Supporting Information

Controllable transformation of indoles using iodine(III) reagent

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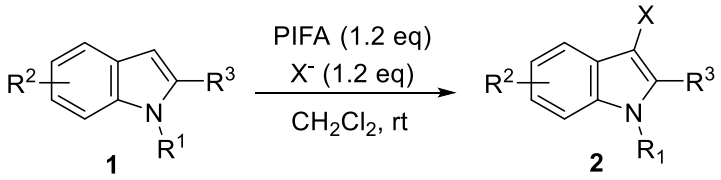
1. General information

All materials were purchased from commercial sources (Acros, Aldrich, Adamas, Casmart) and used without any further treatment unless otherwise stated. When required, unless specifically mentioning, dry solvents were obtained directly prior to use by distillation from CaH_2 or sodium/benzophenone. All reactions were performed in oven-dried glassware under an argon atmosphere unless otherwise noted. Removal of solvents *in vacuo* was achieved using both a GreatWall® rotary evaporator (bath temperatures up to 45 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature Reactions requiring anhydrous conditions were run under a dry atmosphere of nitrogen or argon. Flash column chromatography (FCC) was performed using silica gel (Qindao Haiyang, 200-300). Thin layer chromatography (TLC) was performed using aluminium backed $60F_{254}$ silica plates. Visualisation was achieved by UV fluorescence or a basic $KMnO_4$ solution and heat. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. ^{13}C NMR spectra were recorded at 101 MHz or 151 MHz as stated. ^1H chemical shifts are reported in ppm relative to solvent peak, $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), CD_3OD (δ = 3.30 ppm). ^{13}C chemical shifts are reported in ppm using $CDCl_3$ (δ = 77.16 ppm), DMSO-d_6 (δ = 39.52 ppm), CD_3OD (δ = 49.00 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on BioTOFQ.

2. <u>Experimental Procedures</u>

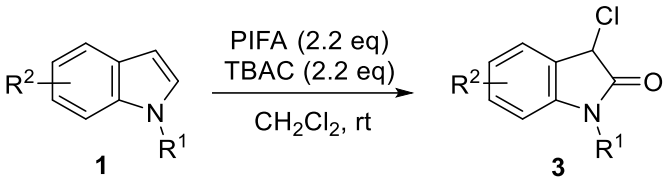
<u>General Procedure A:</u> for the conversion of indoles into 3-halo-indoles



PIFA (0.24 mmol, 120 mol%) was added dropwise to a solution of indoles (**1**) (0.20 mmol, 100 mol%) and *n*-$Bu_4NCl•H_2O$ (TBAC) (0.24mmol, 120 mol%) in CH_2Cl_2 (2.0 mL)

with stirring under open-air conditions at room temperature. The resulting solution was stirred for further 1–3 min. Upon completion as detected by TLC, solvent was removed by rotary evaporation and the residue was purified though FCC or preparative TLC (PTLC) to obtain the products (**2**).

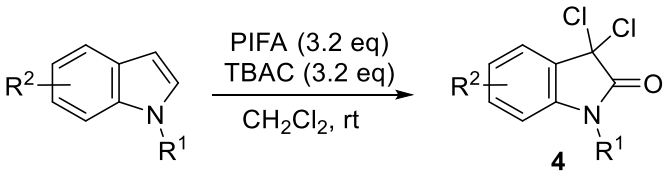
<u>General Procedure B:</u> for the chlorination-oxidation indoles into 3-Cl-2-oxindoles



1 **3**

PIFA (0.44 mmol, 220 mol%) was added dropwise to a solution of indoles (**1**) (0.20 mmol, 100 mol%) and *n*-$Bu_4NCl•H_2O$ (TBAC) (0.44 mmol, 220 mol%) in CH_2Cl_2 (2.0 mL) with stirring under open-air conditions at room temperature. The resulting solution was stirred for further 1–5 min. Upon completion as detected by TLC, solvent was removed by rotary evaporation and the residue was purified though FCC or preparative TLC (PTLC) to obtain 3-Cl-2-oxindoles (**3**).

<u>General Procedure C:</u> for the chlorination-oxidation indoles into 3,3-di-Cl-2-oxindoles

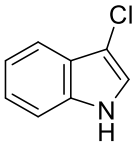


4

PIFA (0.64 mmol, 320 mol%) was added dropwise to a solution of indoles (0.20 mmol, 100 mol%) and *n*-$Bu_4NCl•H_2O$ (TBAC) (0.64 mmol, 320 mol%) in CH_2Cl_2 (2.0 mL) with stirring under open-air conditions at room temperature. The resulting solution was stirred for further 1.5–2 h. Upon completion as detected by TLC, solvent was removed by rotary evaporation and the residue was purified though FCC or preparative TLC (PTLC) to obtain 3,3-di-Cl-2-oxindoles (**4**)**.**

3. <u>Substrate synthesis and Data</u>

3-Chloro-1*H*-indole (2a)

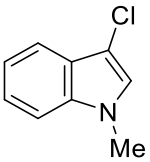


Compound 2a was prepared by the **general procedure A:** Purified by FCC (eluent: 10% EtOAc/hexanes) afforded **2a** (28.2 mg, 93% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (br, s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.19 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.97, 125.40, 123.14, 120.84, 120.49, 118.28, 111.50, 106.57.

The spectroscopic properties were consistent with our previously reported one.[1]

3-Chloro-1-methyl-1*H*-indole (2b)

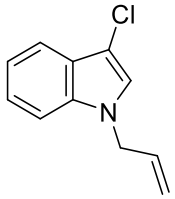


Compound 2b was prepared by the **general procedure A:** Purified by FCC (eluent: 10% EtOAc/hexanes) afforded **2b** (30.8 mg, 93% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 7.06 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.97, 125.86, 125.36, 122.73, 120.02, 118.50, 109.61, 104.53, 33.07. ESI-HRMS: m/z calcd for C_9H_9ClN $[M + H]^+$: 166.0418, found 166.0422.

The spectroscopic properties were consistent with the data available in the literature.[2]

1-Allyl-3-chloro-1*H*-indole (2c)



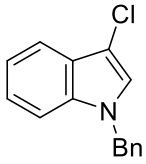
Compound 2c was prepared by the **general procedure A:** Purified by FCC (eluent: 10% EtOAc/hexanes) afforded **2c** (35.3 mg, 92% yield) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 1H), 7.36 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.11 (s, 1H), 6.05 – 5.96 (m, 1H), 5.28 - 5.25 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.18 – 5.13 (m, 1H), 4.72 (dt, *J* = 5.4, 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.40, 133.04, 126.05, 124.38, 122.79, 120.19, 118.59, 117.93, 109.96, 105.11, 49.05. ESI-HRMS: m/z calcd for

$C_{11}H_{11}ClN$ [M + H]$^+$: 192.0575, found 193.0581.

The spectroscopic properties were consistent with the data available in the literature.[2]

1-Benzyl-3-chloro-1*H*-indole (2d)

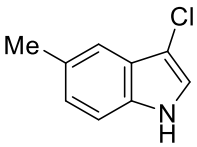


Compound 2d was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2d** (45.0 mg, 93% yield) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 7.42 – 7.41 (m, 1H), 7.36 – 7.32 (m, 4H), 7.30 – 7.21 (m, 2H), 7.18 – 7.15 (m, 2H), 7.13 (s, 1H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.94, 135.63, 129.00, 128.55 , 128.02, 127.77, 127.04, 126.12, 124.73, 122.97, 120.30, 118.64, 110.06, 105.43, 72.26, 50.36. ESI-HRMS: m/z calcd for $C_{15}H_{13}ClN$ [M + H]$^+$: 242.0731, found 242.0735.

The spectroscopic properties were consistent with the data available in the literature.[2]

3-Chloro-5-methyl-1*H*-indole (2e)

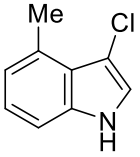


Compound 2e was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2e** (31.1 mg, 94% yield) as a light grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br, s, 1H), 7.48 – 7.47 (m, 1H), 7.29 – 7.26 (m, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 7.13 – 7.11 (m, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.44, 130.07, 125.69, 124.95, 121.01, 117.87, 111.29, 106.09, 21.54. ESI-HRMS: m/z calcd for C_9H_7ClN [M - H]$^-$: 164.0273, found 164.0273.

The spectroscopic properties were consistent with the data available in the literature.[3]

3-Chloro-4-methyl-1*H*-indole (2f)

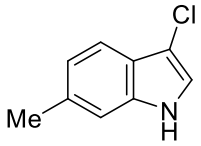


Compound 2f was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2f** (30.1 mg, 91% yield) as a light grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, s, 1H), 7.22 – 7.20 (m, 1H), 7.16– 7.12 (m, 2H), 6.94 – 6.92(m, 1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.46, 130.99, 123.29, 122.06, 121.18, 109.59, 106.87, 19.25. ESI-HRMS: m/z calcd for C_9H_9ClN $[M + H]^+$: 166.0418, found 166.0421.

The spectroscopic properties were consistent with the data available in the literature.[4]

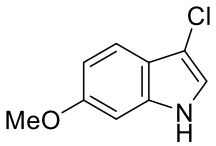
3-Chloro-6-methyl-1*H*-indole (2g)



Compound 2g was prepared by the **general procedure A:** Purified by FCC (eluent: 10% EtOAc/hexanes) afforded **2g** (27.7 mg, 85% yield) as a grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br, s, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.17 (s, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.55, 133.22, 123.45, 122.44, 120.24, 118.03, 111.46, 106.55, 21.82. ESI-HRMS: m/z calcd for C_9H_9ClN $[M + H]^+$: 166.0418, found 166.0421.

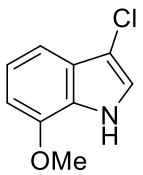
3-Chloro-6-methoxy-1*H*-indole (2h)



Compound 2h was prepared by the **general procedure A:** Purified by FCC (eluent: 10% EtOAc/hexanes) afforded **2h** (22.9 mg, 80% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br, s, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.39, 135.89, 119.98, 119.64, 119.10, 110.86, 106.63, 94.82, 55.81. ESI-HRMS: m/z calcd for C_9H_9ClN $[M + H]^+$: 182.0367, found 182.0369.

3-Chloro-7-methoxy-1*H*-indole (2i)



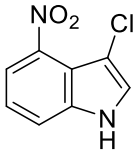
Compound 2i was prepared by the **general procedure A:** Purified by FCC (eluent: 10%

EtOAc/hexanes) afforded **2i** (31.2 mg, 86% yield) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (br, s, 1H), 7.32 – 7.29 (m, 1H), 7.19 – 7.14 (m, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.19, 126.74, 125.77, 121.00, 120.58, 110.93, 106.85, 102.80, 55.52. ESI-HRMS: m/z calcd for C_9H_9ClN $[M + H]^+$: 182.0367, found 182.0368.

The spectroscopic properties were consistent with the data available in the literature.[3]

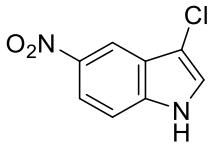
3-Chloro-4-nitro-1*H*-indole (2j)



Compound 2j was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2j** (35.0 mg, 89% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (br, s, 1H), 7.88 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.33 (td, *J* = 8.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.24, 137.38, 128.11, 121.18, 118.30, 117.07, 115.24, 102.72. ESI-HRMS: m/z calcd for $C_8H_6ClN_2O_2$ $[M + H]^+$: 197.0112, found 197.0116.

3-Chloro-5-nitro-1*H*-indole (2k)

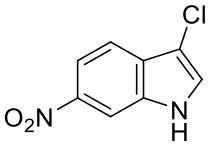


Compound 2k was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2k** (34.2 mg, 87% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (br, s, 1H), 8.36 (d, *J* = 2.3 Hz, 1H), 8.04 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.20, 137.93, 126.53, 123.94, 117.41, 114.09, 112.95, 105.66. ESI-HRMS: m/z calcd for $C_8H_4ClN_2O_2$ $[M - H]^-$: 194.9967, found 194.9971.

The spectroscopic properties were consistent with the data available in the literature.[5]

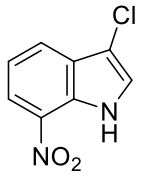
3-Chloro-6-nitro-1*H*-indole (2l)



Compound 2l was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2l** (35.4 mg, 92% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.13 (br, s, 1H), 8.35 (d, J = 2.0 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.62 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.80, 133.27, 129.25, 128.89, 117.57, 114.78, 109.07, 104.28. ESI-HRMS: m/z calcd for $C_8H_4ClN_2O_2$ [M - H]$^-$: 194.9967, found 194.9967.

3-Chloro-7-nitro-1*H*-indole (2m)

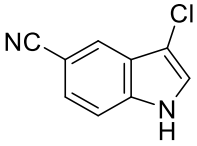


Compound 2m was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2m** (33.8 mg, 86% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.13 (br, s, 1H), 8.19 (dd, J = 8.0, 0.6 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 2.7 Hz, 1H), 7.34(t, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 132.97, 128.66, 127.10, 125.85, 125.75, 119.87, 119.59, 105.49. ESI-HRMS: m/z calcd for $C_8H_4ClN_2O_2$ [M - H]$^-$: 194.9967, found 194.9970.

The spectroscopic properties were consistent with the data available in the literature.[6]

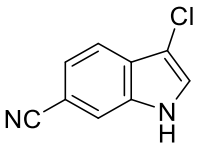
3-Chloro-1*H*-indole-5-carbonitrile (2n)



Compound 2n was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2n** (31.8 mg, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (br, s, 1H), 7.98 (s, 1H), 7.75 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.66, 125.36, 124.93, 124.49, 122.92, 120.17, 113.64, 104.21, 102.14. ESI-HRMS: m/z calcd for $C_9H_6ClN_2$ [M + H]$^+$: 177.0214, found 177.0214.

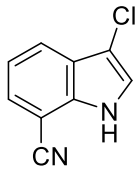
3-Chloro-1*H*-indole-6-carbonitrile (2o)



Compound 2o was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2o** (31.1 mg, 88% yield) as a grey solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 7.96 (s, 1H), 7.84 (d, J = 2.8 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.43 (dd, J = 8.3, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 133.69, 127.40, 127.04, 122.35, 120.11, 118.32, 117.34, 104.06, 103.87. ESI-HRMS: m/z calcd for $C_9H_6ClN_2$ $[M + H]^+$: 177.0214, found 177.0216.

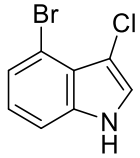
3-Chloro-1*H*-indole-7-carbonitrile (2p)



Compound 2p was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2p** (31.8 mg, 90% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.33 (br, s, 1H), 7.85 – 7.80 (m, 1H), 7.72 – 7.68 (m, 2H), 7.25 (dd, J = 15.5, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 134.31, 127.83, 127.78, 125.61, 124.74, 124.70, 122.99,122.95, 119.98, 119.94, 116.80, 104.67, 94.73. ESI-HRMS: m/z calcd for $C_9H_4ClN_2$ $[M - H]^-$: 175.0068, found 175.0067.

4-Bromo-3-chloro-1*H*-indole (2q)

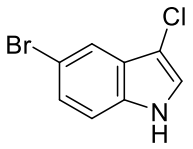


Compound 2q was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2q** (40.6 mg, 88% yield) as a grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (br, s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.29 – 7.29 (m, 1H), 7.21 – 7.20 (m, 1H), 7.06 – 7.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.22, 125.43, 123.99, 123.06, 122.62, 113.31, 111.21. ESI-HRMS: m/z calcd for C_8H_4BrClN $[M - H]^-$: 227.9221, found 227.9226.

The spectroscopic properties were consistent with the data available in the literature.[4]

5-Bromo-3-chloro-1*H*-indole (2r)

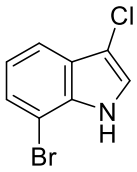


Compound 2r was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2r** (42.4 mg, 92% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (br, s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.67, 127.13, 126.21, 122.18, 121.02, 113.86, 113.11, 106.05. ESI-HRMS: m/z calcd for C_8H_4BrClN [M - H]$^{-}$: 227.9221, found 227.9225.

The spectroscopic properties were consistent with the data available in the literature.[5]

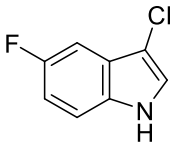
7-Bromo-3-chloro-1*H*-indole (2s)



Compound 2s was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2s** (38.7 mg, 84% yield) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (br, s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.26 – 7.23 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.65, 126.68, 125.58, 121.72, 121.69, 117.80, 107.70, 105.13. ESI-HRMS: m/z calcd for C_8H_4BrClN [M - H]$^{-}$: 227.9221, found 227.9222.

3-Chloro-5-fluoro-1*H*-indole (2t)



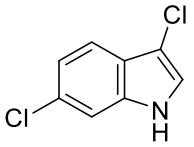
Compound 2t was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2t** (30.5 mg, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (br, s, 1H), 7.33 – 7.29 (m, 2H), 7.23 (d, *J* = 2.6 Hz, 1H), 7.03 (td, *J* = 9.1, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.41 (d, *J* = 237.4 Hz, 1C),

131.58, 125.98 (d, *J* = 10.1 Hz, 1C), 122.73, 112.53 (d, *J* = 9.6 Hz, 1C), 111.95 (d, *J* = 27.3 Hz, 1C), 106.63 (d, *J* = 5.1 Hz, 1C), 103.46 (d, *J* = 25.3 Hz, 1C). ESI-HRMS: m/z calcd for C_8H_4FClN [M - H]$^-$: 168.0022, found 168.0023.

The spectroscopic properties were consistent with the data available in the literature.[5]

3,6-Dichloro-1*H*-indole (2u)

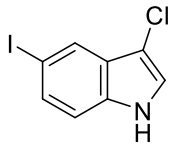


Compound 2u was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2u** (33.1 mg, 89% yield) as a grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br, s, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 1.3, 0.4 Hz, 1H), 7.18 – 7.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.33, 129.32, 124.19, 121.60, 121.46, 119.41, 111.53, 106.96. ESI-HRMS: m/z calcd for $C_8H_4Cl_2N$ [M - H]$^-$: 183.9726, found 183.9729.

The spectroscopic properties were consistent with the data available in the literature.[4]

3-Chloro-5-iodo-1*H*-indole (2v)

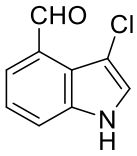


Compound 2v was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2v** (51.1 mg, 92% yield) as a grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (br, s, 1H), 7.98 (d, *J* = 0.9 Hz, 1H), 7.50 - 7.47 (m, 1H), 7.13 – 7.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.12, 131.63, 127.84, 127.32, 127.29, 121.75, 113.54, 105.71, 83.93. ESI-HRMS: m/z calcd for C_8H_4IClN [M - H]$^-$: 275.9082, found 275.9084.

The spectroscopic properties were consistent with the data available in the literature.[4]

3-Chloro-1*H*-indole-4-carbaldehyde (2w)

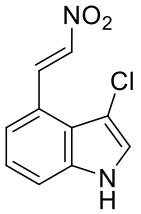


Compound 2w was prepared by the **general procedure A:** Purified by FCC (eluent:

12.5% EtOAc/hexanes) afforded **2w** (33.8 mg, 94% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.94 (br, s, 1H), 11.02 (s, 1H), 7.82 – 7.76 (m, 2H), 7.71 (d, J = 7.5 Hz, 1H), 7.33 (td, J = 7.9, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.82, 136.55, 128.08, 126.73, 123.44, 121.76, 120.42, 118.65, 102.18. ESI-HRMS: m/z calcd for C_9H_7ClNO $[M + H]^+$: 180.0211, found 180.0213.

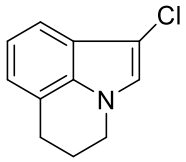
(*E*)-3-Chloro-4-(2-nitrovinyl)-1*H*-indole (2x)



Compound 2x was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2x** (41.0 mg, 92% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (br, s, 1H), 9.18 (d, J = 13.4 Hz, 1H), 8.20 (d, J = 13.4 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.63 (d, J = 8.1 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.25, 135.90, 135.35, 126.21, 122.46, 122.40, 121.05, 120.60, 116.59, 102.50. ESI-HRMS: m/z calcd for $C_{10}H_8ClN_2O_2$ $[M + H]^+$: 223.0269, found 223.0271.

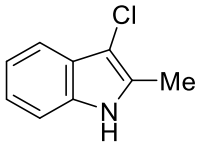
1-Chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (2y)



Compound 2y was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2y** (34.9 mg, 91% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.2, 2.1 Hz, 1H), 7.10 (d, J = 1.9 Hz, 1H), 7.05 (s, 1H), 6.97 (d, J = 7.1 Hz, 1H), 4.11 (t, J = 5.7 Hz, 2H), 3.01 (t, J = 6.1 Hz, 2H), 2.27 – 2.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.35, 123.43, 122.82, 121.98, 120.42, 119.49, 115.84, 104.43, 44.23, 24.53, 22.86. ESI-HRMS: m/z calcd for $C_{11}H_{11}ClN$ $[M + H]^+$: 192.0580, found 192.0585.

3-Chloro-2-methyl-1*H*-indole (2z)

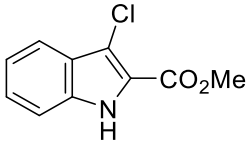


Compound 2z was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2z** (28.5 mg, 86% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (br, s, 1H), 7.60 – 7.57 (m, 1H), 7.30 – 7.27 (m, 1H), 7.22 – 7.20 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.16, 130.63, 126.32, 122.22, 120.33, 117.54, 110.79, 103.59, 11.32. ESI-HRMS: m/z calcd for C_9H_7ClN $[M - H]^-$: 164.0273, found 164.0277.

The spectroscopic properties were consistent with the data available in the literature.[4]

Methyl 3-chloro-1*H*-indole-2-carboxylate (2aa)

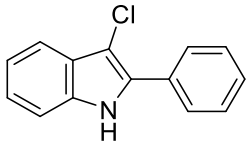


Compound 2aa was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2aa** (30.6 mg, 73% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.26 – 7.20 (m, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.58, 134.89, 126.69, 126.19, 122.19, 121.36, 120.28, 112.55, 112.13, 52.28. ESI-HRMS: m/z calcd for $C_{10}H_9ClNO_2$ $[M + H]^+$: 210.0316, found 210.0316.

The spectroscopic properties were consistent with the data available in the literature.[7]

3-Chloro-2-phenyl-1*H*-indole (2ab)



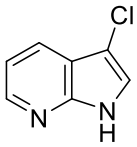
Compound 2ab was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2ab** (41.4 mg, 91% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br, s, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 15.3, 7.7 Hz, 2H), 7.30 – 7.21 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.63, 132.34, 130.88, 128.93, 128.29, 127.31, 127.28, 123.52,

120.81, 118.50, 111.21, 103.72. ESI-HRMS: m/z calcd for $C_{14}H_9ClN$ [M - H]$^{\cdot-}$: 226.0429, found 226.0430.

The spectroscopic properties were consistent with the data available in the literature.[4]

3-Chloro-1*H*-pyrrolo[2,3-*b*]pyridine (2ac)

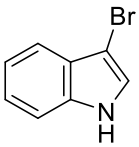


Compound 2ac was prepared by the **general procedure A:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **2ac** (24.4 mg, 80% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (br, s, 1H), 8.32 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.66 (s, 1H), 7.17 (ddd, *J* = 7.9, 4.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.11, 143.31, 126.31, 123.37, 117.54, 116.14, 102.11. ESI-HRMS: m/z calcd for $C_7H_6ClN_2$ [M + H]$^+$: 153.0214, found 153.0214.

The spectroscopic properties were consistent with the data available in the literature.[8]

3-Bromo-1*H*-indole (2ae)

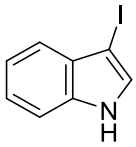


Compound 2ae was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2ae** (35.3 mg, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (br, s, 1H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.45 (t, *J* = 8.6 Hz, 2H), 7.23–7.17 (m, 1H), 7.16–7.11 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 135.84, 126.58, 125.23, 122.68, 120.33, 118.38, 112.56, 89.18. ESI-HRMS: m/z calcd for C_8H_5BrN [M - H]$^{\cdot-}$: 193.9611, found 193.9610.

The spectroscopic properties were consistent with the data available in the literature.[5]

3-Iodo-1*H*-indole (2af)



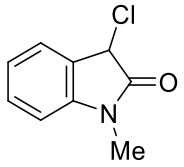
Compound 2af was prepared by the **general procedure A:** Purified by FCC (eluent: 8% EtOAc/hexanes) afforded **2af** (40.4 mg, 83% yield) as a grey solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.55 (br, s, 1H), 7.57 (d, J = 2.5 Hz, 1H), 7.46–7.42 (m, 1H), 7.33–7.28 (m, 1H), 7.21–7.15 (m, 1H), 7.15–7.09 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.40, 130.13, 129.82, 122.64, 120.40, 120.27, 112.38, 56.39.

ESI-HRMS: m/z calcd for C_8H_5IN [M - H]$^-$: 241.9472, found 241.9477.

The spectroscopic properties were consistent with the data available in the literature.[5]

3-Chloro-1-methylindolin-2-one (3a)

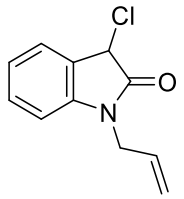


Compound 3a was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3a** (28.3 mg, 78% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.5, 1.3 Hz, 1H), 7.36 (tt, J = 7.8, 1.0 Hz, 1H), 7.12 (td, J = 7.6, 1.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.13 (s, 1H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ172.19, 143.96, 130.64, 125.76, 123.53, 108.83, 51.62, 26.80. ESI-HRMS: m/z calcd for C_9H_7ClNO [M - H]$^-$: 180.0222, found 180.0220.

The spectroscopic properties were consistent with the data available in the literature.[9]

1-Allyl-3-chloroindolin-2-one (3b)

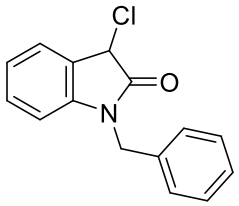


Compound 3b was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3b** (29.1 mg, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 5.84 (ddd, J = 22.0, 10.5, 5.3 Hz, 1H), 5.33 – 5.20 (m, 2H), 5.16 (s, 1H), 4.35 (d, J = 5.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.81, 143.29, 131.86, 130.77, 126.18, 125.96, 123.45, 117.54, 110.23, 52.05, 42.23. ESI-HRMS: m/z calcd for $C_{11}H_{11}ClNO$ [M + H]+: 208.0524, found 208.0530.

The spectroscopic properties were consistent with the data available in the literature.[10]

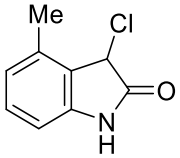
1-Benzyl-3-chloroindolin-2-one (3c)



Compound 3c was prepared by the **general procedure B:** Purified by FCC (eluent: 12.5% EtOAc/hexanes) afforded **3c** (40.7 mg, 79% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.08 (td, *J* = 7.6, 1.0 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.22 (s, 1H), 4.92 (d, *J* = 3.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 143.11, 135.16, 130.54, 129.05, 128.04, 127.44, 125.86, 123.56, 109.86, 51.64, 44.31.

The spectroscopic properties were consistent with the data available in the literature.[11]

3-Chloro-4-methylindolin-2-one (3d)

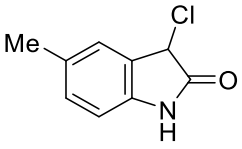


Compound 3d was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3d** (23.3 mg, 64% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.57 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.01, 142.49, 136.23, 130.38, 124.29, 123.70, 107.69, 52.06, 17.69. ESI-HRMS: m/z calcd for C_9H_7ClNO $[M - H]^{-}$: 180.0222, found 180.0218.

The spectroscopic properties were consistent with the data available in the literature.[12]

3-Chloro-5-methylindolin-2-one (3e)



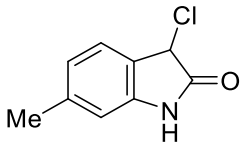
Compound 3e was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3e** (23.9 mg, 66% yield) as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (br, s, 1H), 7.23 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.12 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 138.56,

133.32, 131.02, 126.73, 126.37, 110.35, 52.15, 21.16. ESI-HRMS: m/z calcd for C_9H_9ClNO $[M + H]^+$: 182.0367, found 182.0369.

The spectroscopic properties were consistent with the data available in the literature.[9]

3-Chloro-6-methylindolin-2-one (3f)

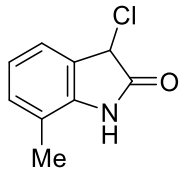


Compound 3f was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3f** (25.4 mg, 70% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 7.18 (s, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 5.52 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ173.10, 139.88, 131.33, 130.50, 126.49, 126.11, 109.86, 52.34, 20.49. ESI-HRMS: m/z calcd for C_9H_7ClNO $[M - H]^-$: 180.0222, found 180.0223.

The spectroscopic properties were consistent with the data available in the literature.[13]

3-Chloro-7-methylindolin-2-one (3g)

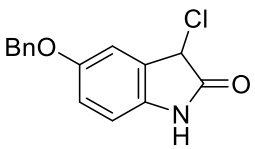


Compound 3g was prepared by the **general procedure B:** Purified by FCC (eluent: 17% EtOAc/hexanes) afforded **3g** (30.5 mg, 84% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.80 (br, s, 1H), 7.19 (d, J = 7.4 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 5.57 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.05, 141.42, 131.89, 126.59, 123.35, 122.70, 120.12, 53.03, 16.74. ESI-HRMS: m/z calcd for C_9H_7ClNO $[M - H]^-$: 180.0222, found 180.0217.

The spectroscopic properties were consistent with the data available in the literature.[14]

5-(Benzyloxy)-3-chloroindolin-2-one (3h)

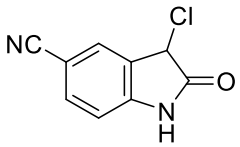


Compound 3h was prepared by the **general procedure B:** Purified by PTLC

(developing solvent: 40% EtOAc/hexanes) afforded **3h** (33.4 mg, 61% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.48 – 7.30 (m, 5H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 5.12 (s, 1H), 5.05 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.48, 154.69, 137.53, 136.26, 128.88, 128.29, 128.13, 128.02, 116.99, 113.58, 111.18, 70.33, 53.00. ESI-HRMS: m/z calcd for $C_{15}H_{11}ClNO_2$ [M - H]$^-$: 272.0484, found 272.0485.

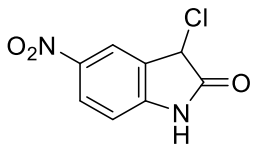
3-Chloro-2-oxoindoline-5-carbonitrile (3i)



Compound 3i was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 40% EtOAc/hexanes) afforded **3i** (21.6 mg, 56% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (br, s, 1H), 7.88 (s, 1H), 7.80 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 5.65 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.53, 147.20, 135.97, 129.72, 128.21, 119.34, 111.55, 104.89, 51.45. ESI-HRMS: m/z calcd for $C_9H_4ClN_2O$ [M - H]$^-$: 191.0018, found 191.0016.

3-Chloro-5-nitroindolin-2-one (3j)

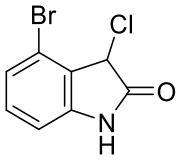


Compound 3j was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 40% EtOAc/hexanes) afforded **3j** (24.7 mg, 58% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (br, s, 1H), 8.27 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.23 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 5.72 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.92, 149.24, 142.97, 128.04, 127.79, 121.69, 110.98, 51.54. ESI-HRMS: m/z calcd for $C_8H_4ClN_2O_3$ [M - H]$^-$: 210.9916, found 210.9913.

The spectroscopic properties were consistent with the data available in the literature.[9]

4-Bromo-3-chloroindolin-2-one (3k)

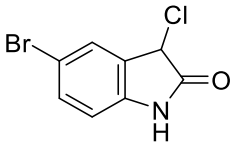


Compound 3k was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 33% EtOAc/hexanes) afforded **3k** (39.4 mg, 80% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.98 (s, 2H), 7.28 – 7.19 (m, 2H), 6.89 (dd, J = 7.5, 1.2 Hz, 2H), 5.48 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.01, 144.43, 132.38, 125.60, 125.40, 119.97, 109.52, 52.81. ESI-HRMS: m/z calcd for $C_8H_4BrClNO$ [M - H]$^-$: 243.9170, found 243.9179.

The spectroscopic properties were consistent with the data available in the literature.[13]

5-Bromo-3-chloroindolin-2-one (3l)

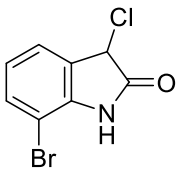


Compound 3l was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 33% EtOAc/hexanes) afforded **3l** (30.1 mg, 61% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 8.3, 2.0 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 5.58 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.74, 141.72, 133.00, 128.88, 128.37, 113.73, 112.15, 51.62. ESI-HRMS: m/z calcd for $C_8H_4BrClNO$ [M - H]$^-$: 243.9170, found 243.9160.

The spectroscopic properties were consistent with the data available in the literature.[9]

7-Bromo-3-chloroindolin-2-one (3m)

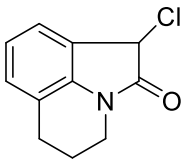


Compound 3m was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 33% EtOAc/hexanes) afforded **3m** (42.4 mg, 86% yield) as a grey solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.10 (br, s, 1H), 7.51 (dd, J = 8.2, 0.5 Hz, 1H), 7.39 (d, J =

7.4 Hz, 1H), 7.03 – 6.99 (m, 1H), 5.71 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.40, 142.26, 133.54, 128.67, 125.22, 124.43, 102.70, 53.05. ESI-HRMS: m/z calcd for $C_8H_4BrClNO$ [M - H]$^-$: 243.9170, found 243.9169.

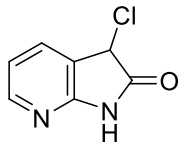
1-Chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (3n)



Compound 3n was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **3n** (19.5 mg, 47% yield) as a grey solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 5.14 (s, 1H), 3.77 – 3.73 (m, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.06 – 2.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 139.79, 129.32, 124.46, 123.30, 122.91, 120.92, 52.63, 39.33, 24.35, 21.00. ESI-HRMS: m/z calcd for $C_{11}H_{10}ClNONa$ [M + Na]$^+$: 208.0524, found 208.0526; [M + Na]$^+$: 230.0343, found 230.0346.

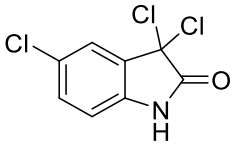
3-Chloro-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (3o)



Compound 3o was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 50% EtOAc/hexanes) afforded **3o** (19.9 mg, 59% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.45 (br, s, 1H), 8.19 – 8.18 (m, 1H), 7.78 – 7.76 (m, 1H), 7.07 (dd, *J* = 7.4, 5.3 Hz, 1H), 5.66 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.24, 157.30, 149.32, 133.97, 121.64, 118.94, 51.84. ESI-HRMS: m/z calcd for $C_7H_4ClN_2O$ [M - H]$^-$: 167.0018, found 167.0018.

3,3,5-Trichloroindolin-2-one (4a)



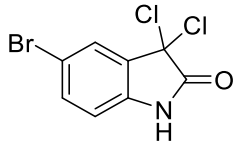
Compound 4a was prepared by the **general procedure C:** Purified by PTLC (developing

solvent: 20% EtOAc/hexanes) afforded **4a** (40.8 mg, 86% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (br, s, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.06, 136.51, 132.22, 131.12, 129.94, 125.57, 112.78, 74.07.

The spectroscopic properties were consistent with the data available in the literature.[15]

5-Bromo-3,3-dichloroindolin-2-one (4b)

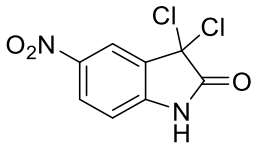


Compound 4b was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4b** (53.2 mg, 95% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (br, s, 1H), 7.88 (s, 1H), 7.60 (dd, *J* = 6.4 Hz, 1H), 6.94 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.68, 138.45, 135.19, 130.74, 127.54, 114.92, 113.40, 74.18.

The spectroscopic properties were consistent with the data available in the literature.[11]

3,3-Dichloro-5-nitroindolin-2-one (4c)

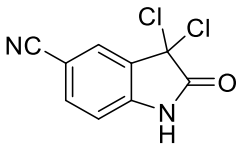


Compound 4c was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 50% EtOAc/hexanes) afforded **4c** (46.7 mg, 94% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (br, s, 1H), 8.48 (d, *J* = 2.3 Hz, 1H), 8.34 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.61, 144.58, 143.77, 130.53, 128.49, 121.40, 111.71, 73.03.

The spectroscopic properties were consistent with the data available in the literature.[16]

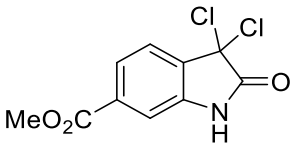
3,3-Dichloro-5-nitrile-2-one (4d)



Compound 4d was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4d** (36.8 mg, 81% yield) as a yellow solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.01 (d, *J* = 1.6 Hz, 1H), 7.77 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 171.08, 144.58, 137.95, 131.97, 129.87, 119.01, 113.17, 108.09, 74.36. ESI-HRMS: m/z calcd for $C_9H_4Cl_2N_2ONa$ $[M + Na]^+$: 248.9593, found 248.9552.

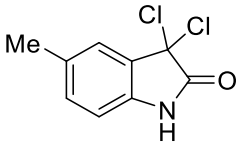
Methyl 3,3-dichloro-2-oxoindoline-6-carboxylate (4e)



Compound 4e was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 33% EtOAc/hexanes) afforded **4e** (49.9 mg, 96% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.54 (br, s, 1H), 7.81 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.43 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 168.72, 165.08, 139.55, 139.37, 133.03, 125.16, 124.67, 111.31, 74.15, 52.61. ESI-HRMS: m/z calcd for $C_{10}H_8Cl_2NO_3$ $[M + H]^+$: 259.9876, found 259.9879.

3,3-Dichloro-5-methylindolin-2-one (4f)

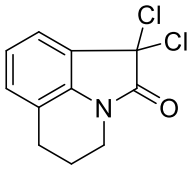


Compound 4f was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4f** (25.9 mg, 60% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.20 (br, s, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.23 – 7.20 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.10, 135.48, 134.37, 132.57, 129.80, 125.70, 111.10, 74.93, 29.84.

The spectroscopic properties were consistent with the data available in the literature.[16]

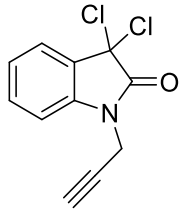
1,1-Dichloro-5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (4g)



Compound 4g was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4g** (30.0 mg, 62% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 3.76 (t, *J* = 5.9 Hz, 2H), 2.78 (t, *J* = 6.1 Hz, 2H), 2.05 (p, *J* = 6.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.86, 136.64, 130.71, 128.09, 123.71, 122.36, 121.45, 75.52, 39.59, 24.27, 20.83. ESI-HRMS: m/z calcd for $C_{11}H_9Cl_2NONa$ $[M + Na]^+$: 242.0134, found 242.0131; $[M + Na]^+$: 263.9953, found 263.9950.

3,3-Dichloro-1-(prop-2-yn-1-yl)indolin-2-one (4h)



Compound 4h was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4h** (40.8 mg, 85% yield) as a yellow liquid.

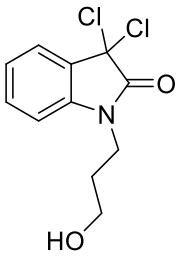
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.45 – 7.39 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10-7.04 (dd, *J* = 16.0, 8.2 Hz, 1H), 4.52 (d, *J* = 2.7 Hz, 2H), 2.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.01, 138.86, 131.98, 129.16, 124.96, 124.67, 110.31, 75.59, 74.13, 73.75, 30.39. ESI-HRMS: m/z calcd for $C_{11}H_8Cl_2NO$ $[M + H]^+$: 239.9977, found 239.9974.

The spectroscopic properties were consistent with the data available in the literature.[15]

This compound contains about 23% overchloridized impurity as detected by ^{13}C NMR.

Spectroscopic data for overchloridized impurity. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 137.35, 131.96, 130.49, 130.11, 125.36, 111.58, 75.20, 74.19, 73.38, 30.54. ESI-HRMS: m/z calcd for $C_{11}H_7Cl_3NO$ $[M + H]^+$: 273.9593, found 273.9589.

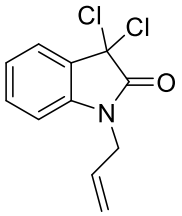
3,3-Dichloro-1-(3-hydroxypropyl)indolin-2-one (4i)



Compound 4i was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 50% EtOAc/hexanes) afforded **4i** (42.7 mg, 82% yield) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 3.65 (t, *J* = 5.7 Hz, 2H), 2.35 (br, s, 1H), 1.93 (p, *J* = 6.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.06, 139.89, 132.09, 129.64, 125.15, 124.49, 109.58, 74.31, 58.75, 37.34, 29.79. ESI-HRMS: m/z calcd for $C_{11}H_{11}Cl_2NO_2Na$ $[M + Na]^+$: 282.0059, found 282.0056.

1-Allyl-3,3-dichloroindolin-2-one (4j)

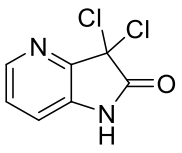


Compound 4j was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **4j** (16.0 mg, 33% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.18(t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.88 – 5.80 (m, 1H), 5.28 – 5.24 (m, 2H), 4.36 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.83, 140.00, 131.90, 130.16, 129.42, 125.00, 124.29, 118.47, 110.12, 74.37, 43.09. ESI-HRMS: m/z calcd for $C_{11}H_9Cl_2NONa$ $[M + Na]^+$: 263.9953, found 263.9954.

The spectroscopic properties were consistent with the data available in the literature.[15]

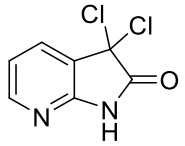
3,3-Dichloro-1,3-dihydro-2H-pyrrolo[3,2-*b*]pyridin-2-one (4k)



Compound 4k was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 50% EtOAc/hexanes) afforded **4k** (37.4 mg, 92% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.54 (br, s, 1H), 8.33 (d, J = 1.6 Hz, 1H), 7.44 – 7.42 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.56, 146.12, 144.30, 135.05, 127.09, 119.17, 73.90. ESI-HRMS: m/z calcd for $C_7H_4Cl_2N_2ONa$ $[M + Na]^+$: 224.9593, found 224.9551.

3,3-Dichloro-1,3-dihydro-2H-pyrrolo[2,3-*b*]pyridin-2-one (4l)

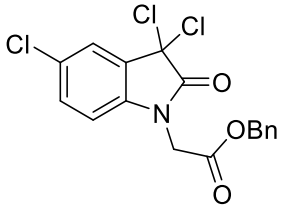


Compound 4l was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 50% EtOAc/hexanes) afforded **4l** (36.5 mg, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.09 (br, s, 1H), 8.31 (d, J = 5.0 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 6.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.74, 153.41, 151.11, 133.24, 123.35, 119.72, 73.97. ESI-HRMS: m/z calcd for $C_7H_5Cl_2N_2O$ $[M + H]^+$: 202.9773, found 202.9776.

The spectroscopic properties were consistent with the data available in the literature.[11]

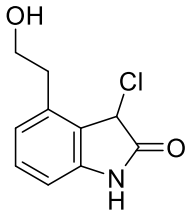
Benzyl 2-(3,3,5-trichloro-2-oxoindolin-1-yl)acetate (10)



Compound 10 was prepared by the **general procedure C:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **10** (60.8 mg, 79% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 2.0 Hz, 1H), 7.58 (dd, J = 8.5, 2.0 Hz, 1H), 7.39 – 7.32 (m, 5H), 7.29 (d, J = 8.5 Hz, 1H), 5.19 (s, 2H), 4.80 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.92, 166.91, 138.53, 135.33, 132.36, 129.52, 128.60, 128.46, 128.29, 128.02, 124.83, 112.48, 73.30, 66.90, 54.89, 41.99. ESI-HRMS: m/z calcd for $C_{17}H_{12}Cl_3NO_3Na$ $[M + Na]^+$: 405.9775, found 405.9783.

3-Chloro-4-(2-hydroxyethyl)indolin-2-one (12)

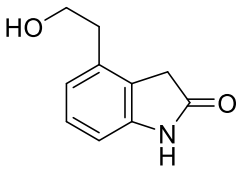


Compound 12 was prepared by the **general procedure B:** Purified by PTLC (developing solvent: 20% EtOAc/hexanes) afforded **12** (21.6 mg, 51% yield) as a brown solid.

^{1}H NMR (400 MHz, CD_3OD) δ 7.27 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 3.89 (ddd, *J* = 10.7, 7.5, 5.7 Hz, 1H), 3.79 (dt, *J* = 10.7, 7.5 Hz, 1H), 3.08 (dt, *J* = 14.6, 7.5 Hz, 1H), 2.93 – 2.84 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 174.62, 142.22, 137.94, 130.30, 125.01, 123.76, 108.12, 61.69, 51.82, 34.86. ESI-HRMS: m/z calcd for $C_{10}H_9ClNO_2$ $[M - H]^-$: 210.0327, found 210.0321.

The spectroscopic properties were consistent with our previously reported one.[1]

4-(2-Hydroxyethyl)indolin-2-one (13)



To a solution of **12** (20.3 mg, 0.10 mmol) in MeOH (3 mL) was added 20% Pd-C (5.0 mg). The mixture was stirred at room temperature under H_2 atmosphere for 2 h. Upon completion as detected by TLC, the mixture was filtered over diatomaceous earth, and concentrated in vacuo, purified by silica gel flash column chromatography (50% EtOAc/hexanes) to afford compound **13** (15.9 mg, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, CD_3OD) δ 7.15 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 3.78 (t, *J* = 6.9 Hz, 2H), 3.50 (s, 2H), 2.78 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 178.53, 142.92, 135.42, 127.61, 124.89, 122.65, 107.44, 61.64, 35.96, 34.74. ESI-HRMS: m/z calcd for $C_{10}H_{12}NO_2$ $[M + H]^+$: 178.0863, found 178.0860.

The spectroscopic properties were consistent with the data available in the literature.[17]

4. References

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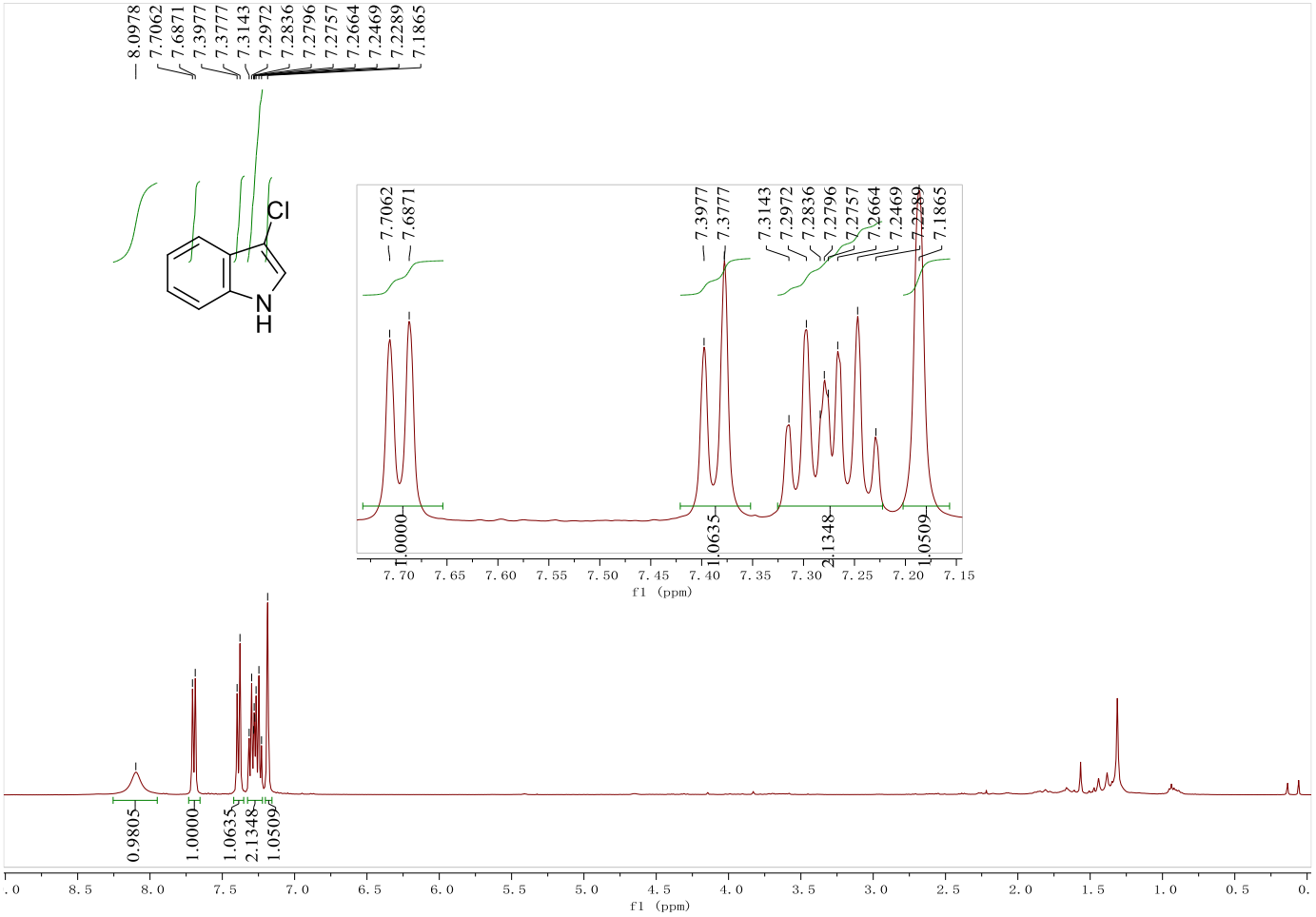
5. Copies of NMR Spectra

^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-1*H*-indole (2a)



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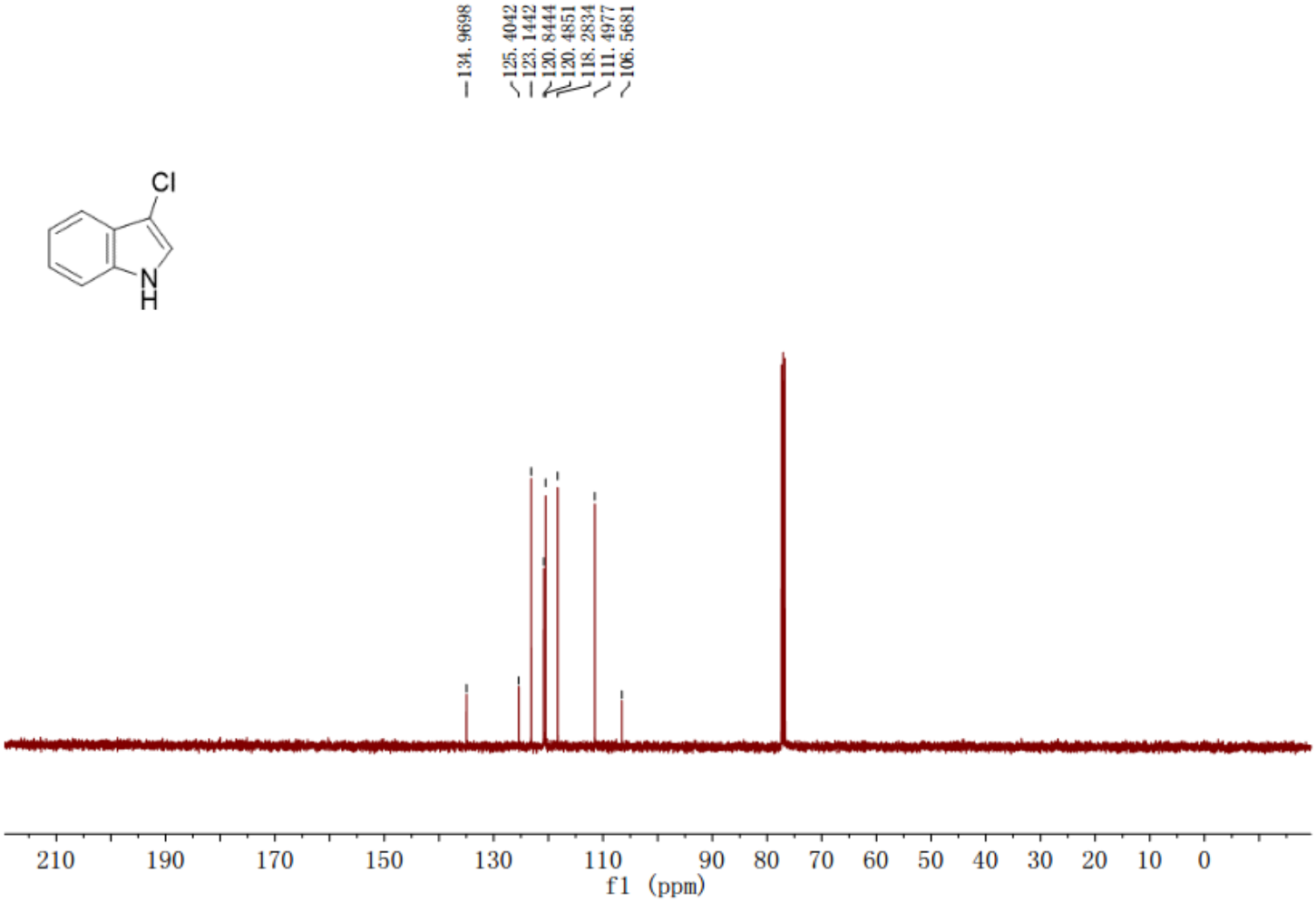
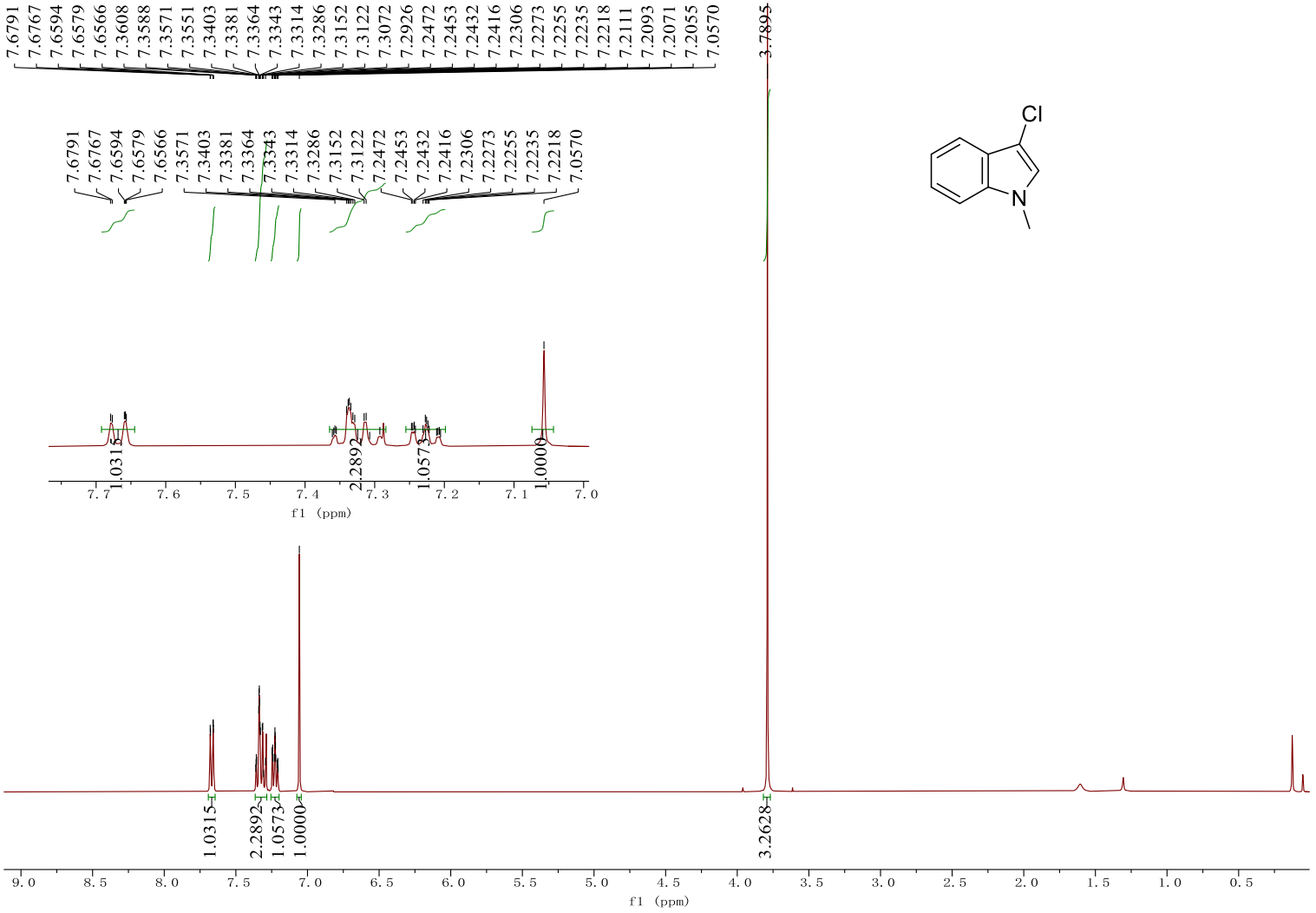


^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-1-methyl-1*H*-indole (2b)



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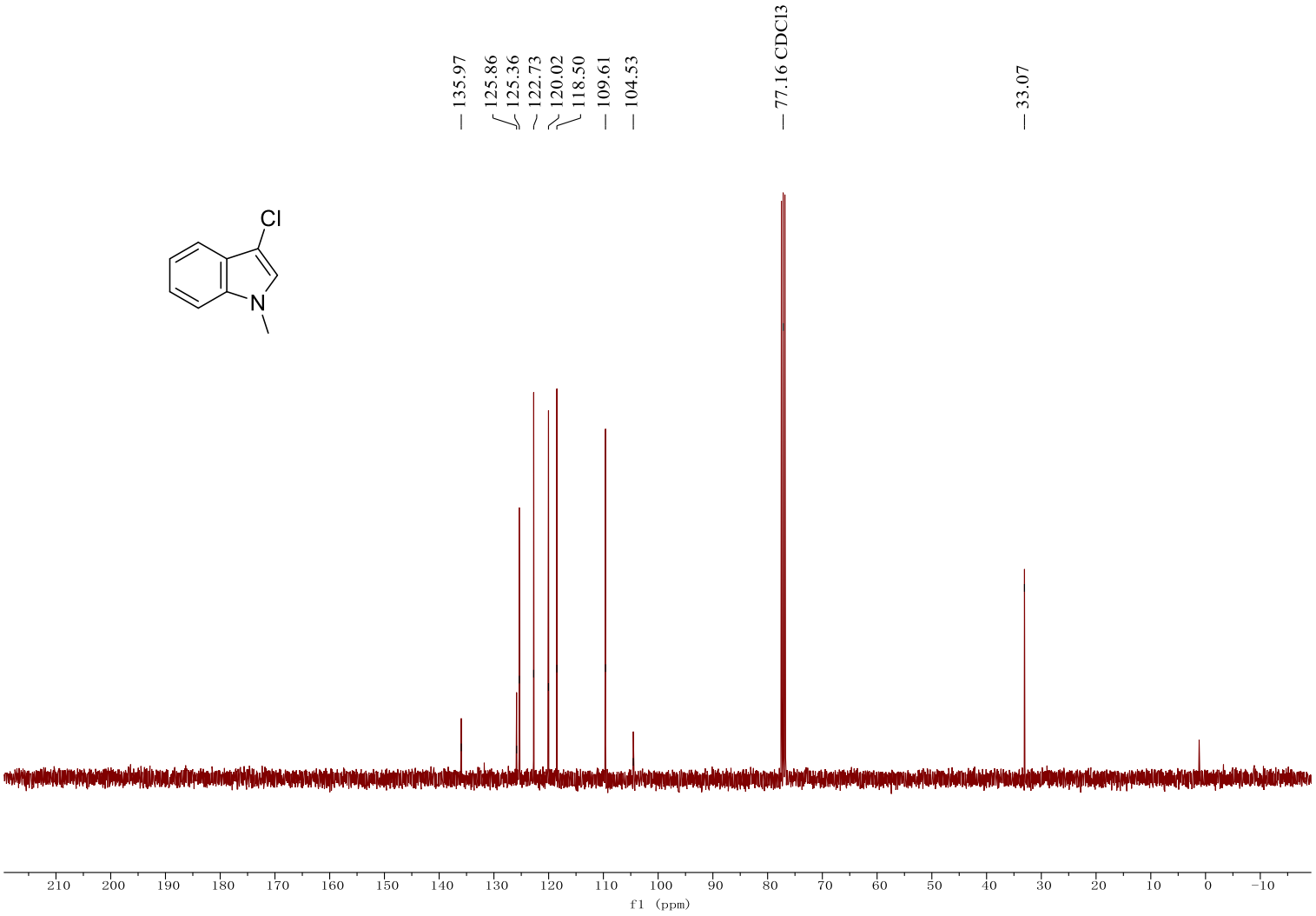
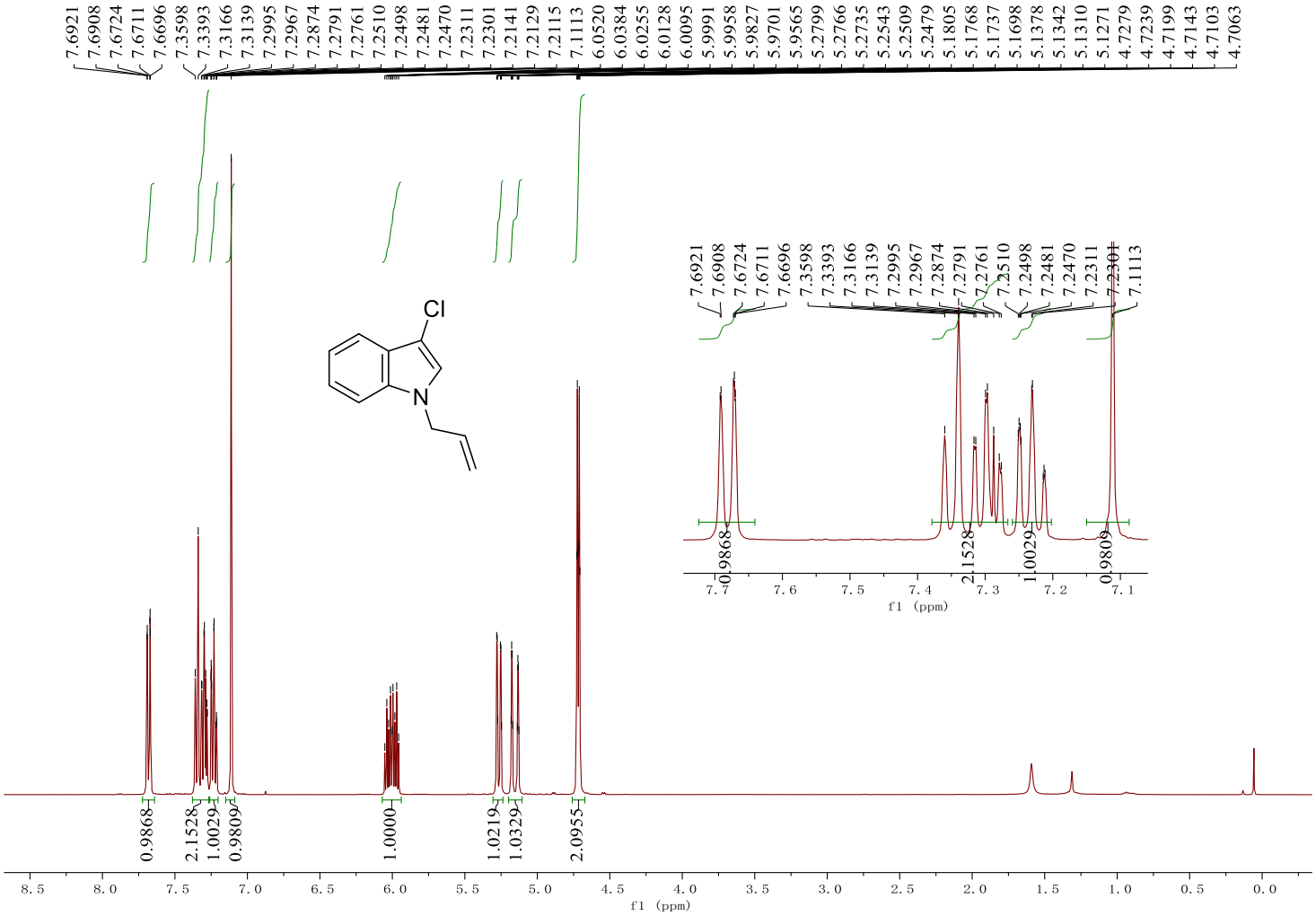


