Facile Synthesis of Azaarene-Substituted 3-Hydroxy-2-Oxindoles via Brønsted Acid-Catalyzed sp^3 C-H Functionalization

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Supporting information

Table of contents

	Page
General methods	S2
General Procedure	S3
Characterization of products	S3
^1H and ^{13}C spectra	S12

General methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Commercial grade solvents and reagents were used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

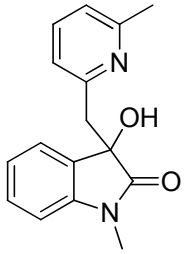
High Resolution Mass (**HRMS**) spectra were obtained using Finnigan MAT95XP GC/HRMS (Thermo Electron Corporation).

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for 1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet).

General Procedure for Synthesis of Azaarene-Substituted 3-Hydroxy-2-Oxindoles via Organocatalytic Brønsted Acid-Catalyzed sp^3 C-H Functionalization

To an 25 mL pressure tube equipped with a magnetic stirrer bar were added dioxane (1 mL) and 1-methylindoline-2,3-dione **2a** (0.3 mmol) before addition of T_fOH (0.03 mmol) and 2,6-lutidine **1a** (1.2 mmol). The mixture was then stirred at 120 ^oC for 48 h. The reaction mixture was cooled down and the solvent was removed. The residue was then purified by column chromatography on silica gel (hexane/ethyl acetate = 4:1-1:1) to afford the desired product **3a** as a yellow solid (68.4 mg, 85% yield).

3-hydroxy-1-methyl-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3a)



Yellow solid, mp 126-127 °C;

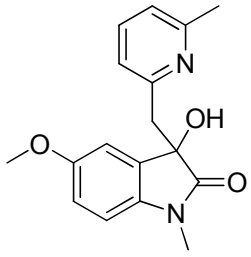
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.26 (m, *J* = 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.92 (m, 1H), 6.79 (m, 3H), 3.30 (d, *J* = 14.7 Hz, 1H), 3.18 (s, 3H), 2.99 (d, *J* = 14.7 Hz, 1H), 2.59 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.7, 157.1, 156.9, 142.8, 137.3, 131.1, 129.2, 123.7, 122.6, 121.8, 121.4, 108.1, 76.1, 42.2, 26.1, 24.2;

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ 269.1290 $[M+H]^+$, found 269.1291 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3281, 1696, 1618, 1470, 1094, 756, 601.

3-hydroxy-5-methoxy-1-methyl-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3b)



Red solid, mp 212-215 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.38 (s, 1H), 3.65 (d, *J* = 0.8 Hz, 3H),

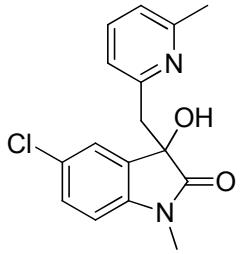
3.30 (d, *J* = 14.7 Hz, 1H), 3.15 (d, *J* = 0.8 Hz, 3H), 2.97 (d, *J* = 14.7 Hz, 1H), 2.59 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.4, 157.0, 156.7, 155.8, 137.2, 136.2, 132.2, 121.7, 121.4, 113.4, 111.1, 108.5, 76.3, 55.5, 42.2, 26.1, 24.1;

HRMS (ESI): calcd. for $C_{17}H_{19}N_2O_3$ 299.1396 $[M+H]^+$, found 299.1392 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3170,1702,1594, 1356, 1156,1033.

5-chloro-3-hydroxy-1-methyl-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3c)



Yellow solid, mp 145-147 °C;

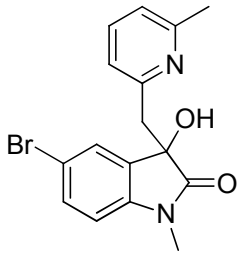
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.88 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.33 (d, *J* = 14.8 Hz, 1H), 3.23 (s, 3H), 3.05 (d, *J* = 14.8 Hz, 1H), 2.72 – 2.61 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.3, 157.4, 156.5, 142.0, 137.5, 133.2, 132.0, 127.3, 122.1, 121.5, 115.3, 109.7, 77.3, 77.0, 76.7, 76.1, 42.0, 26.3, 24.3;

HRMS (ESI): calcd. for $C_{16}H_{16}ClN_2O_2$ 303.0900 $[M+H]^+$, found 303.0901 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3354,1700,1611,1361, 1103,639.

5-bromo-3-hydroxy-1-methyl-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3d)



Yellow solid, mp 136-138 °C;

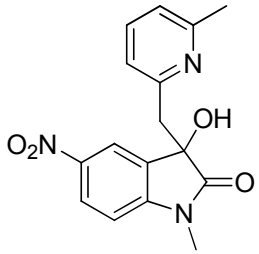
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.3 Hz, 2H), 3.28 (d, *J* = 14.8 Hz, 1H), 3.16 (s, 3H), 2.98 (d, *J* = 14.8 Hz, 1H), 2.60 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.3, 157.3, 156.4, 141.5, 137.5, 132.8, 129.1, 127.9, 124.4, 122.1, 121.4, 109.2, 76.1, 42.0, 26.2, 24.2;

HRMS (ESI): calcd. for $C_{16}H_{16}BrN_2O_2$ 347.0395 $[M+H]^+$, found 347.0396 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3350,1701,1612,1456,1103,812.

3-hydroxy-1-methyl-3-((6-methylpyridin-2-yl)methyl)-5-nitroindolin-2-one (3e)



Yellow solid, mp 141-143 °C;

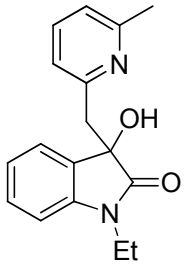
^{1}H NMR (400 MHz, CDCl3) δ = 8.22 (d, *J* = 8.6 Hz, 1H), 8.22 (s, 1H), 7.64 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.87 (dd, *J* = 15.5, 8.1 Hz, 2H), 3.38 – 3.16 (m, 4H), 3.02 (d, *J* = 14.9 Hz, 1H), 2.60 (s, 3H));

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.9, 157.5, 155.8, 148.6, 143.3, 137.7, 131.9, 126.4, 122.3, 121.4, 119.8, 107.9, 75.6, 41.7, 26.5, 24.2;

HRMS (ESI): calcd. for $C_{16}H_{16}N_3O_4$ 314.1141 $[M+H]^+$, found 314.1143 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3336,1716,1615,1511,1331,1066.

1-ethyl-3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3f)



Yellow solid, mp 126-128 °C;

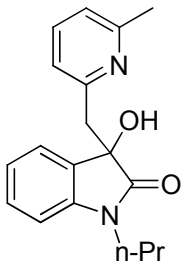
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 2H), 6.78 (d, *J* = 7.4 Hz, 1H), 3.91 – 3.59 (m, 2H), 3.30 (d, *J* = 14.7 Hz, 1H), 2.99 (d, *J* = 14.7 Hz, 1H), 2.60 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.4, 157.2, 157.0, 142.0, 137.3, 131.4, 129.2, 124.0, 122.4, 121.8, 121.5, 108.3, 76.1, 42.4, 34.6, 24.3, 12.5;

HRMS (ESI): calcd. for $C_{17}H_{19}N_2O_2$ 283.1447 $[M+H]^+$, found 283.1451 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3308, 2949, 1692, 1456, 1205, 1114, 739, 600.

3-hydroxy-3-((6-methylpyridin-2-yl)methyl)-1-propylindolin-2-one (3g)



Yellow solid, mp 101-103 °C;

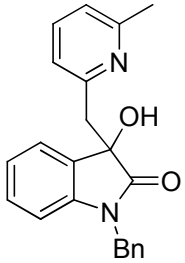
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.22 (td, *J* = 7.7, 1.2 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.92 – 6.76 (m, 4H), 3.72 – 3.54 (m, 2H), 3.32 – 3.24 (m, 1H), 2.98 (d, *J* = 14.7 Hz, 1H), 2.60 (d, *J* = 18.8 Hz, 3H), 1.69 (dt, *J* = 14.6, 7.3 Hz, 2H), 0.93 (dd, *J* = 9.7, 5.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.7, 157.1, 156.9, 142.3, 137.3, 131.3, 129.1, 123.9, 122.3, 121.8, 121.4, 108.4, 76.0, 42.5, 41.3, 24.2, 20.5, 11.2;

HRMS (ESI): calcd. for $C_{18}H_{21}N_2O_2$ 297.1603 $[M+H]^+$, found 297.1600 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3344,1694,1616,1471,1202,750

1-benzyl-3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3h)



Yellow solid, mp 176-178 °C;

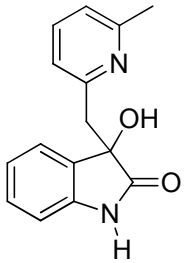
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.28 (m, 5H), 7.14 (s, 2H), 6.85 (m, 3H), 6.69 (d, *J* = 6.7 Hz, 1H), 4.88 (m, 2H), 3.34 (d, *J* = 15.0 Hz, 1H), 3.06 (d, *J* = 14.6 Hz, 1H), 2.61 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.83, 157.18, 156.77, 141.87, 137.34, 135.62, 131.16, 129.07, 128.66, 127.48, 127.16, 123.83, 122.61, 121.87, 121.45, 109.17, 76.15, 43.54, 42.46, 24.21;

HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_2$ 345.1603 $[M+H]^+$, found 345.1659 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3166, 2921, 1722, 1617, 1353, 1078, 751, 605.

3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3i)



Red solid, mp 177-179 °C;

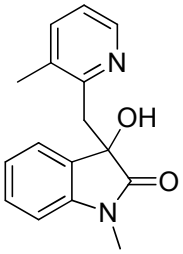
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.10 (m, 2H), 6.93 – 6.80 (m, 3H), 6.73 (d, *J* = 6.5 Hz, 1H), 3.33 (d, *J* = 14.8 Hz, 1H), 3.01 (d, *J* = 14.9 Hz, 1H), 2.61 (s, 3H). One labile proton was not resolved due to significant broadening.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.0, 157.3, 156.9, 140.0, 137.4, 131.7, 129.2, 124.2, 122.6, 122.0, 121.6, 110.1, 76.6, 42.4, 24.3;

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O_2$ 255.1134 $[M+H]^+$, found 255.1133 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3261, 1710, 1475, 1006, 779, 738, 656, 520, 476.

3-hydroxy-1-methyl-3-((3-methylpyridin-2-yl)methyl)indolin-2-one (3J)



Red solid, mp 116-118 °C;

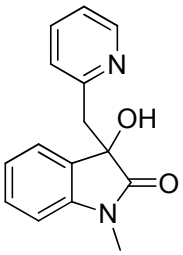
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 – 8.40 (m, 1H), 8.20 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.26 (td, *J* = 7.8, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.94 – 6.87 (m, 1H), 6.87 – 6.79 (m, 2H), 3.32 (d, *J* = 15.5 Hz, 1H), 3.20 (s, 3H), 3.02 (d, *J* = 15.5 Hz, 1H), 2.07 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.8, 156.5, 145.3, 142.9, 138.5, 132.5, 131.6, 129.2, 123.8, 122.7, 122.2, 108.2, 76.1, 38.3, 26.2, 18.8;

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ 269.1290 $[M+H]^+$, found 269.1288 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 2922, 1717, 1611, 1467, 1345, 1092, 751.

3-hydroxy-1-methyl-3-(pyridin-2-ylmethyl)indolin-2-one (3k)



Yellow solid, mp 135-137°C;

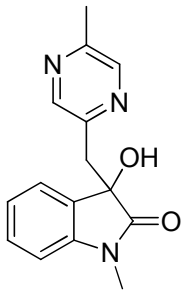
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.58 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52(s,1H),7.26 (ddd, *J* = 7.7, 5.0, 1.3 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.93 (td, *J* = 7.6, 0.9 Hz, 1H), 6.83 – 6.78 (m, 2H), 3.33 (d, *J* = 14.8 Hz, 1H), 3.18 (s, 3H), 3.08 (d, *J* = 14.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 148.2, 143.0, 140.3, 137.1, 131.0, 129.4, 124.6, 123.9, 122.7, 122.3, 108.2, 76.2, 42.6, 26.2;

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O_2$ 255.1134 $[M+H]^+$, found 255.1132 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3353, 2963, 1715, 1612, 1471, 1091, 752.

3-hydroxy-1-methyl-3-((5-methylpyrazin-2-yl)methyl)indolin-2-one (3l)



Red solid, mp 101−103 °C;

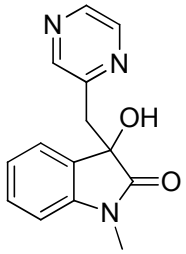
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 8.23 (s, 1H), 7.28 (s, 1H), 6.99 (d, *J* = 3.4 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.91 (s, 1H), 3.30 (d, *J* = 14.3 Hz, 1H), 3.23 (d, *J* = 14.5 Hz, 1H), 3.14 (s, 3H), 2.54 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.8, 152.4, 149.0, 144.4, 142.9, 142.7, 129.8, 129.7, 123.9, 122.9, 108.3, 75.9, 40.9, 26.1, 21.1;

HRMS (ESI): calcd. for $C_{15}H_{16}N_3O_2$ 270.1243 $[M+H]^+$, found 270.1245 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3373, 2919, 1713, 1613, 1471, 1346, 1087, 753.

3-hydroxy-1-methyl-3-(pyrazin-2-ylmethyl)indolin-2-one (3m)



Red solid, mp 135-137 °C;

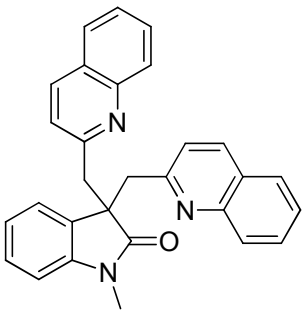
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.52 – 8.48 (m, 2H), 8.37 (s, 1H), 7.35 – 7.22 (m, 1H), 7.01 (d, *J* = 4.4 Hz, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.60 (s, 1H), 3.34 (d, *J* = 14.5 Hz, 1H), 3.29 (d, *J* = 14.5 Hz, 1H), 3.15 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.7, 152.6, 145.7, 143.4, 143.0, 143.0, 129.9, 129.7, 123.9, 123.0, 108.5, 76.0, 41.4, 26.2;

HRMS (ESI): calcd. for $C_{14}H_{14}N_3O_2$ 256.1086 $[M+H]^+$, found 256.1083 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3266, 2919, 1698, 1616, 1470, 1113, 1020, 768.

1-methyl-3,3-bis(quinolin-2-ylmethyl)indolin-2-one (3nb)



Yellow solid, mp 167-170 °C;

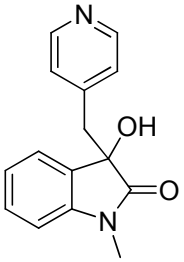
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (m, 4H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 3.76 (d, *J* = 13.8 Hz, 2H), 3.68 (d, *J* = 13.8 Hz, 2H), 3.08 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.3, 157.2, 147.4, 143.7, 135.3, 130.4, 129.0, 129.0, 127.5, 127.2, 126.6, 125.8, 124.3, 122.3, 121.4, 107.2, 53.0, 45.6, 26.1;

HRMS (ESI): calcd. for $C_{29}H_{24}N_3O$ 430.1919 $[M+H]^+$, found 430.1914 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3394, 2913, 1717, 1611, 1598, 823, 745.

3-hydroxy-1-methyl-3-(pyridin-4-ylmethyl)indolin-2-one (3o)



Yellow solid, mp 201-203 °C;

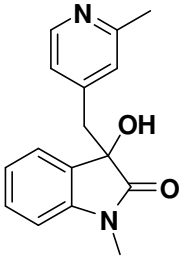
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 2H), 7.26 (m, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 4.7 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 3.30 (d, *J* = 12.6 Hz, 1H), 3.13 (d, *J* = 12.6 Hz, 1H), 2.97 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.4, 148.8, 143.7, 142.9, 129.9, 128.9, 125.5, 124.2, 123.0, 108.4, 76.7, 43.9, 25.9;

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O_2$ 255.1134 $[M+H]^+$, found 255.1132 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3083, 1711, 1611, 1472, 1373, 1228, 811, 588, 492.

3-hydroxy-1-methyl-3-((2-methylpyridin-4-yl)methyl)indolin-2-one (3pa)



Yellow solid, mp 138-140 °C;

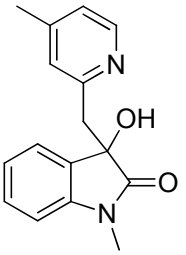
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 4.9 Hz, 1H), 7.30 (dd, *J* = 14.8, 7.1 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.79 (s, 1H), 6.69 (dd, *J* = 13.8, 6.3 Hz, 2H), 4.65 (s, 1H), 3.31 (d, *J* = 12.6 Hz, 1H), 3.14 (d, *J* = 12.6 Hz, 1H), 3.01 (s, 3H), 2.38 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.56, 157.51, 147.87, 143.98, 142.89, 129.72, 129.09, 125.11, 124.25, 122.87, 122.52, 108.28, 76.69, 43.79, 25.84, 23.67;

HRMS (ESI): calcd. for $C_{14}H_{14}N_3O_2$ 256.1086 $[M+H]^+$, found 256.1088 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3054, 2935, 1718, 1614, 1472, 1351, 1092, 752, 473.

3-hydroxy-1-methyl-3-((4-methylpyridin-2-yl)methyl)indolin-2-one (3pb)



Yellow solid, mp 151-153°C;

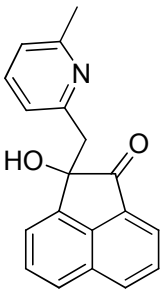
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 5.0 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.80 (d, *J* = 7.5 Hz, 2H), 3.29 (d, *J* = 14.9 Hz, 1H), 3.18 (s, 3H), 3.00 (d, *J* = 14.8 Hz, 1H), 2.32 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.8, 157.5, 148.4, 147.8, 142.9, 131.2, 129.3, 125.4, 123.9, 123.3, 122.7, 108.2, 76.2, 42.3, 26.2, 21.1;

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ 269.1290 $[M+H]^+$, found 269.1292 $[M+H]^+$;

IR (KBr) ν/cm^{-1}: 3049, 2920, 1720, 1608, 1474, 1374, 1085, 747.

2-hydroxy-2-((6-methylpyridin-2-yl)methyl)acenaphthylen-1(2H)-one (5a)



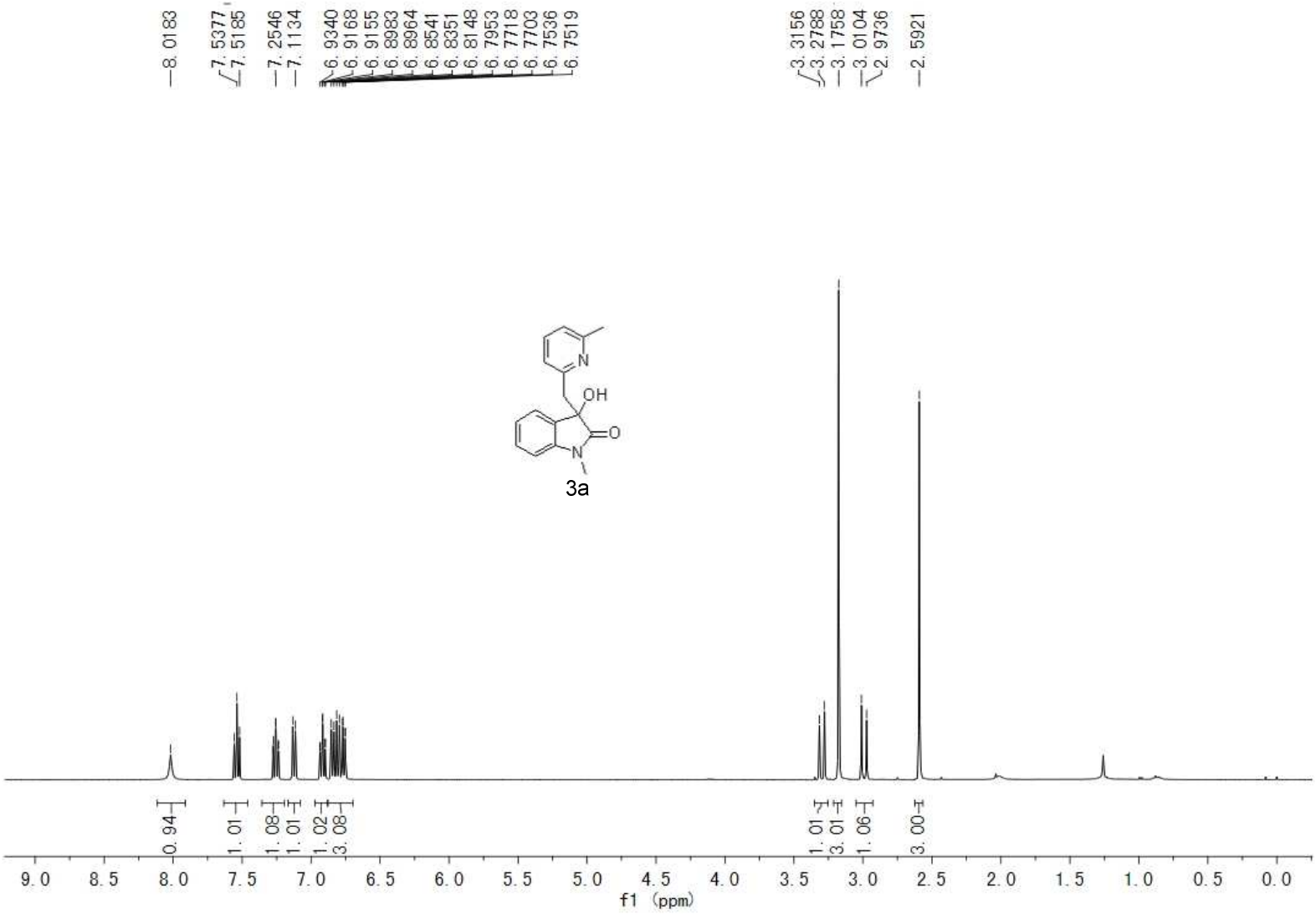
Yellow oil.

