Supporting Information

Redox-Neutral α-Functionalization of Pyrrolidines: Facile Access to α-Aryl Substituted Pyrrolidines

Feng-Xian Tian, Fan-Fan Liu, Jian Wei, Jia-Xi Xiao and Jin Qu*

The State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

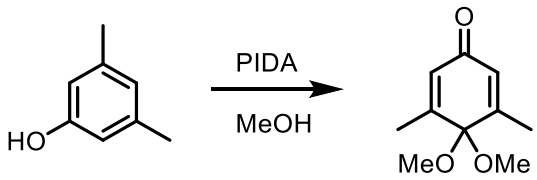
E-mail: qujin@nankai.edu.cn

Table of Contents

General Information.

Unless specially indicated, all materials were used as received from commercial sources without further purification. 2,2,2-trifluoroethanol (TFE) was purchased from J&K Scientific®. Analytical thin layer chromatography (TLC) was performed on Huanghai precoated (0.25 mm thickness) silica gel plates with F254 indicator. Visualization was accomplished with UV light (254 nm) or phosphomolybdic acid (PMA) stain solution. Flash chromatography was carried out with silica gel (200-300 mesh) supplied by Yantai Jiangyou Silica Gel Development Corporation. Melting points were measured by use of a microscope apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard in $CDCl_3$. ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.00 ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. Mass spectral analyses were performed for high-resolution MS (HRMS) on Varian 7.0T FTMS mass spectrometer (ESI).

Preparation of Quinone Monoacetal 2.



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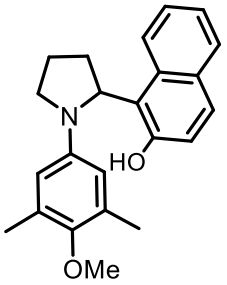
A dry nitrogen flushed round bottomed flask containing a magnetic stir bar was charged with 3,5-dimethylphenol (611 mg, 5 mmol) and dry methanol (10 mL). A solution of PIDA ((diacetoxyiodo)benzene) (3.22 g, 10 mmol) in methanol (25 mL) was slowly transferred via a double ended needle to the stirred phenol solution at room temperature. The resulting mixture was stirred for 40 min. The solvent was then removed and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 10:1) to give *p*-quinone monoacetal **2** (556 mg) in 61% yield as a light-yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 2H), 3.06 (s, 6H), 1.94 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 155.1, 131.8, 98.0, 50.8, 16.3. ^{1}H and ^{13}C NMR spectra are consistent with those of previous report.[1]

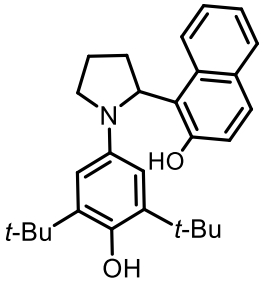
Preparation and Characterization of α-Substituted Pyrrolidines.

1-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-2-ol (3a)



A mixture of pyrrolidine (24 mg, 0.33 mmol), quinone monoacetal **2** (55 mg, 0.3 mmol), β-naphthol (66 mg, 0.45 mmol), and DABCO (7 mg, 0.06 mmol) in toluene (0.6 mL) were stirred and heated at 60 ºC for 11 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) to give **3a** as a light yellow solid (95 mg, 91%). M.p. 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.55−7.45 (m, 1H), 7.40−7.30 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.51 (s, 2H), 5.26 (dd, *J* = 8.6, 4.5 Hz, 1H), 3.94−3.83 (m, 1H), 3.61 (s, 3H), 3.31−3.19 (m, 1H), 2.66–2.48 (m, 1H), 2.26–2.03 (m, 3H), 2.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 151.4, 144.7, 131.5, 131.4, 129.0, 128.93, 128.89, 126.5, 122.6, 121.3, 119.8, 116.5, 116.2, 63.3, 59.8, 52.6, 34.7, 24.6, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{25}NO_2 + H]^+$ 348.1958, found 348.1962.

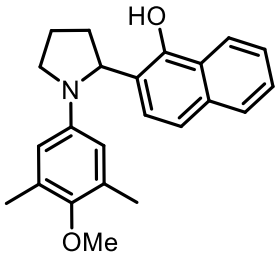
1-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)pyrrolidin-2-yl)naphthalen-2-ol (3a')



A mixture of pyrrolidine (24 mg, 0.33 mmol), quinone monoacetal **1** (55 mg, 0.3 mmol), β-naphthol (66 mg, 0.45 mmol), and DABCO (3.5 mg, 0.03 mmol) in toluene (0.6 mL) were stirred and heated at 60 ºC for 11 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) to give

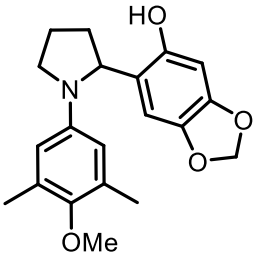
3a' as a brown solid (37 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.71 (s, 2H), 5.23 (t, *J* = 7.4 Hz, 1H), 4.75 (s, 1H), 4.02−3.90 (m, 1H), 33.34−3.20 (m, 1H), 2.65−2.51 (m, 1H), 2.31−2.20 (m, 1H), 2.20−2.06 (m, 2H), 1.19 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 148.2, 141.3, 136.4, 131.5, 128.9, 128.8, 126.4, 122.5, 120.9, 119.5, 116.6, 113.8, 62.8, 52.8, 34.4, 33.6, 29.9, 24.3; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{25}NO_2 + H]^+$ 348.1958, found 348.1962.

2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-1-ol (3b)



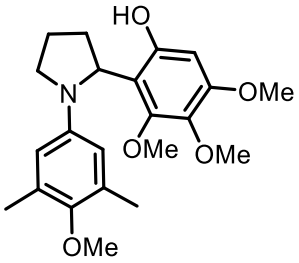
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 13.5 h, compound **3b** (92 mg, 88%) was obtained as a brown solid. M.p. 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.47–7.39 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.55 (s, 2H), 4.63 (dd, *J* = 7.5, 6.2 Hz, 1H), 3.95–3.86 (m, 1H), 3.61 (s, 3H), 3.31–3.19 (m, 1H), 2.50–2.37 (m, 1H), 2.24–2.09 (m, 2H), 2.16 (s, 6H), 2.08–1.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 151.1, 144.6, 133.4, 131.2, 127.2, 125.9, 125.6, 125.3, 124.9, 122.0, 119.3, 119.1, 116.6, 66.8, 59.8, 53.0, 35.7, 24.4, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{25}NO_2 + H]^+$ 348.1958, found 348.1956.

6-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)benzo[d][1,3]dioxol-5-ol (3c)



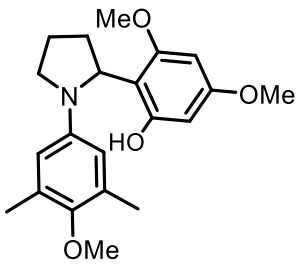
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 22.5 h, compound **3c** (95 mg, 93%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (brs, 1H), 6.58 (s, 1H), 6.51 (s, 2H), 6.32 (s, 1H), 5.89 (d, *J* = 12.6 Hz, 2H), 4.37 (t, *J* = 6.6 Hz, 1H), 3.85–3.75 (m, 1H), 3.64 (s, 3H), 3.25–3.12 (m, 1H), 2.41–2.28 (m, 1H), 2.20 (s, 6H), 2.15–2.02 (m, 2H), 2.01–1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 151.0, 147.0, 144.5, 140.7, 131.2, 118.1, 116.6, 106.7, 100.8, 99.0, 65.9, 59.8, 53.0, 35.4, 23.9, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{20}H_{23}NO_4 + H]^+$ 342.1700, found 342.1701.

3,4,5-trimethoxy-2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)phenol (3d)



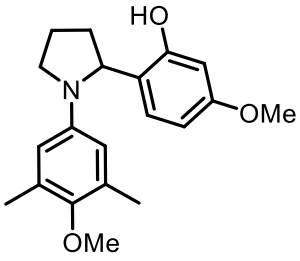
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 22.5 h, compound **3d** (90 mg, 77%) was obtained as a pale brown solid. M.p. 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (brs, 1H), 6.55 (s, 2H), 6.13 (s, 1H), 4.82 (dd, *J* = 8.1, 6.3 Hz, 1H), 3.99 (s, 3H), 3.82 (s, 3H), 3.81–3.75 (m, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 3.19–3.07 (m, 1H), 2.44–2.31 (m, 1H), 2.19 (s, 6H), 2.16–2.08 (m, 1H), 2.06–1.94 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 152.8, 151.2, 150.5, 144.7, 135.0, 131.1, 116.9, 111.6, 96.5, 60.92, 60.87, 60.3, 59.7, 55.6, 53.0, 34.6, 24.2, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{22}H_{29}NO_5 + H]^+$ 388.2118, found 388.2122.

3,5-dimethoxy-2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)phenol (3e)



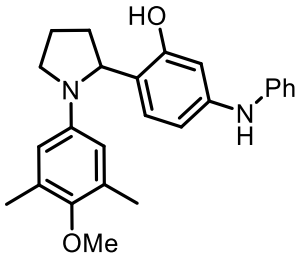
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 22.5 h, compound **3e** (73 mg, 68%) was obtained as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (brs, 1H), 6.51 (s, 2H), 6.04 (s, 1H), 5.97 (s, 1H), 4.84 (dd, *J* = 8.2, 5.8 Hz, 1H), 3.83 (s, 3H), 3.81–3.76 (m, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 3.17–3.06 (m, 1H), 2.39–2.28 (m, 1H), 2.19 (s, 6H), 2.13–2.03 (m, 1H), 2.01–1.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 158.5, 157.6, 151.2, 144.8, 131.0, 116.8, 107.1, 93.9, 90.5, 60.0, 59.8, 55.6, 55.1, 52.8, 34.1, 24.3, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{21}H_{27}NO_4 + H]^+$ 358.2013, found 358.2014.

5-methoxy-2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)phenol (3f)



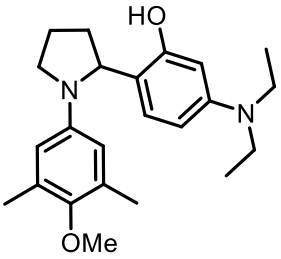
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 23.5 h, compound **3f** (51 mg, 52%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (brs, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 2H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 4.46 (t, *J* = 7.1 Hz, 1H), 3.85– 3.78 (m, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.23–3.12 (m, 1H), 2.38–2.29 (m, 1H), 2.18 (s, 6H), 2.08 (m, 2H), 2.01–1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 157.2, 151.0, 144.6, 131.1, 128.2, 119.1, 116.7, 106.0, 102.0, 65.6, 59.8, 55.2, 53.0, 35.6, 23.9, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{20}H_{25}NO_3 + H]^+$ 328.1907, found 328.1902.

2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)-5-(phenylamino)phenol (3g)



Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 24 h, compound **3g** (92 mg, 79%) was obtained as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (brs, 1H), 7.28–7.19 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.58–6.54 (m, 1H), 6.53 (s, 2H), 6.49 (s, 1H), 5.65 (s, 1H), 4.45 (t, *J* = 6.9 Hz, 1H), 3.86–3.74 (m, 1H), 3.62 (s, 3H), 3.23–3.12 (m, 1H), 2.39–2.29 (m, 1H), 2.19 (s, 6H), 2.15–2.02 (m, 2H), 2.01–1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 150.8, 144.6, 143.2, 142.8, 131.1, 129.2, 128.3, 120.9, 119.5, 118.1, 116.6, 109.1, 105.4, 65.5, 59.8, 52.9, 35.5, 23.9, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{25}H_{28}N_2O_2 + H]^+$ 389.2224, found 389.2226..

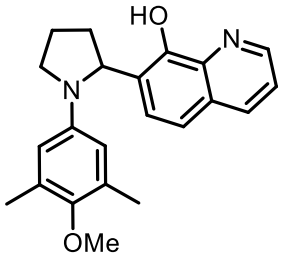
5-(diethylamino)-2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)phenol (3h)



Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 24 h, compound **3h** (64 mg, 58%) was obtained as a violet solid. M.p. 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (brs, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.53 (s, 2H), 6.20 (d, *J* = 8.4 Hz, 1H), 6.08 (s, 1H), 4.44 (t, *J* = 6.2 Hz, 1H), 3.83–3.71 (m, 1H), 3.63 (s, 3H), 3.28 (q, *J* = 7.0 Hz, 4H), 3.21–3.09 (m, 1H),

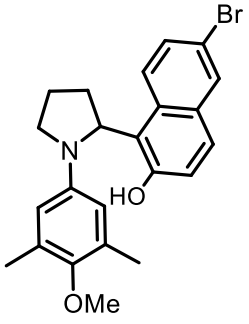
2.35–2.23 (m, 1H), 2.19 (s, 6H), 2.13–2.01 (m, 2H), 1.99–1.86 (m, 1H), 1.13 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 150.4, 148.0, 144.9, 130.8, 128.2, 116.3, 114.0, 103.7, 99.7, 65.2, 59.7, 52.7, 44.1, 35.6, 23.9, 16.3, 12.6; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{32}N_2O_2 + H]^+$ 369.2537, found 369.2539.

7-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)quinolin-8-ol (3i)



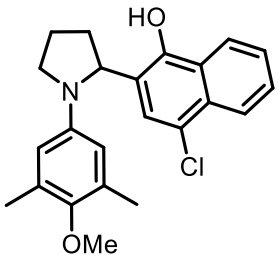
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated at 60 ºC for 24 h, compound **3i** (26 mg, 25%) was obtained as a yellow solid. M.p. 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.2 Hz, 1H), 8.55 (brs, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 6.20 (s, 2H), 5.19 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.78–3.70 (m, 1H), 3.62 (s, 3H), 3.46–3.34 (m, 1H), 2.50–2.38 (m, 1H), 2.16 (s, 6H), 2.11–2.05 (m, 1H), 2.05–1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.8, 143.7, 138.0, 136.0, 131.1, 127.3, 126.6, 126.3, 121.1, 117.2, 112.0, 60.0, 57.9, 49.5, 34.3, 23.7, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{22}H_{24}N_2O_2 + H]^+$ 349.1911, found 349.1905.

6-bromo-1-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-2-ol (3j)



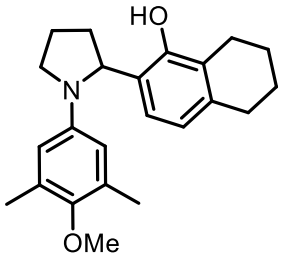
A mixture of pyrrolidine (24 mg, 0.33 mmol), quinone monoacetal **2** (55 mg, 0.3 mmol), 6-bromo-2-naphthol (101 mg, 0.45 mmol), DABCO (7 mg, 0.06 mmol), and 4Å molecular sieves (100 mg) in toluene (0.6 mL) were stirred and heated at 60 ºC for 23 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) to give **3j** as a brown solid (85 mg, 66%). M.p. 157−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.58–7.55 (m, 1H), 7.55–7.52 (m, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.48 (s, 2H), 5.19 (dd, *J* = 8.9, 5.0 Hz, 1H), 3.93–3.84 (m, 1H), 3.62 (s, 3H), 3.29–3.19 (m, 1H), 2.62–2.49 (m, 1H), 2.28–2.16 (m, 1H), 2.12 (s, 6H), 2.11–2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 151.6, 144.5, 131.4, 130.9, 130.2, 130.0, 129.6, 128.1, 123.0, 121.0, 116.6, 116.1, 63.1, 59.8, 52.7, 34.7, 24.6, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{24}BrNO_2 + H]^+$ 426.1063, found 426.1059.

4-chloro-2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-1-ol (3k)



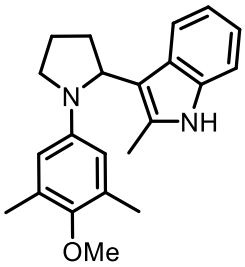
Following the general procedure for the preparation of **3a** and the reaction was stirred and heated for 28.5 h, compound **3k** (109 mg, 95%) was obtained as a yellow solid. M.p. 100−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.16 (dd, *J* = 13.8, 8.3 Hz, 2H), 7.60–7.52 (m, 1H), 7.52–7.44 (m, 1H), 7.31 (s, 1H), 6.54 (s, 2H), 4.59 (dd, *J* = 8.3, 5.4 Hz, 1H), 3.95–3.82 (m, 1H), 3.62 (s, 3H), 3.32–3.16 (m, 1H), 2.49–2.41 (m, 1H), 2.18 (s, 6H), 2.22–2.09 (m, 2H), 2.08–1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 151.2, 144.3, 131.4, 130.3, 127.0, 126.5, 125.6, 125.3, 123.9, 122.5, 121.8, 119.6, 116.6, 66.5, 59.8, 53.0, 35.8, 24.4, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{24}NO_2Cl + H]^+$ 382.1568, found 382.1564.

2-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)-5,6,7,8-tetrahydronaphthalen-1-ol (3l)



Following the general procedure for the preparation of **3a** and the reaction was stirred and heated for 22.5 h, compound **3l** (77 mg, 68%) was obtained as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (brs, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 2H), 4.46 (dd, *J* = 7.6, 6.5 Hz, 1H), 3.87–3.79 (m, 1H), 3.63 (s, 3H), 3.24–3.15 (m, 1H), 2.75–2.68 (m, 2H), 2.61–2.54 (m, 2H), 2.37–2.28 (m, 1H), 2.19 (s, 6H), 2.15–2.03 (m, 2H), 2.01–1.89 (m, 1H), 1.81–1.67 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 150.8, 144.8, 137.0, 131.0, 124.9, 124.2, 122.8, 120.0, 116.6, 66.0, 59.8, 53.2, 35.6, 29.5, 24.1, 22.85, 22.77, 22.7, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{29}NO_2 + H]^+$ 352.2271, found 352.2266.

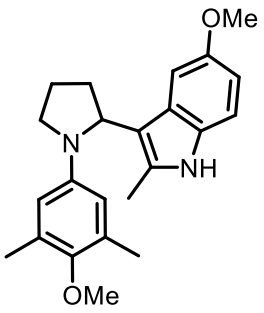
3-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)-2-methyl-1H-indole (3m)



A mixture of pyrrolidine (107 mg, 1.5 mmol), quinone monoacetal **2** (55 mg, 0.3 mmol), 2-methylindole (394 mg, 1.5 mmol), and DABCO (7 mg, 0.06 mmol) in toluene (0.6 mL) were stirred and heated at 60 ºC for 24 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 10:1) to give **3m** as a brown solid (56 mg, 56%). M.p. 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

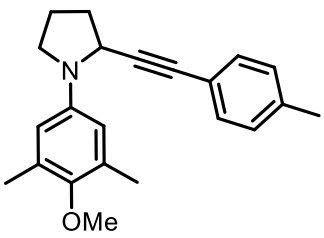
7.63 (brs, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 11.1 Hz, 1H), 7.12–7.01 (m, 2H), 6.20 (s, 2H), 4.94 (d, *J* = 7.7 Hz, 1H), 3.67–3.56 (m, 1H), 3.60 (s, 3H), 3.39–3.26 (m, 1H), 2.35–2.26 (m, 1H), 2.24 (s, 3H), 2.15 (s, 6H), 2.10–2.02 (m, 2H), 2.02–1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 144.2, 135.1, 130.8, 130.5, 127.4, 120.7, 119.0, 118.4, 113.7, 111.7, 110.1, 59.9, 56.5, 49.4, 35.0, 24.5, 16.5, 12.0; HRMS (ESI) (*m*/*z*): calcd for $[C_{22}H_{27}N_2O + H]^+$ 335.2118, found 335.2120.

5-methoxy-3-(1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)-2-methyl-1H-indole (3n)



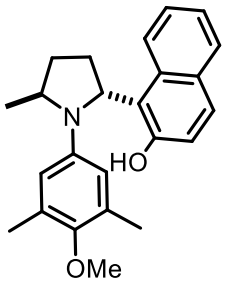
Following the general procedure for the preparation of **3m**, compound **3n** (67 mg, 60%) was obtained as a brown solid. M.p. 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (brs, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.97 (s, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.20 (s, 2H), 4.89 (d, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.65–3.57 (m, 1H), 3.60 (s, 3H), 3.39–3.27 (m, 1H), 2.34–2.25 (m, 1H), 2.22 (s, 3H), 2.15 (s, 6H), 2.09–1.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 147.5, 144.1, 131.5, 130.8, 130.3, 127.8, 113.4, 111.7, 110.6, 109.9 101.2, 59.9, 56.4, 55.9, 49.4, 34.9, 24.6, 16.5, 12.1; HRMS (ESI) (*m*/*z*): calcd for $[C_{23}H_{28}N_2O_2 + H]^+$ 365.2224, found 365.2222.

1-(4-methoxy-3,5-dimethylphenyl)-2-(p-tolylethynyl)pyrrolidine (3o)



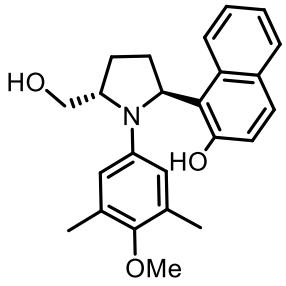
A mixture of pyrrolidine (24 mg, 0.33 mmol), quinone monoacetal **2** (55 mg, 0.3 mmol), DABCO (7 mg, 0.06 mmol), and copper iodide (9 mg, 0.045 mmol) was added in toluene (0.6 mL) in a round bottom flask and stirred at room temperature for 30 min under argon. 4-Ethynyltoluene (52 mg, 0.45 mmol) was then added in portions and the reaction mixture was stirred and heated at 80 ºC for 24 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) to give **3o** as a yellow liquid (29 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.44 (s, 2H), 4.47 (dd, *J* = 6.4, 2.9 Hz, 1H), 3.67 (s, 3H), 3.47–3.37 (m, 1H), 3.29–3.19 (m, 1H), 2.31 (s, 3H), 2.28 (s, 6H), 2.26–2.17 (m, 3H), 2.08–2.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 143.2, 137.9, 131.6, 131.1, 128.8, 120.2, 112.5, 89.5, 82.6, 60.0, 50.5, 48.0, 34.0, 24.3, 21.4, 16.5; HRMS (ESI) (*m*/*z*): calcd for $[C_{22}H_{25}NO + H]^+$ 320.2009, found 320.2005.

1-(1-(4-methoxy-3,5-dimethylphenyl)-5-methylpyrrolidin-2-yl)naphthalen-2-ol (4a)



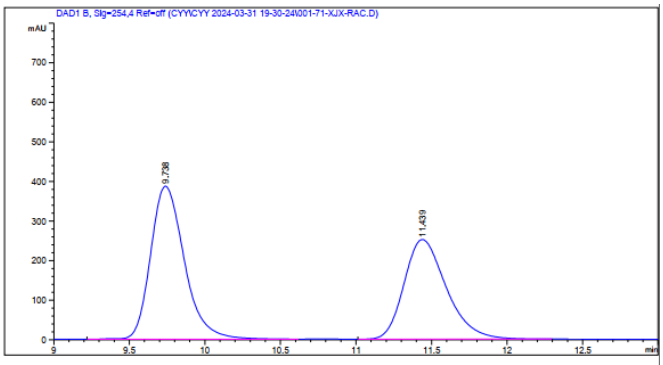
Following the general procedure for the preparation of **3a**, compound **4a** (76 mg, 70%) was obtained as light brown solid. M.p. 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (brs, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.47–7.39 (m, 1H), 7.32–7.24 (m, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.65 (s, 2H), 5.24 (t, *J* = 7.3 Hz, 1H), 3.83–3.69 (m, 1H), 3.59 (s, 3H), 2.53–2.42 (m, 1H), 2.25–2.14 (m, 1H), 2.13 (s, 6H), 2.11–2.07 (m, 1H), 1.90–1.77 (m, 1H), 1.49 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 152.2, 144.1, 131.5, 131.2, 128.9, 128.8, 128.6, 126.3, 122.4, 121.1, 119.7, 118.4, 116.0, 66.4, 60.5, 59.6, 32.6, 32.4, 21.3, 16.3; HRMS (ESI) (*m*/*z*): calcd for $[C_{24}H_{27}NO_2 + H]^+$ 362.2115, found 362.2108.

1-((2*S*,5*S*)-5-(hydroxymethyl)-1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-2-ol (4b)



1-((2*S*,5*S*)-5-(hydroxymethyl)-1-(4-methoxy-3,5-dimethylphenyl)pyrrolidin-2-yl)naphthalen-2-ol

Following the general procedure for the preparation of **3a**, compound **4b** (57 mg, 50%) was obtained as a light-red solid using (*S*)-Prolinol as the substrate. M.p. 191−193 °C; $[\alpha]_D^{22}$ = −351.6 (*c* = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (brs, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.52–7.43 (m, 1H), 7.37–7.27 (m, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.71 (s, 2H), 5.33 (t, *J* = 7.8 Hz, 1H), 4.02–3.91 (m, 2H), 3.91–3.81 (m, 1H), 3.59 (s, 3H), 2.60–2.49 (m, 1H), 2.26 (brs, 1H), 2.22–2.12 (m, 2H), 2.10 (s, 6H), 2.07–2.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.3, 144.5, 131.7, 131.3, 129.0, 128.9, 128.8, 126.5, 122.5, 120.9, 119.7, 118.6, 115.5, 66.7, 65.4, 64.9, 59.7, 32.2, 27.4, 16.4; HRMS (ESI) (*m*/*z*): calcd for $[C_{24}H_{27}NO_3 + H]^+$ 378.2064, found 378.2059. The enantiomeric purity (>99 %) was determined by HPLC column: chiralpak IC-3; solvent 2-propanol: hexane (1:9); light: 254 nm; flow :1 mL/min; t_R = 11.4 min (2*S*, 5*S*, major), 9.7 min (2*R*, 5*R*, minor).



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面积百分比报告

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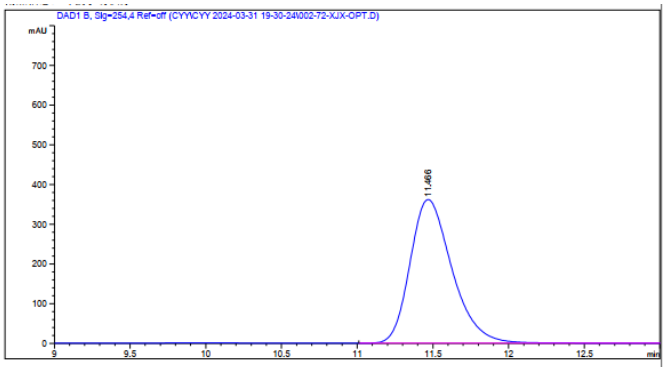
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=254,4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.738	BB	0.2433	6008.23730	386.61212	55.1279
2	11.439	BB	0.2966	4890.48438	251.83028	44.8721

总量 : 1.08987e4 638.44240



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面积百分比报告

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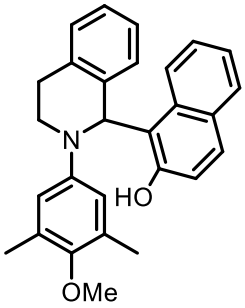
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=254,4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.466	BB	0.2943	6952.99658	361.71466	100.0000

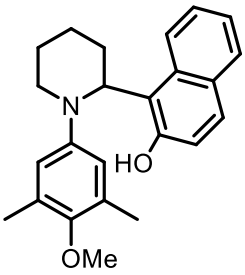
总量 : 6952.99658 361.71466

1-(2-(4-methoxy-3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol (4c)



Following the general procedure for the preparation of **3a**, compound **4c** (48 mg, 39%) was obtained as a white solid. M.p. 167−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (brs, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.66–7.46 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20–7.13 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.95 (s, 2H), 6.94 (d, *J* = 9.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.34 (s, 1H), 3.62–3.57 (m, 1H), 3.59–3.47 (m, 1H), 3.54 (s, 3H), 3.38–3.25 (m, 1H), 3.03–2.92 (m, 1H), 2.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 154.4, 145.3, 136.5, 133.6, 133.4, 131.2, 129.4, 128.9, 128.4, 128.2, 127.5, 127.0, 126.6, 126.4, 123.2, 122.4, 121.0, 119.6, 118.7, 59.5, 59.4, 55.6, 30.6, 16.1; HRMS (ESI) (*m*/*z*): calcd for $[C_{28}H_{27}NO_2 + H]^+$ 410.2115, found 410.2112.