^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-allyl-3-chloro-1*H*-indole (2c)



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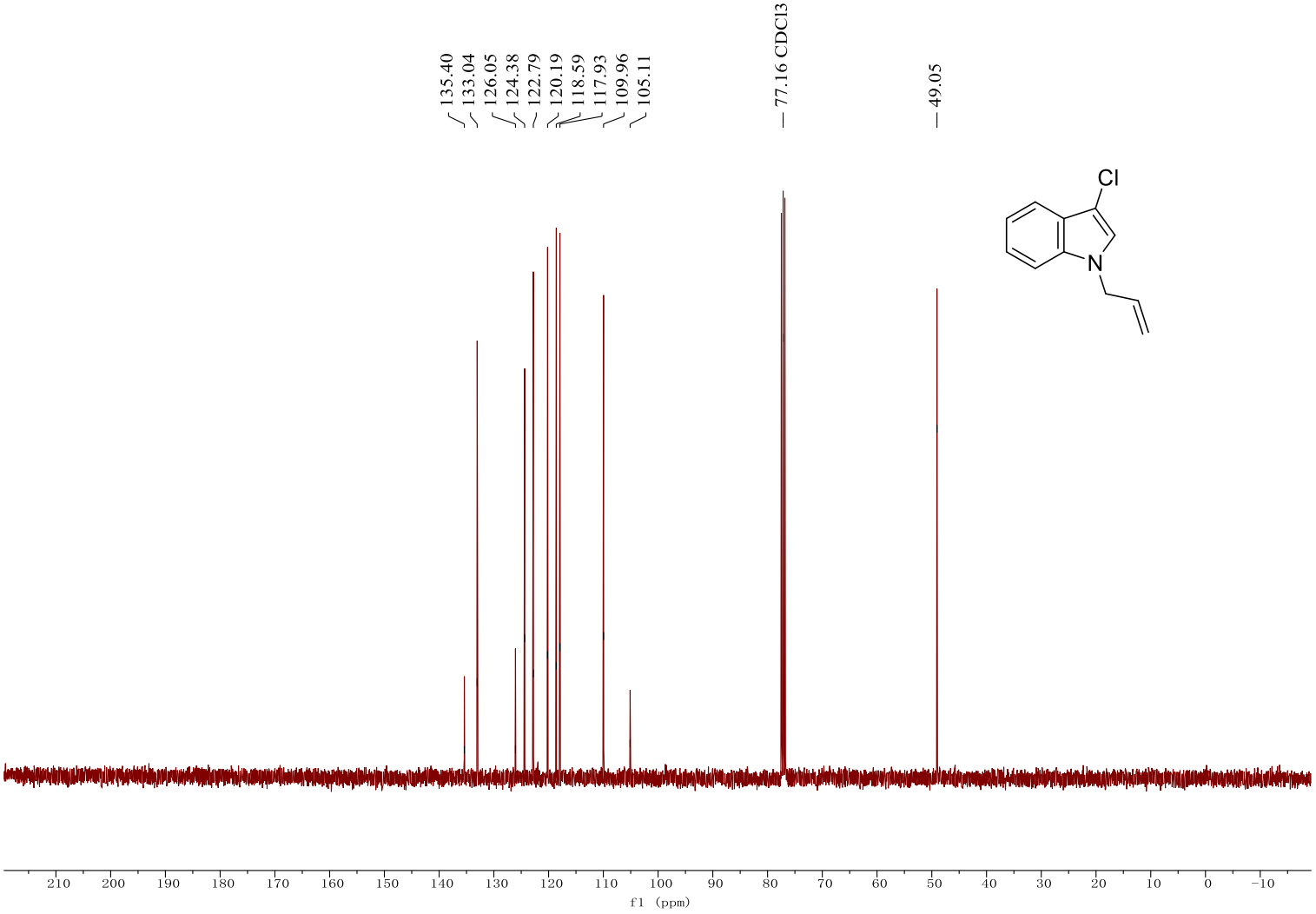

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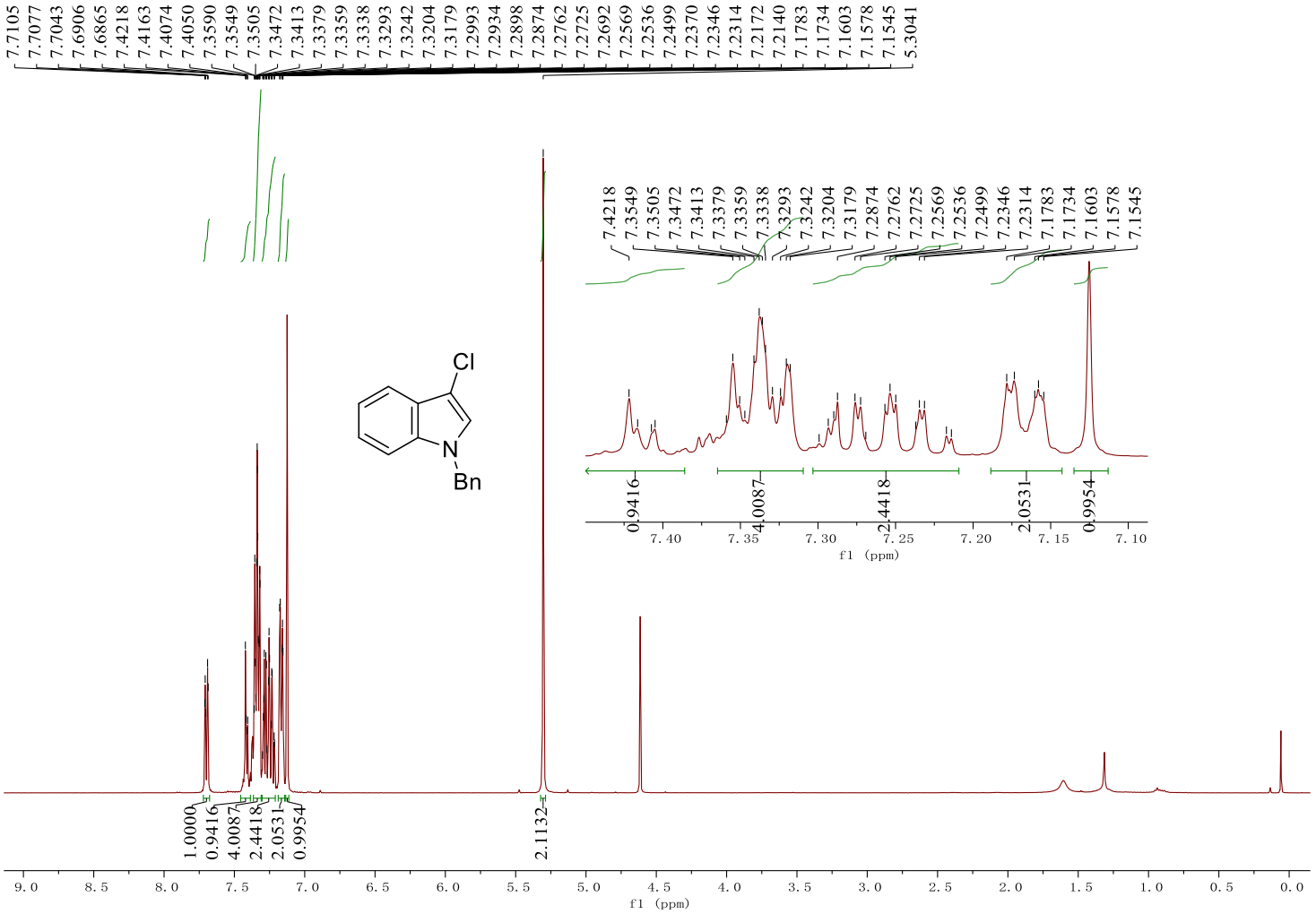

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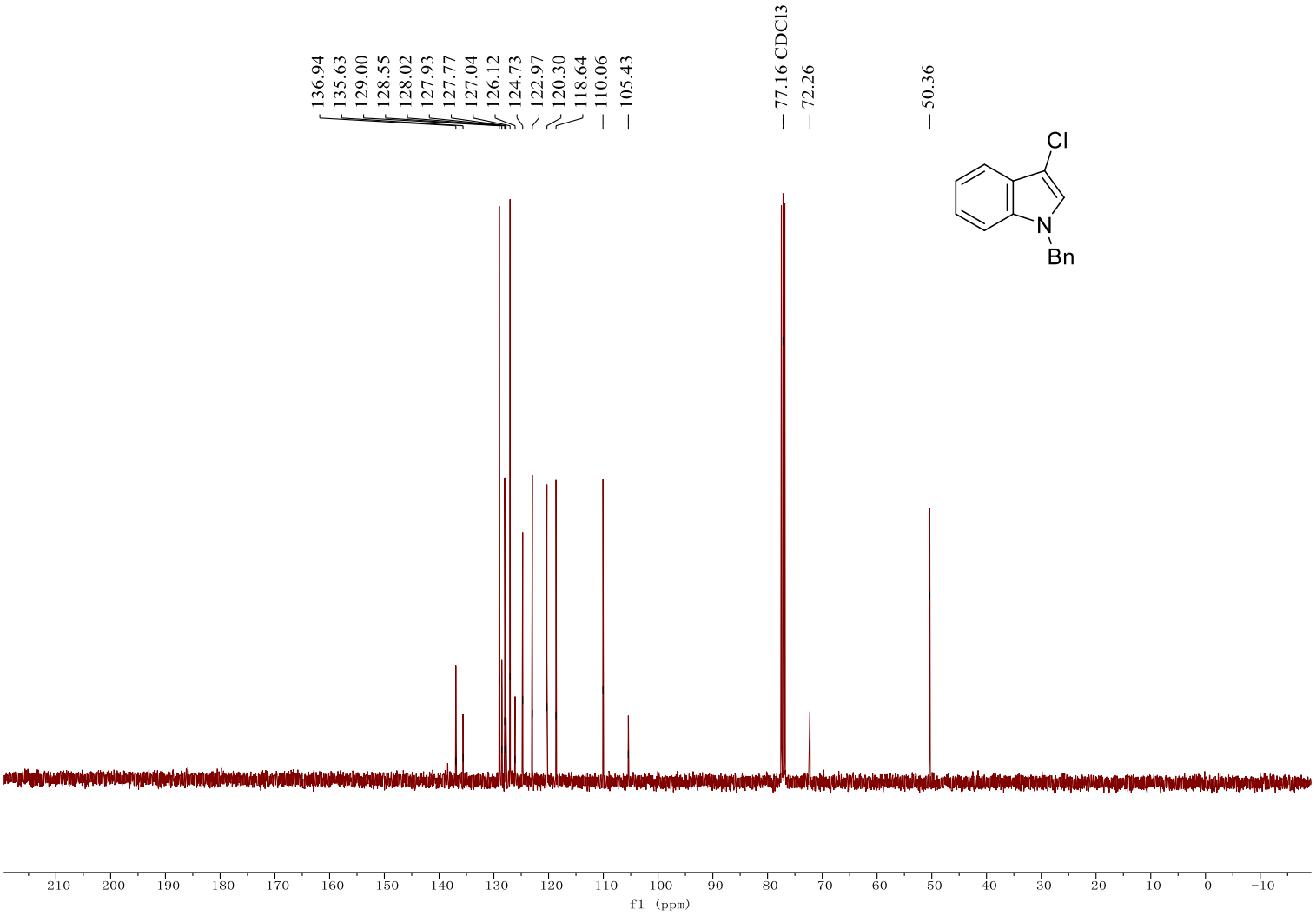

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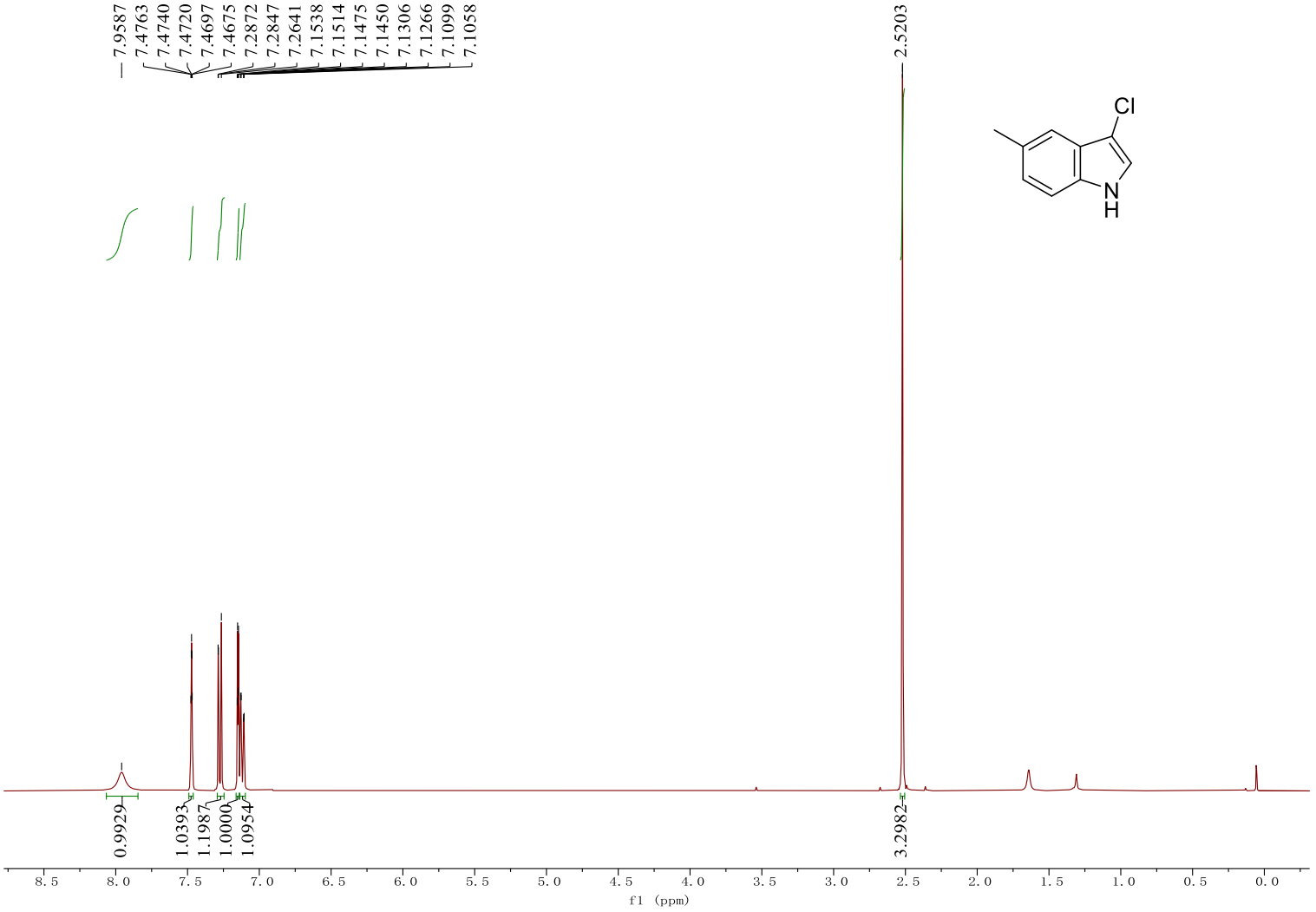

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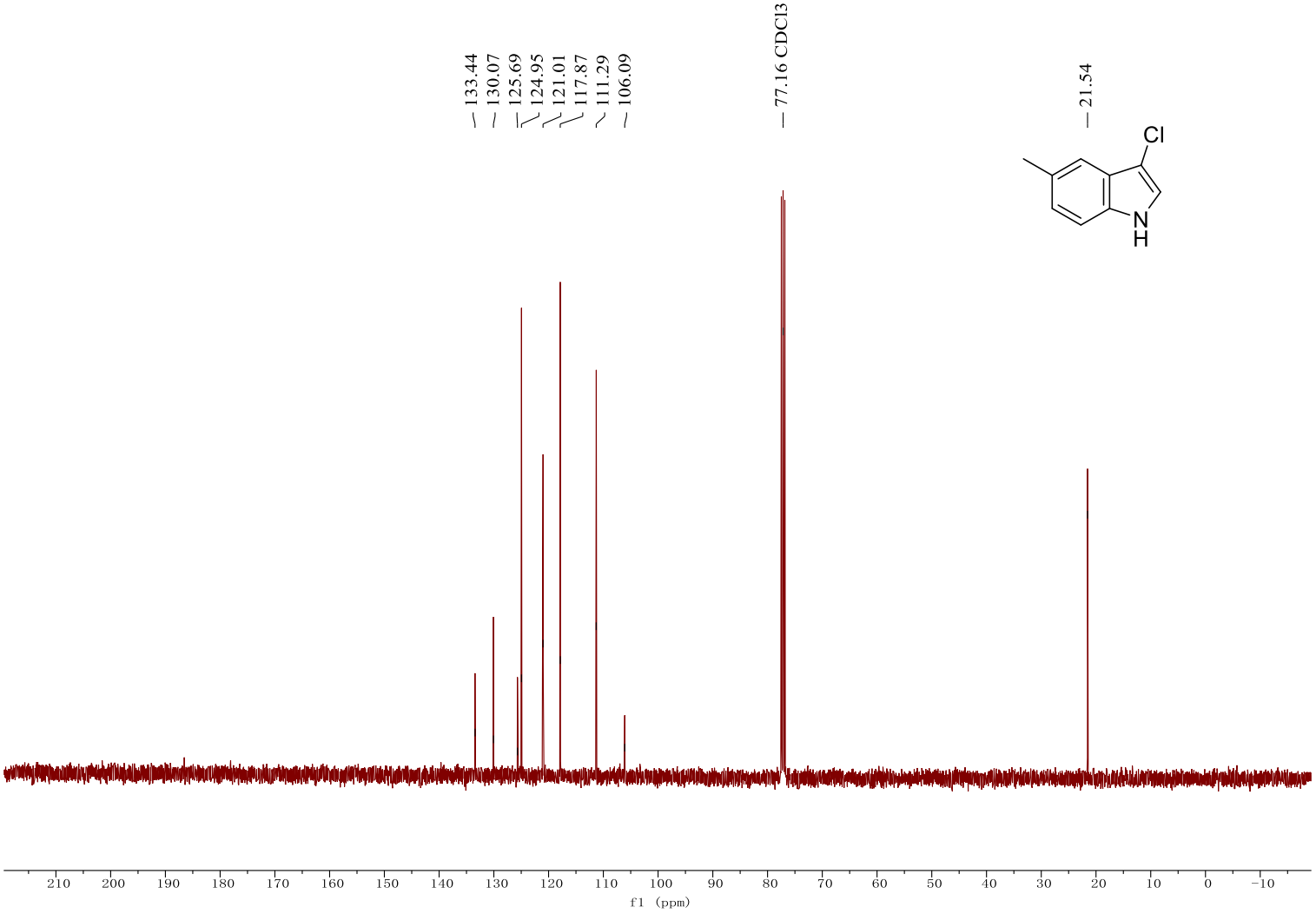

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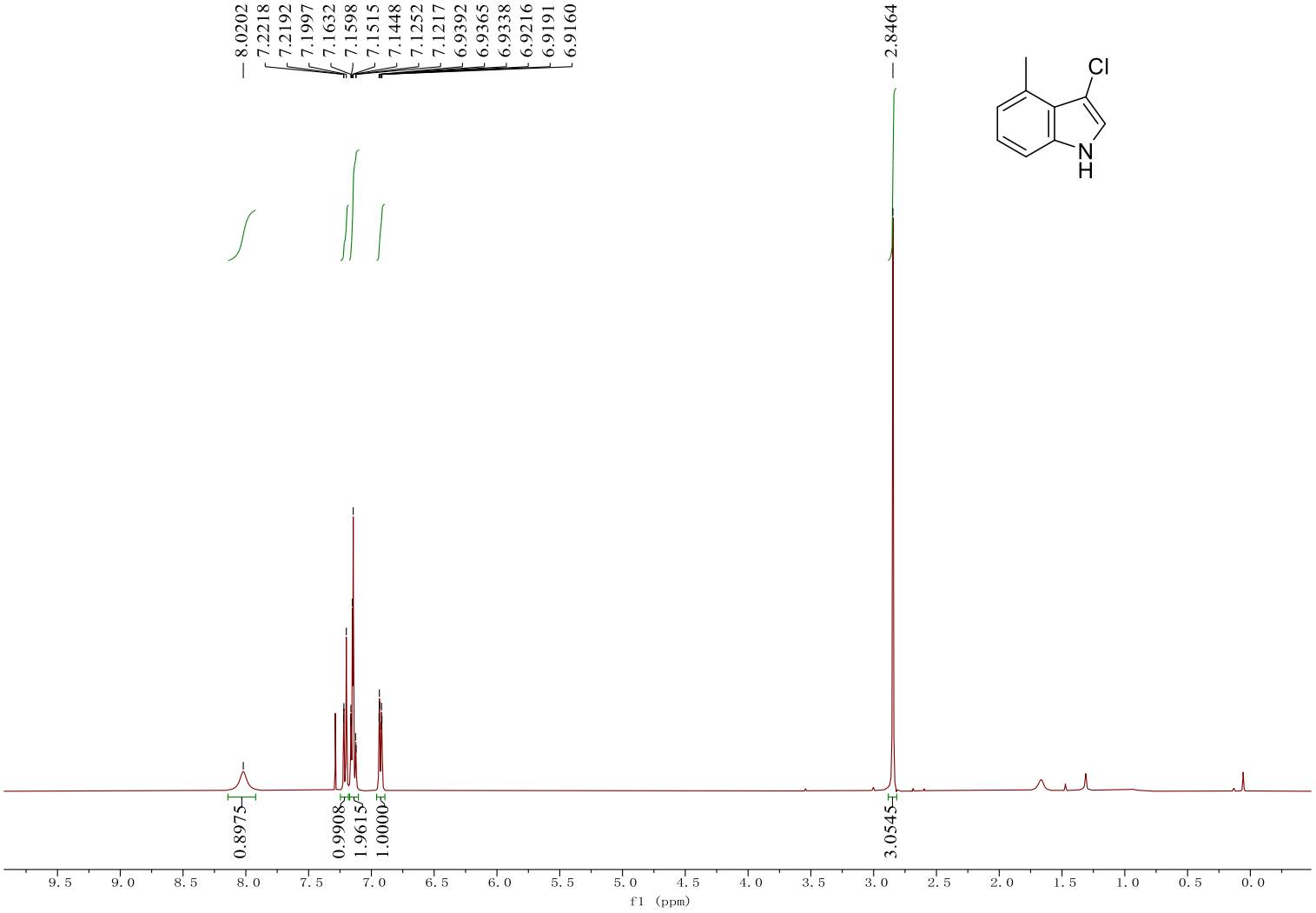

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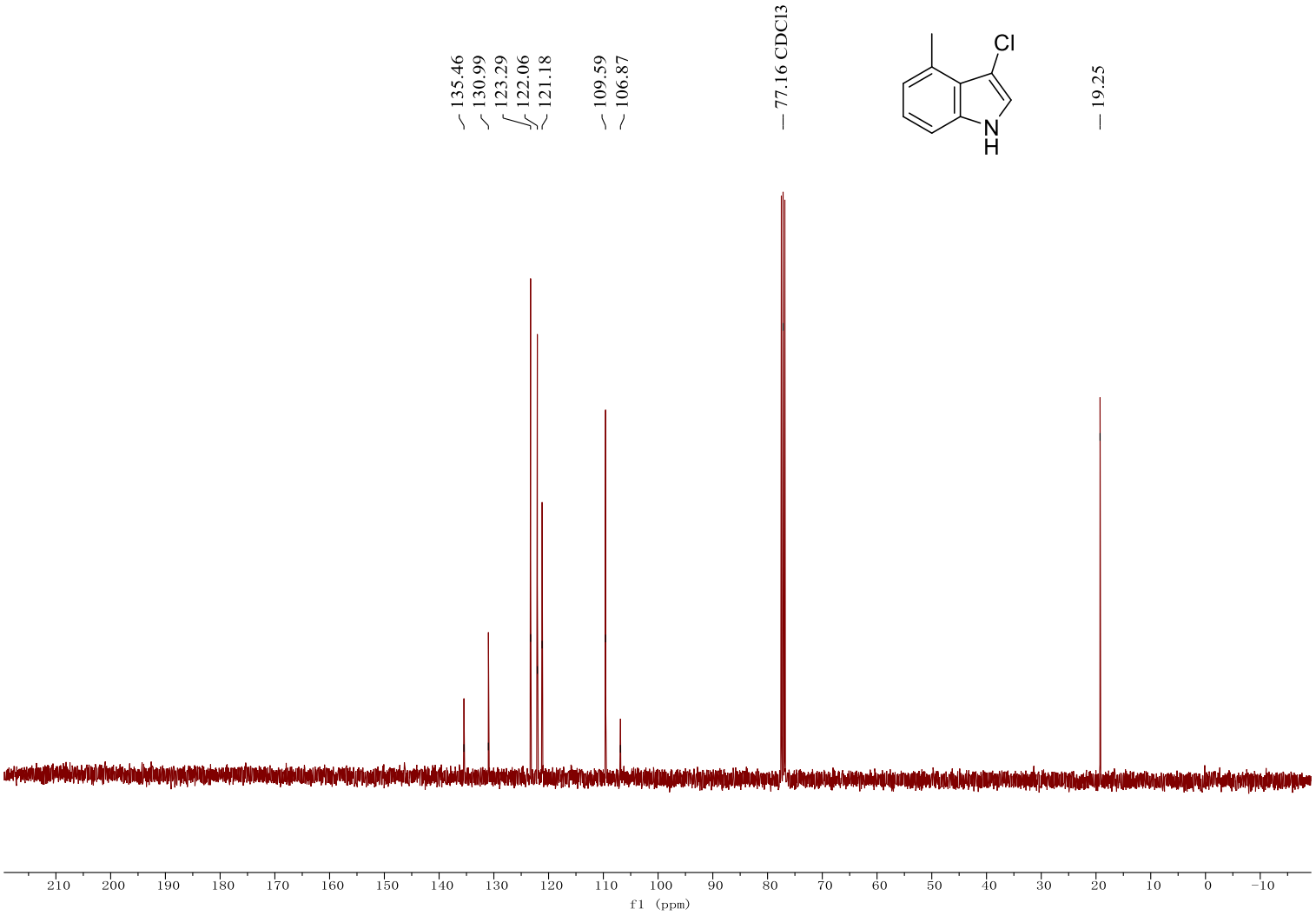

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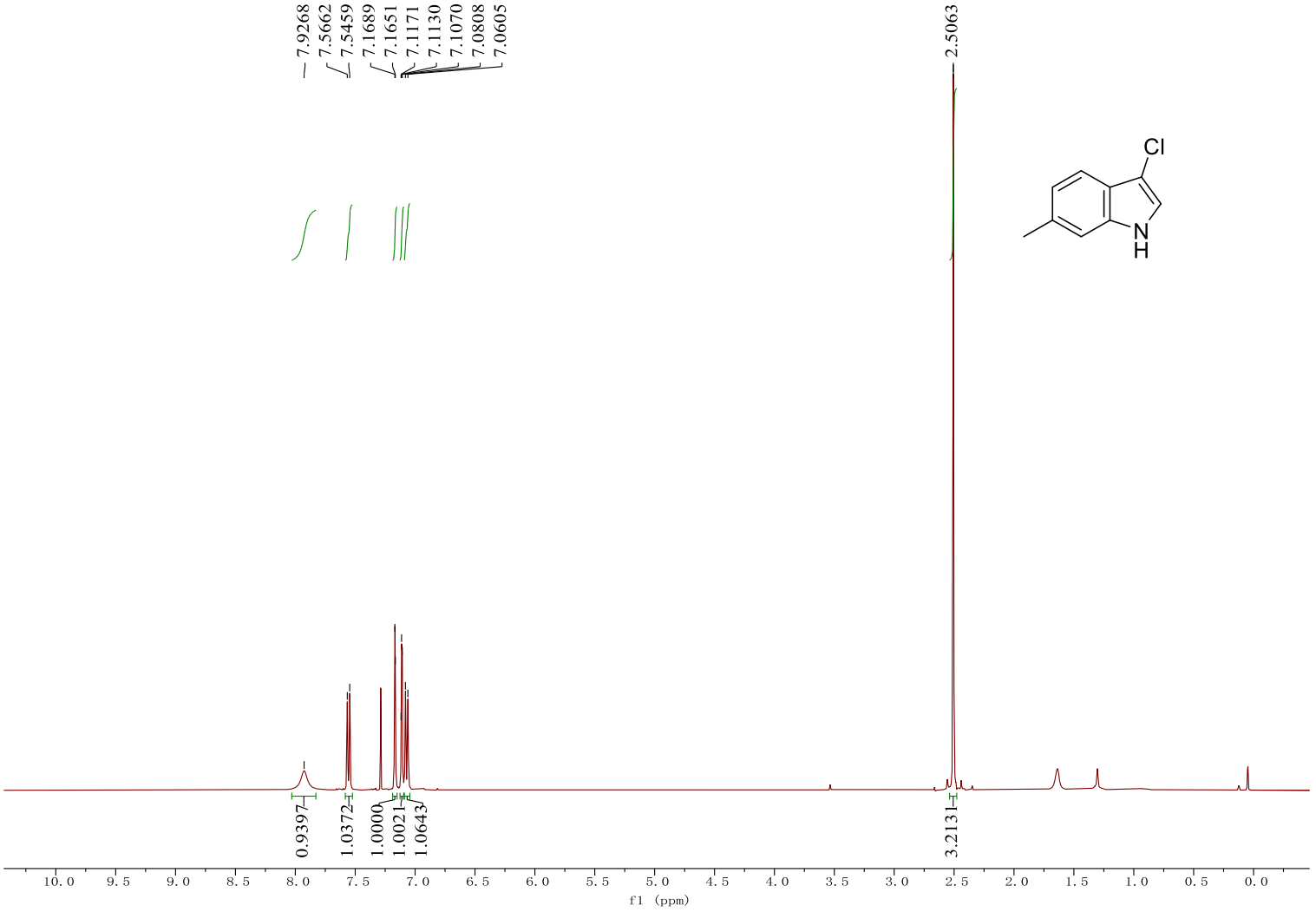

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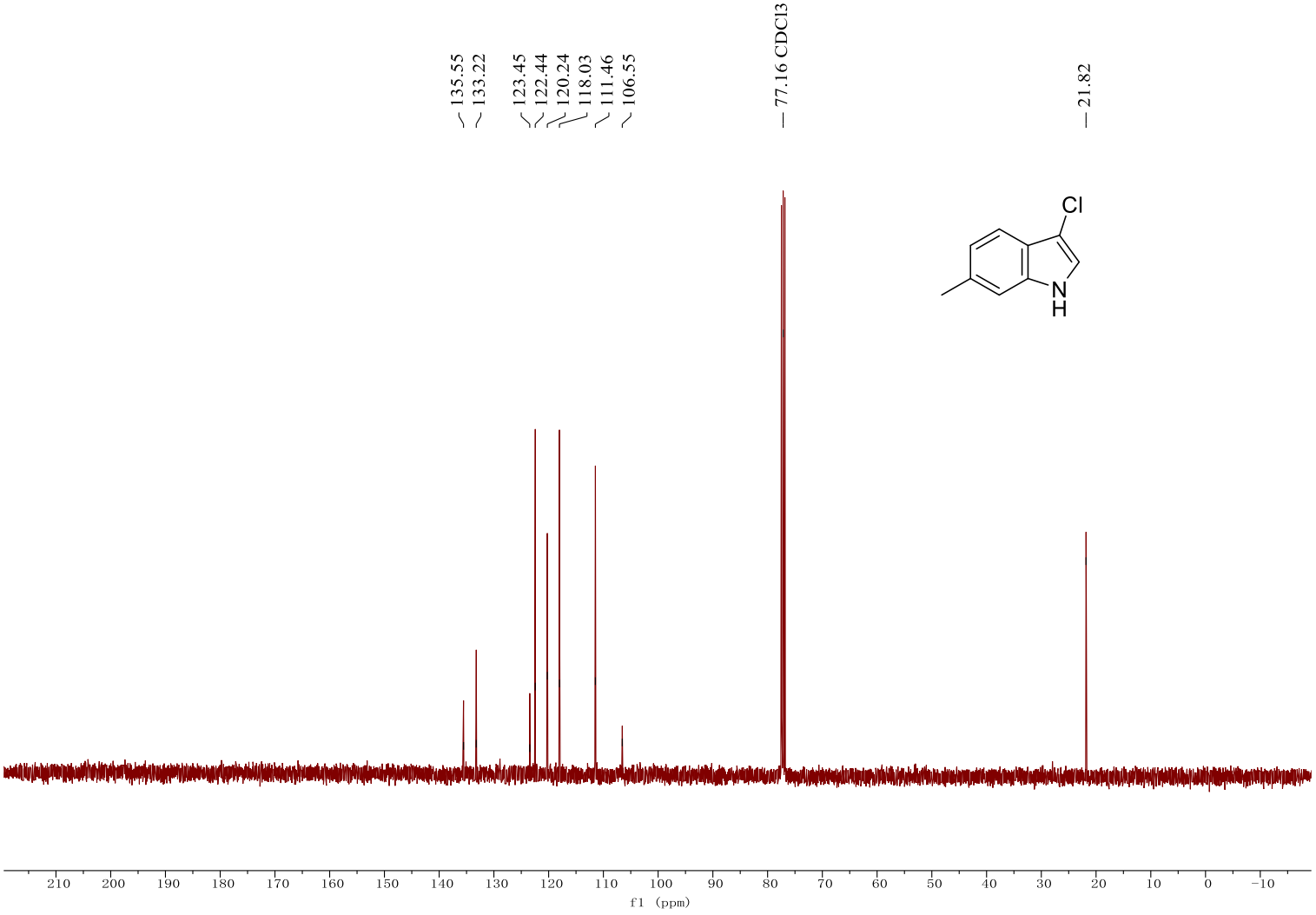

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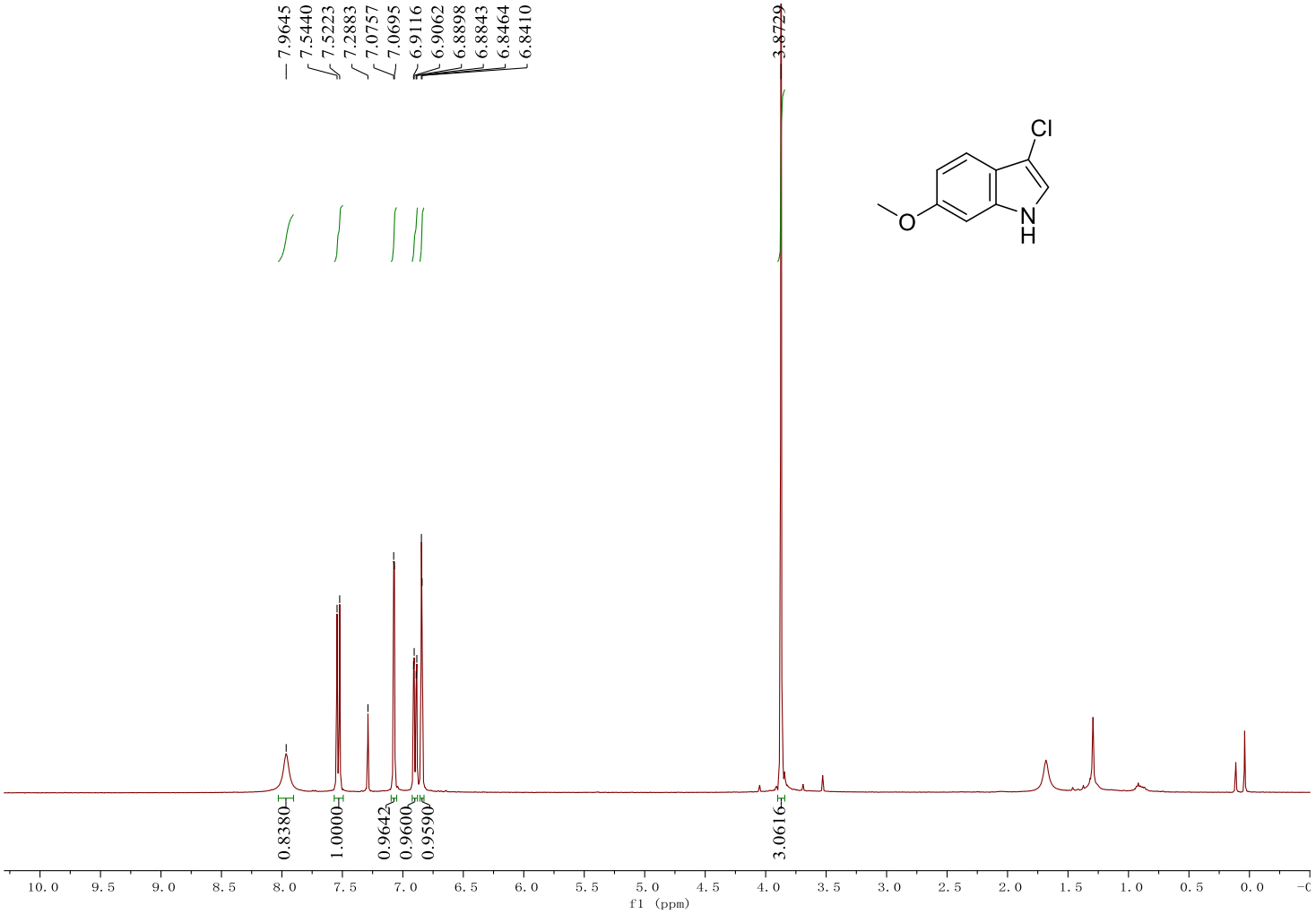

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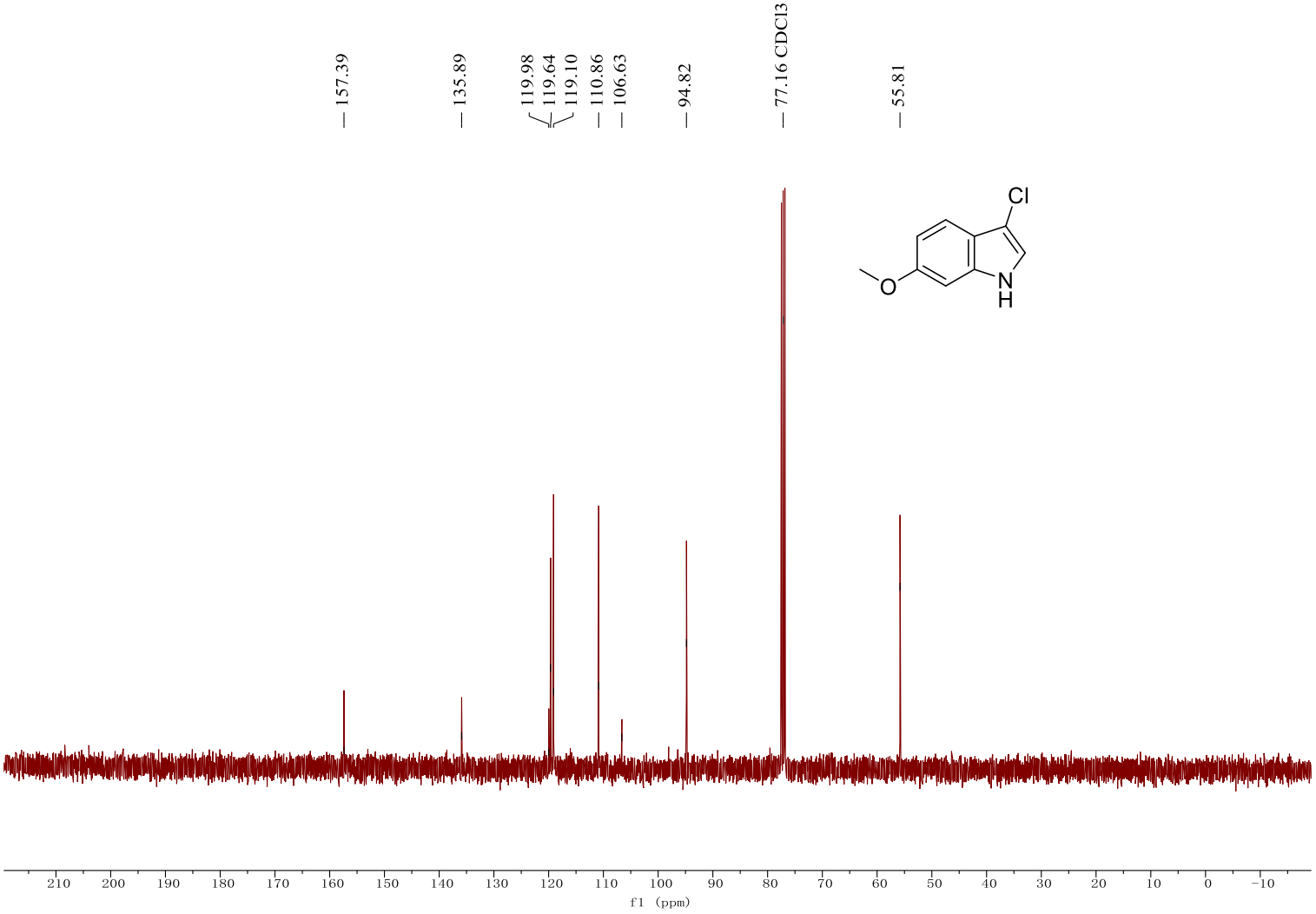

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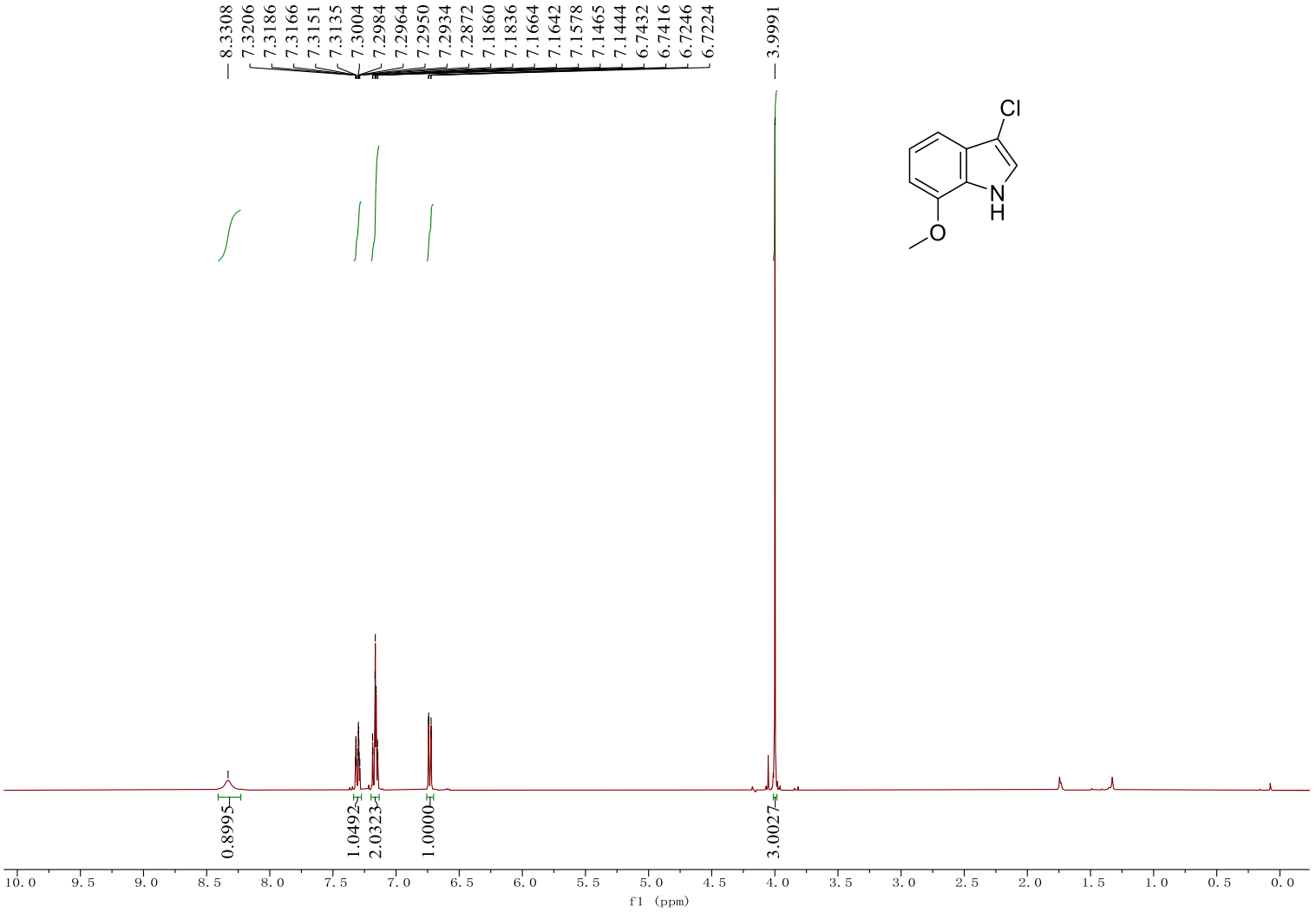

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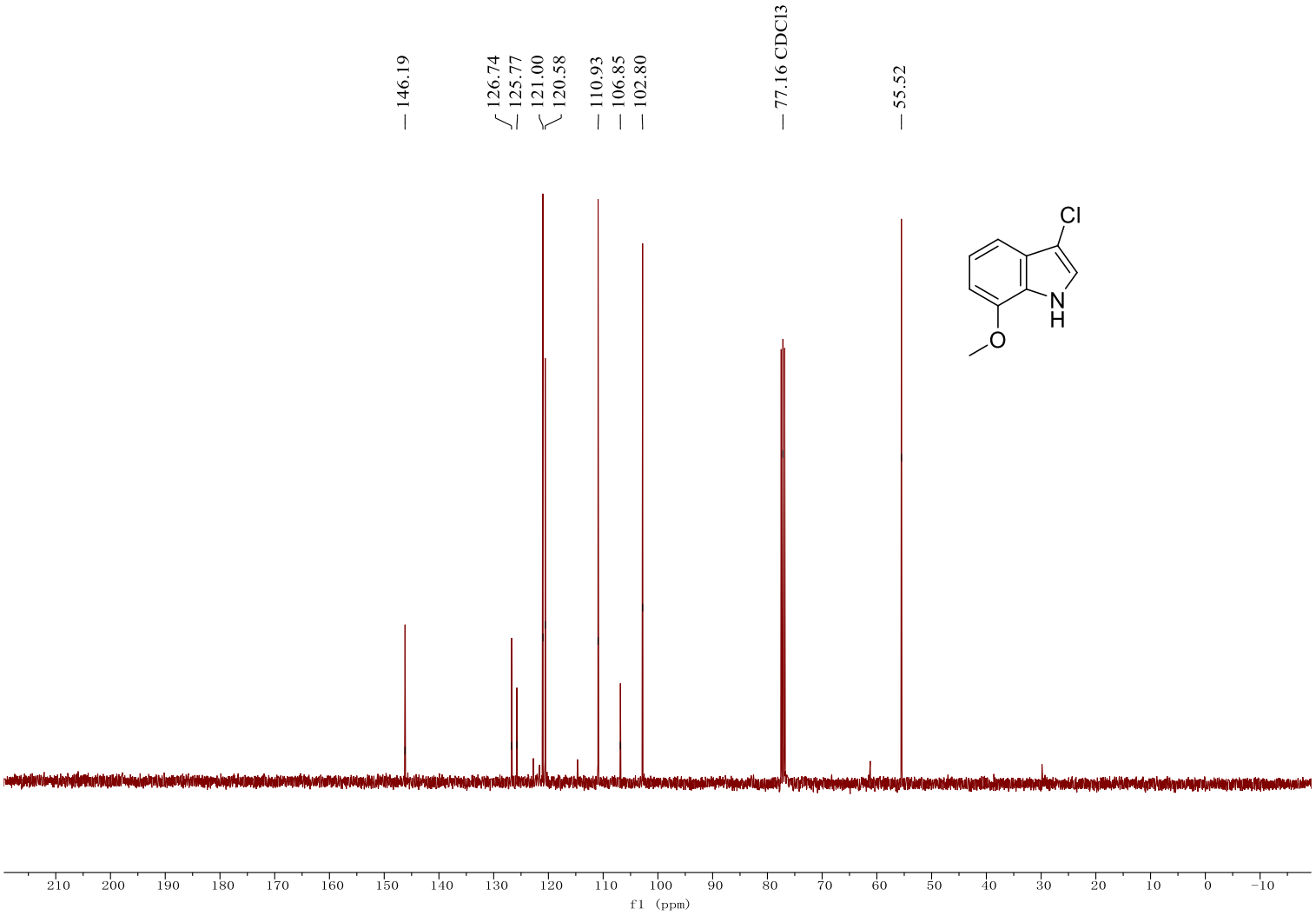
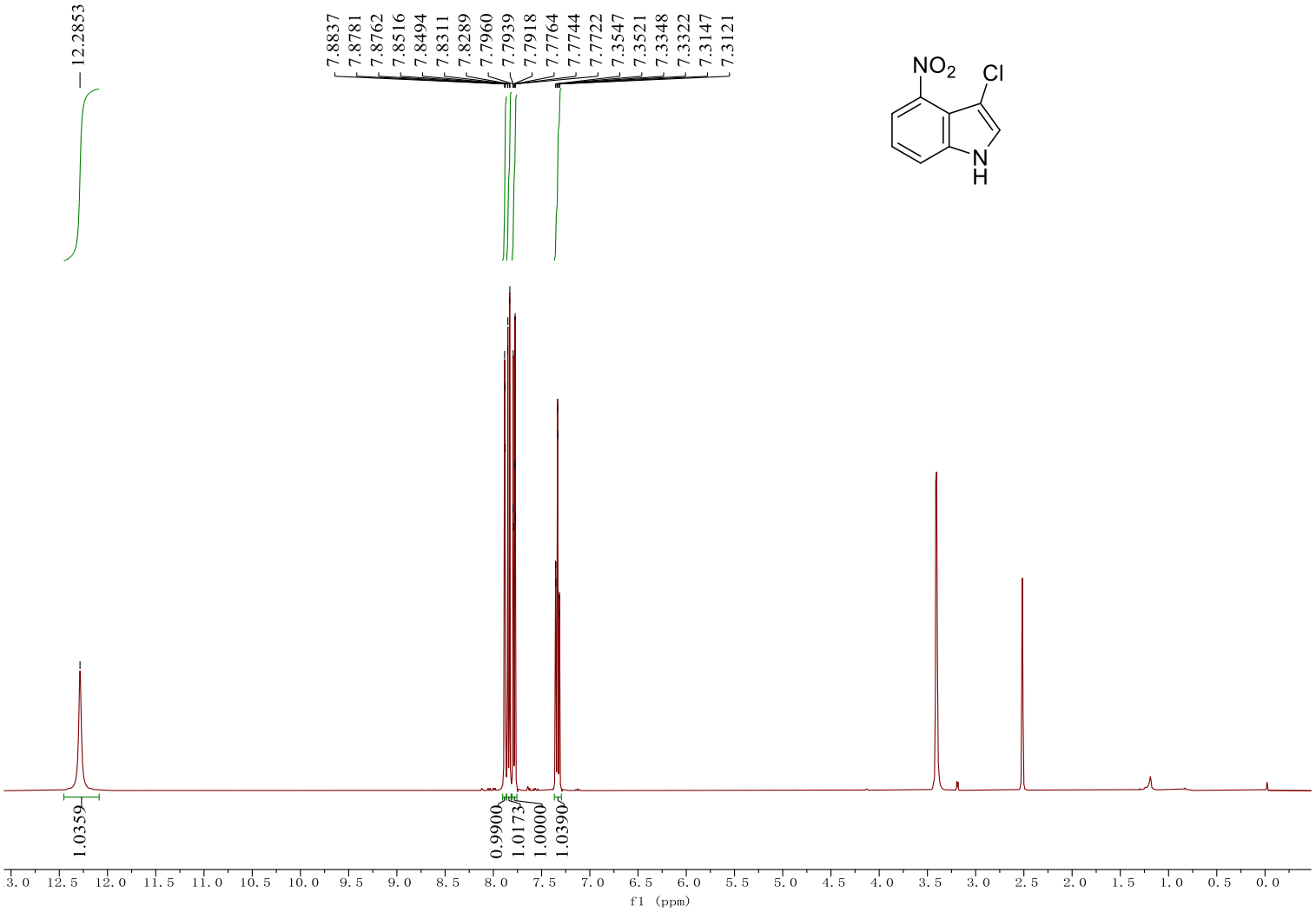


^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-4-nitro-1*H*-indole (2j)



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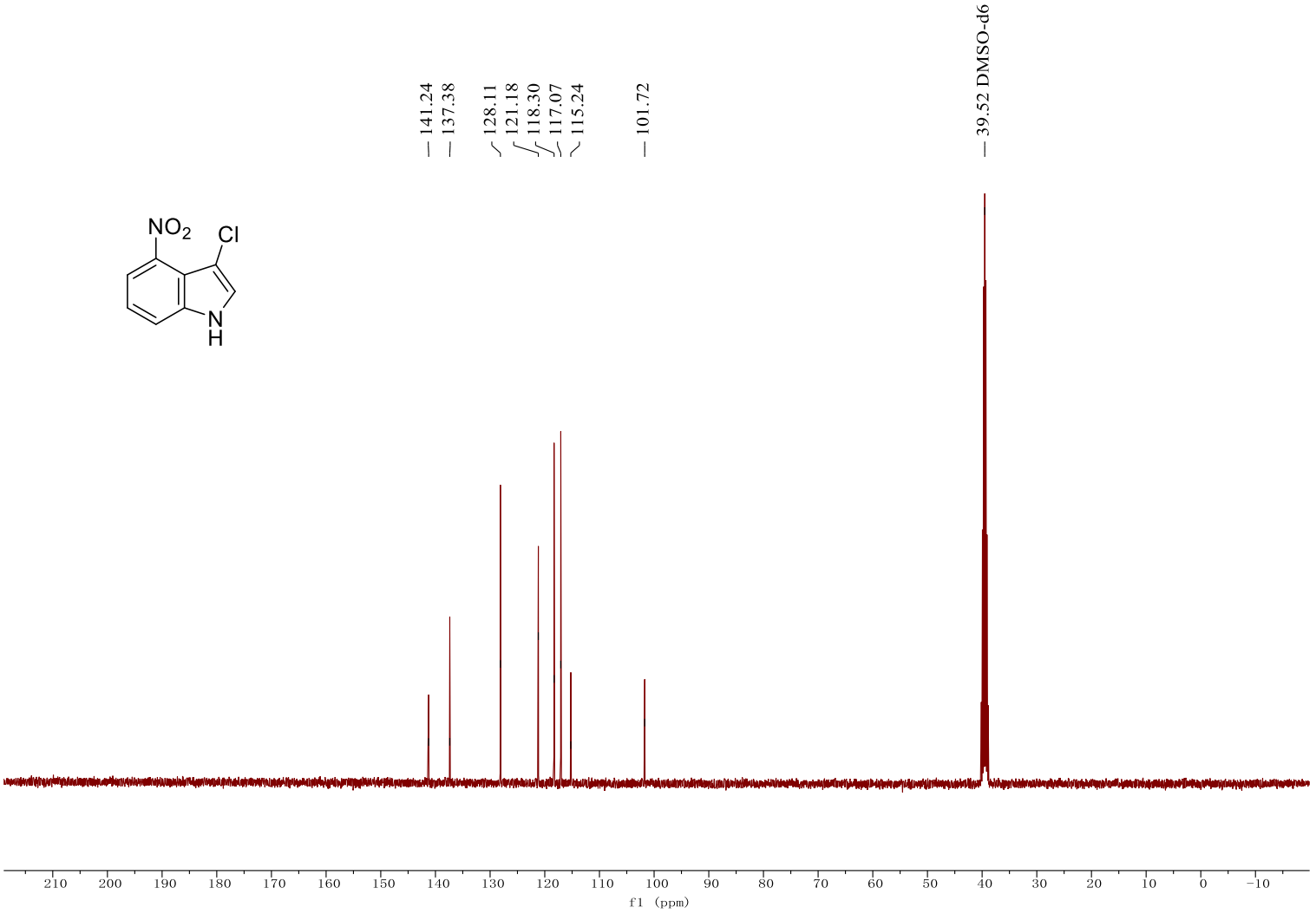

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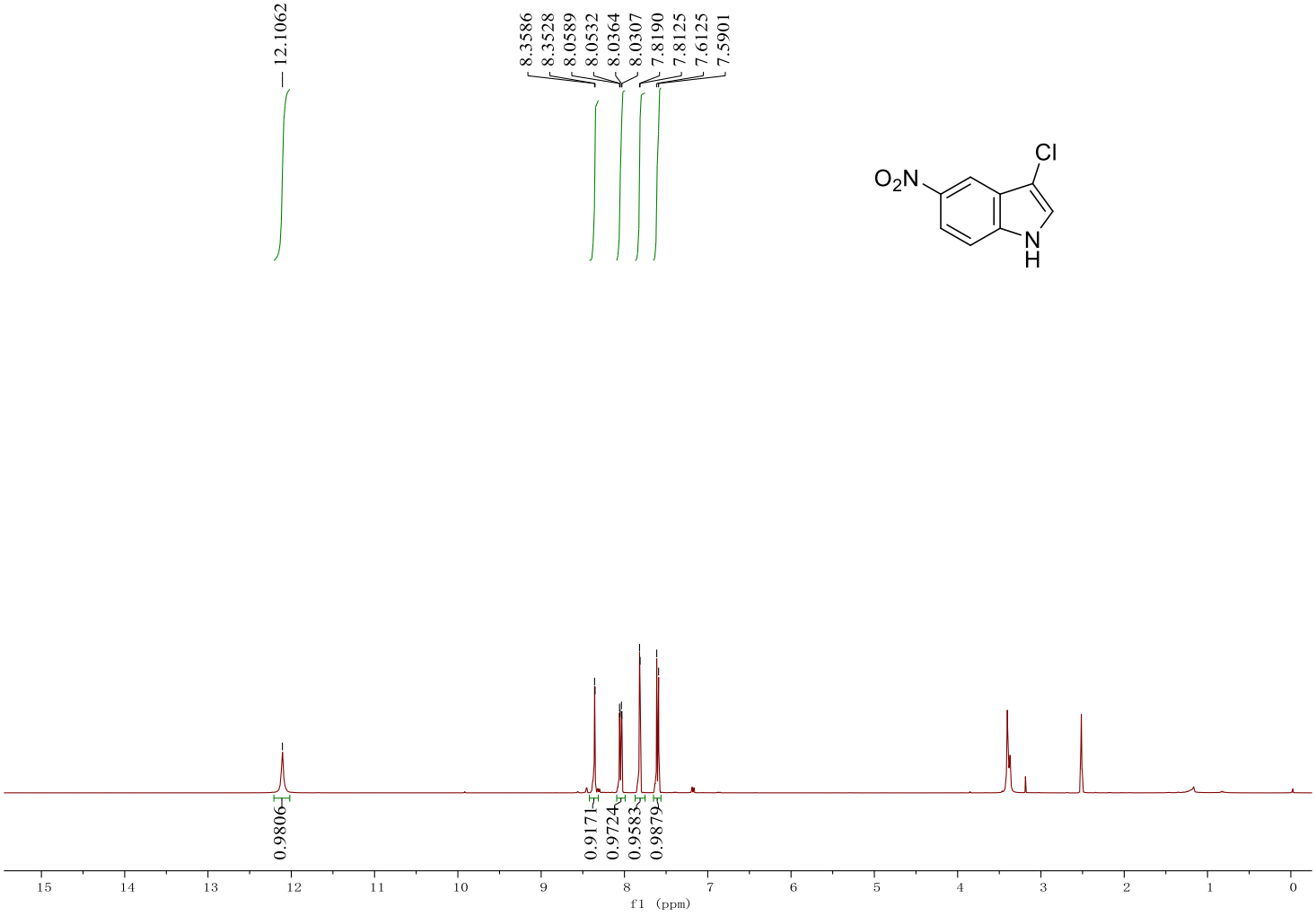

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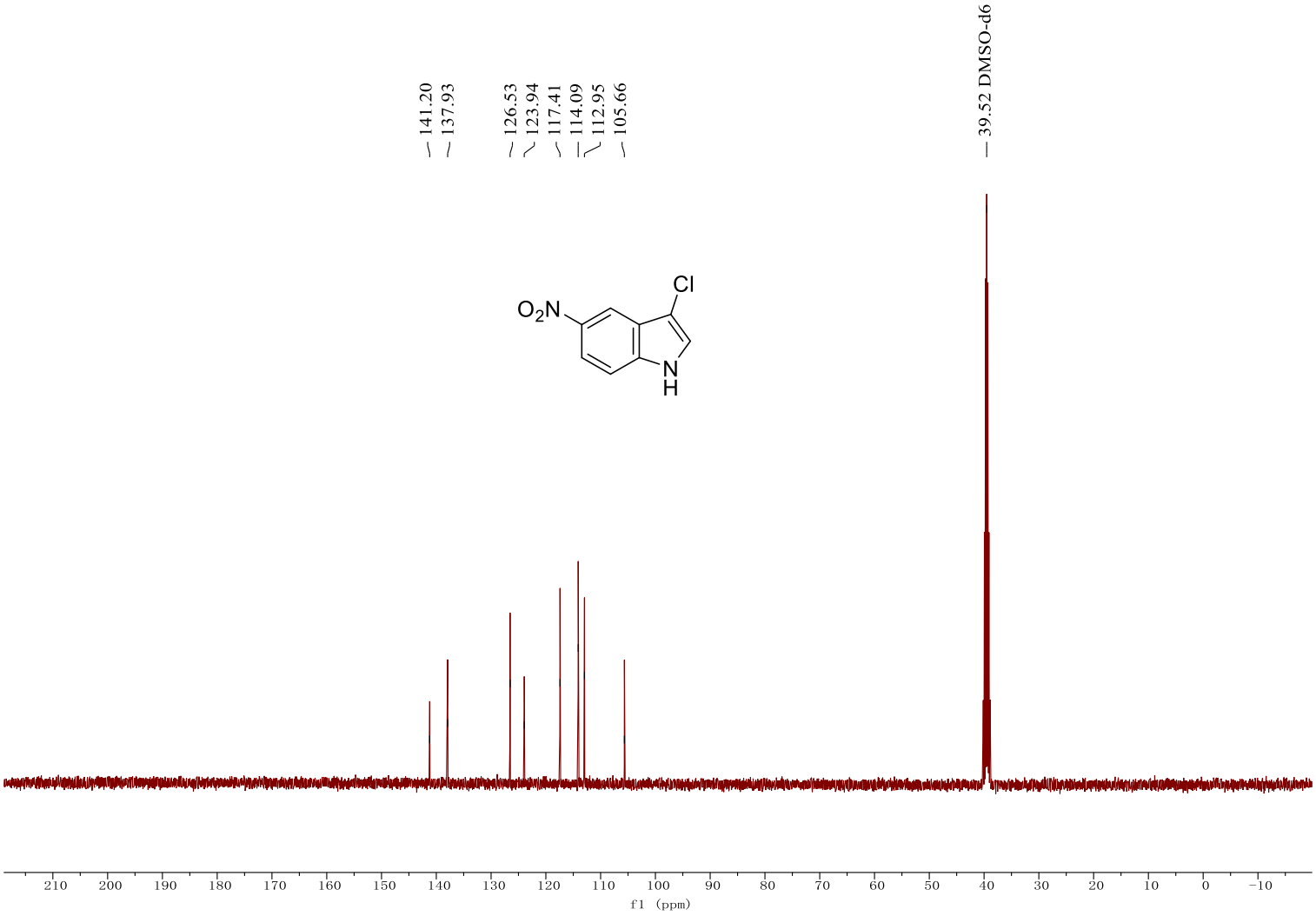