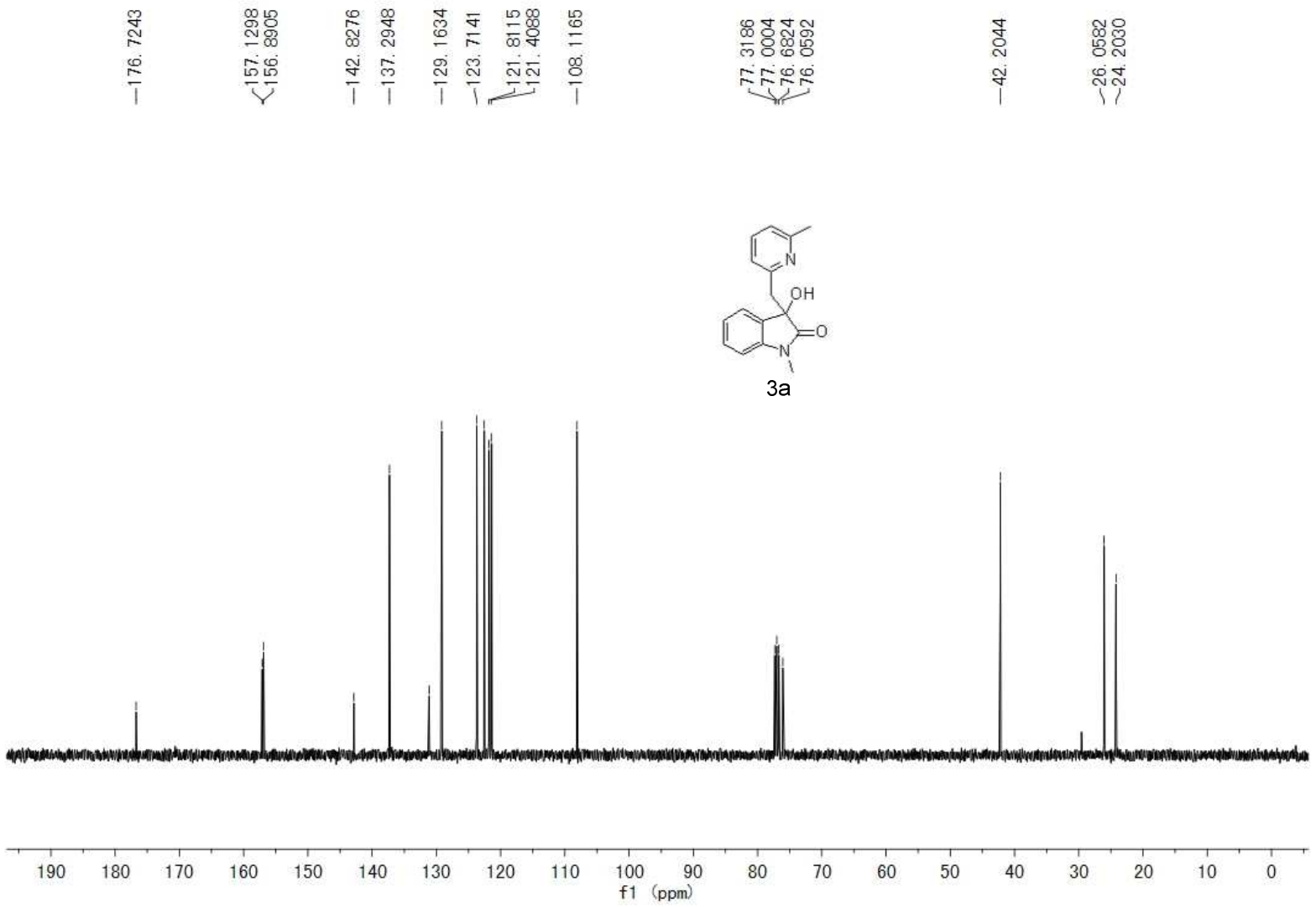
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (m, 2H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.51 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.39 (d, *J* = 14.7 Hz, 1H), 3.05 (d, *J* = 14.7 Hz, 1H), 2.60 (s, 3H);

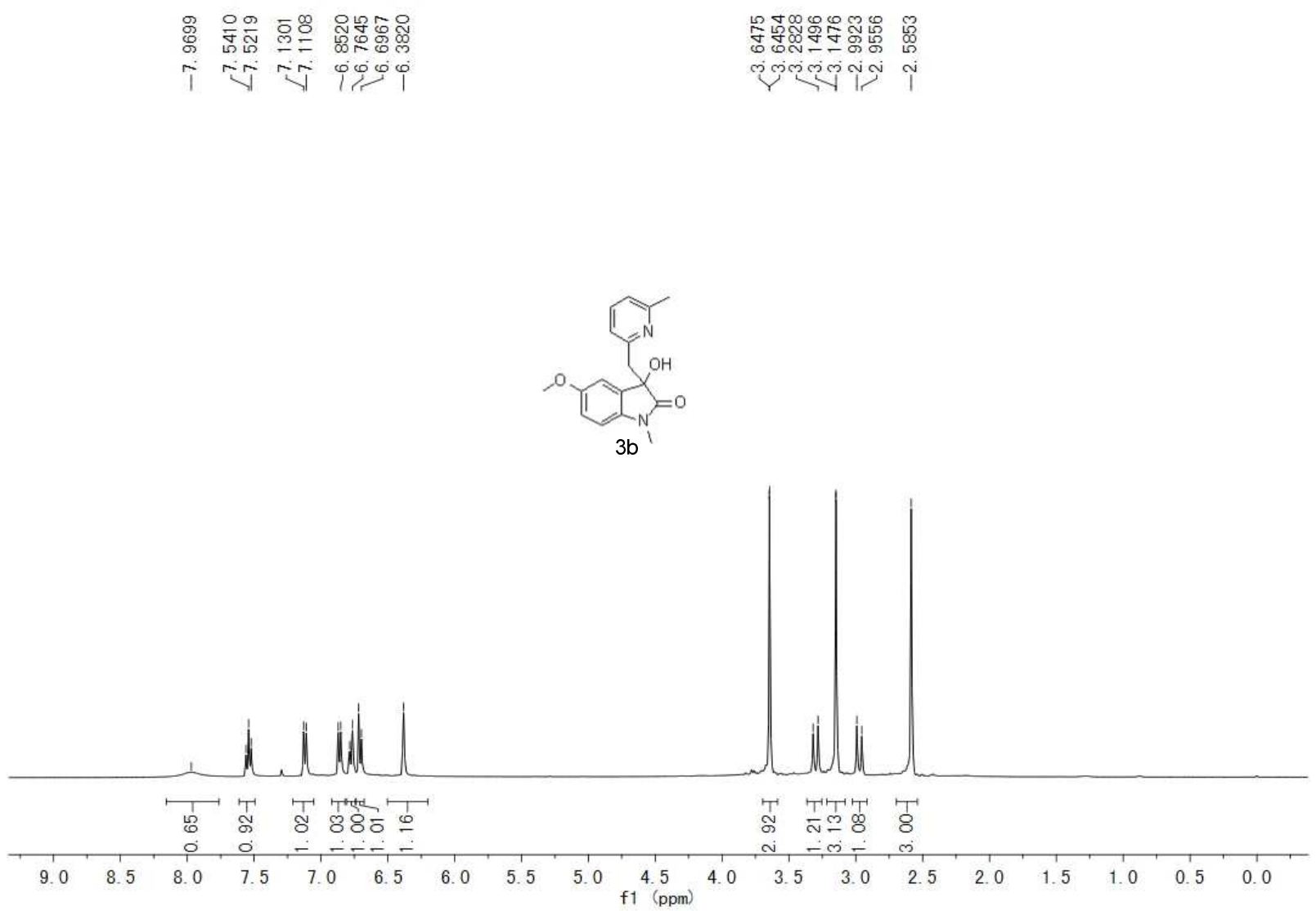
^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.5, 157.4, 157.2, 140.8, 140.7, 137.3, 131.7, 130.5, 128.4, 128.1, 127.3, 124.9, 121.9, 121.8, 121.3, 120.2, 79.9, 42.2, 24.2;

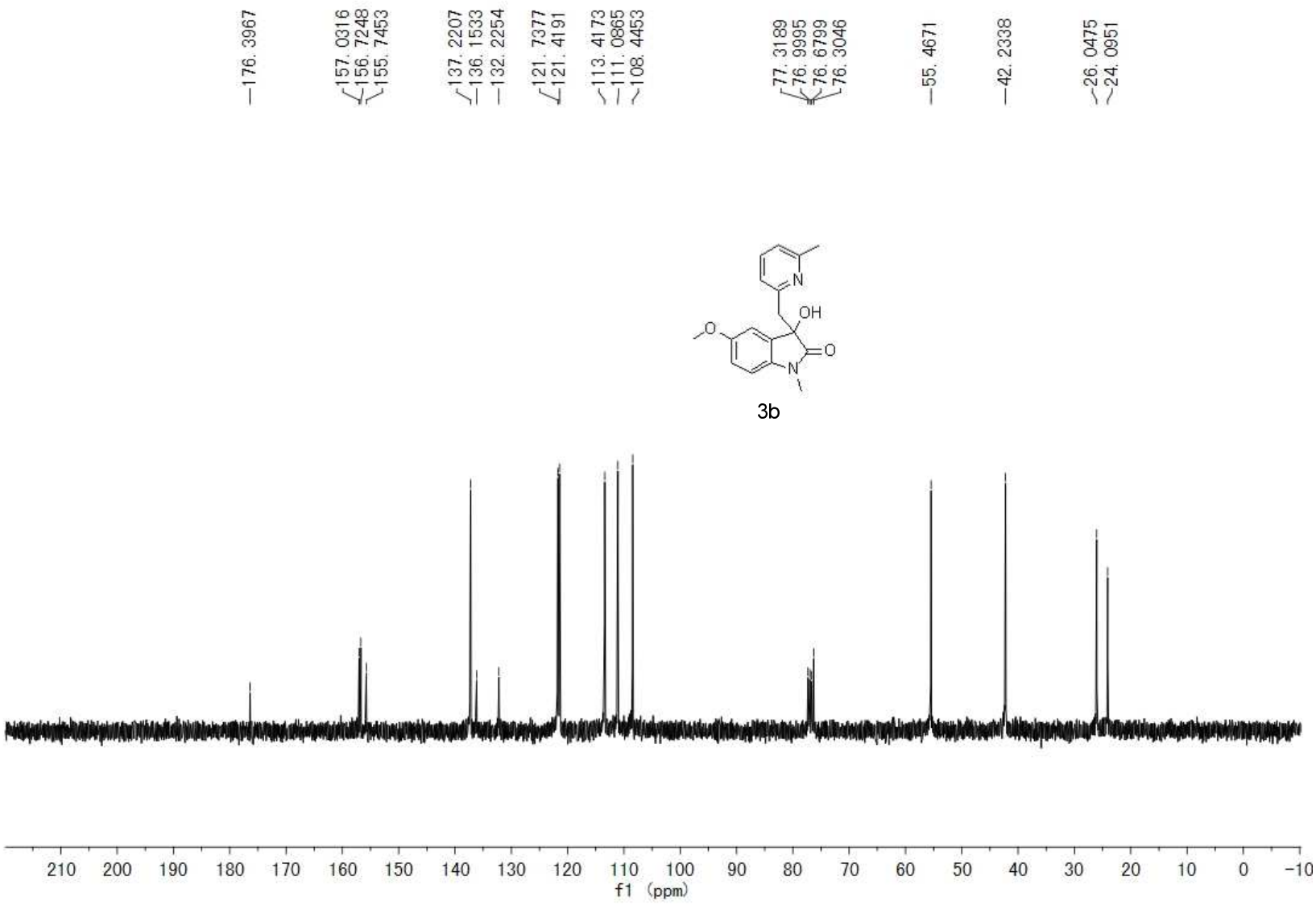
HRMS (ESI): calcd. for $C_{19}H_{16}NO_2$ 290.1181 $[M+H]^+$, found 290.1188 $[M+H]^+$;

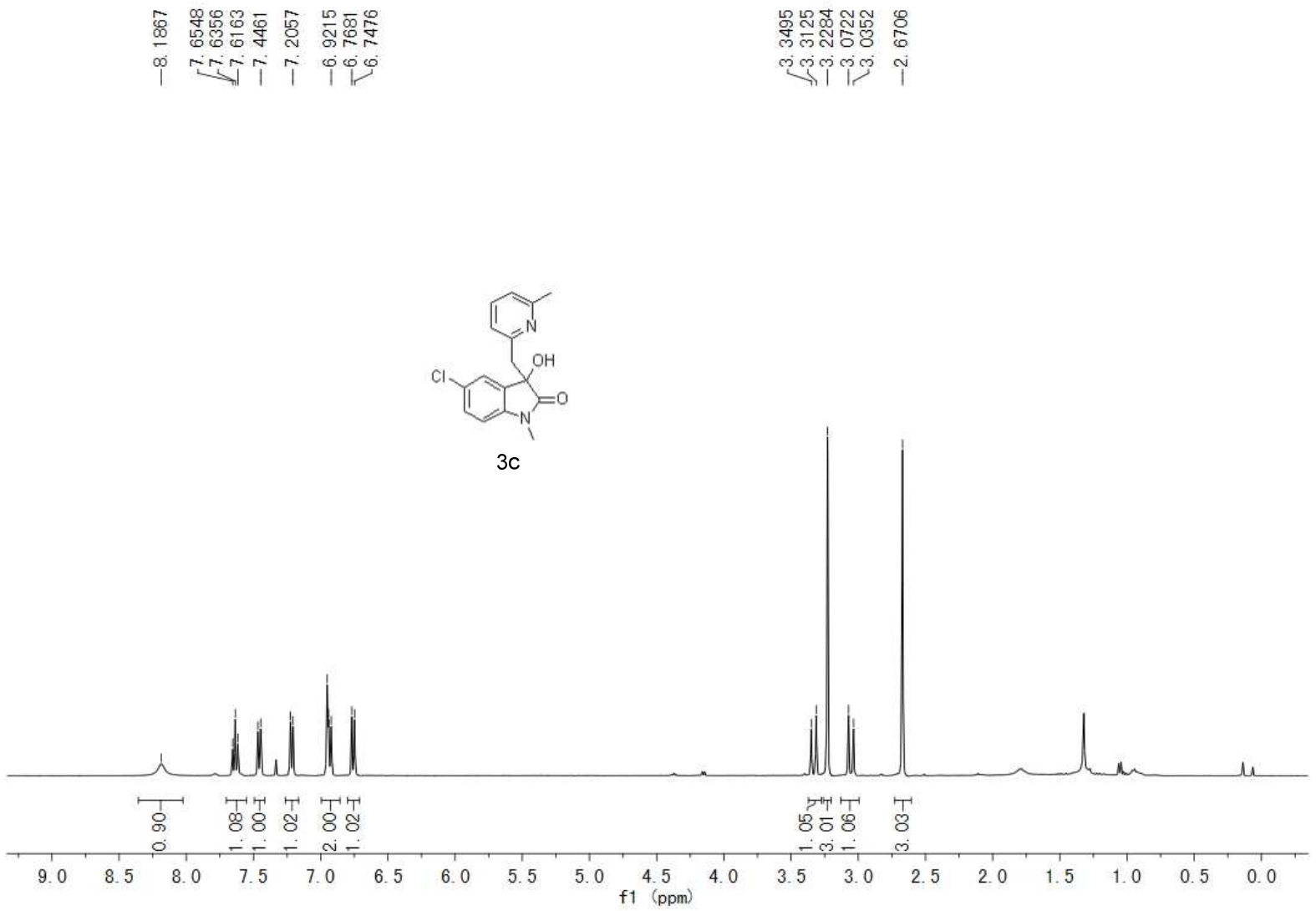
IR (KBr) ν/cm^{-1}: 3296, 1721, 1357, 1110, 801, 601.


8.0183
7.5377
7.5185
7.2546
7.1134
6.9340
6.9168
6.9155
6.8983
6.8964
6.8541
6.8351
6.8148
6.7953
6.7718
6.7703
6.7536
6.7519
3.3156
3.2788
3.1758
3.0104
2.9736
2.5921
OH
O
N
3a
0.94
1.01
1.08
1.01
1.02
3.08
1.01
3.01
1.06
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)

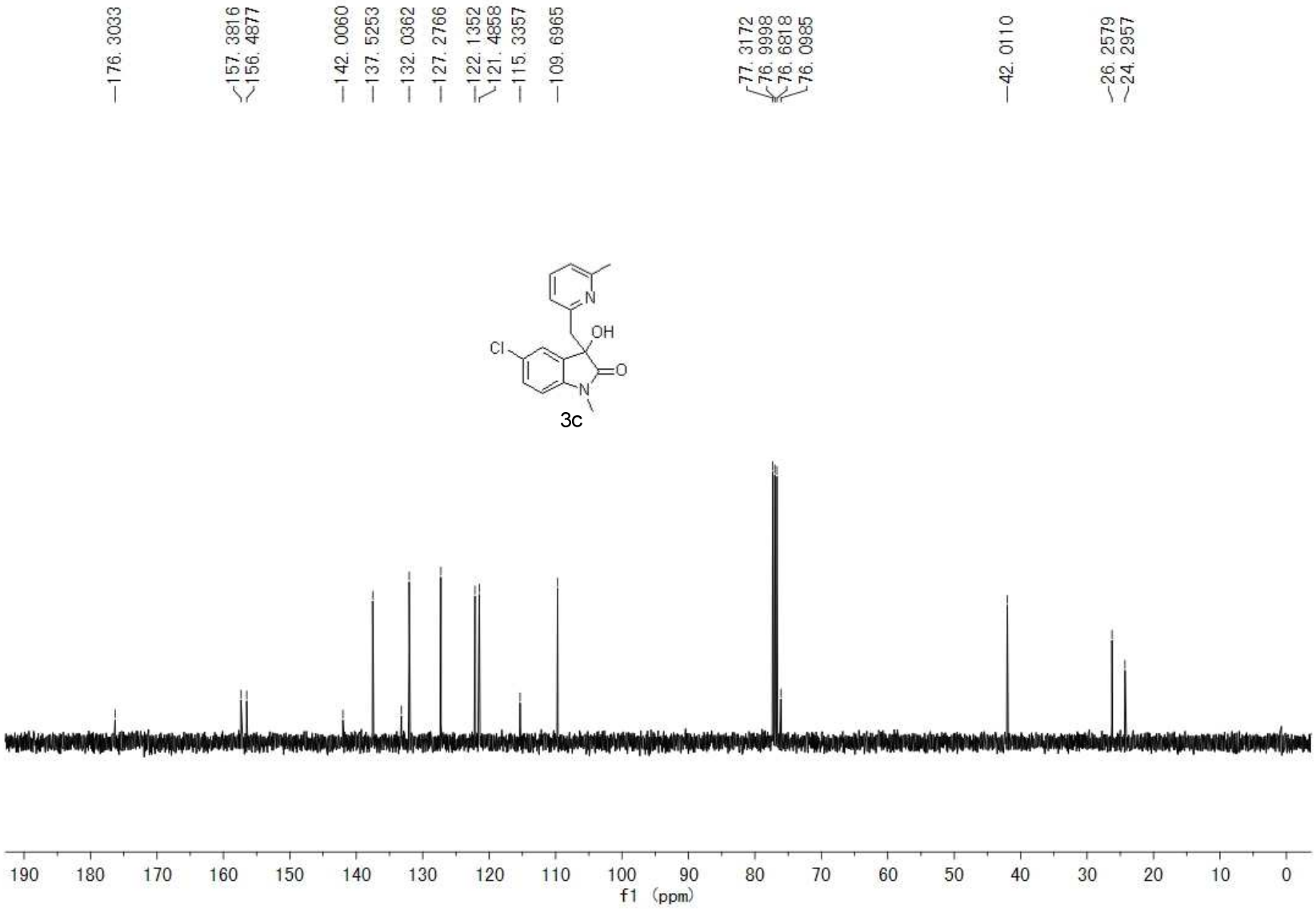

176.7243
157.1298
156.8905
142.8276
137.2948
129.1634
123.7141
121.8115
121.4088
108.1165
77.3186
77.0004
76.6824
76.0592
42.2044
26.0582
24.2030
OH
O
N
N
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

