Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

DBU-Catalyzed Substitution-Controlled Synthesis of Oxa[3.3.1] Bridged Ring and Naphthylamine Derivatives

Shiyu Xu,[a] Zhihui Sun,[a] Pengyutian Liu,[b] Yuanlin Wei,[a] Fan Sun,[a] Man Zhao,[b] Ying Wang,[b] Ming Zhang,*[b] Guofeng Li,*[b] and Liang Hong*[a]

[a]Guangdong Key Laboratory of Chiral Molecule and Drug Discovery, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China.

[b]School of Pharmacy, Shenzhen University Medical School, Shenzhen University, Shenzhen, 518055, China.

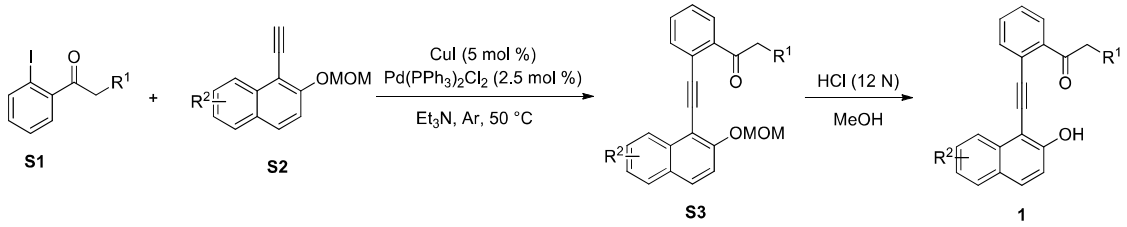
E-mail: hongliang@sysu.edu.cn, liguofeng@szu.edu.cn, zhangm383@mail.sysu.edu.cn.

Index:

General information

Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were purified and dried according to standard methods prior to use. NMR spectra were recorded on Brucker AV 400 or AV 500 spectrometer at 400 MHz or 500 MHz for ^{1}H NMR, at 101 or 126 MHz for ^{13}C NMR and at 376 or 470 MHz for ^{19}F NMR and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources.

General procedure and spectral data for the synthesis of 1



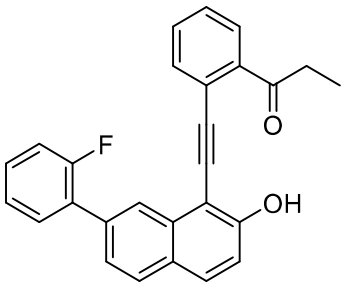
General procedure for the synthesis of S3

Under argon atmosphere, to a stirred solution of **S1** (10 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (2.5 mol %), CuI (5 mol %) in dry Et_3N (30 mL) was added **S2** (15 mmol, 1.5 equiv). Then the mixture was stirred in an oil bath at 50°C overnight. After the completion of the reaction which was indicated by TLC, Et_3N was evaporated in vacuo and the resulting crude residue was extracted with EA and washed with water. Then organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by flash chromatography (PE/EA 10:1) to afford **S3** as a yellow oil. The preparation of **S1**[1] and **S2**[2] was followed the literature procedure.

General procedure for the synthesis of 1

To a stirred solution of **S3** (2.0 mmol, 1.0 equiv) in MeOH (10 mL) was added a few drops of 12N HCl aq. at room temperature. The mixture was stirred at room temperature until the completion of the reaction. Then the reaction mixture is filtered, and the filter residue is dried in an oven to afford **1**.

1-(2-((7-(2-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1a)



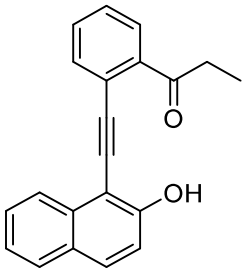
1a

Appearance: yellow solid.
Yield: 86%.
m.p: 143-145°C.
IR: 3291, 2982, 2940, 2177, 1893, 1681, 1483, 1376, 1209, 1140, 1040, 863 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.40 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.84 (t, *J* = 9.1 Hz, 2H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.63 (td, *J* = 7.7, 1.7 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.45 – 7.35

[1] T. Xu, K. Chen, H.-Y. Zhu, W.-*J*. Hao, S.-*J*. Tu and B. *J*iang, *Org. Lett.*, 2020, **22**, 2414-2418.
[2] X. Abel-Snape, G. Wycich and M. Lautens, *ACS Catal.*, 2022, **12**, 3291-3301.

(m, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 3.09 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 201.26, 160.98, 159.74, 159.01, 136.16, 134.69, 133.92, 133.55, 132.23, 131.10, 131.07, 130.95, 129.91, 129.27, 129.17, 129.14, 129.07, 128.27, 127.70, 127.39, 125.02, 125.00, 124.96, 124.93, 124.46, 124.43, 122.43, 117.73, 116.28, 116.10, 102.93, 101.35, 88.28, 33.22, 8.43.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.36.
HRMS (ESI): $C_{27}H_{19}FO_2$ + Na, Calc: 417.1267, Found: 417.1270.

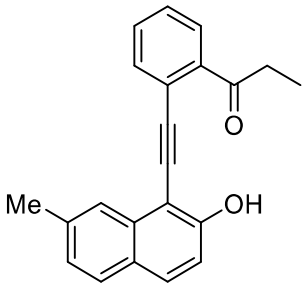
1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1b)



1b

Appearance: yellow solid.
Yield: 78%.
m.p: 115-117 °C.
IR: 3342, 3068, 2941, 2187, 1926, 1668, 1482, 1383, 1211, 1123, 952, 829 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.24 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.80 (dd, J = 14.1, 6.8 Hz, 3H), 7.57 (dd, J = 12.4, 7.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 8.9 Hz, 1H), 3.08 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 201.27, 159.42, 136.22, 133.79, 133.56, 132.21, 131.25, 129.91, 128.24, 128.13, 127.66, 127.19, 124.74, 123.74, 122.52, 117.38, 102.61, 101.01, 88.41, 33.23, 8.44.
HRMS (ESI): $C_{21}H_{16}O_2$ + Na, Calc: 323.1048, Found: 323.1047.

1-(2-((2-hydroxy-7-methylnaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1c)



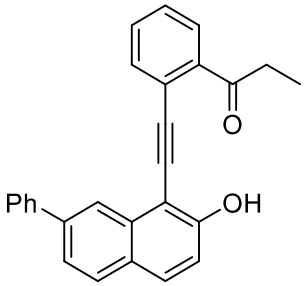
1c

Appearance: yellow solid.
Yield: 48%.
m.p: 158-160°C.
IR: 3368, 2982, 2970, 2935, 2196, 1675, 1622, 1579, 1444, 1413, 1298, 1207, 832 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.04 – 7.89 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 8.2 Hz, 2H), 3.08 (q, J = 7.2 Hz, 2H), 2.58 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.27, 159.54, 137.18, 136.24, 133.80, 133.76, 132.16, 131.06, 129.88, 128.08, 127.57, 126.35, 125.93, 123.93, 122.62, 116.37, 102.00, 100.91, 88.64, 33.24, 22.00, 8.44.

HRMS (ESI): $C_{22}H_{18}O_2$ + Na, Calc: 337.1204, Found: 337.1200.

1-(2-((2-hydroxy-7-phenylnaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1d)



1d

Appearance: yellow solid.

Yield: 54%.

m.p: 176-178°C.

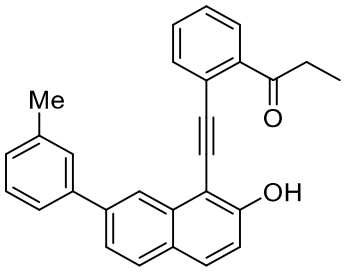
IR: 3377, 3059, 2991, 2195, 1896, 1788, 1603, 1373, 1271, 1170, 1036, 868 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.43 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.76 (m, 5H), 7.66 – 7.51 (m, 4H), 7.48 – 7.38 (m, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 3.10 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 201.26, 159.80, 141.38, 139.99, 136.22, 133.88, 133.84, 132.23, 130.99, 129.93, 128.86, 128.75, 127.70, 127.56, 127.42, 127.33, 123.52, 122.86, 122.49, 117.41, 102.90, 101.37, 88.41, 33.23, 8.45.

HRMS (ESI): $C_{27}H_{20}O_2$ + Na, Calc: 399.1361, Found: 399.1359.

1-(2-((2-hydroxy-7-(m-tolyl)naphthalen-1-yl)ethynyl)phenyl)propan-1-one (1e)



1e

Appearance: yellow solid.

Yield: 71%.

m.p: 158-160°C.

IR: 3324, 3030, 2935, 2192 1890, 1678, 1481, 1377, 1210, 1141, 1041, 884 cm^{-1}.

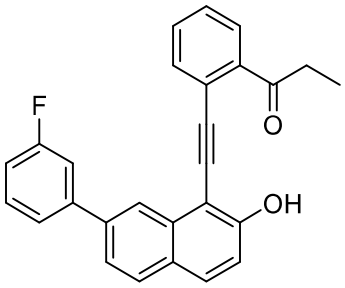
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (d, *J* = 17.6 Hz, 1H), 8.29 (s, 1H), 7.86 (dd, *J* = 16.0, 7.6 Hz, 1H), 7.69 (ddd, *J* = 8.7, 7.5, 5.5 Hz, 3H), 7.52 – 7.42 (m, 4H), 7.30 (ddd, *J* = 15.6, 9.8, 5.8 Hz, 2H), 7.18 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.14 (s, 1H), 2.97 (tt, *J* = 14.4, 7.2 Hz, 2H), 2.38 (d, *J* = 4.1 Hz, 3H), 1.17 (dd, *J* = 7.2, 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 201.26, 159.81, 141.41, 140.18, 138.45, 136.20, 133.84, 132.24,

131.00, 129.94, 128.80, 128.78, 128.70, 128.37, 128.21, 127.69, 127.31, 124.71, 123.64, 122.84, 122.50, 117.34, 102.90, 101.38, 88.48, 33.23, 21.64, 8.46.

HRMS (ESI): $C_{28}H_{22}O_2$ + Na, Calc: 413.1517, Found: 413.1512.

1-(2-((7-(3-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1f)



1f

Appearance: yellow solid.

Yield: 52%.

m.p: 172-174C.

IR: 3341, 2922, 2853, 2193, 1674, 1589, 1511, 1373, 1210, 1141, 1013, 895 cm^{-1}.

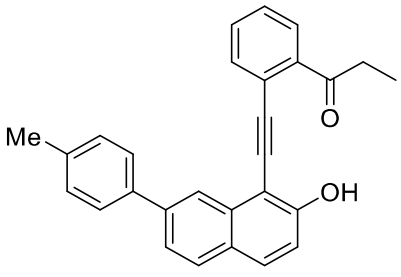
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.39 (d, *J* = 1.7 Hz, 1H), 8.01 – 7.94 (m, 1H), 7.87 – 7.77 (m, 3H), 7.62 – 7.54 (m, 3H), 7.46 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.15 – 7.07 (m, 1H), 3.09 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.26, 164.47, 162.03, 159.90, 143.69, 143.61, 138.64, 138.62, 136.24, 133.91, 133.77, 132.29, 130.95, 130.35, 130.26, 129.94, 128.93, 127.78, 127.58, 123.17, 122.96, 122.40, 117.75, 114.45, 114.29, 114.24, 114.08, 102.98, 101.51, 88.19, 33.23, 8.44.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.93.

HRMS (ESI): $C_{27}H_{19}FO_2$ + Na, Calc: 417.1267, Found: 417.1270.

1-(2-((2-hydroxy-7-(p-tolyl)naphthalen-1-yl)ethynyl)phenyl)propan-1-one (1g)



1g

Appearance: yellow solid.

Yield: 65%.

m.p: 189-191°C.

IR: 3747, 3364, 2940, 2193, 1924, 1672, 1618, 1374, 1207, 1137, 1061, 870 cm^{-1}.

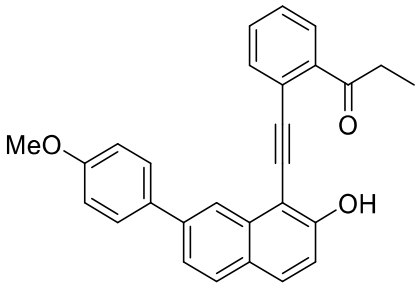
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.31 (s, 1H), 7.88 (d, *J* = 6.1 Hz, 1H), 7.76 – 7.68 (m, 3H), 7.60 (d, *J* = 5.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 7.2, 5.5 Hz, 1H), 7.33 (t, *J* = 6.4 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 2H), 7.21 – 7.16 (m, 1H), 3.06 – 2.87 (m, 2H), 2.36 (d, *J* = 1.7 Hz, 3H), 1.24 – 1.15 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 201.23, 159.76, 139.92, 138.47, 137.26, 136.18, 133.85, 132.21,

130.98, 129.92, 129.59, 128.68, 127.66, 127.38, 127.19, 123.45, 122.53, 122.51, 117.22, 102.82, 101.33, 88.47, 33.22, 21.15, 8.44.

HRMS (ESI): $C_{28}H_{22}O_2$ + Na, Calc: 413.1517, Found: 413.1510.

1-(2-((2-hydroxy-7-(4-methoxyphenyl)naphthalen-1-yl)ethynyl)phenyl)propan-1-one (1h)



1h

Appearance: yellow solid.

Yield: 77%.

m.p: 176-178°C.

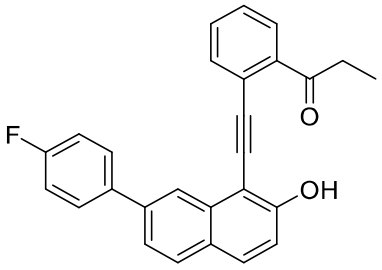
IR: 3283, 2966, 2926, 2179, 1893, 1679, 1505, 1479, 1384, 1168, 1032, 880 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.37 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 8.8 Hz, 3H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.09 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.25, 159.78, 159.33, 139.58, 136.22, 133.91, 133.85, 133.82, 132.21, 130.99, 129.92, 128.69, 128.55, 127.66, 127.02, 123.32, 122.53, 122.11, 117.08, 114.33, 102.74, 101.32, 88.51, 55.37, 33.23, 8.45.

HRMS (ESI): $C_{28}H_{22}O_3$ + Na, Calc: 429.1467, Found: 429.1468.

1-(2-((7-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1i)



1i

Appearance: yellow solid.

Yield: 49%.

m.p: 207-209°C.

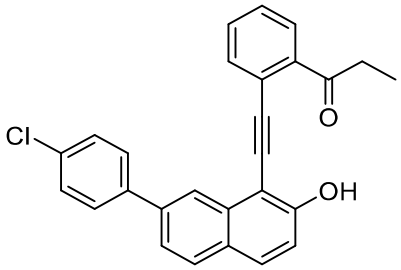
IR: 3379, 2922, 2853, 2196, 1905, 1670, 1483, 1373, 1208, 1138, 1062, 881 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.36 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.68 (m, 5H), 7.59 (dd, *J* = 16.2, 8.5 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 2H), 3.11 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.31, 159.89, 139.02, 137.49, 136.31, 133.89, 133.84, 132.27, 131.00, 129.97, 129.15, 129.07, 128.87, 127.78, 127.28, 123.34, 122.71, 122.48, 117.51, 115.86, 115.64, 102.85, 101.40, 99.96, 88.33, 33.28, 8.47.

19F NMR (376 MHz, $CDCl_3$): δ -115.48.
HRMS (ESI): $C_{27}H_{19}FO_2$ + Na, Calc: 417.1267, Found: 417.1265.

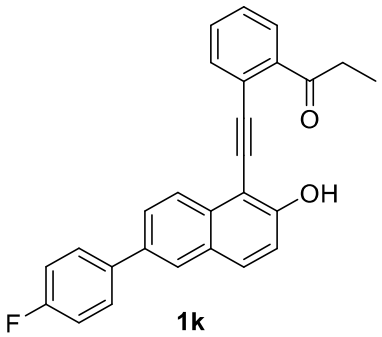
1-(2-((7-(4-chlorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1j)



1j

Appearance: yellow solid.
Yield: 57%.
m.p: 191-193°C.
IR: 3367, 2194, 1672, 1619, 1580, 11513, 1482, 1375, 1210, 1138, 1095, 887 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.37 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.76 (m, 3H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.51 – 7.42 (m, 3H), 7.30 (d, *J* = 8.9 Hz, 1H), 3.10 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.29, 159.88, 139.83, 138.73, 136.28, 133.87, 133.81, 133.56, 132.27, 130.98, 129.96, 129.01, 128.93, 128.77, 127.79, 127.43, 123.14, 122.80, 122.43, 117.65, 102.91, 101.46, 88.24, 33.26, 8.46.
HRMS (ESI): $C_{27}H_{19}ClO_2$ + Na, Calc: 433.0971, Found: 433.0965.

1-(2-((6-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)propan-1-one (1k)

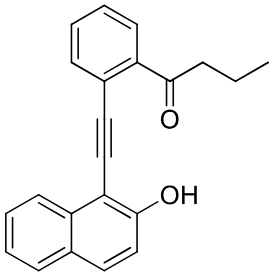


1k

Appearance: yellow solid.
Yield: 46%.
m.p: 167-169°C.
IR: 3312, 3063, 2922, 2183, 1886, 1784, 1481, 1384, 1202, 1193, 1046, 867 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 1.4 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 2H), 7.75 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 3.09 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.27, 163.60, 161.15, 159.54, 137.08, 137.05, 136.22, 135.54, 133.81, 132.66, 132.24, 131.42, 129.94, 128.74, 128.66, 128.32, 127.73, 126.57, 126.01, 125.40, 122.45, 117.94, 115.77, 115.56, 102.57, 101.09, 88.26, 33.22, 8.43.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.86.
HRMS (ESI): $C_{27}H_{19}FO_2$ + Na, Calc: 417.1267, Found: 417.1271.

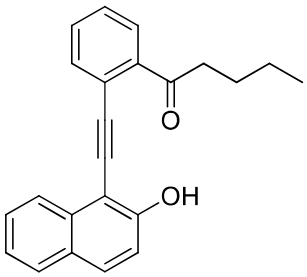
1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)butan-1-one (1l)



1l

Appearance: yellow solid.
Yield: 56%.
m.p: 129-130°C.
IR: 3310, 3056, 2961, 2925, 2191, 1895, 1678, 1594, 1559, 1311, 1283, 1211 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.91 – 7.74 (m, 3H), 7.57 (dd, *J* = 13.7, 7.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 1.96 – 1.76 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.13, 159.49, 136.66, 133.82, 133.63, 132.21, 131.29, 129.97, 128.29, 128.20, 127.67, 127.24, 124.80, 123.78, 122.61, 117.44, 102.65, 100.96, 88.45, 42.03, 18.05, 13.82.
HRMS (ESI): $C_{22}H_{18}O_2$ + Na, Calc: 337.1199, Found: 337.1204.

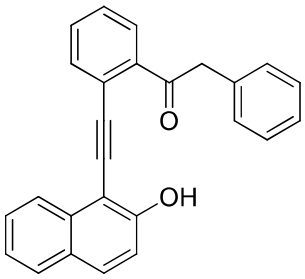
1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)pentan-1-one (1m)



1m

Appearance: yellow solid.
Yield: 81%.
m.p: 92-93°C.
IR: 3342, 3063, 2957, 2936, 2896, 2185, 1674, 1619, 1484, 1282, 1197, 964 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.73 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.40 (dt, *J* = 19.6, 7.5 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 3.15 – 2.97 (m, 2H), 1.91 – 1.70 (m, 2H), 1.44 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.16, 159.44, 136.46, 133.77, 133.55, 132.17, 131.23, 129.96, 128.23, 128.12, 127.62, 127.18, 124.74, 123.73, 122.53, 117.38, 102.60, 100.96, 88.39, 39.83, 26.63, 22.42, 13.92.
HRMS (ESI): $C_{23}H_{20}O_2$ + Na, Calc: 351.1356, Found: 351.1351.

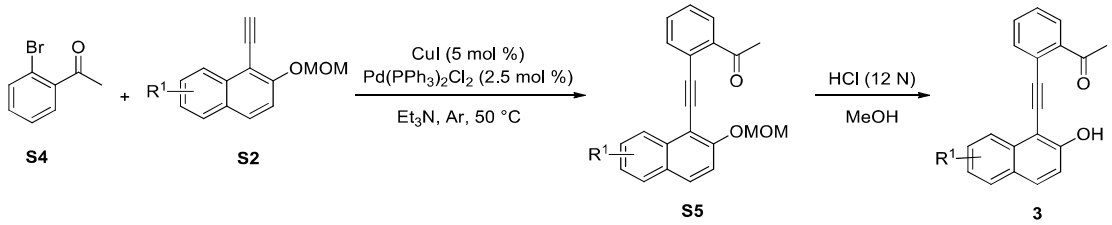
1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-2-phenylethanone (1n)



1n

Appearance: yellow solid.
Yield: 62%.
m.p: 139-141°C.
IR: 3518, 3383, 3054, 2188, 1658, 1592, 1481, 1458, 1283, 1165, 1023, 919 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.38 (ddd, *J* = 7.1, 6.1, 2.1 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.28 – 7.21 (m, 2H), 4.35 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.17, 159.40, 135.84, 134.27, 133.94, 133.56, 132.44, 131.35, 130.67, 129.22, 128.80, 128.26, 128.14, 127.62, 127.24, 127.01, 124.73, 123.77, 123.24, 117.36, 102.54, 100.88, 88.78, 47.03.
HRMS (ESI): $C_{26}H_{18}O_2$ + Na, Calc: 385.1199, Found: 385.1188.

General procedure and spectral data for the synthesis of 3



General procedure for the synthesis of S5

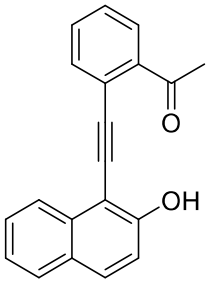
Similar to what has been described previously, under argon atmosphere, to a stirred solution of **S4** (10 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (2.5 mol %), CuI (5 mol %) in dry Et_3N (30 mL) was added **S2** (15 mmol, 1.5 equiv). Then the mixture was stirred in an oil bath at 50°C overnight. After the completion of the reaction which was indicated by TLC, Et_3N was evaporated in vacuo and the resulting crude residue was extracted with EA and washed with water. Then organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by flash chromatography (PE/EA 10:1) to afford **S5** as a yellow oil.

General procedure for the synthesis of 3

Similar to what has been described previously, to a stirred solution of **S5** (2 mmol, 1.0 equiv) in MeOH (10 mL) was added a few drops of 12N HCl aq. at room temperature. The mixture was stirred at room temperature until the completion of the reaction. Then the reaction mixture is filtered, and

the filter residue is dried in an oven to afford **3**.

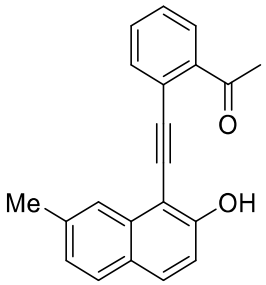
1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3a)



3a

Appearance: yellow solid.
Yield: 77%.
m.p: 167-169°C.
IR: 3351, 3053, 2197, 1949, 1752, 1669, 1484, 1357, 1209, 1137, 1050, 877 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.84 – 7.77 (m, 3H), 7.57 (qd, *J* = 7.7, 1.1 Hz, 2H), 7.42 (td, *J* = 7.8, 1.2 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.42, 159.54, 136.14, 133.79, 133.55, 132.49, 131.31, 130.89, 128.25, 128.13, 127.66, 127.20, 124.73, 123.73, 122.54, 117.38, 102.55, 101.01, 88.67, 28.17.
HRMS (ESI): $C_{20}H_{14}O_2$ + Na, Calc: 309.0891, Found: 309.0893.

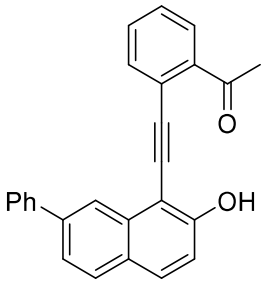
1-(2-((2-hydroxy-7-methylnaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3b)



3b

Appearance: yellow solid.
Yield: 52%.
m.p: 163-165°C.
IR: 3353, 2983, 2942, 2180, 1674, 1621, 1482, 1382, 1213, 1141, 1043, 830 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.02 – 7.88 (m, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 2H), 2.71 (s, 3H), 2.58 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.41, 159.65, 137.17, 136.06, 133.77, 133.72, 132.44, 131.09, 130.87, 128.07, 127.56, 126.31, 125.91, 123.90, 122.59, 116.34, 101.93, 100.93, 88.88, 28.15, 21.98.
HRMS (ESI): $C_{21}H_{16}O_2$ + Na, Calc: 323.1048, Found: 323.1046.

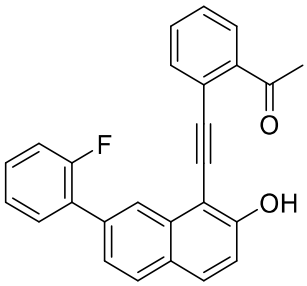
1-(2-((2-hydroxy-7-phenylnaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3c)



3c

Appearance: yellow solid.
Yield: 68%.
m.p: 171-173°C.
IR: 3350, 3059, 2189, 1674, 1619, 1602, 1482, 1379, 1212, 1142, 958, 884 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.42 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.72 (m, 5H), 7.67 – 7.57 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.38 (m, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 2.74 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 198.47, 159.95, 141.40, 140.03, 136.18, 133.90, 133.83, 132.55, 131.06, 130.93, 128.87, 128.77, 127.72, 127.57, 127.44, 127.33, 123.53, 122.86, 122.54, 117.43, 102.82, 101.34, 88.71, 28.22.
HRMS (ESI): $C_{26}H_{18}O_2$ + Na, Calc: 385.1204, Found: 385.1206.

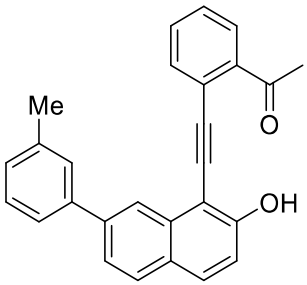
1-(2-((7-(2-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3d)



3d

Appearance: yellow solid.
Yield: 53%.
m.p: 159-160°C.
IR: 3349, 2982, 2921, 2185, 1675, 1620, 1481, 1358, 1210, 1141, 1043, 830 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.33 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.83 – 7.69 (m, 3H), 7.61 – 7.47 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.25 – 7.23 (m, 1H), 7.18 (dd, *J* = 19.3, 7.5 Hz, 2H), 2.66 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.47, 159.89, 136.18, 134.73, 133.95, 133.57, 132.53, 131.11, 131.08, 131.02, 130.89, 129.16, 129.07, 128.29, 127.72, 127.41, 125.03, 125.00, 124.97, 124.94, 124.46, 124.43, 122.51, 117.75, 116.32, 116.10, 102.87, 101.32, 88.59, 28.21.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.36.
HRMS (ESI): $C_{26}H_{17}FO_2$ + Na, Calc: 403.1110, Found: 403.1104.

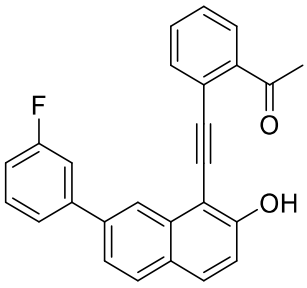
1-(2-((2-hydroxy-7-(m-tolyl)naphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3e)



3e

Appearance: yellow solid.
Yield: 57%.
m.p: 180-182°C.
IR: 3354, 3059, 2190, 1675, 1620, 1605, 1482, 1378, 1357, 1334, 1042, 885 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.40 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.75 (m, 3H), 7.67 – 7.53 (m, 4H), 7.48 – 7.38 (m, 2H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.73 (s, 3H), 2.50 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 198.47, 159.92, 141.42, 140.20, 138.44, 136.18, 133.86, 133.81, 132.54, 131.06, 130.92, 128.77, 128.68, 128.37, 128.19, 127.70, 127.30, 124.70, 123.64, 122.83, 122.54, 117.34, 102.79, 101.30, 88.75, 28.22, 21.62.
HRMS (ESI): $C_{27}H_{20}O_2$ + Na, Calc: 399.1361, Found: 399.1358.

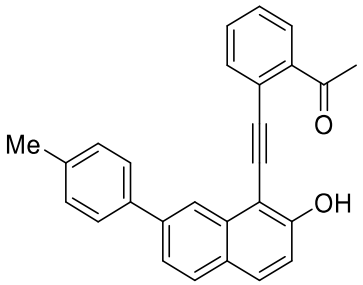
1-(2-((7-(3-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3f)



3f

Appearance: yellow solid.
Yield: 59%.
m.p: 173-174°C.
IR: 3351, 2980, 2941, 2178, 1679, 1621, 1480, 1361, 1209, 1139, 1040, 869 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.29 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.41 – 7.33 (m, 3H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.01 (td, *J* = 8.3, 2.0 Hz, 1H), 2.63 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.48, 164.46, 162.02, 160.01, 143.67, 143.60, 138.64, 136.13, 133.91, 133.73, 132.60, 131.01, 130.95, 130.35, 130.26, 128.94, 127.79, 127.56, 123.17, 122.93, 122.41, 117.74, 114.45, 114.30, 114.24, 114.09, 102.90, 101.49, 88.45, 28.19.
^{19}F NMR (376 MHz, $CDCl_3$): δ -112.93.
HRMS (ESI): $C_{26}H_{17}FO_2$ + Na, Calc: 403.1110, Found: 403.1111.

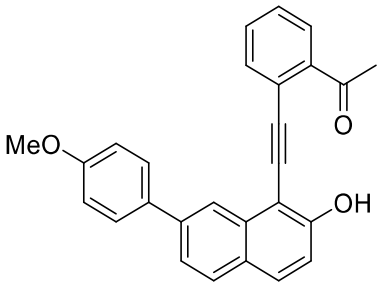
1-(2-((2-hydroxy-7-(p-tolyl)naphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3g)



3g

Appearance: yellow solid.
Yield: 62%.
m.p: 184-186°C.
IR: 3366, 2957, 2918, 2191, 1929, 1671, 1504, 1482, 1249, 1190, 1066, 826 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.40 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.87 – 7.75 (m, 3H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.60 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.73 (s, 3H), 2.45 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 198.44, 159.91, 139.96, 138.49, 137.27, 136.14, 133.86, 132.52, 131.05, 130.92, 129.60, 128.70, 127.68, 127.40, 127.20, 123.47, 122.56, 122.54, 117.24, 102.75, 101.31, 88.77, 28.21, 21.15.
HRMS (ESI): $C_{27}H_{20}O_2$ + Na, Calc: 399.1361, Found: 399.1357.

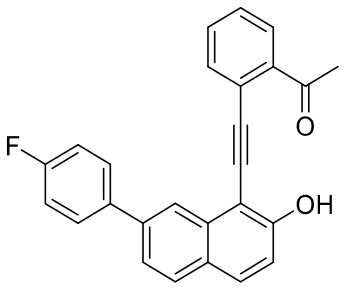
1-(2-((2-hydroxy-7-(4-methoxyphenyl)naphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3h)



3h

Appearance: yellow solid.
Yield: 73%.
m.p: 169-171°C.
IR: 3414, 2957, 2198, 1669, 1604, 1502, 1484, 1362, 1247, 1183, 1073, 825 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.31 (d, *J* = 1.1 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 8.4 Hz, 3H), 7.71 – 7.63 (m, 2H), 7.60 – 7.50 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.09 – 6.97 (m, 2H), 3.84 (s, 3H), 2.68 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.45, 159.91, 159.33, 139.60, 136.14, 133.89, 133.86, 133.82, 132.52, 131.06, 130.92, 128.71, 128.55, 127.67, 127.01, 123.32, 122.56, 122.10, 117.09, 114.33, 102.67, 101.31, 88.79, 55.37, 28.20.
HRMS (ESI): $C_{27}H_{20}O_3$ + Na, Calc: 415.1310, Found: 415.1306.

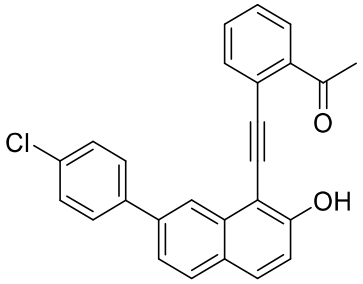
1-(2-((7-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3i)



3i

Appearance: yellow solid.
Yield: 63%.
m.p: 163-165°C.
IR: 3352, 2980, 2920, 2179, 1682, 1621, 1480, 1356, 1232, 1140, 1040, 830 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H), 8.63 (s, 1H), 7.95 (m, 5H), 7.79 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 8.7 Hz, 2H), 7.25 (d, J = 8.8 Hz, 1H), 2.76 (s, 3H).
^{13}C NMR (126 MHz, DMSO-d_6): δ 200.11, 163.53, 161.58, 159.26, 139.59, 138.48, 137.00, 136.97, 135.01, 134.29, 132.32, 131.06, 129.92, 129.71, 129.64, 129.55, 128.69, 127.17, 123.11, 122.38, 121.87, 118.45, 116.32, 116.15, 103.08, 98.25, 89.76, 29.89.
^{19}F NMR (376 MHz, DMSO-d_6): δ -115.20.
HRMS (ESI): $C_{26}H_{17}FO_2$ + Na, Calc: 403.1110, Found: 403.1109.

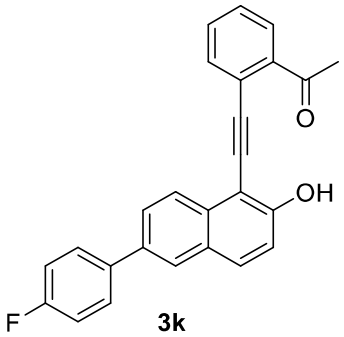
1-(2-((7-(4-chlorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3j)



3j

Appearance: yellow solid.
Yield: 83%.
m.p: 181-183°C.
IR: 3314, 3068, 2940, 2188, 1908, 1675, 1481, 1367, 1290, 1140, 1092, 813 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.36 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.88 – 7.76 (m, 3H), 7.71 (d, J = 8.5 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.56 (dd, J = 8.4, 1.7 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.30 (d, J = 8.9 Hz, 1H), 2.74 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.49, 160.04, 139.85, 138.76, 136.21, 133.89, 133.80, 133.58, 132.59, 131.05, 130.97, 129.02, 128.95, 128.79, 127.81, 127.43, 123.16, 122.79, 122.47, 117.67, 102.84, 101.45, 88.53, 28.24.
HRMS (ESI): $C_{26}H_{17}ClO_2$ + Na, Calc: 419.0815, Found: 419.0810.

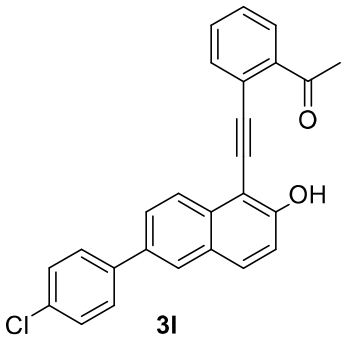
1-(2-((6-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3k)



3k

Appearance: yellow solid.
Yield: 61%.
m.p: 179-180°C.
IR: 3351, 2979, 2942, 2179, 1889, 1621, 1480, 1379, 1232, 1142, 1043, 891 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.06 – 7.98 (m, 1H), 7.92 (d, *J* = 1.7 Hz, 1H), 7.84 (dd, *J* = 5.0, 4.1 Hz, 2H), 7.76 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.71 – 7.57 (m, 3H), 7.47 (td, *J* = 7.8, 1.2 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.22 – 7.12 (m, 2H), 2.74 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.55, 163.67, 161.22, 159.73, 137.17, 137.13, 136.27, 135.64, 133.90, 132.71, 132.62, 131.54, 131.00, 128.82, 128.74, 128.39, 127.82, 126.67, 126.10, 125.45, 122.56, 118.02, 115.84, 115.63, 102.55, 101.10, 88.59, 28.28.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.89.
HRMS (ESI): $C_{26}H_{17}FO_2$ + Na, Calc: 403.1110, Found: 403.1106.

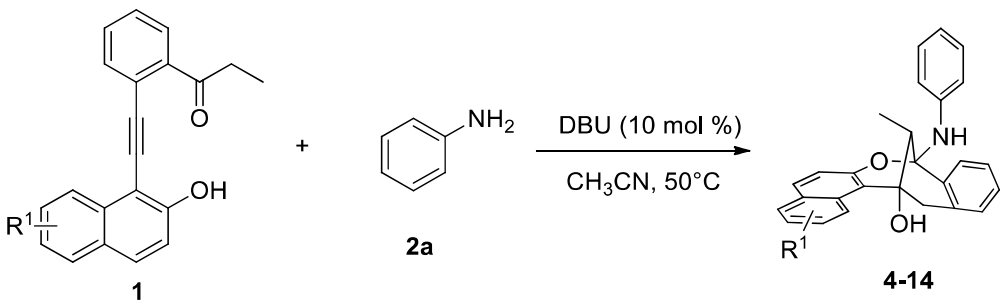
1-(2-((6-(4-chlorophenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (3l)



3l

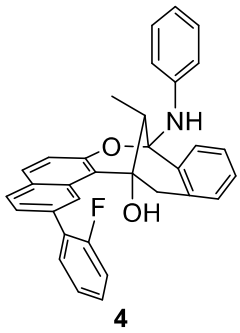
Appearance: yellow solid.
Yield: 56%.
m.p: 180-181°C.
IR: 3315, 2981, 2940, 2188, 1908, 1620, 1493, 1384, 1183, 1140, 1069, 892 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H), 8.42 (d, *J* = 8.7 Hz, 1H), 8.20 (s, 1H), 7.89 (m, 6H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.7 Hz, 3H), 7.29 (d, *J* = 8.9 Hz, 1H), 2.79 (s, 3H).
^{13}C NMR (126 MHz, DMSO-d_6): δ 200.39, 159.15, 139.92, 139.13, 134.33, 134.27, 134.01, 132.65, 132.27, 131.85, 129.69, 129.42, 128.93, 128.85, 128.24, 126.71, 126.38, 125.78, 121.71, 118.86, 102.56, 97.81, 90.05, 30.12.
HRMS (ESI): $C_{26}H_{17}ClO_2$ + Na, Calc: 419.0815, Found: 419.0816.

General procedure for the synthesis of 4-14



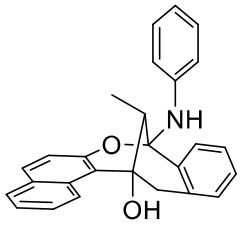
To a solution of substrate **1** (0.1 mmol) and DBU (0.01 mmol) in the 2 ml CH_3CN was added aniline **2a** (0.2 mmol) at the 50°C. After the reaction performed completely, the solvent was removed under vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **4-14**.

2-(2-fluorophenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (4)



Appearance: white solid.
Yield: 92%.
m.p: 168-169°C.
IR: 3530, 3361, 3054, 2979, 2941, 1619, 1602, 1488, 1225, 1160, 1049, 888 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.36 – 7.26 (m, 4H), 7.25 (d, *J* = 5.5 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 4.69 (s, 1H), 3.77 (d, *J* = 16.3 Hz, 1H), 3.53 (d, *J* = 16.3 Hz, 1H), 3.24 (q, *J* = 6.8 Hz, 1H), 1.96 (s, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 161.23, 158.76, 150.60, 144.28, 134.89, 134.54, 133.40, 131.32, 131.13, 131.09, 130.24, 129.71, 129.58, 129.39, 129.23, 129.13, 129.02, 128.94, 128.81, 127.81, 125.90, 125.87, 125.74, 124.46, 124.43, 124.26, 124.23, 120.34, 119.54, 119.43, 117.80, 116.32, 116.10, 92.43, 73.50, 40.71, 38.58, 8.29.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.70.
HRMS (ESI): $C_{33}H_{26}FNO_2$ + H, Calc: 488.2026, Found: 488.2019.

15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (5)



5

Appearance: white solid.

Yield: 73%.

m.p: 154-156°C.

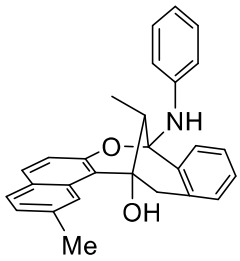
IR: 3288, 3051, 2974, 1621, 1601, 1498, 1462, 1430, 1231, 1160, 1049, 887 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 16.7, 8.1 Hz, 2H), 7.20 (m, 5H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 4.65 (s, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.45 (d, *J* = 16.3 Hz, 1H), 3.18 (q, *J* = 6.8 Hz, 1H), 1.98 (s, 1H), 1.03 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.21, 144.29, 134.91, 134.55, 131.36, 130.52, 130.13, 129.20, 129.09, 129.04, 128.79, 127.76, 126.13, 125.73, 125.34, 123.09, 120.30, 119.28, 118.99, 117.79, 92.32, 73.41, 40.63, 38.39, 8.25.

HRMS (ESI): $C_{27}H_{23}NO_2$ + H, Calc: 394.1807, Found: 394.1804.

2,15-dimethyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (6)



6

Appearance: white solid.

Yield: 69%.

m.p: 161-163°C.

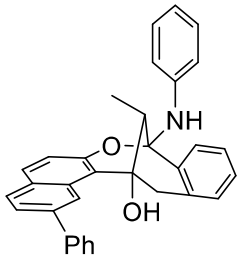
IR: 3534, 3394, 2921, 1618, 1603, 1484, 1422, 1387, 1220, 1172, 1041, 837 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 21.1, 8.4 Hz, 2H), 7.32 – 7.00 (m, 7H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.81 (t, *J* = 6.9 Hz, 1H), 4.55 (s, 1H), 3.63 (d, *J* = 16.2 Hz, 1H), 3.38 (d, *J* = 16.2 Hz, 1H), 3.08 (d, *J* = 6.6 Hz, 1H), 2.46 (s, 3H), 1.82 (s, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.34, 144.33, 135.85, 134.98, 134.62, 131.52, 130.24, 129.19, 129.05, 128.66, 128.30, 127.74, 125.74, 125.22, 124.52, 120.27, 118.71, 118.05, 117.80, 92.25, 73.42, 40.72, 38.34, 22.42, 8.30.

HRMS (ESI): $C_{28}H_{25}NO_2$ + H, Calc: 408.1964, Found: 408.1961.

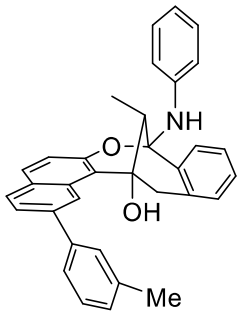
15-methyl-2-phenyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (7)



7

Appearance: white solid.
Yield: 83%.
m.p: 177-179°C.
IR: 3528, 3362, 3054, 2984, 2942, 1617, 1601, 1490, 1246, 1171, 1077, 898 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.03 (d, *J* = 7.1 Hz, 1H), 7.87 – 7.76 (m, 3H), 7.68 – 7.60 (m, 2H), 7.53 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (dt, *J* = 8.6, 3.7 Hz, 3H), 7.21 – 7.16 (m, 2H), 7.05 (dd, *J* = 8.0, 2.8 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.68 (s, 1H), 3.78 (d, *J* = 16.3 Hz, 1H), 3.54 (d, *J* = 16.3 Hz, 1H), 3.23 (q, *J* = 6.8 Hz, 1H), 1.97 (s, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.62, 144.29, 141.61, 138.63, 134.88, 134.55, 131.65, 130.24, 129.33, 129.30, 129.23, 129.14, 129.08, 128.86, 127.81, 127.54, 127.32, 125.74, 123.64, 122.68, 120.35, 119.52, 119.10, 117.82, 92.40, 73.55, 40.73, 38.55, 8.30.
HRMS (ESI): $C_{33}H_{27}NO_2$ + H, Calc: 470.2120, Found: 470.2118.

15-methyl-8-(phenylamino)-2-(m-tolyl)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (8)

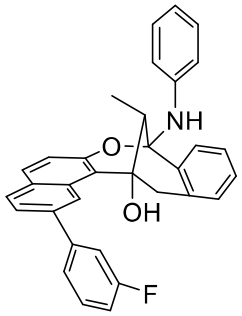


8

Appearance: white solid.
Yield: 69%.
m.p: 157-158°C.
IR: 3535, 3395, 2921, 1618, 1602, 1485, 1451, 1423, 1299, 1173, 1042, 873 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.45 (m, 4H), 7.33 – 7.27 (m, 1H), 7.24 – 7.10 (m, 5H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 4.56 (s, 1H), 3.67 (d, *J* = 16.3 Hz, 1H), 3.42 (d, *J* = 16.3 Hz, 1H), 3.11 (q, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 1.87 (s, 1H), 0.95 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.59, 144.29, 141.65, 138.81, 138.43, 134.90, 134.55, 131.62, 130.24, 129.30, 129.22, 129.12, 129.07, 128.78, 128.25, 128.09, 127.79, 125.73, 124.75, 123.55,

122.83, 120.33, 119.50, 119.01, 117.82, 92.38, 73.53, 40.72, 38.53, 21.64, 8.31.
HRMS (ESI): $C_{34}H_{29}NO_2$ + H, Calc: 484.2277, Found: 484.2274.

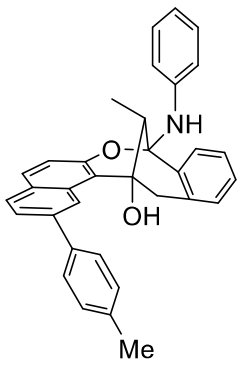
2-(3-fluorophenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (9)



9

Appearance: white solid.
Yield: 71%.
m.p: 176-177°C.
IR: 3531, 3363, 3055, 2983, 2940, 1615, 1600, 1486, 1294, 1162, 1039, 891 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.52 – 7.43 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.21 – 7.17 (m, 2H), 7.08 (m, 3H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.68 (s, 1H), 3.76 (d, *J* = 16.3 Hz, 1H), 3.55 (d, *J* = 16.3 Hz, 1H), 3.22 (q, *J* = 6.7 Hz, 1H), 1.96 (s, 1H), 1.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 164.47, 162.03, 150.73, 144.23, 143.97, 143.90, 137.32, 137.30, 134.78, 134.50, 131.61, 130.32, 130.23, 129.58, 129.45, 129.23, 129.17, 129.07, 127.84, 125.74, 123.79, 123.15, 123.12, 122.36, 120.38, 119.60, 119.42, 117.83, 114.44, 114.22, 114.17, 113.96, 92.43, 73.54, 40.68, 38.62, 8.27.
^{19}F NMR (376 MHz, $CDCl_3$): δ -112.90.
HRMS (ESI): $C_{33}H_{26}FNO_2$ + H, Calc: 488.2026, Found: 488.2026.

15-methyl-8-(phenylamino)-2-(p-tolyl)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (10)

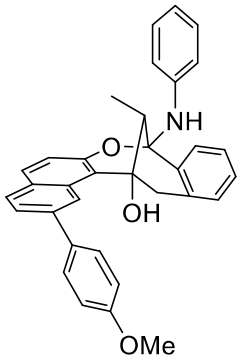


10

Appearance: white solid.
Yield: 66%.
m.p: 172-173°C.

IR: 3538, 2941, 1603, 1497, 1452, 1431, 1385, 1311, 1267, 1193, 1042, 889 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.55 (m, 4H), 7.35 – 7.15 (m, 8H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.91 (t, *J* = 7.1 Hz, 1H), 4.66 (s, 1H), 3.77 (d, *J* = 16.3 Hz, 1H), 3.52 (d, *J* = 16.3 Hz, 1H), 3.21 (q, *J* = 6.6 Hz, 1H), 2.45 (s, 3H), 1.96 (s, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.58, 144.29, 138.69, 138.54, 137.15, 134.90, 134.55, 131.65, 130.22, 129.58, 129.24, 129.22, 129.11, 129.07, 127.78, 127.36, 125.73, 123.26, 122.60, 120.32, 119.44, 118.92, 117.81, 92.37, 73.52, 40.73, 38.51, 21.13, 8.30.
HRMS (ESI): $C_{34}H_{29}NO_2$ + H, Calc: 484.2277, Found: 484.2275.

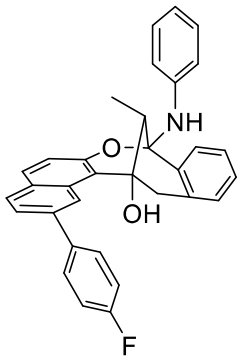
2-(4-methoxyphenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (11)



11

Appearance: white solid.
Yield: 71%.
m.p: 180-181°C.
IR: 3544, 3433, 3374, 2970, 2837, 1621, 1606, 1504, 1242, 1173, 1028, 891 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 15.3, 7.6 Hz, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 11.8, 8.6 Hz, 4H), 6.91 (t, *J* = 7.2 Hz, 1H), 4.66 (s, 1H), 3.89 (s, 3H), 3.76 (d, *J* = 16.4 Hz, 1H), 3.52 (d, *J* = 16.4 Hz, 1H), 3.21 (q, *J* = 6.8 Hz, 1H), 1.95 (s, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.24, 150.61, 144.31, 138.24, 134.91, 134.58, 134.12, 131.70, 130.24, 129.23, 129.13, 129.09, 129.02, 128.55, 127.80, 125.75, 122.89, 122.49, 120.33, 119.37, 118.81, 117.82, 114.32, 92.38, 73.56, 55.40, 40.76, 38.51, 8.33.
HRMS (ESI): $C_{34}H_{29}NO_3$ + H, Calc: 500.2226, Found: 500.2229.

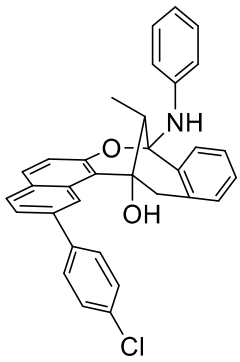
2-(4-fluorophenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (12)



12

Appearance: white solid.
Yield: 59%.
m.p: 179-180°C.
IR: 3540, 3415, 3054, 2976, 2941, 1619, 1603, 1501, 1386, 1222, 1015, 832 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (m, 7H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 4.69 (s, 1H), 3.77 (d, *J* = 16.3 Hz, 1H), 3.55 (d, *J* = 16.3 Hz, 1H), 3.24 (q, *J* = 6.7 Hz, 1H), 1.98 (s, 1H), 1.08 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.74, 161.29, 150.70, 144.25, 137.72, 137.69, 137.62, 134.79, 134.52, 131.64, 130.24, 129.39, 129.23, 129.15, 129.08, 129.06, 129.00, 127.84, 125.75, 123.46, 122.47, 120.38, 119.46, 119.17, 117.83, 115.81, 115.60, 92.41, 73.57, 40.71, 38.55, 8.29.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.61.
HRMS (ESI): $C_{33}H_{26}FNO_2$ + H, Calc: 488.2026, Found: 488.2032.

2-(4-chlorophenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (13)



13

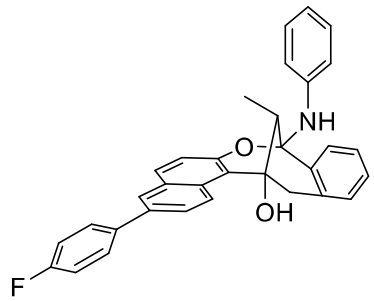
Appearance: white solid.
Yield: 67%.
m.p: 184-185°C.
IR: 3570, 2943, 1619, 1603, 1489, 1451, 1425, 1222, 1173, 1092, 1065, 892 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.05 (dd, *J* = 8.1, 4.1 Hz, 2H), 6.92

(t, *J* = 7.2 Hz, 1H), 4.67 (s, 1H), 3.74 (d, *J* = 16.3 Hz, 1H), 3.53 (d, *J* = 16.3 Hz, 1H), 3.21 (q, *J* = 6.7 Hz, 1H), 1.95 (s, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.75, 144.24, 140.06, 137.37, 134.77, 134.51, 133.43, 131.64, 130.26, 129.47, 129.44, 129.25, 129.18, 129.07, 128.99, 128.75, 127.87, 125.76, 123.57, 122.31, 120.40, 119.53, 119.35, 117.83, 92.44, 73.59, 40.72, 38.59, 8.30.

HRMS (ESI): $C_{33}H_{26}ClNO_2$ + H, Calc: 504.1730, Found: 504.1730

3-(4-fluorophenyl)-15-methyl-8-(phenylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (14)



14

Appearance: white solid.

Yield: 79%.

m.p: 190-191°C.

IR: 3441, 3317, 3053, 2969, 2907, 1622, 1601, 1516, 1498, 1360, 1167, 1125 cm^{-1}.

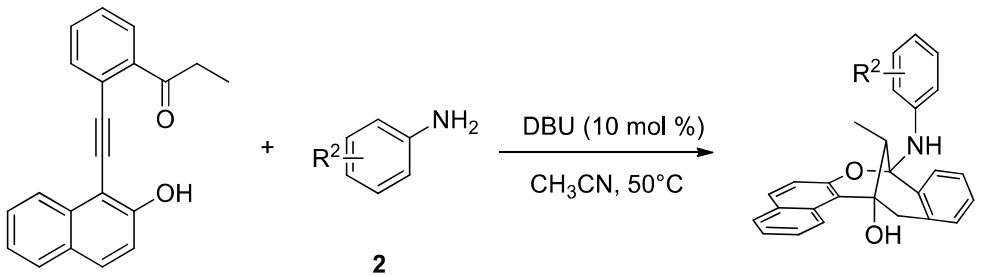
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 1.3 Hz, 1H), 7.68 (dd, *J* = 9.0, 1.7 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 13.9, 5.9 Hz, 3H), 7.19 – 7.10 (m, 4H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 4.65 (s, 1H), 3.66 (d, *J* = 16.4 Hz, 1H), 3.46 (d, *J* = 16.4 Hz, 1H), 3.19 (q, *J* = 6.7 Hz, 1H), 2.01 (s, 1H), 1.02 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.60, 161.16, 150.39, 144.25, 136.89, 136.86, 134.80, 134.69, 134.54, 130.74, 130.49, 130.44, 129.23, 129.16, 129.06, 128.65, 128.57, 127.84, 126.37, 126.01, 125.76, 125.41, 120.36, 119.60, 119.38, 117.81, 115.79, 115.57, 92.46, 73.46, 40.65, 38.54, 8.27.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.85.

HRMS (ESI): $C_{33}H_{26}FNO_2$ + H, Calc: 488.2026, Found: 488.2021.

General procedure for the synthesis of 15-39

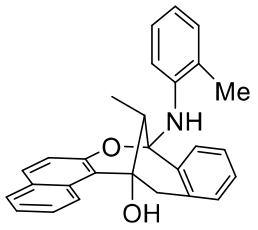


1a **2** **15-39**

To a solution of **1a** (0.1 mmol) and DBU (0.01 mmol) in the 2 ml CH_3CN was added substrate **2** (0.2 mmol) at the 50°C. After the reaction performed completely, the solvent was removed under

vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **15-39**.

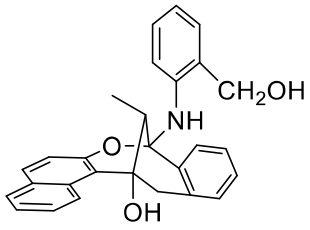
15-methyl-8-(o-tolylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (15)



15

Appearance: white solid.
Yield: 39%.
m.p: 178-179°C.
IR: 3506, 3329, 3054, 2970, 1620, 1600, 1587, 1505, 1463, 1310, 1235, 956 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.33 (dd, *J* = 11.9, 7.6 Hz, 2H), 7.23 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.10 – 7.02 (m, 3H), 6.82 (t, *J* = 7.3 Hz, 1H), 4.58 (s, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.46 (d, *J* = 16.3 Hz, 1H), 3.28 (q, *J* = 6.7 Hz, 1H), 2.22 (s, 3H), 2.00 (s, 1H), 0.93 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.32, 142.24, 134.86, 134.83, 131.40, 130.58, 130.54, 130.15, 129.15, 129.07, 128.81, 127.97, 126.93, 126.14, 125.35, 125.27, 123.84, 123.10, 119.83, 119.32, 119.04, 116.20, 92.29, 73.45, 40.17, 38.38, 17.78, 8.09.
HRMS (ESI): $C_{28}H_{25}NO_2$ + Na, Calc: 430.1783, Found: 430.1786.

8-((2-(hydroxymethyl)phenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (16)

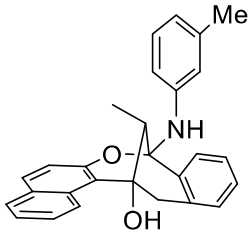


16

Appearance: white solid.
Yield: 65%.
m.p: 173-174°C.
IR: 3565, 3510, 3429, 3397, 2917, 1618, 1600, 1588, 1507, 1233, 1033, 885 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 11.1, 8.6 Hz, 2H), 7.50 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H), 7.15 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.02 (dd, *J* = 8.1, 3.0 Hz, 2H), 6.83 (td, *J* = 7.4, 0.9 Hz, 1H), 6.29 (s, 1H), 4.70 (q, *J* = 12.4 Hz, 2H), 3.71 (d, *J* = 16.2 Hz, 1H), 3.49 (d, *J* = 16.2 Hz, 1H), 3.35 (q, *J* = 6.8 Hz, 1H), 1.95 (s, 1H), 1.72 (s, 1H), 0.99 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.42, 143.99, 134.63, 134.58, 131.42, 130.53, 130.14, 129.43,

129.37, 129.05, 128.96, 128.83, 128.05, 126.32, 126.14, 125.36, 125.29, 123.08, 119.35, 119.19, 119.08, 116.94, 92.10, 73.48, 65.30, 40.29, 38.43, 8.50.
HRMS (ESI): $C_{28}H_{25}NO_3$ + H, Calc: 424.1913, Found: 424.1907.

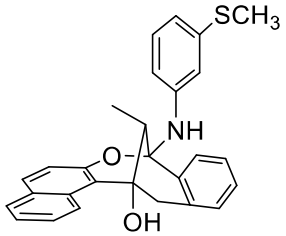
15-methyl-8-(m-tolylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (17)



17

Appearance: white solid.
Yield: 89%.
m.p: 169-170°C.
IR: 3291, 2979, 2936, 1606, 1511, 1488, 1462, 1431, 1335, 1231, 1035, 958 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.07 – 6.89 (m, 4H), 6.72 (d, *J* = 7.4 Hz, 1H), 4.61 (s, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.45 (d, *J* = 16.3 Hz, 1H), 3.19 (q, *J* = 6.7 Hz, 1H), 2.29 (s, 3H), 1.99 (s, 1H), 1.03 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.28, 144.24, 138.93, 134.89, 134.64, 131.38, 130.50, 130.12, 129.04, 129.02, 128.79, 127.75, 126.12, 125.73, 125.36, 123.08, 121.18, 119.28, 119.04, 118.47, 114.91, 92.30, 73.44, 40.67, 38.43, 21.64, 8.31.
HRMS (ESI): $C_{28}H_{25}NO_2$ + H, Calc: 408.1964, Found: 408.1966.

15-methyl-8-((3-(methylthio)phenyl)amino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (18)

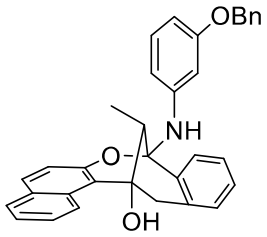


18

Appearance: white solid.
Yield: 77%.
m.p: 155-157°C.
IR: 3385, 3292, 2977, 2918, 2846, 1621, 1591, 1511, 1478, 1432, 1231, 1054 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.09 (s, 1H), 7.04 (t, *J* = 9.6 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.79

(d, *J* = 7.7 Hz, 1H), 4.66 (s, 1H), 3.69 (d, *J* = 16.3 Hz, 1H), 3.46 (d, *J* = 16.3 Hz, 1H), 3.16 (q, *J* = 6.8 Hz, 1H), 2.43 (d, *J* = 6.0 Hz, 3H), 2.00 (s, 1H), 1.04 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.08, 144.81, 139.28, 134.93, 134.39, 131.35, 130.60, 130.15, 129.51, 129.15, 129.06, 128.80, 127.78, 126.15, 125.72, 125.36, 123.15, 119.32, 118.86, 118.30, 115.39, 114.68, 92.27, 73.36, 40.74, 38.37, 15.62, 8.34.
HRMS (ESI): $C_{28}H_{25}NO_2S$ + H, Calc: 440.1684, Found: 440.1685.

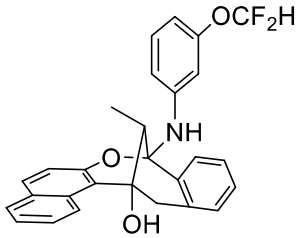
8-((3-(benzyloxy)phenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (19)



19

Appearance: white solid.
Yield: 53%.
m.p: 144-145°C.
IR: 3277, 3029, 1615, 1599, 1510, 1489, 1455, 1432, 1386, 1233, 1017, 975 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 9.4 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.08 (dd, *J* = 16.4, 7.9 Hz, 2H), 7.03 – 6.91 (m, 4H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.54 (ddd, *J* = 10.2, 8.1, 1.7 Hz, 2H), 5.02 (dd, *J* = 28.4, 12.8 Hz, 2H), 4.60 (s, 1H), 3.60 (d, *J* = 16.4 Hz, 1H), 3.37 (d, *J* = 16.3 Hz, 1H), 2.77 (q, *J* = 6.7 Hz, 1H), 1.69 (s, 1H), 0.89 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.15, 150.15, 145.48, 137.49, 134.89, 134.47, 131.47, 130.50, 130.15, 129.95, 129.05, 128.76, 128.44, 127.74, 127.12, 126.95, 126.09, 125.64, 125.45, 123.09, 119.38, 118.88, 110.54, 107.16, 104.07, 92.18, 73.19, 69.42, 40.31, 38.27, 8.15.
HRMS (ESI): $C_{34}H_{29}NO_3$ + H, Calc: 500.2226, Found: 500.2223.

8-((3-(difluoromethoxy)phenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (20)



20

Appearance: white solid.
Yield: 83%.
m.p: 175-176°C.

IR: 3342, 2962, 2934, 1752, 1603, 1543, 1464, 1343, 1243, 1192, 1083, 817 cm^{-1}.

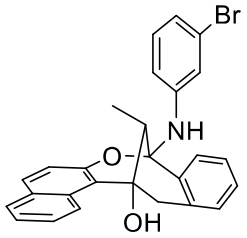
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.21 (dd, *J* = 14.5, 7.3 Hz, 2H), 7.02 (dd, *J* = 8.1, 4.7 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.49 (t, *J* = 74.2 Hz, 1H), 4.76 (s, 1H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.47 (d, *J* = 16.3 Hz, 1H), 3.17 (q, *J* = 6.8 Hz, 1H), 1.99 (s, 1H), 1.05 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.26, 150.00, 145.95, 135.01, 134.19, 131.31, 130.68, 130.31, 130.23, 129.28, 129.13, 128.85, 127.85, 126.21, 125.66, 125.33, 123.24, 119.32, 118.86, 118.57, 115.99, 114.55, 113.42, 110.27, 108.56, 92.17, 73.36, 40.72, 38.31, 8.36.

^{19}F NMR (376 MHz, $CDCl_3$): δ -80.28, -80.48.

HRMS (ESI): $C_{28}H_{23}F_2NO_3$ + H, Calc: 460.1724, Found: 460.1731.

8-((3-bromophenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (21)



21

Appearance: white solid.

Yield: 38%.

m.p: 182-183°C.

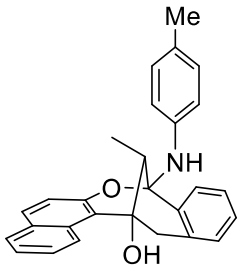
IR: 3333, 2922, 2851, 1620, 1593, 1478, 1462, 1432, 1388, 1233, 1049, 859 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12 – 6.89 (m, 5H), 4.70 (s, 1H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.47 (d, *J* = 16.3 Hz, 1H), 3.16 (q, *J* = 6.8 Hz, 1H), 1.97 (s, 1H), 1.04 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.03, 145.76, 135.00, 134.19, 131.31, 130.67, 130.52, 130.22, 129.28, 129.13, 128.84, 127.86, 126.23, 125.63, 125.35, 123.26, 123.15, 123.02, 120.28, 119.32, 118.90, 116.22, 92.13, 73.38, 40.66, 38.35, 8.37.

HRMS (ESI): $C_{27}H_{22}BrNO_2$ + H, Calc: 472.0912, Found: 472.0909.

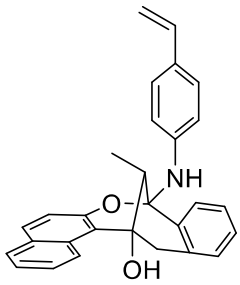
15-methyl-8-(p-tolylamino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (22)



22

Appearance: white solid.
Yield: 92%.
m.p: 177-179°C.
IR: 3539, 3305, 2919, 1620, 1601, 1512, 1433, 1376, 1277, 1234, 1051, 960 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.31 (dd, *J* = 16.9, 8.0 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 – 6.99 (m, 6H), 4.54 (s, 1H), 3.66 (d, *J* = 16.3 Hz, 1H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.13 (q, *J* = 6.7 Hz, 1H), 2.29 (s, 3H), 2.01 (s, 1H), 1.02 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.28, 141.72, 134.88, 134.63, 131.38, 130.48, 130.11, 129.70, 129.65, 129.01, 128.78, 127.71, 126.10, 125.76, 125.35, 123.05, 119.25, 119.03, 118.08, 92.43, 73.44, 40.71, 38.44, 20.56, 8.22.
HRMS (ESI): $C_{28}H_{25}NO_2$ + H, Calc: 408.1964, Found: 408.1965.

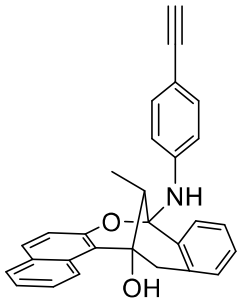
15-methyl-8-((4-vinylphenyl)amino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (23)



23

Appearance: white solid.
Yield: 54%.
m.p: 156-157°C.
IR: 3311, 2922, 2850, 1601, 1580, 1511, 1484, 1462, 1431, 1233, 1125, 959 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 5.6 Hz, 1H), 7.80 – 7.57 (m, 2H), 7.46 (d, *J* = 5.3 Hz, 1H), 7.40 – 7.18 (m, 4H), 7.17 – 6.91 (m, 4H), 6.74 – 6.55 (m, 1H), 5.61 (dd, *J* = 17.6, 4.2 Hz, 1H), 5.14 (dd, *J* = 10.7, 4.3 Hz, 1H), 4.69 (s, 1H), 3.58 (dd, *J* = 16.1, 3.0 Hz, 1H), 3.37 (dd, *J* = 16.2, 3.5 Hz, 1H), 3.21 – 3.04 (m, 1H), 2.38 (s, 1H), 0.95 (d, *J* = 5.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.09, 144.15, 136.43, 134.90, 134.41, 131.35, 130.56, 130.13, 129.88, 129.17, 129.04, 128.78, 127.76, 127.18, 126.17, 125.74, 125.33, 123.12, 119.27, 118.87, 117.82, 110.92, 92.30, 73.36, 40.75, 38.27, 8.11.
HRMS (ESI): $C_{29}H_{25}NO_2$ + H, Calc: 420.1964, Found: 420.1962.

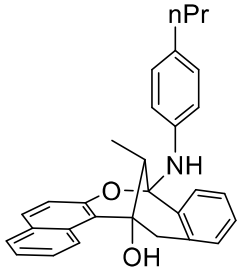
8-((4-ethynylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (24)



24

Appearance: white solid.
Yield: 72%.
m.p: 155-156°C.
IR: 3365, 3250, 2934, 2101, 1605, 1580, 1507, 1488, 1350, 1233, 1170, 983 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.27 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 – 6.93 (m, 4H), 4.79 (s, 1H), 3.69 (d, *J* = 16.4 Hz, 1H), 3.47 (d, *J* = 16.4 Hz, 1H), 3.17 (q, *J* = 6.7 Hz, 1H), 3.00 (s, 1H), 1.95 (s, 1H), 1.02 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.03, 144.98, 135.00, 134.23, 133.32, 131.33, 130.66, 130.23, 129.29, 129.14, 128.86, 127.88, 126.24, 125.66, 125.34, 123.25, 119.35, 118.90, 117.18, 113.22, 92.18, 84.09, 75.66, 73.37, 40.75, 38.36, 8.35.
HRMS (ESI): $C_{29}H_{23}NO_2$ + H, Calc: 418.1807, Found: 418.1815.

15-methyl-8-((4-propylphenyl)amino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (25)

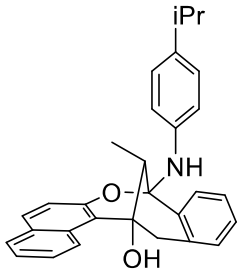


25

Appearance: white solid.
Yield: 96%.
m.p: 161-162°C.
IR: 3307, 3025, 2921, 1616, 1601, 1511, 1480, 1431, 1308, 1233, 1037, 986 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.98 (m, 4H), 4.56 (s, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.46 (d, *J* = 16.3 Hz, 1H), 3.15 (d, *J* = 6.8 Hz, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.95 (s, 1H), 1.66 – 1.57 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.32, 141.90, 134.89, 134.67, 134.57, 131.39, 130.47, 130.12,

129.12, 129.01, 128.79, 127.72, 126.09, 125.77, 125.36, 123.05, 119.27, 119.06, 117.90, 92.41, 73.46, 40.72, 38.46, 37.21, 24.65, 13.77, 8.27.
HRMS (ESI): $C_{30}H_{29}NO_2$ + H, Calc: 436.2277, Found: 436.2275.

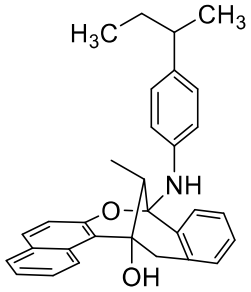
8-((4-isopropylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (26)



26

Appearance: white solid.
Yield: 85%.
m.p: 177-178°C.
IR: 3543, 3304, 2954, 1615, 1601, 1513, 1482, 1432, 1308, 1233, 1001, 887 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 11.4, 4.1 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.09 (s, 4H), 7.02 (dd, *J* = 8.1, 5.4 Hz, 2H), 4.56 (s, 1H), 3.69 (d, *J* = 16.3 Hz, 1H), 3.47 (d, *J* = 16.3 Hz, 1H), 3.16 (q, *J* = 6.7 Hz, 1H), 2.94 – 2.77 (m, 1H), 1.93 (s, 1H), 1.30 – 1.18 (m, 6H), 1.04 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.39, 141.98, 140.81, 134.94, 134.75, 131.45, 130.53, 130.16, 129.07, 128.85, 127.78, 127.10, 126.15, 125.83, 125.41, 123.10, 119.31, 119.13, 117.93, 92.43, 73.52, 40.81, 38.52, 33.28, 24.23, 24.13, 8.39.
HRMS (ESI): $C_{30}H_{29}NO_2$ + H, Calc: 436.2277, Found: 436.2278.

8-((4-(sec-butyl)phenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (27)



27

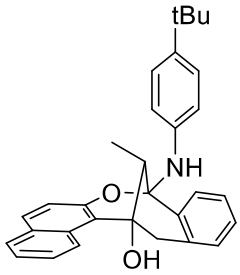
Appearance: white solid.
Yield: 83%.
m.p: 165-166°C.
IR: 3520, 3333, 3053, 2959, 2927, 2872, 1615, 1601, 1579, 1233, 1015, 980 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0

Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 17.0, 8.0 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.06 – 6.91 (m, 4H), 4.56 (s, 1H), 3.66 (d, *J* = 16.3 Hz, 1H), 3.44 (d, *J* = 16.3 Hz, 1H), 3.17 (dd, *J* = 12.9, 6.2 Hz, 1H), 2.53 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.02 (s, 1H), 1.60 – 1.53 (m, 2H), 1.22 (dd, *J* = 6.4, 4.4 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.33, 141.92, 139.51, 134.88, 134.69, 131.39, 130.46, 130.09, 129.00, 128.78, 127.71, 127.68, 126.09, 125.77, 125.34, 123.03, 119.25, 119.06, 117.80, 117.77, 92.38, 73.46, 40.78, 40.69, 38.42, 31.41, 31.22, 21.93, 21.78, 12.22, 8.27.

HRMS (ESI): $C_{31}H_{31}NO_2$ + H, Calc: 450.2433, Found: 450.2430.

8-((4-(tert-butyl)phenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (28)



28

Appearance: white solid.

Yield: 89%.

m.p: 183-184°C.

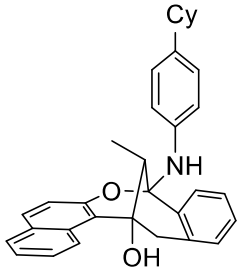
IR: 3552, 3276, 3055, 2956, 2865, 1614, 1602, 1514, 1462, 1432, 1234, 1015, 959 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.21 (dd, *J* = 17.4, 8.0 Hz, 3H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 7.7 Hz, 2H), 4.57 (s, 1H), 3.67 (d, *J* = 16.3 Hz, 1H), 3.45 (d, *J* = 16.3 Hz, 1H), 3.17 (q, *J* = 6.7 Hz, 1H), 2.00 (s, 1H), 1.30 (s, 9H), 1.04 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.34, 142.97, 141.57, 134.89, 134.69, 131.40, 130.46, 130.10, 129.00, 128.79, 127.71, 126.08, 125.95, 125.78, 125.35, 123.03, 119.26, 119.06, 117.49, 92.34, 73.46, 40.75, 38.42, 33.98, 31.46, 8.35.

HRMS (ESI): $C_{31}H_{31}NO_2$ + H, Calc: 450.2433, Found: 450.2432.

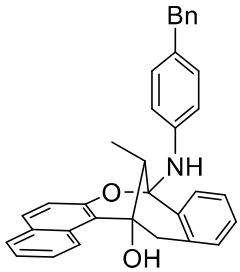
8-((4-cyclohexylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (29)



29

Appearance: white solid.
Yield: 98%.
m.p: 147-148°C.
IR: 3334, 2921, 2849, 1616, 1601, 1513, 1463, 1449, 1388, 1233, 1049, 814 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 – 6.91 (m, 6H), 4.55 (s, 1H), 3.67 (d, *J* = 16.3 Hz, 1H), 3.46 (d, *J* = 16.3 Hz, 1H), 3.16 (q, *J* = 6.6 Hz, 1H), 2.43 (s, 1H), 1.96 (s, 1H), 1.93 – 1.77 (m, 4H), 1.74 (d, *J* = 12.6 Hz, 1H), 1.40 (dd, *J* = 21.0, 10.4 Hz, 4H), 1.27 (d, *J* = 9.3 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.33, 141.92, 140.08, 134.88, 134.69, 131.39, 130.46, 130.09, 129.00, 128.78, 127.71, 127.40, 126.09, 125.77, 125.35, 123.03, 119.25, 119.07, 117.83, 92.36, 73.46, 43.64, 40.73, 38.44, 34.66, 34.57, 26.94, 26.18, 8.31.
HRMS (ESI): $C_{33}H_{33}NO_2$ + H, Calc: 476.2590, Found: 476.2585.

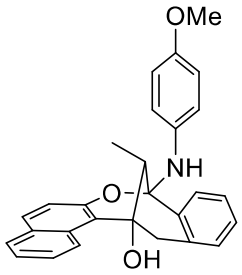
8-((4-benzylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (30)



30

Appearance: white solid.
Yield: 95%.
m.p: 158-159°C.
IR: 3304, 3024, 2975, 2922, 1616, 1602, 1510, 1481, 1488, 1234, 1050, 814 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.02 (s, 1H), 7.73 (s, 1H), 7.62 (s, 1H), 7.51 (s, 1H), 7.31 (s, 4H), 7.22 (s, 4H), 7.11 (s, 2H), 7.05 (d, *J* = 9.9 Hz, 4H), 4.61 (s, 1H), 3.94 (s, 2H), 3.68 (d, *J* = 15.8 Hz, 1H), 3.46 (d, *J* = 15.6 Hz, 1H), 3.17 (s, 1H), 2.03 (s, 1H), 1.04 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.23, 142.34, 141.60, 134.88, 134.58, 132.86, 131.36, 130.48, 130.11, 129.67, 129.04, 129.00, 128.83, 128.78, 128.33, 127.72, 126.09, 125.88, 125.73, 125.33, 123.05, 119.26, 118.98, 117.96, 92.33, 73.40, 41.07, 40.65, 38.40, 8.27.
HRMS (ESI): $C_{34}H_{29}NO_2$ + H, Calc: 484.2277, Found: 484.2270.

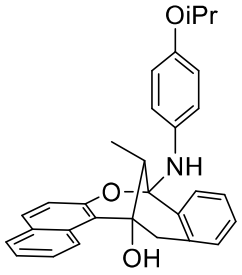
8-((4-methoxyphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (31)



31

Appearance: white solid.
Yield: 98%.
m.p: 177-179°C.
IR: 3359, 2926, 1620, 1600, 1509, 1463, 1432, 1388, 1346, 1233, 1035, 959 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.20 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.03 (dd, *J* = 7.9, 5.8 Hz, 2H), 6.86 – 6.74 (m, 2H), 4.45 (s, 1H), 3.77 (s, 3H), 3.72 – 3.65 (m, 1H), 3.47 (d, *J* = 16.3 Hz, 1H), 3.03 (dd, *J* = 13.1, 6.8 Hz, 1H), 1.87 (s, 1H), 1.03 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.34, 137.71, 134.91, 130.54, 130.17, 129.06, 128.85, 127.76, 126.16, 125.79, 125.39, 123.11, 119.76, 119.08, 114.58, 92.64, 73.53, 55.56, 40.96, 38.60, 8.23.
HRMS (ESI): $C_{28}H_{25}NO_3$ + H, Calc: 424.1913, Found: 424.1913.

8-((4-isopropoxyphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (32)



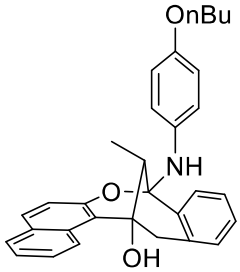
32

Appearance: white solid.
Yield: 63%.
m.p: 135-136°C.
IR: 3351, 3055, 2975, 2936, 1620, 1506, 1463, 1432, 1372, 1233, 1035, 886 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 16.9, 7.9 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.41 (tt, *J* = 12.0, 5.9 Hz, 2H), 3.64 (d, *J* = 16.3 Hz, 1H), 3.42 (d, *J* = 16.3 Hz, 1H), 3.04 (q, *J* = 6.7 Hz, 1H), 2.05 (s, 1H), 1.30 (dd, *J* = 6.0, 1.5 Hz, 6H), 1.00 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 152.10, 150.28, 137.75, 134.86, 134.62, 131.37, 130.45, 130.08,

128.99, 128.77, 127.67, 126.08, 125.74, 125.35, 123.02, 119.64, 119.23, 119.00, 117.24, 92.56, 73.44, 70.62, 40.82, 38.49, 22.13, 22.10, 8.14.

HRMS (ESI): $C_{30}H_{29}NO_3$ + H, Calc: 452.2226, Found: 452.2224.

8-((4-butoxyphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (33)



33

Appearance: white solid.

Yield: 90%.

m.p: 167-168°C.

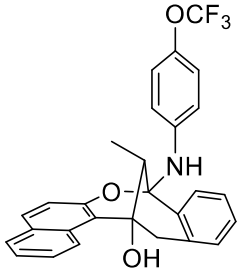
IR: 3338, 2957, 2932, 2872, 1621, 1601, 1508, 1463, 1432, 1234, 1049, 978 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 9.2 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 4.43 (s, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.65 (d, *J* = 16.3 Hz, 1H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.02 (q, *J* = 6.6 Hz, 1H), 1.95 (s, 1H), 1.80 – 1.67 (m, 2H), 1.47 (dq, *J* = 14.1, 7.1 Hz, 2H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.58, 150.30, 137.51, 134.86, 134.62, 131.37, 130.46, 130.10, 128.99, 128.78, 127.68, 126.09, 125.74, 125.35, 123.04, 119.73, 119.22, 119.02, 115.26, 92.60, 73.46, 68.06, 40.88, 38.53, 31.44, 19.25, 13.87, 8.15.

HRMS (ESI): $C_{31}H_{31}NO_3$ + H, Calc: 466.2382, Found: 466.2382.

15-methyl-8-((4-(trifluoromethoxy)phenyl)amino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (34)



34

Appearance: white solid.

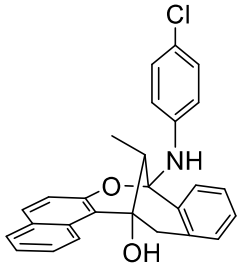
Yield: 35%.

m.p: 180-181°C.

IR: 3378, 3317, 2974, 2921, 1618, 1602, 1506, 1459, 1433, 1230, 1048, 988 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 23.4, 9.0 Hz, 4H), 7.02 (t, *J* = 8.0 Hz, 2H), 4.72 (s, 1H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.48 (d, *J* = 16.3 Hz, 1H), 3.13 (q, *J* = 6.8 Hz, 1H), 1.95 (s, 1H), 1.04 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.03, 143.12, 142.60, 134.98, 134.24, 131.32, 130.67, 130.23, 129.27, 129.13, 128.87, 127.86, 126.25, 125.66, 125.33, 123.25, 122.22, 119.32, 118.87, 118.28, 92.22, 73.39, 40.70, 38.40, 8.35.
^{19}F NMR (376 MHz, $CDCl_3$): δ -58.26.
HRMS (ESI): $C_{28}H_{22}F_3NO_3$ + H, Calc: 478.1630, Found: 478.1635.

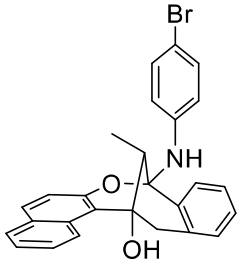
8-((4-chlorophenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (35)



35

Appearance: white solid.
Yield: 72%.
m.p: 179-180°C.
IR: 3382, 3275, 3057, 2921, 1621, 1598, 1490, 1463, 1433, 1233, 1050, 983 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.32 (dd, *J* = 18.5, 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.10 (q, *J* = 8.6 Hz, 4H), 7.00 (t, *J* = 9.0 Hz, 2H), 4.64 (s, 1H), 3.57 (d, *J* = 16.4 Hz, 1H), 3.35 (d, *J* = 16.3 Hz, 1H), 3.08 (d, *J* = 6.8 Hz, 1H), 2.28 (s, 1H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.96, 143.00, 134.89, 134.22, 131.30, 130.63, 130.20, 130.17, 129.25, 129.11, 128.82, 127.81, 126.22, 125.69, 125.30, 123.20, 119.26, 119.10, 118.79, 92.25, 73.32, 40.65, 38.26, 8.08.
HRMS (ESI): $C_{27}H_{22}ClNO_2$ + H, Calc: 428.1417, Found: 428.1412.

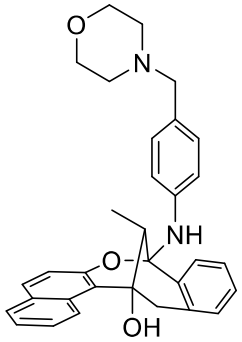
8-((4-bromophenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (36)



36

Appearance: white solid.
Yield: 57%.
m.p: 169-171°C.
IR: 3377, 2964, 1713, 1621, 1593, 1489, 1462, 1433, 1346, 1235, 1080, 983 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.31 (m, 4H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 11.2, 8.8 Hz, 4H), 4.72 (s, 1H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.49 (d, *J* = 16.3 Hz, 1H), 3.16 (q, *J* = 6.7 Hz, 1H), 2.14 (s, 1H), 1.05 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.98, 143.47, 134.93, 134.22, 132.04, 131.31, 130.66, 130.20, 129.26, 129.10, 128.85, 127.84, 126.24, 125.69, 125.32, 123.23, 119.45, 119.29, 118.83, 112.51, 92.23, 73.35, 40.66, 38.34, 8.21.
HRMS (ESI): $C_{27}H_{22}BrNO_2$ + H, Calc: 472.0912, Found: 472.0920.

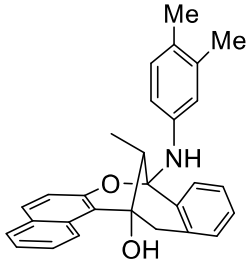
15-methyl-8-((4-(morpholinomethyl)phenyl)amino)-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (37)



37

Appearance: white solid.
Yield: 48%.
m.p: 157-158°C.
IR: 3306, 3025, 2975, 2921, 1616, 1601, 1510, 1481, 1432, 1233, 1037, 985 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.33 – 6.78 (m, 9H), 4.58 (s, 1H), 3.64 – 3.29 (m, 7H), 3.09 (d, *J* = 6.6 Hz, 1H), 2.30 (s, 4H), 2.18 (s, 2H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.17, 143.50, 134.97, 134.52, 131.43, 130.48, 130.34, 130.14, 129.10, 129.06, 128.78, 128.68, 127.75, 126.09, 125.71, 125.44, 123.10, 119.46, 118.96, 117.50, 92.28, 73.25, 66.76, 62.79, 53.22, 40.61, 38.46, 8.32.
HRMS (ESI): $C_{32}H_{32}N_2O_3$ + Na, Calc: 515.2311, Found: 515.2302.

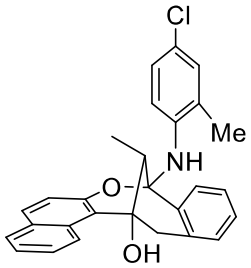
8-((3,4-dimethylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (38)



38

Appearance: white solid.
Yield: 95%.
m.p: 165-166°C.
IR: 3413, 2940, 1618, 1602, 1504, 1490, 1451, 1432, 1387, 1234, 1014, 960 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.62 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.09 – 6.88 (m, 5H), 4.51 (s, 1H), 3.68 (d, *J* = 16.2 Hz, 1H), 3.45 (d, *J* = 16.2 Hz, 1H), 3.16 (d, *J* = 6.6 Hz, 1H), 2.20 (s, 6H), 1.99 (s, 1H), 1.03 (dd, *J* = 6.7, 2.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.40, 142.14, 137.30, 134.93, 134.78, 131.45, 130.52, 130.25, 130.16, 129.05, 128.84, 128.43, 127.76, 126.15, 125.83, 125.43, 123.10, 119.64, 119.32, 119.13, 115.57, 92.47, 73.53, 40.81, 38.55, 20.13, 18.93, 8.36.
HRMS (ESI): $C_{29}H_{27}NO_2$ + H, Calc: 422.2120, Found: 422.2114.

8-((4-chloro-2-methylphenyl)amino)-15-methyl-8,13-dihydro-14H-8,14-methanobenzo[f]naphtho[2,1-b]oxocin-14-ol (39)

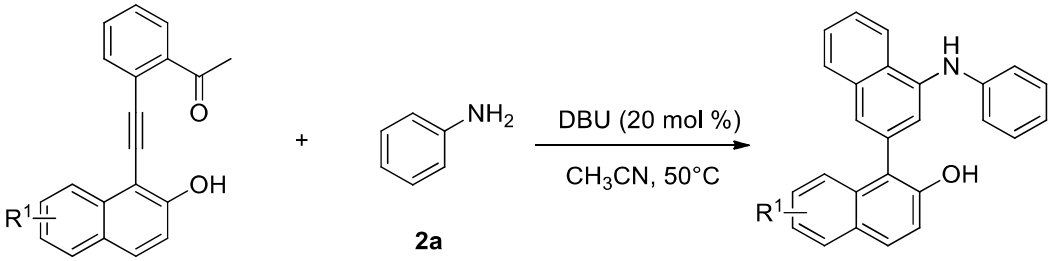


39

Appearance: white solid.
Yield: 64%.
m.p: 187-188°C.
IR: 3544, 3446, 2994, 2969, 2934, 1619, 1599, 1488, 1431, 1235, 1036, 979 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.33 (dd, *J* = 15.7, 7.9 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.07 – 6.97 (m, 3H), 4.54 (s, 1H), 3.69 (d, *J* = 16.4 Hz, 1H), 3.47 (d, *J* = 16.3 Hz, 1H), 3.19 (q, *J* = 6.8 Hz, 1H), 2.19 (s, 3H), 1.98 (s, 1H), 0.93 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.13, 140.89, 134.87, 134.56, 131.34, 130.65, 130.27, 130.21, 129.22, 128.86, 128.04, 126.71, 126.24, 125.73, 125.33, 125.18, 124.50, 123.23, 119.32, 118.91, 117.31, 92.23, 73.41, 40.20, 38.36, 17.66, 8.10.

HRMS (ESI): $C_{28}H_{24}ClNO_2$ + H, Calc: 442.1574, Found: 442.1570.

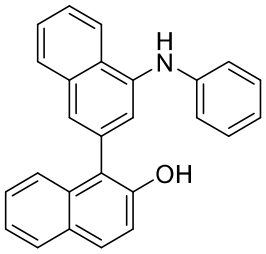
General procedure for the synthesis of 40-51



5 **2a** **40-51**

To a solution of substrate **5** (0.1 mmol) and DBU (0.01 mmol) in the 2 mL CH_3CN was added aniline **2a** (0.2 mmol) at the 50°C. After the reaction performed completely, the solvent was removed under vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **40-51**.

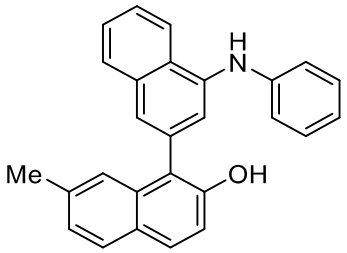
4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (40)



40

Appearance: brown solid.
Yield: 86%.
m.p: 145-146°C.
IR: 3510, 3407, 1618, 1591, 1525, 1509, 1499, 1470, 1438, 1257, 1028, 981 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.05 (m, 1H), 7.88 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.61 – 7.53 (m, 3H), 7.51 – 7.46 (m, 1H), 7.36 – 7.27 (m, 3H), 7.22 (dd, *J* = 8.5, 5.8 Hz, 3H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 5.35 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.23, 143.31, 140.61, 135.14, 133.19, 132.00, 129.53, 129.48, 128.86, 128.77, 128.03, 126.95, 126.51, 126.36, 126.34, 124.68, 123.79, 123.30, 121.51, 121.41, 120.92, 118.56, 117.30, 115.80.
HRMS (ESI): $C_{26}H_{19}NO$ + H, Calc: 362.1545, Found: 362.1545.

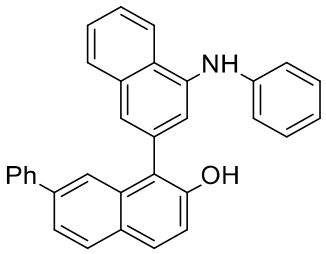
7-methyl-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (41)



41

Appearance: brown solid.
Yield: 43%.
m.p: 136-138°C.
IR: 3510, 3382, 3050, 2918, 1619, 1570, 1513, 1494, 1459, 1253, 1142, 837 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.12 (m, 1H), 8.01 – 7.92 (m, 1H), 7.79 (dd, *J* = 17.0, 8.6 Hz, 2H), 7.64 (s, 3H), 7.42 (s, 1H), 7.35 (s, 1H), 7.34 – 7.20 (m, 4H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.20 (s, 1H), 5.45 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.44, 143.56, 140.60, 136.38, 135.25, 133.42, 132.33, 129.54, 129.35, 128.87, 127.99, 127.22, 126.98, 126.55, 126.37, 125.61, 123.85, 123.80, 121.50, 120.42, 118.53, 116.42, 21.96.
HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 376.1701, Found: 376.1695.

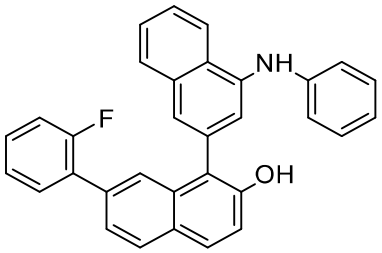
7-phenyl-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (42)



42

Appearance: brown solid.
Yield: 73%.
m.p: 147-149°C.
IR: 3510, 3419, 1595, 1569, 1519, 1497, 1418, 1402, 1309, 1290, 1070, 858 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.09 (m, 1H), 7.93 (t, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.80 (s, 1H), 7.70 – 7.49 (m, 6H), 7.47 – 7.38 (m, 3H), 7.33 (t, *J* = 8.3 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 6.14 (s, 1H), 5.54 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.69, 143.39, 141.39, 140.78, 139.35, 135.19, 133.35, 131.97, 129.43, 129.30, 128.81, 128.69, 128.61, 128.07, 127.40, 127.22, 126.97, 126.54, 126.38, 123.62, 123.12, 122.76, 121.53, 121.39, 121.09, 118.63, 117.39, 116.32.
HRMS (ESI): $C_{32}H_{23}NO$ + H, Calc: 438.1858, Found: 438.1862.

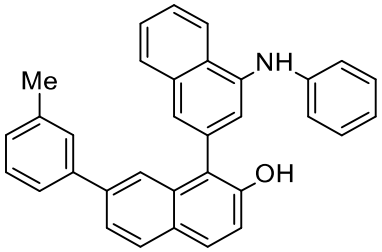
7-(2-fluorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (43)



43

Appearance: brown solid.
Yield: 41%.
m.p: 165-167°C.
IR: 3481, 3366, 2963, 1624, 1597, 1574, 1522, 1488, 1440, 1259, 1016, 974 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 – 7.98 (m, 1H), 7.80 (dd, *J* = 10.7, 5.9 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.61 (s, 1H), 7.54 – 7.47 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.27 (dd, *J* = 9.5, 8.4 Hz, 2H), 7.19 (dd, *J* = 18.0, 8.1 Hz, 2H), 7.12 – 6.96 (m, 6H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.04 (s, 1H), 5.40 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 160.77, 158.80, 150.66, 143.32, 140.79, 135.16, 134.05, 133.12, 131.87, 130.97, 130.94, 129.44, 129.29, 128.94, 128.88, 128.81, 128.14, 128.10, 126.94, 126.44, 126.35, 124.97, 124.96, 124.58, 124.56, 124.26, 124.24, 123.61, 121.57, 121.35, 121.14, 118.73, 117.70, 116.11, 115.98, 115.93.
^{19}F NMR (470 MHz, $CDCl_3$): δ -117.53.
HRMS (ESI): $C_{32}H_{22}FNO$ + H, Calc: 456.1764, Found: 456.1753.

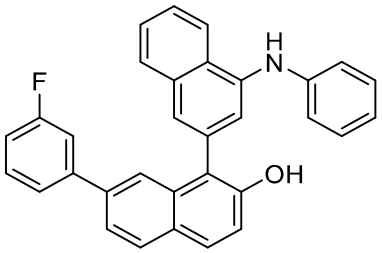
4'-(phenylamino)-7-(m-tolyl)-[1,2'-binaphthalen]-2-ol (44)



44

Appearance: brown solid.
Yield: 78%.
m.p: 130-132°C.
IR: 3511, 3384, 3051, 2919, 1620, 1595, 1513, 1495, 1437, 1253, 1027, 976 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 1H), 7.60 (m, 4H), 7.36 (m, 3H), 7.28 (m, 2H), 7.23 – 7.06 (m, 5H), 6.89 (dd, *J* = 7.7, 6.5 Hz, 1H), 6.14 (s, 1H), 5.50 (s, 1H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.68, 143.36, 141.47, 140.79, 139.59, 138.26, 135.21, 133.32, 132.03, 129.45, 129.31, 128.82, 128.60, 128.53, 128.17, 128.05, 127.99, 126.96, 126.49, 126.36, 124.60, 123.59, 123.28, 122.72, 121.55, 121.40, 121.07, 118.66, 117.31, 116.22, 21.51.
HRMS (ESI): $C_{33}H_{25}NO$ + H, Calc: 452.2014, Found: 452.2007.

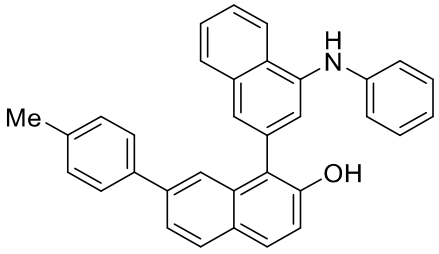
7-(3-fluorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (45)



45

Appearance: brown solid.
Yield: 48%.
m.p: 198-199°C.
IR: 3508, 3420, 3055, 1596, 1569, 1519, 1497, 1464, 1437, 1255, 1070, 995 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 6.2, 3.4 Hz, 1H), 8.03 – 7.86 (m, 2H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.73 (s, 1H), 7.66 – 7.51 (m, 4H), 7.42 – 7.27 (m, 4H), 7.24 (d, *J* = 11.1 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.03 – 6.96 (m, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.15 (s, 1H), 5.52 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 164.29, 161.84, 150.83, 143.74, 143.67, 143.29, 140.97, 138.06, 138.04, 135.20, 133.28, 131.78, 130.18, 130.10, 129.47, 129.31, 128.80, 128.30, 127.05, 126.47, 126.45, 123.50, 123.04, 123.01, 122.89, 122.79, 121.69, 121.38, 121.18, 118.84, 117.73, 115.94, 114.34, 114.12, 114.09, 113.88.
^{19}F NMR (376 MHz, $CDCl_3$): δ -113.03.
HRMS (ESI): $C_{32}H_{22}FNO$ + H, Calc: 456.1764, Found: 456.1768.

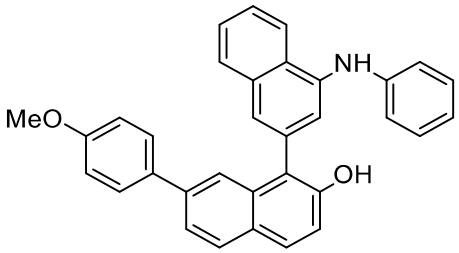
4'-(phenylamino)-7-(p-tolyl)-[1,2'-binaphthalen]-2-ol (46)



46

Appearance: white solid.
Yield: 39%.
m.p: 208-209°C.
IR: 3510, 3406, 3028, 1898, 1618, 1598, 1573, 1502, 1443, 1259, 1035, 993 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.96 – 7.81 (m, 3H), 7.75 (s, 1H), 7.62 (m, 4H), 7.44 (m, 3H), 7.34 – 7.06 (m, 7H), 6.91 (d, *J* = 4.0 Hz, 1H), 6.14 (s, 1H), 5.51 (s, 1H), 2.38 (d, *J* = 3.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.63, 143.40, 140.73, 139.28, 138.50, 137.02, 135.18, 133.38, 132.01, 129.42, 129.40, 129.28, 128.80, 128.54, 127.95, 127.23, 126.94, 126.52, 126.34, 123.65, 123.07, 122.44, 121.50, 121.38, 121.03, 118.61, 117.21, 116.31, 21.05.
HRMS (ESI): $C_{33}H_{25}NO$ + H Calc: 452.2014, Found: 452.2013.

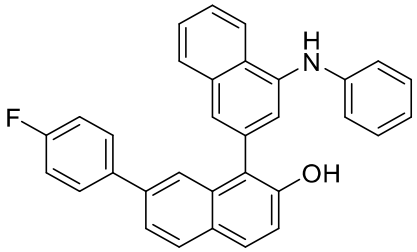
7-(4-methoxyphenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (47)



47

Appearance: brown solid.
Yield: 90%.
m.p: 100-102°C.
IR: 3516, 3379, 3050, 2833, 1675, 1620, 1596, 1497, 1440, 1245, 1026, 972 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.07 (m, 1H), 7.94 – 7.88 (m, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.53 (m, 4H), 7.50 – 7.43 (m, 2H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 7.14 (tt, *J* = 3.8, 1.9 Hz, 2H), 7.11 – 7.04 (m, 2H), 6.98 – 6.80 (m, 3H), 5.48 (s, 1H), 3.79 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.11, 150.65, 143.42, 140.72, 138.91, 135.20, 133.87, 133.42, 132.06, 129.44, 129.28, 128.81, 128.54, 128.38, 127.77, 126.95, 126.54, 126.36, 123.68, 122.93, 122.02, 121.50, 121.41, 120.96, 118.58, 117.09, 116.36, 114.15, 55.31.

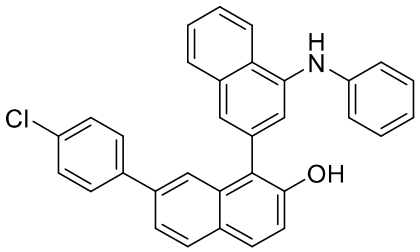
7-(4-fluorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (48)



48

Appearance: Orange solid.
Yield: 50%.
m.p: 179-180°C.
IR: 3508, 3421, 3061, 1621, 1598, 1520, 1501, 1463, 1456, 1288, 1035, 979 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.89 (m, 3H), 7.68 (s, 1H), 7.61 (dd, *J* = 6.5, 3.4 Hz, 3H), 7.54 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.48 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.38 (s, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.11 – 6.96 (m, 4H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 1H), 5.49 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.63, 161.18, 150.78, 143.35, 140.82, 138.33, 137.49, 135.20, 133.33, 131.90, 129.45, 129.31, 128.96, 128.88, 128.82, 128.72, 128.00, 127.03, 126.51, 126.45, 123.60, 122.92, 122.56, 121.61, 121.40, 121.04, 118.66, 117.48, 116.14, 115.67, 115.45.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.66.
HRMS (ESI): $C_{32}H_{22}FNO$ + H, Calc: 456.1764, Found: 456.1758.

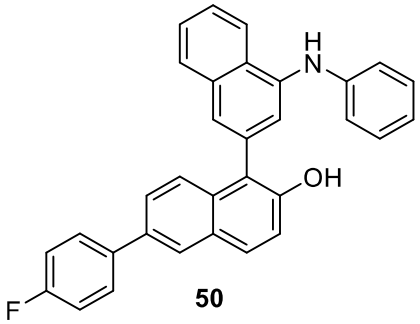
7-(4-chlorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (49)



49

Appearance: brown solid.
Yield: 58%.
m.p: 112-114°C.
IR: 3507, 3390, 3051, 1620, 1594, 1514, 1492, 1455, 1438, 1254, 1012, 976 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 6.2, 3.3 Hz, 1H), 8.00 – 7.85 (m, 2H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.71 (s, 1H), 7.61 (dd, *J* = 6.4, 3.3 Hz, 3H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 12.0 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.15 (s, 1H), 5.51 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.80, 143.31, 140.83, 139.79, 138.04, 135.17, 133.31, 131.81, 129.43, 129.30, 128.81, 128.79, 128.58, 128.15, 127.02, 126.47, 126.44, 123.56, 122.71, 122.65, 121.62, 121.38, 121.10, 118.67, 117.63, 116.03.
HRMS (ESI): $C_{32}H_{22}ClNO$ + H, Calc: 472.1468, Found: 472.1460.

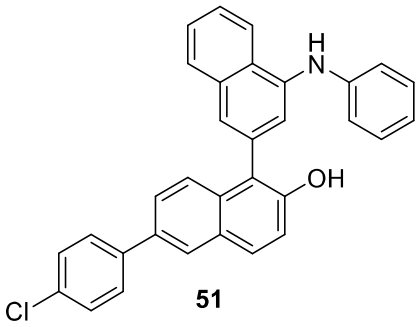
6-(4-fluorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (50)



50

Appearance: brown solid.
Yield: 64%.
m.p: 112-114°C.
IR: 3512, 3393, 3046, 16231, 1592, 1515, 1496, 1410, 1399, 1255, 1013, 962 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 – 8.11 (m, 1H), 7.96 (s, 1H), 7.92 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.66 – 7.53 (m, 7H), 7.37 (d, *J* = 1.1 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.19 – 7.08 (m, 4H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.19 (s, 1H), 5.43 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.36, 160.18, 150.44, 143.25, 140.75, 137.15, 137.13, 135.16, 135.12, 132.33, 131.85, 129.75, 129.52, 129.09, 128.80, 128.75, 128.68, 127.03, 126.41, 126.35, 125.97, 125.82, 125.37, 123.70, 121.62, 121.40, 120.92, 118.68, 117.92, 115.75, 115.58, 115.55.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.99.
HRMS (ESI): $C_{32}H_{22}FNO$ + H, Calc: 456.1764, Found: 456.1758.

6-(4-chlorophenyl)-4'-(phenylamino)-[1,2'-binaphthalen]-2-ol (51)



51

Appearance: brown solid.

Yield: 34%.

m.p: 123-125°C.

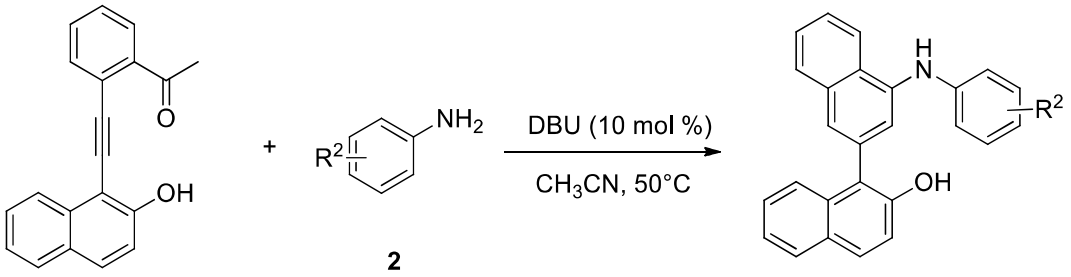
IR: 3506, 3391, 3050, 1620, 1593, 1570, 1491, 1438, 1405, 1234, 1011, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.10 (m, 1H), 8.01 (s, 1H), 7.97 – 7.91 (m, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.53 (m, 7H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.21 (s, 1H), 5.48 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.55, 143.23, 140.73, 139.43, 135.13, 134.78, 133.15, 132.50, 131.79, 129.81, 129.50, 129.04, 128.93, 128.78, 128.38, 127.02, 126.40, 126.33, 125.89, 125.75, 125.44, 123.67, 121.59, 121.40, 120.93, 118.66, 117.97, 115.51.

HRMS (ESI): $C_{32}H_{22}ClNO$ + H, Calc: 472.1468, Found: 472.1472.

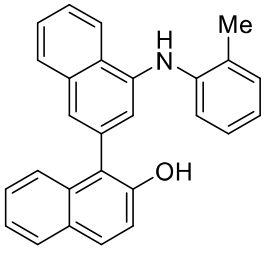
General procedure for the synthesis of 52-76



5a **2** **52-76**

To a solution of **5a** (0.1 mmol) and DBU (0.01 mmol) in the 2 mL CH_3CN was added substrate **2** (0.2 mmol) at the 50°C. After the reaction performed completely, the solvent was removed under vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **52-76**.

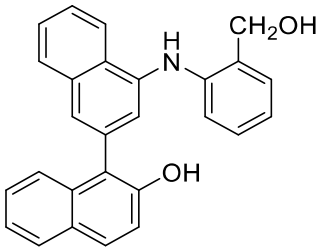
4'-(o-tolylamino)-[1,2'-binaphthalen]-2-ol (52)



52

Appearance: yellow solid.
Yield: 98%.
m.p: 102-104°C.
IR: 3506, 3052, 1619, 1595, 1570, 1501, 1493, 1468, 1409, 1263, 1115, 959 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.95 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.89 – 7.78 (m, 2H), 7.65 (dt, *J* = 6.3, 3.2 Hz, 2H), 7.56 (dd, *J* = 9.1, 6.2 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.09 (m, 2H), 7.03 – 6.88 (m, 2H), 6.04 (s, 1H), 5.42 (s, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.20, 141.51, 141.04, 135.08, 133.19, 132.11, 131.11, 129.44, 129.31, 128.80, 127.99, 127.04, 126.87, 126.44, 126.21, 125.64, 124.72, 123.26, 122.93, 122.90, 121.27, 121.04, 120.66, 117.26, 114.61, 17.90.
HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 376.1701, Found: 376.1702.

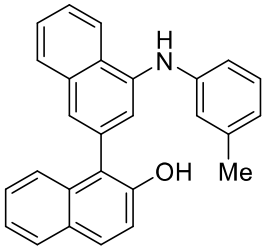
4'-((2-(hydroxymethyl)phenyl)amino)-[1,2'-binaphthalen]-2-ol (53)



53

Appearance: yellow solid.
Yield: 60%.
m.p: 147-149°C.
IR: 3368, 3058, 1621, 1586, 1571, 1515, 1496, 1460, 1410, 1266, 1108, 961 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.86 – 7.77 (m, 2H), 7.75 – 7.51 (m, 5H), 7.42 – 7.30 (m, 4H), 7.28 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 5.44 (s, 1H), 4.83 (s, 2H), 1.96 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.25, 143.26, 140.32, 135.19, 133.22, 131.97, 129.58, 129.48, 129.37, 128.86, 128.74, 128.41, 128.02, 126.91, 126.50, 126.33, 126.09, 124.72, 123.28, 121.47, 121.03, 120.79, 117.67, 117.32, 115.30, 64.90.
HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 414.1470, Found: 414.1467.

4'-(m-tolylamino)-[1,2'-binaphthalen]-2-ol (54)



54

Appearance: brown solid.
Yield: 98%.

m.p: 144-145°C.

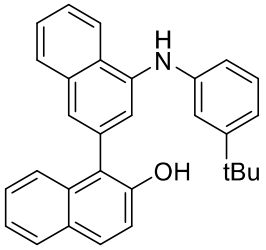
IR: 3506, 3430, 3375, 2920, 1620, 1592, 1496, 1465, 1405, 1262, 1112, 956 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.05 (m, 1H), 7.99 – 7.89 (m, 1H), 7.86 (dd, *J* = 8.4, 3.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 4H), 7.44 – 7.28 (m, 4H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.01 – 6.86 (m, 2H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 5.50 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.21, 143.24, 140.68, 139.30, 135.09, 133.17, 131.99, 129.49, 129.27, 128.86, 128.70, 128.02, 126.87, 126.46, 126.33, 126.23, 124.67, 123.49, 123.27, 122.37, 121.36, 120.90, 119.29, 117.31, 115.96, 115.67, 21.47.

HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 376.1701, Found: 376.1702.

4'-((3-(tert-butyl)phenyl)amino)-[1,2'-binaphthalen]-2-ol (55)



55

Appearance: Orange solid.

Yield: 98%.

m.p: 126-127°C.

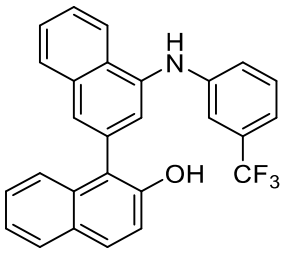
IR: 3389, 3057, 2960, 2865, 1621, 1596, 1497, 1467, 1409, 1264, 1112, 960 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.88 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.78 (dd, *J* = 5.7, 3.0 Hz, 2H), 7.58 (dq, *J* = 6.6, 3.5 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.37 – 7.27 (m, 3H), 7.24 (s, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.94 (dd, *J* = 13.7, 5.1 Hz, 2H), 6.15 (s, 1H), 5.33 (d, *J* = 39.3 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.75, 150.24, 142.71, 141.09, 135.14, 133.19, 132.05, 129.47, 129.08, 128.83, 128.76, 127.99, 126.91, 126.54, 126.21, 126.04, 124.70, 123.24, 123.16, 121.26, 121.00, 119.00, 117.26, 116.54, 116.13, 115.04, 34.65, 31.23.

HRMS (ESI): $C_{30}H_{27}NO$ + H, Calc: 418.2171, Found: 418.2165.

4'-((3-(trifluoromethyl)phenyl)amino)-[1,2'-binaphthalen]-2-ol (56)



56

Appearance: brown solid.

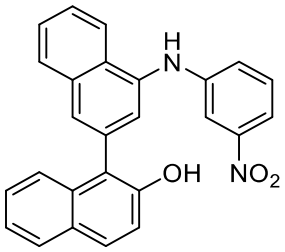
Yield: 71%.

m.p: 116-117°C.

IR: 3392, 3340, 3057, 1618, 1573, 1509, 1470, 1434, 1424, 1266, 1125, 960 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 6.8 Hz, 1H), 7.78 (d, *J* = 4.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.47 (dd, *J* = 5.6, 2.6 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.08 (m, 6H), 7.01 (dd, *J* = 19.2, 7.3 Hz, 2H), 6.04 (s, 1H), 5.27 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.26, 144.73, 139.16, 135.16, 133.14, 132.09, 129.93, 129.72, 128.90, 128.80, 128.10, 127.34, 127.18, 126.74, 126.71, 125.50, 124.43, 123.42, 121.66, 120.48, 120.01, 119.01, 117.35, 117.18, 117.15, 113.75, 113.71, 99.92.
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.79.
HRMS (ESI): $C_{27}H_{18}F_3NO$ + H, Calc: 430.1419, Found: 430.1417.

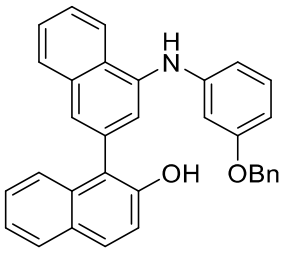
4'-((3-nitrophenyl)amino)-[1,2'-binaphthalen]-2-ol (57)



57

Appearance: Orange solid.
Yield: 41%.
m.p: 124-125°C.
IR: 3362, 1697, 1617, 1598, 1517, 1409, 1338, 1261, 1208, 1141, 1014, 958 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.86 (dd, *J* = 6.2, 3.1 Hz, 1H), 7.74 (dd, *J* = 5.3, 3.0 Hz, 3H), 7.68 (s, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.49 (m, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 1.0 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.28 – 7.21 (m, 2H), 7.21 – 7.14 (m, 2H), 6.19 (s, 1H), 5.32 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.28, 149.30, 145.90, 138.27, 135.20, 133.12, 132.15, 130.10, 129.81, 128.91, 128.88, 128.14, 127.77, 127.31, 127.00, 126.88, 126.51, 124.42, 123.50, 122.01, 121.72, 120.65, 120.28, 117.39, 114.85, 110.71.
HRMS (ESI): $C_{26}H_{18}N_2O_3$ + Na, Calc: 429.1215, Found: 429.1220.

4'-((3-(benzyloxy)phenyl)amino)-[1,2'-binaphthalen]-2-ol (58)

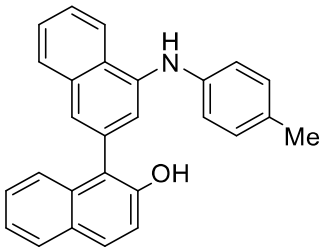


58

Appearance: brown solid.
Yield: 64%.
m.p: 89-91°C.
IR: 3512, 3383, 3058, 2927, 1571, 1515, 1493, 1467, 1408, 1264, 1112, 960 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.05 (m, 1H), 7.92 – 7.86 (m, 1H), 7.84 – 7.76 (m, 2H), 7.63

– 7.54 (m, 3H), 7.54 – 7.49 (m, 1H), 7.44 – 7.21 (m, 9H), 7.13 (t, J = 8.1 Hz, 1H), 6.77 – 6.62 (m, 2H), 6.53 (d, J = 8.2 Hz, 1H), 6.12 (s, 1H), 5.40 (s, 1H), 5.04 – 4.88 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.92, 150.26, 144.97, 140.21, 136.86, 135.12, 133.20, 132.00, 130.23, 129.55, 128.88, 128.73, 128.49, 128.05, 127.89, 127.49, 126.96, 126.73, 126.57, 126.39, 124.64, 124.18, 123.30, 121.60, 120.83, 117.34, 117.11, 110.99, 107.71, 104.73, 69.92.
HRMS (ESI): $C_{33}H_{25}NO_2$ + H, Calc: 468.1964, Found: 468.1957.