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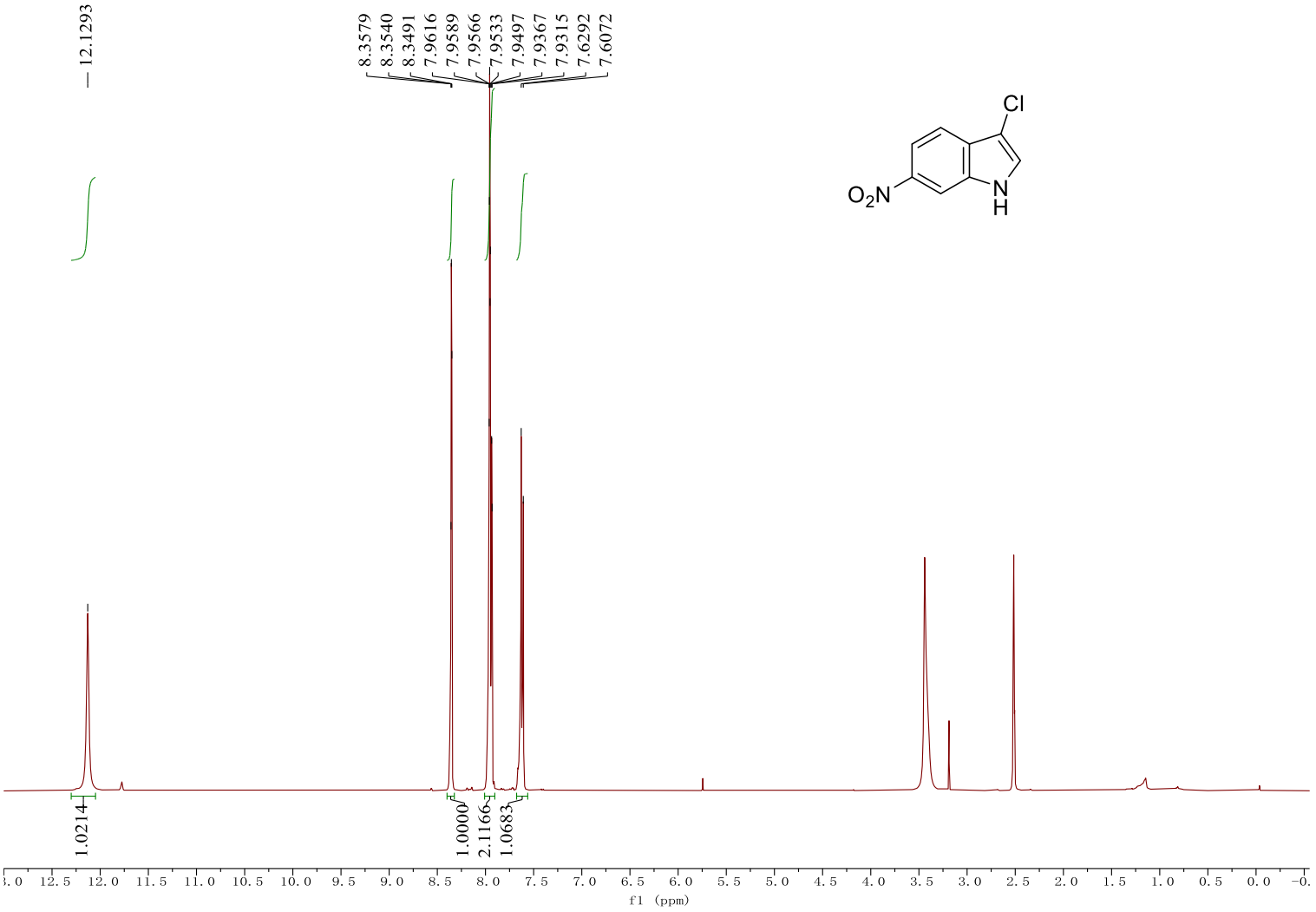

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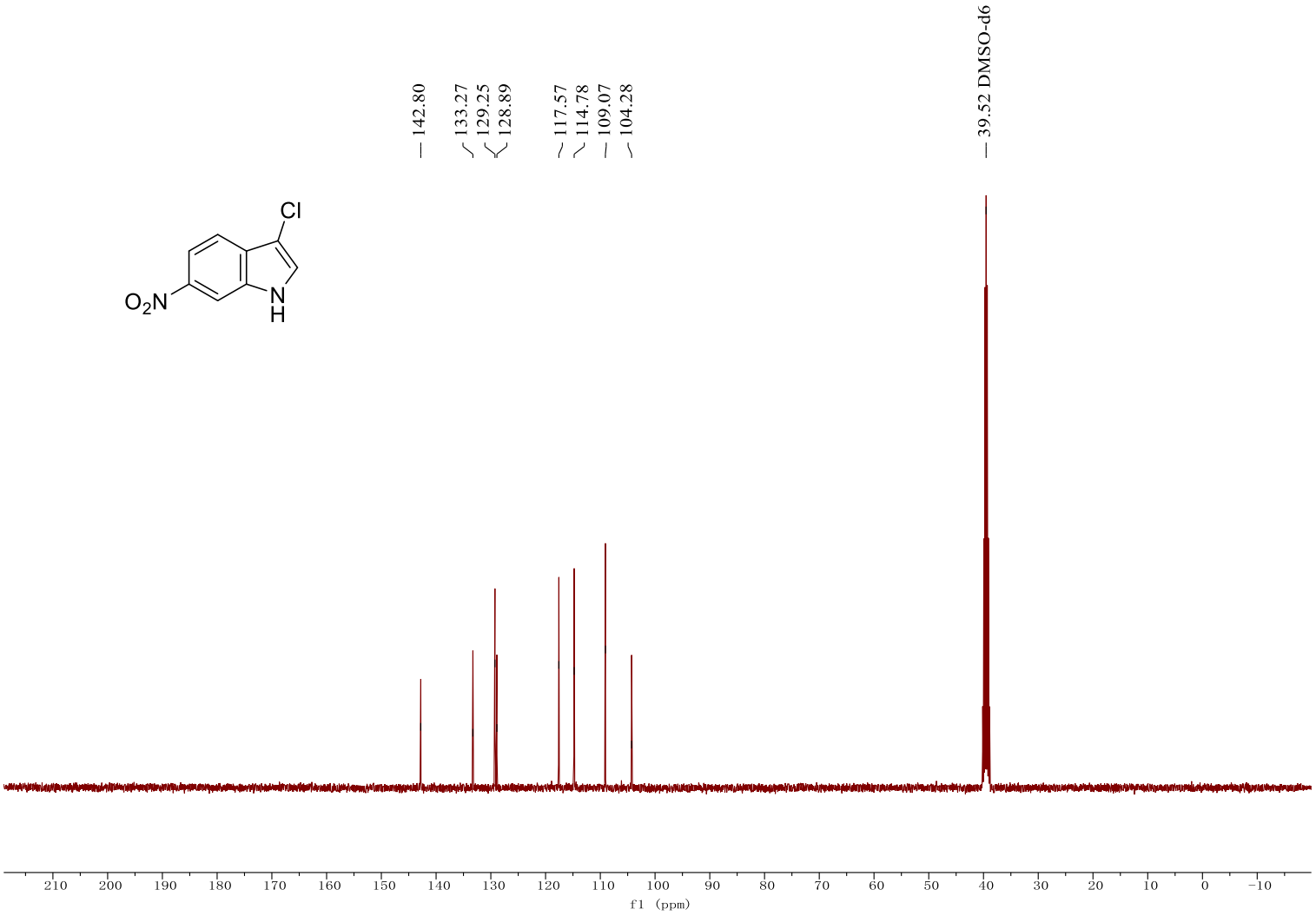
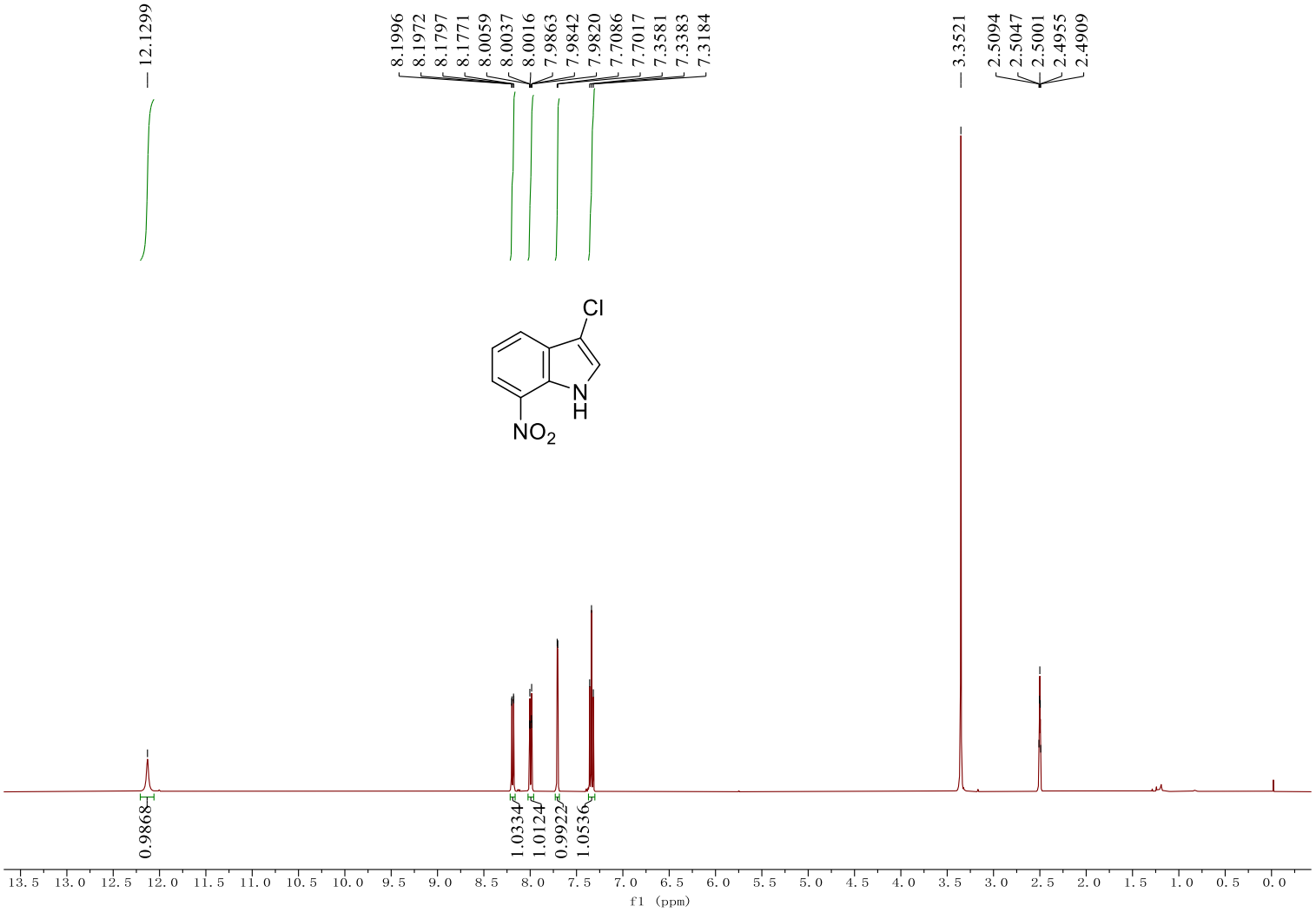
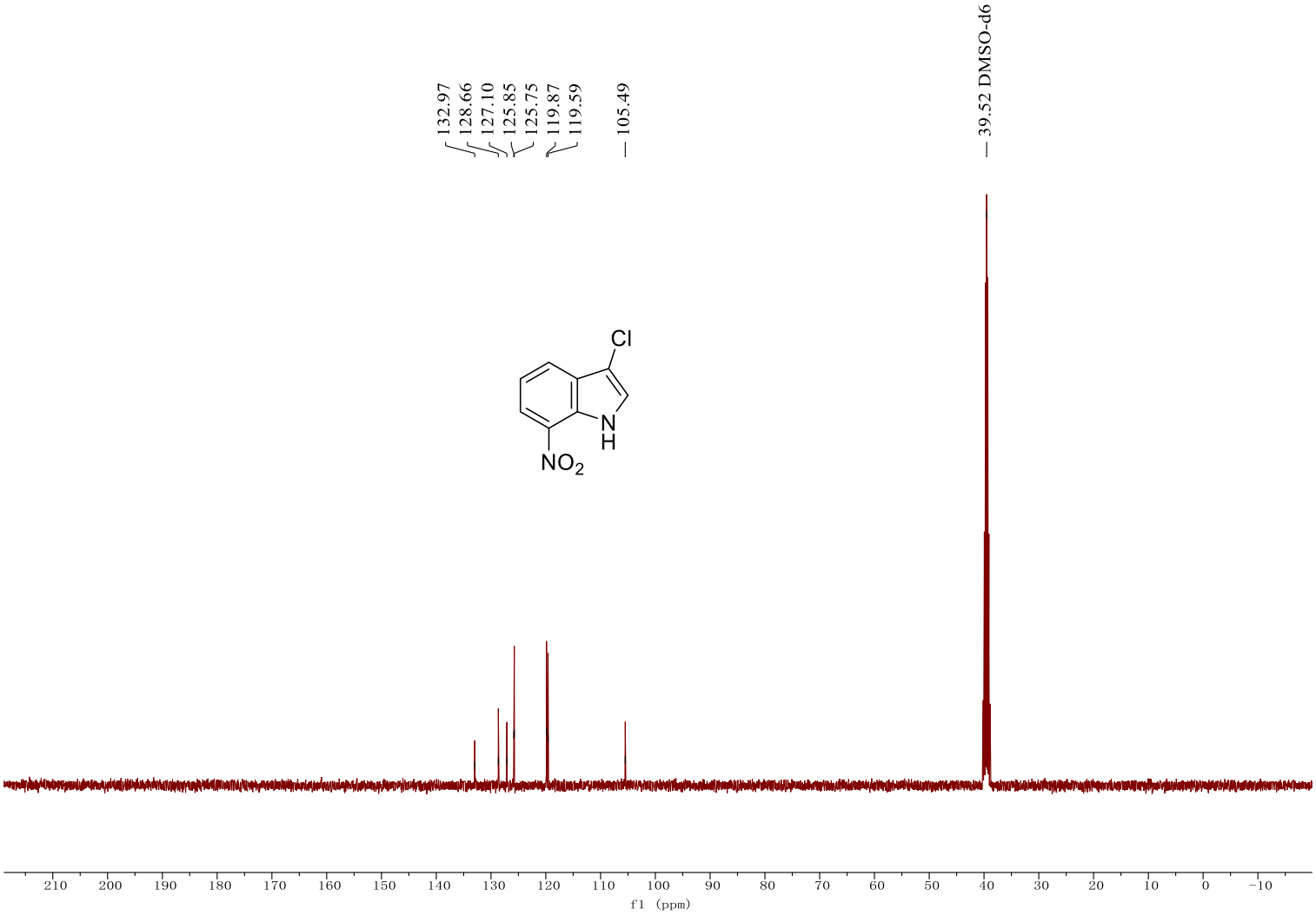


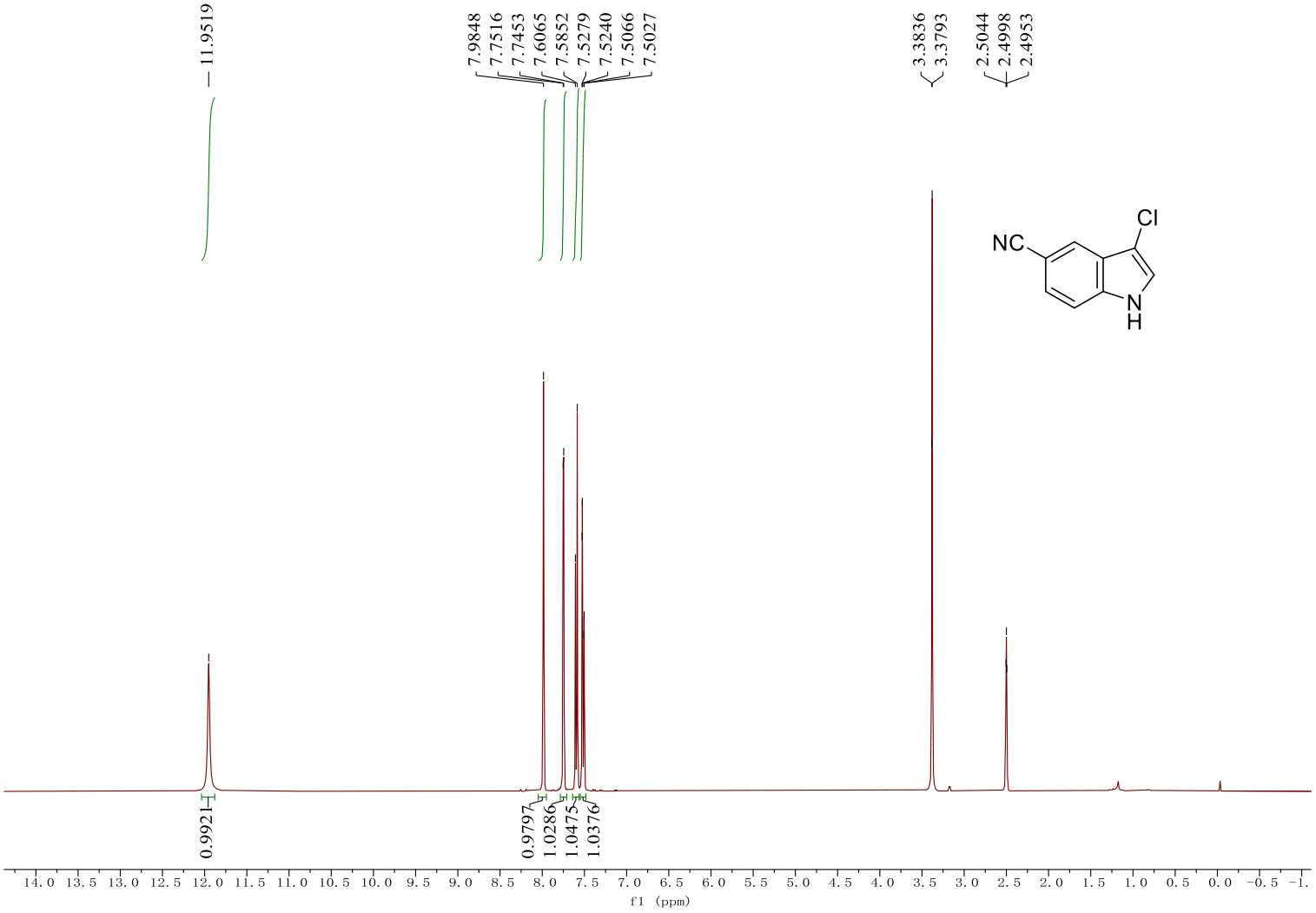
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-7-nitro-1*H*-indole (2m)



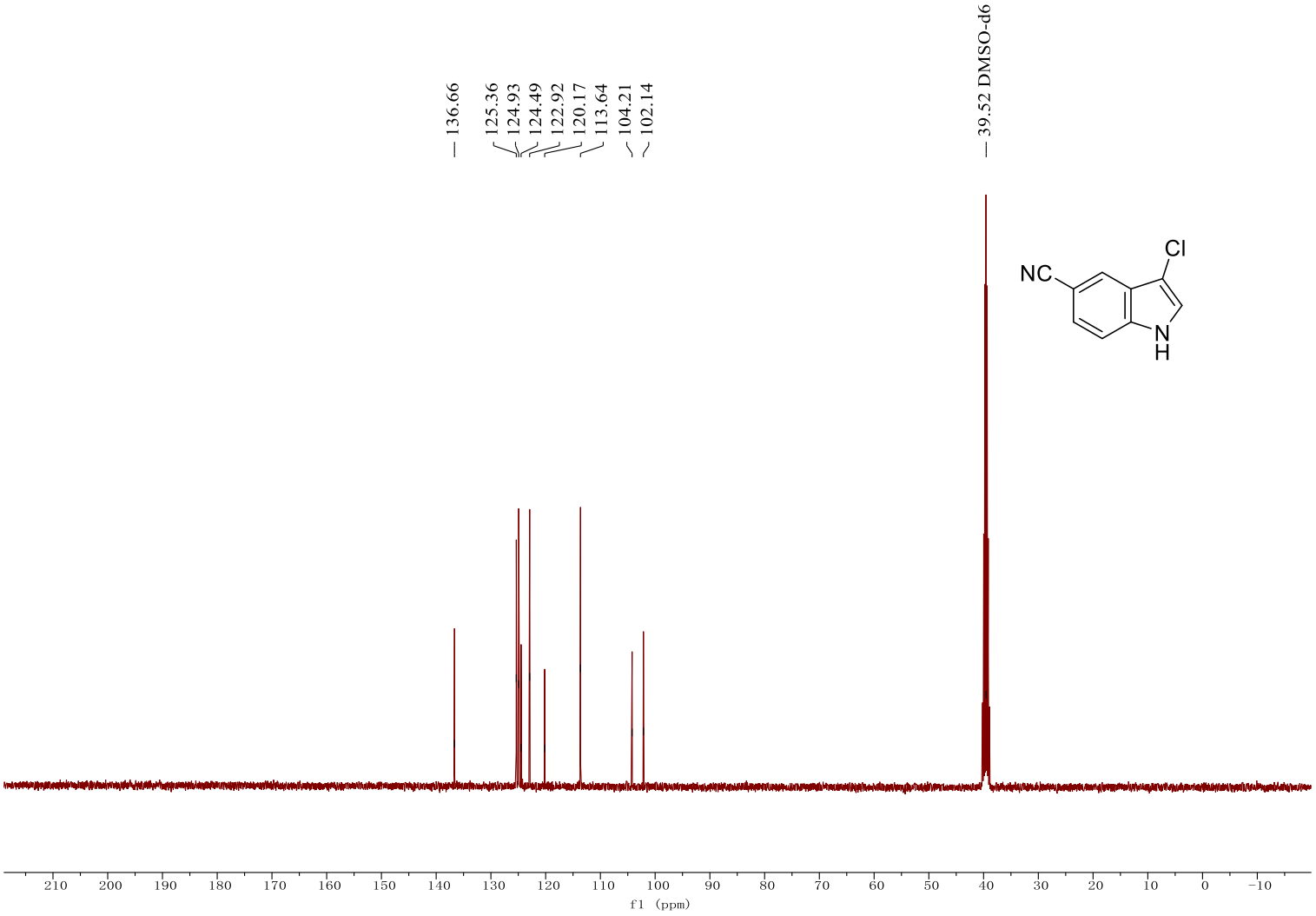
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-7-nitro-1*H*-indole (2m)



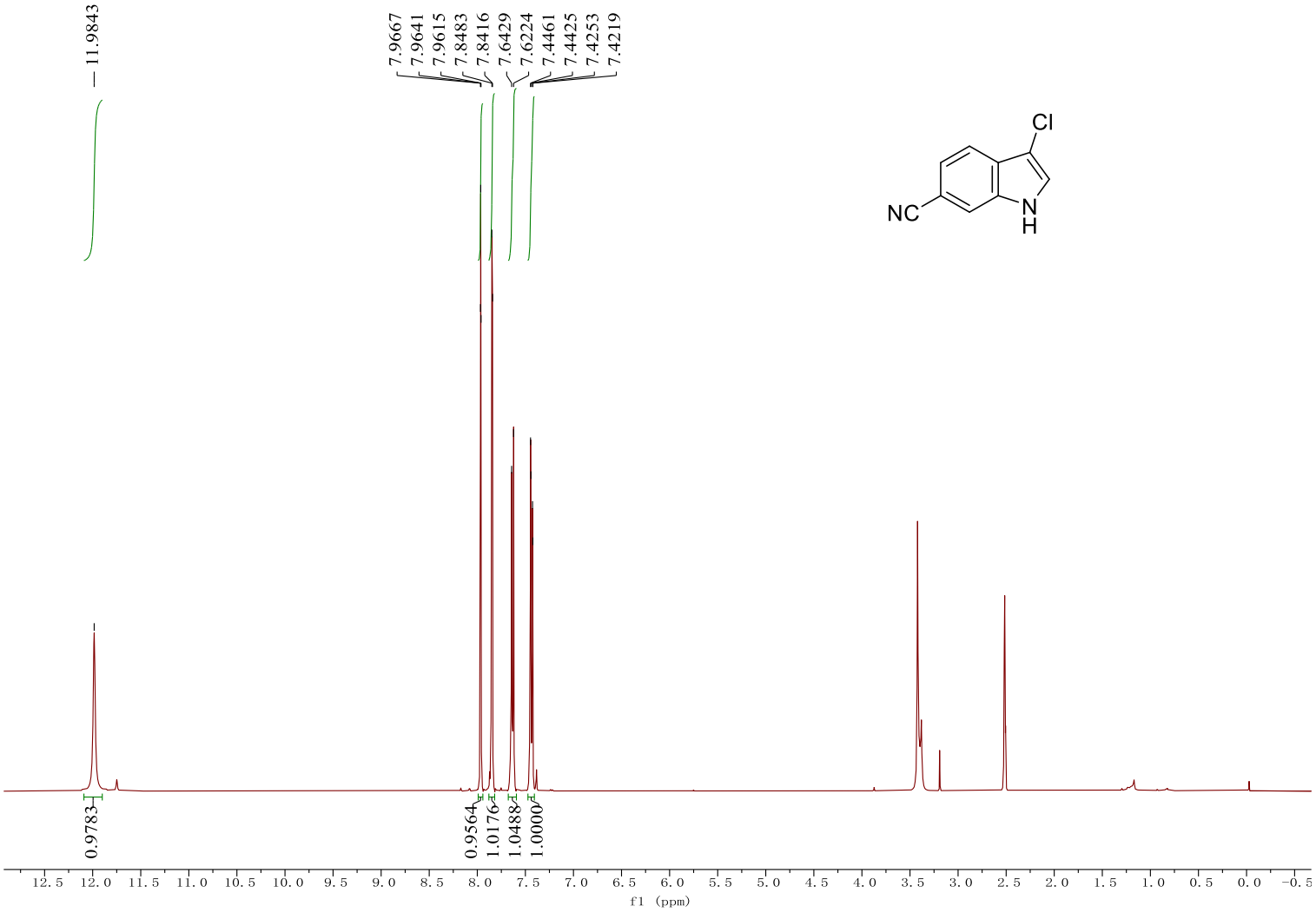
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-5-carbonitrile (2n)



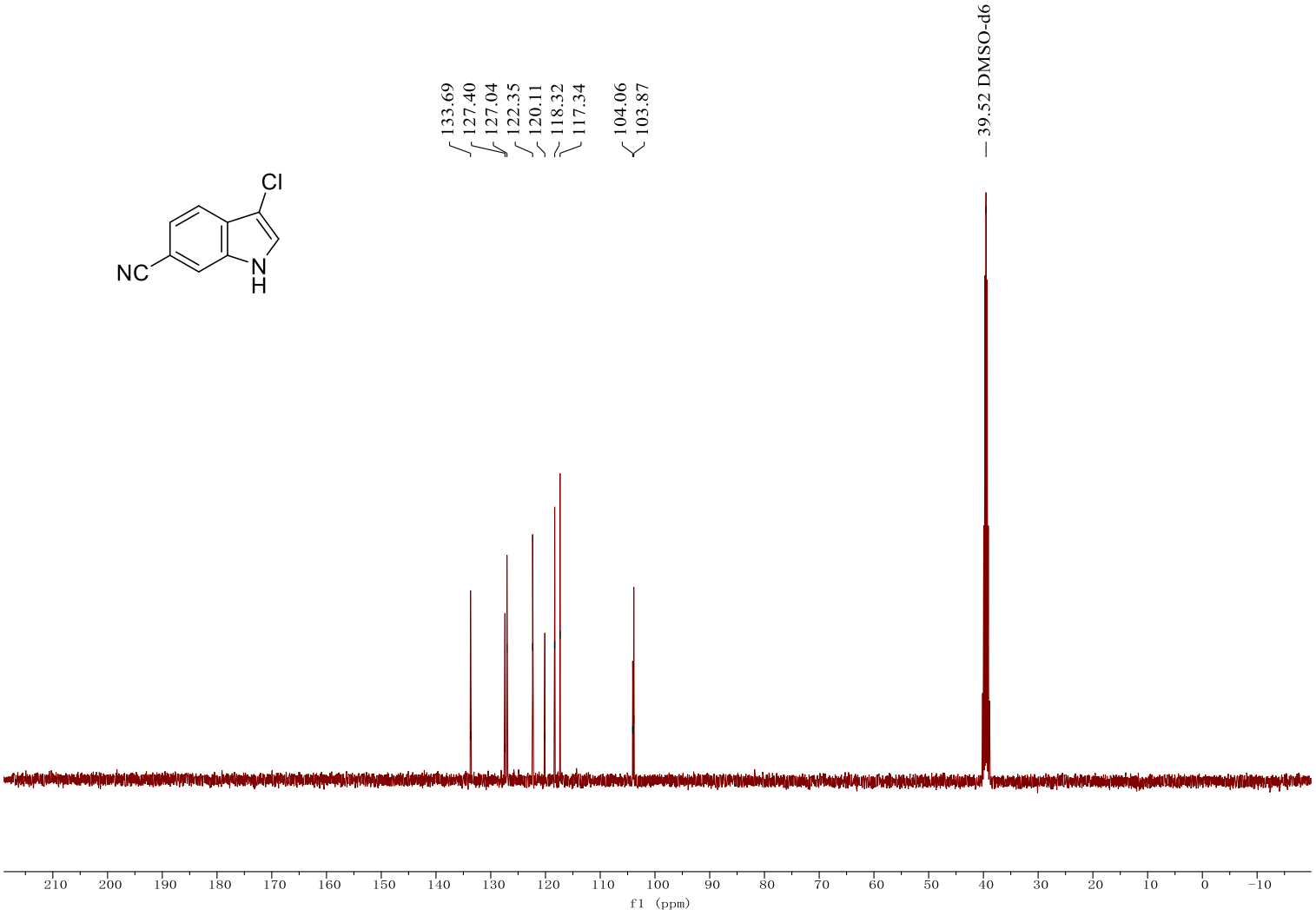
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-5-carbonitrile (2n)



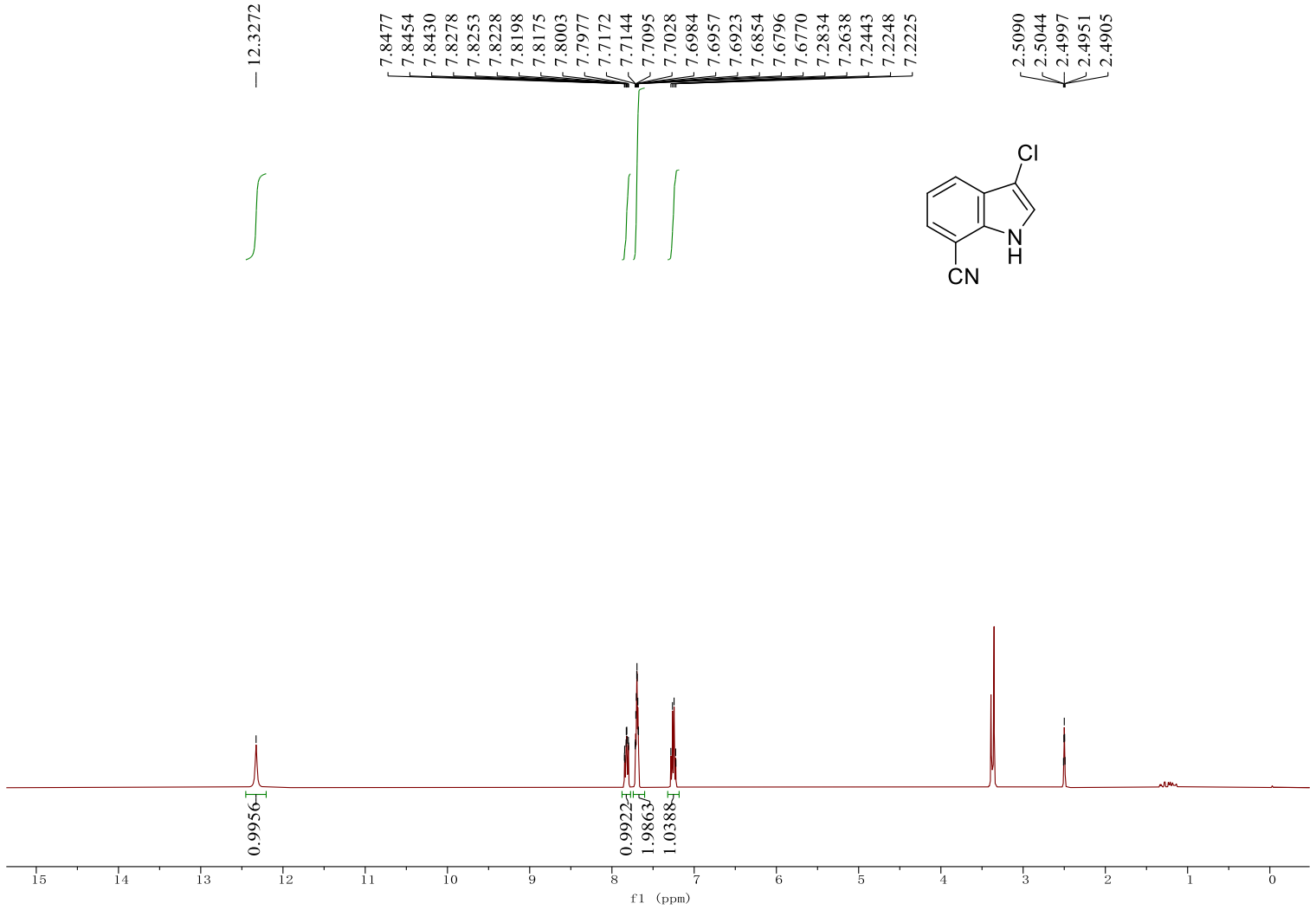
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-6-carbonitrile (2o)



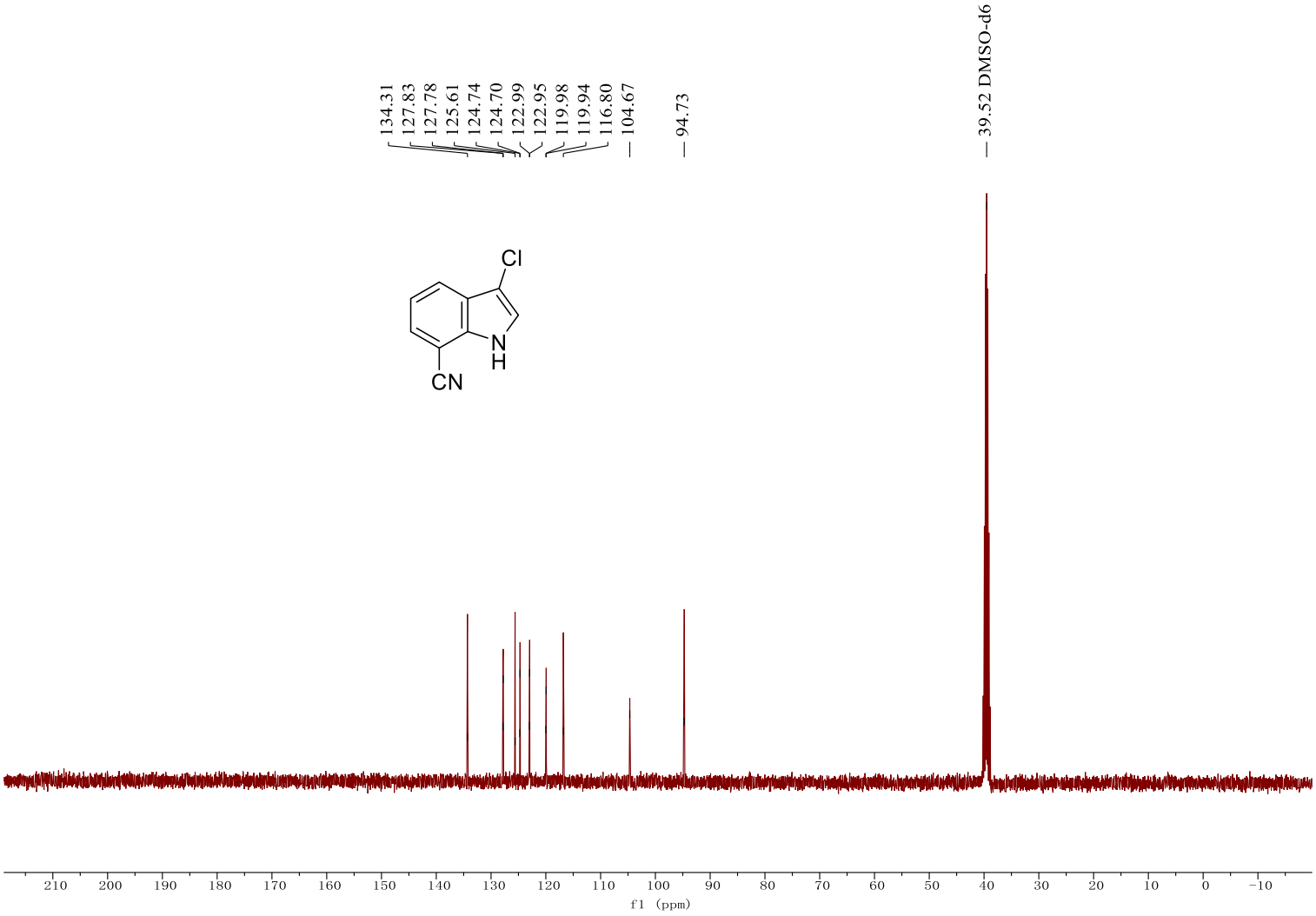
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-6-carbonitrile (2o)



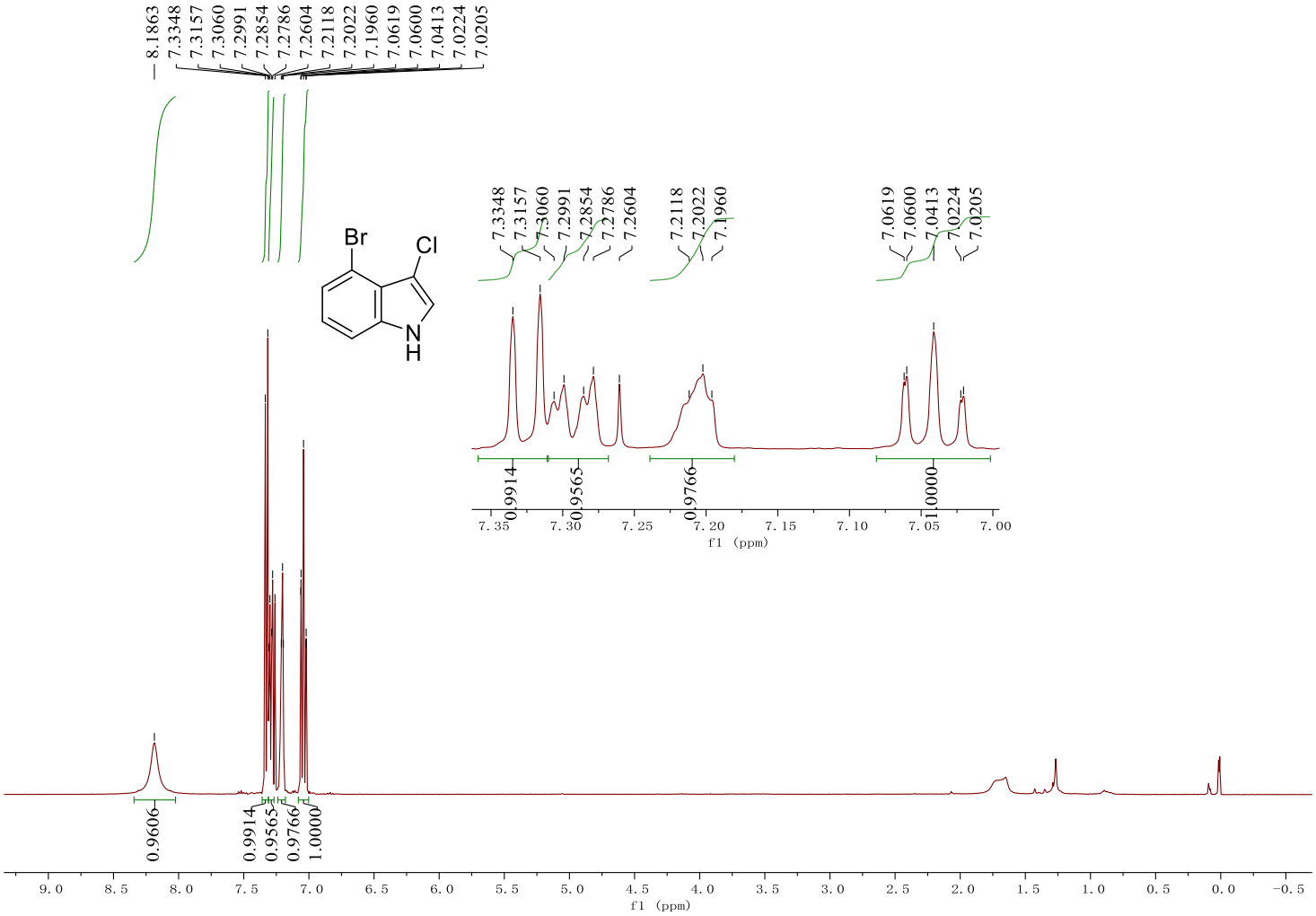
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-7-carbonitrile (2p)



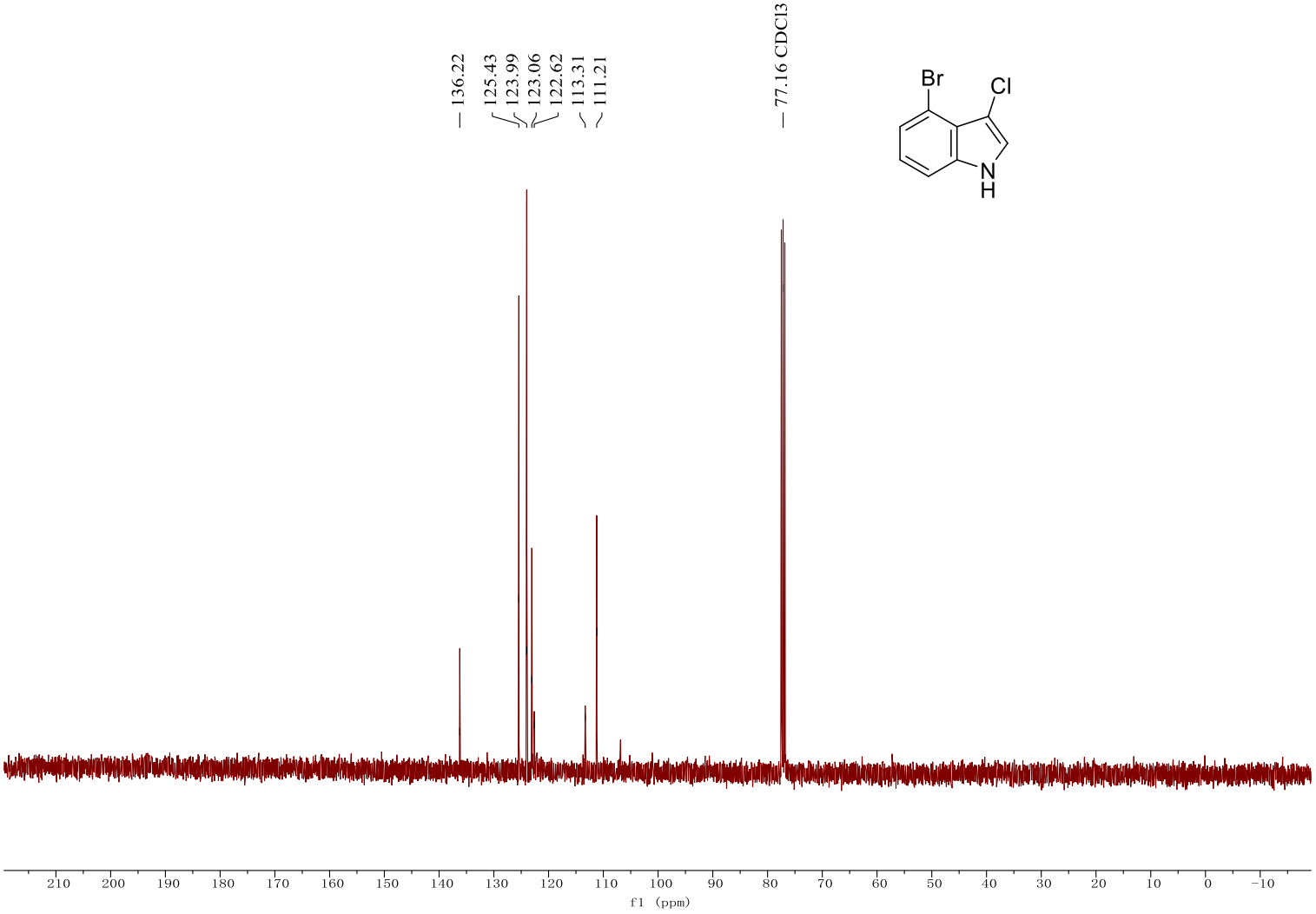
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-7-carbonitrile (2p)



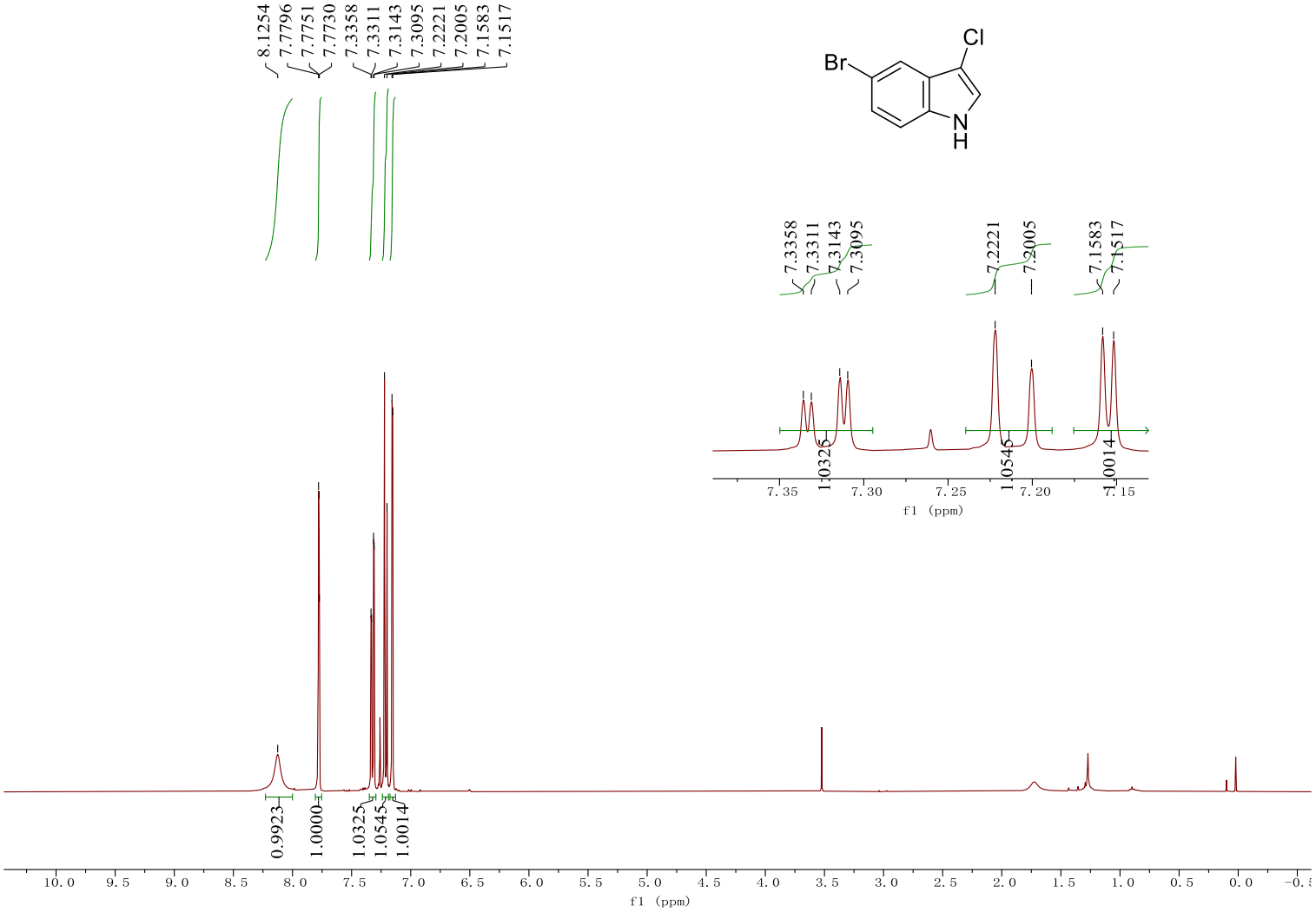
^{1}H NMR (400MHz, $CDCl_3$) spectra of 4-bromo-3-chloro-1*H*-indole (2q)



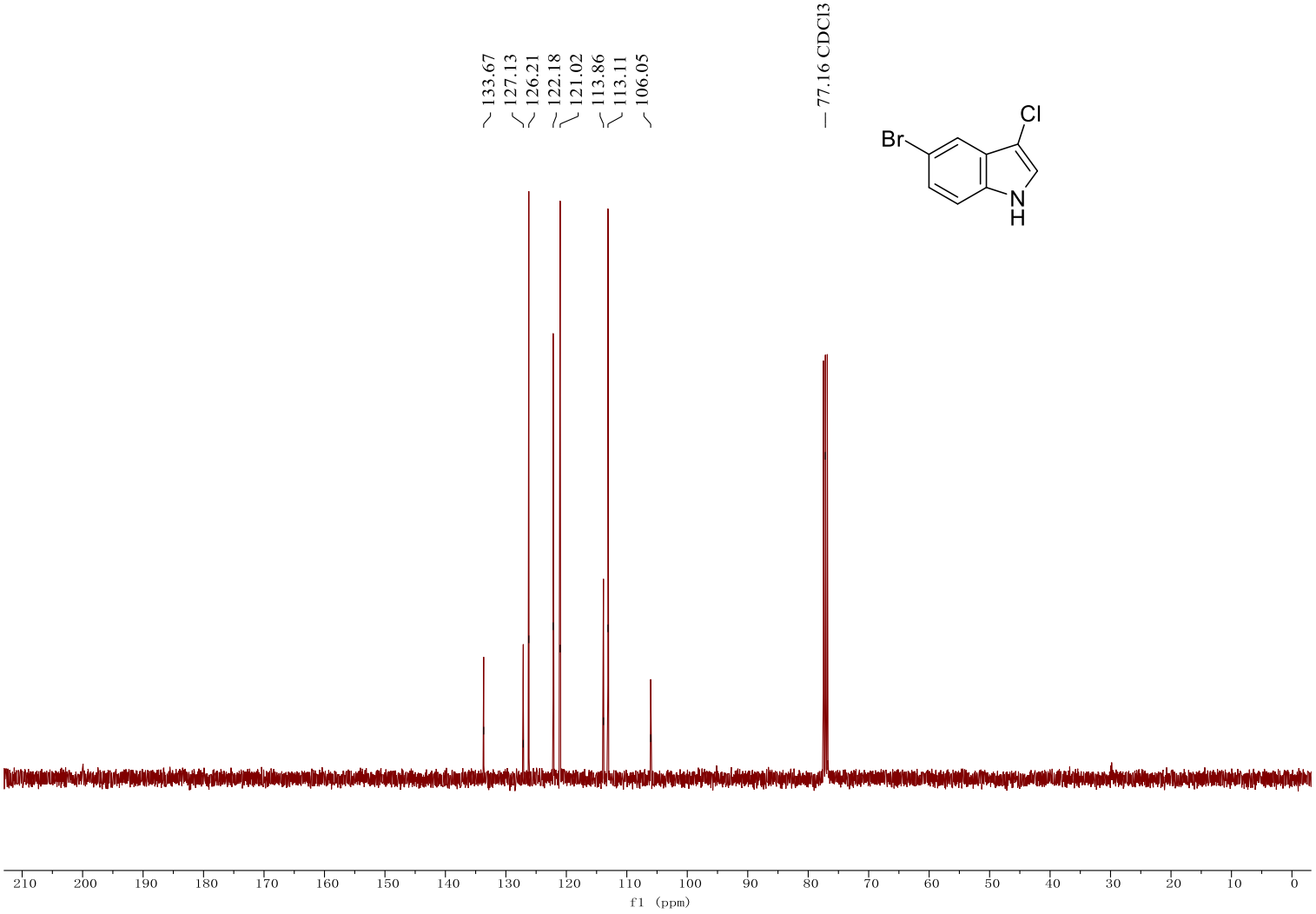
^{13}C NMR (101MHz, $CDCl_3$) spectra of 4-bromo-3-chloro-1*H*-indole (2q)



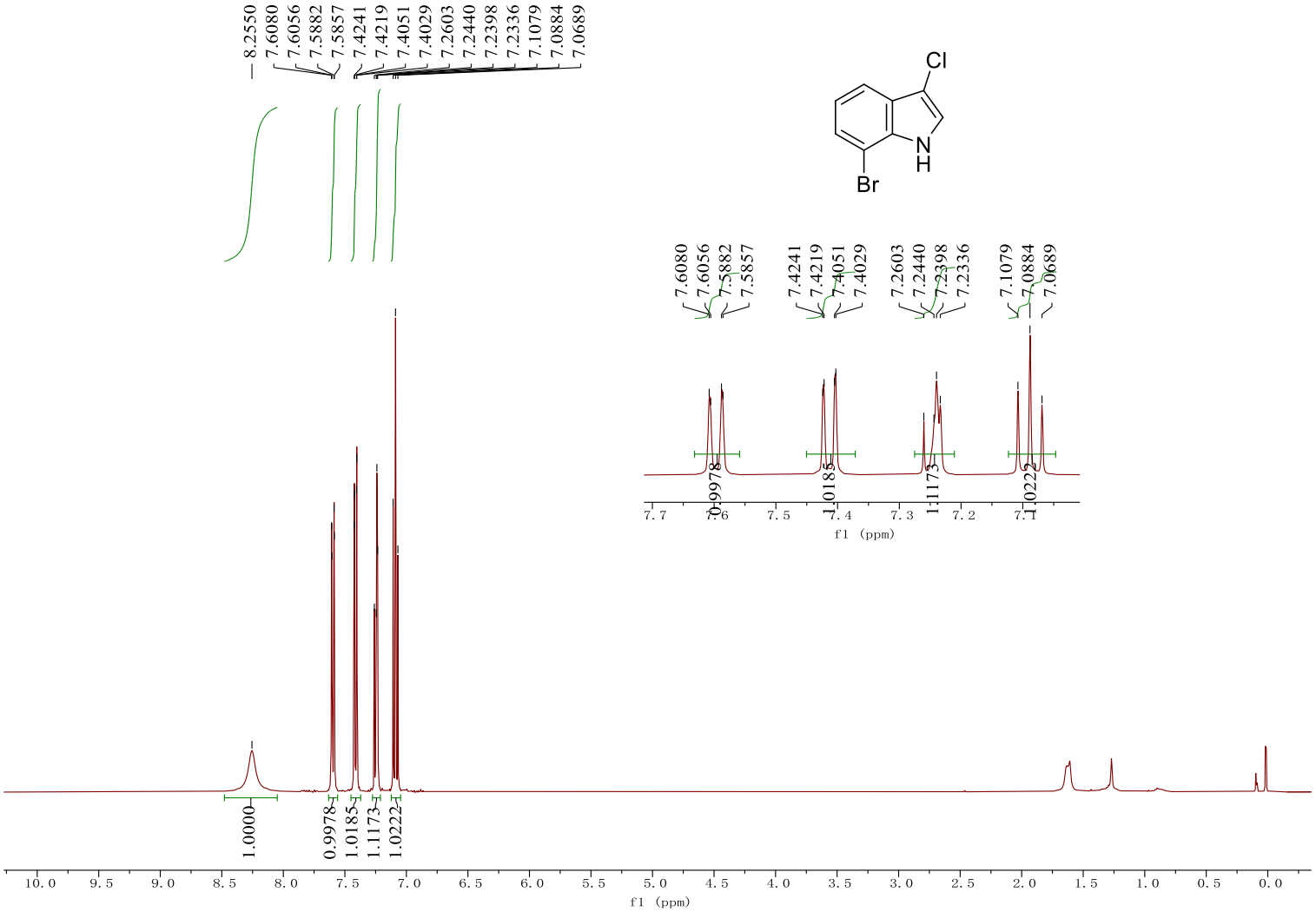
^{1}H NMR (400MHz, $CDCl_3$) spectra of 5-bromo-3-chloro-1*H*-indole (2r)



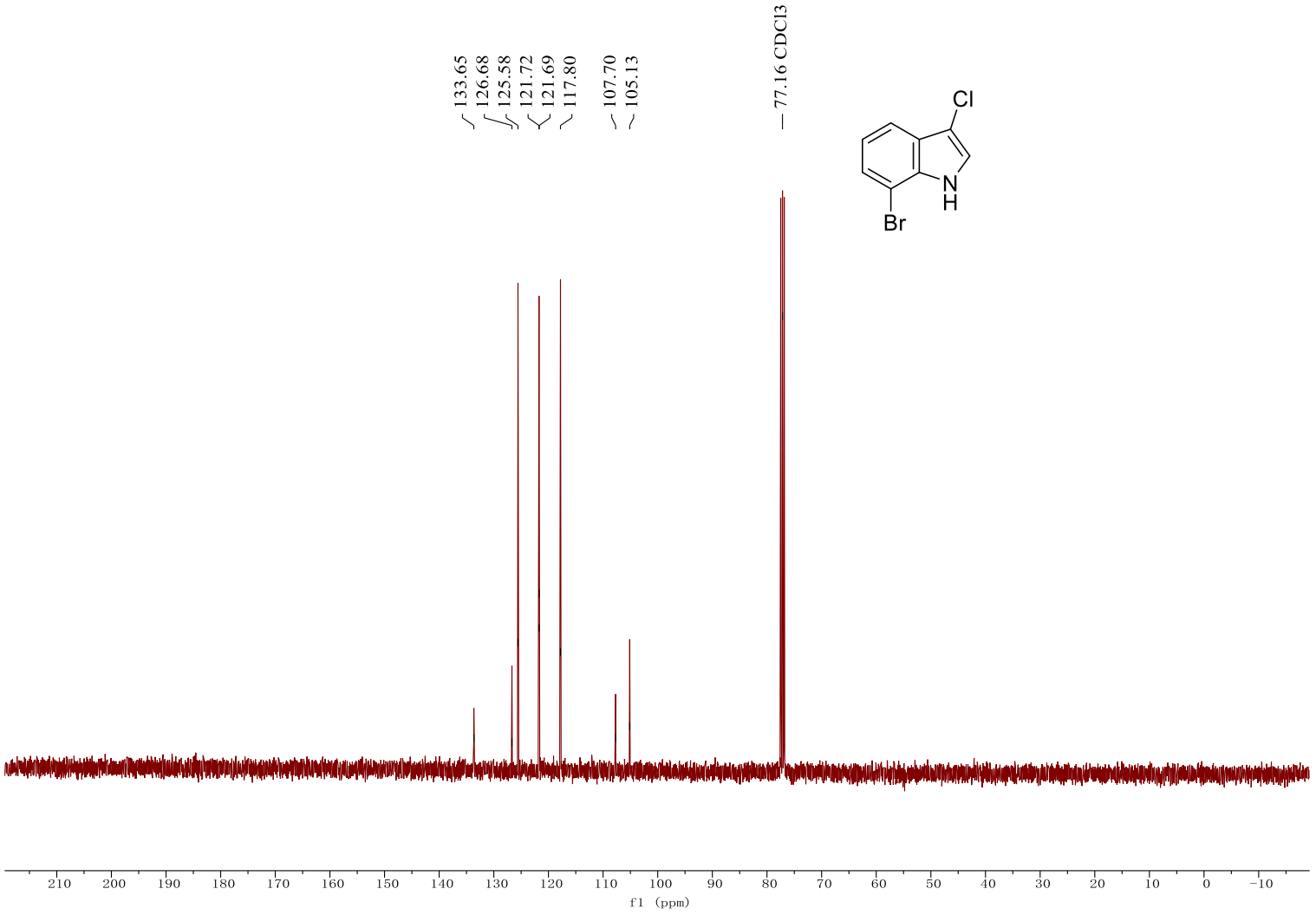
^{13}C NMR (101MHz, $CDCl_3$) spectra of 5-bromo-3-chloro-1*H*-indole (2r)



