Electronic Supplementary Material (ESI) for ChemComm.

Expeditious Synthesis of Multisubstituted Indoles via Multiple Hydrogen Transfers

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Supporting Information

General experimental procedures

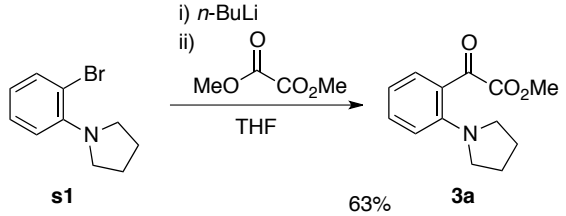
All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry nitrogen. Anhydrous ethereal solvents (THF, Et_2O) were purchased from Kanto Chemical Co., INC., and used directly. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2. Benzene and toluene were distilled over CaH_2, and stored over 4A molecular sieves. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH_2, and stored over 4A molecular sieves.

For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. Column chromatography and preparative TLC (PTLC) were performed on Silica Gel 60N (spherical, neutral), Kanto Chemical Ltd. and Wakogel B-5F, Wako Pure Chemical Industries, respectively.

Melting point (mp) determinations were performed by using a AS ONE ATM-01 instrument and are uncorrected. ^{1}H NMR, ^{13}C NMR were measured on a AL-300 MR (JEOL Ltd., 300 MHz) and ECX-400 (JEOL Ltd., 400 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane for ^{1}H, 0.00 ppm), and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). Elemental analysis (EA) was carried out on Flash2000 instrument (Amco Inc.).

1. Preparation of starting materials.

Scheme S1. Preparation of starting materials **3**. Preparation of **3a** was shown as a representative example.



Synthesis of methyl 2-oxo-2-(2-(pyrrolidin-1-yl)phenyl)acetate (3a):

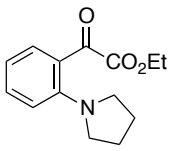
To a solution of **3**[1] (2.45 g, 10.8 mmol) in THF (40.0 mL) was added *n*-BuLi (1.60 M in hexane, 8.10 mL, 13.0 mmol) at –78 °C. After being stirred for 15 min, a solution of dimethyl oxalate (1.93 g, 13.0 mmol) in THF (14.0 mL) was added to the reaction mixture. After the reaction temperature was gradually warmed up to –20 °C for 2 h, the reaction was stopped by adding saturated aqueous NH_4Cl at 0 °C. The crude products were extracted with ether (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 15/1) to give **3a** (1.58 g, 63%) as orange yellow oil.

IR (neat) 3062, 2952, 2871, 1747, 1660, 1652, 1601, 1547, 1480, 1448, 1381, 1353, 1332, 1258, 1197, 1165, 1109, 1050, 997, 959, 908, 873, 835, 818, 790 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.94–2.05 (m, 4H), 3.15 (t, 4H, J = 6.6 Hz), 3.94 (s, 3H), 6.78 (ddd, 1H, J = 1.2, 8.4, 8.4 Hz), 6.90 (d, 1H, J = 8.4 Hz), 7.42 (ddd, 1H, J = 1.2, 8.4, 8.4 Hz), 7.49 (dd, 1H, J =1.2, 8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 52.1, 52.6, 115.0, 116.0, 120.1, 131.5, 134.0, 149.3, 165.1, 184.5.

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.74; H, 6.19; N, 5.89.



Ethyl 2-oxo-2-(2-(pyrrolidin-1-yl)phenyl)acetate (**3b**).

Pale yellow oil.

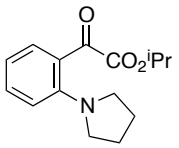
Yield: 50%.

IR (neat) 2974, 2875, 1730, 1658, 1600, 1546, 1493, 1480, 1448, 1370, 1184, 1165, 1108, 1017, 971, 772 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, 3H, *J* = 6.8 Hz), 1.92–2.07 (m, 4H), 3.11–3.21 (m, 4H), 4.41 (q, 2H, *J* = 6.8 Hz), 6.78 (dd, 1H, *J* = 8.0, 8.0 Hz), 6.90 (d, 1H, *J* = 8.0 Hz), 7.41 (ddd, 1H, *J* = 1.2, 8.0, 8.0 Hz), 7.52 (dd, 1H, *J* = 1.2, 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 25.7, 52.1, 62.1, 114.8, 115.9, 120.2, 131.7, 134.0, 149.3, 165.0, 185.0.

Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.26; H, 6.74; N, 5.75.



Isopropyl 2-oxo-2-(2-(pyrrolidin-1-yl)phenyl)acetate (**3c**).

Pale yellow oil.

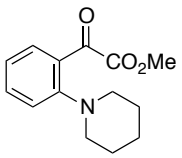
Yield: 43%.

IR (neat) 2978, 2871, 1725, 1660, 1600, 1546, 1493, 1480, 1448, 1375, 1325, 1262, 1186, 1167, 1099, 1050, 979, 955, 844, 745 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (d, 6H, *J* = 6.4 Hz), 1.90–2.02 (m, 4H), 3.10–3.20 (m, 4H), 5.26 (sept, 1H, *J* = 6.4 Hz), 6.76 (dd, 1H, *J* = 8.0, 8.0 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 7.39 (ddd, 1H, *J* = 1.2, 8.0, 8.0 Hz), 7.49 (dd, 1H, *J* = 1.2, 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 25.6, 52.0, 70.1, 114.7, 115.6, 119.9, 131.5, 119.9, 149.1, 164.6, 185.3.

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.70; H, 7.51; N, 5.14.



Methyl 2-oxo-2-(2-(piperidin-1-yl)phenyl)acetate (**3d**).

Yellow solid.

Yield: 46%.

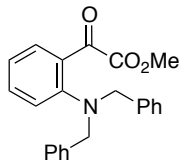
Mp. 76–79 °C.

IR (KBr) 2942, 2856, 2812, 1748, 1734, 1683, 1595, 1484, 1452, 1381, 1299, 1258, 1199, 1161, 1116, 1099, 1064, 1011, 921, 861, 815, 788 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.46–1.57 (m, 2H), 1.58–1.75 (m, 4H), 2.84 (t, 3H, J = 5.1 Hz), 3.88 (s, 3H), 7.22 (dd, 1H, J = 8.1, 8.1 Hz), 7.27 (d, 1H, J = 8.1 Hz), 7.57 (ddd, 1H, J = 1.5, 8.1, 8.1 Hz), 7.69 (dd, 1H, J = 1.5, 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 25.4, 52.1, 55.0, 120.7, 124.3, 130.0, 131.3, 134.4, 155.7, 164.7, 189.0.

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.74; H, 6.19; N, 5.89.



Methyl 2-(2-(dibenzylamino)phenyl)-2-oxoacetate (**3e**).

Yellow solid.

Yield: 64%.

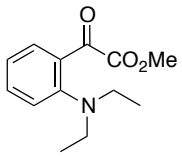
Mp. 59–61 °C.

IR (KBr) 3063, 3029, 2952, 2849, 1735, 1674, 1593, 1484, 1452, 1372, 1267, 1200, 1119, 1081, 1009, 913, 821 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.10 (s, 4H), 6.95 (d, 1H, J = 7.8 Hz), 7.00–7.09 (m, 4H), 7.16 (dd, 1H, J = 7.8, 7.8 Hz), 7.21–7.30 (m, 6H), 7.46 (ddd, 1H, J = 1.8, 7.8, 7.8 Hz), 7.72 (dd, 1H, J = 1.5, 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 57.5, 122.4, 122.9, 127.5, 128.2, 129.2, 129.3, 131.4, 133.9, 136.1, 152.8, 165.0, 188.5.

Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 76.98; H, 5.64; N, 3.74.



Methyl 2-(2-(diethylamino)phenyl)-2-oxoacetate (**3f**).

Yellow oil.

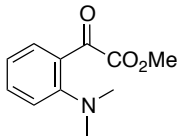
Yield: 41%.

IR (neat) 3068, 2976, 2873, 1734, 1680, 1594, 1485, 1452, 1381, 1318, 1300, 1261, 1236, 1201, 1178, 1100, 1063, 1045, 1011, 918, 896, 818, 787 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 6H, *J* = 7.2 Hz), 3.02 (q, 4H, *J* = 7.2 Hz), 3.84 (s, 3H), 7.13–7.21 (m, 2H), 7.54 (dd, 1H, *J* = 7.8, 7.8 Hz), 7.72 (d, 1H, *J* = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 10.8, 48.2, 52.0, 122.9, 123.9, 130.3, 131.8, 134.0, 152.9, 165.4, 189.3.

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.51; H, 7.13; N, 6.15.



Methyl 2-(2-(dimethylamino)phenyl)-2-oxoacetate (**3g**).

Yellow oil.

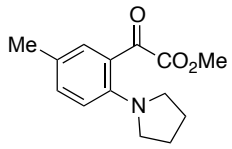
Yield: 83%.

IR (neat) 3068, 2985, 2951, 2868, 2837, 2794, 1736, 1684, 1595, 1488, 1456, 1433, 1317, 1302, 1252, 1151, 1117, 1100, 1043, 1011, 944, 920, 819, 790 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.65 (s, 6H), 3.80 (s, 3H), 7.12 (ddd, 1H, *J* = 0.9, 7.8, 7.8 Hz), 7.19 (d, 1H, *J* = 7.8 Hz), 7.52 (ddd, 1H, *J* = 1.5, 7.8, 7.8 Hz), 7.67 (dd, 1H, *J* = 1.5, 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 45.4, 51.9, 120.0, 123.4, 129.4, 130.2, 134.7, 155.4, 165.2, 188.4.

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.95; H, 6.14; N, 6.83.



Methyl 2-(5-methyl-2-(pyrrolidin-1-yl)phenyl)-2-oxoacetate (**3h**).

Yellow oil.

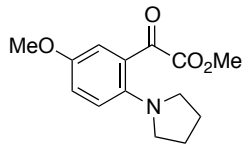
Yield: 55%.

IR (neat) 2952, 2923, 2871, 1736, 1660, 1618, 1572, 1543, 1500, 1483, 1462, 1434, 1415, 1355, 1284, 1262, 1247, 1223, 1184, 1159, 1122, 1033, 1012, 995, 960, 936, 876, 809, 774, cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.85–2.10 (m, 4H), 2.29 (s, 3H), 3.12 (t, 3H, J = 6.3 Hz), 3.93 (s, 3H), 6.89 (d, 1H, J = 8.2 Hz), 7.18–7.38 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 25.4, 52.4, 52.4, 115.9, 121.5, 126.4, 130.8, 135.4, 148.0, 165.2, 185.2.

Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.15; H, 7.11; N, 5.86.



Methyl 2-(5-methoxy-2-(pyrrolidin-1-yl)phenyl)-2-oxoacetate (**3i**).

Orange oil.

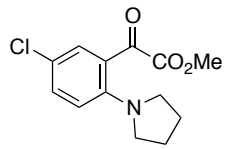
Yield: 64%.

IR (neat) 2953, 2873, 2837, 1733, 1676, 1606, 1574, 1548, 1496, 1463, 1445, 1420, 1353, 1333, 1286, 1263, 1232, 1194, 1159, 1113, 1022, 960, 876, 830, 802, 773 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.85–2.05 (m, 4H), 3.02 (t, 4H, J = 6.3 Hz), 3.80 (s, 3H), 3.87 (s, 3H), 7.03–7.20 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 24.9, 52.2, 53.7, 55.7, 112.5, 120.4, 122.9, 127.5, 145.8, 154.2, 164.9, 187.0.

Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.68; H, 6.78; N, 5.08.



Methyl 2-(5-chloro-2-(pyrrolidin-1-yl)phenyl)-2-oxoacetate (**3j**).

Orange oil.

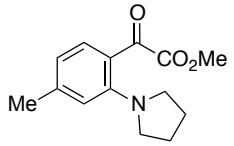
Yield: 64%.

IR (neat) 2953, 2871, 1735, 1667, 1599, 1534, 1494, 1480, 1462, 1435, 1416, 1354, 1331, 1280, 1270, 1247, 1193, 1166, 1115, 1001, 959, 918 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (t, 4H, J = 6.4 Hz), 3.12 (t, 4H, J = 6.4 Hz), 3.96 (s, 3H), 6.85 (d, 1H, J = 8.8 Hz), 7.35 (dd, 1H, J = 2.0, 8.8 Hz), 7.49 (d, 1H, J = 2.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 52.4, 52.8, 116.5, 120.7, 120.8, 130.4, 133.9, 147.9, 164.3, 183.4.

Anal. Calcd for $C_{13}H_{17}ClNO_3$: C, 58.32; H, 5.27; N, 5.23. Found: C, 58.03; H, 5.48; N, 5.46.



Methyl 2-(4-methyl-2-(pyrrolidin-1-yl)phenyl)-2-oxoacetate (**3k**).

Yellow solid.

Yield: 48%.

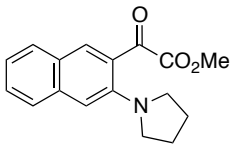
Mp. 81–83 °C.

IR (neat) 2952, 2871, 1735, 1655, 1609, 1539, 1495, 1449, 1349, 1335, 1260, 1207, 1192, 1174, 1122, 999, 909, 880, 834, 801, 746 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.88–1.98 (m, 4H), 2.35 (s, 3H), 3.16 (t, 4H, J = 6.3 Hz), 3.92 (s, 3H), 6.61 (dd, 1H, J = 1.2, 8.1 Hz), 6.70 (s, 1H), 7.42 (d, 1H, J = 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 25.6, 52.1, 52.6, 115.2, 117.6, 117.9, 131.9, 145.3, 149.7, 165.5, 183.9.

Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.25; H, 6.78; N, 5.46.



Methyl 2-oxo-2-(3-(pyrrolidin-1-yl)naphthalen-2-yl)acetate (**3l**).

Yellow oil.

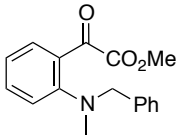
Yield: 44%.

IR (neat) 3055, 2952, 2872, 2835, 1736, 1684, 1625, 1591, 1497, 1458, 1364, 1342, 1296, 1242, 1162, 1146, 1118, 1043, 1003, 956, 909, 879, 819 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.84–1.92 (m, 4H), 3.08 (t, 4H, J = 6.3 Hz), 3.84 (s, 3H), 7.13–7.27 (m, 2H), 7.40 (ddd, 1H, J = 1.2, 8.1, 8.1 Hz), 7.61 (d, 1H, J = 8.1 Hz), 7.71 (d, 1H, J = 8.1 Hz), 8.05 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 52.7, 52.9, 112.3, 124.0, 126.5, 127.2, 127.3, 128.9, 129.2, 132.4, 136.9, 146.1, 164.7, 187.5.

Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 71.87; H, 6.23; N, 5.21.



Methyl 2-(2-(benzyl(methyl)amino)phenyl)-2-oxoacetate (**3m**).

Yellow oil.

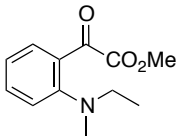
Yield: 85%.

IR (neat) 3067, 3030, 2951, 2845, 2804, 1733, 1677, 1593, 1485, 1453, 1299, 1260, 1200, 1179, 1100, 1010, 914, 768 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (s, 3H), 3.74 (s, 3H), 4.01 (s, 2H), 6.94–7.04 (m, 3H), 7.11 (dd, 1H, J = 7.8, 7.8 Hz), 7.16–7.26 (m, 3H), 7.45 (dd, 1H, J = 7.8, 7.8 Hz), 7.66 (d, 1H, J = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 41.7, 52.2, 62.4, 121.6, 123.6, 127.5, 128.1, 129.4, 129.8, 130.7, 134.3, 135.9, 154.2, 165.1, 188.5.

Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.01; H, 5.86; N, 5.12.



Methyl 2-(2-(ethyl(methyl)amino)phenyl)-2-oxoacetate (**3n**).

Yellow oil.

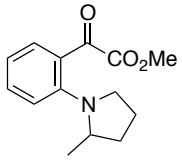
Yield: 61%.

IR (neat) 3068, 2976, 2952, 2874, 2851, 2807, 1746, 1733, 1682, 1594, 1486, 1454, 1435, 1385, 1301, 1267, 1243, 1201, 1180, 1150, 1124, 1100, 1078, 1060, 1042, 1011, 920, 890, 819, 790 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, 3H, *J* = 7.2 Hz), 2.66 (s, 3H), 2.96 (q, 2H, *J* = 7.2 Hz), 3.85 (s, 3H), 7.15–7.29 (m, 2H), 7.57 (ddd, 1H, *J* = 1.2, 7.8, 7.8 Hz), 7.74 (dd, 1H, *J* = 1.2, 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 42.0, 52.0, 52.2, 121.7, 124.1, 130.1, 131.0, 134.5, 154.5, 165.2, 188.8.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.38; H, 6.54; N, 6.47.



Methyl 2-(2-(2-methylpyrrolidin-1-yl)phenyl)-2-oxoacetate (**3o**).

Orange oil.

Yield: 54%.

IR (neat) 3032, 2967, 2872, 2842, 1735, 1679, 1595, 1547, 1484, 1453, 1378, 1341, 1291, 1200, 1171, 1110, 1011, 790, 750 cm^{-1}.

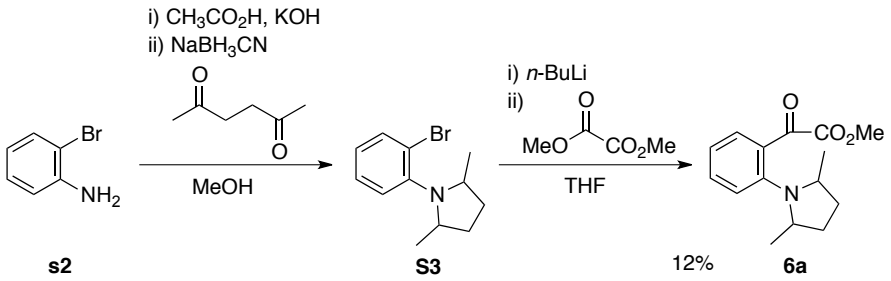
^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (d, 3H, *J* = 6.4 Hz), 1.52–1.66 (m, 1H), 1.69–1.82 (m, 1H), 1.85–1.98 (m, 1H), 2.13–2.25 (m, 1H), 2.72–2.82 (m, 1H), 3.38–3.48 (m, 1H), 3.60–3.70 (m, 1H), 3.88 (s, 3H), 7.00 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.10 (d, 1H, *J* = 7.6 Hz), 7.49 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.63 (dd, 1H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 23.7, 33.6, 52.3, 55.6, 56.6, 118.4, 120.2, 126.8, 130.0, 134.2, 150.1, 165.4, 187.0.

Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.26; H, 6.65; N,

6.74.

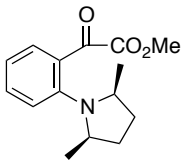
Scheme S2. Preparation of starting materials **6**. Preparation of **6a** was shown as a representative example.[2]



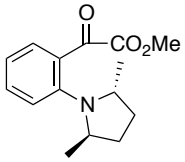
Synthesis of methyl 2-(2-(2,5-dimethylpyrrolidin-1-yl)phenyl)-2-oxoacetate (cis-6a):

To a solution of commercially available **s2** (1.33 g, 7.74 mmol) in MeOH (3.9 mL) were successively added AcOH (0.49 mL, 8.51 mmol) and KOH (24.0 mg, 0.428 mmol) at –10 °C. After being stirred for 5 min, 2,4-hexanedione (0.90 mL, 7.7 mmol) was added to the reaction mixture at –10 °C. After being stirred for 20 h, the reaction temperature was warmed-up to room temperature. After being stirred for 2 h, the reaction was stopped by adding saturated aqueous $NaHCO_3$ at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc =100/1) to give **s3** (455 mg) with inseparable impurities. This material was used to next reaction without further purification.

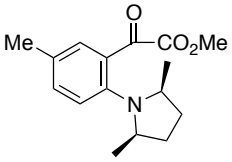
To a solution of **s3** (455 mg, 1.74 mmol) in THF (5.7 mL) was added *n*-BuLi (1.60 M in hexane, 1.30 mL, 2.09 mmol) at –78 °C. After being stirred for 15 min, a solution of dimethyl oxalate (321 mg, 2.71 mmol) in THF (3.0 mL) was added to the reaction mixture. After the reaction temperature was gradually warmed up to –20 °C for 2 h, the reaction was stopped by adding saturated aqueous NH_4Cl at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 20/1) to give **6a** (242 mg, 12% from **s2**) as yellow solid.



Mp. 60–62 °C (recrystallized from Hexane, which was subjected to the X-ray analysis).
IR (KBr) 2965, 2872, 2840, 1735, 1680, 1594, 1483, 1452, 1434, 1377, 1319, 1301, 1273, 1242, 1200, 1180, 1165, 1105, 1048, 1012, 926, 918, 790, 765 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, 6H, *J* = 6.8 Hz), 1.40–1.53 (m, 2H), 1.93–2.06 (m, 2H), 3.03–3.15 (m, 2H), 3.88 (s, 3H), 7.30 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.35 (d, 1H, *J* = 8.0 Hz), 7.62 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.79 (d, 1H, *J* = 8.0 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 31.0, 52.0, 62.4, 122.3, 125.3, 129.9, 134.7, 135.2, 150.1, 165.7, 189.9.
Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.77; H, 7.16; N, 5.15.



Methyl 2-(2-(2,5-dimethylpyrrolidin-1-yl)phenyl)-2-oxoacetate (*trans*-**6a**).
Yellow amorphous.
Yield: 5% (from **s2**).
IR (neat) 2966, 2931, 2872, 1735, 1679, 1593, 1574, 1481, 1454, 1434, 1377, 1350, 1286, 124, 1199, 1178, 1163, 1142, 1104, 1051, 1009, 789 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) δ 0.54–0.73 (brm, 3H), 1.07–1.15 (brm, 3H), 1.35–1.60 (brm, 2H), 2.10–2.23 (brm, 2H), 3.68–3.86 (brm, 2H), 3.84 (s, 3H), 7.02–7.10 (m, 1H), 7.09 (d, 1H, *J* = 8.0 Hz), 7.51 (ddd, 1H, *J* = 1.6, 8.0, 8.0 Hz), 7.66 (dd, 1H, *J* = 1.6, 8.0 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 18.6, 31.1, 32.6, 52.0, 52.3, 62.2, 121.8, 122.0, 130.5, 130.6, 133.7, 148.7, 165.7, 188.9.
Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.99; H, 7.42; N, 5.26.



Methyl 2-(2-(2,5-dimethylpyrrolidin-1-yl)-5-methylphenyl)-2-oxoacetate (**6b**).

Orange solid.

Yield: 32%.

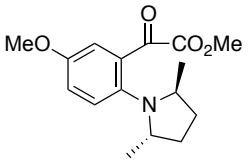
Mp. 101–107 °C.

IR (neat) 2963, 2871, 2363, 1735, 1680, 1609, 1495, 1457, 1376, 1316, 1271, 1225, 1154, 1119, 1037, 995 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, 6H, *J* = 6.4 Hz), 1.38–1.52 (m, 2H), 1.91–2.06 (m, 2H), 2.34 (s, 3H), 2.98–3.10 (m, 2H), 3.87 (s, 3H), 7.24 (d, 1H, *J* = 8.0 Hz), 7.43 (dd, 1H, *J* = 1.6, 8.0 Hz), 7.60 (d, 1H, *J* = 1.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 20.7, 31.0, 51.9, 62.5, 122.1, 130.0, 135.2, 135.4, 135.7, 147.6, 165.8, 190.3.

Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.57; H, 7.83; N, 4.89.



Methyl 2-(2-(2,5-dimethylpyrrolidin-1-yl)-5-methoxyphenyl)-2-oxoacetate (**6c**).

Yellow amorphous.

Yield: 22%.

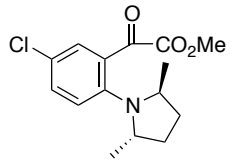
IR (neat) 2963, 2871, 2837, 1735, 1675, 1607, 1571, 1494, 1464, 1419, 1378, 1282, 1263, 1231, 1194, 1163, 1142, 1109, 1040, 1021, 946, 875 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.63 (d, 1H, *J* = 7.0 Hz), 1.05 (d, 1H, *J* = 7.0 Hz), 1.32–1.57 (m, 2H), 2.07–2.23 (m, 2H), 3.53–3.74 (m, 2H), 3.82 (s, 3H), 3.85 (s, 3H), 7.07 (d, 1H, *J* = 8.8 Hz), 7.13 (dd, 1H, *J* = 3.2, 8.8 Hz), 7.21 (d, 1H, *J* = 3.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 18.3, 30.7, 32.6, 52.1, 52.3, 55.6, 62.6, 112.5, 121.8, 123.9, 132.1, 142.6, 155.4, 165.7, 189.1.

Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81. Found: C, 66.21; H, 7.14; N,

4.73.



Methyl 2-(5-chloro-2-(-2,5-dimethylpyrrolidin-1-yl)phenyl)-2-oxoacetate (**6d**).

Yellow amorphous.

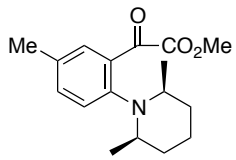
Yield: 31%.

IR (neat) 2966, 2931, 2872, 1735, 1684, 1591, 1478, 1435, 1407, 1378, 1349, 1290, 1244, 1194, 1174, 1148, 1117, 1046, 1021, 957, 933 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.59–0.73 (brm, 3H), 1.01–1.15 (brm, 3H), 1.41–1.62 (brm, 2H), 2.12–2.25 (brm, 2H), 3.66–3.81 (brm, 2H), 3.85 (s, 3H), 7.04 (d, 1H, J = 8.8 Hz), 7.46 (dd, 1H, J = 2.4, 8.8 Hz), 7.61 (d, 1H, J = 2.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 18.6, 31.2, 32.6, 52.3, 52.6, 62.3, 123.1, 127.3, 129.9, 131.5, 133.6, 147.2, 165.0, 187.6.

Anal. Calcd for $C_{15}H_{18}ClNO_3$: C, 60.91; H, 6.13; N, 4.74. Found: C, 60.79; H, 6.25; N, 4.48.



Methyl 2-(2-(2,6-dimethylpiperidin-1-yl)-5-methylphenyl)-2-oxoacetate (**6e**).

Yellow solid.

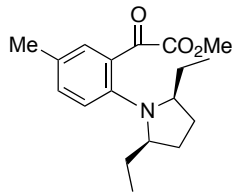
Yield: 25%.

IR (neat) 2973, 2935, 2858, 2799, 1736, 1673, 1607, 1574, 1495, 1455, 1435, 1406, 1375, 1318, 1261, 1223, 1156, 1119, 1085, 1037, 996, 851, 822, 801, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (d, 6H, J = 6.4 Hz), 1.22–1.84 (m, 6H), 2.38 (s, 3H), 2.69–2.85 (m, 2H), 3.93 (s, 3H), 7.25 (d, 1H, J = 8.0 Hz), 7.41 (d, 1H, J = 8.0 Hz), 7.66 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.7, 24.7, 34.3, 51.9, 60.1, 124.3, 129.6, 134.8, 135.6, 135.8, 149.9, 165.8, 189.9.

Anal. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.78; H, 7.84; N, 4.62.



Methyl 2-(2-(2,5-diethylpyrrolidin-1-yl)-5-methylphenyl)-2-oxoacetate (**6f**).

Yellow oil.

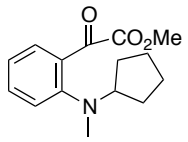
Yield: 22% (reaction with octane-3,6-dione).

IR (neat) 2962, 2928, 2874, 1724, 1620, 1589, 1477, 1462, 1361, 1283, 1226, 1148, 1064, 860, 782 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, 6H, J = 7.2 Hz), 1.18–1.46 (m, 6H), 1.98–2.12 (m, 2H), 2.38 (s, 3H), 2.75–2.93 (m, 2H), 3.85 (s, 3H), 7.24–7.31 (m, 2H), 7.42 (d, 1H, J = 8.0 Hz), 7.58 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 20.8, 25.5, 28.6, 52.0, 122.3, 130.0, 135.4, 136.0, 148.0, 165.7, 190.3.

Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62. Found: C, 71.48; H, 8.16; N, 4.53.



Methyl 2-(2-(cyclopentyl(methyl)amino)phenyl)-2-oxoacetate (**6g**).

Yellow oil.

Yield: 60%.

IR (neat) 2956, 2870, 2799, 1733, 1681, 1594, 1484, 1454, 1434, 1358, 1321, 1300, 1200, 1101, 1012, 920, 774, 746 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.29–1.80 (m, 8H), 2.60 (s, 3H), 3.32 (quint, 1H, J = 8.0 Hz), 3.87 (s, 3H), 7.22–7.28 (m, 1H), 7.31 (d, 1H, J = 8.0 Hz), 7.31 (ddd, 1H, J = 1.6, 8.0, 8.0 Hz), 7.77 (dd, 1H, J = 1.6, 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 30.5, 42.6, 52.0, 66.5, 123.3, 124.9, 129.8, 132.3, 134.5, 155.2, 165.1, 189.2.

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.73; H, 7.47; N, 5.58.

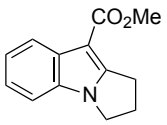
2. Synthesis of multisubstituted indoles.

General Procedure of the formation of 3-methoxycarbonylindoles.

To a solution of *o*-amino ketoester **3** (0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) were successively added DMC (1 M in CH_2Cl_2, 100 μl, 0.10 mmol) and $TiCl_4$ (1 M in CH_2Cl_2, 30 μl, 0.030 mmol)), and the mixture was heated at reflux. After completion of the reaction, the reaction mixture was filtered through a short pad of silica-gel and the resulting filtrate was concentrated in vacuo. The residue was purified by preparative TLC to give 3-alkoxycarbonylindoles **4**.

General Procedure of the formation of 3-alkylindole derivatives.

To a solution of ketoester **6** (0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added $TiCl_4$ (1 M in CH_2Cl_2, 100 μl, 0.10 mmol)), and the mixture was heated at reflux. After completion of the reaction, the reaction mixture was filtered through a short pad of silica-gel and the resulting filtrate was concentrated in vacuo. The residue was purified by preparative TLC to give 3-alkylindoles **8**.



Methyl 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4a**).

White solid.

Yield: 77%.

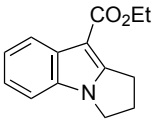
Mp. 90–92 °C.

IR (KBr) 3052, 2948, 2895, 1693, 1615, 1548, 1478, 1455, 1442, 1421, 1377, 1336, 1301, 1286, 1261, 1206, 1150, 1125, 1108, 1032, 1012, 783, 749 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.67 (tt, 2H, *J* = 7.5, 7.5 Hz), 3.21 (t, 2H, *J* = 7.5 Hz), 4.12 (t, 2H, *J* = 7.5 Hz), 3.93 (s, 3H), 7.20–7.30 (m, 3H), 8.10–8.17 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 26.5, 44.3, 50.6, 98.9, 109.7, 121.3, 121.5, 121.6, 130.8, 132.6, 152.8, 165.8.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.37; H, 5.82; N, 6.27.



Ethyl 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4b**).

Yellow solid.

Yield: 64%.

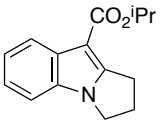
Mp. 96–97 °C.