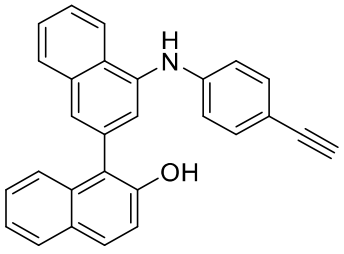
4'-(p-tolylamino)-[1,2'-binaphthalen]-2-ol (59)



59

Appearance: brown solid.
Yield: 87%.
m.p: 197-198°C.
IR: 3508, 3388, 3051, 1593, 1573, 1515, 1471, 1415, 1384, 1257, 1142, 954 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 4.1 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.89 – 7.78 (m, 2H), 7.68 – 7.60 (m, 2H), 7.56 (s, 2H), 7.43 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.19 – 7.04 (m, 4H), 6.16 (s, 1H), 5.46 (s, 1H), 2.38 – 2.24 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.20, 141.48, 140.26, 135.11, 133.19, 132.03, 131.61, 130.02, 129.44, 128.84, 128.77, 127.99, 126.86, 126.45, 126.15, 125.67, 124.73, 123.25, 122.82, 121.12, 121.07, 119.77, 117.27, 114.08, 20.65.
HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 376.1701 Found: 376.1702.

4'-((4-ethynylphenyl)amino)-[1,2'-binaphthalen]-2-ol (60)

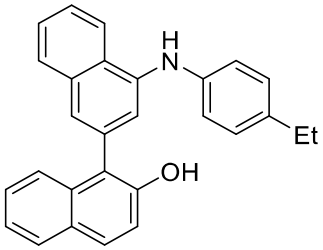


60

Appearance: brown solid.
Yield: 66%.
m.p: 221-222°C.
IR: 3494, 3379, 1620, 1597, 1581, 1507, 1468, 1415, 1385, 1264, 1143, 957 cm^{-1}.
^{1}H NMR (400 MHz, Acetone-d_6): δ 8.23 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 8.00 – 7.95 (m, 1H), 7.90 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.67 (s, 1H), 7.60 – 7.52 (m, 3H), 7.50 (s, 1H), 7.36 (d, J = 6.9 Hz, 1H), 7.31 (dt, J = 10.7, 6.0 Hz, 4H), 7.13 (d, J = 8.5 Hz, 2H), 3.42 (s, 1H).
^{13}C NMR (101 MHz, Acetone-d_6): δ 151.79, 146.43, 138.36, 135.20, 133.86, 133.03, 129.17,

128.80, 128.55, 128.01, 127.57, 126.41, 126.32, 125.62, 125.60, 124.48, 122.85, 122.51, 121.30, 120.50, 118.38, 115.94, 112.40, 84.07, 76.12.
HRMS (ESI): $C_{28}H_{19}NO$ + H, Calc: 386.1545, Found: 386.1546.

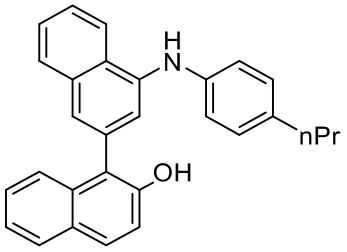
4'-((4-ethylphenyl)amino)-[1,2'-binaphthalen]-2-ol (61)



61

Appearance: brown solid.
Yield: 89%.
m.p: 174-175°C.
IR: 3749, 3495, 1616, 1596, 1571, 1515, 1468, 1410, 1383, 1262, 1172, 954 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 – 8.07 (m, 1H), 7.93 – 7.88 (m, 1H), 7.83 (dd, *J* = 8.8, 4.3 Hz, 2H), 7.60 (dd, *J* = 6.0, 3.4 Hz, 2H), 7.54 (d, *J* = 6.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.10 (q, *J* = 8.4 Hz, 4H), 6.15 (s, 1H), 5.44 (s, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.20, 141.34, 140.45, 138.01, 135.10, 133.20, 132.01, 129.43, 128.82, 128.75, 127.98, 126.85, 126.45, 126.14, 125.70, 124.74, 123.24, 122.86, 121.11, 121.08, 119.59, 117.27, 114.12, 28.11, 15.64.
HRMS (ESI): $C_{28}H_{23}NO$ + H, Calc: 390.1858, Found: 390.1855.

4'-((4-propylphenyl)amino)-[1,2'-binaphthalen]-2-ol (62)

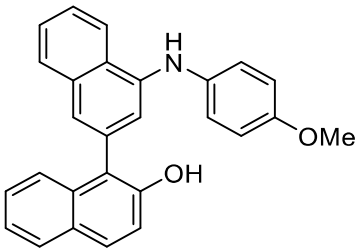


62

Appearance: pink solid.
Yield: 83%.
m.p: 154-157°C.
IR: 3504, 3380, 1616, 1593, 1569, 1515, 1466, 1407, 1383, 1263, 1140, 955 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 5.1, 4.4 Hz, 1H), 7.91 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.65 – 7.51 (m, 4H), 7.38 (dt, *J* = 5.6, 3.4 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.20 – 7.02 (m, 4H), 6.16 (s, 1H), 5.47 (s, 1H), 2.63 – 2.45 (m, 2H), 1.72 – 1.55 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.20, 141.28, 140.48, 136.42, 135.10, 133.20, 132.00, 129.43, 129.41, 128.83, 128.75, 127.99, 126.84, 126.45, 126.13, 125.72, 124.74, 123.25, 122.87, 121.12,

121.09, 119.39, 117.28, 114.17, 37.30, 24.57, 13.82.
HRMS (ESI): $C_{29}H_{25}NO$ + H, Calc: 404.2014, Found: 404.2016.

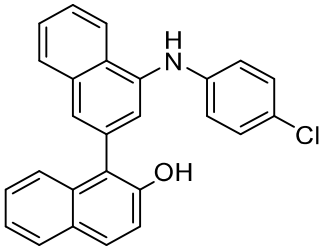
4'-((4-methoxyphenyl)amino)-[1,2'-binaphthalen]-2-ol (63)



63

Appearance: Purple solid.
Yield: 89%.
m.p: 165-166°C.
IR: 3495, 3392, 1621, 1595, 1572, 1512, 1467, 1416, 1384, 1255, 1142, 955 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.87 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.79 (dd, *J* = 8.9, 4.1 Hz, 2H), 7.57 (dt, *J* = 6.3, 3.3 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 (s, 1H), 7.35 – 7.28 (m, 2H), 7.24 (s, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.04 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.08 (s, 1H), 5.41 (s, 1H), 3.74 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.68, 150.18, 142.67, 135.34, 135.08, 133.19, 132.09, 129.38, 128.81, 127.97, 126.83, 126.41, 126.01, 124.76, 124.74, 123.22, 123.01, 122.97, 121.83, 121.22, 120.71, 117.26, 114.89, 112.03, 55.50.
HRMS (ESI): $C_{27}H_{21}NO_2$ + H, Calc: 392.1651, Found: 392.1647.

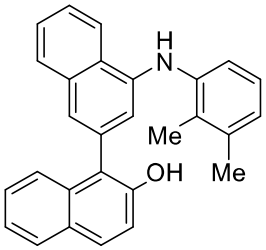
4'-((4-chlorophenyl)amino)-[1,2'-binaphthalen]-2-ol (64)



64

Appearance: yellow solid.
Yield: 79%.
m.p: 192-193°C.
IR: 3509, 3382, 1623, 1590, 1571, 1516, 1471, 1416, 1385, 1264, 1142, 955 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 5.8 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.61 (dd, *J* = 10.5, 6.1 Hz, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 12.1, 8.8 Hz, 3H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.11 (s, 1H), 5.36 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.24, 142.23, 140.14, 135.14, 133.16, 132.03, 129.64, 129.42, 128.91, 128.82, 128.11, 127.08, 126.57, 126.53, 126.04, 124.55, 124.46, 123.36, 121.47, 120.72, 119.45, 117.33, 116.73.
HRMS (ESI): $C_{26}H_{18}ClNO$ + H, Calc: 396.1155, Found: 396.1155.

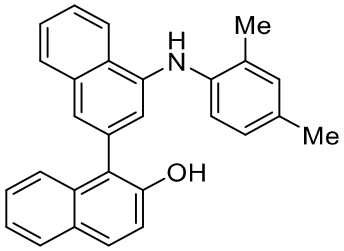
4'-((2,3-dimethylphenyl)amino)-[1,2'-binaphthalen]-2-ol (65)



65

Appearance: Orange solid.
Yield: 81%.
m.p: 140-141°C.
IR: 3508, 3461, 1620, 1596, 1572, 1516, 1470, 1410, 1384, 1265, 1139, 960 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 4.5 Hz, 1H), 7.93 (s, 1H), 7.82 (dd, *J* = 10.7, 6.6 Hz, 2H), 7.62 (d, *J* = 9.2 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.44 – 7.32 (m, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 6.0 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.09 (s, 1H), 5.42 (d, *J* = 8.9 Hz, 1H), 2.32 (d, *J* = 8.8 Hz, 3H), 2.25 (d, *J* = 8.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.19, 142.49, 140.46, 138.17, 135.04, 132.15, 129.74, 129.36, 128.80, 127.95, 126.80, 126.35, 126.30, 126.06, 125.67, 124.92, 124.80, 123.23, 122.01, 121.17, 121.02, 120.49, 117.24, 113.12, 20.58, 13.89.
HRMS (ESI): $C_{28}H_{23}NO$ + H, Calc: 390.1858, Found: 390.1856

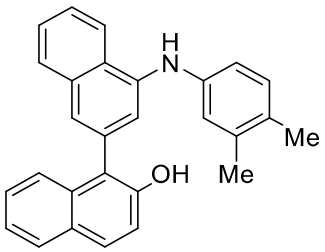
4'-((2,4-dimethylphenyl)amino)-[1,2'-binaphthalen]-2-ol (66)



66

Appearance: Orange solid.
Yield: 80%.
m.p: 94-95°C.
IR: 3507, 1620, 1594, 1572, 1501, 1465, 1409, 1383, 1345, 1264, 1140, 961 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.06 (m, 1H), 7.96 – 7.87 (m, 1H), 7.81 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 (s, 1H), 7.35 (dd, *J* = 9.2, 4.8 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.12 – 6.99 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 5.99 (s, 1H), 5.41 (s, 1H), 2.29 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.18, 142.41, 137.81, 135.05, 133.41, 133.20, 132.16, 131.88, 130.86, 129.35, 128.81, 127.95, 127.63, 126.78, 126.37, 126.00, 124.82, 124.78, 123.21, 122.59, 121.81, 121.21, 120.94, 117.23, 112.62, 20.72, 17.80.
HRMS (ESI): $C_{28}H_{23}NO$ + H, Calc: 390.1858, Found: 390.1864.

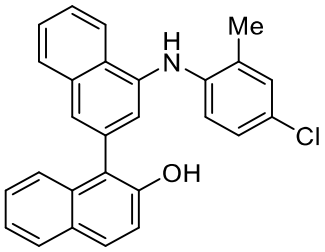
4'-((3,4-dimethylphenyl)amino)-[1,2'-binaphthalen]-2-ol (67)



67

Appearance: Orange solid.
Yield: 81%.
m.p: 147-148°C.
IR: 3513, 3394, 1616, 1596, 1583, 1504, 1457, 1433, 1388, 1260, 1141, 956 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 – 8.06 (m, 1H), 7.91 – 7.86 (m, 1H), 7.84 – 7.77 (m, 2H), 7.57 (dt, *J* = 14.7, 6.9 Hz, 3H), 7.52 (s, 1H), 7.37 – 7.30 (m, 2H), 7.26 (dd, *J* = 12.3, 8.6 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 1H), 5.47 (s, 1H), 2.18 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.22, 141.55, 140.55, 137.70, 135.10, 133.19, 132.05, 130.47, 130.37, 129.42, 128.85, 128.74, 127.99, 126.82, 126.42, 126.09, 125.67, 124.74, 123.23, 122.58, 121.24, 121.09, 121.05, 117.28, 117.18, 114.23, 19.93, 18.96.
HRMS (ESI): $C_{28}H_{23}NO$ + H, Calc: 390.1858, Found: 390.1857.

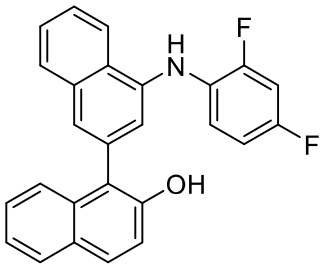
4'-((4-chloro-2-methylphenyl)amino)-[1,2'-binaphthalen]-2-ol (68)



68

Appearance: brown solid.
Yield: 92%.
m.p: 150-152°C.
IR: 3513, 3395, 1621, 1596, 1571, 1515, 1487, 1436, 1384, 1263, 1140, 961 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 1H), 7.93 – 7.87 (m, 1H), 7.80 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.55 (s, 1H), 7.49 – 7.43 (m, 1H), 7.36 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.04 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.90 (s, 1H), 5.89 (s, 1H), 5.32 (s, 1H), 2.29 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.24, 141.11, 139.94, 135.12, 133.19, 132.16, 130.93, 130.85, 129.60, 128.89, 128.11, 127.58, 127.03, 126.99, 126.53, 126.42, 125.82, 124.63, 123.54, 123.36, 121.63, 121.32, 120.88, 117.33, 115.36, 17.84.
HRMS (ESI): $C_{27}H_{20}ClNO$ + H, Calc: 410.1312, Found: 410.1311

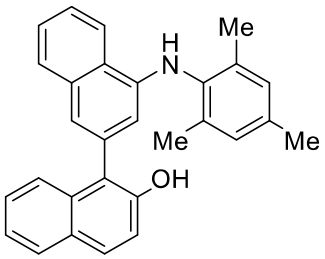
4'-((2,4-difluorophenyl)amino)-[1,2'-binaphthalen]-2-ol (69)



69

Appearance: brown solid.
Yield: 53%.
m.p: 82-84°C.
IR: 3517, 3398, 1620, 1596, 1573, 1506, 1467, 1407, 1384, 1260, 1137, 960 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 – 8.09 (m, 1H), 7.96 – 7.90 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 6.3 Hz, 3H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 9.7, 4.6 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.17 (dd, *J* = 13.8, 7.8 Hz, 2H), 6.91 (t, *J* = 9.6 Hz, 1H), 6.75 (t, *J* = 8.3 Hz, 1H), 6.11 (s, 1H), 5.41 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.31, 152.71, 150.31, 140.19, 135.13, 133.23, 132.01, 129.68, 128.94, 128.89, 128.14, 127.75, 127.15, 126.62, 126.21, 124.65, 124.23, 123.42, 121.23, 120.82, 120.71, 120.66, 117.41, 115.32, 111.44, 111.41, 111.26, 111.23, 104.70, 104.51, 104.30.
^{19}F NMR (376 MHz, $CDCl_3$): δ -118.52, -125.72.
HRMS (ESI): $C_{26}H_{17}F_2NO$ + H, Calc: 398.1356, Found: 398.1351.

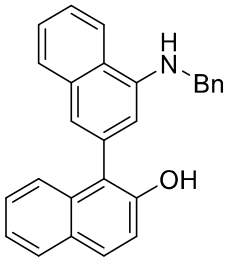
4'-(mesitylamino)-[1,2'-binaphthalen]-2-ol (70)



70

Appearance: brown solid.
Yield: 74%.
m.p: 167-168°C.
IR: 3495, 3059, 1620, 1595, 1572, 1516, 1468, 1414, 1384, 1266, 1141, 959 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.78 (t, *J* = 8.7 Hz, 2H), 7.67 – 7.58 (m, 2H), 7.48 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.36 (s, 1H), 7.30 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.90 (s, 2H), 6.20 (s, 1H), 5.89 (s, 1H), 5.39 (s, 1H), 2.23 (d, *J* = 8.3 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.10, 143.07, 135.65, 135.03, 134.87, 133.19, 132.40, 129.47, 129.21, 128.91, 128.72, 127.89, 126.66, 126.25, 125.69, 124.81, 123.21, 123.14, 121.44, 120.29, 119.98, 117.15, 108.46, 20.82, 17.99.
HRMS (ESI): $C_{29}H_{25}NO$ + H, Calc: 404.2014, Found: 404.2004.

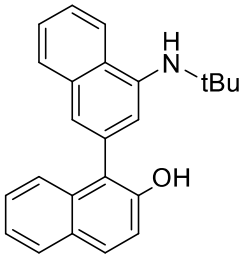
4'-(benzylamino)-[1,2'-binaphthalen]-2-ol (71)



71

Appearance: yellow solid.
Yield: 81%.
m.p: 101-103°C.
IR: 3495, 3059, 1620, 1595, 1572, 1516, 1468, 1414, 1384, 1266, 1141, 959 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.76 (m, 4H), 7.55 (dd, *J* = 9.3, 5.3 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.26 (m, 6H), 6.65 (s, 1H), 5.51 (s, 1H), 4.90 (s, 1H), 4.46 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.22, 144.36, 138.42, 134.76, 133.17, 132.37, 129.32, 128.88, 128.85, 128.79, 127.93, 127.83, 127.58, 126.62, 126.38, 125.55, 124.91, 123.18, 121.55, 119.95, 119.31, 117.27, 107.09, 48.46.
HRMS (ESI): $C_{27}H_{21}NO$ + H, Calc: 376.1701, Found: 376.1696.

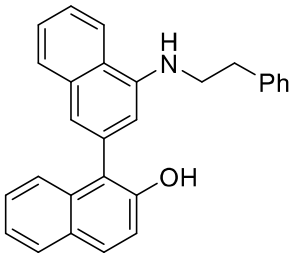
4'-(tert-butylamino)-[1,2'-binaphthalen]-2-ol (72)



72

Appearance: white solid.
Yield: 97%.
m.p: 187-188°C.
IR: 3326, 2969, 1626, 1598, 1583, 1507, 1476, 1436, 1390, 1267, 1144, 965 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dt, *J* = 16.5, 5.6 Hz, 4H), 7.70 – 7.62 (m, 1H), 7.53 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.44 – 7.28 (m, 4H), 6.91 (s, 1H), 5.63 (s, 1H), 4.55 (s, 1H), 1.49 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.25, 142.94, 135.05, 133.25, 131.89, 129.25, 128.99, 128.90, 128.00, 126.39, 126.31, 125.38, 124.90, 124.32, 123.19, 121.76, 120.11, 118.73, 117.32, 110.57, 77.32, 77.00, 76.68, 51.54, 29.71.
HRMS (ESI): $C_{24}H_{23}NO$ + H, Calc: 342.1858, Found: 342.1857.

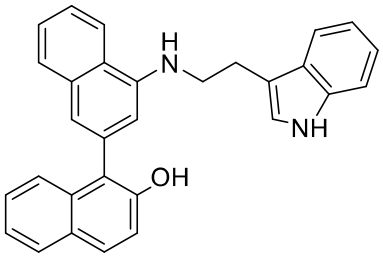
4'-(phenethylamino)-[1,2'-binaphthalen]-2-ol (73)



73

Appearance: brown solid.
Yield: 59%.
m.p: 91-92°C.
IR: 3500, 3366, 1621, 1595, 1573, 1517, 1466, 1454, 1384, 1264, 1142, 961 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.84 (m, 3H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.59 – 7.51 (m, 2H), 7.44 – 7.34 (m, 6H), 7.32 – 7.26 (m, 3H), 6.71 (s, 1H), 5.62 (s, 1H), 4.64 (s, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 3.09 (t, *J* = 6.9 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.21, 144.41, 138.92, 134.72, 133.23, 132.36, 129.29, 128.85, 128.78, 128.72, 128.68, 128.53, 127.96, 126.57, 126.49, 126.36, 125.41, 124.93, 123.18, 123.03, 121.69, 119.76, 119.05, 117.27, 106.68, 44.90, 35.13.
HRMS (ESI): $C_{28}H_{23}NO$ + H, Calc: 390.1858, Found: 390.1859.

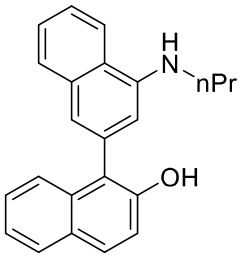
4'-((2-(1H-indol-3-yl)ethyl)amino)-[1,2'-binaphthalen]-2-ol (74)



74

Appearance: green solid.
Yield: 60%.
m.p: 121-123°C.
IR: 3417, 3056, 1620, 1594, 1573, 1515, 1466, 1418, 1384, 1266, 1142, 960 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.82 (t, *J* = 8.7 Hz, 3H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.59 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.48 (dt, *J* = 15.0, 7.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.33 (dd, *J* = 6.8, 3.7 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.03 (m, 2H), 6.65 (s, 1H), 5.53 (s, 1H), 4.73 (s, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.24 (t, *J* = 6.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.21, 144.74, 136.42, 134.74, 132.38, 129.28, 128.87, 128.78, 127.97, 126.47, 126.37, 125.34, 124.99, 123.19, 123.10, 122.34, 122.01, 121.75, 119.92, 119.59, 118.90, 118.72, 117.26, 113.22, 111.27, 106.66, 44.01, 24.76.
HRMS (ESI): $C_{30}H_{24}N_2O$ + H, Calc: 515.2311, Found: 515.2302.

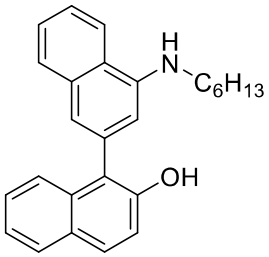
4'-(propylamino)-[1,2'-binaphthalen]-2-ol (75)



75

Appearance: brown solid.
Yield: 65%.
m.p: 188-189°C.
IR: 3295, 3161, 1626, 1598, 1574, 1511, 1465, 1410, 1380, 1266, 1142, 960 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (s, 1H), 8.25 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 8.0 Hz, 3H), 7.45 (d, J = 7.6 Hz, 3H), 7.35 – 7.17 (m, 3H), 7.05 (s, 1H), 6.42 (s, 1H), 6.16 (s, 1H), 3.12 (d, J = 5.5 Hz, 2H), 1.70 (dd, J = 14.0, 6.9 Hz, 2H), 0.94 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, DMSO-d_6): δ 152.20, 144.44, 135.37, 134.71, 134.21, 128.86, 128.54, 128.38, 128.31, 126.47, 126.19, 125.01, 124.30, 122.90, 122.86, 122.79, 122.14, 118.94, 117.79, 106.91, 45.66, 21.96, 12.30.
HRMS (ESI): $C_{23}H_{21}NO$ + H, Calc: 429.1967, Found: 429.1960.

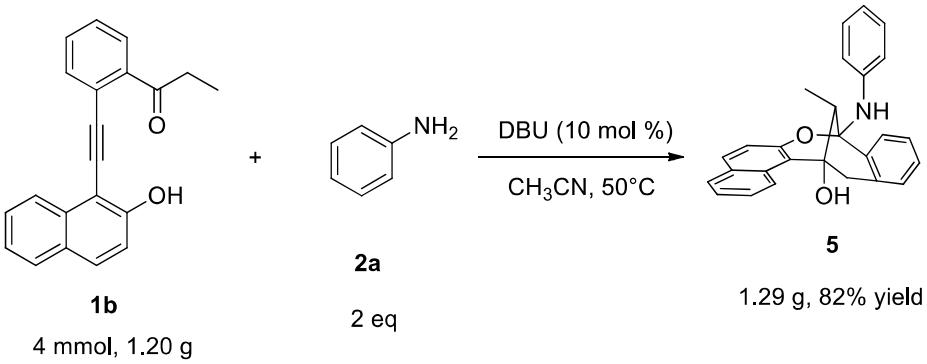
4'-(hexylamino)-[1,2'-binaphthalen]-2-ol (76)



76

Appearance: brown solid.
Yield: 60%.
m.p: 188-189°C.
IR: 3296, 2929, 1625, 1574, 1512, 1476, 1412, 1338, 1266, 1142, 961, 847 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.90 (m, 1H), 7.87 (dt, J = 5.1, 2.9 Hz, 3H), 7.69 – 7.63 (m, 1H), 7.60 – 7.52 (m, 2H), 7.42 – 7.34 (m, 3H), 7.33 (s, 1H), 6.64 (s, 1H), 5.62 (s, 1H), 4.57 (s, 1H), 3.27 (t, J = 7.1 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.48 (dd, J = 14.4, 7.2 Hz, 2H), 1.38 (dt, J = 7.2, 3.6 Hz, 4H), 0.95 (t, J = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.22, 144.85, 134.74, 133.25, 132.40, 129.24, 128.85, 128.82, 127.94, 126.46, 126.32, 125.32, 125.00, 123.16, 122.90, 121.80, 119.80, 118.65, 117.26, 106.37, 44.13, 31.59, 29.26, 26.92, 22.56, 14.00.
HRMS (ESI): $C_{26}H_{27}NO$ + H, Calc: 328.1701, Found: 328.1693.

Experimental procedure for the gram-scale synthesis of 5 and 40



1b

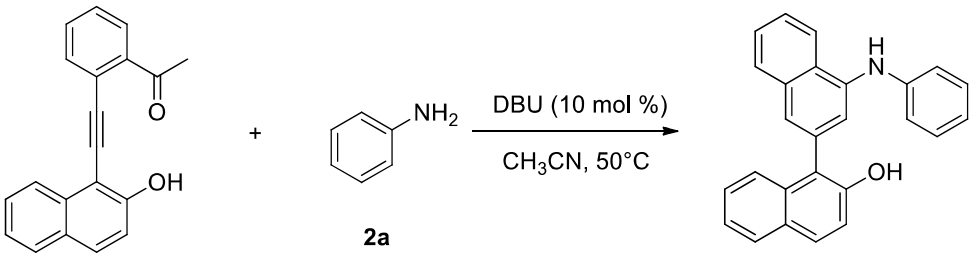
4 mmol, 1.20 g

2a

2 eq

5

1.29 g, 82% yield



3a

4 mmol, 1.14 g

2a

2 eq

40

1.30 g, 90% yield

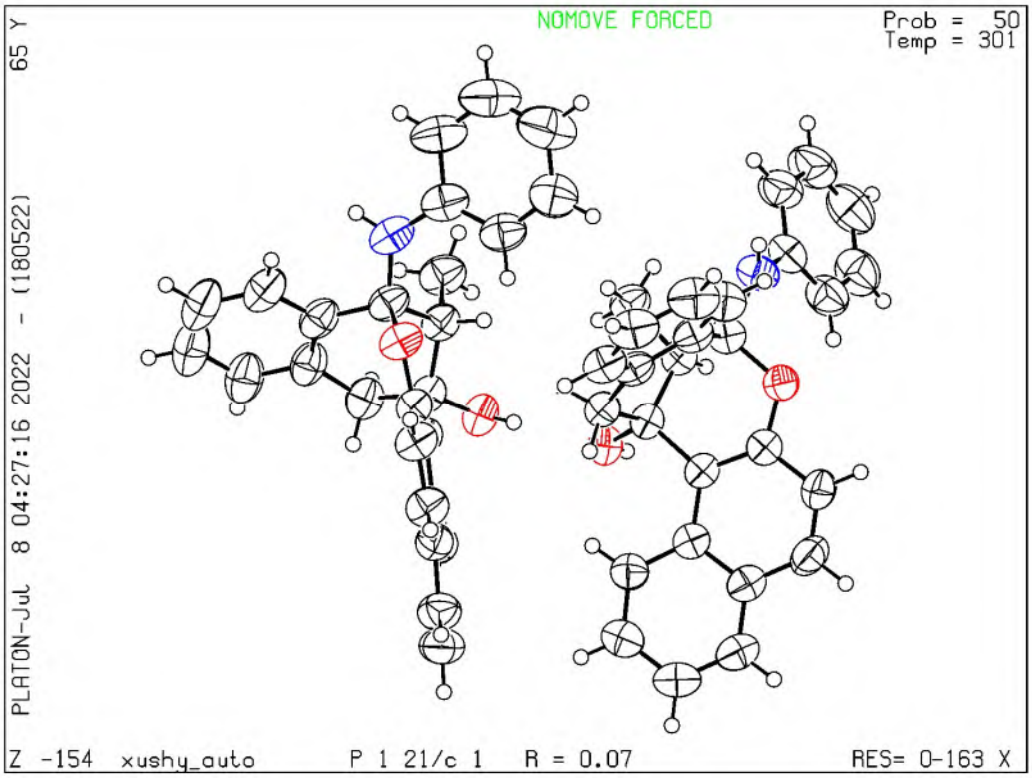
To a solution of substrate **1b** (4 mmol, 1.20 g) and DBU (0.4 mmol, 60.9 mg) in the 30 ml CH_3CN was added aniline **2a** (8 mmol, 0.74 g) at the 50°C. After the reaction performed completely, the solvent was removed under vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **5** (1.29g, 82% yield).

To a solution of substrate **3a** (4 mmol, 1.14 g) and DBU (0.4 mmol, 60.9 mg) in the 30 ml CH_3CN was added aniline **2a** (8 mmol, 0.74 g) at the 50°C. After the reaction performed completely, the solvent was removed under vacuum and residue was purified by flash column chromatography (PE/EA 10:1) to give the pure desired products **40** (1.30g, 90% yield).

X-ray Structure of 5 and 40

X-ray Structure of **5** (The ellipsoid contour percent probability level is 50%)

The solvent system and method for crystal growth: To a solution of **5** (30 mg) in dichloromethane (10 mL) was added distilled hexane (3 mL) in a 25 mL clean and smooth round bottom flask. After the solvent was thoroughly mixed, the round bottom flask was transferred to the refrigerator (0°C) to stand still. After a certain amount of solvent was volatilized, acicular crystals will be precipitated out.



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) xushy_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR

PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: xushy_auto

Bond precision:	C-C = 0.0042 A		Wavelength=1.54184
Cell:	a=14.4846(5)	b=27.7314(7)	c=13.2721(4)
	alpha=90	beta=116.935(4)	gamma=90
Temperature: 301 K			

	Calculated	Reported
Volume	4752.8(3)	4752.8(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C27 H23 N O2 [+ solvent]	C27 H23 N O2
Sum formula	C27 H23 N O2 [+ solvent]	C27 H23 N O2
Mr	393.46	393.46
Dx,g cm-3	1.100	1.100

Z	8	8
Mu (mm-1)	0.543	0.543
F000	1664.0	1664.0
F000'	1668.71	
h,k,lmax	18,34,16	18,34,16
Nref	9907	9744
Tmin,Tmax	0.973,0.973	0.861,1.000
Tmin'	0.973	

Correction method= # Reported T Limits: Tmin=0.861 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.984 Theta(max)= 75.841

R(reflections)= 0.0651(6969) wR2(reflections)= 0.1946(9744)

S = 1.061 Npar= 545

Experimental

Single crystals of $C_{27}H_{23}NO_2$ **[xushy_auto]** were **[]**. A suitable crystal was selected and **[]** on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 300.6(7) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.*J*., Gildea, R.*J*, Howard, *J*.A.K. & Puschmann, H. (2009), *J*. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

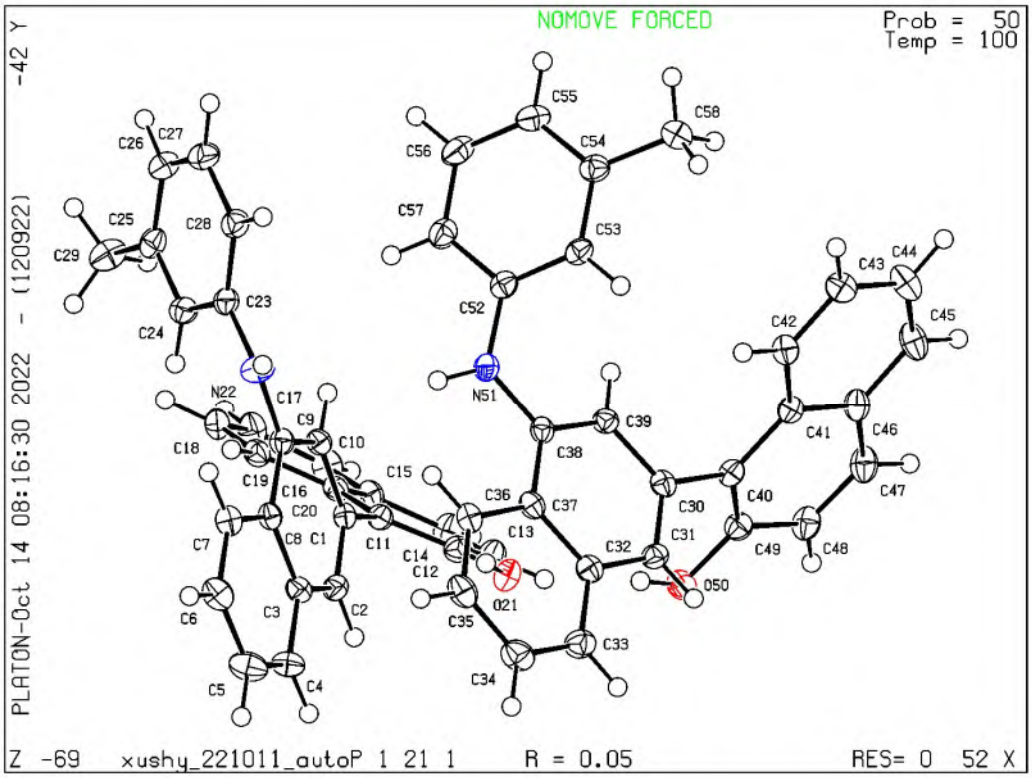
Crystal structure determination of [xushy_auto]

Crystal Data for $C_{27}H_{23}NO_2$ (*M* =393.46 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.4846(5) Å, *b* = 27.7314(7) Å, *c* = 13.2721(4) Å, *β* = 116.935(4)°, *V* = 4752.8(3) Å^3, *Z* = 8, *T* = 300.6(7) K, μ(Cu Kα) = 0.543 mm^{-1}, *Dcalc* = 1.100 g/cm^3, 58062 reflections measured (6.374° ≤ 2Θ ≤ 151.682°), 9744 unique (R_{int} = 0.0602, R_{sigma} = 0.0422) which were used in all calculations. The final R_1 was 0.0651 (I > 2σ(I)) and wR_2 was 0.1946 (all data).

X-ray Structure of **40** (The ellipsoid contour percent probability level is 50%)

The solvent system and method for crystal growth: To a solution of **40** (30 mg) in dichloromethane (10 mL) was added distilled hexane (3 mL) in a 25 mL clean and smooth round bottom flask. After the solvent was thoroughly mixed, the round bottom flask was transferred to the refrigerator (0°C)

to stand still. After a certain amount of solvent was volatilized, acicular crystals will be precipitated out.



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) xushy_221011_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR

PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: xushy_221011_auto

Bond precision:	C-C = 0.0037 A		Wavelength=1.54184
Cell:	a=8.9835(1)	b=21.7218(2)	c=10.6939(1)
	alpha=90	beta=111.112(1)	gamma=90
Temperature: 100 K			

	Calculated	Reported
Volume	1946.72(4)	1946.71(4)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C27 H21 N O	C27 H21 N O

Sum formula	C27 H21 N O	C27 H21 N O
Mr	375.45	375.45
Dx,g cm-3	1.281	1.281
Z	4	4
Mu (mm-1)	0.600	0.600
F000	792.0	792.0
F000'	794.16	
h,k,lmax	11,27,13	11,27,13
Nref	8391[4310]	7750
Tmin,Tmax	0.931,0.942	0.631,1.000
Tmin'	0.835	

Correction method= # Reported T Limits: Tmin=0.631 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.92 Theta(max)= 78.638

R(reflections)= 0.0503(7440) wR2(reflections)= 0.1341(7750)

S = 1.040 Npar= 530

Experimental

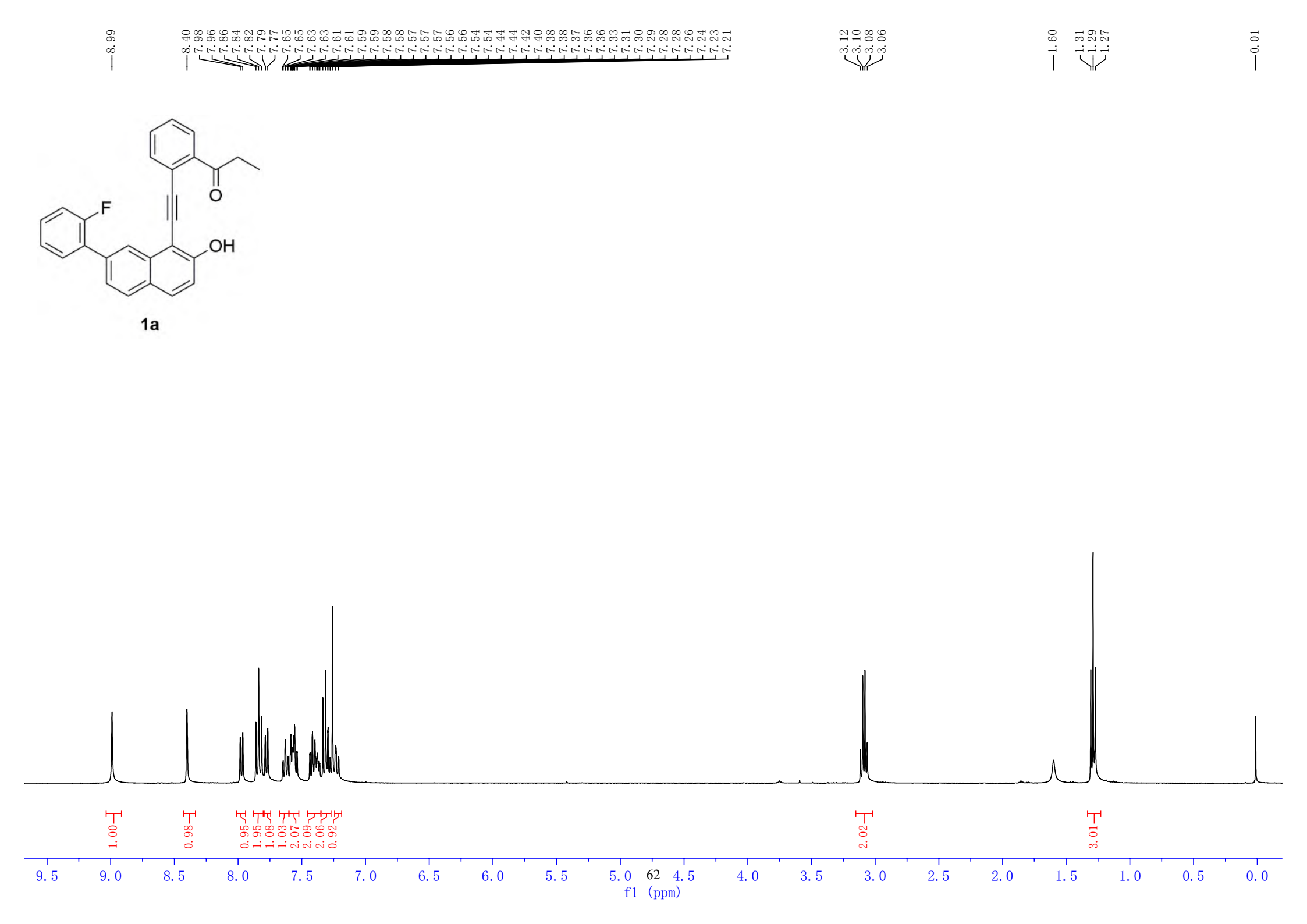
Single crystals of $C_{27}H_{21}NO$ **[xushy_221011_auto]** were **[]**. A suitable crystal was selected and **[]** on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100.00(13) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

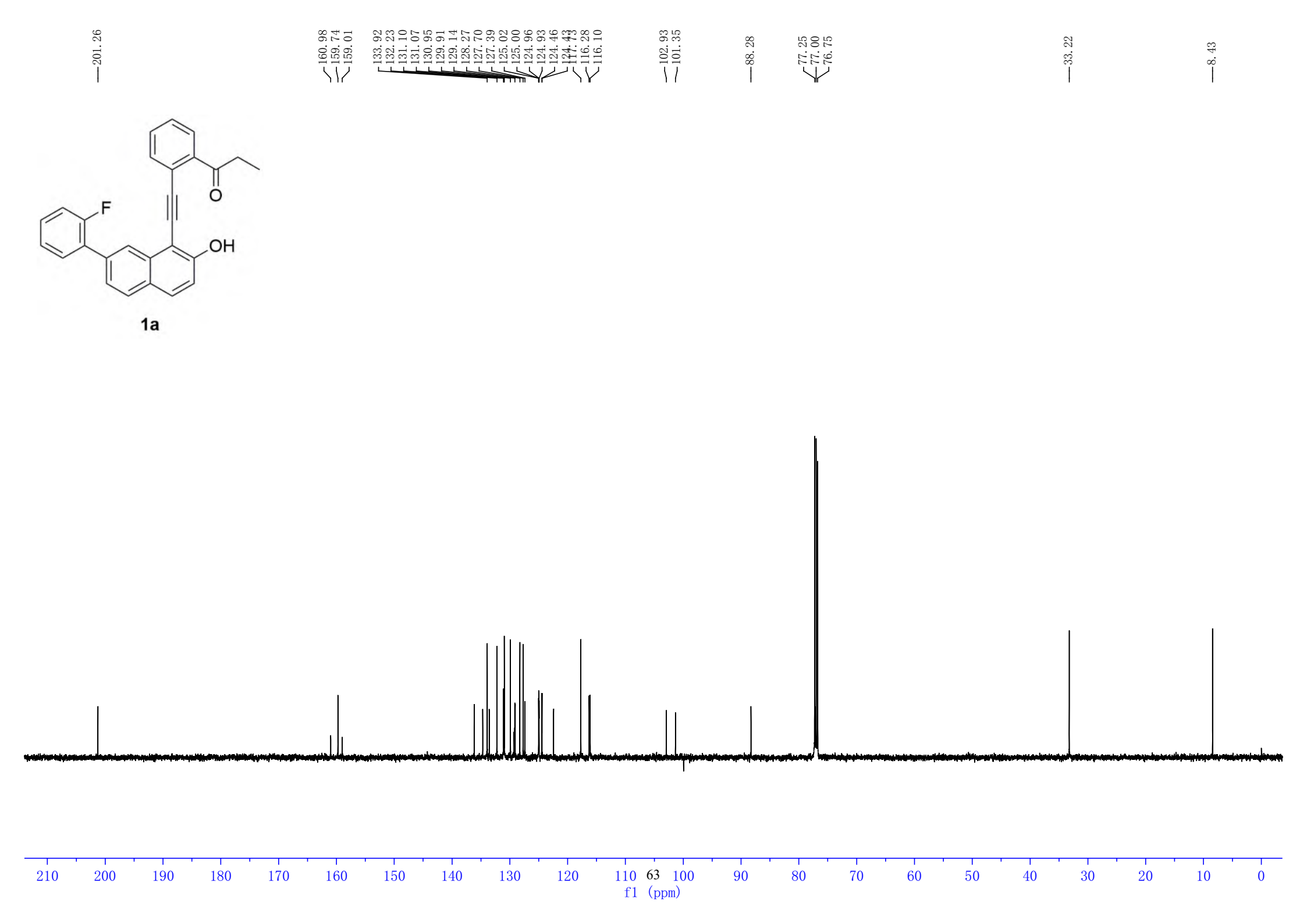
1. Dolomanov, O.V., Bourhis, L.*J*., Gildea, R.*J*, Howard, *J*.A.K. & Puschmann, H. (2009), *J*. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [xushy_221011_auto]

Crystal Data for $C_{27}H_{21}NO$ (M =375.45 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 8.98350(10) Å, b = 21.7218(2) Å, c = 10.69390(10) Å, β = 111.1120(10)°, V = 1946.71(4) Å^3, Z = 4, T = 100.00(13) K, μ(Cu Kα) = 0.600 mm^{-1}, *Dcalc* = 1.281 g/cm^3, 38572 reflections measured (8.14° ≤ 2Θ ≤ 157.276°), 7750 unique (R_{int} = 0.0388, R_{sigma} = 0.0296) which were used in all calculations. The final R_1 was 0.0503 (I > 2σ(I)) and wR_2 was 0.1341 (all data).

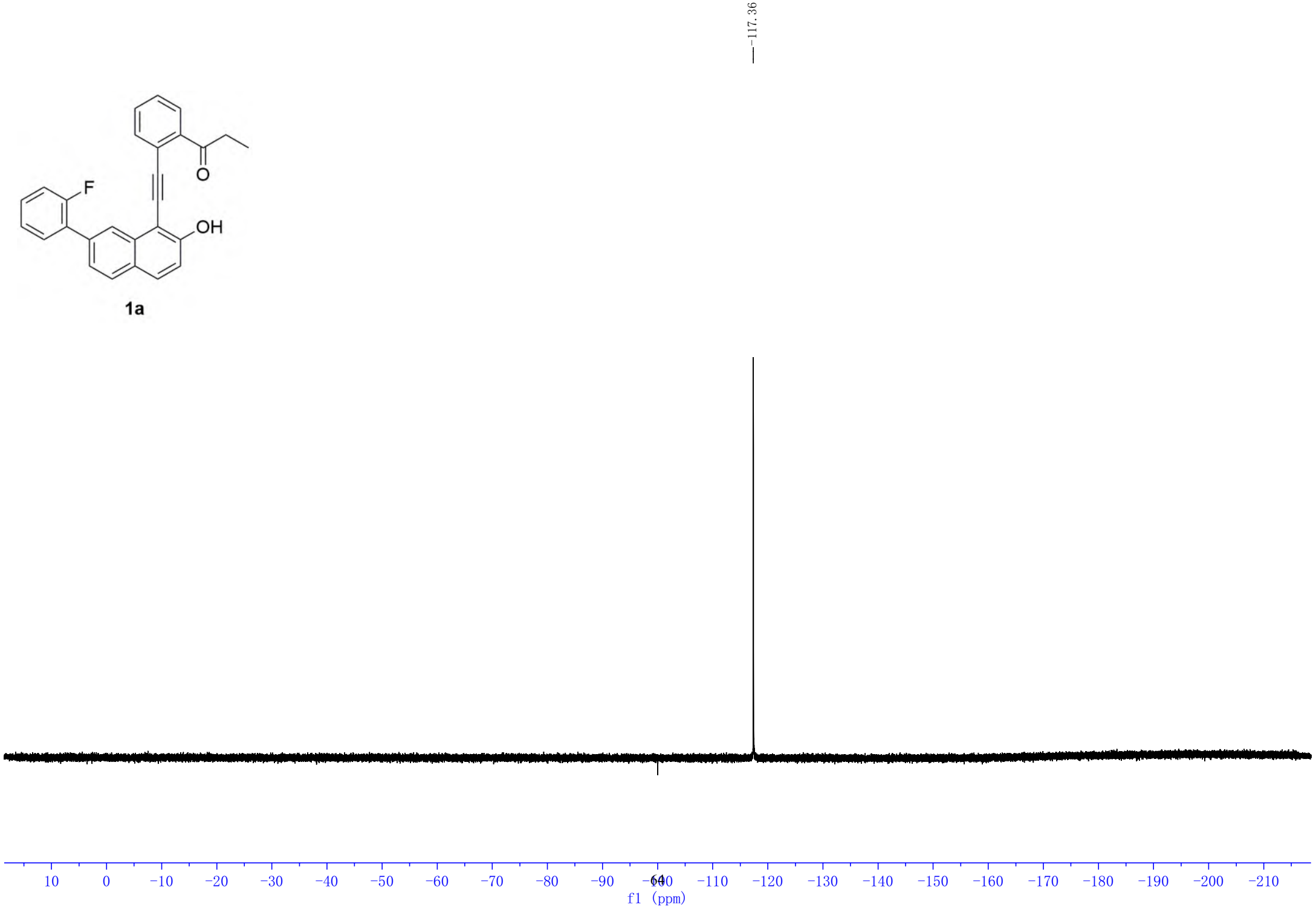
Copies of NMR spectrum

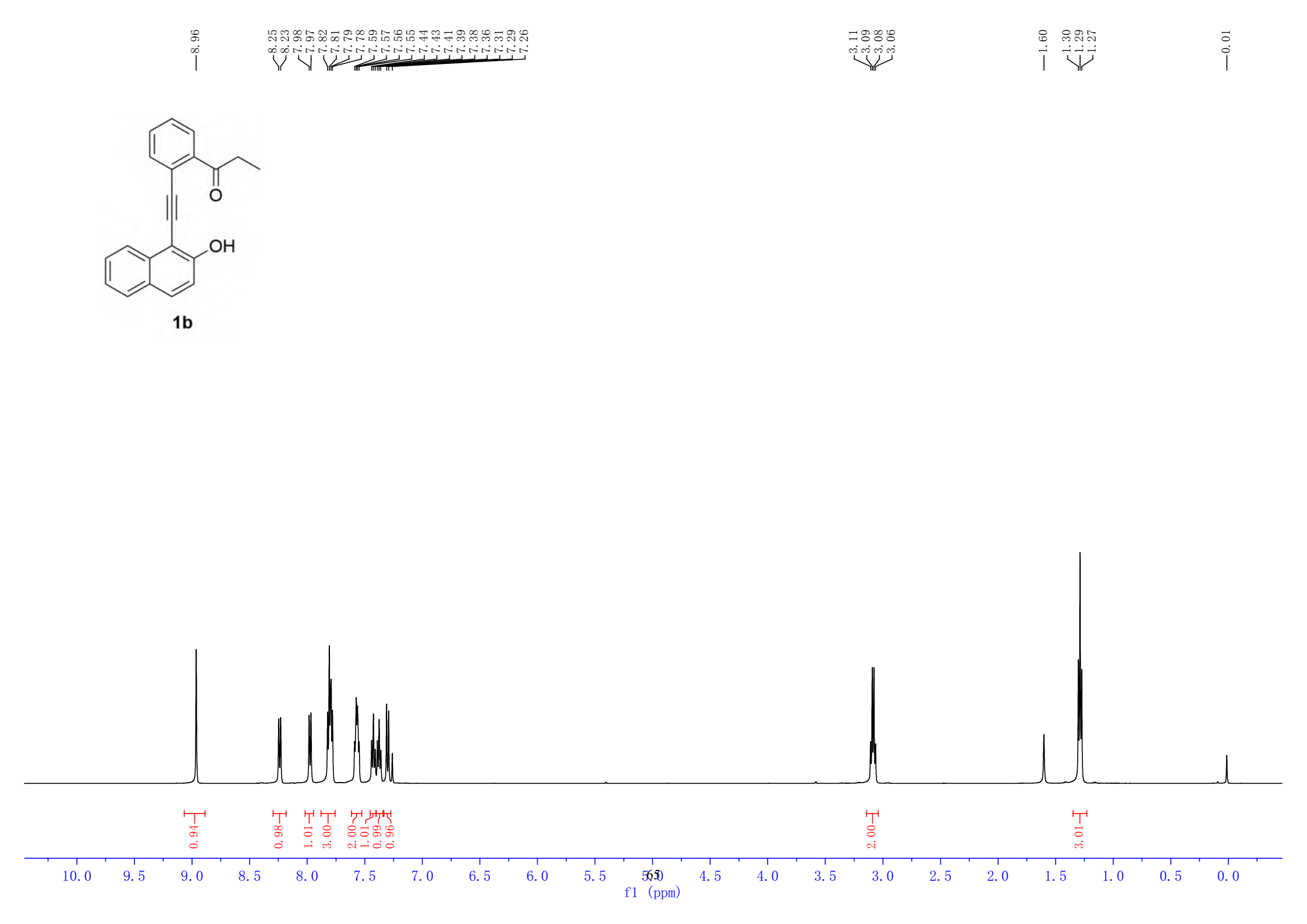

8.99
8.40
7.98
7.96
7.86
7.84
7.82
7.79
7.77
7.65
7.65
7.63
7.63
7.61
7.61
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.54
7.54
7.44
7.44
7.42
7.40
7.38
7.38
7.37
7.36
7.36
7.33
7.31
7.30
7.29
7.28
7.28
7.26
7.24
7.23
7.21
3.12
3.10
3.08
3.06
1.60
1.31
1.29
1.27
0.01
F
O
OH
1a
1.00
0.98
0.95
1.95
1.08
1.03
2.07
2.09
2.06
0.92
2.02
3.01
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
f1 (ppm)

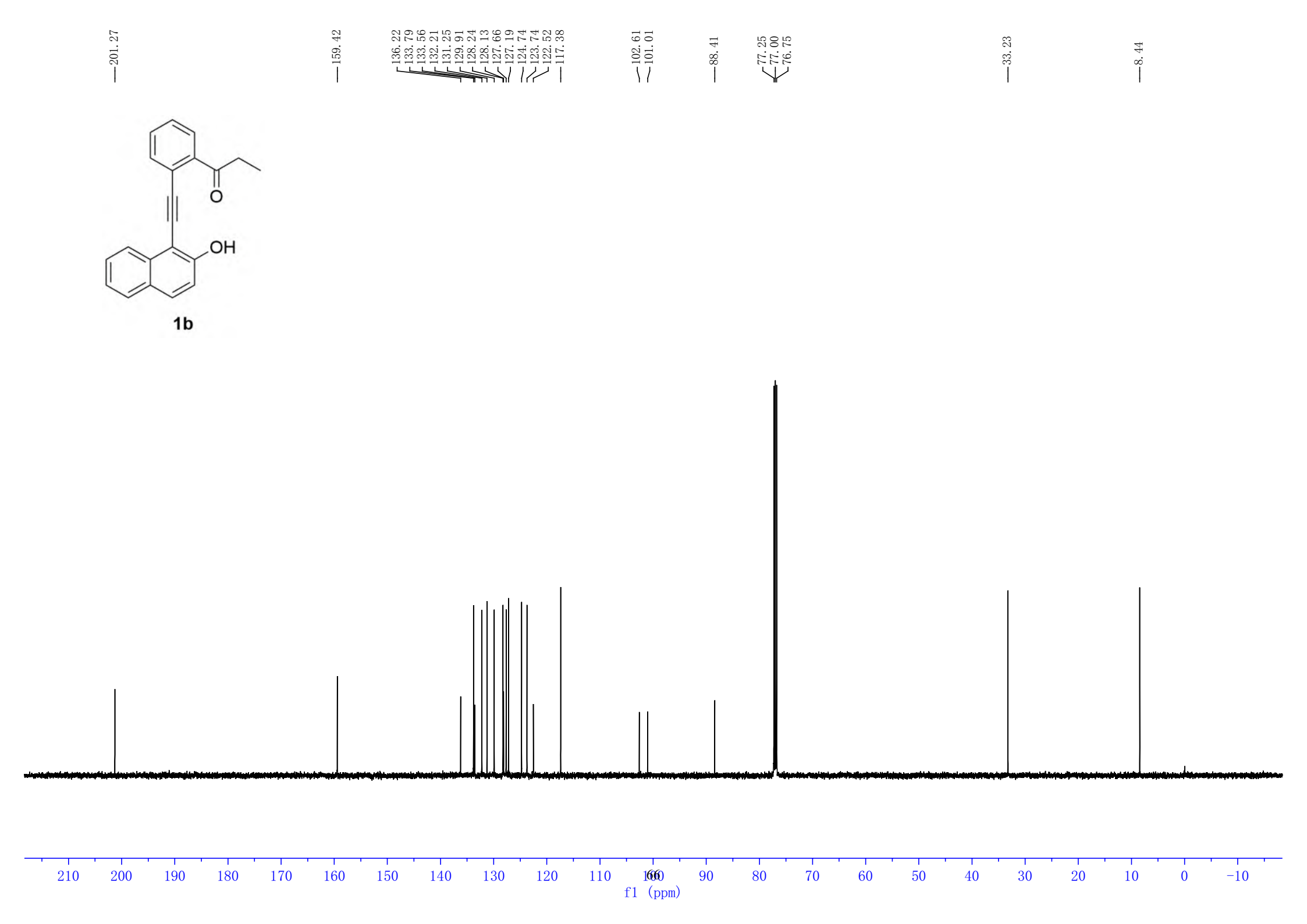

201.26
160.98
159.74
159.01
133.92
132.23
131.10
131.07
130.95
129.91
129.14
128.27
127.70
127.39
125.02
125.00
124.96
124.93
124.46
116.28
116.10
102.93
101.35
88.28
77.25
77.00
76.75
33.22
8.43
F
O
OH
1a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

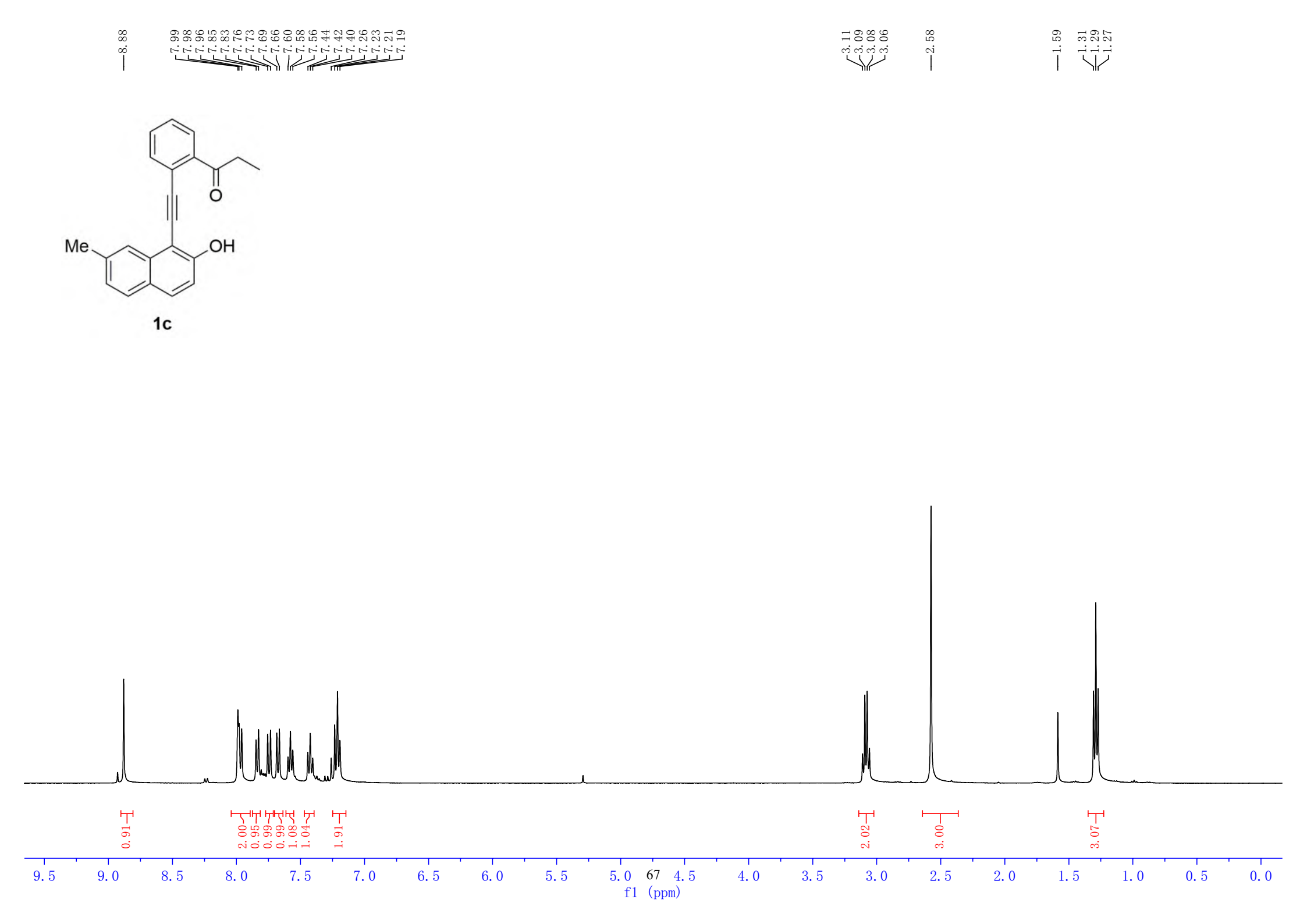
F
O
OH

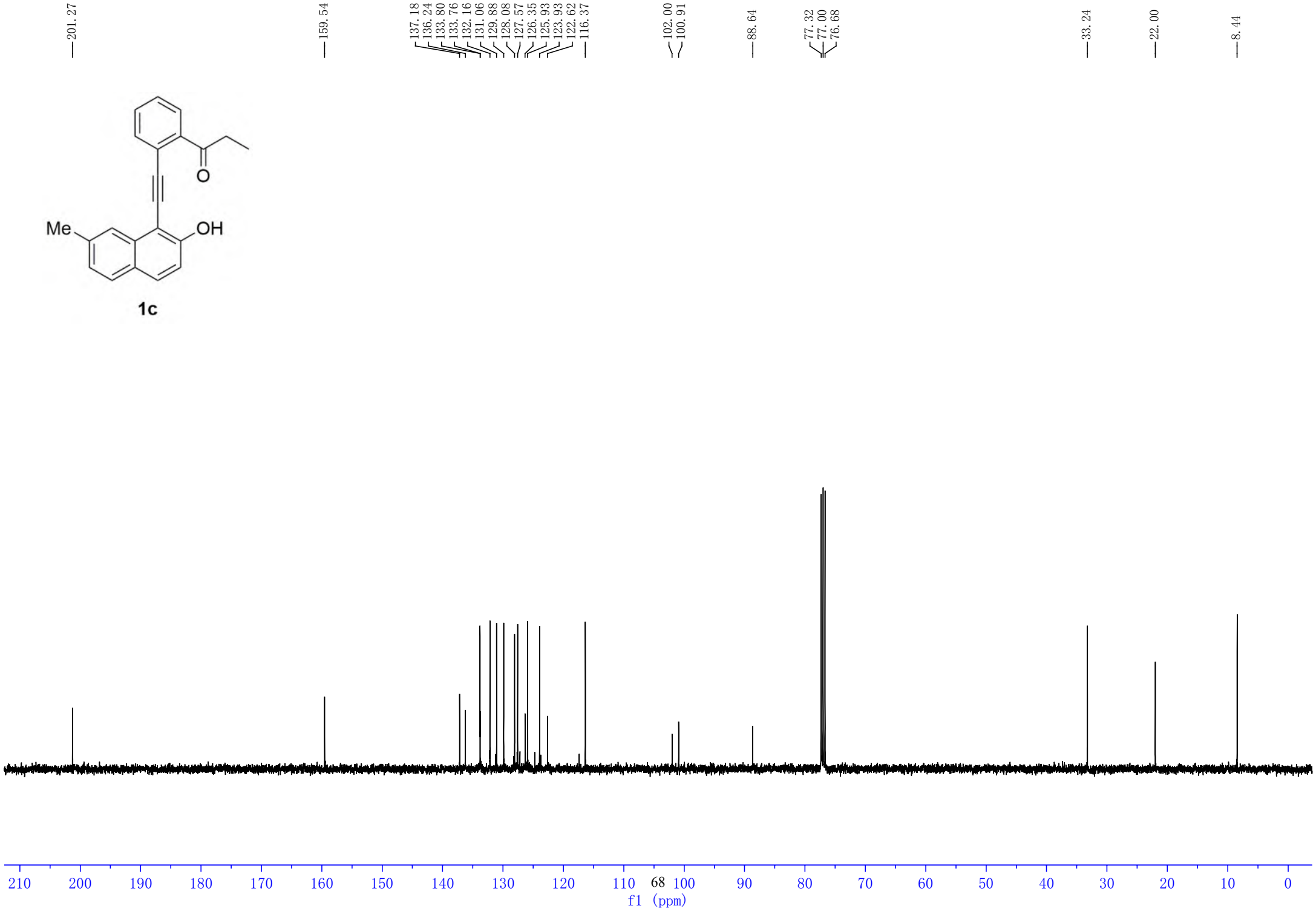
1a


-117.36
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.96
8.25
8.23
7.98
7.97
7.82
7.81
7.79
7.78
7.59
7.57
7.56
7.55
7.44
7.43
7.41
7.39
7.38
7.36
7.31
7.29
7.26
3.11
3.09
3.08
3.06
1.60
1.30
1.29
1.27
0.01
O
OH
1b
0.94
0.98
1.01
3.00
2.00
1.01
0.99
0.96
2.00
3.01
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
f1 (ppm)

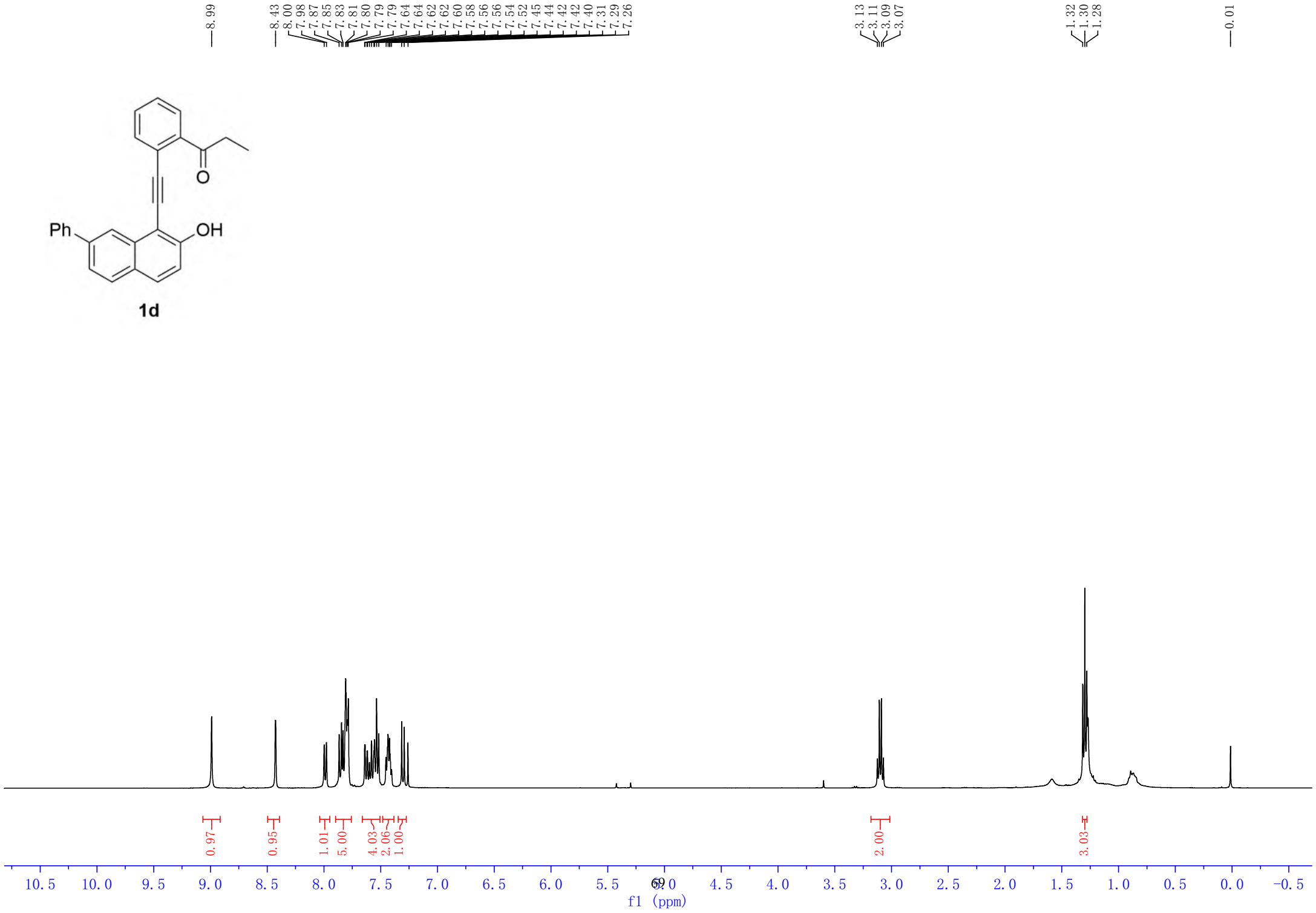

201.27
159.42
136.22
133.79
133.56
132.21
131.25
129.91
128.24
128.13
127.66
127.19
124.74
123.74
122.52
117.38
102.61
101.01
88.41
77.25
77.00
76.75
33.23
8.44
O
OH
1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

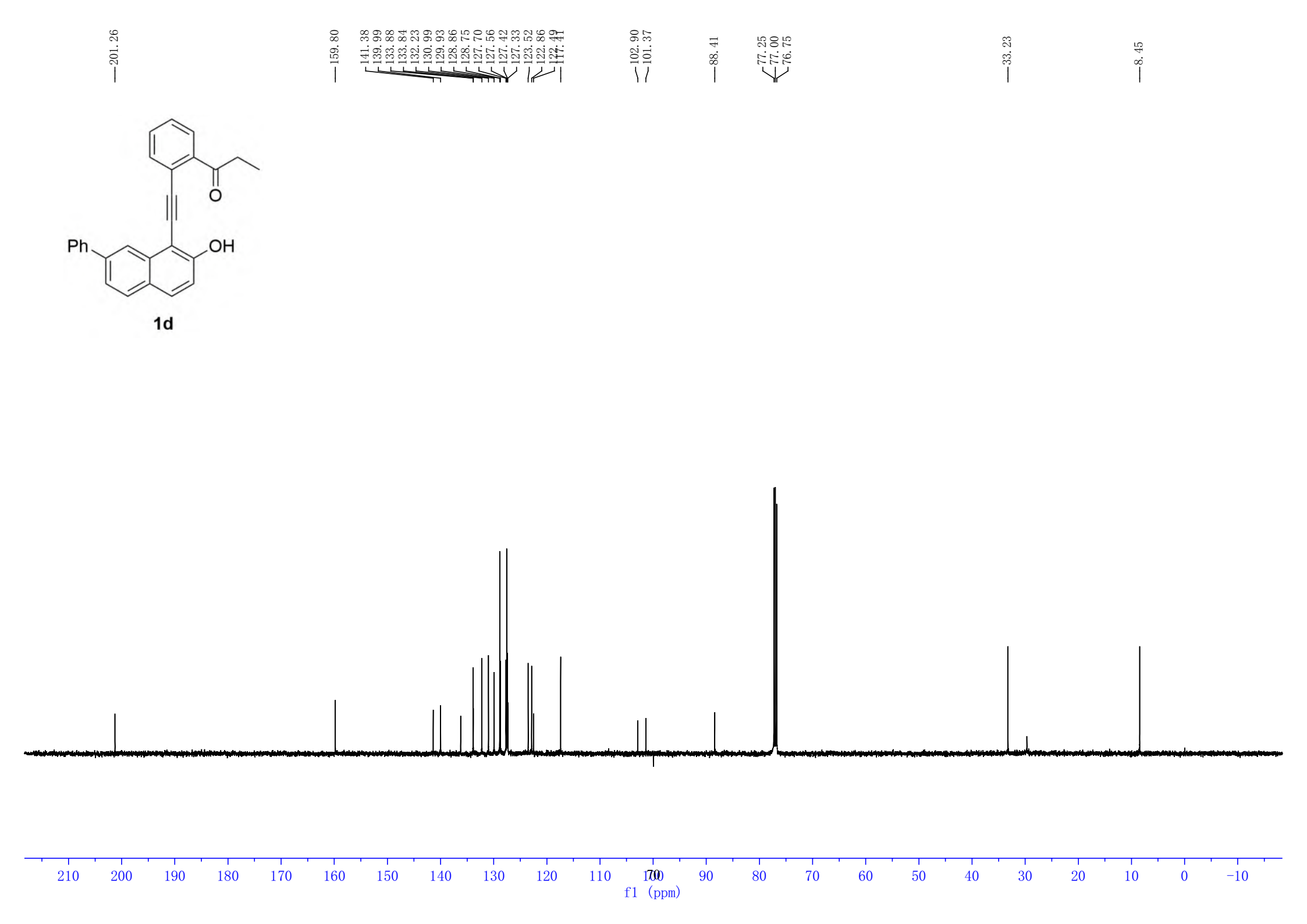

8.88
7.99
7.98
7.96
7.85
7.83
7.76
7.73
7.69
7.66
7.60
7.58
7.56
7.44
7.42
7.40
7.26
7.23
7.21
7.19
3.11
3.09
3.08
3.06
2.58
1.59
1.31
1.29
1.27
O
Me
OH
1c
0.91
2.00
0.95
0.99
0.99
1.08
1.04
1.91
2.02
3.00
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

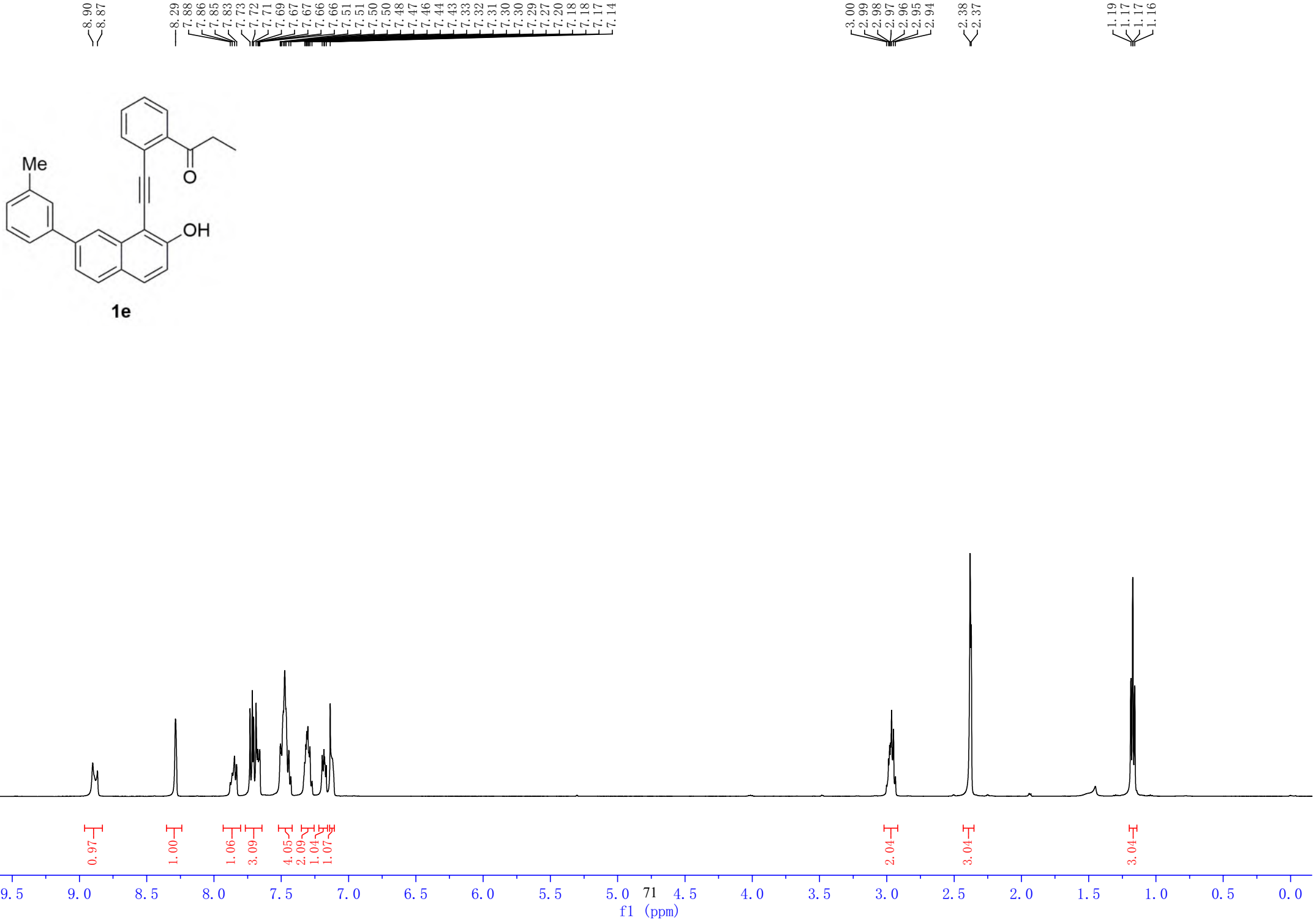

201.27
159.54
137.18
136.24
133.80
133.76
132.16
131.06
129.88
128.08
127.57
126.35
125.93
123.93
122.62
116.37
102.00
100.91
88.64
77.32
77.00
76.68
33.24
22.00
8.44
O
Me
OH
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

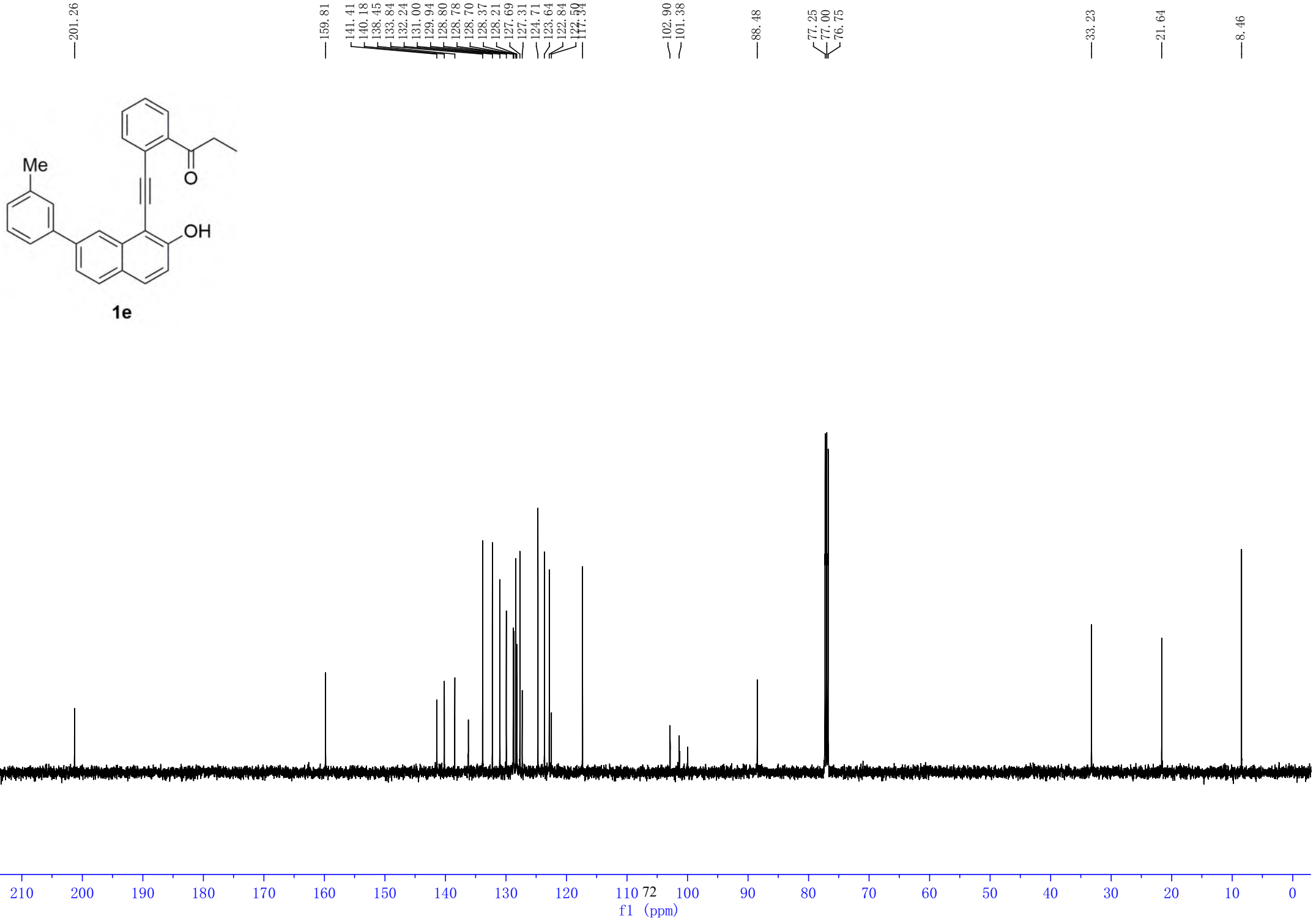
O
Ph
OH

1d


8.99
8.43
8.00
7.98
7.87
7.85
7.83
7.81
7.80
7.79
7.79
7.64
7.64
7.62
7.62
7.60
7.58
7.56
7.56
7.54
7.52
7.45
7.44
7.42
7.42
7.40
7.31
7.29
7.26
3.13
3.11
3.09
3.07
1.32
1.30
1.28
0.01
0.97
0.95
1.01
5.00
4.03
2.06
1.00
2.00
3.03
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
f1 (ppm)

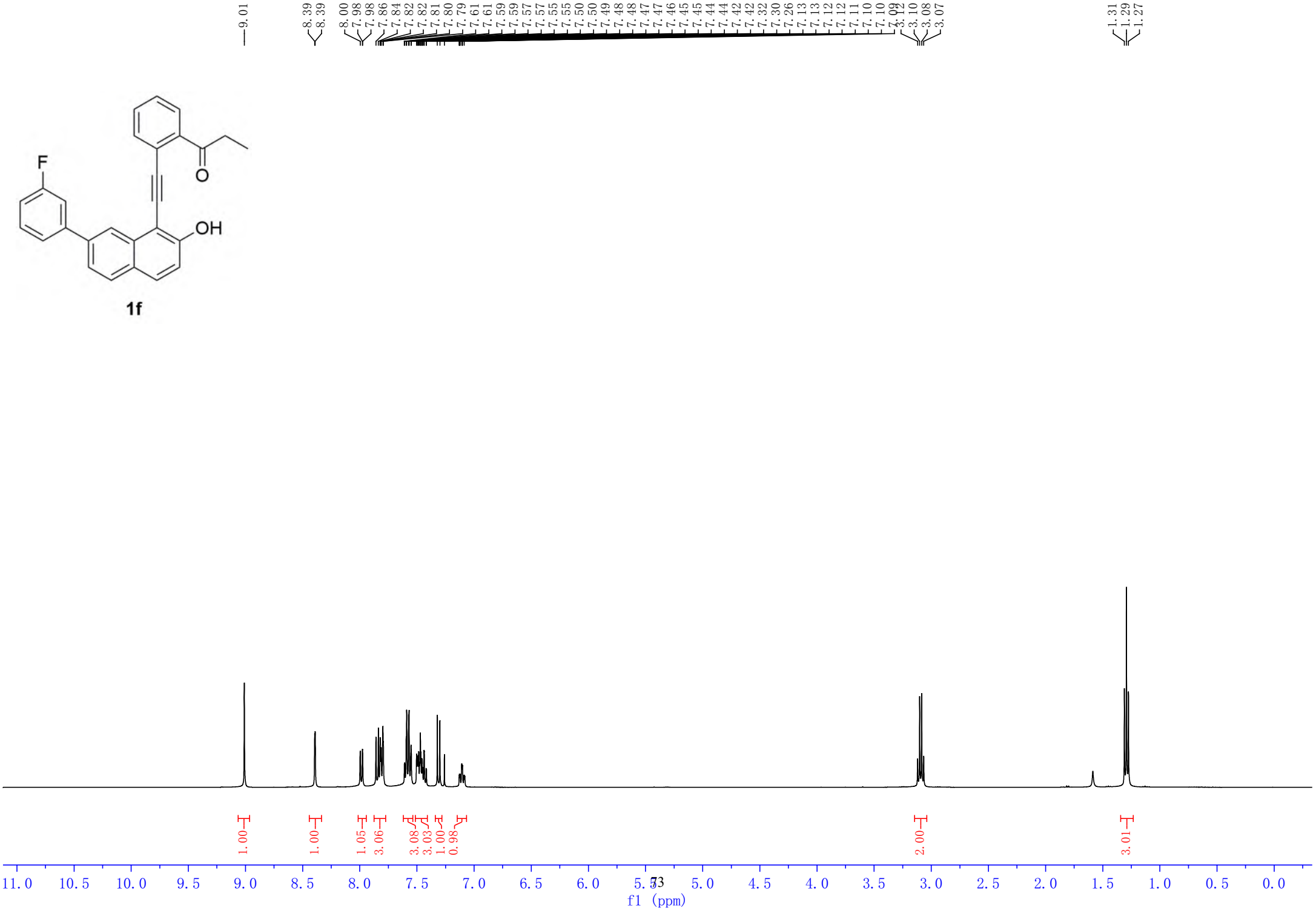

201.26
159.80
141.38
139.99
133.88
133.84
132.23
130.99
129.93
128.86
128.75
127.70
127.56
127.42
127.33
123.52
122.86
122.49
117.41
102.90
101.37
88.41
77.25
77.00
76.75
33.23
8.45
O
Ph
OH
1d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

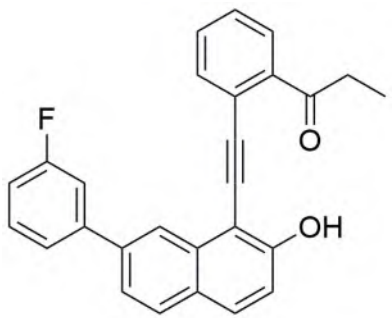

8.90
8.87
8.29
7.88
7.86
7.85
7.83
7.73
7.72
7.71
7.69
7.67
7.67
7.66
7.66
7.51
7.51
7.50
7.50
7.48
7.47
7.46
7.44
7.43
7.33
7.32
7.31
7.30
7.30
7.29
7.27
7.20
7.18
7.18
7.17
7.14
3.00
2.99
2.98
2.97
2.96
2.95
2.94
2.38
2.37
1.19
1.17
1.17
1.16
Me
O
OH
1e
0.97
1.00
1.06
3.09
4.05
2.09
1.04
1.07
2.04
3.04
3.04
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
f1 (ppm)


201.26
159.81
141.41
140.18
138.45
133.84
132.24
131.00
129.94
128.80
128.78
128.70
128.37
128.21
127.69
127.31
124.71
123.64
122.84
102.90
101.38
88.48
77.25
77.00
76.75
33.23
21.64
8.46
Me
O
OH
1e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

F
O
OH

1f


9.01
8.39
8.39
8.00
7.98
7.98
7.86
7.84
7.82
7.82
7.81
7.80
7.79
7.61
7.61
7.59
7.59
7.57
7.57
7.55
7.55
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.44
7.42
7.42
7.32
7.30
7.26
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
3.12
3.10
3.08
3.07
1.31
1.29
1.27
1.00
1.00
1.05
3.06
3.08
3.03
1.00
0.98
2.00
3.01
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
f1 (ppm)

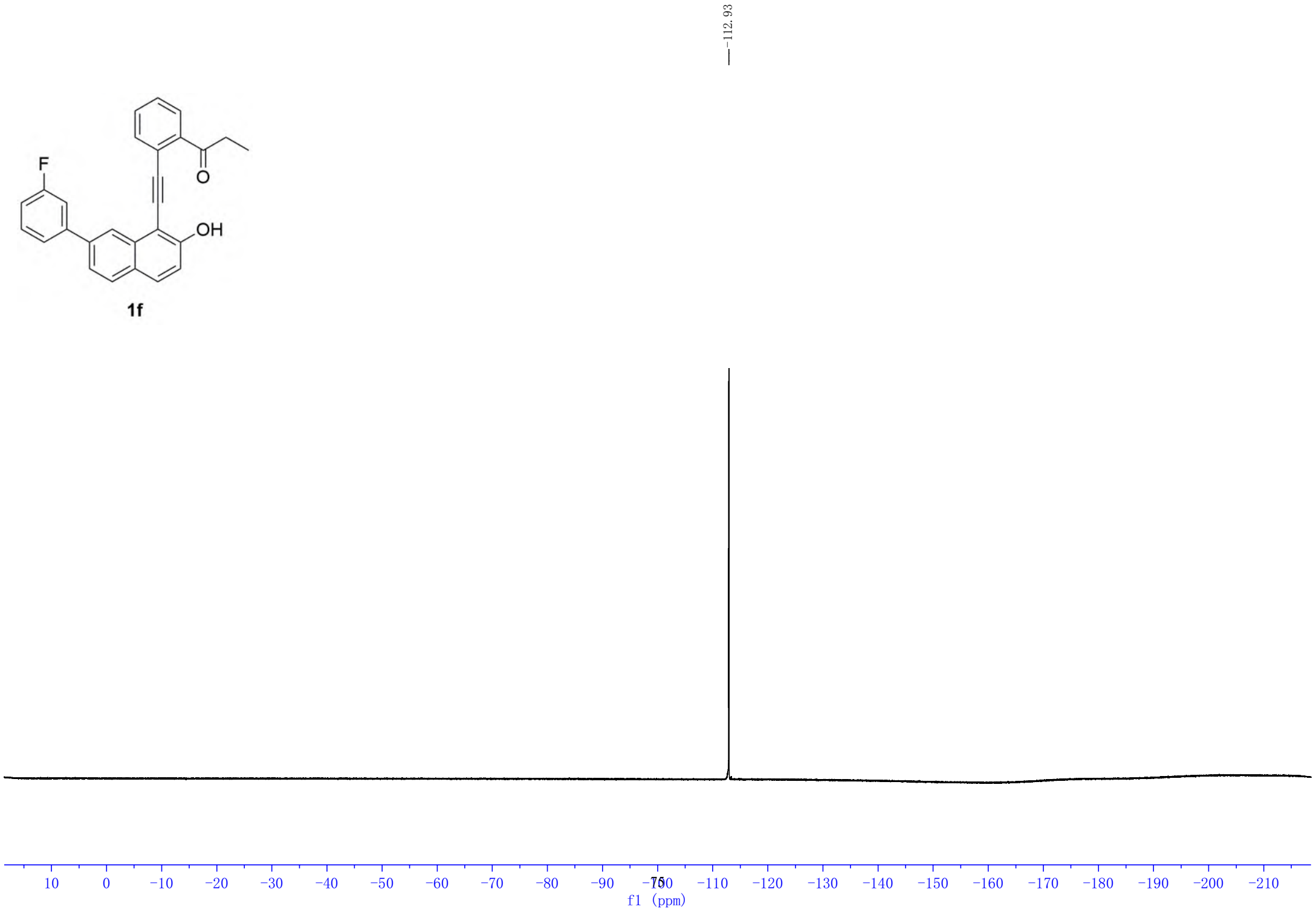


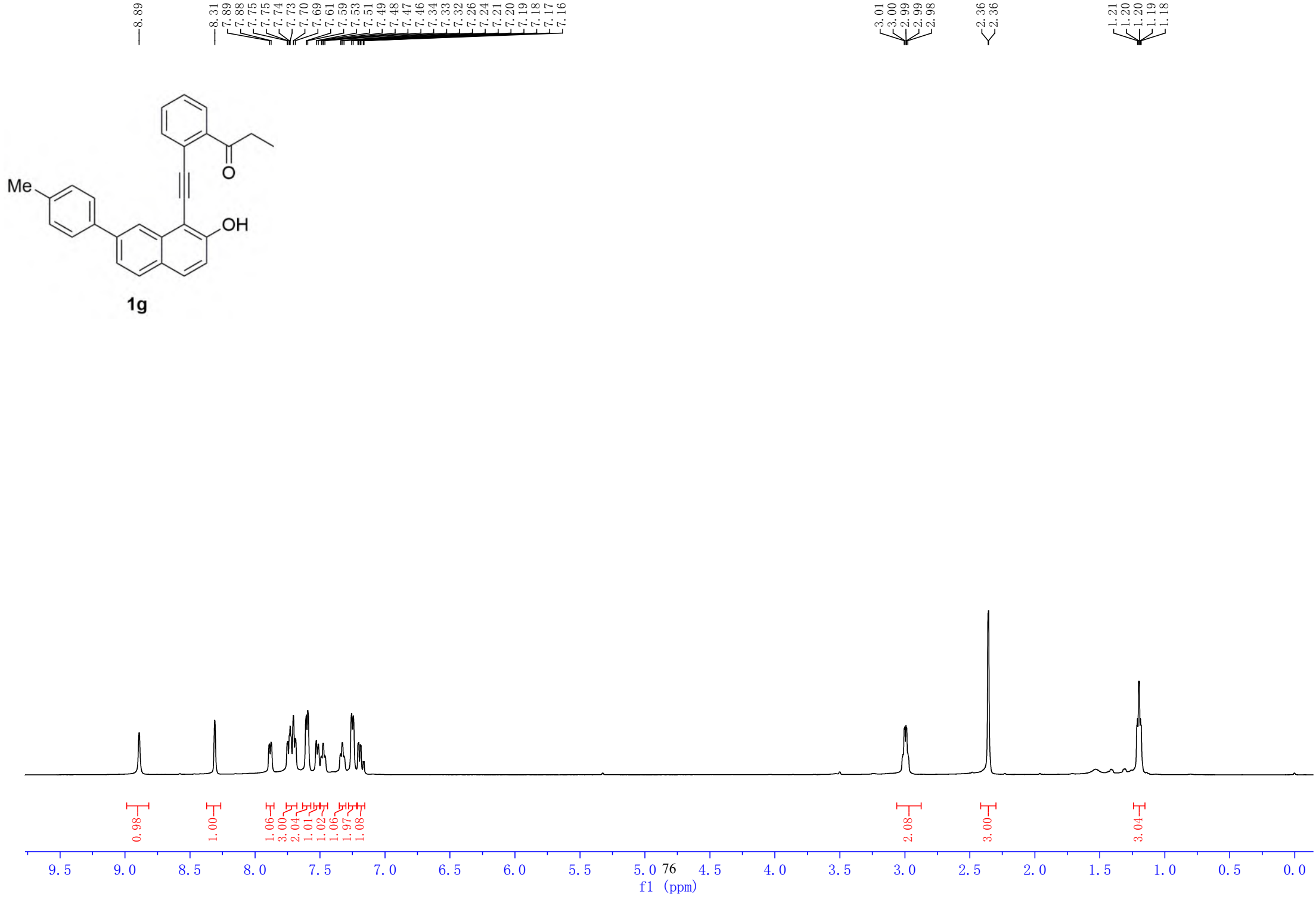
1f

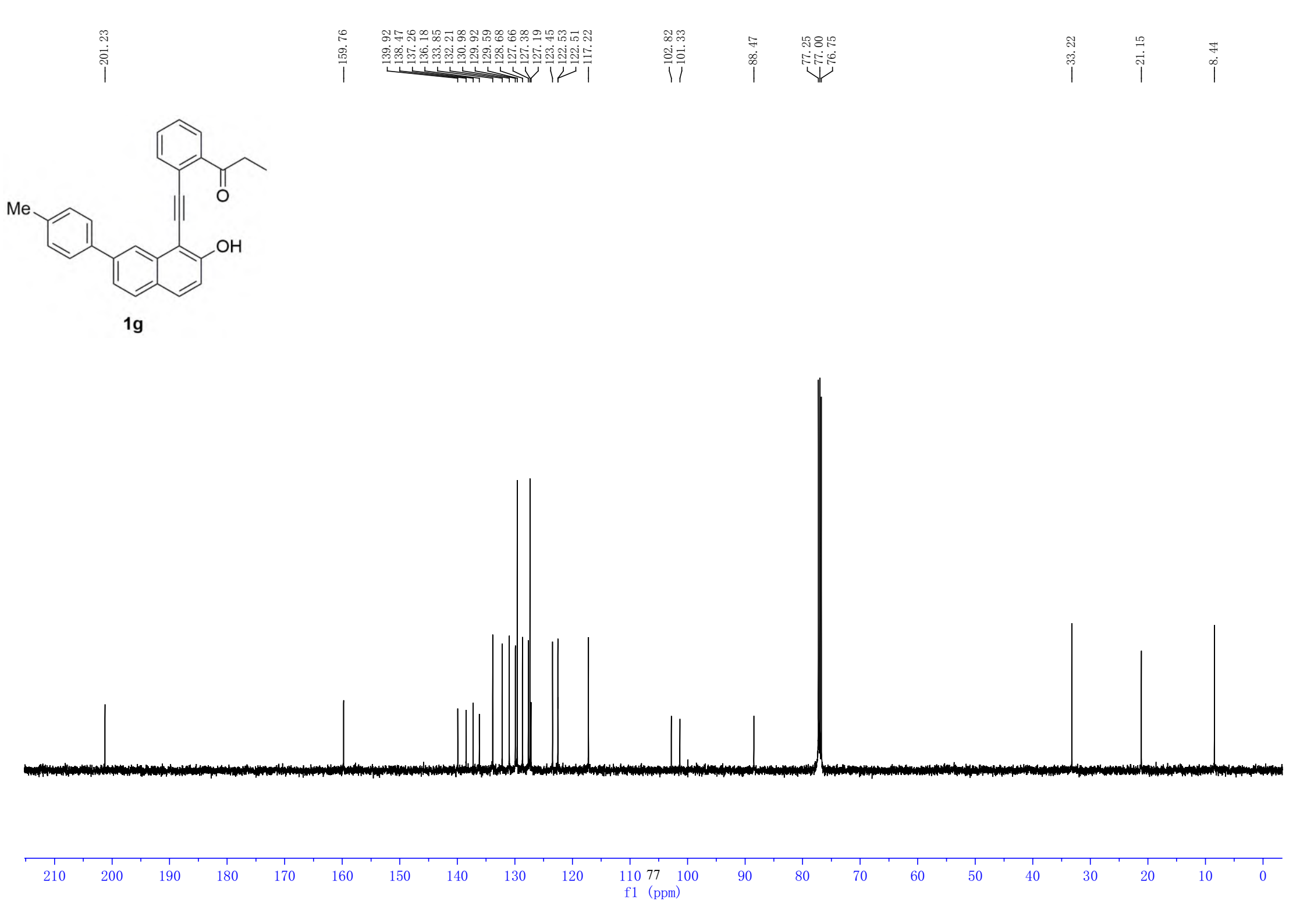
201.26
164.47
162.03
159.90
143.69
143.61
133.91
132.29
130.95
130.35
129.94
128.93
127.78
123.17
114.45
114.29
114.24
114.08
102.98
101.51
88.19
77.32
77.00
76.68
33.23
8.44

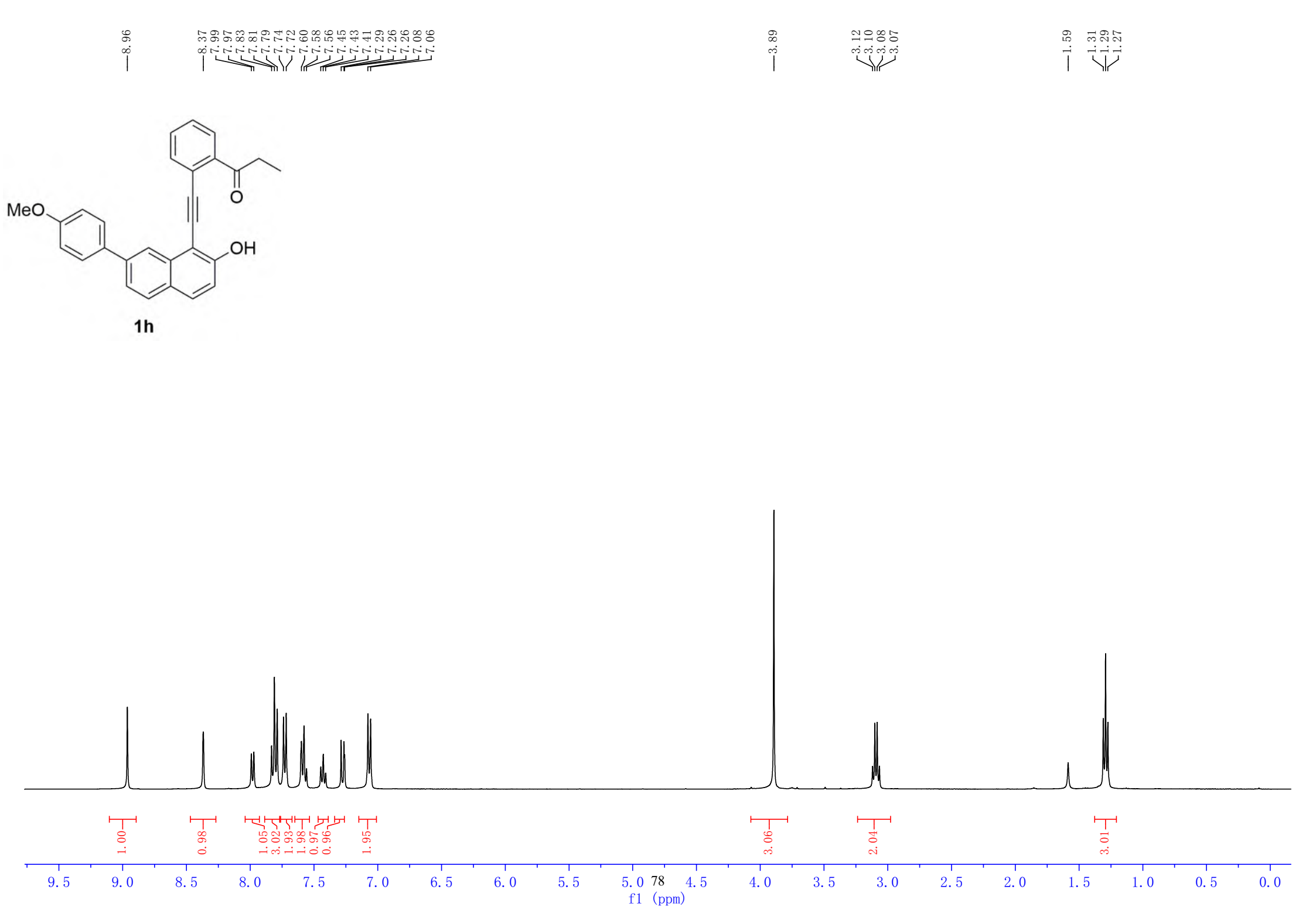
F
O
OH

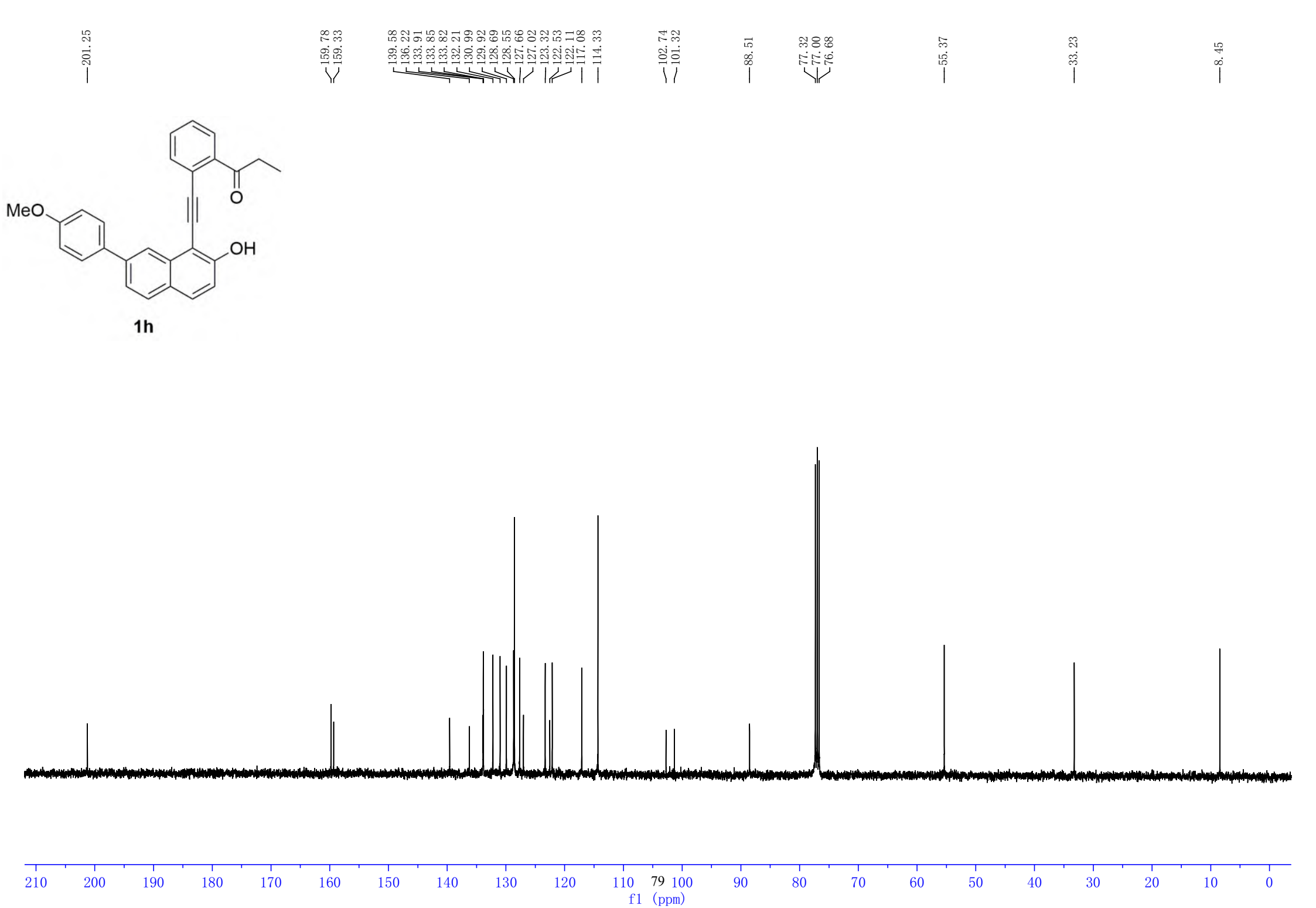
1f

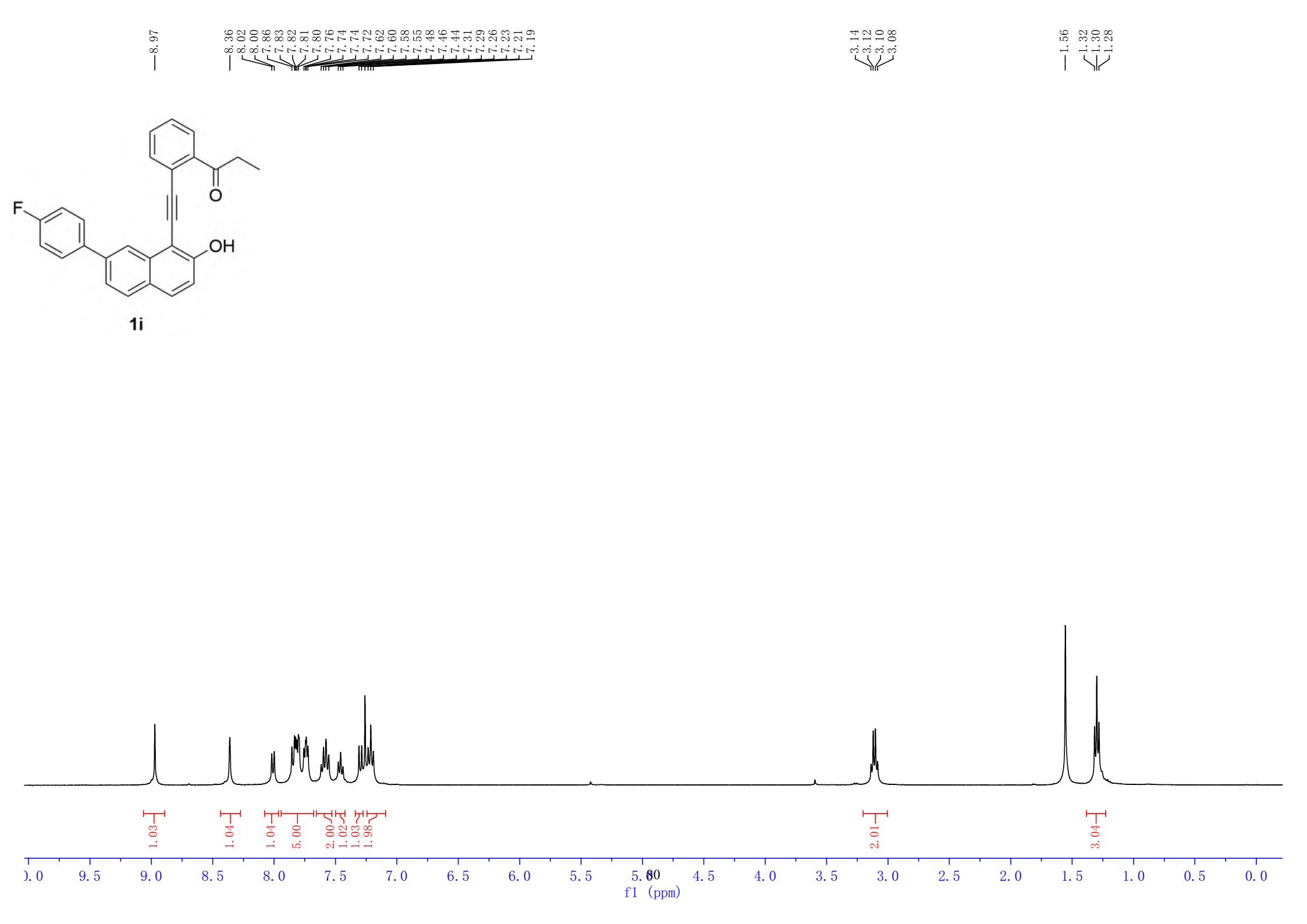

-112.93
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

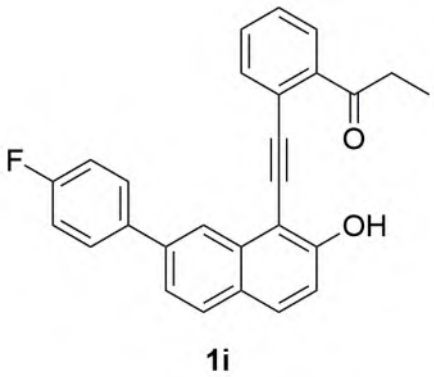

8.89
8.31
7.89
7.88
7.75
7.75
7.74
7.73
7.70
7.69
7.61
7.59
7.53
7.51
7.49
7.48
7.47
7.46
7.34
7.33
7.32
7.26
7.24
7.21
7.20
7.19
7.18
7.17
7.16
3.01
3.00
2.99
2.99
2.98
2.36
2.36
1.21
1.20
1.20
1.19
1.18
Me
O
OH
1g
0.98
1.00
1.06
3.00
2.04
1.01
1.02
1.06
1.97
1.08
2.08
3.00
3.04
9.5
9.0
8.5
8.0
7.5
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
f1 (ppm)


201.23
159.76
139.92
138.47
137.26
136.18
133.85
132.21
130.98
129.92
129.59
128.68
127.66
127.38
127.19
123.45
122.53
122.51
117.22
102.82
101.33
88.47
77.25
77.00
76.75
33.22
21.15
8.44
Me
O
OH
1g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.96
8.37
7.99
7.97
7.83
7.81
7.79
7.74
7.72
7.60
7.58
7.56
7.45
7.43
7.41
7.29
7.26
7.26
7.08
7.06
3.89
3.12
3.10
3.08
3.07
1.59
1.31
1.29
1.27
MeO
O
OH
1h
1.00
0.98
1.05
3.02
1.93
1.98
0.97
0.96
1.95
3.06
2.04
3.01
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
f1 (ppm)


201.25
159.78
159.33
139.58
136.22
133.91
133.85
133.82
132.21
130.99
129.92
128.69
128.55
127.66
127.02
123.32
122.53
122.11
117.08
114.33
102.74
101.32
88.51
77.32
77.00
76.68
55.37
33.23
8.45
MeO
O
OH
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.97
8.36
8.02
8.00
7.86
7.83
7.82
7.81
7.80
7.76
7.74
7.74
7.72
7.62
7.60
7.58
7.55
7.48
7.46
7.44
7.31
7.29
7.26
7.23
7.21
7.19
3.14
3.12
3.10
3.08
1.56
1.32
1.30
1.28
F
O
OH
1i
1.03
1.04
1.04
5.00
2.00
1.02
1.03
1.98
2.01
3.04
f1 (ppm)

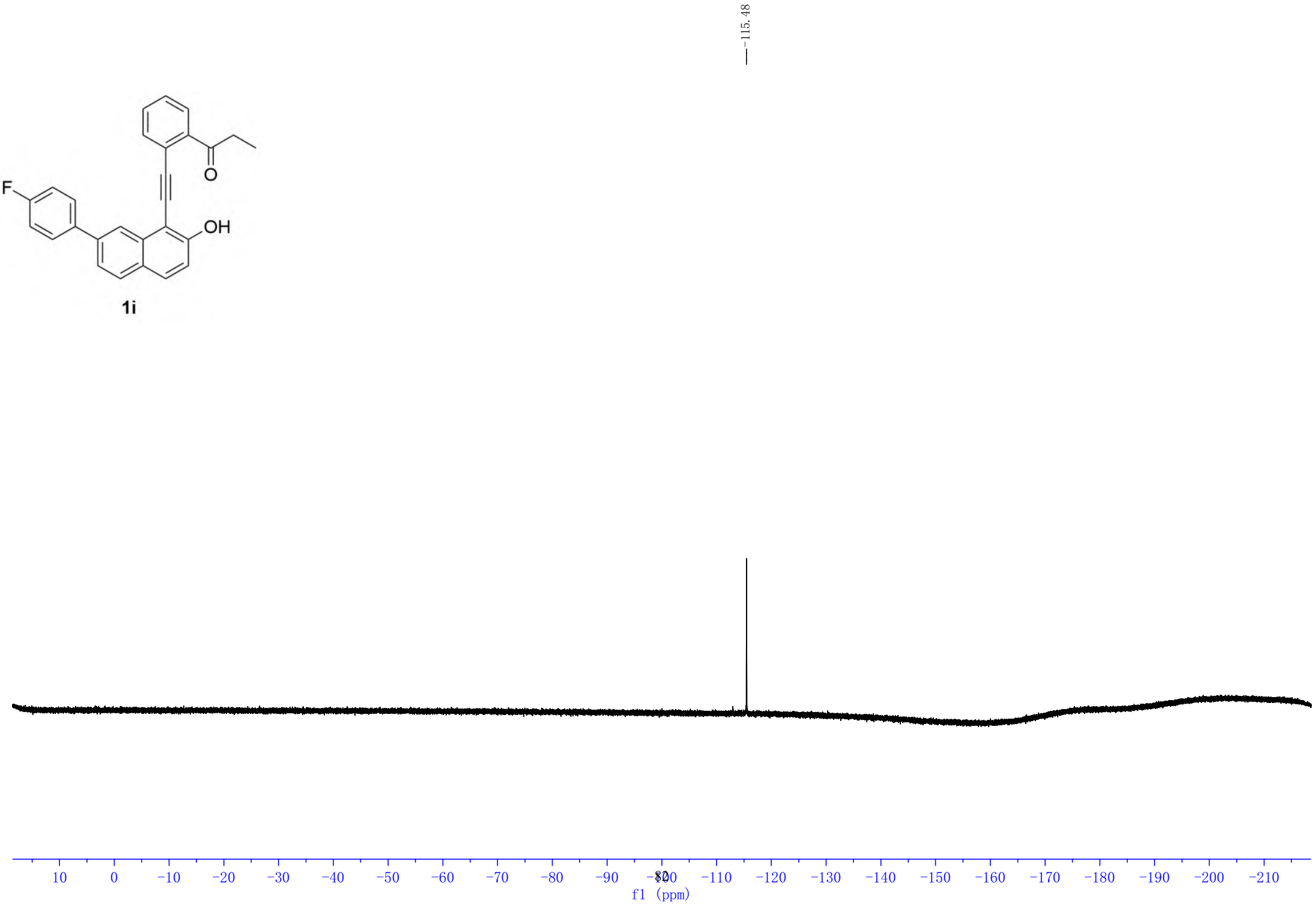


1i

201.31
159.89
139.02
137.49
136.31
133.89
133.84
132.27
131.00
129.97
129.15
129.07
128.87
127.78
127.28
123.34
122.71
122.48
117.51
115.86
115.64
102.85
101.40
99.96
88.33
77.32
77.00
76.68
33.28
8.47

