Supporting Information

A rapid approach to specific carbazolelactam system related to calothrixin B

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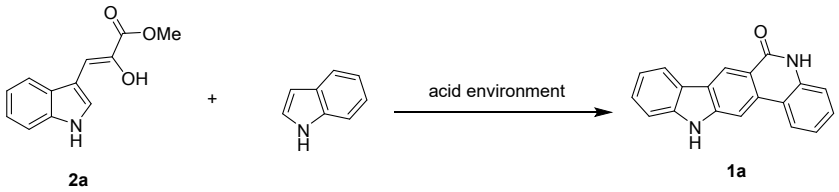
Column chromatographic purifications were performed on SDZF silica gel 160. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on a Bruker NMR spectrometer at 600 MHz, 150 MHz and 565 MHz, respectively, referenced internally based on the residual solvent signal. The data reported for the ^{1}H NMR spectra are as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet), coupling constant in hertz, and number of protons. The data reported for the ^{13}C spectra are given as chemical shift (δ, ppm). The data reported for the ^{19}F spectra are given as chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer by electrospray ionization-time of flight (ESI-TOF) analysis. Melting points were measured with a melting point instrument without correction. All the chemical reagents and solvents were purchased from commercial sources and used as received.

Table 1. Failed attempts for the one-pot construction of **1a**[a]



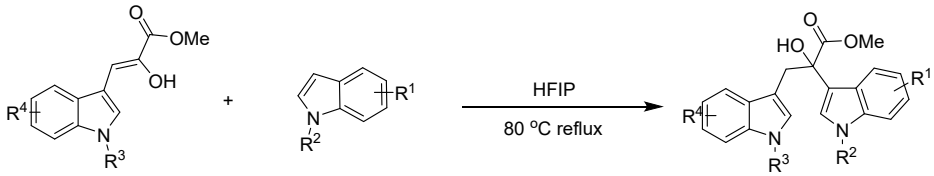
2a **1a**

Entry	Conditions	Temp (°C)	Results[a]
1	AcOH	80	unknown product
2	3.0 eq HCl in MeOH	65	decomposition
3	1.0 eq TFA in DCE	60	no reaction
4	1.0 eq TfOH in DCE	80	decomposition
5	5.0 eq H_3PO_4 in MeOH	65	no reaction
6	Conc. H_3PO_4: EtOH (5:2)	80	decomposition
7	5.0 eq P_2O_5 in Sulfolane Ar	80	decomposition
8	5.0 eq P_2O_5 in DCE Ar	80	decomposition
9	1.0 eq $SnCl_4$ in DCE	60	decomposition
10	1.0 eq $SnCl_4$ in HFIP	60	decomposition
11	1.0 eq $BF_3.Et_2O$ in DCE	84	decomposition
12	1.0 eq $FeCl_3$ in DCE	84	decomposition
13	1.0 eq $ZnCl_2$ in DCE	80	decomposition
14	1.0 eq $Fe(OTf)_3$ in DCE	80	decomposition
15	1.0 eq $Sc(OTf)_3$ in DCE	80	**1a** (trace)
16	1.0 eq $La(OTf)_3$ in DCE	60	no reaction
17	1.0 eq $Yb(OTf)_3$ in DCE	60	no reaction
18	1.0 eq $CoCl_2$ in DCE	80	no reaction
19	1.0 eq $AlCl_3$ in DCE	80	no reaction
20	1.0 eq $TiCl_4$ in DCE	60	**1a** (trace)

[a]Reactions were performed using compound **2a** (200 mg, 0.92 mmol) and indole (129 mg, 1.10 mmol) in acidic solvents for 2-24 h.

2. Experimental and spectroscopic data for compounds **3a-p**, **4a-b**, **1a-p**: **Page S3-14**.

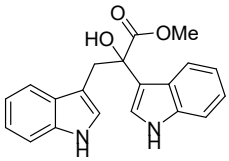
2.1 Synthesis of compounds **3a-p**



2 **3a-p**

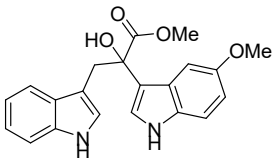
To a solution of compound **2** (2.0 g, 9.22 mmol) in 20 mL HFIP was added indole (1.29 g, 11.06 mmol), and the solution was stirred at 80 °C for 24 h. The solution was concentrated under reduce pressure. The obtained crude products were purified by flash column silica gel chromatography to give compound **3**.

Methyl 2-hydroxy-2,3-di(1H-indol-3-yl) propanoate (3a)



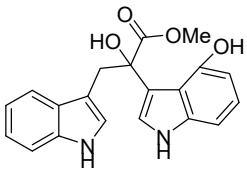
Purified by flash column silica gel chromatography (DCM/MeOH=300:1) to give **3a** as a beige solid (2.24 g, yield 75 %). m.p. 77.1-77.9 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (s, 1H), 10.81 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 2.3 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.11 – 7.06 (m, 2H), 7.01 (dt, J = 21.4, 7.4 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 5.36 (s, 1H), 3.77 (d, J = 14.5 Hz, 1H), 3.48 (s, 3H), 3.45 (d, J = 14.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 136.8, 136.0, 128.2, 125.2, 124.0, 122.6, 122.2, 122.0, 120.8, 120.0, 119.5, 119.3, 117.2, 111.5, 111.2, 109.6, 52.9, 34.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_3Na$ 357.1210; Found 357.1199.

Methyl 2-hydroxy-3-(1H-indol-3-yl)-2-(5-methoxy-1H-indol-3-yl) propanoate (3b)



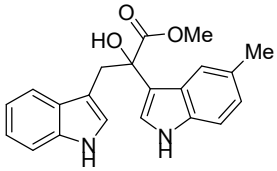
Purified by flash column silica gel chromatography (DCM/MeOH=300:1) to give **3b** as a white solid (1.78 g, yield 53%). m.p. 163.5-164.3 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.90 (s, 1H), 10.81 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 5.7 Hz, 2H), 7.10 (d, J = 1.7 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.74 (dd, J = 8.8, 2.3 Hz, 1H), 5.37 (s, 1H), 3.76 (s, 1H), 3.73 (s, 3H), 3.50 (s, 3H), 3.44 (d, J = 14.5 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.7, 152.9, 135.7, 131.8, 128.4, 125.7, 124.3, 123.5, 120.5, 119.1, 118.1, 117.28, 112.1, 111.1, 111.0, 109.3, 102.6, 76.5, 55.3, 51.7, 34.57. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2O_4Na$ 387.1315; Found 387.1299.

Methyl 2-hydroxy-2-(4-hydroxy-1H-indol-3-yl)-3-(1H-indol-3-yl) propanoate (3c)



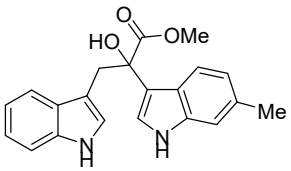
Purified by flash column silica gel chromatography (DCM/MeOH=200:1-100:1) to give **3c** as a yellow solid (1.71 g, yield 53%). m.p. 87.6-88.5 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.07 (s, 1H), 10.84 (s, 1H), 10.21 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.11 (d, J = 1.8 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.95 (dt, J = 15.6, 7.6 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.37 (d, J = 7.5 Hz, 1H), 3.78 (d, J = 14.7 Hz, 1H), 3.53 (s, 3H), 3.42 (d, J = 14.7 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.5, 149.9, 135.7, 128.3, 124.4, 122. 8, 121.3, 120.6, 119.0, 118.2, 116.7, 115.0, 108.9, 104.0, 102.9, 76.5, 51.9, 35.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_4Na$ 373.1159; Found 373.1149.

Methyl 2-hydroxy-3-(1H-indol-3-yl)-2-(5-methyl-1H-indol-3-yl) propanoate (3d)



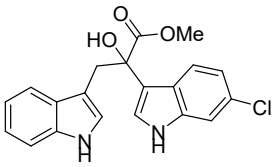
Purified by flash column silica gel chromatography (DCM) to give **3d** as a white solid (2.79 g, yield 87%). m.p. 75.7-76.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 10.2 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 2.2 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 4.01 (d, J = 14.4 Hz, 1H), 3.84 (s, 1H), 3.66 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.6, 136.0, 135.1, 129.3, 128.2, 125.5, 123.9, 123.9, 122.5, 122.0, 120.4, 119.5, 119.3, 116.9, 111.2, 111.0, 109.7, 52.8, 34.7, 21.7. HRMS (ESI-TOF) *m/z*: $[M - H]^-$ Calcd for $C_{21}H_{19}N_2O_3$ 347.1390; found 347.1396.

Methyl 2-hydroxy-3-(1H-indol-3-yl)-2-(6-methyl-1H-indol-3-yl) propanoate (3e)



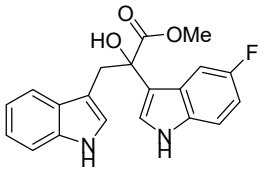
Purified by flash column silica gel chromatography (DCM) to give **3e** as a beige solid (1.83 g, yield 57%). m.p. 86.1-87.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 27.0 Hz, 2H), 7.91 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.23 – 7.17 (m, 2H), 7.16 (d, J = 2.1 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 4.03 (d, J = 14.4 Hz, 1H), 3.67 (s, 3H), 3.64 (d, J = 14.5 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 137.4, 136.0, 132.1, 128.3, 124.0, 123.2, 122.0, 122.0, 121.9, 120.5, 119. 6, 119.4, 117.3, 111.4, 111.2, 109.8, 52.9, 34. 8, 21.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2O_3Na$ 371.1366; found 371.1356.

Methyl 2-(6-chloro-1H-indol-3-yl)-2-hydroxy-3-(1H-indol-3-yl) propanoate (3f)



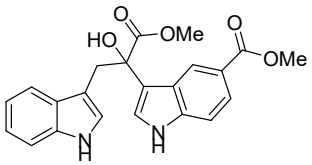
Purified by flash column silica gel chromatography (DCM/MeOH=300:1-150:1) to give **3f** as a white solid (1.46 g, yield 43 %). m.p. 87.3-88.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 41.7 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 13.8, 4.8 Hz, 2H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 3.97 (d, *J* = 14.4 Hz, 1H), 3.67 (s, 3H), 3.62 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$+DMSO-d_6) δ 175.3, 137.3, 136.1, 128.1, 127.1, 124.2, 123.9, 123.5, 121. 6, 121.2, 119.7, 118.9, 118.8, 116.9, 111.3, 111.3, 108.8, 76.7, 52.5, 35.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+ C_{20}H_{17}N_2O_3ClNa$ 391.0820; found 391.0808.

Methyl 2-(5-fluoro-1H-indol-3-yl)-2-hydroxy-3-(1H-indol-3-yl) propanoate (3g)



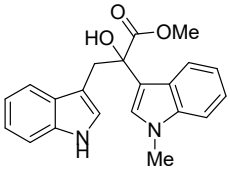
Purified by flash column silica gel chromatography (DCM) to give **3g** as a beige solid (1.91 g, yield 59 %). m.p. 69.8-70.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.19 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.32 (dd, *J* = 8.4, 4.9 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H), 3.98 (d, *J* = 14.4 Hz, 1H), 3.68 (s, 3H), 3.60 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.4, 157.2(d, *J* = 233.0 Hz), 136.0, 133.3, 128.1, 125.6 (d, *J* = 10.2 Hz), 124.3, 124.0, 122.1, 119.7, 119.3, 117. 4 (d, *J* = 4.7 Hz), 112.1 (d, *J* = 9.8 Hz), 111.3, 110.8 (d, *J* = 26.1 Hz), 109.4, 105.9 (d, *J* = 24.0 Hz), 52.9, 34.8. ^{19}F NMR (565 MHz, DMSO-d_6) δ -123. 7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+ C_{20}H_{17}N_2O_3FNa$ 375.1115; found 375.1104.

Methyl 3-(2-hydroxy-3-(1H-indol-3-yl)-1-methoxy-1-oxopropan-2-yl)-1H-indole-5-carboxylate (3h)



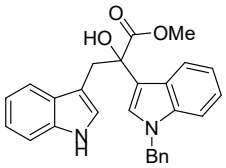
Purified by flash column silica gel chromatography (DCM) to give **3h** as white solid (2.35 g, yield 65%). m.p. 218.9-219.7 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.45 (s, 1H), 10.81 (s, 1H), 8.58 (s, 1H), 7.73 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.55 (t, *J* = 5.2 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 5.57 (s, 1H), 3.85 (s, 3H), 3.75 (d, *J* = 14.5 Hz, 1H), 3.50 (s, 3H), 3.47 (d, *J* = 14.6 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.4, 167.4, 139.2, 135.7, 128.3, 125.0, 124.8, 124.3, 123. 6, 122.0, 120.6, 120.2, 119.1, 118.9, 118.1, 111.5, 111.1, 109.0, 76.4, 51.8, 51.7, 35.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}N_2O_5Na$ 415.1264; Found 415.1253.

Methyl 2-hydroxy-3-(1H-indol-3-yl)-2-(1-methyl-1H-indol-3-yl) propanoate (3i)



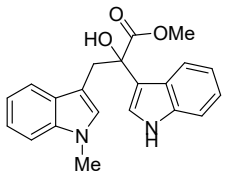
Purified by flash column silica gel chromatography (DCM/MeOH=300:1-150:1) to give **3i** as a white solid (2.57 g, yield 80%). m.p. 155.2-155.9 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.45 (s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 7.05 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 5.40 (s, 1H), 3.79 (s, 1H), 3.77 (s, 3H), 3.49 (s, 3H), 3.45 (d, J = 14.5 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 175.1, 137.4, 136.2, 128.8, 127.7, 126.1, 124.8, 121. 6, 121.2, 121.0, 119.5, 119.3, 118.6, 117.3, 111.6, 110.2, 109.6, 76. 9, 52.1, 35.3, 32.9. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_3Na$ 371.1366; found 371.1351.

Methyl 2-(1-benzyl-1H-indol-3-yl)-2-hydroxy-3-(1H-indol-3-yl) propanoate (3j)



Purified by flash column silica gel chromatography (DCM) to give **3j** as a beige solid. (1.91 g, yield 49 %). m.p. 59.8-60.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.39 (s, 1H), 7.35 – 7.29 (m, 5H), 7.25 – 7.21 (m, 2H), 7.16 (dd, J = 13.1, 7.0 Hz, 3H), 7.07 (d, J = 2.2 Hz, 1H), 5.31 (s, 2H), 4.02 (d, J = 14.4 Hz, 1H), 3.84 (s, 1H), 3.63 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.6, 137.3, 137.3, 136.0, 128.9, 128.2, 127. 8, 127.0, 126.7, 126.1, 124.0, 122.1, 122.0, 121.3, 119.9, 119.6, 119.4, 116. 7, 111.2, 110.1, 109.9, 52.9, 50.3, 35.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{27}H_{24}N_2O_3Na$ 447.1679; found 447.1668.

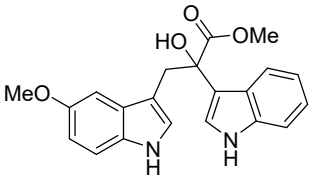
Methyl 2-hydroxy-2-(1H-indol-3-yl)-3-(1-methyl-1H-indol-3-yl) propanoate (3k)



Purified by flash column silica gel chromatography (DCM) to give **3k** as a beige solid (1.73 g, yield 54 %). m.p. 68.1-68.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.44 (dd, J = 8.6, 5.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.32 (dd, J = 16.8, 9.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.09 (s, 1H), 4.06 (d, J = 14.4 Hz, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 3.64 (d, J = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175. 7, 136.9, 128.7, 125.4, 122.5, 122.3, 121.6, 121.0, 120.1, 119.4, 119.1, 117.6, 111.5, 109.3, 108.2, 52.9, 34.9, 32.9. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_3Na$ 371.1366; found 371.1354.

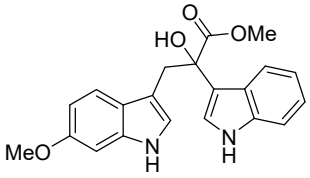
Methyl 2-hydroxy-3-(1H-indol-3-yl)-2-(5-methoxy-1H-indol-3-yl)propanoate (3l)

Purification by flash column silica gel chromatography (DCM/MeOH=300:1-100:1) to give **3l** as a beige solid (2.45 g, yield 83 %). m.p. 91.8-92.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.06 (s, 1H), 7.99 (d, J =



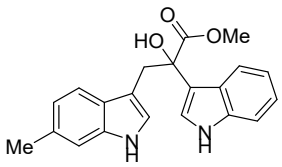
7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.24 – 7.18 (m, 2H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 3.64 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.8, 152.9, 136.6, 130.9, 128.7, 125.4, 125.1, 123.0, 121.0, 120.5, 118.6, 117.5, 111.7, 111.5, 110.8, 109.1, 100.8, 76.5, 55.2, 51.8, 34.7. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_4Na$ 387.1315; found 387.1297.

Methyl 2-hydroxy-2-(1H-indol-3-yl)-3-(6-methoxy-1H-indol-3-yl)propanoate (3m)



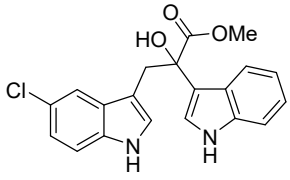
Purification by flash column silica gel chromatography (DCM/MeOH=300:1-100:1) to give **3m** as a beige solid (2.24 g, yield 76 %). m.p. 93.6-94.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.10 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 4.00 (d, *J* = 14.4 Hz, 1H), 3.91 (s, 3H), 3.68 (s, 3H), 3.63 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 156.5, 136.9, 136.8, 125.3, 122.7, 122.7, 122.6, 122.3, 120.9, 120.1, 120.0, 117.4, 111.5, 109.7, 109.7, 94.6, 55.7, 52.9, 35.0. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_4Na$ 387.1315; found 387.1300.

Methyl 2-hydroxy-2-(1H-indol-3-yl)-3-(6-methyl-1H-indol-3-yl) propanoate (3n)



Purified by flash column silica gel chromatography (DCM) to give **3n** as a beige solid (2.60 g, yield 81 %). m.p. 79.8-80.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.38 (dd, *J* = 15.4, 5.3 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 3.98 (d, *J* = 14.4 Hz, 1H), 3.64 (s, 3H), 3.59 (d, *J* = 14.4 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 175.2, 137.1, 136.6, 129.9, 126.7, 125.8, 124.1, 123.3, 121.4, 121.0, 120.3, 119.2, 119.1, 118.1, 111.9, 111.4, 109.5, 76.9, 52.2, 35.2, 21.9. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{20}N_2O_3Na$ 371.1366; found 371.1355.

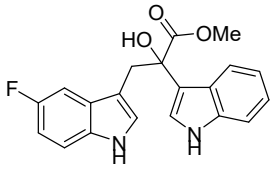
Methyl 2-(5-chloro-1H-indol-3-yl)-2-hydroxy-3-(1H-indol-3-yl)propanoate (3o)



Purification by flash column silica gel chromatography (DCM/MeOH=300:1-100:1) to give **3o** as a white solid (1.96 g, yield 67 %). m.p. 81.1-89.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 33.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J*

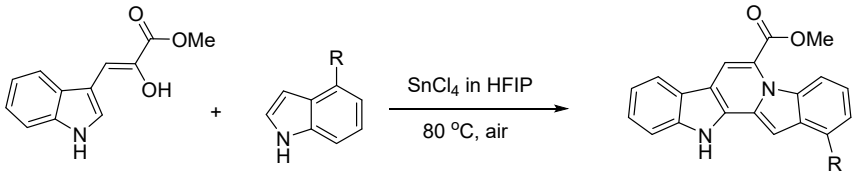
= 1.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.21 (dd, *J* = 15.0, 7.8 Hz, 2H), 7.14 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.11 (d, *J* = 2.3 Hz, 1H), 3.90 (d, *J* = 14.4 Hz, 1H), 3.65 (s, 3H), 3.55 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.6, 136.6, 134.3, 129.6, 126.3, 125.3, 123.0, 122.9, 121.0, 120.5, 120.5, 118.7, 118.7, 117.5, 112.6, 111.5, 109.5, 76.6, 51.7, 34.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{17}ClN_2O_3Na$ 391.0820; found 391.0804.

Methyl 3-(5-fluoro-1H-indol-3-yl)-2-hydroxy-2-(1H-indol-3-yl) propanoate (3p)



Purified by flash column silica gel chromatography (DCM) to give **3p** as a brown solid (480 mg, yield 15 %). ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.07 (s, 1H), 10.93 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.88 (td, *J* = 9.1, 2.5 Hz, 1H), 3.75 (d, *J* = 14.5 Hz, 1H), 3.52 (s, 3H), 3.46 (d, *J* = 14.5 Hz, 1H). The High-resolution mass spectra (HRMS), melting point, ^{13}C NMR and ^{19}F NMR spectra of **3p** could not be obtained due to poor stability of the compound.

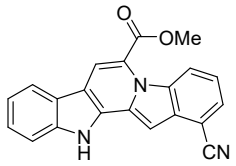
2.2 Synthesis of compounds **4a-b**



2a **4a-b**

To a solution of compound **2a** (100 mg, 0.46 mmol) and indole fragment (0.55 mmol) in 5 mL HFIP was added $SnCl_4$ (179 mg, 80 μL, 0.69 mmol), and the reaction mixtures were stirred at 80 °C for 1 h. The reaction mixture were concentrated under reduce pressure. Then saturated sodium bicarbonate was added, the mixtures were extracted with EA, the combined organic layers were washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by flash column silica gel chromatography to give compound **4**.

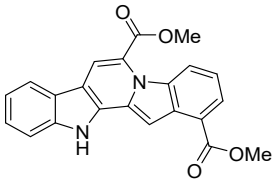
Methyl 1-cyano-12H-pyrido[1,2-a:3,4-b'] diindole-6-carboxylate (4a)



Purified by flash column silica gel chromatography (DCM/MeOH=200:1-60:1) to give **4a** as a yellow solid (81 mg, yield 52%). m.p. 282.4-283.2 °C. ^{1}H NMR (600 MHz,

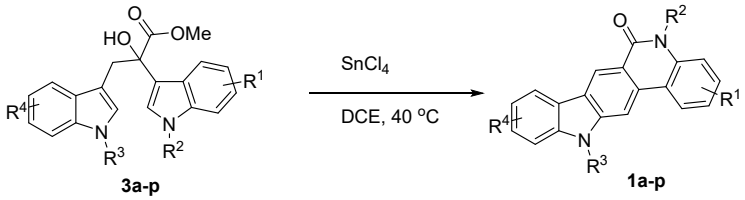
DMSO-d_6) δ 12.70 (s, 1H), 8.21 (s, 1H), 8.15 (dd, J = 15.2, 8.3 Hz, 2H), 7.85 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.7, 139.0, 131.0, 130.8, 130.5, 130.0, 127.8, 125.2, 123.1, 121.9, 121.0, 120.4, 120.1, 119.5, 118.6, 113.8, 112.2, 110.9, 101.0, 90.4, 52.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{13}N_3O_2Na$ 362.0900; found 362.0882.

Dimethyl 12H-pyrido[1,2-a:3,4-b'] diindole-1,6-dicarboxylate (4b)



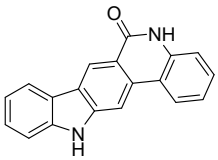
Purified by flash column silica gel chromatography (DCM/MeOH=200:1-80:1) to give **4b** as a pink solid (90 mg, yield 53%). m.p. 248.2-249.1 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.80 (s, 1H), 8.15 (s, 1H), 8.12 (d, J = 7.9 Hz, 1H), 8.07 (dd, J = 15.2, 7.9 Hz, 2H), 7.93 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.32 (dd, J = 8.3, 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 4.05 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.9, 164.1, 139.0, 132.3, 131.0, 130.3, 128.3, 125.7, 125.0, 123.3, 121.9, 120.9, 120.0, 119.1, 113.3, 113.2, 112.1, 110.4, 93.4, 93.4, 52.9, 51.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{16}N_2O_4Na$ 395.1002; found 395.0984.

2.3 Synthesis of compounds **1a-p**



To a solution of compound **3** (0.30 mmol) in 3.0 mL DCE was added $SnCl_4$ (117 mg, 57μL, 0.45 mmol), and the reaction mixtures were stirred at 40 °C for 1 h. The reaction mixtures were concentrated under reduce pressure. Then saturated sodium bicarbonate was added, the mixture was extracted with EA, the combined organic layers were washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude products were purified by trituration with DCM or acetone to give compound **1**.

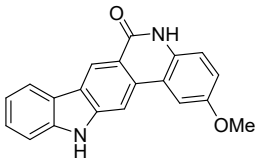
5,12-Dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1a)



Purified by trituration with DCM to give **1a** as a beige solid (73 mg, yield 86%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.73 (s, 1H), 11.49 (s, 1H), 9.15 (s, 1H), 8.47 – 8.40 (m, 2H), 8.33 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.48 (dt, J = 15.1, 7.1 Hz, 2H), 7.38 (d, J = 7.3 Hz, 1H), 7.27 (q, J = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.7, 143.0, 141.5, 136.4, 132.0,

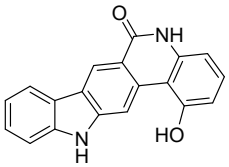
128.9, 127.1, 123.6, 123.1, 122.3, 122.0, 121.0, 120.3, 119.6, 118.5, 118.0, 116.1, 111.3, 102.6. The NMR data is consistent with literature values.[1]

2-Methoxy-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1b)



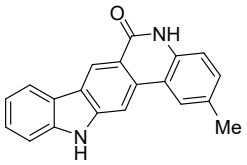
Purified by trituration with DCM to give **1b** as a beige solid (80 mg, yield 93%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.67 (s, 1H), 11.37 (s, 1H), 9.14 (s, 1H), 8.45 (s, 1H), 8.33 (d, J = 7.7 Hz, 1H), 7.91 (d, J = 2.6 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 7.13 (dd, J = 8.8, 2.7 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.3, 154.7, 142.8, 141.6, 131.8, 130.5, 127.1, 123.6, 122.3, 121.0, 120.3, 119.6, 119.2, 118.2, 117.3, 116.8, 111.3, 106.4, 103.0, 55.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}N_2O_2Na$ 337.0947; found 337.0934.

1-Hydroxy-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1c)



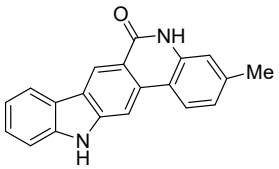
Purified by trituration with acetone to give **1c** as a beige solid (51 mg, isolated yield 59%). m.p. 348.5-349.2 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.71 (s, 1H), 11.35 (s, 1H), 10.74 (s, 1H), 9.47 (s, 1H), 9.15 (s, 1H), 8.30 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.28 – 7.20 (m, 2H), 6.88 (dd, J = 8.0, 0.9 Hz, 1H), 6.79 (dd, J = 8.0, 1.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.7, 156.5, 142.8, 141.3, 138.3, 132.2, 128.7, 126.7, 122.3, 121.9, 120.9, 119.8, 119.4, 117.8, 111.1, 109.4, 108.4, 107.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{12}N_2O_2Na$ 323.0791; found 323.0781.

2-Methyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1d)



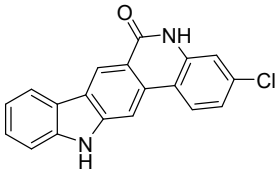
Purified by trituration with DCM to give **1d** as a beige solid (81 mg, yield 95%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.68 (s, 1H), 11.40 (s, 1H), 9.13 (s, 1H), 8.41 (s, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.24 (s, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.33 – 7.22 (m, 3H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.6, 142.9, 141.5, 134.2, 132.0, 130.9, 130.0, 127.1, 123.5, 123.0, 122.3, 121.0, 120.3, 119.6, 118.3, 118.1, 116.0, 111.3, 102.6, 20.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}N_2ONa$ 321.0998; found 321.0987. The NMR data is consistent with literature values.[1]

3-Methyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1e)



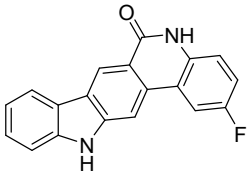
Purified by trituration with DCM to give **1e** as a beige solid (76 mg, yield 89%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.67 (s, 1H), 11.39 (s, 1H), 9.11 (s, 1H), 8.35 (s, 1H), 8.31 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.4 Hz, 1H), 7.16 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.9, 143.0, 141.5, 138.6, 136.4, 132.2, 127.0, 123.3, 123.1, 122.4, 120.9, 120.2, 119.6, 117.7, 116.1, 116.0, 111.3, 102.2, 21.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{14}N_2ONa$ 321.0998; found 321.0988.

3-Chloro-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1f)



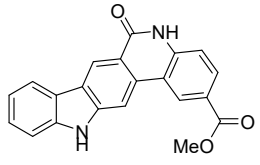
Purified by trituration with DCM to give **1f** as a brown solid (52 mg, yield 60%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.76 (s, 1H), 11.55 (s, 1H), 9.12 (s, 1H), 8.46 (d, J = 8.7 Hz, 1H), 8.39 (s, 1H), 8.33 (d, J = 7.7 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.55 – 7.46 (m, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.33 – 7.24 (m, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.7, 142.9, 141.6, 137.4, 133.0, 131.2, 127.2, 125.1, 123.8, 122.2, 121.8, 121.1, 120.3, 119.7, 117.7, 117.5, 115.2, 111.3, 102.9. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{11}N_2OClNa$ 341.0452; found 341.0439.

3-Fluoro-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1g)



Purified by trituration with DCM to give **1g** as a brown solid (65 mg, yield 76%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.90 (s, 1H), 11.56 (s, 1H), 9.13 (s, 1H), 8.45 (s, 1H), 8.37 – 8.26 (m, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42 (dd, J = 8.9, 5.2 Hz, 1H), 7.34 (td, J = 8.5, 2.7 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.4, 158.6(d, J = 235.6 Hz), 142.8, 141. 7, 132.9, 131.2(d, J = 2.3 Hz), 127.2, 124.0, 122.2, 121.1, 120.2, 119.8 (d, J = 7.7 Hz),119.6, 117.9, 117.7 (d, J = 8.4 Hz), 116.5 (d, J = 23.6 Hz), 111.4, 109.1 (d, J = 23.8 Hz), 103.4. ^{19}F NMR (565 MHz, DMSO-d_6) δ -120.8. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{11}N_2OFNa$ 325.0748; found 325.0734.

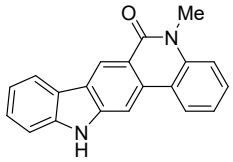
Methyl 6-oxo-6,12-dihydro-5H-indolo[3,2-j] phenanthridine-2-carboxylate (1h)



Purified by trituration with DCM to give **1h** as a beige solid (64 mg, yield 74%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.78 (s, 1H), 11.63 (s, 1H), 9.12 (s, 1H), 8.90 (s, 1H), 8.41 (s, 1H), 8.33 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 7.3

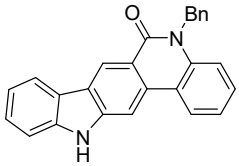
Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.0, 161.8, 143.0, 141. 4, 140.0, 131.1 129.4, 127.3, 124.5, 123.9, 123.0, 122.1, 121.2, 120.3, 119.7, 118.1, 117.7, 116.3, 111.4, 102.7, 52.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{14}N_2O_3Na$ 365.0897; found 365.0885.

5-Methyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1i)



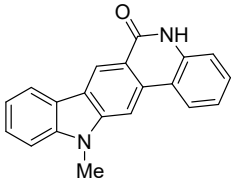
Purified by trituration with DCM to give **1i** as a beige solid (30 mg, yield 36%). m.p. 320.8-321.5 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.73 (s, 1H), 9.17 (s, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.44 (s, 1H), 8.34 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.2, 142.9, 141.6, 137.4, 131.0, 129.3, 127.1, 123.8, 123.4, 122.3, 122.3, 121.1, 120.9, 119.6, 119.3, 117.4, 115.5, 111.3, 102.3, 29.6. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{14}N_2ONa$ 321.0998; found 321.0988.

4-Benzyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1j)



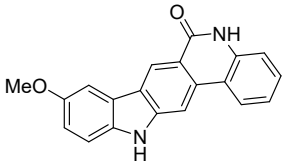
Purified by trituration with DCM to give **1j** as a brown solid (21 mg, yield 24%). m.p. 283.2-284.2 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.76 (s, 1H), 9.25 (s, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.48 (s, 1H), 8.36 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.26 (m, 6H), 7.23 (t, *J* = 7.1 Hz, 1H), 5.69 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.6, 143.1, 141.6, 137.3, 136.5, 131.2, 129.2, 128.7, 127.2, 126.9, 126.5, 123.9, 123.7, 122.5, 122.3, 121.1, 119.7, 119.6, 117.1, 116.1, 111.3, 102.4, 45.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{26}H_{18}N_2ONa$ 397.1311; found 397.1300.

12-Methyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1k)



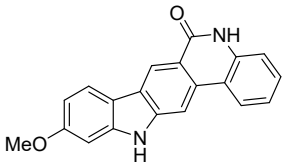
Purified by trituration with DCM to give **1k** as a beige solid (65 mg, yield 76%). m.p. 366.4-367.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$ + CF_3CO_2D) δ 8.63 (s, 1H), 8.27 (d, *J* = 7.1 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.74 (s, 1H), 7.62 – 7.55 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.27 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$ + CF_3CO_2D) δ 145.0, 142.6, 130.8, 130.4, 128.9, 126.8, 124.8, 122.6, 121.5, 121.3, 121.0, 120.4, 119.5, 118.5, 117.5, 115.6, 113.7, 111.8, 109.2, 28.9. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{14}N_2ONa$ 321.0998; found 321.0987.

9-Methoxy-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1l)



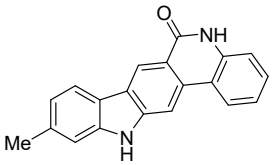
Purified by trituration with DCM to give **1l** as a beige solid (59 mg, yield 69%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.51 (s, 1H), 11.42 (s, 1H), 9.16 (s, 1H), 8.42 (d, J = 7.9 Hz, 1H), 8.37 (s, 1H), 7.94 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.13 (dd, J = 8.7, 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.8, 153.7, 143.5, 136.3, 136.2, 131.8, 128.9, 123.7, 123.1, 122.8, 122.0, 120.6, 118.5, 117.6, 116.2, 116.1, 112.0, 103.9, 102.6, 55.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}N_2O_2Na$ 337.0947; found 337.0931.

10-Methoxy-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1m)



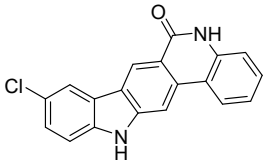
Purified by trituration with DCM to give **1m** as a beige solid (44 mg, yield 51%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.58 (s, 1H), 11.46 (s, 1H), 9.02 (s, 1H), 8.40 (d, J = 7.8 Hz, 1H), 8.37 (s, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.38 (dd, J = 8.1, 1.0 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.08 (d, J = 2.2 Hz, 1H), 6.86 (dd, J = 8.5, 2.3 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.8, 159.6, 143.1, 143.1, 136.2, 130.9, 128.7, 123.9, 123.0, 122.0, 121.9, 119.0, 118.6, 118.1, 116.1, 115.9, 108.6, 102.4, 95.0, 55.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}N_2O_2Na$ 337.0947; found 337.0932.

10-Methyl-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1n)



Purified by trituration with DCM to give **1n** as a beige solid (58 mg, yield 68%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.59 (s, 1H), 11.44 (s, 1H), 9.06 (s, 1H), 8.41 (d, J = 7.9 Hz, 1H), 8.37 (s, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.7, 143.0, 142.0, 136.9, 136.3, 131.6, 128. 8, 123.7, 123.0, 122.0, 121.1, 120.7, 120.0, 119.7, 118.5, 117.9, 116.1, 111.3, 102.5, 21.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}N_2ONa$ 321.0998; found 321.0990. The NMR data is consistent with literature values.[1]

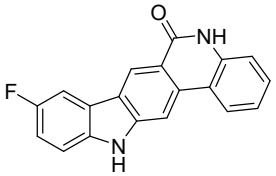
9-Chloro-5,12-dihydro-6H-indolo[3,2-j]phenanthridin-6-one (1o)



Purified by trituration with DCM to give **1o** as a beige solid (59 mg, yield 68%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.84 (s, 1H), 11.48 (s, 1H), 9.20 (s,

1H), 8.43 (d, J = 5.2 Hz, 3H), 7.59 (d, J = 8.5 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.6, 143.4, 140.0, 136.4, 132.6, 129.2, 126.8, 123.9, 123.7, 123.3, 122.6, 122.1, 121.1, 120.8, 118.4, 118.3, 116.1, 112.7, 103.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{11}ON_2ClNa$ 341.0452; found 341.0435.

9-Fluoro-5,12-dihydro-6H-indolo[3,2-j] phenanthridin-6-one (1p)

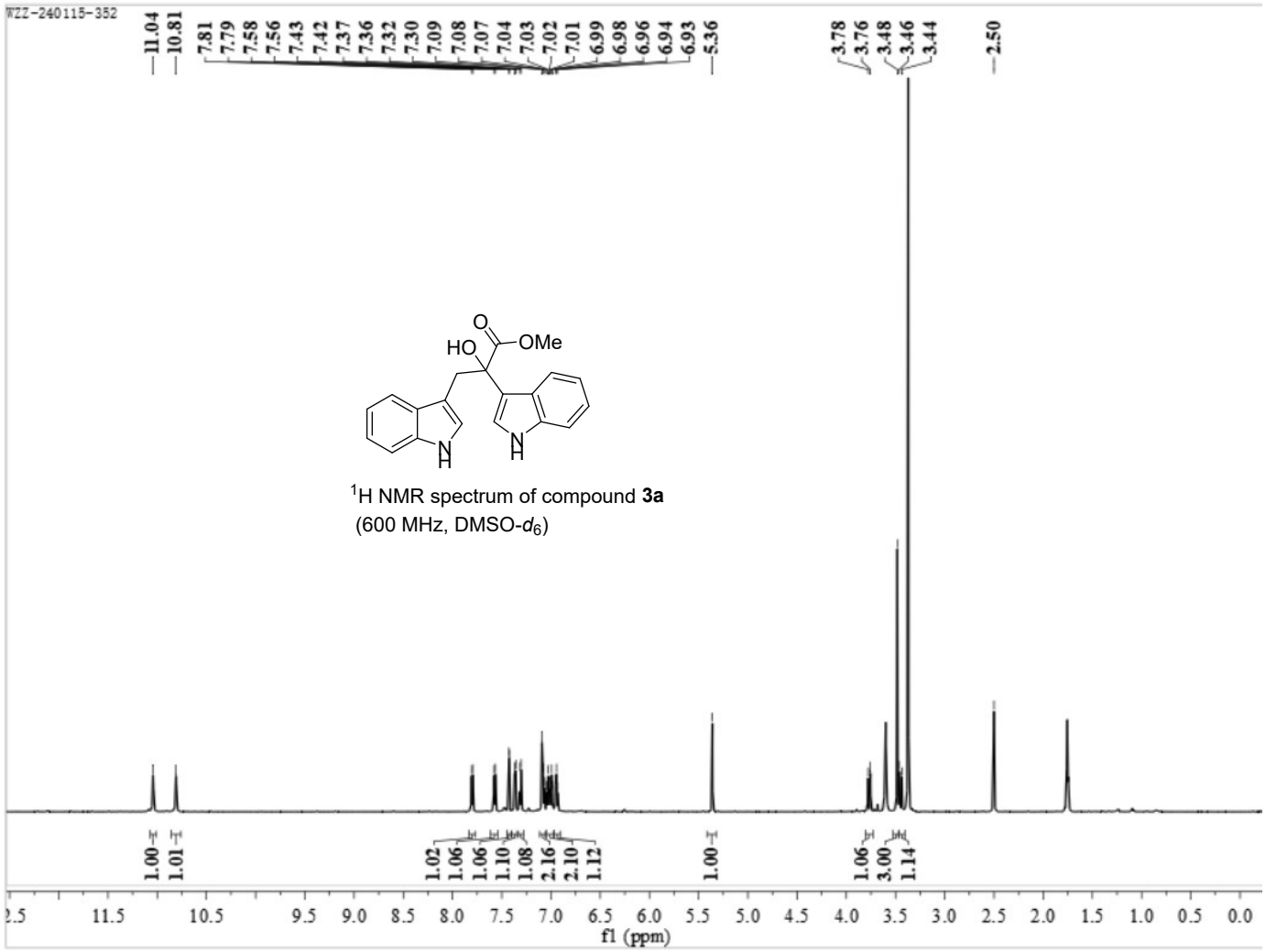


Purified by trituration with DCM to give **1p** as a brown solid (20 mg, yield 23%). m.p. > 370 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.74 (s, 1H), 11.46 (s, 1H), 9.18 (s, 1H), 8.50 – 8.37 (m, 2H), 8.21 (dd, J = 9.1, 2.4 Hz, 1H), 7.58 (dd, J = 8.7, 4.3 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.27 (t, J = 7.5 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.6, 157. 7(d, J = 232.0 Hz), 143.8, 137.9, 136.4, 132.4, 129.1, 123.2 (d, J = 4.8 Hz), 123.0 (d, J = 9.9 Hz), 122.0, 121.1, 118.3, 118.0, 116.1, 114.7 (d, J = 25.5 Hz), 112.2 (d, J = 9.3 Hz), 102.9 (d, J = 6.9 Hz). ^{19}F NMR (565 MHz, DMSO-d_6) δ -118.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{11}N_2OFNa$ 325.0748; found 325.0738.