IR (KBr) 3052, 2948, 2895, 1693, 1615, 1548, 1478, 1455, 1442, 1421, 1377, 1336, 1301, 1286, 1261, 1206, 1150, 1125, 1108, 1032, 1012, 783, 749 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, 3H, *J* = 6.8 Hz), 2.61 (tt, 2H, *J* = 7.2, 7.2 Hz), 3.24 (t, 2H, *J* = 7.2 Hz), 4.05 (t, 2H, *J* = 7.2 Hz), 4.35 (q, 2H, *J* = 6.8 Hz), 7.14–7.27 (m, 3H), 8.10 (d, 1H, *J* = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 26.0, 26.5, 44.3, 59.2, 99.2, 109.7, 121.3, 121.5, 121.6, 130.9, 132.6, 152.8, 165.5.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.11; H, 6.57; N, 6.03.



Isopropyl 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4c**).

Yellow solid.

Yield: 67%.

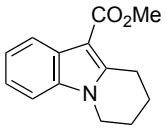
Mp. 94–96 °C.

IR (KBr) 3053, 2979, 2933, 1687, 1544, 1480, 1451, 1427, 1383, 1340, 1301, 1262, 1206, 1152, 1128, 1094, 1018, 784 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, 6H, *J* = 6.4 Hz), 2.64 (tt, 2H, *J* = 7.2, 7.2 Hz), 3.28 (t, 2H, *J* = 7.2 Hz), 4.09 (t, 2H, *J* = 7.2 Hz), 4.35 (sept, 1H, *J* = 6.4 Hz), 7.17–7.29 (m, 3H), 8.10 (dd, 1H, *J* = 1.2, 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 26.1, 26.6, 44.4, 66.4, 99.7, 109.7, 121.4, 121.5, 121.6, 130.9, 132.6, 152.7, 165.1.

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.86; H, 7.95; N, 6.02.



Methyl 6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-carboxylate (**4d**).

Yellow solid.

Yield: 71%.

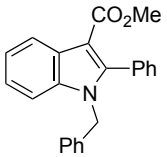
Mp. 106–108 °C.

IR (KBr) 3053, 2947, 2870, 1690, 1531, 1476, 1458, 1419, 1377, 1319, 1271, 1208, 1145, 1114, 1071, 1040, 1015, 783, 752 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.89–1.98 (m, 2H), 2.04–2.14 (m, 2H), 3.33 (t, 2H, J = 6.3 Hz), 3.92 (s, 3H), 4.06 (t, 2H, J = 6.3 Hz), 7.18–7.30 (m, 3H), 8.08–8.15 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 22.5, 24.5, 42.4, 50.5, 102.3, 108.8, 121.0, 121.6, 121.9, 126.5, 135.9, 145.9, 166.3.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.08; H, 6.36; N, 5.95.



Methyl 1-benzyl-2-phenyl-1*H*-indole-3-carboxylate (**4e**).

Yellow solid.

Yield: 63%.

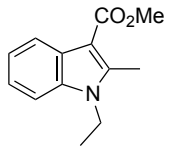
Mp. 136–138 °C.

IR (KBr) 3060, 3033, 2947, 1696, 1605, 1541, 1482, 1460, 1403, 1350, 1282, 1233, 1149, 1118, 1083, 1029, 913, 790 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.23 (s, 2H), 6.91–6.98 (m, 2H), 7.23–7.55 (m, 11H), 8.31 (d, 1H, J = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 47.5, 50.7, 110.7, 122.0, 122.2, 123.1, 126.0, 126.7, 127.4, 128.0, 128.7, 129.0, 130.1, 131.2, 136.3, 136.8, 147.1, 165.5.

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.75; H, 5.38; N, 3.82.



Methyl 1-ethyl-2-methyl-1*H*-indole-3-carboxylate (**4f**).

Yellow solid.

Yield: 55%.

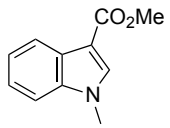
Mp. 44–46 °C.

IR (KBr) 3051, 2981, 2947, 1693, 1612, 1538, 1463, 1438, 1414, 1372, 1341, 1285, 1256, 1214, 1186, 1156, 1135, 1108, 1053, 1021, 999, 955, 928, 785 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, 3H, J = 7.2 Hz), 2.78 (s, 3H), 3.93 (s, 3H), 4.18 (q, 2H, J = 7.2 Hz), 7.19–7.38 (m, 3H), 8.08–8.18 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 14.8, 37.8, 50.6, 103.8, 109.0, 121.5, 121.5, 121.9, 126.7, 135.3, 144.5, 166.6.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.95; H, 7.12; N, 6.27.



Methyl 1-methyl-1*H*-indole-3-carboxylate (**4g**).

Brown solid.

Yield: 49%.

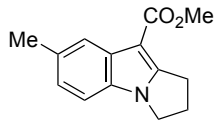
Mp. 78–80 °C.

IR (KBr) 3118, 3052, 2947, 2850, 1697, 1536, 1468, 1437, 1383, 1336, 1263, 1226, 1190, 1152, 1128, 1104, 1063, 1022, 929, 775 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.87 (s, 3H), 7.18-7.39 (m, 3H), 7.72 (s, 1H), 8.08-8.20 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4, 50.9, 106.8, 109.7, 121.5, 121.8, 122.7, 126.5, 135.1, 137.1, 165.4.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.65; H, 6.00; N, 7.69.



Methyl 7-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4h**).

Yellow solid.

Yield: 67%.

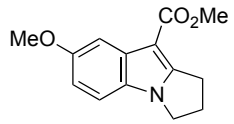
Mp. 145–147 °C.

IR (KBr) 2945, 2917, 2853, 1690, 1546, 1455, 1423, 1375, 1318, 1279, 1213, 1189, 1153, 1112, 809, 782 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.63 (tt, 2H, *J* = 7.5, 7.5 Hz), 3.27 (t, 2H, *J* = 7.5 Hz), 3.89 (s, 3H), 4.07 (t, 2H, *J* = 7.5 Hz), 7.01 (d, 1H, *J* = 8.1 Hz), 7.13 (d, 1H, *J* = 8.1 Hz), 7.90 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 26.1, 26.5, 44.4, 50.6, 98.5, 109.4, 121.1, 123.0, 130.9, 131.0, 131.1, 152.8, 166.0.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.15; H, 6.33; N, 6.23.



Methyl 7-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4i**).

White solid.

Yield: 57%.

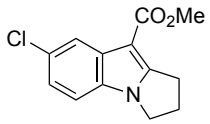
Mp. 103–105 °C.

IR (KBr) 2984, 2948, 2901, 2834, 1691, 1620, 1575, 1542, 1476, 1454, 1377, 1321, 1298, 1263, 1228, 1195, 1158, 1129, 1106, 1041, 1019, 982, 853, 799, 779 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.61 (tt, 2H, *J* = 7.5, 7.5 Hz), 3.24 (t, 2H, *J* = 7.5 Hz), 3.88 (s, 3H), 3.89 (s, 3H), 4.04 (t, 2H, *J* = 7.5 Hz), 6.82 (d, 1H, *J* = 8.7 Hz), 7.10 (d, 1H, *J* = 8.7 Hz), 7.62 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 26.5, 44.6, 50.6, 55.8, 98.7, 103.4, 110.5, 111.5, 127.7, 131.8, 152.9, 155.6, 165.9.

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.37; H, 5.96; N, 5.92.



Methyl 7-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4j**).

White solid.

Yield: 73%.

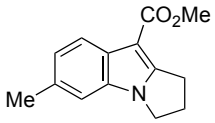
Mp. 124–127 °C.

IR (KBr) 2982, 2948, 2899, 1694, 1613, 1550, 1487, 1453, 1433, 1423, 1372, 1318, 1245, 1204, 1137, 1112, 1062, 1030, 973, 876 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (tt, 2H, *J* = 7.6, 7.6 Hz), 3.23 (t, 2H, *J* = 7.6 Hz), 3.88 (s, 3H), 3.89 (s, 3H), 4.04 (t, 2H, *J* = 7.6 Hz), 7.07 (d, 1H, *J* = 8.8 Hz), 7.09 (d, 1H, *J* = 2.0, 8.8 Hz), 8.03 (d, 1H, *J* = 2.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 26.5, 44.6, 50.8, 98.9, 110.7, 120.8, 121.8, 127.4, 130.9, 131.7, 153.9, 165.4.

Anal. Calcd for $C_{13}H_{13}ClNO_2$: C, 62.53; H, 4.84; N, 5.61. Found: C, 62.76; H, 4.74; N, 5.43.



Methyl 6-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4k**).

Pale green solid.

Yield: 64%.

Mp. 150–152 °C.

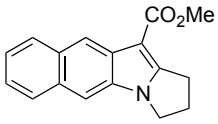
IR (KBr) 2947, 2921, 2849, 1692, 1547, 1441, 1420, 1381, 1335, 1300, 1279, 1262, 1207, 1129, 1104, 1027, 810, 743 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 2.60 (tt, 2H, *J* = 7.5, 7.5 Hz), 3.23 (t, 2H, *J* = 7.5 Hz), 3.89 (s, 3H), 4.01 (t, 2H, *J* = 7.5 Hz), 7.02 (s, 1H), 7.05 (d, 1H, *J* = 8.1 Hz), 7.96 (d, 1H, *J* = 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 26.0, 26.5, 44.2, 50.6, 98.8, 109.8, 120.9, 123.1, 128.6, 131.4, 132.9, 152.3, 165.9.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.08; H, 6.47; N,

6.26.



Methyl 2,3-dihydro-1*H*-benzo[*f*]pyrrolo[1,2-*a*]indole-11-carboxylate (**4l**).

Brown solid.

Yield: 61%.

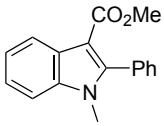
Mp. 152–154 °C.

IR (KBr) 3050, 2947, 2898, 2849, 1691, 1558,, 1450, 1420, 1381, 1365, 1320, 1301, 1262, 1217, 1193, 1161, 1102, 1013, 983, 908, 885, 856, 829, 780 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ 2.68 (tt, 2H, *J* = 7.2 Hz), 3.33 (t, 2H, *J* = 7.2 Hz), 3.95 (s, 3H), 4.13 (t, 2H, *J* = 7.2 Hz), 7.34-7.44 (m, 2H), 7.60 (s, 1H), 7.82-7.94 (m, 1H), 7.95-8.05 (m, 1H), 8.57 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 26.4, 44.3, 50.7, 97.7, 105.4, 118.8, 123.3, 123.9, 127.3, 128.4, 129.6, 129.8, 131.7, 133.3, 157.7, 165.7.

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.25; H, 5.46; N, 5.07.



Methyl 1-methyl-2-phenyl-1*H*-indole-3-carboxylate (**4m**).

Orange oil.

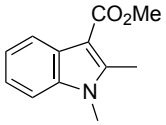
Yield: 63%.

IR (neat) 3053, 2947, 1703, 1539, 1468, 1439, 1394, 1274, 1232, 1196, 1102, 1022, 820, 790 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 3.76 (s, 3H), 7.22–7.55 (m, 8H), 8.20–8.30 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8, 50.7, 104.9, 109.7, 121.9, 122.1, 122.8, 126.5, 128.0, 128.9, 130.2, 131.4, 136.7, 146.9, 165.5.

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.80; H, 5.46; N, 5.18.



Methyl 1-ethyl-2-methyl-1*H*-indole-3-carboxylate (**4n**).

Red solid.

Yield: 52%.

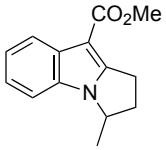
Mp. 96–98 °C.

IR (KBr) 3072, 2941, 1691, 1533, 1439, 1407, 1274, 1211, 1160, 1105, 783 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.78 (s, 3H), 3.70 (s, 3H), 3.95 (s, 3H), 7.20–7.35 (m, 3H), 8.09–8.16 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.7, 29.4, 50.6, 103.6, 109.0, 121.3, 121.5, 121.9, 126.4, 136.4, 145.3, 166.5.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.24; H, 6.39; N, 7.08.



Methyl 3-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (**4o**).

Pale yellow solid.

Yield: 75%.

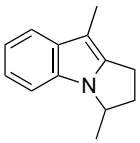
Mp. 88–90 °C.

IR (KBr) 3049, 2970, 2948, 2927, 1694, 1612, 1554, 1482, 1458, 1441, 1420, 1374, 1290, 1205, 1152, 1129, 1108, 1084, 1051, 784, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (d, 3H, J = 6.4 Hz), 2.19–2.30 (m, 1H), 2.75–2.89 (m, 1H), 3.18–3.38 (m, 2H), 3.89 (s, 3H), 4.58–4.70 (m, 1H), 7.15–7.26 (m, 2H), 7.32 (d, 1H, J = 8.4 Hz), 8.11 (d, 1H, J = 8.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 25.1, 35.1, 50.7, 53.7, 98.8, 109.9, 121.5, 121.5, 121.5, 131.1, 132.0, 152.4, 166.0.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.51; H, 6.79; N, 6.38.



3,9-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**8a**).

Yellow solid.

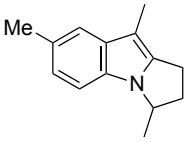
Yield: 31% from *cis*-**6a**; 27% from *trans*-**6a**.

IR (KBr) 2963, 2924, 2855, 1734, 1684, 1653, 1617, 1559, 1540, 1507, 1458, 1355, 1325, 1301, 1230 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, 1H, J = 6.4 Hz), 2.12–2.23 (m, 1H), 2.24 (s, 3H), 2.67–3.04 (m, 3H), 4.46–4.57 (m, 1H), 7.01–7.12 (m, 1H), 7.27 (d, 1H, J = 7.6 Hz), 7.47 (d, 1H, J = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 20.4, 21.9, 36.2, 52.4, 100.3, 109.1, 118.2, 118.4, 119.8, 131.9, 133.3, 141.0.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.11; H, 8.03; N, 7.73.



3,7,9-Trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**8b**).

Yellow amorphous.

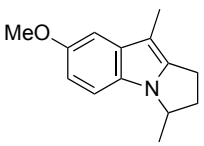
Yield: 35%.

IR (neat) 2965, 2919, 2856, 1700, 1593, 1456, 1406, 1371, 1354, 1309, 1281, 1233, 1149, 1083, 1040, 863, 786 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H, J = 6.4 Hz), 2.09–2.20 (m, 1H), 2.20 (s, 3H), 2.44 (s, 3H), 2.65–3.04 (m, 3H), 4.42–4.53 (m, 1H), 6.90 (d, 1H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.25 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 8.8, 20.4, 21.5, 22.0, 36.2, 52.4, 99.8, 108.8, 118.2, 121.3, 127.3, 130.2, 133.6, 141.1.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.56; H, 8.38; N, 7.25.



7-Methoxy-3,9-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**8c**).

Colorless amorphous.

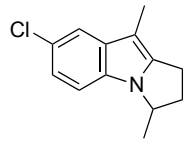
Yield: 30%.

IR (neat) 2965, 2926, 2857, 2828, 1592, 1568, 1480, 1454, 1412, 1374, 1352, 1308, 1226, 1179, 1146, 1048, 1030, 889 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H, J = 6.4 Hz), 2.09–2.20 (m, 1H), 2.21 (s, 3H), 2.66–3.04 (m, 3H), 3.86 (s, 3H), 4.42–4.53 (m, 1H), 6.74 (dd, 1H, J = 2.4, 8.8 Hz), 6.94 (d, 1H, J = 2.4 Hz), 7.17 (d, 1H, J = 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 20.4, 22.1, 36.2, 52.6, 56.0, 100.0, 100.9, 109.6, 109.8, 127.3, 133.6, 141.9, 153.4.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.25; H, 8.27; N, 6.75.



7-Chloro-3,9-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**8d**).

Colorless amorphous.

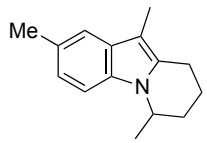
Yield: 38%.

IR (neat) 2967, 2924, 2858, 1464, 1406, 1368, 1354, 1297, 1262, 1230, 1066, 843 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H, J = 6.4 Hz), 2.12–2.24 (m, 1H), 2.19 (s, 3H), 2.68–3.04 (m, 3H), 4.43–4.55 (m, 1H), 7.02 (dd, 1H, J = 2.4, 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.42 (d, 1H, J = 2.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 8.7, 20.3, 22.0, 36.1, 52.6, 100.3, 110.0, 117.9, 119.9, 124.0, 130.2, 134.3, 142.6.

Anal. Calcd for $C_{13}H_{14}ClN$: C, 71.07; H, 6.42; N, 6.38. Found: C, 70.94; H, 6.49; N, 6.54.



2,6,10-Trimethyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**8e**).

Yellow amorphous.

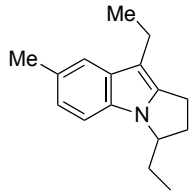
Yield: 34%.

IR (neat) 3013, 2966, 2938, 2858, 1734, 1582, 1466, 1419, 1375, 1354, 1343, 1327, 1314, 1293, 1261, 1243, 1215, 1185, 1172, 1161, 1097, 1065, 1024, 863, 789 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, 3H, *J* = 6.4 Hz), 1.81–2.22 (m, 4H), 2.16 (s, 3H), 2.45 (s, 3H), 2.65–2.78 (m, 1H), 2.91–3.03 (m, 1H), 4.51–4.65 (m, 1H), 6.93 (d, 1H, *J* = 8.4 Hz), 7.15 (d, 1H, *J* = 8.0 Hz), 7.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 8.1, 16.7, 19.9, 21.5, 22.4, 30.2, 47.0, 103.9, 108.8, 117.6, 121.3, 127.7, 129.1, 132.3, 133.2.

Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.65; H, 9.16; N, 6.73.



3,9-Diethyl-7-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**8f**).

Yellow amorphous.

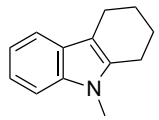
Yield: 42%.

IR (neat) 2962, 2928, 2874, 1724, 1620, 1589, 1477, 1463, 1361, 1283, 1225, 1148, 1064, 861, 782 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.26 (t, 3H, *J* = 7.6 Hz), 1.68–1.80 (m, 1H), 1.96–2.13 (m, 1H), 2.21–2.33 (m, 1H), 2.45 (s, 3H), 2.60–2.76 (m, 3H), 2.82–3.01 (m, 2H), 4.29–4.40 (m, 1H), 6.89 (d, 1H, *J* = 8.4 Hz), 7.15 (d, 1H, *J* = 8.4 Hz), 7.29 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 14.9, 17.9, 21.6, 22.6, 27.3, 33.2, 57.7, 106.6, 109.2, 118.3, 121.2, 127.3, 130.5, 132.7, 140.7.

Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.28; H, 9.26; N, 6.41.



9-Methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**8g**).

Yellow oil.

Yield: 25%.

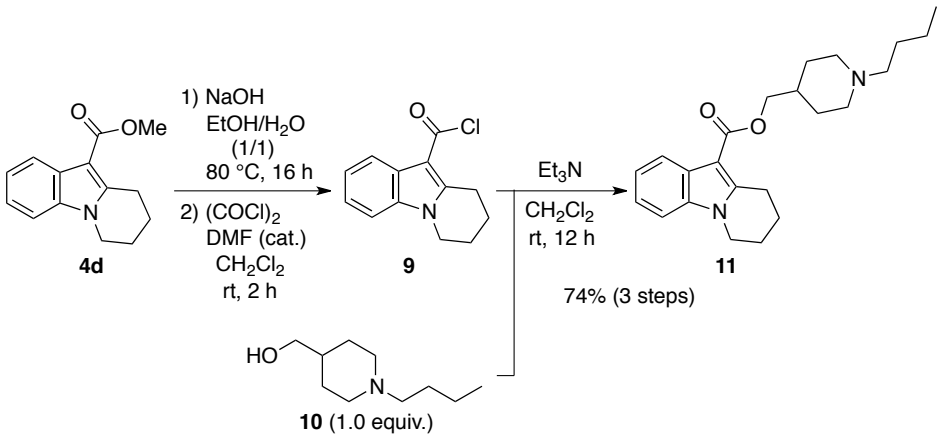
I IR (neat) 3024, 2934, 2912, 2846, 1734, 1614, 1565, 1475, 1441, 1417, 1379, 1336, 1313, 1254, 1244, 1185, 1127, 914, 748, 734 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.80–2.00 (m, 4H), 2.67–2.78 (m, 4H), 3.61 (s, 3H), 7.06 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.14 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.24 (d, 1H, *J* = 7.6 Hz), 7.46 (d, 1H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 22.1, 23.2, 23.2, 28.9, 108.4, 109.2, 117.7, 118.5, 120.4, 127.1, 135.7, 136.7.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.03; H, 8.39; N, 7.41.

Scheme S3. Synthesis of biologically active molecule **11**.



Synthesis of 3,9-dimethyl-2,3-dihydro-1H-pyrrolo[1,2-a]indole (11):

To a solution of **4d** (64.6 mg, 0.282 mol) in EtOH (1.76 mL) and H_2O (0.80 mL) was added NaOH (113 mg, 2.82 mmol) at 0 °C, and then heated at 80 °C. After being stirred for 16 h at 80 °C, the reaction was stopped by adding 1 M HCl at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to afford crude acid. This material was used next reaction without further purification.

To a solution of acid in CH_2Cl_2 (2.82 mL) were successively added oxalyl chloride (1 M in CH_2Cl_2, 366 μl, 0.366 mmol) and one drop of DMF at 0 °C. After being stirred for 2 h at room temperature, the reaction mixture was concentrated in vacuo to afford acid chloride **9**. This material was used next reaction without further purification.

To a solution of **9** in CH_2Cl_2 (1.40 mL) were successively added a solution of **10** (48.3 mg, 2.82 mmol) in CH_2Cl_2 (1.4 mL) and Et_3N (80 μL, 0.574 mmol) at 0 °C. After being stirred for 12 h at room temperature, the reaction was stopped by adding H_2O at

0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH = 20/1) to give **11** (77.0 mg, 74%) as yellow solid.

Mp. 45–47 °C.

IR (neat) 2934, 2871, 2804, 2766, 1689, 1532, 1476, 1457, 1423, 1362, 1321, 1270, 1215, 1205, 1170, 1155, 1144, 1112, 1036 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$,) δ 0.92 (t, 3H, *J* = 7.6 Hz), 1.21–1.55 (m, 6H), 1.78–2.15 (m, 9H), 2.28–2.39 (m, 2H), 2.92–3.04 (m, 2H), 3.32 (t, 2H, *J* = 6.0 Hz), 4.07 (t, 2H, *J* = 6.0Hz), 4.20 (d, 2H, *J* = 6.0 Hz), 7.16–7.32 (m, 3H), 8.10 (d, 1H, *J* = 7.6 Hz).

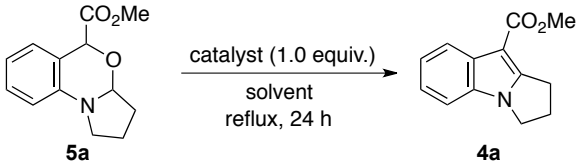
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.0, 20.9, 22.5, 24.6, 29.1, 29.2, 35.7, 42.4, 53.4, 58.8, 67.8, 102.4, 108.8, 121.0, 121.6, 122.0, 126.6, 135.9, 145.9, 165.9.

Anal. Calcd for $C_{23}H_{32}N_2O_2$: C, 74.96; H, 8.75; N, 7.60. Found: C, 74.74; H, 8.93; N, 7.39.

2. Detailed screening of the reaction conditions

Table S1 illustrates the screening of the catalysts with *N*,*O*-acetal **5a** as a substrate, which suggested that $TiCl_4$ was the catalyst of choice as in the case of ketoester **3a**. Although good chemical yield was achieved (62%) when $TiCl_4$ was employed as a catalyst (entry 1), most of the catalysts such as some common Lewis acids (TMSOTf, BF_3•OEt_2, $AlCl_3$), lanthanoid triflates ($Yb(OTf)_3$, $Gd(OTf)_3$), and strong Brønsted acids (TfOH, Tf_2NH) resulted in only recovery of **5a** (Entries 3-10). Except for $TiCl_4$, only $SnCl_4$ promoted the reaction, however, the chemical yield of **4a** was low (11%, Entry 2). The selection of solvent was also important, and chemical of **4a** was decreased to 26% even with $TiCl_4$ when toluene was used instead of $ClCH_2CH_2Cl$.

Table S1. Examination of the reaction conditions from **5a**.[a]



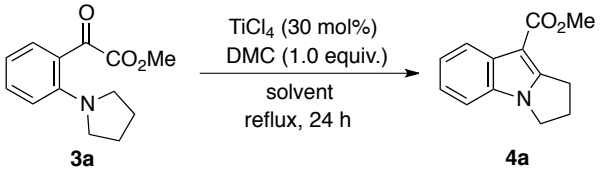
5a **4a**

Entry	catalyst	Yield (%)[b]
1	$TiCl_4$	62
2	$SnCl_4$	11 (60)
3	BF_3•OEt_2	0 (98)
4	TMSOTf	0 (56)
5	$AlCl_3$	0 (95)
6	$Yb(OTf)_3$	0 (69)
7	$Gd(OTf)_3$	0 (95)
8	$Hf(OTf)_4$	0 (93)
9	TfOH	0 (95)
10	Tf_2NH	0 (73)
11[c]	$TiCl_4$	26 (55)

[a] Unless otherwise noted, all reactions were conducted with 0.10 mmol of **5a** in the presence of 1.0 equiv. of catalyst in solvent (1.0 mL) at refluxing temperature for 24 h. [b] Recovery of **5a** is shown in parenthesis. [c] In toluene.

The importance of solvent selection is also observed when the reaction starts from ketoester **3a** (Table S2). Entry 1 shows the result with $ClCH_2CH_2Cl$. Various solvents such as benzene, toluene, *o*-xylene, *p*-xylene, and CH_3CN were examined under the optimized reaction conditions. The desired indole **4a** was obtained in all cases, however, the chemical yield of **4a** remained low to moderate (24–41%, Entries 2–6), and substantial amount of **3a** was recovered.

Table S2. Examination of the solvent effect with ketoester **3a**.[a]



3a **4a**

Entry	solvent	Yield (%)[b]
1	$ClCH_2CH_2Cl$	77
2	toluene	27 (63)
3	benzene	35 (39)
4	*o*-xylene	26 (43)
5	*p*-xylene	41 (32)
6	CH_3CN	24 (20)

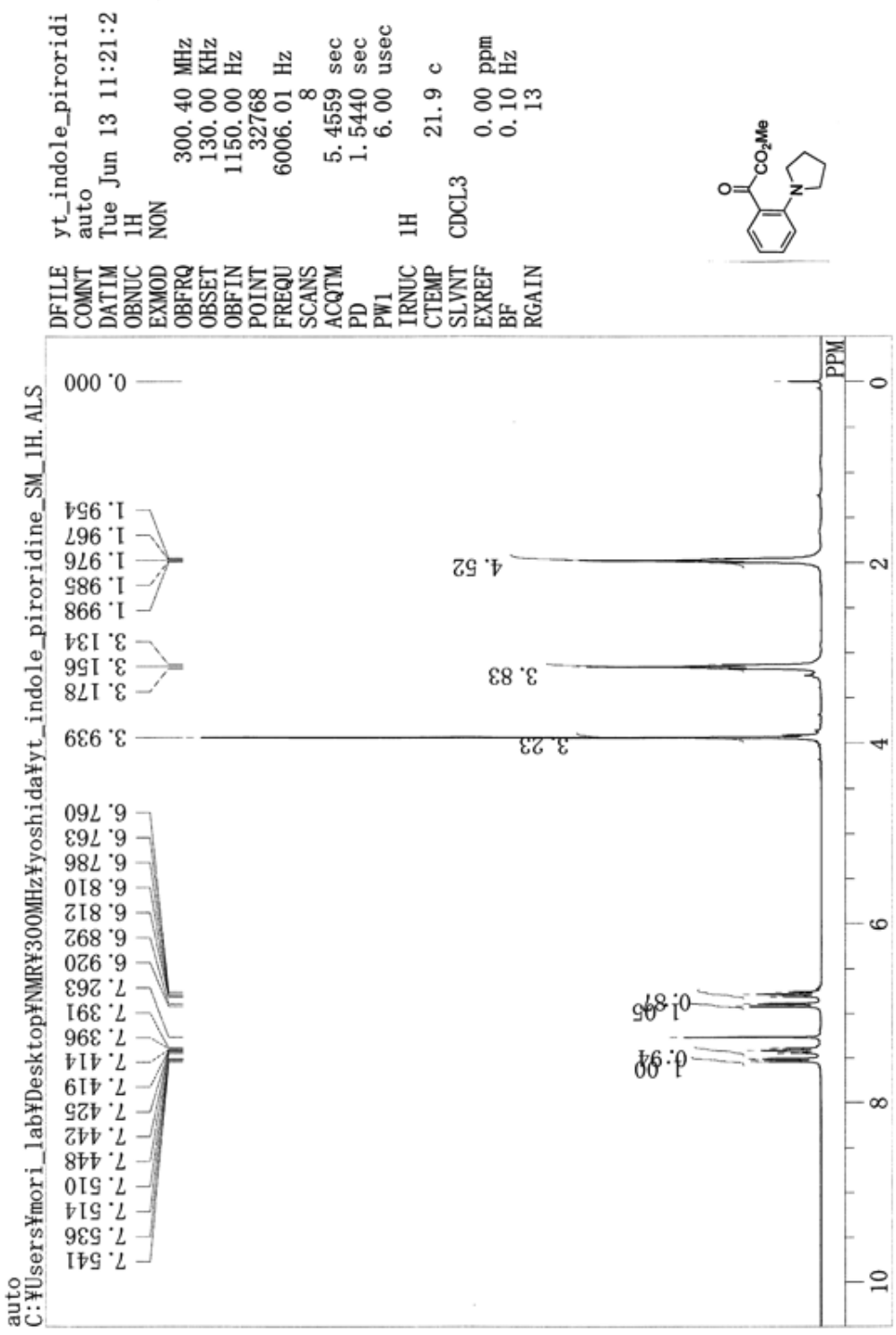
[a] Unless otherwise noted, all reactions were conducted with 0.10 mmol of **3a** in the presence of 30 mol% of catalyst and 1.0 equiv. of DMC in solvent (1.0 mL) at refluxing temperature for 24 h. [b] Recovery of **3a** is shown in parenthesis.