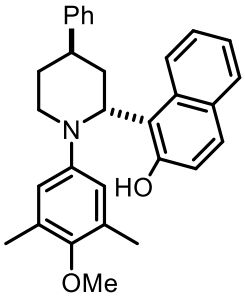
1-(1-(4-methoxy-3,5-dimethylphenyl)piperidin-2-yl)naphthalen-2-ol (4d)



Following the general procedure for the preparation of **3a**, compound **4d** (13 mg, 12%) was obtained as a light yellow solid. M.p. 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (brs, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.57–7.45 (m, 2H), 7.31–7.24 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.82 (s, 2H), 4.96–4.85 (m, 1H), 3.53 (s, 3H), 3.53–3.41 (m, 1H), 2.73–2.59 (m, 1H), 2.03 (s, 6H), 2.01–1.93 (m, 3H), 1.93–1.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 146.0, 131.5, 130.9, 129.4, 128.9, 128.6, 128.5, 126.4, 123.2, 122.2, 120.2, 119.3, 118.5, 59.8, 59.5, 58.5, 30.8,

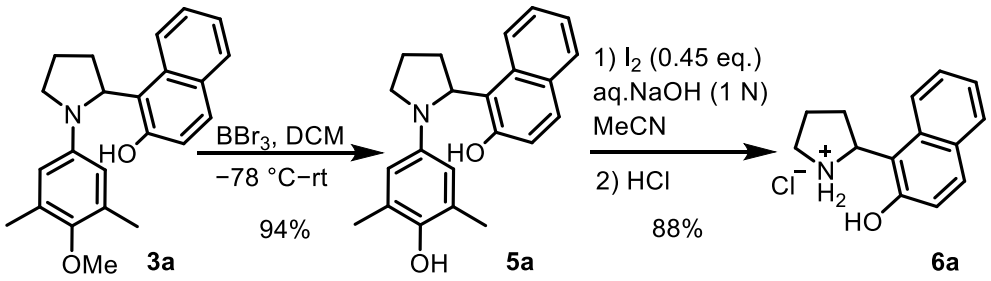
26.5, 24.5, 16.2; HRMS (ESI) (*m*/*z*): calcd for $[C_{24}H_{27}NO_2 + H]^+$ 362.2115, found 362.2107.

1-(1-(4-methoxy-3,5-dimethylphenyl)-4-phenylpiperidin-2-yl)naphthalen-2-ol (4e)



Following the general procedure for the preparation of **3a**, compound **4e** (30 mg, 23%) was obtained as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (brs, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.56–7.45 (m, 2H), 7.30–7.22 (m, 5H), 7.20–7.12 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 2H), 5.16–5.06 (m, 1H), 3.68–3.59 (m, 1H), 3.54 (s, 3H), 2.97–2.82 (m, 2H), 2.25–2.17 (m, 2H), 2.18–2.06 (m, 2H), 2.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 154.1, 145.5, 144.8, 131.4, 131.1, 128.9, 128.8, 128.6, 128.4, 126.7, 126.5, 126.4, 123.2, 122.3, 120.1, 119.3, 117.8, 59.6, 59.5, 58.5, 42.4, 38.0, 33.9, 16.2; HRMS (ESI) (*m*/*z*): calcd for $[C_{30}H_{31}NO_2 + H]^+$ 438.2428, found 438.2423.

2-(2-hydroxynaphthalen-1-yl)pyrrolidin-1-ium chloride (6a)

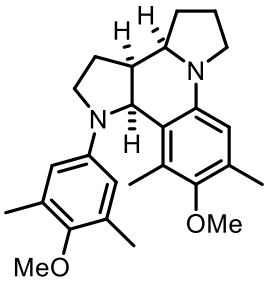


To the solution of **3a** (174 mg, 0.5 mmol) in DCM (5 mL) at −78 °C was slowly added BBr_3 (501 mg, 2 mmol) under argon protection. Then the reaction temperature

was allowed to rise to room temperature. After completion, 15% aqueous solution of $NaHCO_3$ (5 mL) was poured into the reaction at 0 °C. The aqueous layer was extracted with EtOAc (20 mL×3) and the combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (PE: EtOAc = 20:1) to give product **5a** (157 mg, 94%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (brs, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.53–7.43 (m, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.53 (s, 2H), 5.27–5.17 (m, 1H), 4.30 (br, 1H), 3.92–3.80 (m, 1H), 3.25–3.14 (m, 1H), 2.64–2.49 (m, 1H), 2.27–2.15 (m, 1H), 2.14–2.02 (m, 2H), 2.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 147.1, 141.9, 131.6, 129.0, 128.9, 128.8, 126.4, 123.8, 122.5, 121.2, 119.8, 117.0, 116.2, 63.3, 53.1, 34.5, 24.5, 16.3.

Compound **5a** (157 mg, 0.48 mmol) was dissolved in the mixed solvent of MeCN (9 mL) and aq. NaOH (1 N, 14 mL), and iodine (55 mg, 0.22 mmol) were added subsequently. After 10 min, the reaction mixture was extracted with DCM (20 mL×3). The combined organic layer was washed with aqueous 2M HCl (20 mL×2). The combined acidic aqueous solution was washed with hexane (20 mL×2) and then concentrated under reduced pressure. The residue containing the product was washed with DCM, dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford **6a** (103 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, CD_3OD) δ 8.03 (d, *J* = 8.6 Hz, 1H), 7.86–7.78 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 5.48 (t, *J* = 8.7 Hz, 1H), 3.74–3.63 (m, 1H), 3.57–3.46 (m, 1H), 2.47–2.36 (m, 2H), 2.36–2.16 (m, 2H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.7, 133.8, 132.2, 130.2, 129.9, 128.6, 124.4, 122.2, 118.7, 112.7, 58.9, 47.2, 30.9, 26.0.

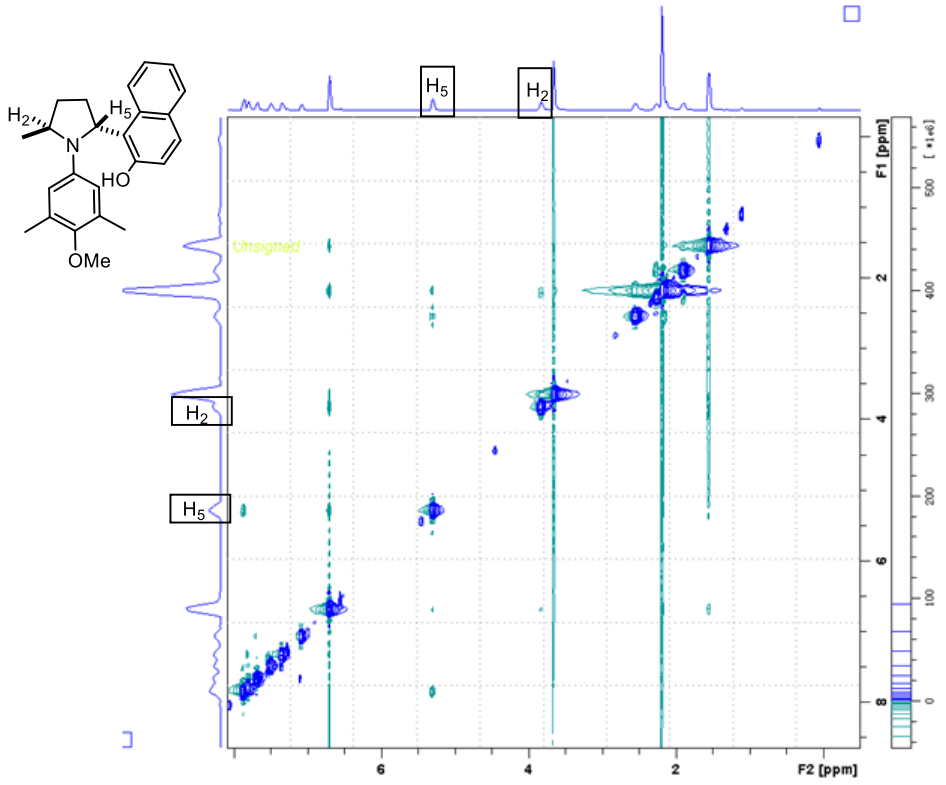
Synthesis of Octahydro-Dipyrroloquinoline Framework 7.



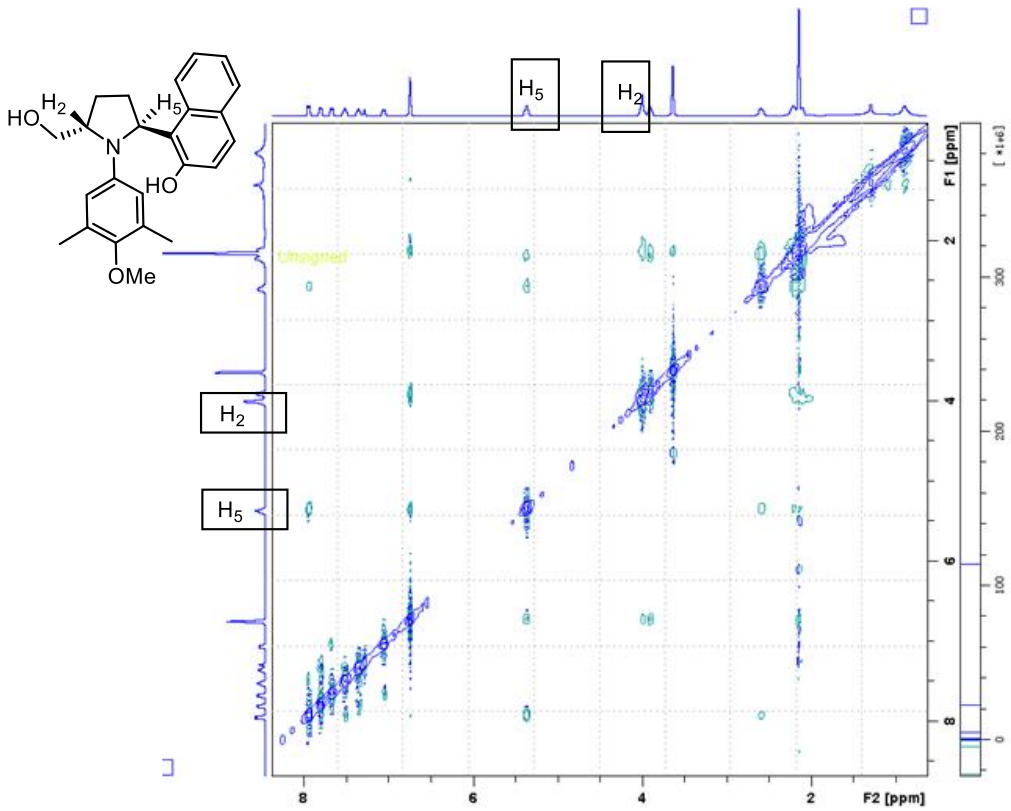
A mixture of pyrrolidine (78 mg, 1.1 mmol,), quinone monoacetal **2** (182 mg, 1 mmol), and DIPEA (*N*, *N*-diisopropylethylamine) (13 mg, 0.1 mmol) in trifluoroethanol (10 mL) were stirred and heated under reflux for 3 hours. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (PE: Et_2O = 9:1, 0.5% of Et_3N was added into the eluent) to give **7** as a colorless solid (166 mg, 82%). M.p. 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (s, 2H), 6.20 (s, 1H), 4.99 (d, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 3.59 (s, 3H), 3.49–3.39 (m, 1H), 3.38–3.25 (m, 2H), 3.20–3.09 (m, 1H), 3.02–2.93 (m, 1H), 2.75–2.65 (m, 1H), 2.25 (s, 3H), 2.24 (s, 6H), 2.05 (s, 3H), 2.03–1.98 (m, 1H), 1.96–1.79 (m, 4H), 1.73–1.59 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 148.6, 147.1, 143.9, 132.2, 130.7, 129.5, 121.5, 116.1, 111.1, 60.0, 59.9, 59.6, 59.2, 50.8, 47.8, 40.2, 29.7, 24.1, 22.9, 16.5, 16.4, 13.3. HRMS (ESI) (*m*/*z*): calcd for $[C_{26}H_{34}N_2O_2 + H]^+$ 407.2693, found 407.2694.

NOESY Spectra of 4a, 4b, and 4e.

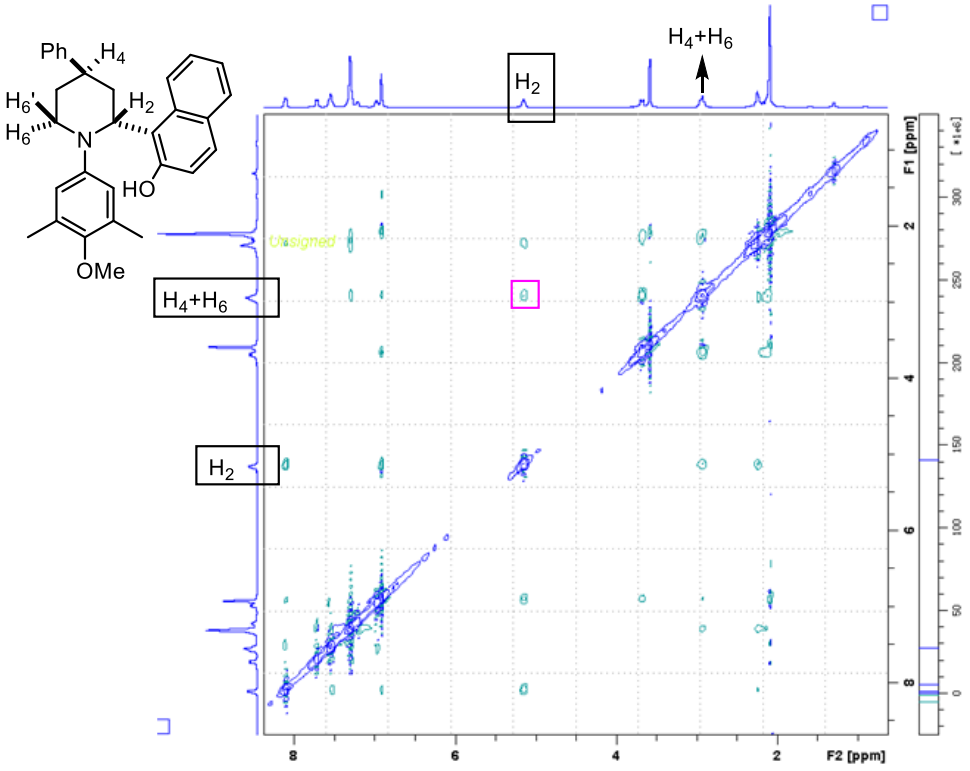
NOESY spectrum of **4a**



NOESY spectrum of **4b**



NOESY spectrum of **4e**



X-ray Crystallographic Data for Octahydro-Dipyrroloquinoline Framework 7

Crystal data and X-ray molecular structure with the CCDC number are reported as follows.

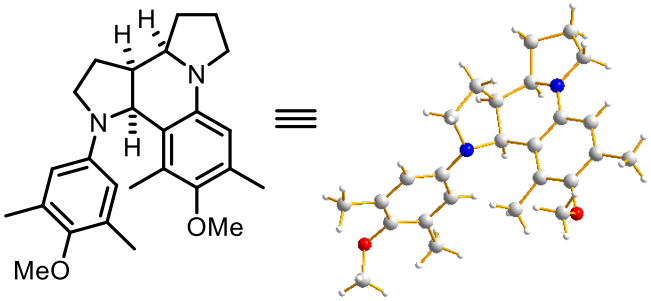


Table 1. Crystal data and structure refinement

Empirical formula	$C_{26}H_{34}N_2O_2$
Formula weight	406.55
Temperature/K	113(2)
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a/Å	10.168(2)
b/Å	10.859(2)
c/Å	11.191(2)
α/°	82.43(3)
β/°	64.17(3)
γ/°	76.64(3)
Volume/Å^3	1081.4(5)
Z	2
ρ_{calc}g/cm^3	1.249
Absorption coefficient/mm^{-1}	0.078
F(000)	440
Crystal size/mm^3	0.200 × 0.180 × 0.120
Theta range for data collection	2.269 to 27.868
Limiting indices	-13<=h<=13, -14<=k<=14, -14<=l<=14
Reflections collected	12877
Independent reflections	5108 [R(int) = 0.0280]
Completeness to theta = 25.242	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9060
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5108 / 0 / 277

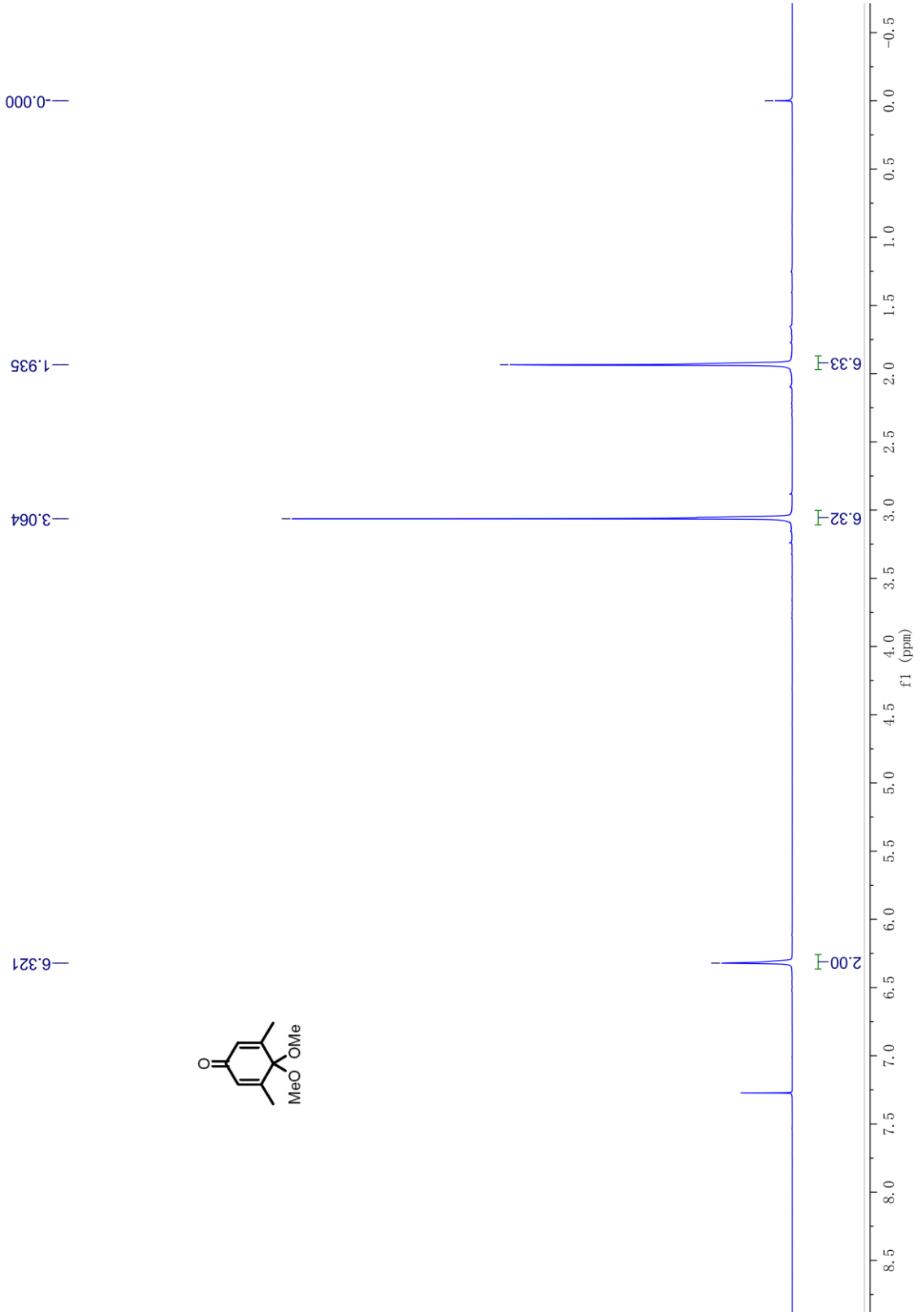
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1359
Final R indexes [all data]	R_1 = 0.0580, wR_2 = 0.1458
Extinction coefficient	n/a
Largest diff. peak/hole / e $Å^{-3}$	0.324 and -0.329
CCDC	2292799

Reference.

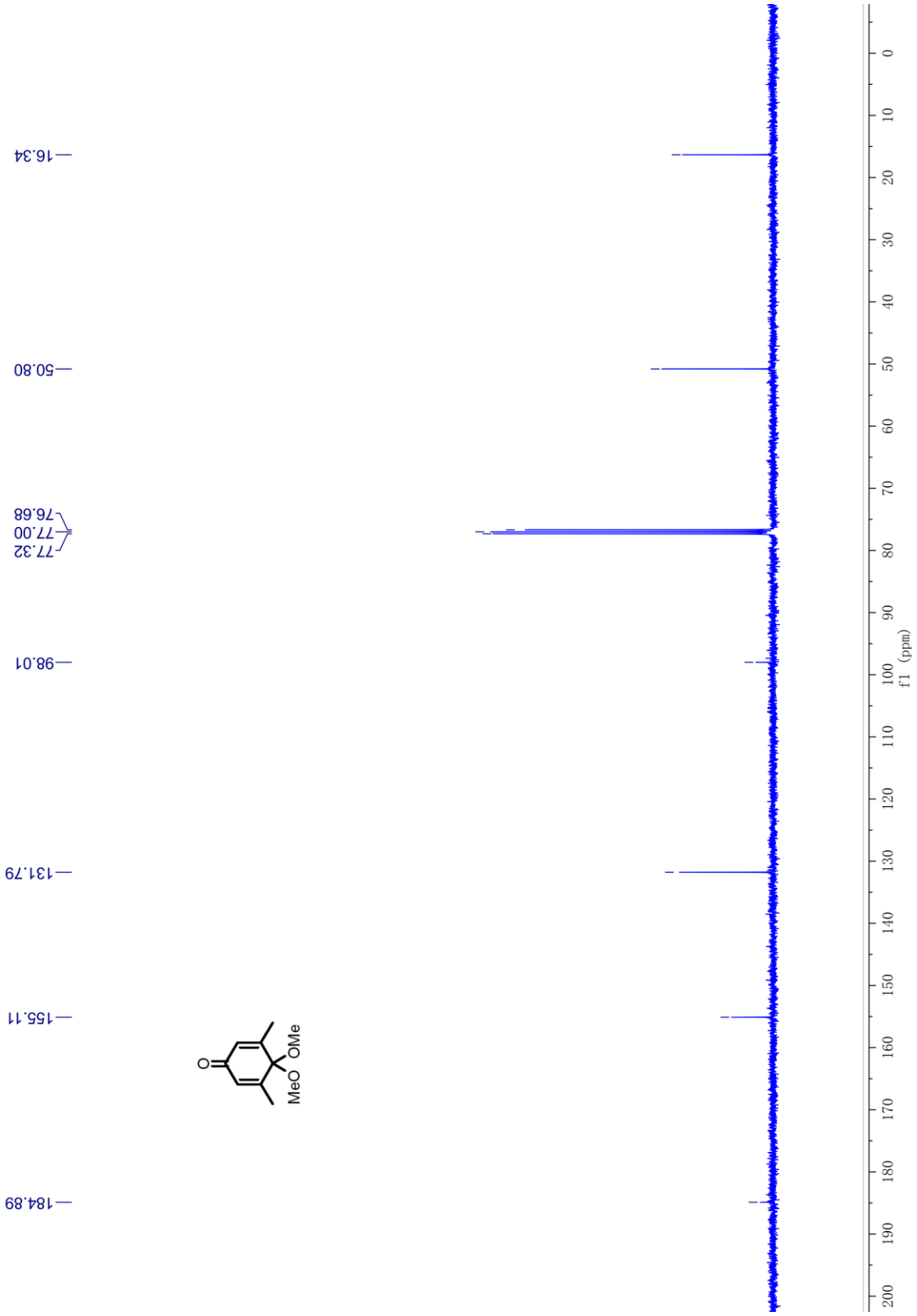
1. J.-Z. Zhang, Z.-W. Yin, P. Leonard, J. Wu, K. Sioson, C. Liu, R. Lapo and S.-P. Zheng, *Angew. Chem., Int. Ed*., 2013, **52**, 13273−13275.

NMR spectra.

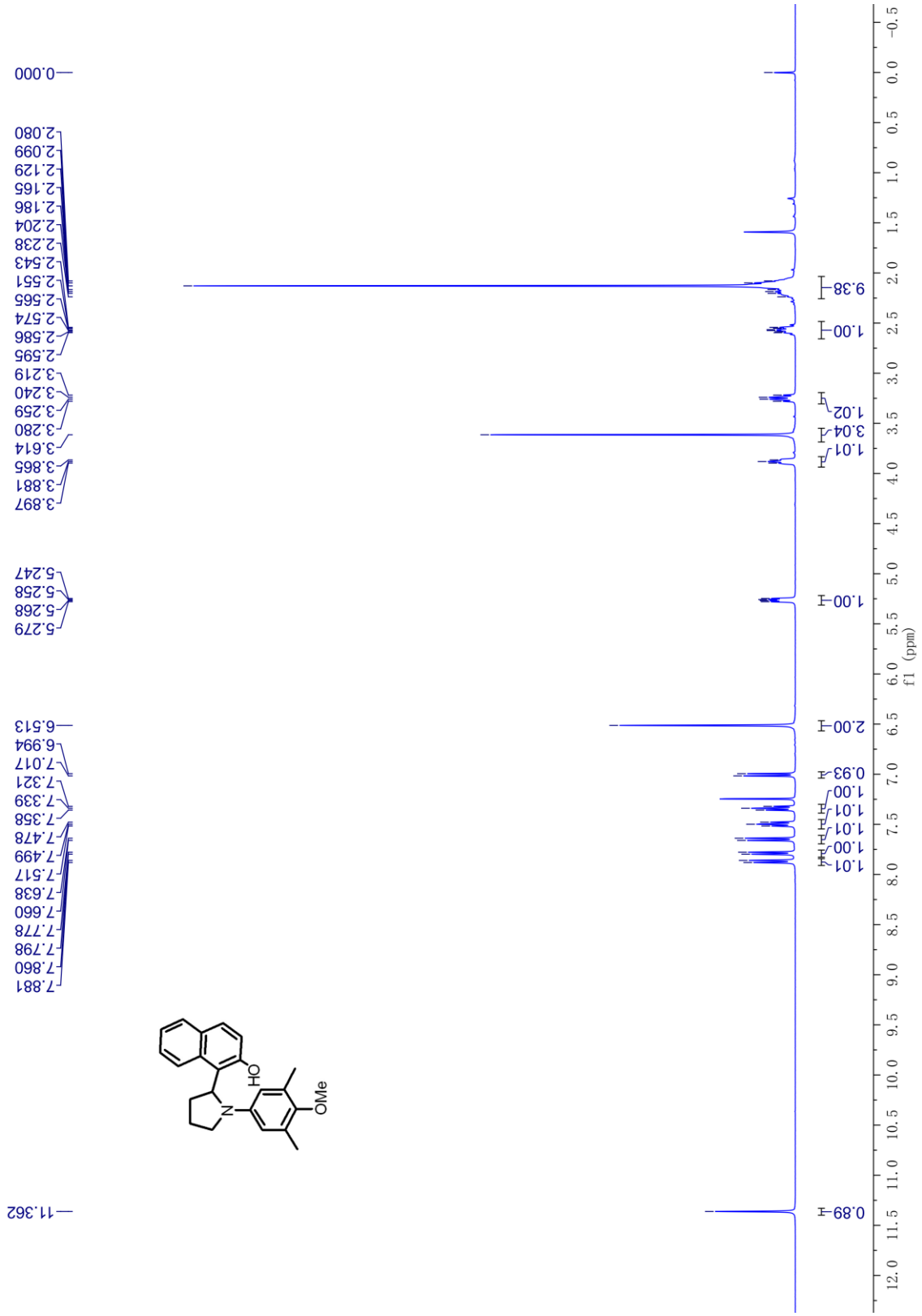
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of quinone monoacetal **2**