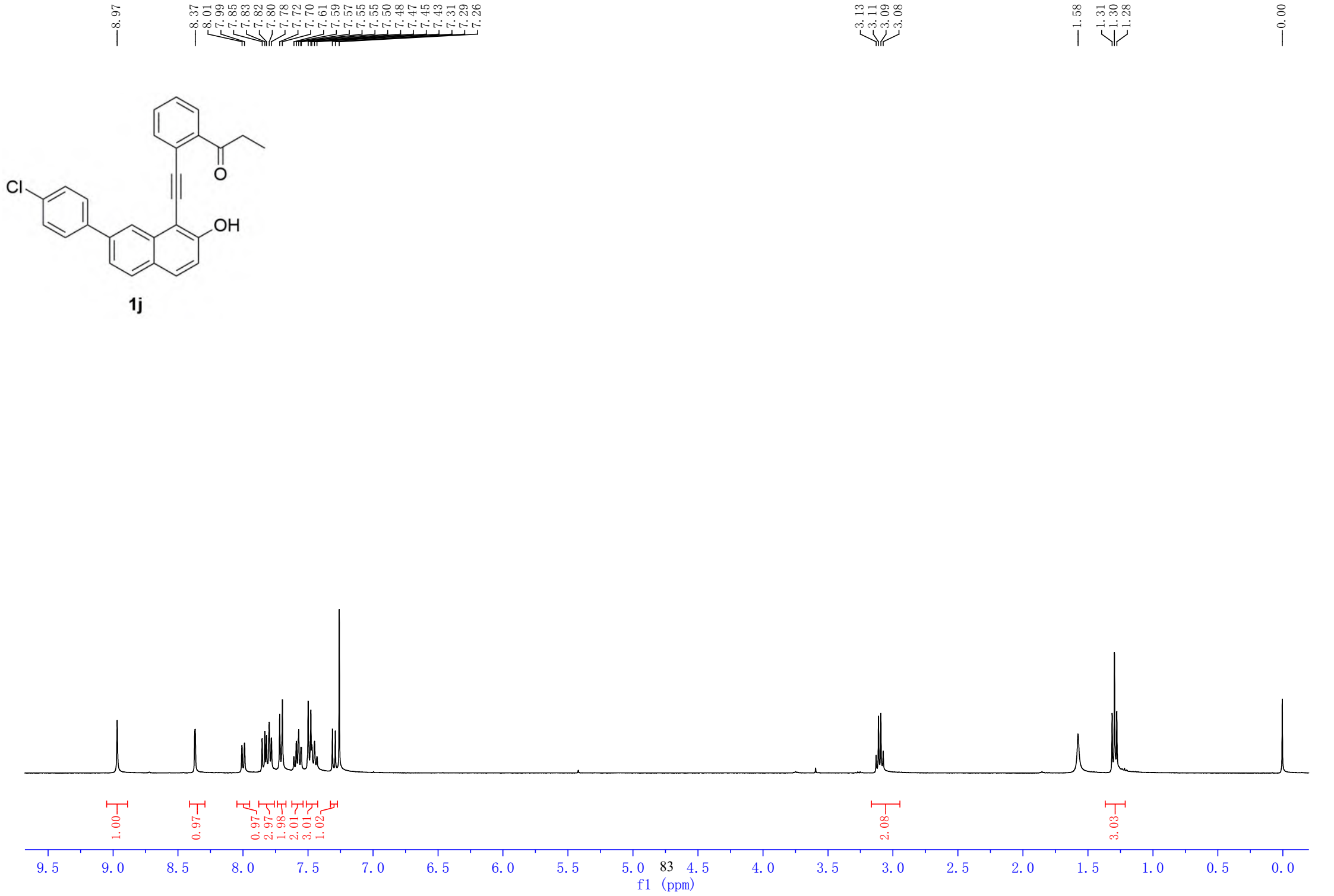
F
O
OH

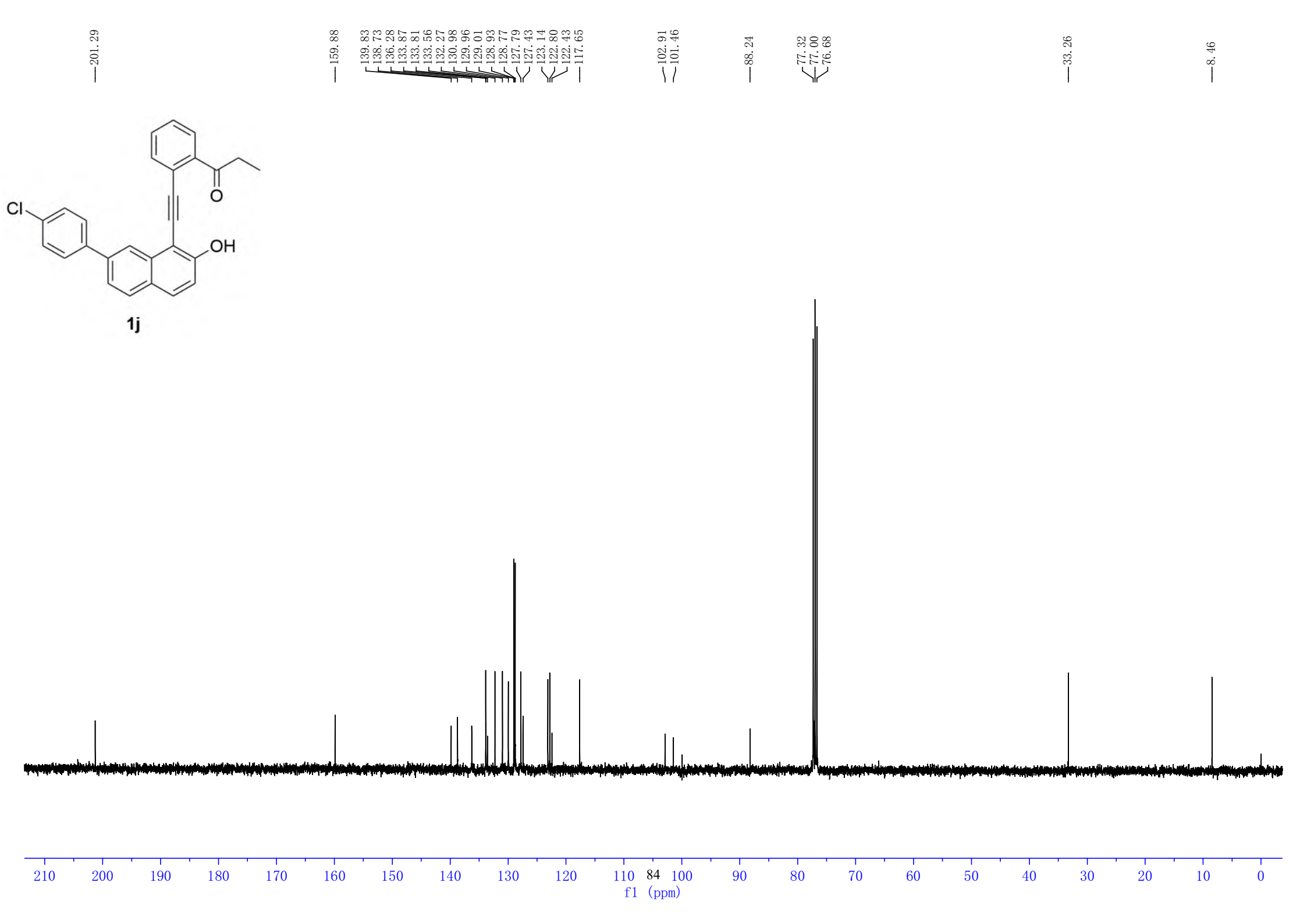
1i

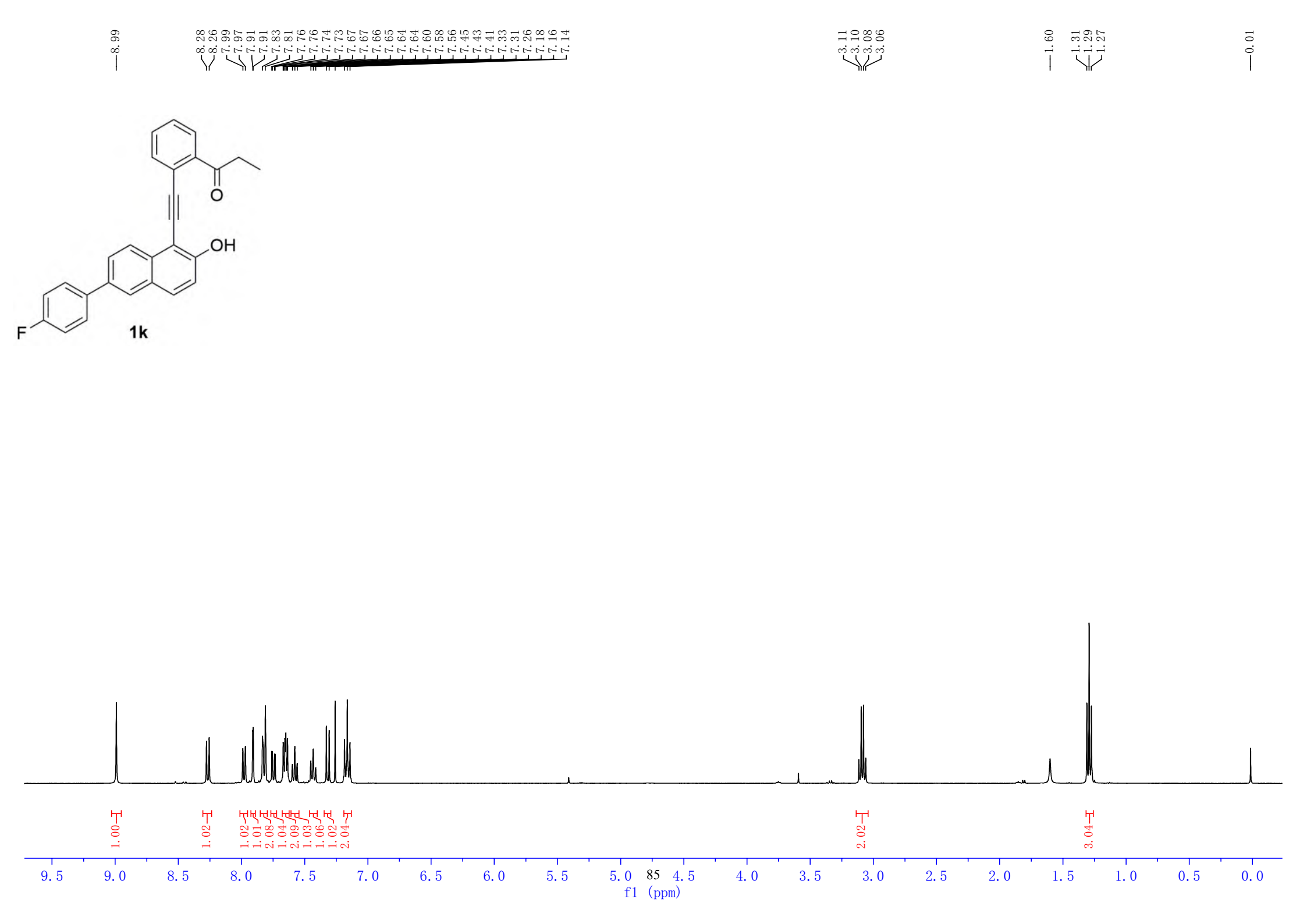

-115.48
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

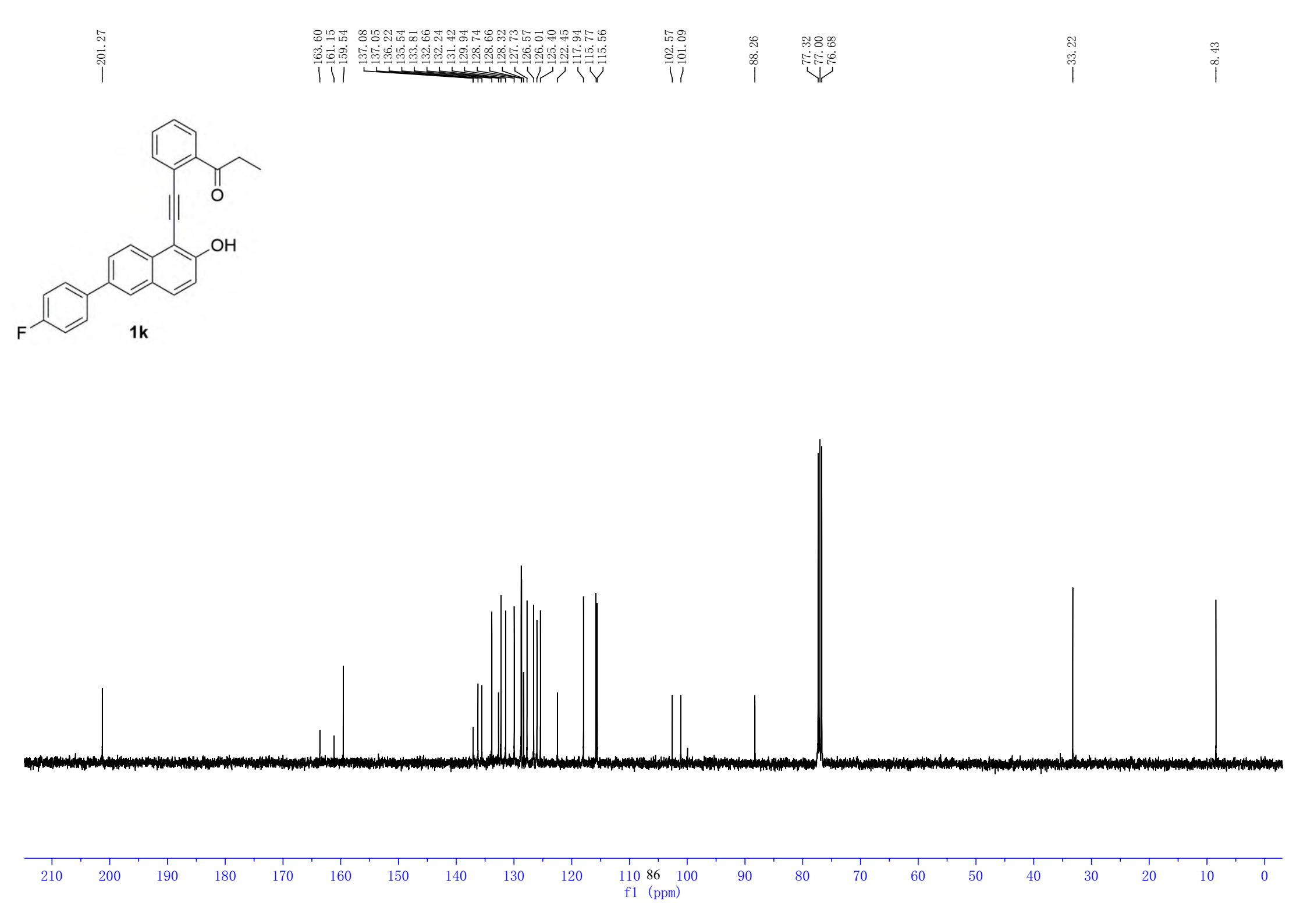
Cl
O
OH

1j


8.97
8.37
8.01
7.99
7.85
7.83
7.82
7.80
7.78
7.72
7.70
7.61
7.59
7.57
7.55
7.55
7.50
7.48
7.47
7.45
7.43
7.31
7.29
7.26
3.13
3.11
3.09
3.08
1.58
1.31
1.30
1.28
0.00
1.00
0.97
0.97
2.97
1.98
2.01
3.01
1.02
2.08
3.03
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
f1 (ppm)

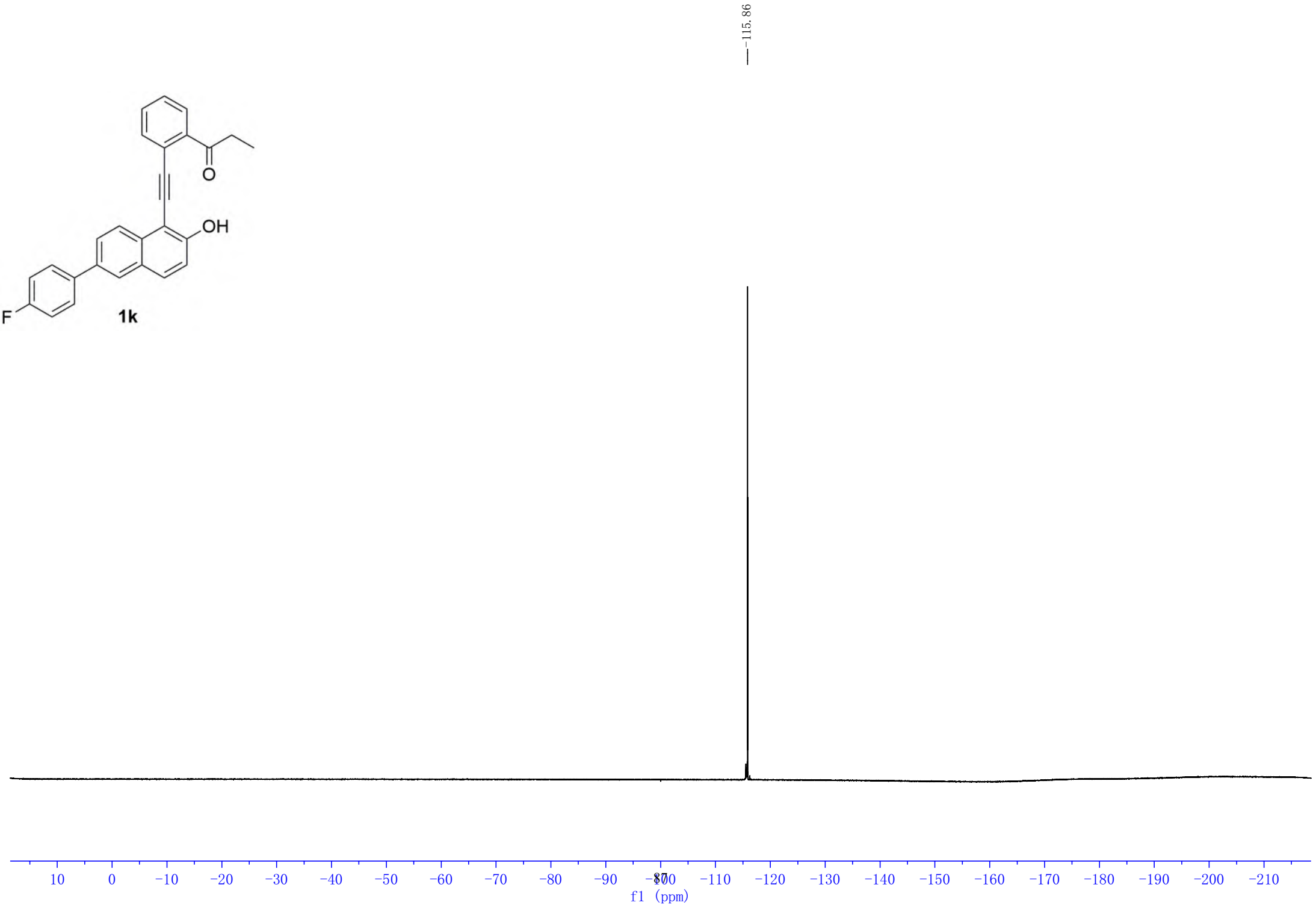

201.29
159.88
139.83
138.73
136.28
133.87
133.81
133.56
132.27
130.98
129.96
129.01
128.93
128.77
127.79
127.43
123.14
122.80
122.43
117.65
102.91
101.46
88.24
77.32
77.00
76.68
33.26
8.46
Cl
O
OH
1j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

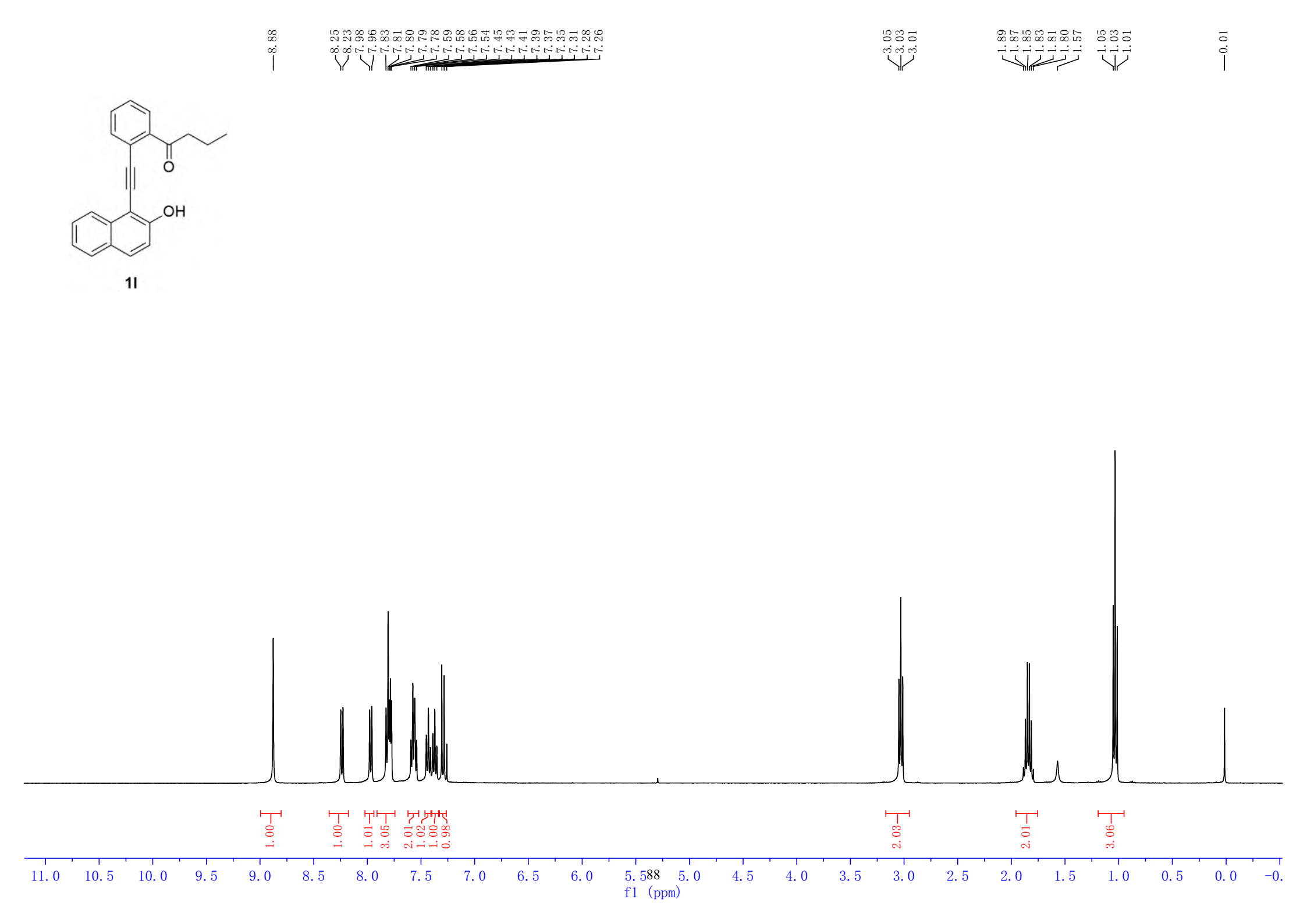

8.99
8.28
8.26
7.99
7.97
7.91
7.91
7.83
7.81
7.76
7.76
7.74
7.73
7.67
7.67
7.66
7.65
7.64
7.64
7.60
7.58
7.56
7.45
7.43
7.41
7.33
7.31
7.26
7.18
7.16
7.14
3.11
3.10
3.08
3.06
1.60
1.31
1.29
1.27
0.01
O
OH
F
1k
1.00
1.02
1.02
1.01
2.08
1.04
2.09
1.03
1.06
1.02
2.04
2.02
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)


201.27
163.60
161.15
159.54
137.08
137.05
136.22
135.54
133.81
132.66
132.24
131.42
129.94
128.74
128.66
128.32
127.73
126.57
126.01
125.40
122.45
117.94
115.77
115.56
102.57
101.09
88.26
77.32
77.00
76.68
33.22
8.43
O
OH
F
1k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

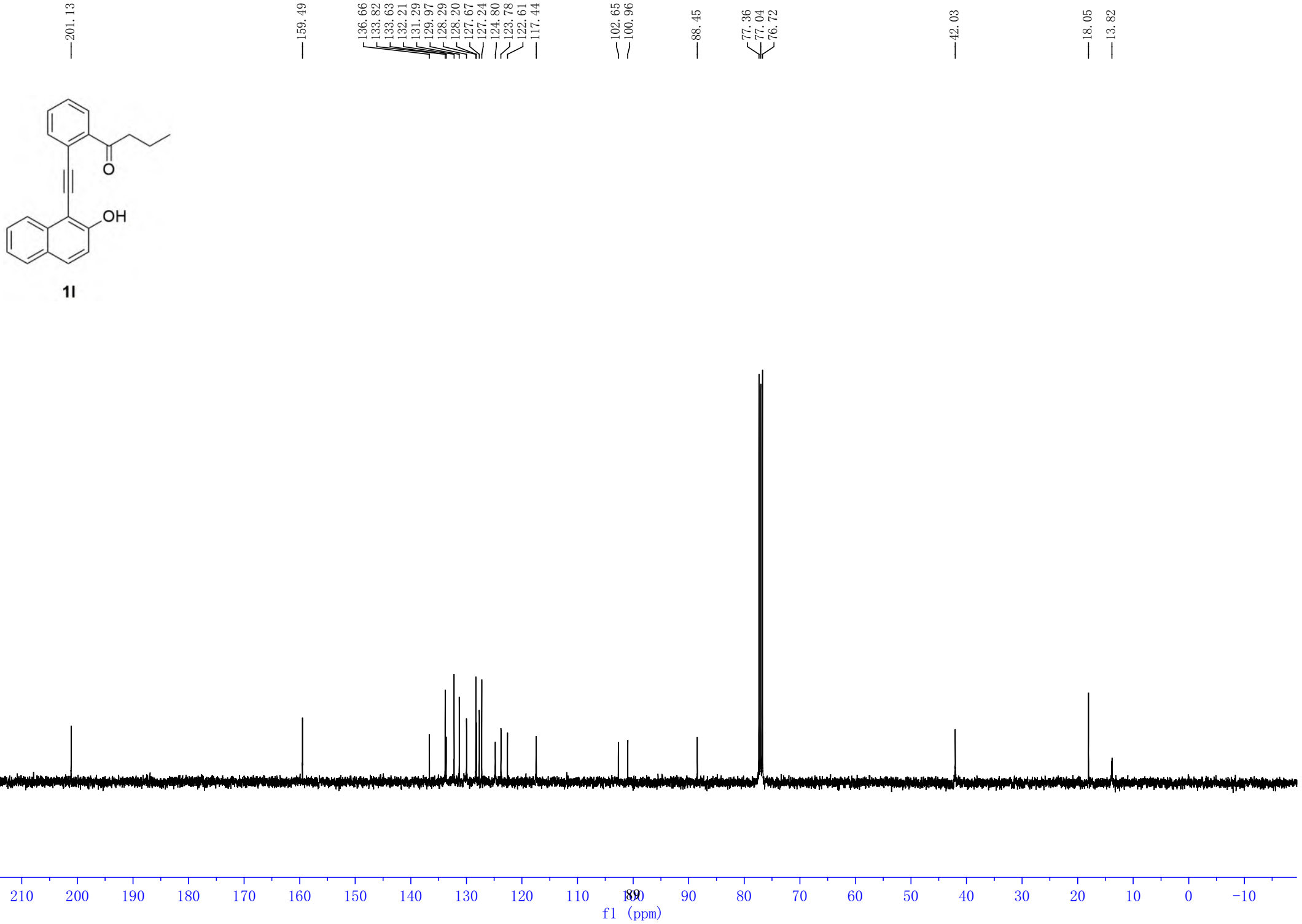
O
OH
F

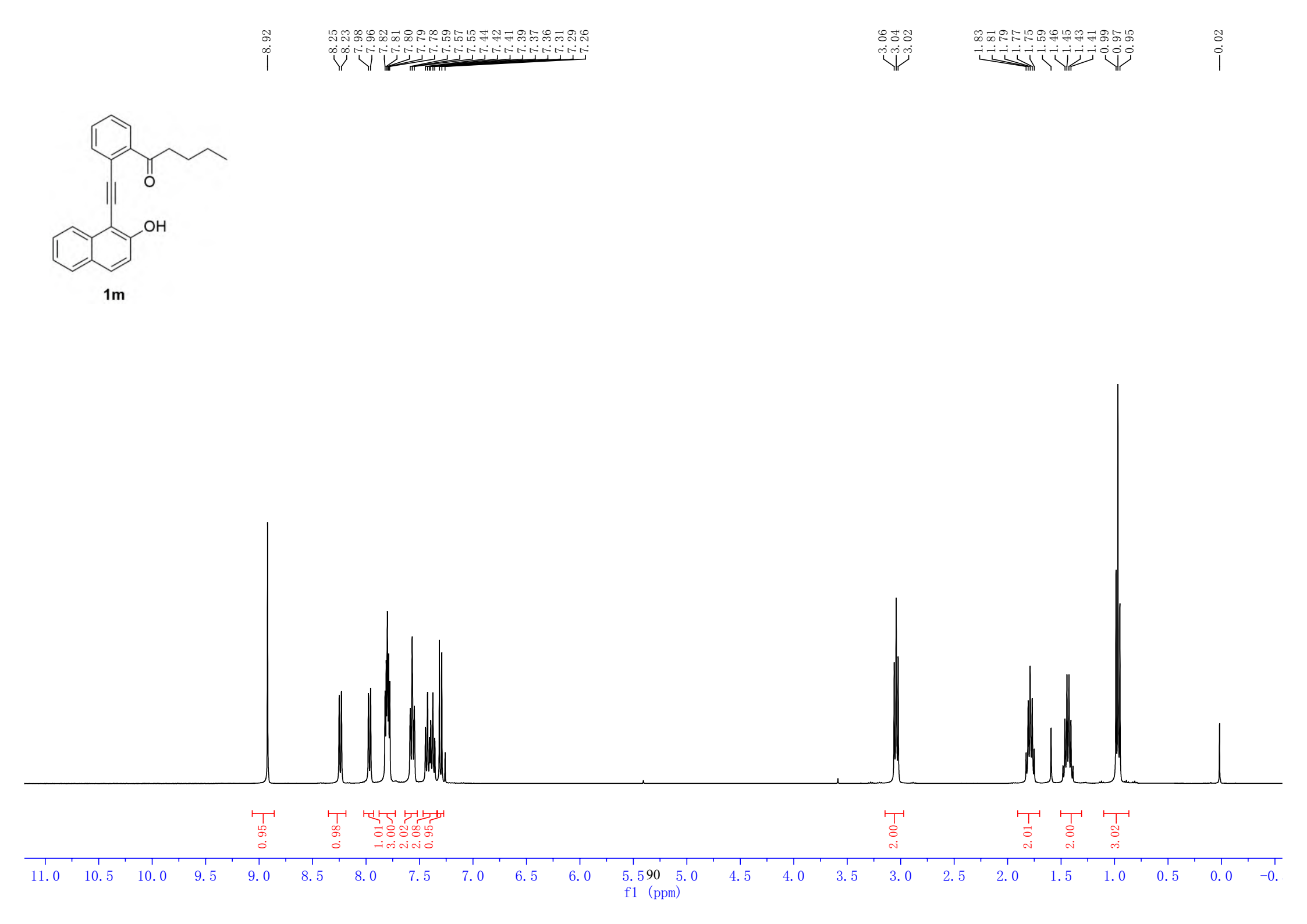
1k

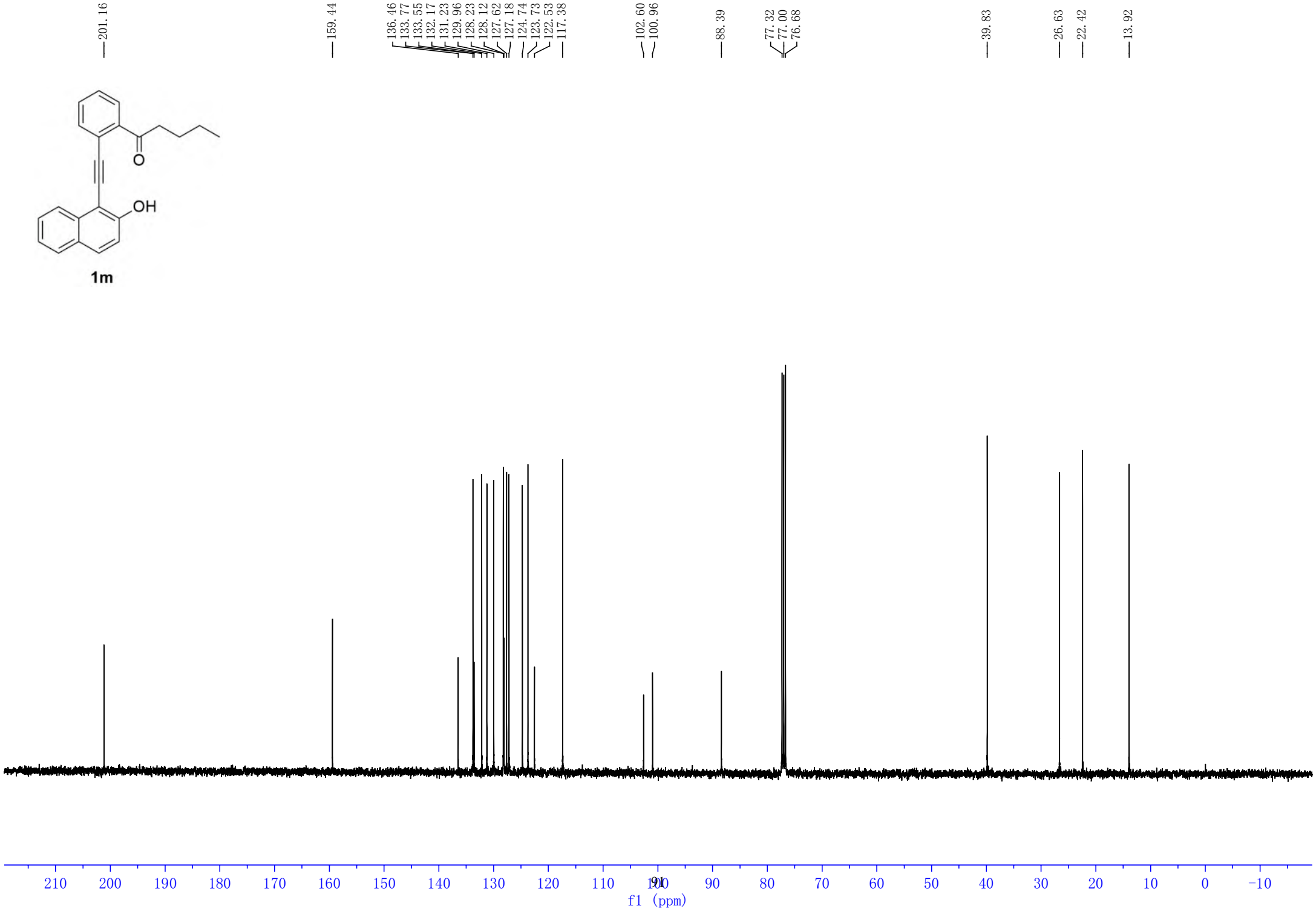

-115.86
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

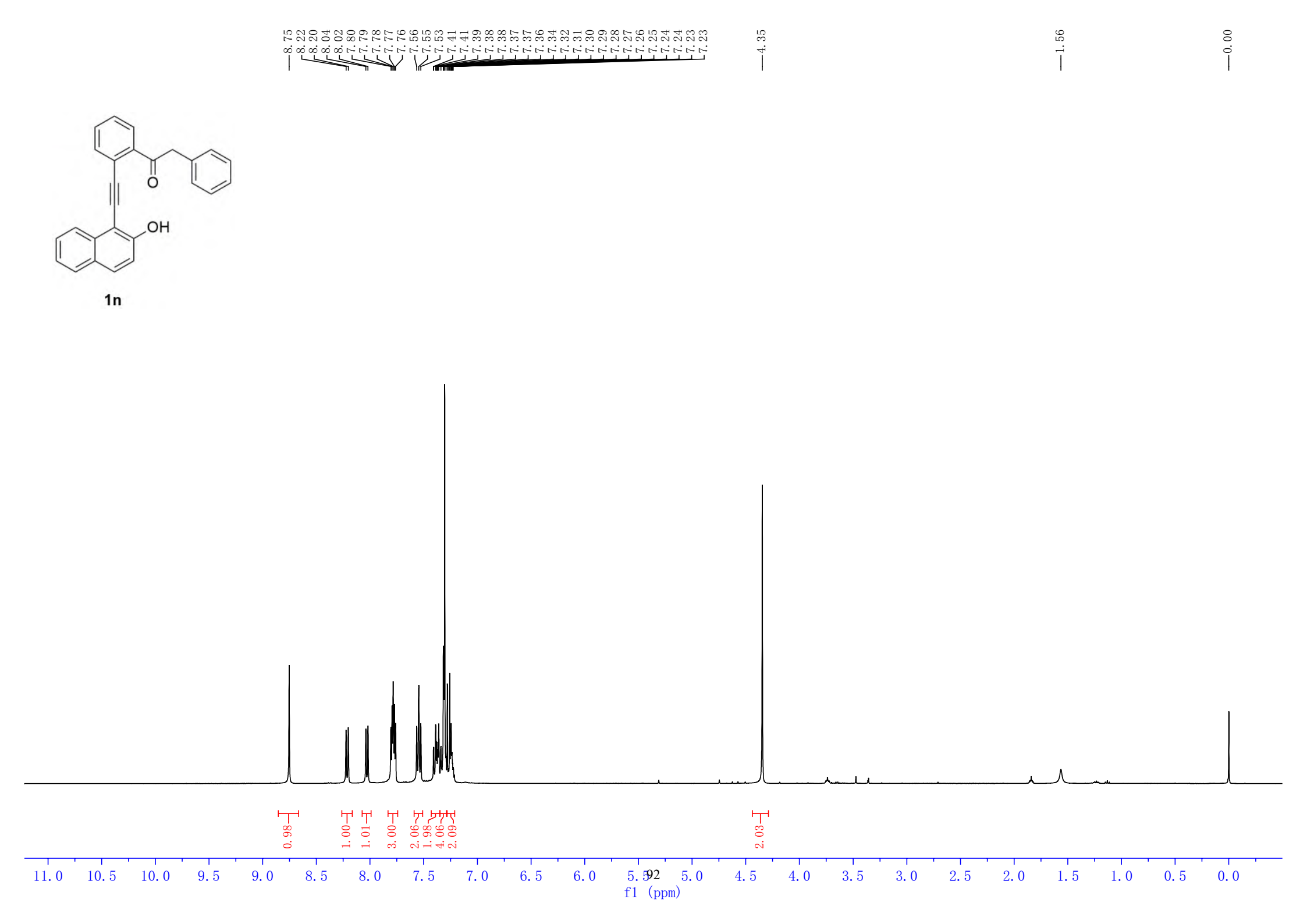

8.88
8.25
8.23
7.98
7.96
7.83
7.81
7.80
7.79
7.78
7.59
7.58
7.56
7.54
7.45
7.43
7.41
7.39
7.37
7.35
7.31
7.28
7.26
3.05
3.03
3.01
1.89
1.87
1.85
1.83
1.81
1.80
1.57
1.05
1.03
1.01
0.01
O
OH
1.00
1.00
1.01
3.05
2.01
1.02
1.00
0.98
2.03
2.01
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

1l

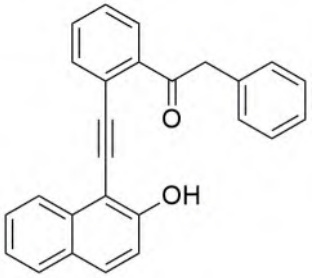

201.13
159.49
136.66
133.82
133.63
132.21
131.29
129.97
128.29
128.20
127.67
127.24
124.80
123.78
122.61
117.44
102.65
100.96
88.45
77.36
77.04
76.72
42.03
18.05
13.82
O
OH
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.92
8.25
8.23
7.98
7.96
7.82
7.81
7.80
7.79
7.78
7.59
7.57
7.55
7.44
7.42
7.41
7.39
7.37
7.36
7.31
7.29
7.26
3.06
3.04
3.02
1.83
1.81
1.79
1.77
1.75
1.59
1.46
1.45
1.43
1.41
0.99
0.97
0.95
0.02
O
OH
1m
0.95
0.98
1.01
3.00
2.02
2.08
0.95
2.00
2.01
2.00
3.02
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
f1 (ppm)

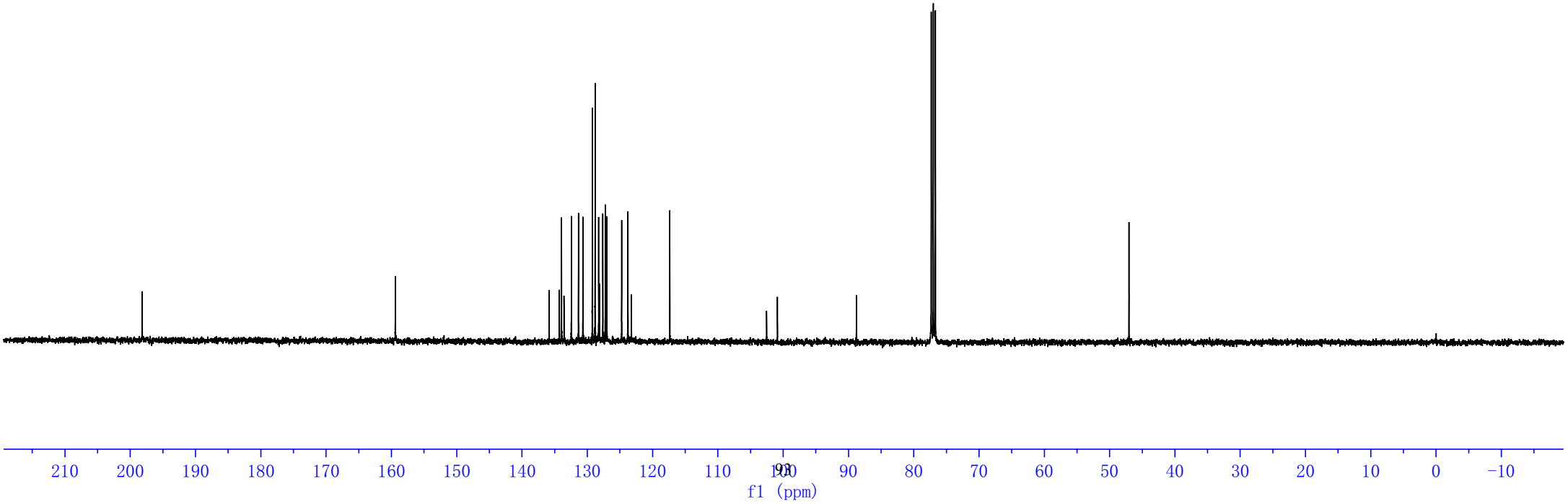

201.16
159.44
136.46
133.77
133.55
132.17
131.23
129.96
128.23
128.12
127.62
127.18
124.74
123.73
122.53
117.38
102.60
100.96
88.39
77.32
77.00
76.68
39.83
26.63
22.42
13.92
O
OH
1m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

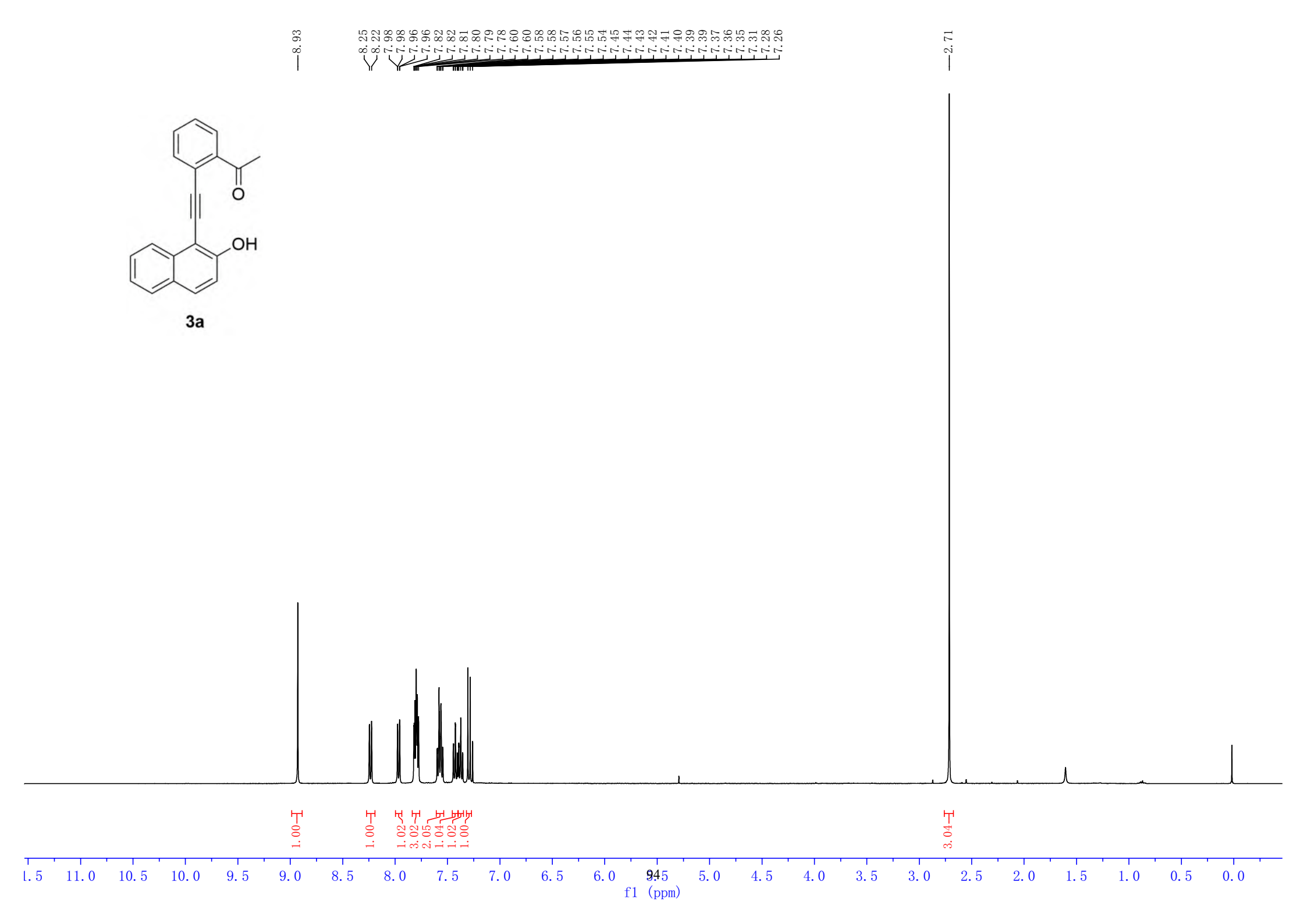

8.75
8.22
8.20
8.04
8.02
7.80
7.79
7.78
7.77
7.76
7.56
7.55
7.53
7.41
7.41
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.23
4.35
1.56
0.00
O
OH
1n
0.98
1.00
1.01
3.00
2.06
1.98
4.06
2.09
2.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.17
159.40
135.84
134.27
133.94
132.44
131.35
130.67
129.22
128.80
128.26
128.14
127.62
127.24
127.01
124.73
123.77
123.24
117.36
102.54
100.88
88.78
77.32
77.00
76.68
47.03

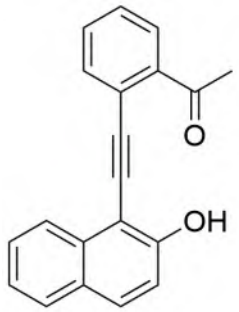


1n

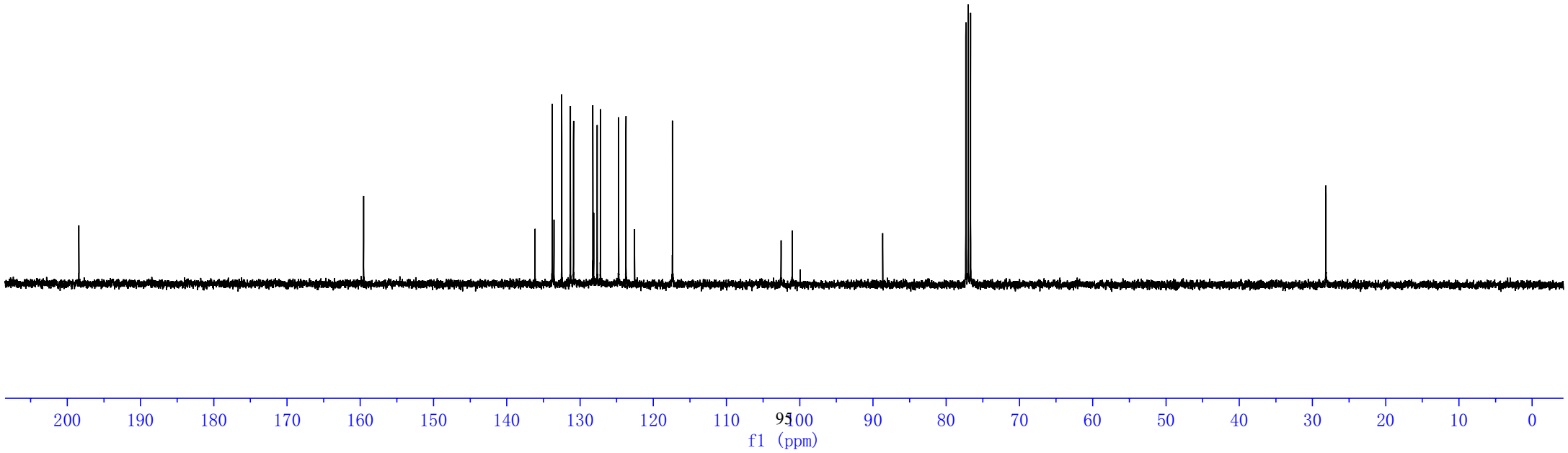


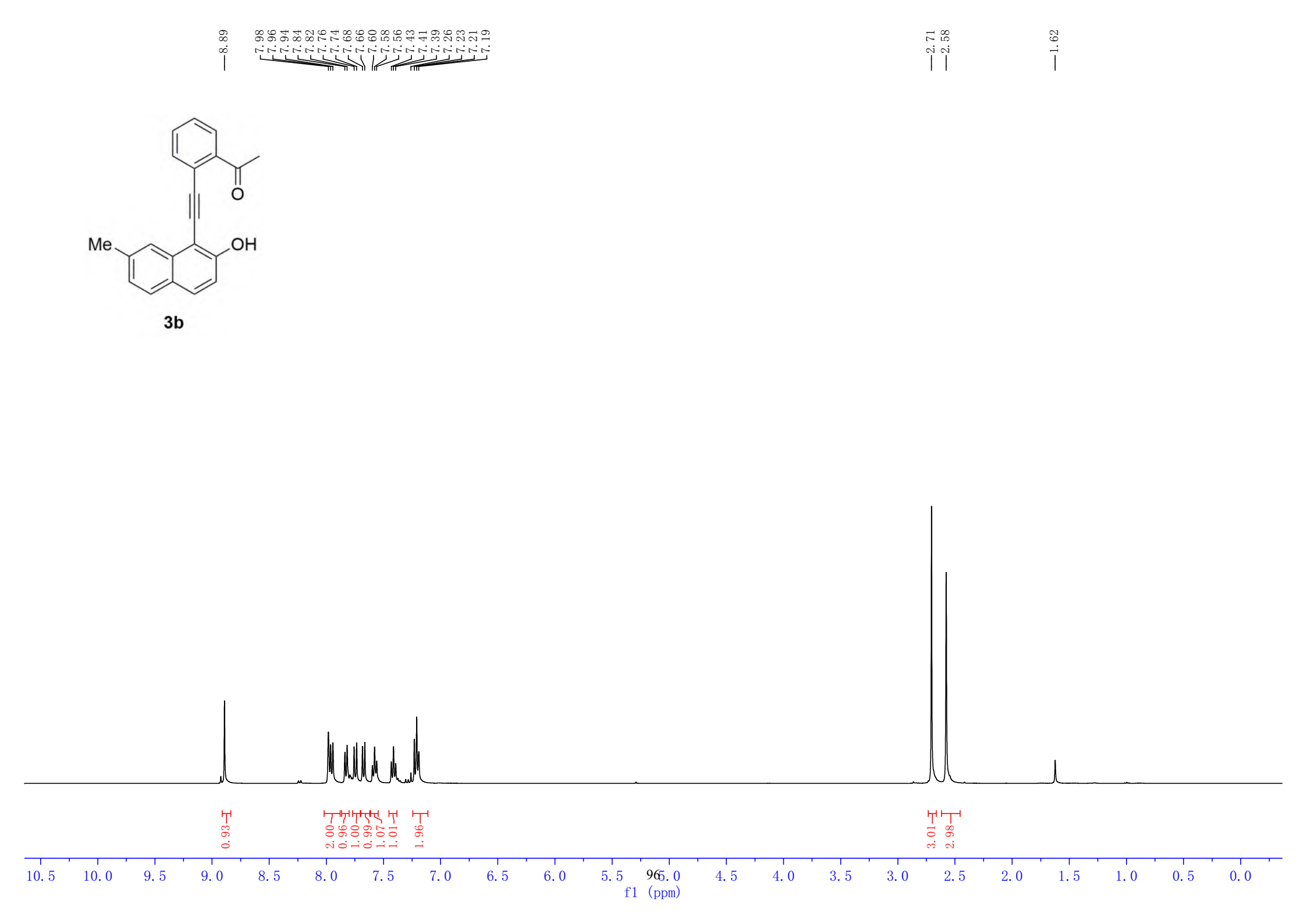

8.93
8.25
8.22
7.98
7.98
7.96
7.96
7.82
7.82
7.81
7.80
7.79
7.78
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.54
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.37
7.36
7.35
7.31
7.28
7.26
2.71
O
OH
3a
1.00
1.00
1.02
3.02
2.05
1.04
1.02
1.00
3.04
f1 (ppm)

198.42
159.54
136.14
133.79
133.55
132.49
131.31
130.89
128.25
128.13
127.66
127.20
124.73
123.73
122.54
117.38
102.55
101.01
88.67
77.32
77.00
76.68
28.17

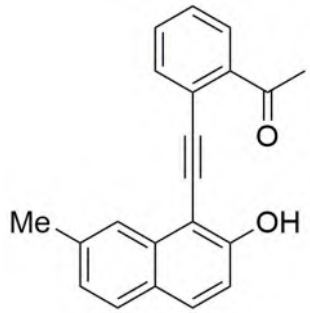


3a

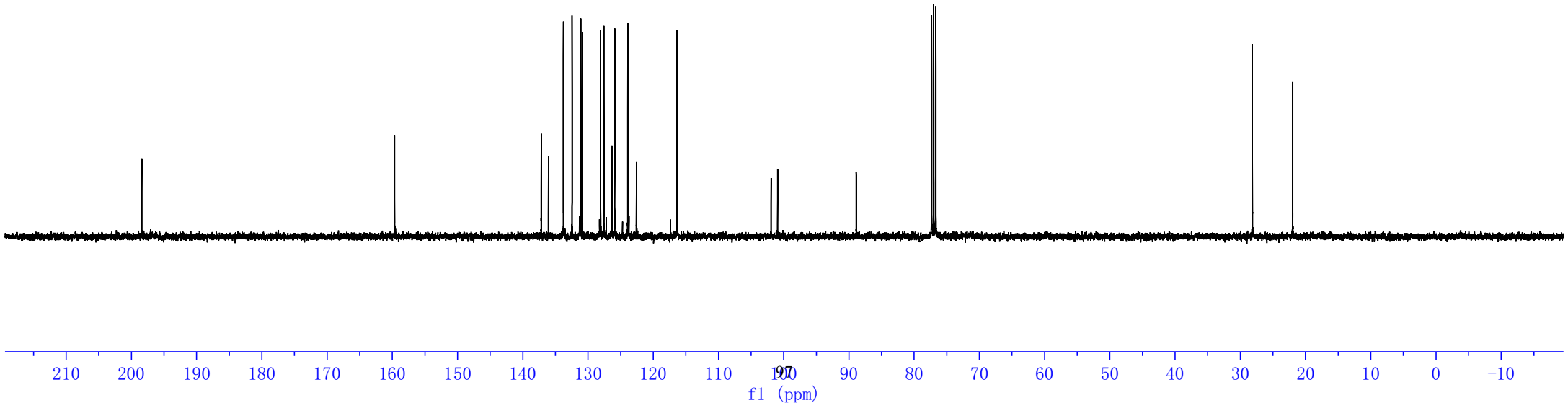


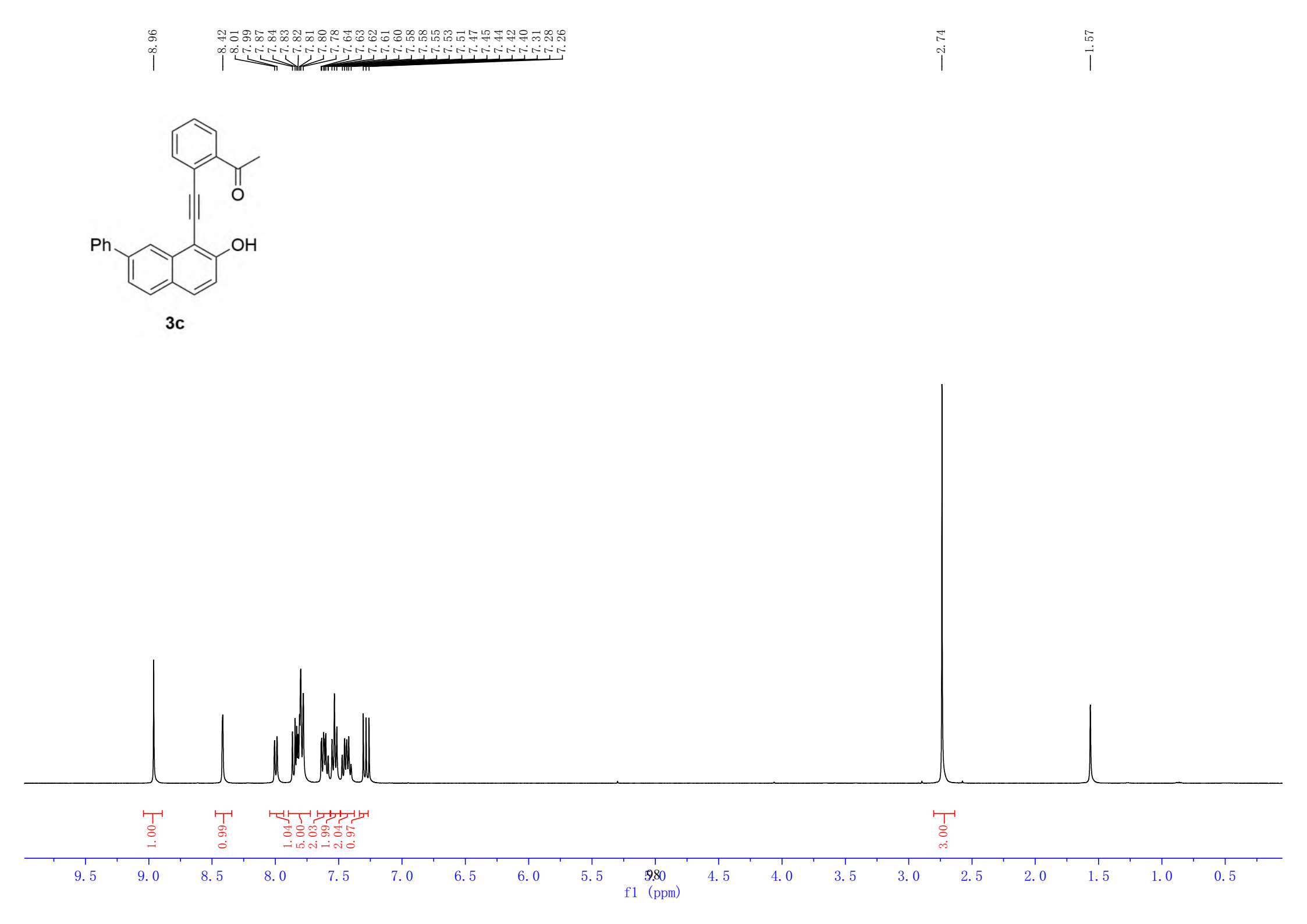

8.89
7.98
7.96
7.94
7.84
7.82
7.76
7.74
7.68
7.66
7.60
7.58
7.56
7.43
7.41
7.39
7.26
7.23
7.21
7.19
2.71
2.58
1.62
O
Me
OH
3b
0.93
2.00
0.96
1.00
0.99
1.07
1.01
1.96
3.01
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

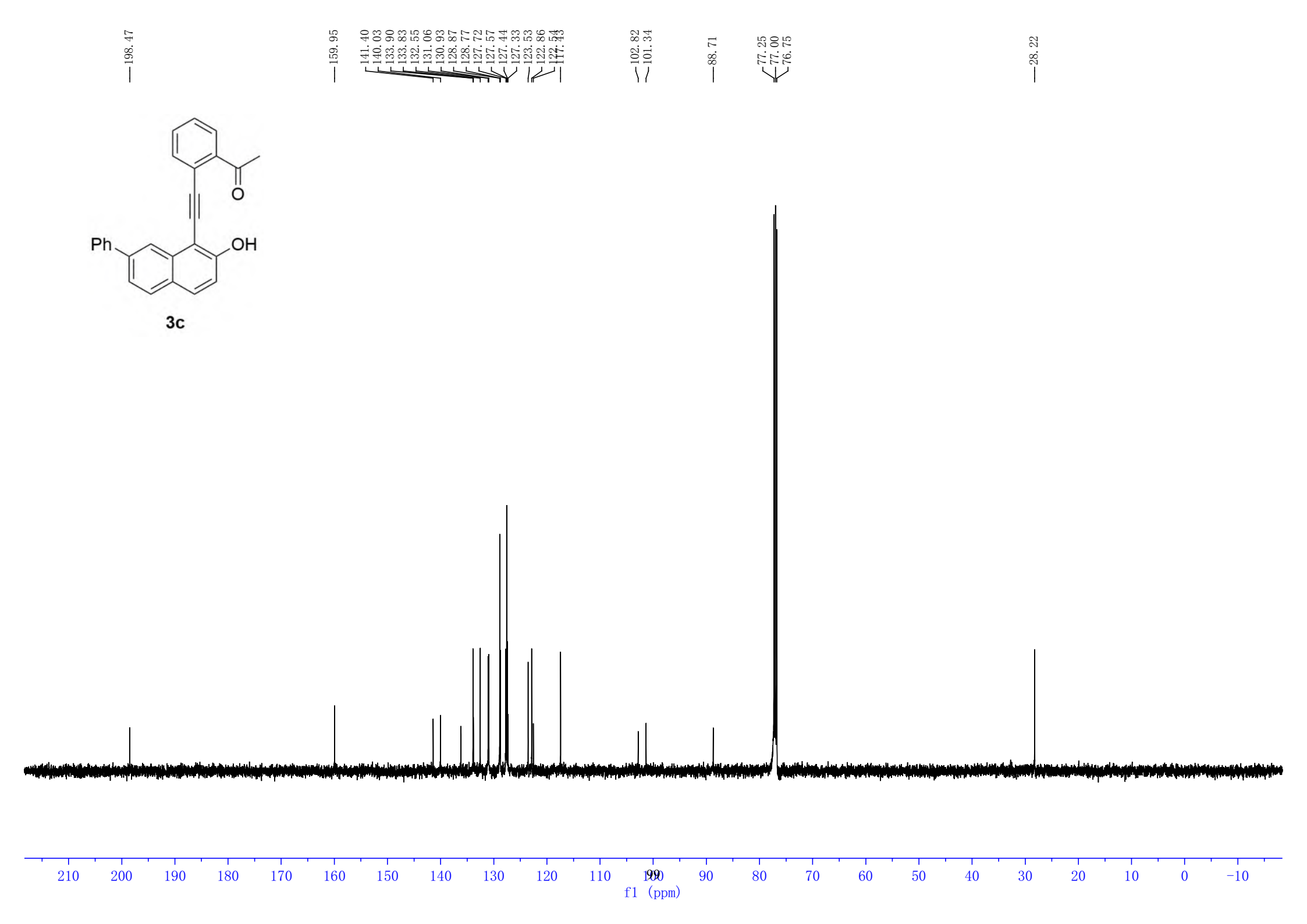
198.41
159.65
137.17
136.06
133.77
133.72
132.44
131.09
130.87
128.07
127.56
126.31
125.91
123.90
122.59
116.34
101.93
100.93
88.88
77.32
77.00
76.68
28.15
21.98

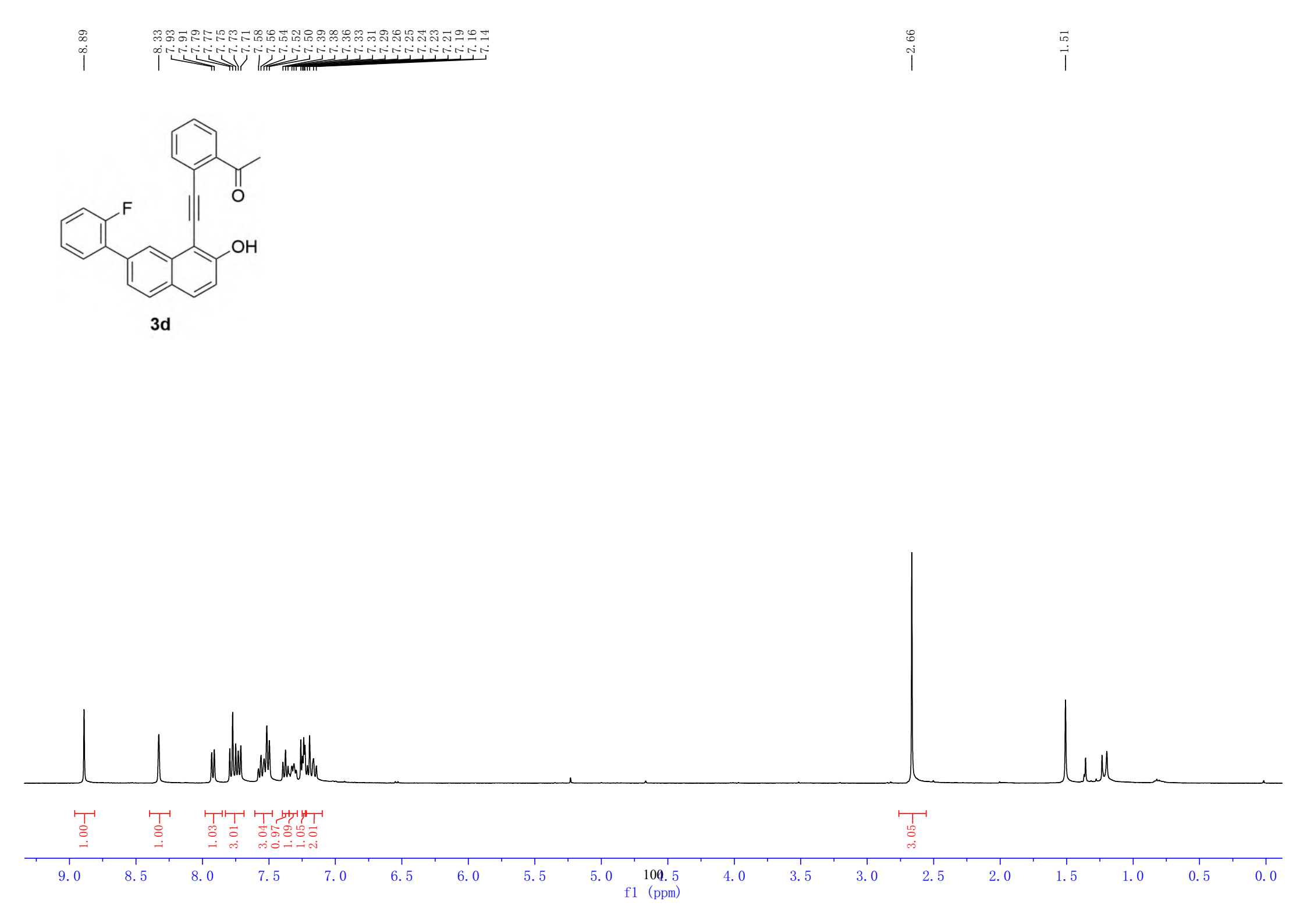


3b

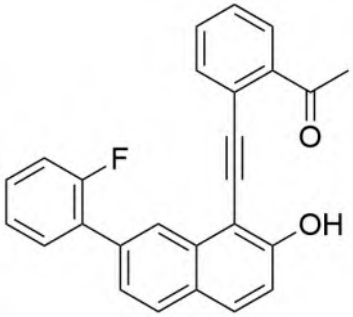



8.96
8.42
8.01
7.99
7.87
7.84
7.83
7.82
7.81
7.80
7.78
7.64
7.63
7.62
7.61
7.60
7.58
7.55
7.53
7.51
7.47
7.45
7.44
7.42
7.40
7.31
7.28
7.26
2.74
1.57
O
Ph
OH
3c
1.00
0.99
1.04
5.00
2.03
1.99
2.04
0.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

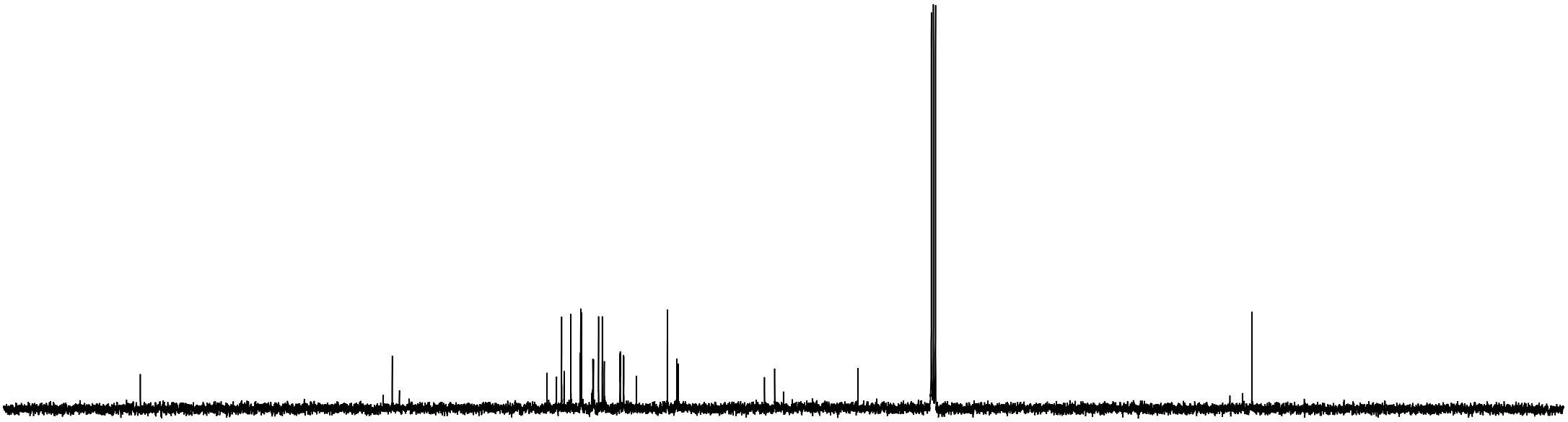

198.47
159.95
141.40
140.03
133.90
133.83
132.55
131.06
130.93
128.87
128.77
127.72
127.57
127.44
127.33
123.53
122.86
122.54
117.43
102.82
101.34
88.71
77.25
77.00
76.75
28.22
O
Ph
OH
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

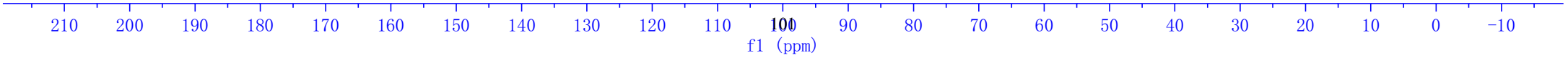

8.89
8.33
7.93
7.91
7.79
7.77
7.75
7.73
7.71
7.58
7.56
7.54
7.52
7.50
7.39
7.38
7.36
7.33
7.31
7.29
7.26
7.25
7.24
7.23
7.21
7.19
7.16
7.14
2.66
1.51
F
O
OH
3d
1.00
1.00
1.03
3.01
3.04
0.97
1.09
1.05
2.01
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.47
159.89
136.18
133.95
133.57
132.53
131.11
131.08
131.02
130.89
129.16
129.07
128.29
127.72
127.41
125.03
125.00
124.97
124.94
124.46
124.43
117.75
116.32
102.87
101.32
88.59
77.32
77.00
76.68
28.21



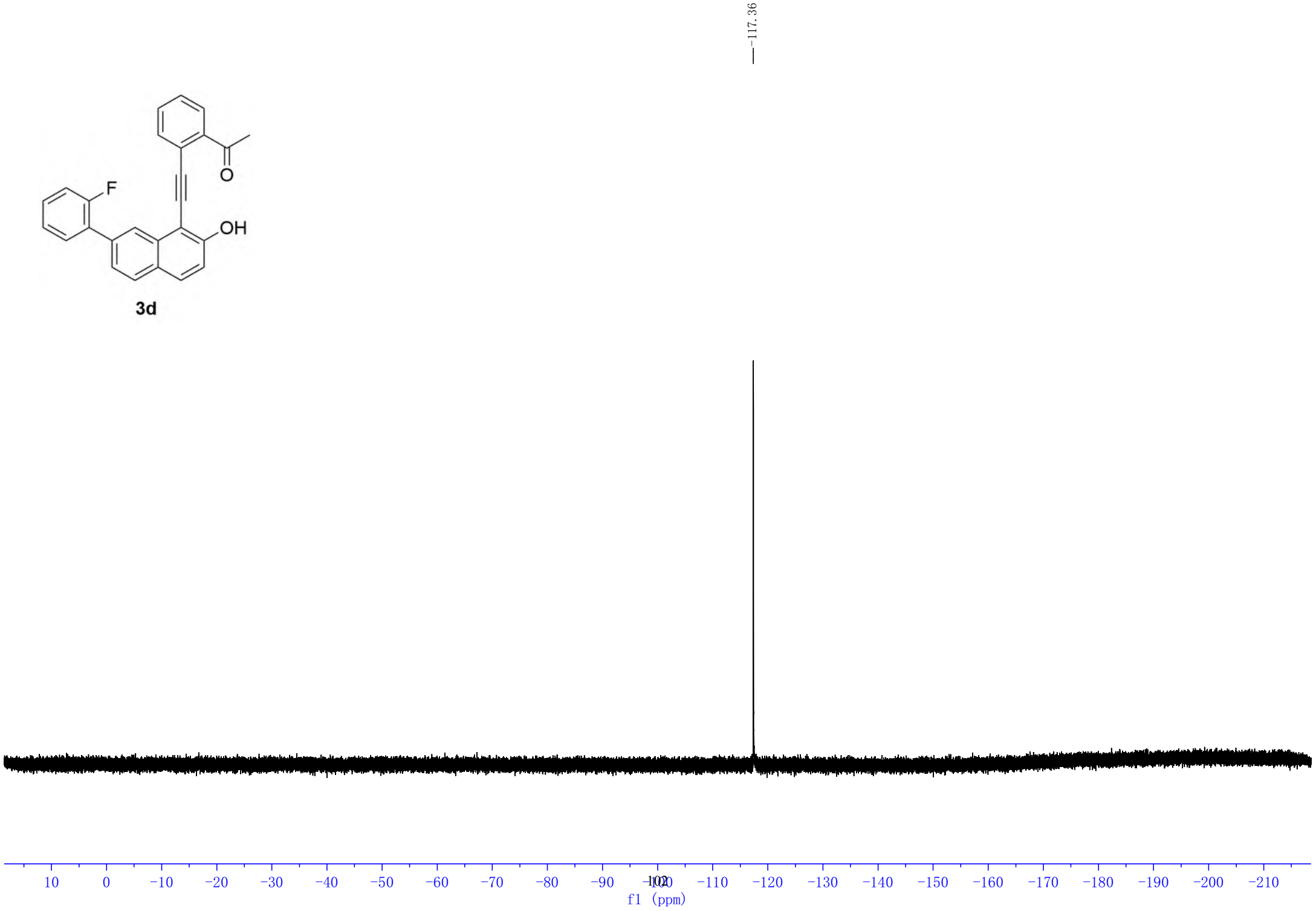
3d





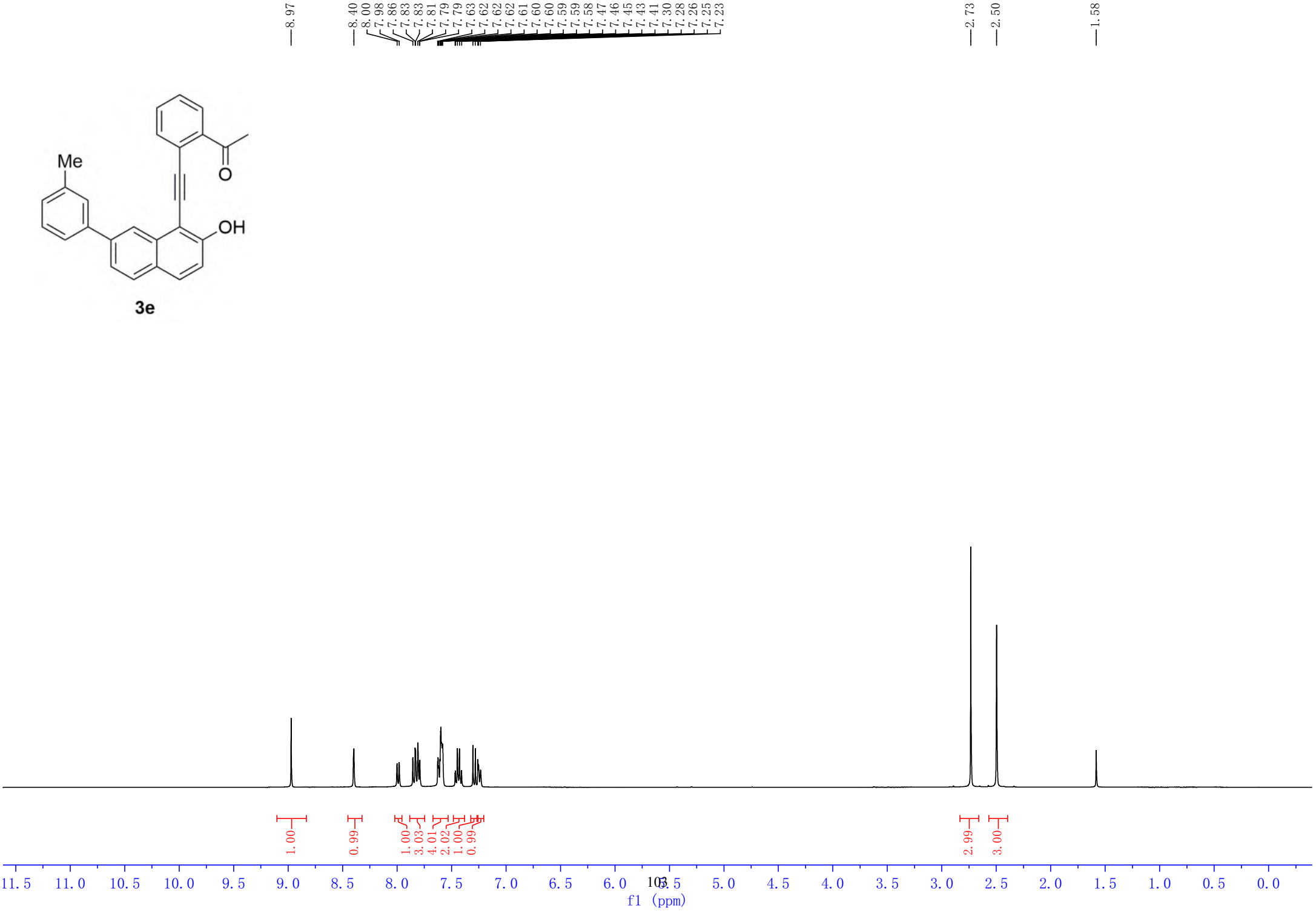
F
O
OH

3d

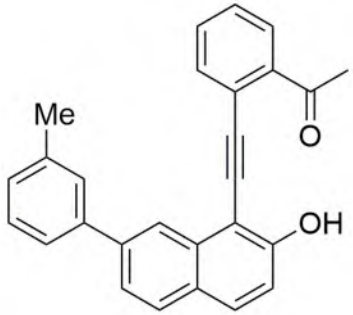

-117.36
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Me
O
OH

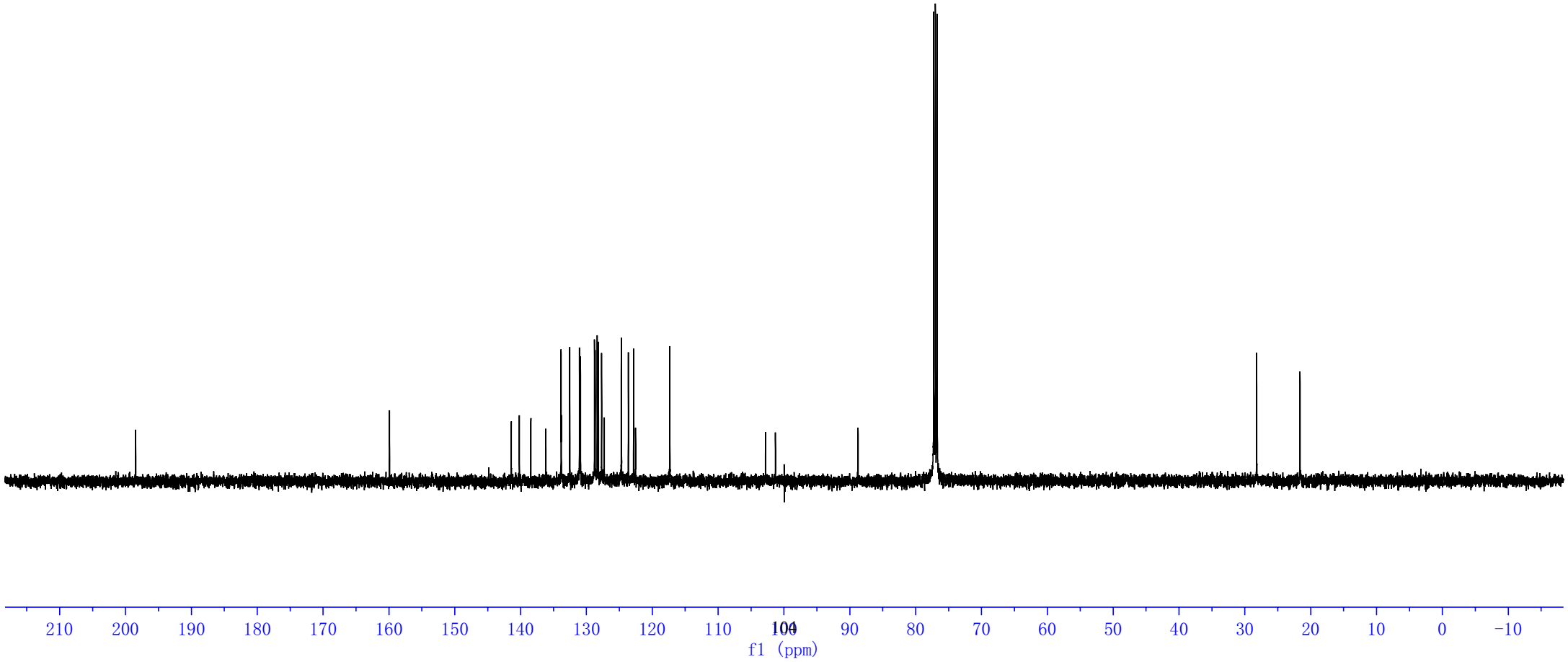
3e

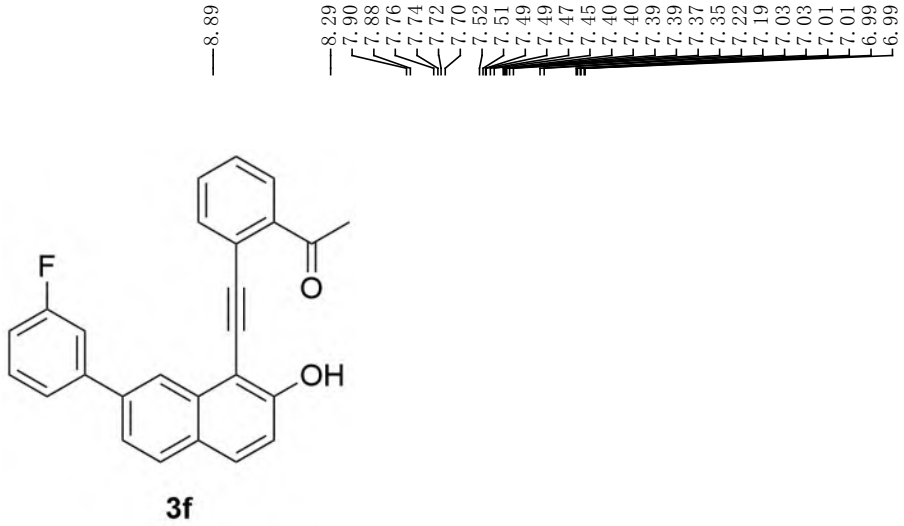

8.97
8.40
8.00
7.98
7.86
7.83
7.83
7.81
7.79
7.79
7.63
7.62
7.62
7.62
7.61
7.60
7.60
7.59
7.59
7.58
7.47
7.46
7.45
7.43
7.41
7.30
7.28
7.26
7.25
7.23
2.73
2.50
1.58
1.00
0.99
1.00
3.03
4.01
2.02
1.00
0.99
2.99
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.47
159.92
140.20
138.44
133.86
133.81
132.54
131.06
130.92
128.77
128.68
128.37
128.19
127.70
127.30
124.70
123.64
122.83
117.34
102.79
101.30
88.75
77.25
77.00
76.75
28.22
21.62

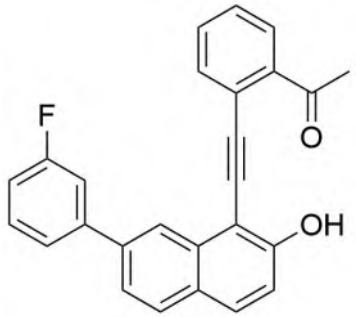


3e

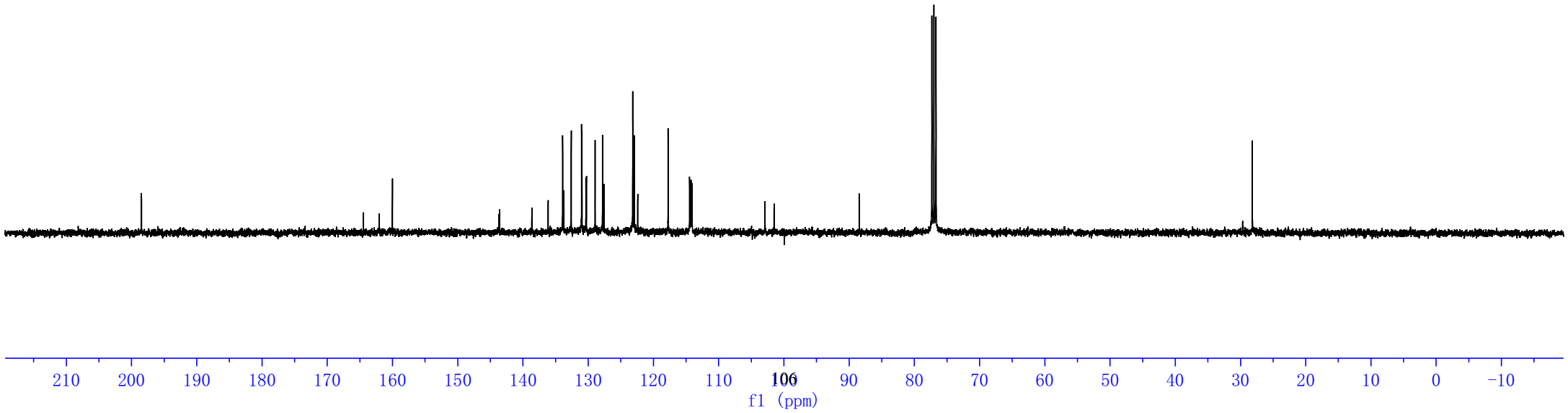



8.89
8.29
7.90
7.88
7.76
7.74
7.72
7.70
7.52
7.51
7.49
7.49
7.47
7.45
7.40
7.40
7.39
7.39
7.37
7.35
7.22
7.19
7.03
7.03
7.01
7.01
6.99
6.99
2.63
F
O
OH
3f
0.99
1.00
1.03
1.02
2.01
3.08
2.99
1.06
1.06
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

198.48
164.46
162.02
160.01
143.67
143.60
133.91
132.60
131.01
130.95
130.35
130.26
128.94
127.79
123.17
122.93
117.74
114.45
114.30
114.24
102.90
101.49
88.45
77.32
77.00
76.68
28.19

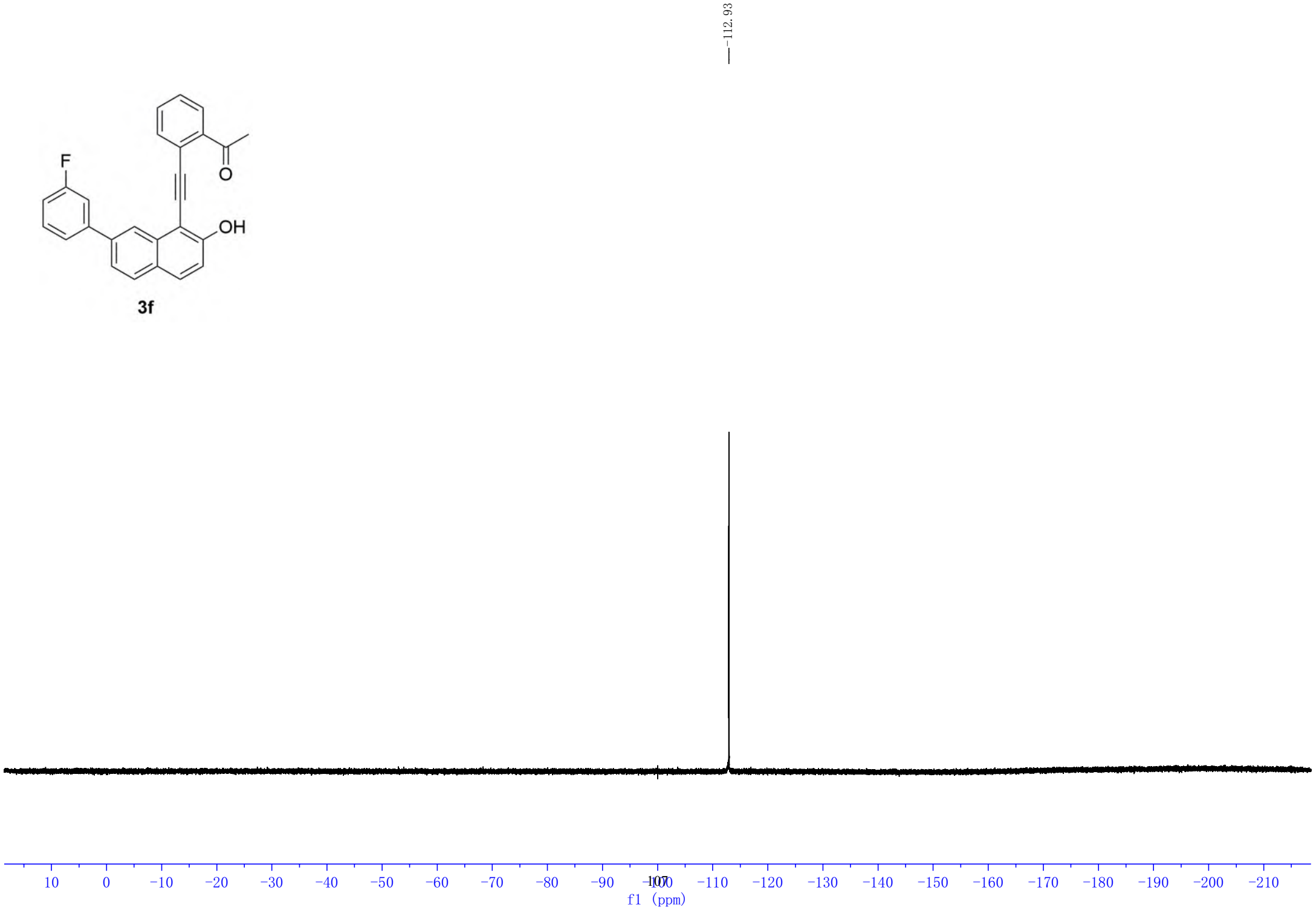


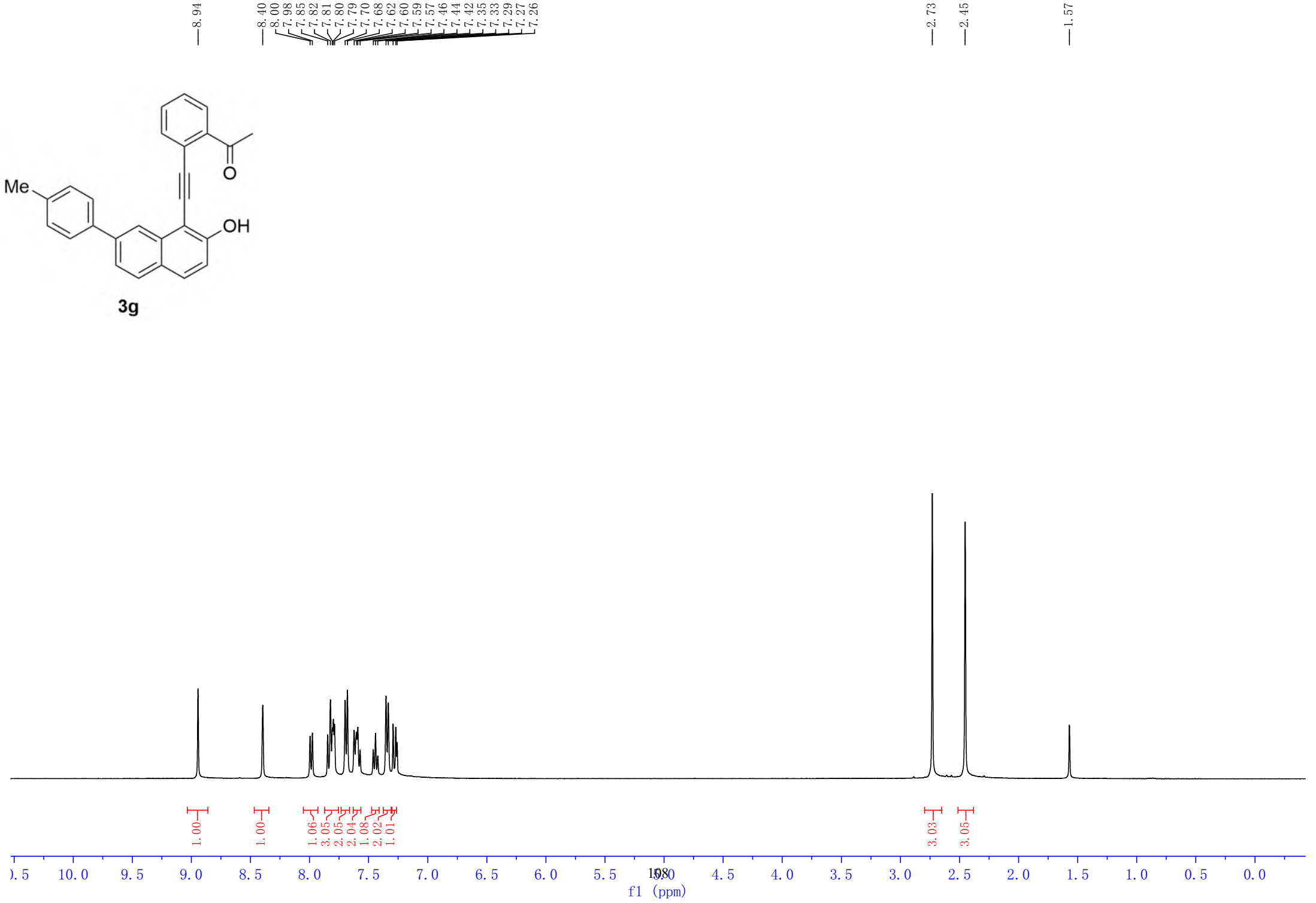
3f



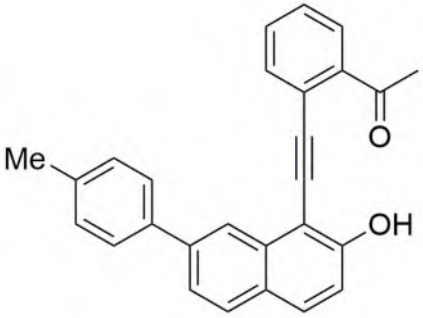
F
O
OH

3f

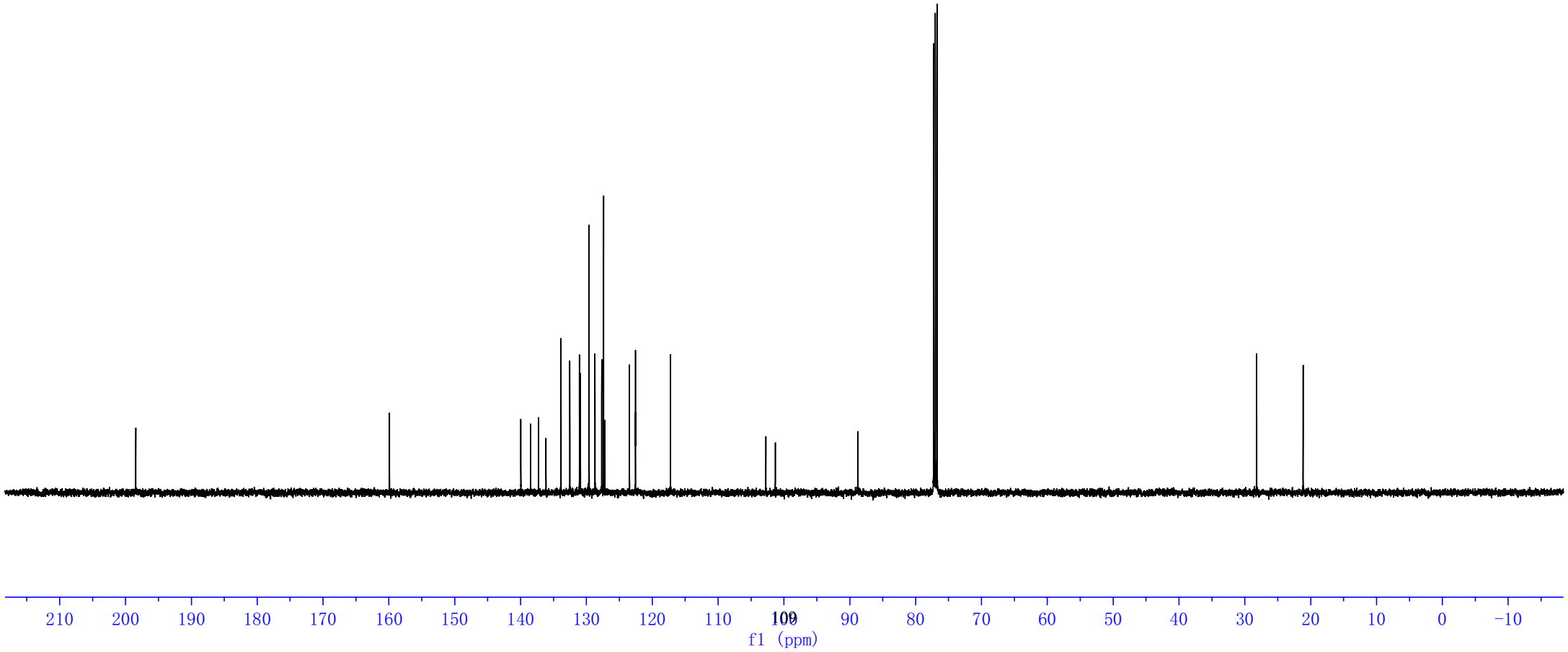

-112.93
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

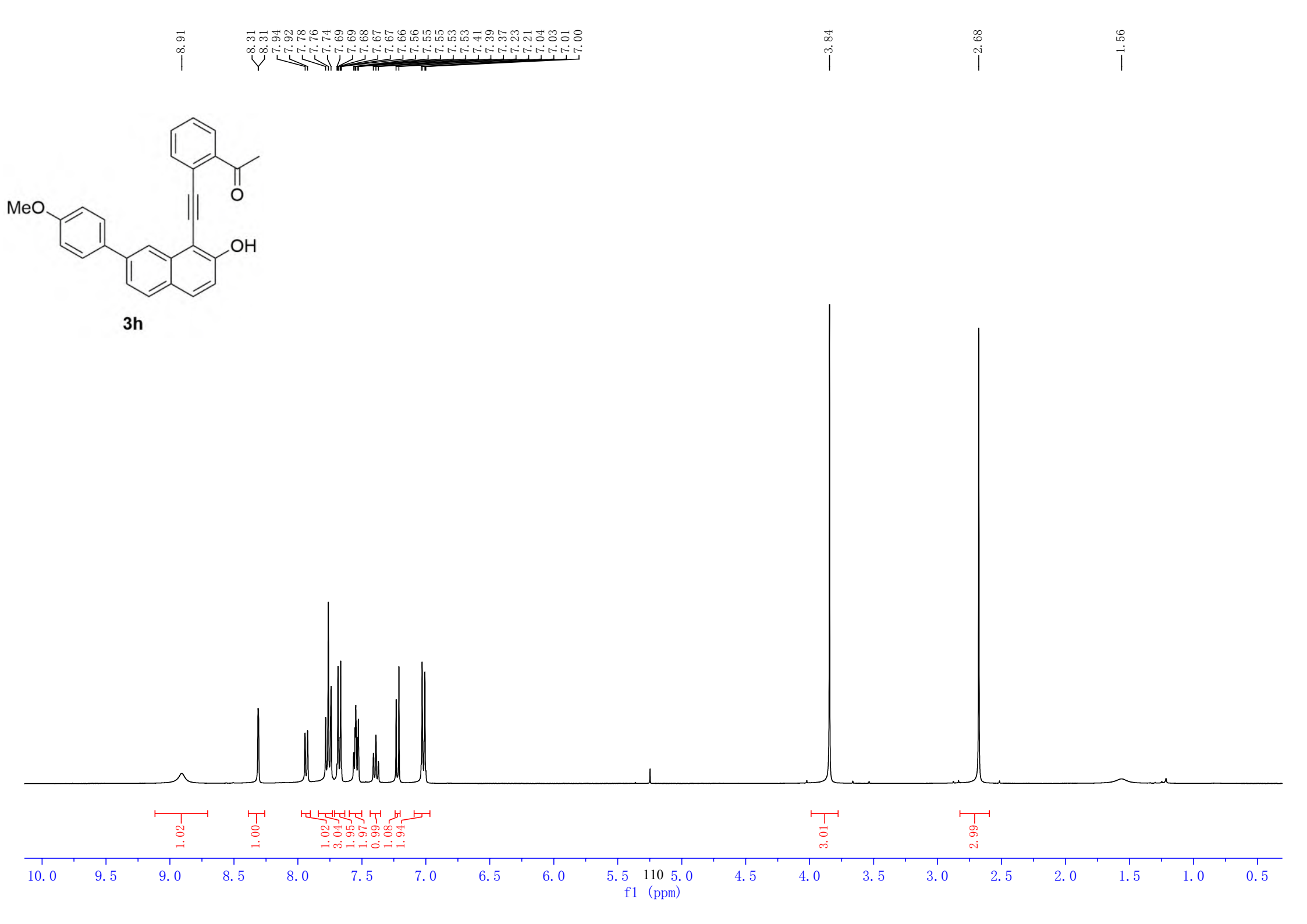

8.94
8.40
8.00
7.98
7.85
7.82
7.81
7.80
7.79
7.70
7.68
7.62
7.60
7.59
7.57
7.46
7.44
7.42
7.35
7.33
7.29
7.27
7.26
2.73
2.45
1.57
Me
O
OH
3g
1.00
1.00
1.06
3.05
2.05
2.04
1.08
2.02
1.01
3.03
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.44
159.91
139.96
138.49
137.27
136.14
133.86
132.52
131.05
130.92
129.60
128.70
127.68
127.40
127.20
123.47
122.56
122.54
117.24
102.75
101.31
88.77
77.25
77.00
76.75
28.21
21.15

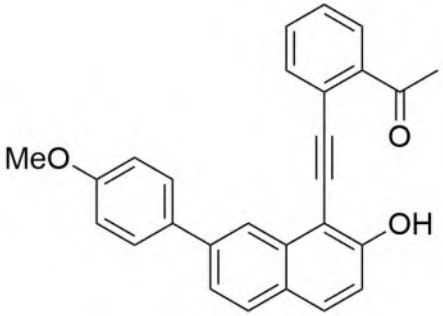


3g

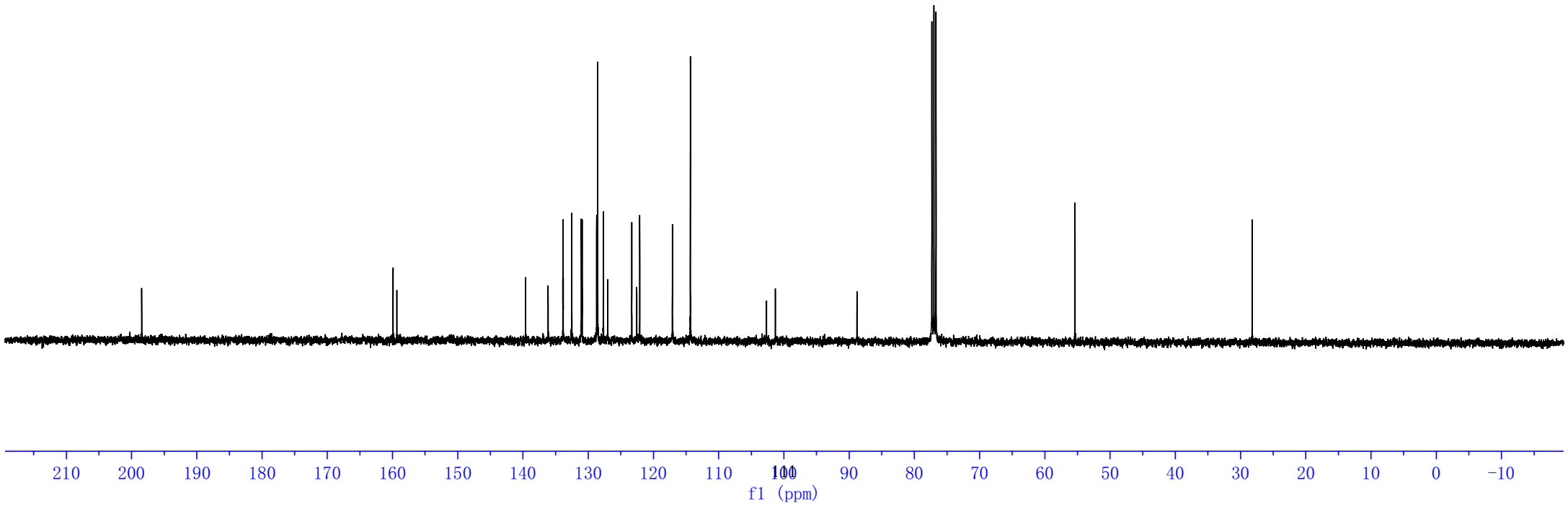


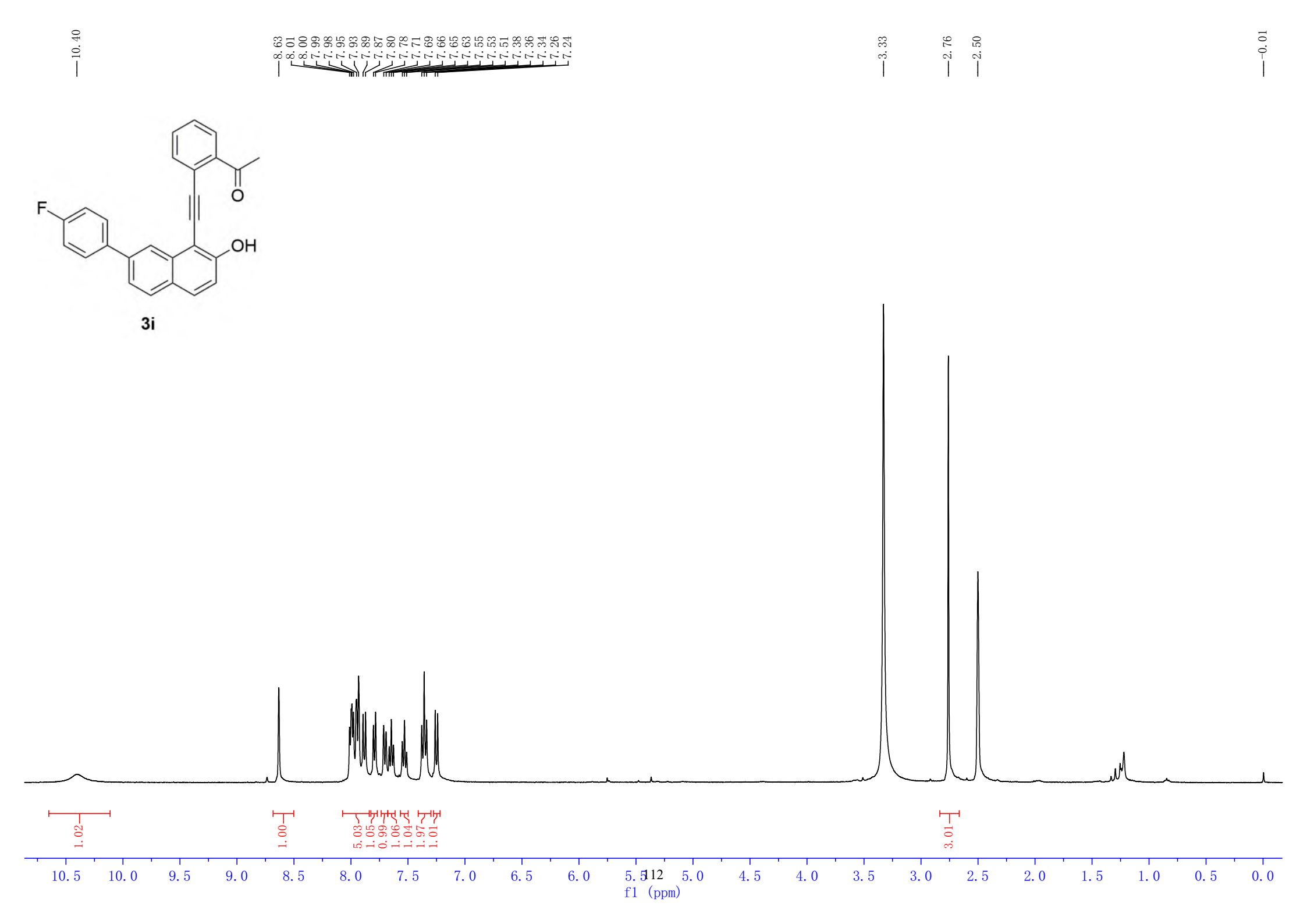

8.91
8.31
8.31
7.94
7.92
7.78
7.76
7.74
7.69
7.69
7.68
7.67
7.67
7.66
7.56
7.55
7.55
7.53
7.53
7.41
7.39
7.37
7.23
7.21
7.04
7.03
7.01
7.00
3.84
2.68
1.56
MeO
O
OH
3h
1.02
1.00
1.02
3.04
1.95
1.97
0.99
1.08
1.94
3.01
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

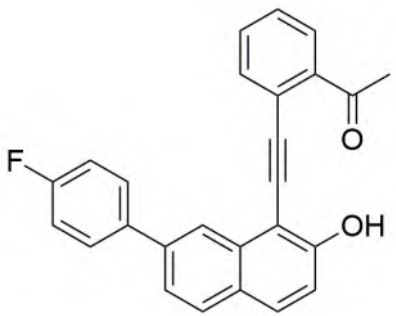
198.45
159.91
159.33
139.60
136.14
133.89
133.86
133.82
132.52
131.06
130.92
128.71
128.55
127.67
127.01
123.32
122.56
122.10
117.09
114.33
102.67
101.31
88.79
77.32
77.00
76.68
55.37
28.20



3h




10.40
8.63
8.01
8.00
7.99
7.98
7.95
7.93
7.89
7.87
7.80
7.78
7.71
7.69
7.66
7.65
7.63
7.55
7.53
7.51
7.38
7.36
7.34
7.26
7.24
3.33
2.76
2.50
0.01
F
O
OH
3i
1.02
1.00
5.03
1.05
0.99
1.06
1.04
1.97
1.01
3.01
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
f1 (ppm)