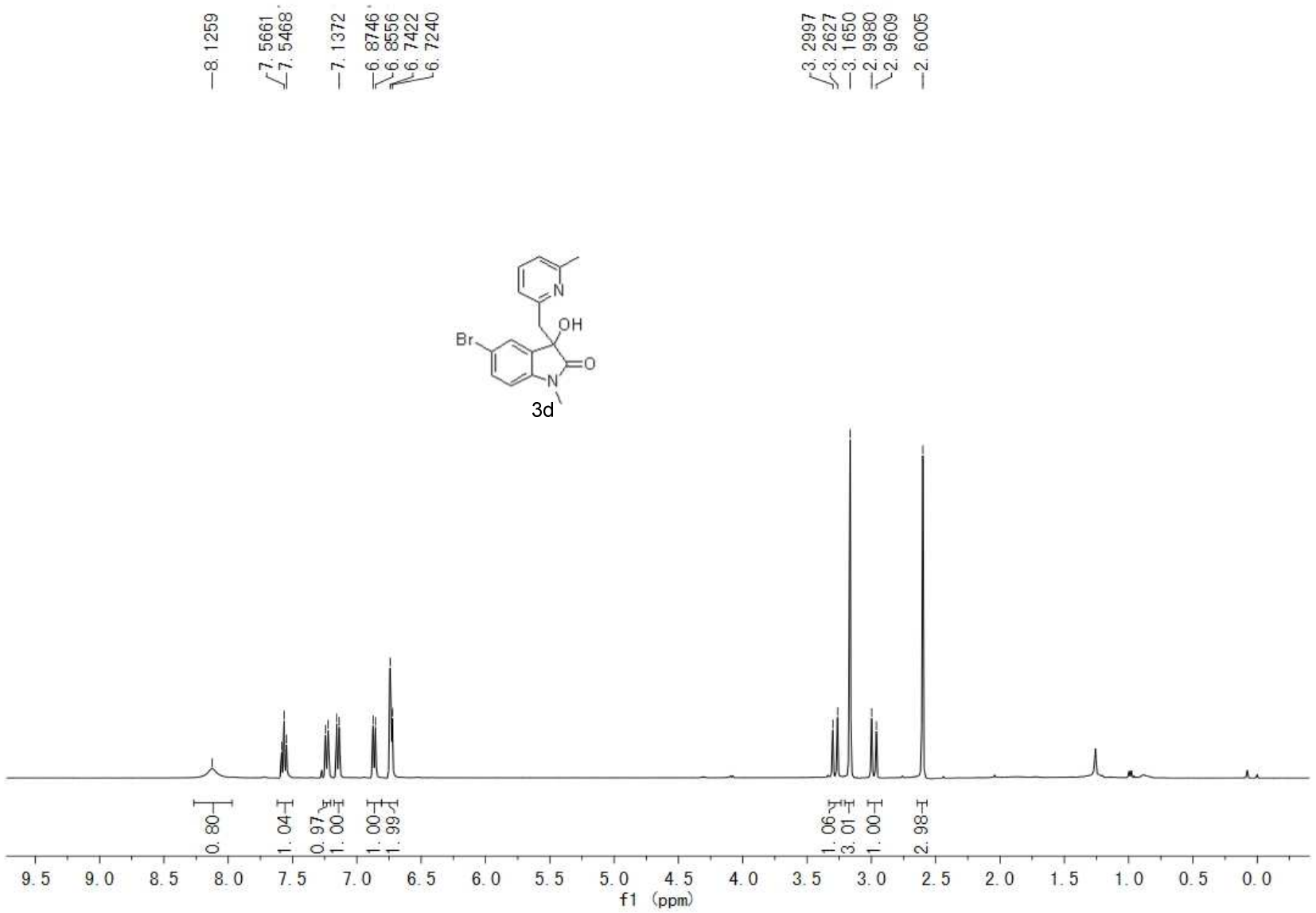

7.9699
7.5410
7.5219
7.1301
7.1108
6.8520
6.7645
6.6967
6.3820
3.6475
3.6454
3.2828
3.1496
3.1476
2.9923
2.9556
2.5853
OH
O
N
O
N
3b
0.65
0.92
1.02
1.03
1.00
1.01
1.16
2.92
1.21
3.13
1.08
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

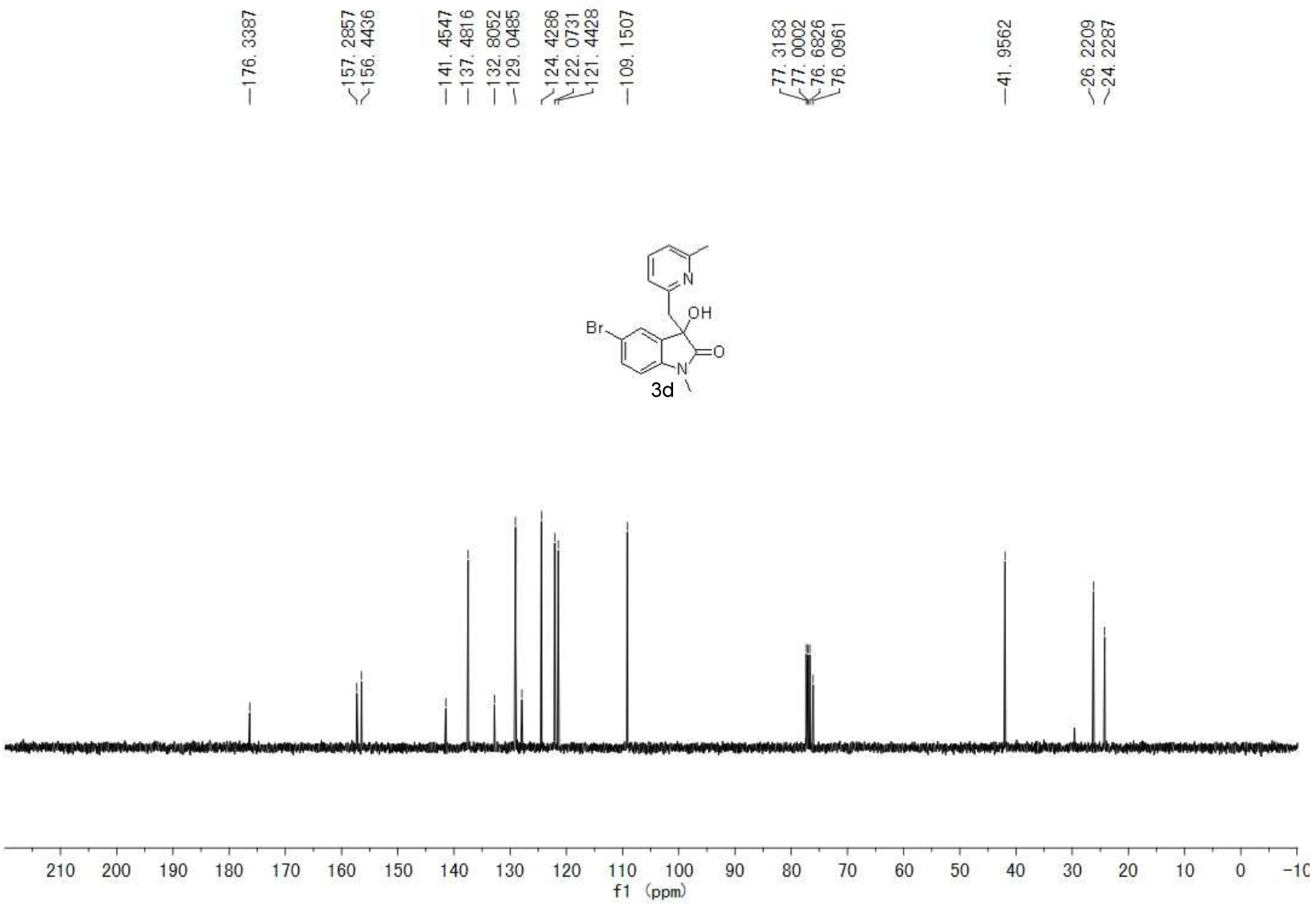

176.3967
157.0316
156.7248
155.7453
137.2207
136.1533
132.2254
121.7377
121.4191
113.4173
111.0865
108.4453
77.3189
76.9995
76.6799
76.3046
55.4671
42.2338
26.0475
24.0951
OH
O
N
O
N
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

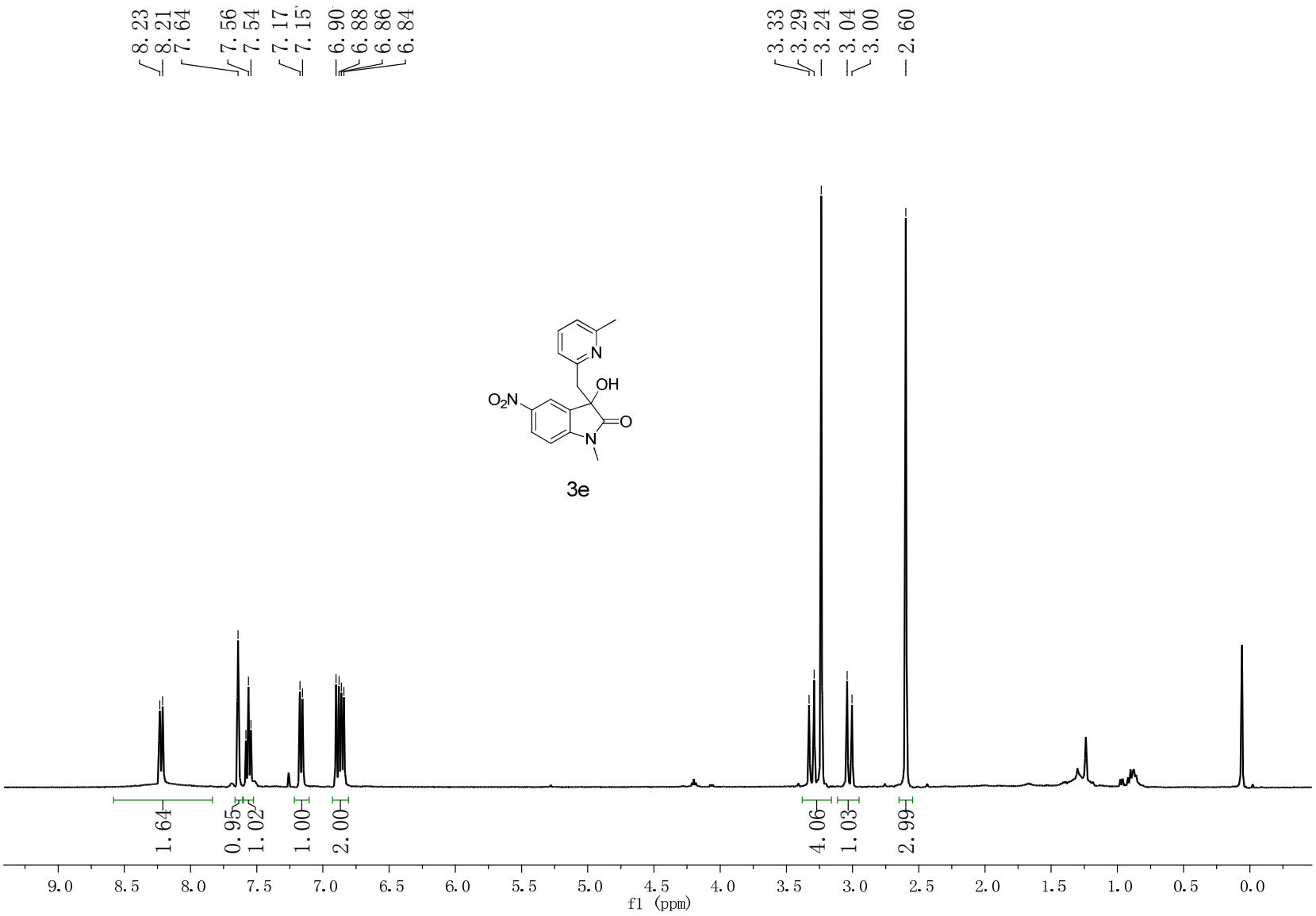

8.1867
7.6548
7.6356
7.6163
7.4461
7.2057
6.9215
6.7681
6.7476
3.3495
3.3125
3.2284
3.0722
3.0352
2.6706
OH
Cl
O
N
N
0.90
1.08
1.00
1.02
2.00
1.02
1.05
3.01
1.06
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

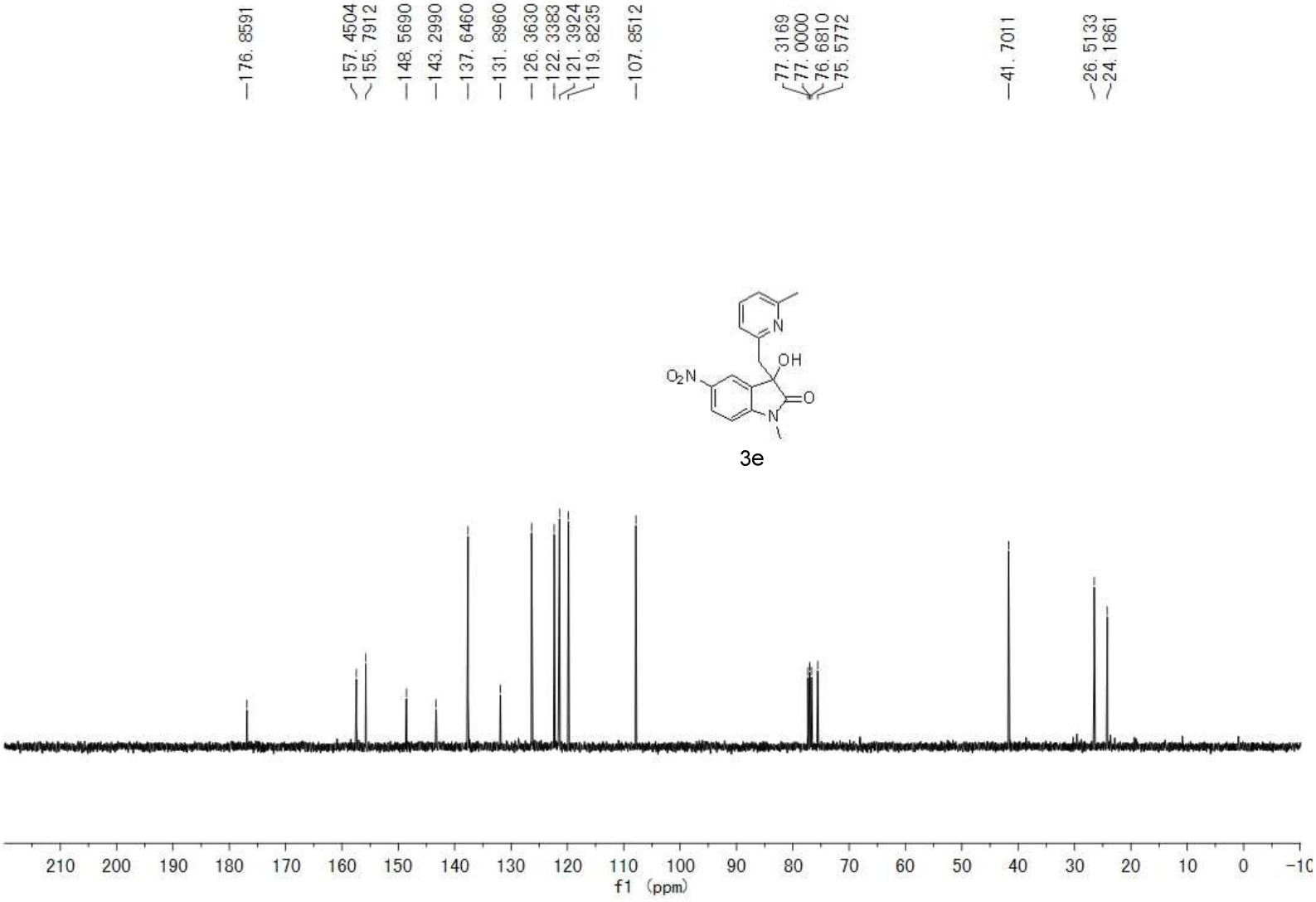
3c

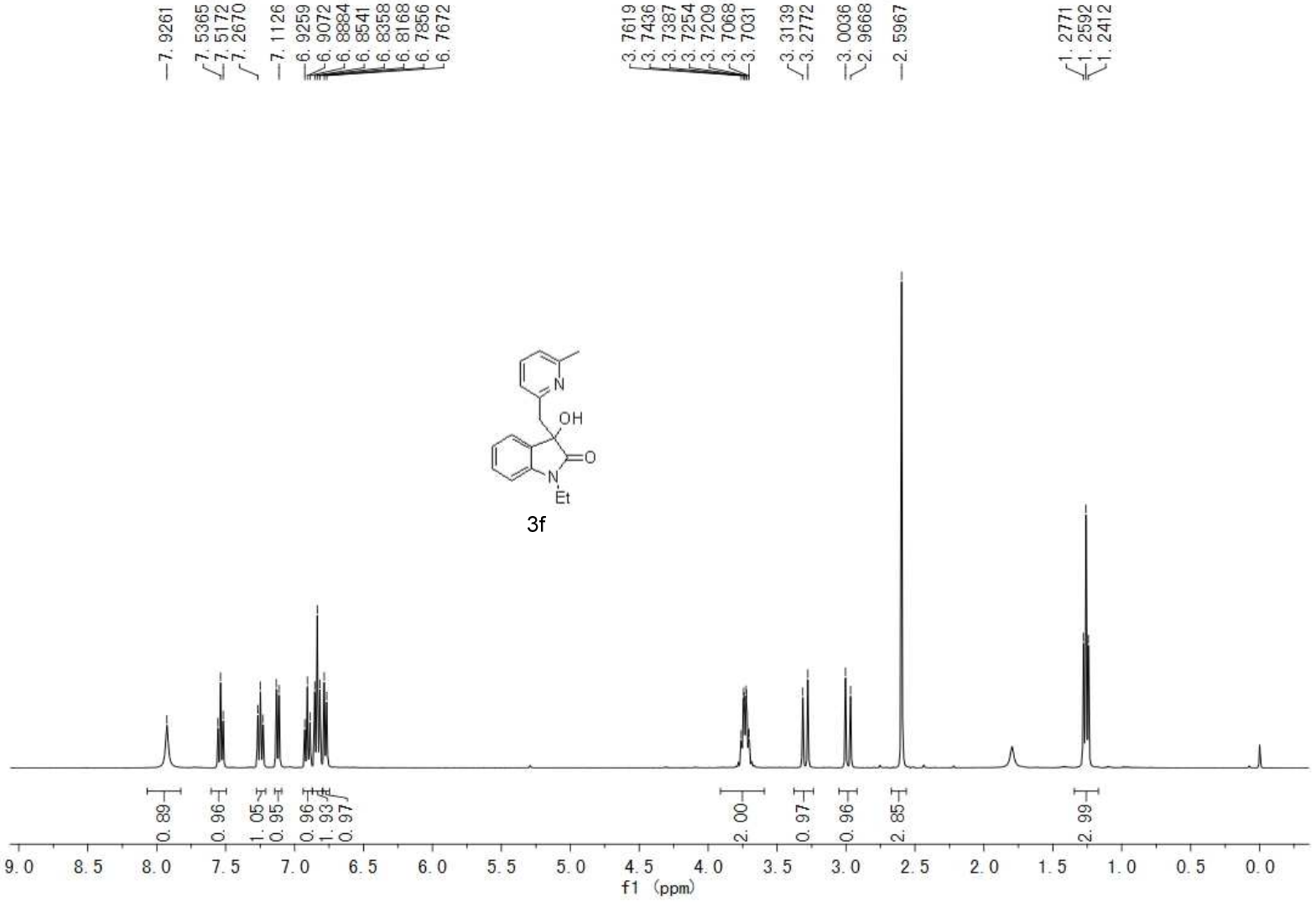

176.3033
157.3816
156.4877
142.0060
137.5253
132.0362
127.2766
122.1352
121.4858
115.3357
109.6965
77.3172
76.9998
76.6818
76.0985
42.0110
26.2579
24.2957
Cl
OH
O
N
N
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