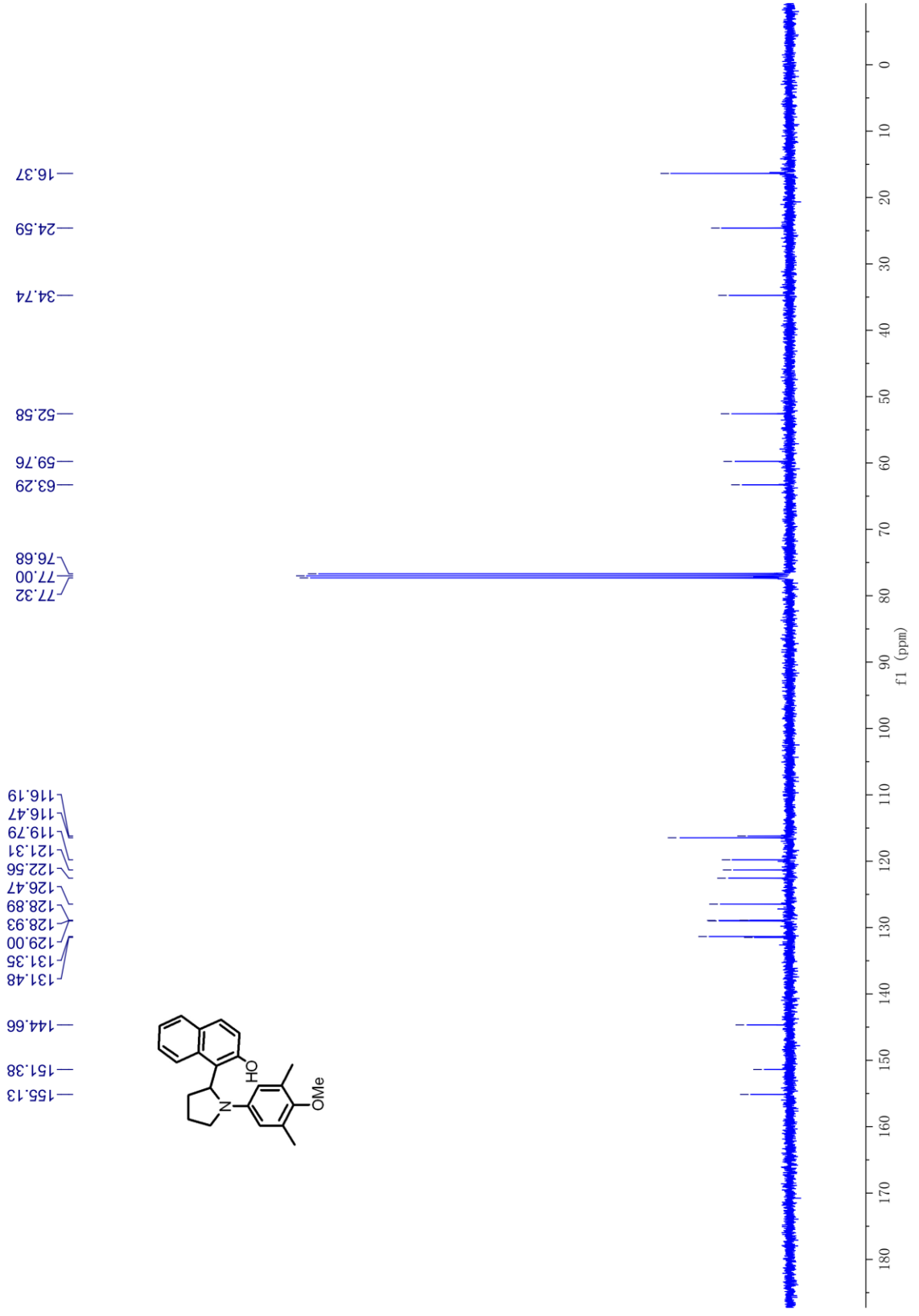
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of quinone monoacetal **2**



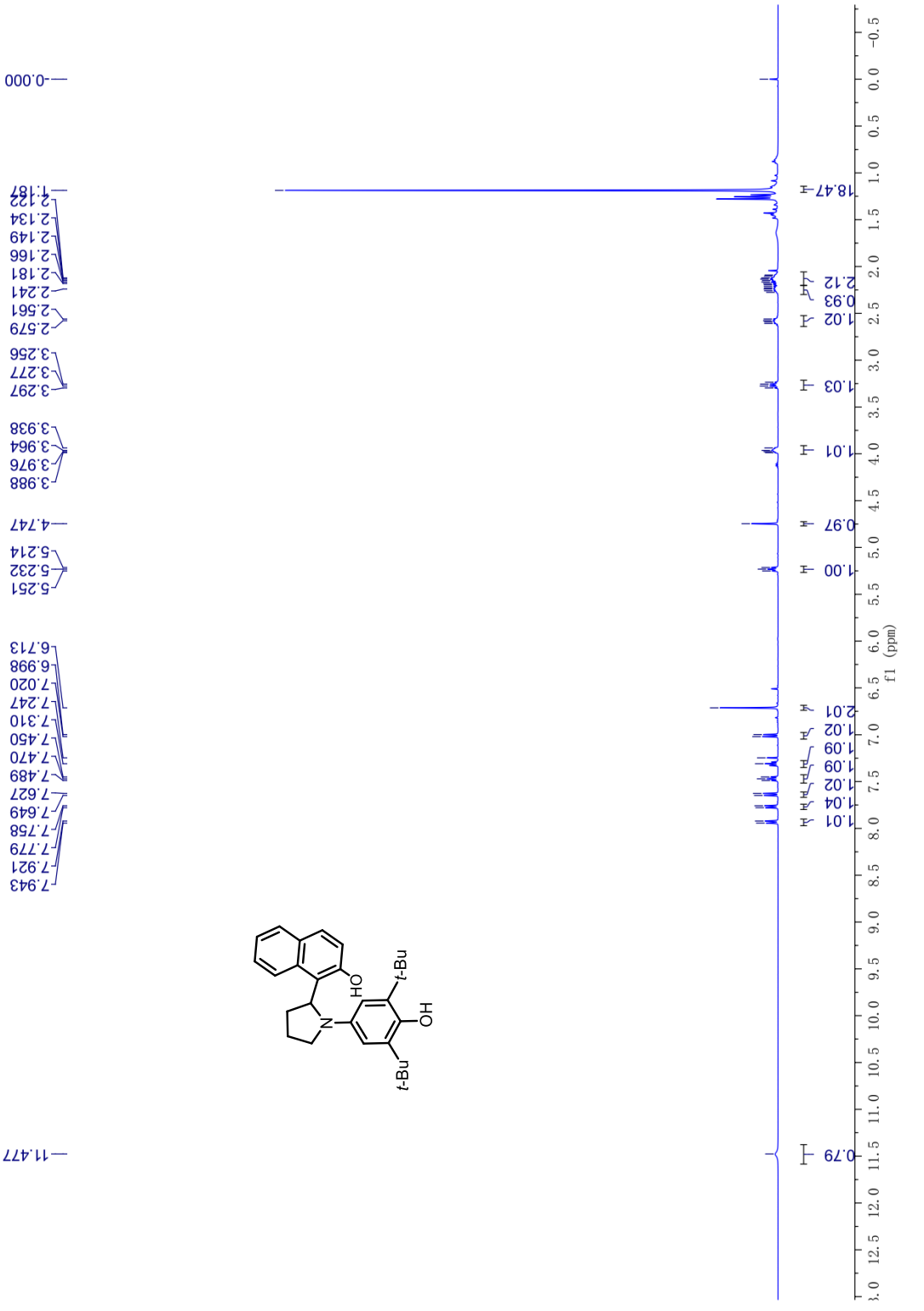
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



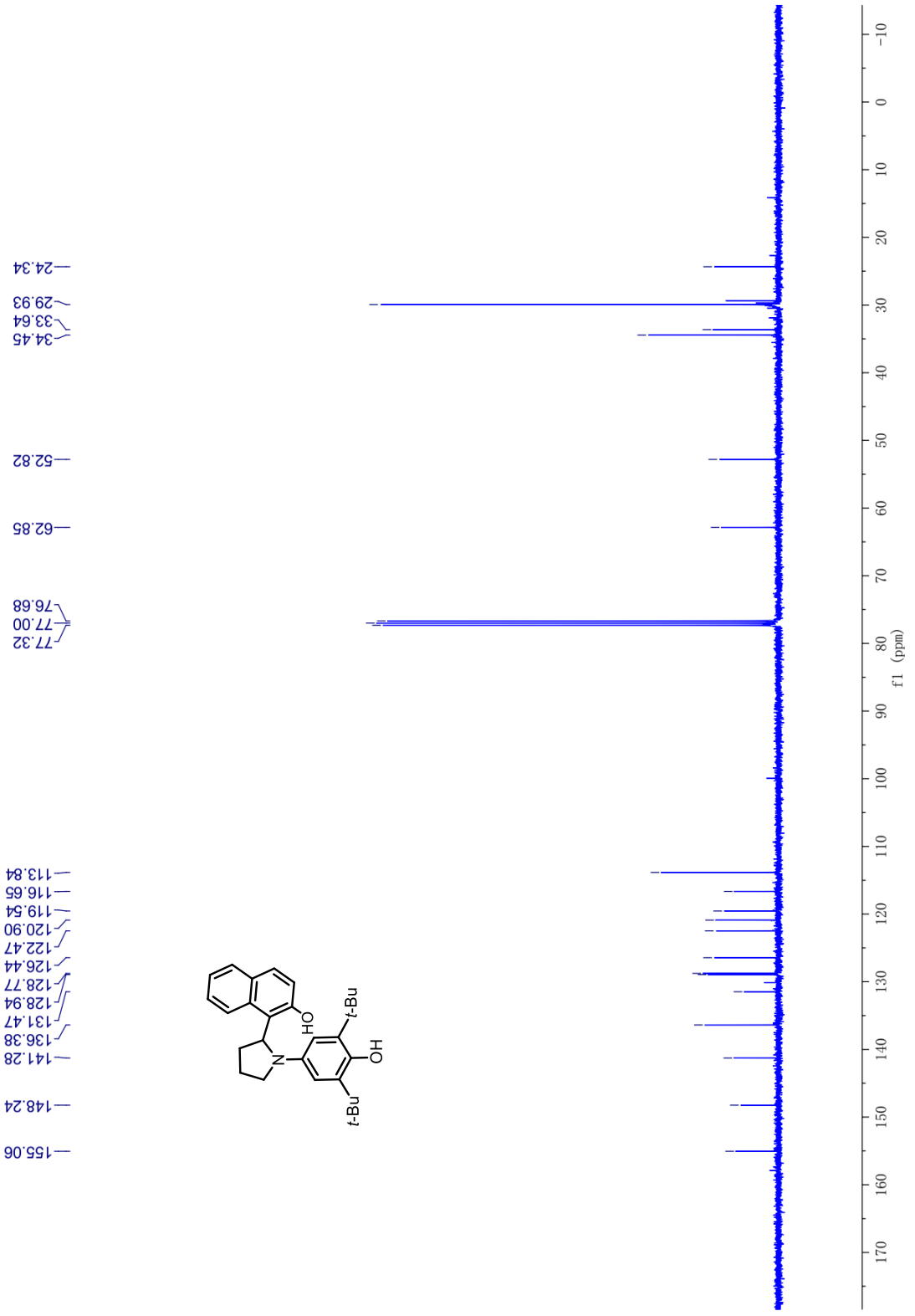
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**



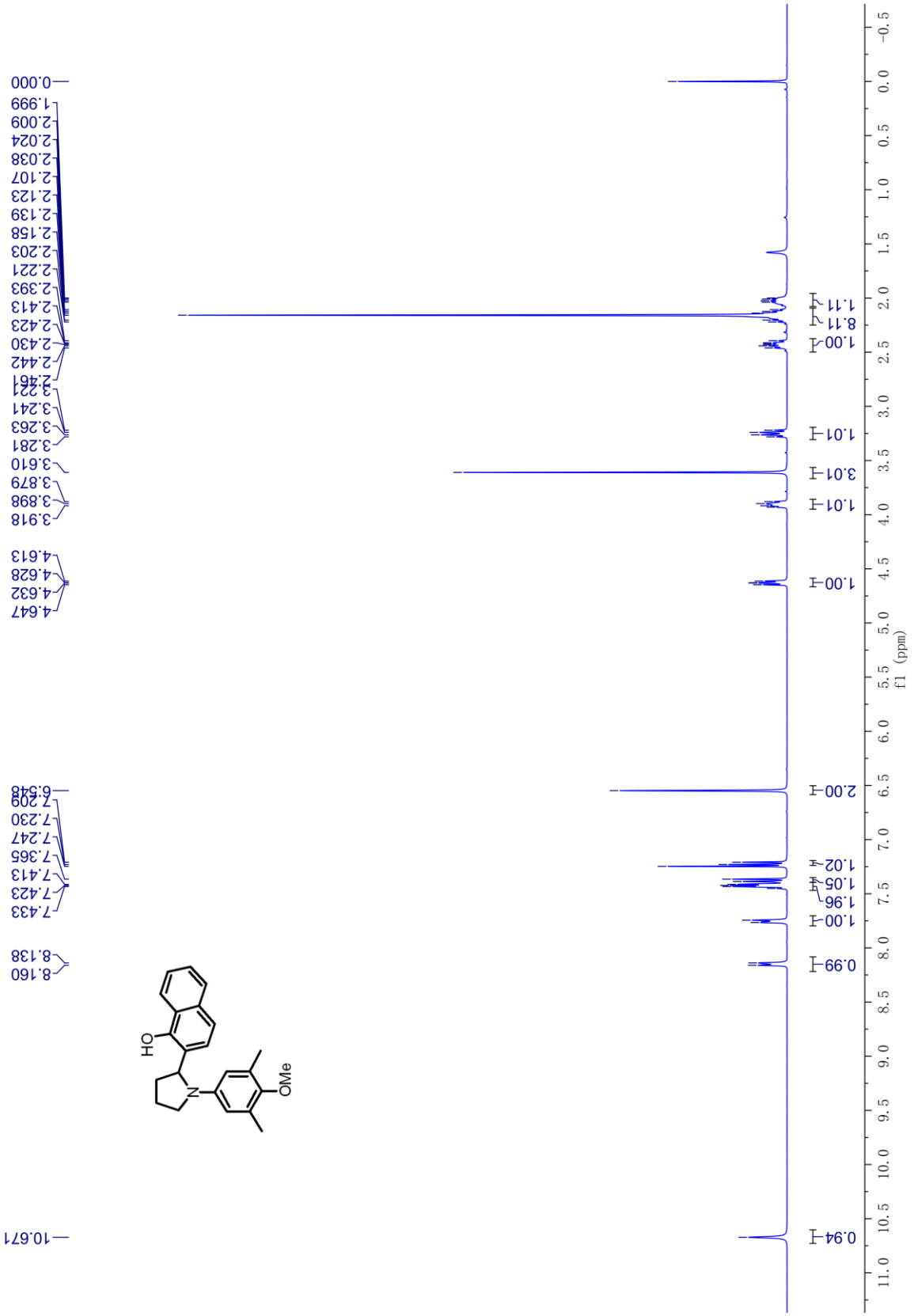
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a'**



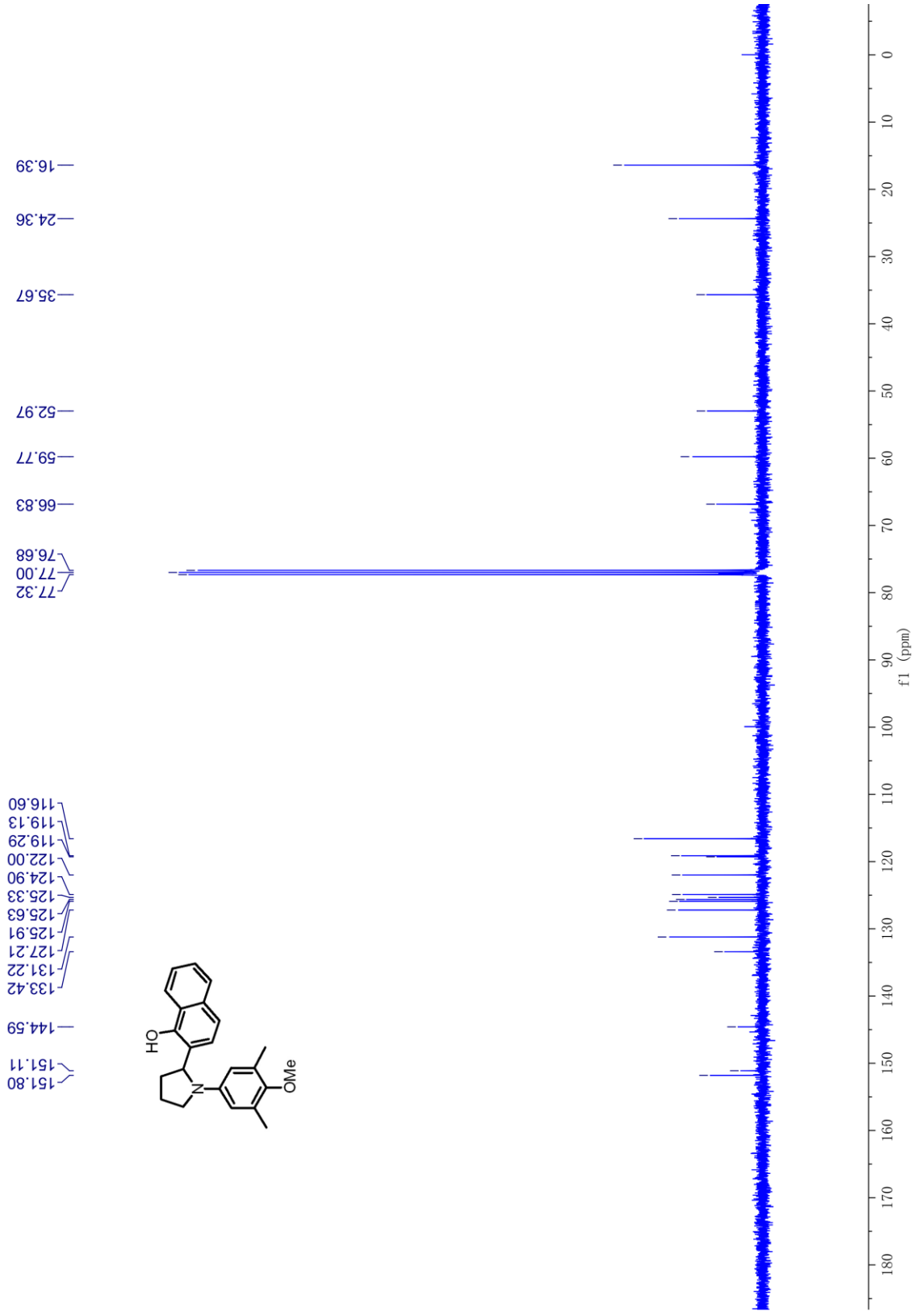
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a'**



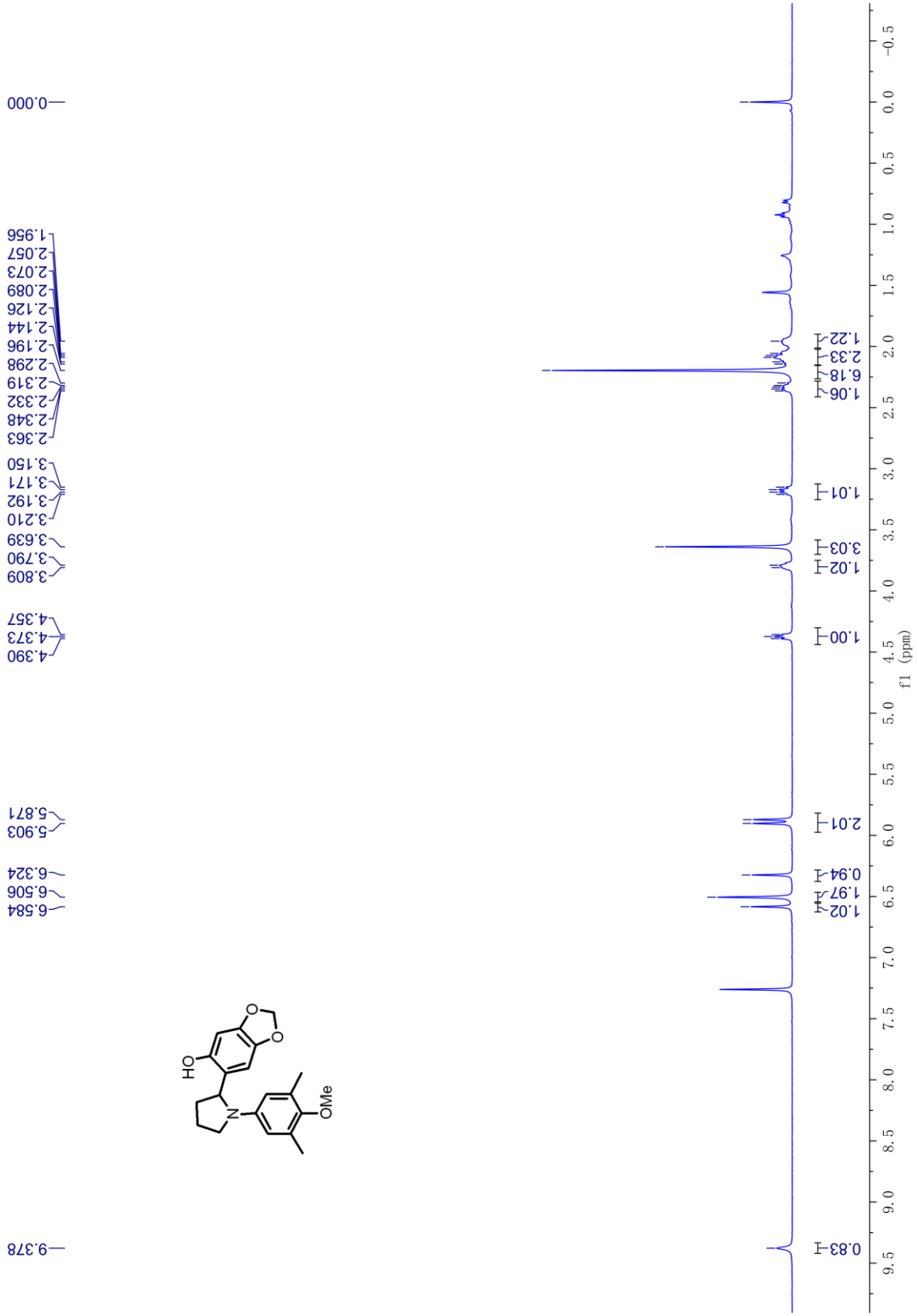
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



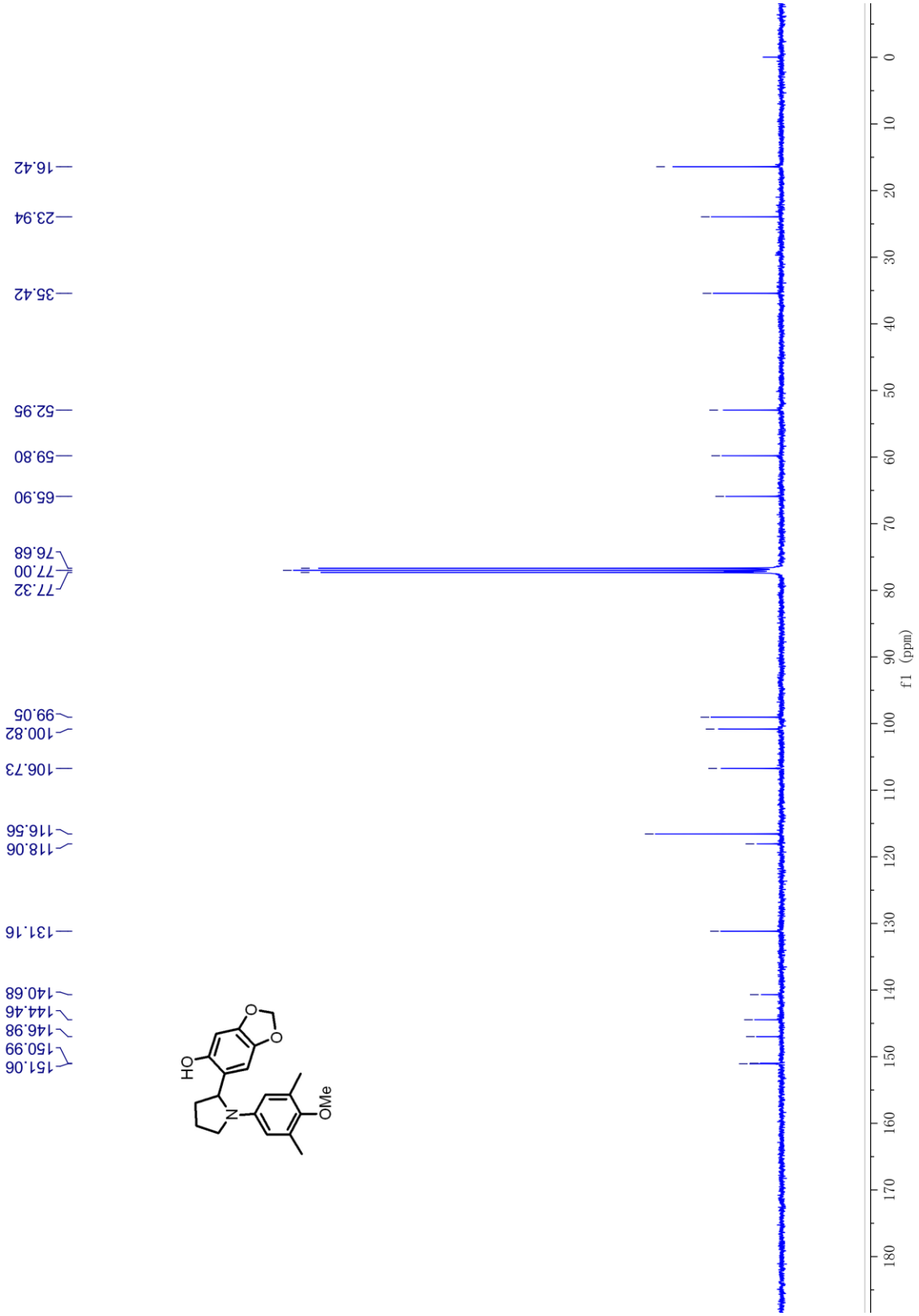
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**



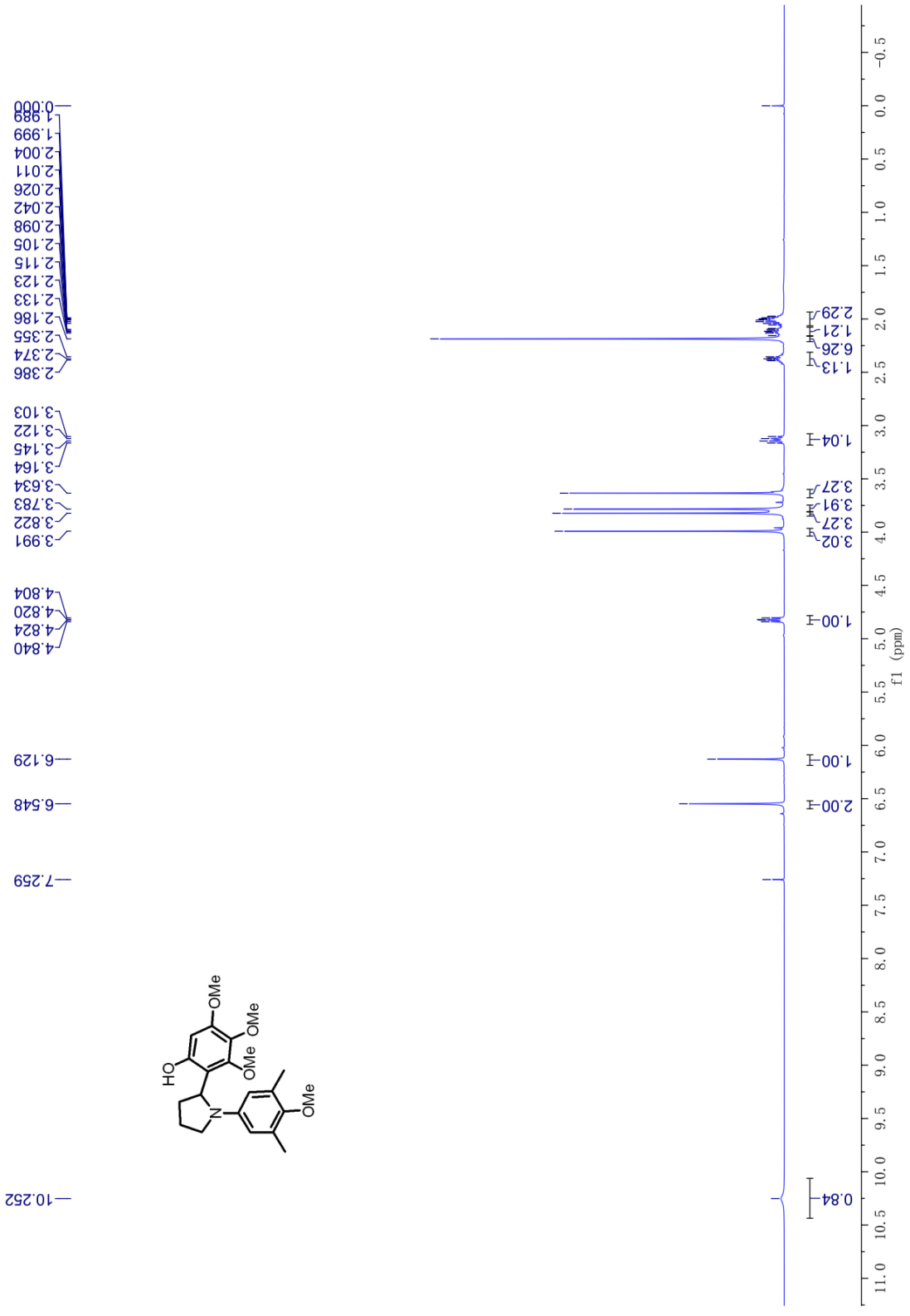
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