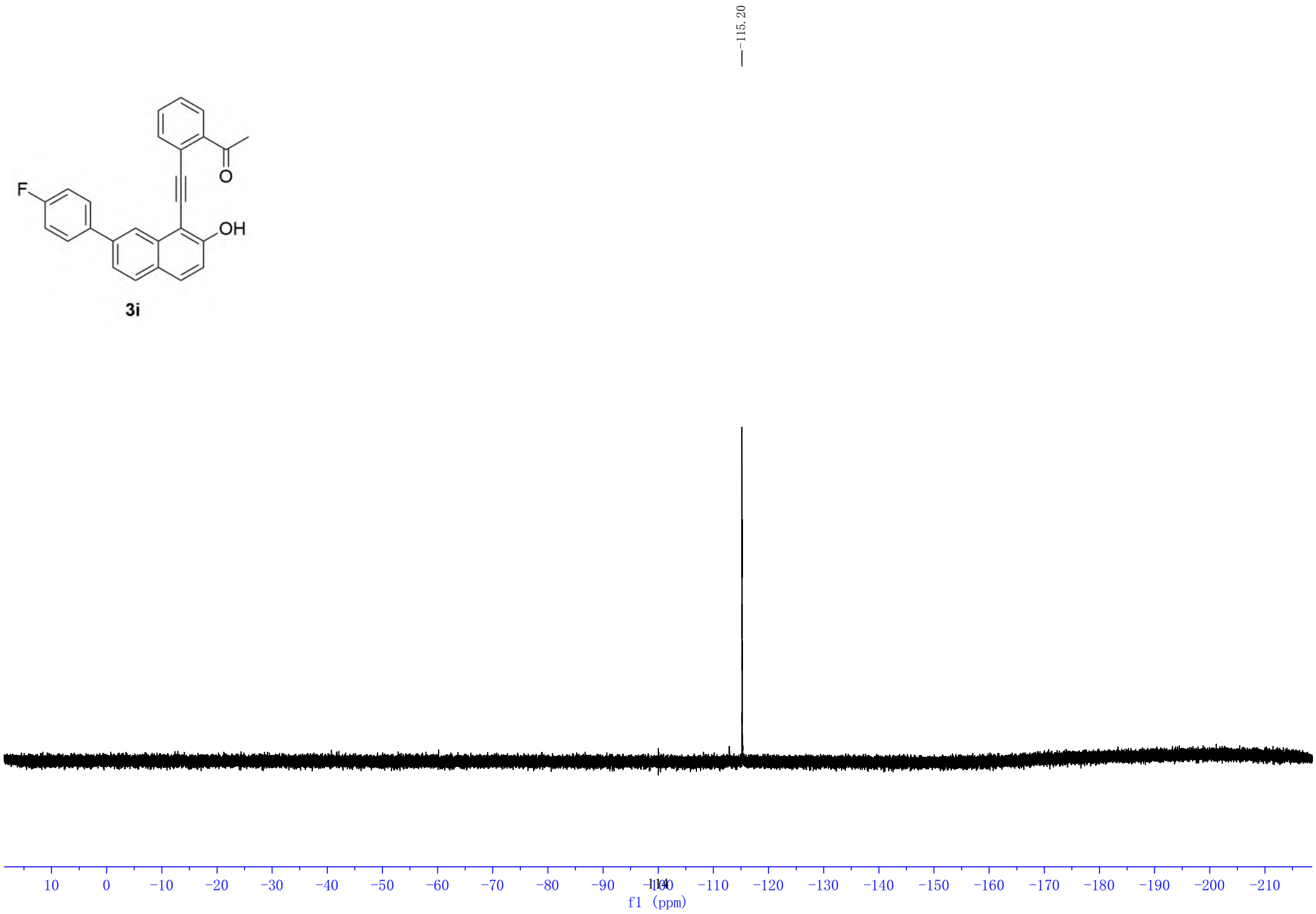
3i

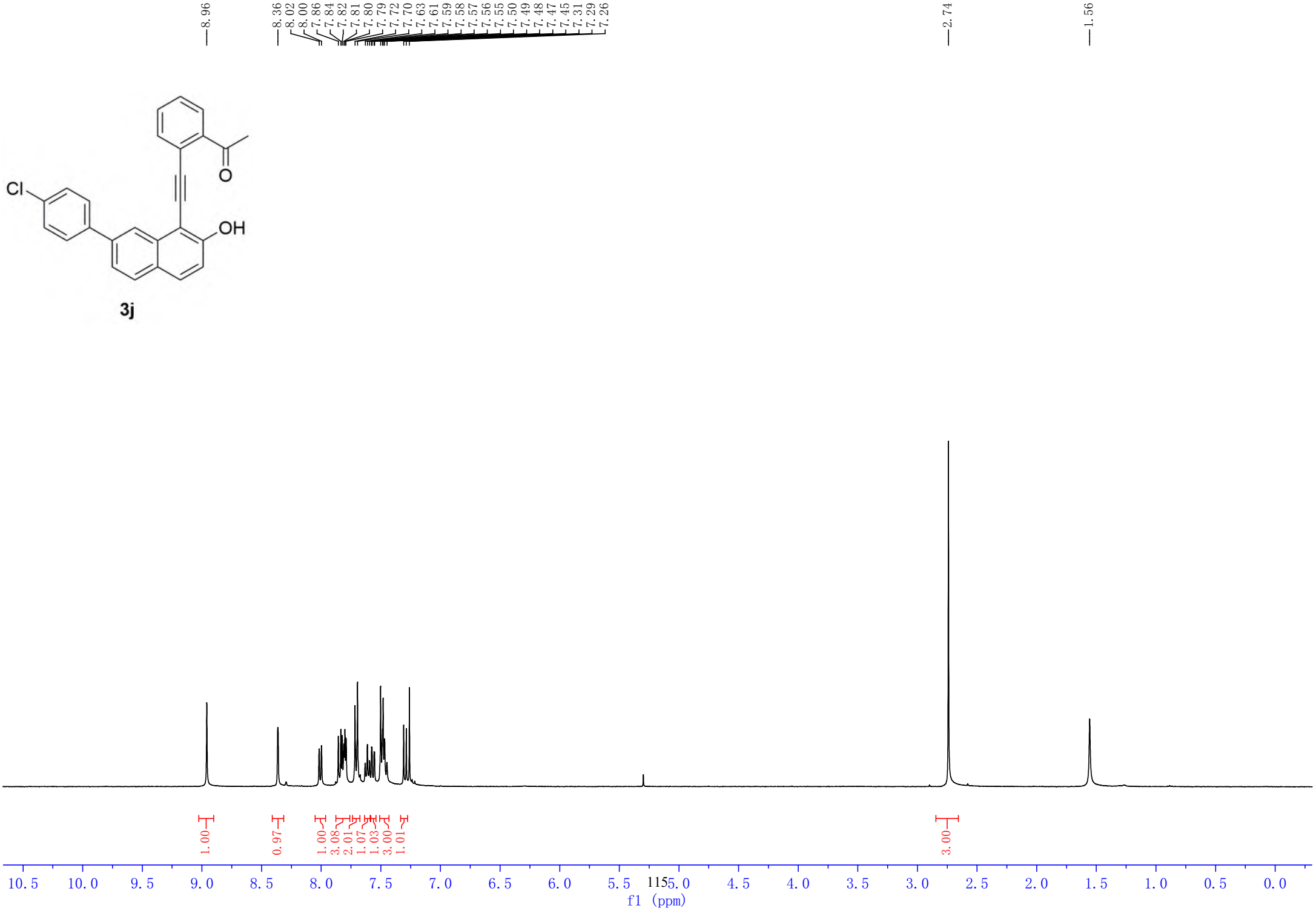
200.11
163.53
161.58
159.26
139.59
138.48
137.00
136.97
135.01
134.29
132.32
131.06
129.92
129.71
129.64
129.55
128.69
127.17
123.11
122.38
121.87
118.45
116.32
116.15
103.08
98.25
89.76
40.49
40.33
40.16
39.82
39.66
39.49
29.89

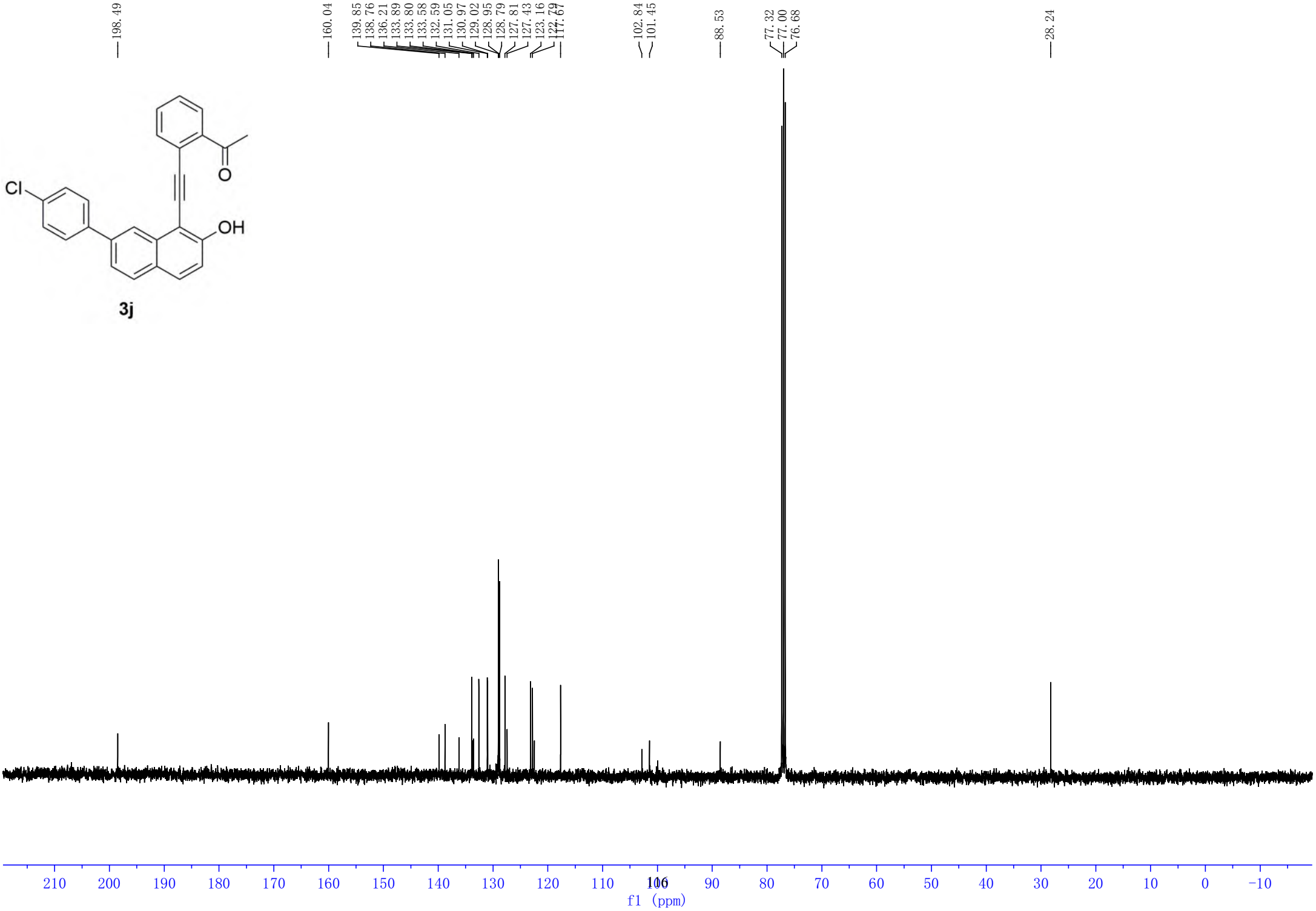
f1 (ppm)

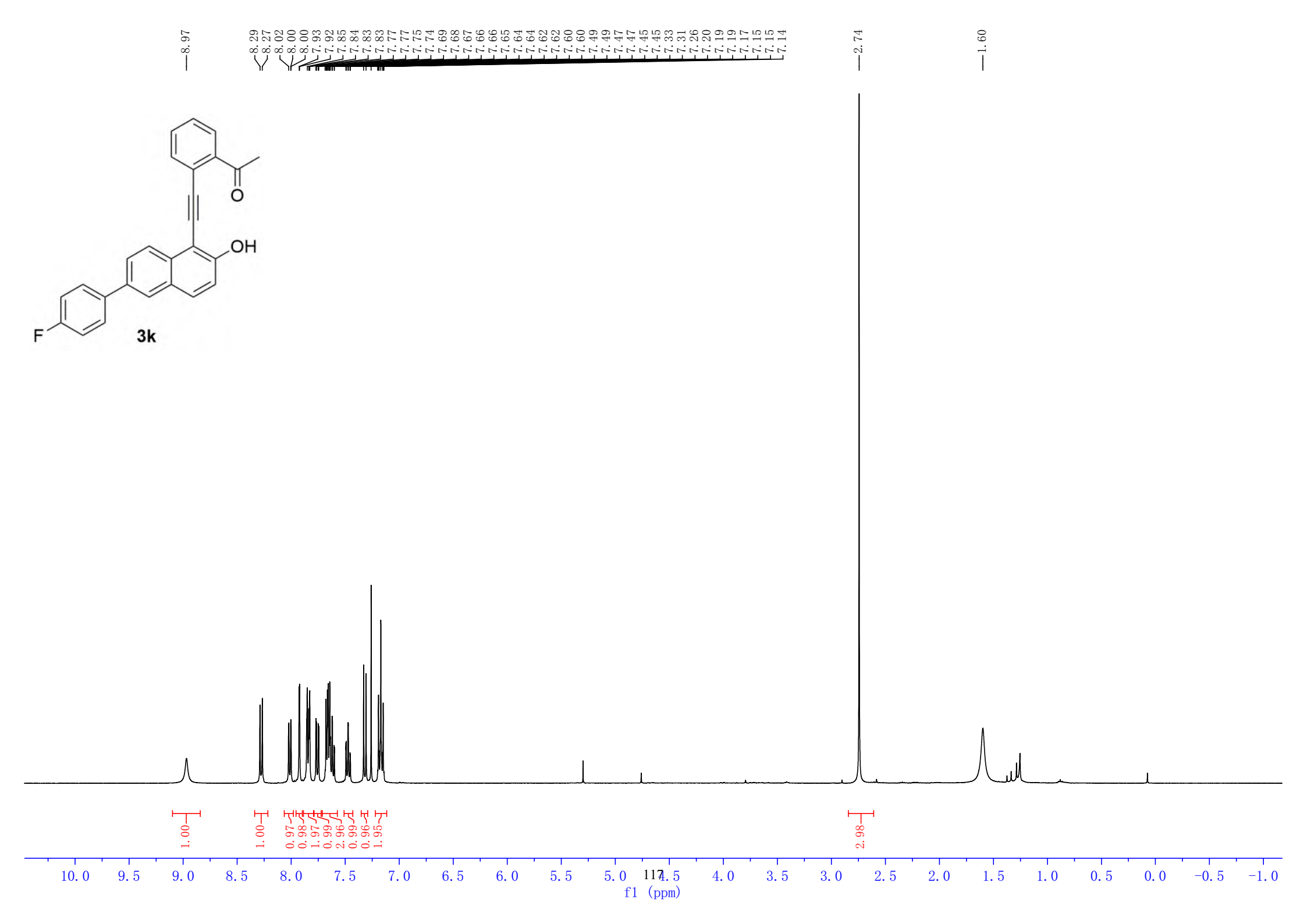
F
O
OH

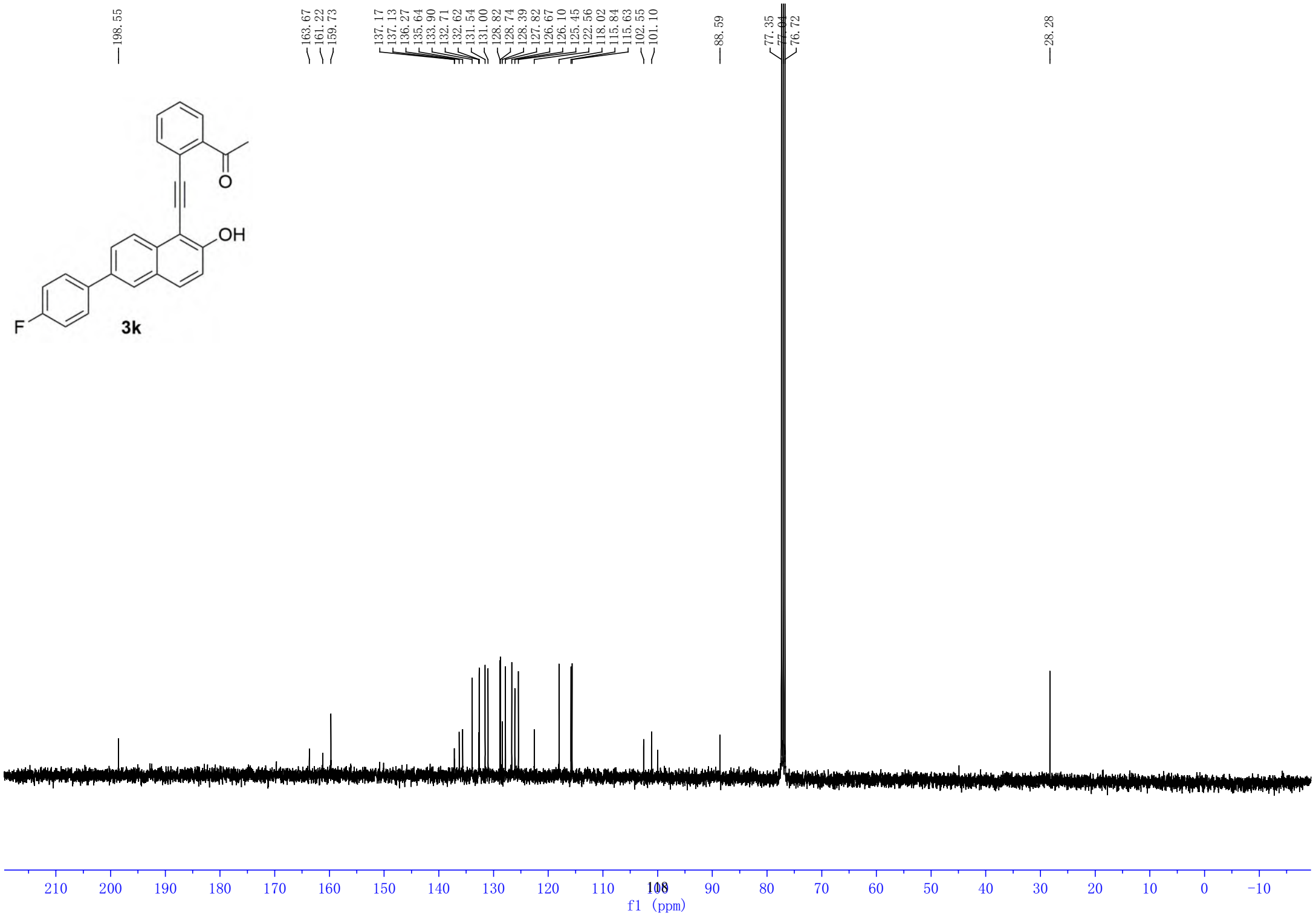
3i


-115.20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.96
8.36
8.02
8.00
7.86
7.84
7.82
7.81
7.80
7.79
7.72
7.70
7.63
7.61
7.59
7.58
7.57
7.56
7.55
7.50
7.49
7.48
7.47
7.45
7.31
7.29
7.26
2.74
1.56
Cl
O
OH
3j
1.00
0.97
1.00
3.08
2.01
1.07
1.03
3.00
1.01
3.00
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
f1 (ppm)

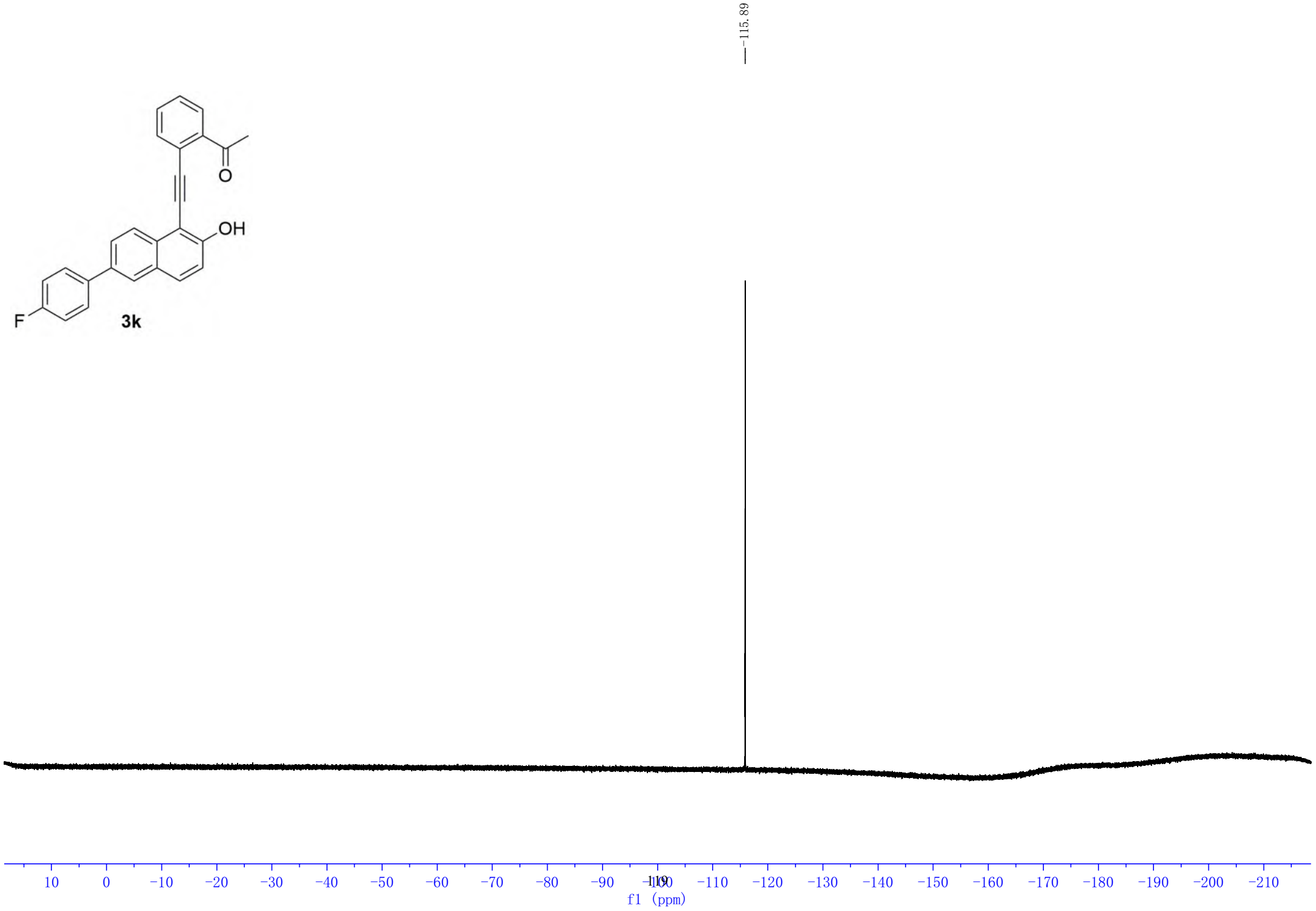

198.49
160.04
139.85
138.76
136.21
133.89
133.80
133.58
132.59
131.05
130.97
129.02
128.95
128.79
127.81
127.43
123.16
122.79
117.67
102.84
101.45
88.53
77.32
77.00
76.68
28.24
Cl
O
OH
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

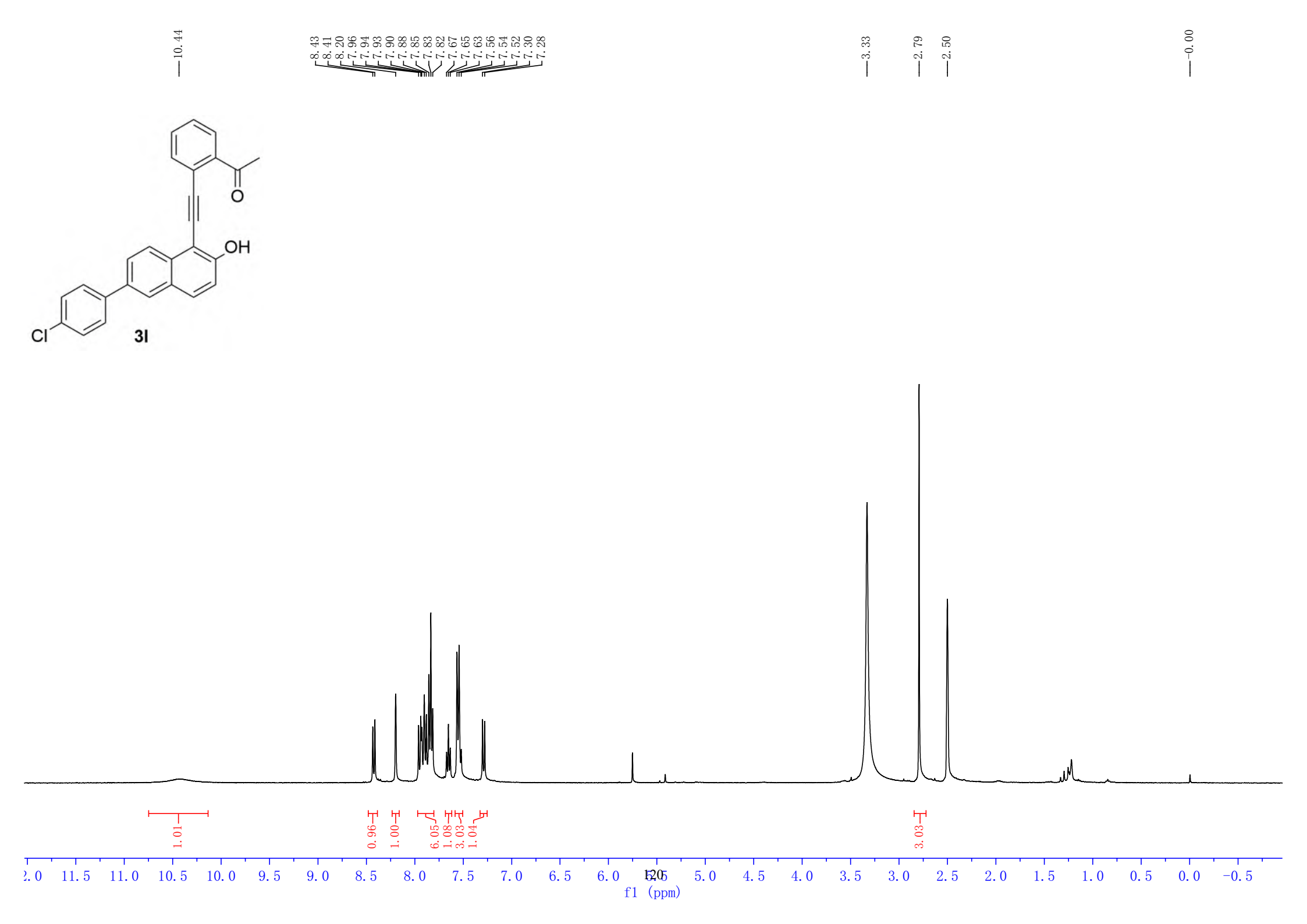

8.97
8.29
8.27
8.02
8.00
8.00
7.93
7.92
7.85
7.84
7.83
7.83
7.77
7.77
7.75
7.74
7.69
7.68
7.67
7.66
7.66
7.65
7.64
7.64
7.62
7.62
7.60
7.60
7.49
7.49
7.47
7.47
7.45
7.45
7.33
7.31
7.26
7.20
7.19
7.19
7.17
7.15
7.15
7.14
2.74
1.60
O
OH
F
3k
1.00
1.00
0.97
0.98
1.97
0.99
2.96
0.99
0.96
1.95
2.98
10.0
9.5
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
-1.0
f1 (ppm)

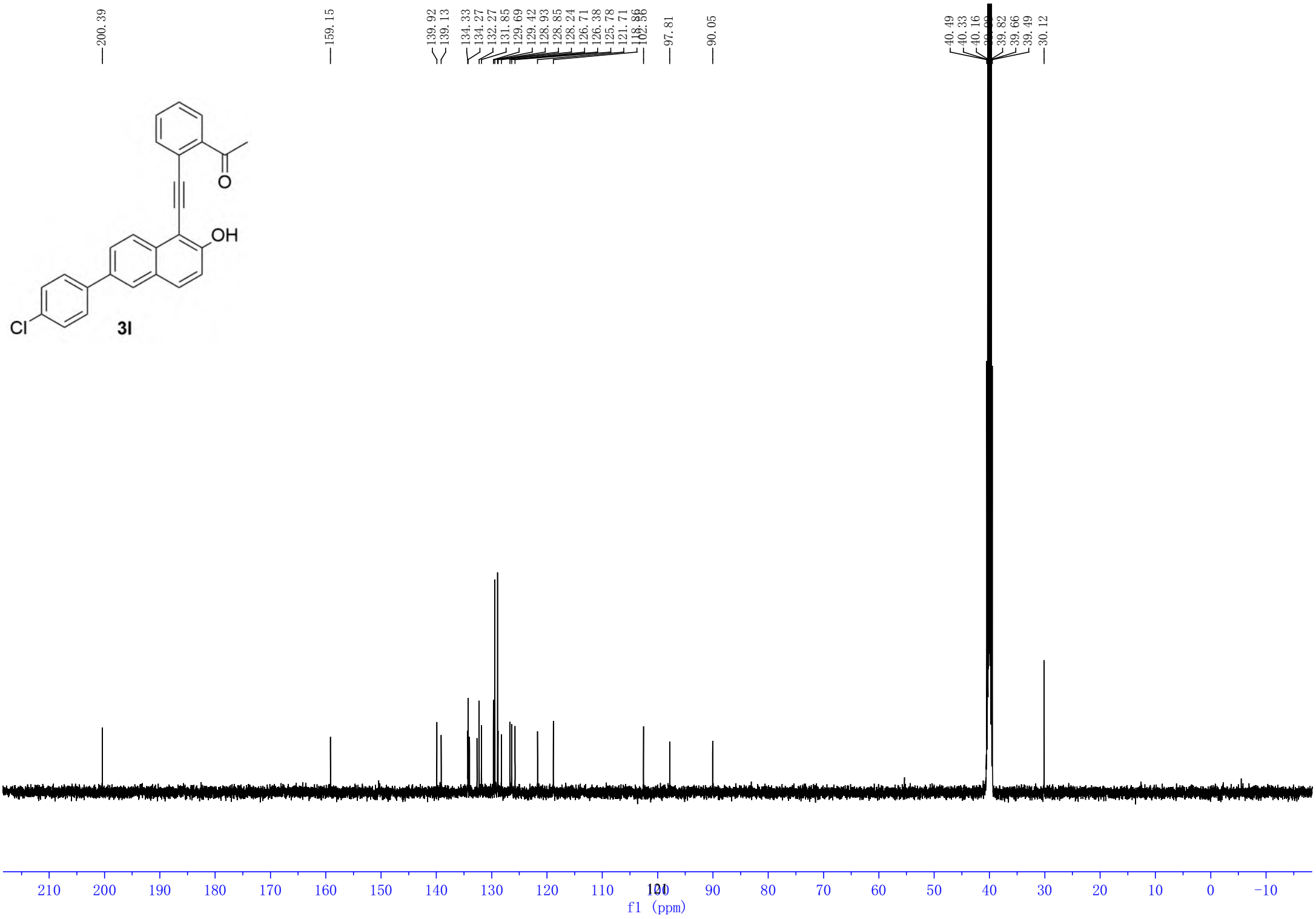

198.55
163.67
161.22
159.73
137.17
137.13
136.27
135.64
133.90
132.71
132.62
131.54
131.00
128.82
128.74
128.39
127.82
126.67
126.10
125.45
122.56
118.02
115.84
115.63
102.55
101.10
88.59
77.35
77.04
76.72
28.28
O
OH
F
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

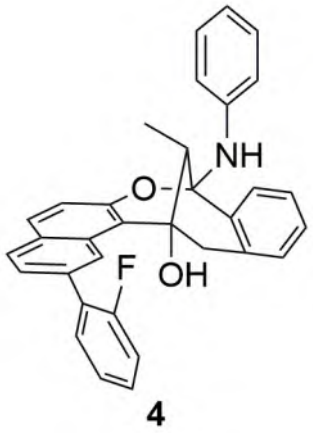
O
OH
F

3k

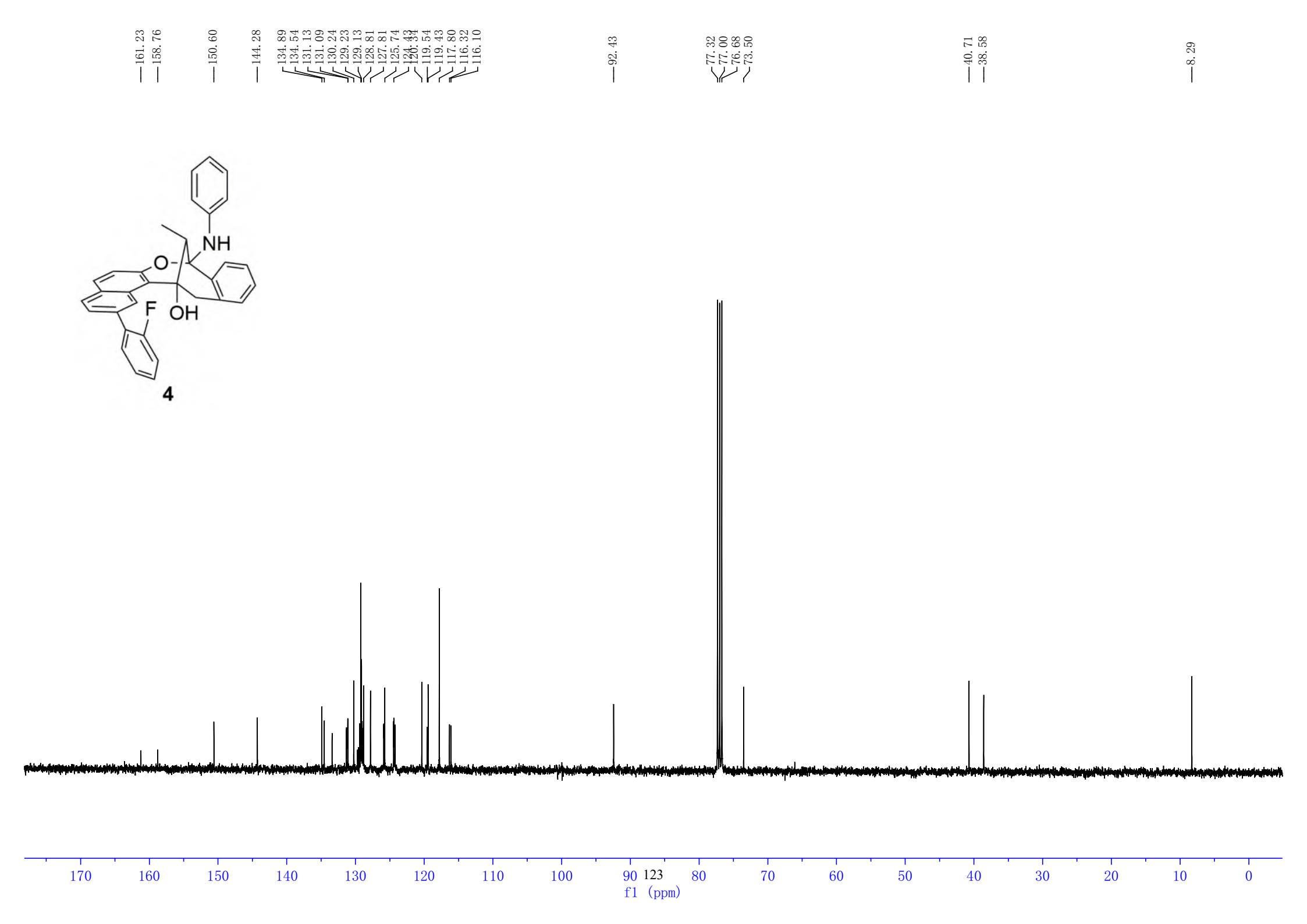

-115.89
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


10.44
8.43
8.41
8.20
7.96
7.94
7.93
7.90
7.88
7.85
7.83
7.82
7.67
7.65
7.63
7.56
7.54
7.52
7.30
7.28
3.33
2.79
2.50
0.00
O
OH
Cl
3l
1.01
0.96
1.00
6.05
1.08
3.03
1.04
3.03
f1 (ppm)


200.39
159.15
139.92
139.13
134.33
134.27
132.27
131.85
129.69
129.42
128.93
128.85
128.24
126.71
126.38
125.78
121.71
97.81
90.05
40.49
40.33
40.16
39.82
39.66
39.49
30.12
O
OH
Cl
3l
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)

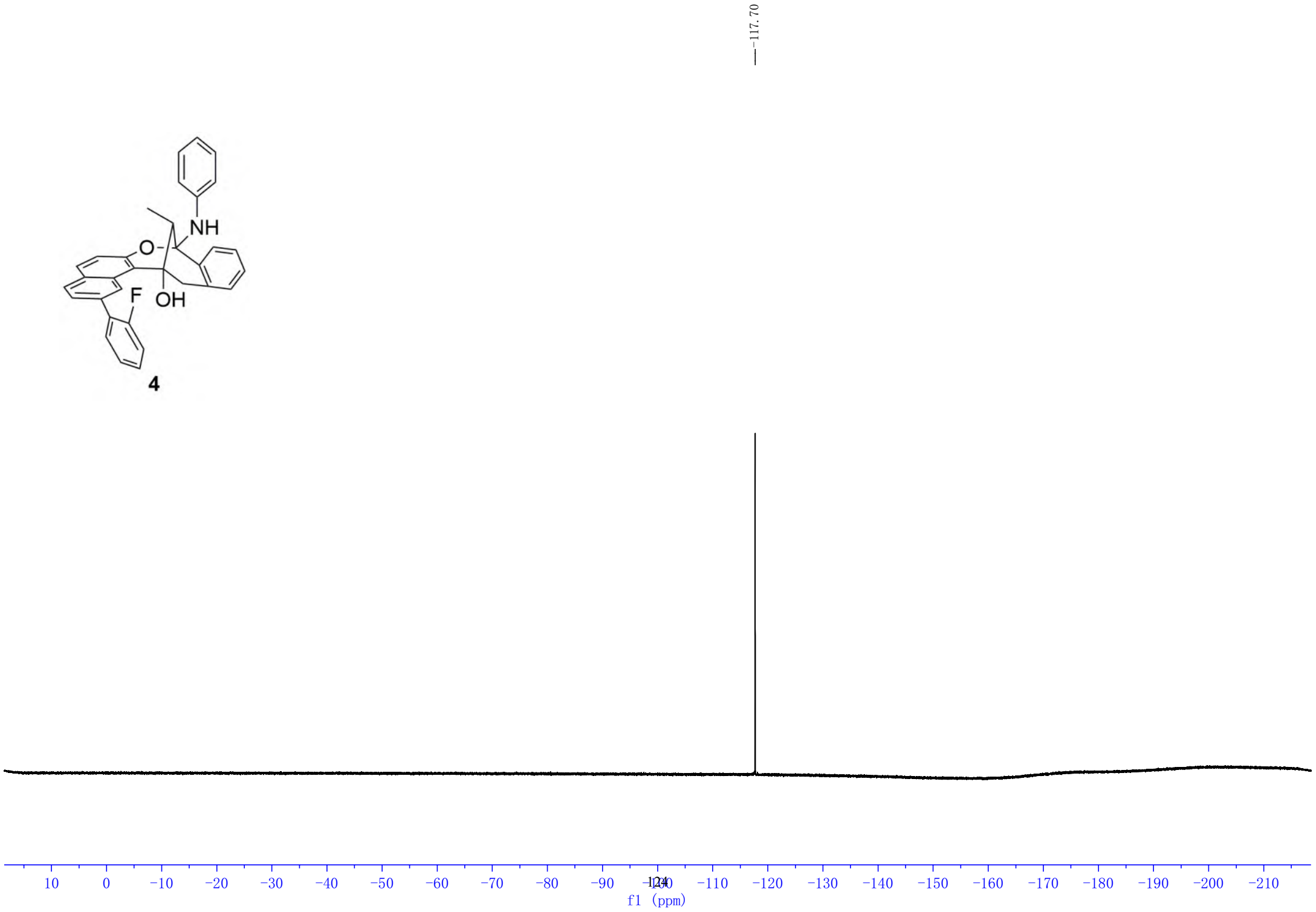


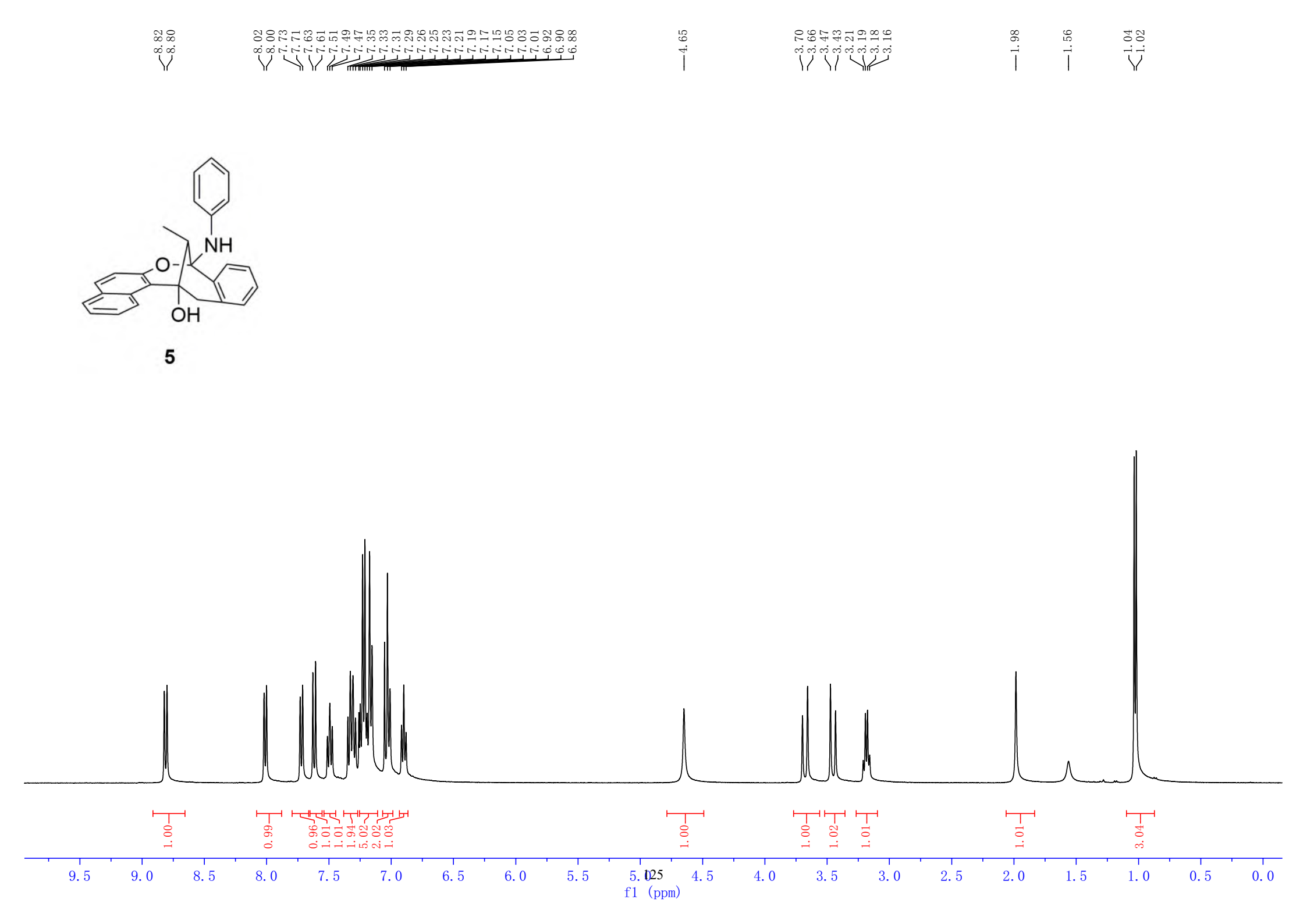
4


161.23
158.76
150.60
144.28
134.89
134.54
131.13
131.09
130.24
129.23
129.13
128.81
127.81
125.74
92.43
77.32
77.00
76.68
73.50
40.71
38.58
8.29
NH
O
F
OH
4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

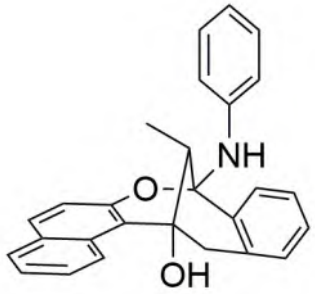
NH
O
F
OH

4

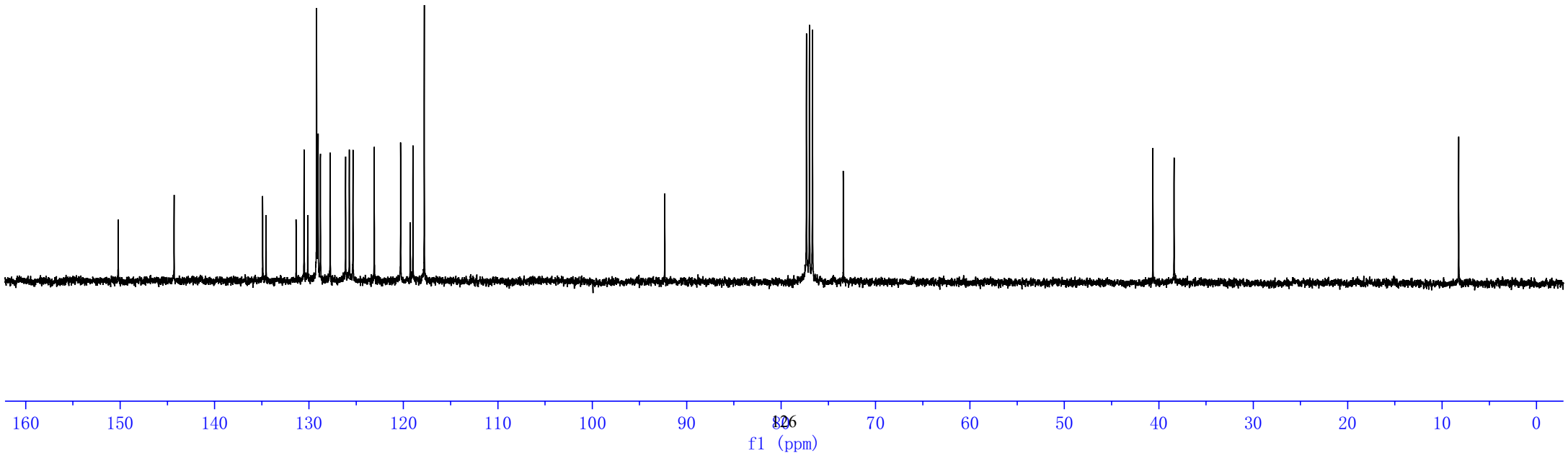

-117.70
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

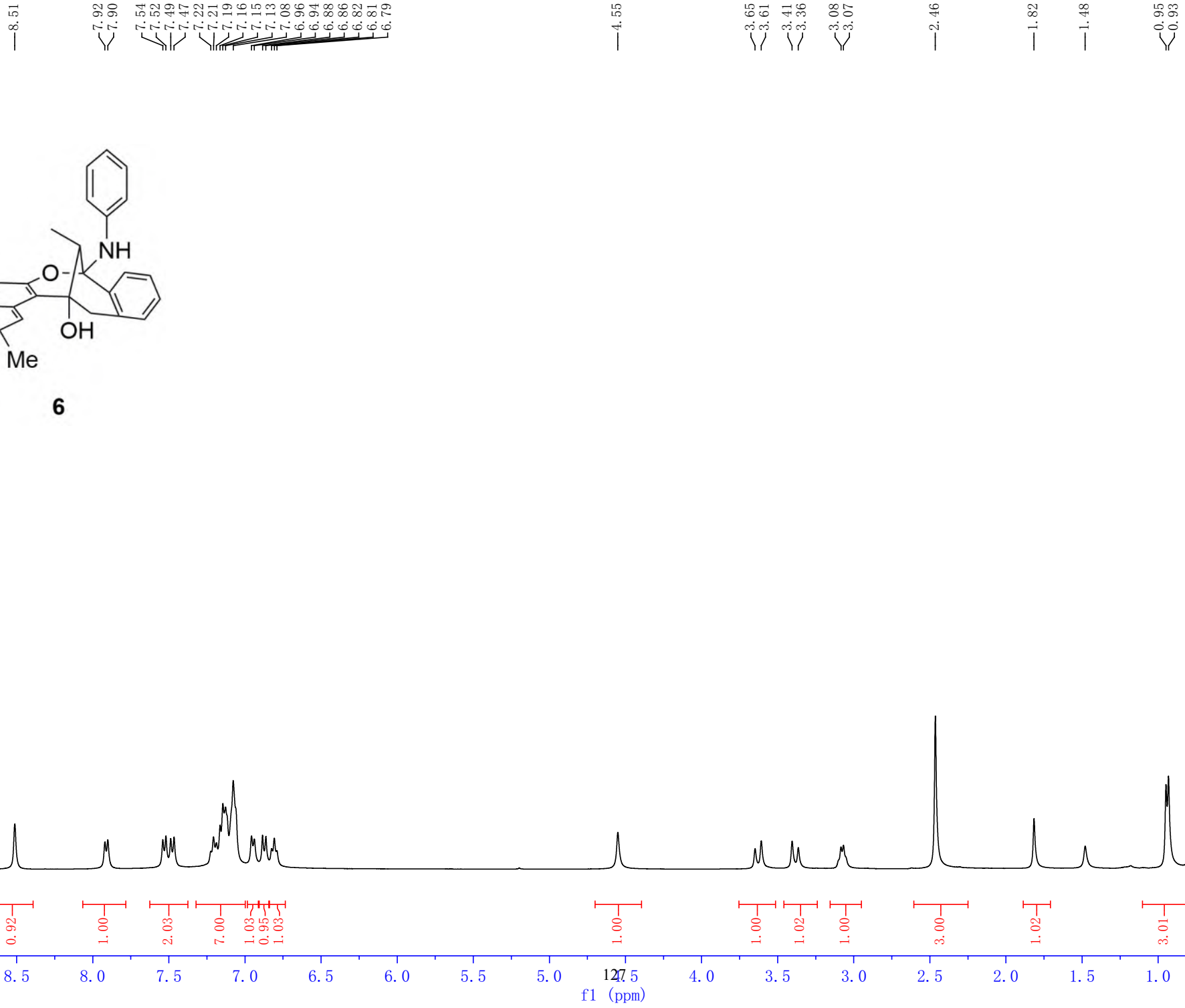

8.82
8.80
8.02
8.00
7.73
7.71
7.63
7.61
7.51
7.49
7.47
7.35
7.33
7.31
7.29
7.26
7.25
7.23
7.21
7.19
7.17
7.15
7.05
7.03
7.01
6.92
6.90
6.88
4.65
3.70
3.66
3.47
3.43
3.21
3.19
3.18
3.16
1.98
1.56
1.04
1.02
NH
O-
OH
5
1.00
0.99
0.96
1.01
1.01
1.94
5.02
2.02
1.03
1.00
1.00
1.02
1.01
1.01
3.04
9.5
9.0
8.5
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
f1 (ppm)

150.21
144.29
134.91
134.55
131.36
130.52
130.13
129.20
129.09
129.04
128.79
127.76
126.13
125.73
125.34
123.09
120.30
119.28
118.99
117.79
92.32
77.32
77.00
76.68
73.41
40.63
38.39
8.25



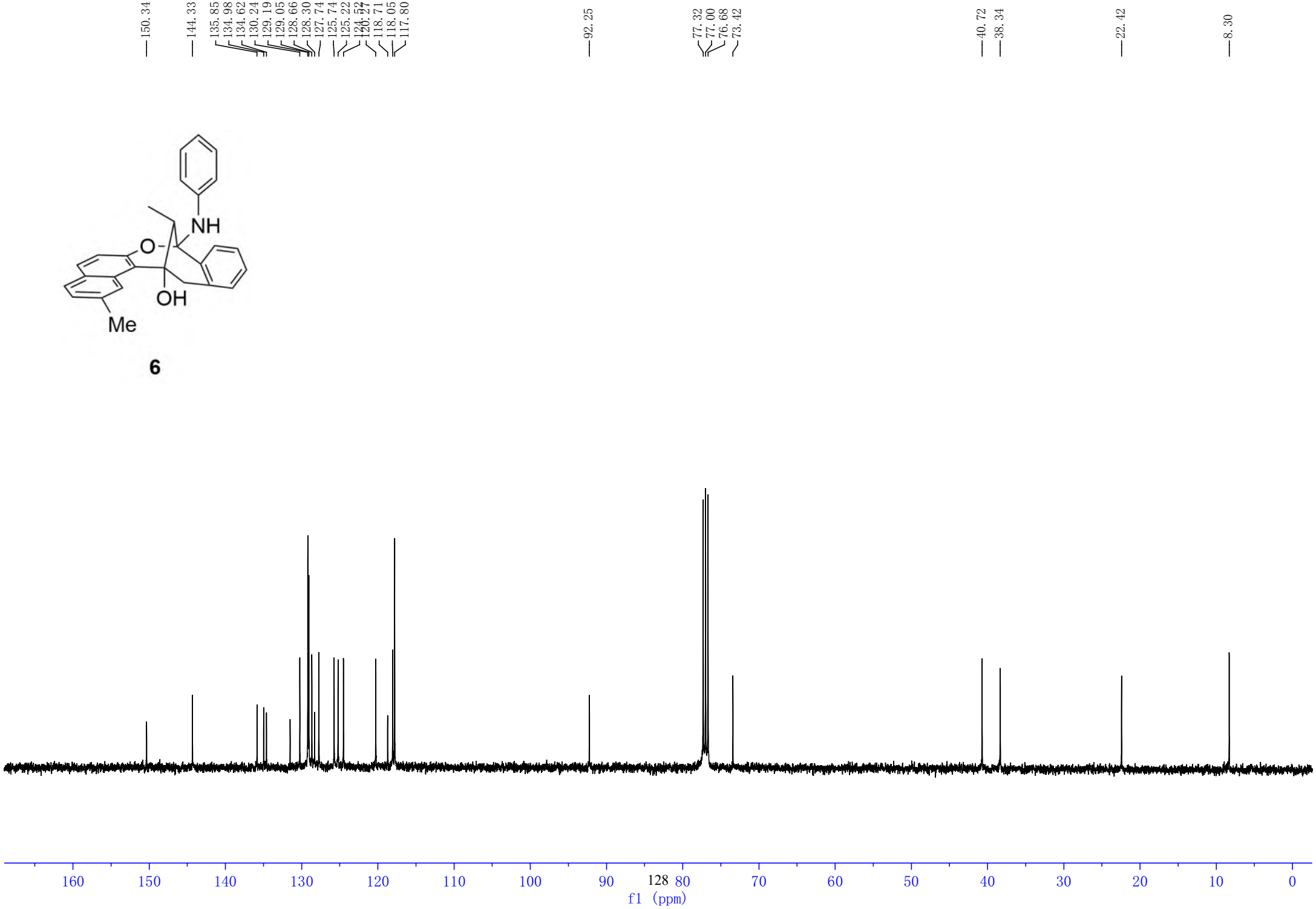
5

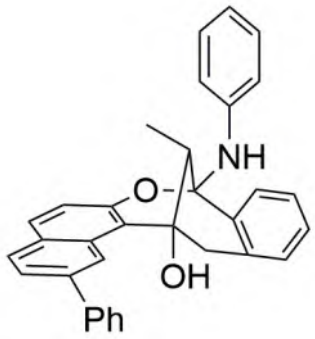



8.51
7.92
7.90
7.54
7.52
7.49
7.47
7.22
7.21
7.19
7.16
7.15
7.13
7.08
6.96
6.94
6.88
6.86
6.82
6.81
6.79
4.55
3.65
3.61
3.41
3.36
3.08
3.07
2.46
1.82
1.48
0.95
0.93
NH
O
OH
Me
6
0.92
1.00
2.03
7.00
1.03
0.95
1.03
1.00
1.00
1.02
1.00
3.00
1.02
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

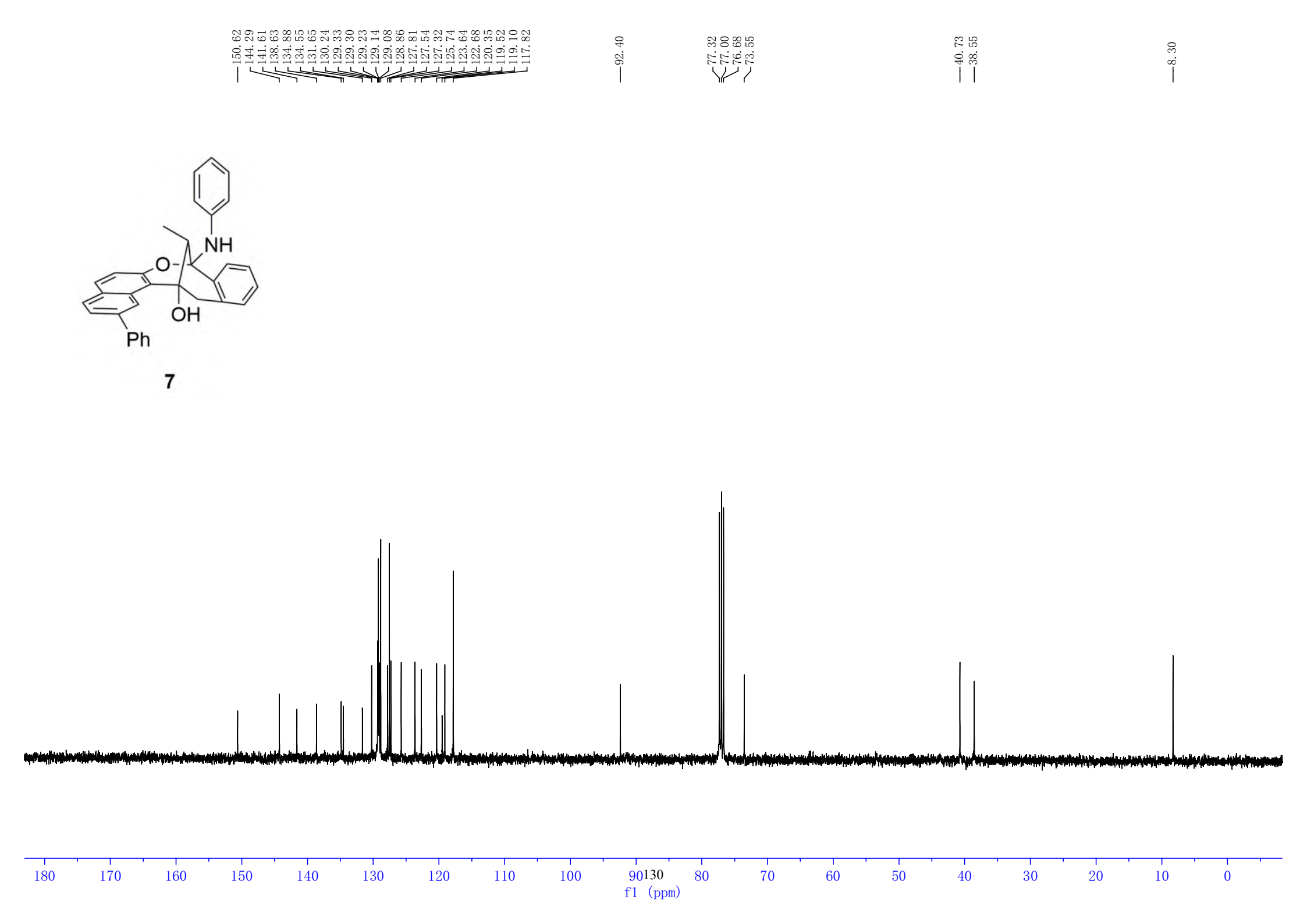
NH
O
OH
Me

6


150.34
144.33
135.85
134.98
134.62
130.24
129.19
129.05
128.66
128.30
127.74
125.74
125.22
124.52
118.71
118.05
117.80
92.25
77.32
77.00
76.68
73.42
40.72
38.34
22.42
8.30
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

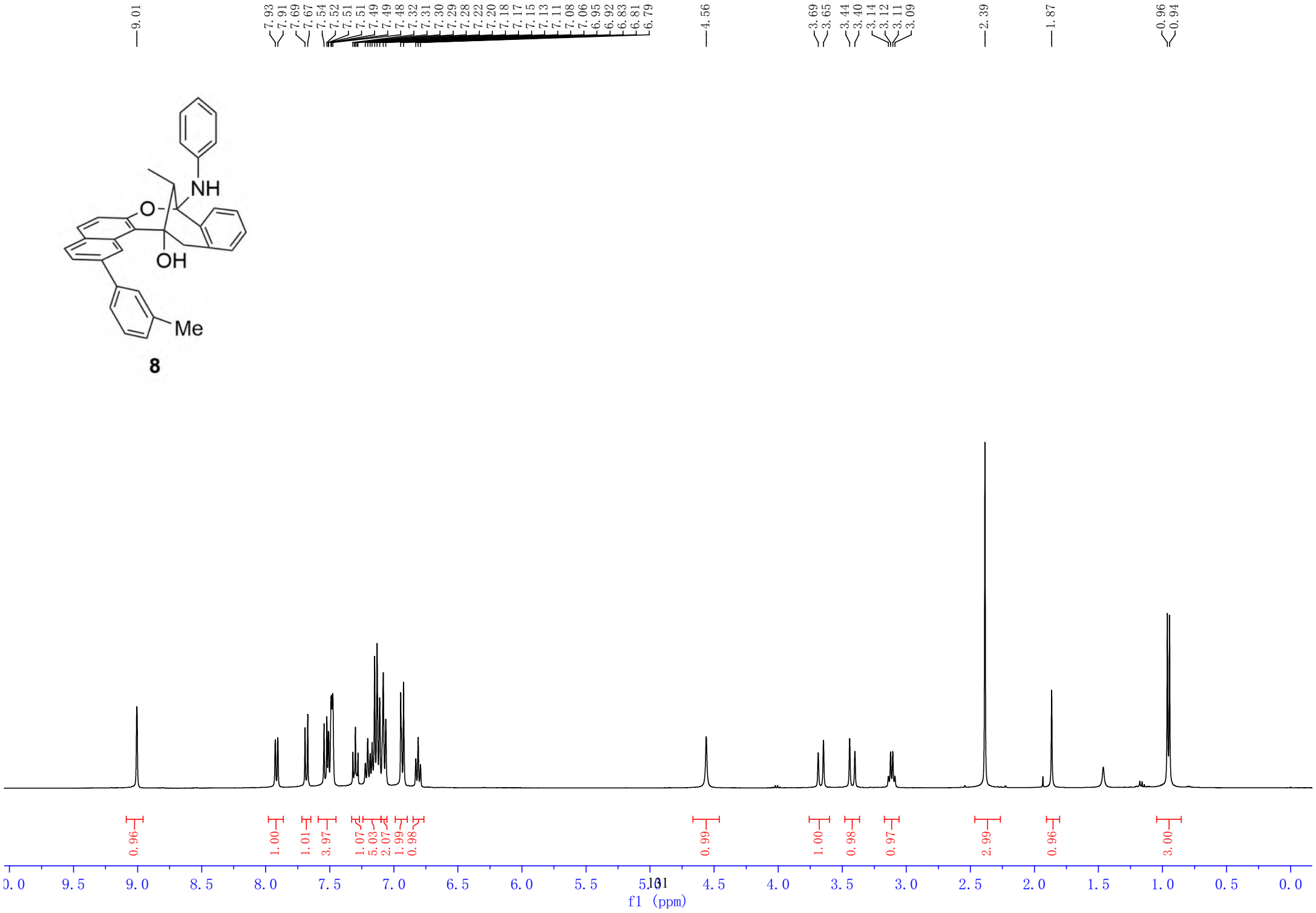


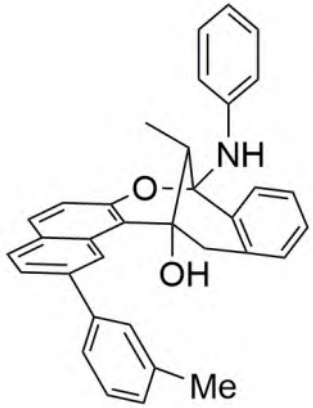
7


150.62
144.29
141.61
138.63
134.88
134.55
131.65
130.24
129.33
129.30
129.23
129.14
129.08
128.86
127.81
127.54
127.32
125.74
123.64
122.68
120.35
119.52
119.10
117.82
92.40
77.32
77.00
76.68
73.55
40.73
38.55
8.30
NH
O
OH
Ph
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

NH
O
OH
Me

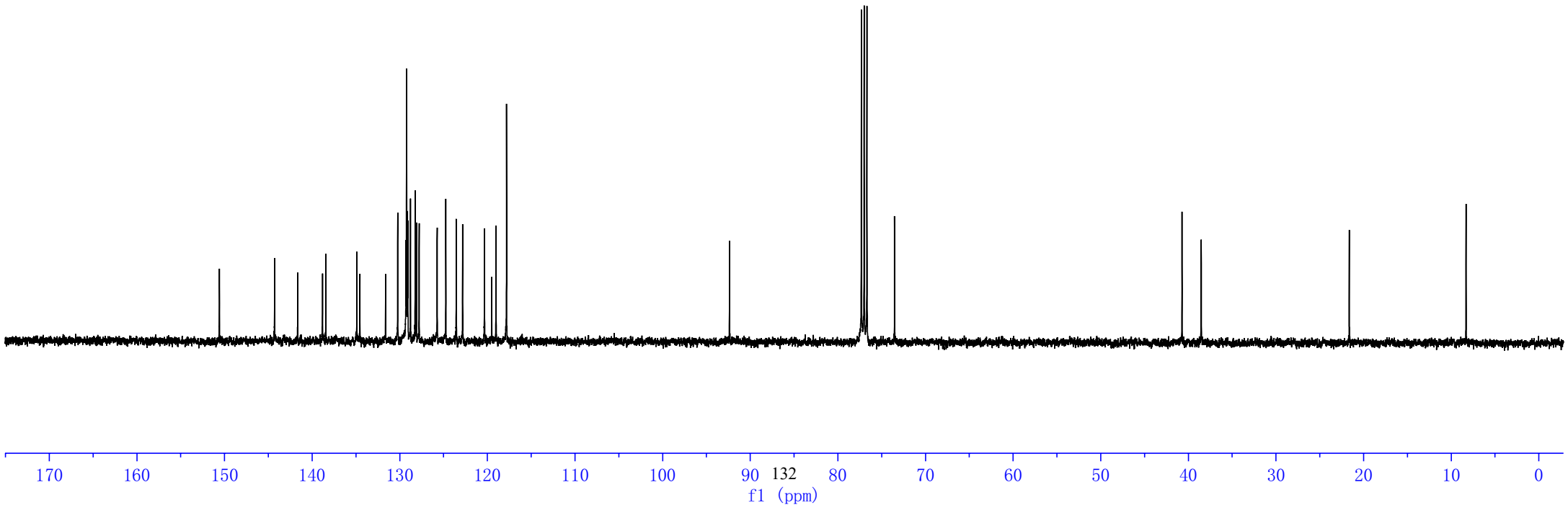
8

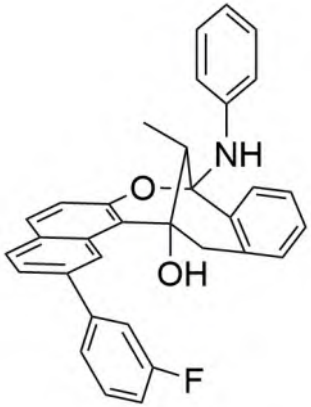

9.01
7.93
7.91
7.69
7.67
7.54
7.52
7.51
7.51
7.49
7.49
7.48
7.32
7.31
7.30
7.29
7.28
7.22
7.20
7.18
7.17
7.15
7.13
7.11
7.08
7.06
6.95
6.92
6.83
6.81
6.79
4.56
3.69
3.65
3.44
3.40
3.14
3.12
3.11
3.09
2.39
1.87
0.96
0.94
0.96
1.00
1.01
3.97
1.07
5.03
2.07
1.99
0.98
0.99
1.00
0.98
0.97
2.99
0.96
3.00
f1 (ppm)



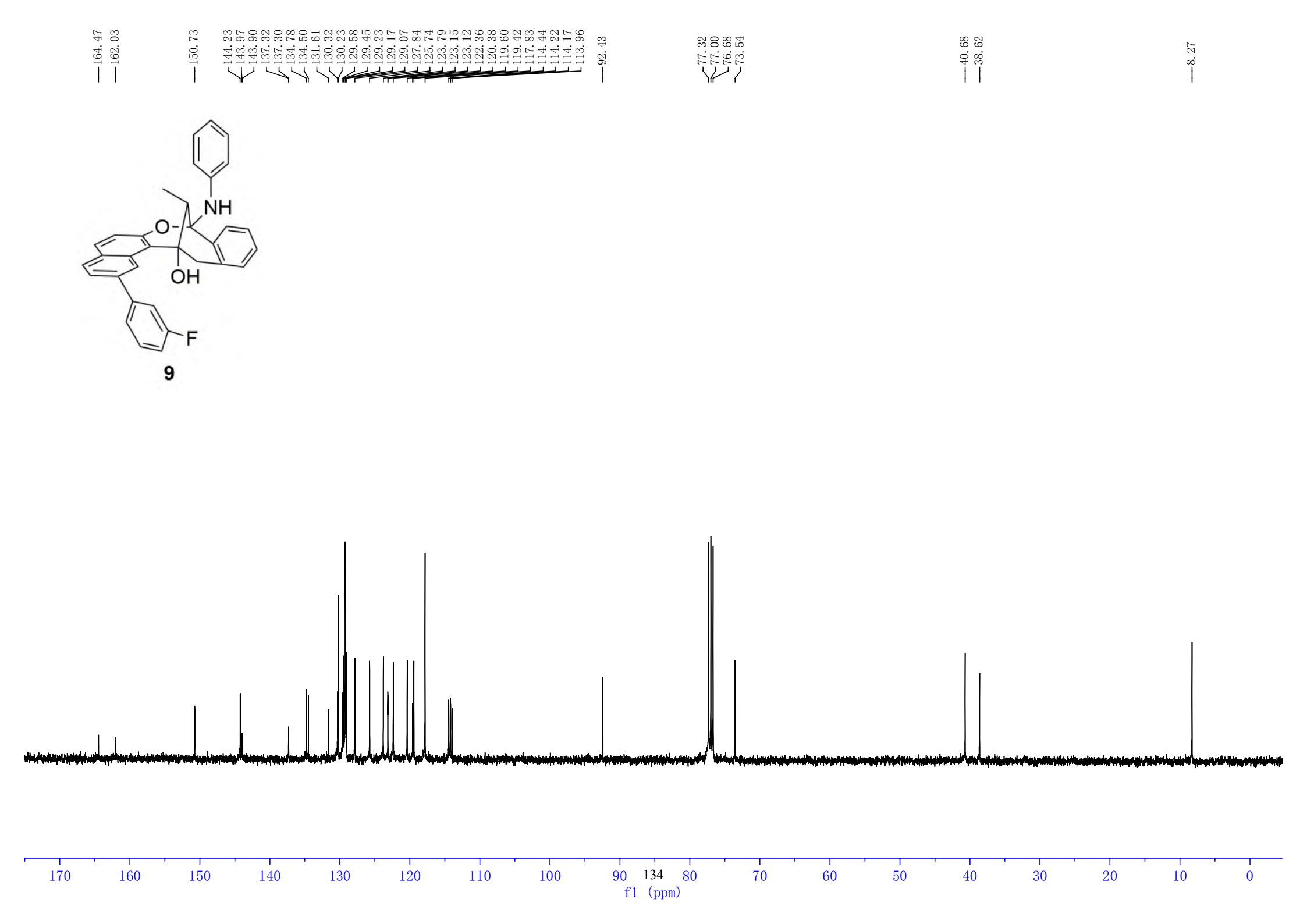
8

150.59
144.29
141.65
138.81
138.43
134.90
134.55
131.62
130.24
129.30
129.22
129.12
129.07
128.78
128.25
128.09
127.79
125.73
124.75
123.55
122.83
120.33
119.50
119.01
117.82
92.38
77.32
77.00
76.68
73.53
40.72
38.53
21.64
8.31



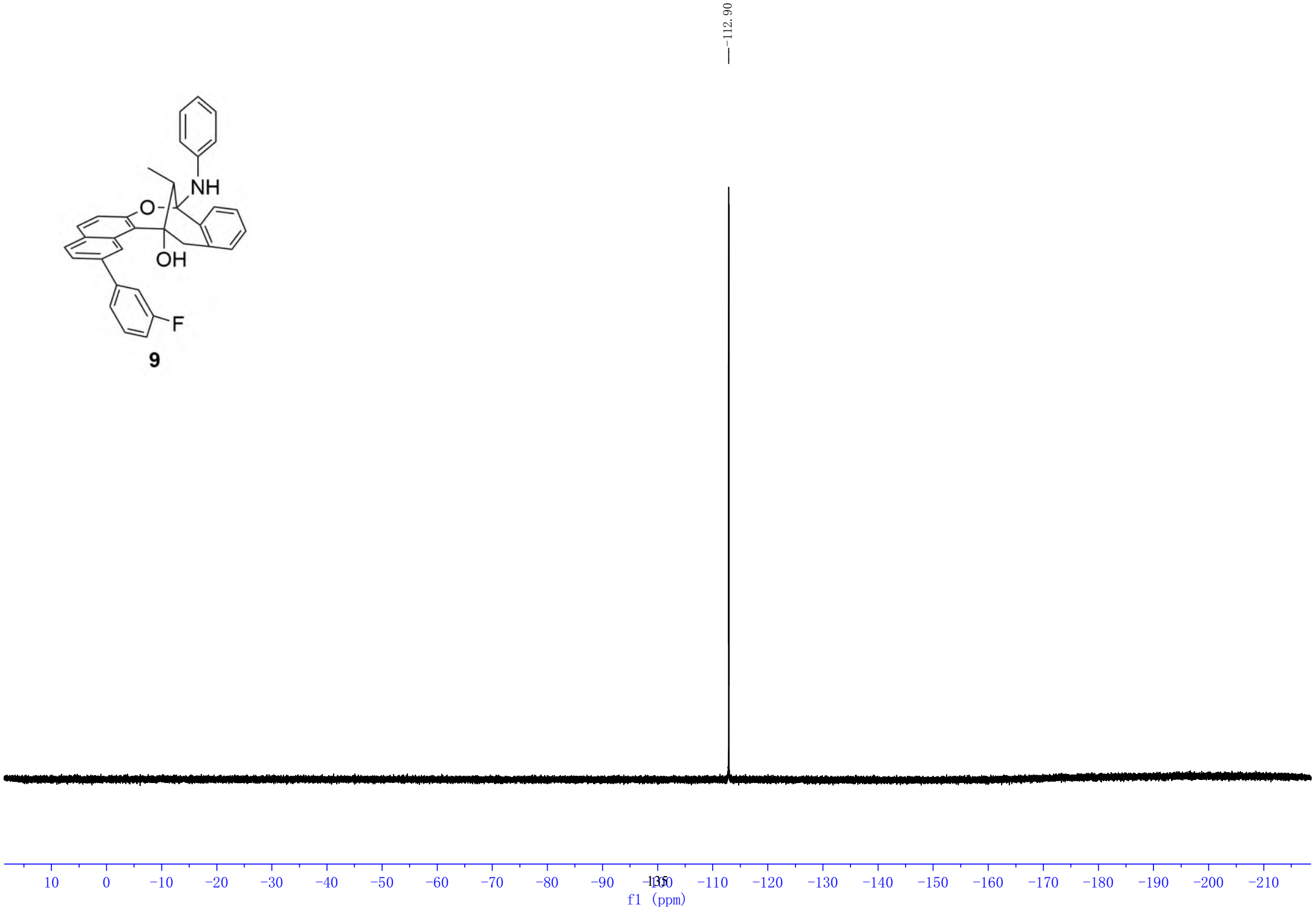


9


164.47
162.03
150.73
144.23
143.97
143.90
137.32
137.30
134.78
134.50
131.61
130.32
130.23
129.58
129.45
129.23
129.17
129.07
127.84
125.74
123.79
123.15
123.12
122.36
120.38
119.60
119.42
117.83
114.44
114.22
114.17
113.96
92.43
77.32
77.00
76.68
73.54
40.68
38.62
8.27
NH
O
OH
F
9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

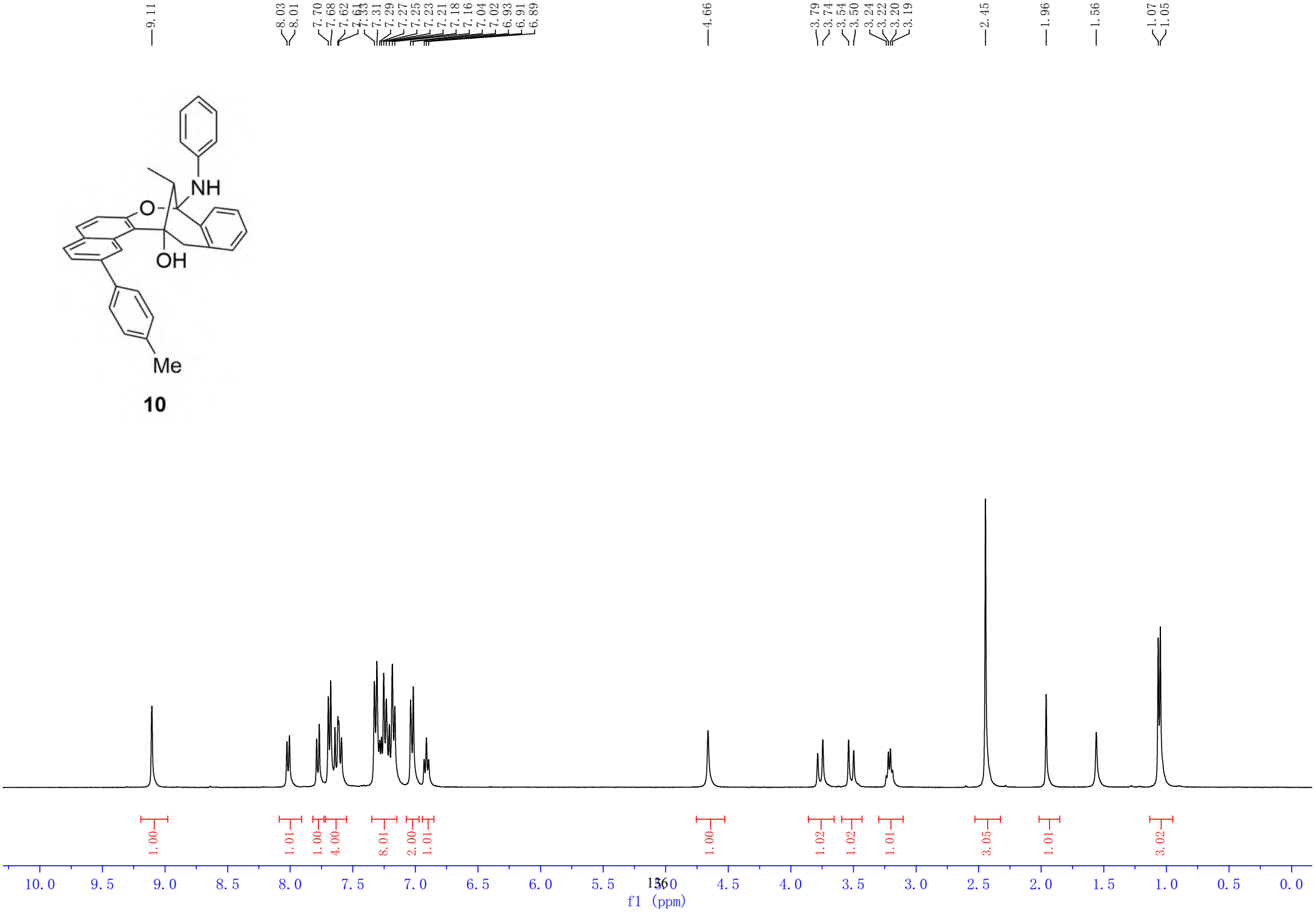
NH
O
OH
F

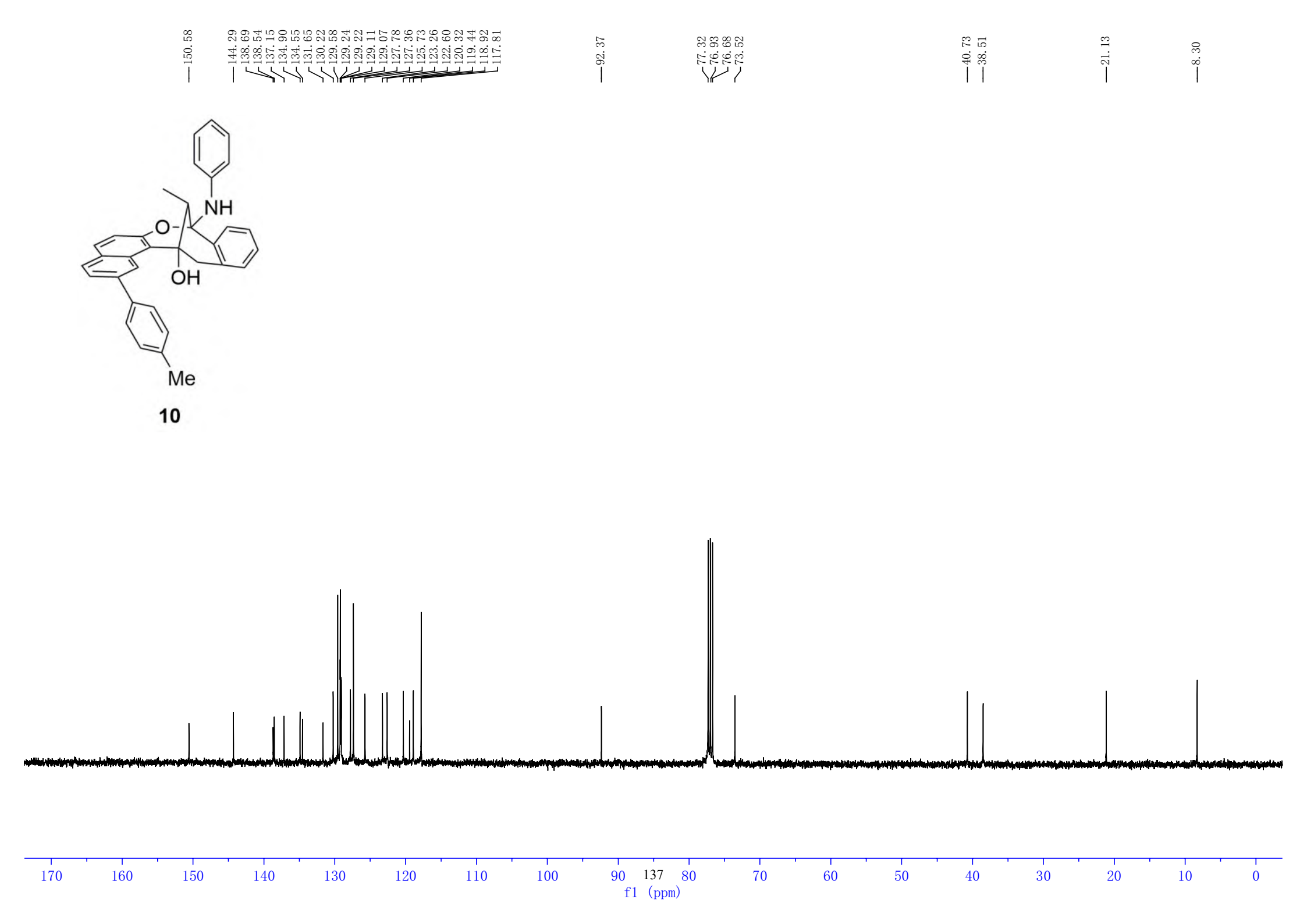
9

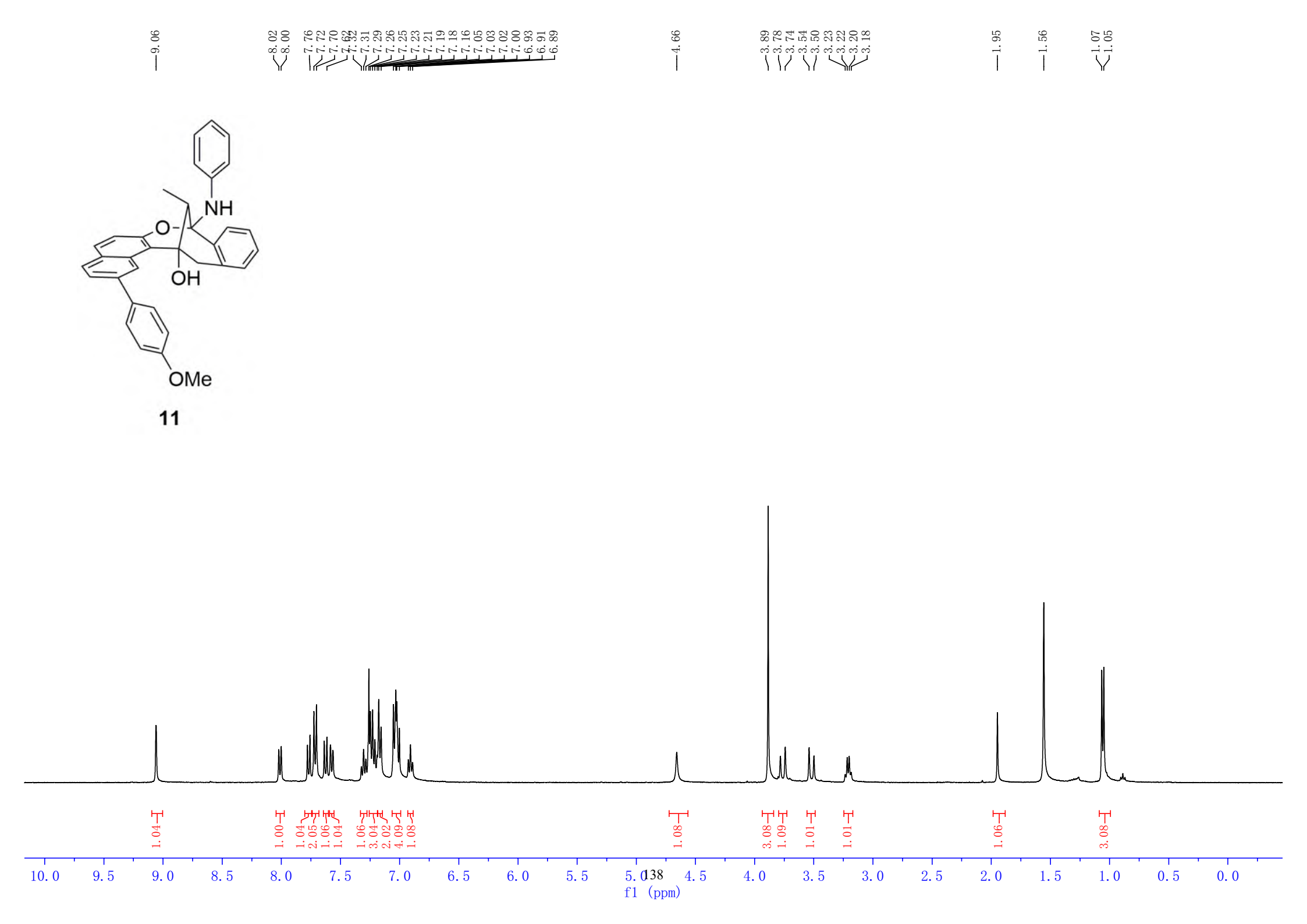

-112.90
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

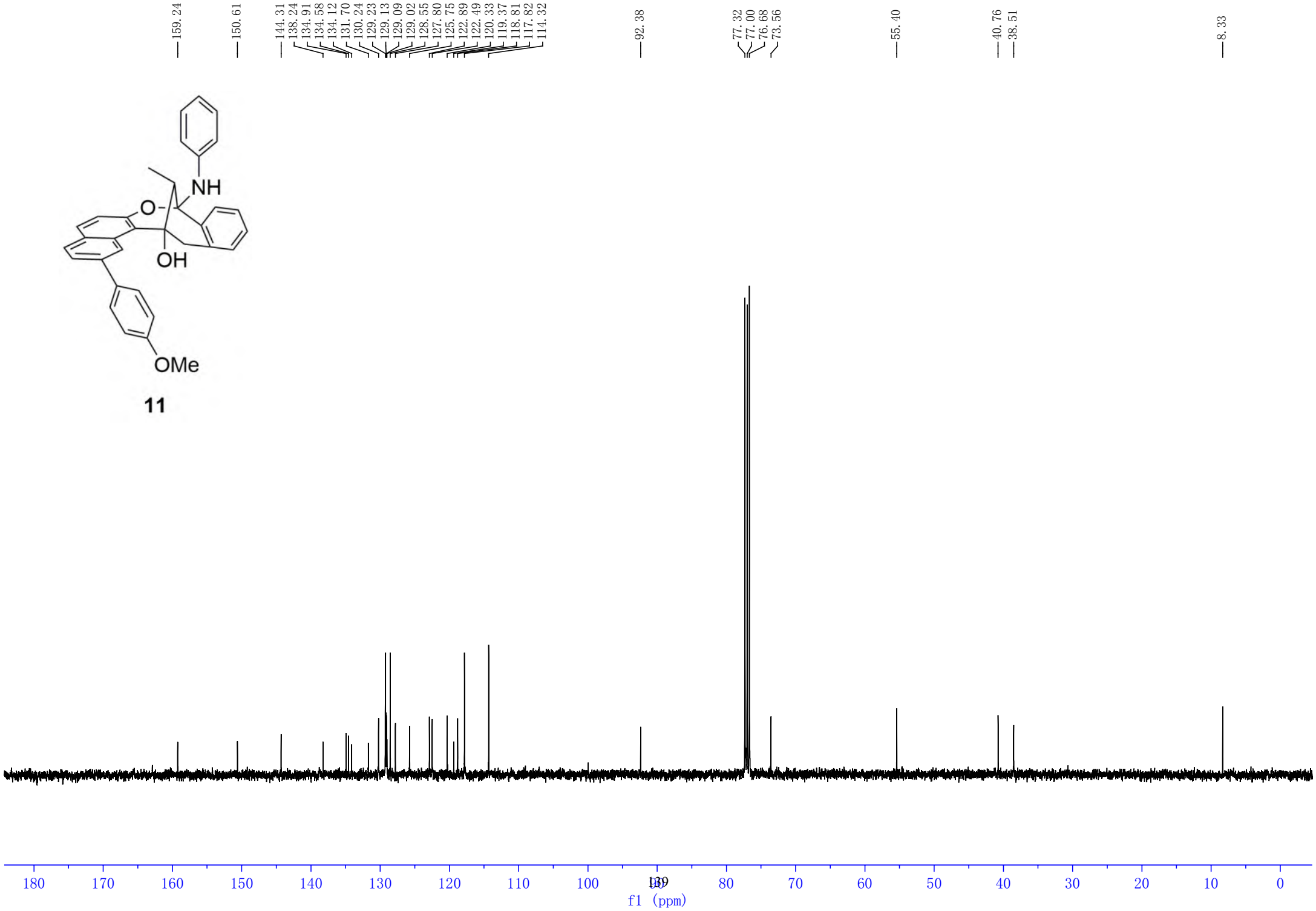
NH
O
OH
Me

10


9.11
8.03
8.01
7.70
7.68
7.62
7.61
7.33
7.31
7.29
7.27
7.25
7.23
7.21
7.18
7.16
7.04
7.02
6.93
6.91
6.89
4.66
3.79
3.74
3.54
3.50
3.24
3.22
3.20
3.19
2.45
1.96
1.56
1.07
1.05
1.00
1.01
1.00
4.00
8.01
2.00
1.01
1.00
1.02
1.02
1.01
3.05
1.01
3.02
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
f1 (ppm)

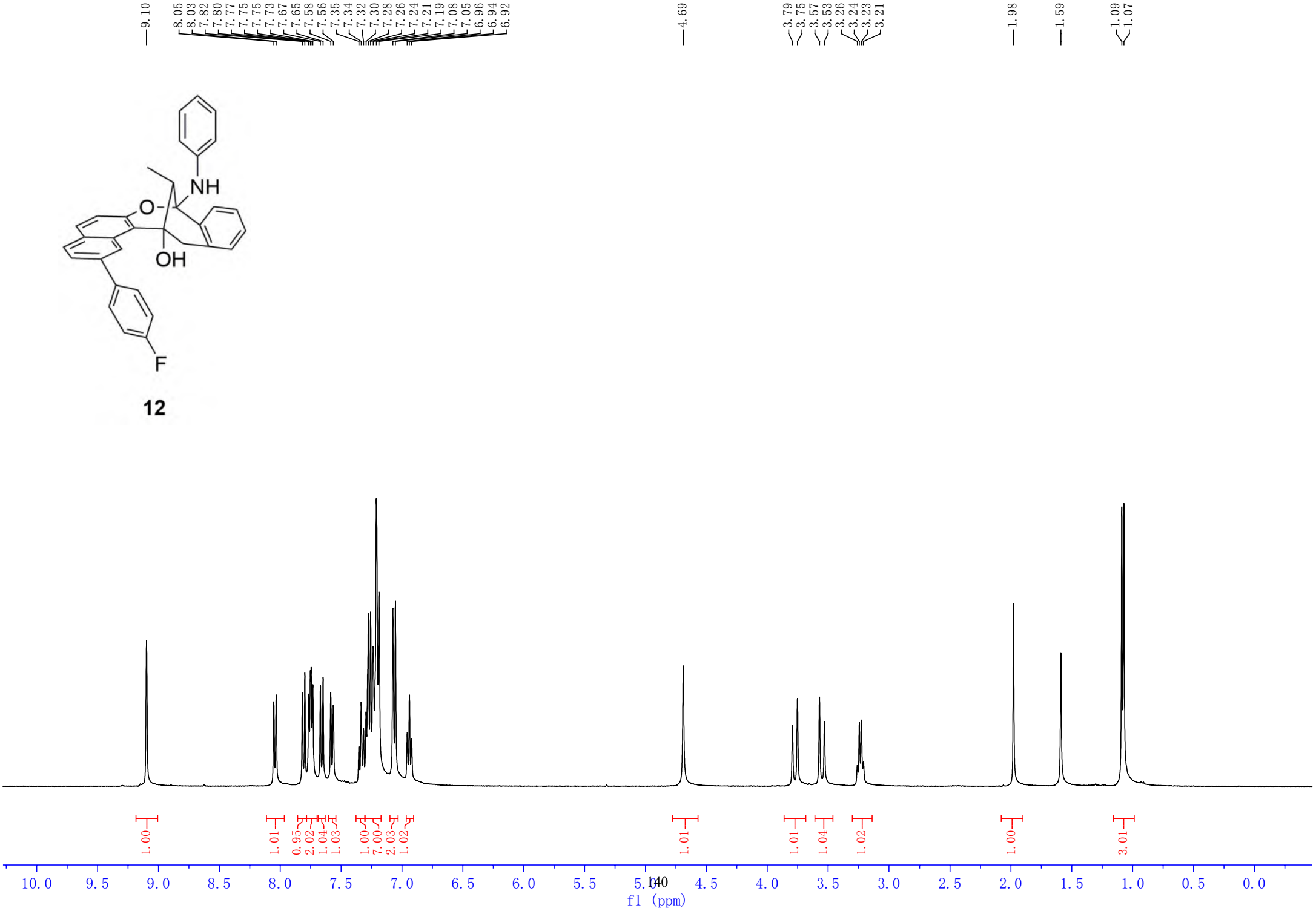

150.58
144.29
138.69
138.54
137.15
134.90
134.55
131.65
130.22
129.58
129.24
129.22
129.11
129.07
127.78
127.36
125.73
123.26
122.60
120.32
119.44
118.92
117.81
92.37
77.32
76.93
76.68
73.52
40.73
38.51
21.13
8.30
NH
O
OH
Me
10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

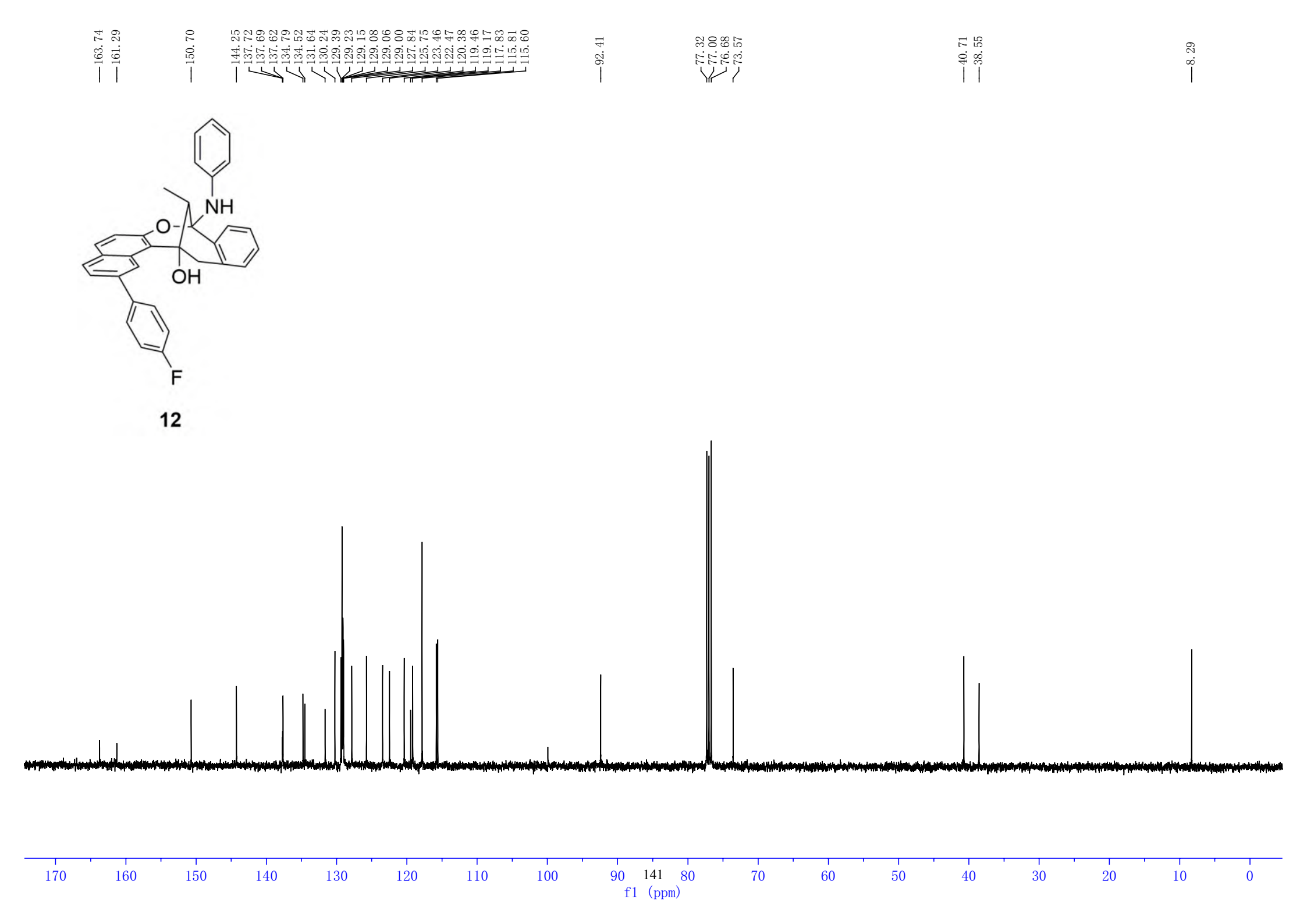

9.06
8.02
8.00
7.76
7.72
7.70
7.62
7.32
7.31
7.29
7.26
7.25
7.23
7.21
7.19
7.18
7.16
7.05
7.03
7.02
7.00
6.93
6.91
6.89
4.66
3.89
3.78
3.74
3.54
3.50
3.23
3.22
3.20
3.18
1.95
1.56
1.07
1.05
NH
O
OH
OMe
11
1.04
1.00
1.04
2.05
1.06
1.04
1.06
3.04
2.02
4.09
1.08
1.08
3.08
1.09
1.01
1.01
1.06
3.08
10.0
9.5
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
f1 (ppm)


159.24
150.61
144.31
138.24
134.91
134.58
134.12
131.70
130.24
129.23
129.13
129.09
129.02
128.55
127.80
125.75
122.89
122.49
120.33
119.37
118.81
117.82
114.32
92.38
77.32
77.00
76.68
73.56
55.40
40.76
38.51
8.33
NH
O
OH
OMe
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

NH
O
OH
F

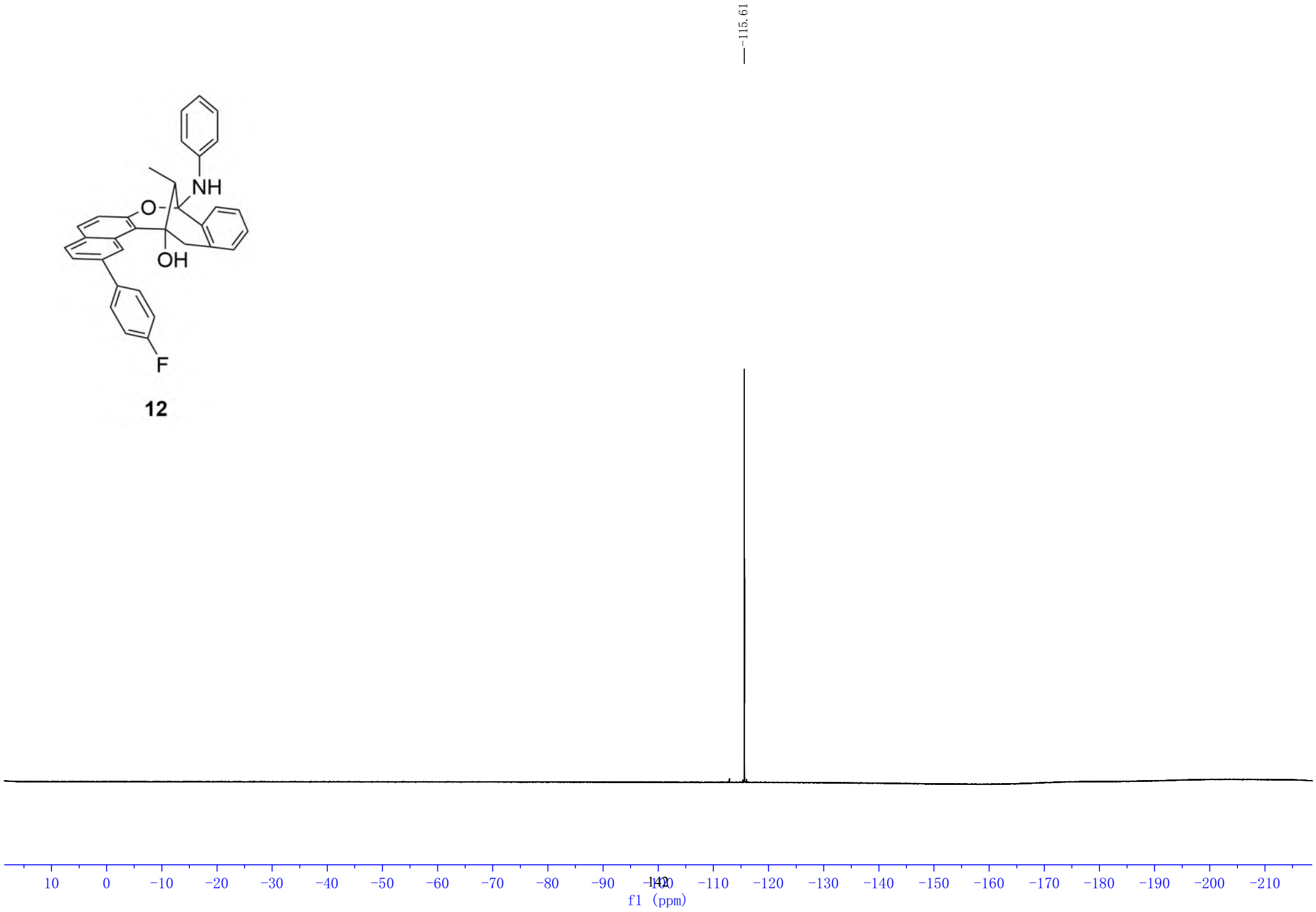
12


9.10
8.05
8.03
7.82
7.80
7.77
7.75
7.75
7.73
7.67
7.65
7.58
7.56
7.35
7.34
7.32
7.30
7.28
7.26
7.24
7.21
7.19
7.08
7.05
6.96
6.94
6.92
4.69
3.79
3.75
3.57
3.53
3.26
3.24
3.23
3.21
1.98
1.59
1.09
1.07
1.00
1.01
0.95
2.02
1.04
1.03
1.00
7.00
2.03
1.02
1.01
1.01
1.04
1.02
1.00
3.01
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
f1 (ppm)


163.74
161.29
150.70
144.25
137.72
137.69
137.62
134.79
134.52
131.64
130.24
129.39
129.23
129.15
129.08
129.06
129.00
127.84
125.75
123.46
122.47
120.38
119.46
119.17
117.83
115.81
115.60
92.41
77.32
77.00
76.68
73.57
40.71
38.55
8.29
NH
O
OH
F
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

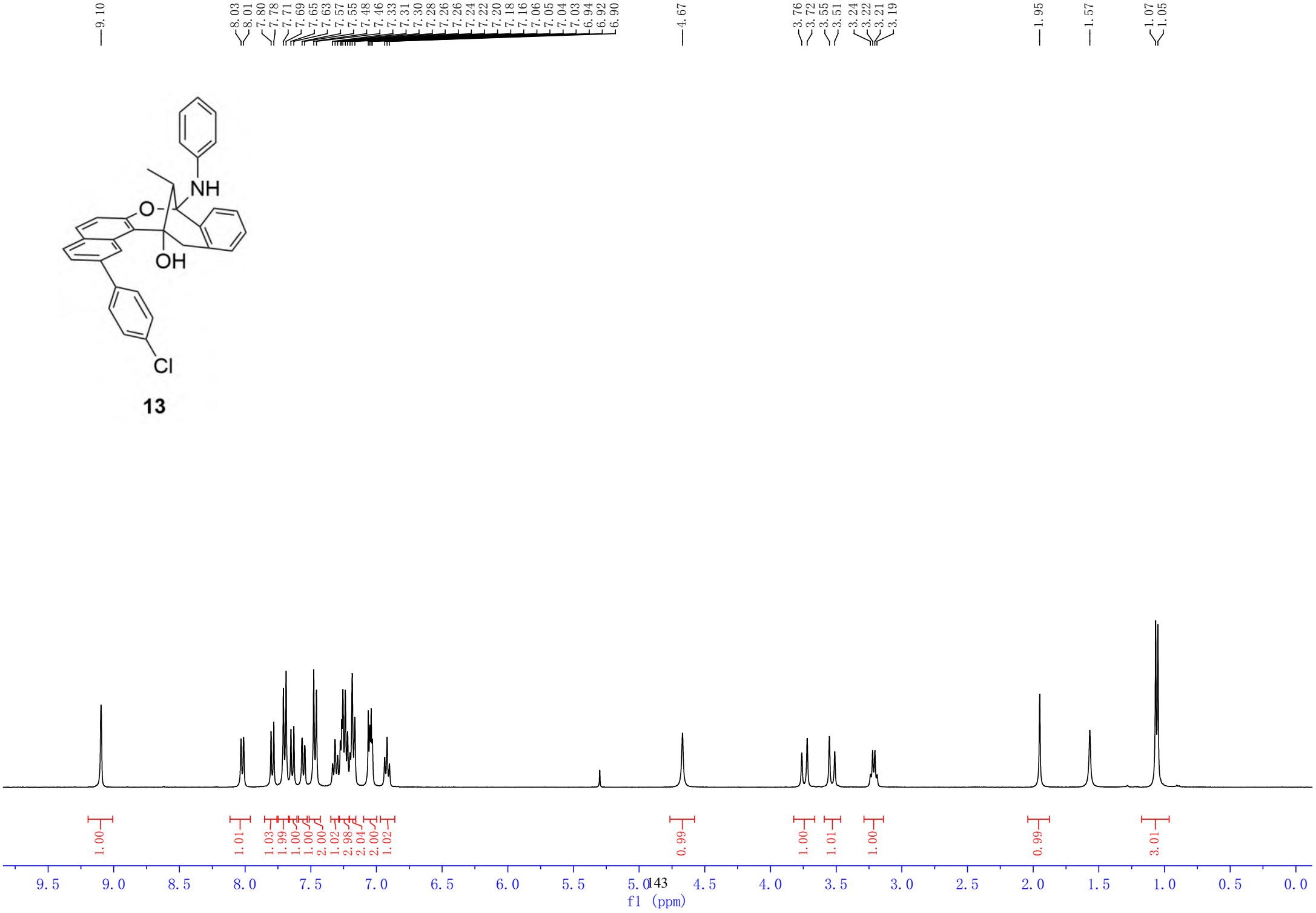
NH
O
OH
F

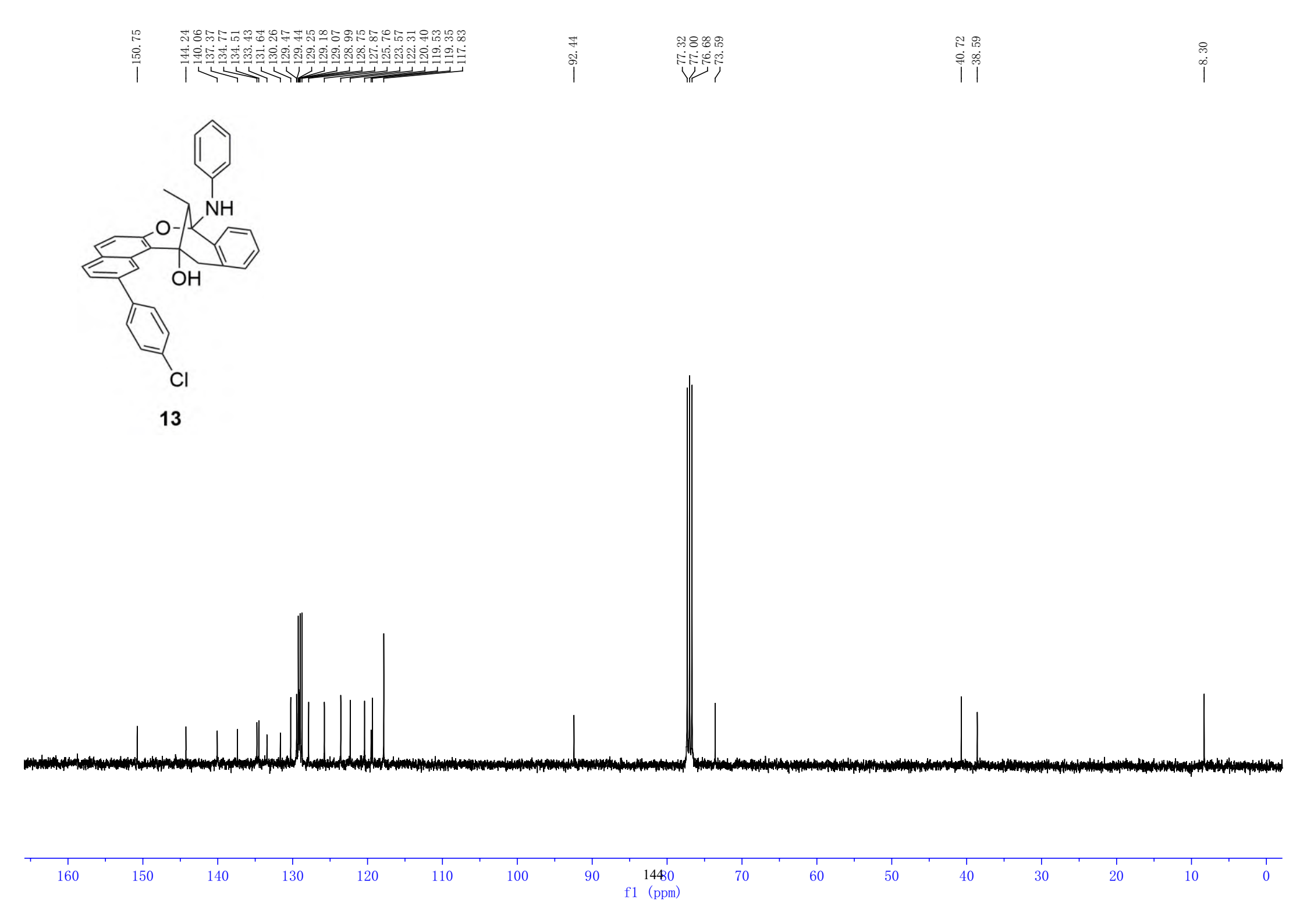
12


-115.61
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

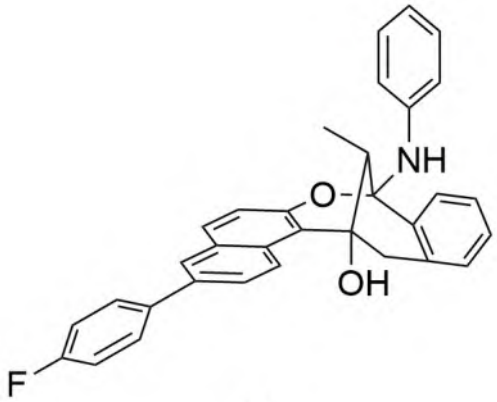
NH
O
OH
Cl

13

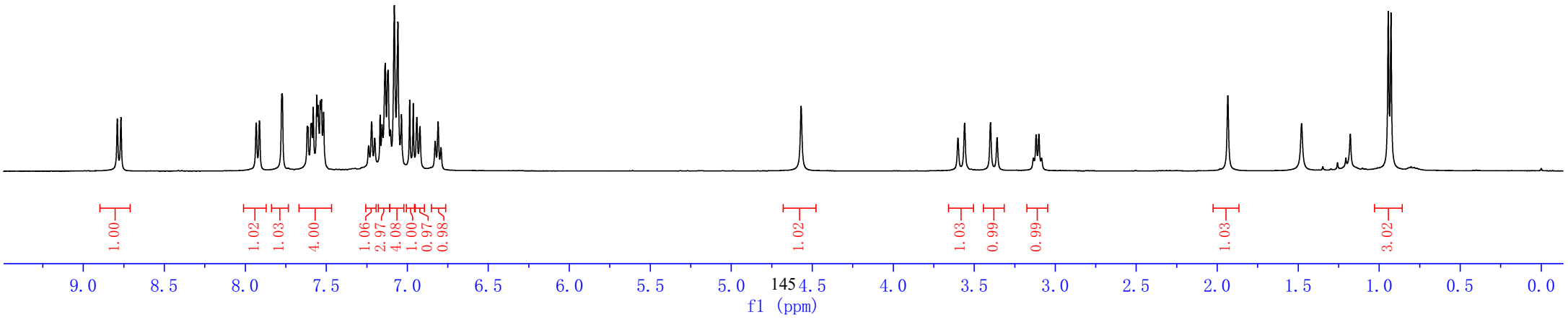

9.10
8.03
8.01
7.80
7.78
7.71
7.69
7.65
7.63
7.57
7.55
7.48
7.46
7.33
7.31
7.30
7.28
7.26
7.26
7.24
7.22
7.20
7.18
7.16
7.06
7.05
7.04
7.03
6.94
6.92
6.90
4.67
3.76
3.72
3.55
3.51
3.24
3.22
3.21
3.19
1.95
1.57
1.07
1.05
1.00
1.01
1.03
1.99
1.00
1.00
2.00
1.02
2.98
2.04
2.00
1.02
0.99
1.00
1.01
1.00
0.99
3.01
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
f1 (ppm)