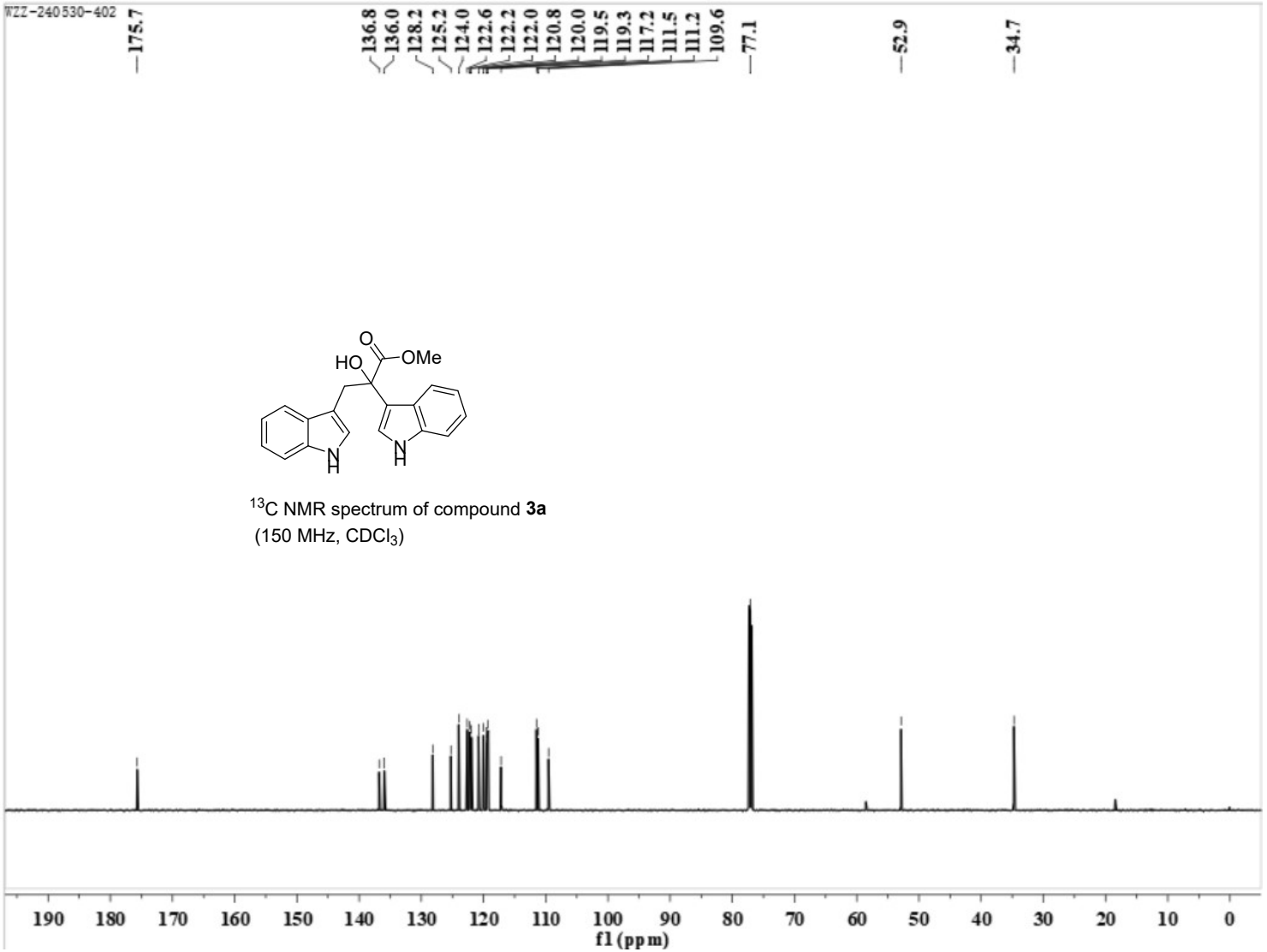
References:

(1) Y. Liu, M. Xu, K. Xie and S. Liu, Total synthesis of calothrixin B via an intramolecular baylishillman cyclization/6 π electrocyclization/dehydro-aromatization sequence and a specific oxidative quinone formation, Adv. Synth. Catal., 2021, 363, 737-741.

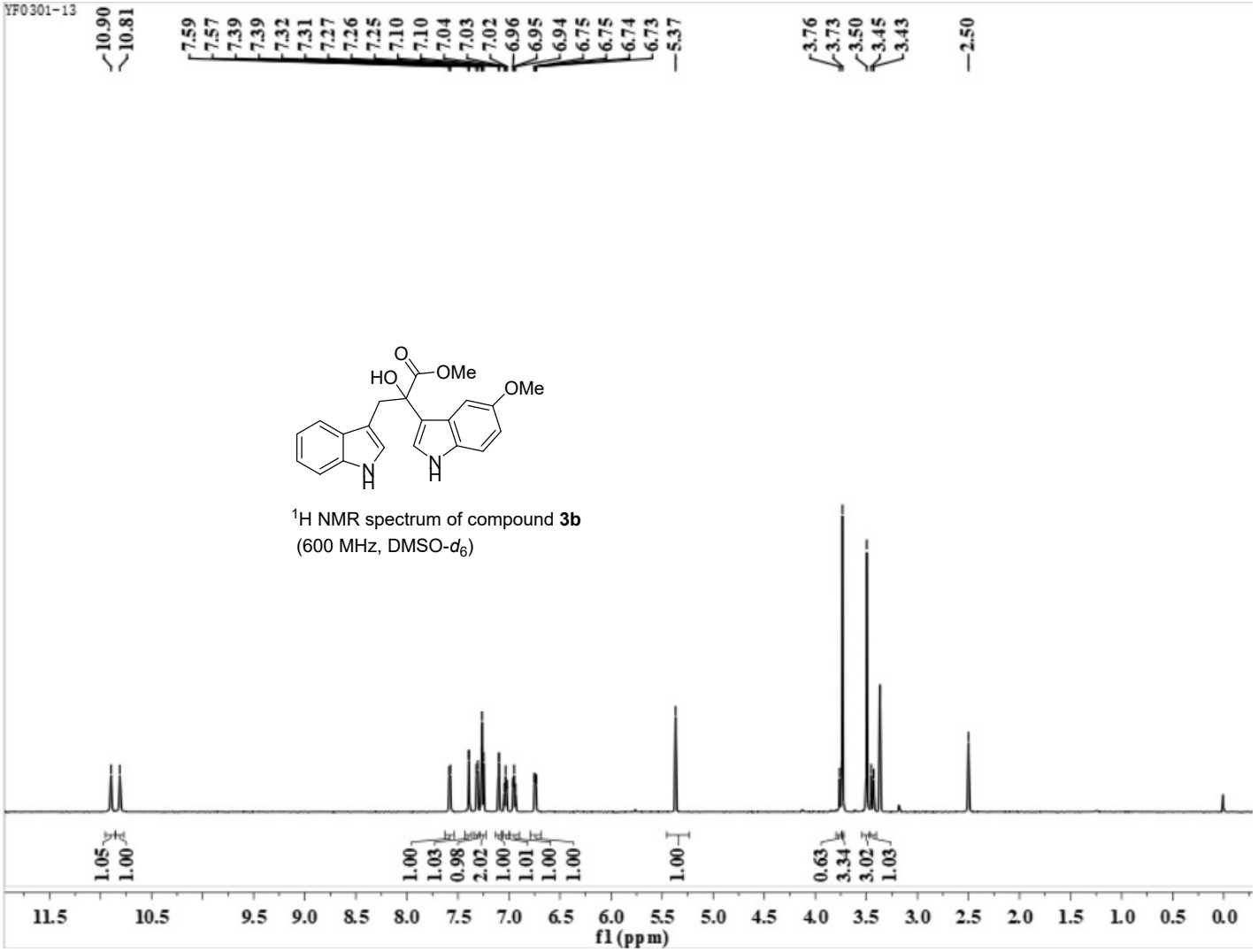
3. NMR spectra for compounds **3a-p**, **4a-b**, **1a-p**: **Page S15-85**.



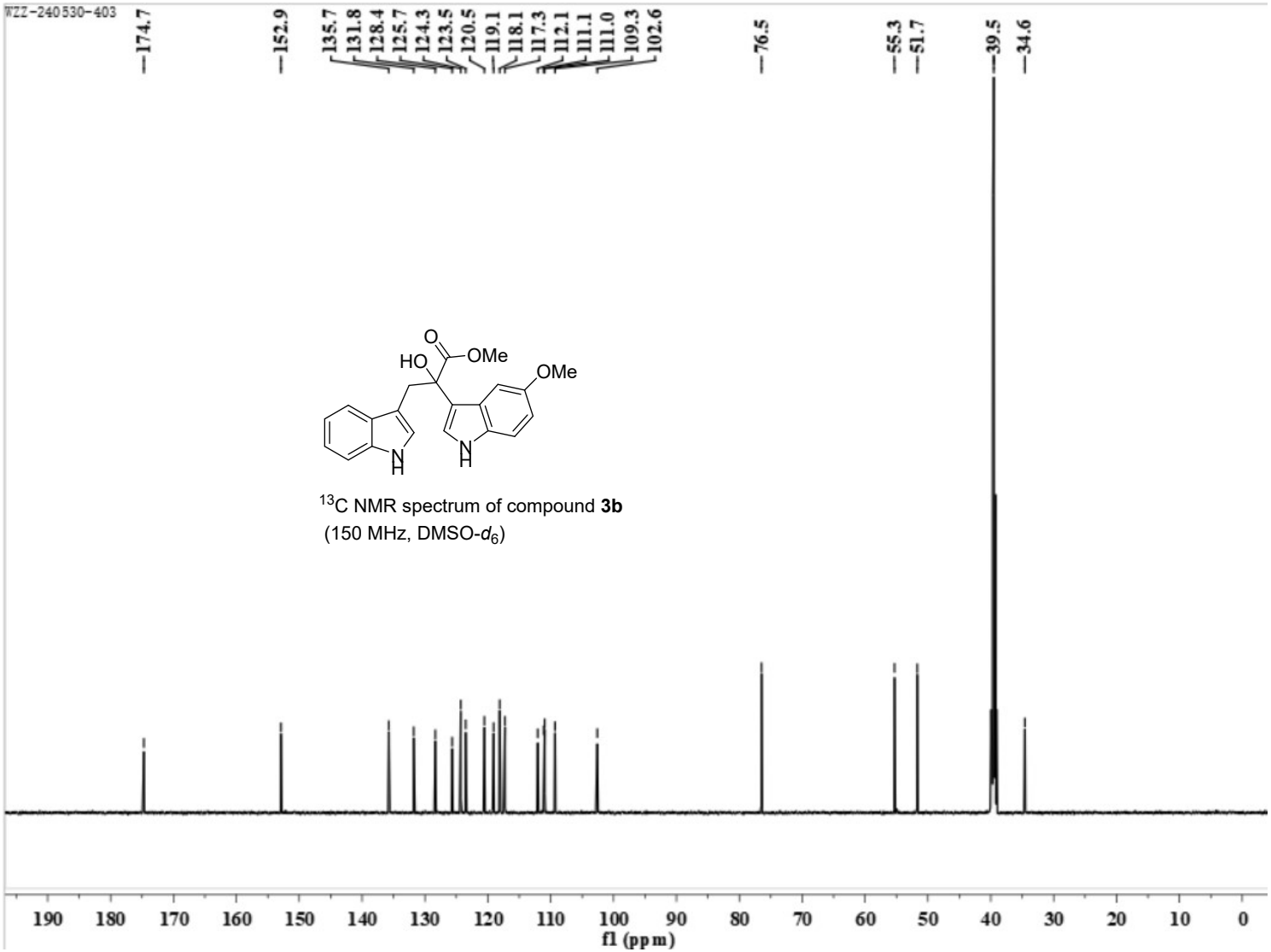
^{1}H NMR spectrum of compound **3a**
(600 MHz, DMSO-d_6)



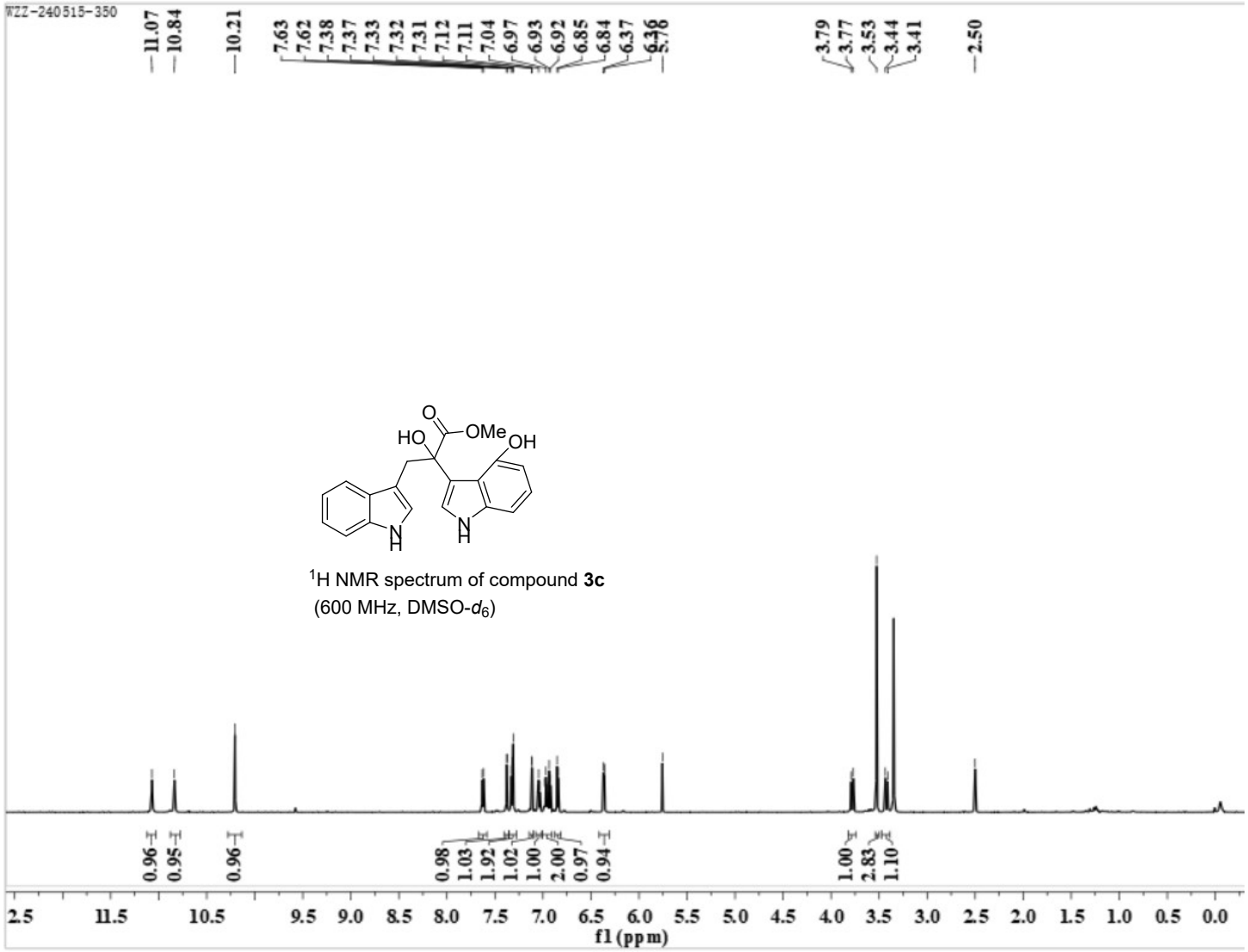
^{13}C NMR spectrum of compound **3a**
(150 MHz, $CDCl_3$)



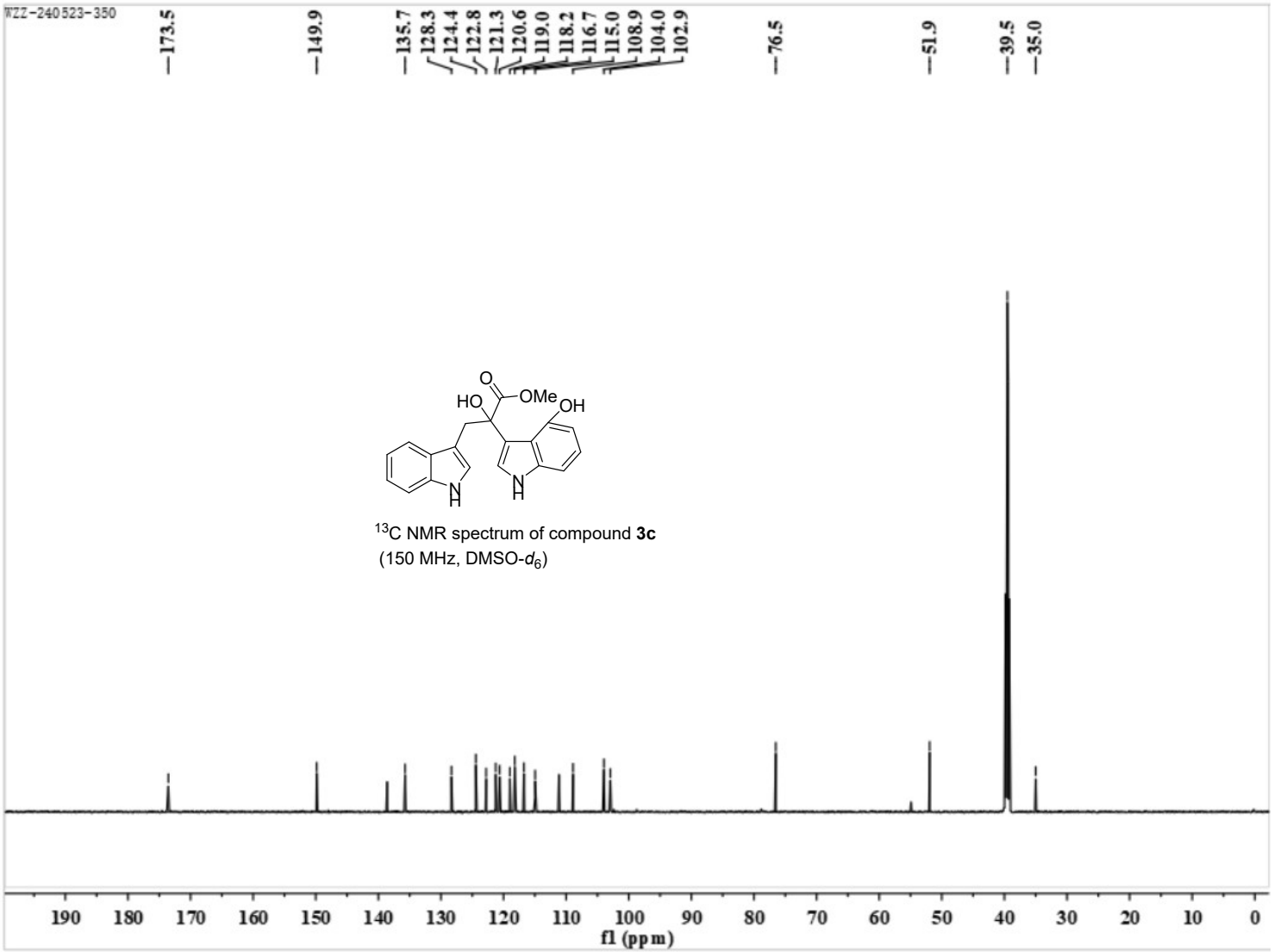
^{1}H NMR spectrum of compound **3b**
(600 MHz, DMSO-d_6)



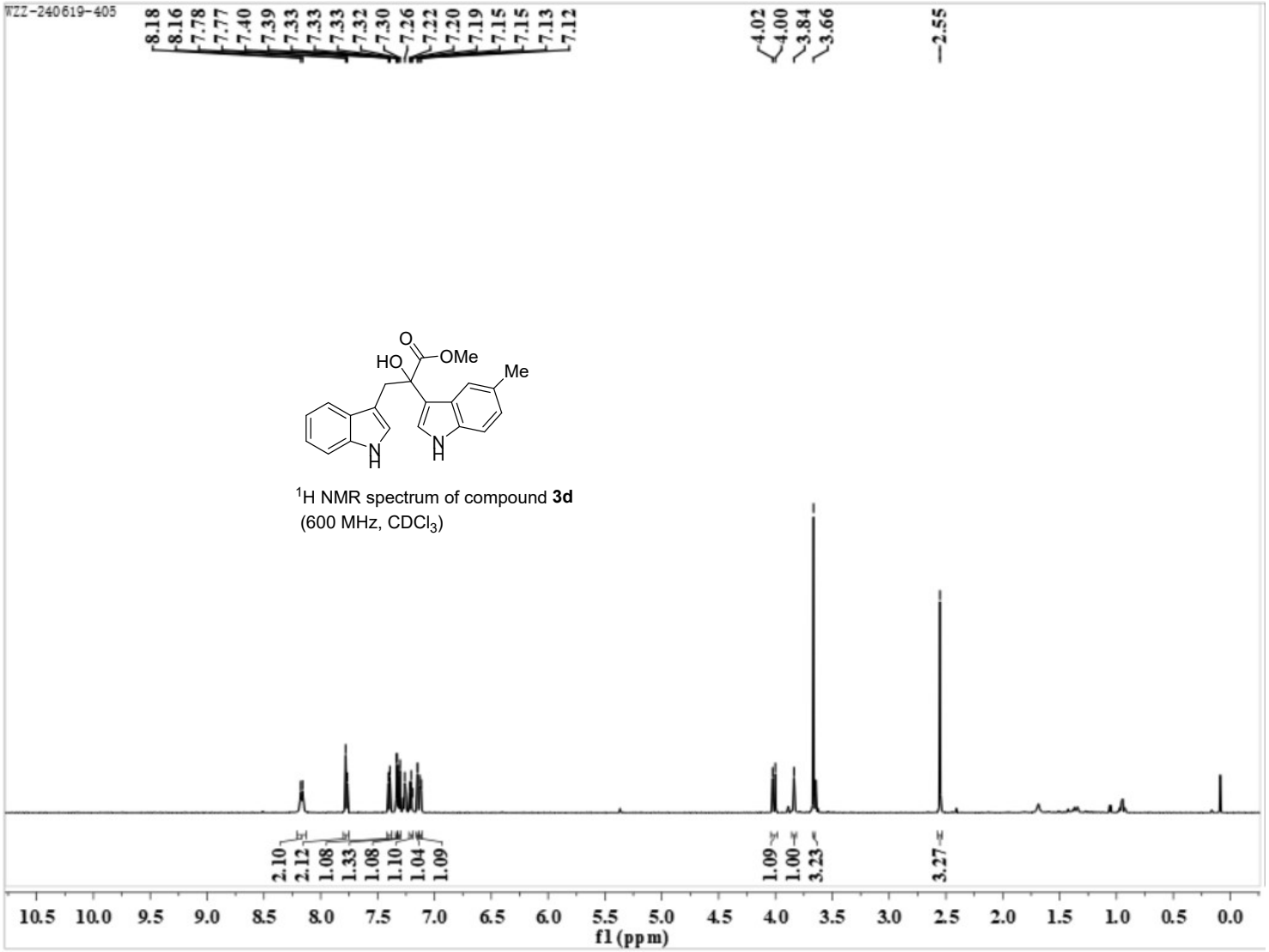
^{13}C NMR spectrum of compound **3b**
(150 MHz, DMSO-d_6)



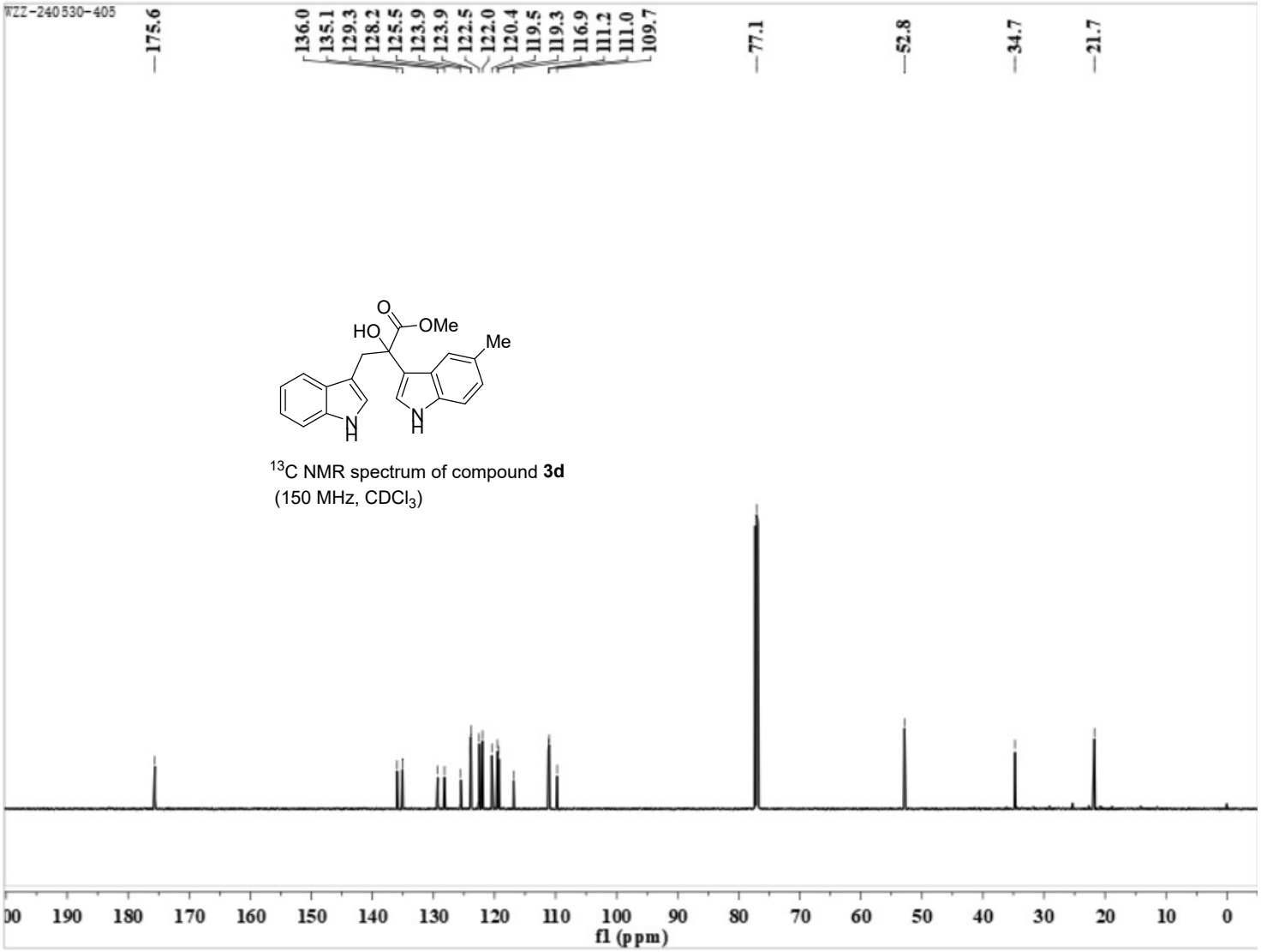
^{1}H NMR spectrum of compound **3c**
(600 MHz, DMSO-d_6)



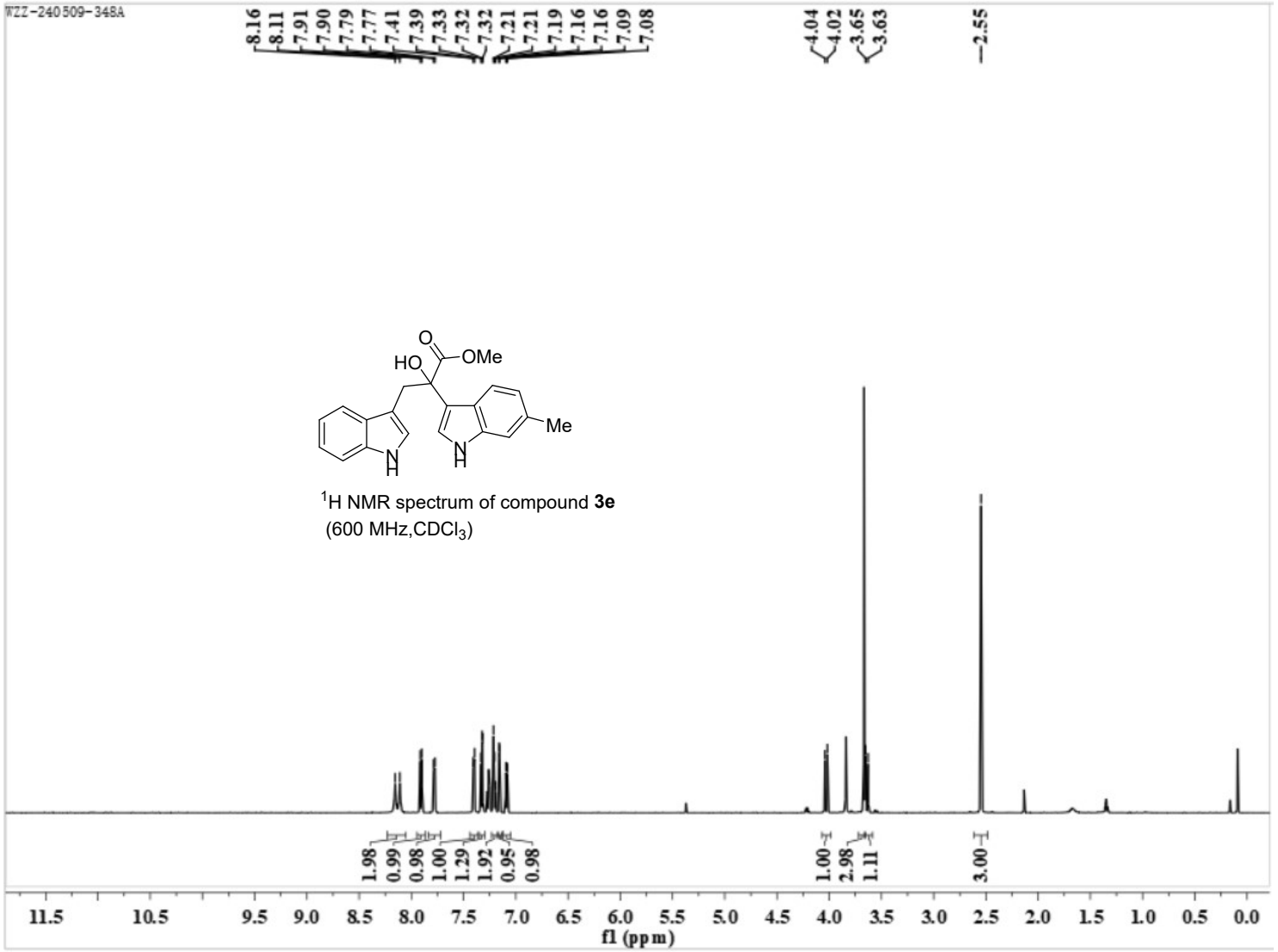
^{13}C NMR spectrum of compound **3c**
(150 MHz, DMSO-d_6)



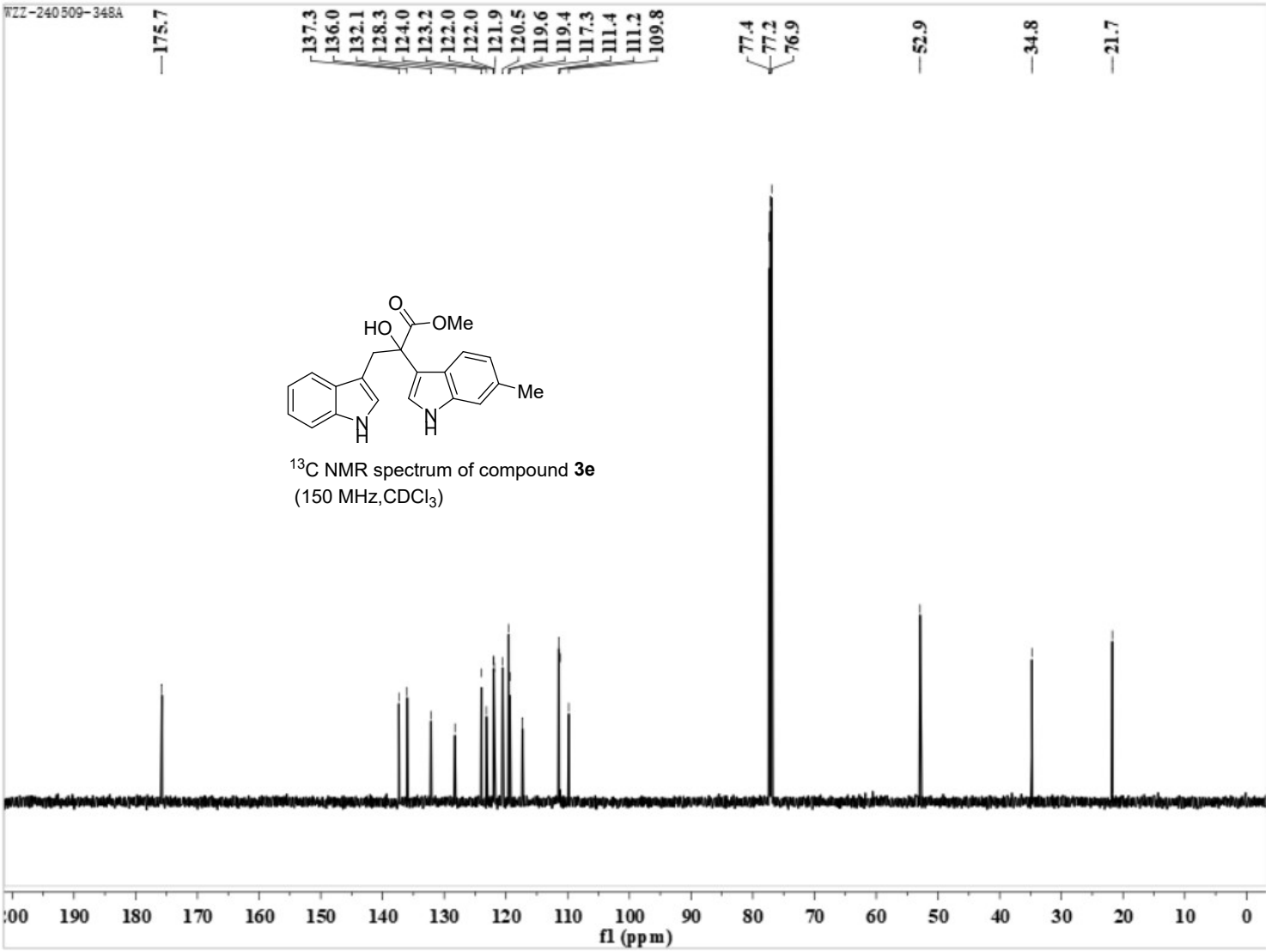
^{1}H NMR spectrum of compound **3d**
(600 MHz, $CDCl_3$)



