Supplementary Information

Metal-Free Heteroarene C(sp^2)-H Aminations with Unprotected (Hetero)arylamines

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1. General Information

All reactions under standard conditions were carried out under nitrogen and monitored by thin-layer chromatography (TLC) on gel F254 plates. Hexane and ethyl acetate were used as eluents. All solvents were purified and dried by standard techniques and distilled prior to use. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on *Agilent ProPulse* AM-400 MHz instruments and the spectral data were reported in ppm relative to tetramethylsilane (0.00 ppm) or residual undeuterated solvent $CHCl_3$ (7.26 ppm) and DMSO (2.50 pm) as internal standard for ^{1}H NMR and deuterated solvent $CDCl_3$ (77.0 ppm) and DMSO-d_6 (39.5 ppm) as internal standard for ^{13}C NMR. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, hept = heptet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, tt = triplet of triplet, ttt = triplet of triplet of triplets). High-resolution mass spectral analysis (HRMS) data were measured on an *Agilent* 7890-5975C spectrometer by means of the ESI technique.

Known componds:

1a-1, **1a-2**, **1a-3**, **1a-4**, **1a-5**, **1a-9**, **1a-15**, **1a-17**, **1a-19**, **1a-28**, **1a-29**;

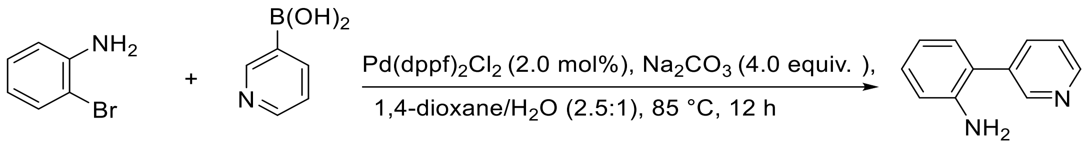
1b-1, **1b-2**, **1b-5**, **1b-8**, **1b-15**, **1b-19**, **1b-21**, **1b-22**, **1b-23**;

2a-1, **2a-2**, **2a-3**, **2a-4**, **2a-5**, **2a-7**, **2a-8**, **2a-9**, **2a-10**, **2a-14**, **2a-15**, **2a-16**, **2a-17**, **2a-18**, **2a-19**, **2a-20**, **2a-28**, **2a-29**, **2a-30**, **2a-31**;

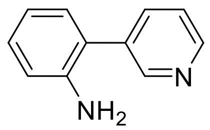
2b-1, **2b-2**, **2b-4,** **2b-5**, **2b-6**, **2b-10**, **2b-11**, **2b-12**, **2b-13**, **2b-16**, **2b-18**, **2b-19**, **2b-21**, **2b-22**, **2b-23**, **2b-25**.

2. Preparation of Starting Materials

2.1 General procedure 1: for the synthesis of 2-(pyridin-3-yl)aniline derivatives **1a-1-1a-10**, **1a-12-1a-20**, **1a-22-1a-34**, **1b-1-1b-25**

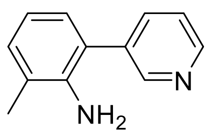


A clean, oven-dried Schlenk tube with previously placed magnetic stir-bar was charged with 2-bromoaniline (860.0 mg, 1.0 equiv.), pyridin-3-ylboronic acid (738.0 mg, 1.2 equiv.), Pd(dppf)$_2$Cl$_2$ (76.2 mg, 2.0 mmol%) and Na_2CO_3 (2.12 g, 4.0 equiv.). The reaction was evacuated and back filled with nitrogen and this sequence was repeated for three additional times. Under the positive flow of nitrogen, a 2.5/1 mixture of 1,4-dioxane (25 mL) and water (10 mL) was added to the reaction mixture. The reaction mixture was vigorously stirred at 85 °C for 12 h. Next, the reaction was allowed to cool at room temperature and the reaction mixture was extracted with ethyl acetate (3×50 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel to give the desired **1a-1**. Substrates **1a-1-1a-10**, **1a-12-1a-20**, **1a-22-1a-34**, **1b-1-1b-25** were prepared by this method. [1]



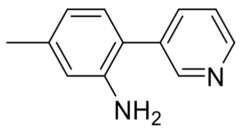
2-(pyridin-3-yl)aniline (1a-1)[2]

Prepared according to general procedure 1 to afford **1a-1** (807 mg, 95% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.59 (d, J = 3.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.37 (dd, J = 7.8, 4.9 Hz, 1H), 7.20 (t, J = 8.2 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 3.35 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.8, 148.2, 143.8, 136.6, 135.6, 130.6, 129.4, 123.8, 123.7, 118.9, 115.9. HRMS (m/z): calcd for $C_{11}H_{10}N_2$ [M+H]$^+$: 171.0917, Found: 171.0922.



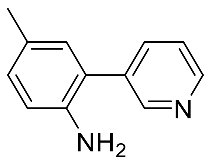
2-methyl-6-(pyridin-3-yl)aniline (1a-2)[3]

Prepared according to general procedure 1 to afford **1a-2** (298 mg, 81% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.36 (d, J = 4.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.14 (dd, J = 7.5, 4.6 Hz, 1H), 6.91 (d, J = 7.3 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.62-6.56 (m, 1H), 3.56 (s, 2H), 2.03 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.2, 142.0, 136.7, 135.7, 130.5, 128.4, 123.6, 123.4, 122.7, 118.2, 17.8. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, Found: 185.1072.



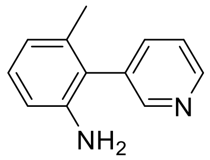
3-methyl-6-(pyridin-3-yl)aniline (1a-3)[4]

Prepared according to general procedure 1 to afford **1a-3** (290 mg, 79% yield) as a brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.56 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 6.3 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 6.59 (s, 1H), 3.62 (s, 2H), 2.29 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.1, 143.6, 139.4, 136.5, 135.4, 130.4, 123.6, 121.0, 119.8, 116.5, 21.2. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, Found: 185.1085.



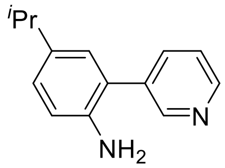
4-methyl-2-(pyridin-3-yl)aniline (1a-4)[2]

Prepared according to general procedure 1 to afford **1a-4** (294 mg, 80% yield) as a brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.38 (s, 1H), 7.65-7.58 (m, 1H), 7.16 (dd, J = 8.2, 4.0 Hz, 1H), 6.86-6.79 (m, 1H), 6.75 (s, 1H), 6.53 (dd, J = 8.0, 2.8 Hz, 1H), 3.58 (s, 2H), 2.12 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.9, 148.1, 141.4, 136.6, 135.5, 130.9, 129.9, 128.0, 123.6, 123.5, 116.1, 20.4. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, Found: 185.1082.



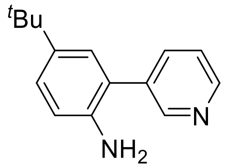
3-methyl-2-(pyridin-3-yl)aniline (1a-5)

Prepared according to general procedure 1 to afford **1a-5** (258 mg, 70% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.58 (dd, J = 4.8, 1.7 Hz, 1H), 8.49 (d, J = 2.1 Hz, 1H), 7.59 (dt, J = 7.7, 2.0 Hz, 1H), 7.38 (dd, J = 7.7, 4.9 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 3.38 (s, 2H), 1.97 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.8, 148.5, 144.3, 137.9, 137.1, 134.1, 128.8, 124.0, 123.5, 120.1, 113.0, 20.7. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1073, Found: 185.1082.



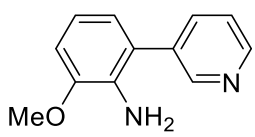
5-isopropyl-2-(pyridin-3-yl)aniline (1a-6)

Prepared according to general procedure 1 to afford **1a-6** (256 mg, 61% yield) as a brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 2.2 Hz, 1H), 8.55 (d, J = 4.6 Hz, 1H), 7.81 (dt, J = 7.5, 1.6 Hz, 1H), 7.33 (dd, J = 7.8, 4.8 Hz, 1H), 7.06 (dd, J = 8.2, 2.1 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 6.73 (d, J = 0.6 Hz, 1H), 3.67 (s, 2H), 2.84 (hept, J = 6.9 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.2, 141.7, 139.4, 136.6, 135.6, 128.4, 127.3, 123.6, 123.5, 116.1, 33.2, 24.3. HRMS (m/z): calcd for $C_{14}H_{16}N_2$ $[M+H]^+$: 213.1386, Found: 213.1400.



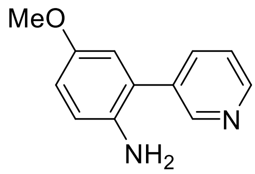
4-(*tert*-butyl)-2-(pyridin-3-yl)aniline (1a-7)

Prepared according to general procedure 1 to afford **1a-7** (360 mg, 80% yield) as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.56 (d, J = 4.3 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.37-7.31 (m, 1H), 7.23 (dd, J = 8.3, 1.8 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.68 (s, 2H), 1.31 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.1, 148.2, 141.7, 141.4, 136.6, 135.9, 127.3, 126.3, 123.5, 123.3, 115.8, 34.0, 31.6. HRMS (m/z): calcd for $C_{15}H_{18}N_2$ $[M+H]^+$: 227.1543, Found: 227.1552.



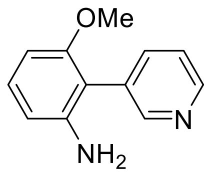
2-methoxy-6-(pyridin-3-yl)aniline (1a-8)

Prepared according to general procedure 1 to afford **1a-8** (240 mg, 60% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.52 (dd, J = 4.9, 1.5 Hz, 1H), 7.78 (dt, J = 7.8, 1.9 Hz, 1H), 7.30 (dd, J = 7.8, 4.9 Hz, 1H), 6.82-6.69 (m, 3H), 3.84 (s, 3H), 3.77 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.2, 147.3, 136.4, 135.2, 133.9, 123.5, 123.5, 122.4, 117.9, 110.0, 55.7. HRMS (m/z): calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022, Found: 201.1032.



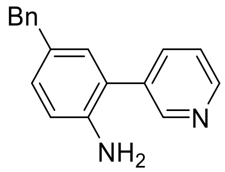
4-methoxy-2-(pyridin-3-yl)aniline (1a-9)[2]

Prepared according to general procedure 1 to afford **1a-9** (256 mg, 64% yield) as a yellowish-brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.58 (d, J = 5.1 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.37 (dd, J = 7.9, 4.8 Hz, 1H), 6.80 (dd, J = 8.7, 2.9 Hz, 1H), 6.77-6.64 (m, 2H), 3.76 (s, 3H), 3.21 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 152.9, 149.9, 148.4, 137.4, 136.6, 135.3, 124.8, 123.5, 117.3, 115.7, 115.3, 55.8. HRMS (m/z): calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022, Found: 201.1030.



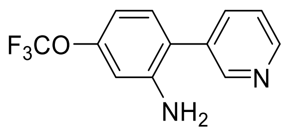
3-methoxy-2-(pyridin-3-yl)aniline (1a-10)

Prepared according to general procedure 1 to afford **1a-10** (260 mg, 56% yield) as a brown solid, (m.p. 118-119 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.59-8.52 (m, 2H), 7.67 (dt, J = 7.8, 1.9 Hz, 1H), 7.35 (dd, J = 7.8, 4.8 Hz, 1H), 7.12 (t, J = 8.2 Hz, 1H), 6.40 (t, J = 8.5 Hz, 2H), 3.66 (s, 3H), 3.51 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.7, 151.6, 148.2, 145.4, 138.5, 131.1, 129.6, 123.6, 112.3, 108.6, 100.9, 55.5. HRMS (m/z): calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022, Found: 201.1018.



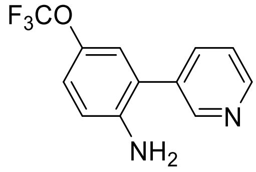
4-benzyl-2-(pyridin-3-yl)aniline (1a-12)

Prepared according to general procedure 1 to afford **1a-12** (411 mg, 79% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 2.2 Hz, 1H), 8.29 (d, J = 3.1 Hz, 1H), 7.50 (dt, J = 7.8, 2.0 Hz, 1H), 7.07-6.92 (m, 6H), 6.78 (d, J = 8.1 Hz, 1H), 6.73 (s, 1H), 6.44 (d, J = 8.1 Hz, 1H), 3.67 (s, 2H), 3.50 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.2, 142.3, 142.3, 141.7, 136.6, 135.5, 131.5, 130.9, 129.9, 128.9, 128.6, 126.1, 123.8, 123.6, 116.3, 41.1. HRMS (m/z): calcd for $C_{18}H_{16}N_2$ $[M+H]^+$: 261.1386, Found: 261.1393.



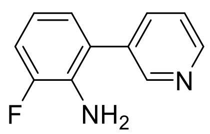
2-(pyridin-3-yl)-5-(trifluoromethoxy)aniline (1a-13)

Prepared according to general procedure 1 to afford **1a-13** (366 mg, 72% yield) as a yellow solid, (m.p. 56-57 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.40 (d, J = 4.3 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.20 (dd, J = 7.9, 4.8 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.54-6.47 (m, 2H), 3.97 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0 (q, J = 1.8 MHz), 149.7, 148.5, 145.5, 136.5, 134.2, 131.5, 123.6, 121.9, 121.7, 110.3, 107.6. HRMS (m/z): calcd for $C_{12}H_9F_3N_2O$ $[M+H]^+$: 255.0744, Found: 255.0748.



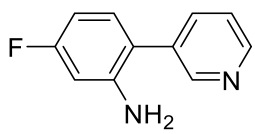
2-(pyridin-3-yl)-4-(trifluoromethoxy)aniline (1a-14)

Prepared according to general procedure 1 to afford **1a-14** (386 mg, 76% yield) as a brown liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.43 (d, J = 4.6 Hz, 1H), 7.64 (dt, J = 7.8, 2.0 Hz, 1H), 7.24 (dd, J = 7.8, 4.8 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 6.51 (s, 1H), 3.89 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0 (q, J = 1.9 MHz), 149.7, 148.5, 145.5, 136.6, 134.2, 131.6, 123.7, 121.9, 121.7, 119.1, 110.4, 107.6. HRMS (m/z): calcd for $C_{12}H_9F_3N_2O$ $[M+H]^+$: 255.0744, Found: 255.0750.



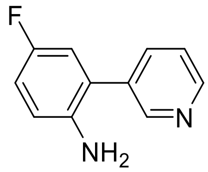
2-fluoro-6-(pyridin-3-yl)aniline (1a-15)[5]

Prepared according to general procedure 1 to afford **1a-15** (229 mg, 61% yield) as a gray solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.61 (d, J = 4.7 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 6.3 Hz, 1H), 7.03 (t, J = 9.5 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 6.76 (q, J = 7.4 Hz, 1H), 3.74 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 152.9, 150.6, 149.8, 148.7, 136.4, 134.2, 132.5 (d, J = 13.0 Hz), 125.6 (d, J = 3.0 Hz), 123.6, 118.0 (d, J = 8.0 Hz), 114.8 (d, J = 19.0 Hz). HRMS (m/z): calcd for $C_{11}H_9FN_2$ $[M+H]^+$: 189.0823, Found: 189.0827.



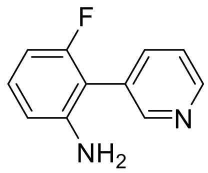
5-fluoro-2-(pyridin-3-yl)aniline (1a-16)

Prepared according to general procedure 1 to afford **1a-16** (331 mg, 88% yield) as a pale-yellow solid, (m.p. 73-74 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.68-8.55 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.36 (dd, J = 7.8, 4.8 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.58-6.43 (m, 2H), 3.82 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.8, 162.4, 150.1, 148.5, 145.5 (d, J = 11.0 Hz), 136.6, 134.5, 131.8 (d, J = 10.0 Hz), 123.6, 105.5 (d, J = 22.0 Hz), 102.3 (d, J = 24.0 Hz). HRMS (m/z): calcd for $C_{11}H_9FN_2$ $[M+H]^+$: 189.0823, Found: 189.0829.



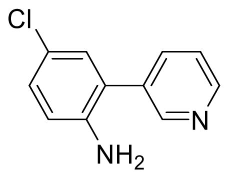
4-fluoro-2-(pyridin-3-yl)aniline (1a-17)[2]

Prepared according to general procedure 1 to afford **1a-17** (282 mg, 75% yield) as a light gray oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.61 (d, J = 4.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 7.8, 4.9 Hz, 1H), 6.91 (td, J = 8.5, 2.9 Hz, 1H), 6.84 (dd, J = 9.0, 2.9 Hz, 1H), 6.72 (dd, J = 8.8, 4.8 Hz, 1H), 3.40 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.5, 155.1, 149.8, 148.8, 139.9, 136.4, 134.4, 123.6, 116.80 ,116.7 (d, J = 30.0 Hz), 115.8 (d, J = 22.0 Hz). HRMS (m/z): calcd for $C_{11}H_9FN_2$ $[M+H]^+$: 189.0823, Found: 189.0827.



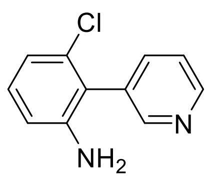
3-fluoro-2-(pyridin-3-yl)aniline (1a-18)

Prepared according to general procedure 1 to afford **1a-18** (226 mg, 60% yield) as a black solid, (m.p. 78-79 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71-8.54 (m, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 6.3 Hz, 1H), 7.12 (q, J = 7.6 Hz, 1H), 6.56 (d, J = 6.8 Hz, 2H), 3.75 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 161.9, 159.5, 151.0 (d, J = 1.3 Hz), 149.02, 145.8 (d, J = 5.6 Hz), 138.0 (d, J = 1.3 Hz), 123.0 (d, J = 10.5 Hz), 128.6, 123.7, 111.0 (d, J = 2.8 Hz), 105.1 (d, J = 22.8 Hz). HRMS (m/z): calcd for $C_{11}H_9FN_2$ $[M+H]^+$: 189.0823, Found: 189.0829.



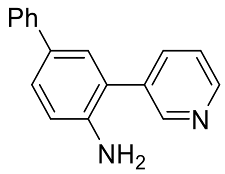
4-chloro-2-(pyridin-3-yl)aniline (1a-19)[2]

Prepared according to general procedure 1 to afford **1a-19** (258 mg, 63% yield) as a brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.61 (dd, J = 4.9, 1.6 Hz, 1H), 7.77 (dt, J = 7.9, 2.0 Hz, 1H), 7.38 (dd, J = 7.8, 4.9 Hz, 1H), 7.14 (dd, J = 8.6, 2.4 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 3.72 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.8, 148.9, 142.4, 136.4, 134.1, 130.0, 129.1, 125.0, 123.7, 123.4, 117.0. HRMS (m/z): calcd for $C_{11}H_9ClN_2$ $[M+H]^+$: 205.0527, Found: 205.0523.



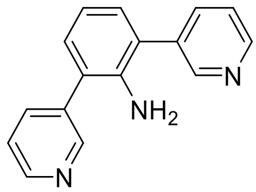
3-chloro-2-(pyridin-3-yl)aniline (1a-20)[2]

Prepared according to general procedure 1 to afford **1a-20** (247 mg, 60% yield) as a brown solid, (m.p. 110-112 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.58 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 7.8, 4.7 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 3.52 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.9, 149.0, 145.9, 138.1, 134.2, 132.3, 129.8, 124.0, 122.1, 119.1, 113.7. HRMS (m/z): calcd for $C_{11}H_9ClN_2$ $[M+H]^+$: 205.0527, Found: 205.0535.



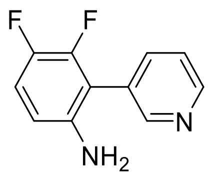
3-(pyridin-3-yl)-[1,1'-biphenyl]-4-amine (1a-22)

Prepared according to general procedure 1 to afford **1a-22** (247 mg, 70% yield) as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.50 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 7.9, 4.7 Hz, 1H), 7.20 (t, J = 7.9 Hz, 2H), 6.92 (dd, J = 22.6, 7.7 Hz, 3H), 6.84 (dd, J = 8.6, 2.7 Hz, 1H), 6.77 (d, J = 2.7 Hz, 1H), 6.68 (d, J = 8.6 Hz, 1H), 3.45 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.5, 149.8, 148.9, 148.6, 140.0, 136.5, 134.7, 129.6, 124.8, 123.6, 122.4, 121.9, 121.1, 117.4, 117.1. HRMS (m/z): calcd for $C_{17}H_{14}N_2$ $[M+H]^+$: 247.1230, Found: 247.1236.



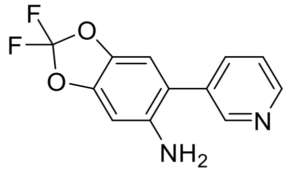
2,6-di(pyridin-3-yl)aniline (1a-23)

Prepared according to general procedure 1 to afford **1a-23** (198 mg, 40% yield) as a yellow solid, (m.p. 184-185 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.60 (s, 2H), 7.84 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 4.3 Hz, 2H), 7.13 (d, J = 6.3 Hz, 2H), 6.92 (t, J = 6.6 Hz, 1H), 3.71 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.1, 148.6, 141.2, 136.8, 135.1, 130.7, 124.4, 123.6, 118.7. HRMS (m/z): calcd for $C_{16}H_{13}N_3$ $[M+H]^+$: 248.1182, Found: 248.1197.



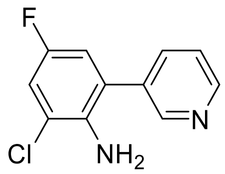
3,4-difluoro-2-(pyridin-3-yl)aniline (1a-24)

Prepared according to general procedure 1 to afford **1a-24** (313 mg, 76% yield) as a gray solid, (m.p. 92-94 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.41 (dd, J = 7.9, 4.9 Hz, 1H), 6.99 (q, J = 9.1 Hz, 1H), 6.49-6.41 (m, 1H), 3.36 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.8 (d, J = 1.5 Hz), 149.4, 147.0 (d, J = 13.6 Hz), 145.0 (d, J = 13.6 Hz), 142.5 (d, J = 13.6 Hz), 137.9, 127.8, 123.8, 117.1 (dd, J = 18.0, 2.0 Hz), 113.3 (d, J = 15.6 Hz), 110.0 (q, J = 3.7 Hz). HRMS (m/z): calcd for $C_{11}H_8F_2N_2$ $[M+H]^+$: 207.0728, Found: 207.0735.



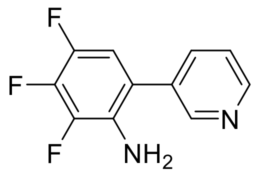
2,2-difluoro-6-(pyridin-3-yl)benzo[*d*][1,3]dioxol-5-amine (1a-25)

Prepared according to general procedure 1 to afford **1a-25** (360 mg, 72% yield) as a brown solid, (m.p. 125-127 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 15.4 Hz, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 6.5 Hz, 1H), 6.79 (s, 1H), 6.52 (s, 1H), 3.51 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.0, 148.7, 144.4, 140.6, 137.0, 136.8, 134.2, 131.7, 129.2, 117.8, 110.9, 97.8. HRMS (m/z): calcd for $C_{12}H_8F_2N_2O_2$ $[M+H]^+$: 251.0627, Found: 251.0632.



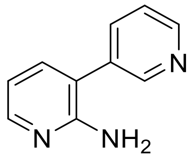
2-chloro-4-fluoro-6-(pyridin-3-yl)aniline (1a-26)

Prepared according to general procedure 1 to afford **1a-26** (293 mg, 66% yield) as a brown solid, (m.p. 126-128 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.73-8.58 (m, 2H), 7.79 (dt, J = 7.9, 2.0 Hz, 1H), 7.41 (dd, J = 7.8, 4.8 Hz, 1H), 7.09 (dd, J = 8.0, 2.9 Hz, 1H), 6.79 (dd, J = 8.6, 2.9 Hz, 1H), 3.95 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.0, 153.6, 149.6, 149.2, 136.6, 133.9, 123.8, 116.5, 116.3, 115.9, 115.7. HRMS (m/z): calcd for $C_{11}H_8ClFN_2$ $[M+H]^+$: 223.0433, Found: 223.0439.



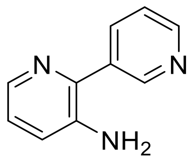
2,3,4-trifluoro-6-(pyridin-3-yl)aniline (1a-27)

Prepared according to general procedure 1 to afford **1a-27** (278 mg, 62% yield) as a white solid, (m.p. 142-143 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (dd, J = 12.7, 3.5 Hz, 2H), 7.75 (d, J = 7.6 Hz, 1H), 7.39 (dd, J = 7.8, 4.9 Hz, 1H), 6.76 (t, J = 8.7 Hz, 1H), 3.76 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.7, 149.3, 144.8 (d, J = 6.9 Hz), 142.4 (d, J = 13.7 Hz), 141.3, 136.4, 132.7, 130.2 (d, J = 10.2 Hz), 123.7, 118.8, 112.4 (dd, J = 14.9, 3.4 Hz). HRMS (m/z): calcd for $C_{11}H_7F_3N_2$ $[M+H]^+$: 225.0634, Found: 225.0633.



[3,3'-bipyridin]-2-amine (1a-28)[6]

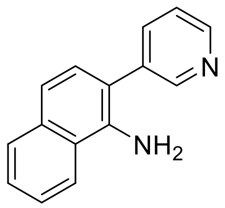
Prepared according to general procedure 1 to afford **1a-28** (250 mg, 73% yield) as a gray solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.57 (d, J = 4.7 Hz, 1H), 8.06 (d, J = 5.0 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.34 (dd, J = 14.8, 6.2 Hz, 2H), 6.73 (dd, J = 7.3, 4.9 Hz, 1H), 4.71 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.0, 149.7, 149.0, 148.1, 138.2, 136.1, 133.9, 123.7, 118.1, 114.5. HRMS (m/z): calcd for $C_{10}H_9N_3$ $[M+H]^+$: 172.0869, Found: 172.0865.



[2,3'-bipyridin]-3-amine (1a-29)[7]

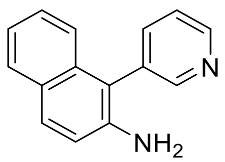
Prepared according to general procedure 1 to afford **1a-29** (250 mg, 68% yield) as a gray solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.54 (s, 1H), 8.06 (d, J = 2.1

Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.36-7.29 (m, 1H), 7.02 (s, 2H), 3.61 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.4, 149.2, 141.5, 140.5, 140.3, 136.2, 134.5, 123.8, 123.6, 123.1. HRMS (m/z): calcd for $C_{10}H_9N_3$ $[M+H]^+$: 172.0869, Found: 172.0865.



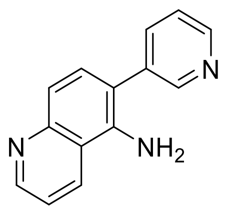
2-(pyridin-3-yl)naphthalen-1-amine (1a-30)

Prepared according to general procedure 1 to afford **1a-30** (440 mg, 75% yield) as a brown solid, (m.p. 117-119 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 8.80 (d, *J* = 1.5 Hz, 1H), 8.61 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.88-7.79 (m, 3H), 7.52-7.45 (m, 2H), 7.37 (dt, *J* = 7.8, 2.1 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 4.36 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* 150.5, 148.3, 139.2, 137.1, 135.9, 134.0, 128.6, 128.2, 126.3, 125.5, 123.8, 123.4, 121.2, 118.7, 117.8. HRMS (m/z): calcd for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1073, Found: 221.1070.



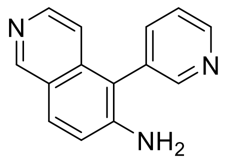
1-(pyridin-3-yl)naphthalen-2-amine (1a-31)

Prepared according to general procedure 1 to afford **1a-31** (304 mg, 69% yield) as a red solid, (m.p. 148-150 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 8.62 (dt, *J* = 4.6, 2.1 Hz, 1H), 8.56 (t, *J* = 2.3 Hz, 1H), 7.70-7.61 (m, 3H), 7.40 (ddd, *J* = 7.6, 4.9, 2.4 Hz, 1H), 7.24-7.13 (m, 2H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.52 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* 151.9, 148.8, 141.7, 139.0, 133.7, 133.1, 129.6, 128.1, 127.9, 126.8, 124.1, 123.5, 122.4, 118.1, 115.4. HRMS (m/z): calcd for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1073, Found: 221.1079.



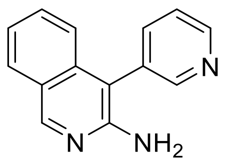
6-(pyridin-3-yl)quinolin-5-amine (1a-32)

Prepared according to general procedure 1 to afford **1a-32** (318 mg, 72% yield) as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, J = 4.1, 1.5 Hz, 1H), 8.73-8.67 (m, 2H), 8.58 (dd, J = 4.8, 1.6 Hz, 1H), 7.91 (dt, J = 7.8, 2.0 Hz, 1H), 7.51 (dd, J = 7.8, 5.1 Hz, 1H), 7.46-7.38 (m, 2H), 7.33 (d, J = 8.6 Hz, 1H), 5.76 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.6, 150.4, 149.0, 148.3, 142.1, 137.2, 135.9, 132.6, 131.8, 124.3, 120.0, 118.3, 117.4, 116.3. HRMS (m/z): calcd for $C_{14}H_{11}N_3$ $[M+H]^+$: 222.1026, Found: 222.1020.



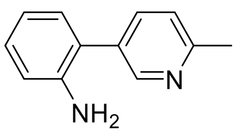
5-(pyridin-3-yl)isoquinolin-6-amine (1a-33)

Prepared according to general procedure 1 to afford **1a-33** (344 mg, 78% yield) as a gray solid, (m.p. 231-233 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.97 (s, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.26-7.14 (m, 3H), 6.84 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.55 (s, 1H), 3.78 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.7, 151.2, 149.5, 145.9, 143.1, 138.7, 137.0, 131.3, 129.8, 124.3, 123.1, 119.1, 116.5. HRMS (m/z): calcd for $C_{14}H_{11}N_3$ $[M+H]^+$: 222.1026, Found: 222,1035.



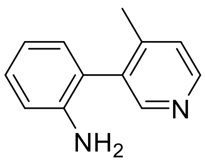
4-(pyridin-3-yl)isoquinolin-3-amine (1a-34)

Prepared according to general procedure 1 to afford **1a-34** (322 mg, 73% yield) as a yellow solid, (m.p. 118-120 °C). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.82 (s, 1H), 8.64-8.54 (m, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.67 (dt, J = 7.8, 1.9 Hz, 1H), 7.39 (dd, J = 7.8, 4.9 Hz, 1H), 7.34 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.20-7.13 (m, 1H), 7.10 (d, J = 8.6 Hz, 1H), 4.37 (s, 2H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 152.1, 152.1, 151.6, 149.2, 138.5, 137.3, 131.8, 130.9, 128.1, 124.1, 123.7, 122.9, 122.2, 107.2. HRMS (m/z): calcd for $C_{14}H_{11}N_3$ [M+H]$^+$: 222.1026, Found: 222.1025.



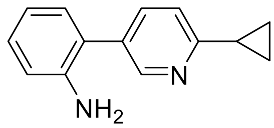
2-(6-methylpyridin-3-yl)aniline (1b-1)[2]

Prepared according to general procedure 1 to afford **1b-1** (272 mg, 74% yield) as a grey solid. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.52 (s, 1H), 7.63 (dd, J = 8.0, 2.3 Hz, 1H), 7.19-7.15 (m, 1H), 7.11 (td, J = 7.7, 1.6 Hz, 1H), 7.02 (dd, J = 7.6, 1.6 Hz, 1H), 6.77 (td, J = 7.4, 1.1 Hz, 1H), 6.70 (dd, J = 8.1, 1.1 Hz, 1H), 3.59 (s, 2H), 2.54 (s, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 157.1, 149.1, 143.8, 137.0, 132.2, 130.5, 129.1, 123.8, 123.2, 118.9, 115.8, 24.1. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ [M+H]$^+$:185.1073, Found: 185.1068.



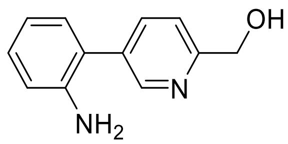
2-(4-methylpyridin-3-yl)aniline (1b-2)[8]

Prepared according to general procedure 1 to afford **1b-2** (346 mg, 94% yield) as a yellow oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.46-8.31 (m, 2H), 7.15 (ddd, J = 9.2, 6.4, 2.5 Hz, 2H), 6.94 (d, J = 6.9 Hz, 1H), 6.80-6.70 (m, 2H), 3.69 (s, 2H), 2.17 (s, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 150.3, 148.6, 146.7, 144.3, 135.0, 130.2, 129.2, 125.2, 122.9, 118.1, 115.2, 19.2. HRMS (m/z): calcd for $C_{12}H_{12}N_2$ [M+H]$^+$:185.1073, Found: 185.1081.



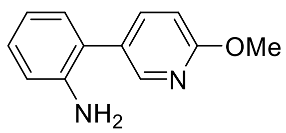
2-(6-cyclopropylpyridin-3-yl)aniline (1b-3)

Prepared according to general procedure 1 to afford **1b-3** (403 mg, 80% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.66 (dd, J = 8.1, 2.0 Hz, 1H), 7.21-7.17 (m, 2H), 7.08 (d, J = 7.5 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 3.62 (s, 2H), 2.13-2.05 (m, 1H), 1.08-1.02 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 161.7, 149.3, 143.8, 136.5, 131.8, 130.5, 129.0, 124.0, 121.0, 118.8, 115.7, 17.0, 10.0. HRMS (m/z): calcd for $C_{14}H_{14}N_2$ $[M+H]^+$: 211.1230, Found: 211.1242.



(5-(2-aminophenyl)pyridin-2-yl)methanol (1b-4)

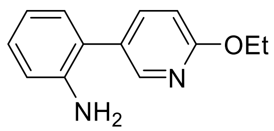
Prepared according to general procedure 1 to afford **1b-4** (352 mg, 88% yield) as a yellow solid, (m.p. 100-101 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.82-7.76 (m, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.79 (s, 2H), 3.96 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.8, 148.6, 143.8, 137.5, 134.0, 130.6, 129.4, 123.4, 120.5, 119.0, 115.9, 64.1. HRMS (m/z): calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$:201.1022, Found: 201.1018.



2-(6-methoxypyridin-3-yl)aniline (1b-5)

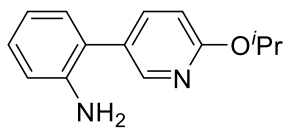
Prepared according to general procedure 1 to afford **1b-5** (280 mg, 70% yield) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.83 (t, J = 7.5 Hz, 2H), 6.75 (d, J = 8.2

Hz, 1H), 3.98 (s, 3H), 3.68 (s, 2H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 163.3, 146.8, 144.0, 139.5, 130.6, 128.9, 128.2, 123.8, 118.8, 115.7, 110.8, 53.5. HRMS (m/z): calcd for $C_{12}H_{12}N_2O$ [M+H]$^+$:201.1022, Found: 201.1028.



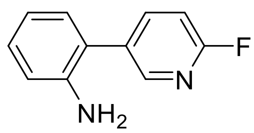
2-(6-ethoxypyridin-3-yl)aniline (1b-6)

Prepared according to general procedure 1 to afford **1b-6** (385 mg, 90% yield) as a yellow solid, (m.p. 49-50 °C). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.25 (dd, J = 2.5, 0.8 Hz, 1H), 7.66 (dd, J = 8.5, 2.5 Hz, 1H), 7.18-7.12 (m, 1H), 7.08 (dd, J = 7.6, 1.6 Hz, 1H), 6.84-6.76 (m, 2H), 6.72 (d, J = 7.8 Hz, 1H), 4.42 (q, J = 7.0 Hz, 2H), 3.75 (s, 2H), 1.44 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 163.0, 146.8, 144.2, 139.5, 130.6, 128.8, 128.1, 123.9, 118.7, 115.7, 110.9, 61.8, 14.8. HRMS (m/z): calcd for $C_{13}H_{14}N_2O$ [M+H]$^+$:215.1179, Found: 215.1189.



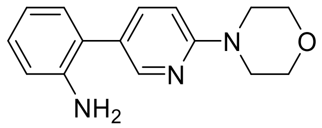
2-(6-isopropoxypyridin-3-yl)aniline (1b-7)

Prepared according to general procedure 1 to afford **1b-7** (342 mg, 75% yield) as a red oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.23 (d, J = 2.5 Hz, 1H), 7.67 (dd, J = 8.5, 2.5 Hz, 1H), 7.20-7.13 (m, 1H), 7.10 (dd, J = 7.5, 1.6 Hz, 1H), 6.83 (td, J = 7.4, 1.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 2H), 5.36 (hept, J = 6.2 Hz, 1H), 3.61 (s, 2H), 1.40 (d, J = 6.2 Hz, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 162.7, 146.8, 144.0, 139.5, 130.6, 128.8, 127.7, 124.0, 118.8, 115.6, 111.4, 68.1, 22.2. HRMS (m/z): calcd for $C_{14}H_{16}N_2O$ [M+H]$^+$: 229.1335, Found: 229.1330.



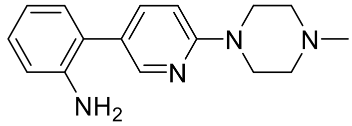
2-(6-fluoropyridin-3-yl)aniline (1b-8)[5]

Prepared according to general procedure 1 to afford **1b-8** (275 mg, 73% yield) as a gray solid, (m.p. 85-87 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.91 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.85 (tdd, J = 7.5, 2.1, 1.1 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 3.64 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.0, 161.6, 147.7 (d, J = 14.4 Hz), 143.8, 141.9 (d, J = 7.9 Hz), 133.0 (d, J = 4.7 Hz), 130.5, 129.5, 119.0, 116.0, 109.5 (d, J = 35.1 Hz). HRMS (m/z): calcd for $C_{11}H_9N_2F$ $[M+H]^+$: 189.0823, Found: 189.0835.



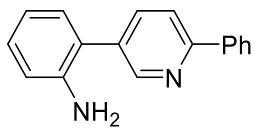
2-(6-morpholinopyridin-3-yl)aniline (1b-9)

Prepared according to general procedure 1 to afford **1b-9** (433 mg, 85% yield) as a brown solid, (m.p. 120-122 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.64 (dd, J = 8.7, 2.4 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.74 (dd, J = 16.0, 8.3 Hz, 2H), 3.85 (t, J = 4.9 Hz, 4H), 3.67 (s, 2H), 3.54 (t, J = 4.9 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.5, 147.8, 144.0, 138.4, 130.5, 128.6, 125.0, 124.3, 118.8, 115.6, 106.7, 66.8, 45.6. HRMS (m/z): calcd for $C_{15}H_{17}N_3O$ $[M+H]^+$: 256.1444, Found: 256.1454.



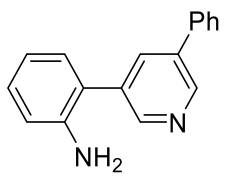
2-(6-(4-methylpiperazin-1-yl)pyridin-3-yl)aniline (1b-10)

Prepared according to general procedure 1 to afford **1b-10** (429 mg, 80% yield) as a yellow solid, (m.p. 130-132 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 2.4 Hz, 1H), 7.62 (dd, J = 8.7, 2.5 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.78-6.70 (m, 2H), 3.70 (s, 2H), 3.66 (t, J = 5.2 Hz, 4H), 2.61 (t, J = 5.0 Hz, 4H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.4, 147.9, 144.1, 138.2, 130.4, 128.4, 124.4, 124.4, 118.6, 115.5, 106.8, 54.9, 46.2, 45.1. HRMS (m/z): calcd for $C_{16}H_{20}N_4$ $[M+H]^+$: 269.1761, Found: 269.1769.



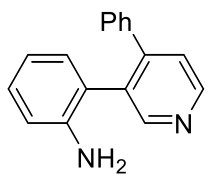
2-(6-phenylpyridin-3-yl)aniline (1b-11)

Prepared according to general procedure 1 to afford **1b-11** (393 mg, 80% yield) as a pale brown solid, (m.p. 90-92 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J = 2.4 Hz, 1H), 8.05 (d, J = 7.1 Hz, 2H), 7.90 (dd, J = 8.2, 2.3 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.25-7.16 (m, 2H), 6.89 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.69 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.0, 149.8, 143.9, 138.9, 137.3, 133.6, 131, 130.5, 129.3, 129.1, 128.8, 126.8, 123.6, 120.4, 119.0, 118.8, 115.9. HRMS (m/z): calcd for $C_{17}H_{14}N_2$ $[M+H]^+$: 247.1230, Found: 247.1234.



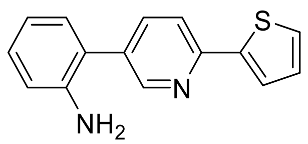
2-(5-phenylpyridin-3-yl)aniline (1b-12)

Prepared according to general procedure 1 to afford **1b-12** (413 mg, 84% yield) as a yellow solid, (m.p. 152-154 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.62 (s, 1H), 7.95 (s, 1H), 7.57-7.51 (m, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.35 (dd, J = 7.1, 1.7 Hz, 1H), 7.14 (tt, J = 7.8, 1.7 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.54 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.4, 146.7, 143.8, 137.4, 136.6, 135.3, 135.0, 130.6, 129.5, 129.1, 128.3, 127.2, 124.4, 124.0, 123.5, 119.0, 115.9. HRMS (m/z): calcd for $C_{17}H_{14}N_2$ $[M+H]^+$: 247.1230, Found: 247.1128.



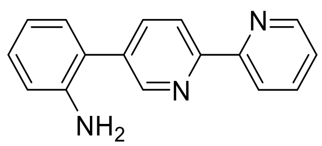
2-(4-phenylpyridin-3-yl)aniline (1b-13)

Prepared according to general procedure 1 to afford **1b-13** (403 mg, 82% yield) as a yellow solid, (m.p. 140-141 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 19.1 Hz, 2H), 7.40 (s, 1H), 7.25 (s, 5H), 7.09 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.71 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 3.37 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.8, 149.1, 148.6, 143.9, 138.2, 131.3, 129.1, 128.5, 128.3, 128.3, 123.1, 118.5, 115.5. HRMS (m/z): calcd for $C_{17}H_{14}N_2$ $[M+H]^+$: 247.1230, Found: 247.1238.



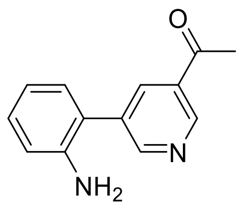
2-(6-(thiophen-2-yl)pyridin-3-yl)aniline (1b-14)

Prepared according to general procedure 1 to afford **1b-14** (413 mg, 82% yield) as a gray solid, (m.p. 78-80 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.86-7.79 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 3.4 Hz, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.16-7.09 (m, 2H), 6.86 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 3.74 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 149.7, 143.9, 137.2, 133.4, 131.0, 130.4, 129.3, 128.2, 127.7, 124.7, 123.5, 119.0, 118.6, 115.9. HRMS (m/z): calcd for $C_{15}H_{12}N_2S$ $[M+H]^+$: 253.0794, Found: 253.0805.



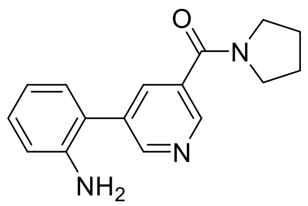
2-([2,2'-bipyridin]-5-yl)aniline (1b-15)[9]

Prepared according to general procedure 1 to afford **1b-15** (430 mg, 87% yield) as a brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.57 (d, J = 4.8 Hz, 1H), 8.32 (dd, J = 13.9, 8.1 Hz, 2H), 7.81 (dd, J = 8.2, 2.2 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.18 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.06 (dd, J = 16.6, 7.7 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.61 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.8, 154.7, 149.4, 149.2, 143.9, 137.4, 137.0, 135.3, 130.5, 129.4, 123.7, 123.5, 121.0, 120.9, 118.9, 115.9. HRMS (m/z): calcd for $C_{16}H_{13}N_3$ $[M+H]^+$: 248.1182, Found: 248.1183.



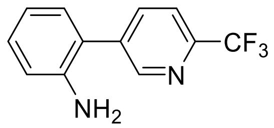
1-(5-(2-aminophenyl)pyridin-3-yl)ethan-1-one (1b-16)

Prepared according to general procedure 1 to afford **1b-16** (335 mg, 79% yield) as a brown solid, (m.p. 244-245 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.04 (d, J = 2.1 Hz, 1H), 8.83 (d, J = 2.2 Hz, 1H), 8.29 (td, J = 2.2, 0.6 Hz, 1H), 7.20-7.13 (m, 1H), 7.05 (dd, J = 7.6, 1.6 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.71 (s, 2H), 2.61 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 196.7, 153.7, 148.2, 143.8, 135.8, 135.5, 132.1, 130.5, 129.8, 122.5, 119.0, 116.1, 26.8. HRMS (m/z): calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213,1022, Found: 213.1018.



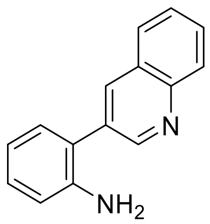
(5-(2-aminophenyl)pyridin-3-yl)(pyrrolidin-1-yl)methanone (1b-17)

Prepared according to general procedure 1 to afford **1b-17** (432 mg, 81% yield) as a brown solid, (m.p. 135-137 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 2H), 7.93 (s, 1H), 7.14-7.06 (m, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.80-6.67 (m, 2H), 3.75 (s, 2H), 3.59 (t, J = 6.8 Hz, 2H), 3.43 (t, J = 6.5 Hz, 2H), 1.88 (dq, J = 19.1, 6.8 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.9, 150.7, 146.4, 144.0, 135.1, 133.0, 130.5, 129.6, 122.6, 118.8, 116.0, 49.5, 46.4, 26.4, 24.4. HRMS (m/z): calcd for $C_{16}H_{17}N_3O$ $[M+H]^+$: 268.1444, Found: 268.1438.



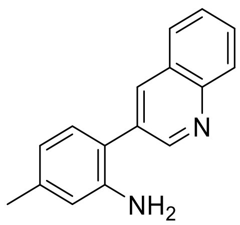
Preparation of 2-(6-(trifluoromethyl)pyridin-3-yl)aniline (1b-18)

Prepared according to general procedure 1 to afford **1b-18** (371 mg, 78% yield) as a brown solid, (m.p. 45-47 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.11 (tt, J = 7.7, 1.8 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 3.62 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.2, 146.6 (q, J = 34.5 Hz), 143.8, 138.4, 137.8, 130.5, 130.1, 123.0, 122.2, 120.4 (q, J = 2.7 Hz), 119.2, 116.2. HRMS (m/z): calcd for $C_{12}H_9N_2F_3$ $[M+H]^+$: 239.0791, Found: 239,0798.



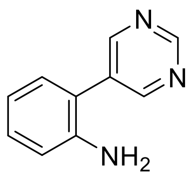
2-(quinolin-3-yl)aniline (1b-19)[5]

Prepared according to general procedure 1 to afford **1b-19** (352 mg, 80% yield) as a gray solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.18 (s, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.69-7,63 (m, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.19-7.10 (m, 2H), 6.82 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.36 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.4, 147.0, 144.0, 135.5, 132.4, 130.8, 129.6, 129.4, 129.2, 127.9, 127.8, 127.0, 123.7, 119.1, 116.0. HRMS (m/z): calcd for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1073, Found: 221.1082.



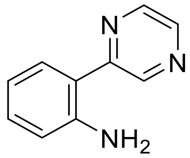
5-methyl-2-(quinolin-3-yl)aniline (1b-20)

Prepared according to general procedure 1 to afford **1b-20** (360 mg, 77% yield) as a gray solid, (m.p. 125-127 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.24 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.60-7.54 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.66 (s, 1H), 3.76 (s, 2H), 2.34 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.7, 147.0, 143.8, 139.5, 135.3, 132.5, 130.7, 129.4, 129.2, 128.0, 127.8, 126.9, 121.0, 120.1, 116.6, 21.3. HRMS (m/z): calcd for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1230, Found: 235.1240.



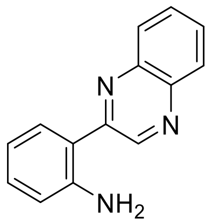
2-(pyrimidin-5-yl)aniline (1b-21)[10]

Prepared according to general procedure 1 to afford **1b-21** (280 mg, 82% yield) as a brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.80 (d, J = 2.2 Hz, 2H), 7.20 -7.14 (m, 1H), 7.02 (dt, J = 7.5, 1.8 Hz, 1H), 6.83-6.73 (m, 1H), 6.74 (dd, J = 8.1, 1.3 Hz, 1H), 3.68 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.4, 157.0, 143.8, 133.4, 130.5, 130.2, 119.9, 119.3, 116.2. HRMS (m/z): calcd for $C_{10}H_9N_3$ $[M+H]^+$: 172.0869, Found: 172.0867.



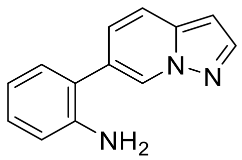
2-(pyrazin-2-yl)aniline (1b-22)[11]

Prepared according to general procedure 1 to afford **1b-22** (273 mg, 80% yield) as a yellowish-brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.51 (s, 1H), 8.42 (d, J = 2.6 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.25-7.18 (m, 1H), 6.84-6.74 (m, 2H), 5.37 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.8, 147.2, 143.7, 141.8, 141.1, 131.0, 129.0, 118.5, 117.8, 117.4. HRMS (m/z): calcd for $C_{10}H_9N_3$ $[M+H]^+$: 172.0869, Found: 172.0867.



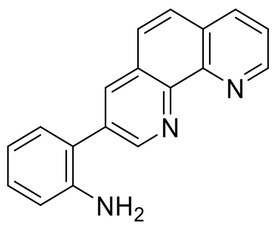
2-(quinoxalin-2-yl)aniline (1b-23)[12]

Prepared according to general procedure 1 to afford **1b-23** (353 mg, 80% yield) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.97 (dd, J = 7.9, 1.9 Hz, 1H), 7.90 (dd, J = 8.1, 1.6 Hz, 1H), 7.71 (dd, J = 8.0, 1.5 Hz, 1H), 7.65-7.56 (m, 2H), 7.14 (ddd, J = 8.4, 7.2, 1.5 Hz, 1H), 6.76-6.69 (m, 2H), 5.64 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 153.5, 148.1, 144.6, 140.4, 140.1, 131.3, 130.1, 129.3, 129.0, 129.0, 128.6, 118.1, 117.5, 117.5. HRMS (m/z): calcd for $C_{14}H_{11}N_3$ $[M+H]^+$: 222.1026, Found: 222.1030.



2-(pyrazolo[1,5-*a*]pyridin-6-yl)aniline (1b-24)

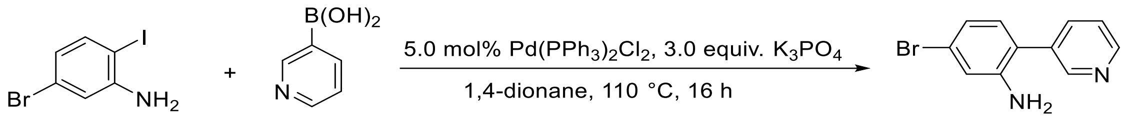
Prepared according to general procedure 1 to afford **1b-24** (301 mg, 72% yield) as a brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.96 (d, J = 2.3 Hz, 1H), 7.57 (d, J = 9.1 Hz, 1H), 7.25-7.13 (m, 3H), 6.83 (td, J = 7.4, 1.1 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 2.3 Hz, 1H), 3.69 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.2, 142.2, 139.1, 130.6, 129.3, 127.7, 125.5, 123.9, 123.0, 118.8, 118.0, 115.8, 96.9. HRMS (m/z): calcd for $C_{13}H_{11}N_3$ $[M+H]^+$: 210.1026, Found: 210.1024.



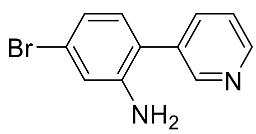
2-(1,10-phenanthrolin-3-yl)aniline (1b-25)

Prepared according to general procedure 1 to afford **1b-25** (443 mg, 80% yield) as a red solid, (m.p. 160-162 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 9.07 (d, J = 3.6 Hz, 1H), 8.33 (d, J = 2.2 Hz, 1H), 8.28 (dd, J = 8.1, 1.7 Hz, 1H), 7.82 (s, 2H), 7.62 (dd, J = 8.1, 4.4 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.82 (dd, J = 13.2, 8.4 Hz, 2H), 3.57 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 152.8, 149.4, 145.8, 144.2, 141.6, 136.5, 128.9, 128.6, 128.4, 128.2, 123.7, 123.2, 122.9, 122.4, 120.5, 120.3, 118.2, 111.8. HRMS (m/z): calcd for $C_{18}H_{13}N_3$ $[M+H]^+$: 272.1182 , Found: 282.1191.

2.2 General procedure 2: for the synthesis of 5-bromo-2-(pyridin-3-yl)aniline derivatives **1a-11**, **1a-21**

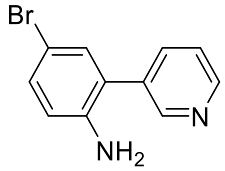


A clean, oven-dried Schlenk tube with previously placed magnetic stir-bar was charged with 5-bromo-2-iodoaniline (594 mg, 1.0 equiv.), pyridin-3-ylboronic acid (295 mg, 1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 5.0 mmol%) and K_3PO_4 (1.27 g, 3.0 equiv.). The reaction was evacuated and back filled with nitrogen and this sequence was repeated for three additional times. Under the positive flow of nitrogen, 1,4-dioxane (10 mL) was added to the reaction mixture. The reaction mixture was vigorously stirred at 110 °C for 16 h. Next, the reaction was allowed to cool at room temperature and the reaction mixture was extracted with ethyl acetate (3×50 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel to give the desired product (**1a-11**).



5-bromo-2-(pyridin-3-yl)aniline (1a-11)

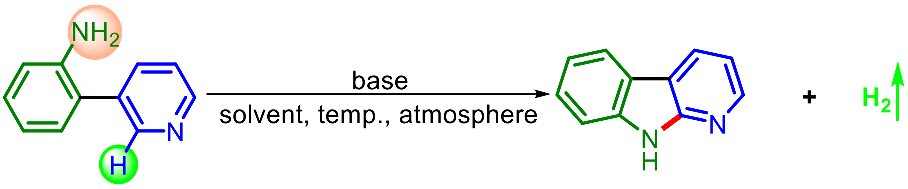
Prepared according to general procedure 2 to afford **1a-11** (373 mg, 75% yield) as a yellow solid, (m.p. 48-50 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 2.1 Hz, 1H), 8.57 (dd, J = 5.1, 1.7 Hz, 1H), 7.74 (dt, J = 7.9, 1.9 Hz, 1H), 7.35 (dd, J = 7.9, 4.8 Hz, 1H), 6.95-6.89 (m, 3H), 3.77 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.8, 148.7, 145.1, 136.5, 134.3, 131.8, 123.7, 123.0, 122.4, 121.7, 118.3. HRMS (m/z): calcd for $C_{11}H_9N_2Br$ $[M+H]^+$: 249.0022, Found: 249.0029.



4-bromo-2-(pyridin-3-yl)aniline (1a-21)

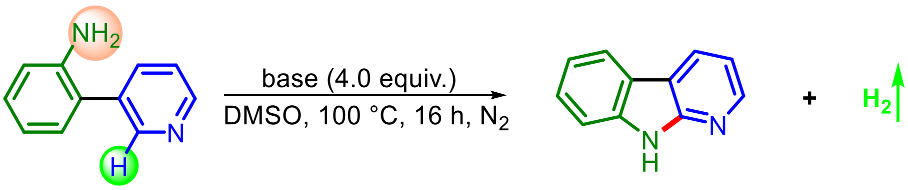
Prepared according to general procedure 2 to afford **1a-21** (348 mg, 70% yield) as a brown solid, (m.p. 72-73 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 2.3 Hz, 1H), 8.54 (dd, J = 4.9, 1.7 Hz, 1H), 7.71 (dt, J = 7.9, 2.0 Hz, 1H), 7.32 (dd, J = 7.9, 4.8 Hz, 1H), 7.21 (dd, J = 8.5, 2.4 Hz, 1H), 7.16 (d, J = 2.3 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 3.80 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.7, 148.8, 143.0, 136.5, 134.0, 132.8, 131.9, 125.3, 123.7, 117.4, 110.2. HRMS (m/z): calcd for $C_{11}H_9BrN_2$ $[M+H]^+$: 249.0922, Found: 249.0029.

3. Detailed Reaction Optimization



The mixture of 2-(pyridin-3-yl)aniline (68.0 mg, 0.4 mmol), base (2-10 equiv.) in dry solvent (X mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at temp.. Next, the reaction was allowed to cool at room temperature and the reaction mixture was extracted with ethyl acetate (3×50 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel to give the substrate (**1a-1**) and product (**2a-1**).

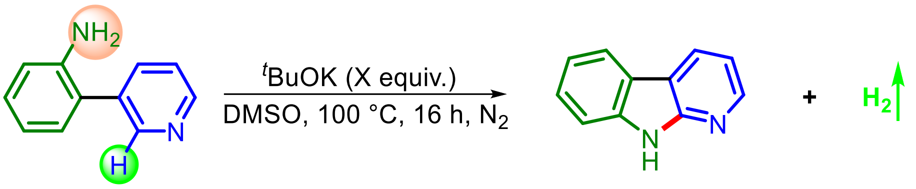
Table S1. Screening of base type [a]



Entry	base (4.0 equiv.)	Yield (%) [b]	Conv. (%) [b]
1	^{t}BuONa	N.R.	0
2	^{t}BuOK	25	30
3	CH_3ONa	N.R.	0
4	CH_3OK	N.R.	0
5	C_2H_5ONa	N.R.	0
6	C_2H_5OK	N.R.	0
7	NaOH	N.R.	0
8	KOH	N.R.	0

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), **base** (4.0 equiv.), DMSO (4 mL), 100 °C, N_2 (1.0 atm), 16 h; [b] Isolated yield.

Table S2. Screening of base equivalent [a]

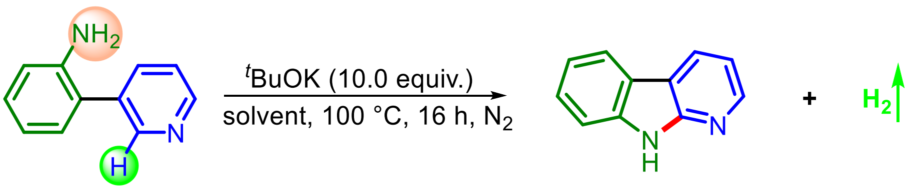


1a-1 **2a-1**

Entry	^{t}BuOK (X equiv.)	Yield (%) [b]	Conv. (%) [b]
1	2.0	4	5
2	4.0	25	30
3	6.0	50	78
4	8.0	60	95
5	10.0	65	100

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (X equiv.), DMSO (4 mL), 100 °C, N_2 (1.0 atm), 16 h; [b] Isolated yield.

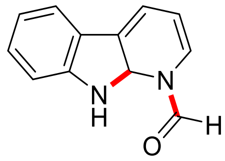
Table S3. Screening of solvent [a]



1a-1 **2a-1**

Entry	solvent	Yield (%) [b]	Conv. (%) [b]
1	DMSO	65	100
2	DMF	0	100
3	1,4-dioxane	70	90
4	THF	61	90
5	toluene	96	100
6	MeOH	0	0

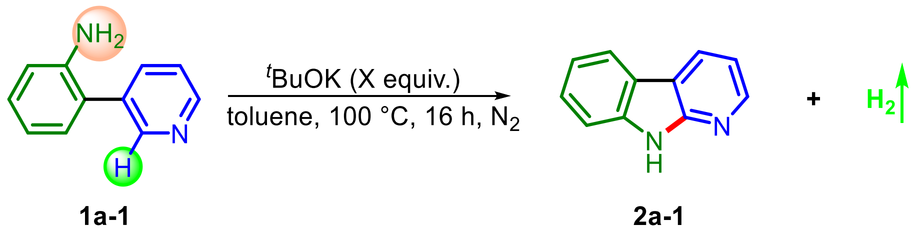
[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (456.0 mg, 10.0 equiv.), solvent (4 mL), 100 °C, N_2 (1.0 atm), 16 h; [b] Isolated yield.



9,9a-dihydro-1*H*-pyrido[2,3-*b*]indole-1-carbaldehyde

The mixture of 2-(pyridin-3-yl)aniline (68.0 mg, 0.4 mmol), ^{t}BuOK (456.0 mg, 10.0 equiv.) in dry DMF (4.0 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100°C for 4 hours. Next, the reaction was allowed to cool at room temperature and the reaction mixture was extracted with ethyl acetate (3×50 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel to give the product **2a-DMF** (85% yield) as a faint yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.61 (d, J = 63.3 Hz, 1H), 8.68-8.49 (m, 2H), 8.22 (d, J = 56.9 Hz, 1H), 7.82 (dd, J = 24.4, 8.6 Hz, 2H), 7.51-7.27 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 162.9, 159.7, 149.6, 148.6, 137.1, 131.2, 130.4, 129.2, 126.1, 125.2, 123.2, 120.9. HRMS (m/z): calcd for $C_{12}H_{10}N_2O$ $[M+H]^+$: 198.0793, Found: 198,0798.

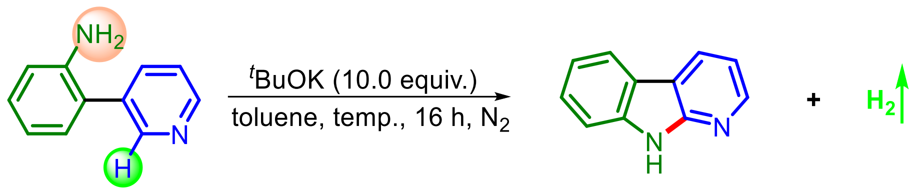
Table S4. Screening of base equivalent [a]



Entry	^{t}BuOK (X equiv.)	Yield (%) [b]	Conv. (%) [b]
1	2.0	4	5
2	4.0	31	35
3	6.0	55	60
4	8.0	79	85
5	9.0	92	95
6	10.0	96	100

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (X equiv.), toluene (4 mL), 100 °C, N_2 (1.0 atm), 16 h; [b] Isolated yield.

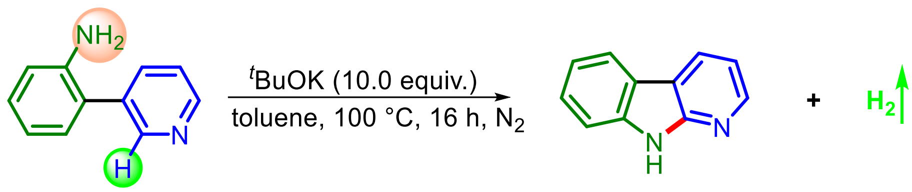
Table S5. Screening of temperature [a]



Entry	temperature (°C)	Yield (%) [b]	Conv. (%) [b]
1	25	0	0
2	40	2	5
3	60	16	20
4	70	25	30
5	80	40	50
6	90	80	85
7	100	96	100
8	110	90	100

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (456.0 mg, 10.0 equiv.), toluene (4 mL), N_2 (1.0 atm), 16 h; [b] Isolated yield.

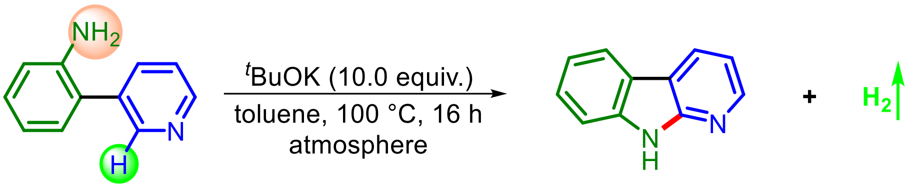
Table S6. Screening of volume of solvent [a]



Entry	Volume (ml)	Yield (%) [b]	Conv. (%) [b]
1	4	96	100
2	6	96	100
3	8	96	100
4	10	96	100

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (456.0 mg, 10.0 equiv.), toluene (X mL), 100 °C, N_2(1.0 atm), 16 h; [b] Isolated yield.

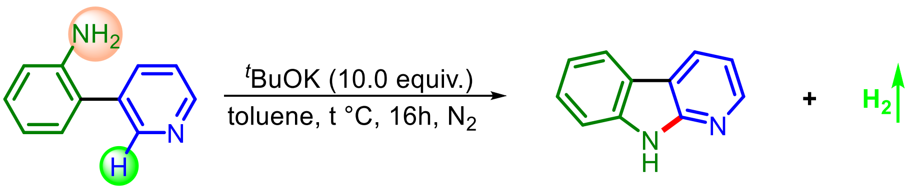
Table S7. Screening of reaction atmosphere [a]



Entry	Atmosphere	Yield (%) [b]	Conv. (%) [b]
1	Air [c]	50	100
2	N_2	96	100
3	O_2 [d]	trace	100

[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (456.0 mg, 10.0 equiv.), toluene (4 mL), 100 °C, N_2 (1.0 atm), 16 h; [b] Isolated yield; [c] Air; [d] O_2 (1.0 atm).

Table S8. Screening of the relationship between base equivalent and time [a]

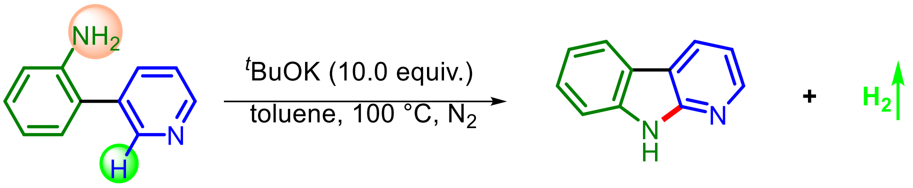


Entry	^{t}BuOK (X equiv.)	Time (h)	Yield (%) [b]	Conv. (%) [b]
1	2	72	55	60
2	4	72	90	95
3	6	72	96	100
4	8	72	96	100
5	2[c]	144	96	100

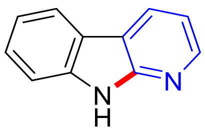
[a] Reaction conditions: **1a-1** (68.0 mg, 0.4 mmol), ^{t}BuOK (X equiv.), toluene (4 mL), 100 °C, N_2 (1.0 atm), 72 h; [b] Isolated yield; [c] ^{t}BuOK (2.0 equiv.), 144 h.

4. Intramolecular C(sp^2)-H Amination of Azines

4.1 General procedure A: for the synthesis of C(sp^2)-H amination of azines product **2a** and **2b**

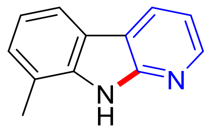


A clean, oven-dried Schlenk tube with previously placed magnetic stir-bar was charged with 2-(pyridin-3-yl)aniline (34.0 mg, 0.2 mmol) and ^{t}BuOK (224 mg, 10 equiv.). The reaction was evacuated and back filled with nitrogen and this sequence was repeated for three additional times. Under the positive flow of nitrogen, dry toluene (2.0 mL) was added to the reaction mixture. The reaction mixture was vigorously stirred at 100 °C for 16 h. Next, the reaction was allowed to cool at room temperature and the reaction mixture was extracted with ethyl acetate (3×50 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel to give the desired **2a-1** as a white solid.



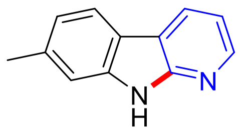
9*H*-pyrido[2,3-*b*]indole (2a-1)[13]

Prepared according to general procedure A to afford **2a-1** (32.2 mg, 96% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.82 (s, 1H), 8.47 (dt, J = 7.7, 1.6 Hz, 1H), 8.43 (dt, J = 4.8, 1.6 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.49-7.43 (m, 1H), 7.24 -7.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.4, 146.5, 139.3, 128.8, 127.0, 121.5, 120.8, 119.8, 115.6, 115.4, 111.7. HRMS (ESI) m/z calcd for $C_{11}H_8N_2$ [M+H]$^+$: 169.0761, Found: 169.0770.



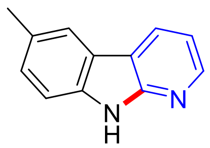
8-methyl-9*H*-pyrido[2,3-*b*]indole (2a-2)

Prepared according to general procedure A to afford **2a-2** (35.8 mg, 98% yield) as a white solid, (m.p. 234-236 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.79 (s, 1H), 8.50-8.39 (m, 2H), 7.96 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.18 (dd, J = 7.7, 4.9 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6, 146.3, 138.5, 128.8, 127.5, 121.1, 120.4, 119.9, 118.9, 116.0, 115.4, 17.5. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ $[M+H]^+$: 183.0917, Found: 183.0920.



7-methyl-9*H*-pyrido[2,3-*b*]indole (2a-3)[13]

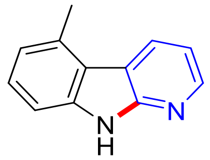
Prepared according to general procedure A to afford **2a-3** (27.8 mg, 76% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.68 (s, 1H), 8.42-8.35 (m, 2H), 8.00 (d, J = 7.9 Hz, 1H), 7.31 (s, 1H), 7.15 (dd, J = 7.6, 4.9 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.4, 145.8, 139.7, 136.7, 128.2, 121.3, 121.3, 118.5, 115.8, 115.2, 111.6, 22.2. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ $[M+H]^+$: 183.0917, Found: 183.0920.



6-methyl-9*H*-pyrido[2,3-*b*]indole (2a-4)[13]

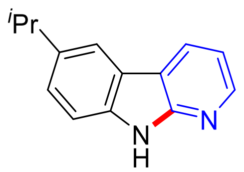
Prepared according to general procedure A to afford **2a-4** (32.2 mg, 87% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.66 (s, 1H), 8.46-8.36 (m, 2H), 7.92

(s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.26 (dd, J = 8.3, 1.6 Hz, 1H), 7.15 (dd, J = 7.7, 4.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6, 146.3, 137.4, 128.6, 128.5, 128.3, 121.3, 120.9, 115.5, 115.1, 111.4, 21.5. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ [M+H]$^+$: 183.0917, Found: 183.0920.



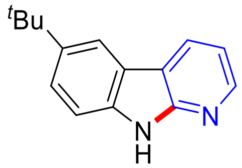
5-methyl-9*H*-pyrido[2,3-*b*]indole (2a-5)[13]

Prepared according to general procedure A to afford **2a-5** (32.1 mg, 87% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.82 (s, 1H), 8.42 (td, J = 6.1, 5.1, 2.7 Hz, 2H), 7.38-7.32 (m, 2H), 7.20 (ddd, J = 7.0, 4.9, 1.9 Hz, 1H), 7.01 (t, J = 2.7 Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.1, 145.7, 139.2, 133.7, 130.3, 126.9, 121.1, 119.4, 116.0, 115.3, 109.2, 20.5. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ [M+H]$^+$: 183.0917, Found: 183.0915.



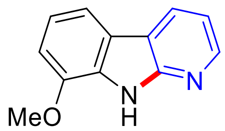
6-isopropyl-9*H*-pyrido[2,3-*b*]indole (2a-6)

Prepared according to general procedure A to afford **2a-6** (29.4 mg, 70% yield) as a white solid, (m.p. 139-141 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.65 (s, 1H), 8.47 (d, J = 7.6 Hz, 1H), 8.38 (d, J = 4.7 Hz, 1H), 8.00 (s, 1H), 7.47-7.29 (m, 2H), 7.16 (dd, J = 7.6, 4.9 Hz, 1H), 3.03 (hept, J = 6.9 Hz, 1H), 1.29 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6, 146.2, 140.0, 137.7, 128.5, 125.9, 120.8, 118.6, 115.7, 115.1, 111.4, 34.0, 25.0. HRMS (ESI) m/z calcd for $C_{14}H_{14}N_2$ [M+H]$^+$: 211.1230, Found: 211.1234.



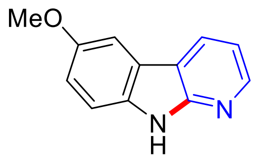
6-(*tert*-butyl)-9*H*-pyrido[2,3-*b*]indole (2a-7)

Prepared according to general procedure A to afford **2a-7** (34.0 mg, 76% yield) as a white solid, (m.p. 185-187 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (s, 1H), 8.51 (d, J = 7.7 Hz, 1H), 8.38 (d, J = 4.8 Hz, 1H), 8.16 (s, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.19-7.14 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6, 146.1, 142.3, 137.3, 128.6, 124.9, 120.5, 117.5, 115.9, 115.1, 111.1, 34.9, 32.2. HRMS (ESI) m/z calcd for $C_{15}H_{16}N_2$ [M+H]$^+$: 225.1386, Found: 225.1393.



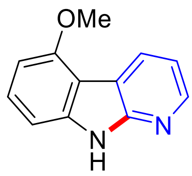
8-methoxy-9*H*-pyrido[2,3-*b*]indole (2a-8)[14]

Prepared according to general procedure A to afford **2a-8** (36.6 mg, 92% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.44 (dd, J = 13.0, 6.2 Hz, 2H), 7.73 (d, J = 7.8 Hz, 1H), 7.21-7.12 (m, 2H), 7.04 (d, J = 7.9 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 146.4, 146.2, 129.2, 128.9, 121.9, 120.4, 115.8, 115.4, 113.8, 107.8, 56.0. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2O$ [M+H]$^+$: 199.0866, Found: 199.0866.



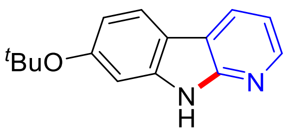
6-methoxy-9*H*-pyrido[2,3-*b*]indole (2a-9)[13]

Prepared according to general procedure A to afford **2a-9** (35.0 mg, 88% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.64 (s, 1H), 8.47 (dd, J = 7.7, 1.6 Hz, 1H), 8.39 (dd, J = 4.9, 1.6 Hz, 1H), 7.75 (d, J = 2.5 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.15 (dd, J = 7.7, 4.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 152.7, 146.4, 133.8, 128.9, 121.2, 116.2, 115.7, 114.9, 112.4, 104.3, 56.0. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2O$ [M+H]$^+$: 199.0866, Found: 199.0866.



5-methoxy-9*H*-pyrido[2,3-*b*]indole (2a-10)[13]

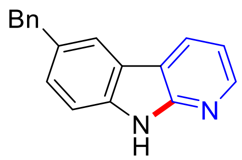
Prepared according to general procedure A to afford **2a-10** (35.8 mg, 90% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.82 (s, 1H), 8.42-8.35 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.18 (dd, J = 7.6, 4.9 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.4, 151.6, 145.4, 140.5, 130.0, 128.1, 115.6, 114.8, 109.7, 104.6, 101.1, 55.8. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2O$ [M+H]$^+$: 199.0866, Found: 199.0867.



7-(tert-butoxy)-9*H*-pyrido[2,3-*b*]indole (2a-11)

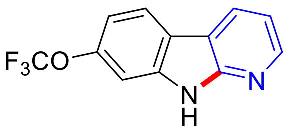
Prepared according to general procedure A to afford **2a-11** (43.0 mg, 90% yield) as a white solid, (m.p. 194-196 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 8.39 (dd, J = 7.7, 1.6 Hz, 1H), 8.34 (dd, J = 4.9, 1.5 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.16 (dd, J = 7.7, 4.9 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.85 (dd, J = 8.5, 2.0 Hz, 1H), 1.35

(s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8, 152.6, 145.5, 140.0, 128.0, 121.7, 117.1, 116.6, 115.7, 115.4, 106.3, 78.8, 29.1. HRMS (m/z): calcd for $C_{15}H_{16}N_2O$ $[M+H]^+$: 241.1335, Found: 241.1340.



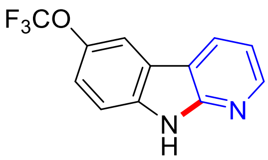
6-benzyl-9*H*-pyrido[2,3-*b*]indole (2a-12)

Prepared according to general procedure A to afford **2a-12** (43.0 mg, 83% yield) as a faint yellow solid, (m.p. 191-193 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (s, 1H), 8.47-8.37 (m, 2H), 8.02 (s, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.36-7.23 (m, 5H), 7.20-7.10 (m, 2H), 4.08 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6, 146.4, 142.6, 137.8, 132.8, 129.0, 128.8, 128.7, 128.1, 126.2, 121.3, 121.0, 115.5, 115.2, 111.6, 41.7. HRMS (ESI) m/z calcd for $C_{18}H_{14}N_2$ $[M+H]^+$: 259.1230, Found: 259.1232.



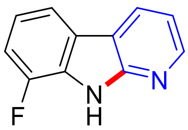
7-(trifluoromethoxy)-9*H*-pyrido[2,3-*b*]indole (2a-13)

Prepared according to general procedure A to afford **2a-13** (29.3 mg, 58% yield) as a white solid, (m.p. 187-189 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.07 (s, 1H), 8.55 (dd, J = 7.8, 1.6 Hz, 1H), 8.46 (dd, J = 4.8, 1.6 Hz, 1H), 8.27 (d, J = 8.5 Hz, 1H), 7.42 (s, 1H), 7.25 (dd, J = 7.7, 4.8 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.9, 147.4(q, J = 1.9 Hz), 139.5, 129.3, 123.1, 122.0, 119.9, 119.4, 116.0, 114.9, 113.0, 104.2. HRMS (m/z): calcd for $C_{12}H_7F_3N_2O$ $[M+H]^+$: 253.0583, Found: 253.0584.



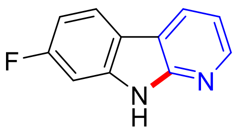
6-(trifluoromethoxy)-9*H*-pyrido[2,3-*b*]indole (2a-14)[15]

Prepared according to general procedure A to afford **2a-14** (26.1 mg, 51% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.08 (s, 1H), 8.56 (d, J = 7.7 Hz, 1H), 8.46 (dd, J = 4.8, 1.6 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 7.42 (s, 1H), 7.25 (dd, J = 7.7, 4.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.9, 147.4 (q, J = 2.0 Hz), 147.0, 139.4, 129.4, 123.2, 122.0, 119.9, 116.0, 114.9, 113.1, 104.2. HRMS (m/z): calcd for $C_{12}H_7F_3N_2O$ [M+H]$^+$: 253.0583, Found: 253.0581.



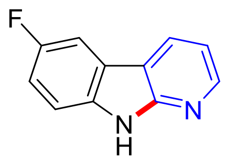
8-fluoro-9*H*-pyrido[2,3-*b*]indole (2a-15)[16]

Prepared according to general procedure A to afford **2a-15** (28.8 mg, 77% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.33 (s, 1H), 8.55 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 4.2 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.32 (dd, J = 11.4, 8.3 Hz, 1H), 7.25 (dd, J = 7.7, 4.8 Hz, 1H), 7.20 (td, J = 7.9, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.5, 148.9 (d, J=22.4 Hz), 147.4, 129.6, 126.9 (d, J = 13.1 Hz), 124.4 (d, J = 5.7 Hz), 120.2 (d, J = 5.9 Hz), 117.7 (d, J = 3.5 Hz), 116.0, 115.5 (d, J = 3.0 Hz), 112.2 (d, J = 16.2 Hz). HRMS (ESI) m/z calcd for $C_{11}H_7FN_2$ [M+H]$^+$: 187.0666, Found: 187.0667.



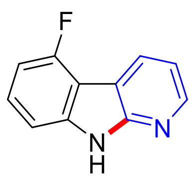
7-fluoro-9H-pyrido[2,3-b]indole (2a-16)[13]

Prepared according to general procedure A to afford **2a-16** (28.4 mg, 76% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.92 (s, 1H), 8.47 (dd, J = 7.7, 1.6 Hz, 1H), 8.39 (dd, J = 4.8, 1.7 Hz, 1H), 8.17 (dd, J = 8.6, 5.6 Hz, 1H), 7.25 (dd, J = 9.9, 2.3 Hz, 1H), 7.21 (dd, J = 7.7, 4.9 Hz, 1H), 7.10-7.02 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.1, 160.7, 152.8 (d, J = 2.0 Hz), 146.1, 140.0 (d, J = 13.0 Hz), 128.6, 123.2 (d, J = 11.0 Hz), 117.5 (d, J = 20.0 Hz) 115.6 (d, J = 47.0 Hz), 107.9 (d, J = 24.0 Hz), 98.2 (d, J = 26.0 Hz). HRMS (ESI) m/z calcd for $C_{11}H_7FN_2$ $[M+H]^+$: 187.0666, Found: 187.0661.



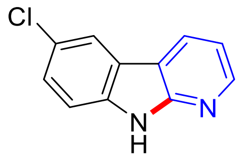
6-fluoro-9H-pyrido[2,3-b]indole (2a-17)[16]

Prepared according to general procedure A to afford **2a-17** (33.0 mg, 88% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.85 (s, 1H), 8.50 (dd, J = 7.7, 1.6 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 8.01 (dd, J = 9.3, 2.6 Hz, 1H), 7.50 (dd, J = 8.8, 4.5 Hz, 1H), 7.30 (td, J = 9.2, 2.6 Hz, 1H), 7.19 (dd, J = 7.7, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.3, 156.0, 153.0, 147.2, 135.6, 129.4, 121.3 (d, J = 10.0 Hz), 115.4 (d, J = 4.0 Hz), 115.3, 114.7 (d, J = 25.0 Hz), 112.7 (d, J = 9.0 Hz), 107.2 (d, J = 24.0 Hz). HRMS (ESI) m/z calcd for $C_{11}H_7FN_2$ $[M+H]^+$: 187.0666, Found: 187.0664.



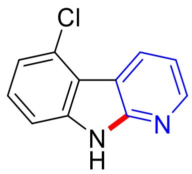
5-fluoro-9H-pyrido[2,3-b]indole (2a-18)[15]

Prepared according to general procedure A to afford **2a-18** (28.4 mg, 76% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.17 (s, 1H), 8.46 (dd, J = 4.9, 1.6 Hz, 1H), 8.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.44 (td, J = 8.0, 5.5 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.22 (dd, J = 7.7, 4.9 Hz, 1H), 7.00 (dd, J = 10.3, 7.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.6, 157.1, 151.8, 146.9, 141.4 (d, J = 9.0 Hz), 130.3 (d, J = 2.7 Hz), 128.0 (d, J = 8.4 Hz), 116.1, 112.7 (d, J = 1.7 Hz), 108.1 (d, J = 3.4 Hz), 105.4 (d, J = 18.1 Hz). HRMS (ESI) m/z calcd for $C_{11}H_7FN_2$ [M+H]$^+$: 187.0666, Found: 187.0665.



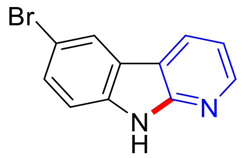
6-chloro-9*H*-pyrido[2,3-*b*]indole (2a-19)[15]

Prepared according to general procedure A to afford **2a-19** (28.8 mg, 71% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 8.55 (d, J = 7.8 Hz, 1H), 8.45 (d, J = 5.0 Hz, 1H), 8.28 (s, 1H), 7.54-7.43 (m, 2H), 7.22 (ddd, J = 7.7, 4.9, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.7, 147.4, 137.6, 129.6, 126.8, 124.2, 122.1, 121.2, 115.8, 114.9, 113.2. HRMS (ESI) m/z calcd for $C_{11}H_7ClN_2$ [M+H]$^+$: 203.0371, Found: 203.0368.



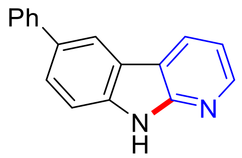
5-chloro-9*H*-pyrido[2,3-*b*]indole (2a-20)

Prepared according to general procedure A to afford **2a-20** (28.7 mg, 71% yield) as a white solid, (m.p. 238-240 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.18 (s, 1H), 8.67 (d, J = 7.5 Hz, 1H), 8.50 (dd, J = 4.8, 1.7 Hz, 1H), 7.53-7.43 (m, 2H), 7.27 (dt, J = 7.9, 2.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.1, 147.3, 140.4, 130.4, 128.2, 127.8, 120.2, 118.0, 115.9, 114.3, 110.7. HRMS (ESI) m/z calcd for $C_{11}H_7ClN_2$ $[M+H]^+$: 203.0371, Found: 203.0368.



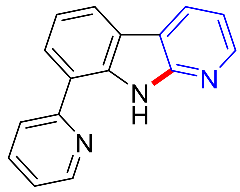
6-bromo-9*H*-pyrido[2,3-*b*]indole (2a-21)

Prepared according to general procedure A to afford **2a-21** (34.9 mg, 70% yield) as a white solid, (m.p. 210-212 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H), 8.55 (d, J = 7.7 Hz, 1H), 8.47-8.43 (m, 1H), 8.42 (d, J = 2.0 Hz, 1H), 7.57 (dd, J = 8.6, 2.0 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.22 (dd, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.4, 147.4, 137.9, 129.6, 129.4, 124.2, 122.8, 115.8, 114.7, 113.7, 111.9. HRMS (ESI) m/z calcd for $C_{11}H_7BrN_2$ $[M+H]^+$: 246.9865, Found: 246.9872.



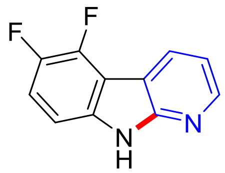
6-phenyl-9*H*-pyrido[2,3-*b*]indole (2a-22)

Prepared according to general procedure A to afford **2a-22** (21.1 mg, 43% yield) as a yellow solid, (m.p. 239-241 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.82 (s, 1H), 8.51-8.40 (m, 2H), 7.92 (dd, J = 4.3, 2.4 Hz, 1H), 7.54 (dd, J = 8.6, 4.1 Hz, 1H), 7.38-7.30 (m, 2H), 7.24-7.13 (m, 2H), 7.09-7,03 (m, 1H), 6.99-6.90 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.2, 152.9, 149.4, 147.0, 136.0, 131.0, 129.4, 122.7, 121.7, 120.2, 117.4, 115.5, 115.3, 112.9, 112.8. HRMS (ESI) m/z calcd for $C_{17}H_{12}N_2$ $[M+H]^+$: 245.1073, Found: 245.1081.



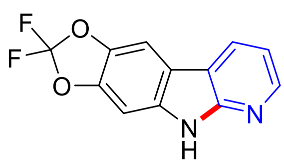
8-(pyridin-2-yl)-9*H*-pyrido[2,3-*b*]indole (2a-23)

Prepared according to general procedure A to afford **2a-23** (44.6 mg, 90% yield) as a white solid, (m.p. 226-228 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.89 (d, J = 1.5 Hz, 1H), 8.64 (dd, J = 4.8, 1.6 Hz, 1H), 8.55 (dd, J = 7.7, 1.6 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 8.12-8.08 (m, 1H), 7.55 (ddd, J = 7.9, 4.8, 0.8 Hz, 1H), 7.48 (dd, J = 7.4, 1.2 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.23 (dd, J = 7.7, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.0, 149.6, 148.8, 146.9, 136.8, 136.7, 134.4, 129.0, 127.6, 124.3, 122.4, 121.9, 121.4, 120.5, 115.8, 115.7. HRMS (ESI) m/z calcd for $C_{16}H_{11}N_3$ [M+H]$^+$: 246.1025, Found: 246.1023.



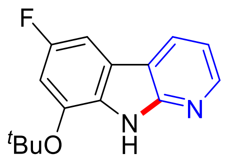
5,6-difluoro-9*H*-pyrido[2,3-*b*]indole (2a-24)

Prepared according to general procedure A to afford **2a-24** (26.6 mg, 72% yield) as a white solid, (m.p. 235-237 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.18 (s, 1H), 8.51 (d, J = 4.9 Hz, 1H), 8.42 (d, J = 7.8 Hz, 1H), 7.52 (q, J = 8.7 Hz, 1H), 7.33-7.25 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.4, 147.7, 146.3 (d, J = 14.9 Hz), 144.7, 143.8 (d, J = 14.8 Hz), 142.5 (d, J = 9.4 Hz), 136.7 (d, J = 8 Hz), 130.7 (d, J = 2.6 Hz), 116.3 (d, J = 18.4 Hz), 116.10, 107.8 (dd, J = 40.0, 31.1 Hz). HRMS (ESI) m/z calcd for $C_{11}H_6F_2N_2$ [M+H]$^+$: 205.0572, Found: 205.0565.



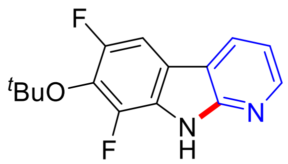
2,2-difluoro-5*H*-[1,3]dioxolo[4,5-*f*]pyrido[2,3-*b*]indole (2a-25)

Prepared according to general procedure A to afford **2a-25** (20.1 mg, 40% yield) as a white solid, (m.p. 241-243 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.06 (s, 1H), 8.58-8.31 (m, 2H), 8.20 (s, 1H), 7.48 (s, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 146.3, 142.5, 137.8, 135.2 134.2, 131.7, 128.8, 115.7, 115.5, 102.8, 94.3. HRMS (ESI) m/z calcd for $C_{12}H_6F_2N_2O_2$ [M+H]$^+$: 249.0470, Found: 249.0468.



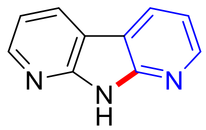
8-(*tert*-butoxy)-6-fluoro-9*H*-pyrido[2,3-*b*]indole (2a-26)

Prepared according to general procedure A to afford **2a-26** (30.9 mg, 60% yield) as a white solid, (m.p. 145-147 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.84 (s, 1H), 8.47 (dd, J = 14.2, 6.2 Hz, 2H), 7.75 (dd, J = 8.7, 2.4 Hz, 1H), 7.19 (dd, J = 7.3, 4.9 Hz, 1H), 7.01 (dd, J = 11.1, 2.0 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.8, 155.5, 152.8, 147.3, 141.6 (d, J = 11.5 Hz), 131.2, 129.5, 121.6 (d, J = 11.9 Hz), 115.3, 109.1 (d, J = 25.7 Hz), 102.0 (d, J = 23.8 Hz), 81.5, 28.7. HRMS (ESI) m/z calcd for $C_{15}H_{15}FN_2O$ [M+H]$^+$: 259.1241, Found: 259.1246.



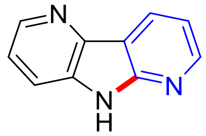
7-(*tert*-butoxy)-6,8-difluoro-9*H*-pyrido[2,3-*b*]indole (2a-27)

Prepared according to general procedure A to afford **2a-27** (35.3 mg, 64% yield) as a white solid, (m.p. 200-202 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.28 (s, 1H), 8.52-8.43 (m, 2H), 7.96 (d, J = 10.2 Hz, 1H), 7.23 (dd, J = 7.8, 4.8 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.5 (d, J = 2.5 Hz), 153.0, 151.1 (d, J = 2.6 Hz), 147.2, 145.2 (d, J = 5.4 Hz), 142.8 (d, J = 5.3 Hz), 129.5, 124.4 (d, J = 12.5 Hz), 115.9, 103.6 (dd, $J = 29.5, 3.7$ Hz), 103.5, 83.5, 28.5. HRMS (ESI) m/z calcd for $C_{15}H_{14}F_2N_2O$ $[M+H]^+$: 277.1147, Found: 277.1151.



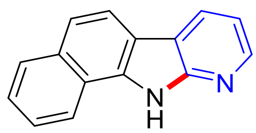
9*H*-pyrrolo[2,3-*b*:5,4-*b*']dipyridine (2a-28)[13]

Prepared according to general procedure A to afford **2a-28** (12.9 mg, 38% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.38 (s, 1H), 8.56 (dd, $J = 7.8, 1.6$ Hz, 2H), 8.48 (dd, $J = 4.9, 1.6$ Hz, 2H), 7.28 (dd, $J = 7.7, 4.9$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ151.7, 147.4, 129.9, 116.3, 114.0. HRMS (ESI) m/z calcd for $C_{10}H_7N_3$ $[M+H]^+$: 170.0713, Found: 170.0714.



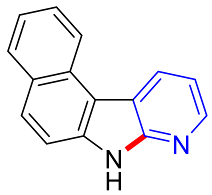
5*H*-pyrrolo[2,3-*b*:4,5-*b*']dipyridine (2a-29)[13]

Prepared according to general procedure A to afford **2a-29** (15.3 mg, 45% yield) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.38 (s, 1H), 8.56 (dd, $J = 7.8$, 1.6 Hz, 2H), 8.48 (dd, $J = 4.9, 1.6$ Hz, 2H), 7.28 (dd, $J = 7.7, 4.9$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.5, 148.6, 142.6, 139.5, 132.9, 129.1, 121.7, 119.0, 116.3, 114.7. HRMS (ESI) m/z calcd for $C_{10}H_7N_3$ $[M+H]^+$: 170.0713, Found: 170.0713.



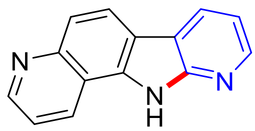
11*H*-benzo[*g*]pyrido[2,3-*b*]indole (2a-30)[17]

Prepared according to general procedure A to afford **2a-30** (39.4 mg, 90% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.79 (s, 1H), 8.63 (d, $J = 8.2$ Hz, 1H), 8.56 (d, J = 7.7 Hz, 1H), 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.72-7.62 (m, 2H), 7.58 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.27 (ddd, J = 7.7, 4.7, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 151.6, 145.7, 135.1, 132.6, 129.0, 128.4, 126.2, 126.2, 122.8, 121.6, 120.4, 120.2, 116.3, 116.0, 115.7. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2$ $[M+H]^+$: 219.0917, Found: 219.0914.



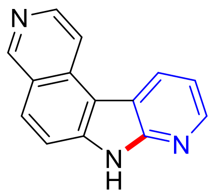
7*H*-benzo[*e*]pyrido[2,3-*b*]indole (2a-31)[13]

Prepared according to general procedure A to afford **2a-31** (38.1 mg, 87% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.79 (s, 1H), 8.63 (d, J = 8.2 Hz, 1H), 8.56 (d, J = 7.7 Hz, 1H), 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.72-7.62 (m, 2H), 7.58 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.27 (ddd, J = 7.7, 4.7, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 151.6, 145.7, 135.1, 132.6, 129.0, 128.4, 126.2, 126.2, 122.8, 121.6, 120.4, 120.2, 116.3, 116.0, 115.7. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2$ $[M+H]^+$: 219.0916, Found: 219.0919.



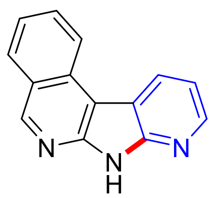
11*H*-pyrido[3',2':4,5]pyrrolo[2,3-*f*]quinoline (2a-32)

Prepared according to general procedure A to afford **2a-32** (30.8 mg, 70% yield) as a white solid, (m.p. >320 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.98 (s, 1H), 9.02 (ddd, J = 8.4, 1.7, 0.8 Hz, 1H), 8.95 (dd, J = 4.3, 1.7 Hz, 1H), 8.64 (dd, J = 7.7, 1.6 Hz, 1H), 8.53-8.47 (m, 2H), 7.82 (d, J = 8.8 Hz, 1H), 7.67 (dd, J = 8.3, 4.3 Hz, 1H), 7.33 (dd, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.8, 150.0, 147.8, 146.2, 134.5, 130.9, 128.9, 123.7, 121.5, 121.3, 116.8, 116.4, 115.9, 115.8. HRMS (ESI) m/z calcd for $C_{14}H_9N_3$ $[M+H]^+$: 220.0869, Found: 220.0868.



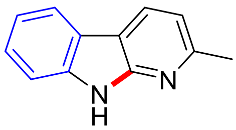
7*H*-pyrido[3',2':4,5]pyrrolo[3,2-*f*]isoquinoline (2a-33)

Prepared according to general procedure A to afford **2a-33** (34.2 mg, 78% yield) as a white solid, (m.p. >320 °C). ^{1}H NMR (400 MHz, DMSO-*d6*): δ 12.60 (s, 1H), 9.37 (s, 1H), 9.01 (d, J = 7.9 Hz, 1H), 8.66 (d, J = 5.7 Hz, 1H), 8.56 (dd, J = 18.5, 5.3 Hz, 2H), 8.16 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.40 (dd, J = 7.8, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.9, 151.1, 145.9, 144.8, 139.6, 132.5, 130.2, 127.7, 124.3, 116.9, 116.8, 115.8, 115.2, 111.4. HRMS (ESI) m/z calcd for $C_{14}H_9N_3$ $[M+H]^+$: 220.0869, Found: 220.0871.



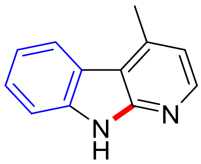
7*H*-pyrido[3',2':4,5]pyrrolo[2,3-*c*]isoquinoline (2a-34)

Prepared according to general procedure A to afford **2a-34** (30.8 mg, 70% yield) as a faint yellow solid, (m.p. >320 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.82 (s, 1H), 9.27 (s, 1H), 8.96 (dd, J = 7.9, 1.5 Hz, 1H), 8.71 (dd, J = 8.4, 1.1 Hz, 1H), 8.53 (dd, J = 4.8, 1.5 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.38 (dd, J = 7.9, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.0, 149.8, 147.8, 145.9, 132.3, 132.0, 130.6, 130.0, 124.8, 124.6, 122.9, 116.7, 114.5, 104.2. HRMS (ESI) m/z calcd for $C_{14}H_9N_3$ $[M+H]^+$: 220.0869, Found: 220.0875.



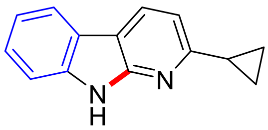
2-methyl-9*H*-pyrido[2,3-*b*]indole (2b-1)[13]

Prepared according to general procedure A to afford **2b-1** (18.3 mg, 50% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.64 (s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.47 (dt, J = 8.1, 1.0 Hz, 1H), 7.40 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.18 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.3, 152.2, 138.9, 129.0, 126.3, 121.1, 121.0, 119.6, 115.0, 113.0, 111.6, 24.8. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ [M+H]$^+$: 183.0917, Found: 183.0921.



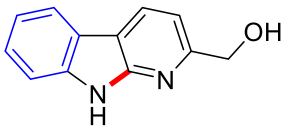
4-methyl-9*H*-pyrido[2,3-*b*]indole (2b-2)[18]

Prepared according to general procedure A to afford **2b-2** (30.4 mg, 83% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.83 (s, 1H), 8.28 (dd, J = 5.0, 1.6 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 4.0 Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 146.2, 142.1, 139.0, 126.4, 123.1, 121.2, 119.8, 117.2, 114.4, 111.5, 20.0. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2$ [M+H]$^+$: 183.0917, Found: 183.0918.



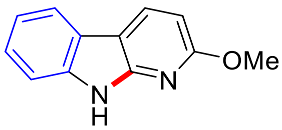
2-cyclopropyl-9*H*-pyrido[2,3-*b*]indole (2b-3)

Prepared according to general procedure A to afford **2b-3** (30.0 mg, 72% yield) as a white solid, (m.p. 173-175 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.63 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 7.4 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.39-7.34 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 2.19 (tt, J = 7.9, 5.0 Hz, 1H), 0.99 (tt, J = 8.1, 2.7 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.0, 152.6, 138.9, 128.7, 126.1, 121.1, 120.9, 119.6, 113.7, 113.1, 111.4, 17.6, 10.5. HRMS (ESI) m/z calcd for $C_{14}H_{12}N_2$ [M+H]$^+$: 209.1073, Found: 209.1074.



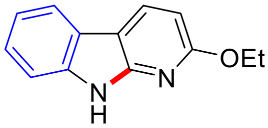
(9*H*-pyrido[2,3-*b*]indol-2-yl)methanol (2b-4)

Prepared according to general procedure A to afford **2b-4** (16.6 mg, 42% yield) as a yellow solid, (m.p. 236-238 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.64 (s, 1H), 8.46 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.42 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.20 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 5.42 (t, J = 5.9 Hz, 1H), 4.68 (d, J = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.4, 151.8, 139.2, 129.1, 126.6, 121.3, 120.9, 119.7, 114.2, 112.2, 111.6, 65.2. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2O$ [M+H]$^+$: 199.0866, Found: 199.0865.



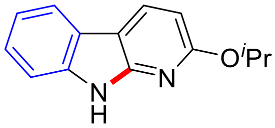
2-methoxy-9*H*-pyrido[2,3-*b*]indole (2b-5)

Prepared according to general procedure A to afford **2b-5** (25.0 mg, 63% yield) as a faint yellow solid, (m.p. 156-158 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.35-7.29 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 6.62 (dd, J = 8.3, 0.9 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.0, 150.7, 138.1, 132.0, 124.9, 121.5, 120.1, 119.8, 111.5, 108.9, 102.4, 53.7. HRMS (ESI) m/z calcd for $C_{12}H_{10}N_2O$ $[M+H]^+$: 199.0866, Found: 199.0868.



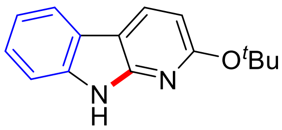
2-ethoxy-9*H*-pyrido[2,3-*b*]indole (2b-6)[18]

Prepared according to general procedure A to afford **2b-6** (26.8 mg, 63% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 8.3 Hz, 1H), 4.39 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.6, 150.7, 138.1, 131.9, 124.8, 121.5, 120.1, 119.8, 111.4, 108.8, 102.6, 61.7, 15.0. HRMS (ESI) m/z calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213.1022, Found: 213.1027.



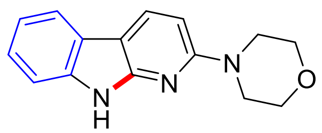
2-isopropoxy-9*H*-pyrido[2,3-*b*]indole (2b-7)

Prepared according to general procedure A to afford **2b-7** (25.0 mg, 55% yield) as a yellow solid, (m.p. 92-94 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.71 (s, 1H), 8.33 (dd, J = 8.3, 4.0 Hz, 1H), 7.98 (dd, J = 7.8, 4.1 Hz, 1H), 7.40 (dd, J = 8.0, 4.1 Hz, 1H), 7.34-7.26 (m, 1H), 7.20-7.10 (m, 1H), 6.54 (dd, J = 8.3, 3.9 Hz, 1H), 5.38-5.27 (m, 1H), 1.35 (dd, J = 6.2, 3.9 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.1, 150.7, 138.0, 132.0, 124.8, 121.5, 120.1, 119.8, 111.4, 108.62, 103.2, 67.8, 22.4. HRMS (ESI) m/z calcd for $C_{14}H_{14}N_2O$ $[M+H]^+$: 227.1178, Found: 227.1179.



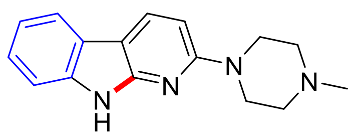
2-(*tert*-butoxy)-9*H*-pyrido[2,3-*b*]indole (2b-8)

Prepared according to general procedure A to afford **2b-8** (16.8 mg, 35% yield) as a yellow solid, (m.p. 133-135 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.60 (s, 1H), 8.29 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.34-7.27 (m, 1H), 7.18-7.11 (m, 1H), 6.49 (d, J = 8.4 Hz, 1H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.1, 154.8, 142.8, 136.3, 129.5, 126.1, 124.8, 124.4, 116.0, 113.1, 109.8, 84.2, 33.6. HRMS (ESI) m/z calcd for $C_{15}H_{16}N_2O$ [M+H]$^+$: 241.1335, Found: 241.1334.



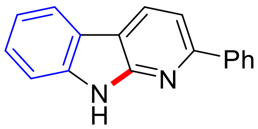
4-(9*H*-pyrido[2,3-*b*]indol-2-yl)morpholine (2b-9)

Prepared according to general procedure A to afford **2b-9** (22.8 mg, 45% yield) as a faint yellow solid, (m.p. 175-177 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.33 (s, 1H), 8.21 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 8.6 Hz, 1H), 3.78-3.71 (m, 4H), 3.56-3.51 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.5, 151.8, 138.1, 130.7, 124.2, 121.9, 119.6, 119.5, 111.1, 106.8, 100.1, 70.2, 66.5, 46.1. HRMS (ESI) m/z calcd for $C_{15}H_{15}N_3O$ [M+H]$^+$: 254.1288, Found: 254.1289.



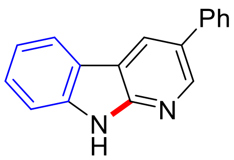
2-(4-methylpiperazin-1-yl)-9*H*-pyrido[2,3-*b*]indole (2b-10)

Prepared according to general procedure A to afford **2b-10** (40.4 mg, 76% yield) as a faint yellow solid, (m.p. 188-190 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 8.45 (dd, J = 7.7, 1.6 Hz, 1H), 8.36 (dd, J = 4.8, 1.6 Hz, 1H), 7.70 (d, J = 2.3 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.19 (dd, J = 8.8, 2.4 Hz, 1H), 7.13 (dd, J = 7.7, 4.8 Hz, 1H), 3.15 (t, J = 4.9 Hz, 4H), 2.54 (t, J = 4.9 Hz, 4H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 146.1, 145.9, 133.8, 128.6, 121.2, 118.8, 115.9, 114.8, 112.0, 108.2, 55.3, 50.7, 46.1. HRMS (ESI) m/z calcd for $C_{16}H_{18}N_4$ $[M+H]^+$: 267.1604, Found: 267.1601.



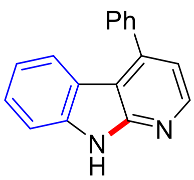
2-phenyl-9*H*-pyrido[2,3-*b*]indole (2b-11)[19]

Prepared according to general procedure A to afford **2b-11** (32.3 mg, 66% yield) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.89 (s, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.16 (dd, J = 12.5, 7.4 Hz, 3H), 7.77 (d, J = 8.1 Hz, 1H), 7.55-7.39 (m, 5H), 7.25-7.20 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.4, 152.5, 139.9, 139.8, 129.6, 129.2, 129.0, 127.1, 127.0, 121.5, 120.8, 112.0, 114.7, 112.4, 111.7. HRMS (ESI) m/z calcd for $C_{17}H_{12}N$ $[M+H]^+$: 245.1073, Found: 245.1075.



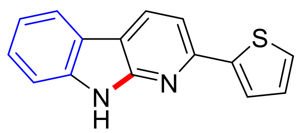
3-phenyl-9*H*-pyrido[2,3-*b*]indole (2b-12)[13]

Prepared according to general procedure A to afford **2b-12** (41.6 mg, 85% yield) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.89 (s, 1H), 8.82 (d, J = 2.2 Hz, 1H), 8.75 (d, J = 2.2 Hz, 1H), 8.25 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.57-7.45 (m, 4H), 7.37 (t, J = 7.3 Hz, 1H), 7.25 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.9, 145.2, 139.9, 139.1, 129.5, 128.1, 127.4, 127.3, 127.2, 127.0, 121.9, 121.0, 112.0, 115.8, 111.8. HRMS (ESI) m/z calcd for $C_{17}H_{12}N$ $[M+H]^+$: 245.1073, Found: 245.1076.



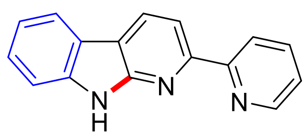
4-phenyl-9*H*-pyrido[2,3-*b*]indole (2b-13)[20]

Prepared according to general procedure A to afford **2b-13** (45.5 mg, 93% yield) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.03 (s, 1H), 8.45 (d, J = 5.0 Hz, 1H), 7.70-7.64 (m, 2H), 7.64-7.47 (m, 5H), 7.44-7.37 (m, 1H), 7.09 (d, J = 4.9 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 146.5, 144.7, 139.4, 138.9, 129.3, 129.2, 128.9, 127.0, 122.3, 120.2, 119.6, 116.3, 112.5, 111.8. HRMS (ESI) m/z calcd for $C_{17}H_{12}N$ $[M+H]^+$: 245.1073, Found: 245.1075.



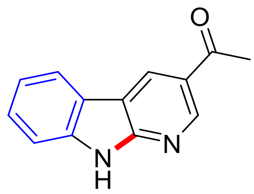
2-(thiophen-2-yl)-9*H*-pyrido[2,3-*b*]indole (2b-14)

Prepared according to general procedure A to afford **2b-14** (47.5 mg, 90% yield) as a white solid, (m.p. 174-176 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.92 (s, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 3.5 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 5.0 Hz, 1H), 7.47-7.38 (m, 2H), 7.21-7.12 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.1, 149.1, 146.0, 139.6, 129.6, 128.8, 128.2, 126.9, 125.4, 121.4, 121.0, 120.1, 114.6, 111.7, 111.1. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2S$ $[M+H]^+$: 251.0637, Found: 251.0639.



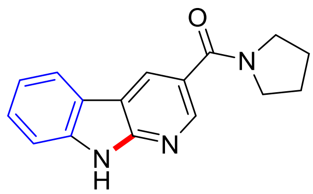
2-(pyridin-2-yl)-9*H*-pyrido[2,3-*b*]indole (2b-15)

Prepared according to general procedure A to afford **2b-15** (45.6 mg, 93% yield) as a white solid, (m.p. 108-110 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.99 (s, 1H), 8.70 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 8.60 (d, J = 8.1 Hz, 1H), 8.49 (dt, J = 8.0, 1.1 Hz, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.95 (td, J = 7.7, 1.8 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.47 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.41 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.23 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.4, 158.6, 154.5, 154.2, 151.0, 142.5, 142.4, 141.0, 135.4, 134.2, 129.2, 125.7, 127.1, 125.5, 122.1, 120.8. HRMS (ESI) m/z calcd for $C_{16}H_{11}N_3$ [M+H]$^+$: 246.1026, Found: 246.1029.



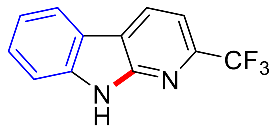
1-(9*H*-pyrido[2,3-*b*]indol-3-yl)ethan-1-one (2b-16)

Prepared according to general procedure A to afford **2b-16** (14.7 mg, 35% yield) as a white solid, (m.p. 178-180 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.26 (s, 1H), 9.07 (dd, J = 15.1, 1.8 Hz, 2H), 8.30 (d, J = 7.8 Hz, 1H), 7.57-7.49 (m, 2H), 7.30 (t, J = 7.3 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.0, 154.2, 148.3, 140.0, 129.2, 127.8, 125.3, 122.2, 121.2, 120.9, 115.3, 112.2, 27.3. HRMS (ESI) m/z calcd for $C_{13}H_{10}N_2$ [M+H]$^+$: 211.0866, Found: 211.0869.



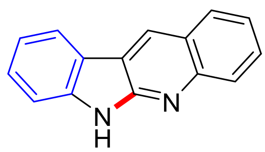
(9*H*-pyrido[2,3-*b*]indol-3-yl)(pyrrolidin-1-yl)methanone (2b-17)

Prepared according to general procedure A to afford **2b-17** (24.4 mg, 46% yield) as a yellow solid, (m.p. 185-187 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.03 (s, 1H), 8.73 (d, J = 2.0 Hz, 1H), 8.61 (d, J = 2.1 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 7.55-7.45 (m, 2H), 7.25 (t, J = 7.4 Hz, 1H), 3.60-3.49 (m, 4H), 1.86 (td, J = 12.5, 6.6 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.8, 152.6, 146.0, 139.8, 128.2, 127.5, 124.7, 122.0, 120.9, 120.3, 114.7, 111.9, 49.7, 46.7, 26.5, 24.5. HRMS (ESI) m/z calcd for $C_{16}H_{15}N_3O$ [M+H]$^+$: 266.1288, Found: 266.1283.



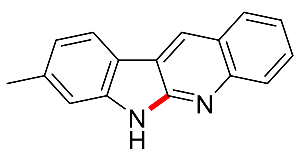
2-(trifluoromethyl)-9*H*-pyrido[2,3-*b*]indole (2b-18)

Prepared according to general procedure A to afford **2b-18** (35.0 mg, 74% yield) as a white solid, (m.p. 200-201 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.29 (s, 1H), 8.77 (d, J = 7.9 Hz, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 3.6 Hz, 2H), 7.34-7.27 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.4, 142.5 (q, J = 33.0 Hz), 140.6, 130.2, 128.7, 124.2, 122.6, 120.7, 119.9, 118.9, 112.1, 111.6 (q, J = 3.0 Hz). HRMS (ESI) m/z calcd for $C_{12}H_7F_3N_2$ [M+H]$^+$: 237.0634, Found: 237.0631.



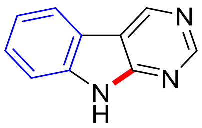
6*H*-indolo[2,3-*b*]quinoline (2b-19)[13]

Prepared according to general procedure A to afford **2b-19** (37.6 mg, 86% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (s, 1H), 9.05 (s, 1H), 8.26 (d, J = 7.7 Hz, 1H), 8.11 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.56-7.42 (m, 3H), 7.27 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.3, 146.7, 141.9, 129.1, 129.1, 128.6, 128.0, 127.4, 124.1, 123.2, 122.3, 120.7, 120.1, 118.3, 111.4. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2$ [M+H]$^+$: 219.0917, Found: 219.0917.



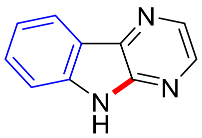
8-methyl-6*H*-indolo[2,3-*b*]quinoline (2b-20)

Prepared according to general procedure A to afford **2b-20** (35.8 mg, 77% yield) as a white solid, (m.p. 226-228 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.61 (s, 1H), 8.95 (s, 1H), 8.14-8.05 (m, 2H), 7.97 (d, J = 8.5 Hz, 1H), 7.70 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.47 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.30 (s, 1H), 7.12-7.06 (m, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.6, 146.5, 142.3, 138.6, 129.0, 128.8, 127.4, 127.2, 124.2, 123.1, 122.0, 121.4, 118.5, 118.3, 111.5, 22.3. HRMS (ESI) m/z calcd for $C_{16}H_{12}N_2$ $[M+H]^+$: 233.1073, Found: 233.1071.



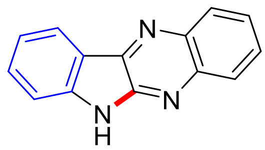
9*H*-pyrimido[4,5-*b*]indole (2b-21)[21]

Prepared according to general procedure A to afford **2b-21** (25.5 mg, 75% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (s, 1H), 9.44 (s, 1H), 8.93 (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.64-7.47 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.5, 154.9, 149.0, 138.8, 128.1, 122.1, 121.4, 119.2, 114.3, 112.3. HRMS (ESI) m/z calcd for $C_{10}H_7N_3$ $[M+H]^+$: 170.0713, Found: 170.0714.



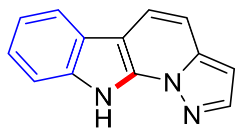
5*H*-pyrazino[2,3-*b*]indole (2b-22)[22]

Prepared according to general procedure A to afford **2b-22** (28.5 mg, 84% yield) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.15 (s, 1H), 8.46 (dd, J = 21.2, 2.6 Hz, 2H), 8.23 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 3.6 Hz, 2H), 7.32 (dt, J = 8.1, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.9, 140.7, 140.3, 136.9, 135.6, 129.4, 121.4, 120.9, 119.7, 112.5. HRMS (ESI) m/z calcd for $C_{10}H_7N_3$ $[M+H]^+$: 170.0713, Found: 170.0713.



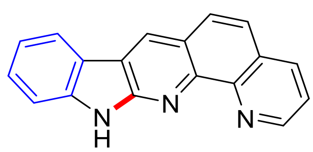
6*H*-indolo[2,3-*b*]quinoxaline (2b-23)[6]

Prepared according to general procedure A to afford **2b-23** (38.2 mg, 87% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.07 (s, 1H), 8.30 (dd, J = 39.8, 7.8 Hz, 2H), 8.07 (d, J = 8.1 Hz, 1H), 7.83-7.48 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.2, 144.4, 140.6, 140.2, 139.0, 131.7, 129.5, 129.2, 127.9, 126.4, 122.7, 121.1, 119.4, 112.4. HRMS (ESI) m/z calcd for $C_{14}H_9N_3$ $[M+H]^+$: 220.0869, Found: 220.0871.



10*H*-pyrazolo[1',5':1,6]pyrido[2,3-*b*]indole (2b-24)

Prepared according to general procedure A to afford **2b-24** (16.6 mg, 40% yield) as a yellow solid, (m.p. 200-202 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.84 (s, 1H), 8.13 (t, J = 2.0 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.99 (dd, J = 9.0, 1.7 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 9.0, 1.8 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.1, 140.2, 136.0, 135.3, 124.0, 123.2, 120.9, 119.8, 119.5, 112.5, 108.4, 104.6, 98.2. HRMS (ESI) m/z calcd for $C_{13}H_9N_3$ $[M+H]^+$: 208.0869, Found: 208.0873.

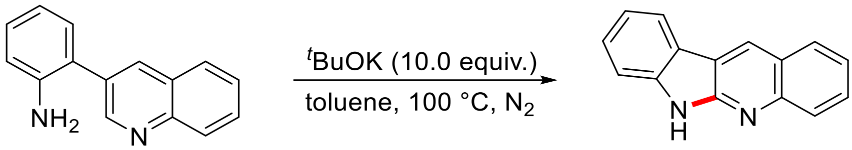


12*H*-indolo[2,3-*b*][1,10]phenanthroline (2b-25)[16]

Prepared according to general procedure A to afford **2b-25** (23.6 mg, 44% yield) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.14 (s, 1H), 9.17 (s, 1H), 9.07 (d, J = 2.6 Hz, 1H), 8.47 (d, J = 7.6 Hz, 1H), 8.33 (d, J = 7.7 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.73 (dd, J = 8.0, 4.3 Hz, 1H), 7.62-7.53 (m, 2H), 7.31 (ddd, J = 8.0, 5.8, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.8, 149.4, 145.8, 144.2, 141.5, 136.5, 128.9, 128.6, 128.4, 128.2, 123.7, 123.2, 122.9, 122.4, 120.5, 120.3, 118.1, 111.8. HRMS (ESI) m/z calcd for $C_{18}H_{11}N_3$ $[M+H]^+$: 270.1025, Found: 270.1027.

5. Synthesis of Important Molecules and Scale-up Experiment

5.1 Synthesis of Norneocryptolepine (2b-19):



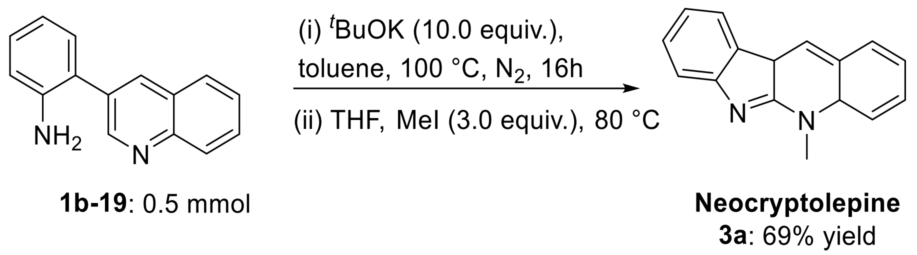
1b-19: 0.5 mmol

Norneocryptolepine
2b-19: 86% yield

The mixture of 2-(quinolin-3-yl)aniline (110.0 mg, 0.5 mmol), ^{t}BuOK (661.0 mg, 10 equiv.) in dry solvent (5 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 °C for 16 hours. After completion (judged by TLC), toluene was removed under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in DCM as eluent) to give 95.0 mg (86%) of the desired product (**2b-19**) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (s, 1H), 9.05 (s, 1H), 8.26 (d, J = 7.7 Hz, 1H), 8.11 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.56-7.42 (m, 3H), 7.27 (t, J = 7.3 Hz, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): δ 153.3, 146.7, 141.9, 129.1, 129.1, 128.6, 128.0, 127.4, 124.1, 123.2, 122.3, 120.7, 120.1, 118.3, 111.4.
HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2$ $[M+H]^+$: 219.0917, Found: 219.0917.

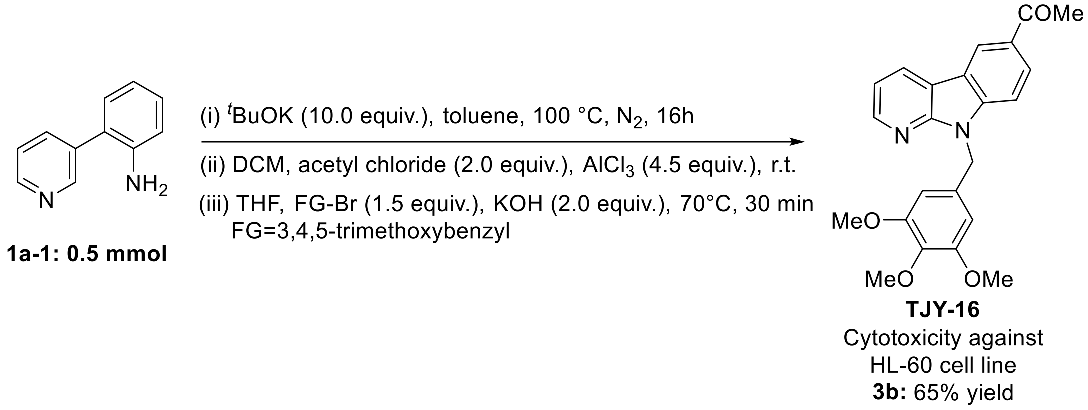
5.2 Synthesis of Neocryptolepine (3a):



The mixture of 2-(quinolin-3-yl)aniline (110.0 mg, 0.5 mmol), ^{t}BuOK (661.0 mg, 10 equiv.) in dry solvent (5 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 ℃ for 16 hours. After completion (judged by TLC), toluene was removed under reduced pressure to afford the crude α-carboline product. To this crude product, THF (4.0 mL) and MeI (94.0 μL, 3.0 equiv.) was added and the microreactor was capped with a teflon pressure cap and placed into a pre-heated aluminum block at 80 ℃[23]. The reaction mixture was stirred for 12 h. After completion (judged by TLC), THF was removed under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in DCM as eluent) to give 80.7 mg (69%) of the desired product (**3a**) as red solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 8.32-8.19 (m, 3H), 8.02 (t, J = 7.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.67-7.57 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 4.39 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.5, 150.6, 141.2, 138.4, 137.6, 135.7, 134.8, 129.7, 128.73, 127.2, 127.2, 127.0, 126.5, 121.3, 119.4, 40.5.
HRMS (ESI) m/z calcd for $C_{16}H_{12}N_2$ $[M+H]^+$: 233.1073, Found: 233.1081

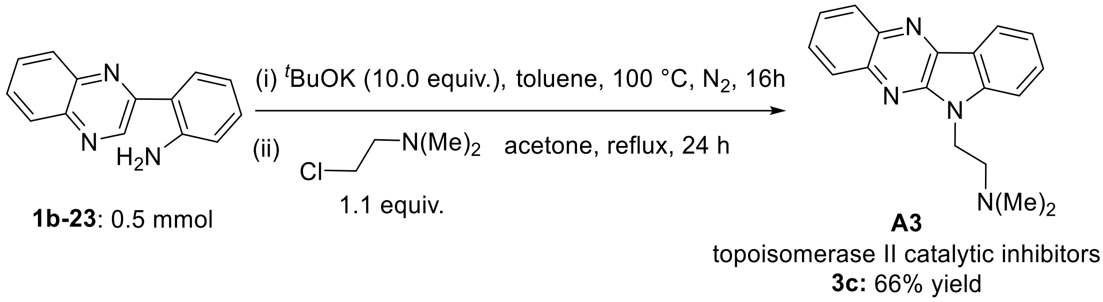
5.3 Synthesis of 1-(9-(3,4,5-trimethoxybenzyl)-9*H*-pyrido[2,3-*b*]indol-6-yl)ethan-1-one (3b):



The mixture of 2-(pyridin-3-yl)aniline (84.0 mg, 0.5 mmol), ^{t}BuOK (661.0 mg, 10 equiv.) in dry solvent (5 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 ℃ for 16 hours. After completion (judged by TLC), the mixture was extracted with ethyl acetate (3×40 mL) and brine solution (3×20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude α-carboline product. To this crude product, $AlCl_3$ (288.0 mg, 4.5 equiv.) and acetyl chloride (75.0 mg, 2.0 equiv.) at 25ºC were added to stirred solution of α-carboline in dried CH_2Cl_2 (10 mL)[24]. The mixture was refluxed for 4 hours and poured into iced water and extracted with ethyl acetate (40 mL). The organic layer was washed with waster, dried over $MgSO_4$, evaporated and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 77 mg (76%) of the desired compound as white solid. Then, the acetylation product, KOH (40.8 mg, 2.0 equiv.) and 5-(bromomethyl)-1,2,3-trimethoxytoluene (104.5 mg, 1.1 equiv.) was added in THF (2.0 mL). The reaction mixture was stirred for 30 min at 70 °C[25]. After completion (judged by TLC), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 128.0 mg (65%) of the desired compound 1-(9-(3,4,5-trimethoxybenzyl)-9*H*-pyrido[2,3-*b*]indol-6-yl)ethan-1-one (**3b**) as white solid.

^{1}H NMR (400 MHz, DMSO): δ 8.89 (d, J = 1.9 Hz, 1H), 8.79 (d, J = 7.1 Hz, 1H), 8.45 (d, J = 6.2 Hz, 1H), 8.07 (dd, J = 8.6, 1.8 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.15-7.10 (m, 1H), 6.97 (s, 2H), 5.83 (s, 2H), 3.71 (s, 6H), 3.61 (s, 3H), 2.65 (s, 3H).
13C-NMR (100 MHz, $CDCl_3$): δ 197.3, 157.0, 154.9, 153.4, 137.9, 135.7, 132.0, 131.8, 128.2, 127.8, 126.4, 123.6, 123.1, 117.5, 109.3, 106.7, 60.4, 56.3, 55.4, 27.0.
HRMS (ESI) m/z calcd for $C_{23}H_{22}N_2O_4$ $[M+H]^+$: 391.1652, Found: 391.1658

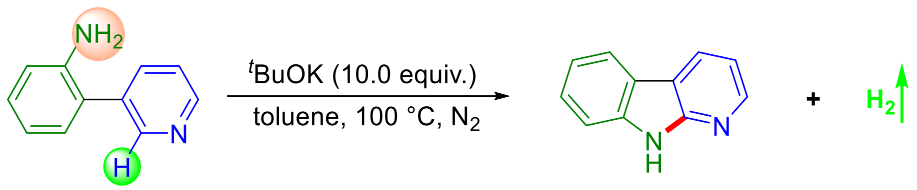
5.4 Synthesis of 2-(6*H*-indolo[2,3-*b*]quinoxalin-6-yl)-N,N-dimethylethan-1-amine (3c):



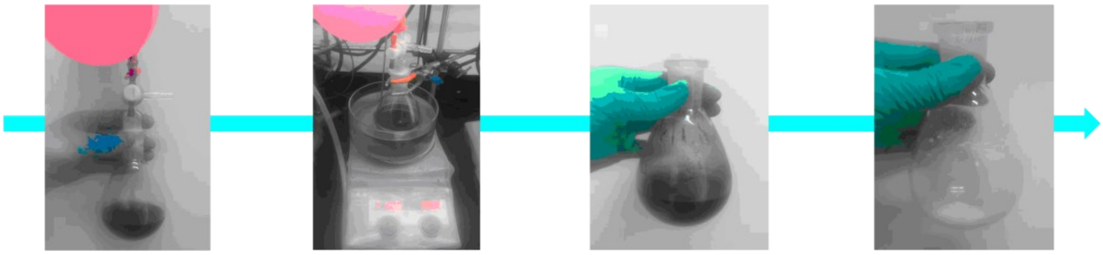
The mixture of 2-(quinoxalin-2-yl)aniline (110.5 mg, 0.5 mmol), ^{t}BuOK (661.0 mg, 10 equiv.) in dry solvent (5 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 ℃ for 16 hours. After completion (judged by TLC), the mixture was extracted with ethyl acetate (3×40 mL) and brine solution (3×20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product. To this crude product, 2-chloro-N,N-dimethylethan-1-amine (59.2 mg, 1.1 equiv.) were added to stirred solution of α-carboline in acetone (10 mL). The mixture was refluxed for 24 hours and poured into iced water and extracted with ethyl acetate (40 mL)[26]. The organic layer was washed with waster, dried over $MgSO_4$, evaporated and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 95.7 mg (66%) of the desired compound 2-(6H-indolo[2,3-b]quinoxalin-6-yl)-N,N-dimethylethan-1-amine (**3c**) as a yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 8.33 (dd, J = 7.7, 1.0 Hz, 1H), 8.26-8.19 (m, 1H), 8.06 (dt, J = 8.4, 0.9 Hz, 1H), 7.80-7.66 (m, 4H), 7.40-7.33 (m, 1H), 4.52 (t, J = 6.6 Hz, 2H), 2.71 (t, J = 6.5 Hz, 2H), 2.18 (d, J = 0.8 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.4, 144.6, 140.3, 139.8, 139.0, 131.7, 129.5, 129.3, 128.0, 126.4, 122.6, 121.3, 119.0, 110.9, 57.2, 45.8.
HRMS (ESI) m/z calcd for $C_{18}H_{18}N_4$ [M+H]$^+$: 291.1604, Found: 291.1613

5.5 Scale-up experiment:



1a-1 **2a-1**

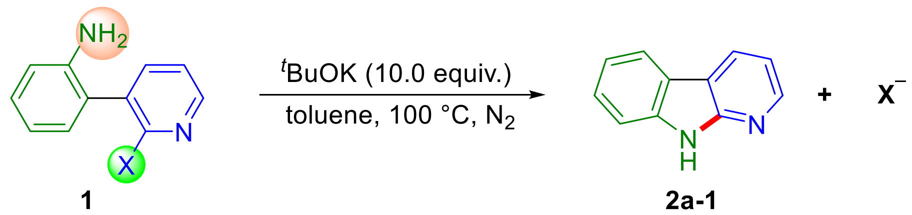


start point (**1a**, 7.5 mmol, 1.26 g) | reaction in progress 16 hours | end point | **2a-1** (1.0 g, 80% yield)

The mixture of 2-(pyridin-3-yl)aniline (1.26 g, 7.5 mmol), ^{t}BuOK (8.55 g, 10 equiv.) was added in a 100 mL round-bottom flask. The flask was evacuated and back filled with nitrogen and this sequence was repeated three additional times. Under the positive flow of nitrogen, toluene (25 ml) was added to the reaction mixture. The reaction was heated at 100 °C for 16 hours. The mixture was extracted with ethyl acetate (3×200 mL) and brine solution (3×100 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel (33% ethyl acetate in hexane as eluent) to give of the product **2a-1** (1.0 g, 80%) as a white solid.

6. Mechanistic Studies

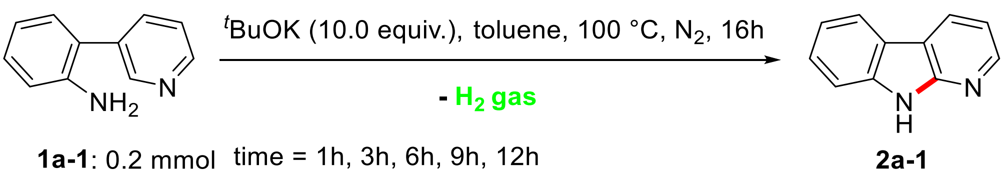
1. Replace 2-H of pyridine with F, Cl, Br, I



Entry	X	Yield
1	F	61%
2	Cl	58%
3	Br	63%
4	I	60%

The mixture of 2-substitution pyridine of substrate (0.2 mmol), ^{t}BuOK (224.0 mg, 10 equiv.) in dry toluene (2 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 °C for 16h. The mixture was extracted with ethyl acetate (3×20 mL) and brine solution (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) to give 20.5 mg (61%), 19.5 mg (58%), 21.2 mg (63%), 20.2 mg (60%) of the product respectively.

2. Real Time ^{1}H NMR Analysis:



The mixture of 2-(pyridin-3-yl)aniline (**1a-1**)(34.0 mg, 0.2 mmol), ^{t}BuOK (224.0 mg, 10 equiv.) in dry solvent (2 mL) was sealed in a 25 mL Schlenk tube in glovebox. The tube was removed from the glovebox and heated at 100 °C. Then, Ethyl acetate (5 ml) was added to quench the reaction when reaction times were one-hour, three-hour, six-hour, nine-hour, twelve-hour, respectively. The mixture was extracted thrice with ethyl acetate (3×20 mL) and brine solution (3×25 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was measured by **^{1}H NMR** spectroscopy using 1,3,5-trimethoxytoluene as an internal standard (**Figure S2**). The residue chromatographic separation with silica gel gave the isolated intermediate **4** (**Figure S3**).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.42 (s, 1H), 8.55 (d, J = 4.5 Hz, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.48-7.42 (m, 2H), 7.42-7,29 (m, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): 13C NMR (101 MHz, dmso): δ 169.0, 149.5, 148.6, 136.4, 135.7, 135.3, 134.1, 130.7, 128.9, 127.8, 126.6, 123.8, 23.3. HRMS (ESI) m/z calcd for $C_{13}H_{11}N_2O$ [M+H]$^+$: 213.0128, Found: 213.1035.

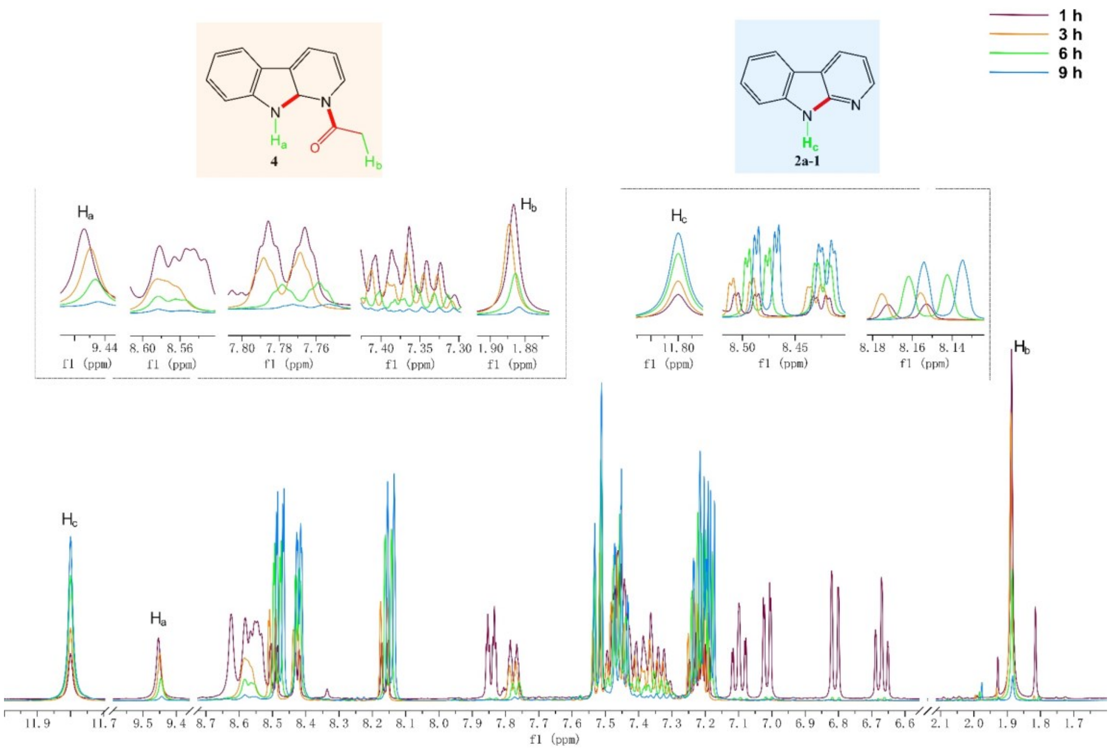
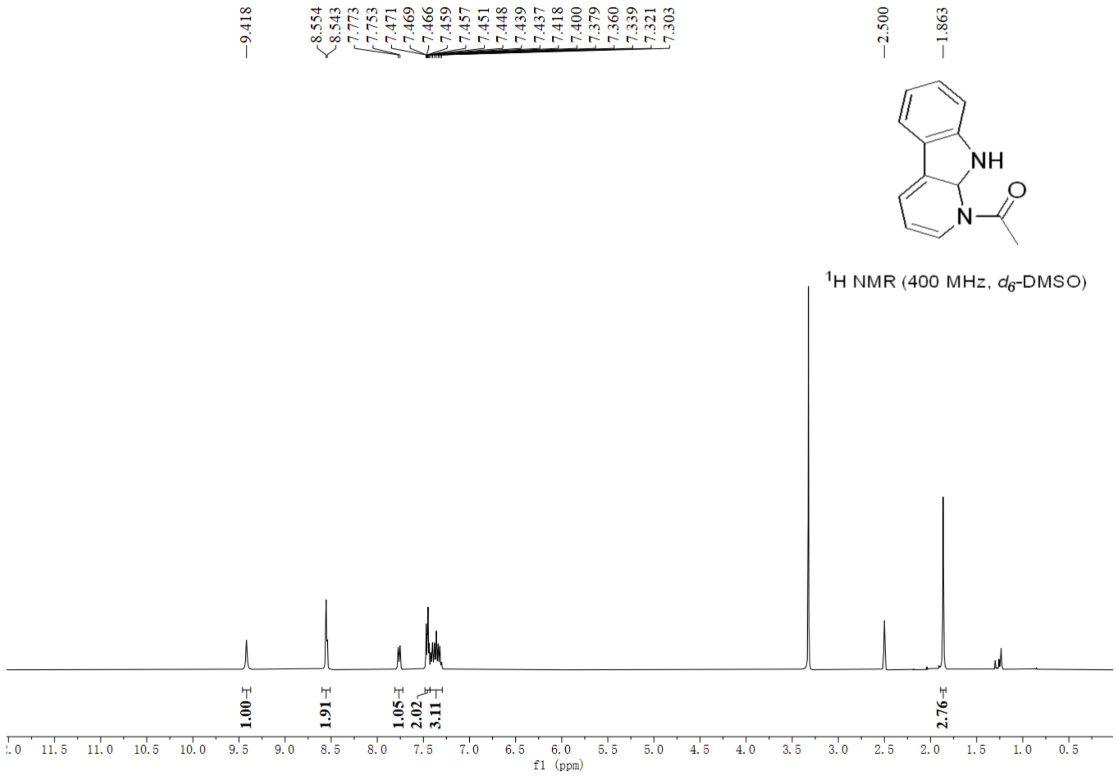


Figure S1. Real time ^{1}H NMR studies.



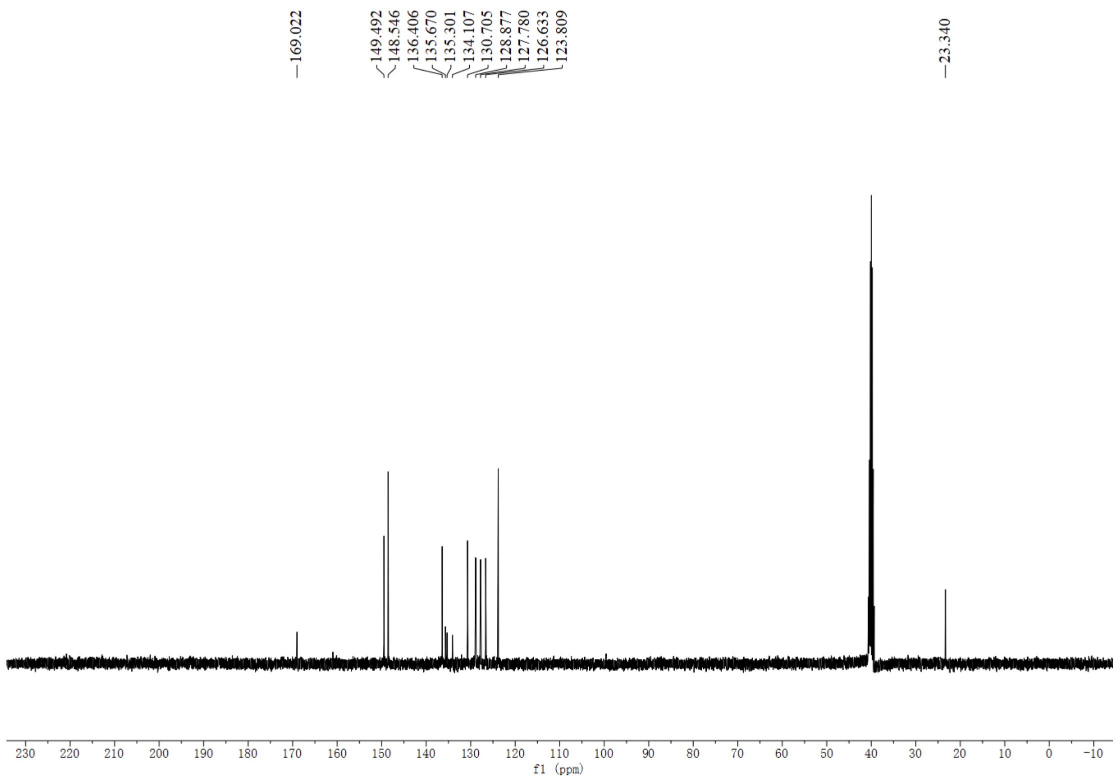


Figure S2. Spectrum of isolated intermediate.