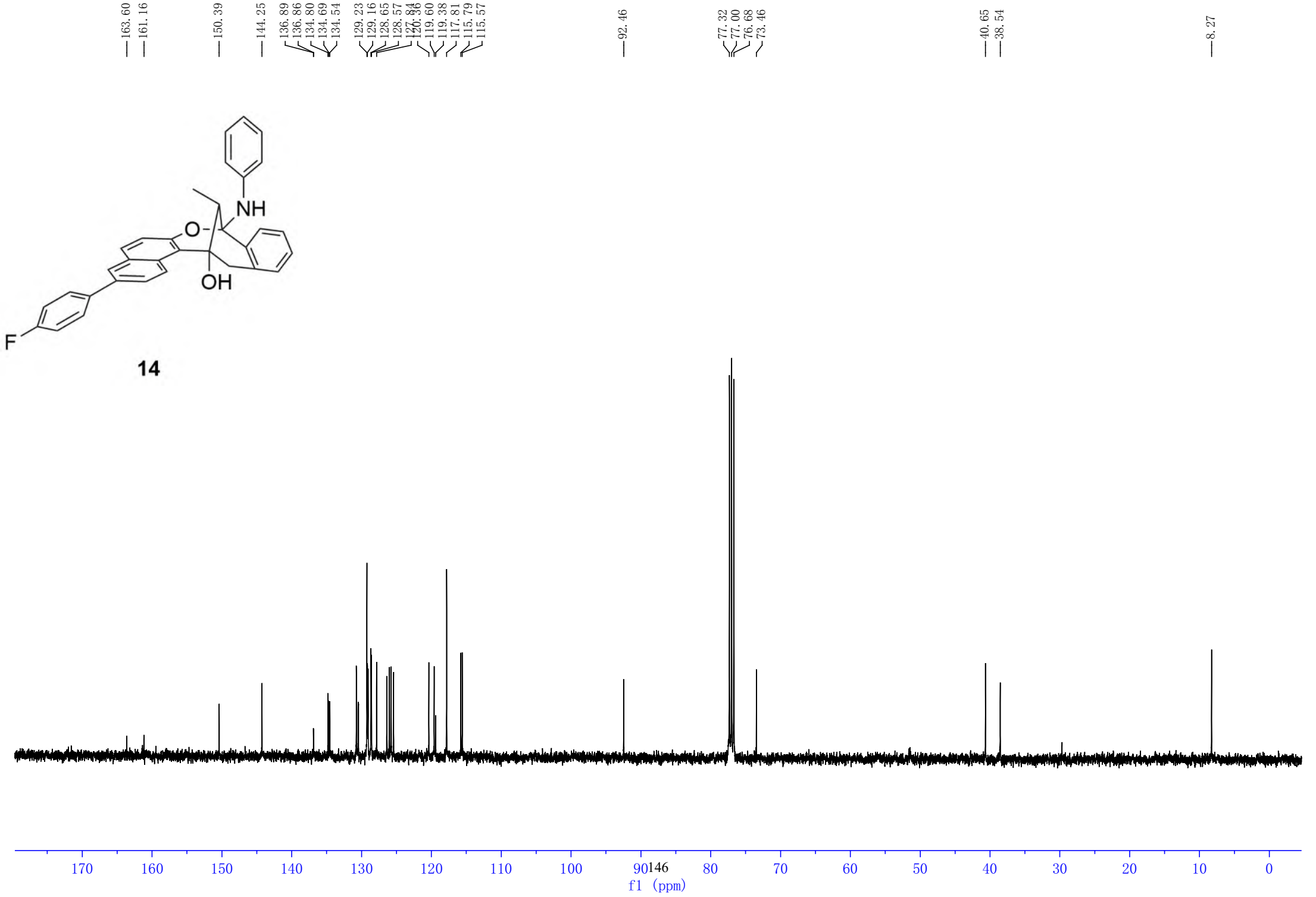

150.75
144.24
140.06
137.37
134.77
134.51
133.43
131.64
130.26
129.47
129.44
129.25
129.18
129.07
128.99
128.75
127.87
125.76
123.57
122.31
120.40
119.53
119.35
117.83
92.44
77.32
77.00
76.68
73.59
40.72
38.59
8.30
NH
O
OH
Cl
13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.79
8.77
7.93
7.91
7.77
7.77
7.62
7.60
7.59
7.58
7.56
7.55
7.54
7.53
7.52
7.22
7.20
7.17
7.16
7.14
7.12
7.10
7.08
7.06
7.04
6.99
6.96
6.94
6.92
6.83
6.81
6.79
4.57
3.60
3.56
3.40
3.36
3.13
3.12
3.10
3.08
1.93
1.48
0.94
0.93


NH
O
OH
F

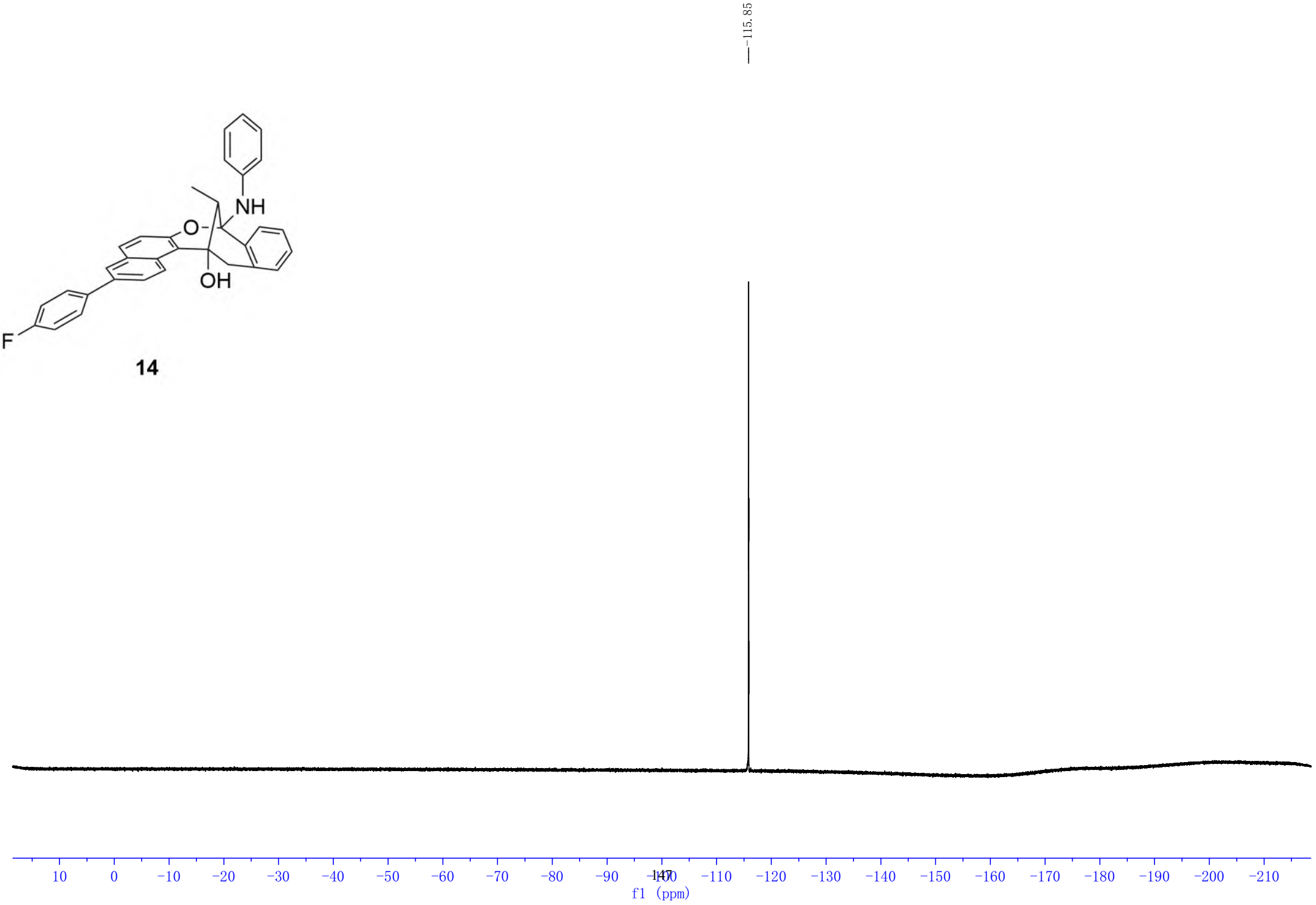
14

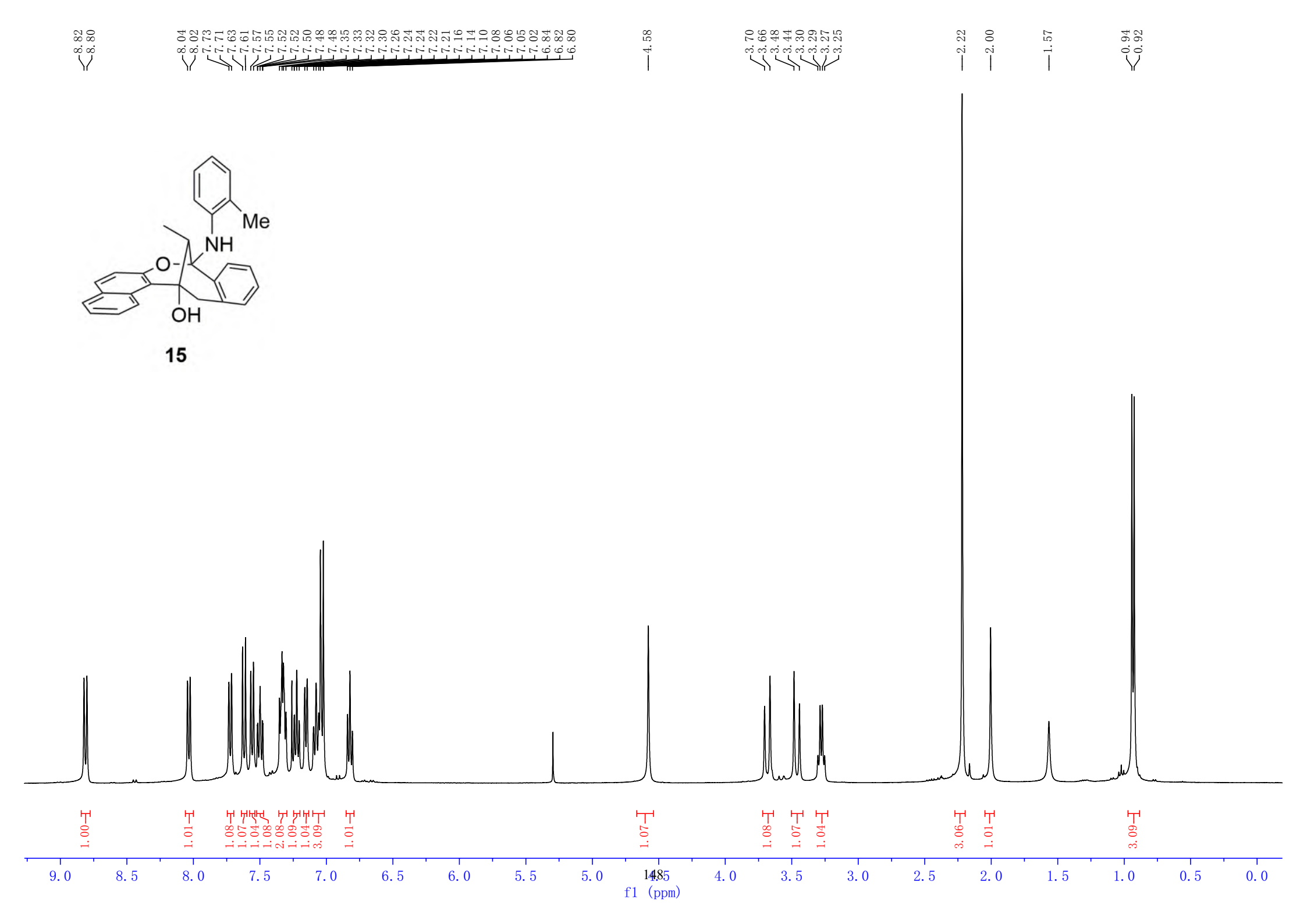

1.00
1.02
1.03
4.00
1.06
2.97
4.08
1.00
0.97
0.98
1.02
1.03
0.99
0.99
1.03
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.60
161.16
150.39
144.25
136.89
136.86
134.80
134.69
134.54
129.23
129.16
128.65
128.57
119.60
119.38
117.81
115.79
115.57
92.46
77.32
77.00
76.68
73.46
40.65
38.54
8.27
NH
O
OH
F
14
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

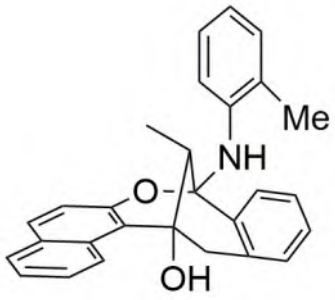
NH
O
OH
F

14

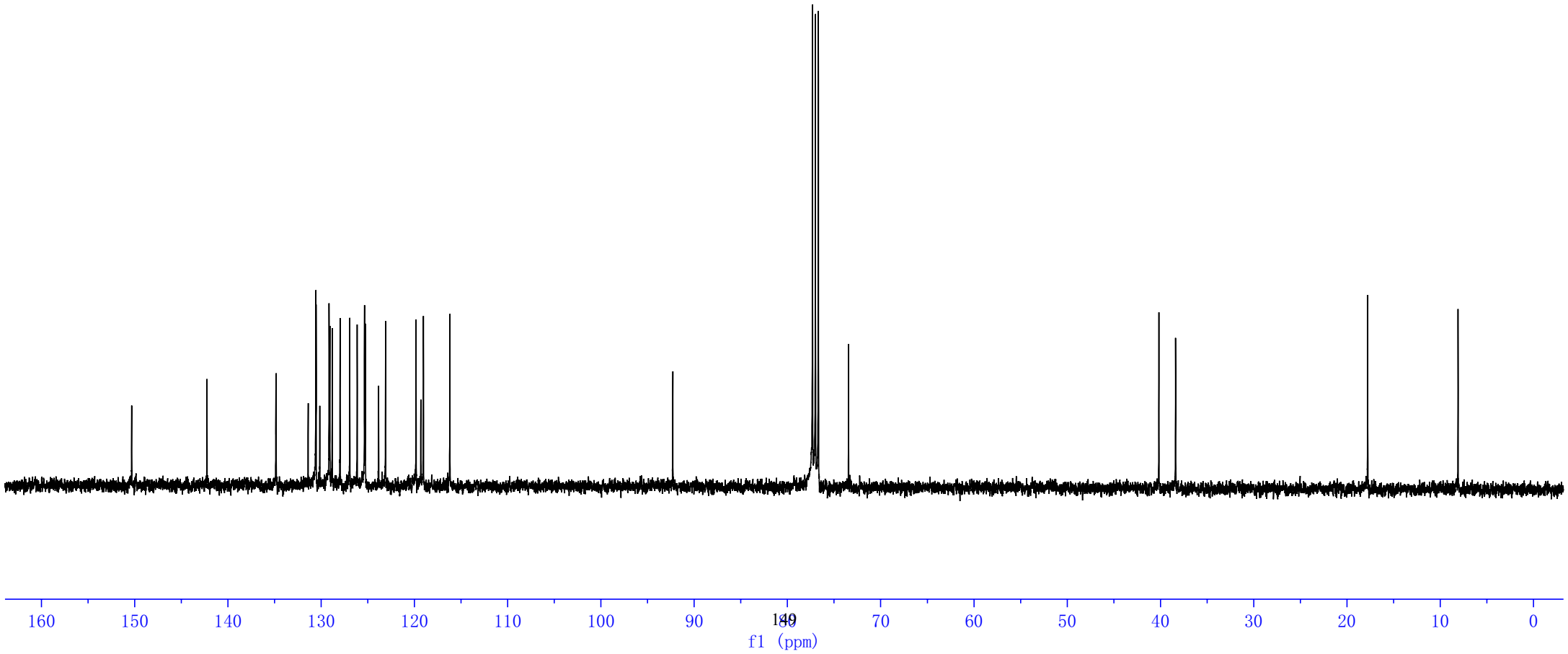

-115.85
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.82
8.80
8.04
8.02
7.73
7.71
7.63
7.61
7.57
7.55
7.52
7.52
7.50
7.48
7.48
7.35
7.33
7.32
7.30
7.26
7.24
7.24
7.22
7.21
7.16
7.14
7.10
7.08
7.06
7.05
7.02
6.84
6.82
6.80
4.58
3.70
3.66
3.48
3.44
3.30
3.29
3.27
3.25
2.22
2.00
1.57
0.94
0.92
Me
NH
O
OH
15
1.00
1.01
1.08
1.07
1.04
1.08
2.08
1.09
1.04
3.09
1.01
1.07
1.08
1.07
1.04
3.06
1.01
3.09
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
f1 (ppm)

150.32
142.24
134.86
134.83
131.40
130.58
130.54
130.15
129.15
129.07
128.81
127.97
126.93
126.14
125.35
125.27
123.84
123.10
119.83
119.32
119.04
116.20
92.29
77.32
77.00
76.68
73.45
40.17
38.38
17.78
8.09

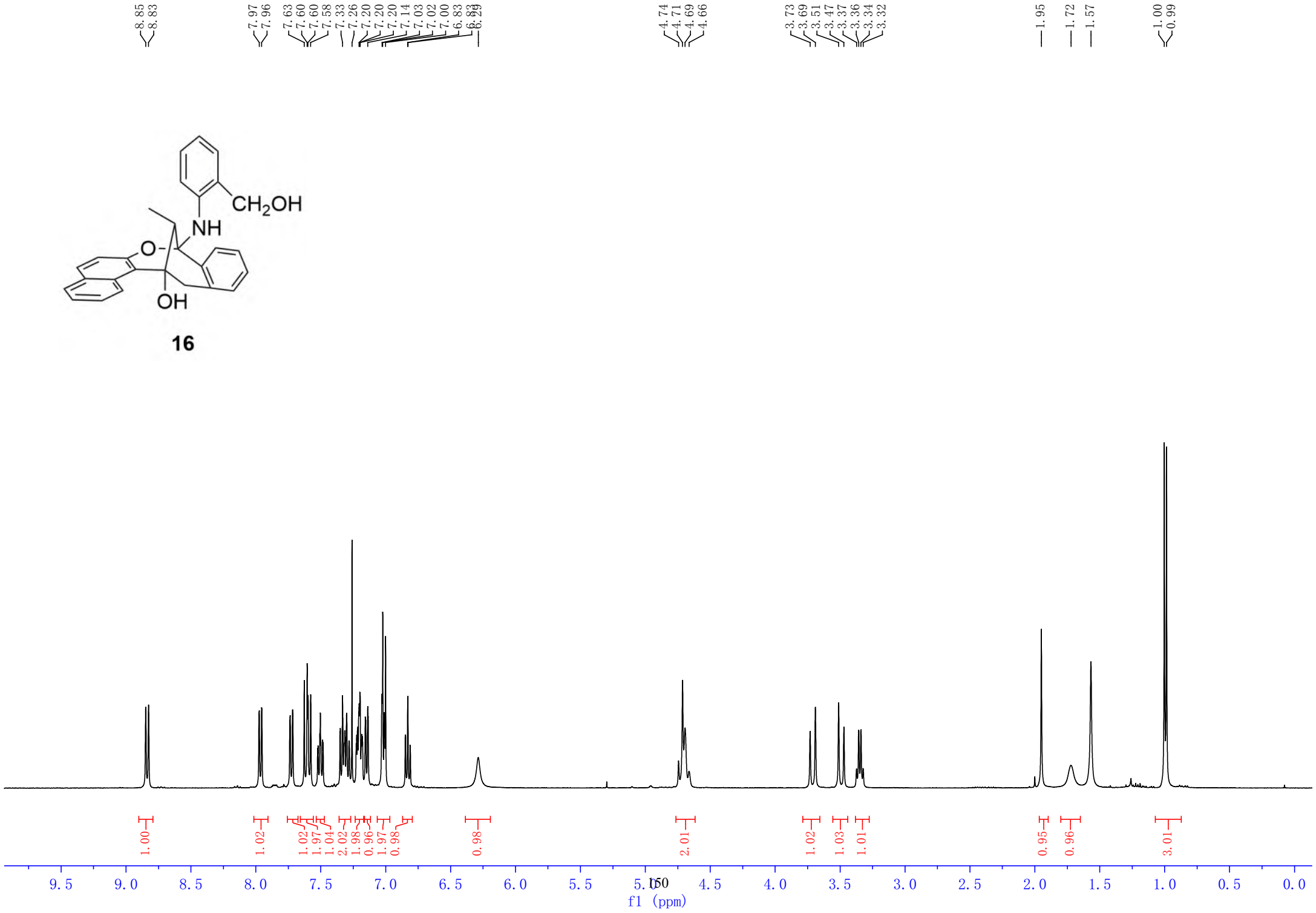


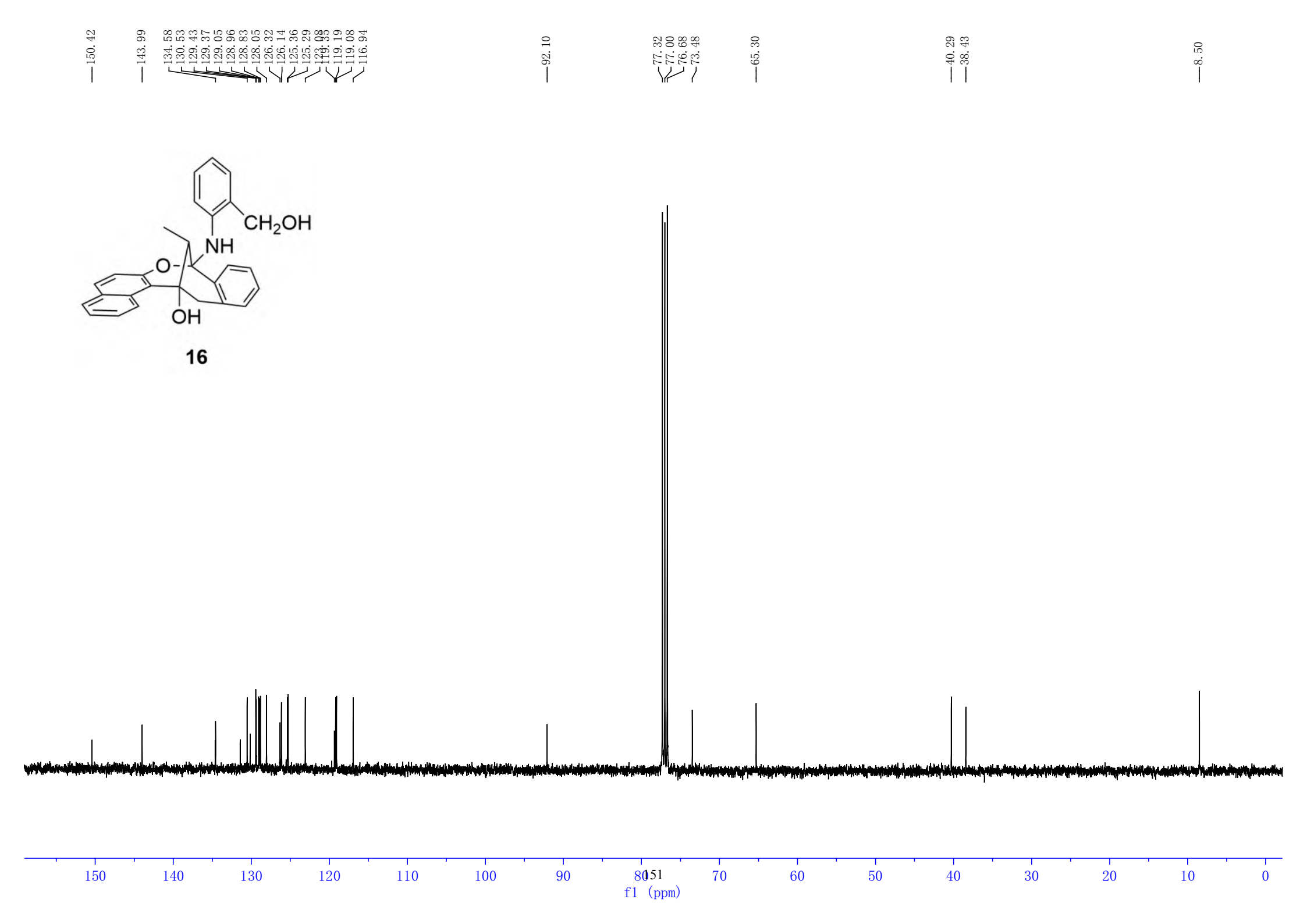
15

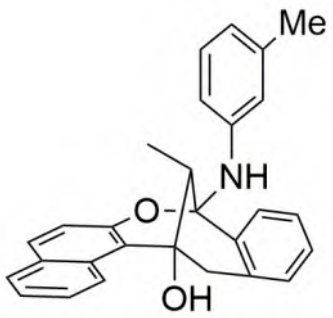


CH2OH
NH
O
OH

16


8.85
8.83
7.97
7.96
7.63
7.60
7.60
7.58
7.33
7.26
7.20
7.20
7.20
7.14
7.03
7.02
7.00
6.83
6.83
6.29
4.74
4.71
4.69
4.66
3.73
3.69
3.51
3.47
3.37
3.36
3.34
3.32
1.95
1.72
1.57
1.00
0.99
1.00
1.02
1.02
1.97
1.04
2.02
1.98
0.96
1.97
0.98
0.98
2.01
1.02
1.03
1.01
0.95
0.96
3.01
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
f1 (ppm)


150.42
143.99
134.58
130.53
129.43
129.37
129.05
128.96
128.83
128.05
126.32
126.14
125.36
125.29
123.08
119.35
119.19
119.08
116.94
92.10
77.32
77.00
76.68
73.48
65.30
40.29
38.43
8.50
CH2OH
NH
O
OH
16
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



17

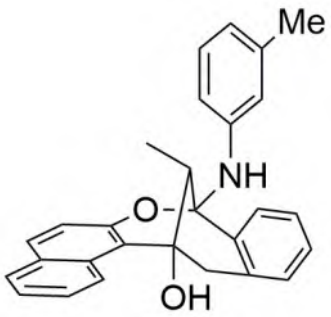
8.83 8.81 8.01 7.99 7.63 7.61 7.33 7.21 7.11 7.06 7.04 7.03 7.00 6.95 6.72 6.71 4.61 3.70 3.66 3.47 3.43 3.22 3.20 3.19 3.17 2.29 1.99 1.58 1.04 1.03

1.00 1.04 1.05 1.02 1.06 2.06 1.04 1.08 4.02 1.00 1.00 1.01 1.01 1.01 3.02 1.03 3.02

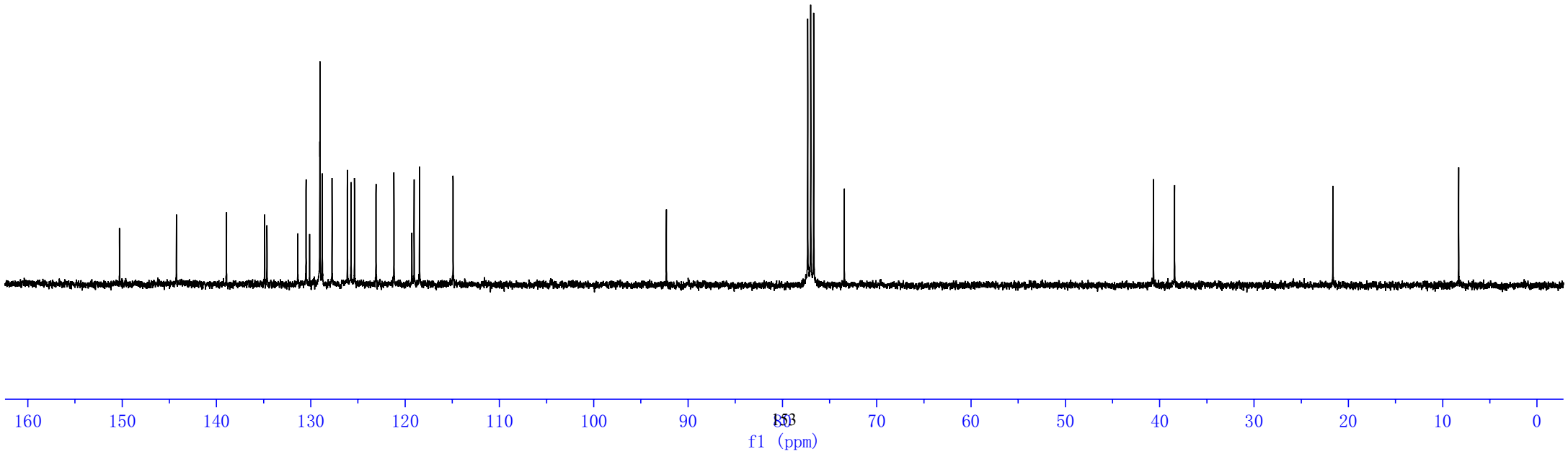
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

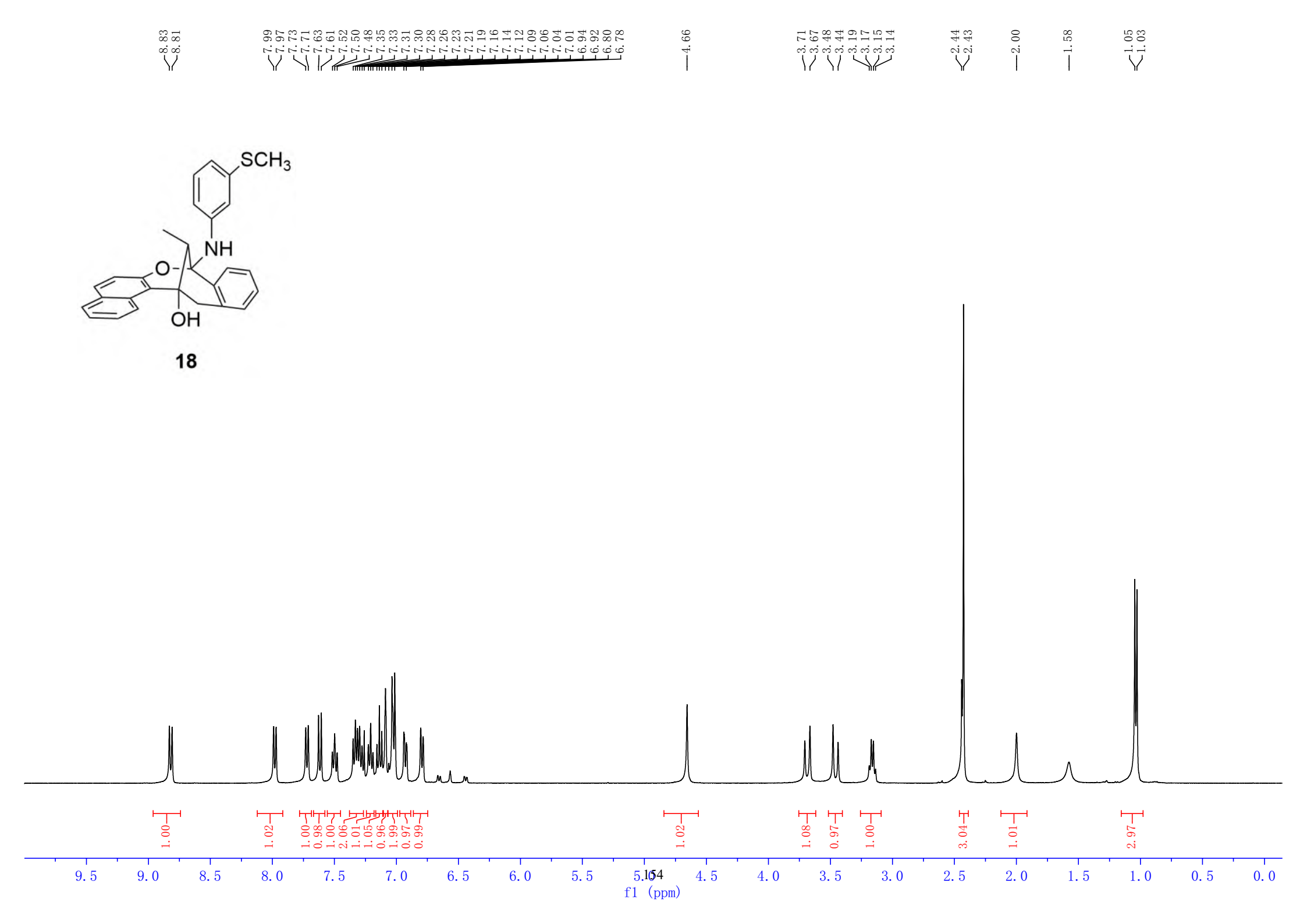
f1 (ppm)

150.28
144.24
138.93
134.89
130.50
129.04
129.02
128.79
127.75
126.12
125.73
125.36
123.08
121.18
119.04
92.30
77.32
77.00
76.68
73.44
40.67
38.43
21.64
8.31

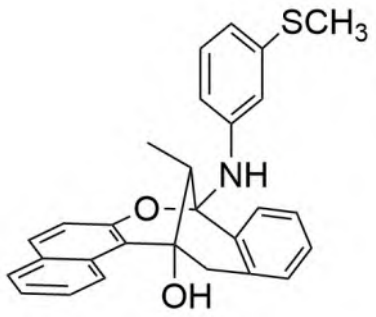


17

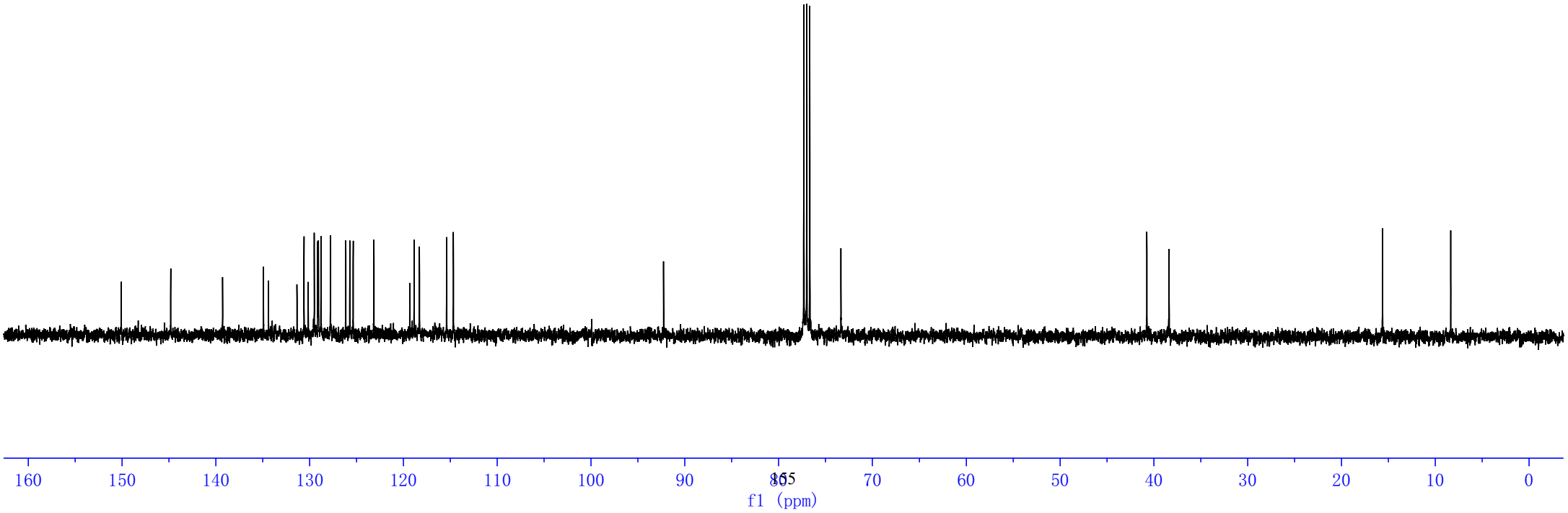


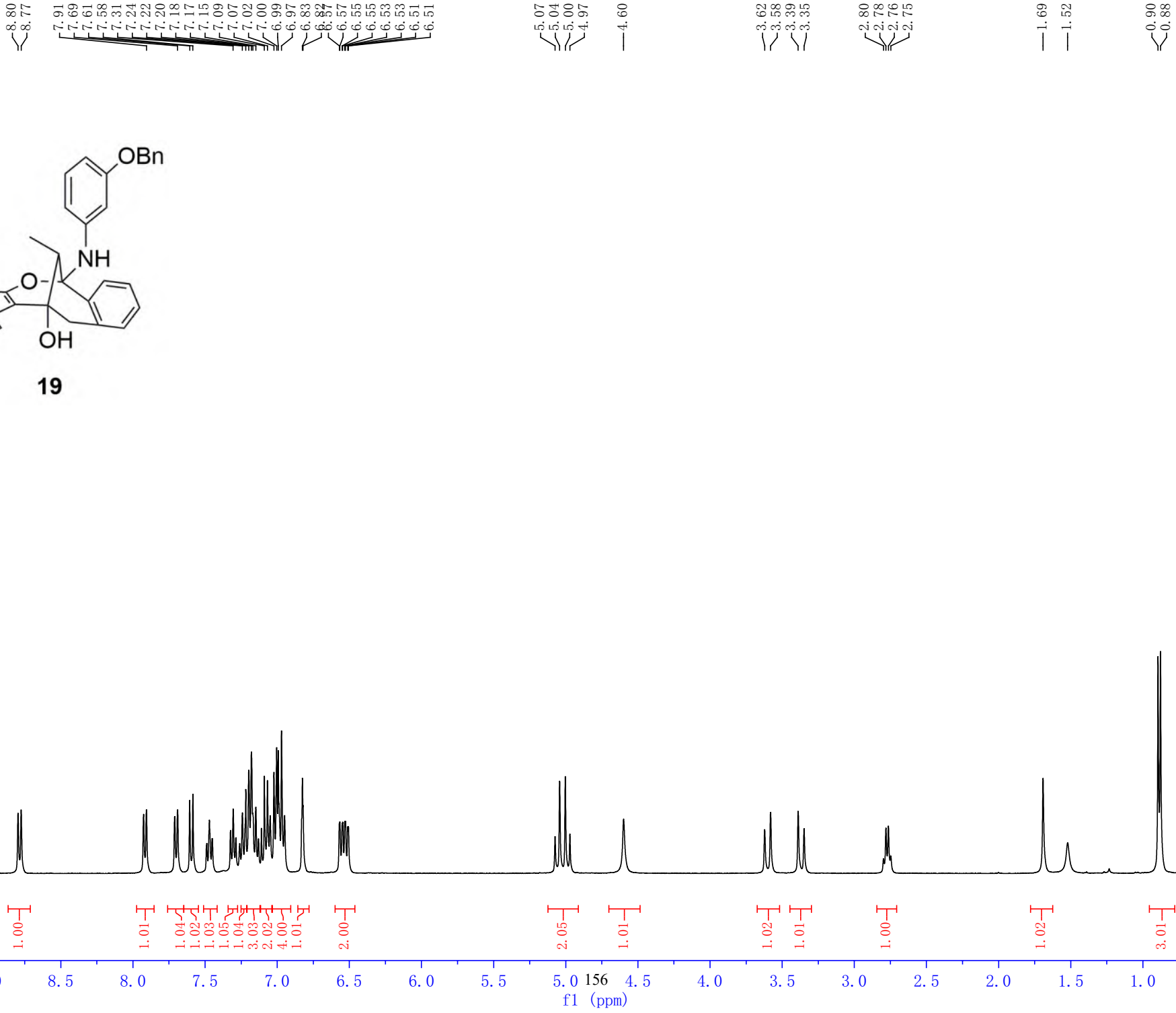

8.83
8.81
7.99
7.97
7.73
7.71
7.63
7.61
7.52
7.50
7.48
7.35
7.33
7.31
7.30
7.28
7.26
7.23
7.21
7.19
7.16
7.14
7.12
7.09
7.06
7.04
7.01
6.94
6.92
6.80
6.78
4.66
3.71
3.67
3.48
3.44
3.19
3.17
3.15
3.14
2.44
2.43
2.00
1.58
1.05
1.03
SCH3
NH
O
OH
18
1.00
1.02
1.00
0.98
1.00
2.06
1.01
1.05
0.96
1.99
0.97
0.99
1.02
1.08
0.97
1.00
3.04
1.01
2.97
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
f1 (ppm)

150.08
144.81
139.28
130.60
129.51
129.15
129.06
128.80
127.78
126.15
125.72
125.36
118.86
118.30
115.39
114.68
92.27
77.32
77.00
76.68
73.36
40.74
38.37
15.62
8.34

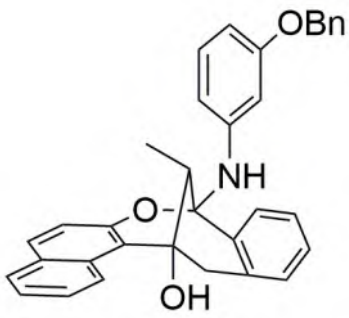


18

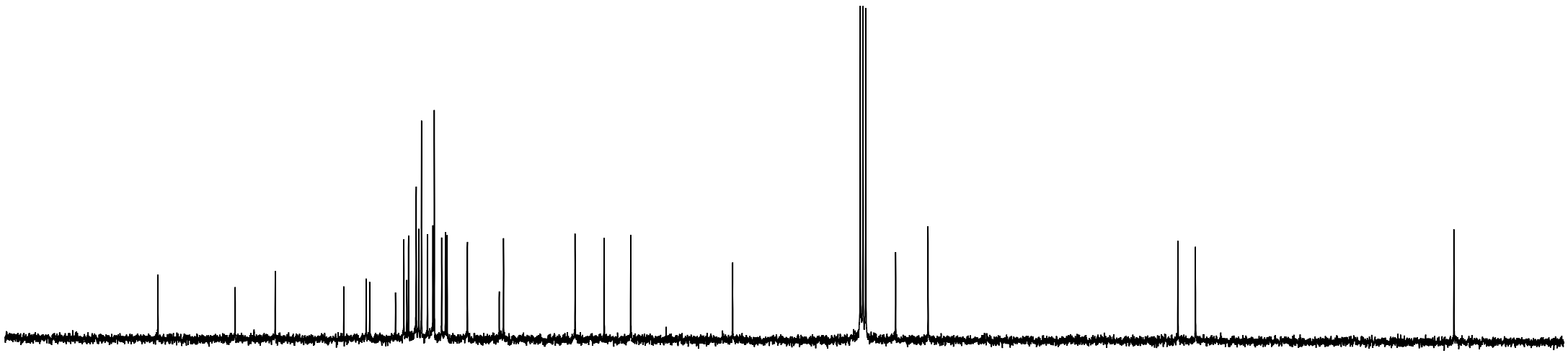


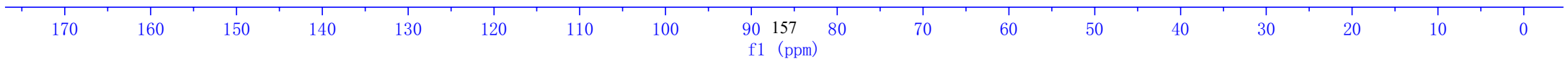

8.80
8.77
7.91
7.69
7.61
7.58
7.31
7.24
7.22
7.20
7.18
7.17
7.15
7.09
7.07
7.02
7.00
6.99
6.97
6.83
6.82
6.57
6.55
6.53
6.53
6.51
6.51
5.07
5.04
5.00
4.97
4.60
3.62
3.58
3.39
3.35
2.80
2.78
2.76
2.75
1.69
1.52
0.90
0.88
OBn
NH
O
OH
19
1.00
1.01
1.04
1.02
1.03
1.05
1.04
3.03
2.02
4.00
1.01
2.00
2.05
1.01
1.02
1.01
1.00
1.02
3.01
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
f1 (ppm)

159.15
150.15
145.48
134.89
130.50
129.95
129.05
128.76
128.44
127.74
127.12
126.95
126.09
125.64
125.45
118.88
110.54
107.16
104.07
92.18
77.32
77.00
76.68
73.19
69.42
40.31
38.27
8.15



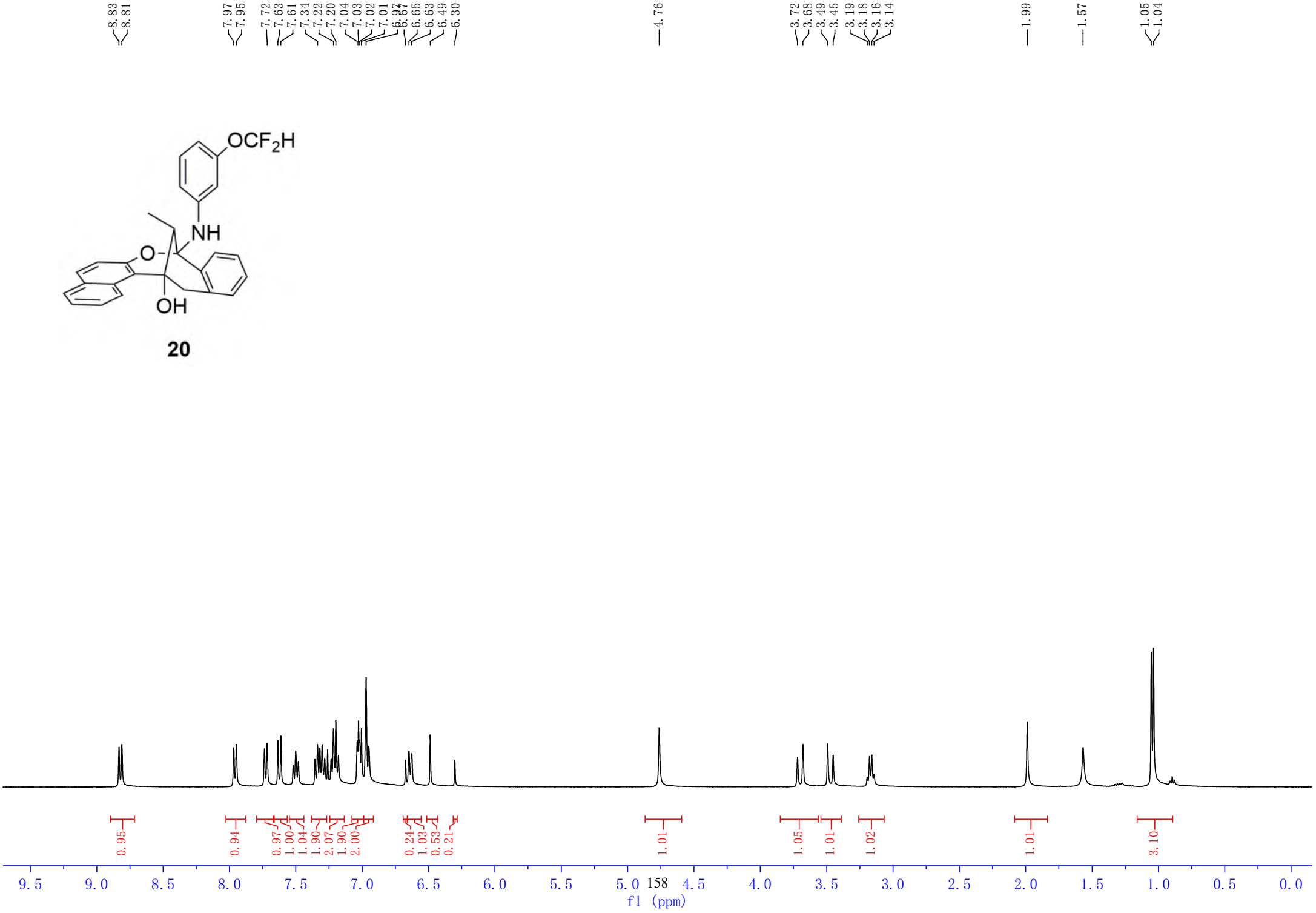
19

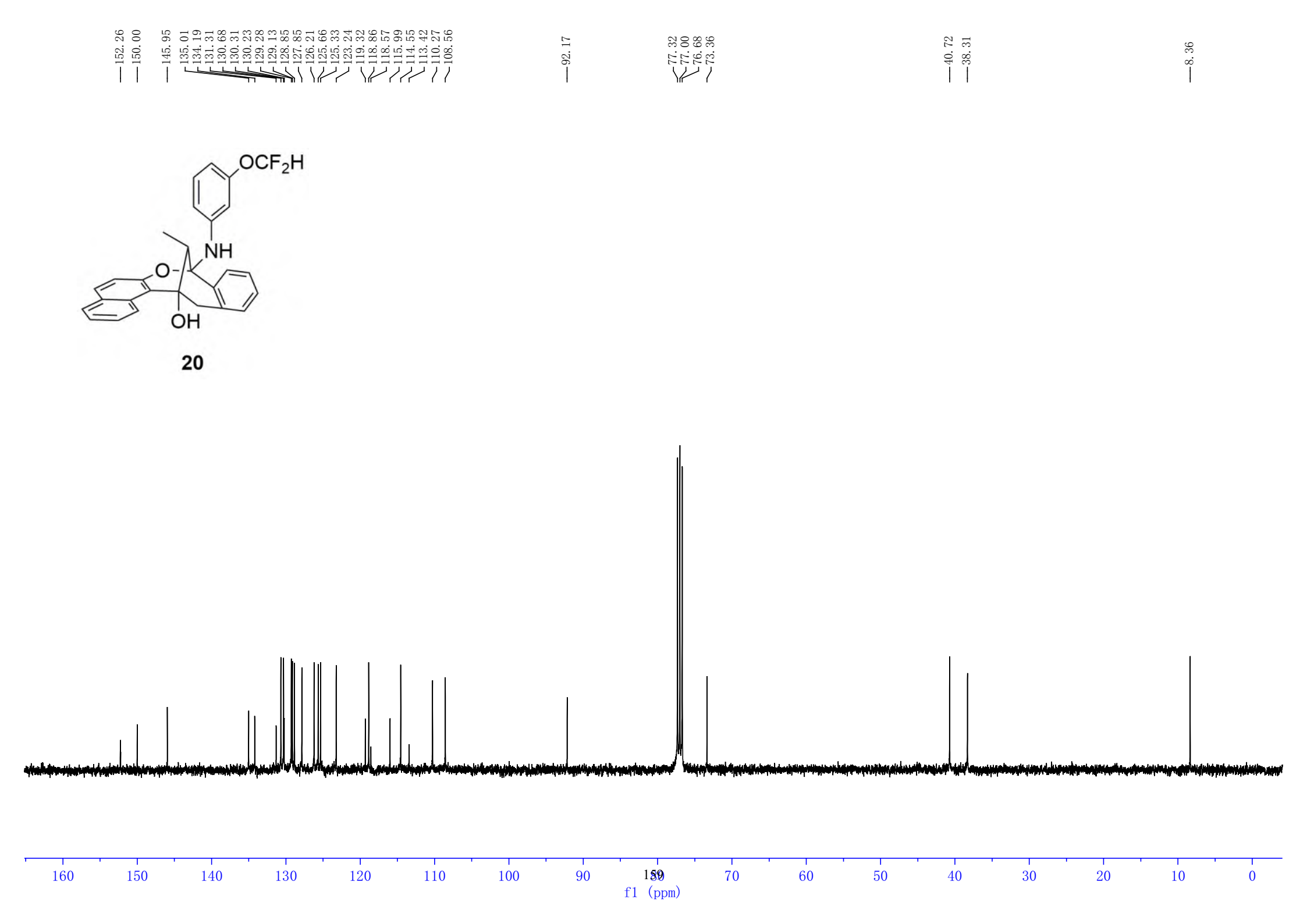




OCF2H
NH
O
OH

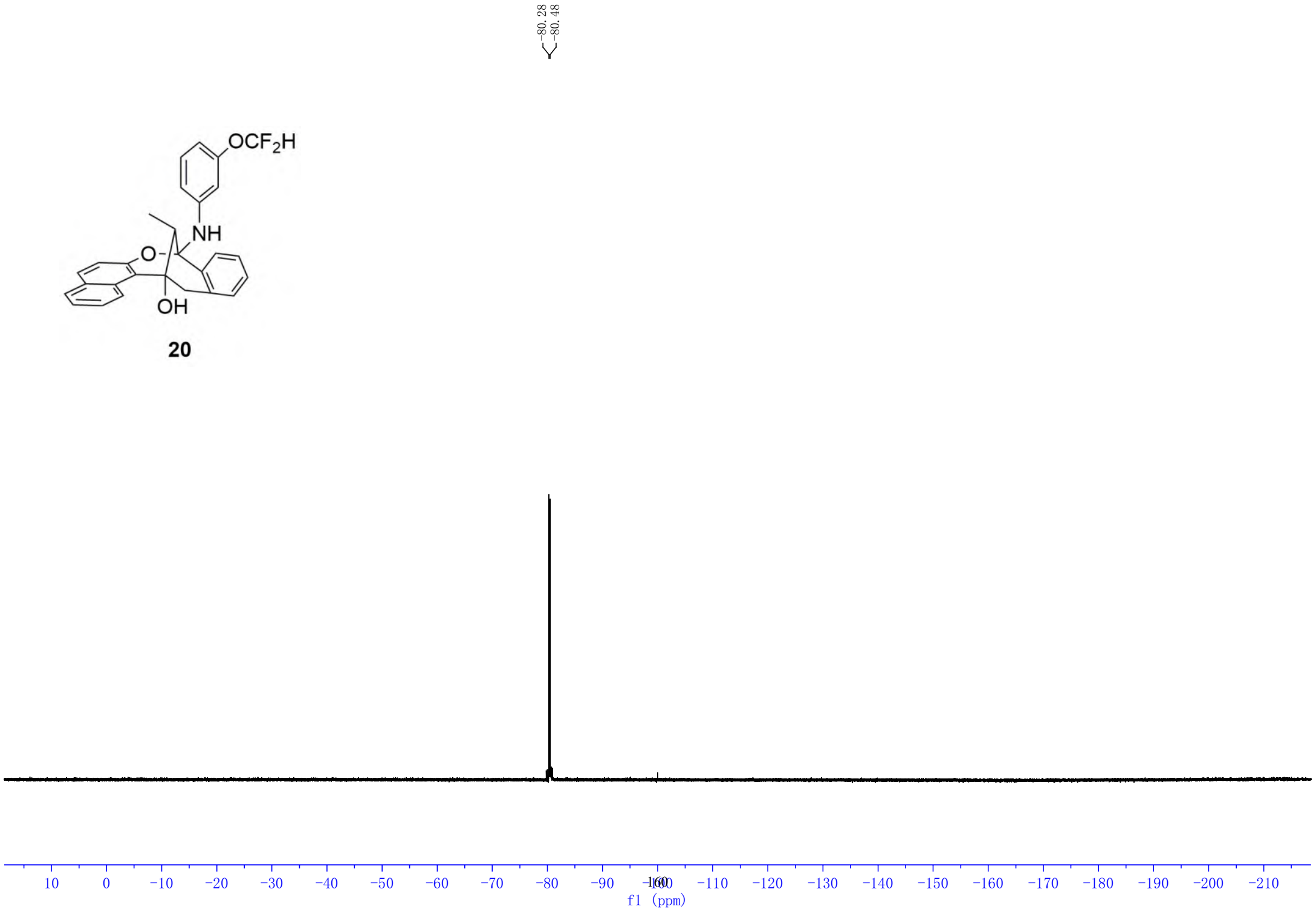
20

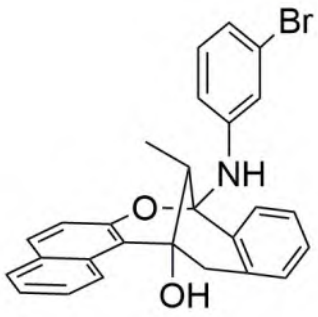

8.83
8.81
7.97
7.95
7.72
7.63
7.61
7.34
7.22
7.20
7.04
7.03
7.02
7.01
6.67
6.65
6.63
6.49
6.30
4.76
3.72
3.68
3.49
3.45
3.19
3.18
3.16
3.14
1.99
1.57
1.05
1.04
0.95
0.94
0.97
1.00
1.04
1.90
2.07
1.90
2.00
0.24
1.03
0.53
0.21
1.01
1.05
1.01
1.02
1.01
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.26
150.00
145.95
135.01
134.19
131.31
130.68
130.31
130.23
129.28
129.13
128.85
127.85
126.21
125.66
125.33
123.24
119.32
118.86
118.57
115.99
114.55
113.42
110.27
108.56
92.17
77.32
77.00
76.68
73.36
40.72
38.31
8.36
OCF2H
NH
O
OH
20
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

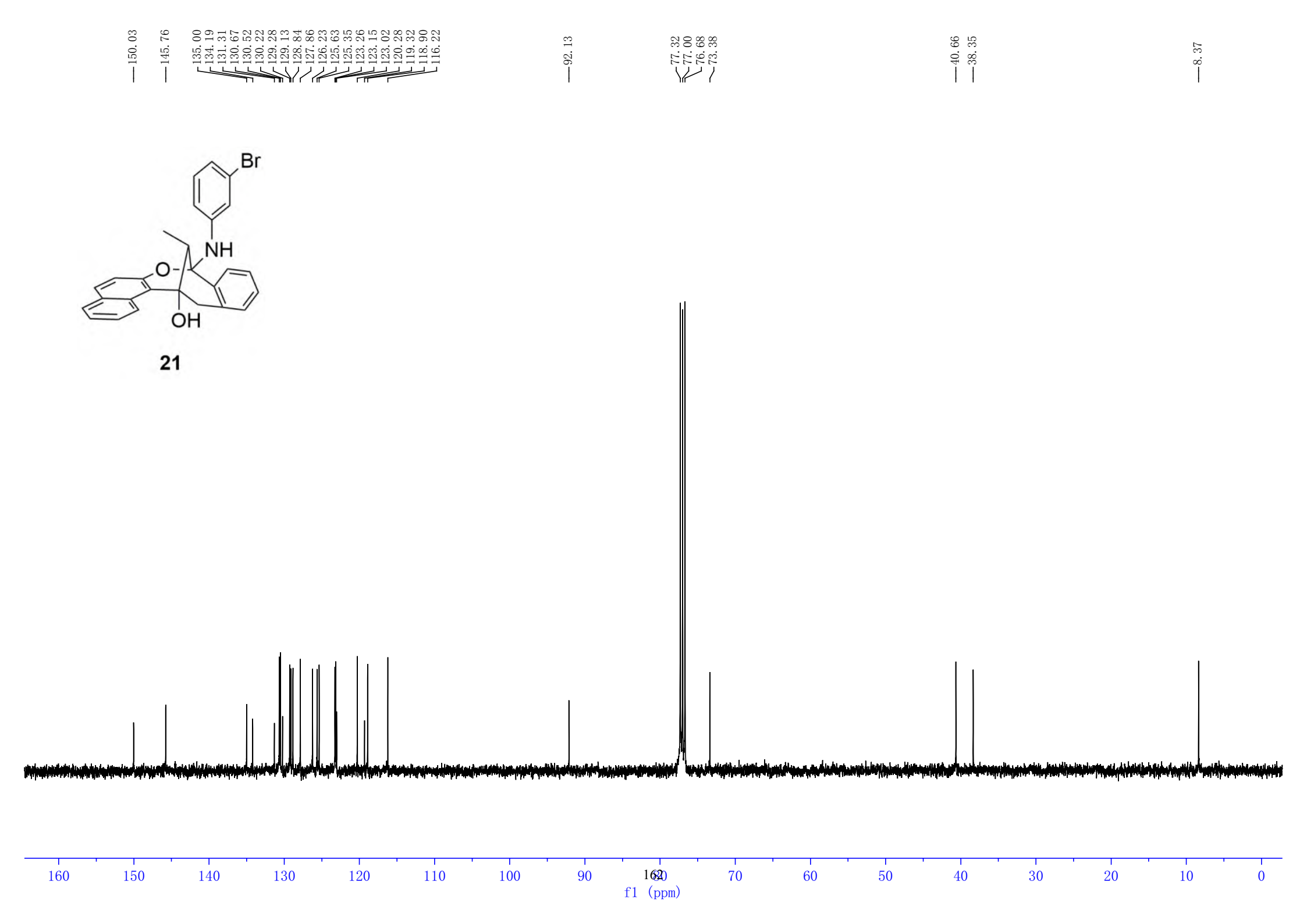
OCF2H
NH
O
OH

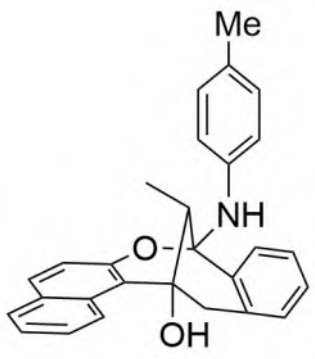
20


-80.28
-80.48
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

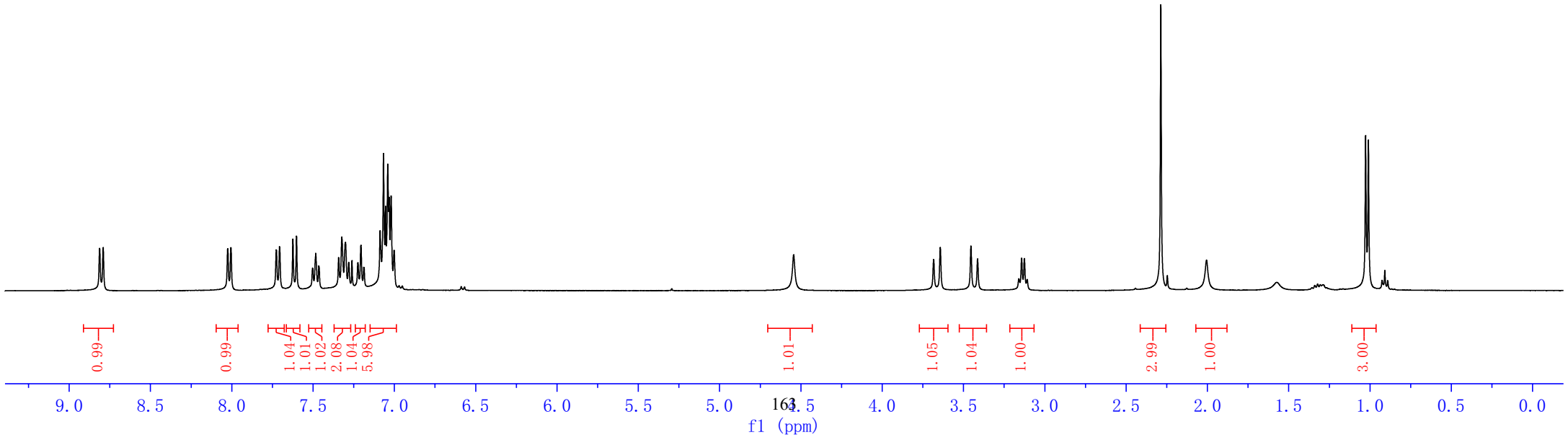


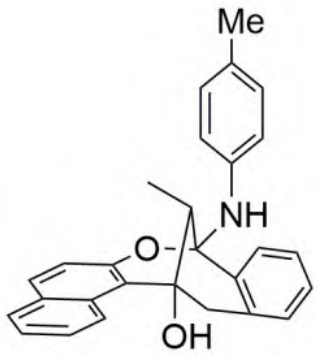
21


150.03
145.76
135.00
134.19
131.31
130.67
130.52
130.22
129.28
129.13
128.84
127.86
126.23
125.63
125.35
123.26
123.15
123.02
120.28
119.32
118.90
116.22
92.13
77.32
77.00
76.68
73.38
40.66
38.35
8.37
Br
NH
O
OH
21
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
NH
O
OH

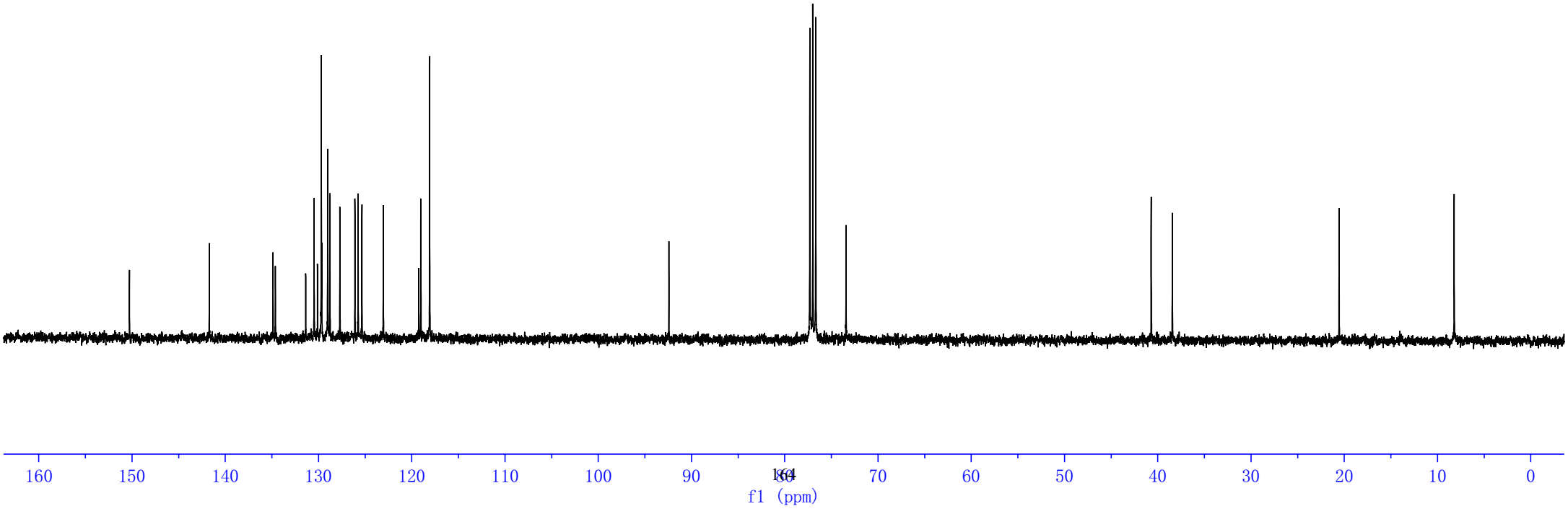
22

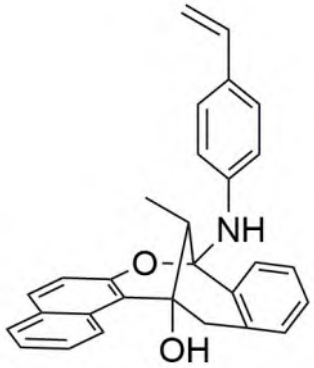

8.81
8.79
8.02
8.01
7.73
7.71
7.62
7.60
7.50
7.48
7.46
7.34
7.32
7.30
7.28
7.26
7.22
7.21
7.19
7.09
7.07
7.05
7.04
7.03
7.02
7.00
4.54
3.68
3.64
3.45
3.41
3.16
3.14
3.13
3.11
2.29
2.01
1.57
1.03
1.01
0.99
0.99
1.04
1.01
1.02
2.08
1.04
5.98
1.01
1.05
1.04
1.00
2.99
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



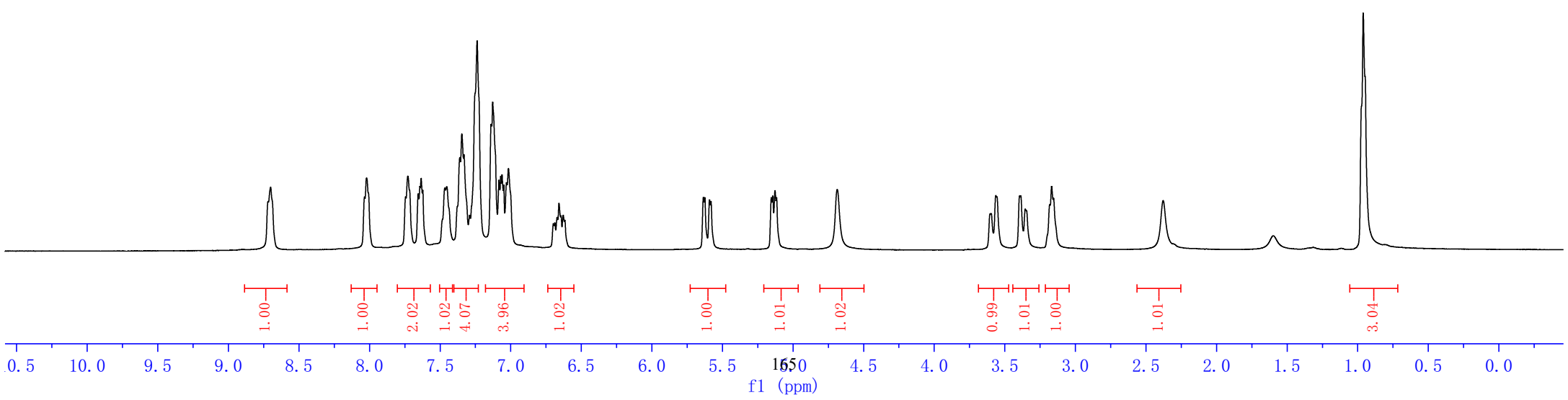
22

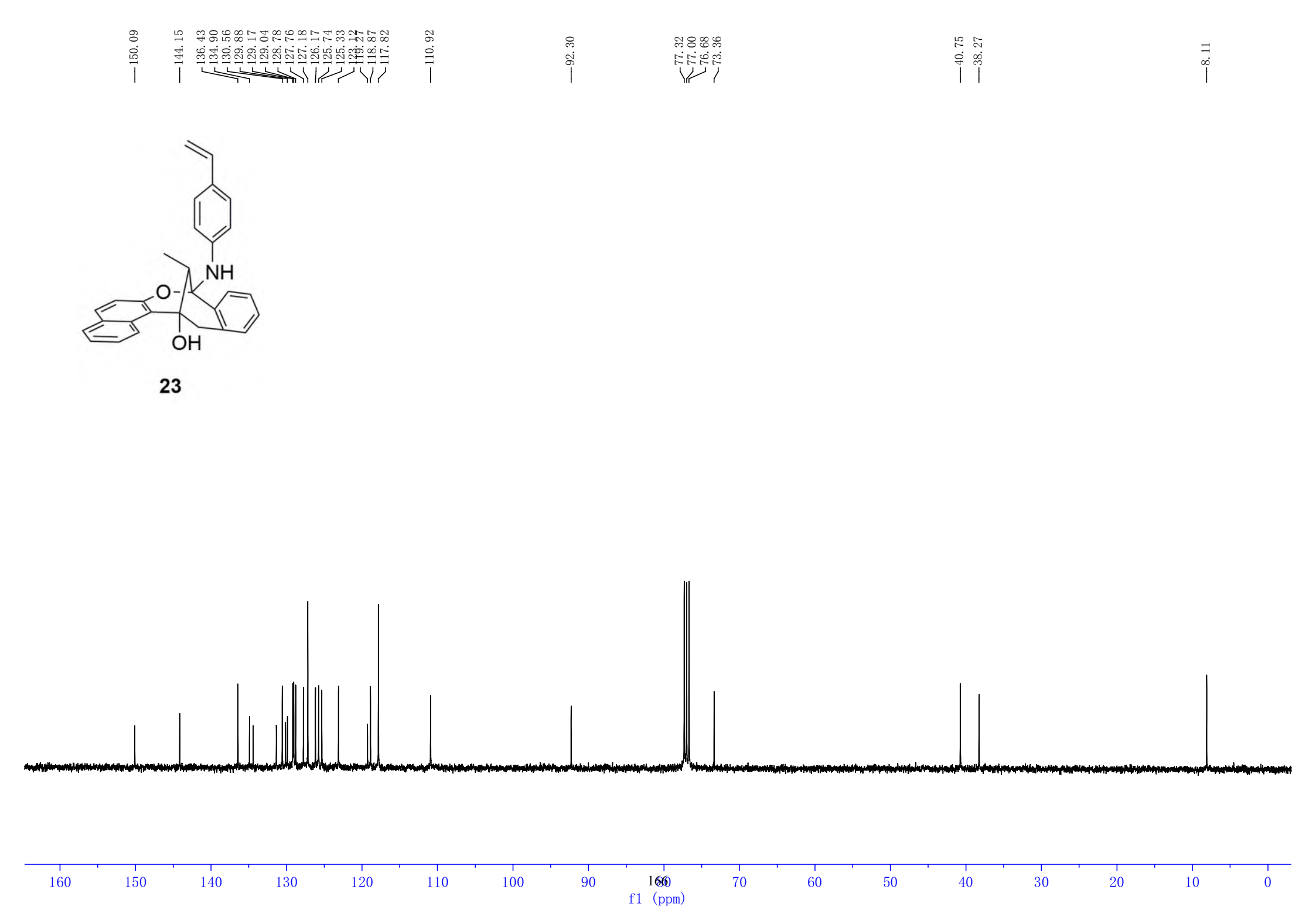
150.28
141.72
134.88
130.48
129.70
129.65
129.01
128.78
127.71
126.10
125.76
125.35
122.95
119.25
119.03
118.08
92.43
77.32
77.00
76.68
73.44
40.71
38.44
20.56
8.22

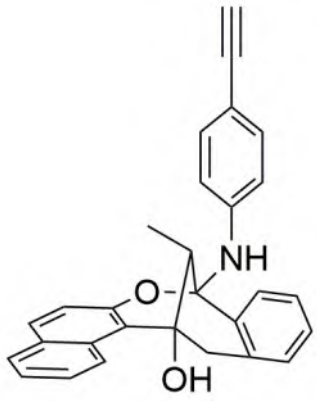



NH
O
OH

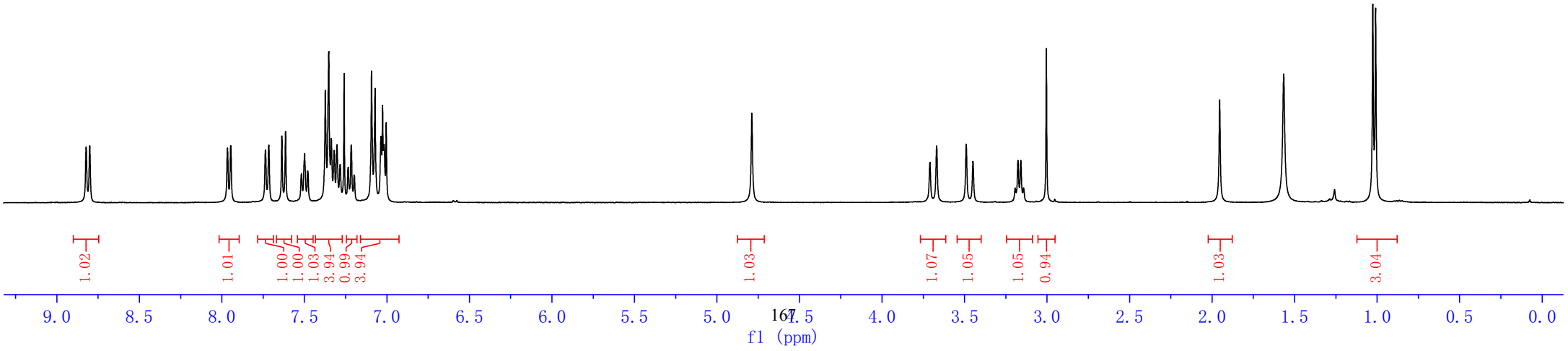
23

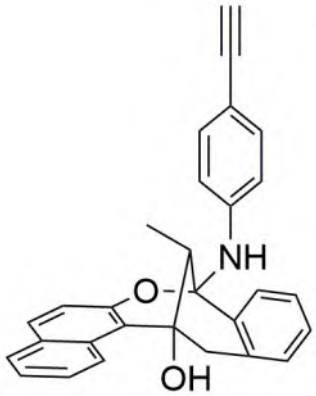

8.72
8.70
8.04
8.02
7.36
7.35
7.33
7.24
7.14
7.13
7.07
7.06
6.69
6.67
6.66
6.64
6.63
6.62
5.64
5.62
5.59
5.58
5.15
5.14
5.13
5.12
4.69
3.60
3.60
3.56
3.40
3.39
3.36
3.35
3.18
3.17
3.15
2.38
1.60
0.96
0.95
1.00
1.00
2.02
1.02
4.07
3.96
1.02
1.00
1.01
1.02
0.99
1.01
1.00
1.01
3.04
f1 (ppm)


150.09
144.15
136.43
134.90
130.56
129.88
129.17
129.04
128.78
127.76
127.18
126.17
125.74
125.33
123.12
118.87
117.82
110.92
92.30
77.32
77.00
76.68
73.36
40.75
38.27
8.11
NH
O
OH
23
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
O
OH

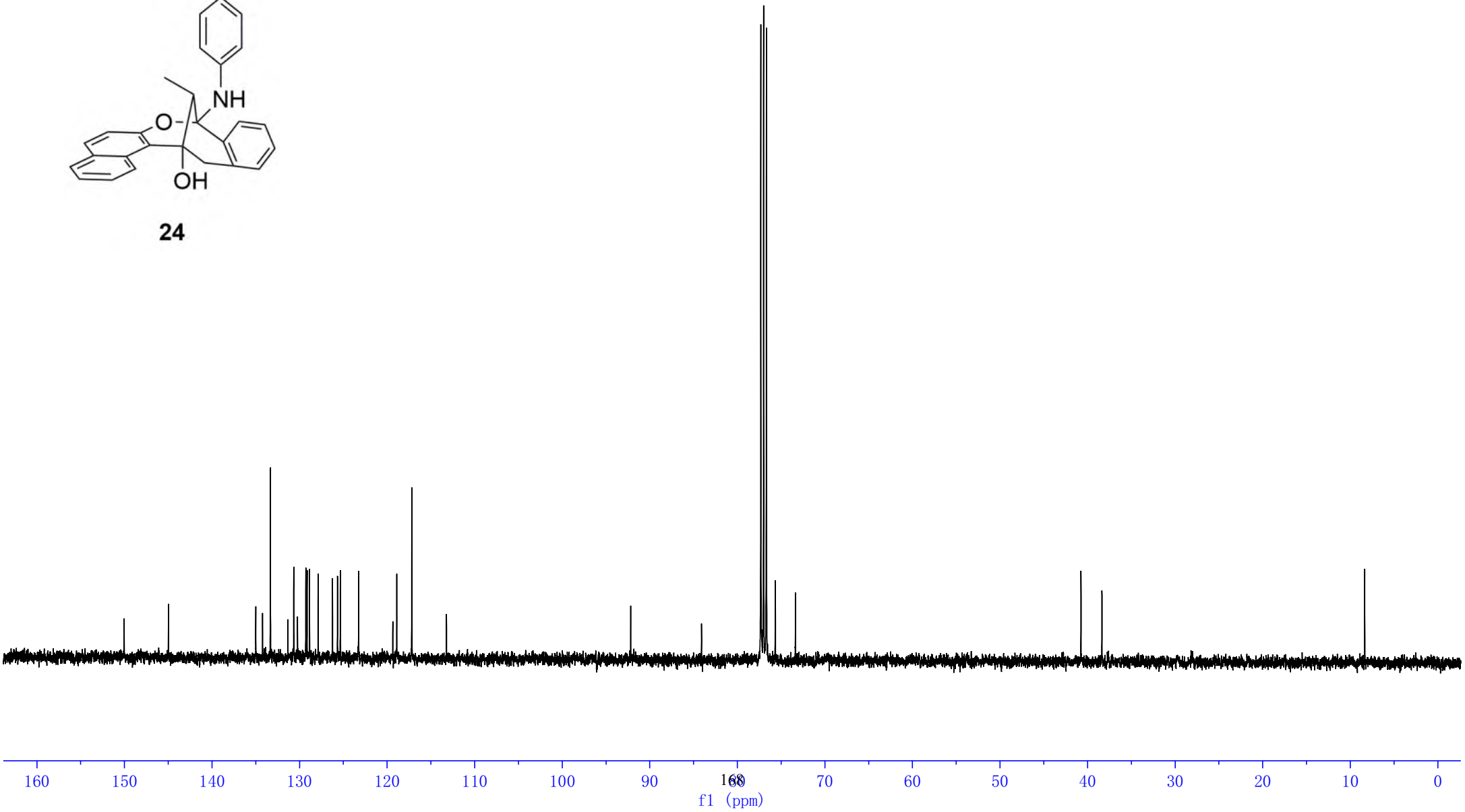
24

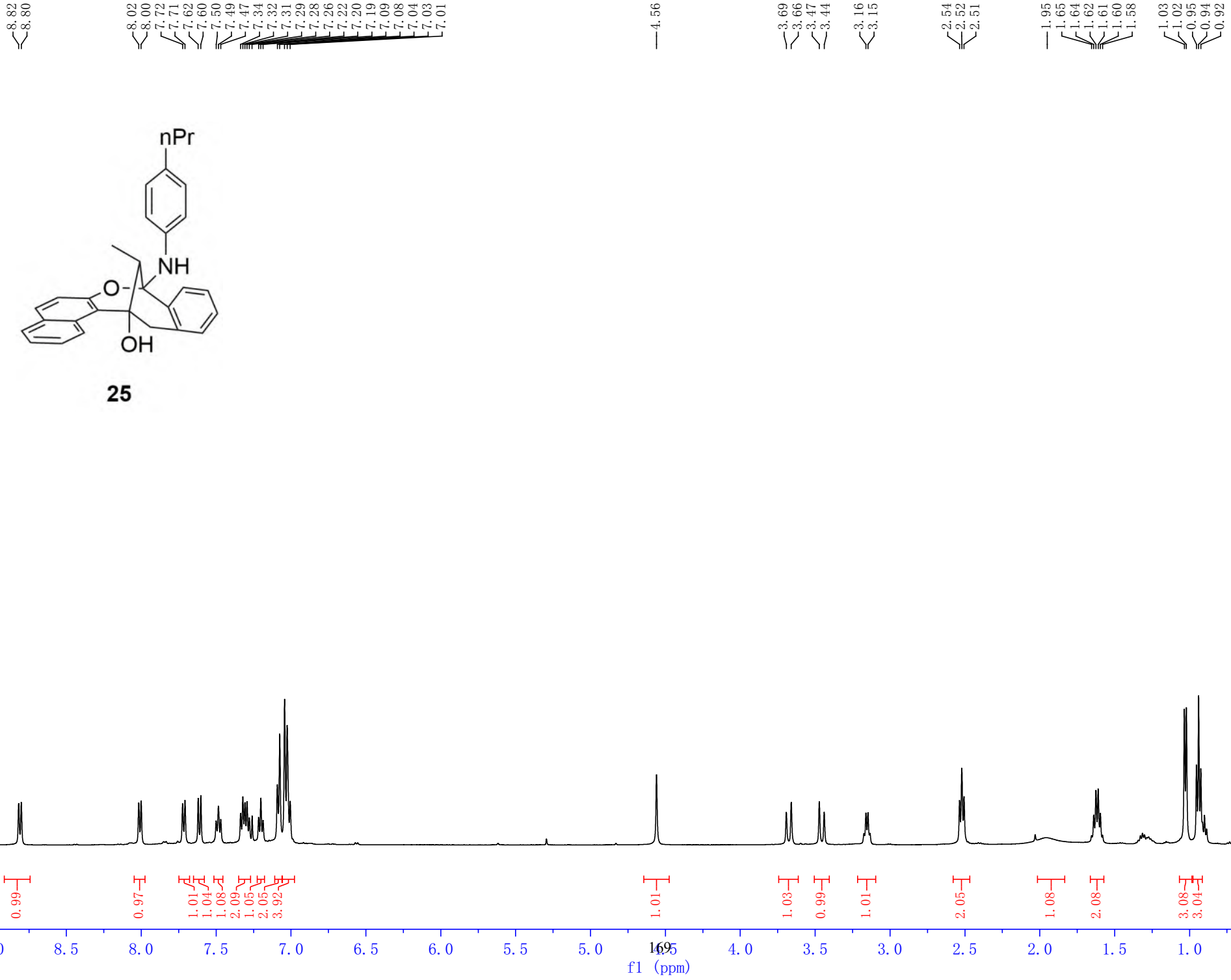

8.82
8.80
7.97
7.95
7.74
7.72
7.64
7.61
7.52
7.50
7.48
7.37
7.35
7.34
7.32
7.30
7.28
7.26
7.23
7.22
7.20
7.09
7.07
7.04
7.03
7.02
7.00
4.79
3.71
3.67
3.49
3.45
3.19
3.18
3.16
3.14
3.00
1.95
1.57
1.03
1.01
1.02
1.01
1.00
1.00
1.03
3.94
0.99
3.94
1.03
1.07
1.05
1.05
0.94
1.03
3.04
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)



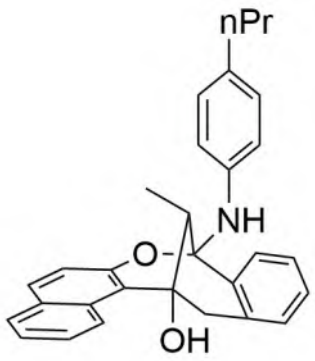
24

150.03
144.98
135.00
134.23
133.32
131.33
130.66
130.23
129.29
129.14
128.86
127.88
126.24
125.66
125.34
123.25
119.35
118.90
117.18
113.22
92.18
84.09
77.32
77.00
76.68
75.66
73.37
40.75
38.36
8.35

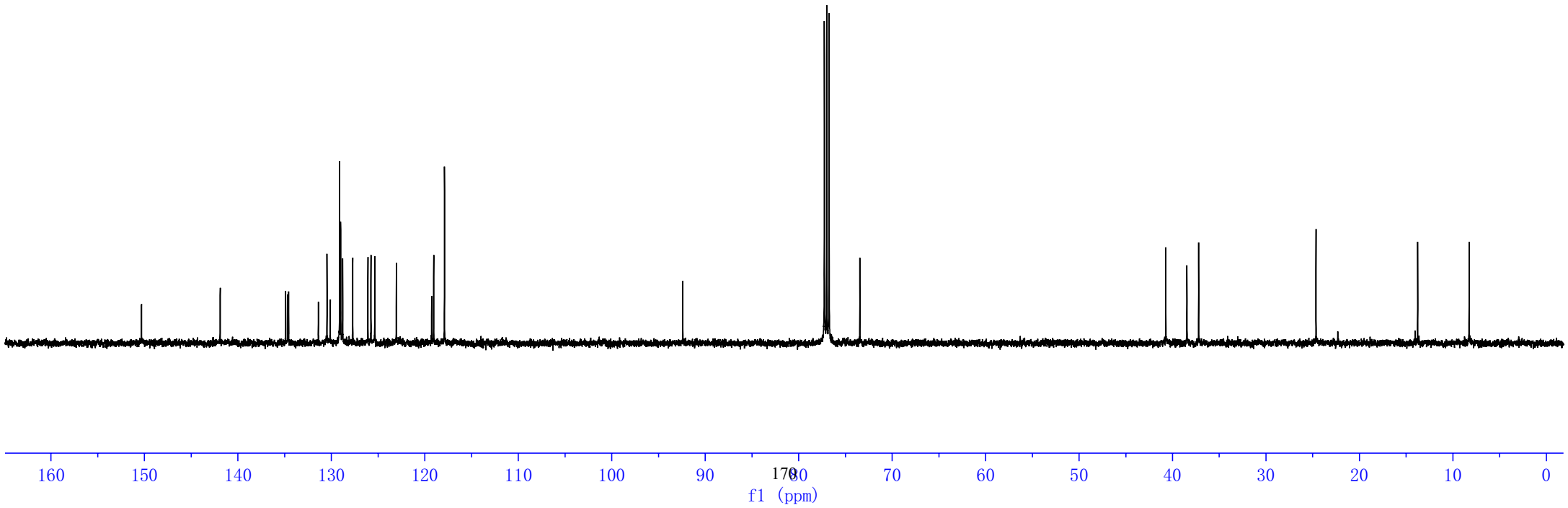


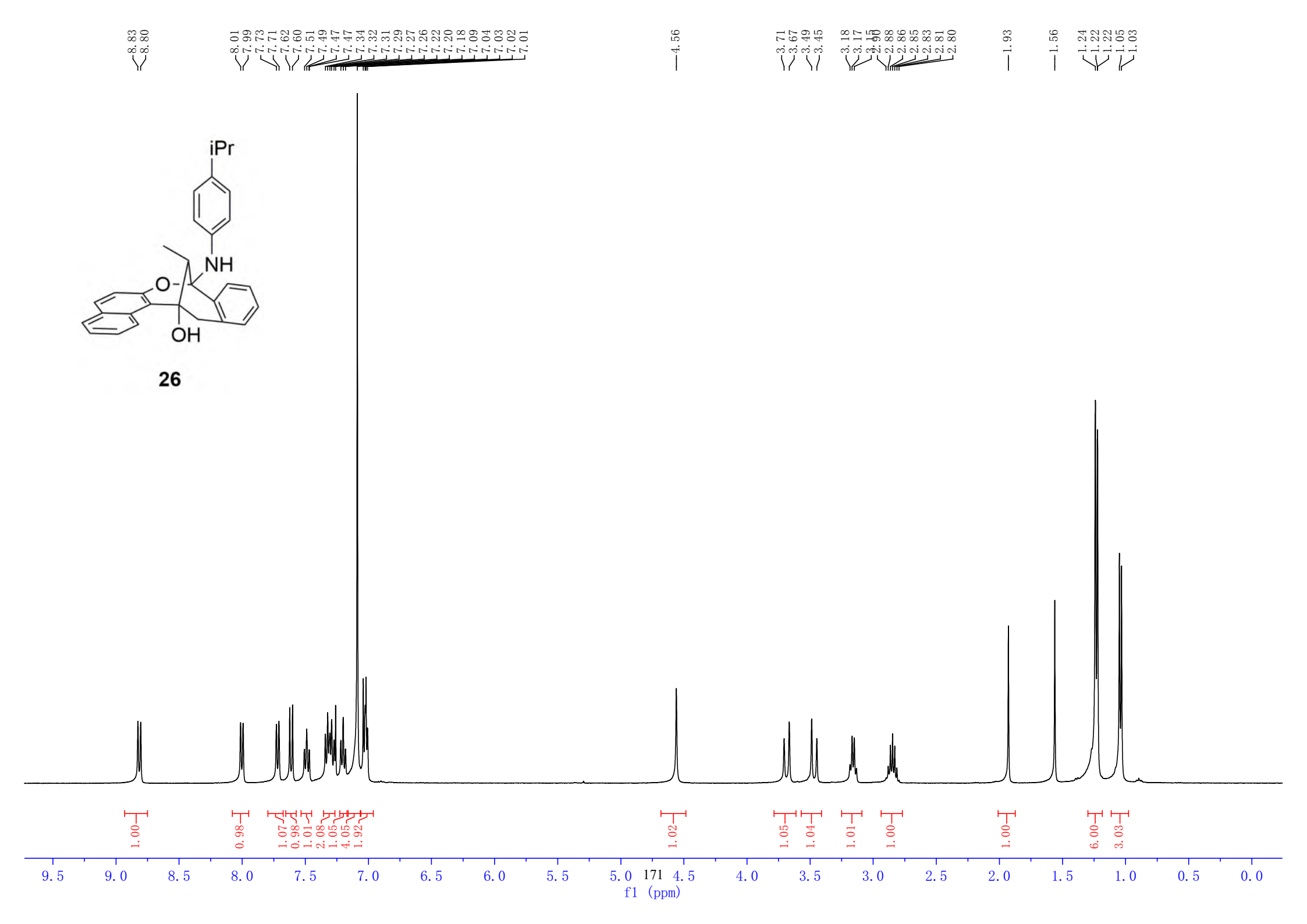

8.82
8.80
8.02
8.00
7.72
7.71
7.62
7.60
7.50
7.49
7.47
7.34
7.32
7.31
7.29
7.28
7.26
7.22
7.20
7.19
7.09
7.08
7.04
7.03
7.01
4.56
3.69
3.66
3.47
3.44
3.16
3.15
2.54
2.52
2.51
1.95
1.65
1.64
1.62
1.61
1.60
1.58
1.03
1.02
0.95
0.94
0.92
nPr
NH
O
OH
25
0.99
0.97
1.01
1.04
1.08
2.09
1.05
2.05
3.92
1.01
1.03
0.99
1.01
2.05
1.08
2.08
3.08
3.04
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
f1 (ppm)

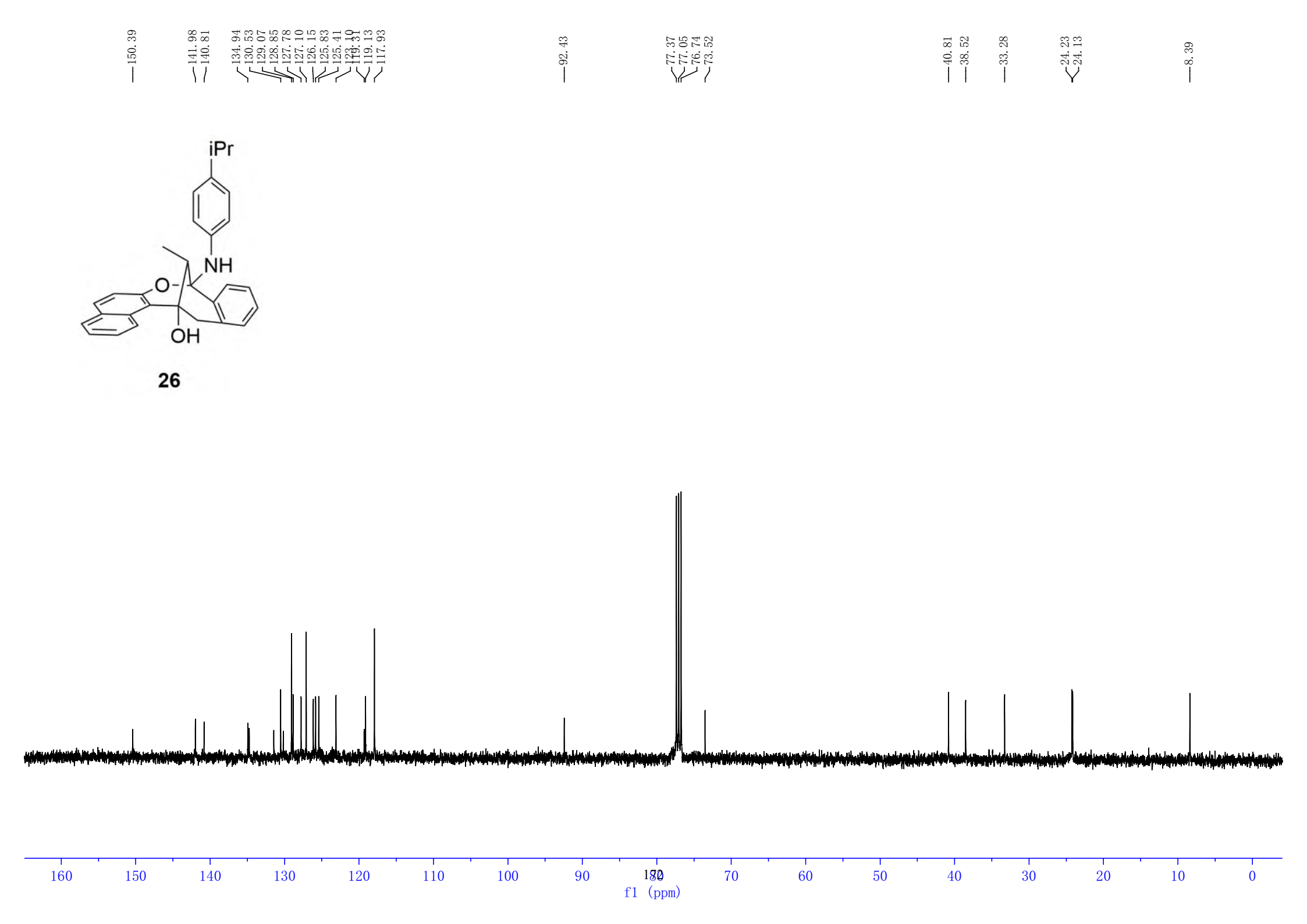
150.32
141.90
134.89
134.57
130.47
129.12
129.01
128.79
127.72
126.09
125.77
125.36
119.27
119.06
117.90
92.41
77.25
77.00
76.75
73.46
40.72
38.46
37.21
24.65
13.77
8.27

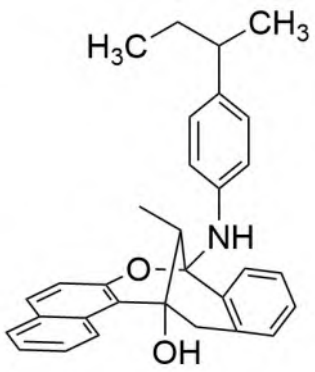


25

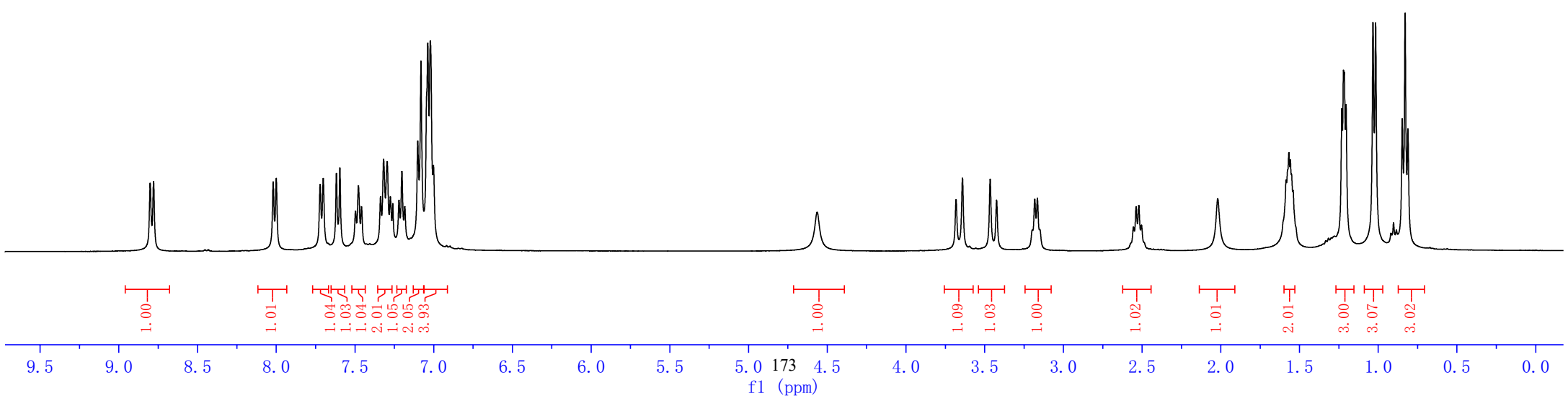



8.83
8.80
8.01
7.99
7.73
7.71
7.62
7.60
7.51
7.49
7.47
7.47
7.34
7.32
7.31
7.29
7.27
7.26
7.22
7.20
7.18
7.09
7.04
7.03
7.02
7.01
4.56
3.71
3.67
3.49
3.45
3.18
3.17
2.88
2.86
2.85
2.83
2.81
2.80
1.93
1.56
1.24
1.22
1.22
1.05
1.03
iPr
NH
O
OH
26
1.00
0.98
1.07
0.98
1.01
2.08
1.05
4.05
1.92
1.02
1.05
1.04
1.01
1.00
1.00
6.00
3.03
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
f1 (ppm)

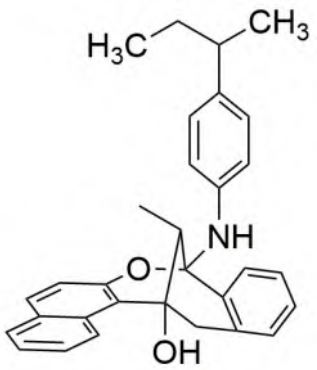

150.39
141.98
140.81
134.94
130.53
129.07
128.85
127.78
127.10
126.15
125.83
125.41
123.10
119.31
119.13
117.93
92.43
77.37
77.05
76.74
73.52
40.81
38.52
33.28
24.23
24.13
8.39
iPr
NH
O
OH
26
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



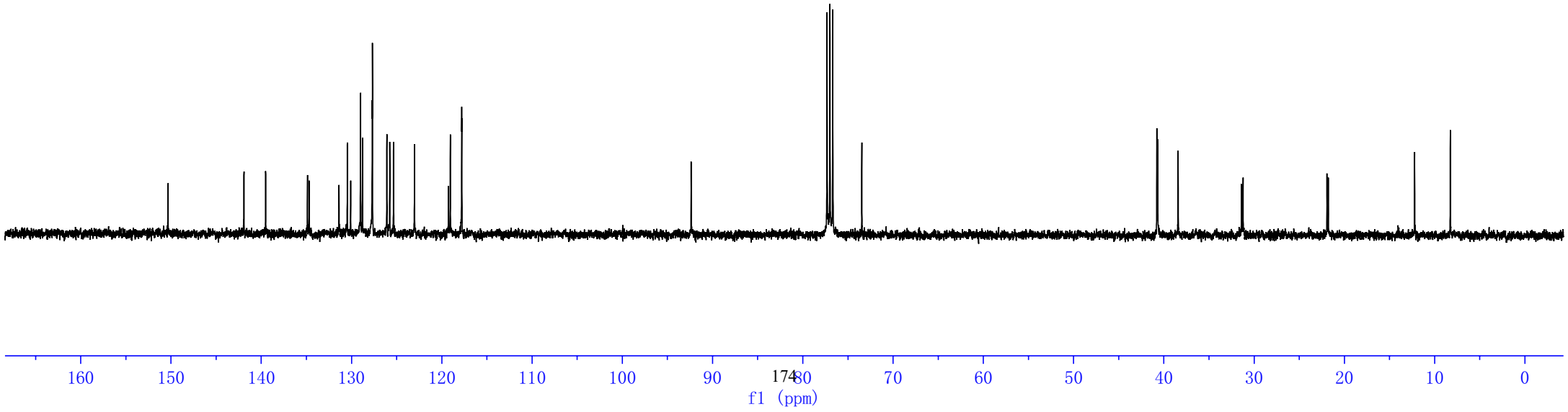
27

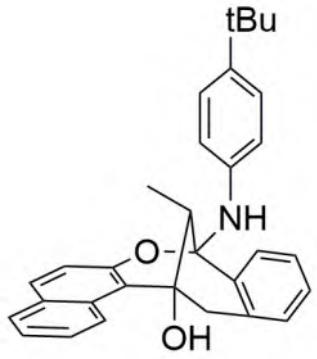


150.33
141.92
139.51
134.88
130.46
129.00
128.78
127.71
127.68
126.09
125.77
125.34
123.03
119.25
119.06
117.80
117.77
92.38
77.32
77.00
76.68
73.46
40.78
40.69
38.42
31.41
31.22
21.93
21.78
12.22
8.27

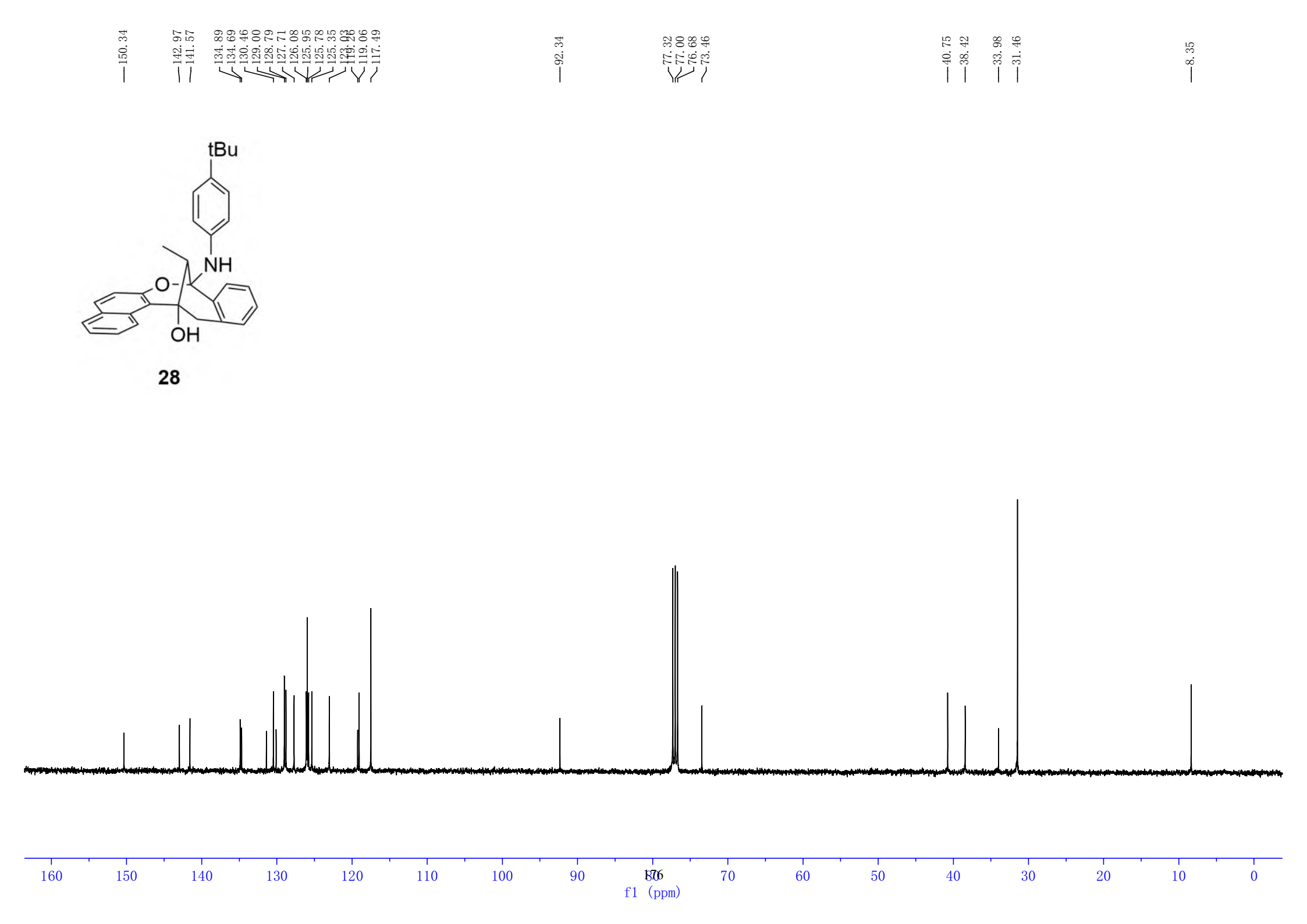


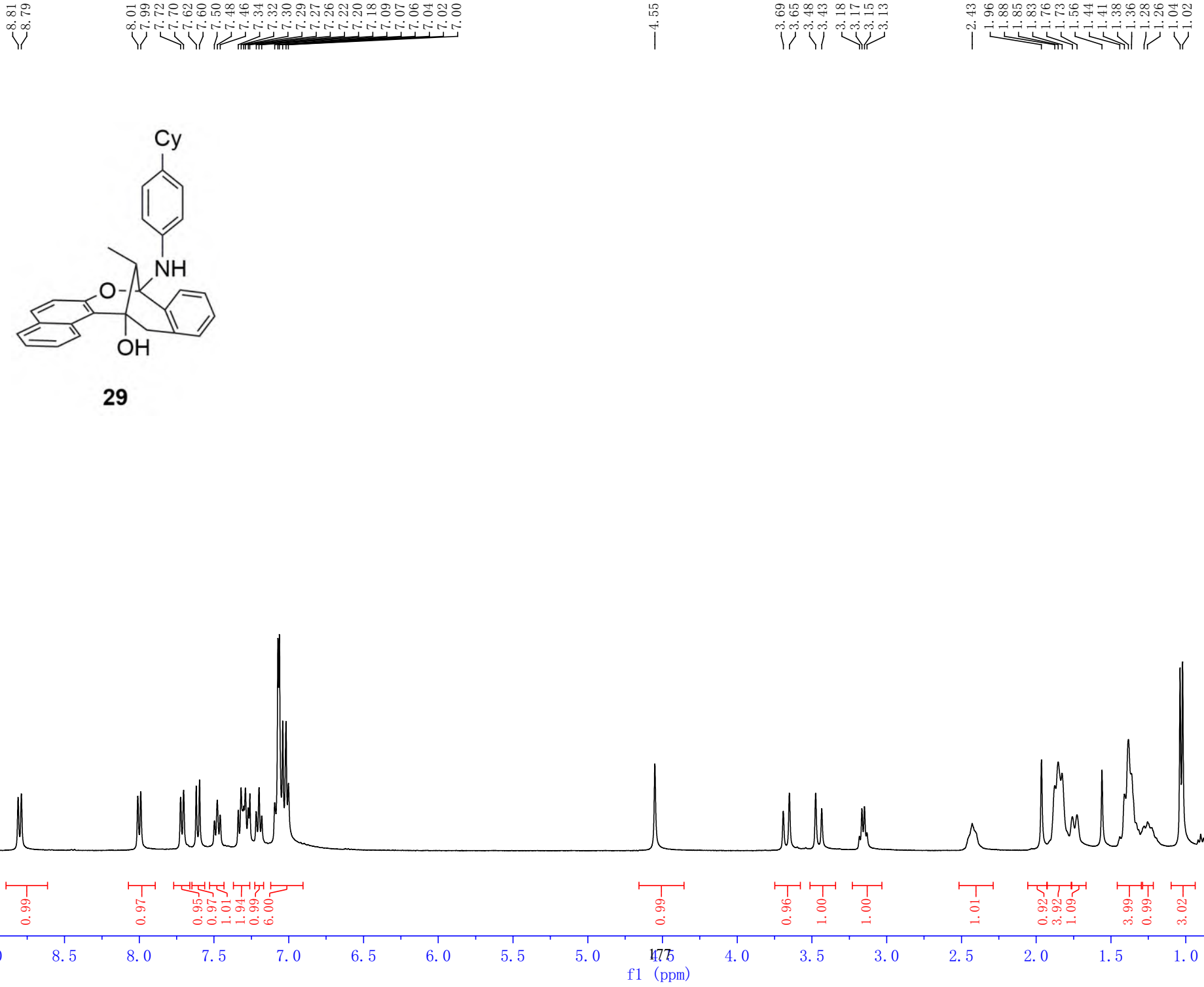
27



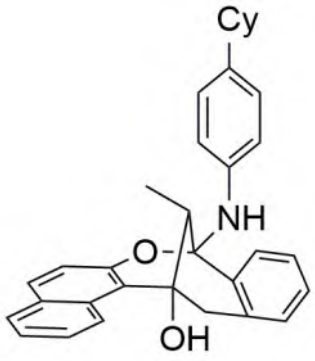


28

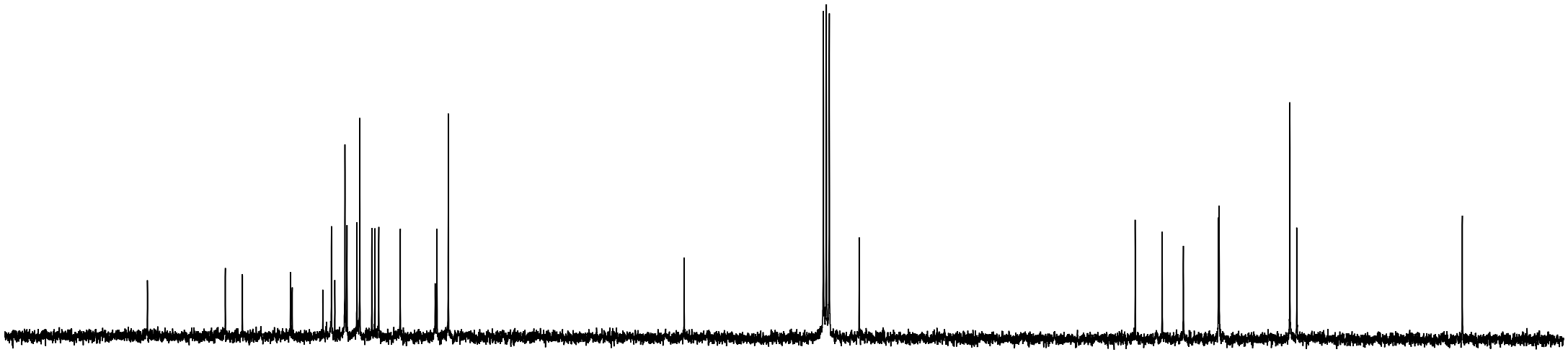

150.34
142.97
141.57
134.89
134.69
130.46
129.00
128.79
127.71
126.08
125.95
125.78
125.35
119.26
119.06
117.49
92.34
77.32
77.00
76.68
73.46
40.75
38.42
33.98
31.46
8.35
tBu
NH
O
OH
28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

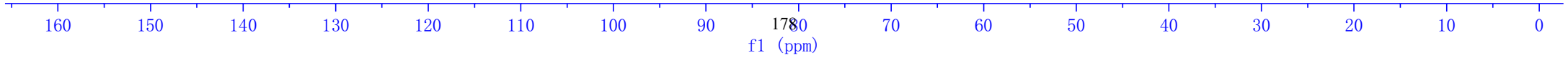

8.81
8.79
8.01
7.99
7.72
7.70
7.62
7.60
7.50
7.48
7.46
7.34
7.32
7.30
7.29
7.27
7.26
7.22
7.20
7.18
7.09
7.07
7.06
7.04
7.02
7.00
4.55
3.69
3.65
3.48
3.43
3.18
3.17
3.15
3.13
2.43
1.96
1.88
1.85
1.83
1.76
1.73
1.56
1.44
1.41
1.38
1.36
1.28
1.26
1.04
1.02
Cy
NH
O
OH
29
0.99
0.97
0.95
0.97
1.01
1.94
0.99
6.00
0.99
0.96
1.00
1.00
1.01
0.92
3.92
1.09
3.99
0.99
3.02
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
f1 (ppm)

150.33
141.92
140.08
134.88
130.46
129.00
128.78
127.71
127.40
126.09
125.77
125.35
119.07
117.83
92.36
77.32
77.00
76.68
73.46
43.64
40.73
38.44
34.66
34.57
26.94
26.18
8.31