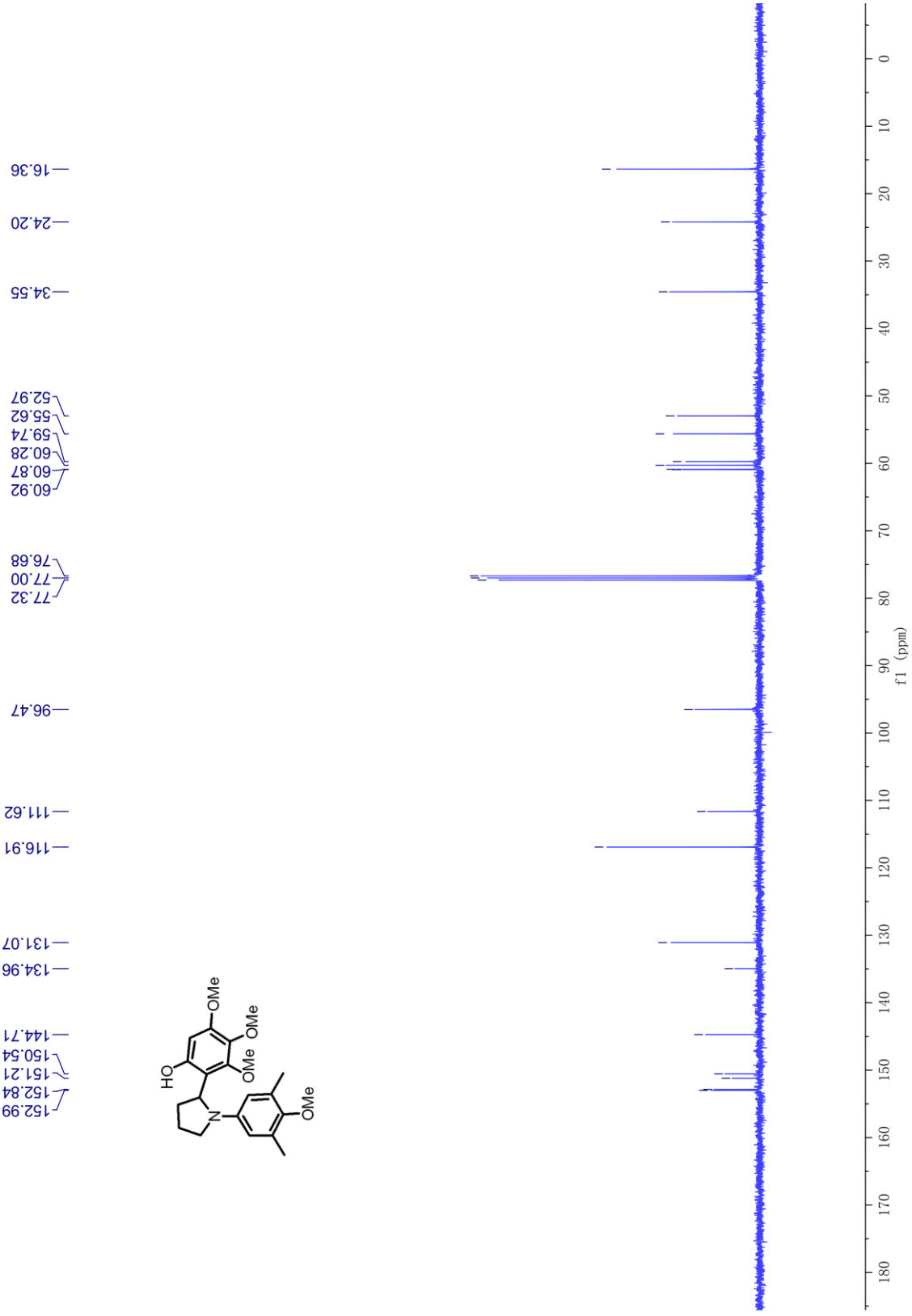
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3c**



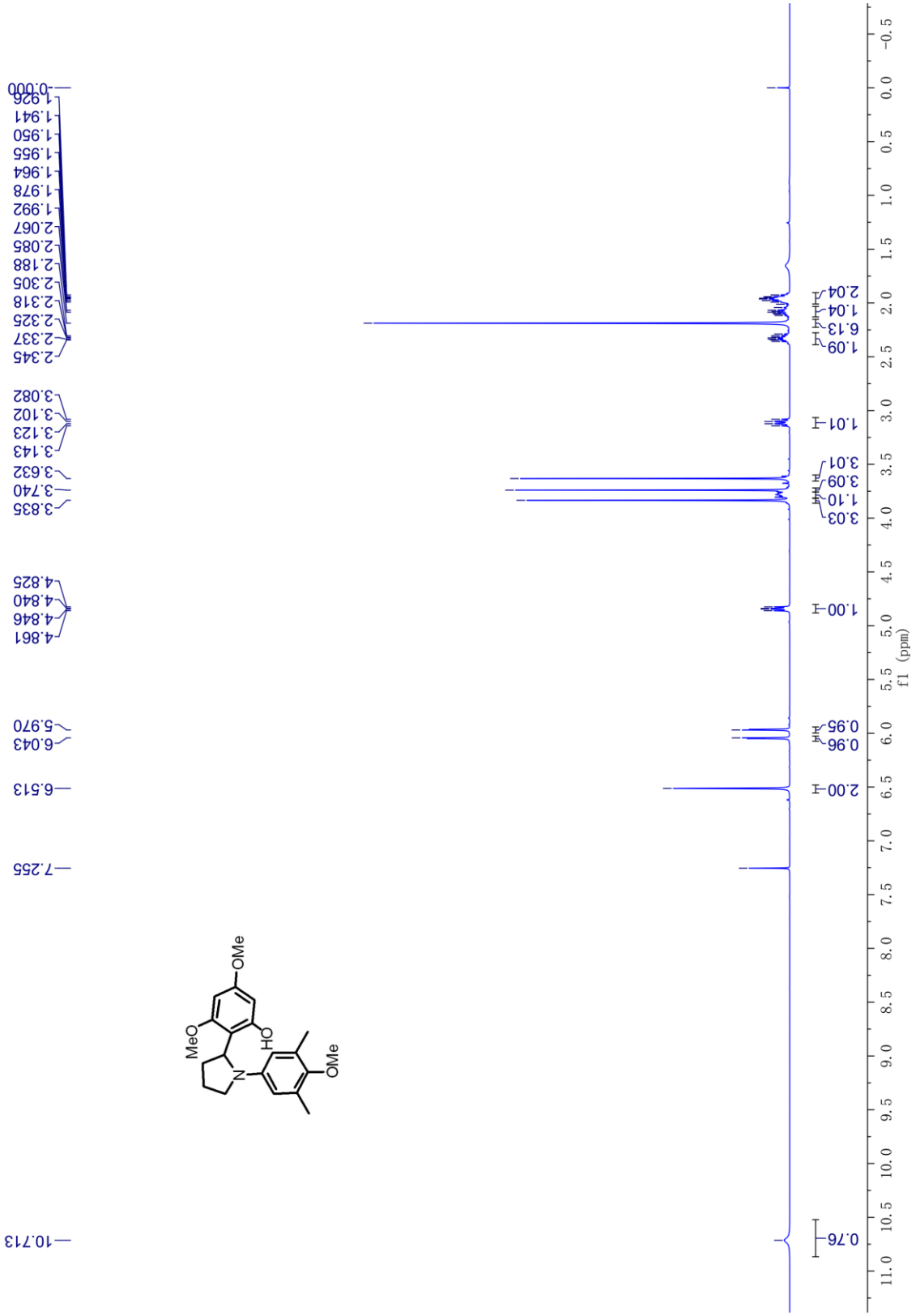
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



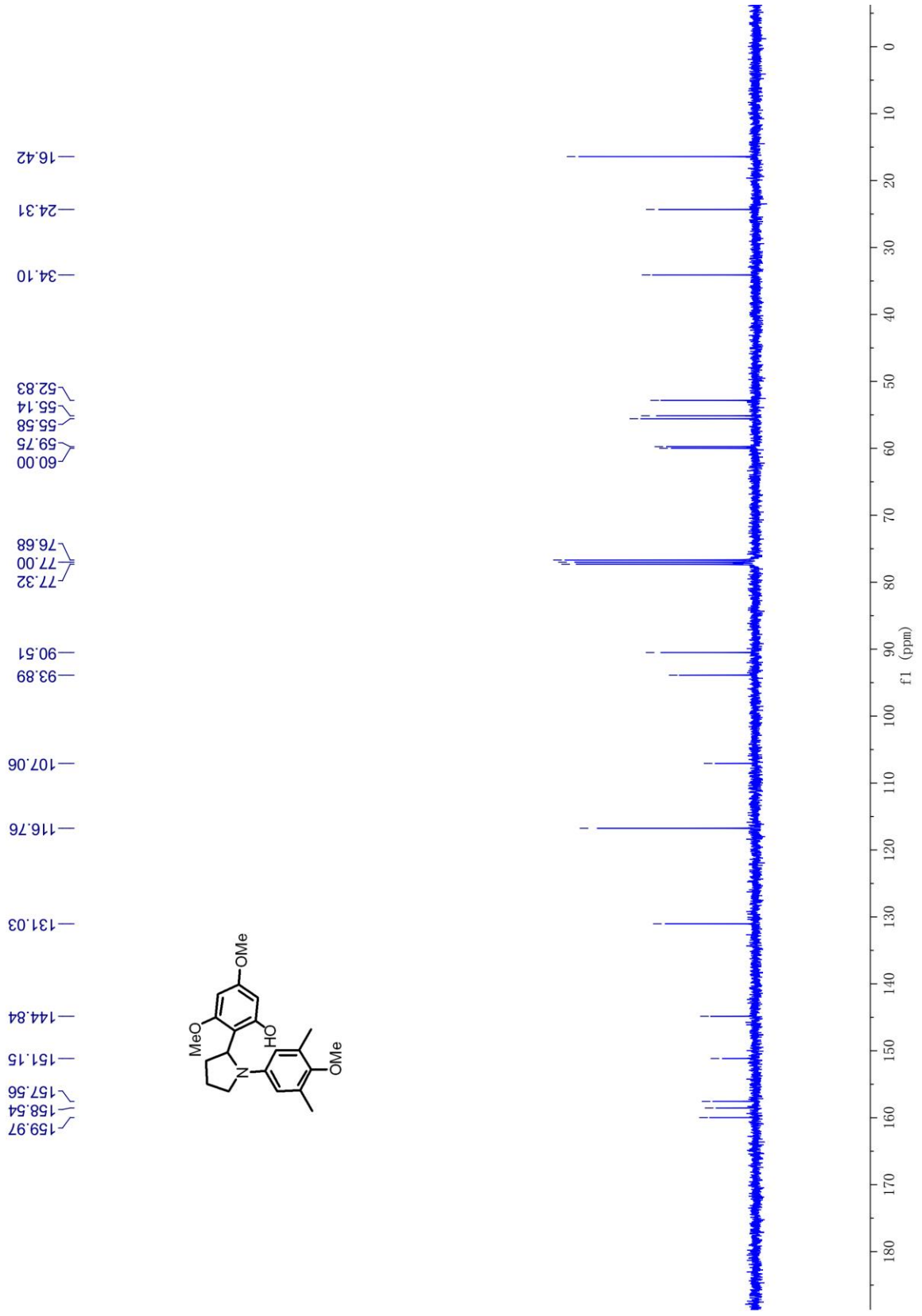
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3d**



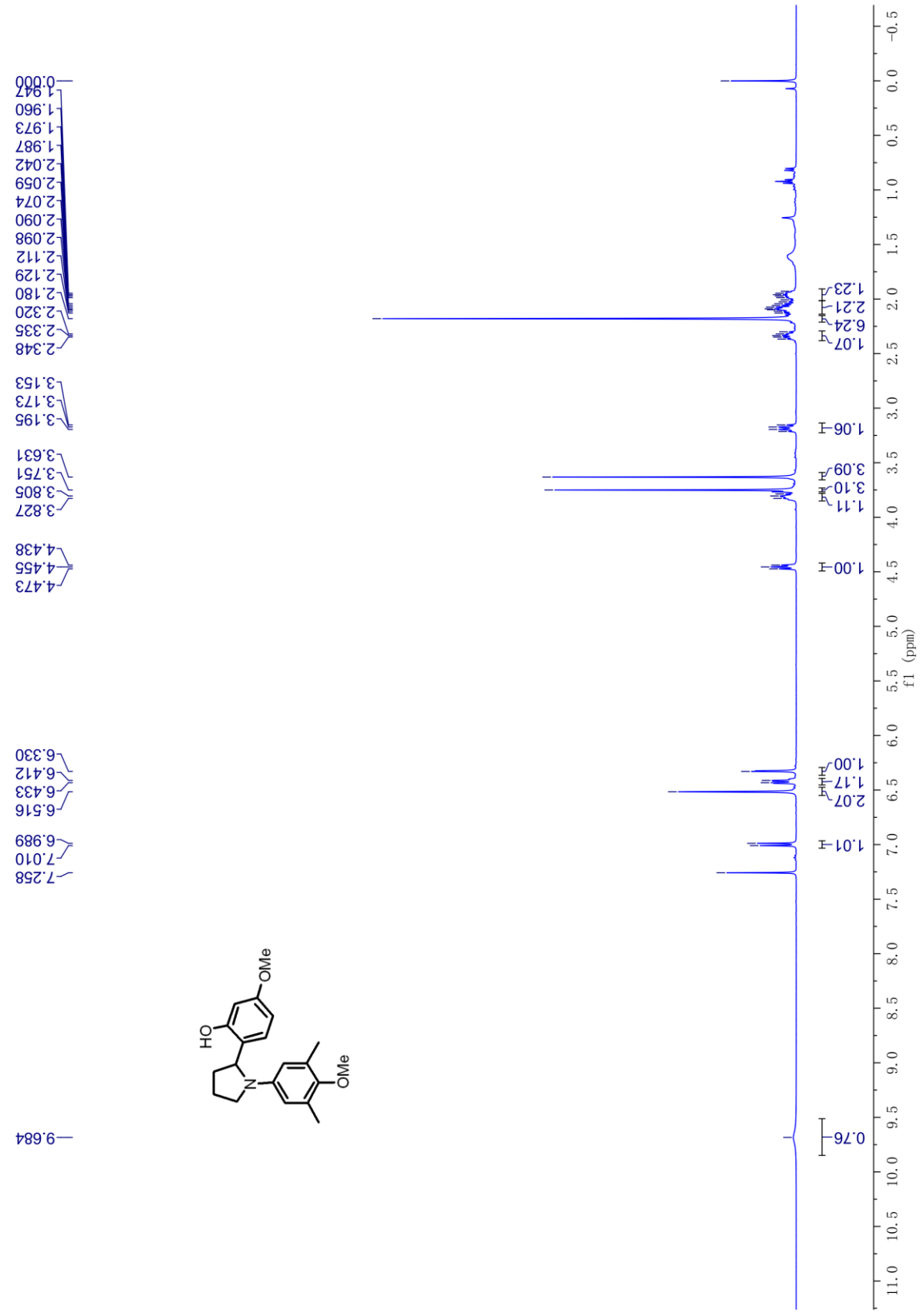
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



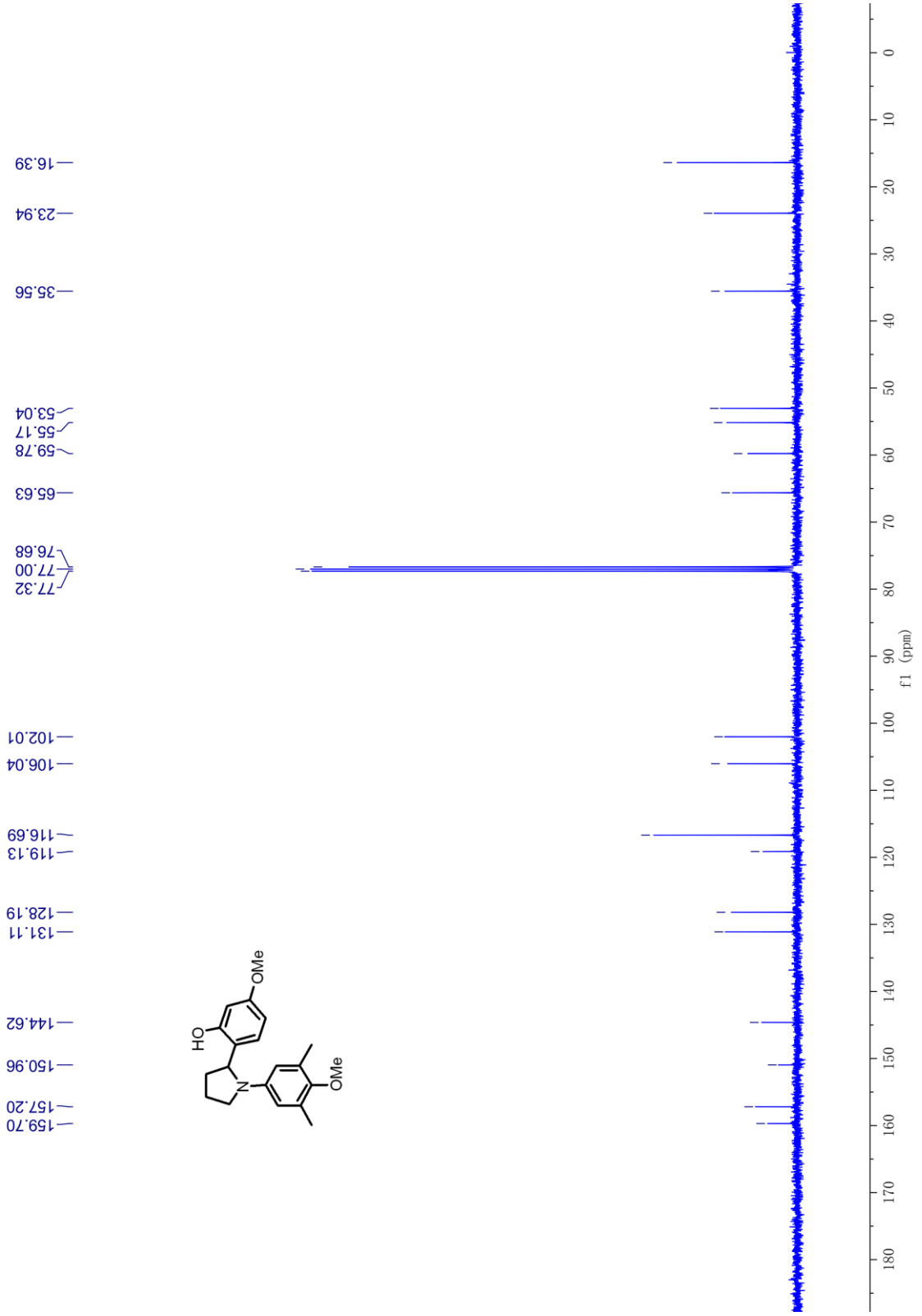
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3e**



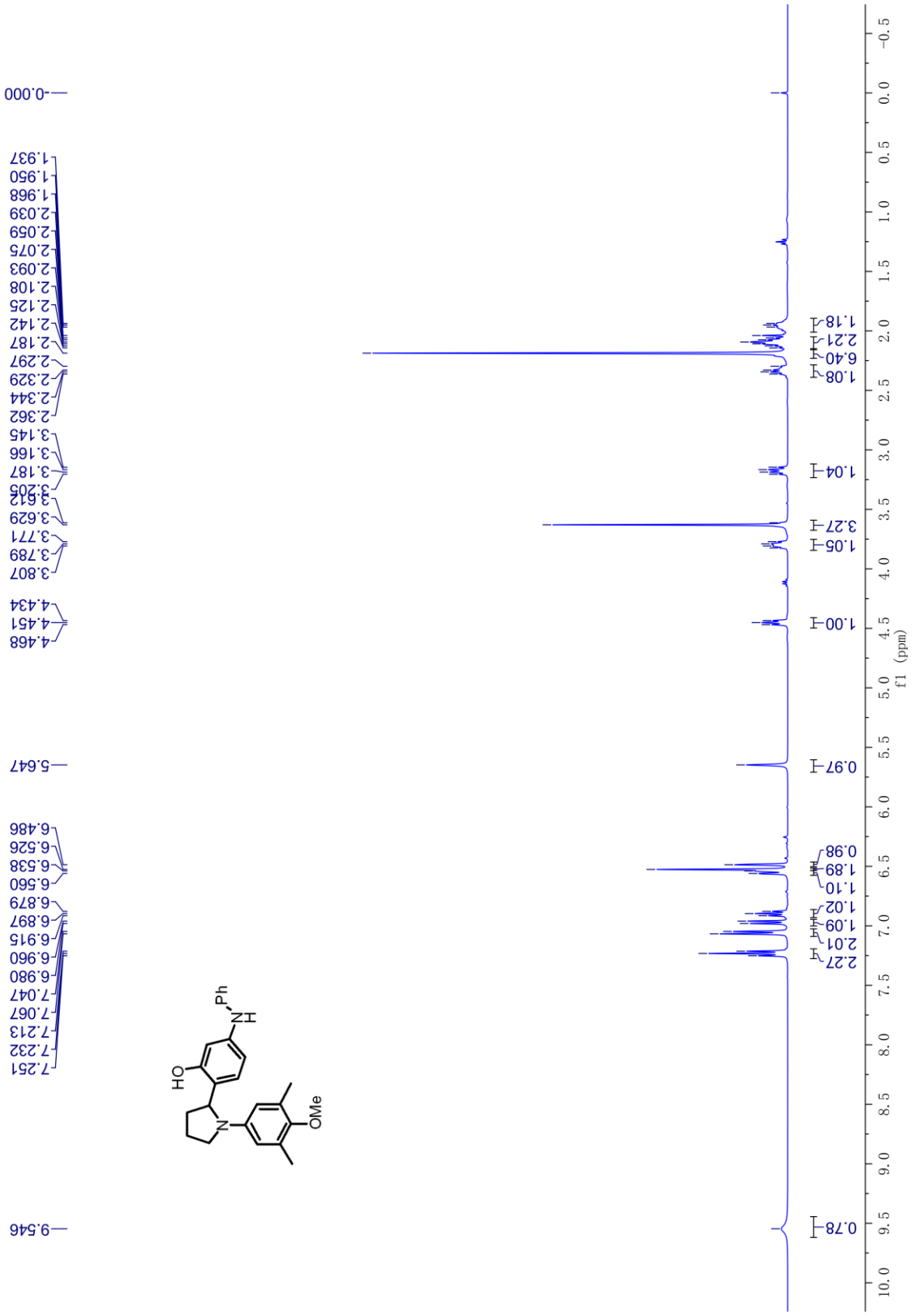
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



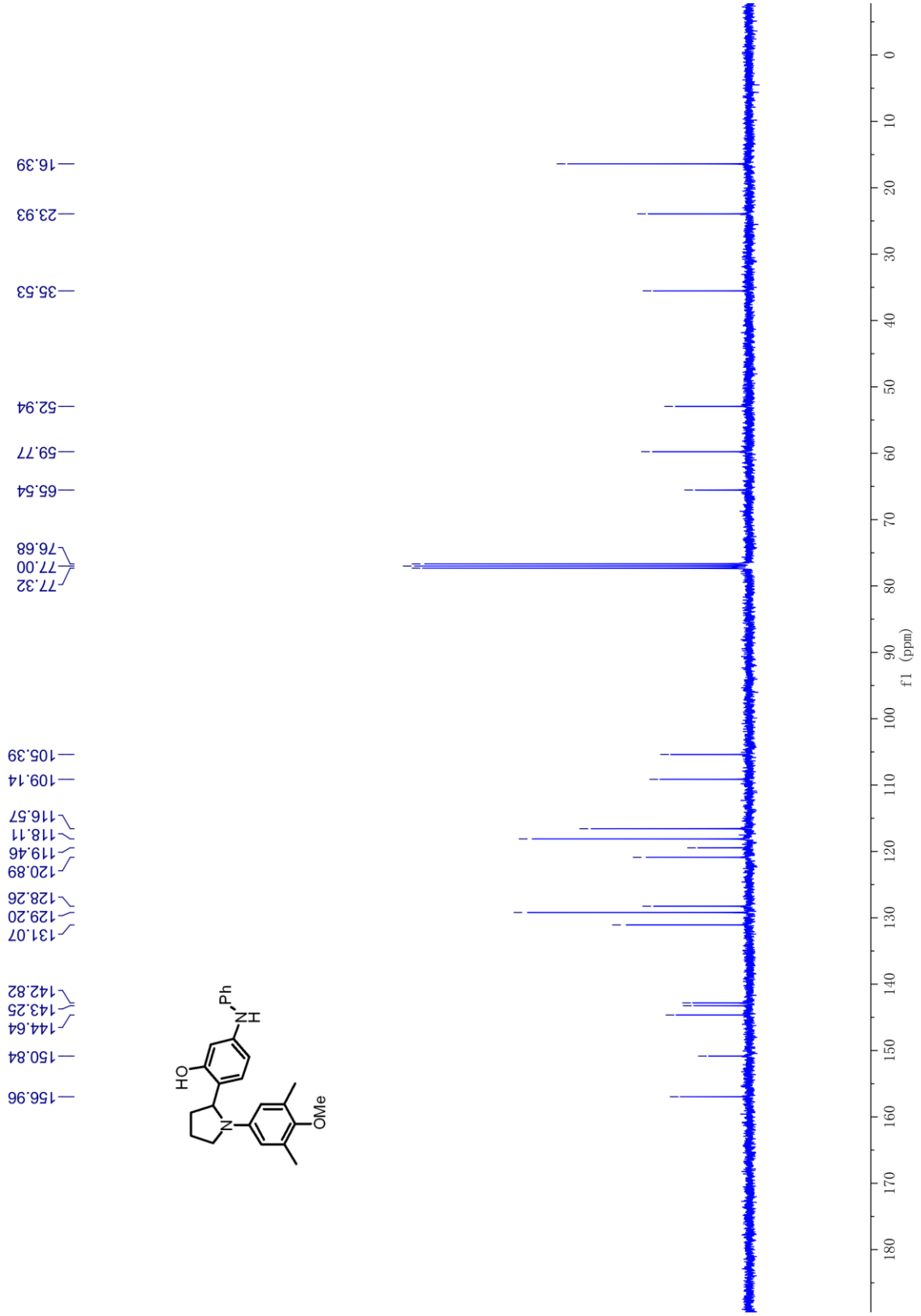
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3f**



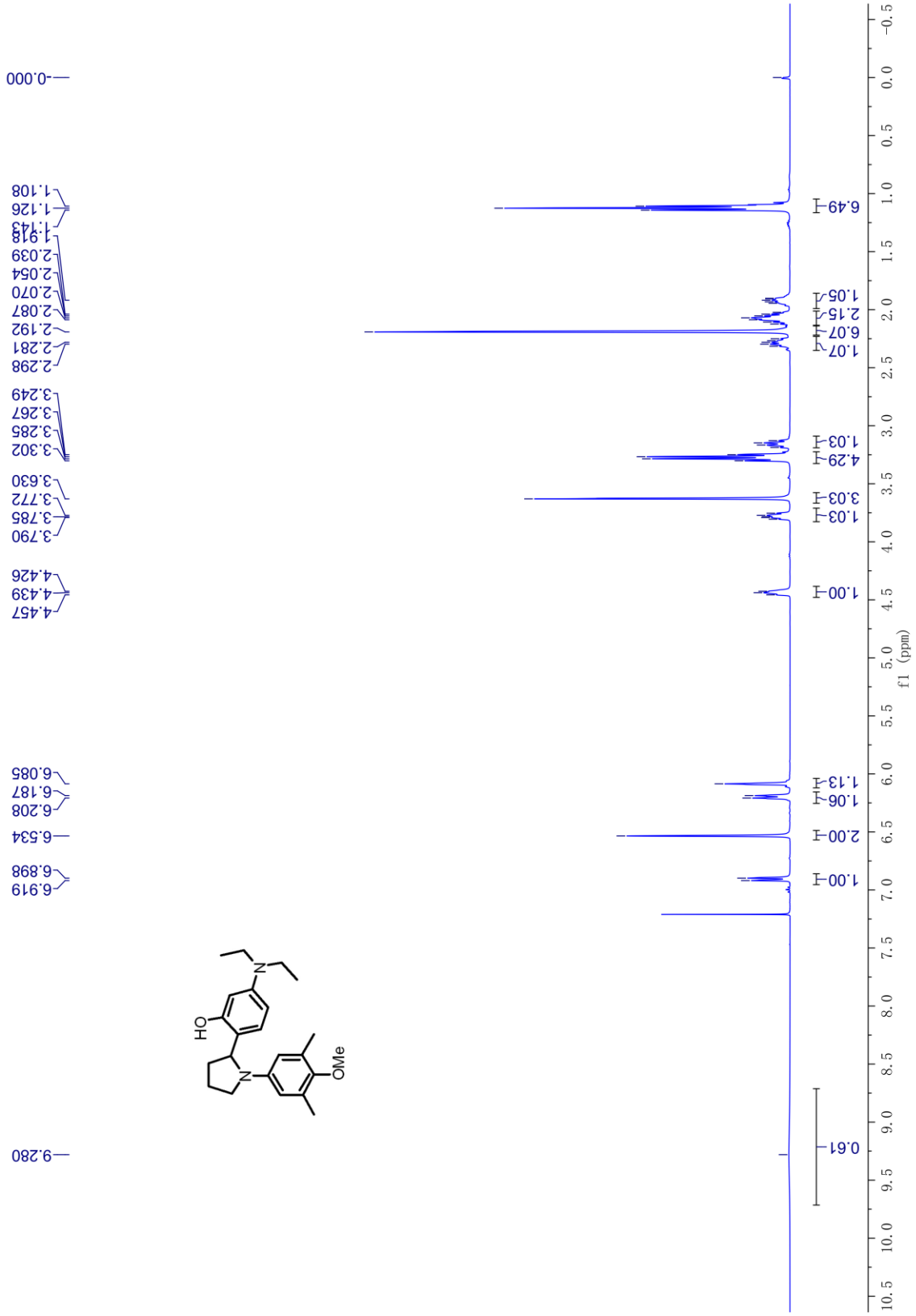
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**