References

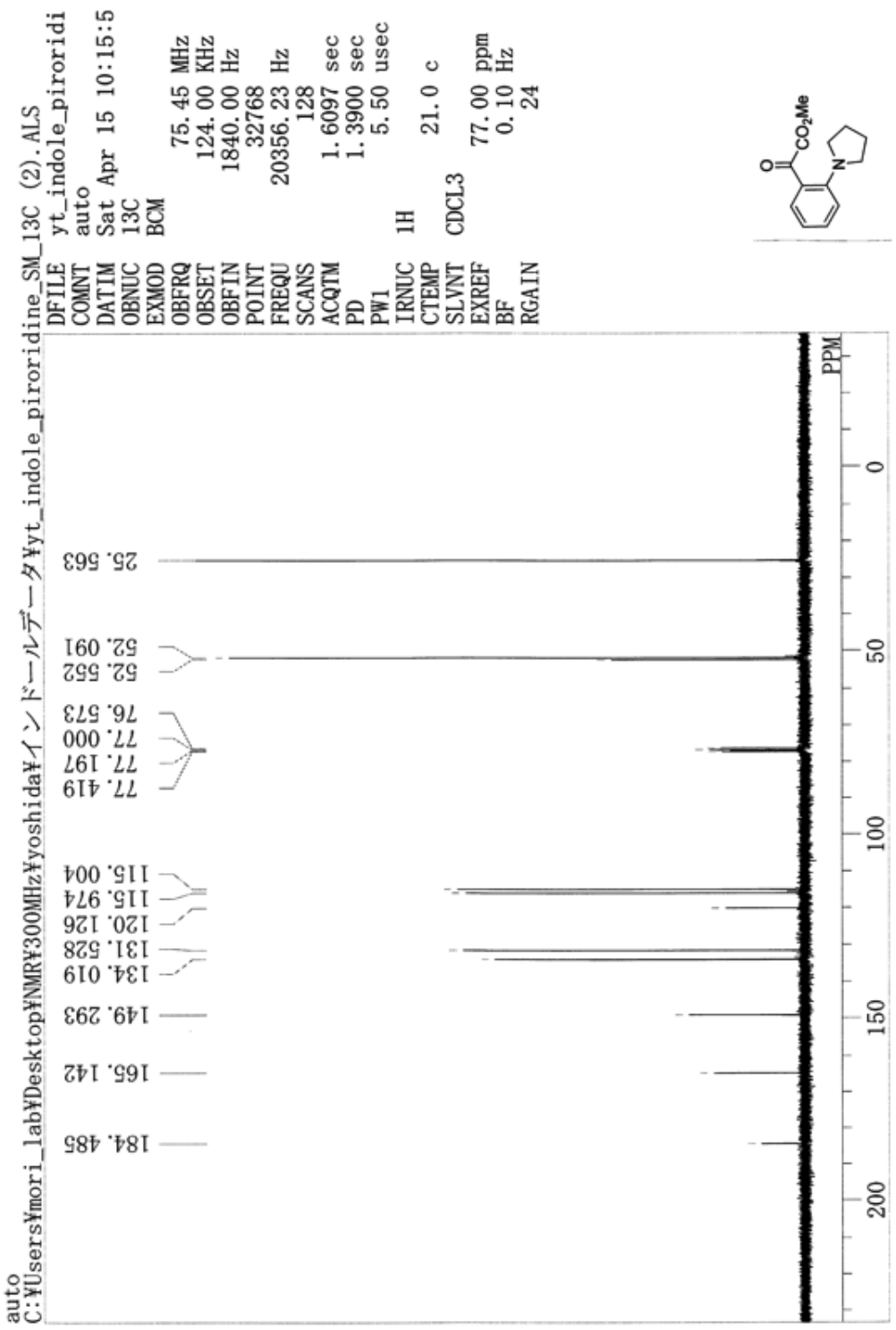
1) Polonka-Báliant, A.; Saraceno, C.; Ludányi, K.; Bényei, A. Mátyus, P. *Synlett.* **2018**, *18*, 2846.

2) Boga, C.; Manescalchi, F.; Savoia, D. *Tetrahedron.* **1994**, *50*, 4709.

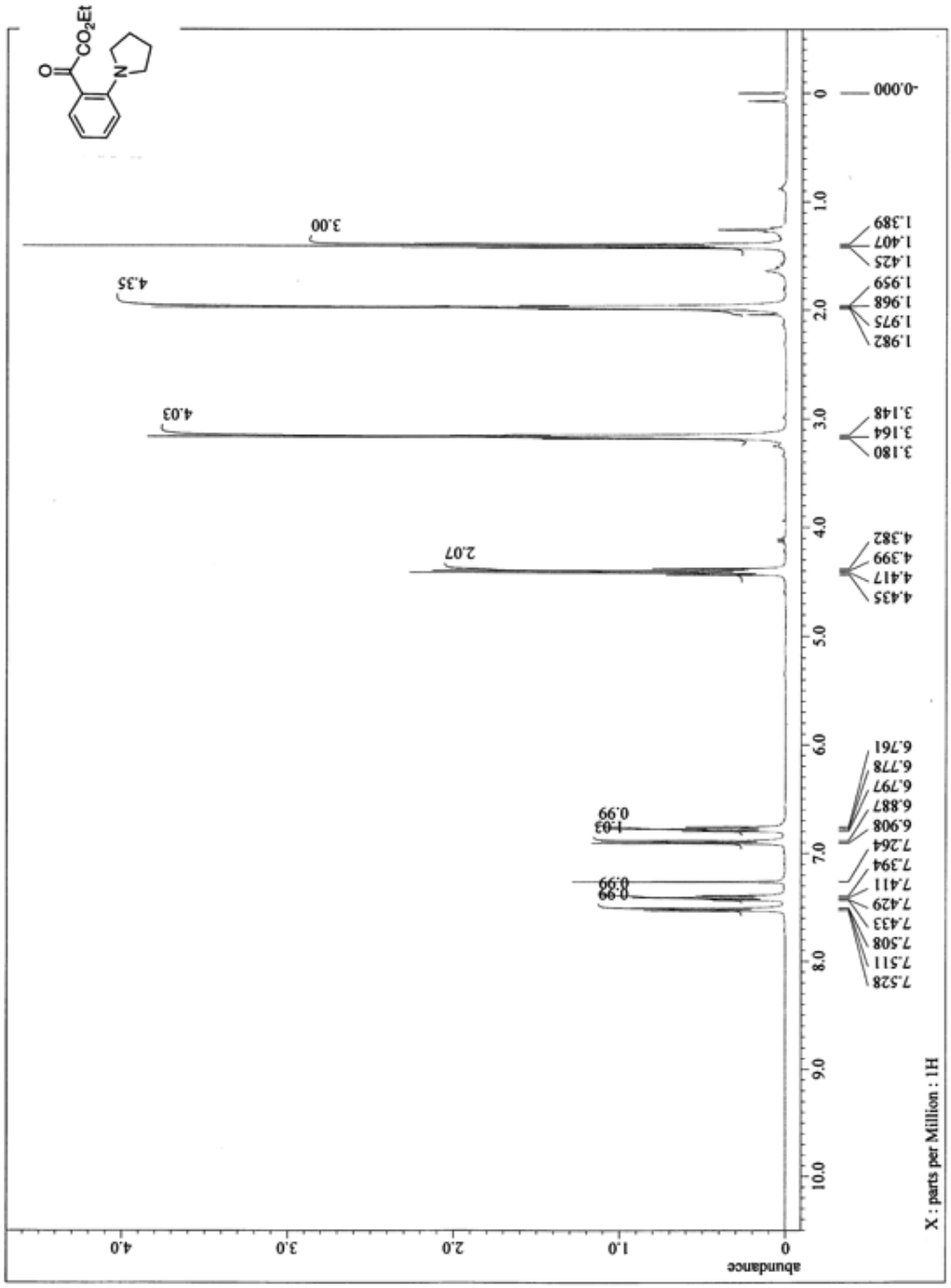
^{1}H NMR spectrum of **3a**.



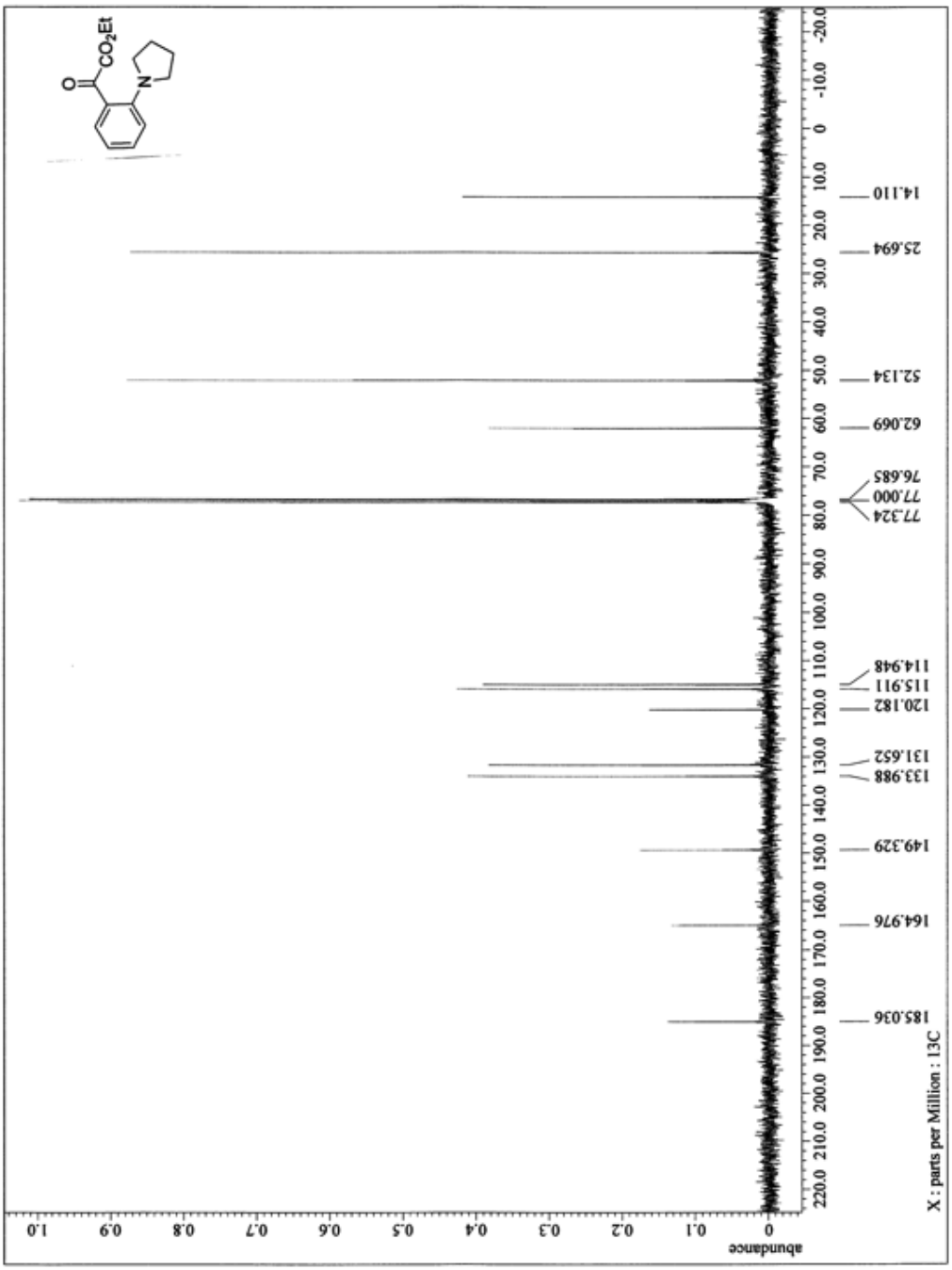
^{13}C NMR spectrum of **3a**.



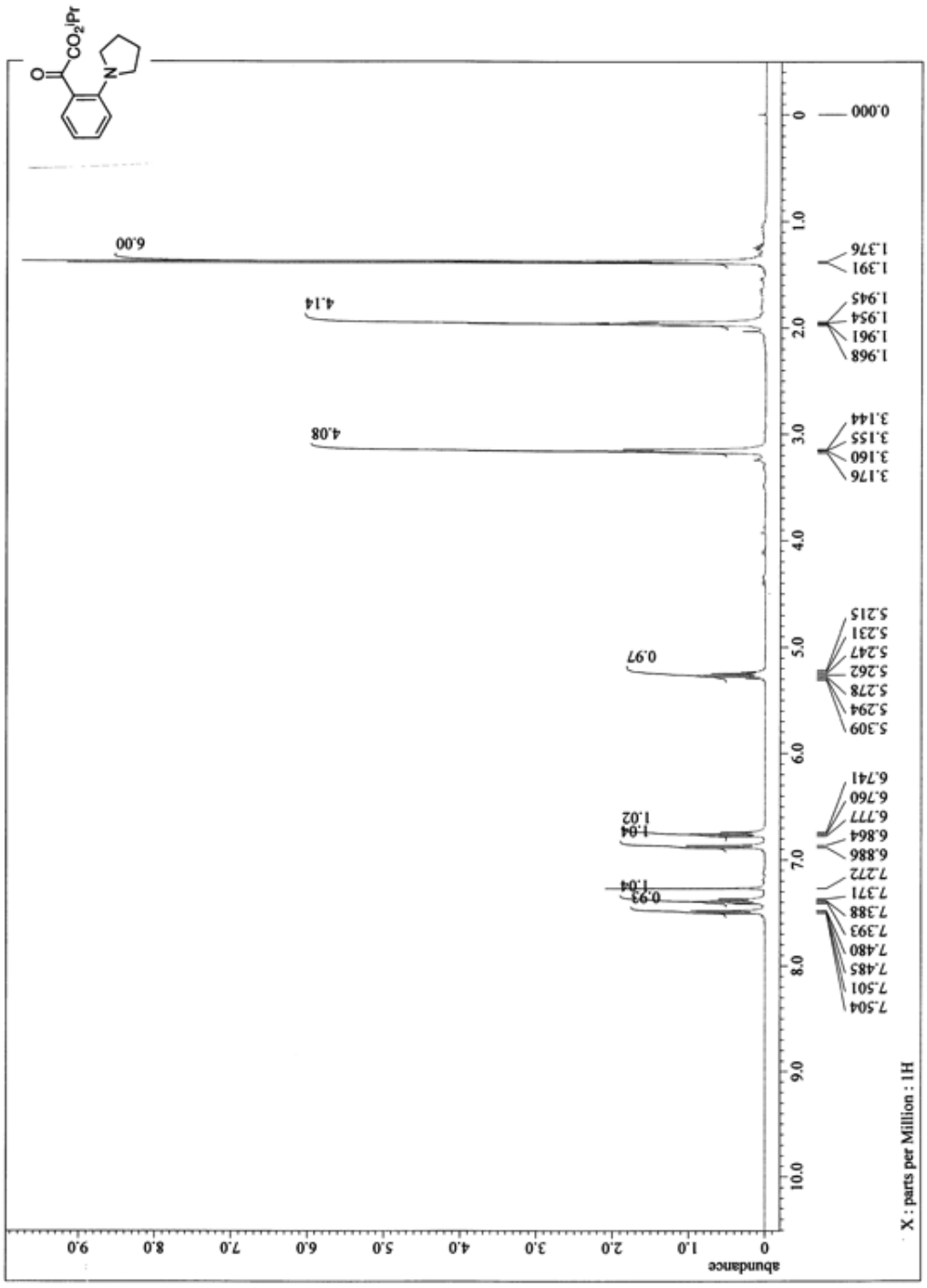
^{1}H NMR spectrum of **3b**.



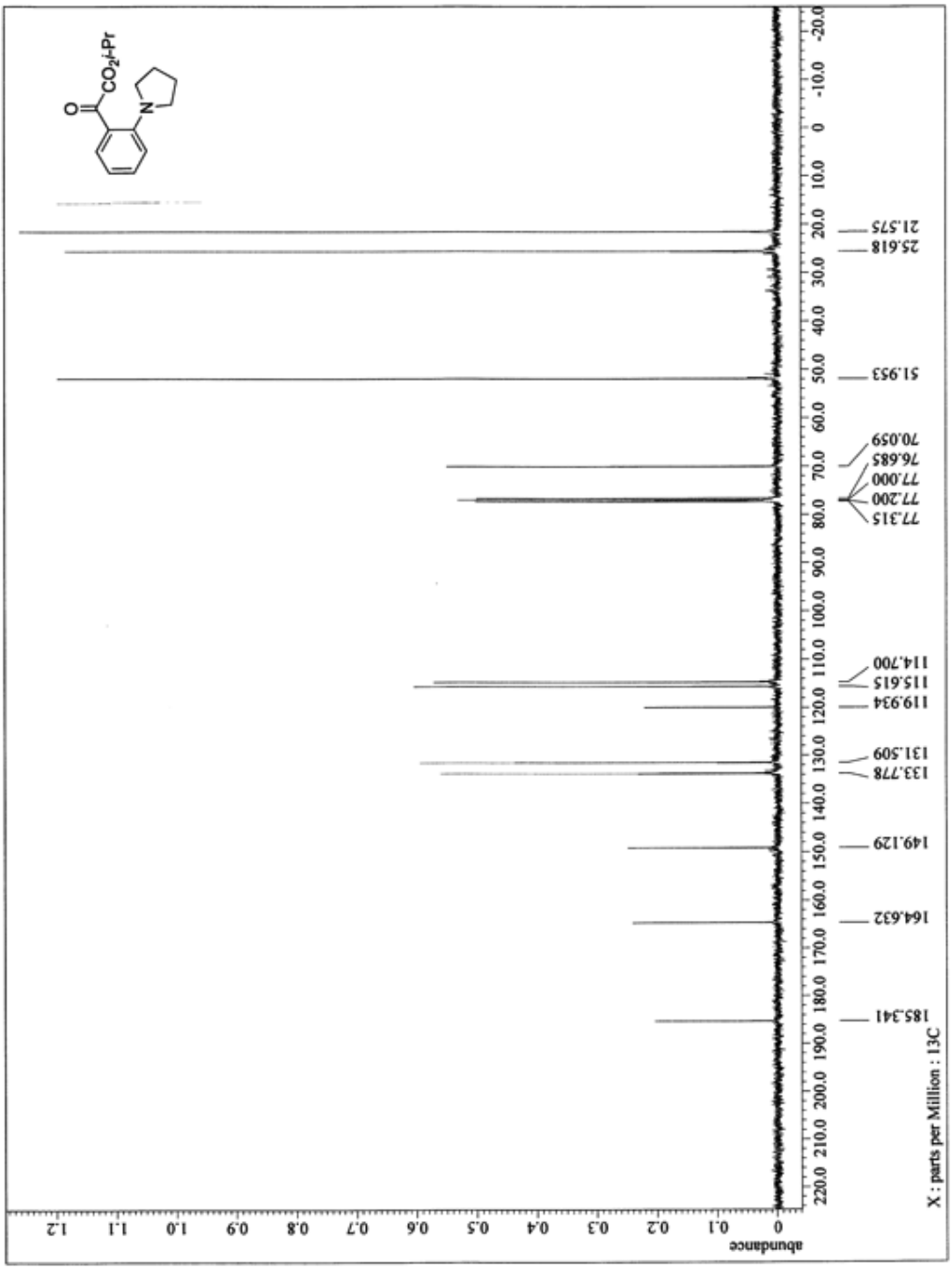
^{13}C NMR spectrum of **3b**.



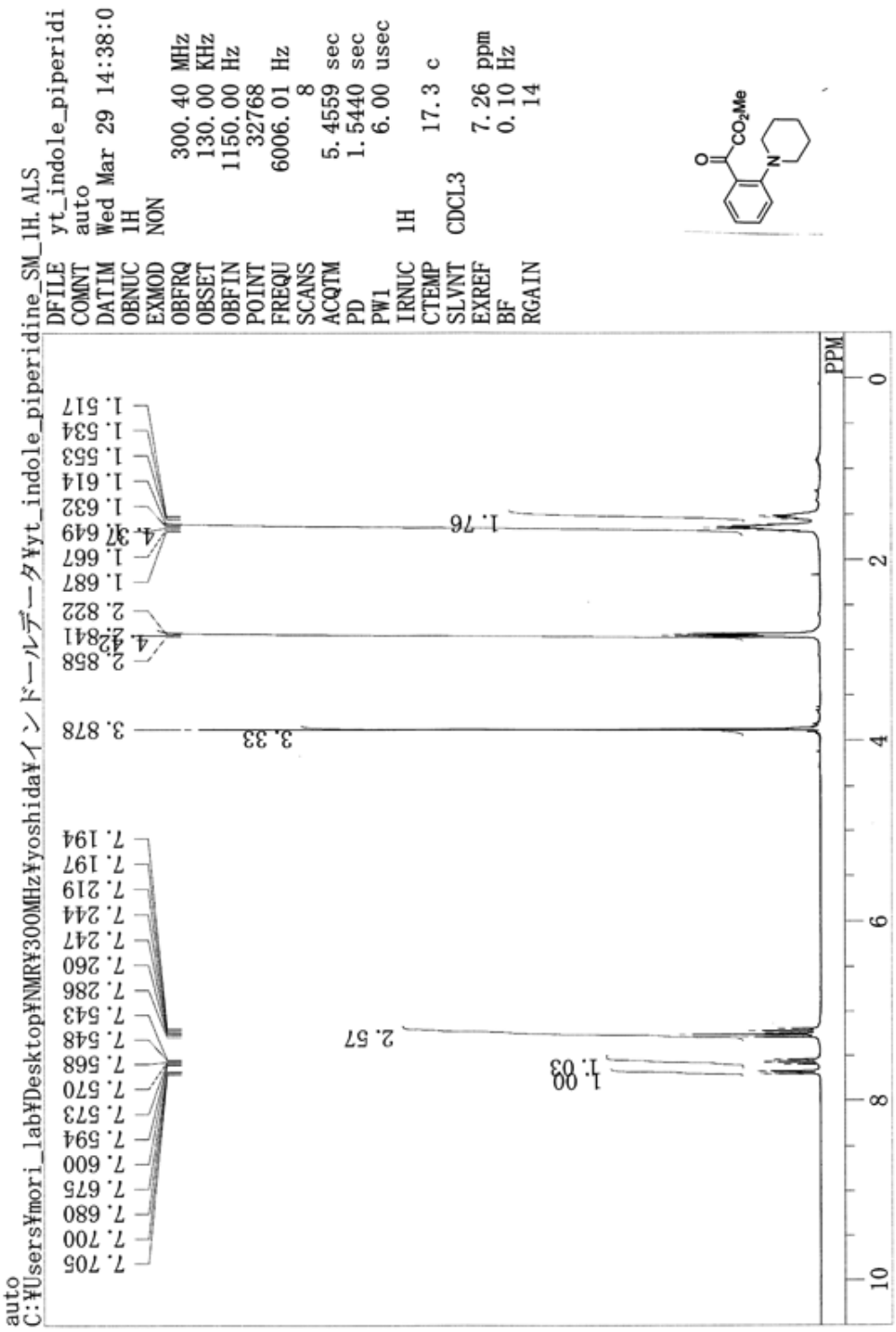
^{1}H NMR spectrum of **3c**.



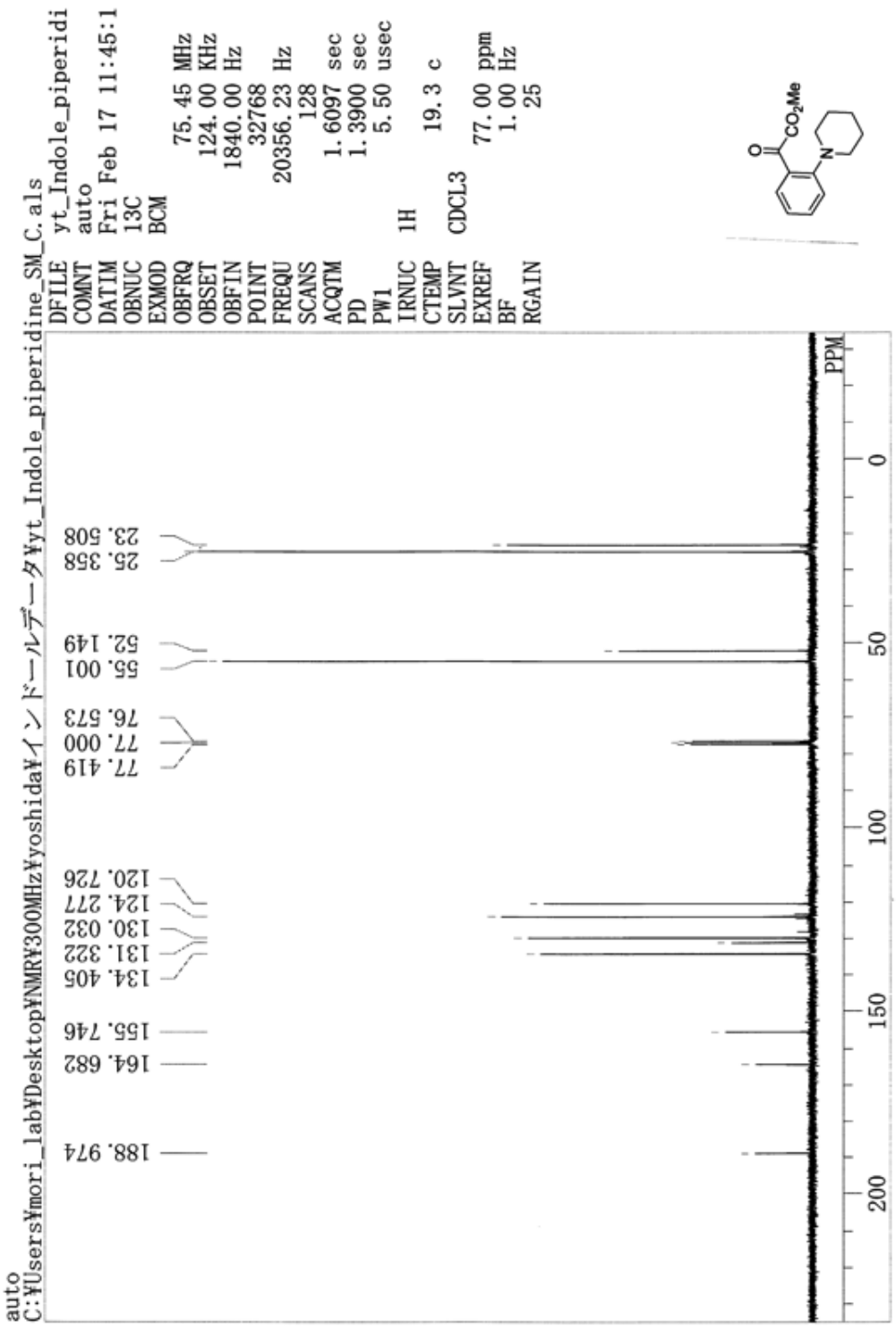
^{13}C NMR spectrum of **3c**.



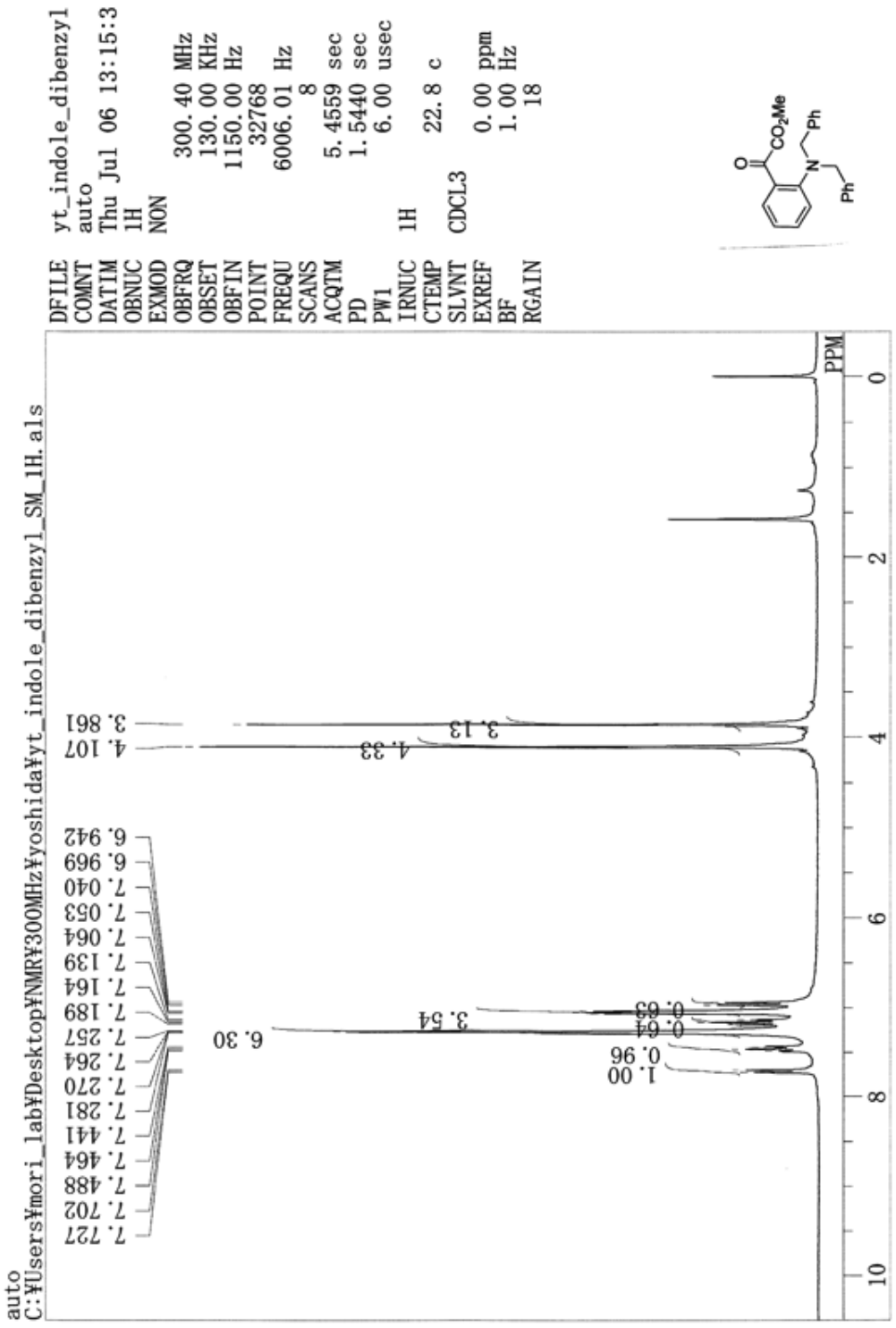
^{1}H NMR spectrum of **3d**.



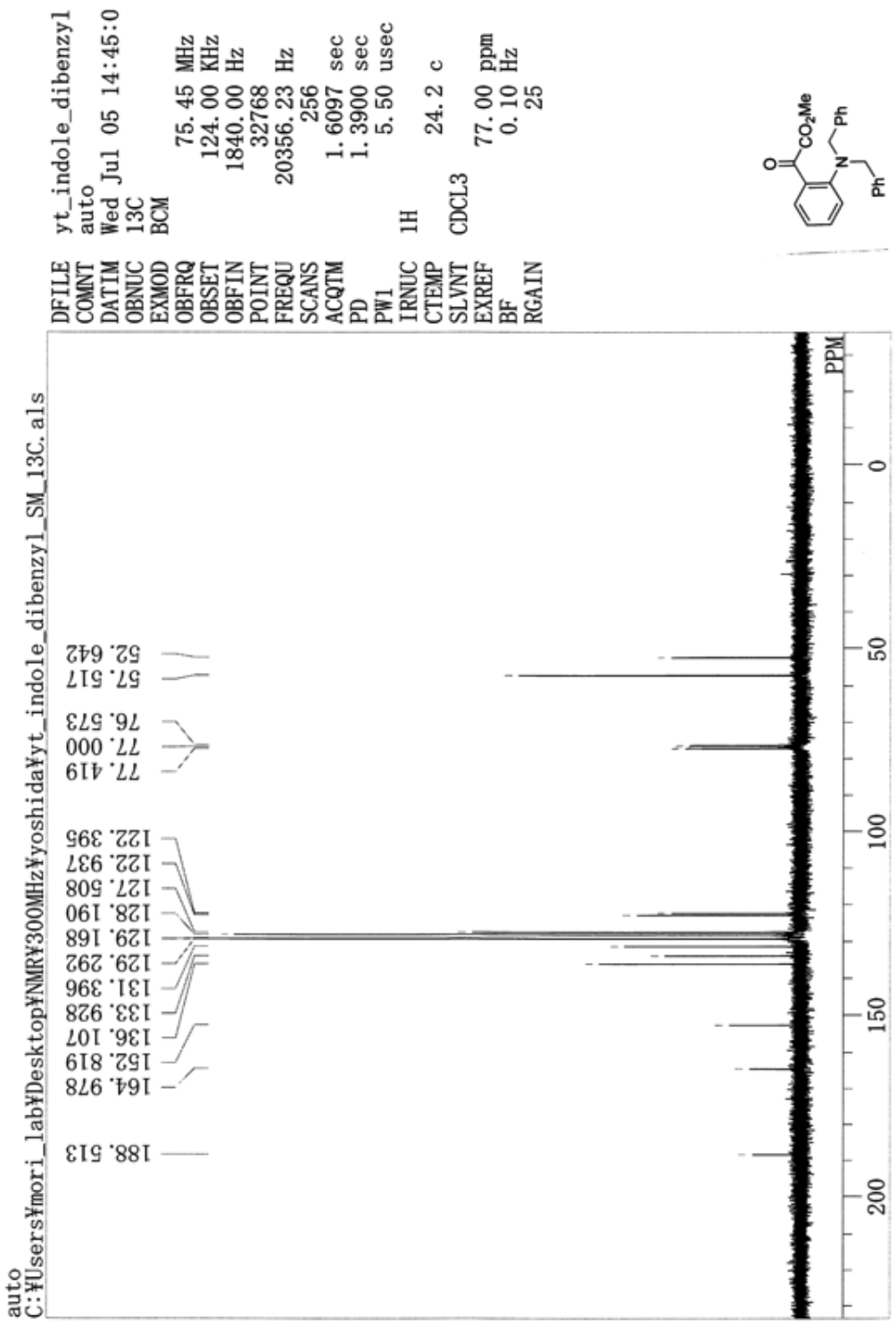
^{13}C NMR spectrum of **3d**.