7. X-Ray Ellipsoid Plots of 2a-31, 2a-34 and 2b-21

Single crystal structure of 2a-31:

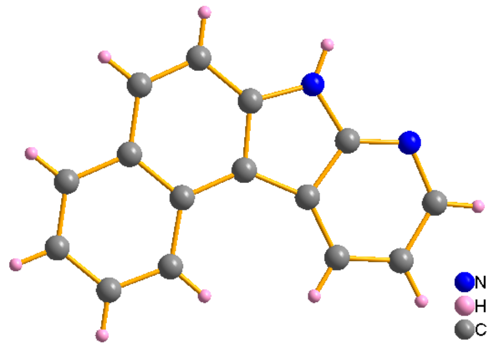


Table S9. Crystal data of compound **2a-31** at room temperature

Compounds	7H-benzo[e]pyrido[2,3-b]indole
CCDC Name	CCDC 2224160
Chemical Formula	$C_{15}H_{10}N_2$
Formula Weight	218.25
Temperature(K)	296
Crystal System	Monoclinic
Space Group	*P 21/n*
a (Å)	5.0243(19)
b (Å)	15.100(6)
c (Å)	14.285(6)
α (°)	90.00
β (°)	93.425(7)
γ (°)	90.00
Volume[Å]^3	1081.8(7)
Z	4
D_{calc} (g/cm^3)	1.340
F(000)	456.0
GOF, *S*	1.182
R_1, wR_2 (obsd data)	0.1310, 0.2497
R_1, wR_2 (all data)	0.1217, 0.2255

Single crystal structure of 2a-34:

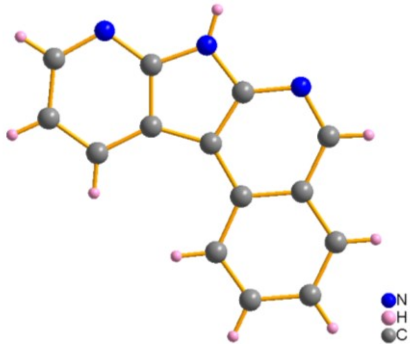


Table S10. Crystal data of compound **2a-34** at room temperature

Compounds	7H-pyrido[3',2':4,5]pyrrolo[2,3-c]isoquinoline
CCDC Name	CCDC 2224157
Chemical Formula	$C_{14}H_9N_3$
Formula Weight	219.24
Temperature(K)	296
Crystal System	Monoclinic
Space Group	*P 21/c*
a (Å)	9.977(3)
b (Å)	5.2487(13)
c (Å)	20.047(5)
α (°)	90.00
β (°)	96.257(4)
γ (°)	90.00
Volume[Å]^3	1043.6(5)
Z	4
D_{calc} (g/cm^3)	1.395
F(000)	456.0
GOF, *S*	1.126
R_1, wR_2 (obsd data)	0.0511, 0.1581
R_1, wR_2 (all data)	0.1577, 0.2359

Single crystal structure of 2b-21:

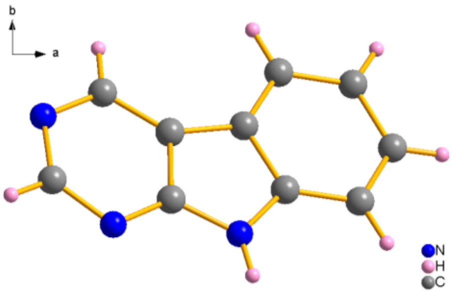
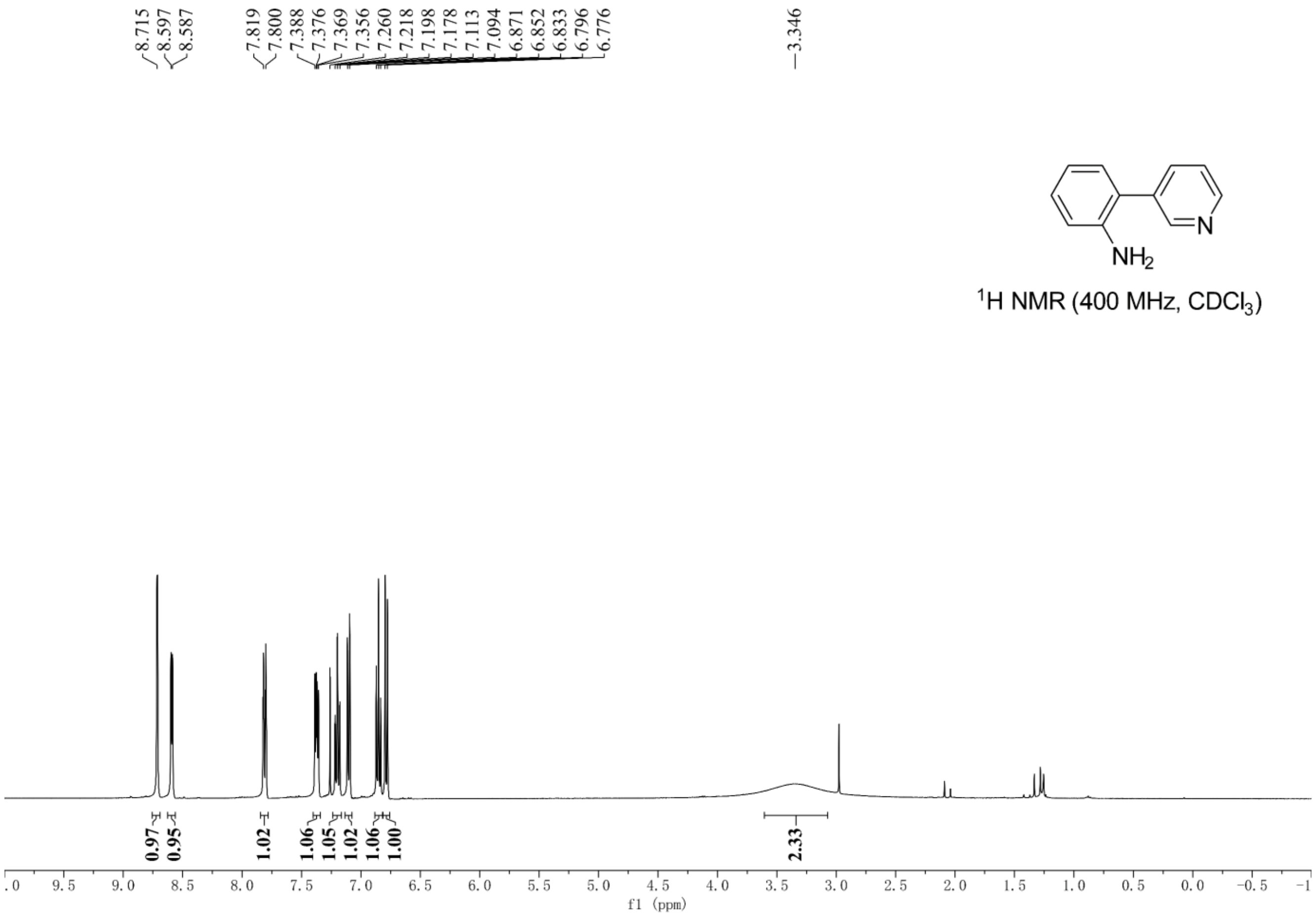
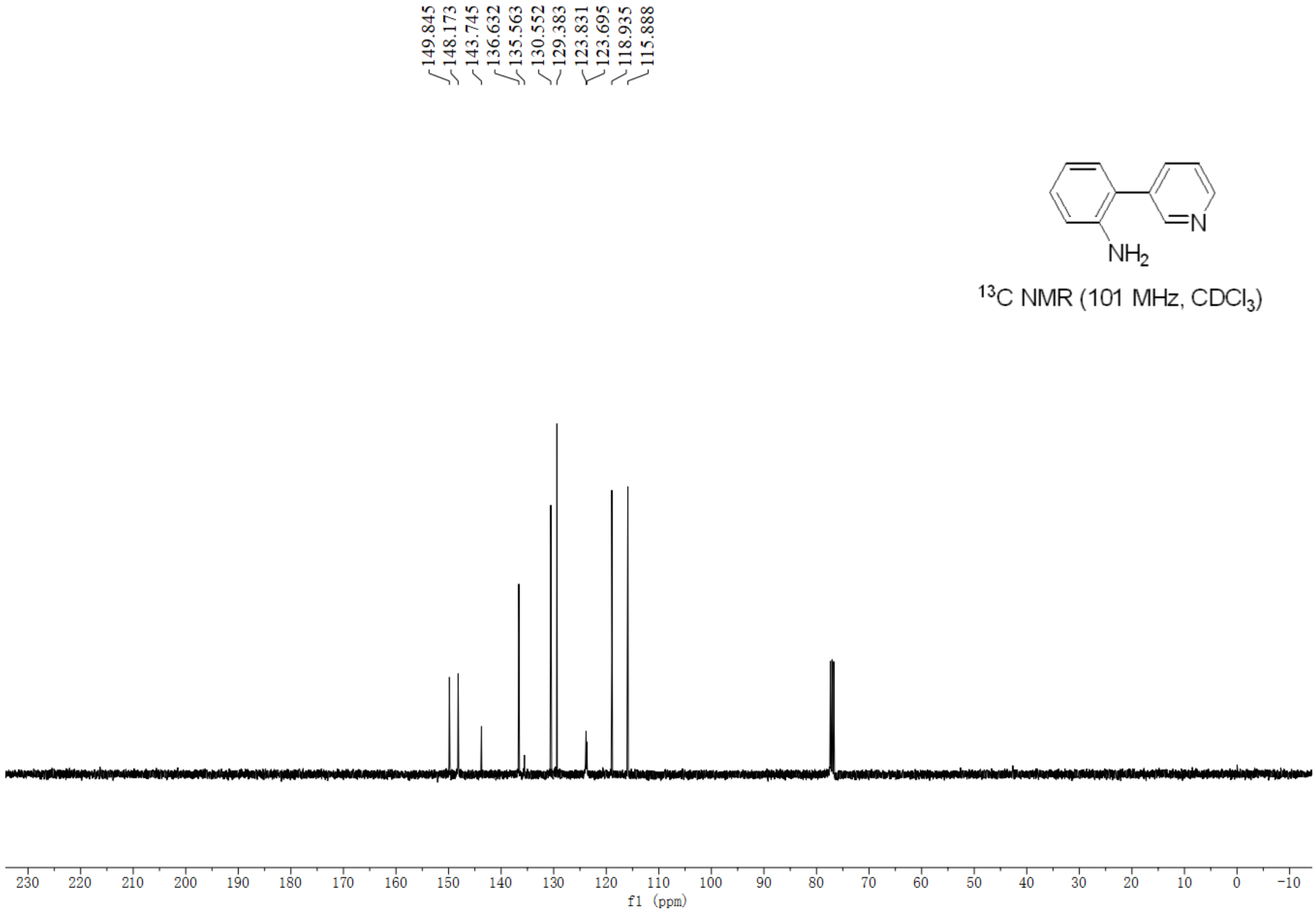


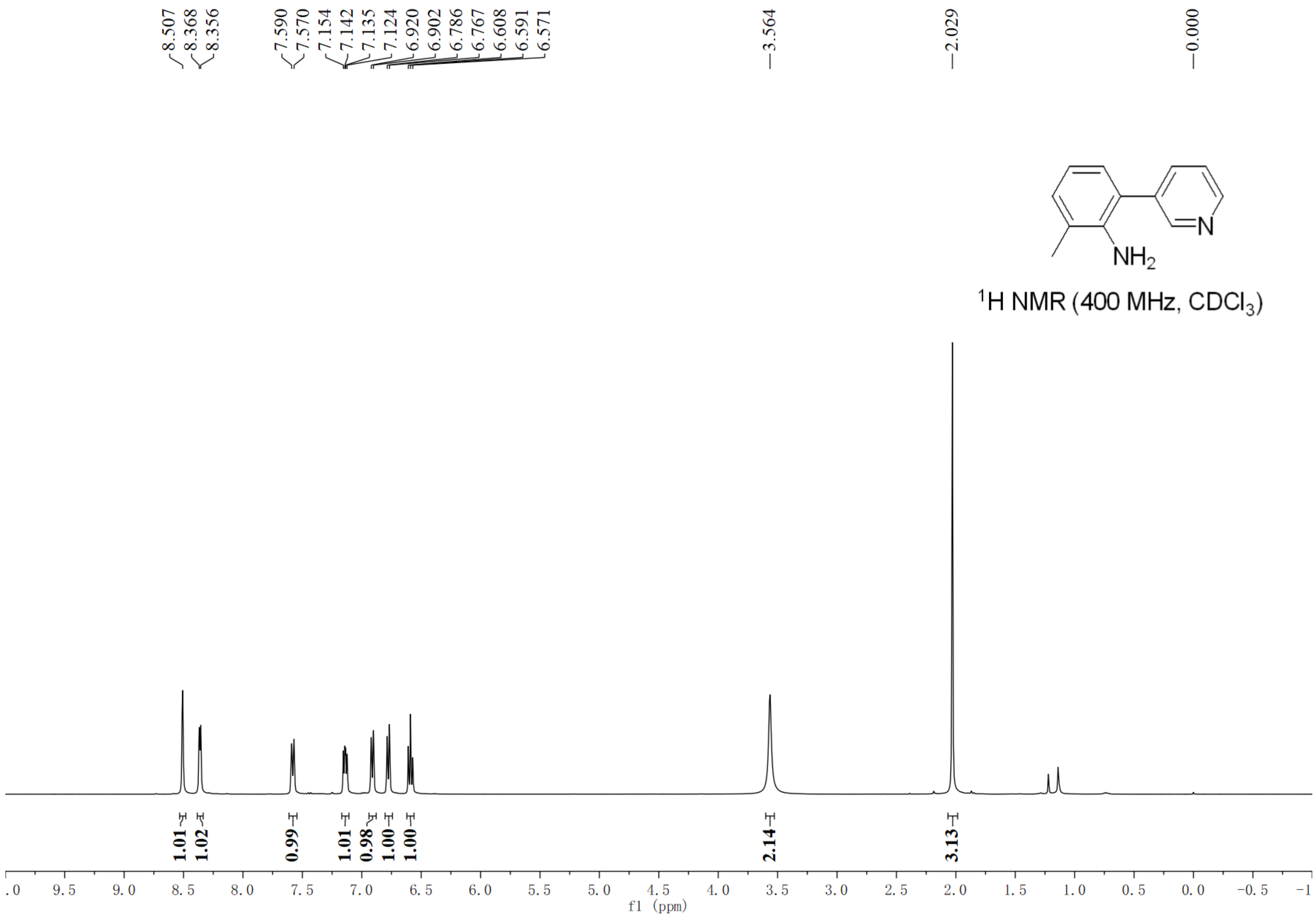
Table S11. Crystal data of compound **2b-21** at room temperature

Compounds	9H-pyrimido[4,5-b]indole
CCDC Name	CCDC 2224156
Chemical Formula	$C_{10}H_7N_3$
Formula Weight	160.19
Temperature(K)	296
Crystal System	Monoclinic
Space Group	*C2/c*
a (Å)	18.096(6)
b (Å)	5.6801(19)
c (Å)	16.380(6)
α (°)	90.00
β (°)	103.239(5)
γ (°)	90.00
Volume[Å]^3	1638.9(10)
Z	8
D_{calc} (g/cm^3)	1.371
F(000)	704.0
GOF, *S*	1.118
R_1, wR_2 (obsd data)	0.0506, 0.1267
R_1, wR_2 (all data)	0.1501, 0.1821

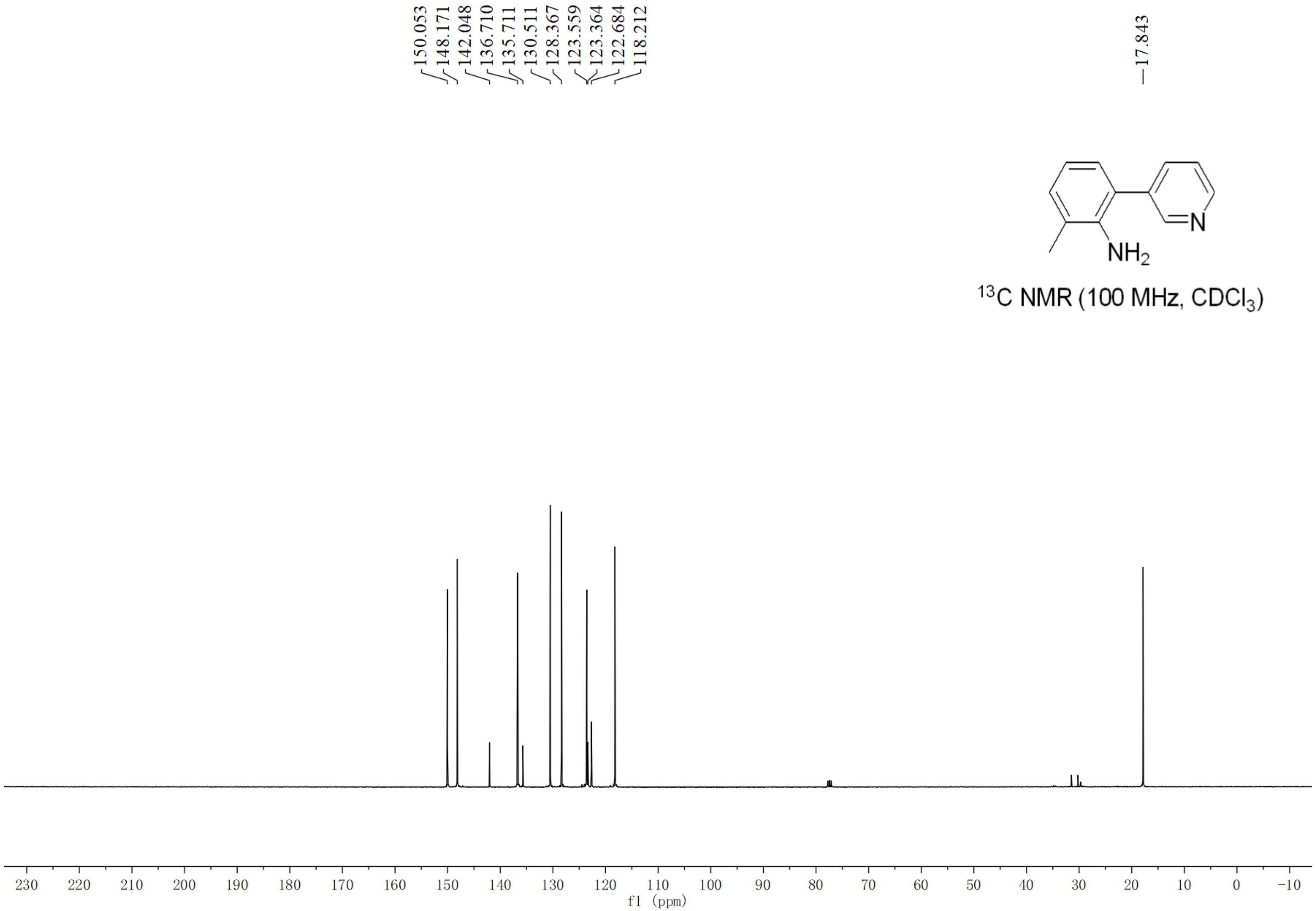
8. NMR Spectra of Substrates and Products



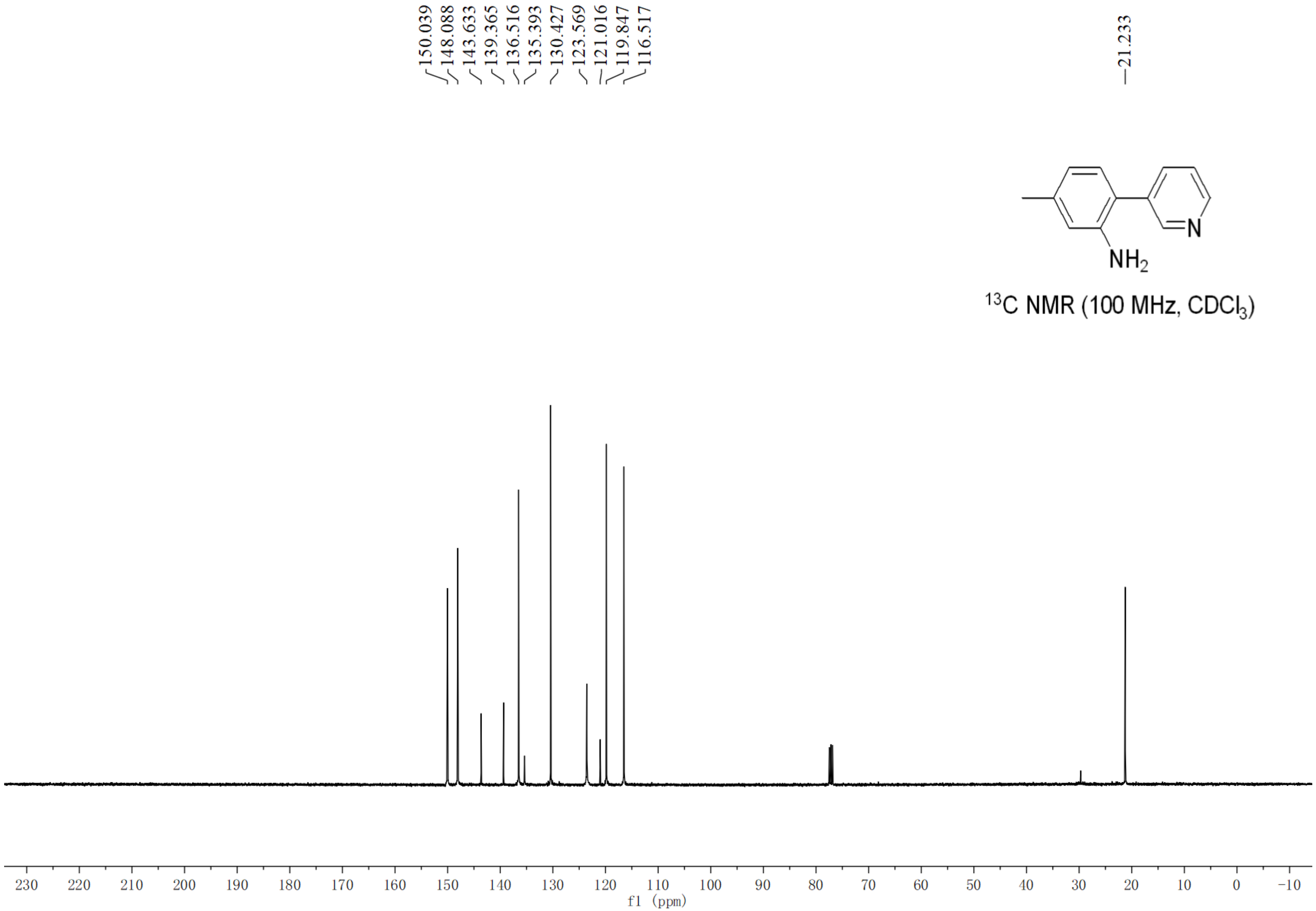

149.845
148.173
143.745
136.632
135.563
130.552
129.383
123.831
123.695
118.935
115.888
NH2
N
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



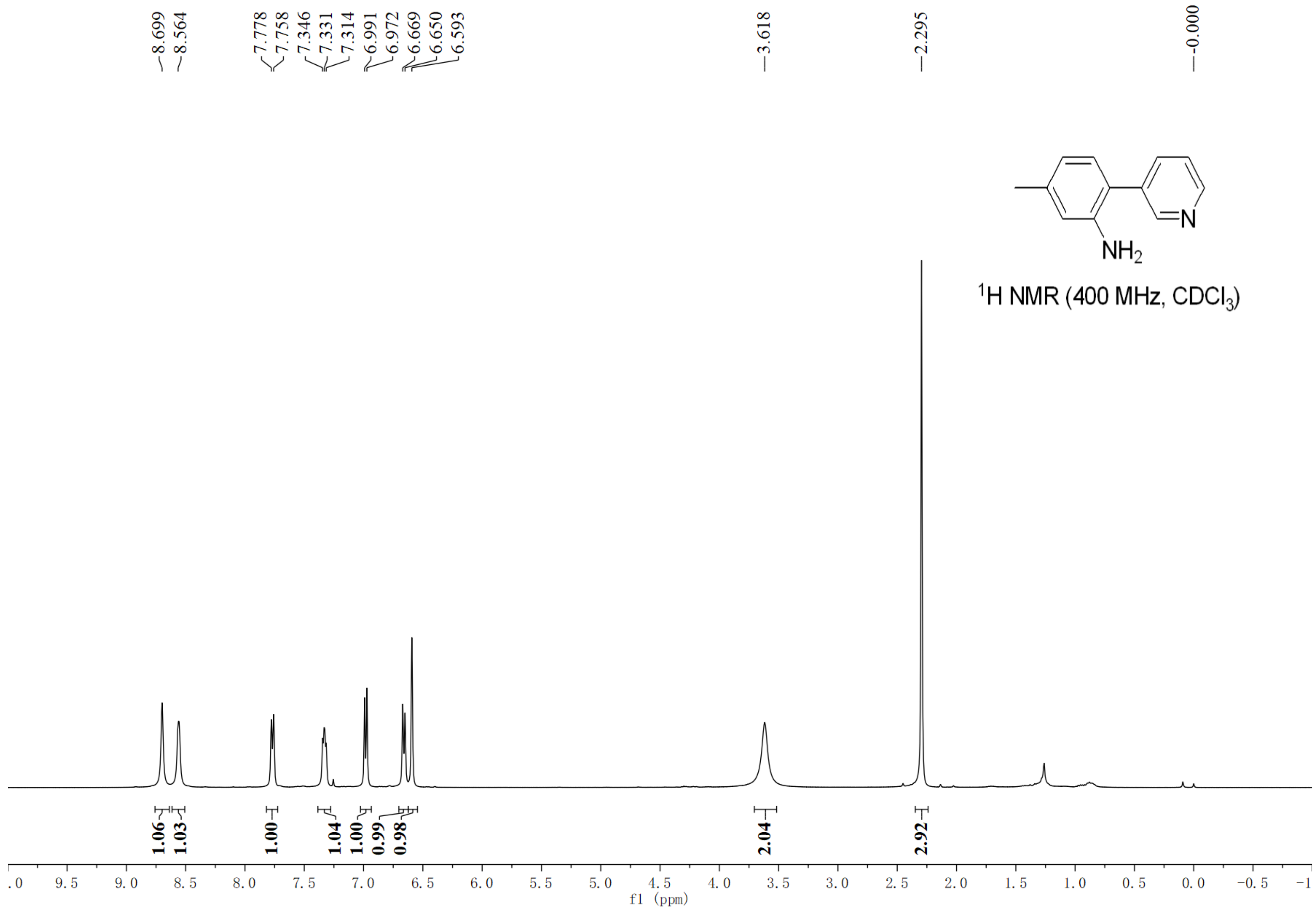
8.507
8.368
8.356
7.590
7.570
7.154
7.142
7.135
7.124
6.920
6.902
6.786
6.767
6.608
6.591
6.571
3.564
2.029
0.000
NH2
N
1H NMR (400 MHz, CDCl3)
1.01
1.02
0.99
1.01
0.98
1.00
1.00
2.14
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



^{13}C NMR (100 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)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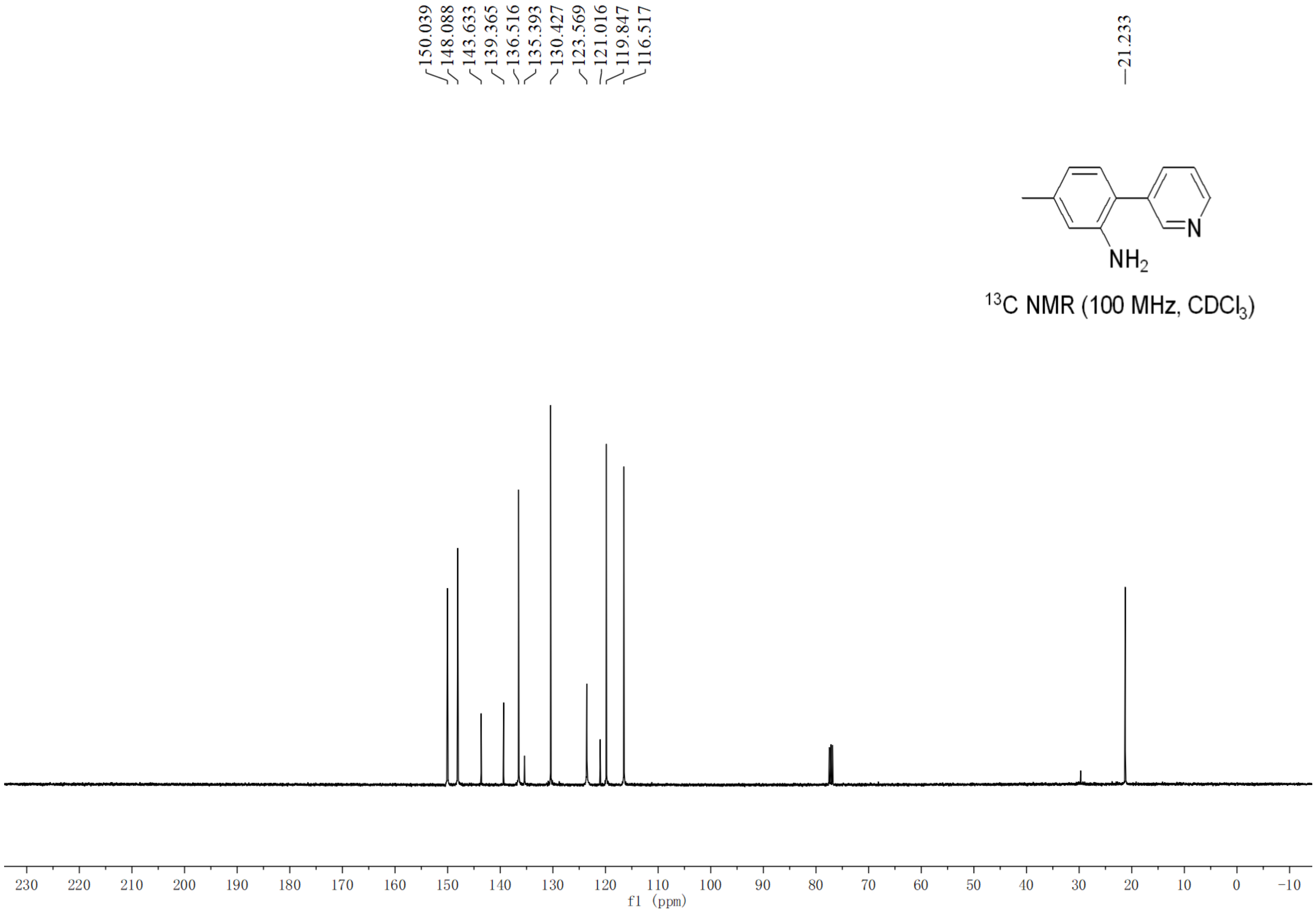
7.758
7.346
7.331
7.314
6.991
6.972
6.669
6.650
6.593
3.618
2.295
0.000
NH2
N
1H NMR (400 MHz, CDCl3)
1.06
1.03
1.00
1.04
1.00
0.99
0.98
2.04
2.92
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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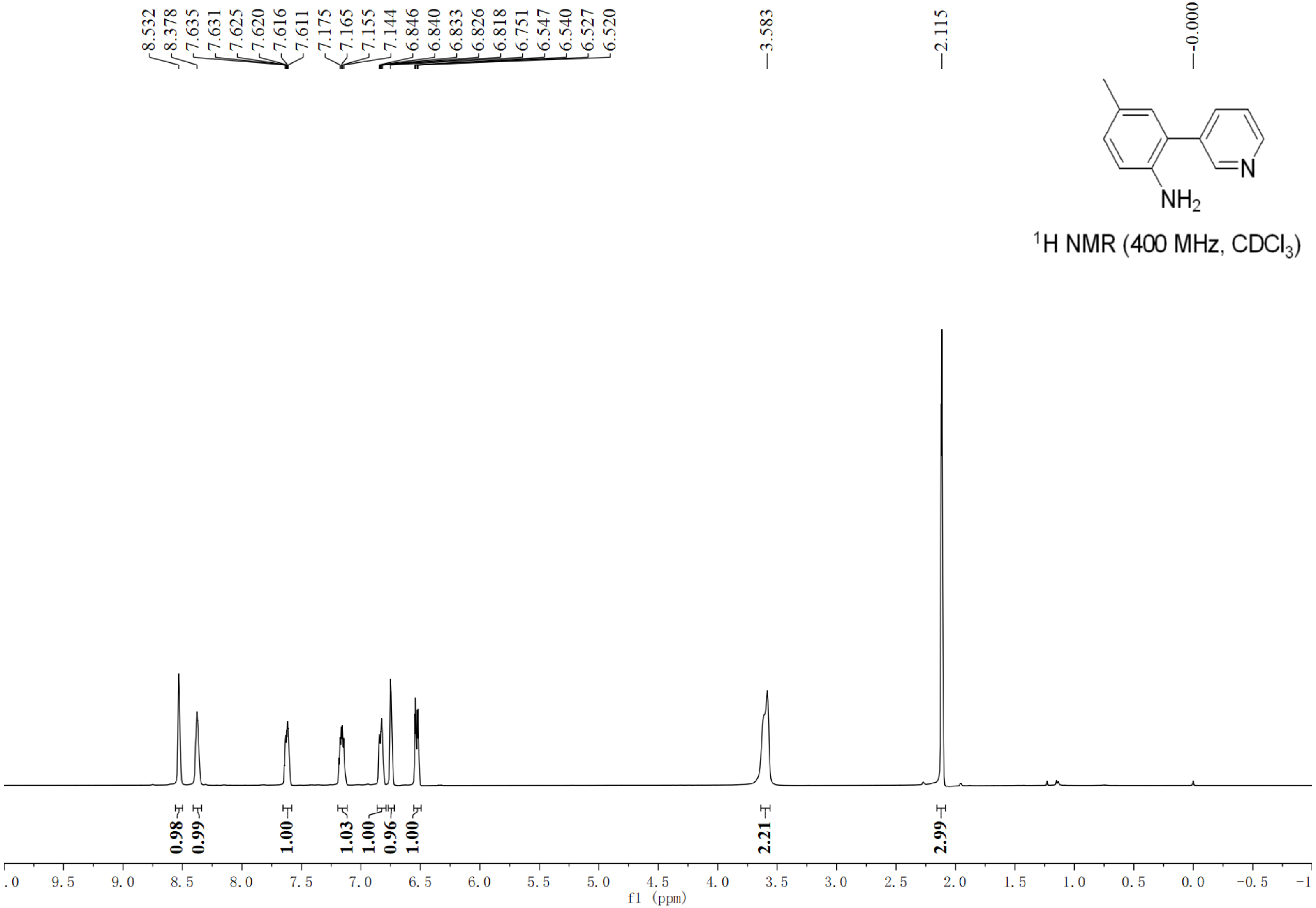
148.088
143.633
139.365
136.516
135.393
130.427
123.569
121.016
119.847
116.517
21.233
NH2
N
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.625
7.620
7.616
7.611
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7.165
7.155
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6.846
6.840
6.833
6.826
6.818
6.751
6.547
6.540
6.527
6.520
3.583
2.115
0.000
NH2
N
1H NMR (400 MHz, CDCl3)
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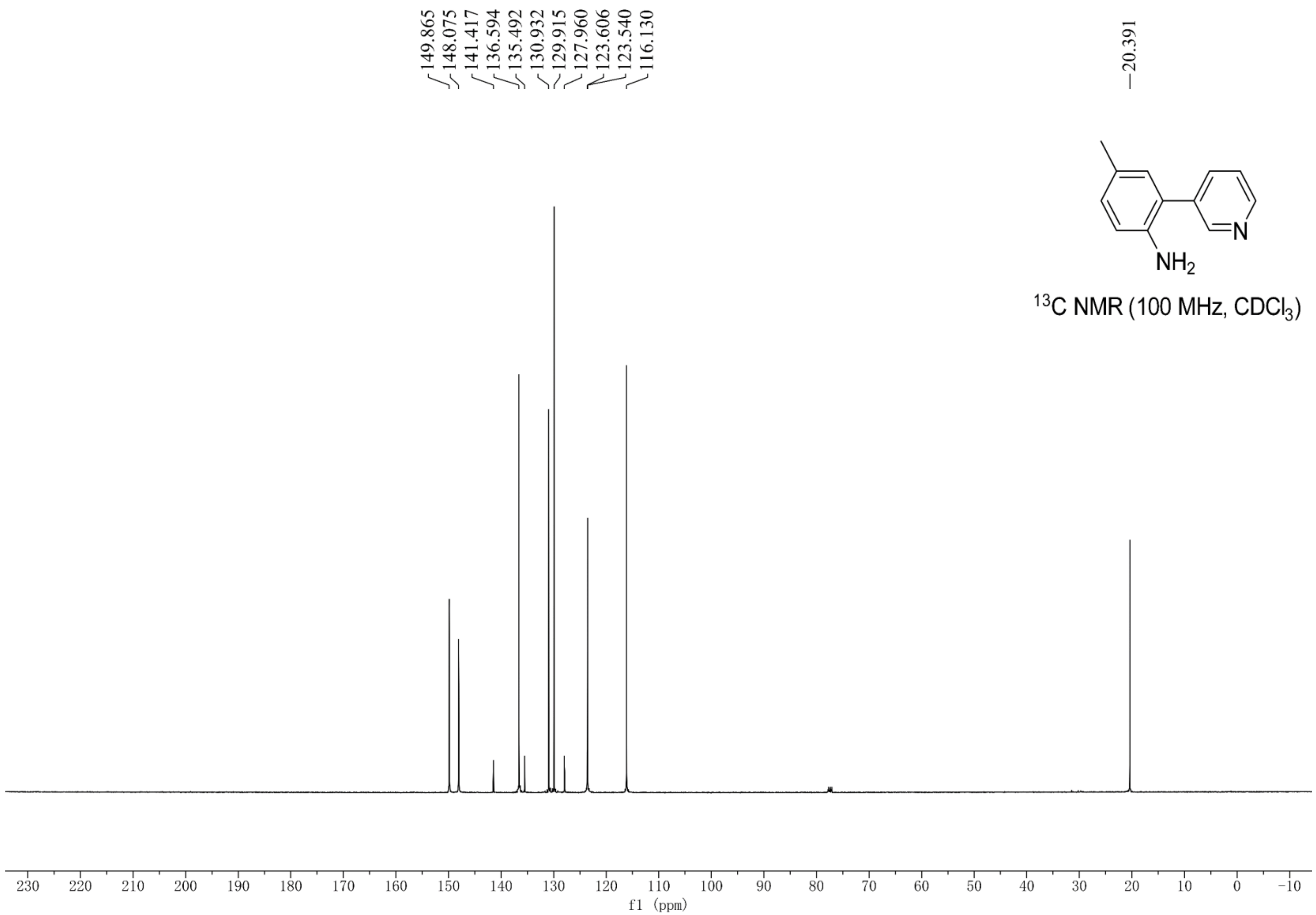
0.99
1.00
1.03
1.00
0.96
1.00
2.21
2.99
f1 (ppm)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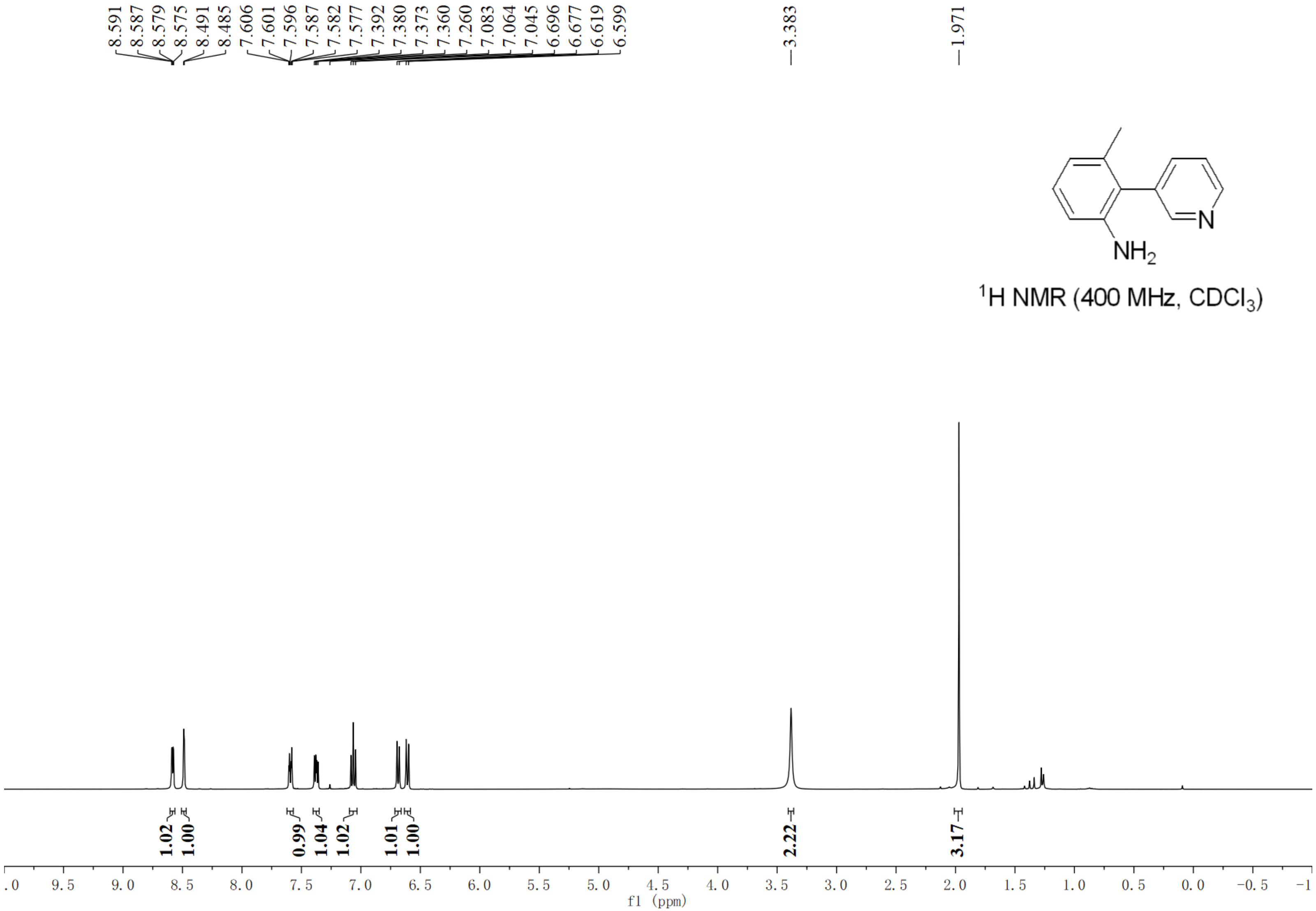
141.417
136.594
135.492
130.932
129.915
127.960
123.606
123.540
116.130
20.391
N
NH2
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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8.587
8.579
8.575
8.491
8.485
7.606
7.601
7.596
7.587
7.582
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7.392
7.380
7.373
7.360
7.260
7.083
7.064
7.045
6.696
6.677
6.619
6.599
3.383
1.971
NH2
N
1H NMR (400 MHz, CDCl3)
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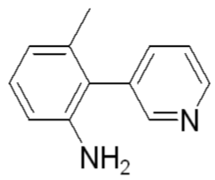
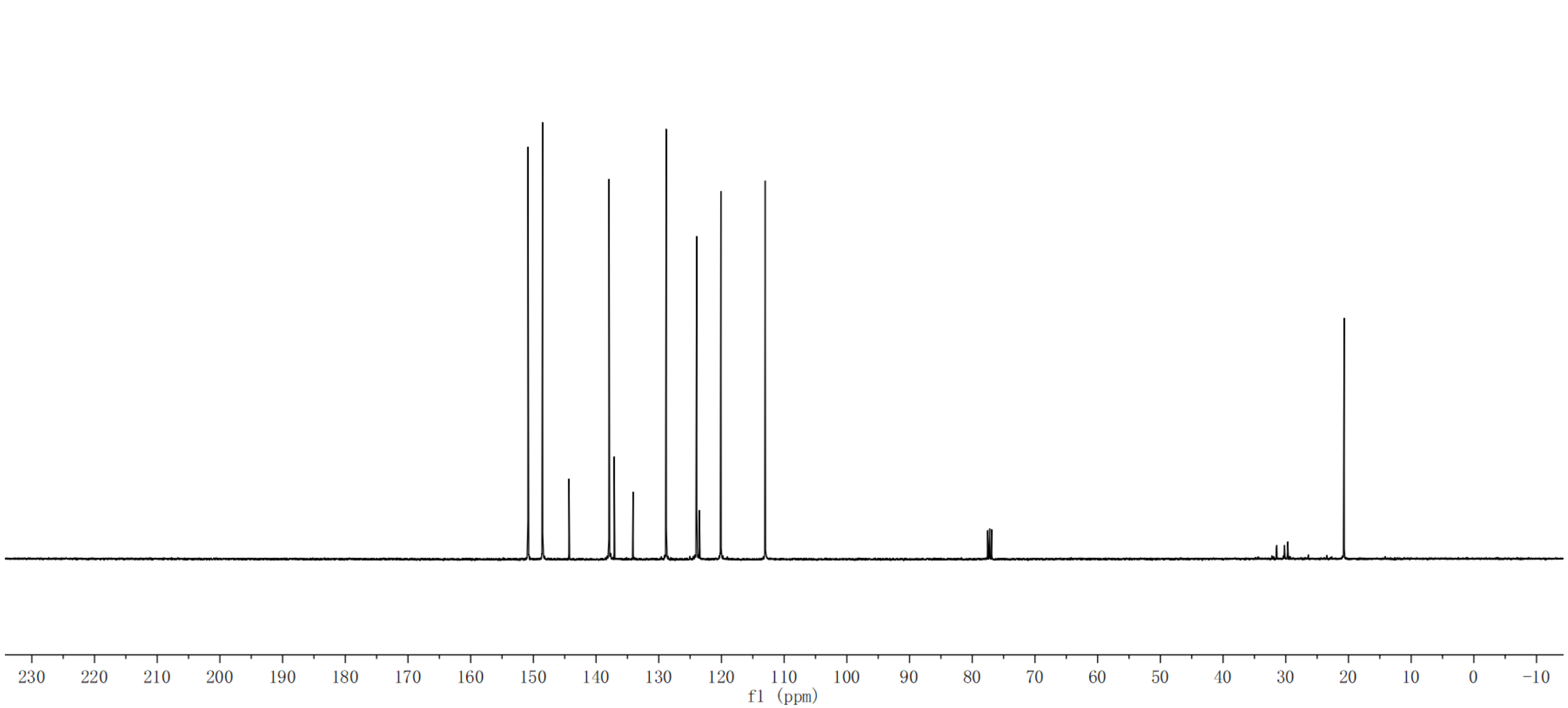
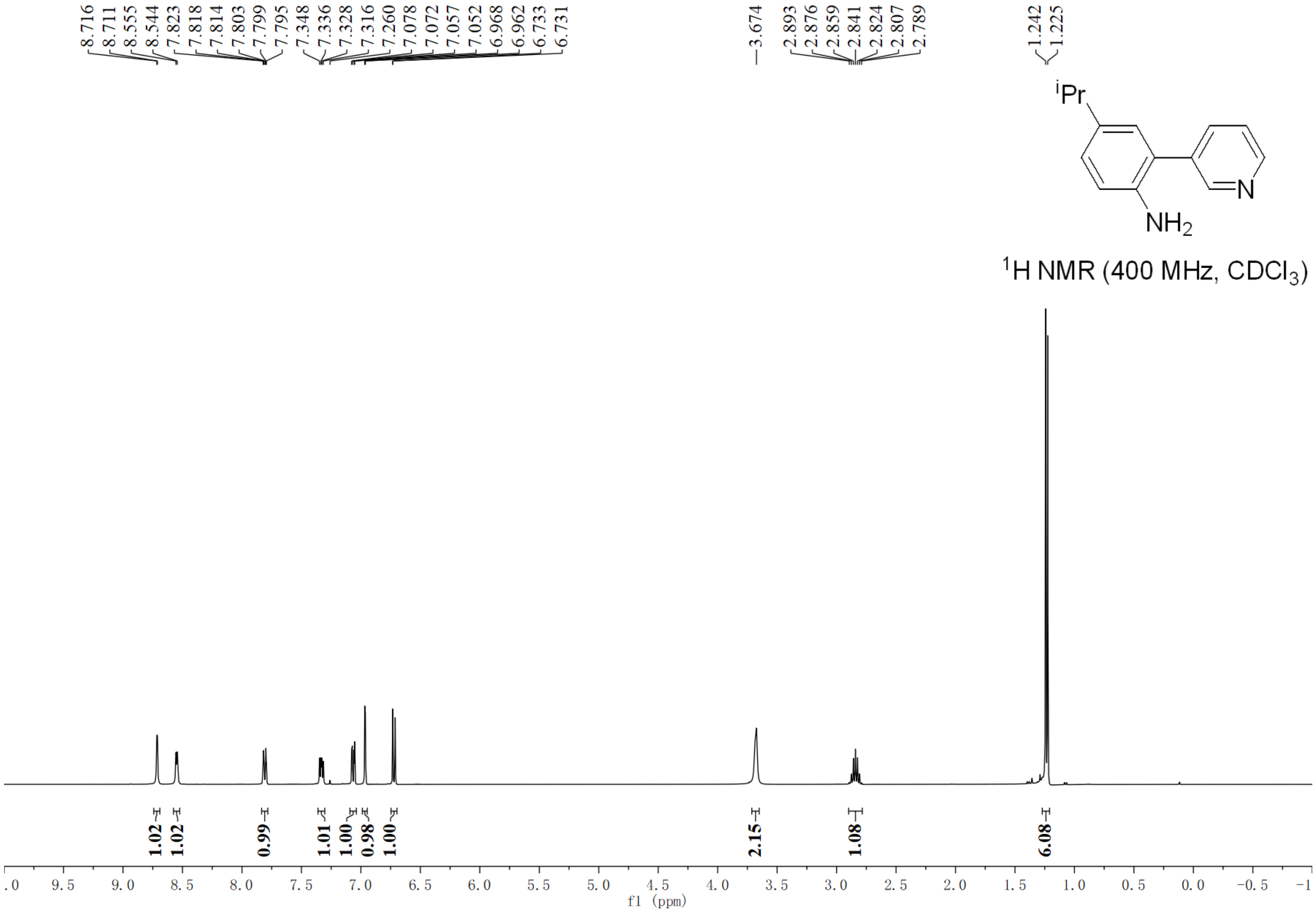
1.00
0.99
1.04
1.02
1.01
1.00
2.22
3.17
f1 (ppm)



^{13}C NMR (100 MHz, $CDCl_3$)

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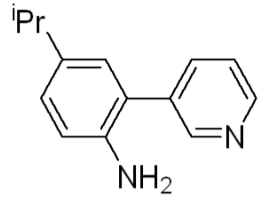
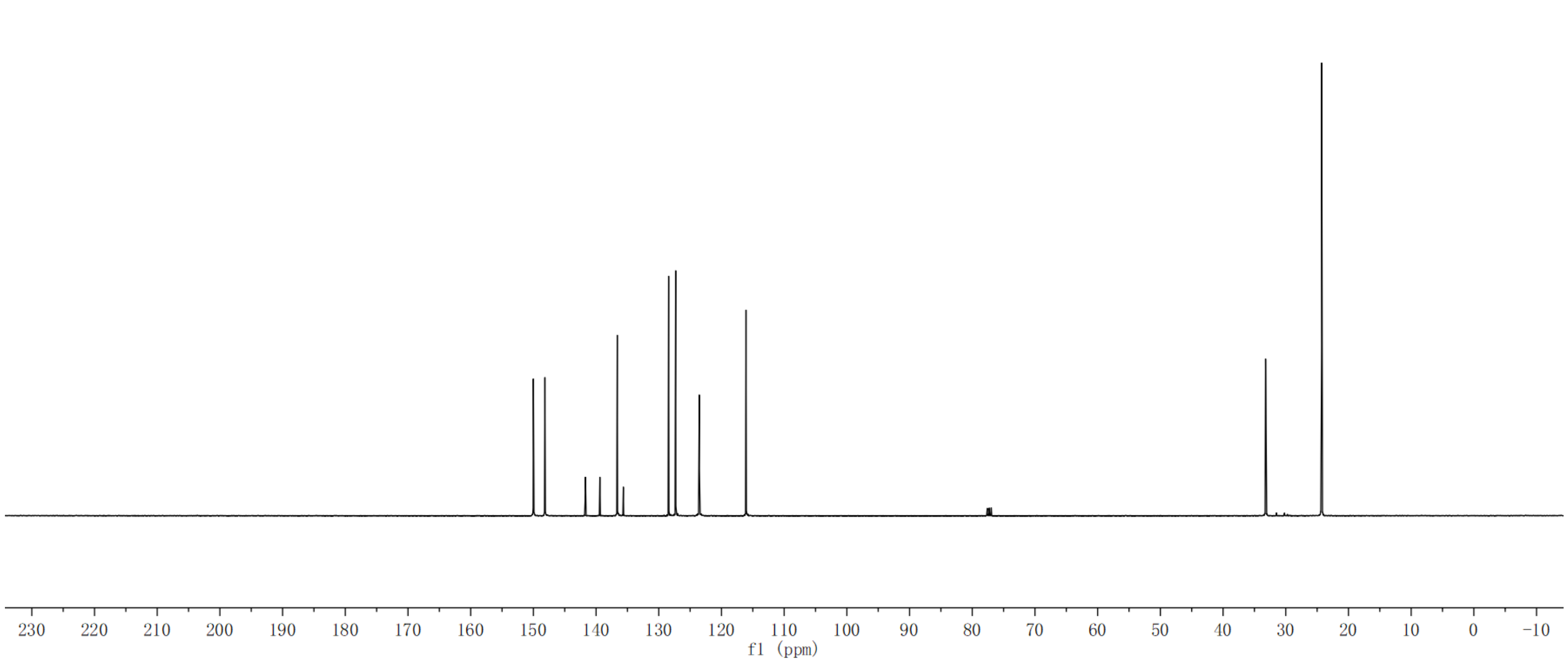
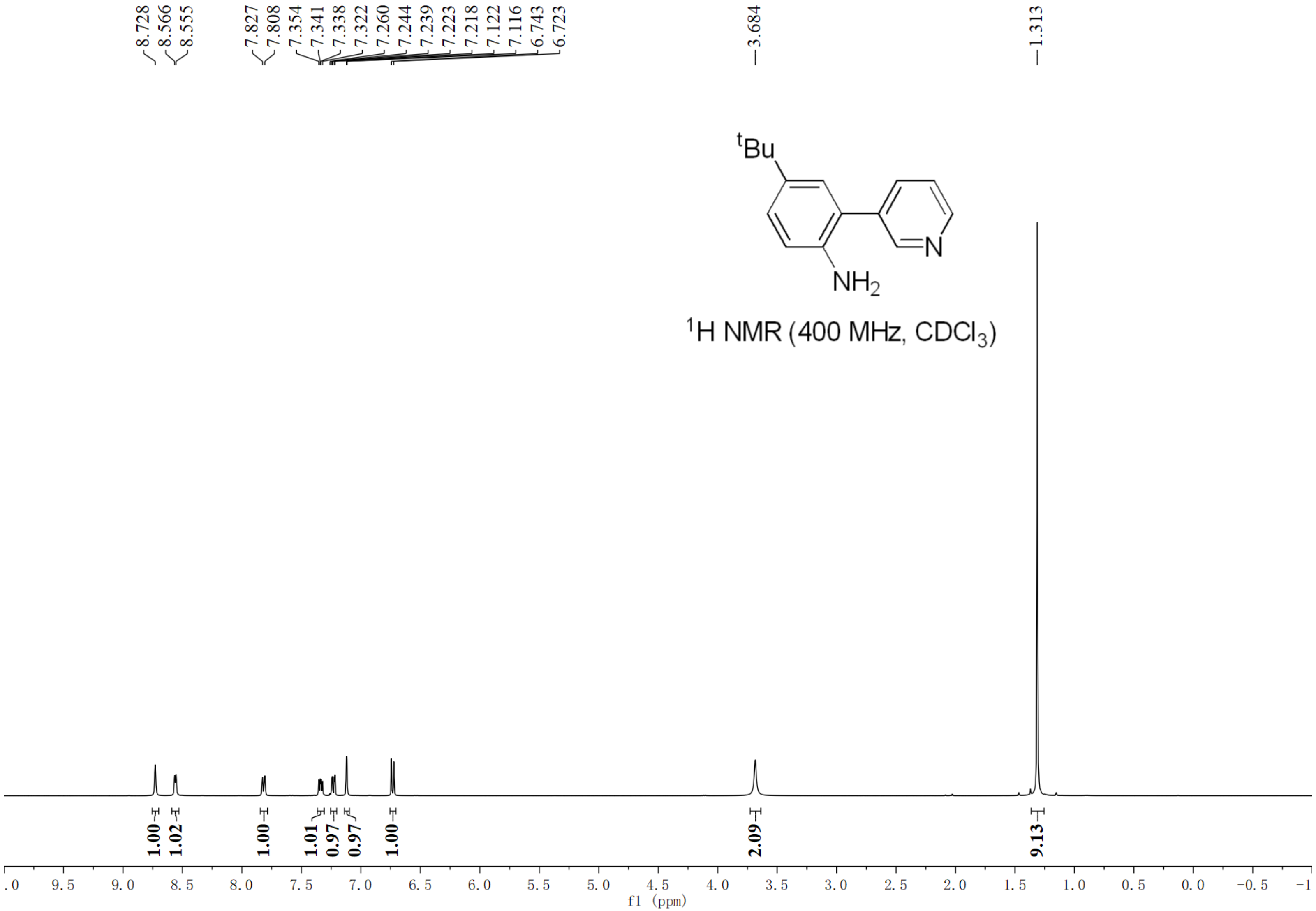
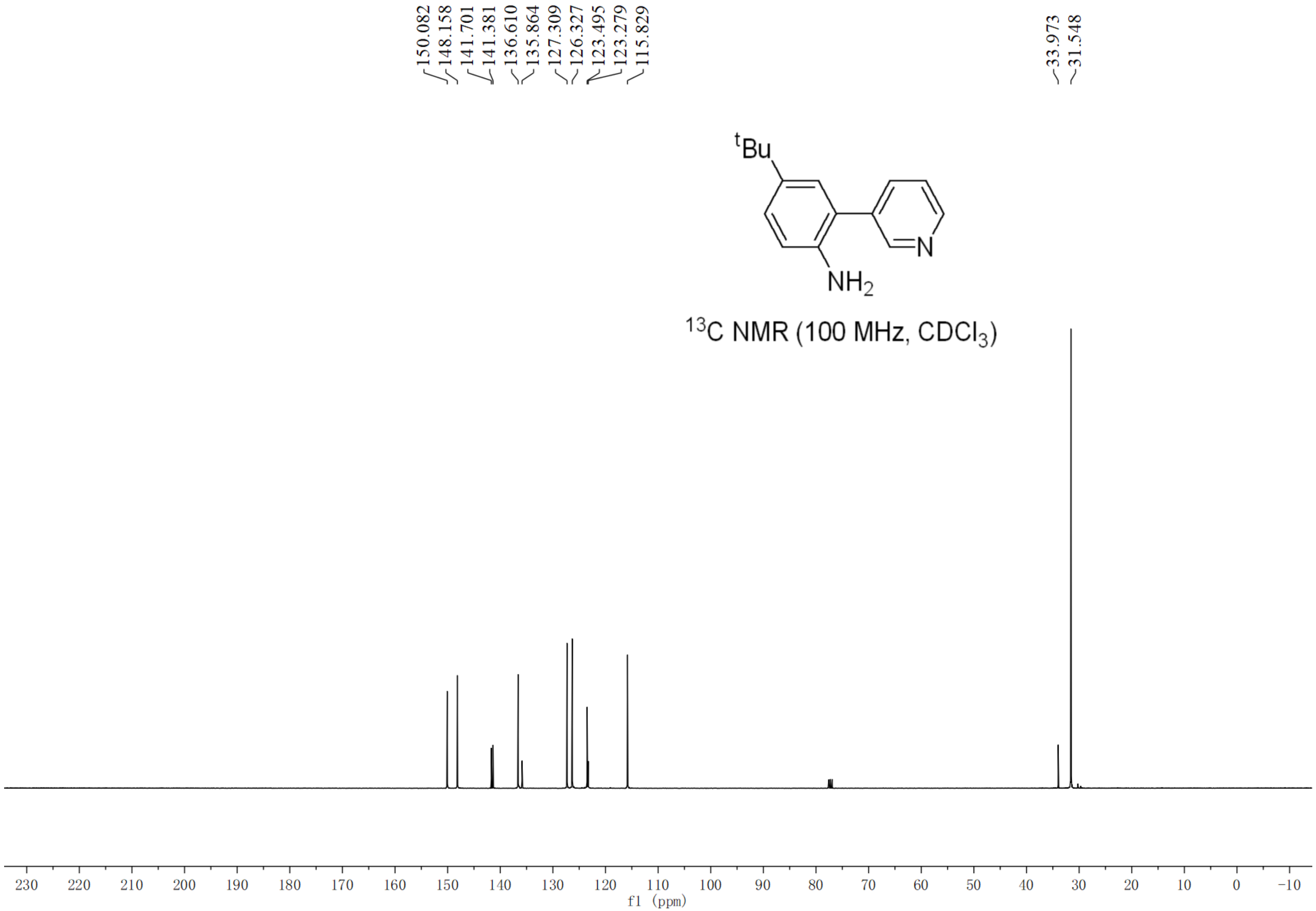
8.555
8.544
7.823
7.818
7.814
7.803
7.799
7.795
7.348
7.336
7.328
7.316
7.260
7.078
7.072
7.057
7.052
6.968
6.962
6.733
6.731
3.674
2.893
2.876
2.859
2.841
2.824
2.807
2.789
1.242
1.225
iPr
N
NH2
1H NMR (400 MHz, CDCl3)
1.02
1.02
0.99
1.01
1.00
0.98
1.00
2.15
1.08
6.08
f1 (ppm)

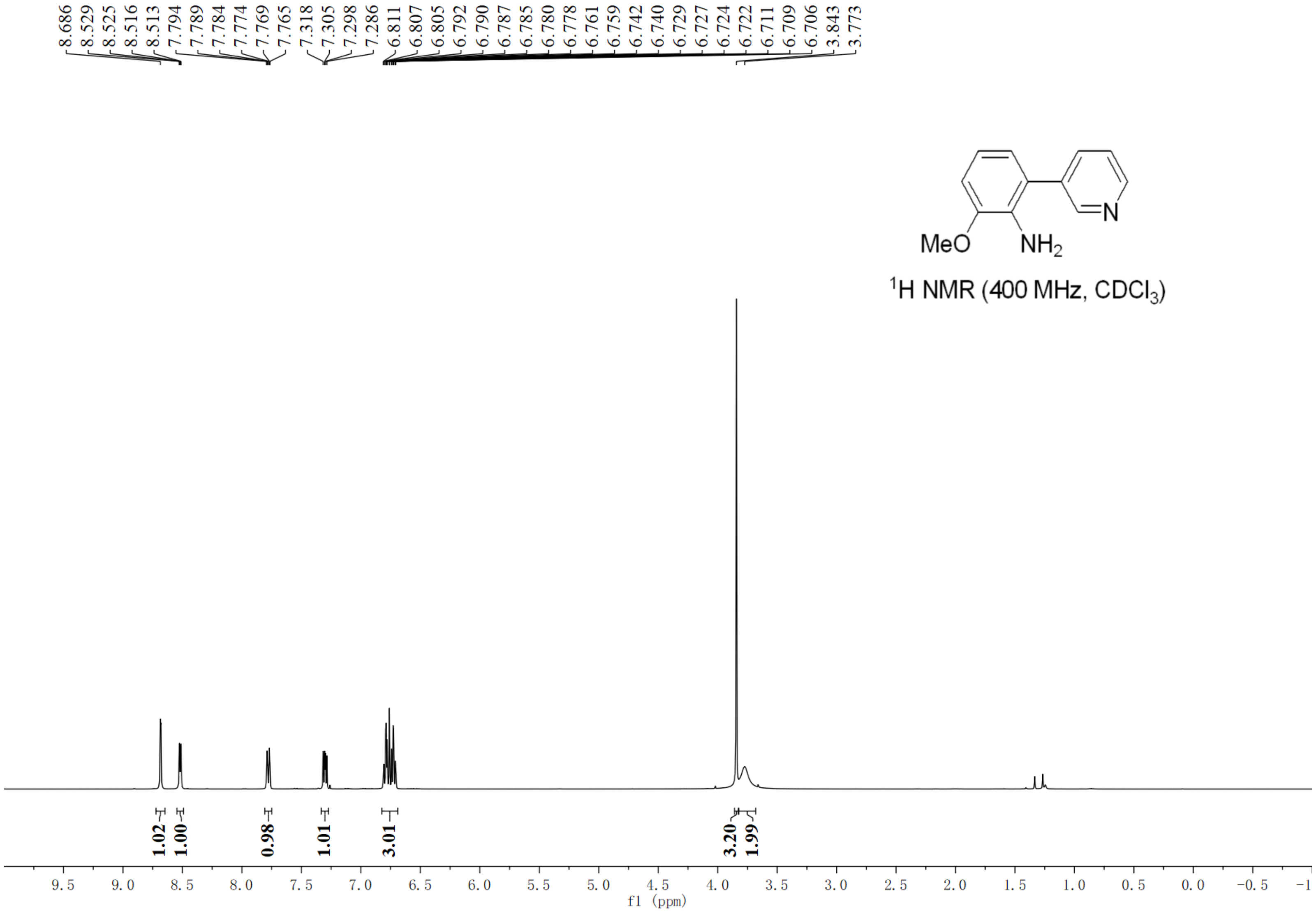


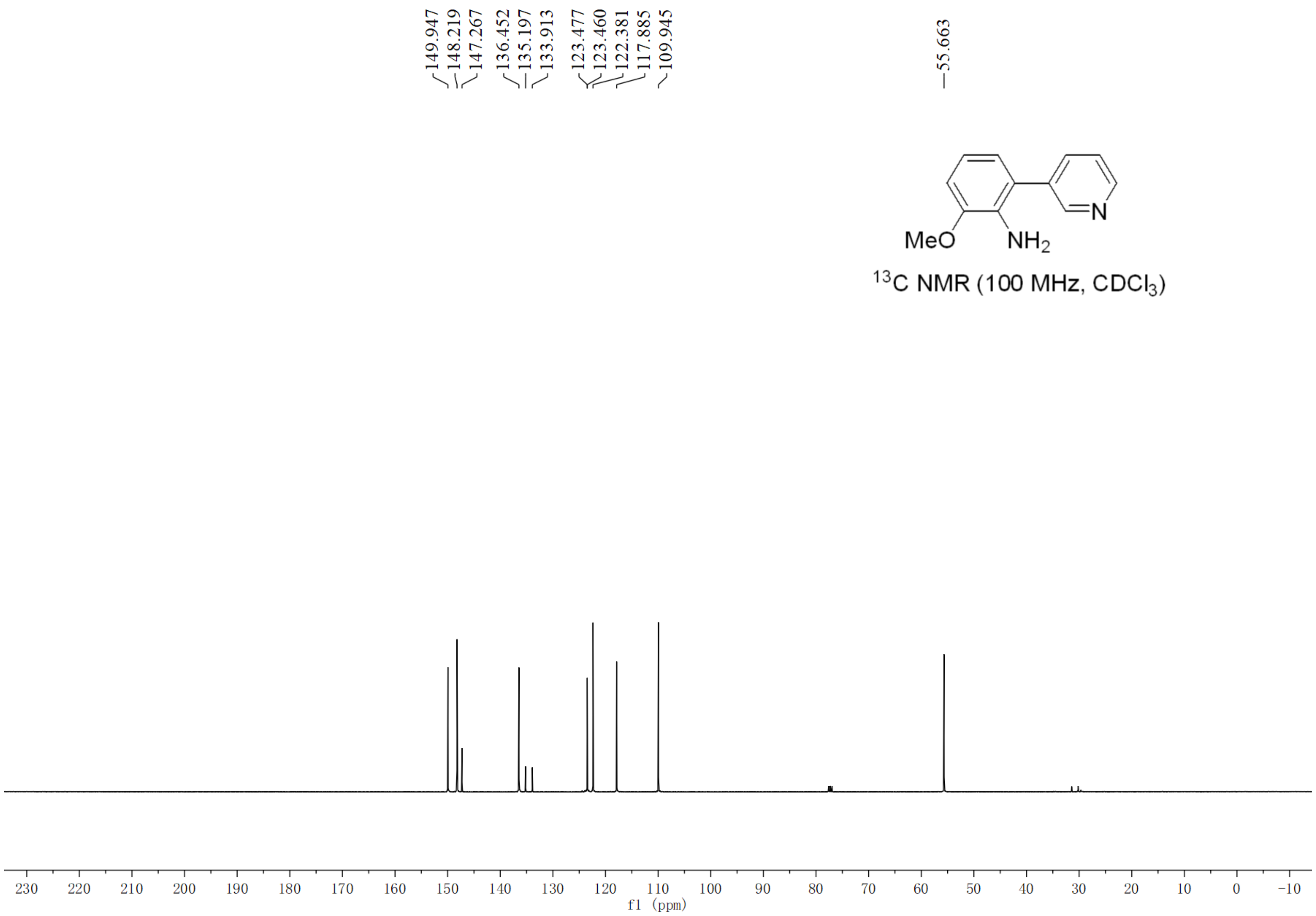
^{13}C NMR (100 MHz, $CDCl_3$)



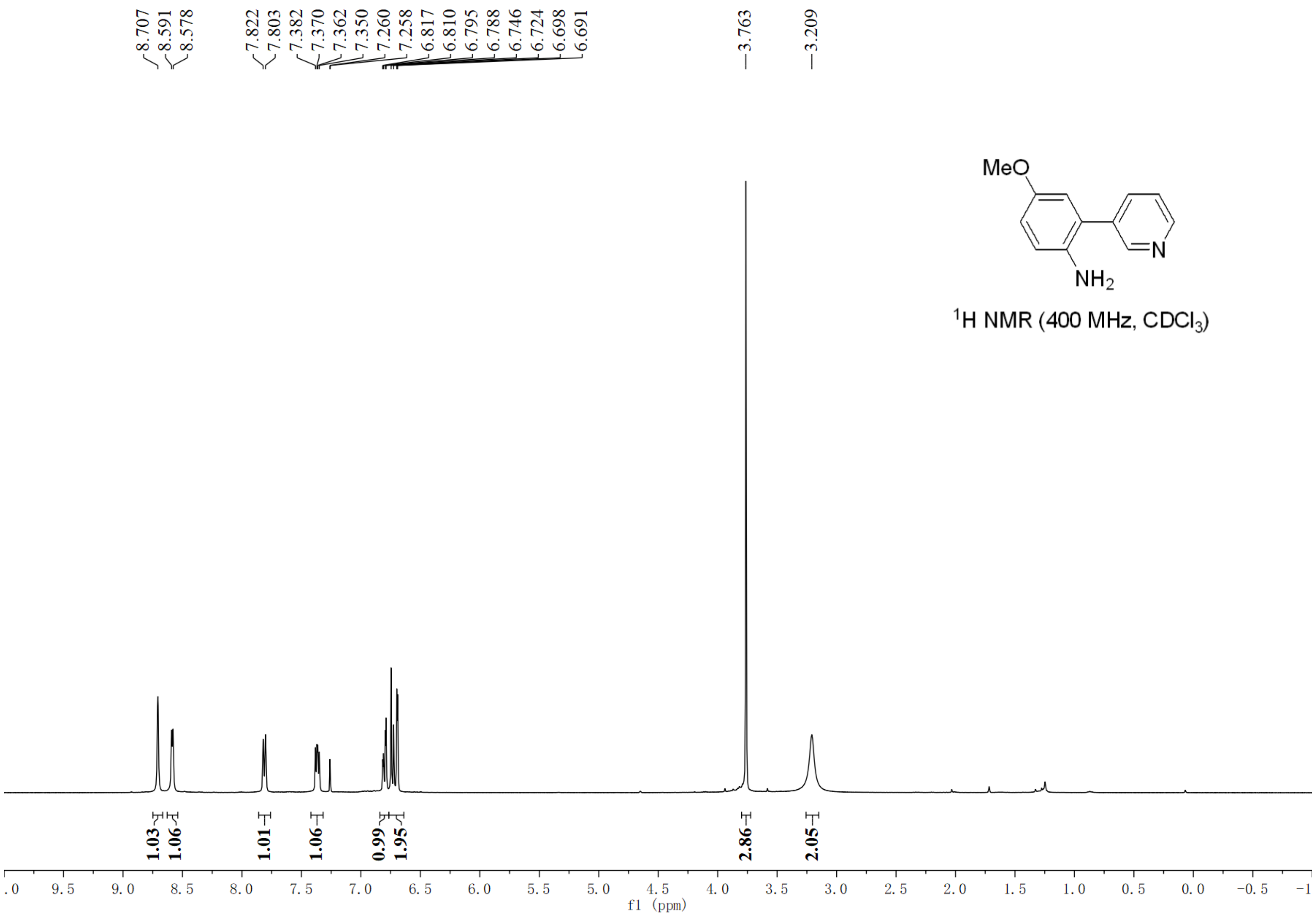

8.728
8.566
8.555
7.827
7.808
7.354
7.341
7.338
7.322
7.260
7.244
7.239
7.223
7.218
7.122
7.116
6.743
6.723
3.684
1.313
tBu
N
NH2
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.00
1.01
0.97
0.97
1.00
2.09
9.13
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


150.082
148.158
141.701
141.381
136.610
135.864
127.309
126.327
123.495
123.279
115.829
33.973
31.548
tBu
N
NH2
13C NMR (100 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

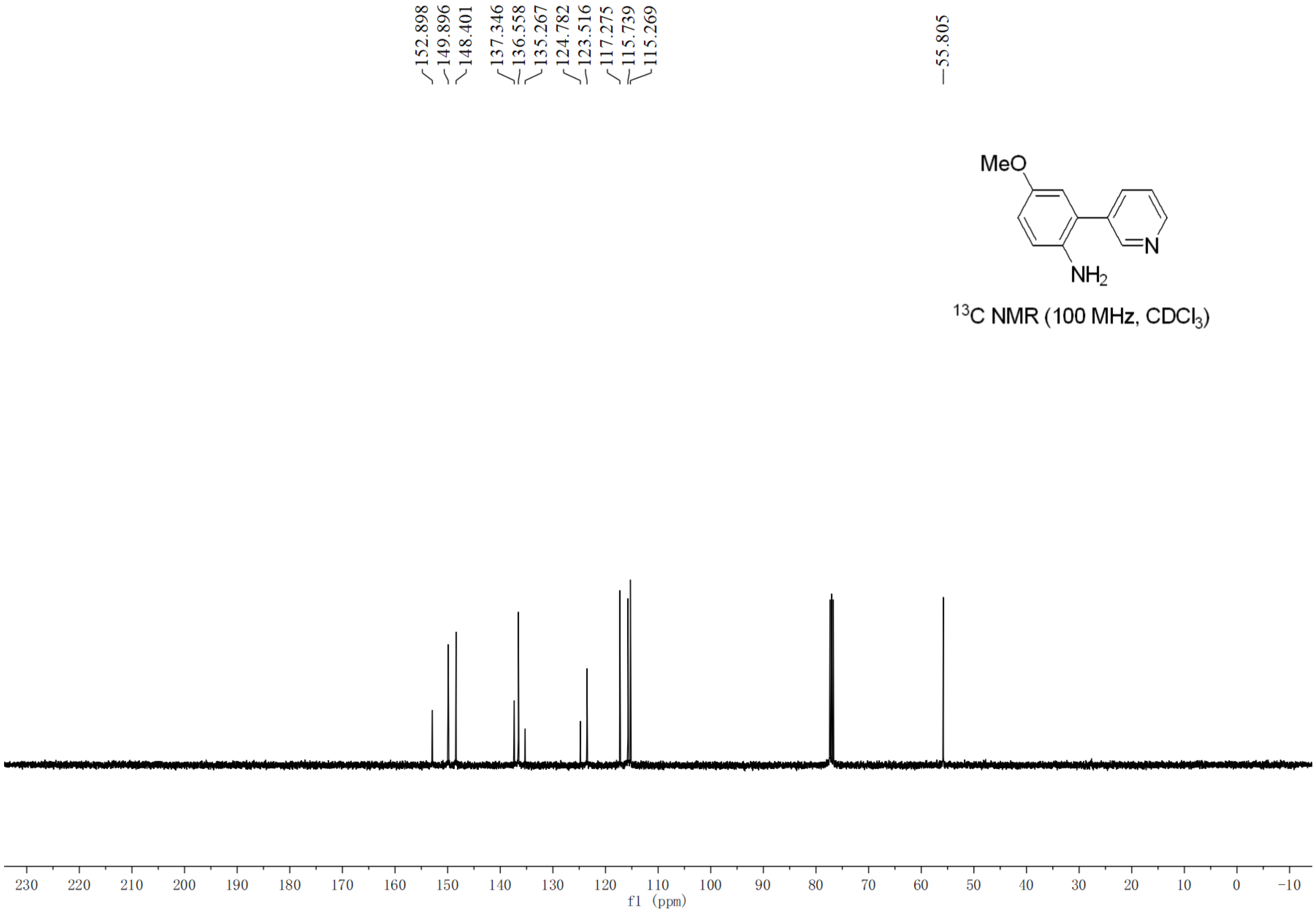

8.686
8.529
8.525
8.516
8.513
7.794
7.789
7.784
7.774
7.769
7.765
7.318
7.305
7.298
7.286
6.811
6.807
6.805
6.792
6.790
6.787
6.785
6.780
6.778
6.761
6.759
6.742
6.740
6.729
6.727
6.724
6.722
6.711
6.709
6.706
3.843
3.773
MeO
NH2
N
1H NMR (400 MHz, CDCl3)
1.02
1.00
0.98
1.01
3.01
3.20
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



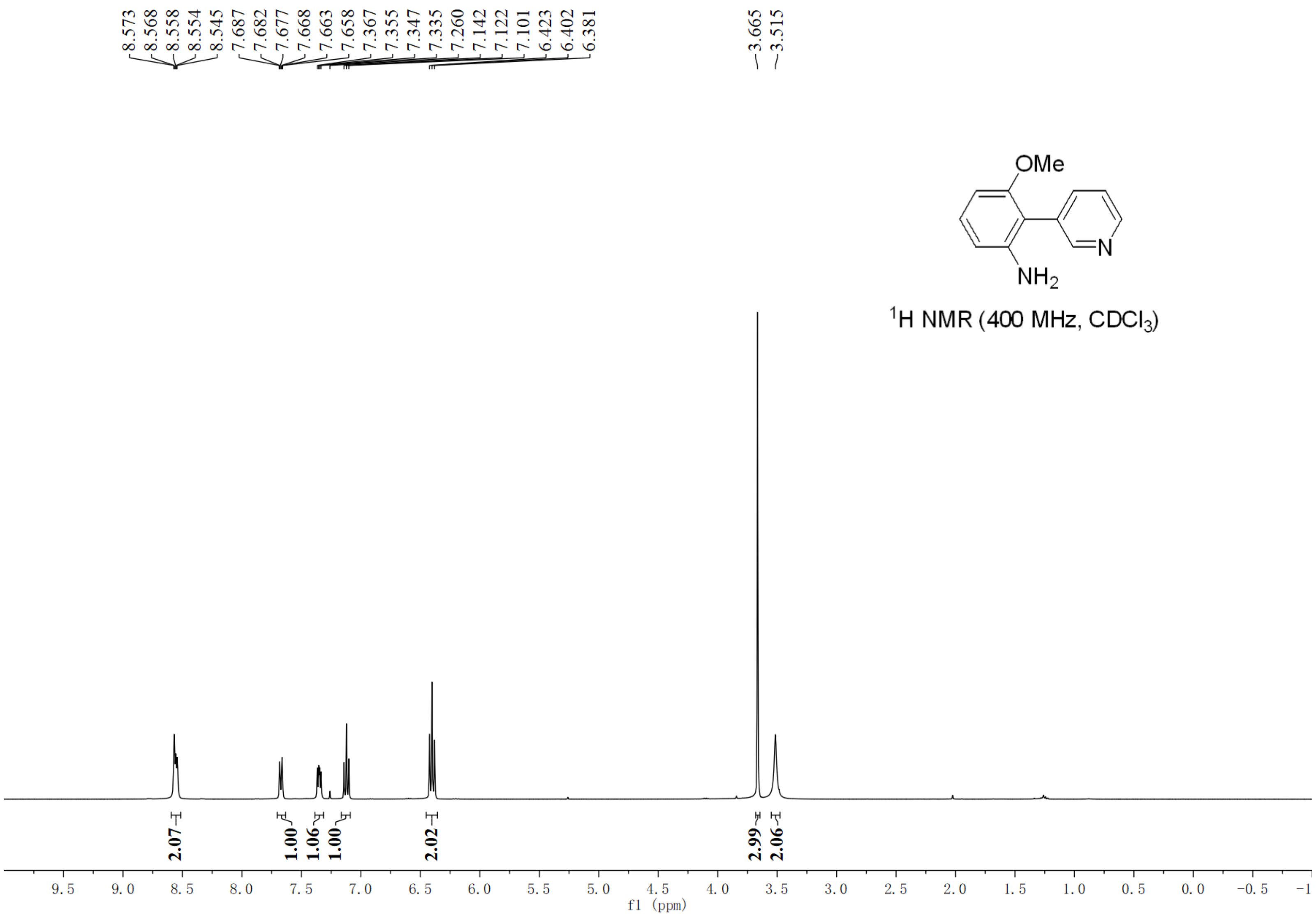
149.947
148.219
147.267
136.452
135.197
133.913
123.477
123.460
122.381
117.885
109.945
55.663
MeO
NH2
N
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



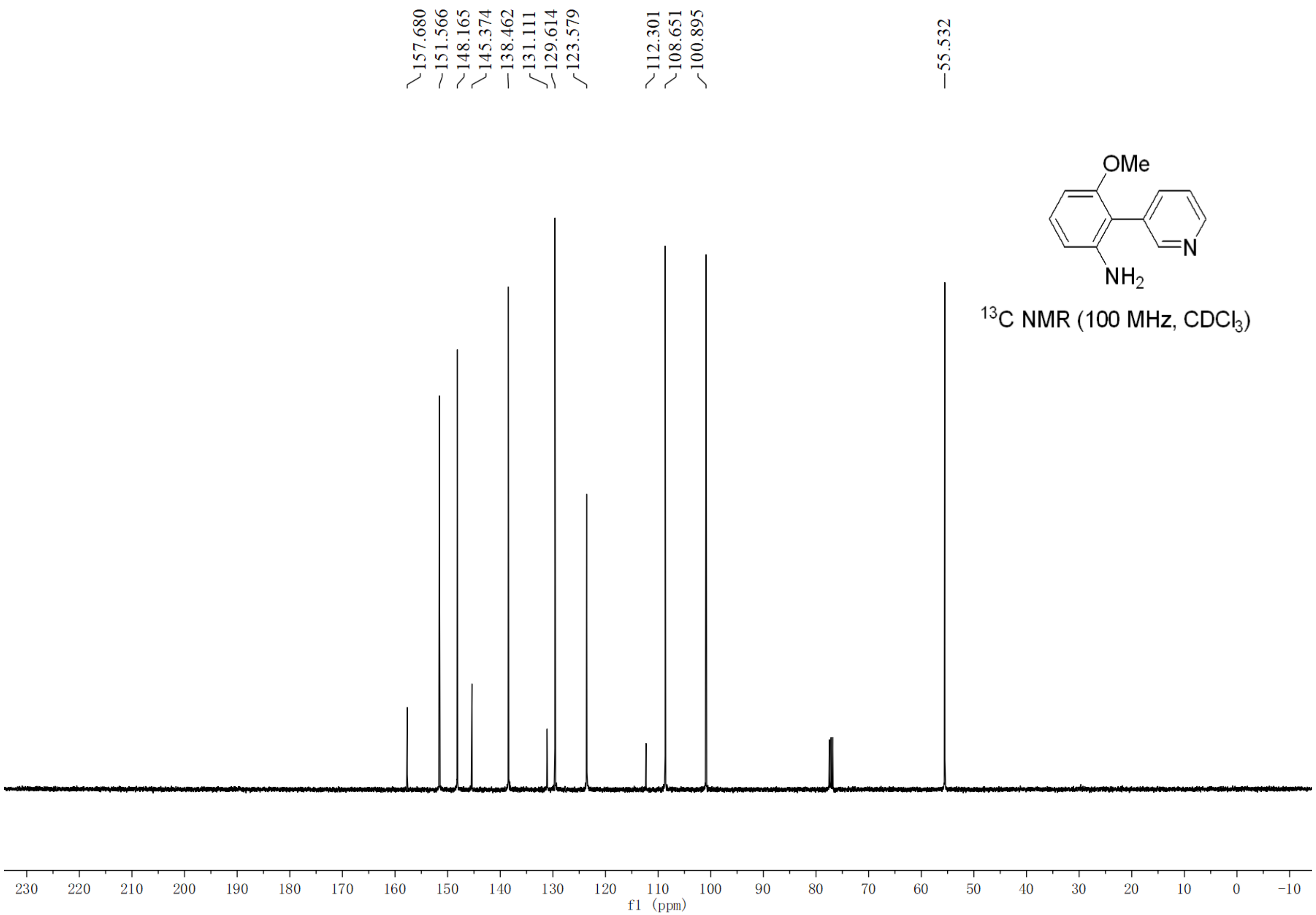
8.707
8.591
8.578
7.822
7.803
7.382
7.370
7.362
7.350
7.260
7.258
6.817
6.810
6.795
6.788
6.746
6.724
6.698
6.691
3.763
3.209
MeO
N
NH_2
^{1}H NMR (400 MHz, $CDCl_3$)
1.03
1.06
1.01
1.06
0.99
1.95
2.86
2.05
f1 (ppm)

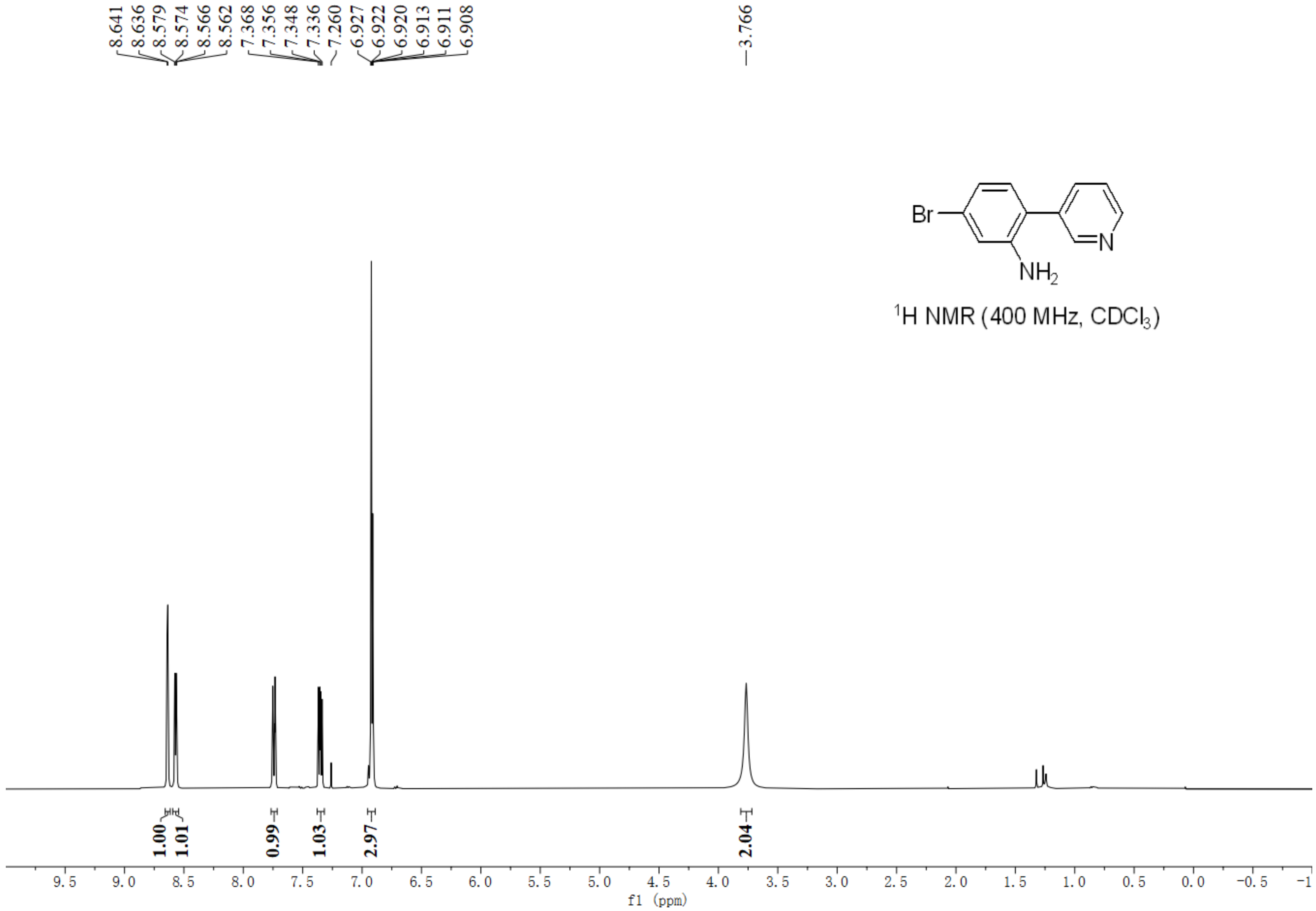


^{13}C NMR (100 MHz, $CDCl_3$)

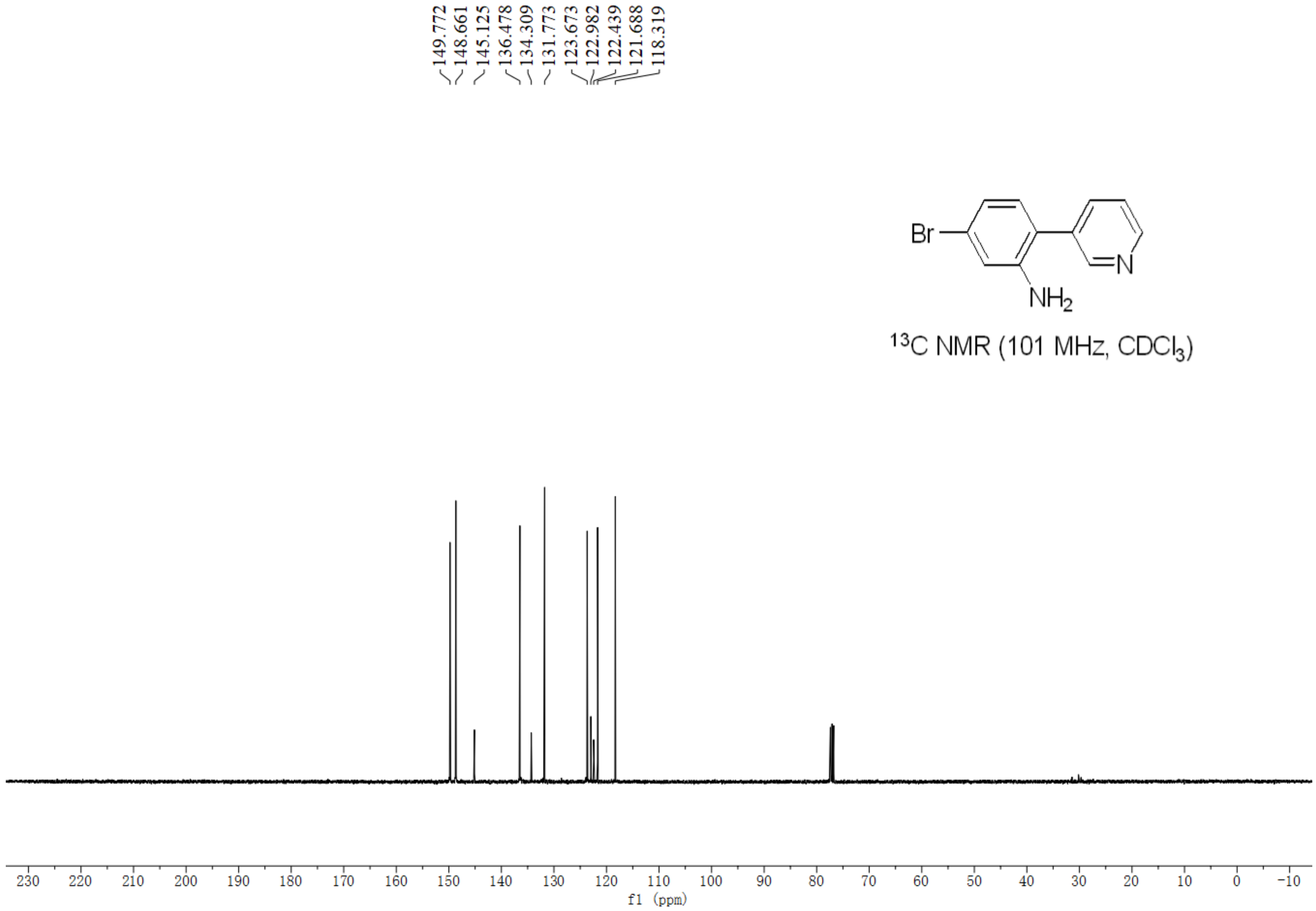


8.573
8.568
8.558
8.554
8.545
7.687
7.682
7.677
7.668
7.663
7.658
7.367
7.355
7.347
7.335
7.260
7.142
7.122
7.101
6.423
6.402
6.381
3.665
3.515
OMe
N
NH2
1H NMR (400 MHz, CDCl3)
2.07
1.00
1.06
1.00
2.02
2.99
2.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

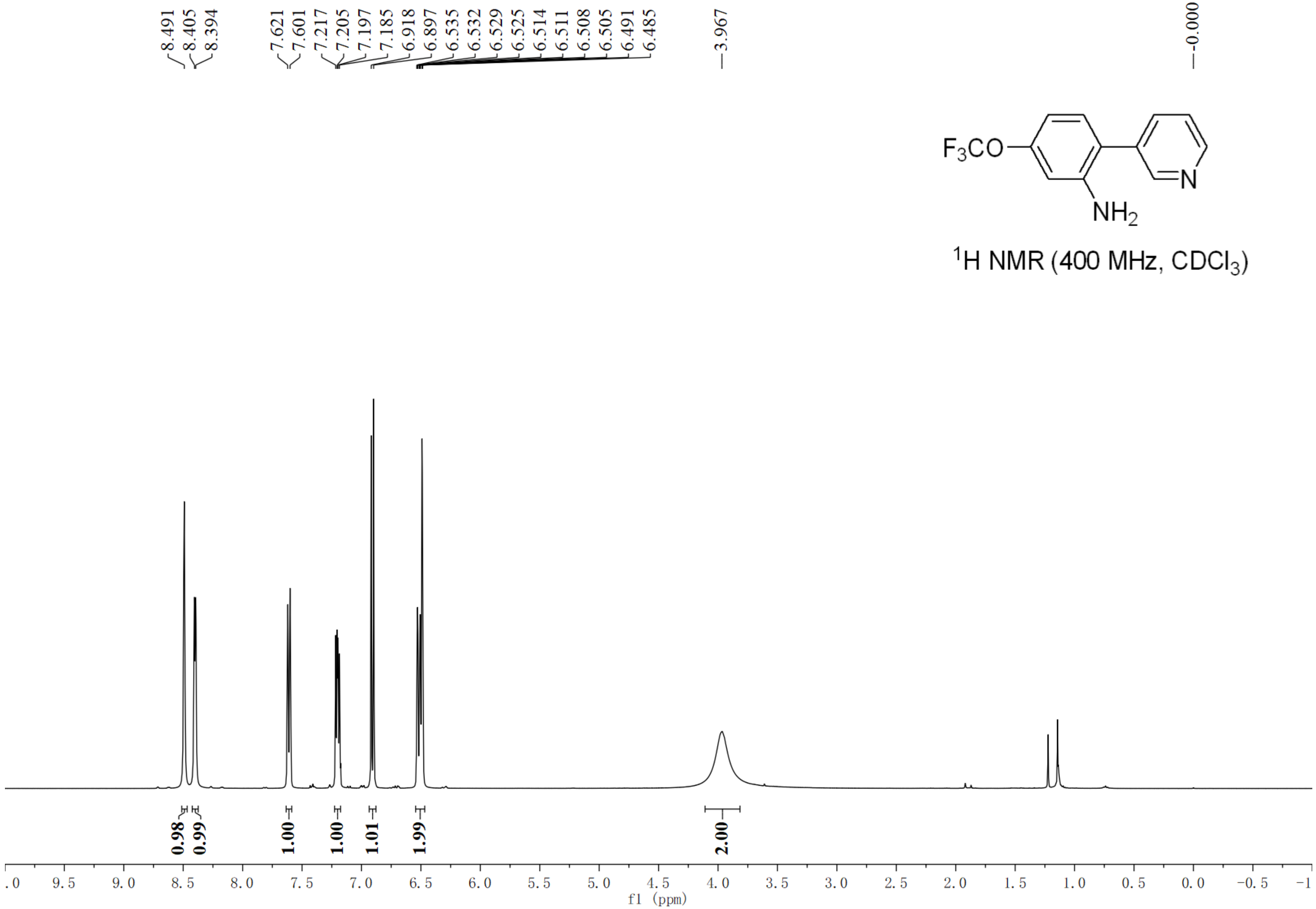

157.680
151.566
148.165
145.374
138.462
131.111
129.614
123.579
112.301
108.651
100.895
55.532
OMe
N
NH2
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



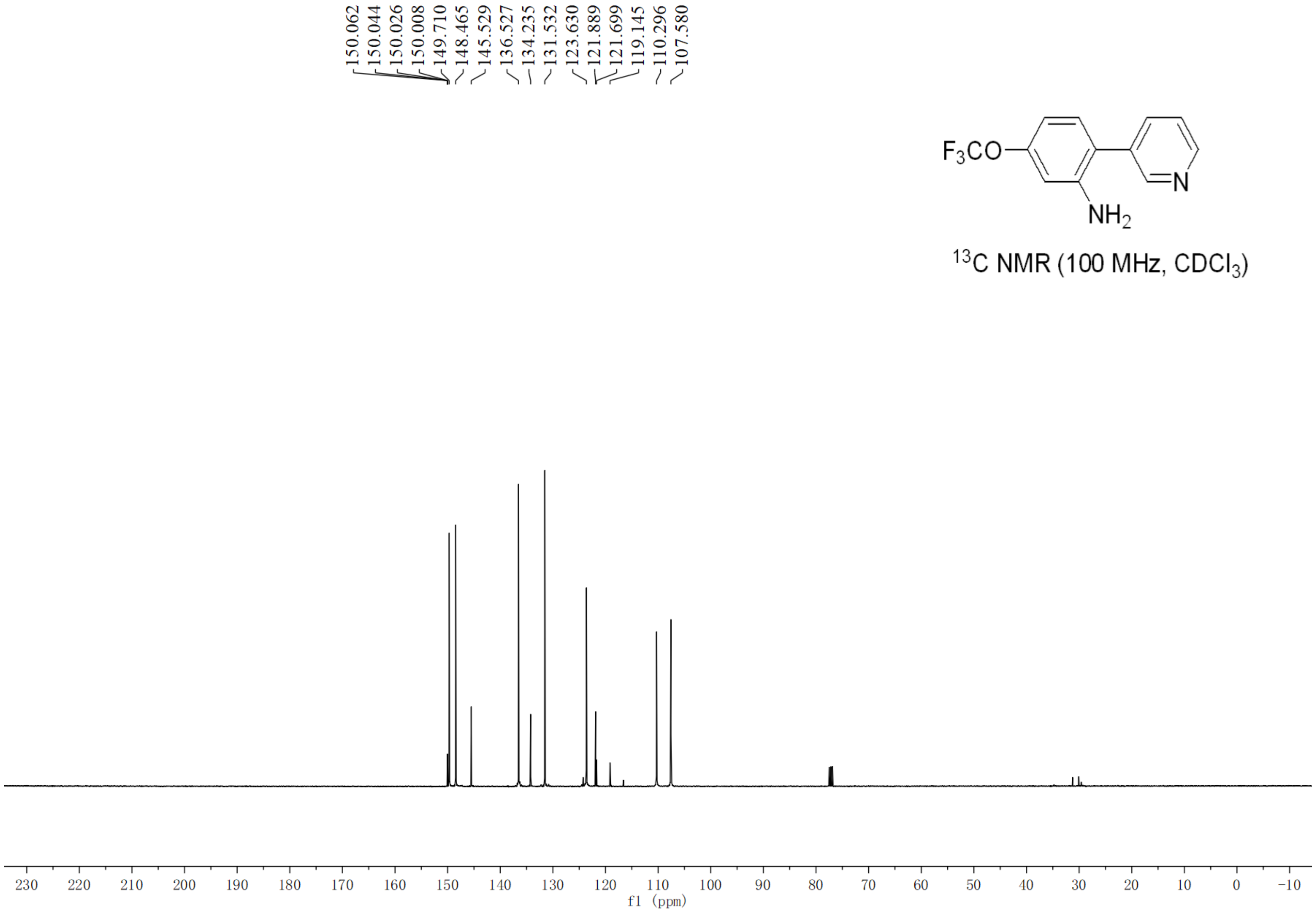
^{1}H NMR (400 MHz, $CDCl_3$)



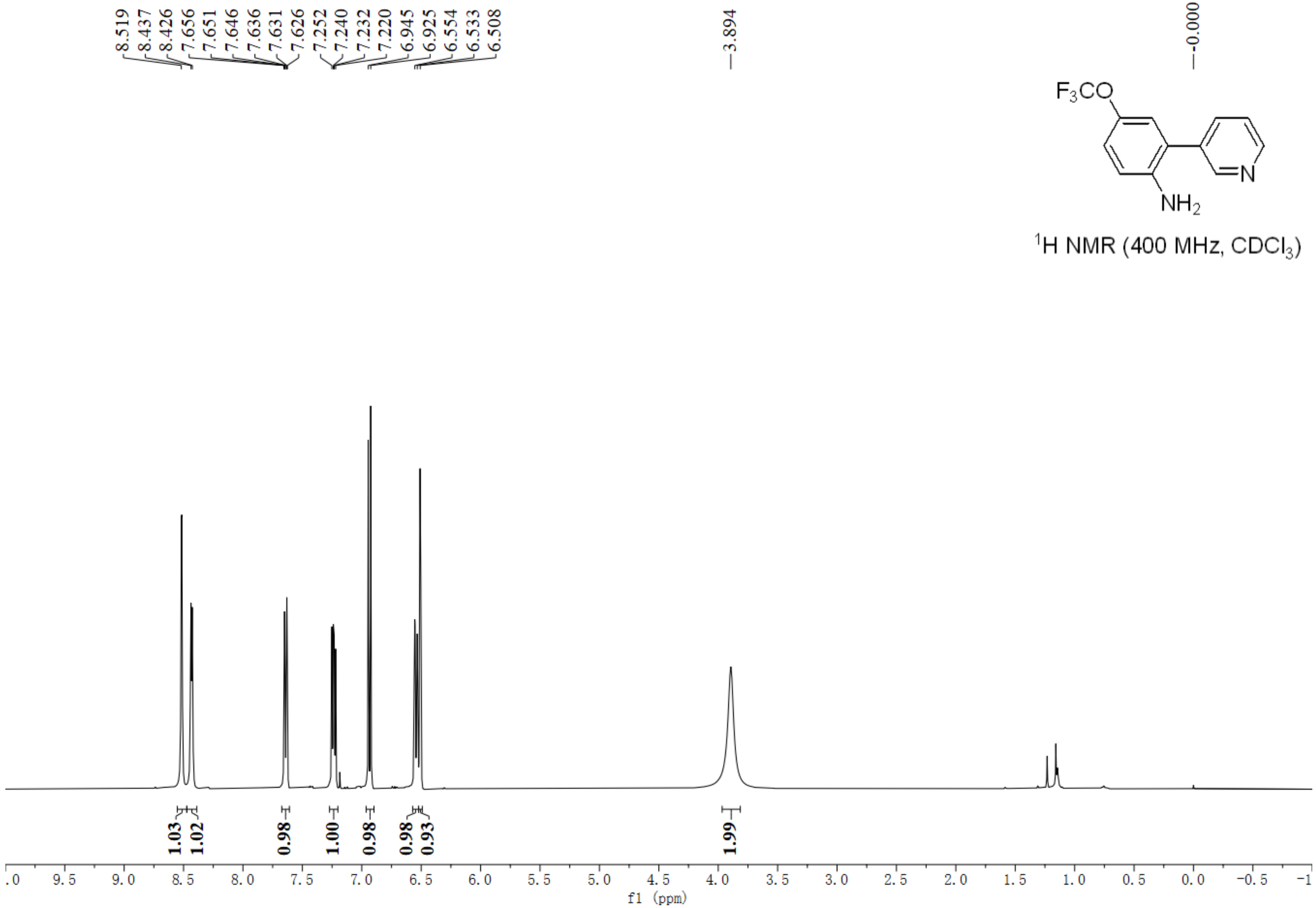
^{13}C NMR (101 MHz, $CDCl_3$)



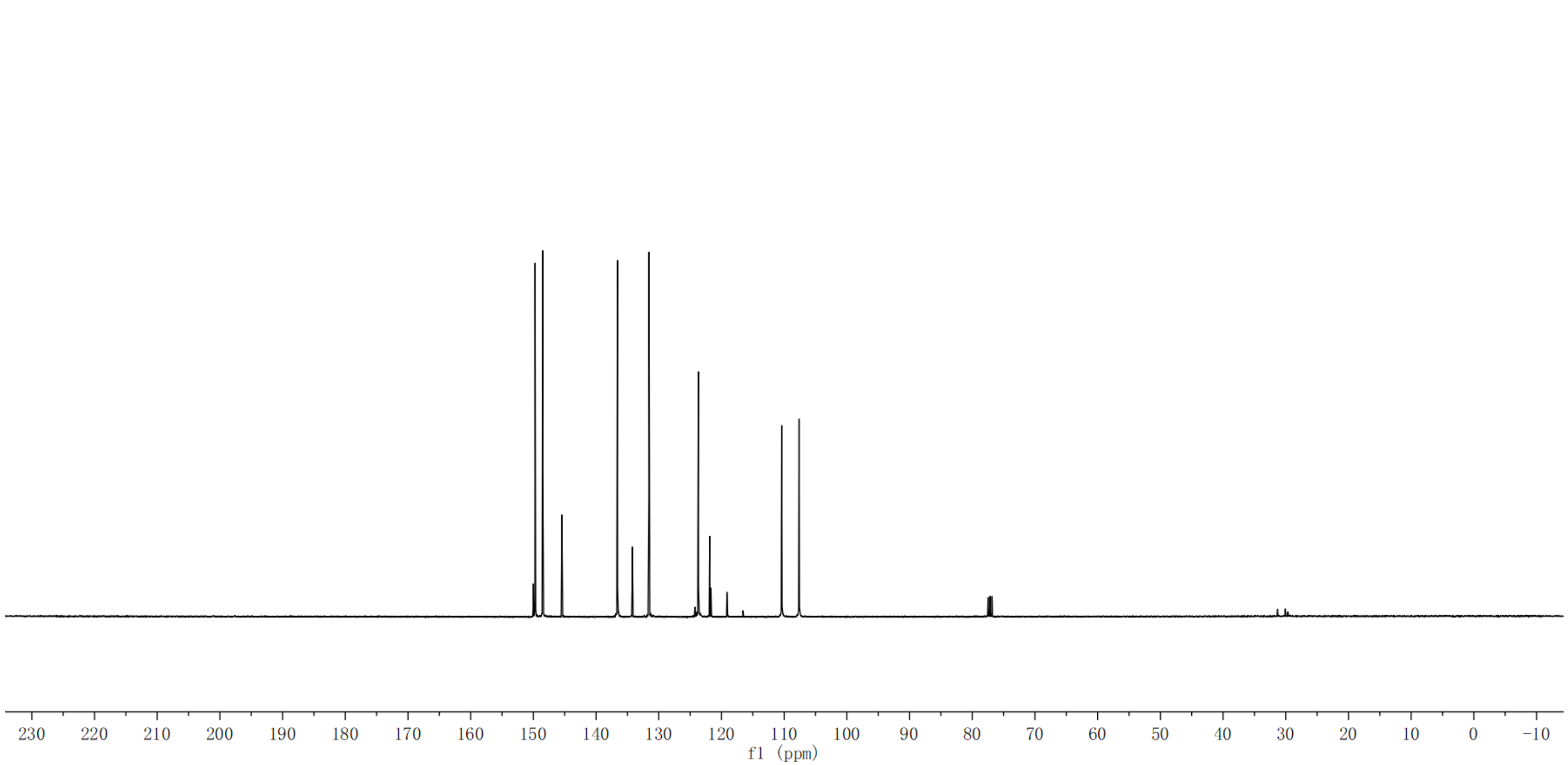
^{1}H NMR (400 MHz, $CDCl_3$)

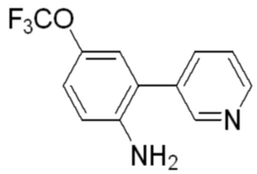


^{13}C NMR (100 MHz, $CDCl_3$)

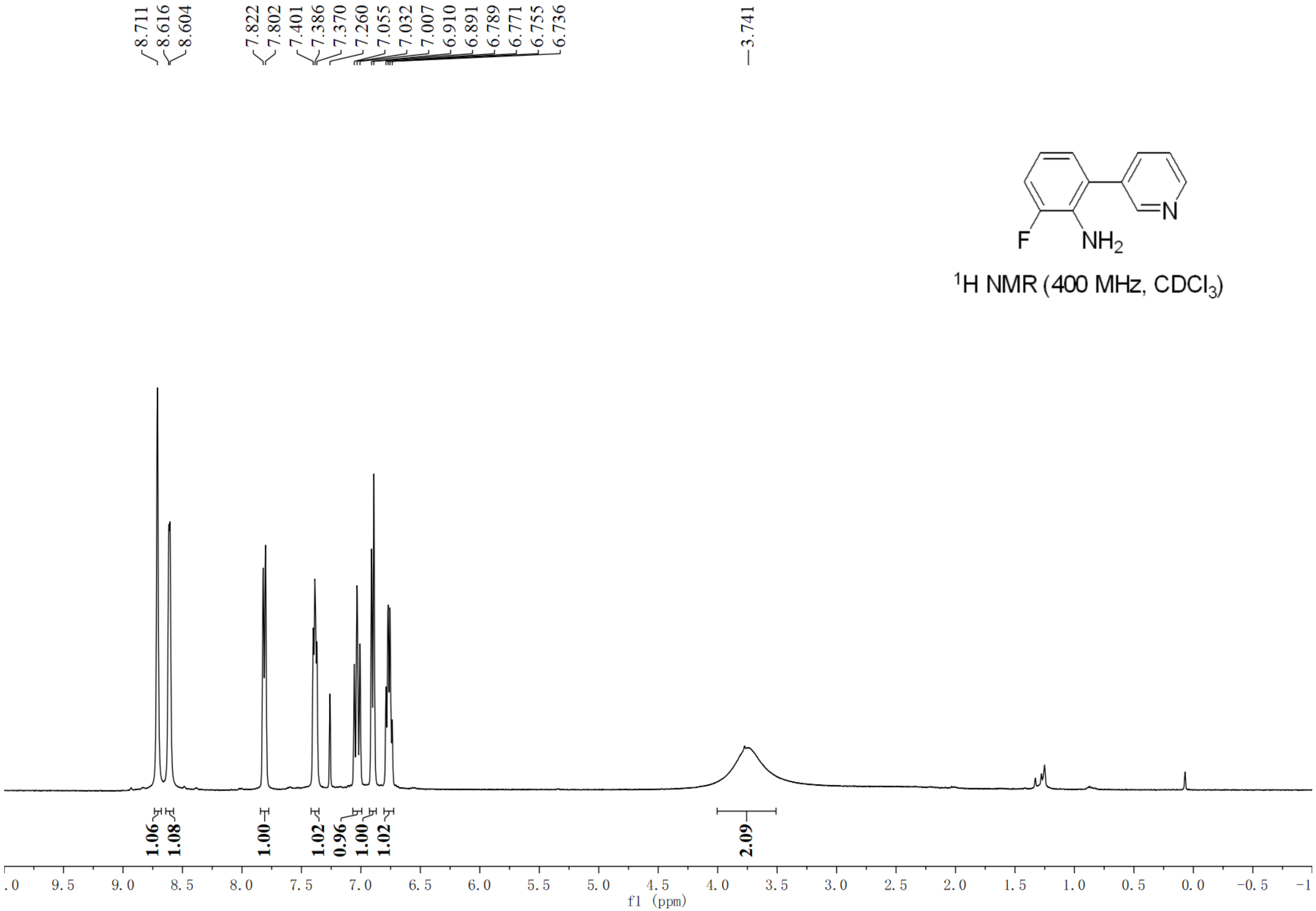


8.519
8.437
8.426
7.656
7.651
7.646
7.636
7.631
7.626
7.252
7.240
7.232
7.220
6.945
6.925
6.554
6.533
6.508
3.894
0.000
F3CO
N
NH2
1H NMR (400 MHz, CDCl3)
1.03
1.02
0.98
1.00
0.98
0.98
0.93
1.99
f1 (ppm)

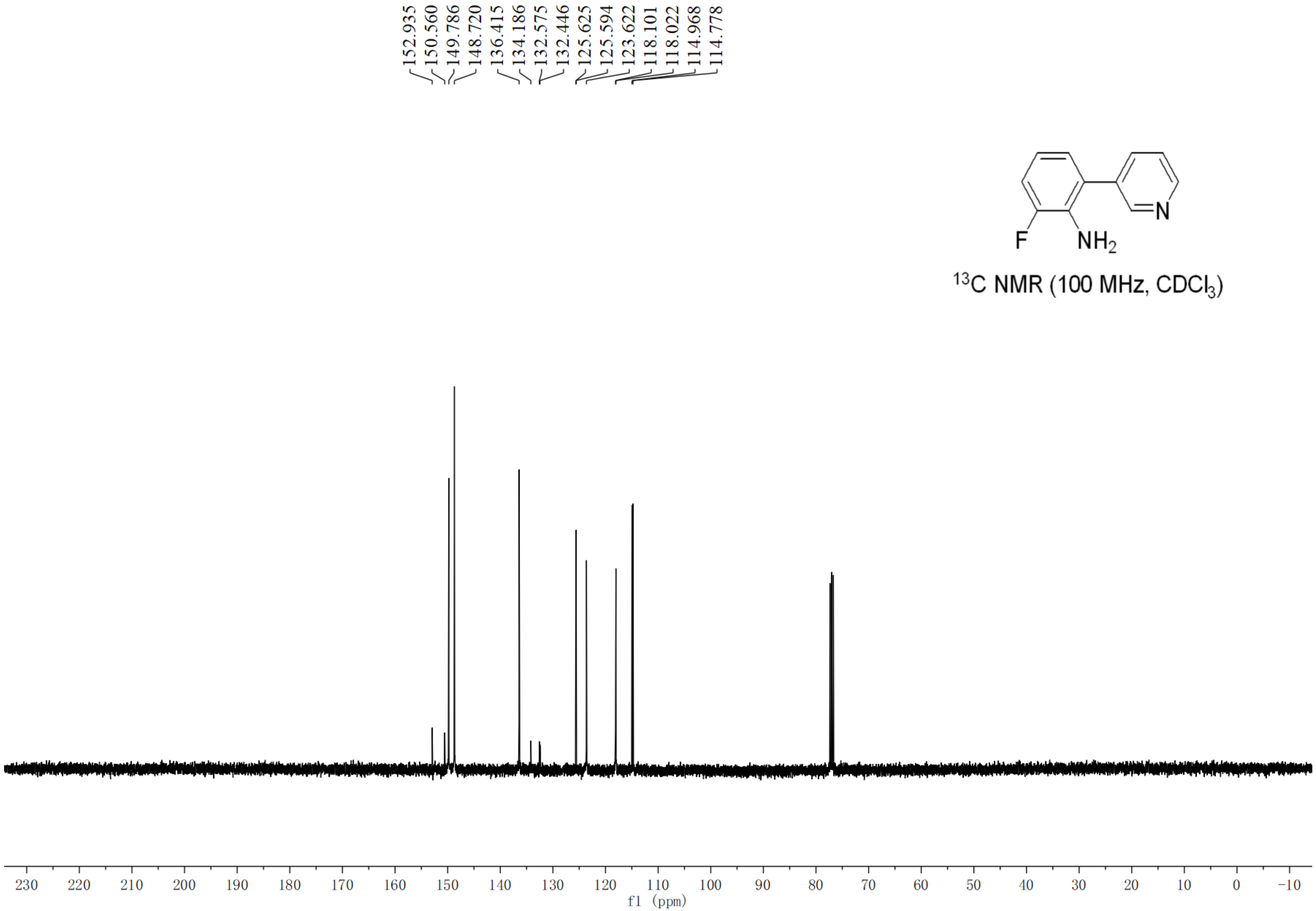


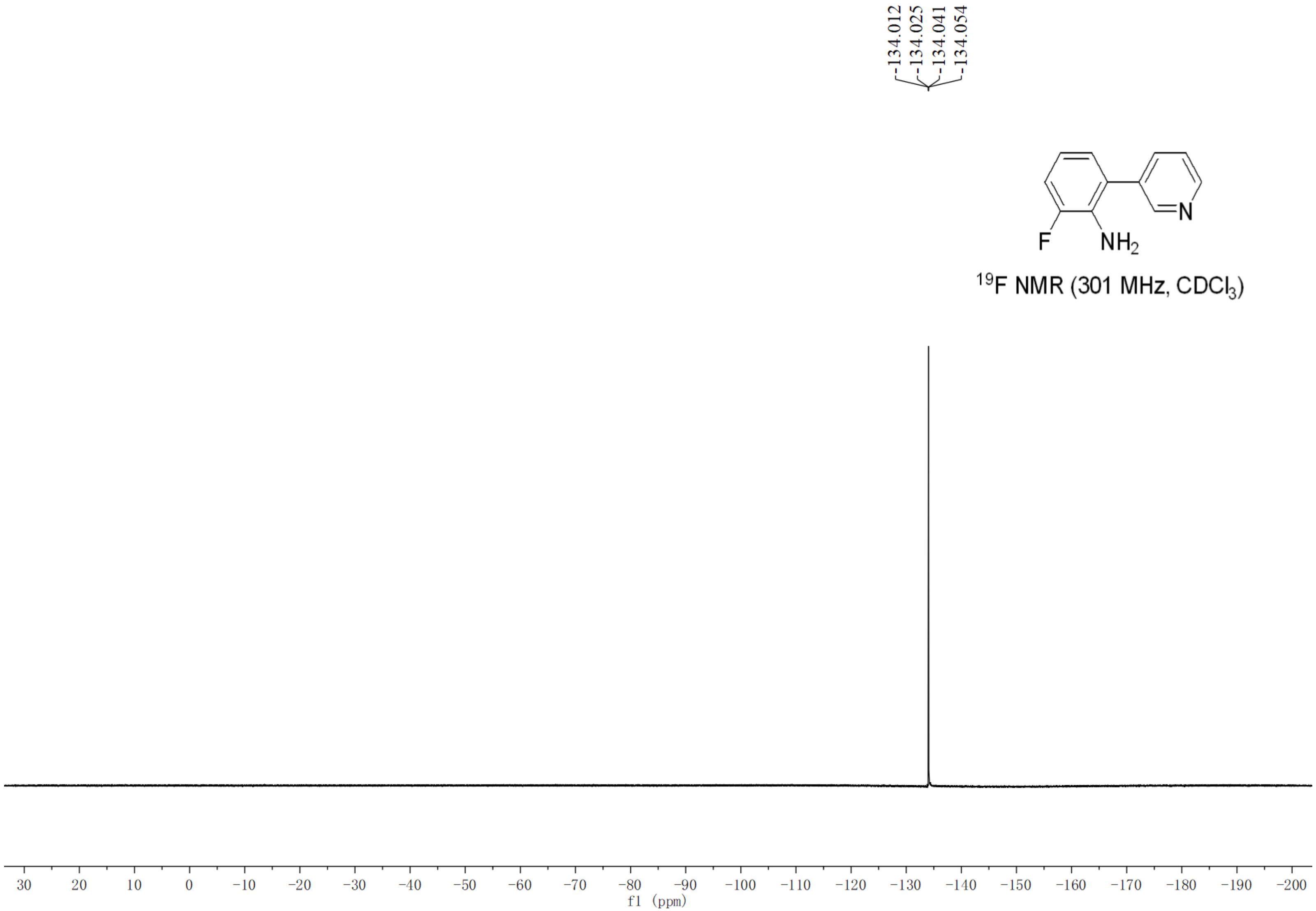


^{13}C NMR (100 MHz, $CDCl_3$)

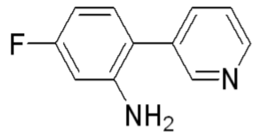


^{1}H NMR (400 MHz, $CDCl_3$)

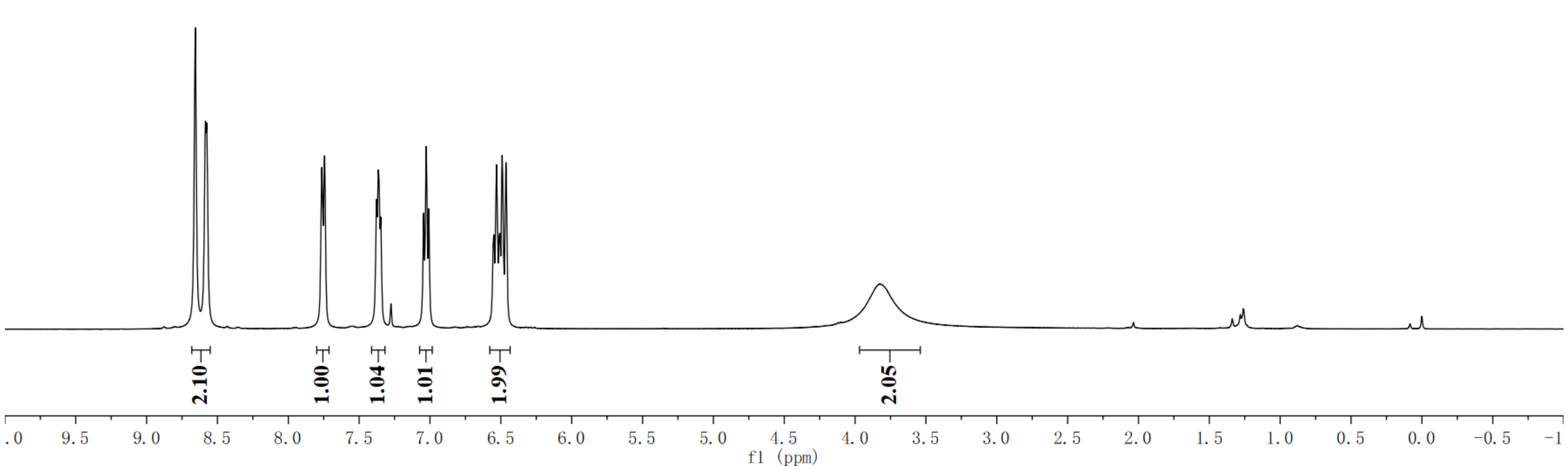

152.935
150.560
149.786
148.720
136.415
134.186
132.575
132.446
125.625
125.594
123.622
118.101
118.022
114.968
114.778
F
NH2
N
^{13}C NMR (100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

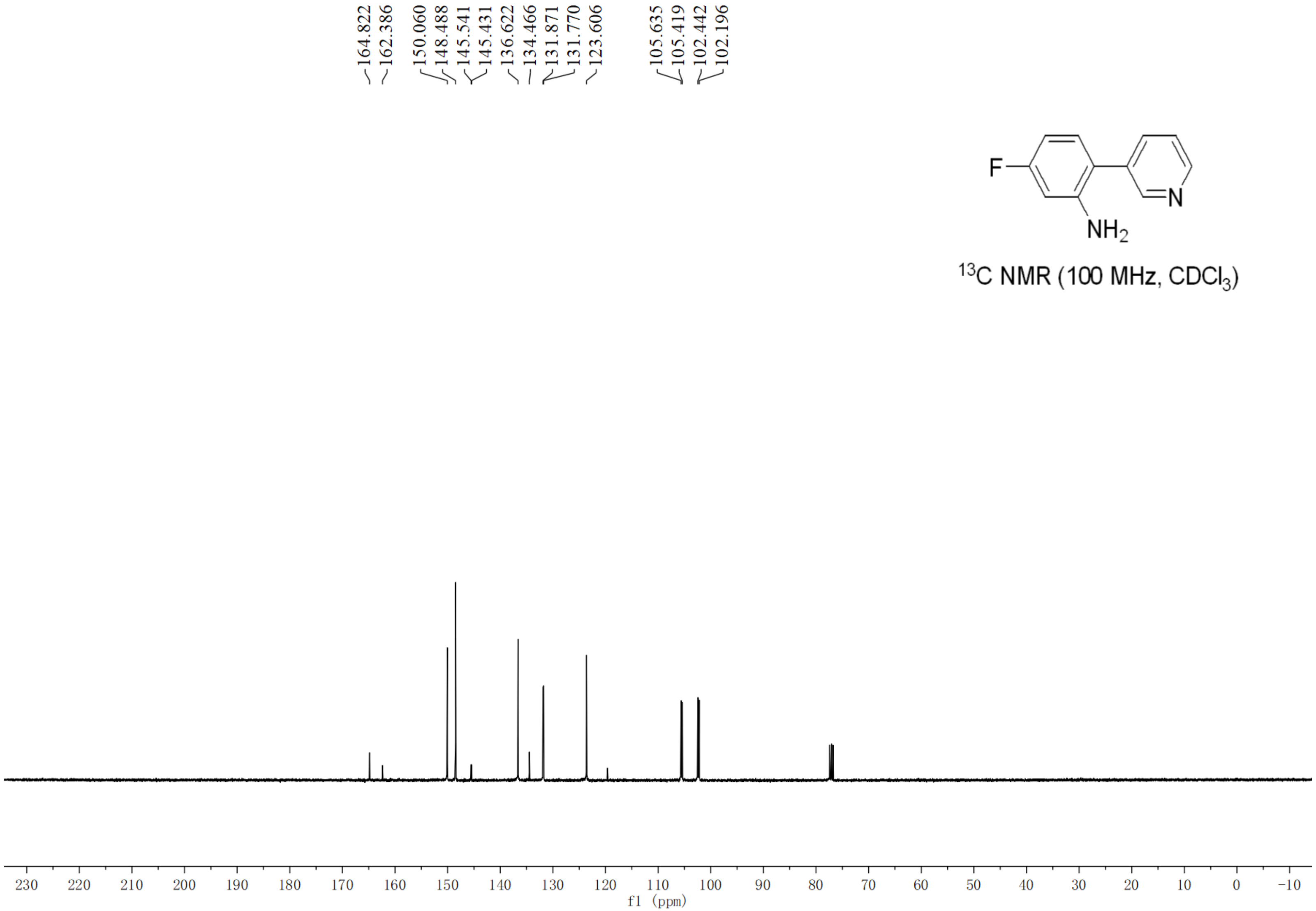


-134.012
-134.025
-134.041
-134.054
F
NH2
N
19F NMR (301 MHz, CDCl3)
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

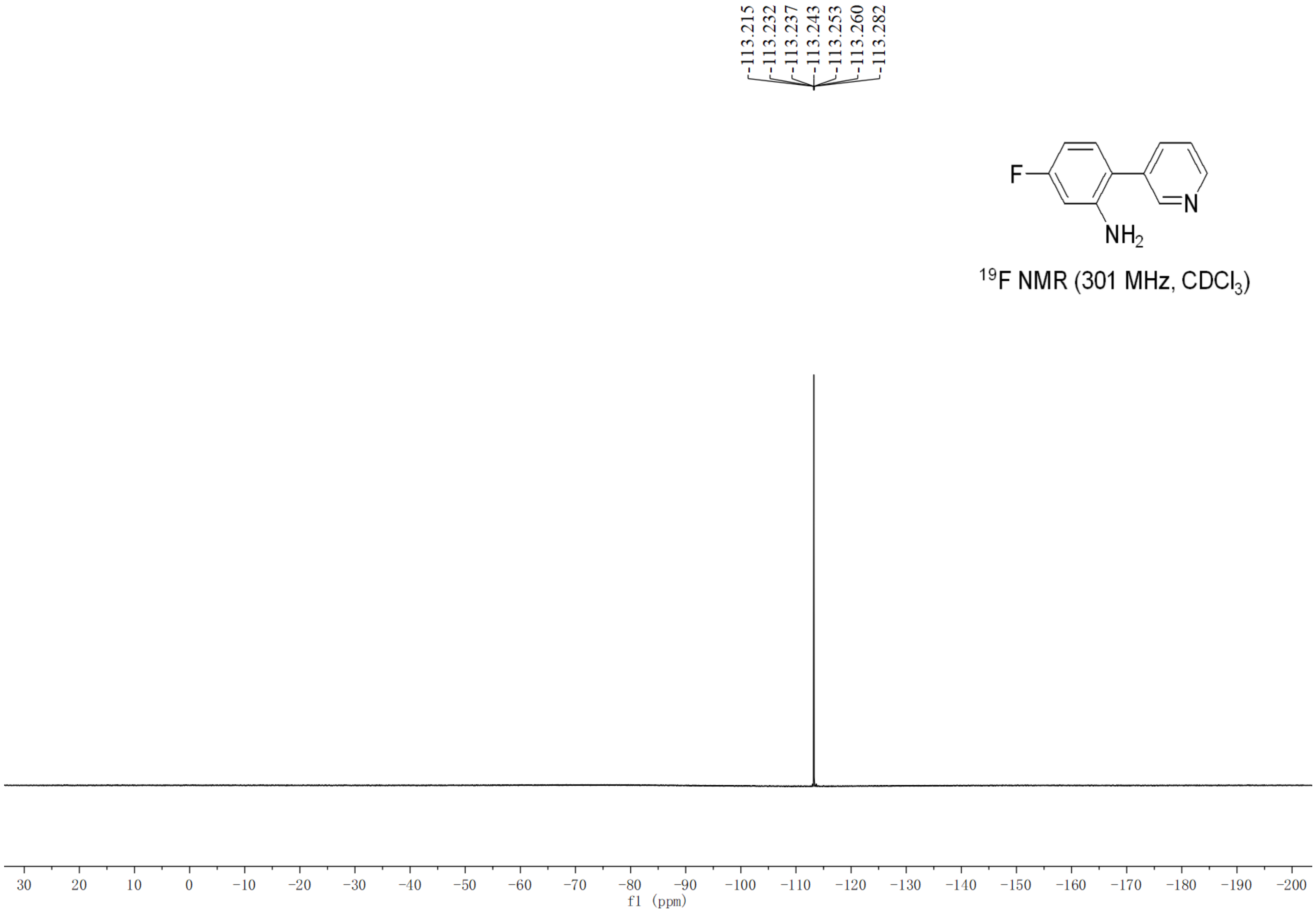


^{1}H NMR (400 MHz, $CDCl_3$)

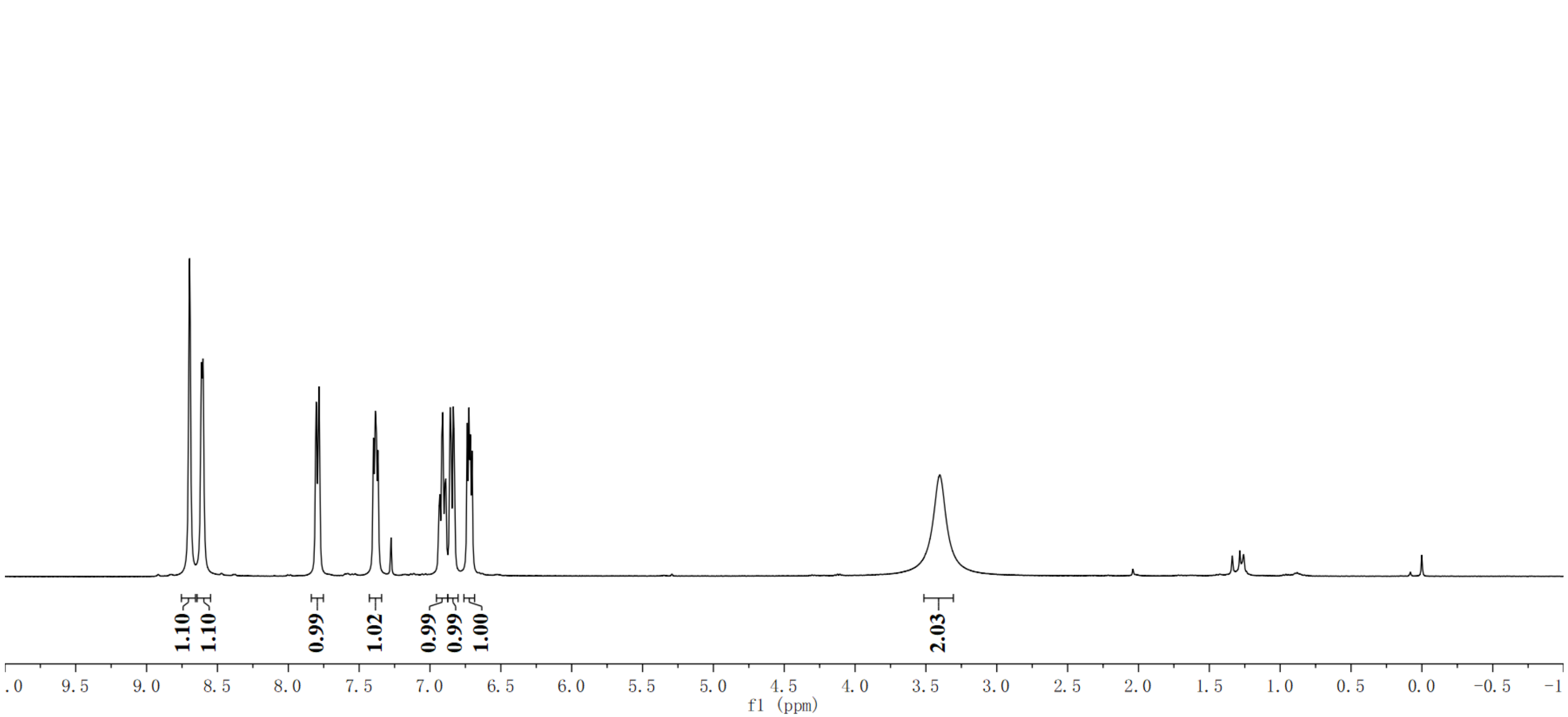


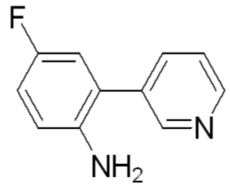


^{13}C NMR (100 MHz, $CDCl_3$)

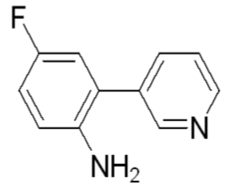


-113.215
-113.232
-113.237
-113.243
-113.253
-113.260
-113.282
F
N
NH2
19F NMR (301 MHz, CDCl3)
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