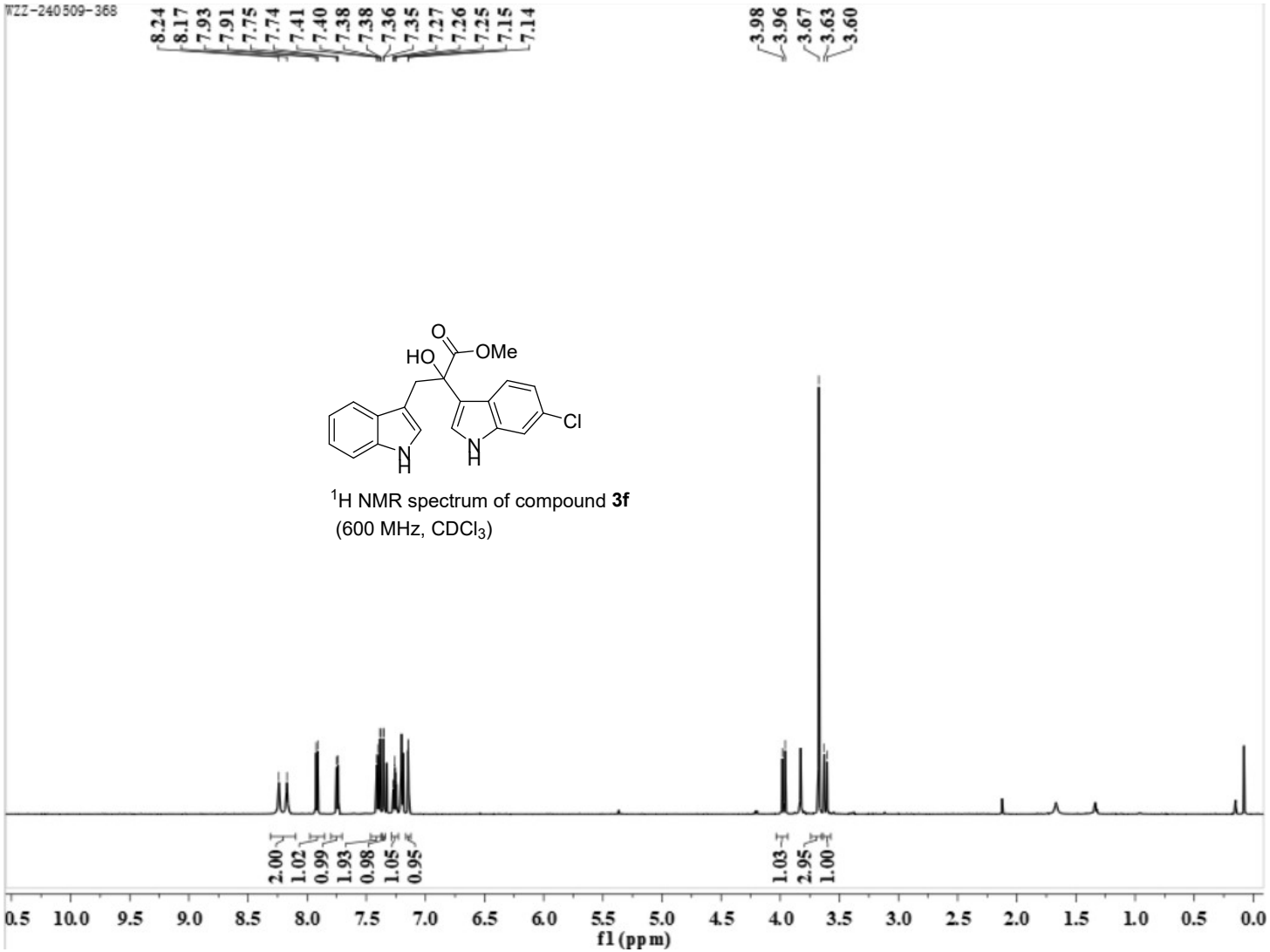
^{13}C NMR spectrum of compound **3d**
(150 MHz, $CDCl_3$)



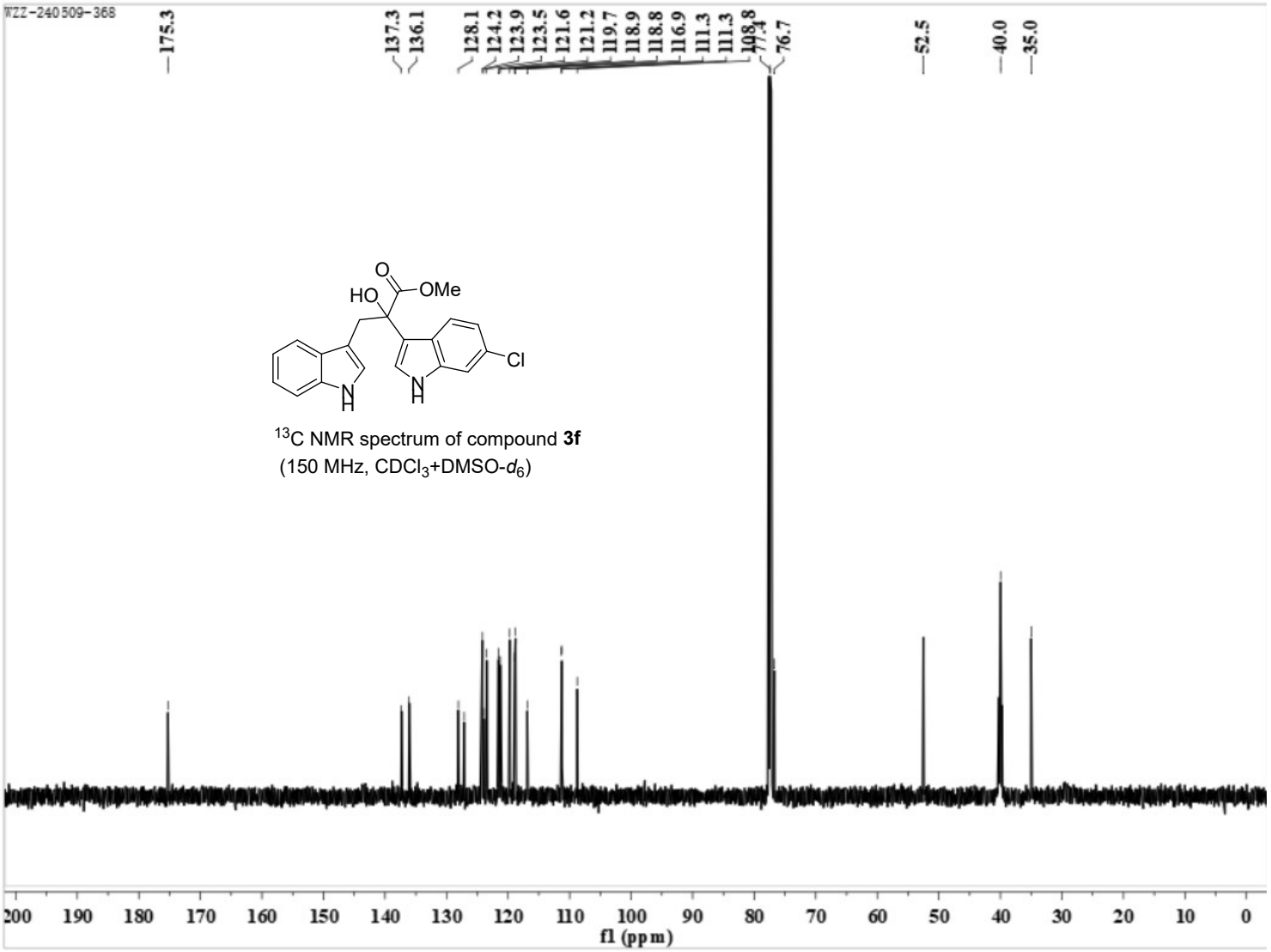
^{1}H NMR spectrum of compound **3e**
(600 MHz,$CDCl_3$)



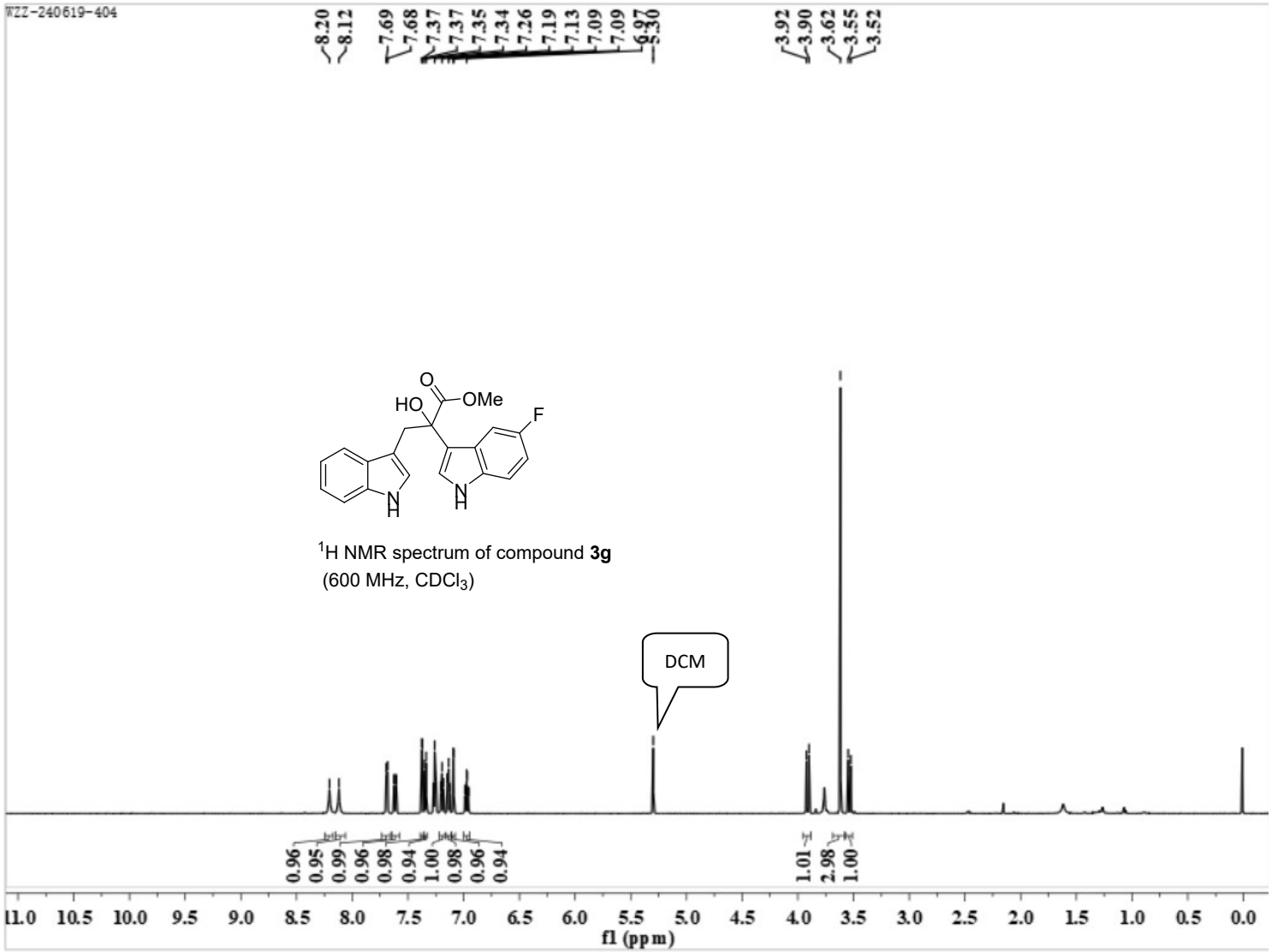
^{13}C NMR spectrum of compound **3e**
(150 MHz,$CDCl_3$)



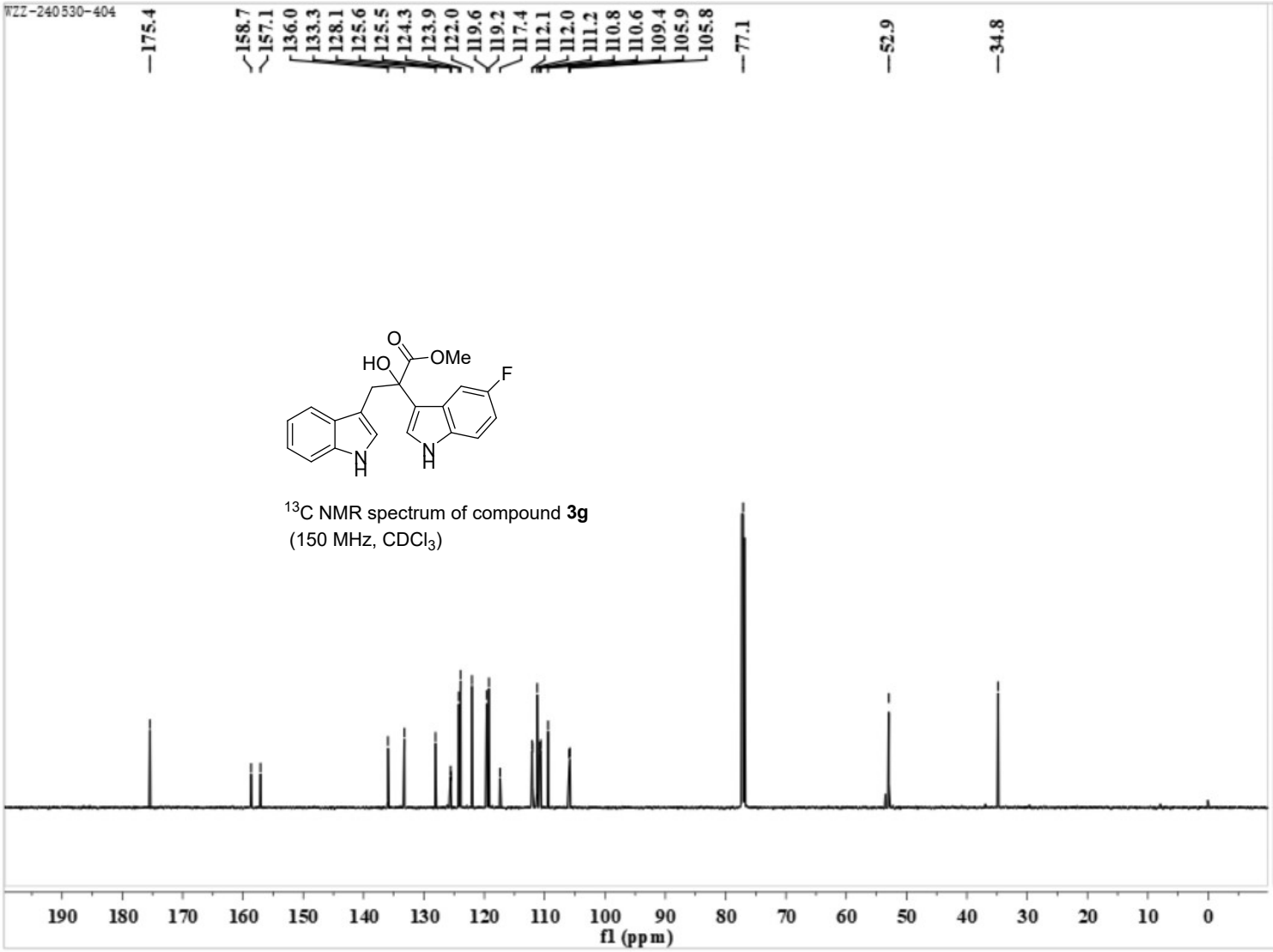
^{1}H NMR spectrum of compound **3f**
(600 MHz, $CDCl_3$)



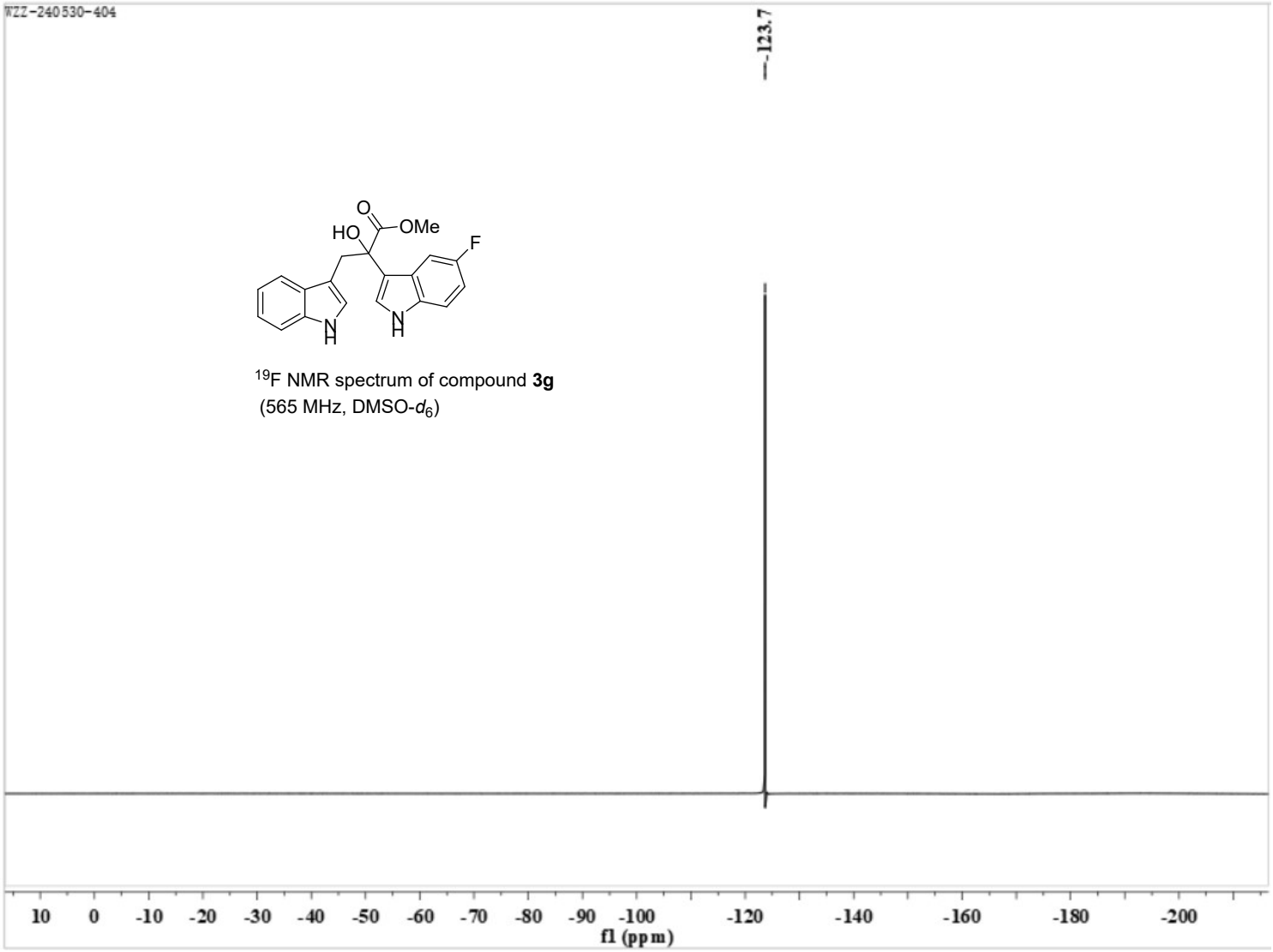
^{13}C NMR spectrum of compound **3f**
(150 MHz, $CDCl_3$+DMSO-d_6)



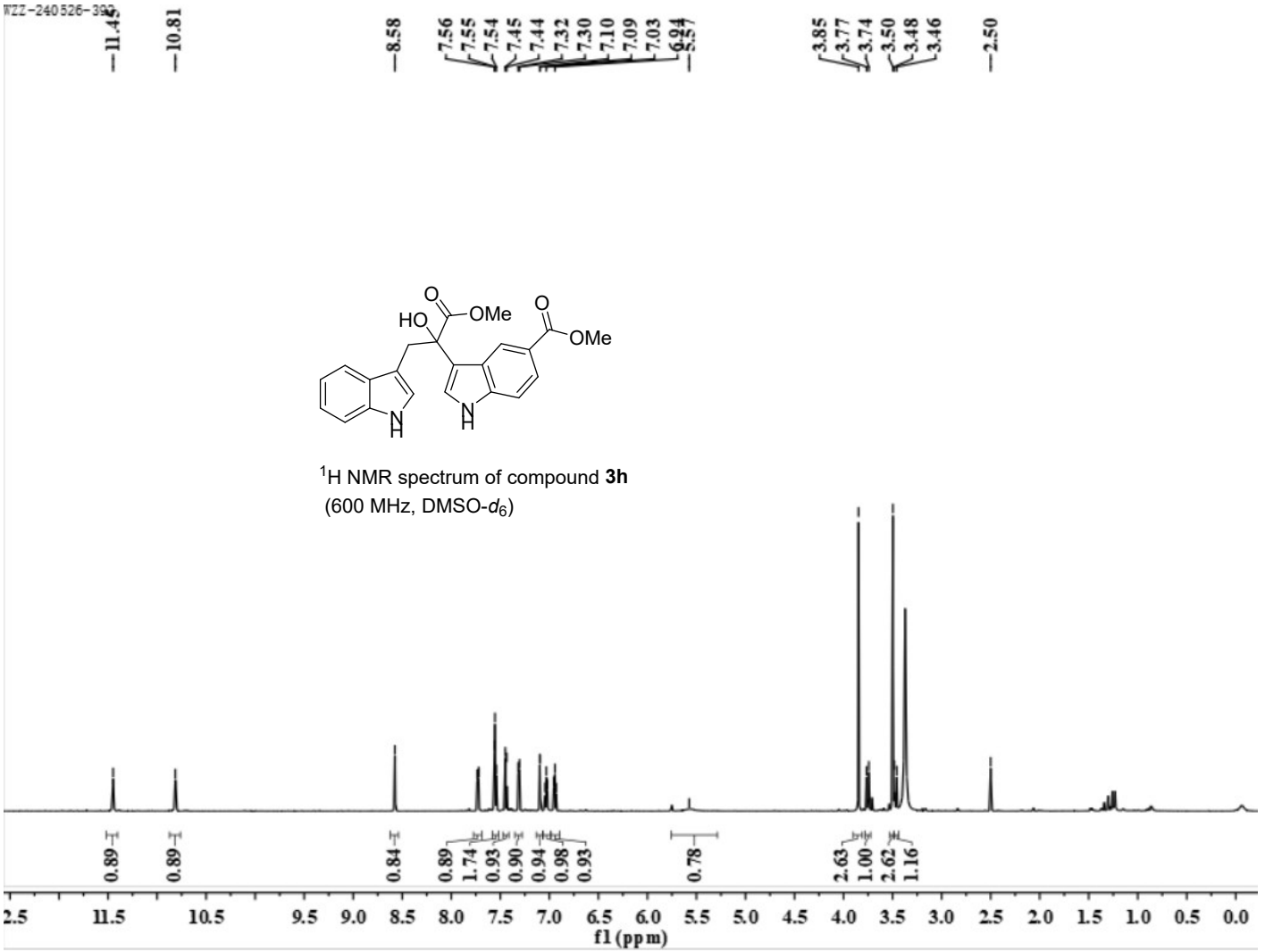
^{1}H NMR spectrum of compound **3g**
(600 MHz, $CDCl_3$)



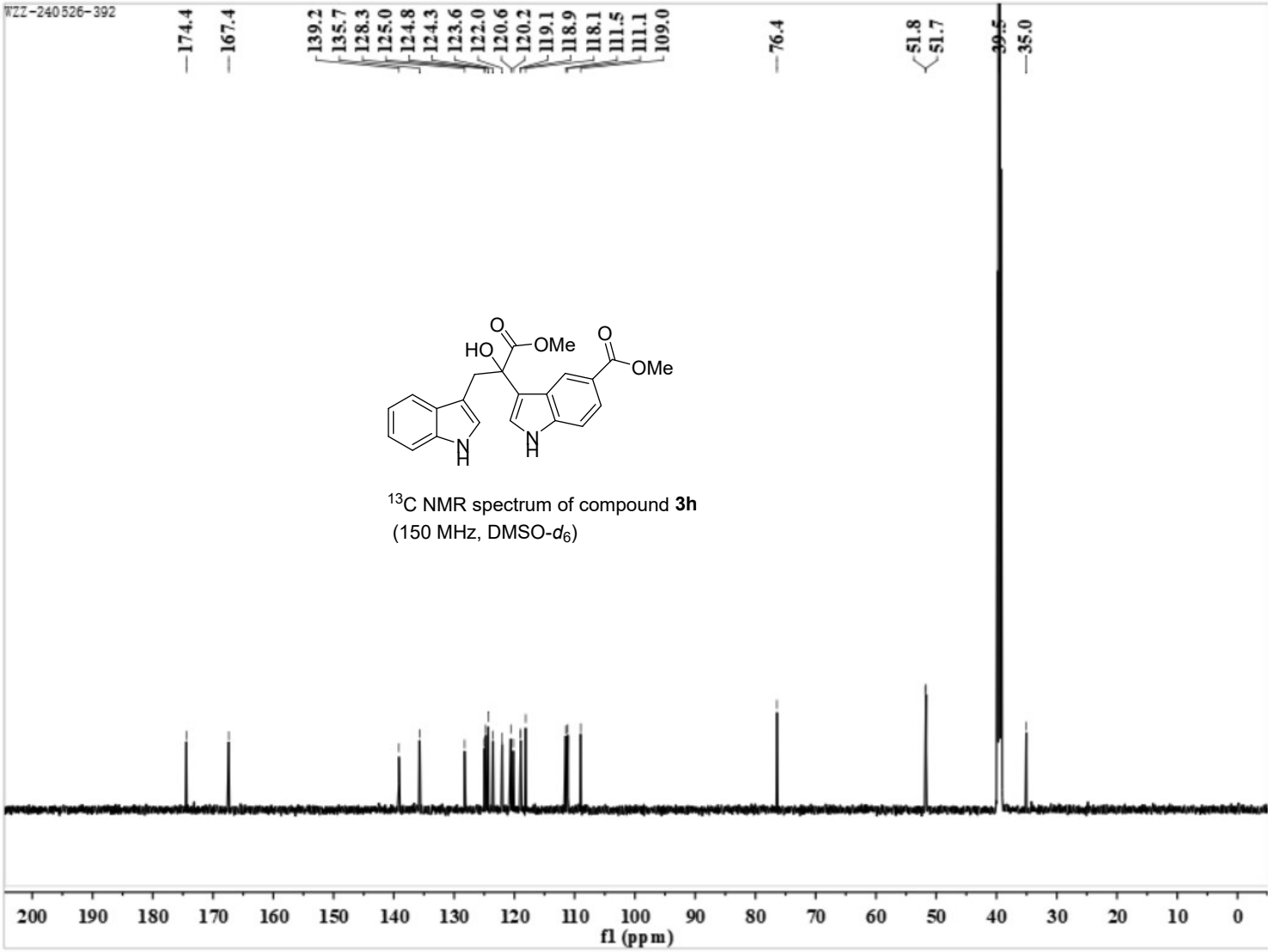
^{13}C NMR spectrum of compound **3g**
(150 MHz, $CDCl_3$)



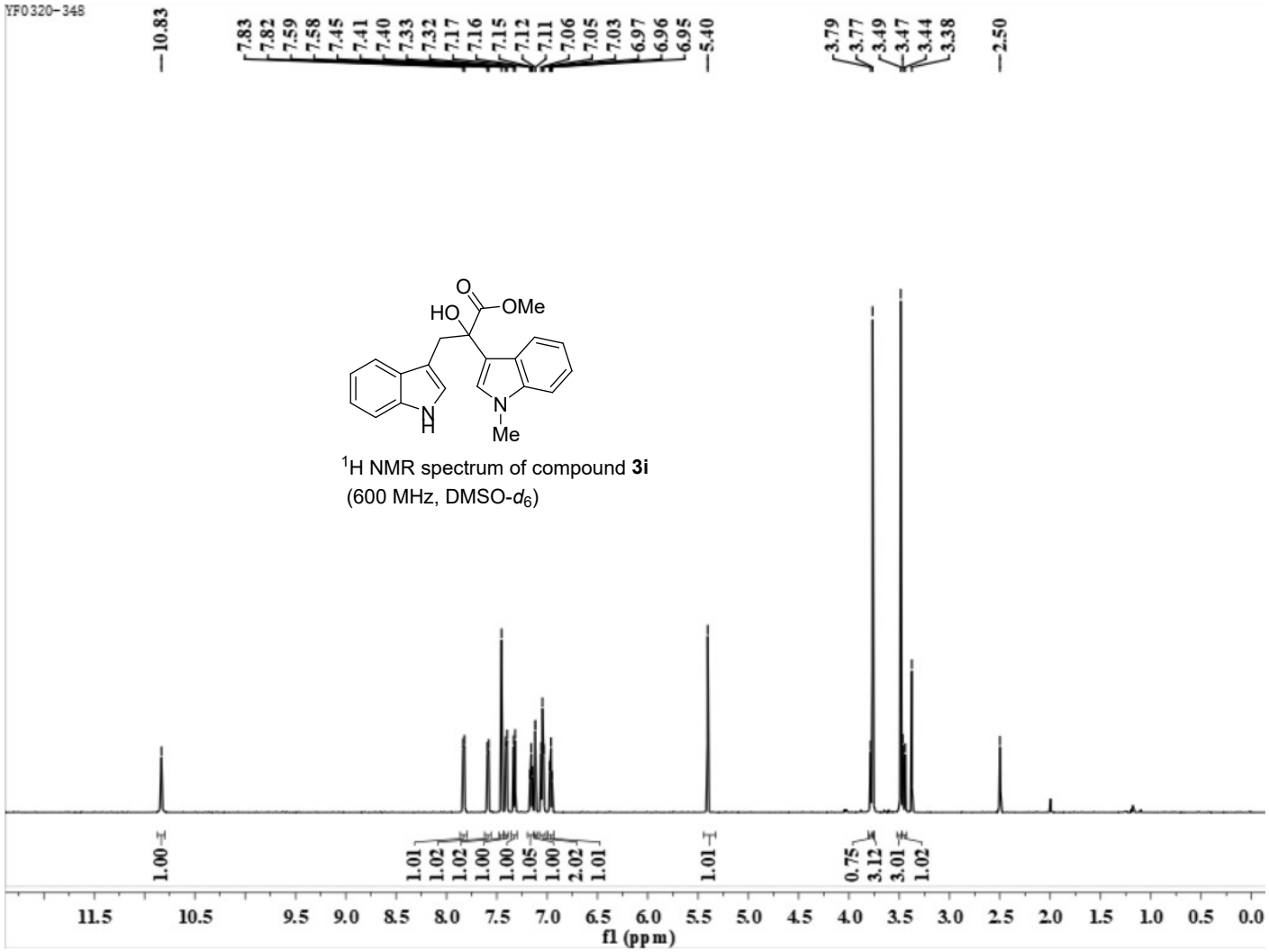
^{19}F NMR spectrum of compound **3g**
(565 MHz, DMSO-d_6)



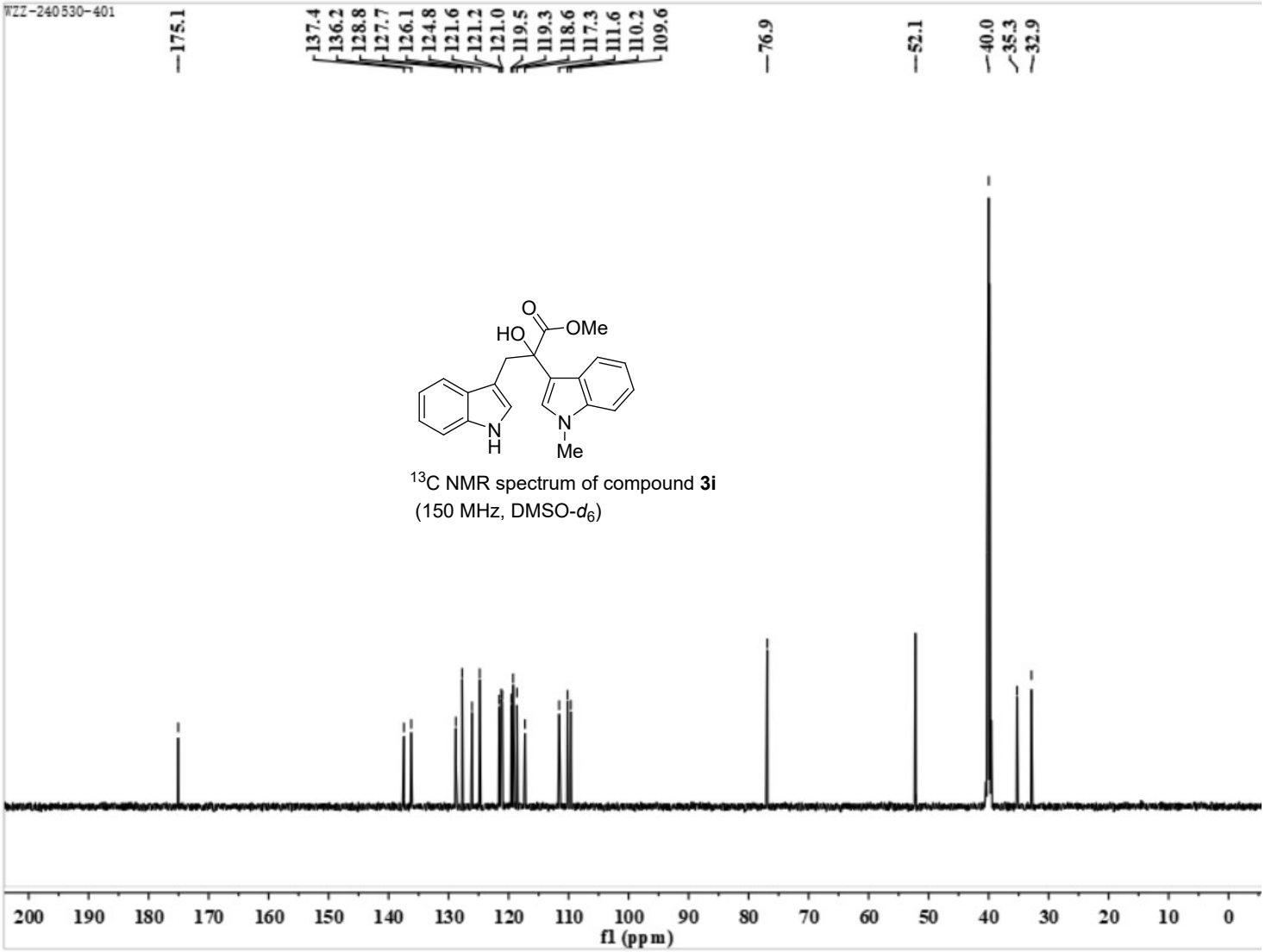
^{1}H NMR spectrum of compound **3h**
(600 MHz, DMSO-d_6)



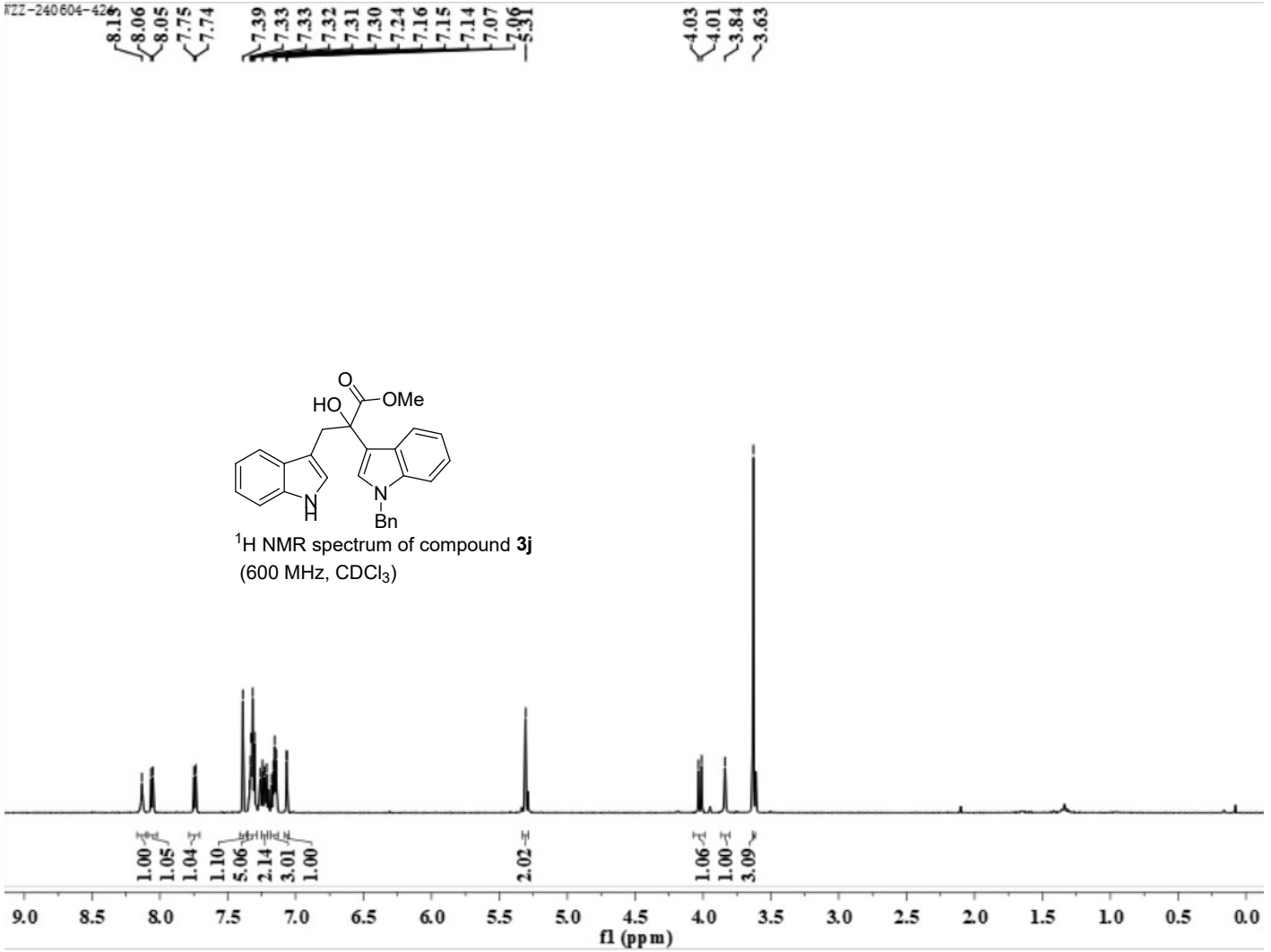
^{13}C NMR spectrum of compound **3h**
(150 MHz, DMSO-d_6)



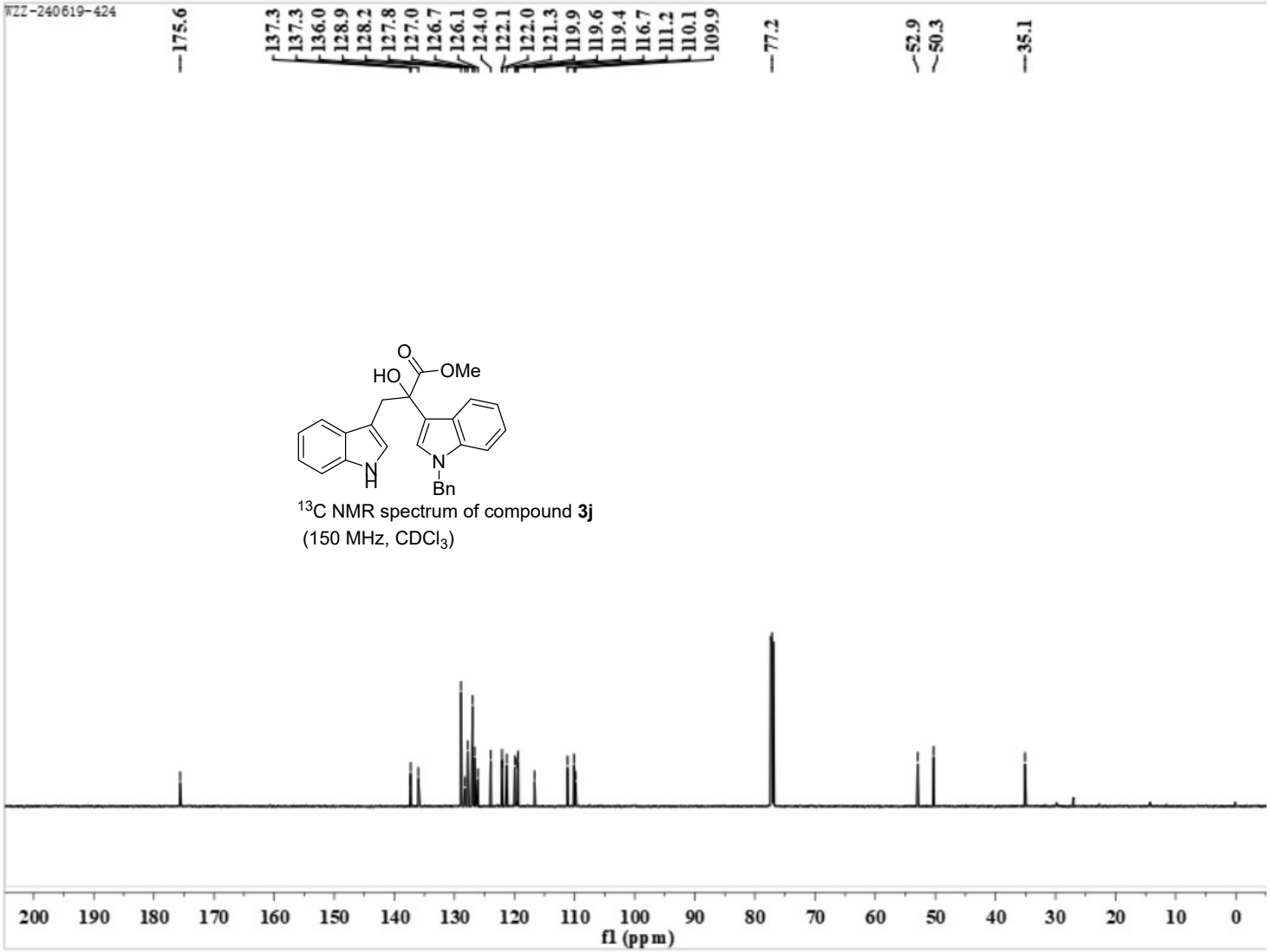
^{1}H NMR spectrum of compound **3i**
(600 MHz, DMSO-d_6)