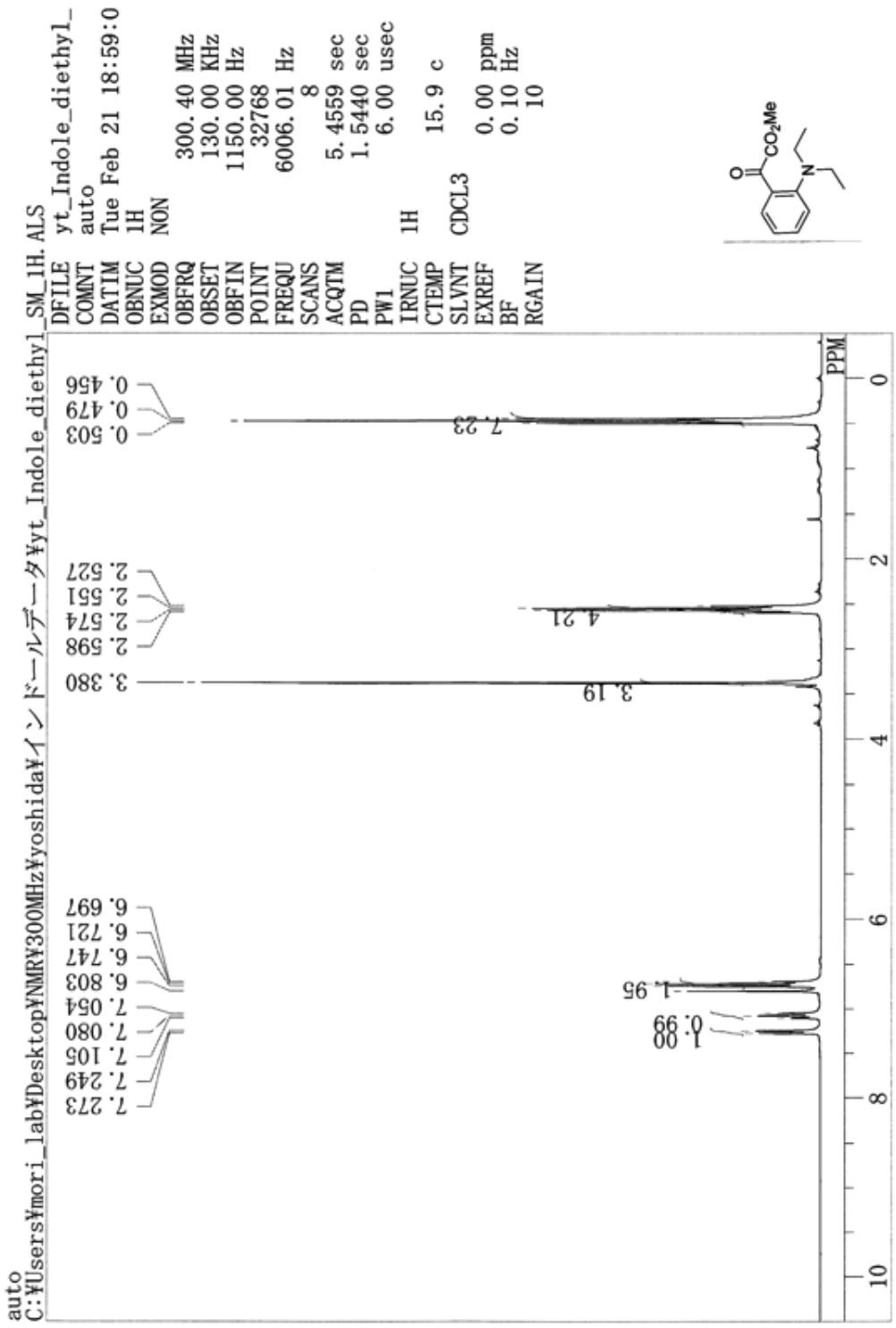
^{1}H NMR spectrum of **3e**.



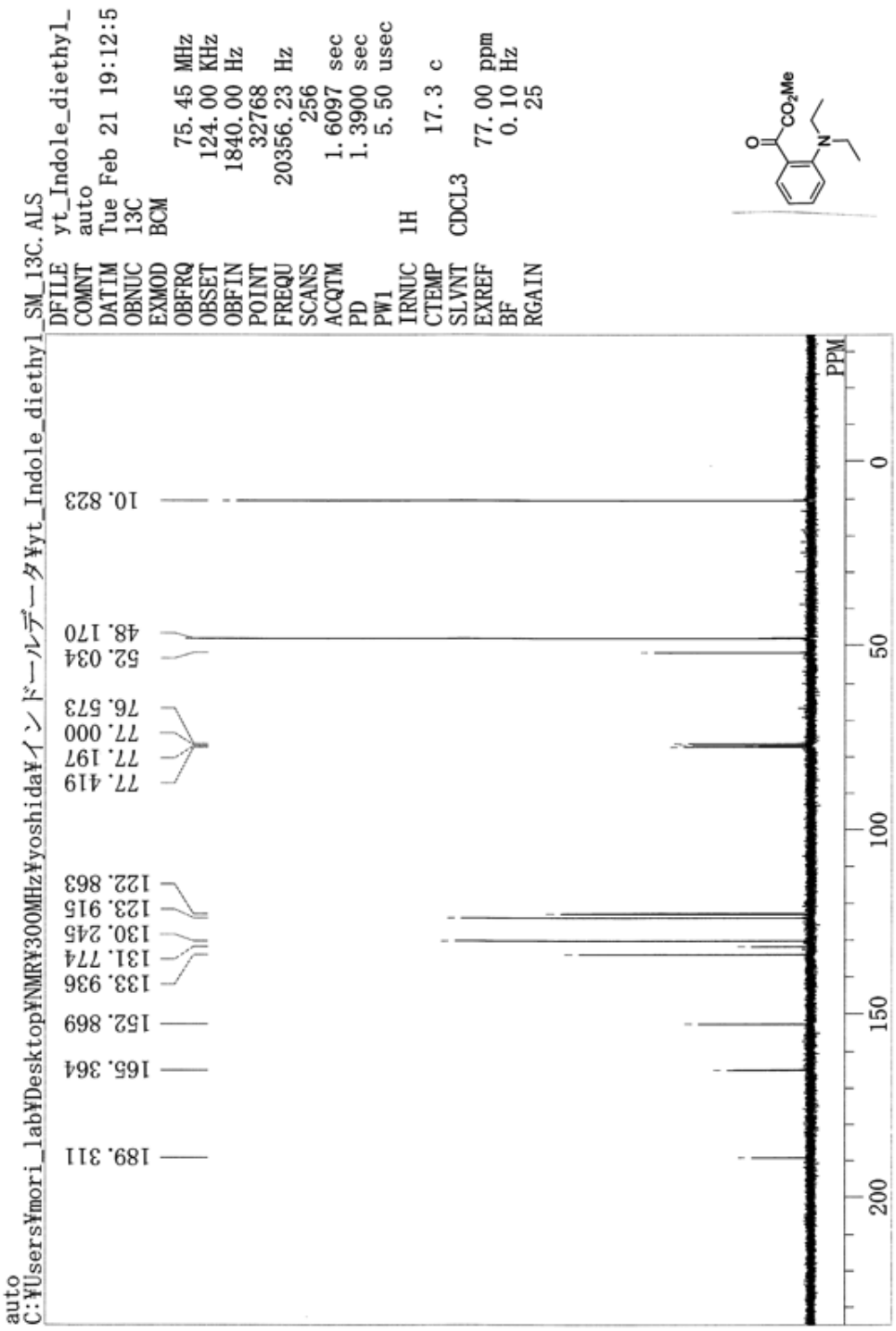
^{13}C NMR spectrum of **3e**.



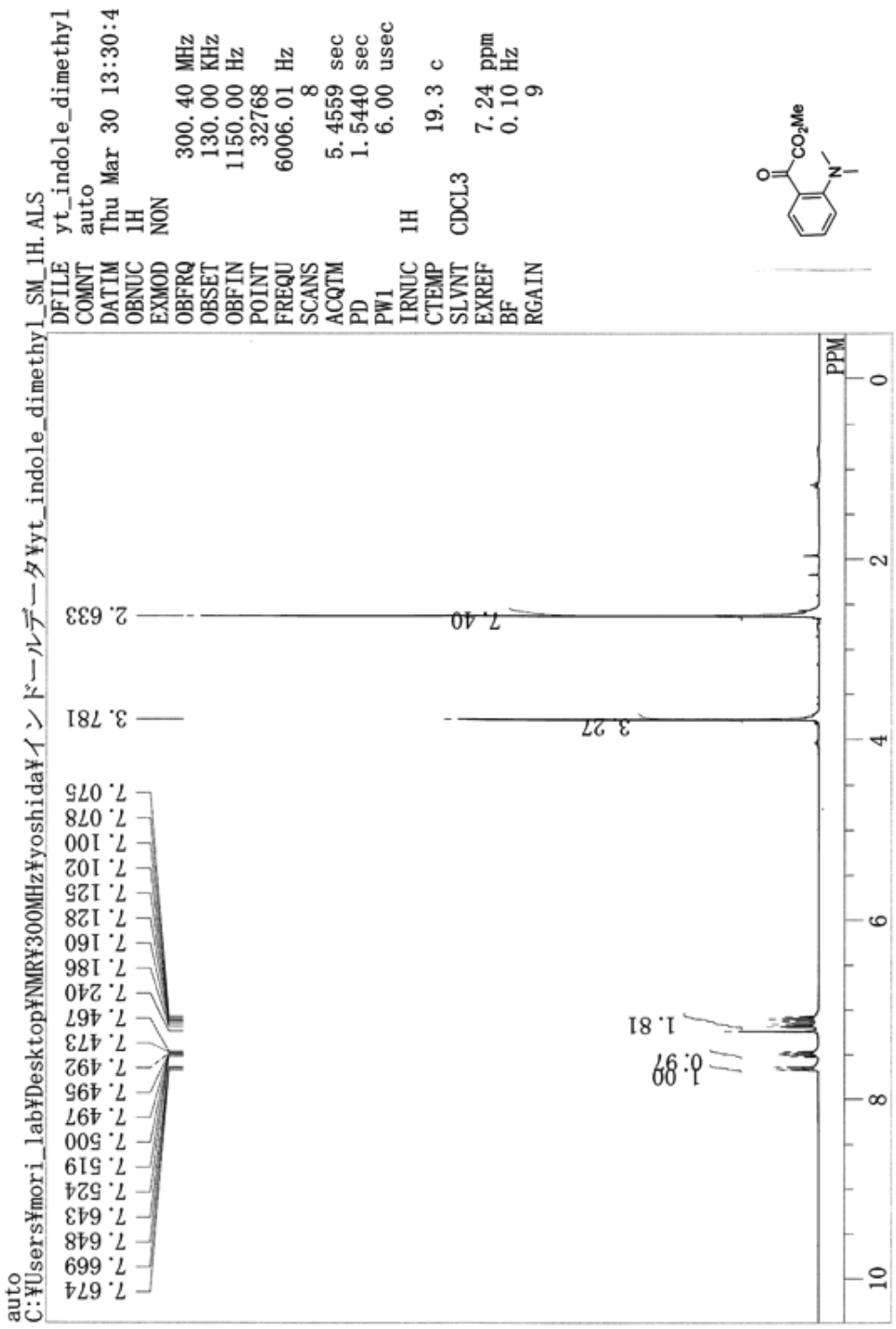
^{1}H NMR spectrum of **3f**.



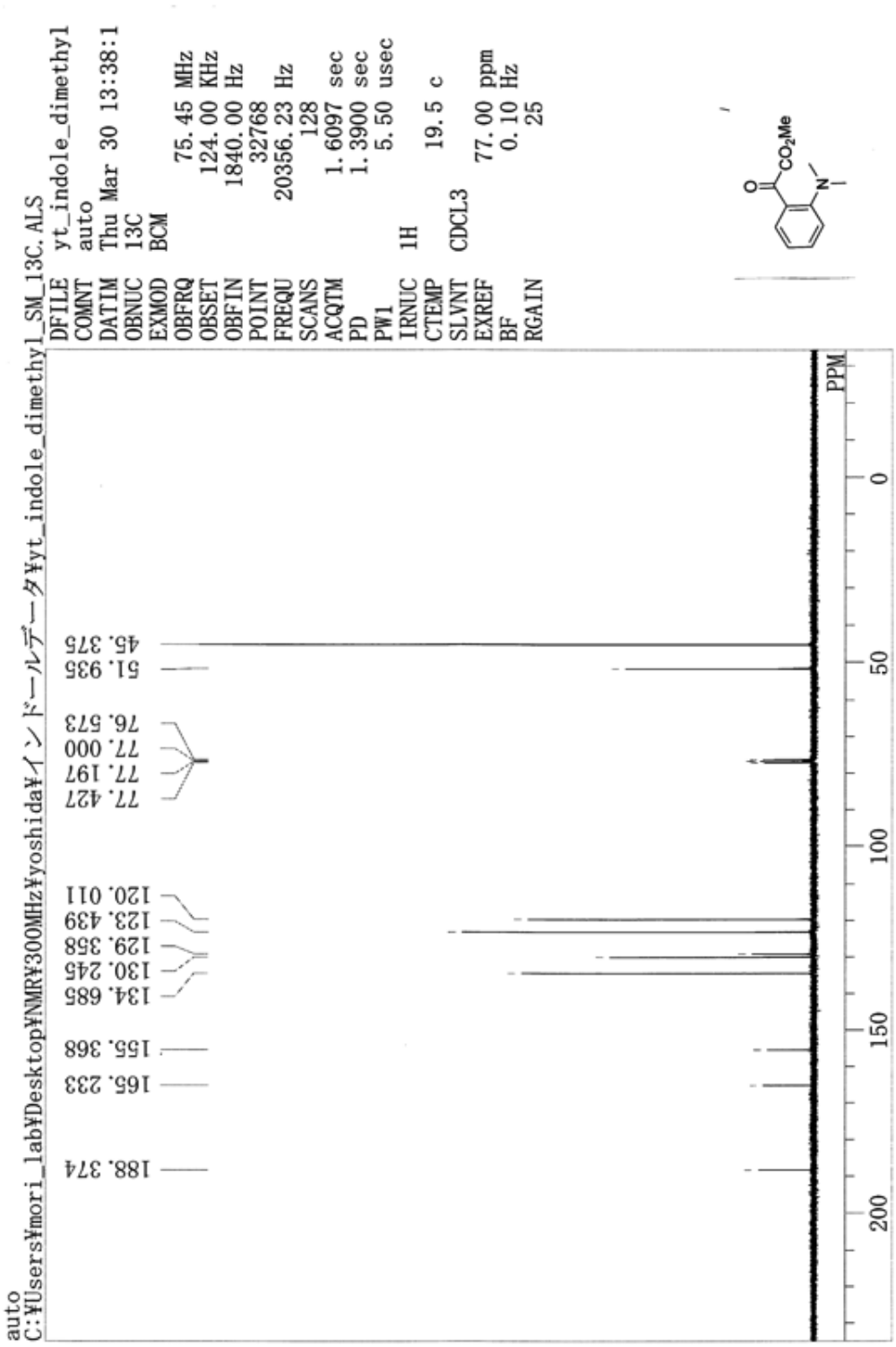
^{13}C NMR spectrum of **3f**.



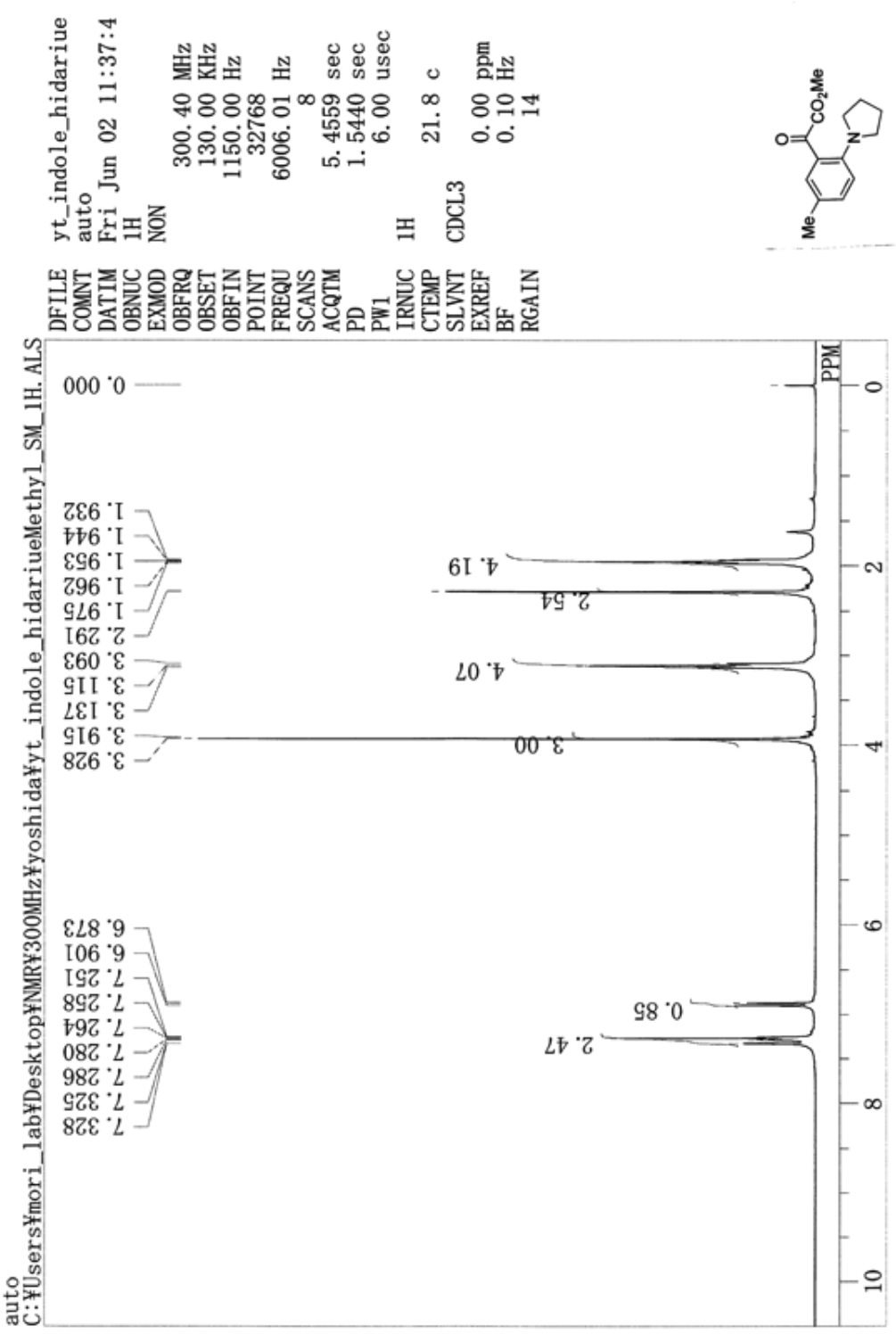
^{1}H NMR spectrum of **3g**.



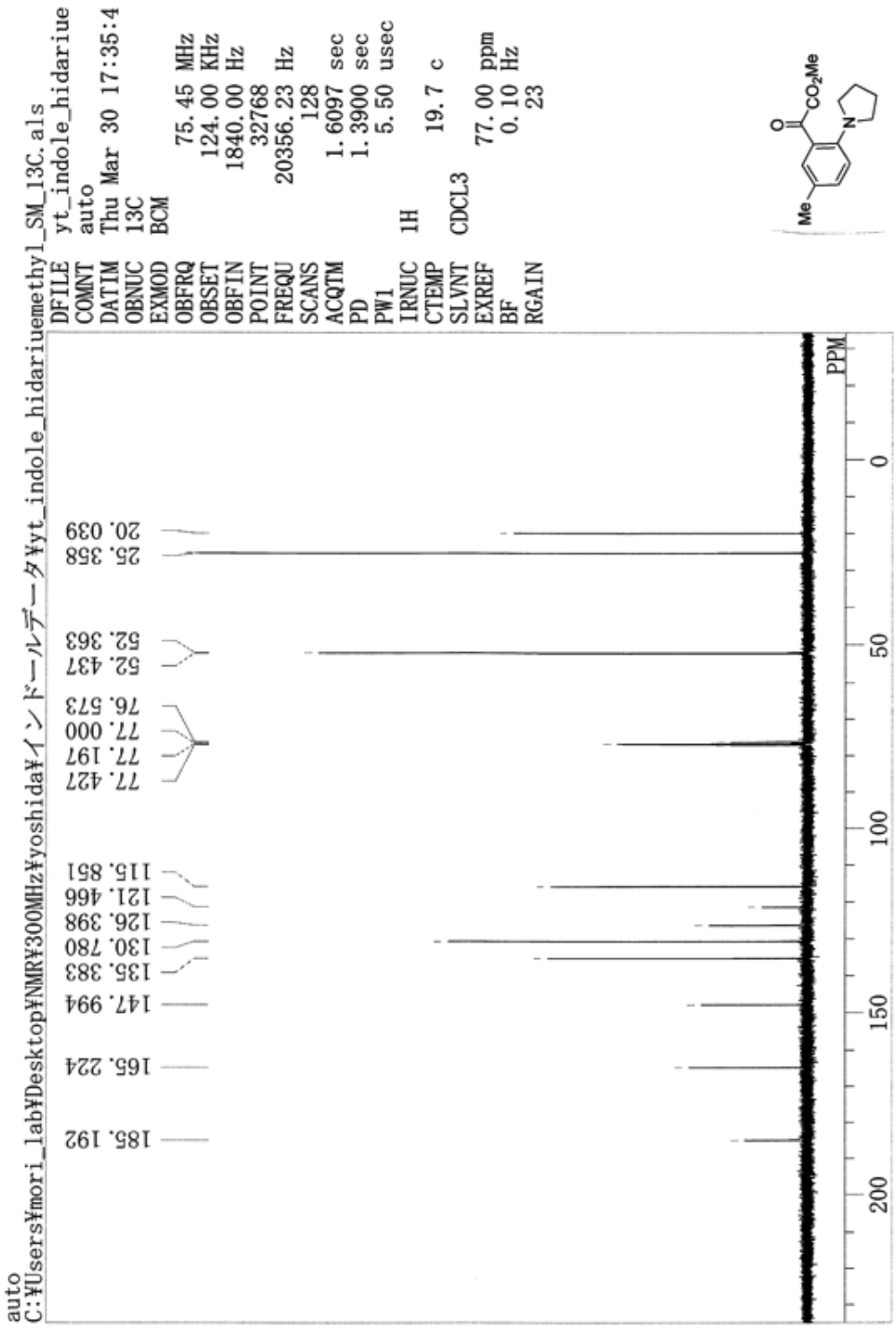
^{13}C NMR spectrum of **3g**.



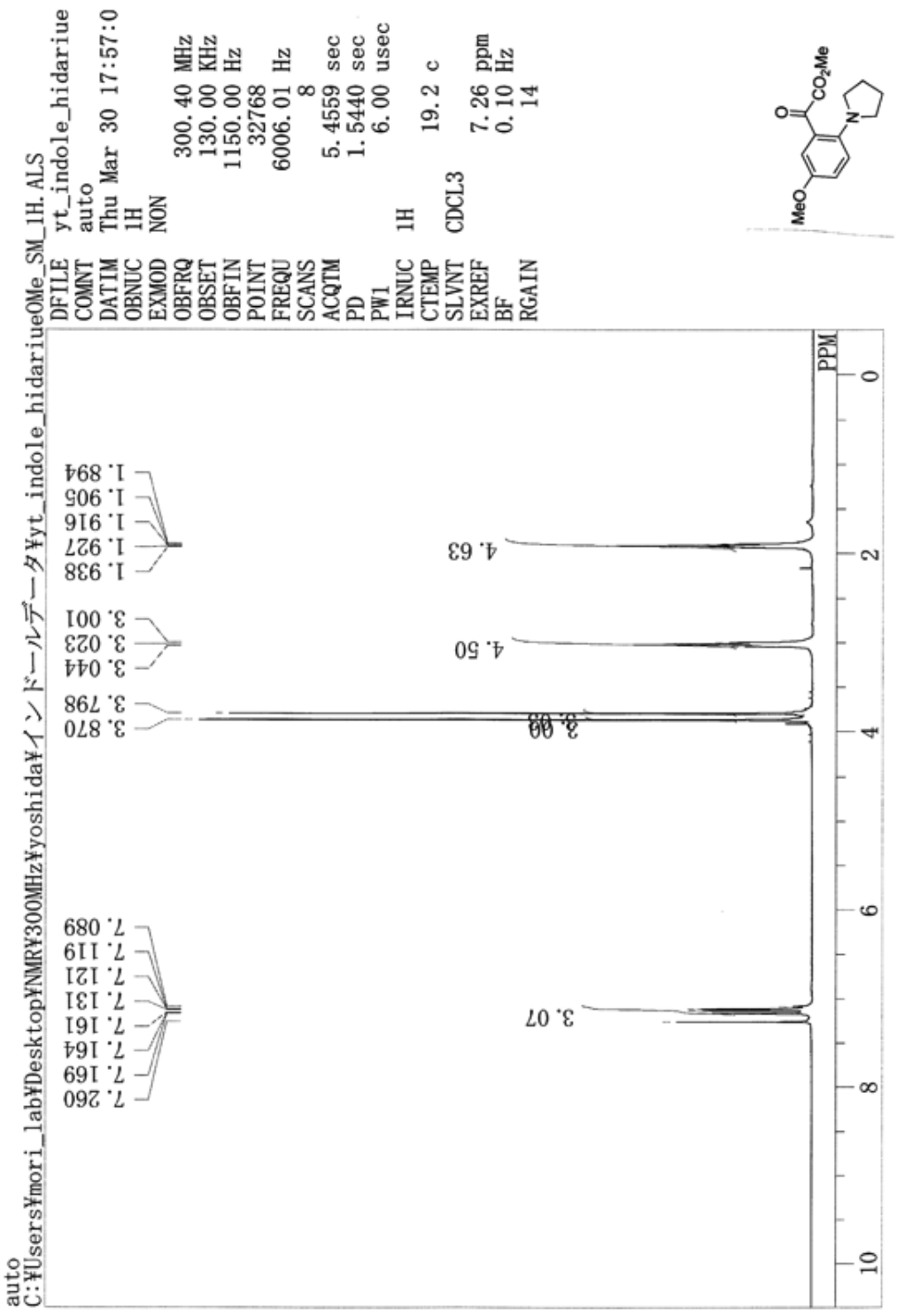
^{1}H NMR spectrum of **3h**.



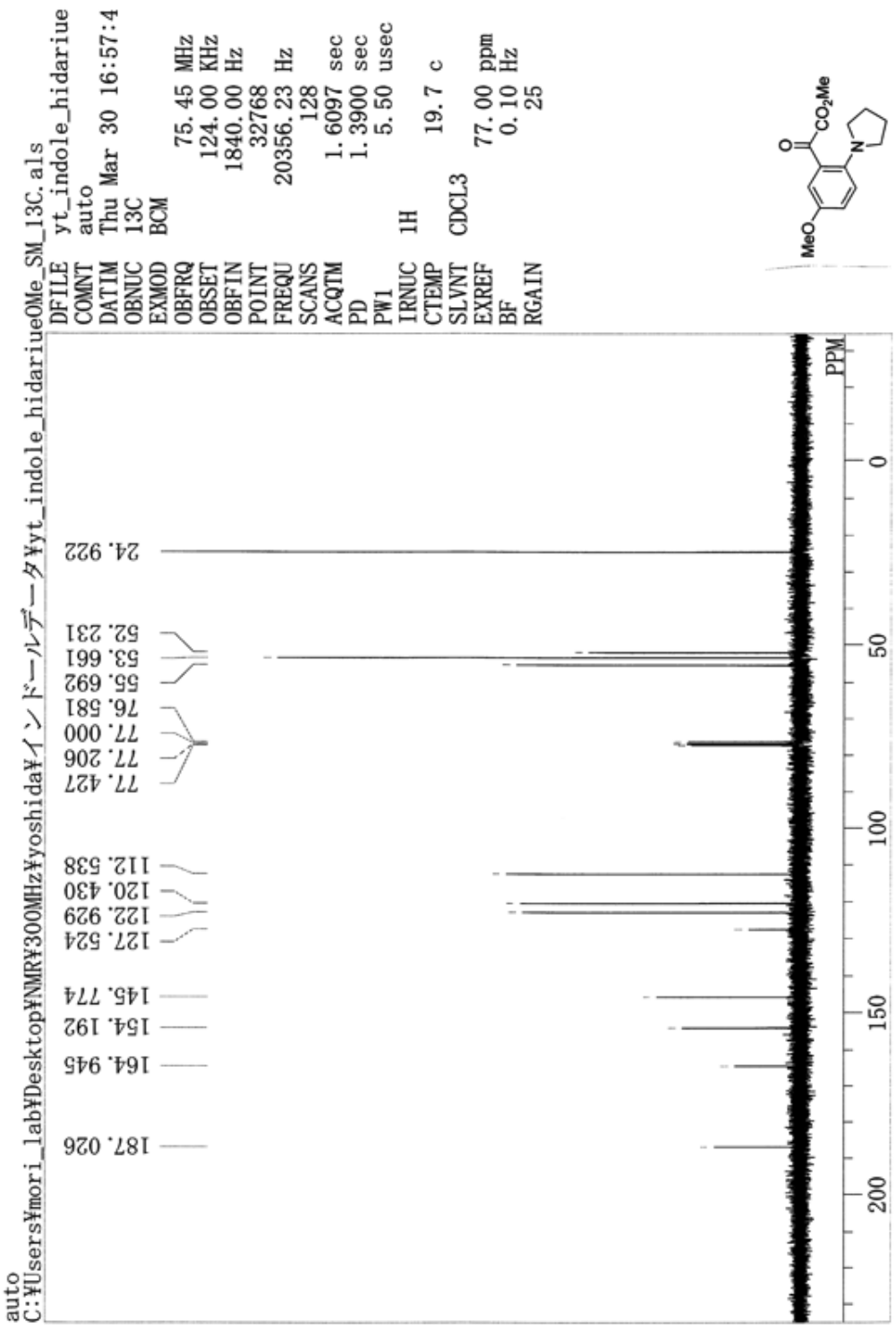
^{13}C NMR spectrum of **3h**.



