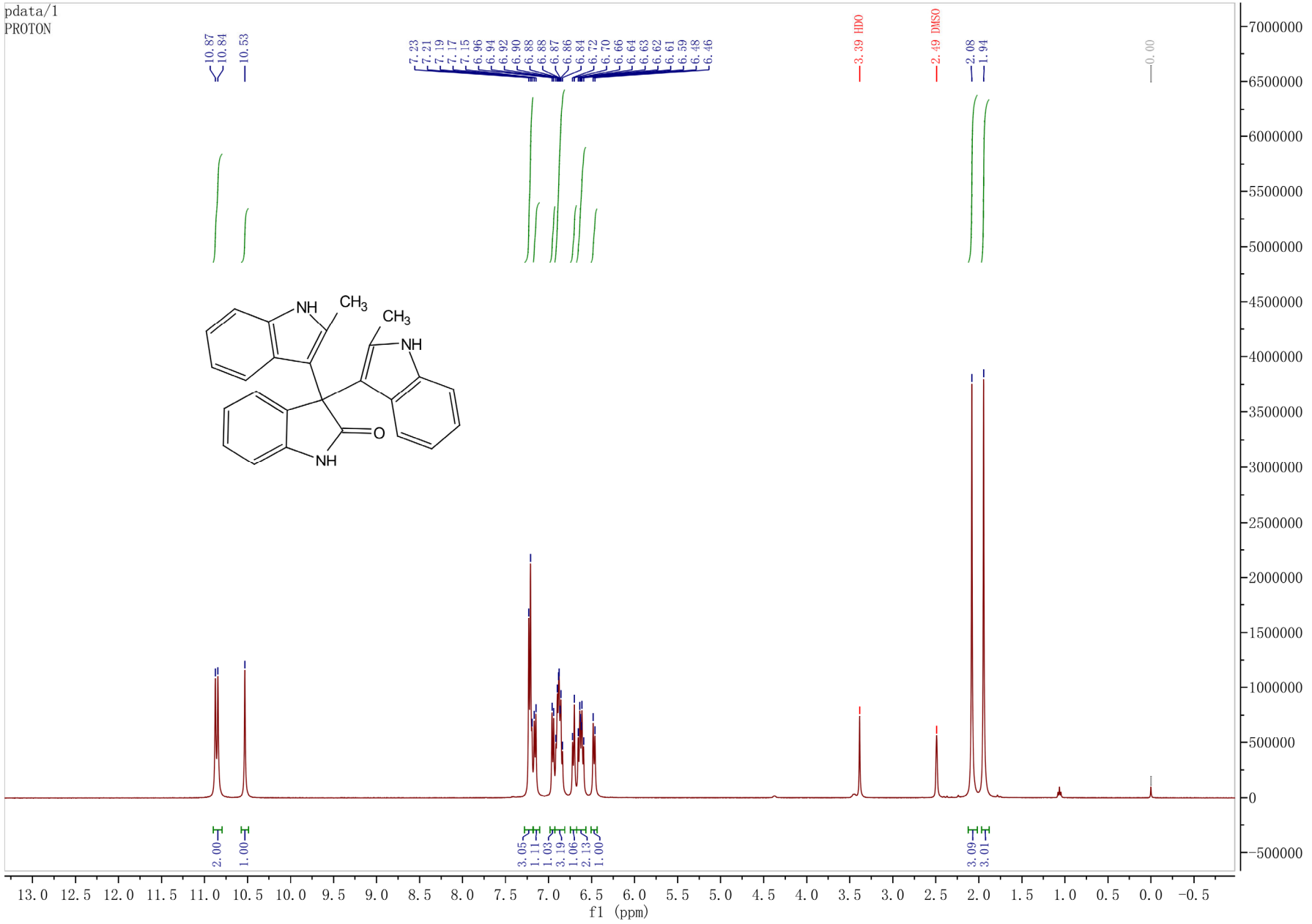
^{1}H NMR spectrum of Compound 3aa (DMSO-d_6, 400 MHz)



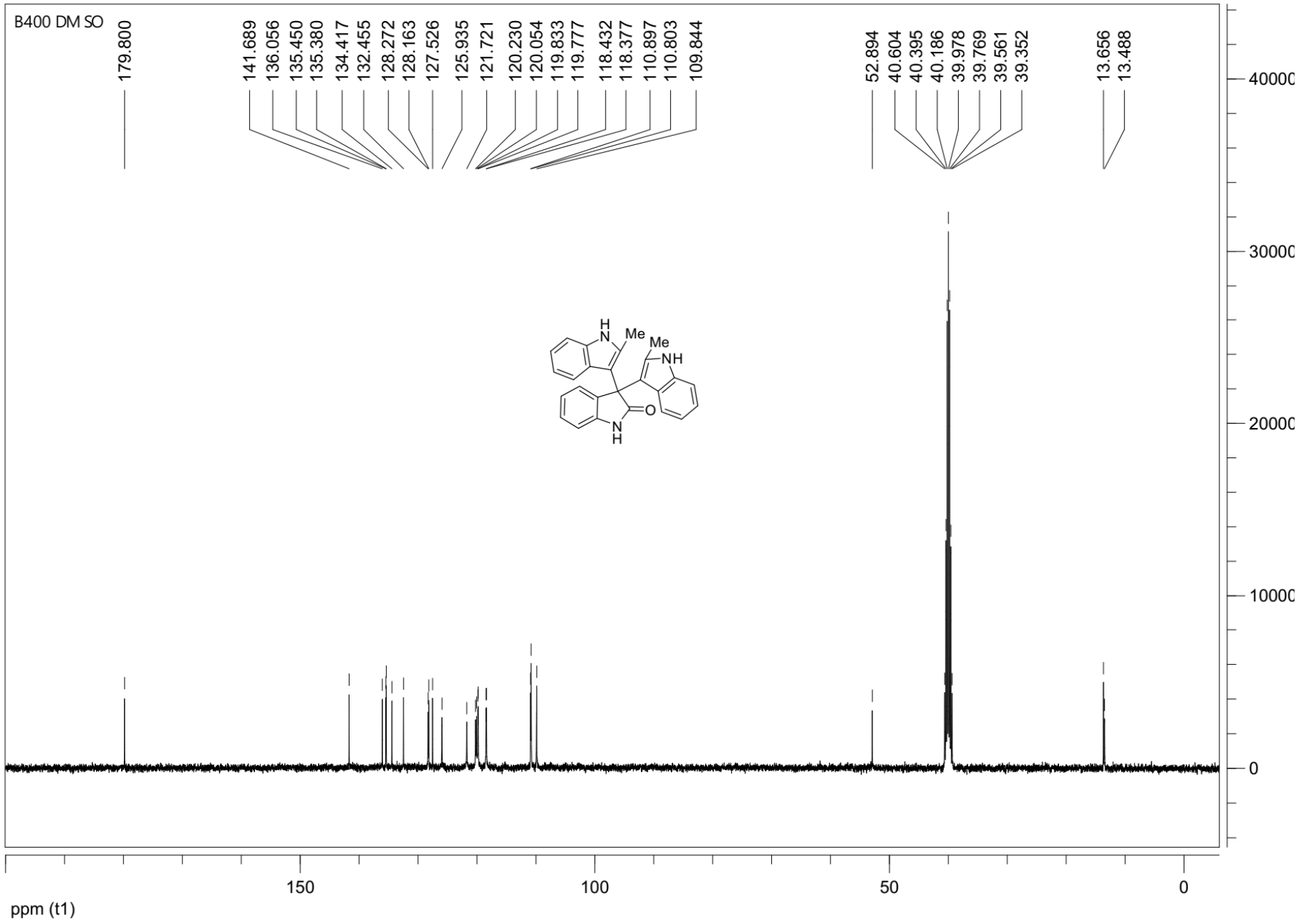
^{13}C NMR spectrum of Compound 3aa (DMSO-d_6, 100 MHz)