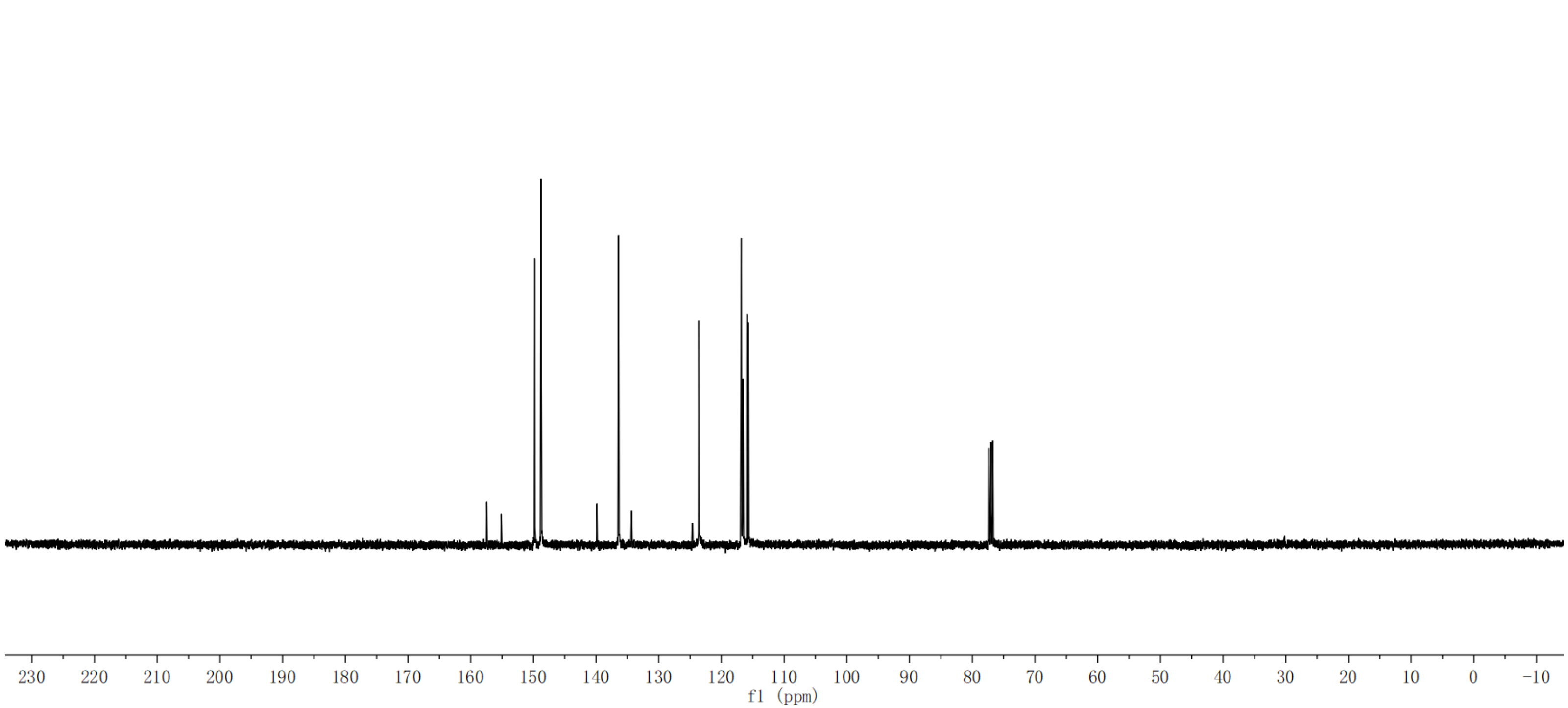


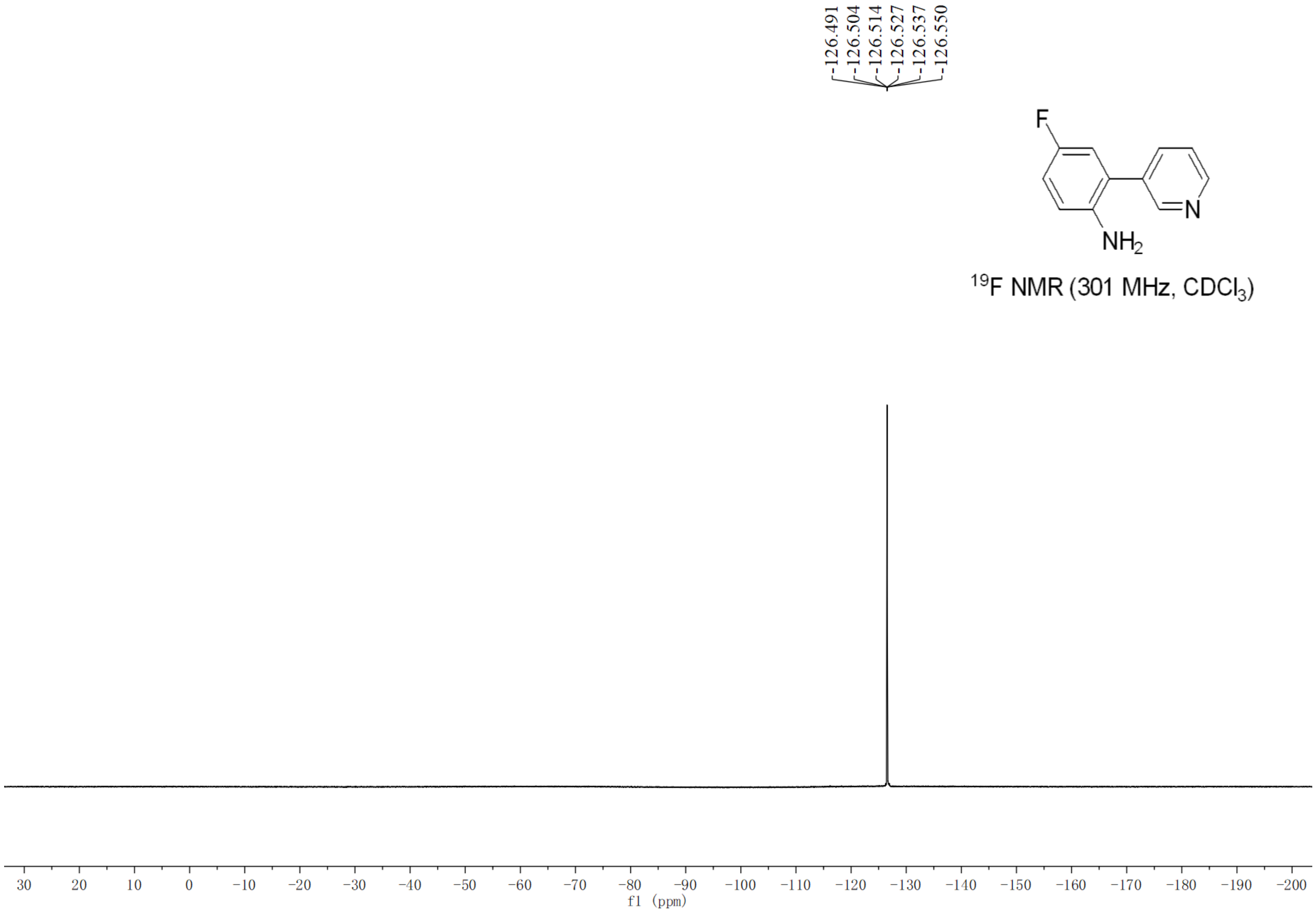


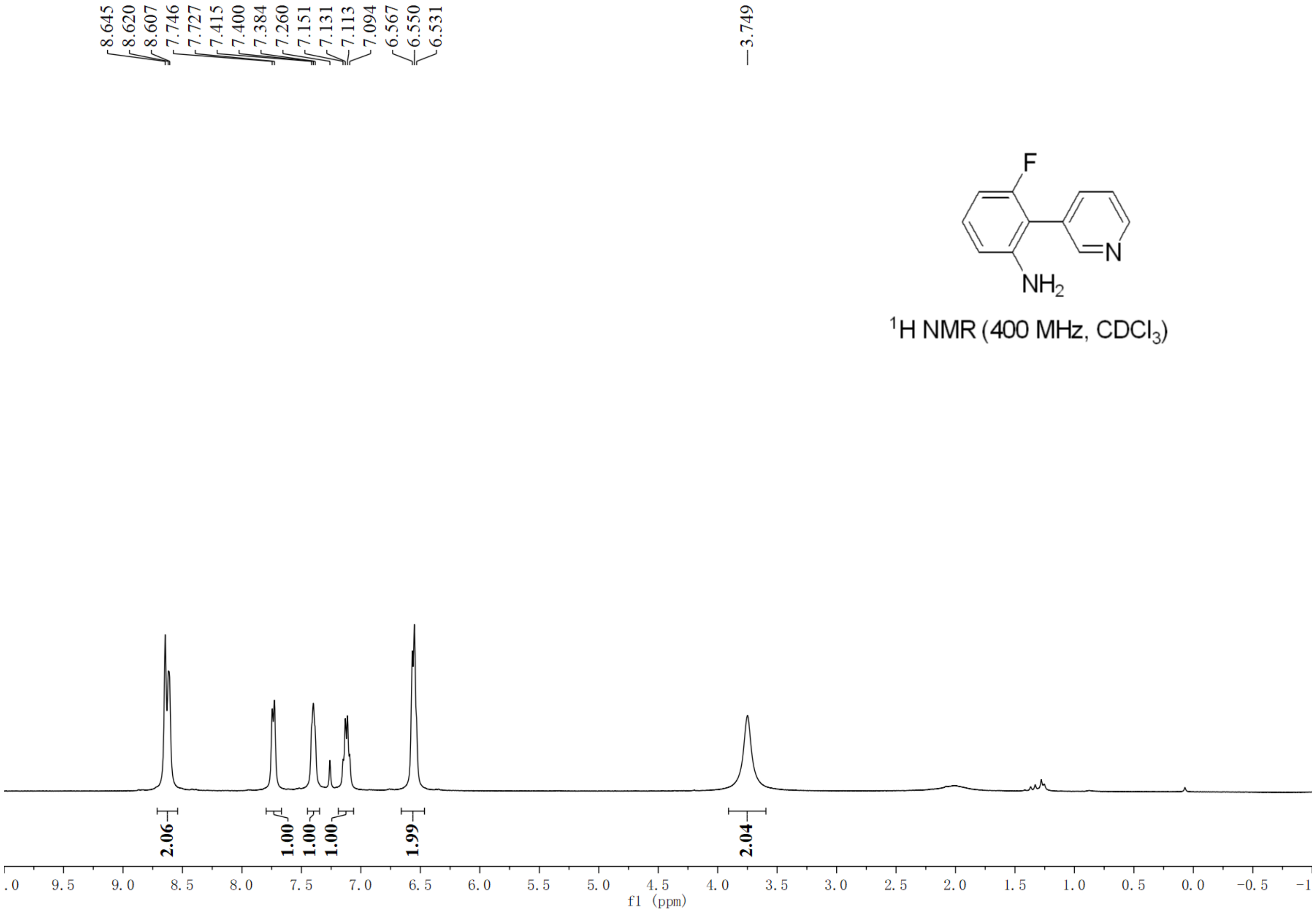
^{1}H NMR (400 MHz, $CDCl_3$)



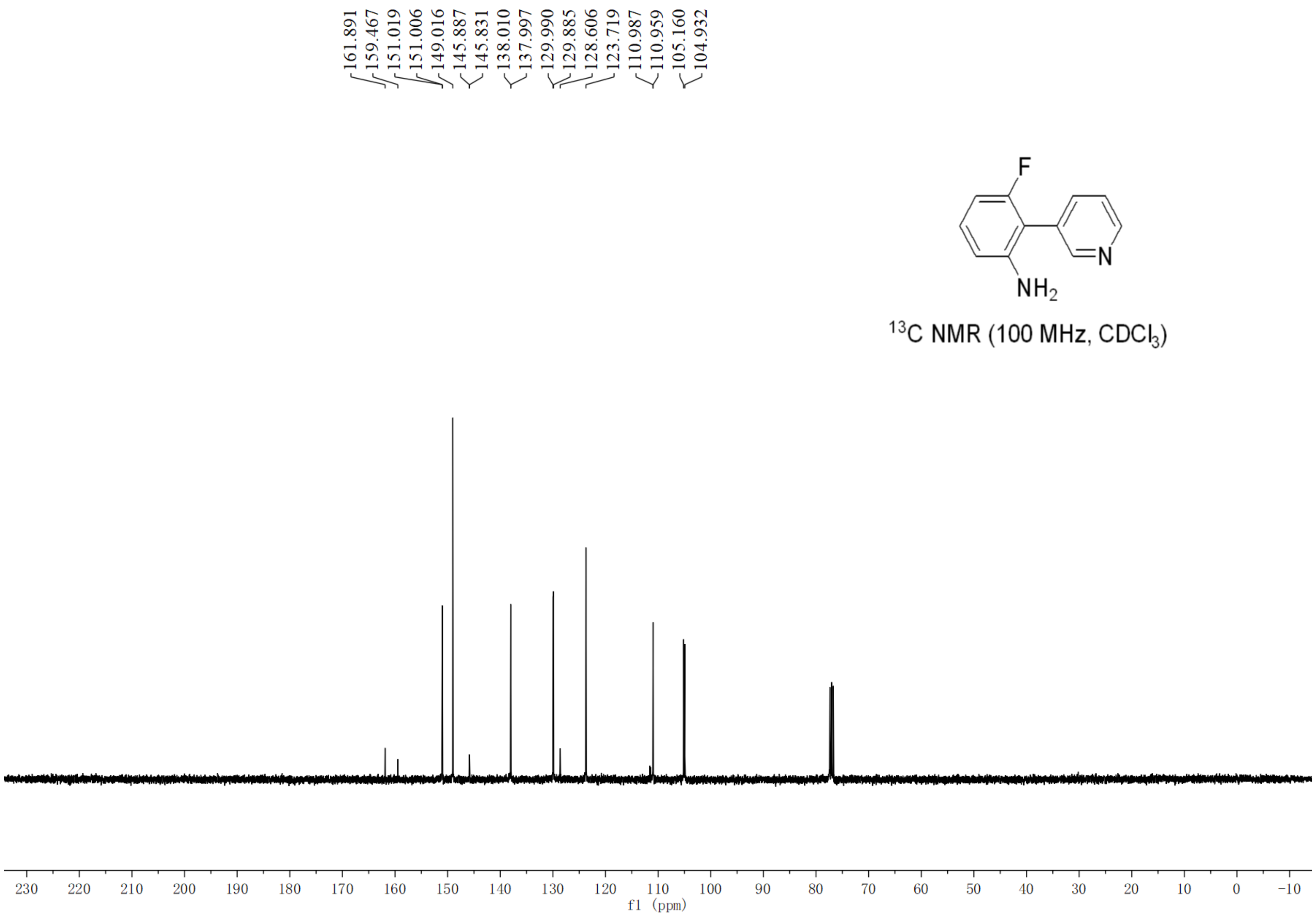
^{13}C NMR (100 MHz, $CDCl_3$)

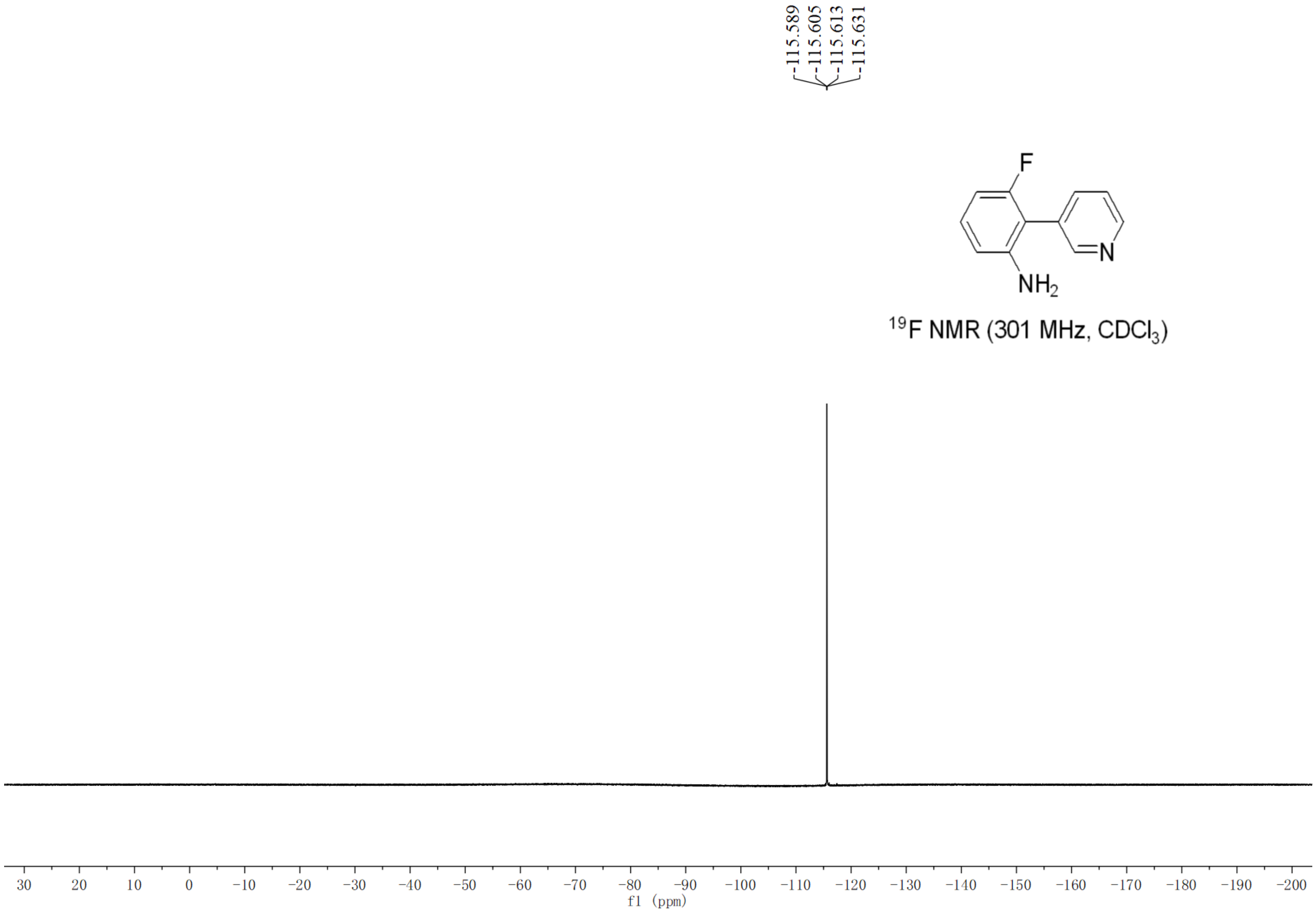



-126.491
-126.504
-126.514
-126.527
-126.537
-126.550
F
N
NH2
19F NMR (301 MHz, CDCl3)
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

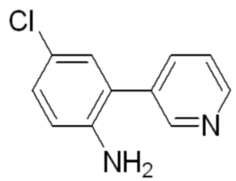


^1H NMR (400 MHz, $CDCl_3$)

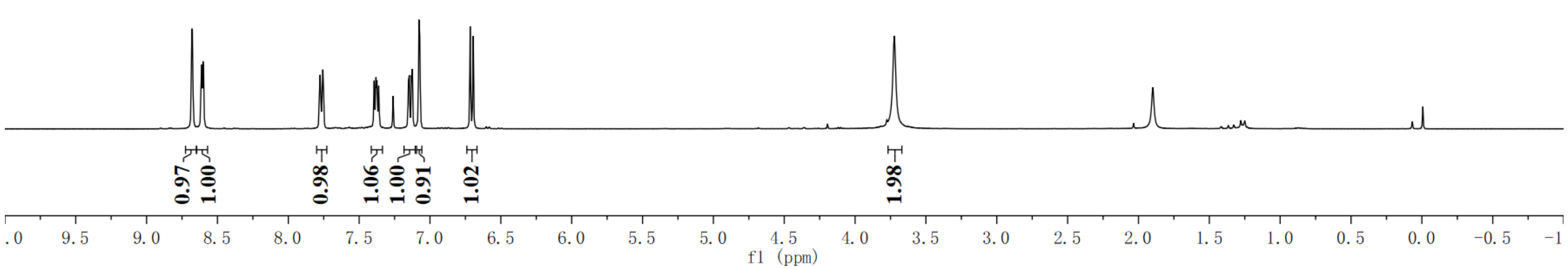

161.891
159.467
151.019
151.006
149.016
145.887
145.831
138.010
137.997
129.990
129.885
128.606
123.719
110.987
110.959
105.160
104.932
F
N
NH2
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

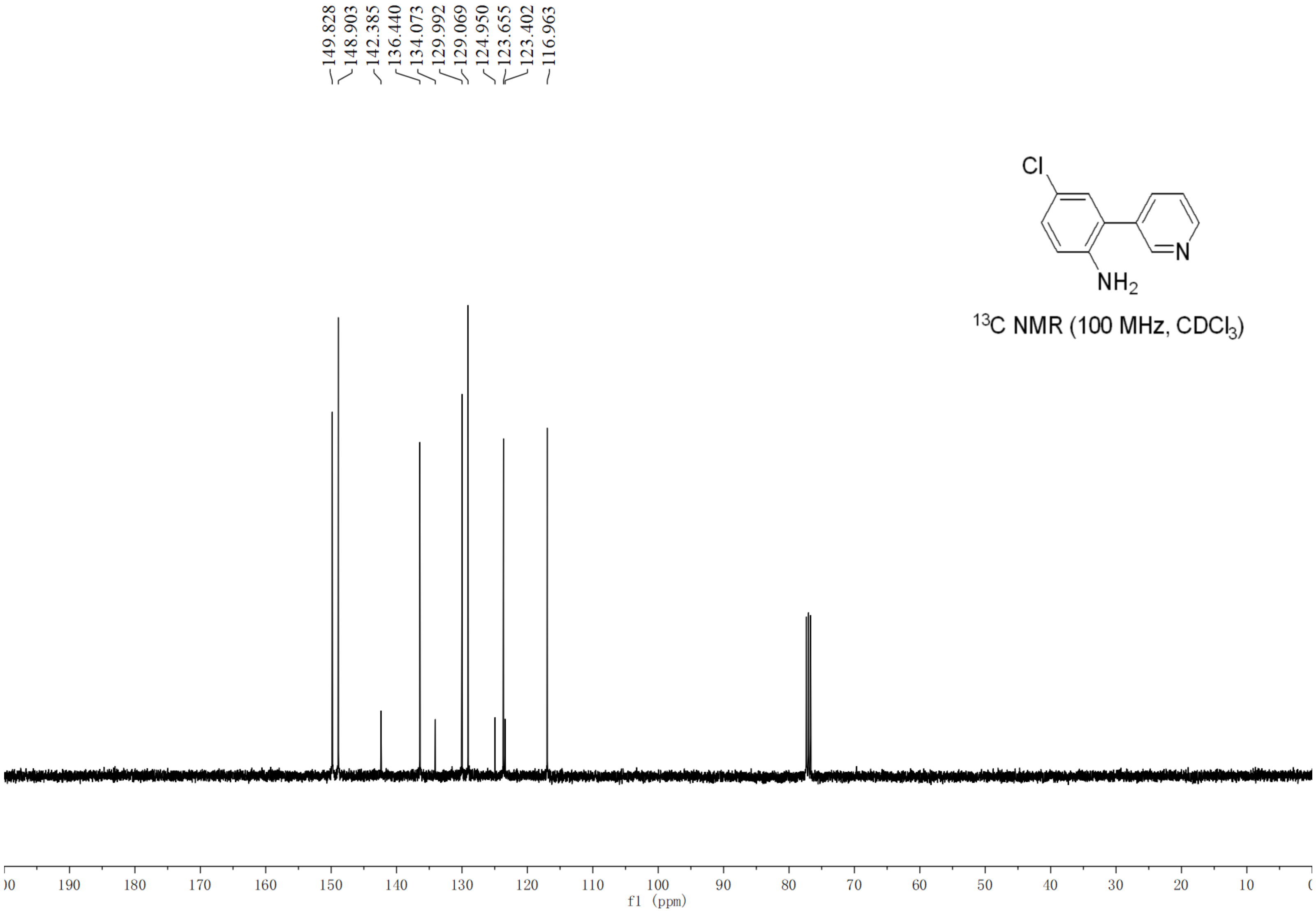


^{19}F NMR (301 MHz, $CDCl_3$)

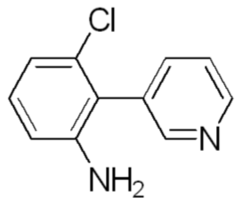


^1H NMR (400 MHz, $CDCl_3$)

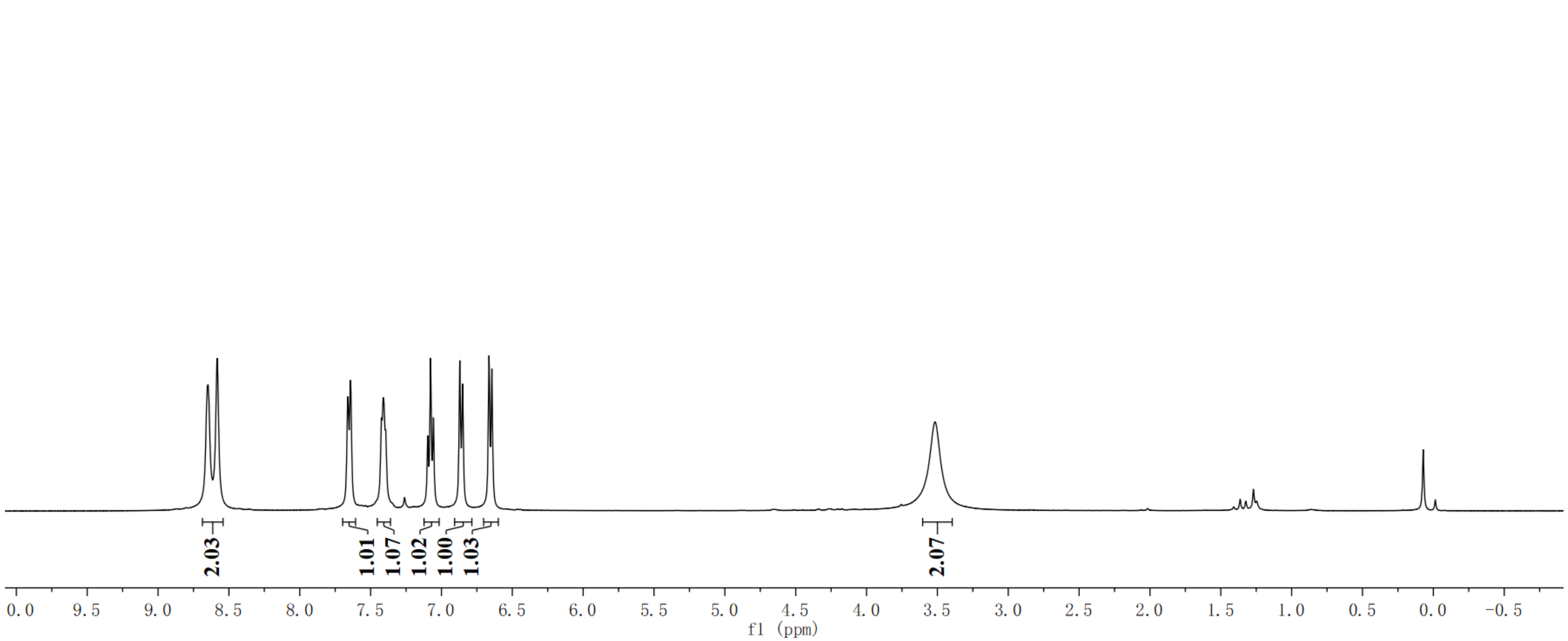


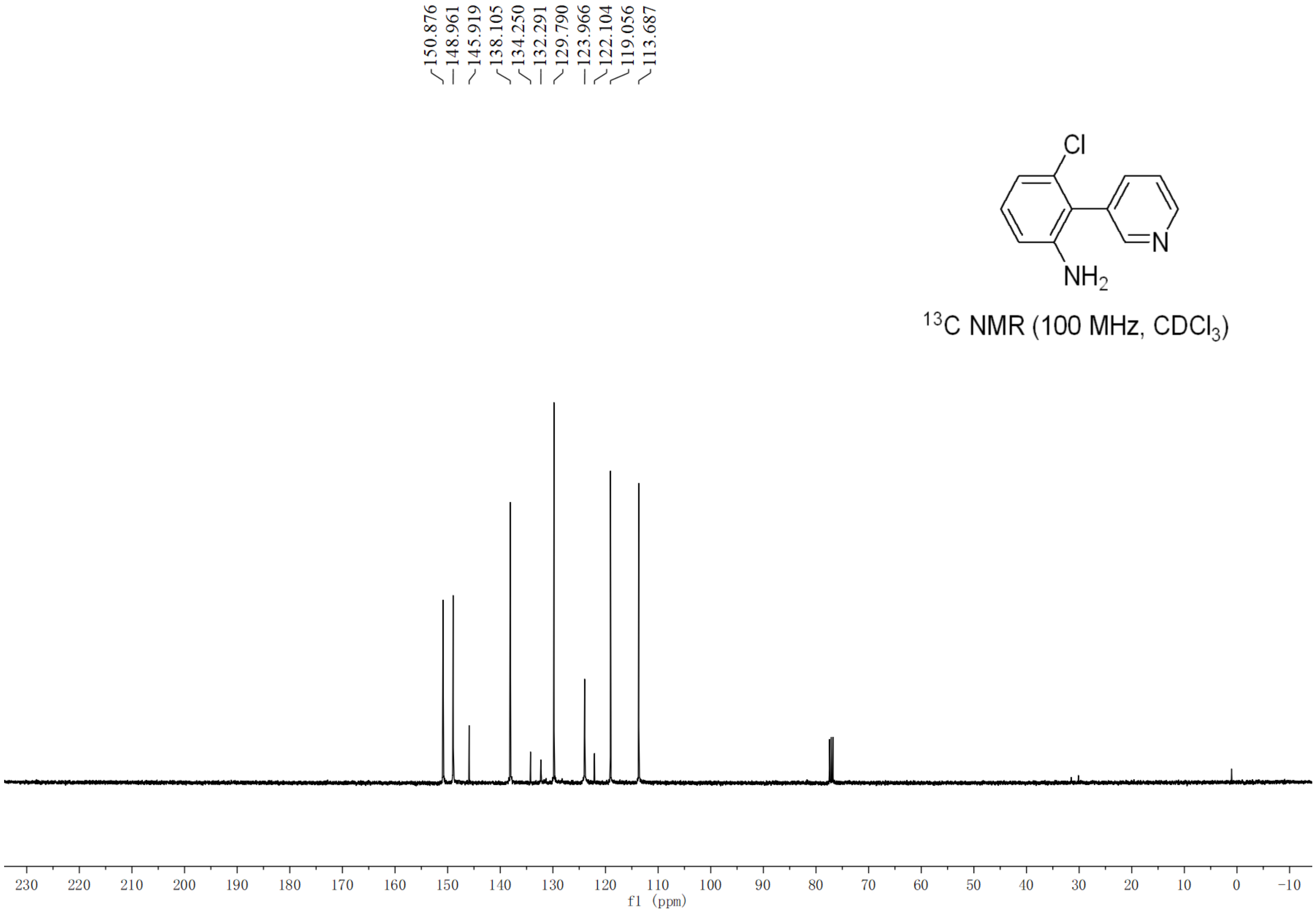


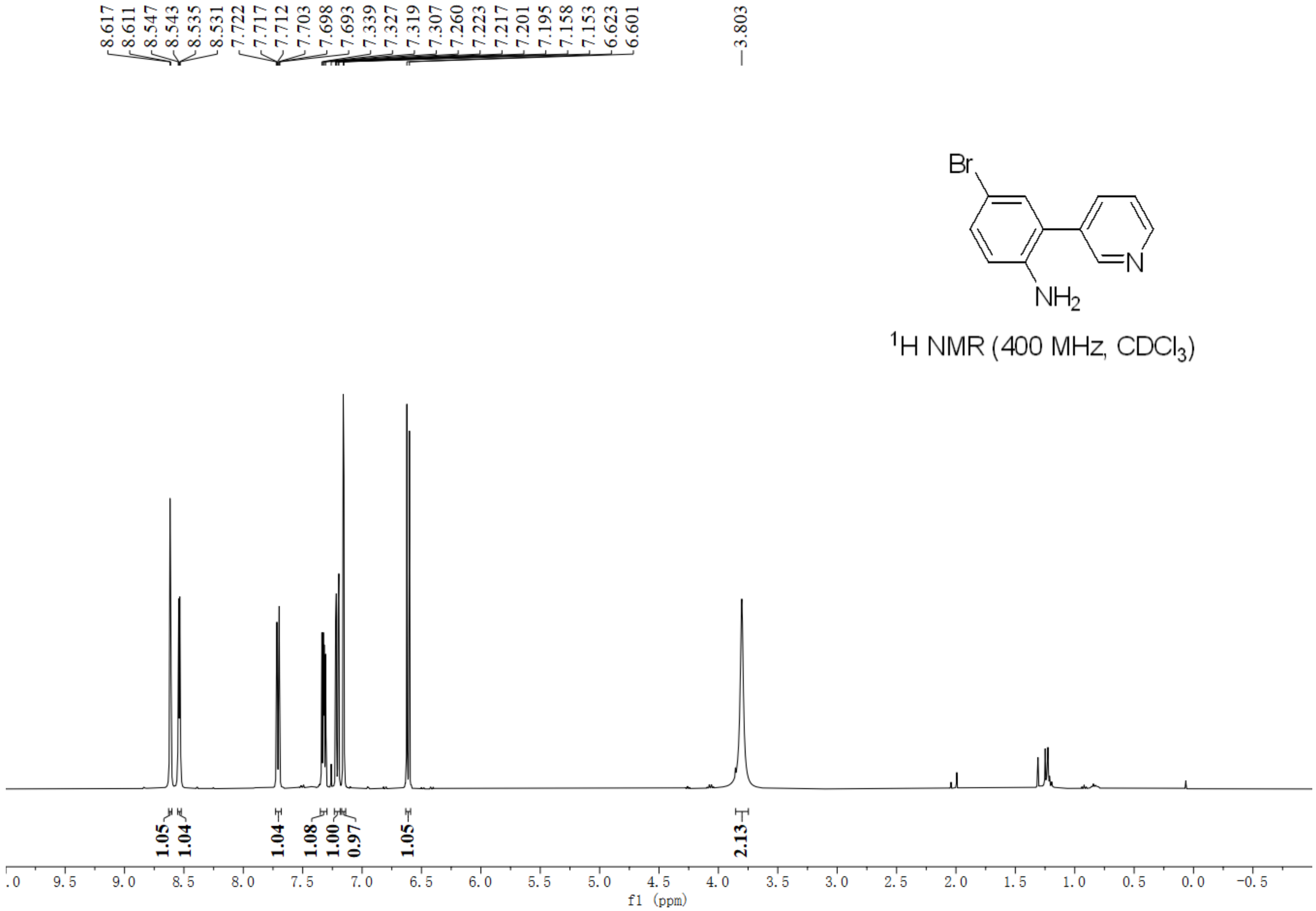
^{13}C NMR (100 MHz, $CDCl_3$)



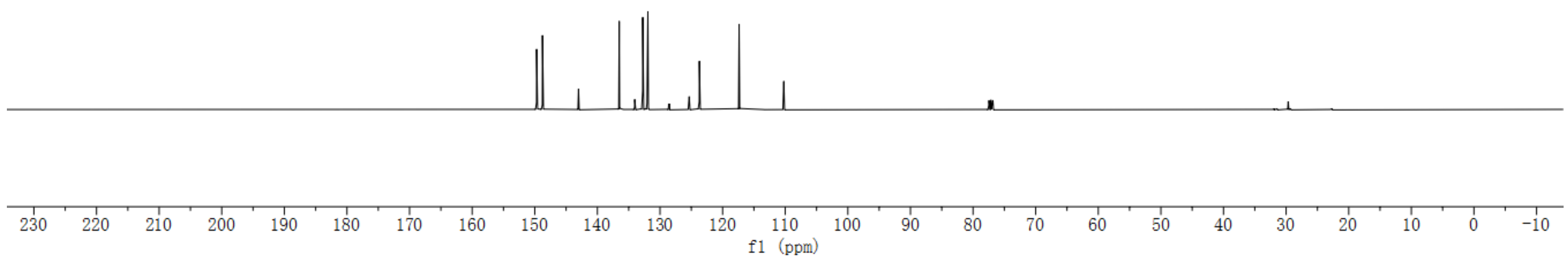
^1H NMR (400 MHz, $CDCl_3$)

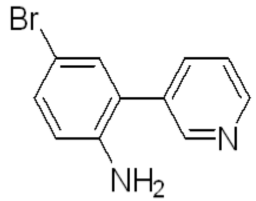



150.876
148.961
145.919
138.105
134.250
132.291
129.790
123.966
122.104
119.056
113.687
Cl
N
NH_2
^{13}C NMR (100 MHz, $CDCl_3$)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

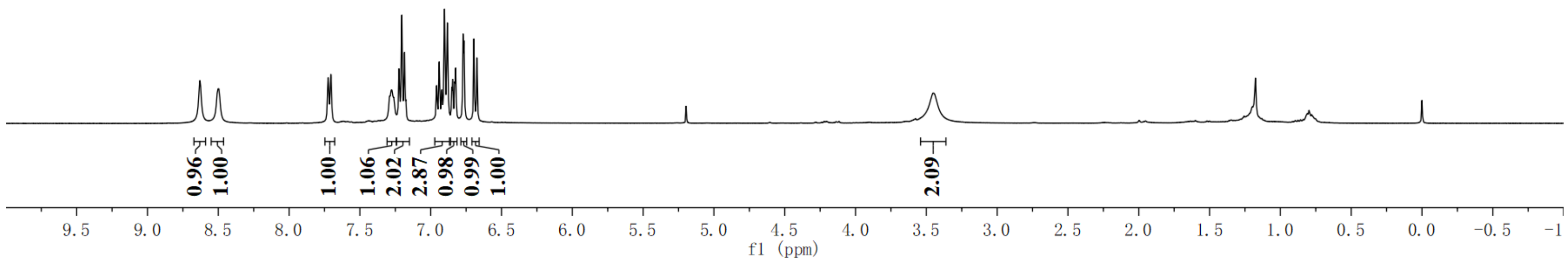


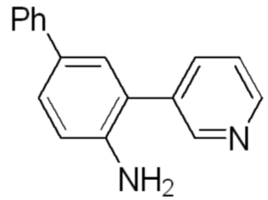
8.617
8.611
8.547
8.543
8.535
8.531
7.722
7.717
7.712
7.703
7.698
7.693
7.339
7.327
7.319
7.307
7.260
7.223
7.217
7.201
7.195
7.158
7.153
6.623
6.601
3.803
Br
N
NH_2
^1H NMR (400 MHz, $CDCl_3$)
1.05
1.04
1.04
1.08
1.00
0.97
1.05
2.13
f1 (ppm)



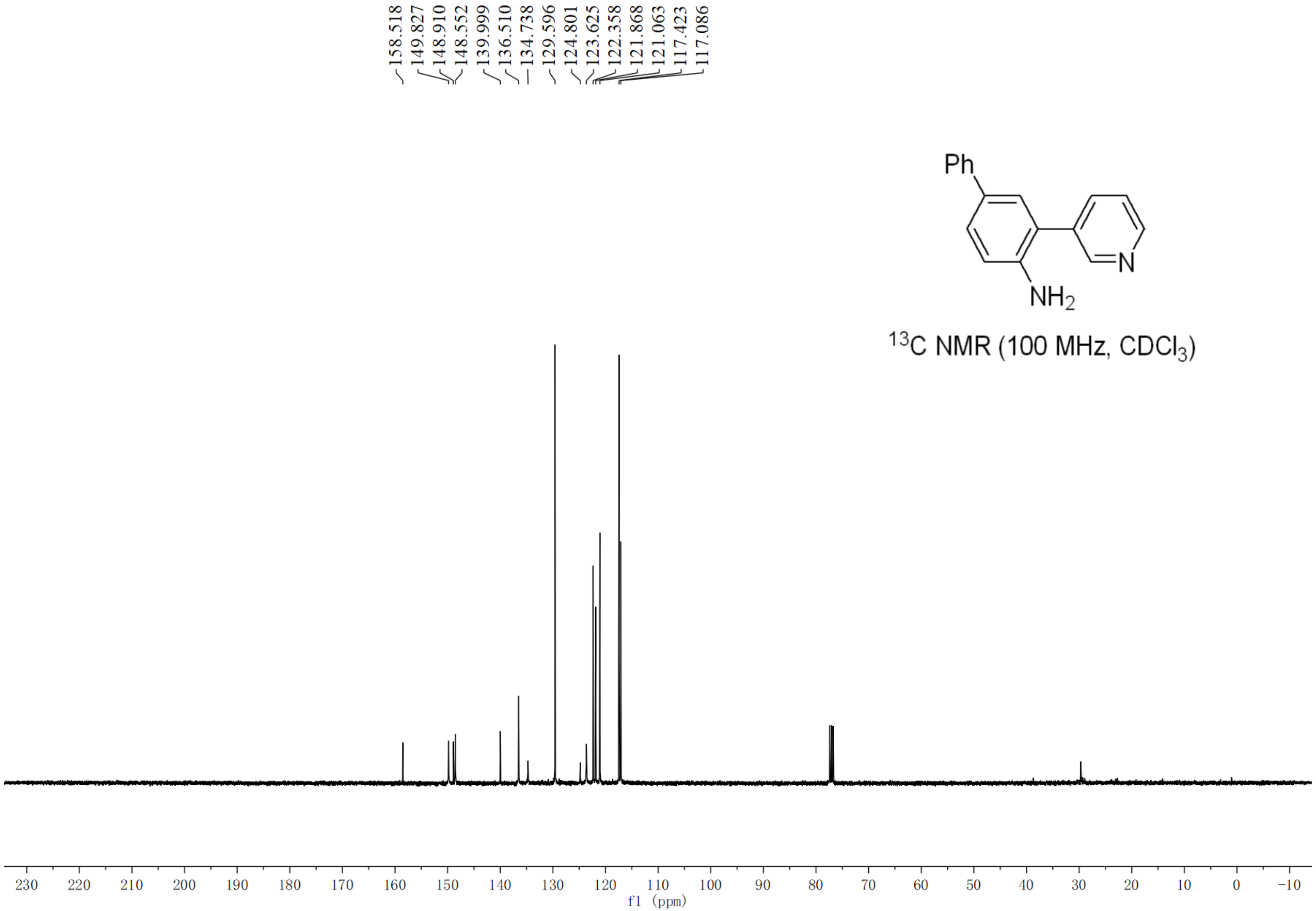


^{13}C NMR (101 MHz, $CDCl_3$)

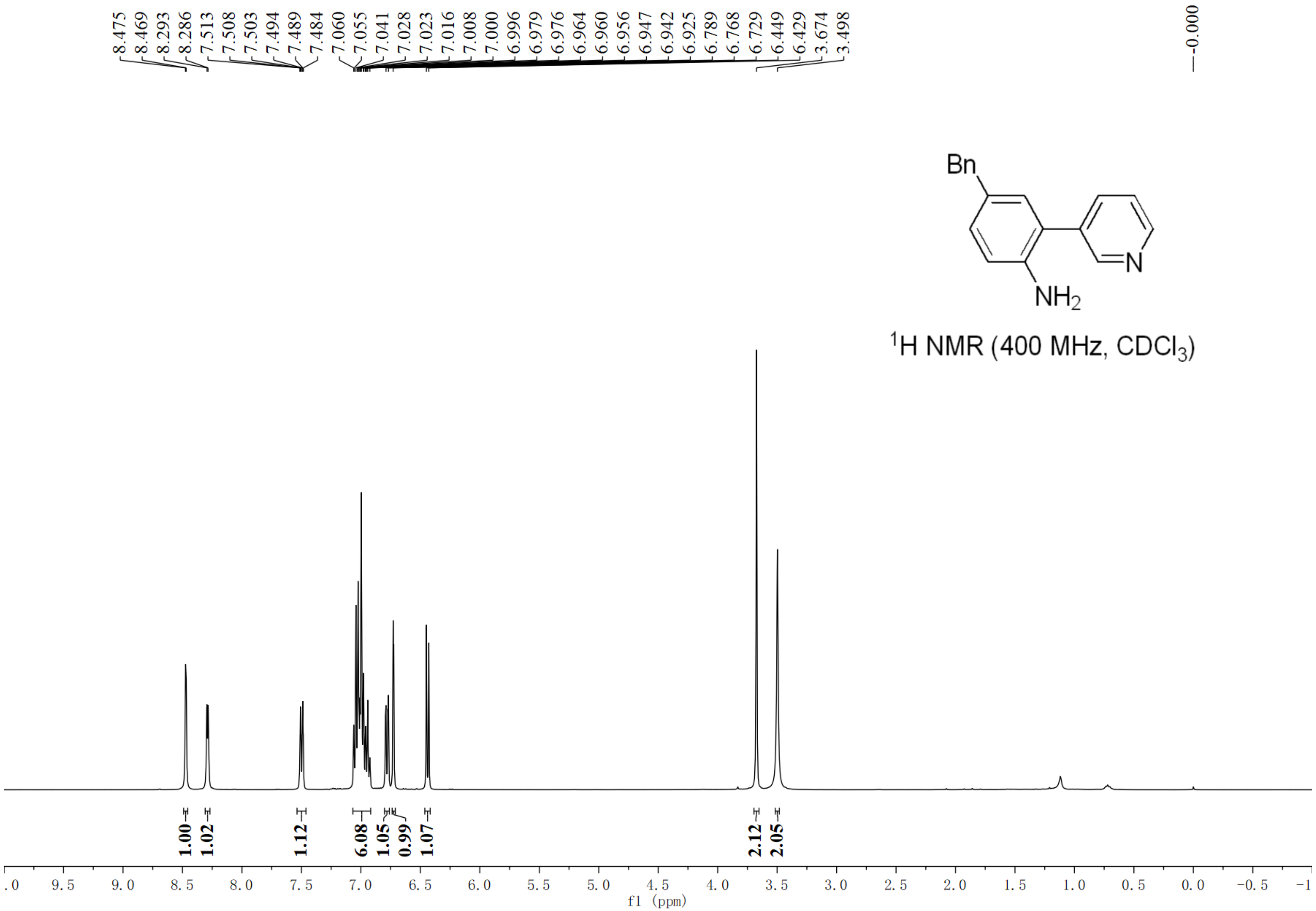


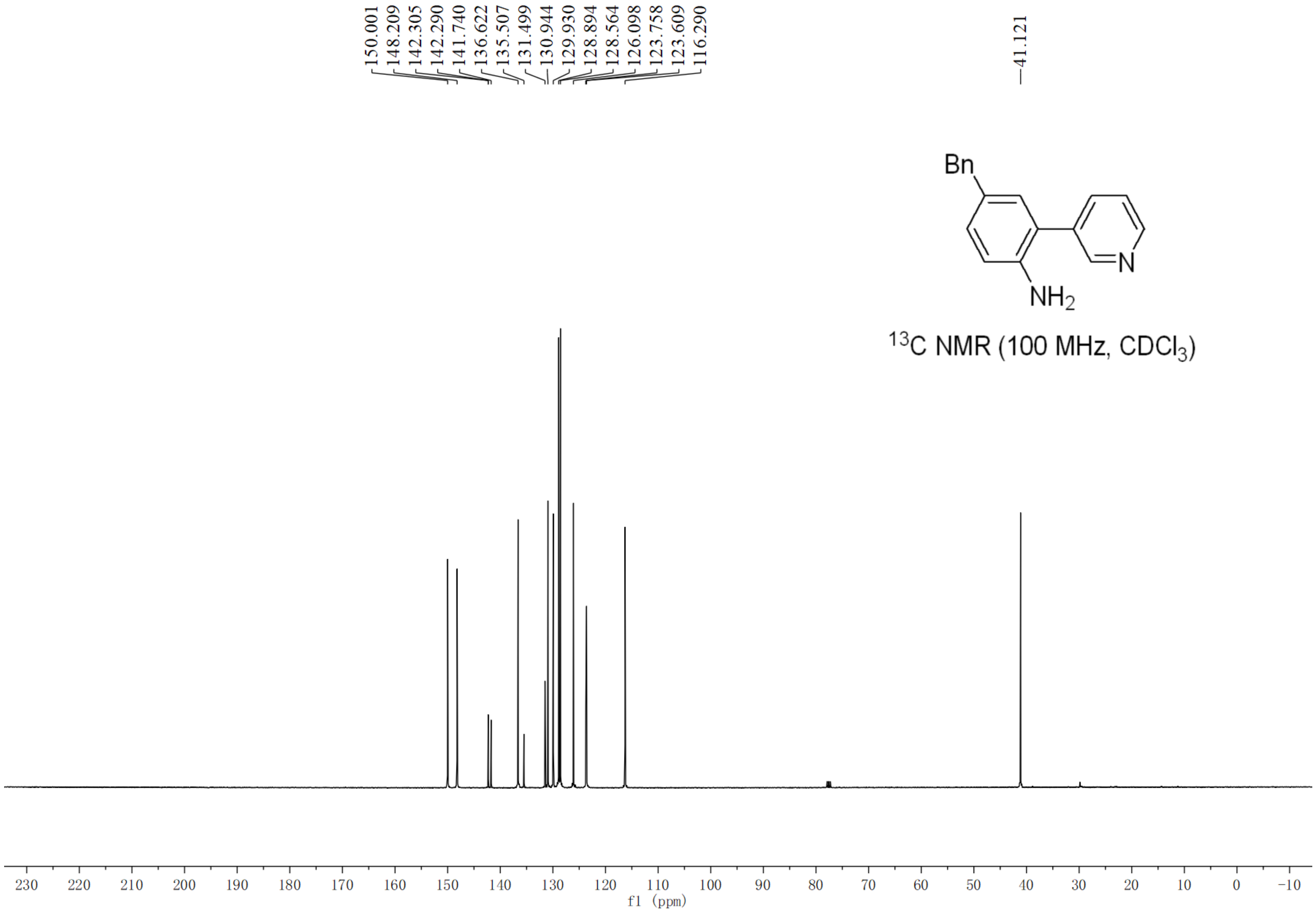


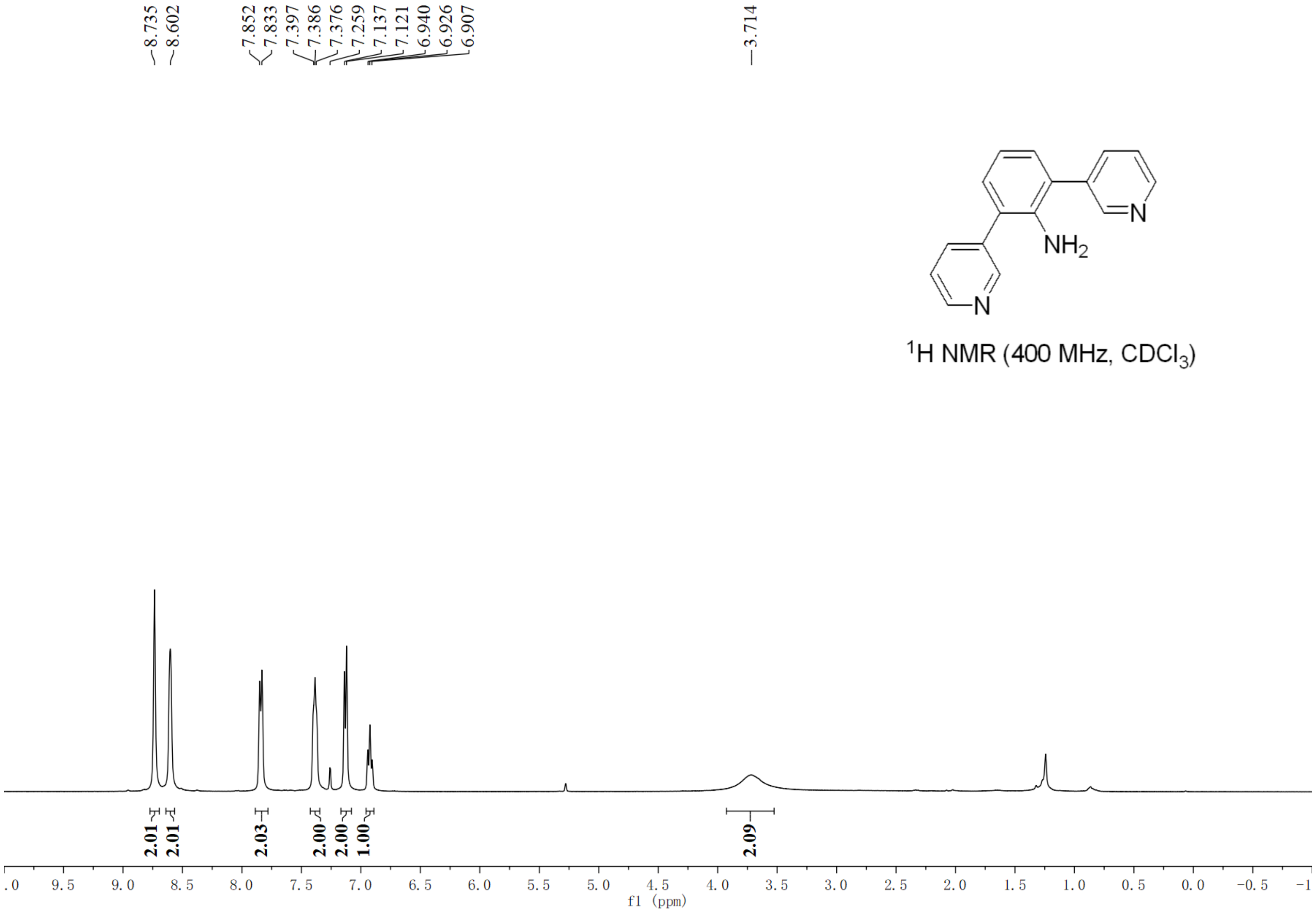
^{1}H NMR (400 MHz, $CDCl_3$)



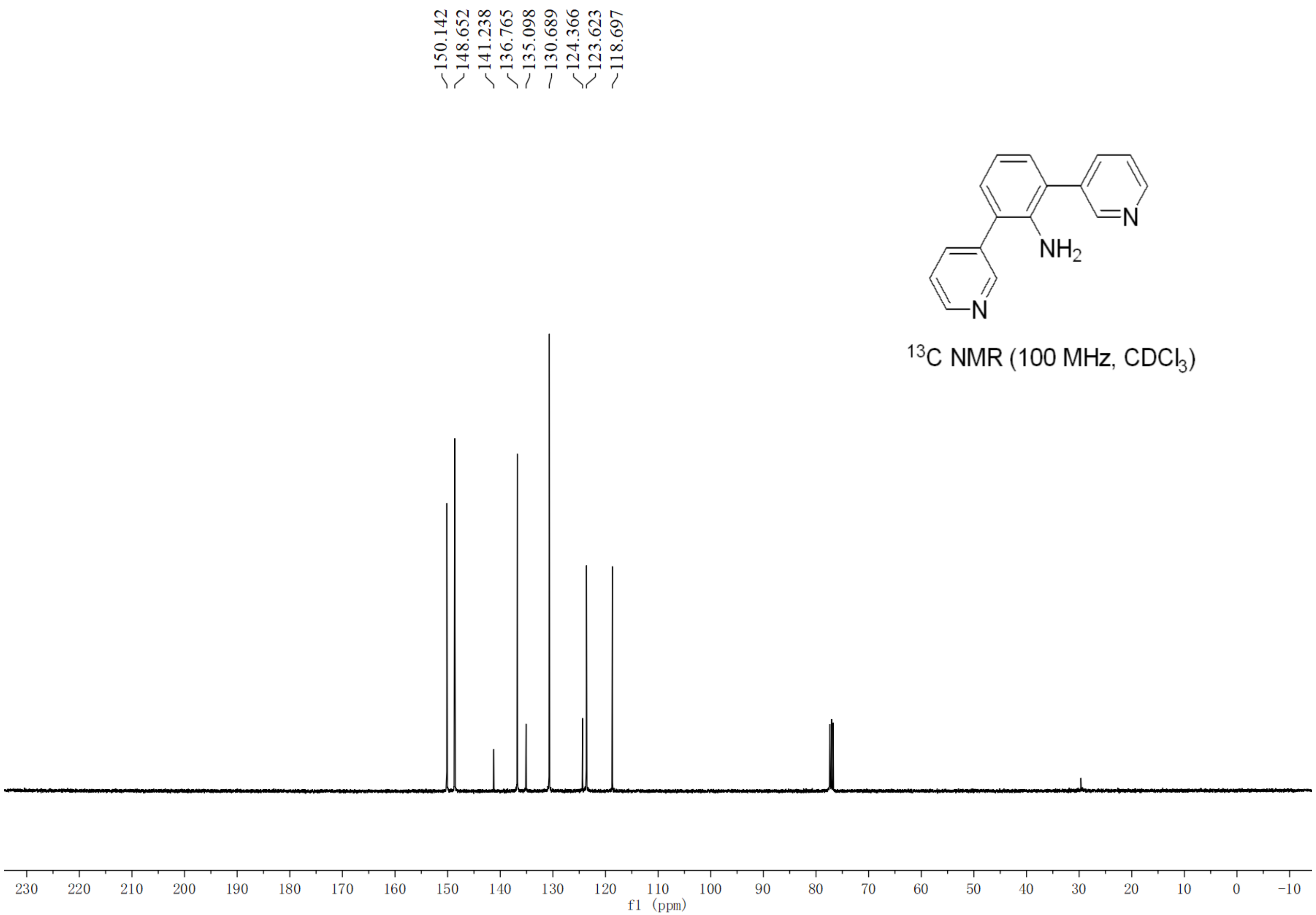
^{13}C NMR (100 MHz, $CDCl_3$)


8.475
8.469
8.293
8.286
7.513
7.508
7.503
7.494
7.489
7.484
7.060
7.055
7.041
7.028
7.023
7.016
7.008
7.000
6.996
6.979
6.976
6.964
6.960
6.956
6.947
6.942
6.925
6.789
6.768
6.729
6.449
6.429
3.674
3.498
0.000
Bn
N
NH2
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.12
6.08
1.05
0.99
1.07
2.12
2.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

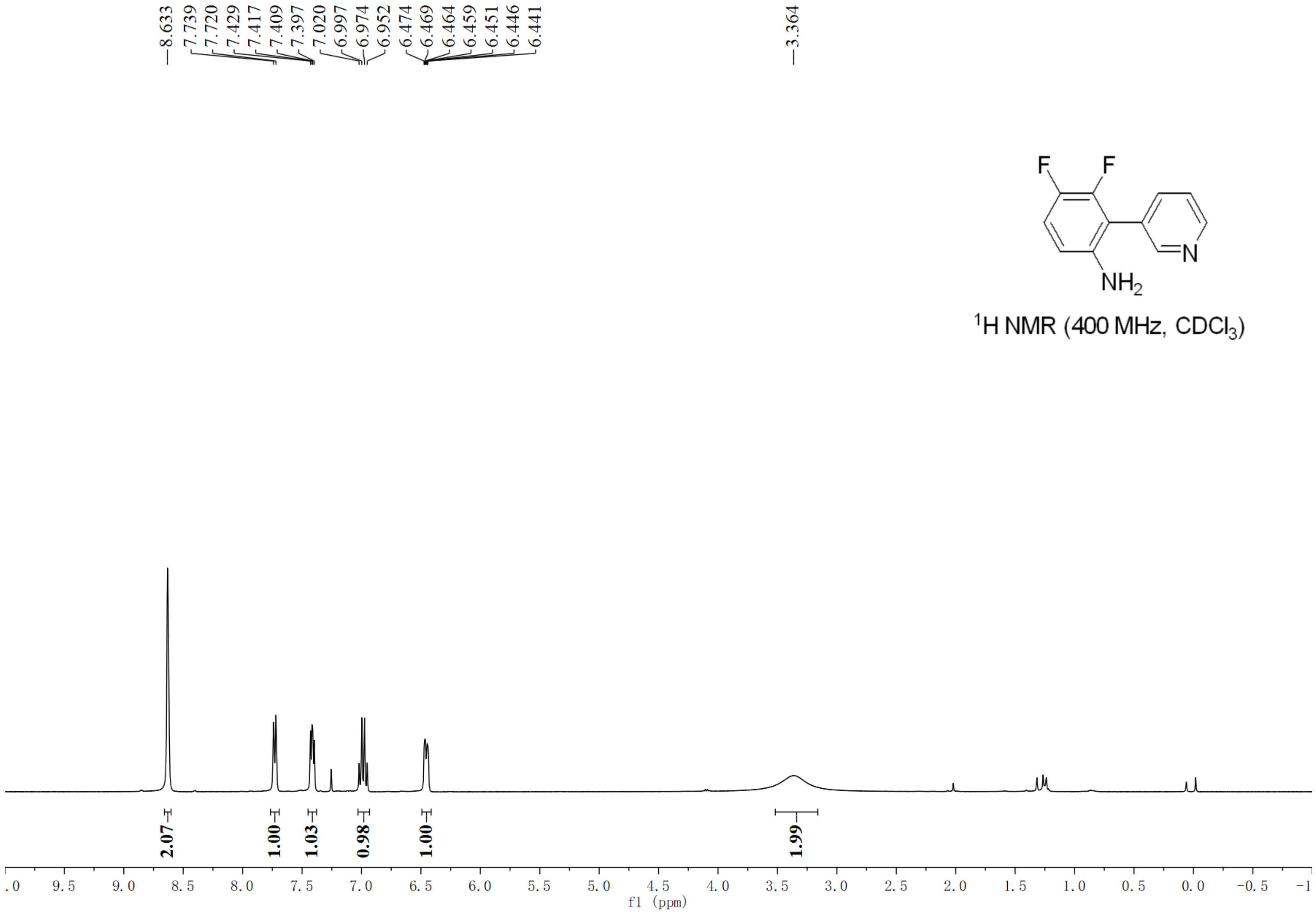

150.001
148.209
142.305
142.290
141.740
136.622
135.507
131.499
130.944
129.930
128.894
128.564
126.098
123.758
123.609
116.290
41.121
Bn
N
NH_2
^{13}C NMR (100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^1H NMR (400 MHz, $CDCl_3$)

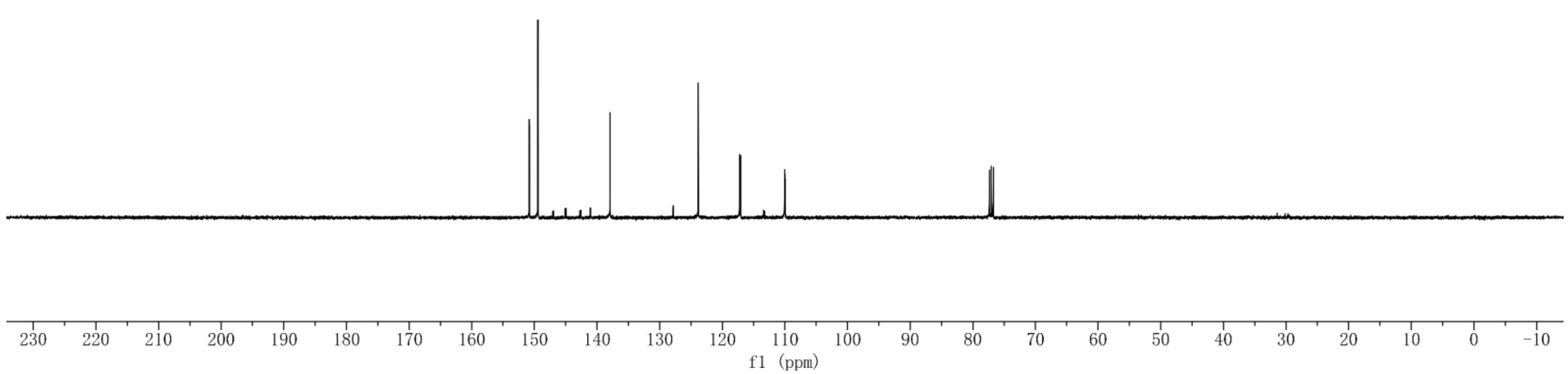


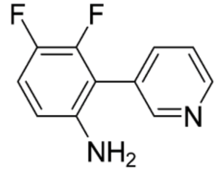
^{13}C NMR (100 MHz, $CDCl_3$)

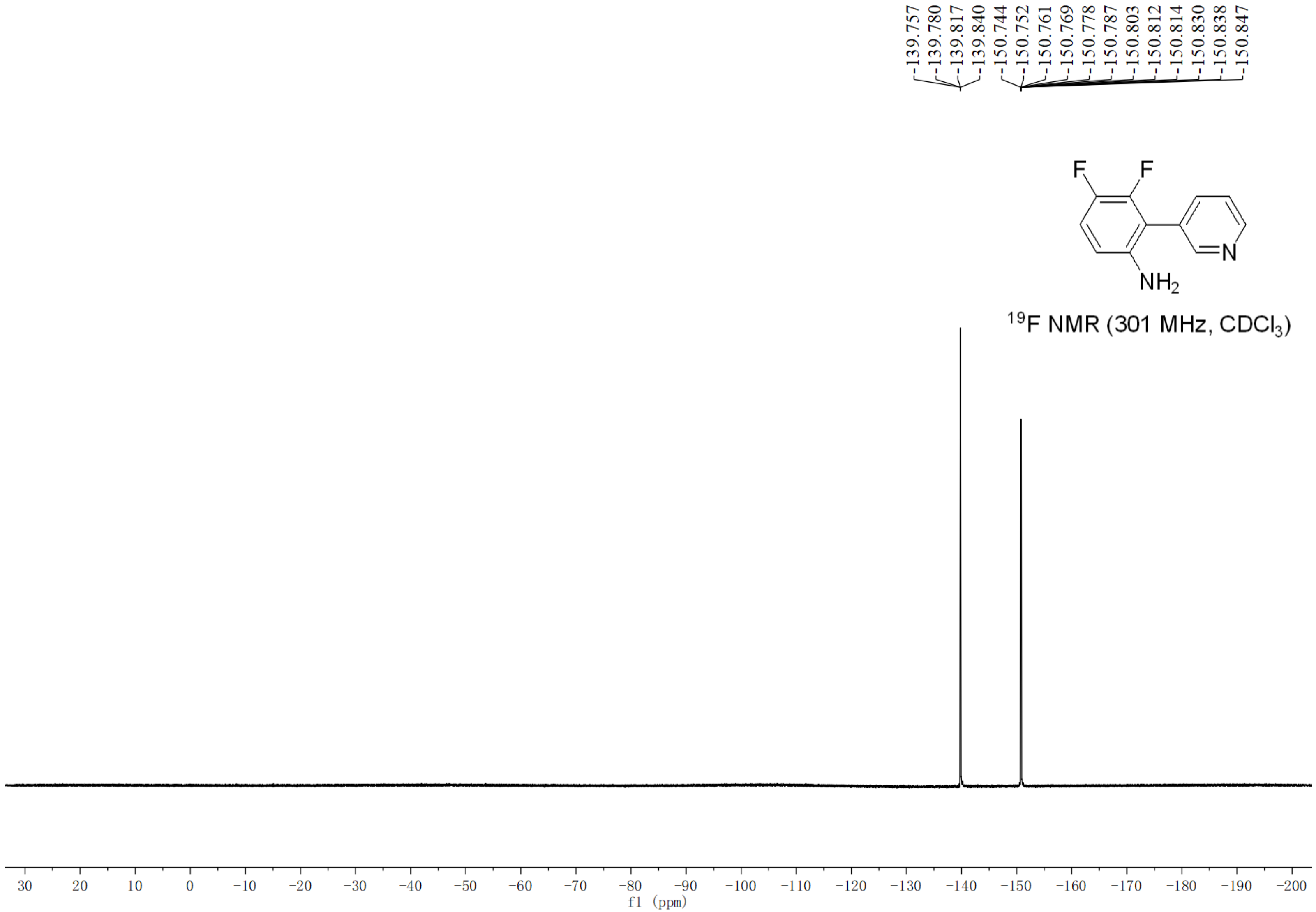


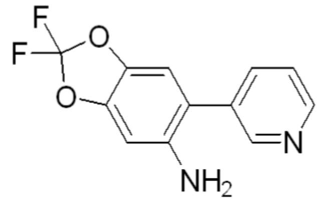
^{1}H NMR (400 MHz, $CDCl_3$)

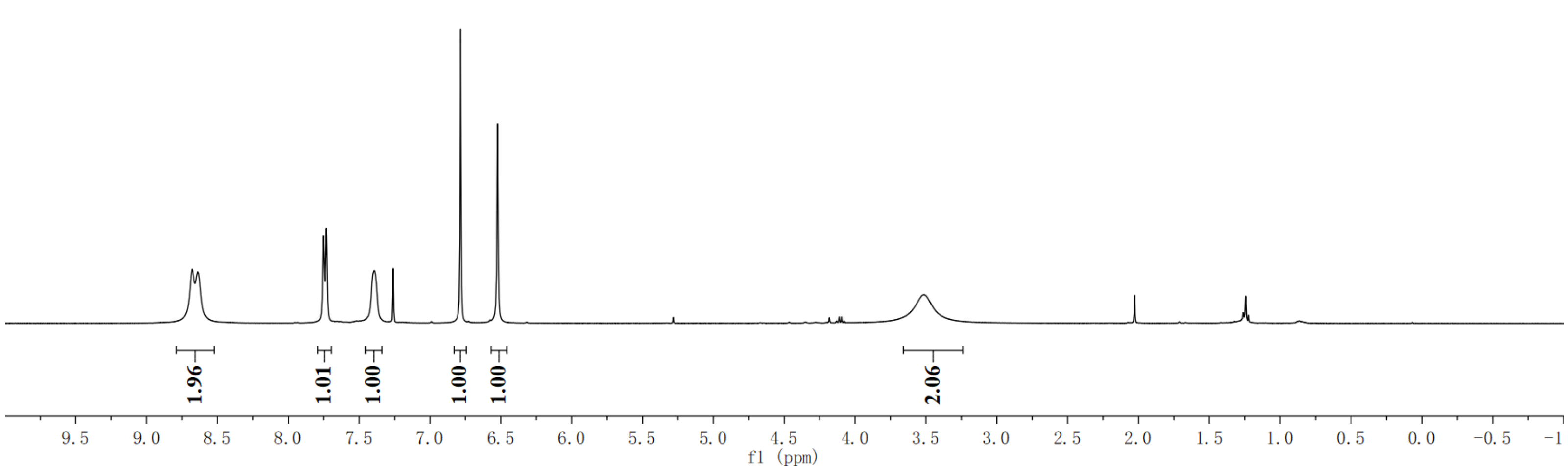
^{13}C NMR (100 MHz, $CDCl_3$)



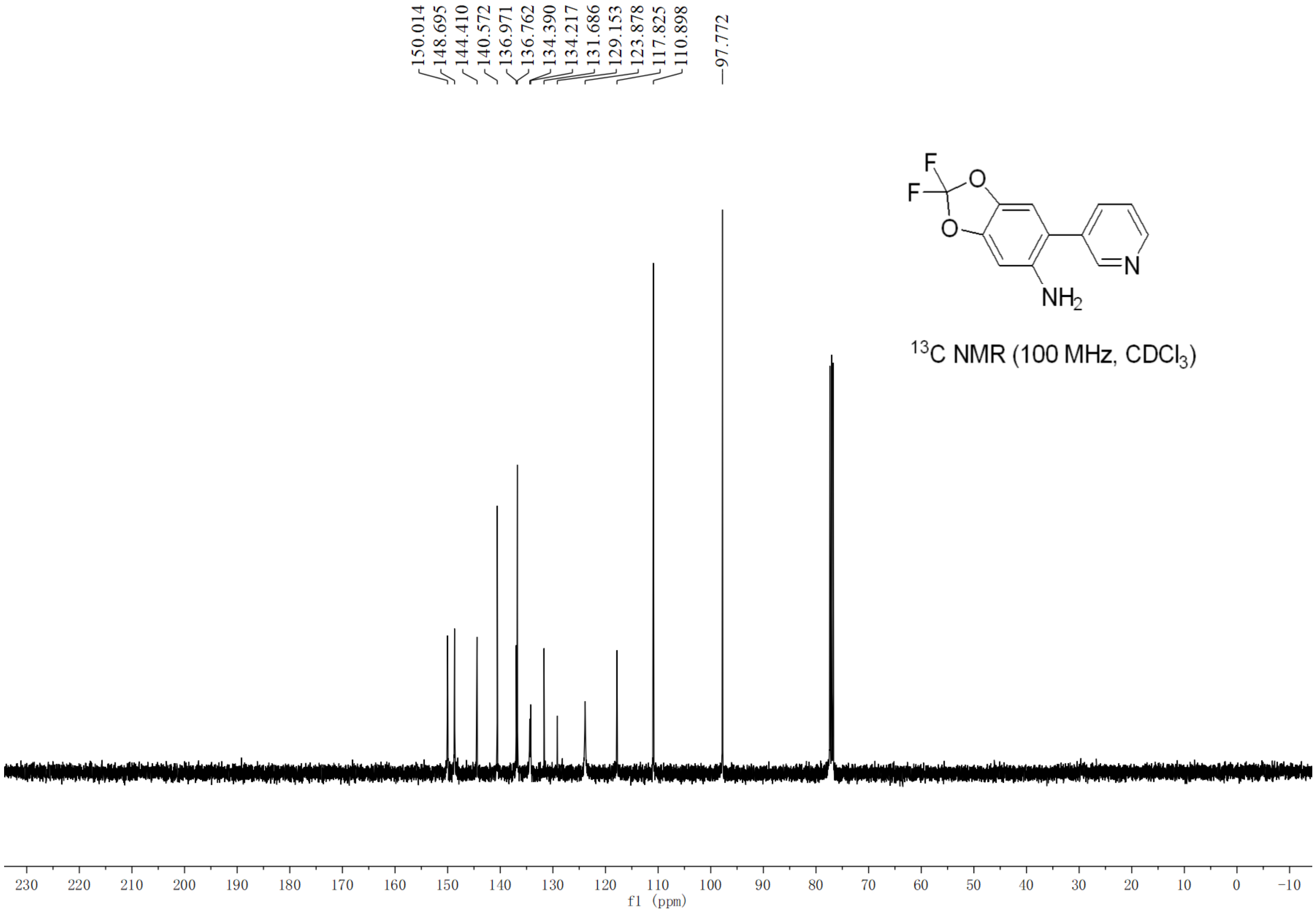


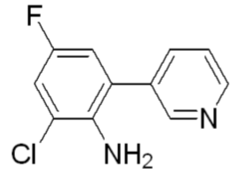

-139.757
-139.780
-139.817
-139.840
-150.744
-150.752
-150.761
-150.769
-150.778
-150.787
-150.803
-150.812
-150.814
-150.830
-150.838
-150.847
F
F
N
NH2
19F NMR (301 MHz, CDCl3)
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)



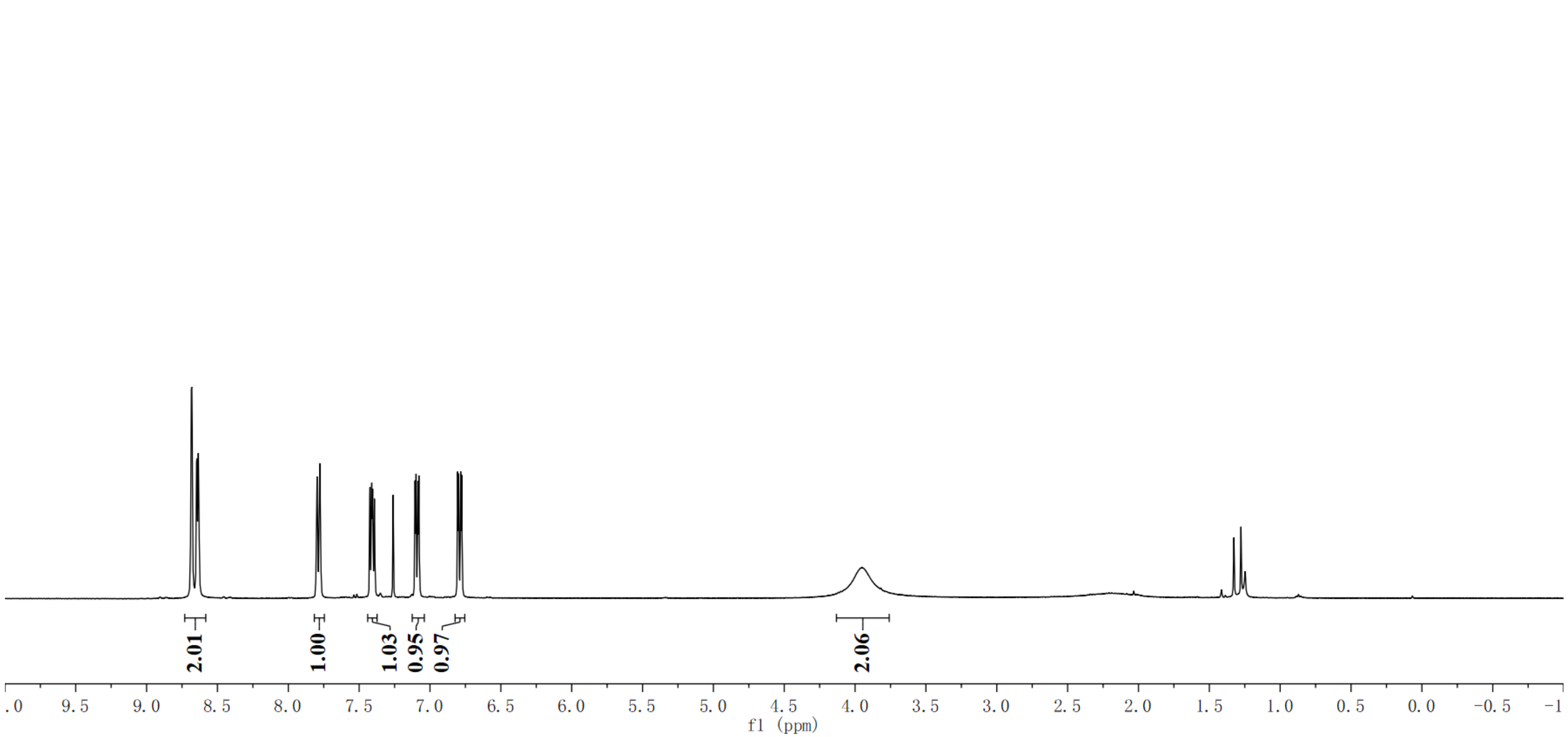


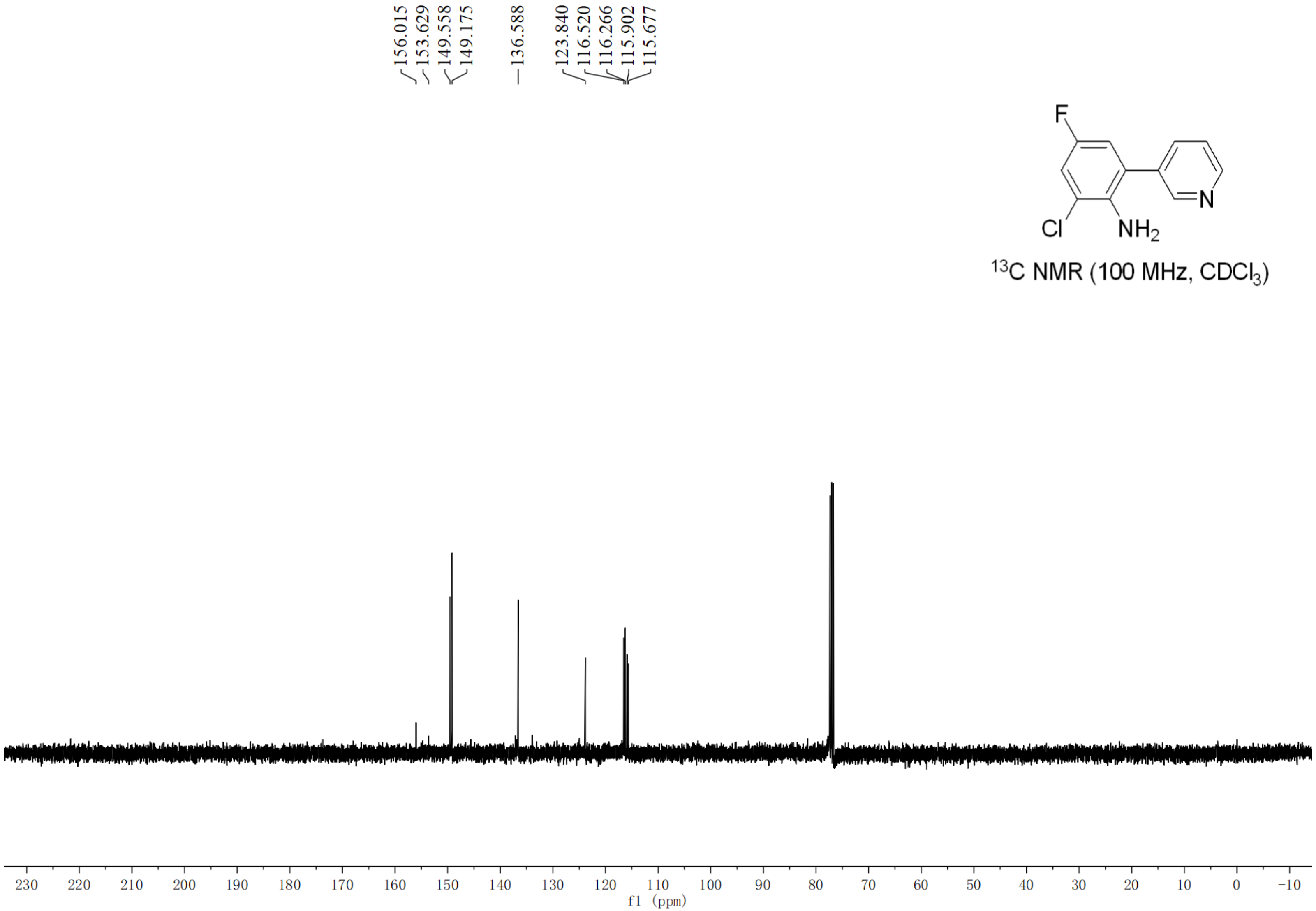
^1H NMR (400 MHz, $CDCl_3$)


150.014
148.695
144.410
140.572
136.971
136.762
134.390
134.217
131.686
129.153
123.878
117.825
110.898
97.772
F
F
O
O
N
NH_2
^{13}C NMR (100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

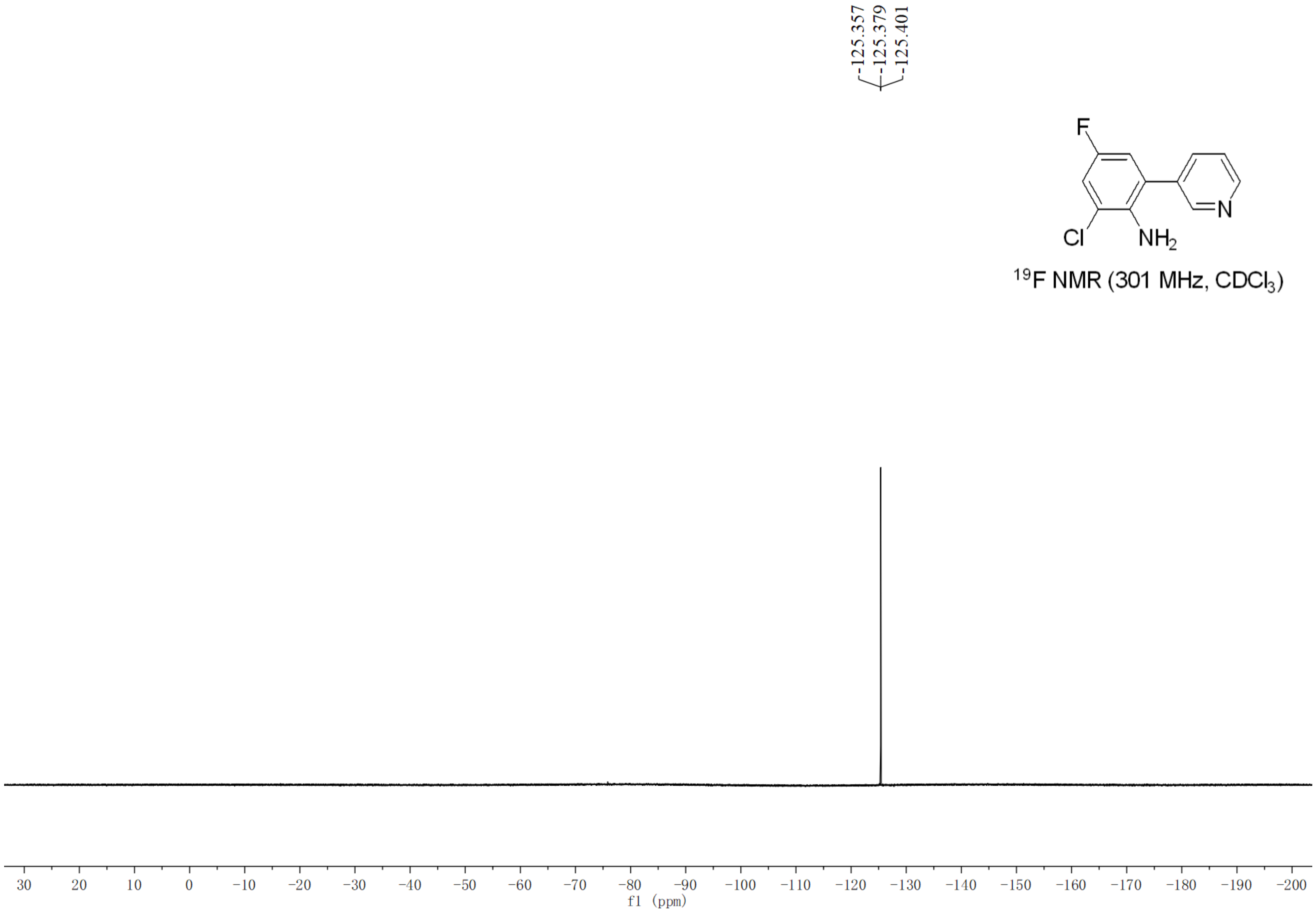


^{1}H NMR (400 MHz, $CDCl_3$)

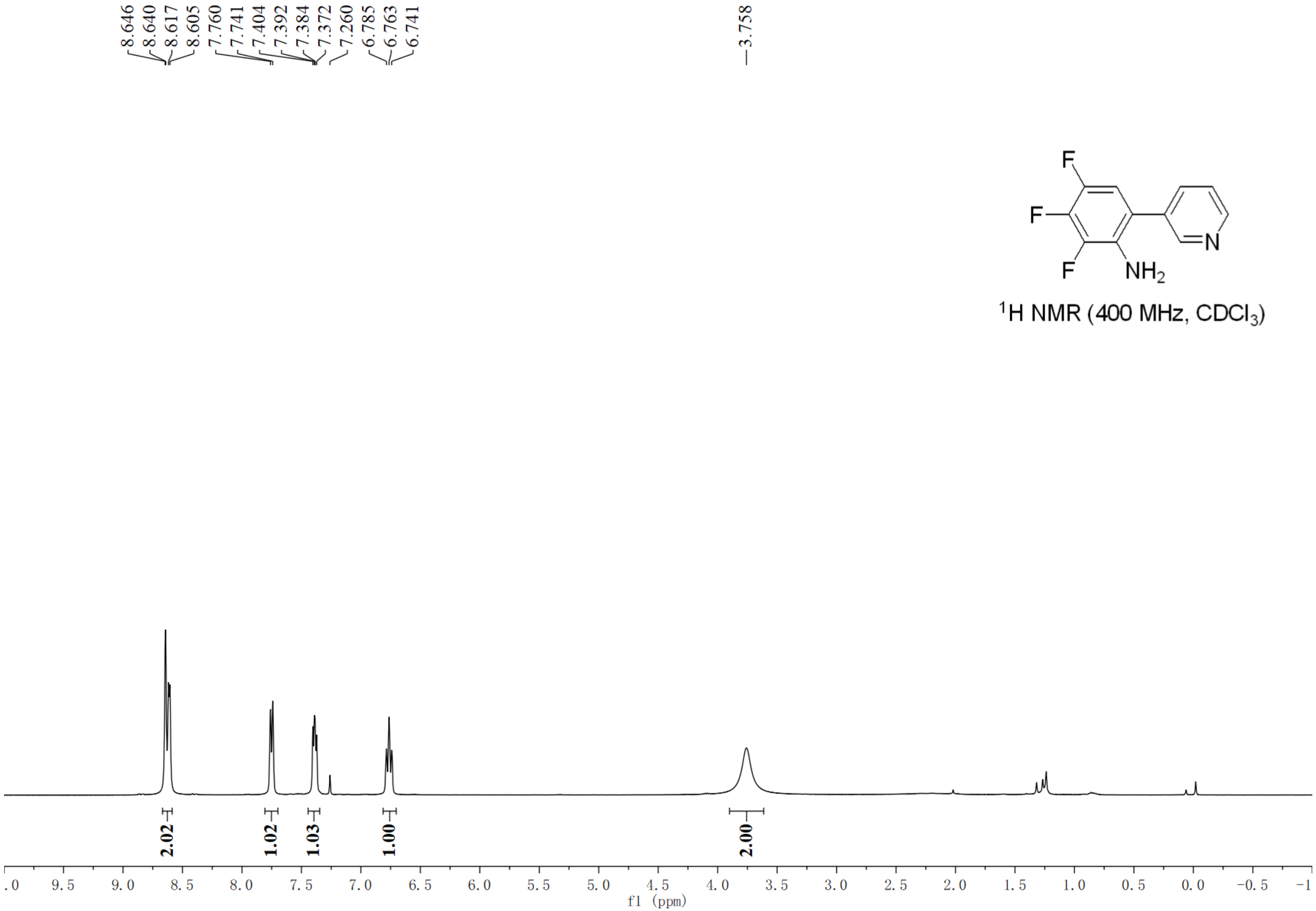




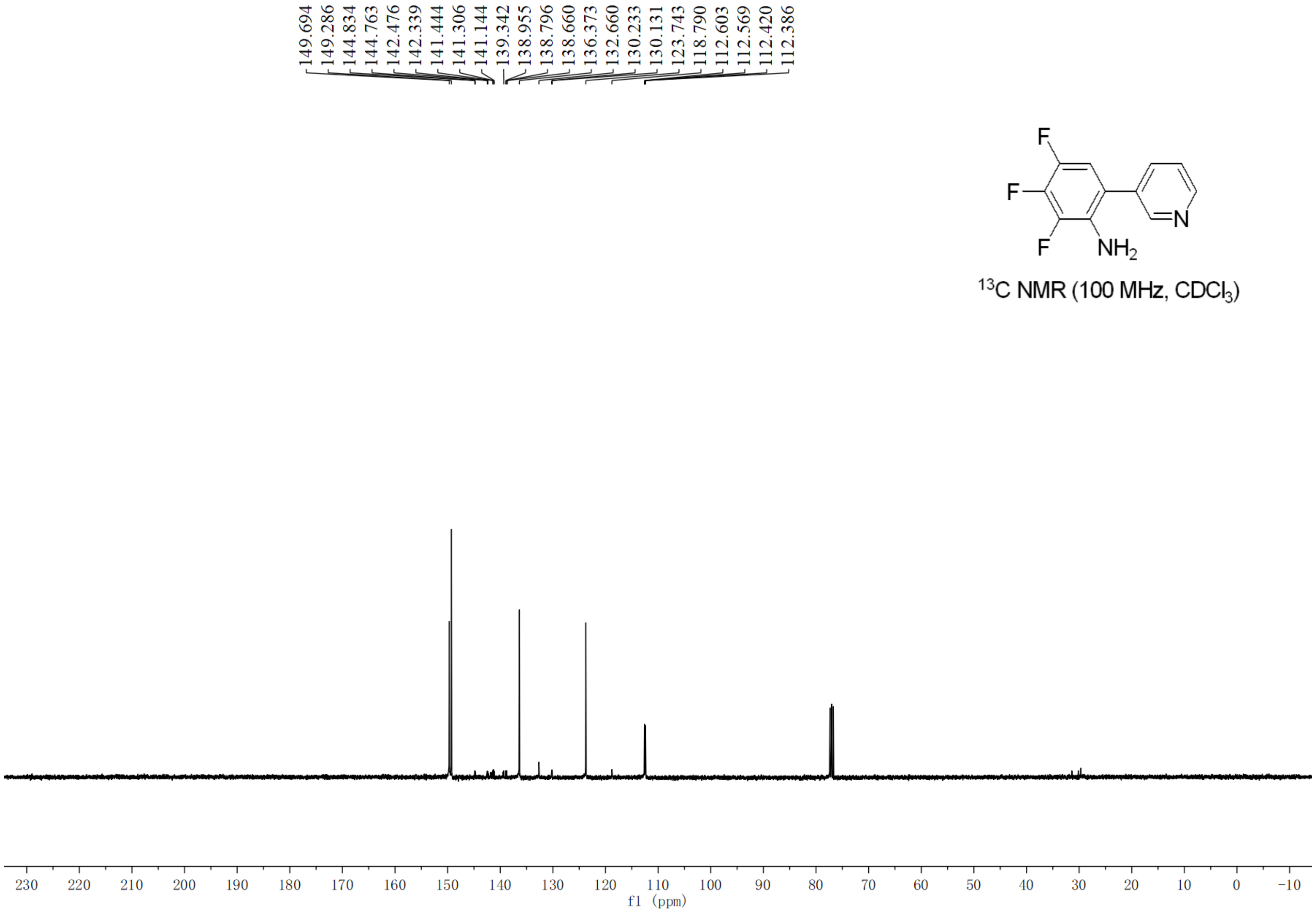
^{13}C NMR (100 MHz, $CDCl_3$)



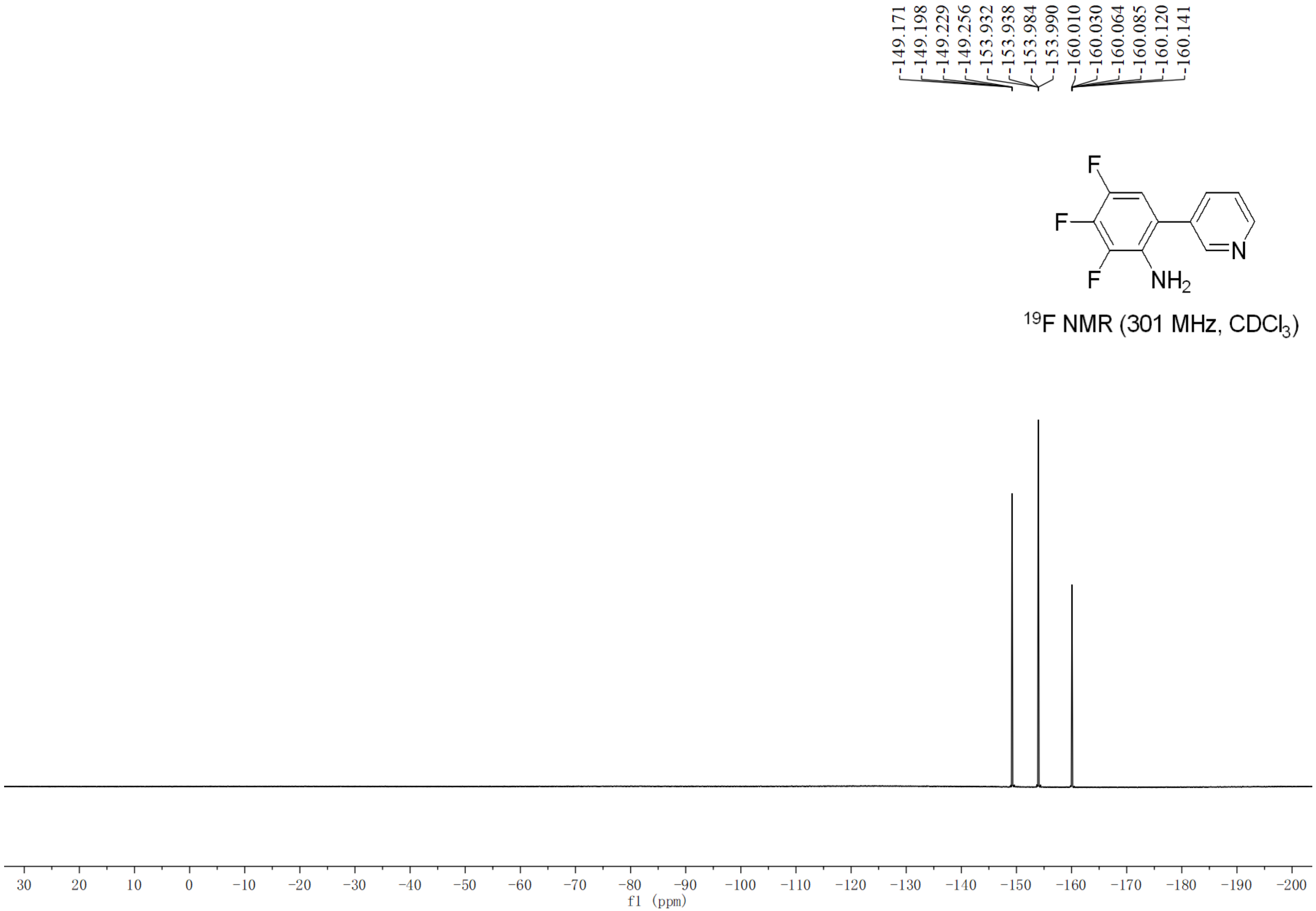
^{19}F NMR (301 MHz, $CDCl_3$)



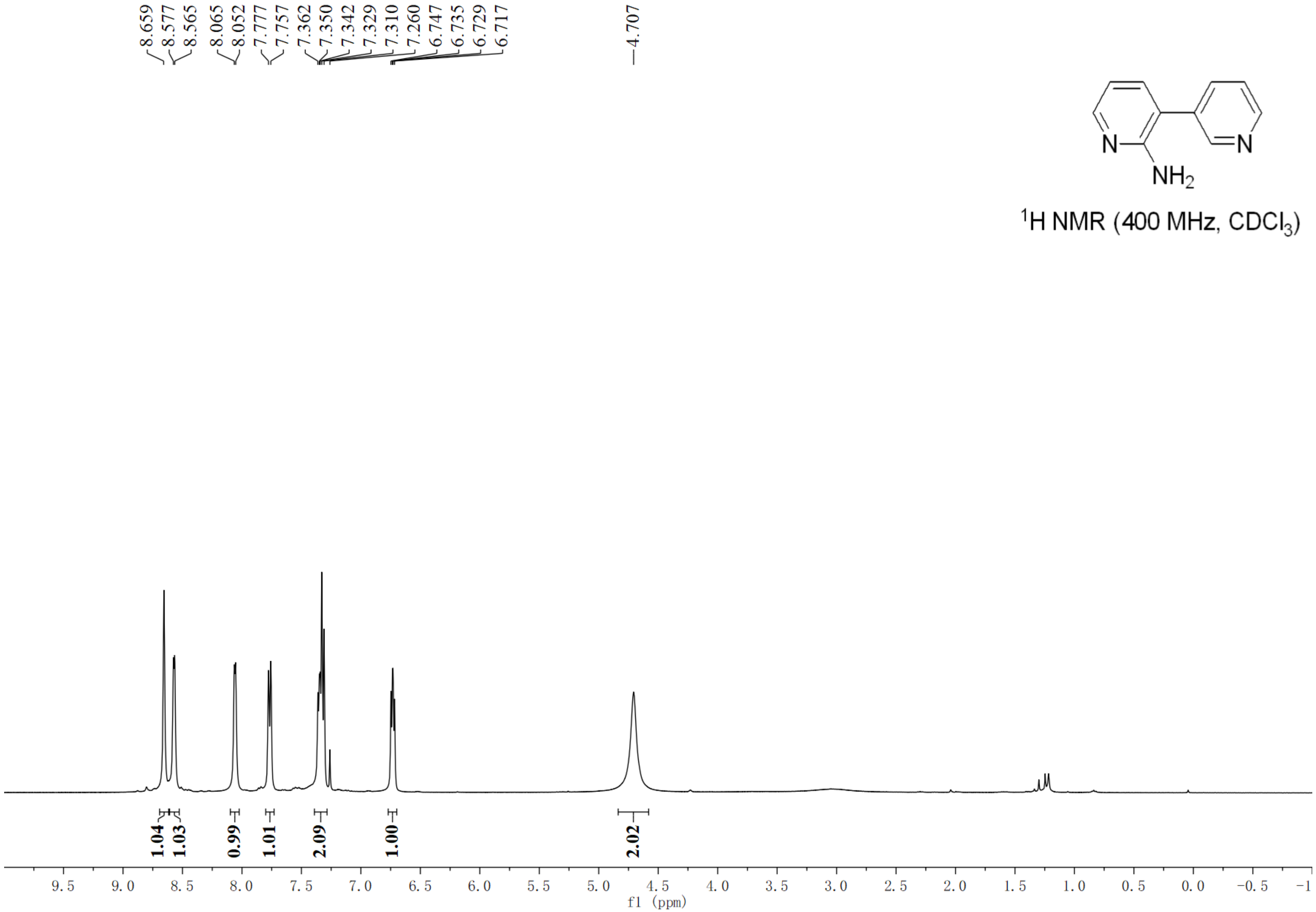
^{1}H NMR (400 MHz, $CDCl_3$)



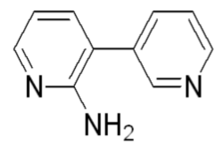
^{13}C NMR (100 MHz, $CDCl_3$)



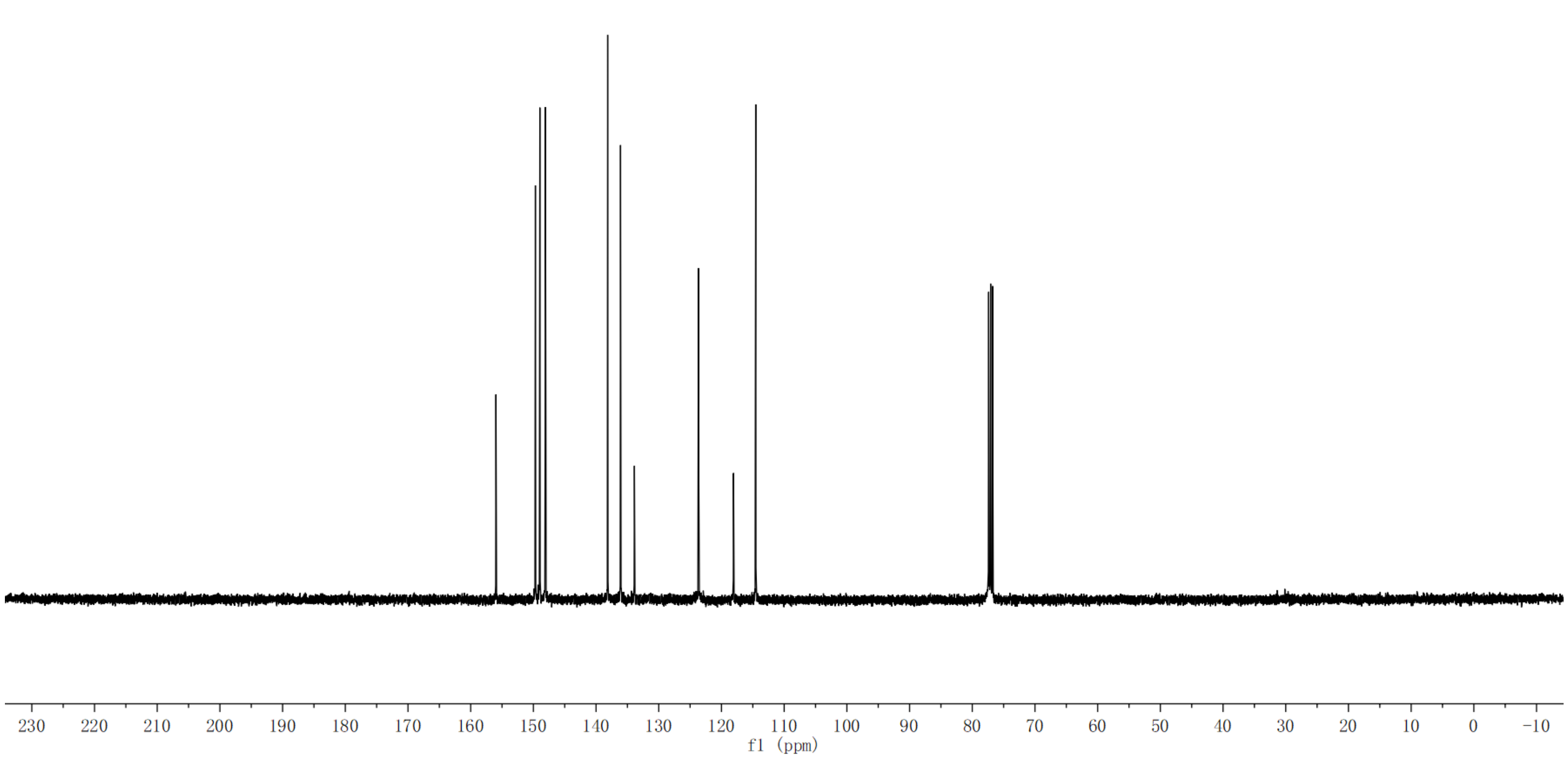
^{19}F NMR (301 MHz, $CDCl_3$)

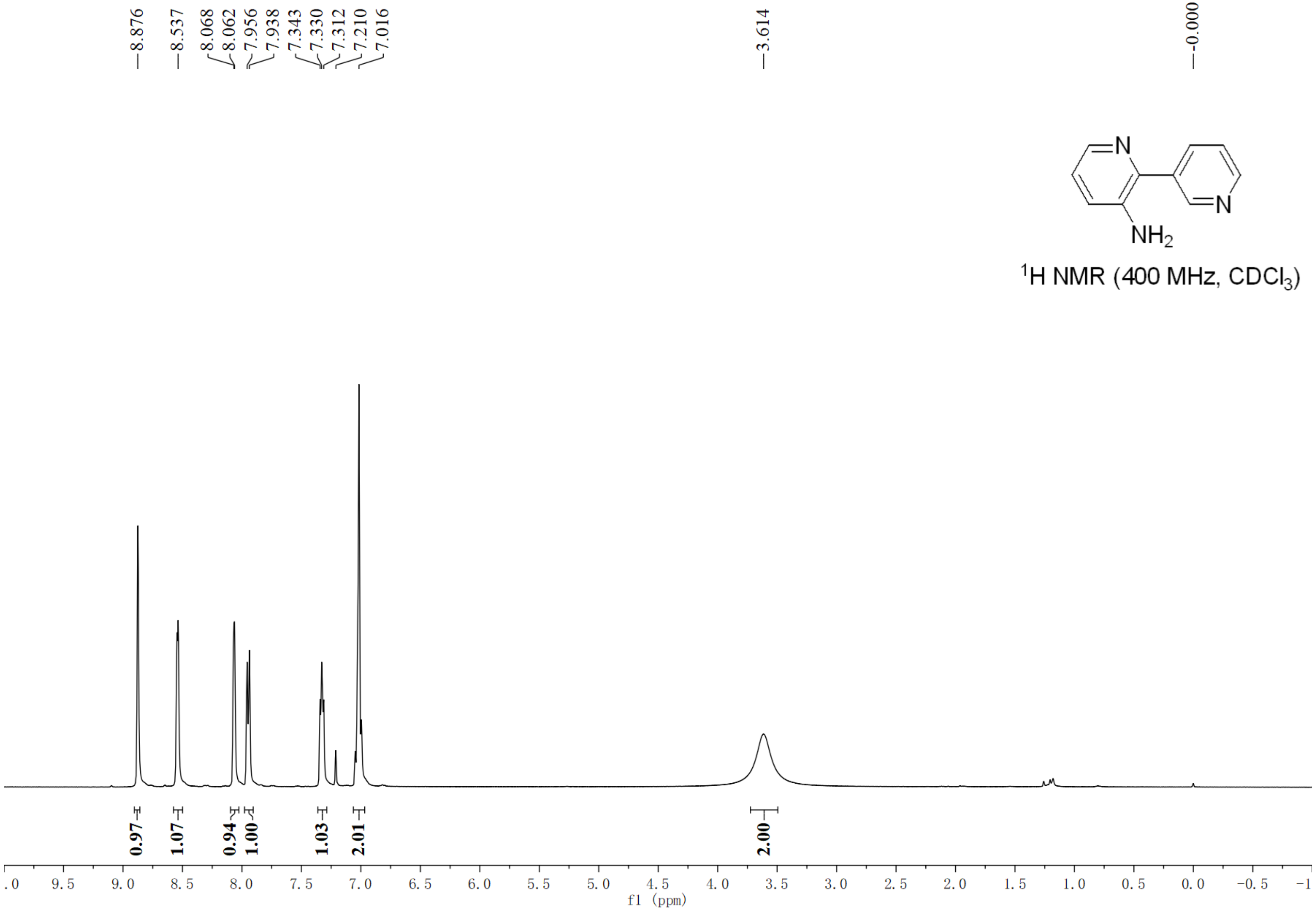


^{1}H NMR (400 MHz, $CDCl_3$)

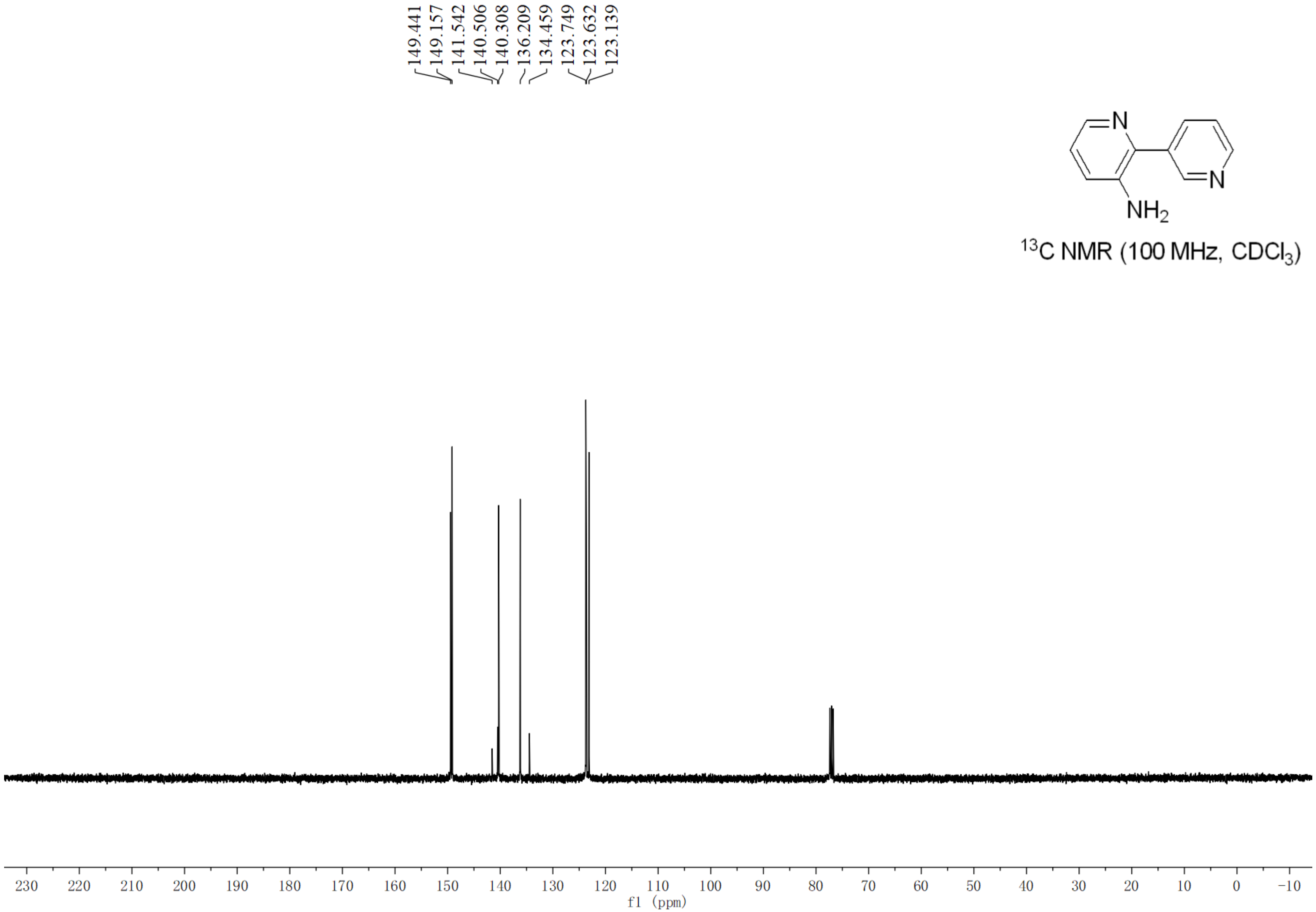


^{13}C NMR (100 MHz, $CDCl_3$)

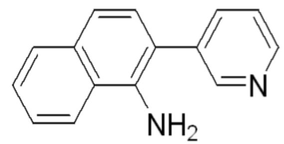




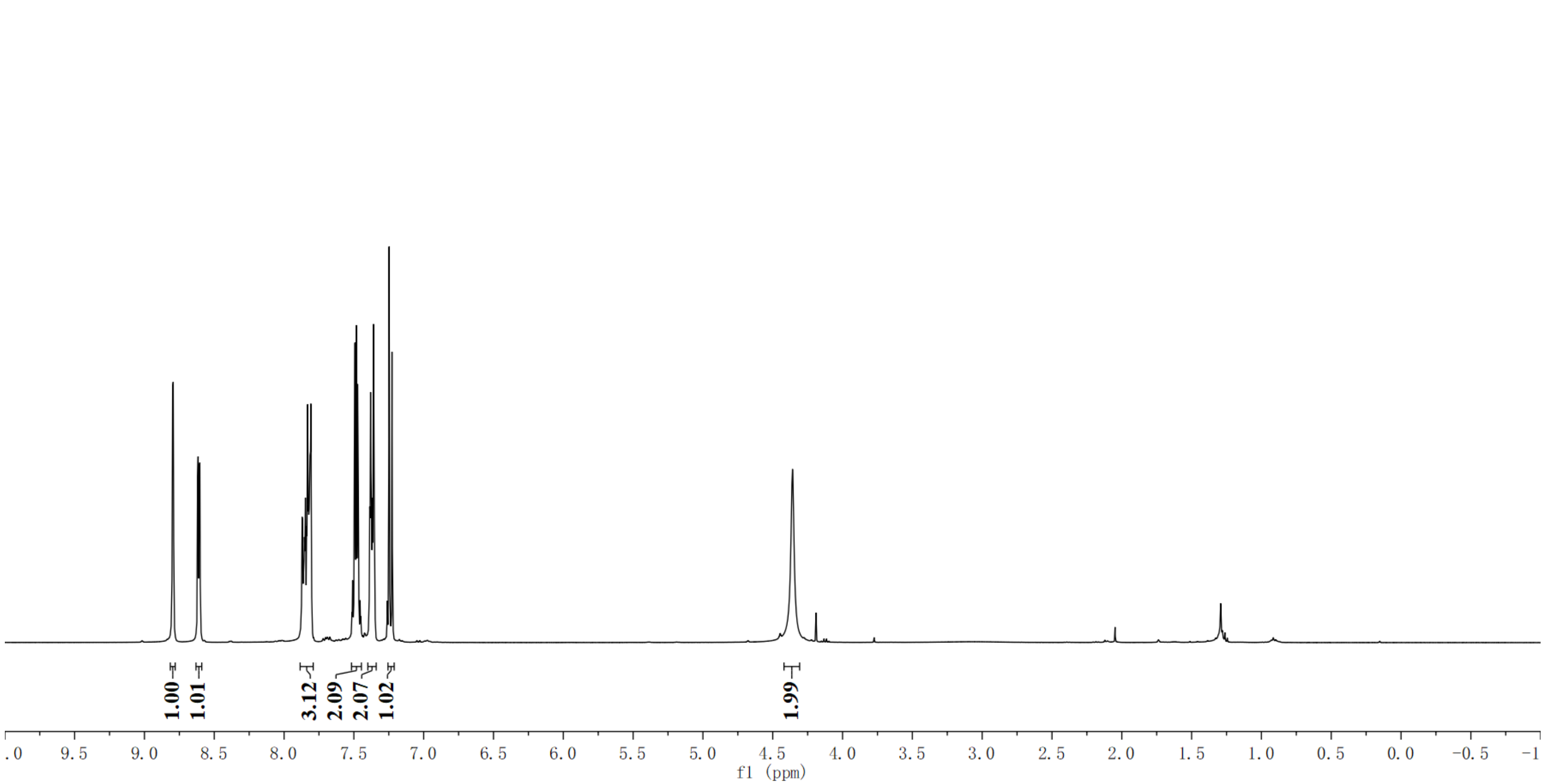
8.876
8.537
8.068
8.062
7.956
7.938
7.343
7.330
7.312
7.210
7.016
3.614
0.000
N
N
NH2
1H NMR (400 MHz, CDCl3)
0.97
1.07
0.94
1.00
1.03
2.01
2.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

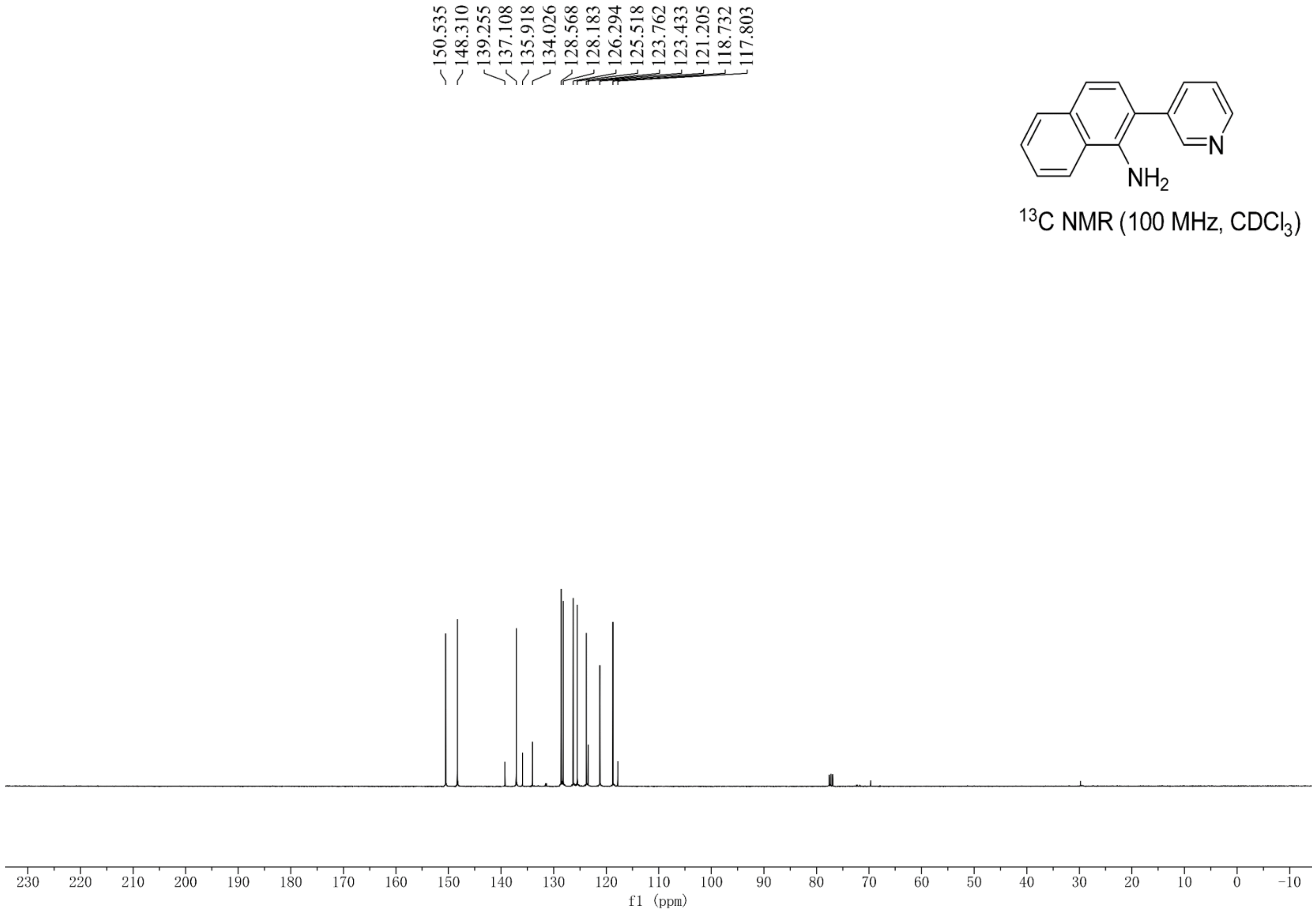


^{13}C NMR (100 MHz, $CDCl_3$)

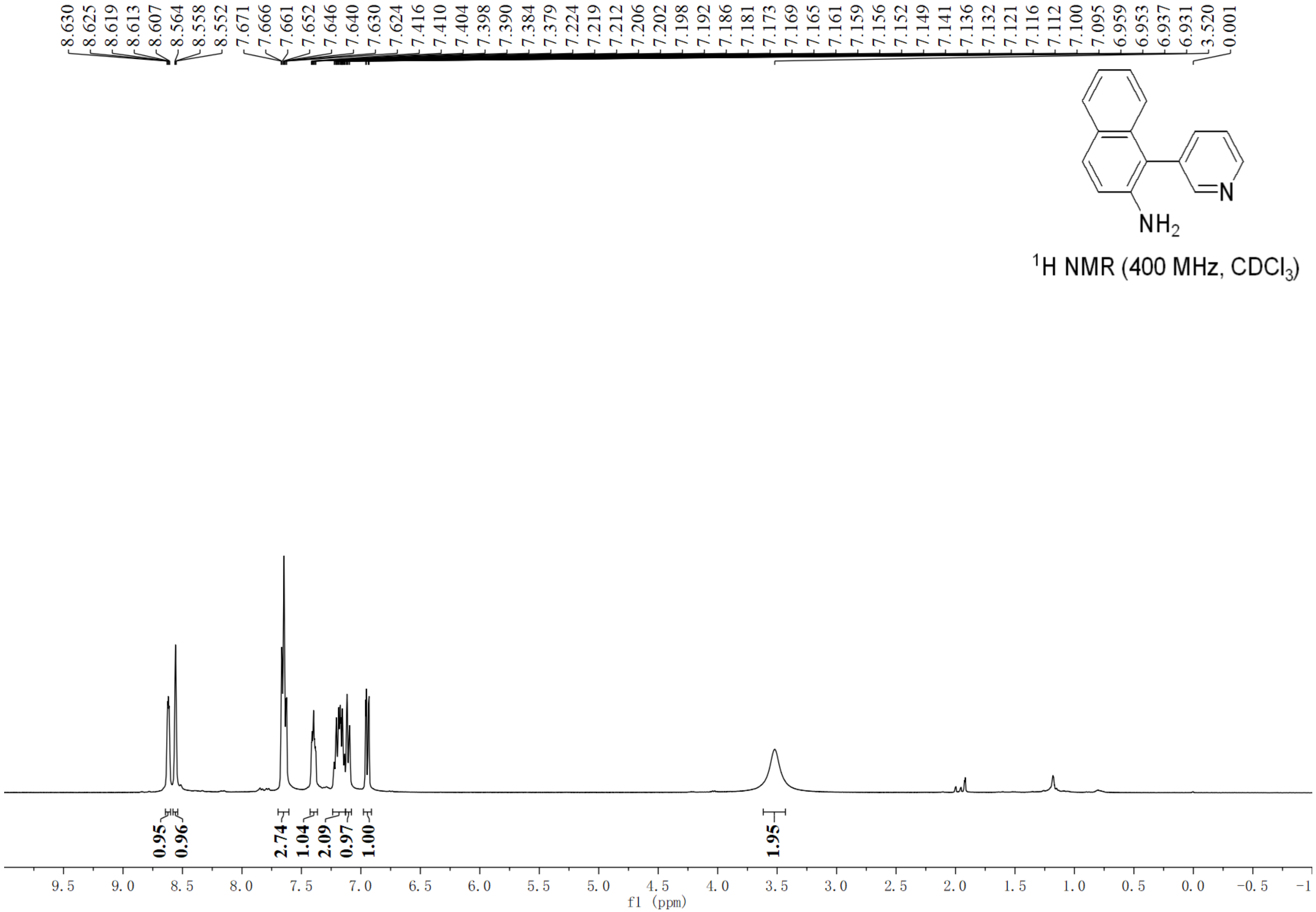


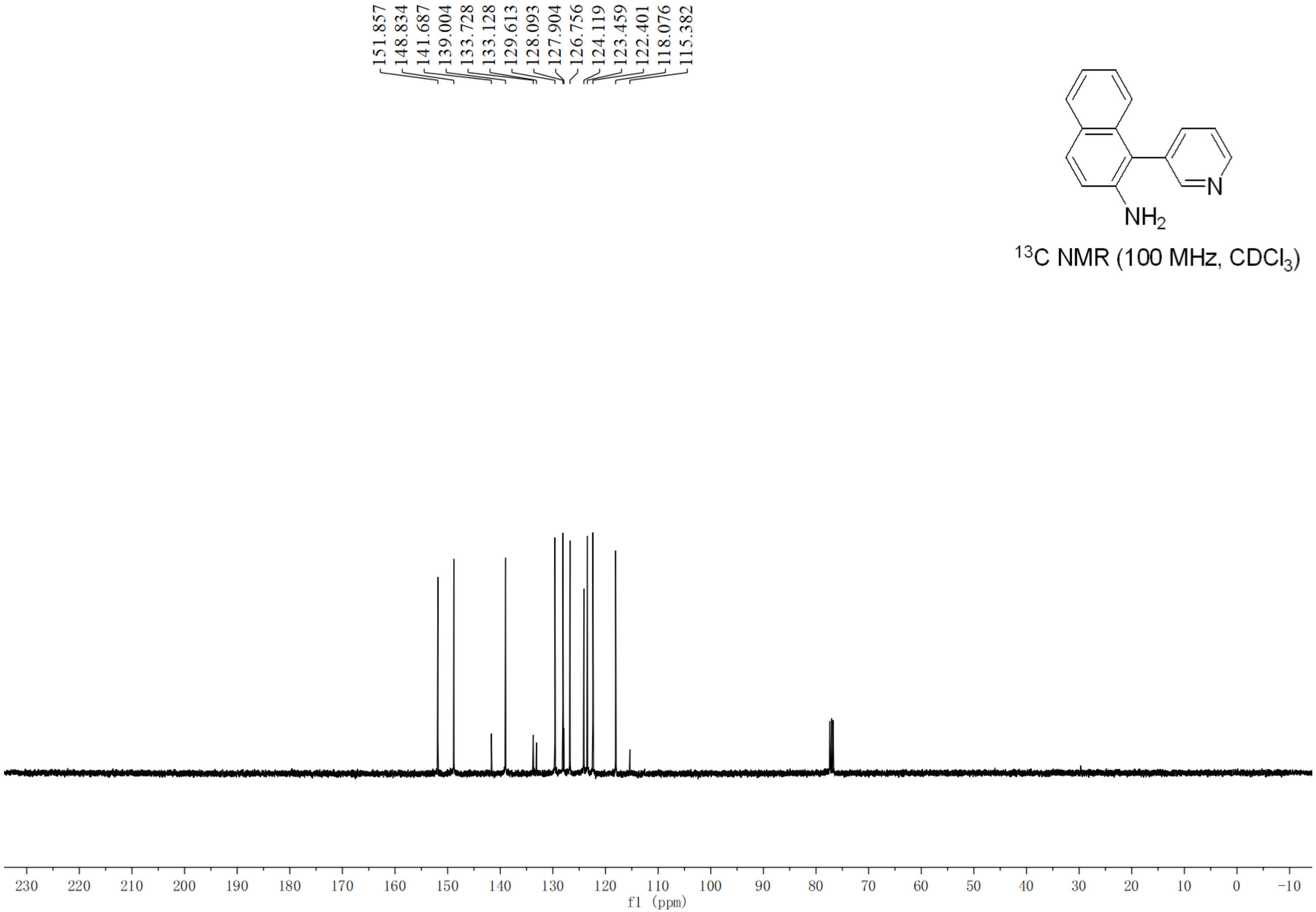
^{1}H NMR (400 MHz, $CDCl_3$)



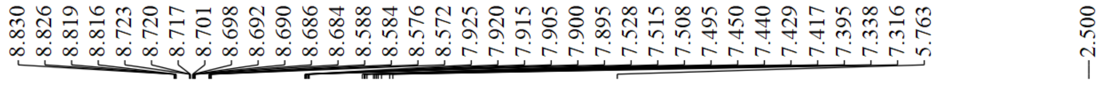


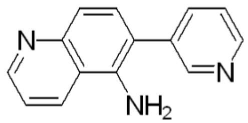
^{13}C NMR (100 MHz, $CDCl_3$)


8.630
8.625
8.619
8.613
8.607
8.564
8.558
8.552
7.671
7.666
7.661
7.652
7.646
7.640
7.630
7.624
7.416
7.410
7.404
7.398
7.390
7.384
7.379
7.224
7.219
7.212
7.206
7.202
7.198
7.192
7.186
7.181
7.173
7.169
7.165
7.161
7.159
7.156
7.152
7.149
7.141
7.136
7.132
7.121
7.116
7.112
7.100
7.095
6.959
6.953
6.937
6.931
3.520
0.001
NH2
N
1H NMR (400 MHz, CDCl3)
0.95
0.96
2.74
1.04
2.09
0.97
1.00
1.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

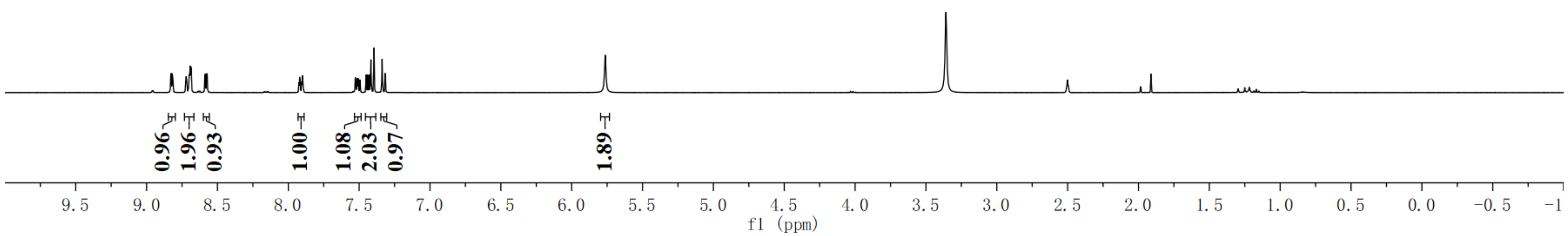


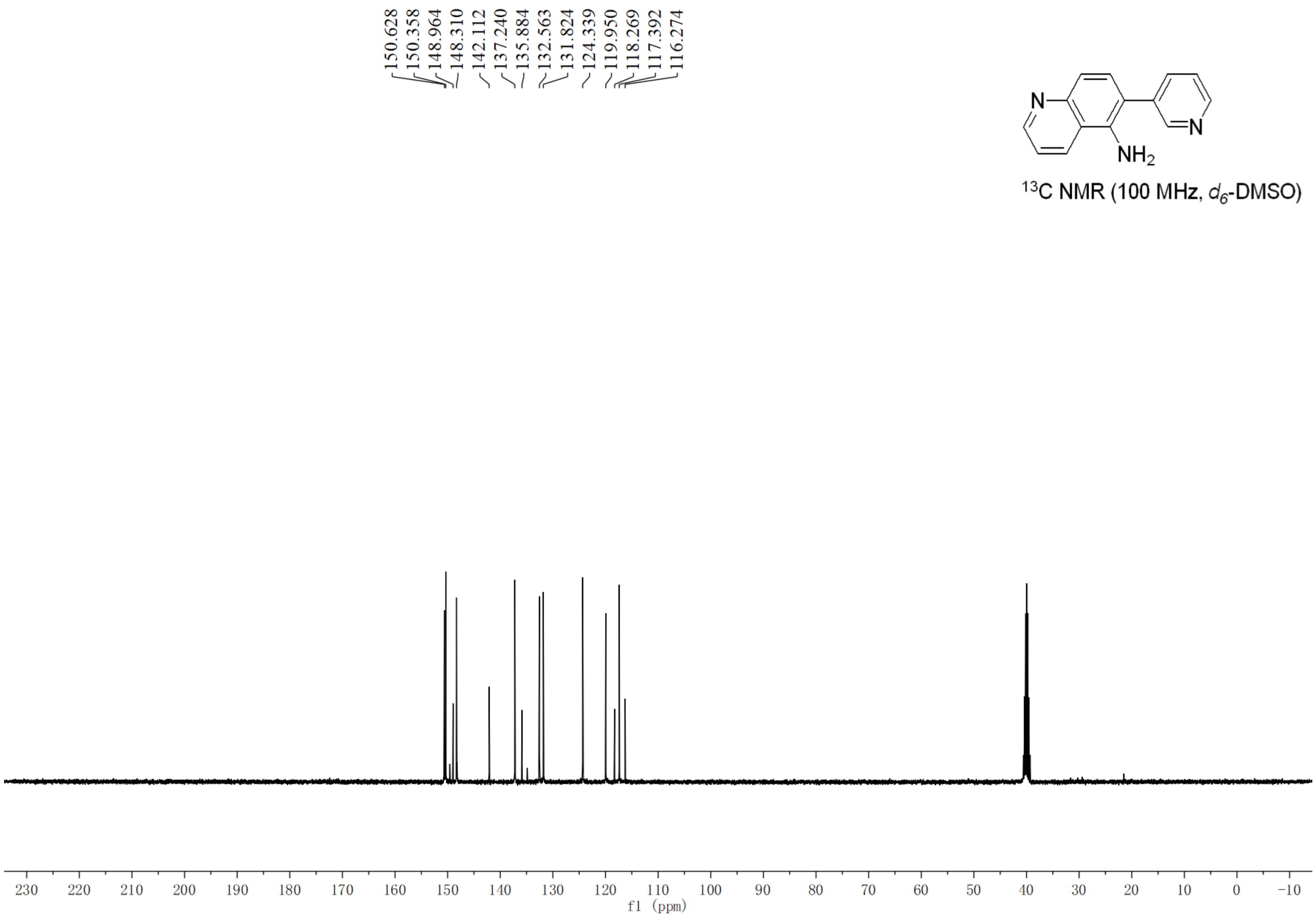
^{13}C NMR (100 MHz, $CDCl_3$)

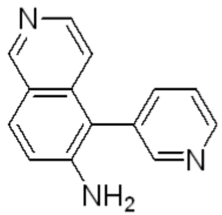




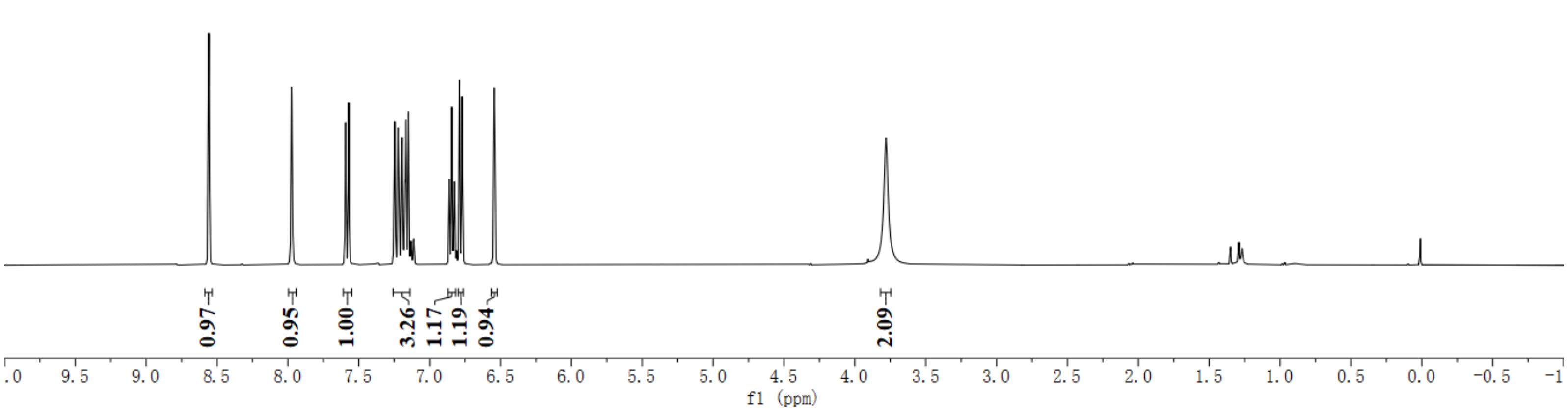
^{1}H NMR (400 MHz, d_6-DMSO)

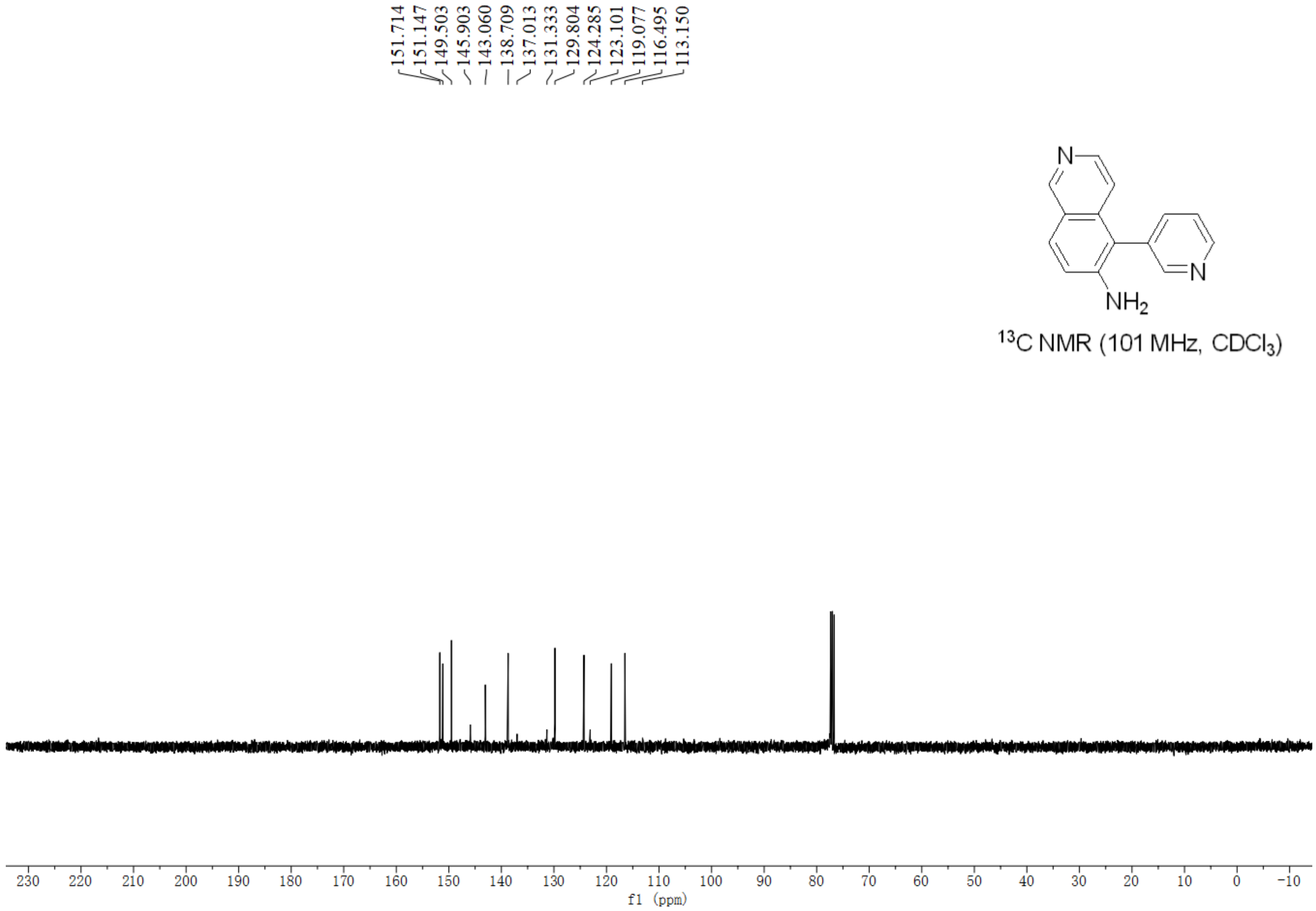



150.628
150.358
148.964
148.310
142.112
137.240
135.884
132.563
131.824
124.339
119.950
118.269
117.392
116.274
N
N
NH2
13C NMR (100 MHz, d6-DMSO)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

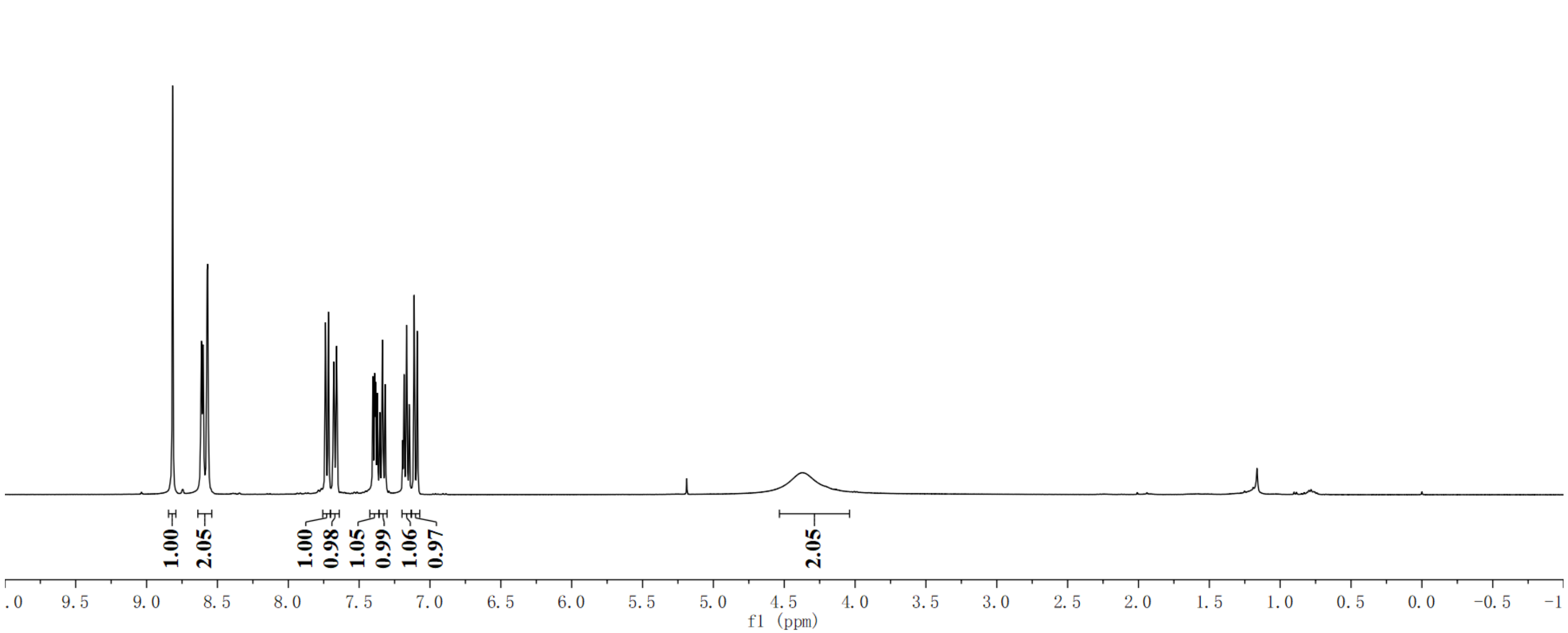


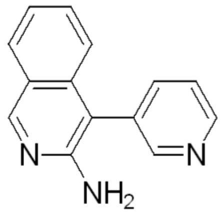
^1H NMR (400 MHz, $CDCl_3$)





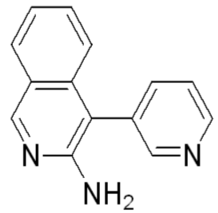
^{13}C NMR (101 MHz, $CDCl_3$)