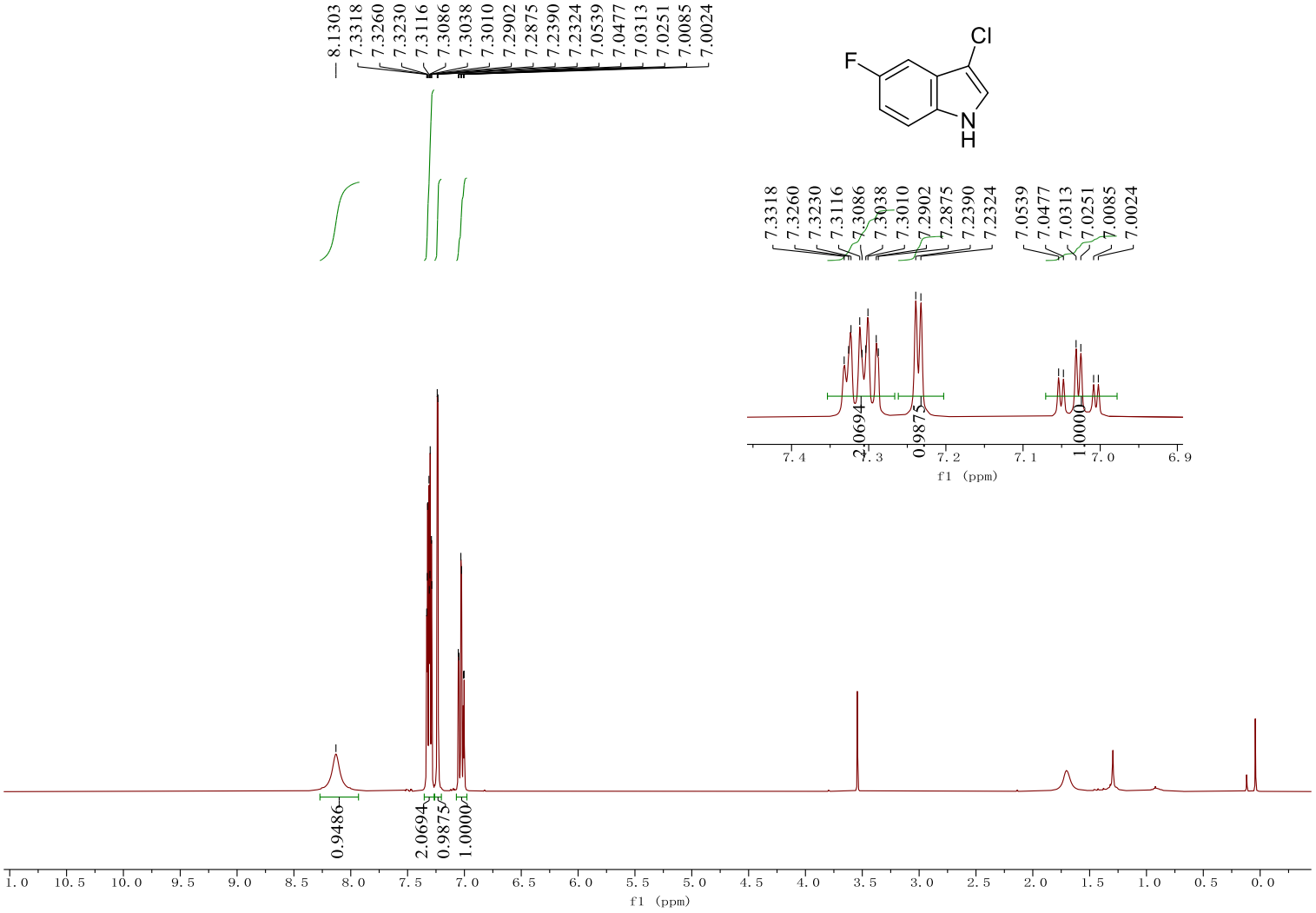
^{1}H NMR (400MHz, $CDCl_3$) spectra of 7-bromo-3-chloro-1*H*-indole (2*s*)



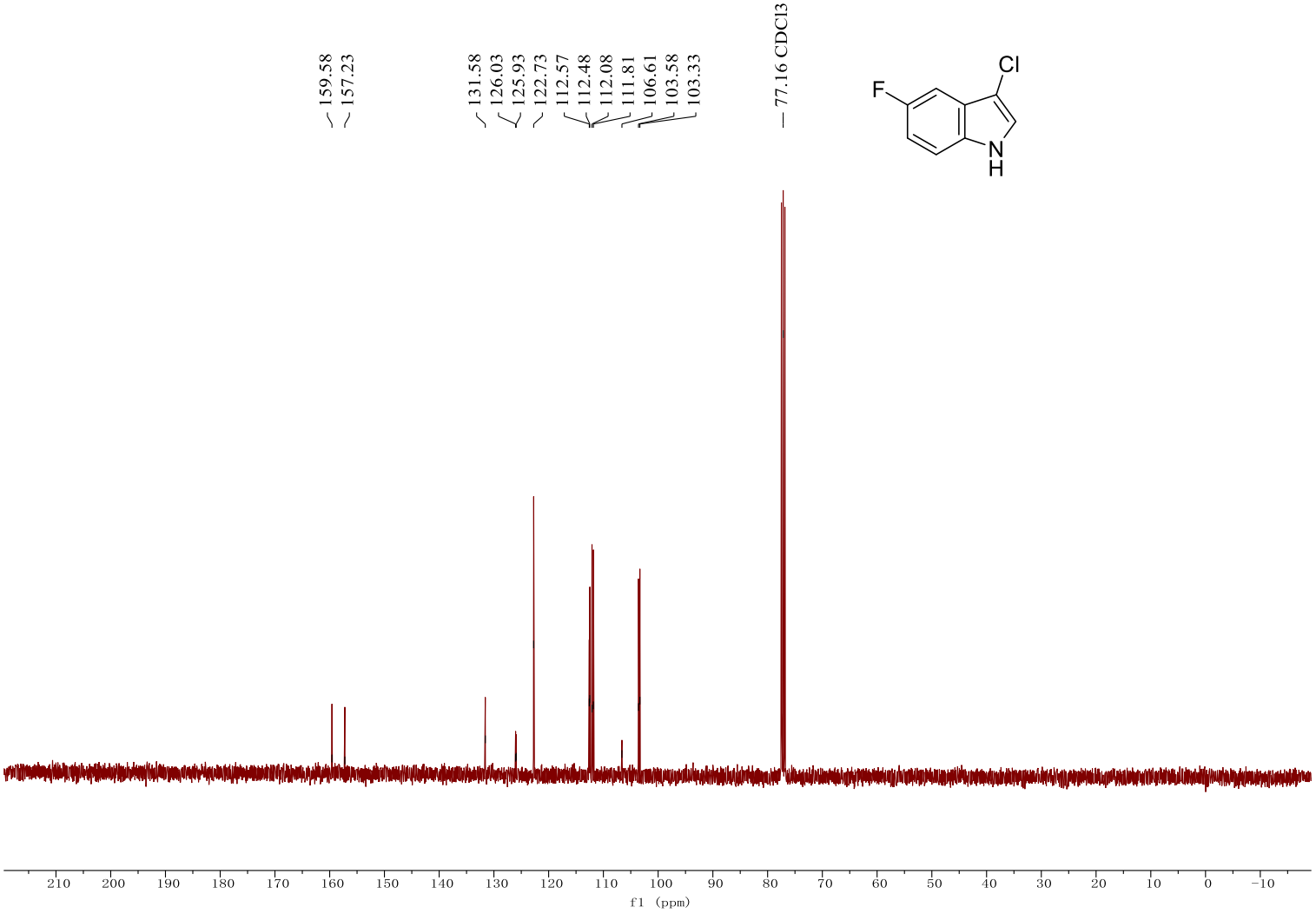
^{13}C NMR (101MHz, $CDCl_3$) spectra of 7-bromo-3-chloro-1*H*-indole (2s)



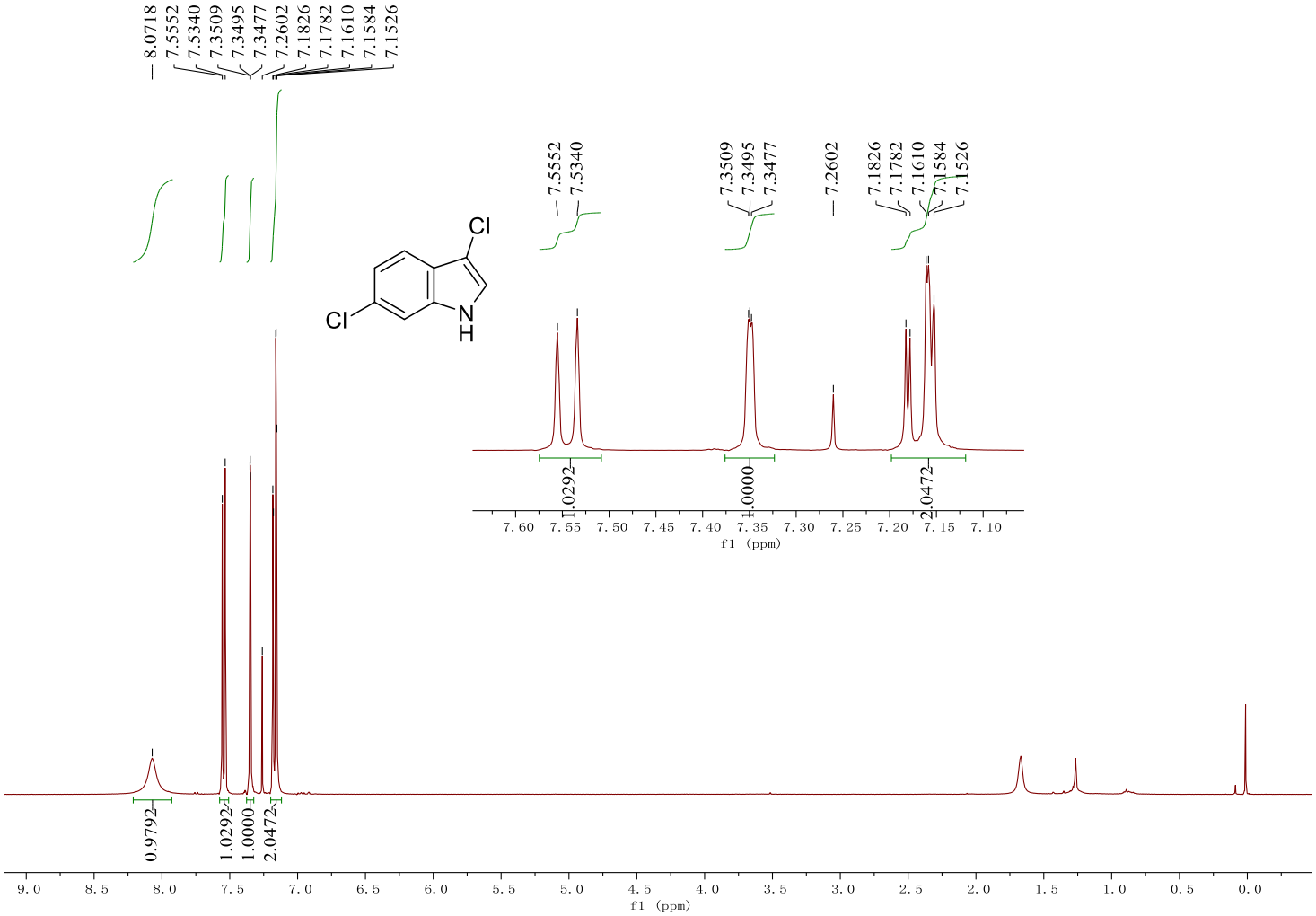
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-5-fluoro-1*H*-indole (2t)



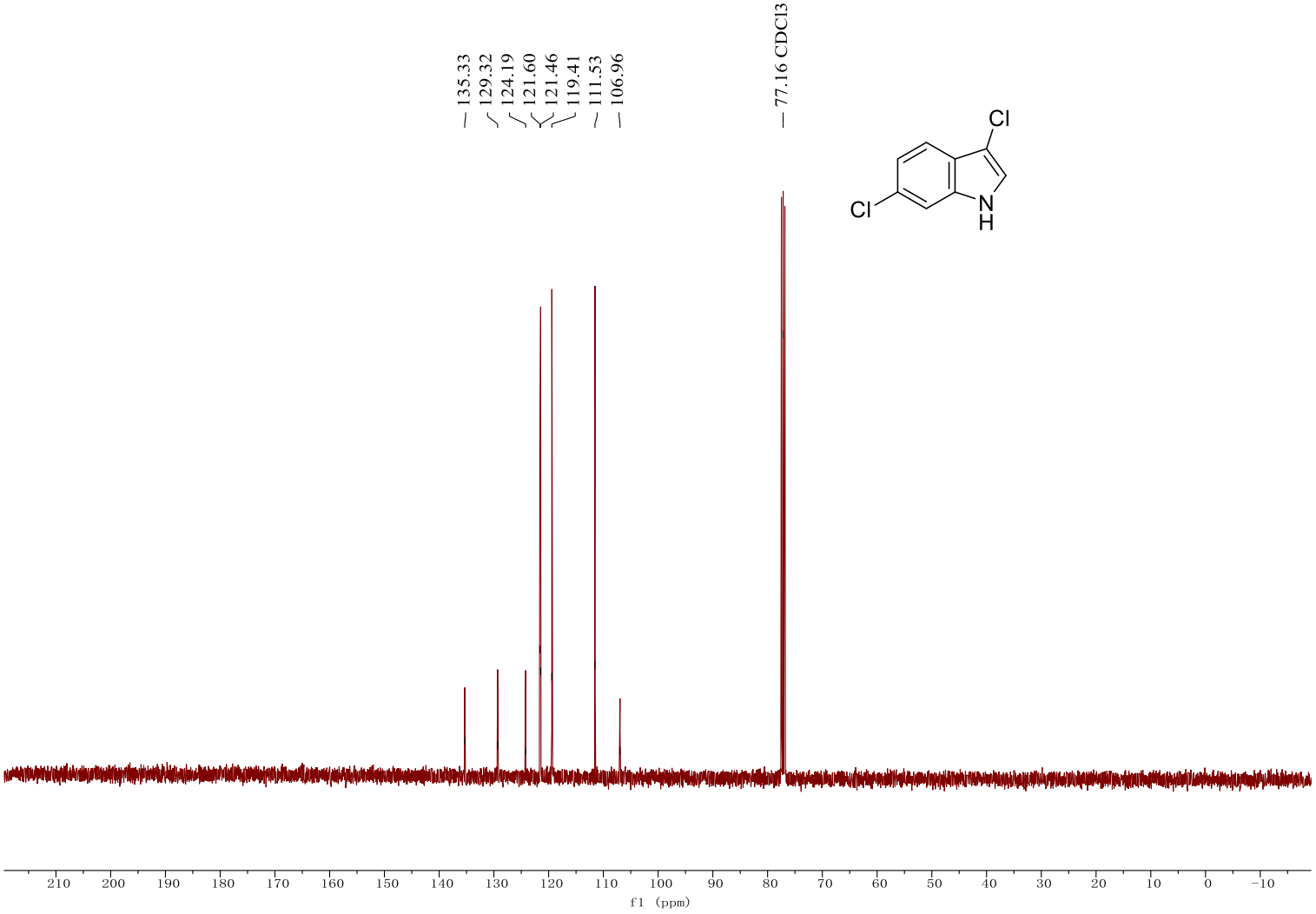
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-5-fluoro-1*H*-indole (2t)



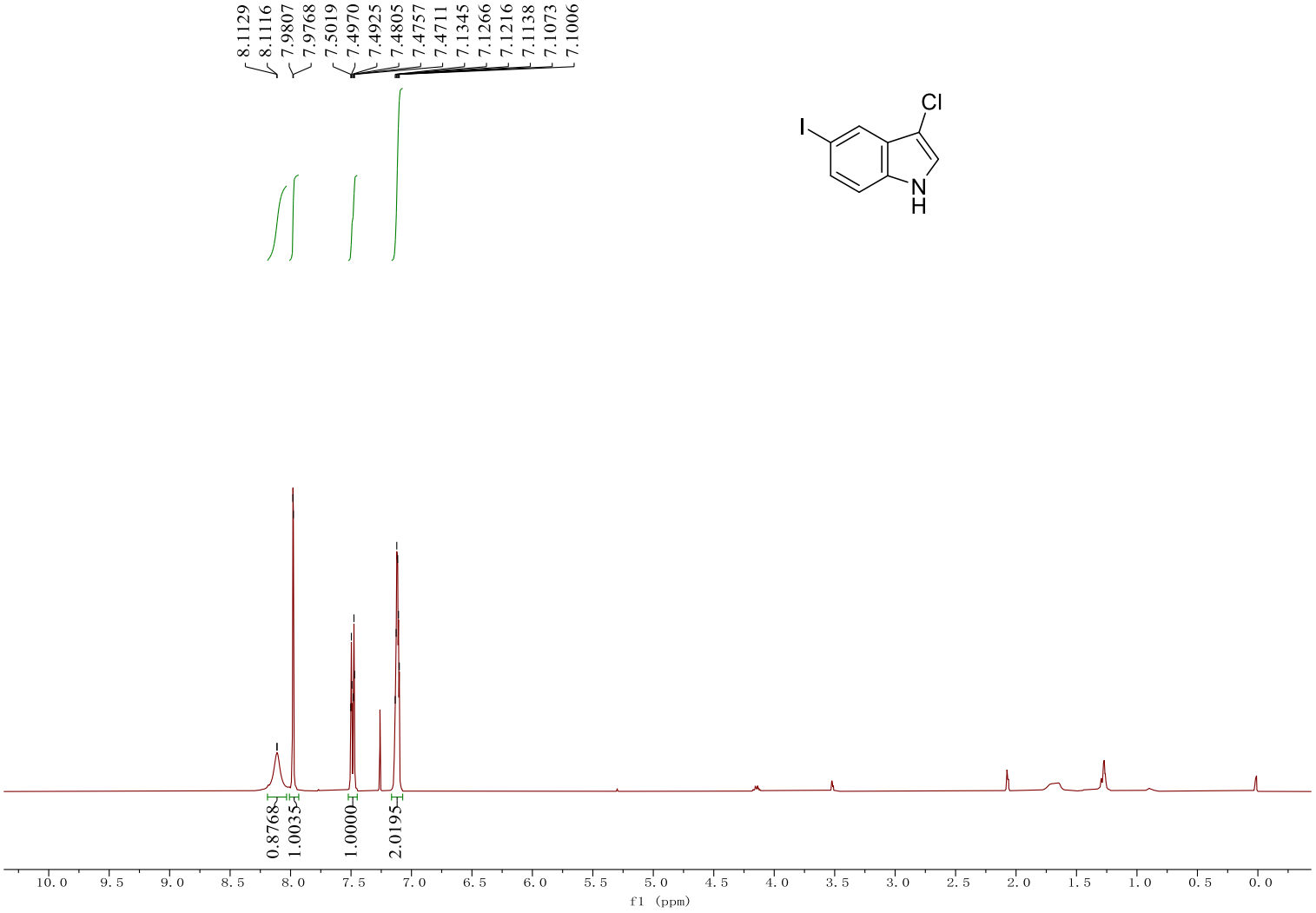
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3,6-dichloro-1*H*-indole (2u)



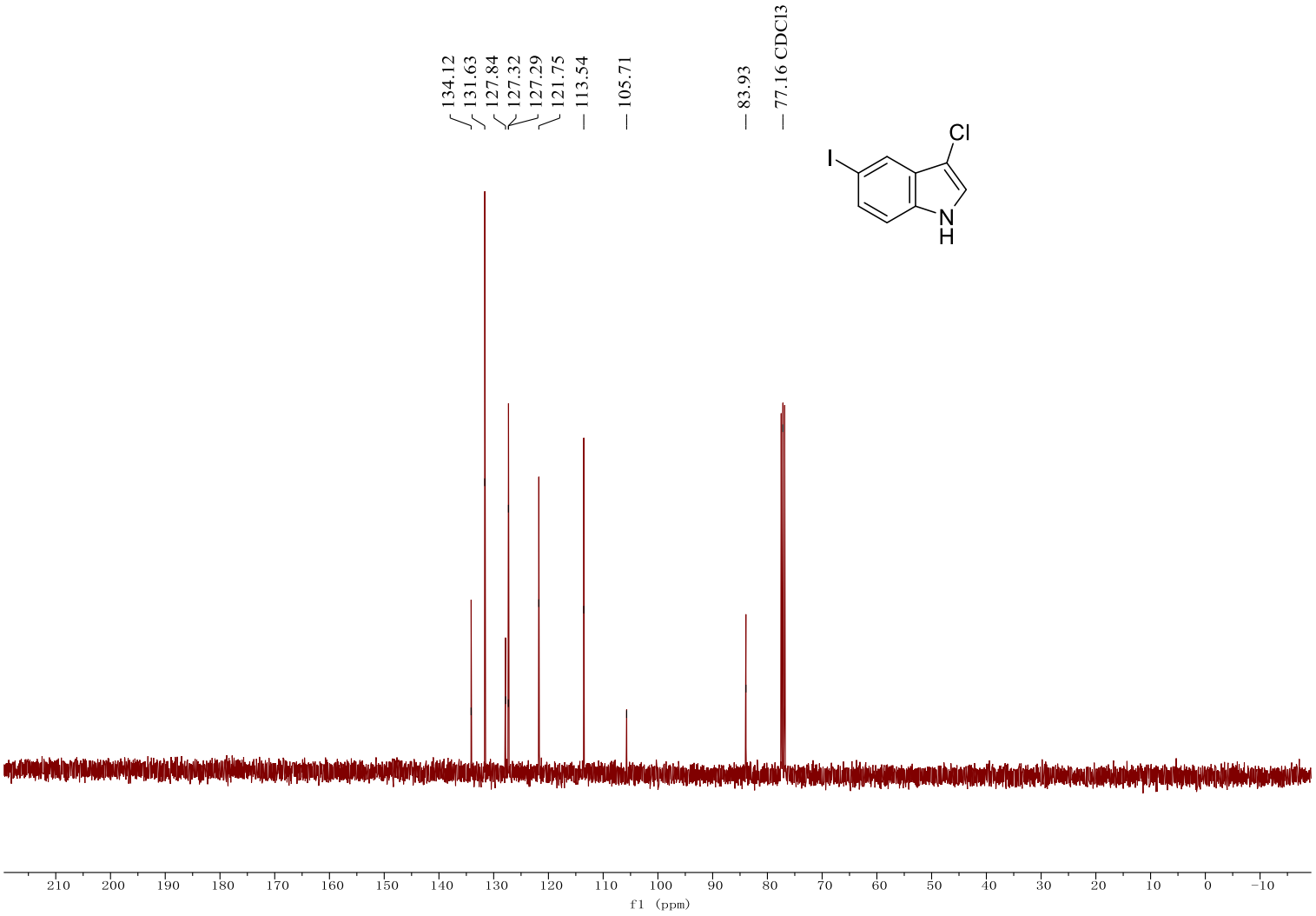
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,6-dichloro-1*H*-indole (2u)



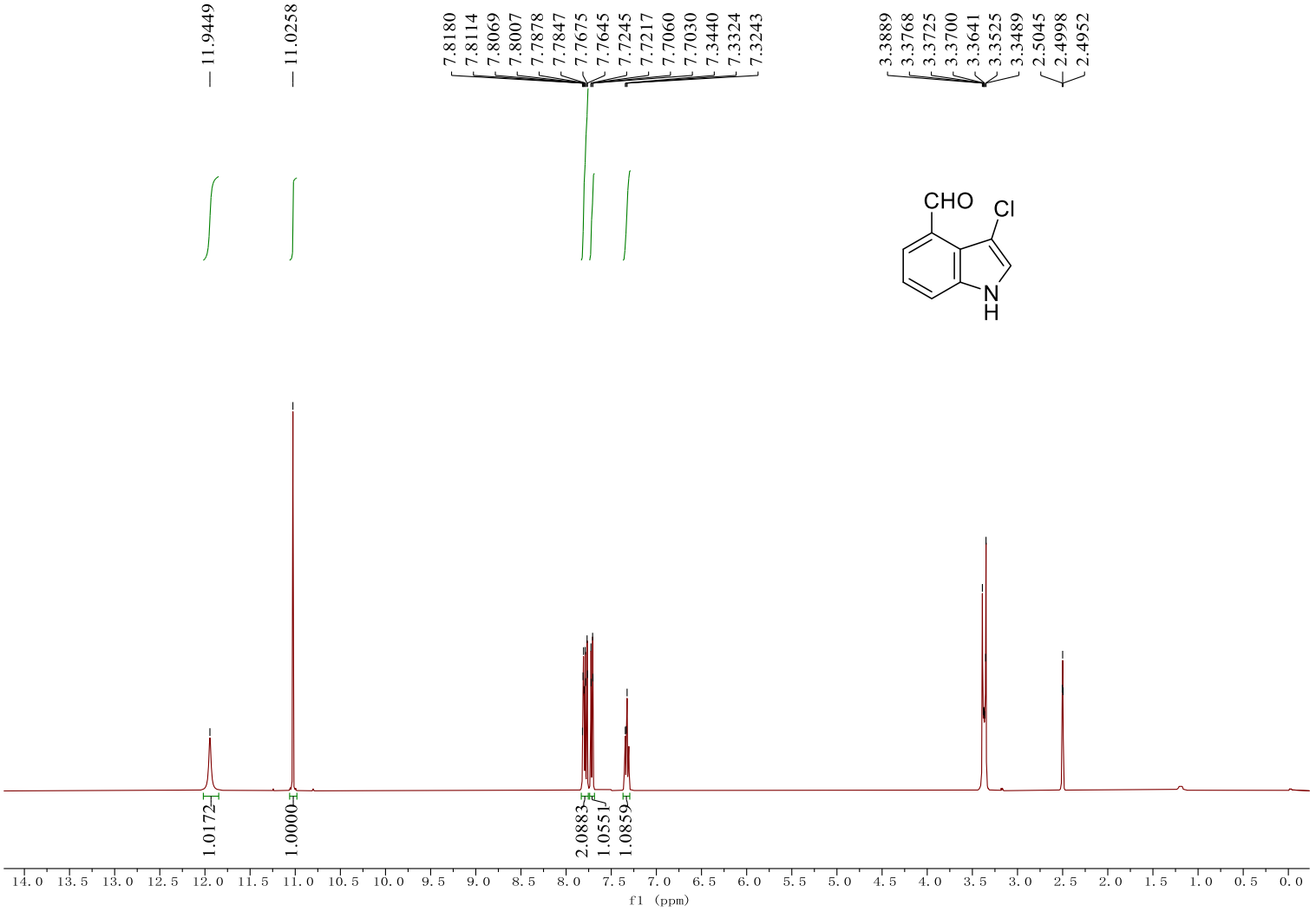
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-5-iodo-1*H*-indole (2v)



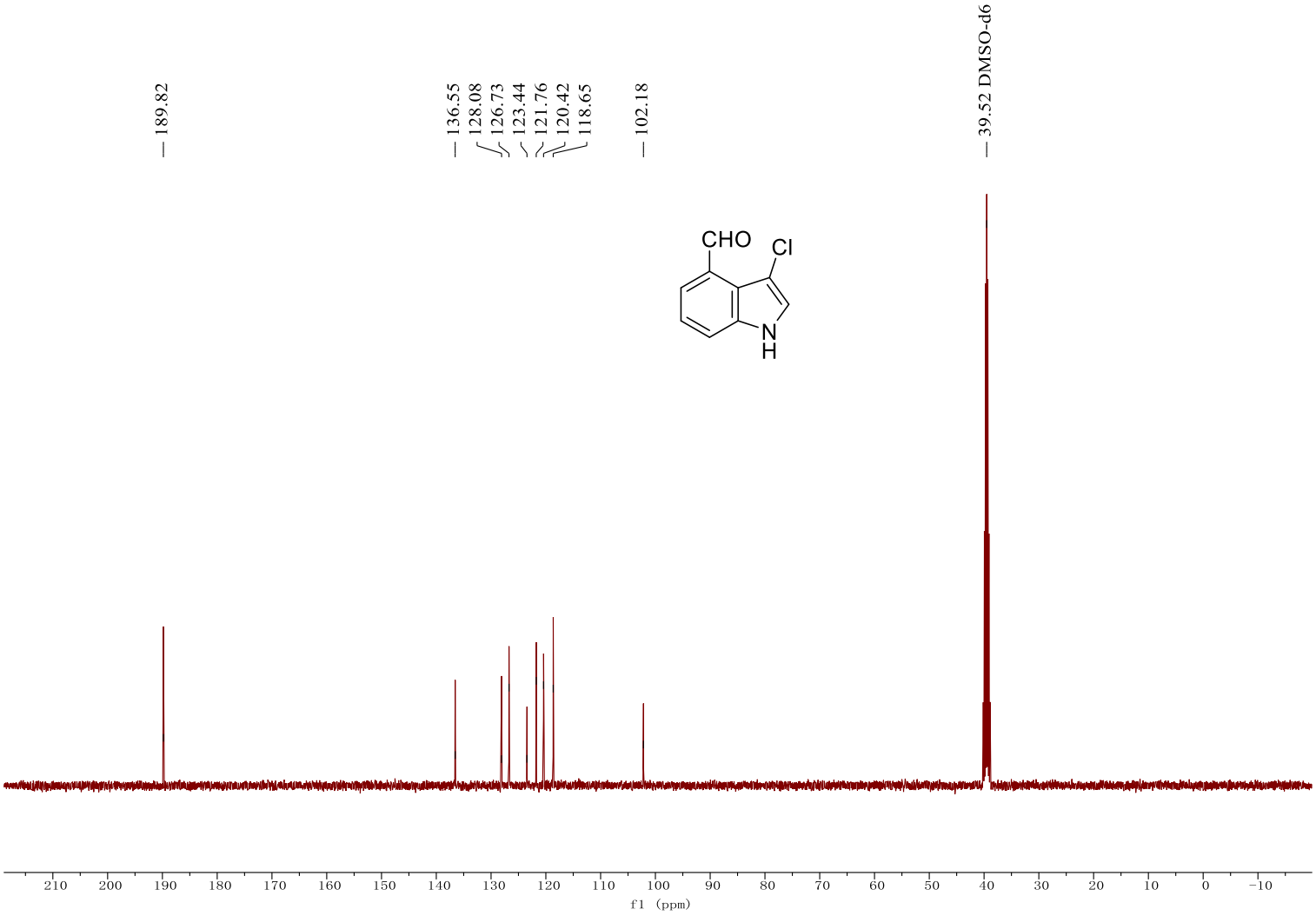
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-5-iodo-1*H*-indole (2v)



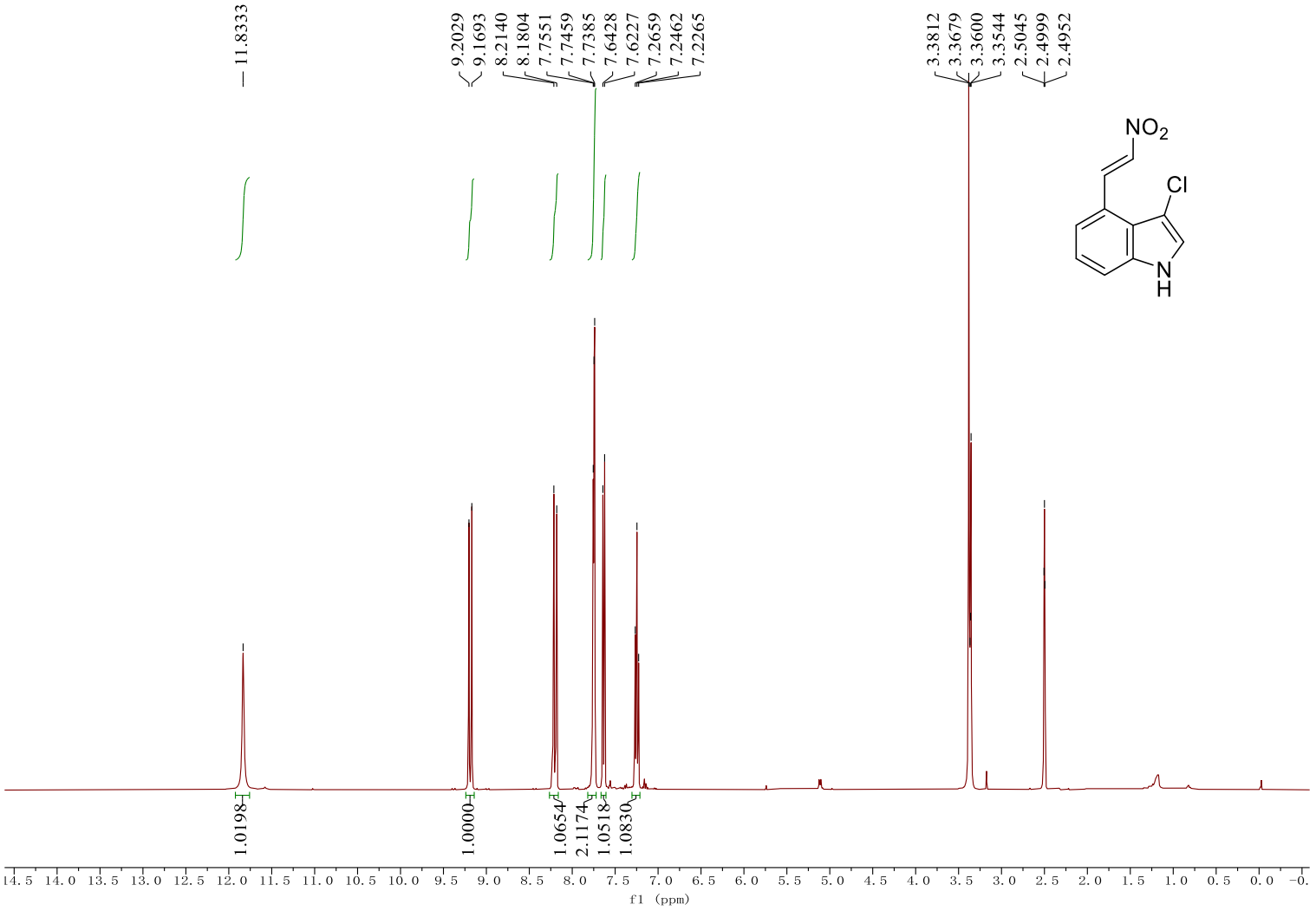
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-4-carbaldehyde (2w)



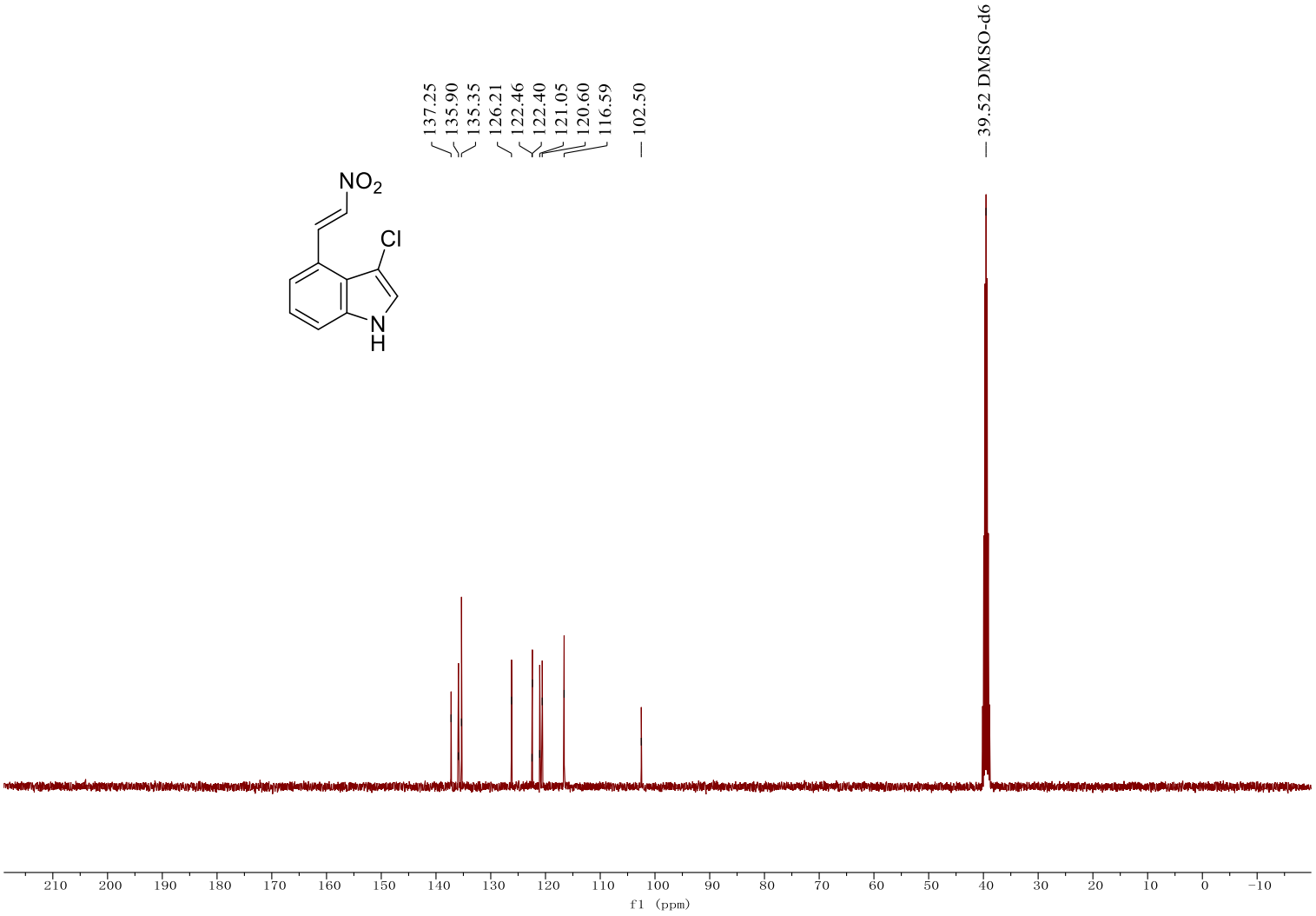
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1*H*-indole-4-carbaldehyde (2w)



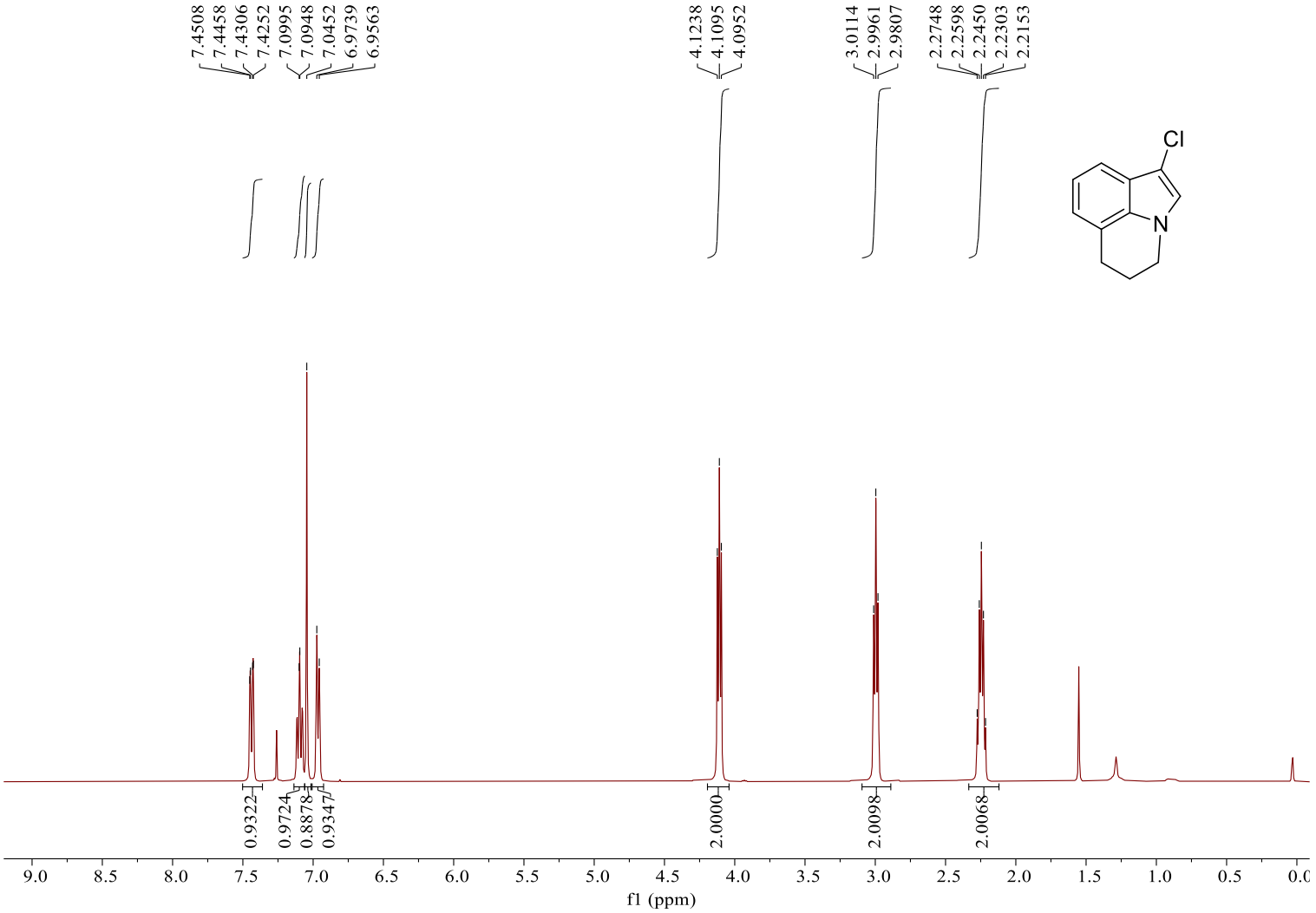
^{1}H NMR (400MHz, DMSO-d_6) spectra of (*E*)-3-chloro-4-(2-nitrovinyl)-1*H*-indole (2x)



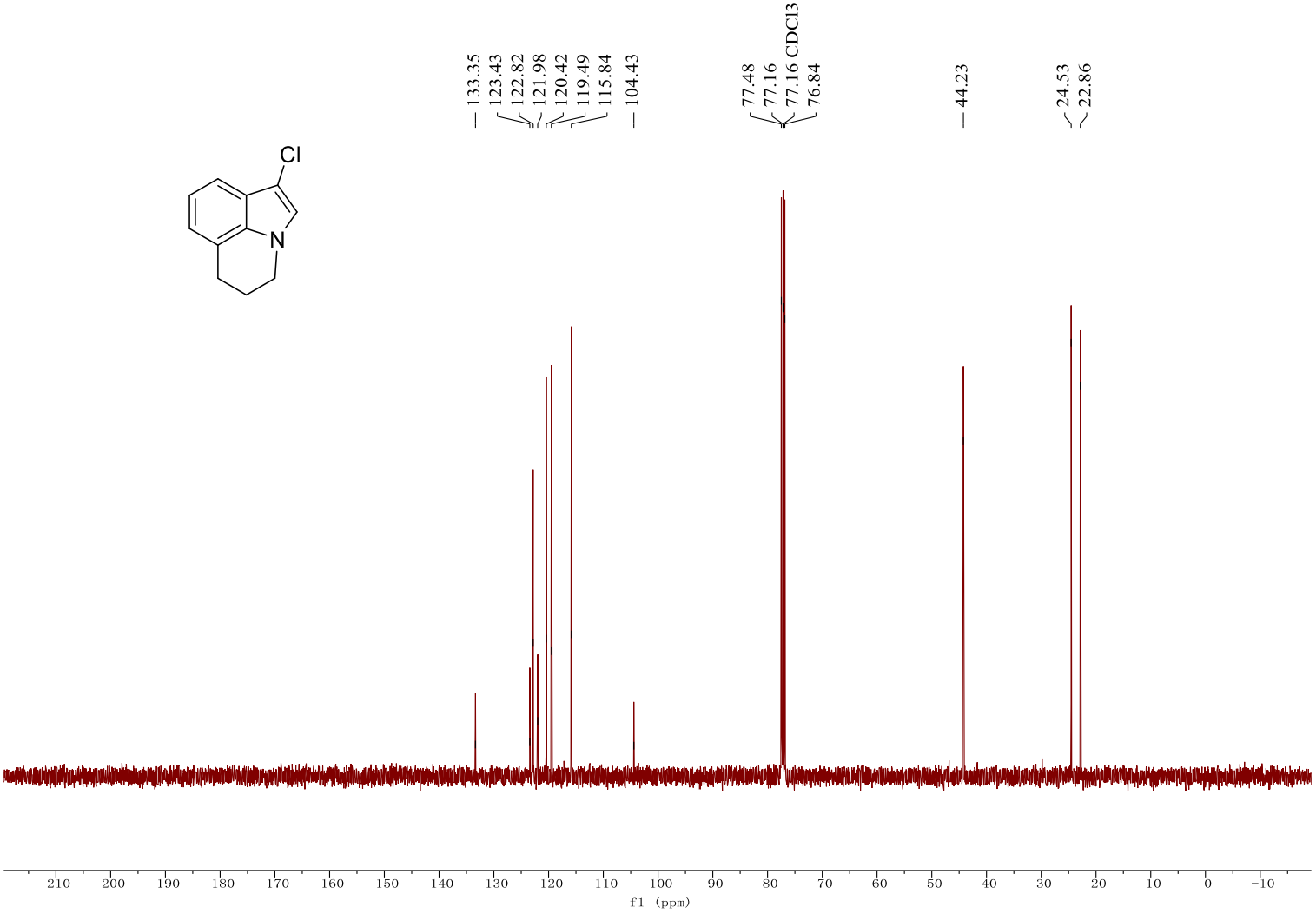
^{13}C NMR (101MHz, DMSO-d_6) spectra of (*E*)-3-chloro-4-(2-nitrovinyl)-1*H*-indole (2x)



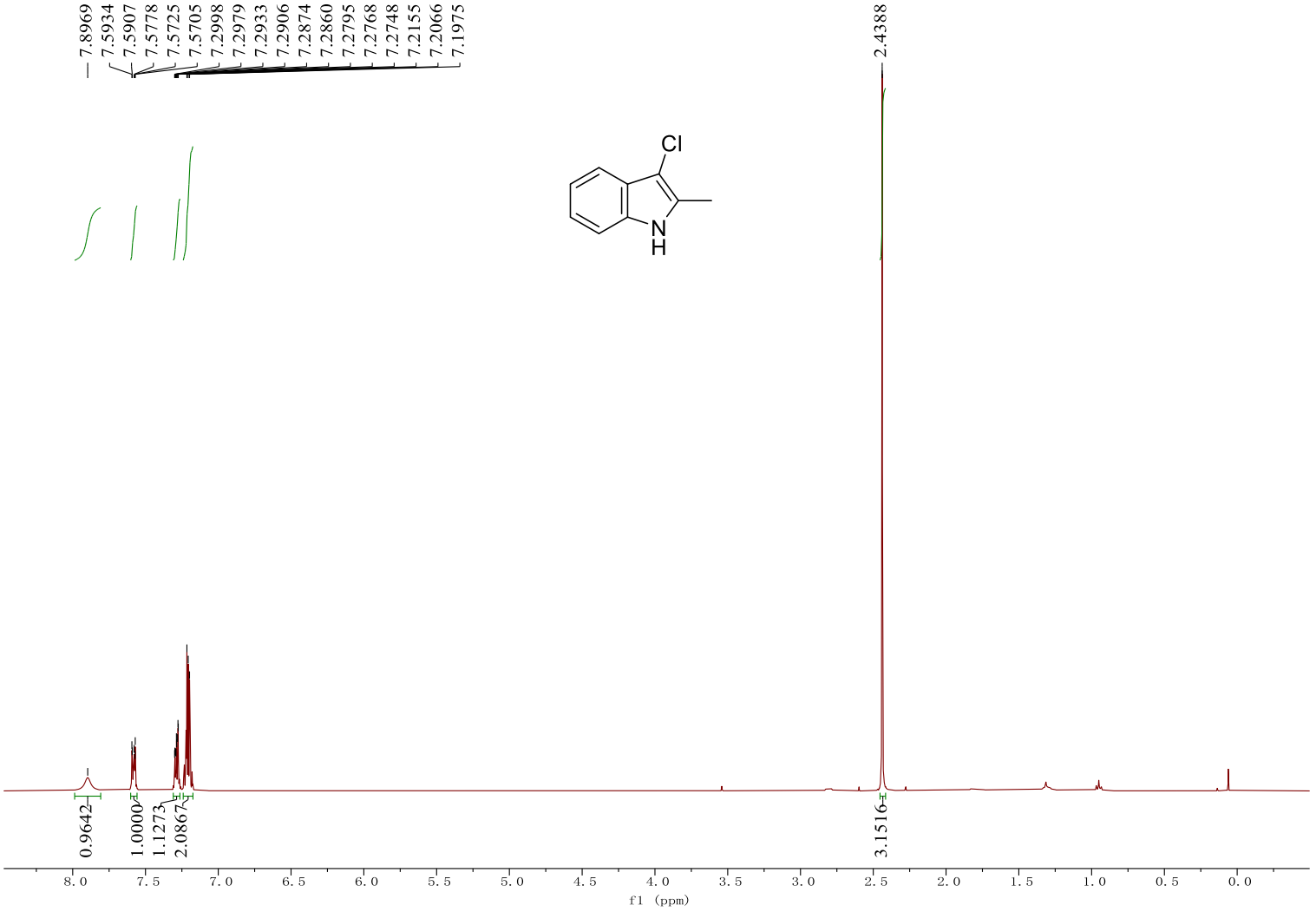
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (2y)



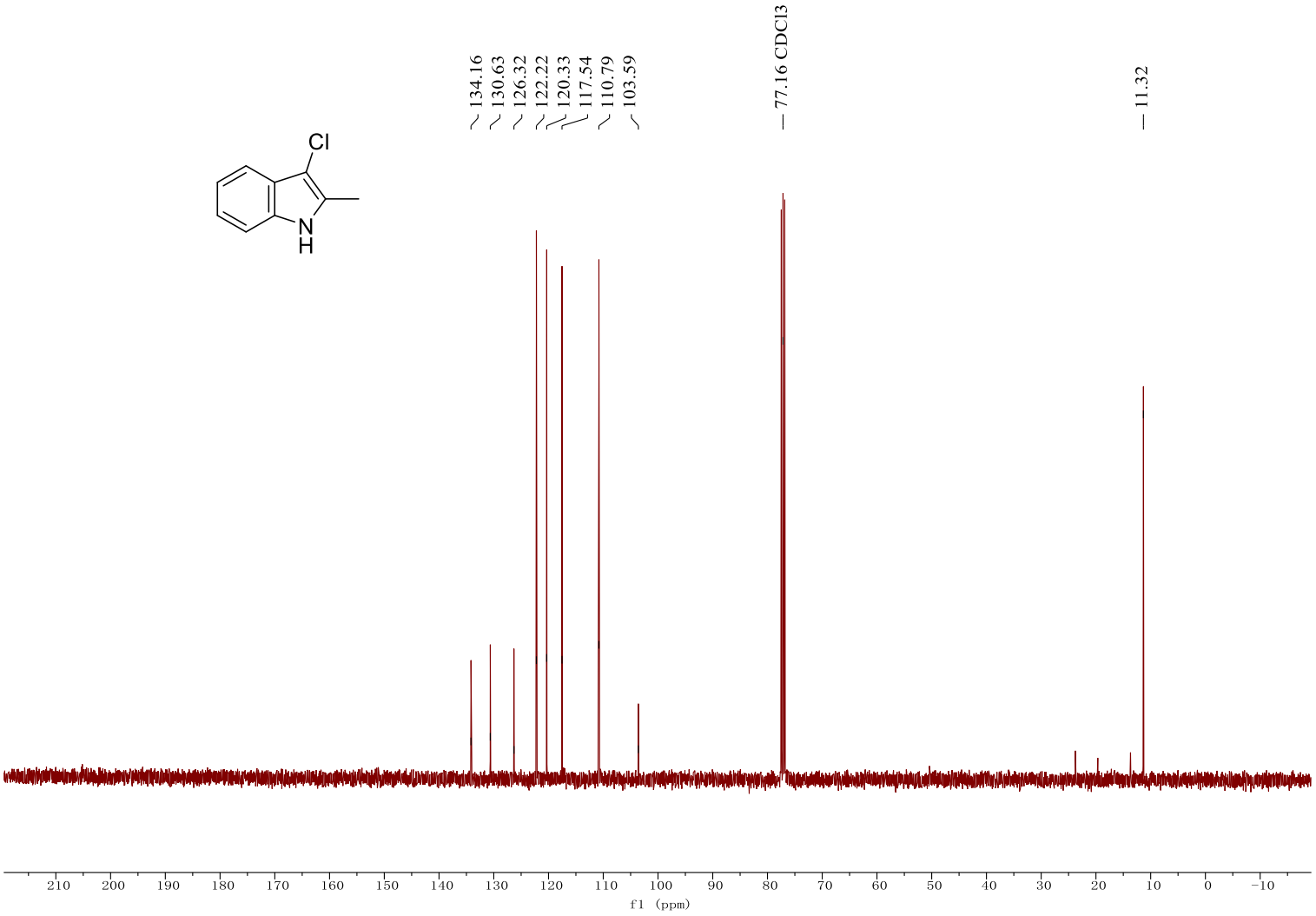
^{13}C NMR (101MHz, $CDCl_3$) spectra of 1-chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (2y)



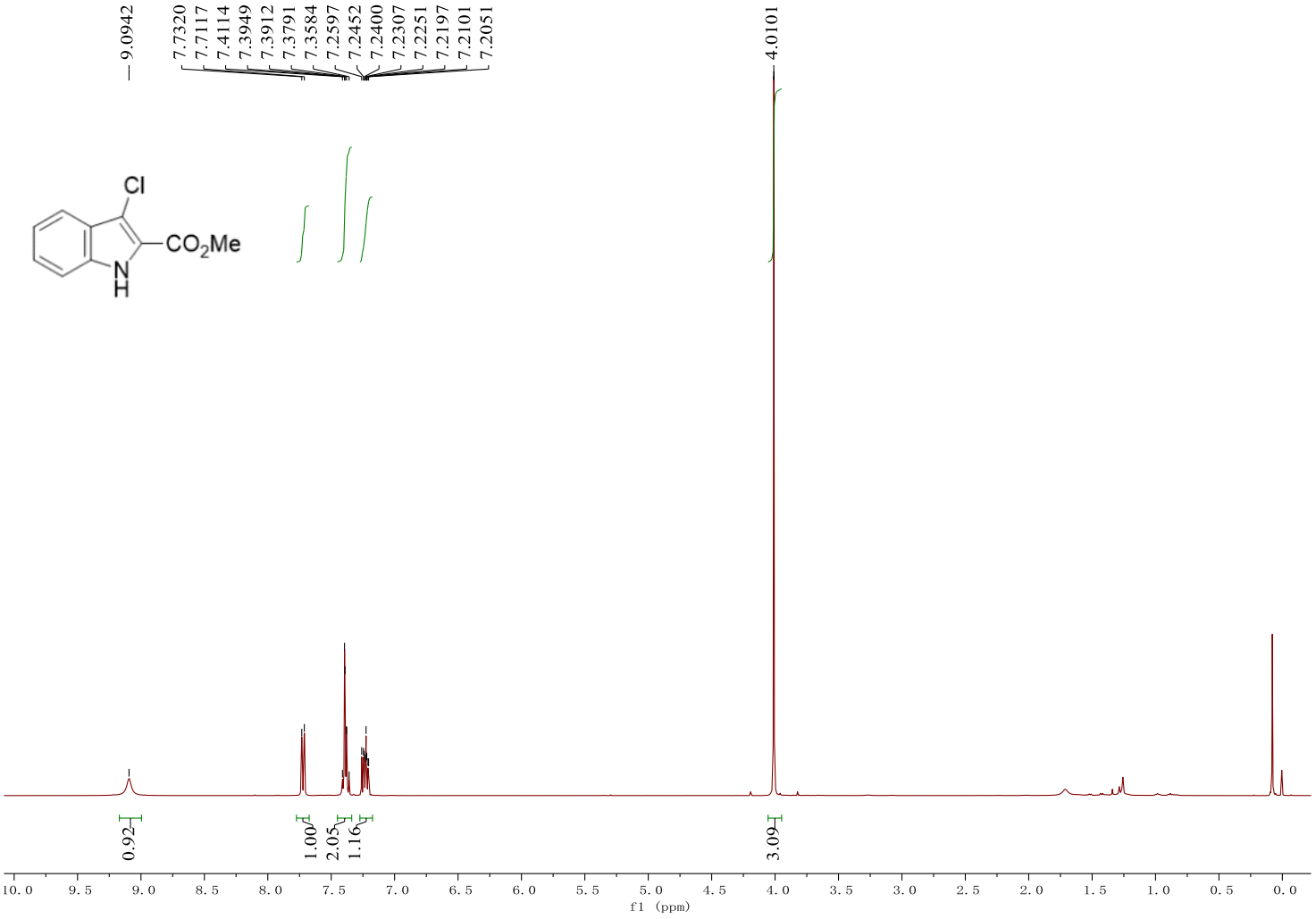
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-2-methyl-1*H*-indole (2z)



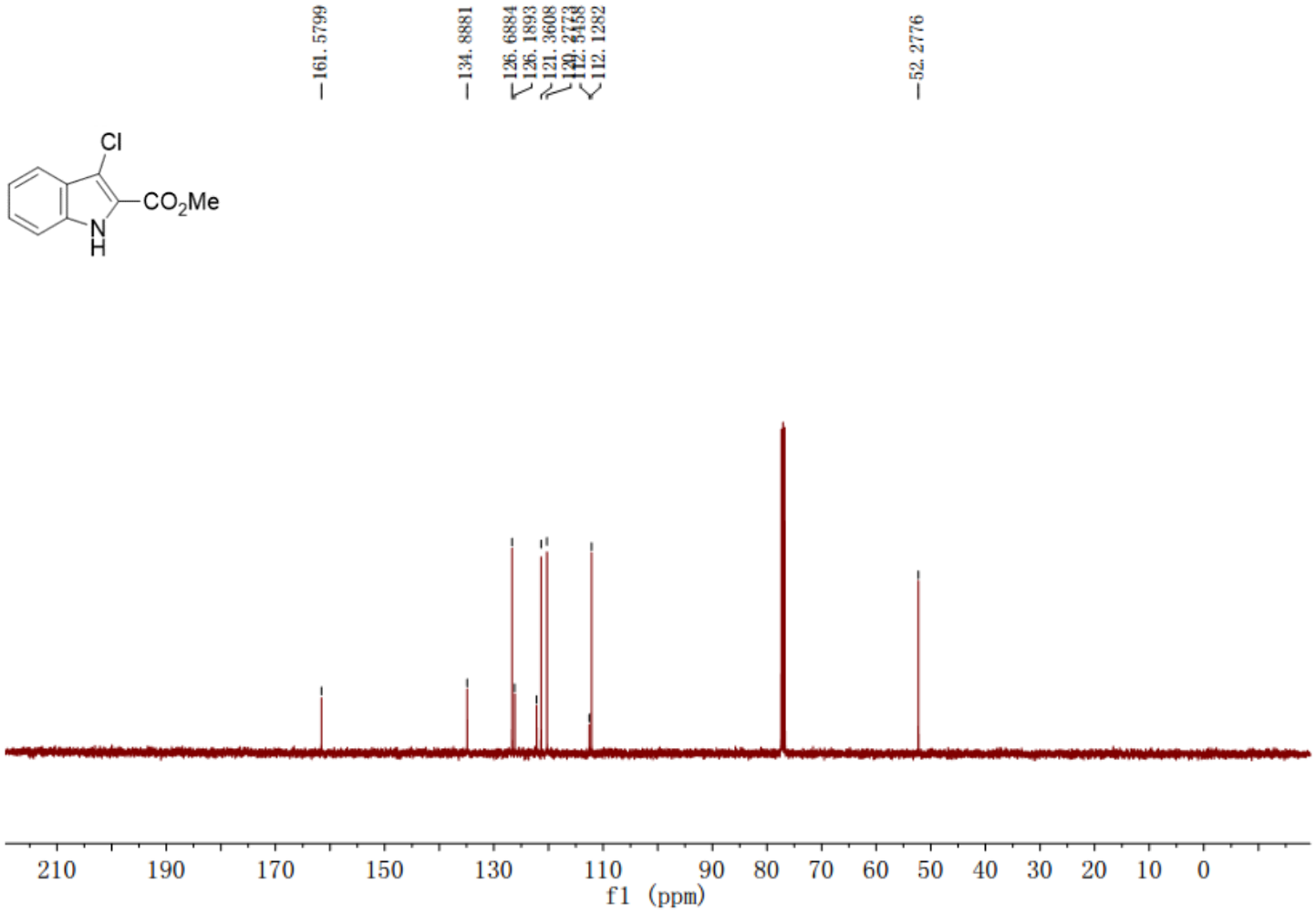
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-2-methyl-1*H*-indole (2z)



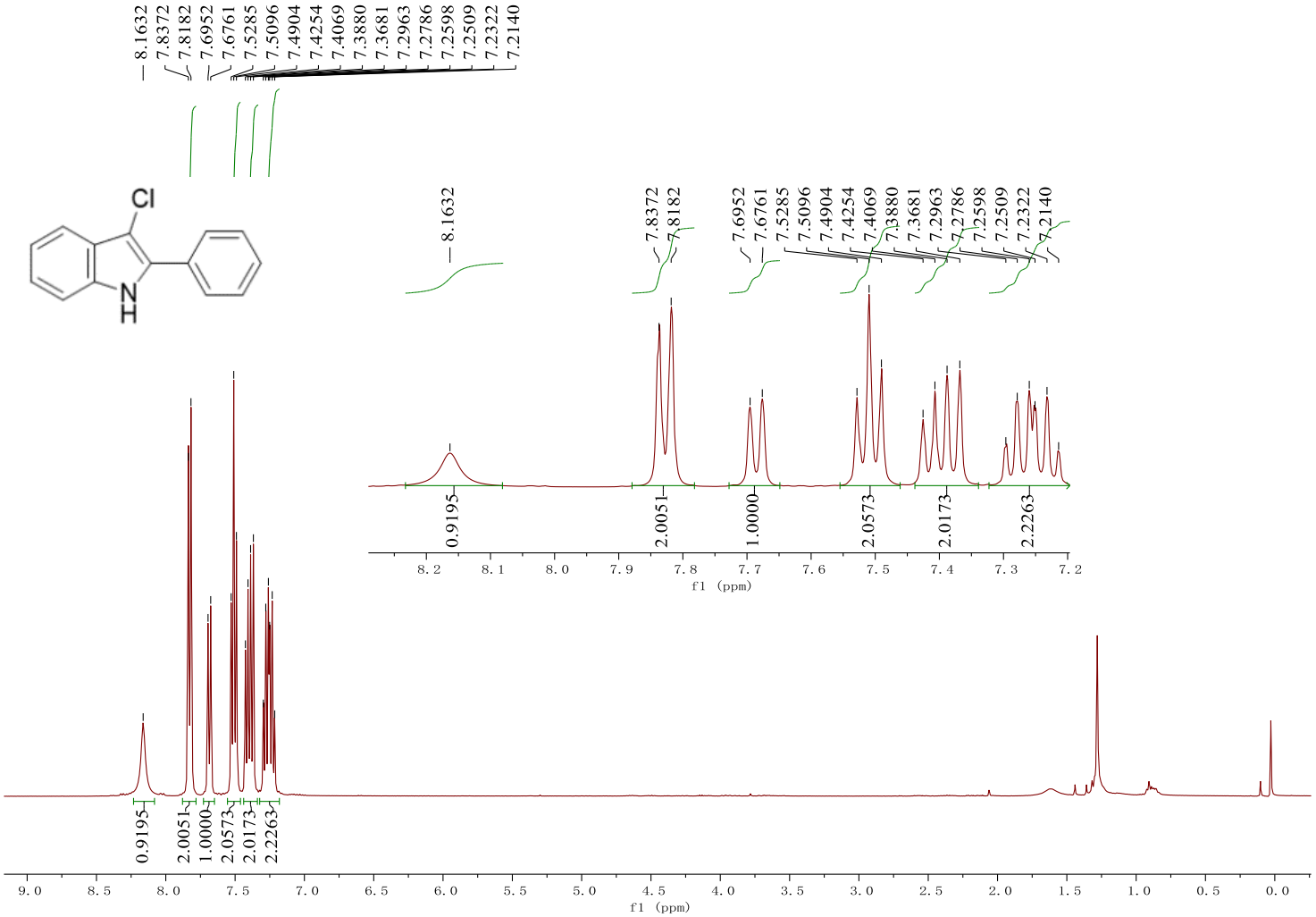
^{1}H NMR (400MHz, $CDCl_3$) spectra of methyl 3-chloro-1*H*-indole-2-carboxylate (2aa)