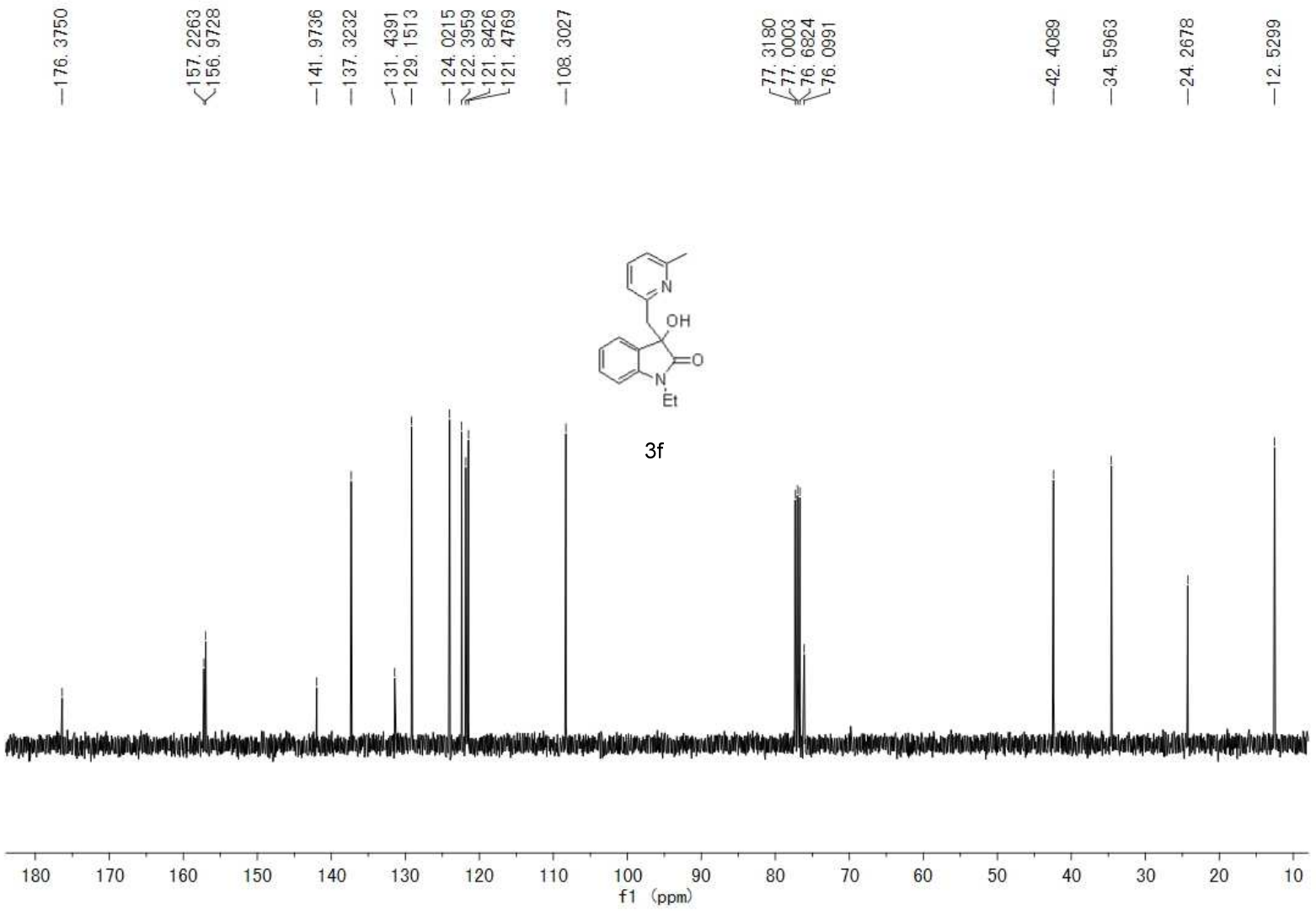

8.1259
7.5661
7.5468
7.1372
6.8746
6.8556
6.7422
6.7240
3.2997
3.2627
3.1650
2.9980
2.9609
2.6005
Br
OH
O
N
N
3d
0.80
1.04
0.97
1.00
1.00
1.99
1.06
3.01
1.00
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.3387
157.2857
156.4436
141.4547
137.4816
132.8052
129.0485
124.4286
122.0731
121.4428
109.1507
77.3183
77.0002
76.6826
76.0961
41.9562
26.2209
24.2287
Br
OH
O
N
N
3d
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)

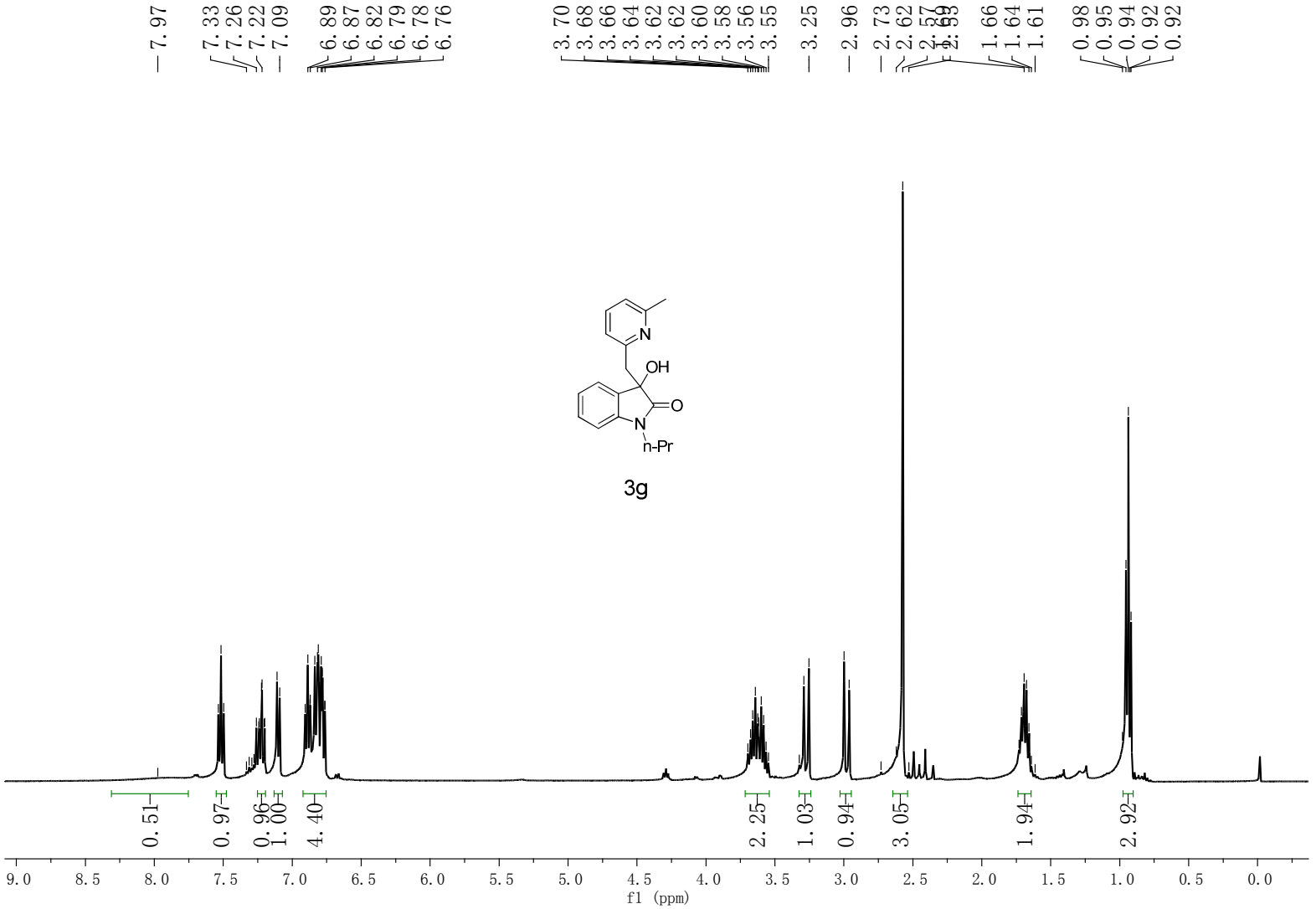

8.23
8.21
7.64
7.56
7.54
7.17
7.15
6.90
6.88
6.86
6.84
3.33
3.29
3.24
3.04
3.00
2.60
OH
O2N
O
N
3e
1.64
0.95
1.02
1.00
2.00
4.06
1.03
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

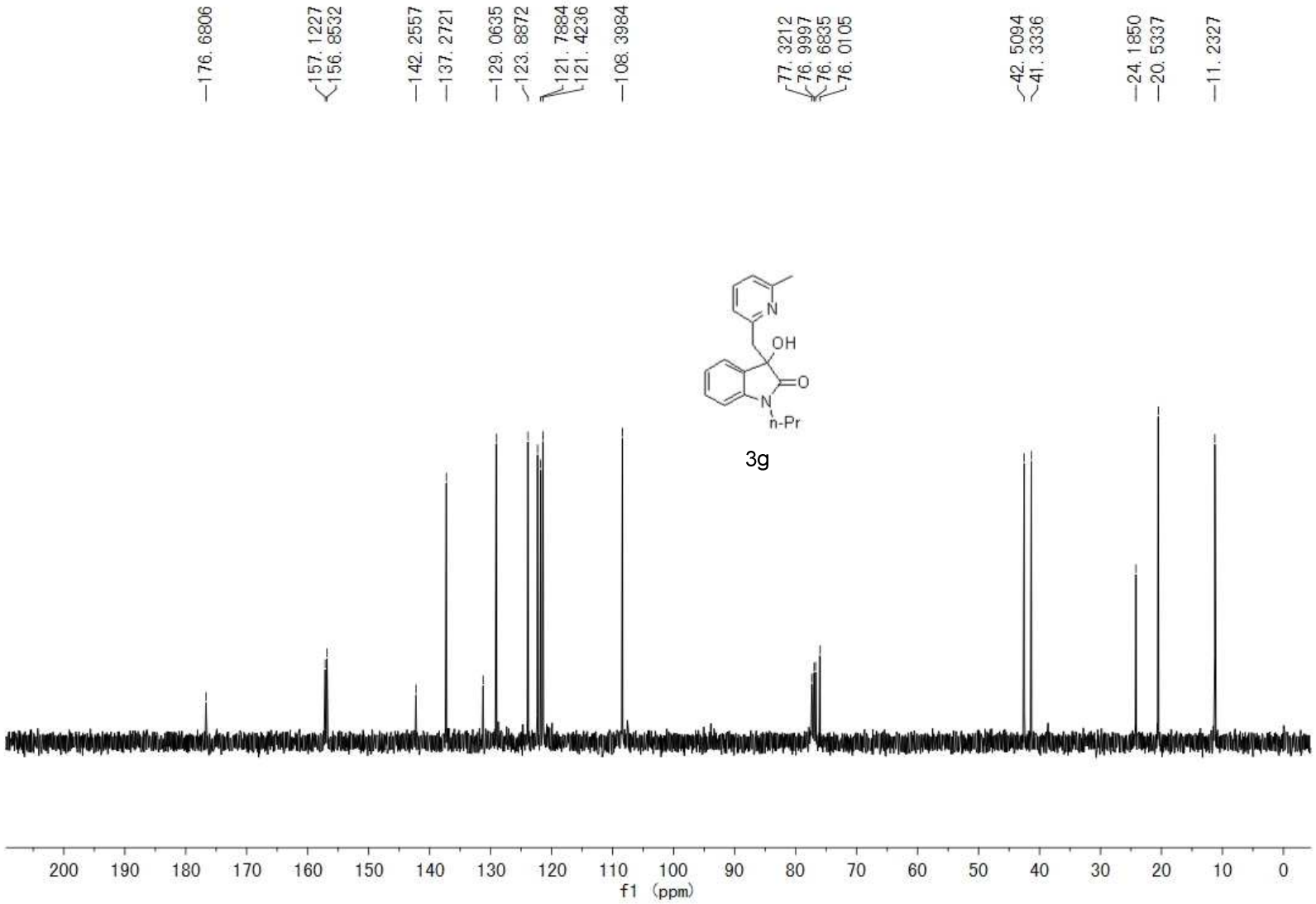

176.8591
157.4504
155.7912
148.5690
143.2990
137.6460
131.8960
126.3630
122.3383
121.3924
119.8235
107.8512
77.3169
77.0000
76.6810
75.5772
41.7011
26.5133
24.1861
OH
O2N
O
N
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

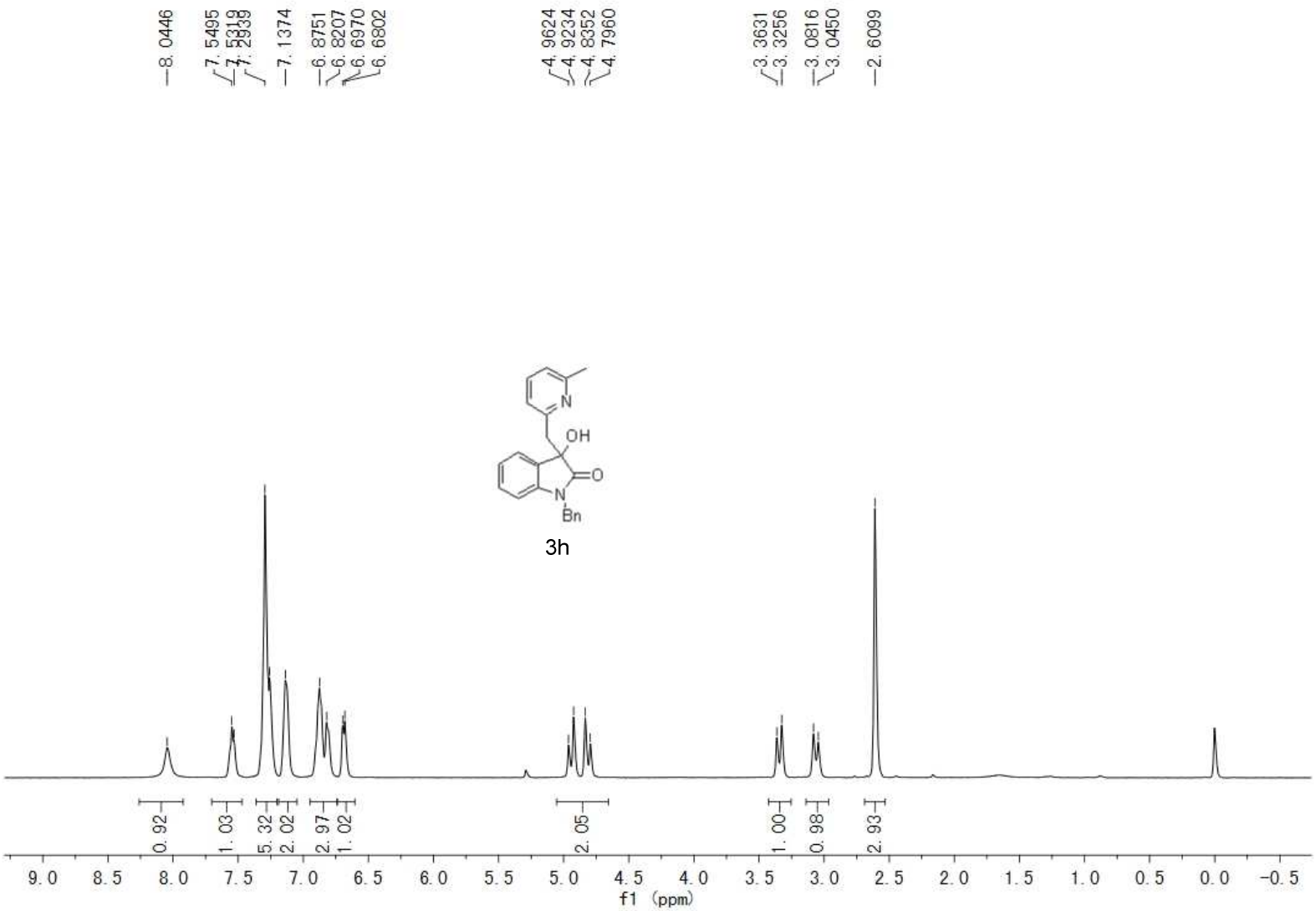

7.9261
7.5365
7.5172
7.2670
7.1126
6.9259
6.9072
6.8884
6.8541
6.8358
6.8168
6.7856
6.7672
3.7619
3.7436
3.7387
3.7254
3.7209
3.7068
3.7031
3.3139
3.2772
3.0036
2.9668
2.5967
1.2771
1.2592
1.2412
OH
O
N
Et
3f
0.89
0.96
1.05
0.95
0.96
1.93
0.97
2.00
0.97
0.96
2.85
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.3750
157.2263
156.9728
141.9736
137.3232
131.4391
129.1513
124.0215
122.3959
121.8426
121.4769
108.3027
77.3180
77.0003
76.6824
76.0991
42.4089
34.5963
24.2678
12.5299
N
OH
O
N
Et
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

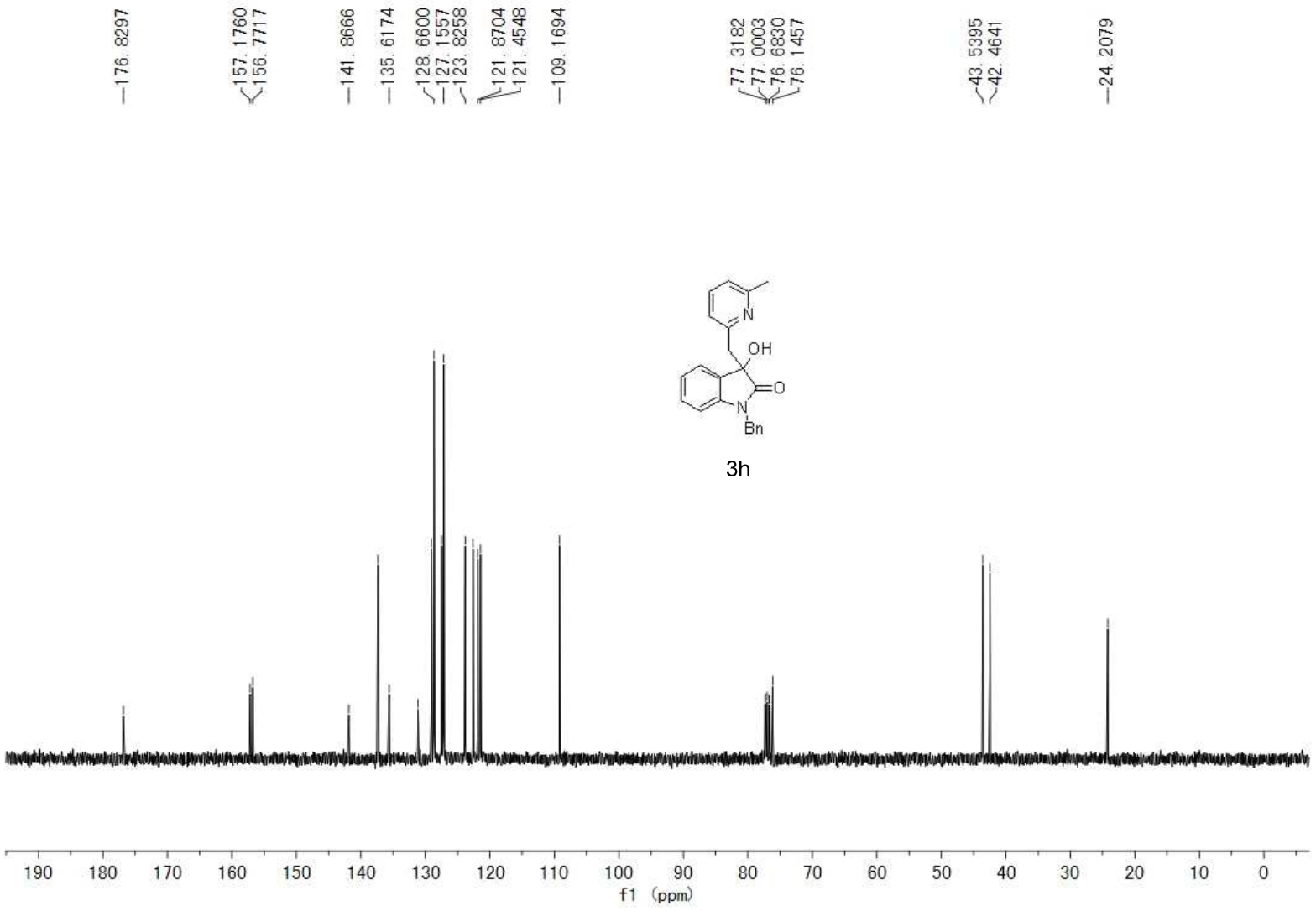
3f


7.97
7.33
7.26
7.22
7.09
6.89
6.87
6.82
6.79
6.78
6.76
3.70
3.68
3.66
3.64
3.62
3.62
3.60
3.58
3.56
3.55
3.25
2.96
2.73
2.62
2.57
1.66
1.64
1.61
0.98
0.95
0.94
0.92
0.92
OH
O
N
n-Pr
3g
0.51
0.97
0.96
1.00
4.40
2.25
1.03
0.94
3.05
1.94
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)