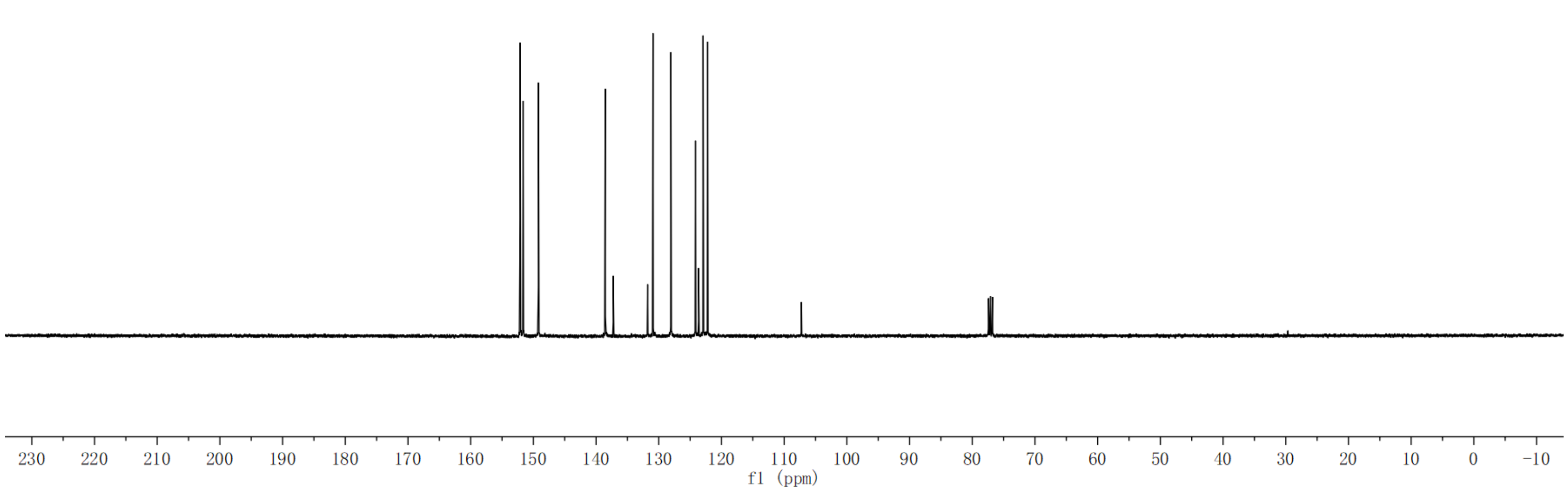


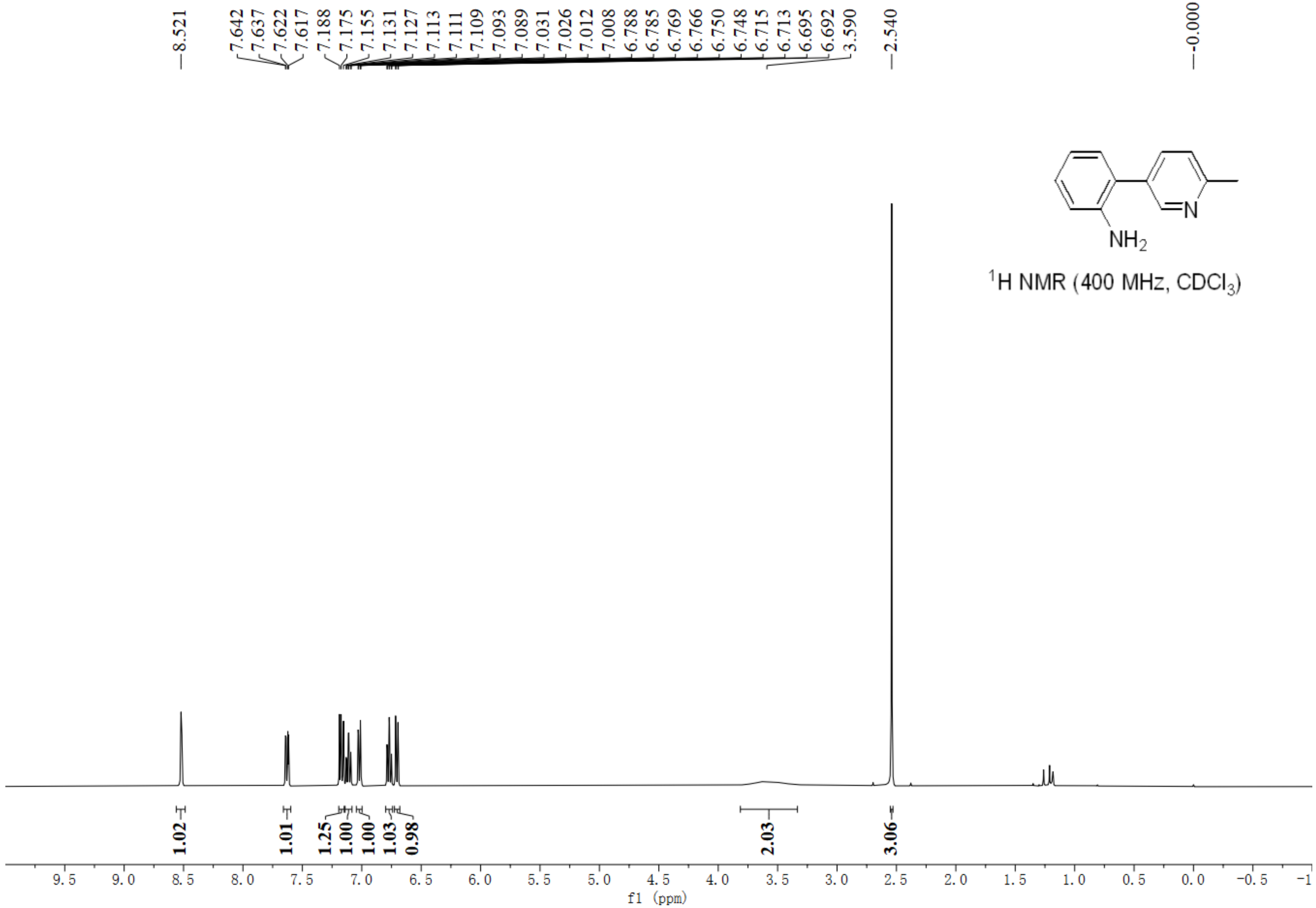
^{1}H NMR (400 MHz, $CDCl_3$)

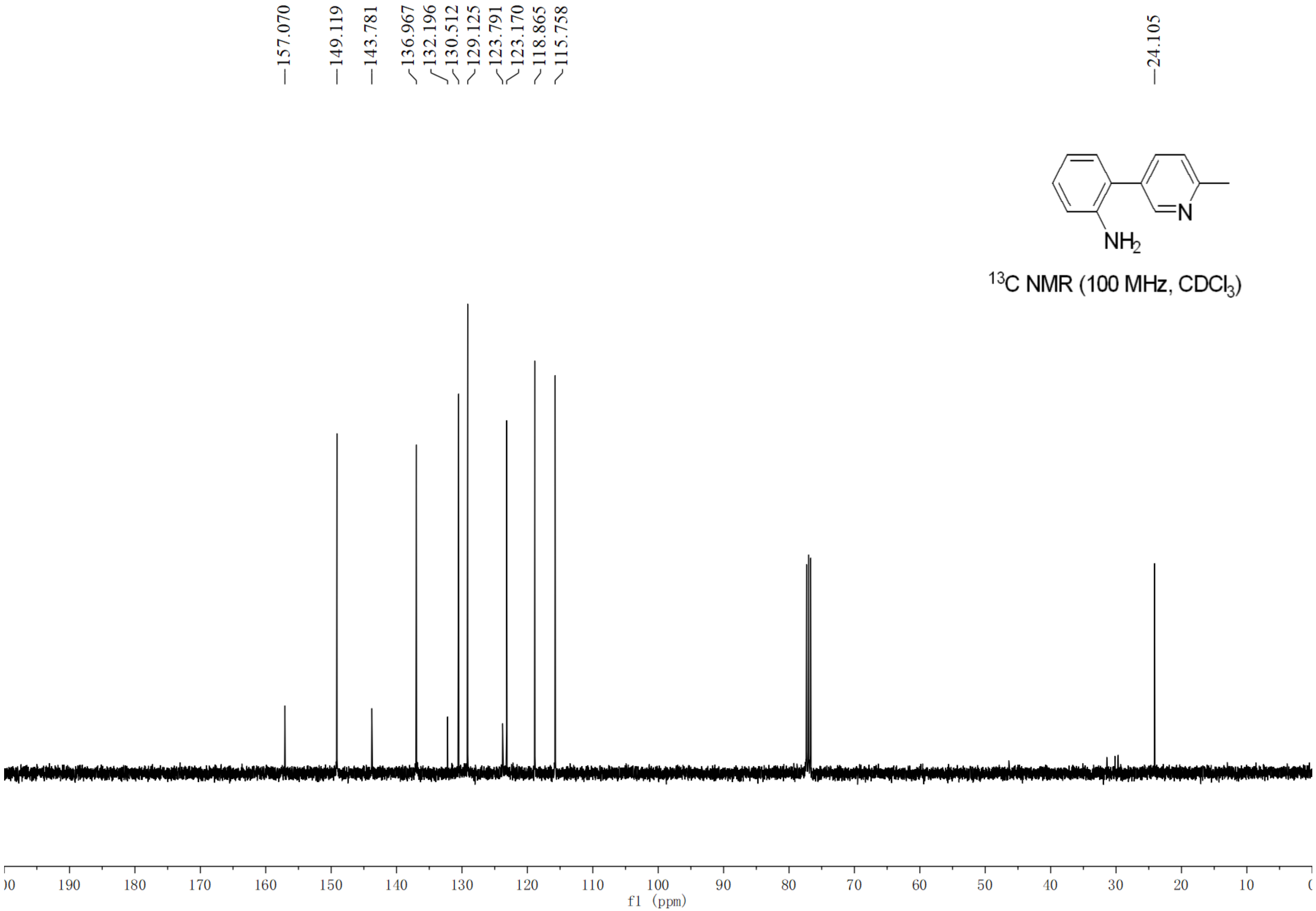
152.126
152.111
151.636
149.193
138.537
137.259
131.774
130.924
128.071
124.144
123.656
122.924
122.209
107.253



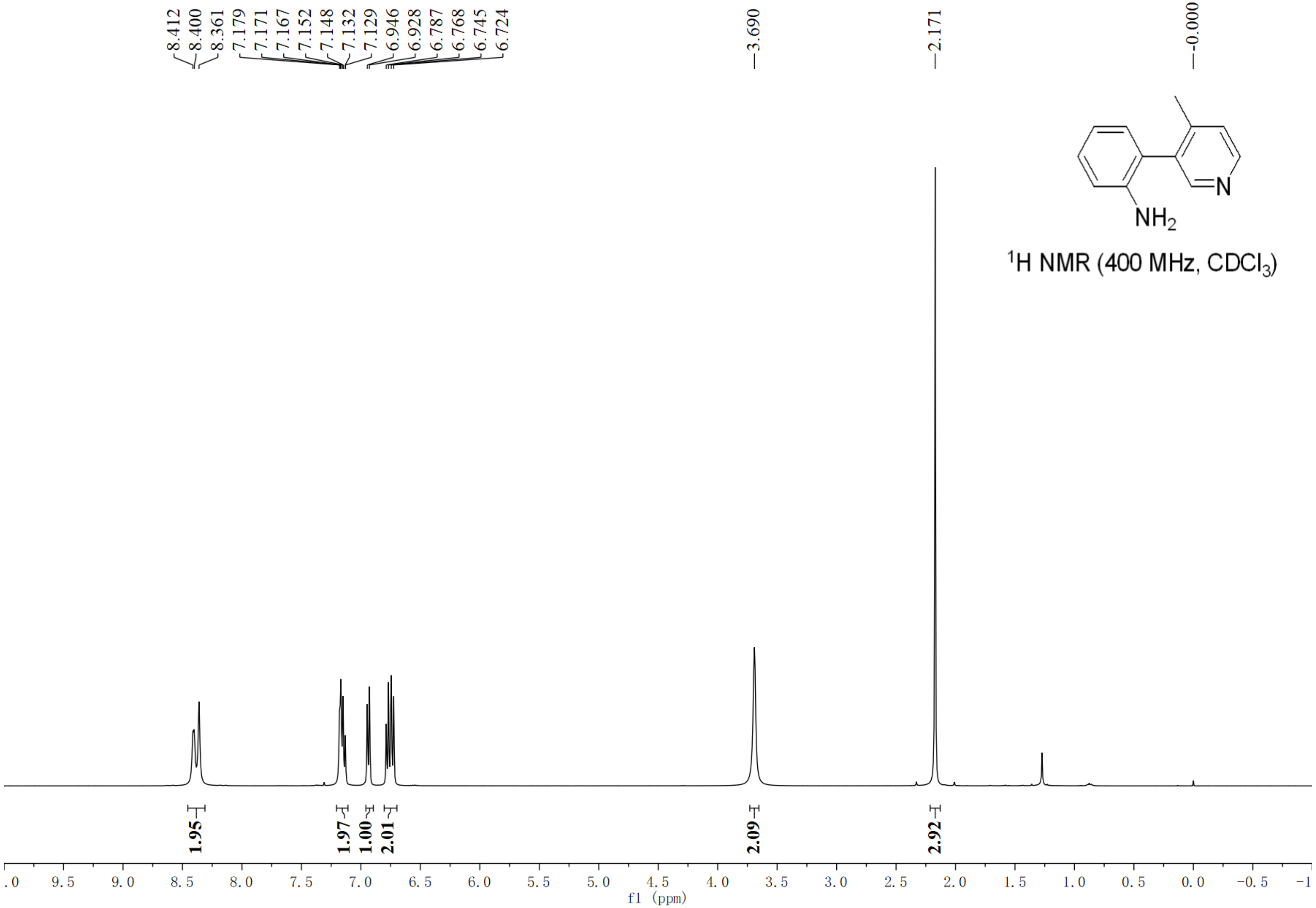
^{13}C NMR (100 MHz, $CDCl_3$)



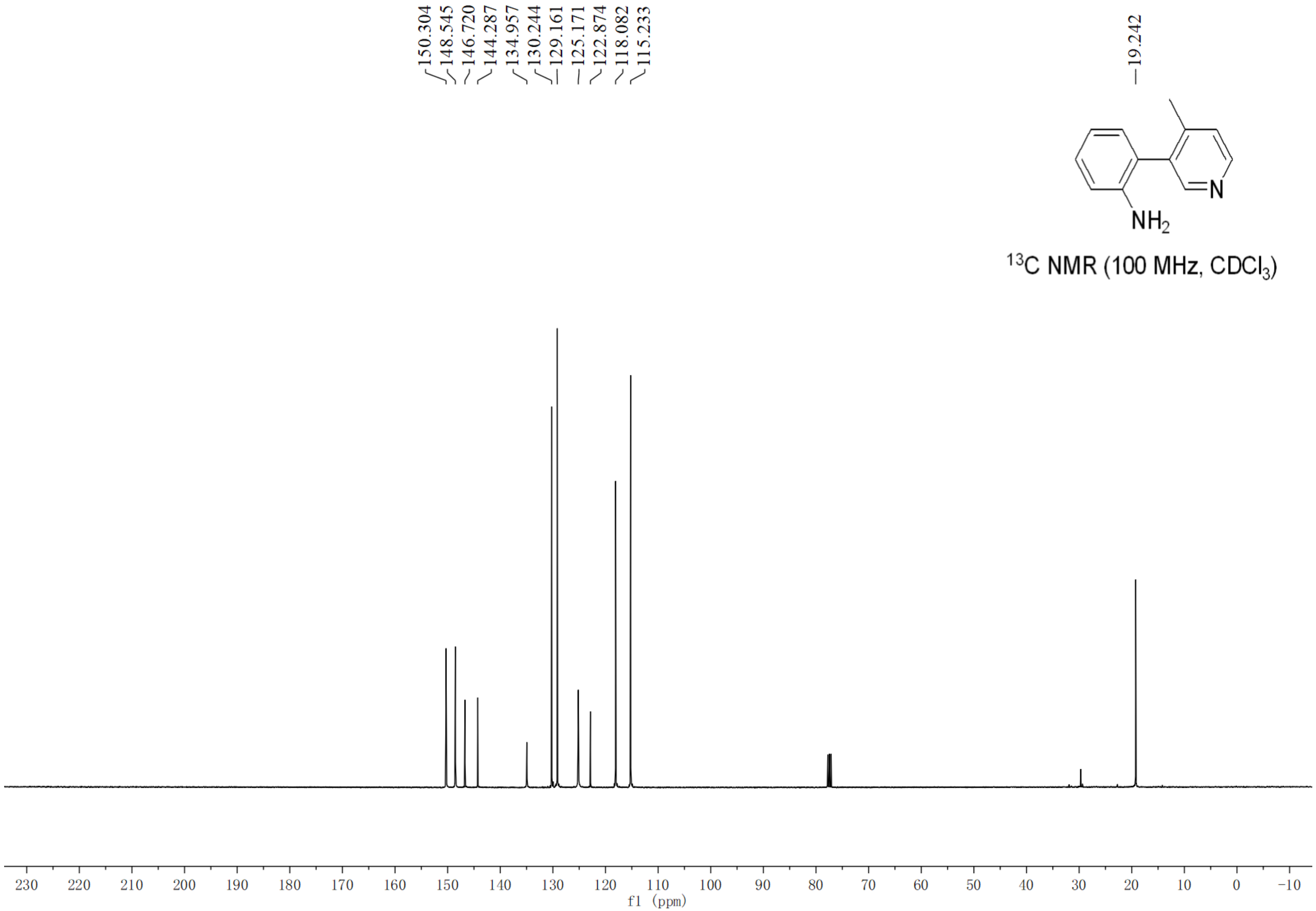

8.521
7.642
7.637
7.622
7.617
7.188
7.175
7.155
7.131
7.127
7.113
7.111
7.109
7.093
7.089
7.031
7.026
7.012
7.008
6.788
6.785
6.769
6.766
6.750
6.748
6.715
6.713
6.695
6.692
3.590
2.540
0.000
NH2
N
1H NMR (400 MHz, CDCl3)
1.02
1.01
1.25
1.00
1.00
1.03
0.98
2.03
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



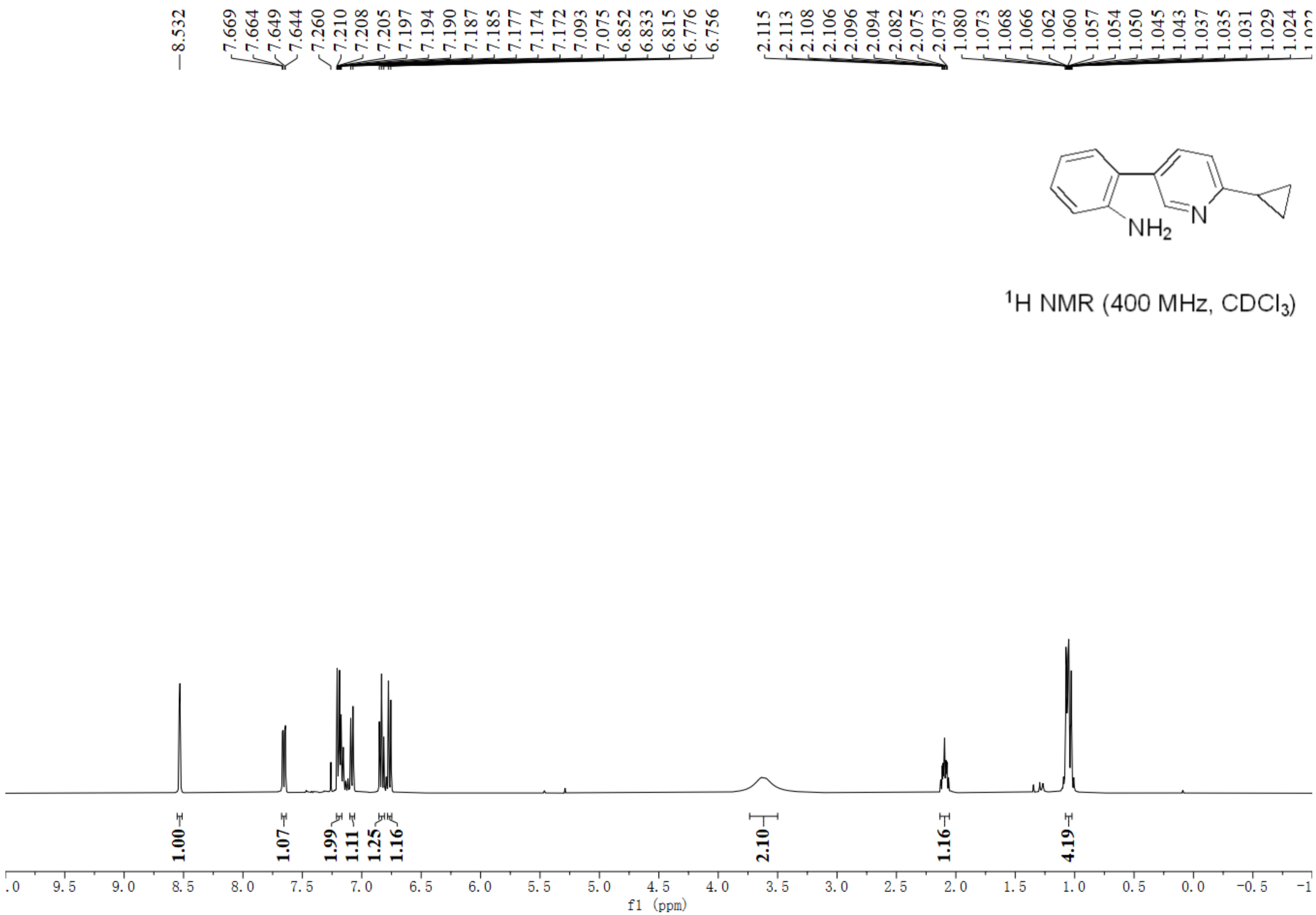
^{13}C NMR (100 MHz, $CDCl_3$)

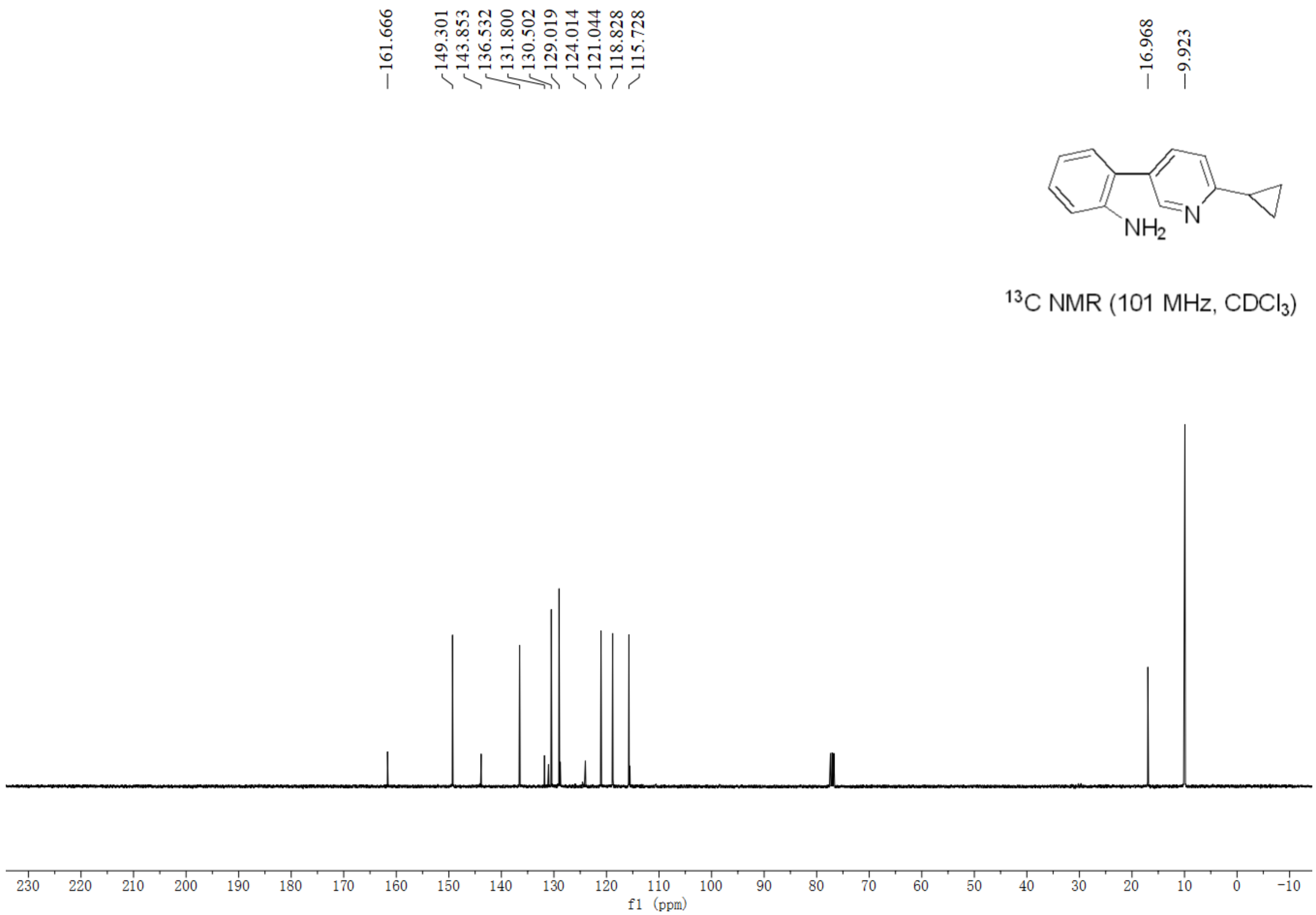


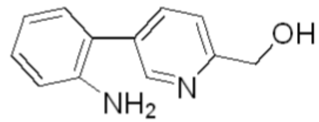
^{1}H NMR (400 MHz, $CDCl_3$)



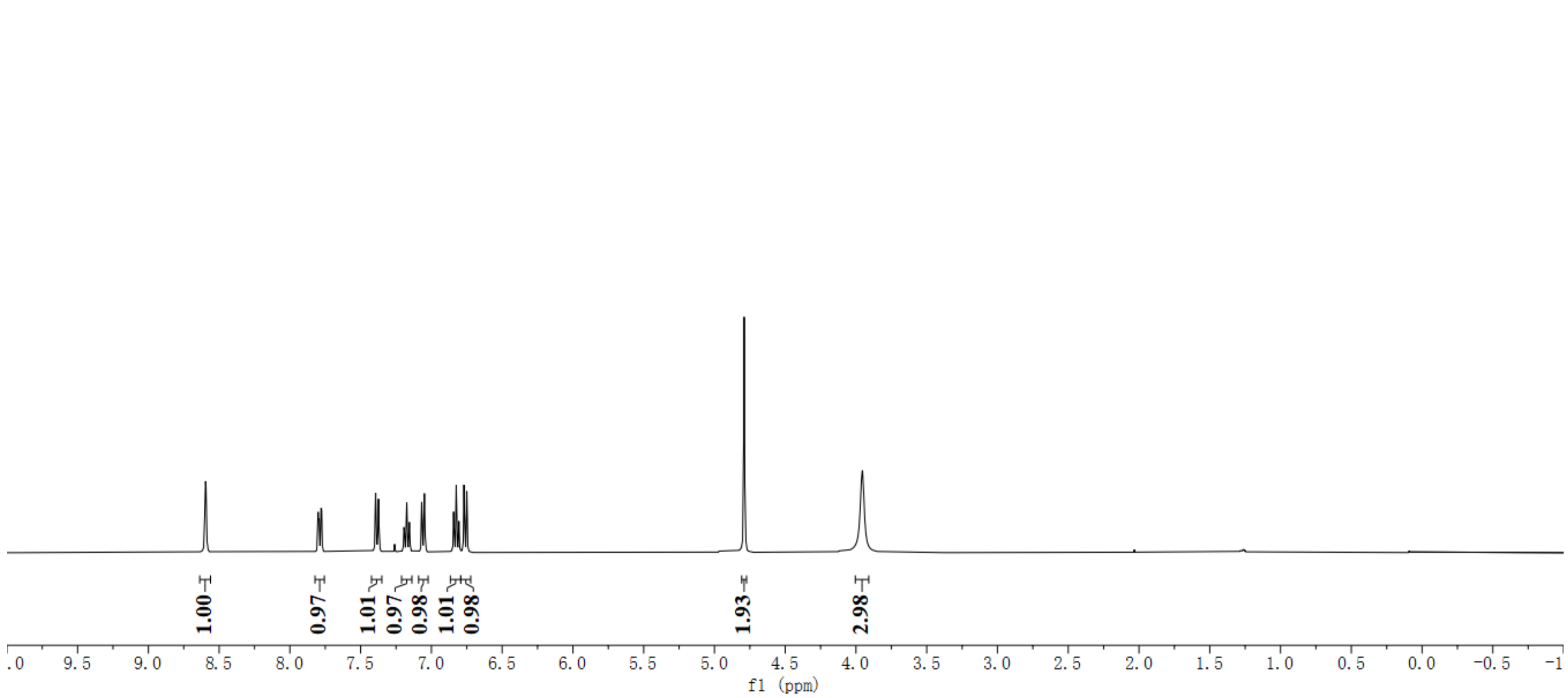
150.304
148.545
146.720
144.287
134.957
130.244
129.161
125.171
122.874
118.082
115.233
19.242
NH2
N
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

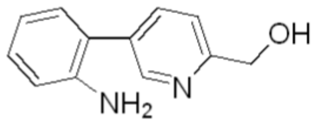

8.532
7.669
7.664
7.649
7.644
7.260
7.210
7.208
7.205
7.197
7.194
7.190
7.187
7.185
7.177
7.174
7.172
7.093
7.075
6.852
6.833
6.815
6.776
6.756
2.115
2.113
2.108
2.106
2.096
2.094
2.082
2.075
2.073
1.080
1.073
1.068
1.066
1.062
1.060
1.057
1.054
1.050
1.045
1.043
1.037
1.035
1.031
1.029
1.024
NH2
N
1H NMR (400 MHz, CDCl3)
1.00
1.07
1.99
1.11
1.25
1.16
2.10
1.16
4.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


161.666
149.301
143.853
136.532
131.800
130.502
129.019
124.014
121.044
118.828
115.728
16.968
9.923
NH2
N
^{13}C NMR (101 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

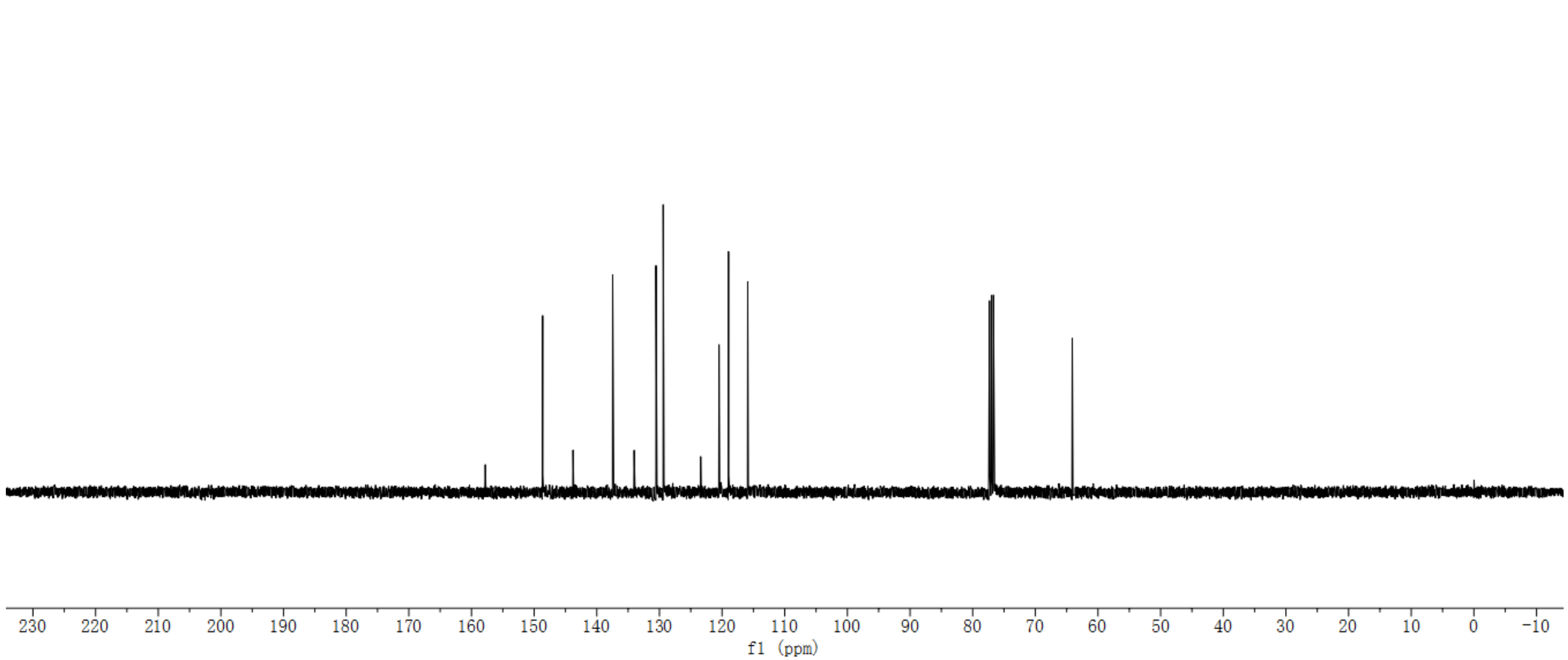


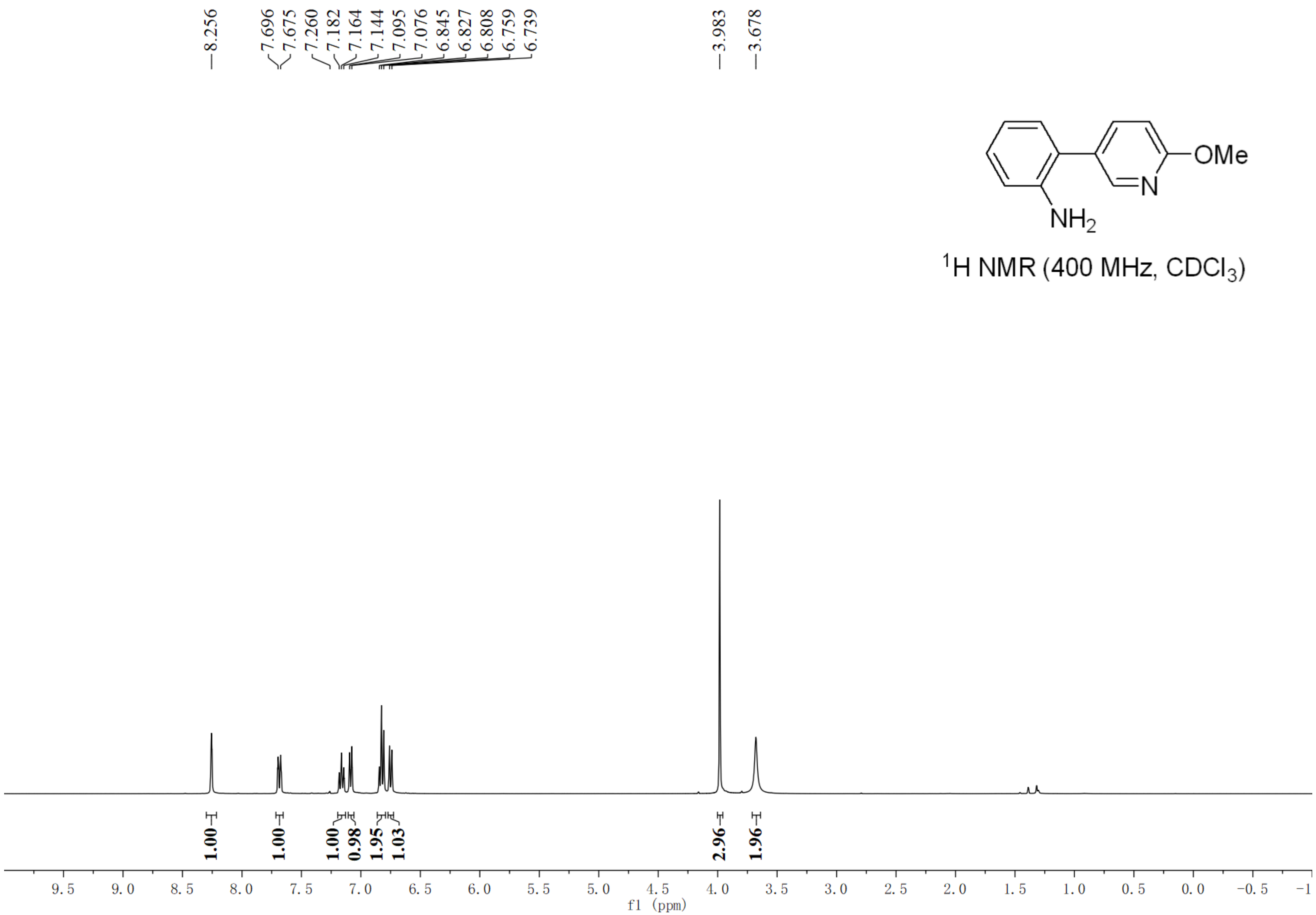
^1H NMR (400 MHz, $CDCl_3$)



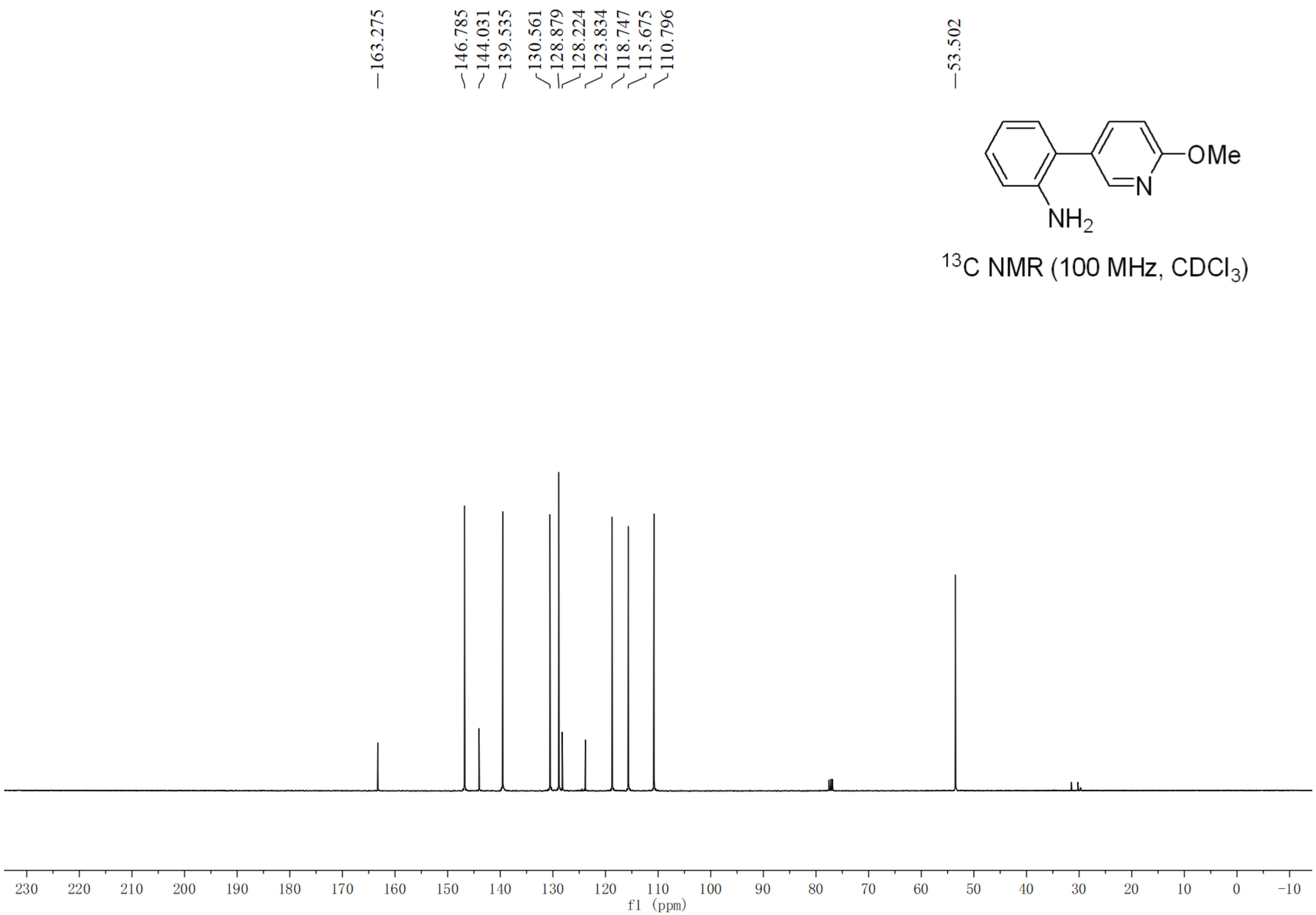


^{13}C NMR (101 MHz, $CDCl_3$)

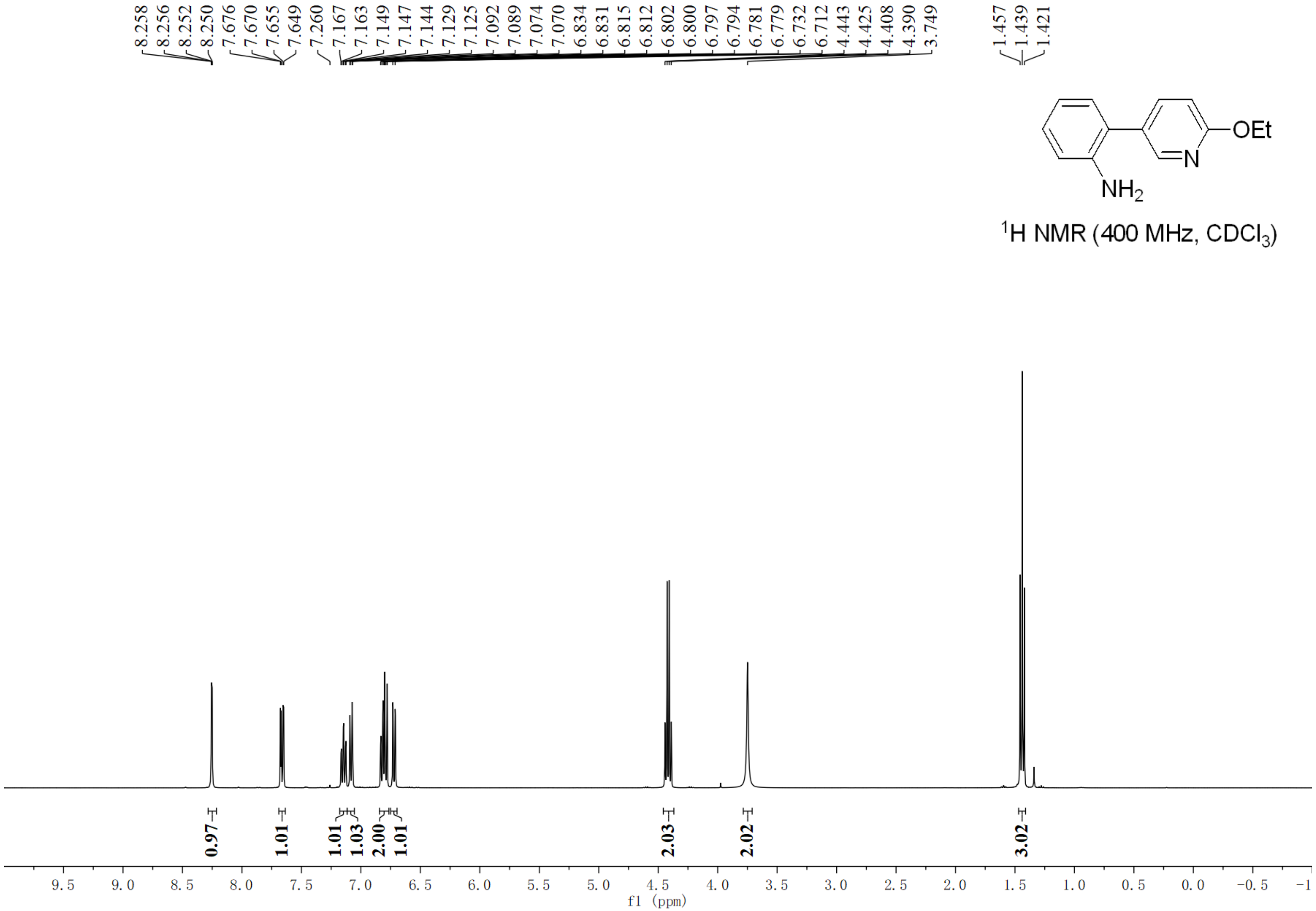


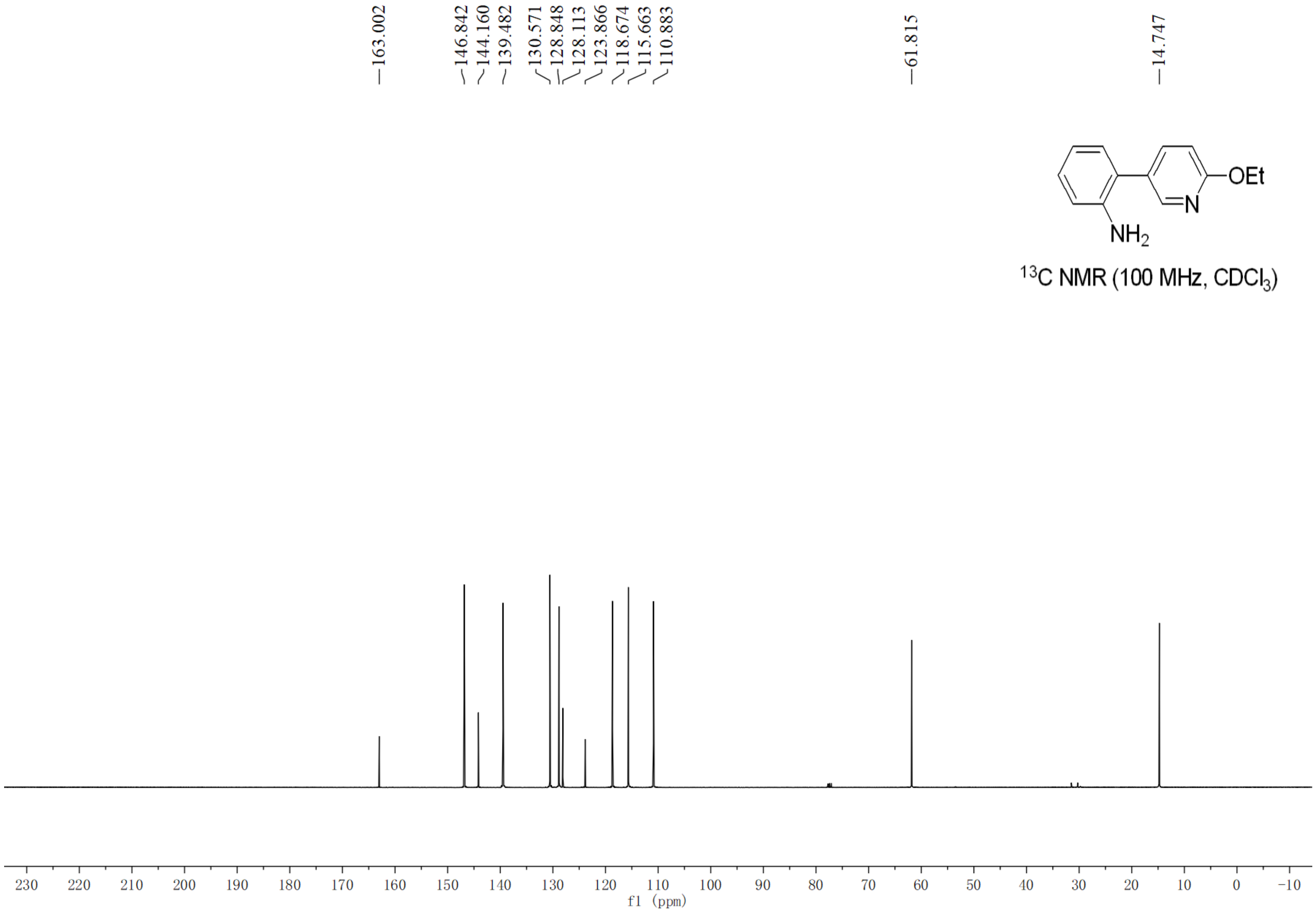


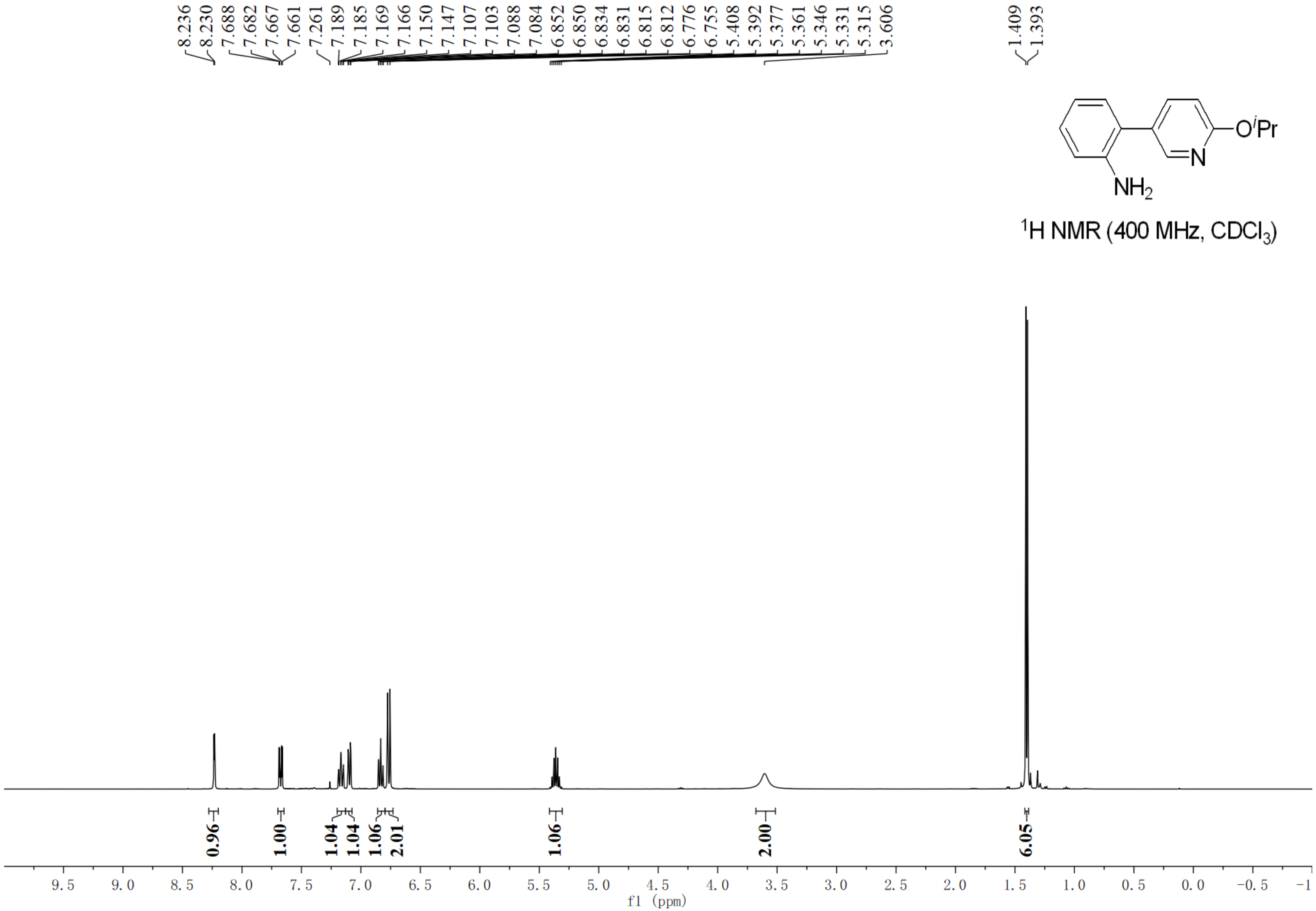
^{1}H NMR (400 MHz, $CDCl_3$)



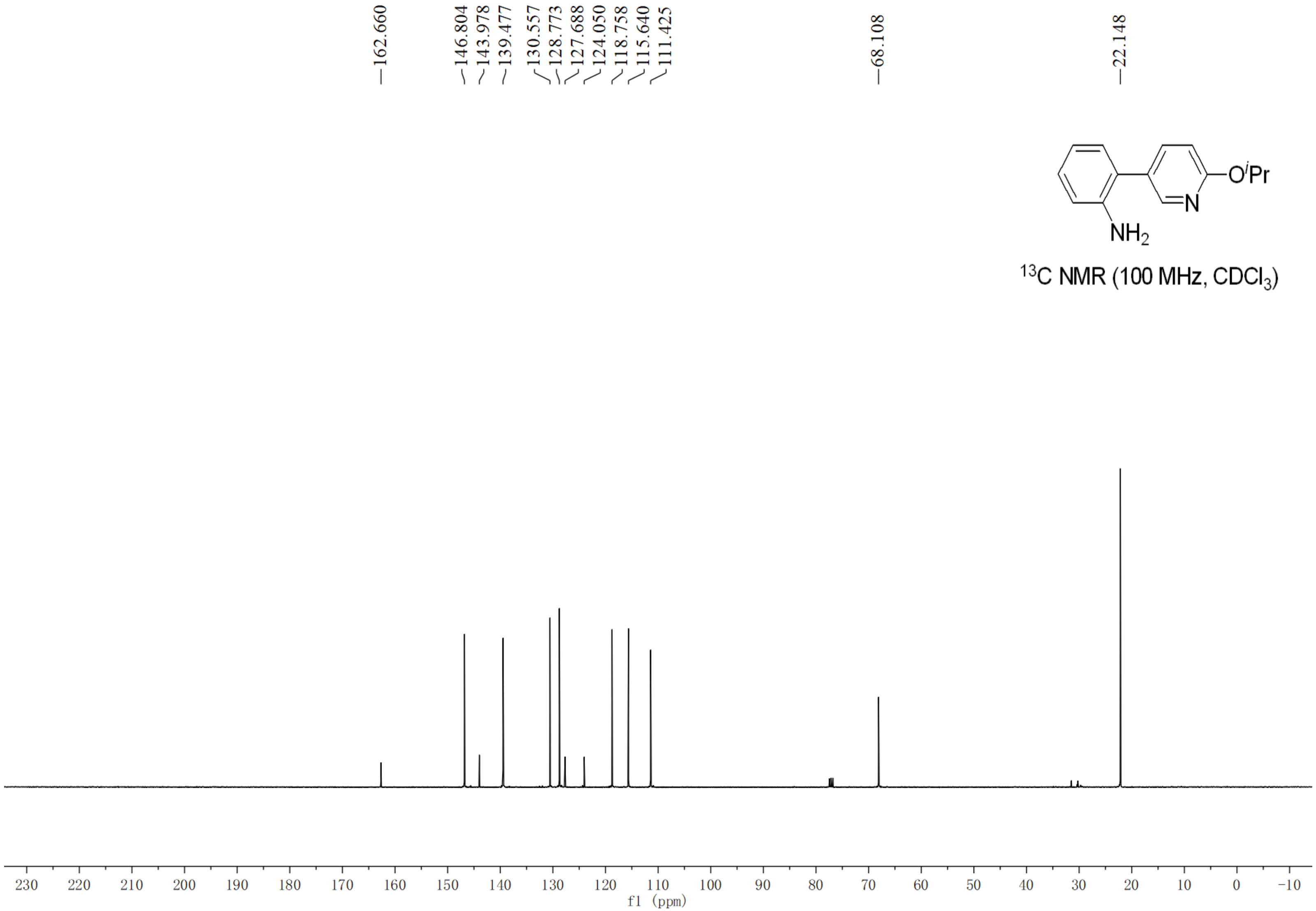
^{13}C NMR (100 MHz, $CDCl_3$)


8.258
8.256
8.252
8.250
7.676
7.670
7.655
7.649
7.260
7.167
7.163
7.149
7.147
7.144
7.129
7.125
7.092
7.089
7.074
7.070
6.834
6.831
6.815
6.812
6.802
6.800
6.797
6.794
6.781
6.779
6.732
6.712
4.443
4.425
4.408
4.390
3.749
1.457
1.439
1.421
OEt
N
NH2
1H NMR (400 MHz, CDCl3)
0.97
1.01
1.01
1.03
2.00
1.01
2.03
2.02
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

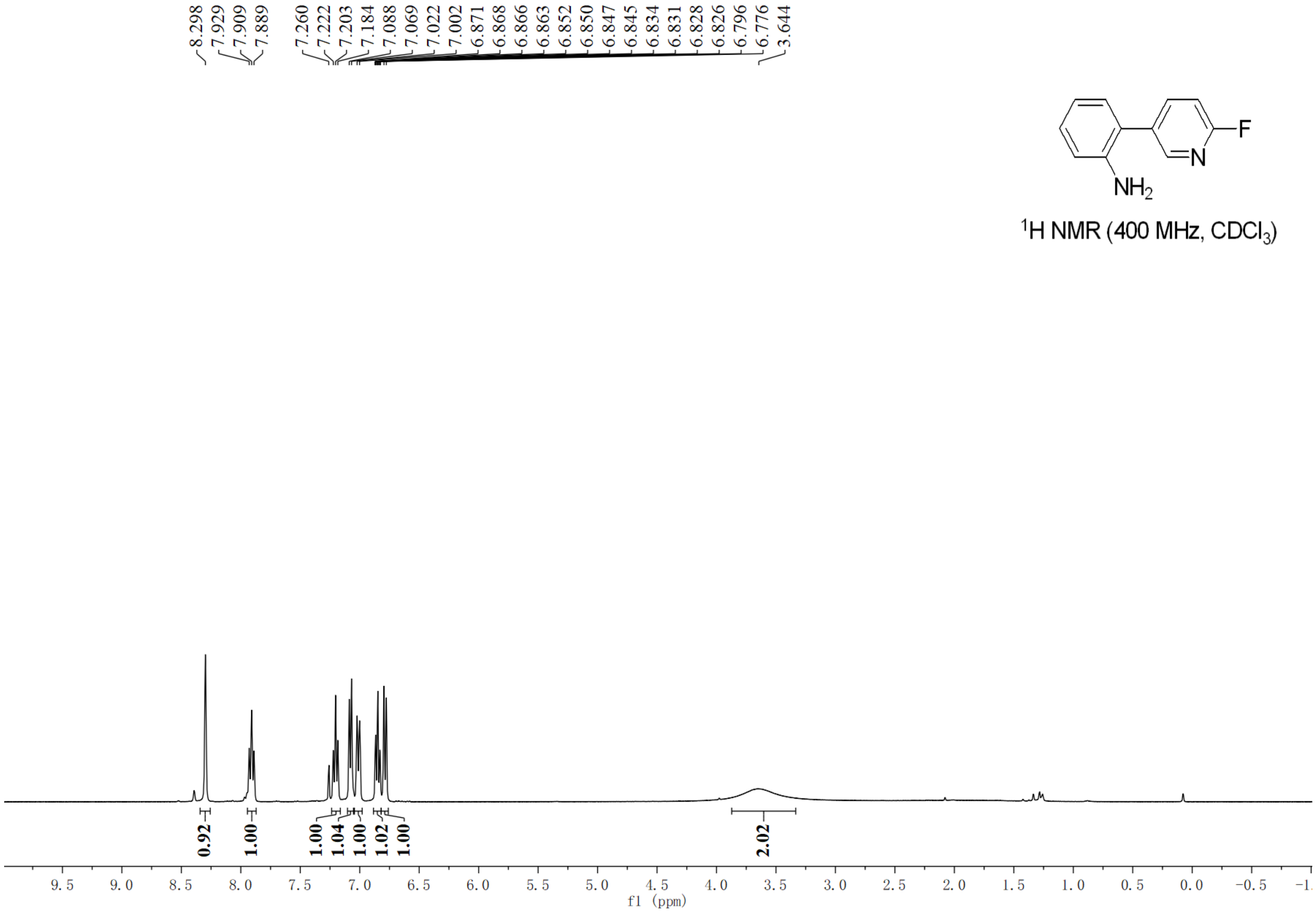

163.002
146.842
144.160
139.482
130.571
128.848
128.113
123.866
118.674
115.663
110.883
61.815
14.747
OEt
N
NH2
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



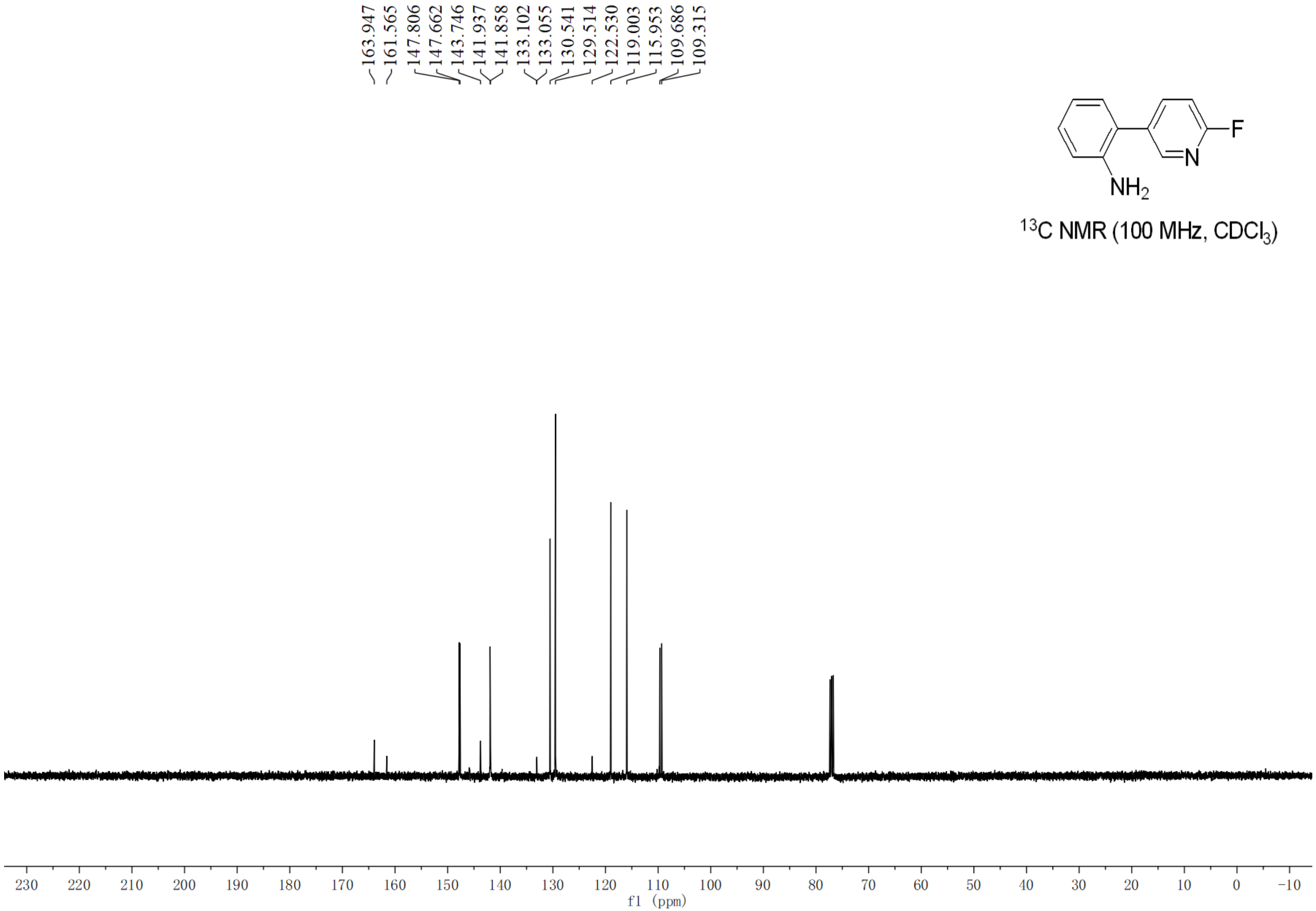
8.236
8.230
7.688
7.682
7.667
7.661
7.261
7.189
7.185
7.169
7.166
7.150
7.147
7.107
7.103
7.088
7.084
6.852
6.850
6.834
6.831
6.815
6.812
6.776
6.755
5.408
5.392
5.377
5.361
5.346
5.331
5.315
3.606
1.409
1.393
O^{i}Pr
N
NH$_2$
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
1.00
1.04
1.04
1.06
2.01
1.06
2.00
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

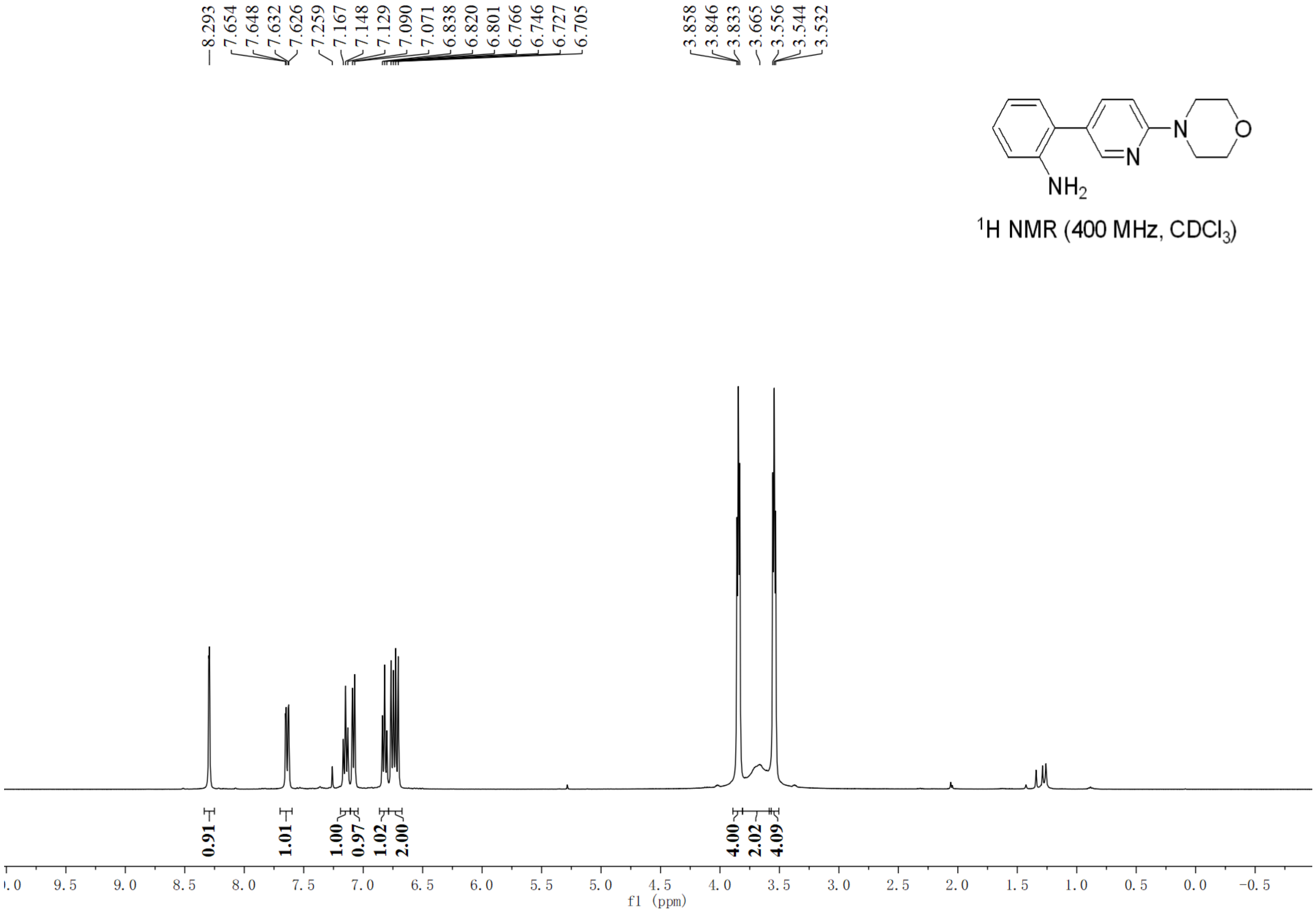


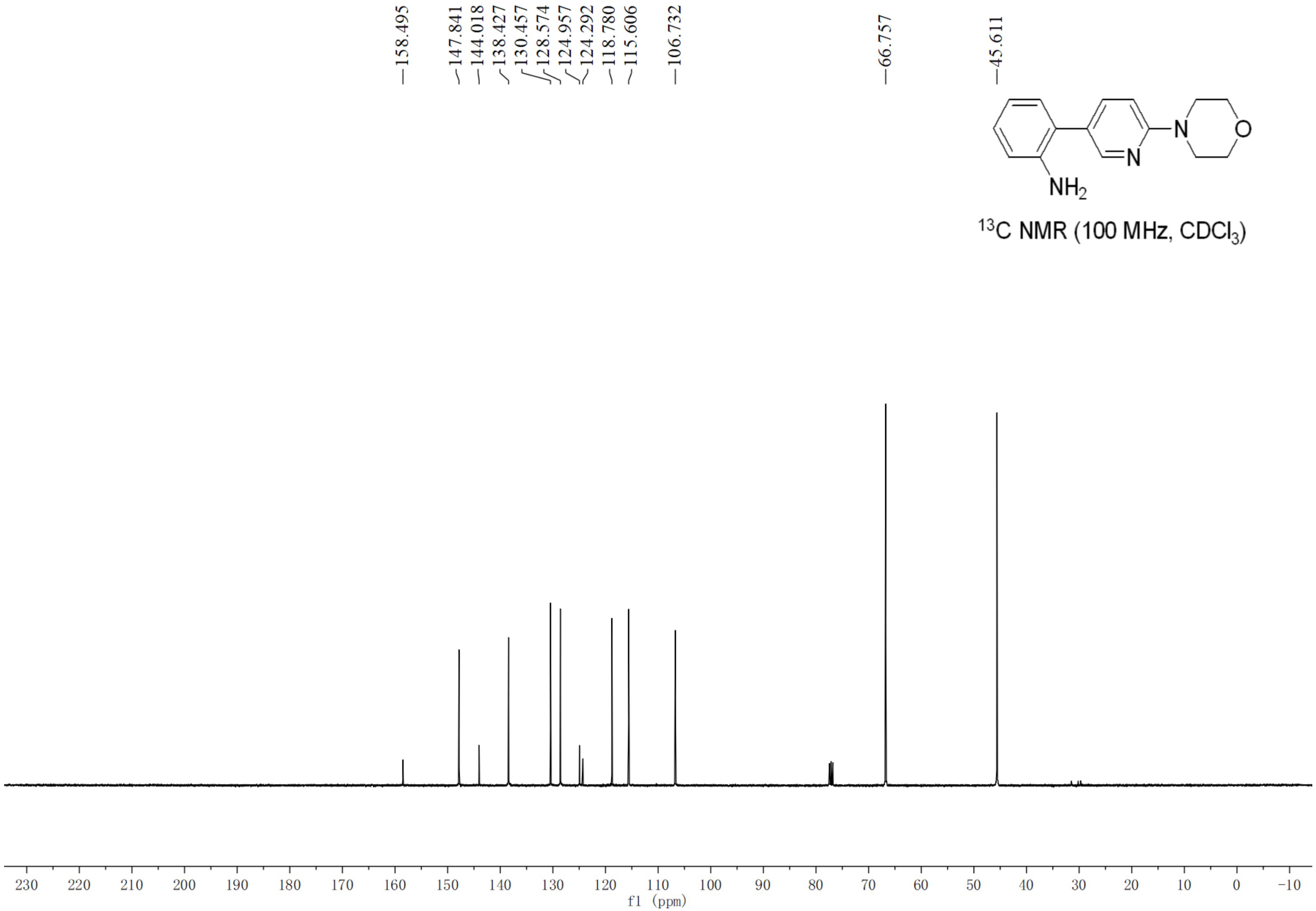
^{13}C NMR (100 MHz, $CDCl_3$)



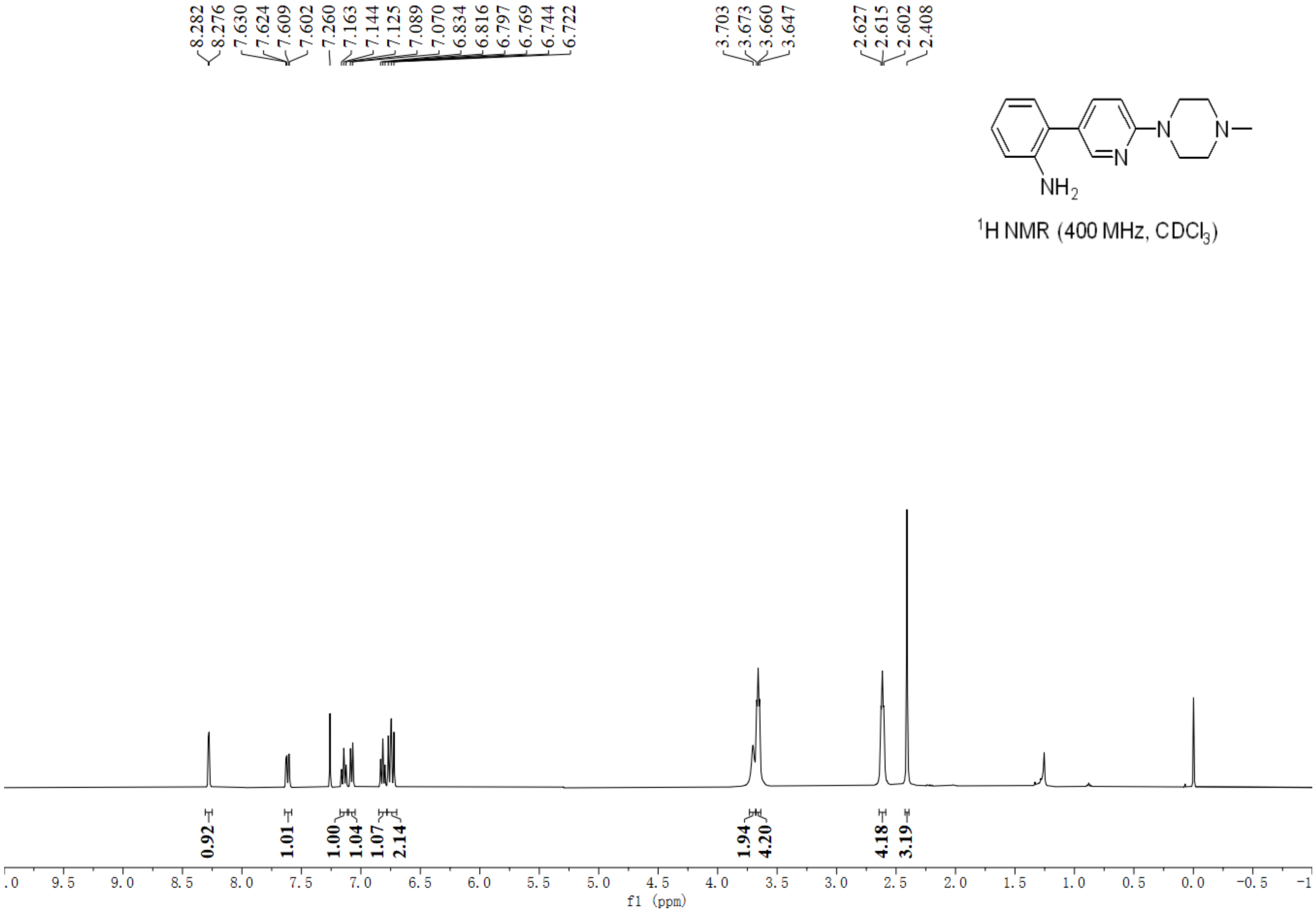
^{1}H NMR (400 MHz, $CDCl_3$)


163.947
161.565
147.806
147.662
143.746
141.937
141.858
133.102
133.055
130.541
129.514
122.530
119.003
115.953
109.686
109.315
F
N
NH_2
^{13}C NMR (100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

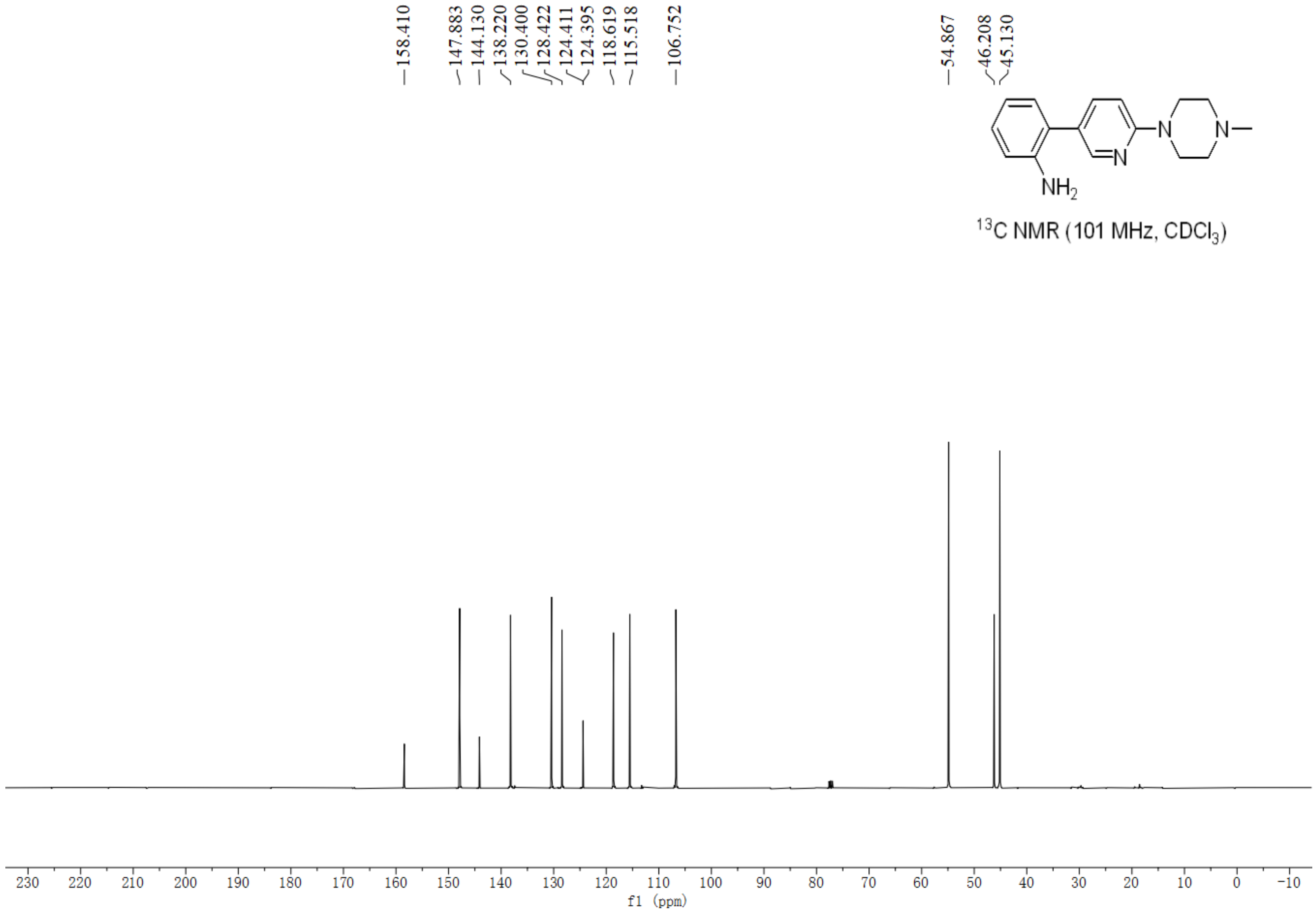

8.293
7.654
7.648
7.632
7.626
7.259
7.167
7.148
7.129
7.090
7.071
6.838
6.820
6.801
6.766
6.746
6.727
6.705
3.858
3.846
3.833
3.665
3.556
3.544
3.532
NH2
N
N
O
1H NMR (400 MHz, CDCl3)
0.91
1.01
1.00
0.97
1.02
2.00
4.00
2.02
4.09
f1 (ppm)



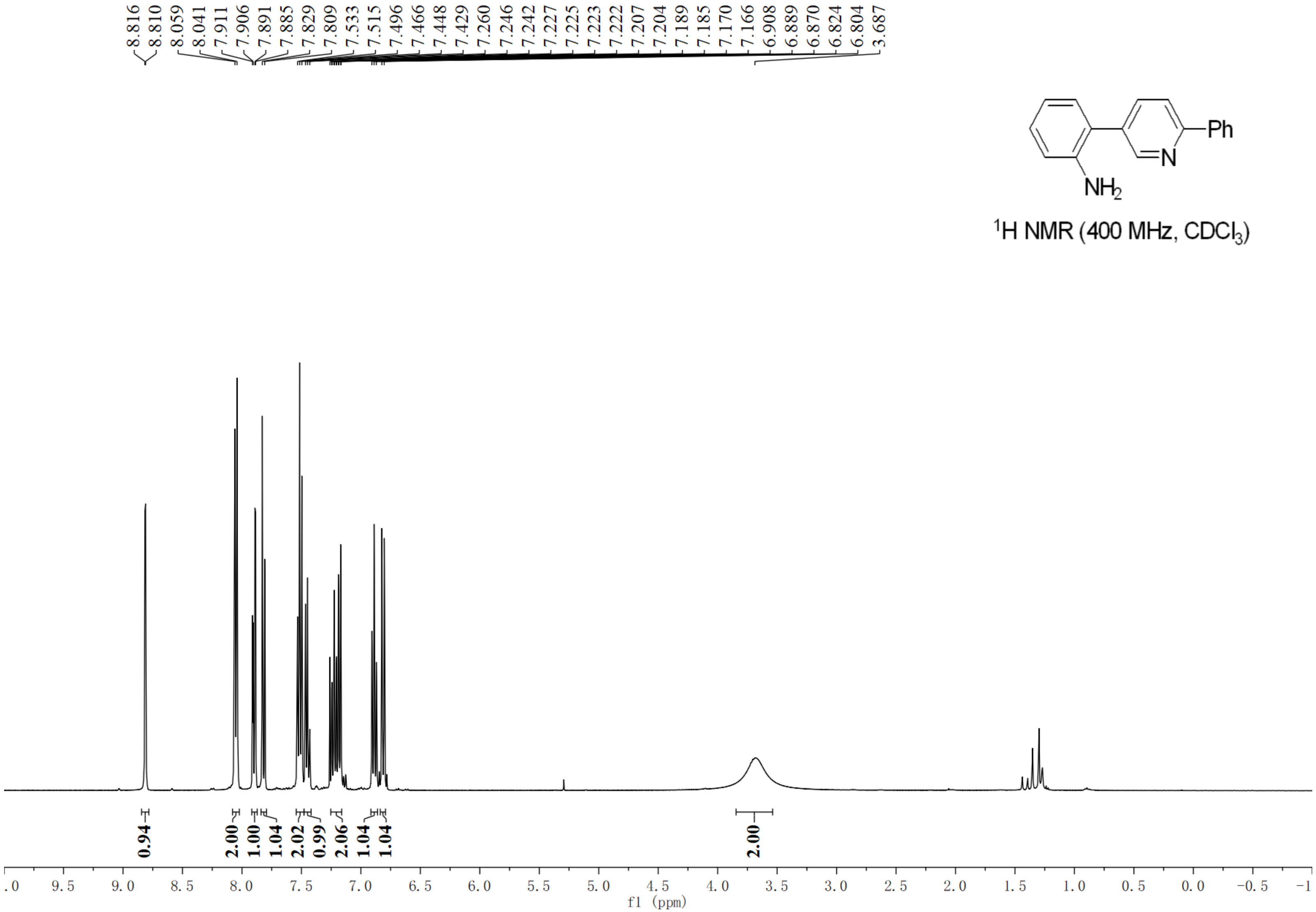
^{13}C NMR (100 MHz, $CDCl_3$)

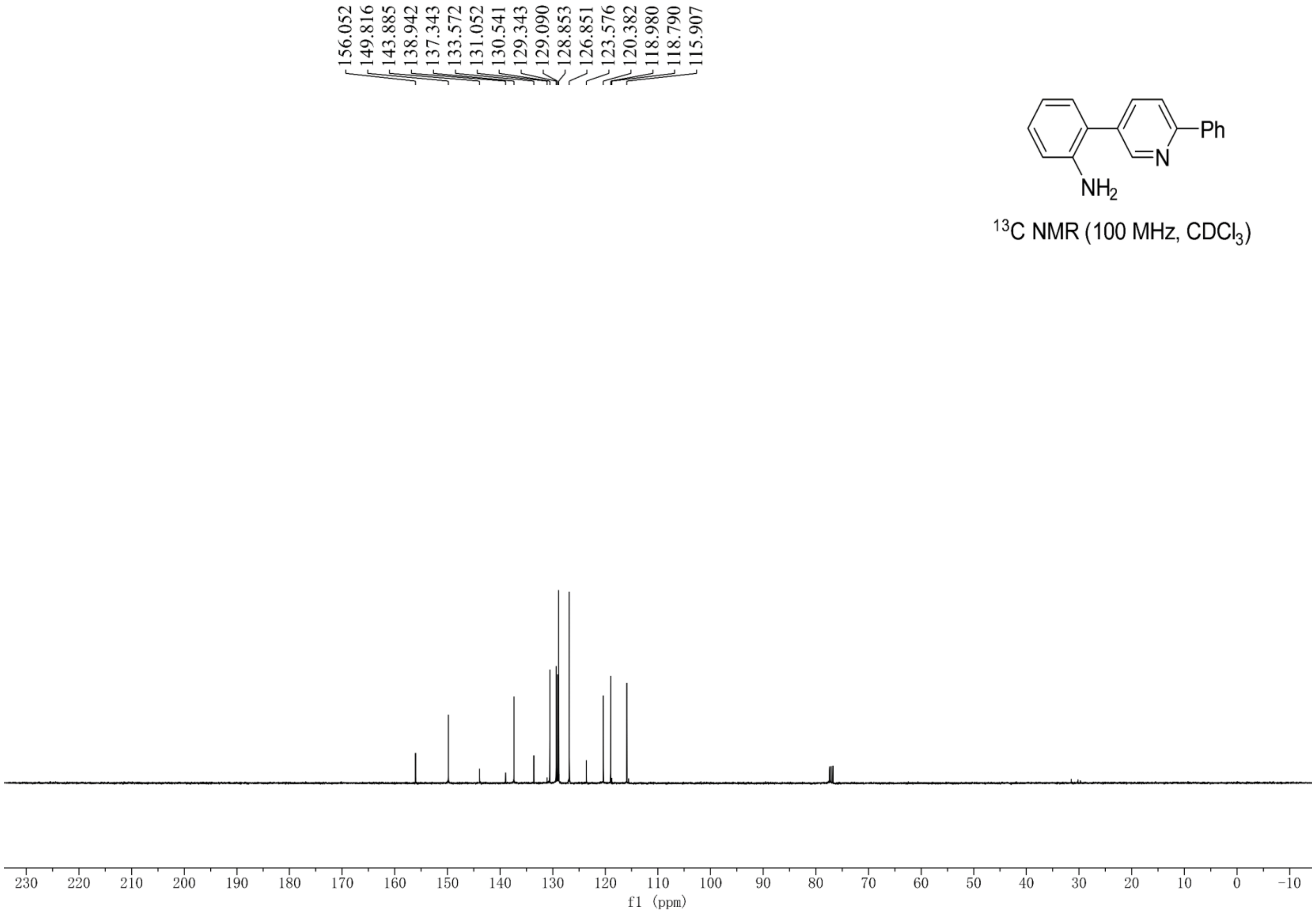


^1H NMR (400 MHz, $CDCl_3$)

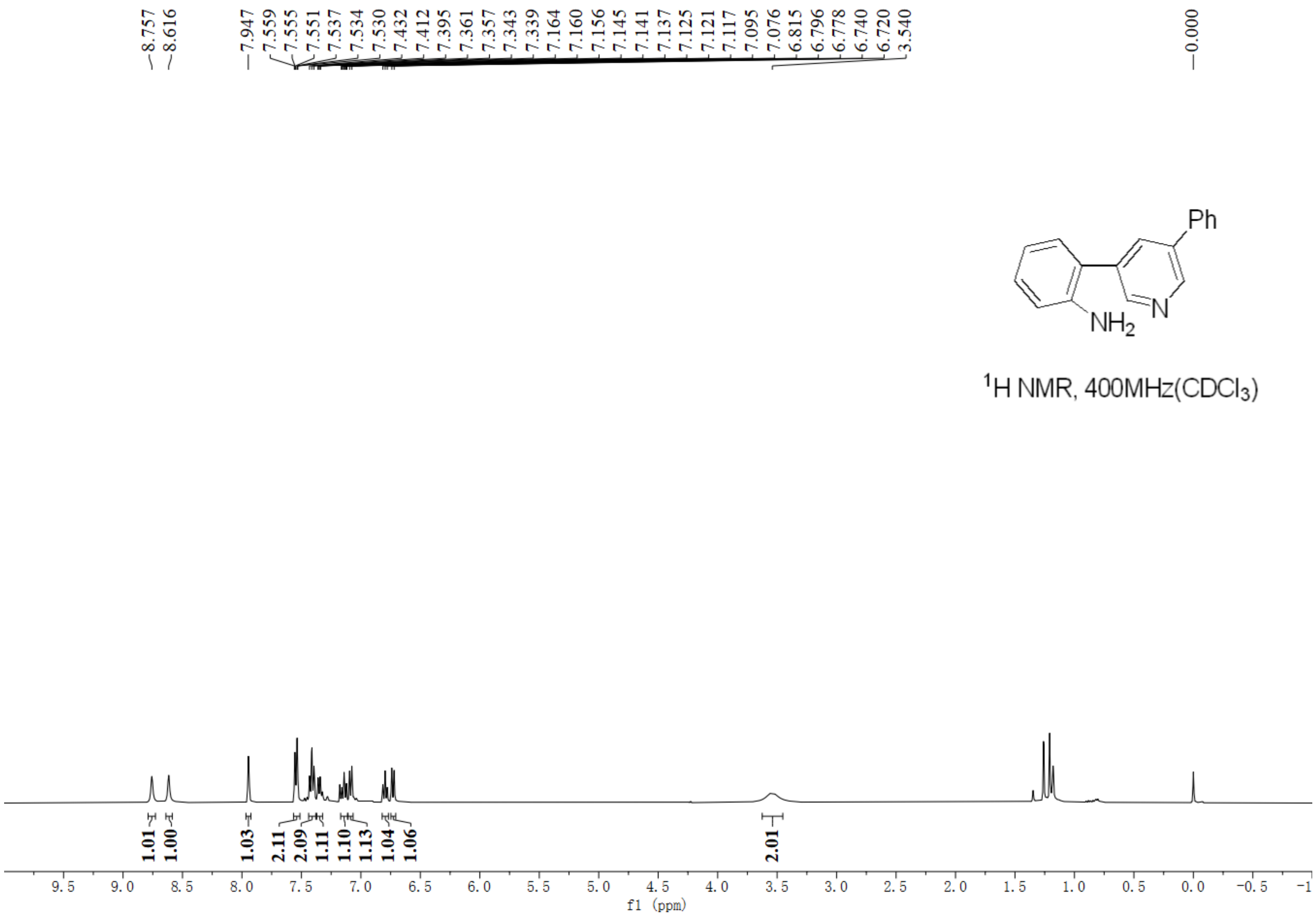


158.410
147.883
144.130
138.220
130.400
128.422
124.411
124.395
118.619
115.518
106.752
54.867
46.208
45.130
NH2
N
N
N
^{13}C NMR (101 MHz, CDCl$_3$)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

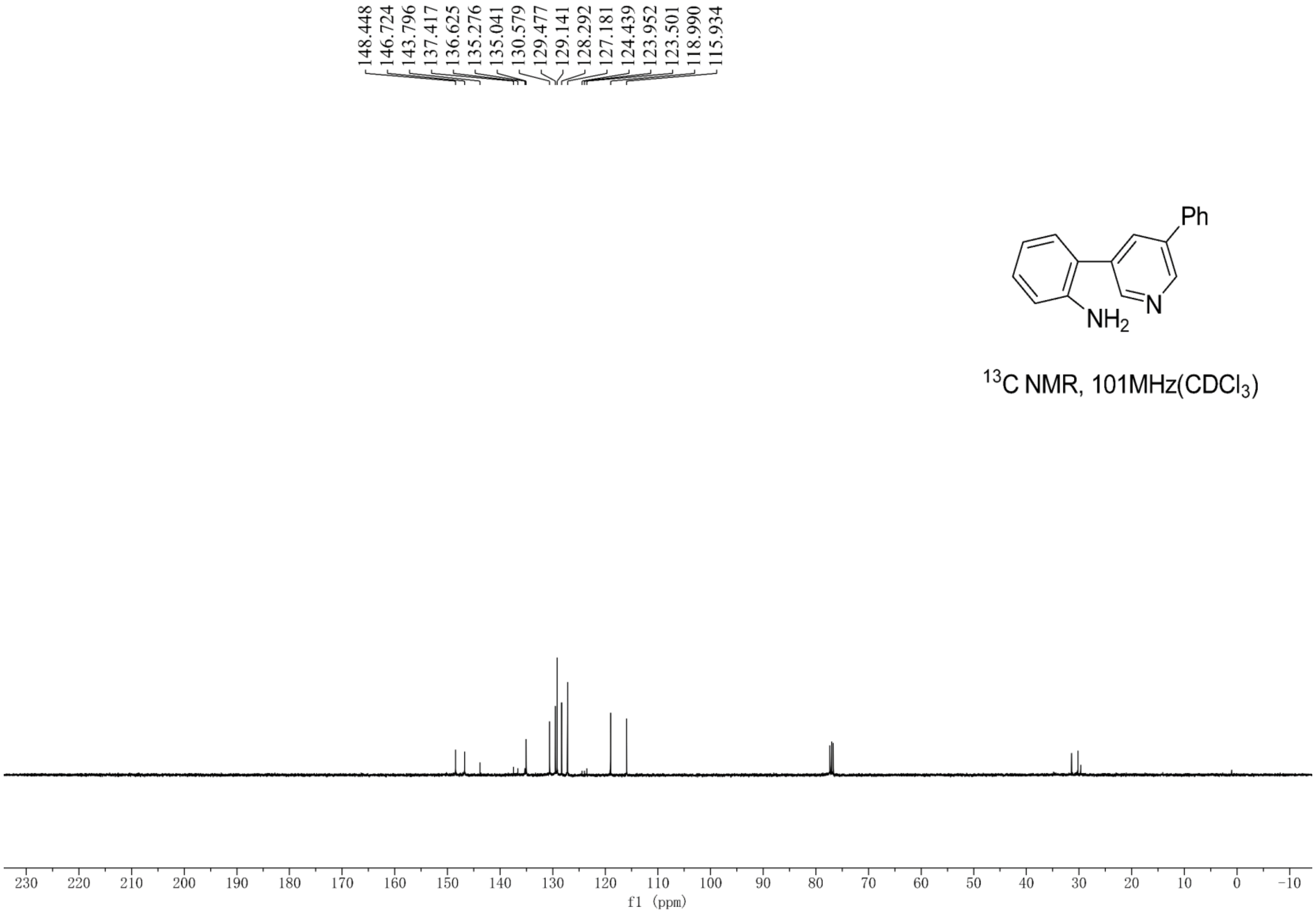

8.816
8.810
8.059
8.041
7.911
7.906
7.891
7.885
7.829
7.809
7.533
7.515
7.496
7.466
7.448
7.429
7.260
7.246
7.242
7.227
7.225
7.223
7.222
7.207
7.204
7.189
7.185
7.170
7.166
6.908
6.889
6.870
6.824
6.804
3.687
Ph
N
NH2
1H NMR (400 MHz, CDCl3)
0.94
2.00
1.00
1.04
2.02
0.99
2.06
1.04
1.04
2.00
f1 (ppm)



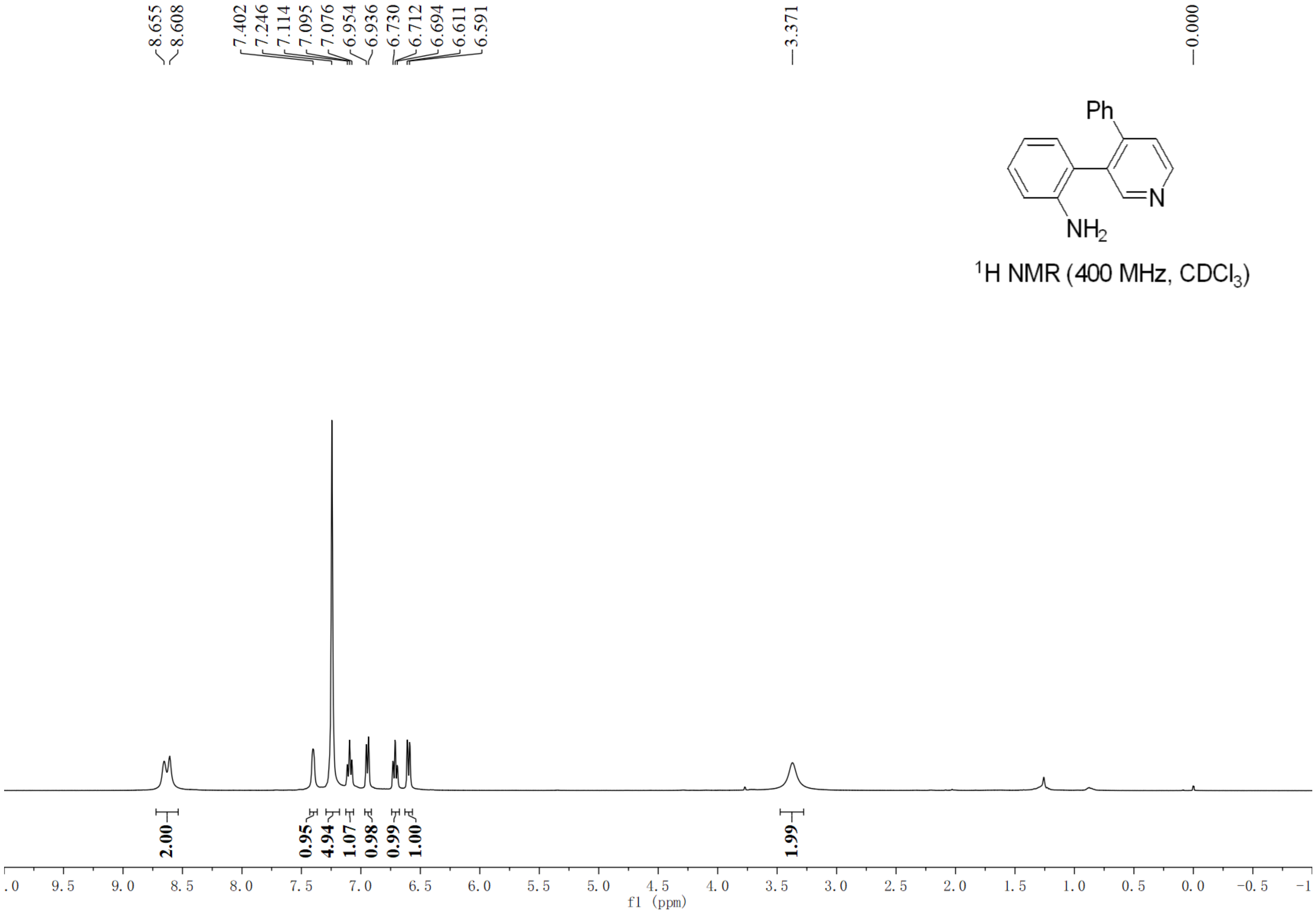
^{13}C NMR (100 MHz, $CDCl_3$)

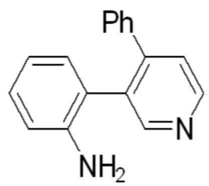


^1H NMR, 400MHz($CDCl_3$)

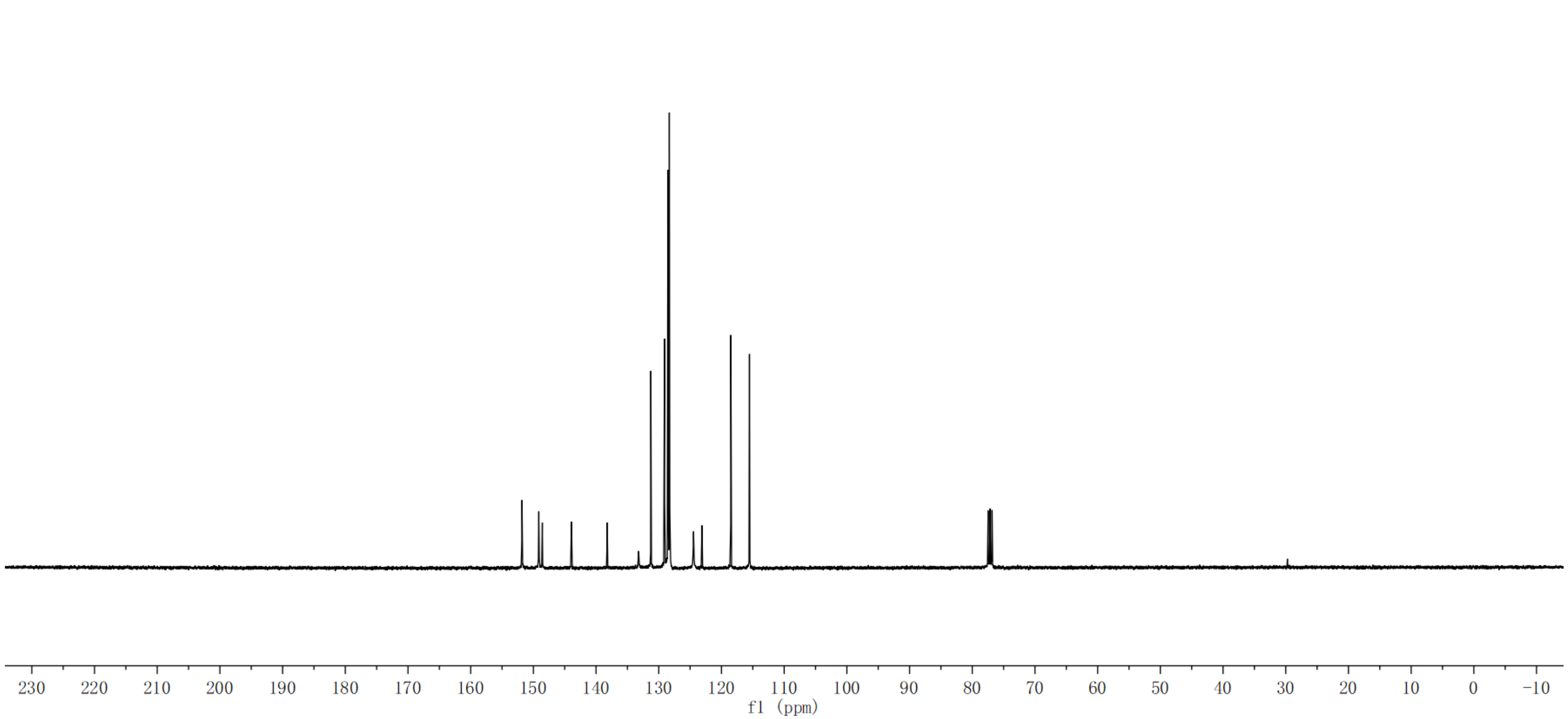


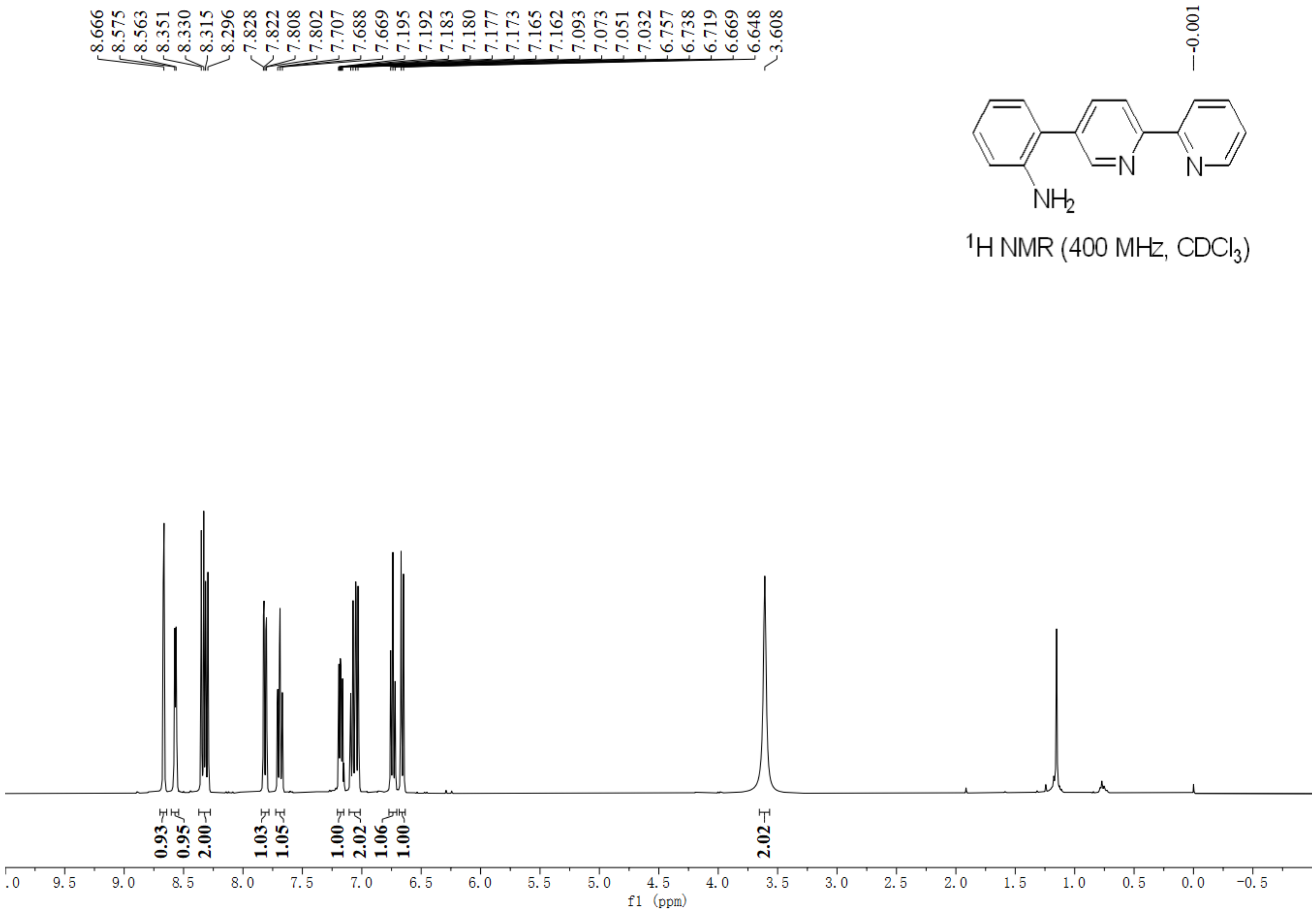
^{13}C NMR, 101MHz($CDCl_3$)

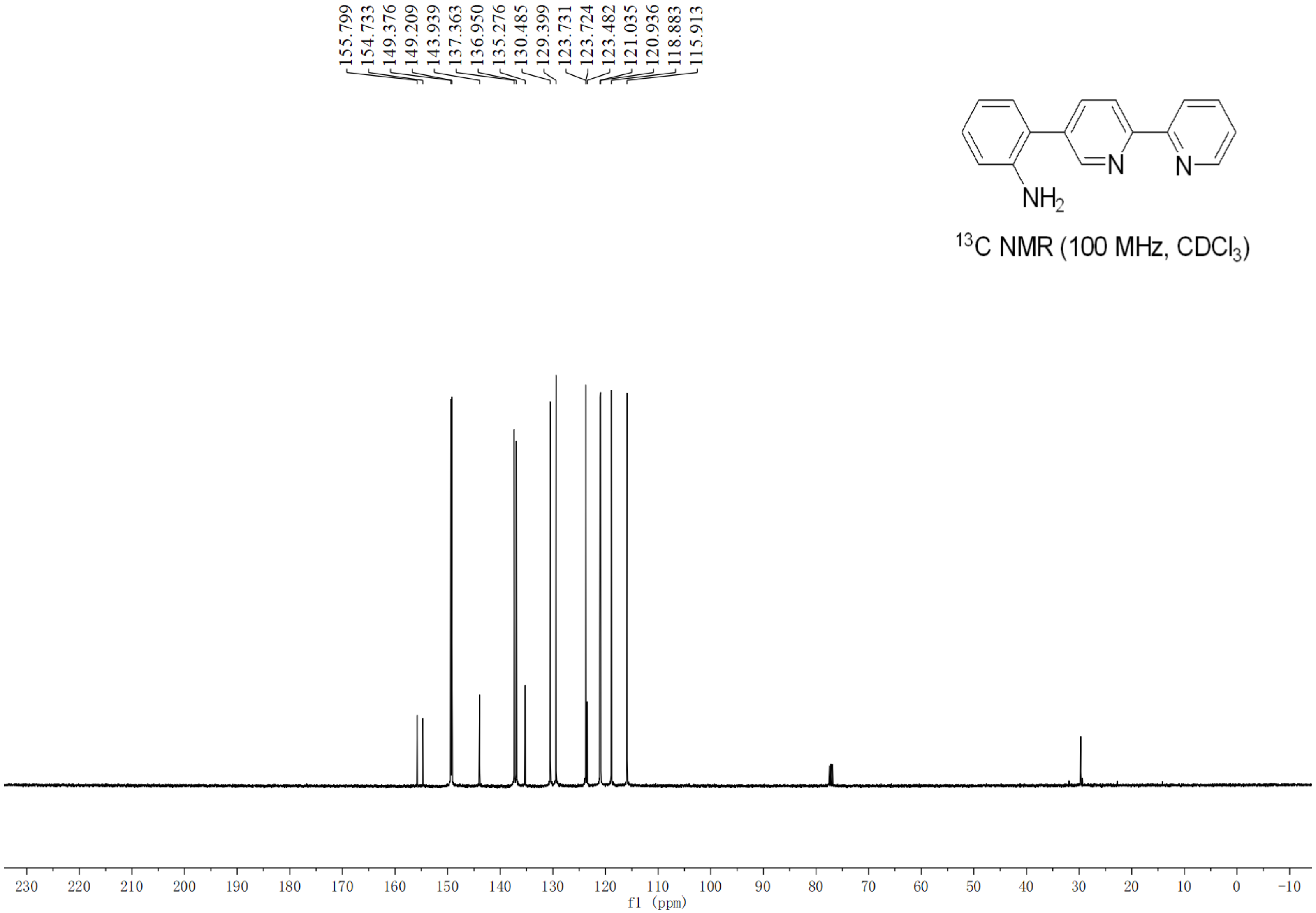

8.655
8.608
7.402
7.246
7.114
7.095
7.076
6.954
6.936
6.730
6.712
6.694
6.611
6.591
3.371
0.000
Ph
N
NH2
1H NMR (400 MHz, CDCl3)
2.00
0.95
4.94
1.07
0.98
0.99
1.00
1.99
f1 (ppm)



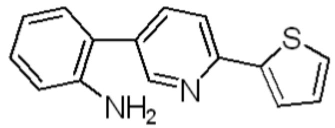
^{13}C NMR (100 MHz, $CDCl_3$)



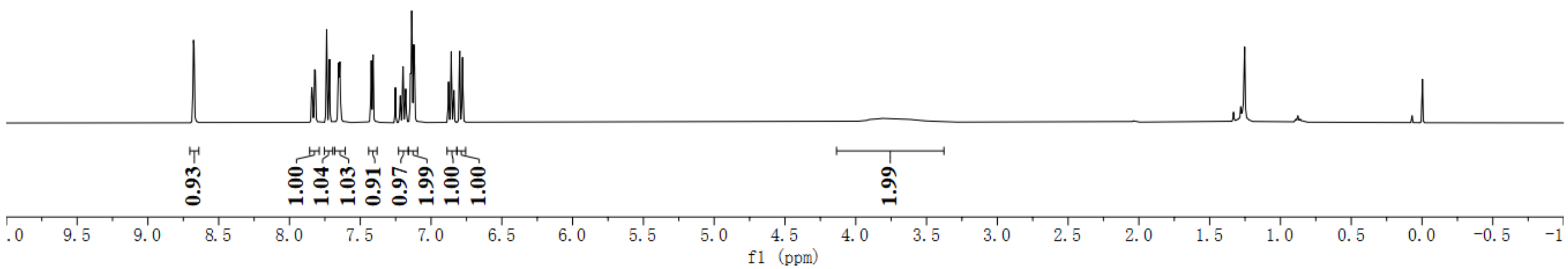

8.666
8.575
8.563
8.351
8.330
8.315
8.296
7.828
7.822
7.808
7.802
7.707
7.688
7.669
7.195
7.192
7.183
7.180
7.177
7.173
7.165
7.162
7.093
7.073
7.051
7.032
6.757
6.738
6.719
6.669
6.648
3.608
-0.001
NH2
N
N
1H NMR (400 MHz, CDCl3)
0.93
0.95
2.00
1.03
1.05
1.00
2.02
1.06
1.00
2.02
f1 (ppm)

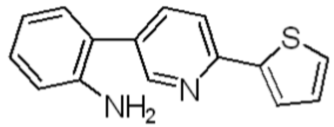


^{13}C NMR (100 MHz, $CDCl_3$)

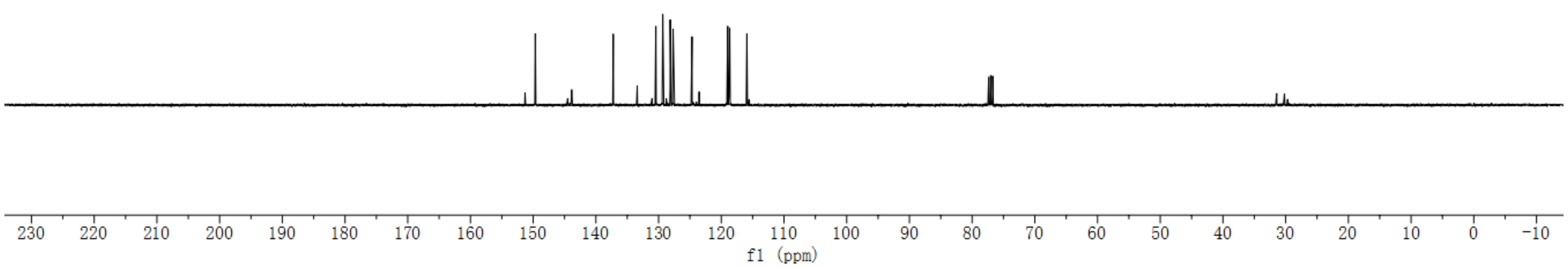


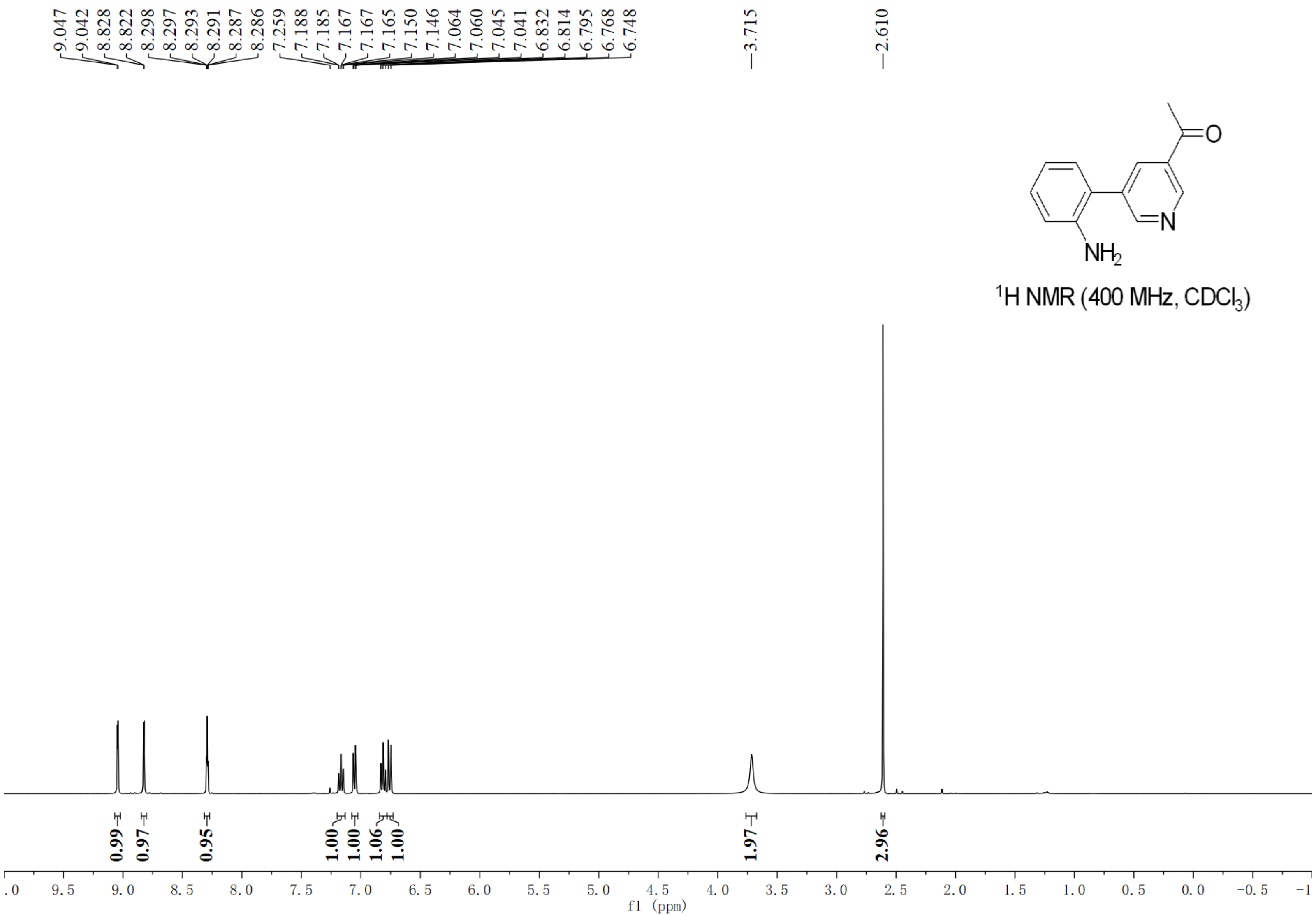
^1H NMR (400 MHz, $CDCl_3$)



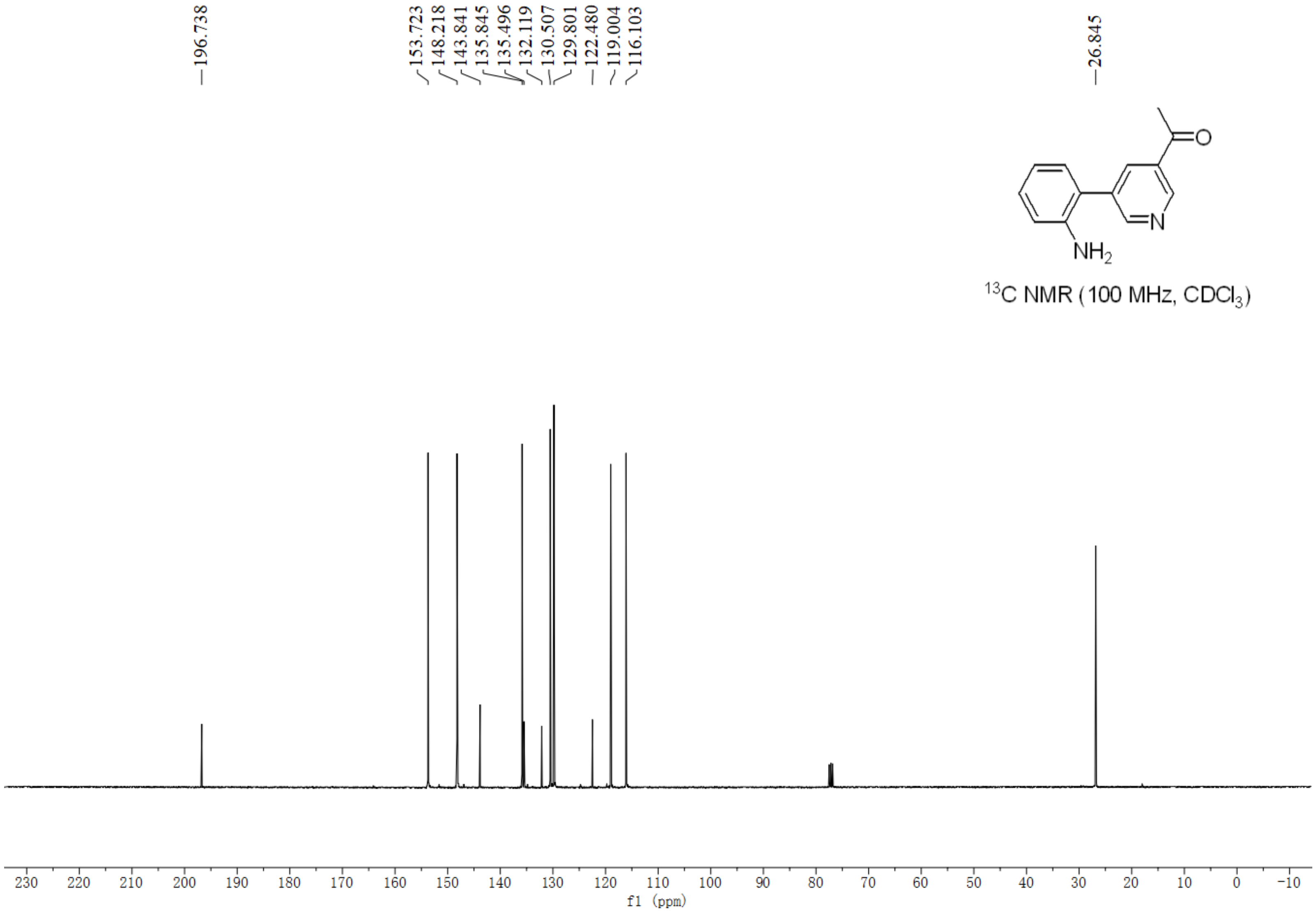


^{13}C NMR (101 MHz, $CDCl_3$)

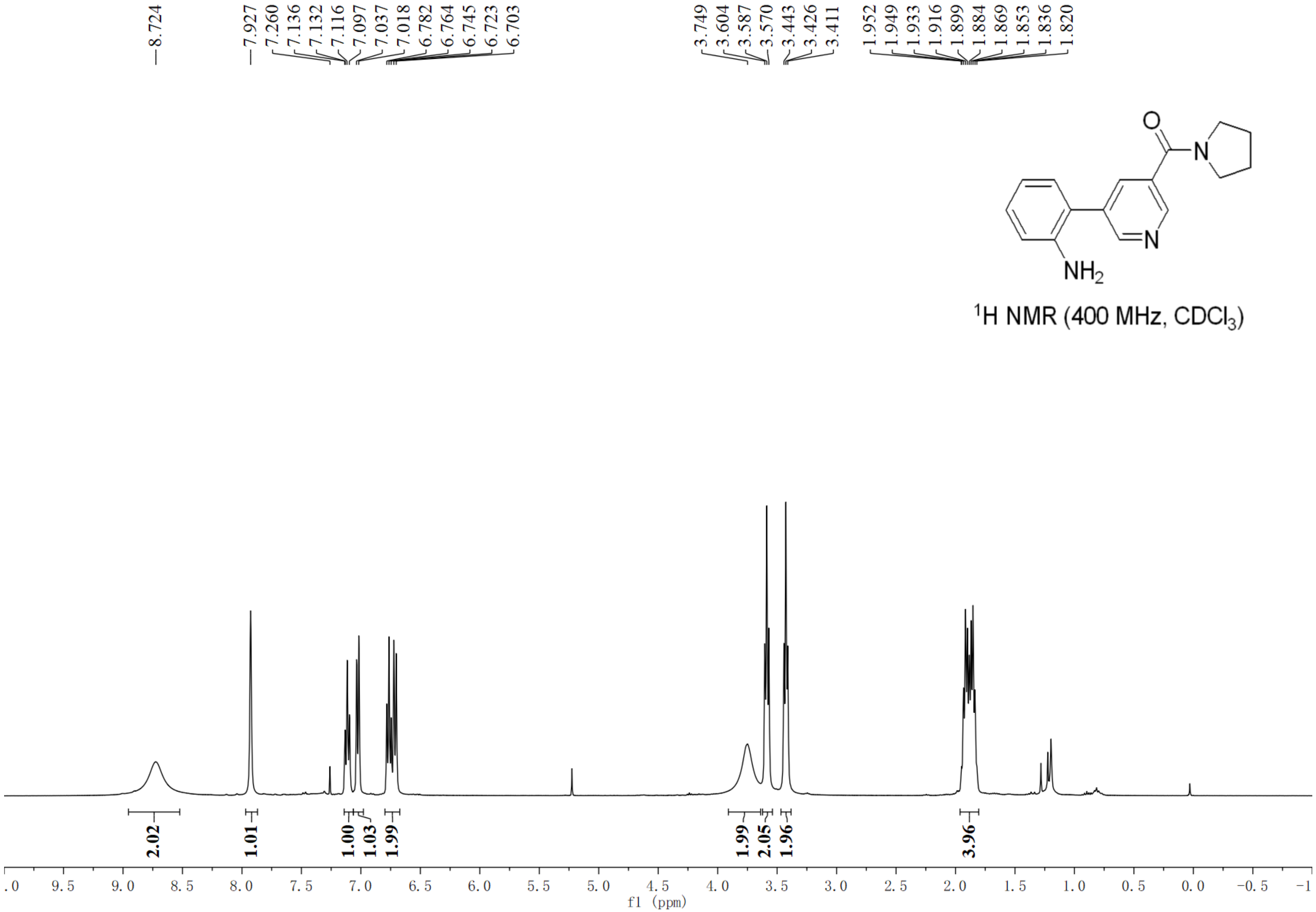




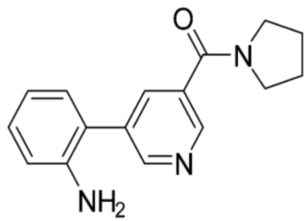
9.047
9.042
8.828
8.822
8.298
8.297
8.293
8.291
8.287
8.286
7.259
7.188
7.185
7.167
7.167
7.165
7.150
7.146
7.064
7.060
7.045
7.041
6.832
6.814
6.795
6.768
6.748
3.715
2.610
NH2
N
O
1H NMR (400 MHz, CDCl3)
0.99
0.97
0.95
1.00
1.00
1.06
1.00
1.97
2.96
f1 (ppm)



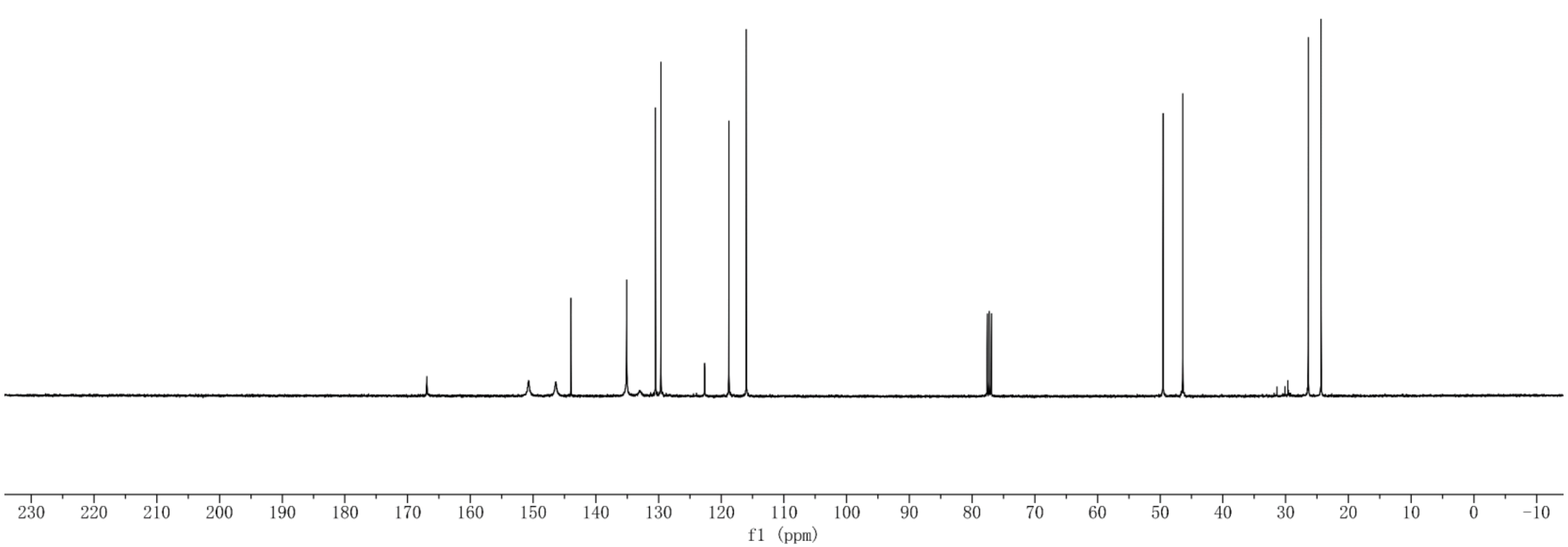
^{13}C NMR (100 MHz, $CDCl_3$)

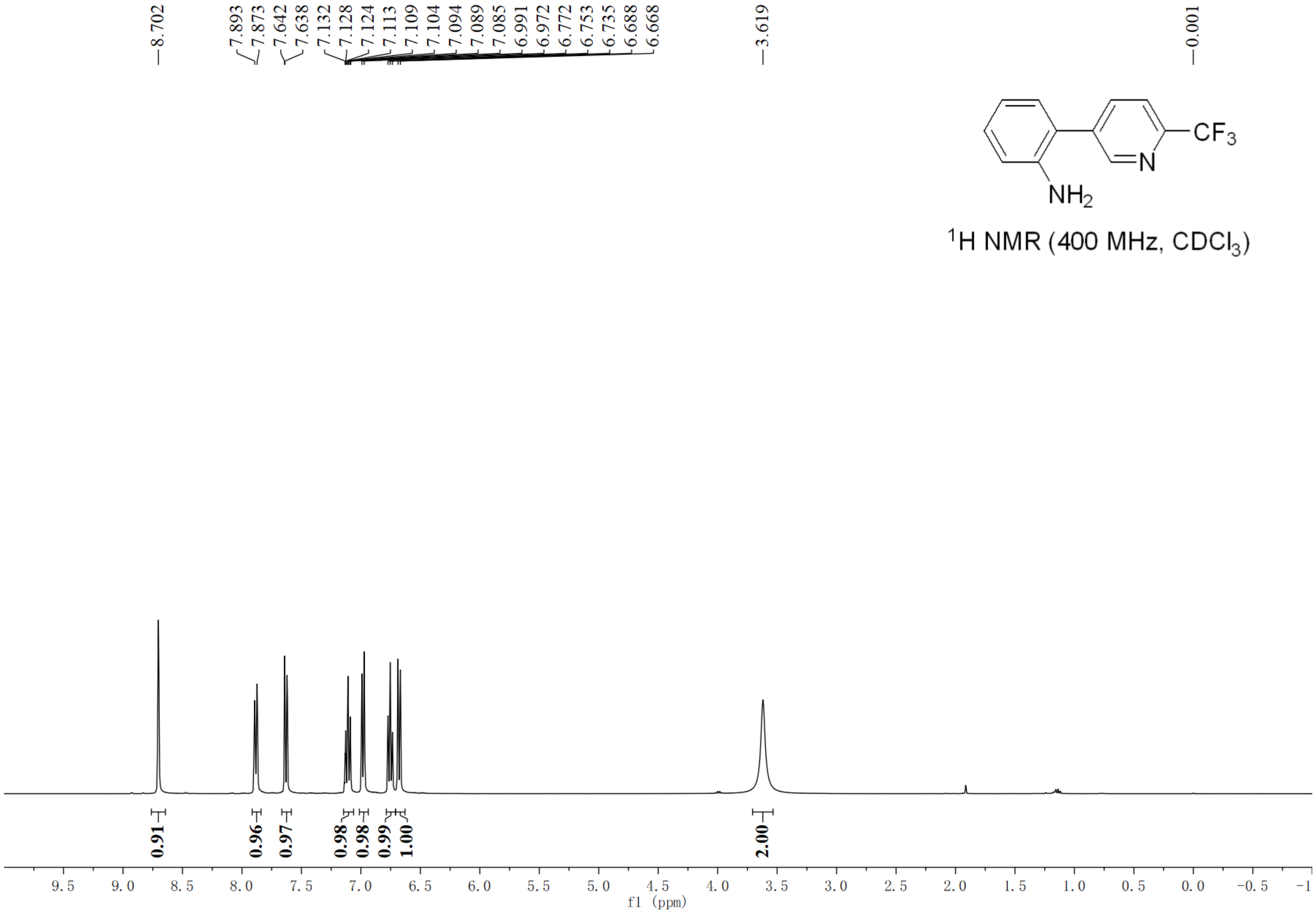


^{1}H NMR (400 MHz, $CDCl_3$)

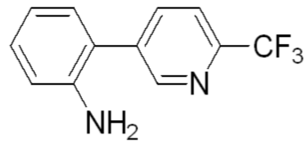


^{13}C NMR (100 MHz, $CDCl_3$)

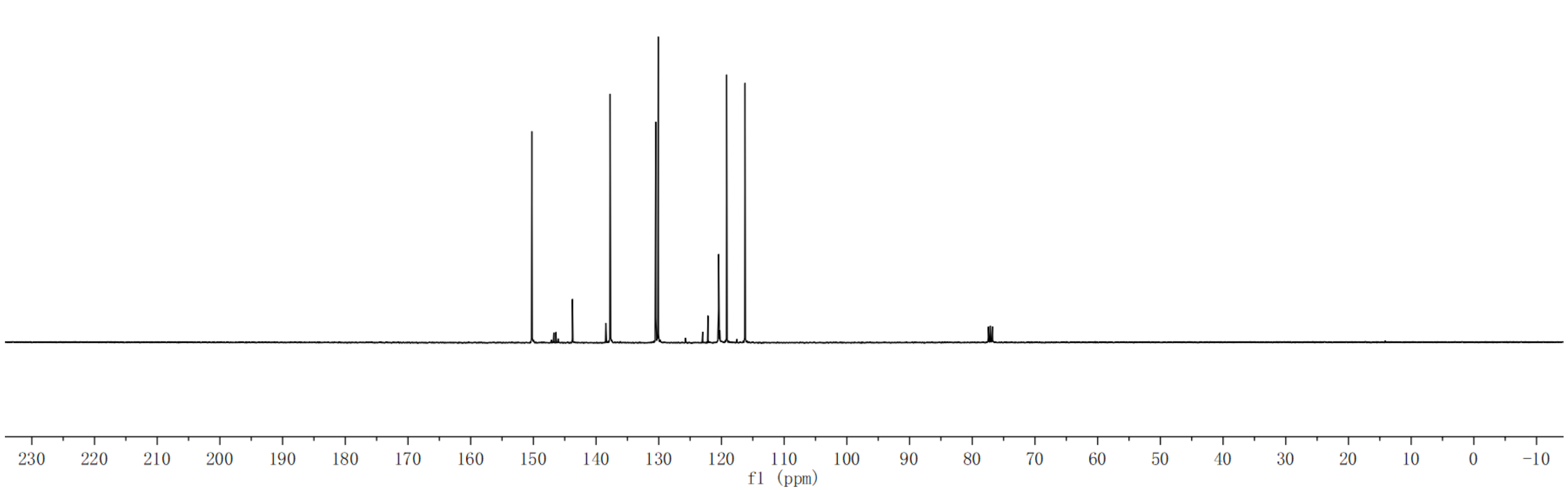


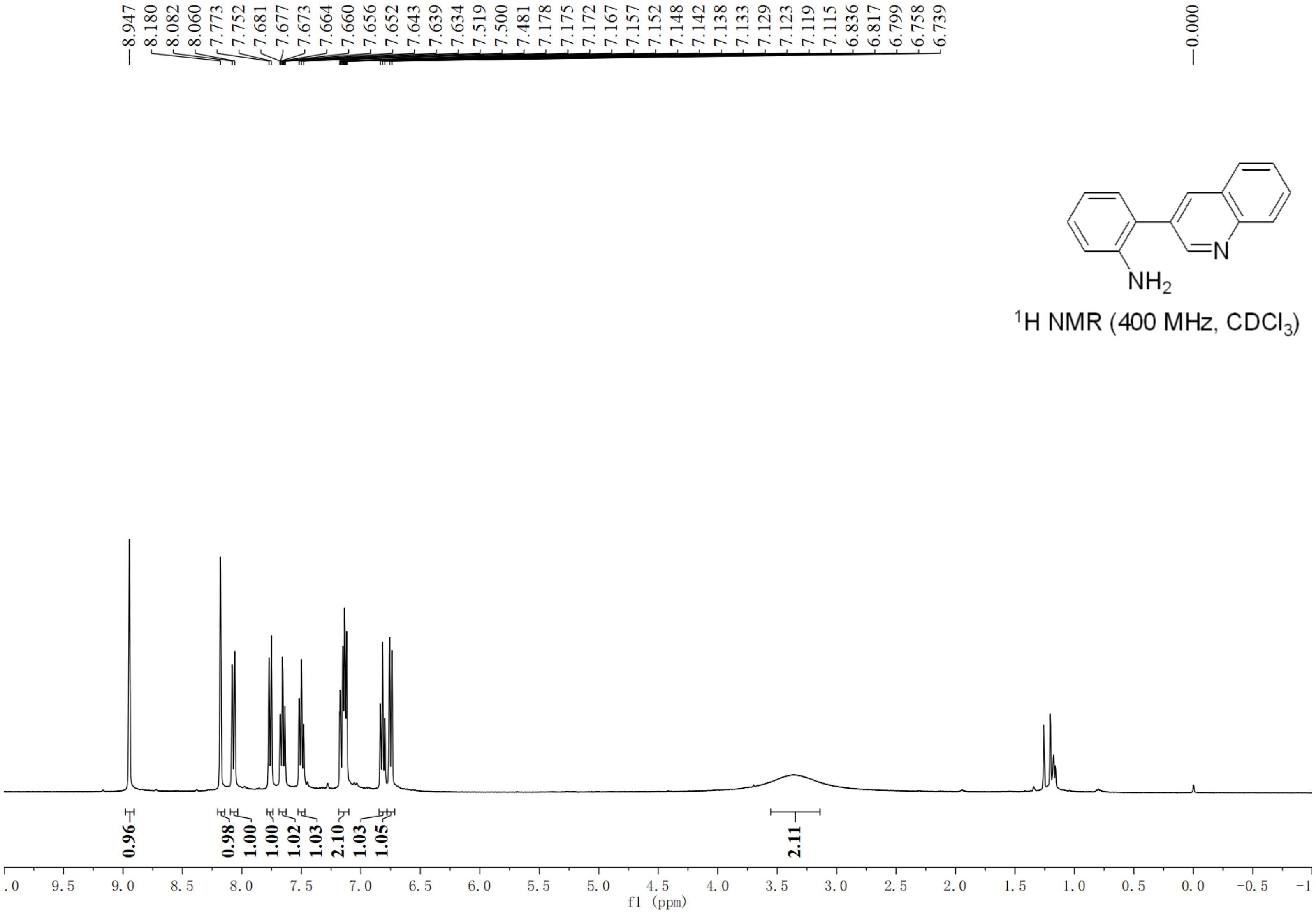


^{1}H NMR (400 MHz, $CDCl_3$)

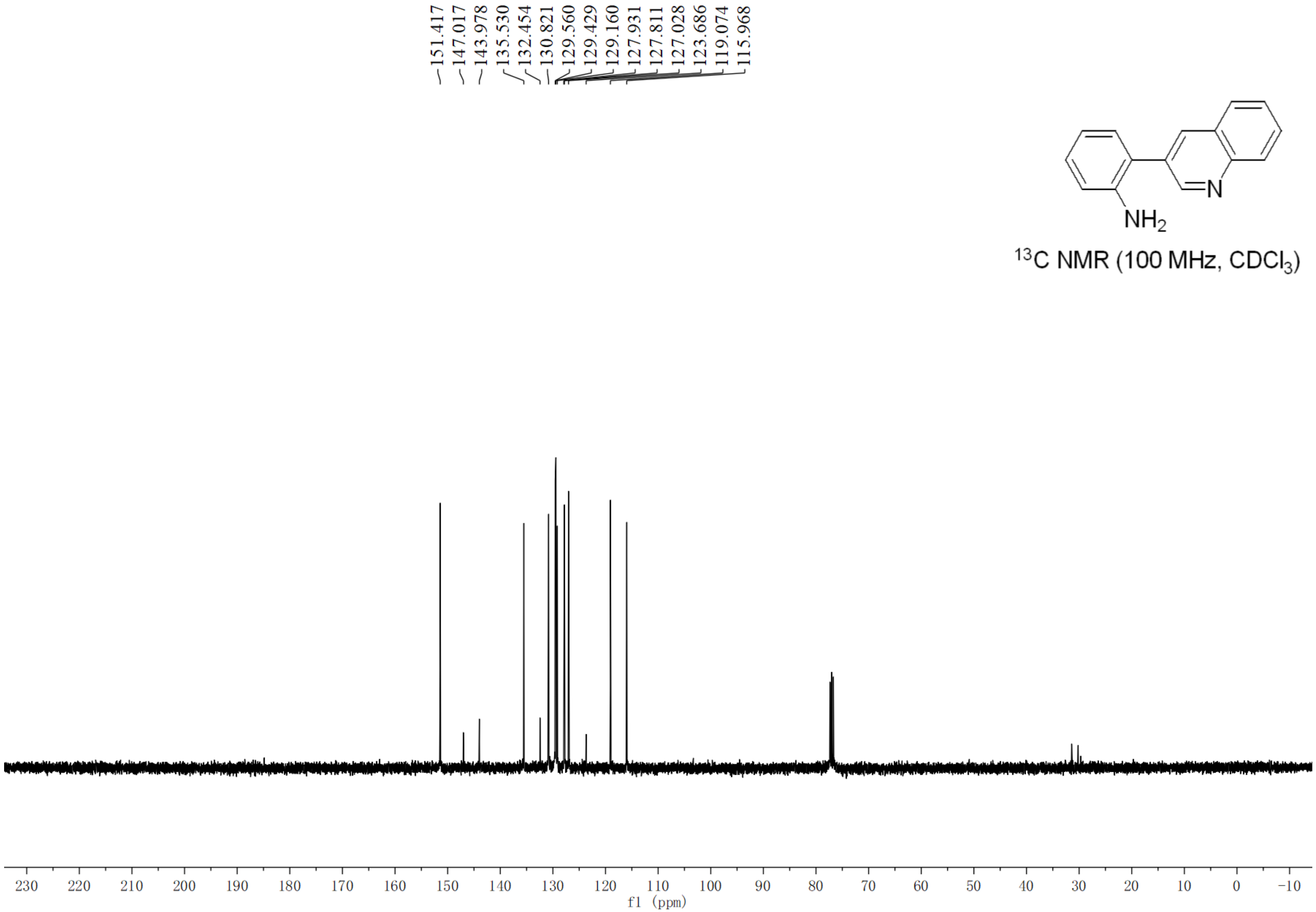


^{13}C NMR (100 MHz, $CDCl_3$)