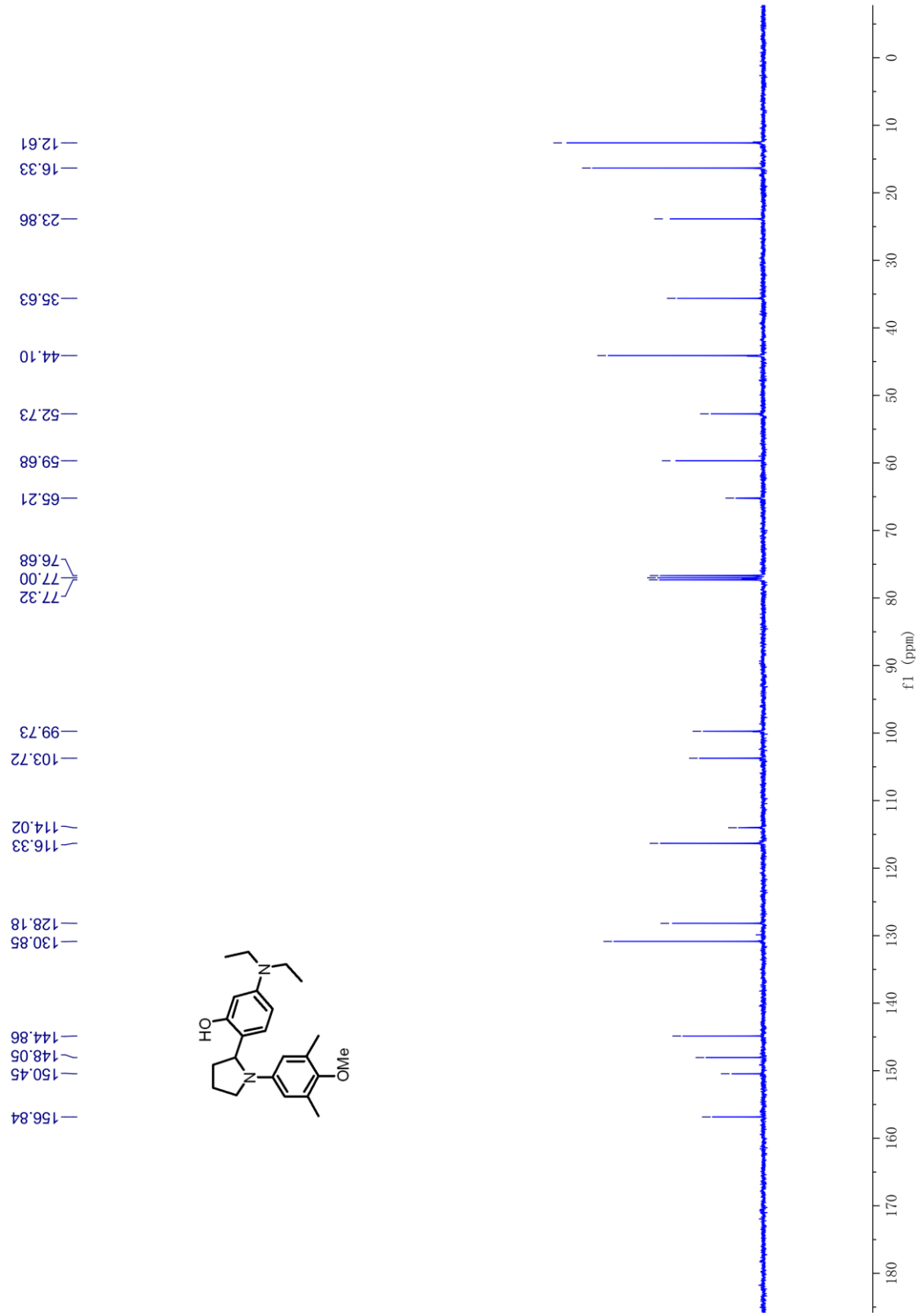
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3g**



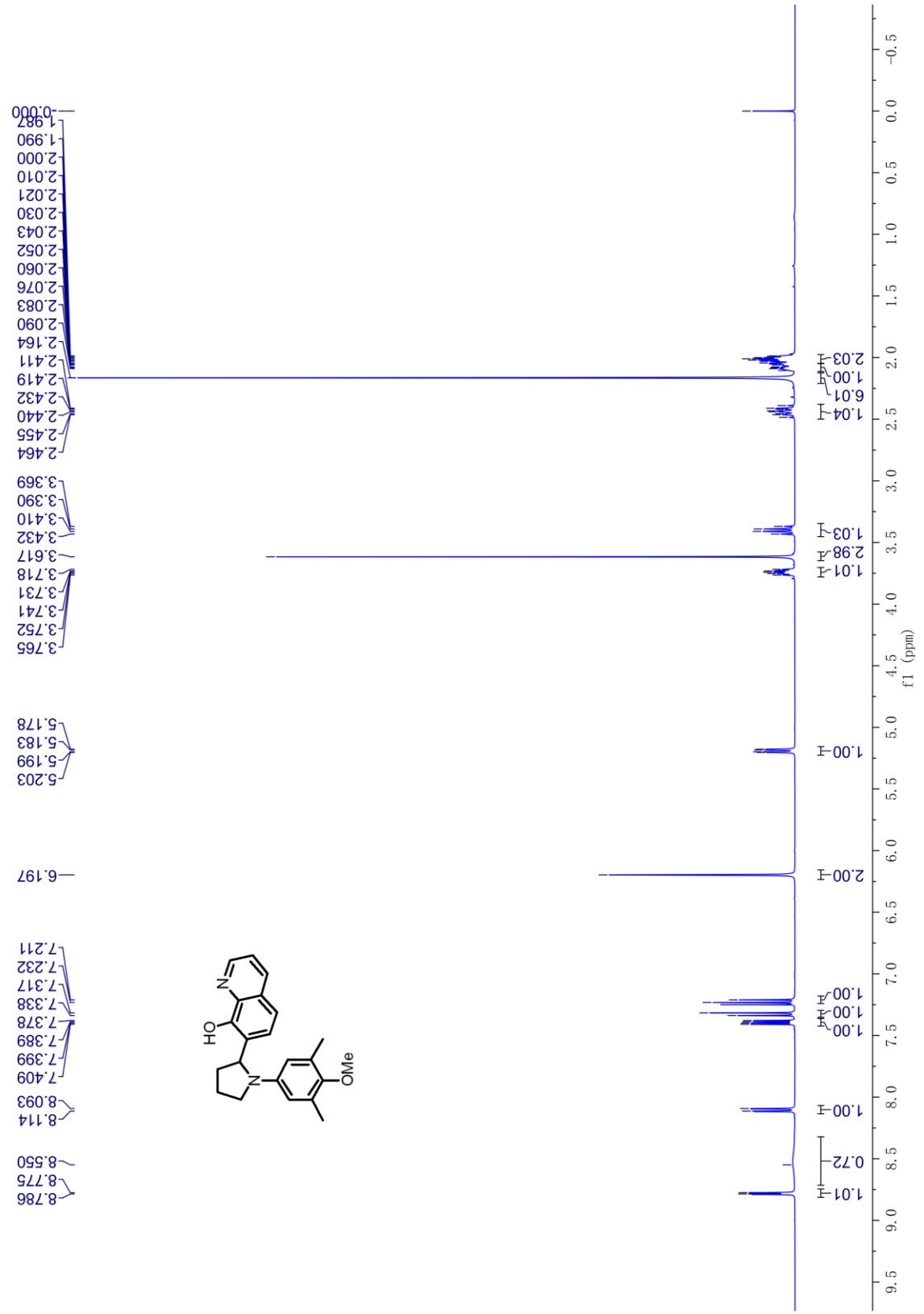
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



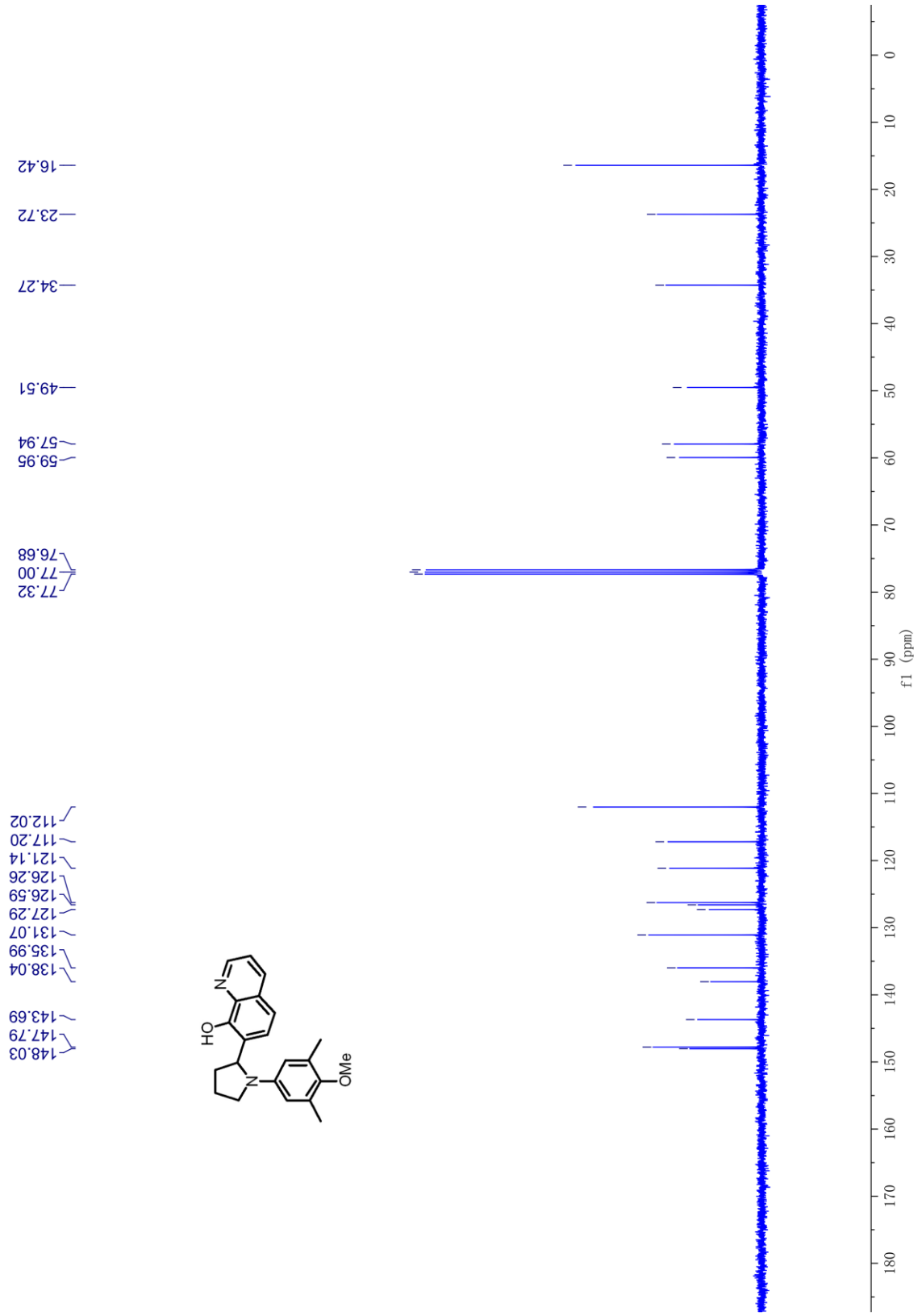
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3h**



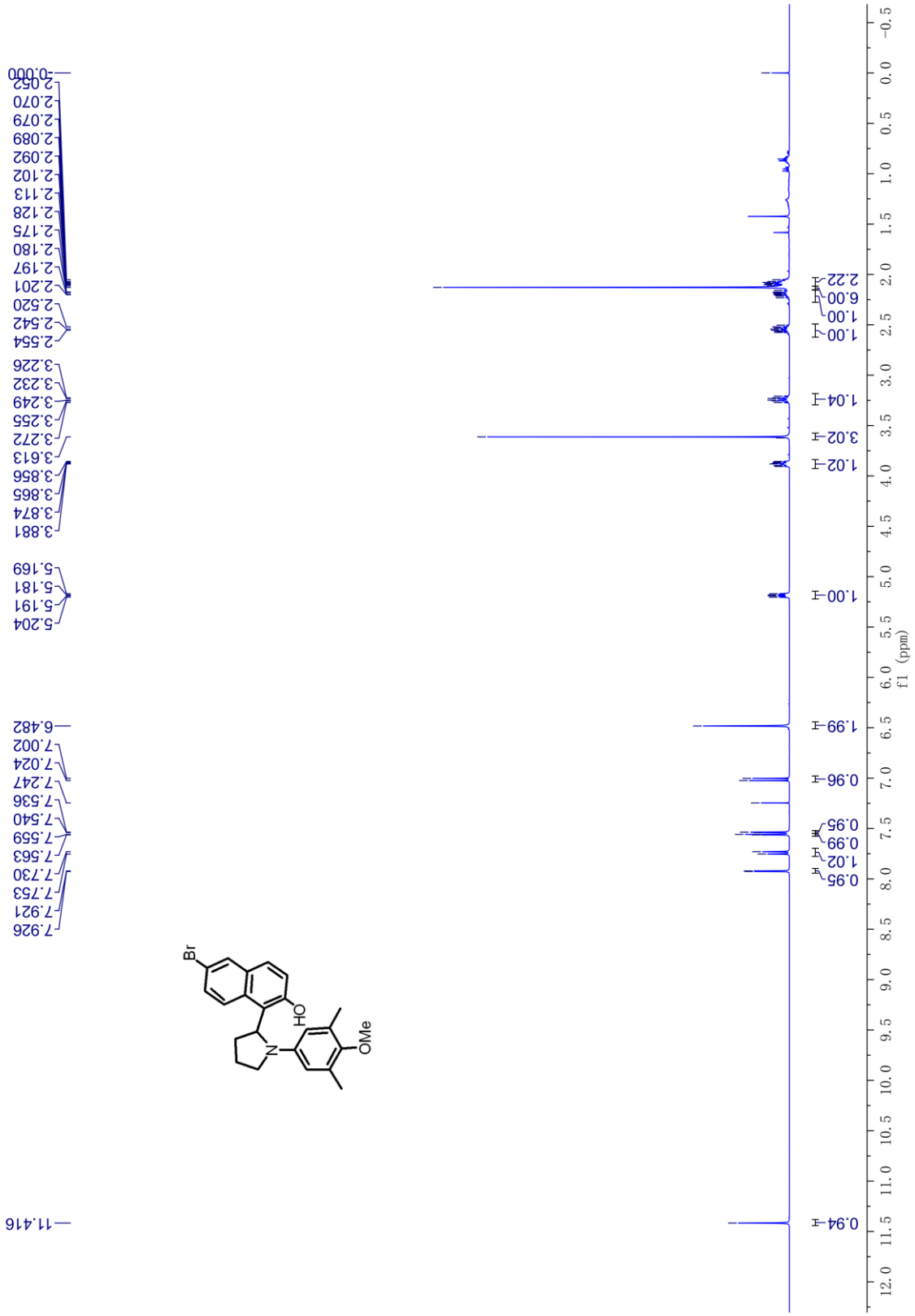
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**



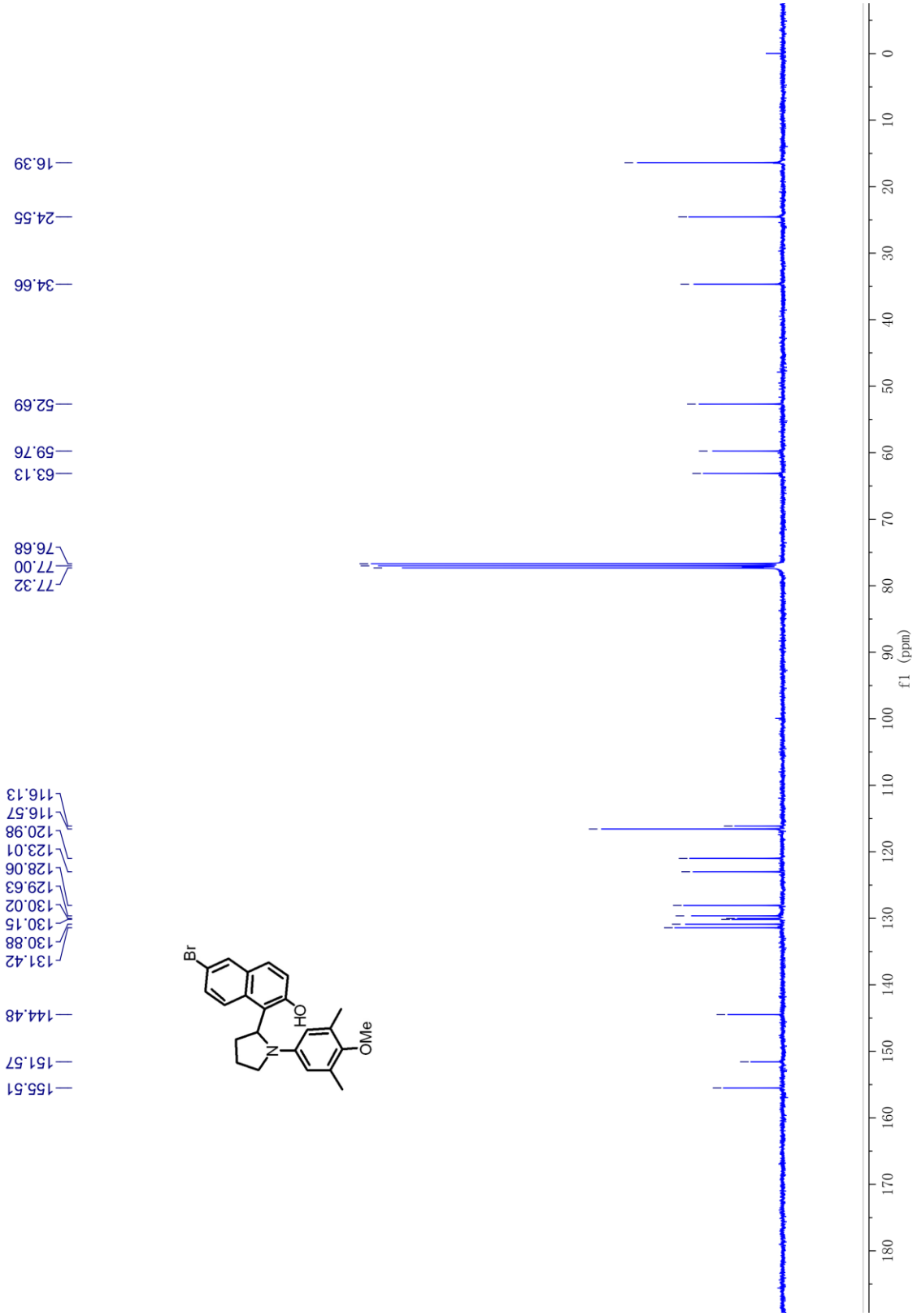
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3i**



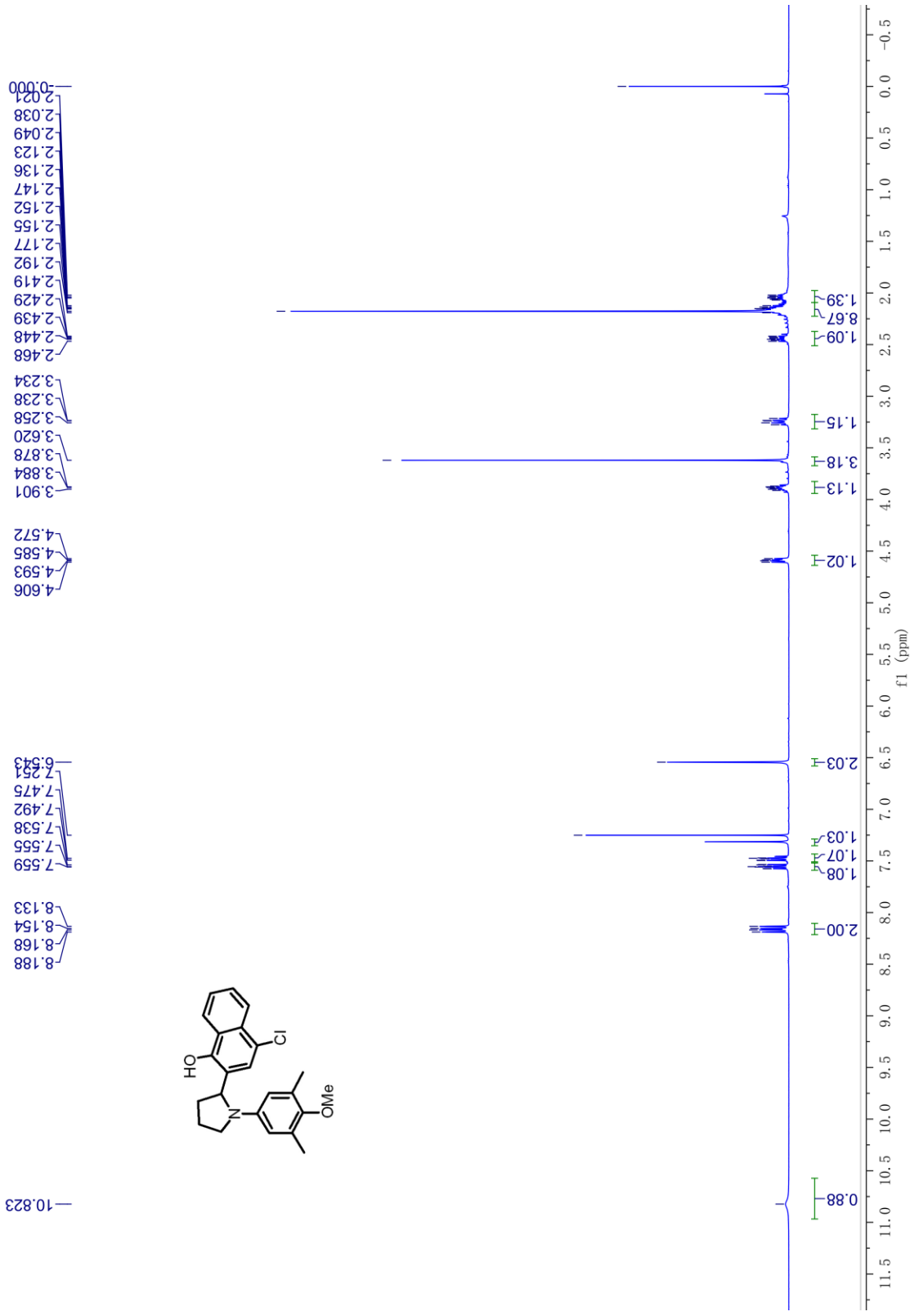
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**



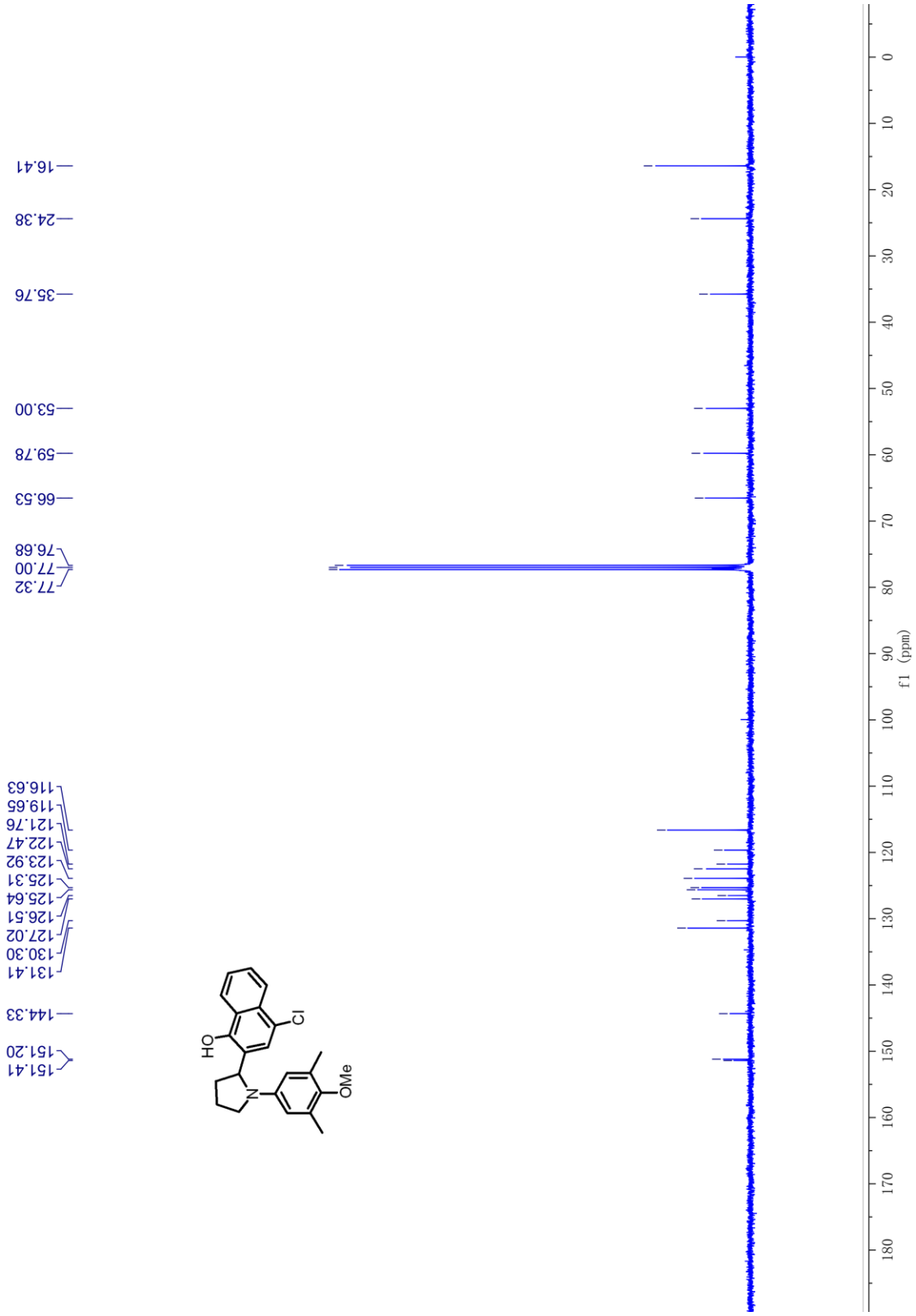
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3j**