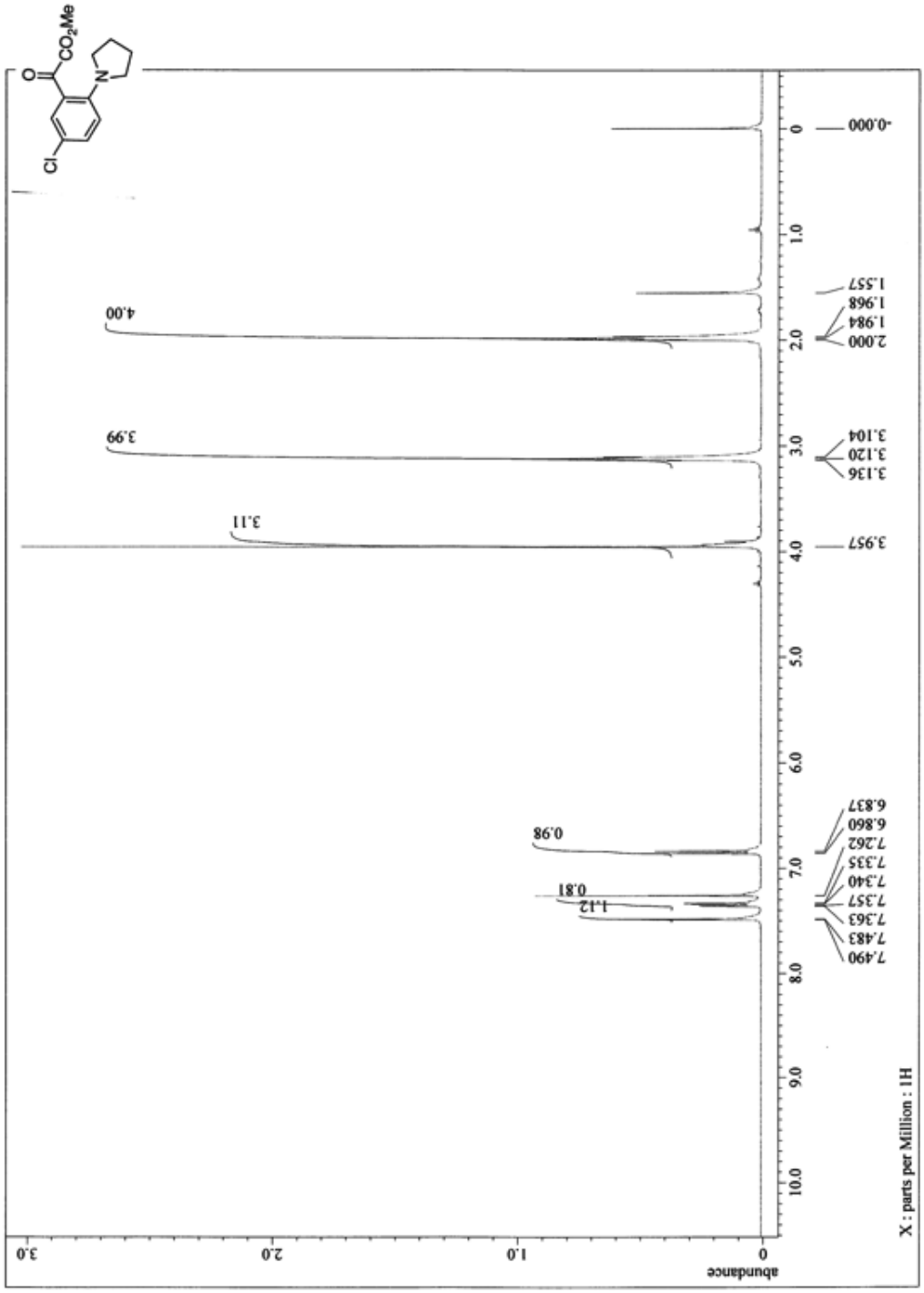
^{1}H NMR spectrum of **3i**.



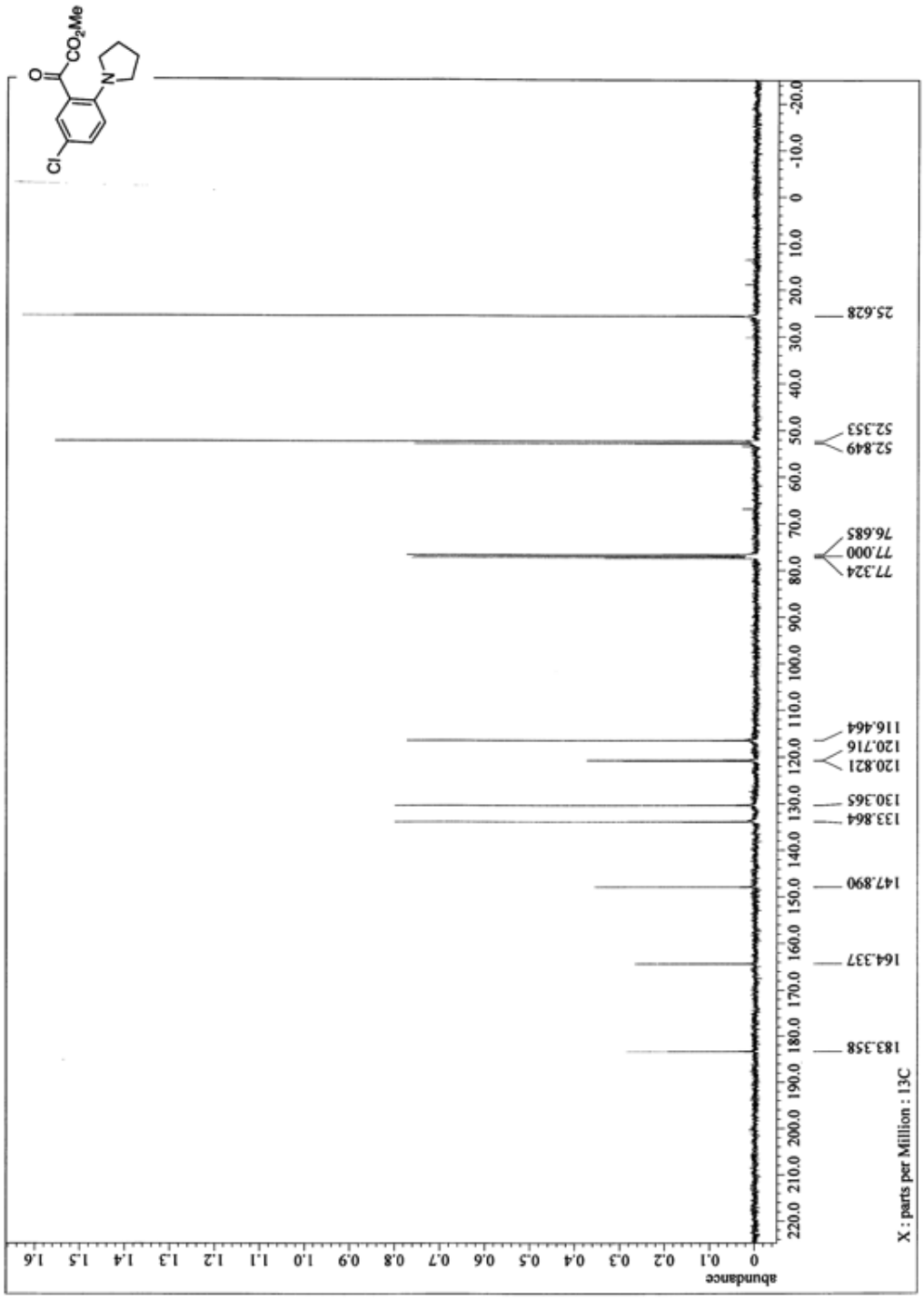
^{13}C NMR spectrum of **3i**.



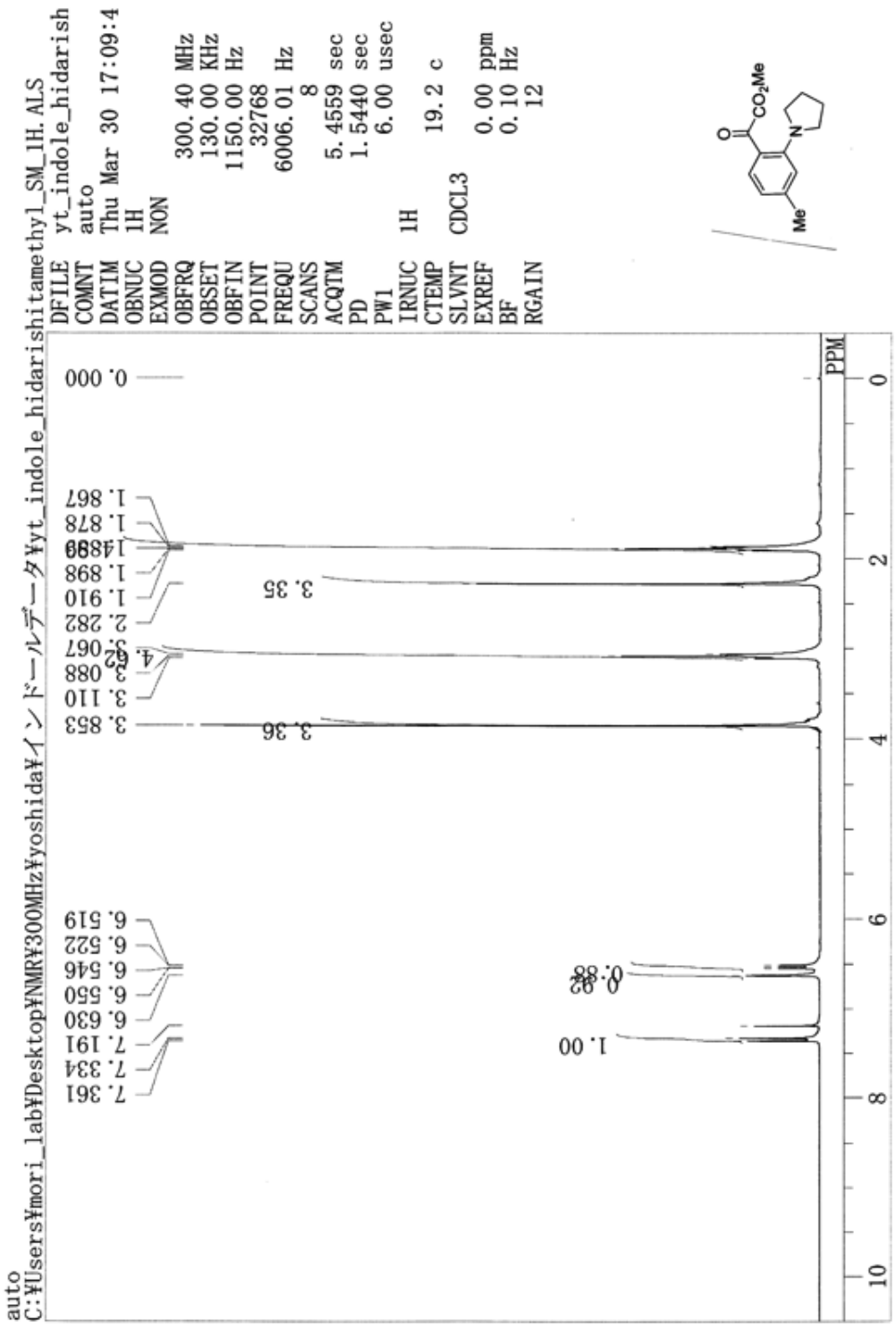
^{1}H NMR spectrum of **3j**.



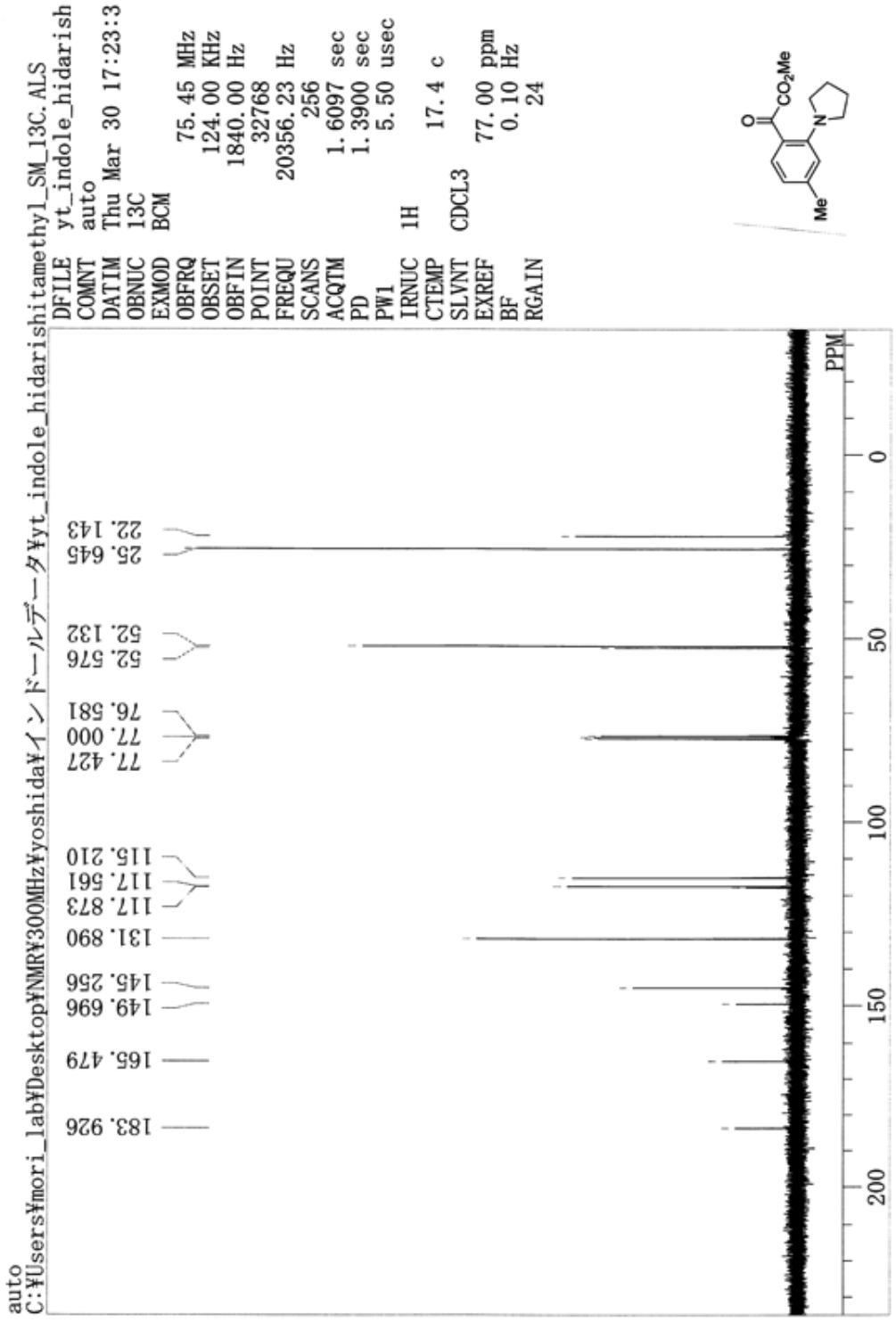
^{13}C NMR spectrum of **3j**.



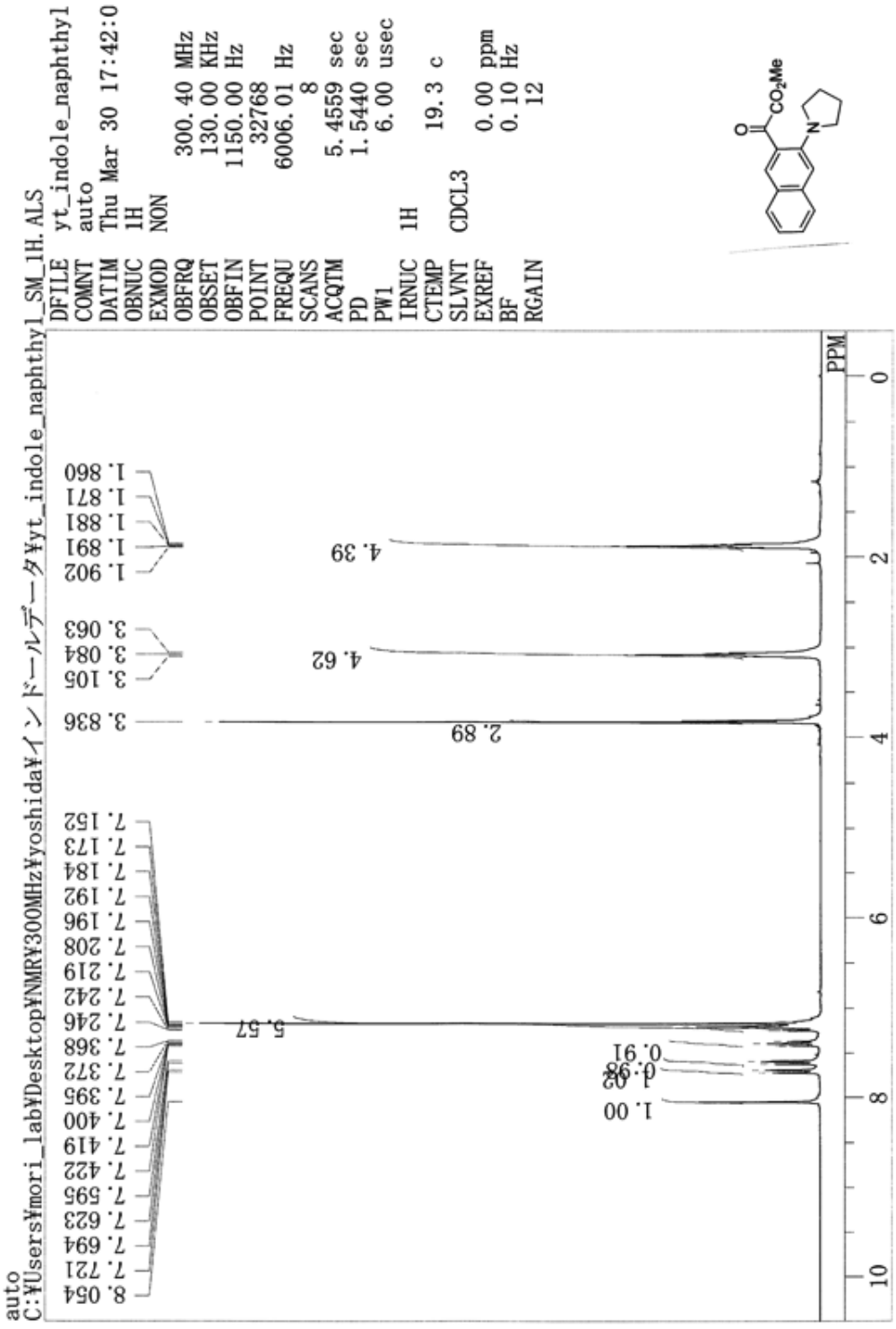
^{1}H NMR spectrum of **3k**.



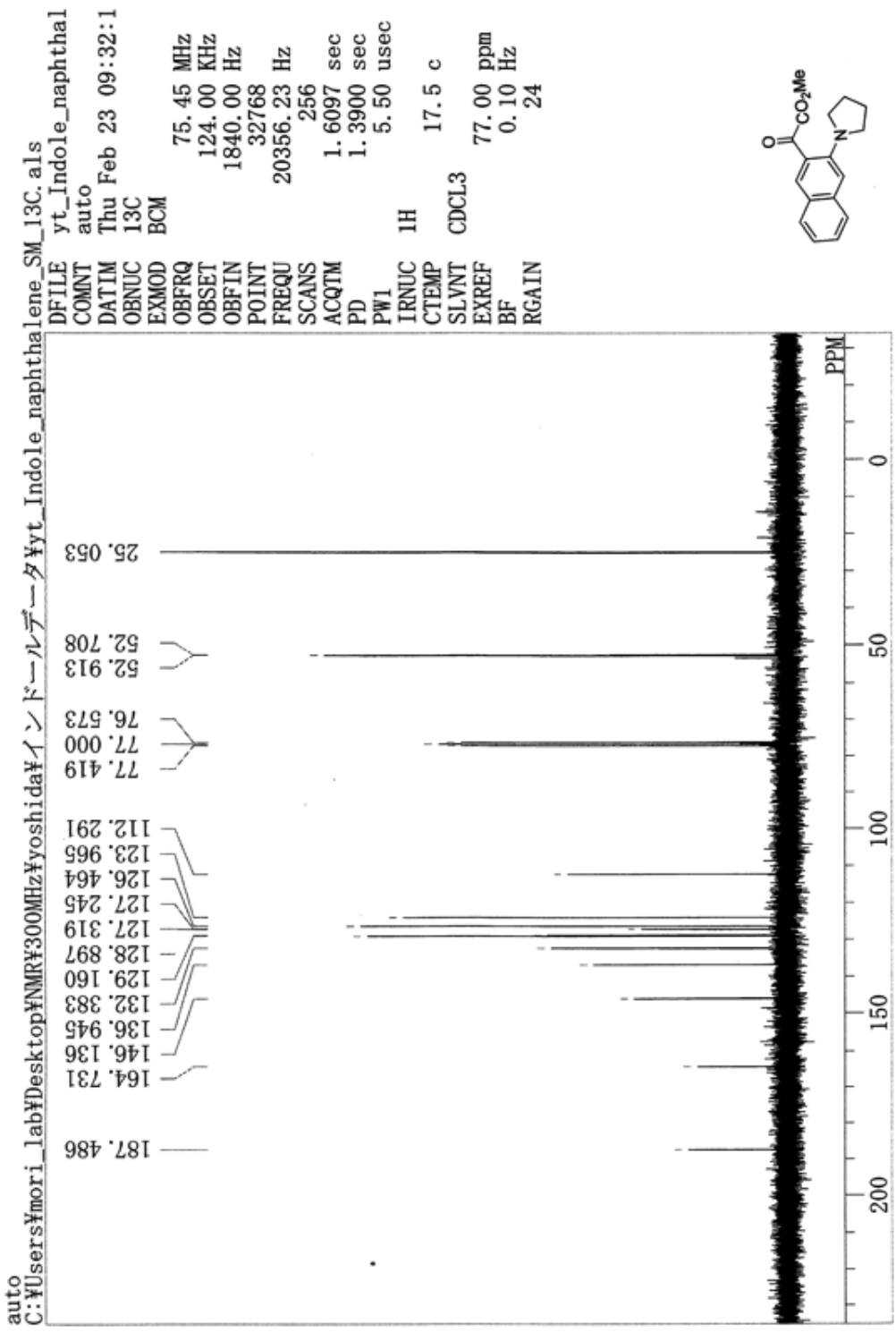
^{13}C NMR spectrum of **3k**.



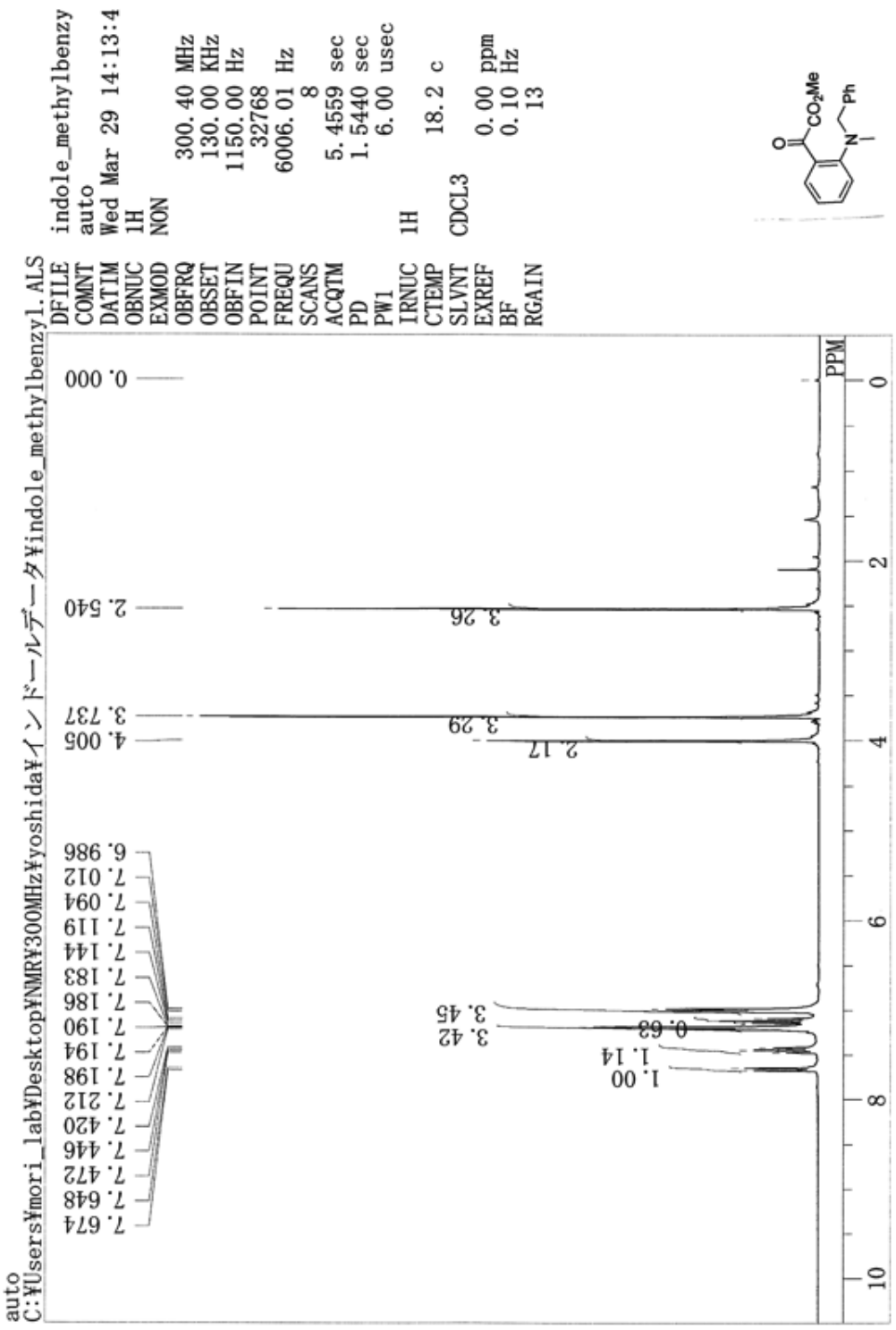
^{1}H NMR spectrum of **3l**.



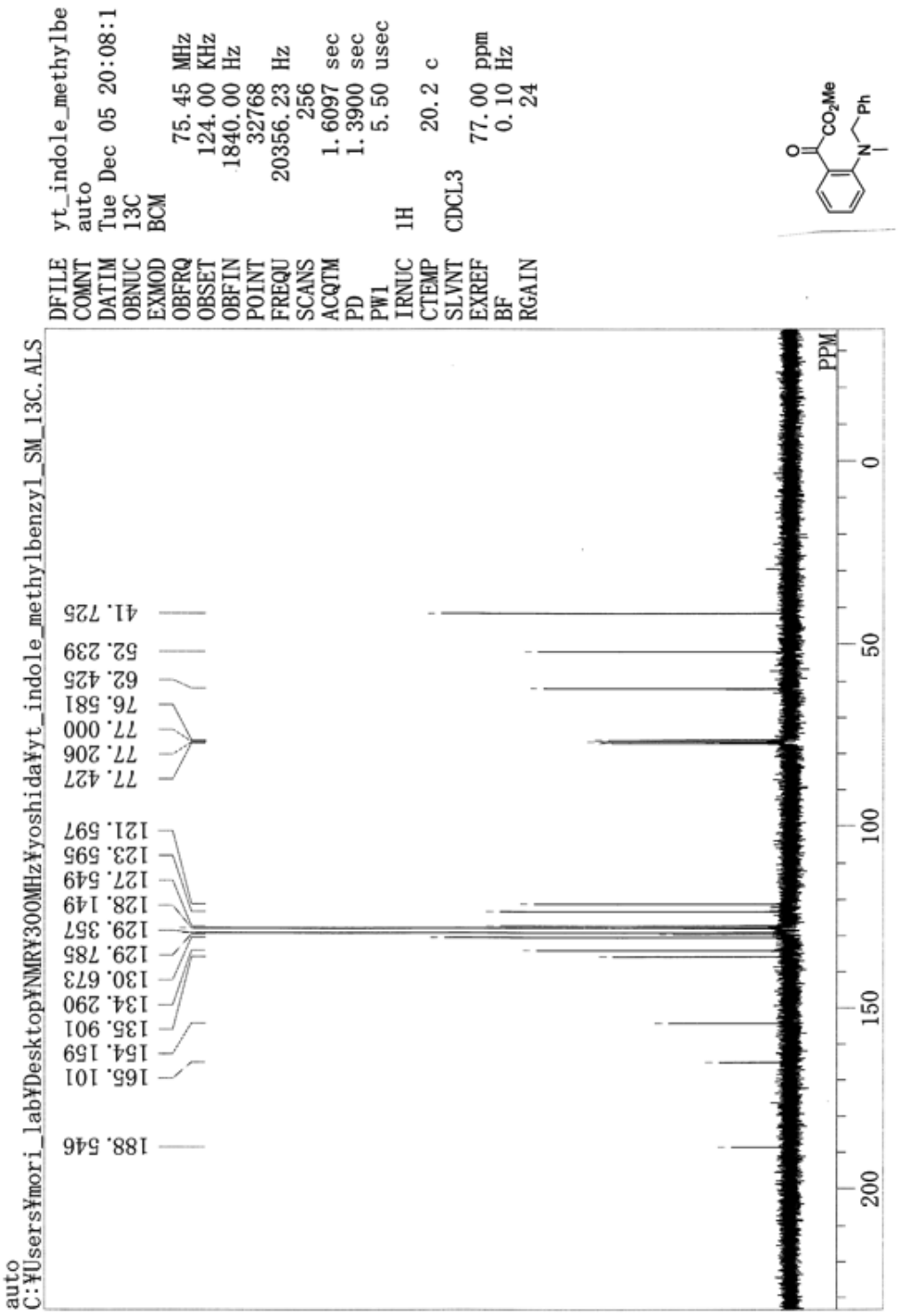
^{13}C NMR spectrum of **3l**.