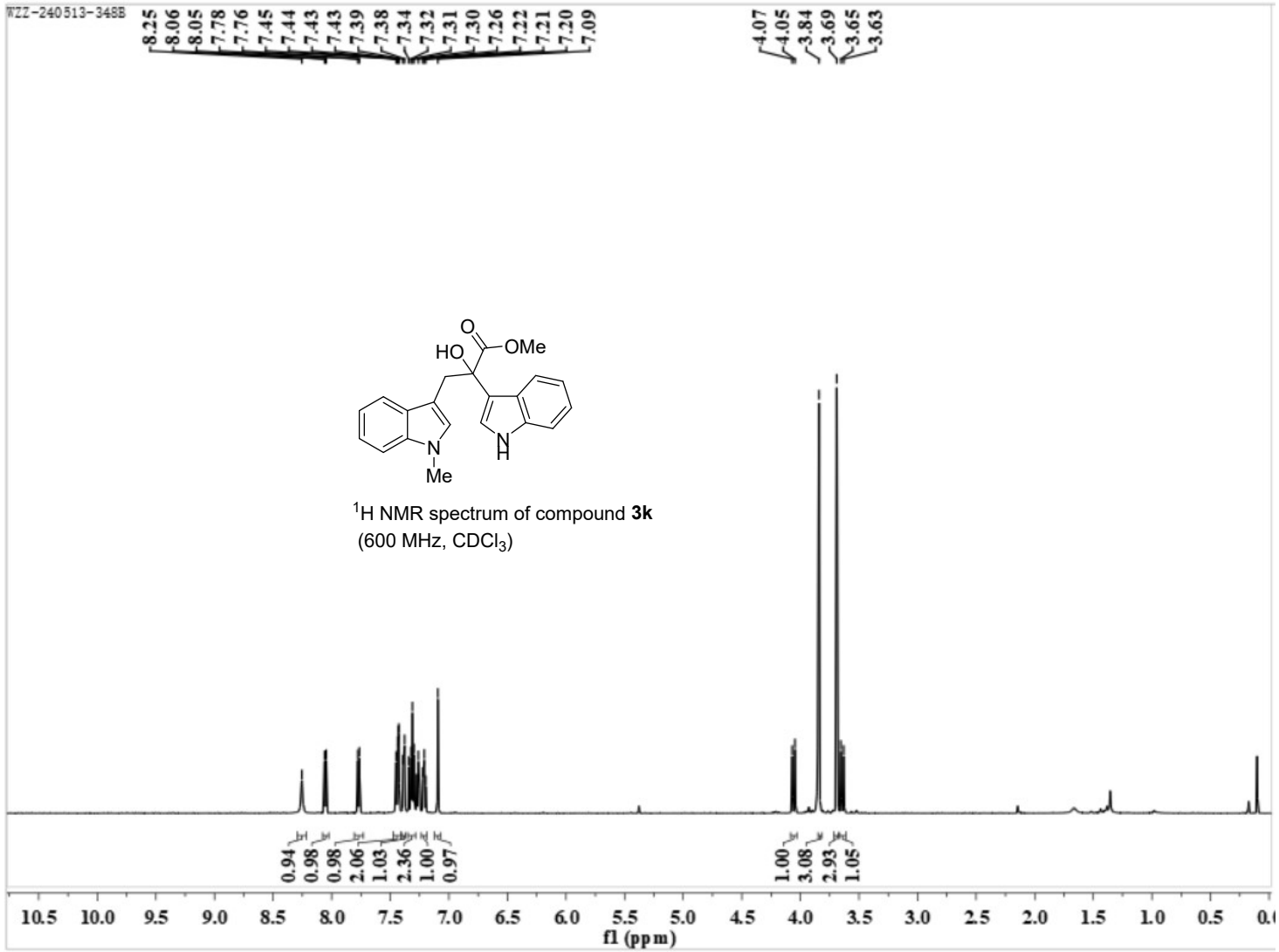
^{13}C NMR spectrum of compound **3i**
(150 MHz, DMSO-d_6)



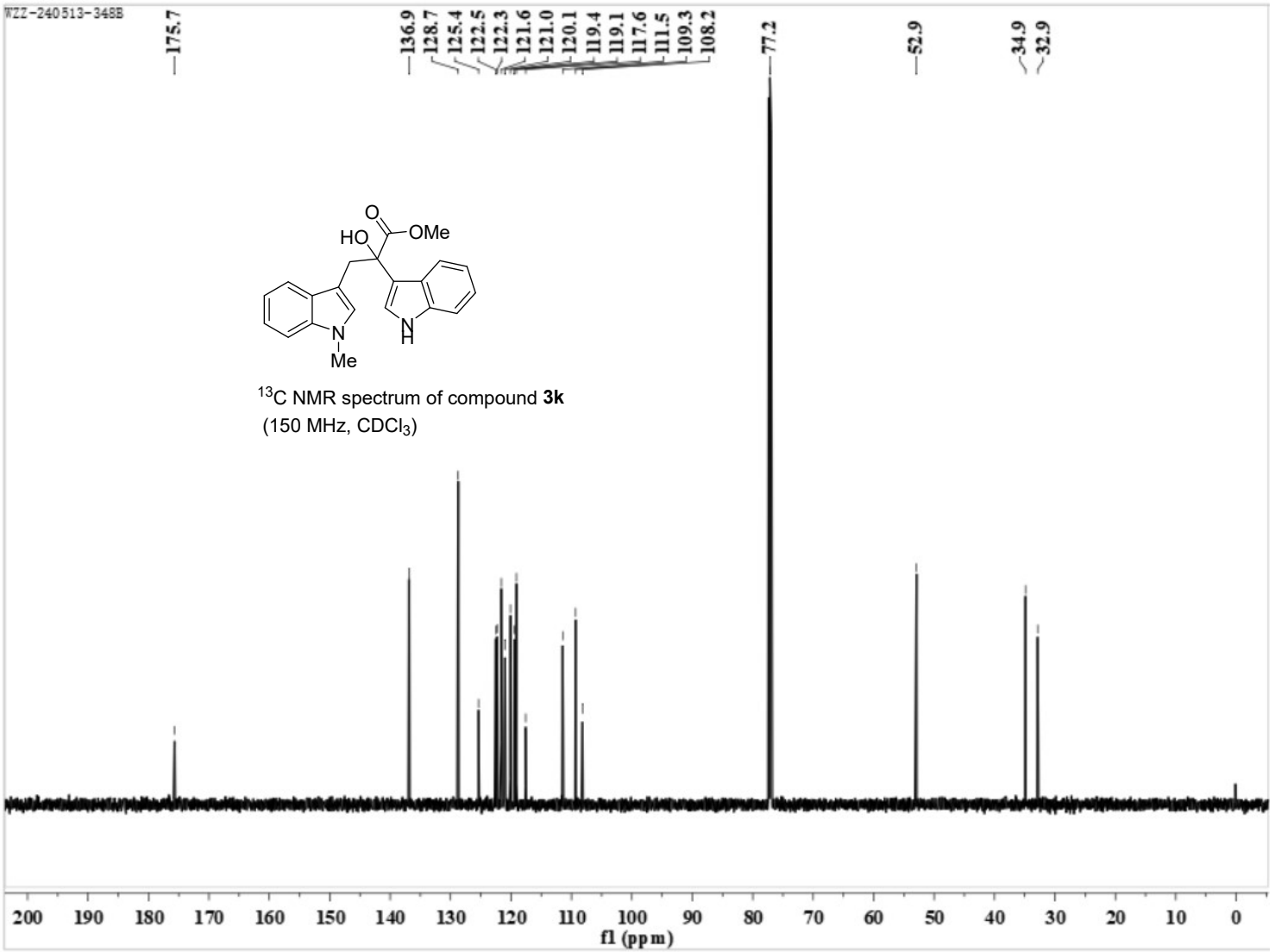
^{1}H NMR spectrum of compound **3j**
(600 MHz, $CDCl_3$)



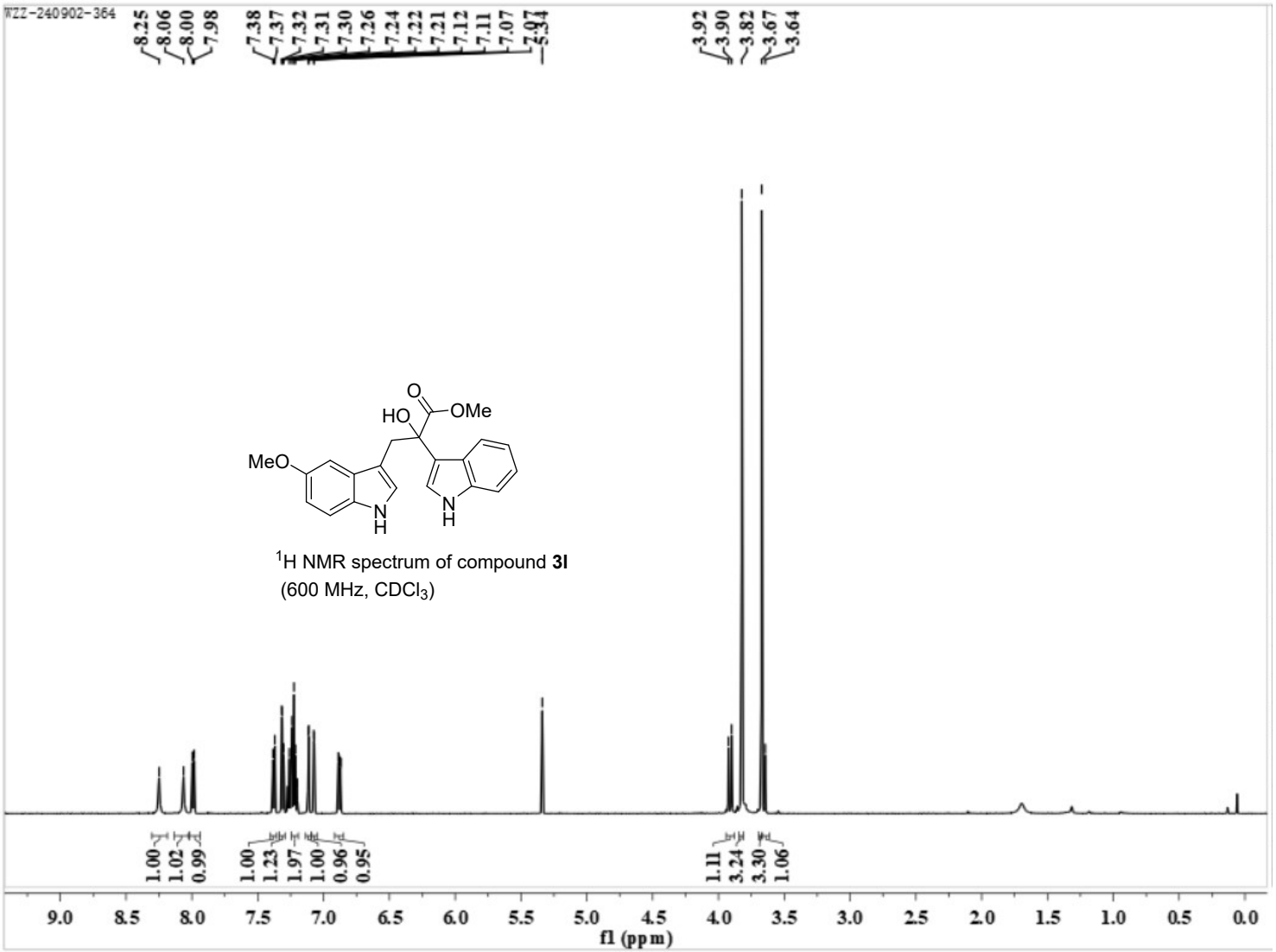
^{13}C NMR spectrum of compound **3j**
(150 MHz, $CDCl_3$)



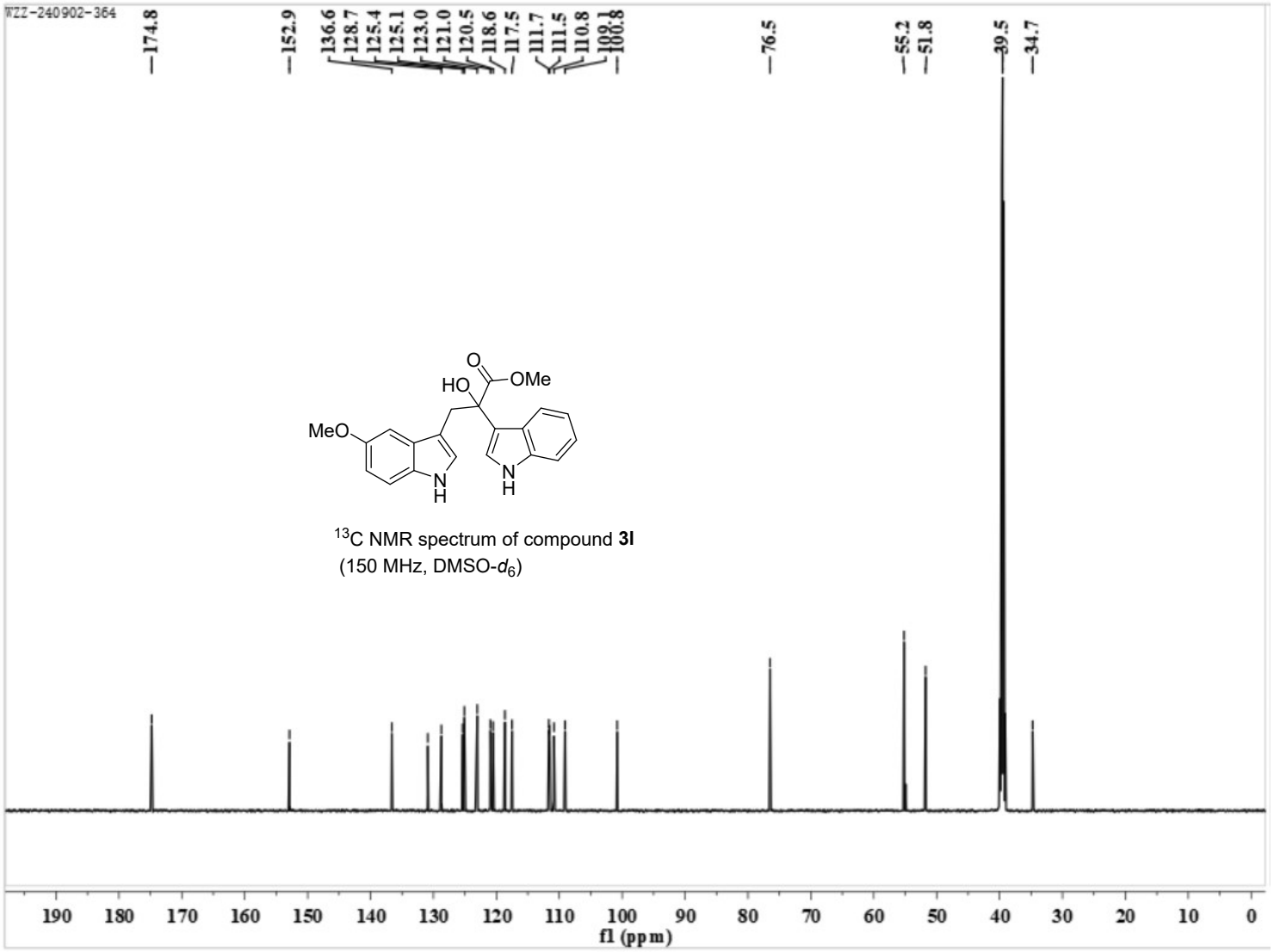
^{1}H NMR spectrum of compound **3k**
(600 MHz, $CDCl_3$)



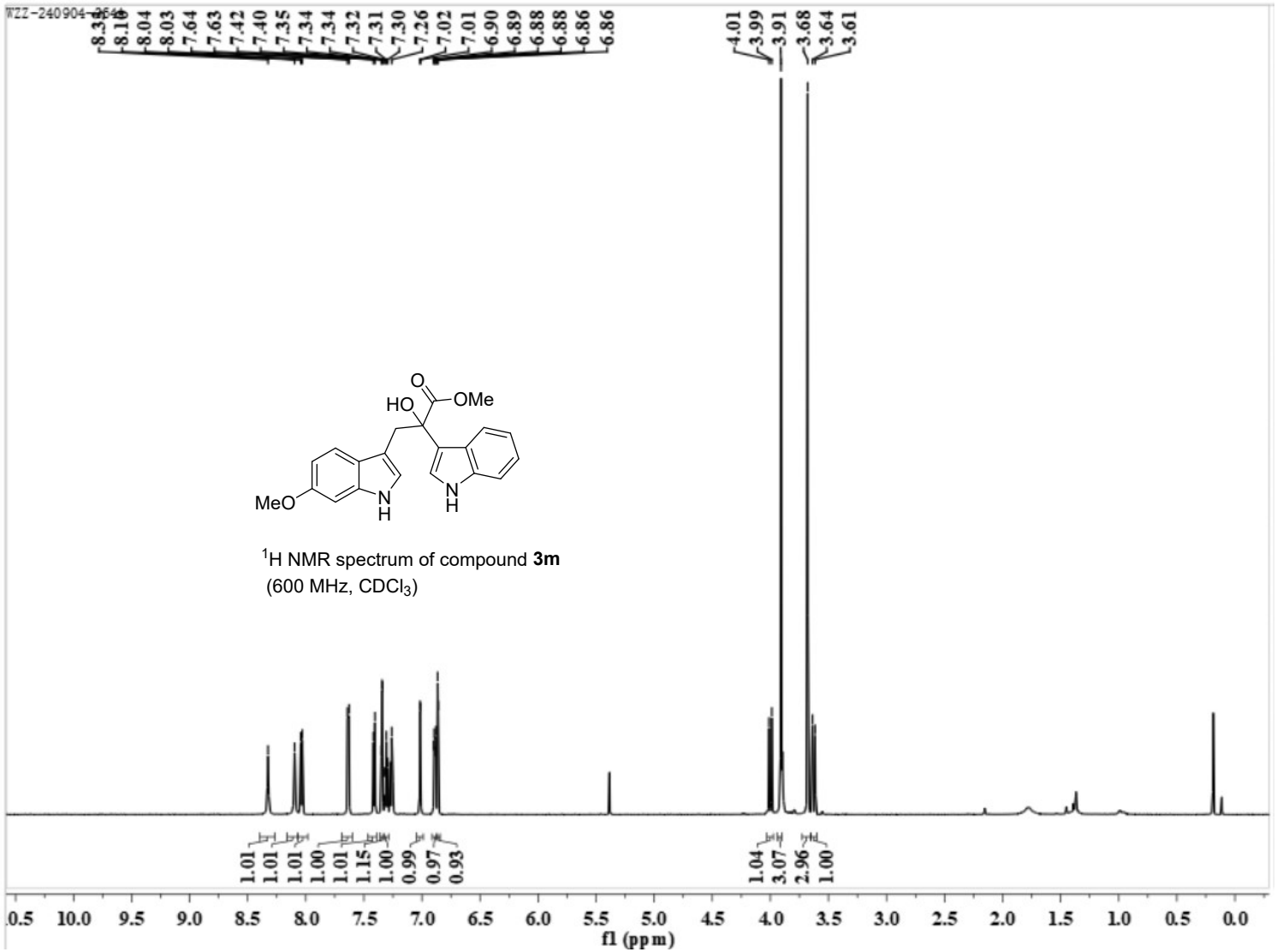
^{13}C NMR spectrum of compound **3k**
(150 MHz, $CDCl_3$)



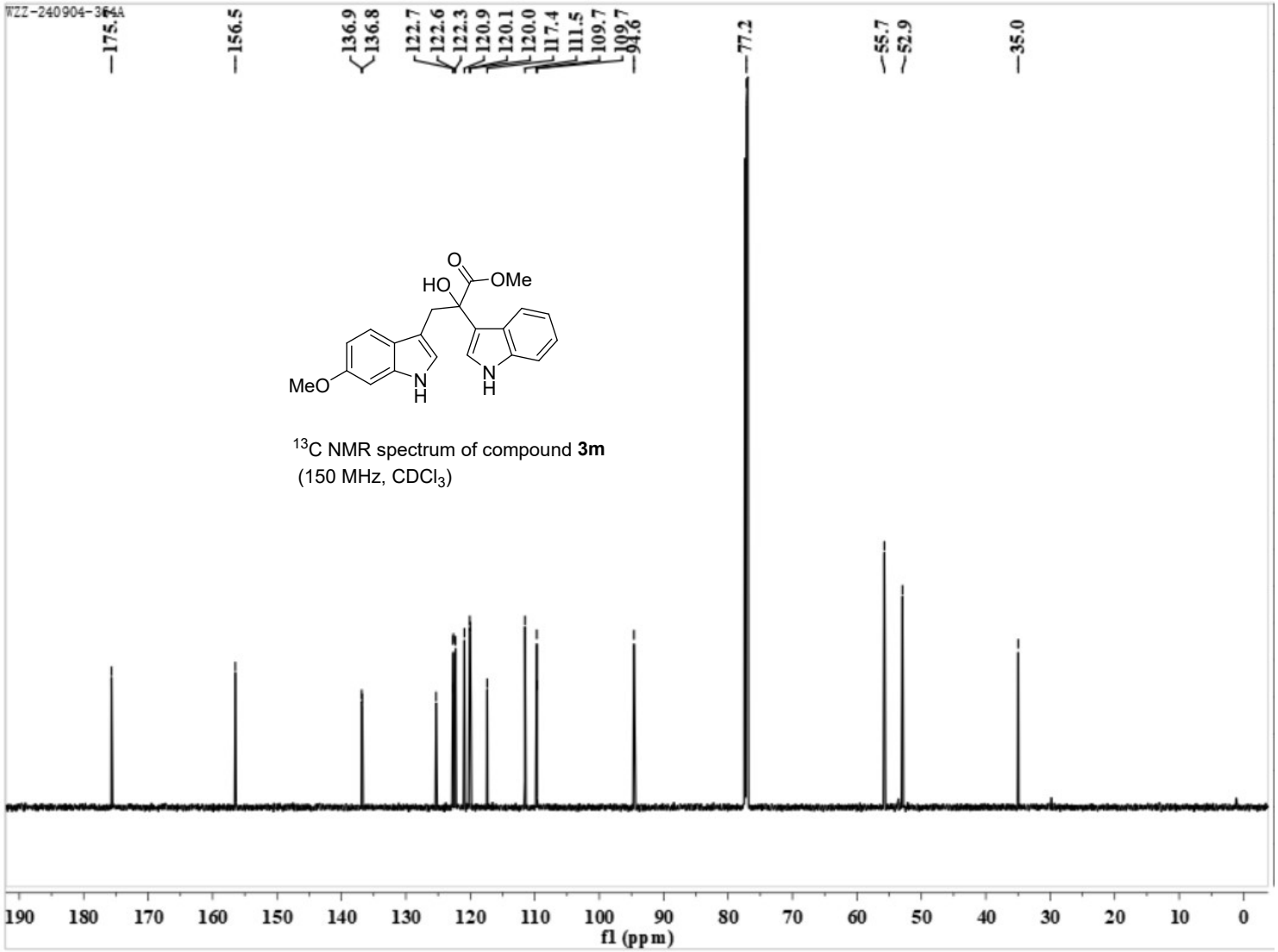
^{1}H NMR spectrum of compound **3l**
(600 MHz, $CDCl_3$)



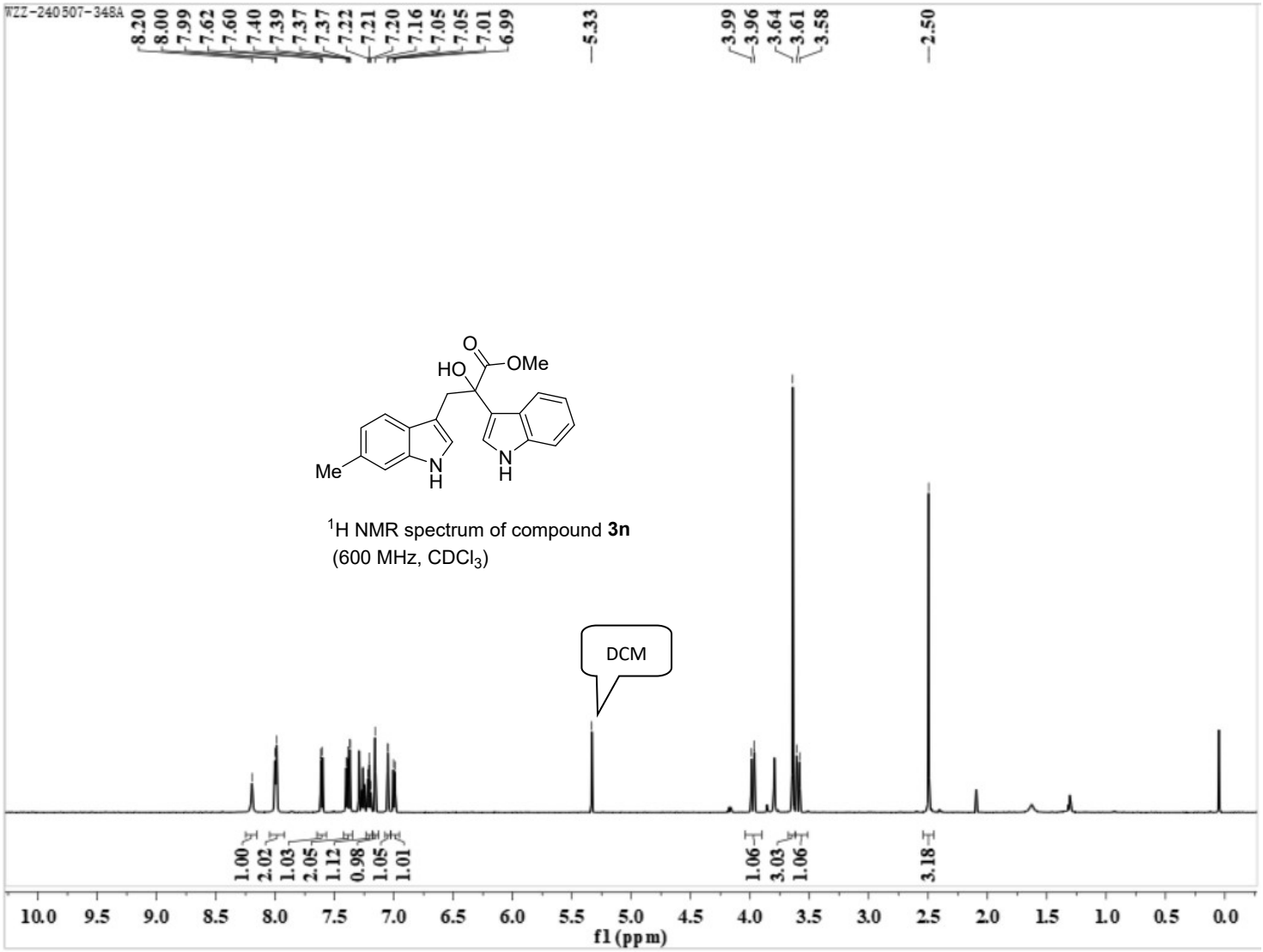
^{13}C NMR spectrum of compound **3l**
(150 MHz, DMSO-d_6)



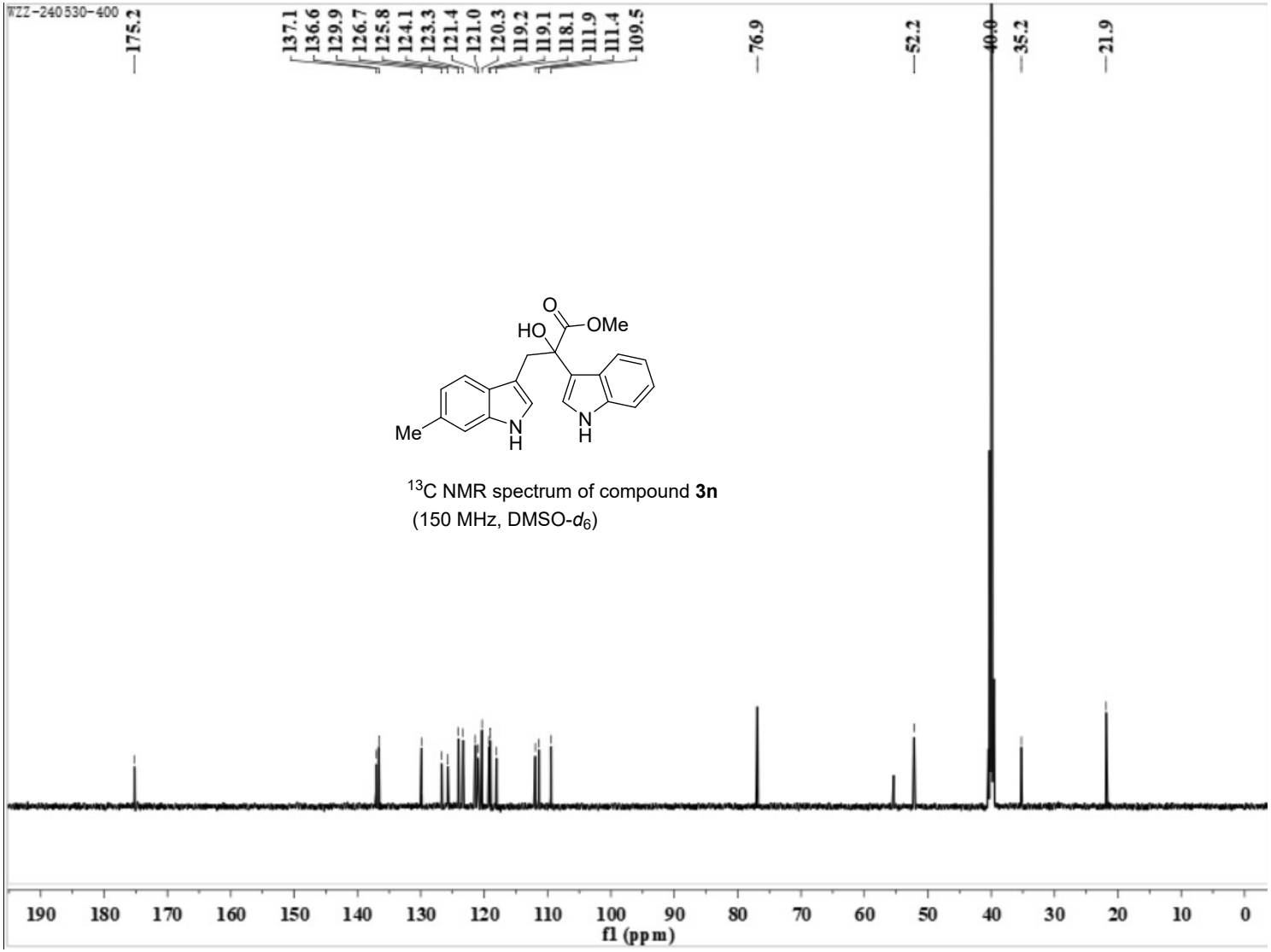
^{1}H NMR spectrum of compound **3m**
(600 MHz, $CDCl_3$)



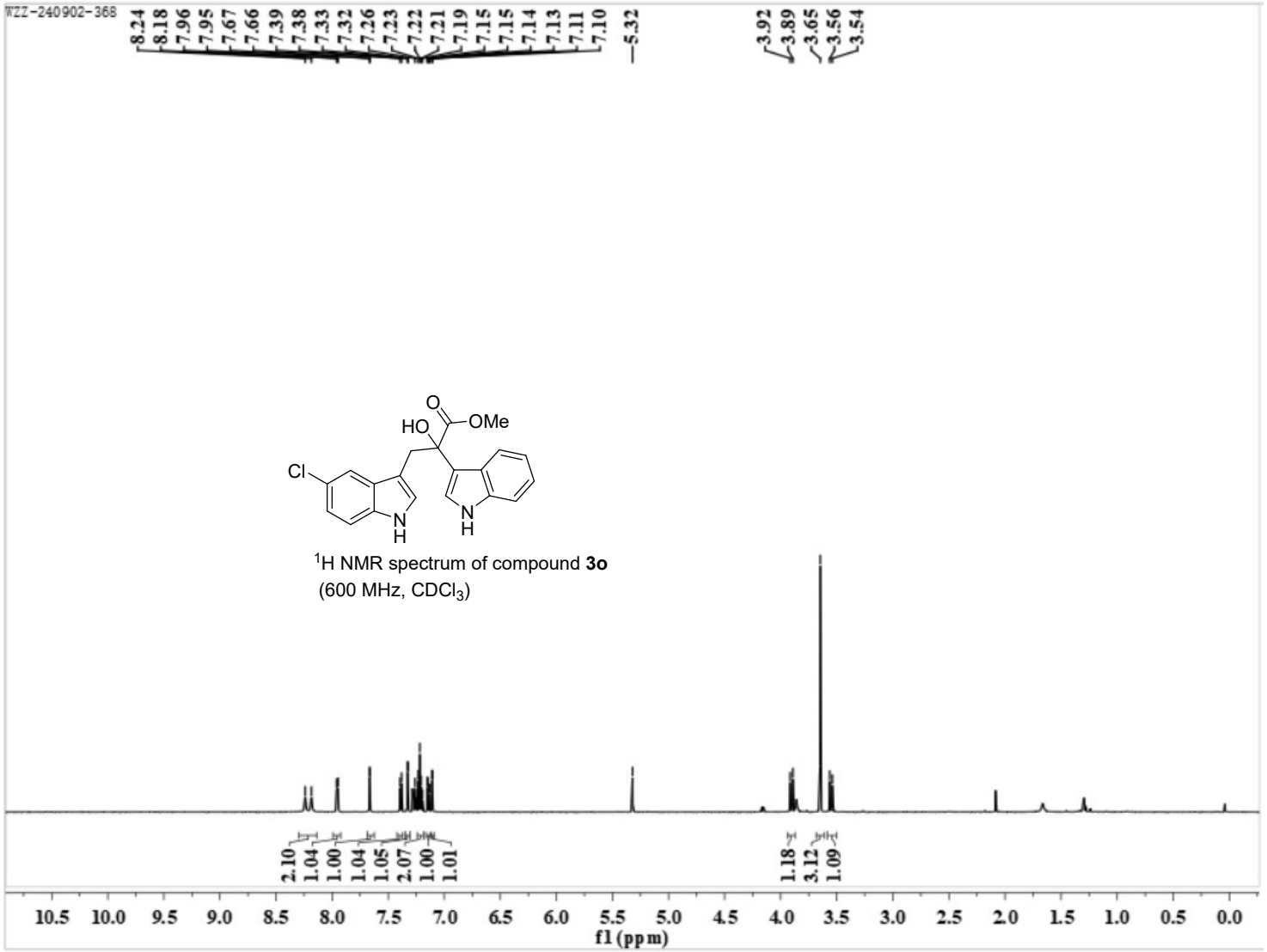
^{13}C NMR spectrum of compound **3m**
(150 MHz, $CDCl_3$)



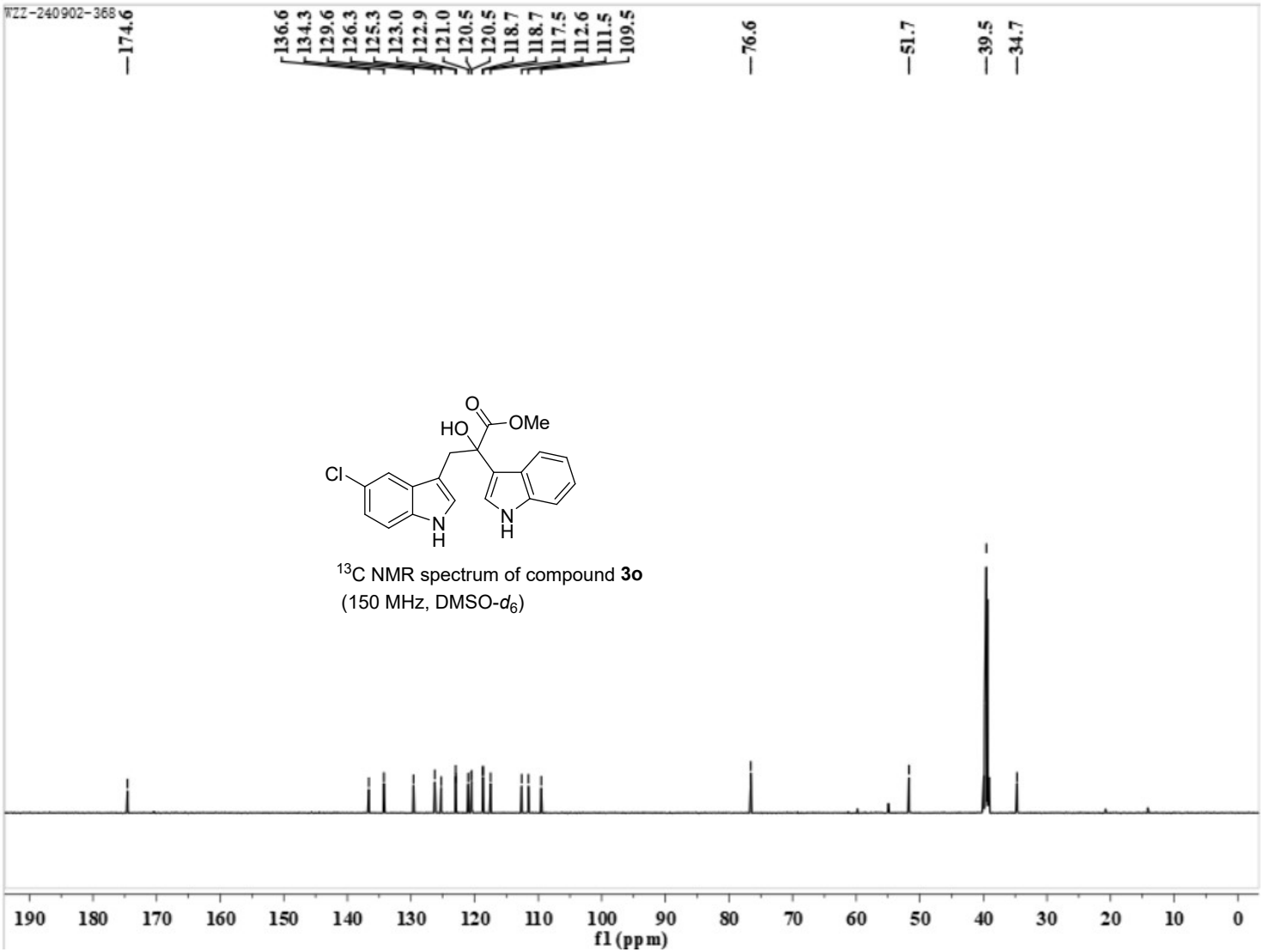
^{1}H NMR spectrum of compound **3n**
(600 MHz, $CDCl_3$)