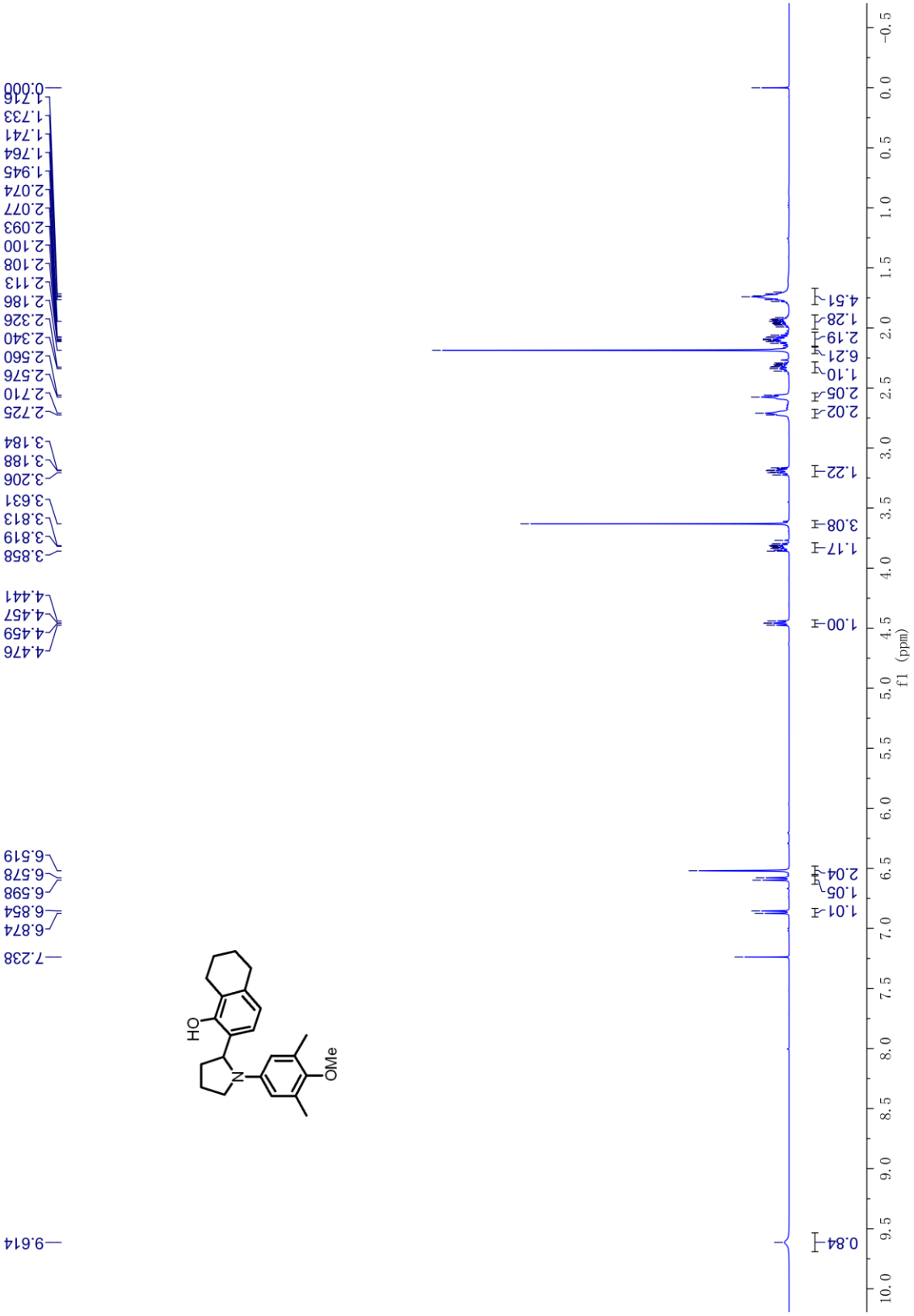
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**



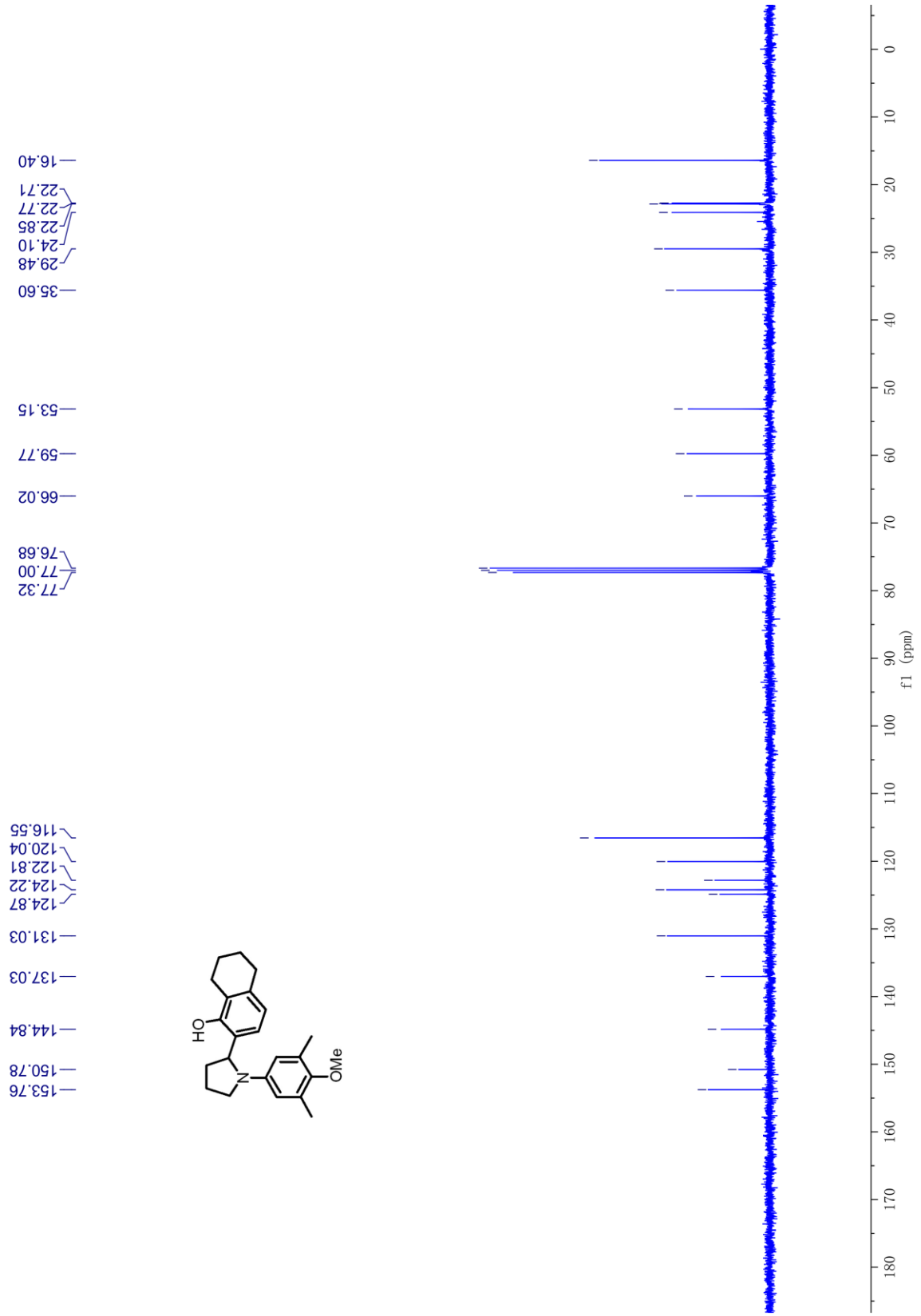
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3k**



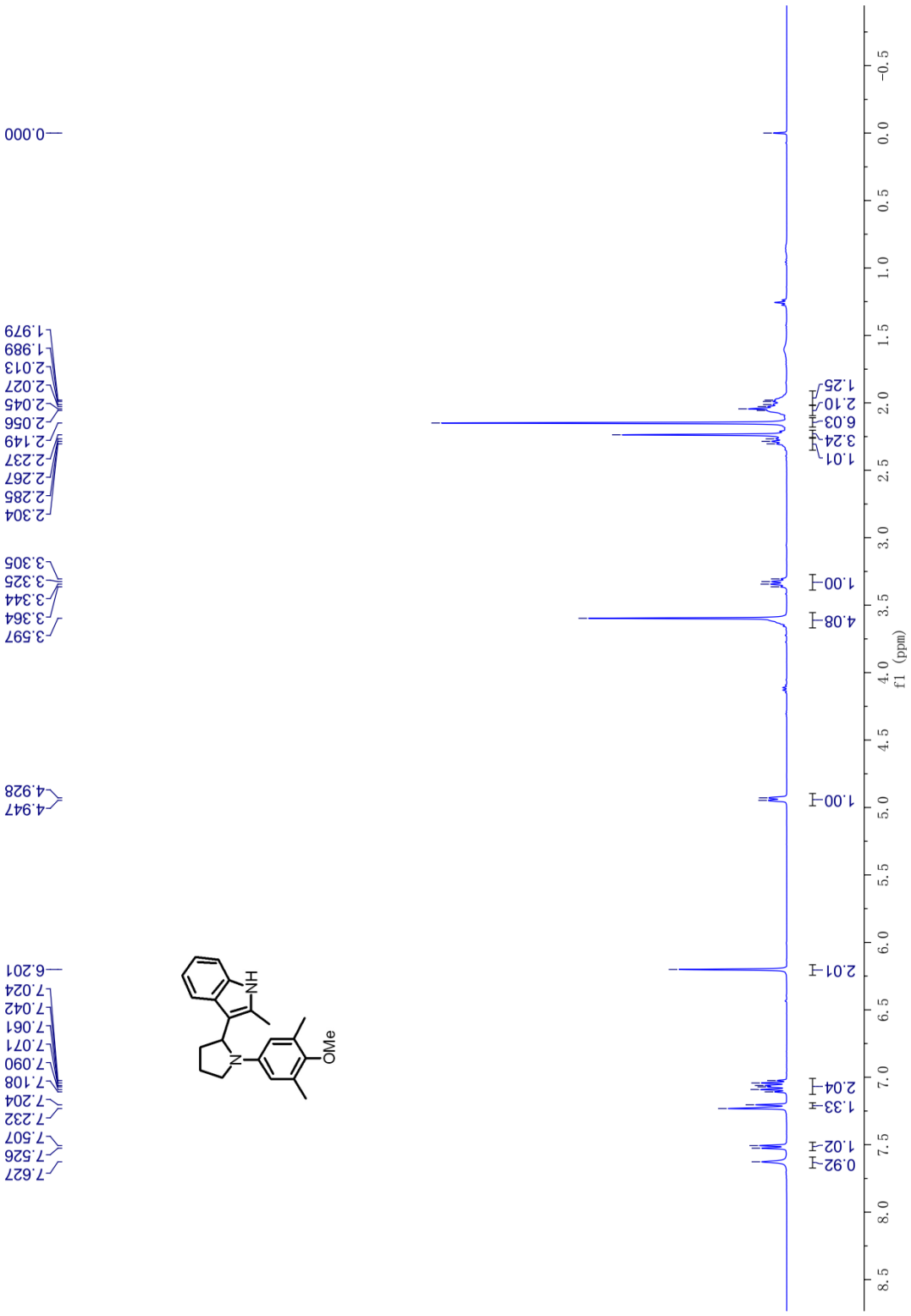
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



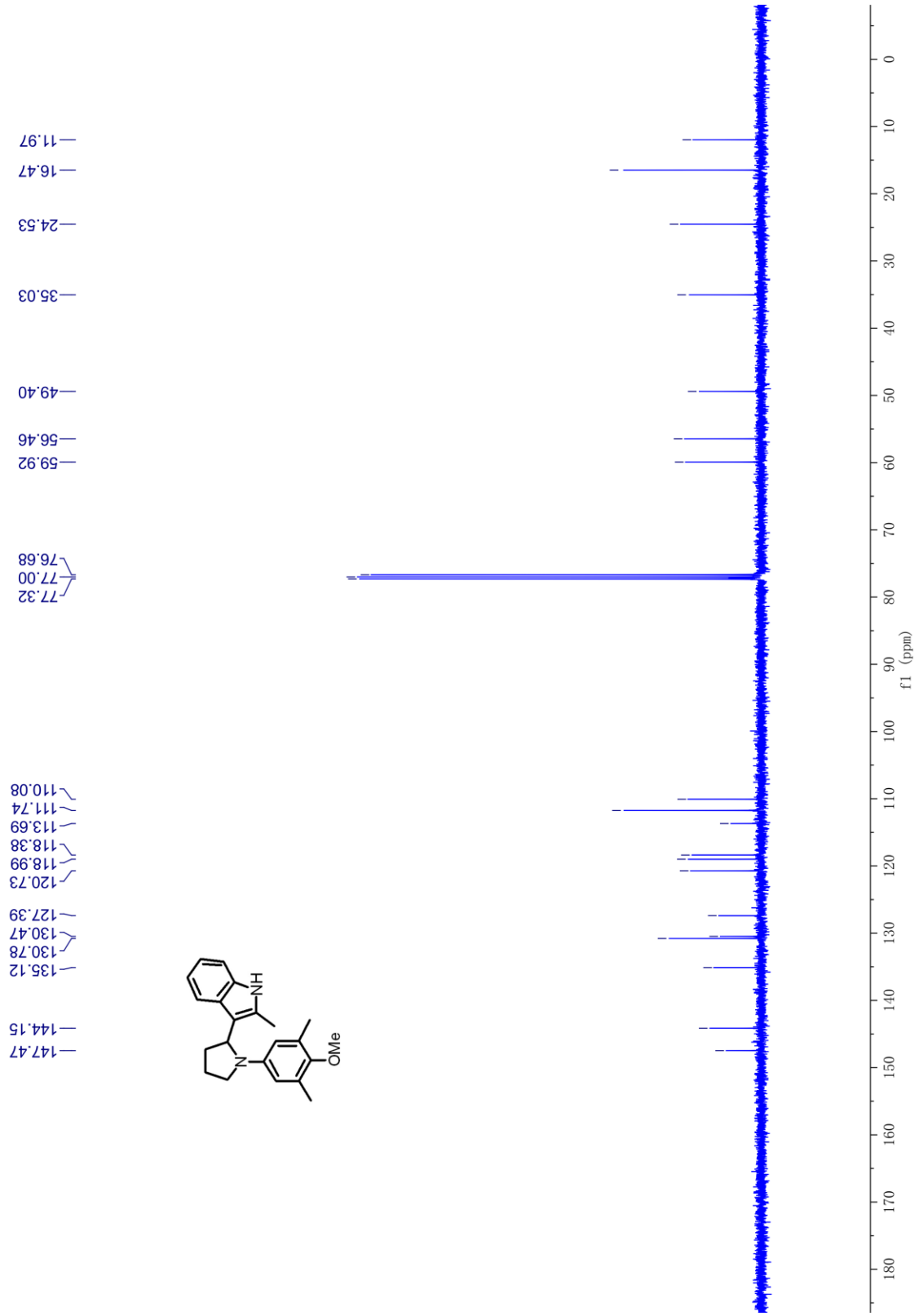
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3l**



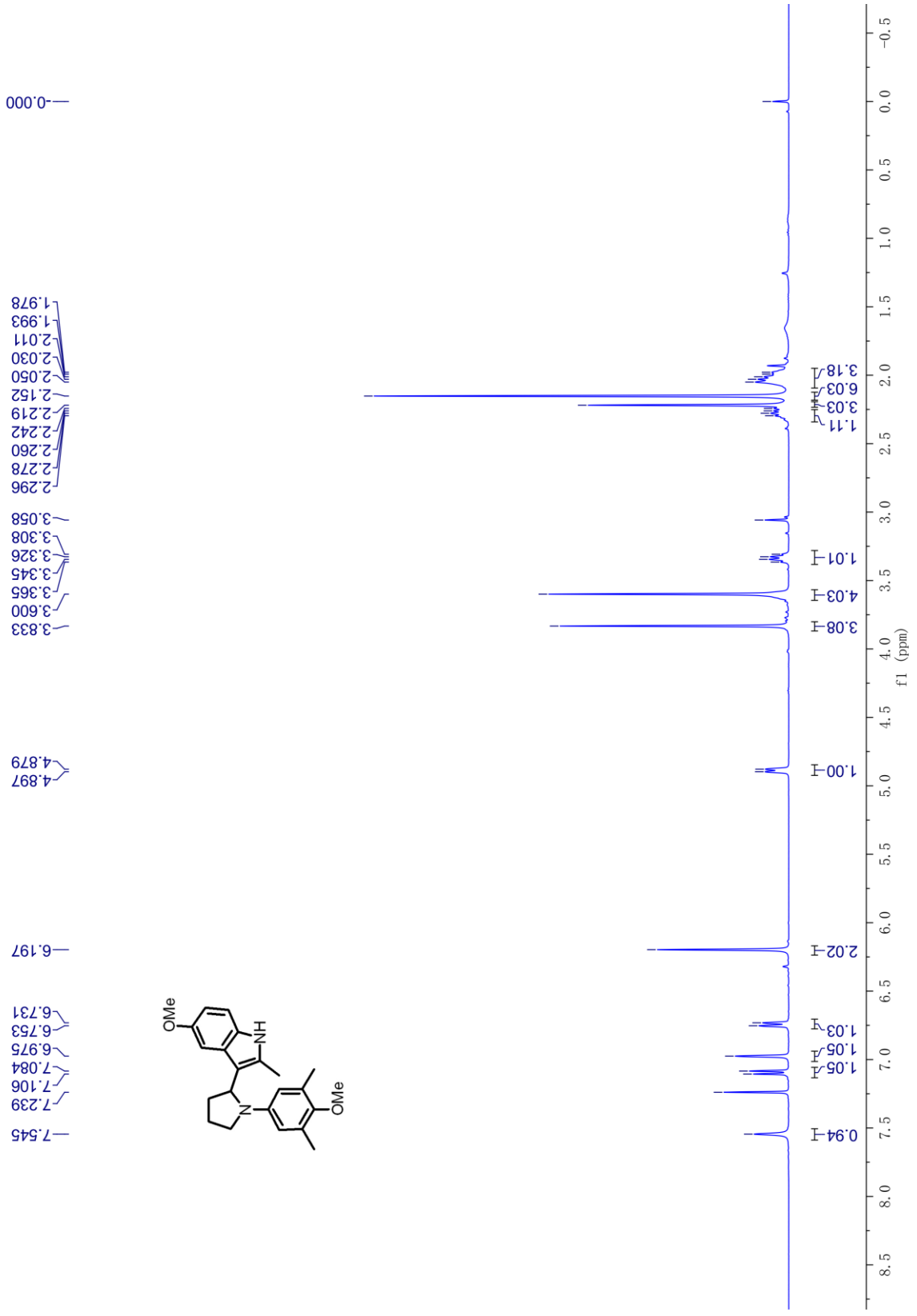
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



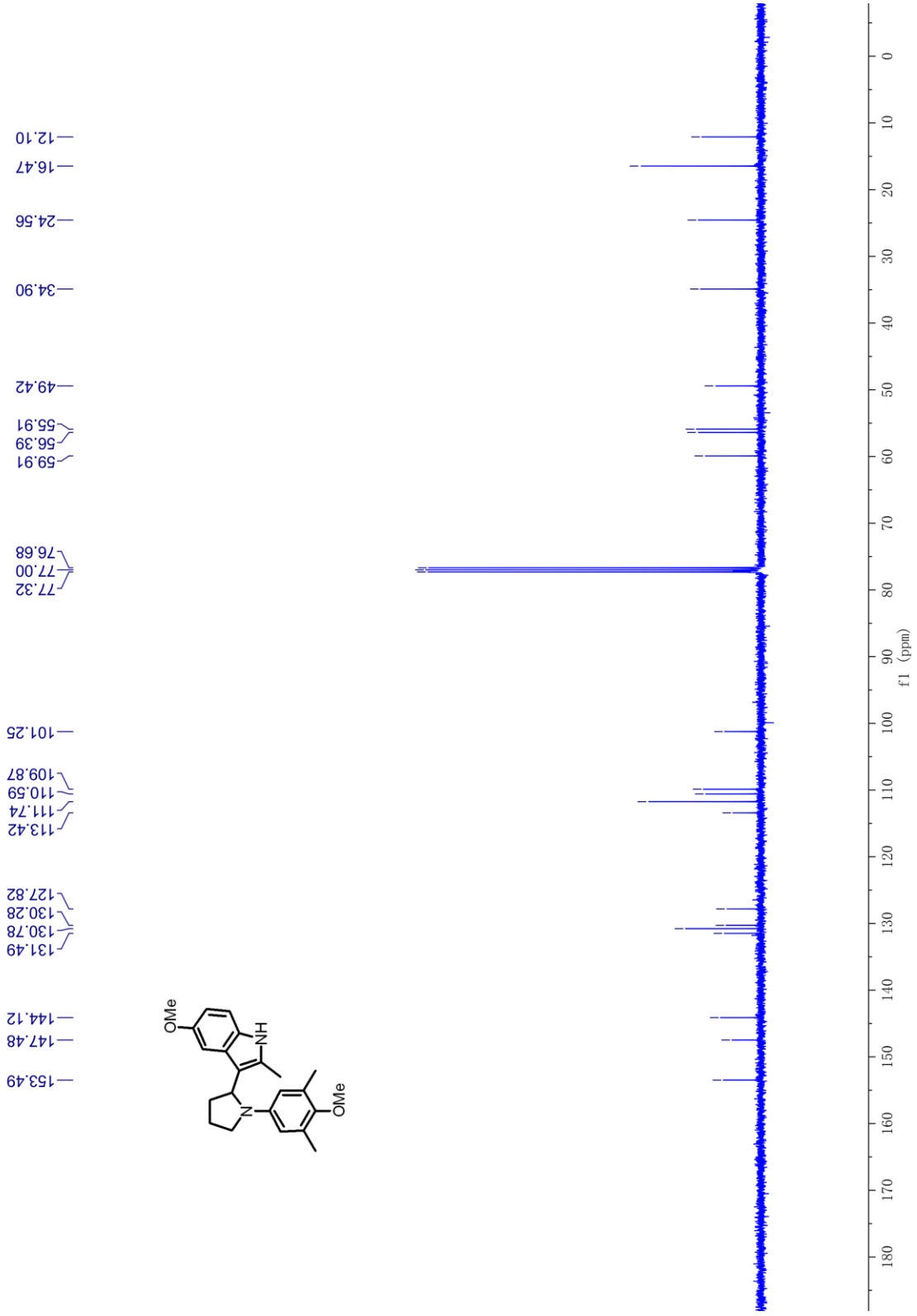
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3m**



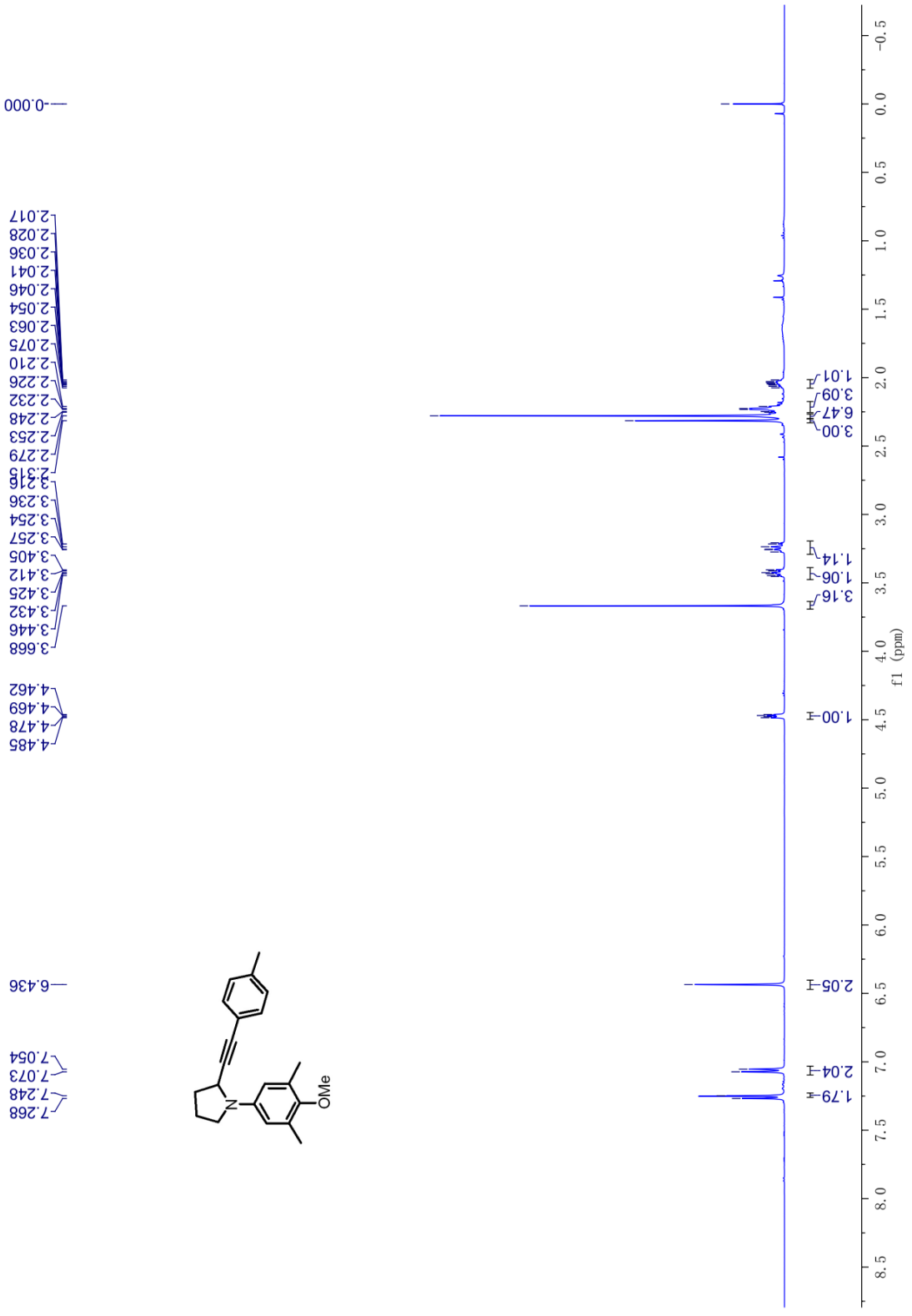
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**



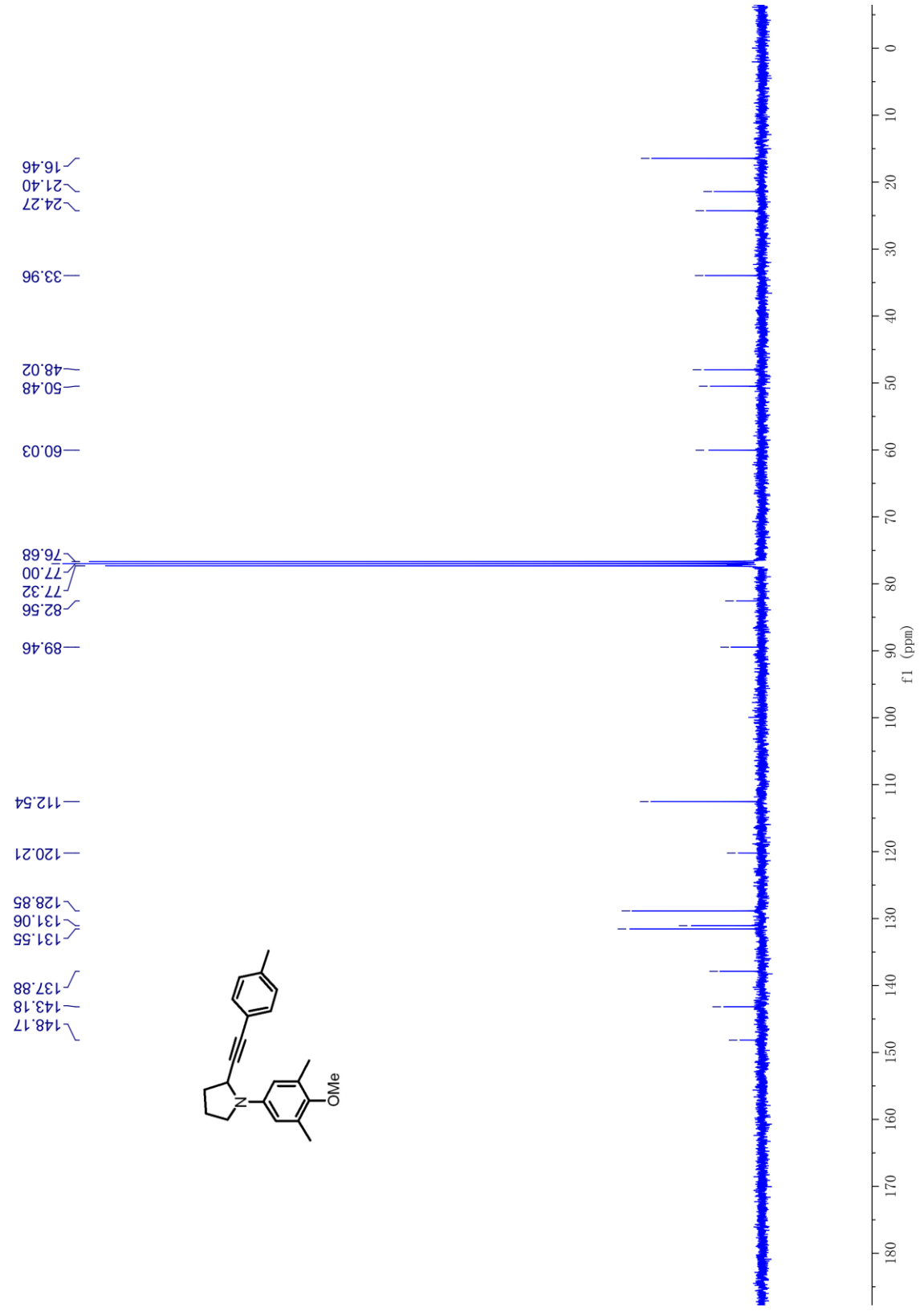
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3n**