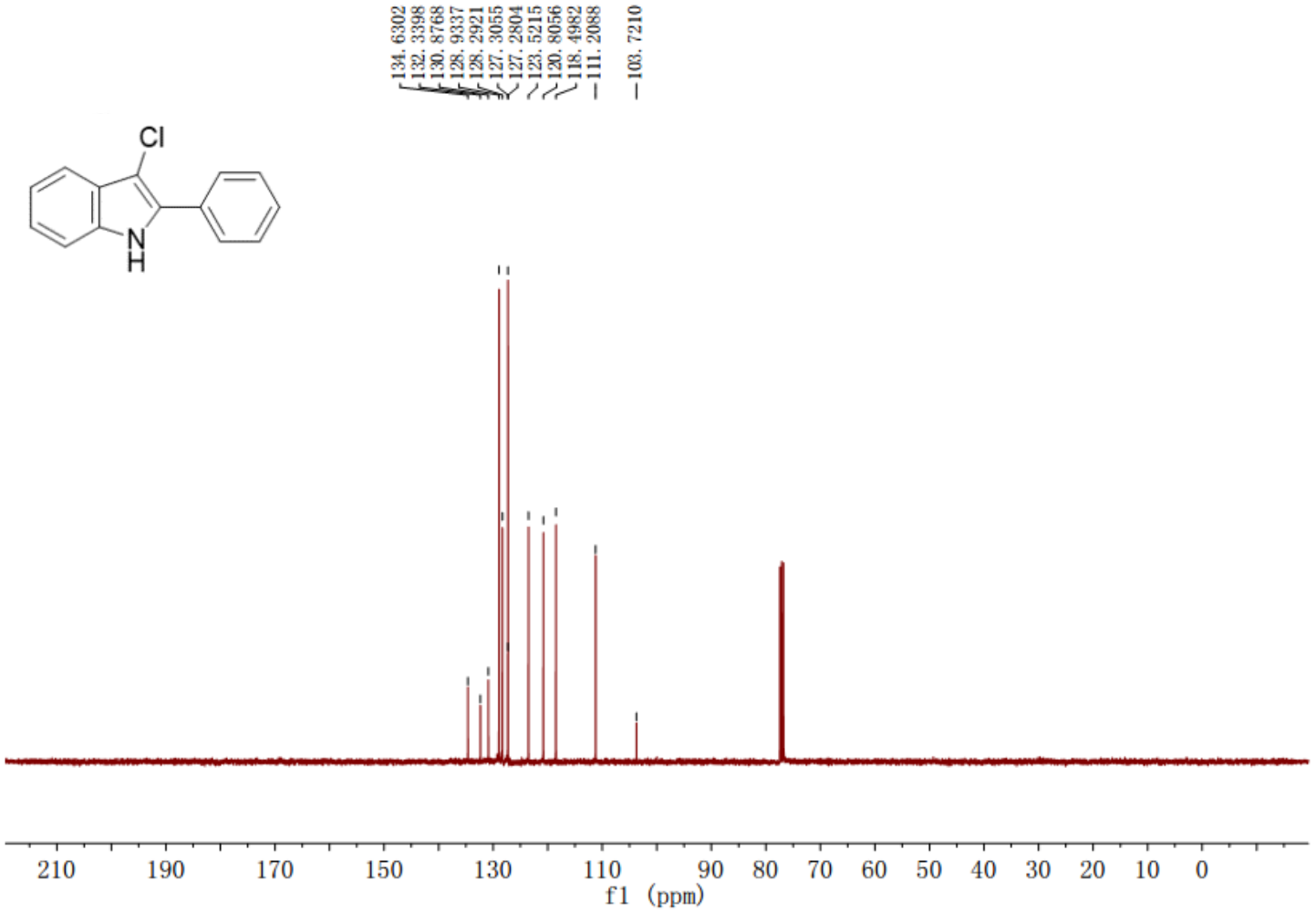
^{13}C NMR (101MHz, $CDCl_3$) spectra of methyl 3-chloro-1*H*-indole-2-carboxylate (2aa)



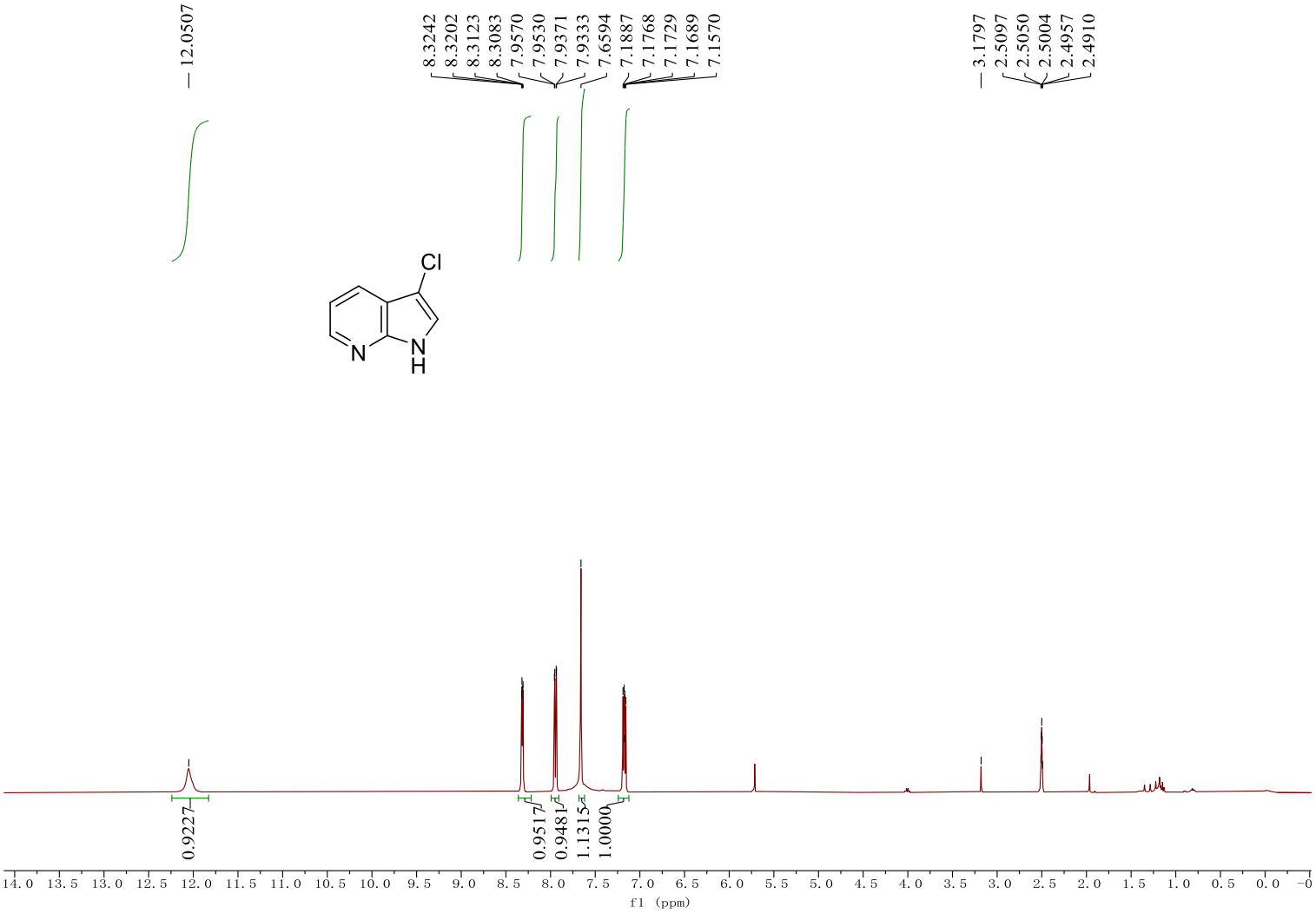
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-2-phenyl-1*H*-indole (2ab)



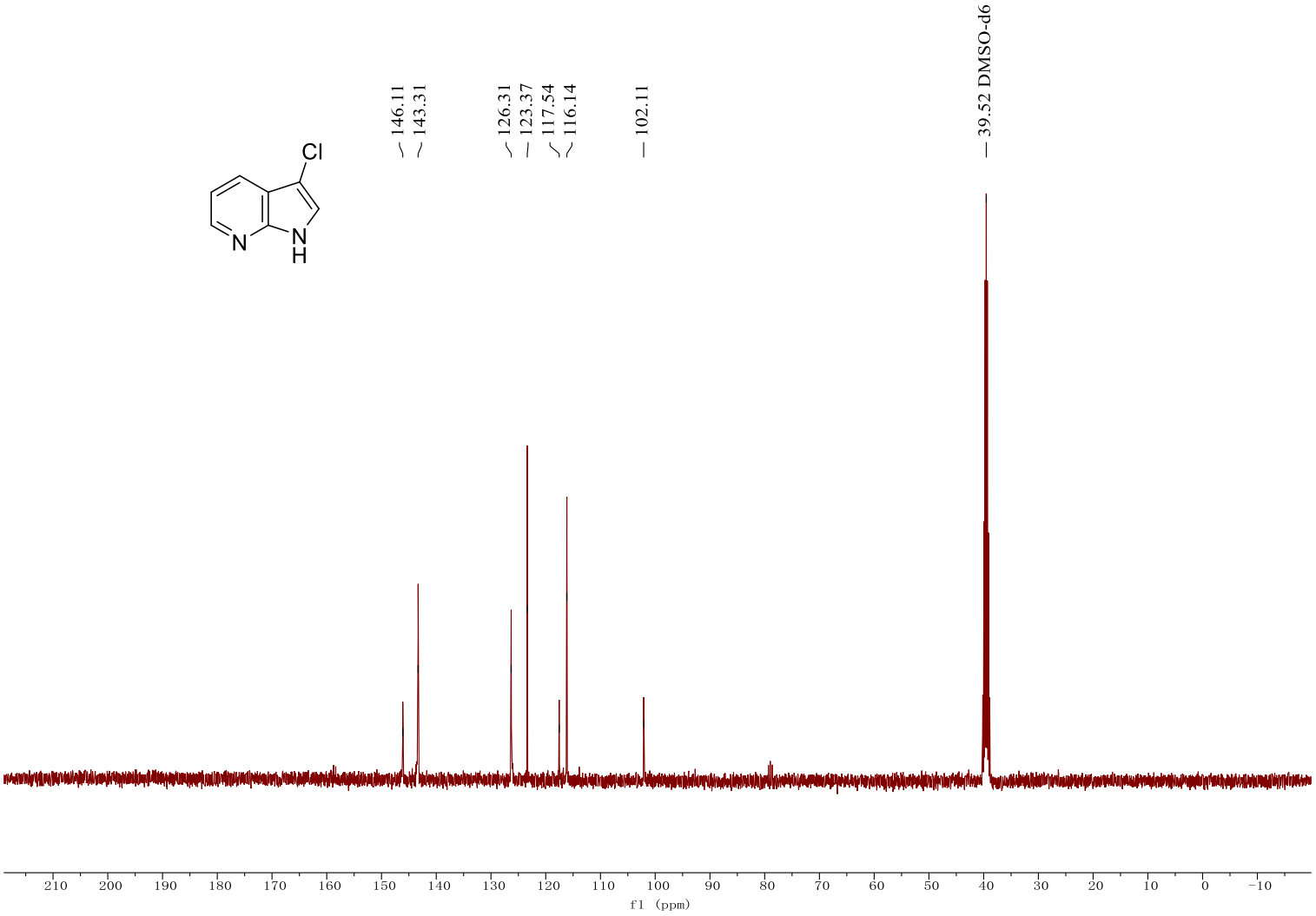
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-2-phenyl-1*H*-indole (2ab)



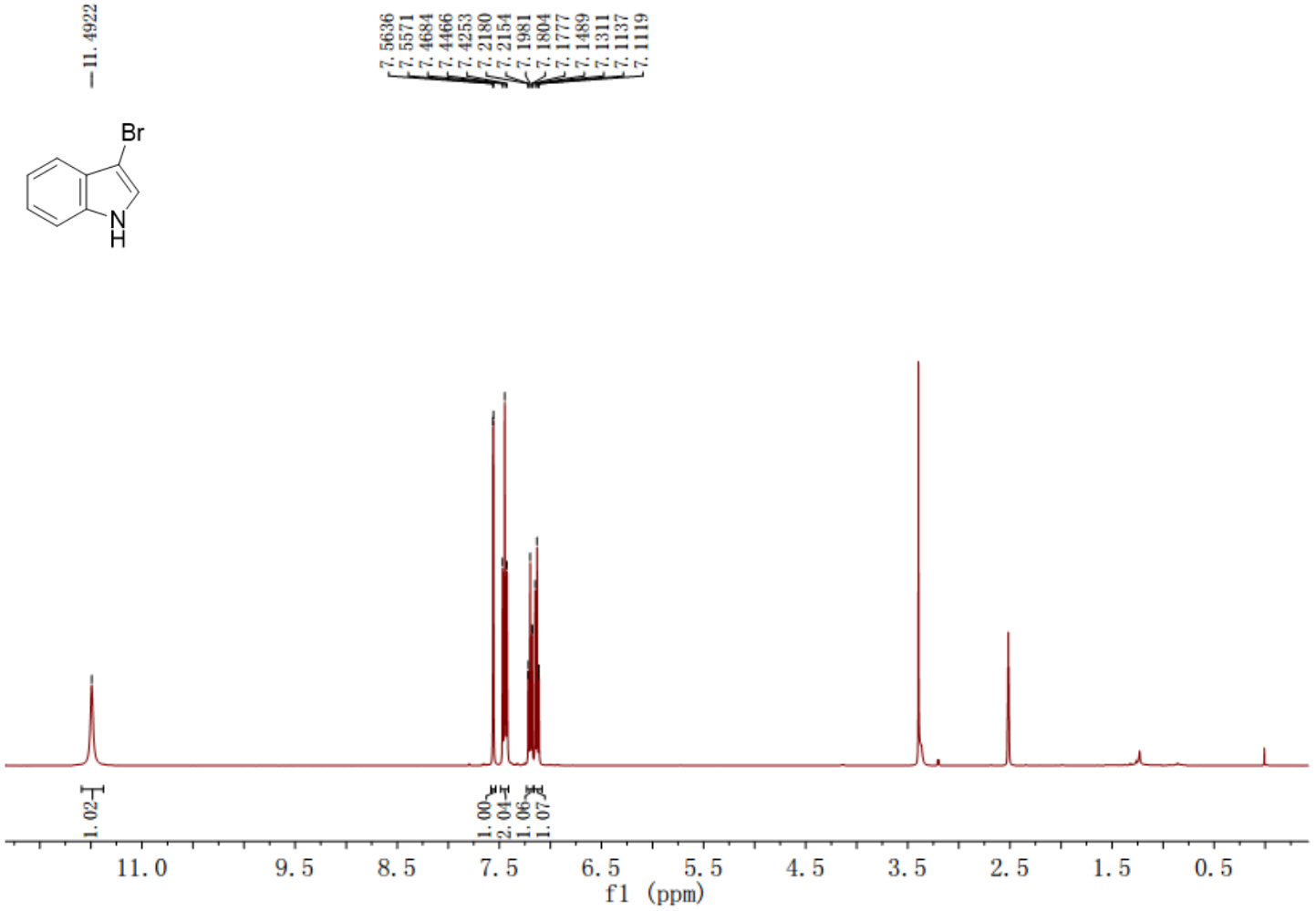
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (2ac)



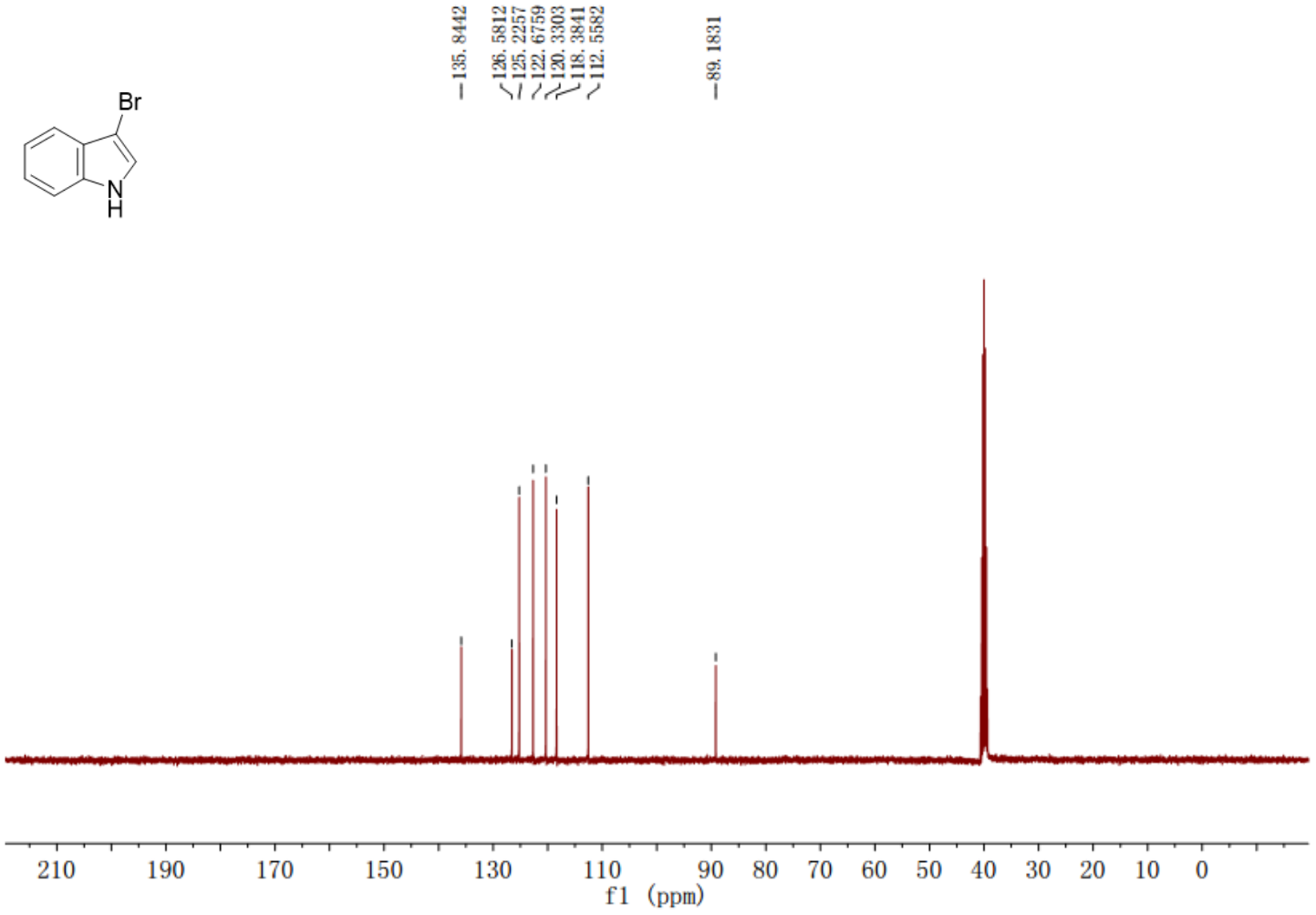
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (2ac)



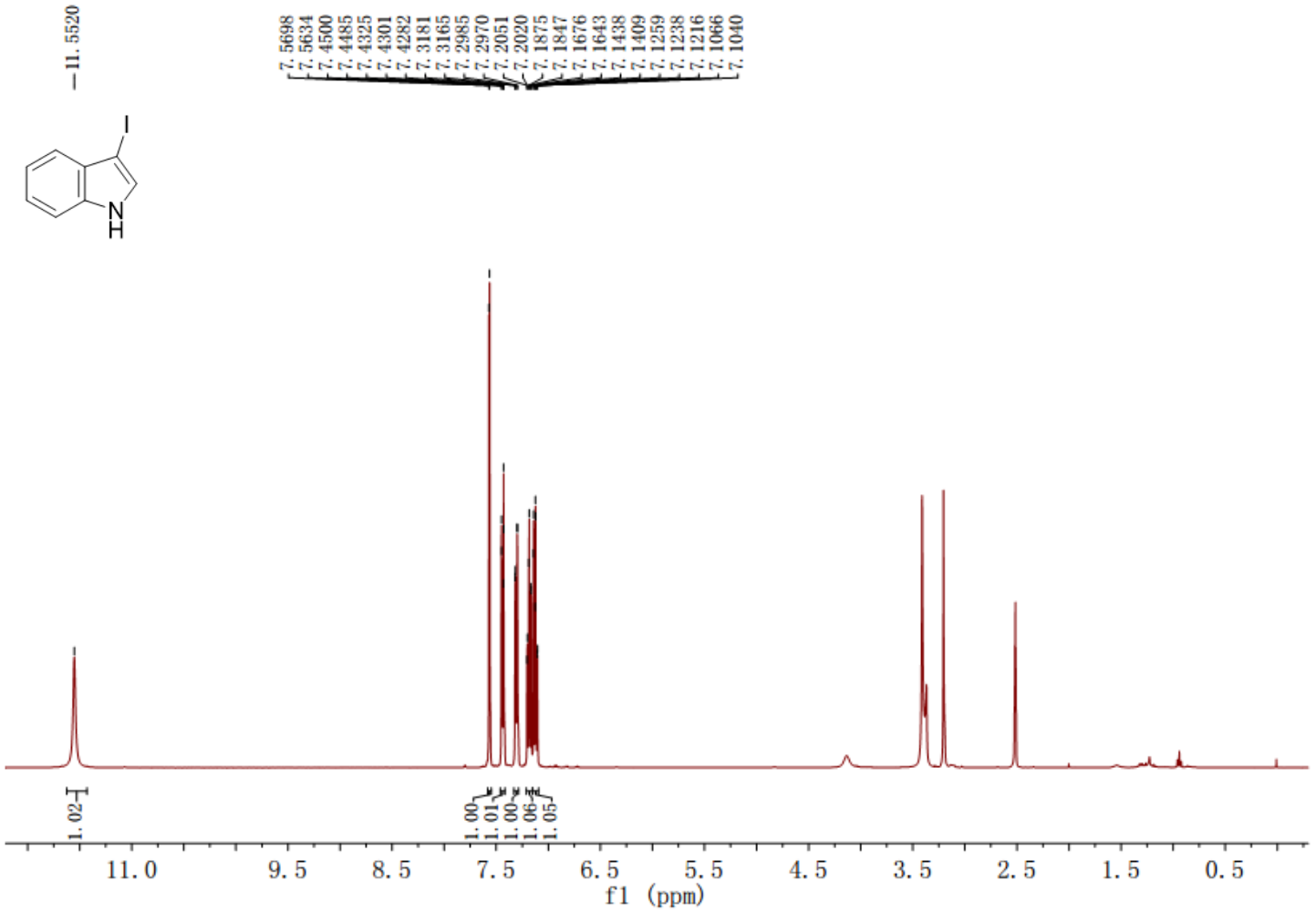
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-bromo-1*H*-indole (2ae)



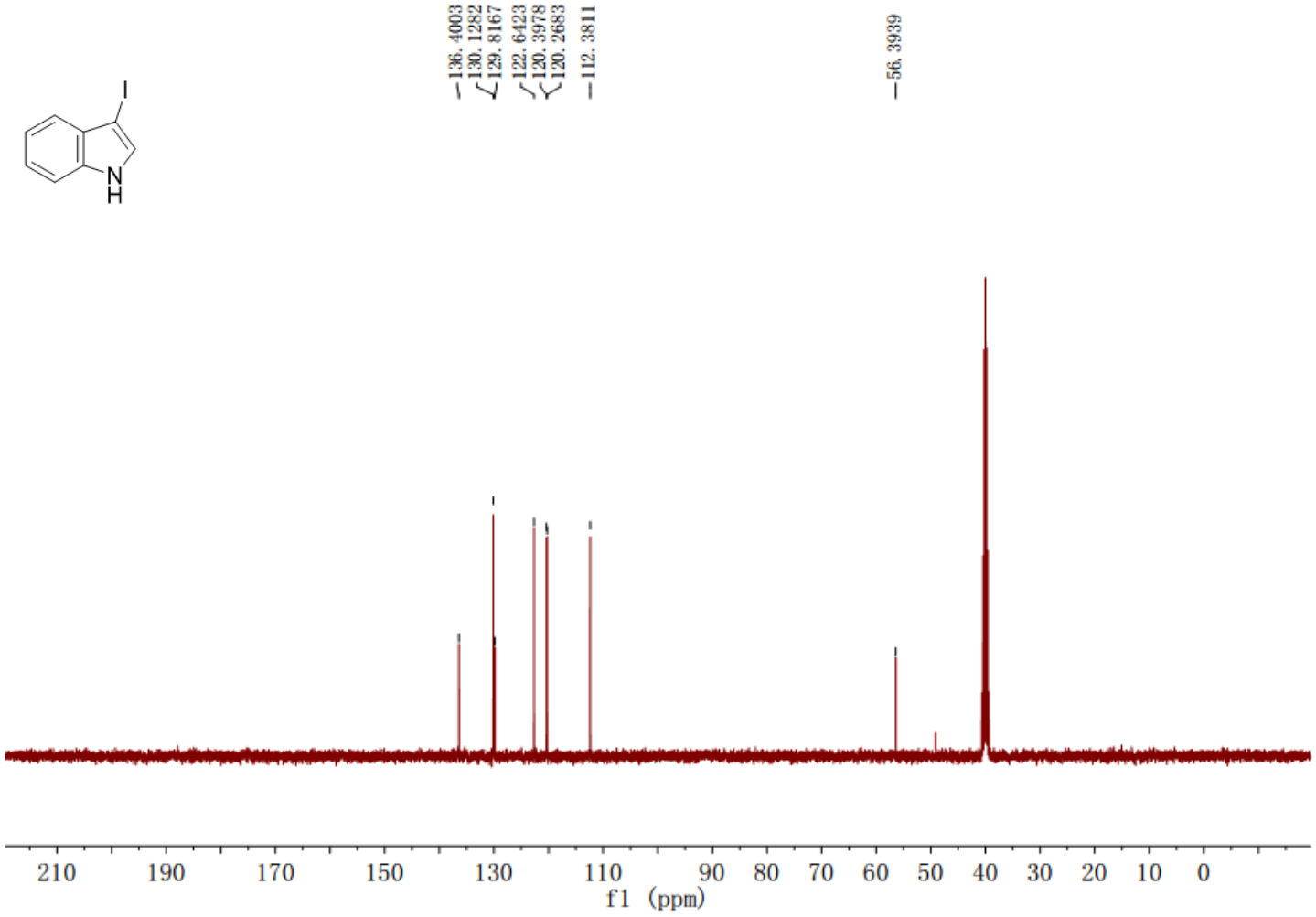
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-bromo-1*H*-indole (2ae)



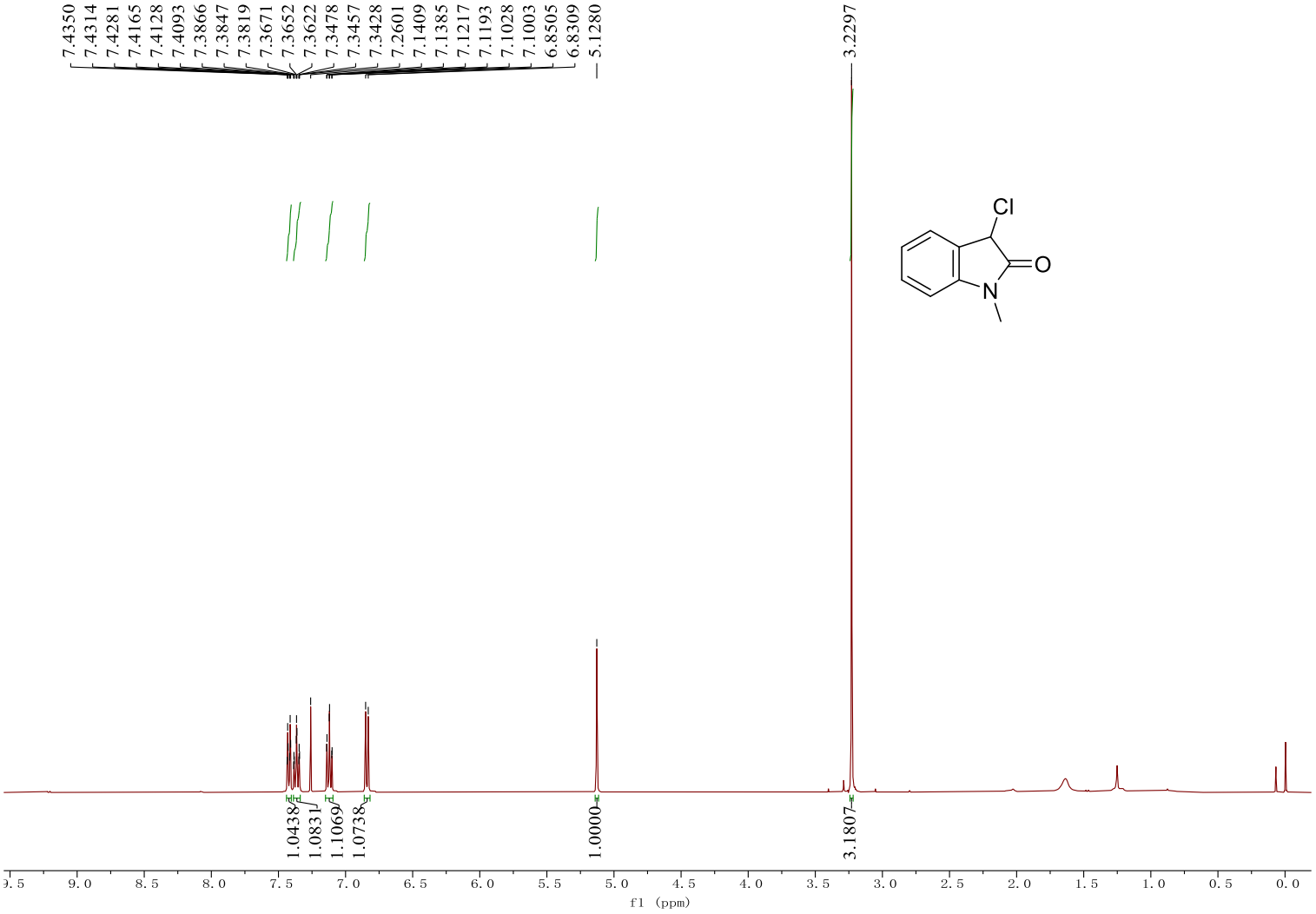
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-iodo-1*H*-indole (2af)



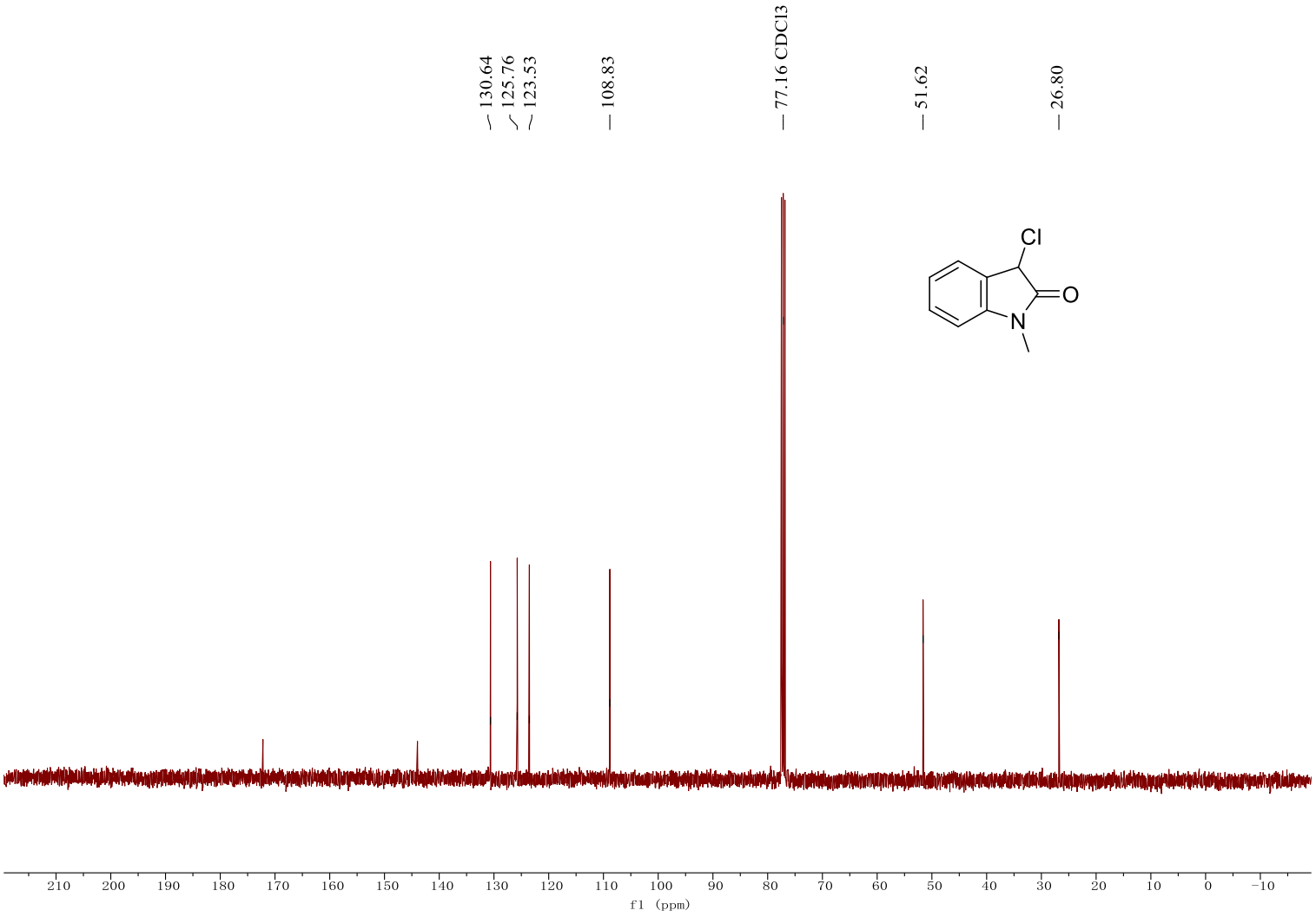
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-iodo-1*H*-indole (2af)



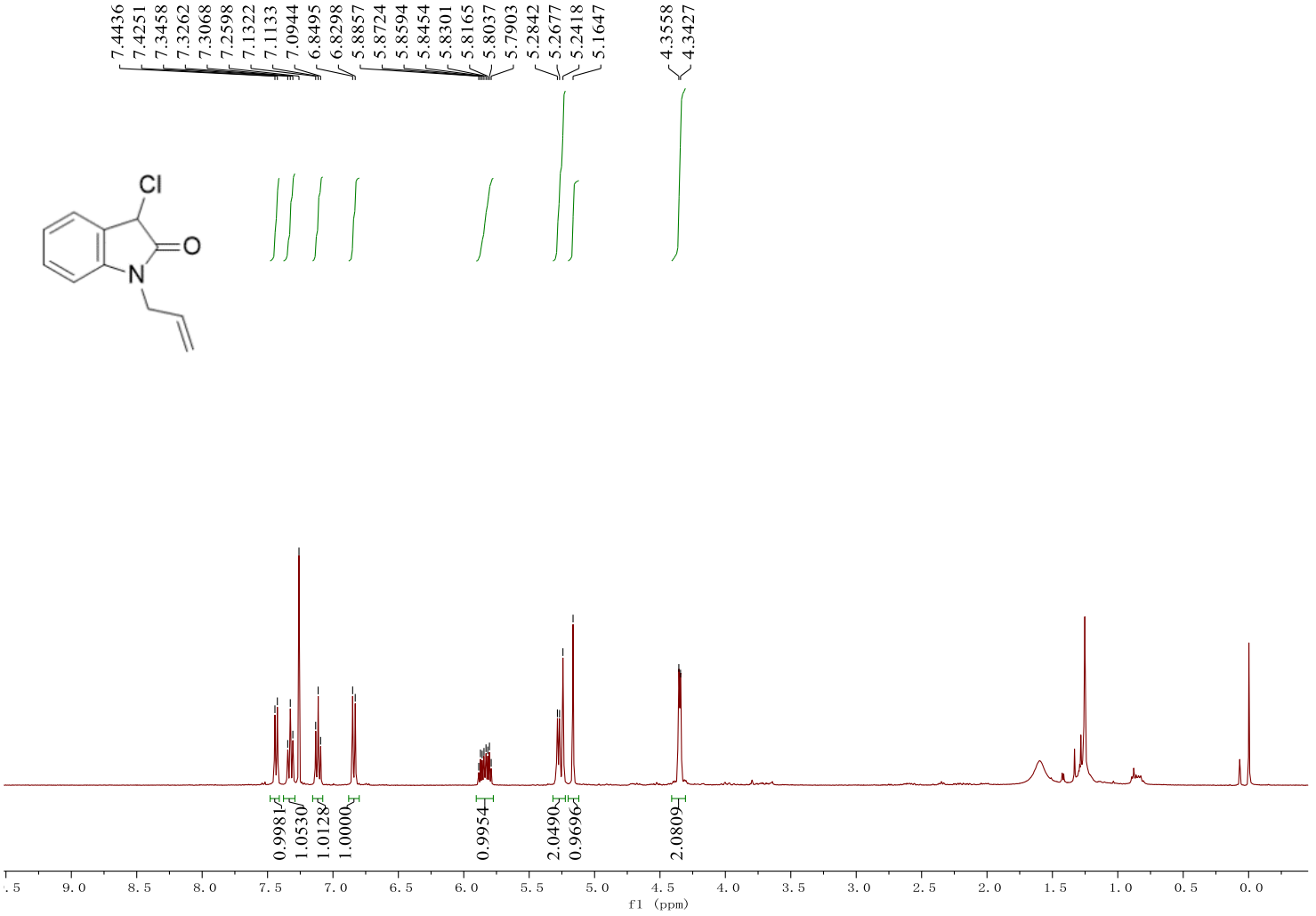
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3-chloro-1-methylindolin-2-one (3a)



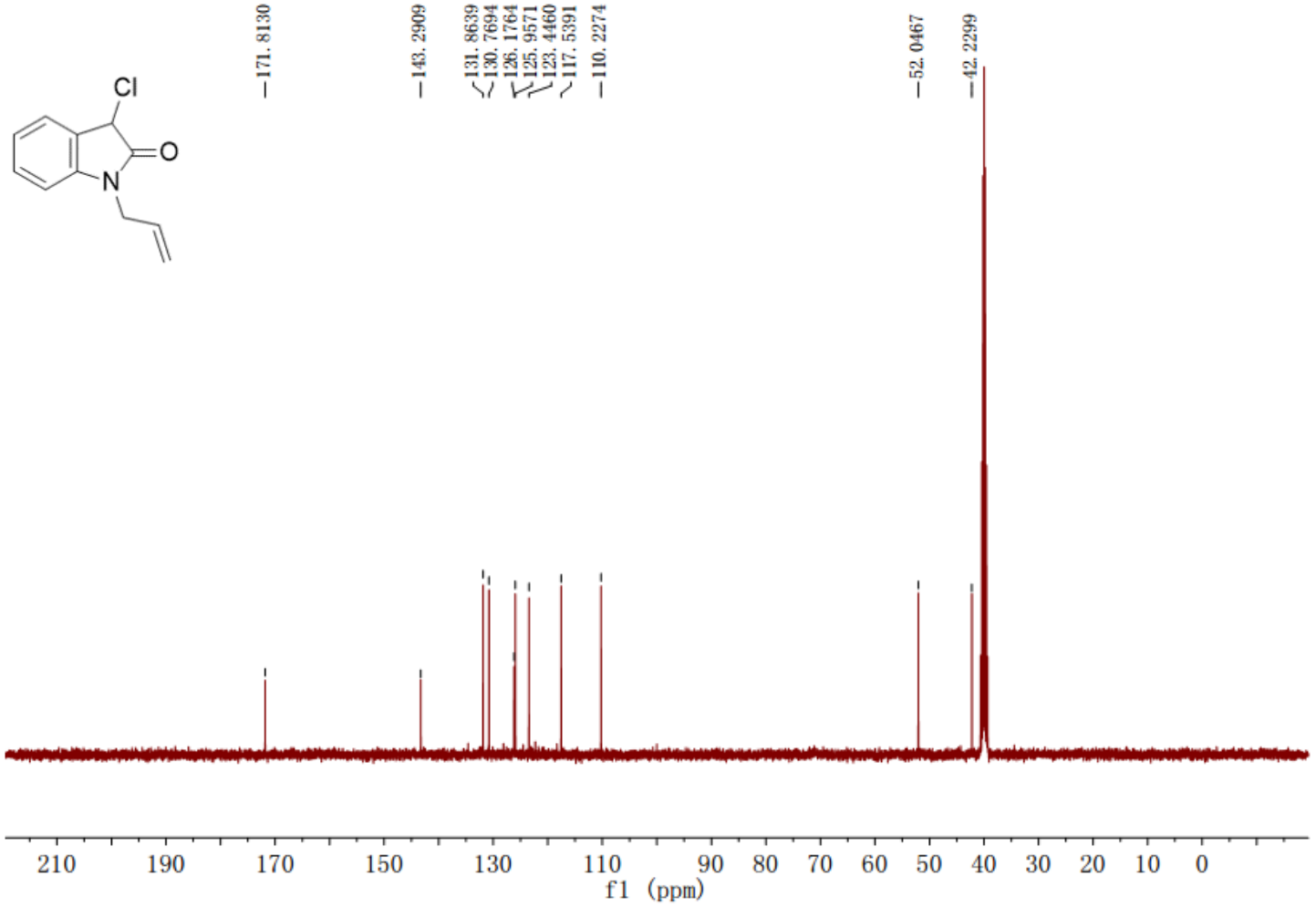
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-1-methylindolin-2-one (3a)



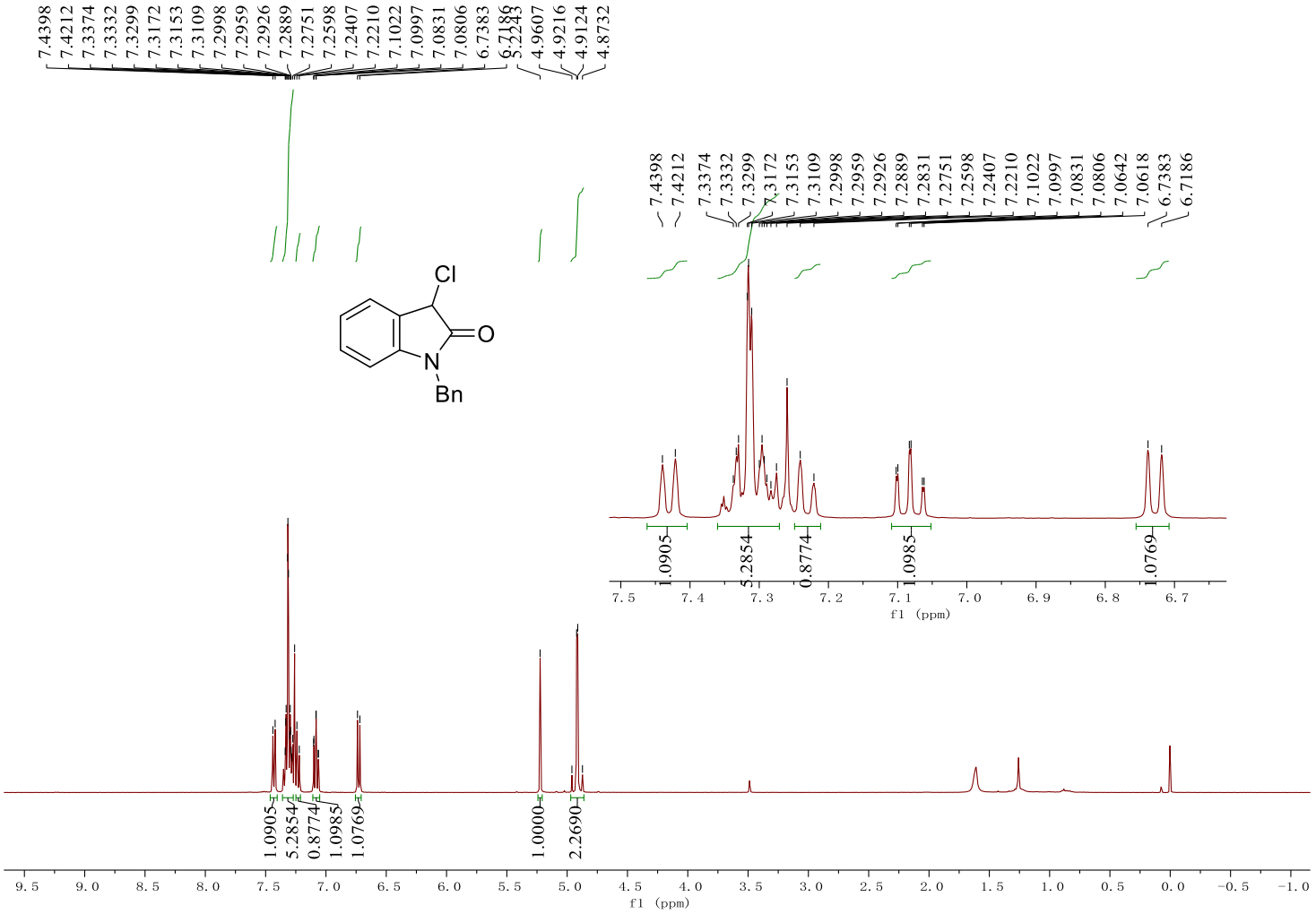
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-allyl-3-chloroindolin-2-one (3b)



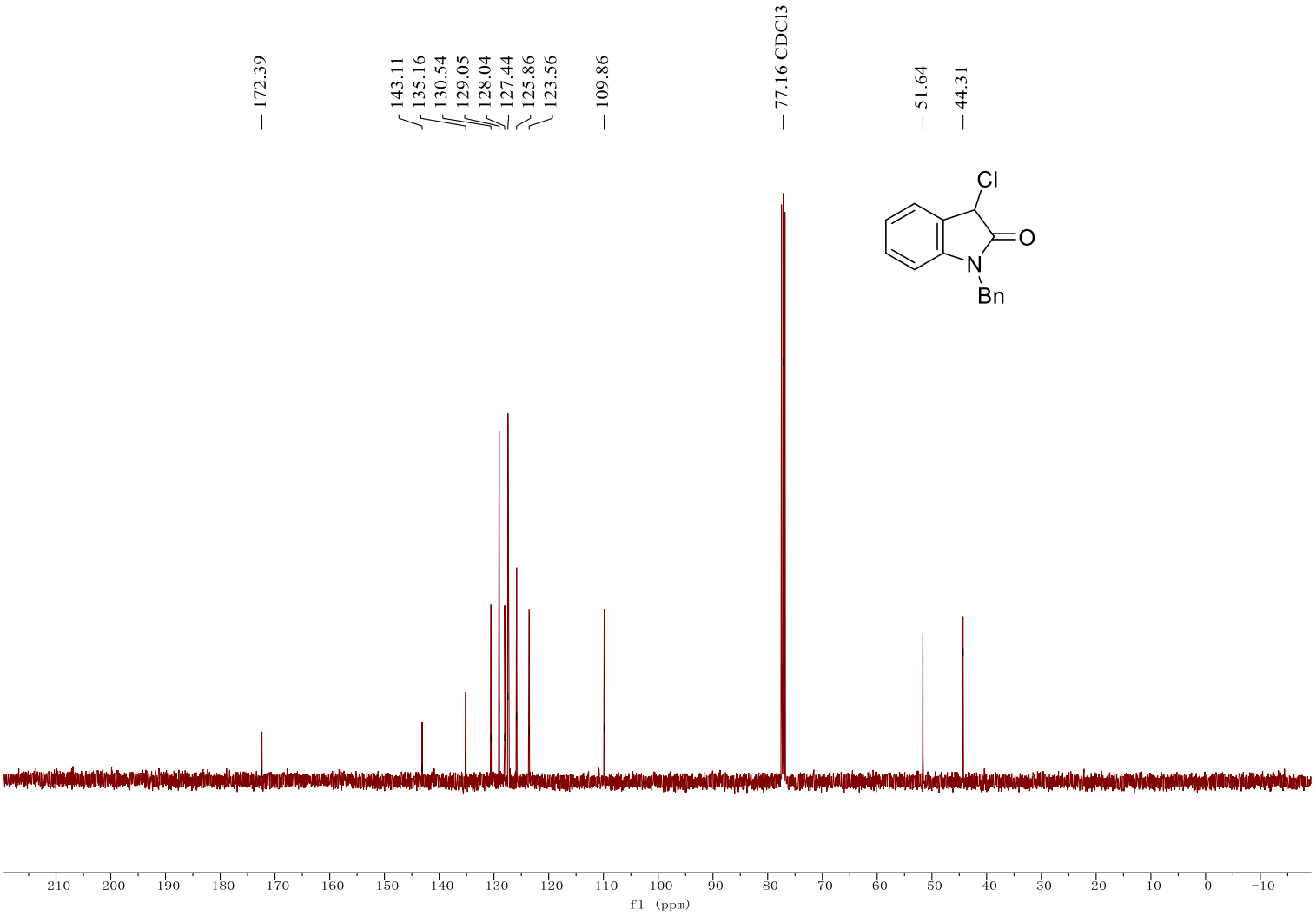
^{13}C NMR (101MHz, DMSO-d_6) spectra of 1-allyl-3-chloroindolin-2-one (3b)



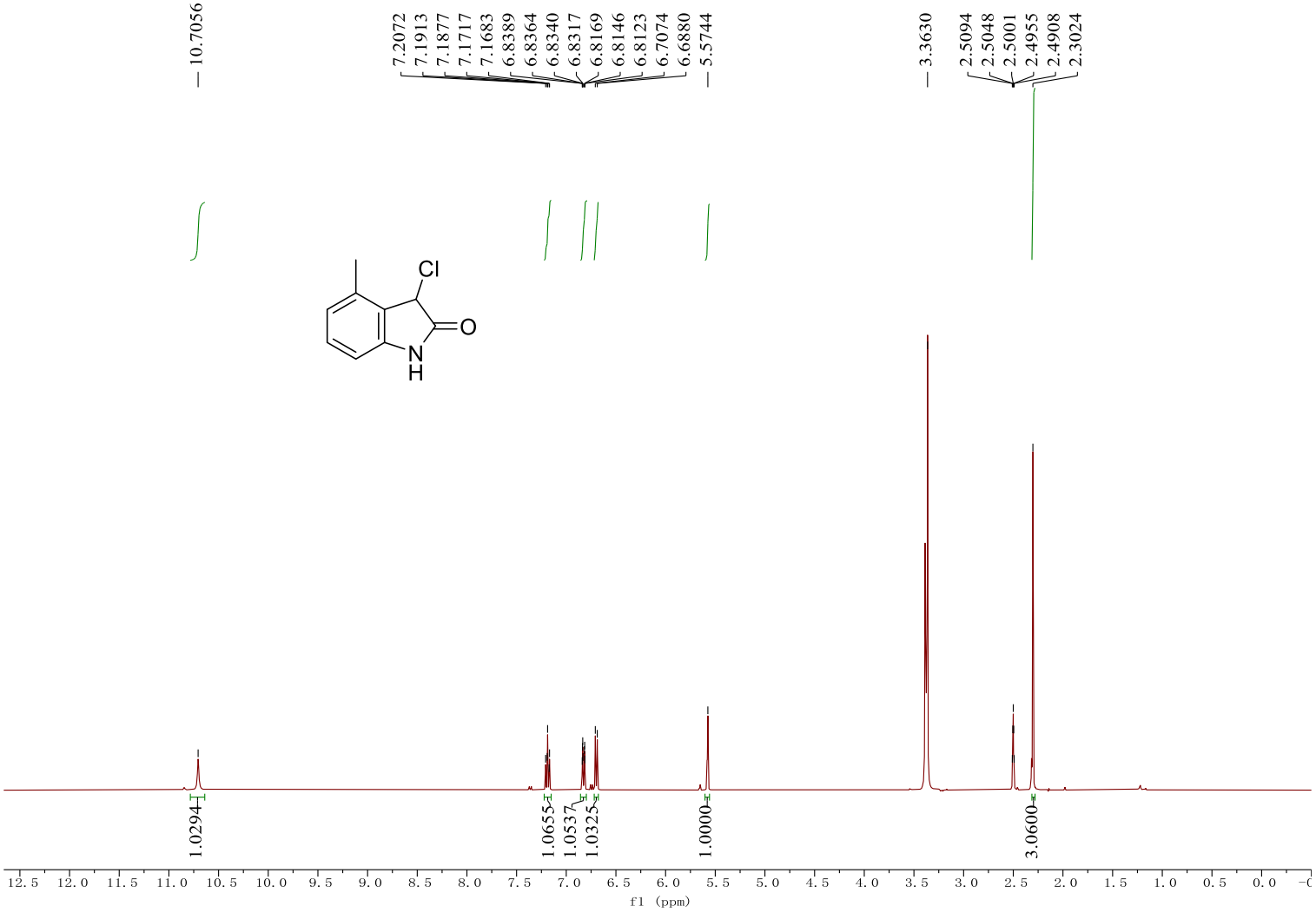
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-benzyl-3-chloroindolin-2-one (3c)



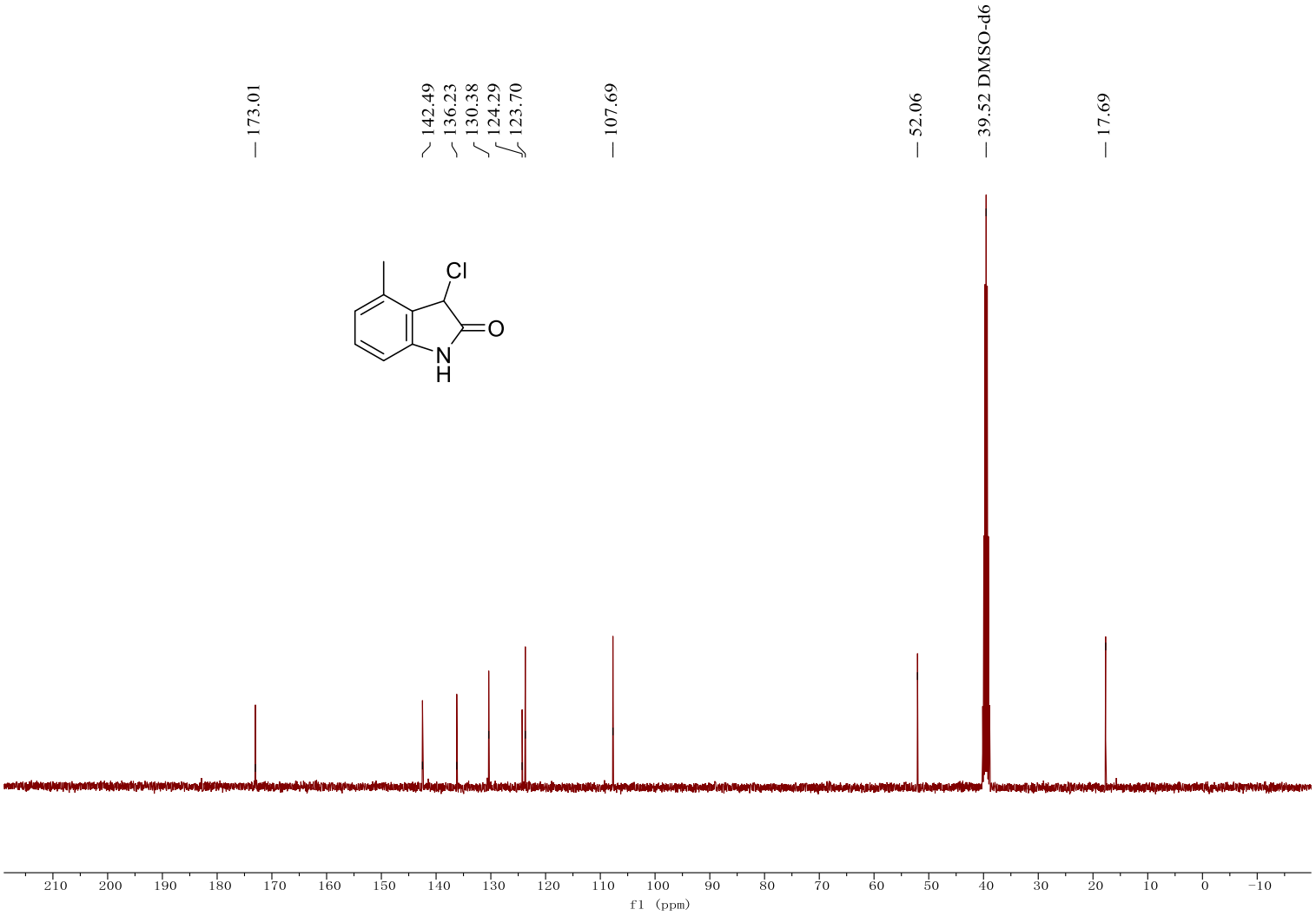
^{13}C NMR (101MHz, $CDCl_3$) spectra of 1-benzyl-3-chloroindolin-2-one (3c)



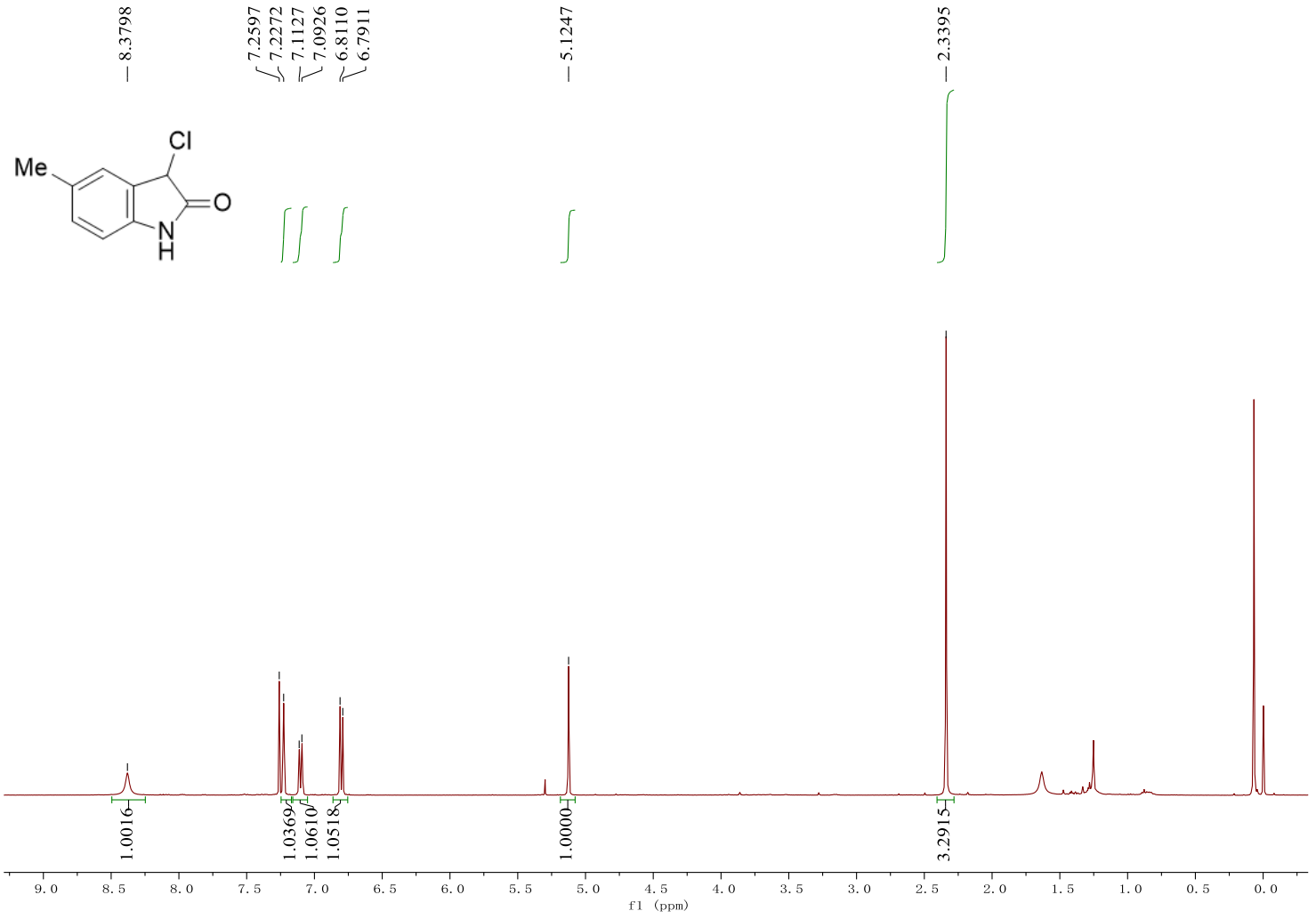
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-4-methylindolin-2-one (3d)



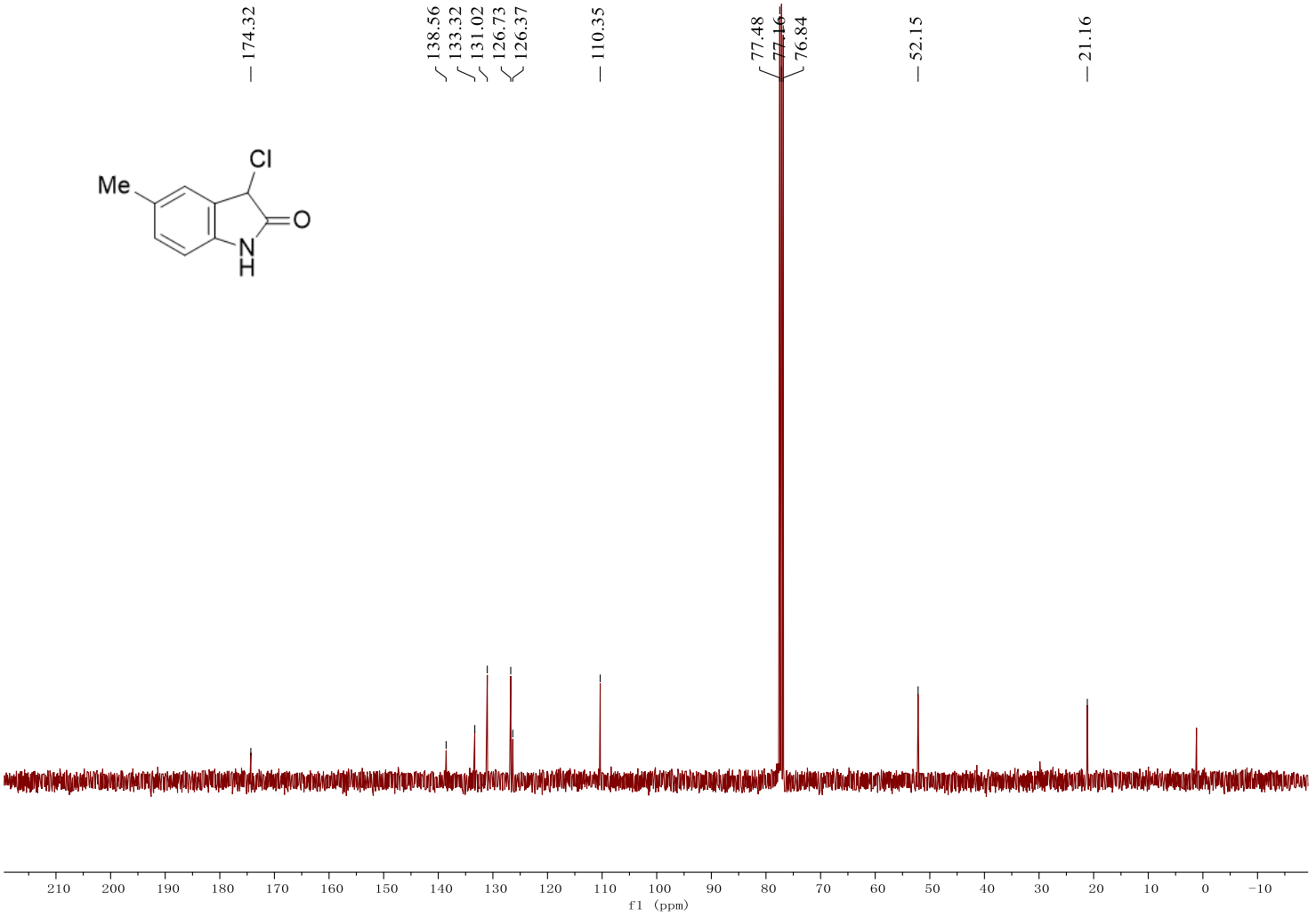
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-4-methylindolin-2-one (3d)