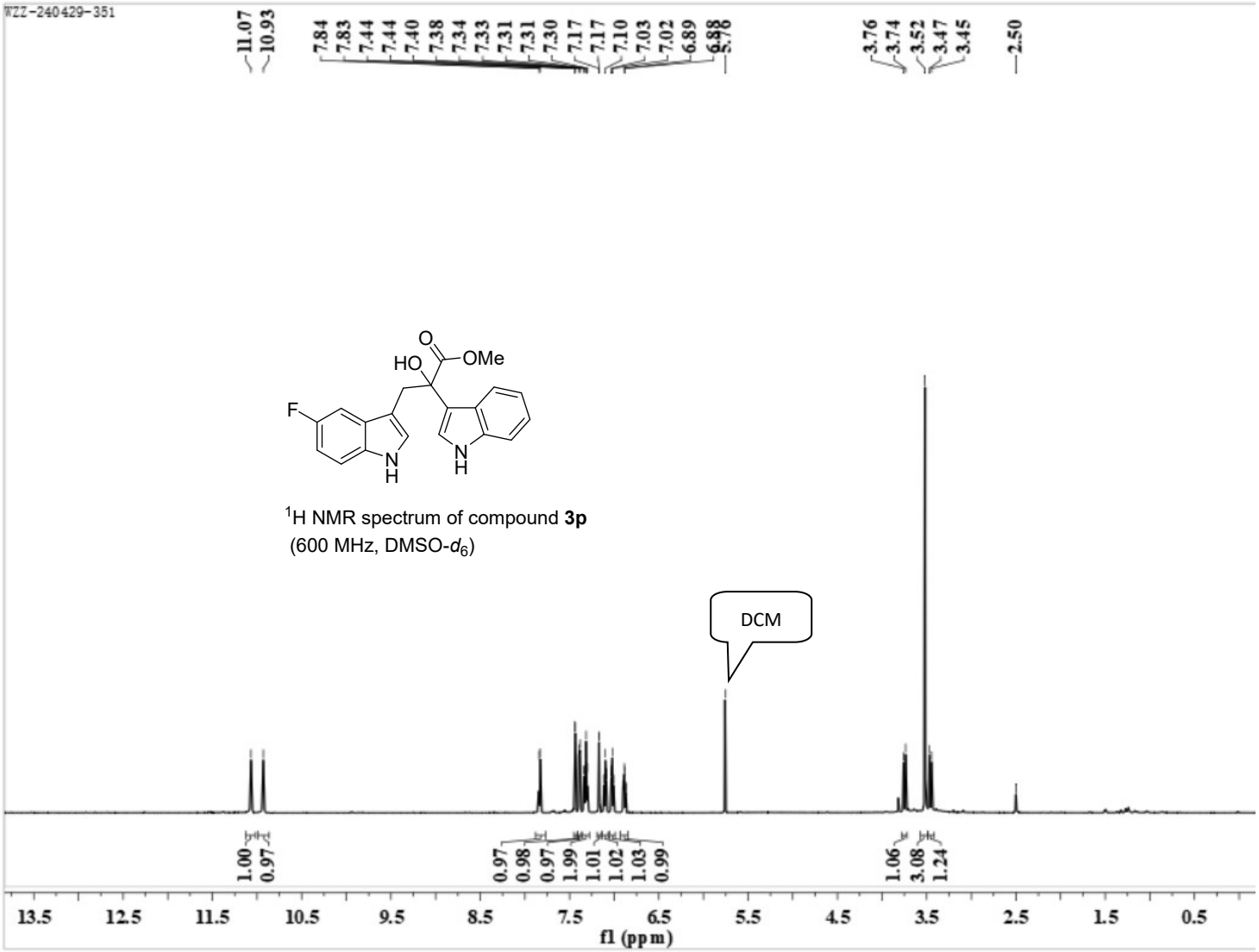
^{13}C NMR spectrum of compound **3n**
(150 MHz, DMSO-d_6)



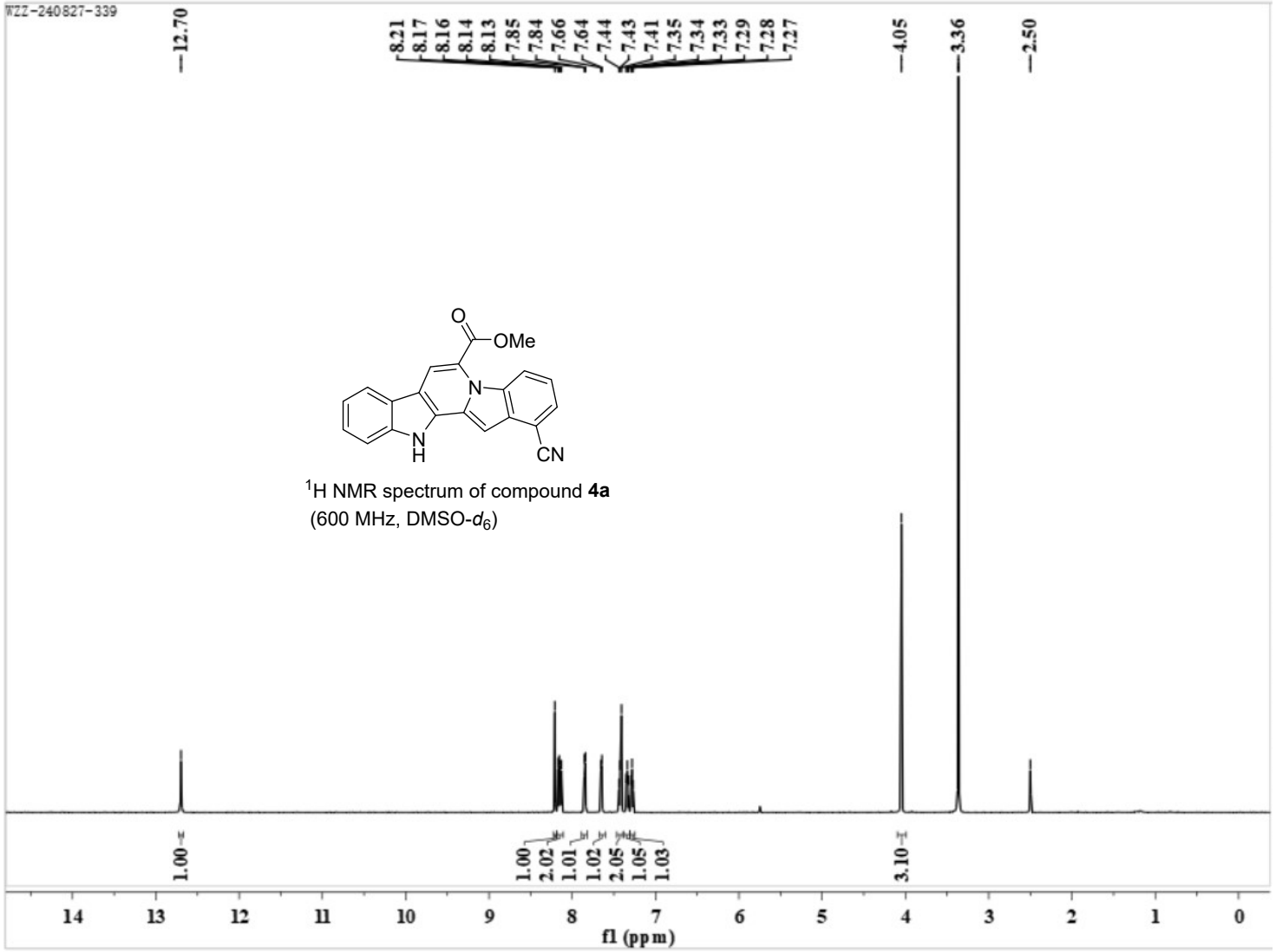
^{1}H NMR spectrum of compound **3o**
(600 MHz, $CDCl_3$)



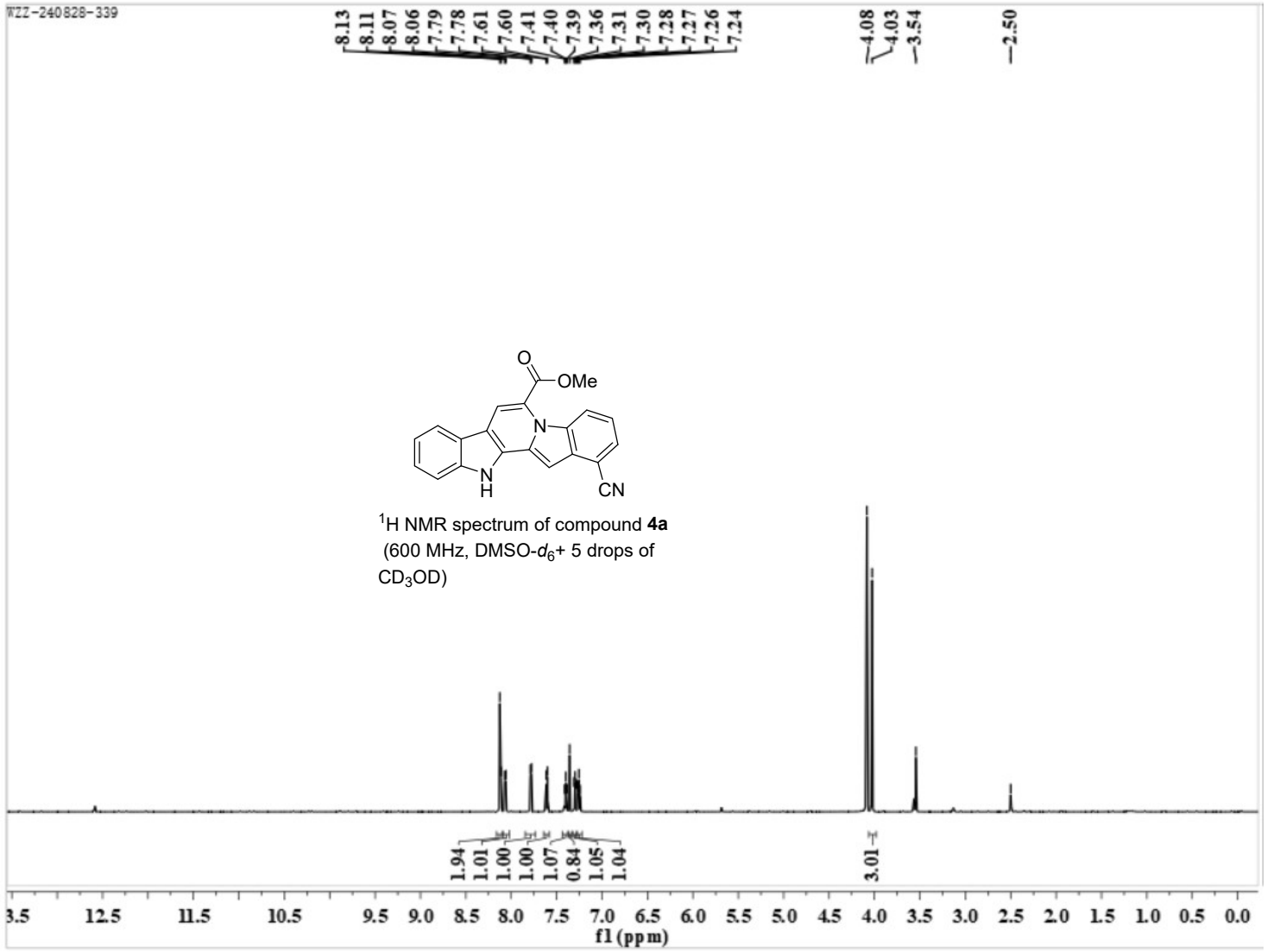
^{13}C NMR spectrum of compound **3o**
(150 MHz, DMSO-d_6)



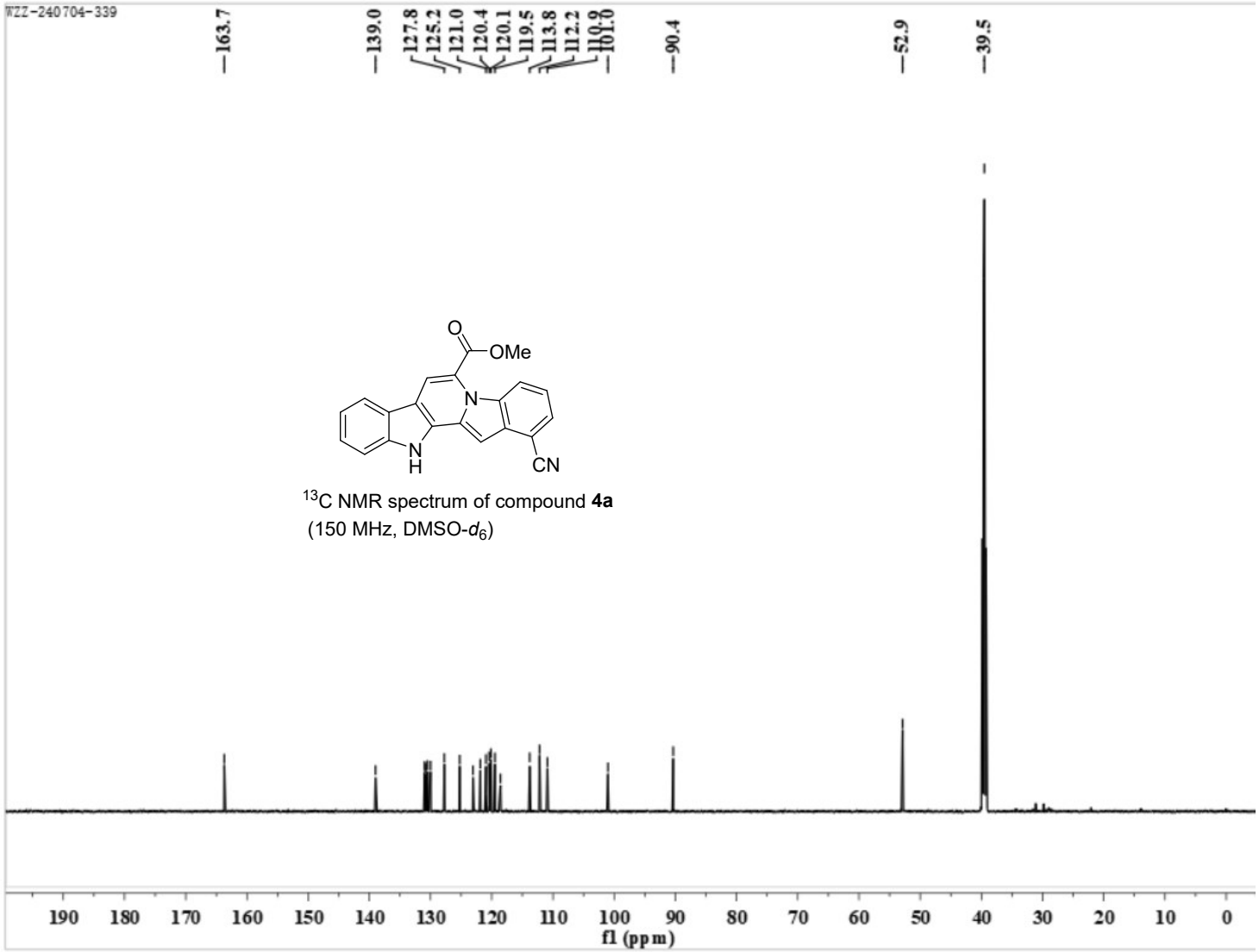
^{1}H NMR spectrum of compound **3p**
(600 MHz, DMSO-d_6)



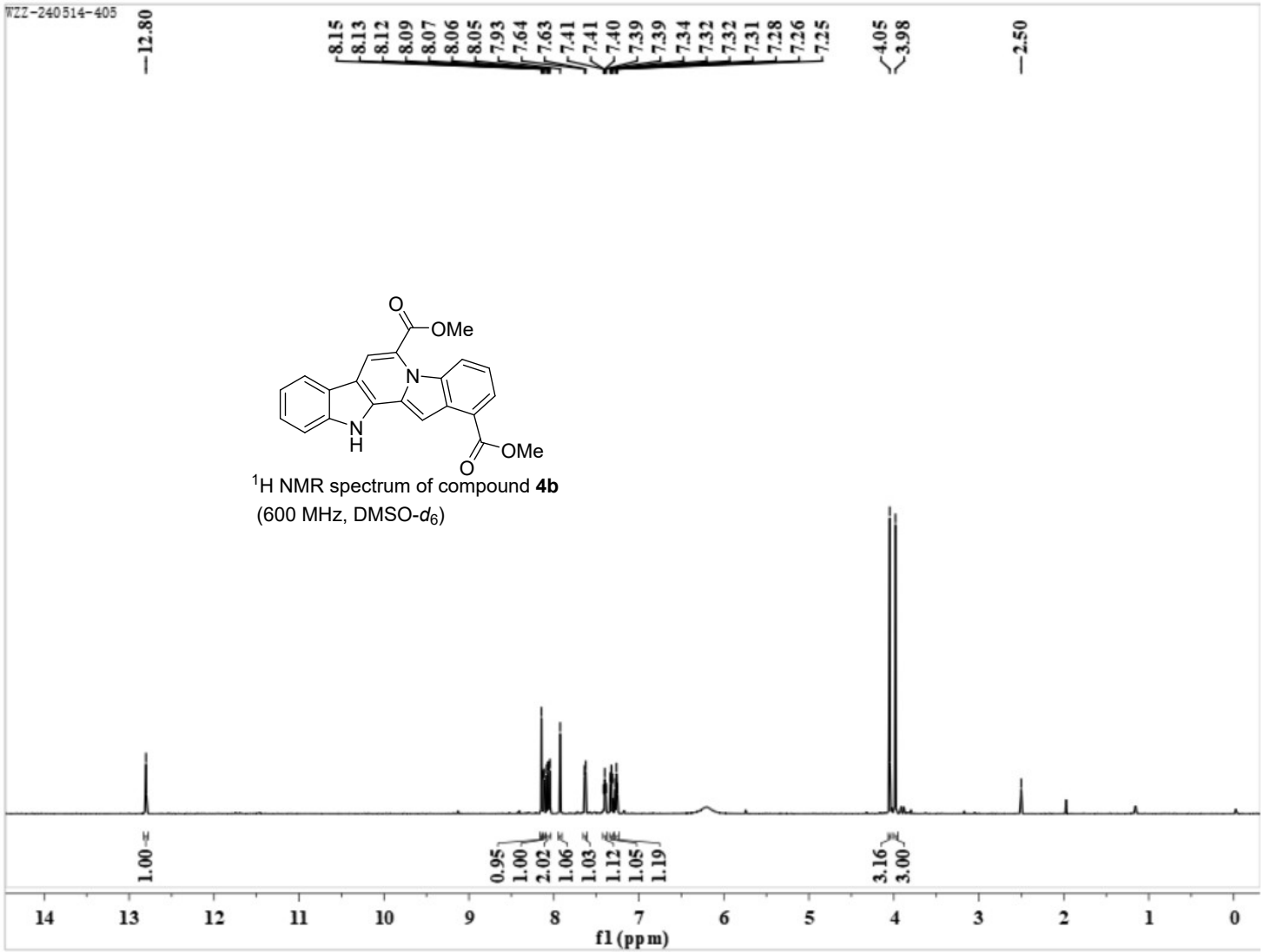
^{1}H NMR spectrum of compound **4a**
(600 MHz, DMSO-d_6)



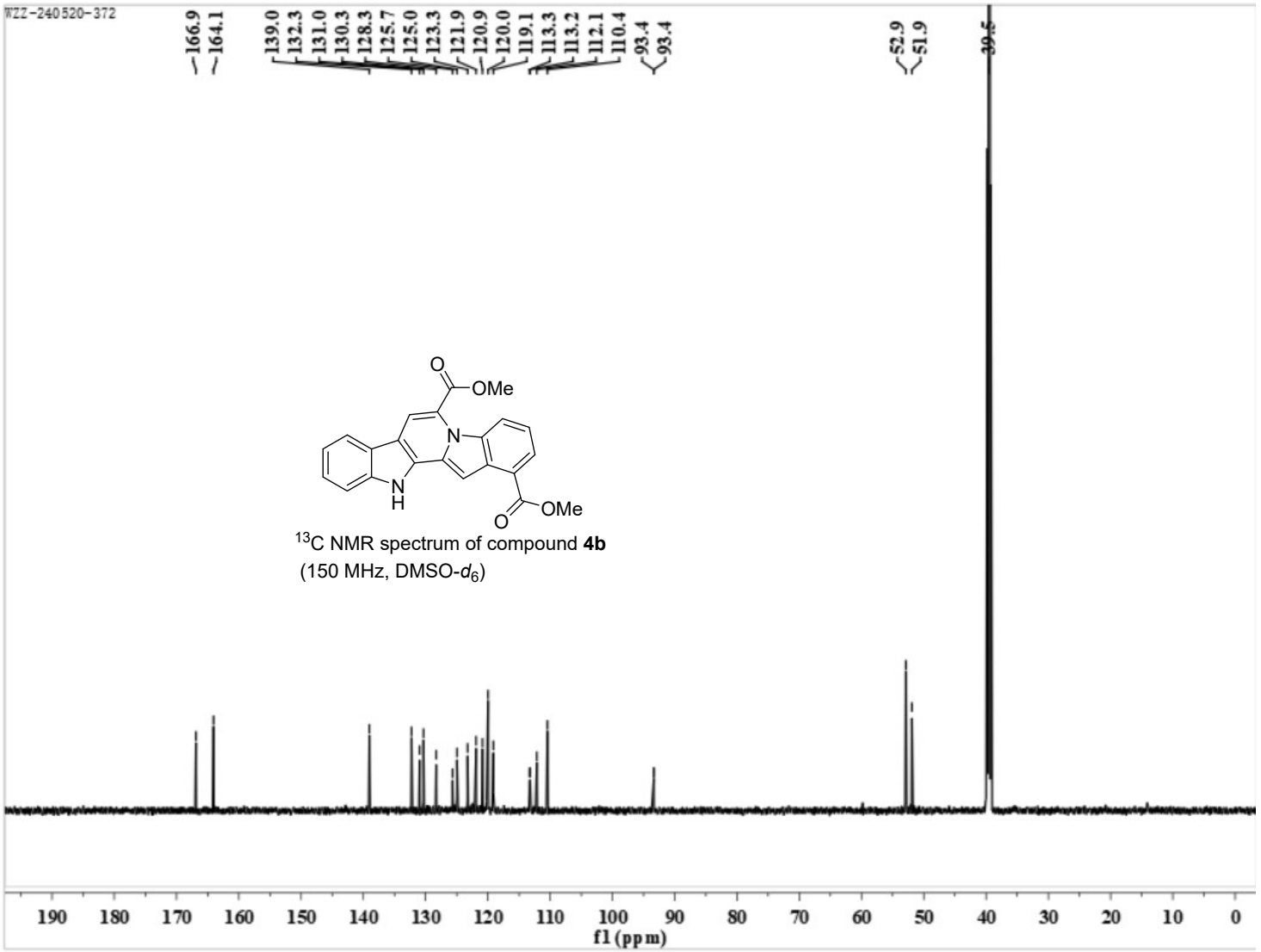
^{1}H NMR spectrum of compound **4a** (600 MHz, DMSO-d_6+ 5 drops of CD_3OD)



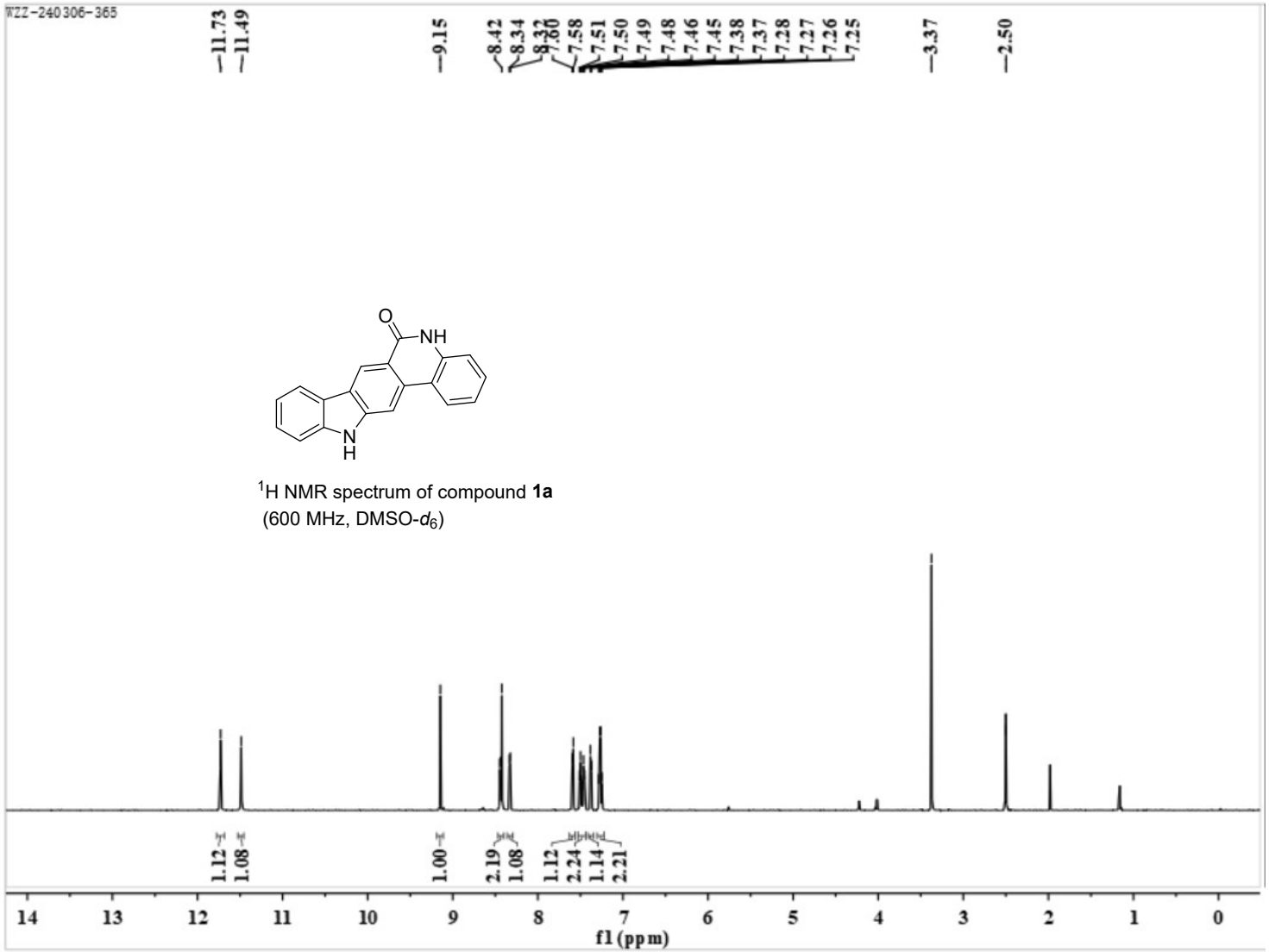
^{13}C NMR spectrum of compound **4a**
(150 MHz, DMSO-d_6)



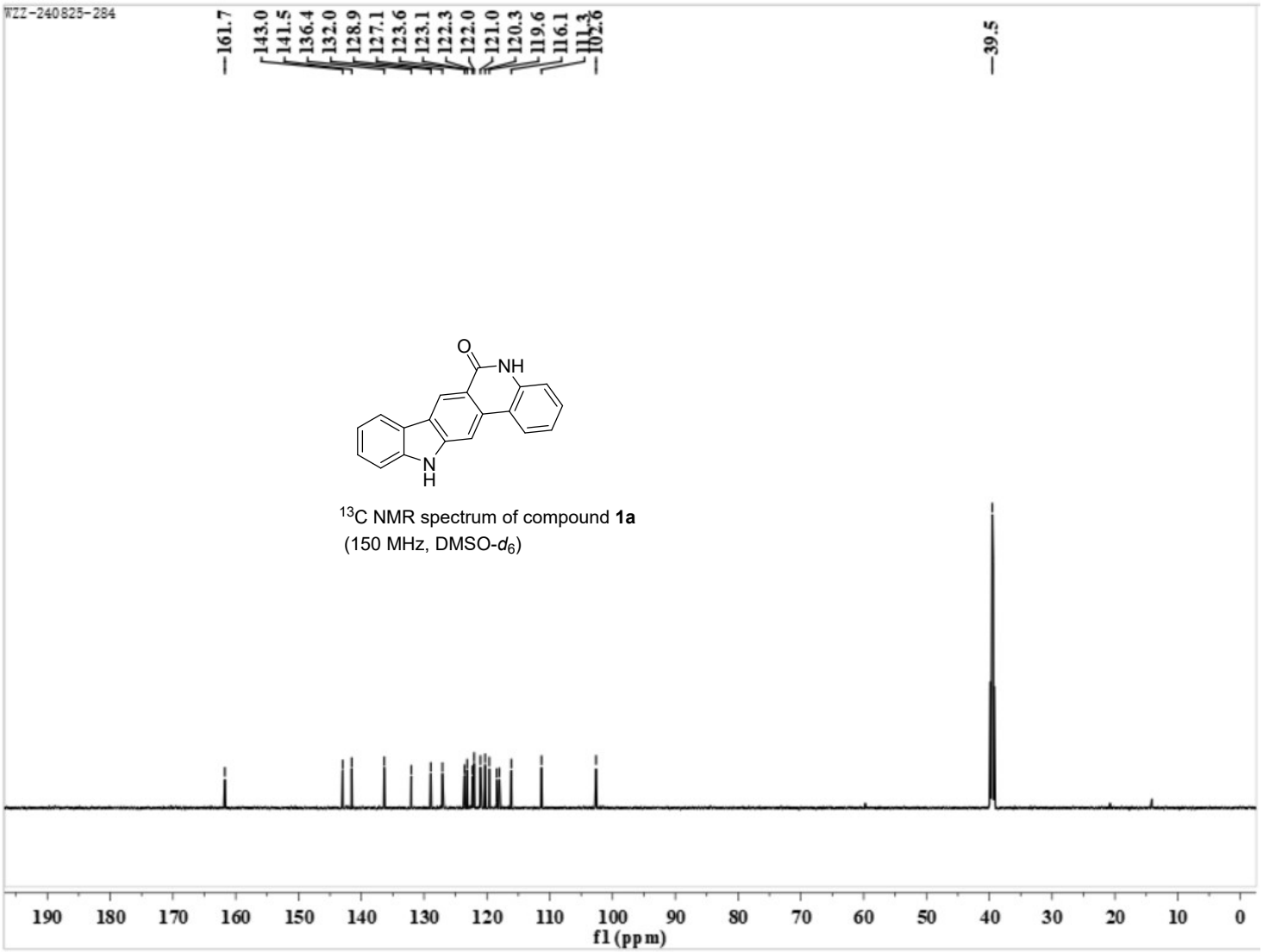
^{1}H NMR spectrum of compound **4b**
(600 MHz, DMSO-d_6)



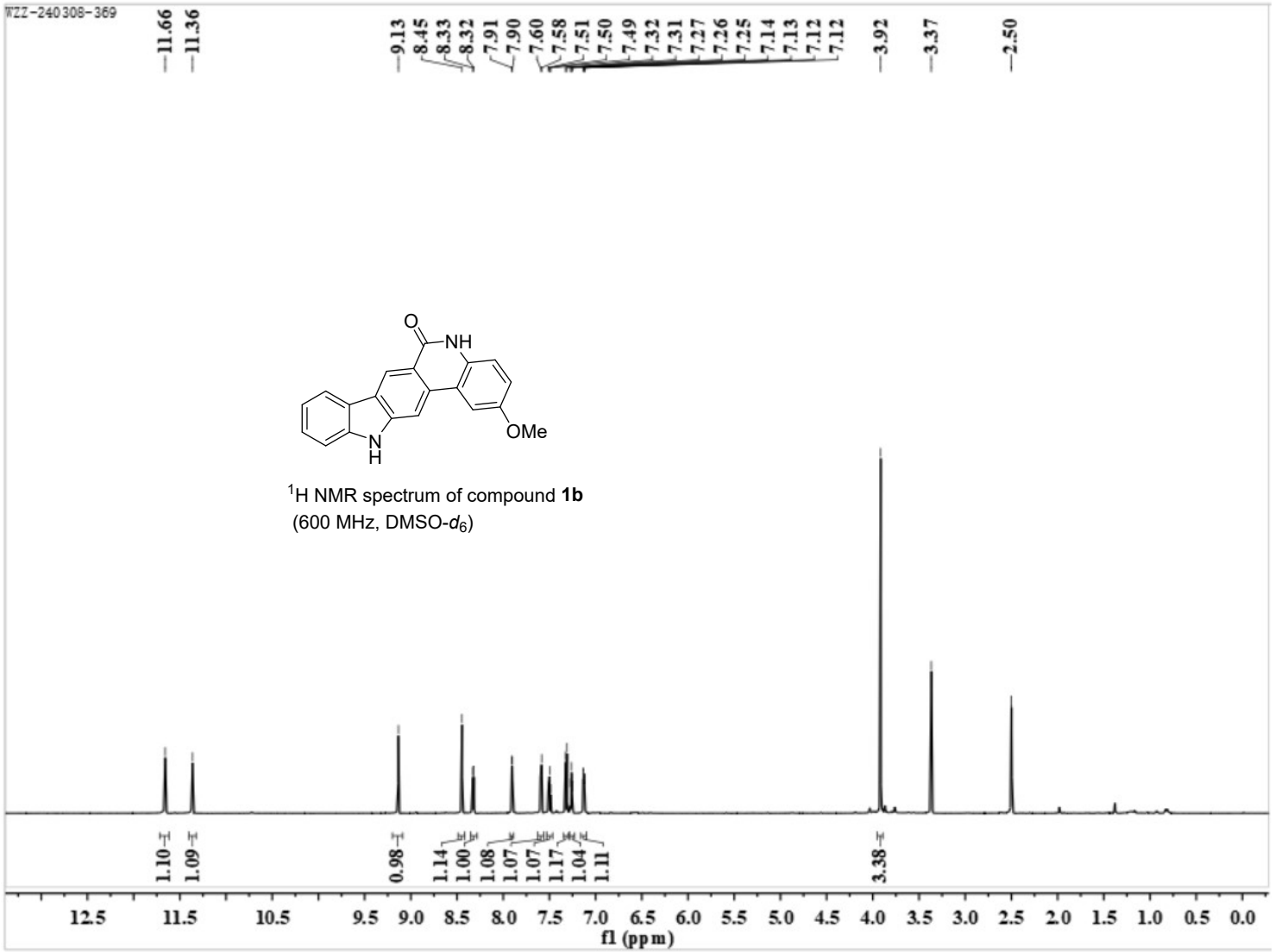
^{13}C NMR spectrum of compound **4b**
(150 MHz, DMSO-d_6)



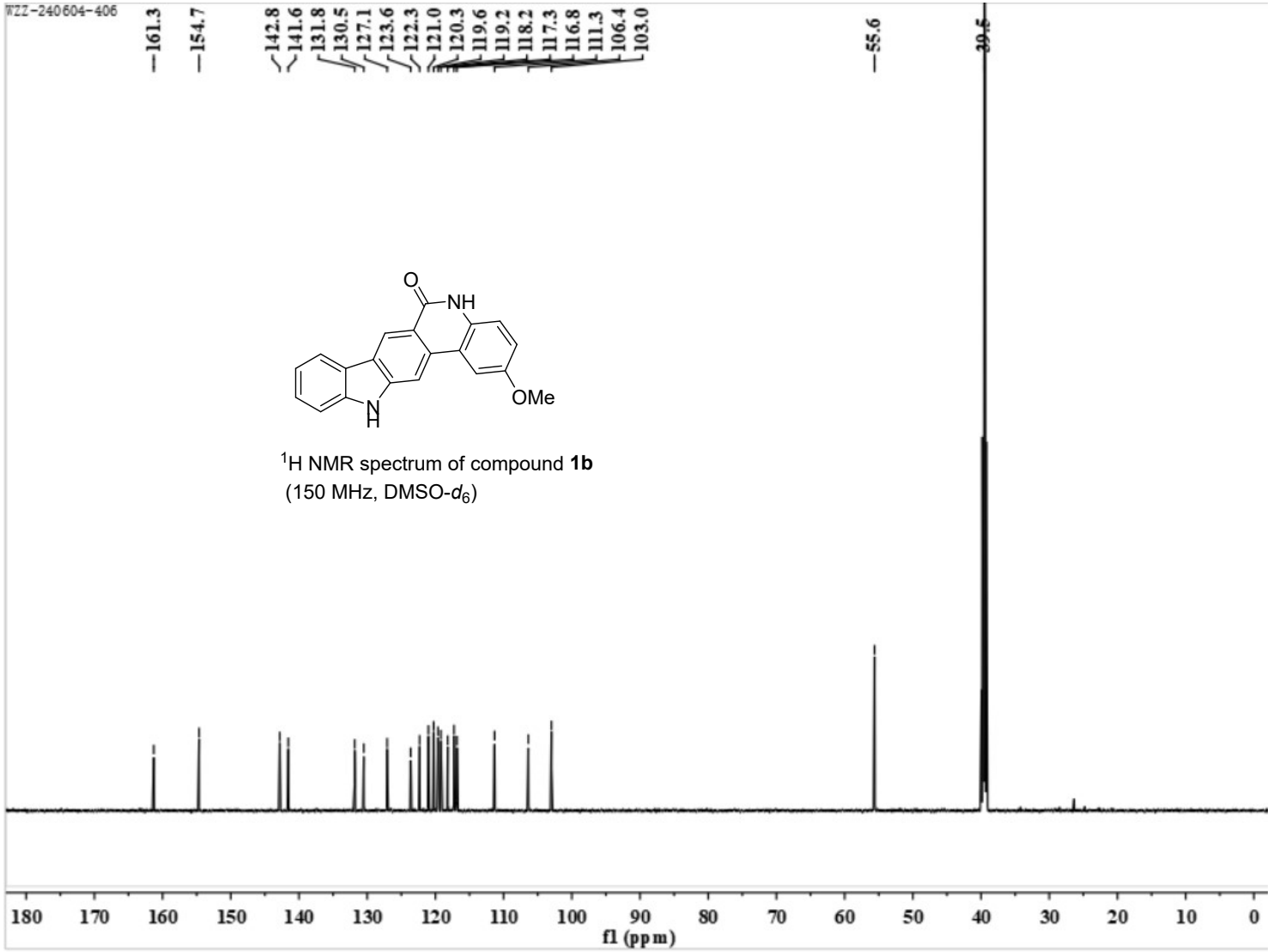
^{1}H NMR spectrum of compound **1a**
(600 MHz, DMSO-d_6)