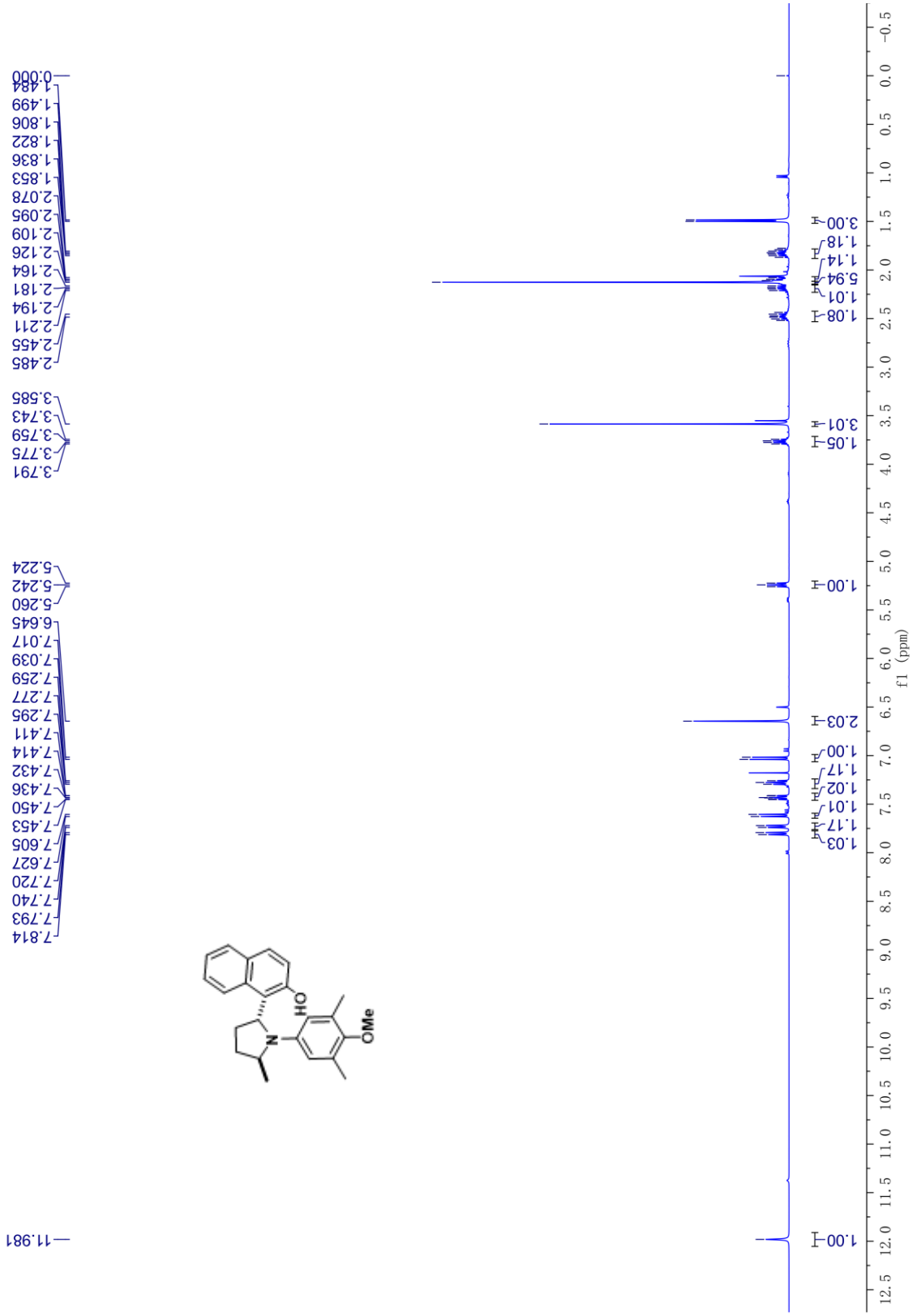
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**



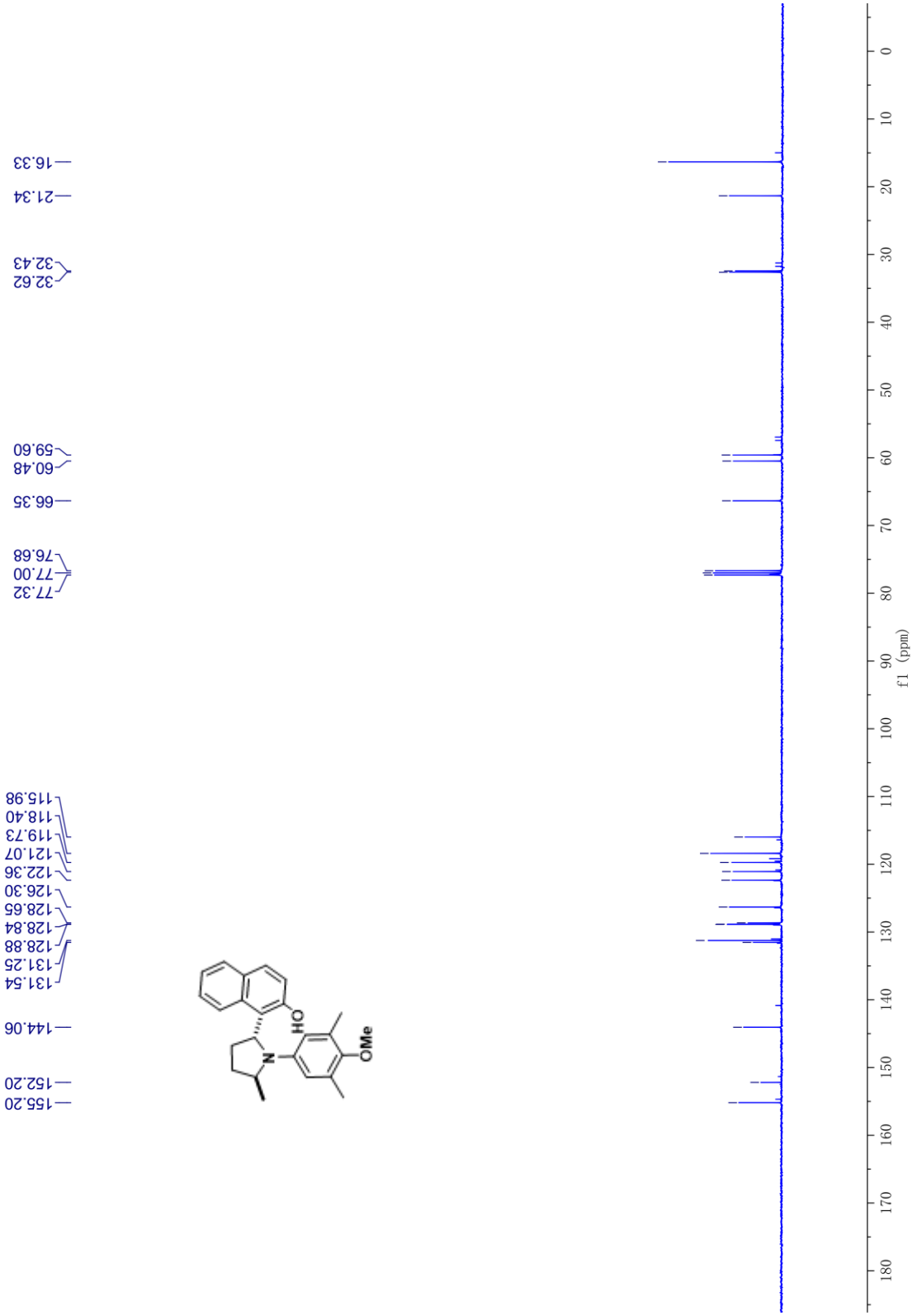
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3o**



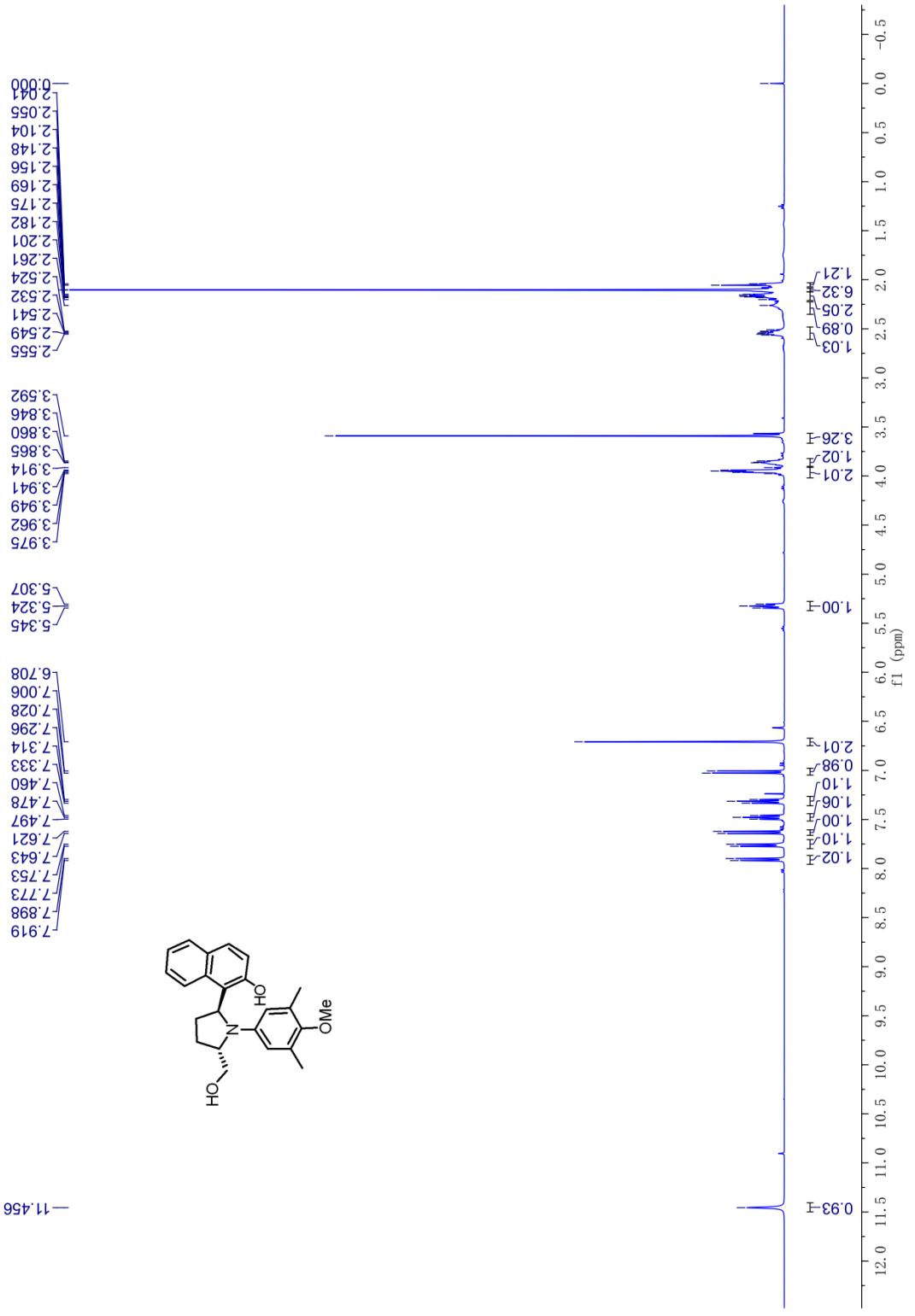
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



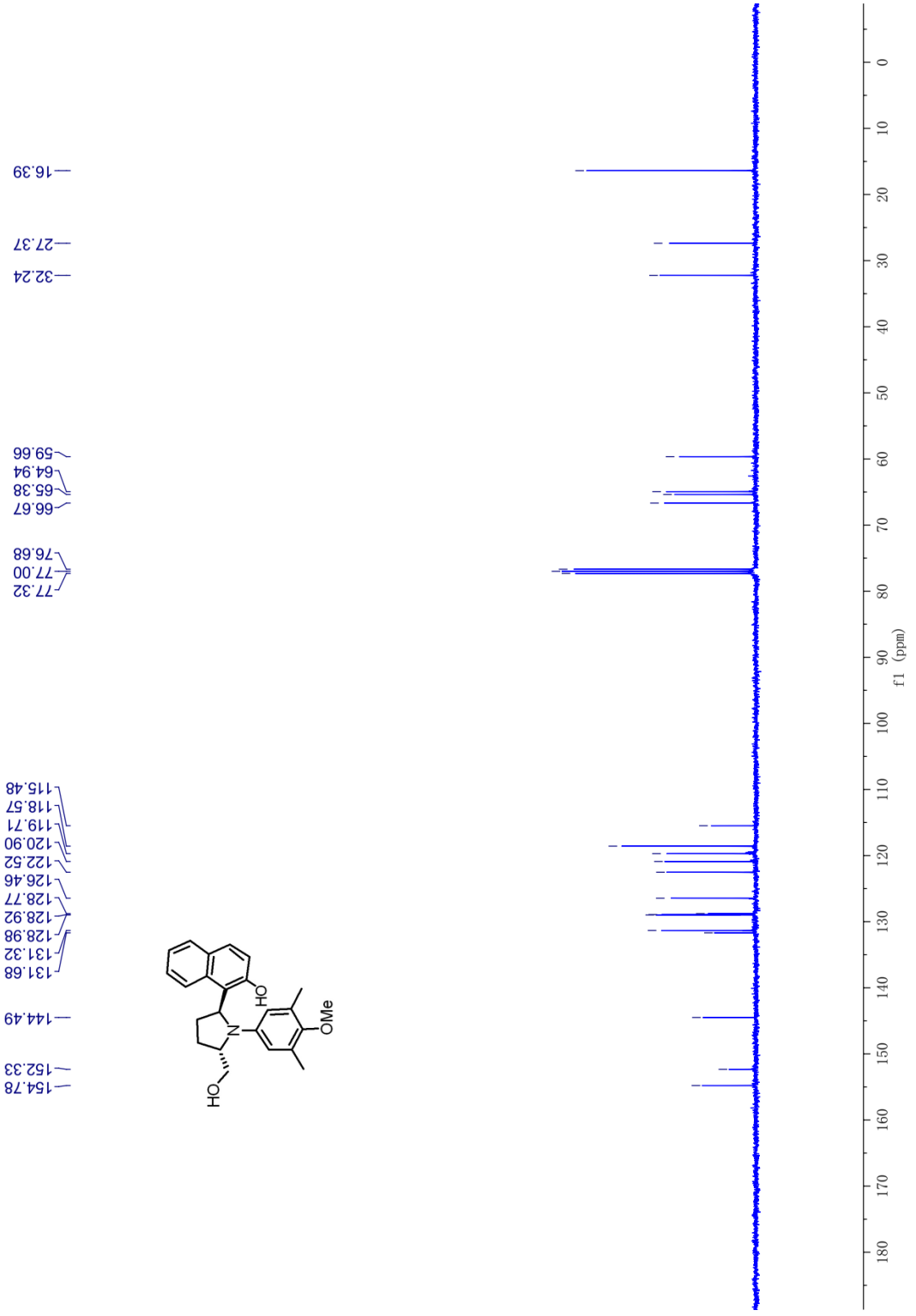
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4a**



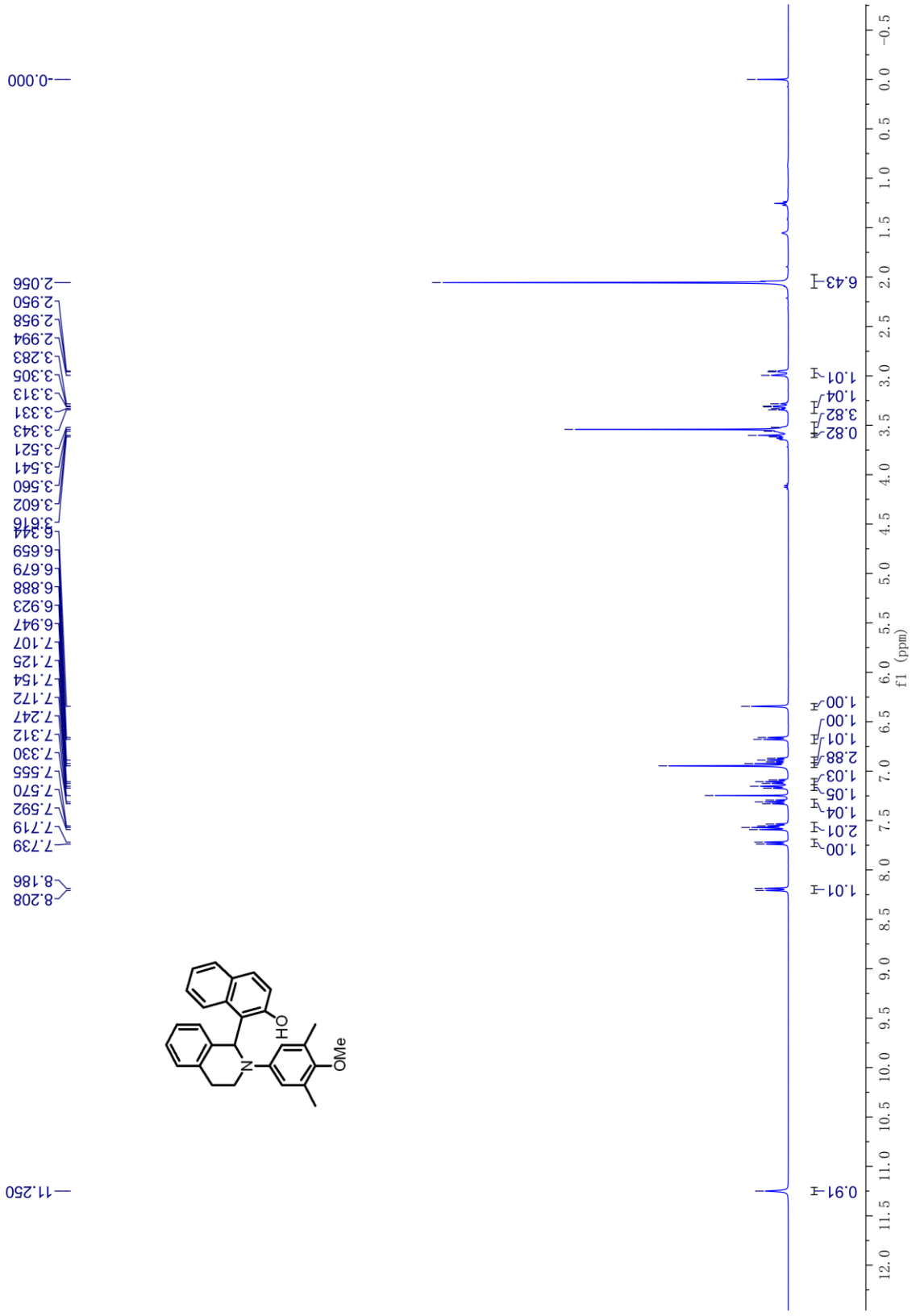
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



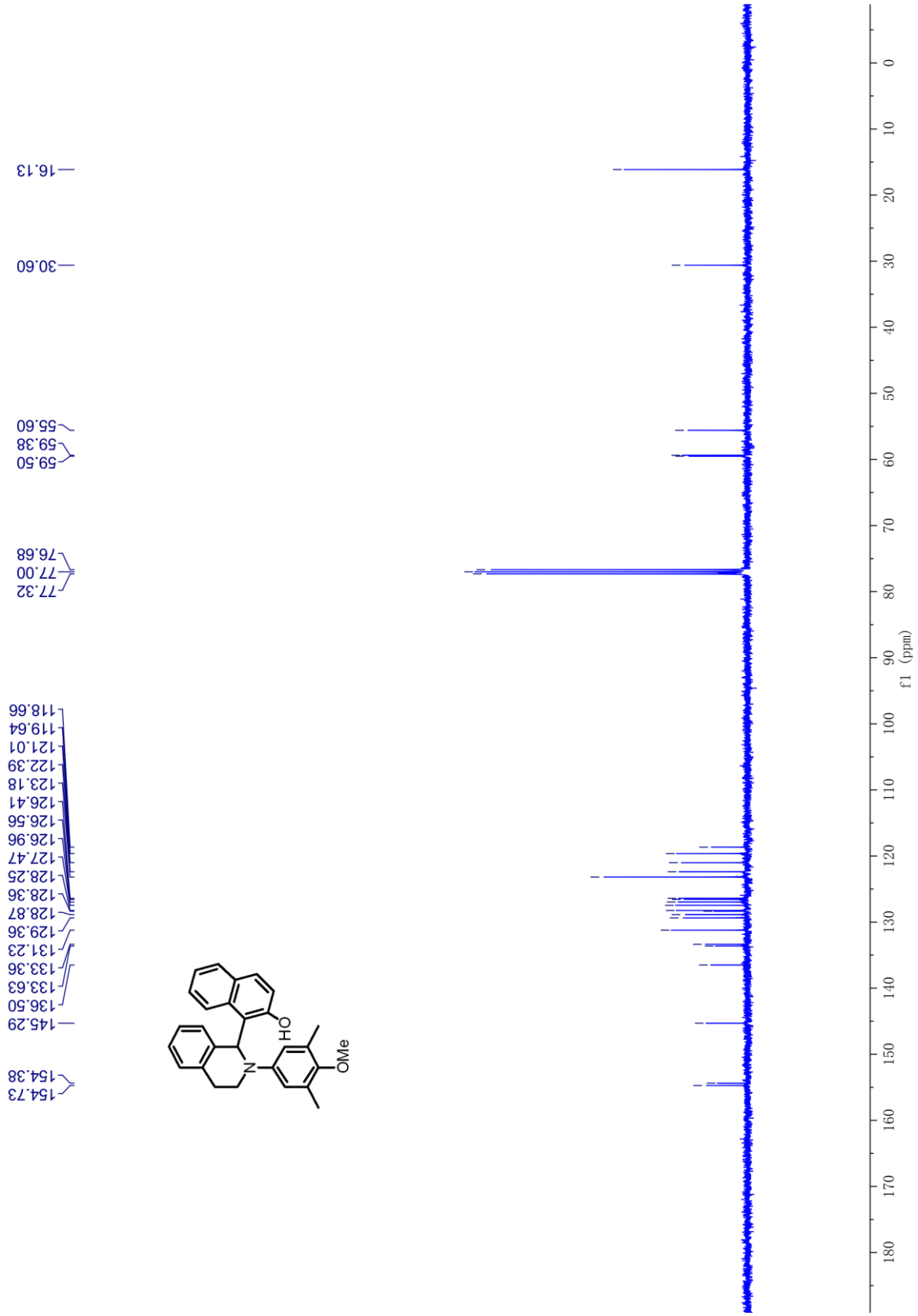
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4b**



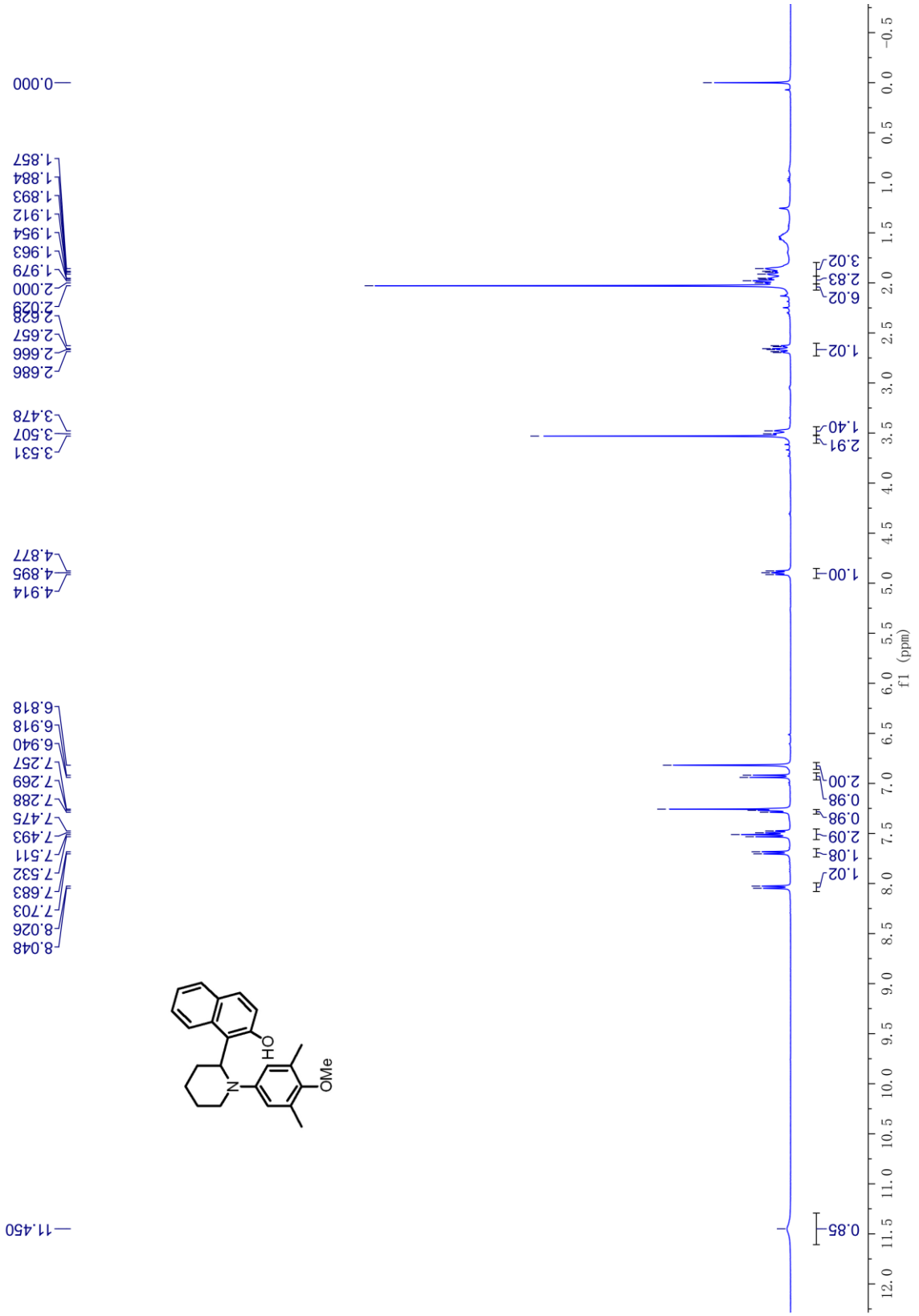
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