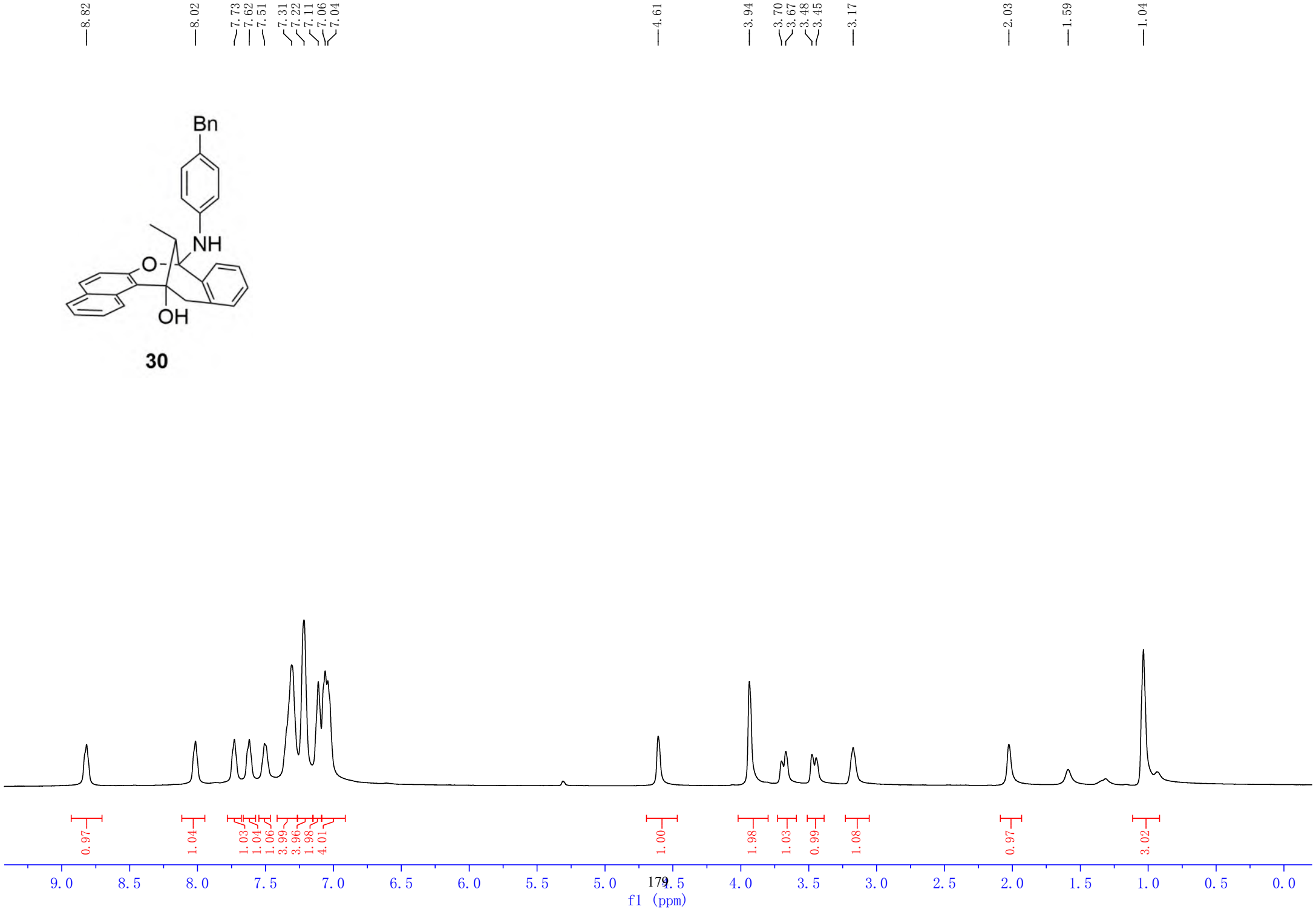
29

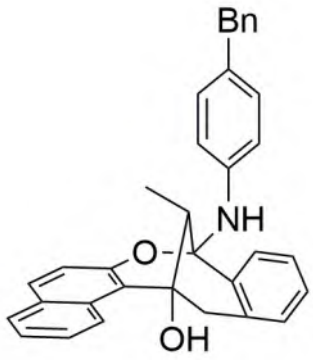




Bn
NH
O
OH

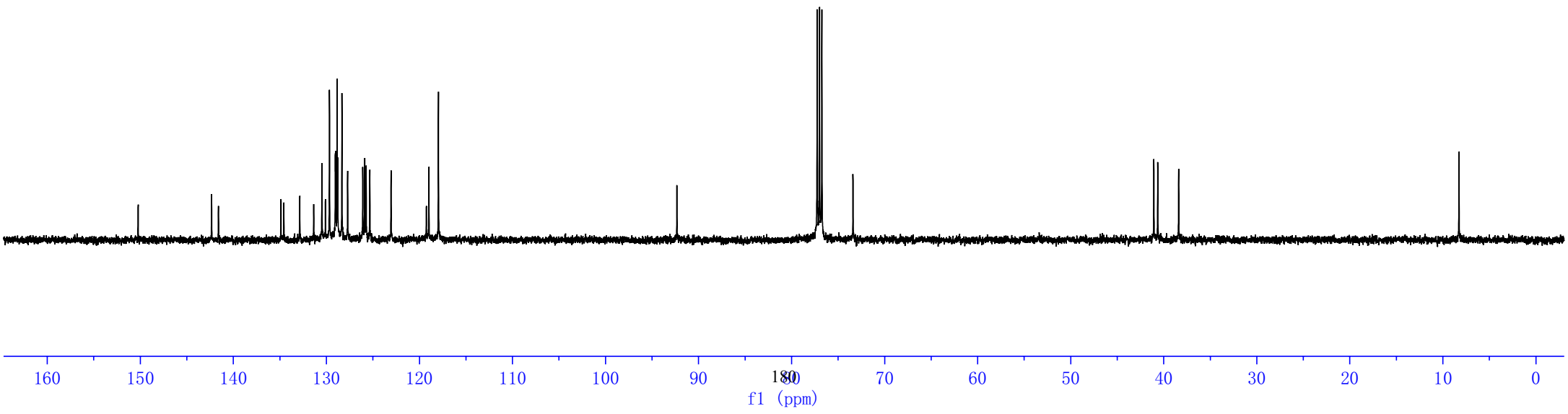
30

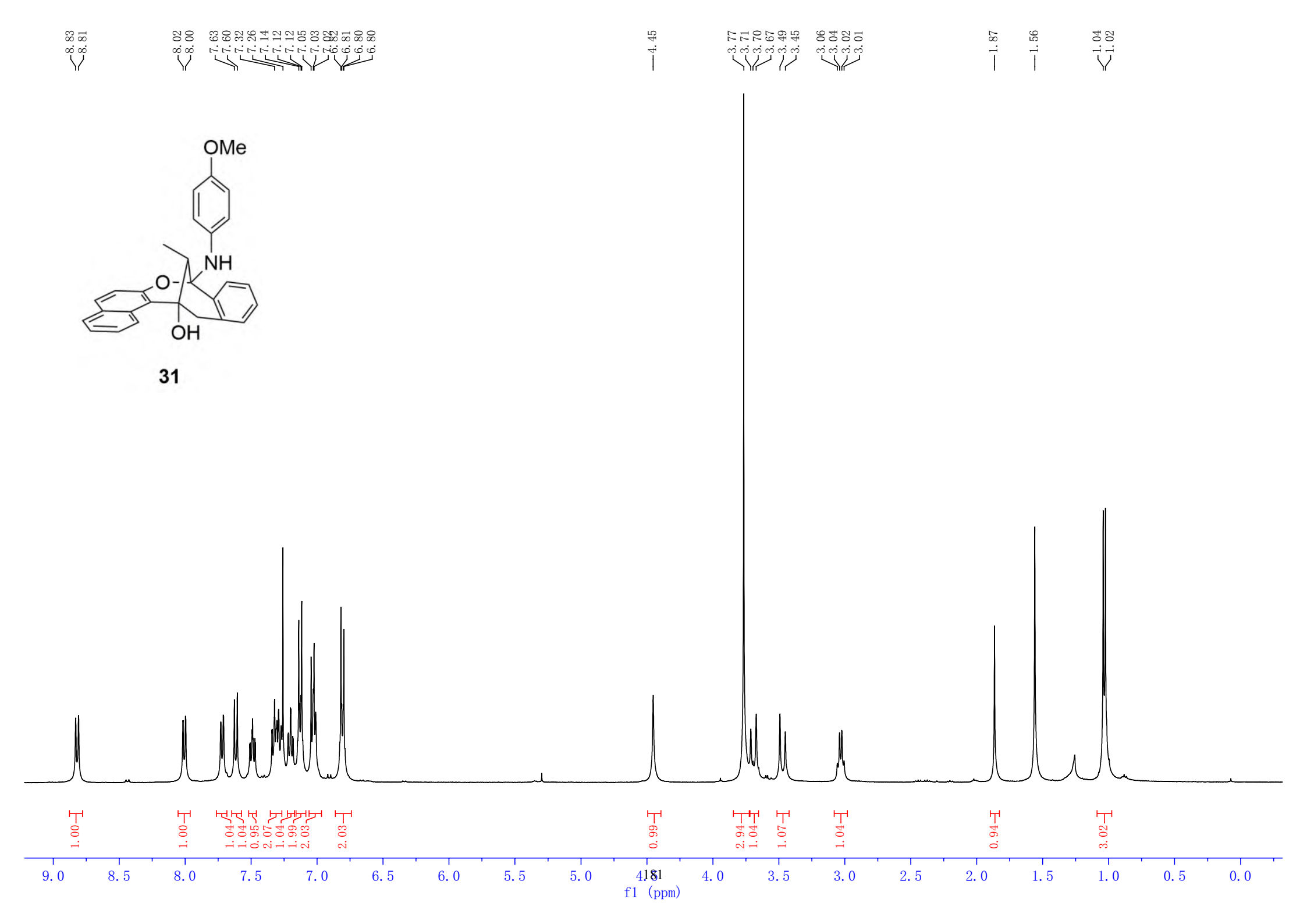

8.82
8.02
7.73
7.62
7.51
7.31
7.22
7.11
7.06
7.04
4.61
3.94
3.70
3.67
3.48
3.45
3.17
2.03
1.59
1.04
0.97
1.04
1.03
1.04
1.06
3.99
3.96
1.98
4.01
1.00
1.98
1.03
0.99
1.08
0.97
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



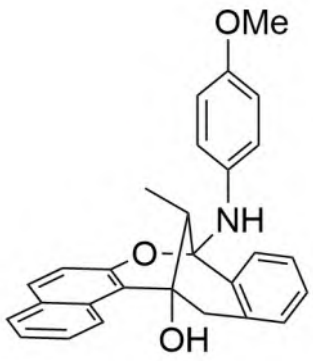
30

150.23
142.34
141.60
130.48
129.67
129.04
129.00
128.83
128.78
128.33
126.09
125.88
125.73
118.98
117.96
92.33
77.25
77.00
76.75
73.40
41.07
40.65
38.40
8.27

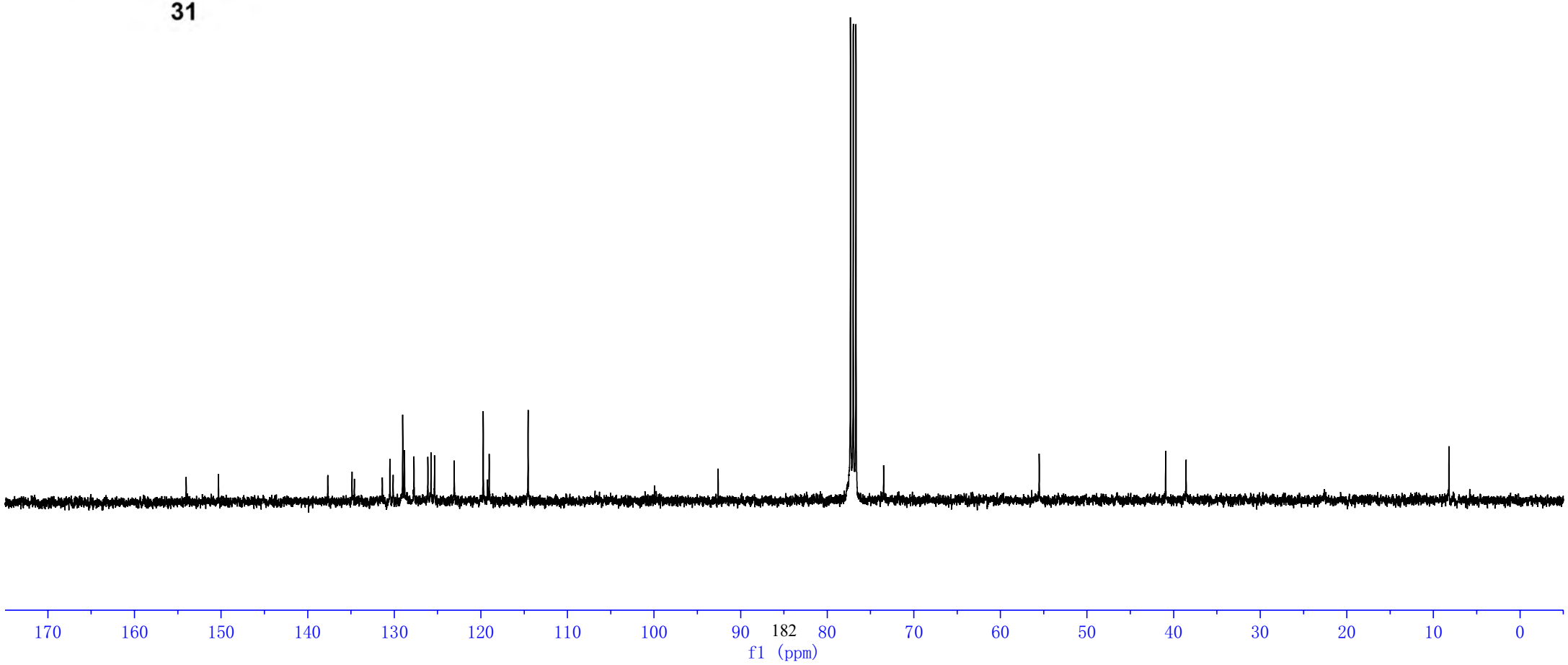



8.83
8.81
8.02
8.00
7.63
7.60
7.32
7.26
7.14
7.12
7.12
7.05
7.03
6.81
6.80
6.80
4.45
3.77
3.71
3.70
3.67
3.49
3.45
3.06
3.04
3.02
3.01
1.87
1.56
1.04
1.02
OMe
NH
O
OH
31
1.00
1.00
1.04
1.04
0.95
2.07
1.04
1.99
2.03
2.03
0.99
2.94
1.04
1.07
1.04
0.94
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

154.03
150.30
137.68
134.88
134.60
131.37
130.50
130.13
129.03
128.82
127.72
126.12
125.75
125.35
123.08
119.73
119.23
119.04
114.54
92.60
77.32
77.00
76.68
73.49
55.52
40.92
38.56
8.20

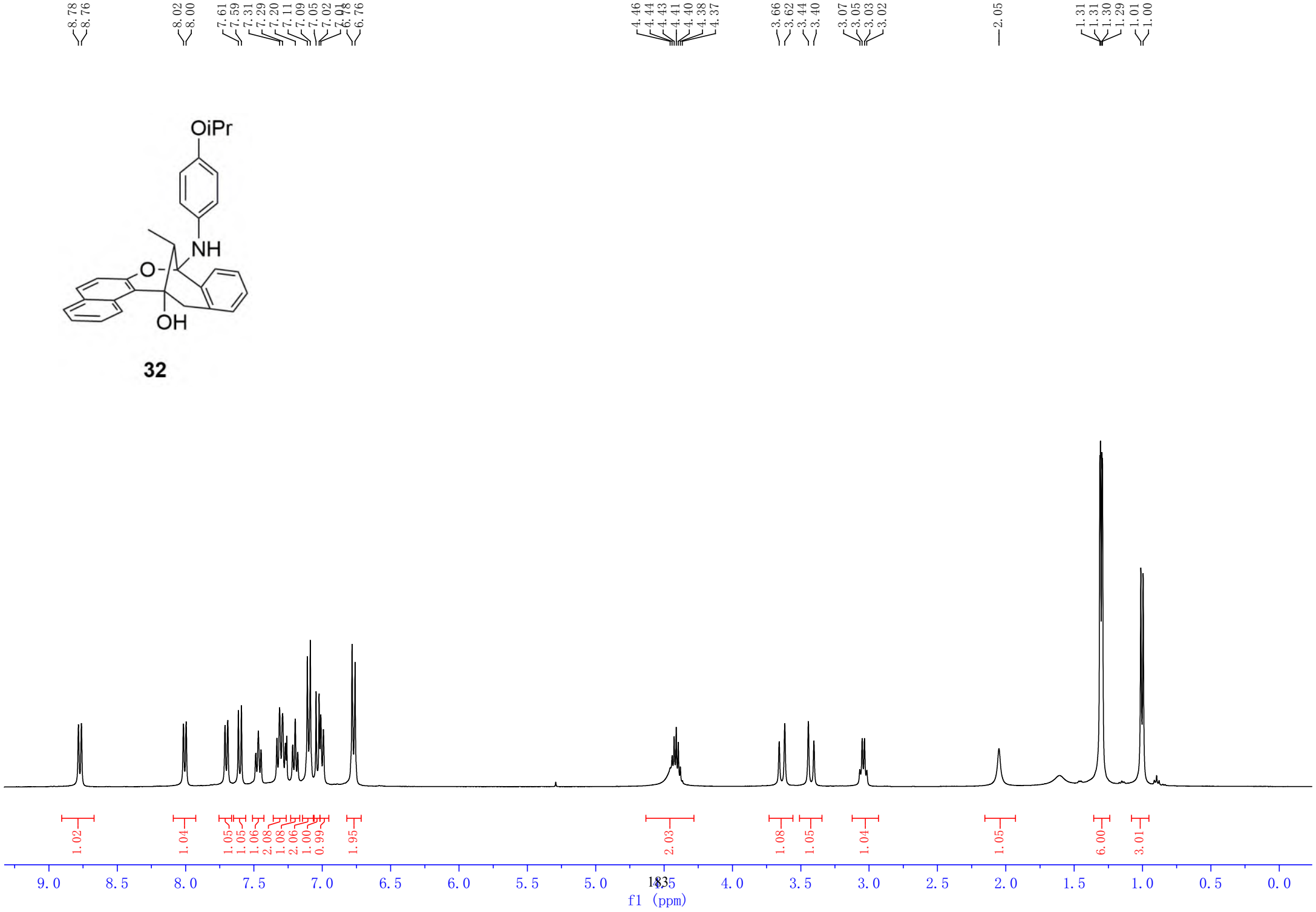


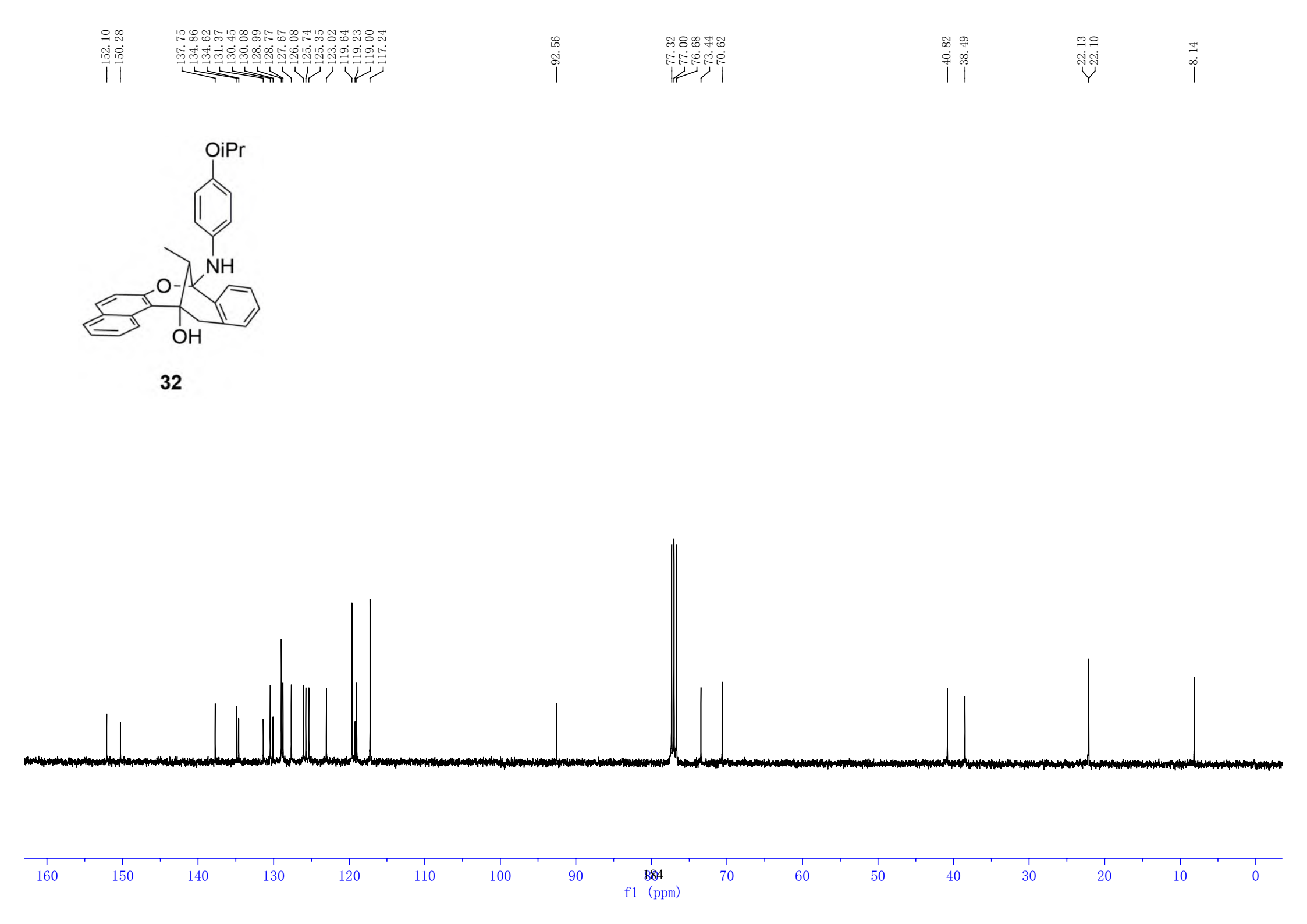
31



OiPr
NH
O
OH

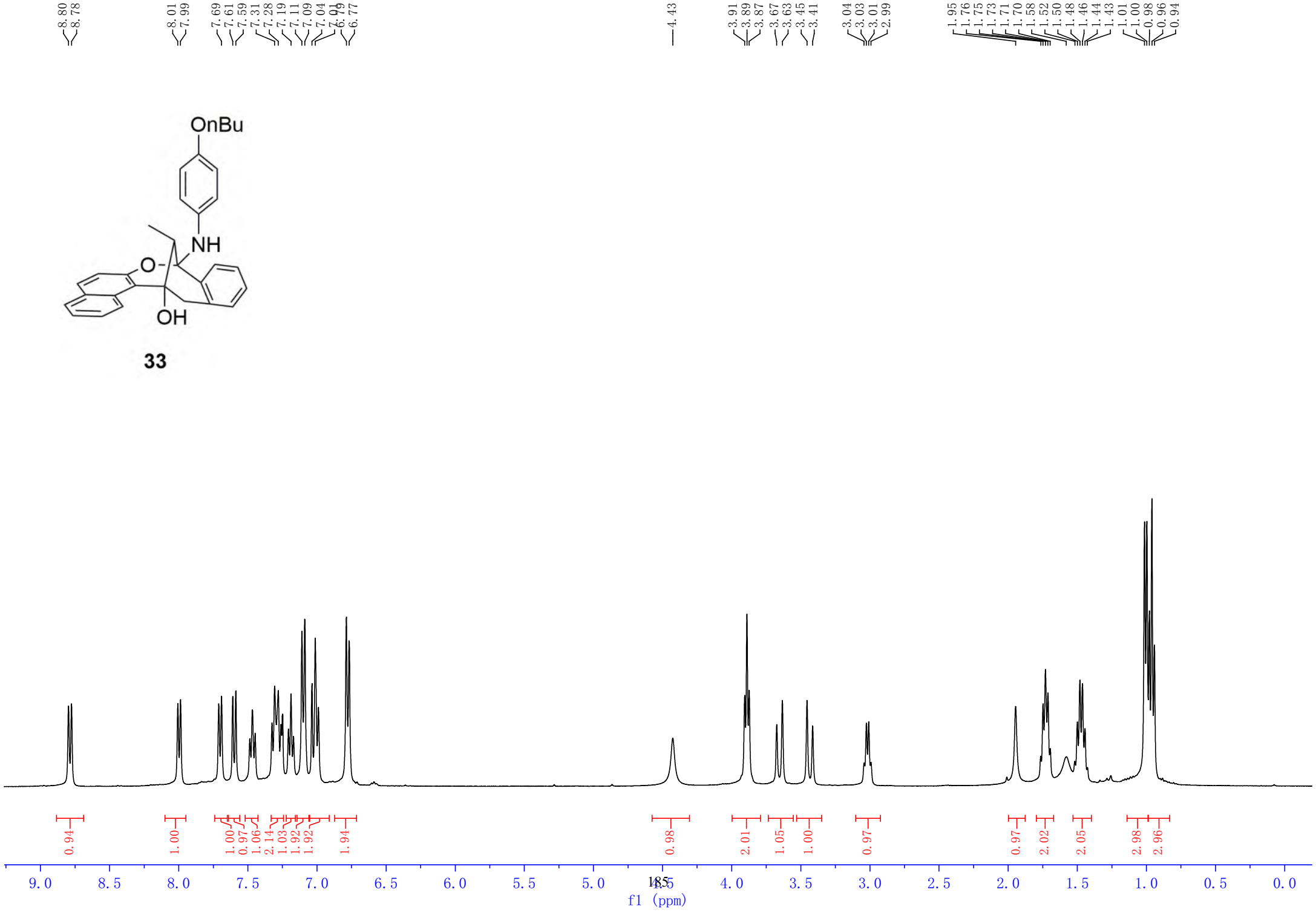
32


8.78
8.76
8.02
8.00
7.61
7.59
7.31
7.29
7.20
7.11
7.09
7.05
7.02
6.76
4.46
4.44
4.43
4.41
4.40
4.38
4.37
3.66
3.62
3.44
3.40
3.07
3.05
3.03
3.02
2.05
1.31
1.31
1.30
1.29
1.01
1.00
1.02
1.04
1.05
1.05
1.06
2.08
1.08
2.06
1.00
0.99
1.95
2.03
1.08
1.05
1.04
1.05
6.00
3.01
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
f1 (ppm)

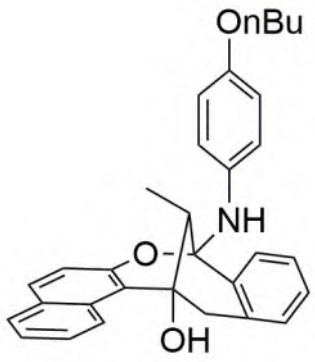

152.10
150.28
137.75
134.86
134.62
131.37
130.45
130.08
128.99
128.77
127.67
126.08
125.74
125.35
123.02
119.64
119.23
119.00
117.24
92.56
77.32
77.00
76.68
73.44
70.62
40.82
38.49
22.13
22.10
8.14
OiPr
NH
O
OH
32
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OnBu
NH
O
OH

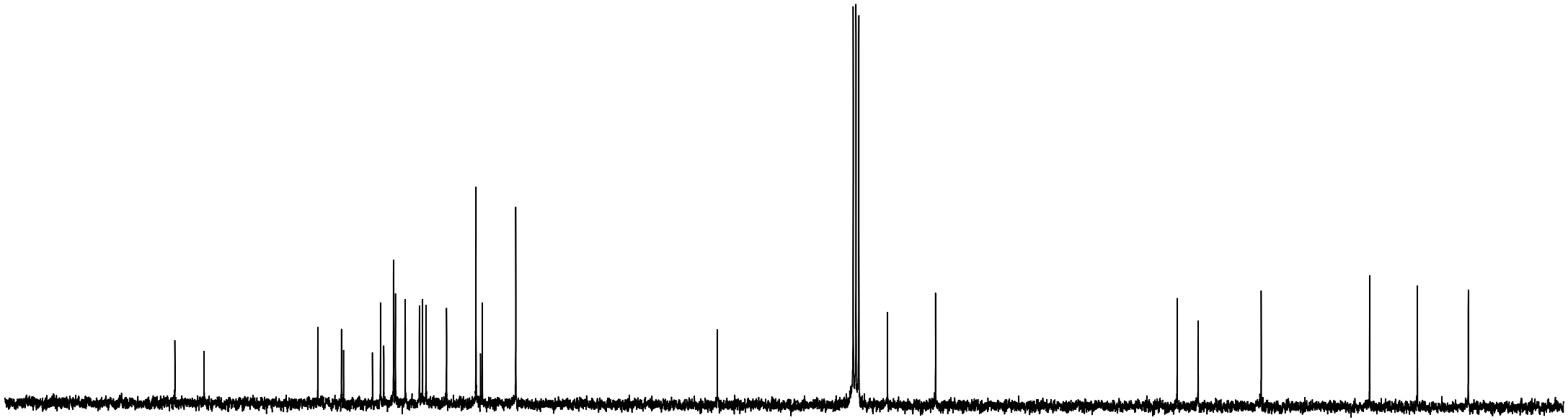
33

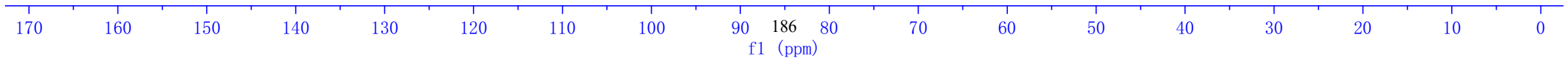

8.80
8.78
8.01
7.99
7.69
7.61
7.59
7.31
7.28
7.19
7.11
7.09
7.04
7.01
6.99
6.77
4.43
3.91
3.89
3.87
3.67
3.63
3.45
3.41
3.04
3.03
3.01
2.99
1.95
1.76
1.75
1.73
1.71
1.70
1.58
1.52
1.50
1.48
1.46
1.44
1.43
1.01
1.00
0.98
0.96
0.94
0.94
1.00
1.00
0.97
1.06
2.14
1.03
1.92
1.92
1.94
0.98
2.01
1.05
1.00
0.97
0.97
2.02
2.05
2.98
2.96
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
f1 (ppm)

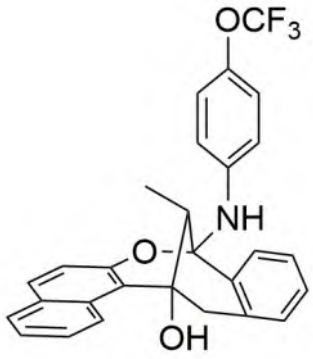
153.58
150.30
137.51
134.86
134.62
131.37
130.46
130.10
128.99
128.78
127.68
126.09
125.74
125.35
123.04
119.73
119.22
119.02
115.26
92.60
77.32
77.00
76.68
73.46
68.06
40.88
38.53
31.44
19.25
13.87
8.15



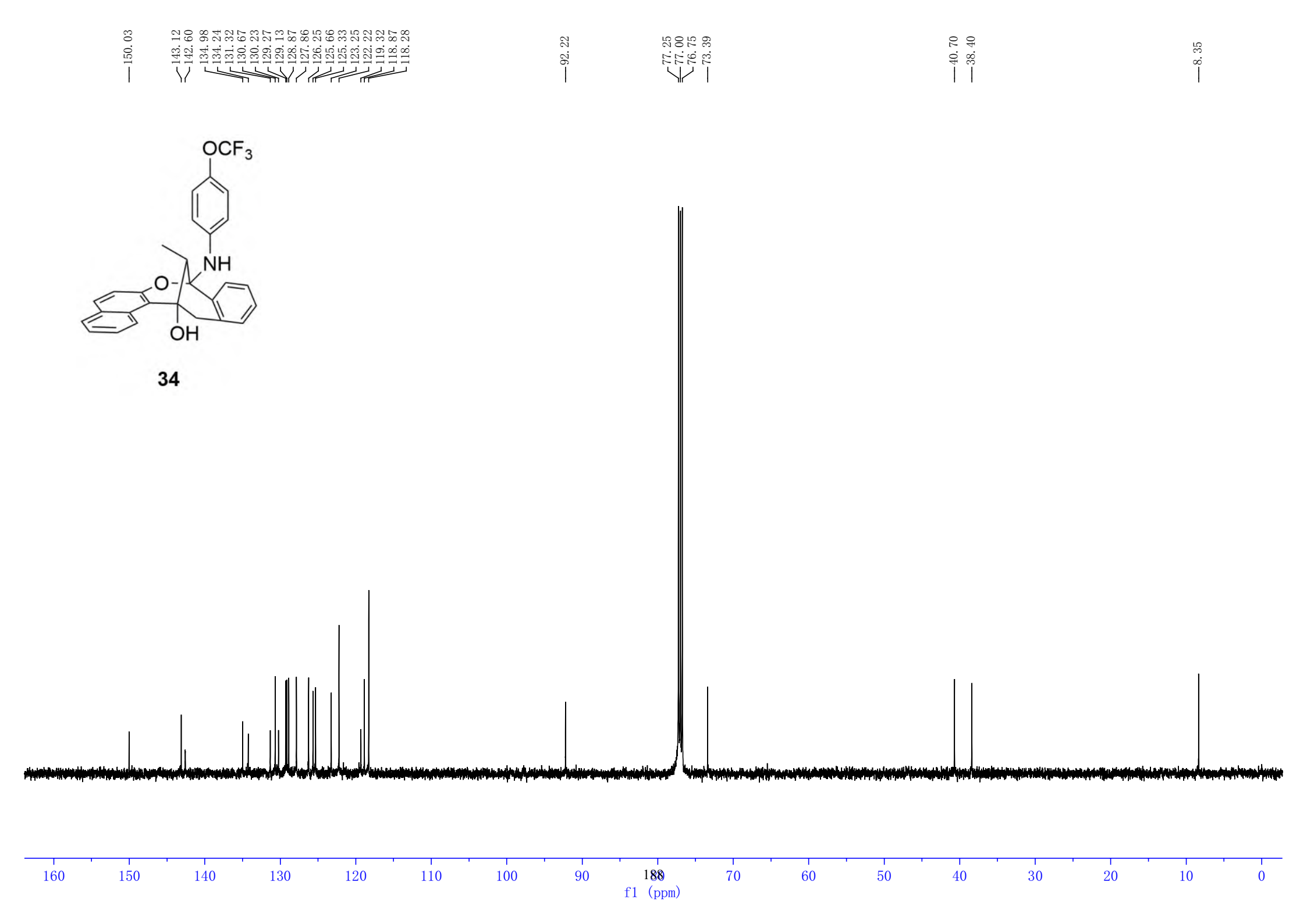
33





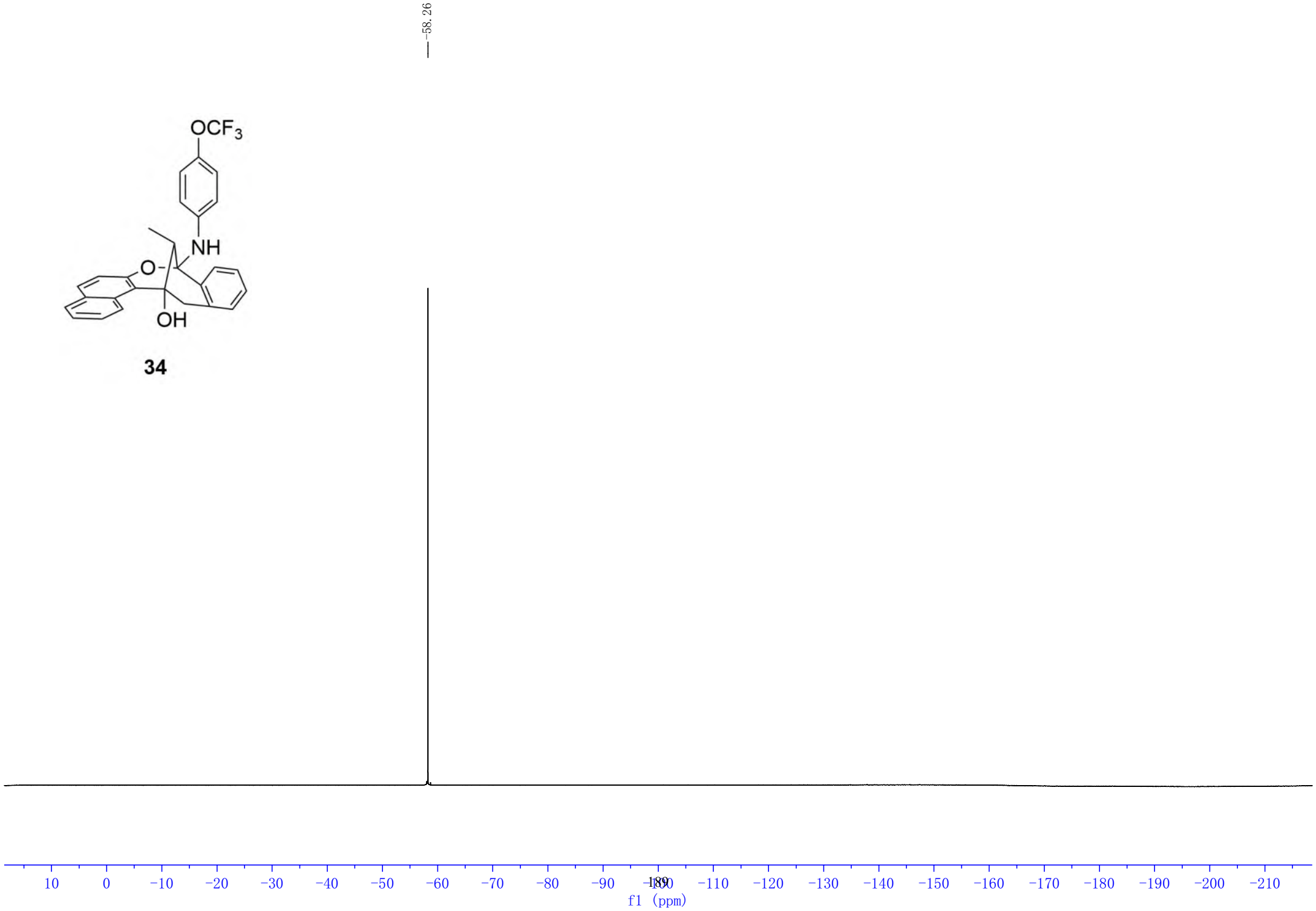


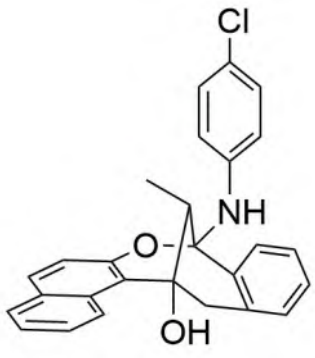
34


150.03
143.12
142.60
134.98
134.24
131.32
130.67
130.23
129.27
129.13
128.87
127.86
126.25
125.66
125.33
123.25
122.22
119.32
118.87
118.28
92.22
77.25
77.00
76.75
73.39
40.70
38.40
8.35
OCF3
NH
O
OH
34
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OCF3
NH
O
OH

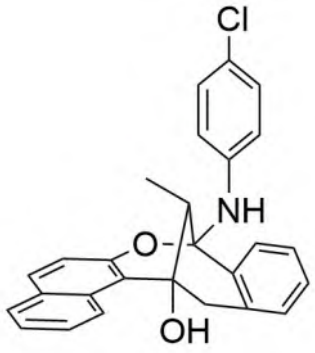
34


-58.26
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

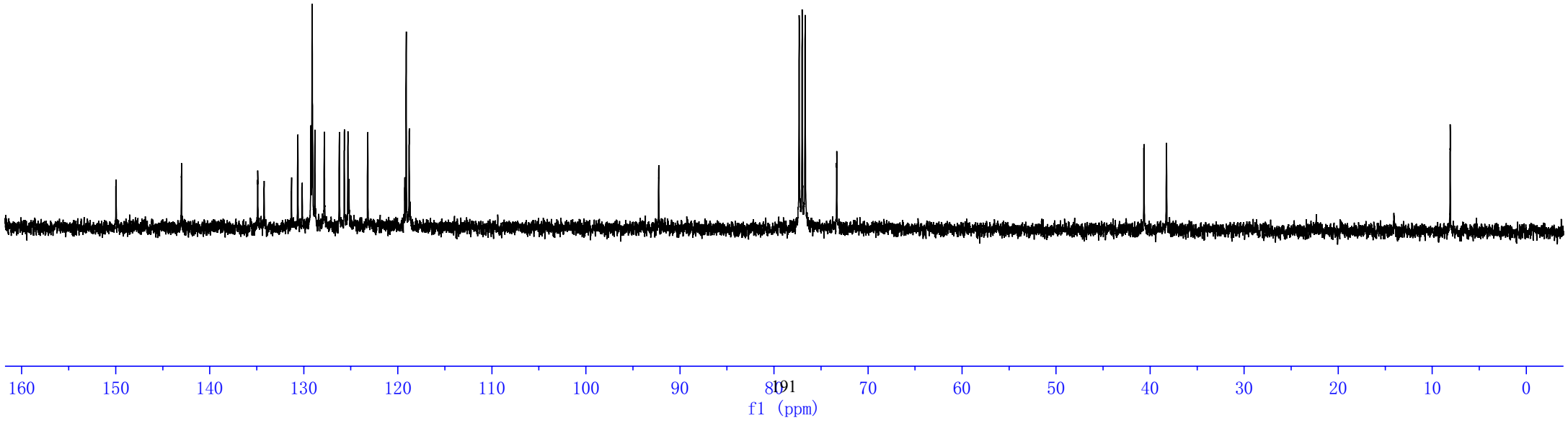


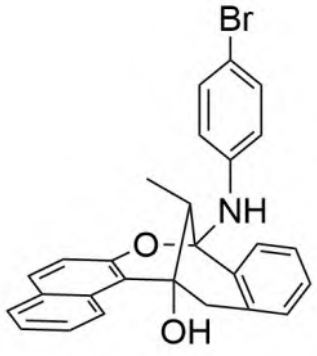
35

149.96
143.00
134.89
134.22
131.30
130.63
129.25
129.11
128.82
127.81
126.22
125.69
125.30
92.25
77.32
77.00
76.68
73.32
40.65
38.26
8.08

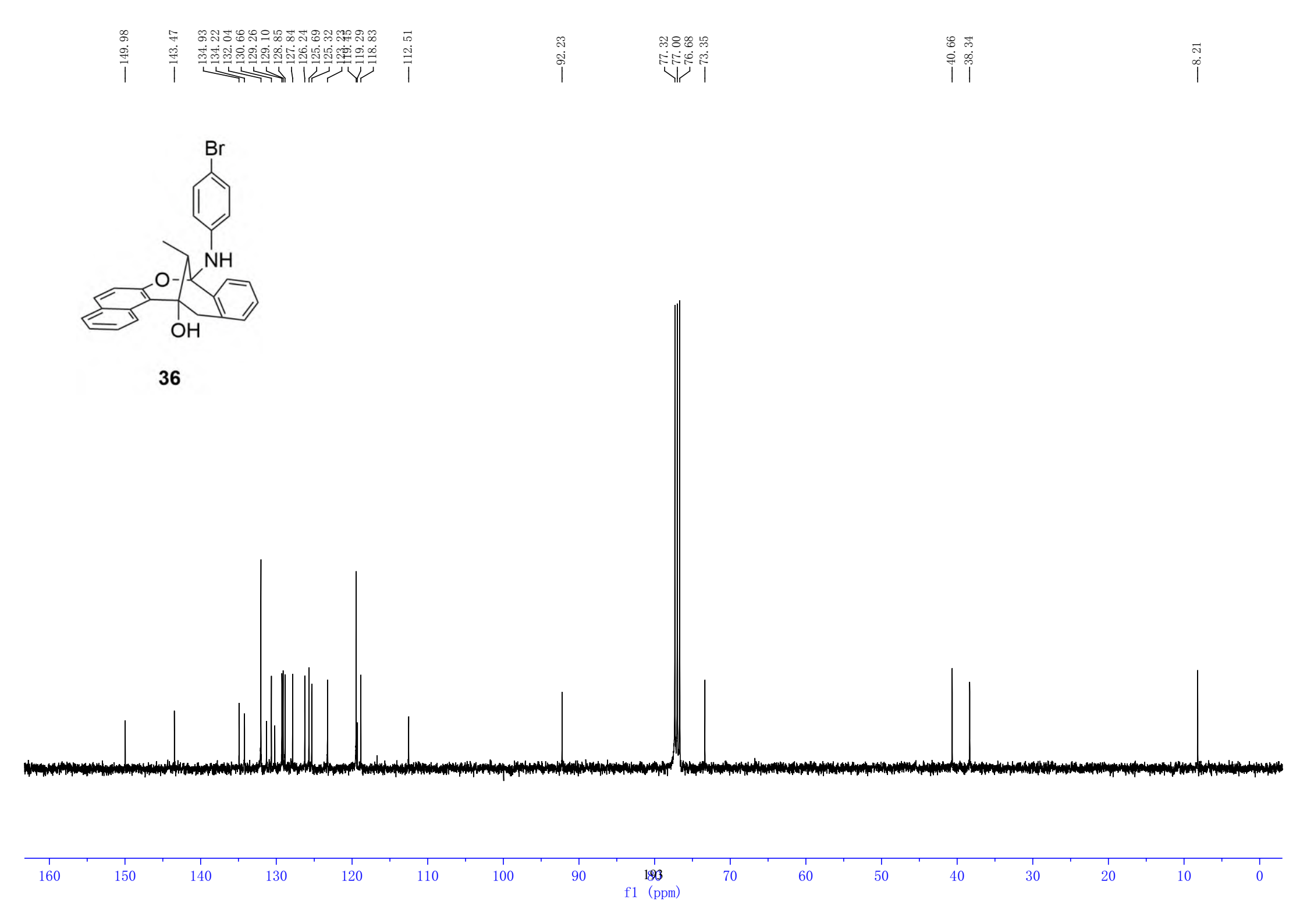


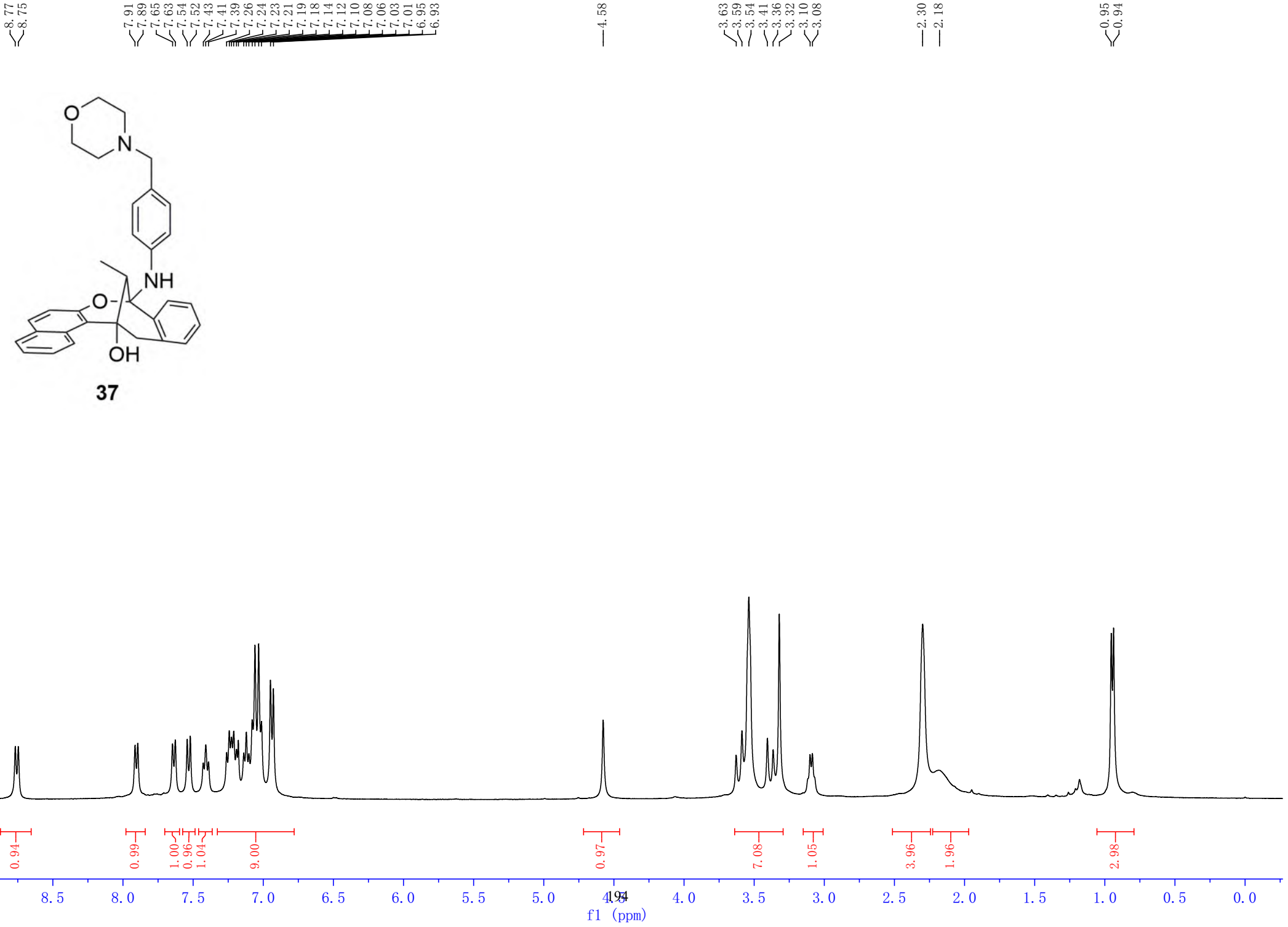
35



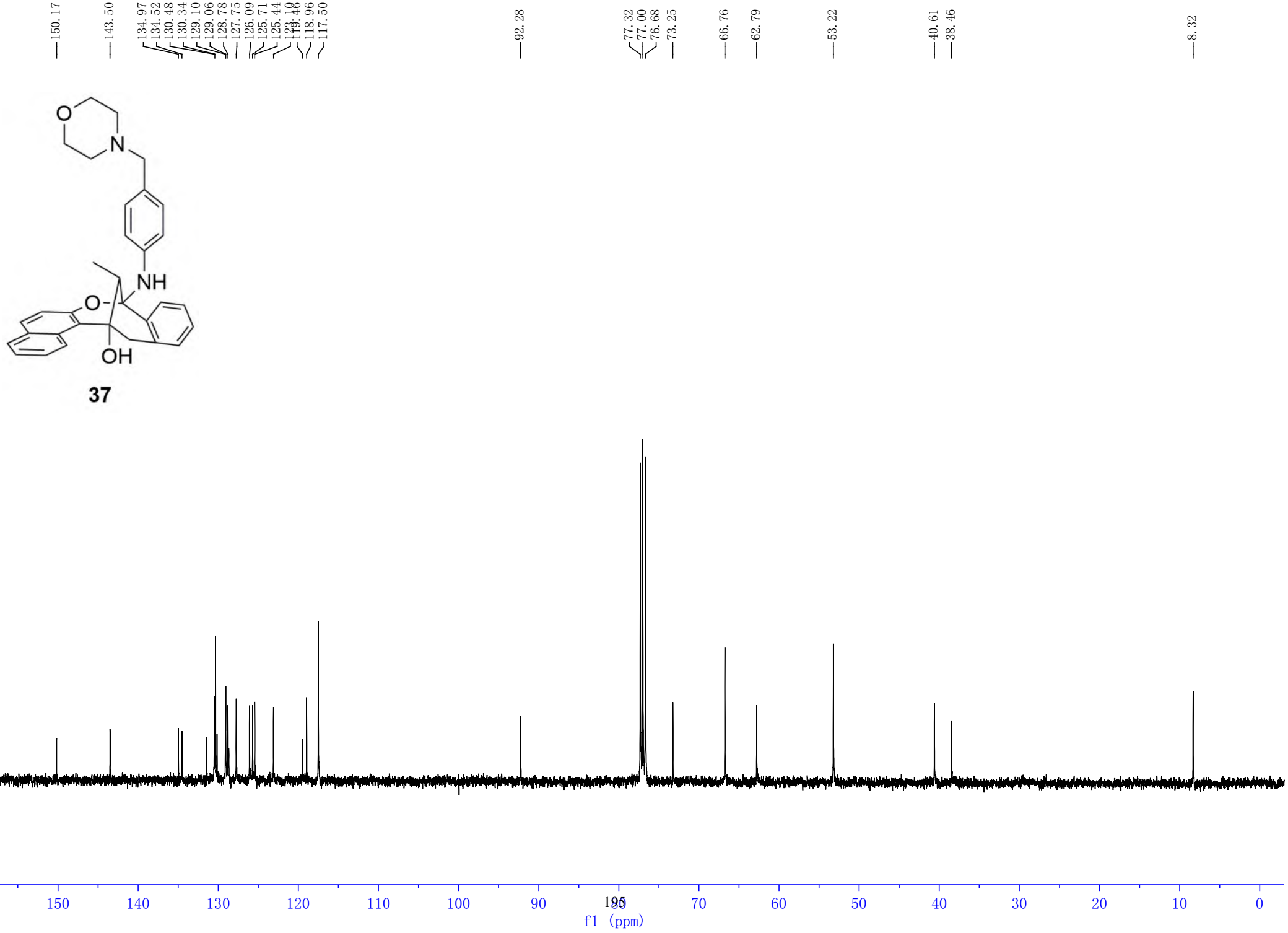


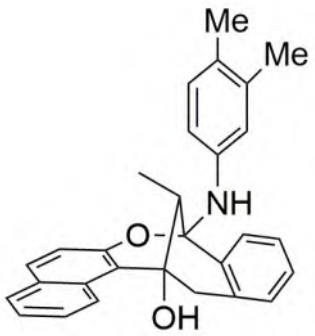
36


149.98
143.47
134.93
134.22
132.04
130.66
129.26
129.10
128.85
127.84
126.24
125.69
125.32
123.23
119.29
118.83
112.51
92.23
77.32
77.00
76.68
73.35
40.66
38.34
8.21
Br
NH
O
OH
36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

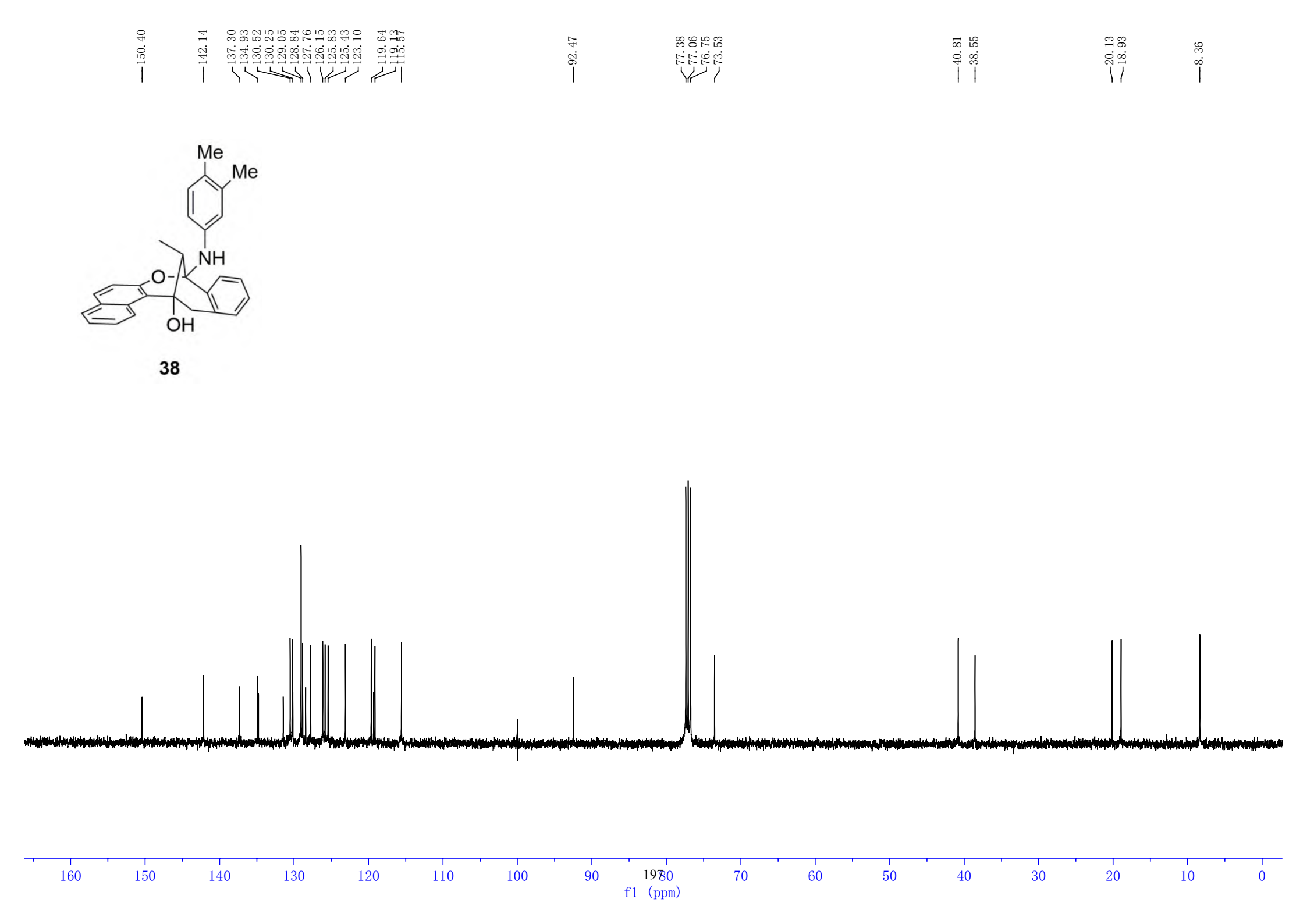

8.77
8.75
7.91
7.89
7.65
7.63
7.54
7.52
7.43
7.41
7.39
7.26
7.24
7.23
7.21
7.19
7.18
7.14
7.12
7.10
7.08
7.06
7.03
7.01
6.95
6.93
4.58
3.63
3.59
3.54
3.41
3.36
3.32
3.10
3.08
2.30
2.18
0.95
0.94
O
N
NH
O
OH
0.94
0.99
1.00
0.96
1.04
9.00
0.97
7.08
1.05
3.96
1.96
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

37


150.17
143.50
134.97
134.52
130.48
130.34
129.10
129.06
128.78
127.75
126.09
125.71
125.44
118.96
117.50
92.28
77.32
77.00
76.68
73.25
66.76
62.79
53.22
40.61
38.46
8.32
O
N
NH
O
OH
37
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

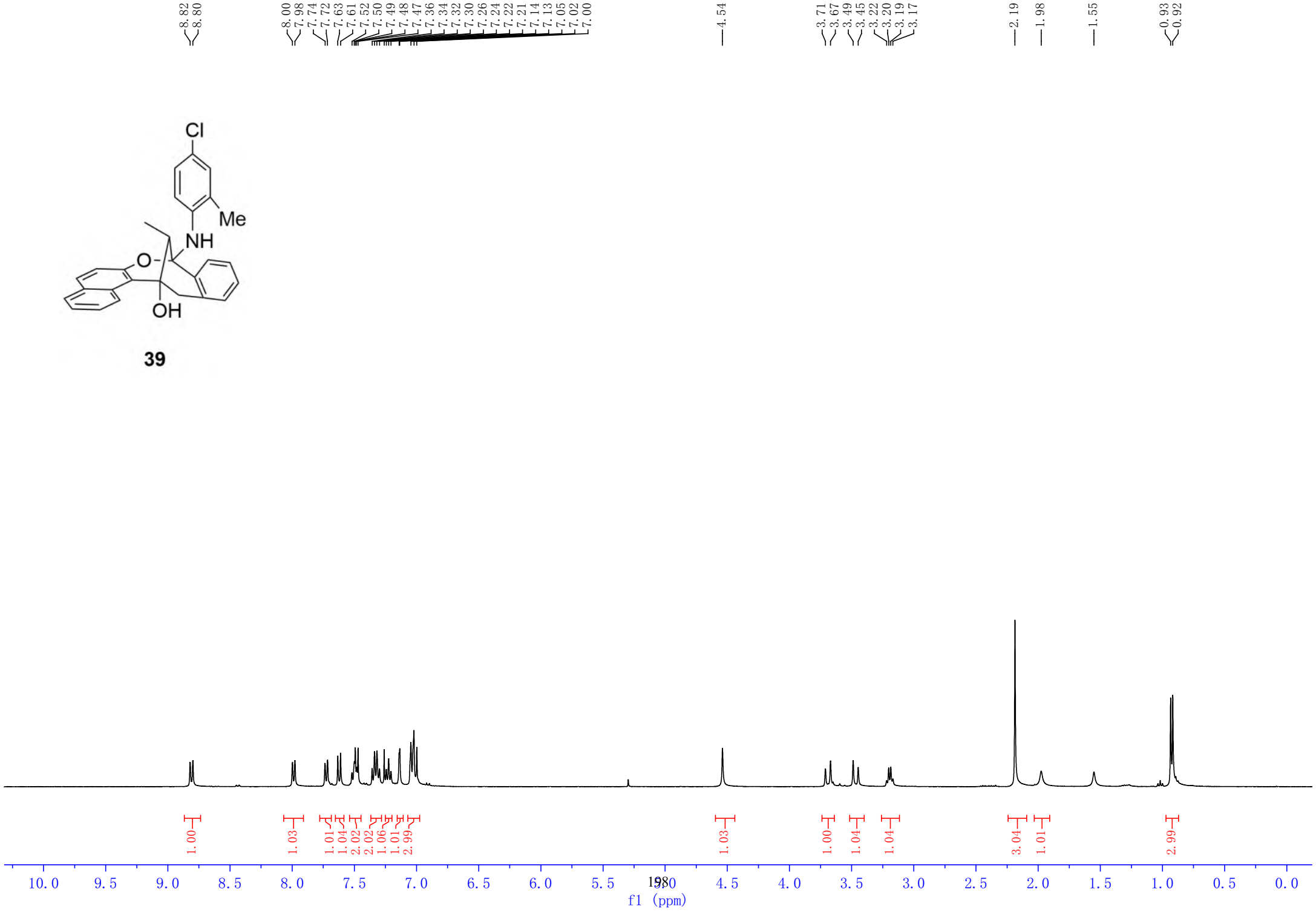


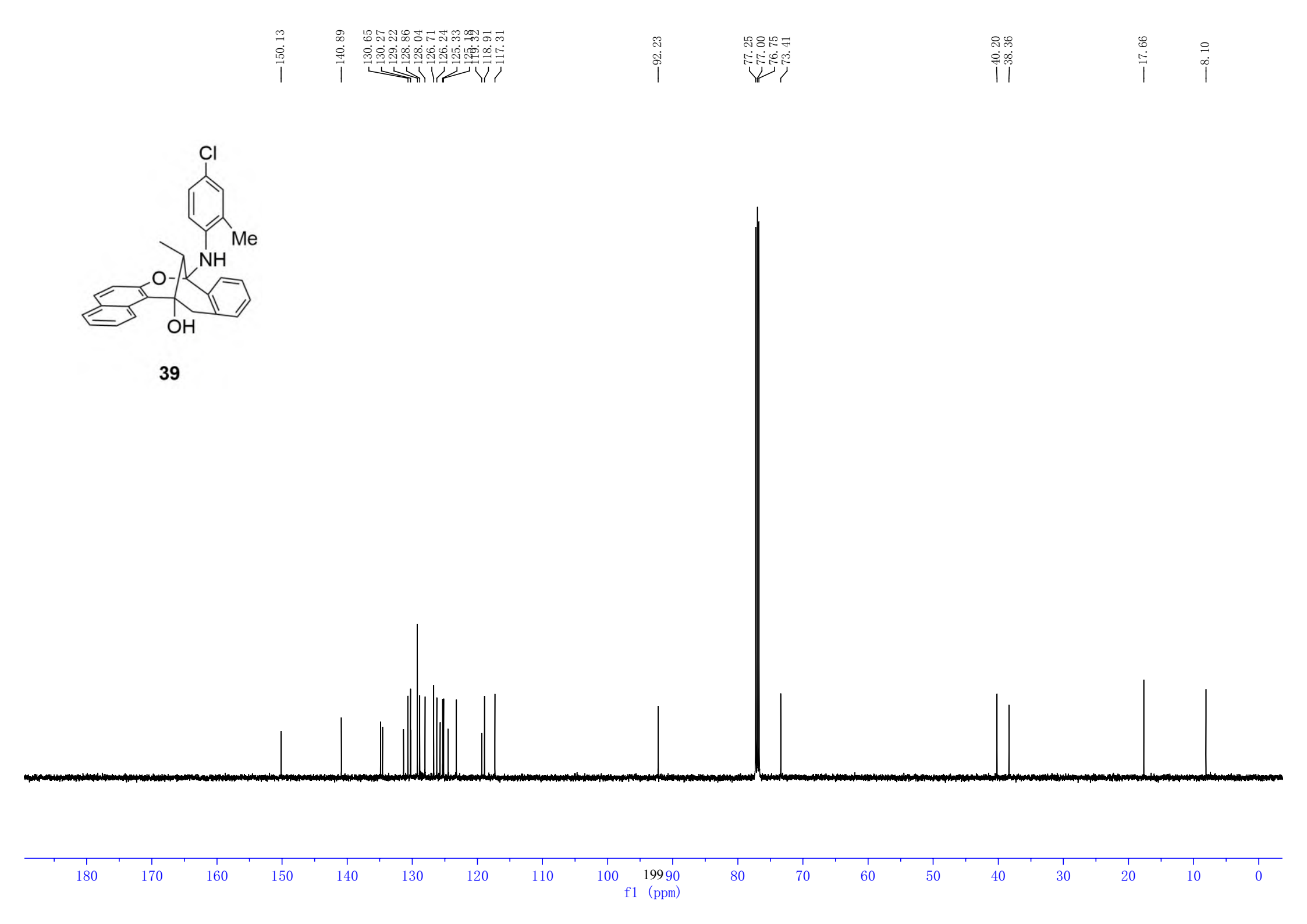
38

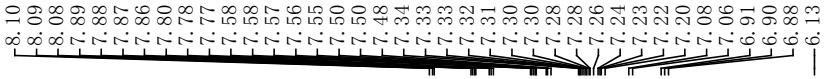

150.40
142.14
137.30
134.93
130.52
130.25
129.05
128.84
127.76
126.15
125.83
125.43
123.10
119.64
92.47
77.38
77.06
76.75
73.53
40.81
38.55
20.13
18.93
8.36
Me
Me
NH
O
OH
38
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

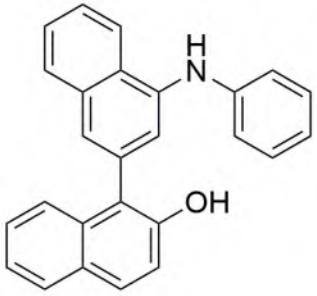
Cl
Me
NH
O
OH

39

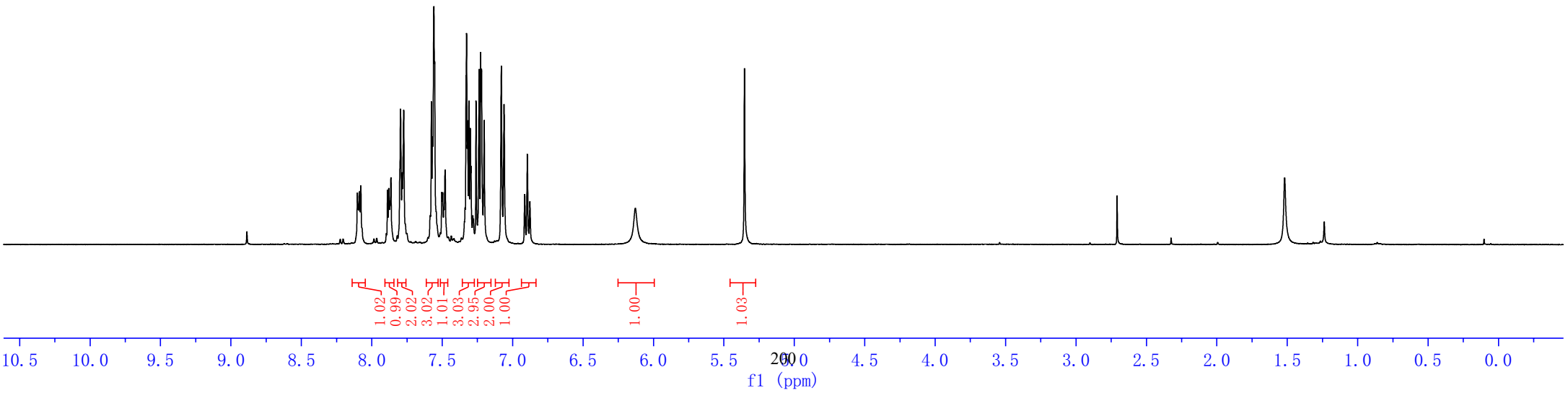

8.82
8.80
8.00
7.98
7.74
7.72
7.63
7.61
7.52
7.50
7.49
7.48
7.47
7.36
7.34
7.32
7.30
7.26
7.24
7.22
7.21
7.14
7.13
7.05
7.02
7.00
4.54
3.71
3.67
3.49
3.45
3.22
3.20
3.19
3.17
2.19
1.98
1.55
0.93
0.92
1.00
1.03
1.01
1.04
2.02
2.02
1.06
1.01
2.99
1.03
1.00
1.04
1.04
3.04
1.01
2.99
10.0
9.5
9.0
8.5
8.0
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
f1 (ppm)

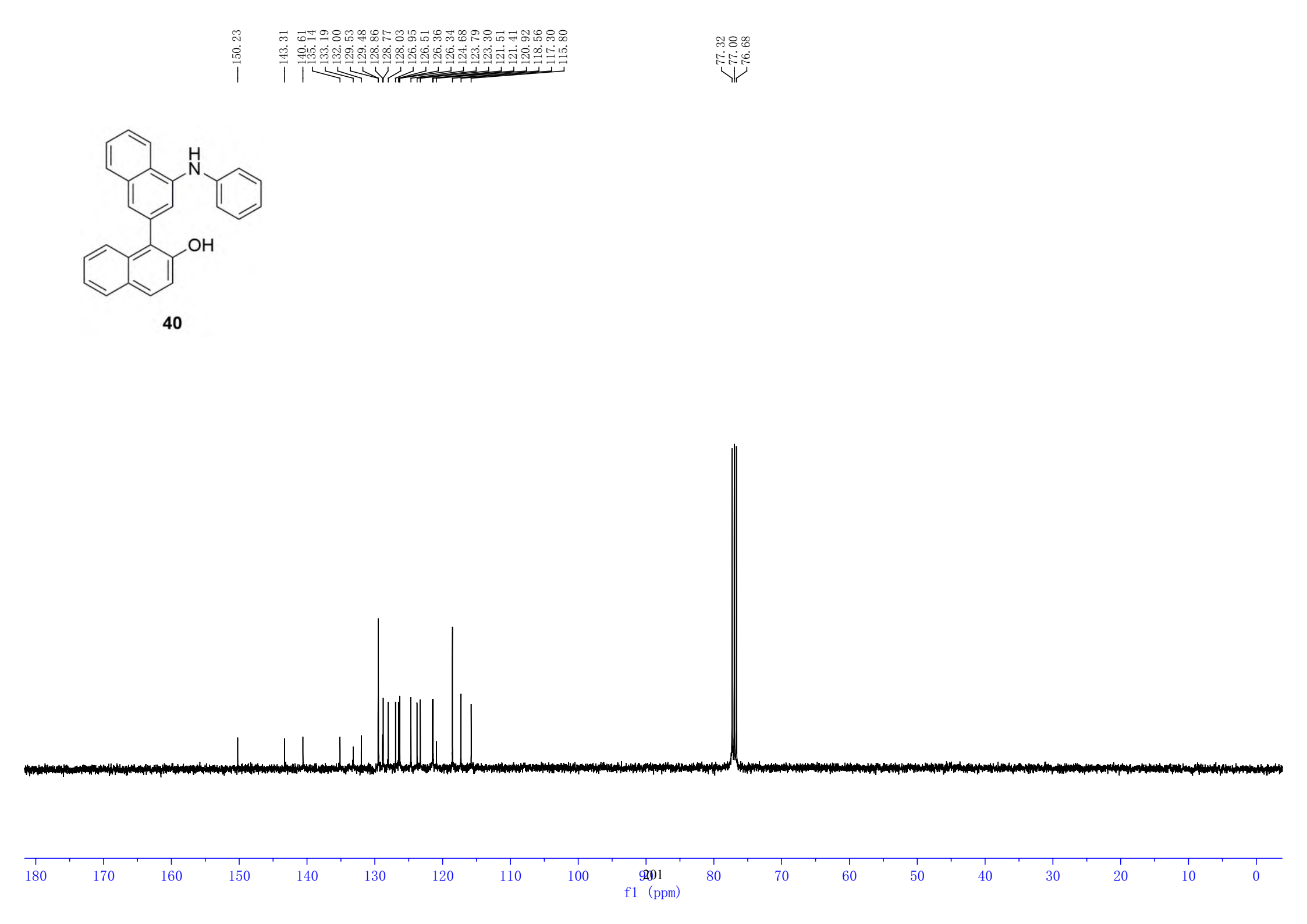

150.13
140.89
130.65
130.27
129.22
128.86
128.04
126.71
126.24
125.33
118.91
117.31
92.23
77.25
77.00
76.75
73.41
40.20
38.36
17.66
8.10
Cl
Me
NH
O
OH
39
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

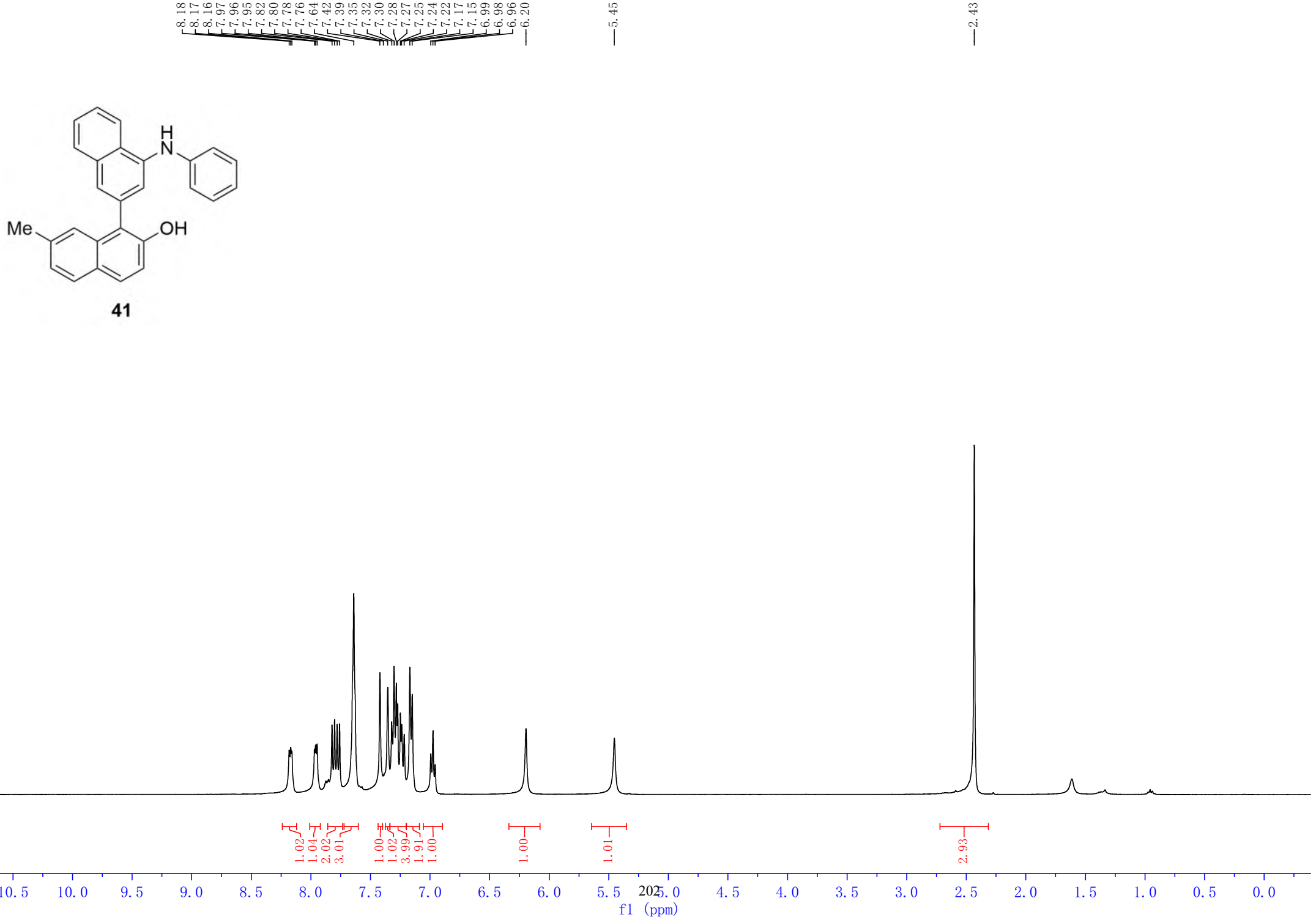

8.10
8.09
8.08
7.89
7.88
7.87
7.86
7.80
7.78
7.77
7.58
7.58
7.57
7.56
7.55
7.50
7.50
7.48
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.28
7.28
7.26
7.24
7.23
7.22
7.20
7.08
7.06
6.91
6.90
6.88
6.13
5.35
1.52

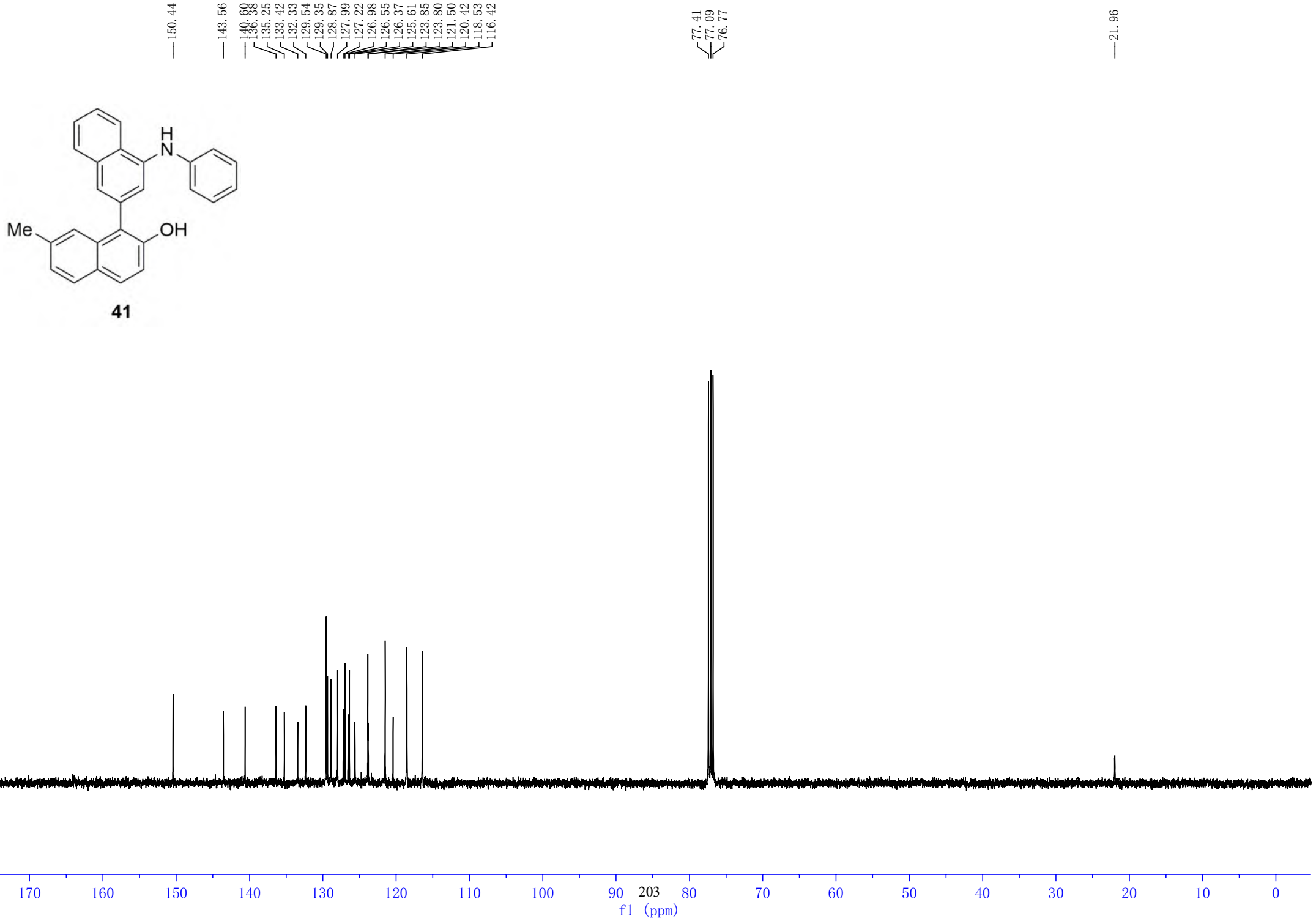

H
N
OH

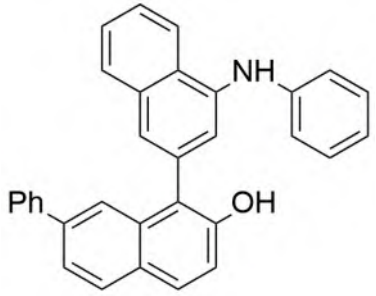
40


1.02
0.99
2.02
3.02
1.01
3.03
2.95
2.00
1.00
1.00
1.03
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
f1 (ppm)

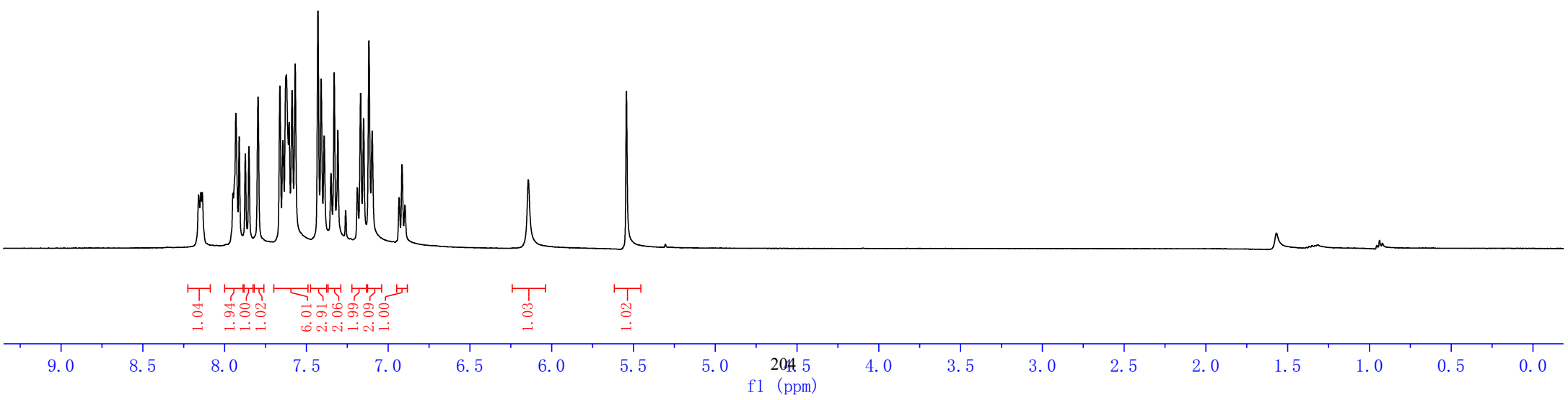

150.23
143.31
140.61
135.14
133.19
132.00
129.53
129.48
128.86
128.77
128.03
126.95
126.51
126.36
126.34
124.68
123.79
123.30
121.51
121.41
120.92
118.56
117.30
115.80
77.32
77.00
76.68
H
N
OH
40
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

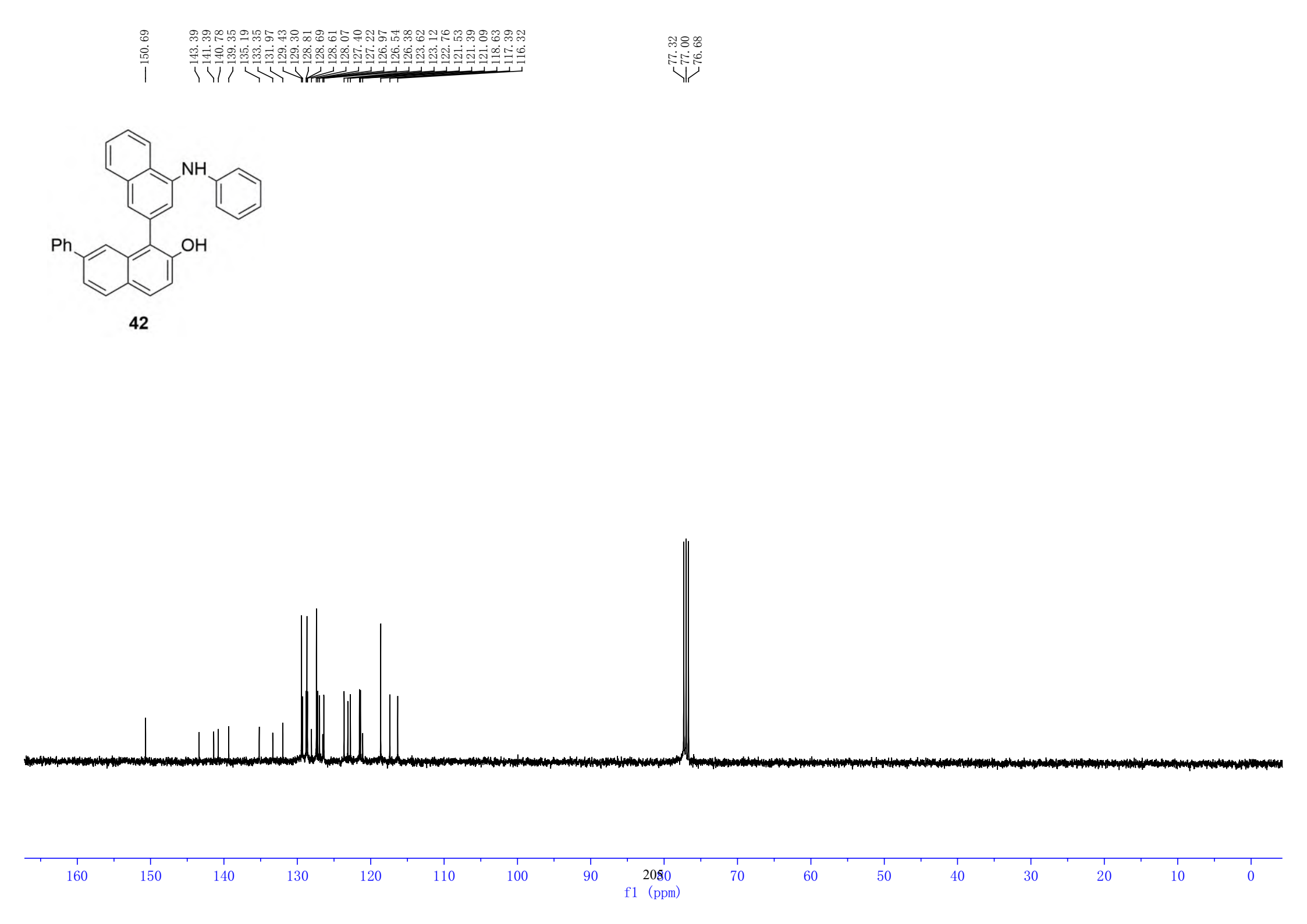

8.18
8.17
8.16
7.97
7.96
7.95
7.82
7.80
7.78
7.76
7.64
7.42
7.39
7.35
7.32
7.30
7.28
7.27
7.25
7.24
7.22
7.17
7.15
6.99
6.98
6.96
6.20
5.45
2.43
H
N
Me
OH
41
1.02
1.04
2.02
3.01
1.00
1.02
3.99
1.91
1.00
1.00
1.01
2.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.44
143.56
140.60
136.38
135.25
133.42
132.33
129.54
129.35
128.87
127.99
127.22
126.98
126.55
126.37
125.61
123.85
123.80
121.50
120.42
118.53
116.42
77.41
77.09
76.77
21.96
H
N
Me
OH
41
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

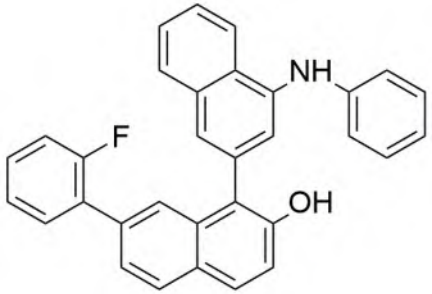

NH
Ph
OH

42

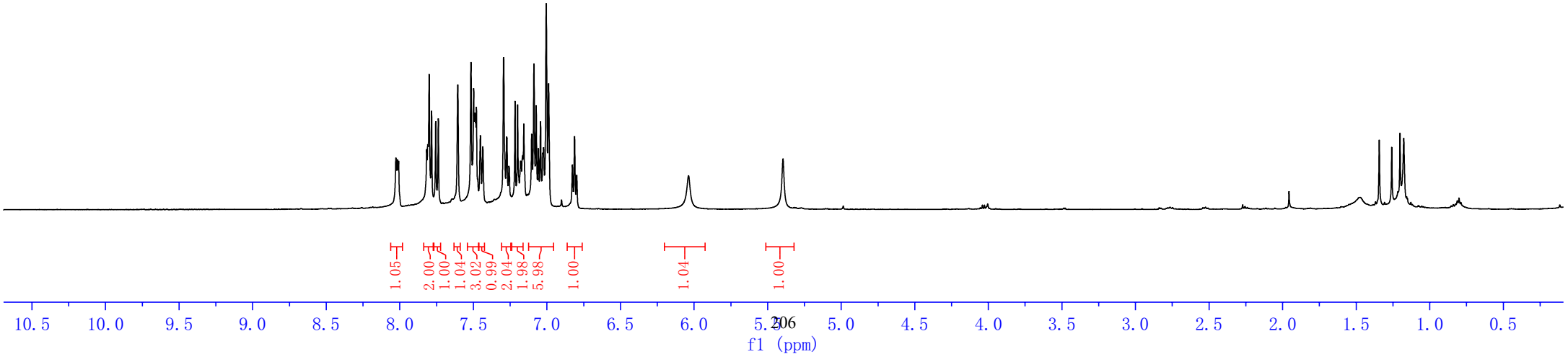

8.16
8.15
8.14
7.95
7.93
7.91
7.87
7.85
7.80
7.66
7.64
7.62
7.61
7.59
7.57
7.43
7.41
7.39
7.35
7.33
7.31
7.26
7.19
7.17
7.15
7.12
7.10
6.93
6.92
6.90
6.14
5.54
1.57
1.04
1.94
1.00
1.02
6.01
2.91
2.06
1.99
2.09
1.00
1.03
1.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

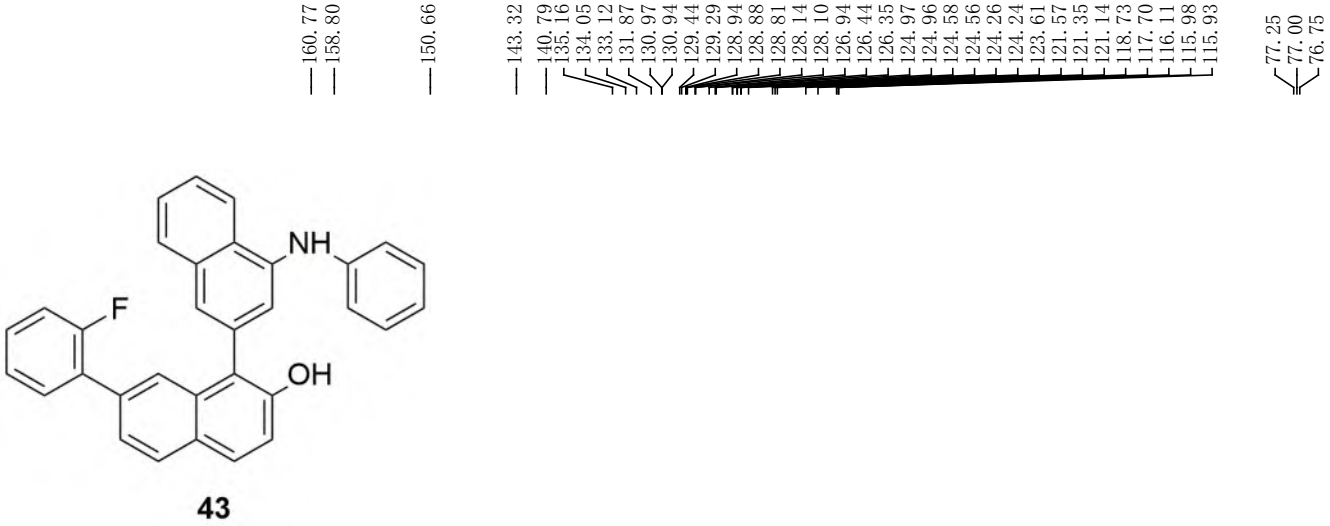

150.69
143.39
141.39
140.78
139.35
135.19
133.35
131.97
129.43
129.30
128.81
128.69
128.61
128.07
127.40
127.22
126.97
126.54
126.38
123.62
123.12
122.76
121.53
121.39
121.09
118.63
117.39
116.32
77.32
77.00
76.68
NH
Ph
OH
42
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.03
8.02
8.01
7.82
7.81
7.80
7.78
7.76
7.74
7.61
7.52
7.50
7.49
7.48
7.45
7.44
7.29
7.27
7.27
7.26
7.22
7.20
7.18
7.16
7.16
7.13
7.10
7.09
7.07
7.06
7.04
7.03
7.02
7.00
6.99
6.83
6.81
6.80
6.04
5.40

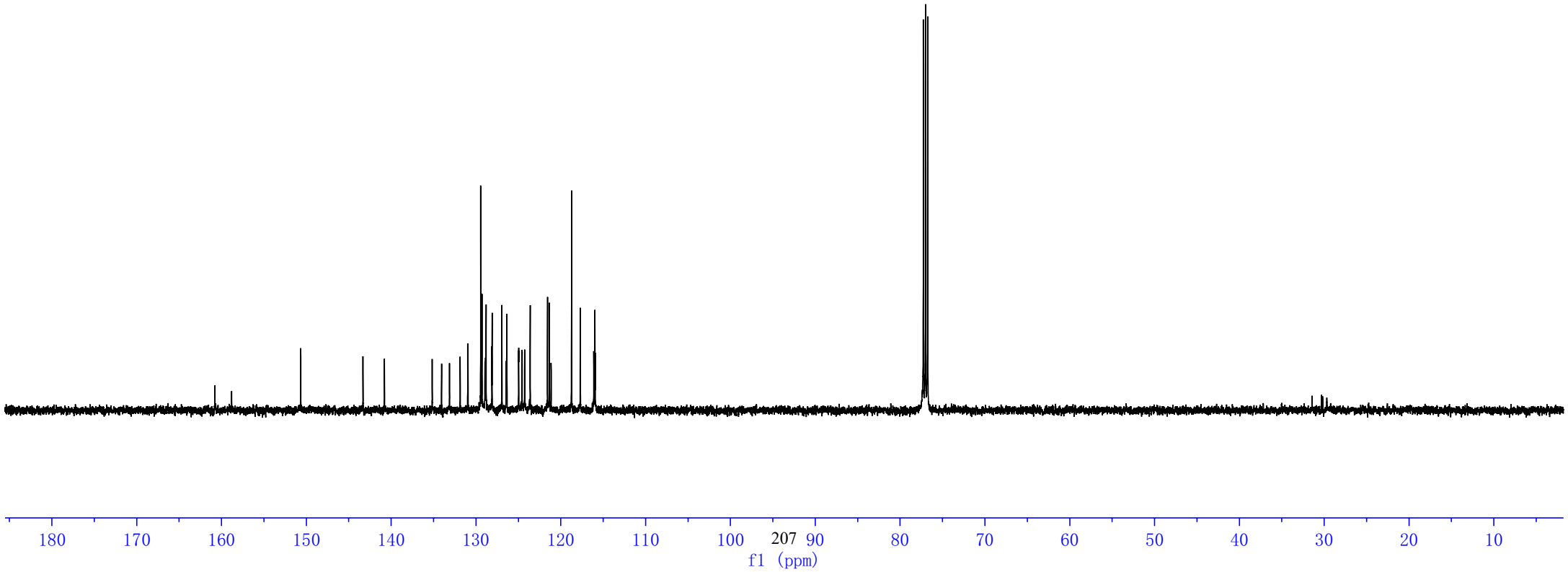

NH
F
OH

43


1.05
2.00
1.00
1.04
3.02
0.99
2.04
1.98
5.98
1.00
1.04
1.00
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
f1 (ppm)

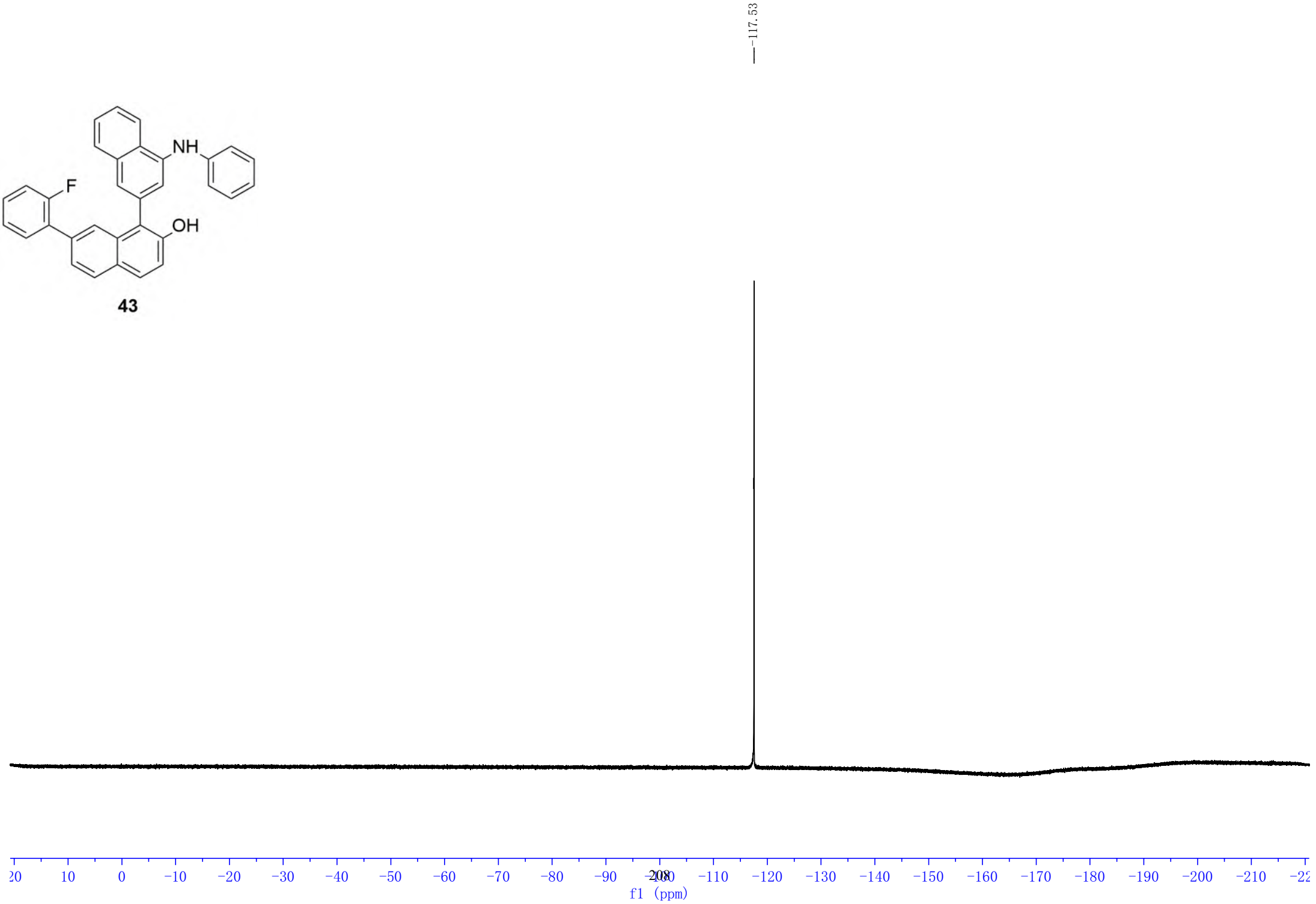

160.77
158.80
150.66
143.32
140.79
135.16
134.05
133.12
131.87
130.97
130.94
129.44
129.29
128.94
128.88
128.81
128.14
128.10
126.94
126.44
126.35
124.97
124.96
124.58
124.56
124.26
124.24
123.61
121.57
121.35
121.14
118.73
117.70
116.11
115.98
115.93
77.25
77.00
76.75
NH
F
OH

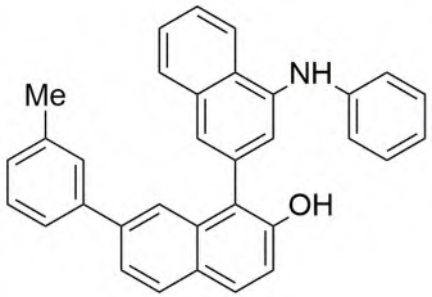
43


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

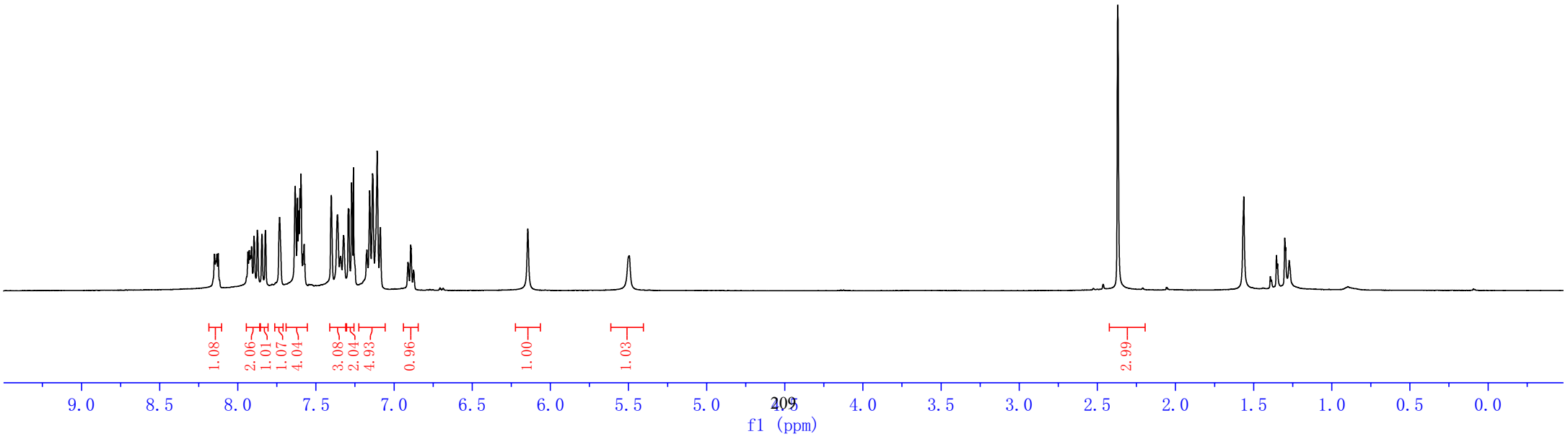
NH
F
OH

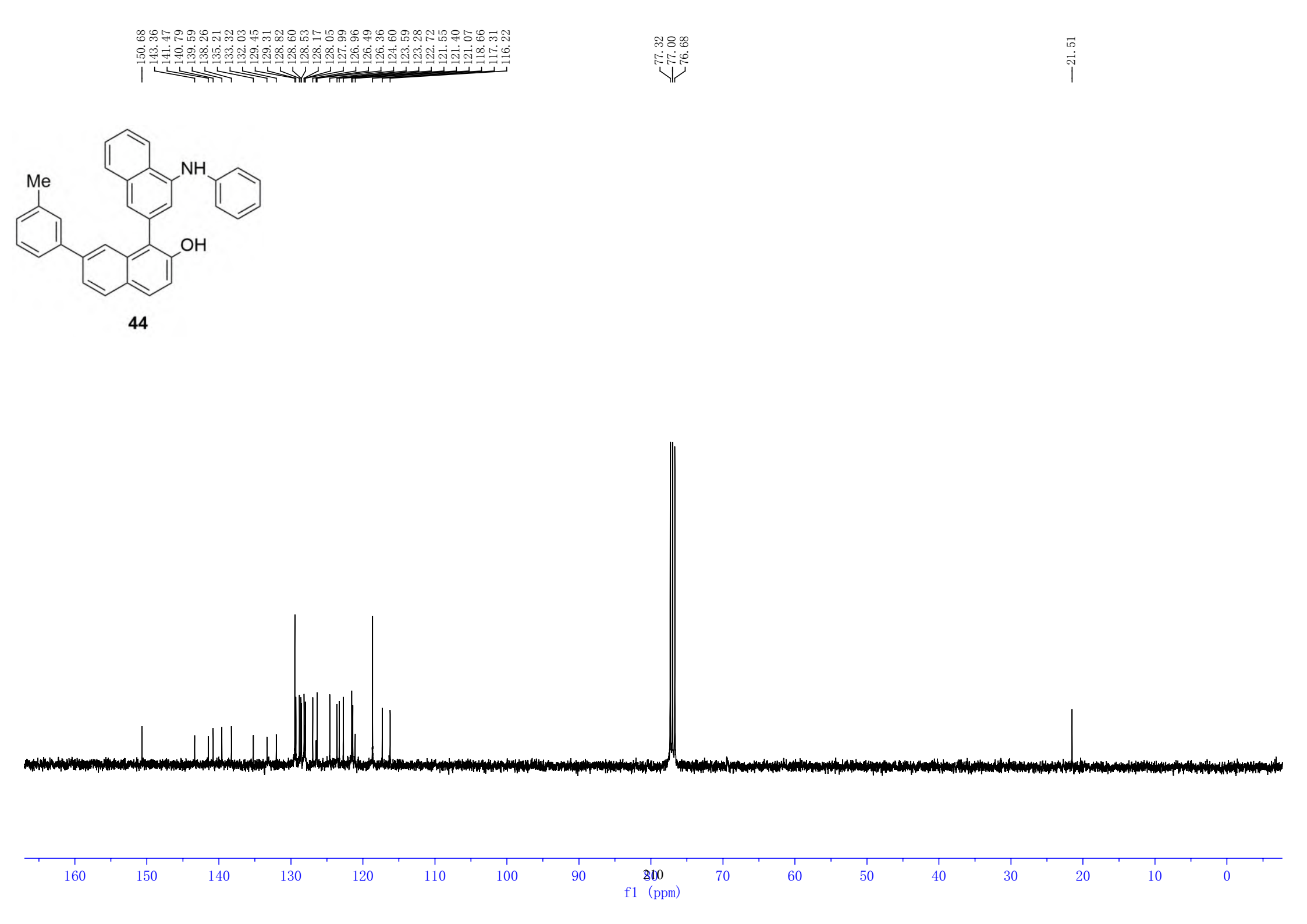
43


-117.53
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


Me
NH
OH

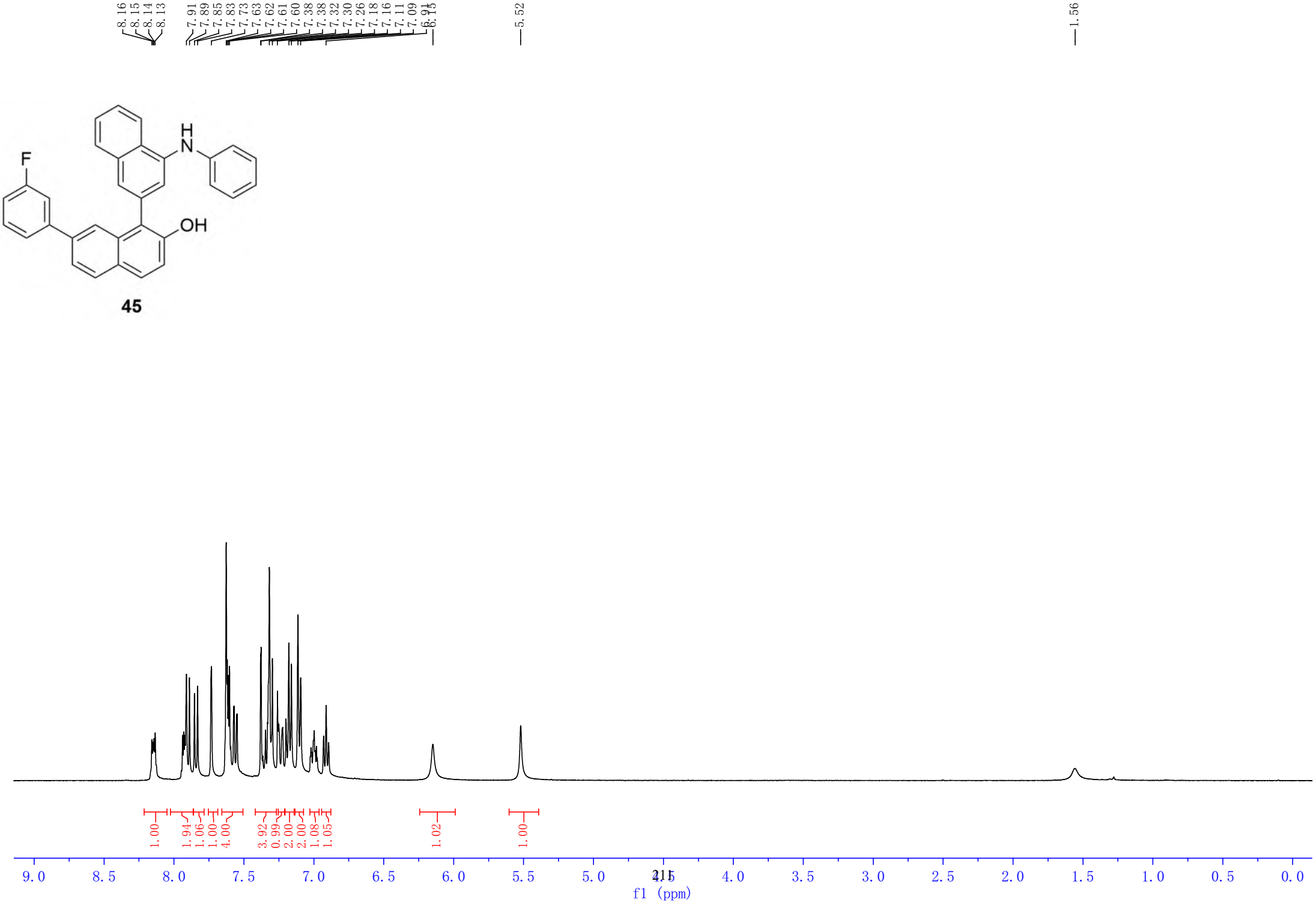
44

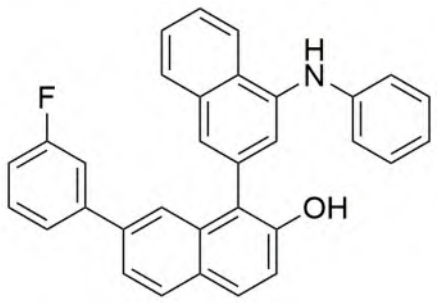

8.15
8.13
8.13
7.94
7.93
7.92
7.91
7.90
7.88
7.85
7.82
7.73
7.63
7.62
7.61
7.60
7.60
7.58
7.40
7.36
7.32
7.29
7.29
7.27
7.26
7.17
7.16
7.14
7.11
7.09
6.89
6.89
6.87
5.50
2.37
1.56
1.08
2.06
1.01
1.07
4.04
3.08
2.04
4.93
0.96
1.00
1.03
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.68
143.36
141.47
140.79
139.59
138.26
135.21
133.32
132.03
129.45
129.31
128.82
128.60
128.53
128.17
128.05
127.99
126.96
126.49
126.36
124.60
123.59
123.28
122.72
121.55
121.40
121.07
118.66
117.31
116.22
77.32
77.00
76.68
21.51
NH
Me
OH
44
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

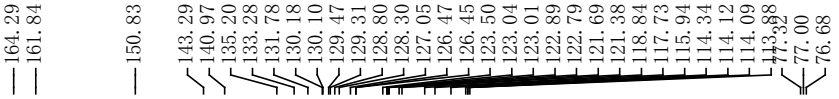
H
N
F
OH

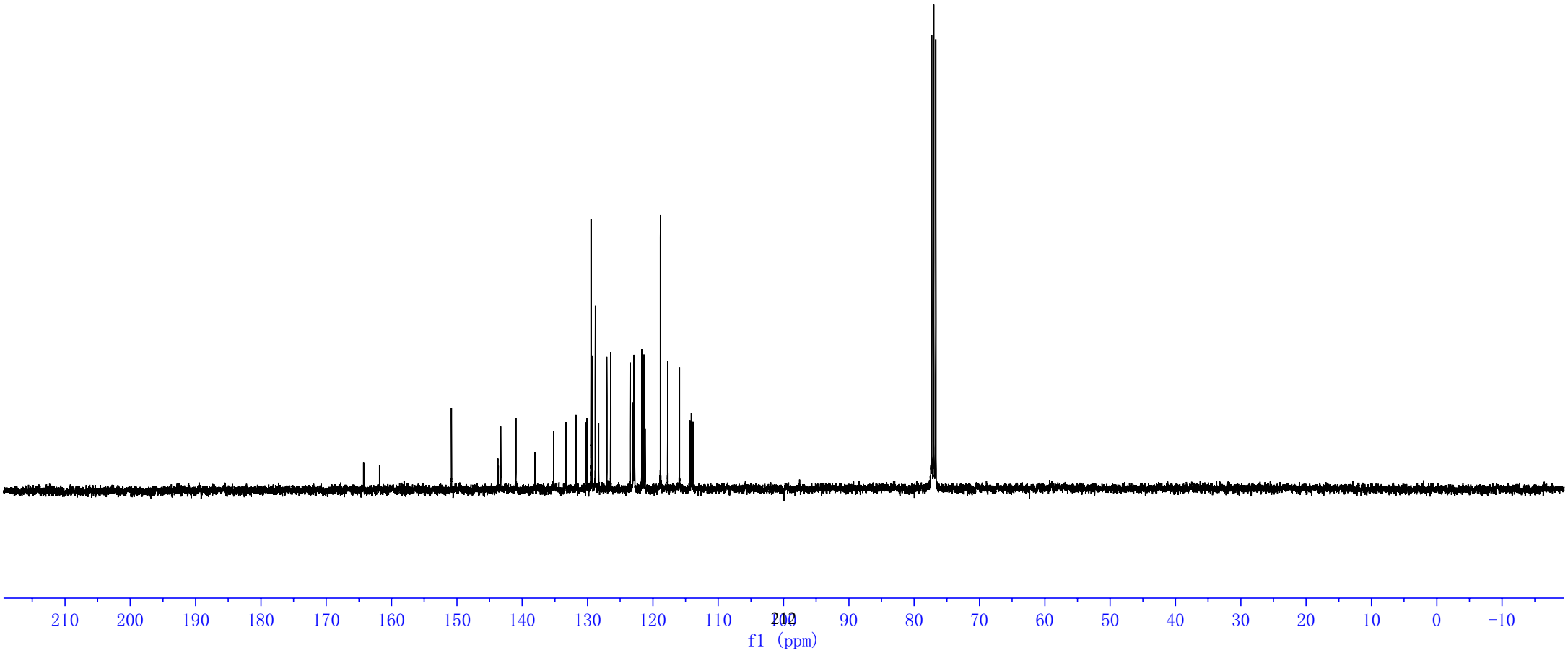
45


8.16
8.15
8.14
8.13
7.91
7.89
7.85
7.83
7.73
7.63
7.62
7.61
7.60
7.38
7.38
7.32
7.30
7.26
7.18
7.16
7.11
7.09
6.91
6.15
5.52
1.56
1.00
1.94
1.06
1.00
4.00
3.92
0.99
2.00
2.00
1.08
1.05
1.02
1.00
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
f1 (ppm)