176.6806
157.1227
156.8532
142.2557
137.2721
129.0635
123.8872
121.7884
121.4236
108.3984
77.3212
76.9997
76.6835
76.0105
42.5094
41.3336
24.1850
20.5337
11.2327
OH
O
N
n-Pr
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.0446
7.5495
7.5319
7.2939
7.1374
6.8751
6.8207
6.6970
6.6802
4.9624
4.9234
4.8352
4.7960
3.3631
3.3256
3.0816
3.0450
2.6099
OH
O
N
Bn
0.92
1.03
5.32
2.02
2.97
1.02
2.05
1.00
0.98
2.93
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)

3h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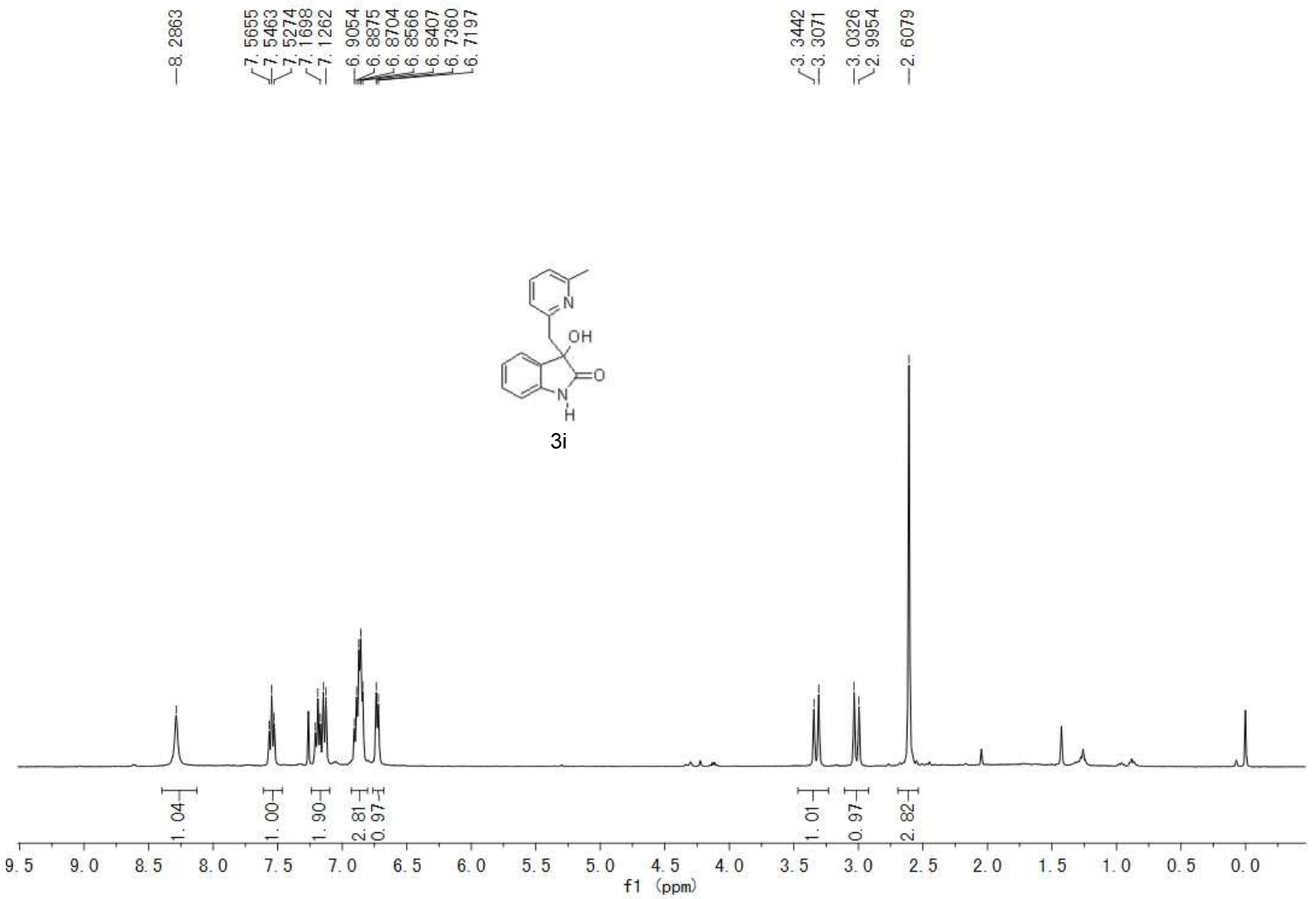
156.7717
141.8666
135.6174
128.6600
127.1557
123.8258
121.8704
121.4548
109.1694
77.3182
77.0003
76.6830
76.1457
43.5395
42.4641
24.2079
OH
O
N
Bn
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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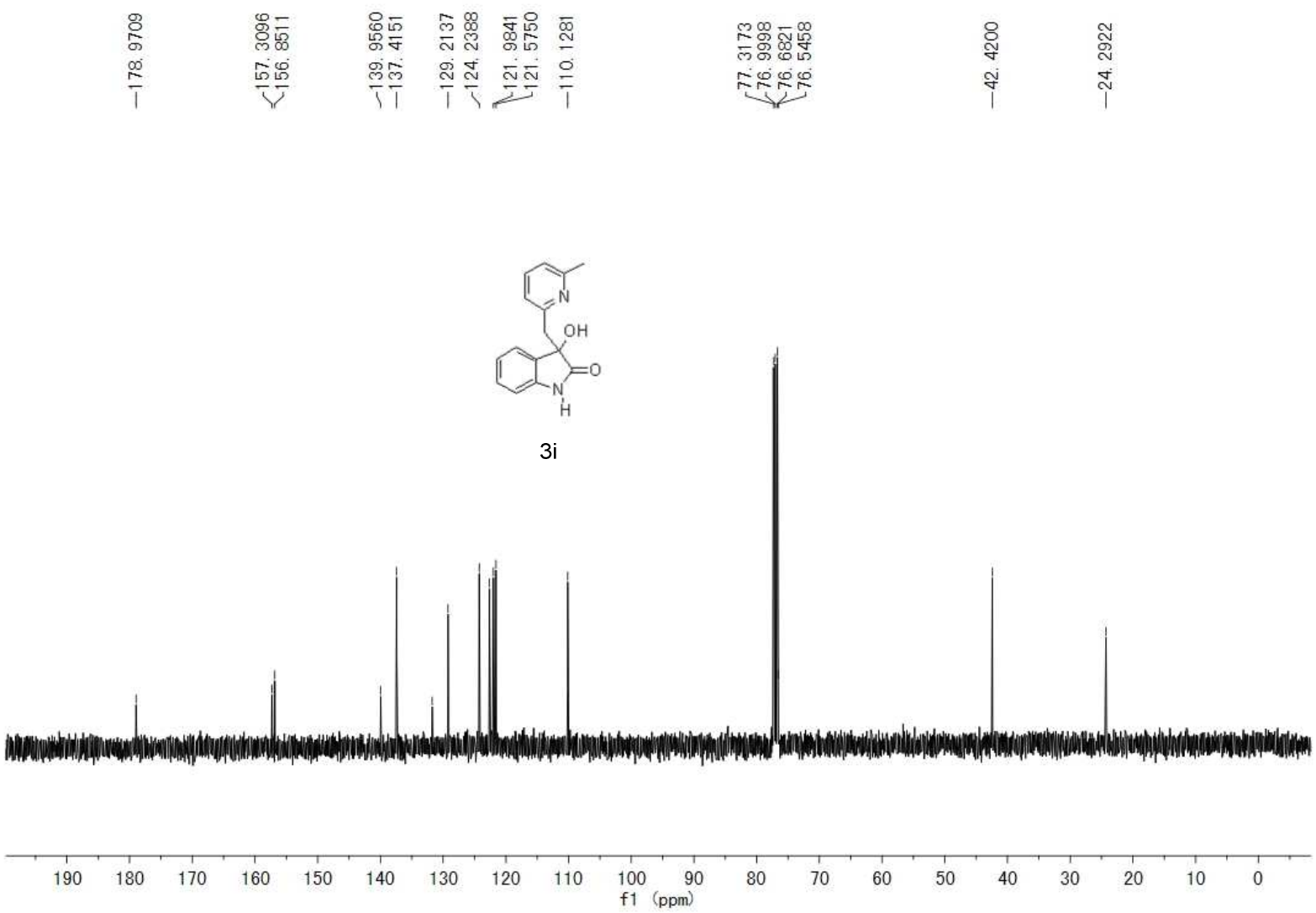
7.5655
7.5463
7.5274
7.1698
7.1262
6.9054
6.8875
6.8704
6.8566
6.8407
6.7360
6.7197
3.3442
3.3071
3.0326
2.9954
2.6079
OH
O
N
H
3i
1.04
1.00
1.90
2.81
0.97
1.01
0.97
2.82
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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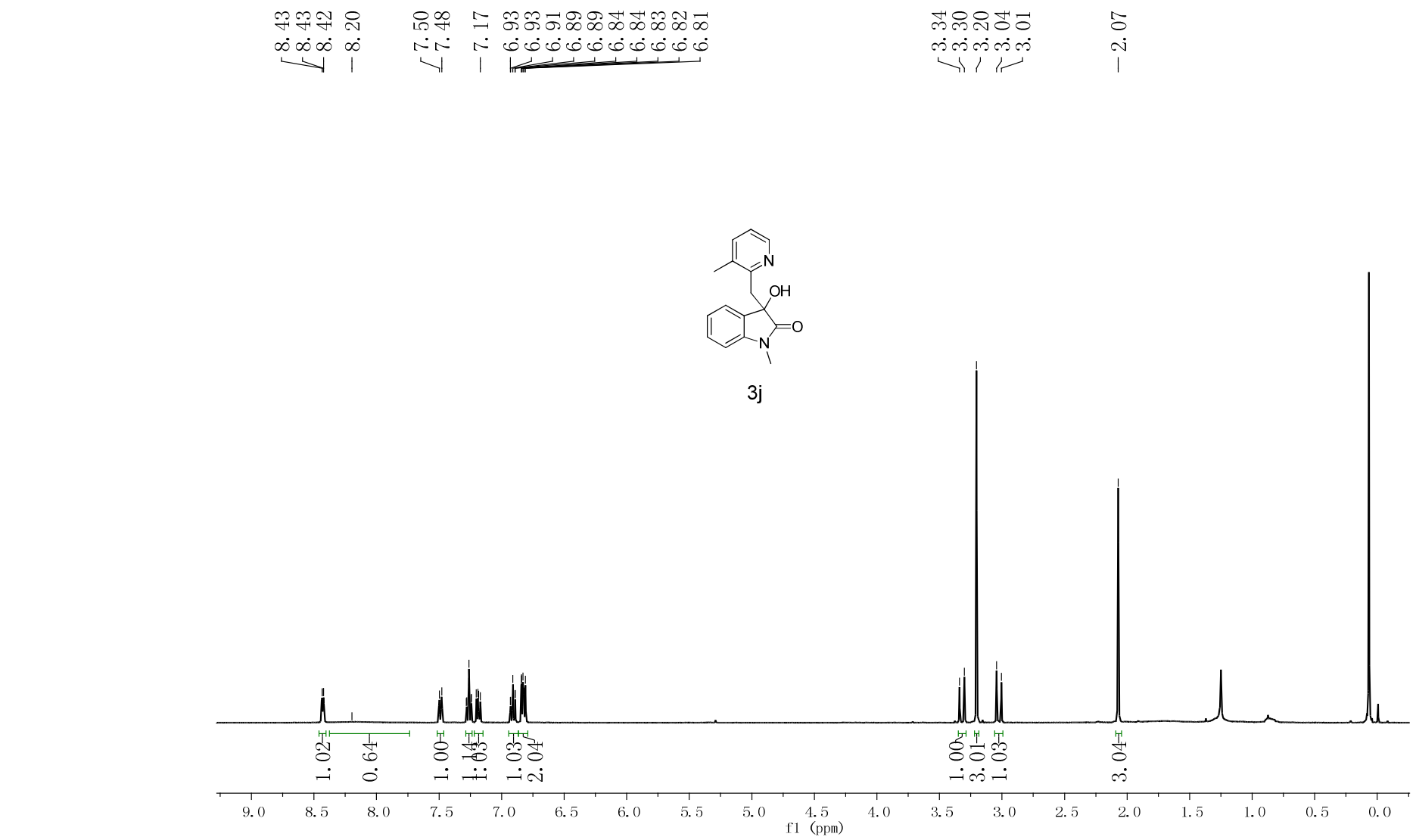
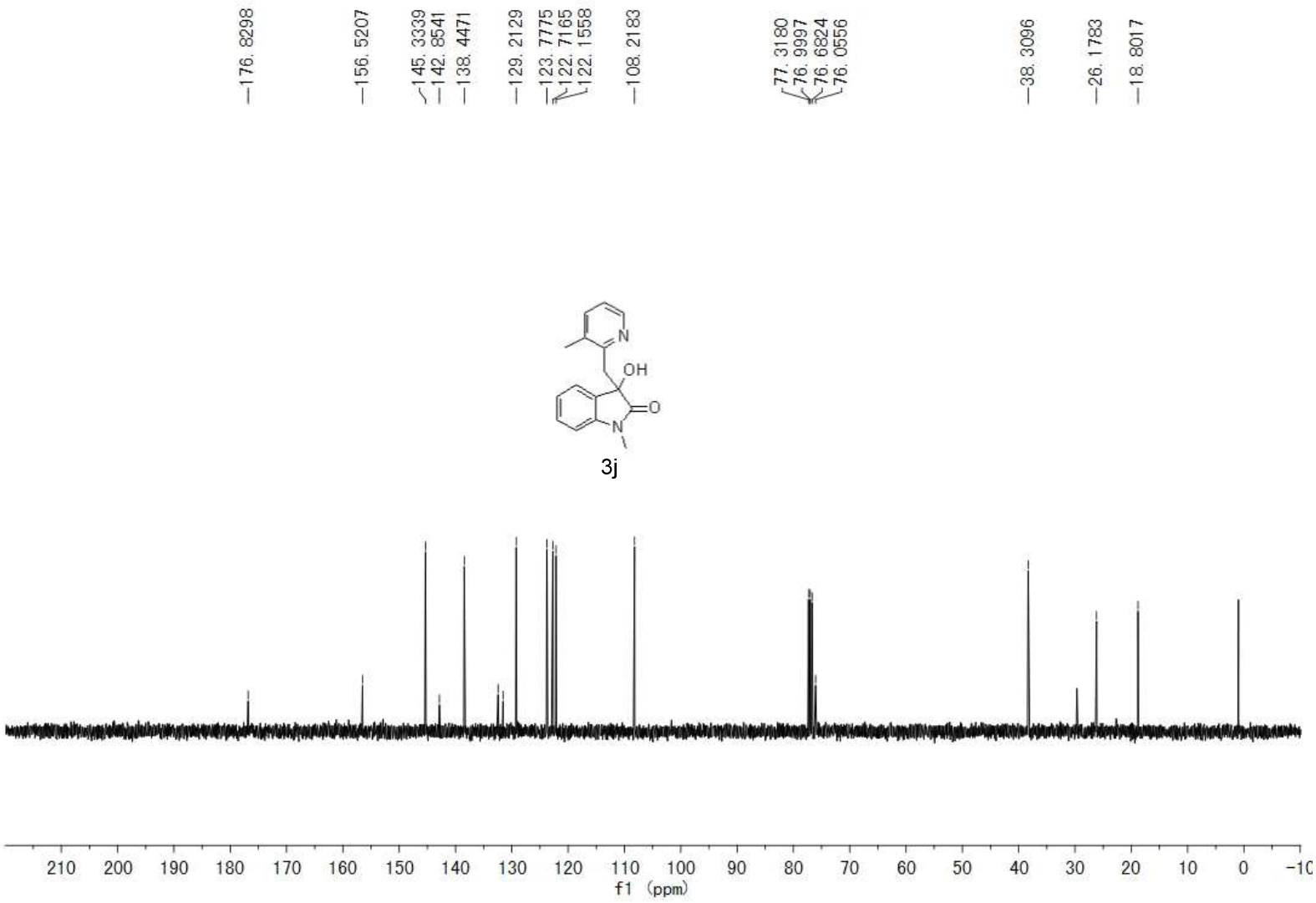
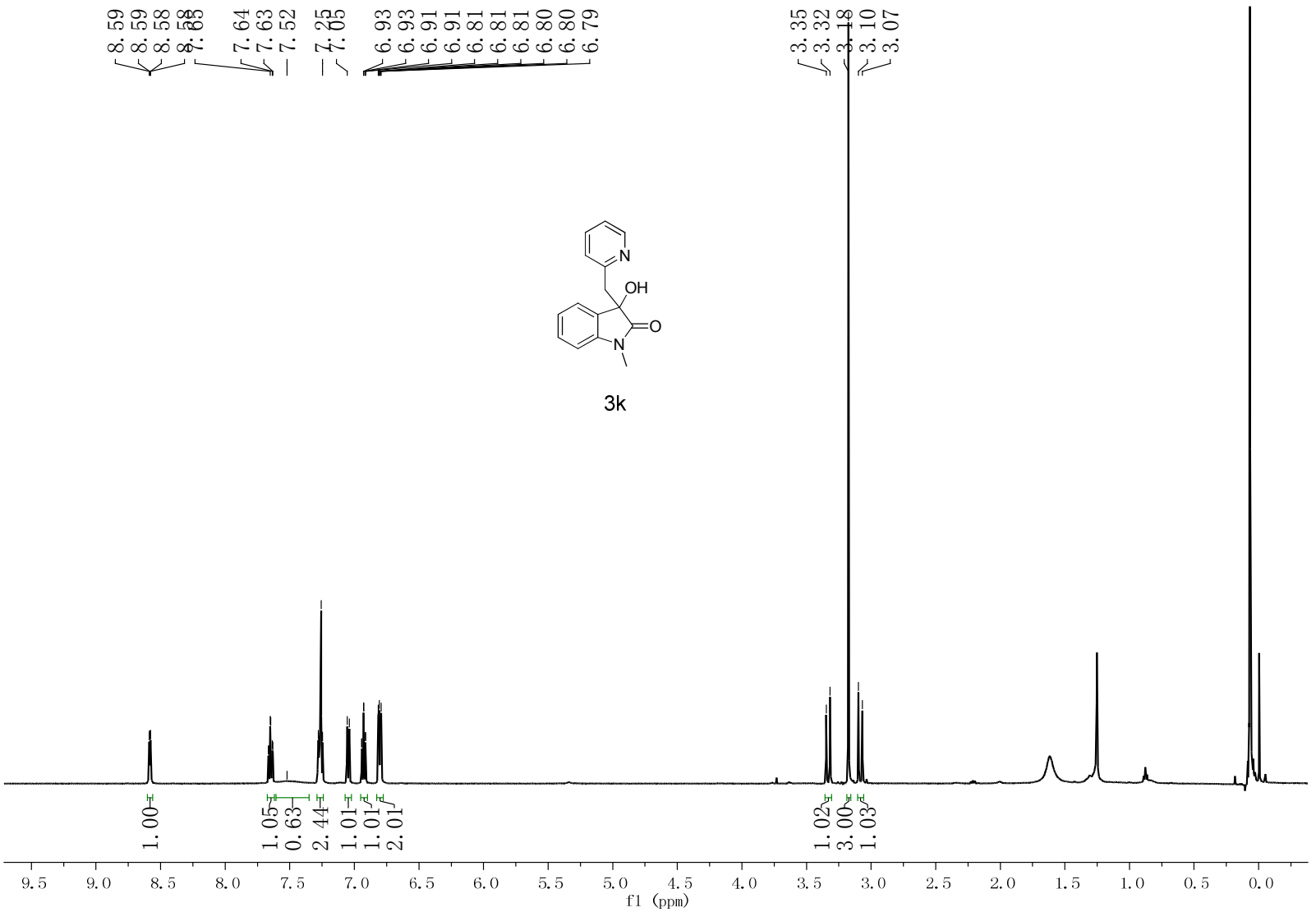
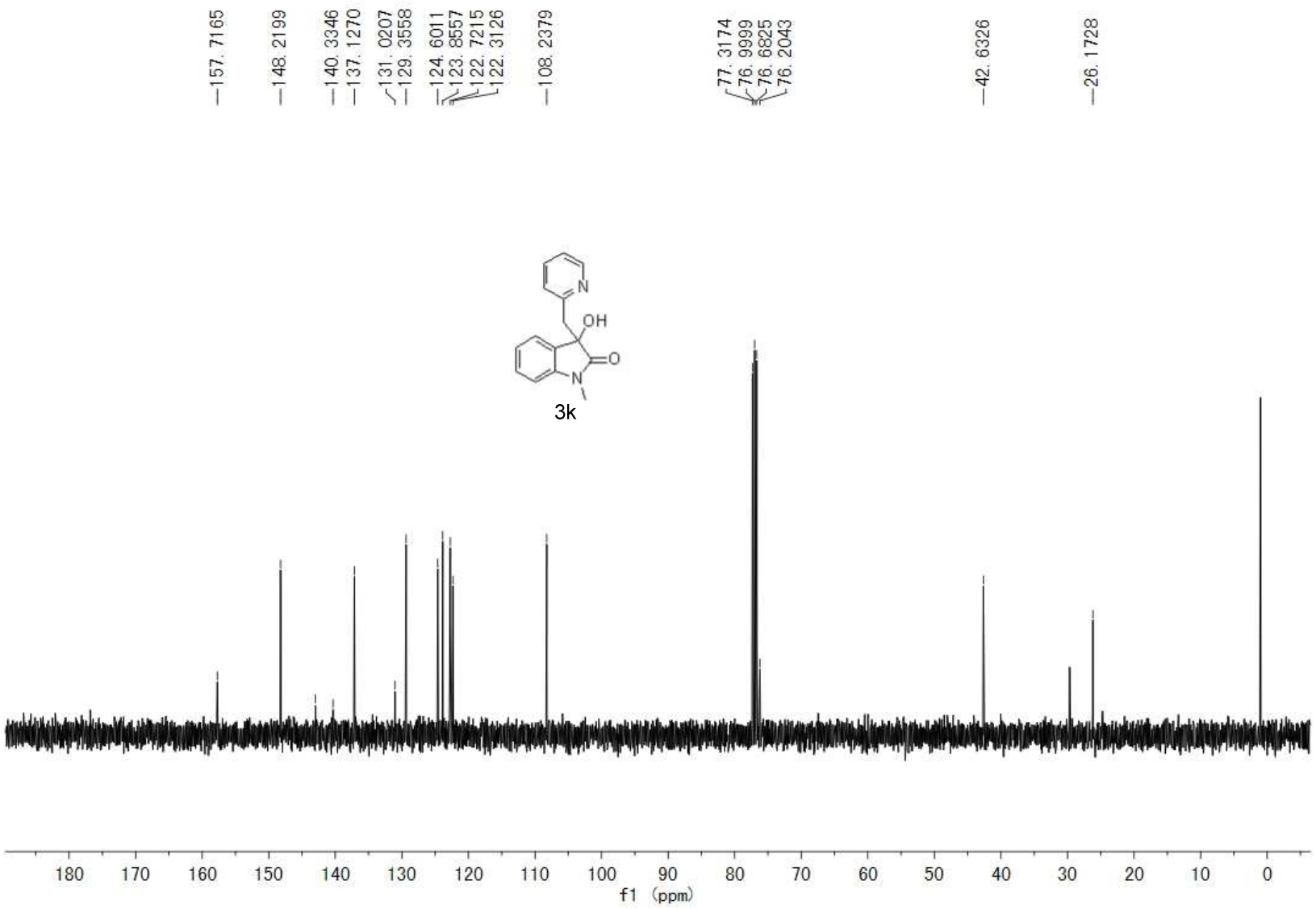
157.3096
156.8511
139.9560
137.4151
129.2137
124.2388
121.9841
121.5750
110.1281
77.3173
76.9998
76.6821
76.5458
42.4200
24.2922
OH
O
N
H
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