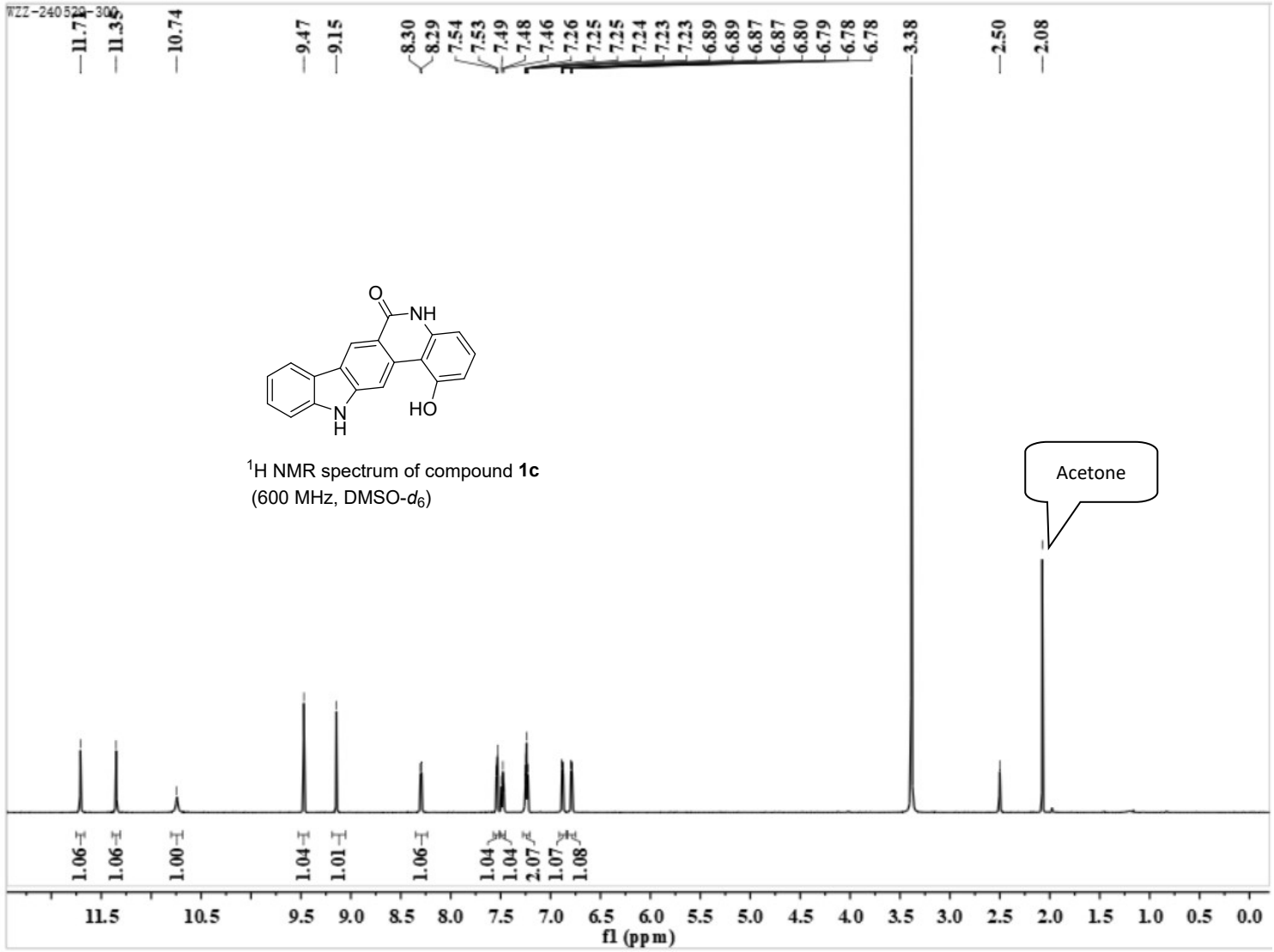
^{13}C NMR spectrum of compound **1a**
(150 MHz, DMSO-d_6)



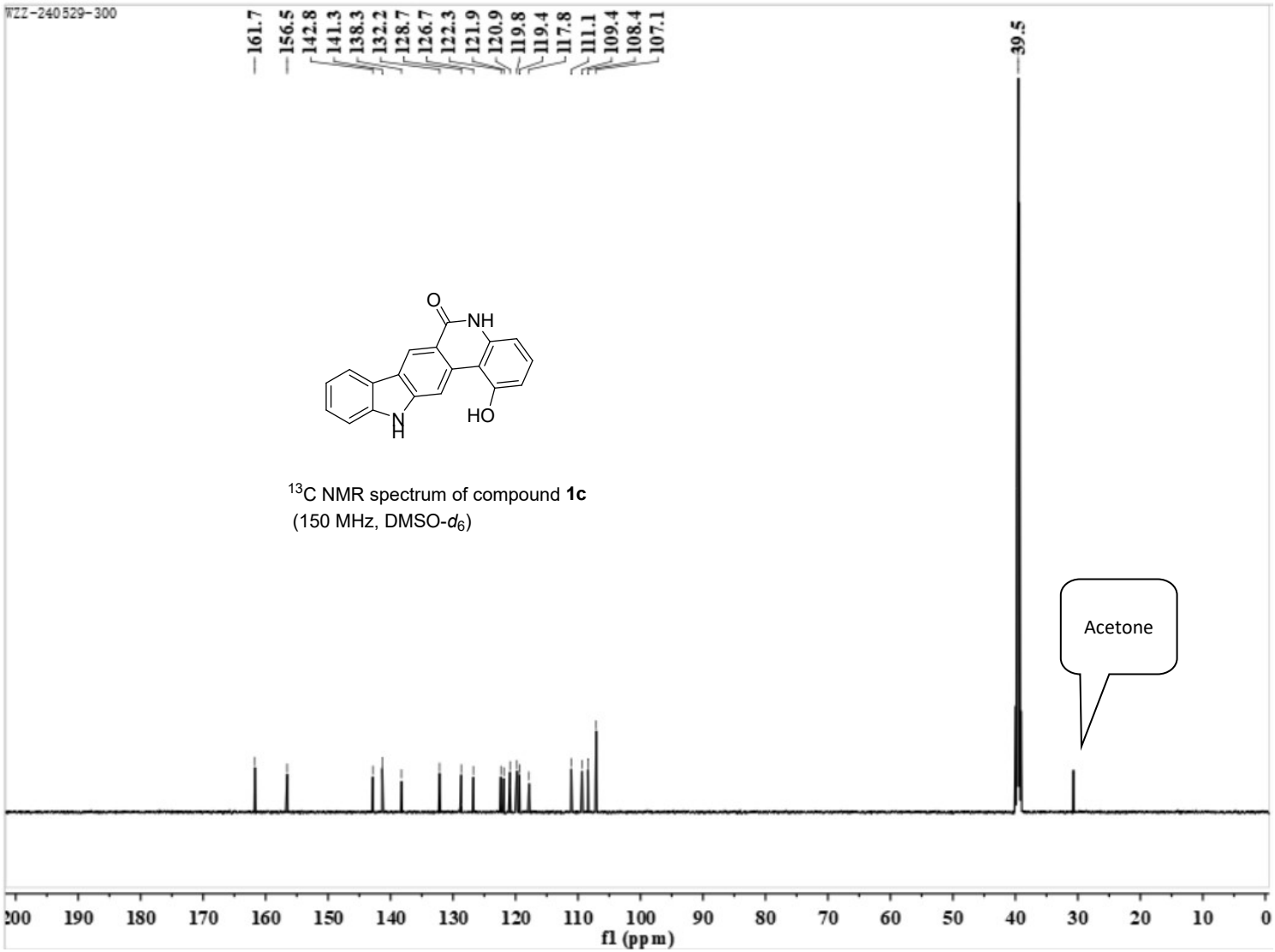
^{1}H NMR spectrum of compound **1b**
(600 MHz, DMSO-d_6)



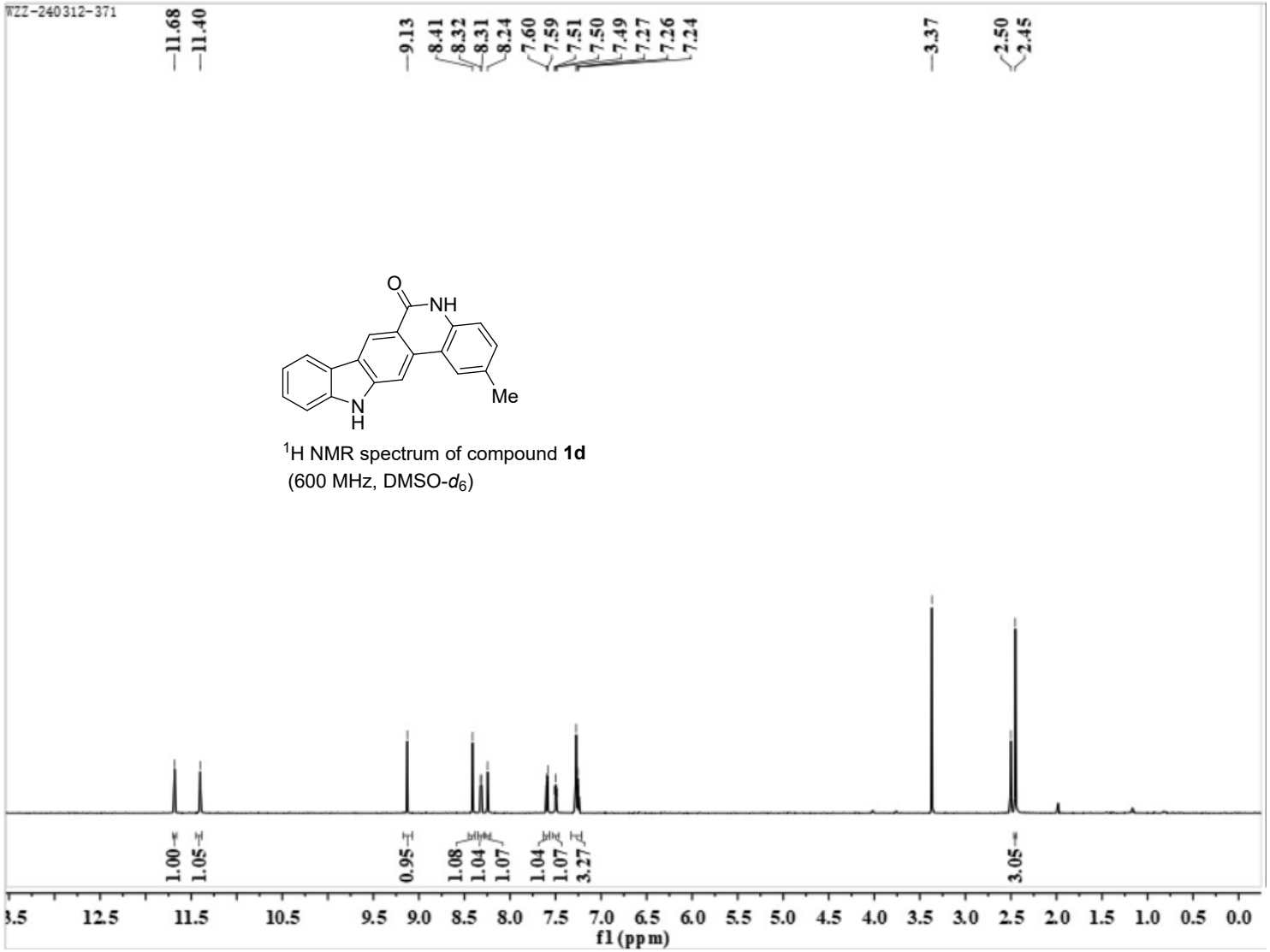
^{1}H NMR spectrum of compound **1b**
(150 MHz, DMSO-d_6)



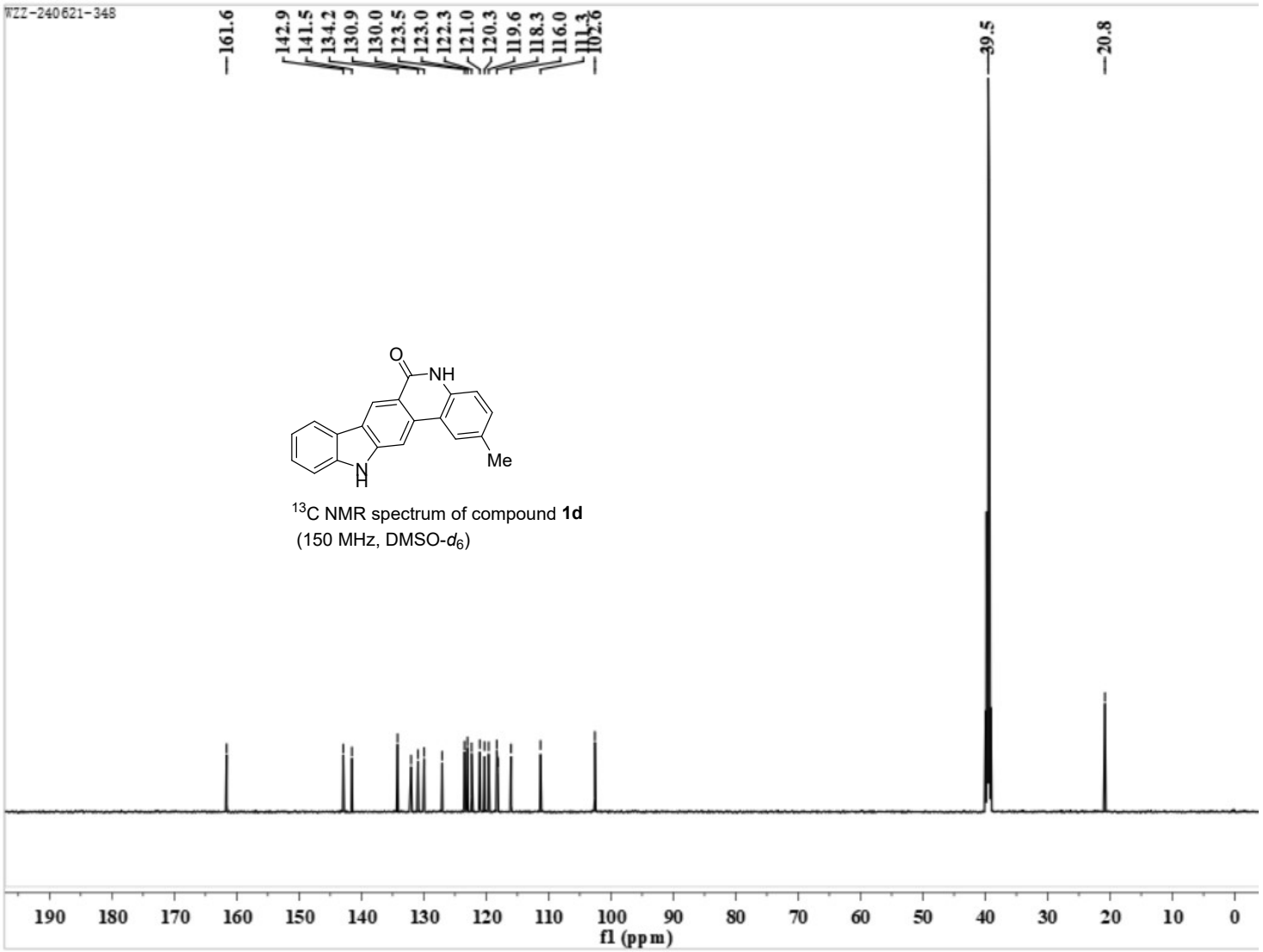
^{1}H NMR spectrum of compound **1c**
(600 MHz, DMSO-d_6)



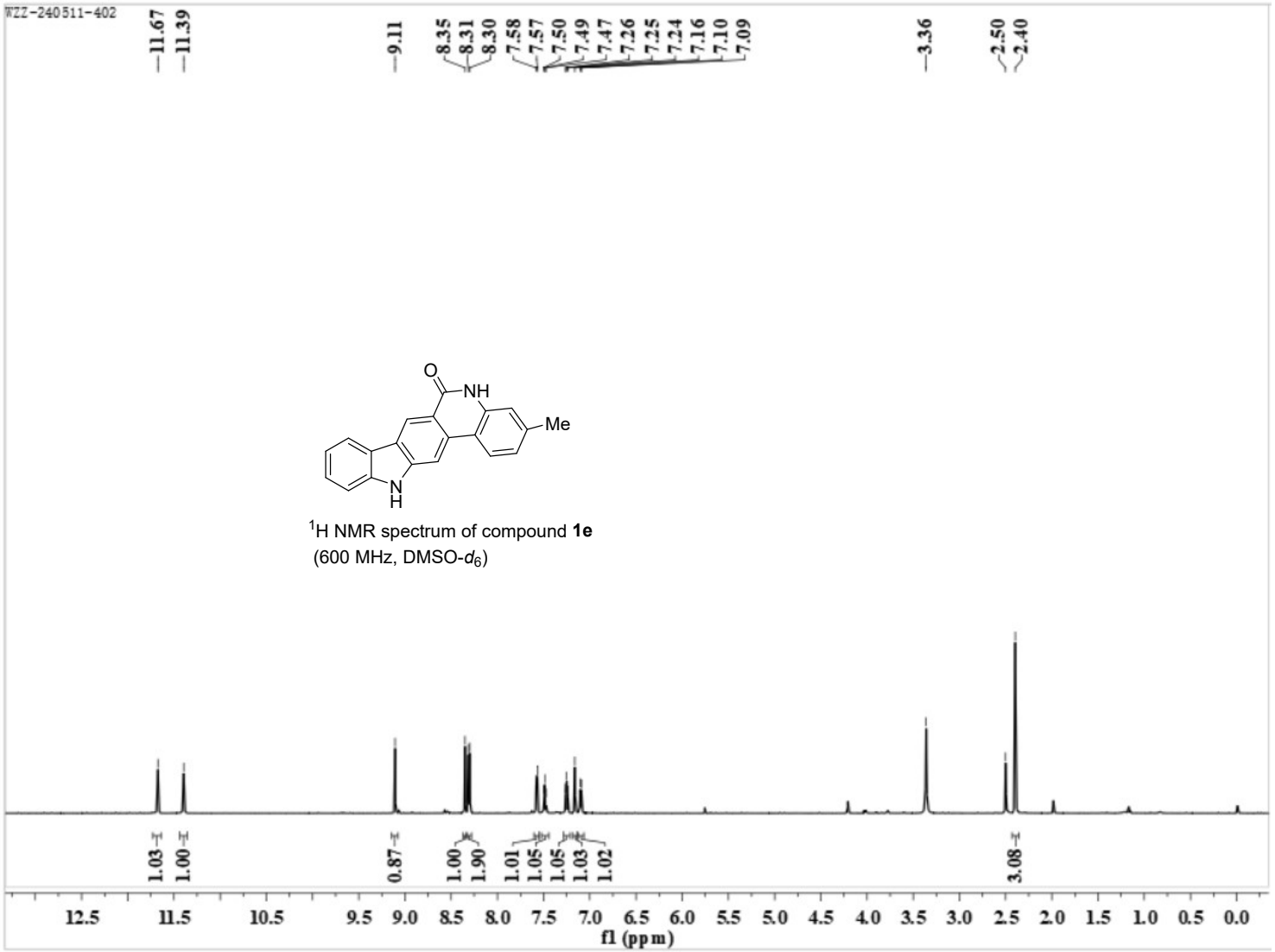
^{13}C NMR spectrum of compound **1c**
(150 MHz, DMSO-d_6)



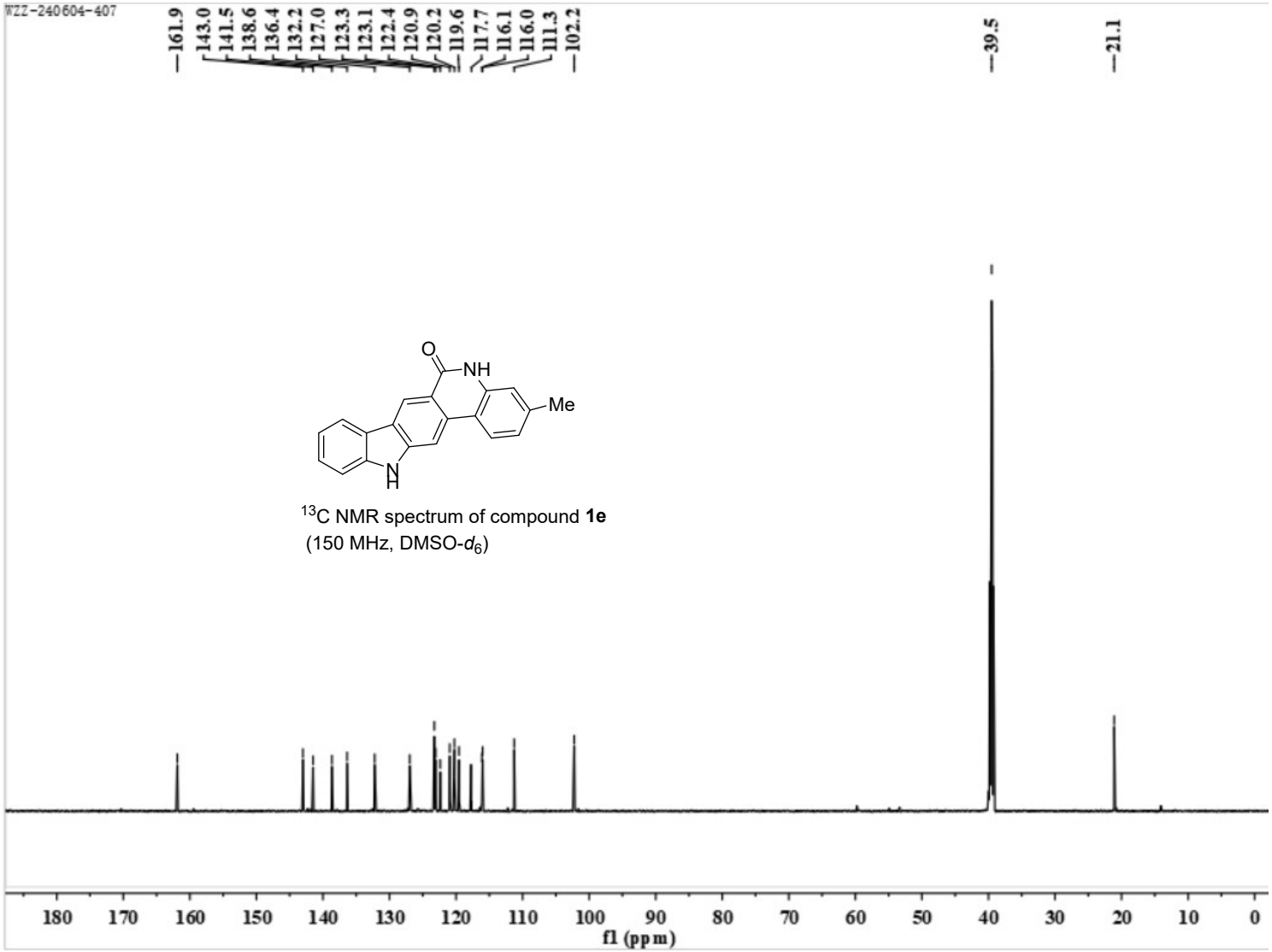
^{1}H NMR spectrum of compound **1d**
(600 MHz, DMSO-d_6)



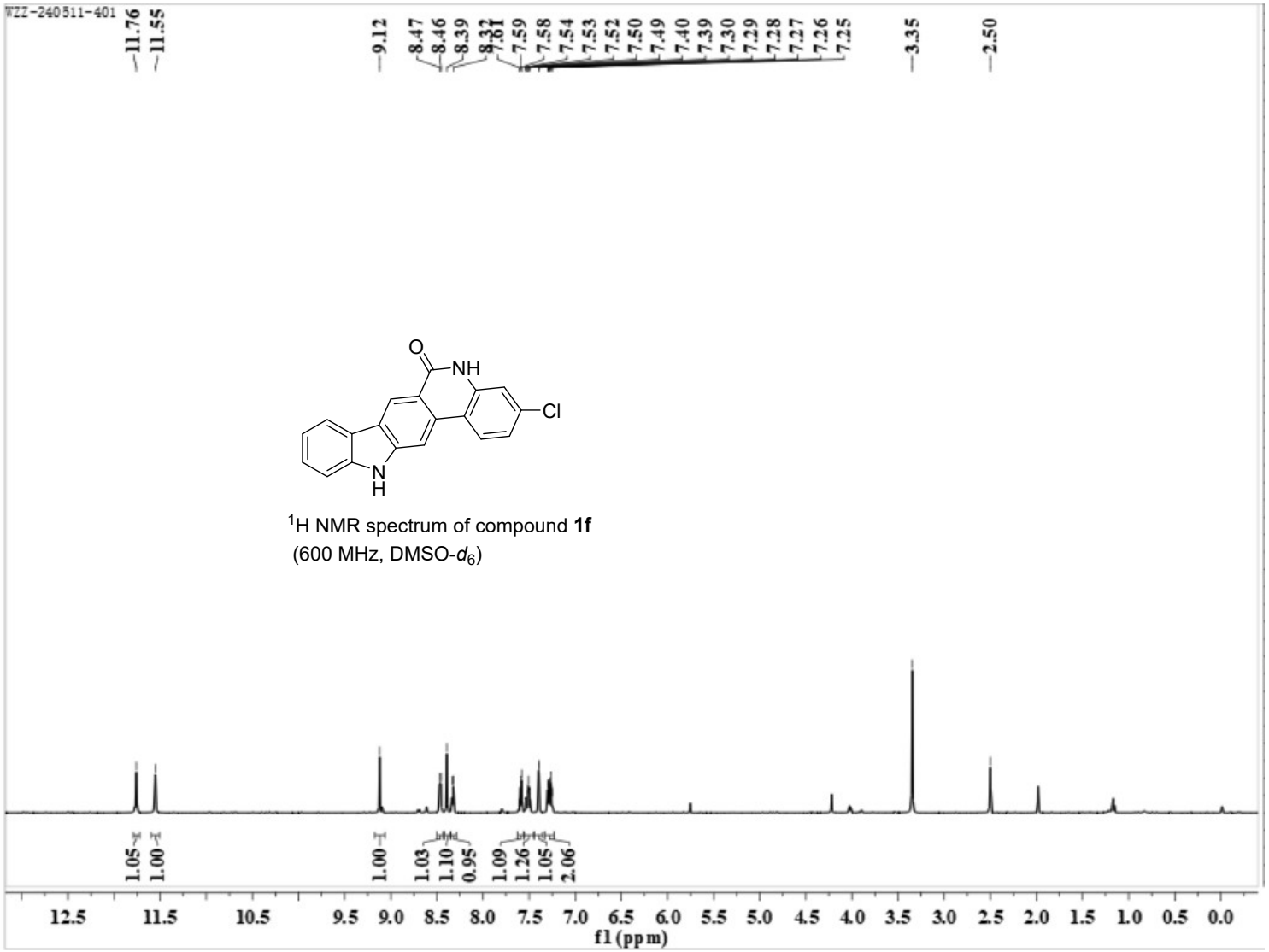
^{13}C NMR spectrum of compound **1d**
(150 MHz, DMSO-d_6)



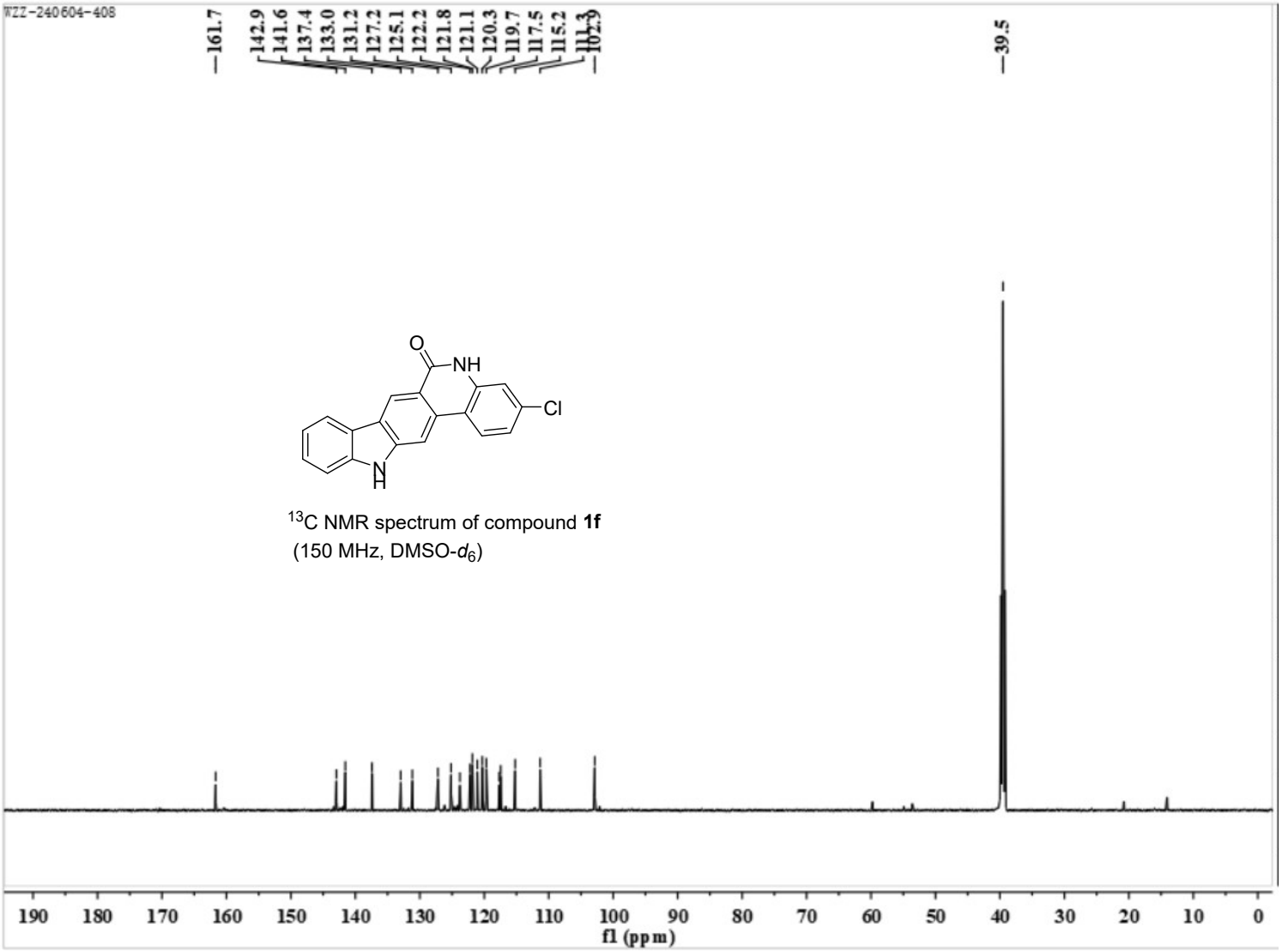
^{1}H NMR spectrum of compound **1e**
(600 MHz, DMSO-d_6)



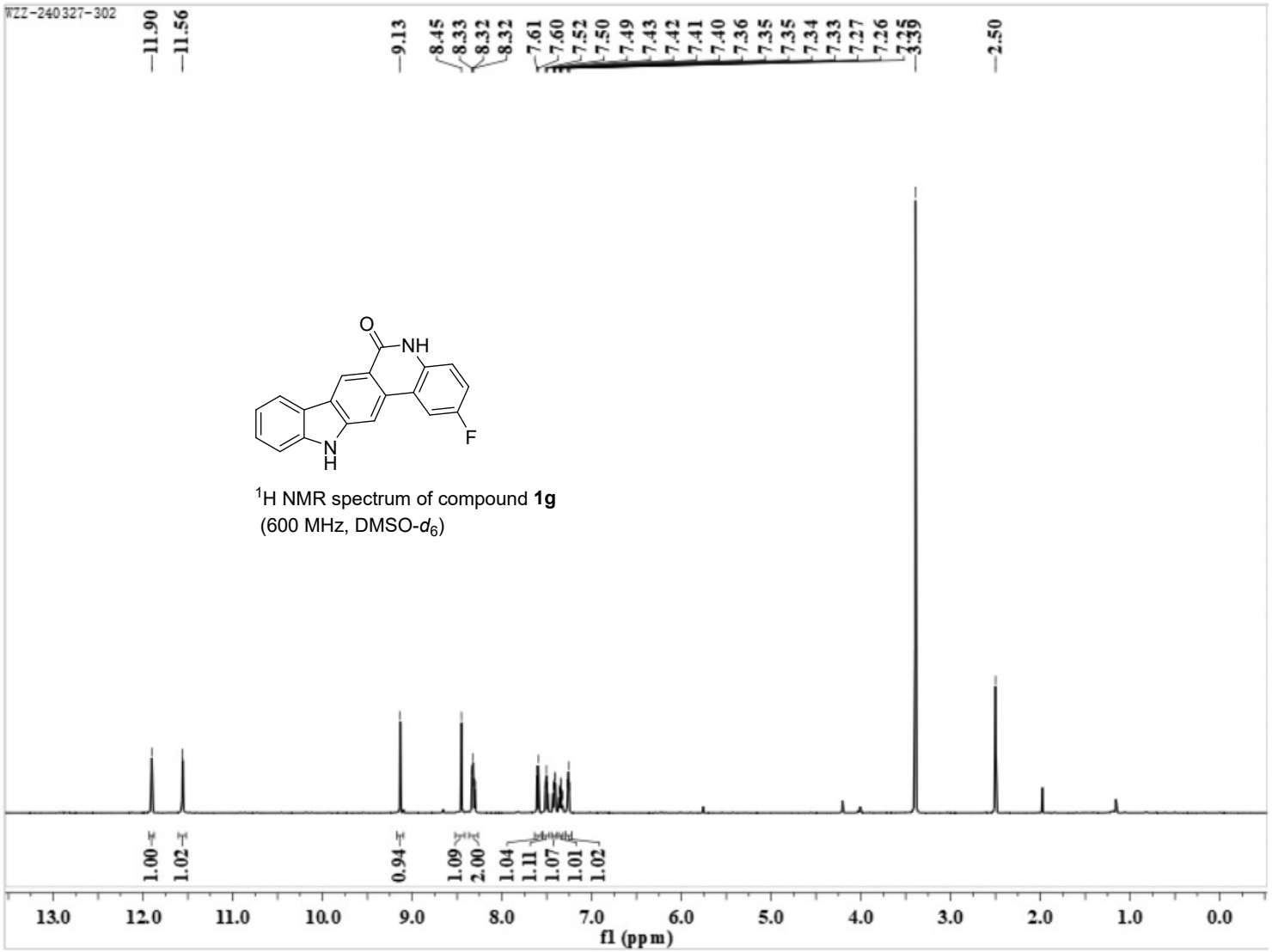
^{13}C NMR spectrum of compound **1e**
(150 MHz, DMSO-d_6)



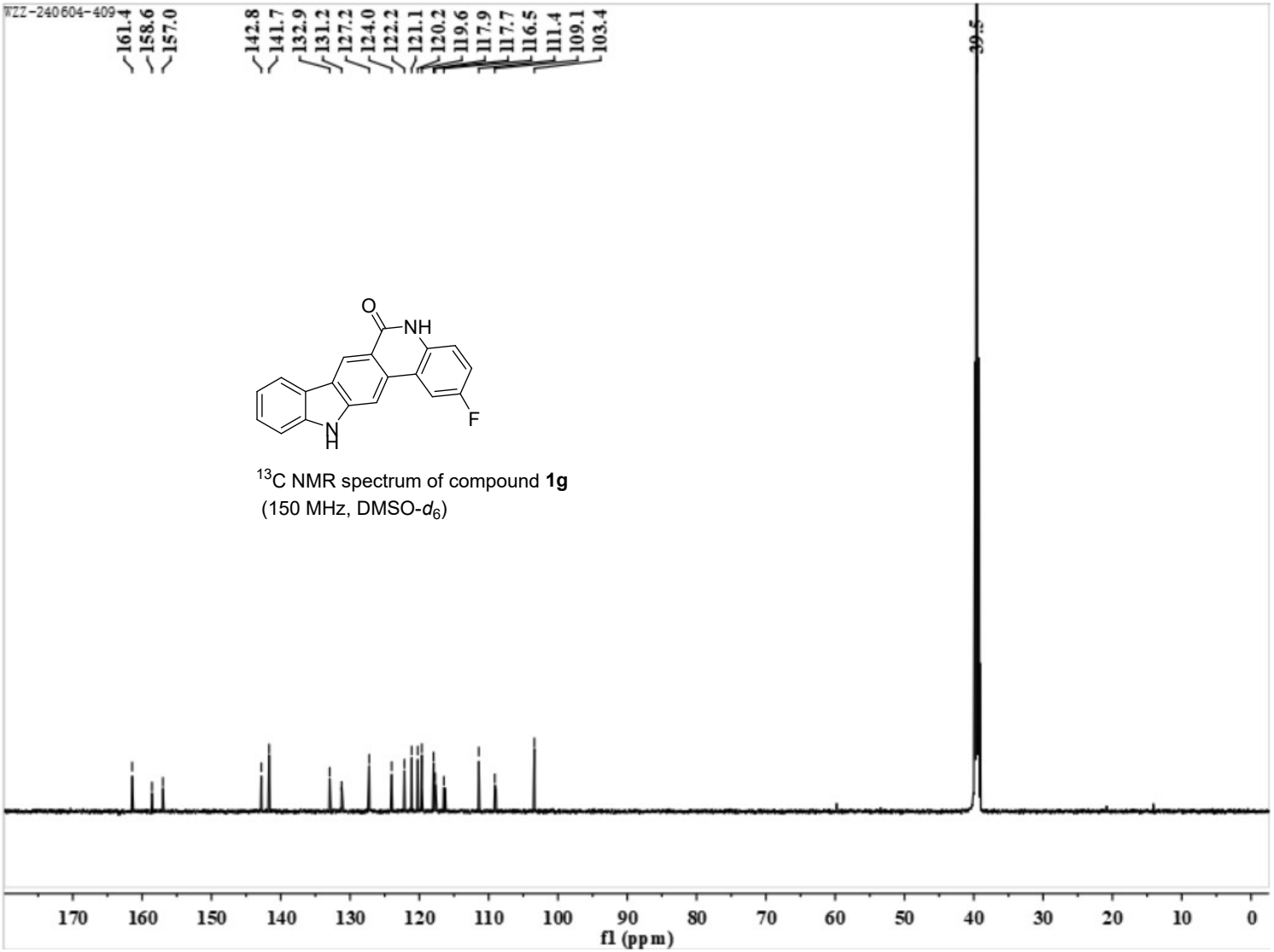
^{1}H NMR spectrum of compound **1f**
(600 MHz, DMSO-d_6)