F
H
N
OH

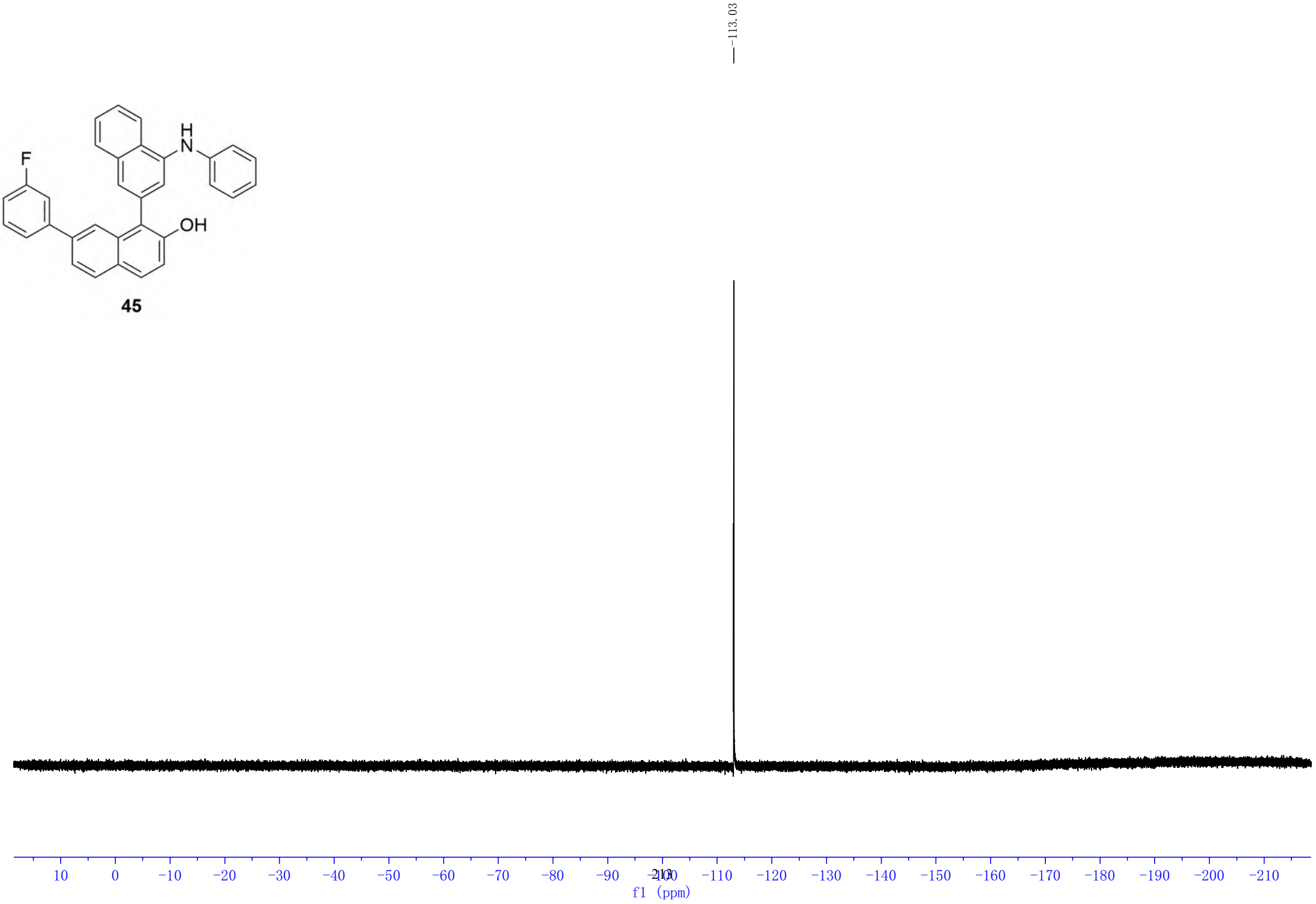
45


164.29
161.84
150.83
143.29
140.97
135.20
133.28
131.78
130.18
130.10
129.47
129.31
128.80
128.30
127.05
126.47
126.45
123.50
123.04
123.01
122.89
122.79
121.69
121.38
118.84
117.73
115.94
114.34
114.12
114.09
113.88
77.32
77.00
76.68


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)

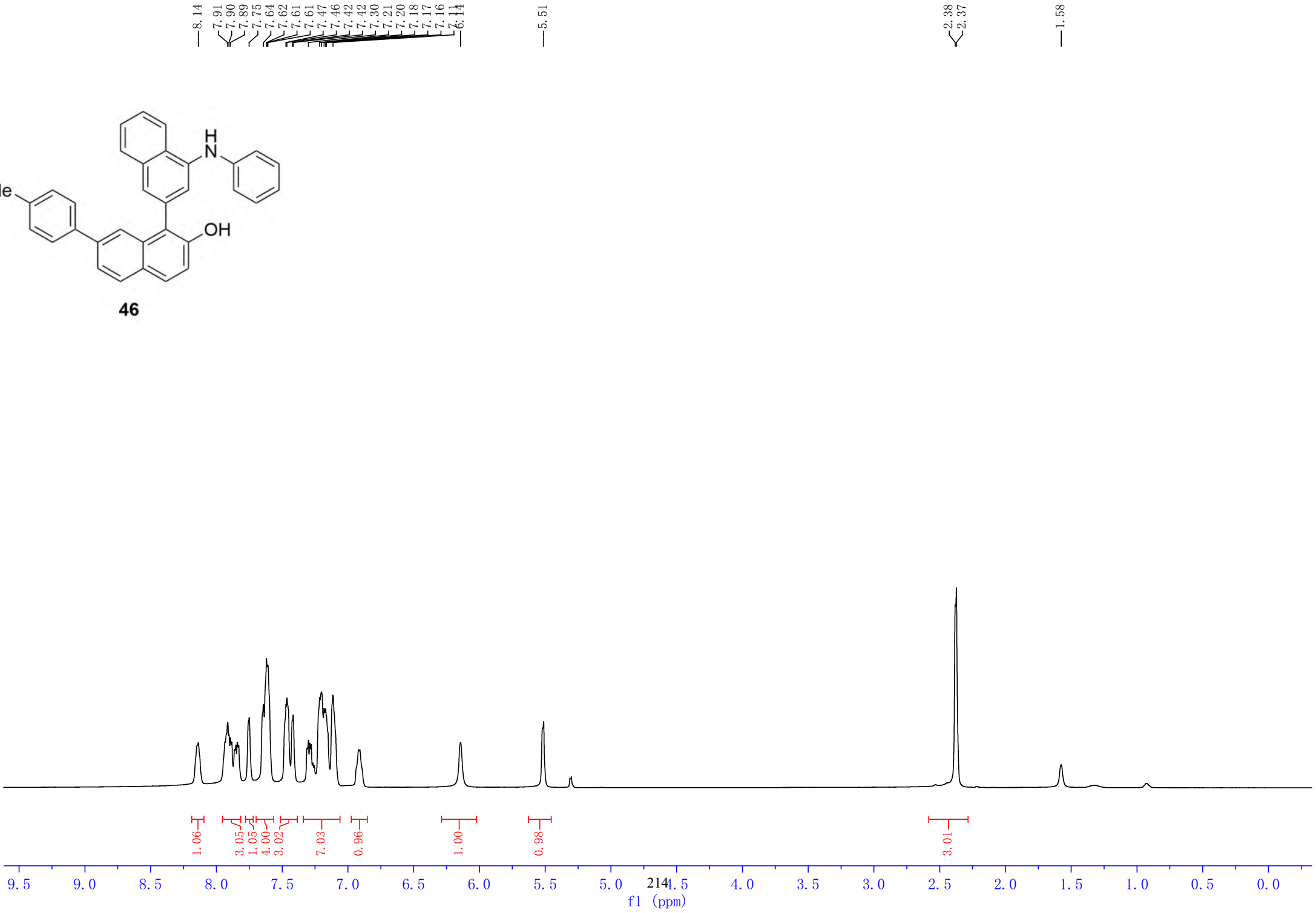
F
H
N
OH

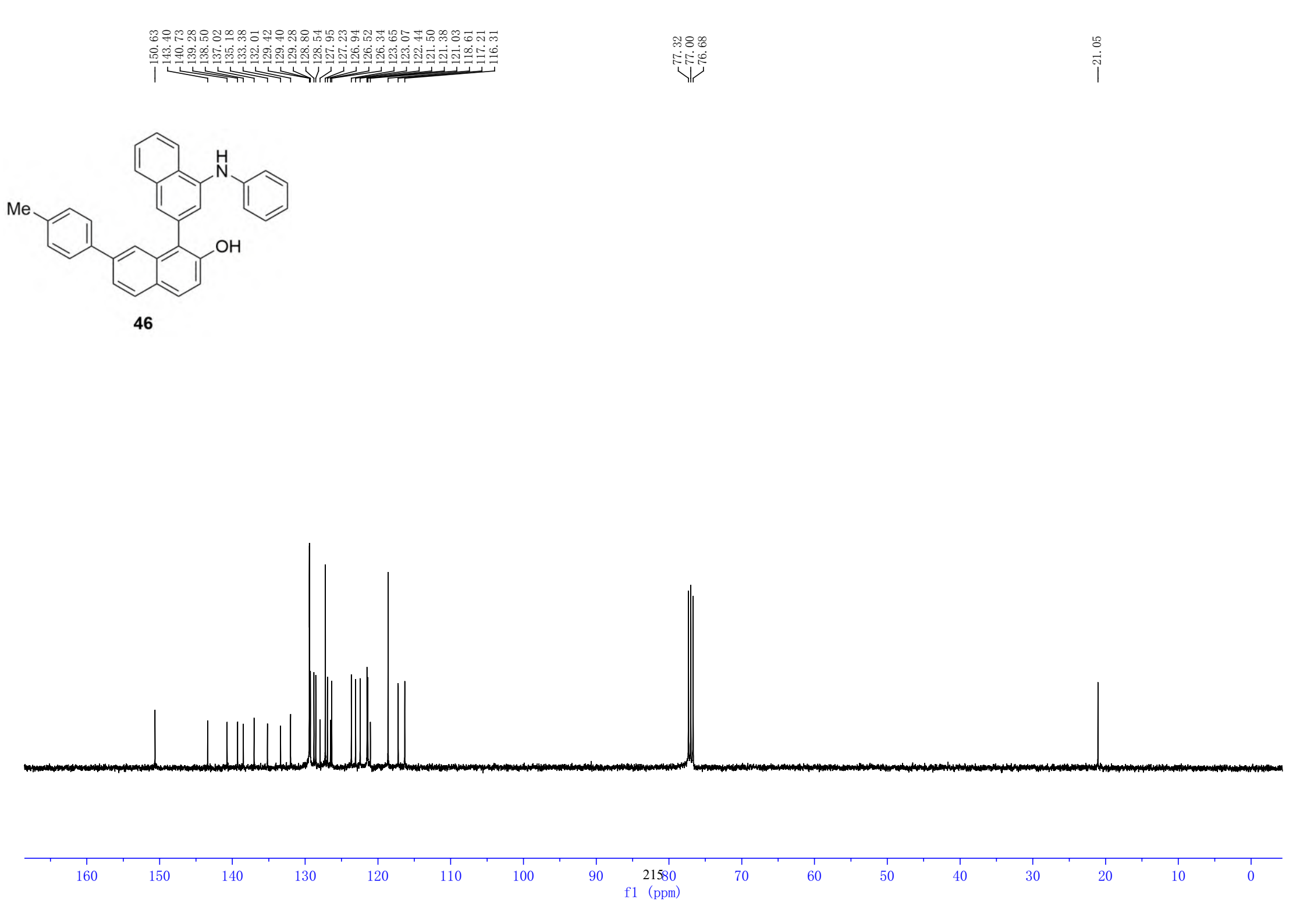
45

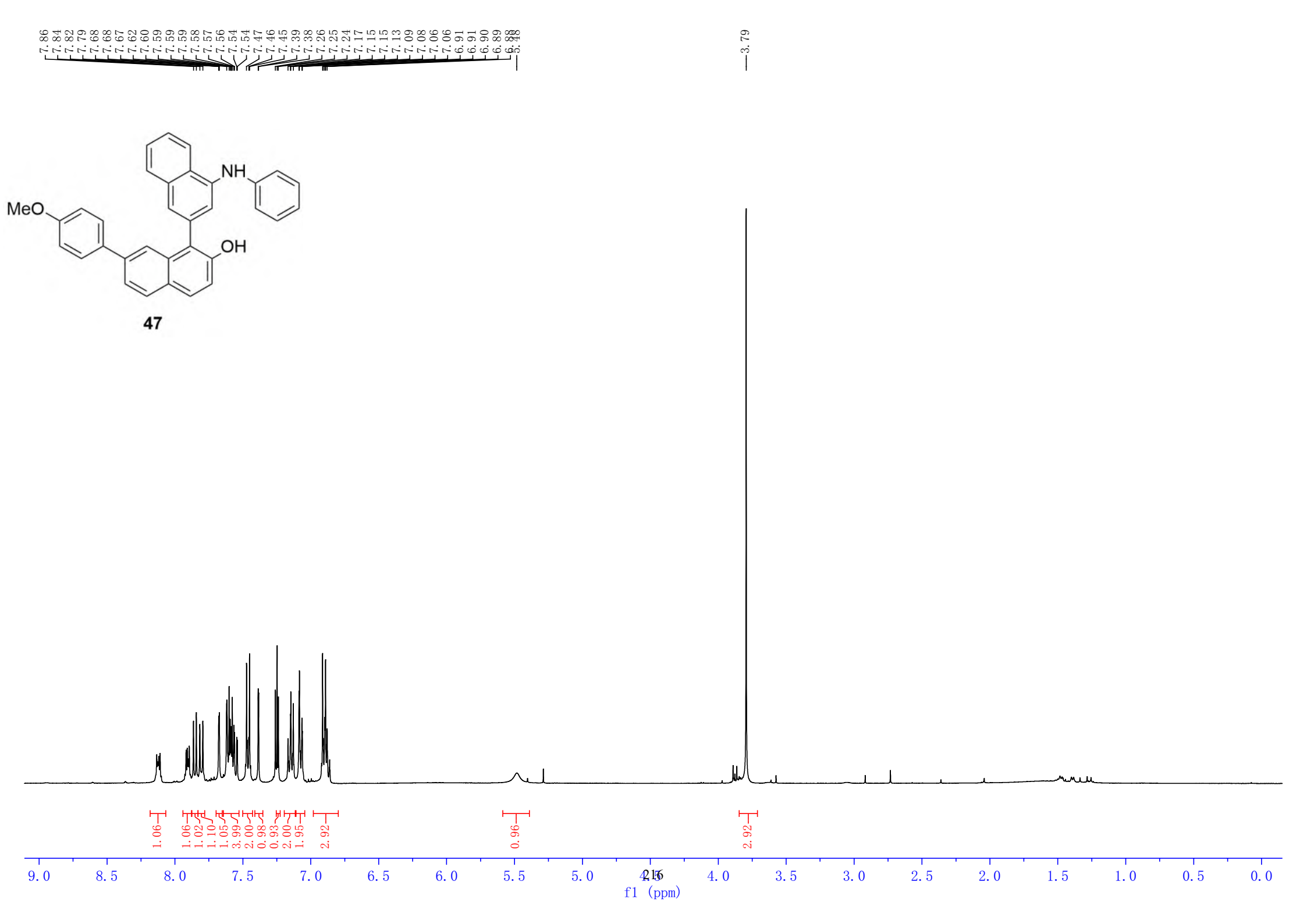

-113.03
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

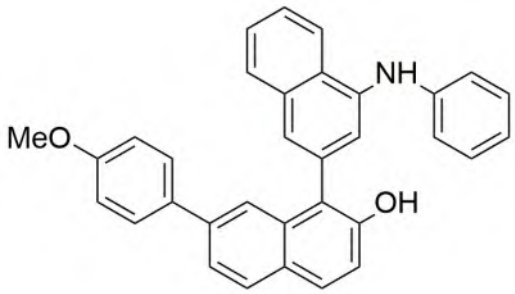
H
N
Me
OH

46


8.14
7.91
7.90
7.89
7.75
7.64
7.62
7.61
7.61
7.47
7.46
7.42
7.42
7.30
7.21
7.20
7.18
7.17
7.16
6.11
5.51
2.38
2.37
1.58
1.06
3.05
1.05
4.00
3.02
7.03
0.96
1.00
0.98
3.01
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
f1 (ppm)

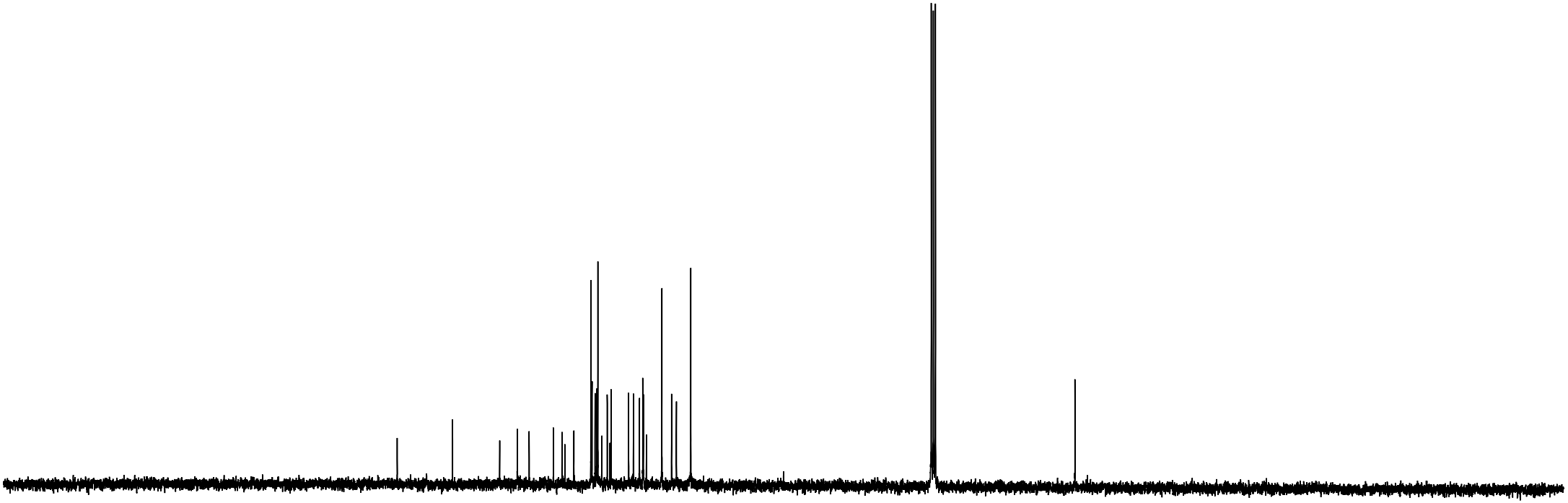

150.63
143.40
140.73
139.28
138.50
137.02
135.18
133.38
132.01
129.42
129.40
129.28
128.80
128.54
127.95
127.23
126.94
126.52
126.34
123.65
123.07
122.44
121.50
121.38
121.03
118.61
117.21
116.31
77.32
77.00
76.68
21.05
H
N
Me
OH
46
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

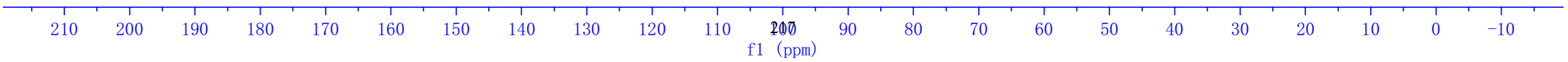

7.86
7.84
7.82
7.79
7.68
7.68
7.67
7.62
7.60
7.59
7.59
7.59
7.58
7.57
7.56
7.54
7.54
7.47
7.46
7.45
7.39
7.38
7.26
7.25
7.24
7.17
7.15
7.15
7.13
7.09
7.08
7.06
7.06
6.91
6.90
6.89
3.79
NH
MeO
OH
47
1.06
1.06
1.02
1.10
1.05
3.99
2.00
0.98
0.93
2.00
1.95
2.92
0.96
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



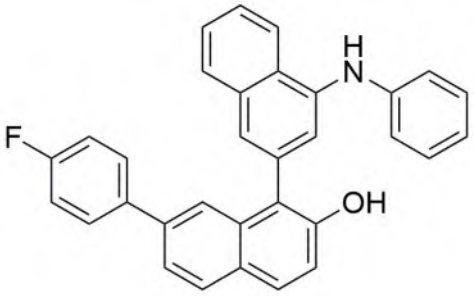
47

159.11
150.65
143.42
140.72
138.91
135.20
133.87
133.42
132.06
129.44
129.28
128.81
128.54
128.38
127.77
126.95
126.54
126.36
123.68
122.93
122.02
121.50
121.41
120.96
118.58
117.09
116.36
114.15
77.32
77.00
76.68
55.31

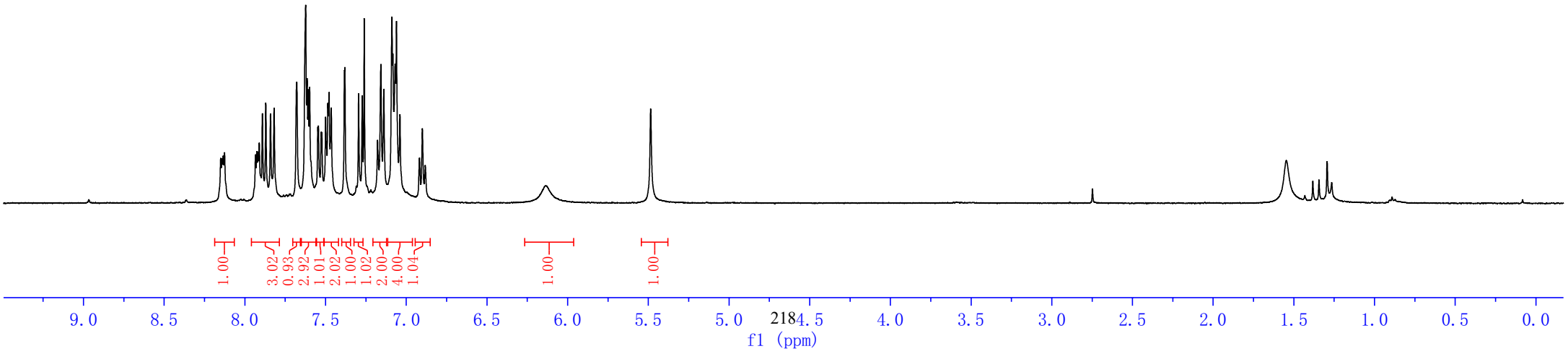


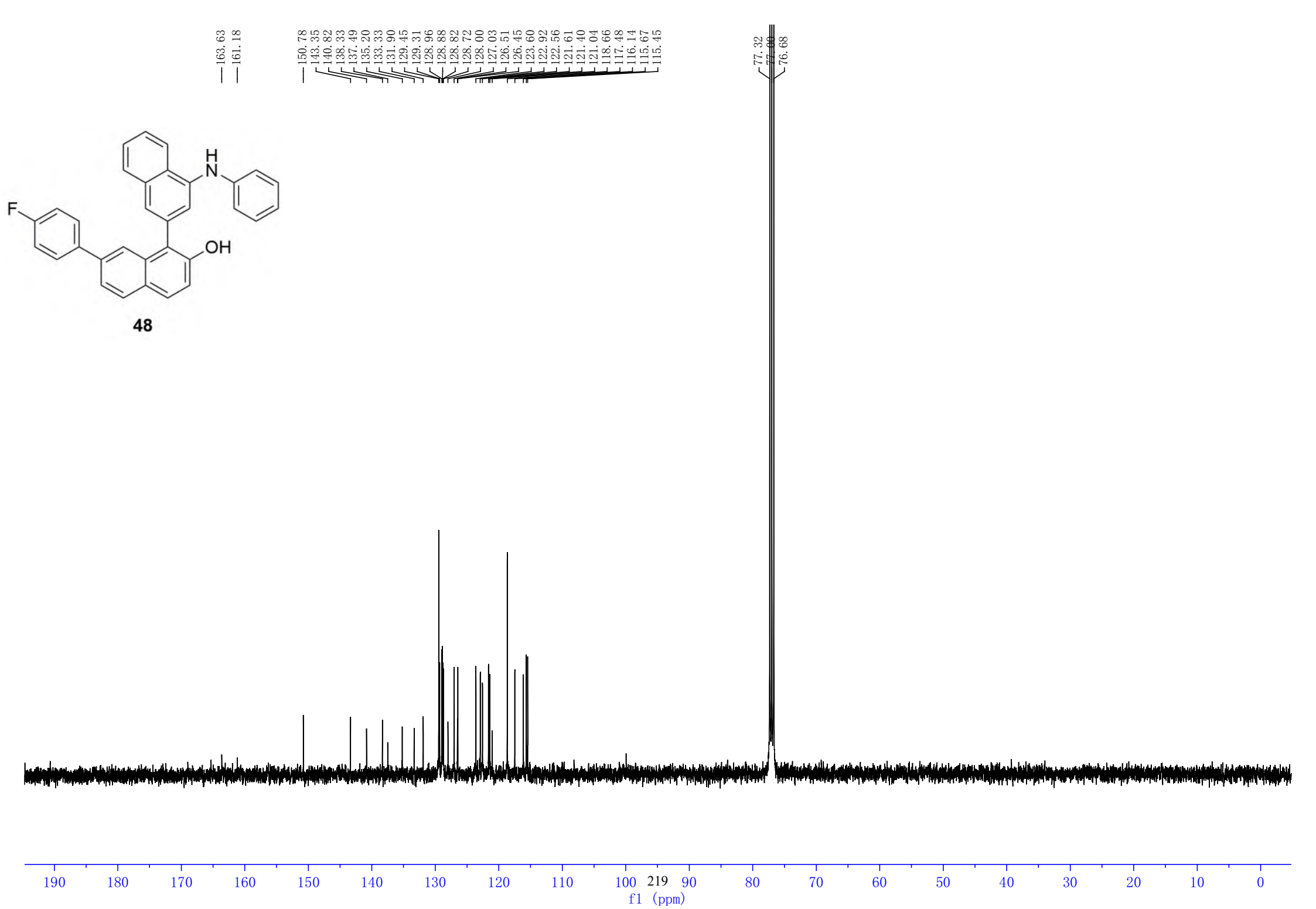



8.13
7.93
7.92
7.91
7.89
7.87
7.84
7.82
7.68
7.62
7.61
7.61
7.60
7.55
7.54
7.53
7.52
7.50
7.49
7.48
7.46
7.38
7.30
7.27
7.26
7.18
7.16
7.14
7.09
7.08
7.07
7.06
7.04
6.90
6.13
5.49
1.55


H
N
F
OH

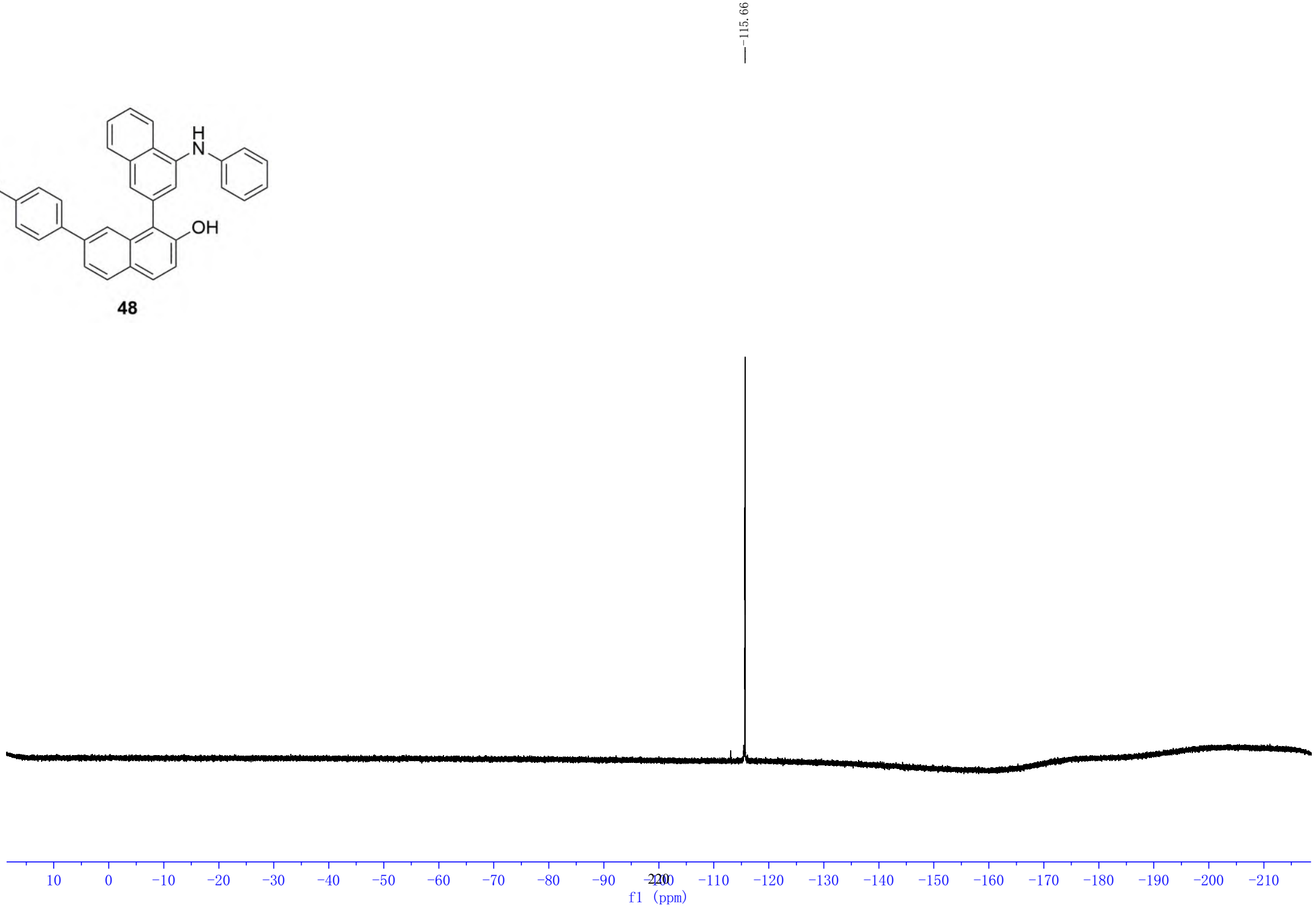
48


1.00
3.02
0.93
2.92
1.01
2.02
1.00
1.02
2.00
4.00
1.04
1.00
1.00
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
f1 (ppm)


163.63
161.18
150.78
143.35
140.82
138.33
137.49
135.20
133.33
131.90
129.45
129.31
128.96
128.88
128.82
128.72
128.00
127.03
126.51
126.45
123.60
122.92
122.56
121.61
121.40
121.04
118.66
117.48
116.14
115.67
115.45
77.32
77.00
76.68
H
N
F
OH
48
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

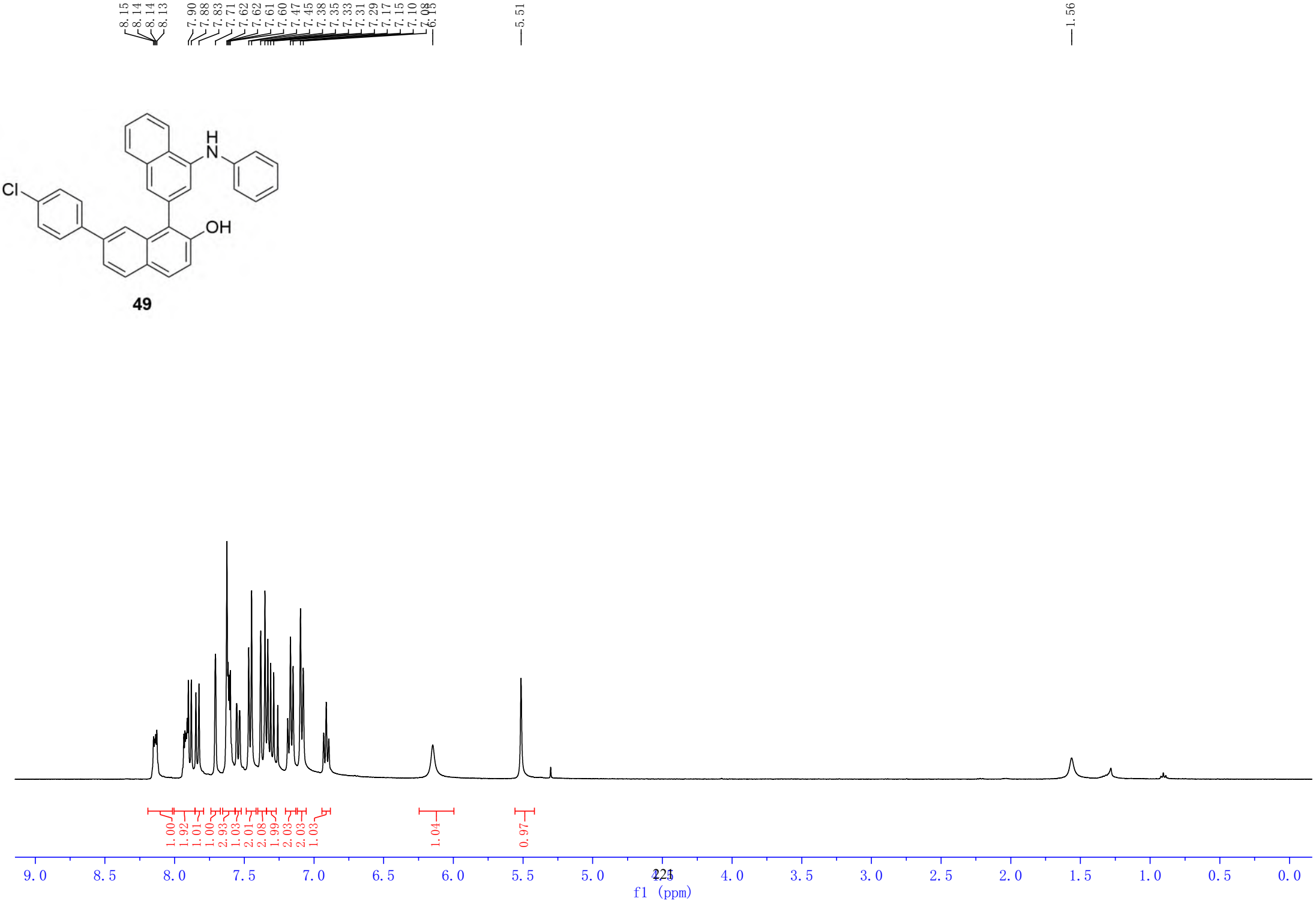
H
N
F
OH

48


-115.66
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

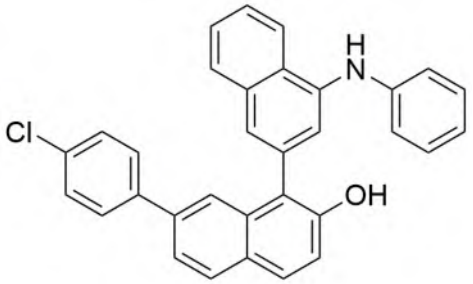
H
N
Cl
OH

49

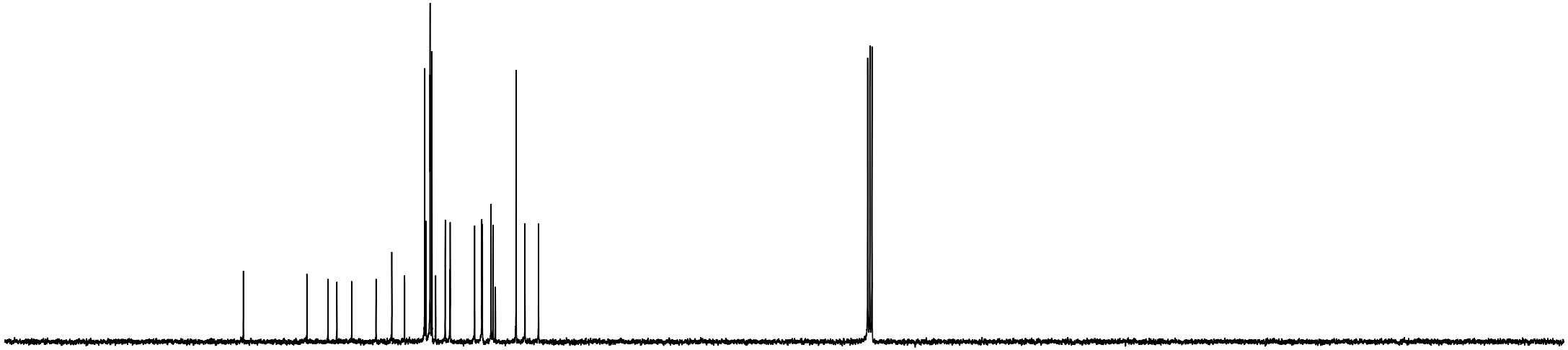

8.15
8.14
8.14
8.13
7.90
7.88
7.83
7.71
7.62
7.62
7.61
7.60
7.47
7.45
7.38
7.35
7.33
7.31
7.29
7.17
7.15
7.10
7.08
6.15
5.51
1.56
1.00
1.92
1.01
1.00
2.93
1.03
2.01
2.08
1.99
2.03
2.03
1.03
1.04
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

150.80
143.31
140.83
139.79
138.04
135.17
133.31
131.81
129.43
129.30
128.81
128.79
128.58
128.15
127.02
126.47
126.44
123.56
122.71
122.65
121.62
121.38
121.10
118.67
117.63
116.03

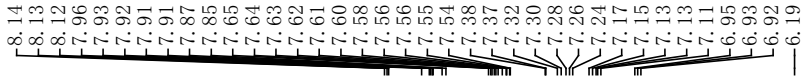
77.25
77.00
76.75

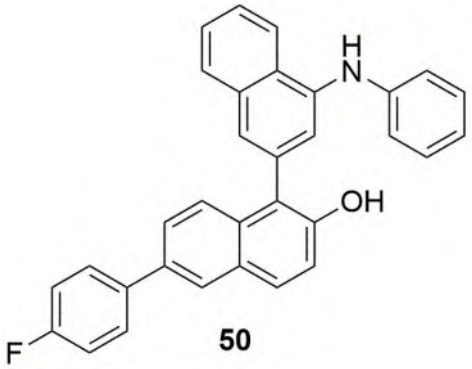


49

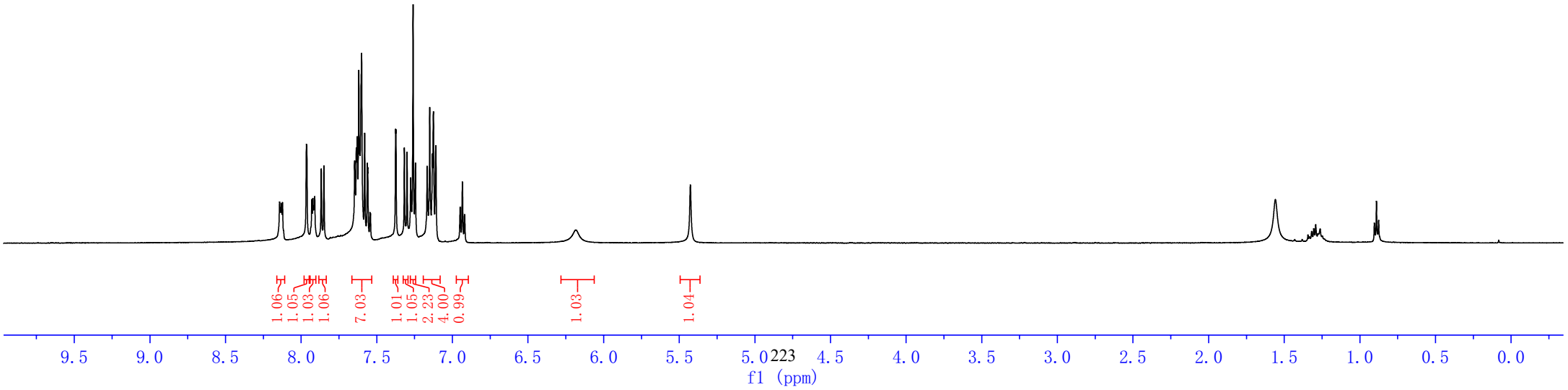


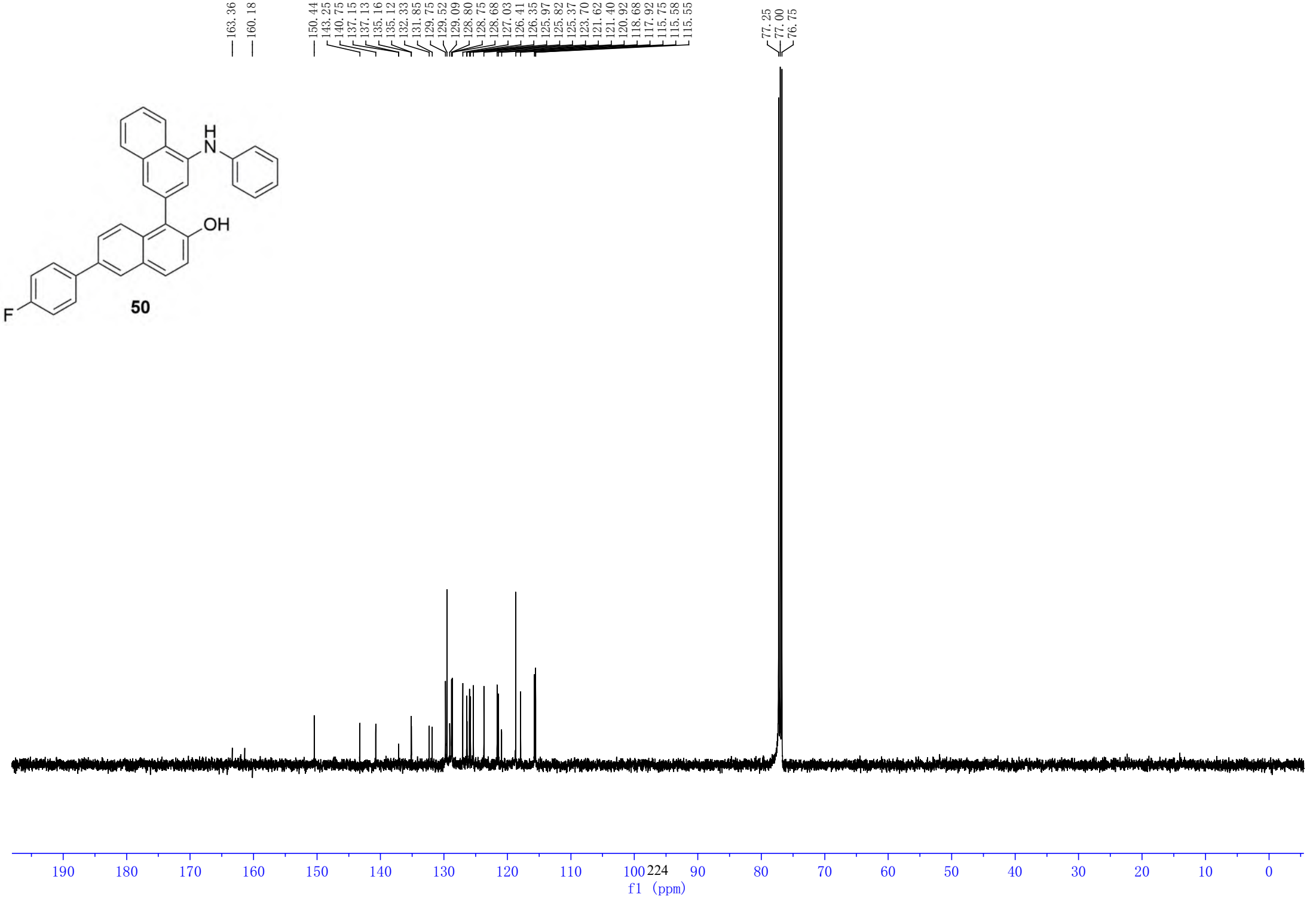
f1 (ppm)


8.14
8.13
8.12
7.96
7.93
7.92
7.91
7.91
7.87
7.85
7.65
7.64
7.63
7.62
7.61
7.60
7.58
7.56
7.56
7.55
7.54
7.38
7.37
7.32
7.30
7.28
7.26
7.24
7.17
7.15
7.13
7.11
6.95
6.93
6.92
6.19
5.43
1.56


H
N
OH
F

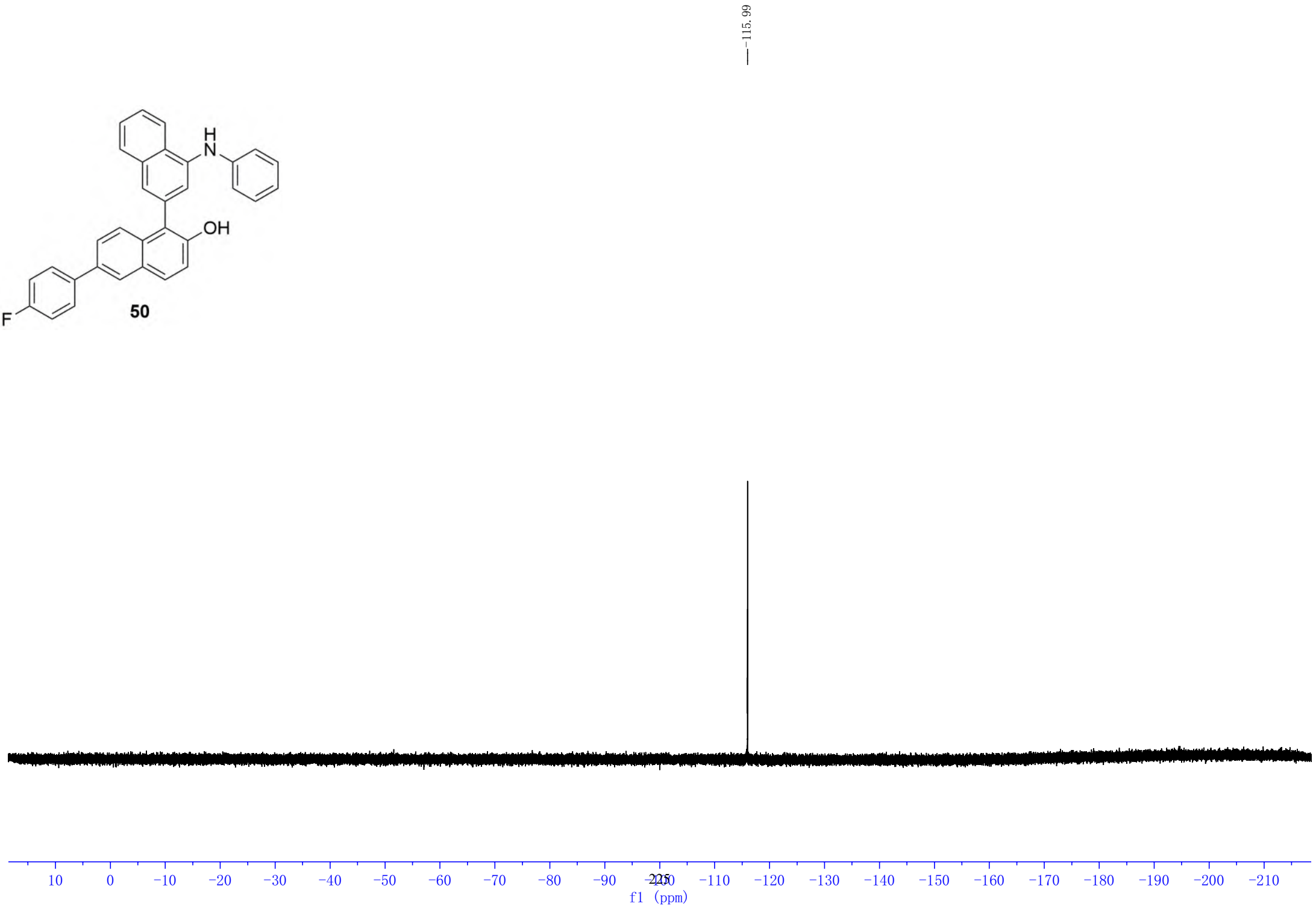
50

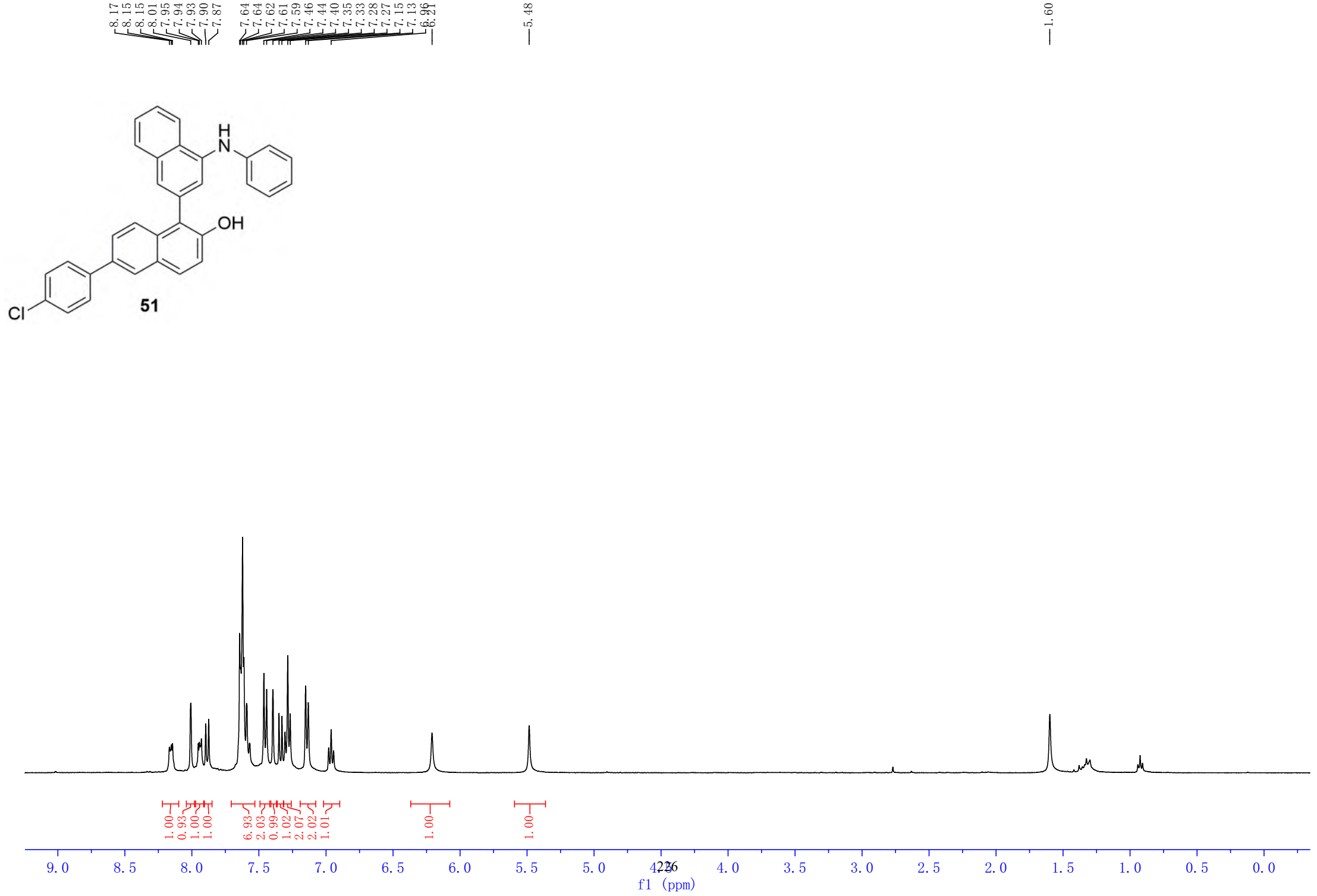

1.06
1.05
1.03
1.06
7.03
1.01
1.05
2.23
4.00
0.99
1.03
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

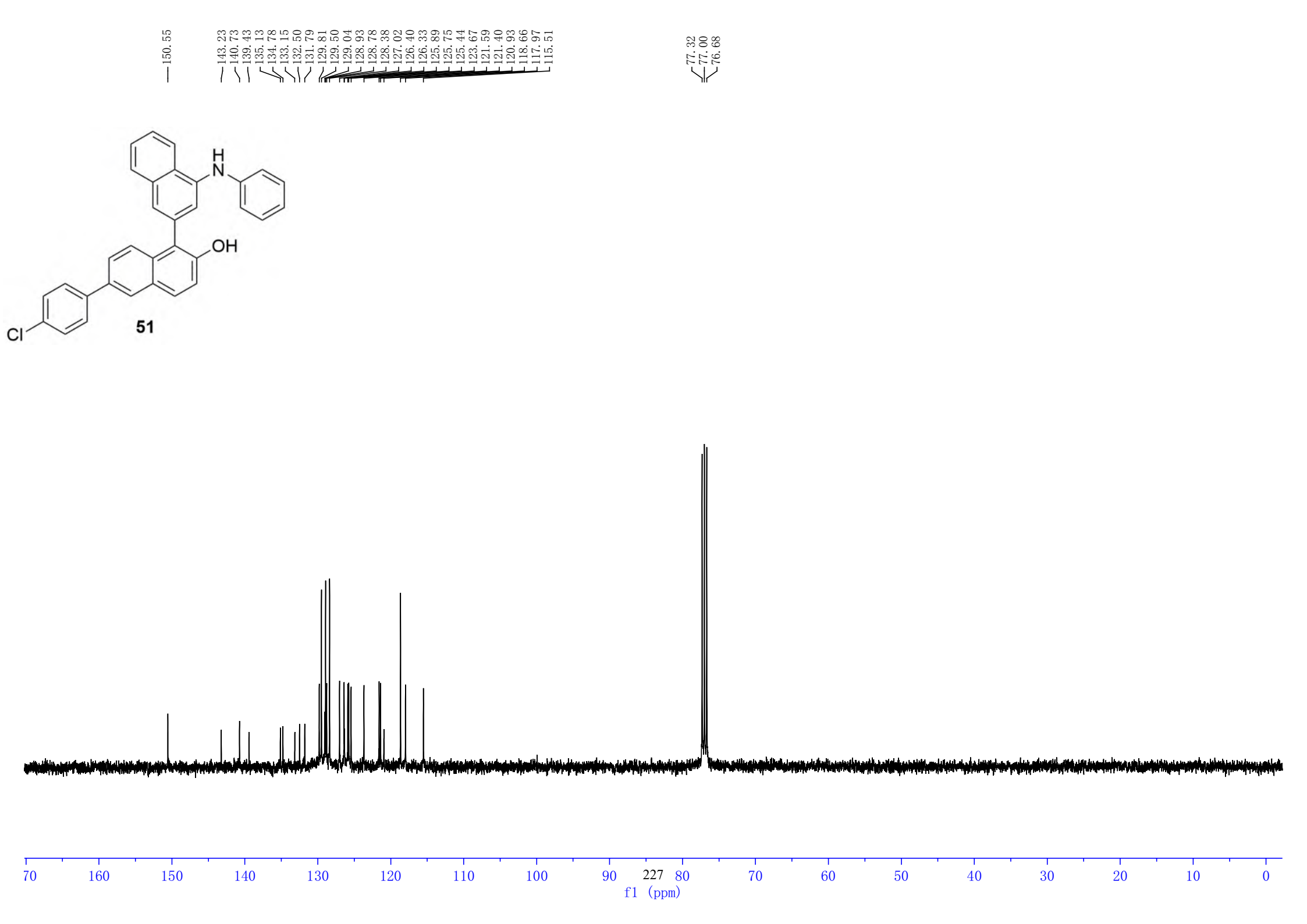

163.36
160.18
150.44
143.25
140.75
137.15
137.13
135.16
135.12
132.33
131.85
129.75
129.52
129.09
128.80
128.75
128.68
127.03
126.41
126.35
125.97
125.82
125.37
123.70
121.62
121.40
120.92
118.68
117.92
115.75
115.58
115.55
77.25
77.00
76.75
H
N
OH
F
50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

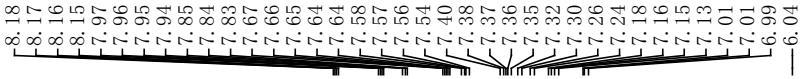
H
N
OH
F

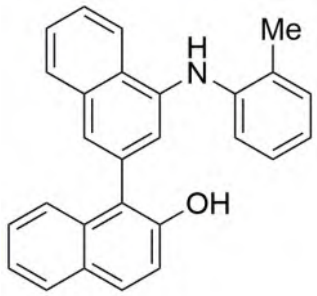
50


-115.99
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

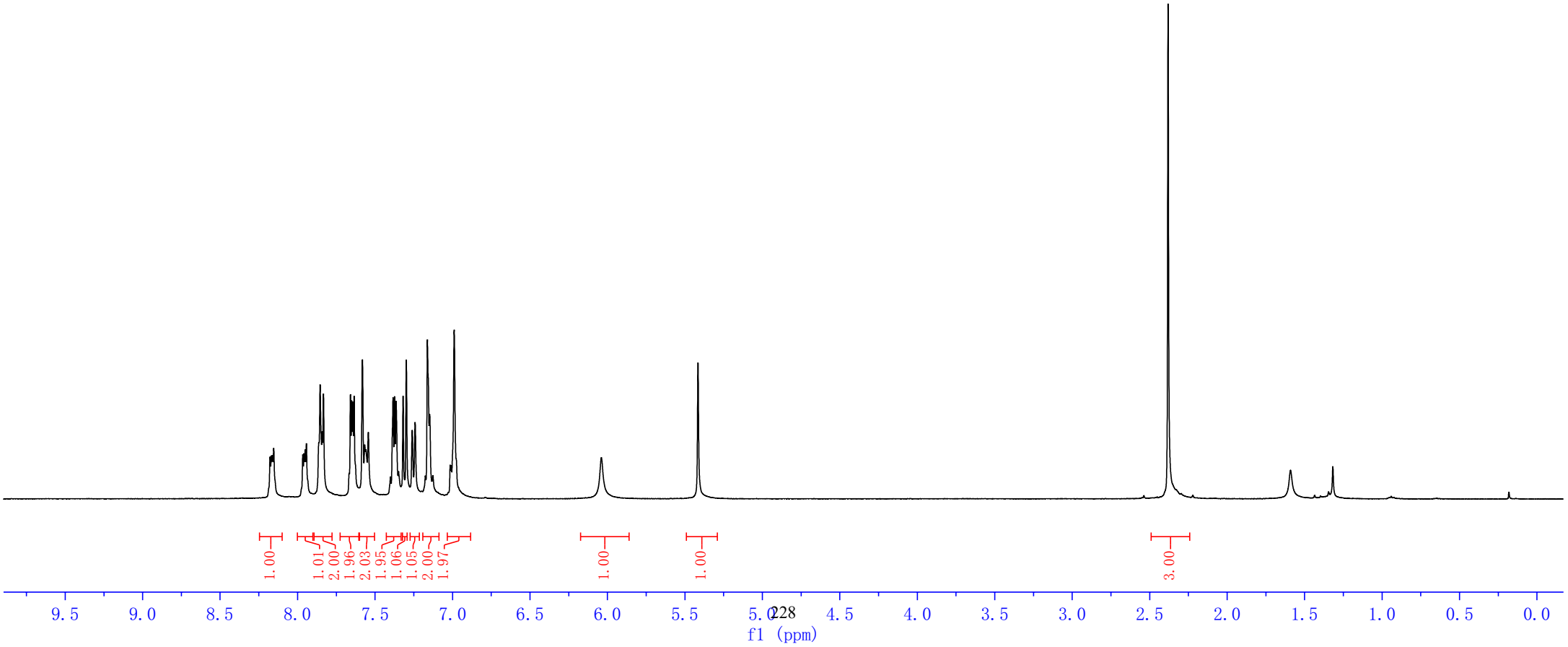

8.17
8.15
8.15
8.01
7.95
7.94
7.93
7.90
7.87
7.64
7.64
7.62
7.61
7.59
7.46
7.44
7.40
7.35
7.33
7.28
7.27
7.15
7.13
6.96
6.21
5.48
1.60
H
N
OH
Cl
51
1.00
0.93
1.00
1.00
6.93
2.03
0.99
1.02
2.07
2.02
1.01
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

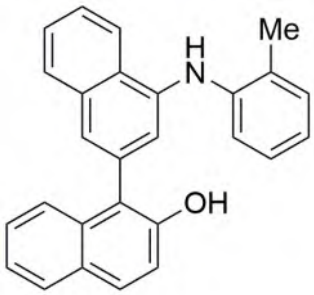

150.55
143.23
140.73
139.43
135.13
134.78
133.15
132.50
131.79
129.81
129.50
129.04
128.93
128.78
128.38
127.02
126.40
126.33
125.89
125.75
125.44
123.67
121.59
121.40
120.93
118.66
117.97
115.51
77.32
77.00
76.68
H
N
OH
Cl
51
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.18
8.17
8.16
8.15
7.97
7.96
7.95
7.94
7.85
7.84
7.83
7.67
7.66
7.65
7.64
7.64
7.58
7.57
7.56
7.54
7.40
7.38
7.37
7.36
7.35
7.32
7.30
7.26
7.24
7.18
7.16
7.15
7.13
7.01
7.01
6.99
6.04
5.42
2.38
1.59


H
N
Me
OH

52

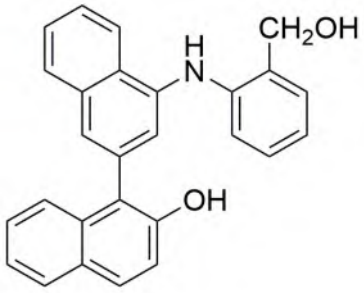

1.00
1.01
2.00
1.96
2.03
1.95
1.06
1.05
2.00
1.97
1.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



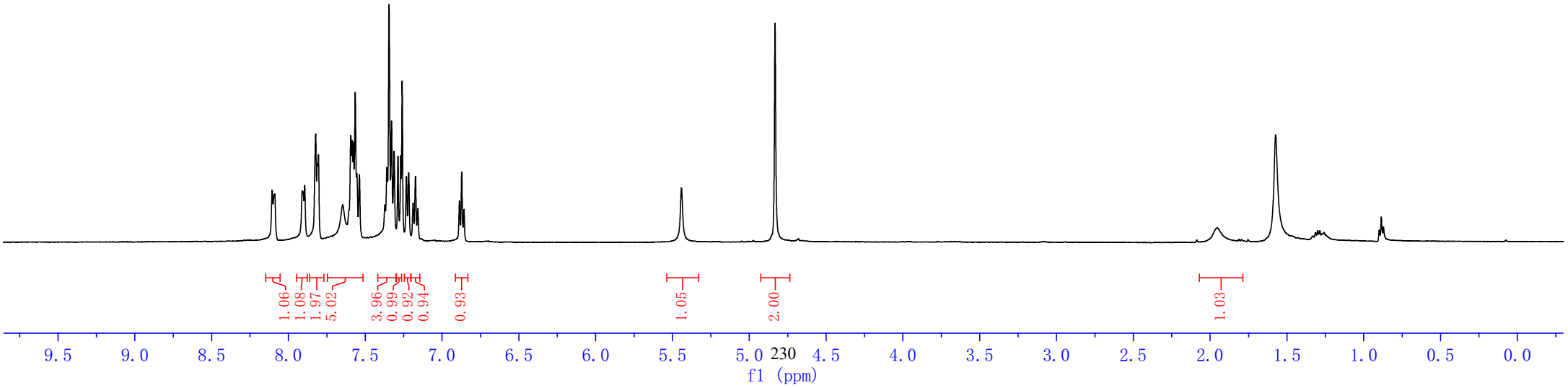
52

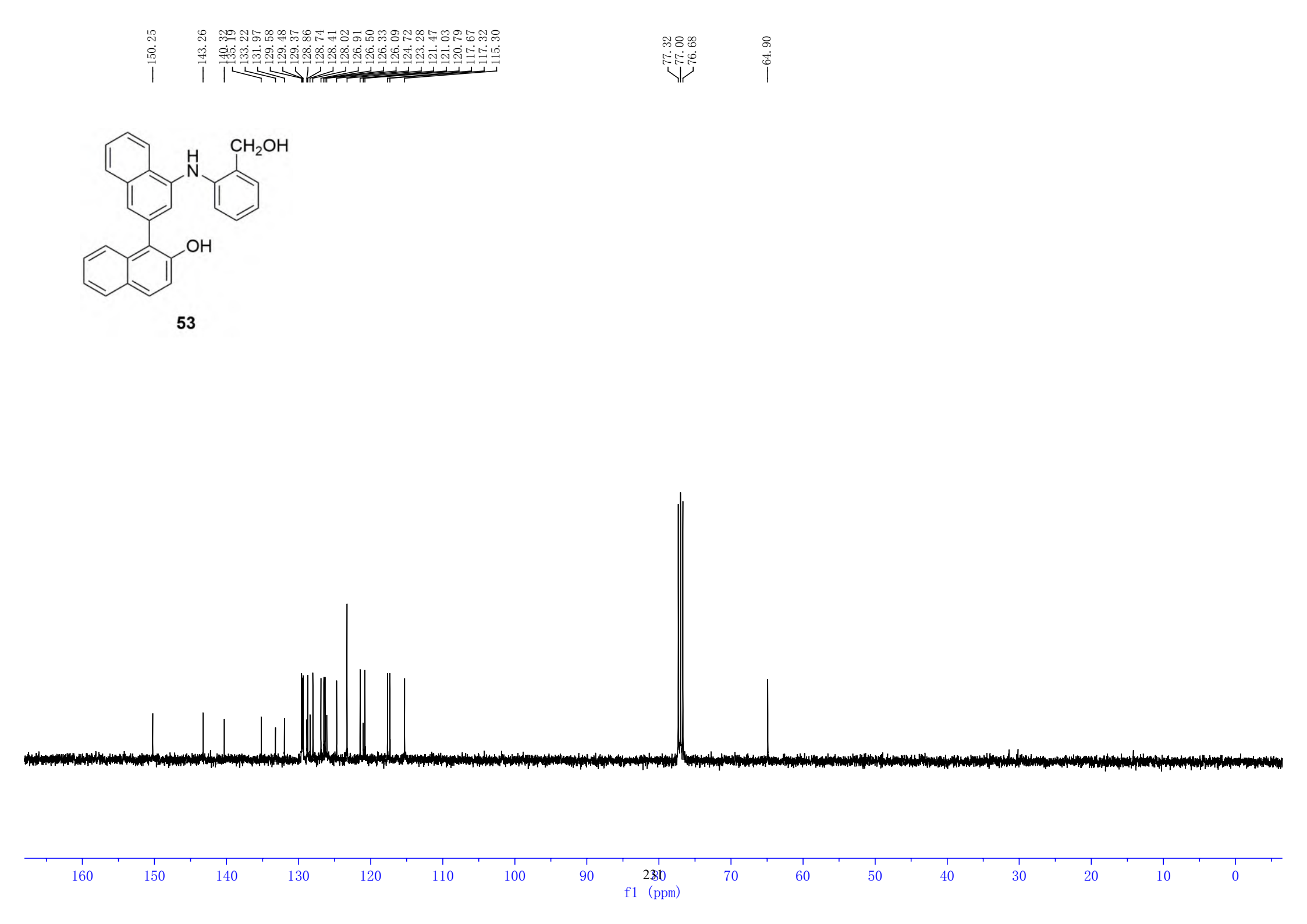
150.20
141.51
141.04
135.08
133.19
132.11
131.11
129.44
129.31
128.80
127.99
127.04
126.87
126.44
126.21
125.64
124.72
123.26
122.93
122.90
121.27
121.04
120.66
117.26
114.61
77.32
77.00
76.68
17.90

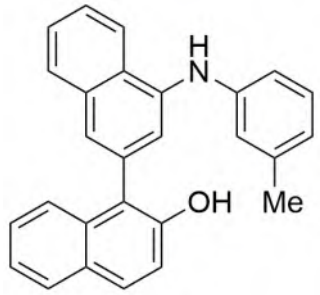

8.11
8.09
7.91
7.91
7.89
7.82
7.81
7.80
7.65
7.59
7.59
7.58
7.57
7.56
7.54
7.37
7.36
7.35
7.33
7.31
7.29
7.27
7.26
7.23
7.22
7.19
6.87
6.86
5.44
4.83
1.96
1.57


H
N
CH2OH
OH

53

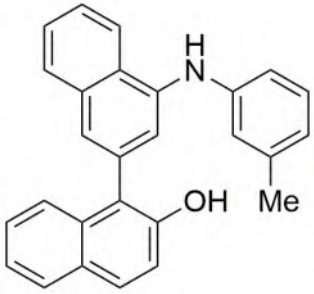

1.06
1.08
1.97
5.02
3.96
0.99
0.92
0.94
0.93
1.05
2.00
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.25
143.26
140.32
135.19
133.22
131.97
129.58
129.48
129.37
128.86
128.74
128.41
128.02
126.91
126.50
126.33
126.09
124.72
123.28
121.47
121.03
120.79
117.67
117.32
115.30
77.32
77.00
76.68
64.90
CH2OH
H
N
OH
53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

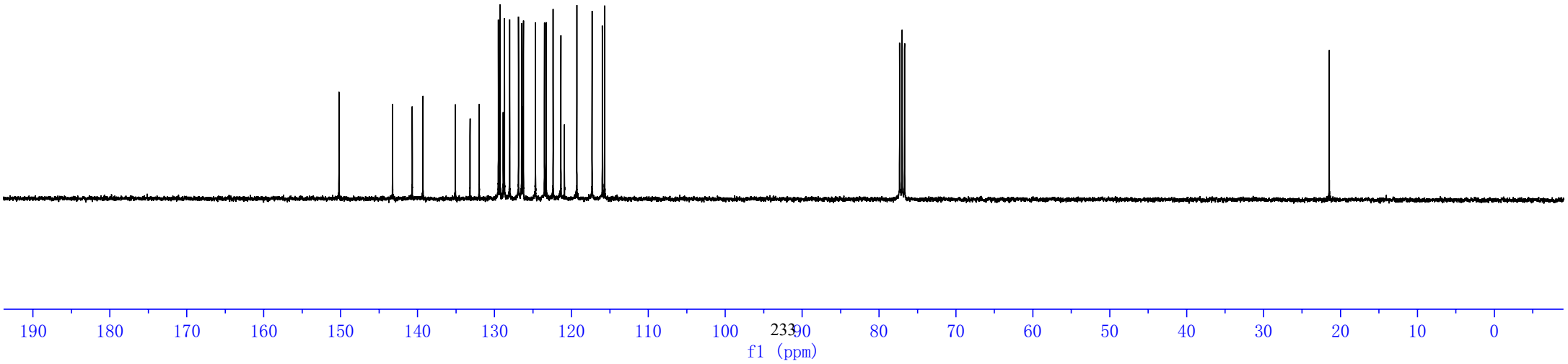


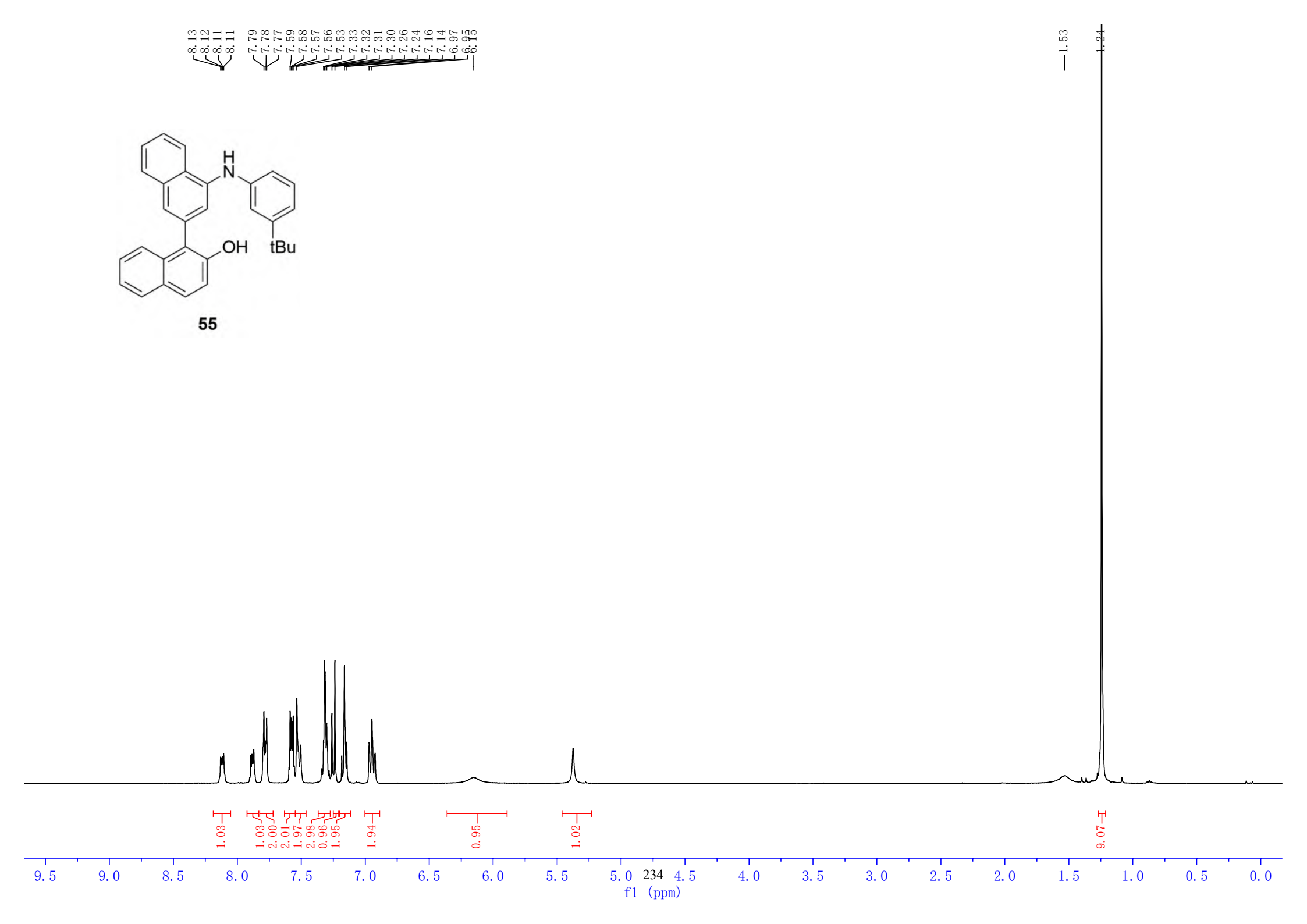
54

150.21
143.24
140.68
139.30
135.09
133.17
131.99
129.49
129.27
128.86
128.70
128.02
126.87
126.46
126.33
126.23
124.67
123.49
123.27
122.37
121.36
120.90
119.29
117.31
115.96
115.67
77.32
77.00
76.68
21.47



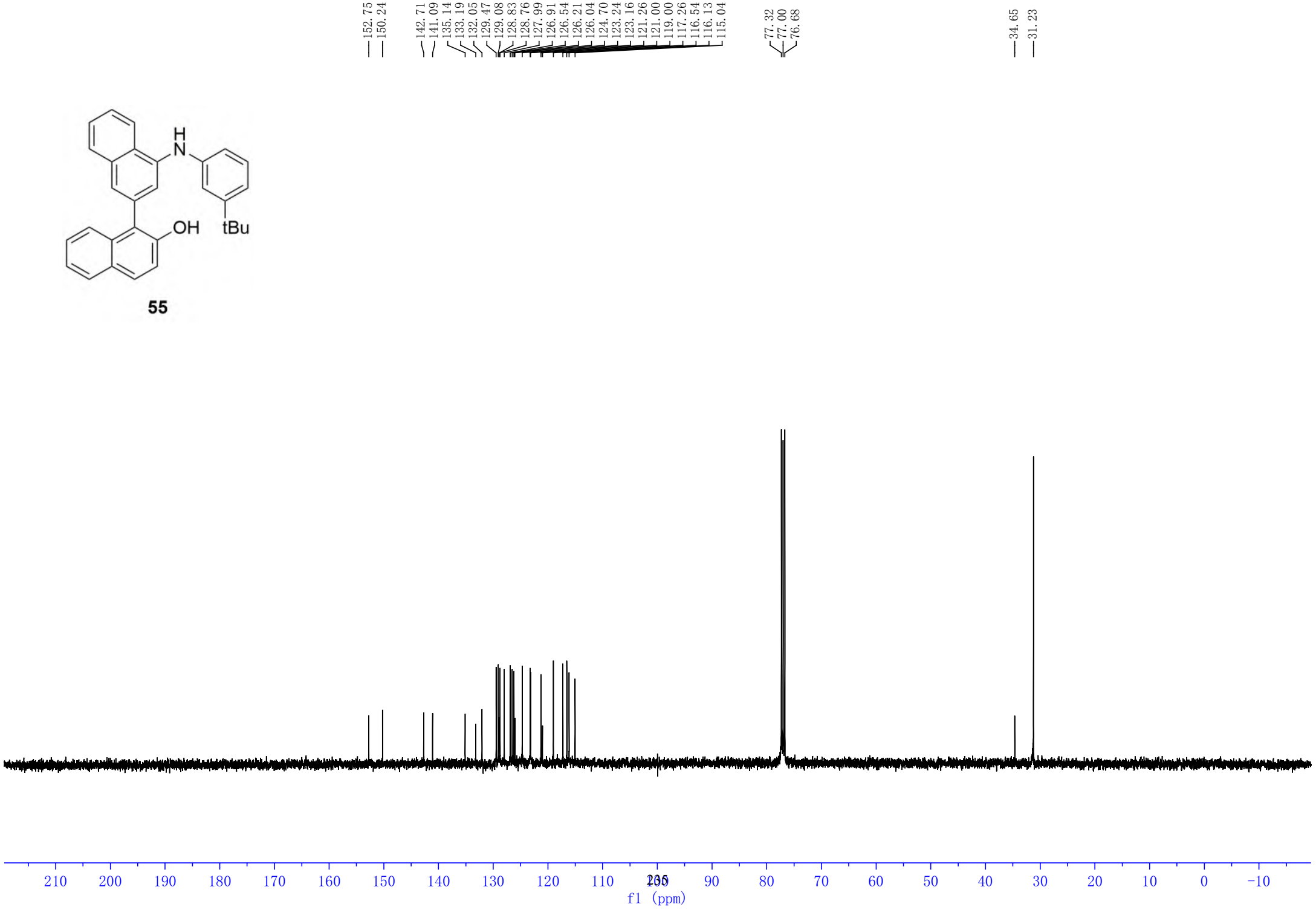
54



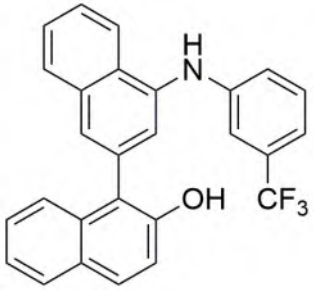

8.13
8.12
8.11
8.11
7.79
7.78
7.77
7.59
7.58
7.57
7.56
7.53
7.33
7.32
7.31
7.30
7.26
7.24
7.16
7.14
6.97
6.95
6.15
1.53
1.24
H
N
OH
tBu
55
1.03
1.03
2.00
2.01
1.97
2.98
0.96
1.95
1.94
0.95
1.02
9.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

H
N
OH
tBu

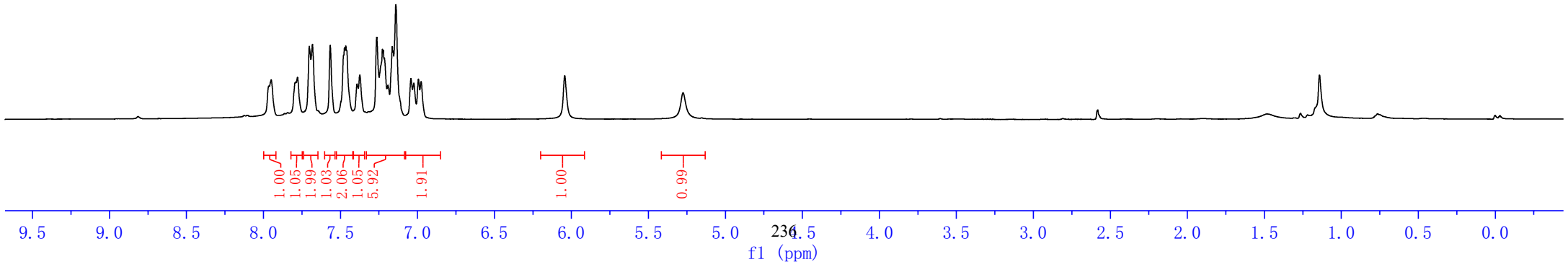
55

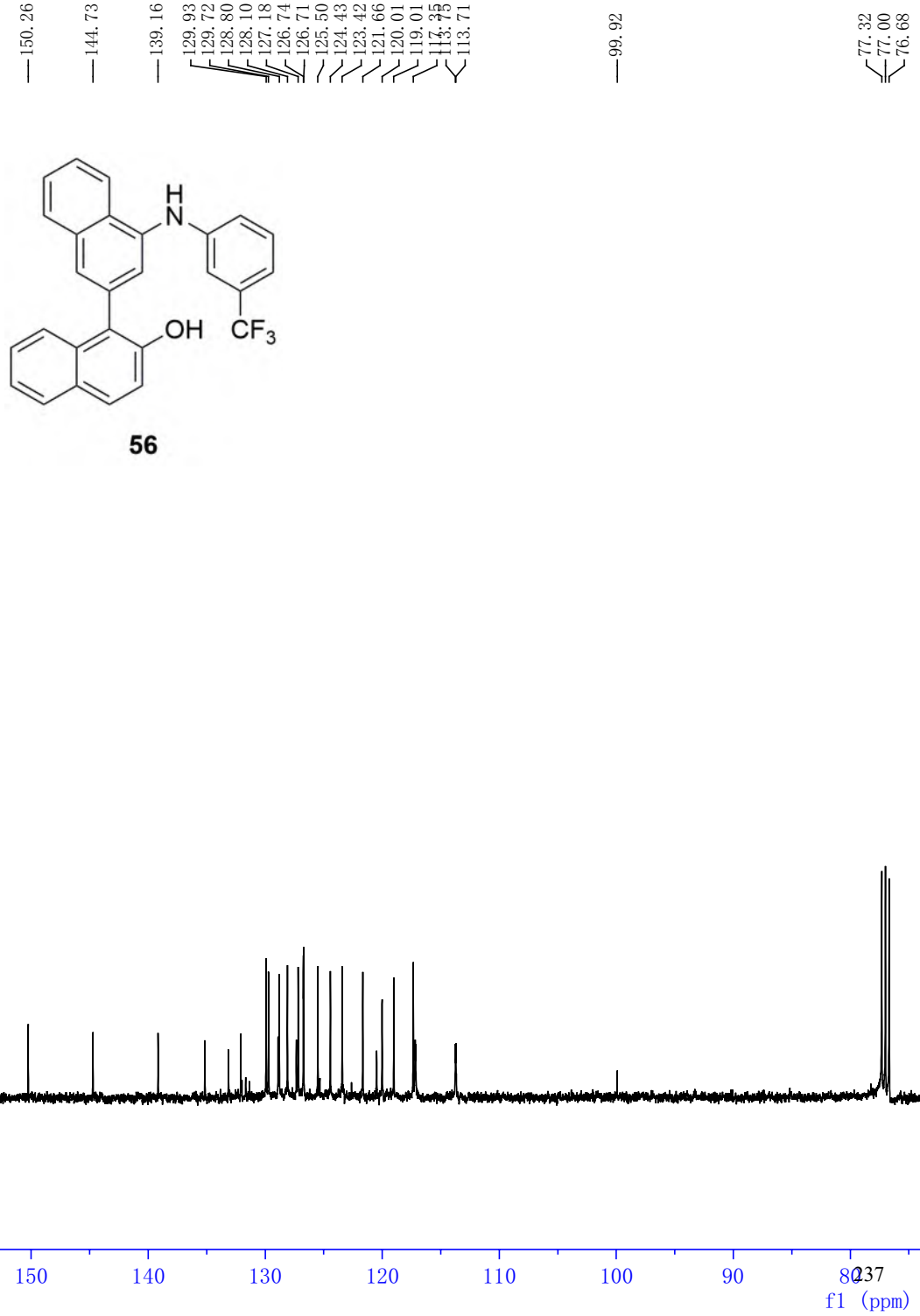

152.75
150.24
142.71
141.09
135.14
133.19
132.05
129.47
129.08
128.83
128.76
127.99
126.91
126.54
126.21
126.04
124.70
123.24
123.16
121.26
121.00
119.00
117.26
116.54
116.13
115.04
77.32
77.00
76.68
34.65
31.23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.97
7.95
7.79
7.78
7.70
7.68
7.57
7.48
7.47
7.47
7.46
7.39
7.37
7.26
7.23
7.22
7.21
7.19
7.16
7.16
7.14
7.04
7.02
6.99
6.98
6.04
5.27


H
N
OH
CF3

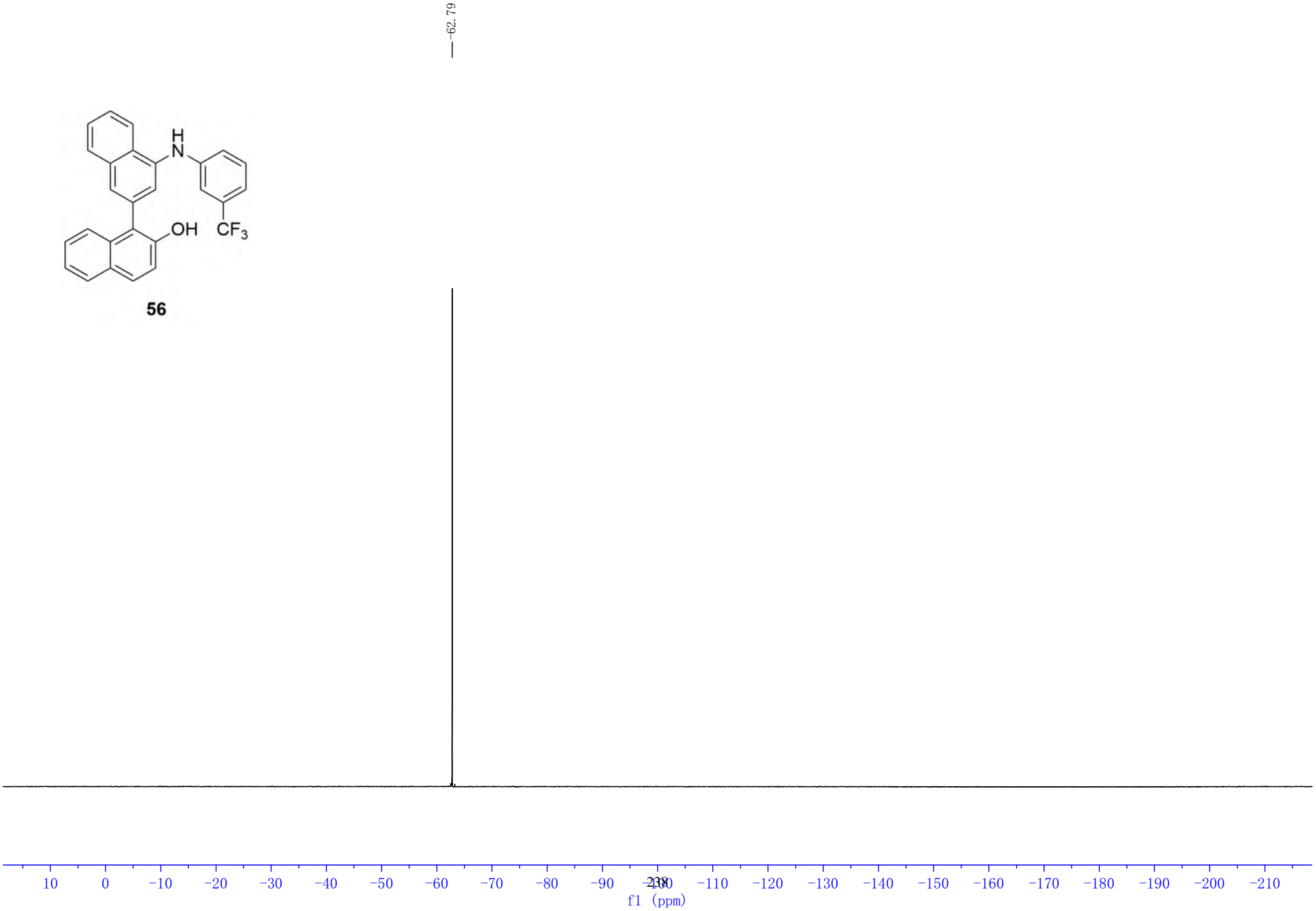
56

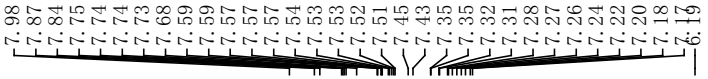

1.00
1.05
1.99
1.03
2.06
1.05
5.92
1.91
1.00
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

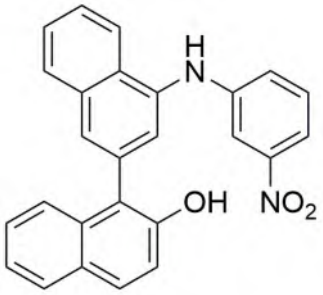

150.26
144.73
139.16
129.93
129.72
128.80
128.10
127.18
126.74
126.71
125.50
124.43
123.42
121.66
120.01
119.01
99.92
77.32
77.00
76.68
H
N
OH
CF3
56
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

H
N
OH
CF3

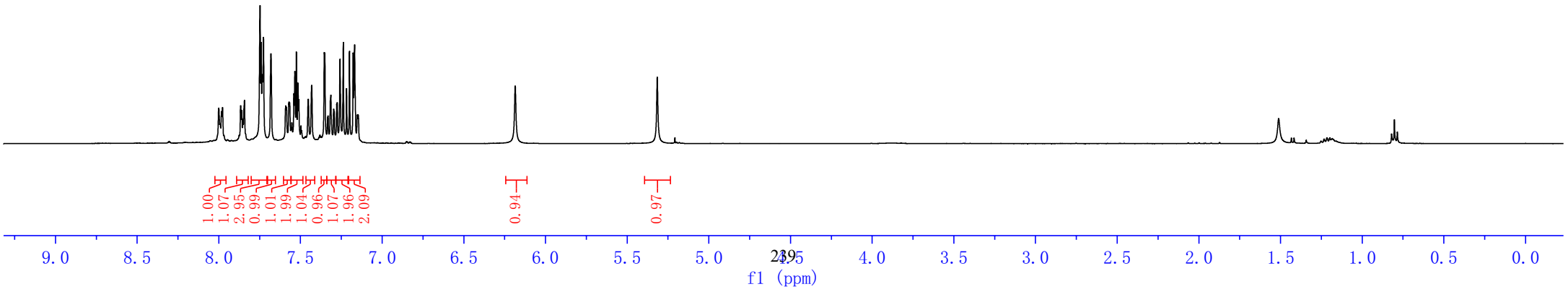
56

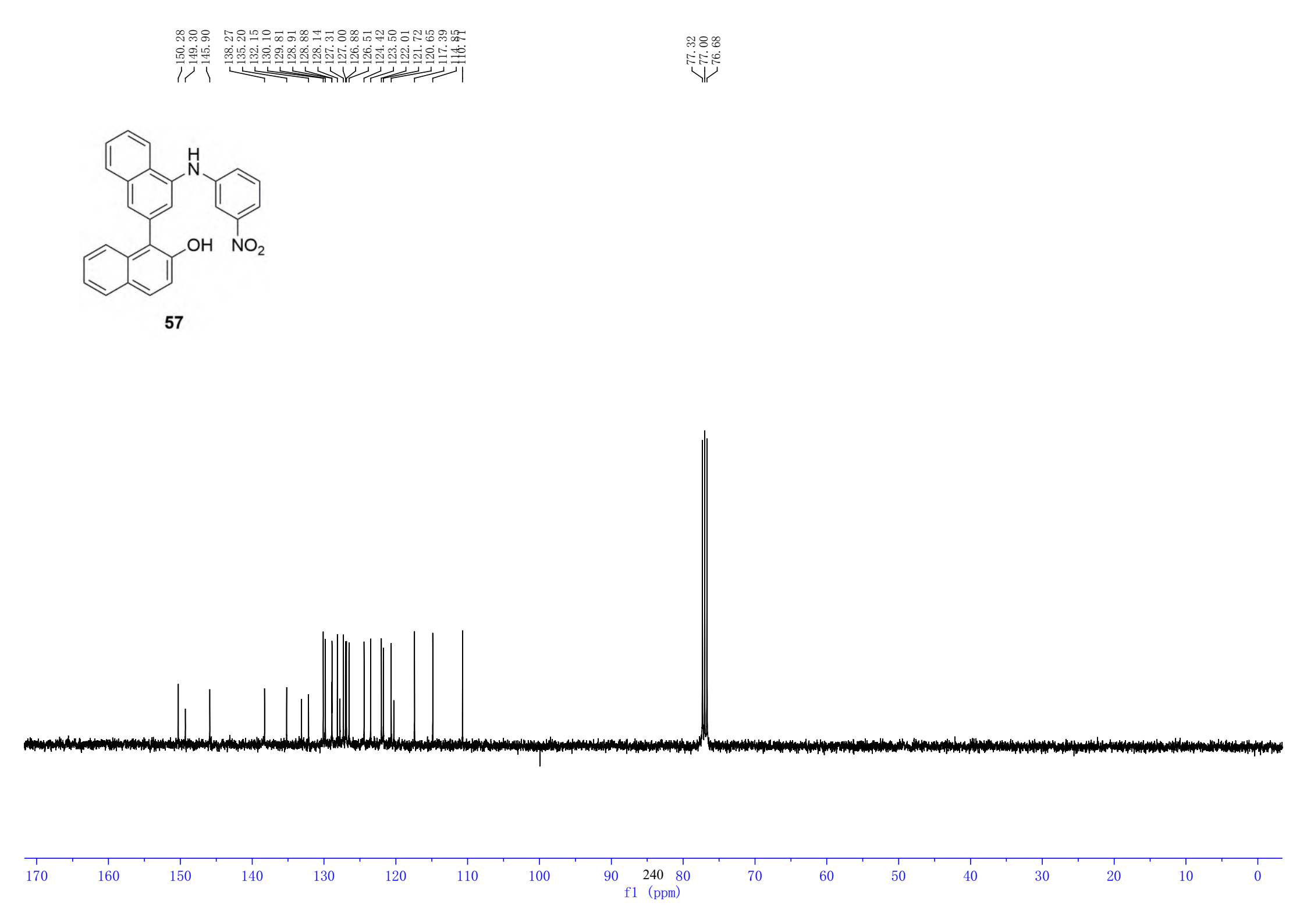

-62.79
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

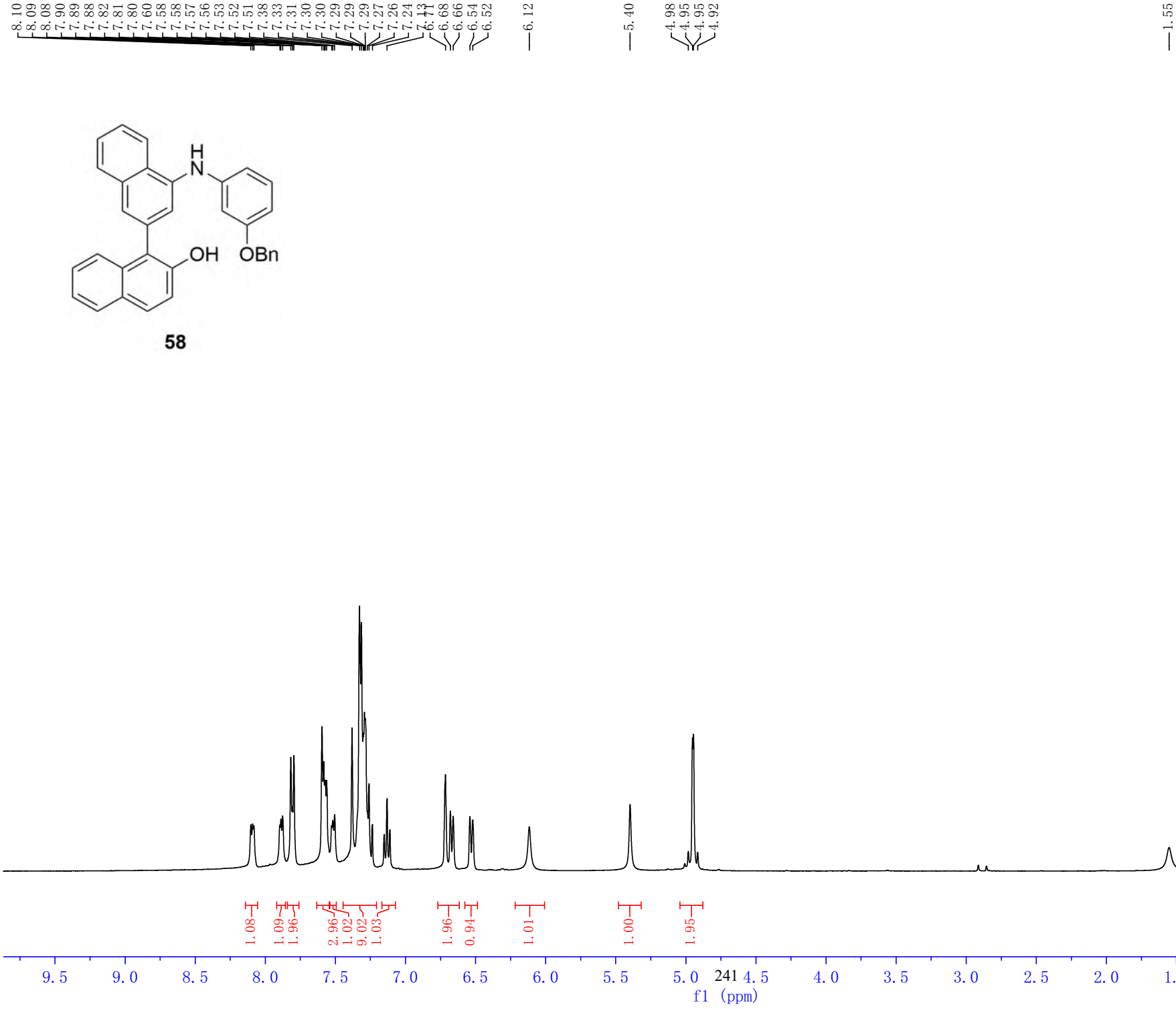

7.98
7.87
7.84
7.75
7.74
7.74
7.73
7.68
7.59
7.59
7.57
7.57
7.57
7.54
7.53
7.53
7.52
7.51
7.45
7.43
7.35
7.35
7.32
7.31
7.28
7.27
7.26
7.24
7.22
7.20
7.18
7.17
6.19
5.32
1.51


H
N
OH
NO2

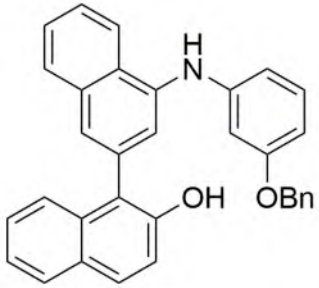
57


1.00
1.07
2.95
0.99
1.01
1.99
1.04
0.96
1.07
1.96
2.09
0.94
0.97
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
f1 (ppm)

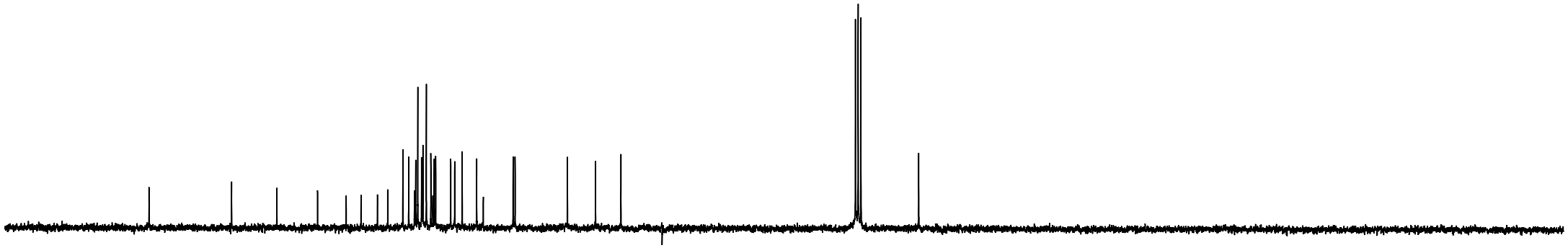

150.28
149.30
145.90
138.27
135.20
132.15
130.10
129.81
128.91
128.88
128.14
127.31
127.00
126.88
126.51
124.42
123.50
122.01
121.72
120.65
117.39
114.85
110.71
77.32
77.00
76.68
H
N
OH
NO2
57
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

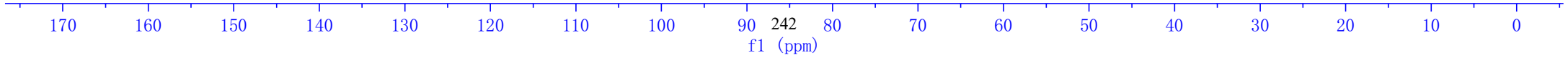

8.10
8.09
8.08
7.90
7.89
7.88
7.82
7.81
7.80
7.60
7.58
7.58
7.57
7.56
7.53
7.52
7.51
7.38
7.33
7.31
7.30
7.30
7.29
7.29
7.29
7.27
7.26
7.24
7.13
6.71
6.68
6.66
6.54
6.52
6.12
5.40
4.98
4.95
4.95
4.92
1.55
H
N
OH
OBn
58
1.08
1.09
1.96
2.96
1.02
9.02
1.03
1.96
0.94
1.01
1.00
1.95
9.5
9.0
8.5
8.0
7.5
7.0
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
f1 (ppm)

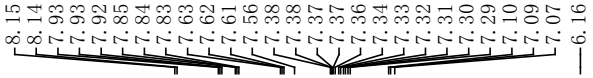
159.92
150.26
144.97
140.21
132.00
130.23
129.55
128.73
128.49
128.05
127.89
127.49
126.96
126.57
126.39
124.64
124.18
123.30
121.60
117.34
107.71
104.73
77.32
77.00
76.68
69.92

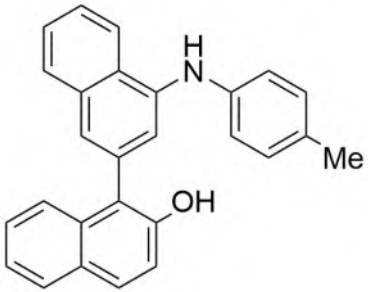


58

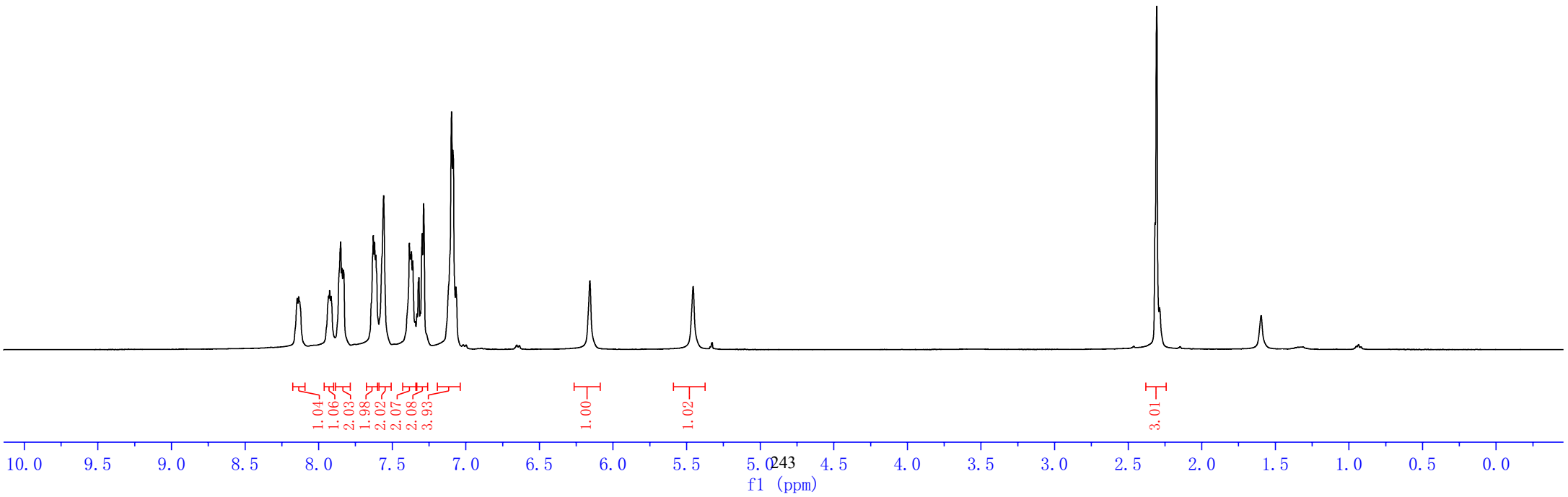


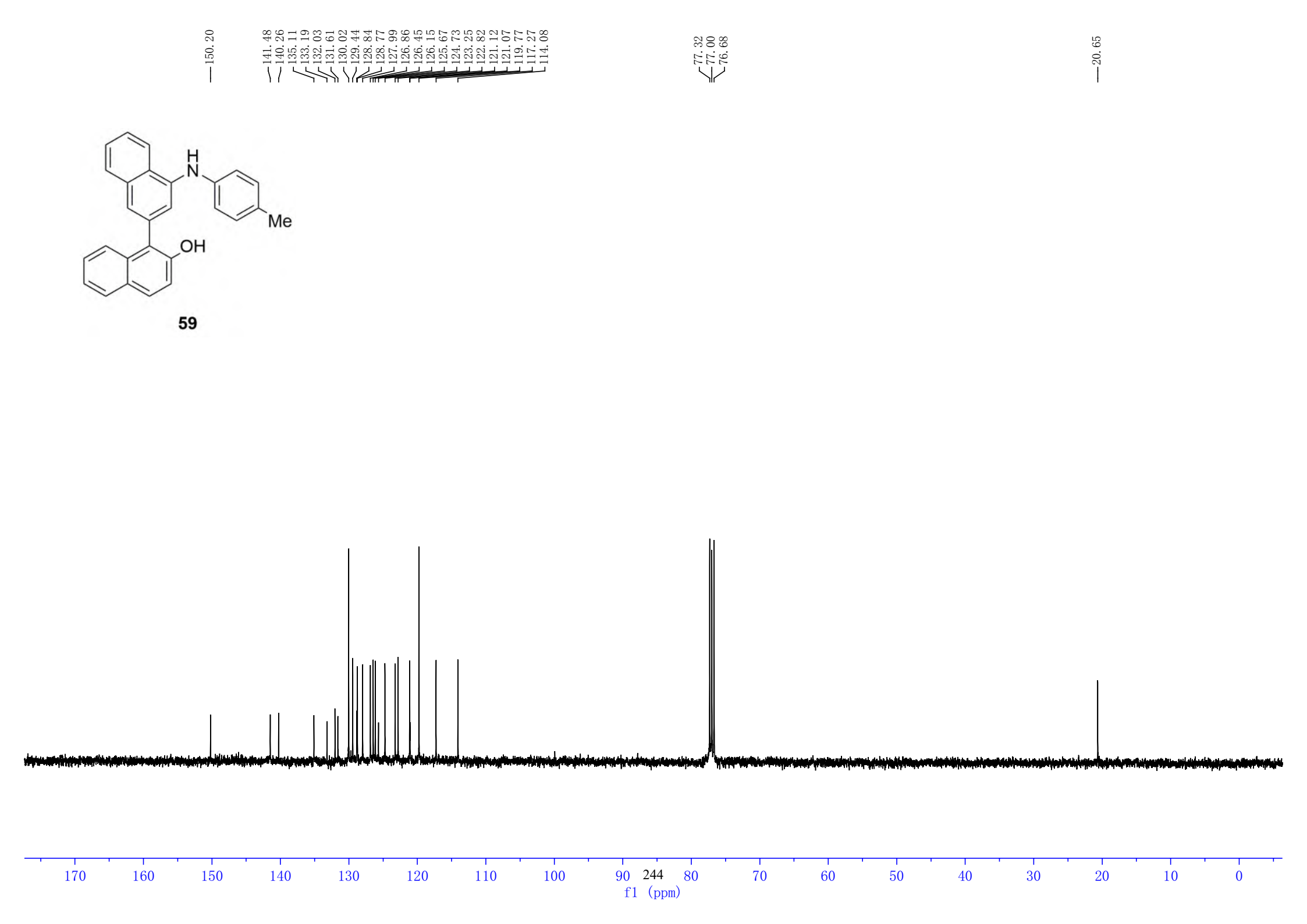


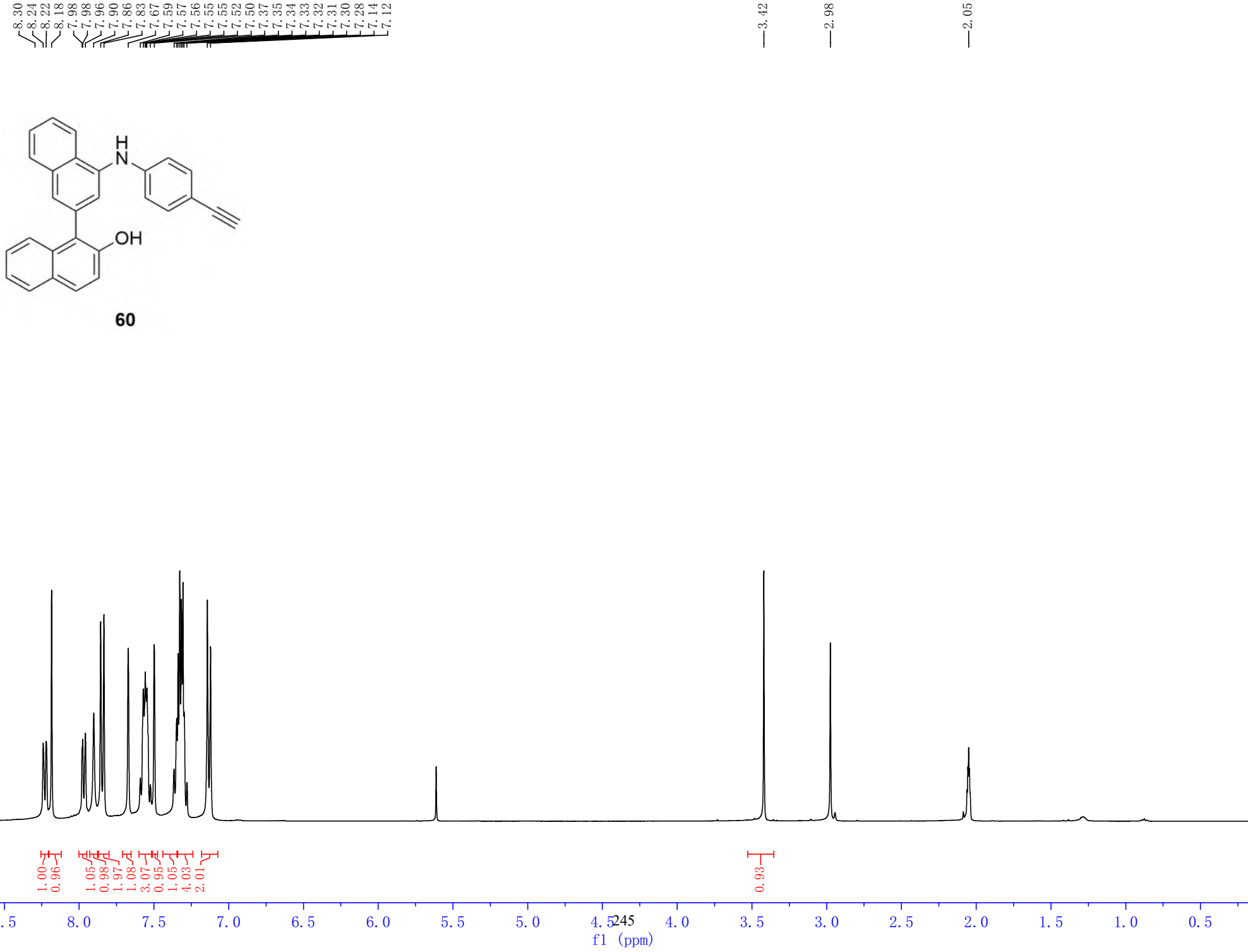

8.15
8.14
7.93
7.93
7.92
7.85
7.84
7.83
7.63
7.62
7.61
7.56
7.38
7.38
7.37
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.29
7.10
7.09
7.07
6.16
5.46
2.32
2.31
2.29
1.60

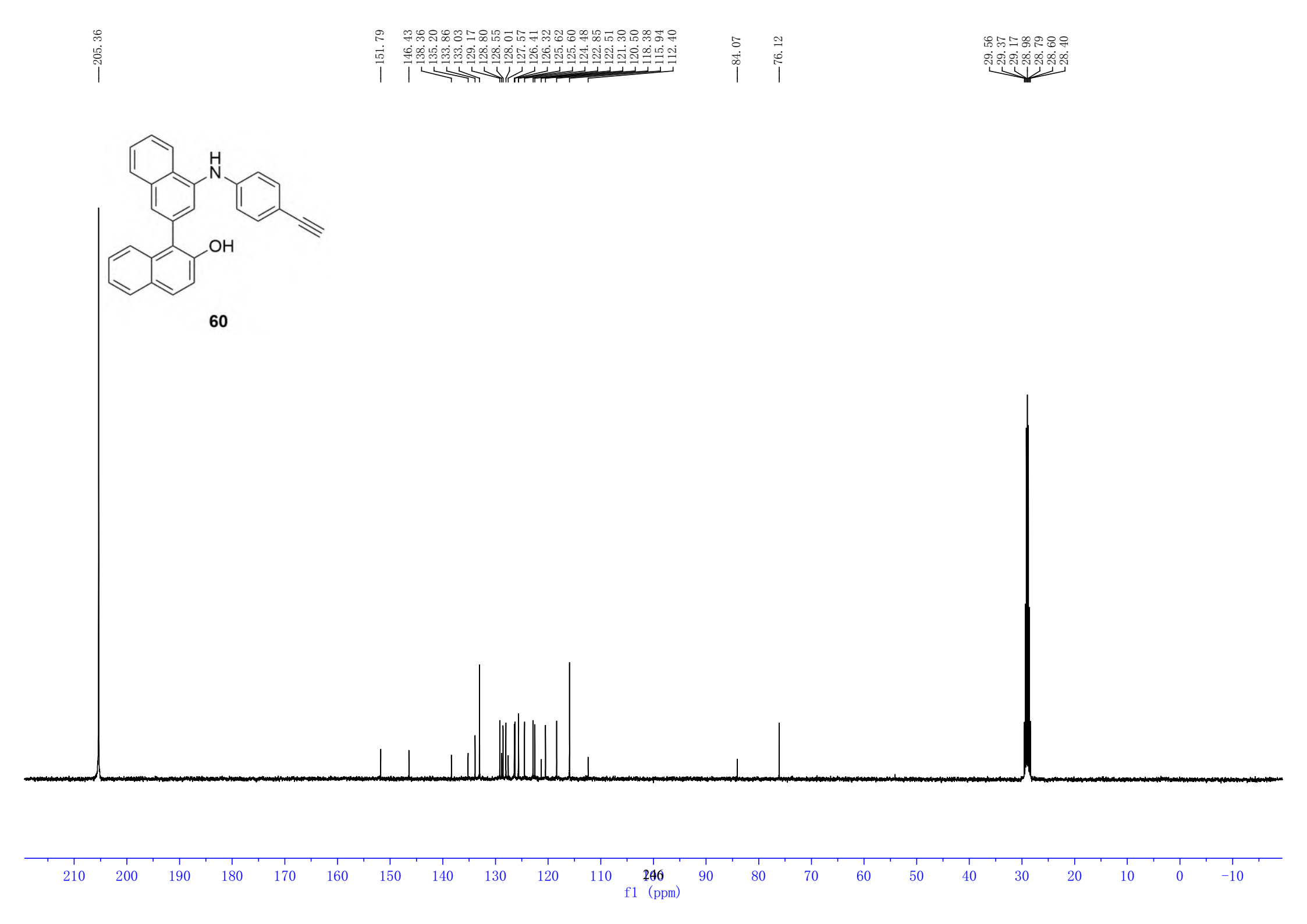

H
N
Me
OH

59


1.04
1.06
2.03
1.98
2.02
2.07
2.08
3.93
1.00
1.02
3.01
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
f1 (ppm)