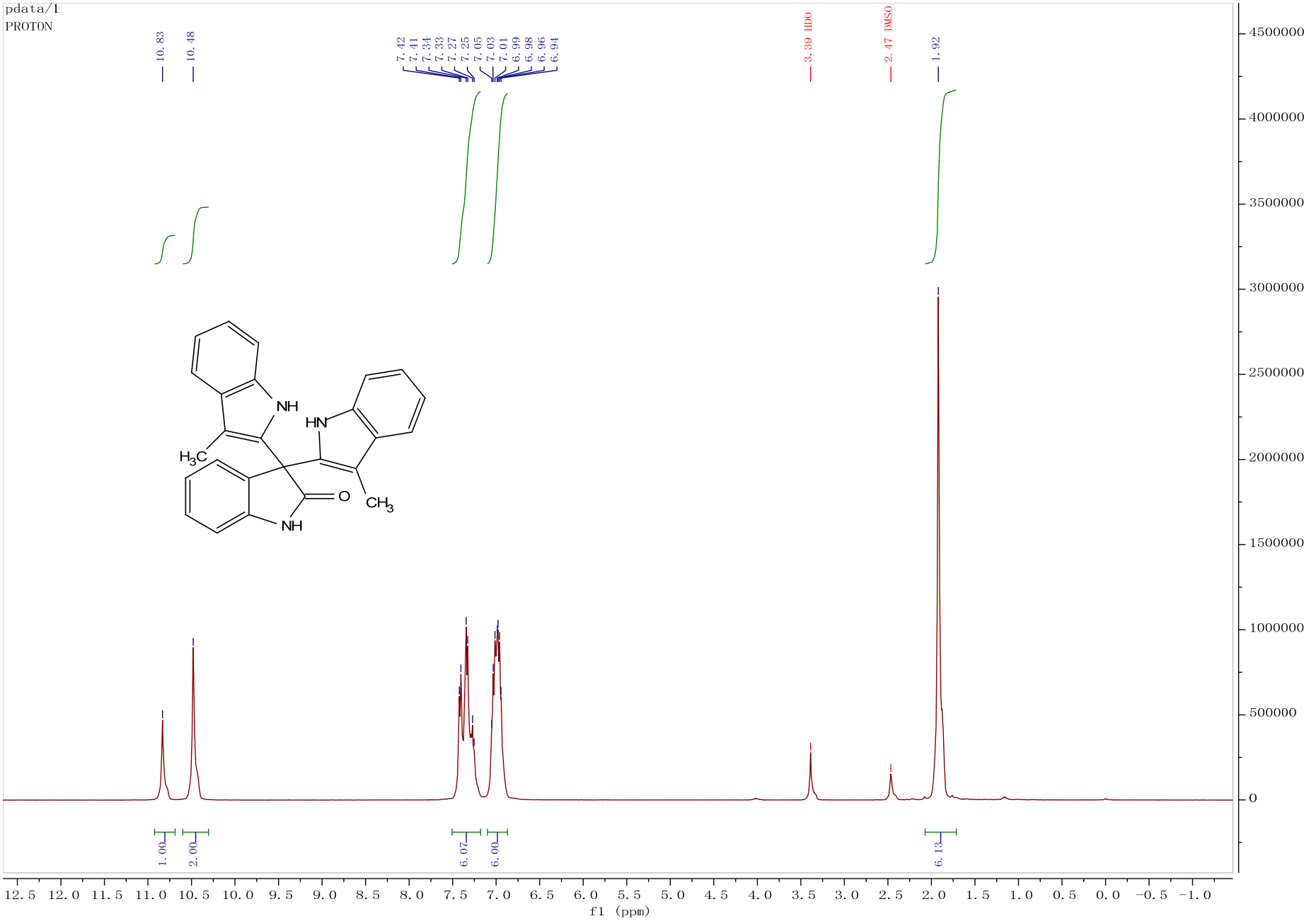
^{1}H NMR spectrum of Compound 3ab (DMSO-d_6, 400 MHz)



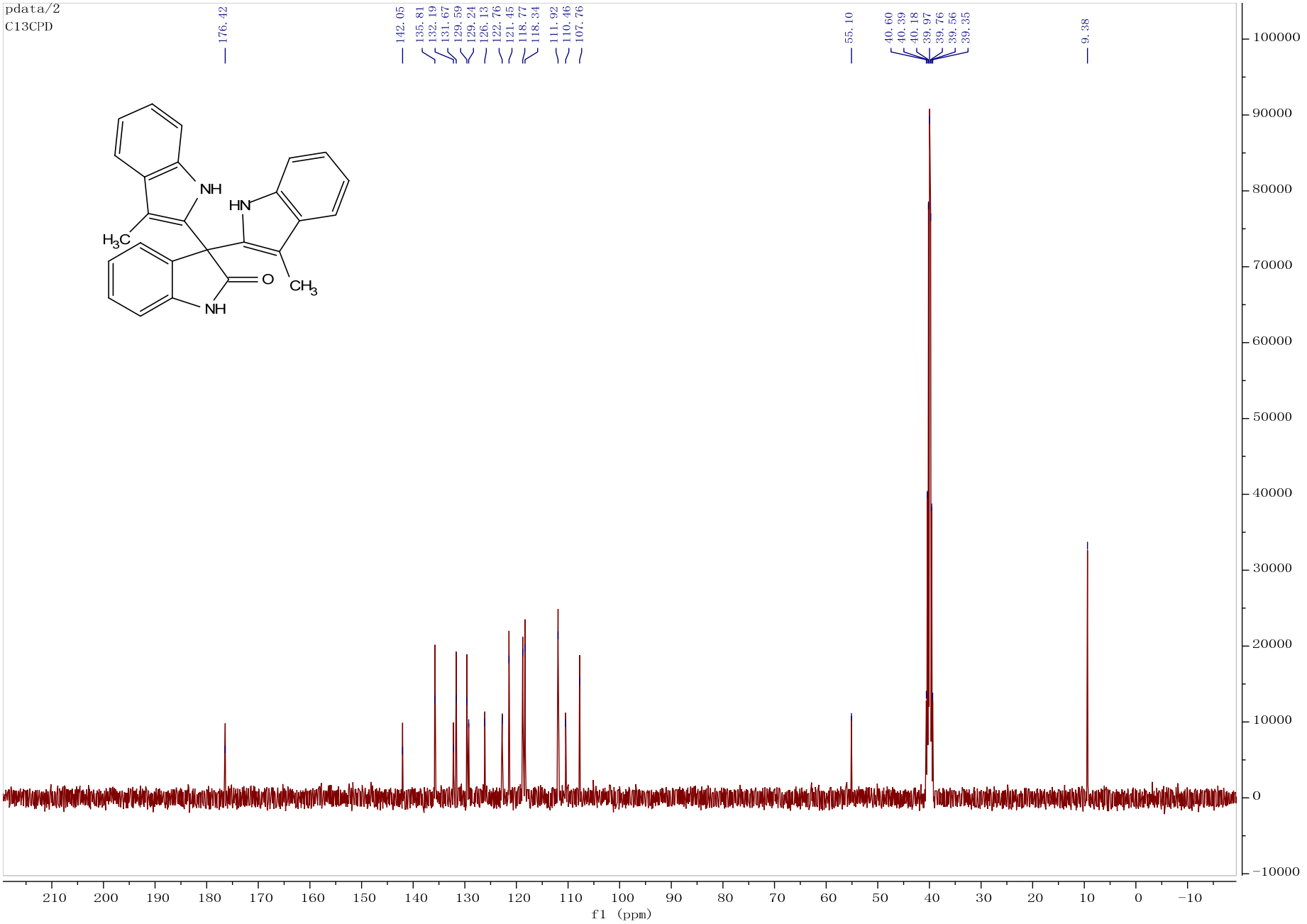
^{13}C NMR spectrum of Compound 3ab (DMSO-d_6, 100 MHz)