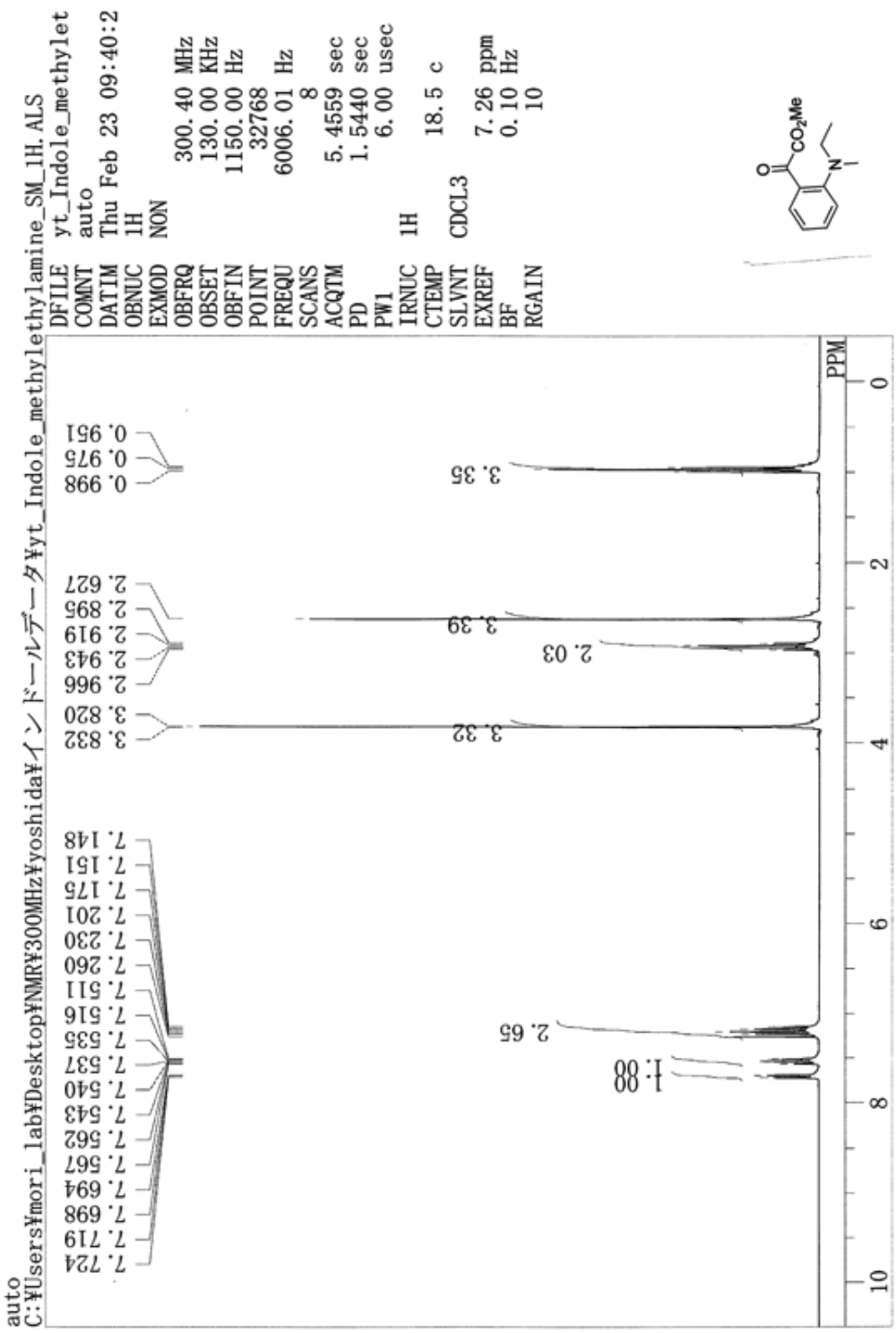
^{1}H NMR spectrum of **3m**.



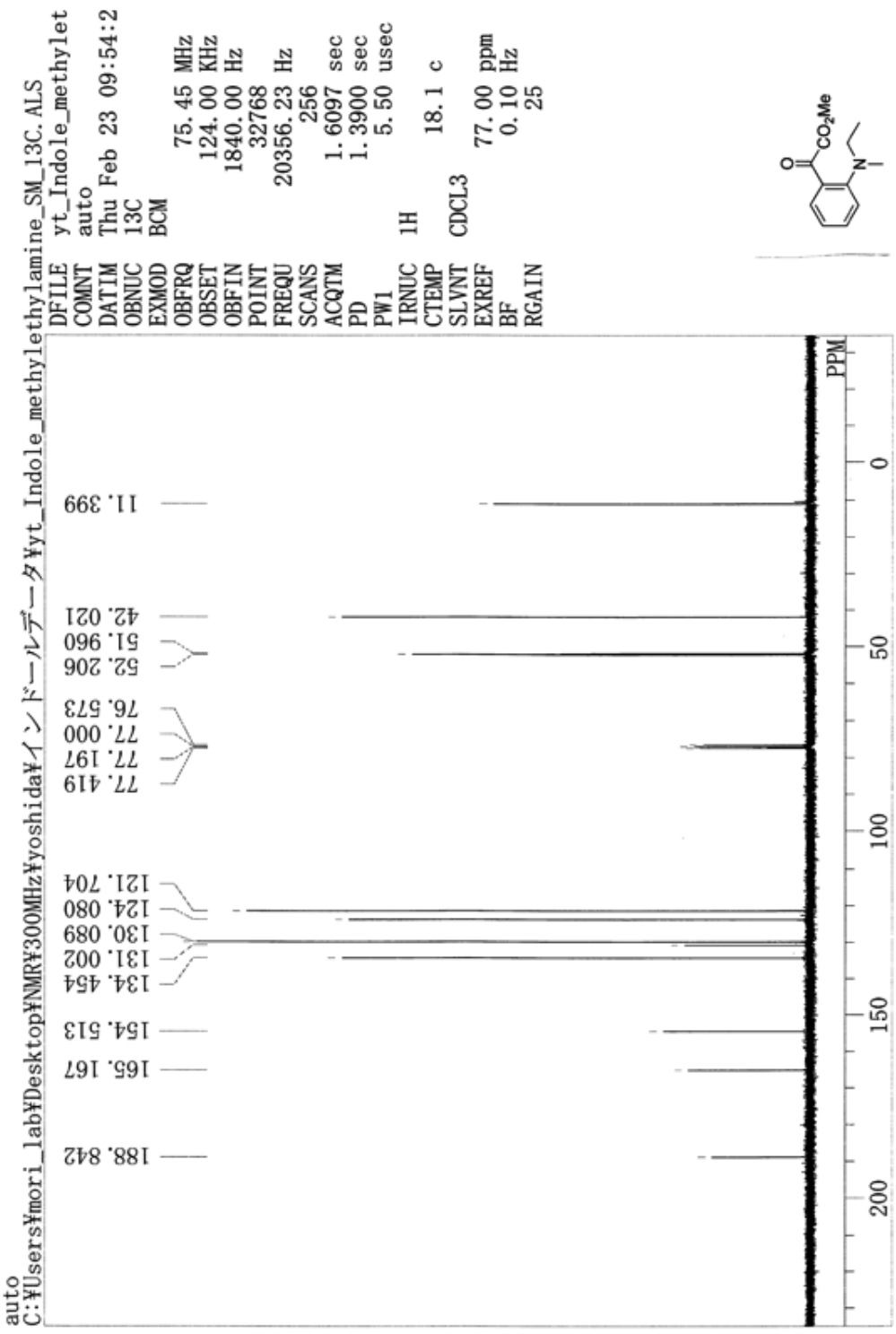
^{13}C NMR spectrum of **3m**.



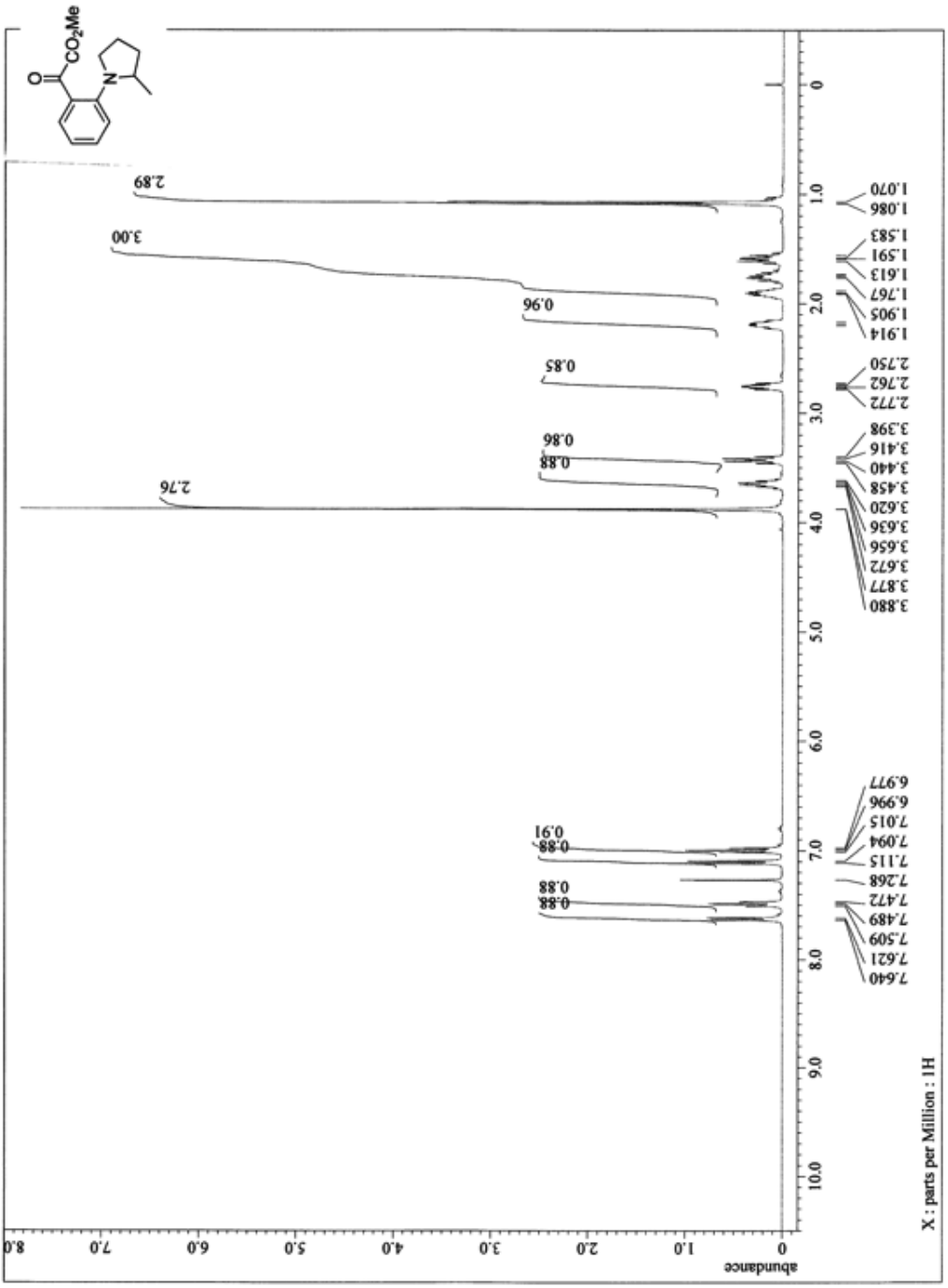
^{1}H NMR spectrum of **3n**.



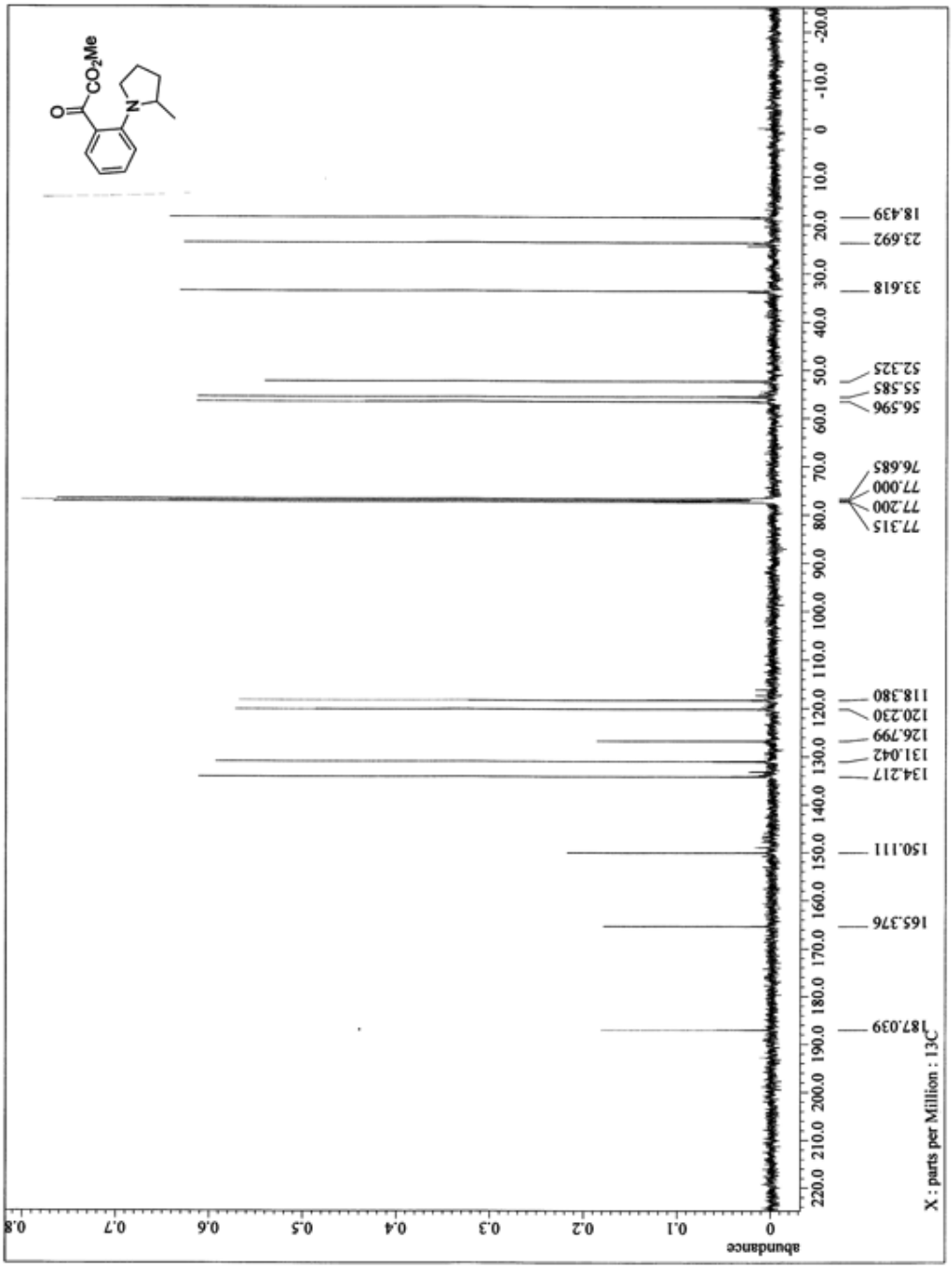
^{13}C NMR spectrum of **3n**.



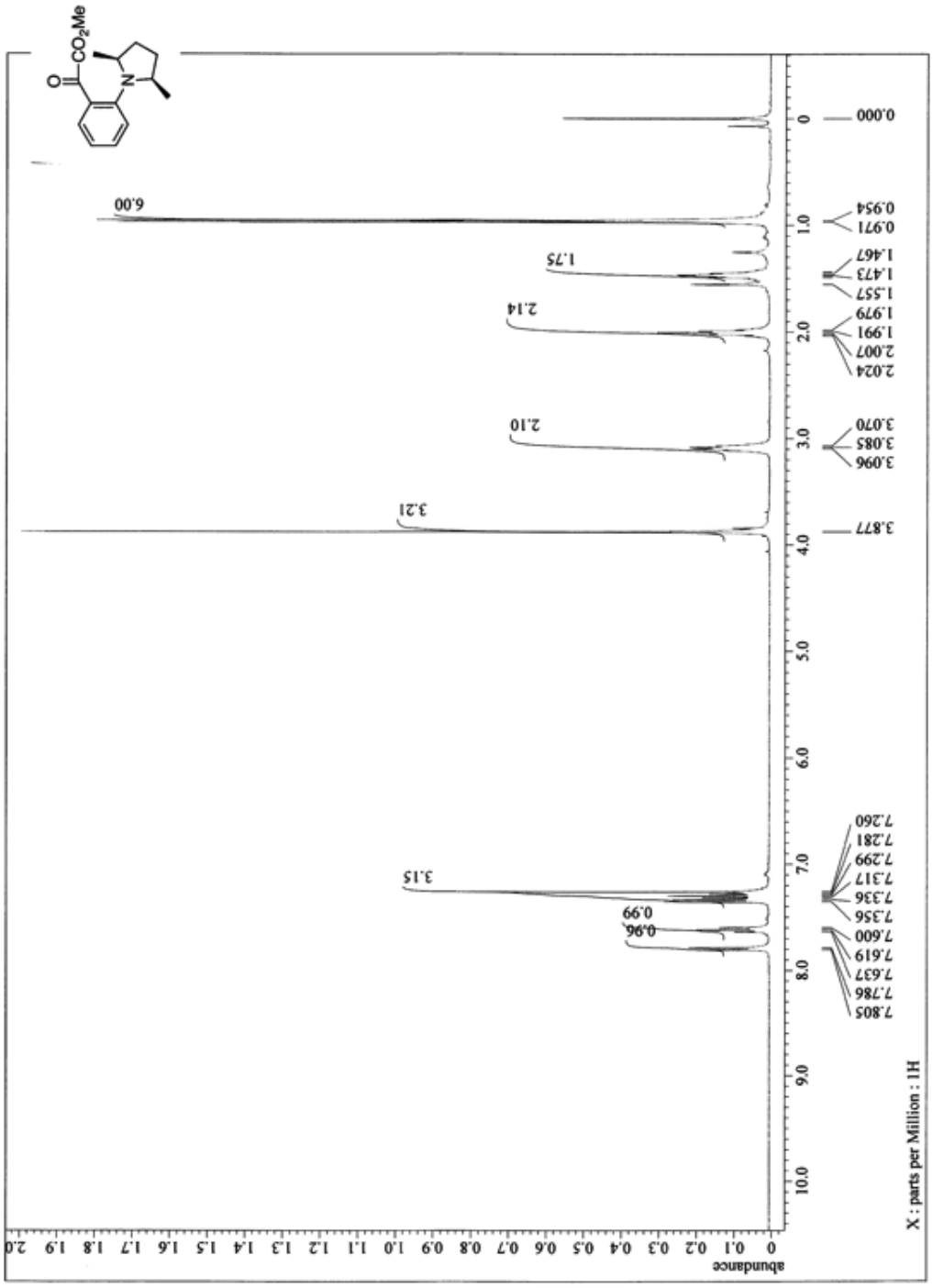
^{1}H NMR spectrum of **3o**.



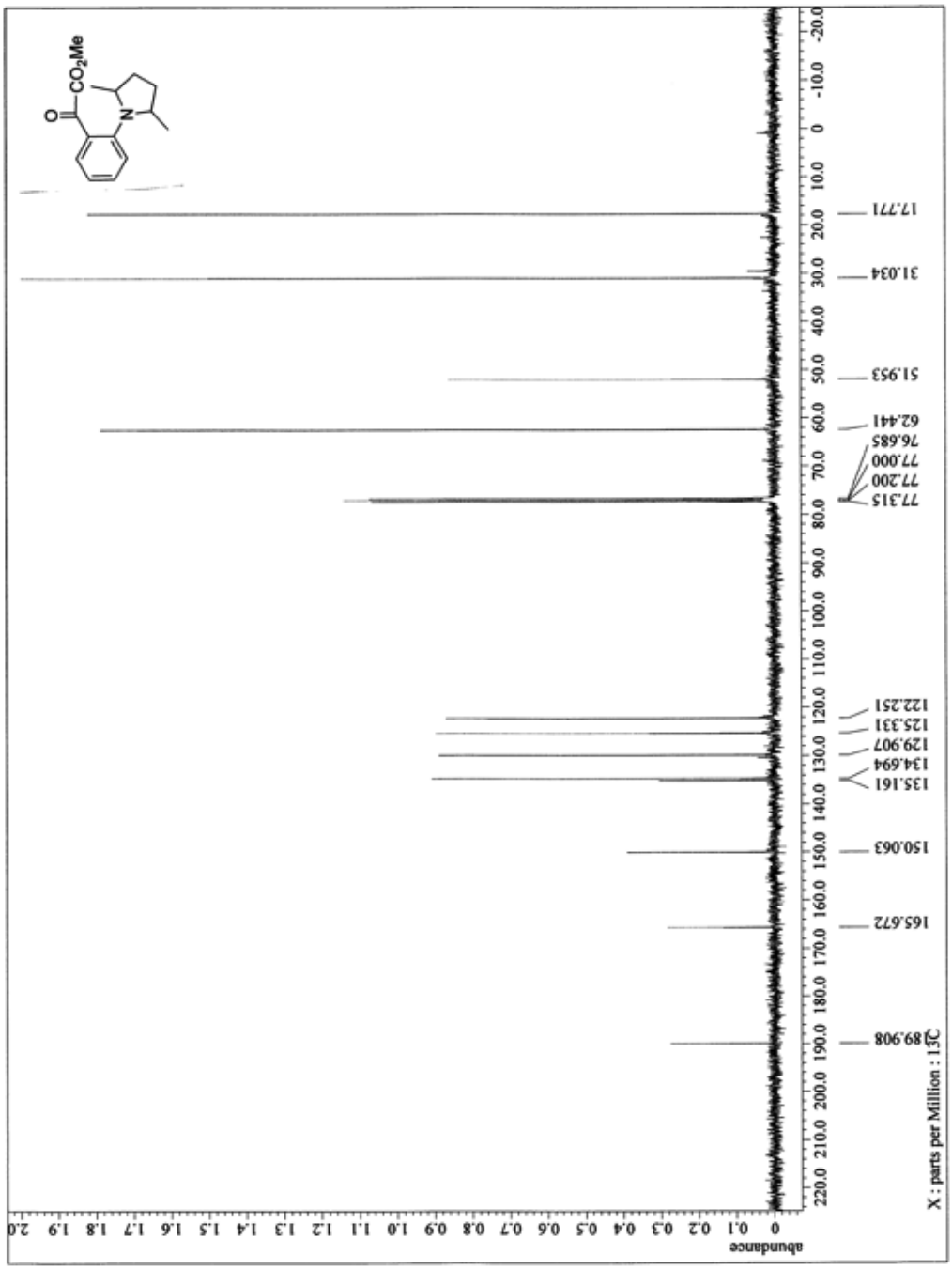
^{13}C NMR spectrum of **3o**.



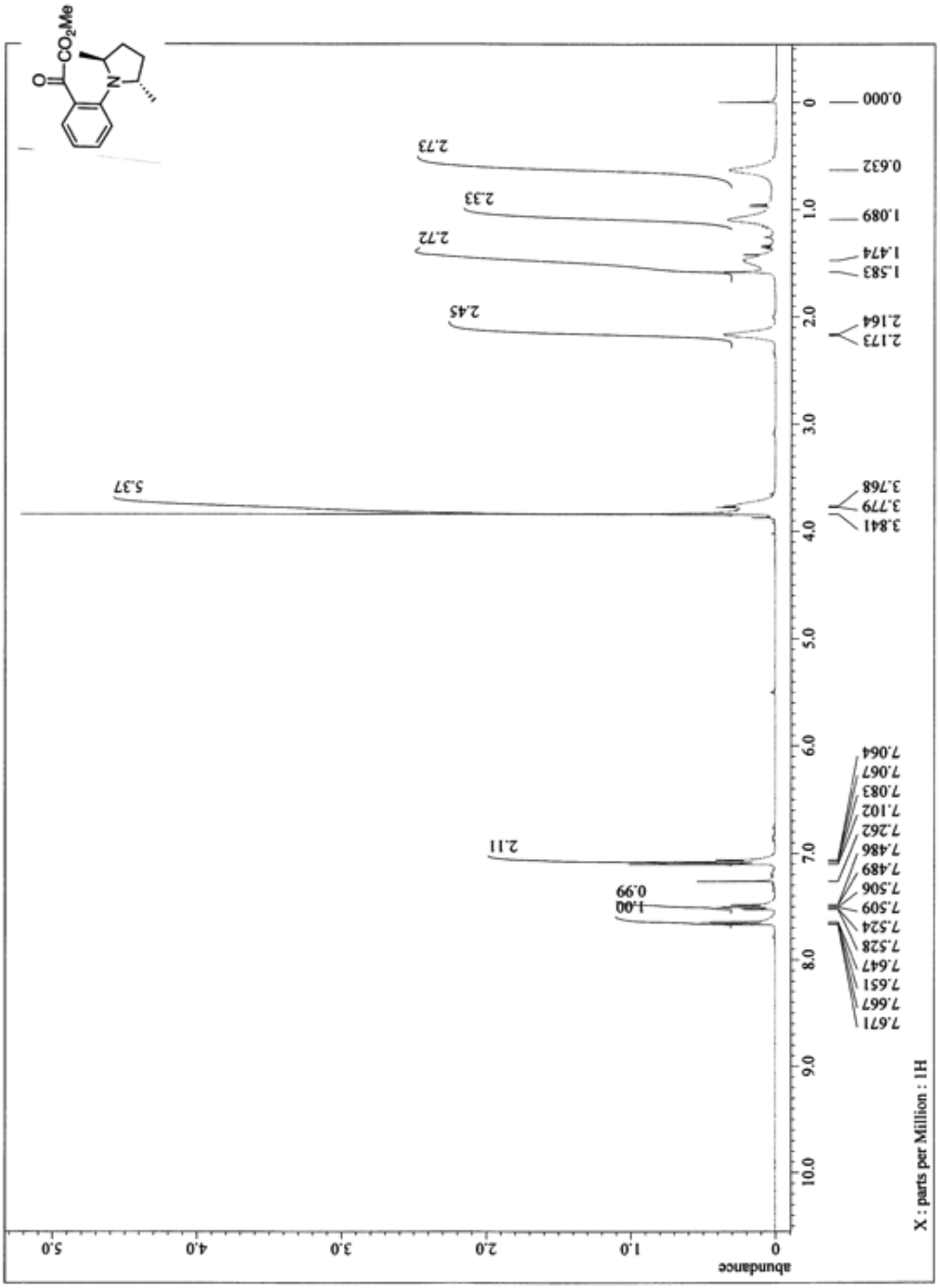
^{1}H NMR spectrum of *cis*-**6a**.



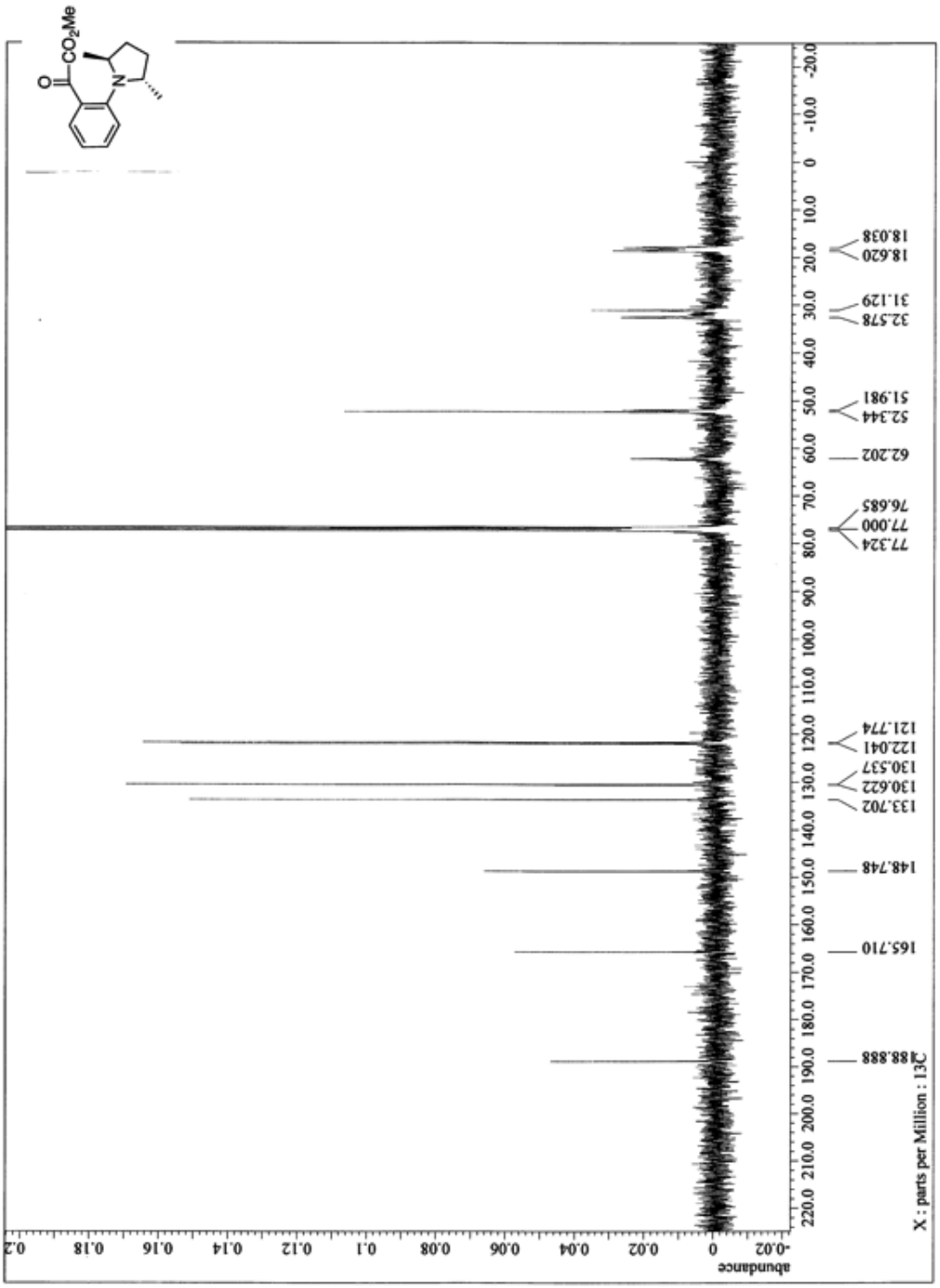
^{13}C NMR spectrum of *cis*-**6a**.



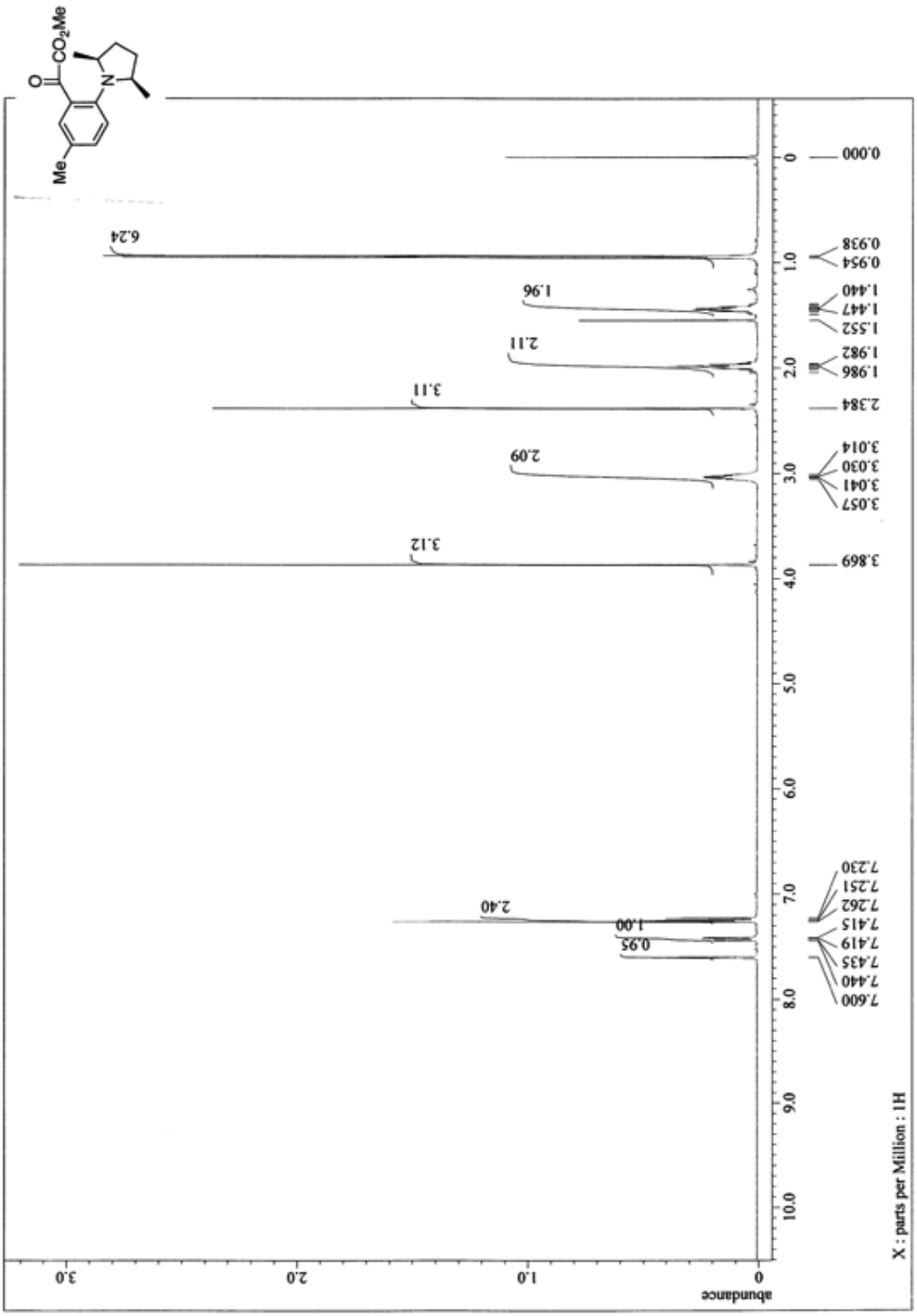
^{1}H NMR spectrum of *trans*-**6a**.