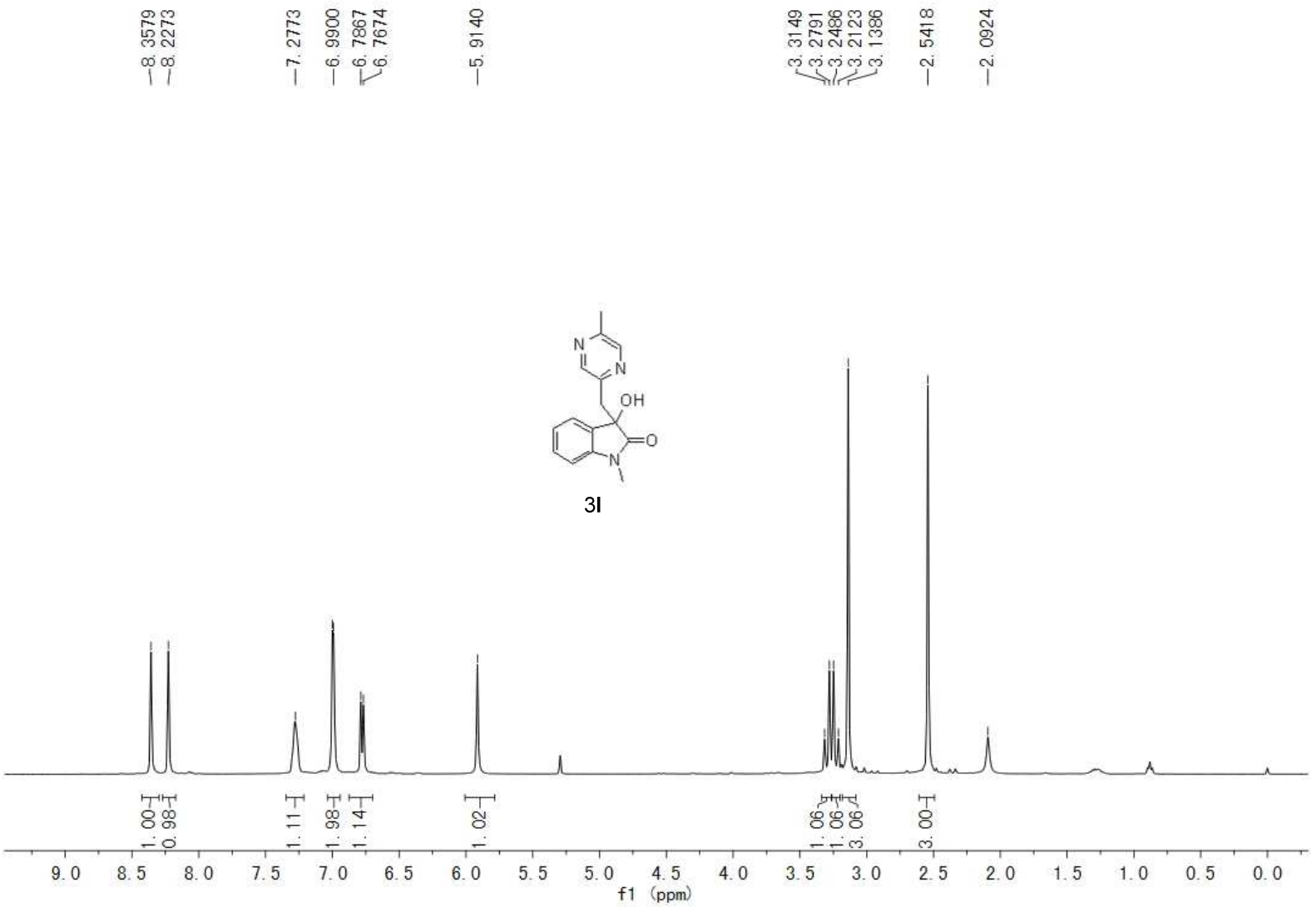

8.43
8.43
8.42
8.20
7.50
7.48
7.17
6.93
6.93
6.91
6.89
6.89
6.84
6.84
6.83
6.82
6.81
3.34
3.30
3.20
3.04
3.01
2.07
N
OH
O
N
3j
1.02
0.64
1.00
1.14
1.03
1.03
2.04
1.00
3.01
1.03
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

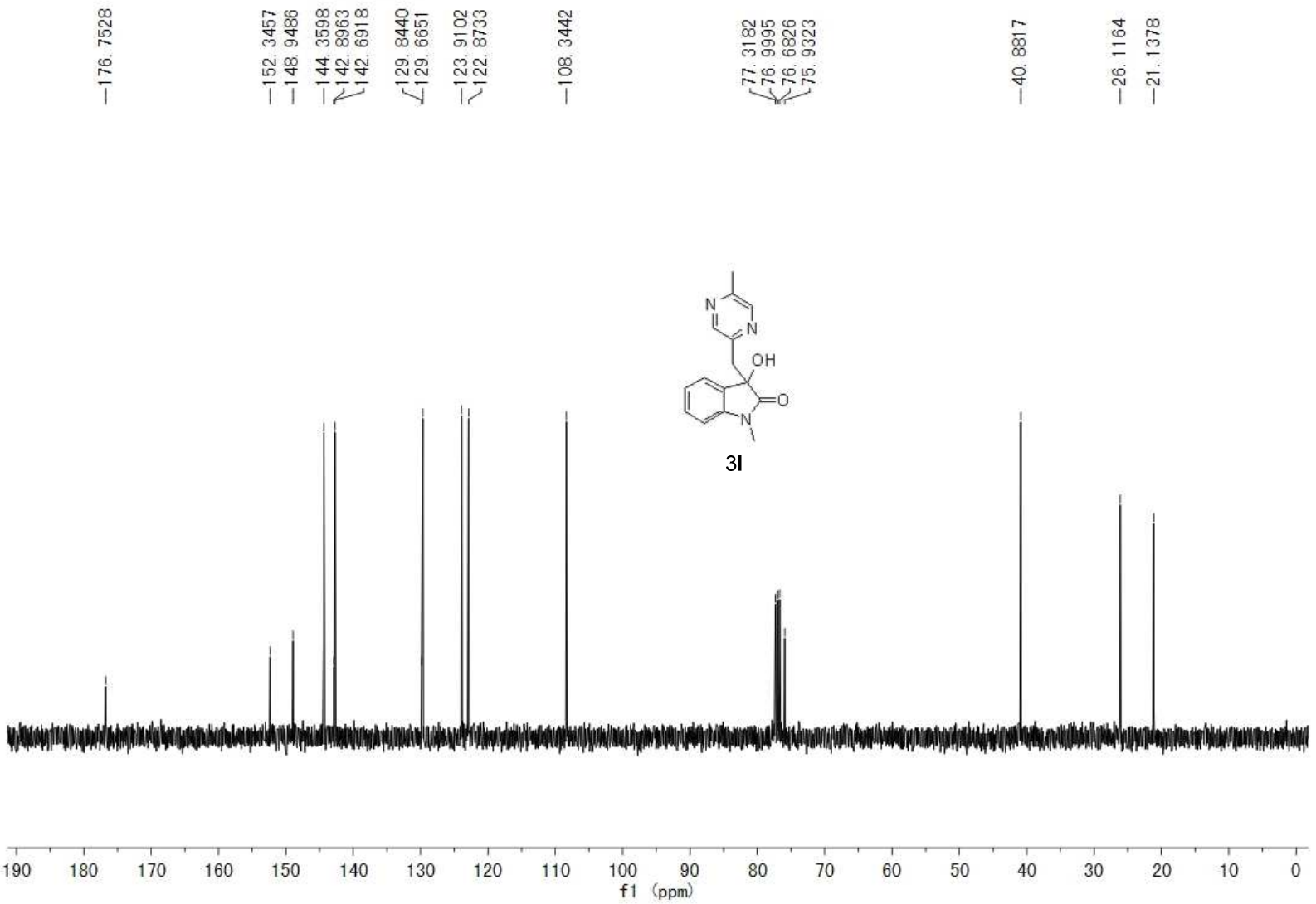

176.8298
156.5207
145.3339
142.8541
138.4471
129.2129
123.7775
122.7165
122.1558
108.2183
77.3180
76.9997
76.6824
76.0556
38.3096
26.1783
18.8017
OH
O
N
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

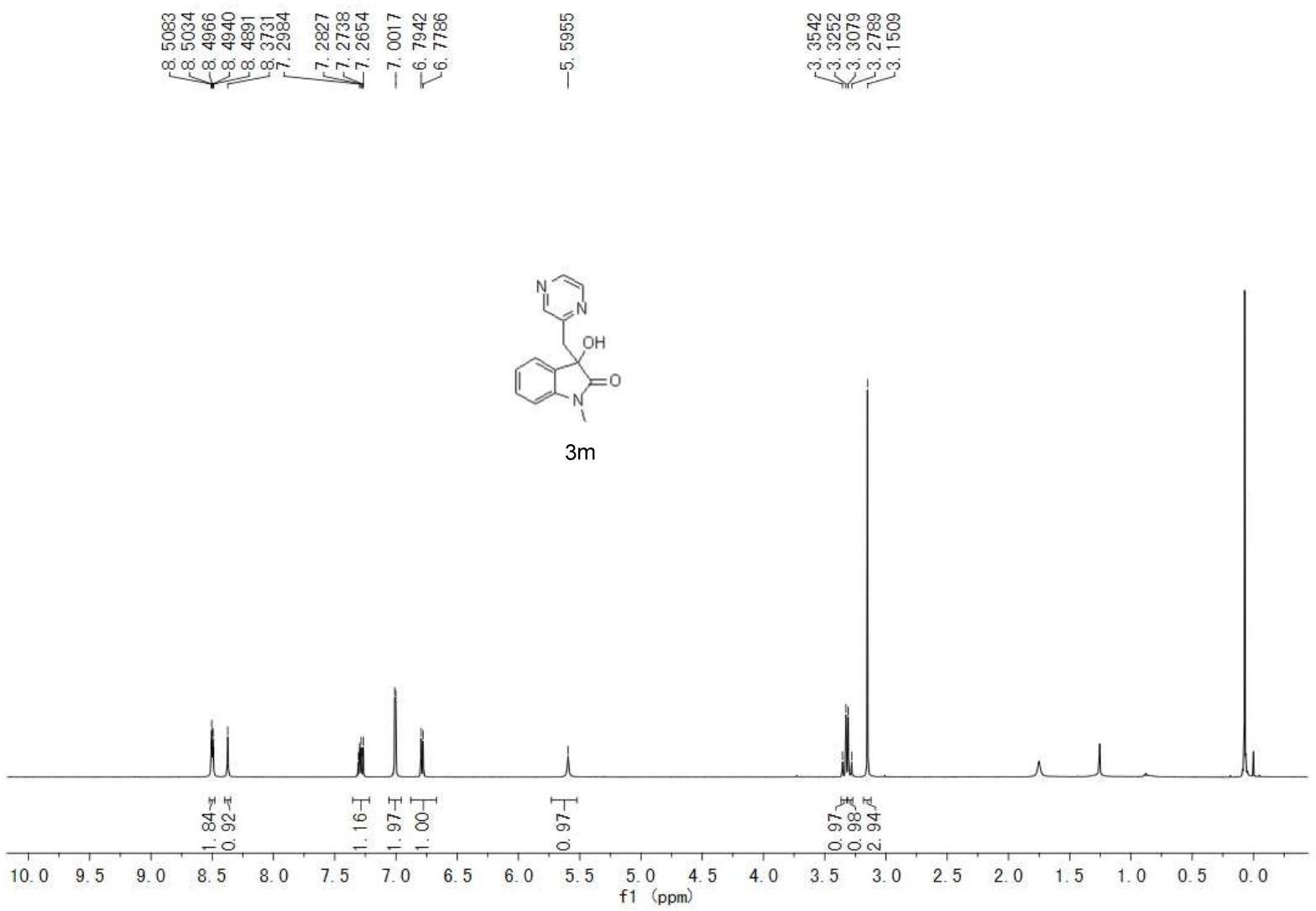

8.59
8.59
8.58
8.58
8.58
8.58
7.64
7.63
7.52
7.25
7.05
6.93
6.93
6.91
6.91
6.81
6.81
6.81
6.80
6.80
6.79
3.35
3.32
3.18
3.10
3.07
N
OH
O
N
1.00
1.05
0.63
2.44
1.01
1.01
2.01
1.02
3.00
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