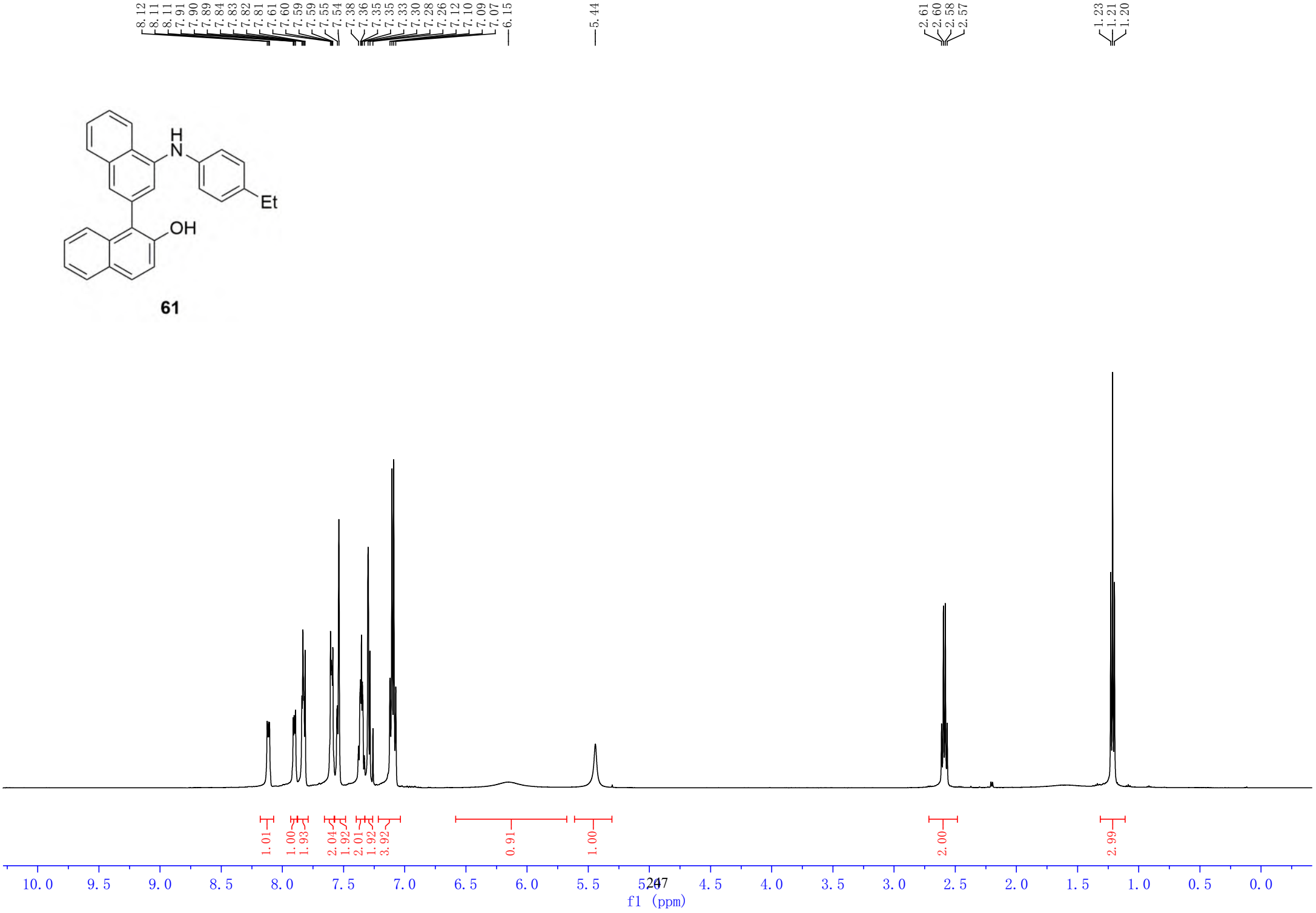

150.20
141.48
140.26
135.11
133.19
132.03
131.61
130.02
129.44
128.84
128.77
127.99
126.86
126.45
126.15
125.67
124.73
123.25
122.82
121.12
121.07
119.77
117.27
114.08
77.32
77.00
76.68
20.65
H
N
Me
OH
59
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.30
8.24
8.22
8.18
7.98
7.98
7.96
7.90
7.86
7.83
7.67
7.59
7.57
7.56
7.55
7.55
7.52
7.50
7.37
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.14
7.12
3.42
2.98
2.05
H
N
OH
60
1.00
0.96
1.05
0.98
1.97
1.08
3.07
0.95
1.05
4.03
2.01
0.93
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
f1 (ppm)


205.36
151.79
146.43
138.36
135.20
133.86
133.03
129.17
128.80
128.55
128.01
127.57
126.41
126.32
125.62
125.60
124.48
122.85
122.51
121.30
120.50
118.38
115.94
112.40
84.07
76.12
29.56
29.37
29.17
28.98
28.79
28.60
28.40
H
N
OH
60
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)

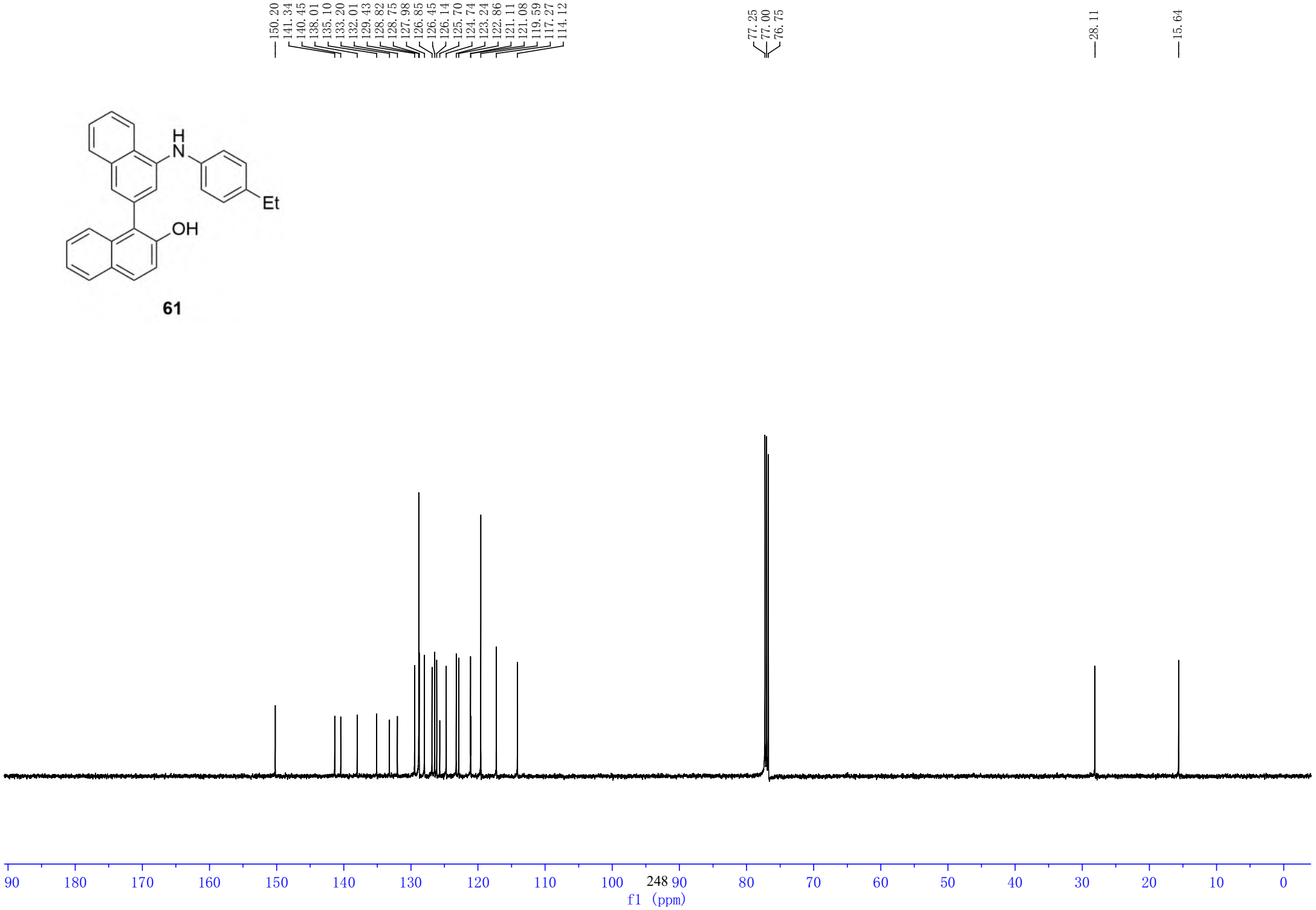
H
N
Et
OH

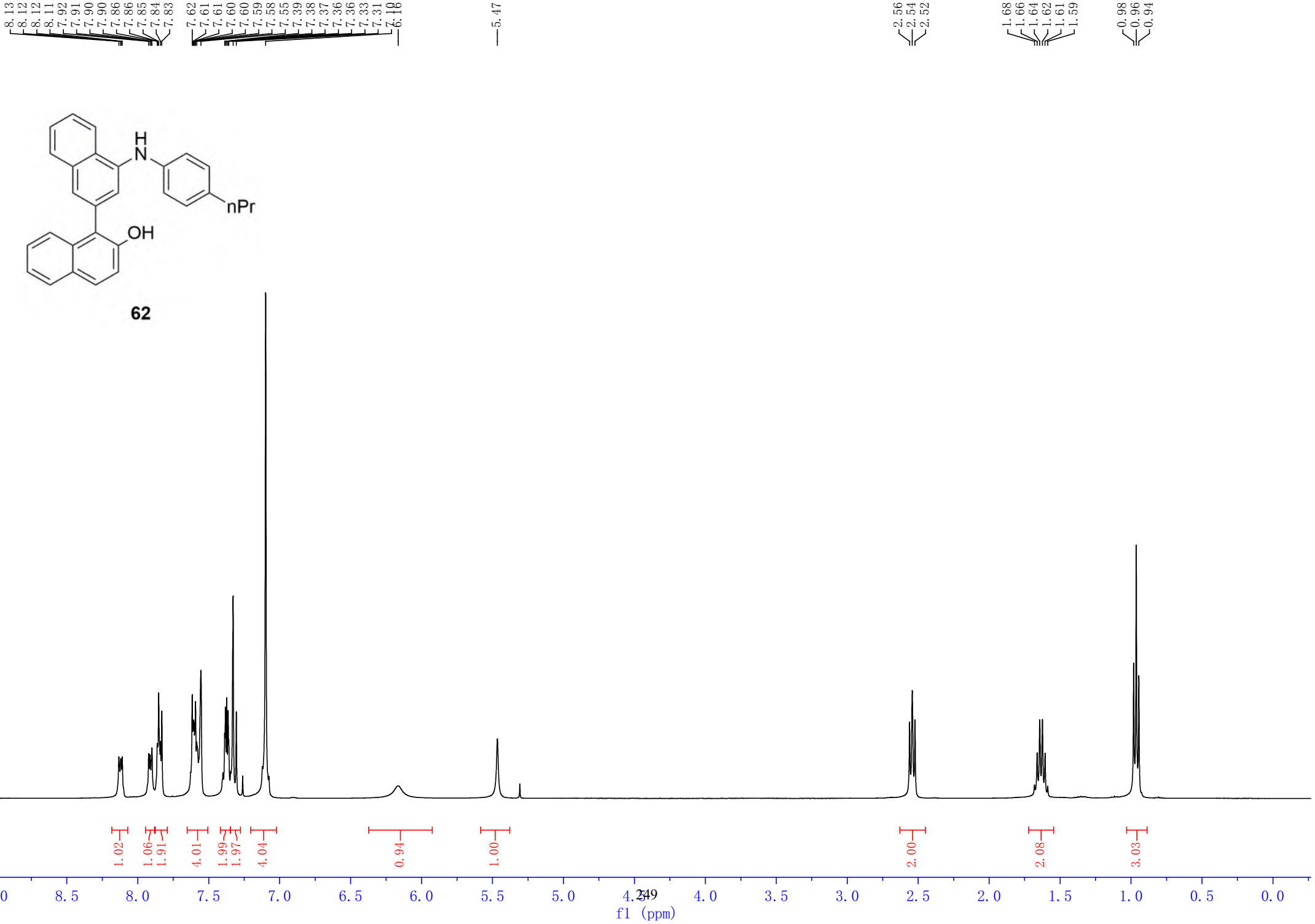
61


8.12
8.11
8.11
7.91
7.90
7.89
7.84
7.83
7.82
7.81
7.61
7.60
7.59
7.59
7.55
7.54
7.38
7.36
7.35
7.33
7.30
7.28
7.26
7.12
7.10
7.09
7.07
6.15
5.44
2.61
2.60
2.58
2.57
1.23
1.21
1.20
1.01
1.00
1.93
2.04
1.92
2.01
1.92
3.92
0.91
1.00
2.00
2.99
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
f1 (ppm)

H
N
Et
OH

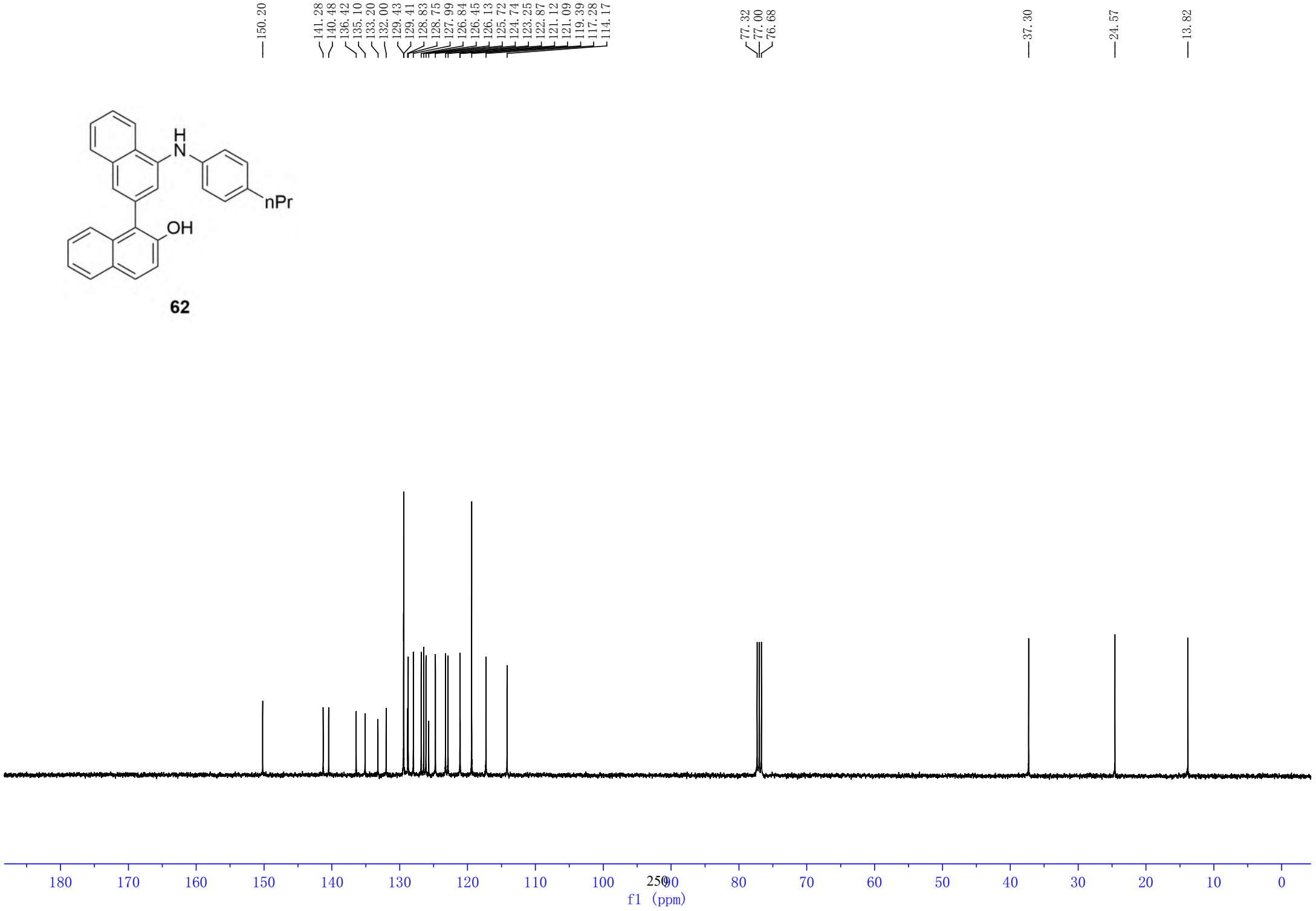
61

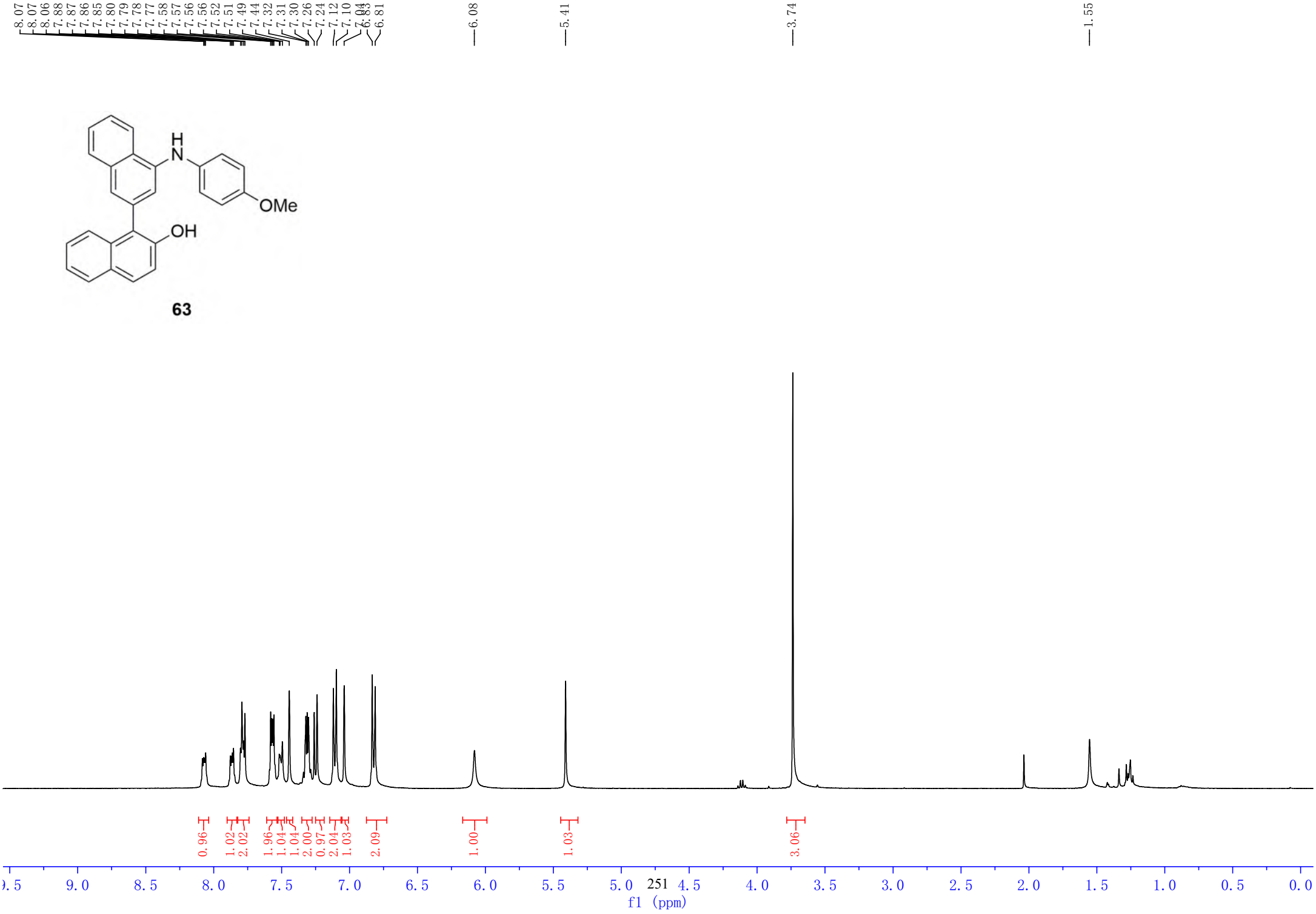

150.20
141.34
140.45
138.01
135.10
133.20
132.01
129.43
128.82
128.75
127.98
126.85
126.45
126.14
125.70
124.74
123.24
122.86
121.11
121.08
119.59
117.27
114.12
77.25
77.00
76.75
28.11
15.64
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.13
8.12
8.12
8.11
7.92
7.91
7.90
7.90
7.86
7.86
7.85
7.84
7.83
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.55
7.39
7.38
7.37
7.36
7.36
7.33
7.31
7.10
6.10
5.47
2.56
2.54
2.52
1.68
1.66
1.64
1.62
1.61
1.59
0.98
0.96
0.94
H
N
nPr
OH
62
1.02
1.06
1.91
4.01
1.99
1.97
4.04
0.94
1.00
2.00
2.08
3.03
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
f1 (ppm)

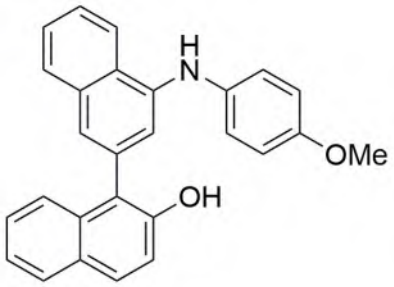
H
N
nPr
OH

62

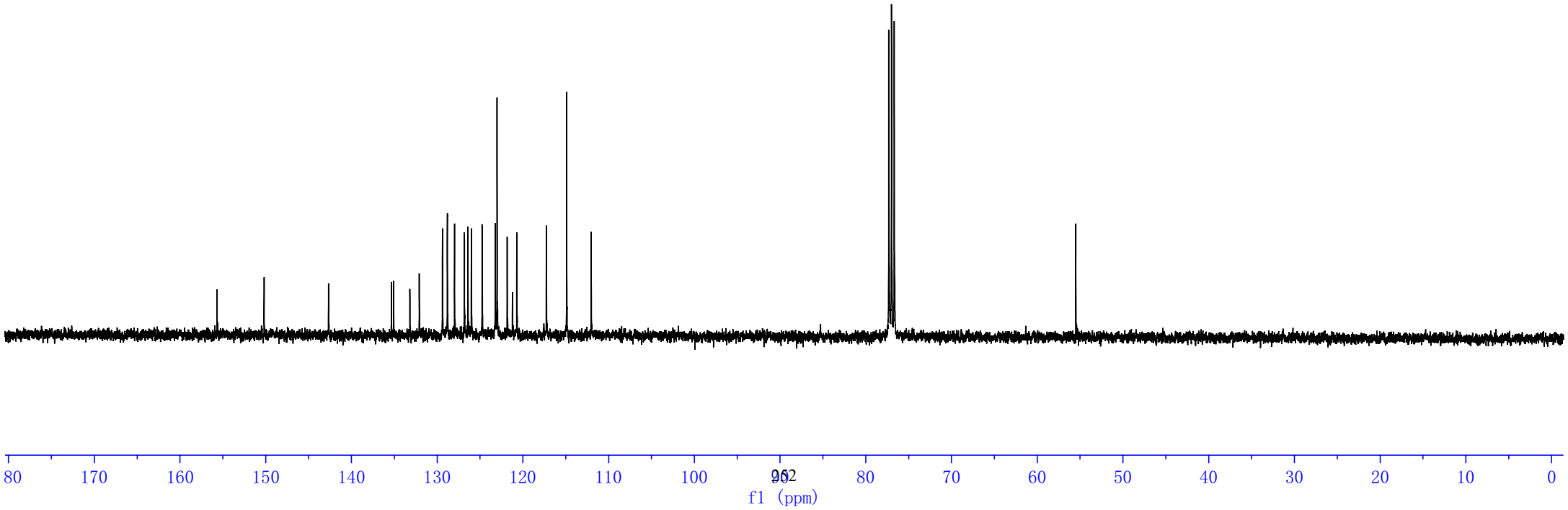

150.20
141.28
140.48
136.42
135.10
133.20
132.00
129.43
129.41
128.83
128.75
127.99
126.84
126.45
126.13
125.72
124.74
123.25
122.87
121.12
121.09
119.39
117.28
114.17
77.32
77.00
76.68
37.30
24.57
13.82
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.07
8.07
8.06
7.88
7.87
7.86
7.85
7.80
7.79
7.78
7.77
7.58
7.57
7.56
7.52
7.51
7.49
7.44
7.32
7.31
7.30
7.26
7.24
7.12
7.10
7.04
6.83
6.81
6.08
5.41
3.74
1.55
H
N
OMe
OH
63
0.96
1.02
2.02
1.96
1.04
1.04
2.00
0.97
2.04
1.03
2.09
1.00
1.03
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
f1 (ppm)

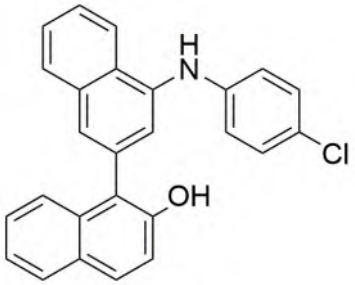
155.68
150.18
142.67
135.34
135.08
133.19
132.09
129.38
128.81
127.97
126.83
126.41
126.01
124.76
124.74
123.22
123.01
122.97
121.83
121.22
120.71
117.26
114.89
112.03
77.32
77.00
76.68
55.50



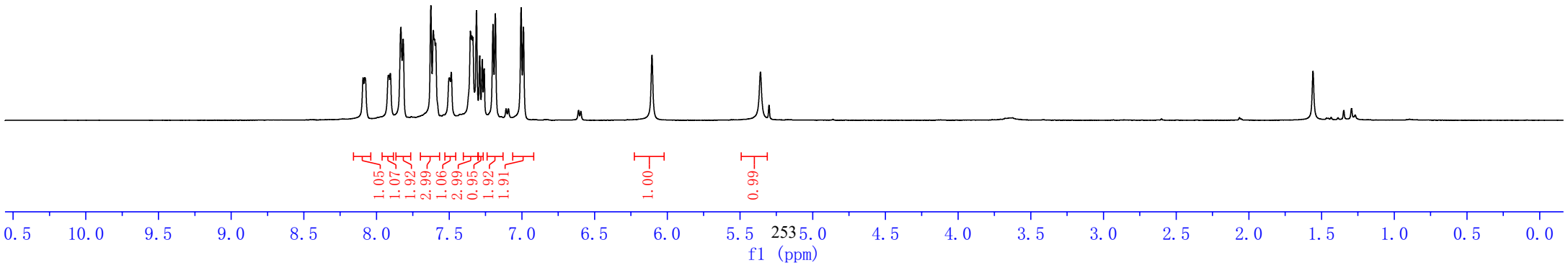
63

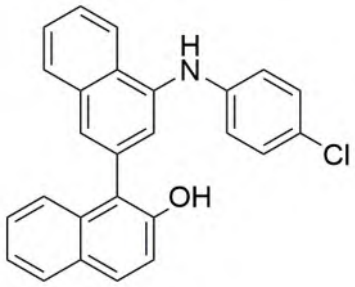



8.09
8.08
7.92
7.92
7.90
7.83
7.82
7.63
7.61
7.60
7.59
7.50
7.49
7.35
7.34
7.34
7.31
7.29
7.27
7.26
7.20
7.18
7.01
6.99
6.11
5.36
1.56


H
N
Cl
OH

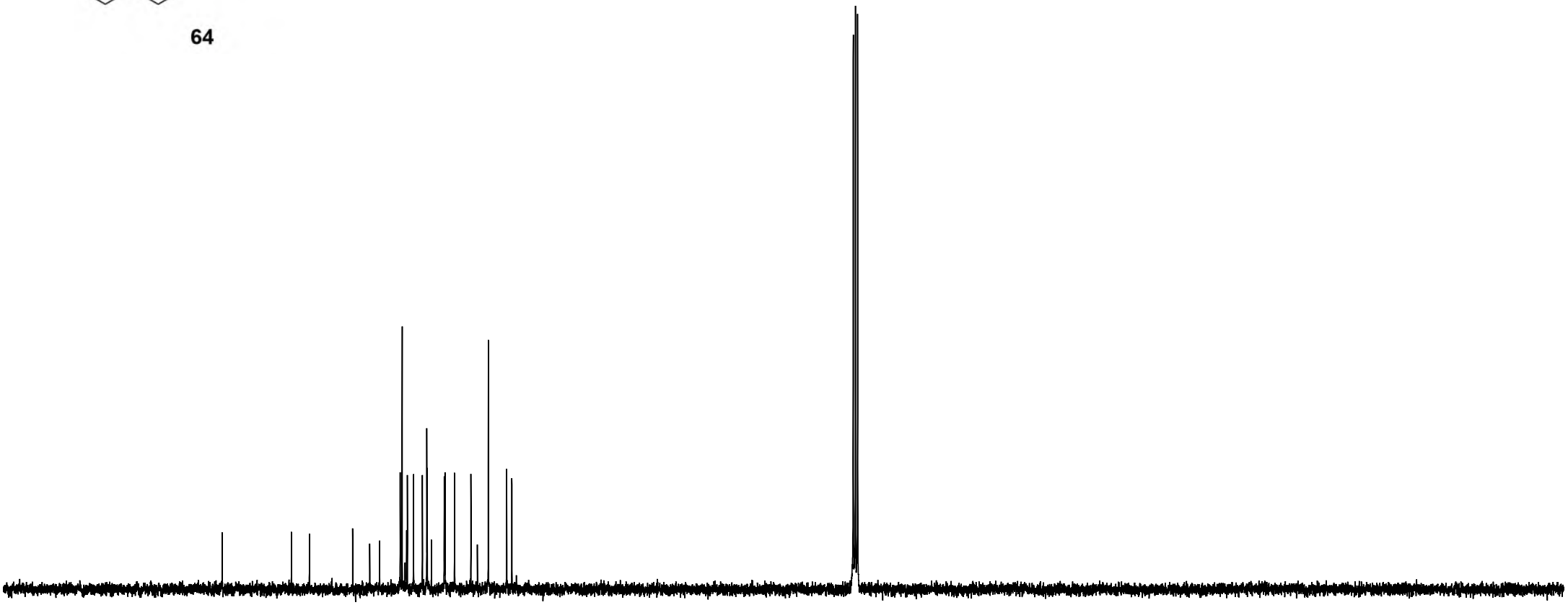
64


1.05
1.07
1.92
2.99
1.06
2.99
0.95
1.92
1.91
1.00
0.99
0.5
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
f1 (ppm)



64

150.24
142.23
140.14
135.14
133.16
132.03
129.64
129.42
128.91
128.82
128.11
127.08
126.57
126.53
126.04
124.55
124.46
123.36
121.47
120.72
119.45
117.33
116.73
77.25
77.00
76.75

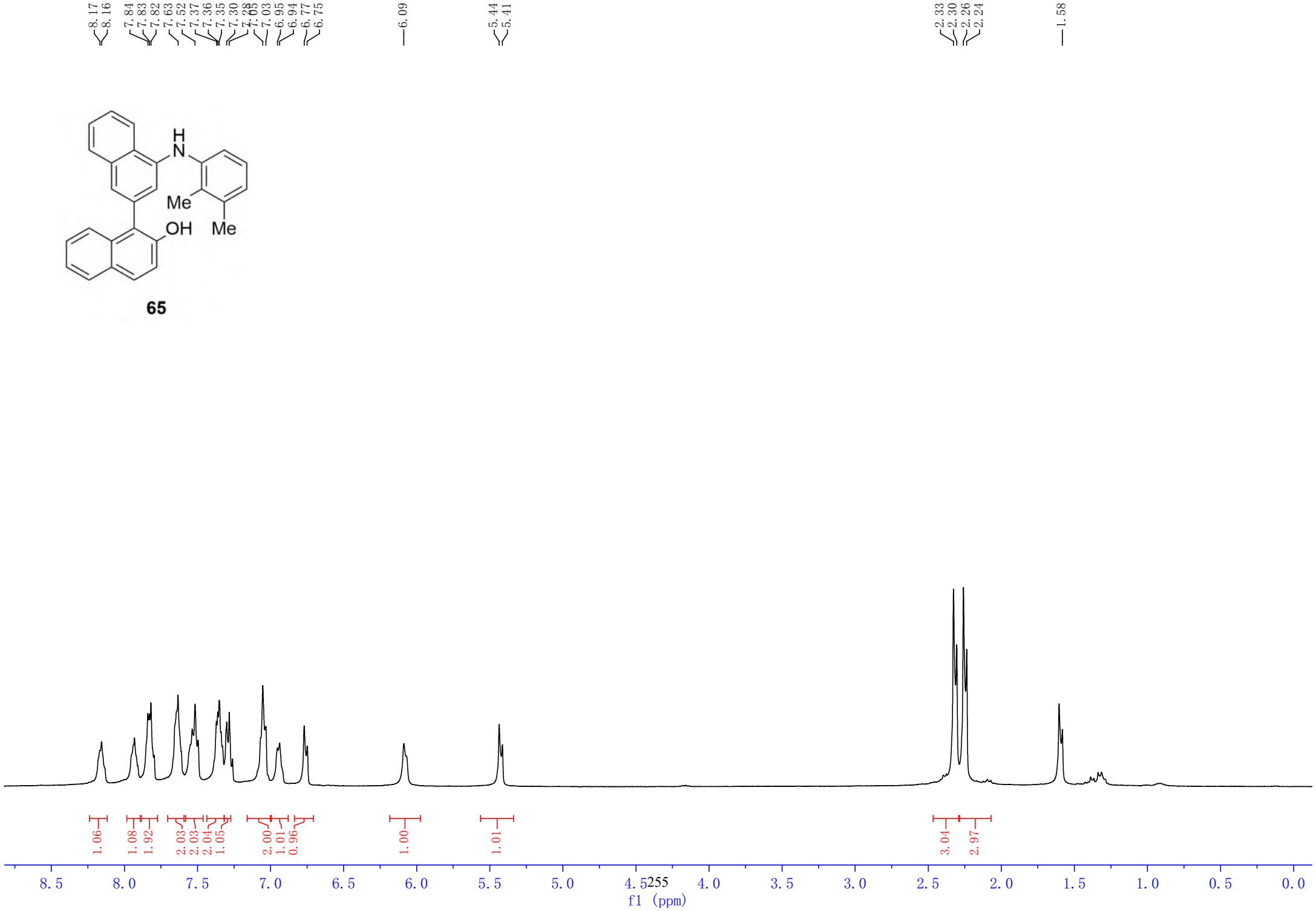


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

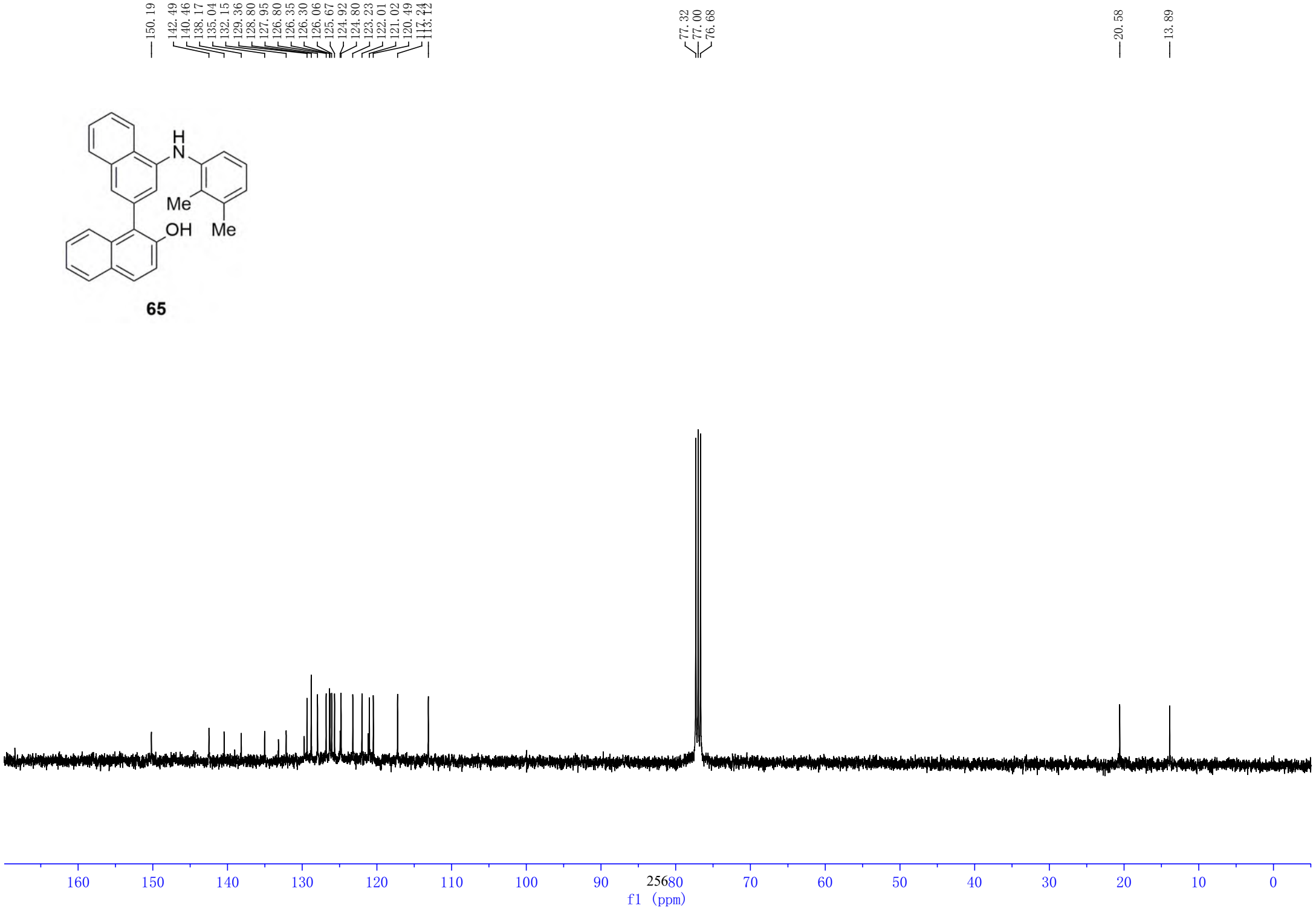
H
N
Me
OH
Me

65

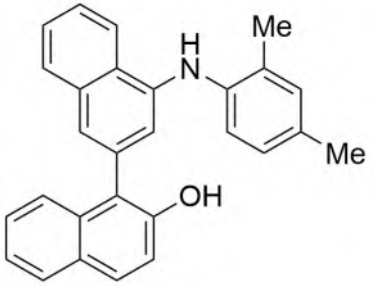

8.17
8.16
7.84
7.83
7.82
7.63
7.52
7.37
7.36
7.35
7.30
7.03
6.95
6.94
6.77
6.75
6.09
5.44
5.41
2.33
2.30
2.26
2.24
1.58
1.06
1.08
1.92
2.03
2.03
2.04
1.05
2.00
1.01
0.96
1.00
1.01
3.04
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

H
N
Me
OH
Me

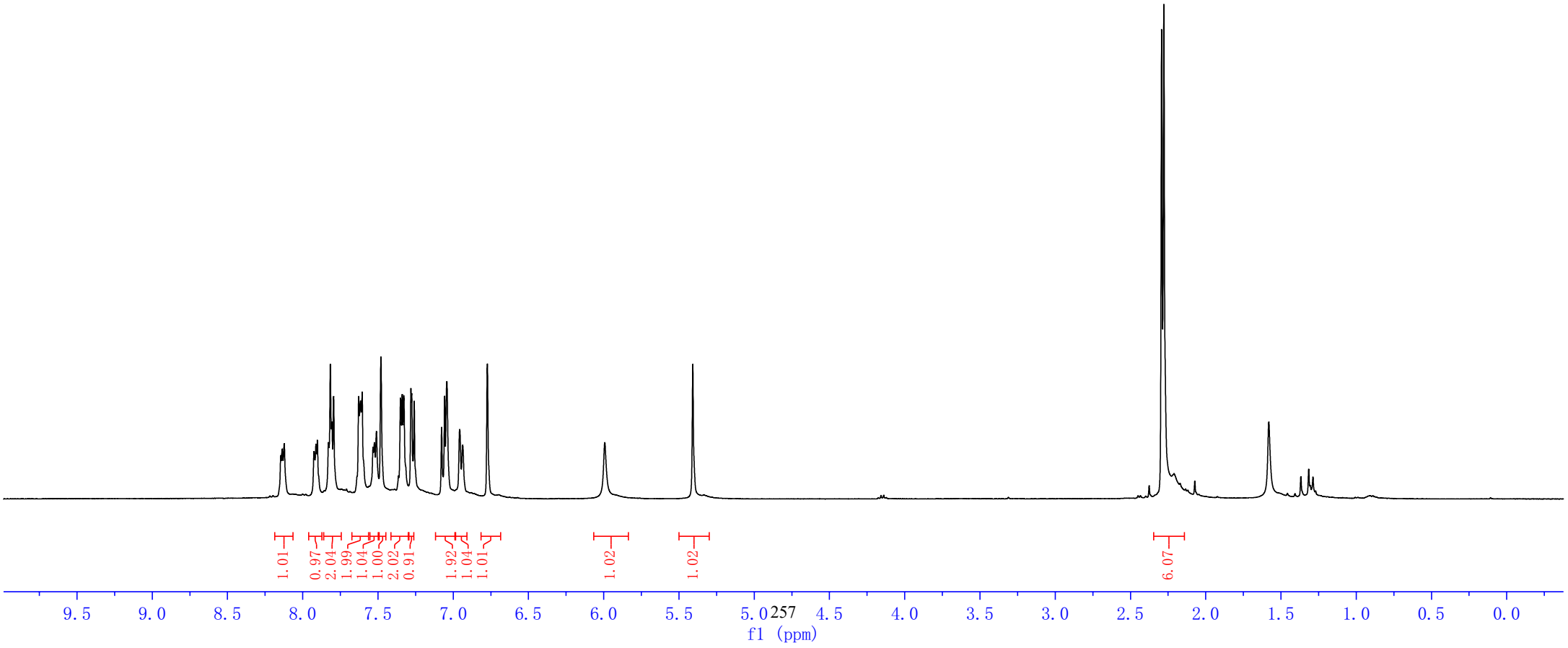
65

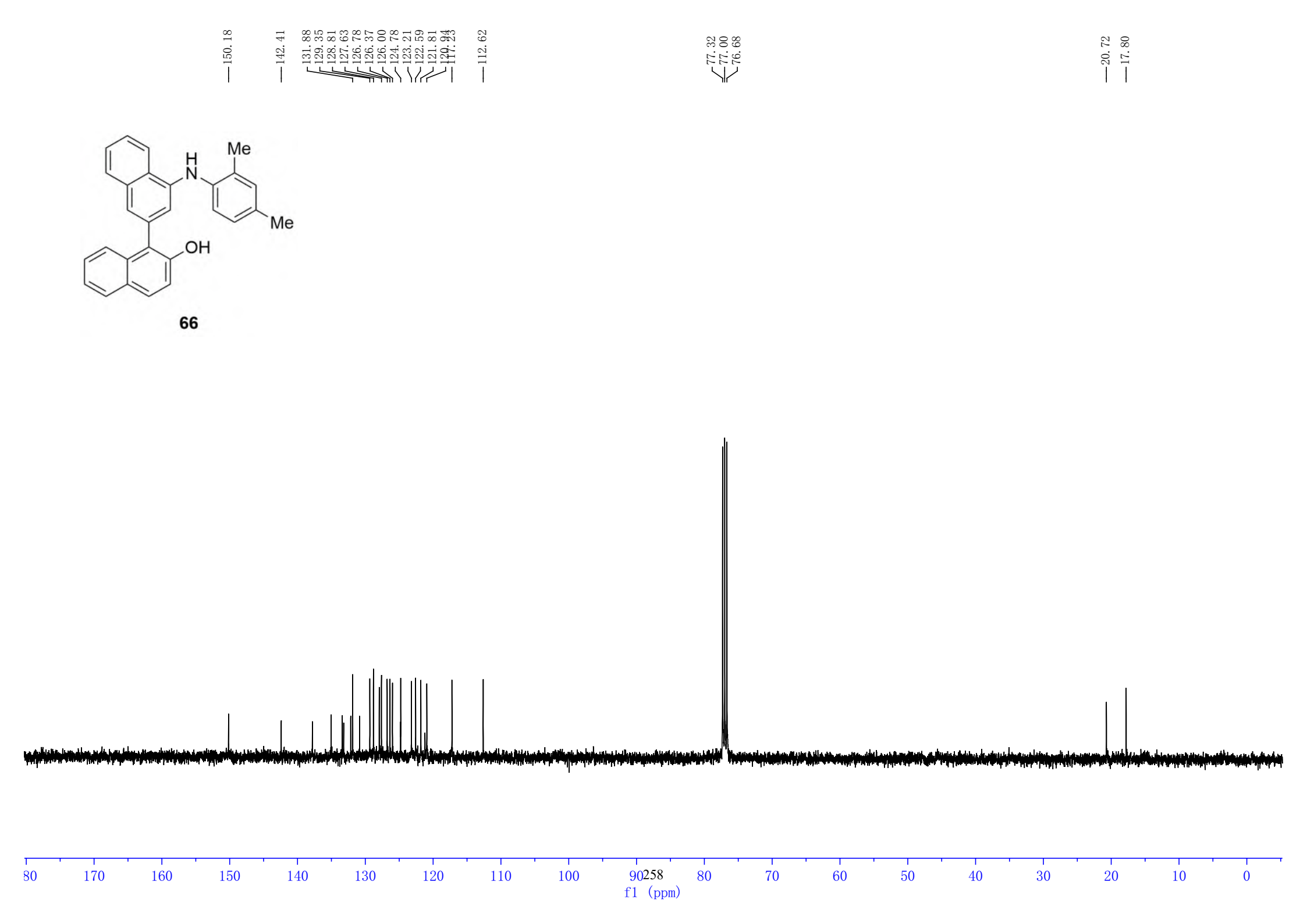

150.19
142.49
140.46
138.17
135.04
132.15
129.36
128.80
127.95
126.80
126.35
126.30
126.06
125.67
124.92
124.80
123.23
122.01
121.02
120.49
77.32
77.00
76.68
20.58
13.89
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

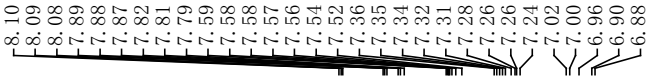

8.15
8.14
8.12
7.93
7.91
7.90
7.83
7.82
7.81
7.79
7.63
7.62
7.61
7.53
7.52
7.51
7.48
7.36
7.35
7.34
7.33
7.28
7.28
7.26
7.08
7.06
7.04
6.96
6.94
6.77
5.99
5.41
2.29
2.28
1.58

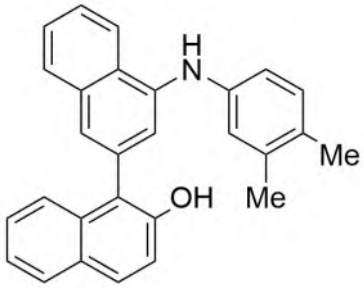

H
N
Me
Me
OH

66

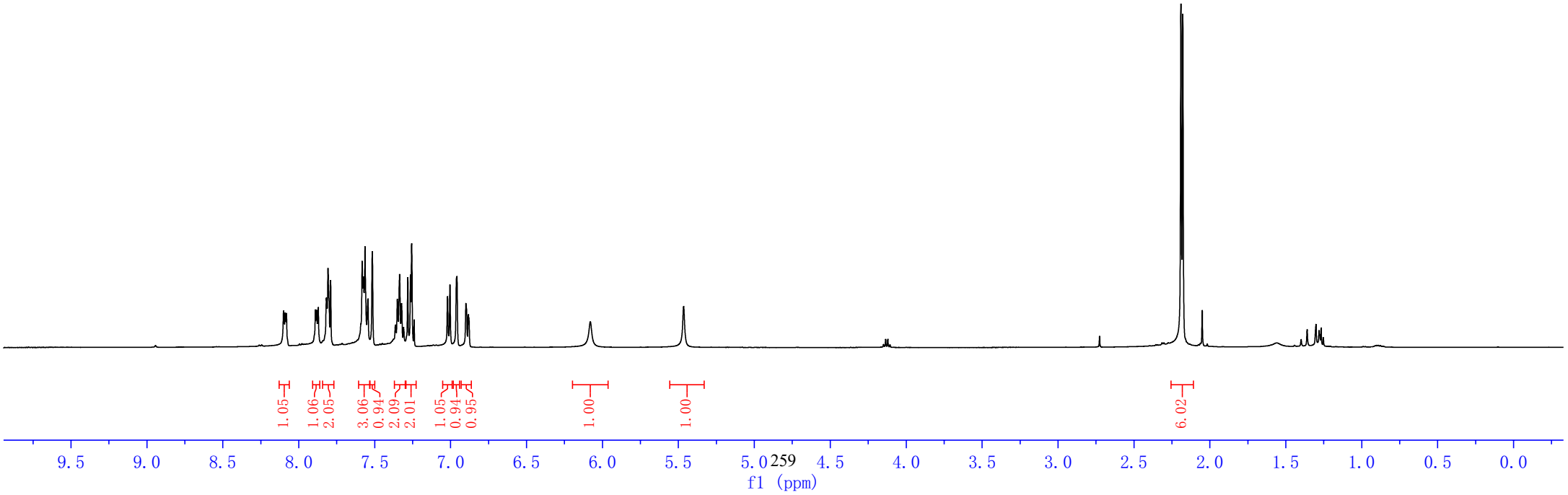

1.01
0.97
2.04
1.99
1.04
1.00
2.02
0.91
1.92
1.04
1.01
1.02
1.02
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

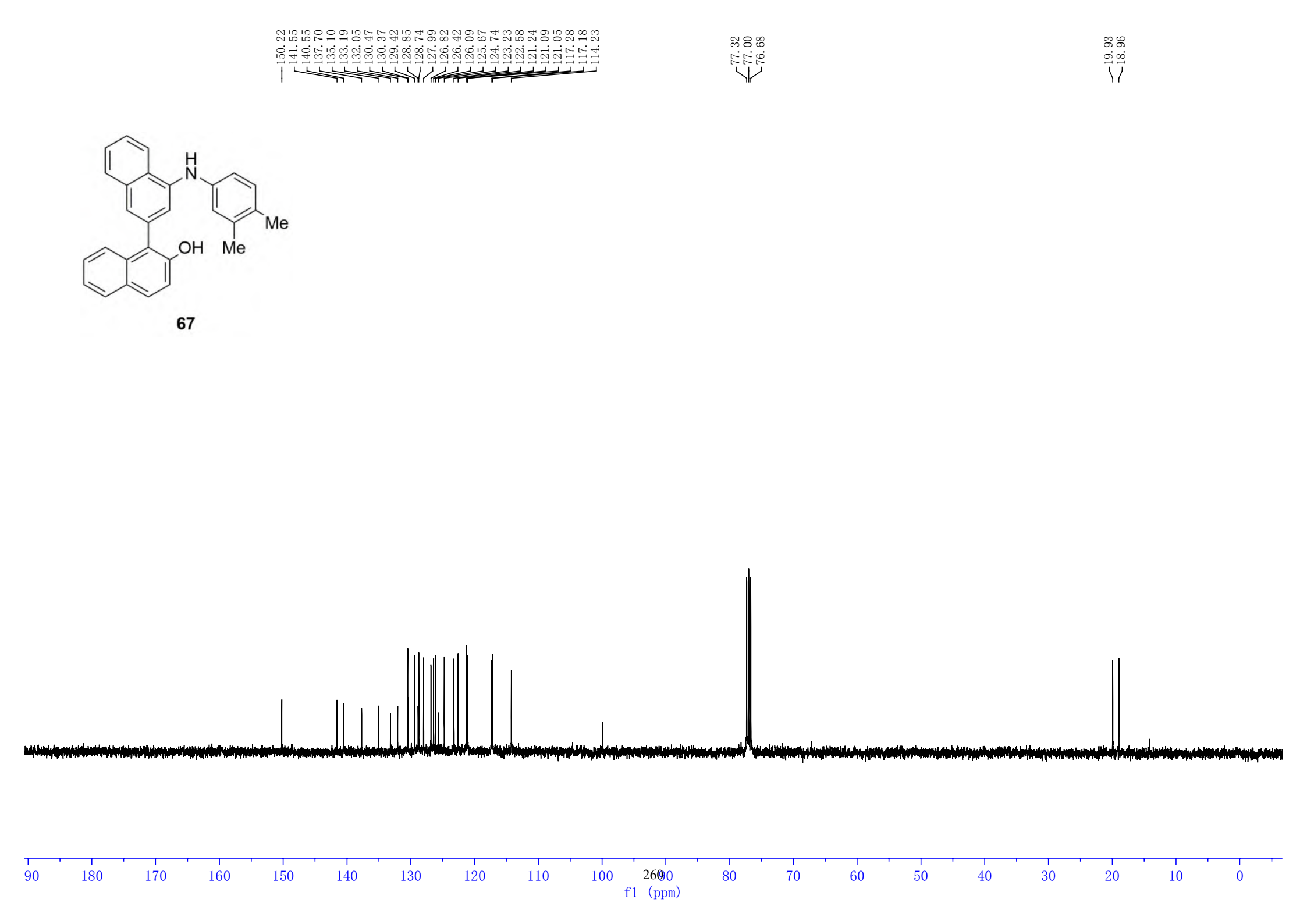

150.18
142.41
131.88
129.35
128.81
127.63
126.78
126.37
126.00
124.78
123.21
122.59
121.81
120.94
117.23
112.62
77.32
77.00
76.68
20.72
17.80
H
N
Me
Me
OH
66
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.10
8.09
8.08
7.89
7.88
7.87
7.82
7.81
7.79
7.59
7.58
7.58
7.57
7.56
7.54
7.52
7.36
7.35
7.34
7.32
7.31
7.28
7.26
7.26
7.24
7.02
7.00
6.96
6.90
6.88
6.08
5.47
2.19
2.18

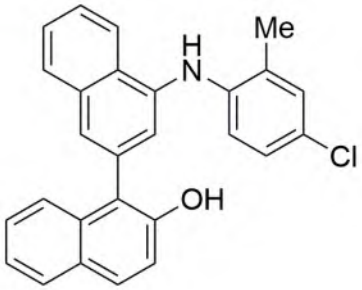

H
N
Me
OH
Me

67

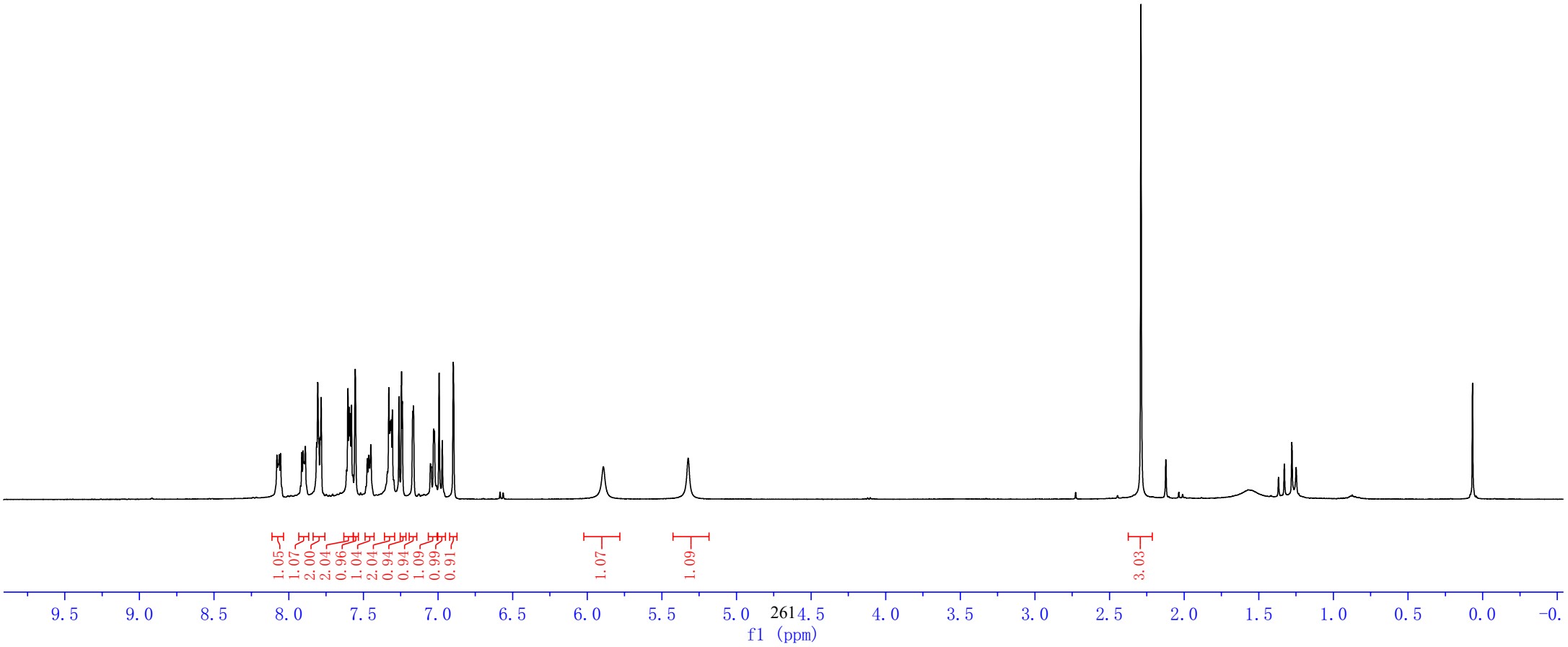

1.05
1.06
2.05
3.06
0.94
2.09
2.01
1.05
0.94
0.95
1.00
1.00
6.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

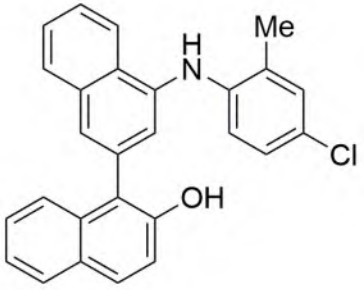

150.22
141.55
140.55
137.70
135.10
133.19
132.05
130.47
130.37
129.42
128.85
128.74
127.99
126.82
126.42
126.09
125.67
124.74
123.23
122.58
121.24
121.09
121.05
117.28
117.18
114.23
77.32
77.00
76.68
19.93
18.96
H
N
Me
OH
Me
67
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.08
8.06
8.06
7.91
7.90
7.90
7.89
7.89
7.81
7.81
7.79
7.78
7.60
7.59
7.58
7.55
7.47
7.46
7.45
7.33
7.32
7.32
7.31
7.31
7.26
7.25
7.24
7.24
7.17
7.16
7.05
7.03
7.02
6.99
6.97
6.90
6.89
5.32
2.29
1.57
0.07


H
N
Me
Cl
OH

68


1.05
1.07
2.00
2.04
0.96
1.04
2.04
0.94
0.94
1.09
0.99
0.91
1.07
1.09
3.03
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.
f1 (ppm)

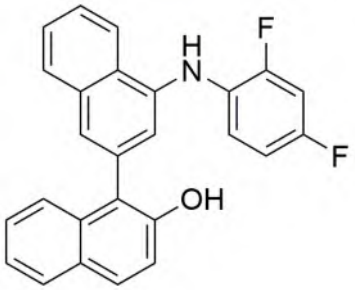


68

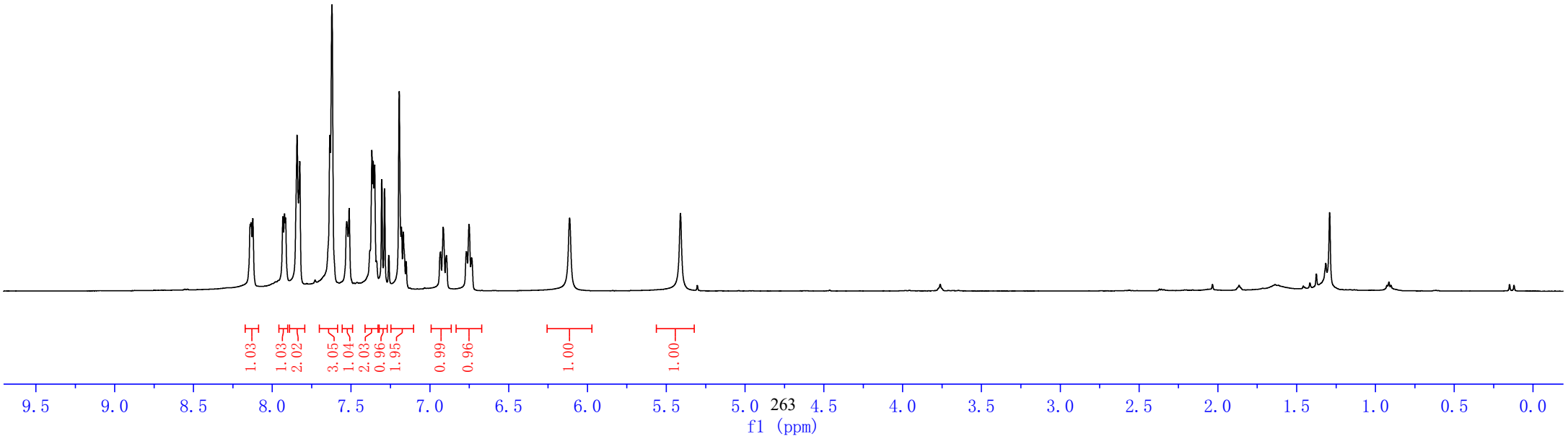
150.24
141.11
139.94
130.85
129.60
128.89
128.11
127.03
126.99
126.53
126.42
124.63
123.36
121.63
115.36
77.36
77.04
76.72
17.84

f1 (ppm)

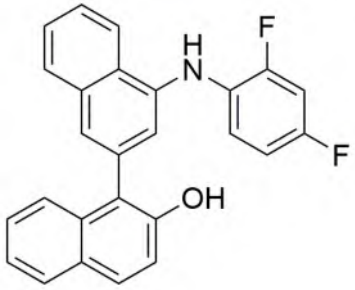

8.14
8.13
8.12
7.93
7.92
7.92
7.84
7.83
7.63
7.62
7.53
7.51
7.37
7.36
7.35
7.34
7.31
7.29
7.26
7.19
7.18
7.17
7.15
6.93
6.92
6.89
6.77
6.75
6.73
6.11
5.41


H
N
F
F
OH

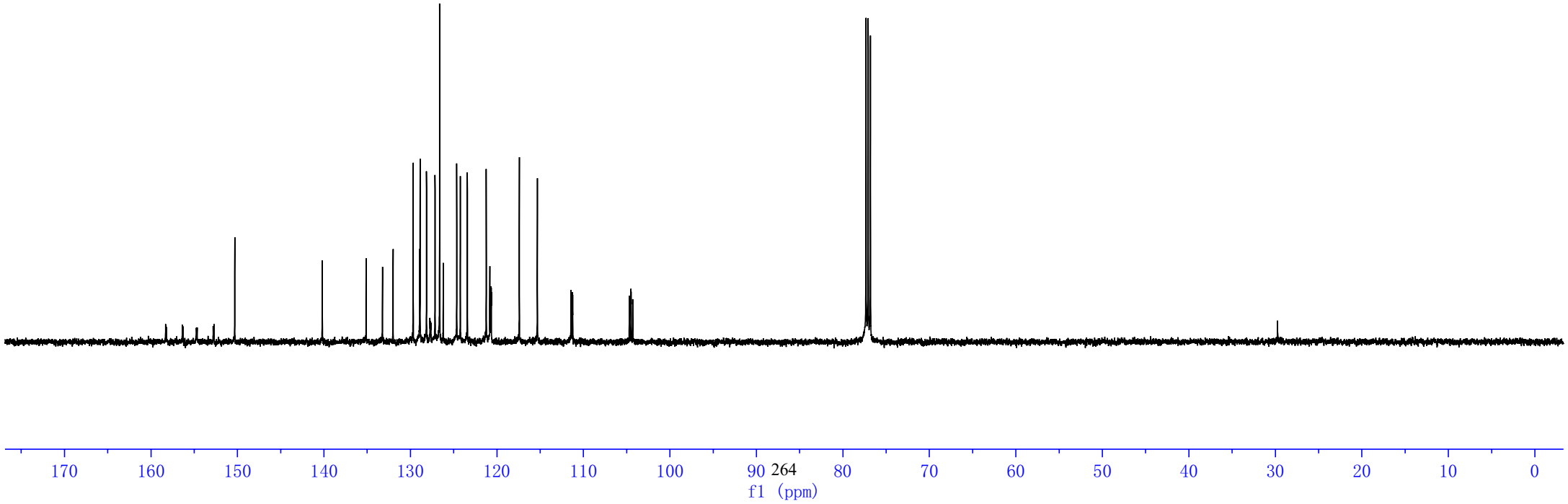
69


1.03
1.03
2.02
3.05
1.04
2.03
0.96
1.95
0.99
0.96
1.00
1.00
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
f1 (ppm)

158.31
152.71
150.31
140.19
135.13
132.01
129.68
128.94
128.89
128.14
127.15
126.62
124.65
124.23
123.42
121.23
117.41
115.32
111.44
111.41
104.51
104.30
77.32
77.07
76.82

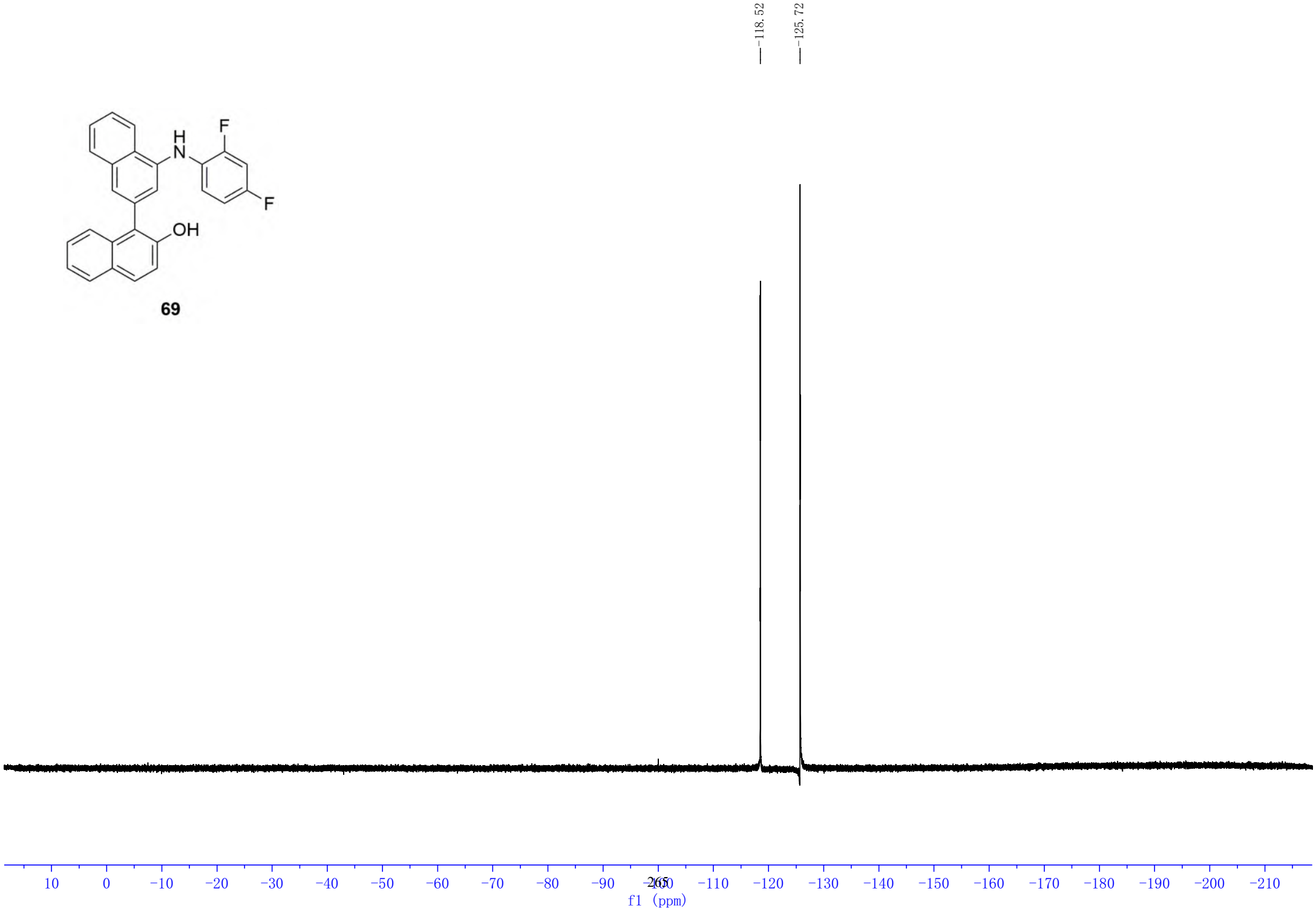


69



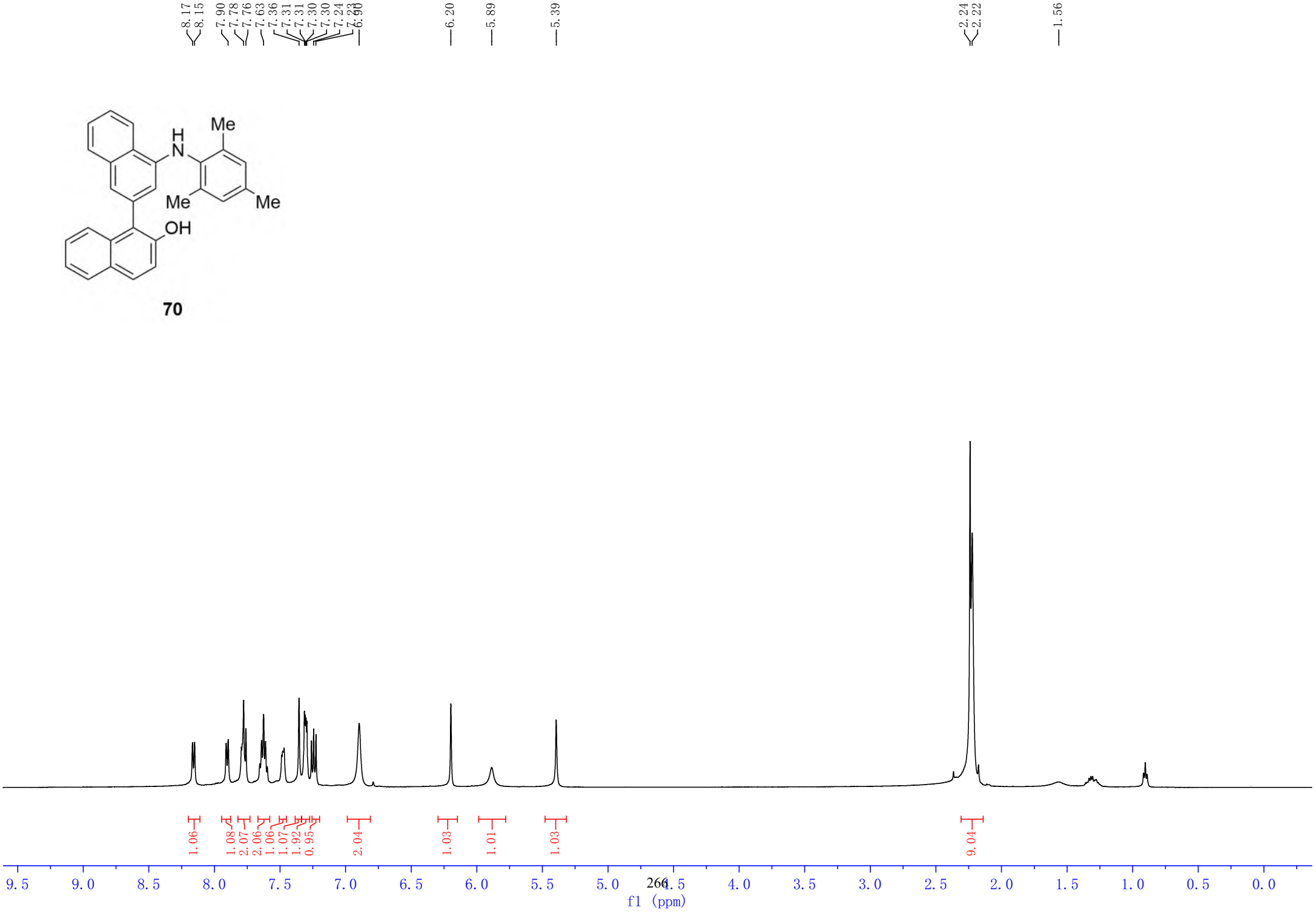
H
N
F
F
OH

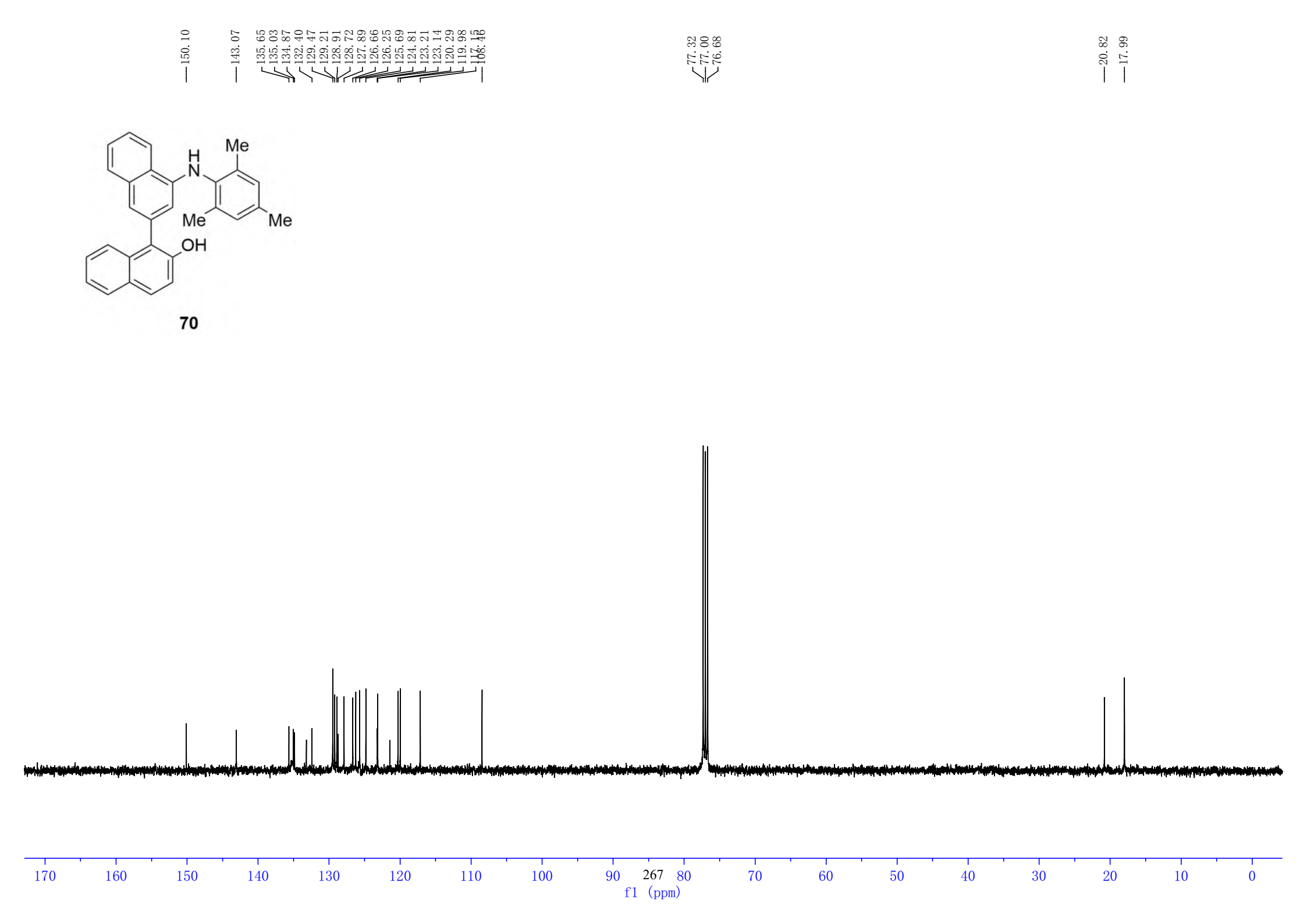
69

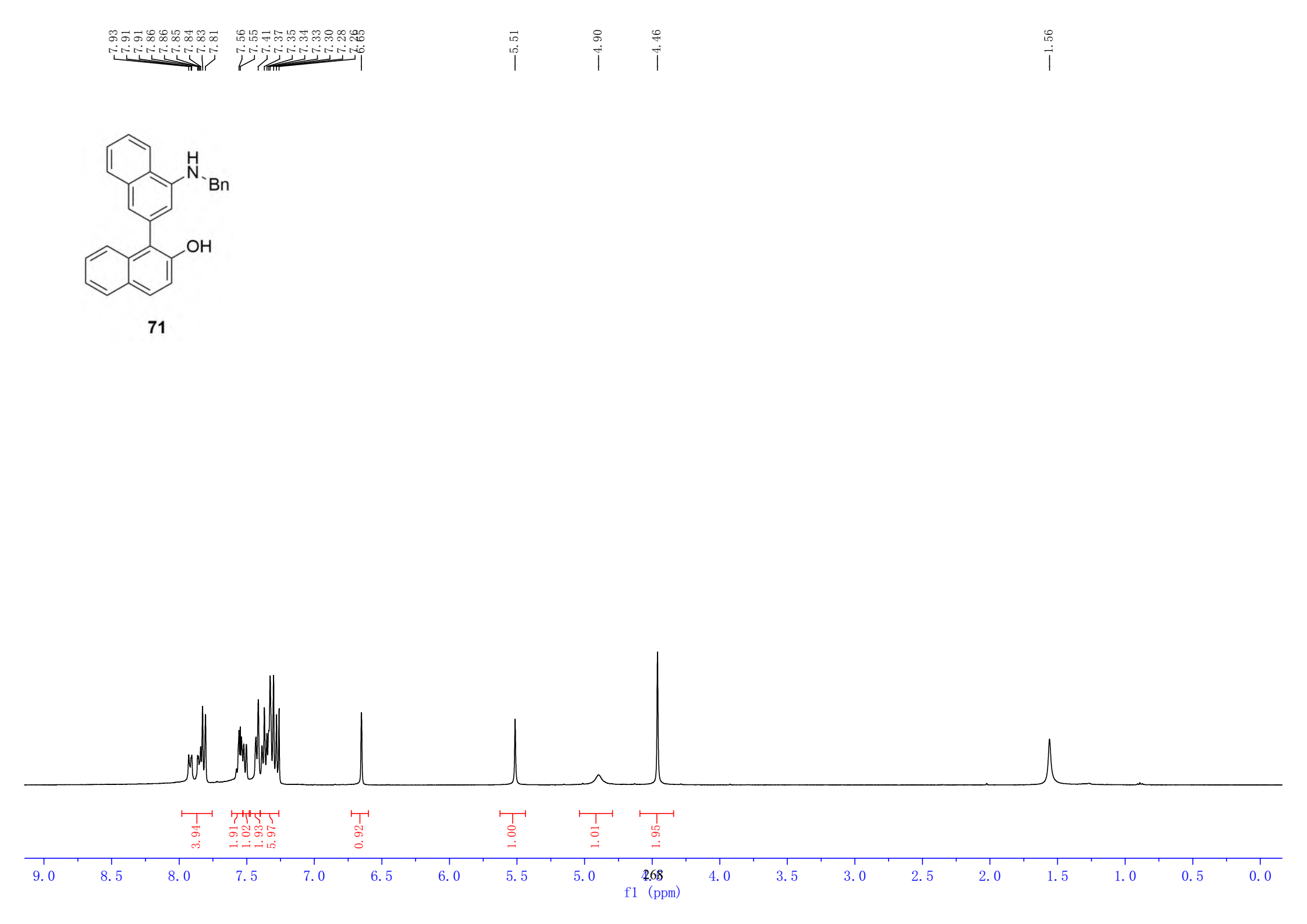

-118.52
-125.72
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

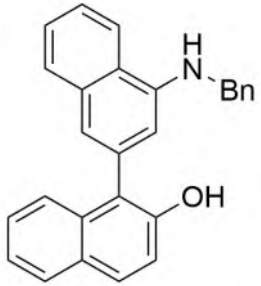
H
N
Me
Me
Me
OH

70


8.17
8.15
7.90
7.78
7.76
7.63
7.36
7.31
7.31
7.30
7.30
7.24
7.23
6.90
6.20
5.89
5.39
2.24
2.22
1.56
1.06
1.08
2.07
2.06
1.06
1.07
1.92
0.95
2.04
1.03
1.01
1.03
9.04
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
f1 (ppm)


150.10
143.07
135.65
135.03
134.87
132.40
129.47
129.21
128.91
128.72
127.89
126.66
126.25
125.69
124.81
123.21
123.14
120.29
119.98
77.32
77.00
76.68
20.82
17.99
H
N
Me
Me
Me
OH
70
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.93
7.91
7.91
7.86
7.86
7.85
7.84
7.83
7.81
7.56
7.55
7.41
7.37
7.35
7.34
7.33
7.30
7.28
7.26
6.65
5.51
4.90
4.46
1.56
H
N
Bn
OH
71
3.94
1.91
1.02
1.93
5.97
0.92
1.00
1.01
1.95
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
f1 (ppm)

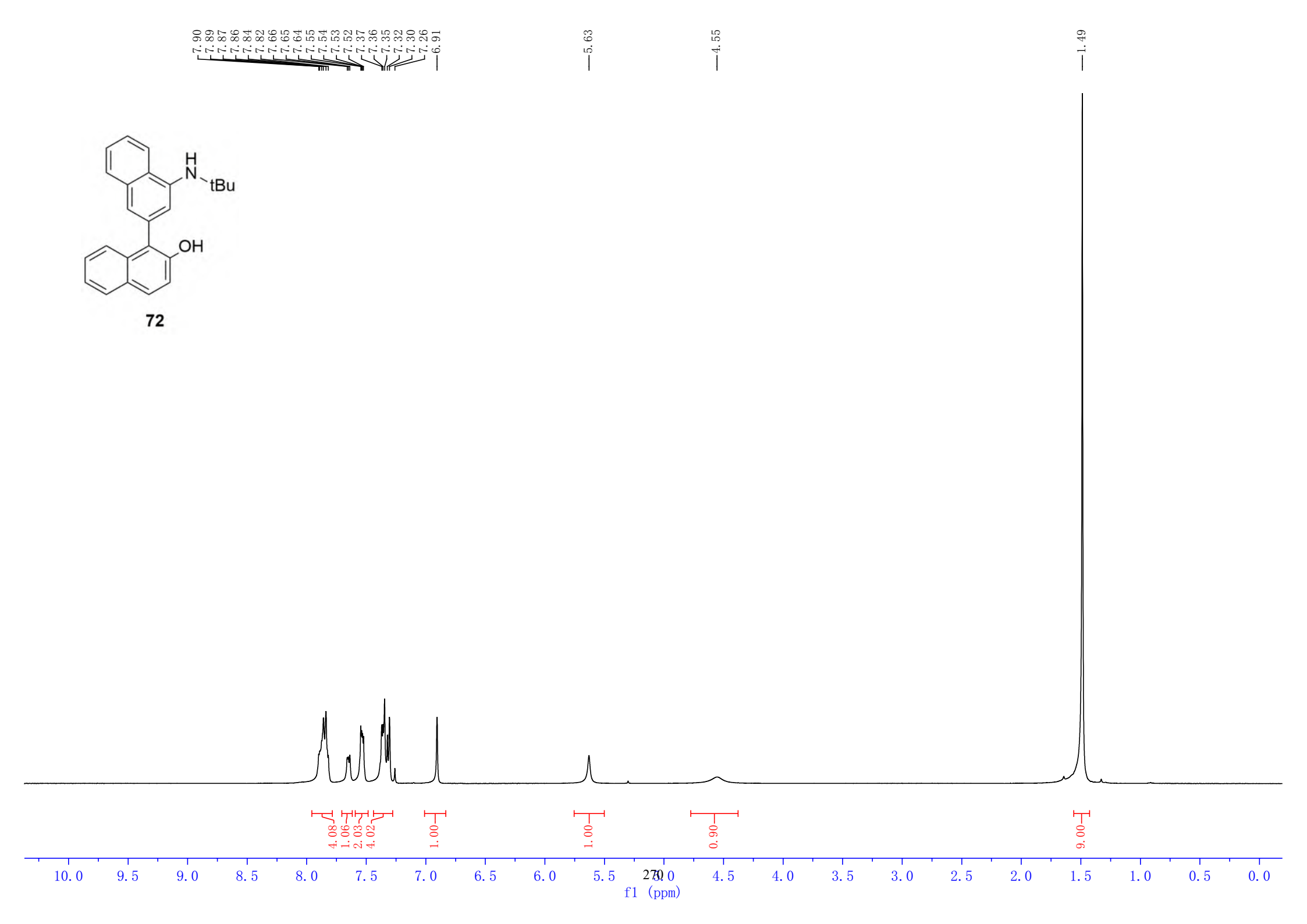


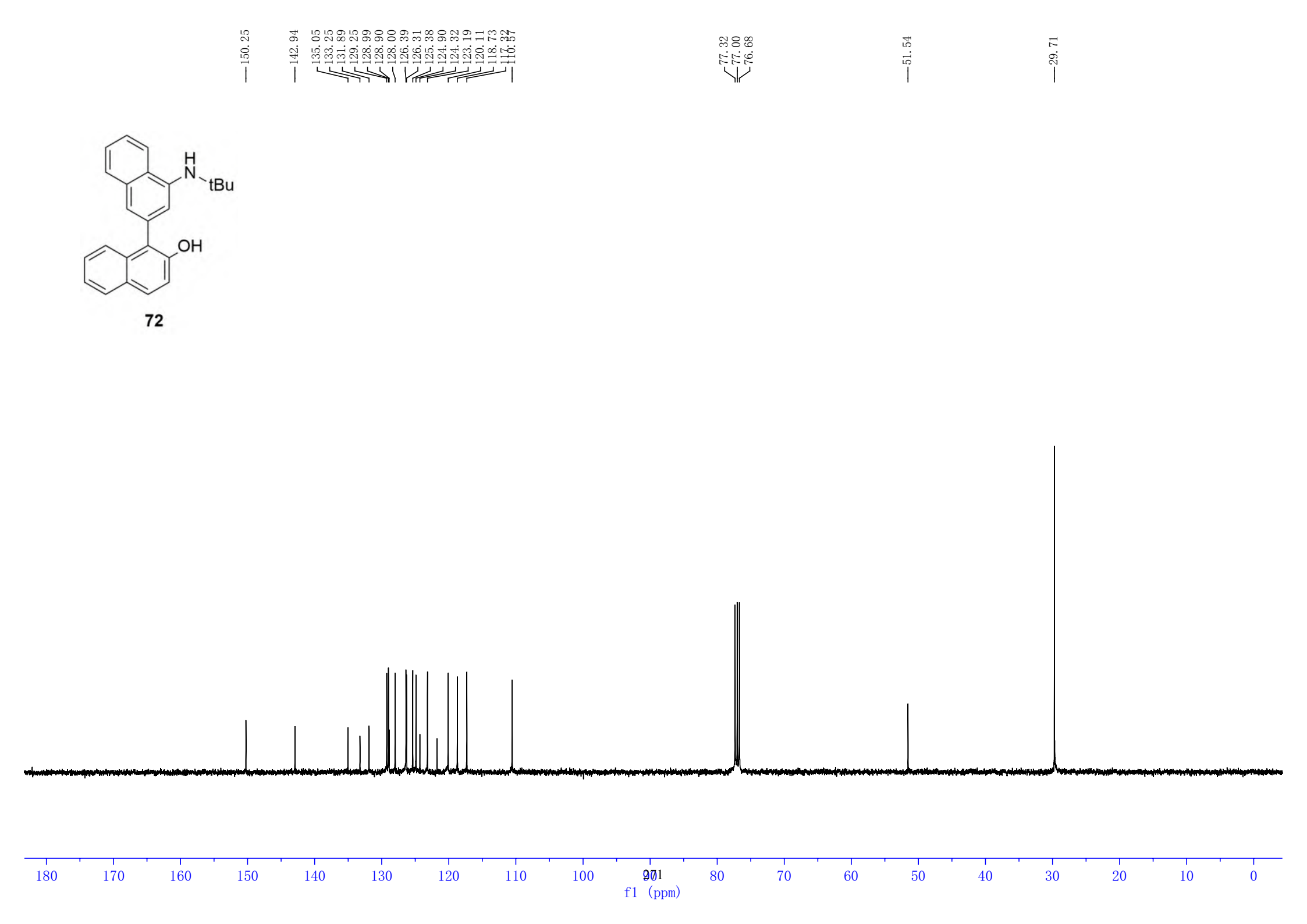
71

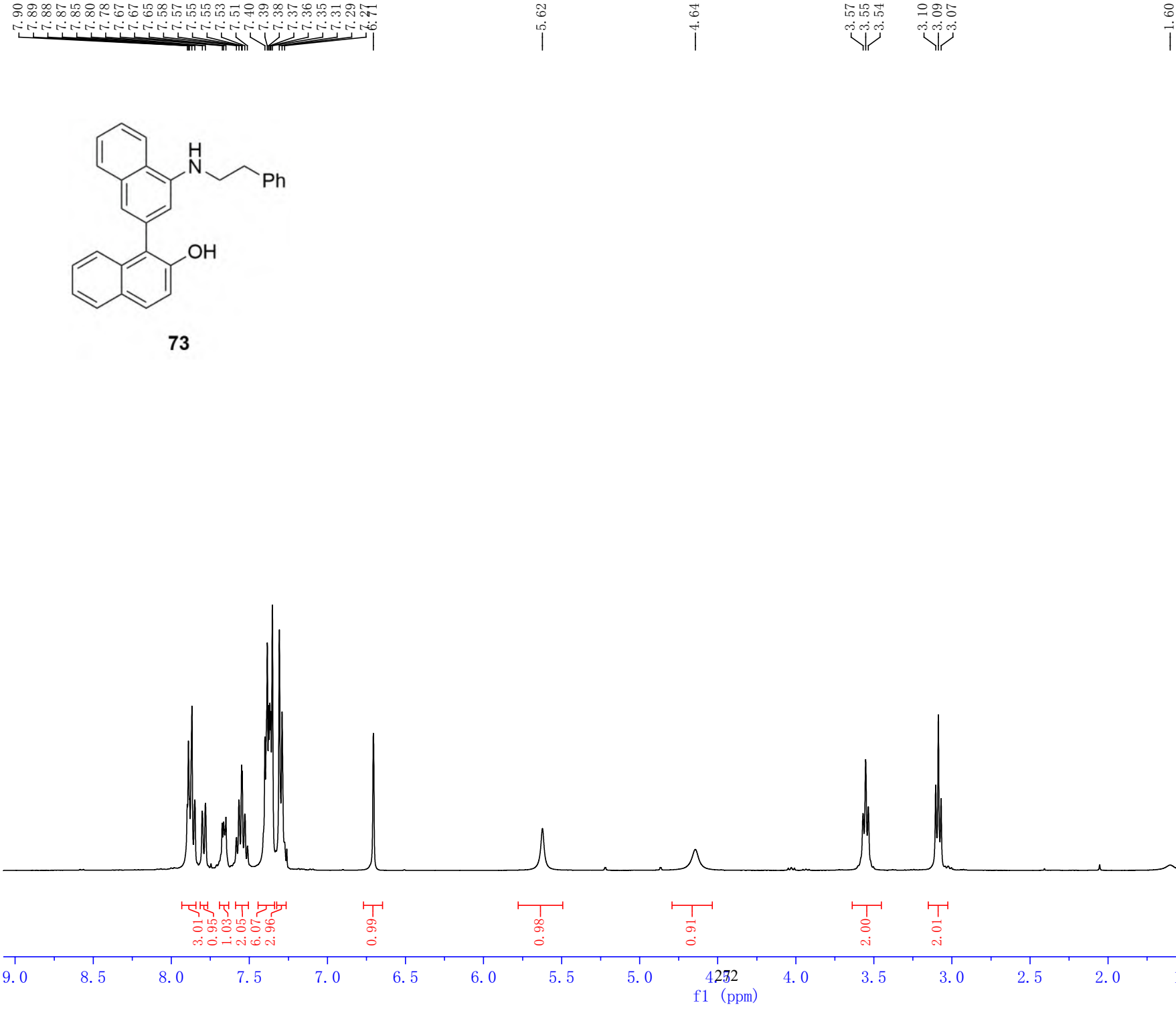
150.22
144.36
138.42
134.76
133.17
132.37
129.32
128.88
128.85
128.79
127.93
127.83
127.58
126.62
126.38
125.55
124.91
123.18
119.95
119.31
77.32
77.00
76.68
48.46

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

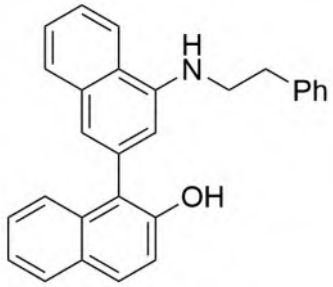
f1 (ppm)


7.90
7.89
7.87
7.86
7.84
7.82
7.66
7.65
7.64
7.55
7.54
7.53
7.52
7.37
7.36
7.35
7.32
7.30
7.26
6.91
5.63
4.55
1.49
H
N
tBu
OH
72
4.08
1.06
2.03
4.02
1.00
1.00
0.90
9.00
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
f1 (ppm)

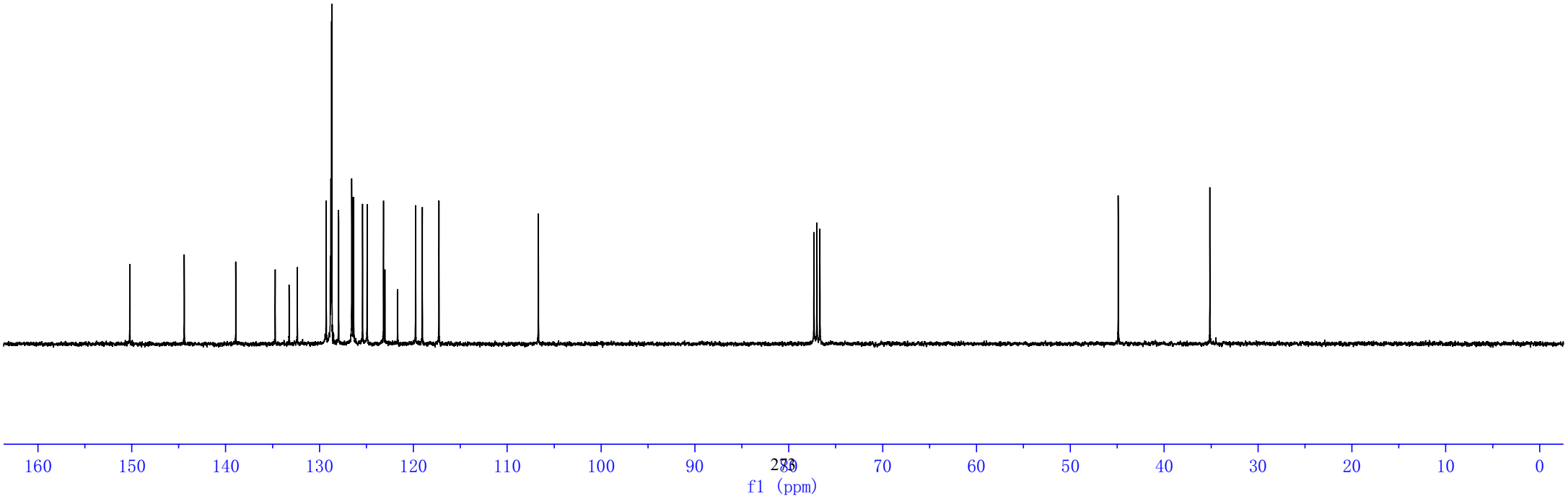

150.25
142.94
135.05
133.25
131.89
129.25
128.99
128.90
128.00
126.39
126.31
125.38
124.90
124.32
123.19
120.11
118.73
117.32
110.37
77.32
77.00
76.68
51.54
29.71
H
N
tBu
OH
72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.90
7.89
7.88
7.87
7.85
7.80
7.78
7.67
7.67
7.65
7.58
7.57
7.55
7.55
7.53
7.51
7.40
7.39
7.38
7.37
7.36
7.35
7.31
7.29
7.27
6.71
5.62
4.64
3.57
3.55
3.54
3.10
3.09
3.07
1.60
H
N
Ph
OH
73
3.01
0.95
1.03
2.05
6.07
2.96
0.99
0.98
0.91
2.00
2.01
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
f1 (ppm)

150.21
144.41
138.92
134.72
132.36
129.29
128.85
128.78
128.72
128.68
127.96
126.57
126.49
126.36
125.41
124.93
123.18
123.03
119.76
119.05
117.27
106.68
77.32
77.00
76.68
44.90
35.13

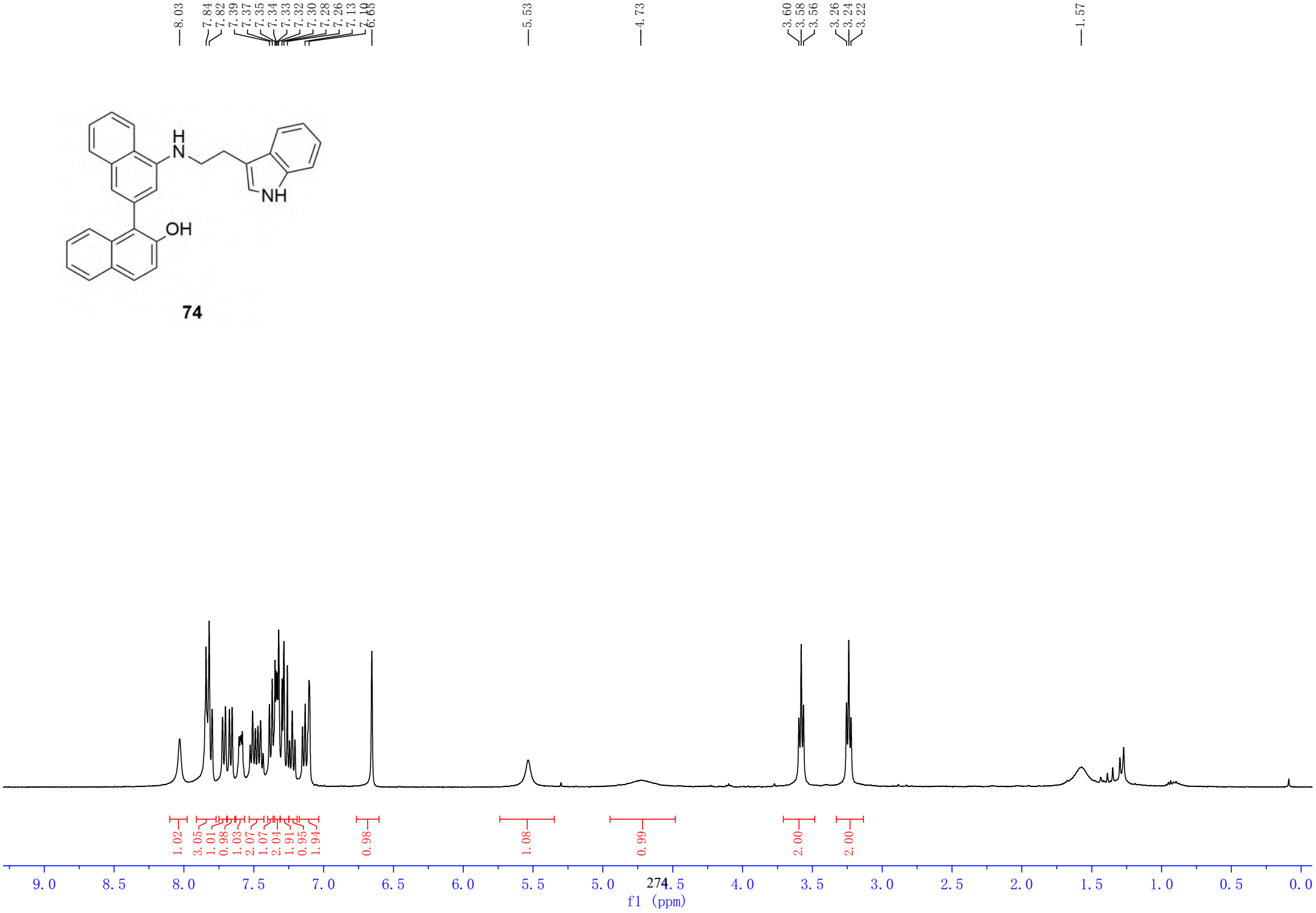


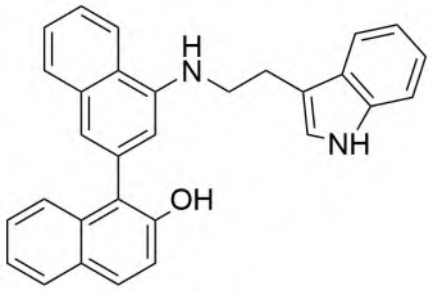
73



H
N
NH
OH

74


8.03
7.84
7.82
7.39
7.37
7.35
7.34
7.33
7.32
7.30
7.28
7.26
7.13
5.53
4.73
3.60
3.58
3.56
3.26
3.24
3.22
1.57
1.02
3.05
1.01
0.98
1.03
2.07
1.07
2.04
1.91
0.95
1.94
0.98
1.08
0.99
2.00
2.00
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
f1 (ppm)

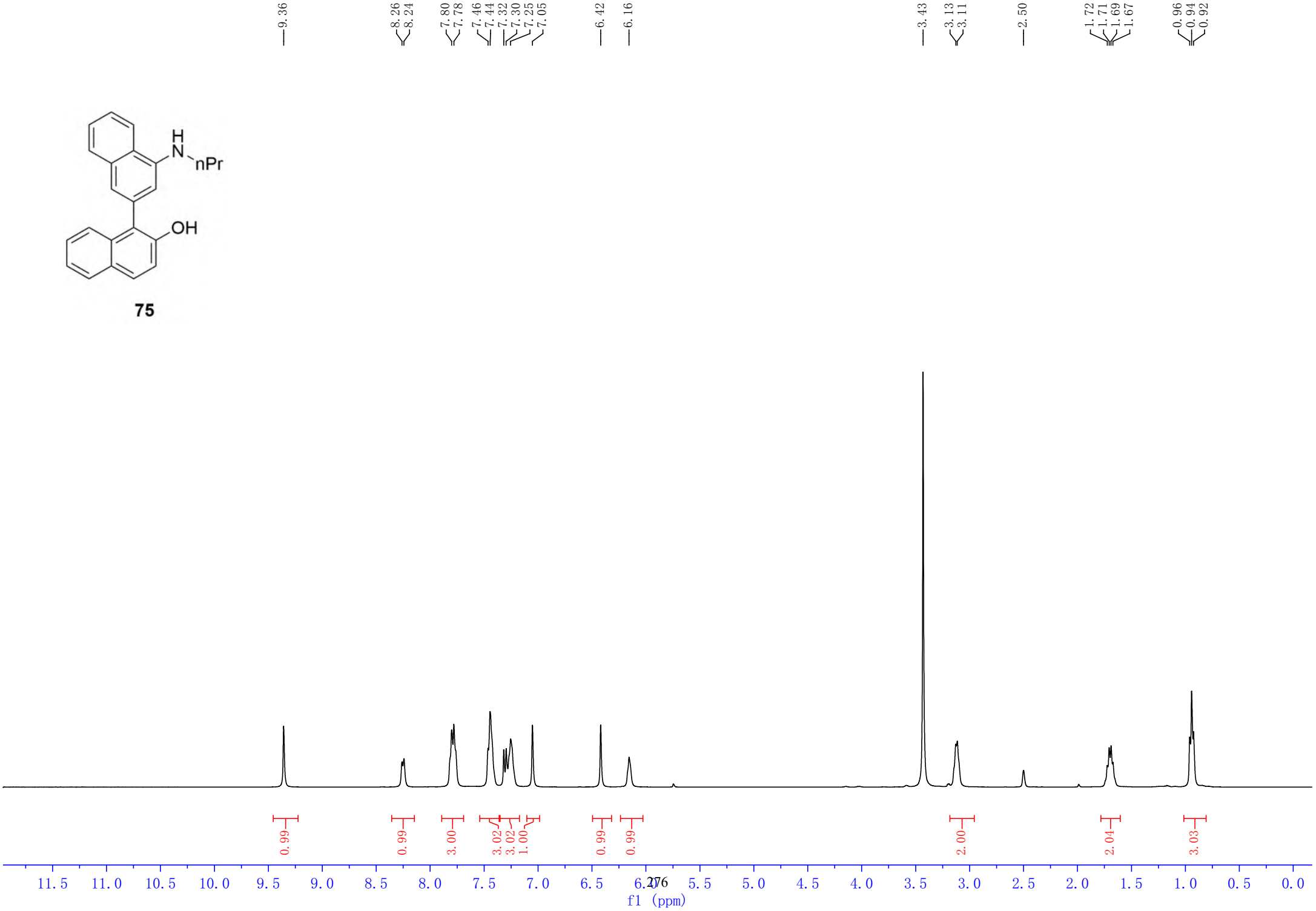


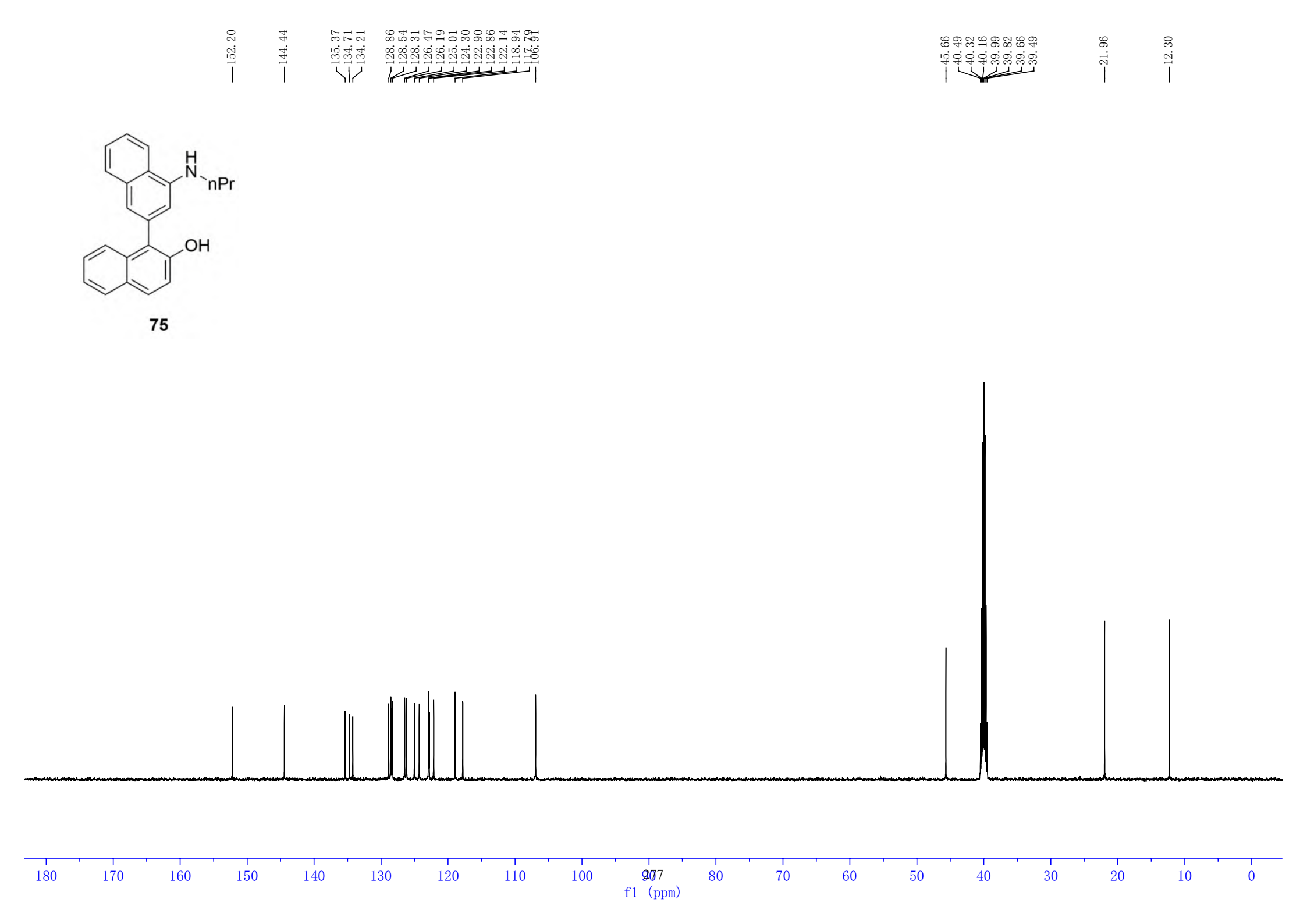
74

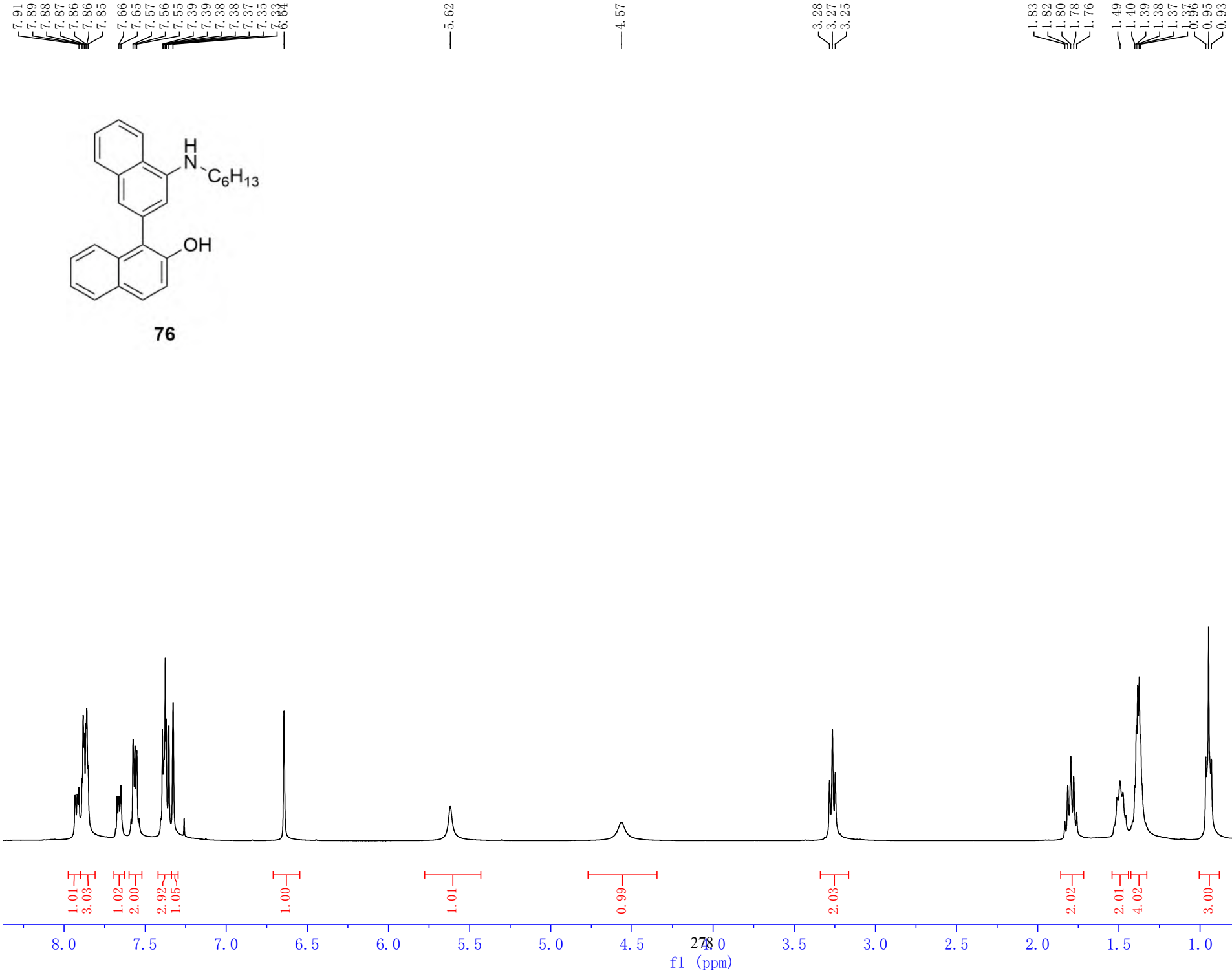
150.21
144.74
136.42
134.74
132.38
129.28
128.87
128.78
127.97
126.47
126.37
125.34
124.99
123.19
123.10
122.34
122.01
121.75
119.92
119.59
118.90
118.72
117.26
113.22
111.27
106.66
77.25
77.00
76.75
44.01
24.76

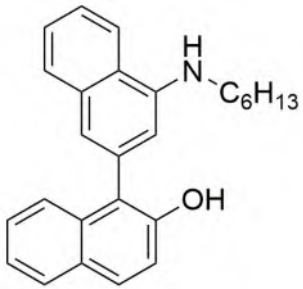
H
N
nPr
OH

75


9.36
8.26
8.24
7.80
7.78
7.46
7.44
7.32
7.30
7.25
7.05
6.42
6.16
3.43
3.13
3.11
2.50
1.72
1.71
1.69
1.67
0.96
0.94
0.92
0.99
0.99
3.00
3.02
3.02
1.00
0.99
0.99
2.00
2.04
3.03
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
f1 (ppm)


152.20
144.44
135.37
134.71
134.21
128.86
128.54
128.31
126.47
126.19
125.01
124.30
122.90
122.86
122.14
118.94
117.79
106.91
45.66
40.49
40.32
40.16
39.99
39.82
39.66
39.49
21.96
12.30
H
N
nPr
OH
75
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.91
7.89
7.88
7.87
7.86
7.86
7.85
7.66
7.65
7.57
7.56
7.55
7.39
7.39
7.38
7.38
7.37
7.35
7.33
6.64
5.62
4.57
3.28
3.27
3.25
1.83
1.82
1.80
1.78
1.76
1.49
1.40
1.39
1.38
1.37
0.96
0.95
0.93
H
N
C6H13
OH
76
1.01
3.03
1.02
2.00
2.92
1.05
1.00
1.01
0.99
2.03
2.02
2.01
4.02
3.00
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
f1 (ppm)



76

150.22
144.85
134.74
132.40
129.24
128.85
128.82
127.94
126.46
126.32
125.32
125.00
123.16
122.90
119.80
118.65
117.26
106.37
77.32
77.00
76.68
44.13
31.59
29.26
26.92
22.56
14.00