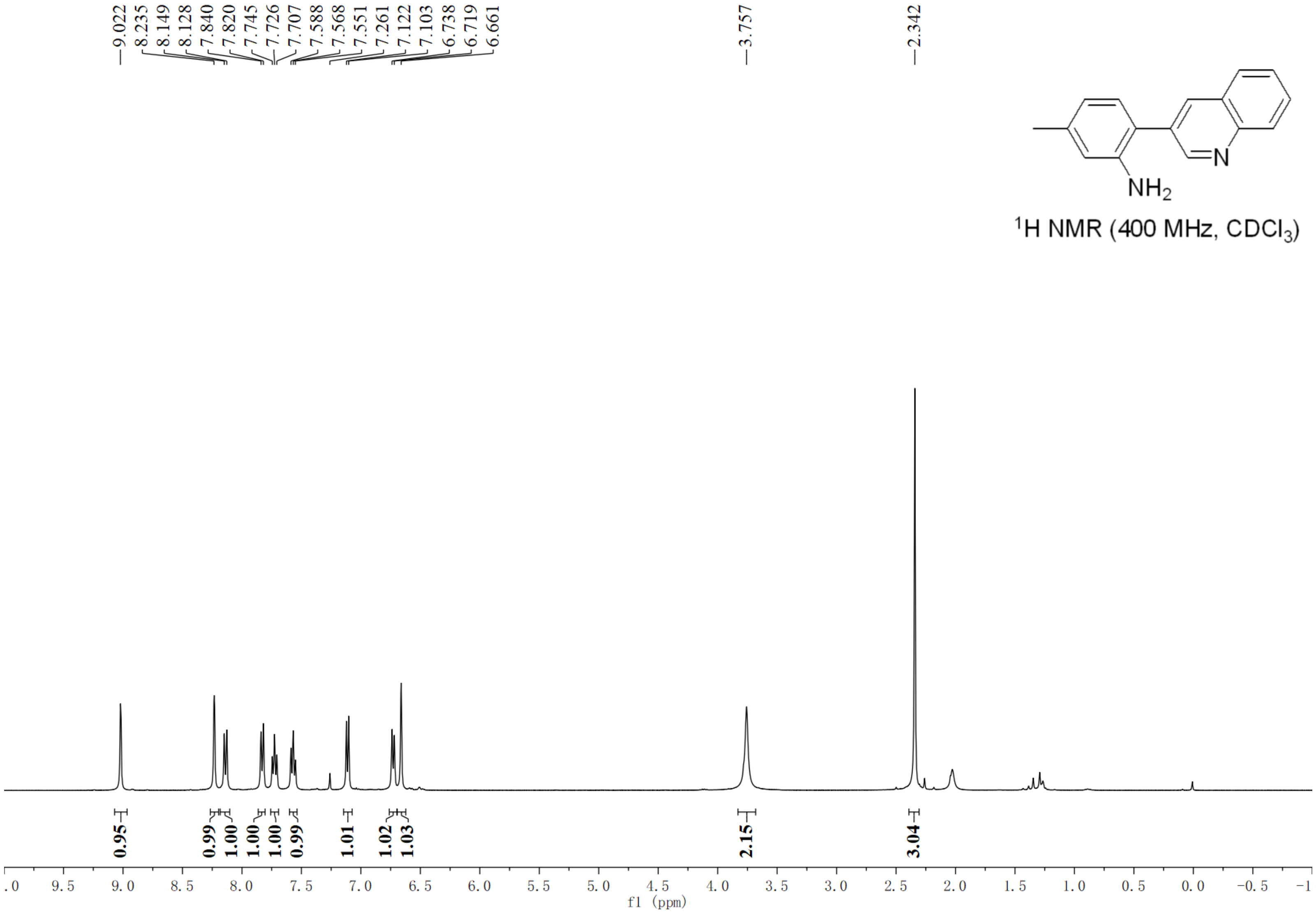




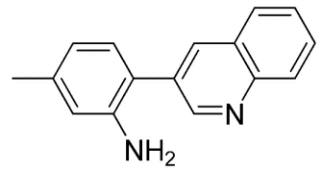
^1H NMR (400 MHz, $CDCl_3$)



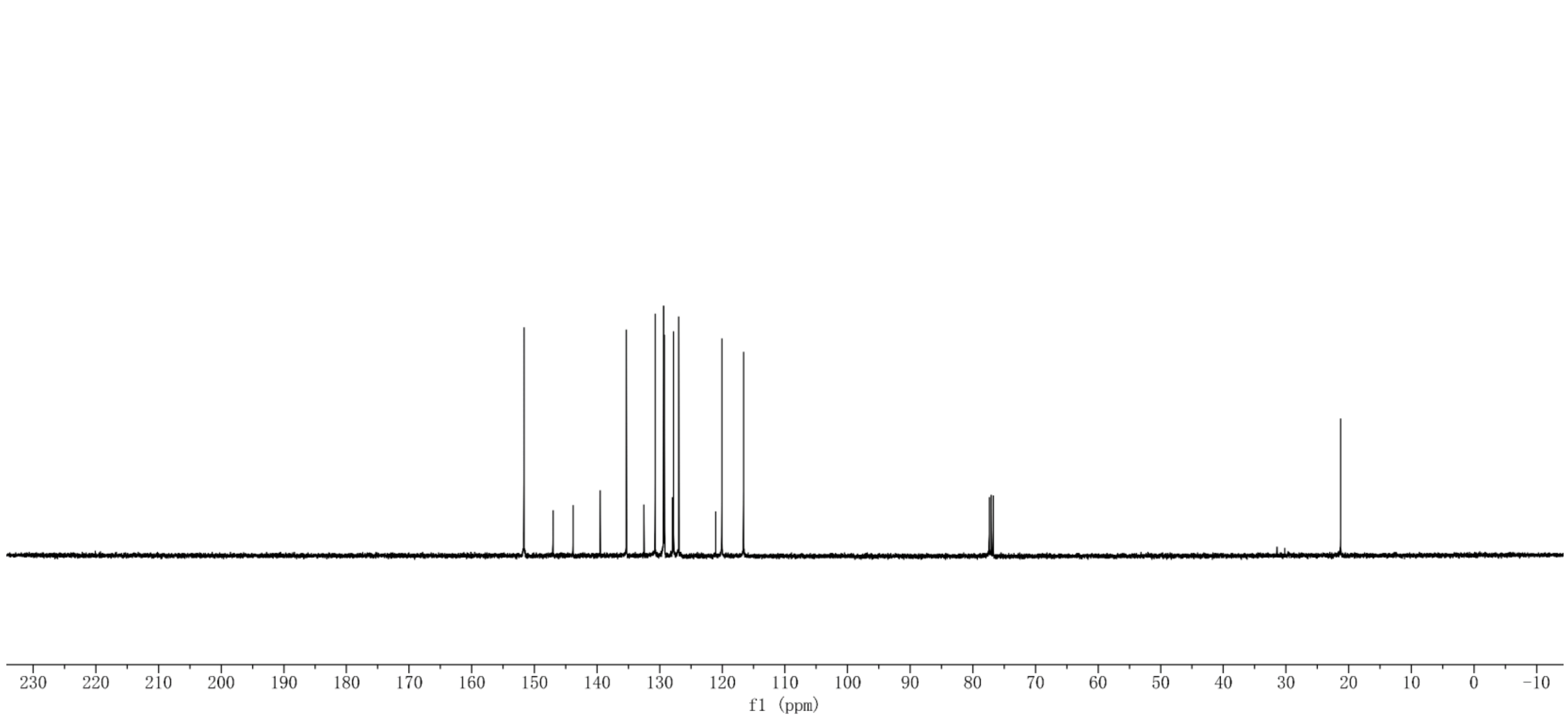
^{13}C NMR (100 MHz, $CDCl_3$)

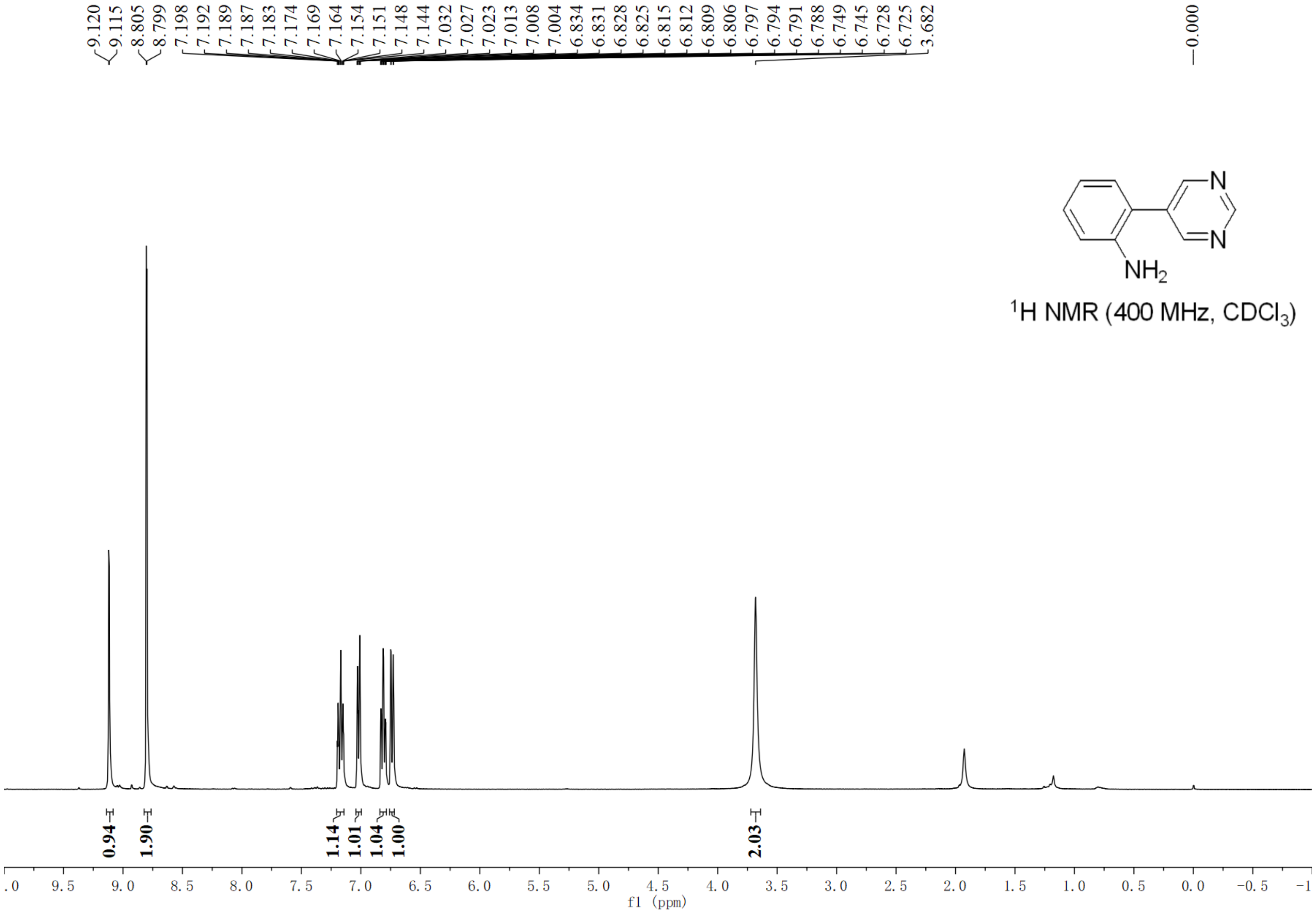


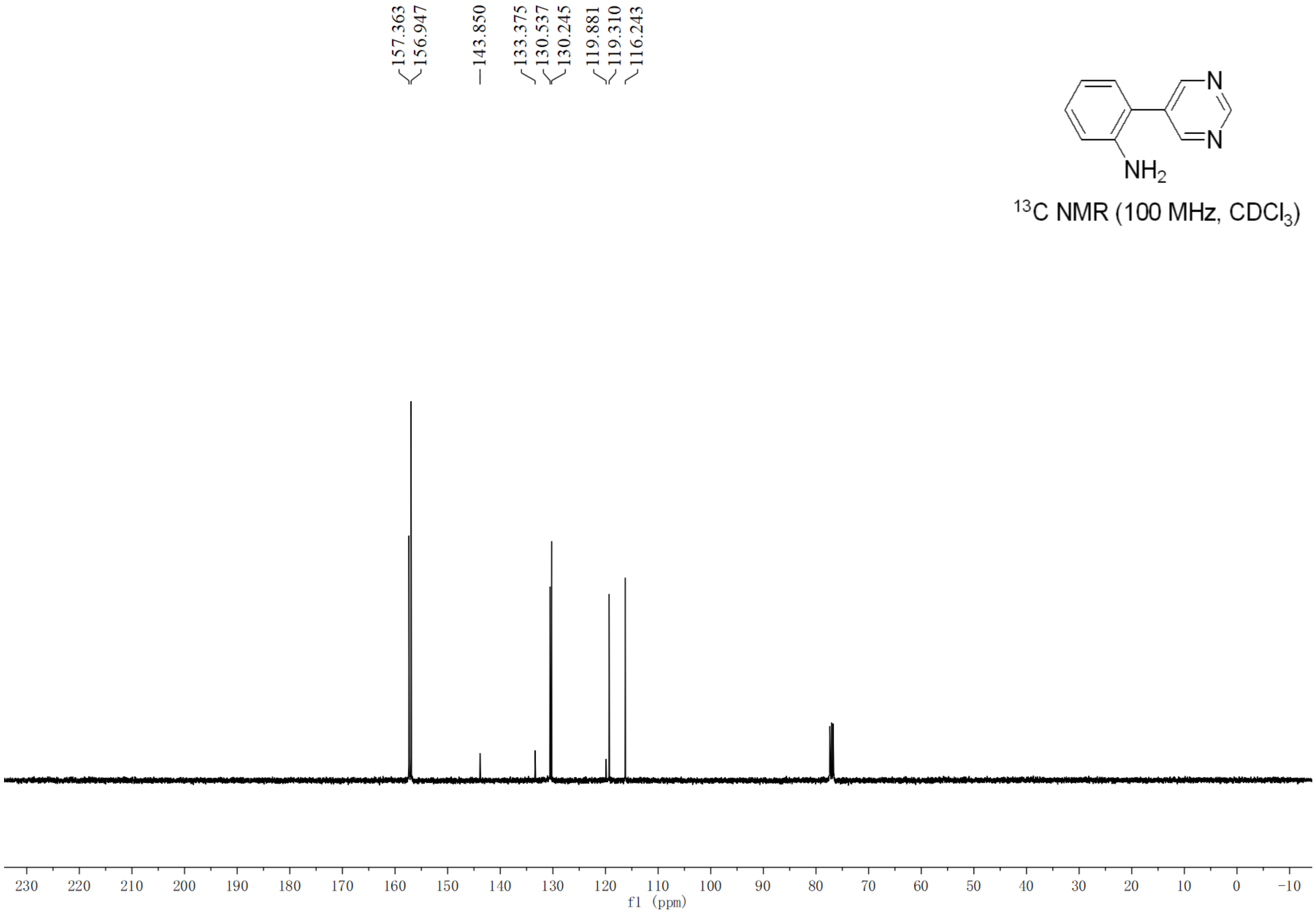
9.022
8.235
8.149
8.128
7.840
7.820
7.745
7.726
7.707
7.588
7.568
7.551
7.261
7.122
7.103
6.738
6.719
6.661
3.757
2.342
NH2
N
1H NMR (400 MHz, CDCl3)
0.95
0.99
1.00
1.00
1.00
0.99
1.01
1.02
1.03
2.15
3.04
f1 (ppm)

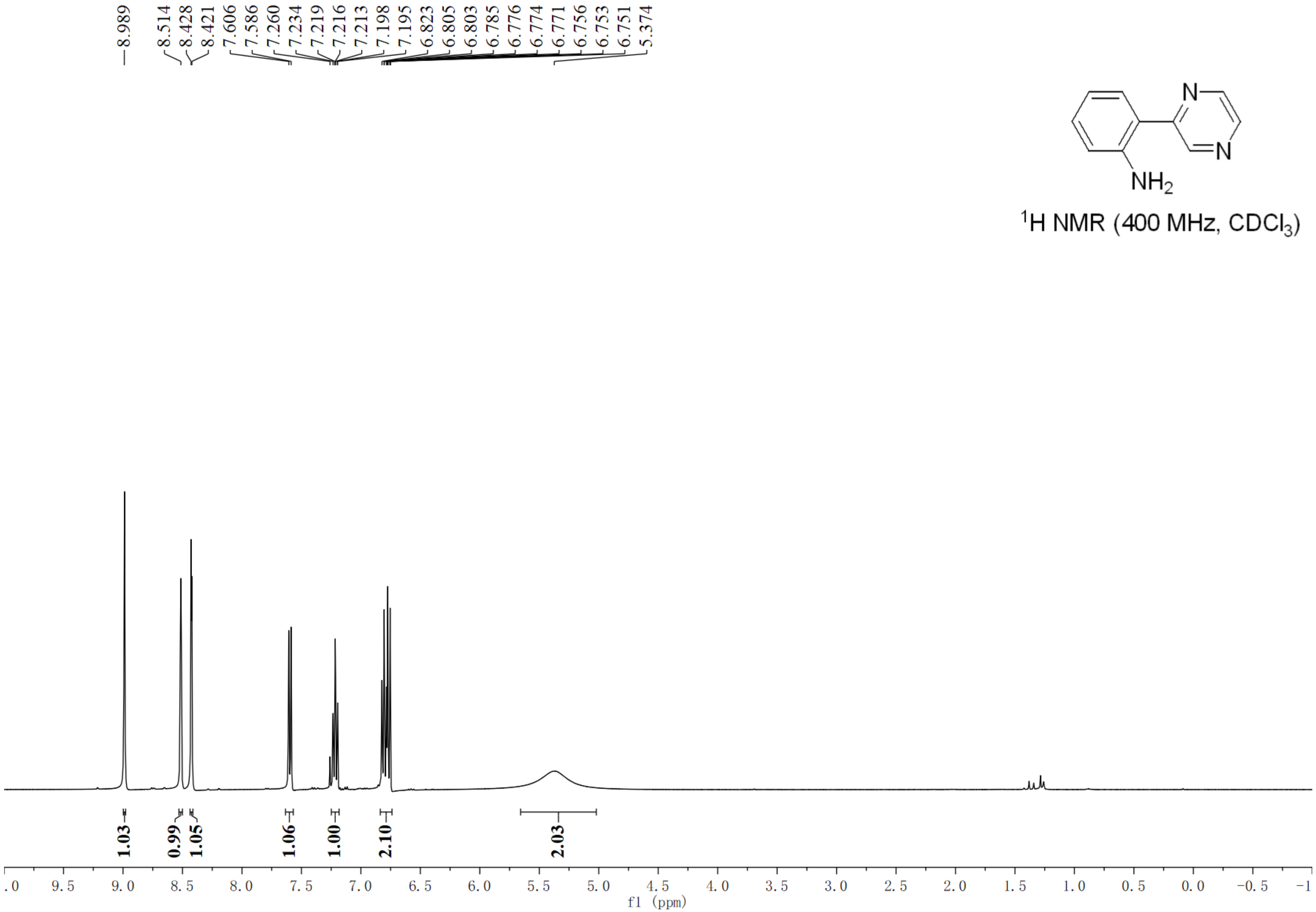


^{13}C NMR (100 MHz, $CDCl_3$)

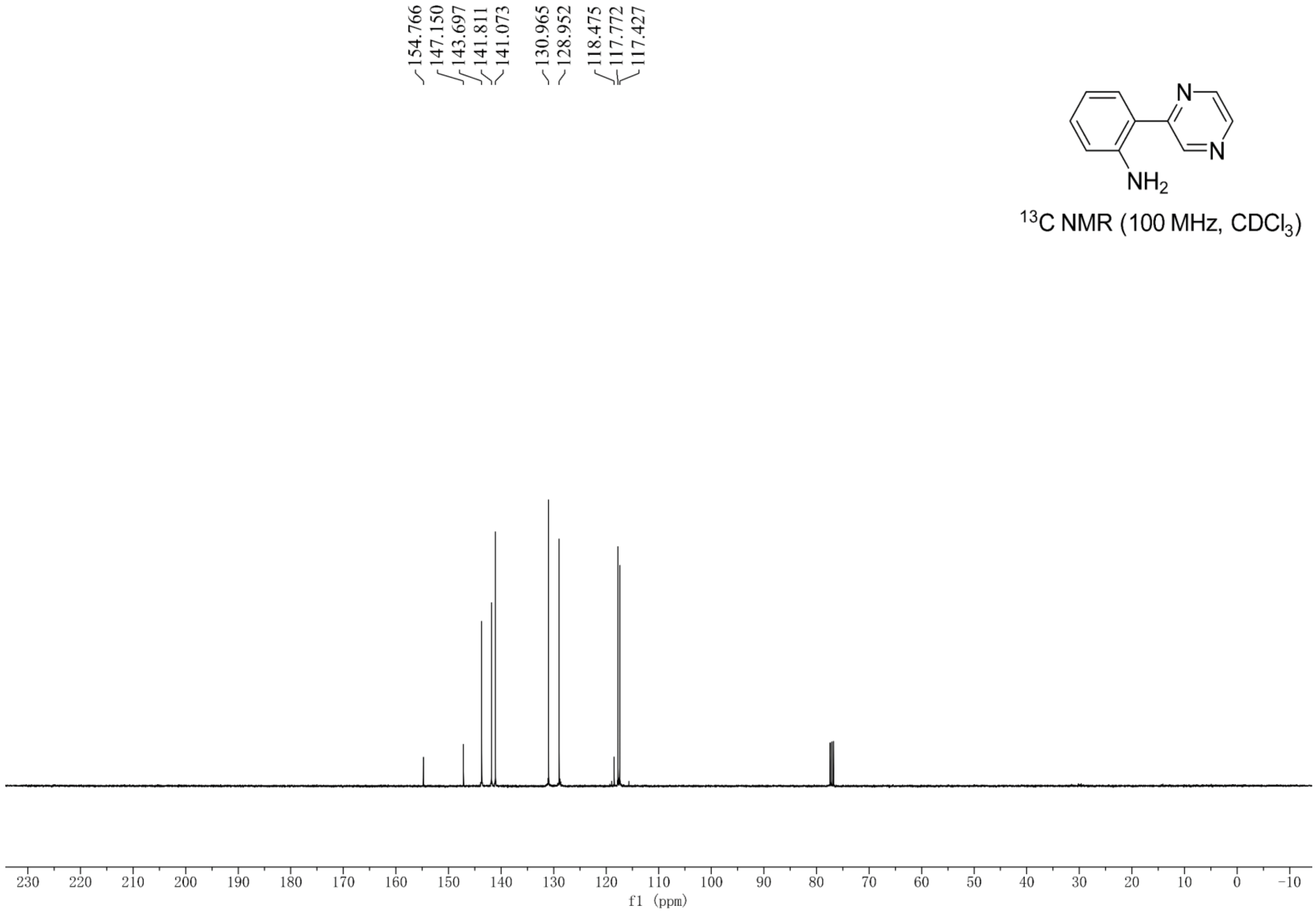



9.120
9.115
8.805
8.799
7.198
7.192
7.189
7.187
7.183
7.174
7.169
7.164
7.154
7.151
7.148
7.144
7.032
7.027
7.023
7.013
7.008
7.004
6.834
6.831
6.828
6.825
6.815
6.812
6.809
6.806
6.797
6.794
6.791
6.788
6.749
6.745
6.728
6.725
3.682
0.000
N
N
NH2
1H NMR (400 MHz, CDCl3)
0.94
1.90
1.14
1.01
1.04
1.00
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

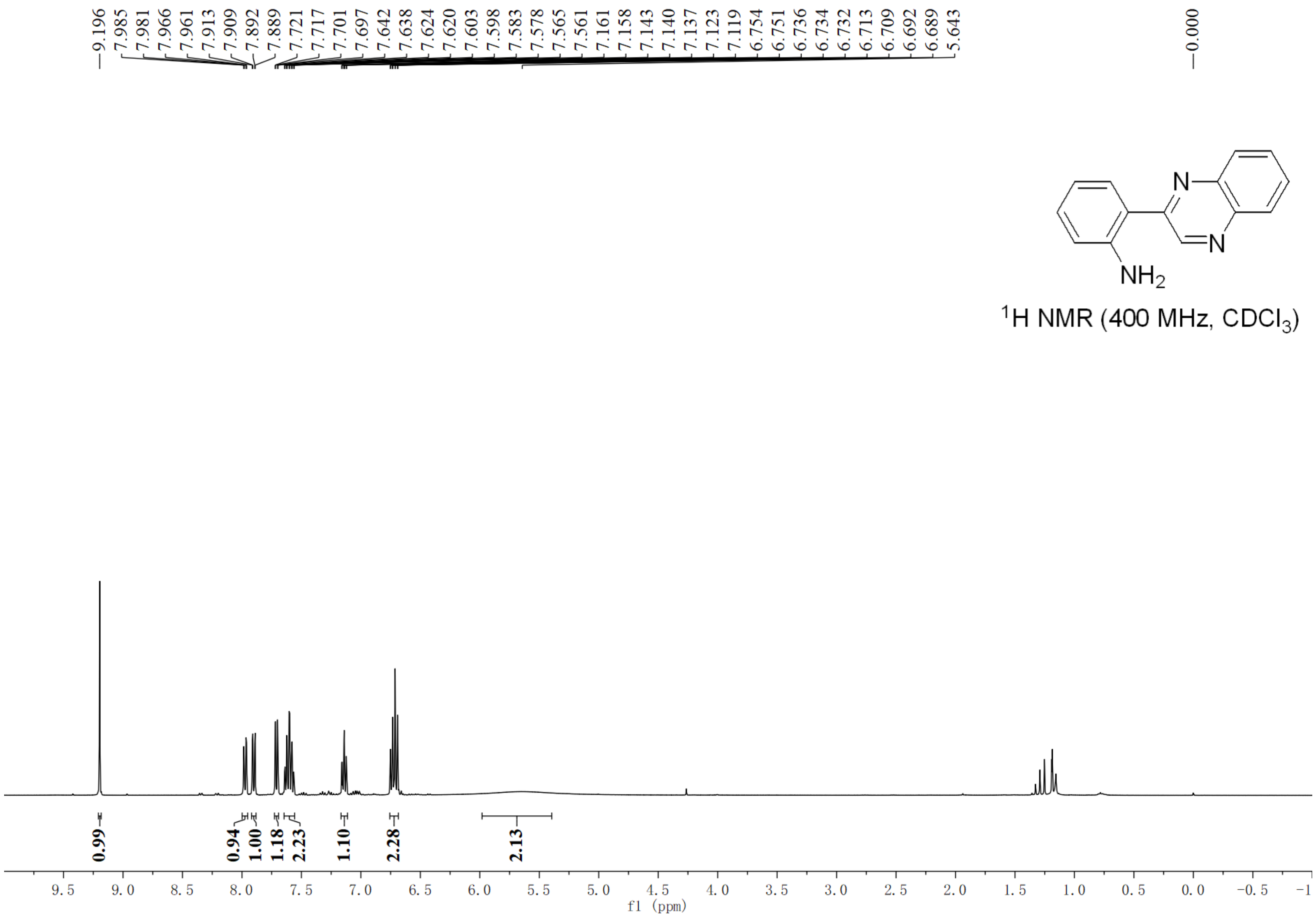

157.363
156.947
143.850
133.375
130.537
130.245
119.881
119.310
116.243
N
N
NH2
13C NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



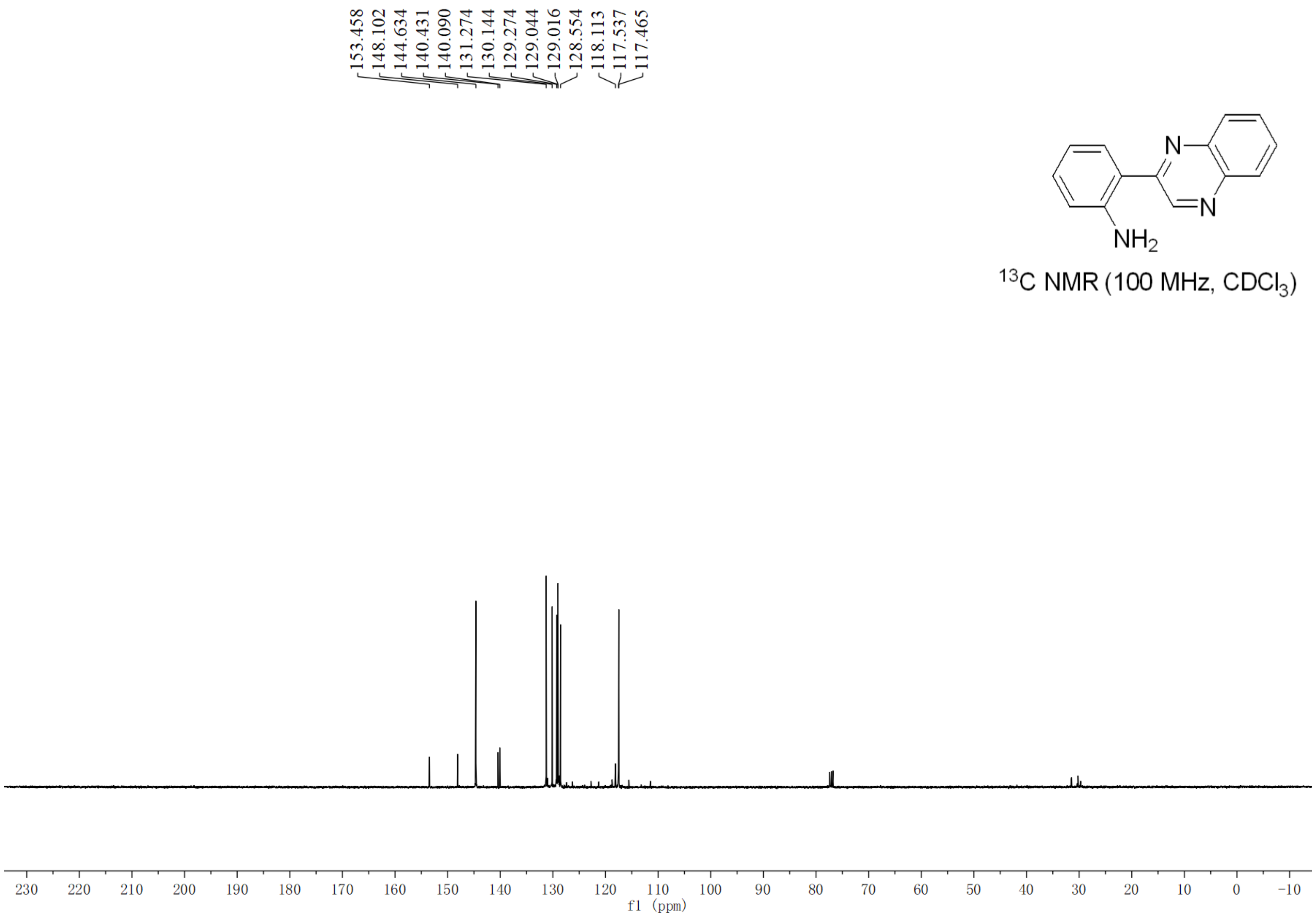
^{1}H NMR (400 MHz, $CDCl_3$)



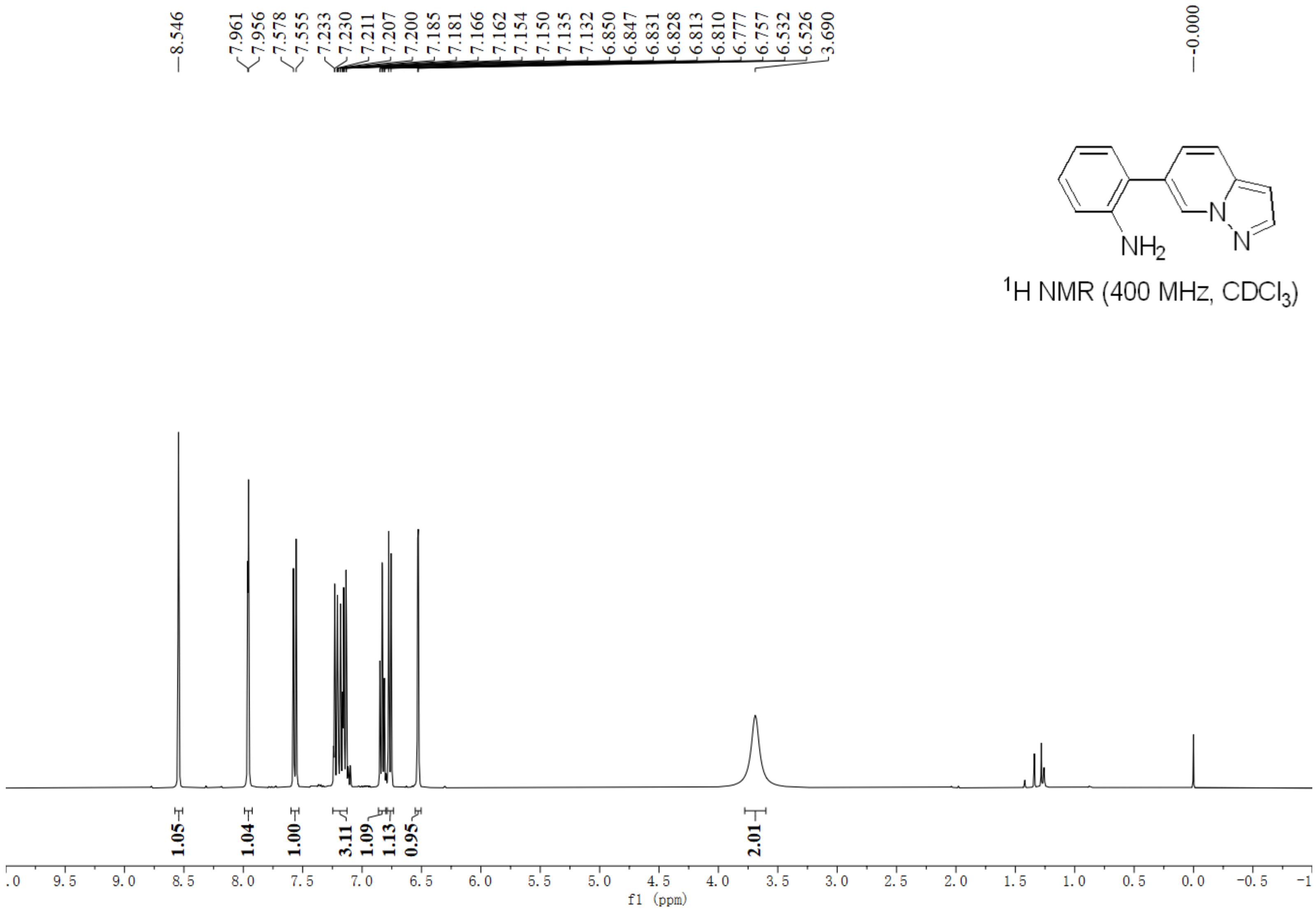
^{13}C NMR (100 MHz, $CDCl_3$)

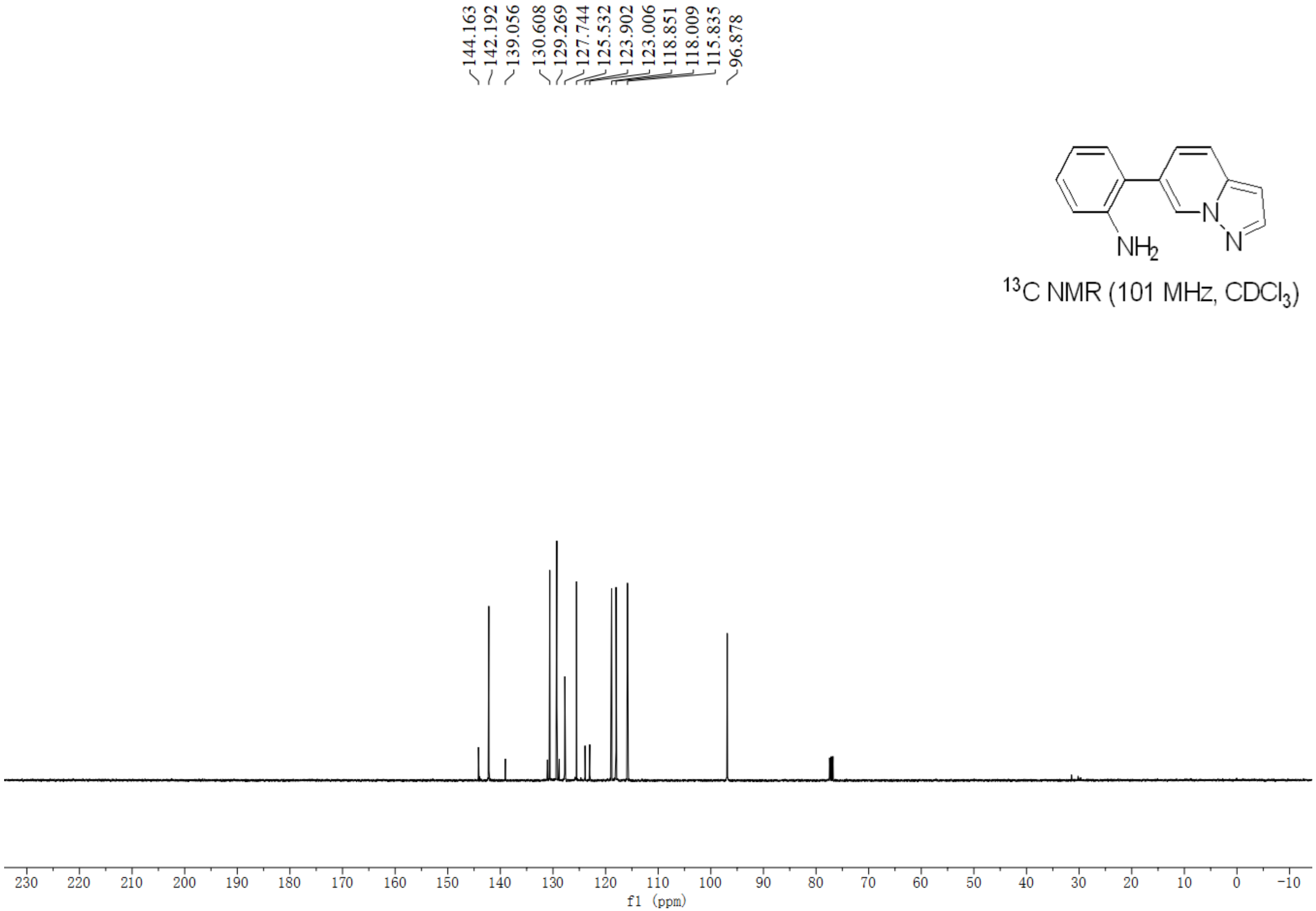


^1H NMR (400 MHz, $CDCl_3$)

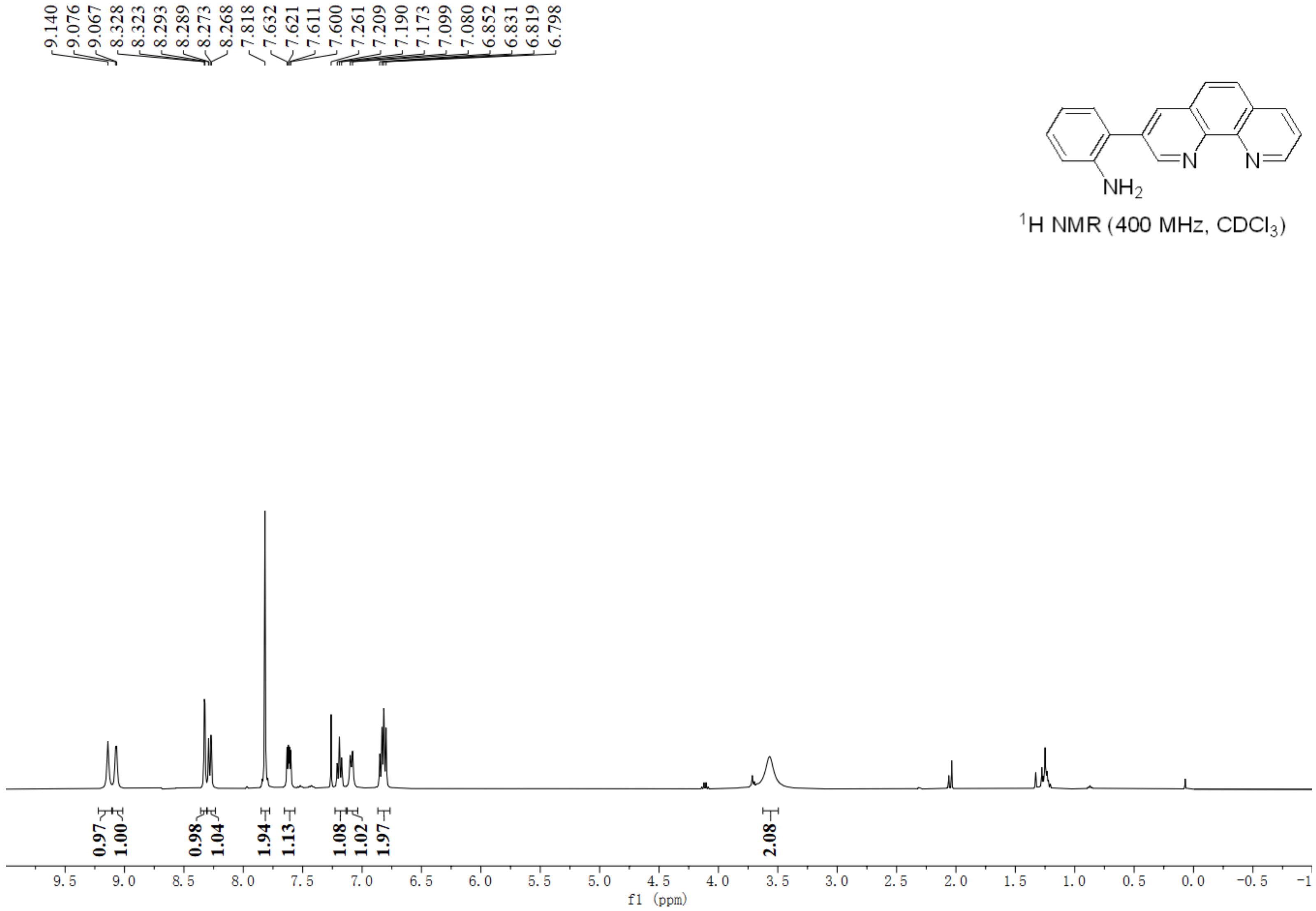


^{13}C NMR (100 MHz, $CDCl_3$)

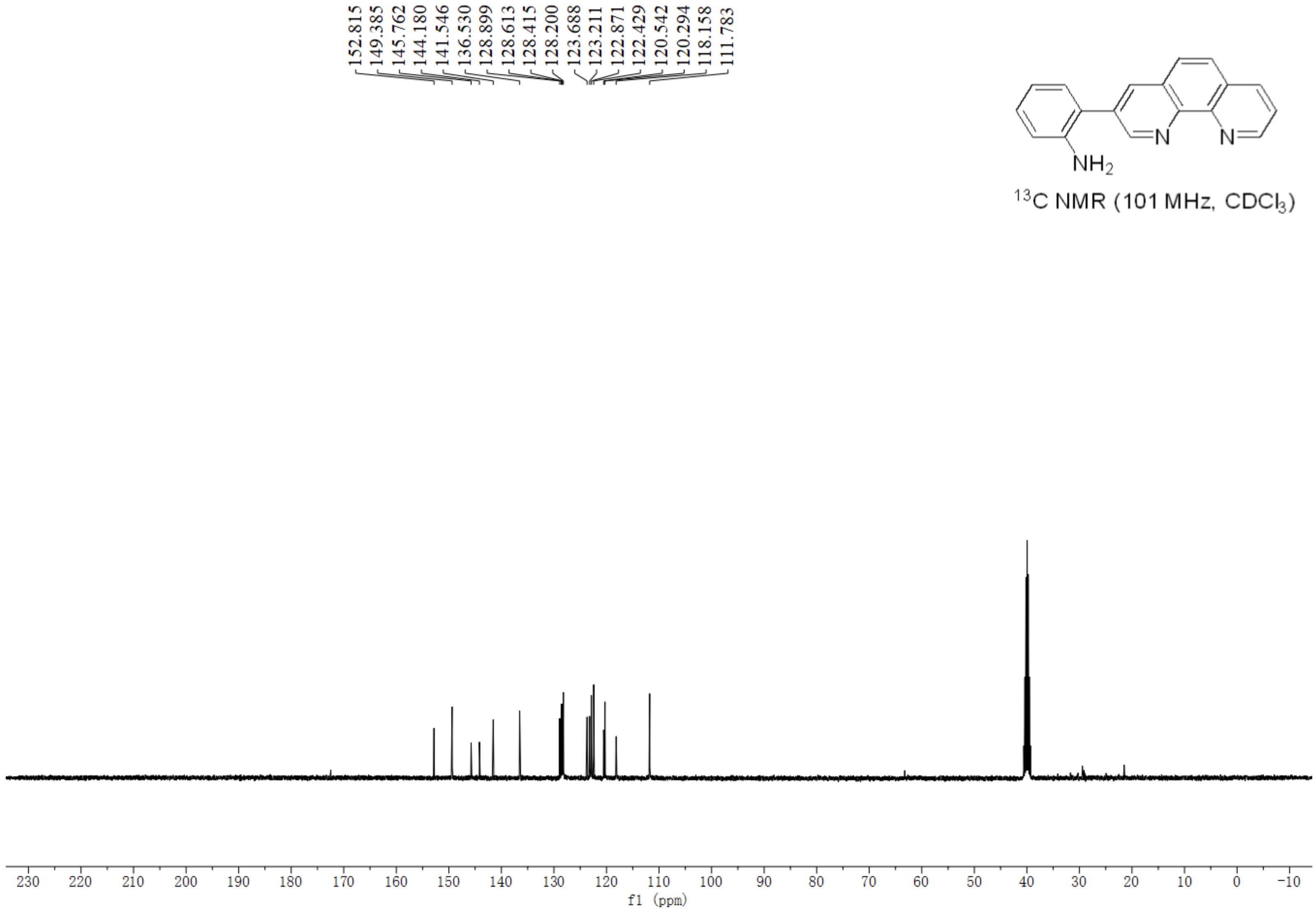

8.546
7.961
7.956
7.578
7.555
7.233
7.230
7.211
7.207
7.200
7.185
7.181
7.166
7.162
7.154
7.150
7.135
7.132
6.850
6.847
6.831
6.828
6.813
6.810
6.777
6.757
6.532
6.526
3.690
0.000
NH2
N
N
1H NMR (400 MHz, CDCl3)
1.05
1.04
1.00
3.11
1.09
1.13
0.95
2.01
f1 (ppm)



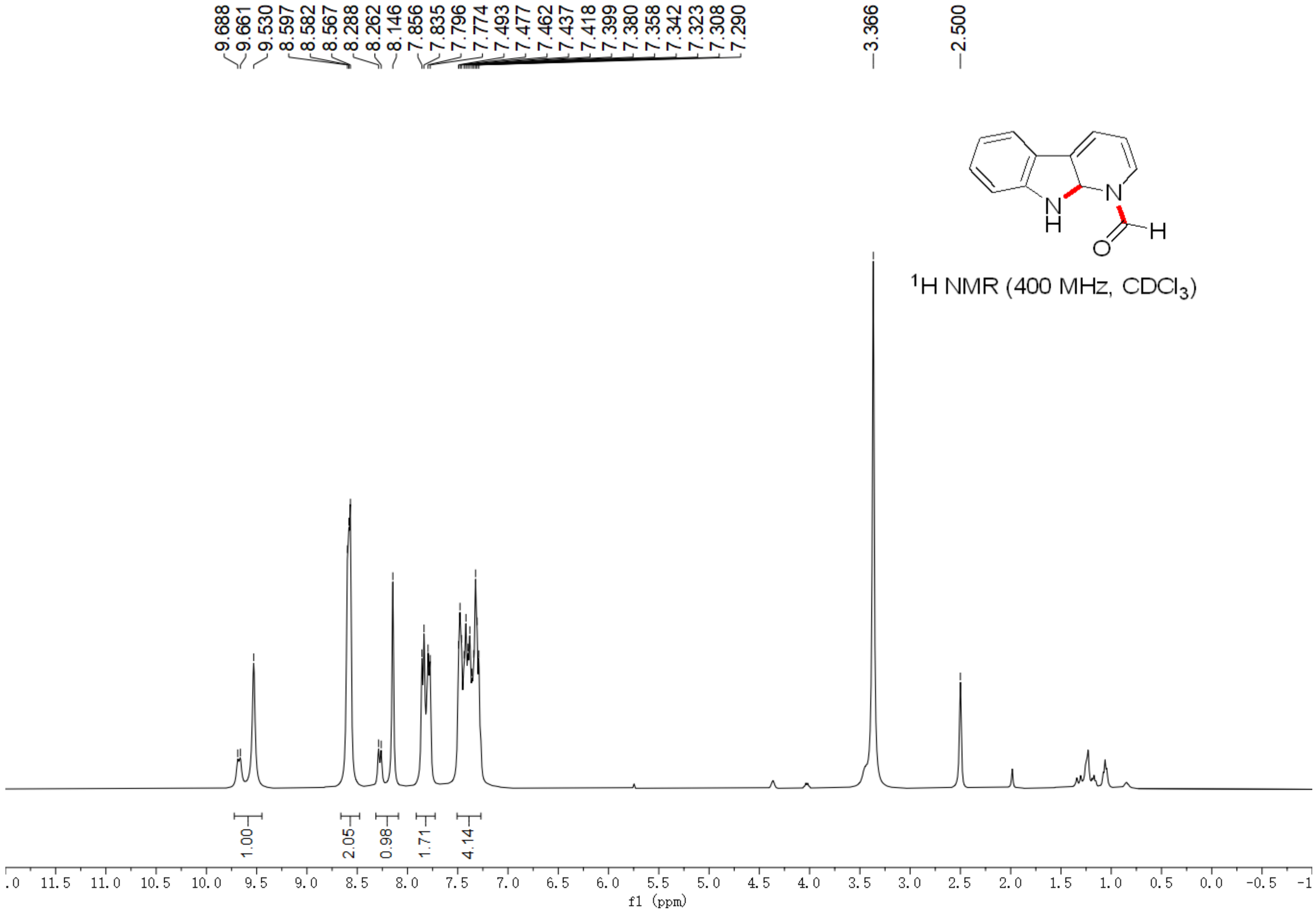
^{13}C NMR (101 MHz, $CDCl_3$)

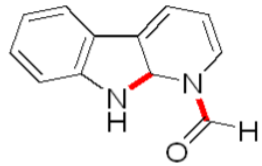


^{1}H NMR (400 MHz, $CDCl_3$)

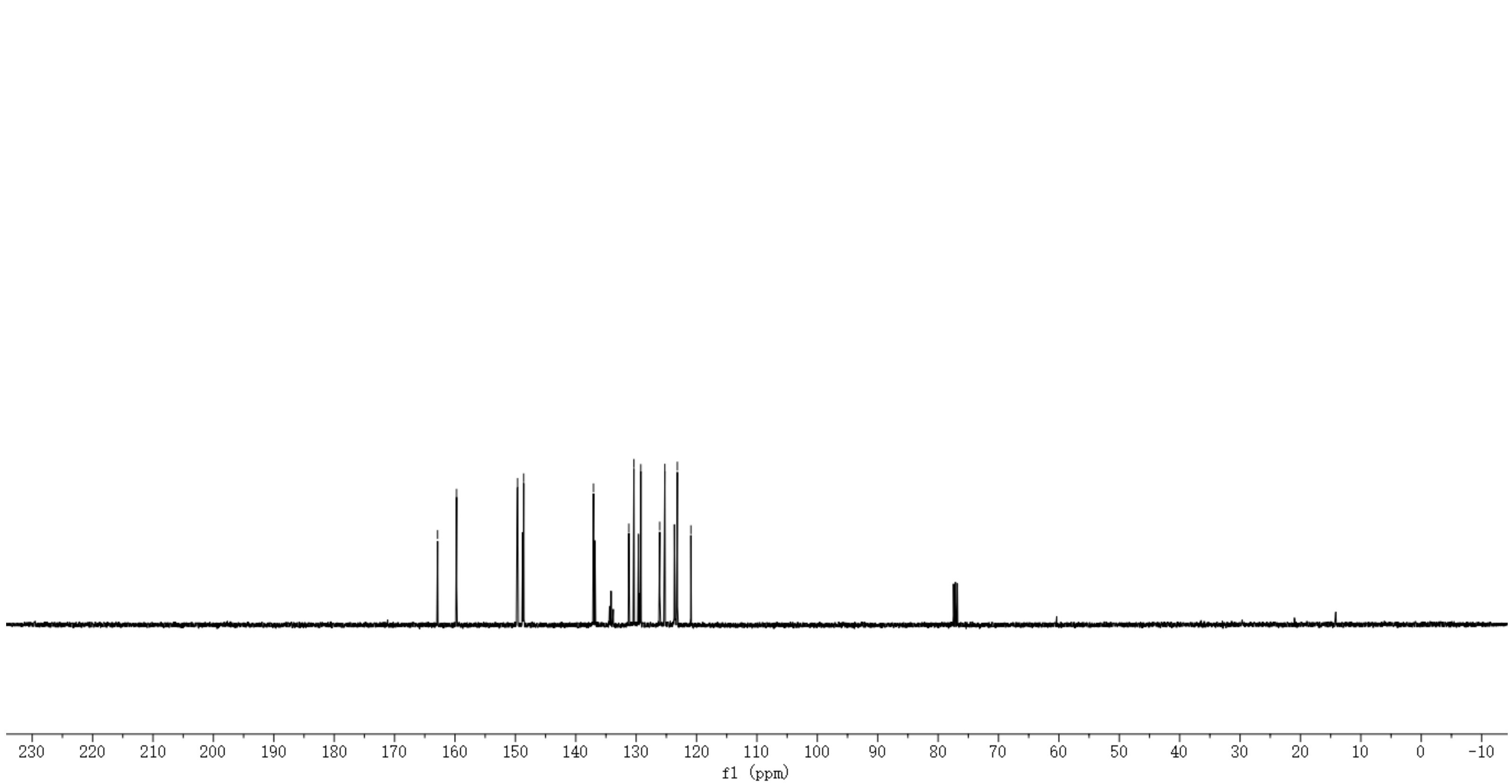


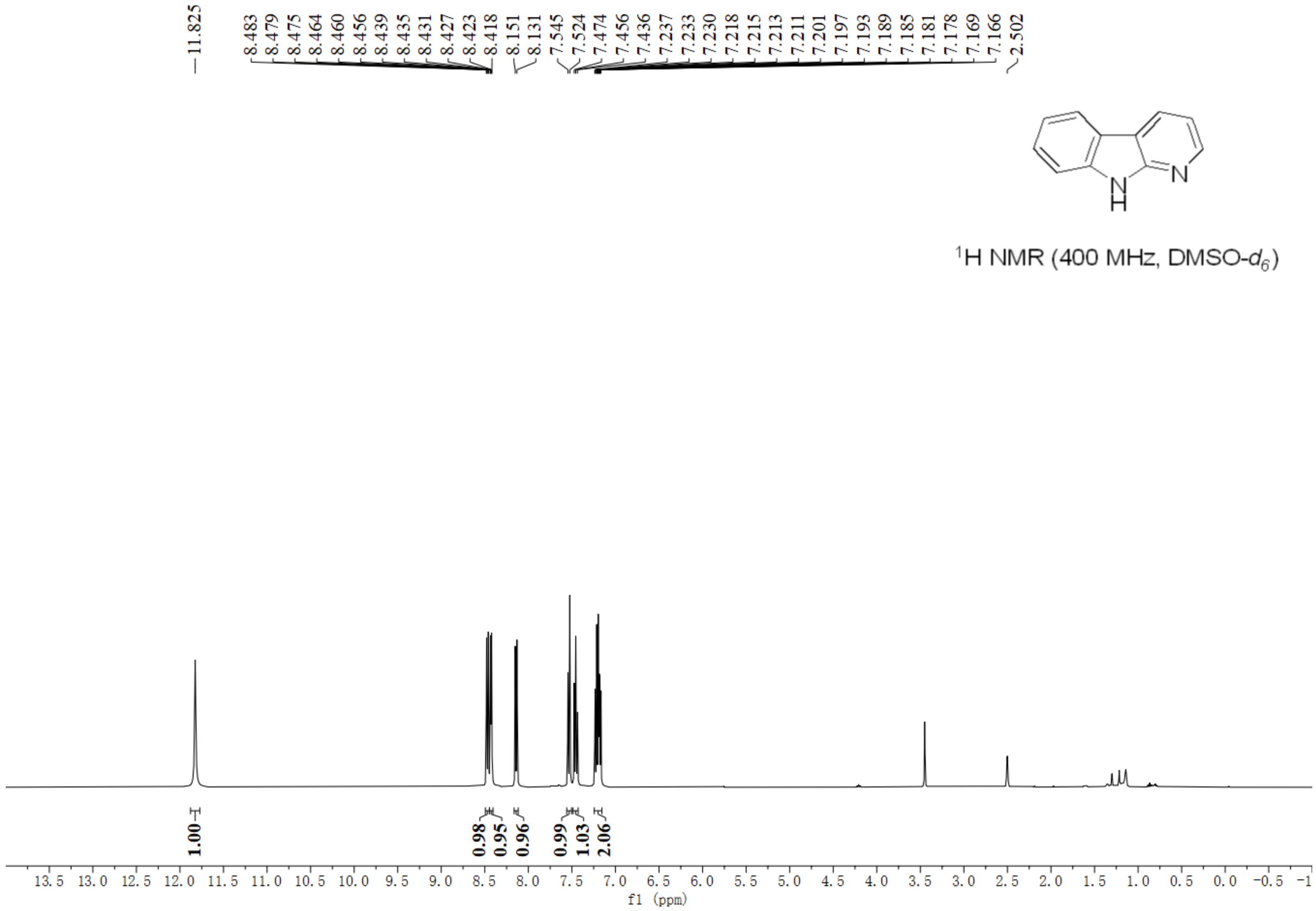
^{13}C NMR (101 MHz, $CDCl_3$)


9.688
9.661
9.530
8.597
8.582
8.567
8.288
8.262
8.146
7.856
7.835
7.796
7.774
7.493
7.477
7.462
7.437
7.418
7.399
7.380
7.358
7.342
7.323
7.308
7.290
3.366
2.500
N
H
N
O
H
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
2.05
0.98
1.71
4.14
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

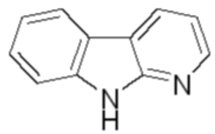


^{13}C NMR (100 MHz, $CDCl_3$)

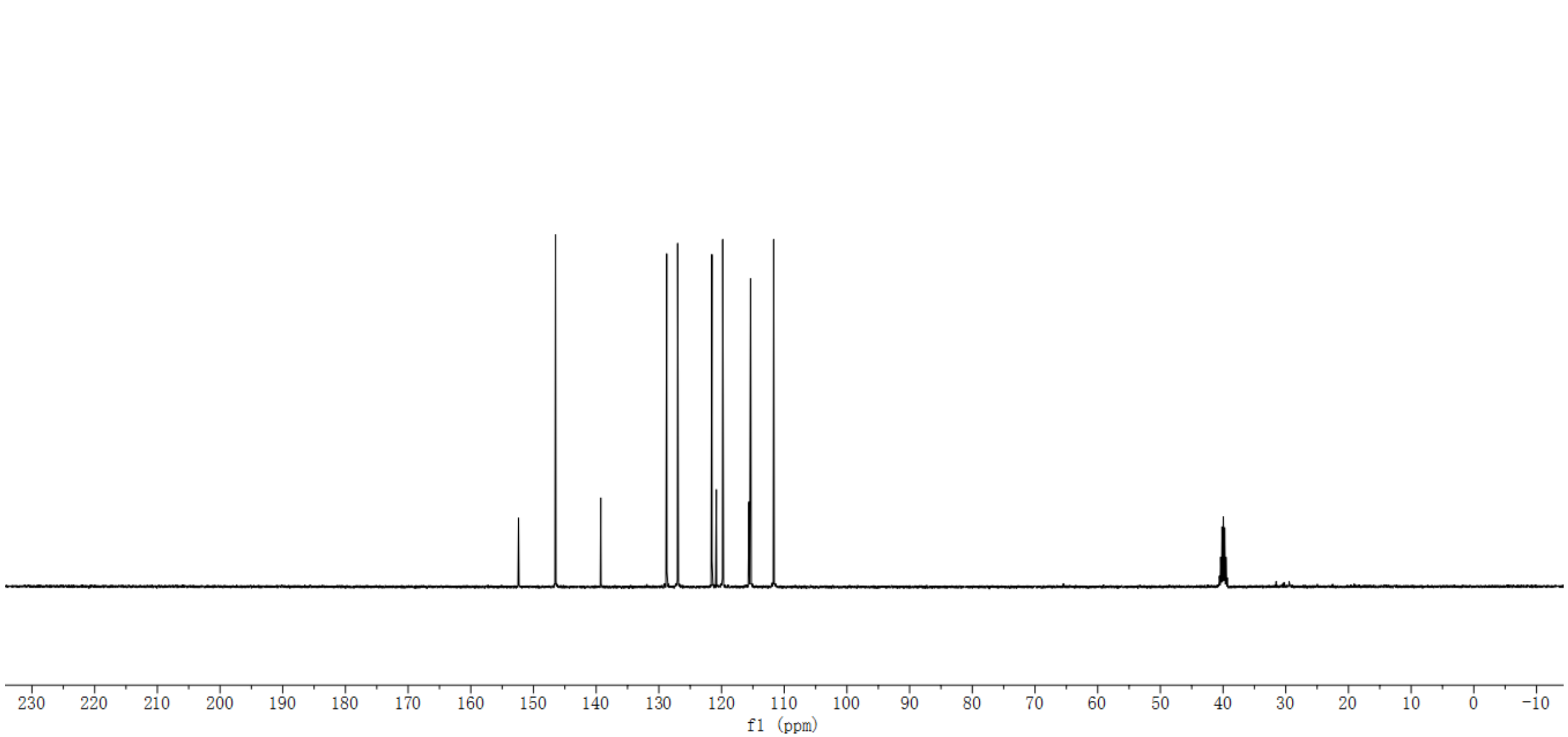


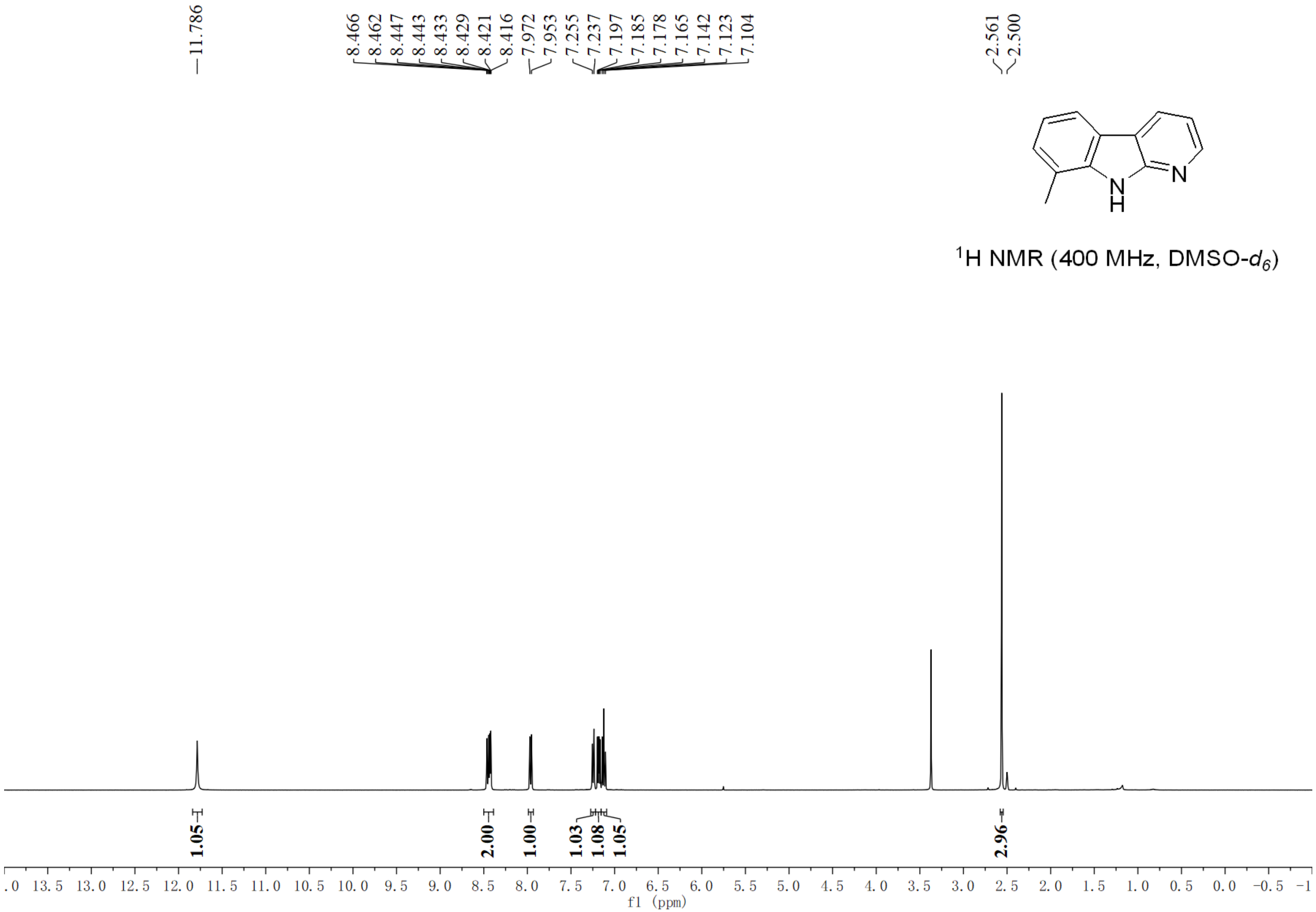


^{1}H NMR (400 MHz, DMSO-d_6)

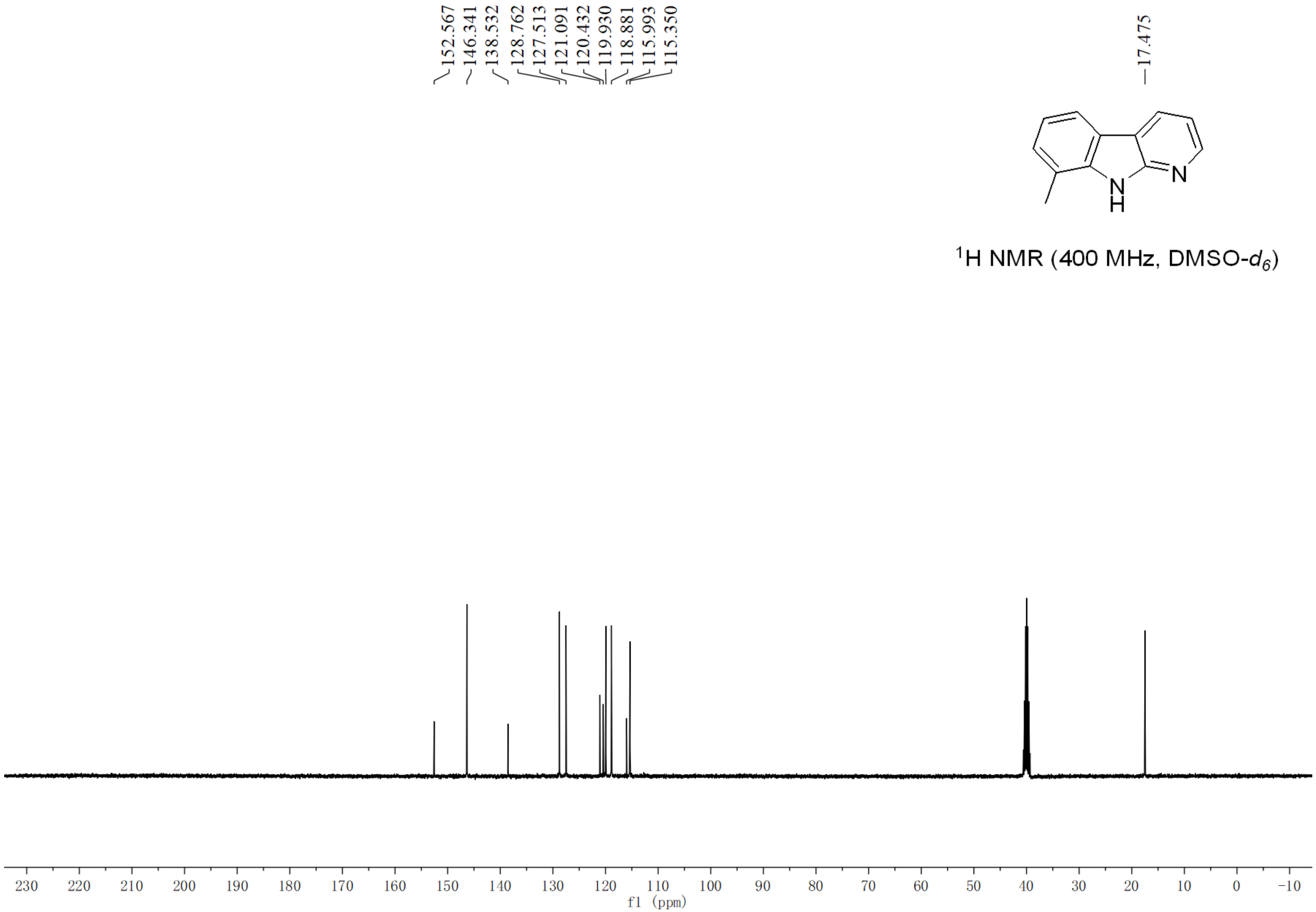


^{13}C NMR (101 MHz, DMSO-d_6)

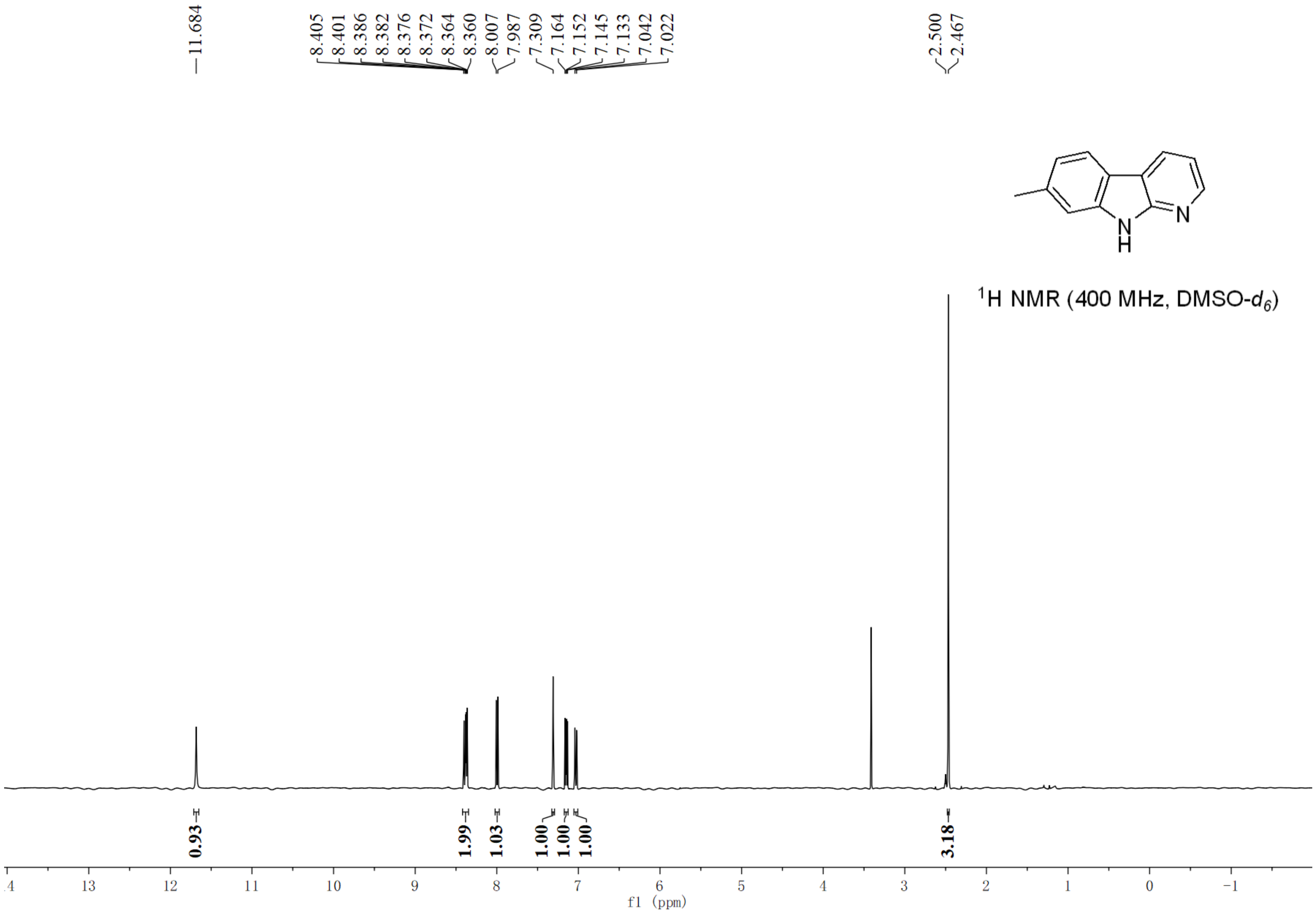




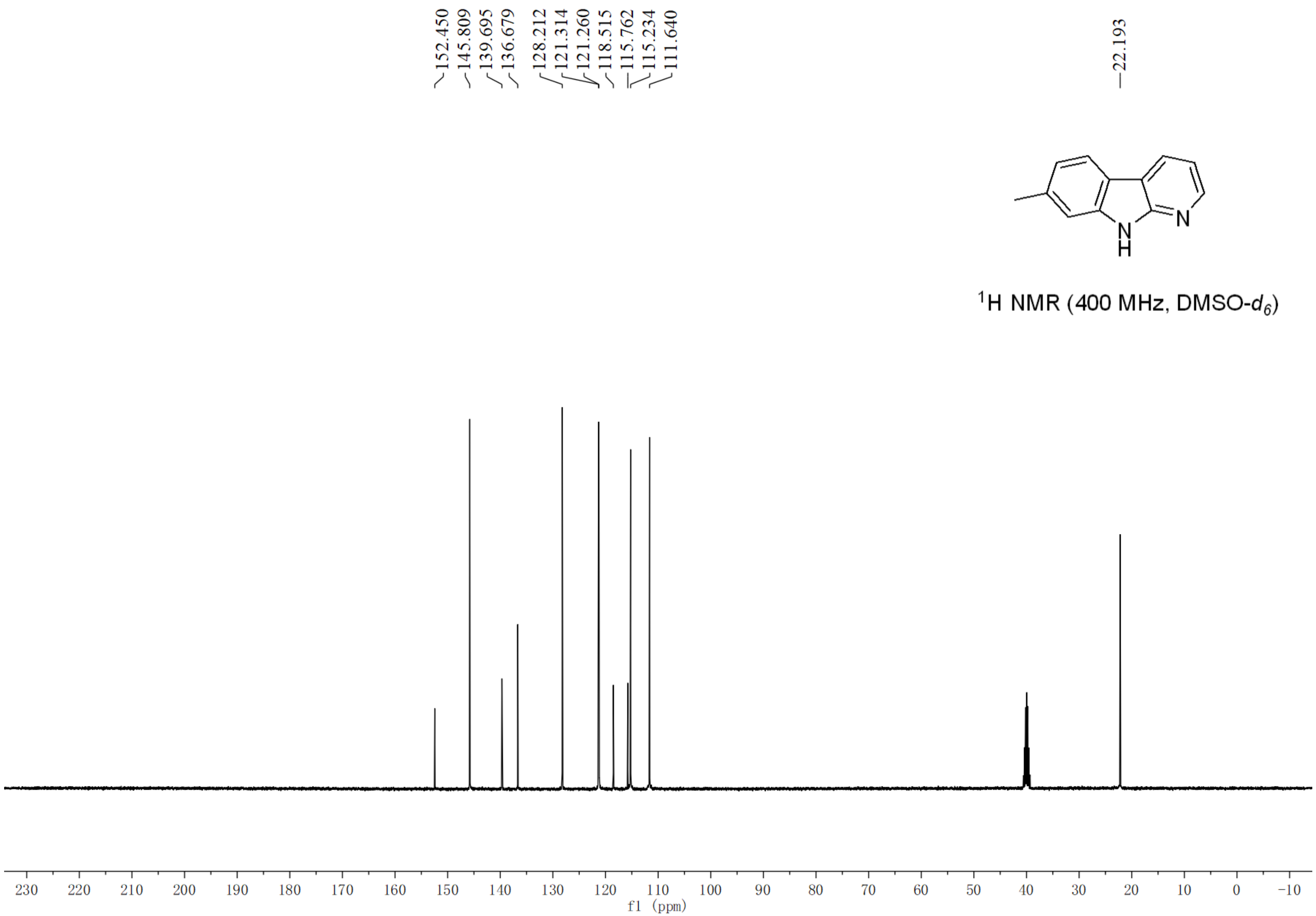
^1H NMR (400 MHz, DMSO-d_6)

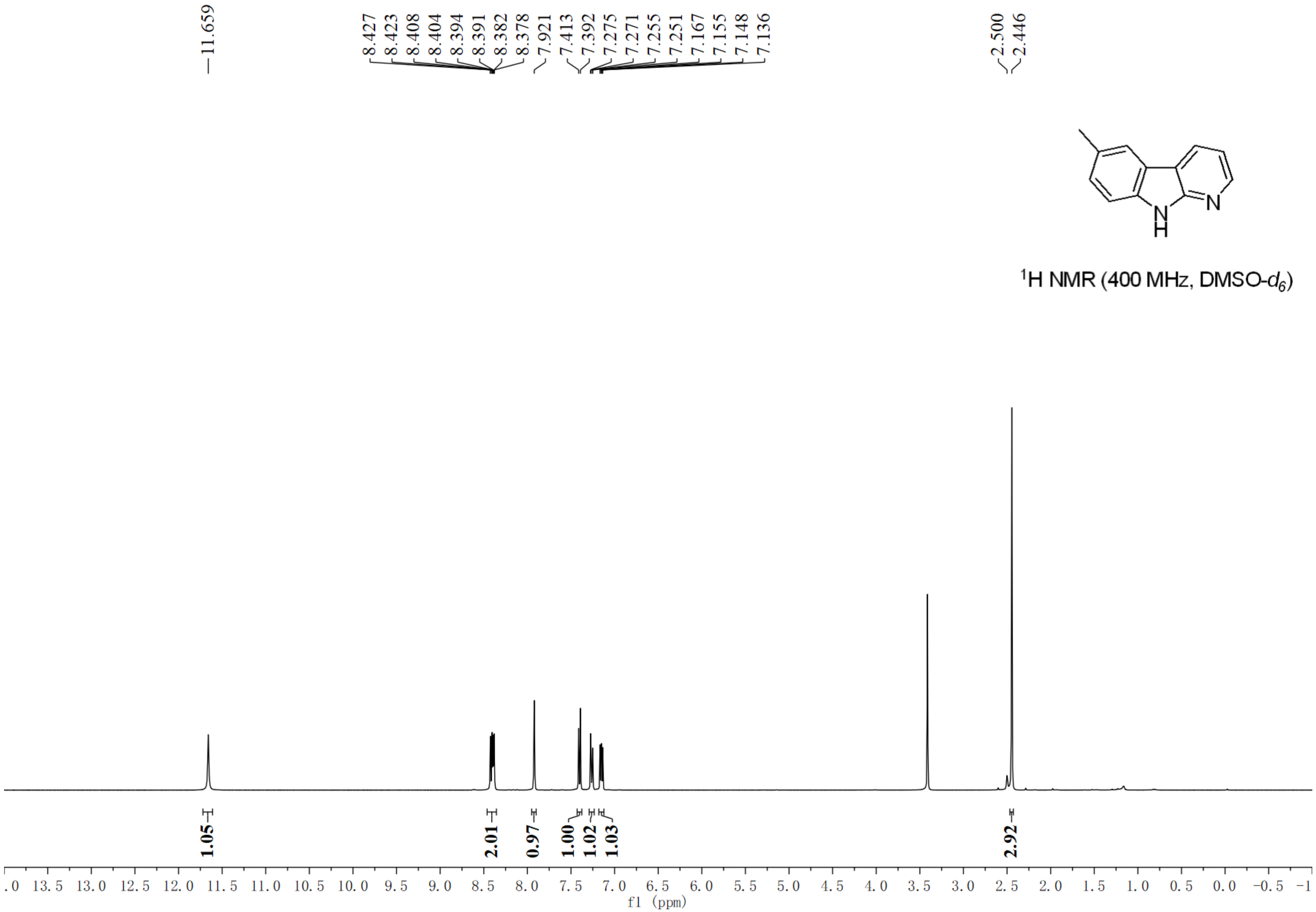


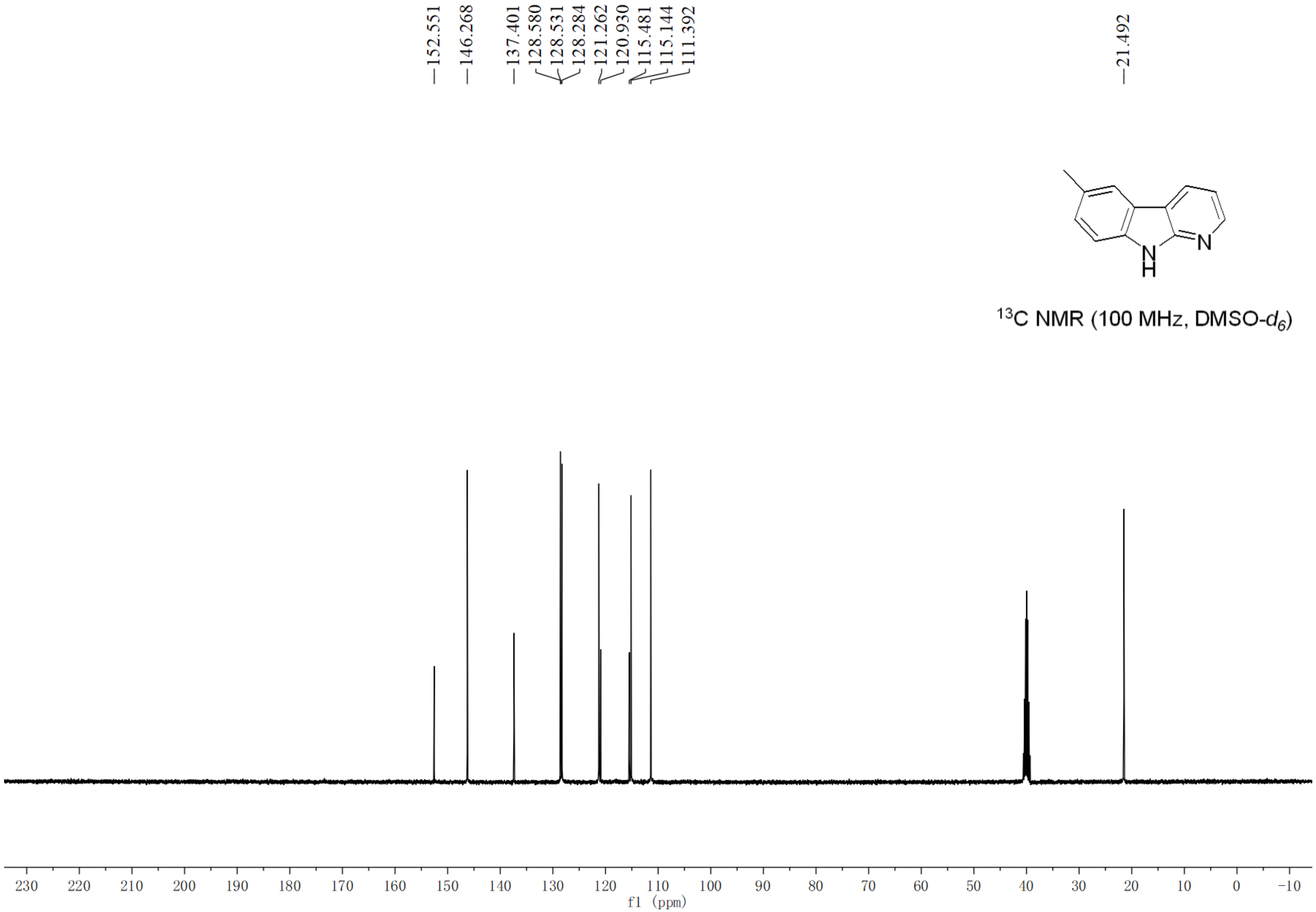
^1H NMR (400 MHz, DMSO-d_6)



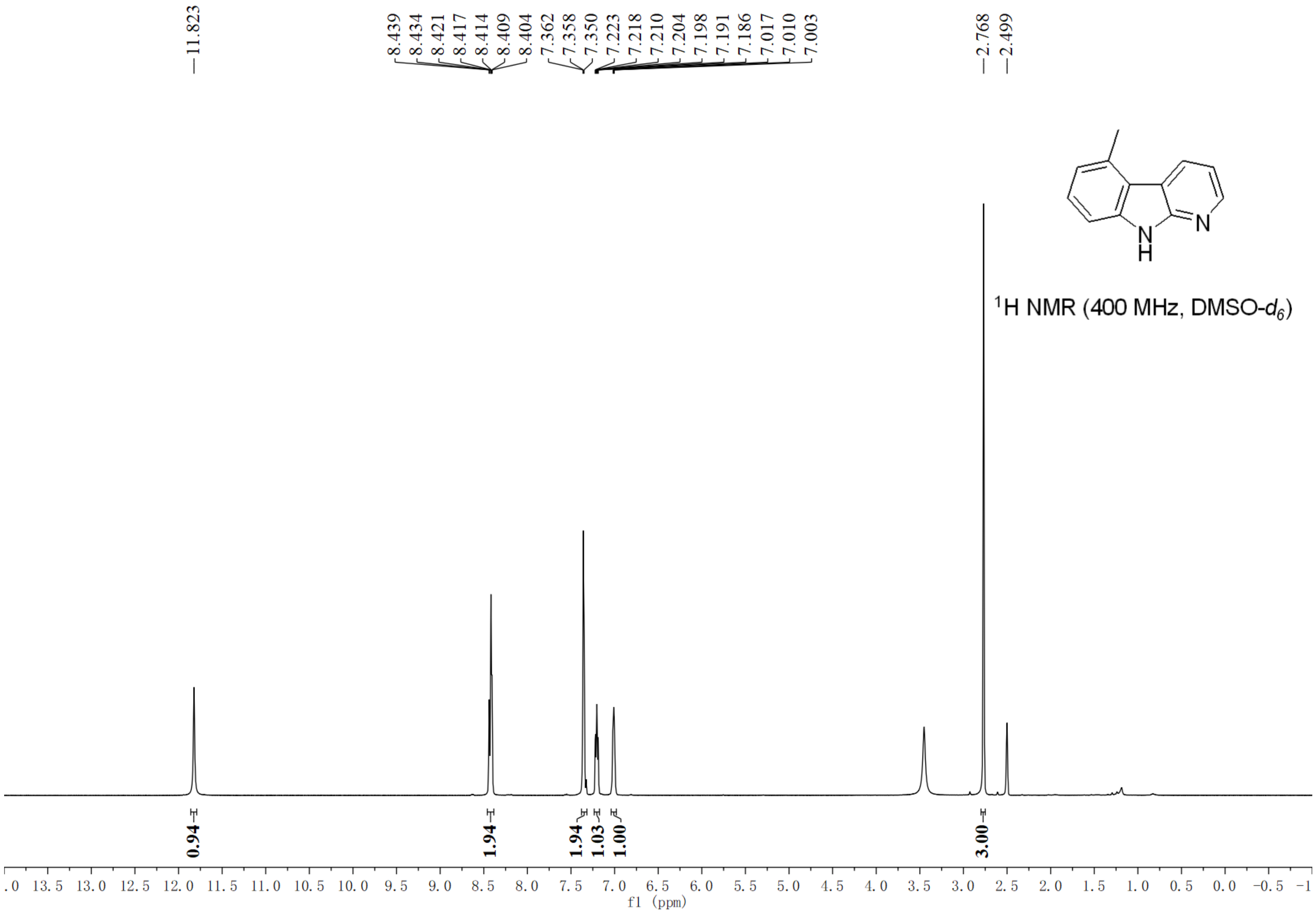
^1H NMR (400 MHz, DMSO-d_6)

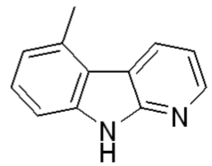

152.450
145.809
139.695
136.679
128.212
121.314
121.260
118.515
115.762
115.234
111.640
22.193
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


11.659
8.427
8.423
8.408
8.404
8.394
8.391
8.382
8.378
7.921
7.413
7.392
7.275
7.271
7.255
7.251
7.167
7.155
7.148
7.136
2.500
2.446
N
H
N
^{1}H NMR (400 MHz, DMSO-d_6)
1.05
2.01
0.97
1.00
1.02
1.03
2.92
f1 (ppm)

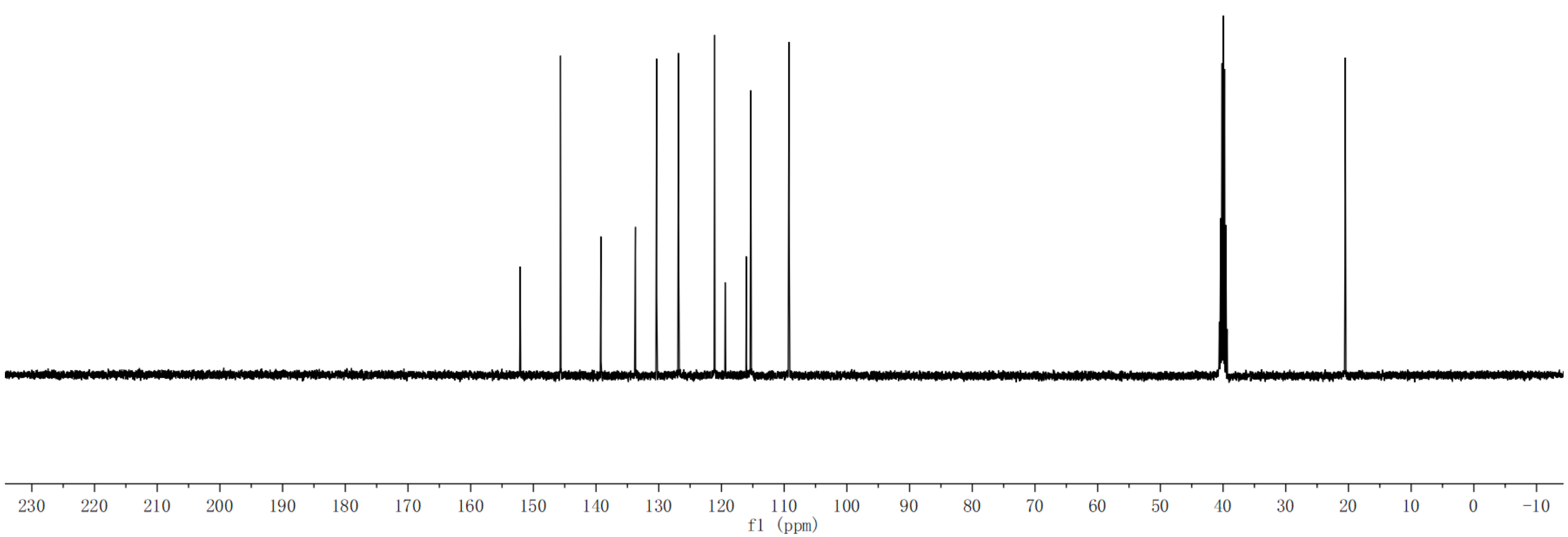


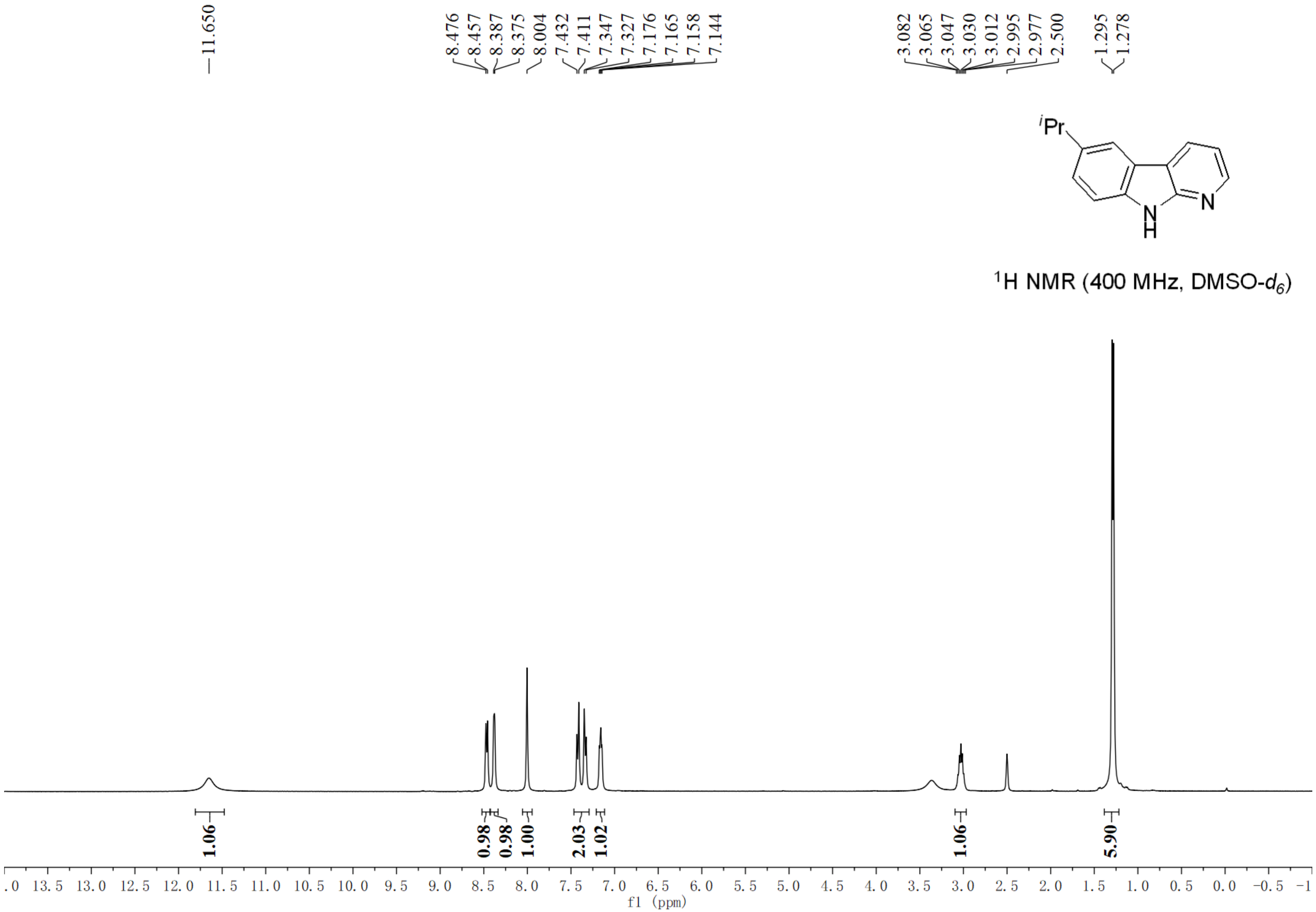
^{13}C NMR (100 MHz, DMSO-d_6)

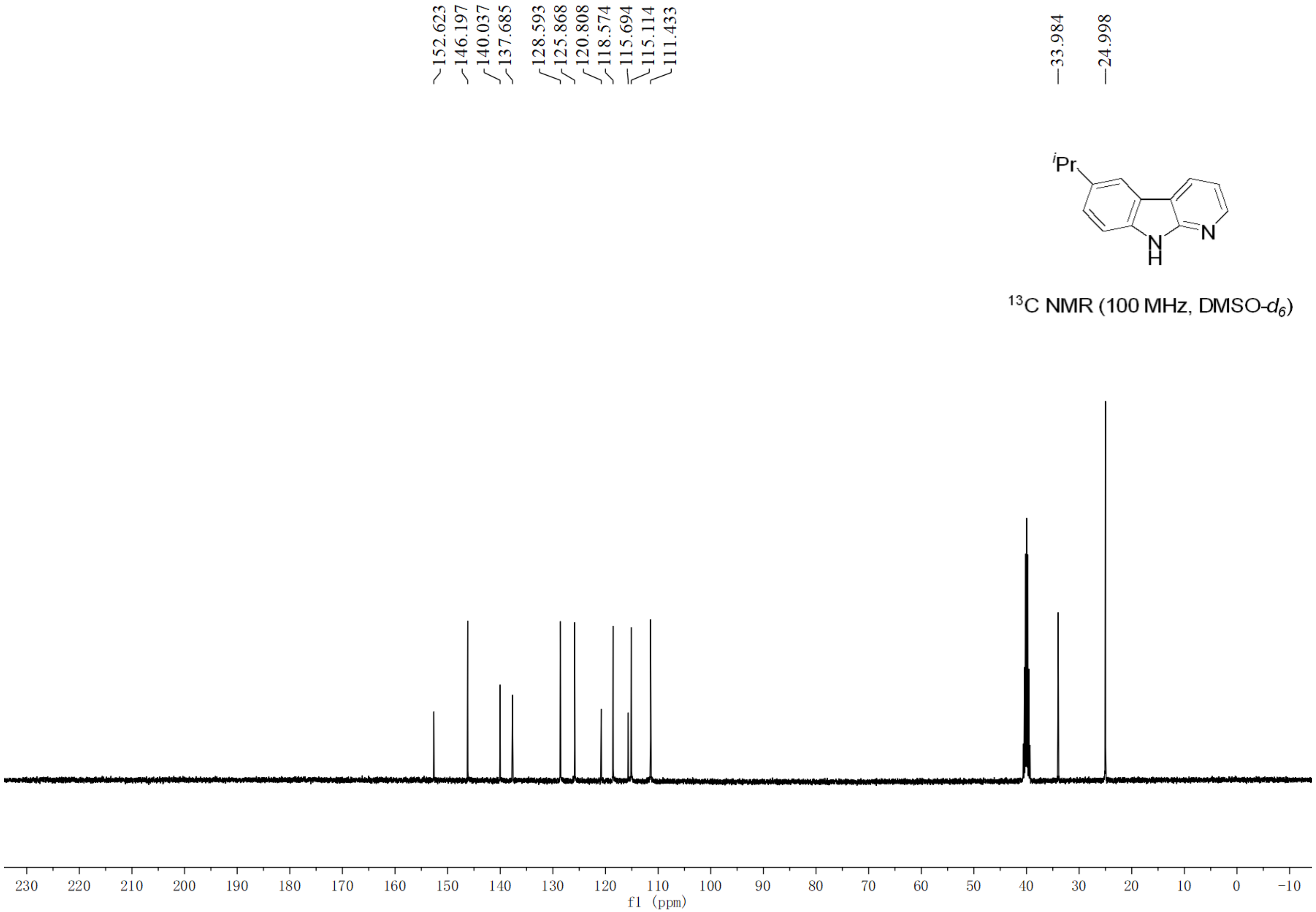

11.823
8.439
8.434
8.421
8.417
8.414
8.409
8.404
7.362
7.358
7.350
7.223
7.218
7.210
7.204
7.198
7.191
7.186
7.017
7.010
7.003
2.768
2.499
N
H
N
1H NMR (400 MHz, DMSO-d6)
0.94
1.94
1.94
1.03
1.00
3.00
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

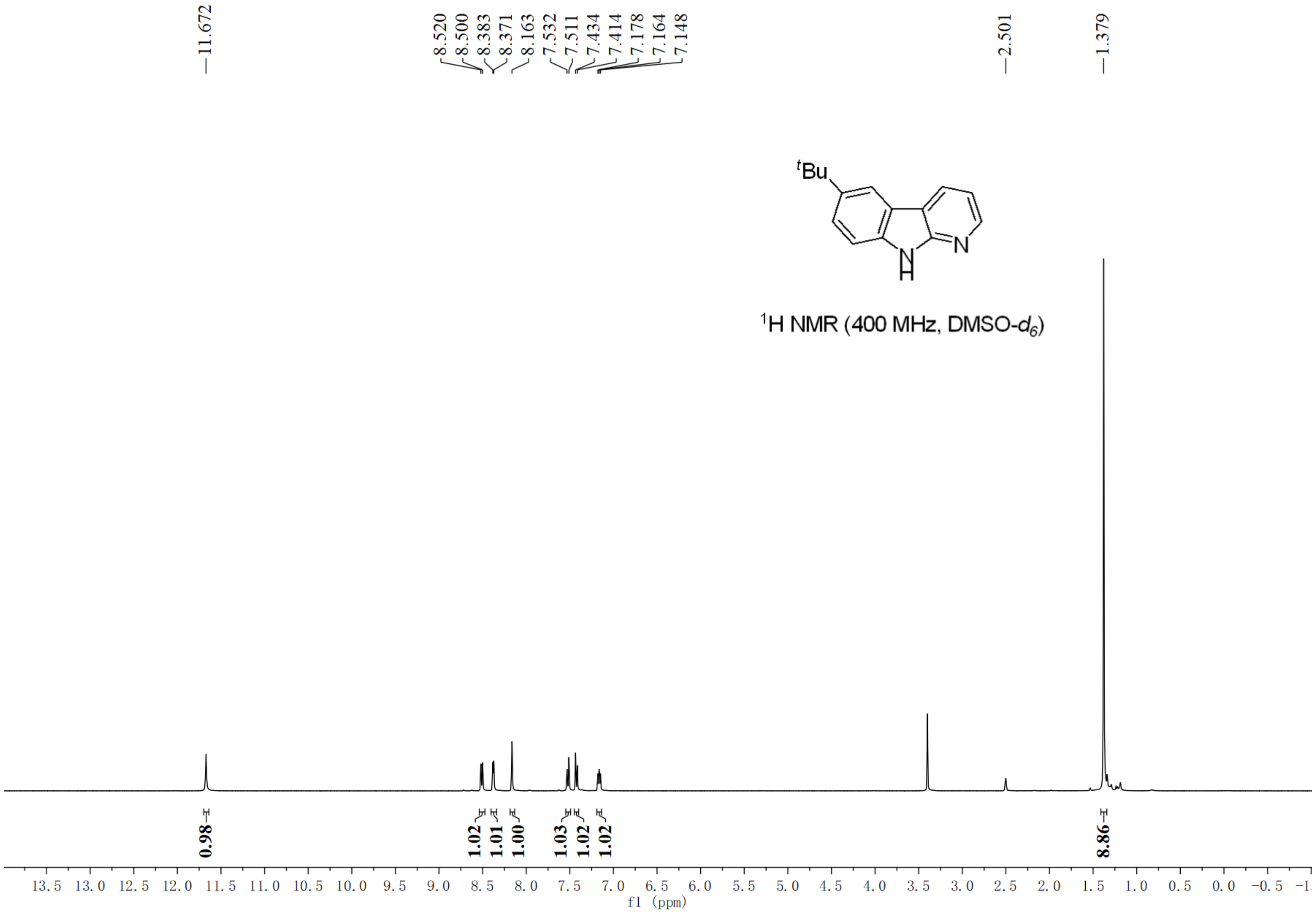


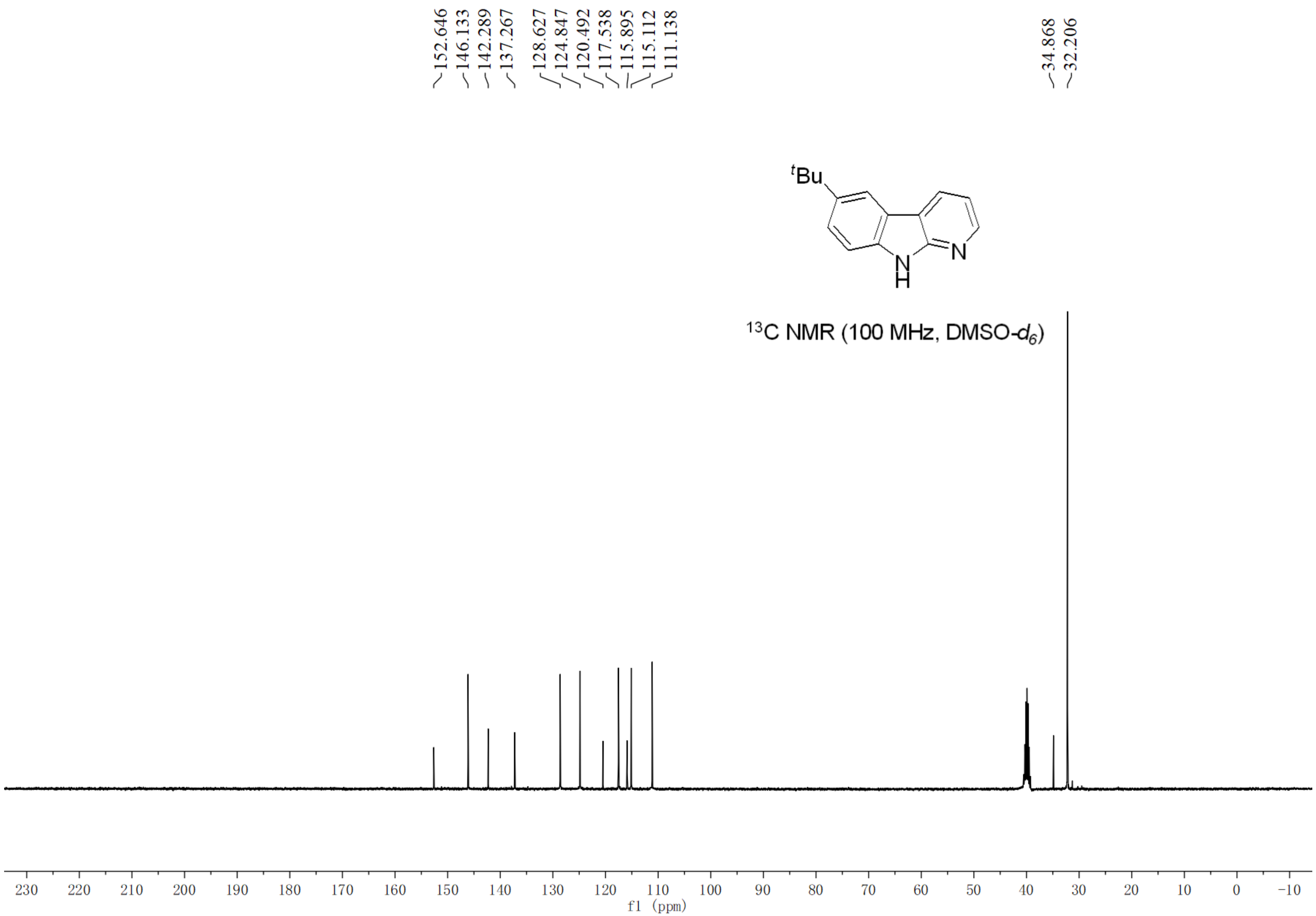
^{13}C NMR (100 MHz, DMSO-d_6)

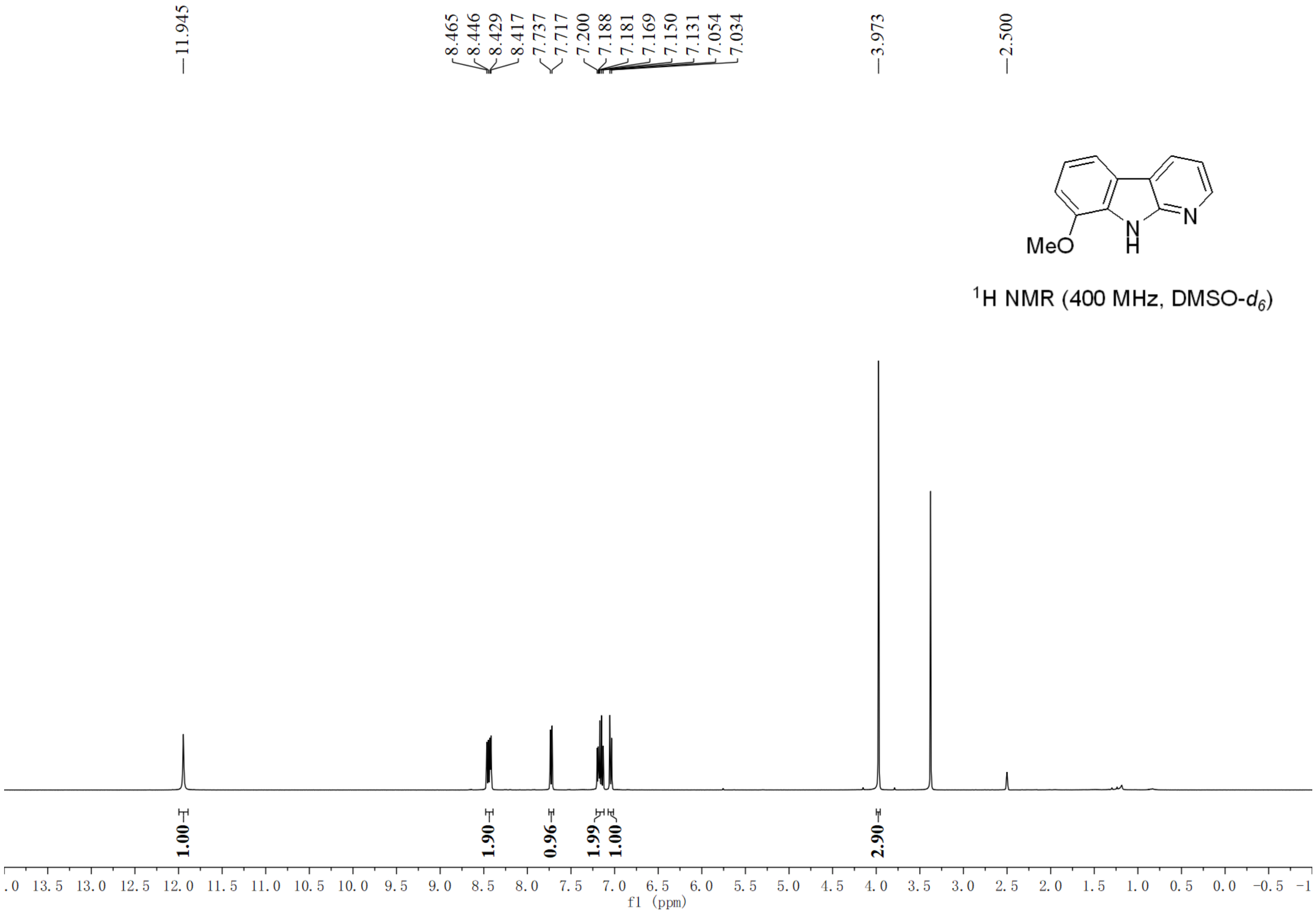


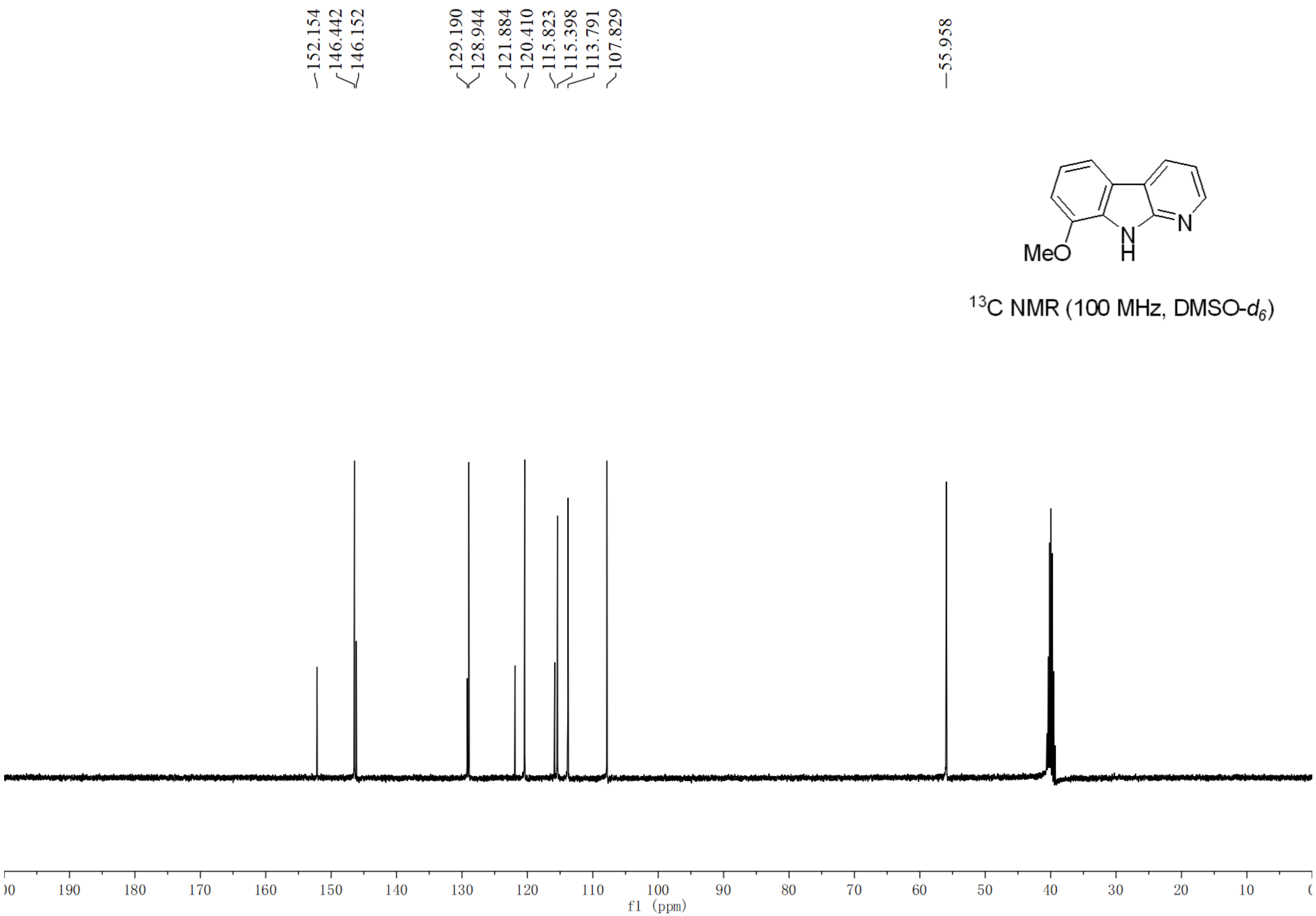

11.650
8.476
8.457
8.387
8.375
8.004
7.432
7.411
7.347
7.327
7.176
7.165
7.158
7.144
3.082
3.065
3.047
3.030
3.012
2.995
2.977
2.500
1.295
1.278
iPr
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.06
0.98
0.98
1.00
2.03
1.02
1.06
5.90
f1 (ppm)

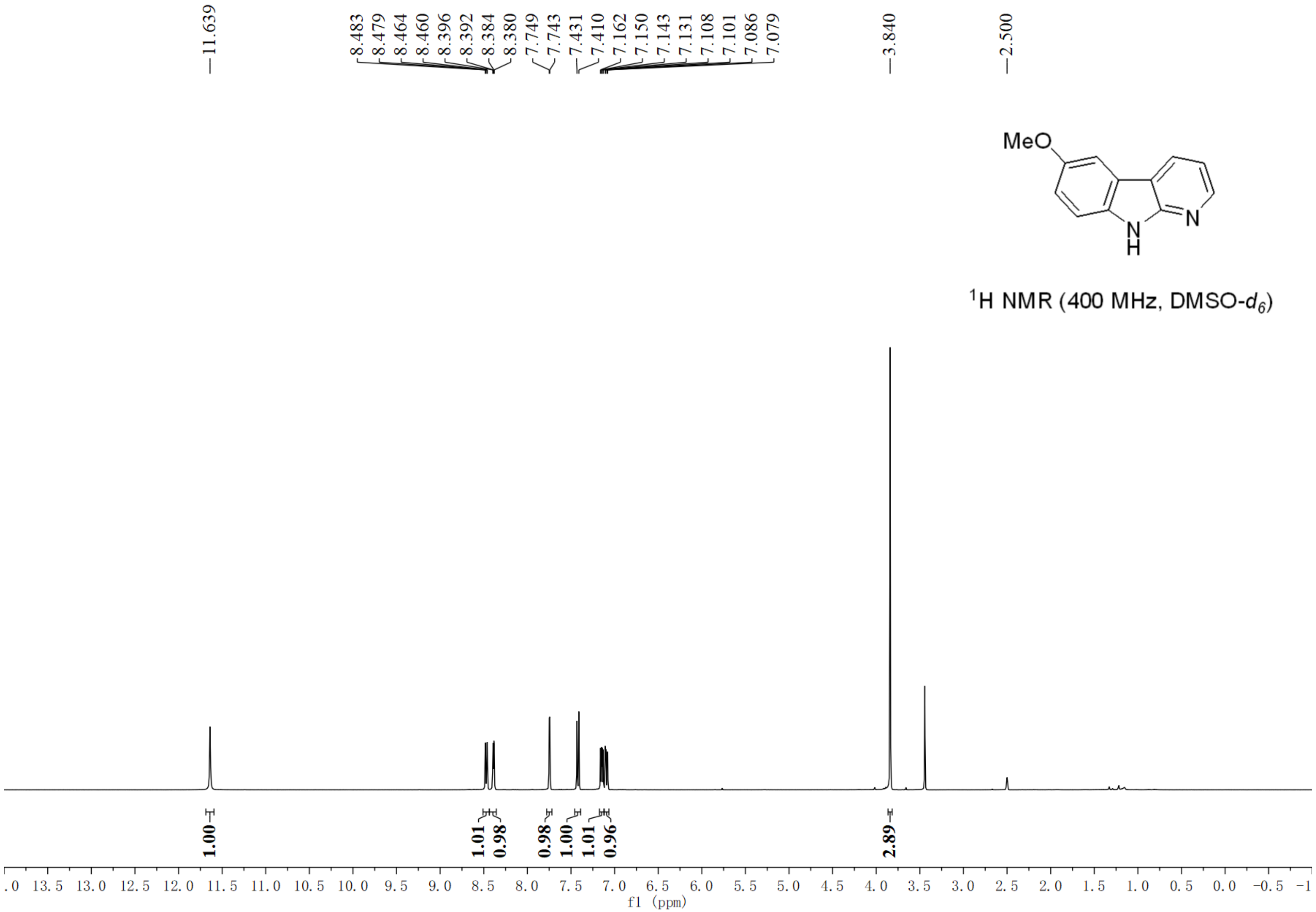

152.623
146.197
140.037
137.685
128.593
125.868
120.808
118.574
115.694
115.114
111.433
33.984
24.998
^{i}Pr
N
H
N
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

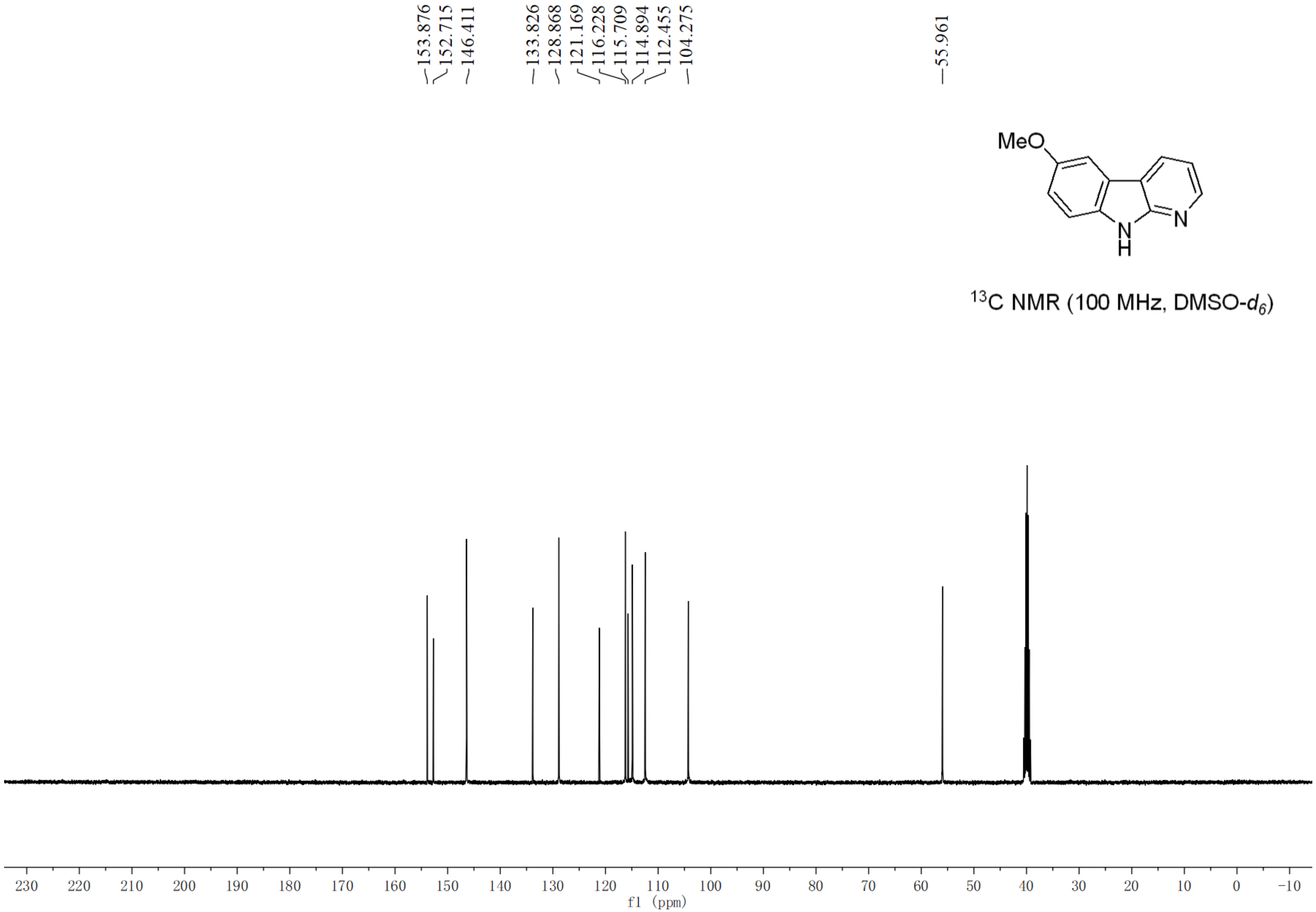

11.672
8.520
8.500
8.383
8.371
8.163
7.532
7.511
7.434
7.414
7.178
7.164
7.148
2.501
1.379
tBu
N
H
N
1H NMR (400 MHz, DMSO-d6)
0.98
1.02
1.01
1.00
1.03
1.02
1.02
8.86
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)


152.646
146.133
142.289
137.267
128.627
124.847
120.492
117.538
115.895
115.112
111.138
34.868
32.206
tBu
N
H
N
13C NMR (100 MHz, DMSO-d6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

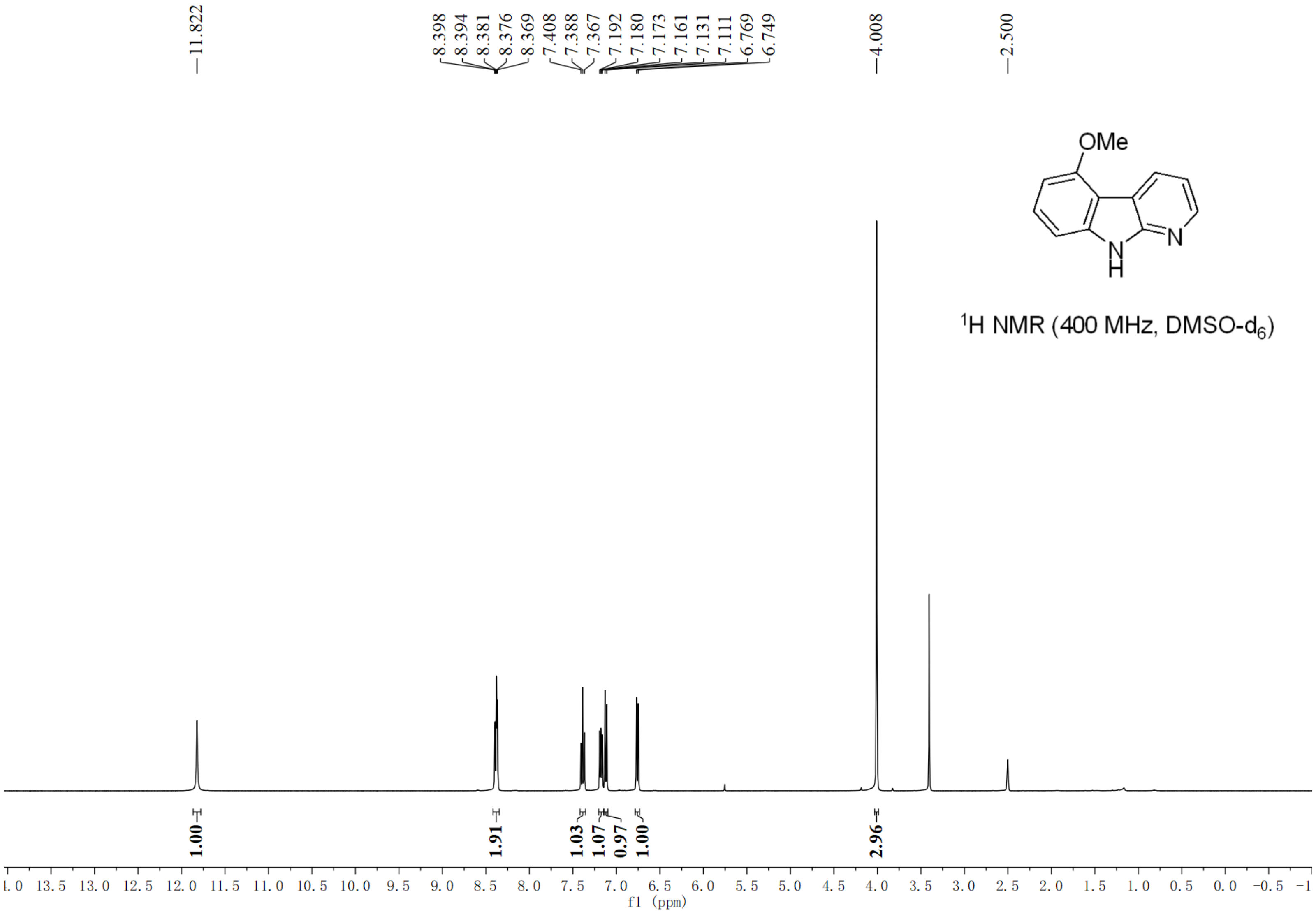

11.945
8.465
8.446
8.429
8.417
7.737
7.717
7.200
7.188
7.181
7.169
7.150
7.131
7.054
7.034
3.973
2.500
MeO
N
H
N
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
1.90
0.96
1.99
1.00
2.90
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

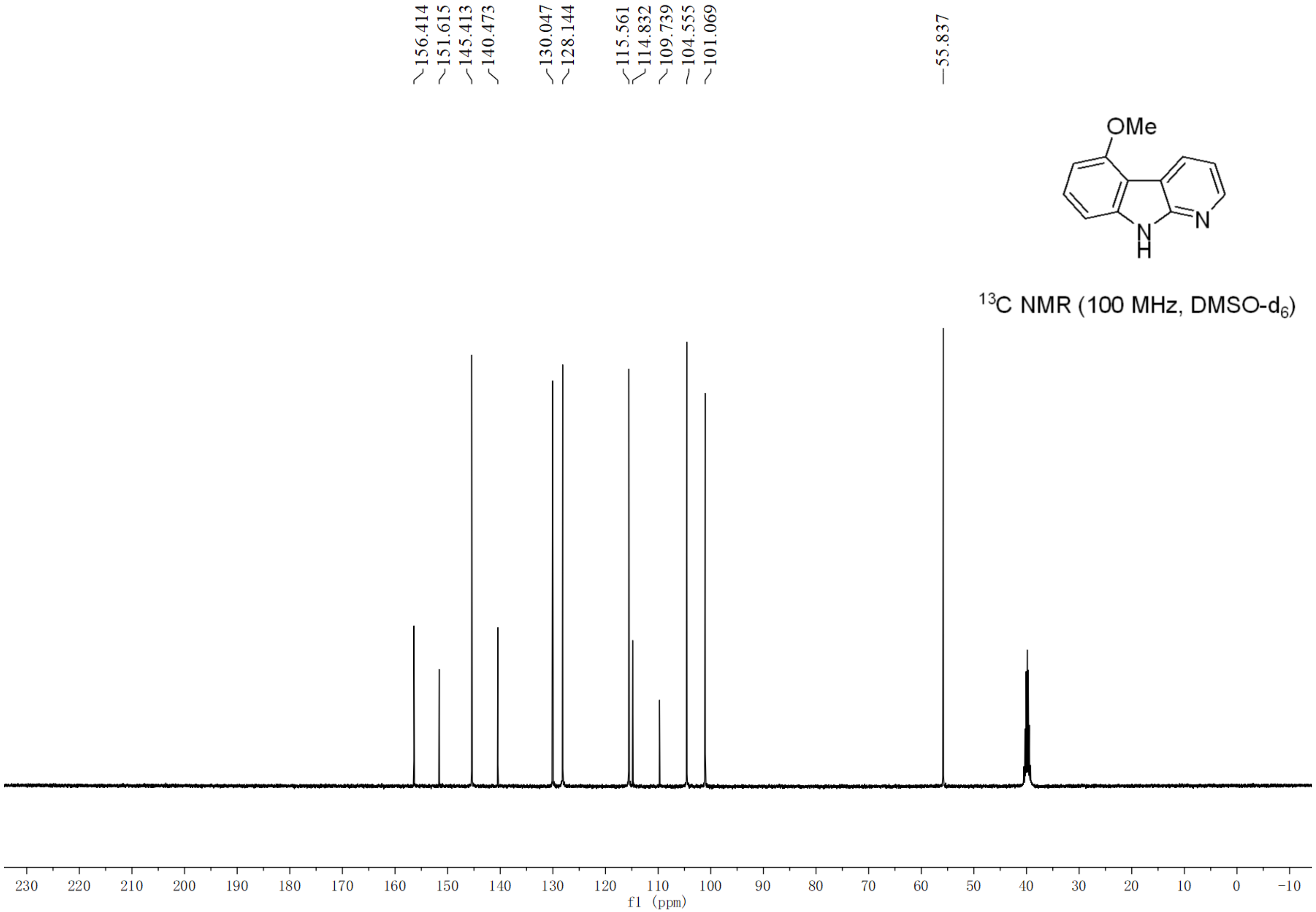

152.154
146.442
146.152
129.190
128.944
121.884
120.410
115.823
115.398
113.791
107.829
55.958
MeO
N
H
N
^{13}C NMR (100 MHz, DMSO-d_6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

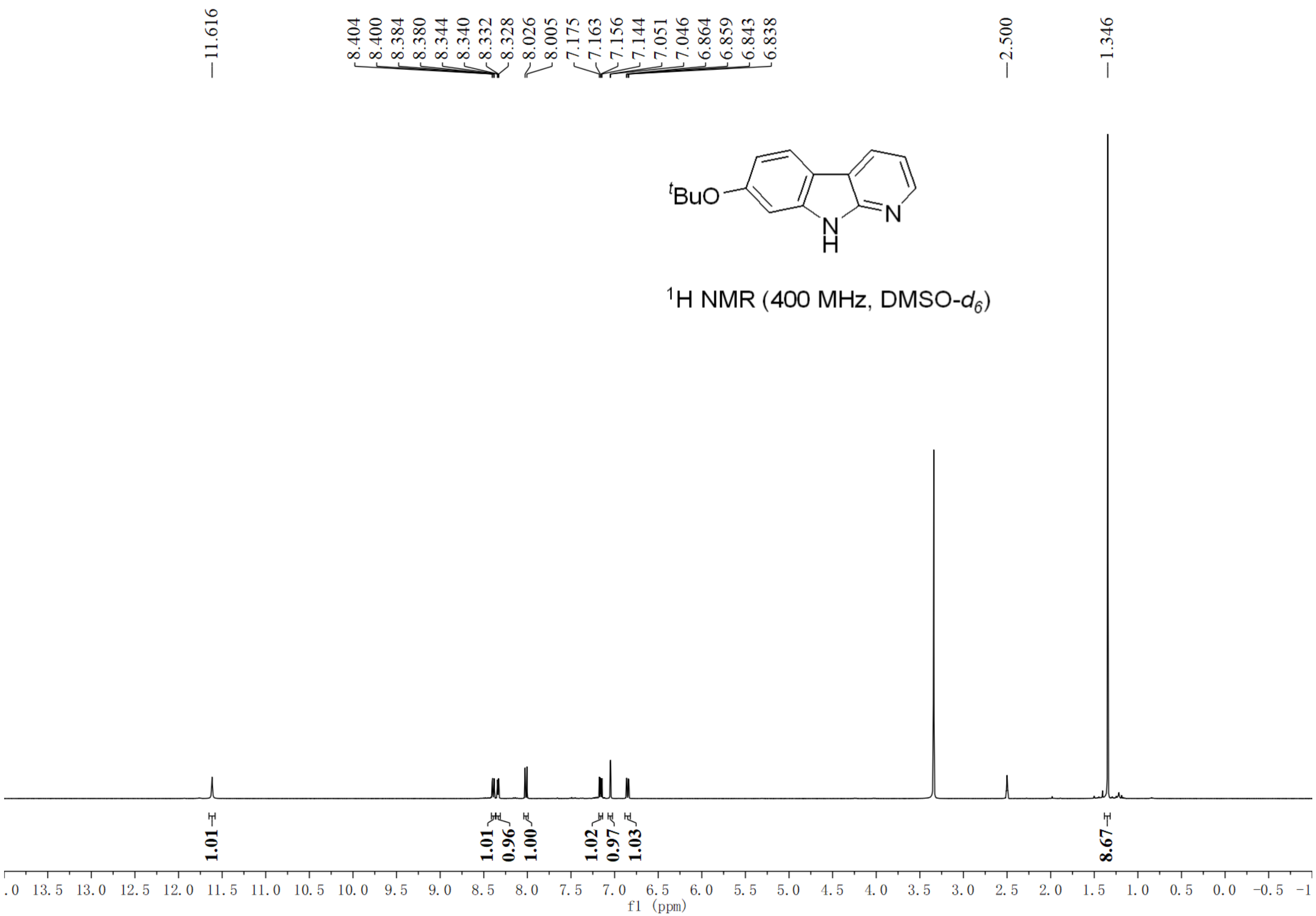

11.639
8.483
8.479
8.464
8.460
8.396
8.392
8.384
8.380
7.749
7.743
7.431
7.410
7.162
7.150
7.143
7.131
7.108
7.101
7.086
7.079
3.840
2.500
MeO
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
1.01
0.98
0.98
1.00
1.01
0.96
2.89
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



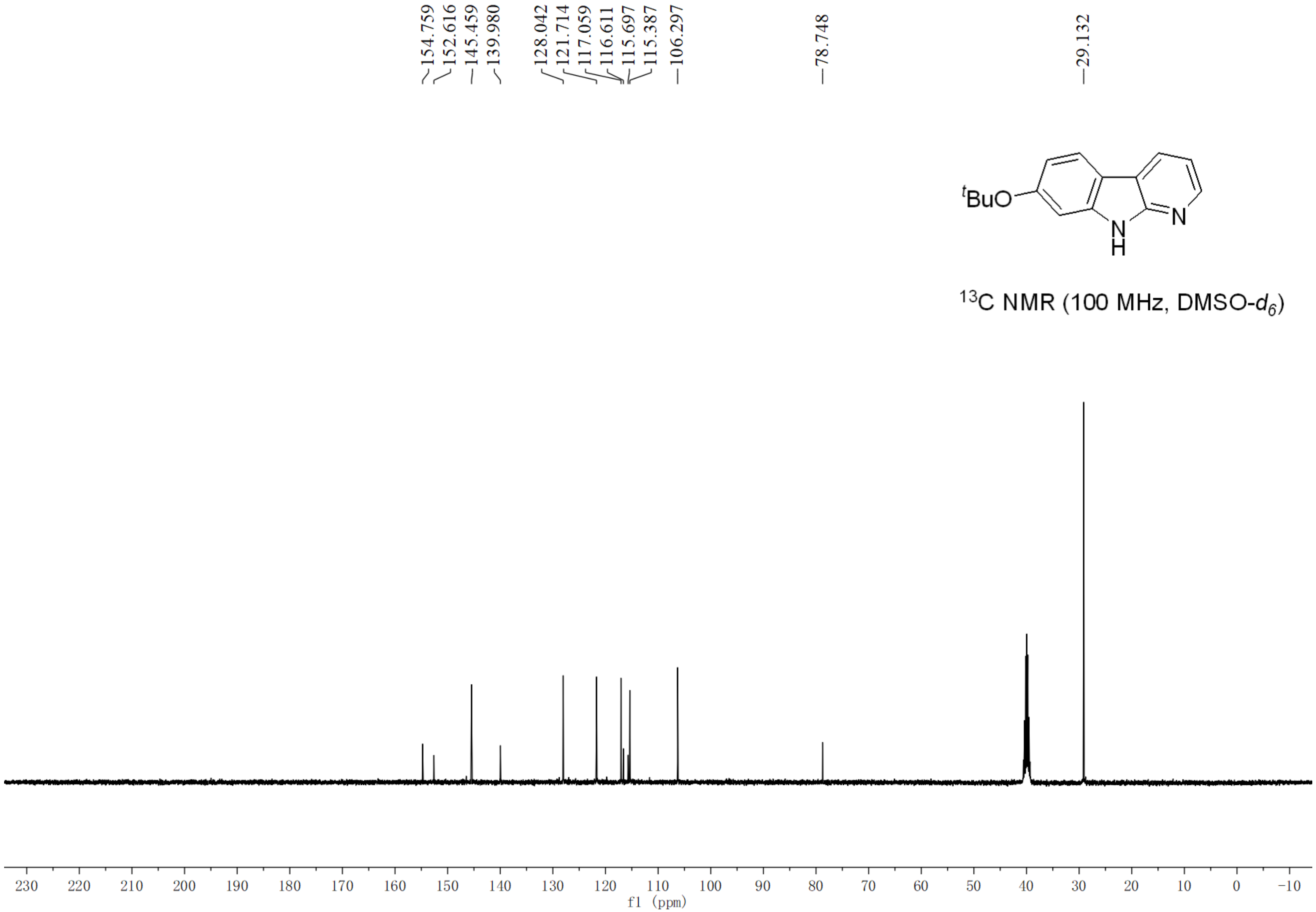
^{13}C NMR (100 MHz, DMSO-d_6)