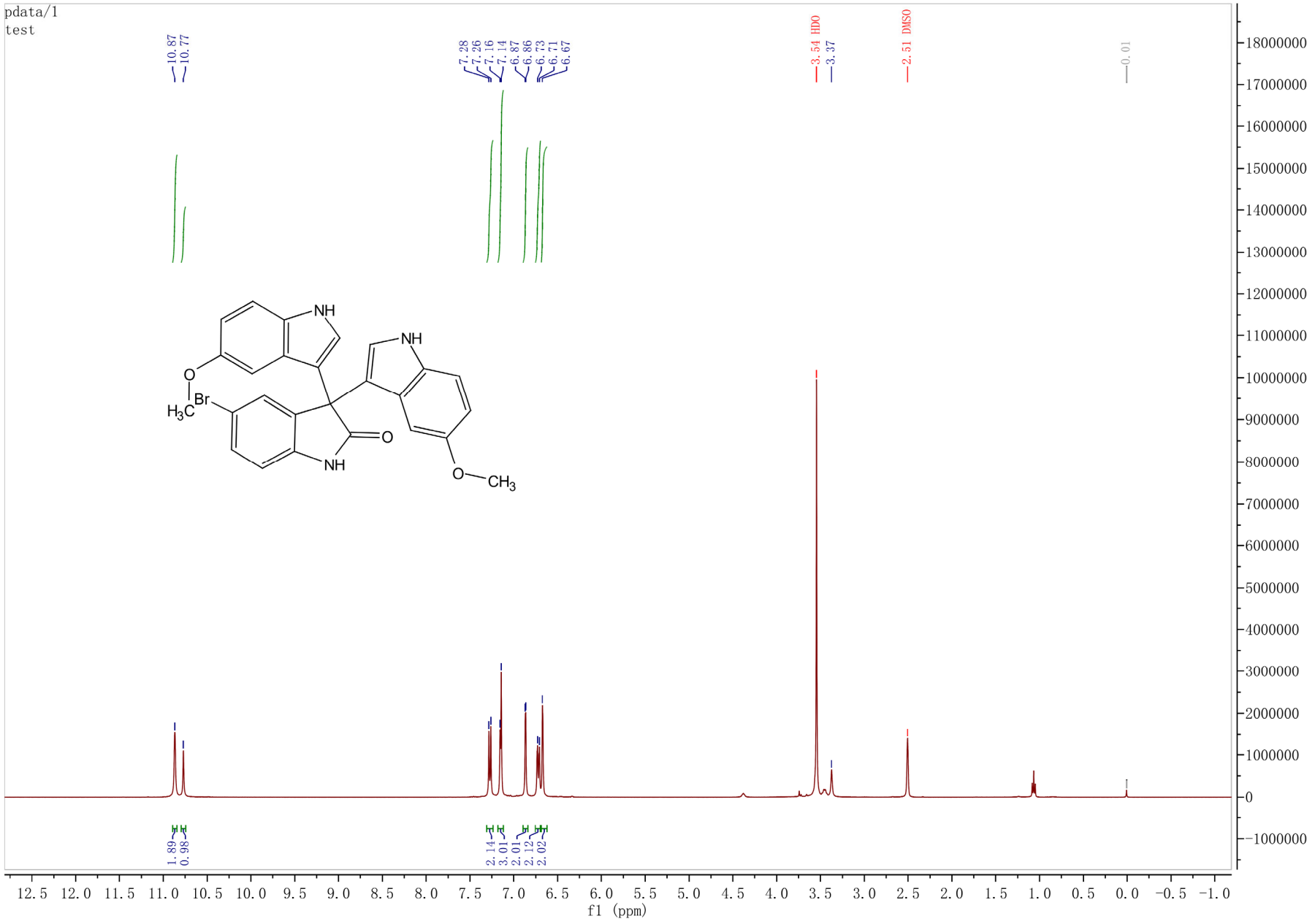
^{1}H NMR spectrum of Compound 3ac (DMSO-d_6, 400 MHz)



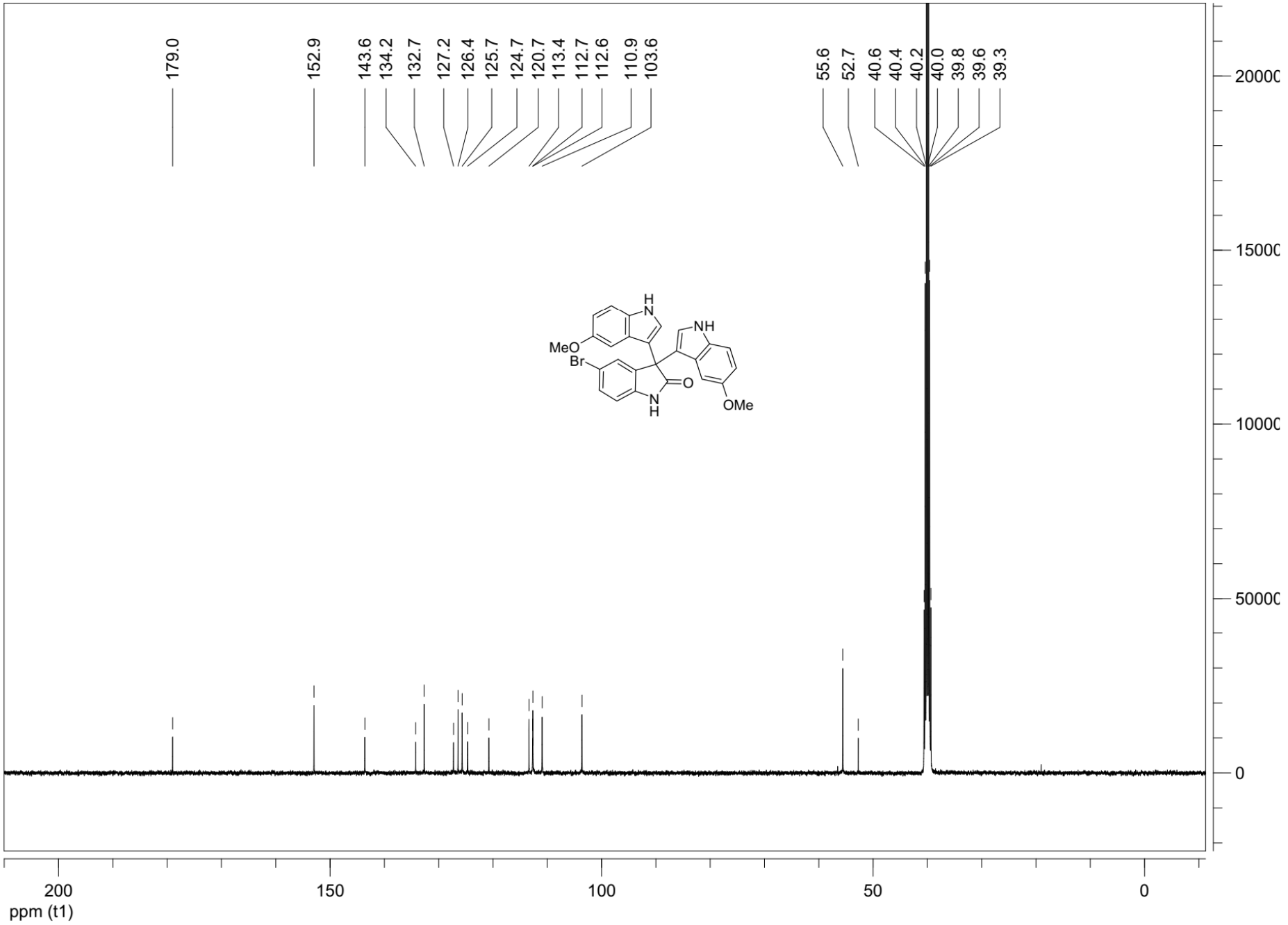