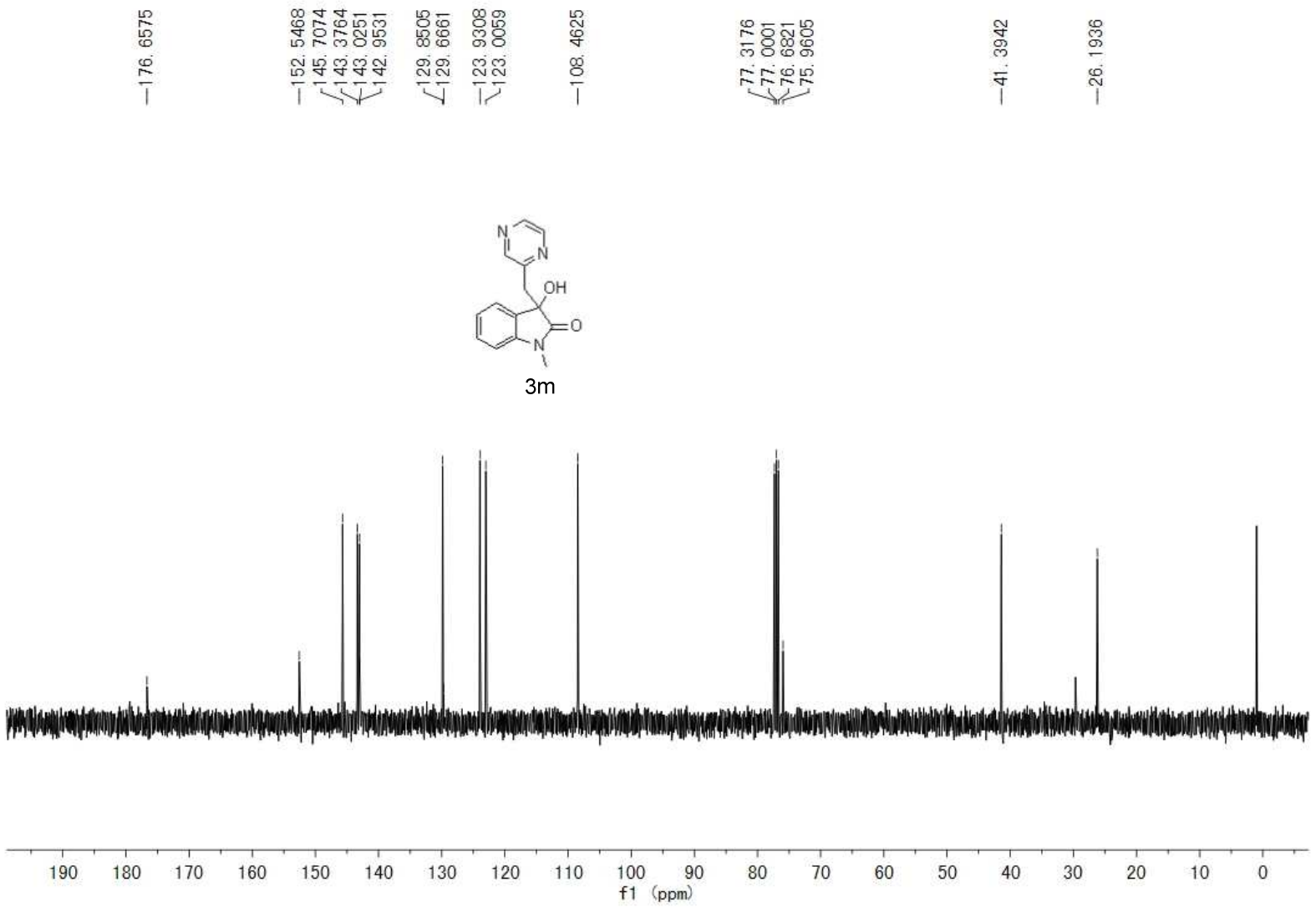
3k

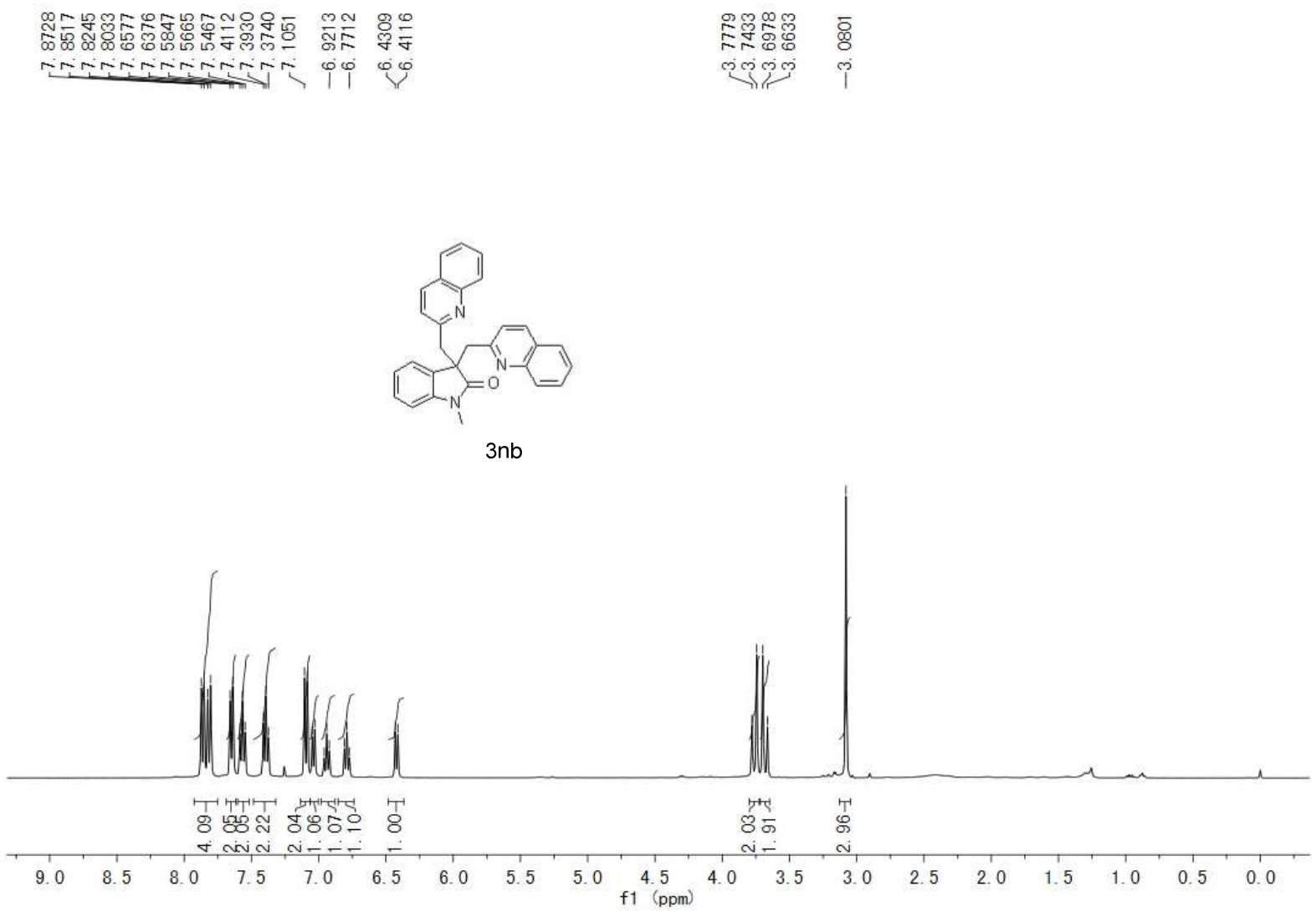

157.7165
148.2199
140.3346
137.1270
131.0207
129.3558
124.6011
123.8557
122.7215
122.3126
108.2379
77.3174
76.9999
76.6825
76.2043
42.6326
26.1728
OH
O
N
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.3579
8.2273
7.2773
6.9900
6.7867
6.7674
5.9140
3.3149
3.2791
3.2486
3.2123
3.1386
2.5418
2.0924
OH
O
N
N
N
3l
1.00
0.98
1.11
1.98
1.14
1.02
1.06
1.06
3.06
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)

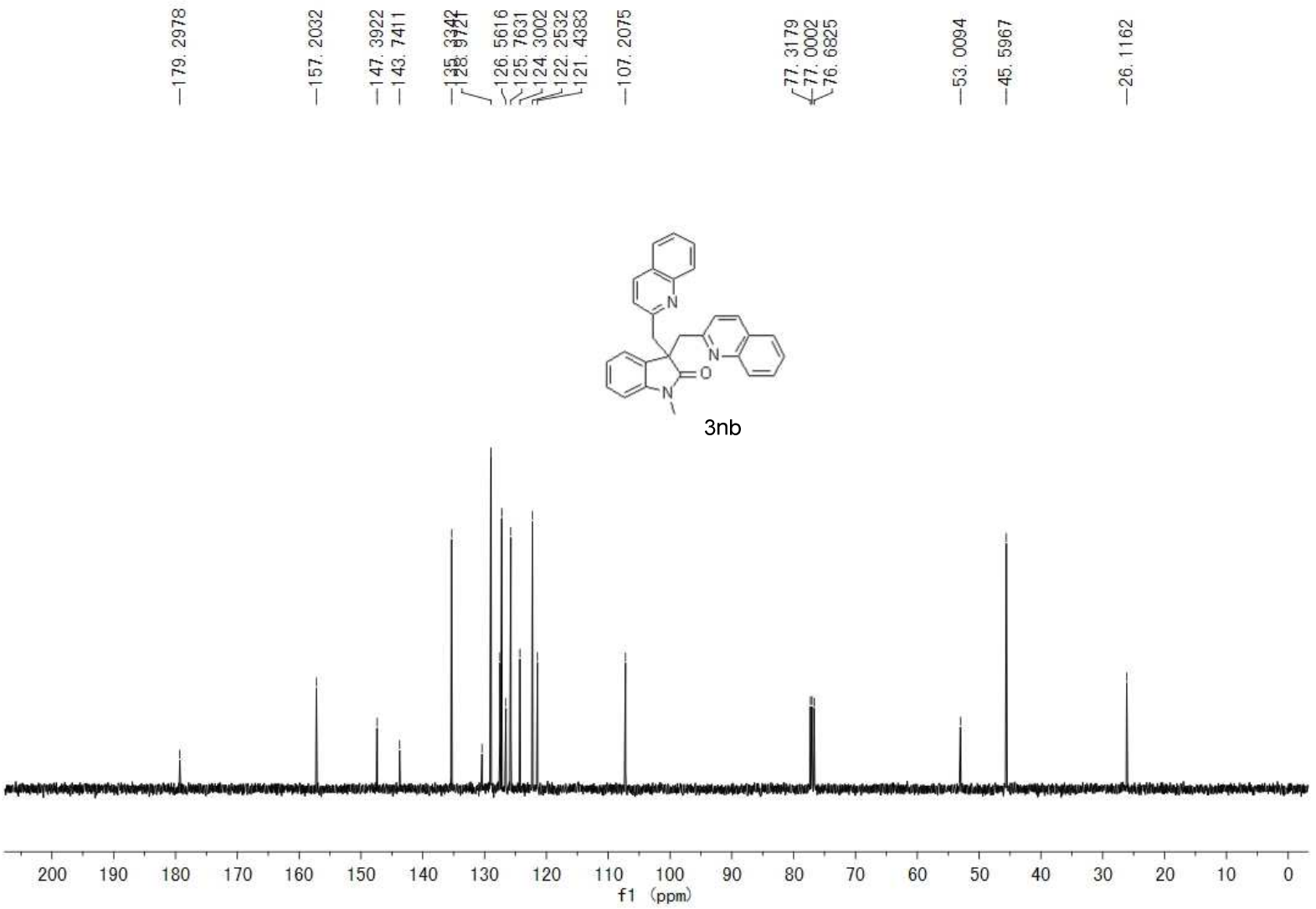

176.7528
152.3457
148.9486
144.3598
142.8963
142.6918
129.8440
129.6651
123.9102
122.8733
108.3442
77.3182
76.9995
76.6826
75.9323
40.8817
26.1164
21.1378
OH
O
N
N
N
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

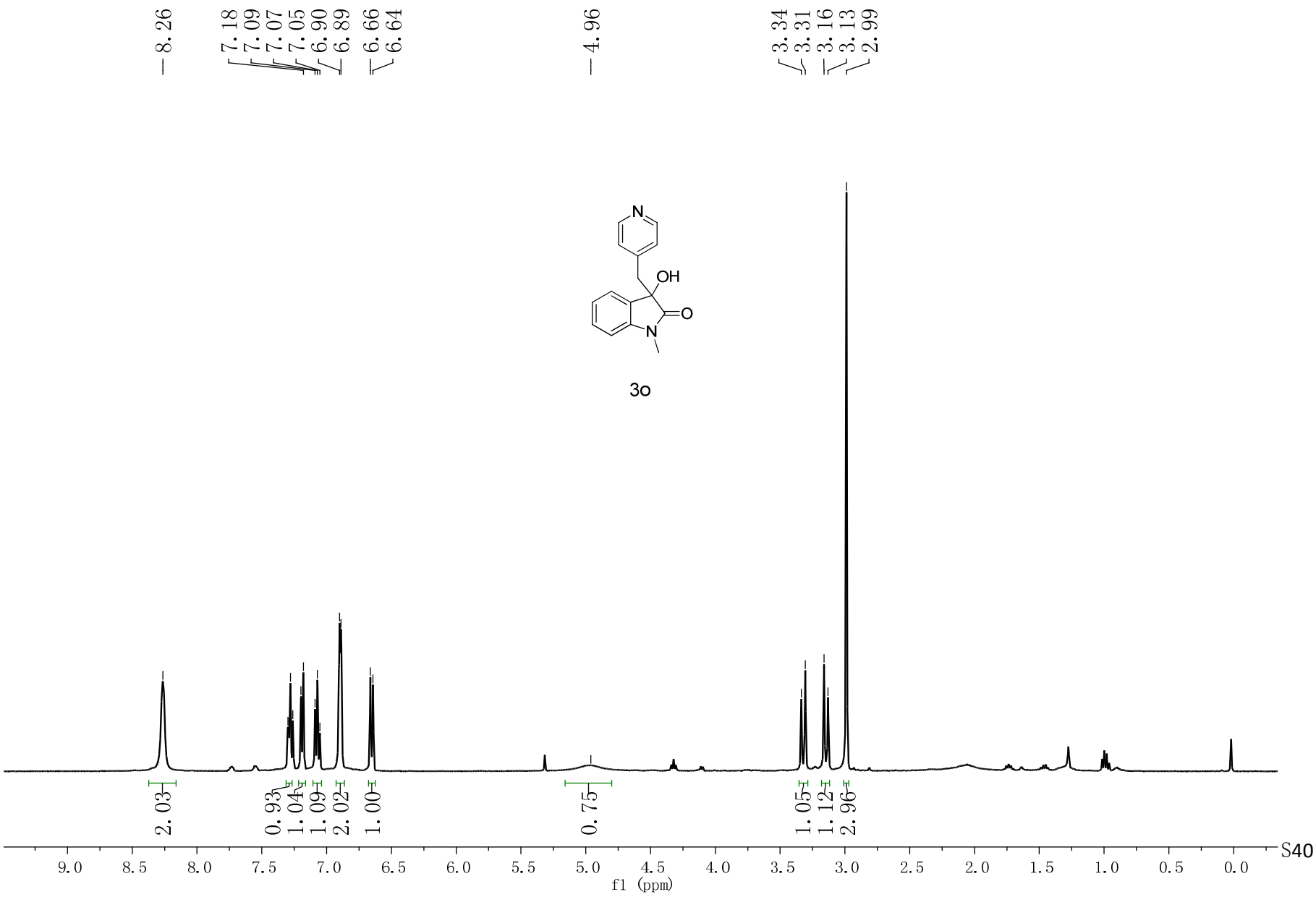

8.5083
8.5034
8.4966
8.4940
8.4891
8.3731
7.2984
7.2827
7.2738
7.2654
7.0017
6.7942
6.7786
5.5955
3.3542
3.3252
3.3079
3.2789
3.1509
N
N
OH
O
N
3m
1.84
0.92
1.16
1.97
1.00
0.97
0.97
0.98
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.6575
152.5468
145.7074
143.3764
143.0251
142.9531
129.8505
129.6661
123.9308
123.0059
108.4625
77.3176
77.0001
76.6821
75.9605
41.3942
26.1936
OH
O
N
N
N
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

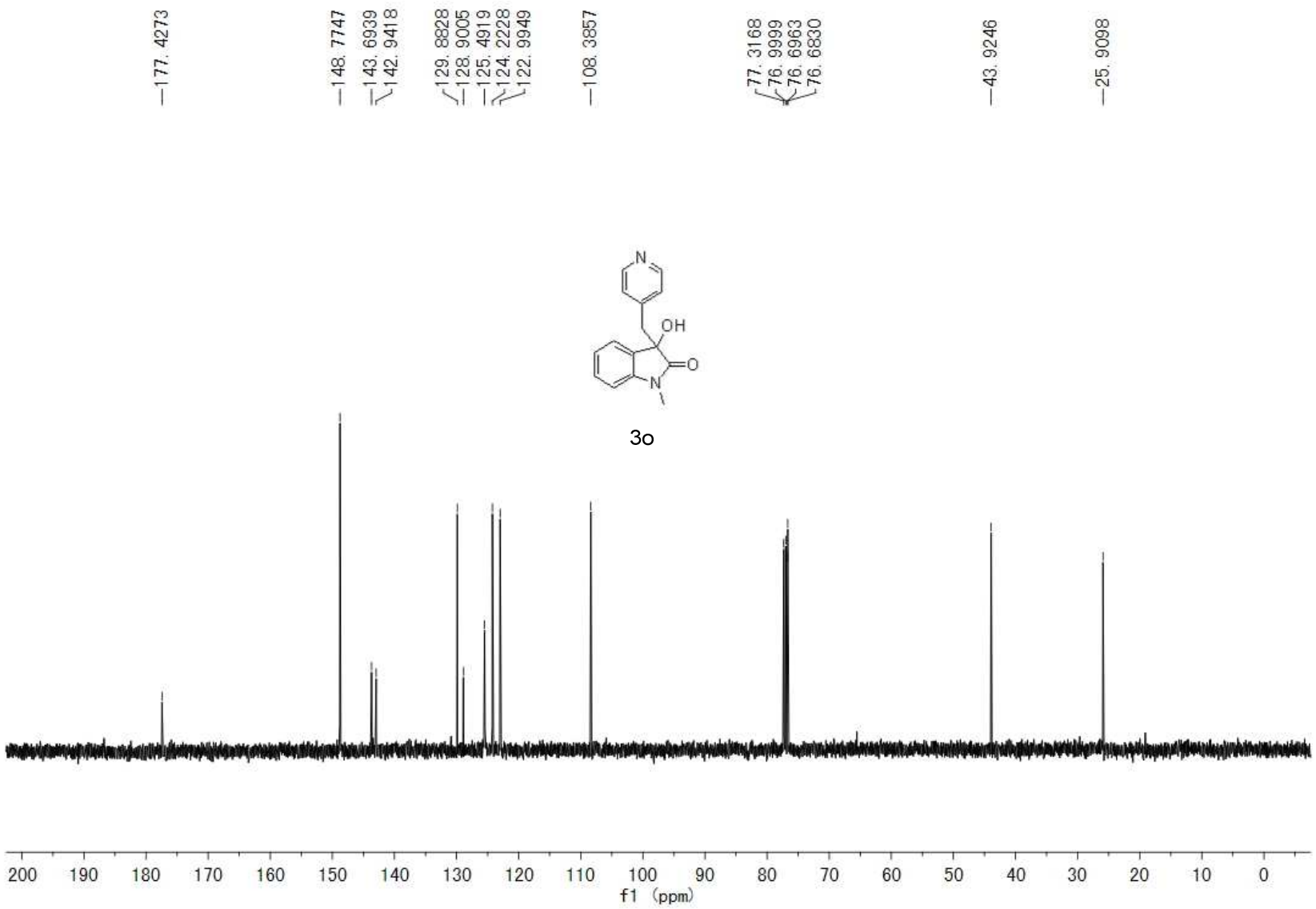

7.8728
7.8517
7.8245
7.8033
7.6577
7.6376
7.5847
7.5665
7.5467
7.4112
7.3930
7.3740
7.1051
6.9213
6.7712
6.4309
6.4116
3.7779
3.7433
3.6978
3.6633
3.0801
N
O
N
N
4.09
2.05
2.85
2.22
2.04
1.06
1.07
1.10
1.00
2.03
1.91
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3nb

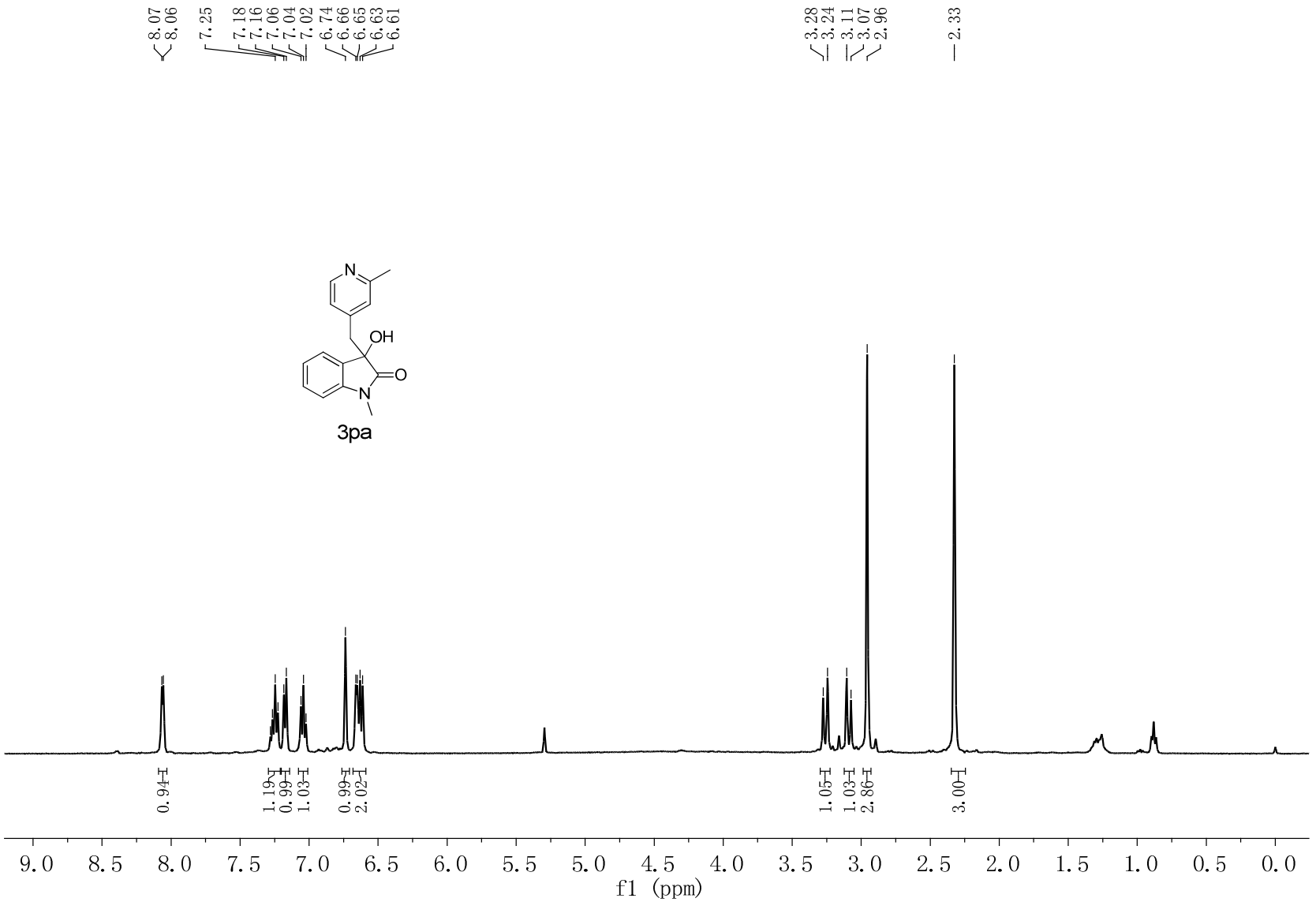

179.2978
157.2032
147.3922
143.7411
135.3342
128.9721
126.5616
125.7631
124.3002
122.2532
121.4383
107.2075
77.3179
77.0002
76.6825
53.0094
45.5967
26.1162
3nb
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