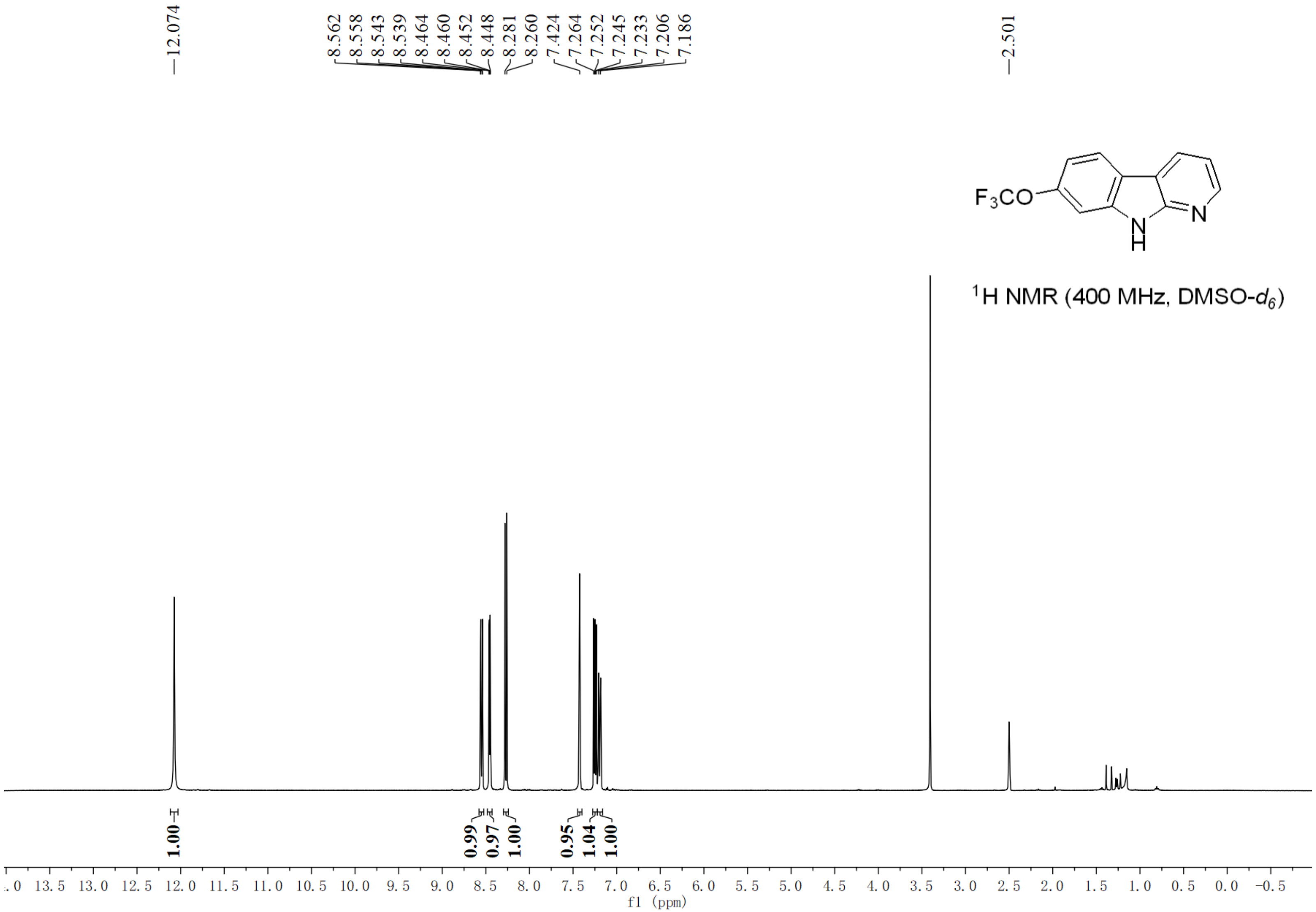

11.822
8.398
8.394
8.381
8.376
8.369
7.408
7.388
7.367
7.192
7.180
7.173
7.161
7.131
7.111
6.769
6.749
4.008
2.500
OMe
N
N
H
^{1}H NMR (400 MHz, DMSO-d$_6$)
1.00
1.91
1.03
1.07
0.97
1.00
2.96
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


156.414
151.615
145.413
140.473
130.047
128.144
115.561
114.832
109.739
104.555
101.069
55.837
OMe
N
H
N
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

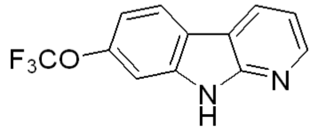


11.616
8.404
8.400
8.384
8.380
8.344
8.340
8.332
8.328
8.026
8.005
7.175
7.163
7.156
7.144
7.051
7.046
6.864
6.859
6.843
6.838
2.500
1.346
^{t}BuO
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.01
1.01
0.96
1.00
1.02
0.97
1.03
8.67
f1 (ppm)

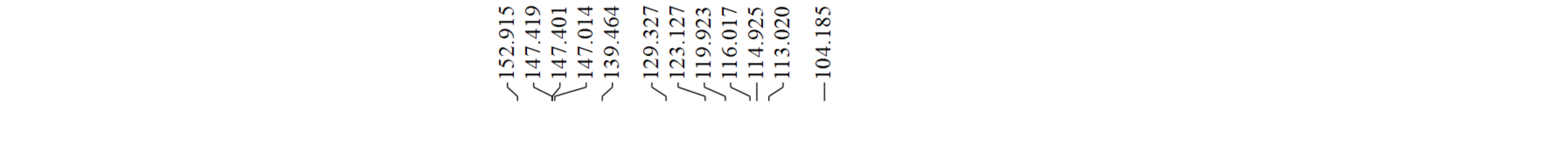

154.759
152.616
145.459
139.980
128.042
121.714
117.059
116.611
115.697
115.387
106.297
78.748
29.132
^{t}BuO
N
H
N
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

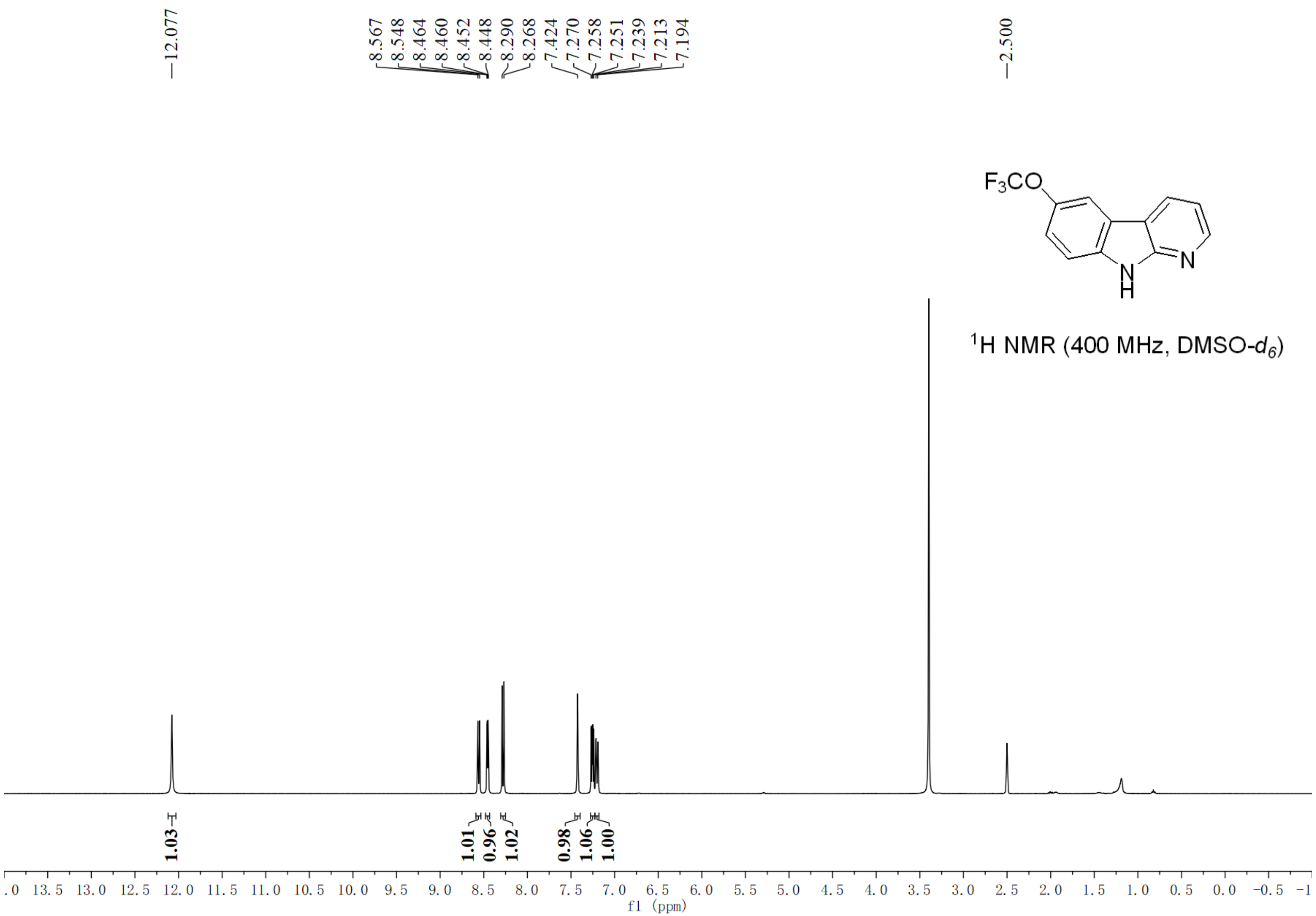


12.074
8.562
8.558
8.543
8.539
8.464
8.460
8.452
8.448
8.281
8.260
7.424
7.264
7.252
7.245
7.233
7.206
7.186
2.501
F3CO
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.00
0.99
0.97
1.00
0.95
1.04
1.00
f1 (ppm)

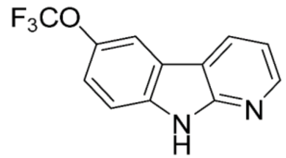


^{13}C NMR (100 MHz, DMSO-d_6)

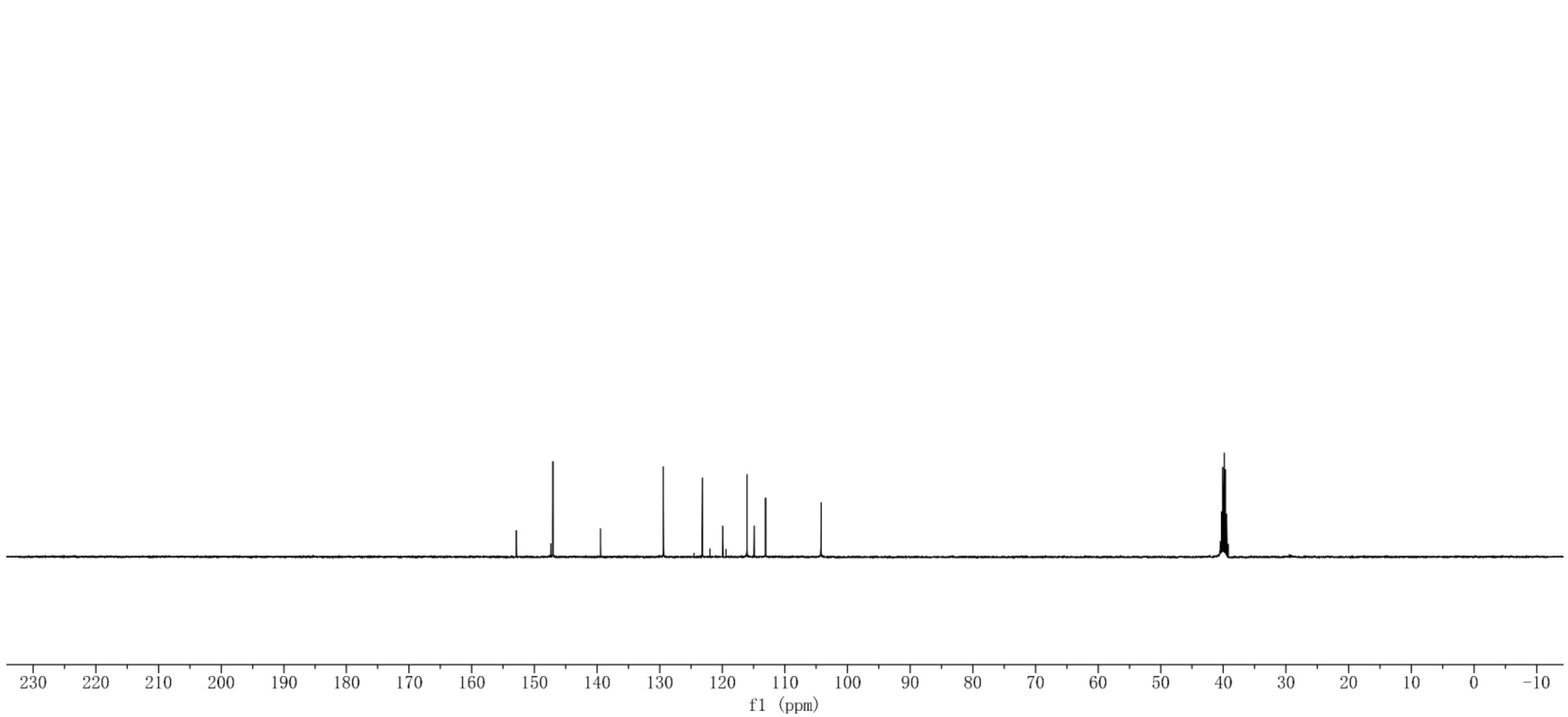


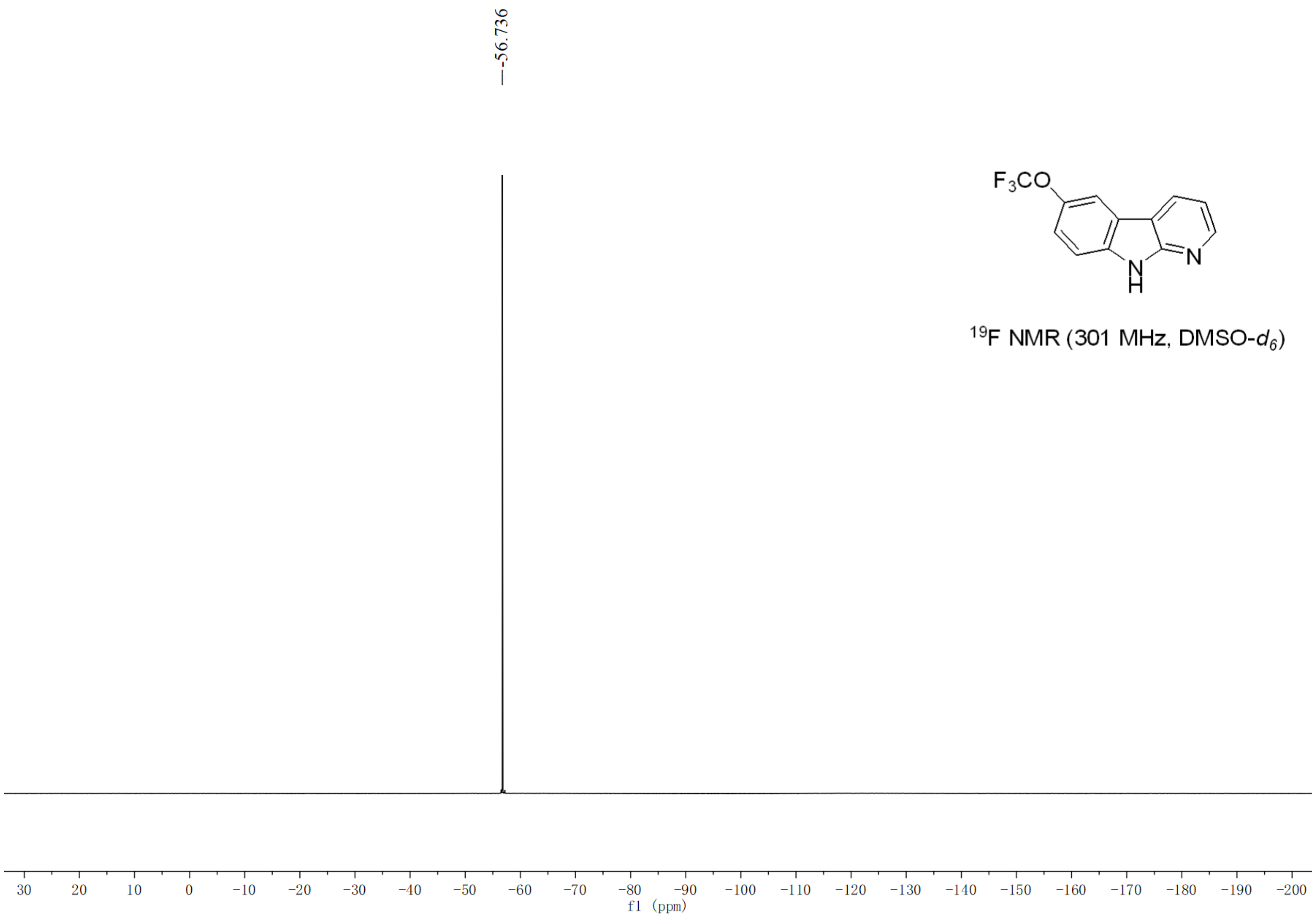


12.077
8.567
8.548
8.464
8.460
8.452
8.448
8.290
8.268
7.424
7.270
7.258
7.251
7.239
7.213
7.194
2.500
F3CO
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.03
1.01
0.96
1.02
0.98
1.06
1.00
f1 (ppm)

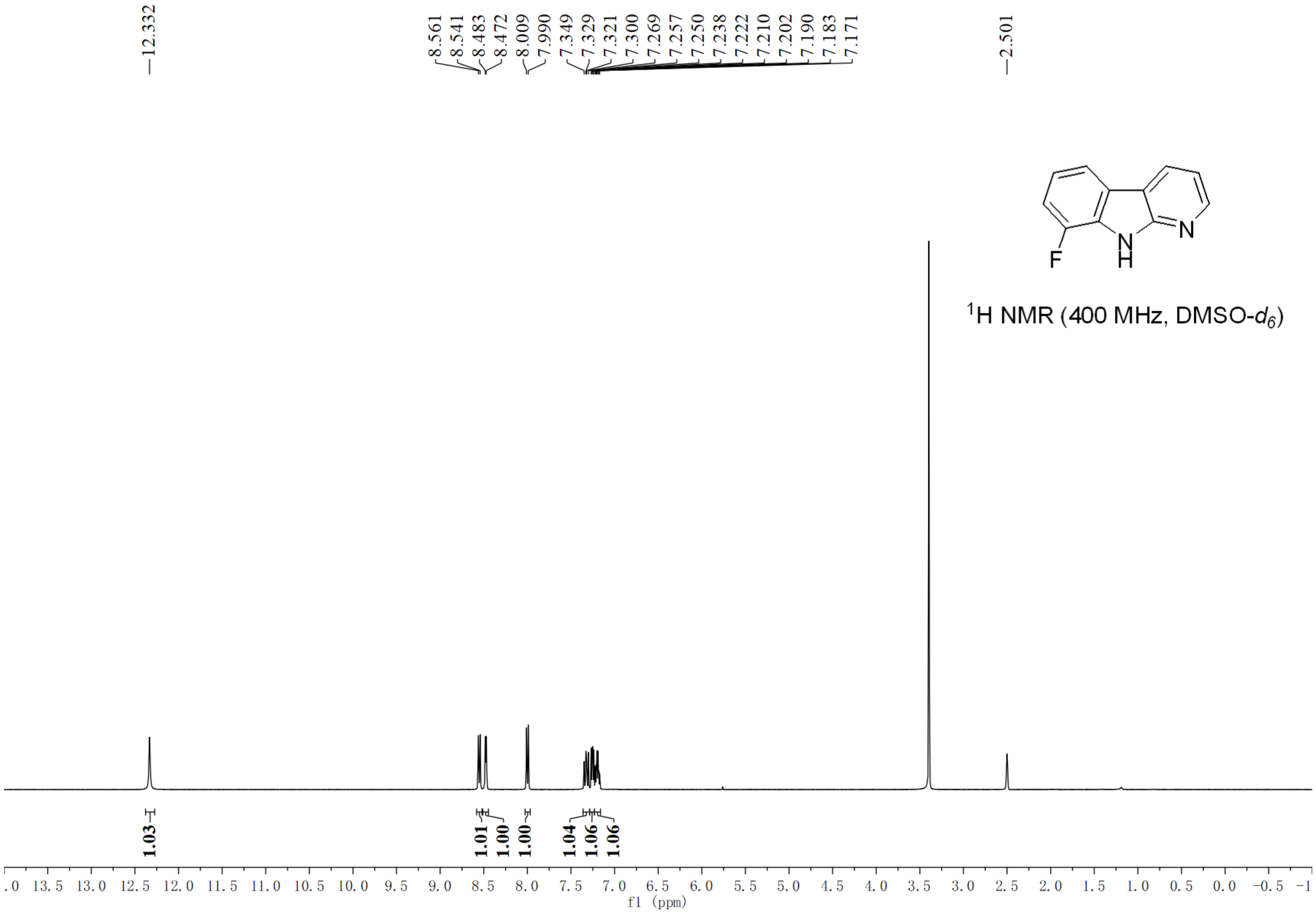


^{13}C NMR (100 MHz, DMSO-d_6)

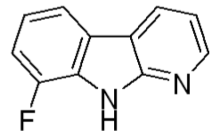




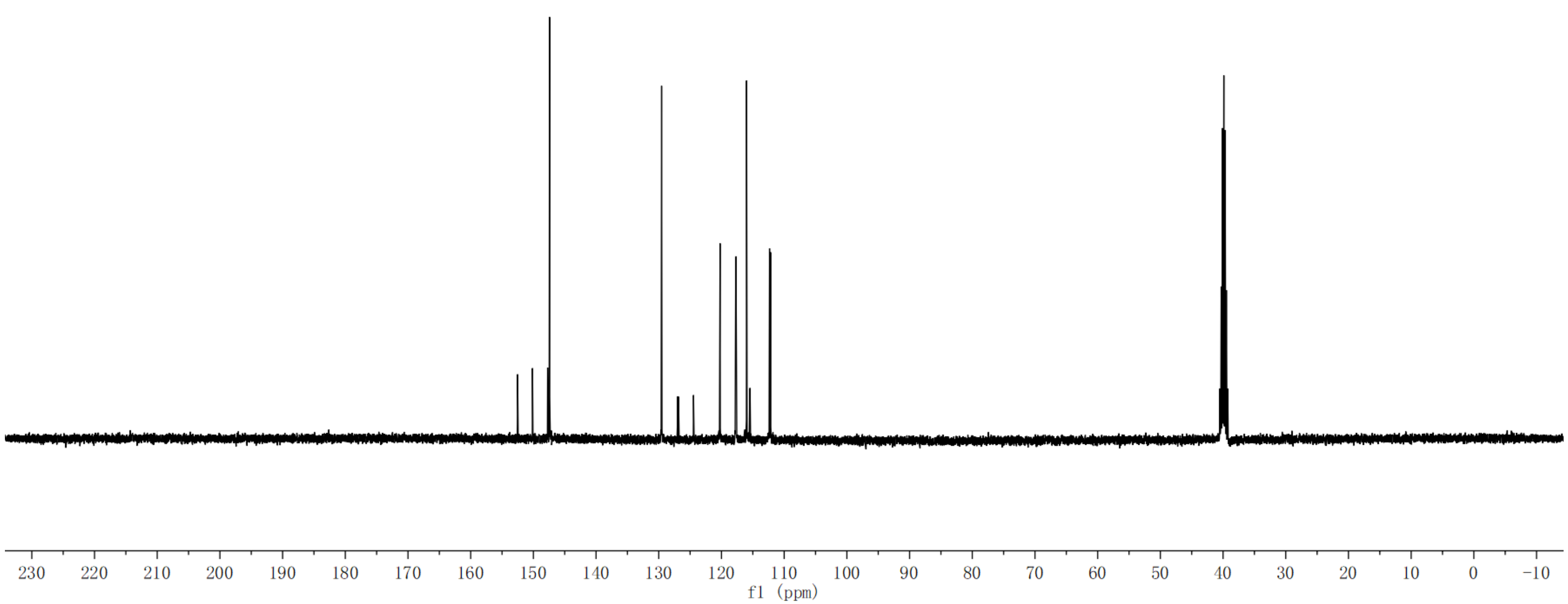
^{19}F NMR (301 MHz, DMSO-d_6)

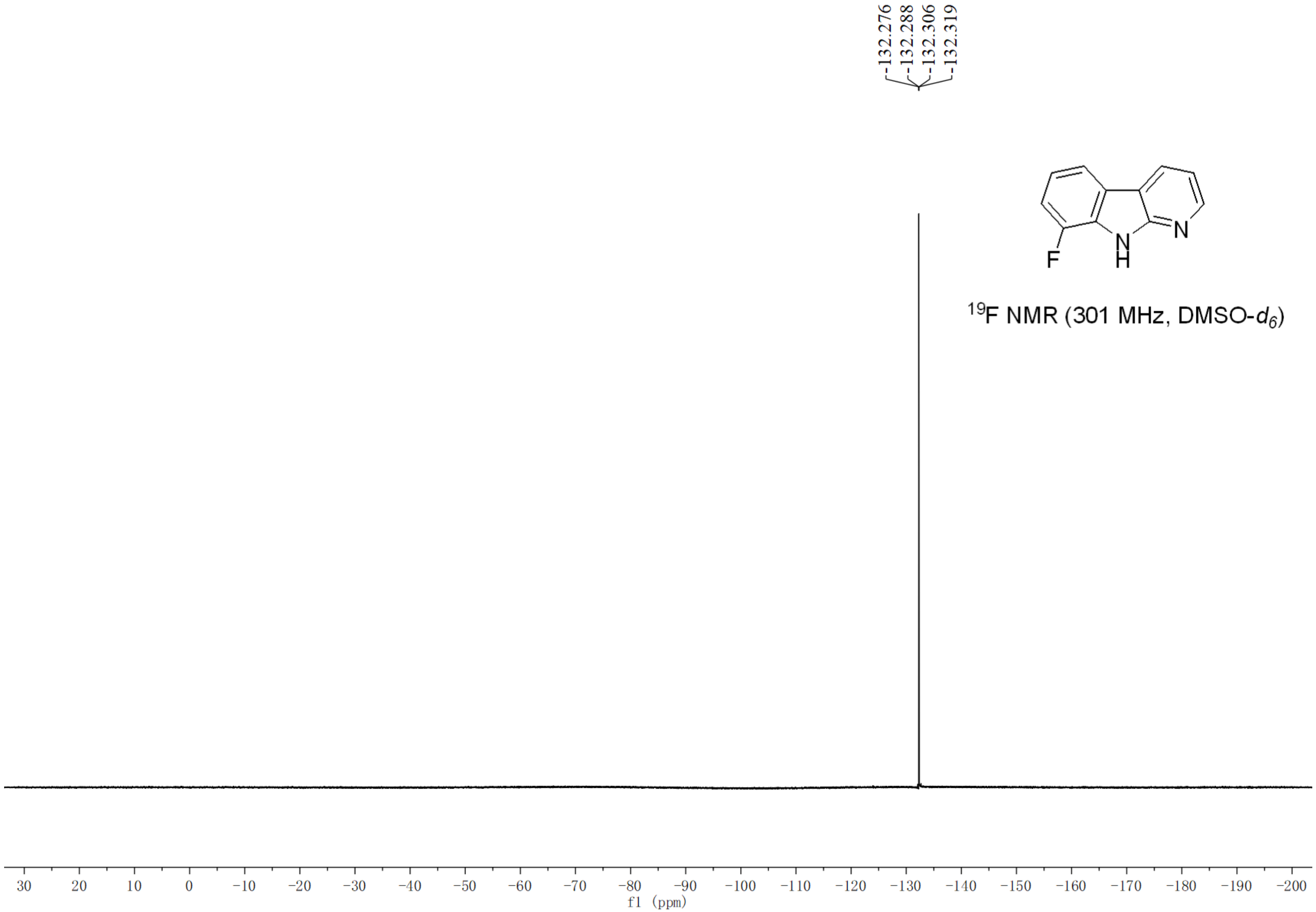


12.332
8.561
8.541
8.483
8.472
8.009
7.990
7.349
7.329
7.321
7.300
7.269
7.257
7.250
7.238
7.222
7.210
7.202
7.190
7.183
7.171
2.501
F
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.03
1.01
1.00
1.00
1.04
1.06
1.06
f1 (ppm)

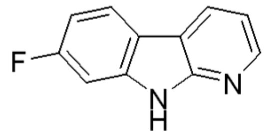


^{13}C NMR (100 MHz, DMSO-d_6)

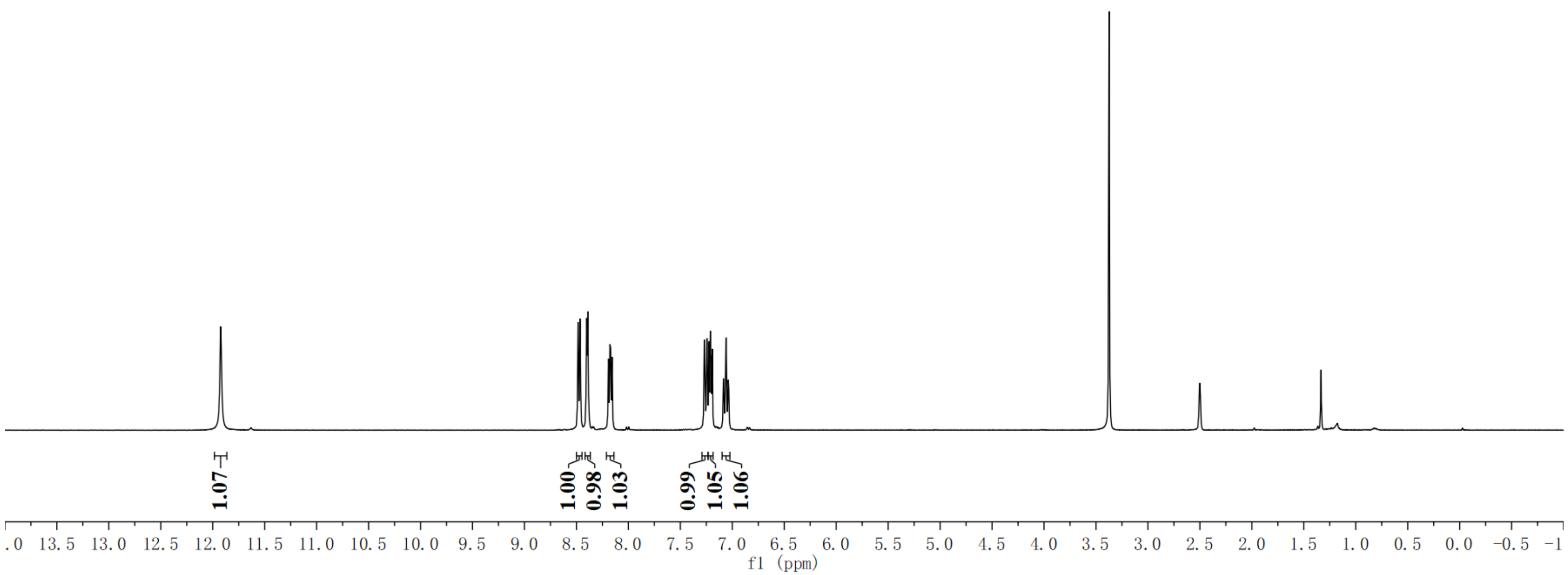


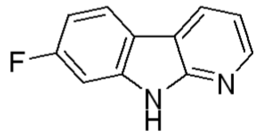


^{19}F NMR (301 MHz, DMSO-d_6)

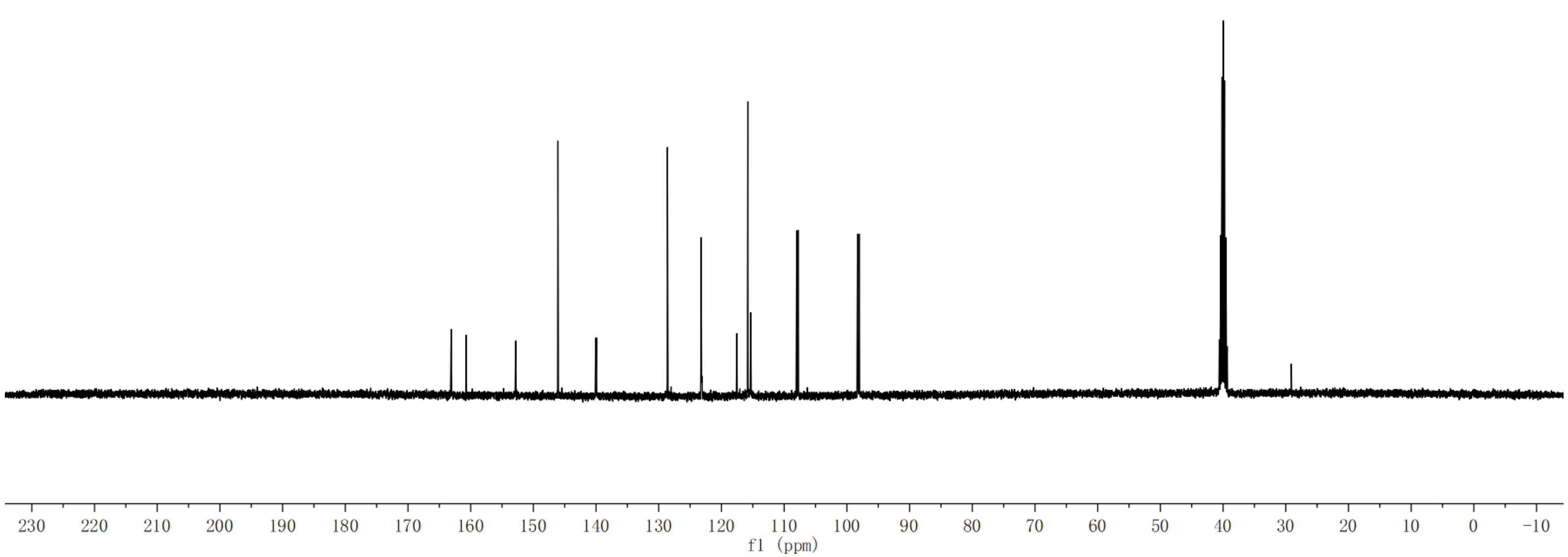


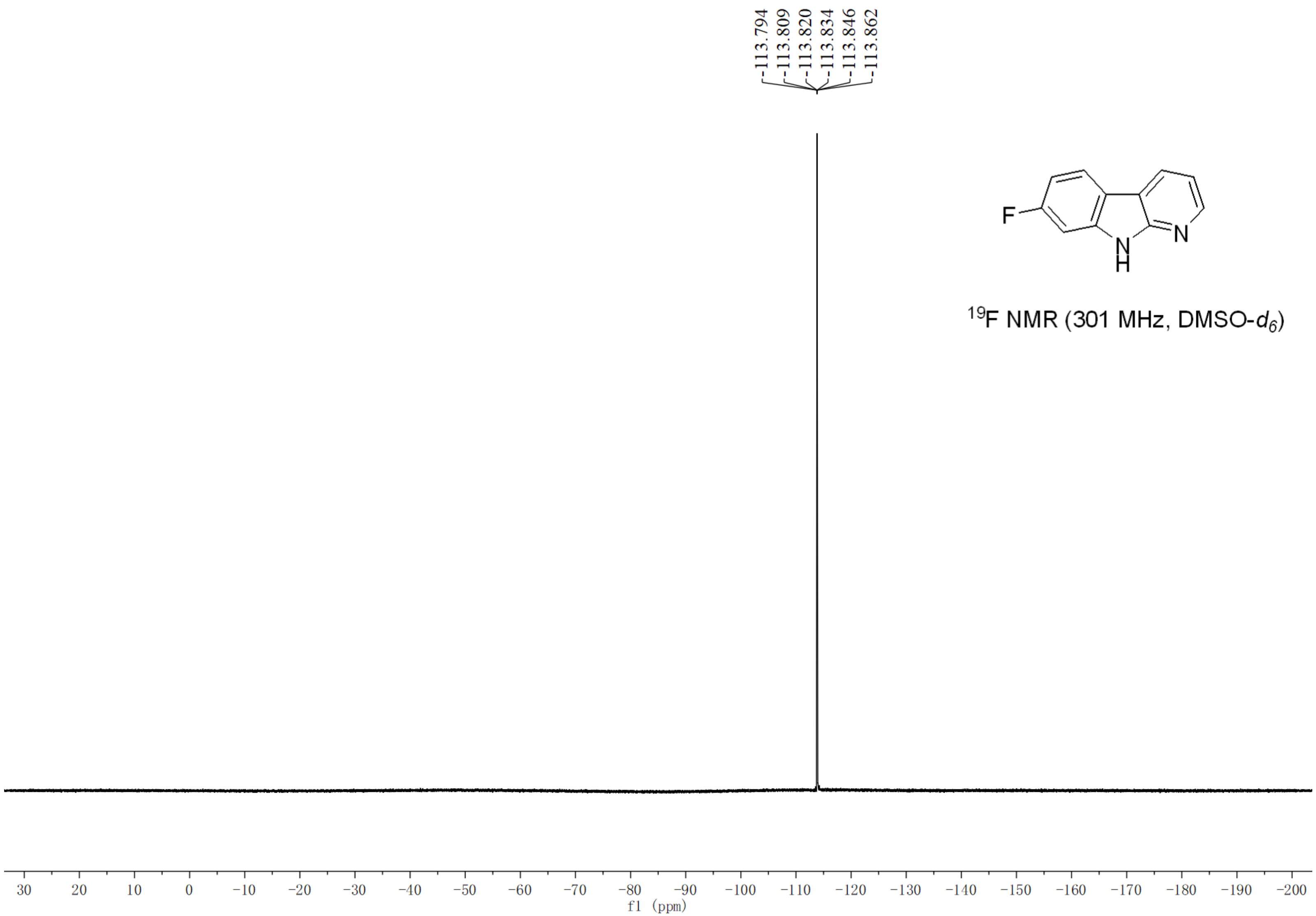
^{1}H NMR (400 MHz, DMSO-d_6)



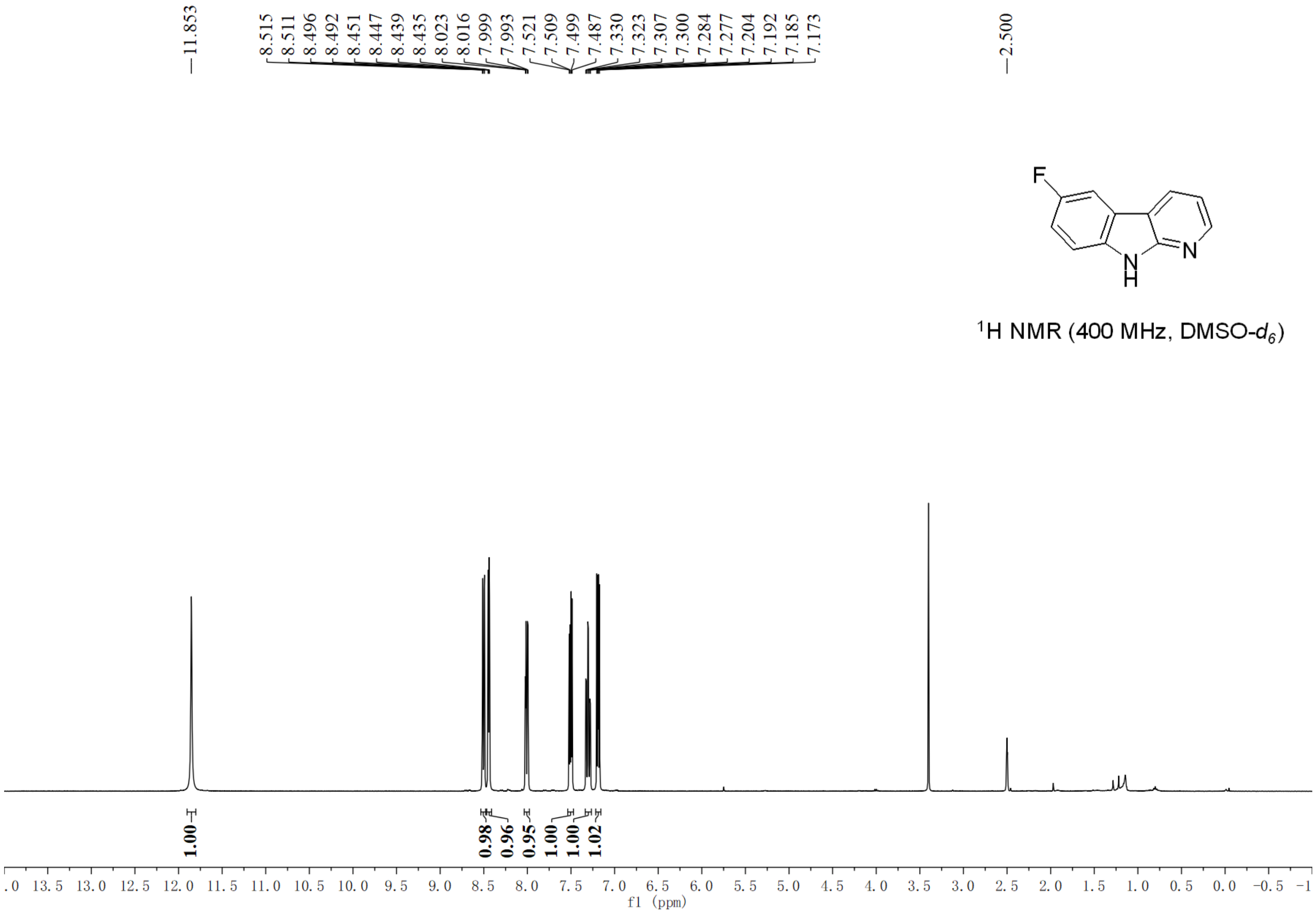


^{13}C NMR (100 MHz, DMSO-d_6)

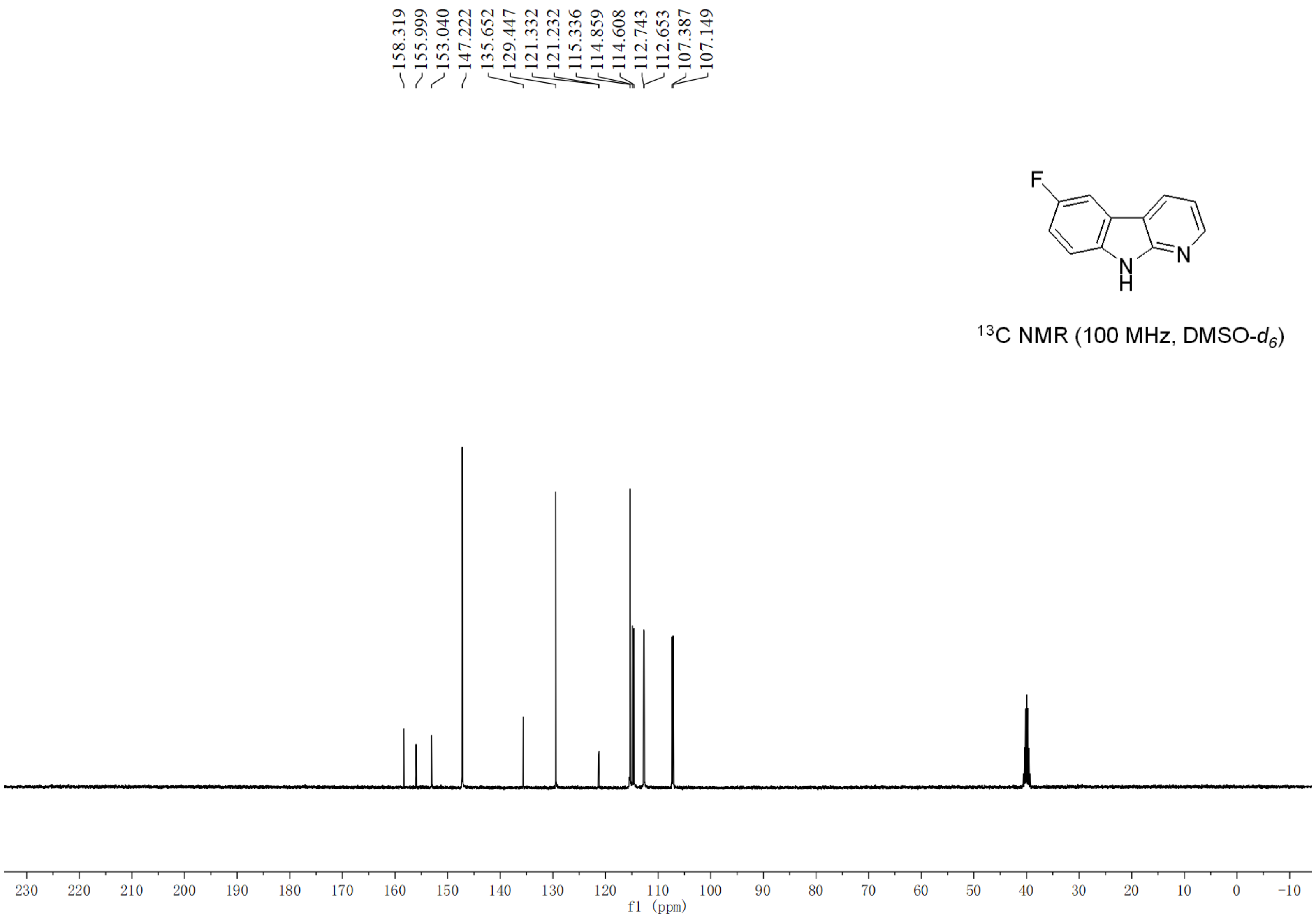




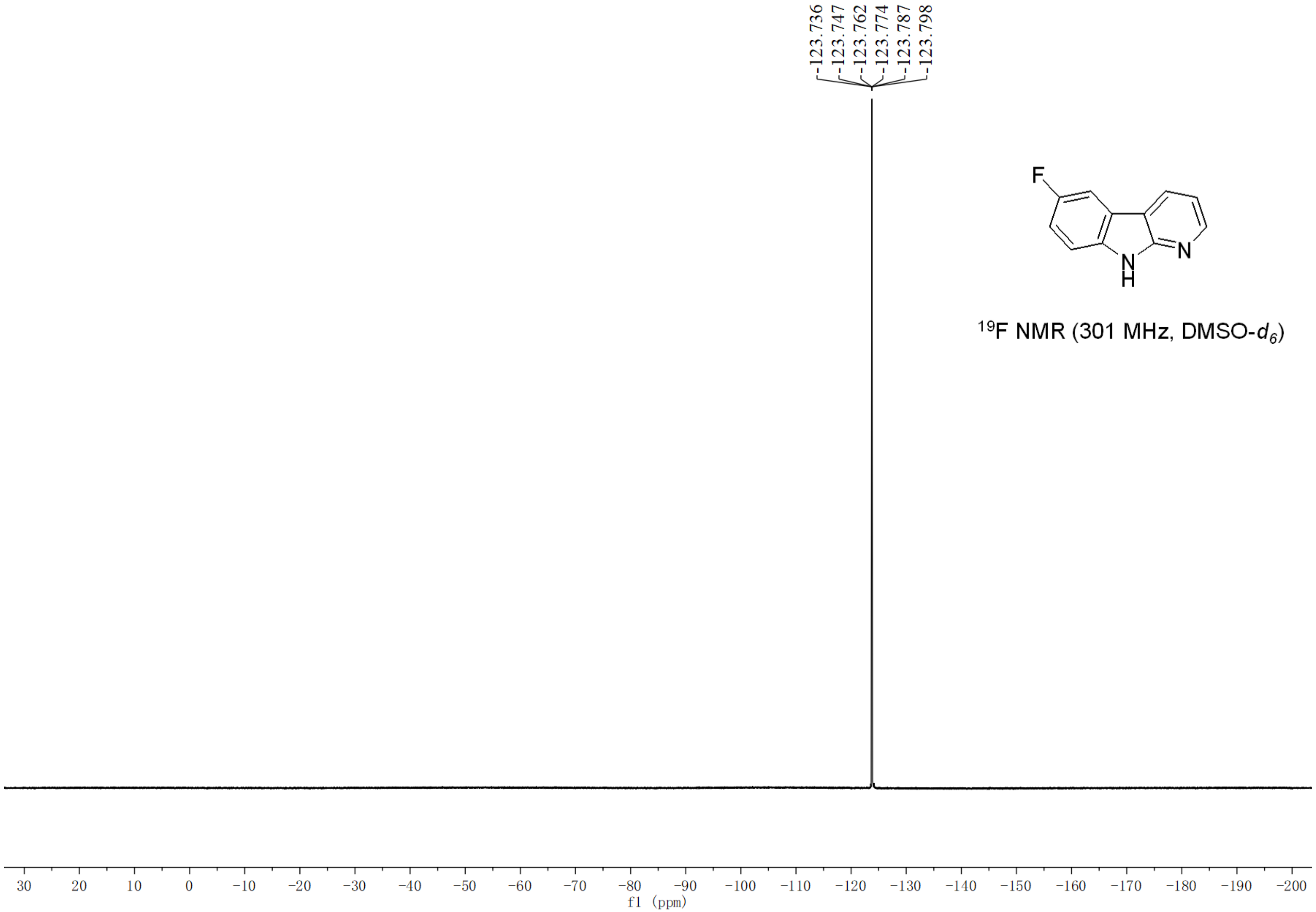
^{19}F NMR (301 MHz, DMSO-d_6)



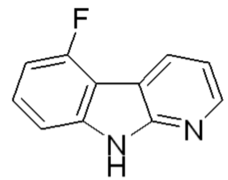
^1H NMR (400 MHz, DMSO-d_6)



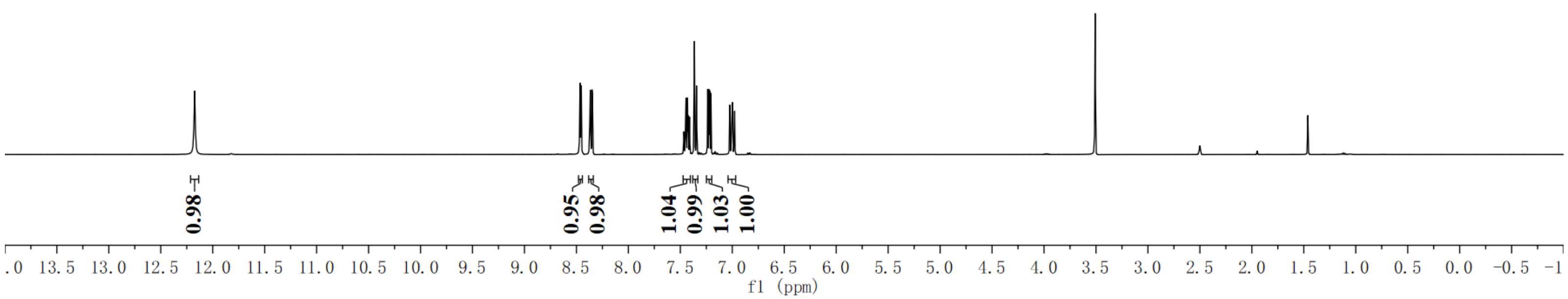
^{13}C NMR (100 MHz, DMSO-d_6)

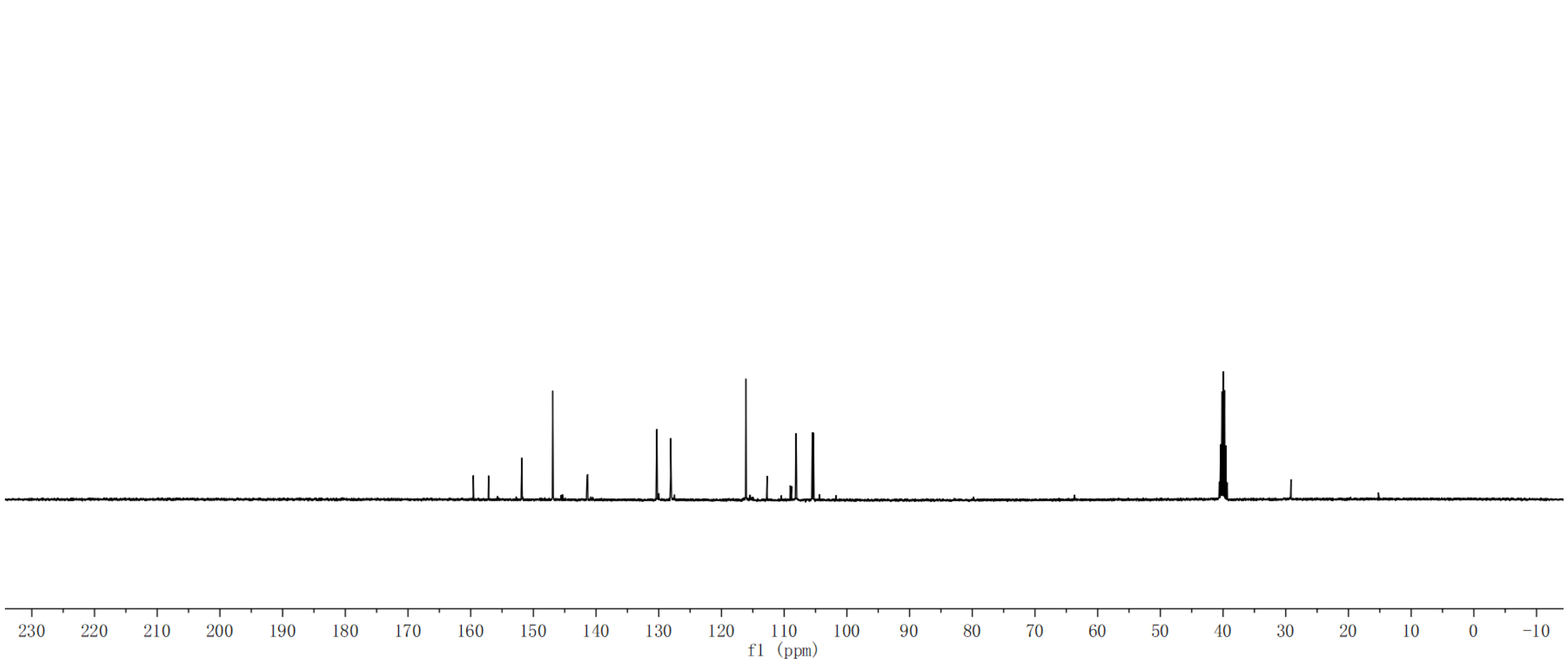


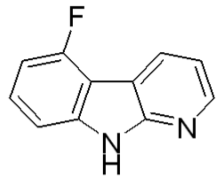
^{19}F NMR (301 MHz, DMSO-d_6)



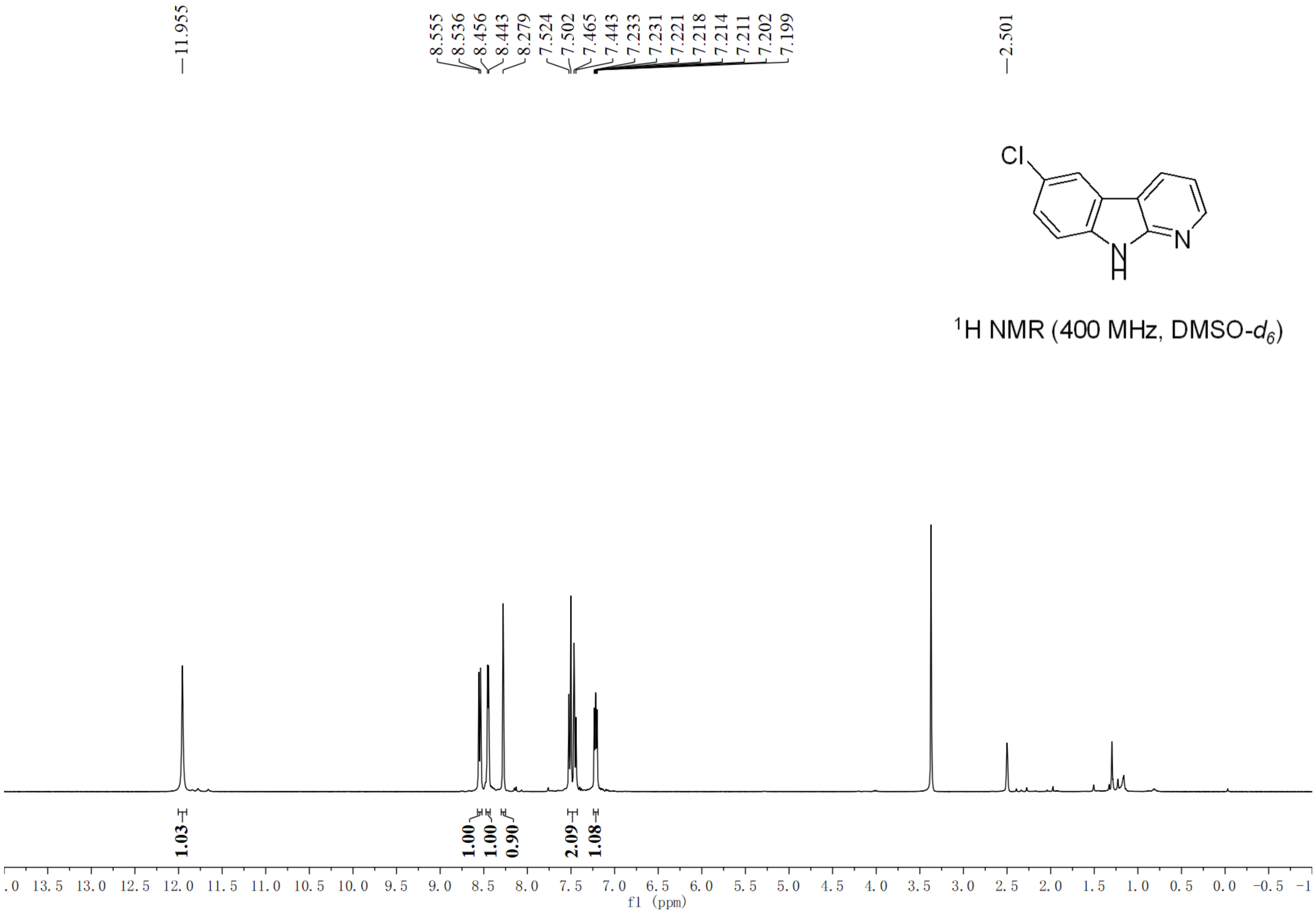
^{1}H NMR (400 MHz, DMSO-d_6)



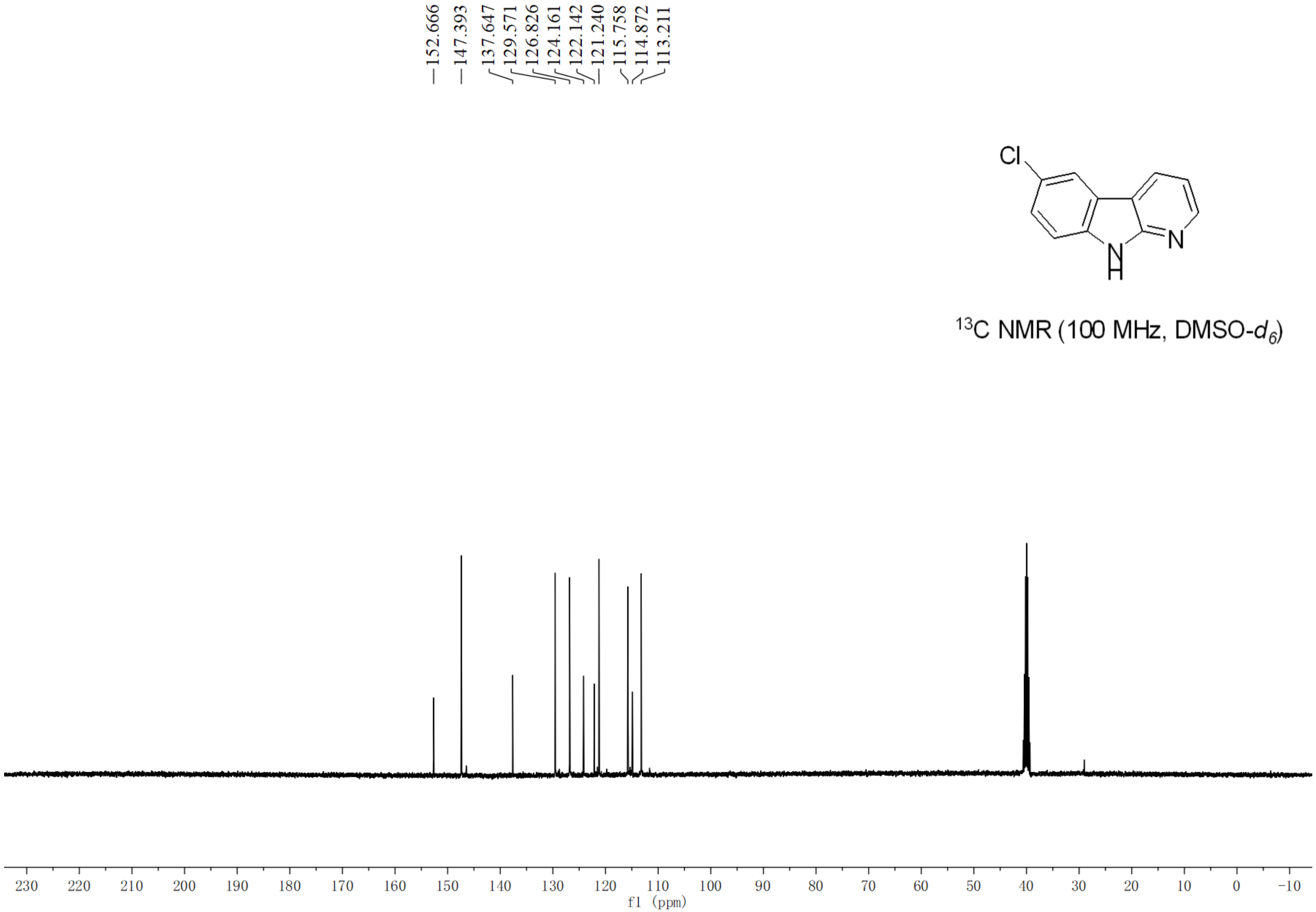




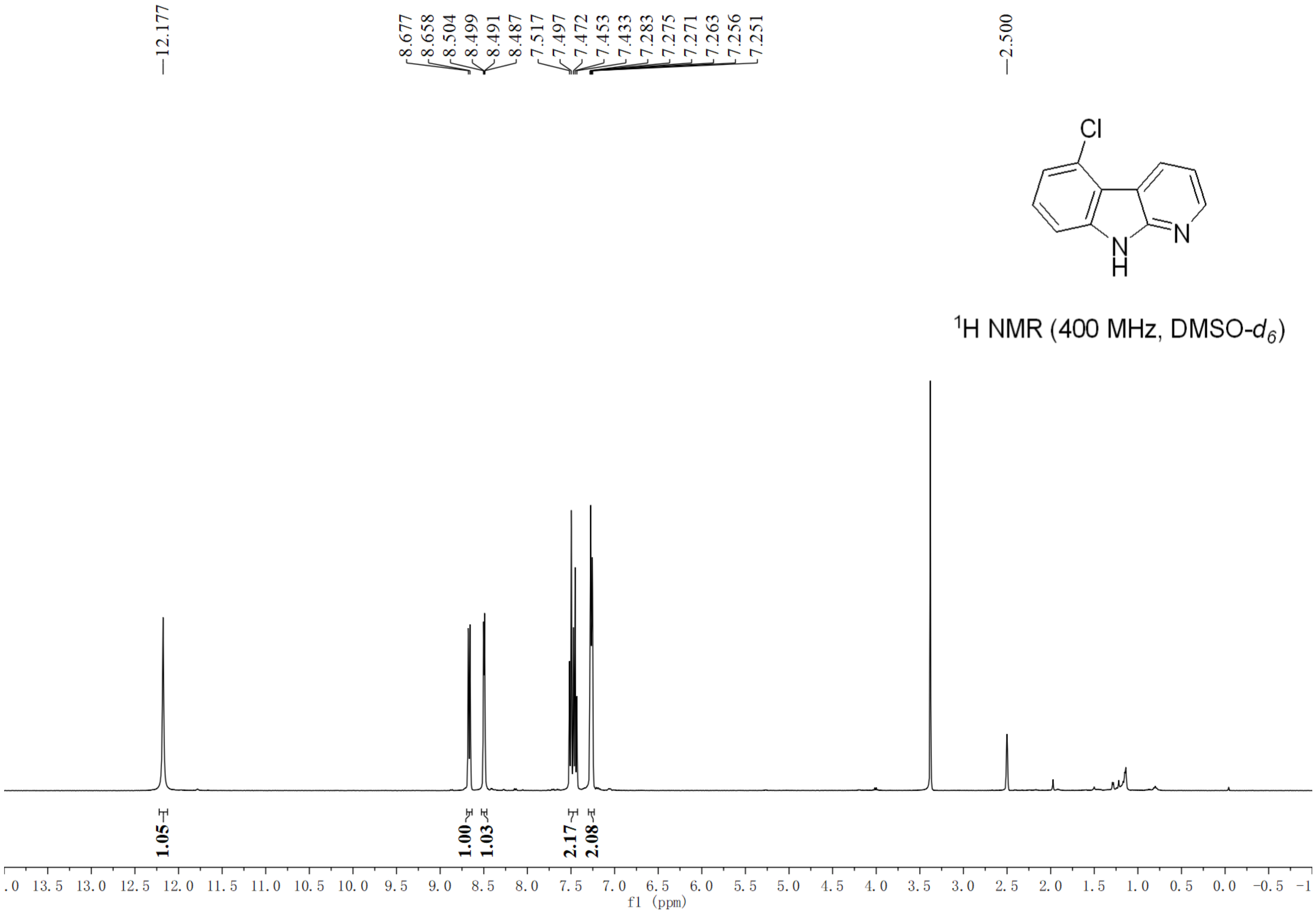
^{13}C NMR (100 MHz, DMSO-d_6)

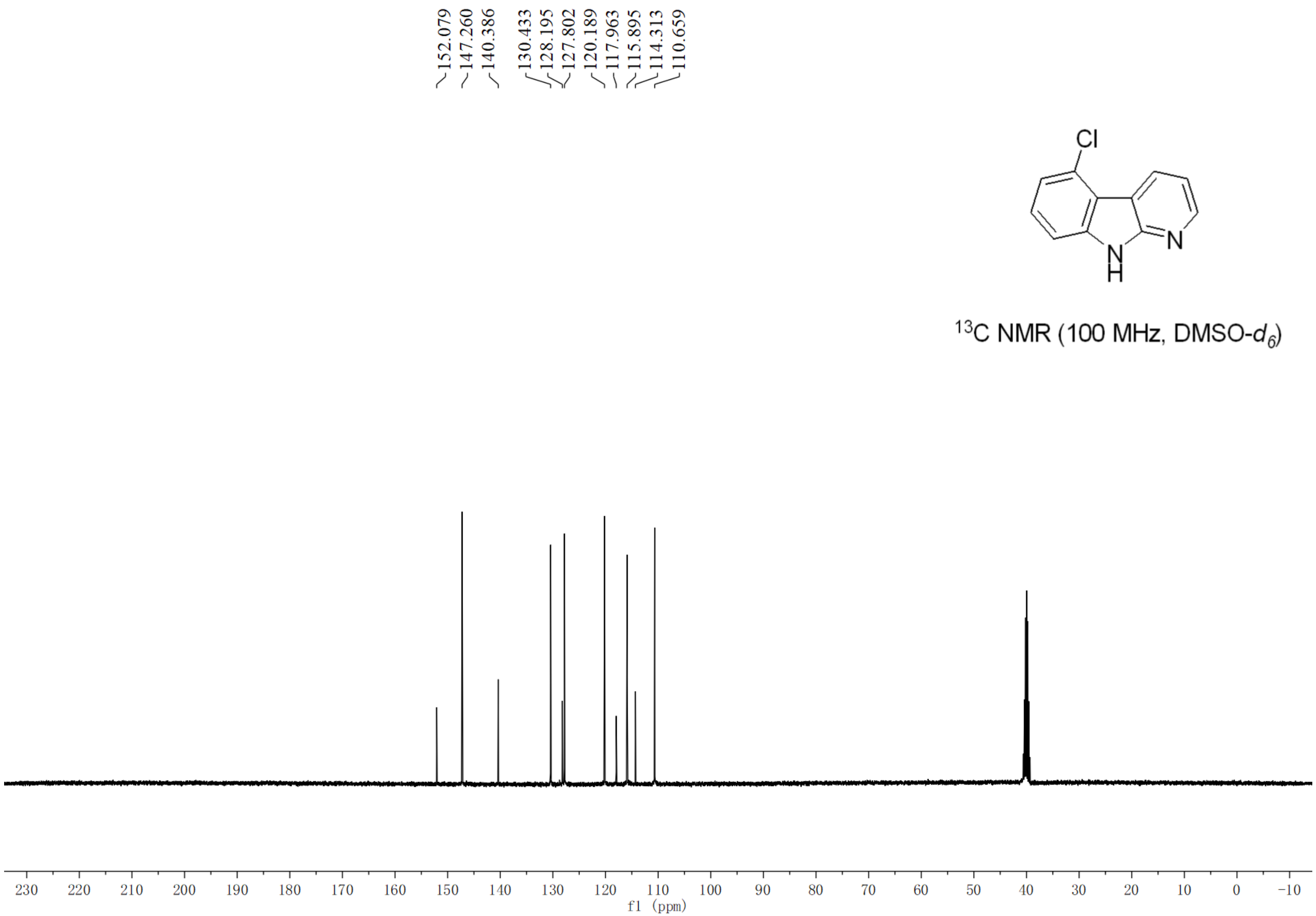


^{1}H NMR (400 MHz, DMSO-d_6)

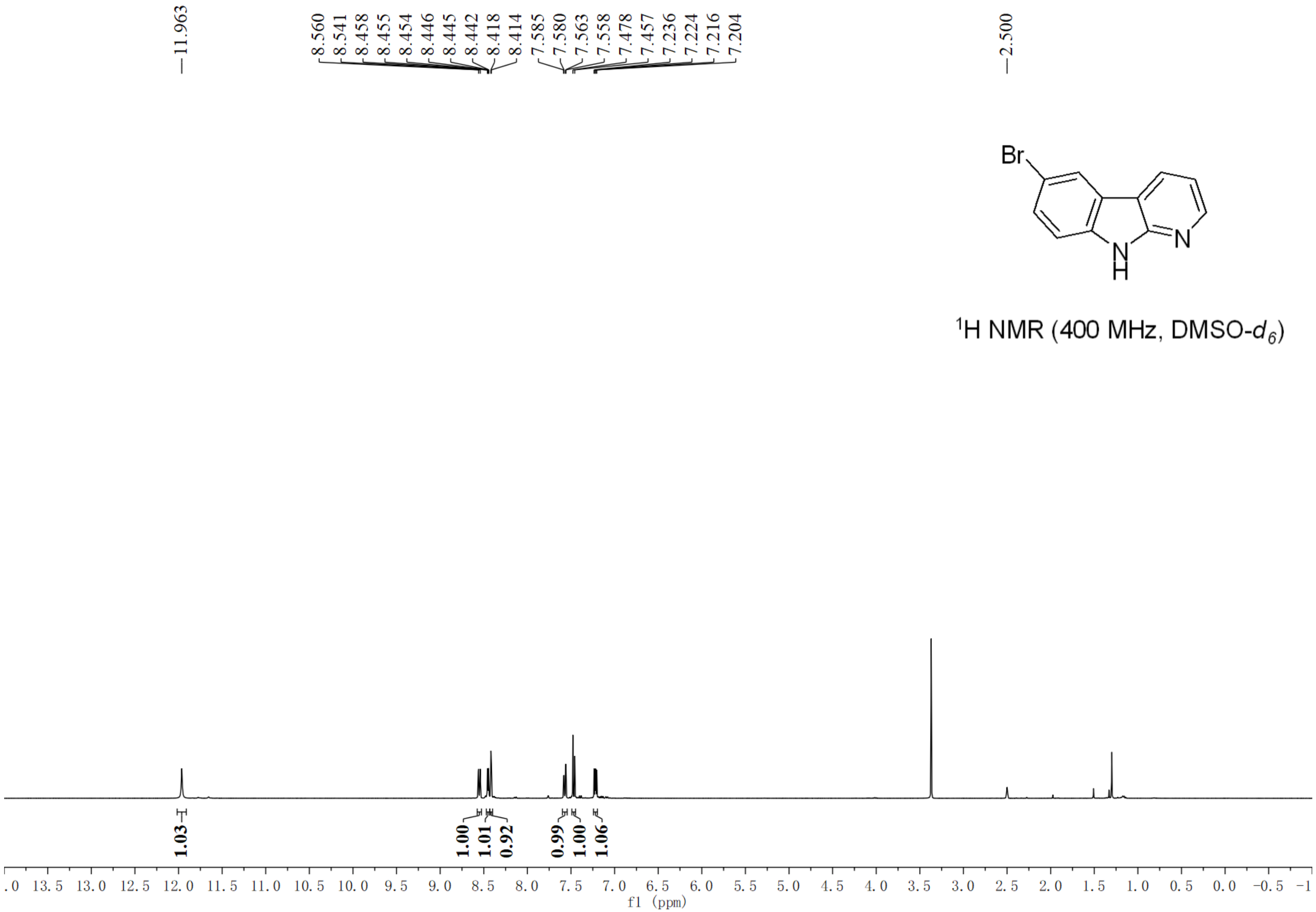


^{13}C NMR (100 MHz, DMSO-d_6)

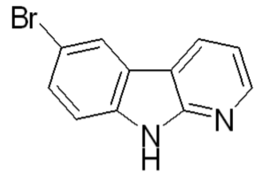

12.177
8.677
8.658
8.504
8.499
8.491
8.487
7.517
7.497
7.472
7.453
7.433
7.283
7.275
7.271
7.263
7.256
7.251
2.500
Cl
N
N
H
1H NMR (400 MHz, DMSO-d6)
1.05
1.00
1.03
2.17
2.08
f1 (ppm)



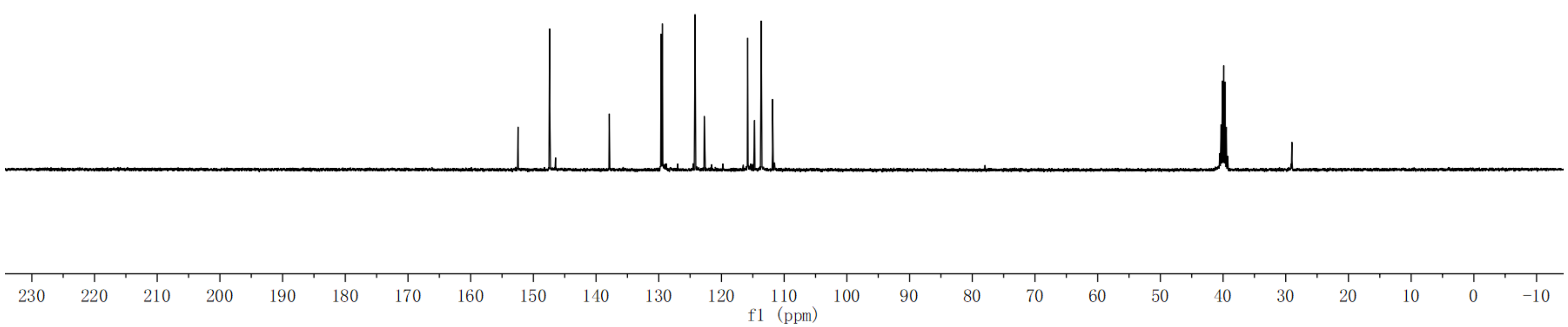
^{13}C NMR (100 MHz, DMSO-d_6)

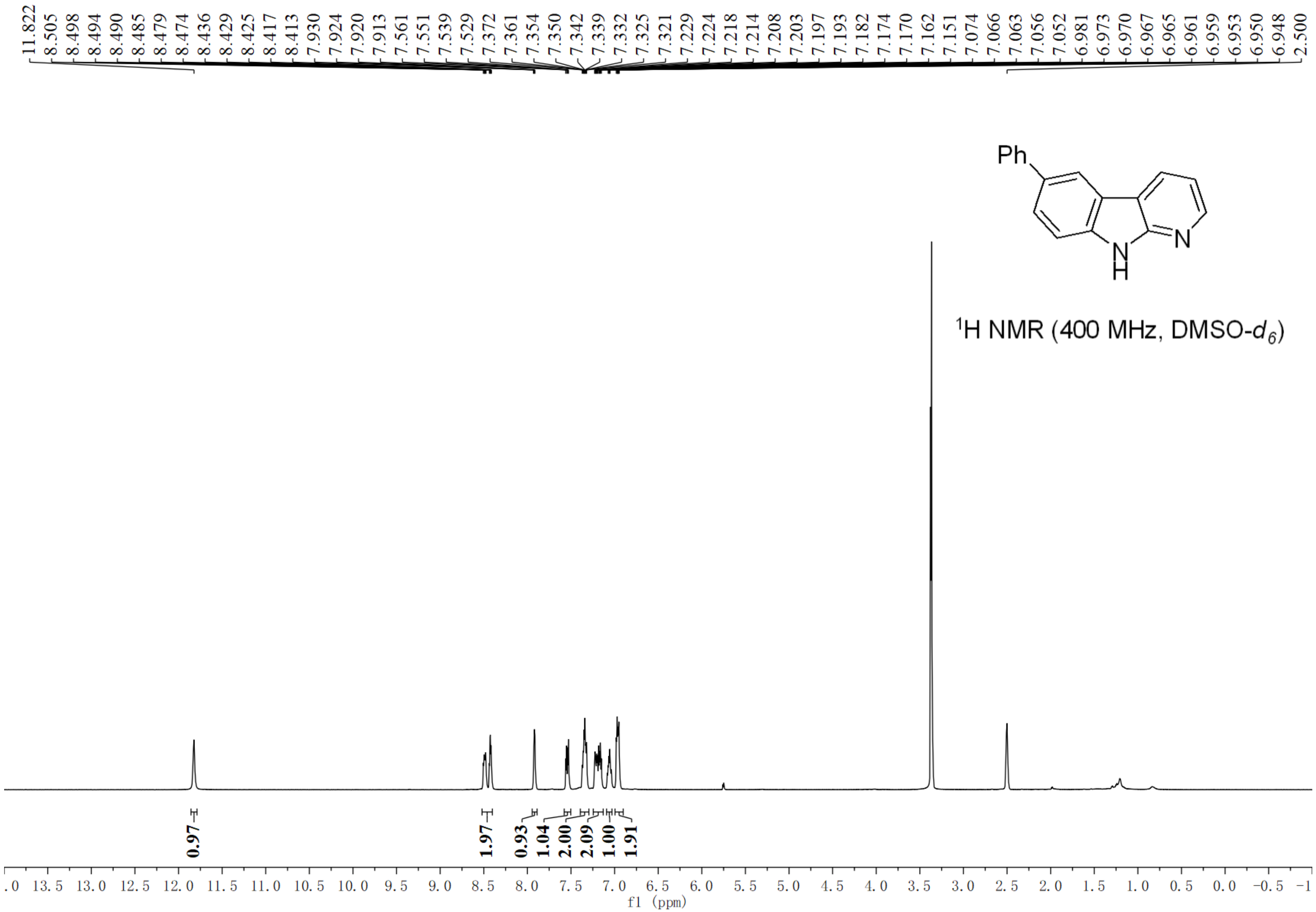


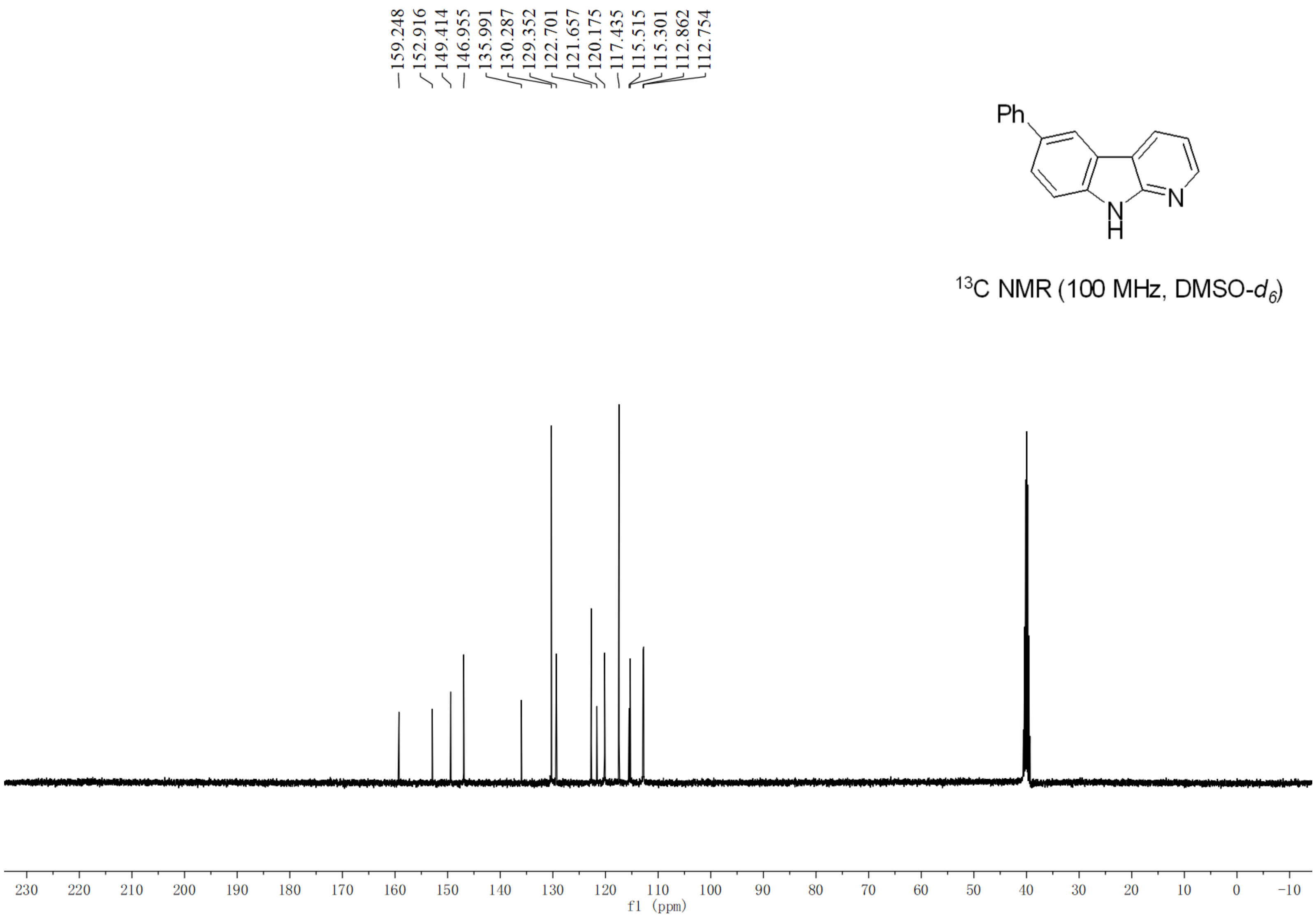
^{1}H NMR (400 MHz, DMSO-d_6)



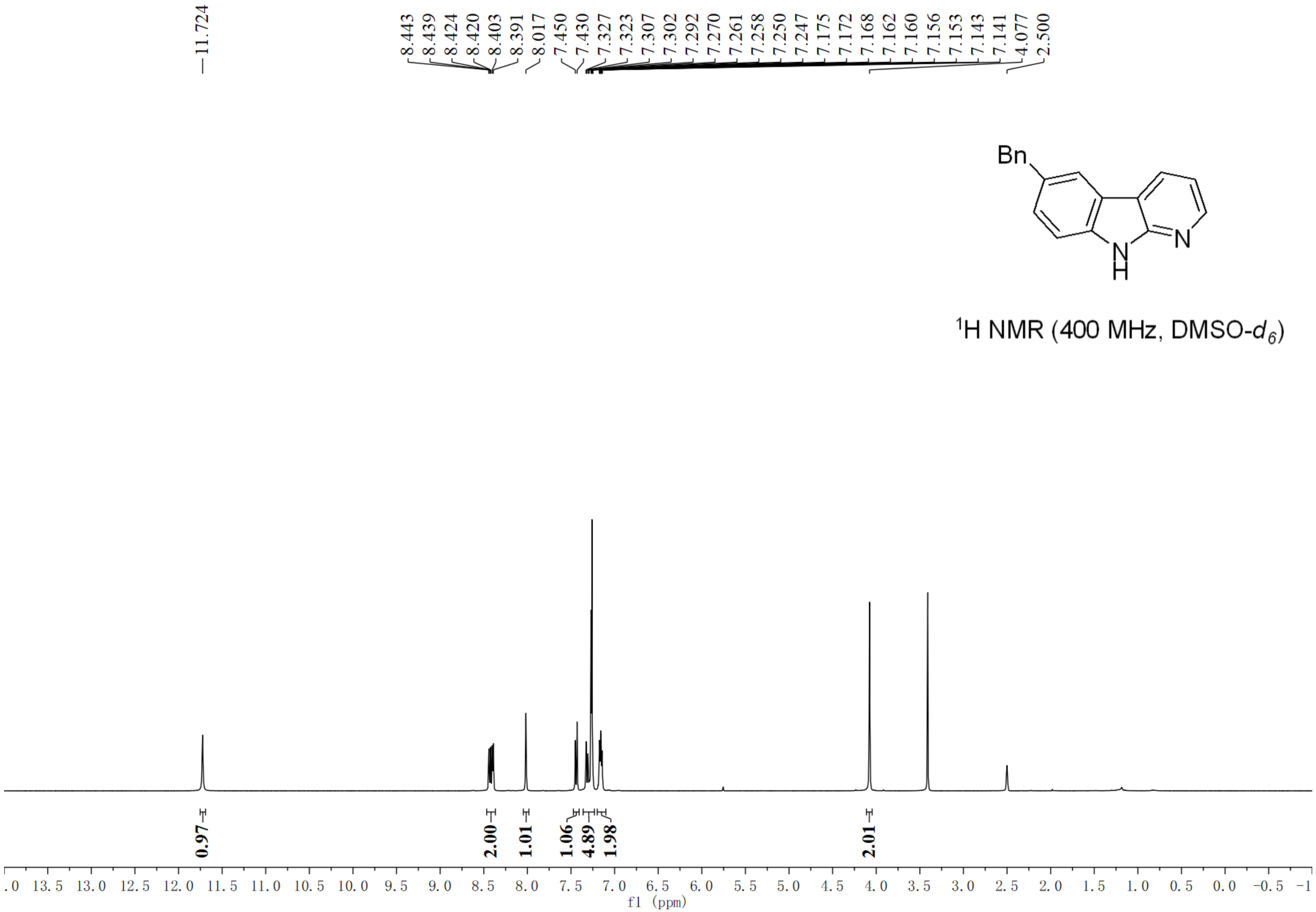
^{13}C NMR (100 MHz, DMSO-d_6)



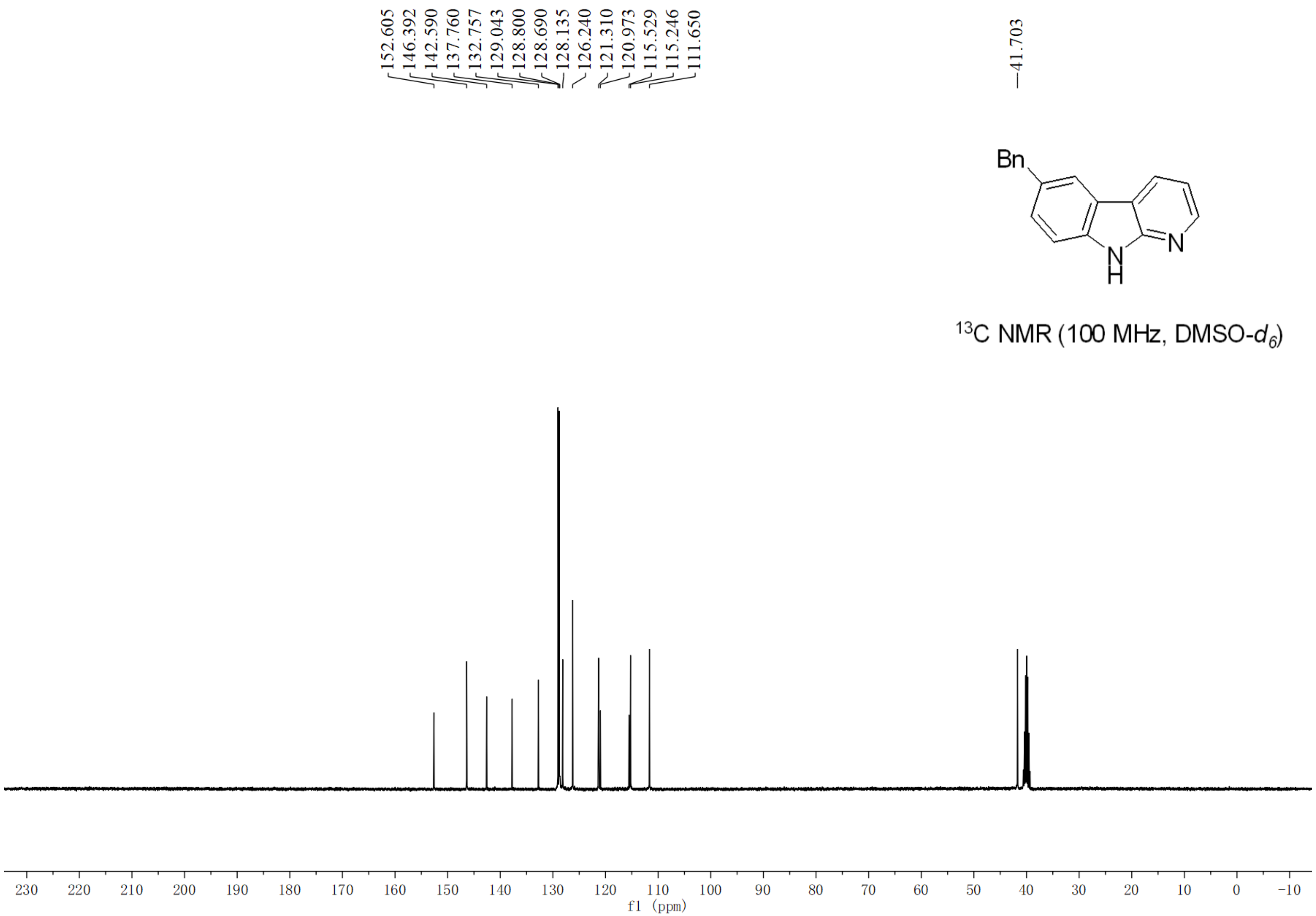

11.822
8.505
8.498
8.494
8.490
8.485
8.479
8.474
8.436
8.429
8.425
8.417
8.413
7.930
7.924
7.920
7.913
7.561
7.551
7.539
7.529
7.372
7.361
7.354
7.350
7.342
7.339
7.332
7.325
7.321
7.229
7.224
7.218
7.214
7.208
7.203
7.197
7.193
7.182
7.174
7.170
7.162
7.151
7.074
7.066
7.063
7.056
7.052
6.981
6.973
6.970
6.967
6.965
6.961
6.959
6.953
6.950
6.948
2.500
Ph
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
0.97
1.97
0.93
1.04
2.00
2.09
1.00
1.91
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



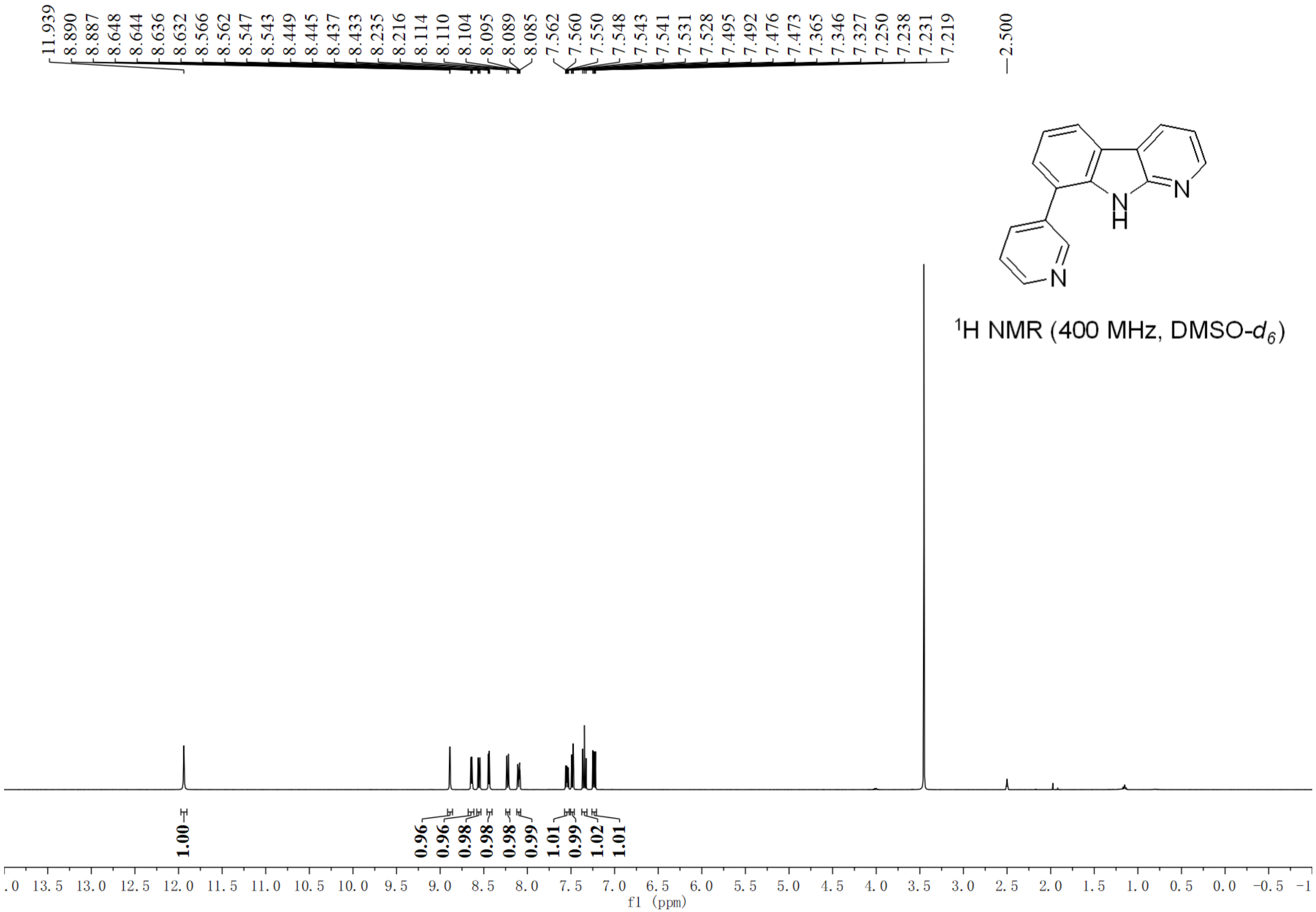
^{13}C NMR (100 MHz, DMSO-d_6)



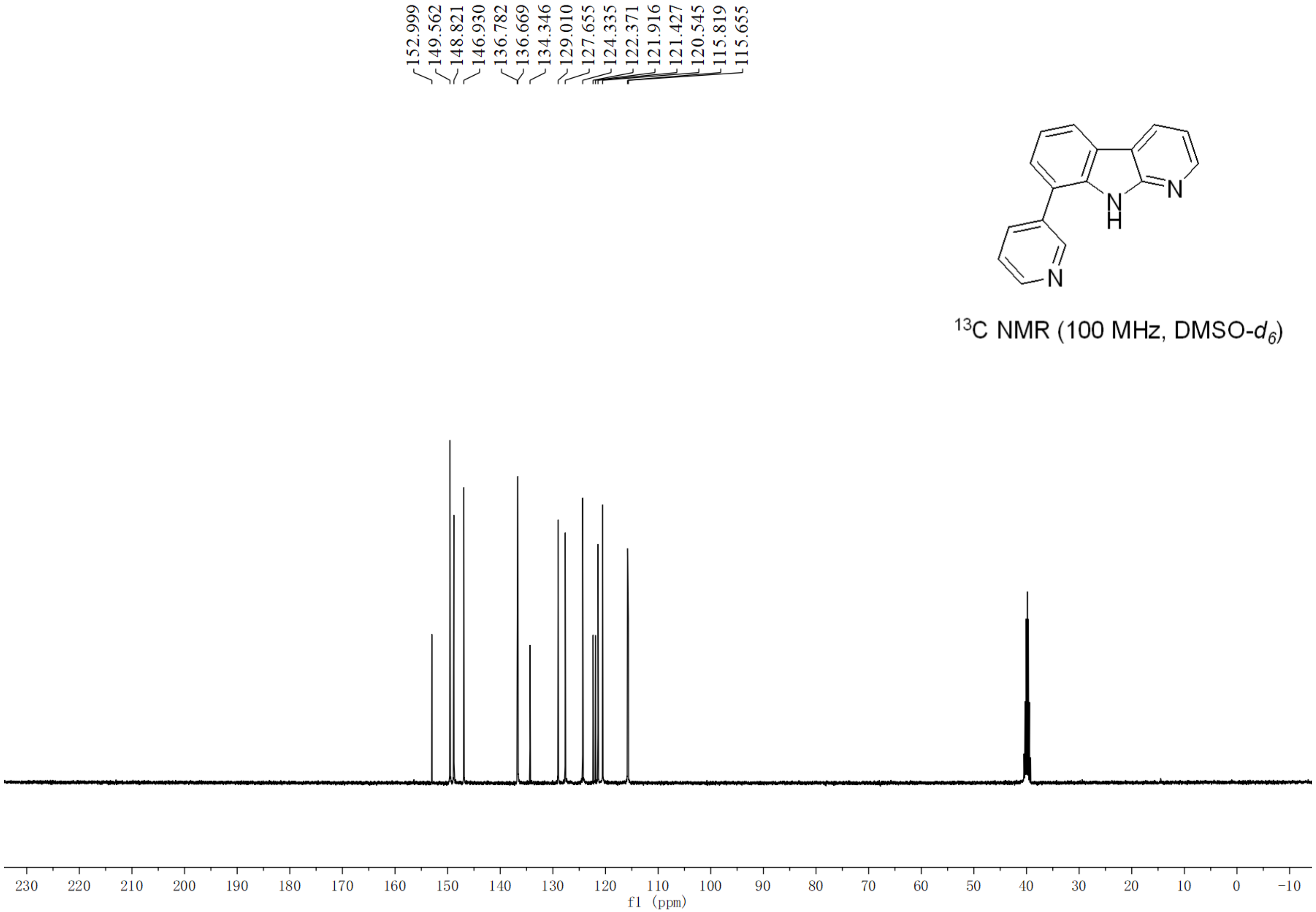
^1H NMR (400 MHz, DMSO-d_6)

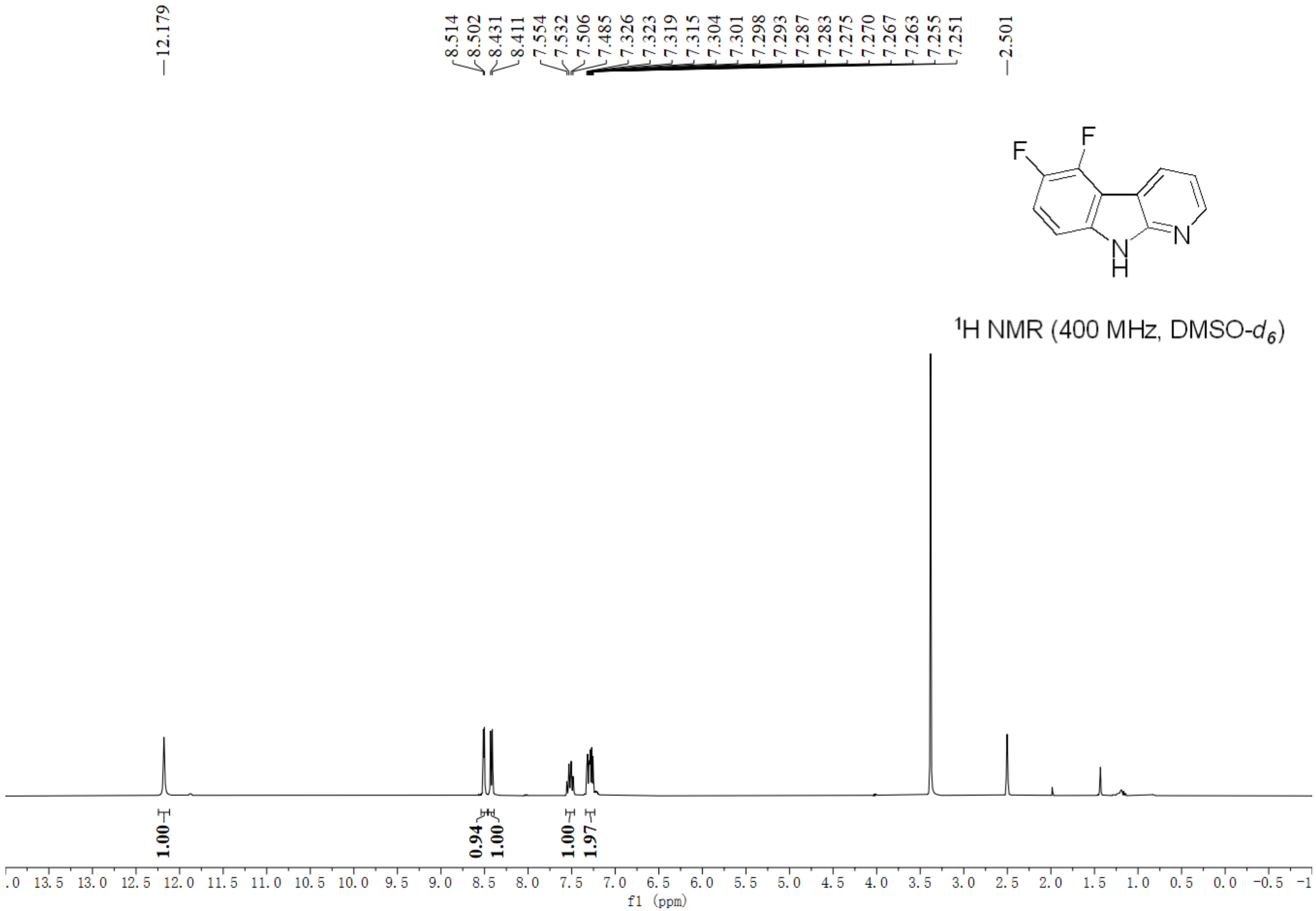


152.605
146.392
142.590
137.760
132.757
129.043
128.800
128.690
128.135
126.240
121.310
120.973
115.529
115.246
111.650
41.703
Bn
N
N
H
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

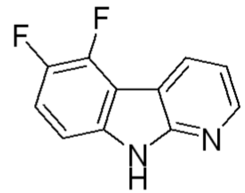

11.939 8.890 8.887 8.648 8.644 8.636 8.632 8.566 8.562 8.547 8.543 8.449 8.445 8.437 8.433 8.235 8.216 8.114 8.110 8.104 8.095 8.089 8.085 7.562 7.560 7.550 7.548 7.543 7.541 7.531 7.528 7.495 7.492 7.476 7.473 7.365 7.346 7.327 7.250 7.238 7.231 7.219
2.500
N
N
H
N
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
0.96 0.96 0.98 0.98 0.98 0.99 1.01 0.99 1.02 1.01
f1 (ppm)

^{13}C NMR (100 MHz, DMSO-d_6)

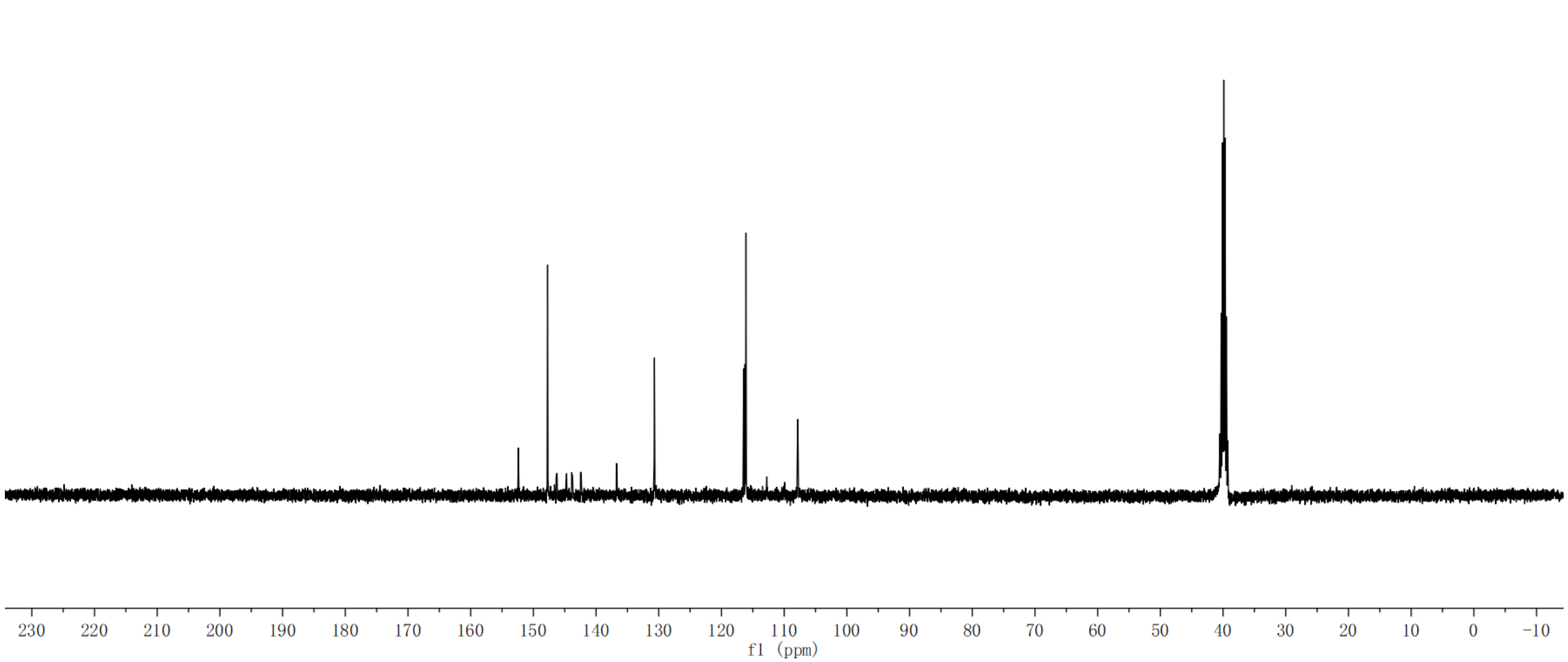


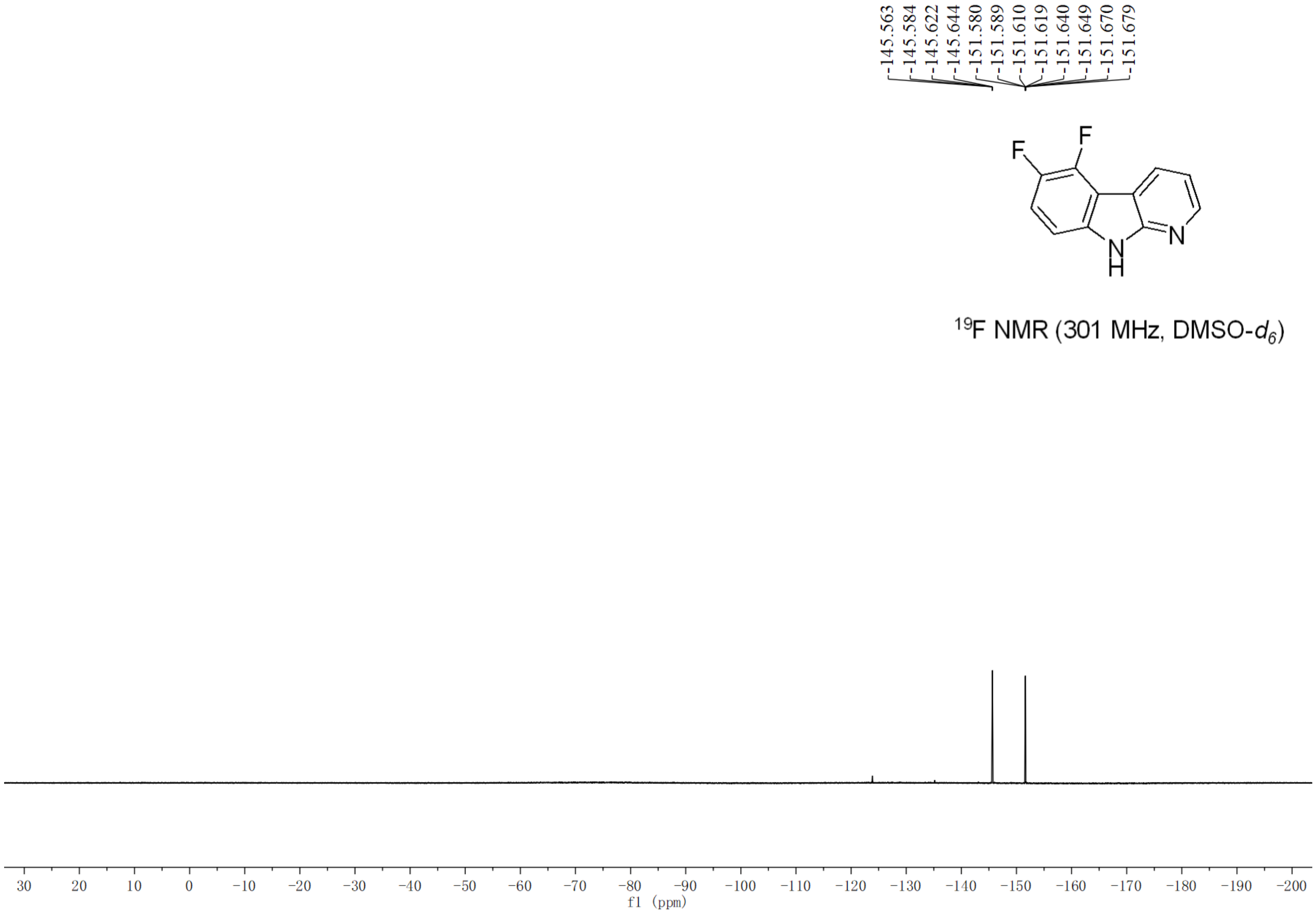


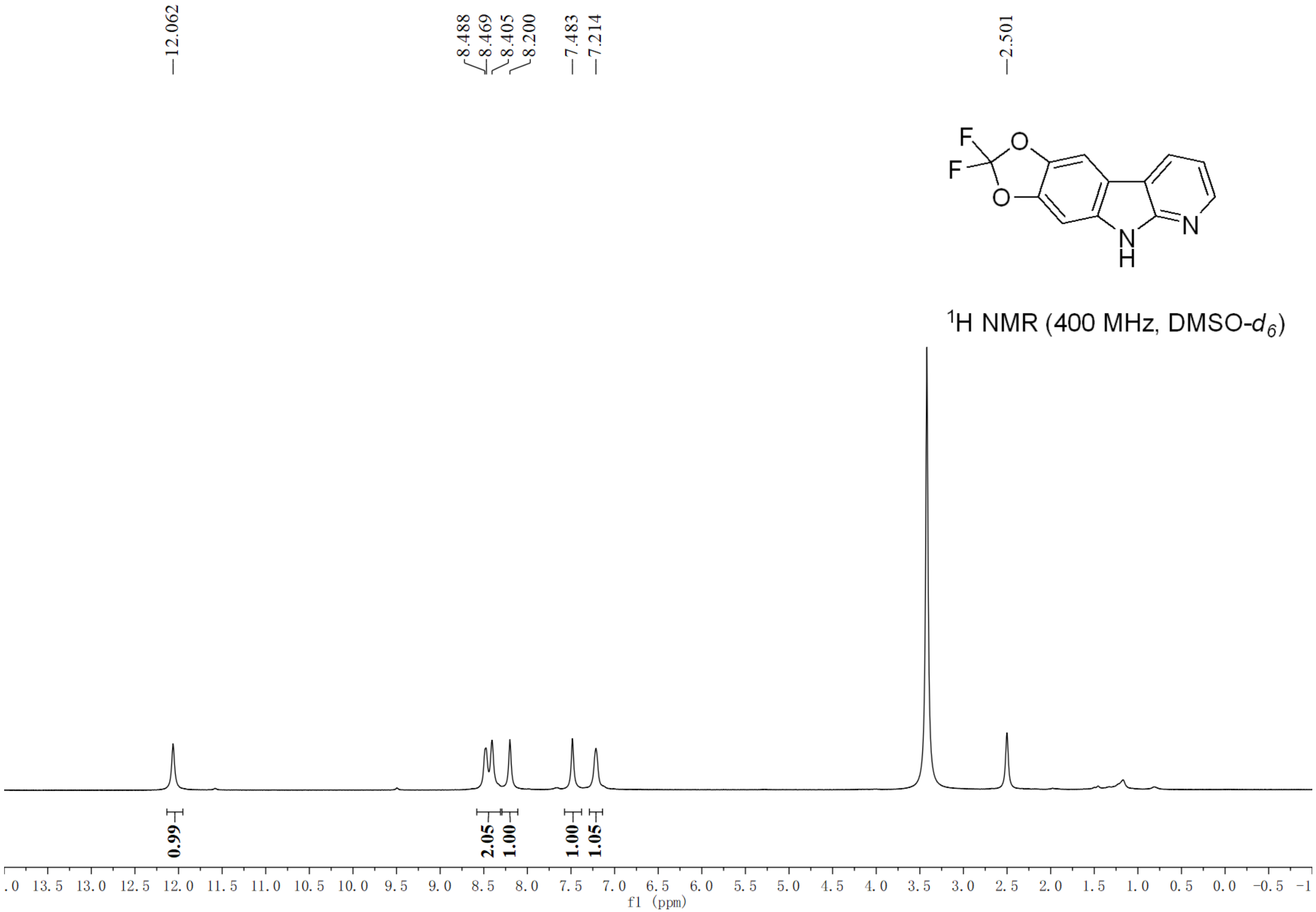
12.179
8.514
8.502
8.431
8.411
7.554
7.532
7.506
7.485
7.326
7.323
7.319
7.315
7.304
7.301
7.298
7.293
7.287
7.283
7.275
7.270
7.267
7.263
7.255
7.251
2.501
F
F
N
N
H
¹H NMR (400 MHz, DMSO-d6)
1.00
0.94
1.00
1.00
1.97
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



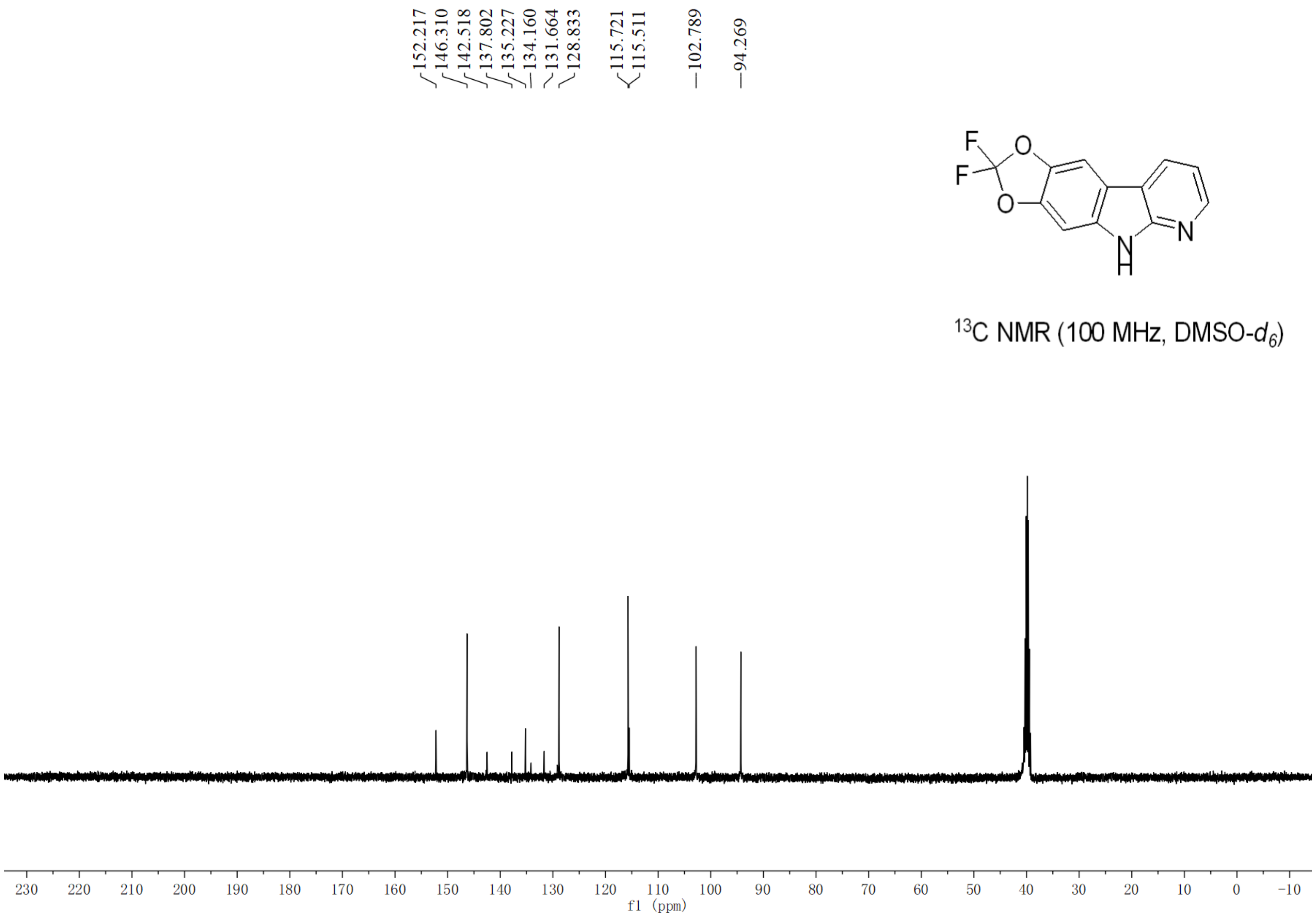
^{13}C NMR (100 MHz, DMSO-d_6)



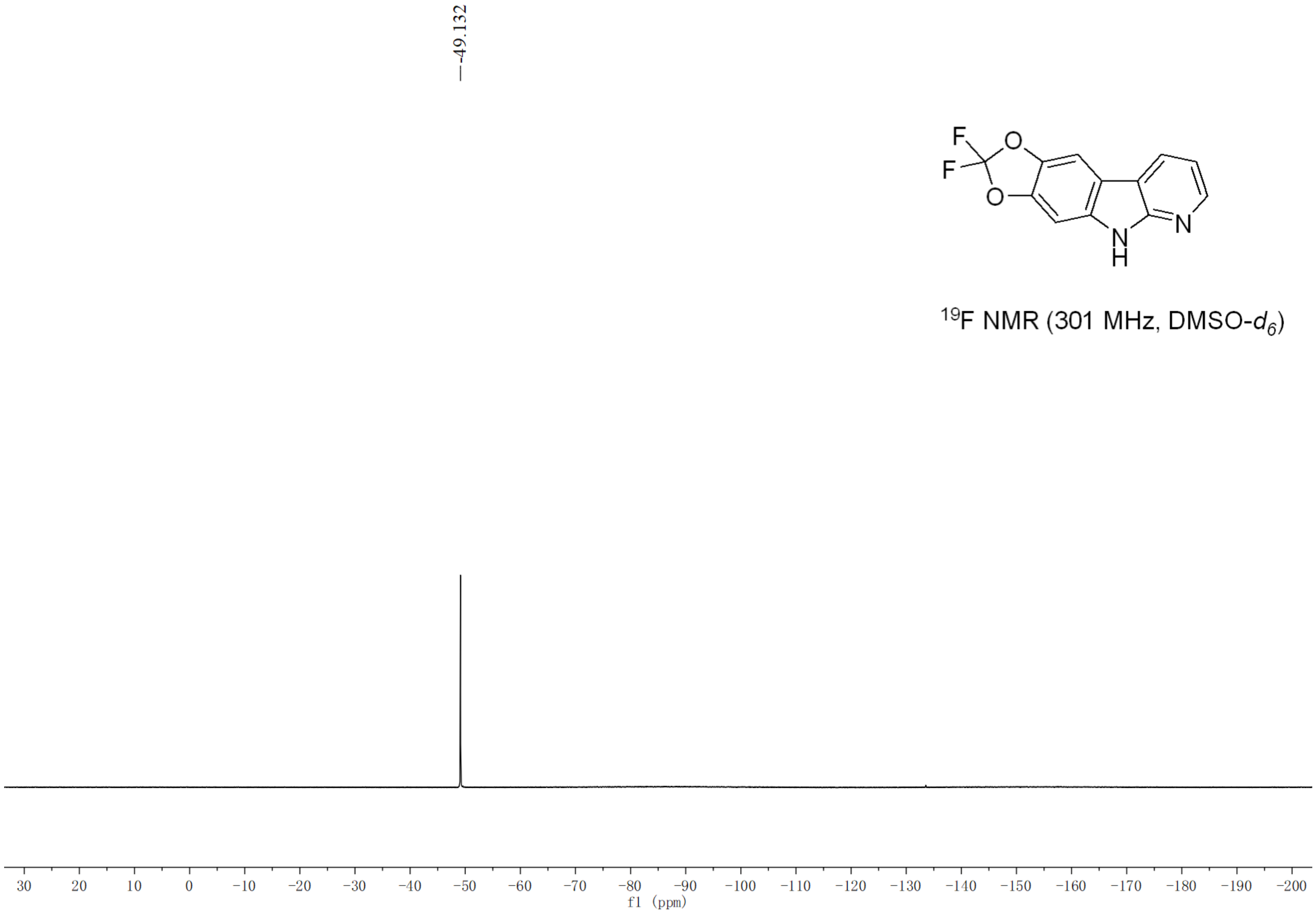

-145.563
-145.584
-145.622
-145.644
-151.580
-151.589
-151.610
-151.619
-151.640
-151.649
-151.670
-151.679
F
F
N
N
H
^{19}F NMR (301 MHz, DMSO-d_6)
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)



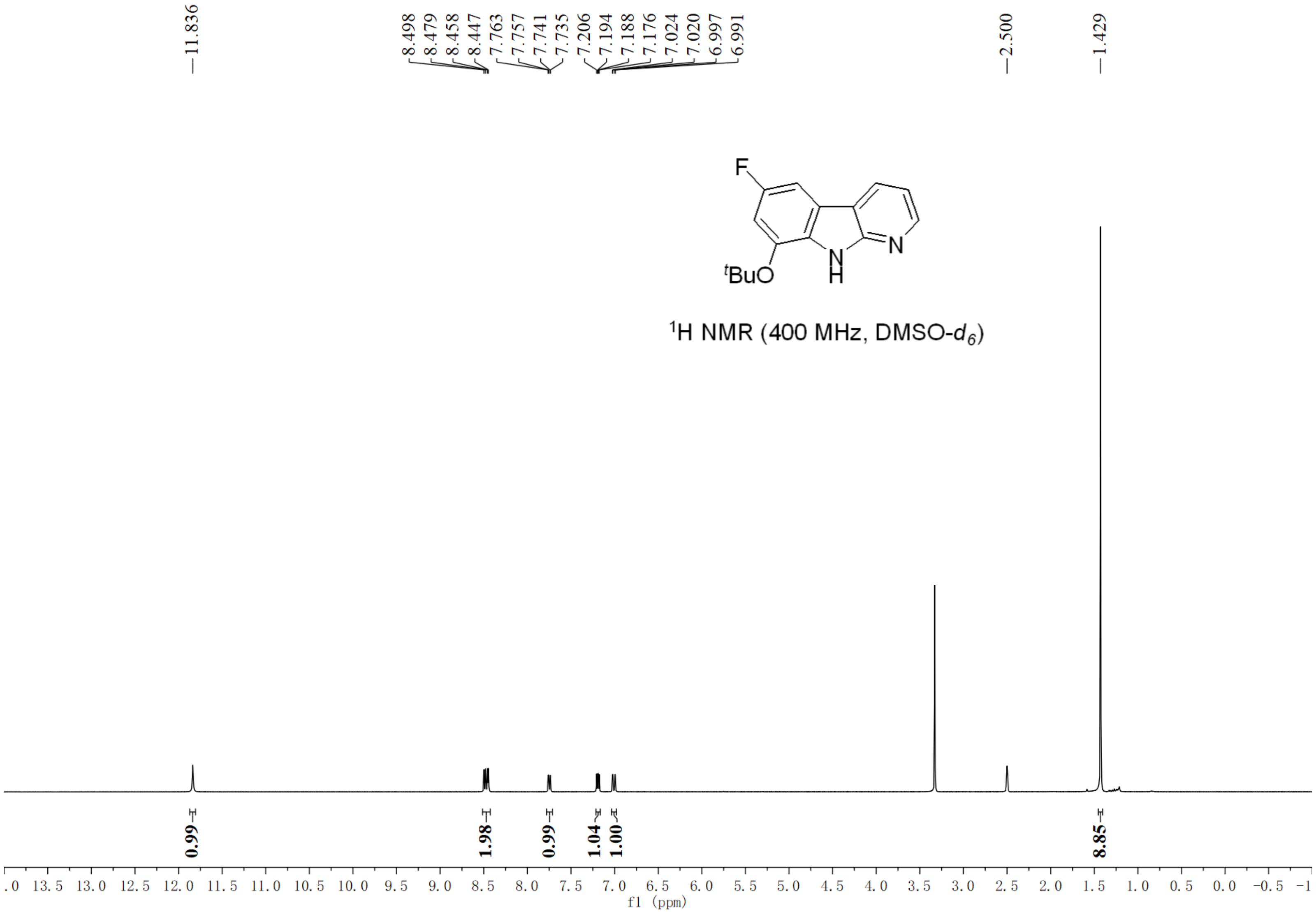
^{1}H NMR (400 MHz, DMSO-d_6)



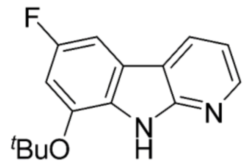
^{13}C NMR (100 MHz, DMSO-d_6)



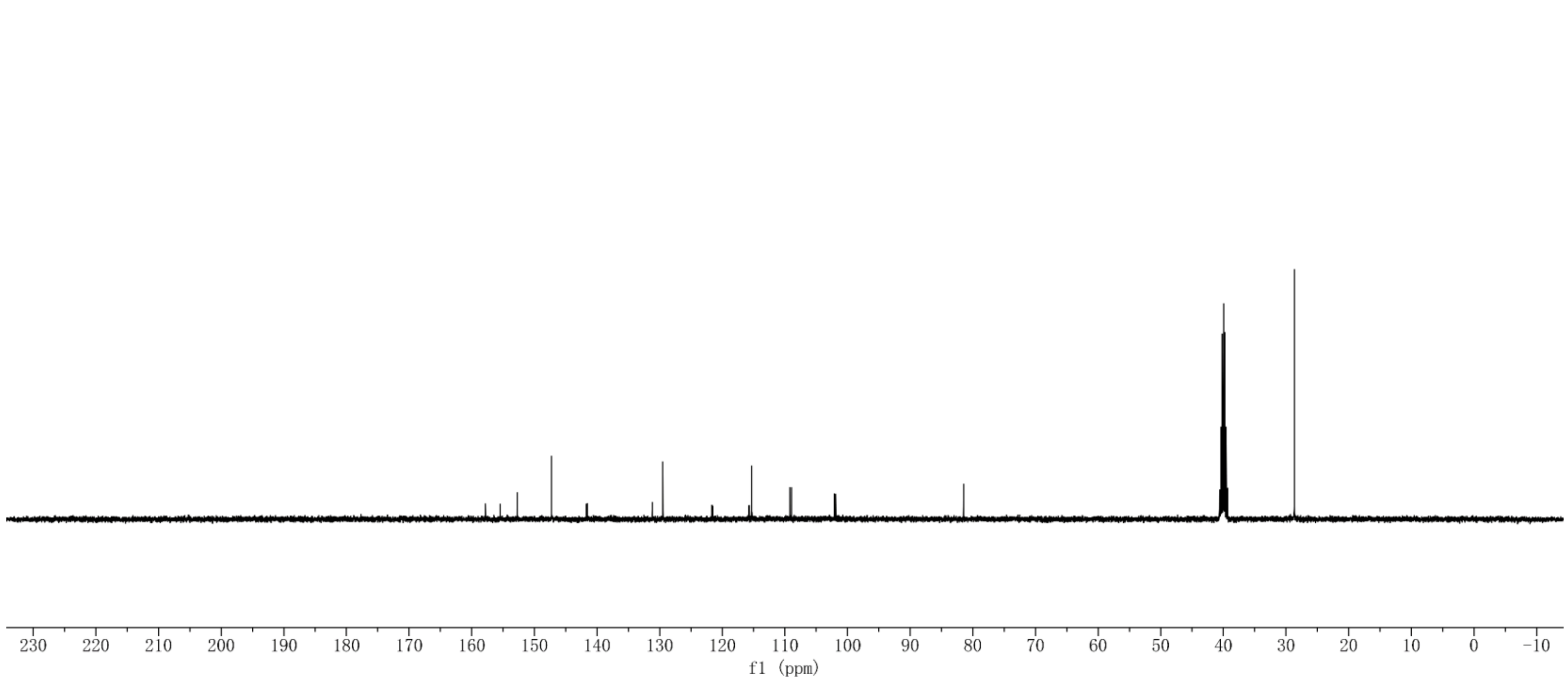
^{19}F NMR (301 MHz, DMSO-d_6)

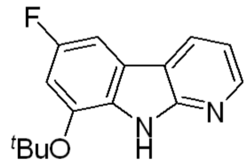


11.836
8.498
8.479
8.458
8.447
7.763
7.757
7.741
7.735
7.206
7.194
7.188
7.176
7.024
7.020
6.997
6.991
2.500
1.429
F
N
N
H
^{t}BuO
^{1}H NMR (400 MHz, DMSO-d_6)
0.99
1.98
0.99
1.04
1.00
8.85
f1 (ppm)

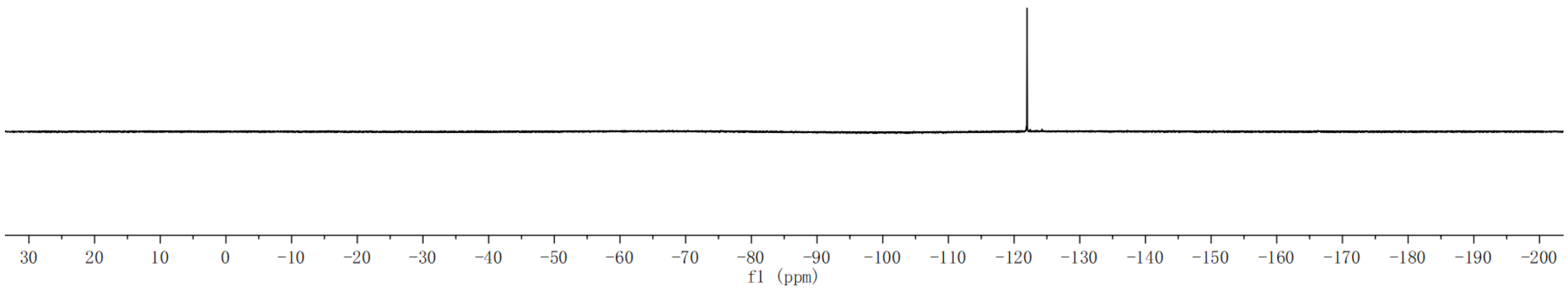


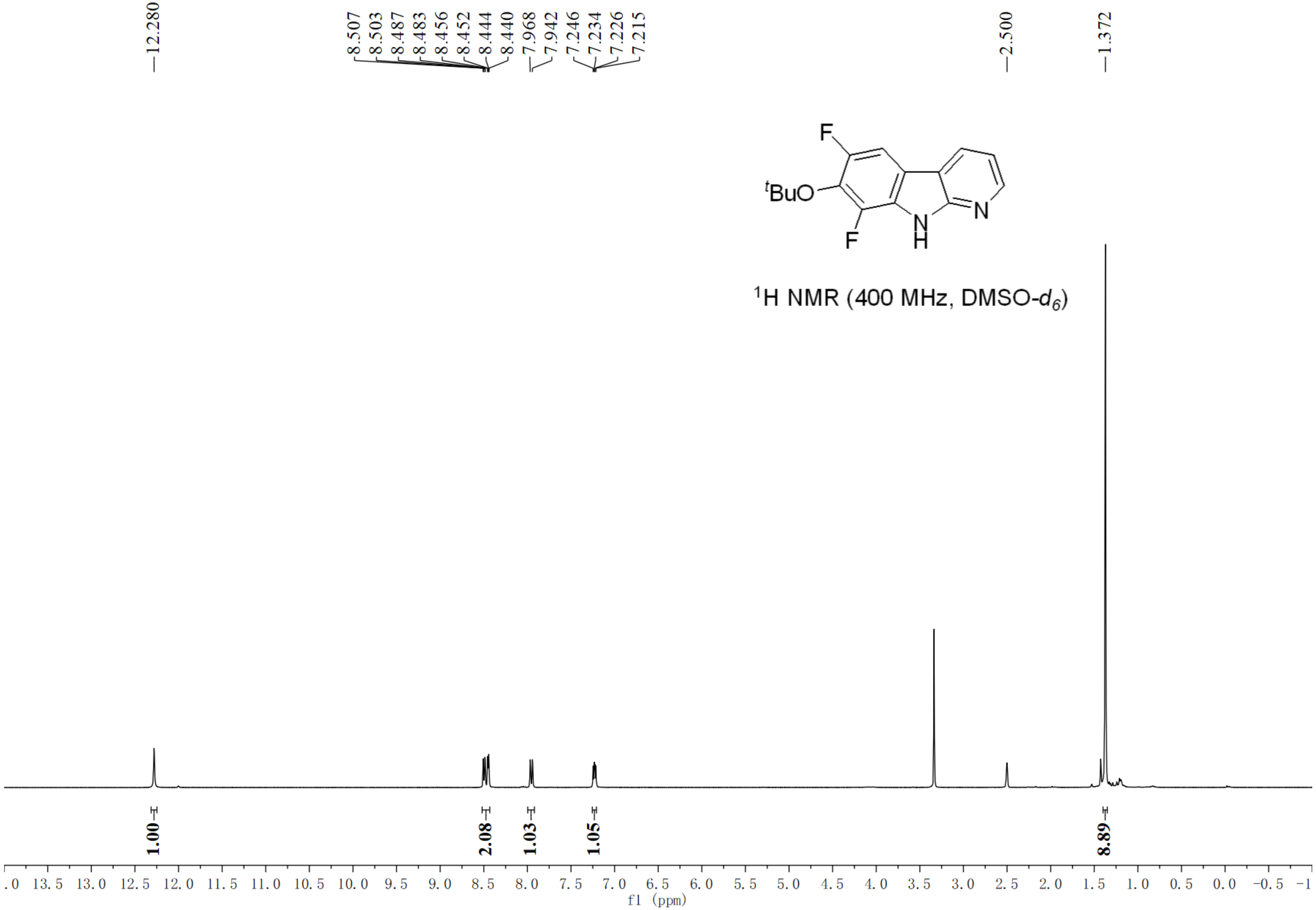
^{13}C NMR (100 MHz, DMSO-d_6)

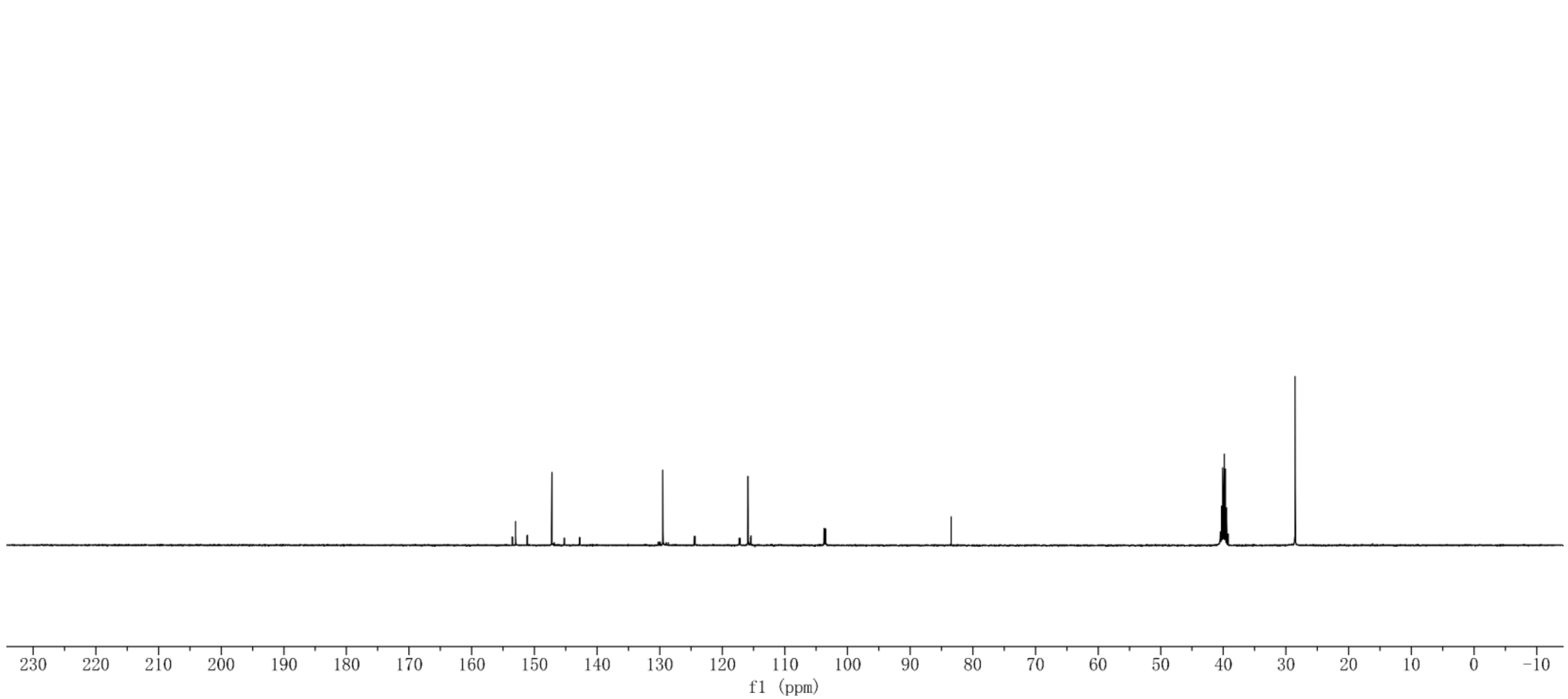


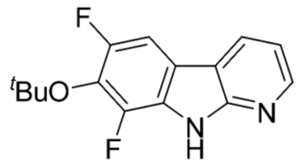


^{19}F NMR (301 MHz, DMSO-d_6)

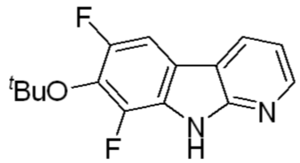



12.280
8.507
8.503
8.487
8.483
8.456
8.452
8.444
8.440
7.968
7.942
7.246
7.234
7.226
7.215
2.500
1.372
F
tBuO
F
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.00
2.08
1.03
1.05
8.89
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