^{13}C NMR spectrum of Compound 3ac (DMSO-d_6, 100 MHz)



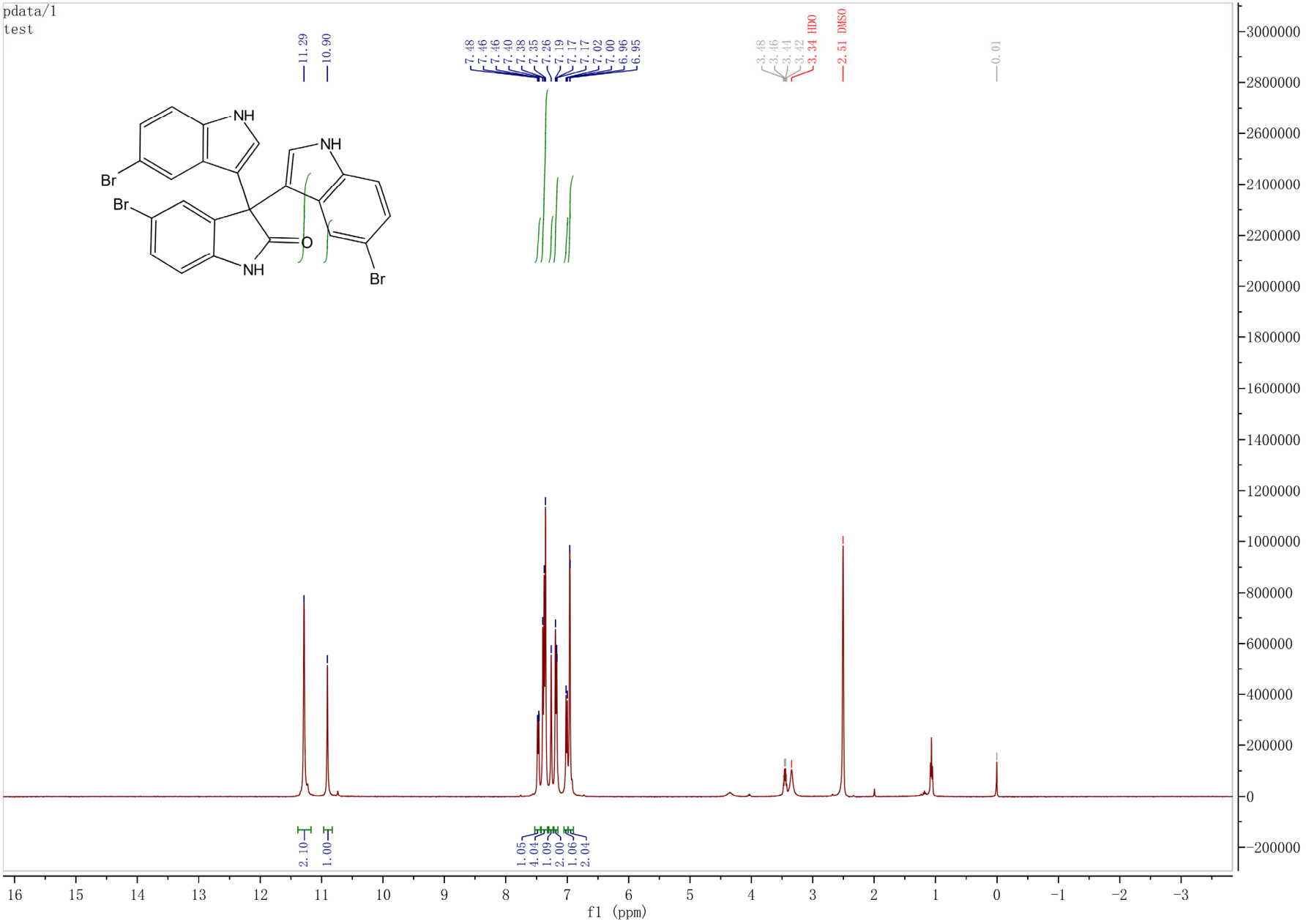
^{1}H NMR spectrum of Compound 3ad (DMSO-d_6, 400 MHz)



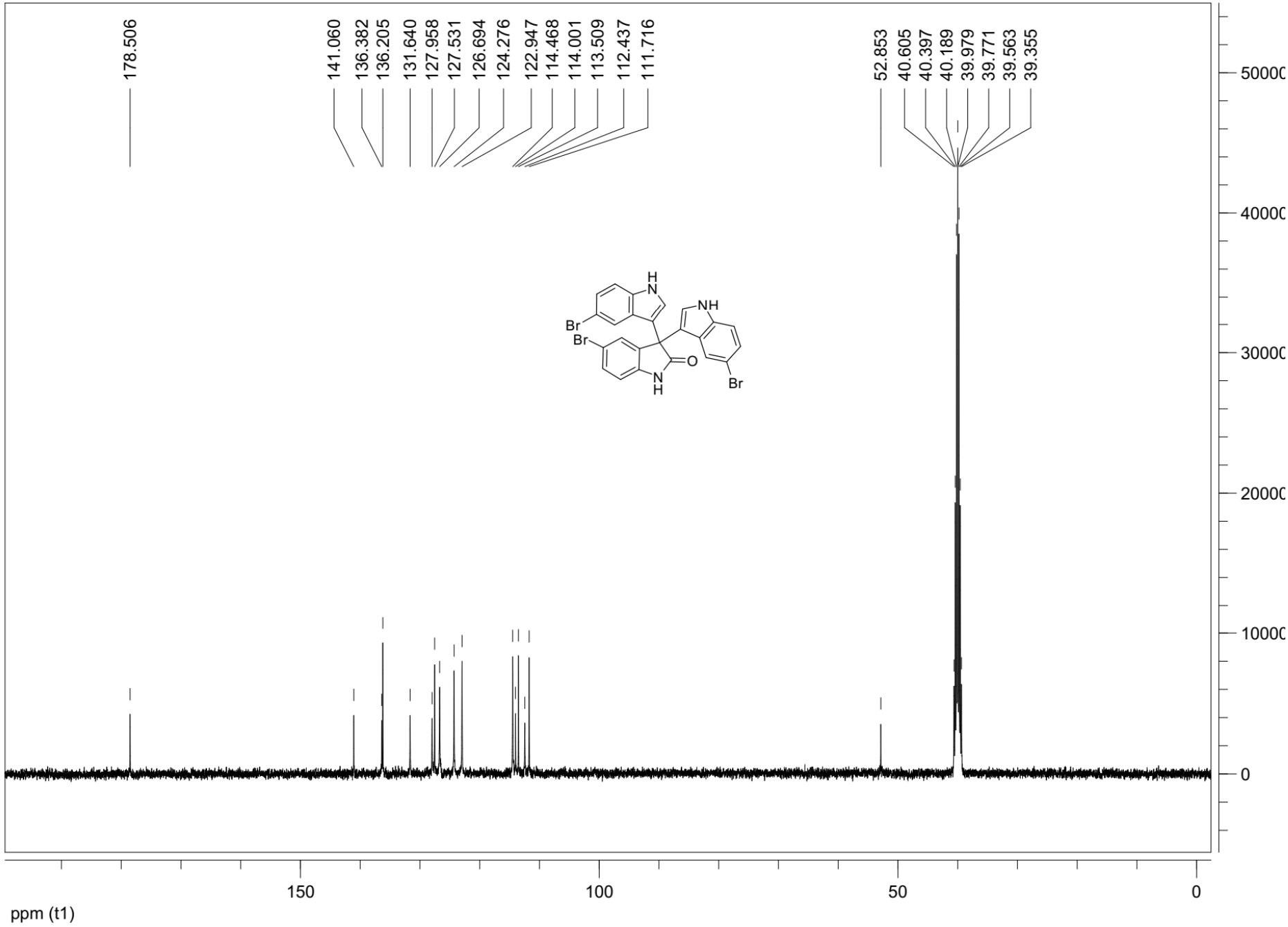