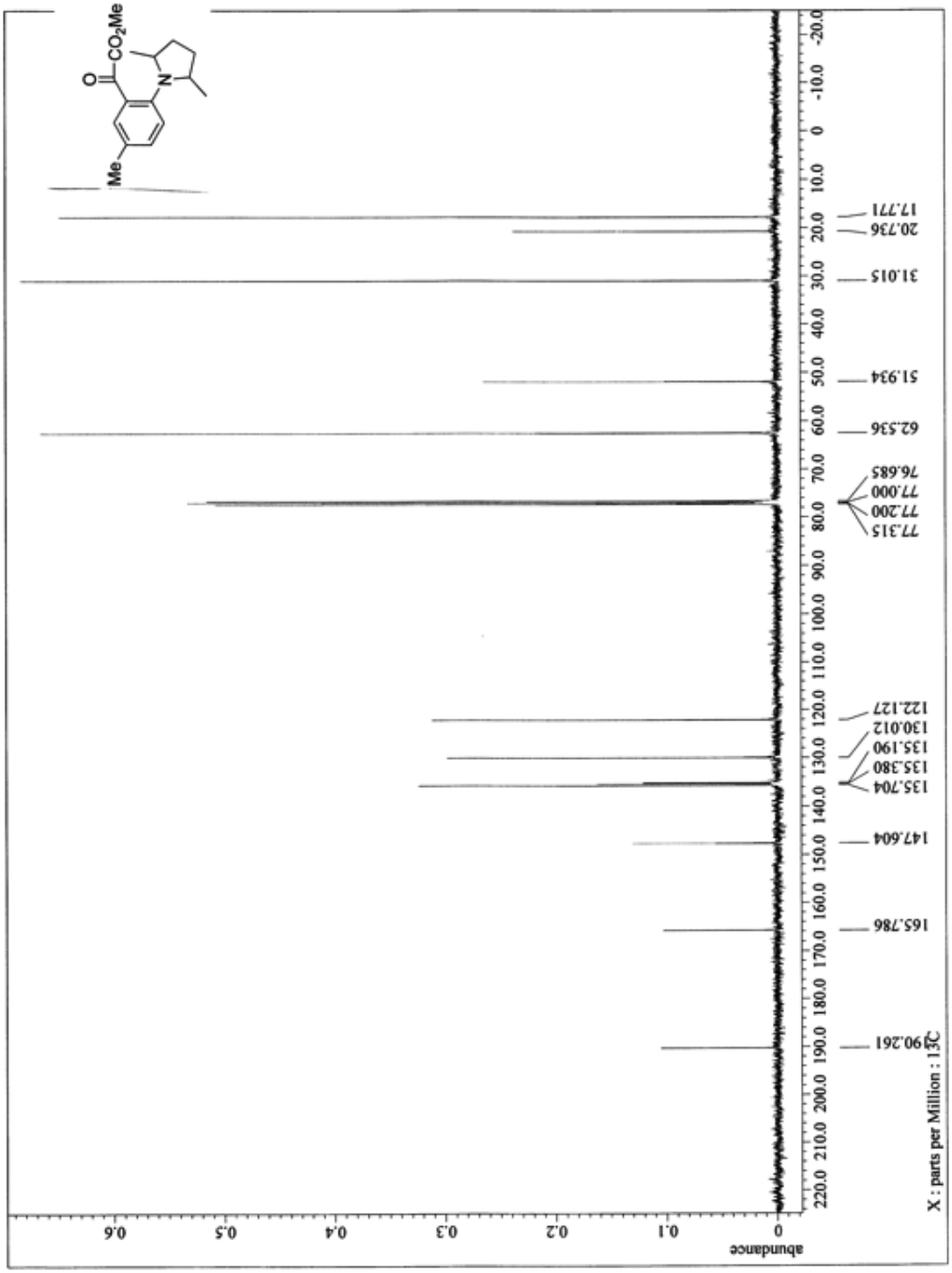
^{13}C NMR spectrum of *trans*-**6a**.



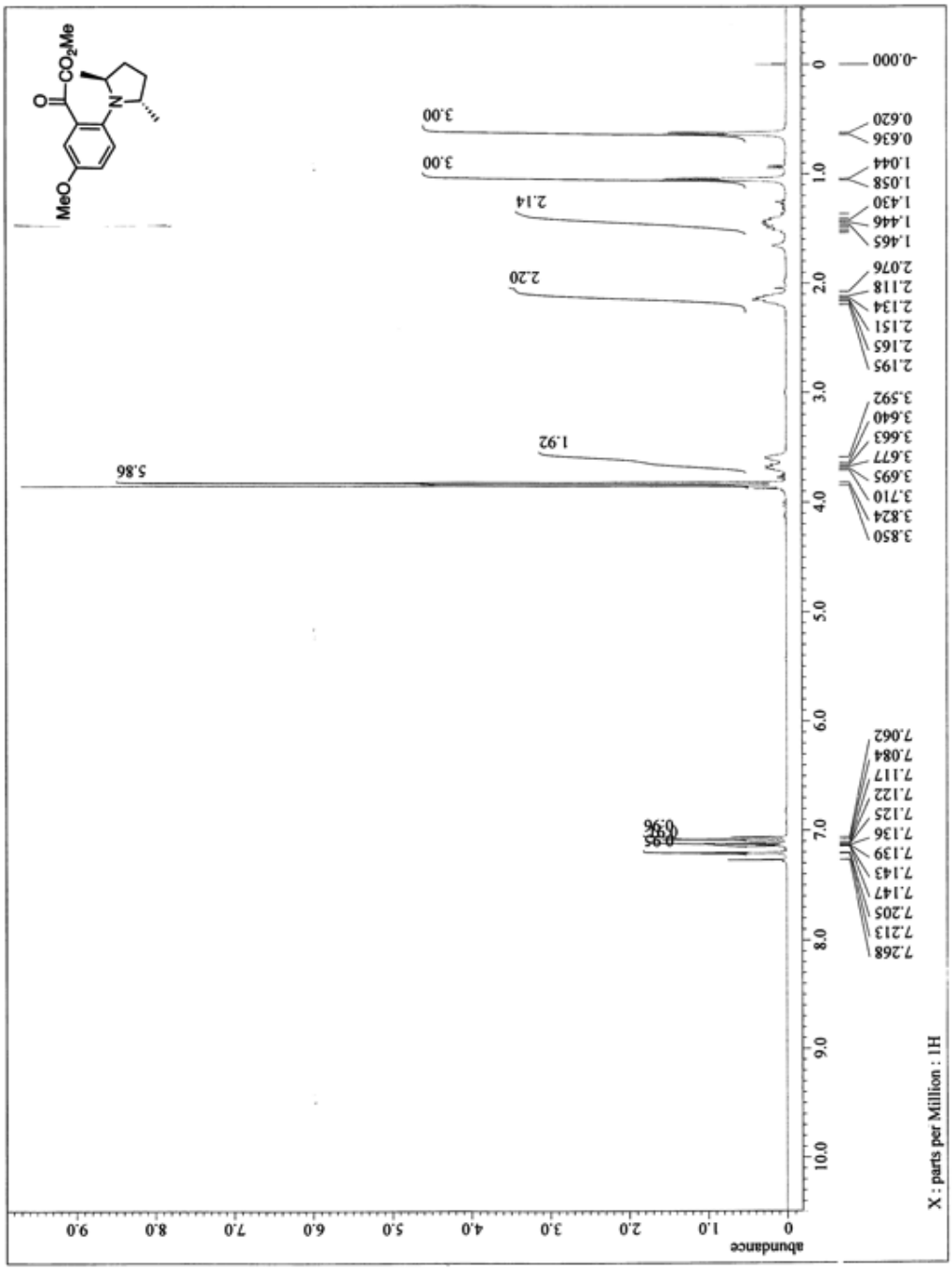
^{1}H NMR spectrum of **6b**.



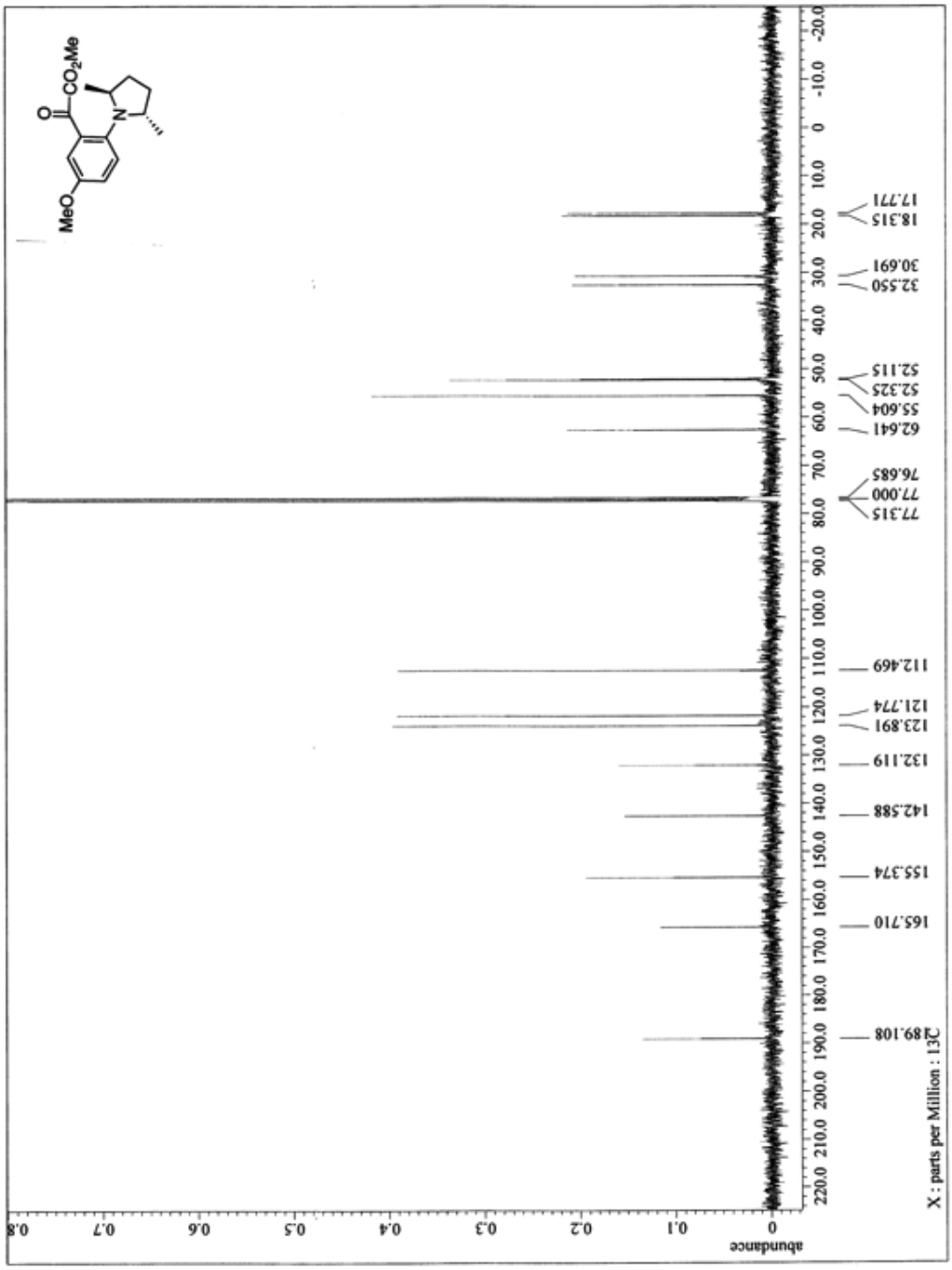
^{13}C NMR spectrum of **6b**.



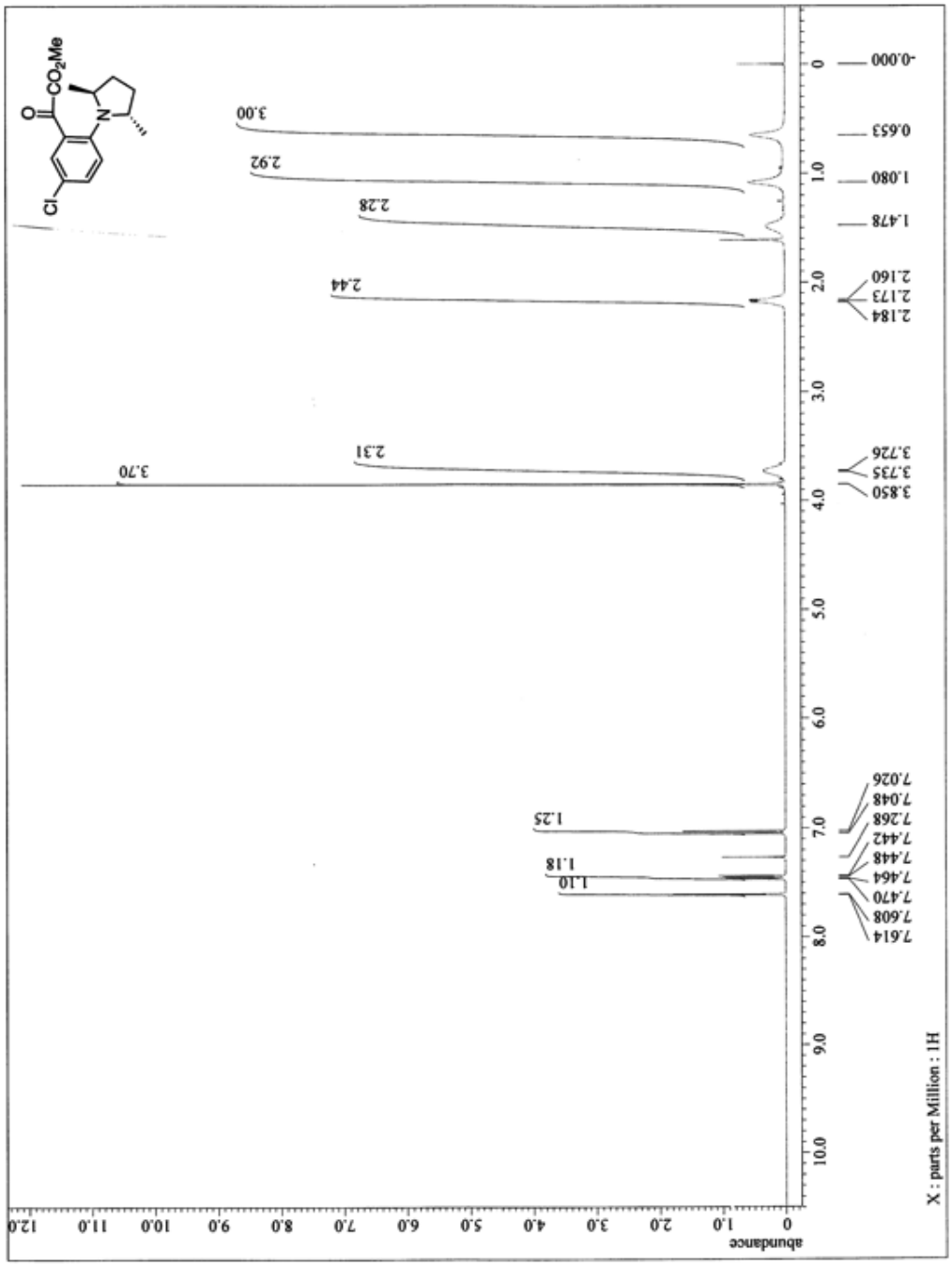
^{1}H NMR spectrum of **6c**.



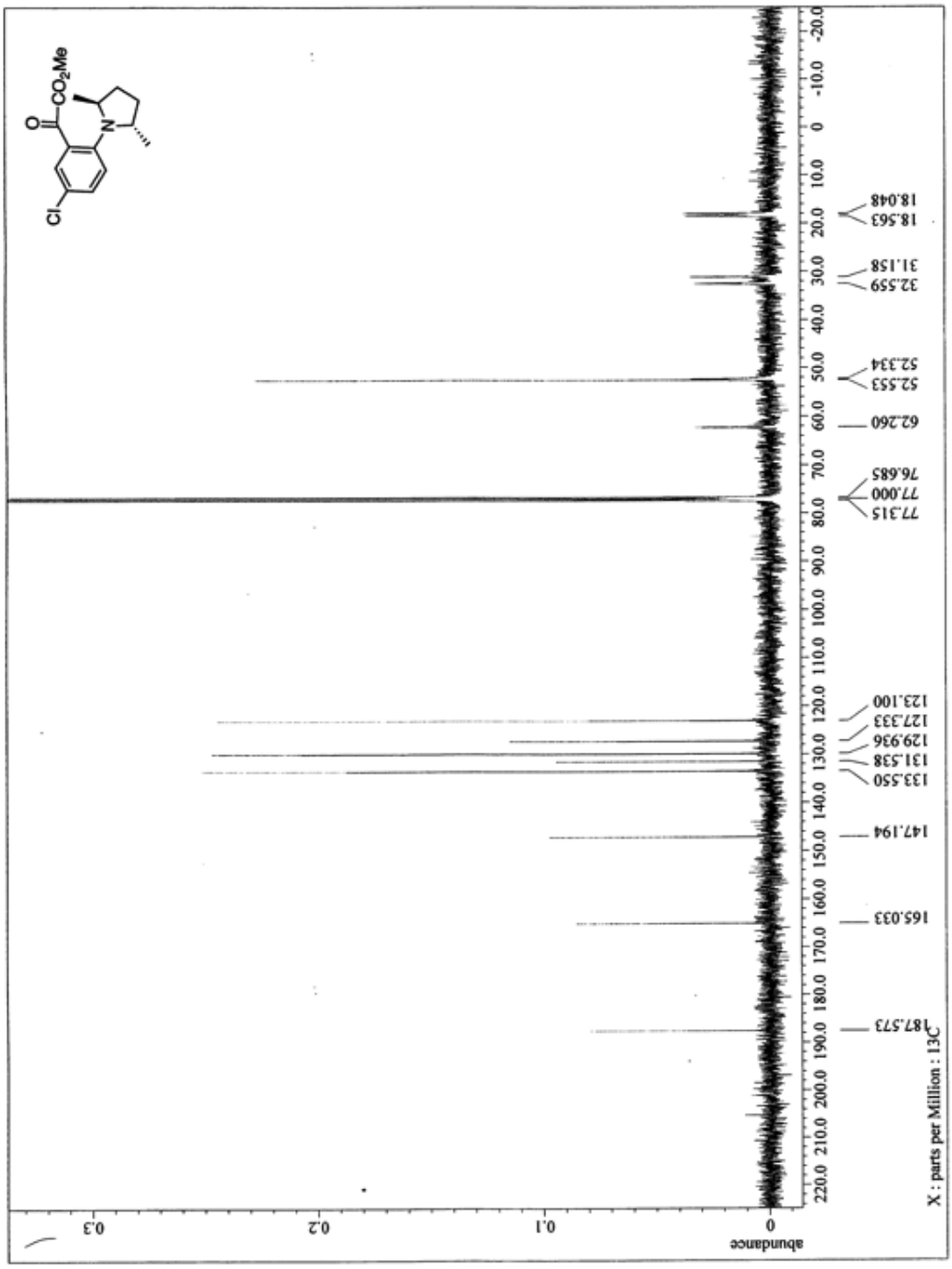
^{13}C NMR spectrum of **6c**.



^{1}H NMR spectrum of **6d**.



^{13}C NMR spectrum of **6d**.



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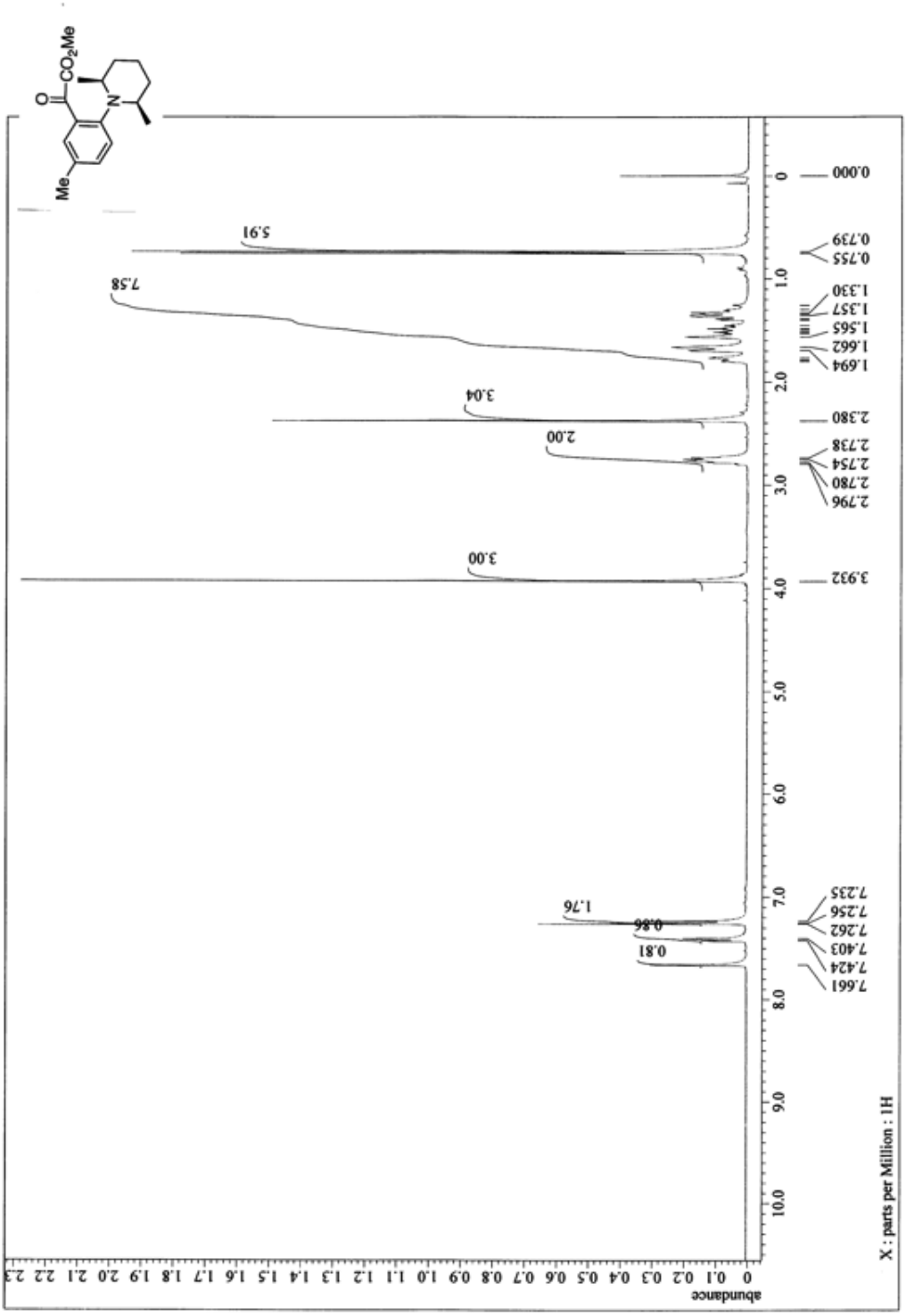
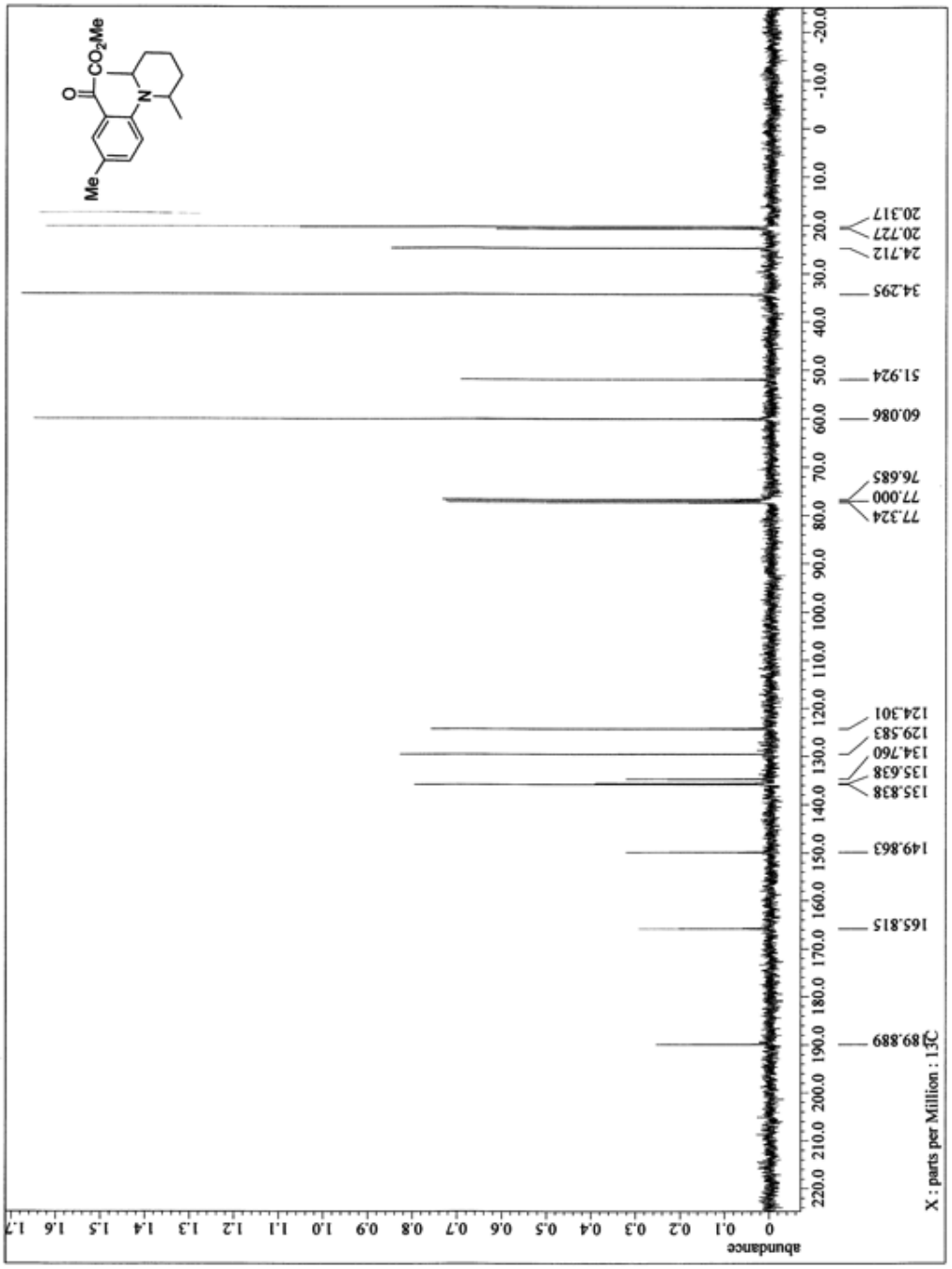
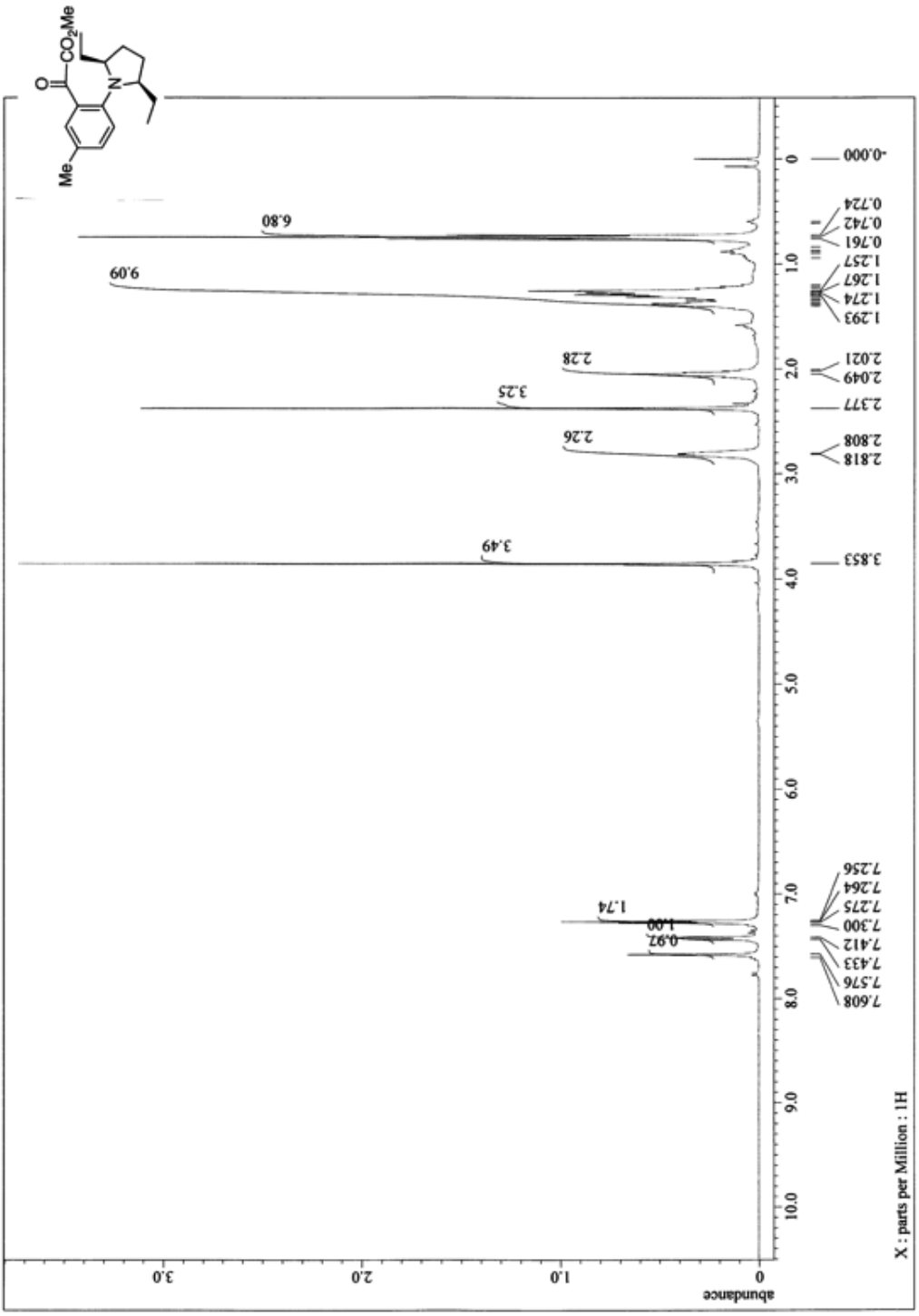
^{1}H NMR spectrum of **6e**.