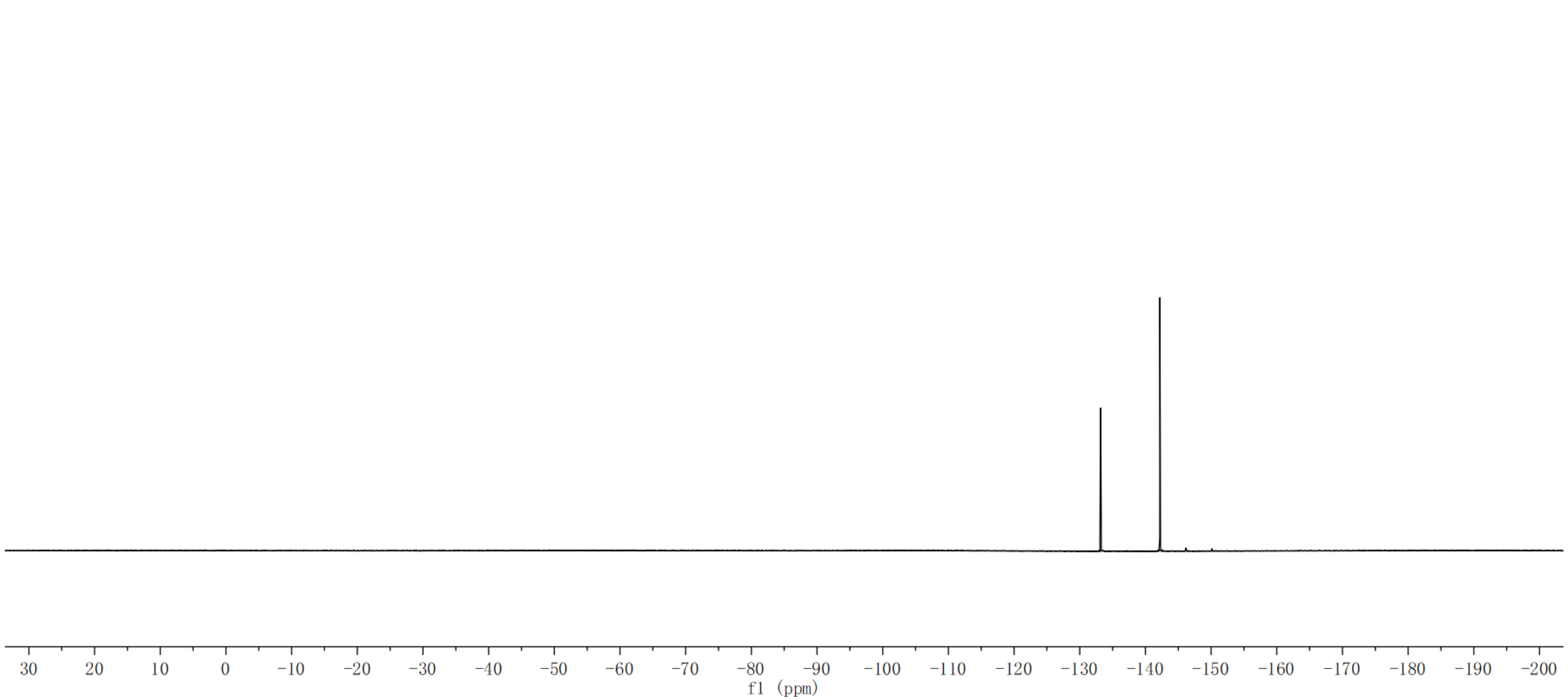


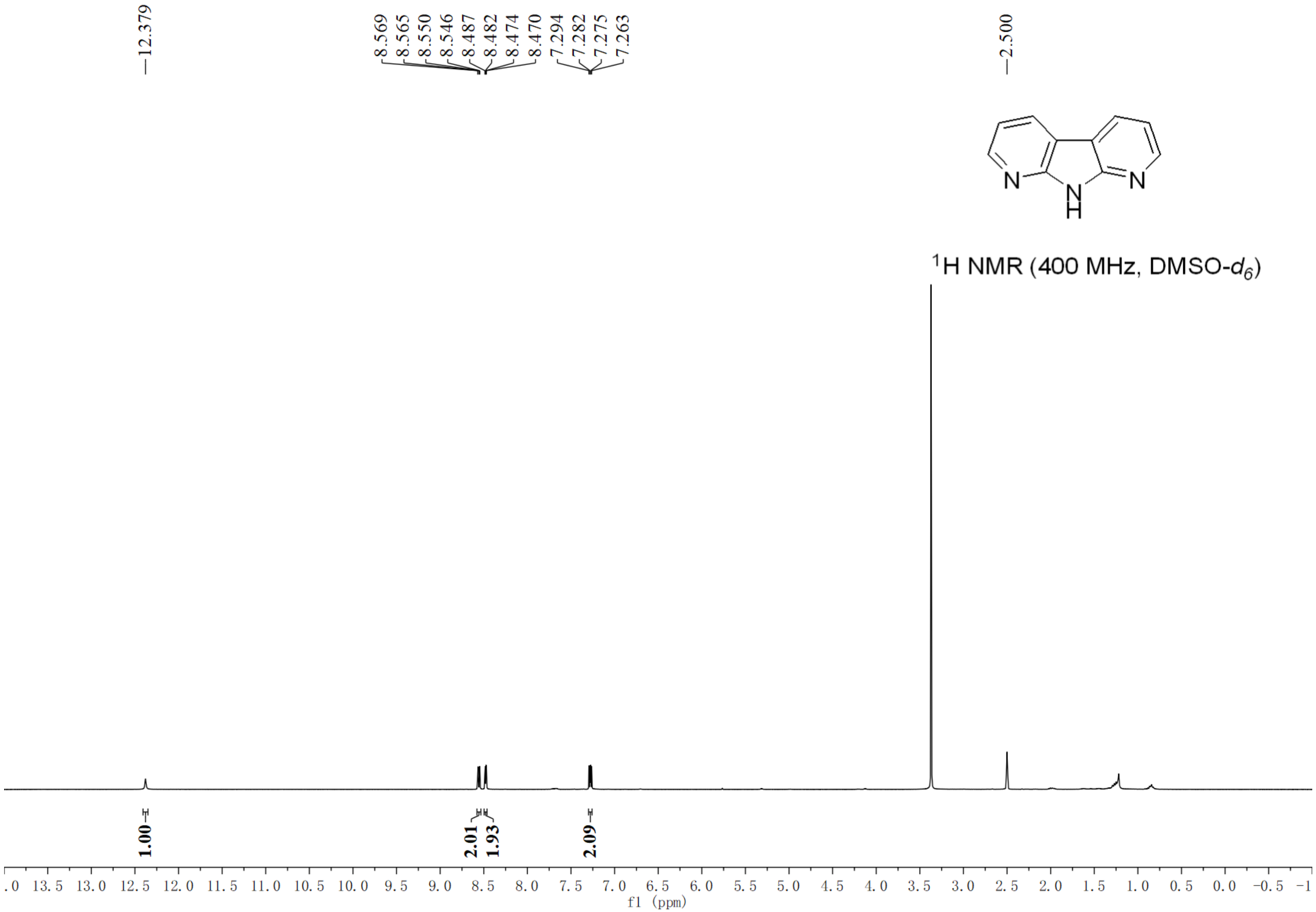


^{13}C NMR (100 MHz, DMSO-d_6)

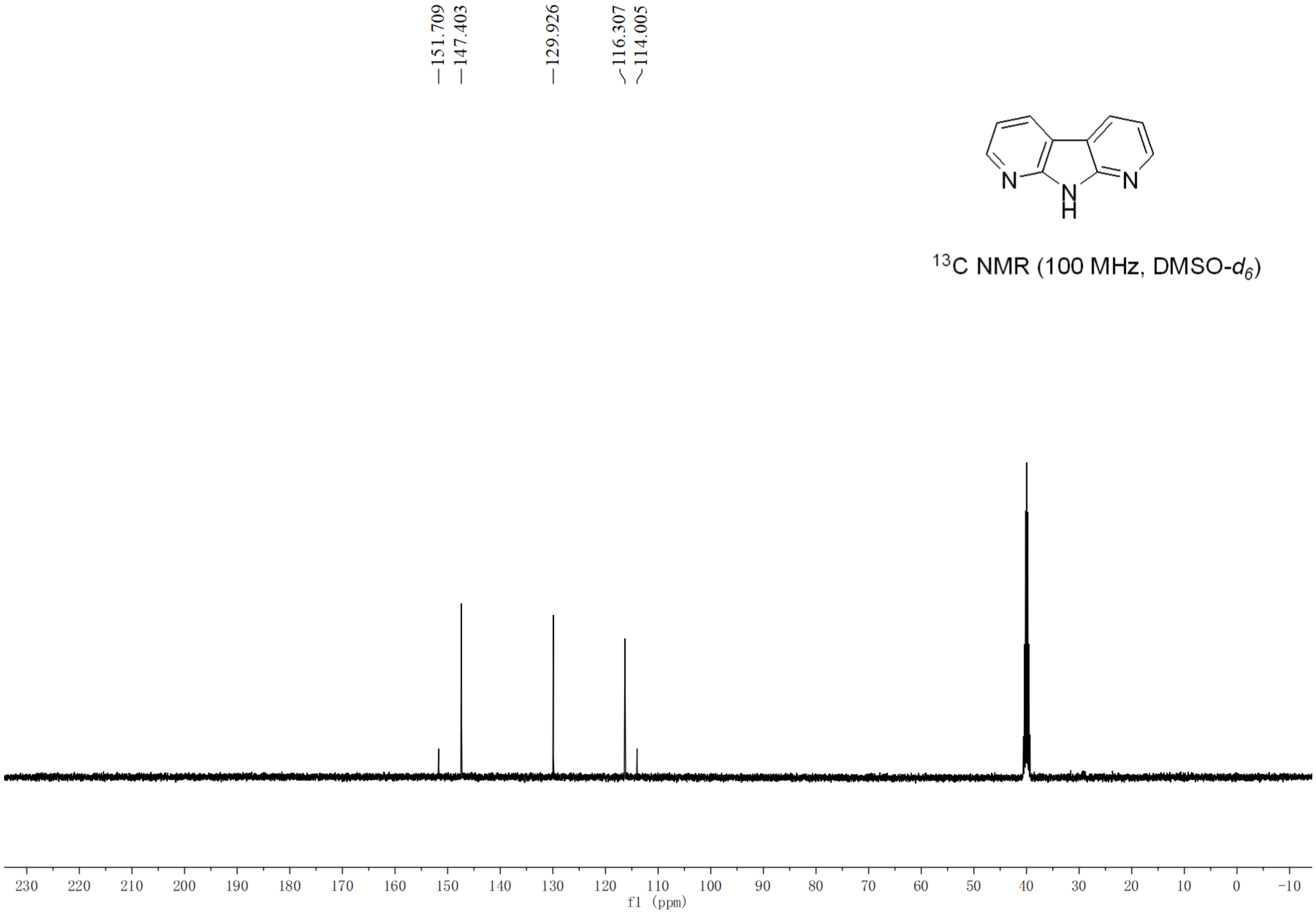


^{19}F NMR (301 MHz, DMSO-d_6)

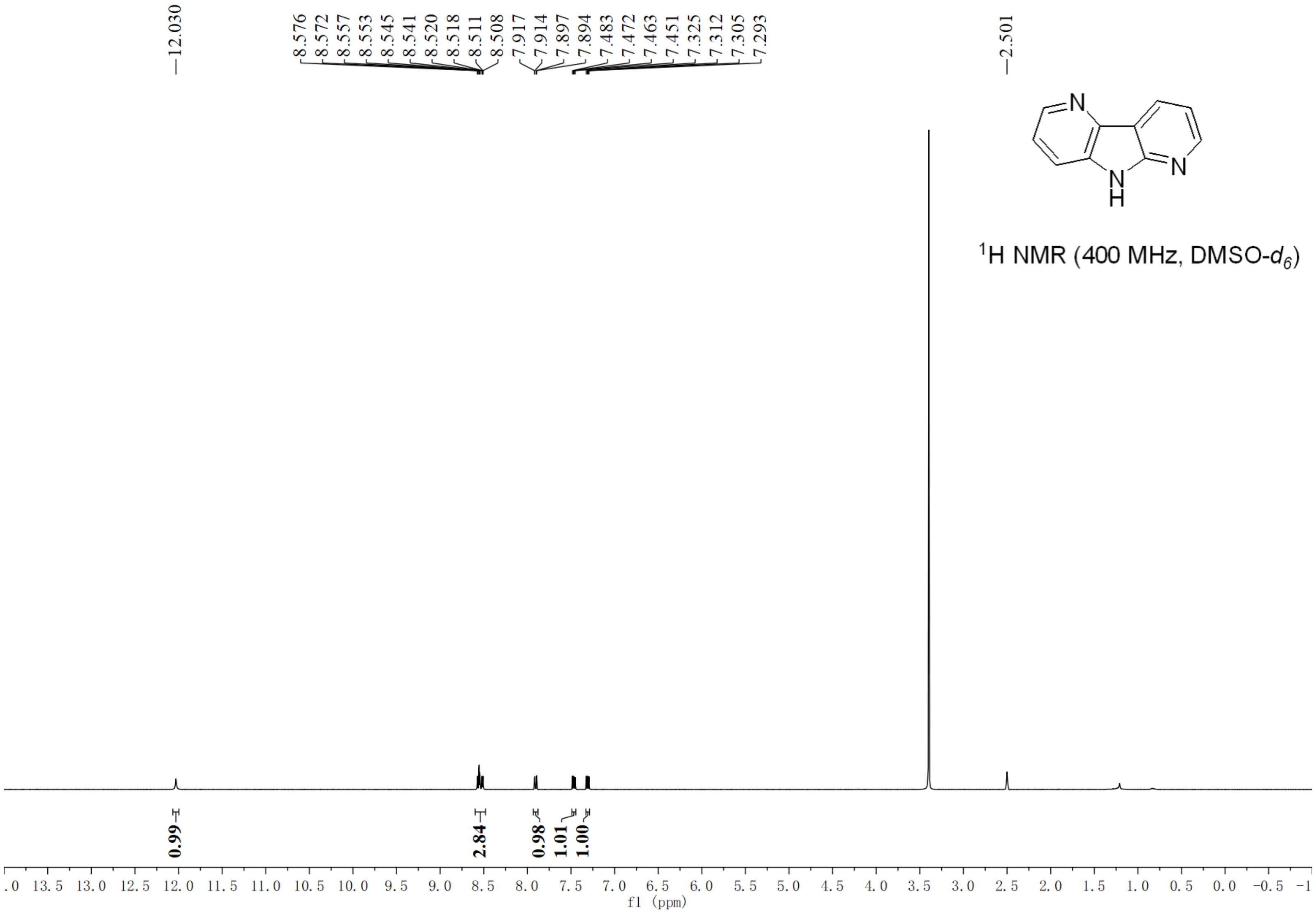




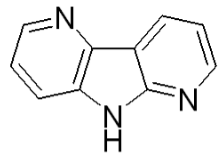
12.379
8.569
8.565
8.550
8.546
8.487
8.482
8.474
8.470
7.294
7.282
7.275
7.263
2.500
N
N
N
H
¹H NMR (400 MHz, DMSO-d_6)
1.00
2.01
1.93
2.09
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)



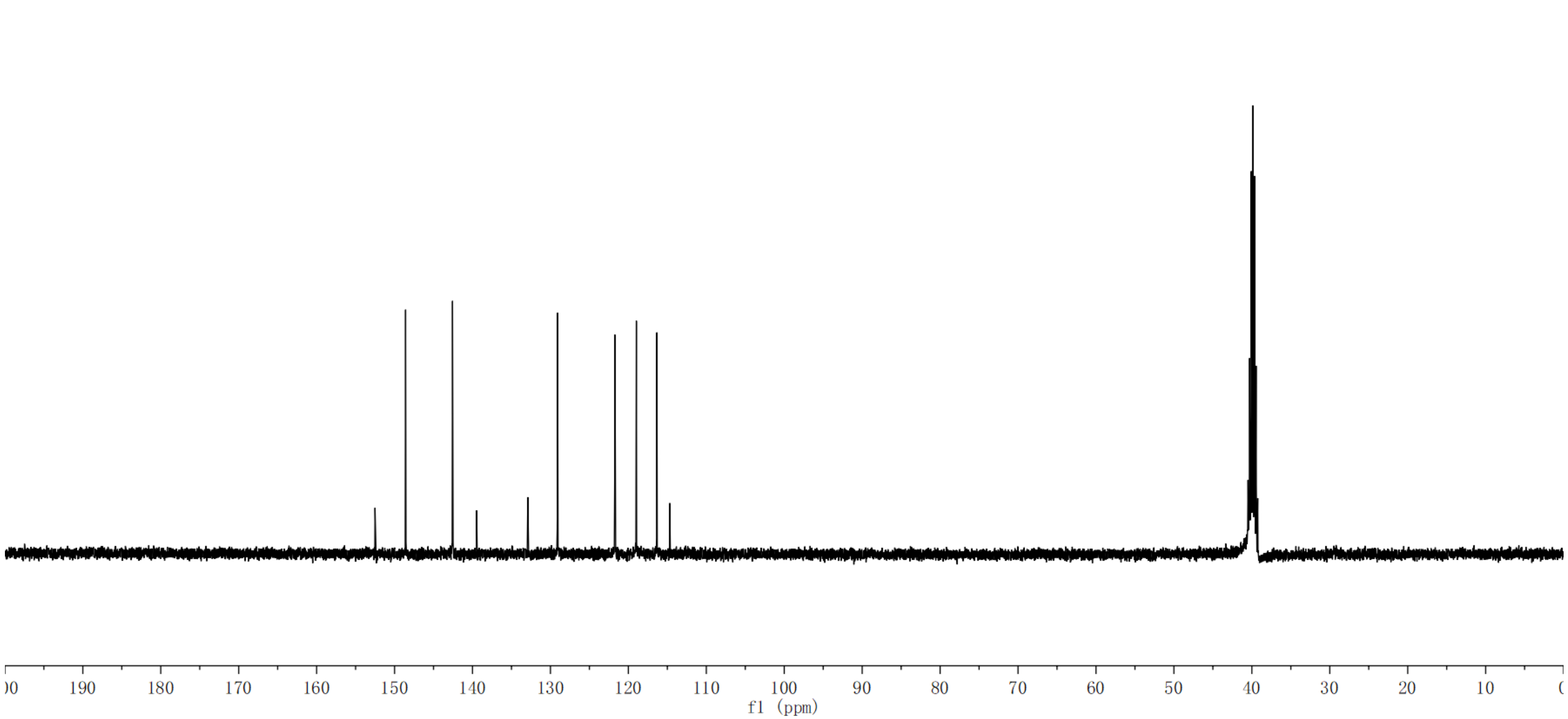
^{13}C NMR (100 MHz, DMSO-d_6)

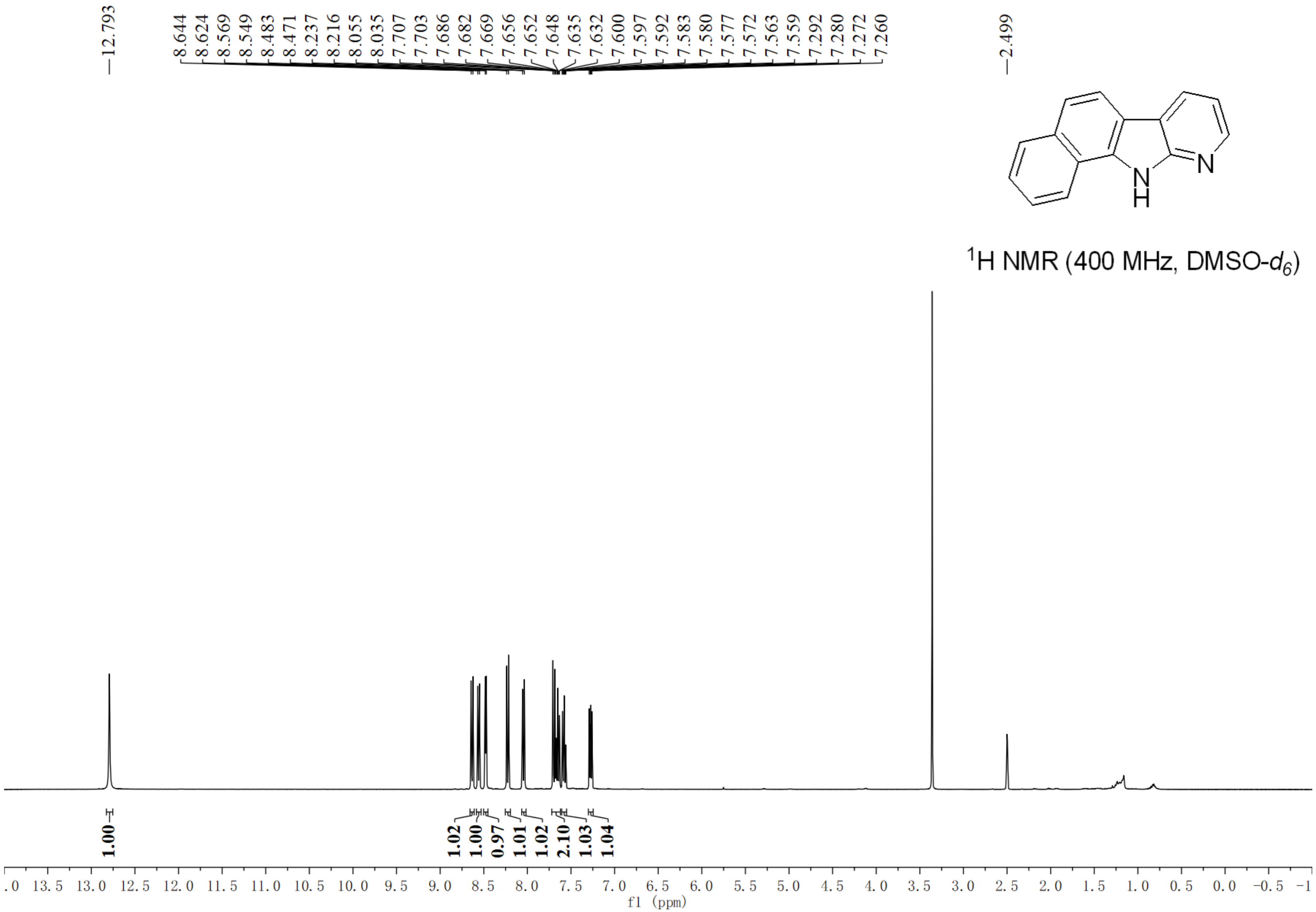


12.030
8.576
8.572
8.557
8.553
8.545
8.541
8.520
8.518
8.511
8.508
7.917
7.914
7.897
7.894
7.483
7.472
7.463
7.451
7.325
7.312
7.305
7.293
2.501
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
0.99
2.84
0.98
1.01
1.00
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

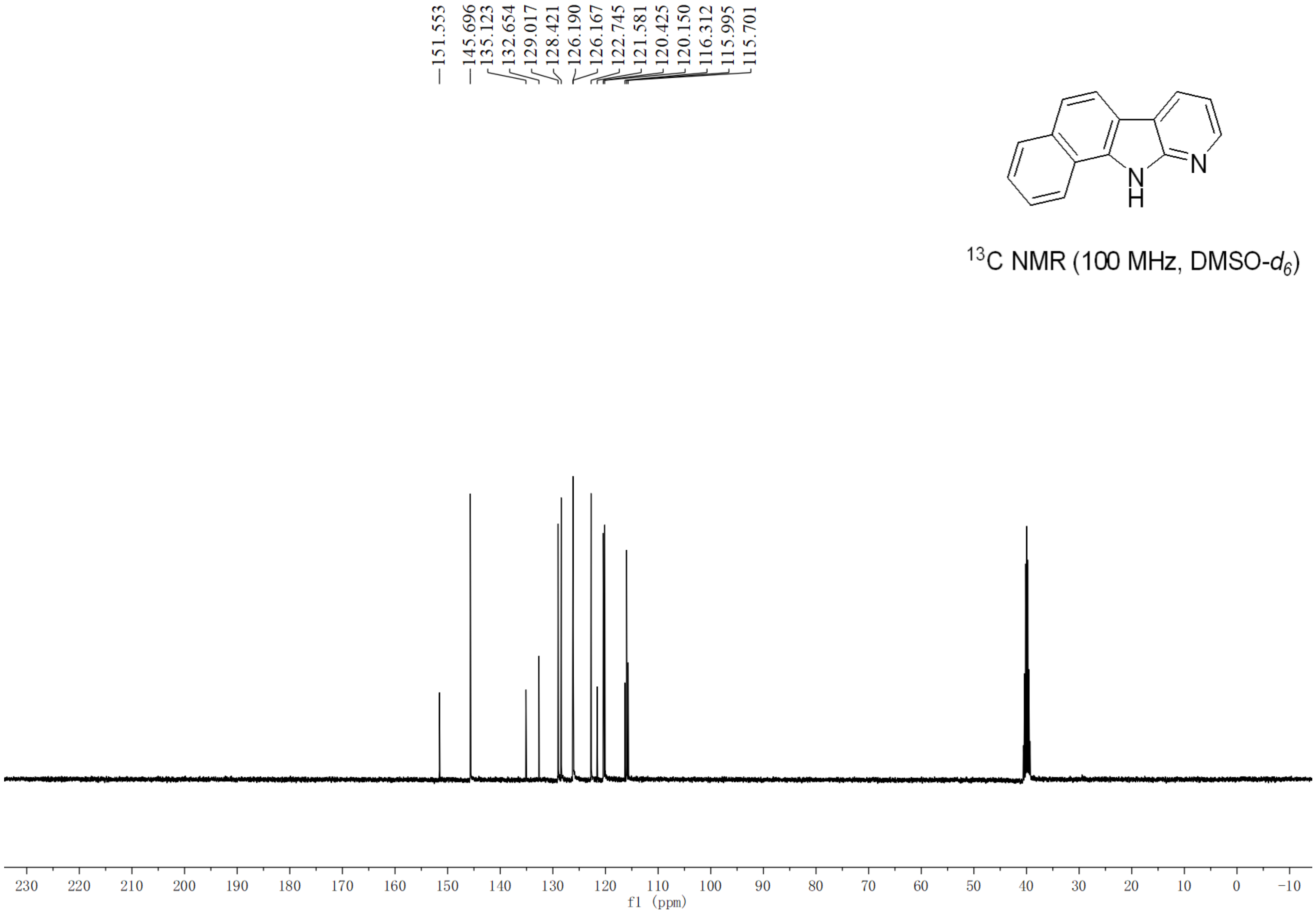


^{1}H NMR (400 MHz, DMSO-d_6)

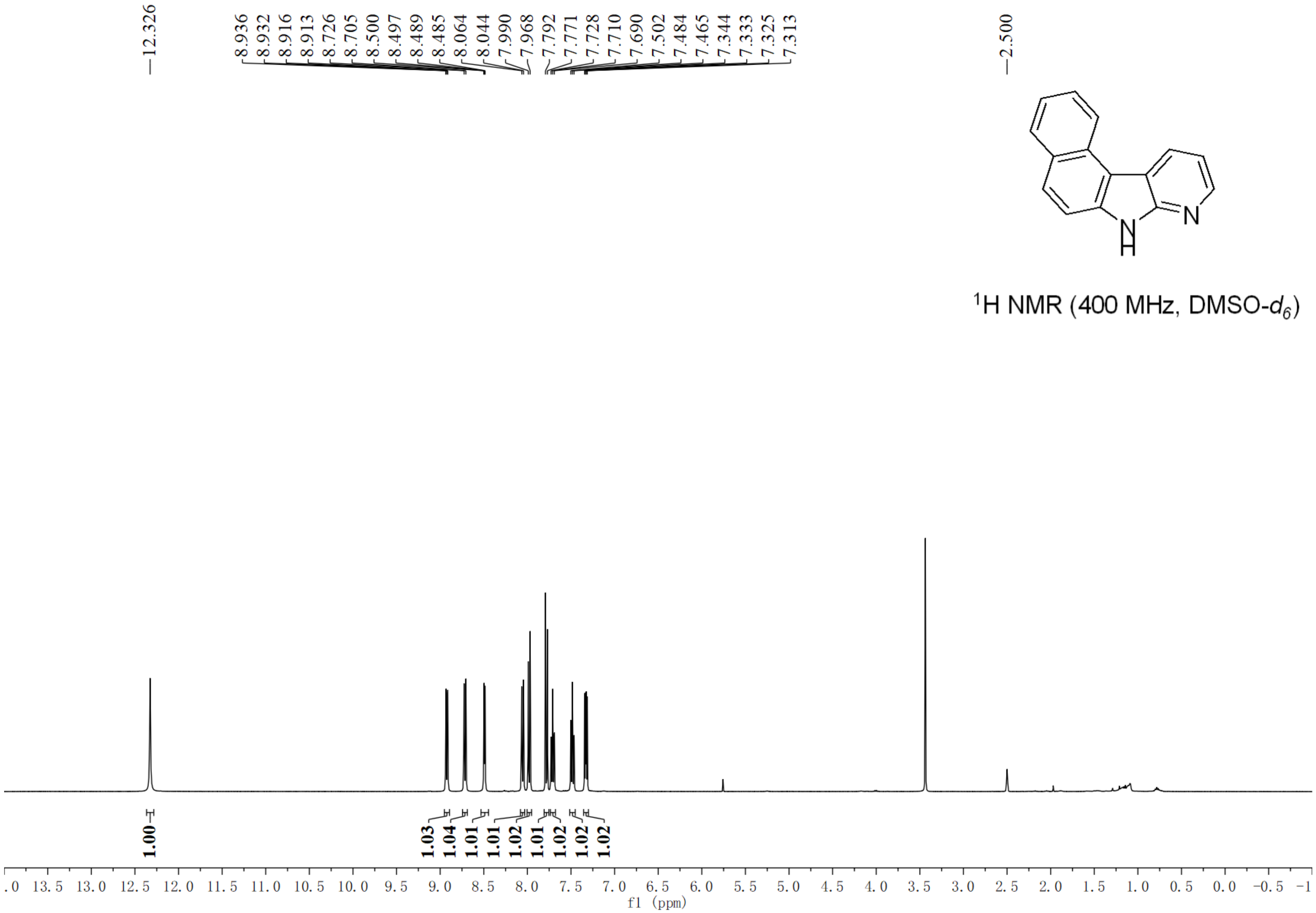




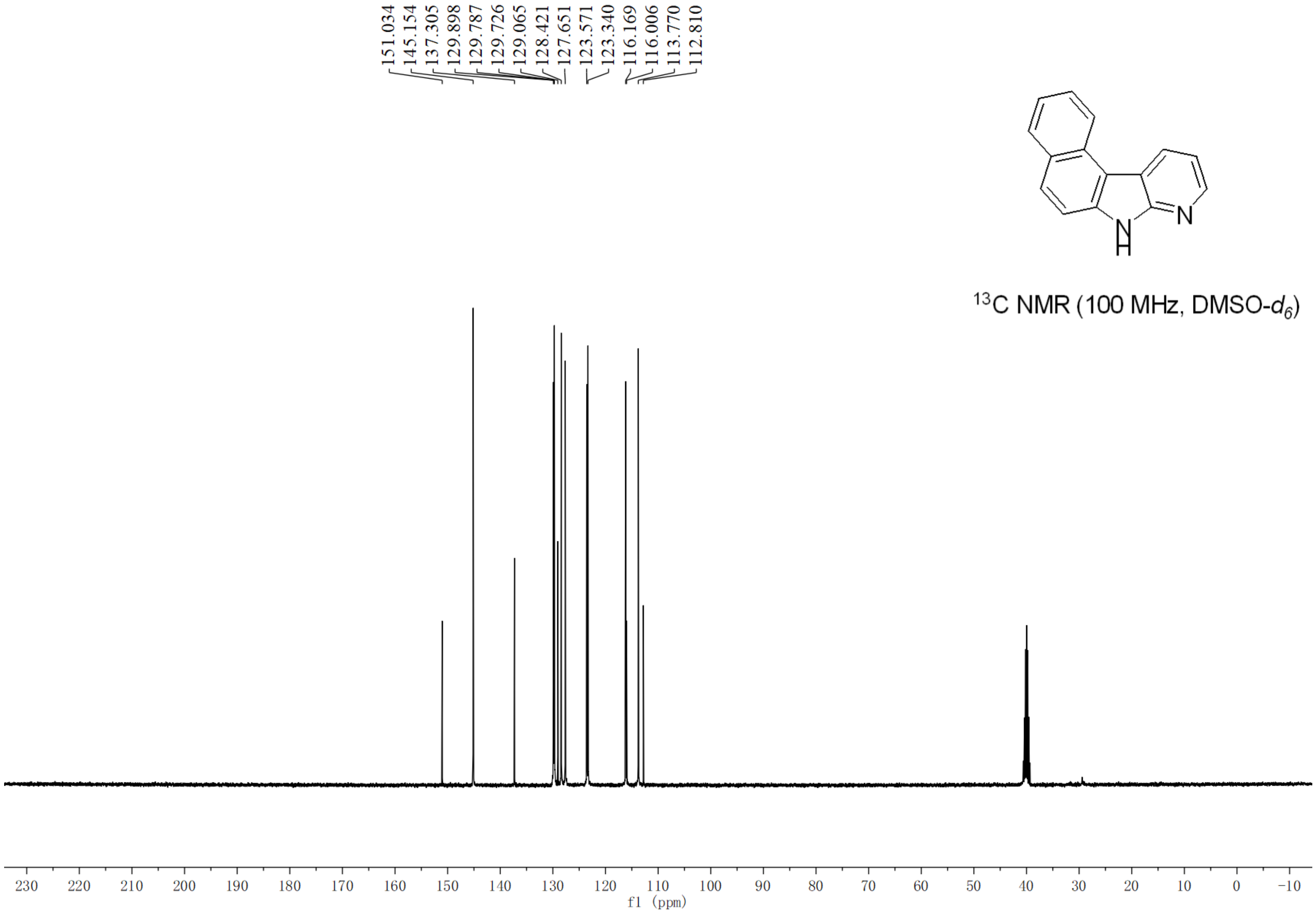
^{1}H NMR (400 MHz, DMSO-d_6)



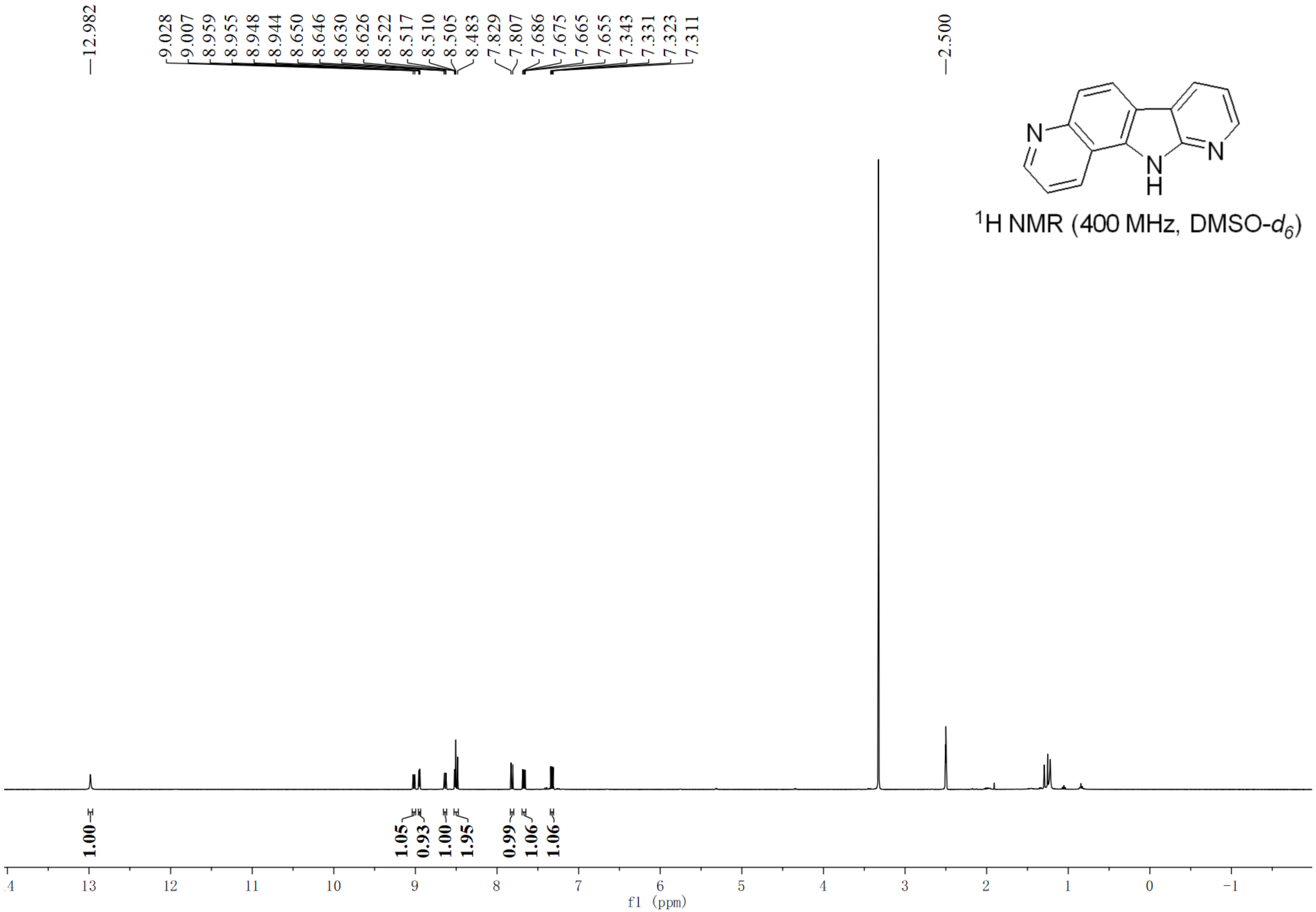
^{13}C NMR (100 MHz, DMSO-d_6)



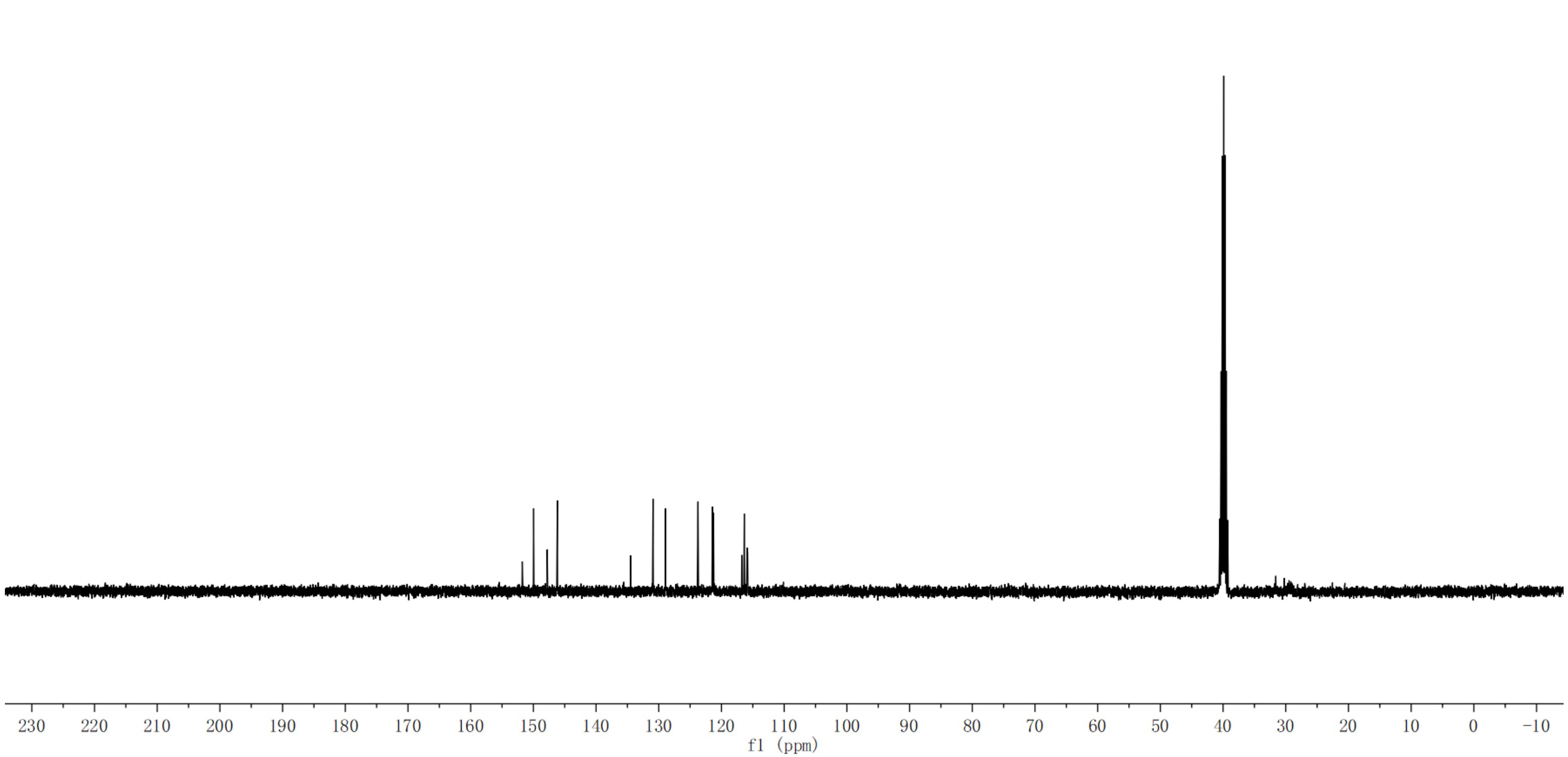
^{1}H NMR (400 MHz, DMSO-d_6)

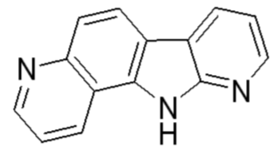


^{13}C NMR (100 MHz, DMSO-d_6)

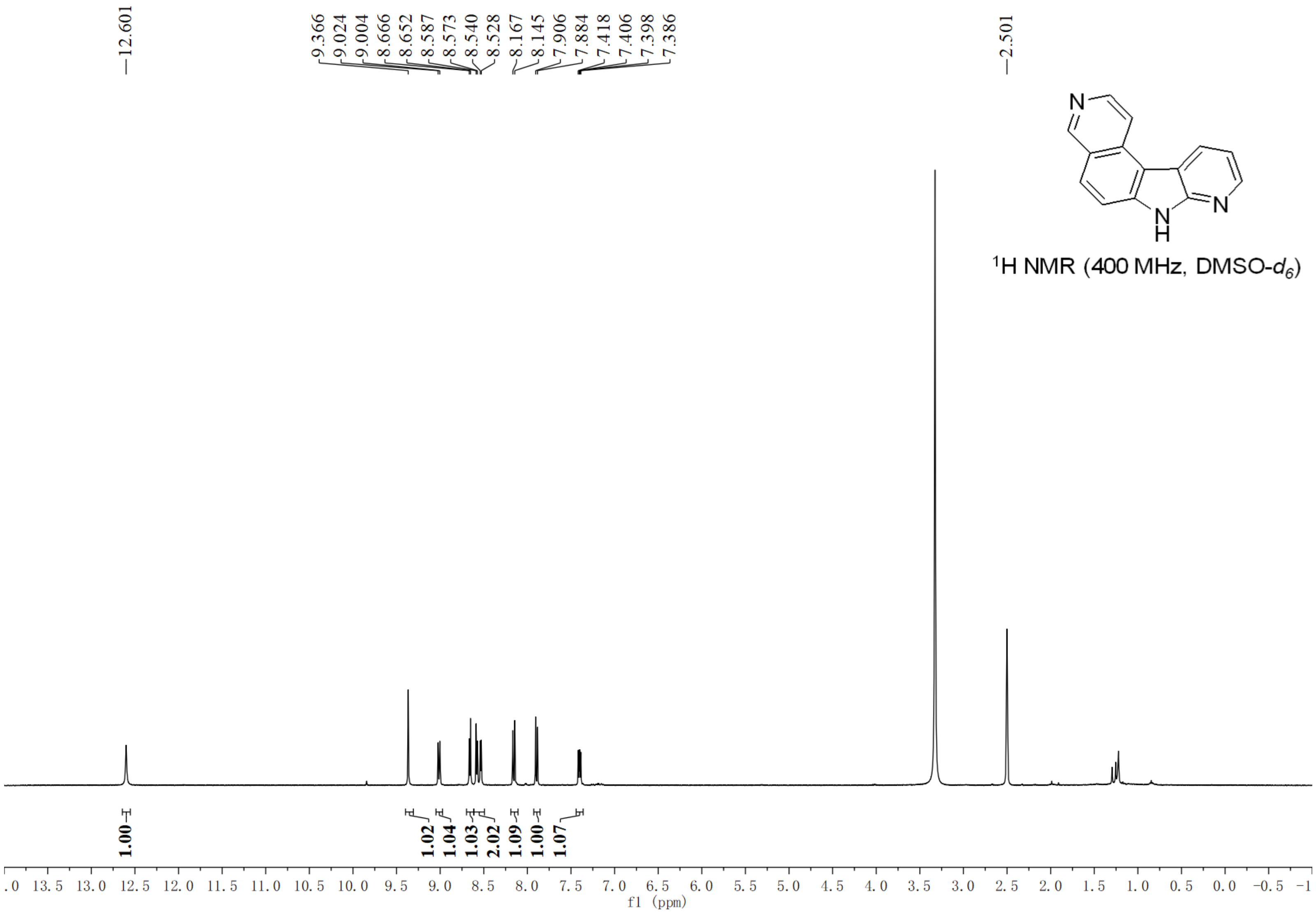


12.982
9.028
9.007
8.959
8.955
8.948
8.944
8.650
8.646
8.630
8.626
8.522
8.517
8.510
8.505
8.483
7.829
7.807
7.686
7.675
7.665
7.655
7.343
7.331
7.323
7.311
2.500
N
N
N
H
1H NMR (400 MHz, DMSO-d6)
1.00
1.05
0.93
1.00
1.95
0.99
1.06
1.06
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

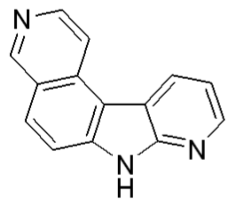




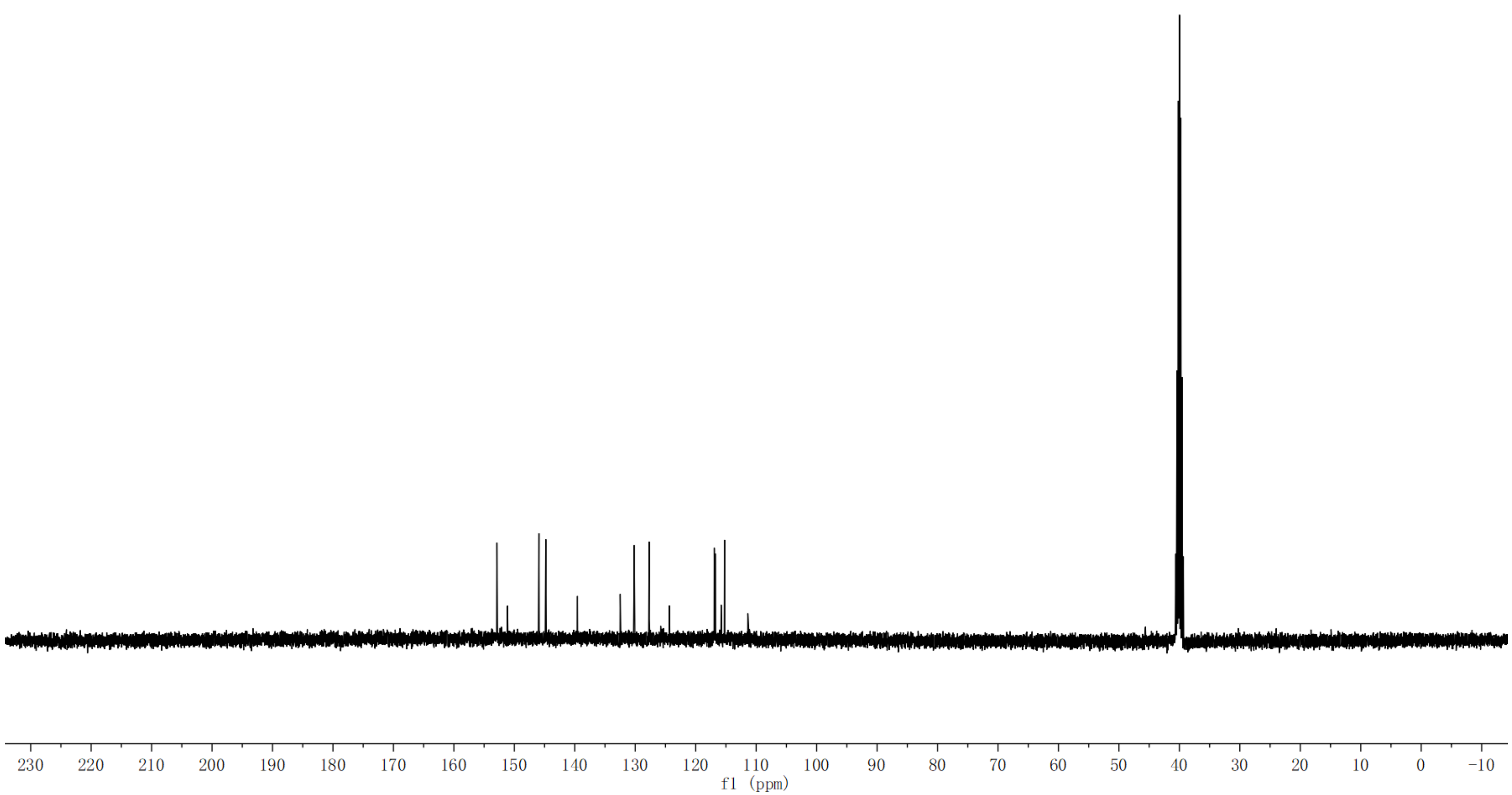
^{13}C NMR (100 MHz, DMSO-d_6)

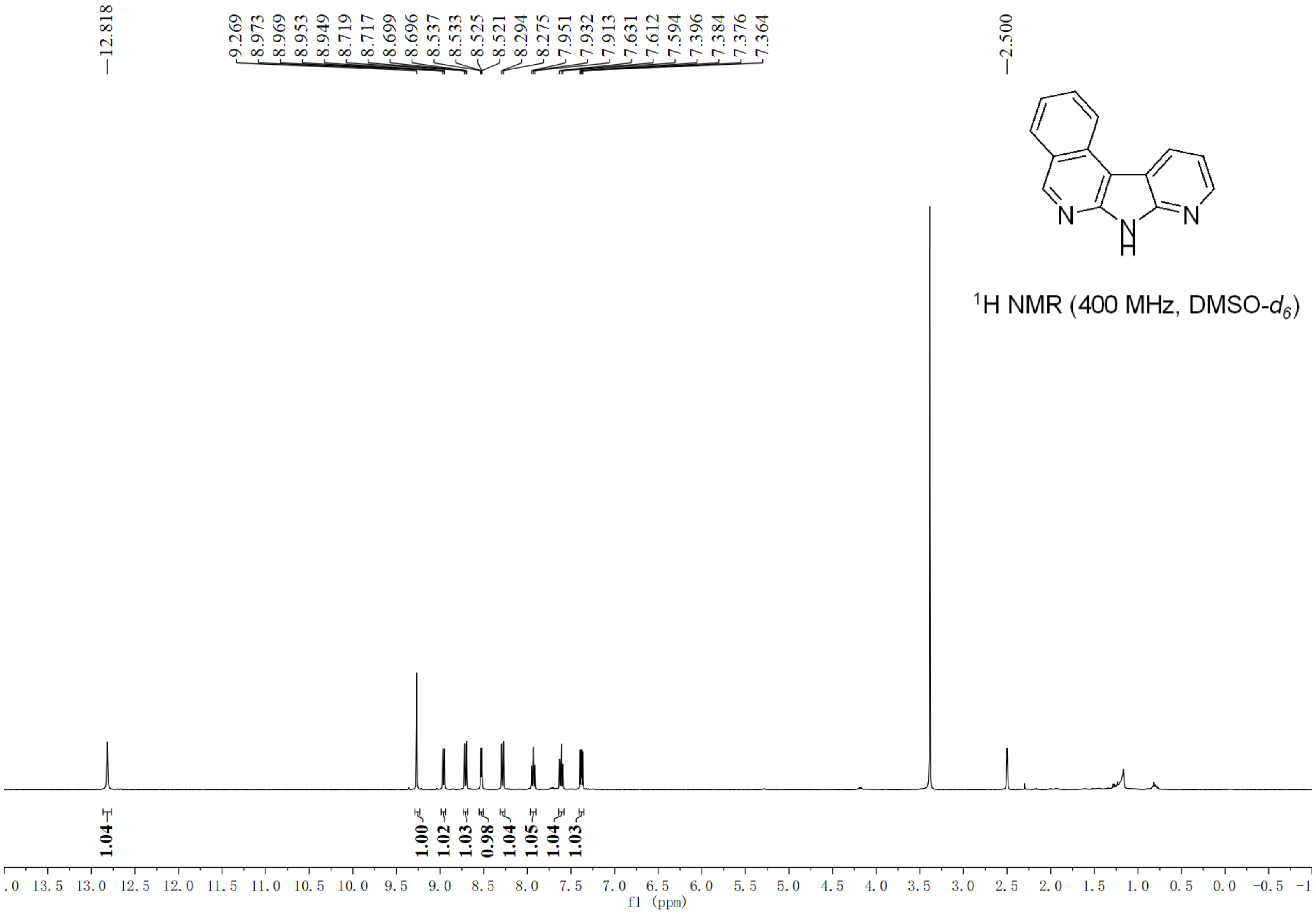


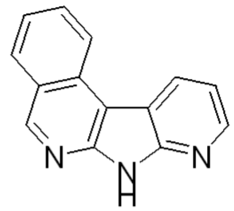
12.601
9.366
9.024
9.004
8.666
8.652
8.587
8.573
8.540
8.528
8.167
8.145
7.906
7.884
7.418
7.406
7.398
7.386
2.501
N
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
1.02
1.04
1.03
2.02
1.09
1.00
1.07
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)



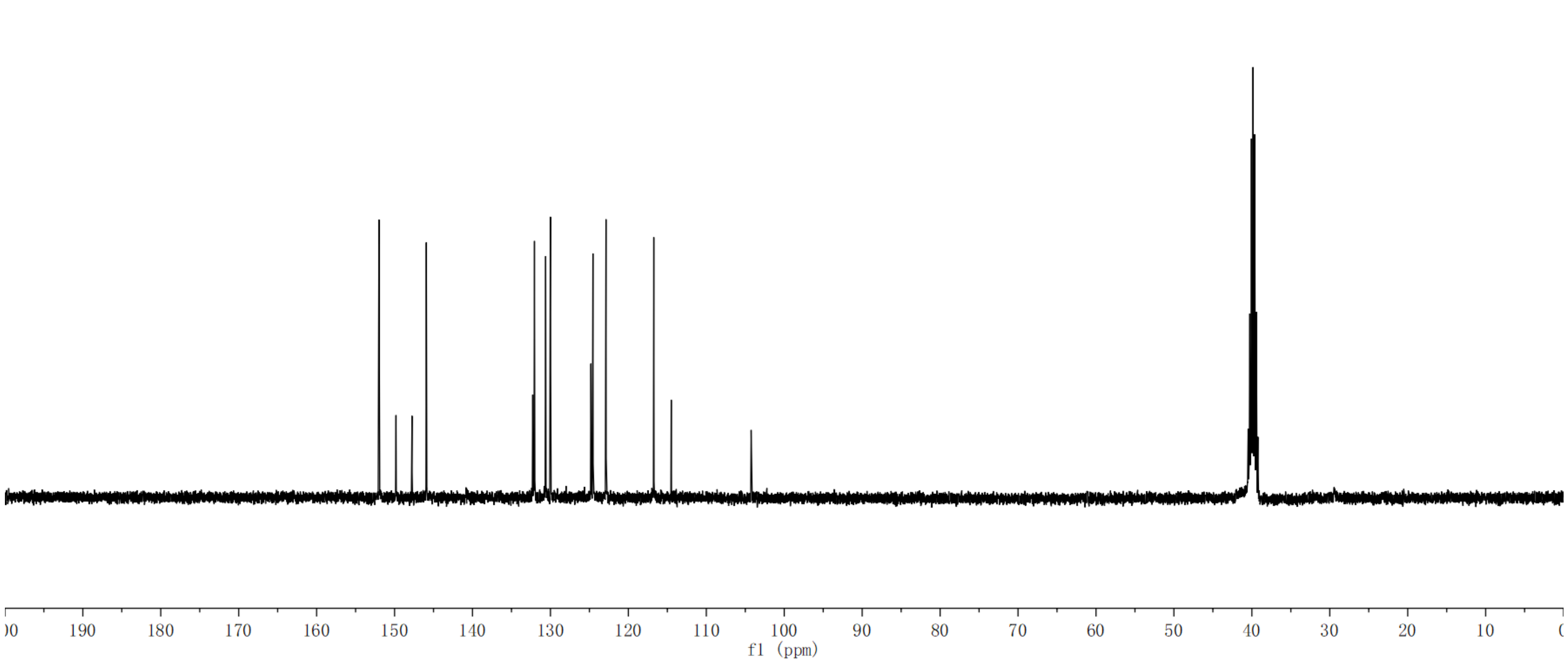
^{13}C NMR (100 MHz, DMSO-d_6)

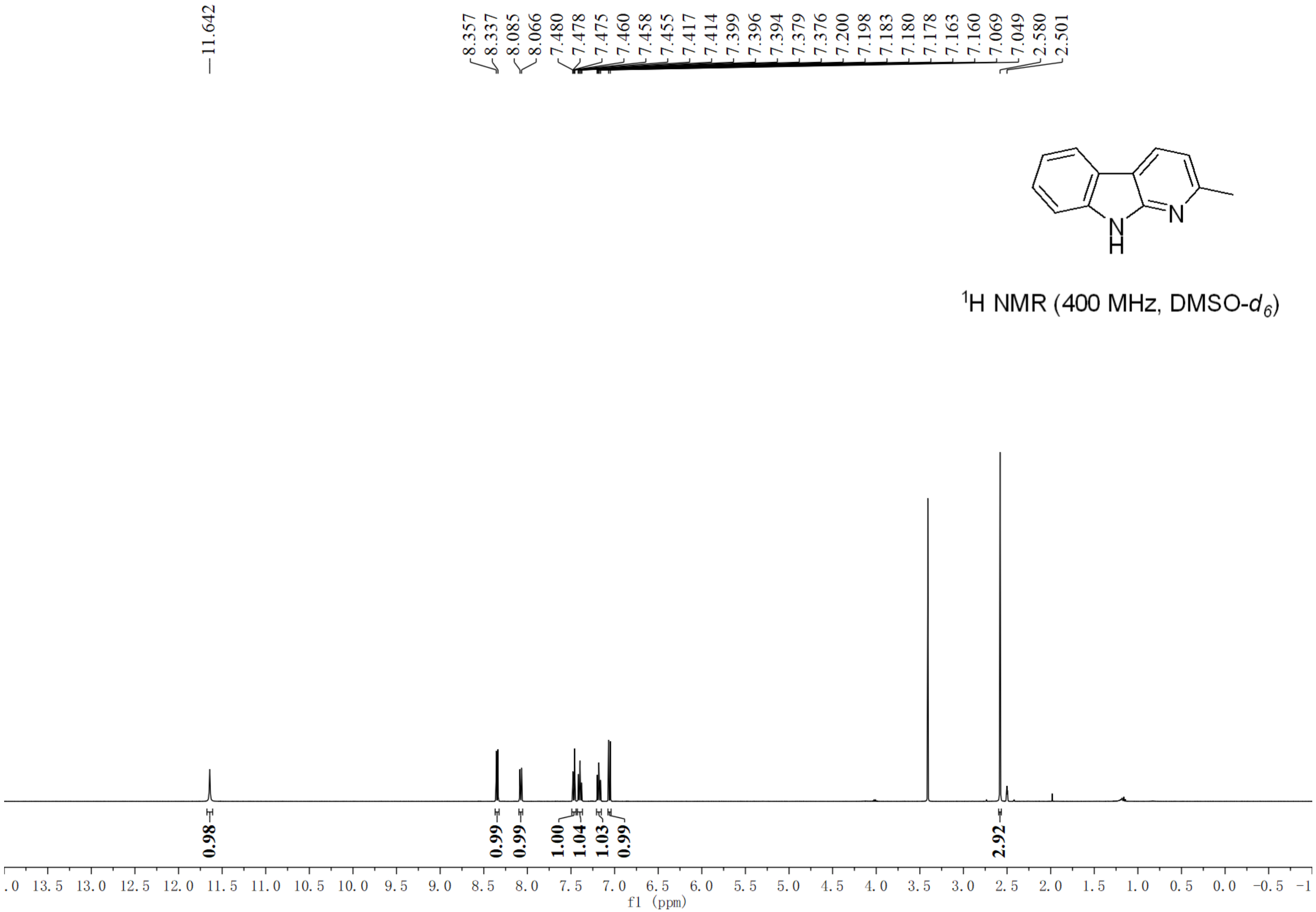


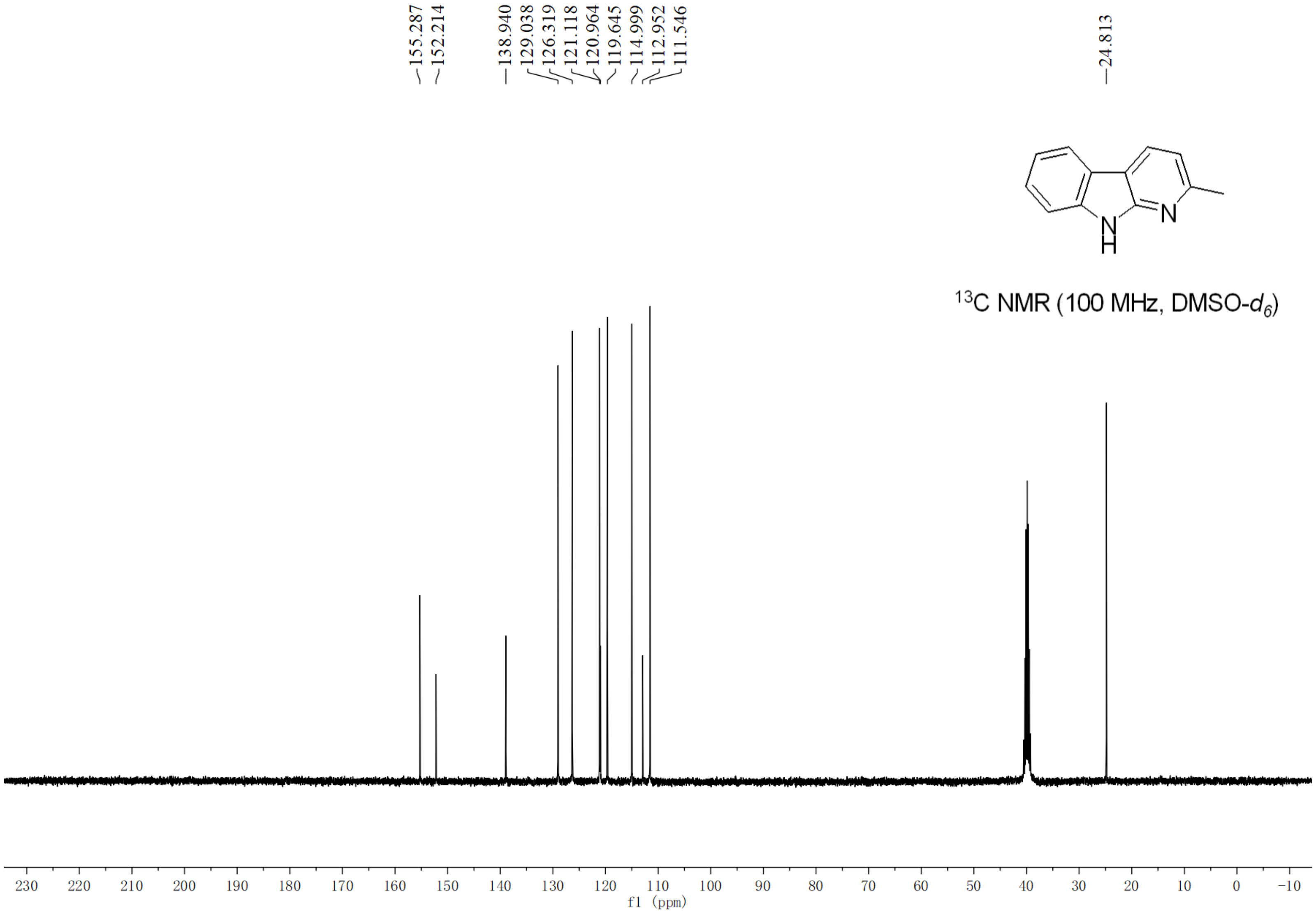

12.818
9.269
8.973
8.969
8.953
8.949
8.719
8.717
8.699
8.696
8.537
8.533
8.525
8.521
8.294
8.275
7.951
7.932
7.913
7.631
7.612
7.594
7.396
7.384
7.376
7.364
2.500
N
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.04
1.00
1.02
1.03
0.98
1.04
1.05
1.04
1.03
f1 (ppm)



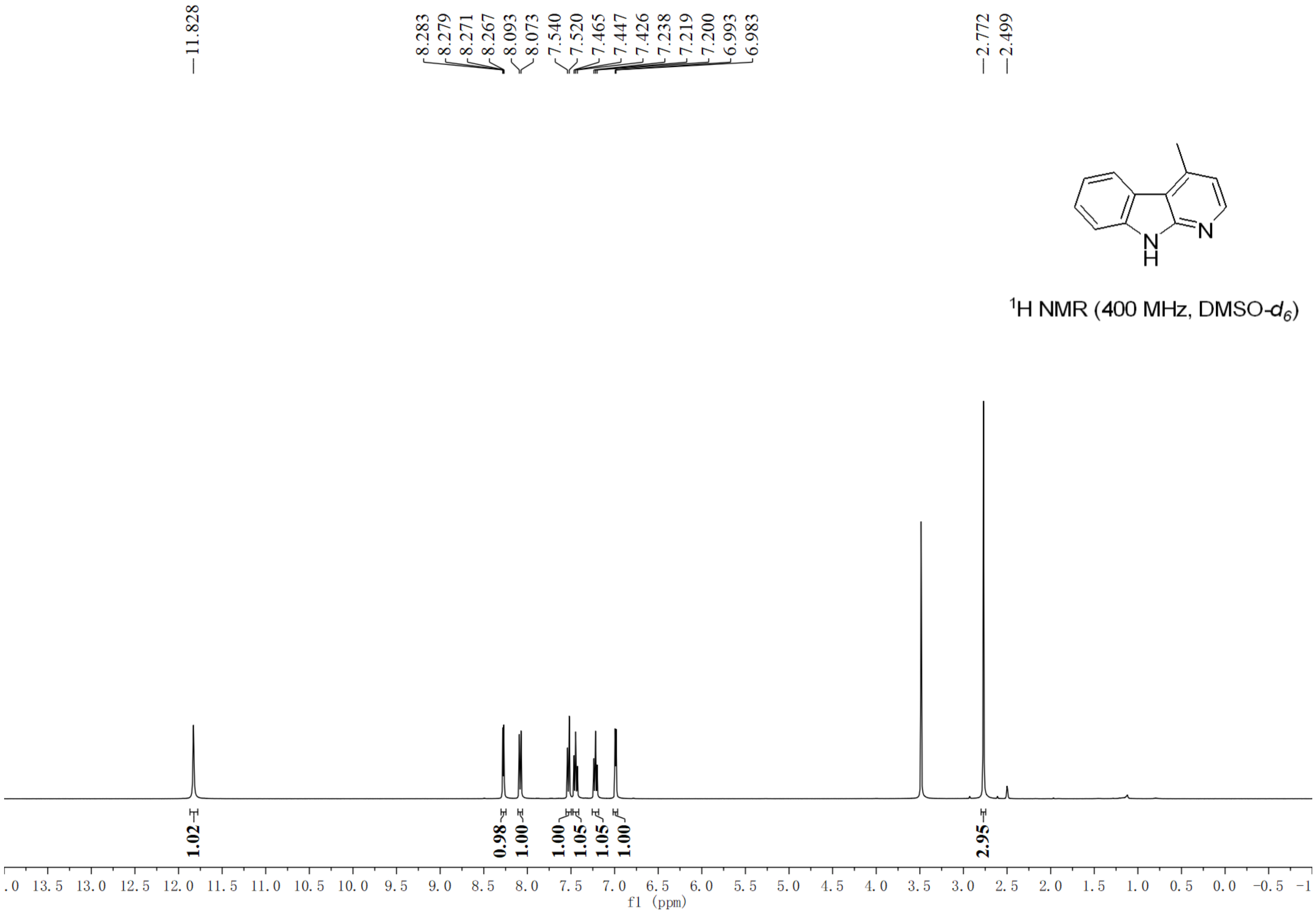
^{13}C NMR (100 MHz, DMSO-d_6)



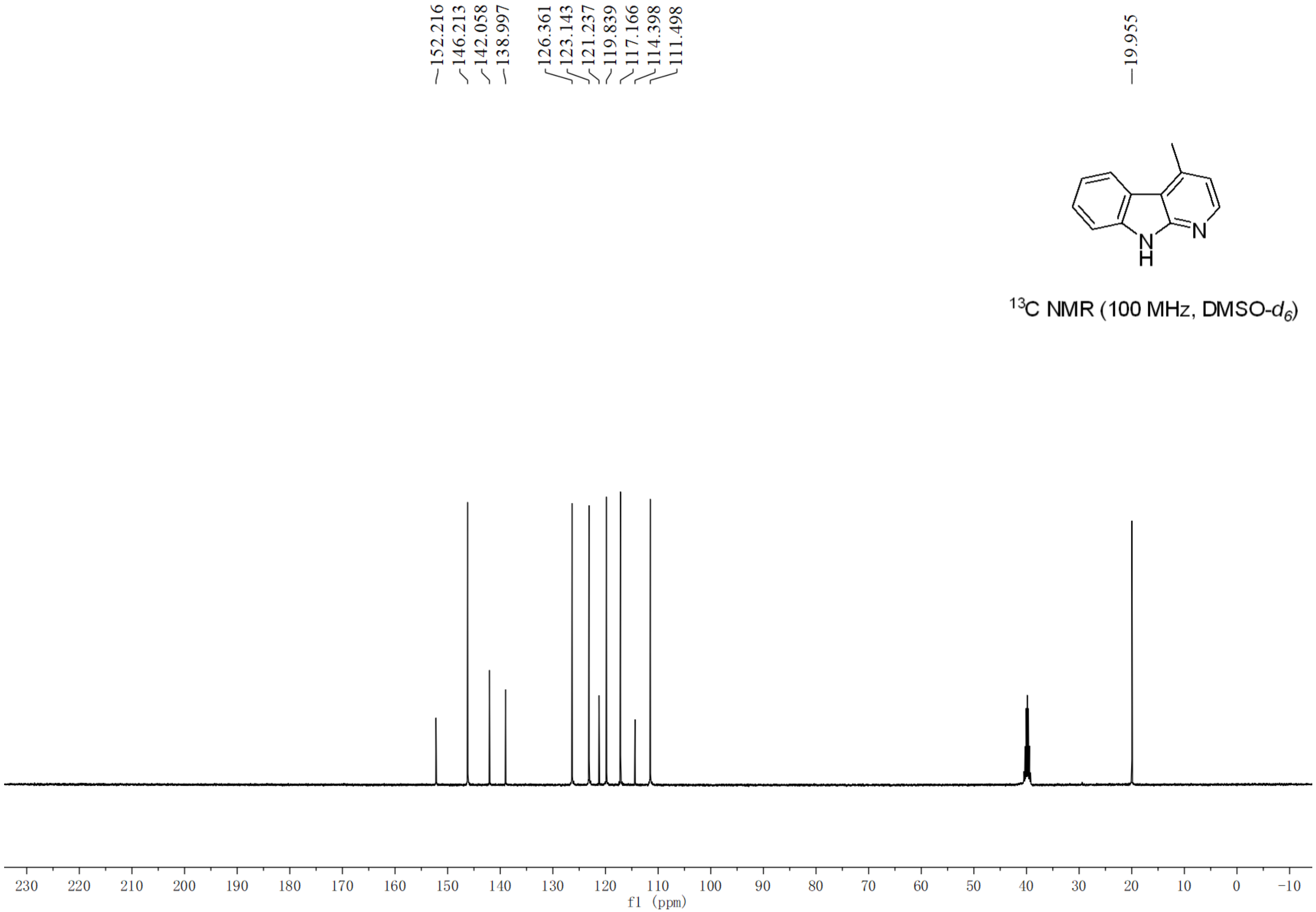

11.642
8.357
8.337
8.085
8.066
7.480
7.478
7.475
7.460
7.458
7.455
7.417
7.414
7.399
7.396
7.394
7.379
7.376
7.200
7.198
7.183
7.180
7.178
7.163
7.160
7.069
7.049
2.580
2.501
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
0.98
0.99
0.99
1.00
1.04
1.03
0.99
2.92
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)



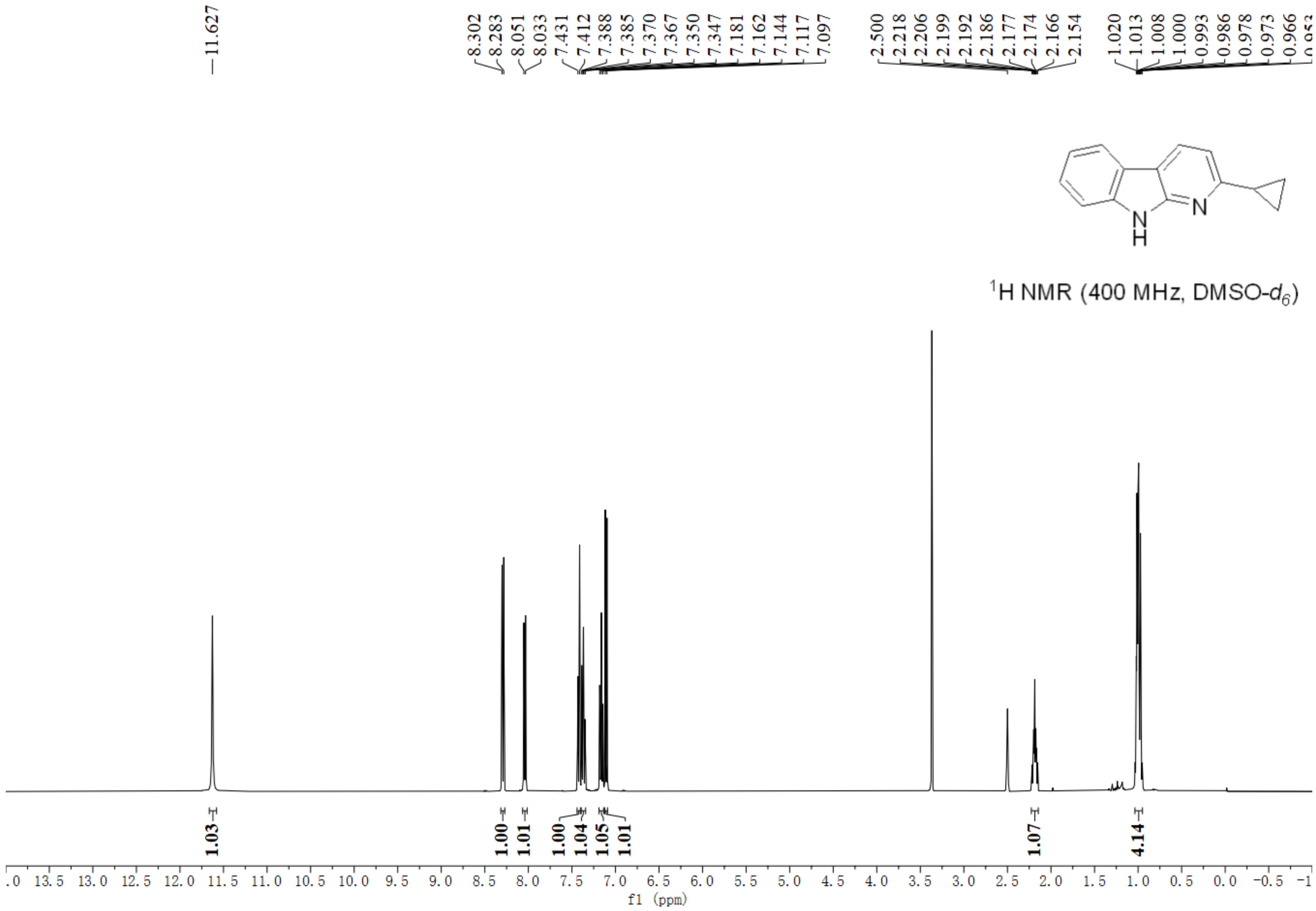
^{13}C NMR (100 MHz, DMSO-d_6)



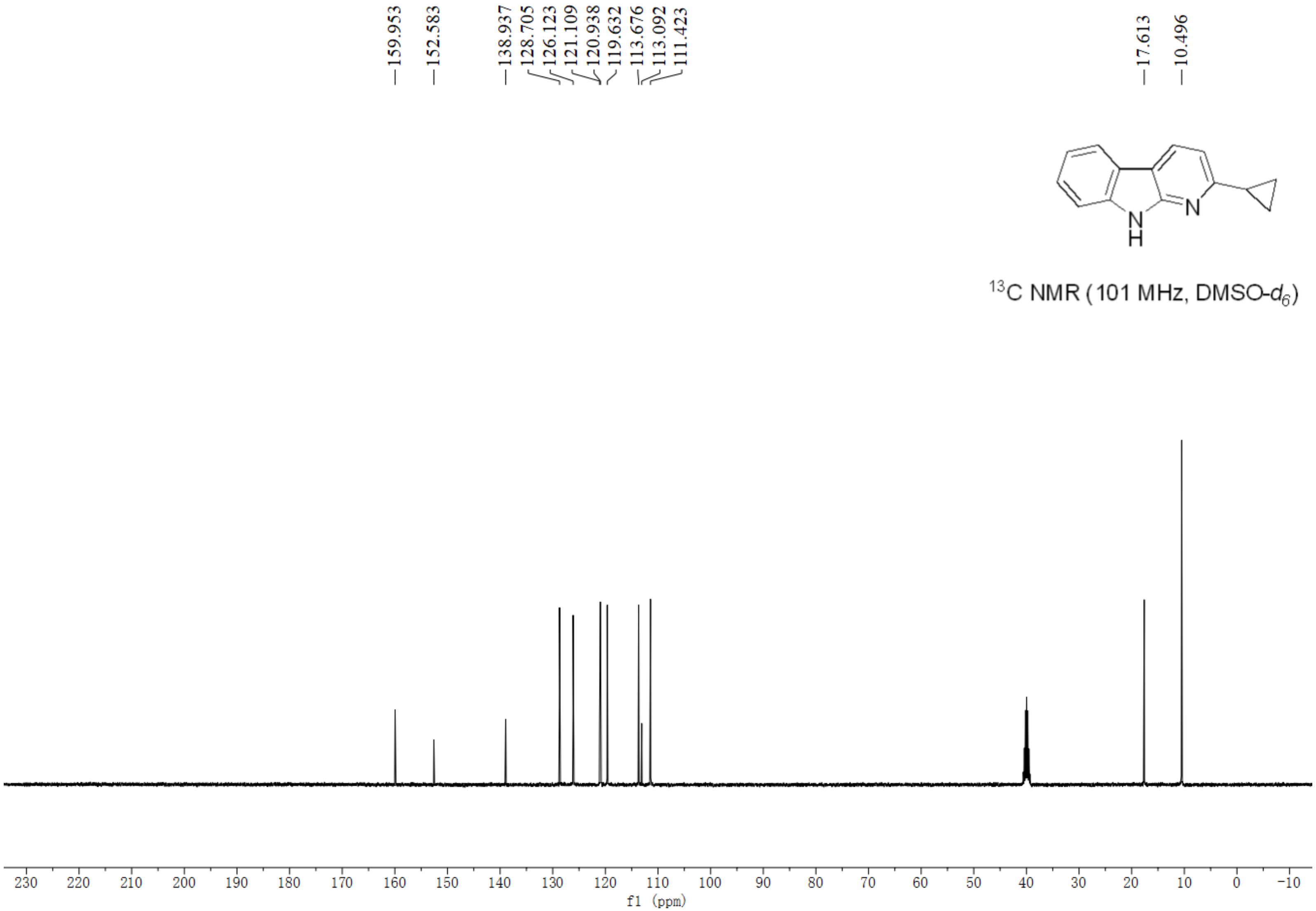
^{1}H NMR (400 MHz, DMSO-d_6)



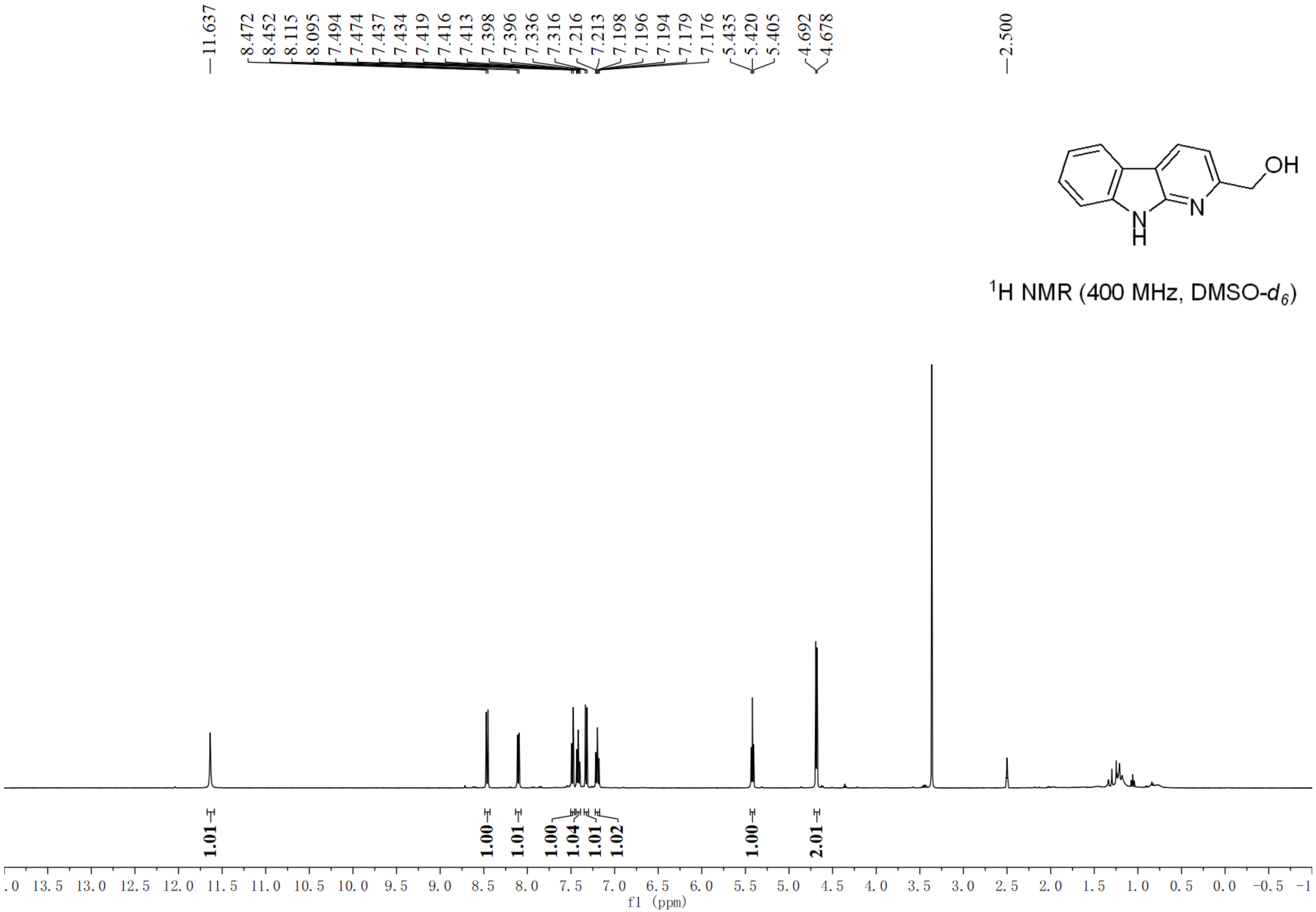
^{13}C NMR (100 MHz, DMSO-d_6)



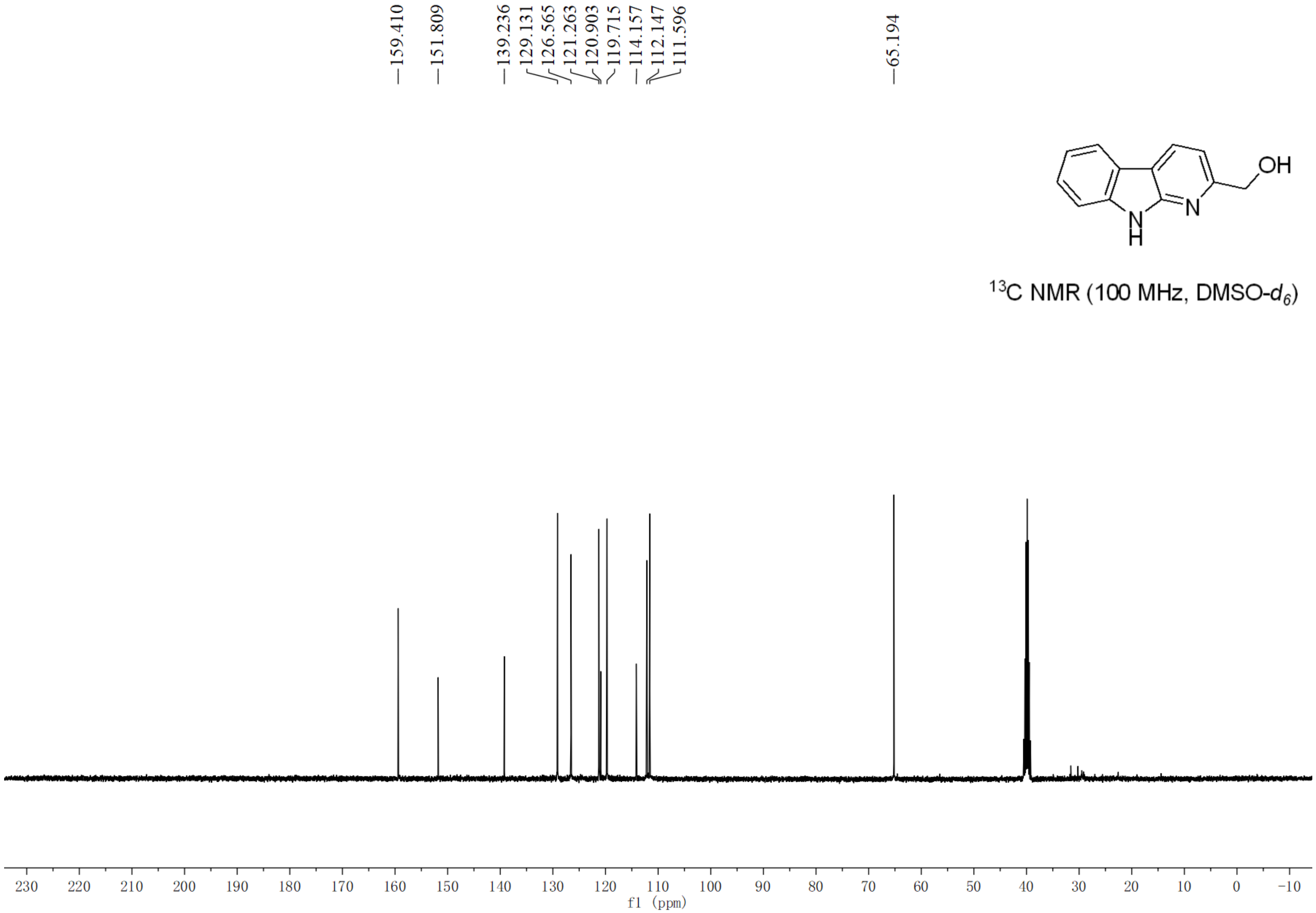
^1H NMR (400 MHz, DMSO-d_6)



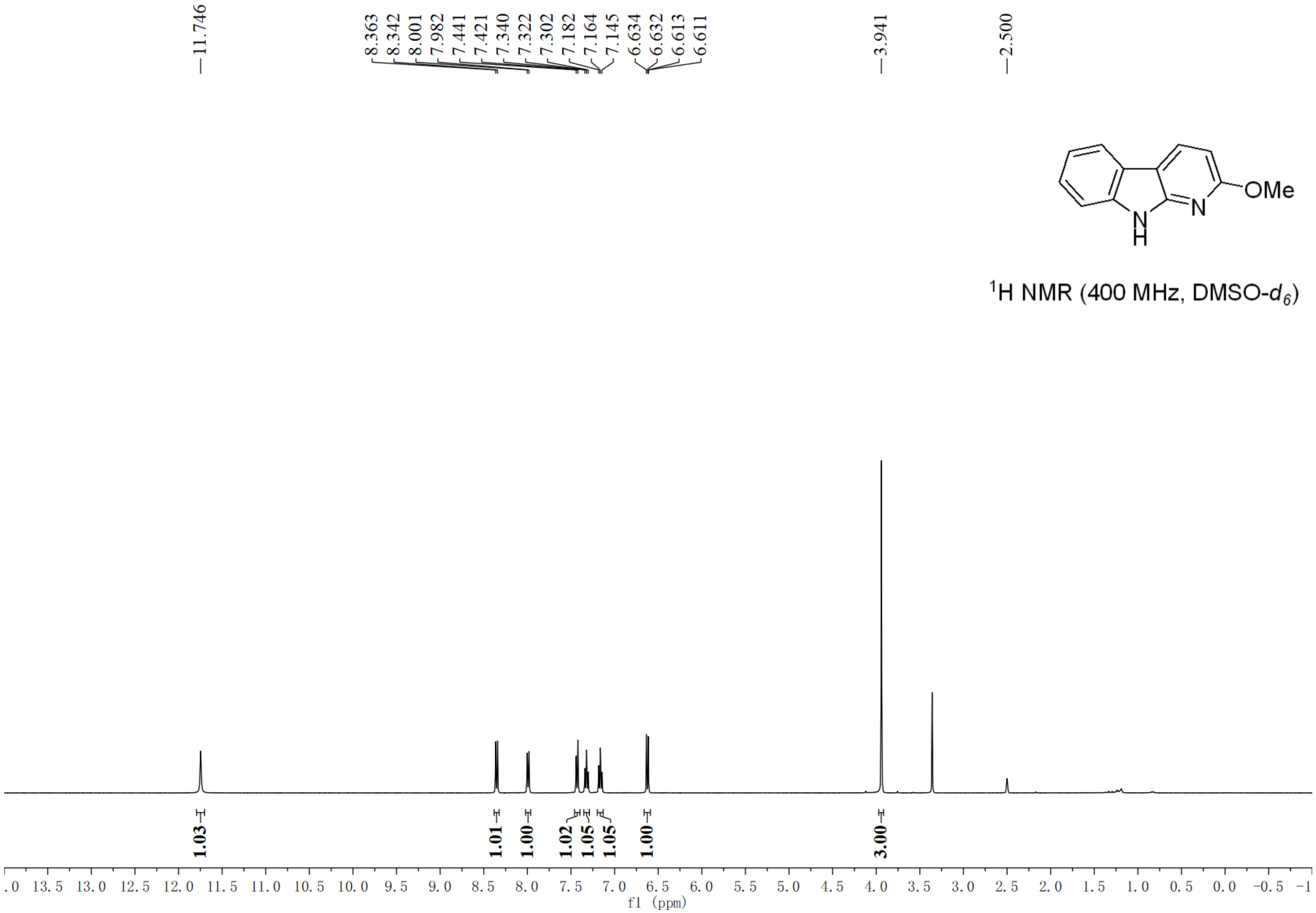
^{13}C NMR (101 MHz, DMSO-d_6)



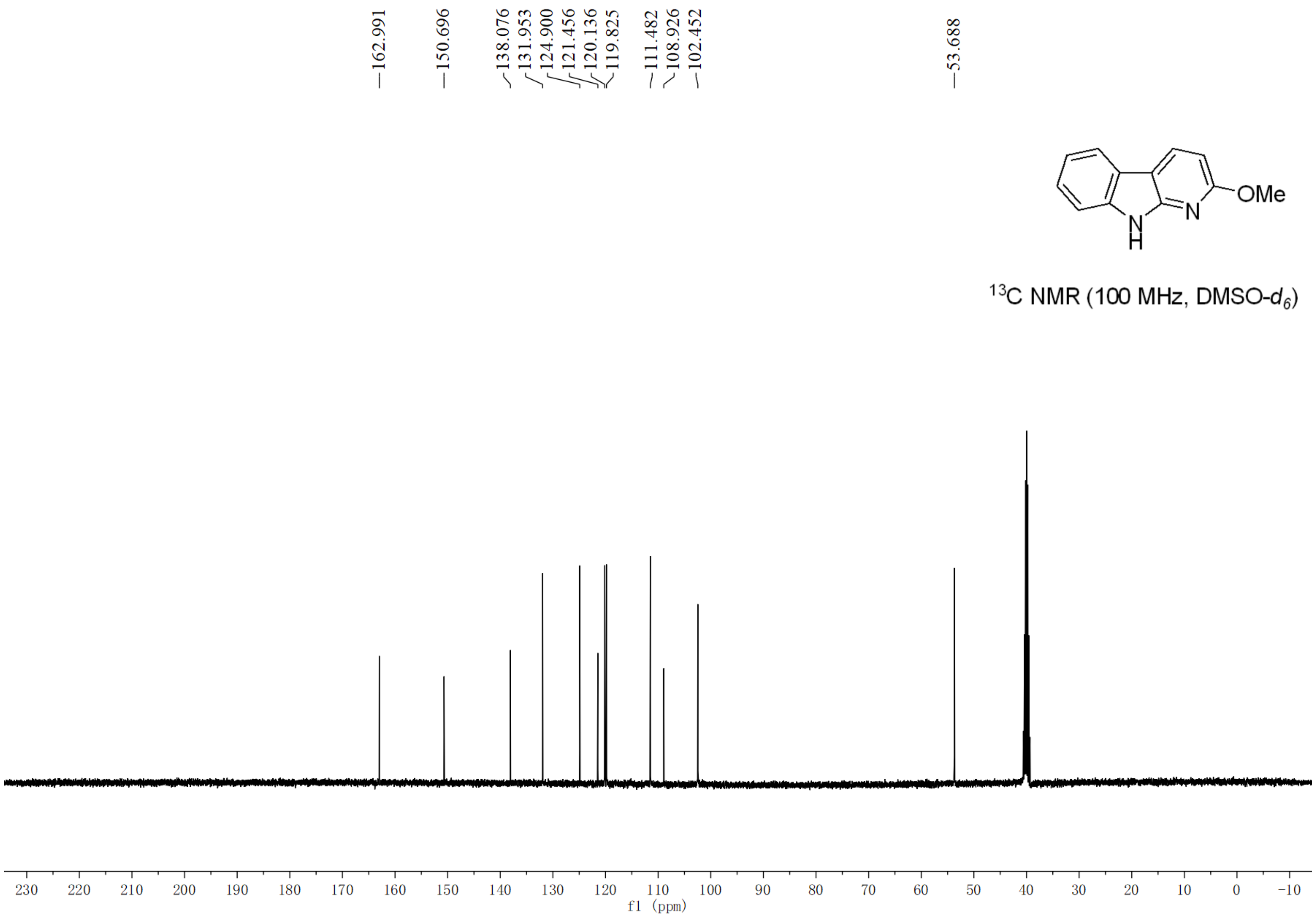
11.637
8.472
8.452
8.115
8.095
7.494
7.474
7.437
7.434
7.419
7.416
7.413
7.398
7.396
7.336
7.316
7.216
7.213
7.198
7.196
7.194
7.179
7.176
5.435
5.420
5.405
4.692
4.678
2.500
OH
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.01
1.00
1.01
1.00
1.04
1.01
1.02
1.00
2.01
f1 (ppm)

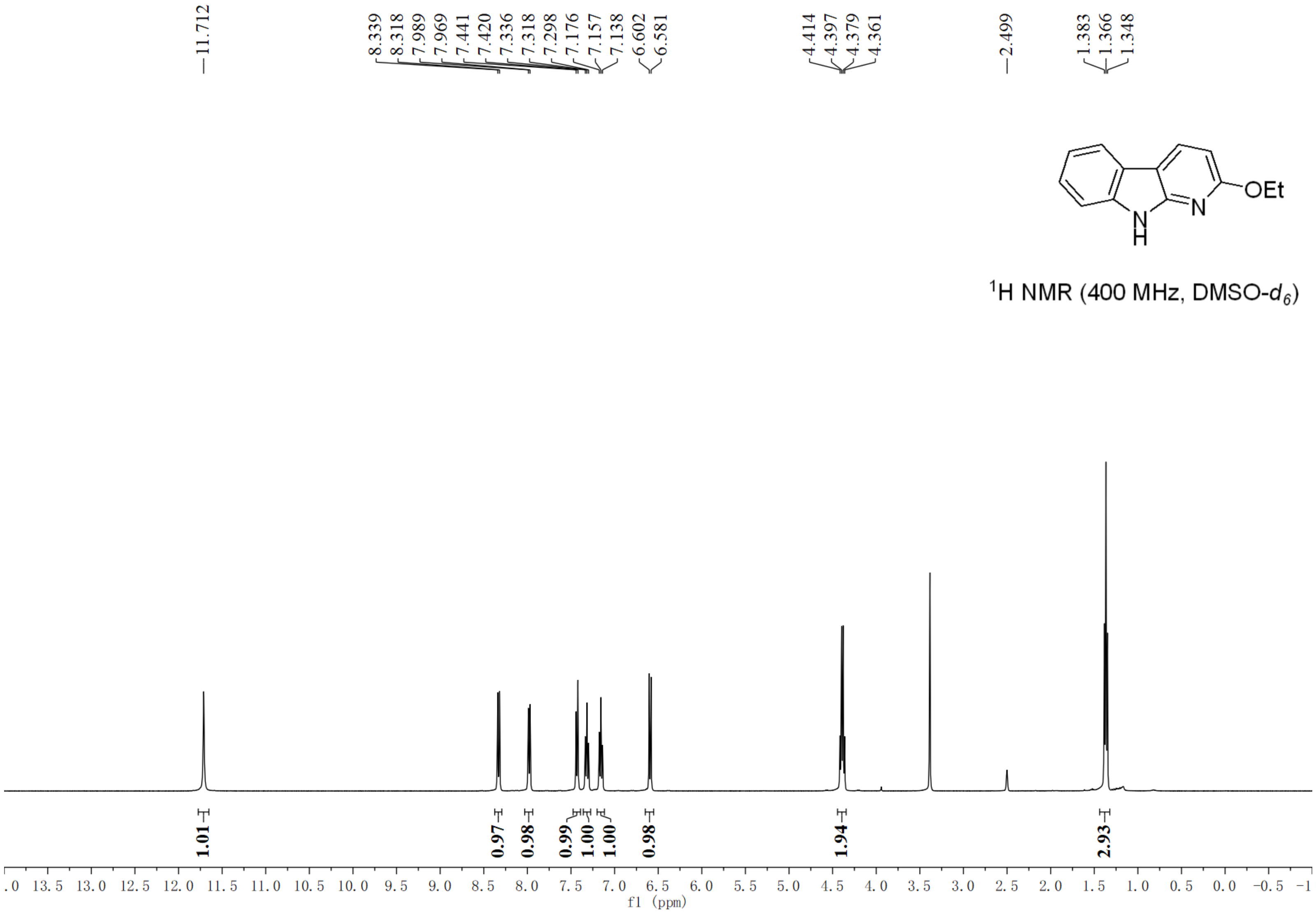


^{13}C NMR (100 MHz, DMSO-d_6)

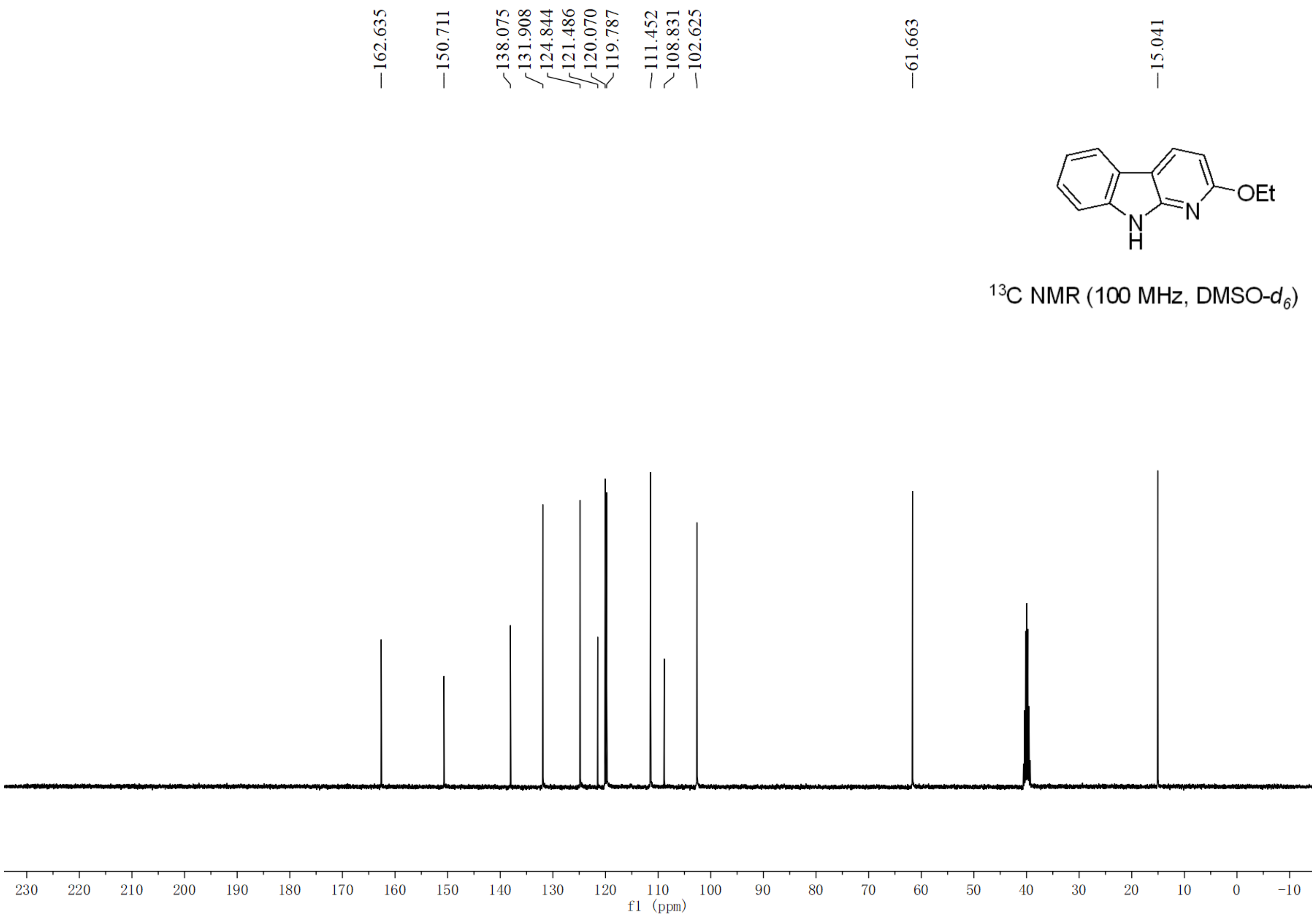


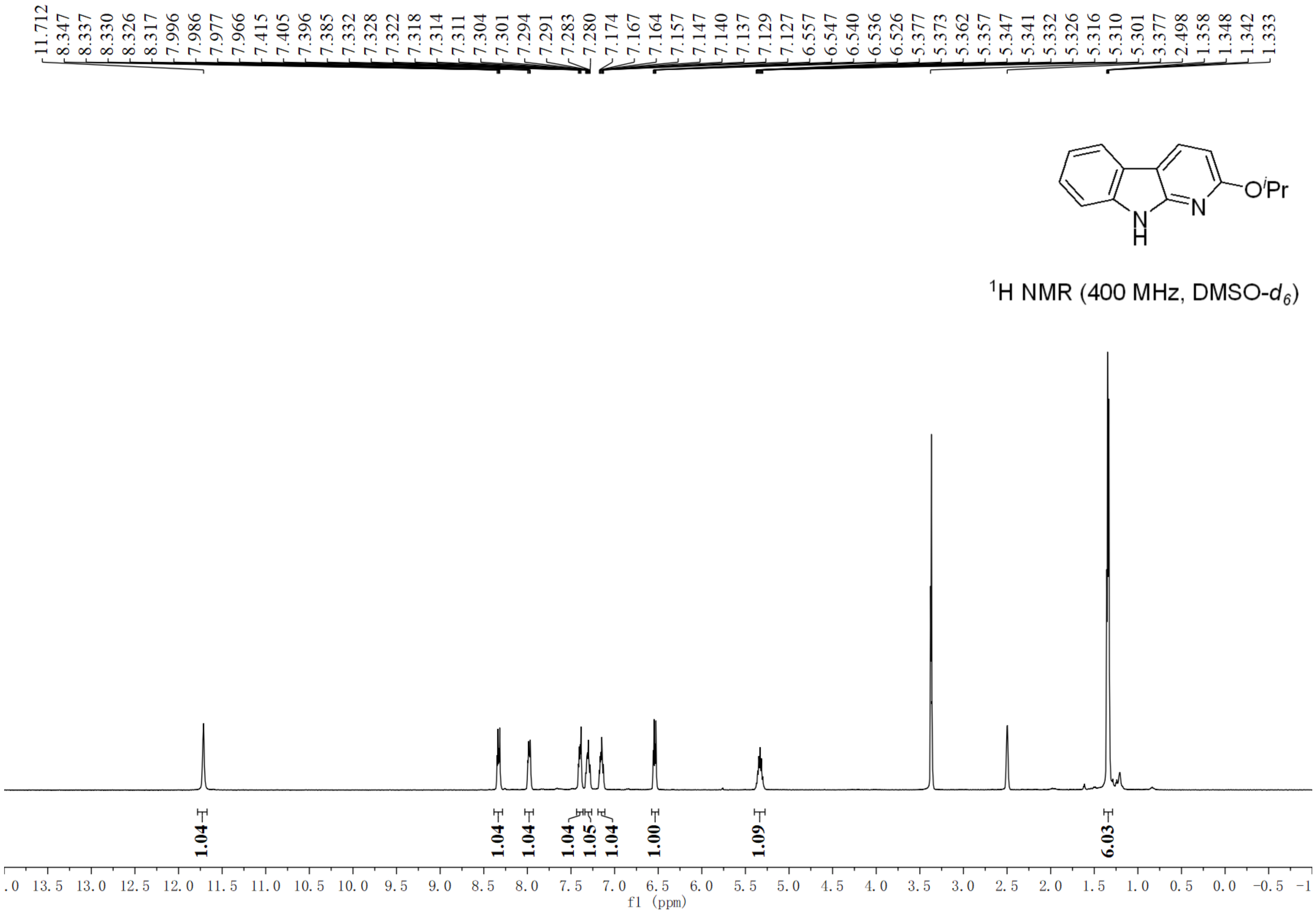
^1H NMR (400 MHz, DMSO-d_6)

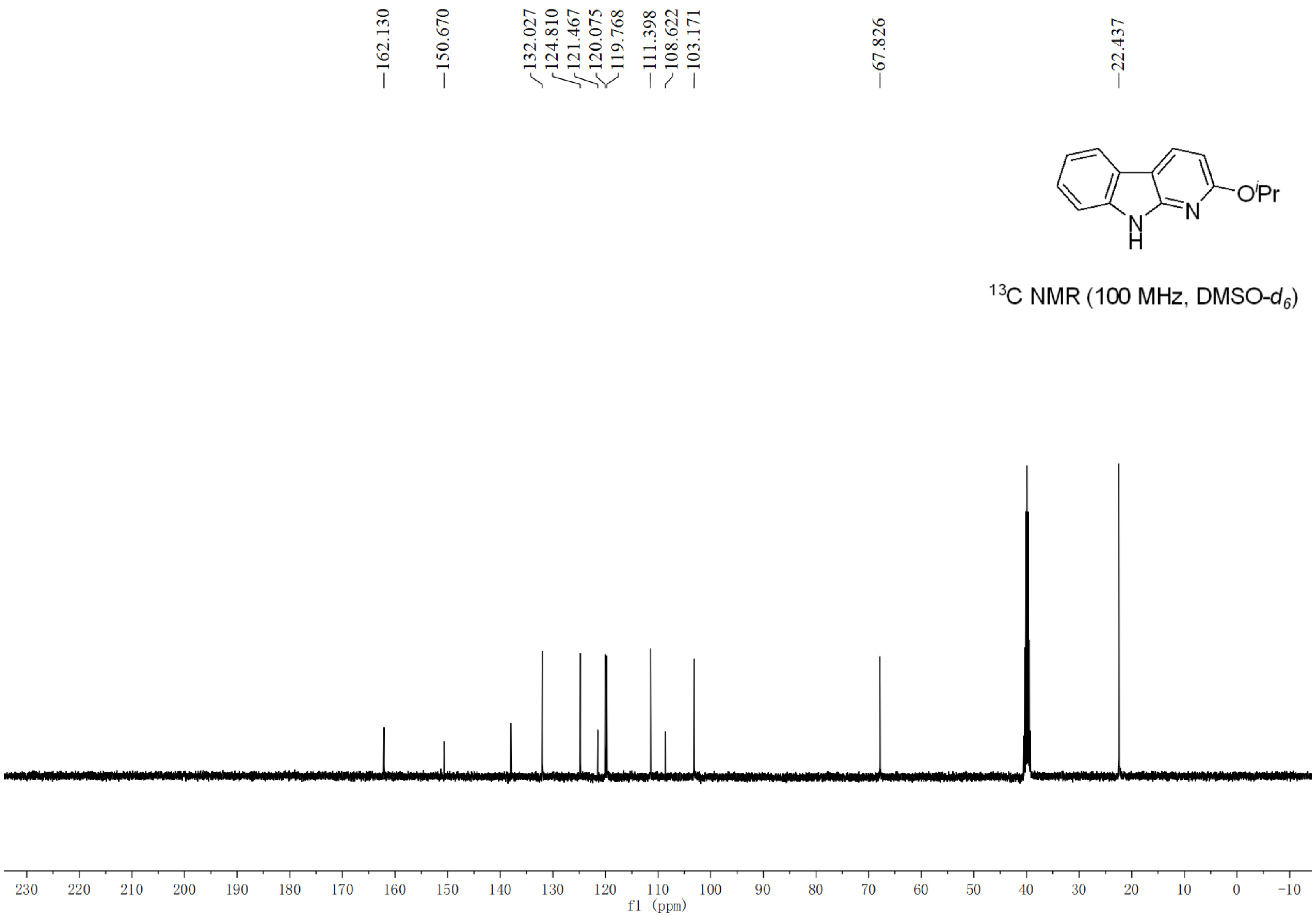

162.991
150.696
138.076
131.953
124.900
121.456
120.136
119.825
111.482
108.926
102.452
53.688
OMe
N
N
H
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

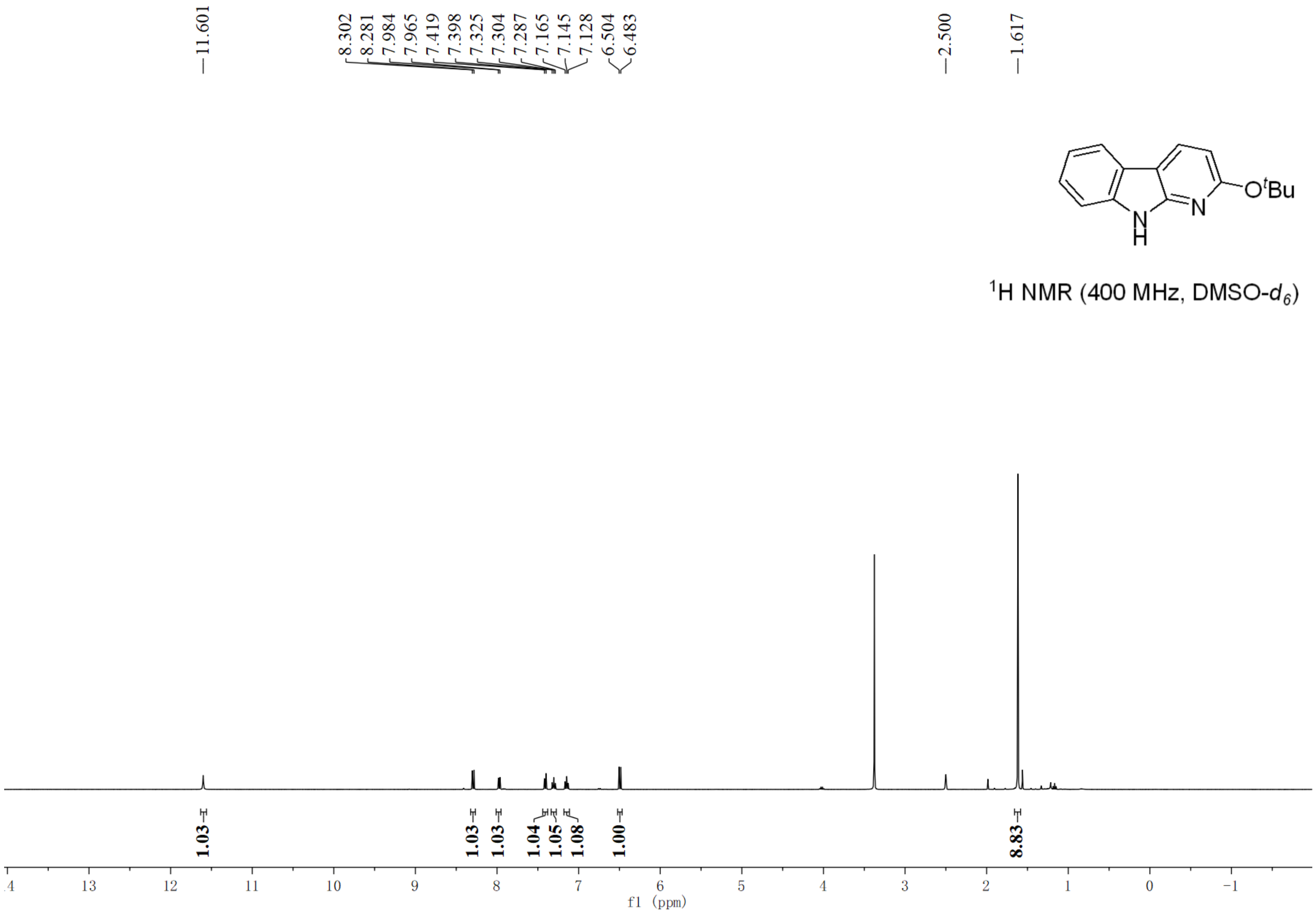


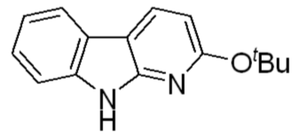
^{1}H NMR (400 MHz, DMSO-d_6)


162.635
150.711
138.075
131.908
124.844
121.486
120.070
119.787
111.452
108.831
102.625
61.663
15.041
OEt
N
N
H
^{13}C NMR (100 MHz, DMSO-d_6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

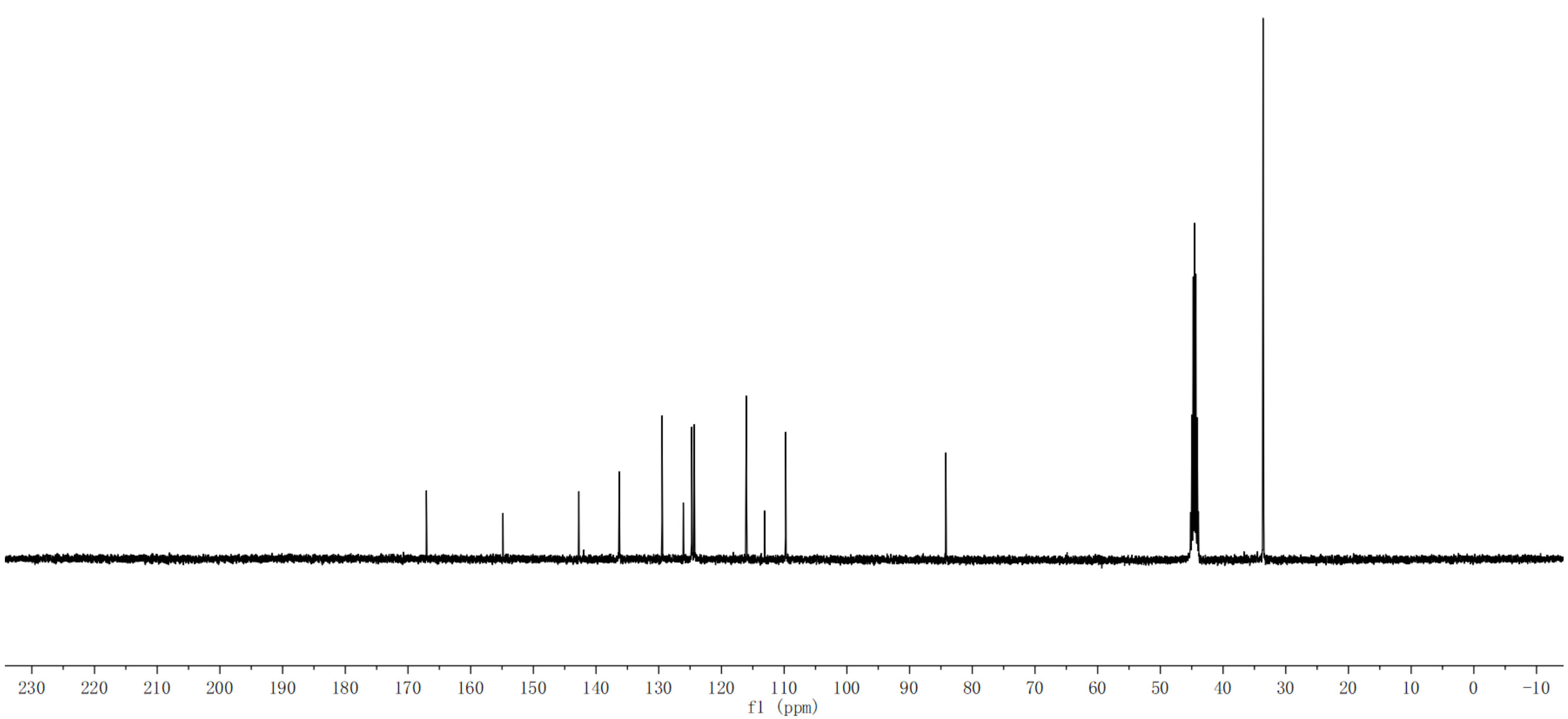

11.712
8.347
8.337
8.330
8.326
8.317
7.996
7.986
7.977
7.966
7.415
7.405
7.396
7.385
7.332
7.328
7.322
7.318
7.314
7.311
7.304
7.301
7.294
7.291
7.283
7.280
7.174
7.167
7.164
7.157
7.147
7.140
7.137
7.129
7.127
6.557
6.547
6.540
6.536
6.526
5.377
5.373
5.362
5.357
5.347
5.341
5.332
5.326
5.316
5.310
5.301
3.377
2.498
1.358
1.348
1.342
1.333
N
H
N
O^{i}Pr
^{1}H NMR (400 MHz, DMSO-d_6)
1.04
1.04
1.04
1.04
1.05
1.04
1.00
1.09
6.03
f1 (ppm)

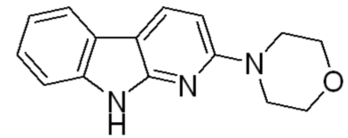

162.130
150.670
132.027
124.810
121.467
120.075
119.768
111.398
108.622
103.171
67.826
22.437
N
H
N
O^{i}Pr
^{13}C NMR (100 MHz, DMSO-d_6)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

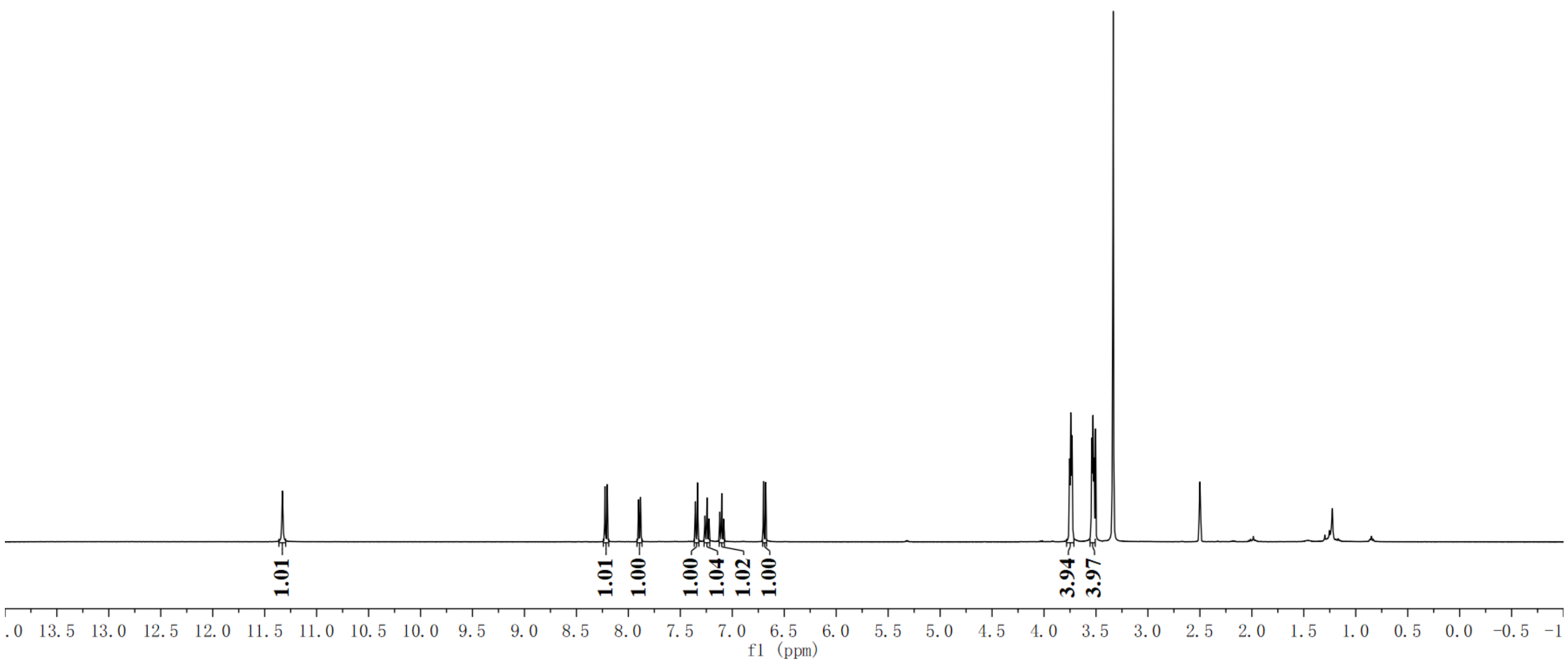

11.601
8.302
8.281
7.984
7.965
7.419
7.398
7.325
7.304
7.287
7.165
7.145
7.128
6.504
6.483
2.500
1.617
O^{t}Bu
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.03
1.03
1.03
1.04
1.05
1.08
1.00
8.83
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)



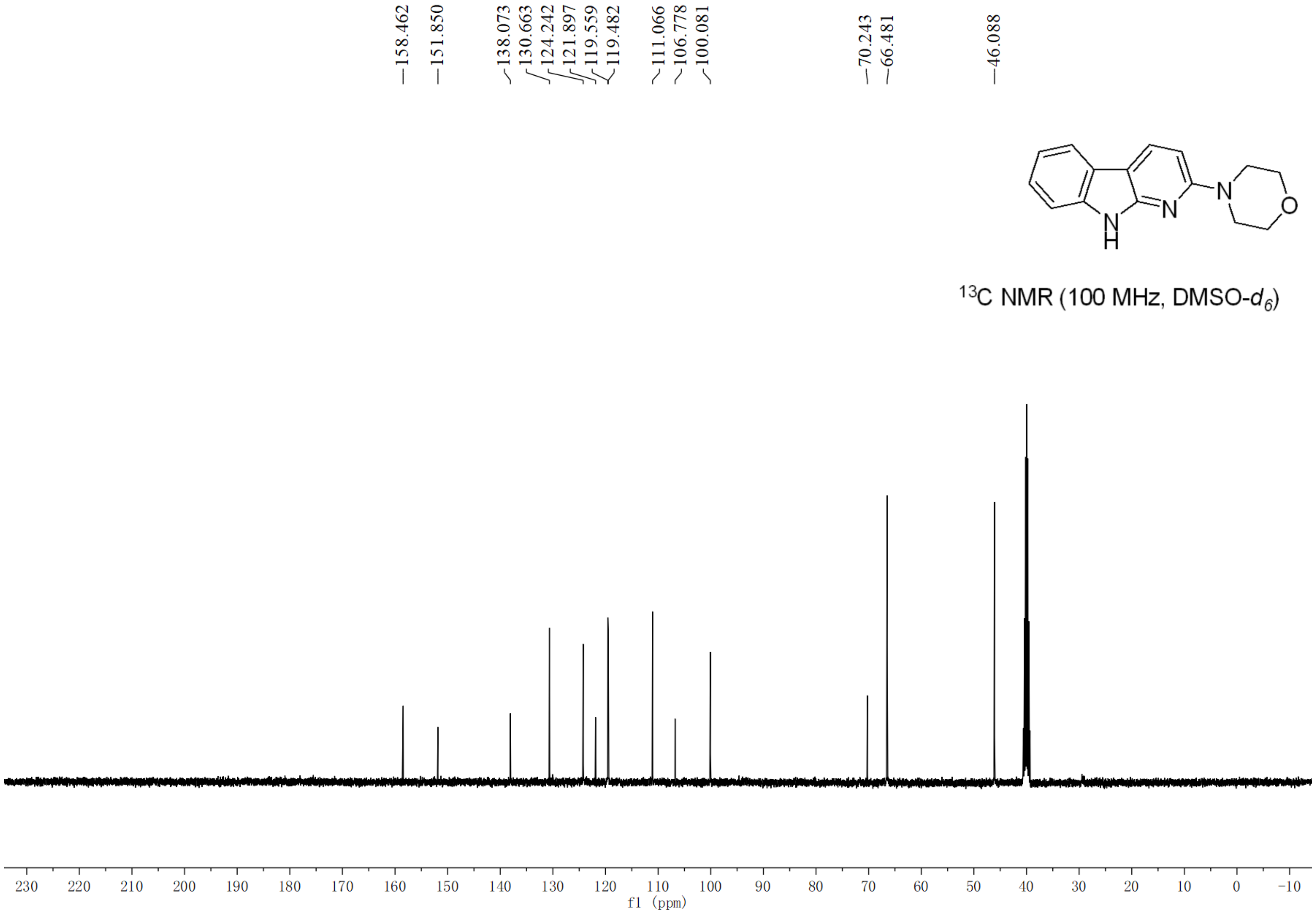
^{13}C NMR (100 MHz, DMSO-d_6)



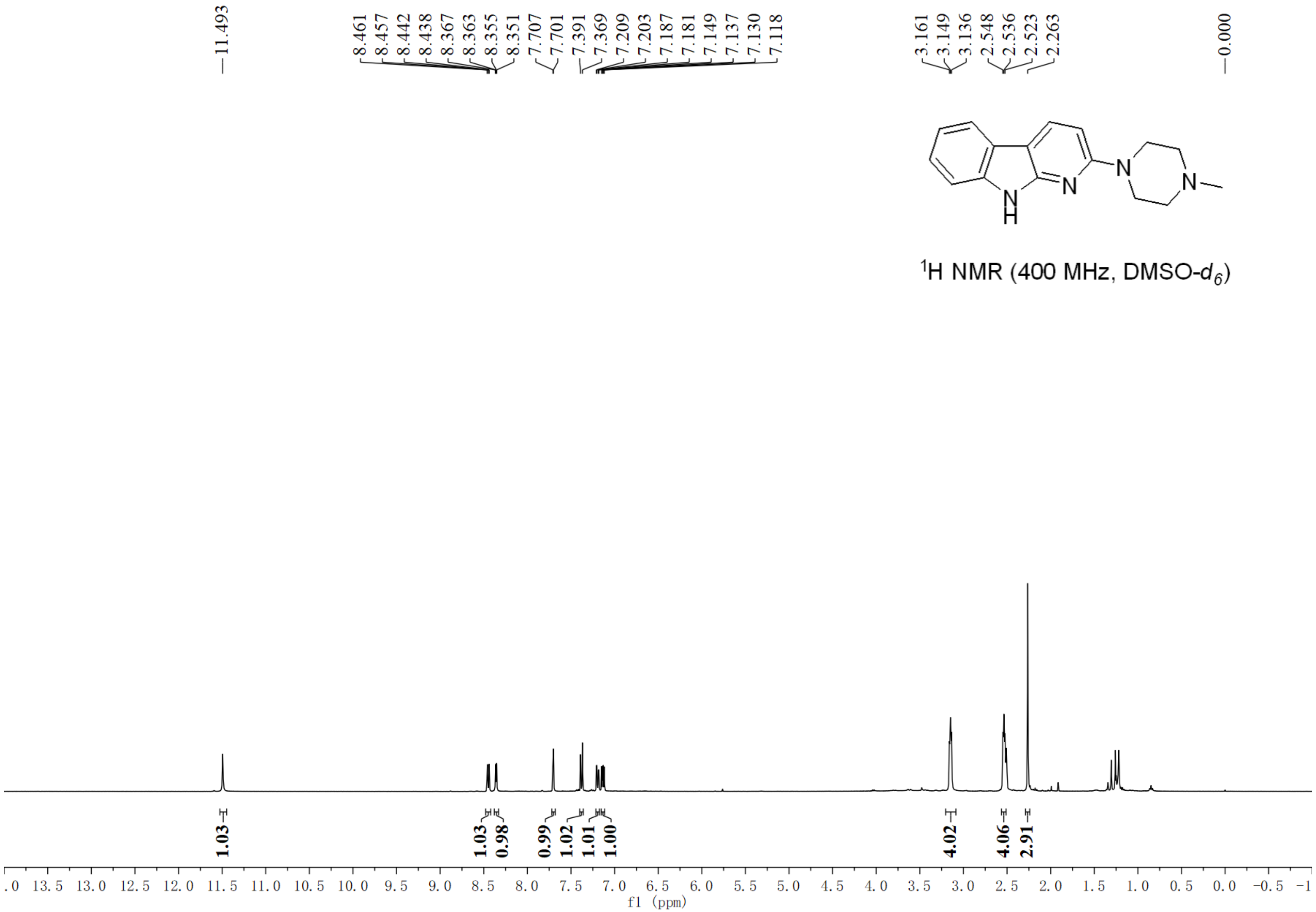




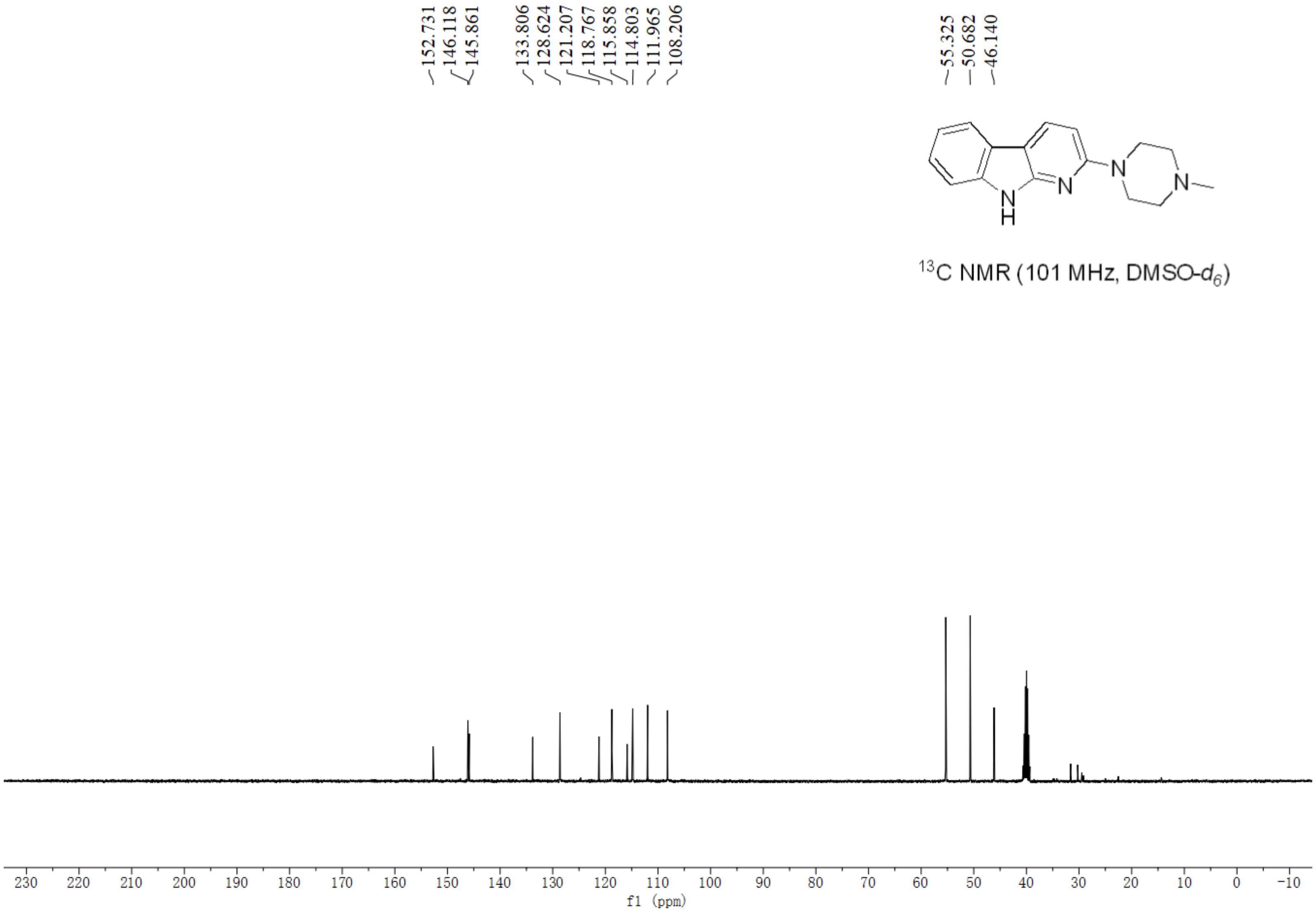
^{1}H NMR (400 MHz, DMSO-d_6)



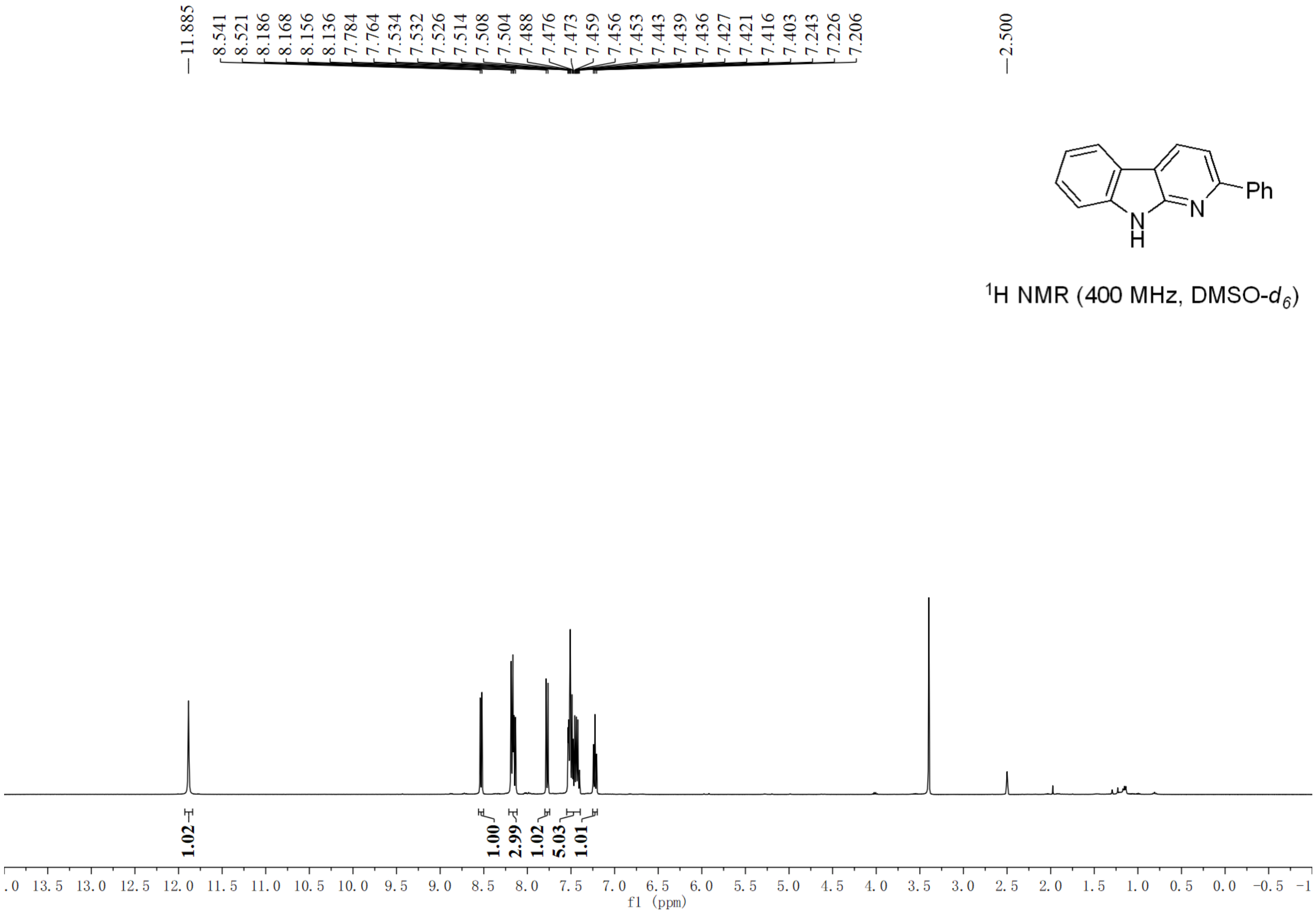
^{13}C NMR (100 MHz, DMSO-d_6)



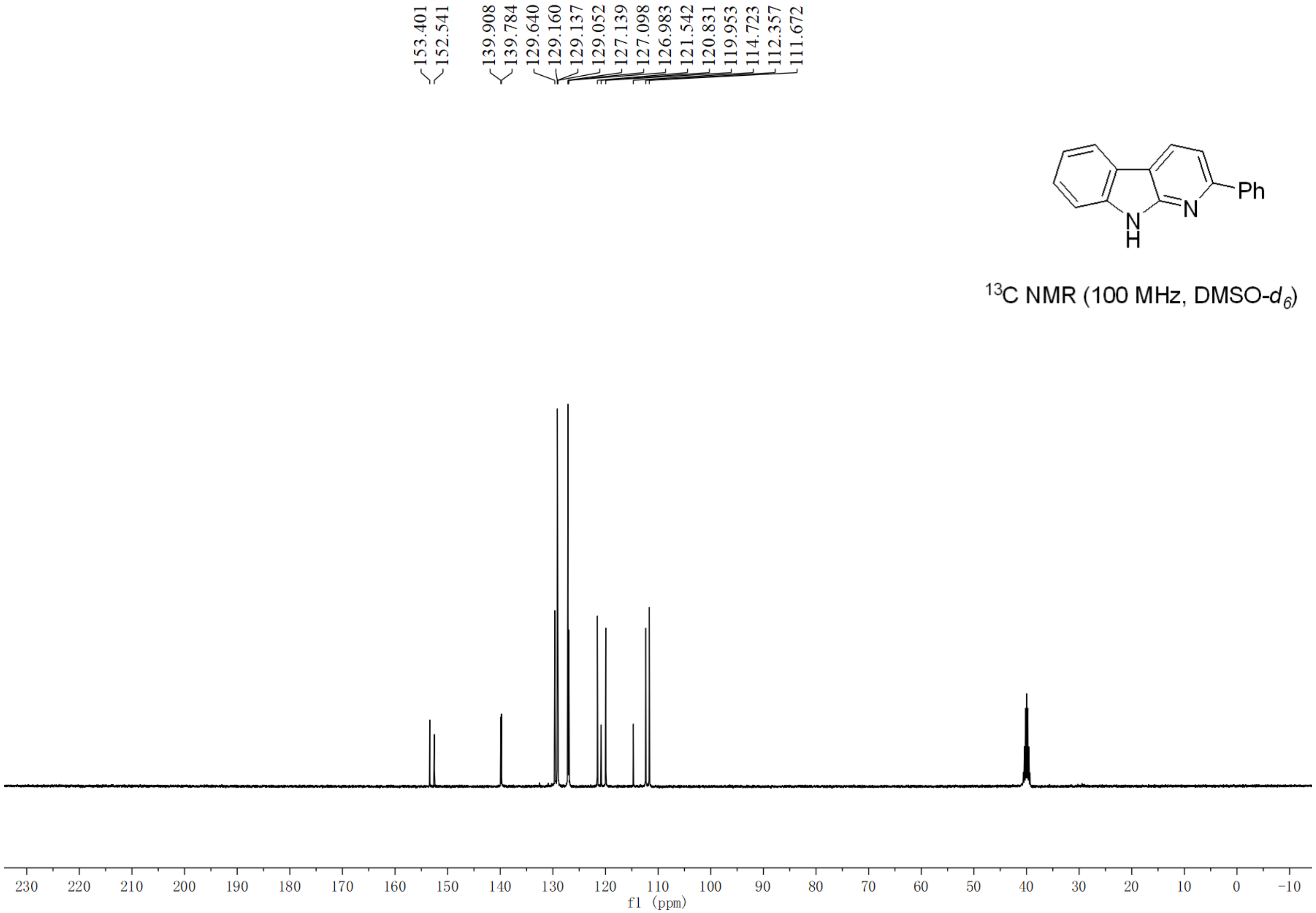
11.493
8.461
8.457
8.442
8.438
8.367
8.363
8.355
8.351
7.707
7.701
7.391
7.369
7.209
7.203
7.187
7.181
7.149
7.137
7.130
7.118
3.161
3.149
3.136
2.548
2.536
2.523
2.263
0.000
N
H
N
N
N
1H NMR (400 MHz, DMSO-d6)
1.03
1.03
0.98
0.99
1.02
1.01
1.00
4.02
4.06
2.91
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