^{13}C NMR spectrum of Compound 3ad (DMSO-d_6, 100 MHz)



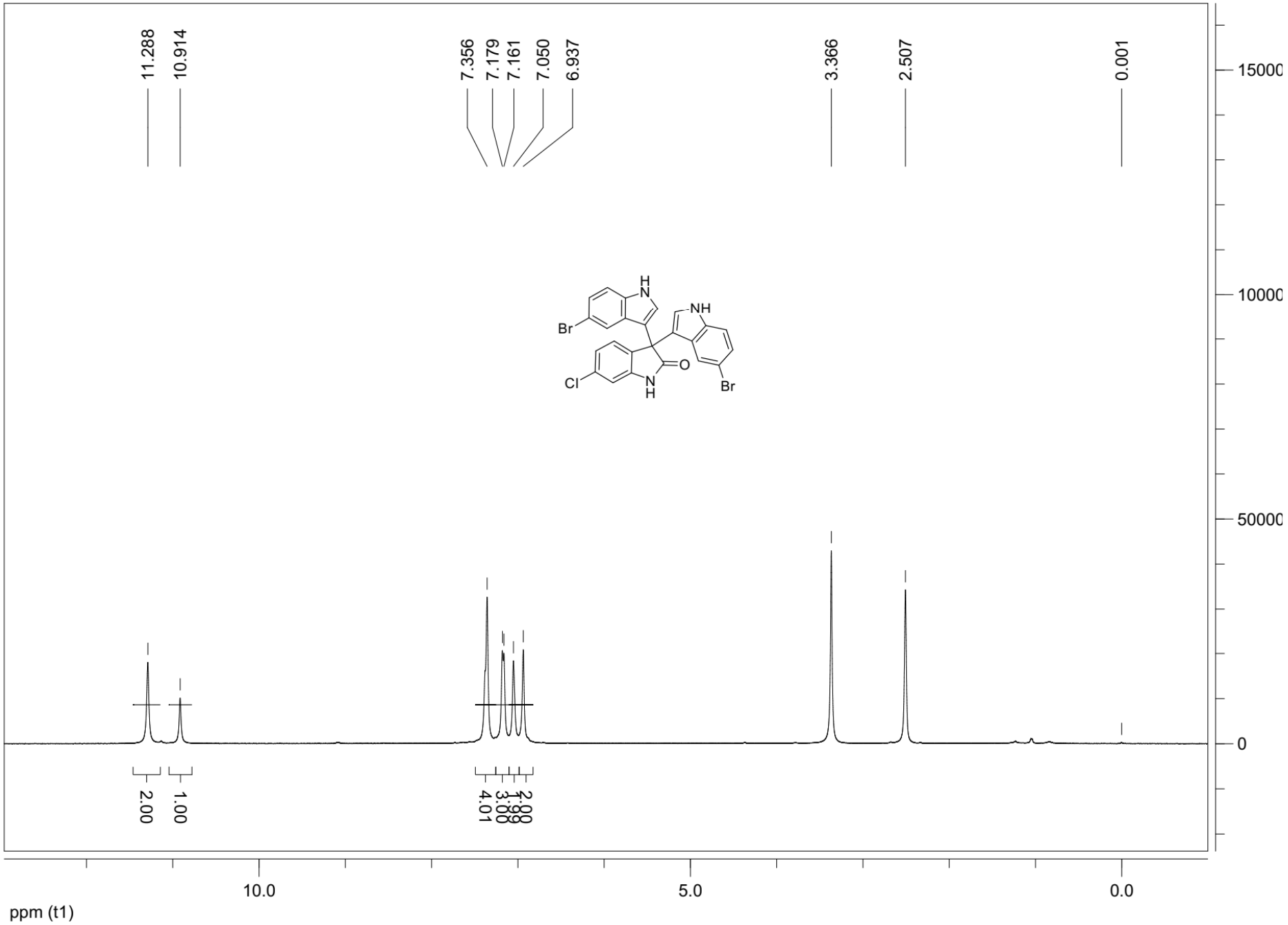
^{1}H NMR spectrum of Compound 3ae (DMSO-d_6, 400 MHz)



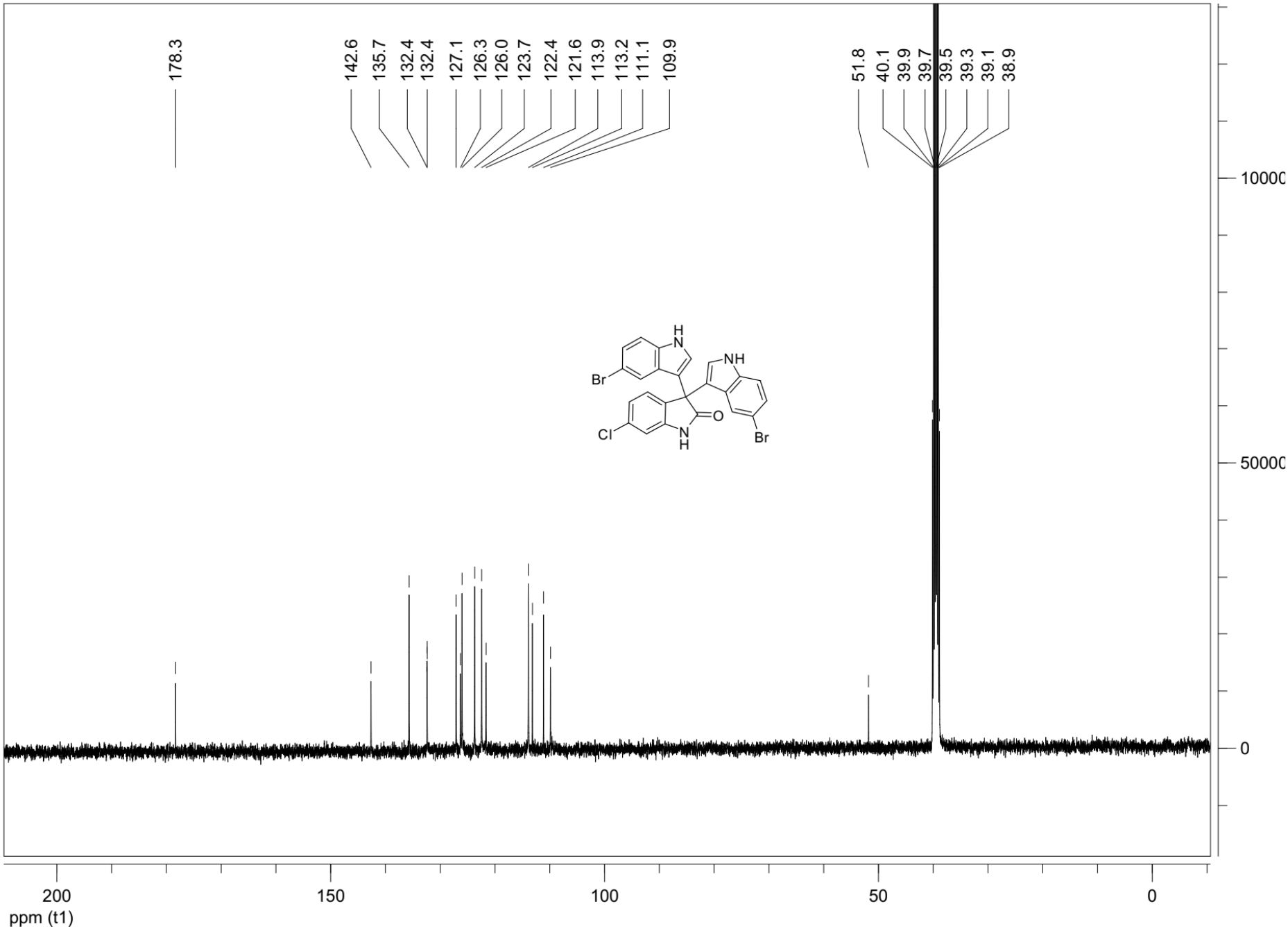