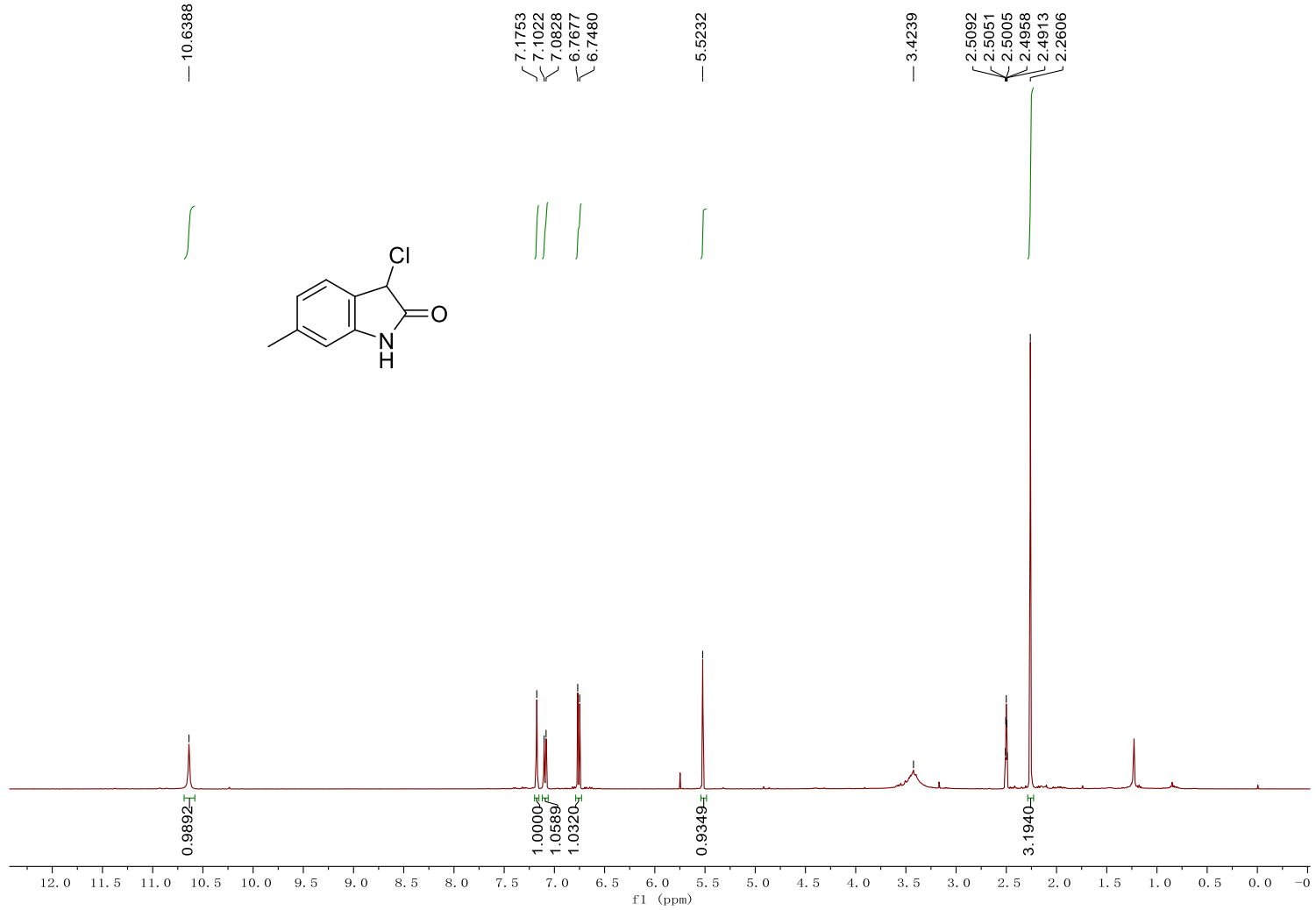
^{1}H NMR (400MHz,$CDCl_3$) spectra of 3-chloro-5-methylindolin-2-one (3e)



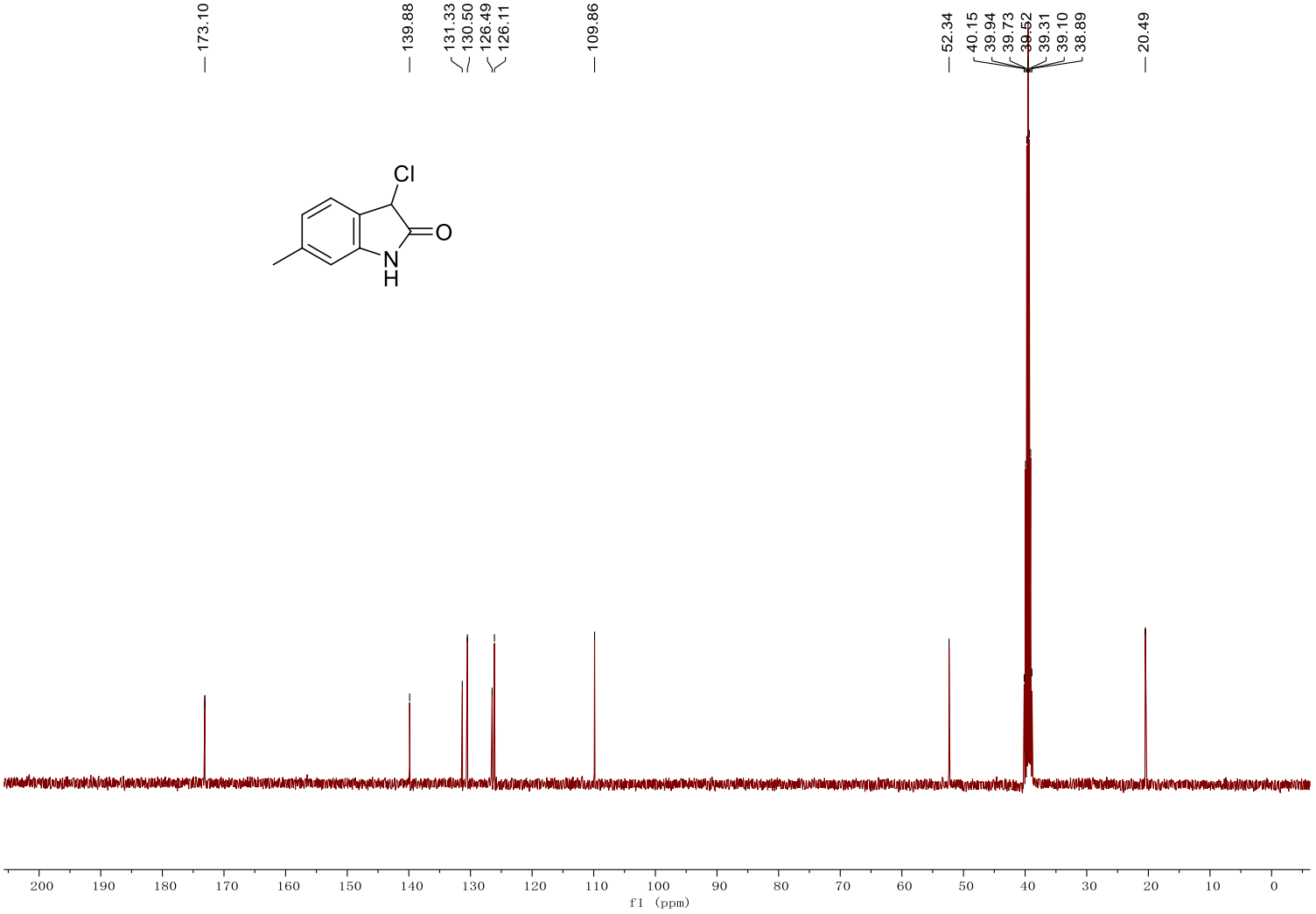
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-chloro-5-methylindolin-2-one (3e)



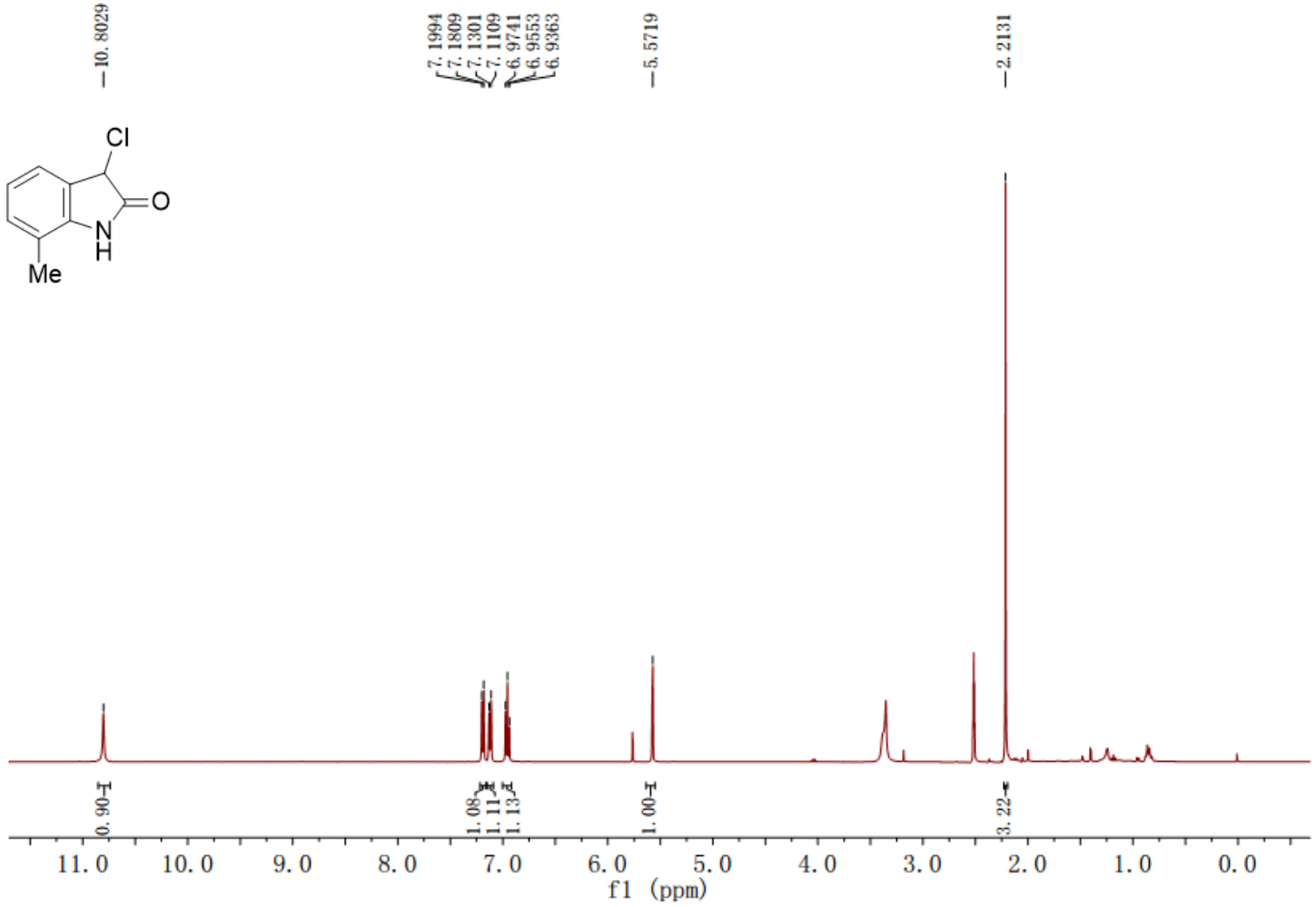
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-6-methylindolin-2-one (3f)



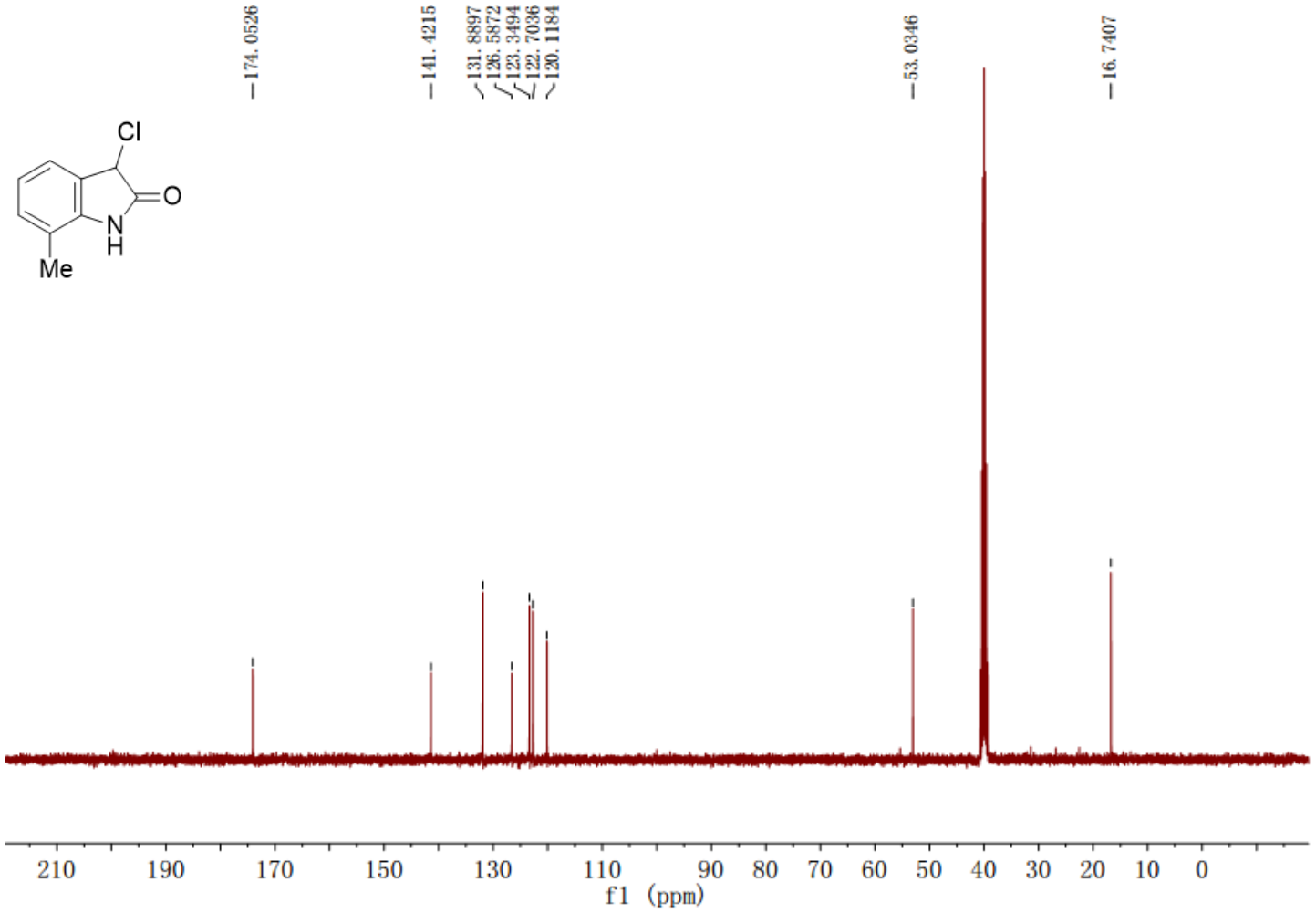
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-6-methylindolin-2-one (3f)



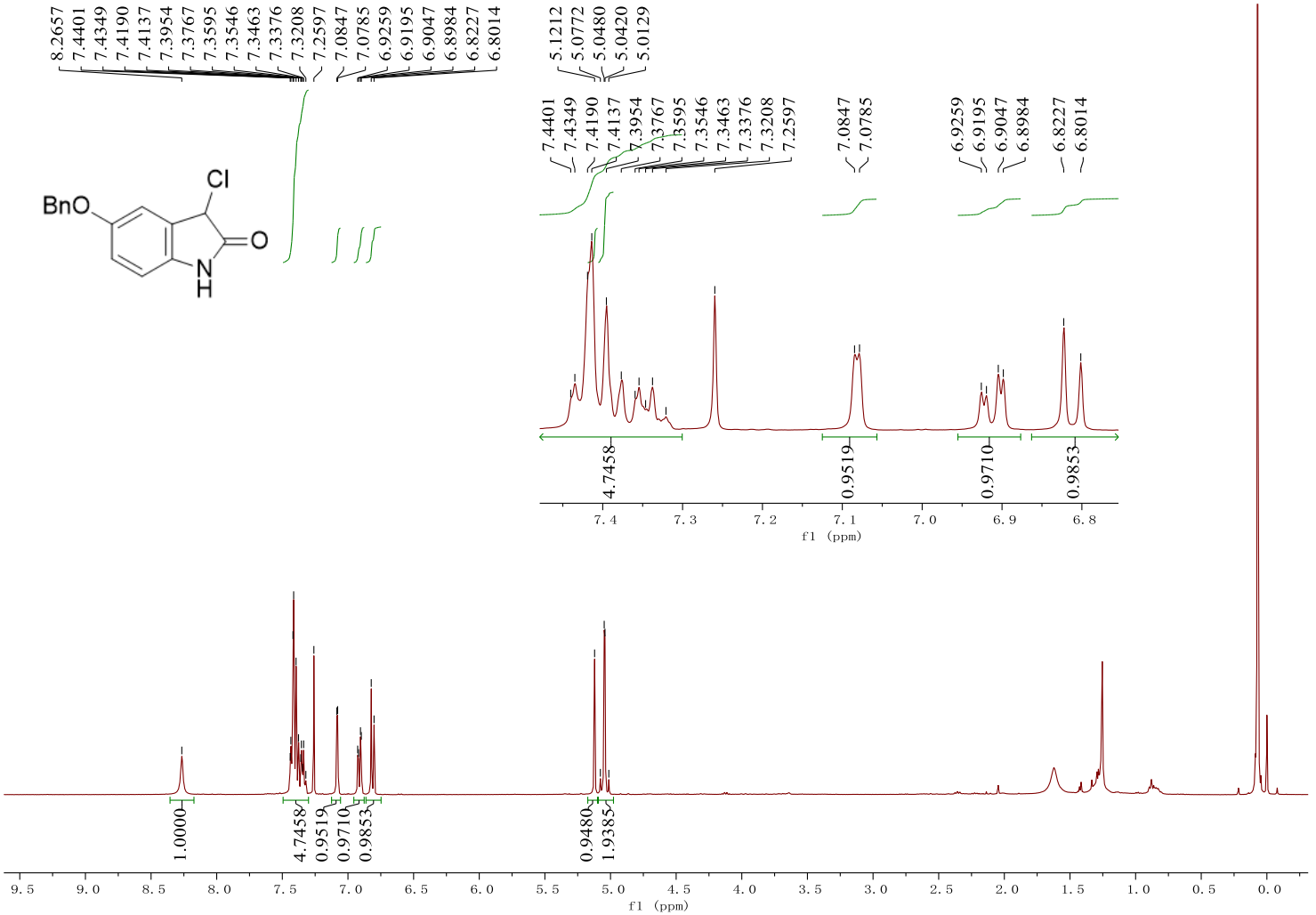
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-7-methylindolin-2-one (3g)



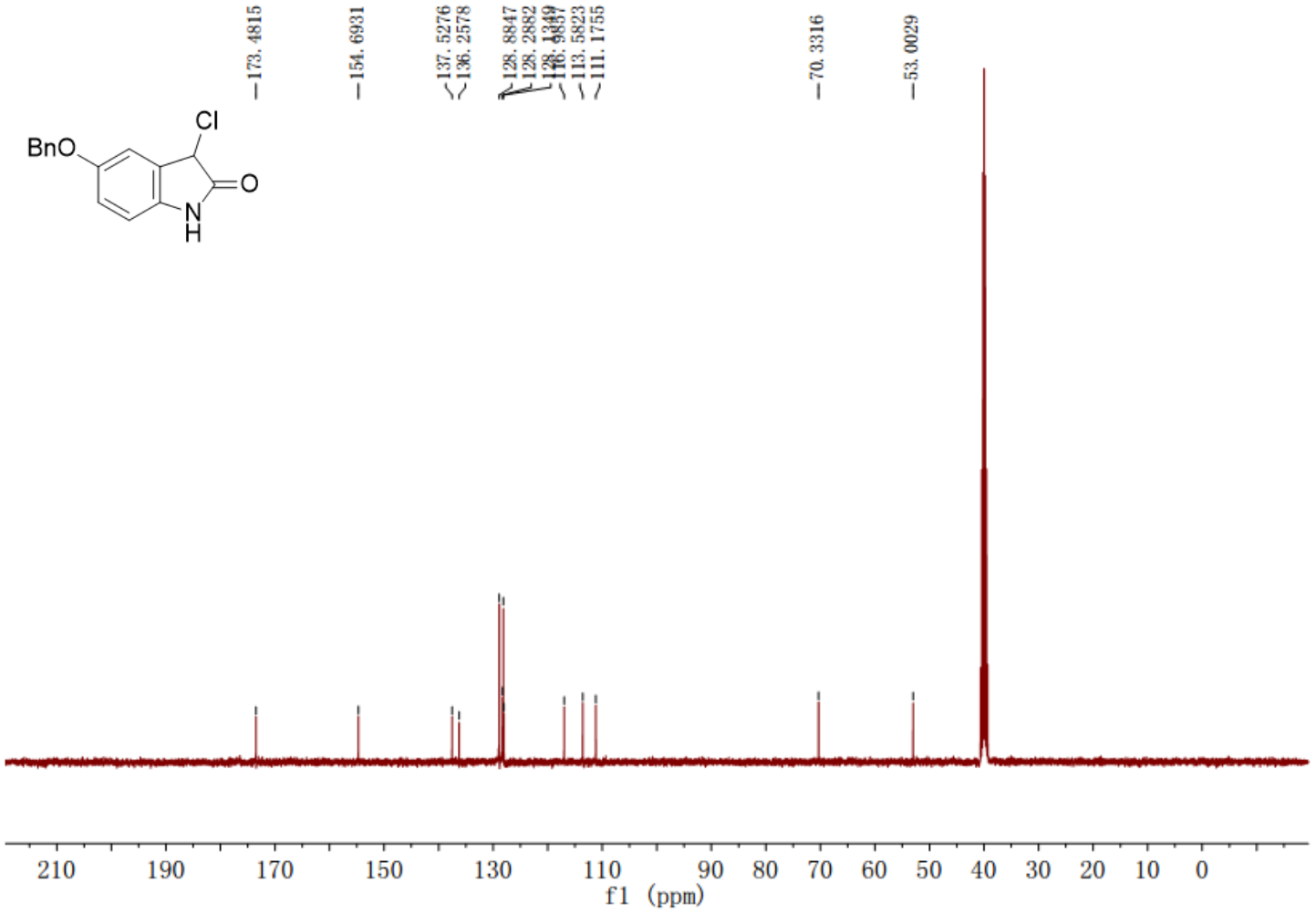
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-7-methylindolin-2-one (3g)



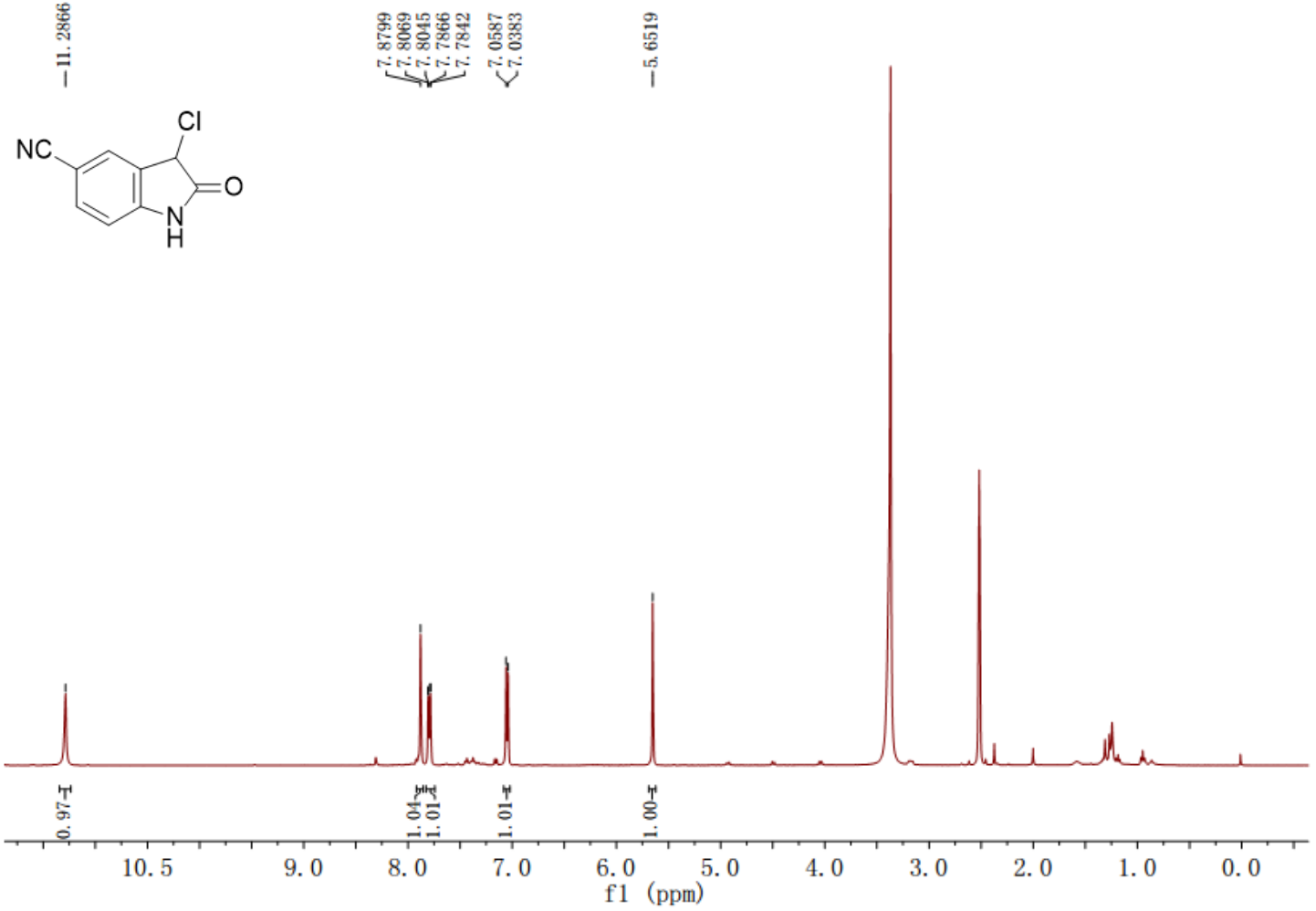
^{1}H NMR (400MHz, $CDCl_3$) spectra of 5-(benzyloxy)-3-chloroindolin-2-one (3h)



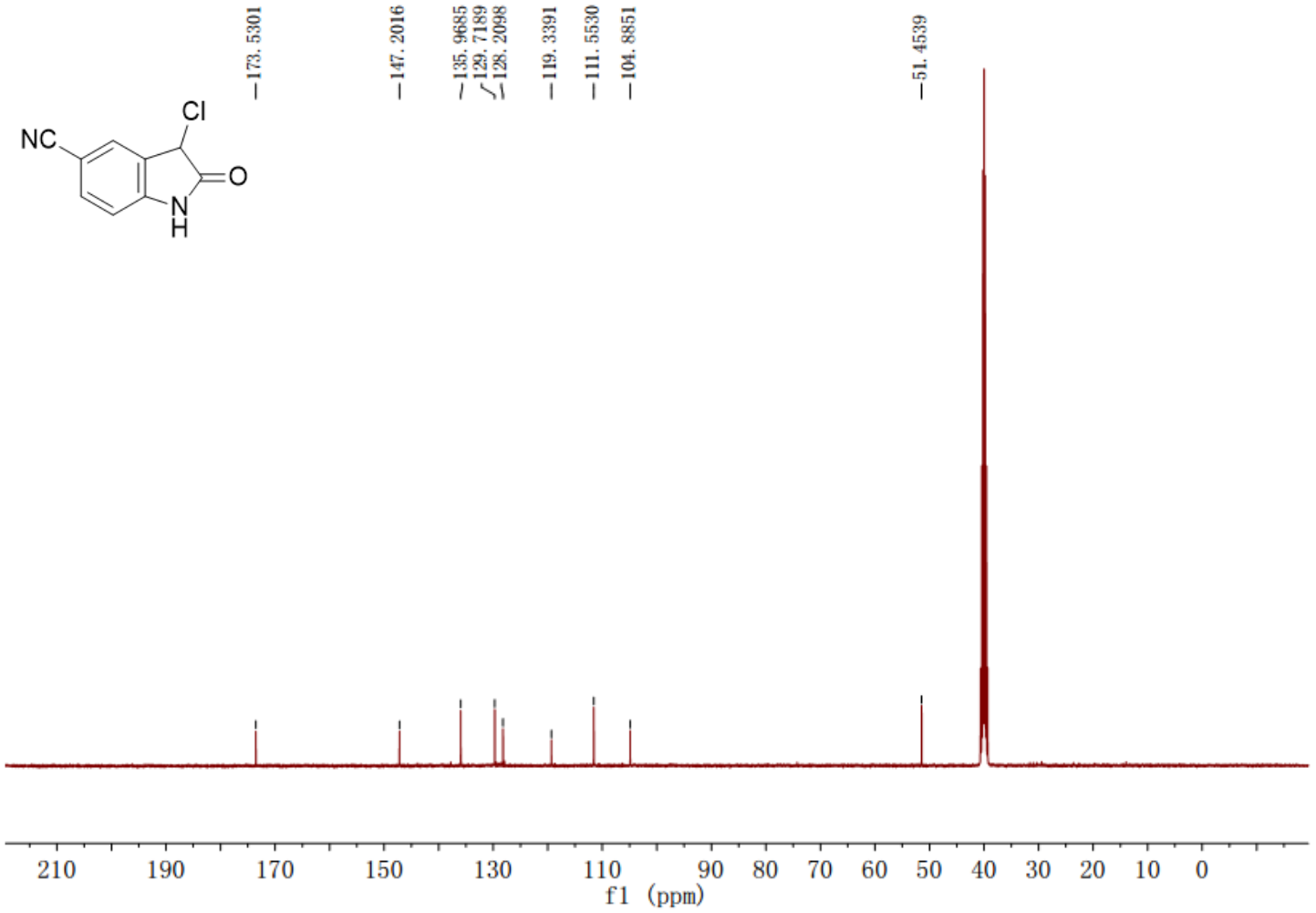
^{13}C NMR (101MHz, DMSO-d_6) spectra of 5-(benzyloxy)-3-chloroindolin-2-one (3h)



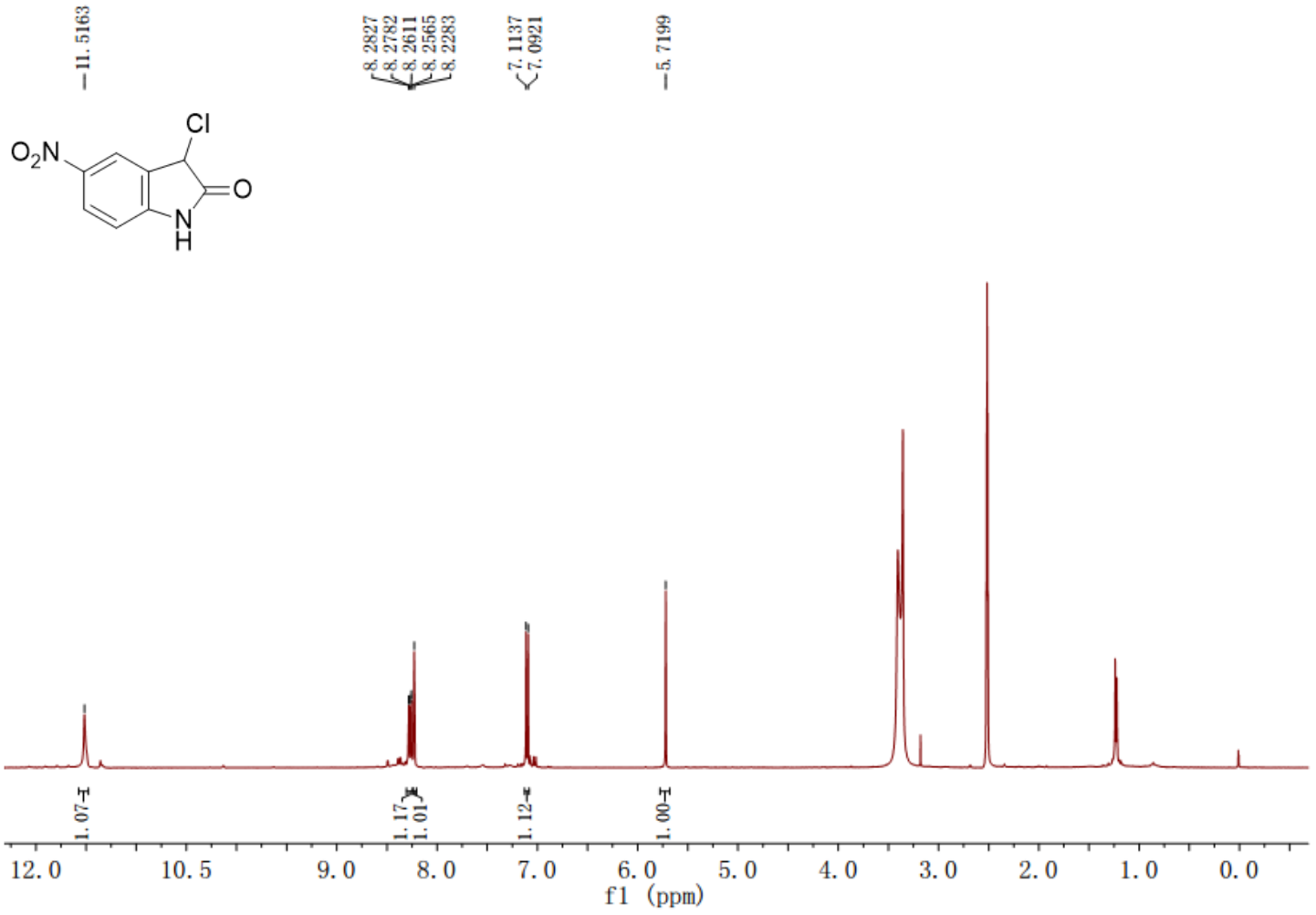
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-2-oxoindoline-5-carbonitrile (3i)



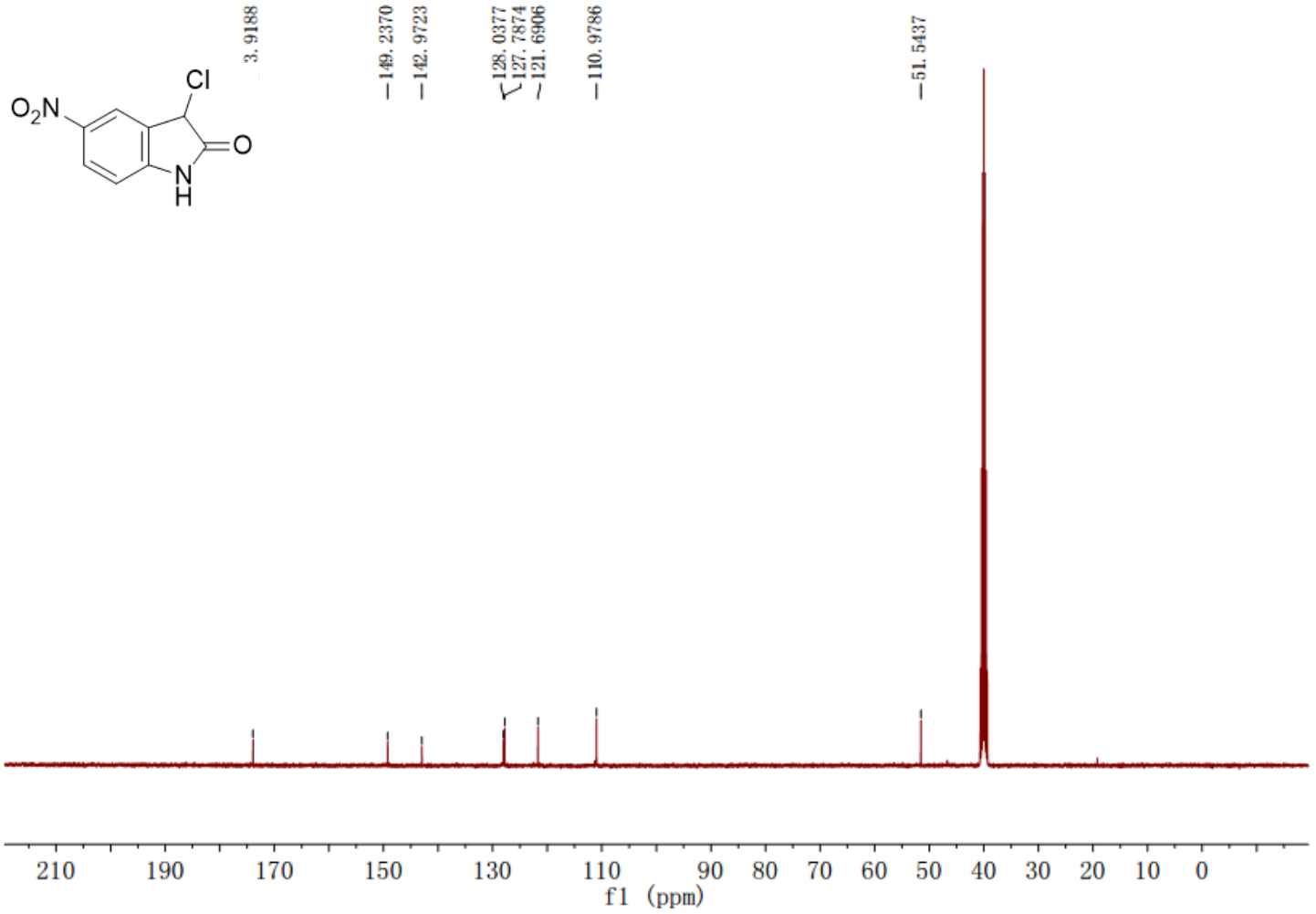
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-2-oxoindoline-5-carbonitrile (3i)



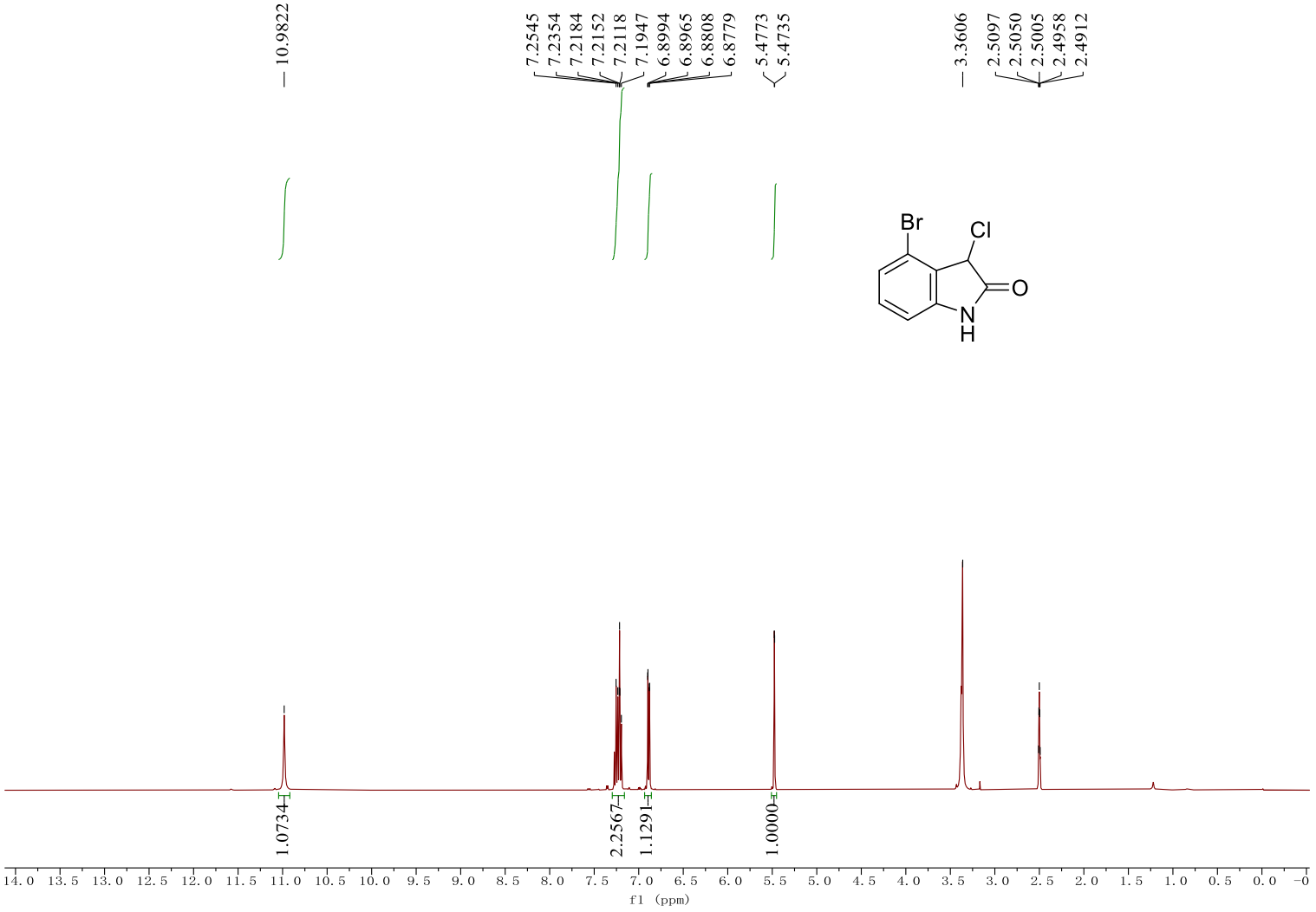
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-5-nitroindolin-2-one (3j)



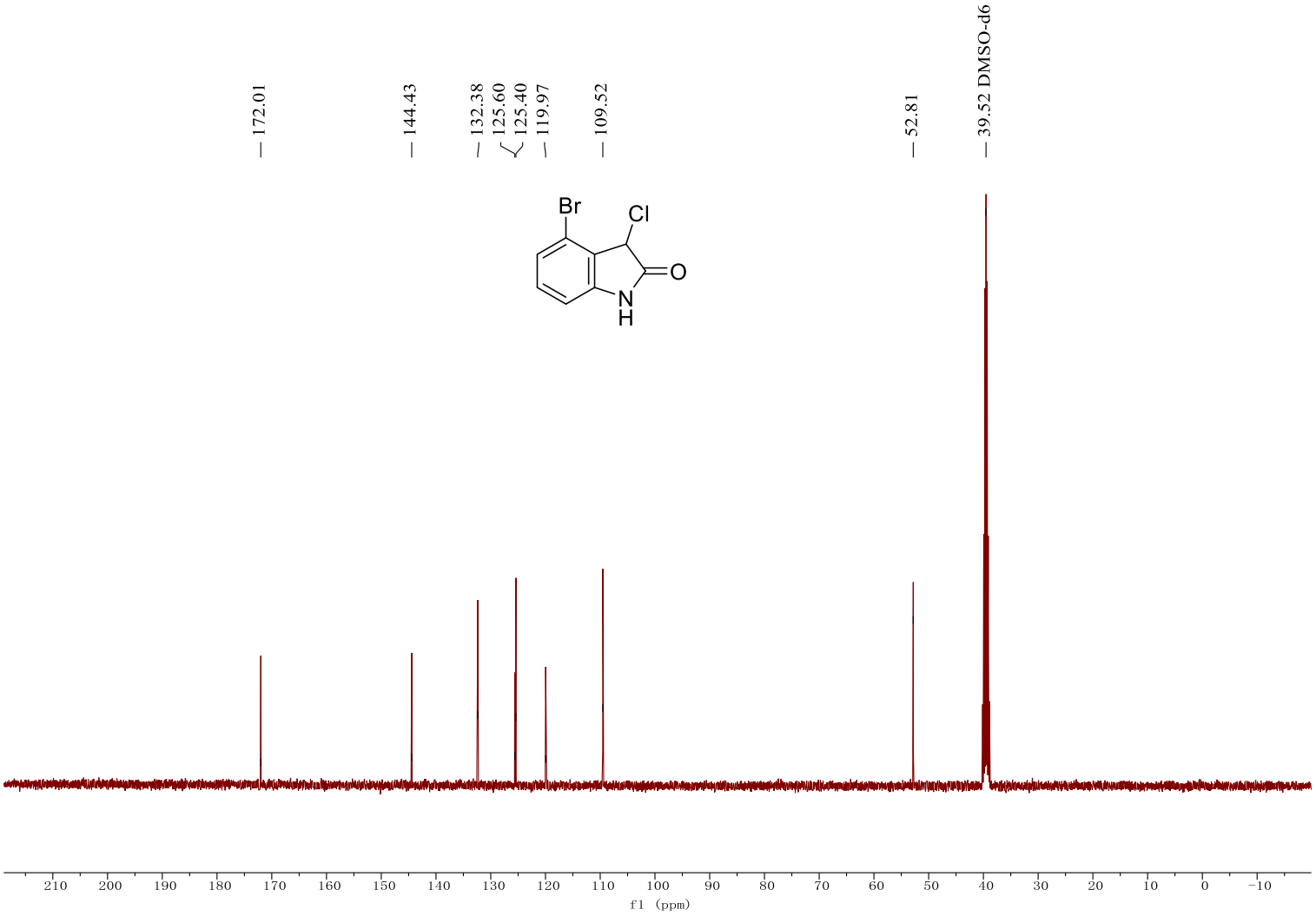
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-5-nitroindolin-2-one (3j)



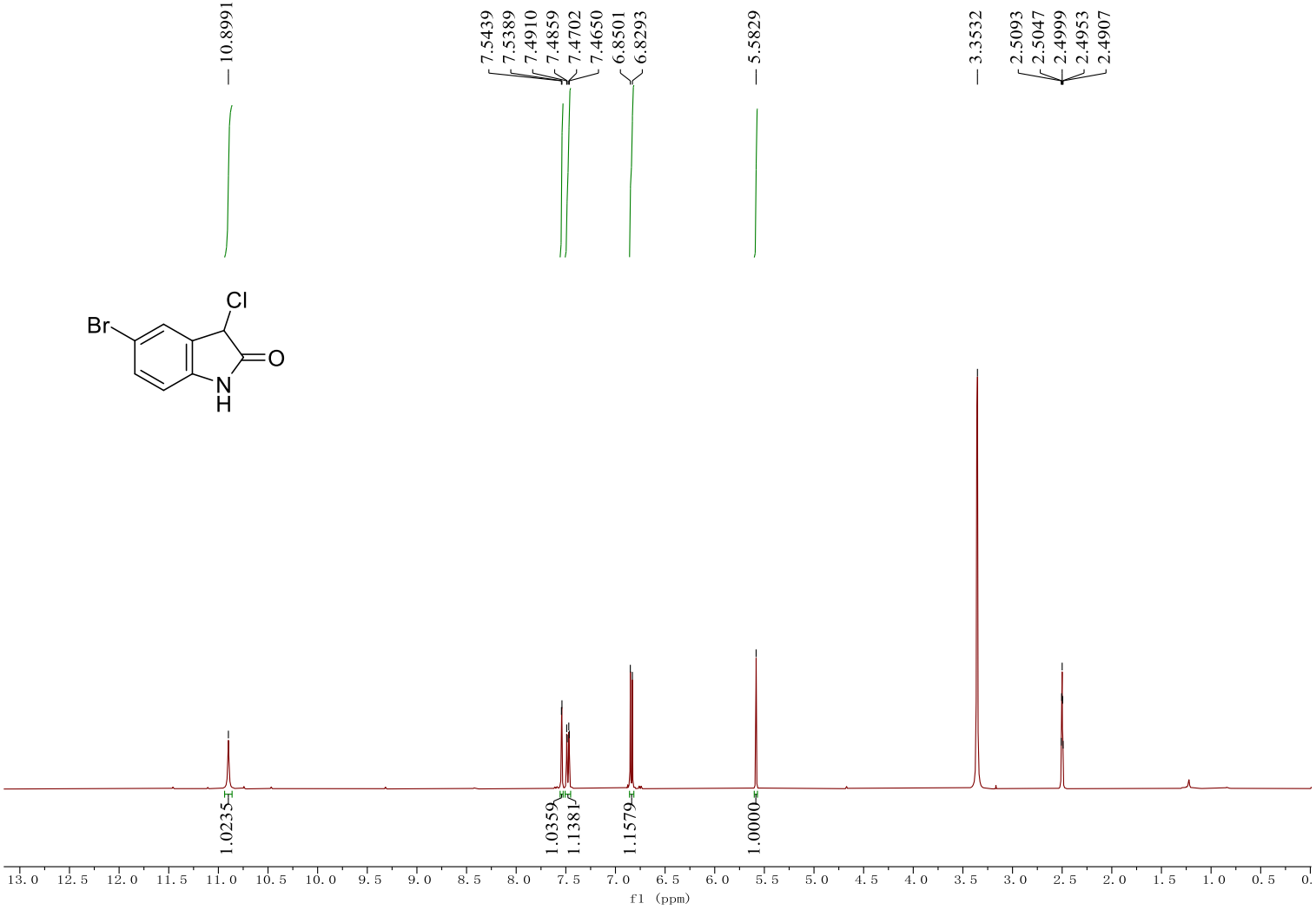
^{1}H NMR (400MHz, DMSO-d_6) spectra of 4-bromo-3-chloroindolin-2-one (3k)



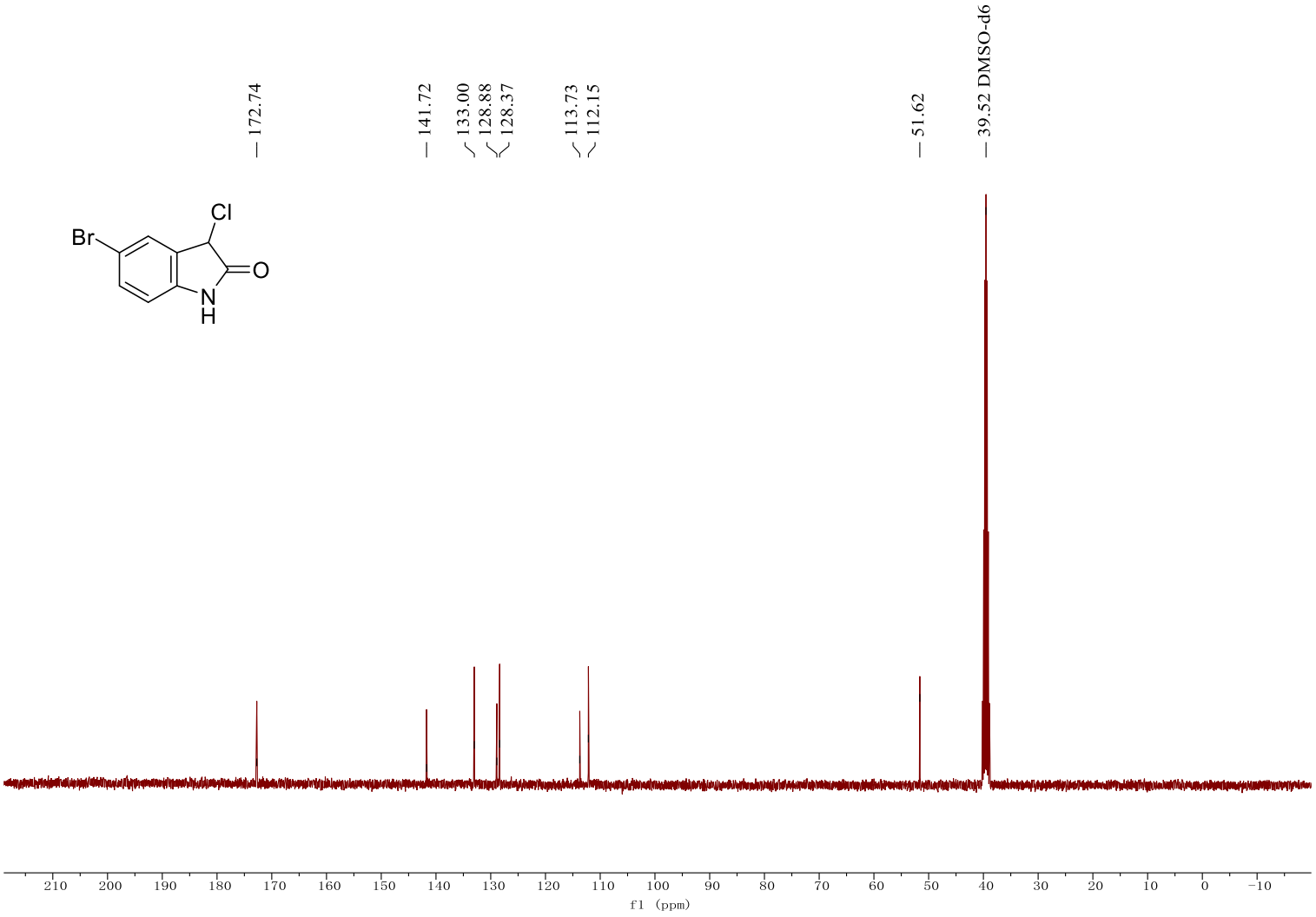
^{13}C NMR (101MHz, DMSO-d_6) spectra of 4-bromo-3-chloroindolin-2-one (3k)



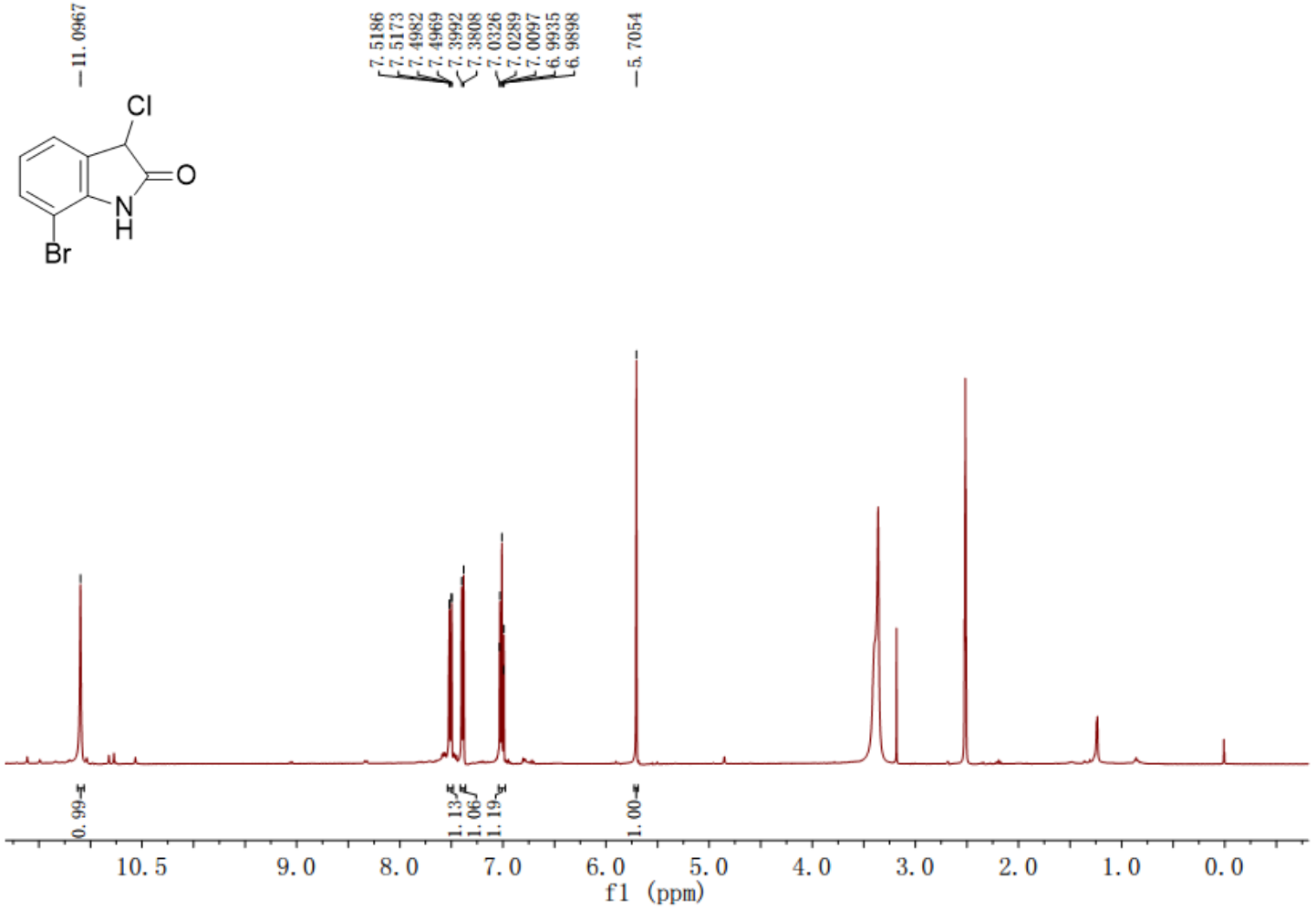
^{1}H NMR (400MHz, DMSO-d_6) spectra of 5-bromo-3-chloroindolin-2-one (3l)



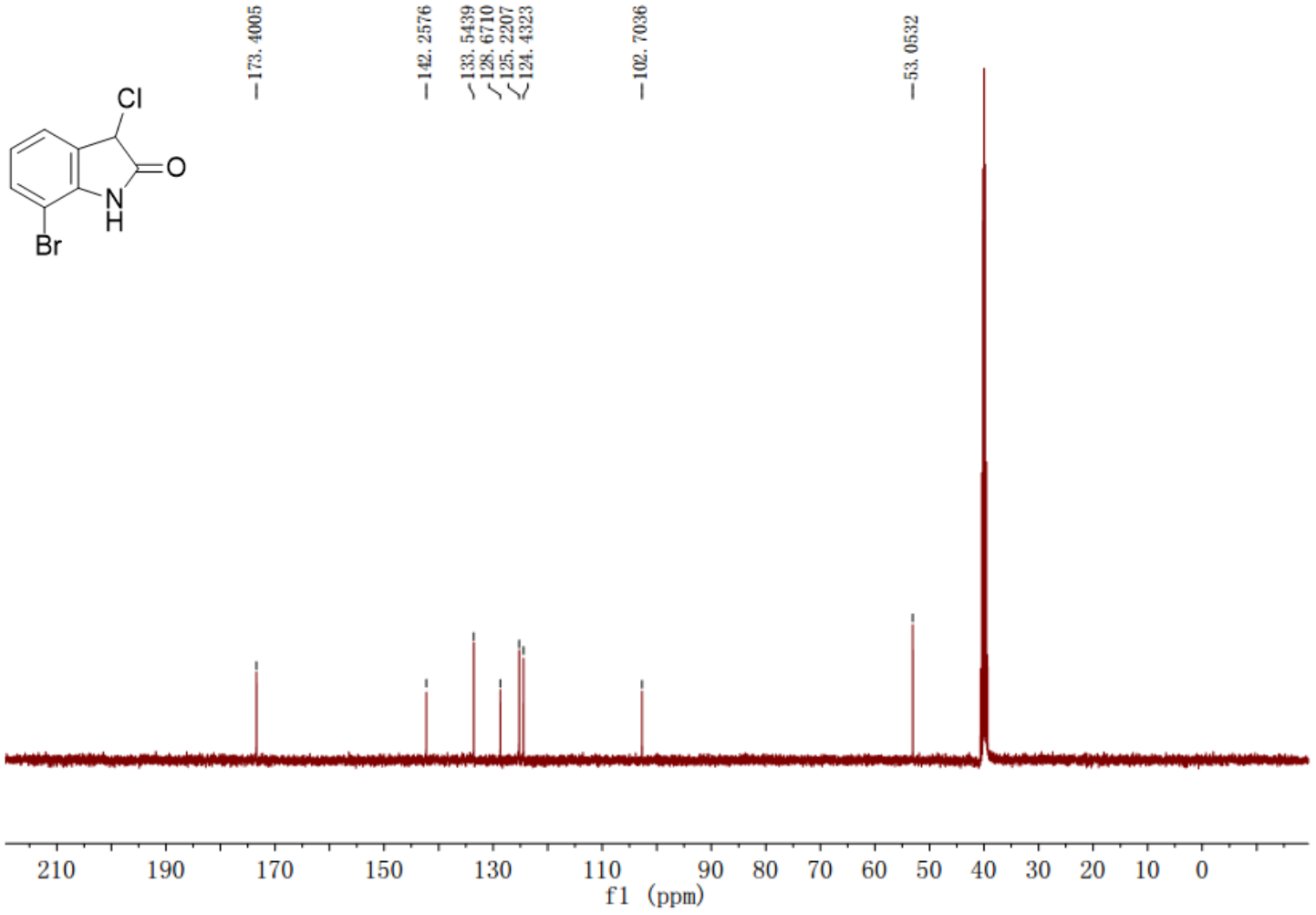
^{13}C NMR (101MHz, DMSO-d_6) spectra of 5-bromo-3-chloroindolin-2-one (3l)