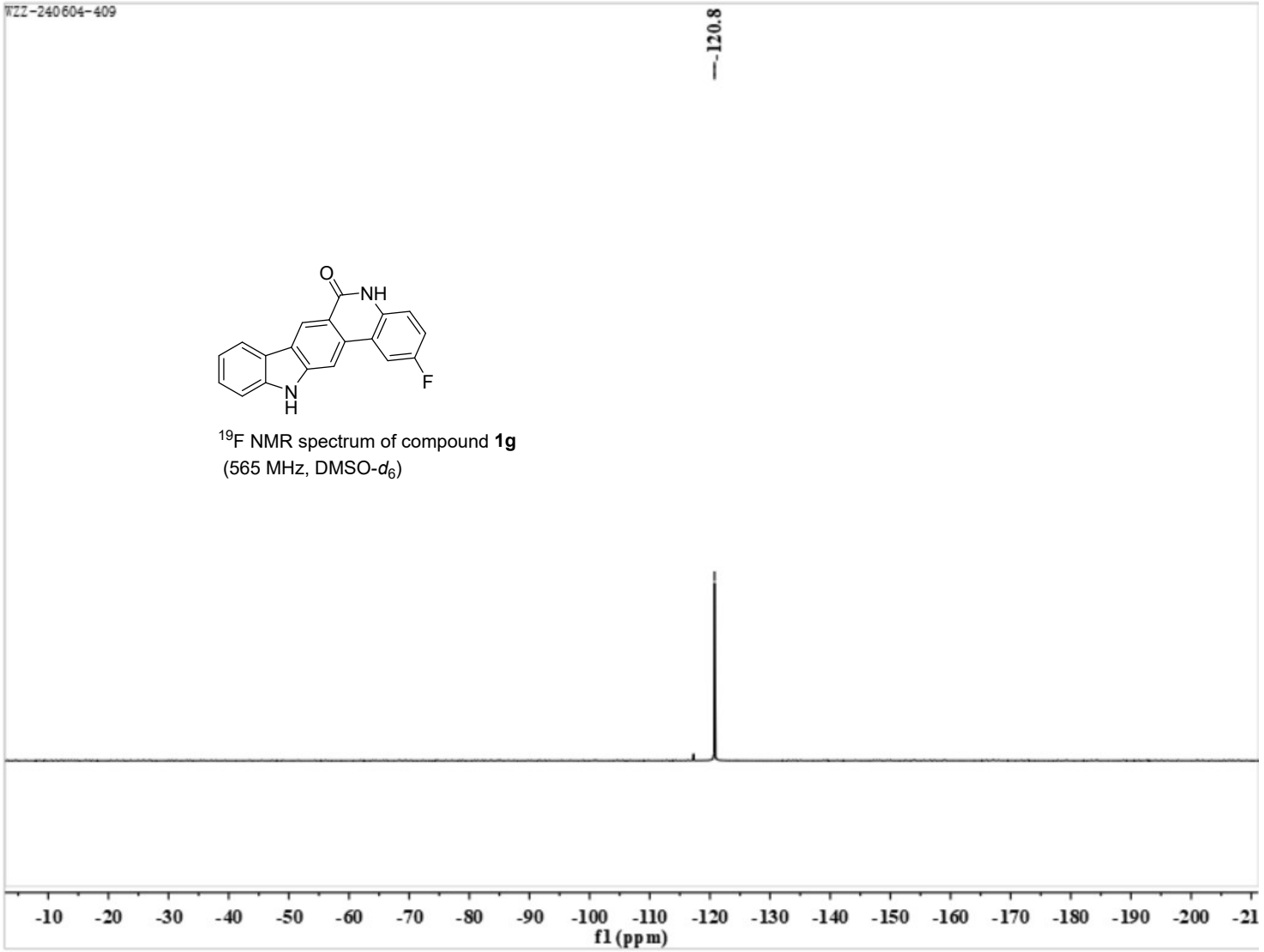
^{13}C NMR spectrum of compound **1f**
(150 MHz, DMSO-d_6)



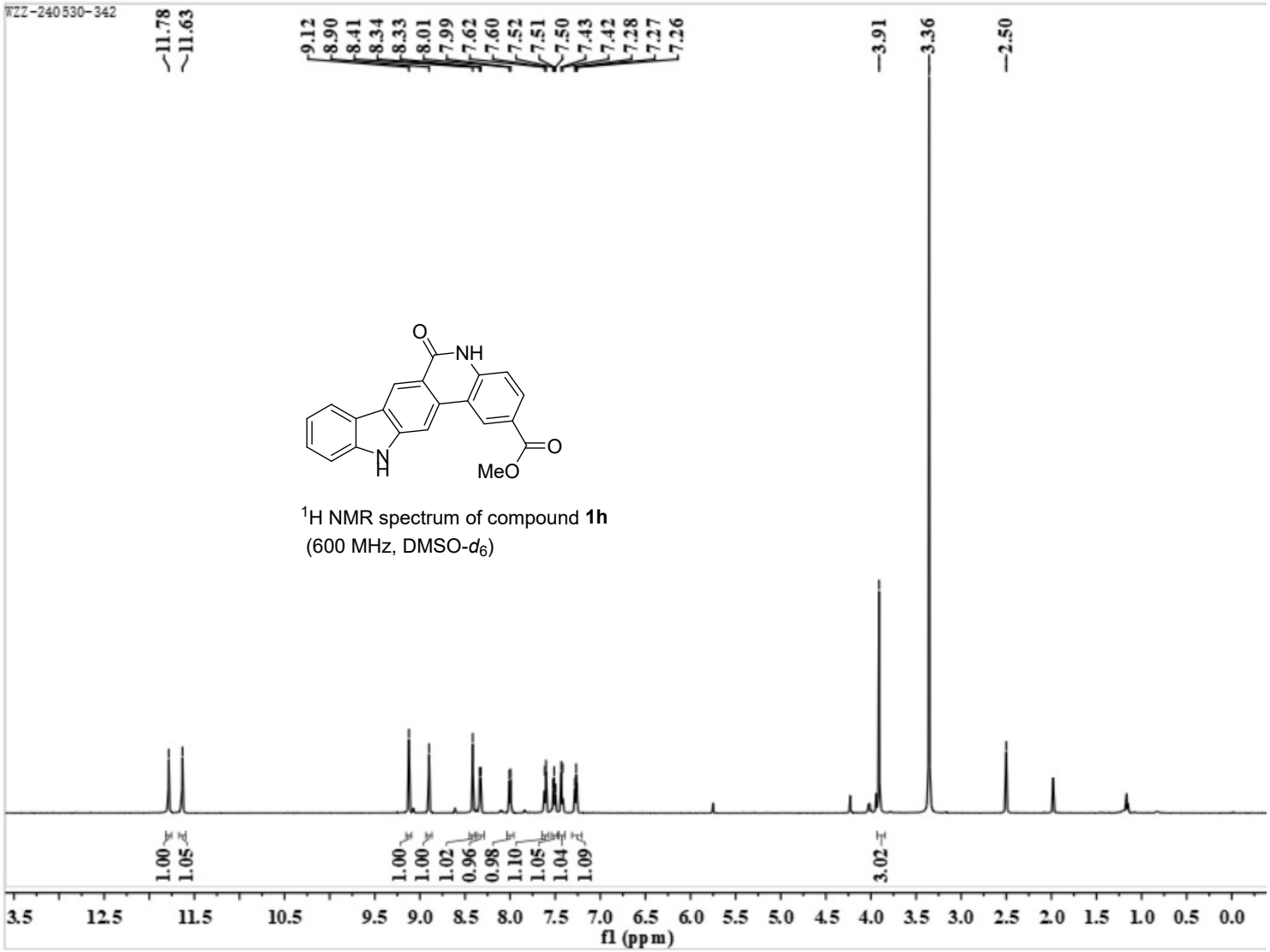
^{1}H NMR spectrum of compound **1g**
(600 MHz, DMSO-d_6)



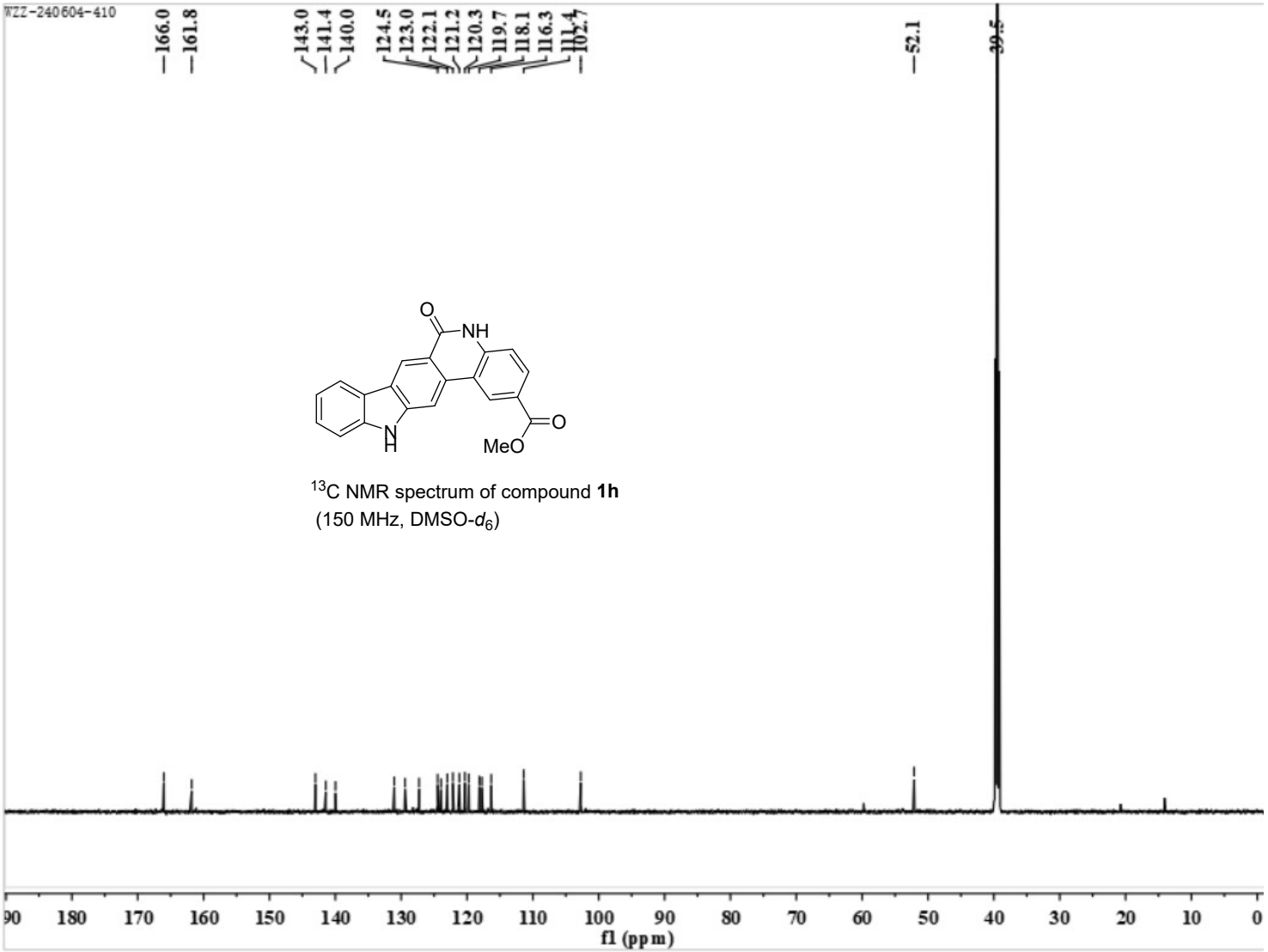
^{13}C NMR spectrum of compound **1g**
(150 MHz, DMSO-d_6)



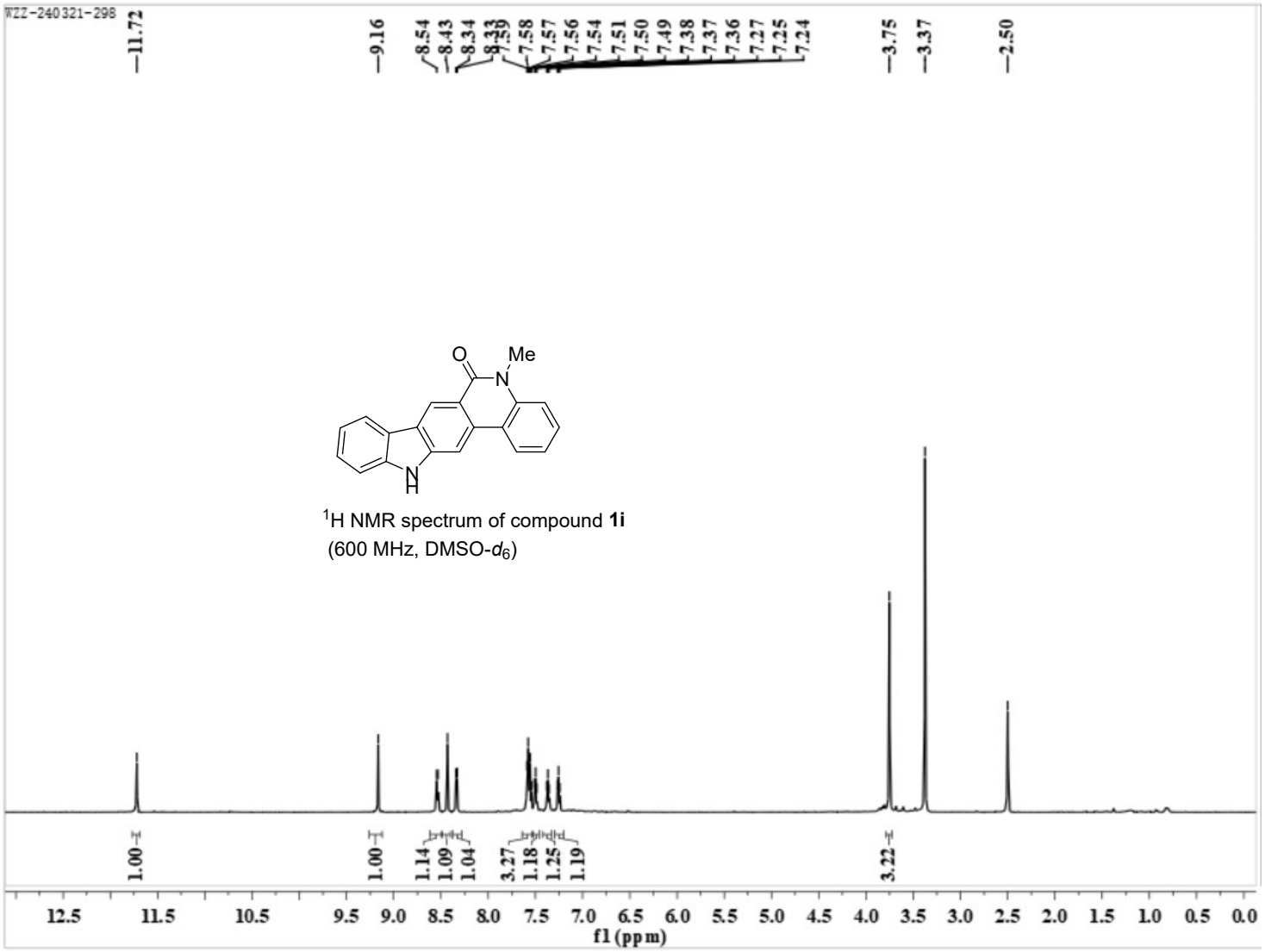
^{19}F NMR spectrum of compound **1g**
(565 MHz, DMSO-d_6)



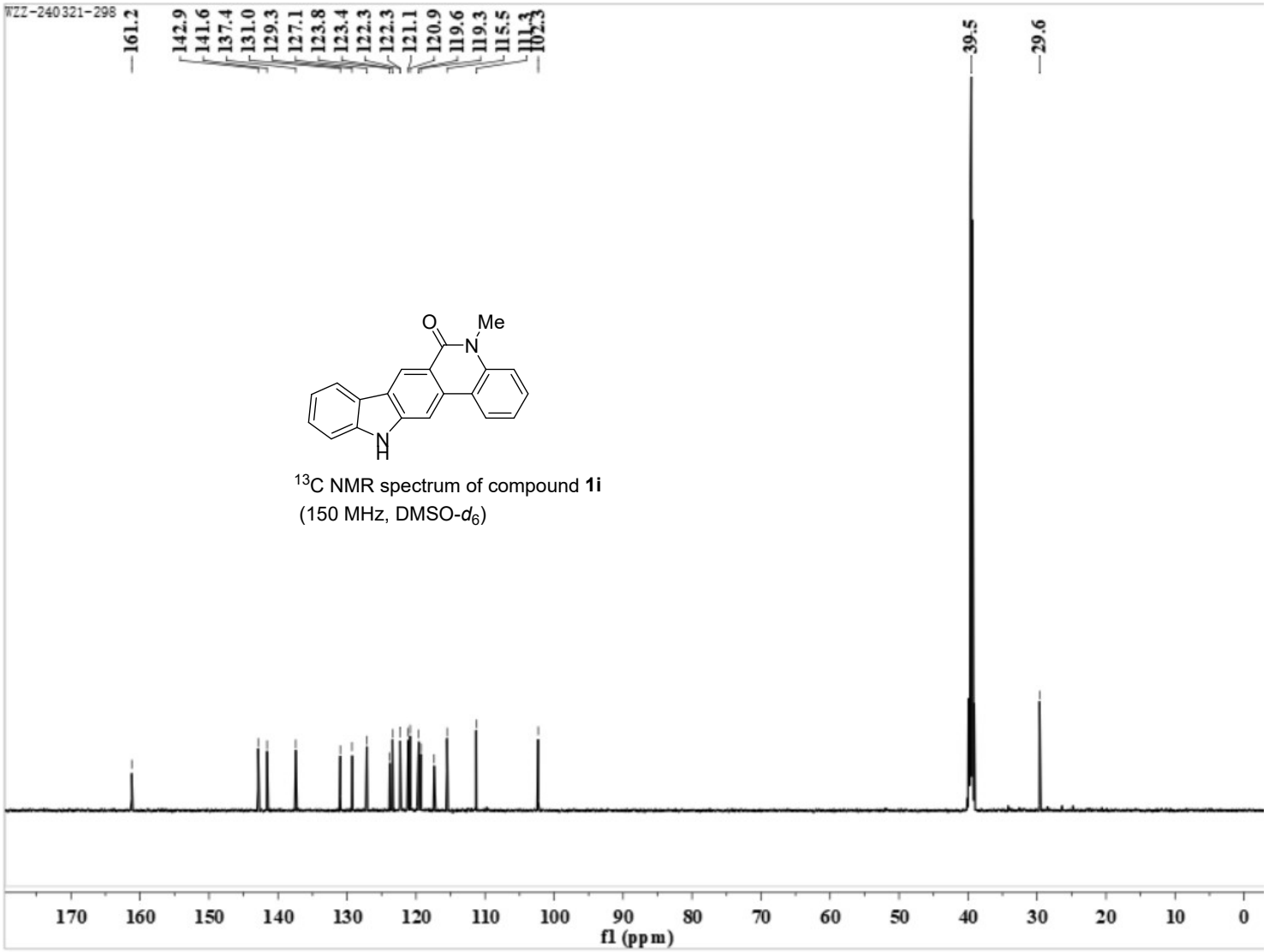
^{1}H NMR spectrum of compound **1h**
(600 MHz, DMSO-d_6)



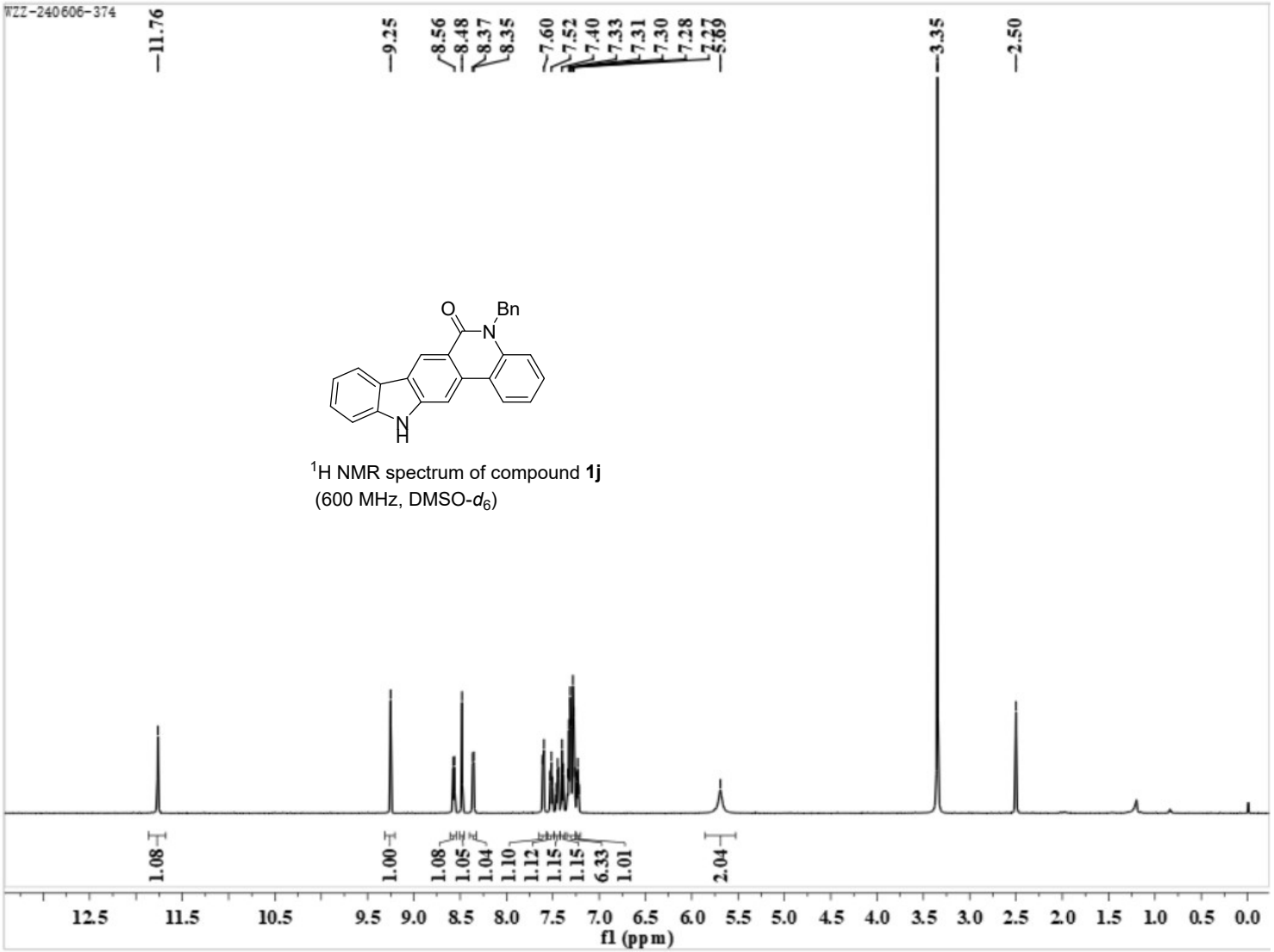
^{13}C NMR spectrum of compound **1h**
(150 MHz, DMSO-d_6)



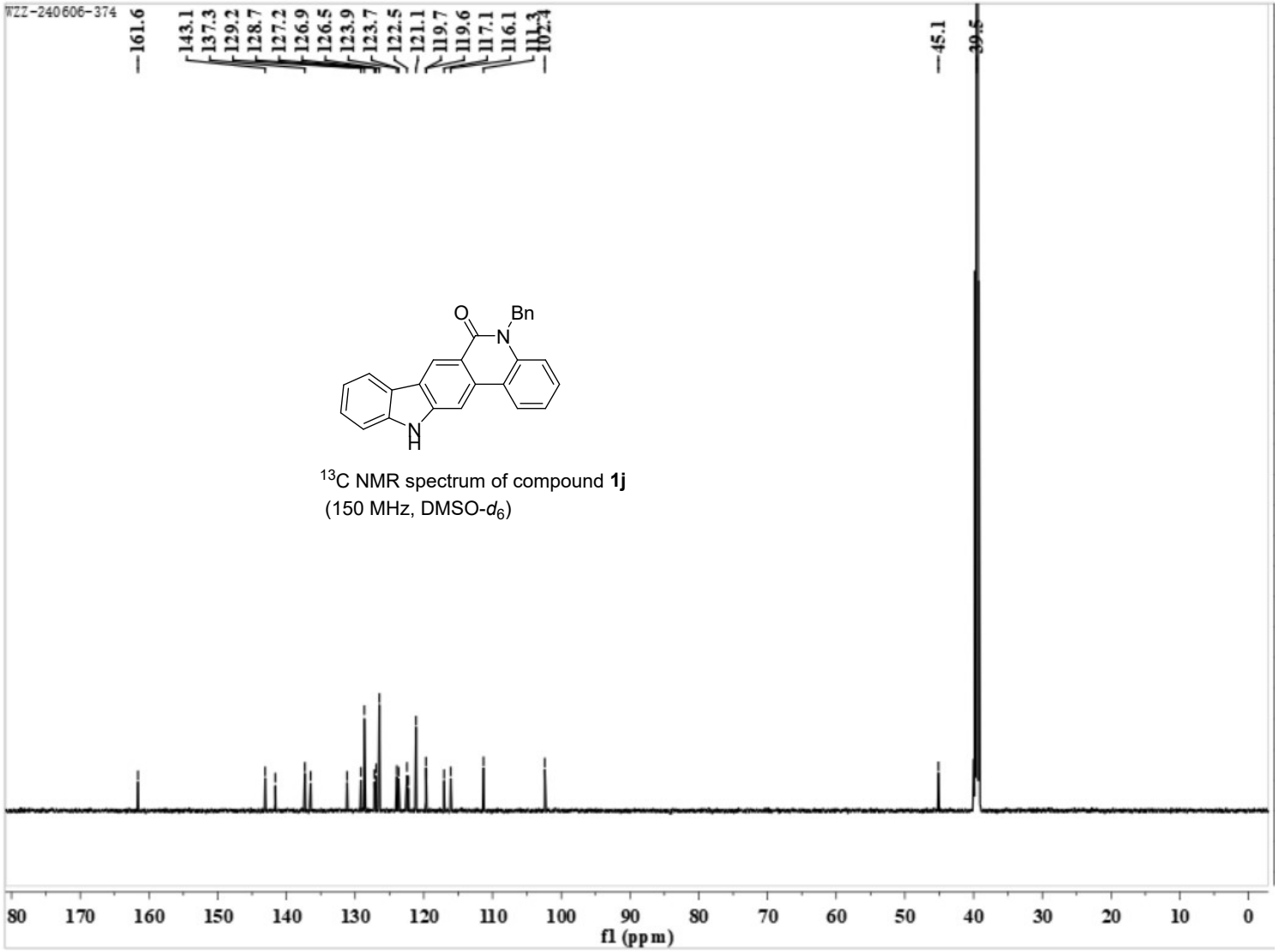
^{1}H NMR spectrum of compound **1i**
(600 MHz, DMSO-d_6)



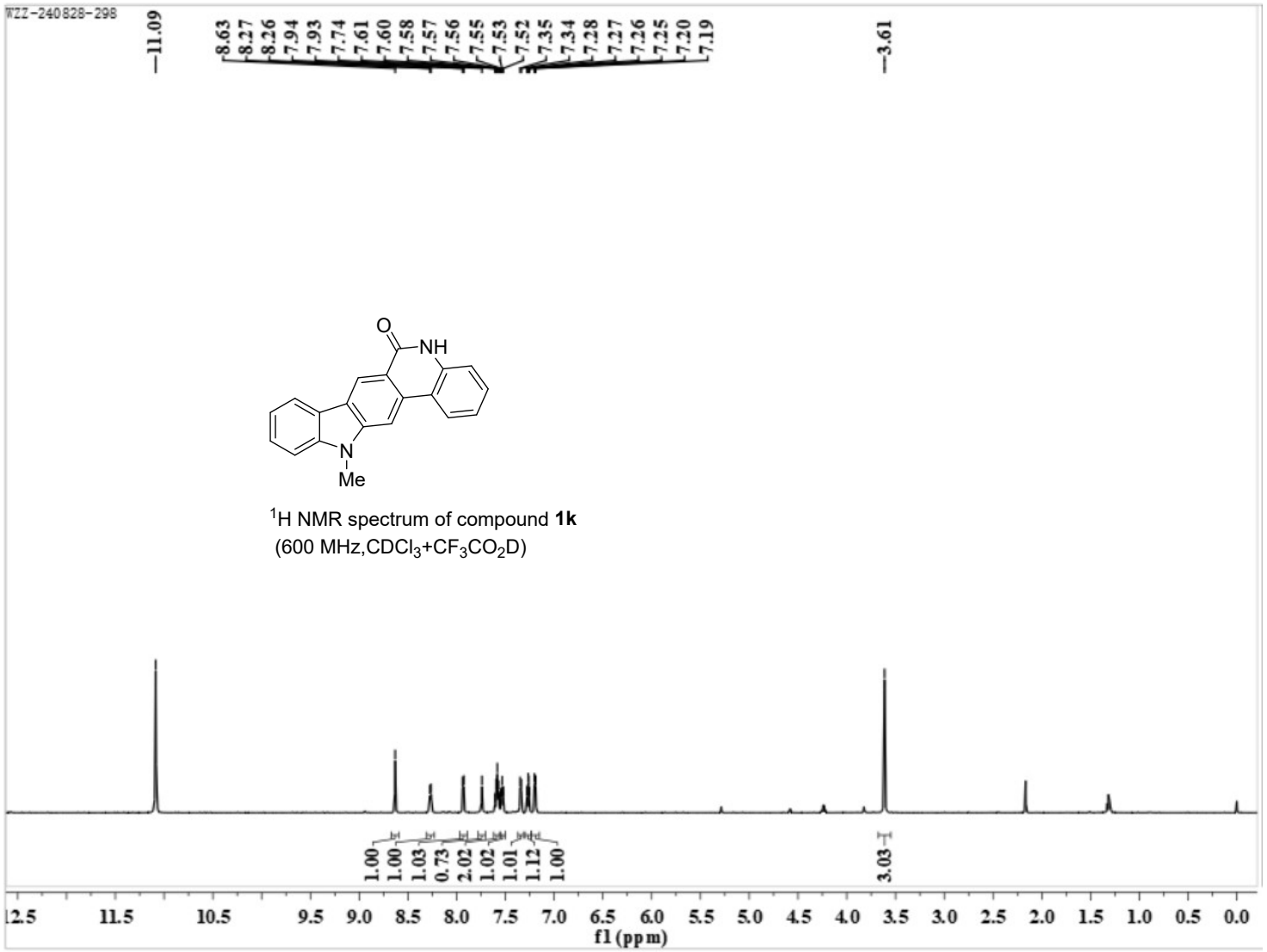
^{13}C NMR spectrum of compound **1i**
(150 MHz, DMSO-d_6)



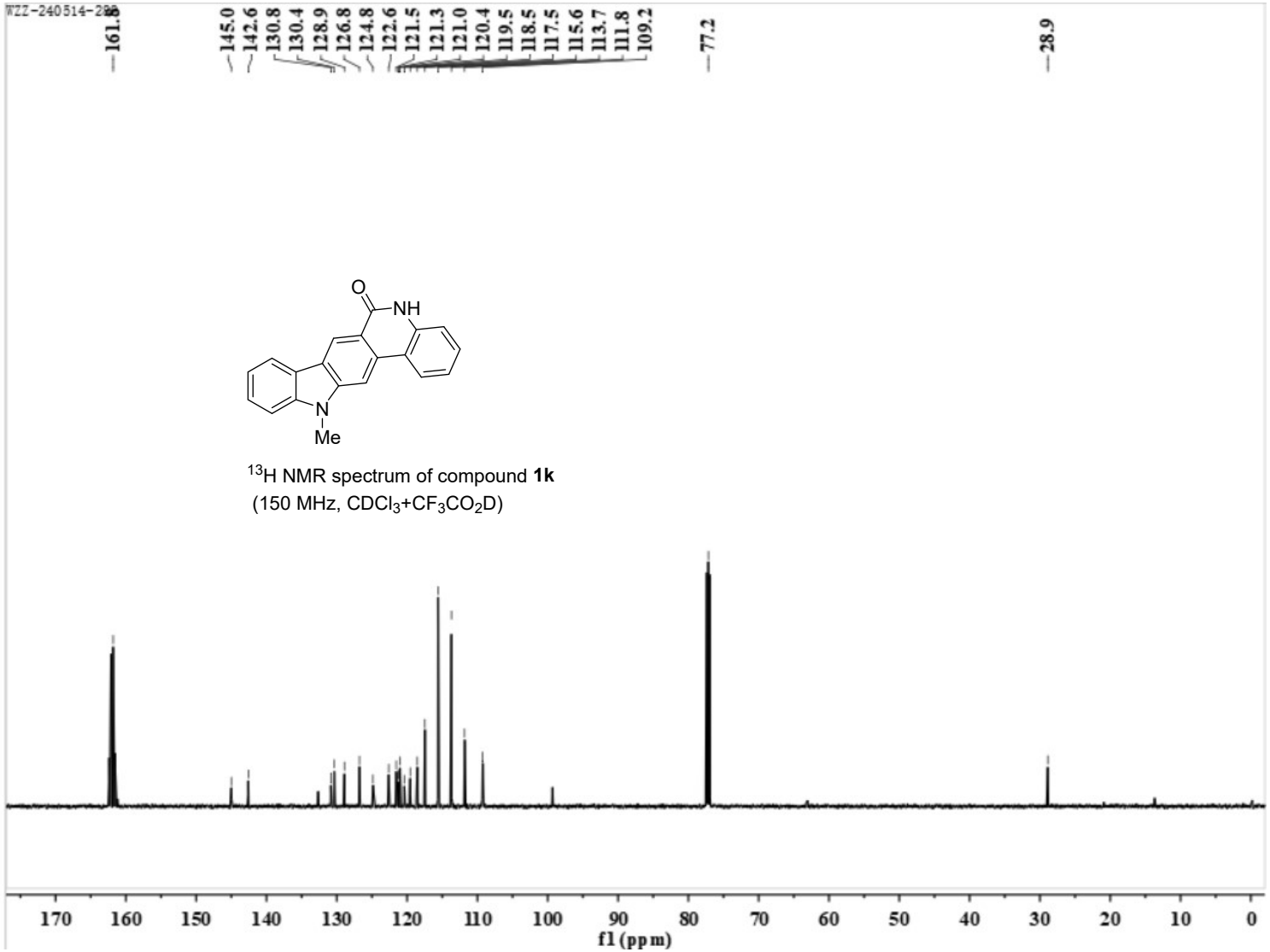
^{1}H NMR spectrum of compound **1j**
(600 MHz, DMSO-d_6)



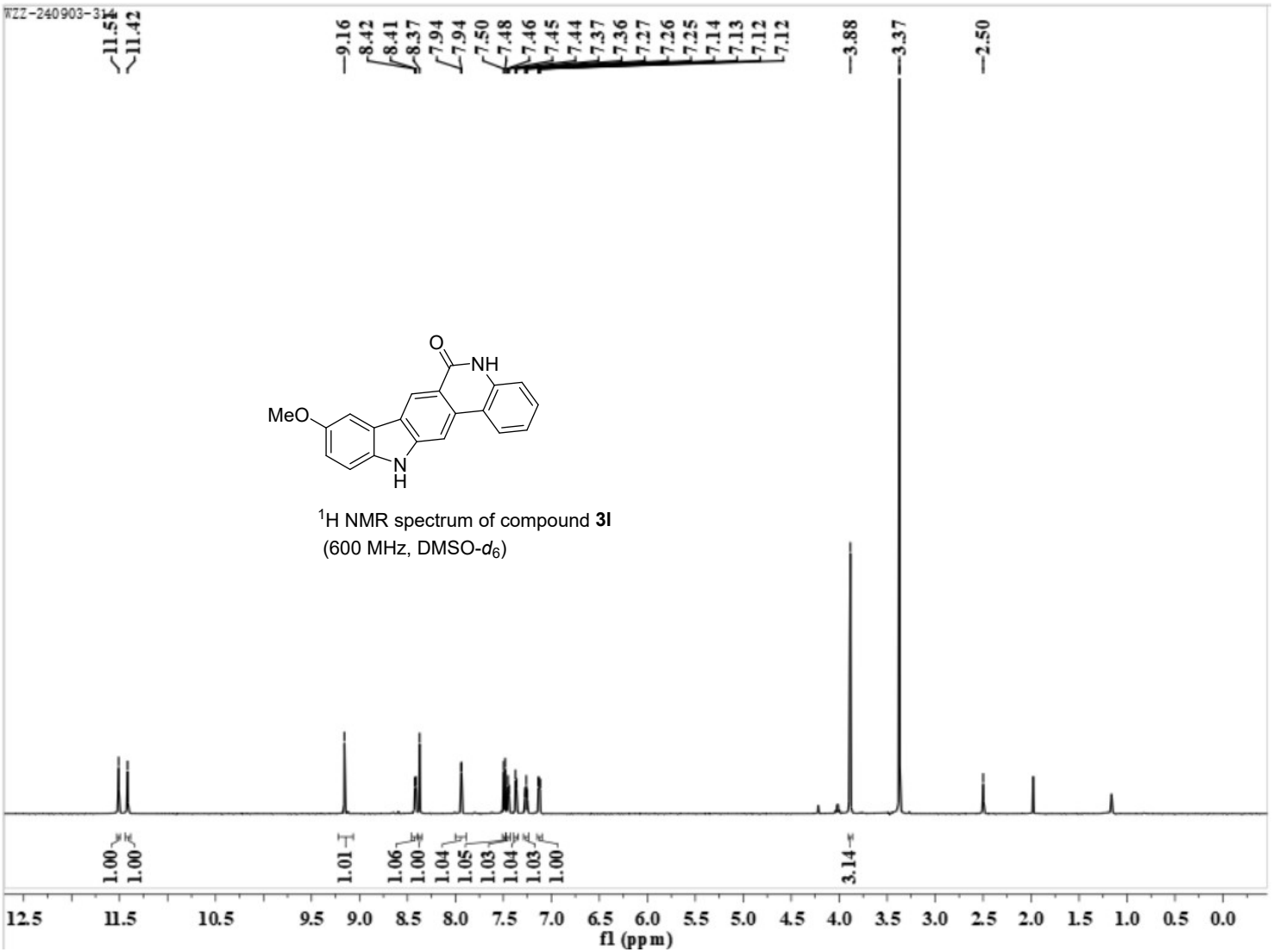
^{13}C NMR spectrum of compound **1j**
(150 MHz, DMSO-d_6)