^{13}C NMR spectrum of Compound 3ae (DMSO-d_6, 100 MHz)



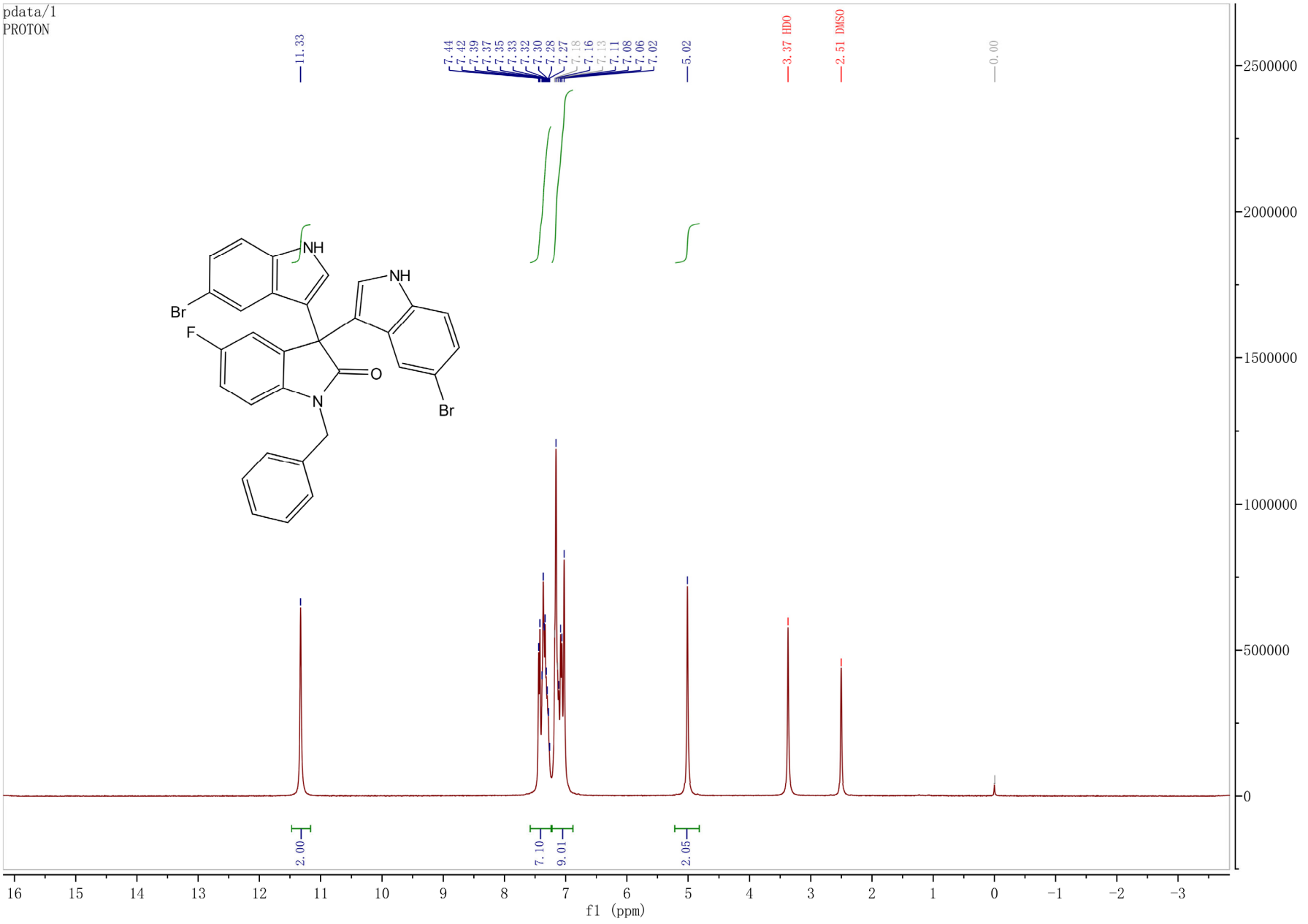
^{1}H NMR spectrum of Compound 3af (DMSO-d_6, 400 MHz)



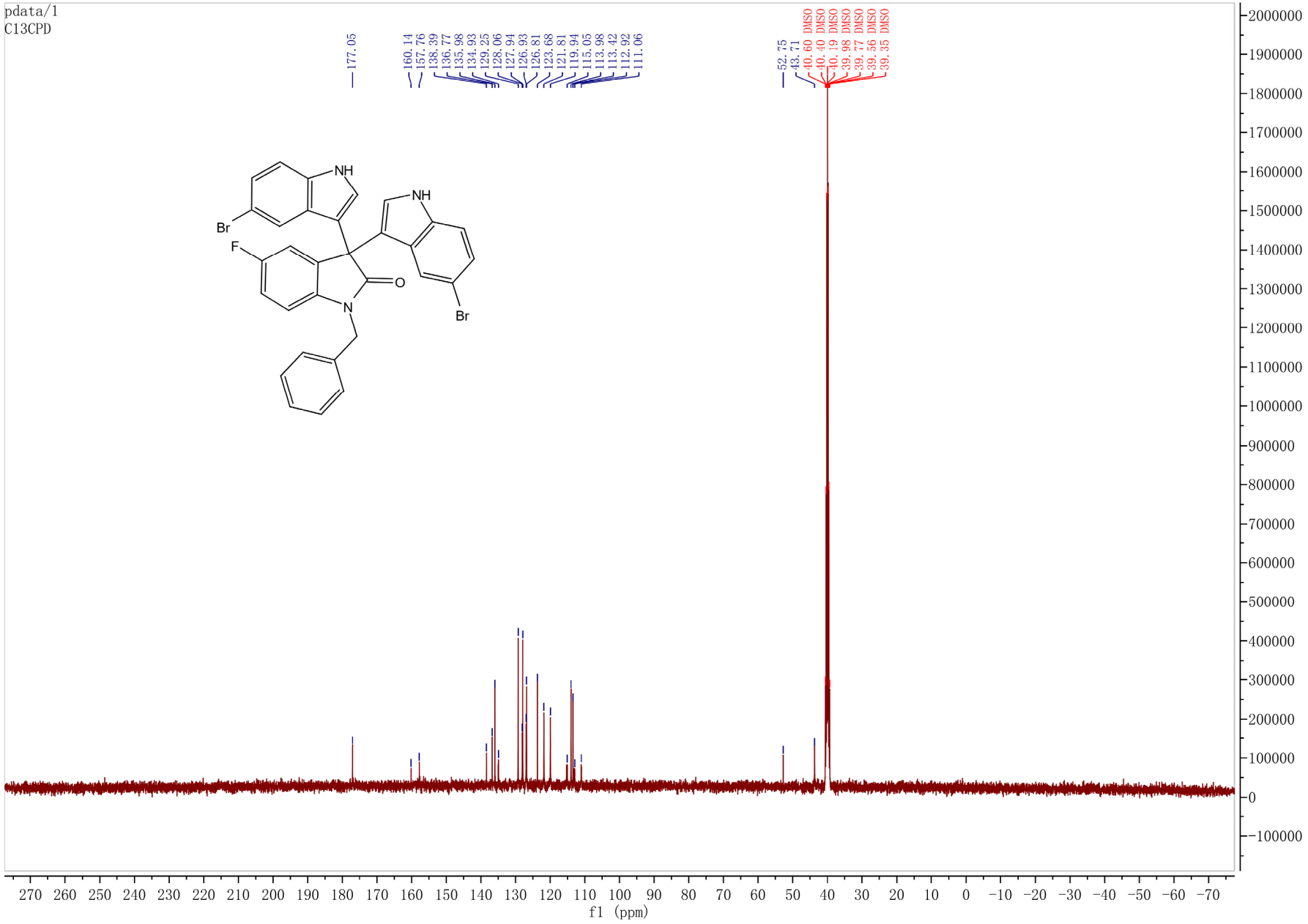