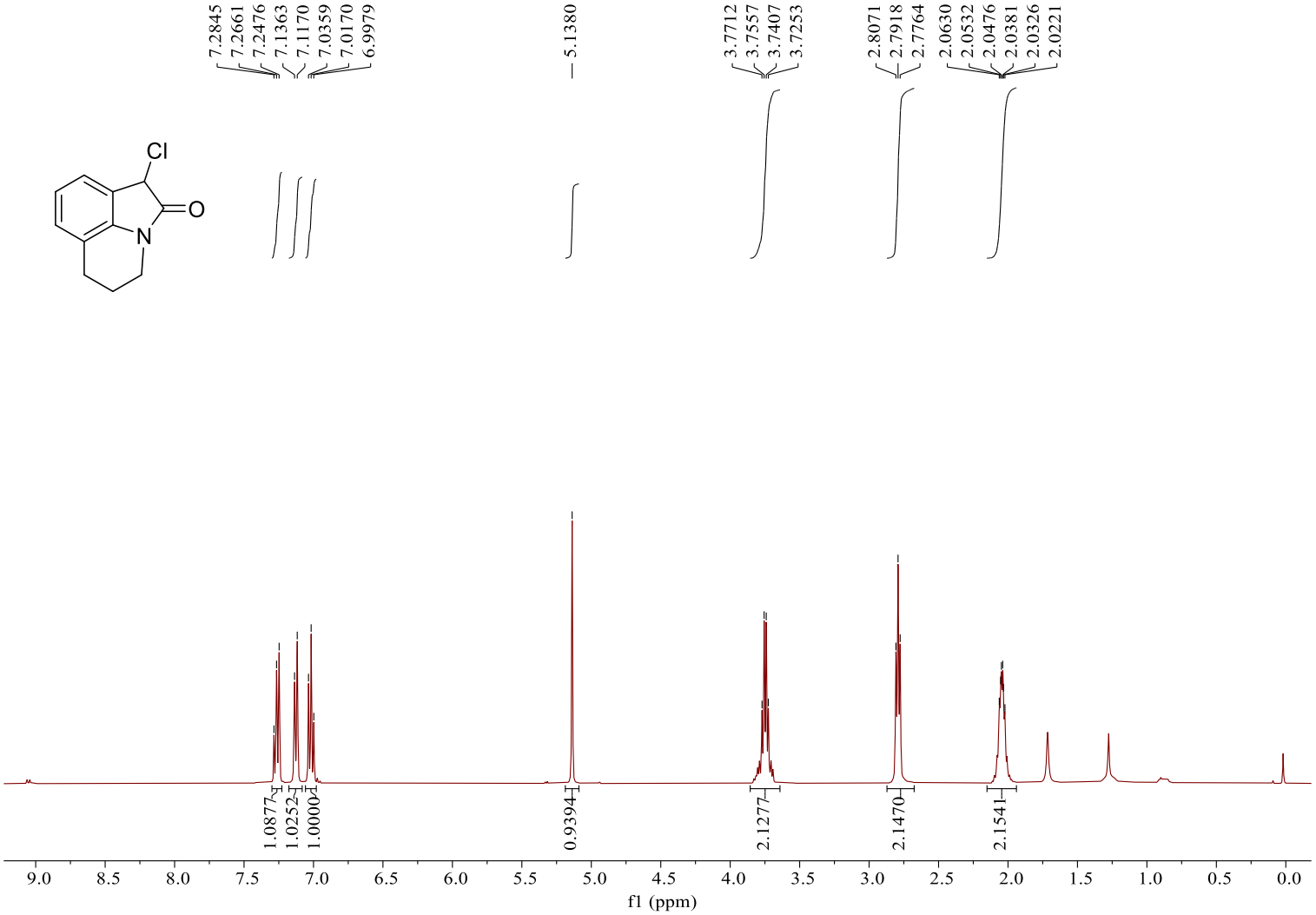
^{1}H NMR (400MHz, DMSO-d_6) spectra of 7-bromo-3-chloroindolin-2-one (3m)



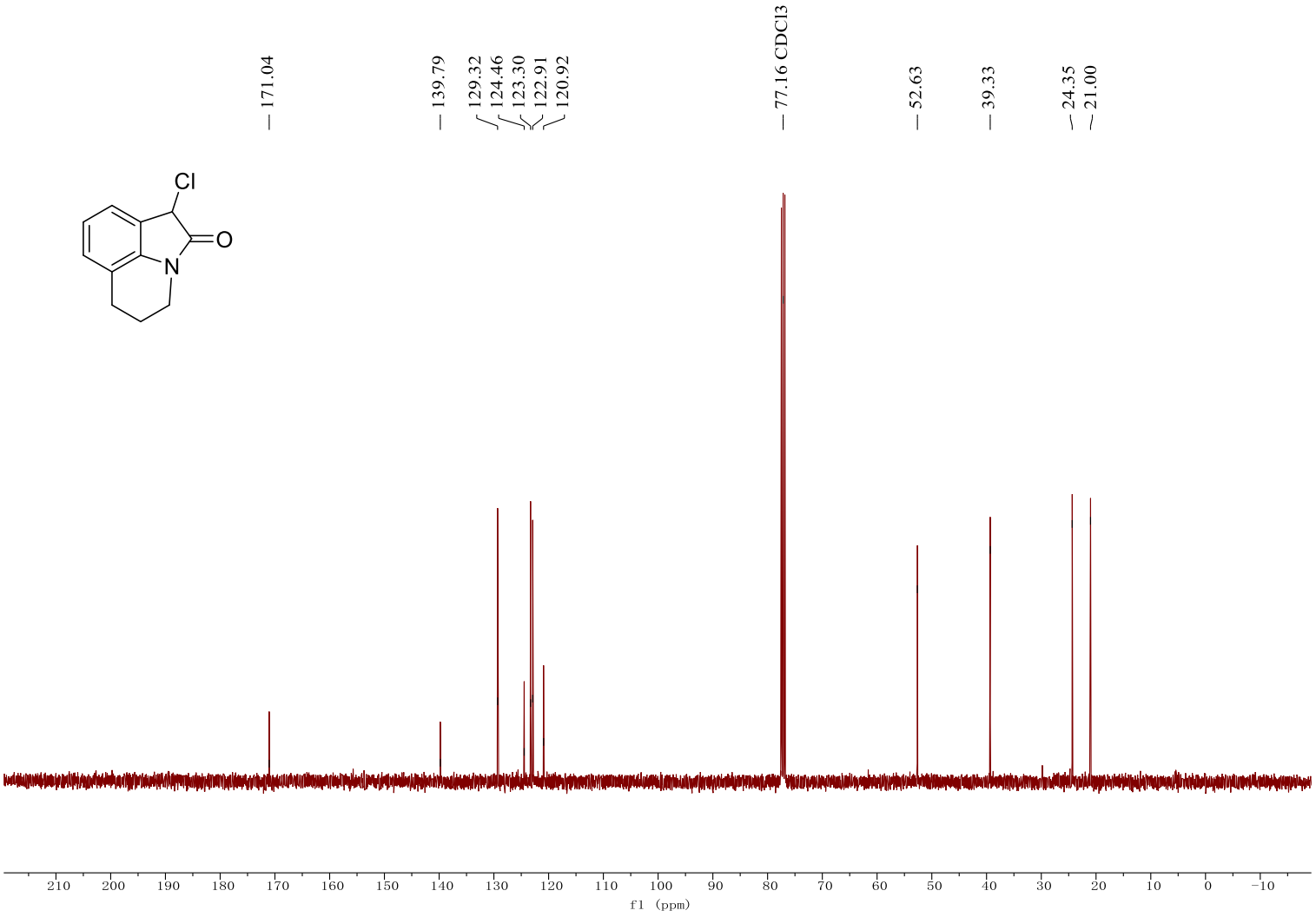
^{13}C NMR (101MHz, DMSO-d_6) spectra of 7-bromo-3-chloroindolin-2-one (3m)



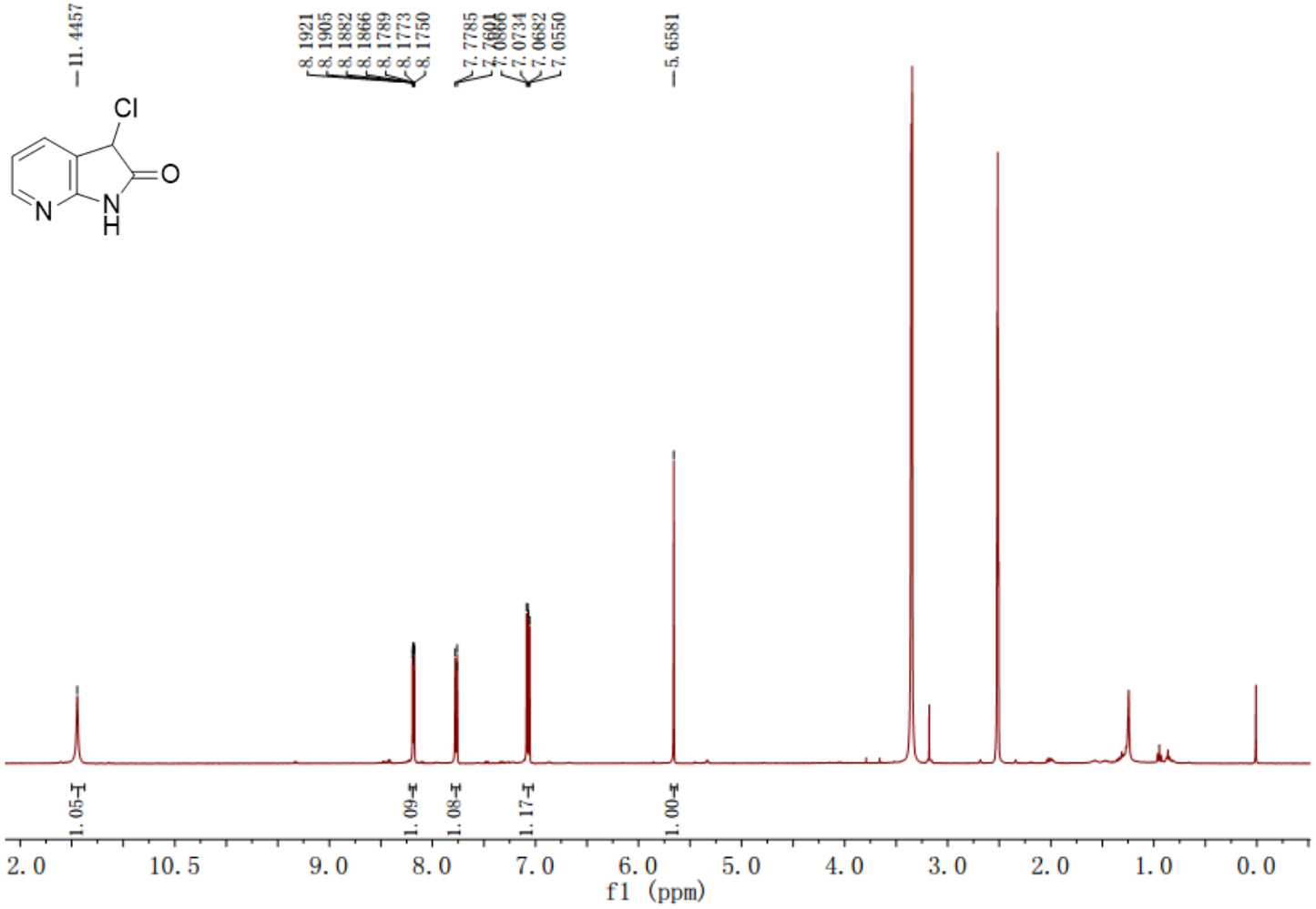
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (3n)



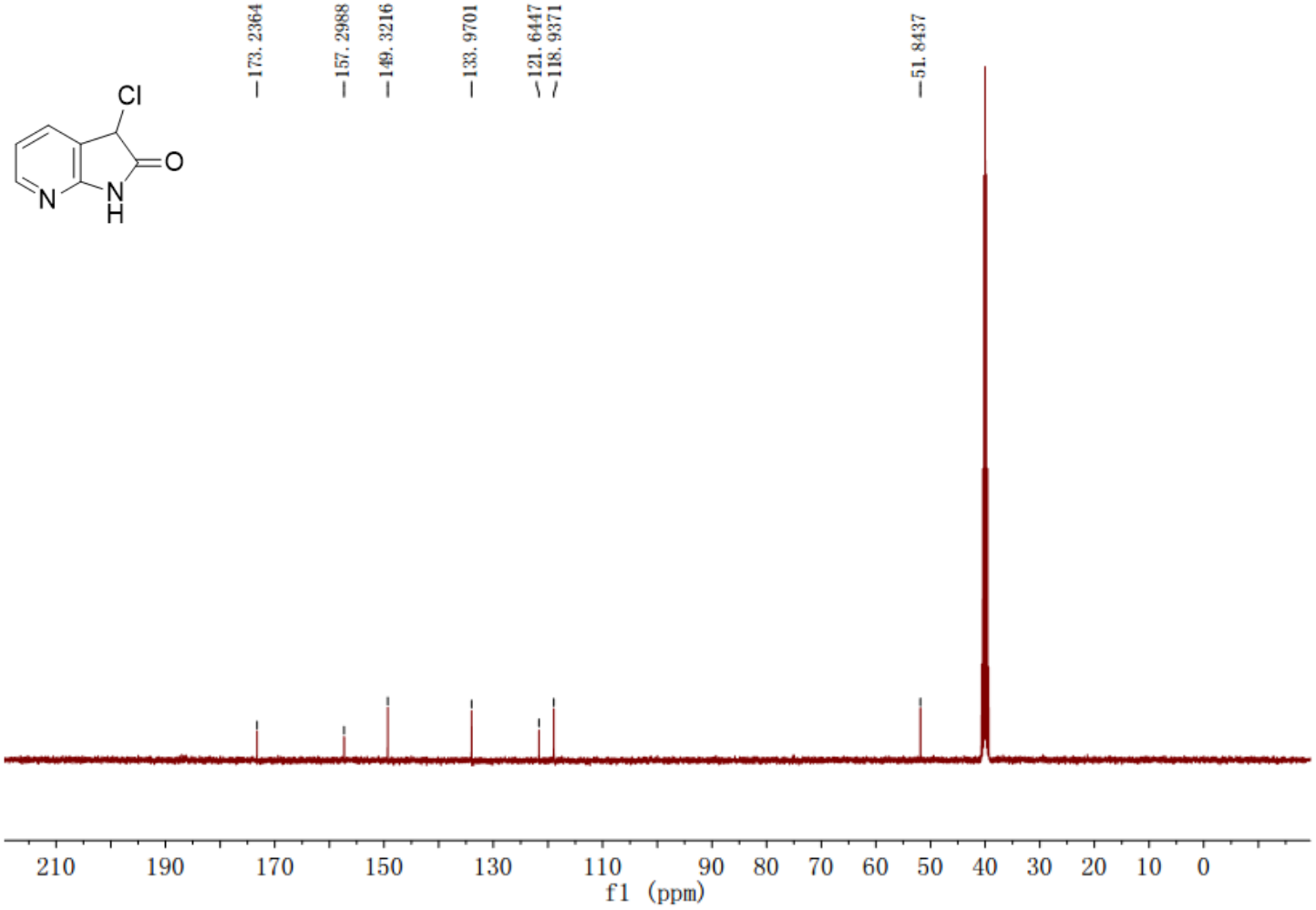
^{13}C NMR (101MHz, $CDCl_3$) spectra of 1-chloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (3n)



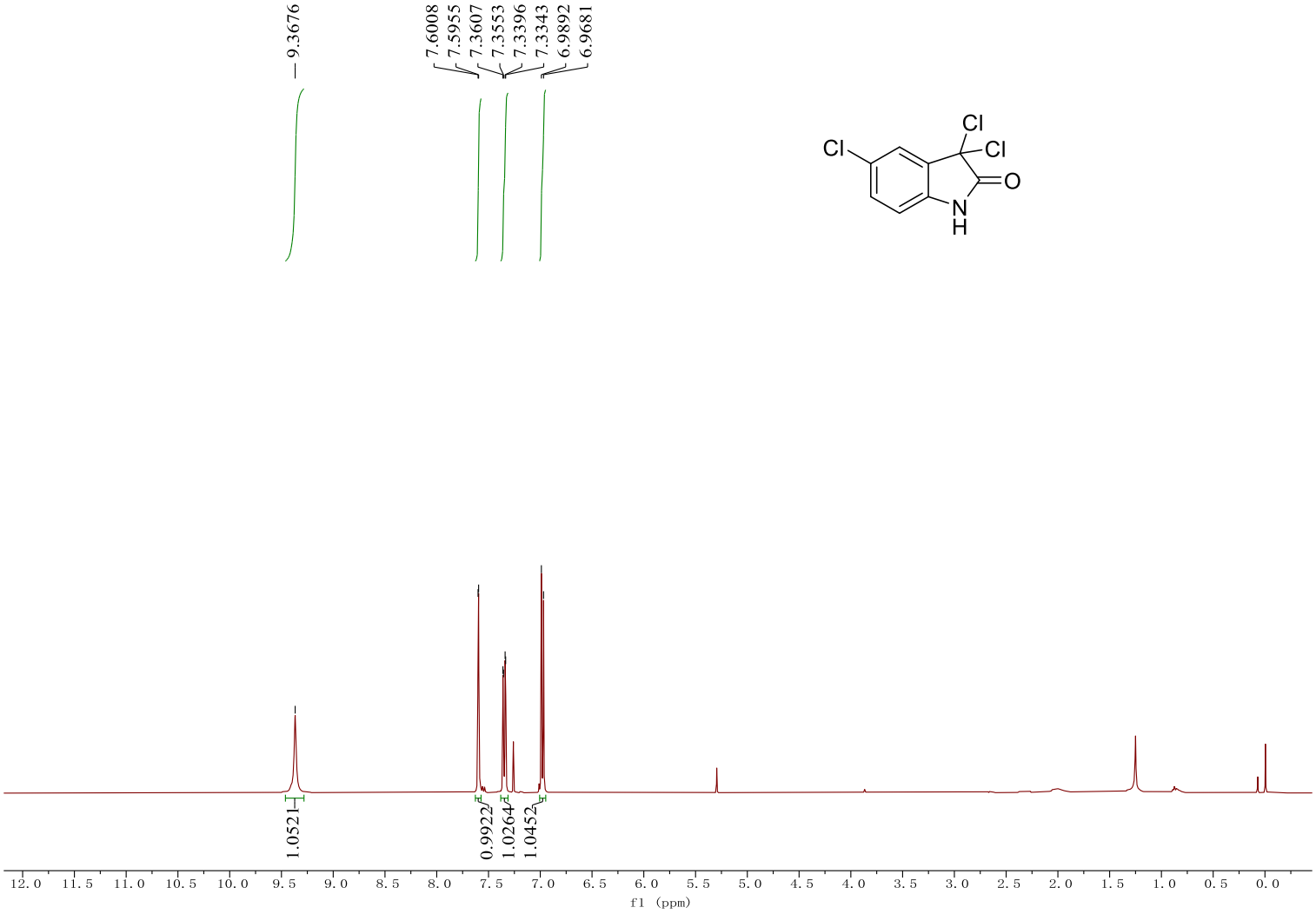
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3-chloro-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (3o)



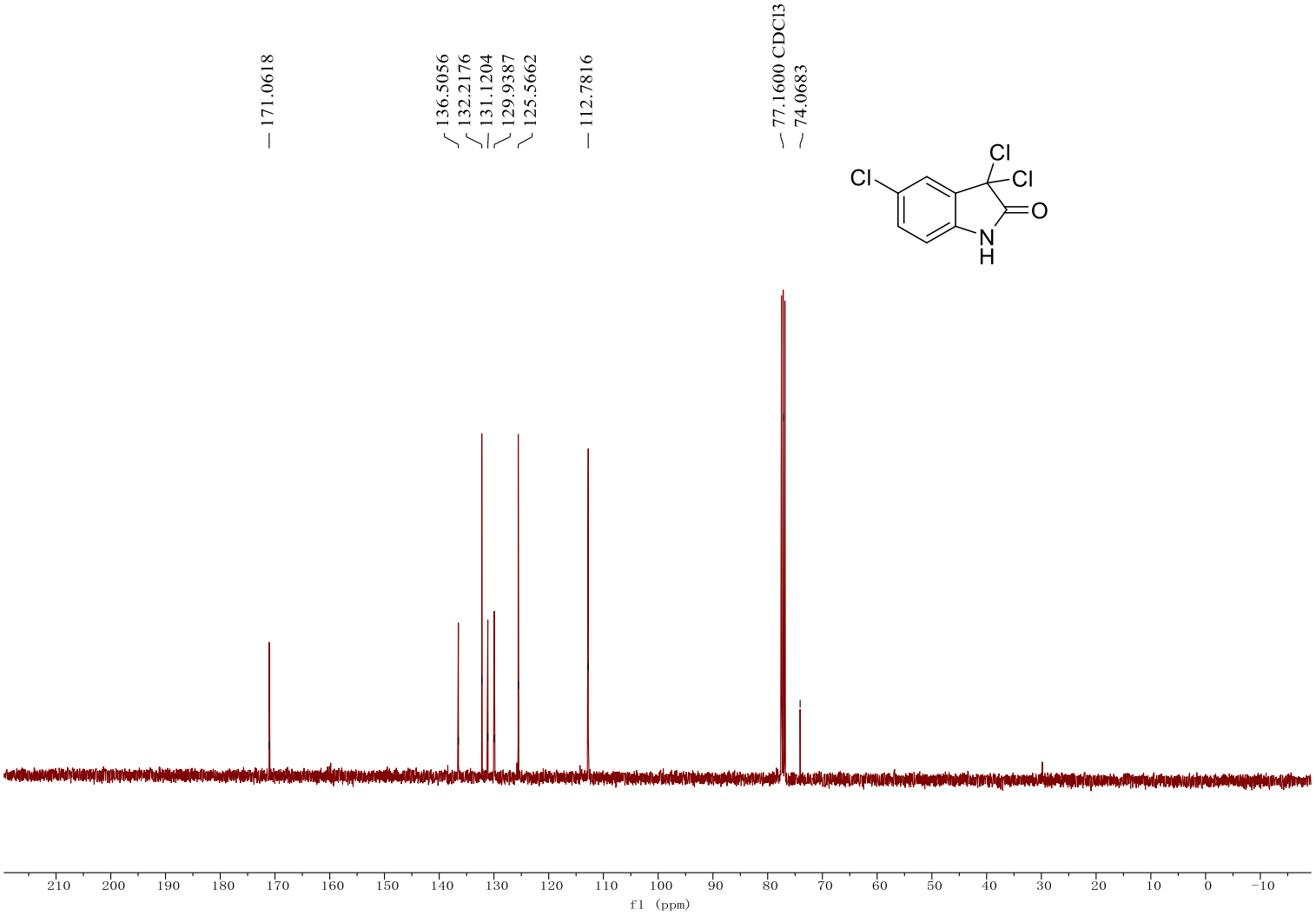
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3-chloro-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (3o)



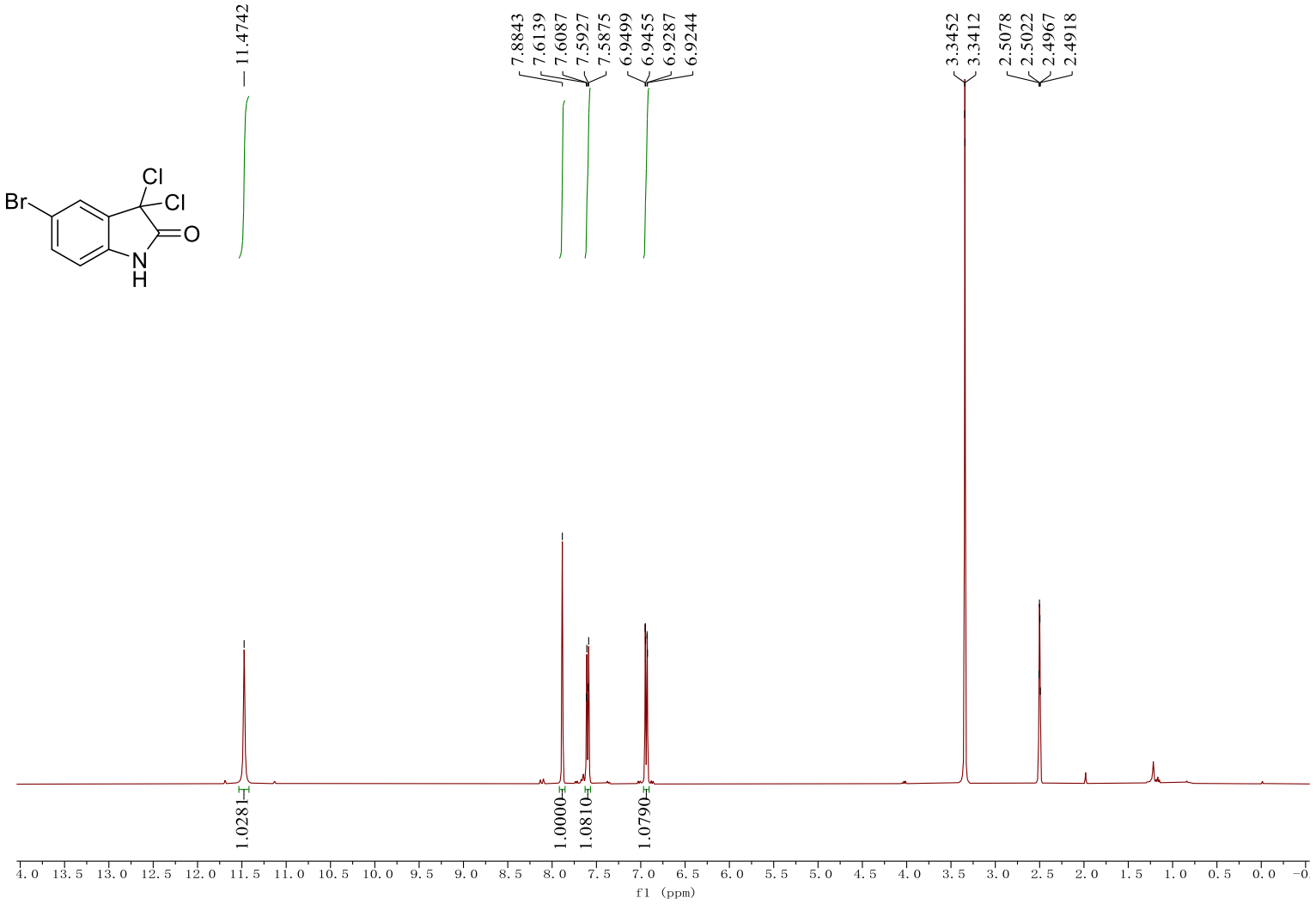
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3,3,5-trichloroindolin-2-one (4a)



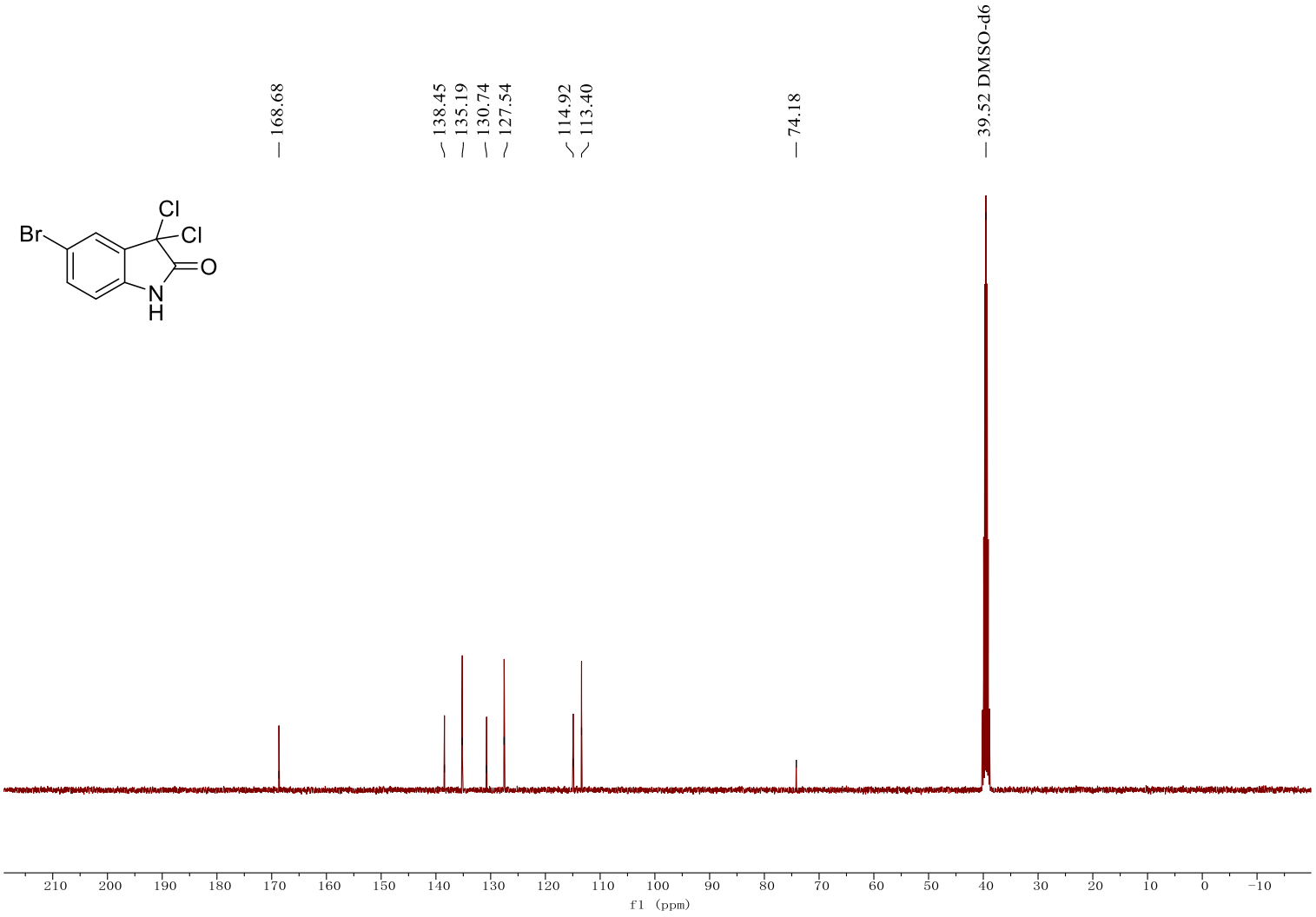
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,3,5-trichloroindolin-2-one (4a)



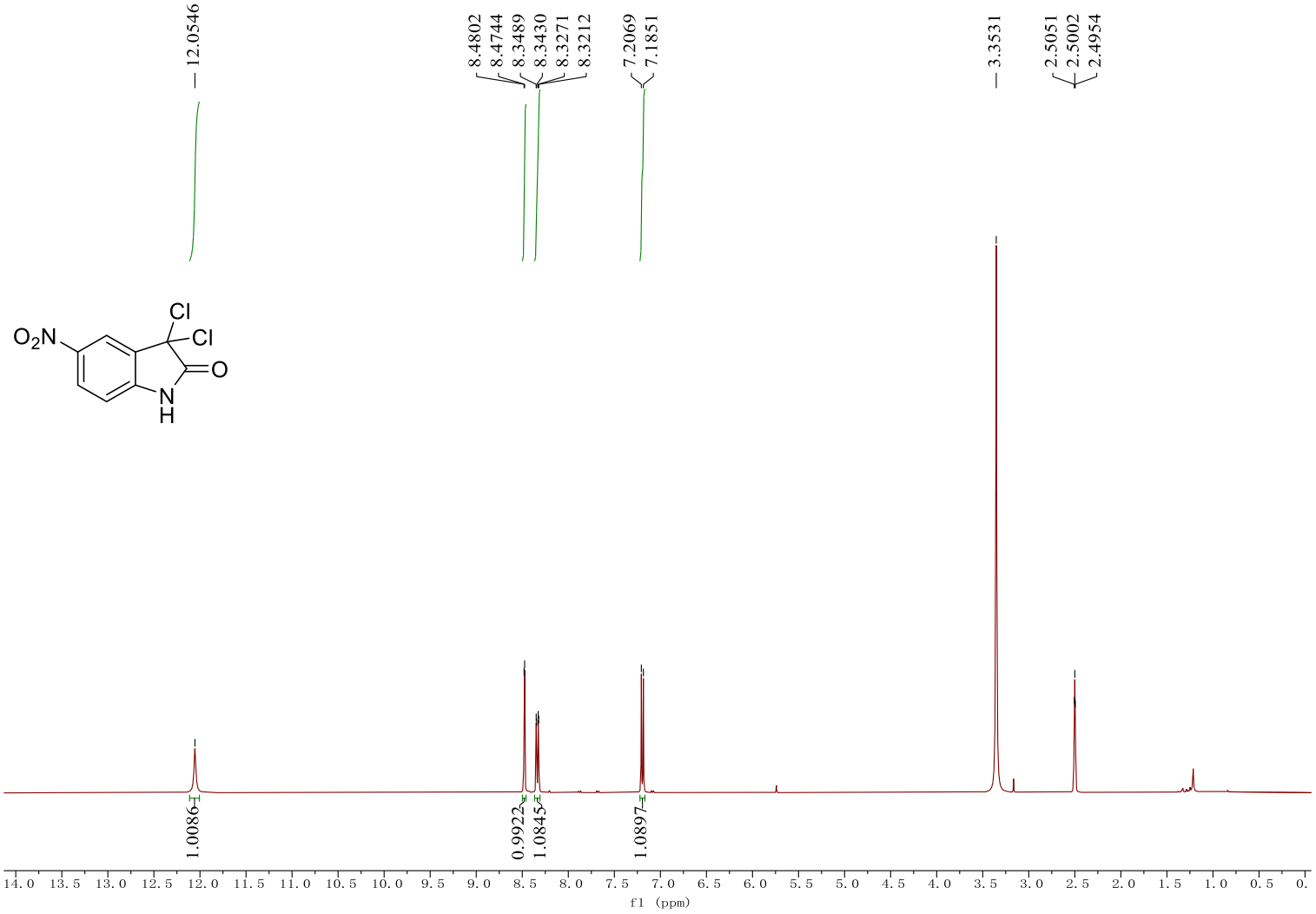
^{1}H NMR (400MHz, DMSO-d_6) spectra of 5-bromo-3,3-dichloroindolin-2-one (4b)



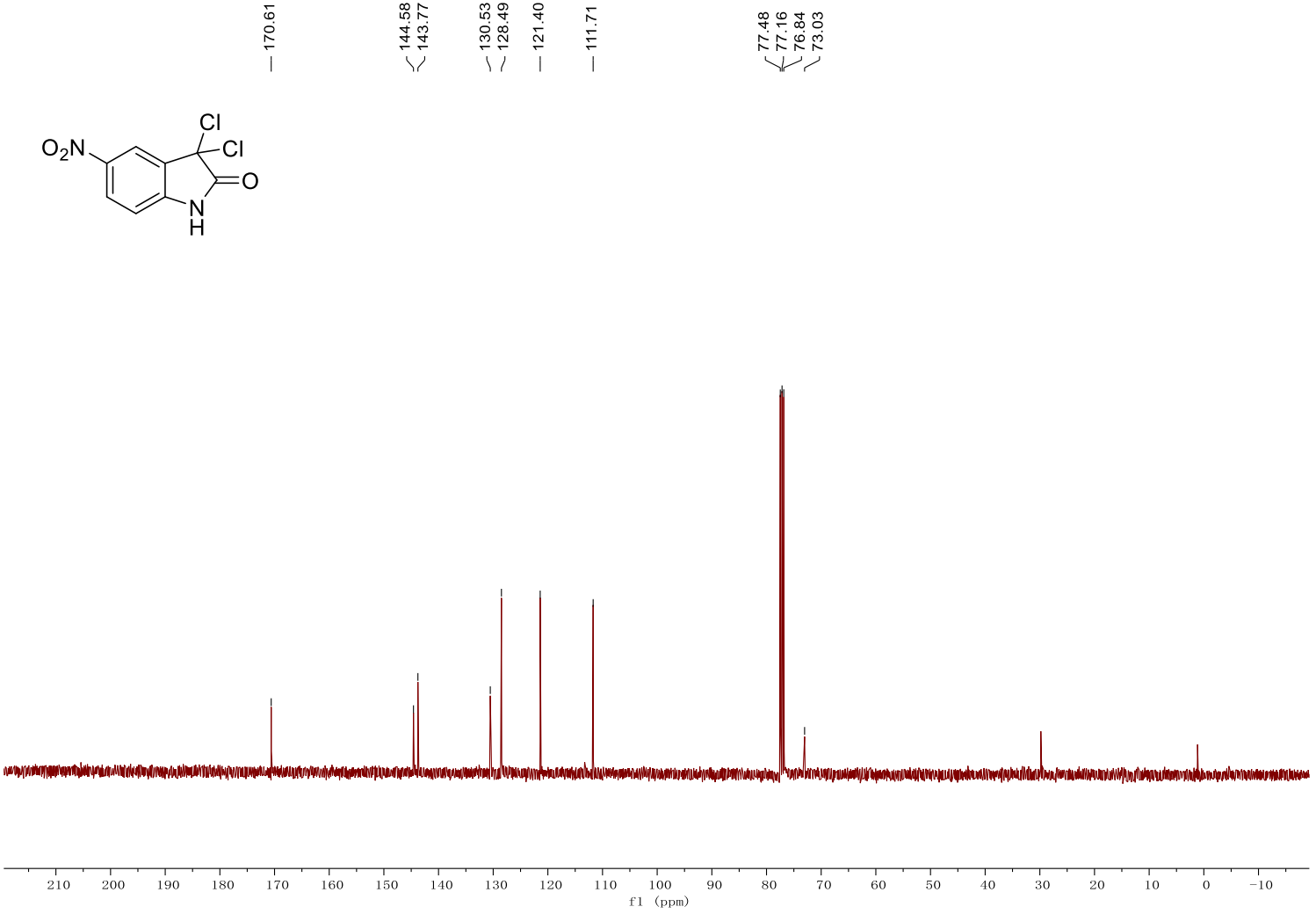
^{13}C NMR (101MHz, DMSO-d_6) spectra of 5-bromo-3,3-dichloroindolin-2-one (4b)



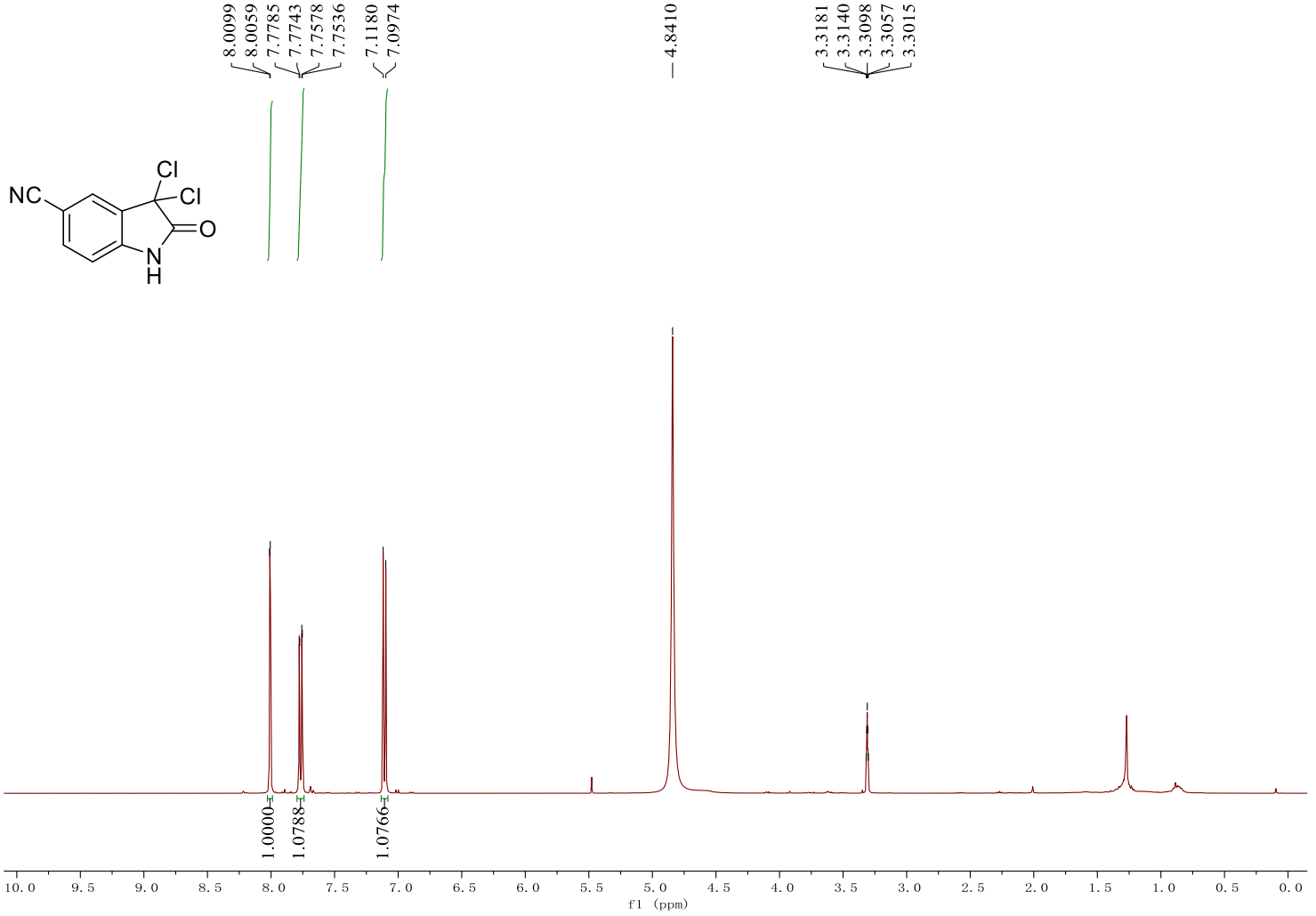
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3,3-dichloro-5-nitroindolin-2-one (4c)



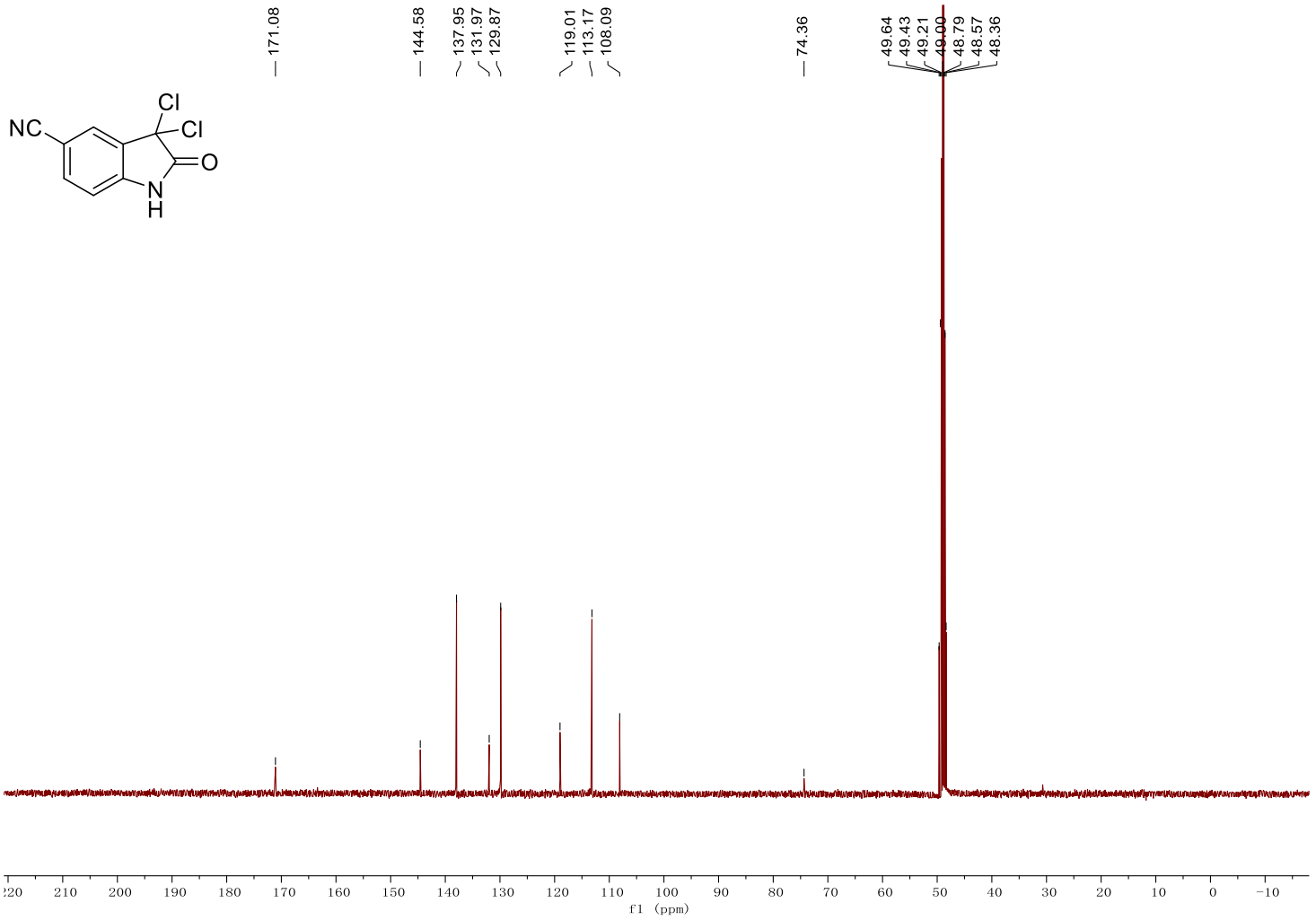
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3,3-dichloro-5-nitroindolin-2-one (4c)



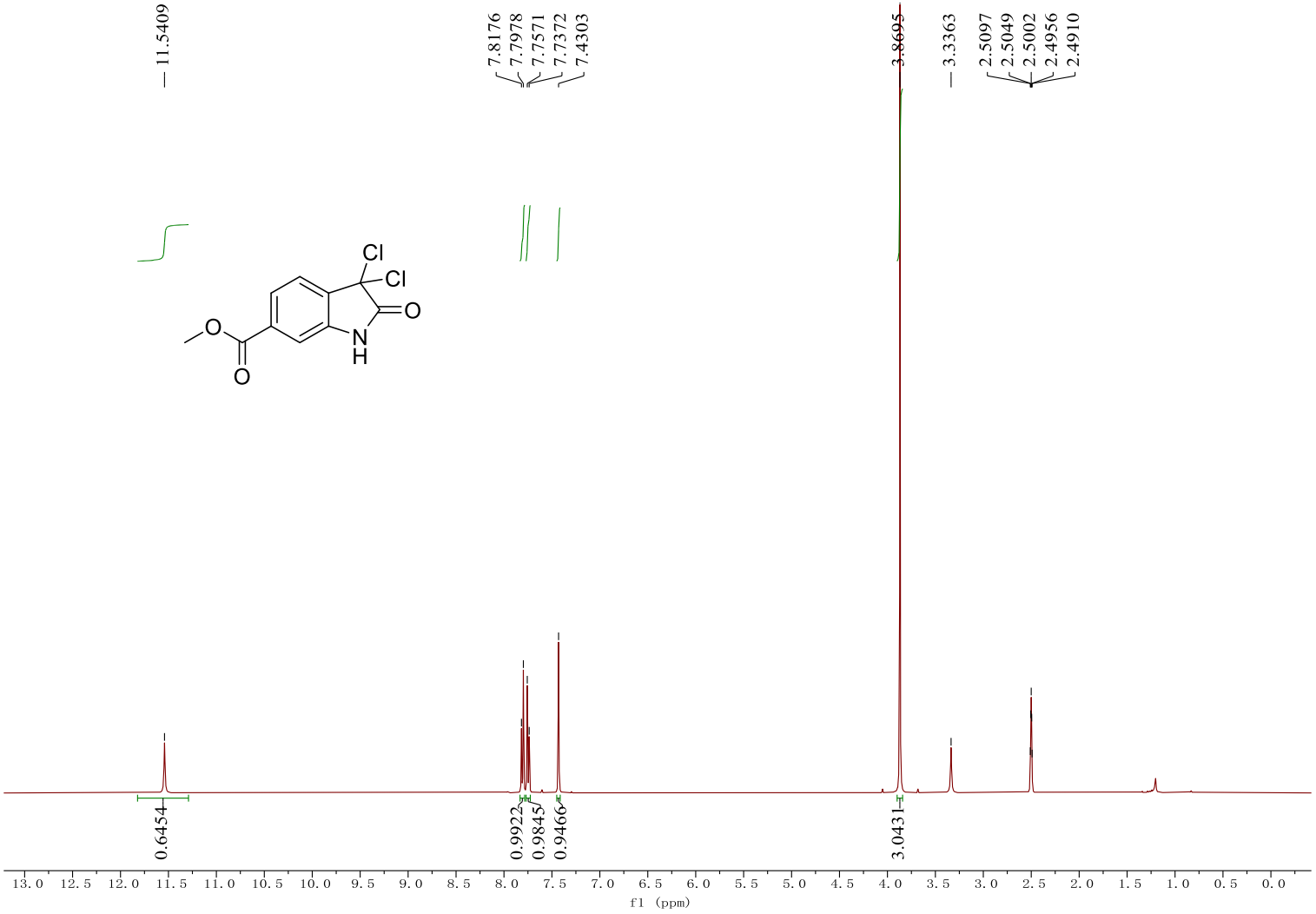
^{1}H NMR (400MHz, CD_3OD) and ^{13}C NMR (101MHz, CD_3OD) spectra of 3,3-dichloro-5-nitrile-2-one (4d)



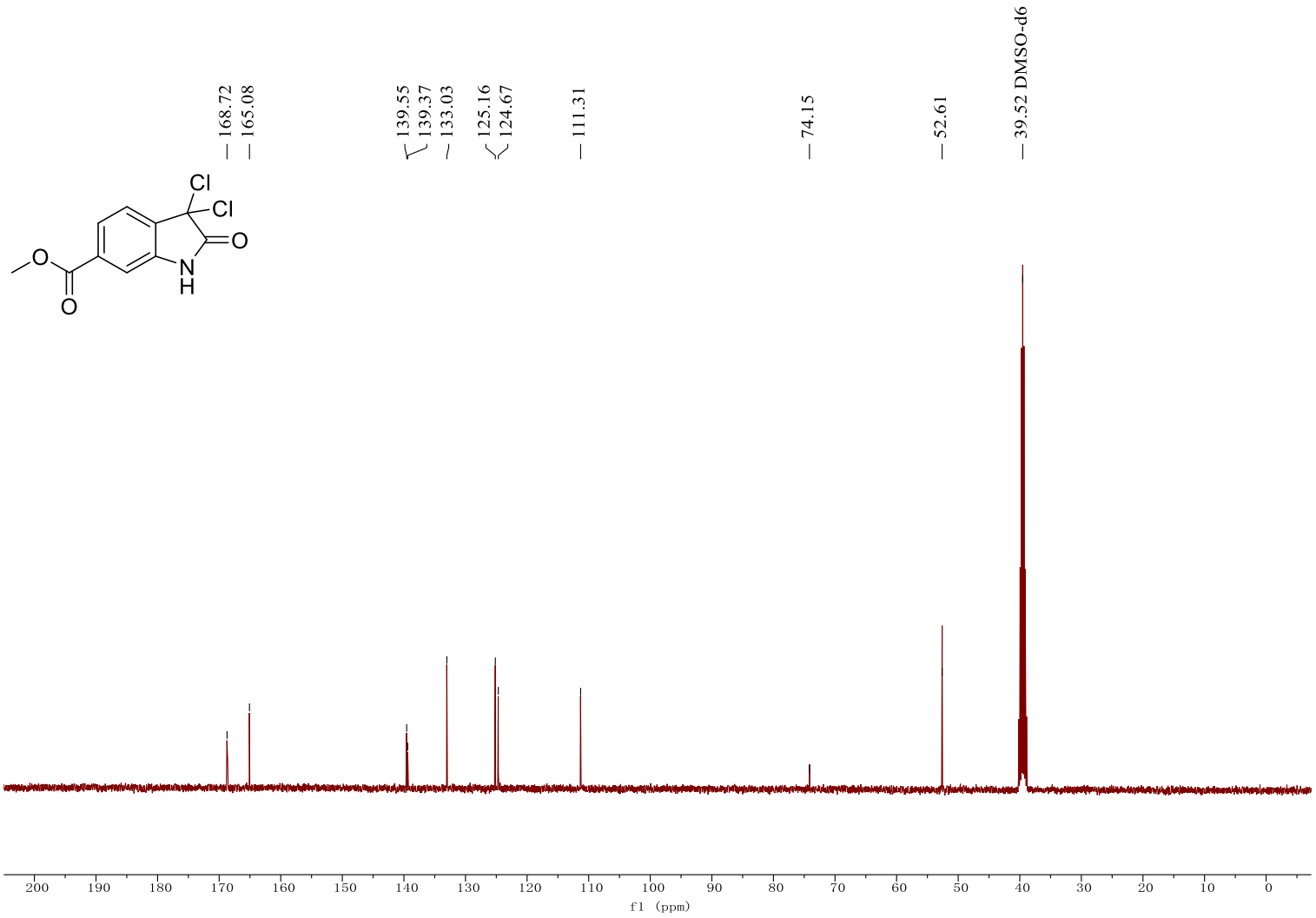
^{13}C NMR (101MHz, CD_3OD) spectra of 3,3-dichloro-5-nitrile-2-one (4d)



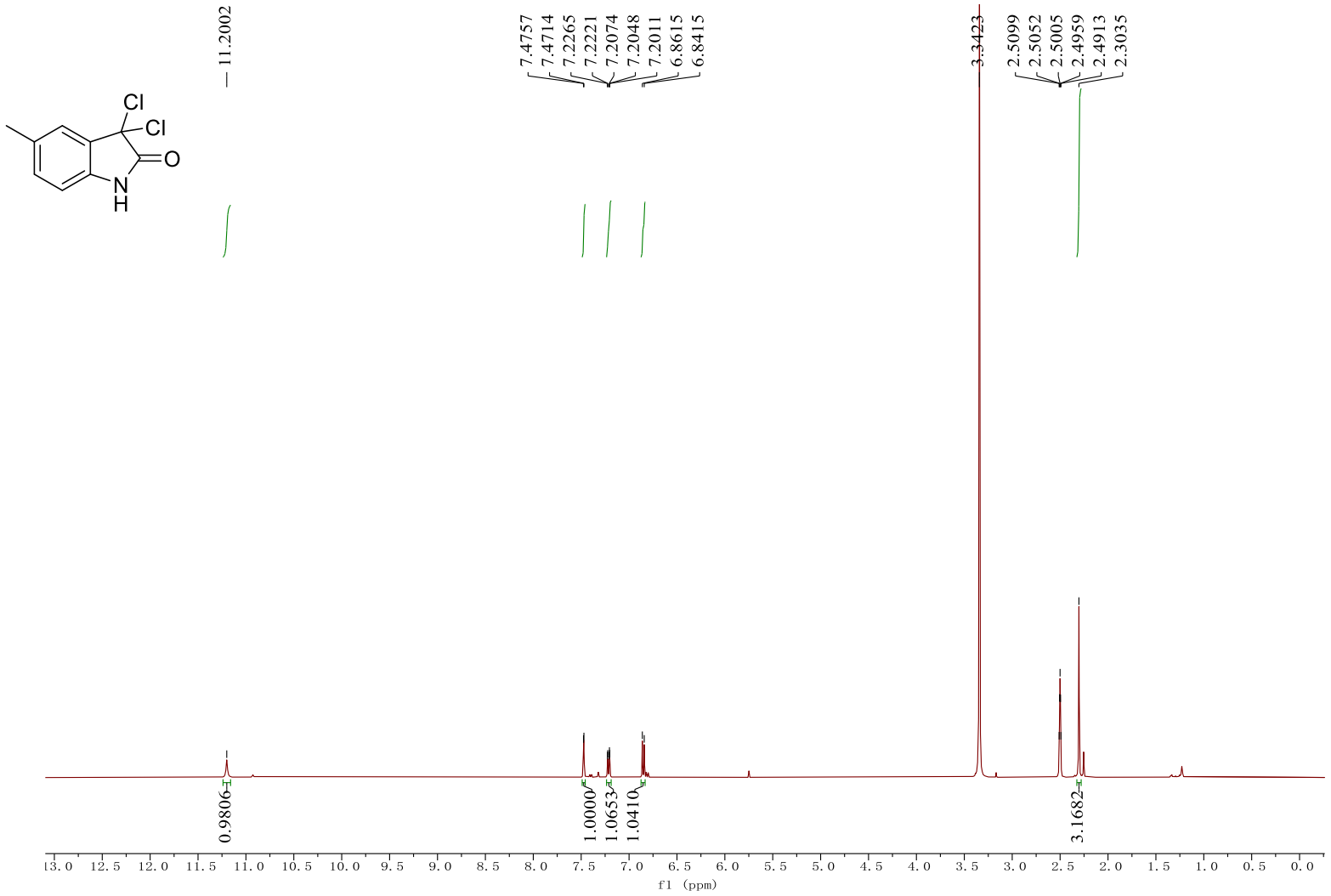
^{1}H NMR (400MHz, DMSO-d_6) spectra of methyl 3,3-dichloro-2-oxoindoline-6-carboxylate (4e)



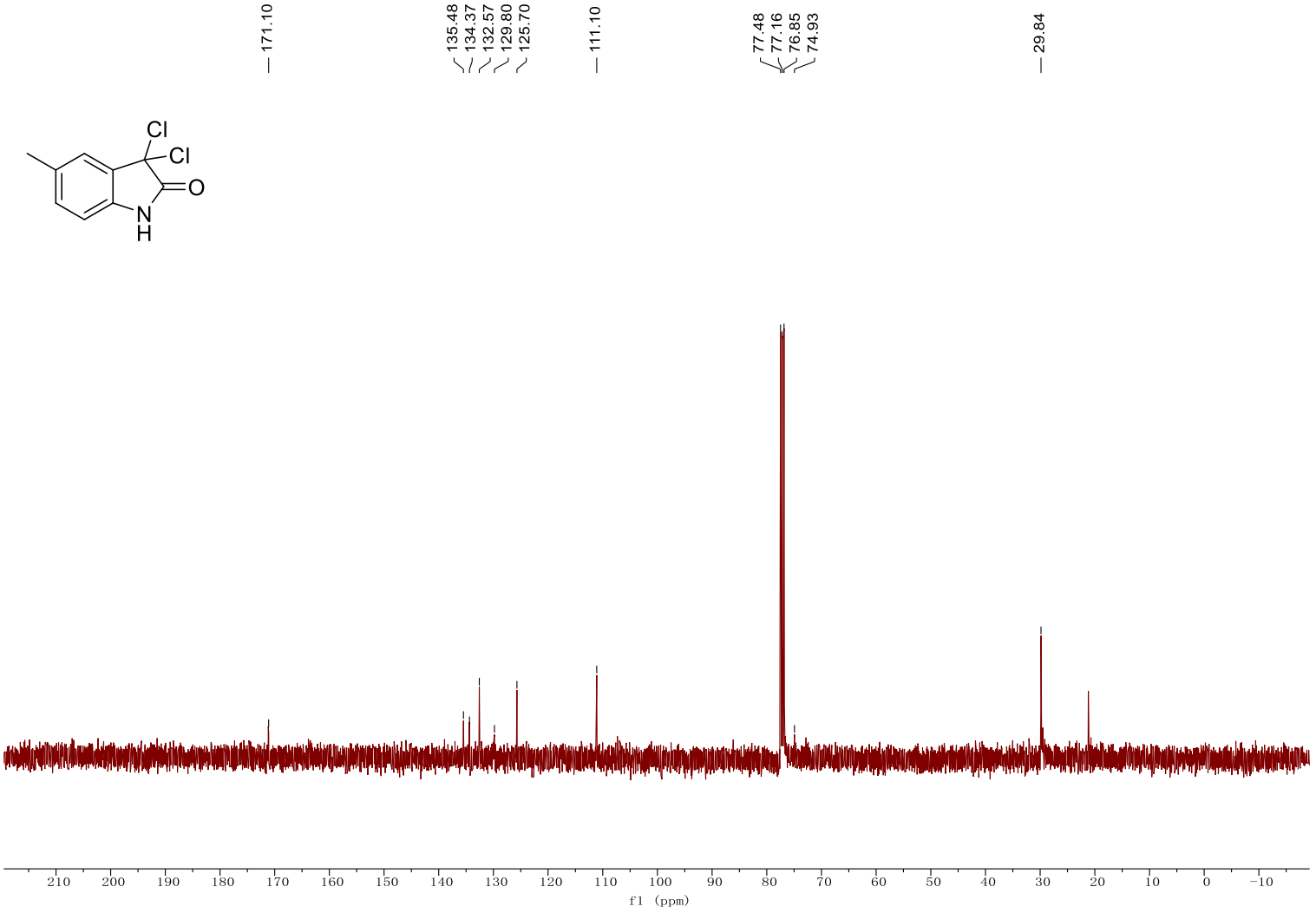
^{13}C NMR (101MHz, DMSO-d_6) spectra of methyl 3,3-dichloro-2-oxoindoline-6-carboxylate (4e)



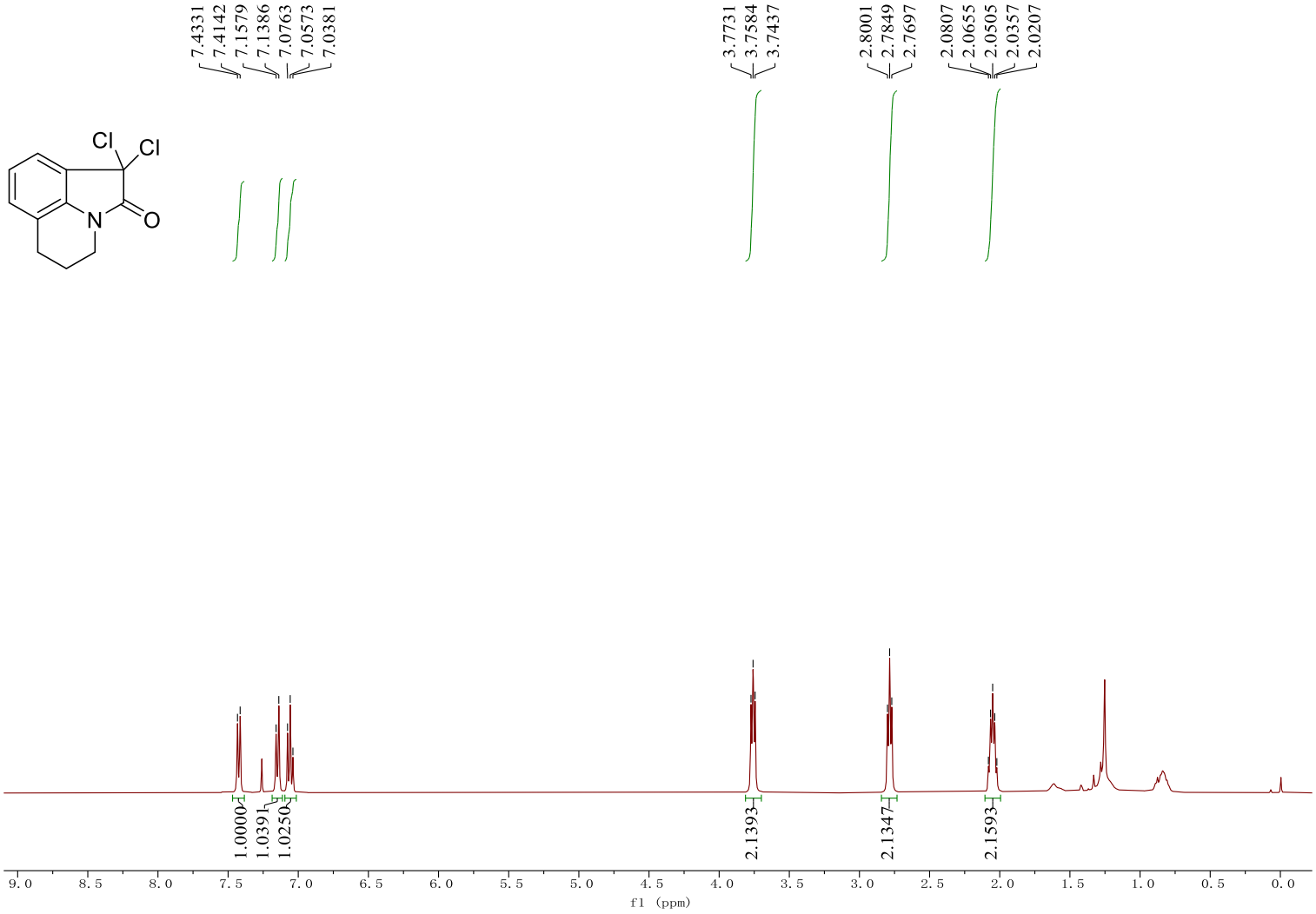
^{1}H NMR (400MHz, DMSO-d_6) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,3-dichloro-5-methylindolin-2-one (4f)