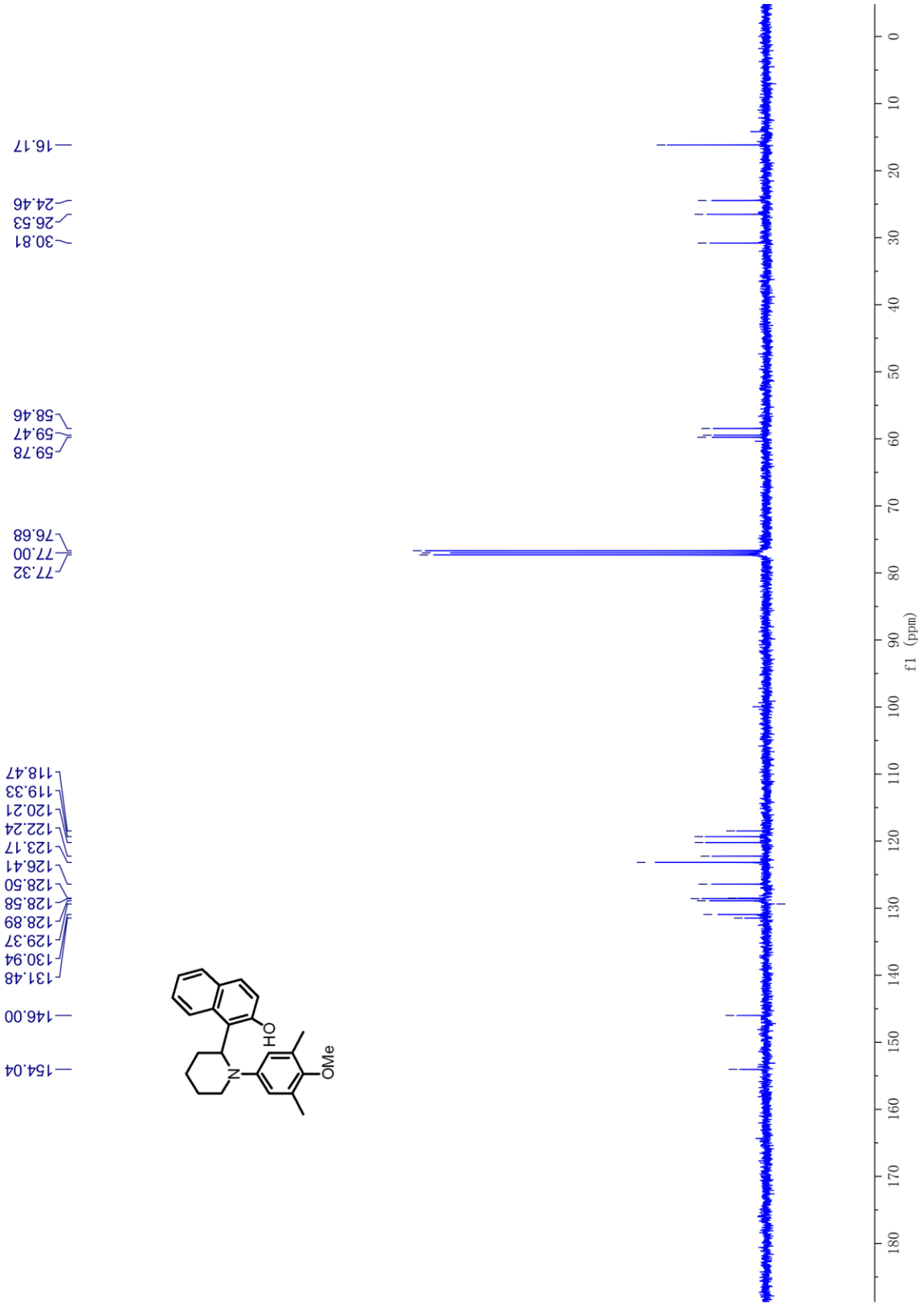
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4c**



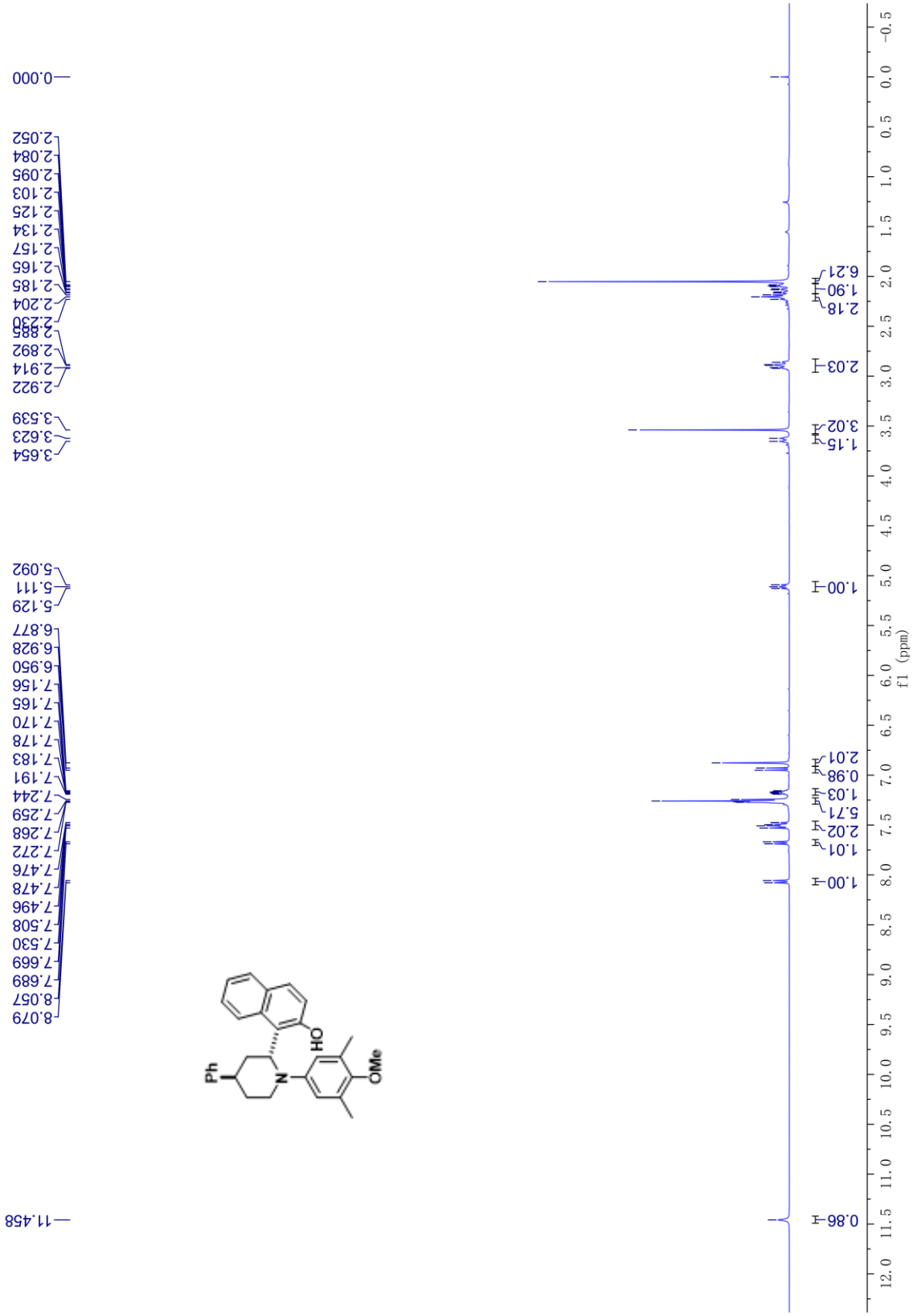
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



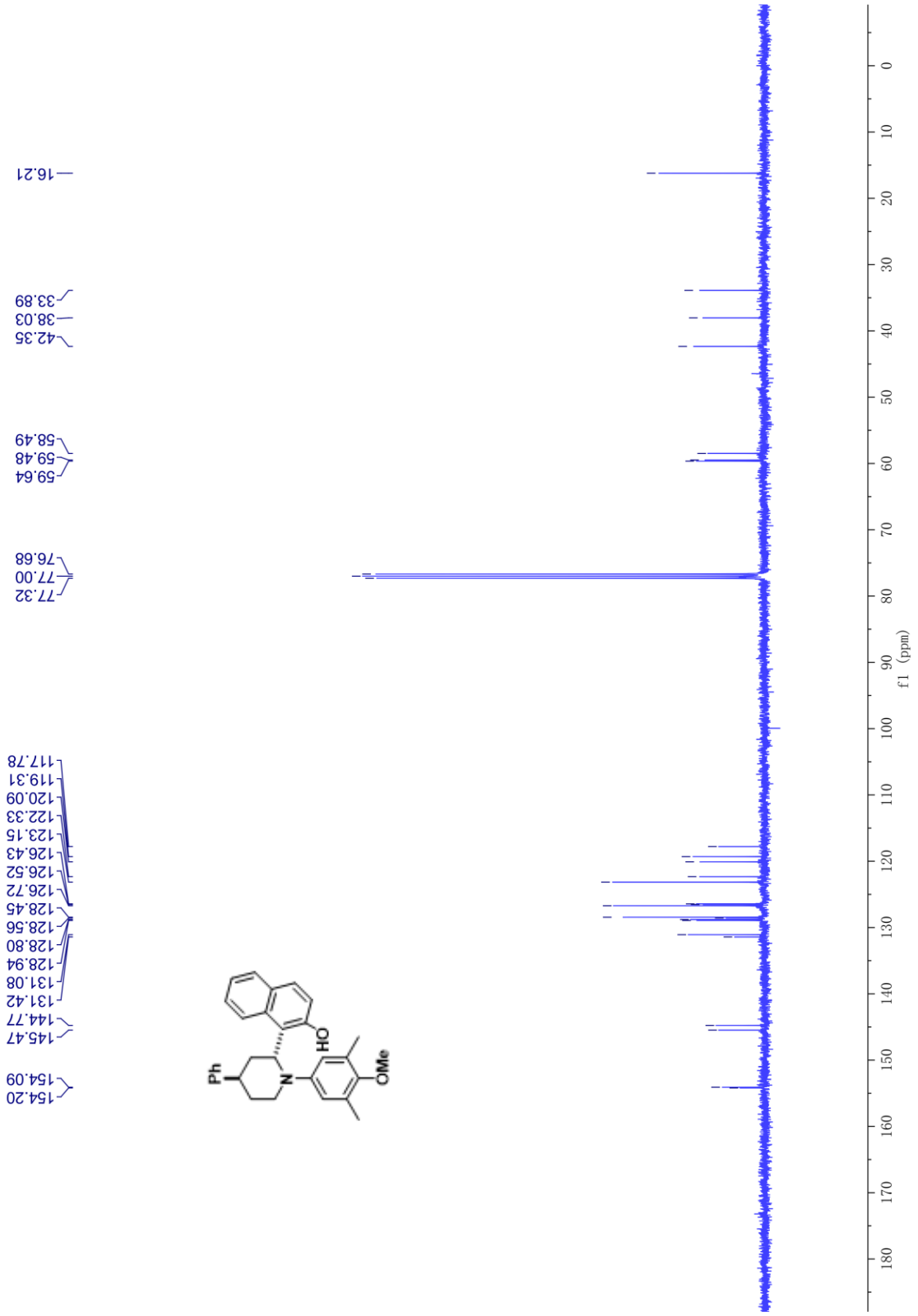
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4d**



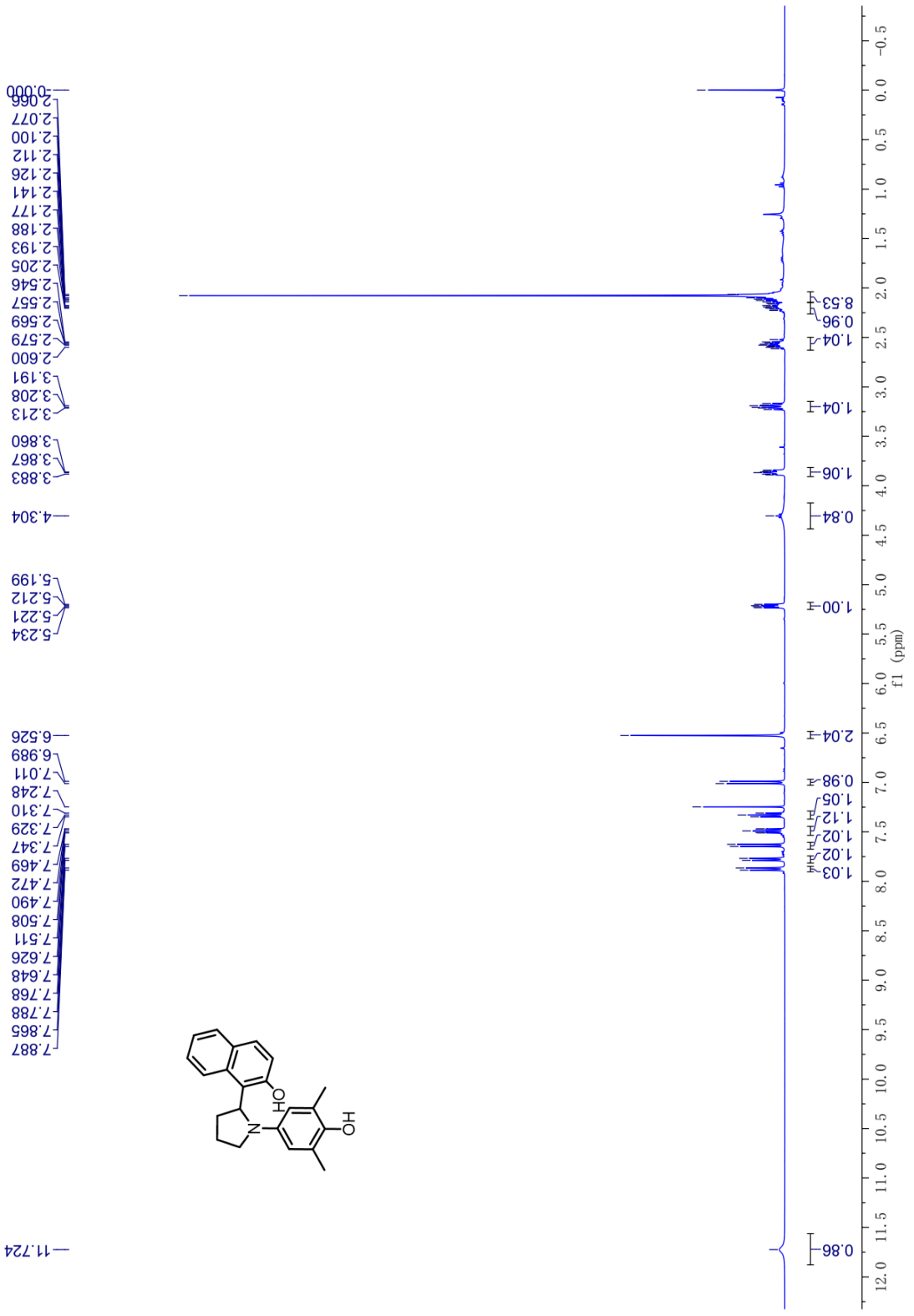
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



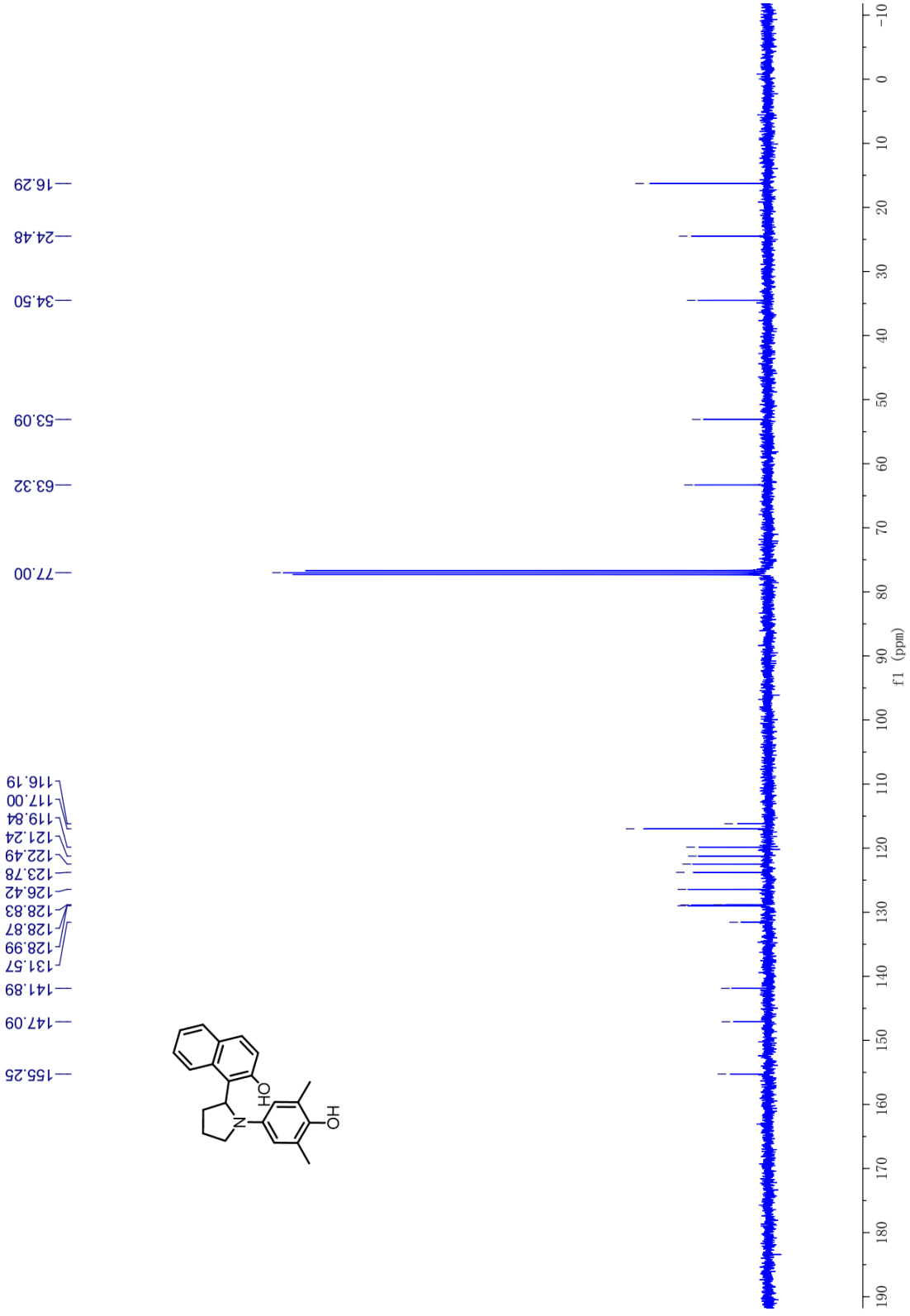
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4e**



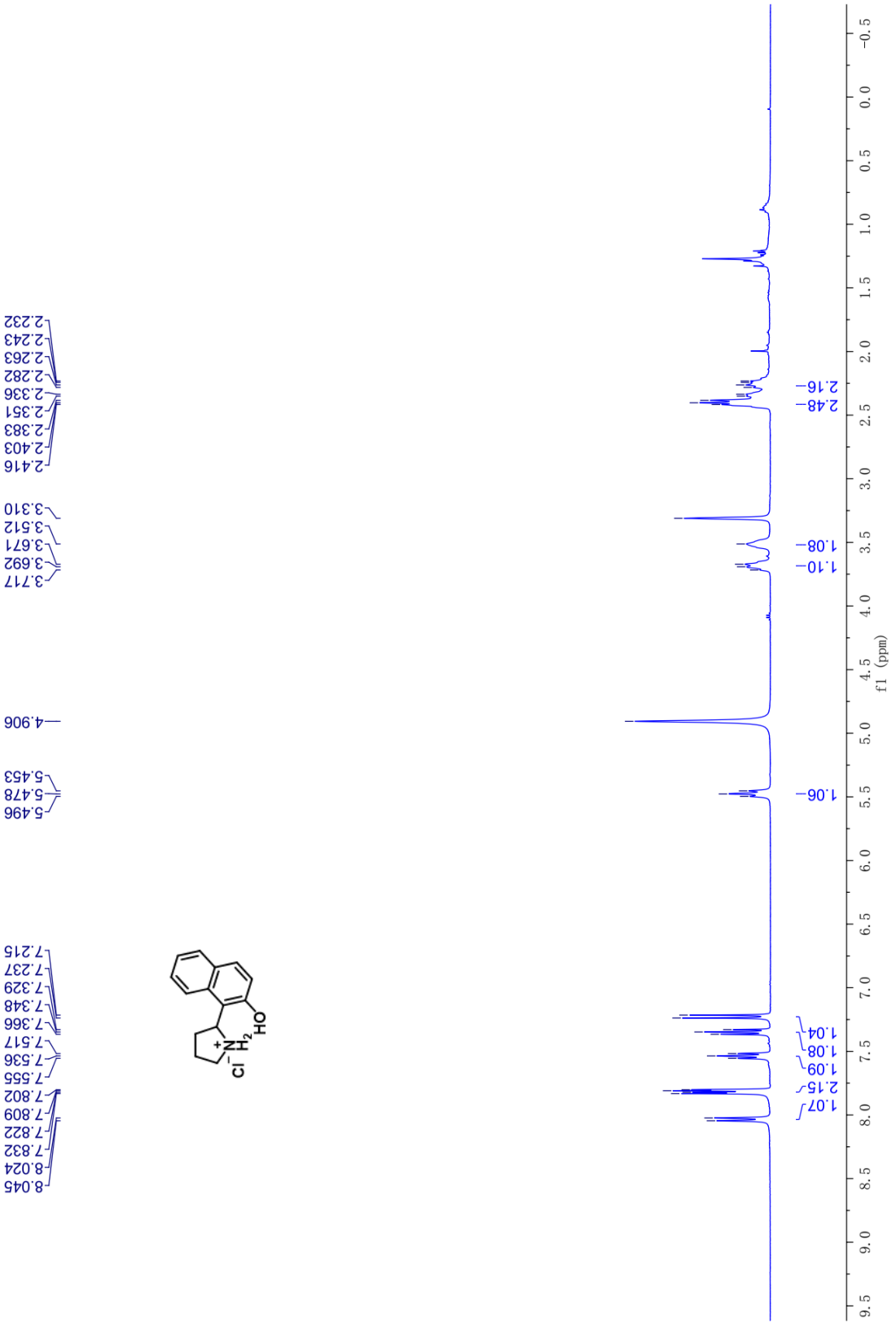
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**



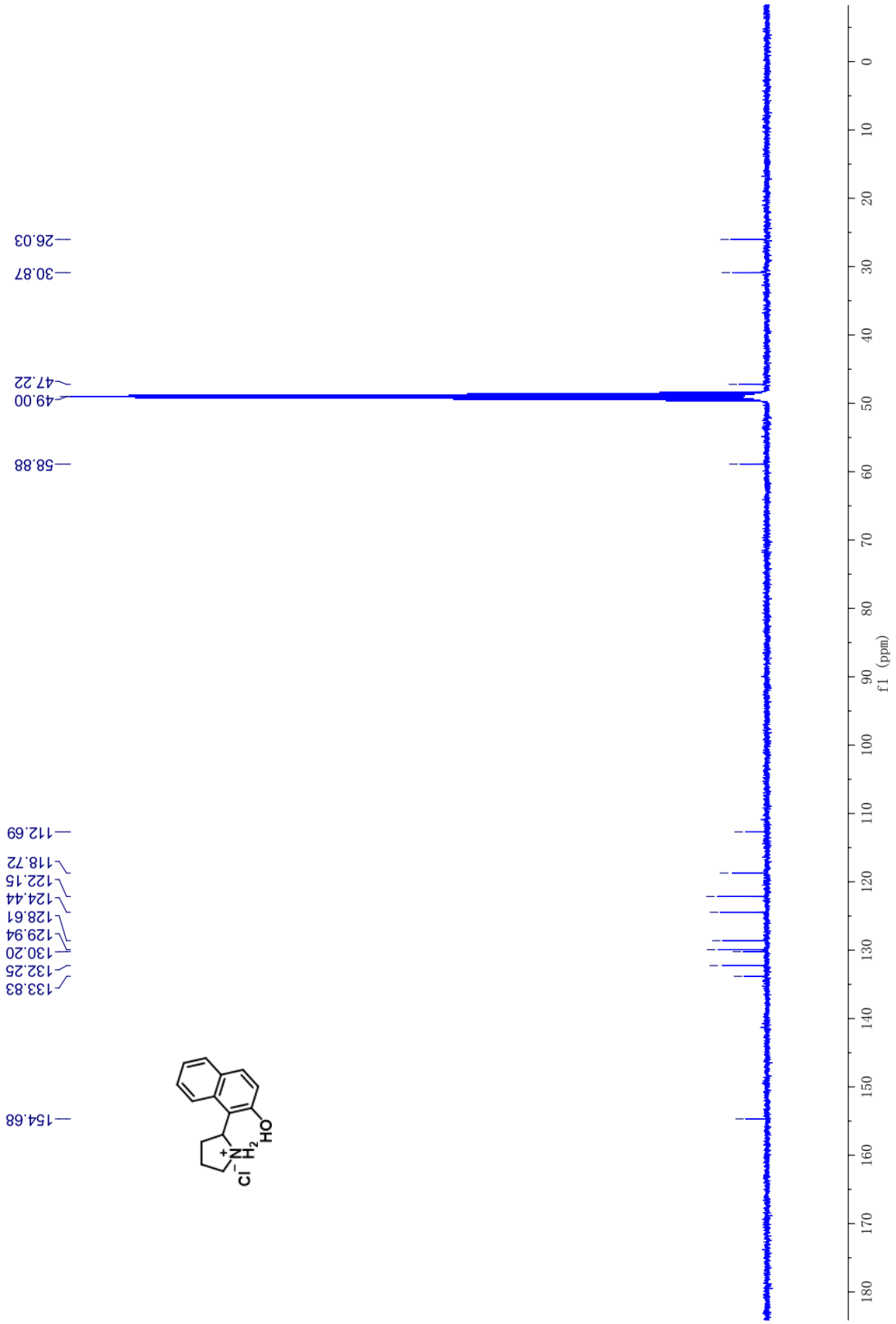
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5a**



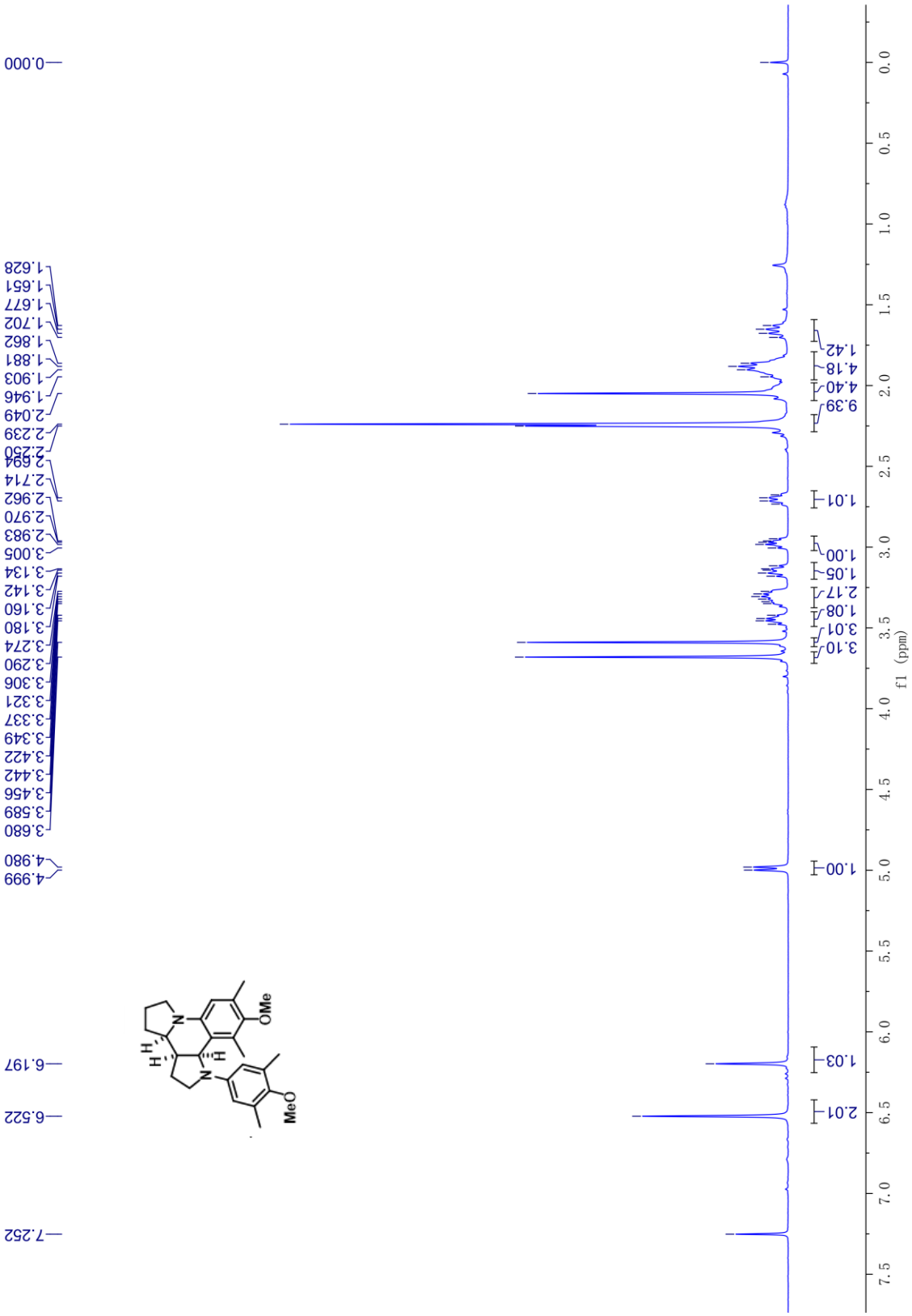
^{1}H NMR (400 MHz, CD_3OD) spectrum of **6a**



^{13}C NMR (101 MHz, CD_3OD) spectrum of **6a**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7**