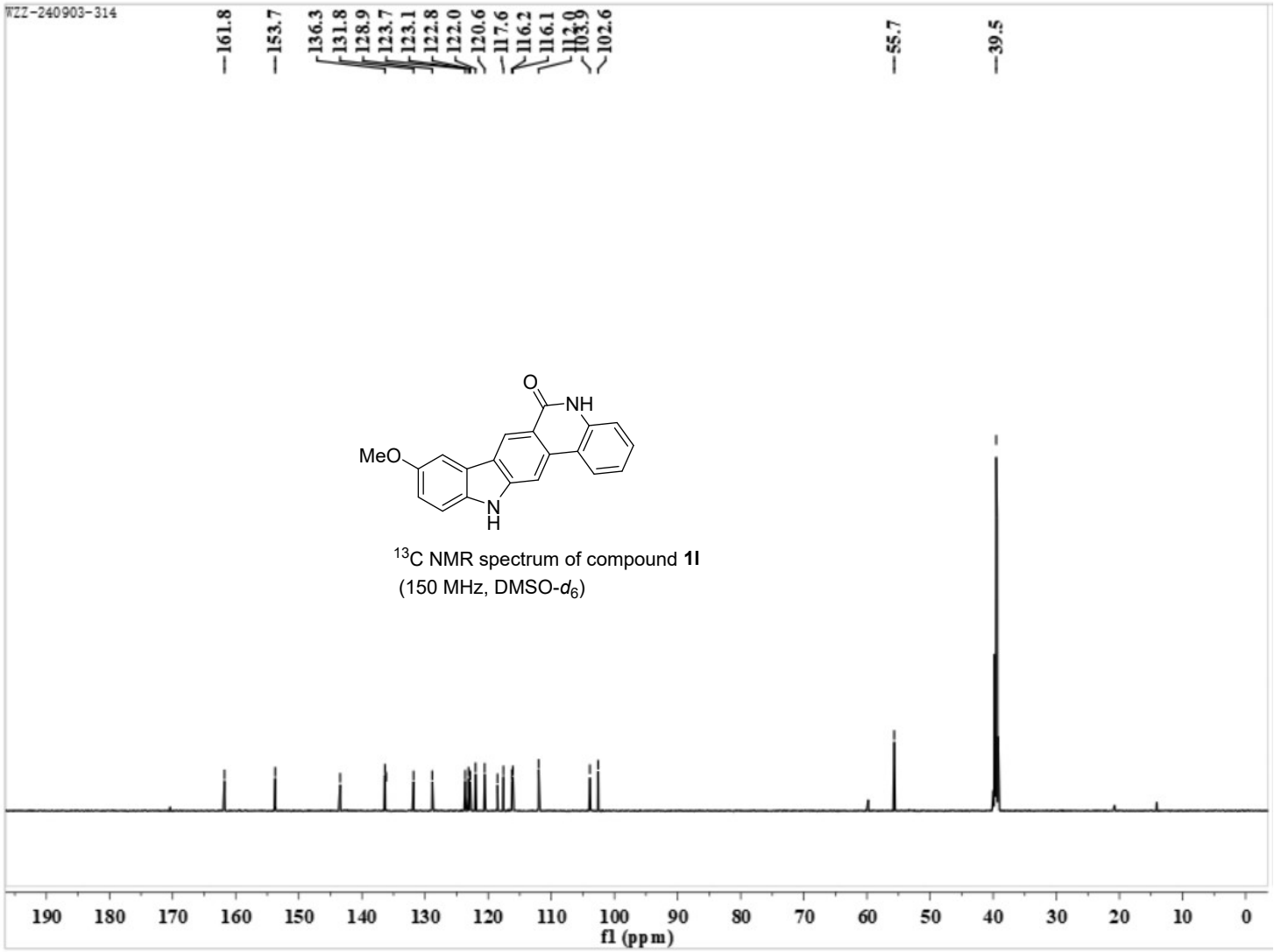
^{1}H NMR spectrum of compound **1k**
(600 MHz,$CDCl_3$+CF_3CO_2D)



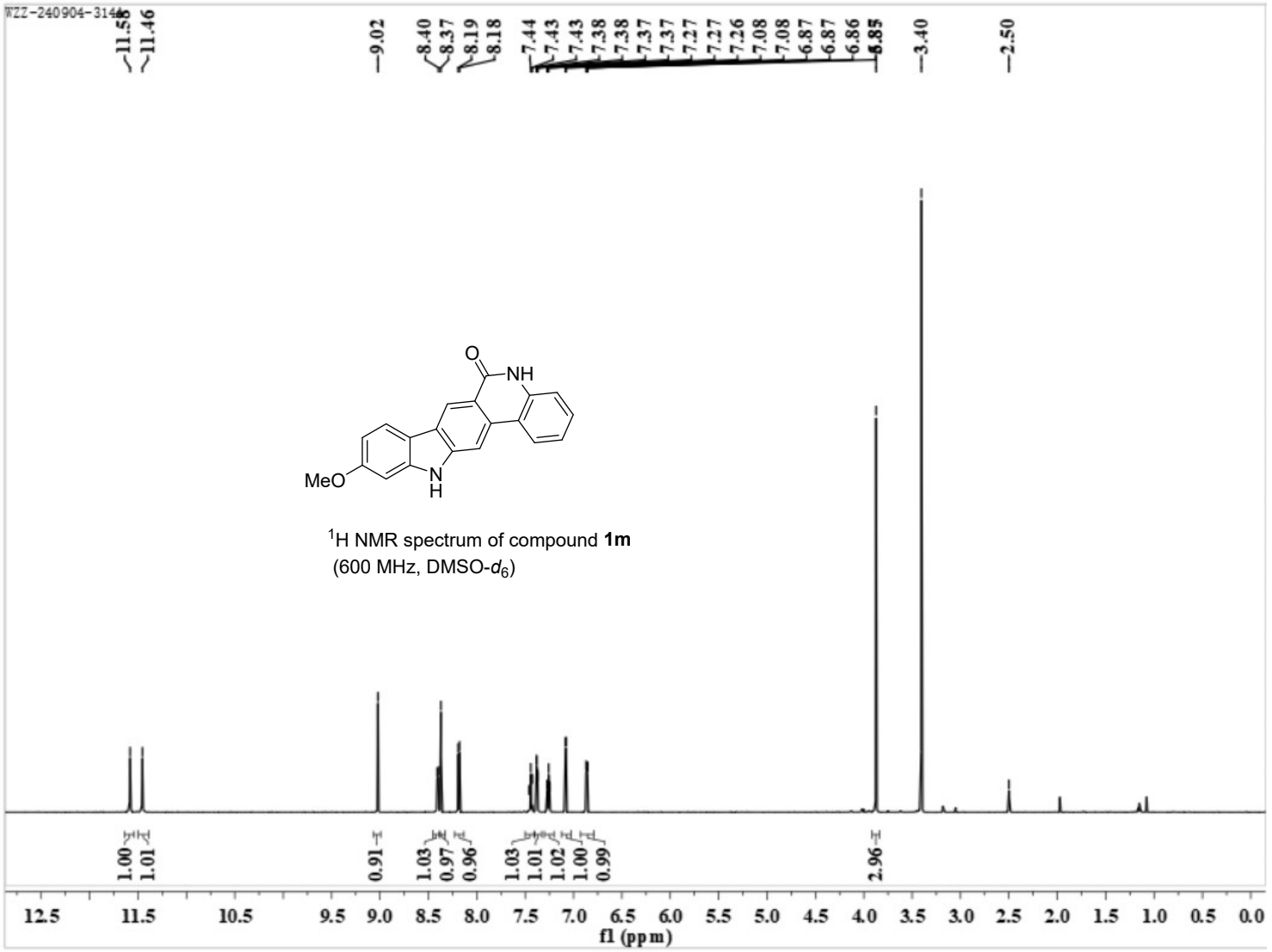
^{13}H NMR spectrum of compound **1k**
(150 MHz, $CDCl_3$+CF_3CO_2D)



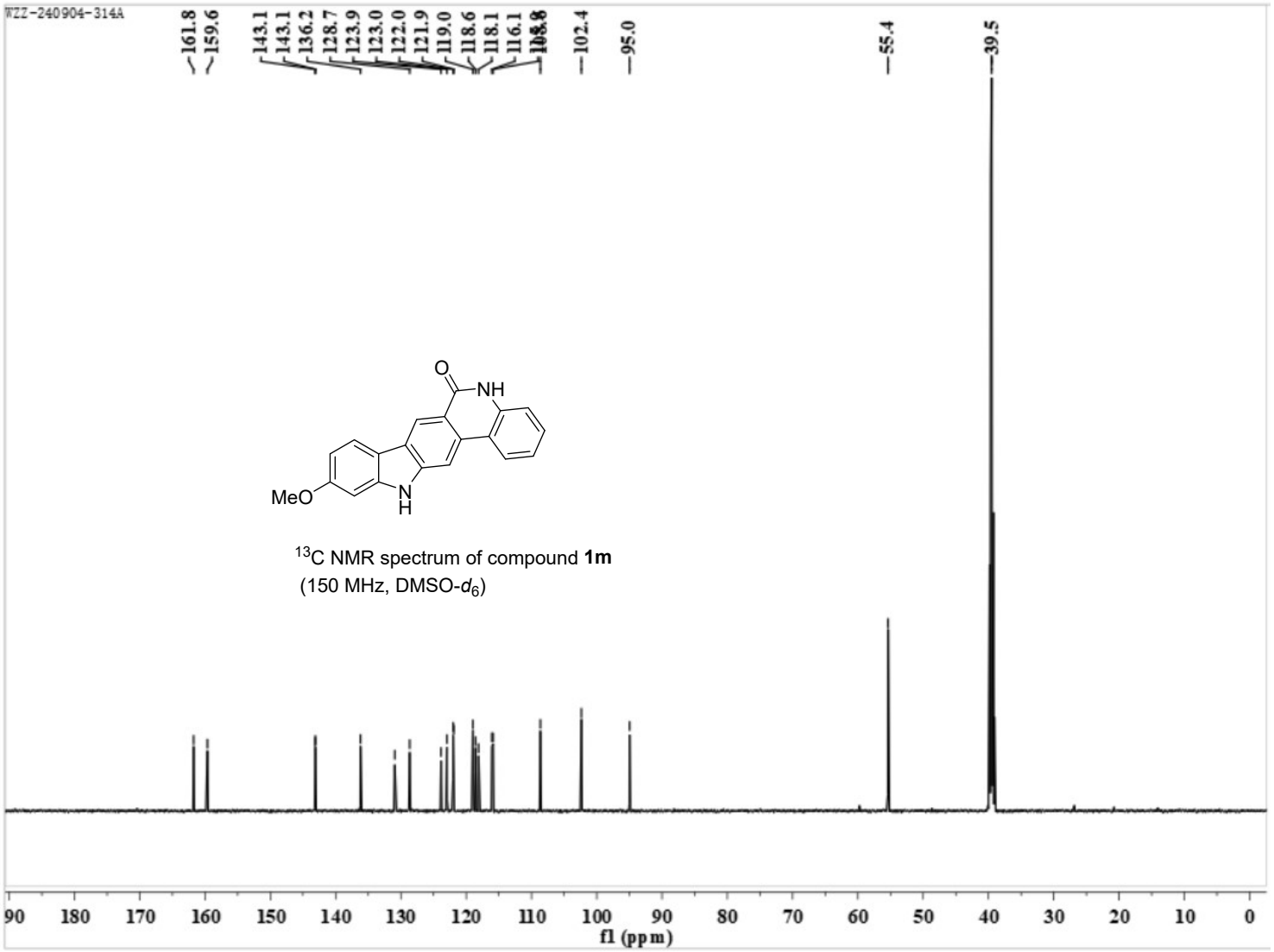
^{1}H NMR spectrum of compound **3l**
(600 MHz, DMSO-d_6)



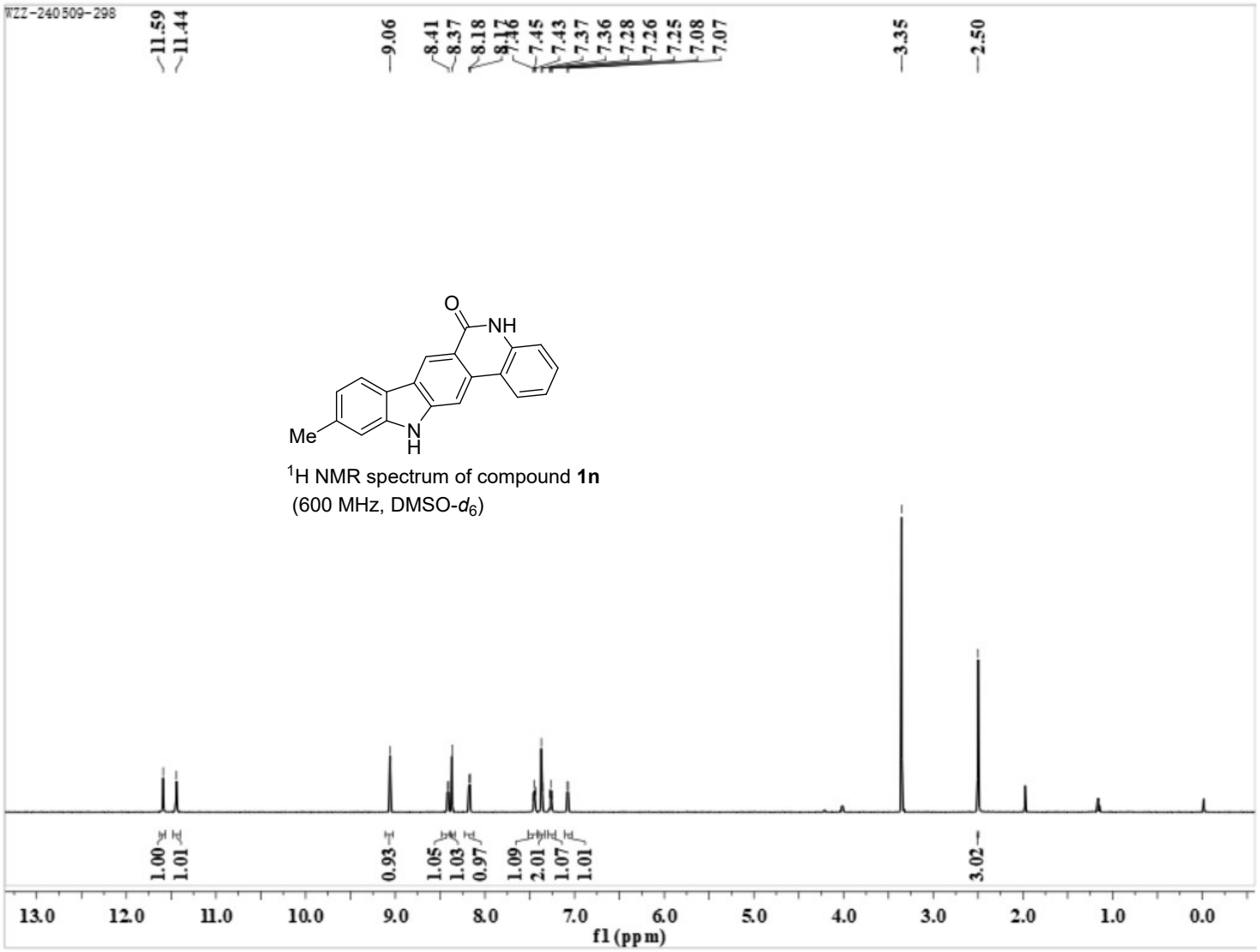
^{13}C NMR spectrum of compound **1l**
(150 MHz, DMSO-d_6)



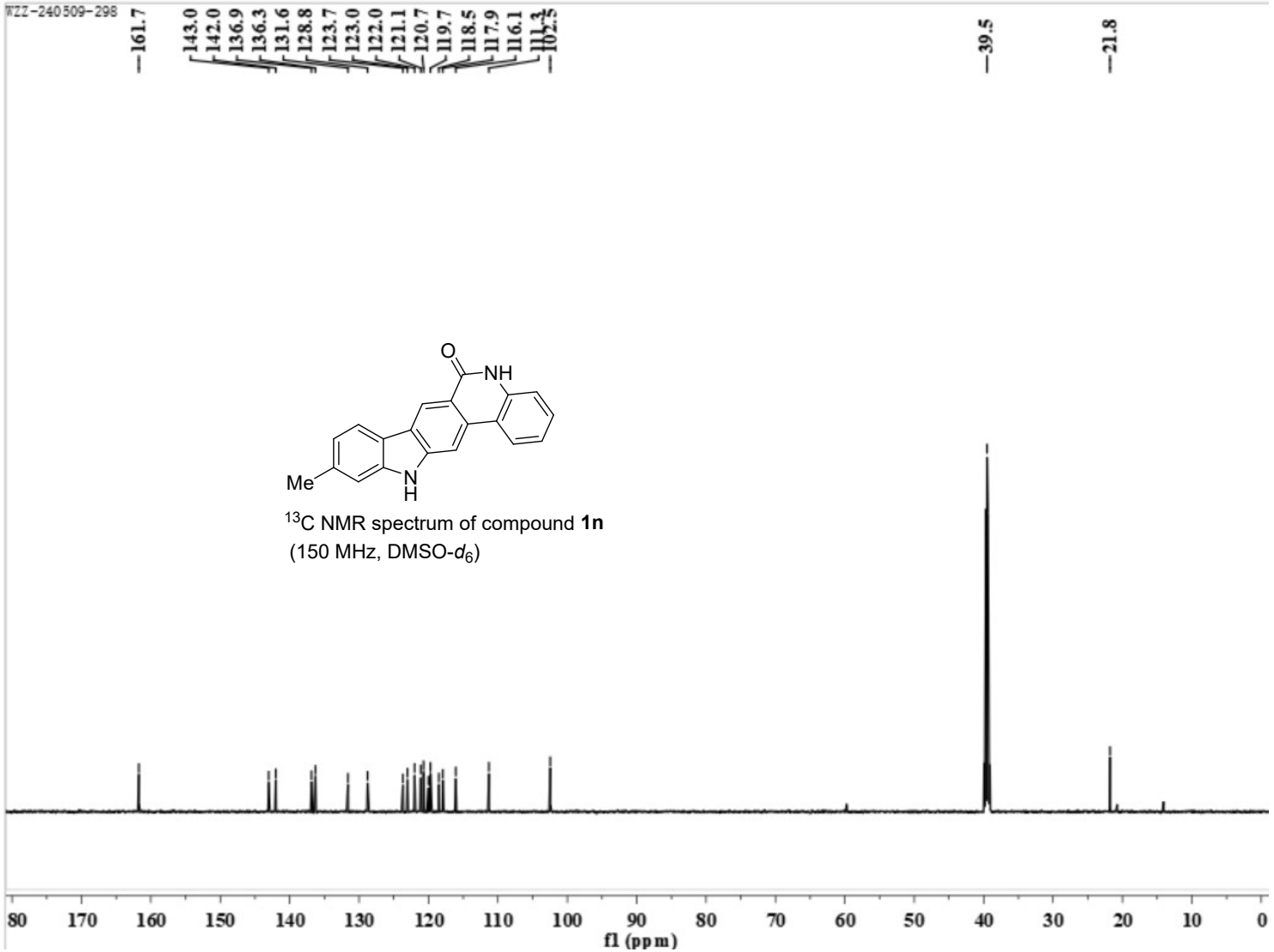
^{1}H NMR spectrum of compound **1m**
(600 MHz, DMSO-d_6)



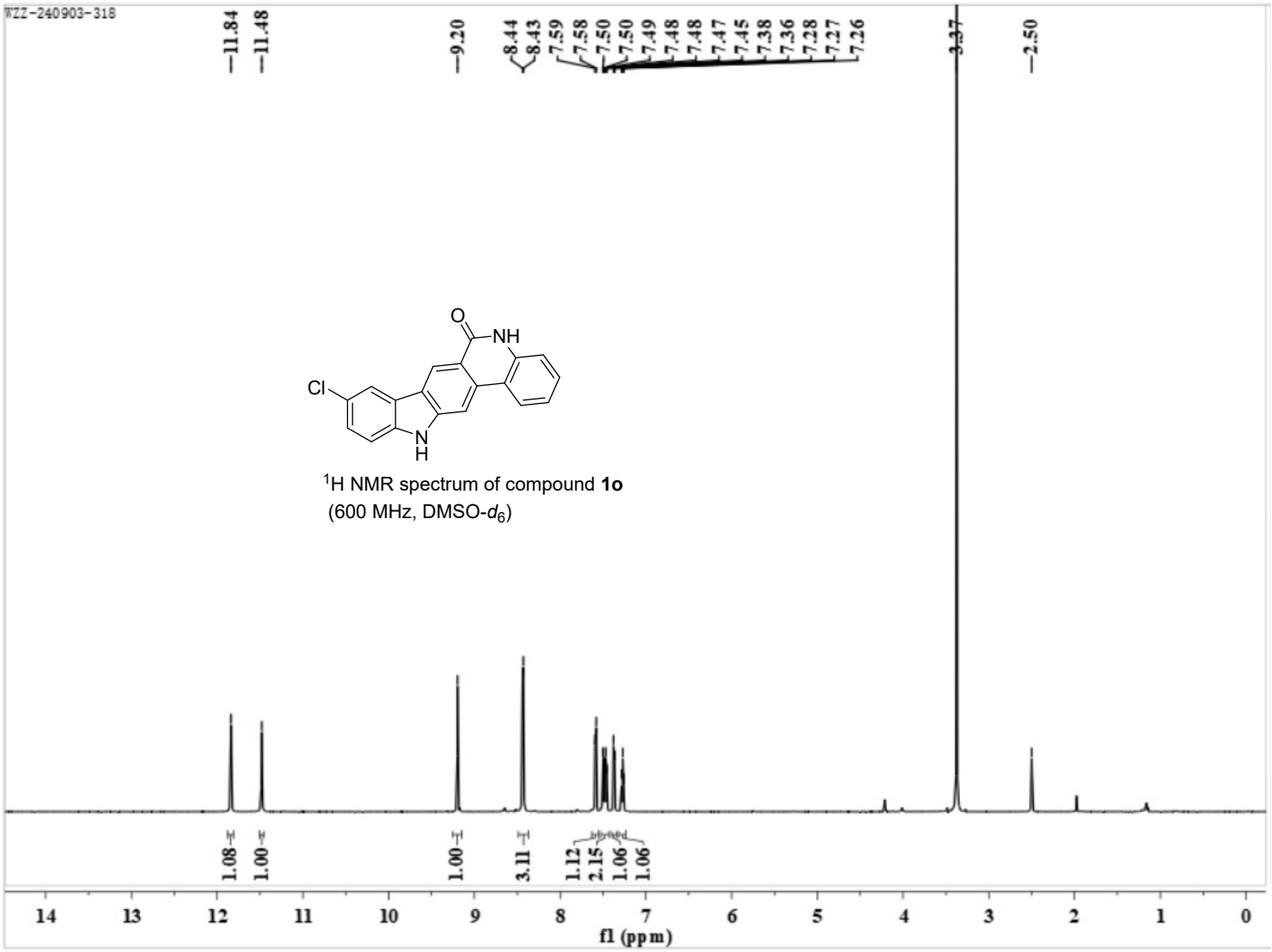
^{13}C NMR spectrum of compound **1m**
(150 MHz, DMSO-d_6)



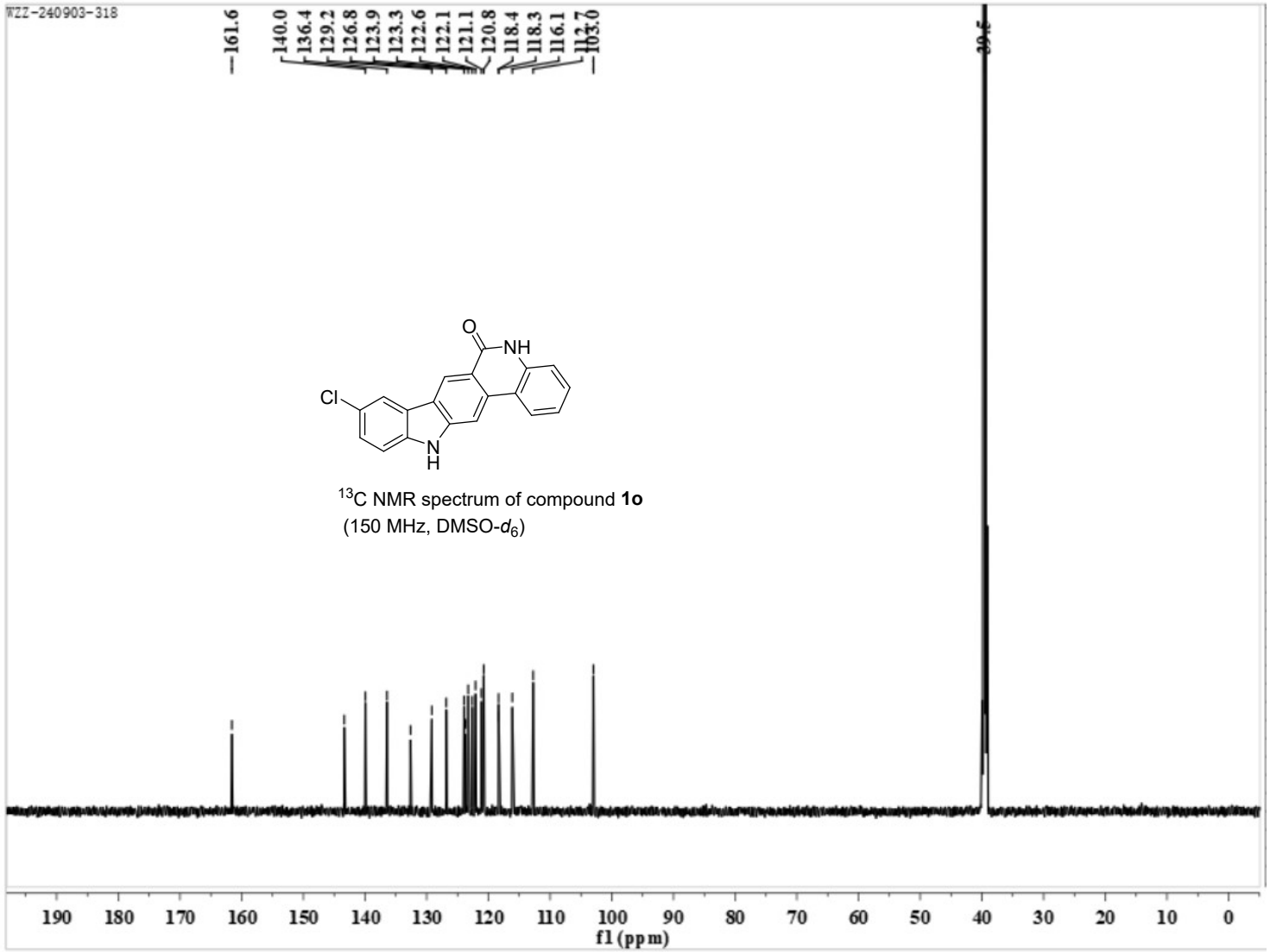
^{1}H NMR spectrum of compound **1n**
(600 MHz, DMSO-d_6)



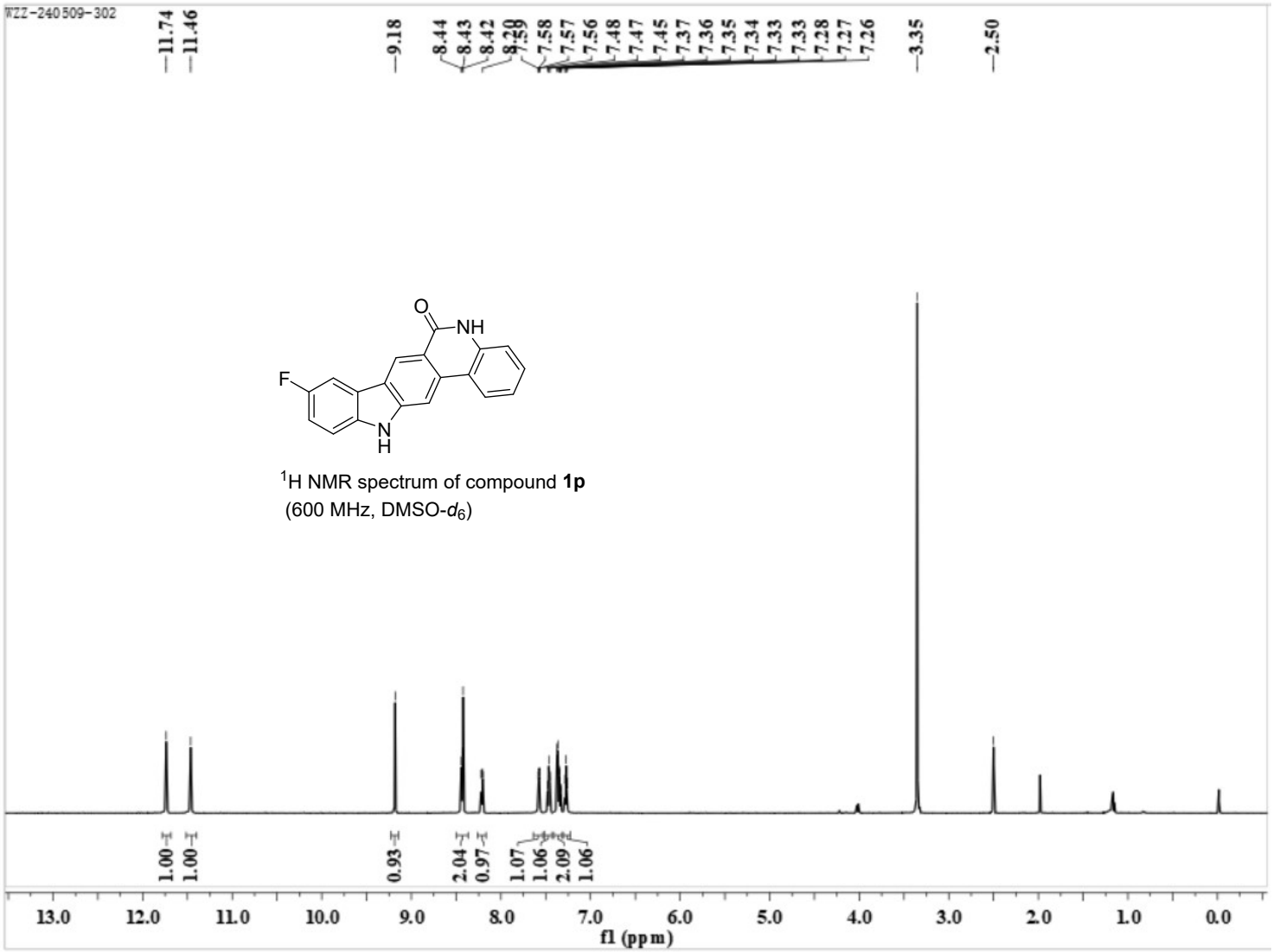
^{13}C NMR spectrum of compound **1n**
(150 MHz, DMSO-d_6)



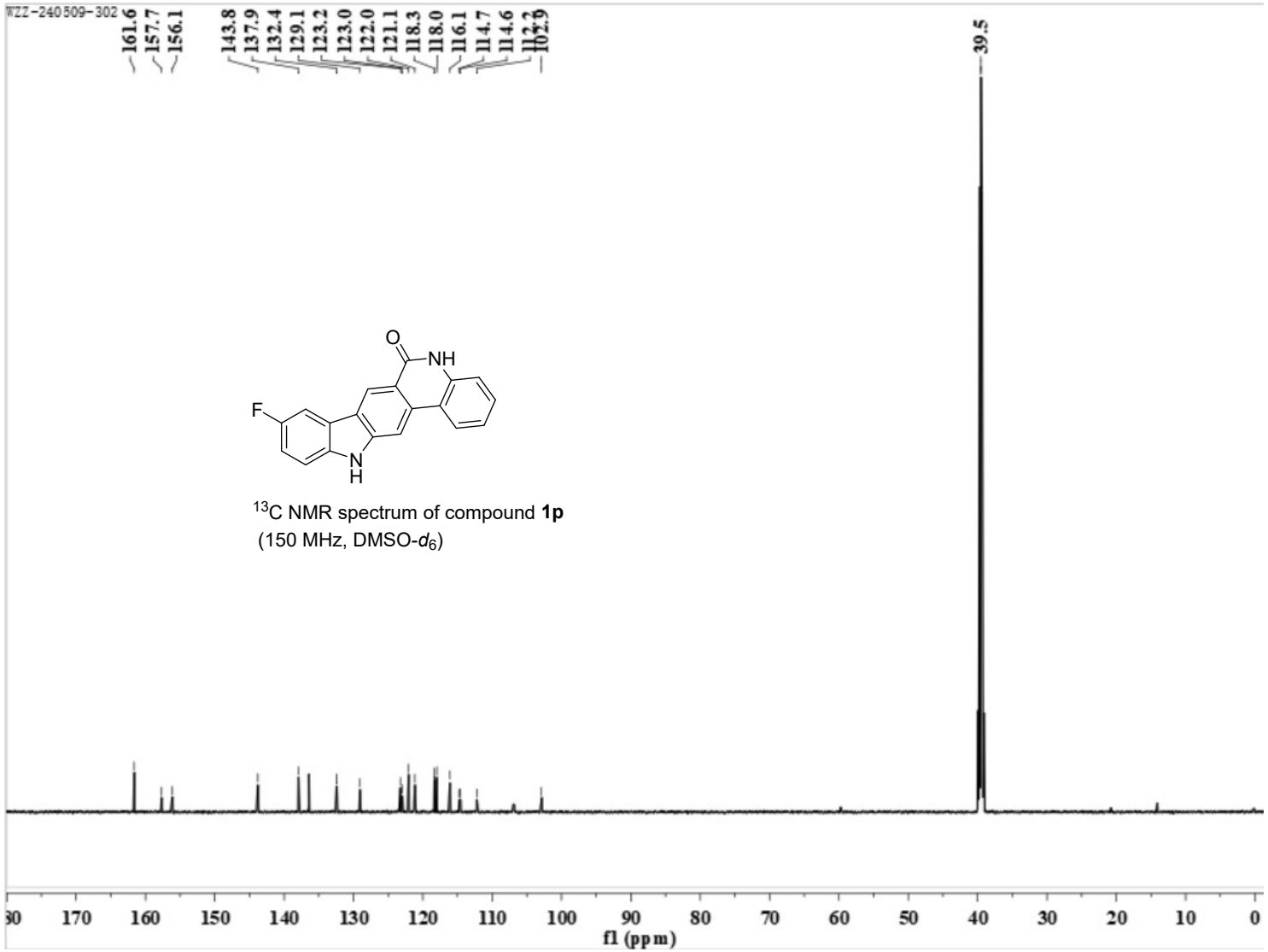
^{1}H NMR spectrum of compound **1o**
(600 MHz, DMSO-d_6)



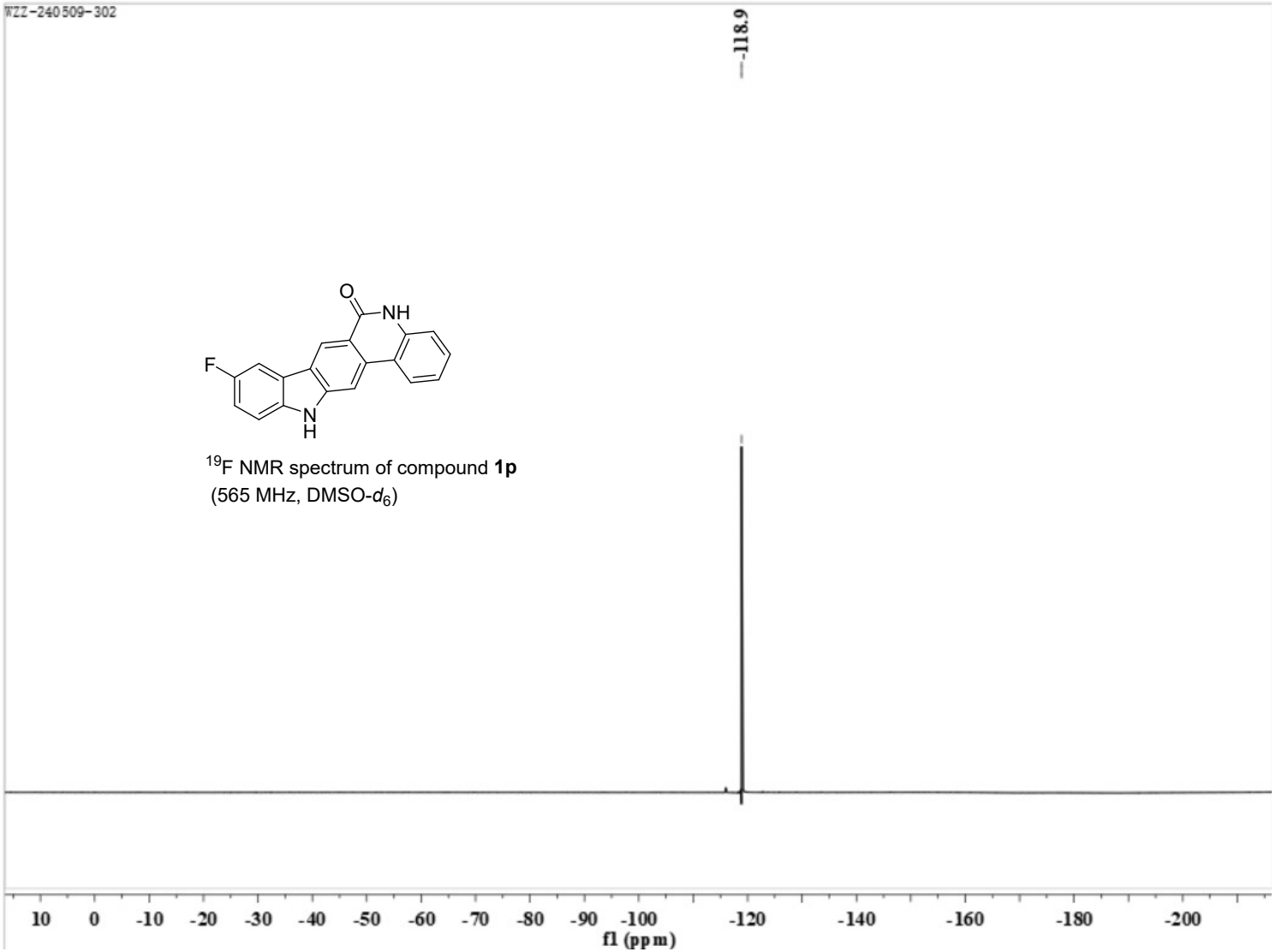
^{13}C NMR spectrum of compound **1o**
(150 MHz, DMSO-d_6)



^{1}H NMR spectrum of compound **1p**
(600 MHz, DMSO-d_6)



^{13}C NMR spectrum of compound **1p**
(150 MHz, DMSO-d_6)



^{19}F NMR spectrum of compound **1p**
(565 MHz, DMSO-d_6)