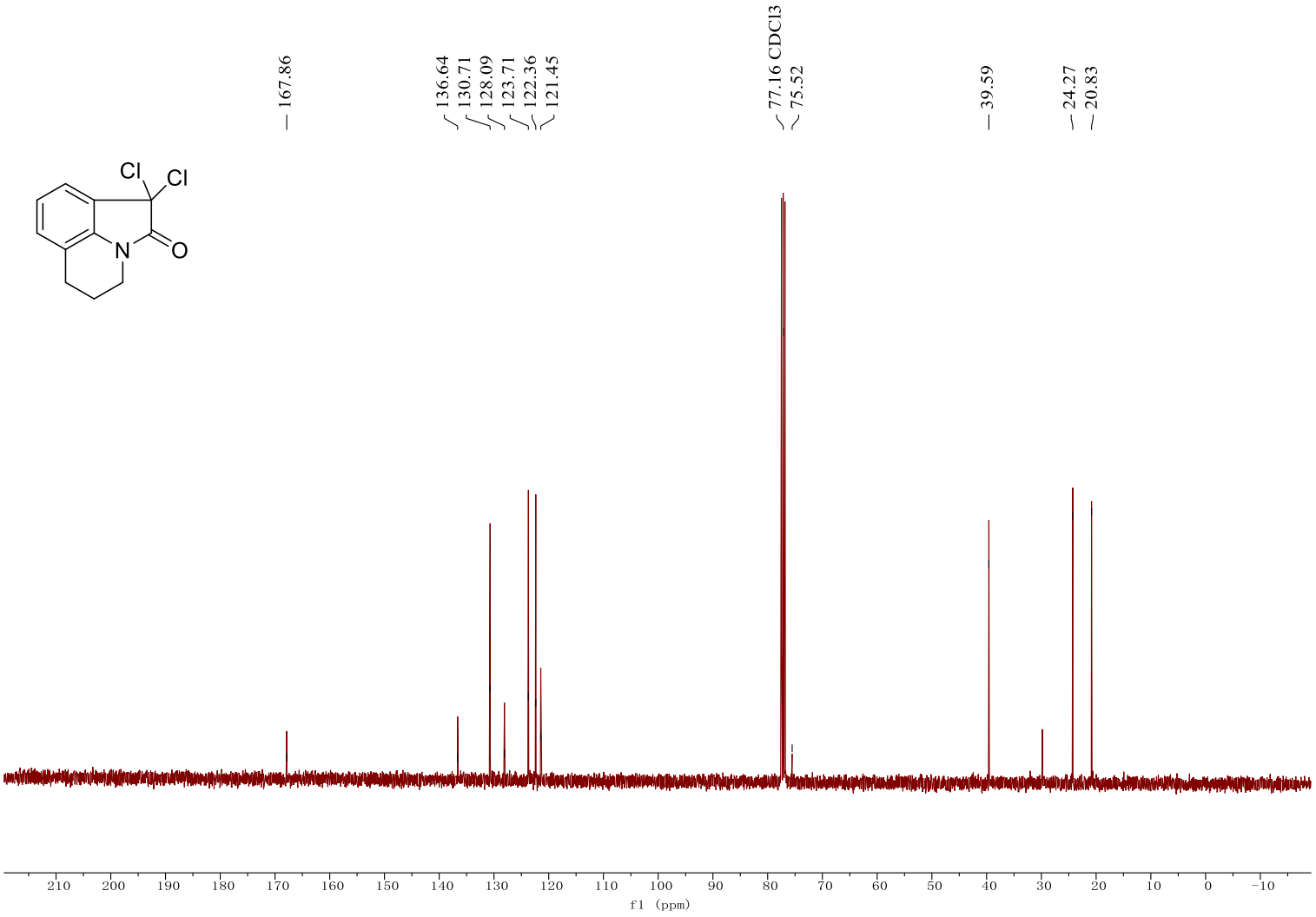
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,3-dichloro-5-methylindolin-2-one (4f)



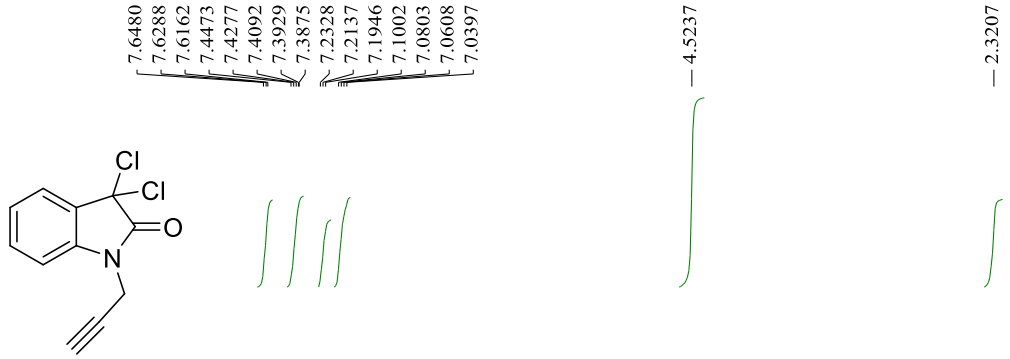
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1,1-dichloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (4g)



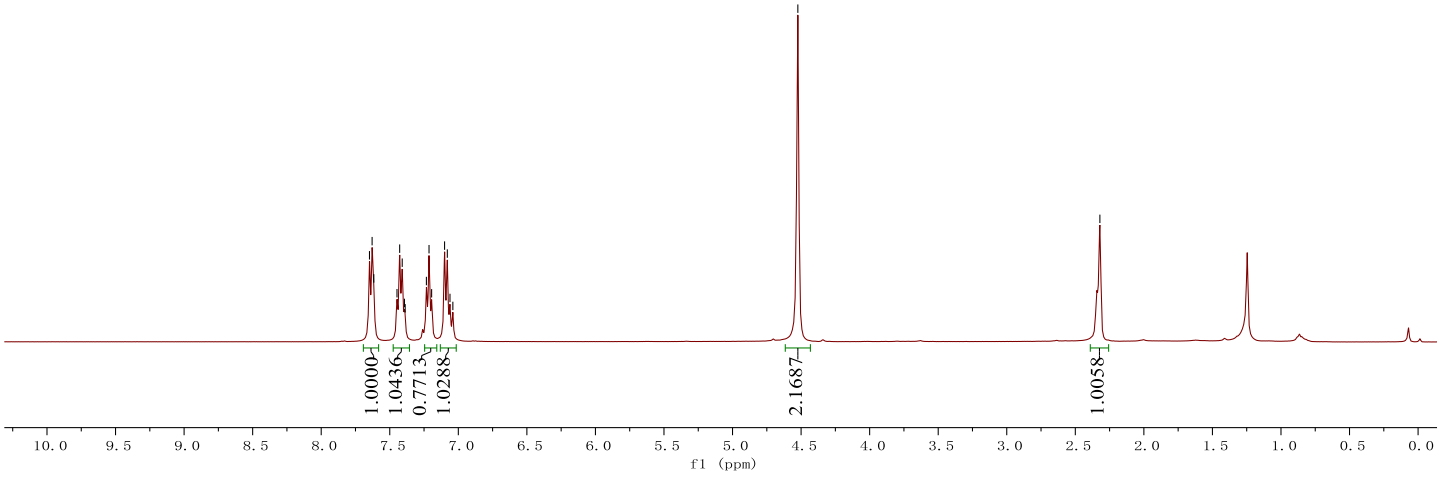
^{13}C NMR (101MHz, $CDCl_3$) spectra of 1,1-dichloro-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (4g)



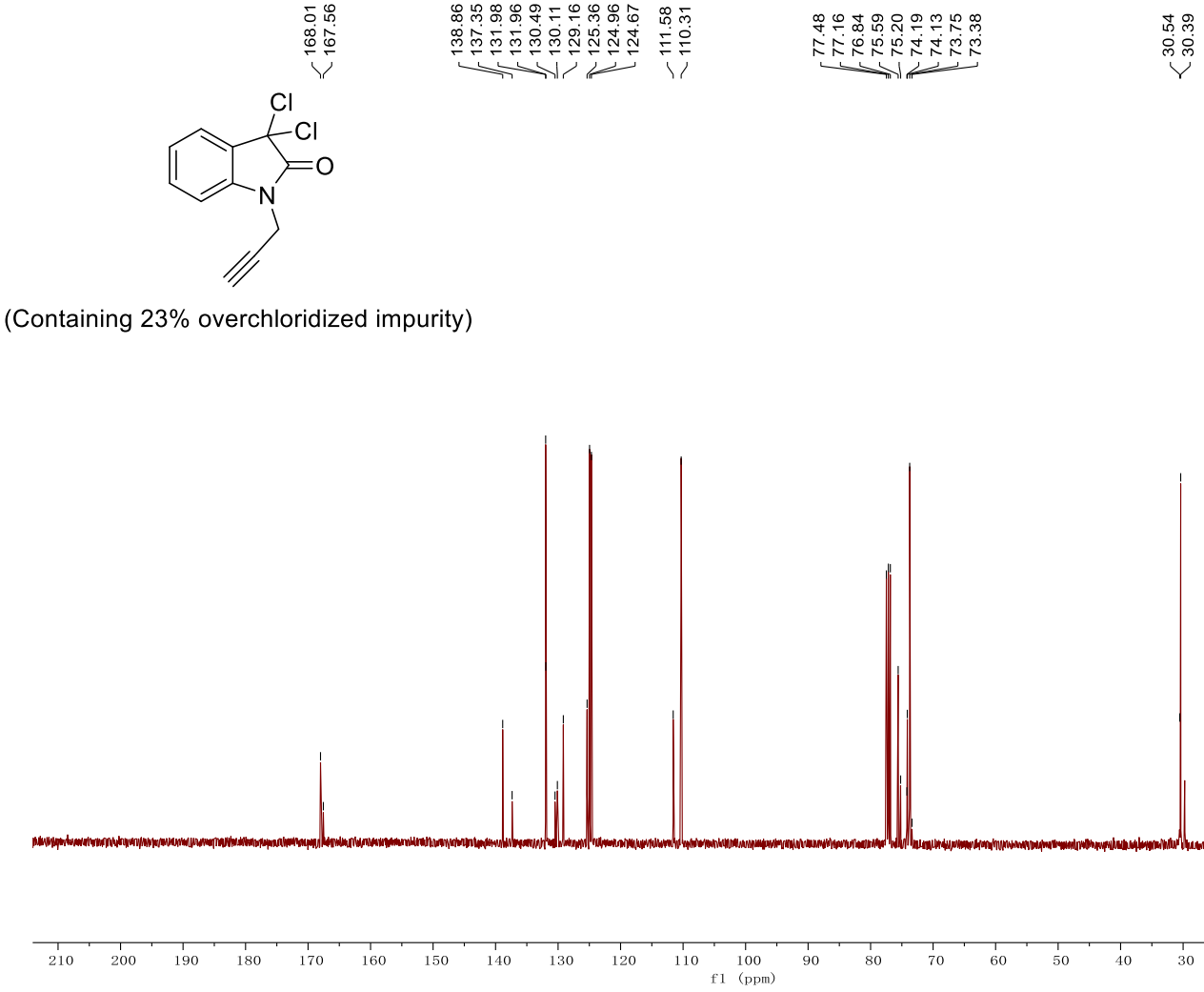
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3,3-dichloro-1-(prop-2-yn-1-yl)indolin- 2-one (4h)



(Containing 23% overchloridized impurity)

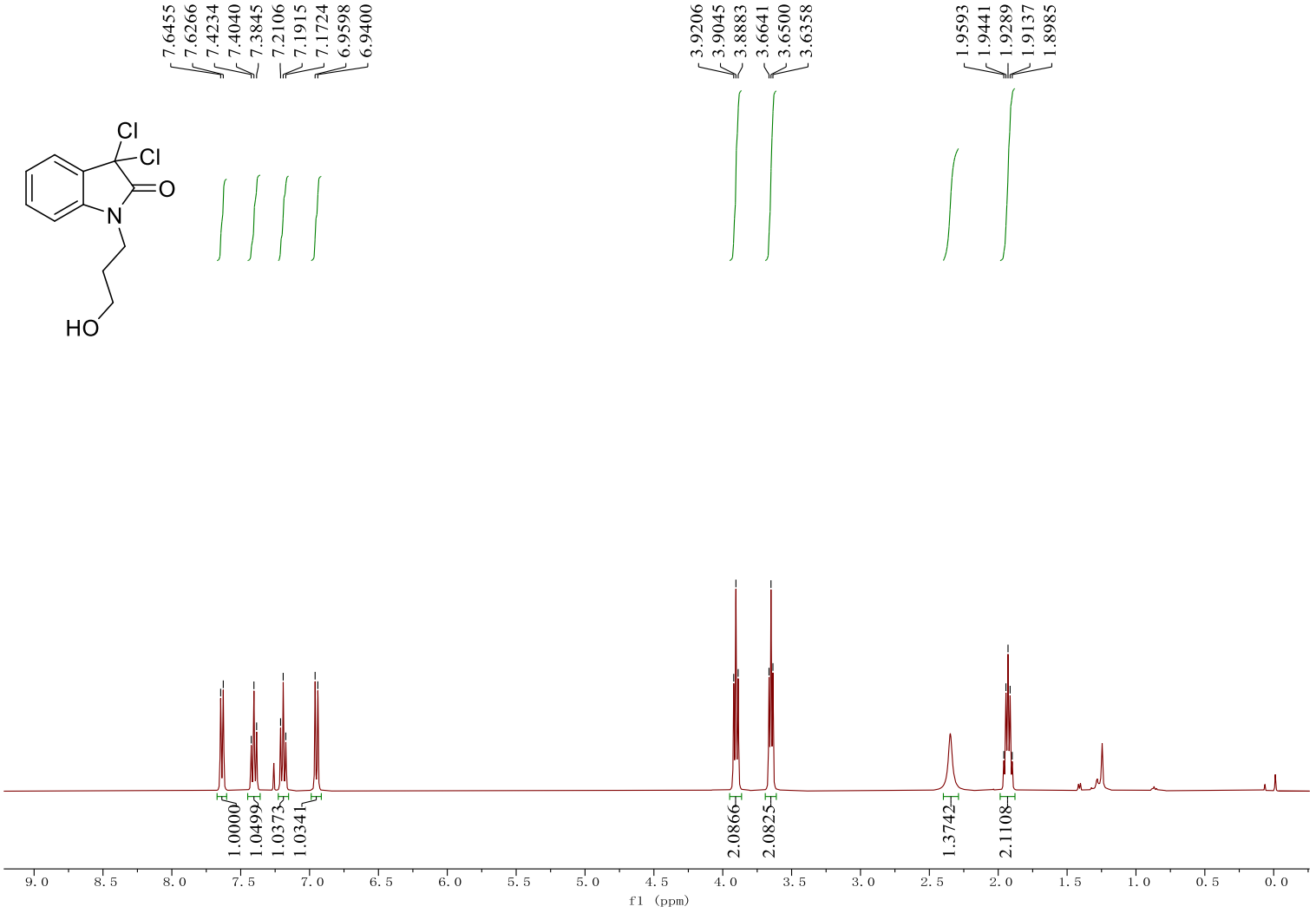


^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,3-dichloro-1-(prop-2-yn-1-yl)indolin- 2-one (4h)

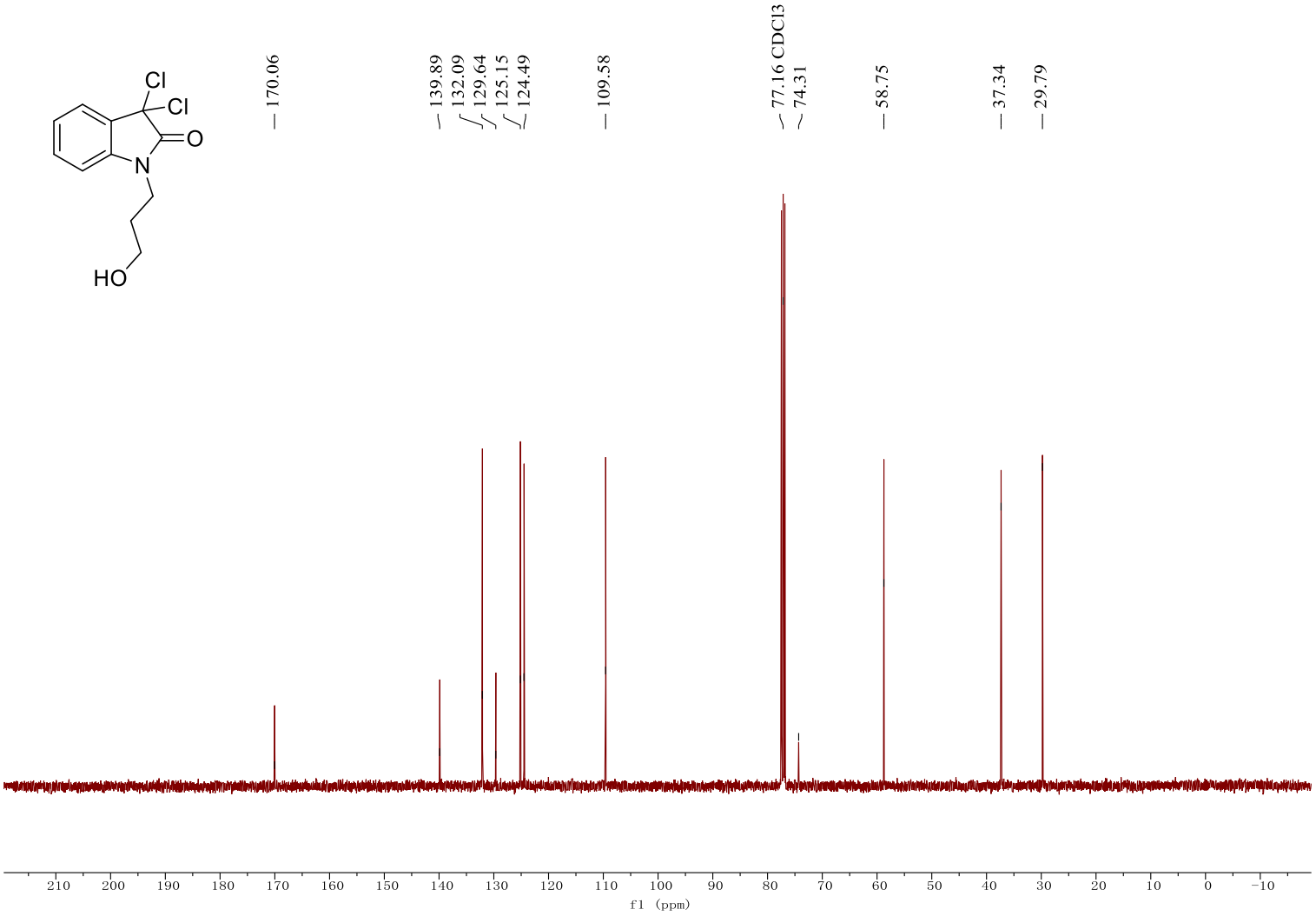


(Containing 23% overchloridized impurity)

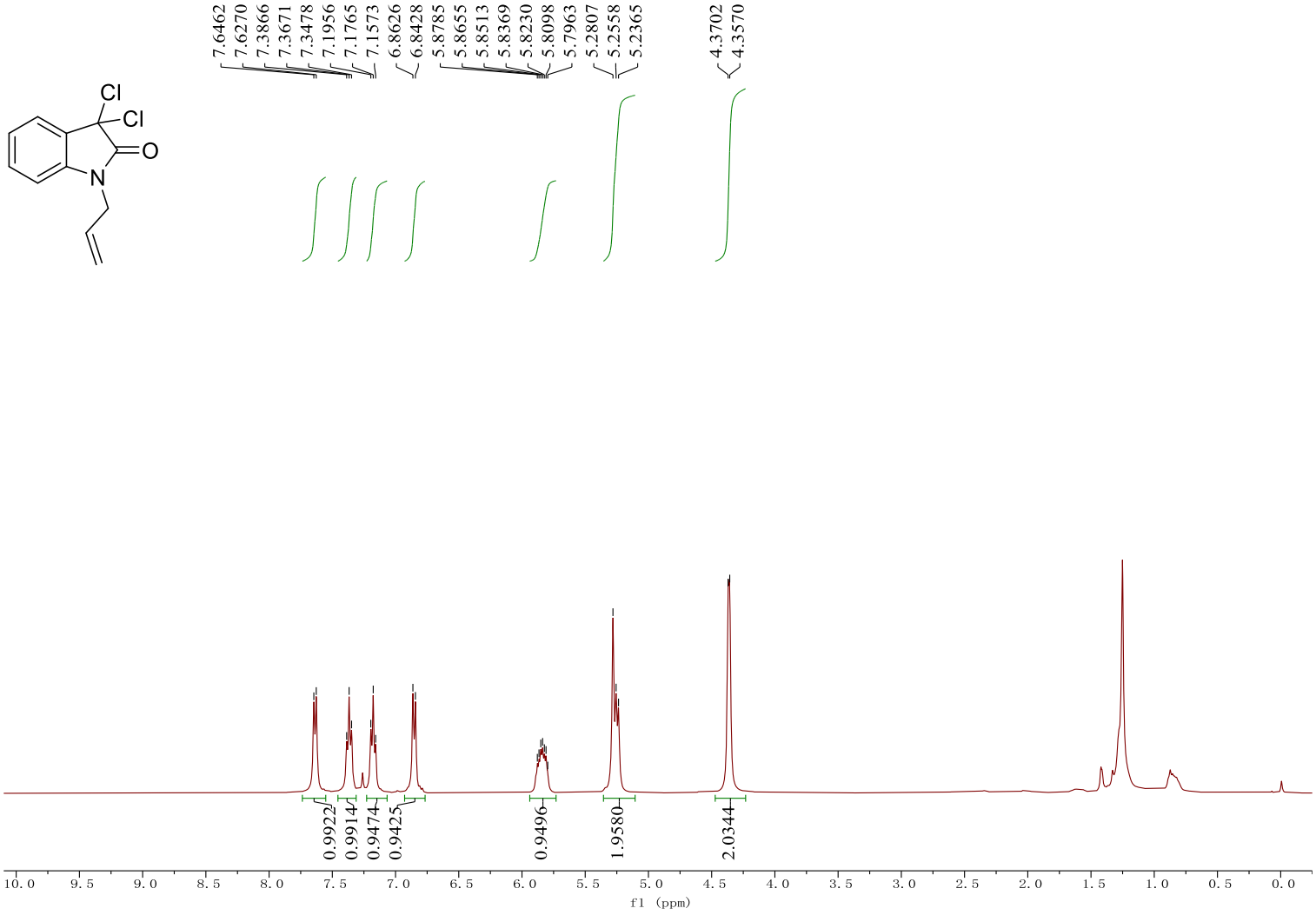
^{1}H NMR (400MHz, $CDCl_3$) spectra of 3,3-dichloro-1-(3-hydroxypropyl)indolin-2-one (4i)



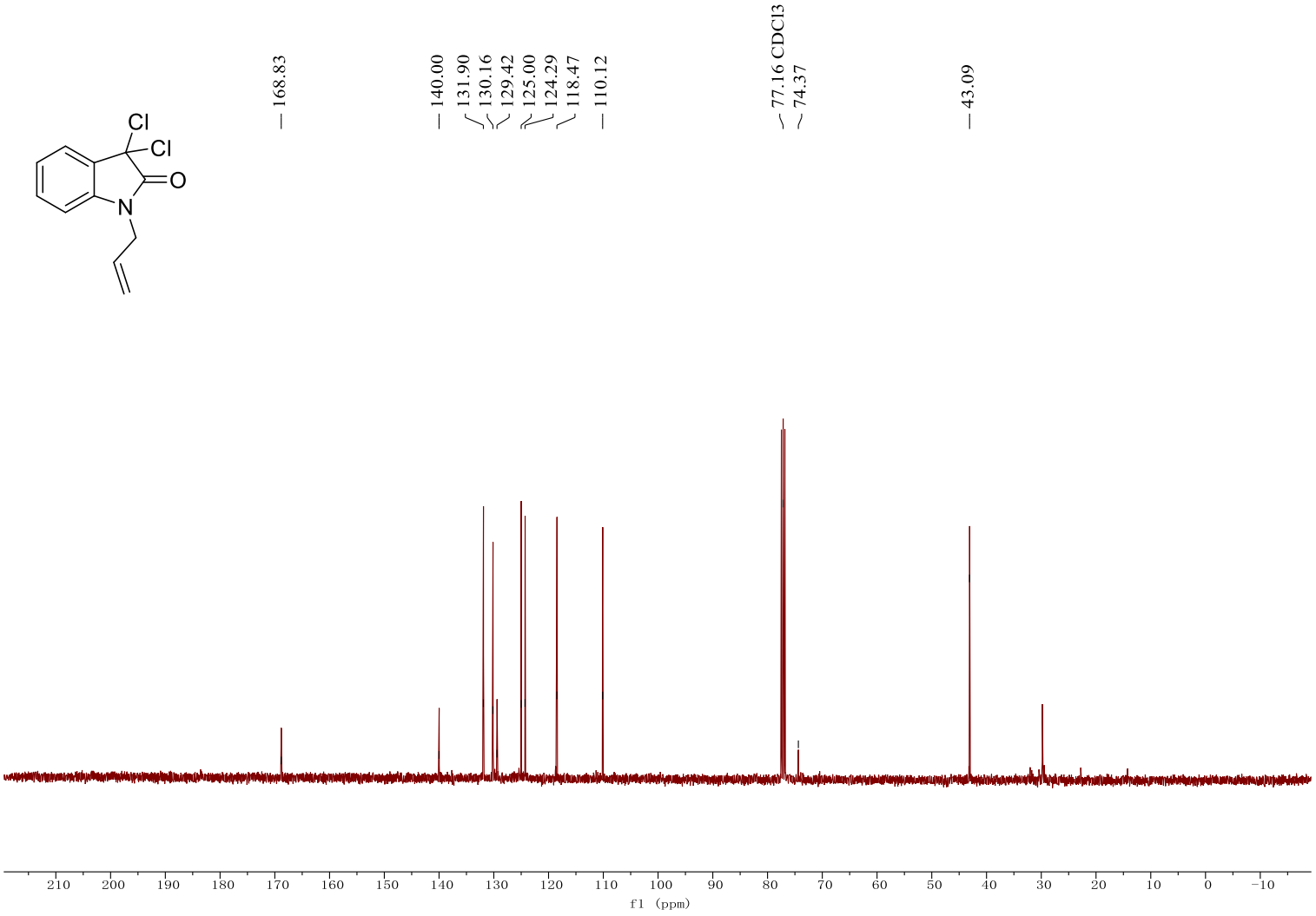
^{13}C NMR (101MHz, $CDCl_3$) spectra of 3,3-dichloro-1-(3-hydroxypropyl)indolin-2-one (4i)



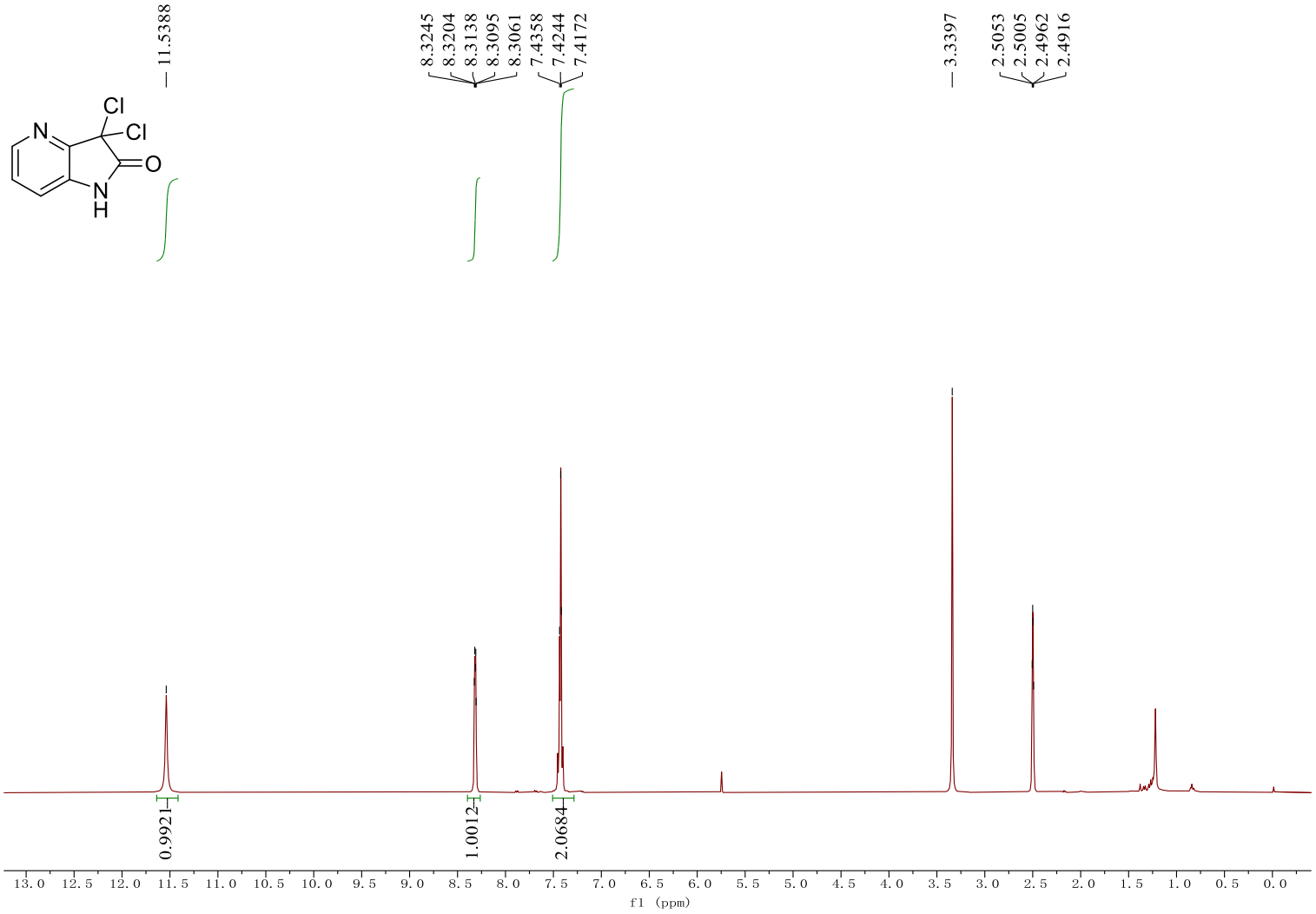
^{1}H NMR (400MHz, $CDCl_3$) spectra of 1-allyl-3,3-dichloroindolin-2-one (4j)



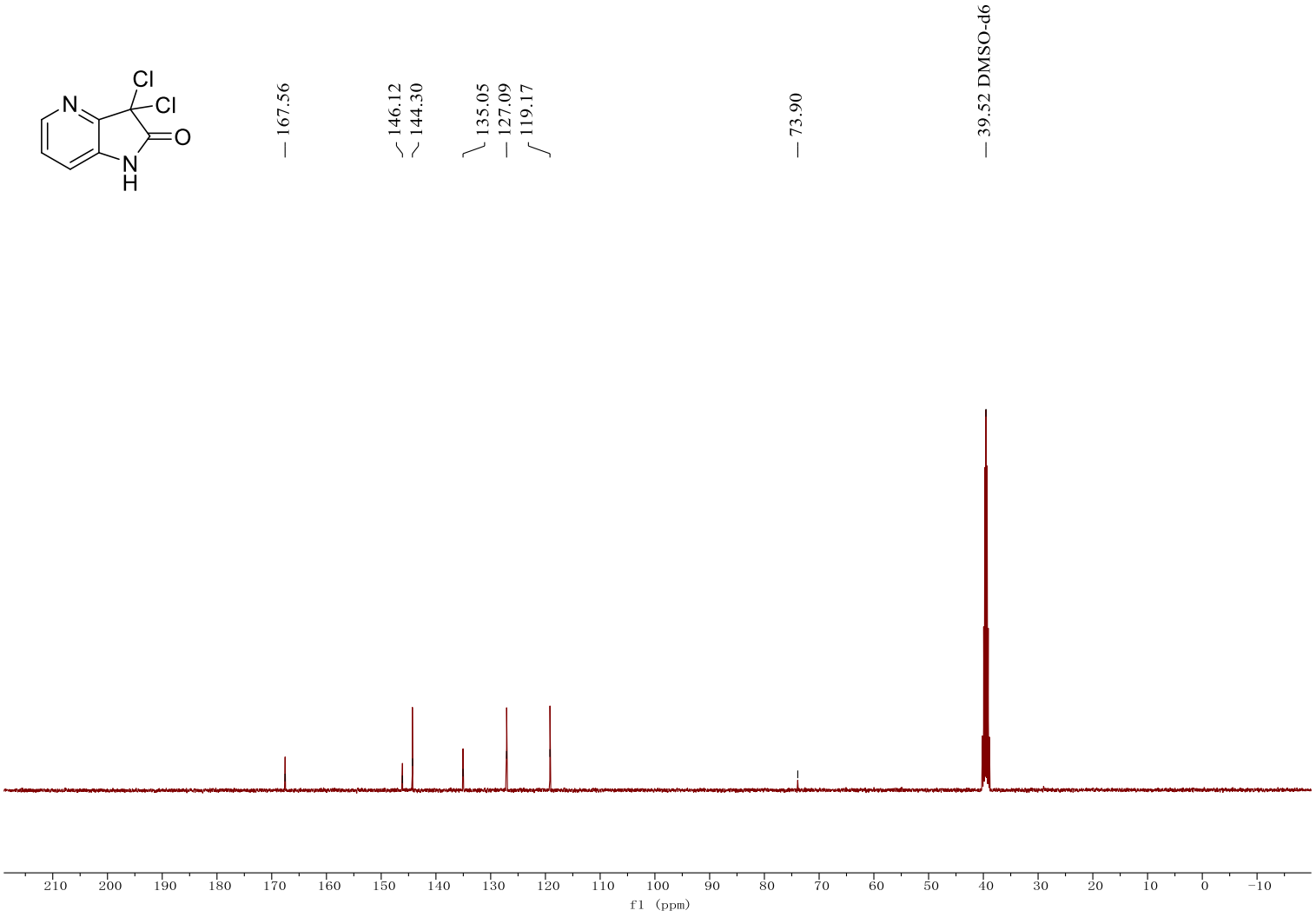
^{13}C NMR (101MHz, $CDCl_3$) spectra of 1-allyl-3,3-dichloroindolin-2-one (4j)



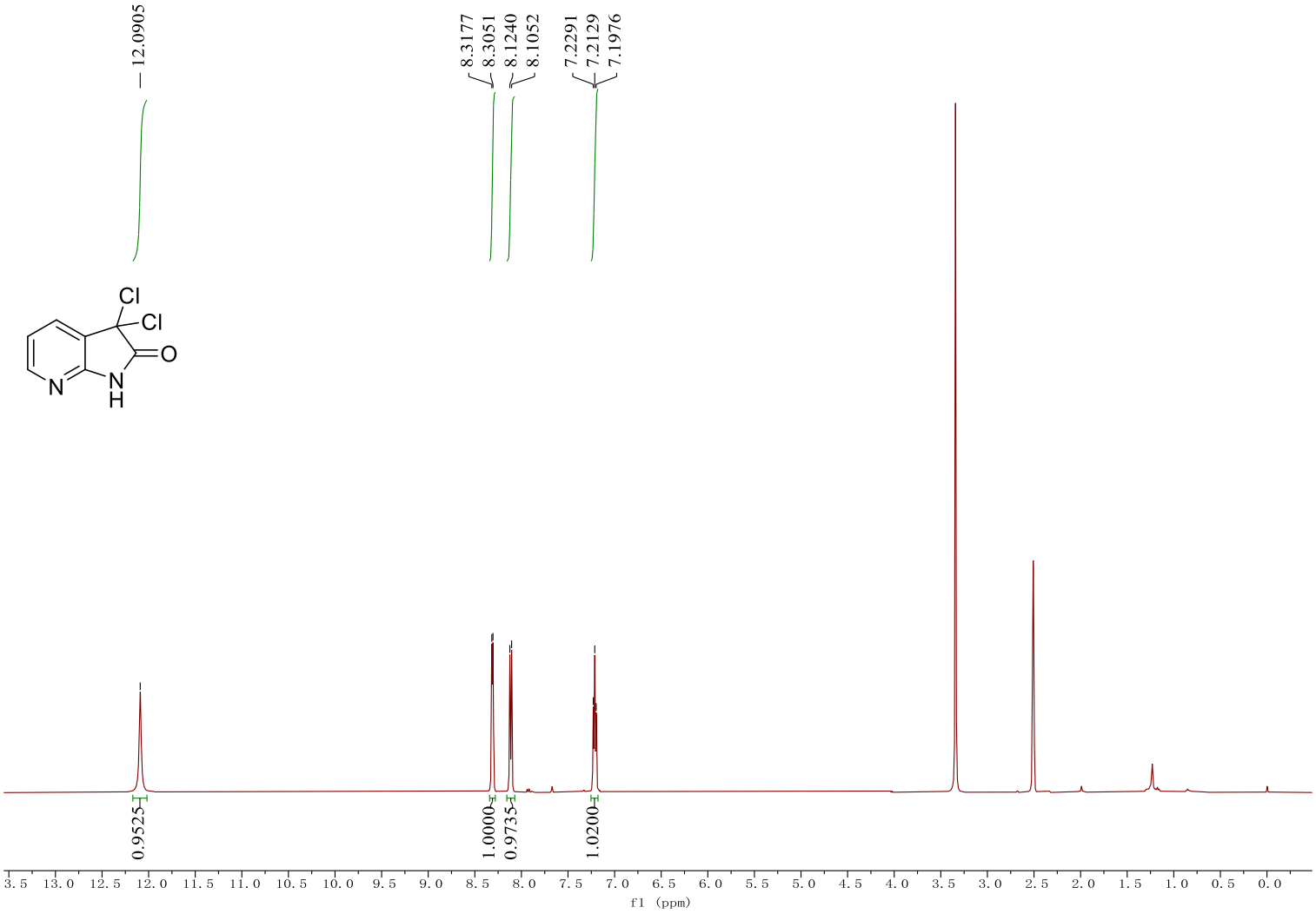
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3,3-dichloro-1,3-dihydro-2H-pyrrolo[3,2-*b*]pyridin-2-one (4k)



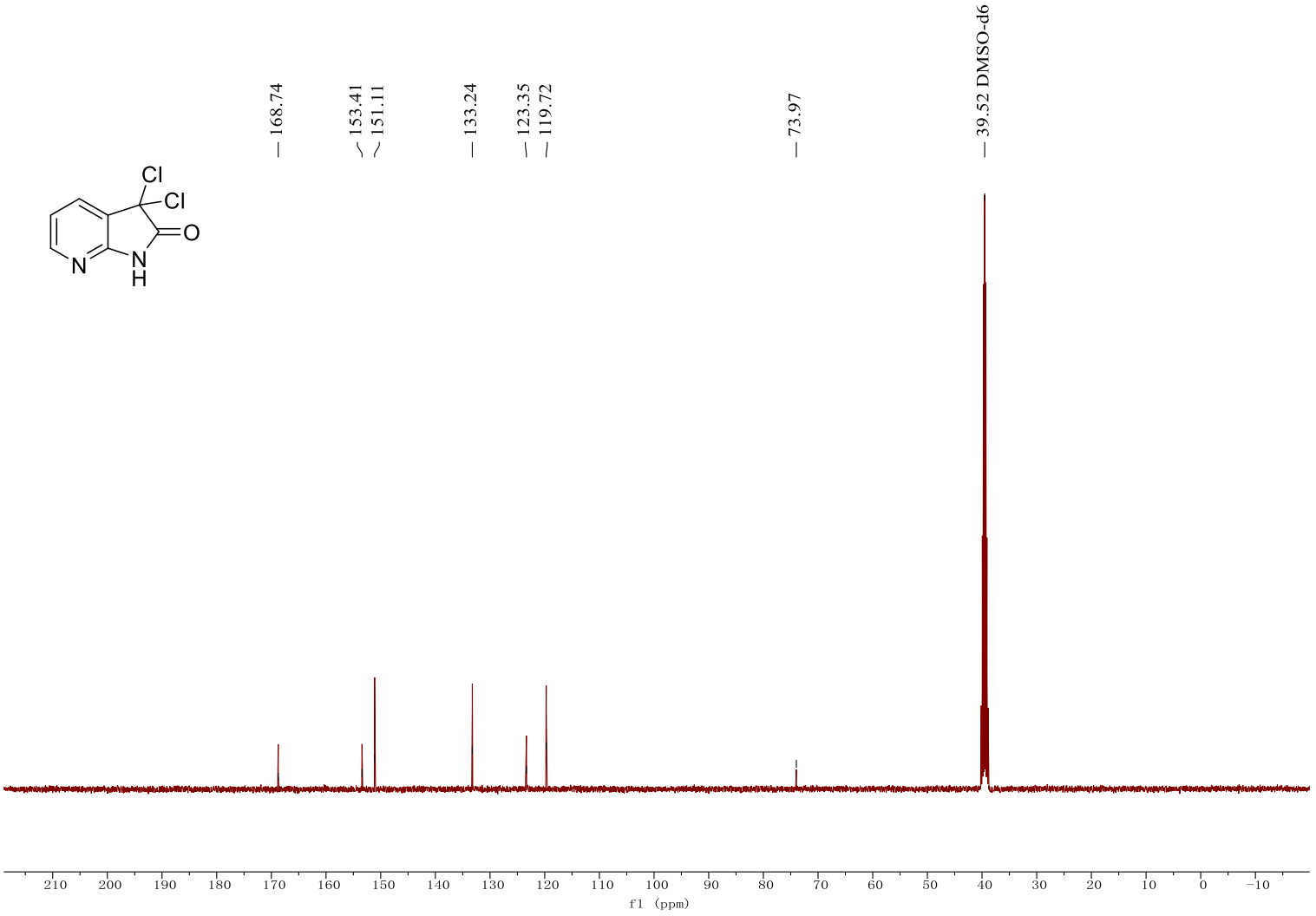
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3,3-dichloro-1,3-dihydro-2H-pyrrolo[3,2-*b*]pyridin-2-one (4k)



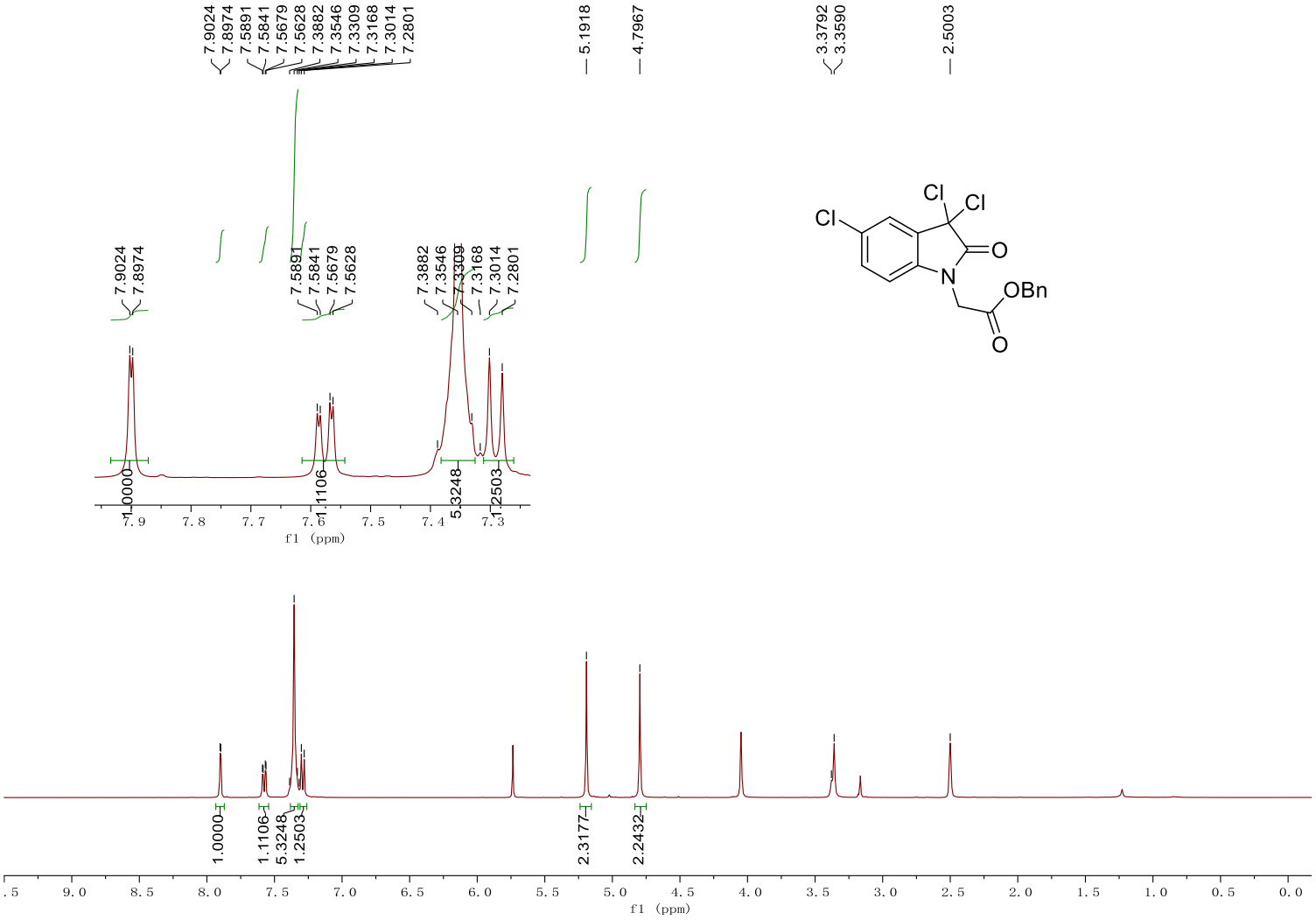
^{1}H NMR (400MHz, DMSO-d_6) spectra of 3,3-dichloro-1,3-dihydro-2H-pyrrolo[2,3-*b*]pyridin-2-one (4l)



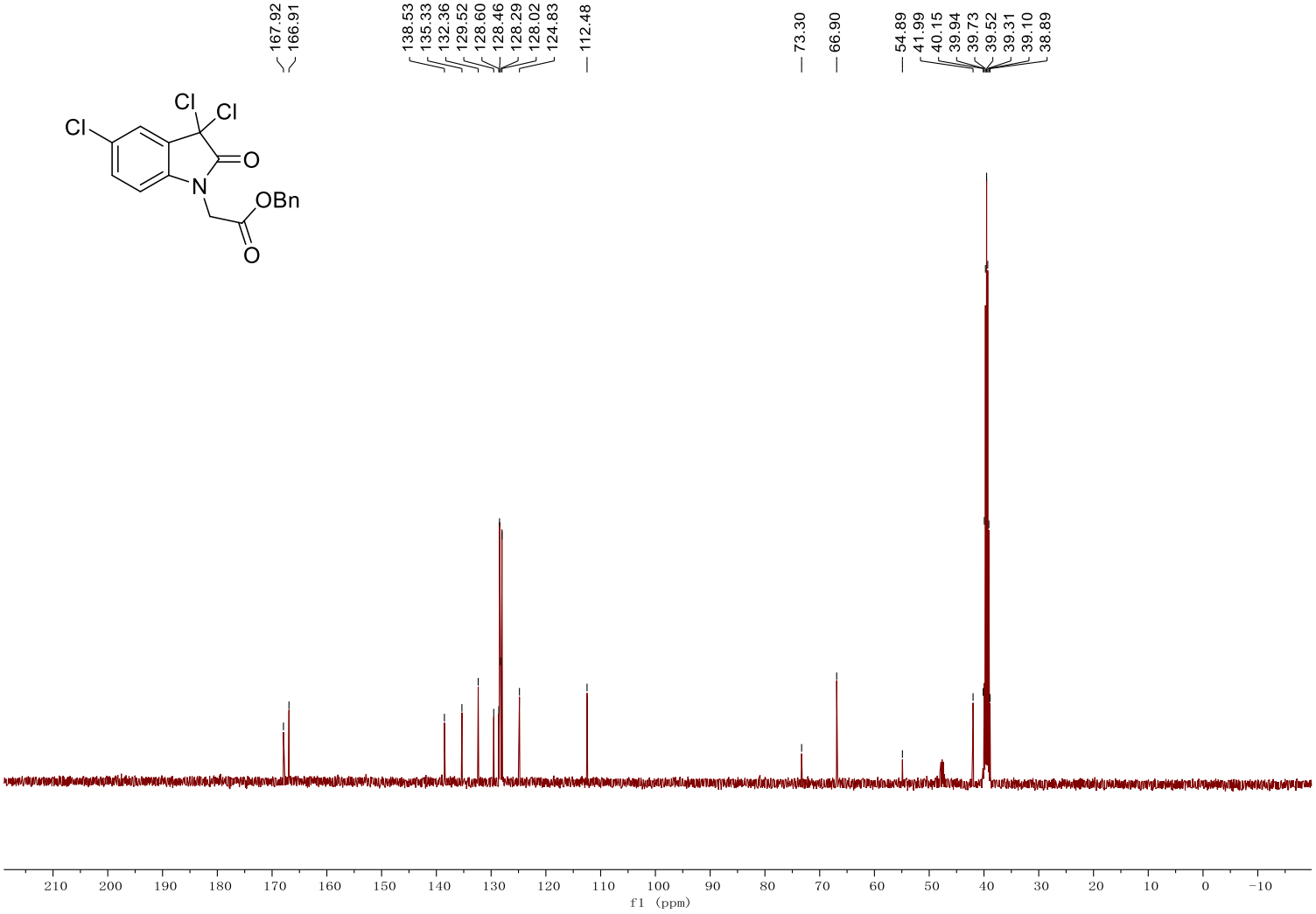
^{13}C NMR (101MHz, DMSO-d_6) spectra of 3,3-dichloro-1,3-dihydro-2H-pyrrolo[2,3-*b*]pyridin-2-one (4l)



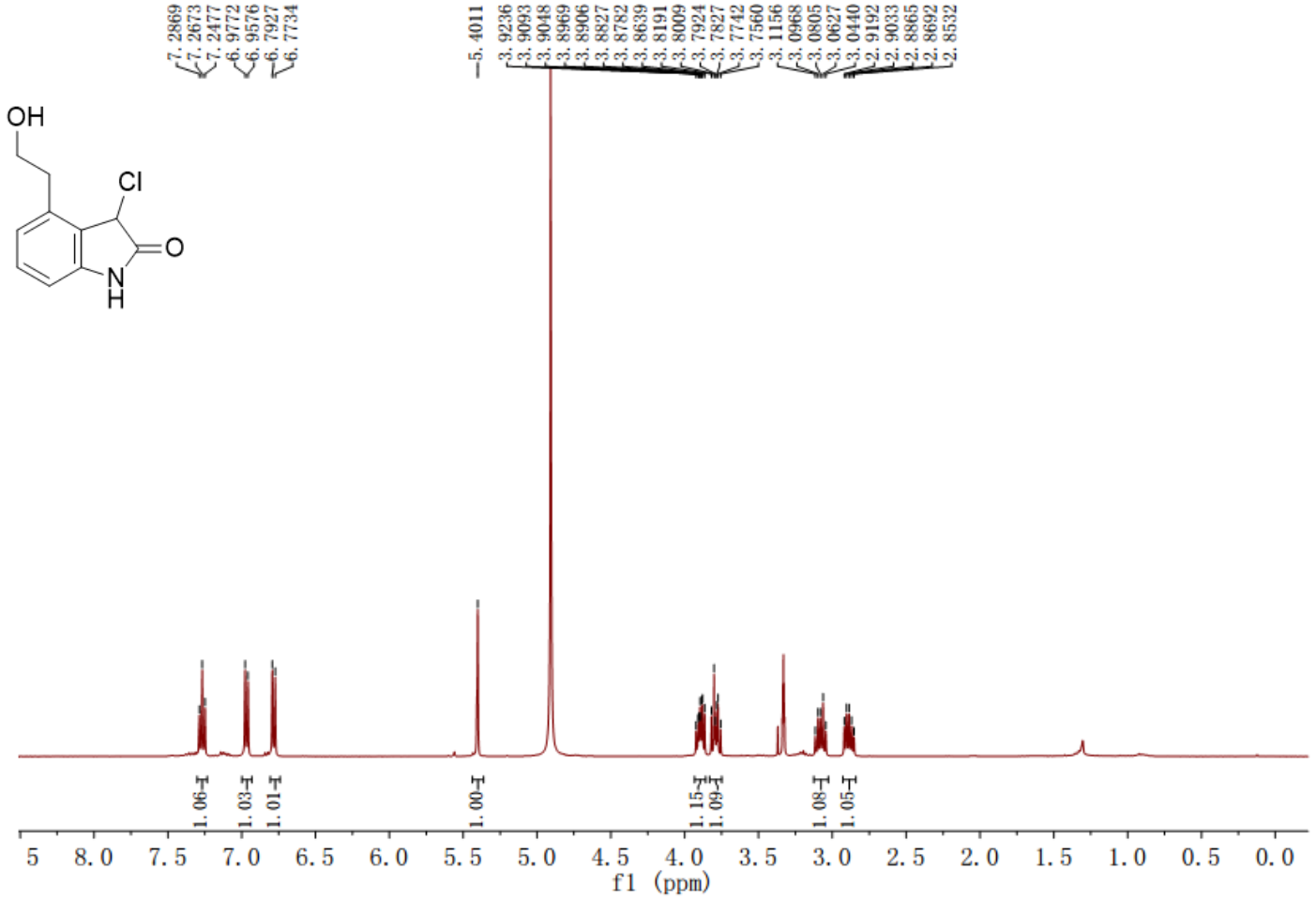
^{1}H NMR (400MHz, DMSO-d_6) spectra of benzyl 2-(3,3,5-trichloro-2-oxoindolin-1-yl)acetate (10)



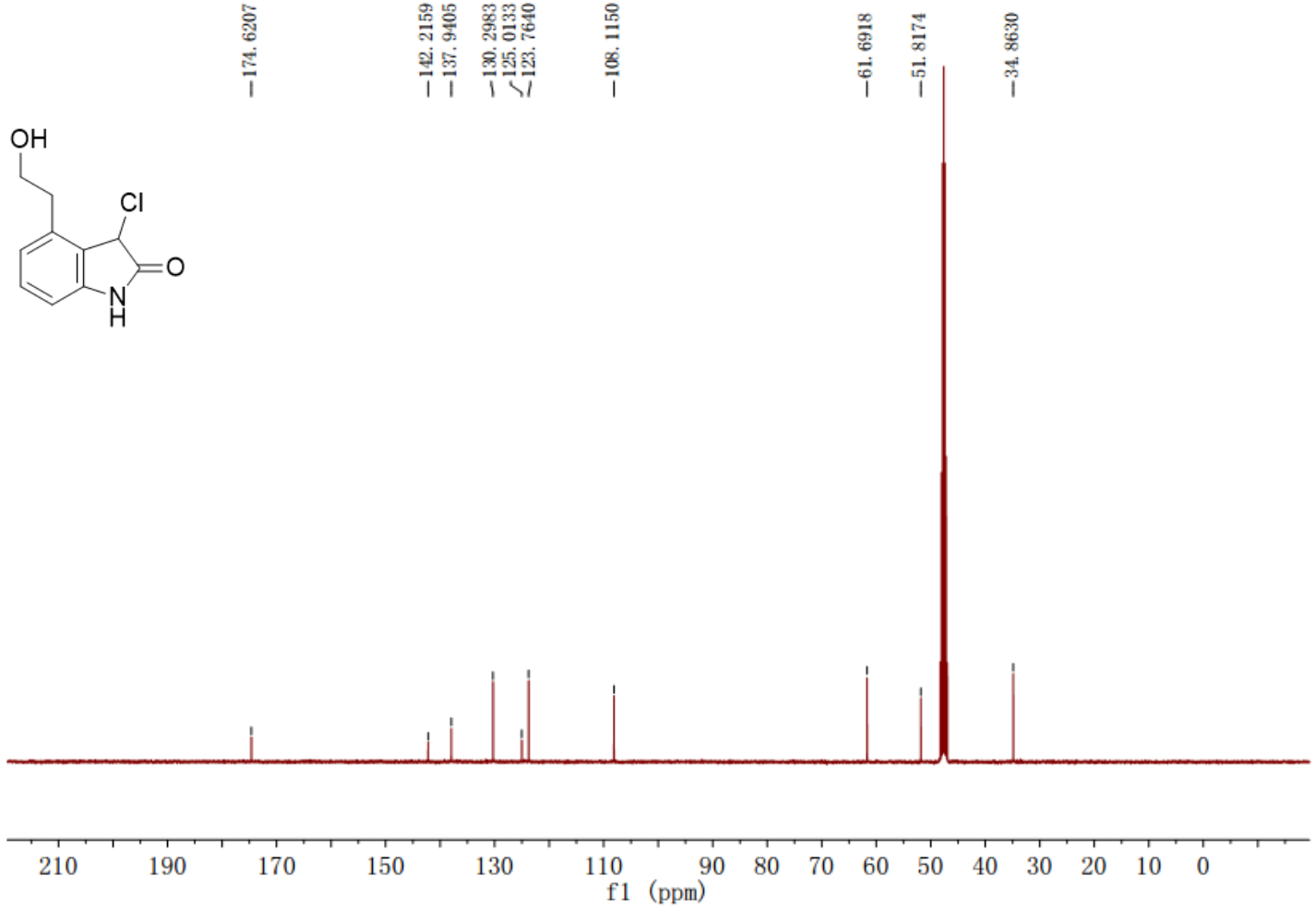
^{13}C NMR (101MHz, DMSO-d_6) spectra of benzyl 2-(3,3,5-trichloro-2-oxoindolin-1-yl)acetate (10)



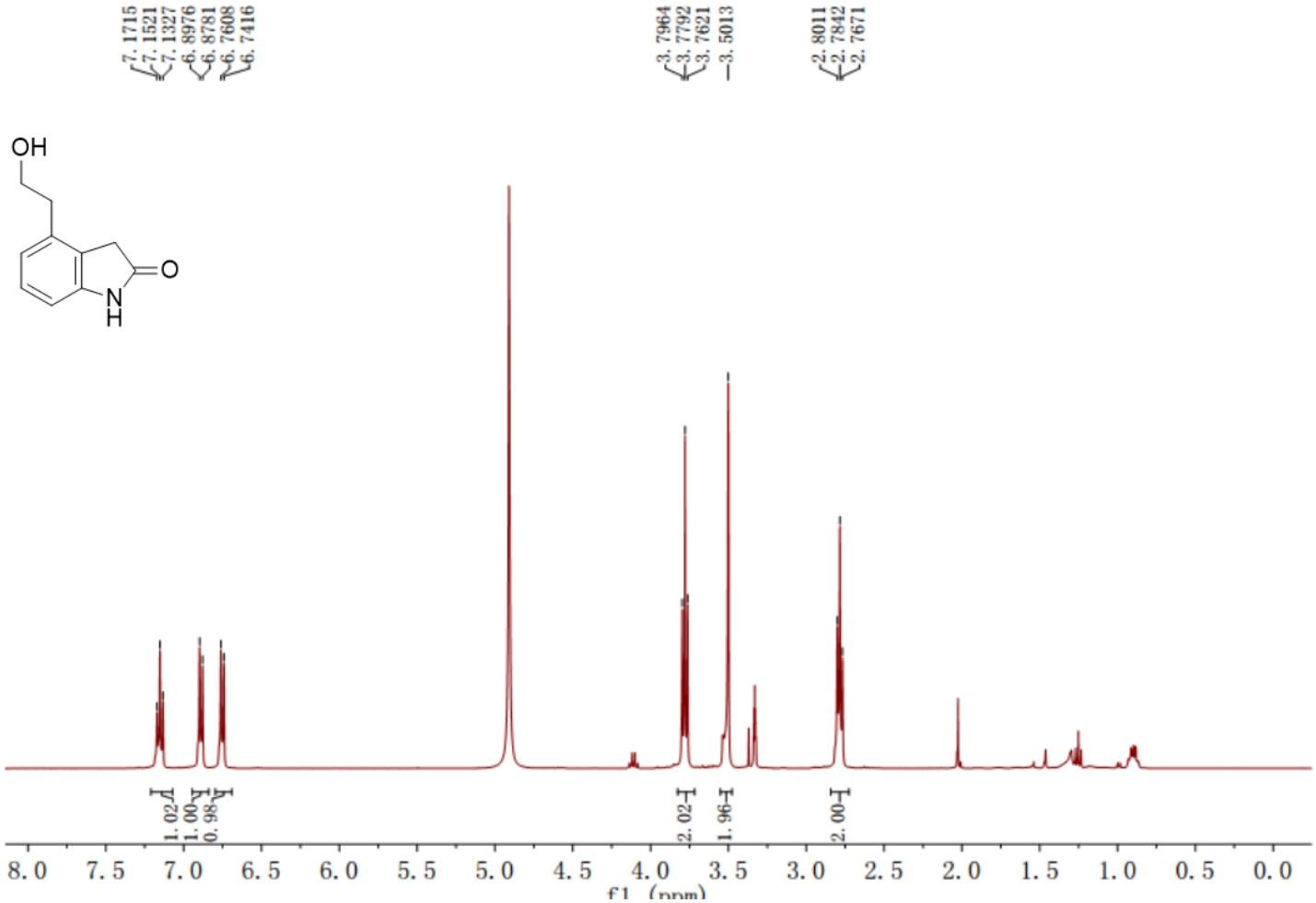
^{1}H NMR (400MHz, CD_3OD) spectra of 3-chloro-4-(2-hydroxyethyl)indolin-2-one (12)



^{13}C NMR (101MHz, CD_3OD) spectra of 3-chloro-4-(2-hydroxyethyl)indolin-2-one (12)



^{1}H NMR (400MHz, CD_3OD) and ^{13}C NMR (101MHz, CD_3OD) spectra of 4-(2-hydroxyethyl)indolin-2-one (13)



^{13}C NMR (101MHz, CD_3OD) spectra of 4-(2-hydroxyethyl)indolin-2-one (13)