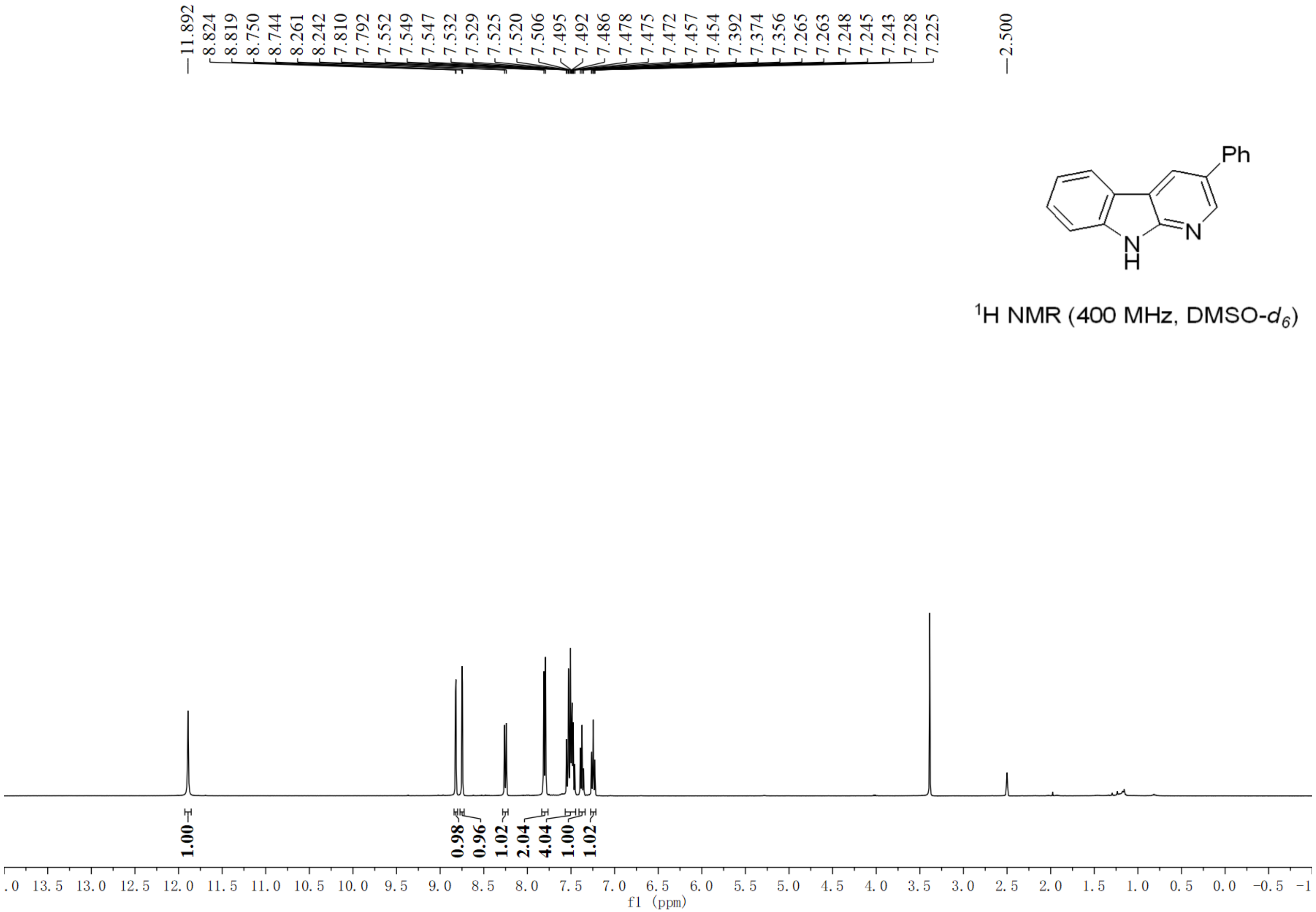
^{13}C NMR (101 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)

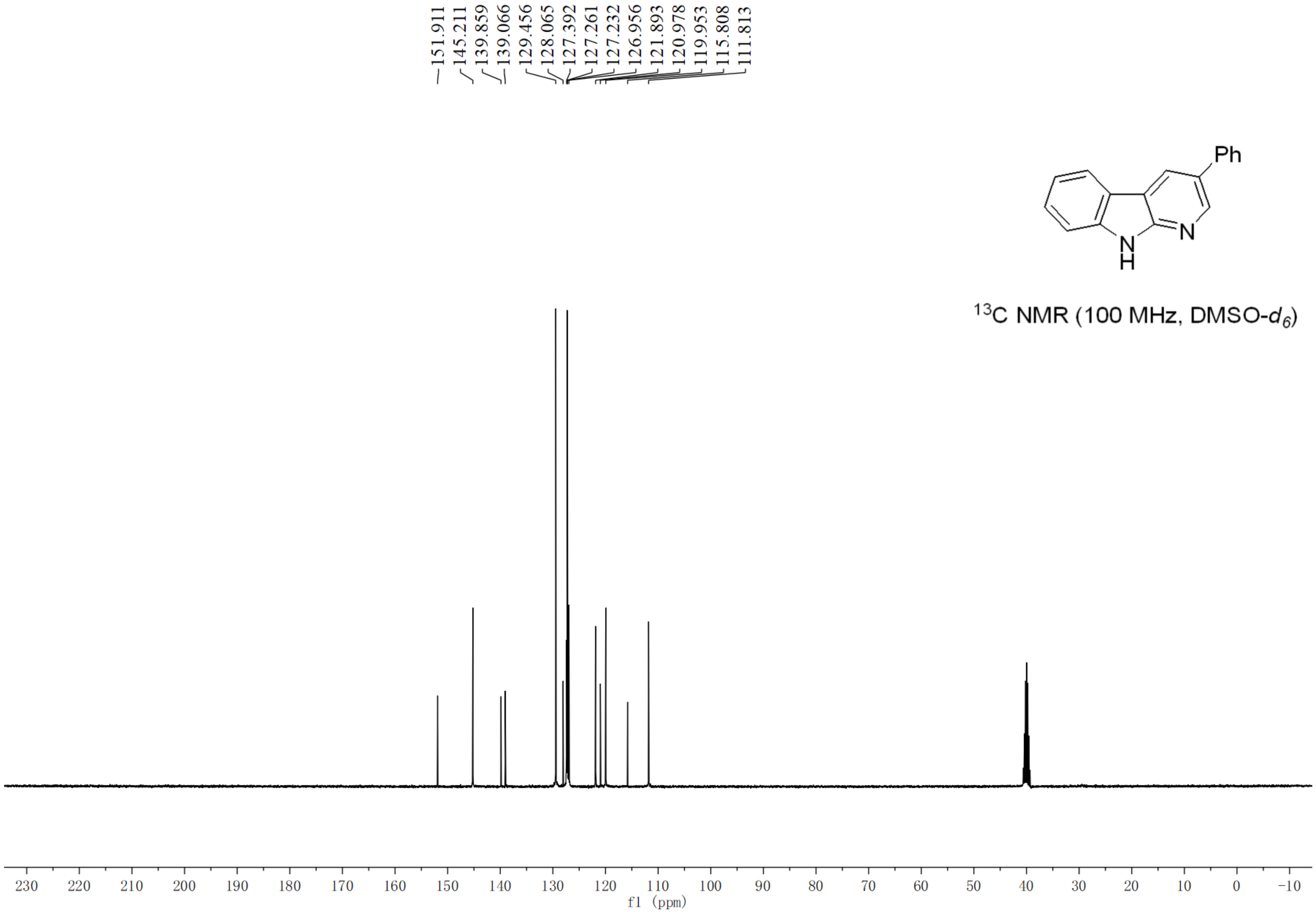


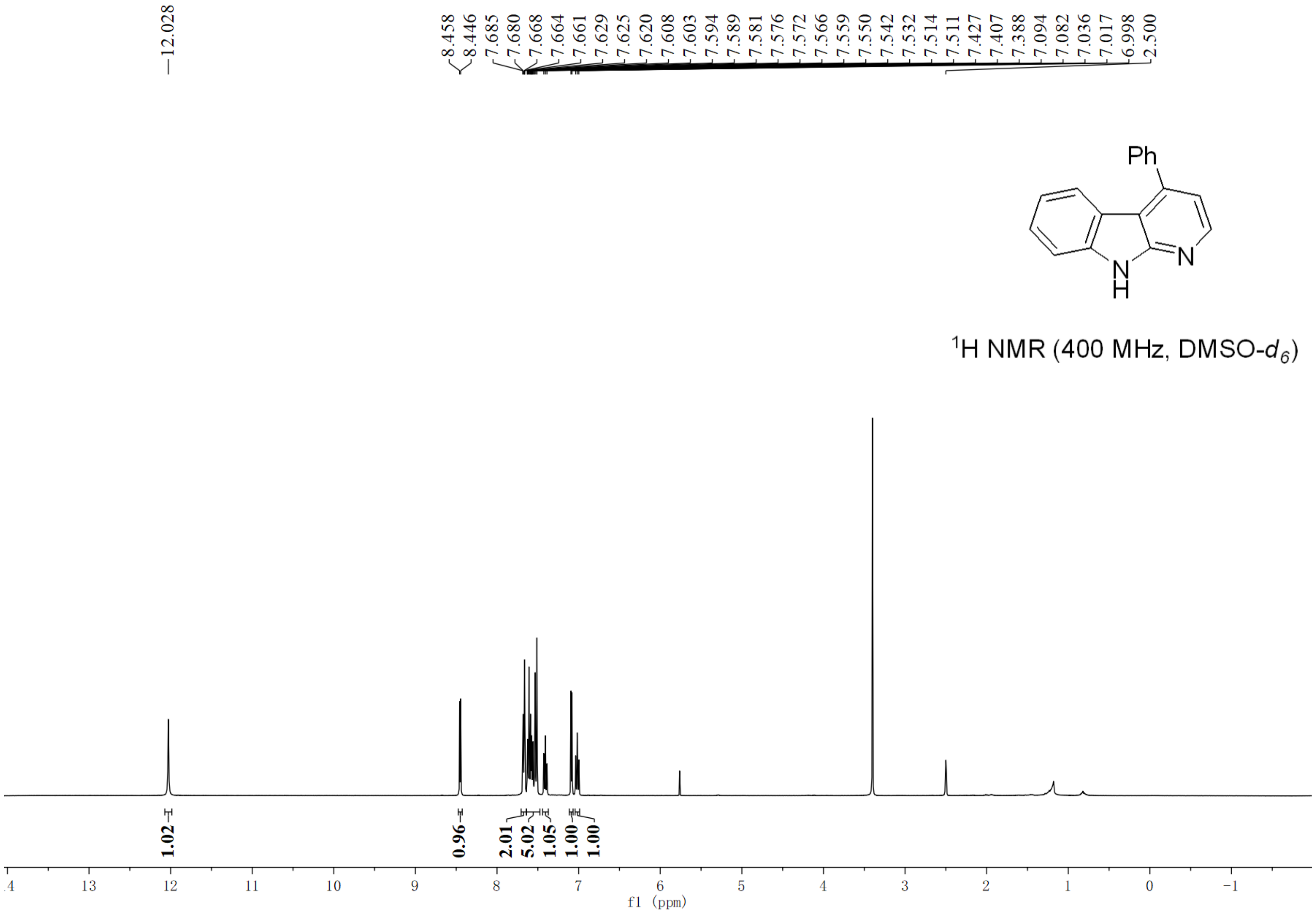
^{13}C NMR (100 MHz, DMSO-d_6)



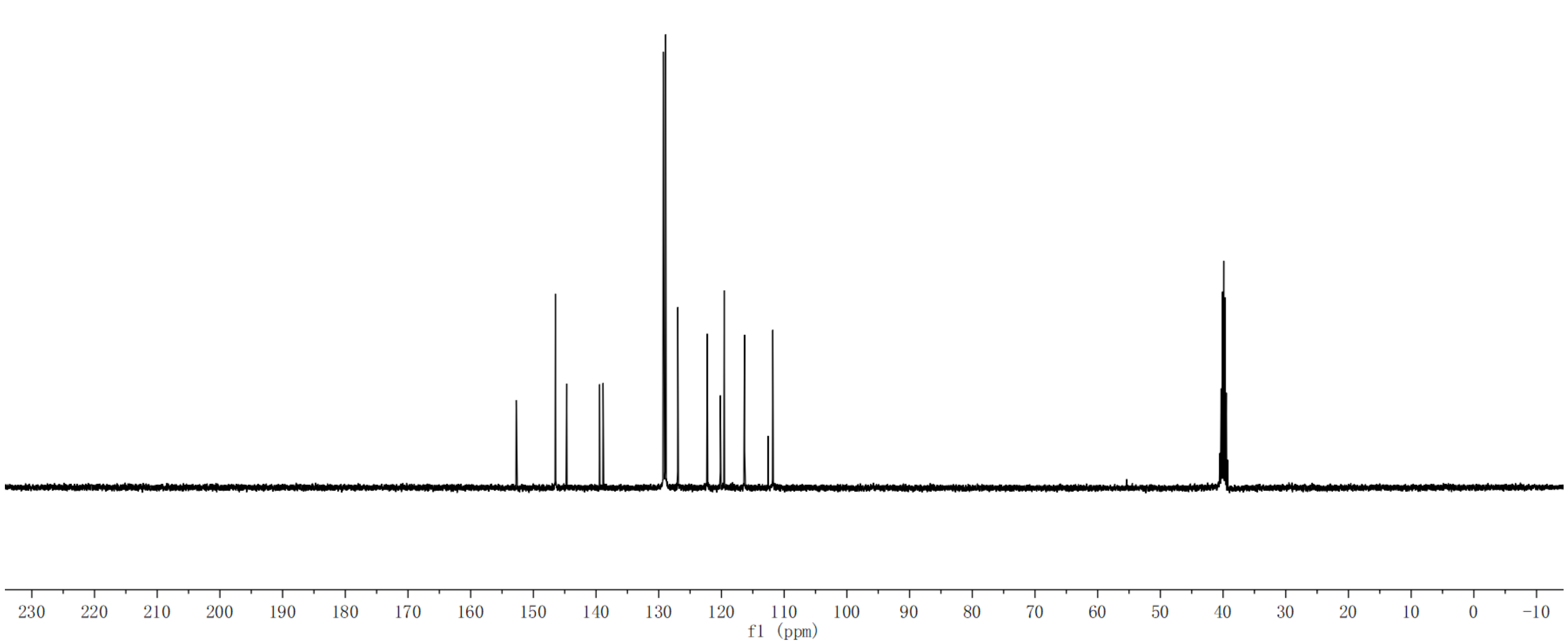
11.892
8.824
8.819
8.750
8.744
8.261
8.242
7.810
7.792
7.552
7.549
7.547
7.532
7.529
7.525
7.520
7.506
7.495
7.492
7.486
7.478
7.475
7.472
7.457
7.454
7.392
7.374
7.356
7.265
7.263
7.248
7.245
7.243
7.228
7.225
2.500
Ph
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
0.98
0.96
1.02
2.04
4.04
1.00
1.02
f1 (ppm)

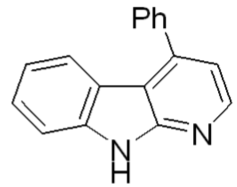
^{13}C NMR (100 MHz, DMSO-d_6)



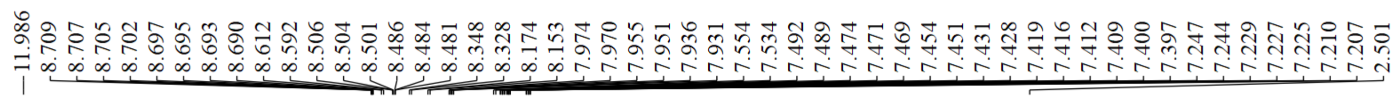


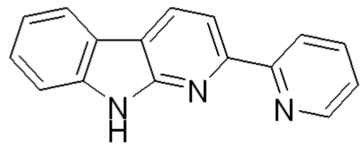
^{1}H NMR (400 MHz, DMSO-d_6)



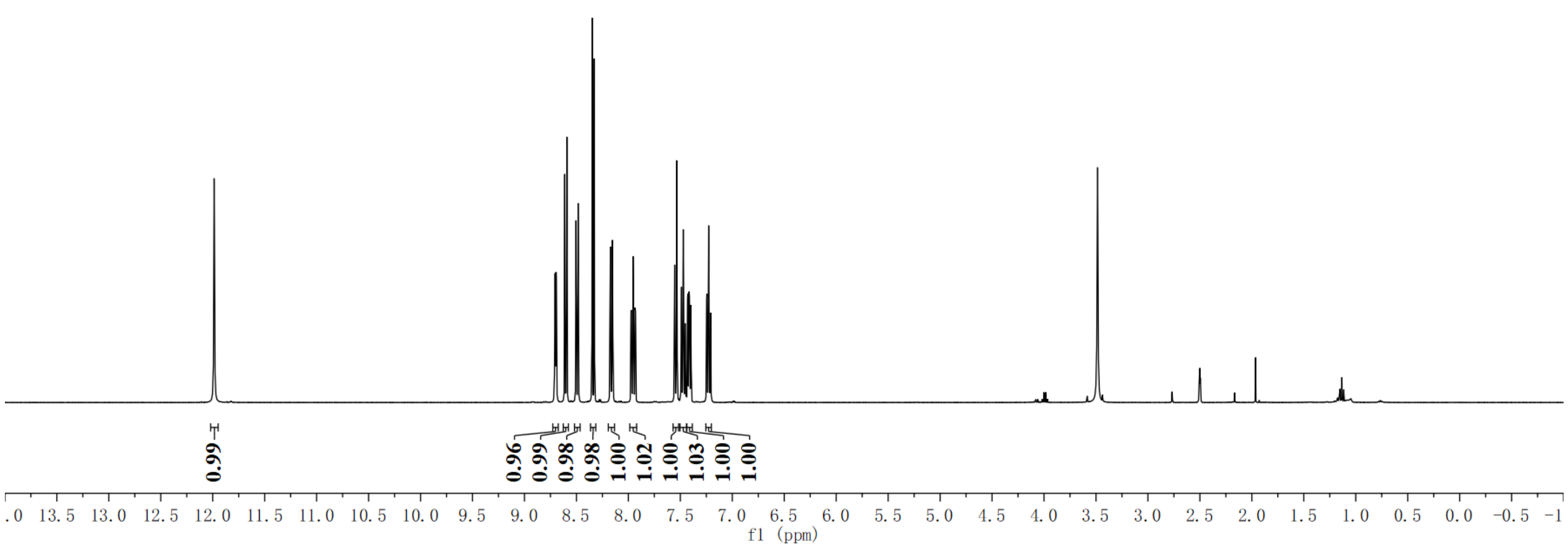


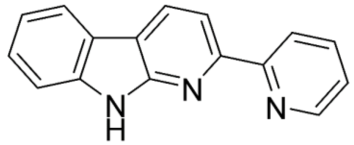
^{13}C NMR (100 MHz, DMSO-d_6)



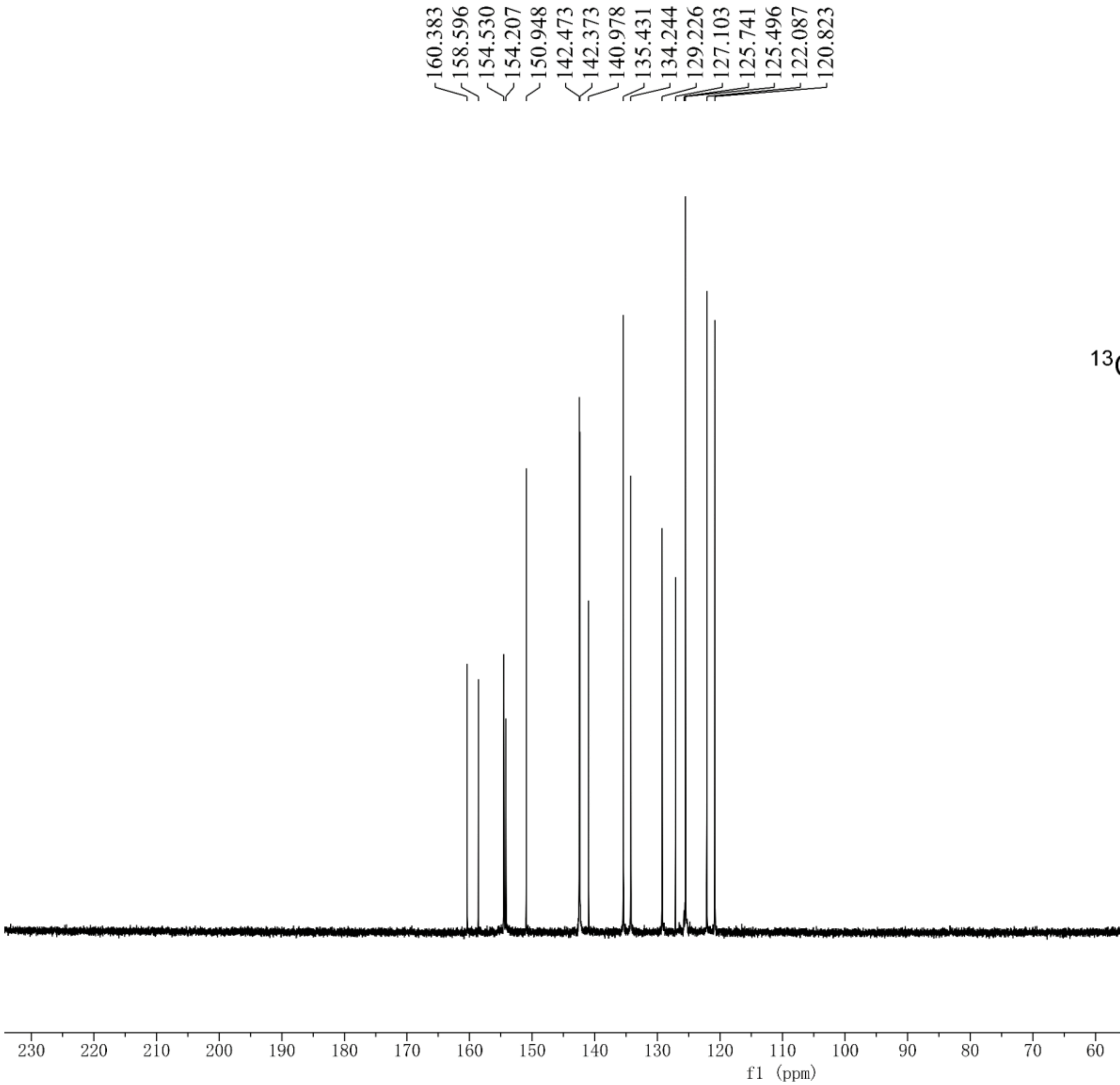


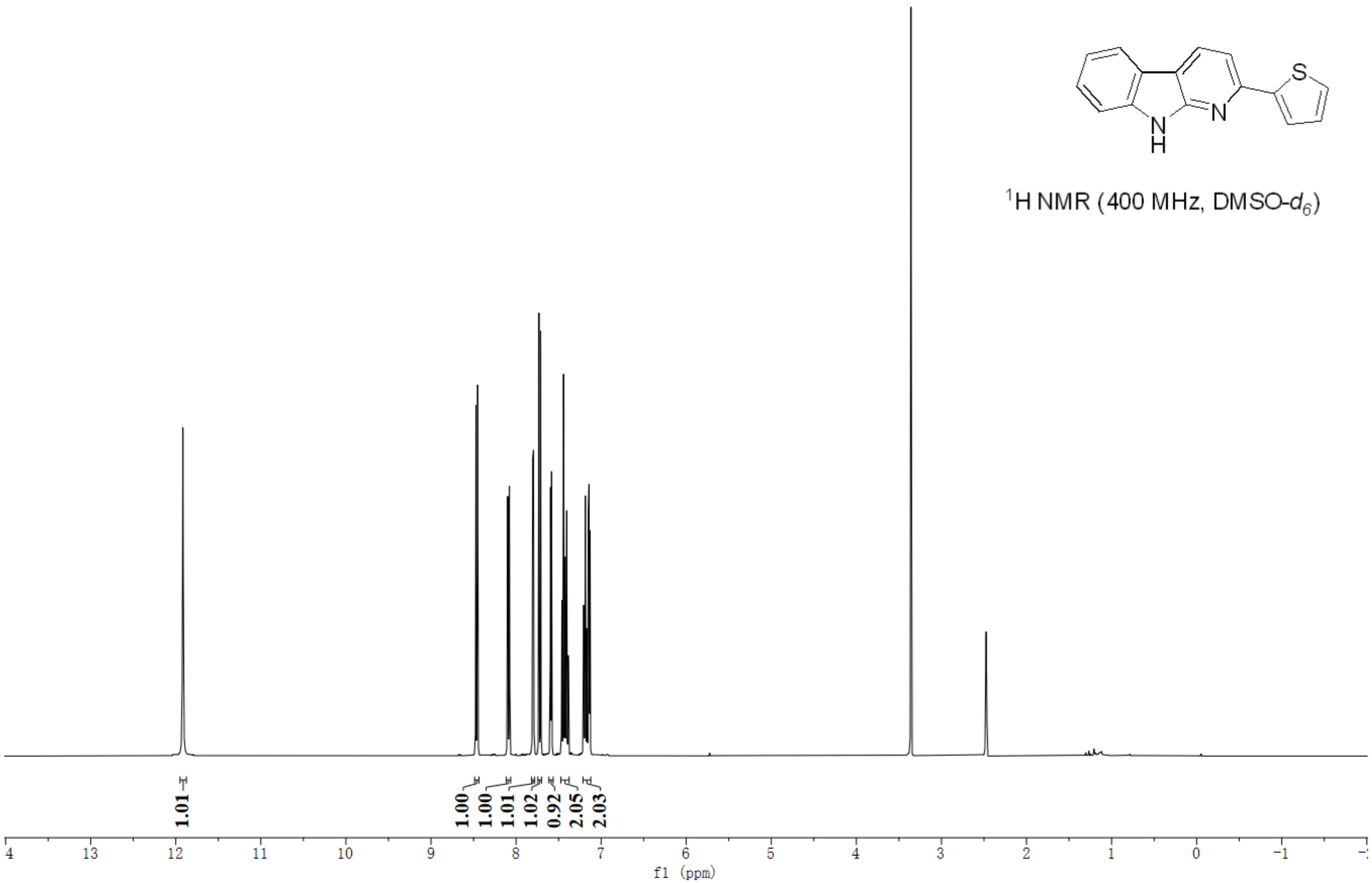
^{1}H NMR (400 MHz, DMSO-d_6)



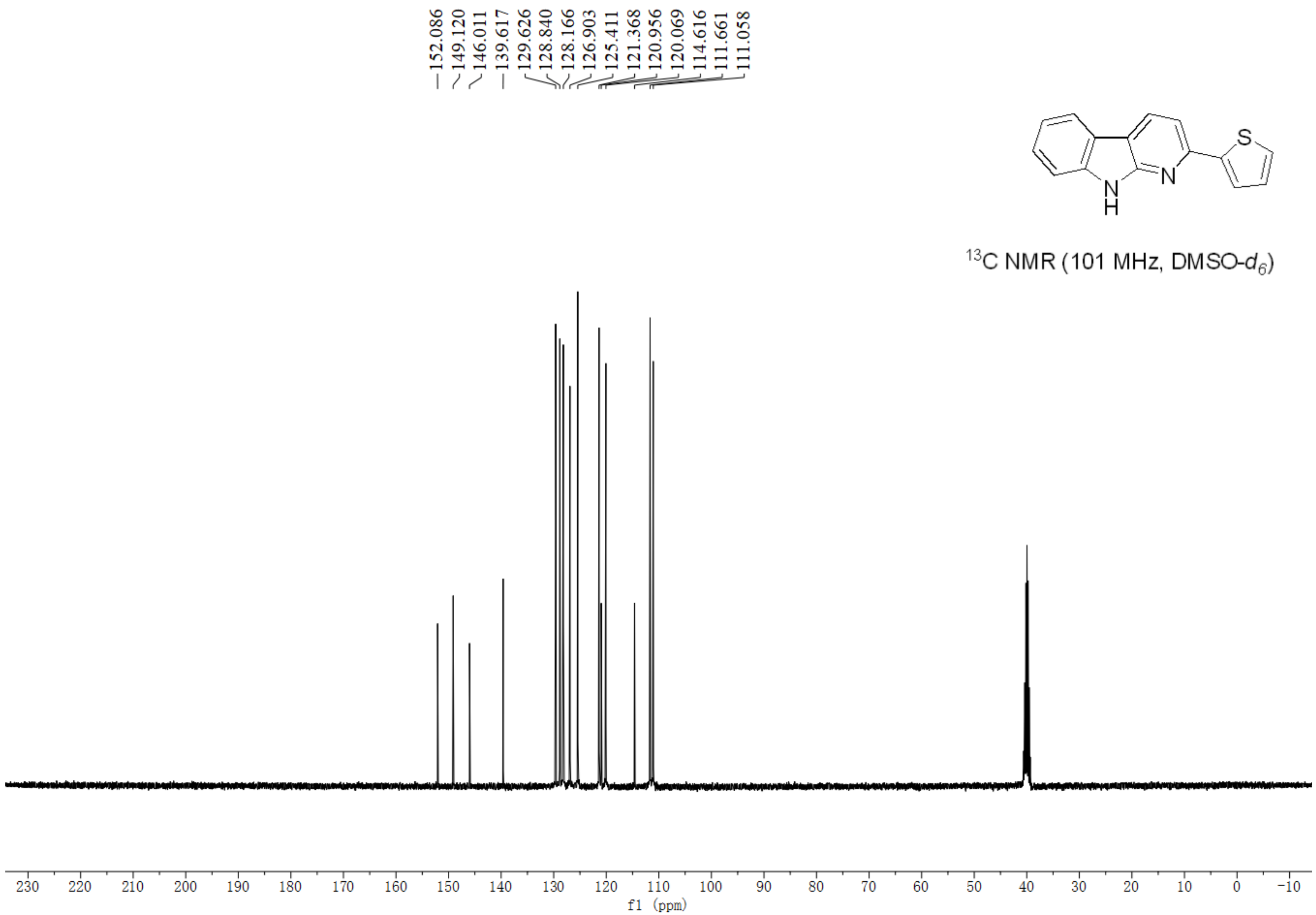


^{13}C NMR (100 MHz, DMSO-d_6)

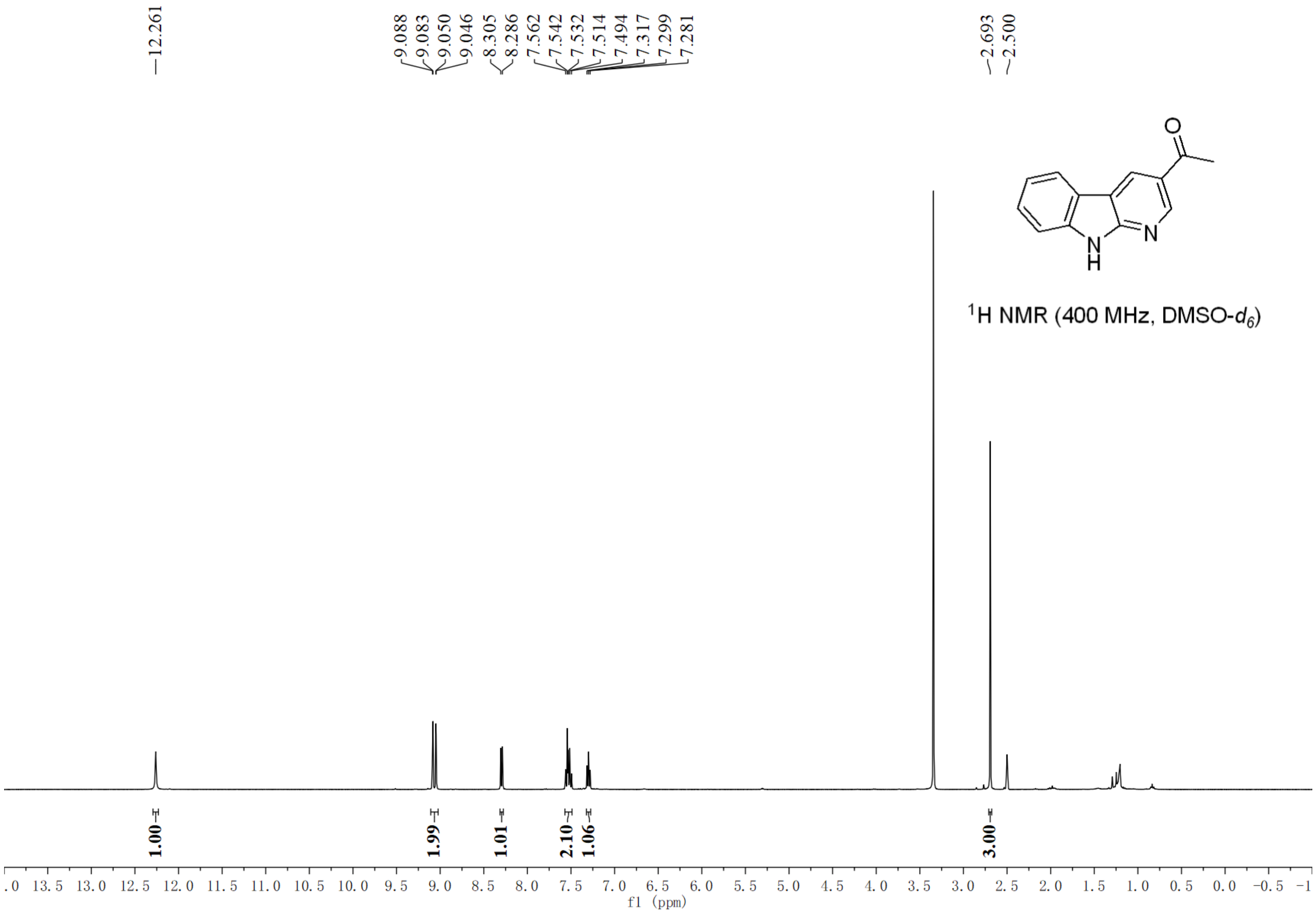




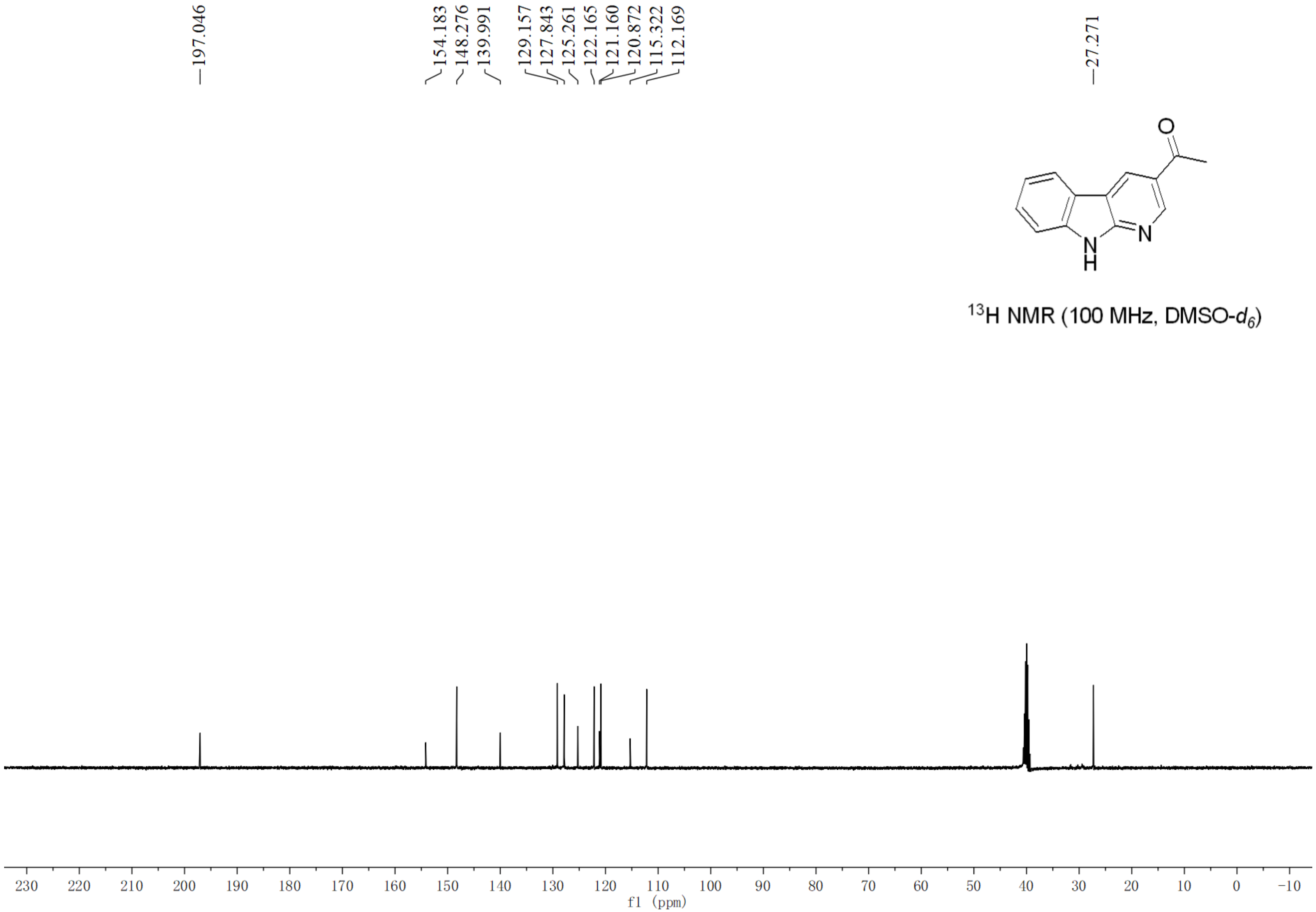
S
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.01
1.00
1.00
1.01
1.02
0.92
2.05
2.03
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



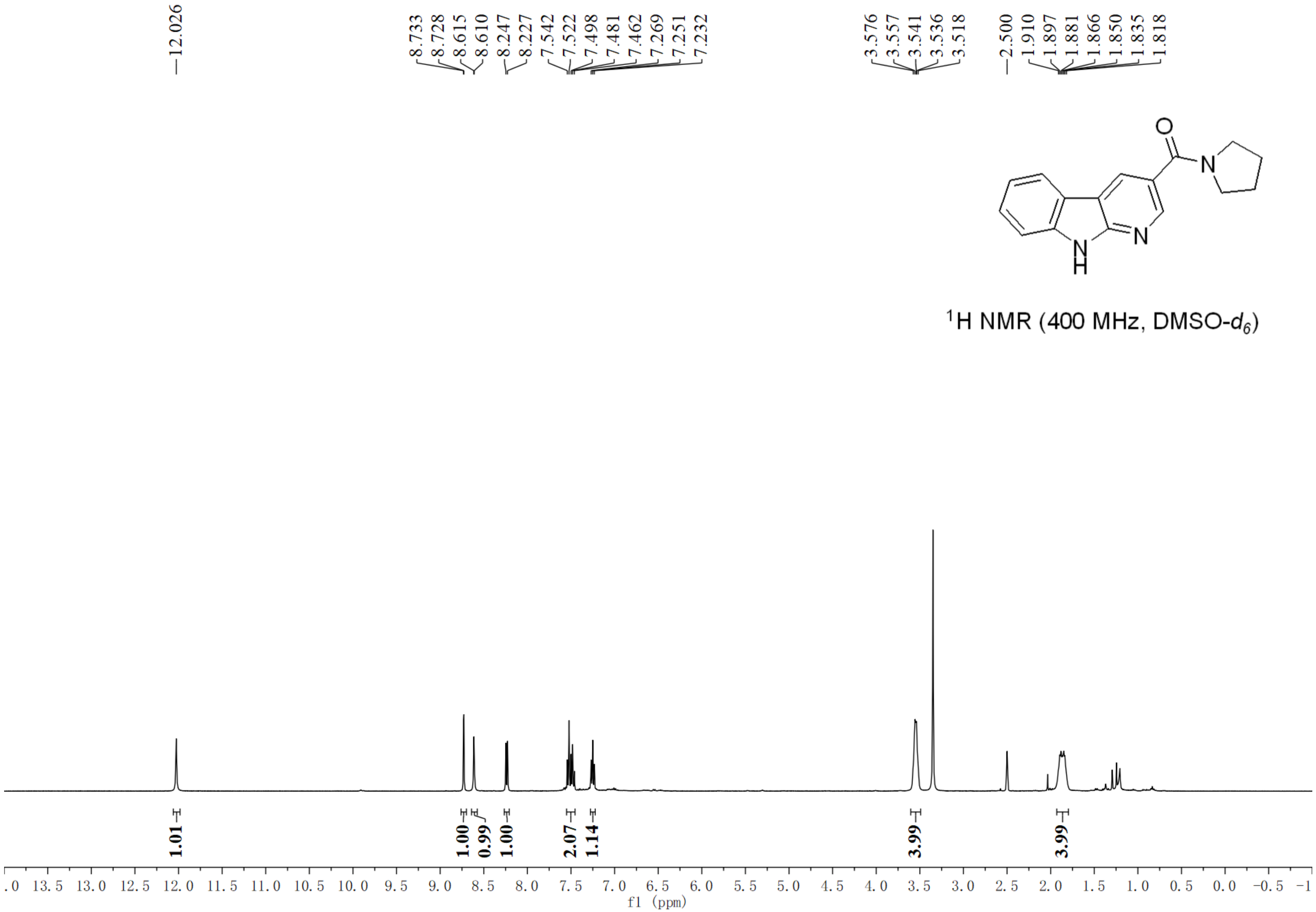
^{13}C NMR (101 MHz, DMSO-d_6)



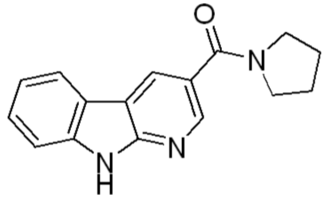
^{1}H NMR (400 MHz, DMSO-d_6)

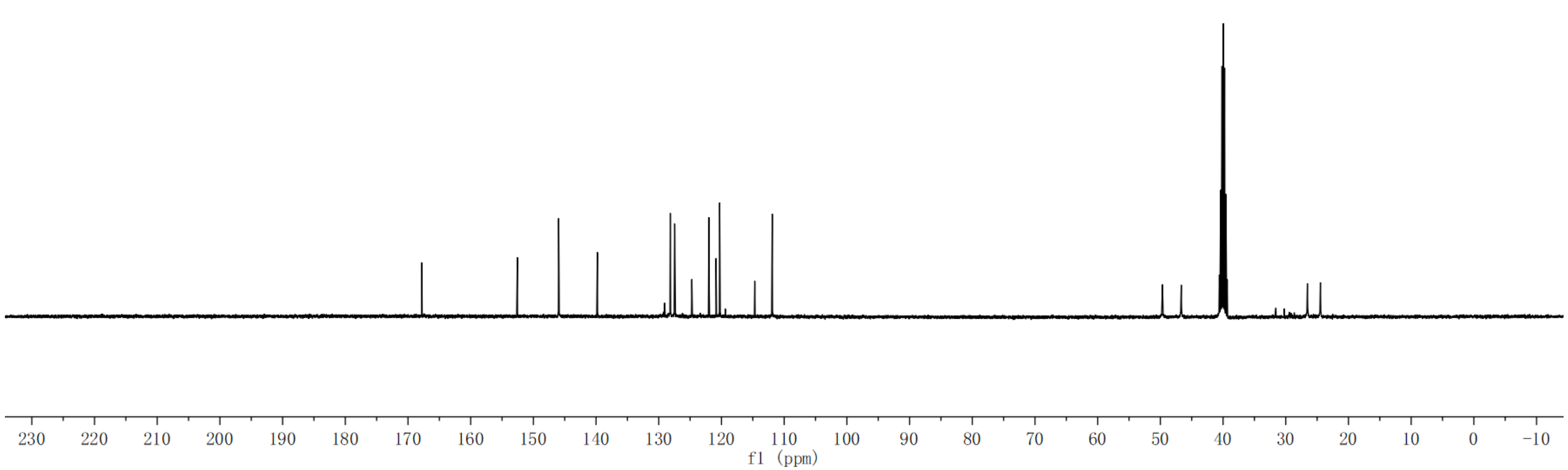


^{13}H NMR (100 MHz, DMSO-d_6)

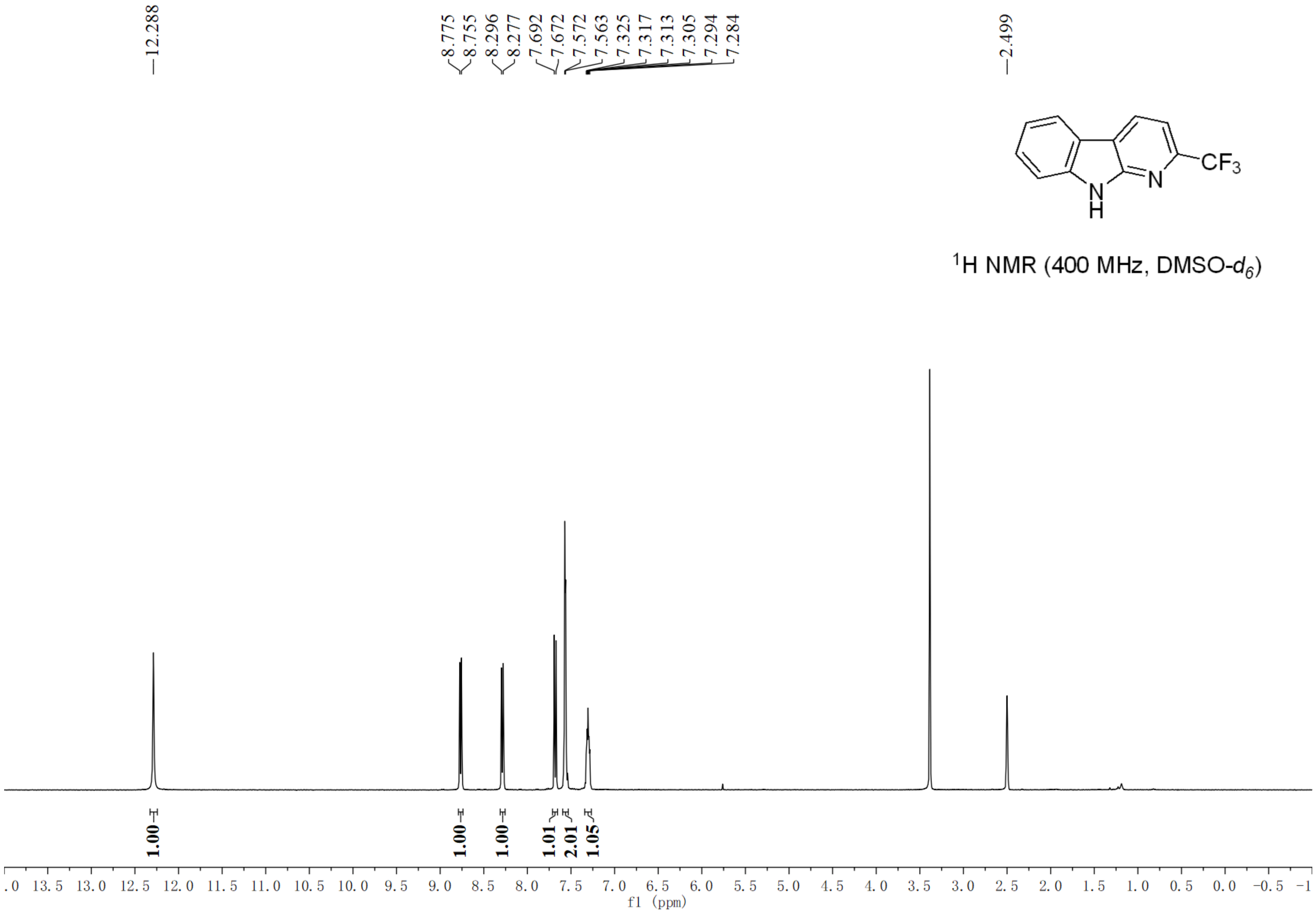


^{1}H NMR (400 MHz, DMSO-d_6)

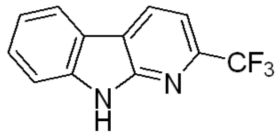




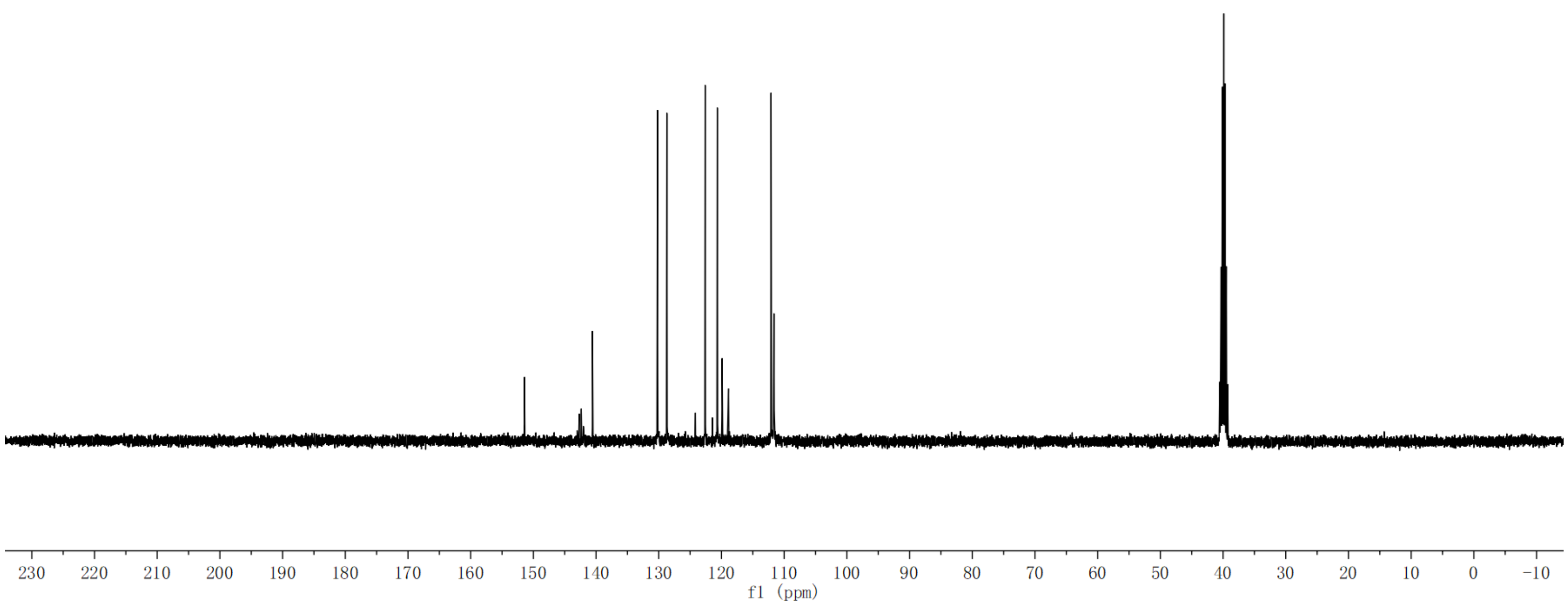
^{13}C NMR (100 MHz, DMSO-d_6)

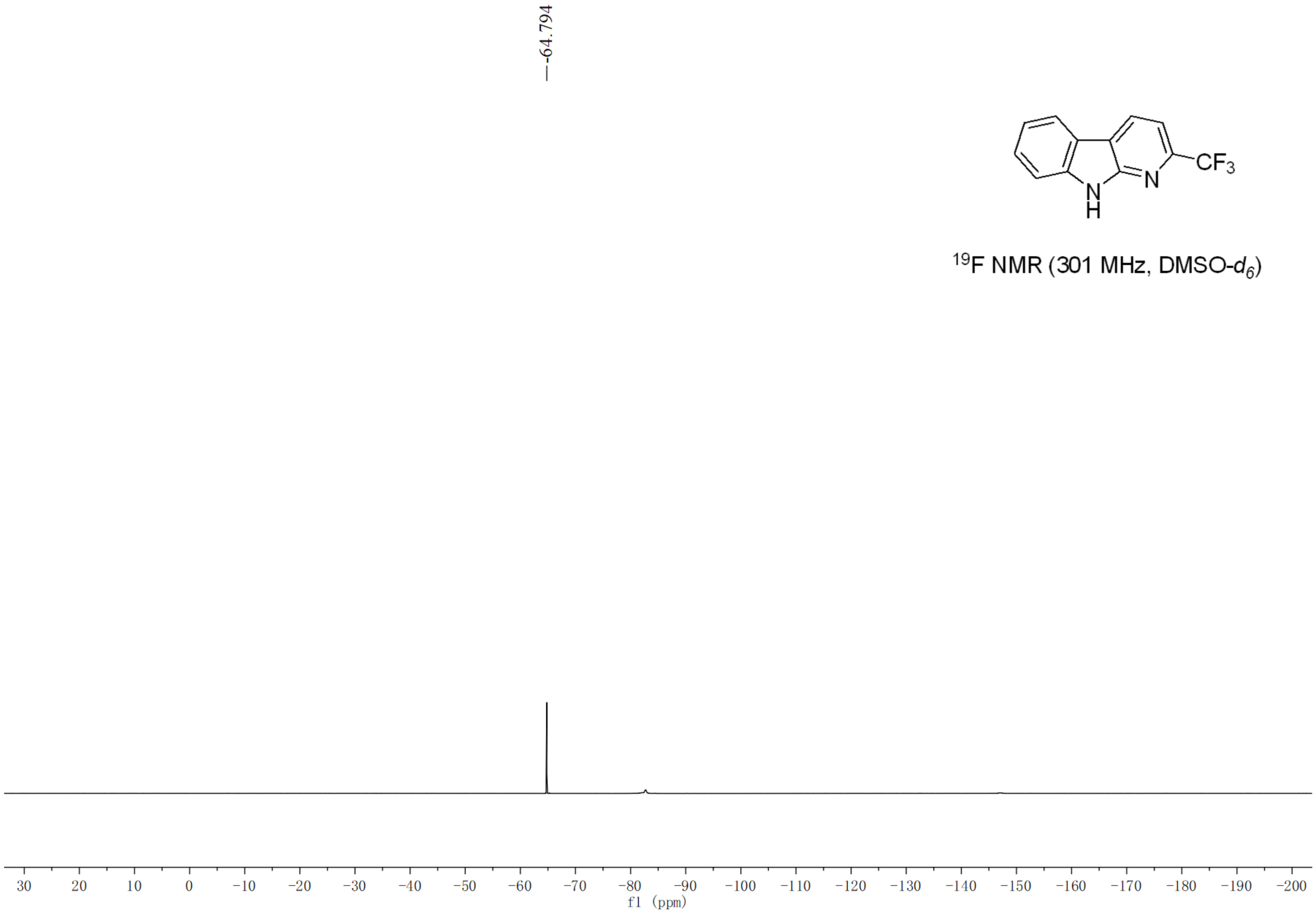


12.288
8.775
8.755
8.296
8.277
7.692
7.672
7.572
7.563
7.325
7.317
7.313
7.305
7.294
7.284
2.499
CF3
N
H
N
1H NMR (400 MHz, DMSO-d6)
1.00
1.00
1.00
1.01
2.01
1.05
f1 (ppm)

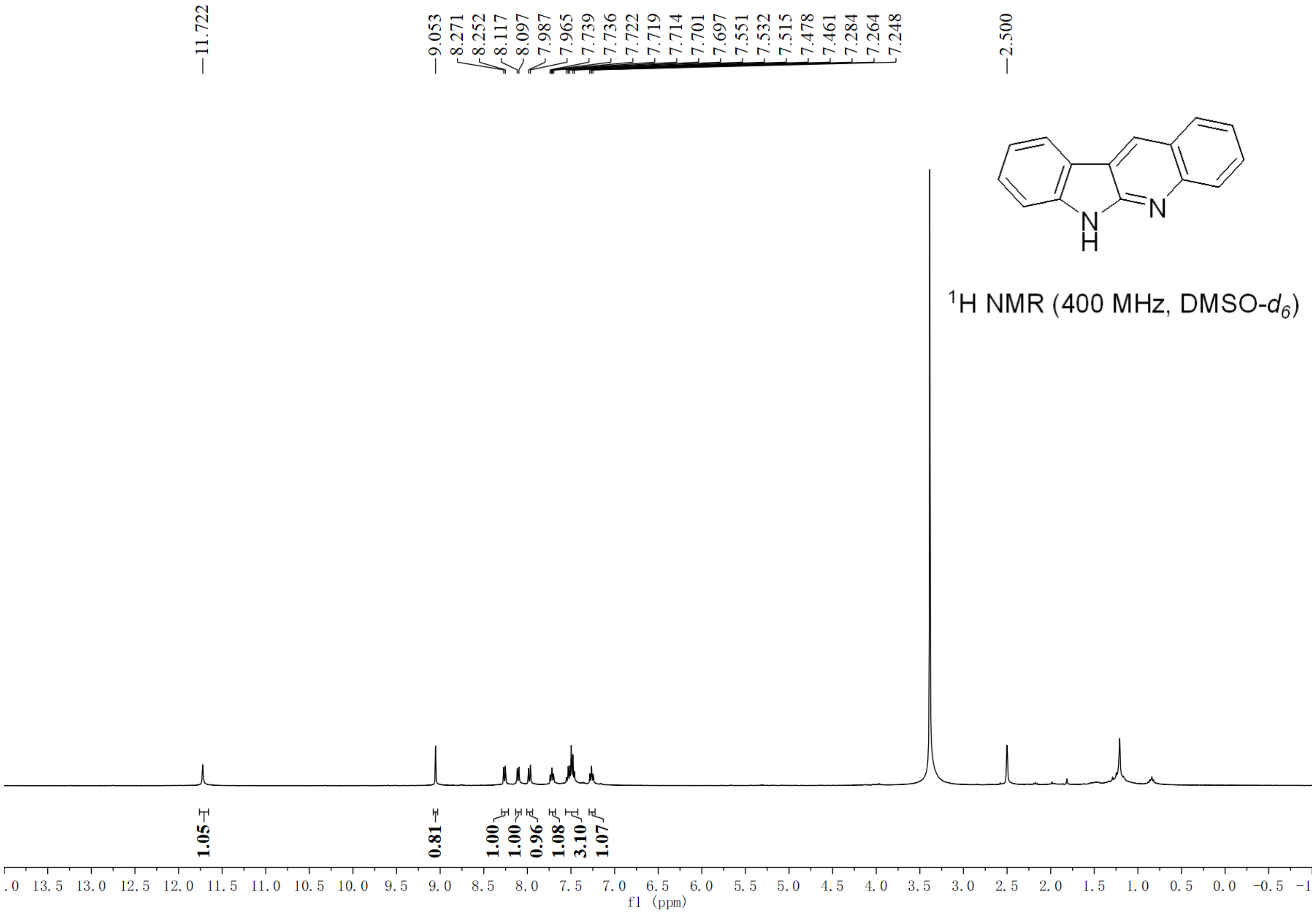


^{13}C NMR (100 MHz, DMSO-d_6)

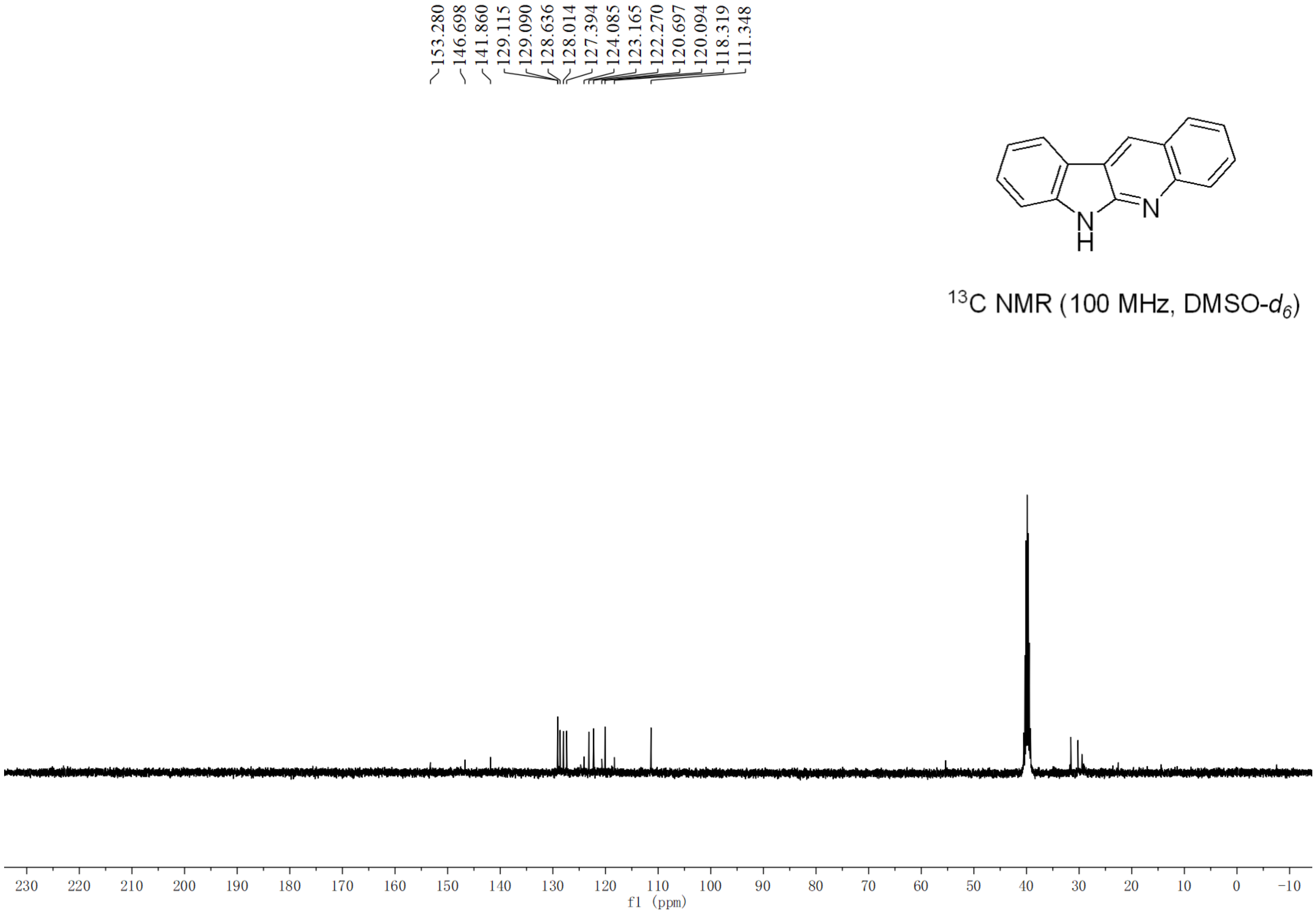




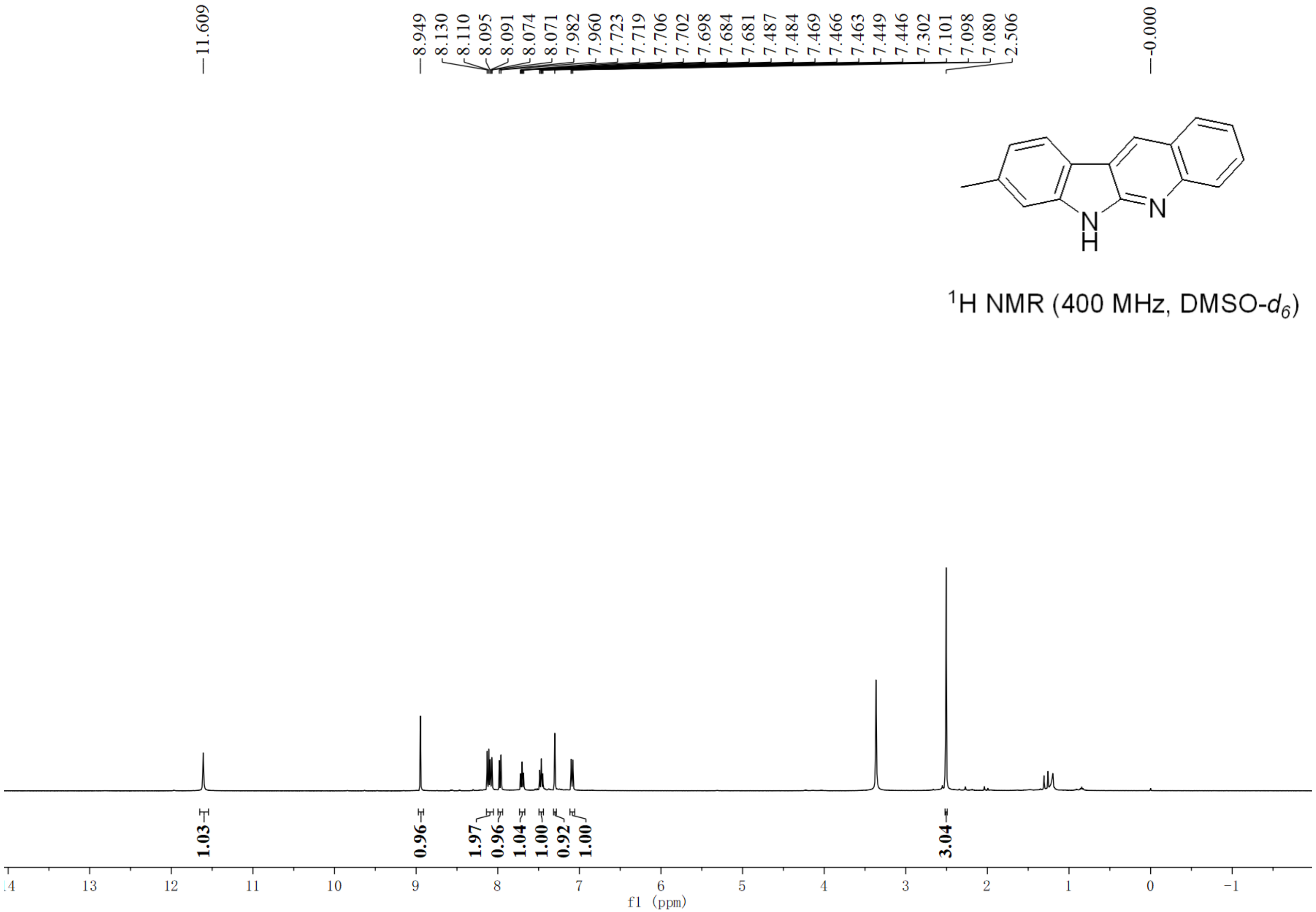
^{19}F NMR (301 MHz, DMSO-d_6)



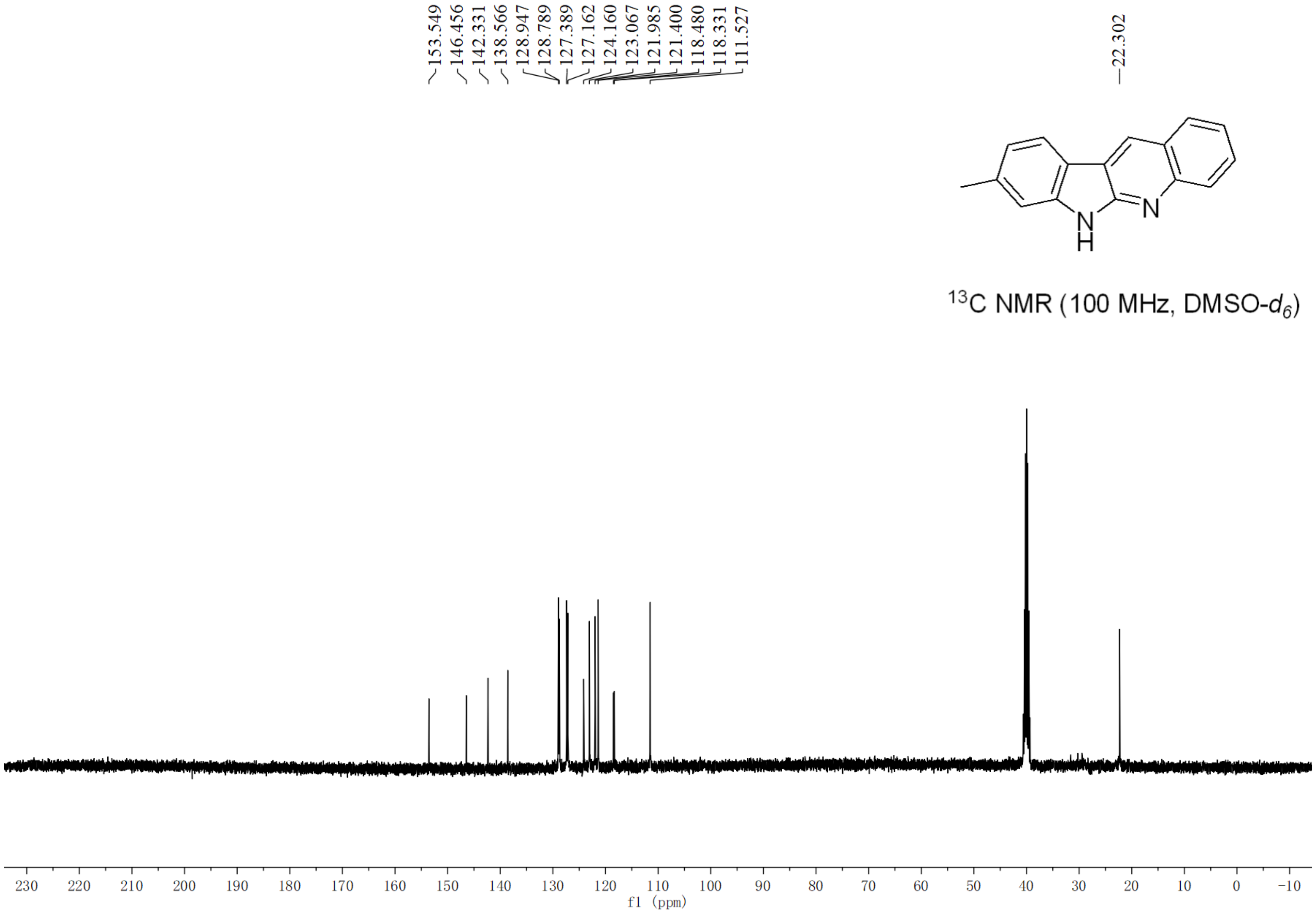
11.722
9.053
8.271
8.252
8.117
8.097
7.987
7.965
7.739
7.736
7.722
7.719
7.714
7.701
7.697
7.551
7.532
7.515
7.478
7.461
7.284
7.264
7.248
2.500
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.05
0.81
1.00
1.00
0.96
1.08
3.10
1.07
.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



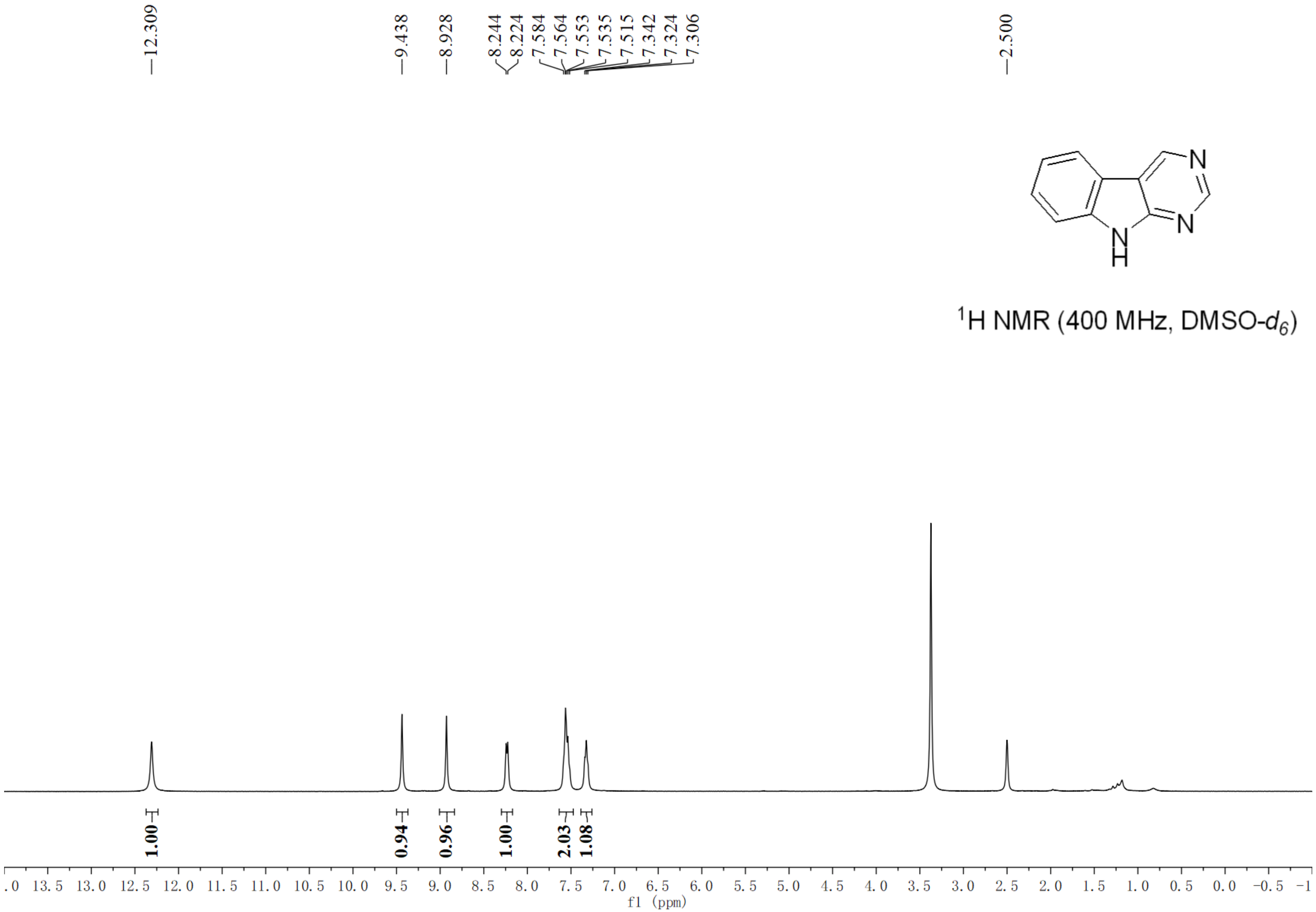
^{13}C NMR (100 MHz, DMSO-d_6)



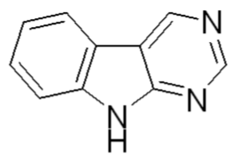
^{1}H NMR (400 MHz, DMSO-d_6)



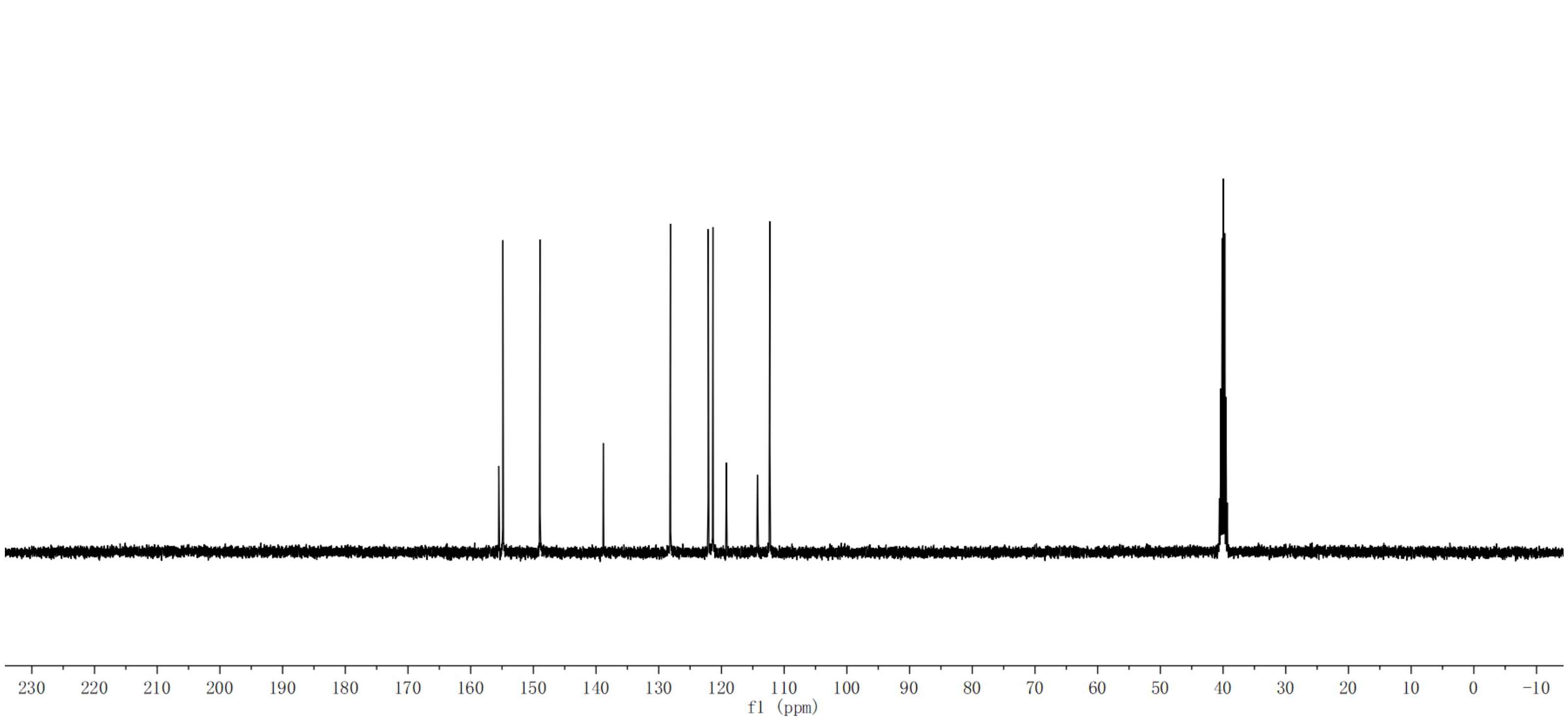
^{13}C NMR (100 MHz, DMSO-d_6)

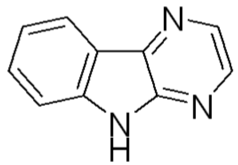


^{1}H NMR (400 MHz, DMSO-d_6)

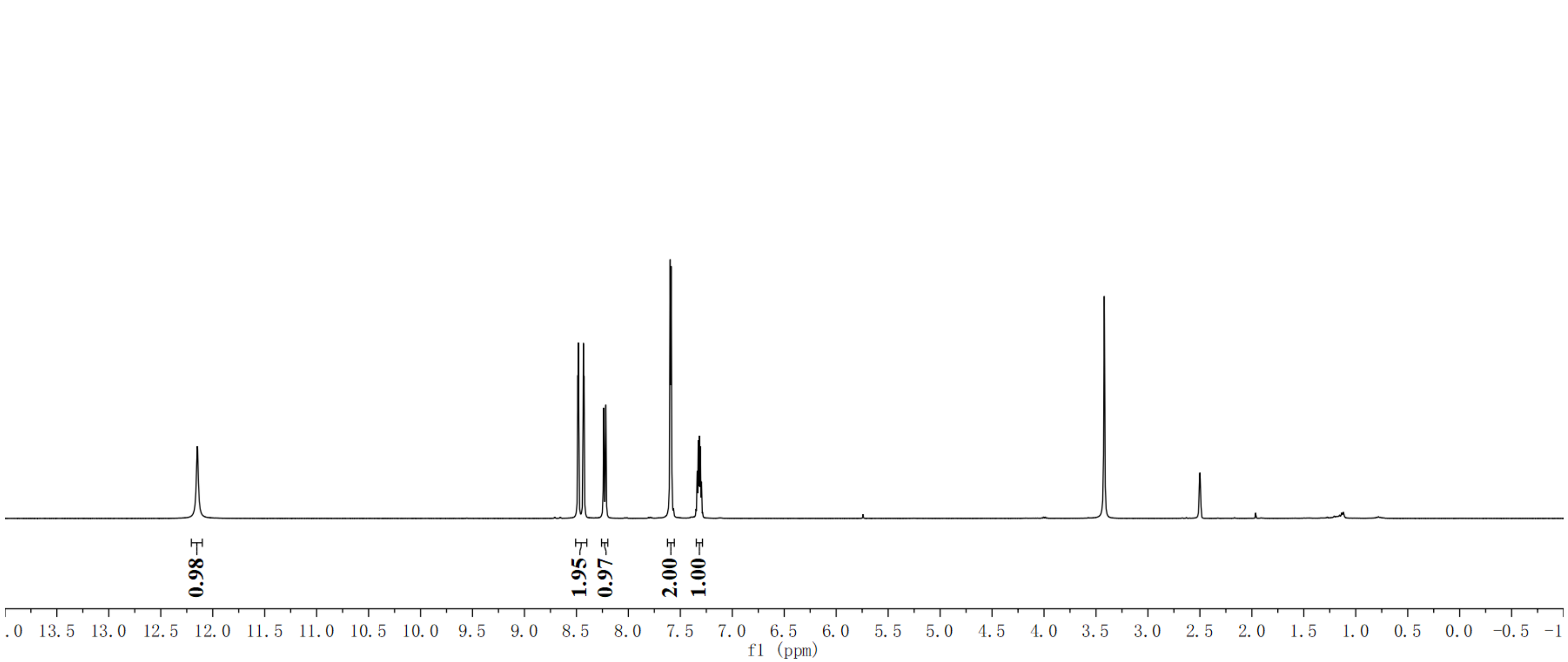


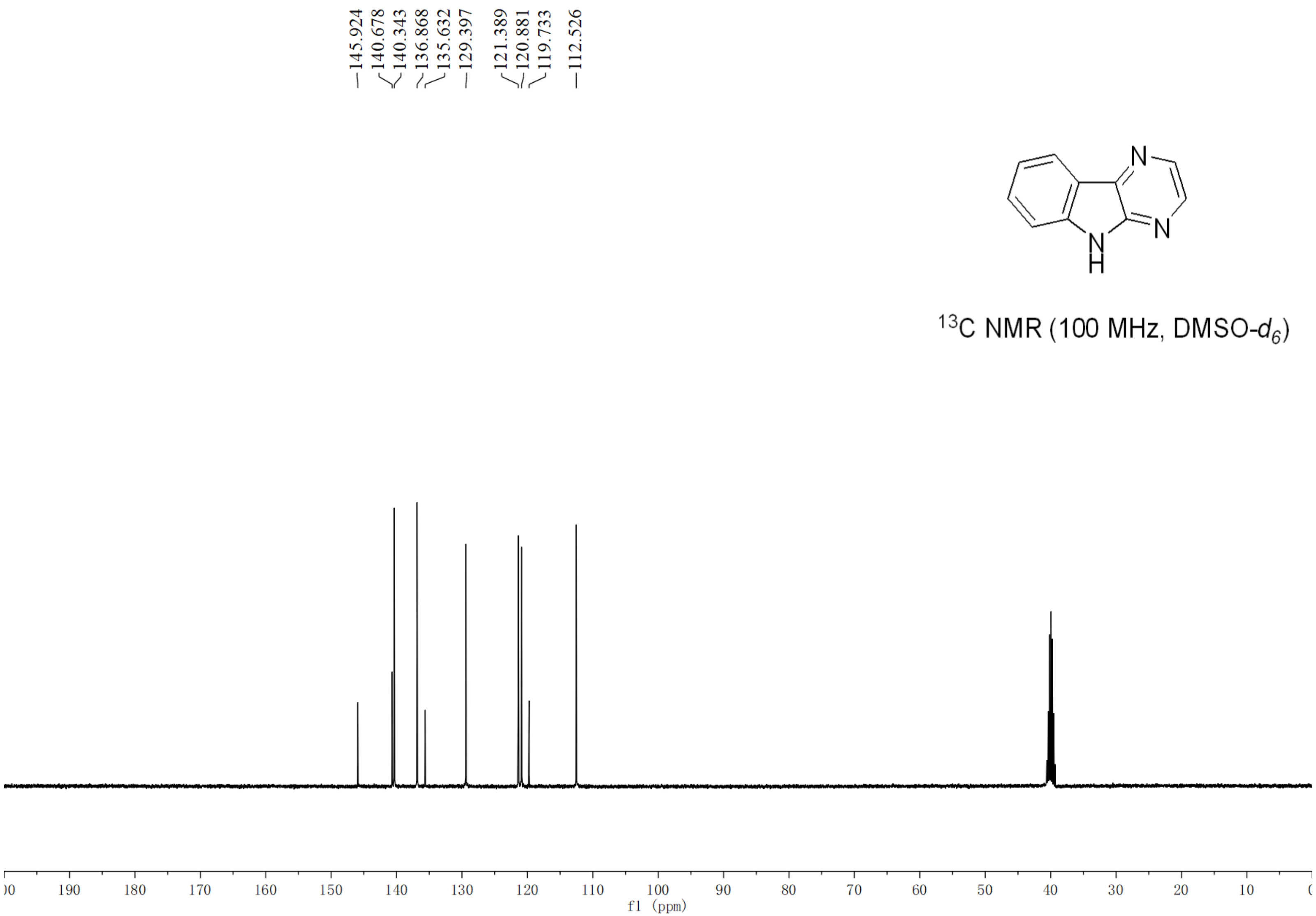
^{1}H NMR (400 MHz, DMSO-d_6)



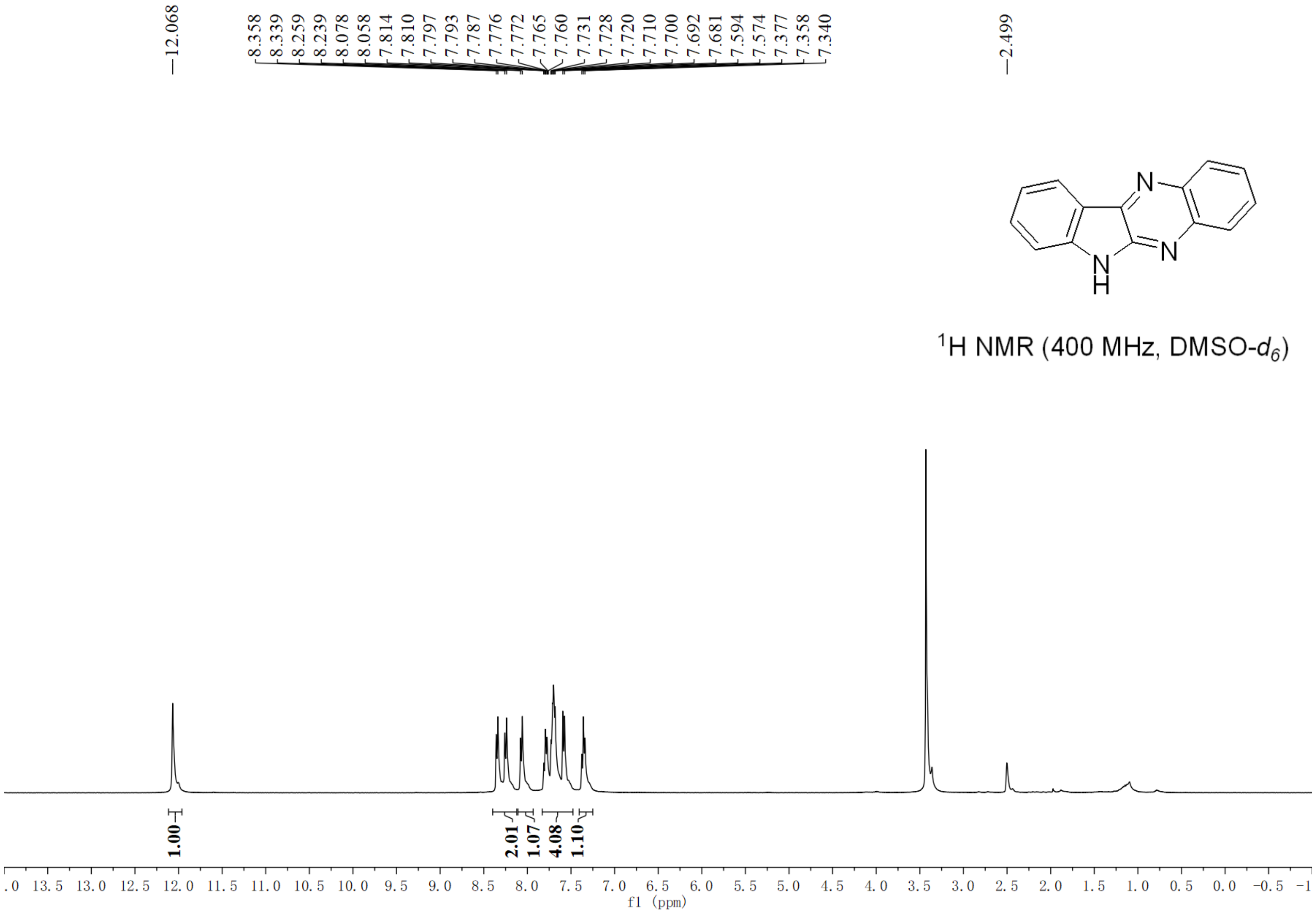


^{1}H NMR (400 MHz, DMSO-d_6)

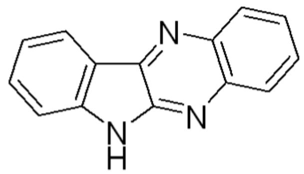




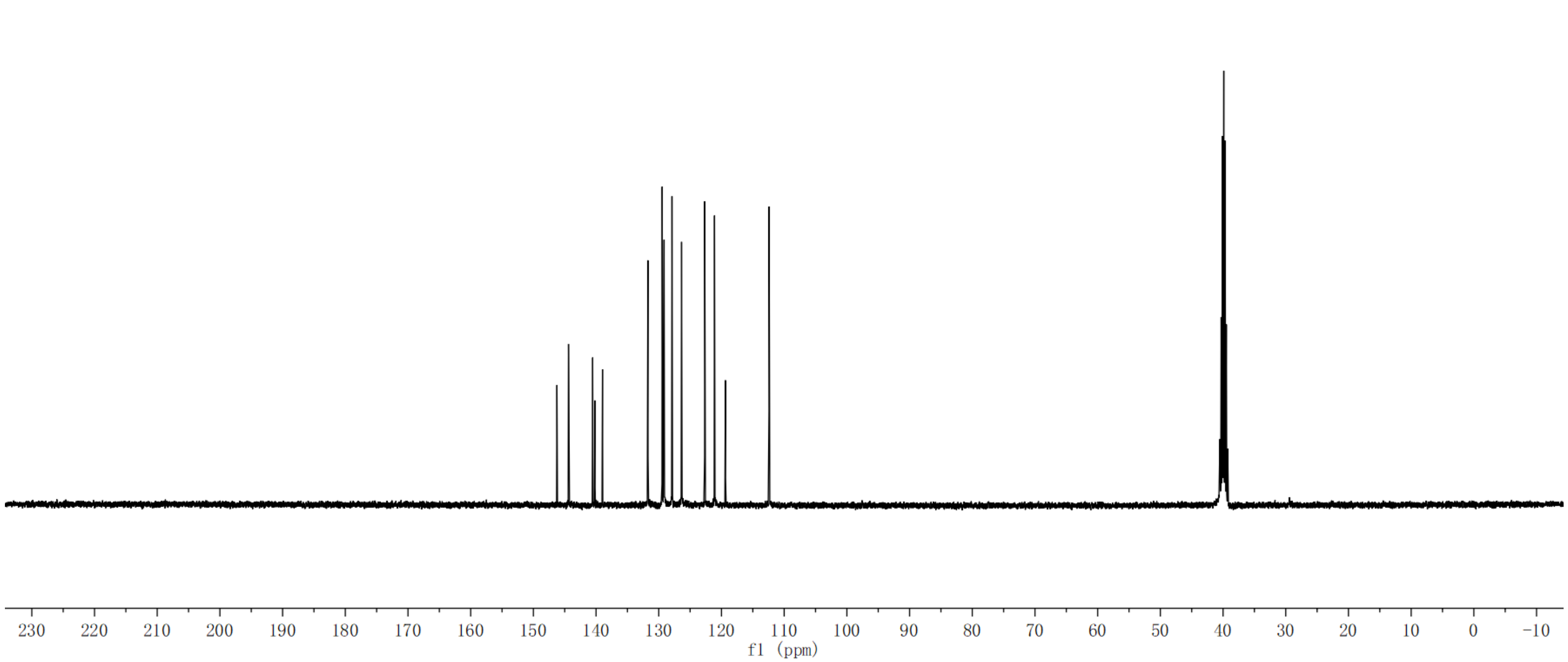
^{13}C NMR (100 MHz, DMSO-d_6)

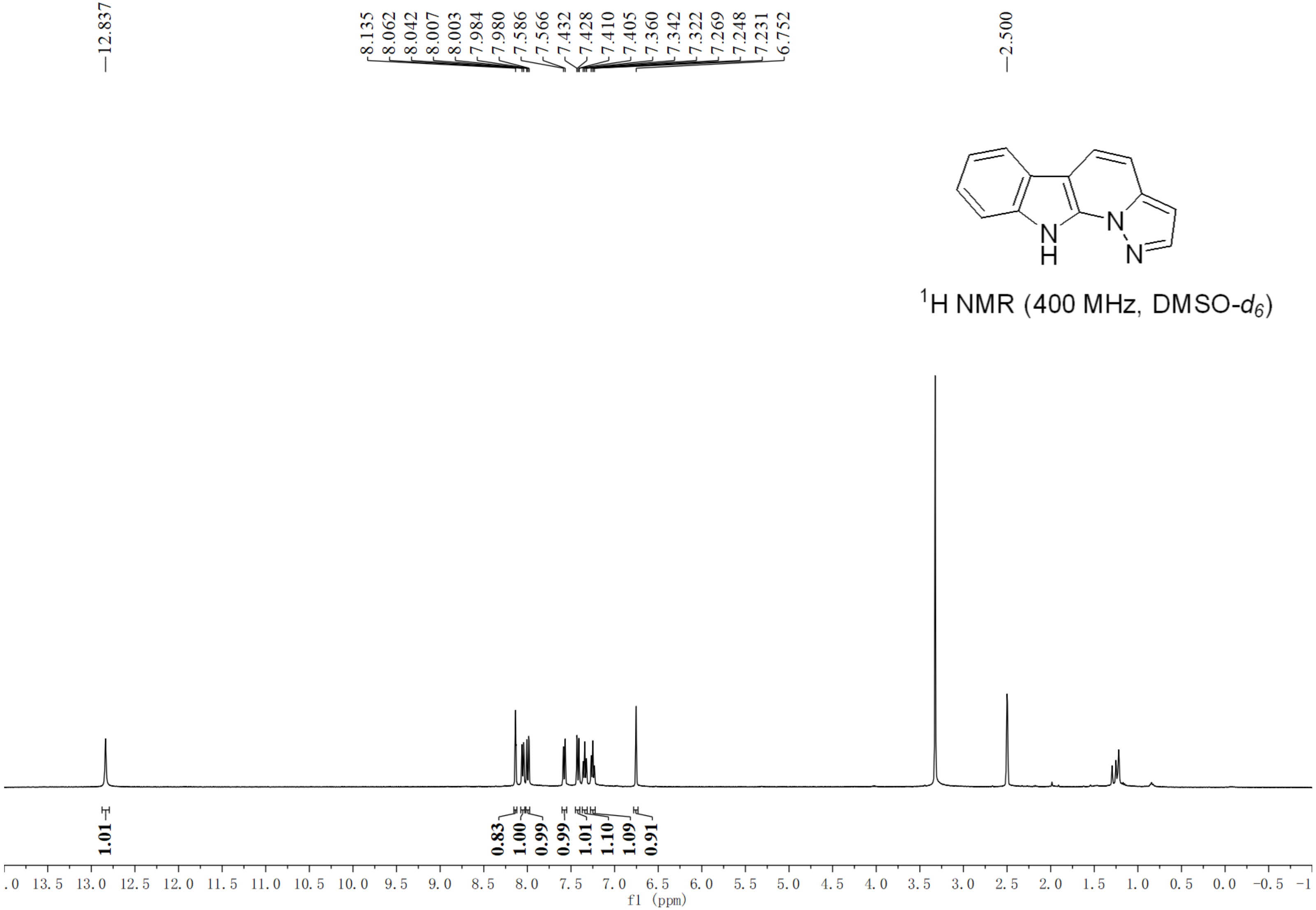


12.068
8.358
8.339
8.259
8.239
8.078
8.058
7.814
7.810
7.797
7.793
7.787
7.776
7.772
7.765
7.760
7.731
7.728
7.720
7.710
7.700
7.692
7.681
7.594
7.574
7.377
7.358
7.340
2.499
N
N
N
H
^{1}H NMR (400 MHz, DMSO-d_6)
1.00
2.01
1.07
4.08
1.10
f1 (ppm)

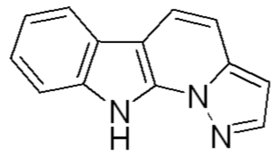


^{13}C NMR (100 MHz, DMSO-d_6)

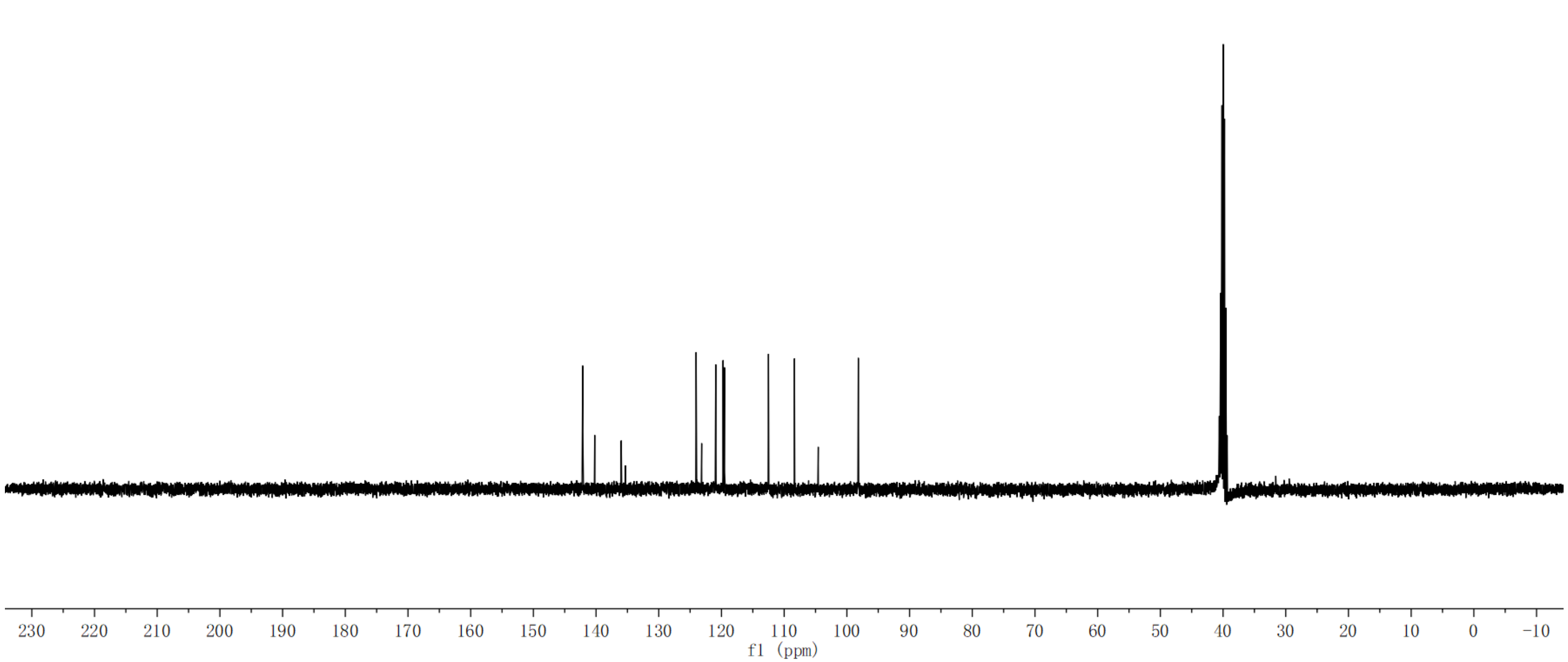


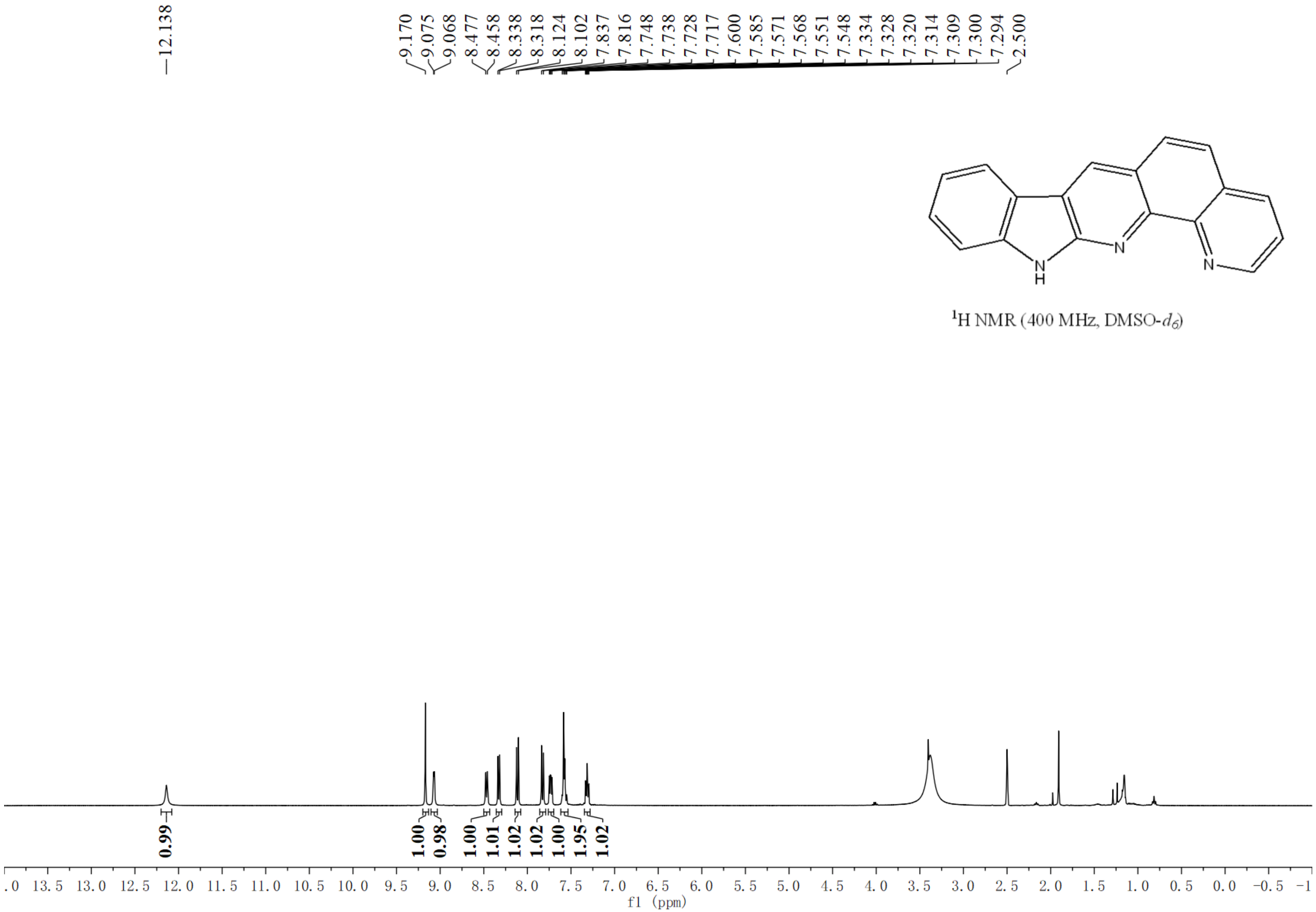


^{1}H NMR (400 MHz, DMSO-d_6)

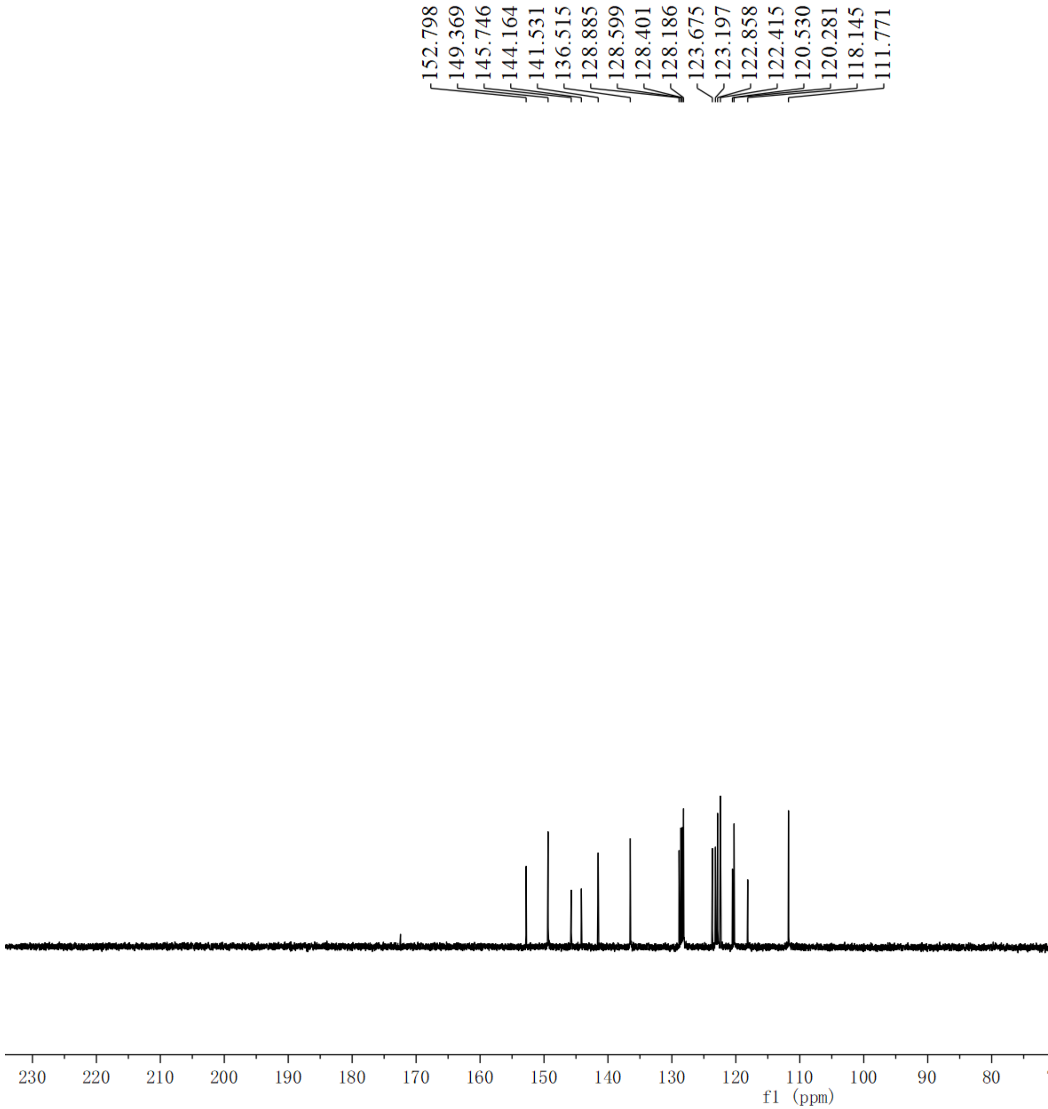


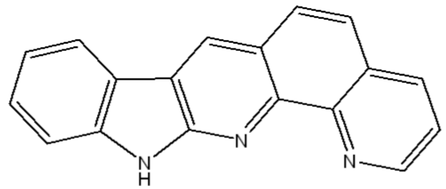
^{13}C NMR (400 MHz, DMSO-d_6)



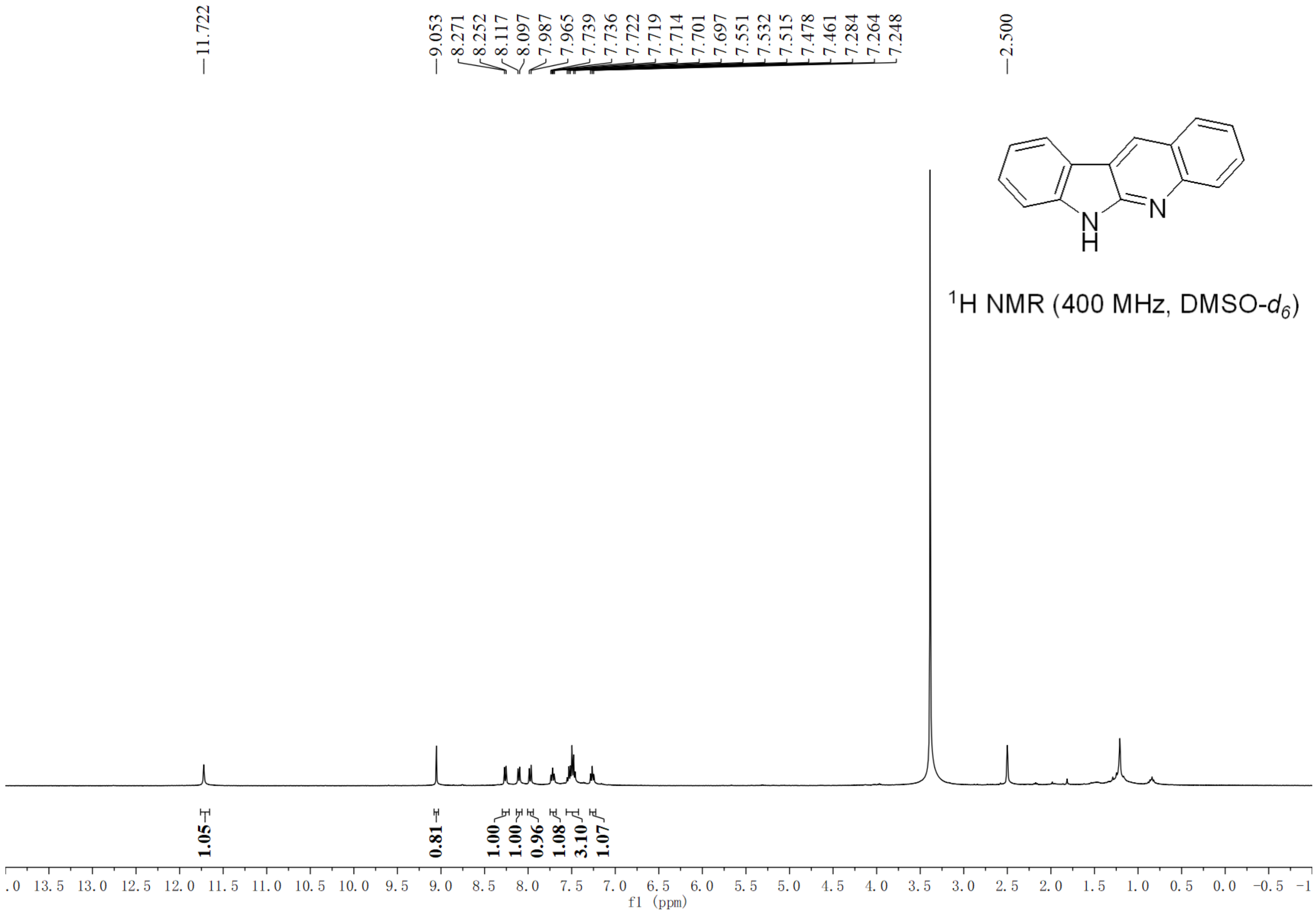


^{1}H NMR (400 MHz, DMSO-d_6)

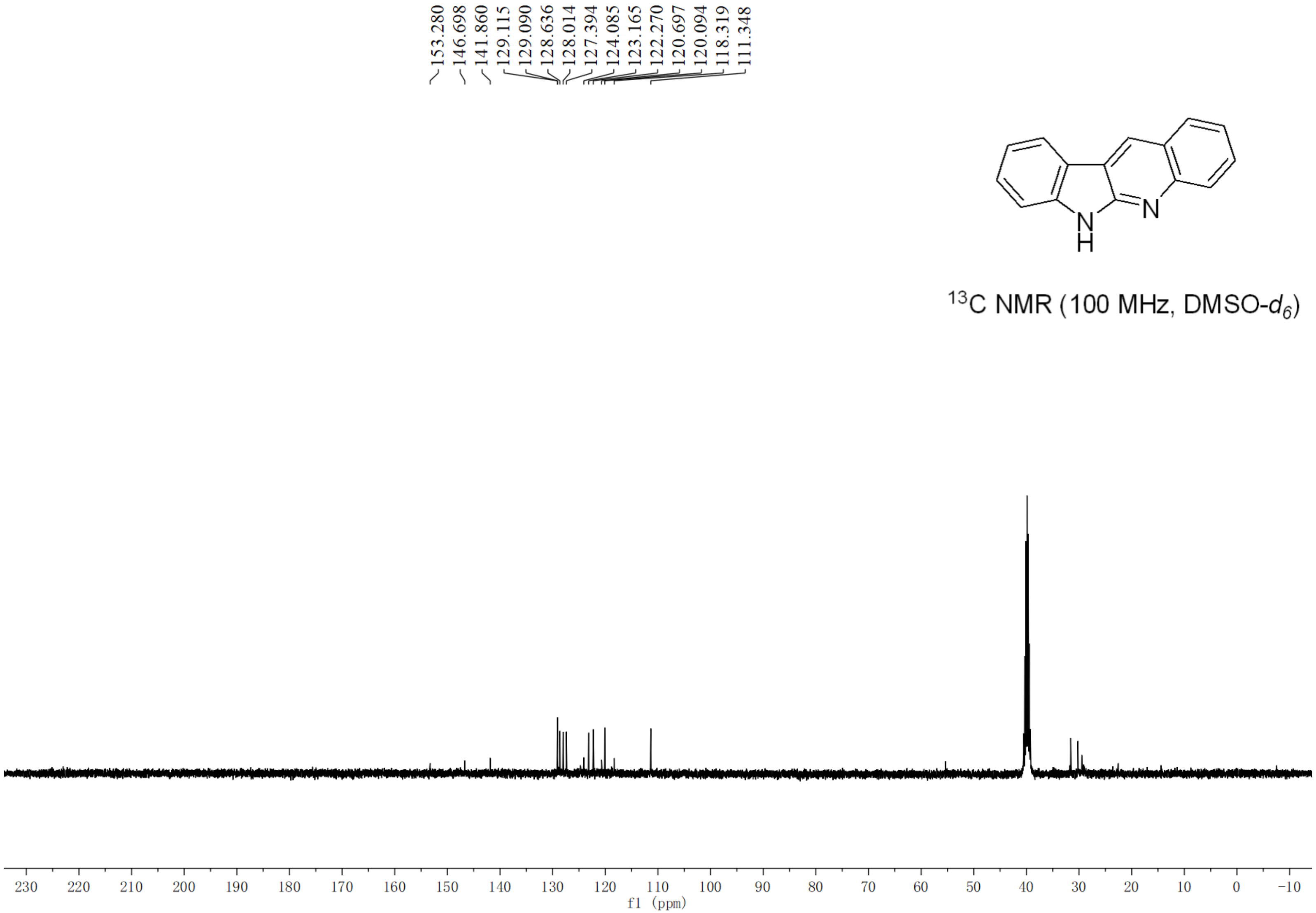




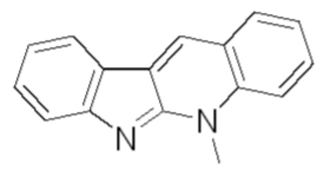
^{13}C NMR (400 MHz DMSO-d_6)



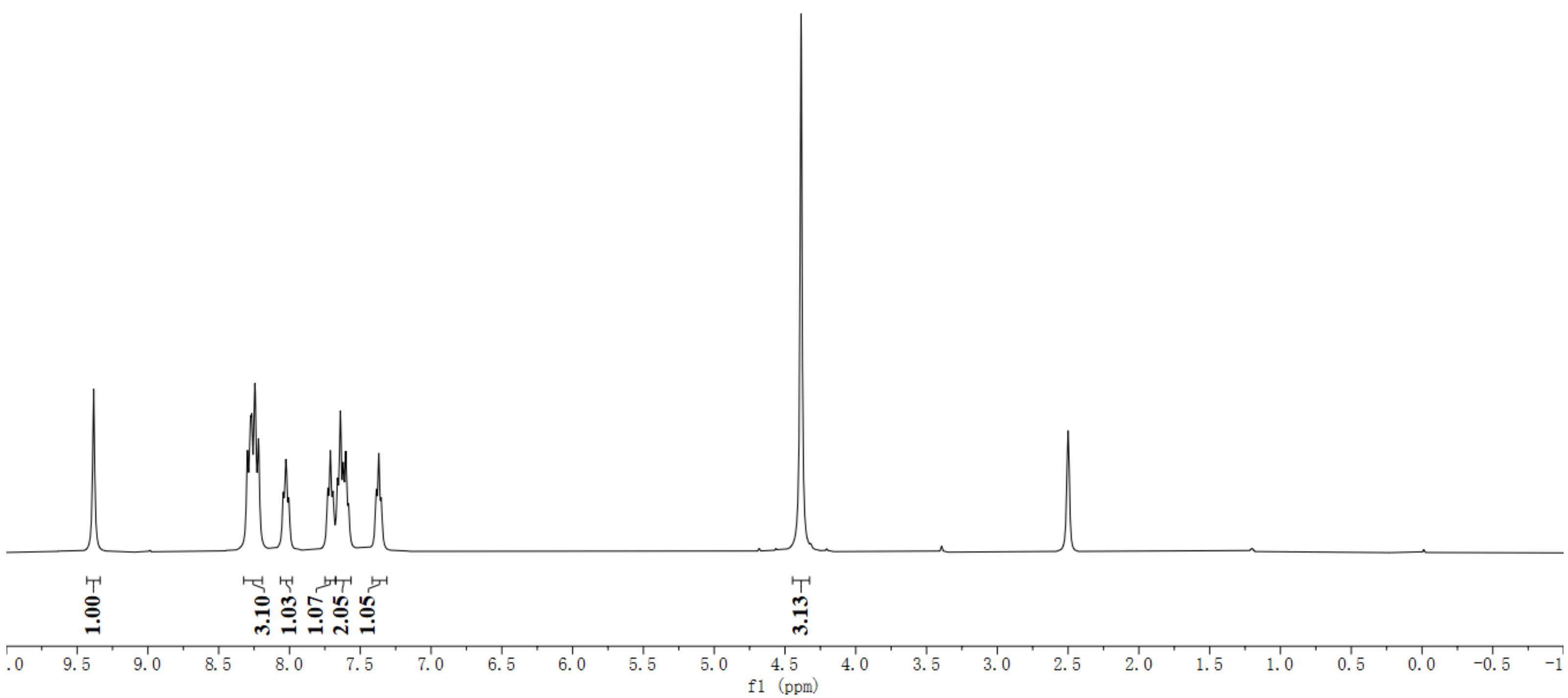
11.722
9.053
8.271
8.252
8.117
8.097
7.987
7.965
7.739
7.736
7.722
7.719
7.714
7.701
7.697
7.551
7.532
7.515
7.478
7.461
7.284
7.264
7.248
2.500
N
H
N
^{1}H NMR (400 MHz, DMSO-d_6)
1.05
0.81
1.00
1.00
0.96
1.08
3.10
1.07
f1 (ppm)

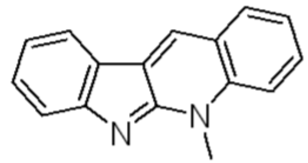


^{13}C NMR (100 MHz, DMSO-d_6)

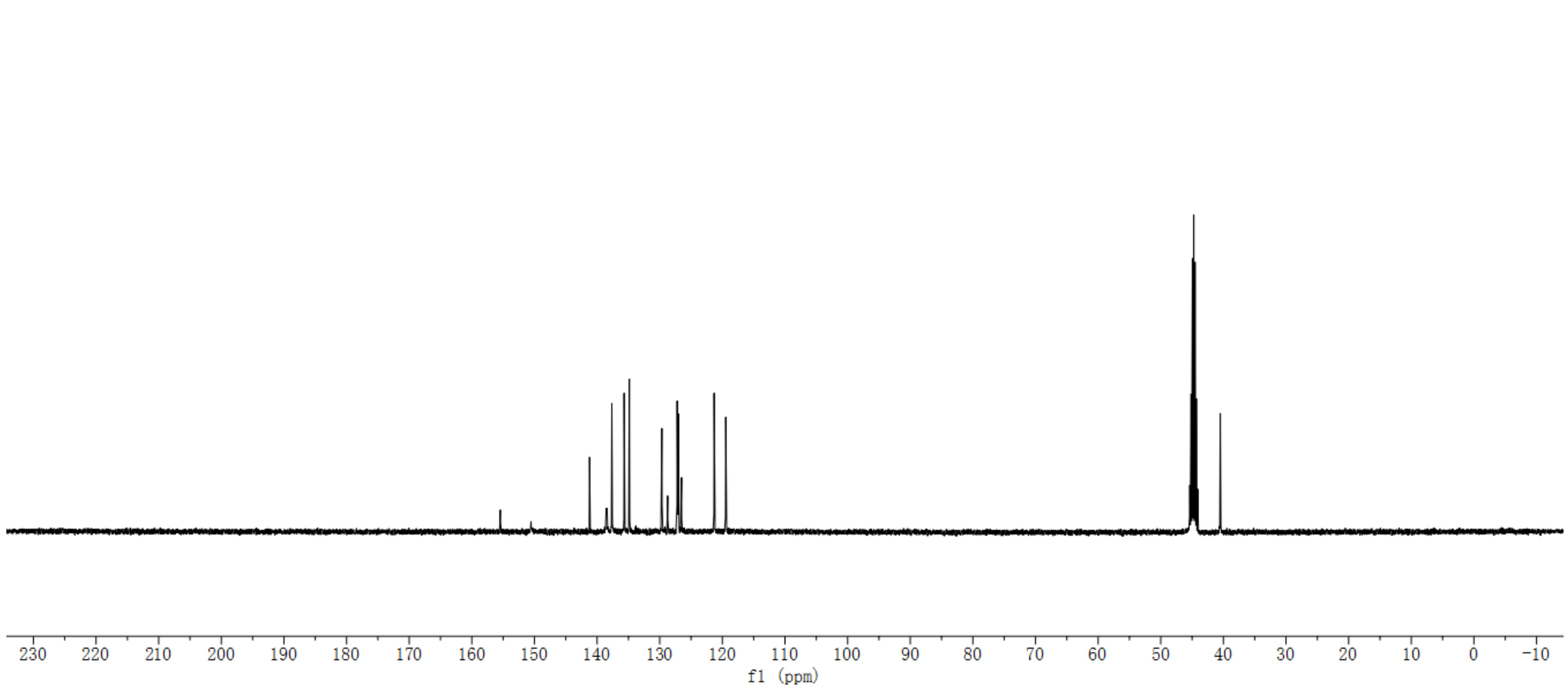


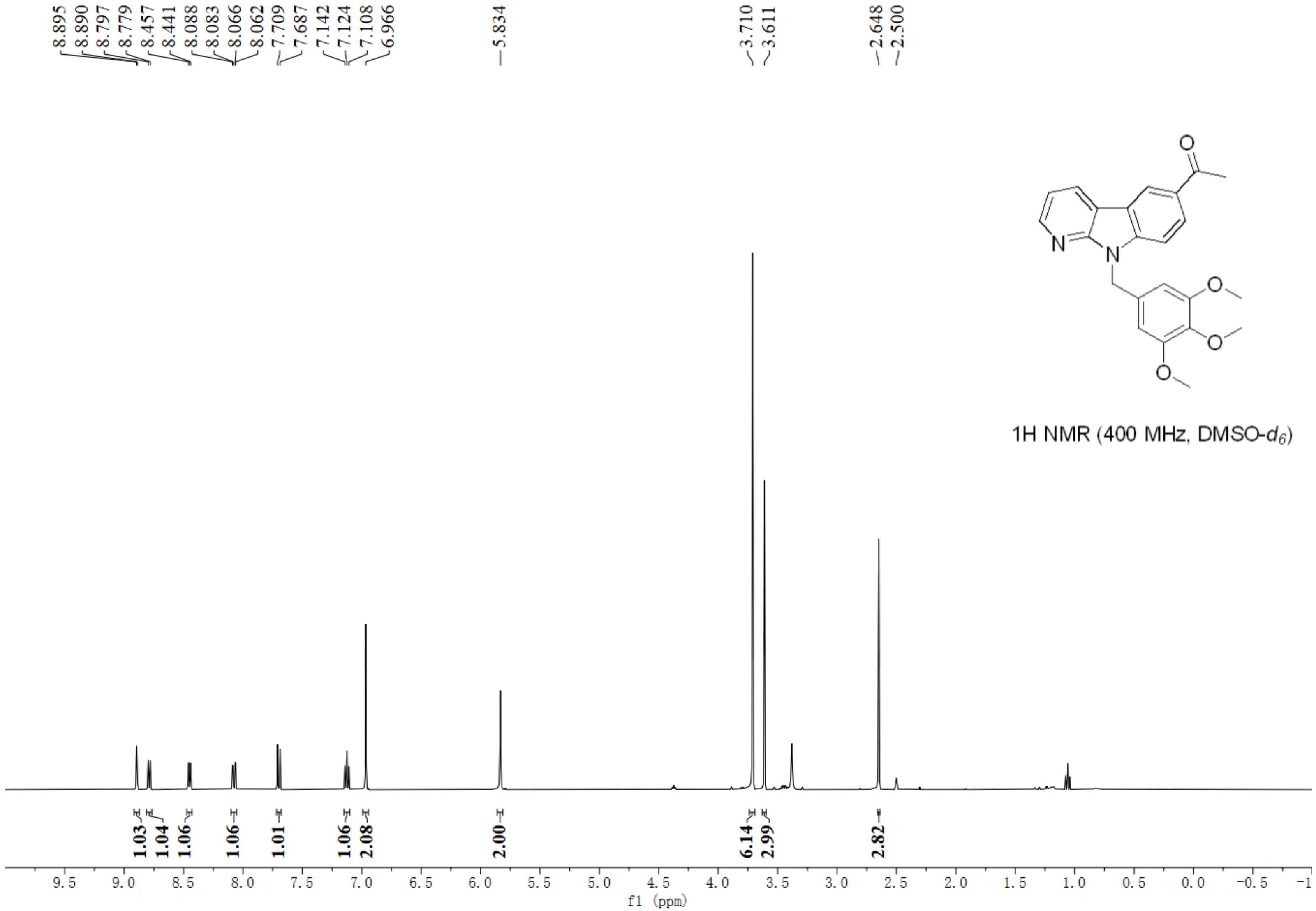
^{1}H NMR (400 MHz, DMSO-d_6)



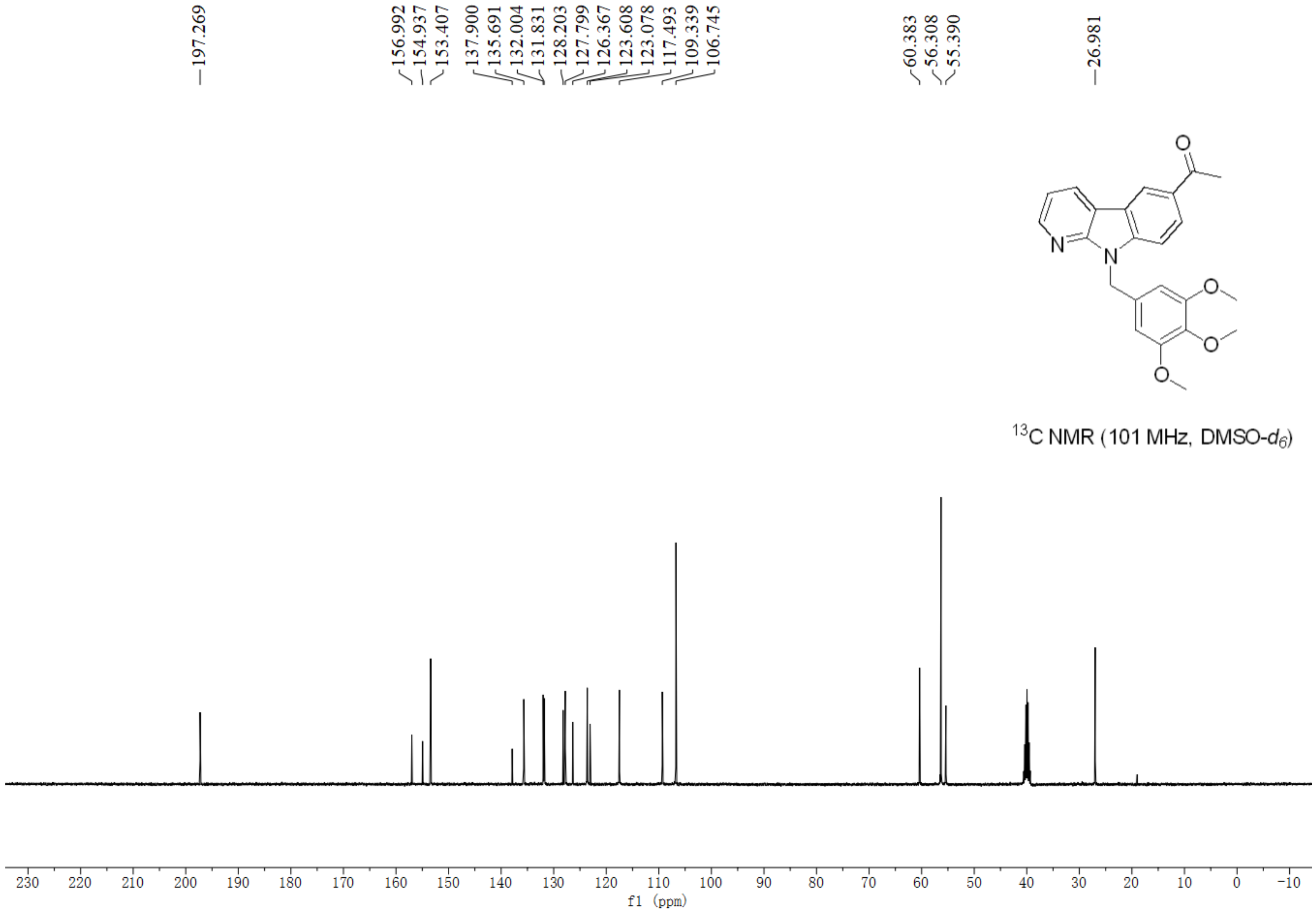


^{13}C NMR (100 MHz, DMSO-d_6)

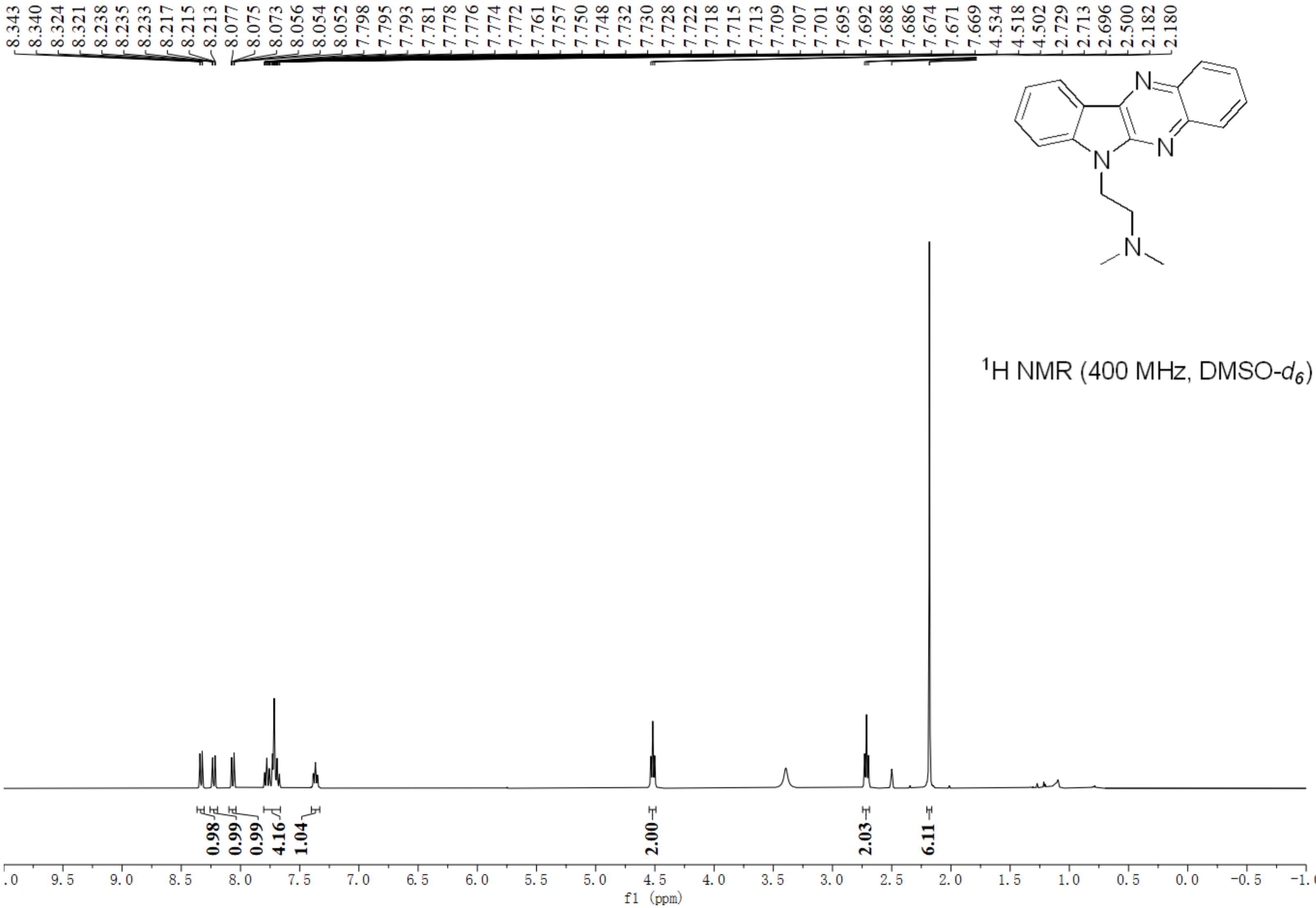


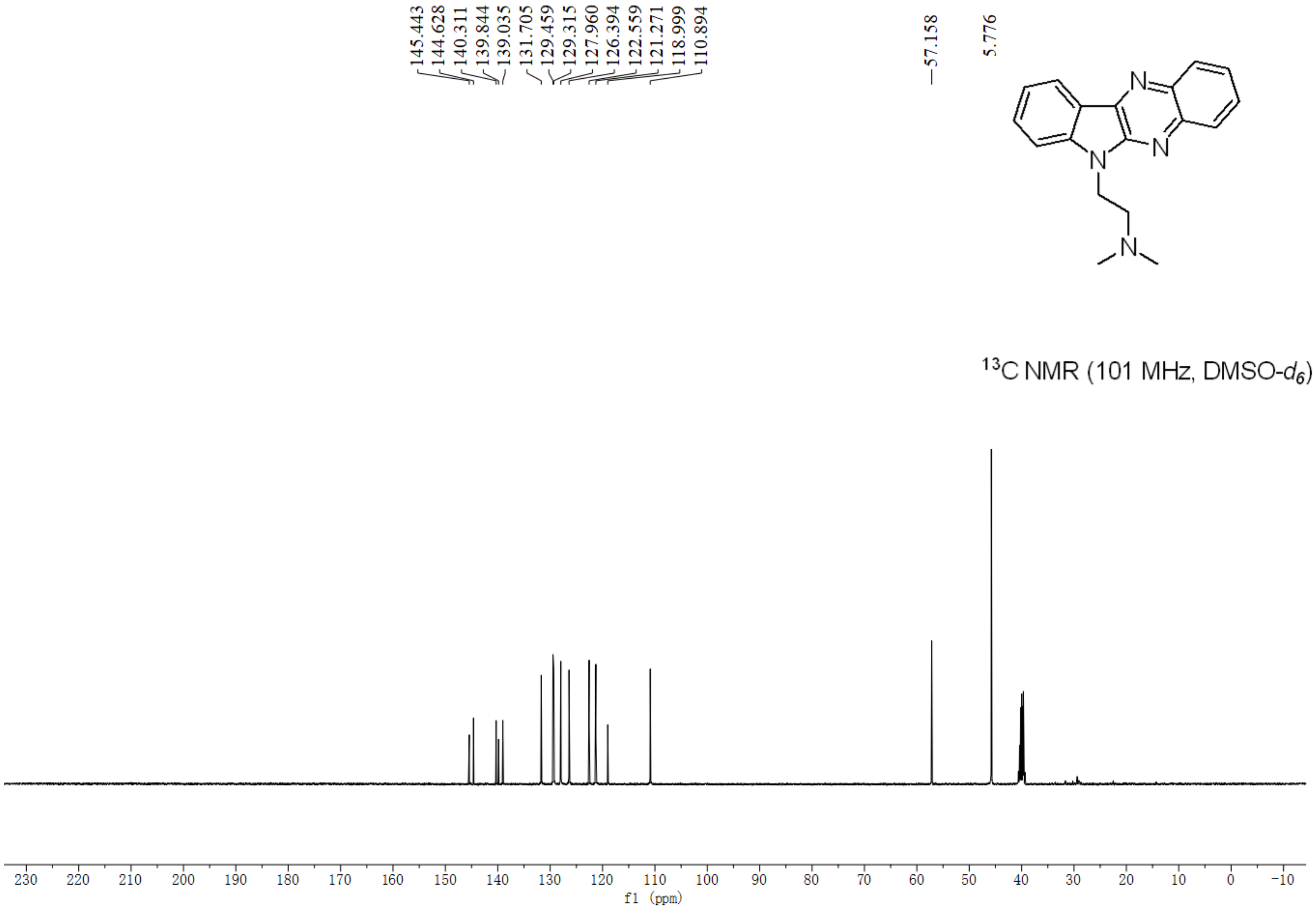


8.895
8.890
8.797
8.779
8.457
8.441
8.088
8.083
8.066
8.062
7.709
7.687
7.142
7.124
7.108
6.966
5.834
3.710
3.611
2.648
2.500
1H NMR (400 MHz, DMSO-d_6)
1.03
1.04
1.06
1.06
1.01
1.06
2.08
2.00
6.14
2.99
2.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)



197.269
156.992
154.937
153.407
137.900
135.691
132.004
131.831
128.203
127.799
126.367
123.608
123.078
117.493
109.339
106.745
60.383
56.308
55.390
26.981
O
N
N
O
O
O
13C NMR (101 MHz, DMSO-d6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.343 8.340 8.324 8.321 8.238 8.235 8.233 8.217 8.215 8.213 8.077 8.075 8.073 8.056 8.054 8.052 7.798 7.795 7.793 7.781 7.778 7.776 7.774 7.772 7.761 7.757 7.750 7.748 7.732 7.730 7.728 7.722 7.718 7.715 7.713 7.709 7.707 7.701 7.695 7.692 7.688 7.686 7.674 7.671 7.669 4.534 4.518 4.502 2.729 2.713 2.696 2.500 2.182 2.180
N
N
N
N
^{1}H NMR (400 MHz, DMSO-d_6)
0.98
0.99
0.99
4.16
1.04
2.00
2.03
6.11
f1 (ppm)



^{13}C NMR (101 MHz, DMSO-d_6)

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