^{13}C NMR spectrum of Compound 3af (DMSO-d_6, 100 MHz)



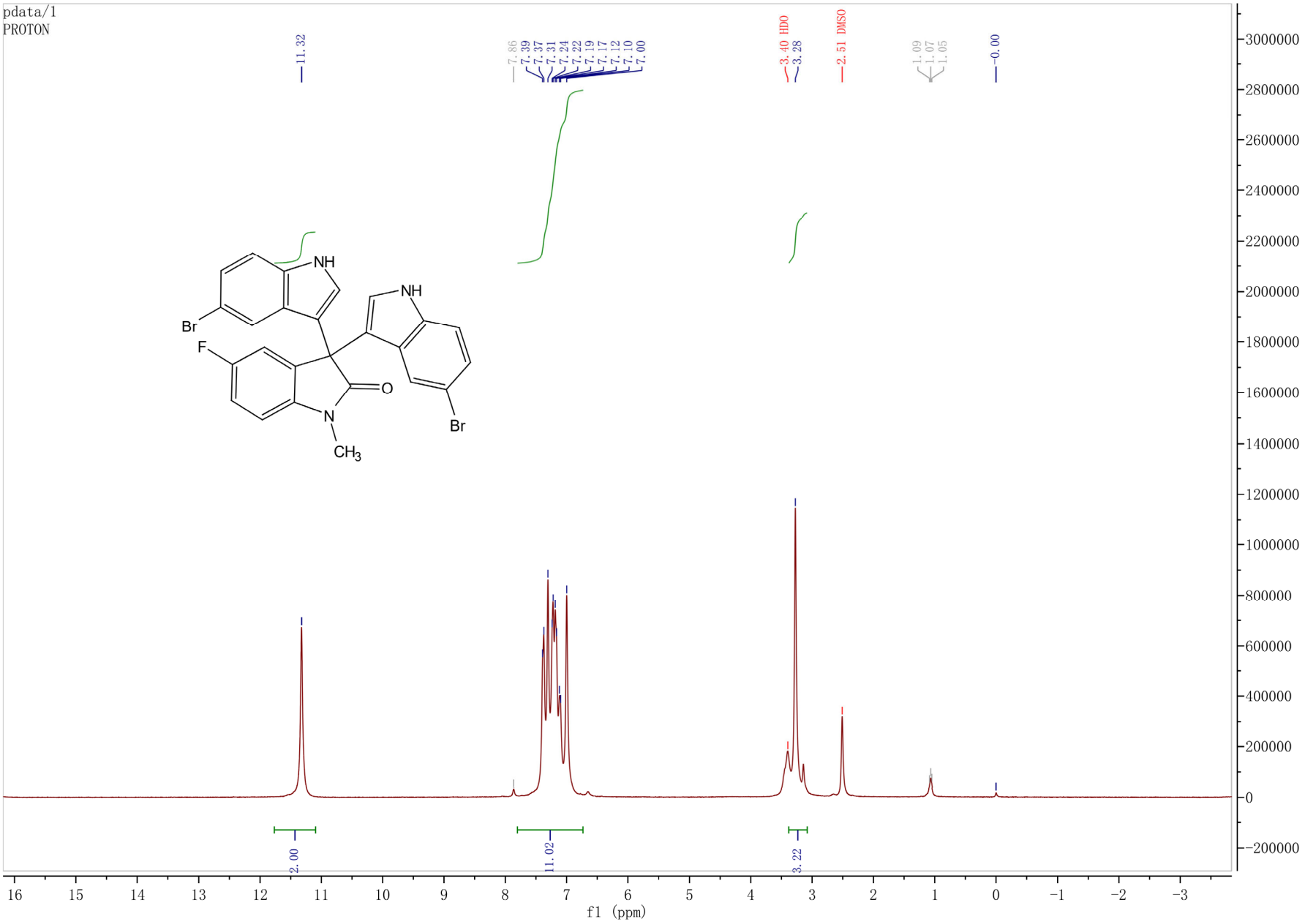
^{1}H NMR spectrum of Compound 3ag (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of Compound 3ag (DMSO-d_6, 100 MHz)



^{1}H NMR spectrum of Compound 3ah (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of Compound 3ah (DMSO-d_6, 100 MHz)