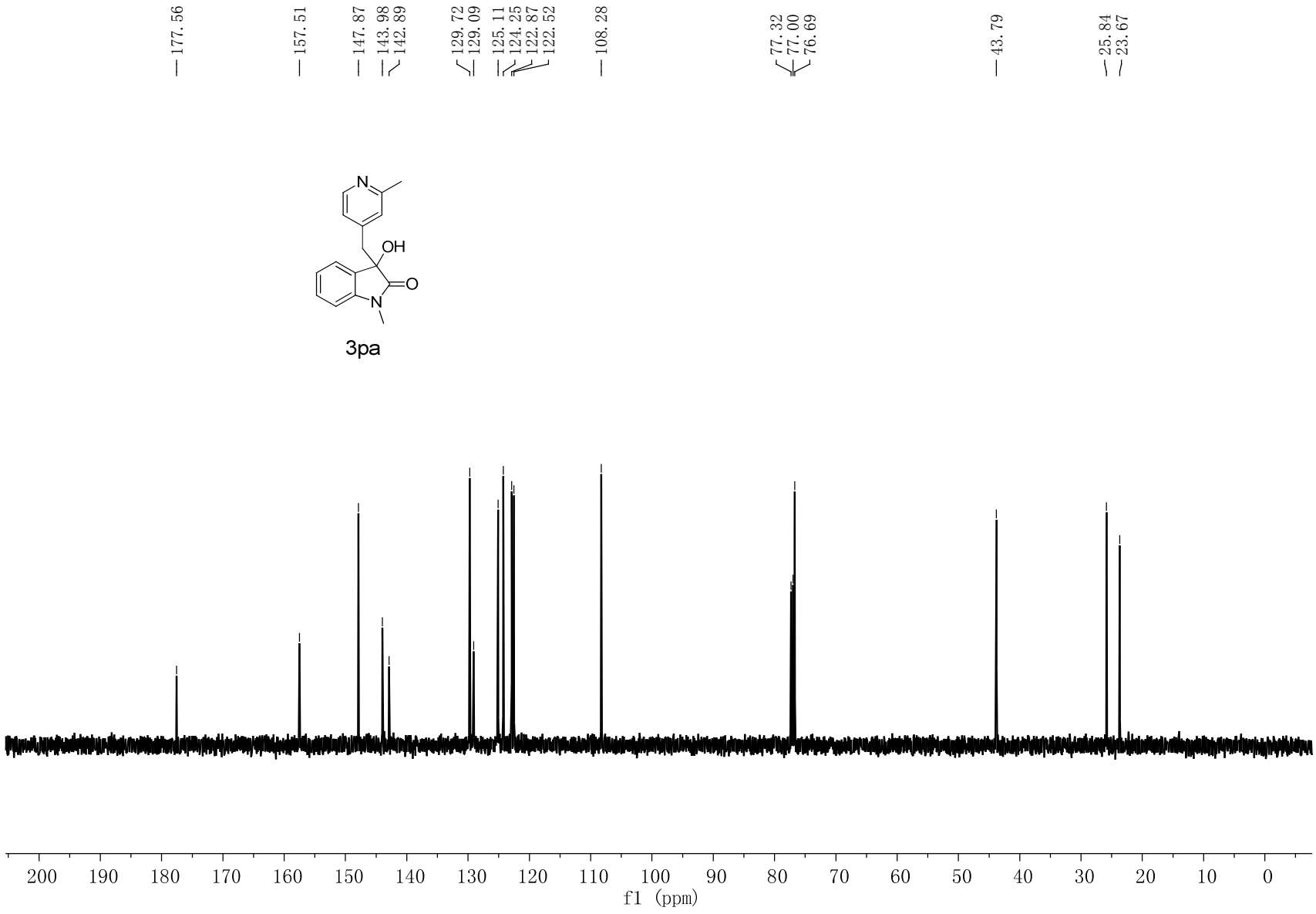

8.26
7.18
7.09
7.07
7.05
6.90
6.89
6.66
6.64
4.96
3.34
3.31
3.16
3.13
2.99
OH
O
N
2.03
0.93
1.04
1.09
2.02
1.00
0.75
1.05
1.12
2.96
f1 (ppm)

3o

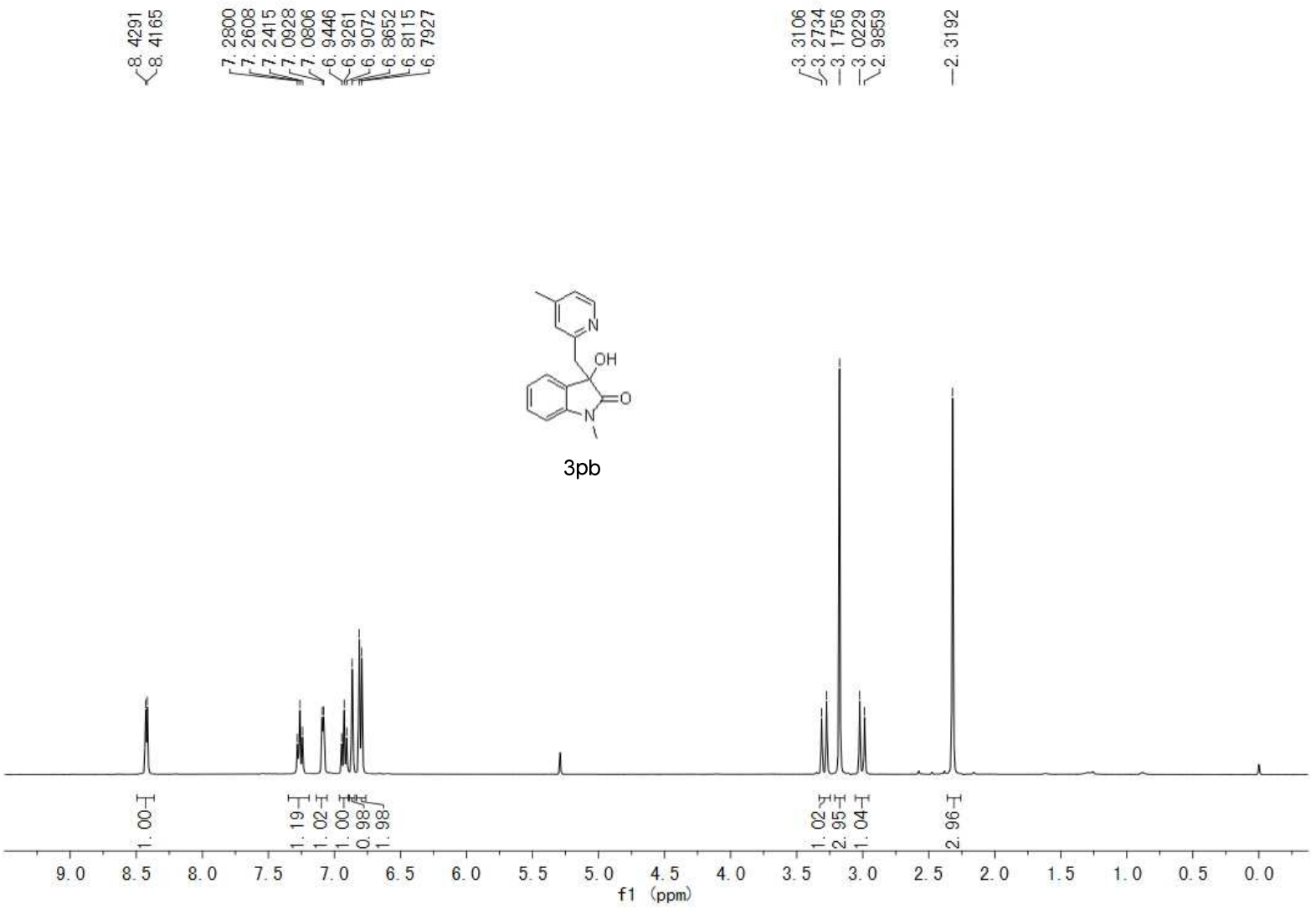

177.4273
148.7747
143.6939
142.9418
129.8828
128.9005
125.4919
124.2228
122.9949
108.3857
77.3168
76.9999
76.6963
76.6830
43.9246
25.9098
N
OH
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

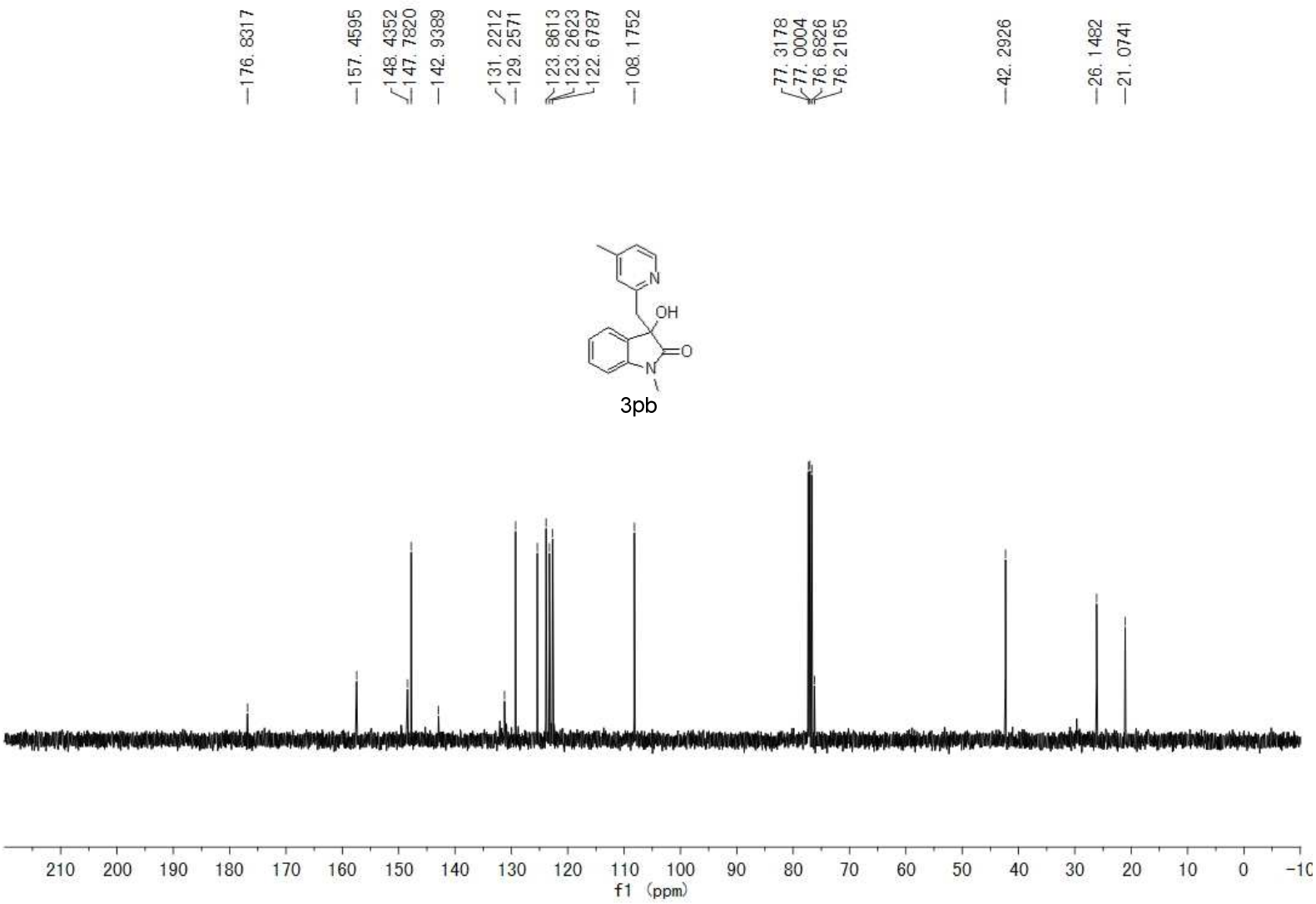
3o

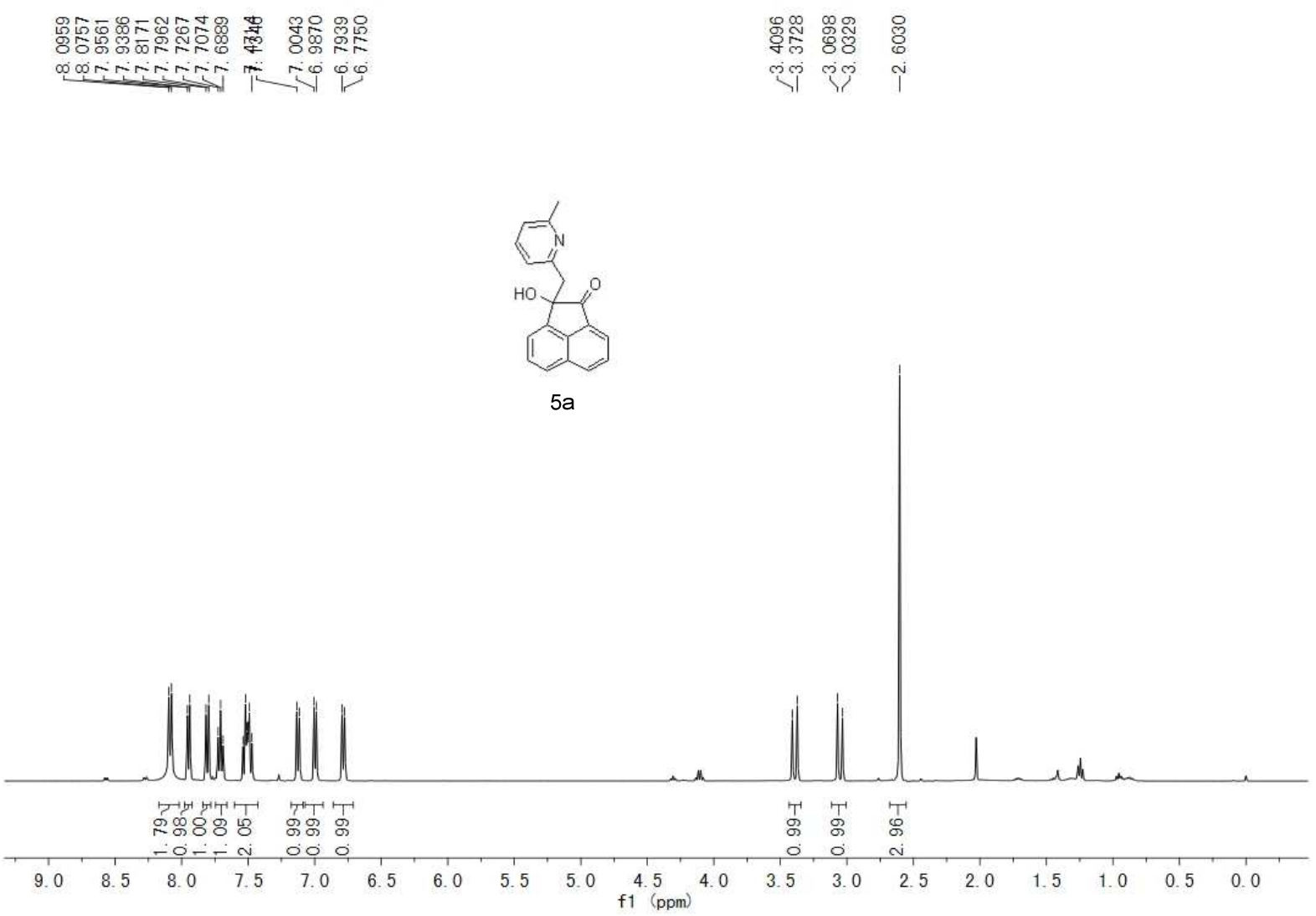

8.07
8.06
7.25
7.18
7.16
7.06
7.04
7.02
6.74
6.66
6.65
6.63
6.61
3.28
3.24
3.11
3.07
2.96
2.33
OH
O
N
3pa
0.94
1.19
0.99
1.03
0.99
2.02
1.05
1.03
2.86
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.56
157.51
147.87
143.98
142.89
129.72
129.09
125.11
124.25
122.87
122.52
108.28
77.32
77.00
76.69
43.79
25.84
23.67
N
OH
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

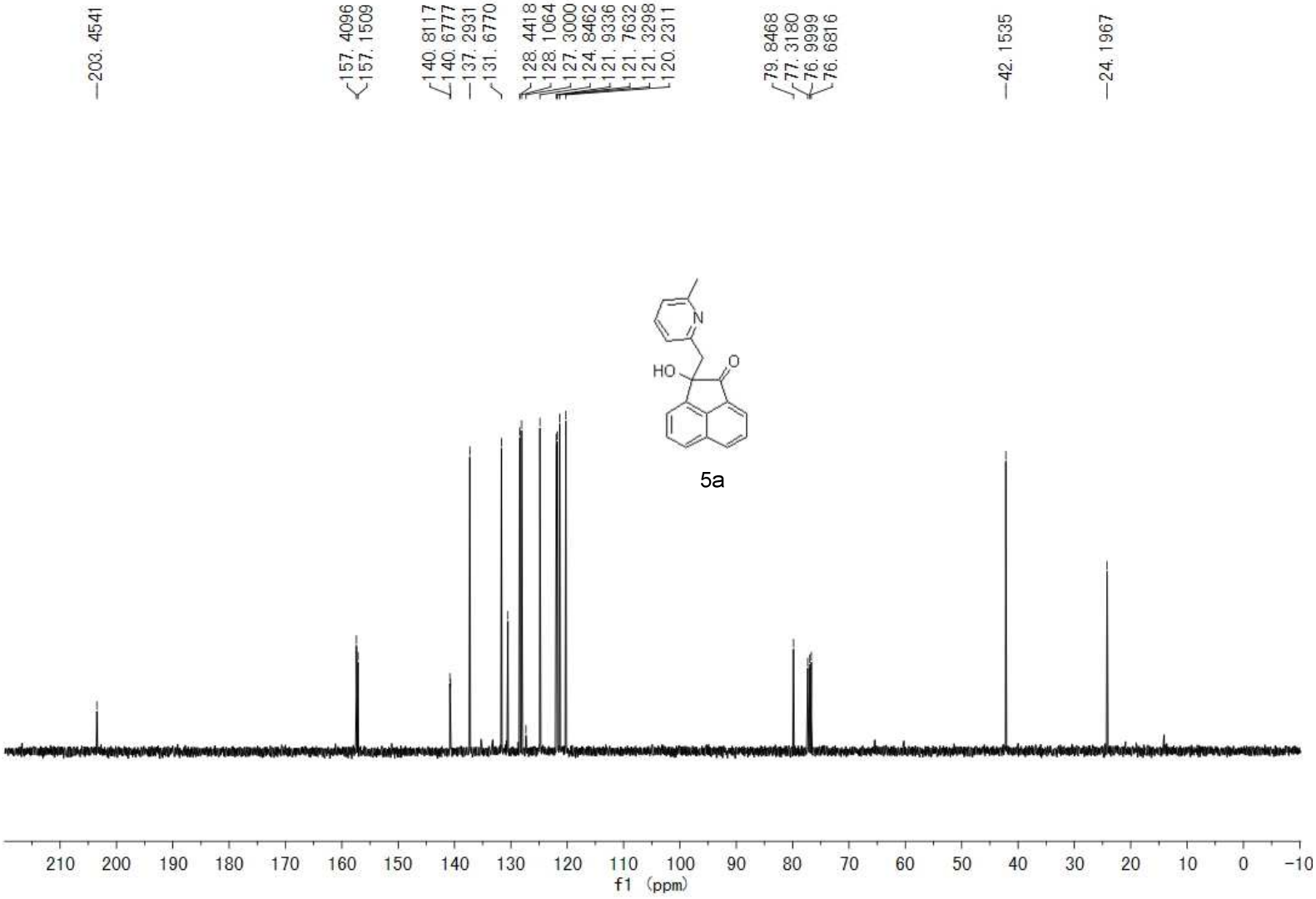
3pa


8.4291
8.4165
7.2800
7.2608
7.2415
7.0928
7.0806
6.9446
6.9261
6.9072
6.8652
6.8115
6.7927
3.3106
3.2734
3.1756
3.0229
2.9859
2.3192
OH
O
N
N
3pb
1.00
1.19
1.02
1.00
0.98
1.98
1.02
2.95
1.04
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)


176.8317
157.4595
148.4352
147.7820
142.9389
131.2212
129.2571
123.8613
123.2623
122.6787
108.1752
77.3178
77.0004
76.6826
76.2165
42.2926
26.1482
21.0741
OH
O
N
N
3pb
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)


8.0959
8.0757
7.9561
7.9386
7.8171
7.7962
7.7267
7.7074
7.6889
7.4346
7.0043
6.9870
6.7939
6.7750
3.4096
3.3728
3.0698
3.0329
2.6030
N
HO
O
1.79
0.98
1.00
1.09
2.05
0.99
0.99
0.99
0.99
0.99
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)

5a


203.4541
157.4096
157.1509
140.8117
140.6777
137.2931
131.6770
128.4418
128.1064
127.3000
124.8462
121.9336
121.7632
121.3298
120.2311
79.8468
77.3180
76.9999
76.6816
42.1535
24.1967
HO
O
N
5a
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)