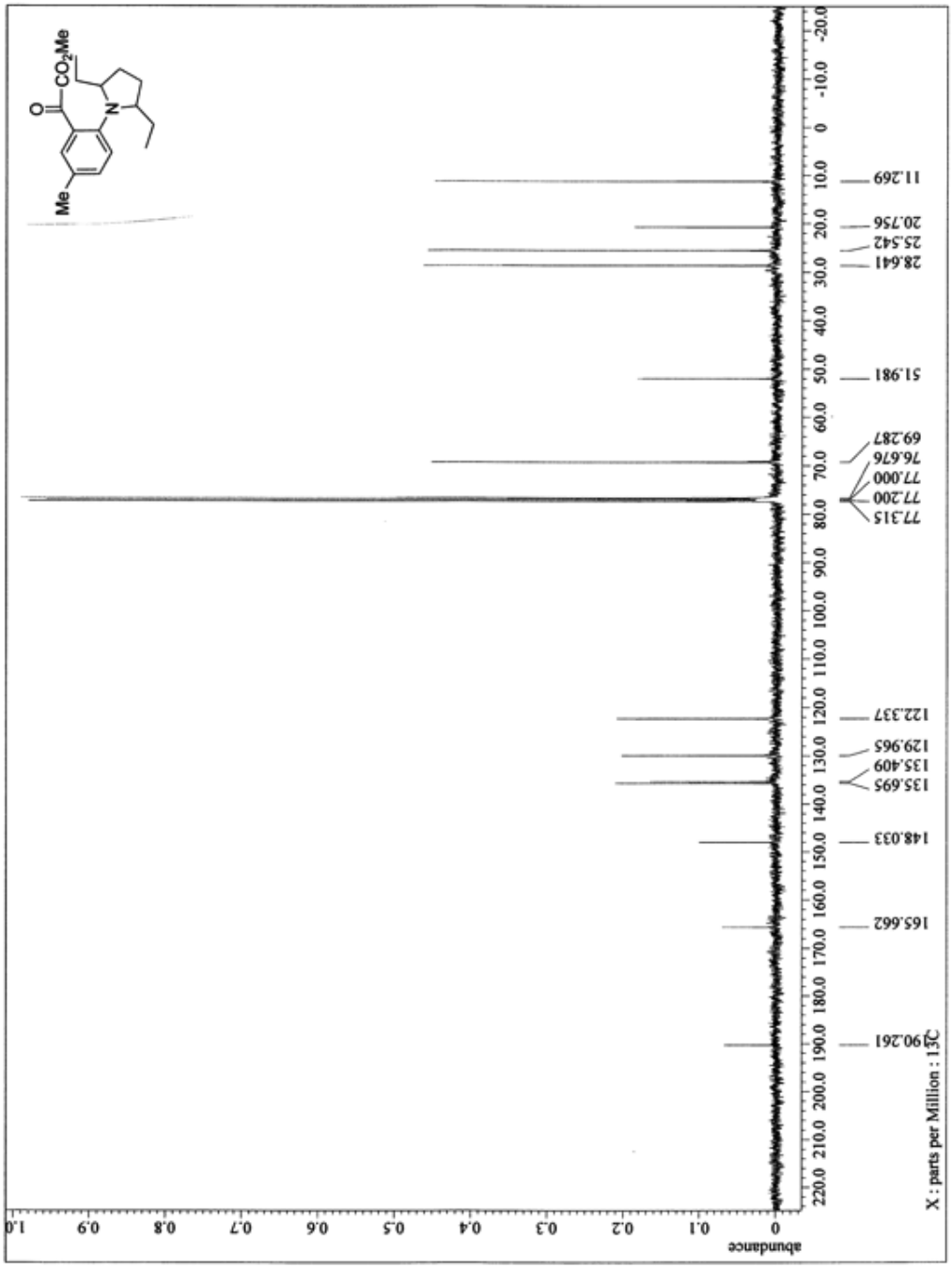
^{13}C NMR spectrum of **6e**.



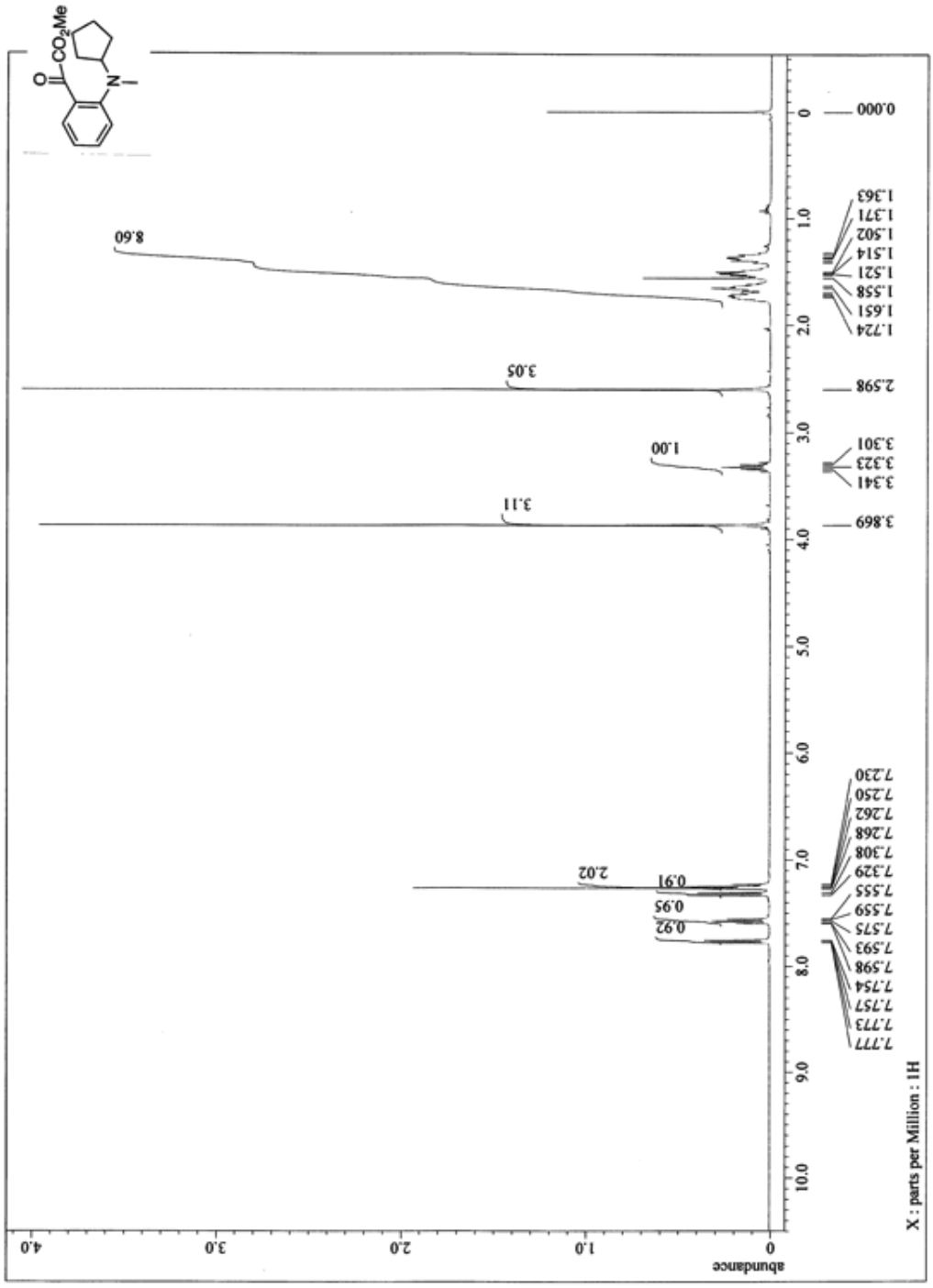
^{1}H NMR spectrum of **6f**.



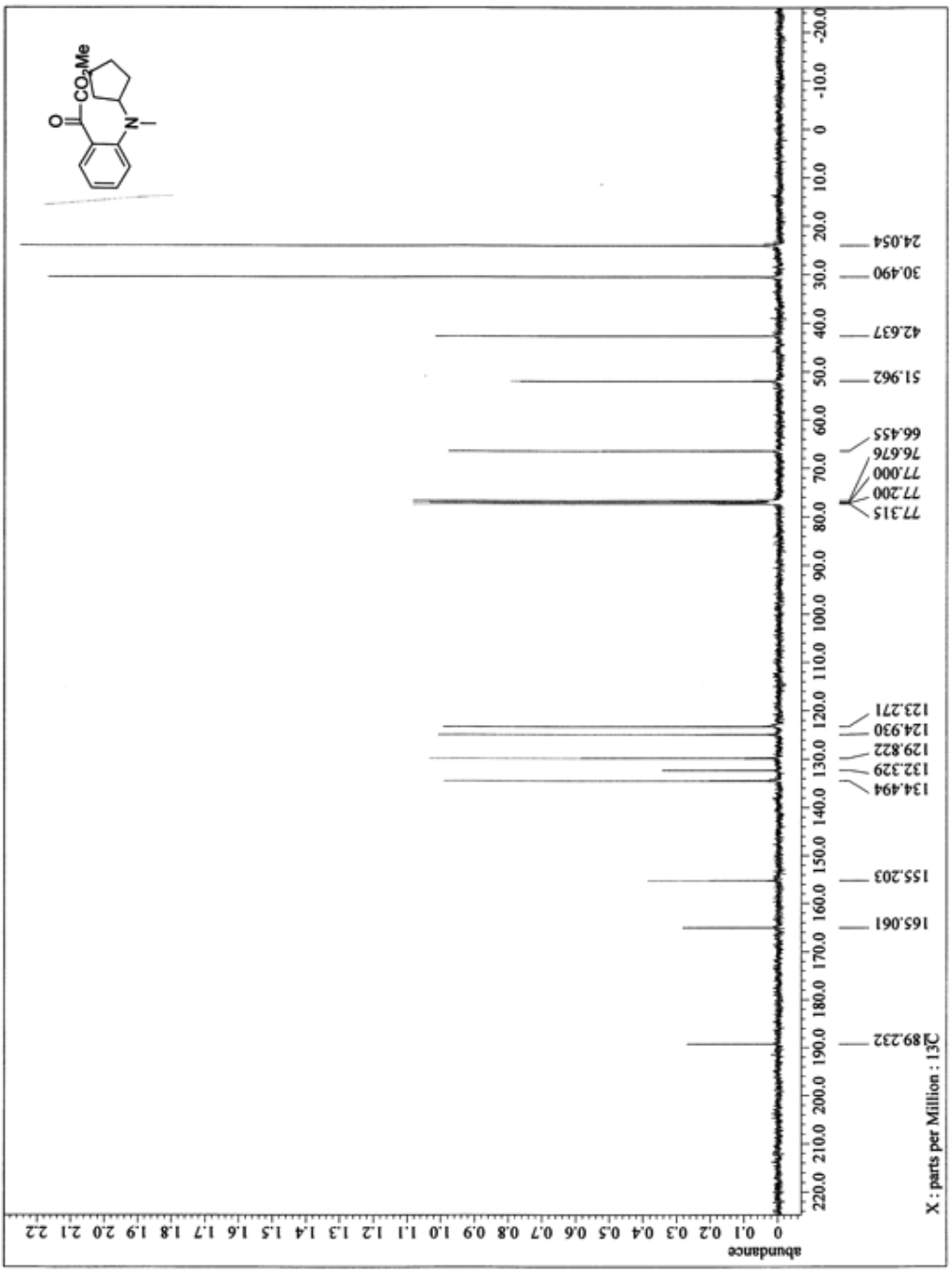
^{13}C NMR spectrum of **6f**.



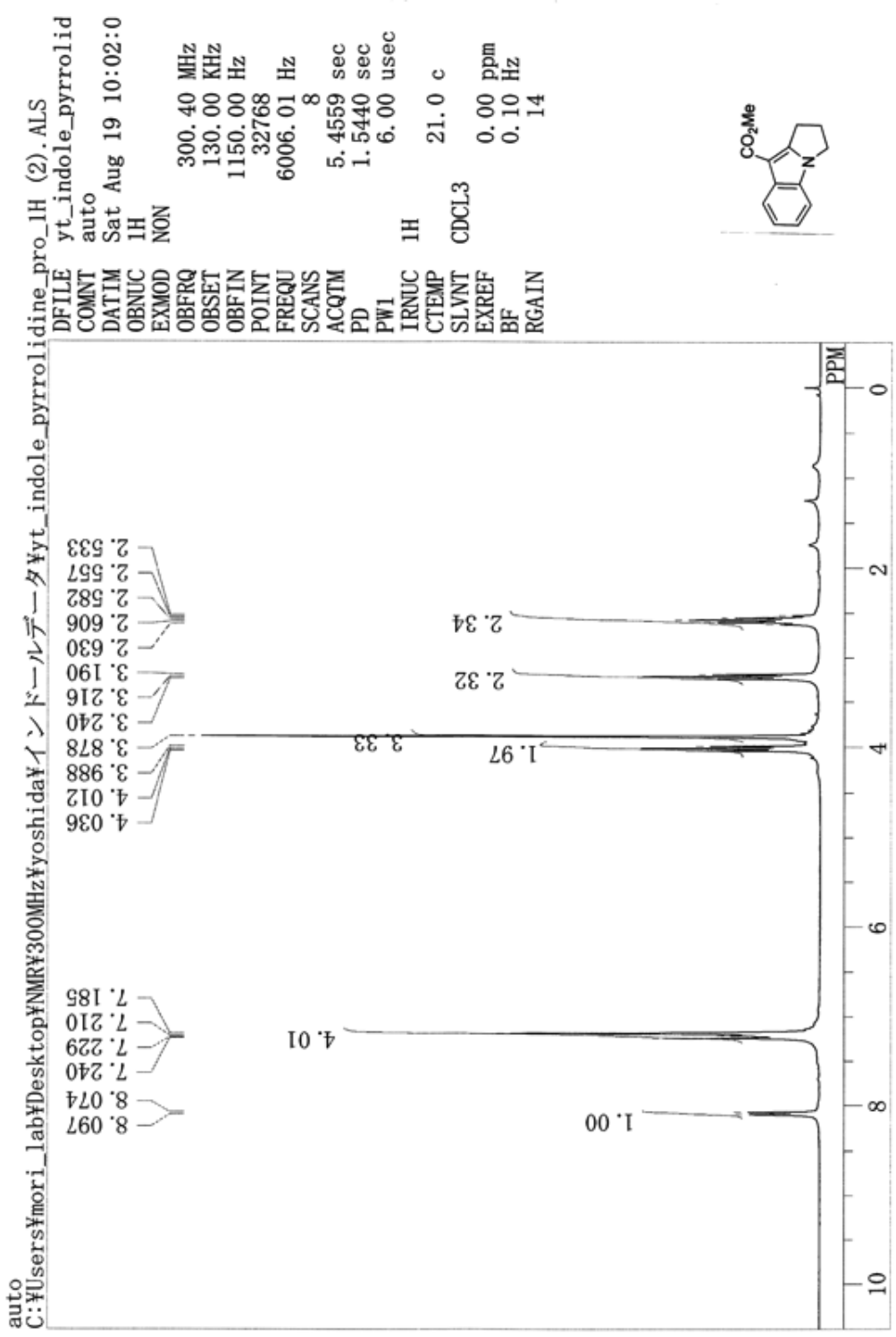
^{1}H NMR spectrum of **6g**



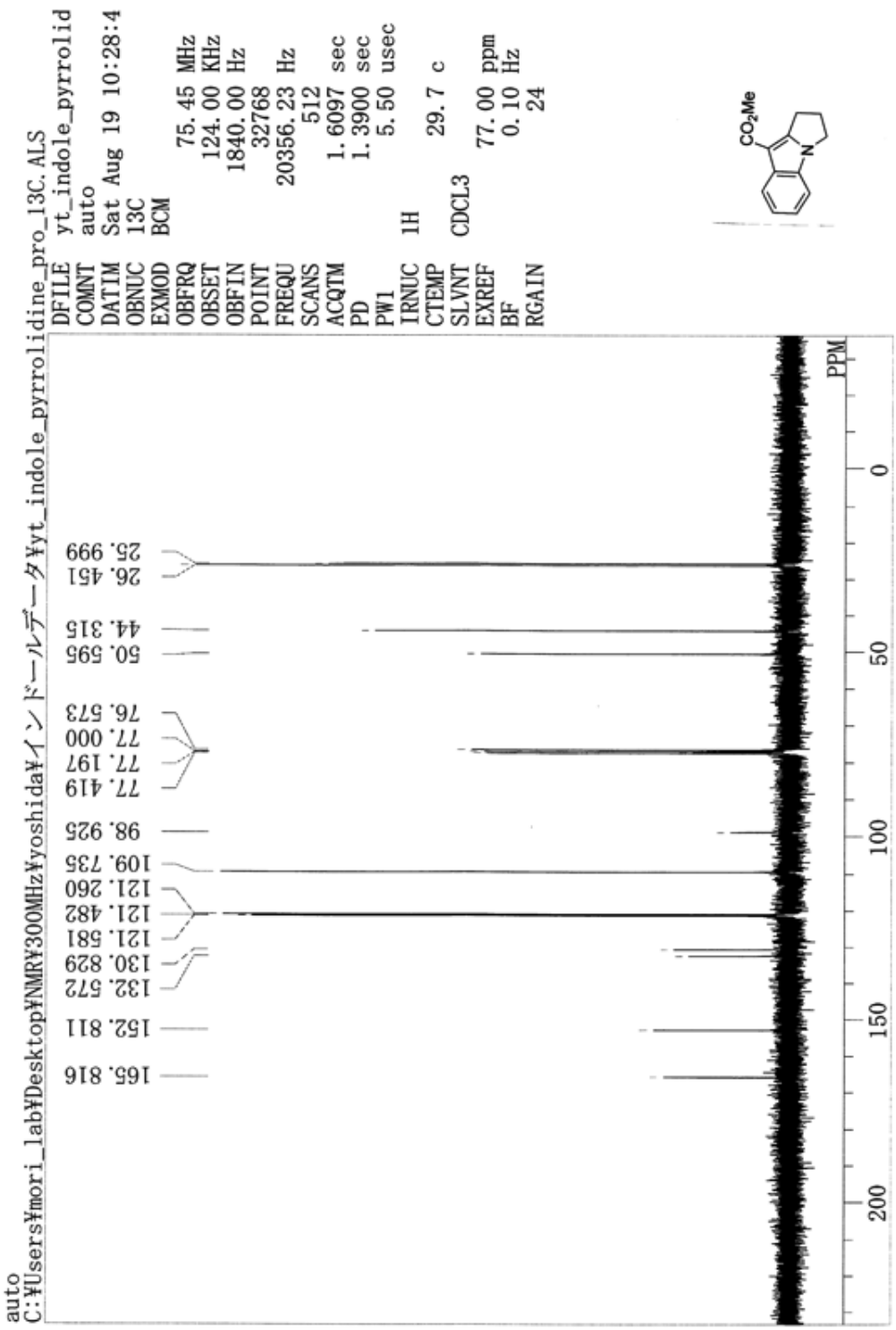
^{13}C NMR spectrum of **6g**.



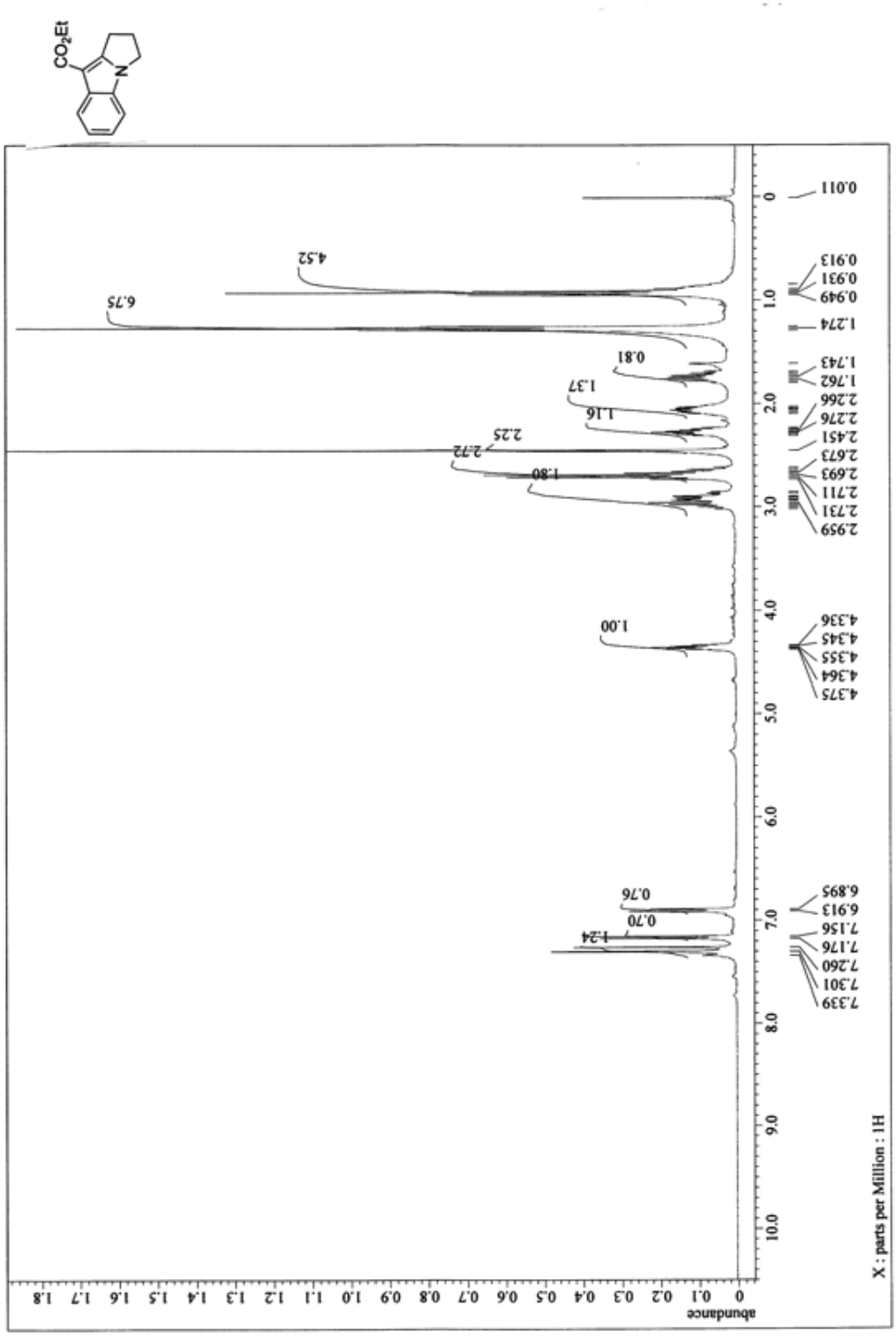
^{1}H NMR spectrum of **4a**.



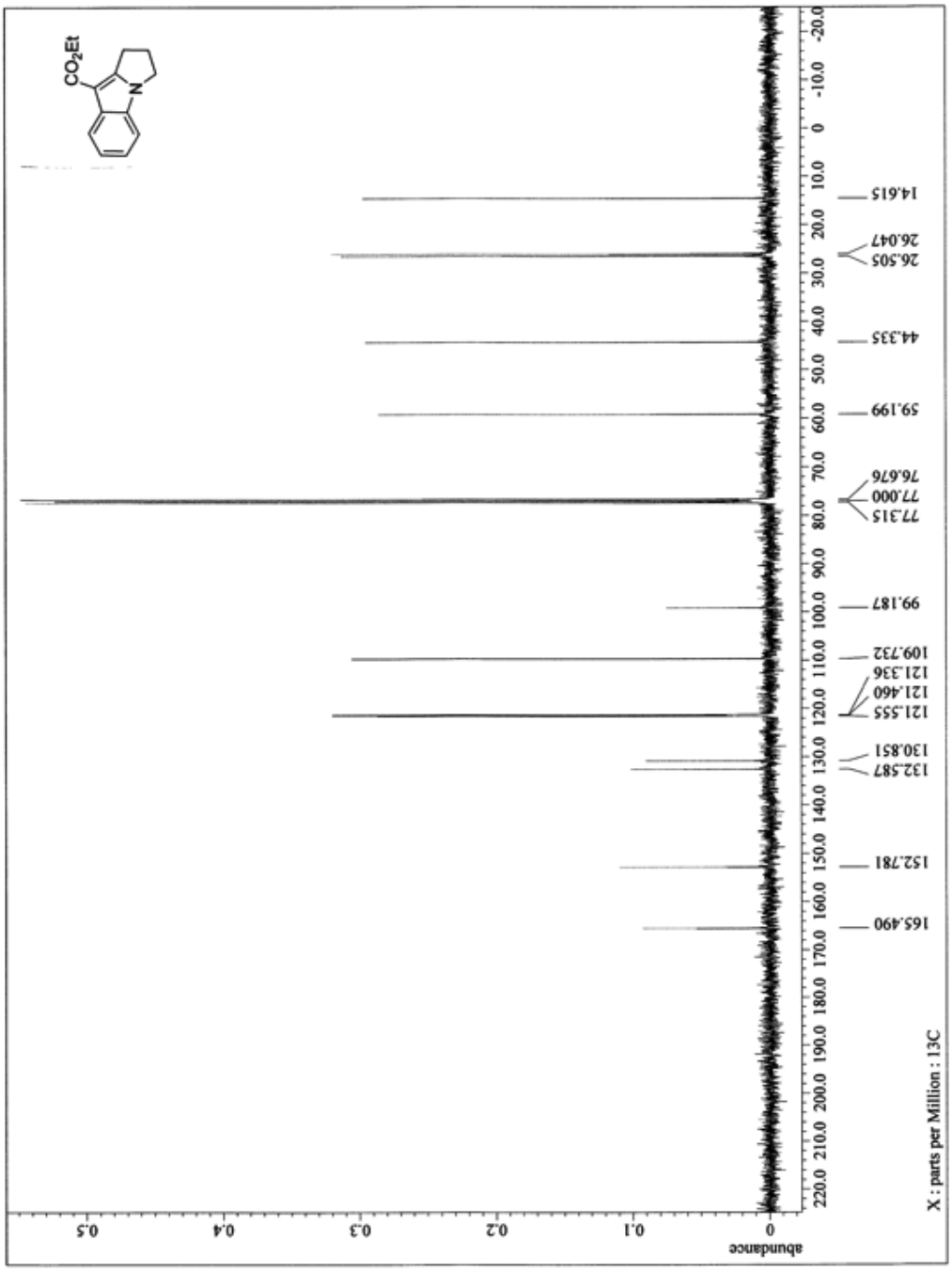
^{13}C NMR spectrum of **4a**.



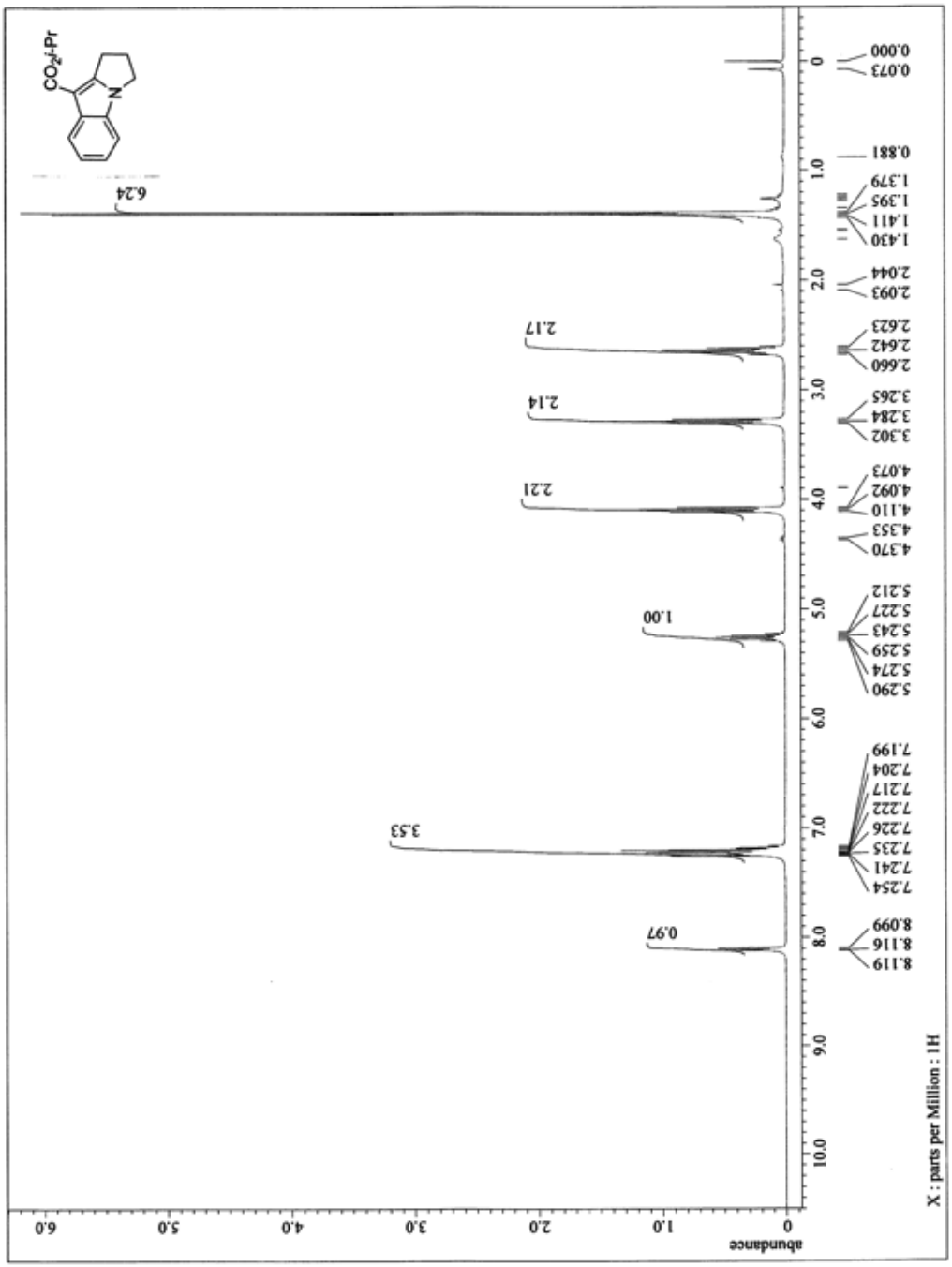
^{1}H NMR spectrum of **4b**.



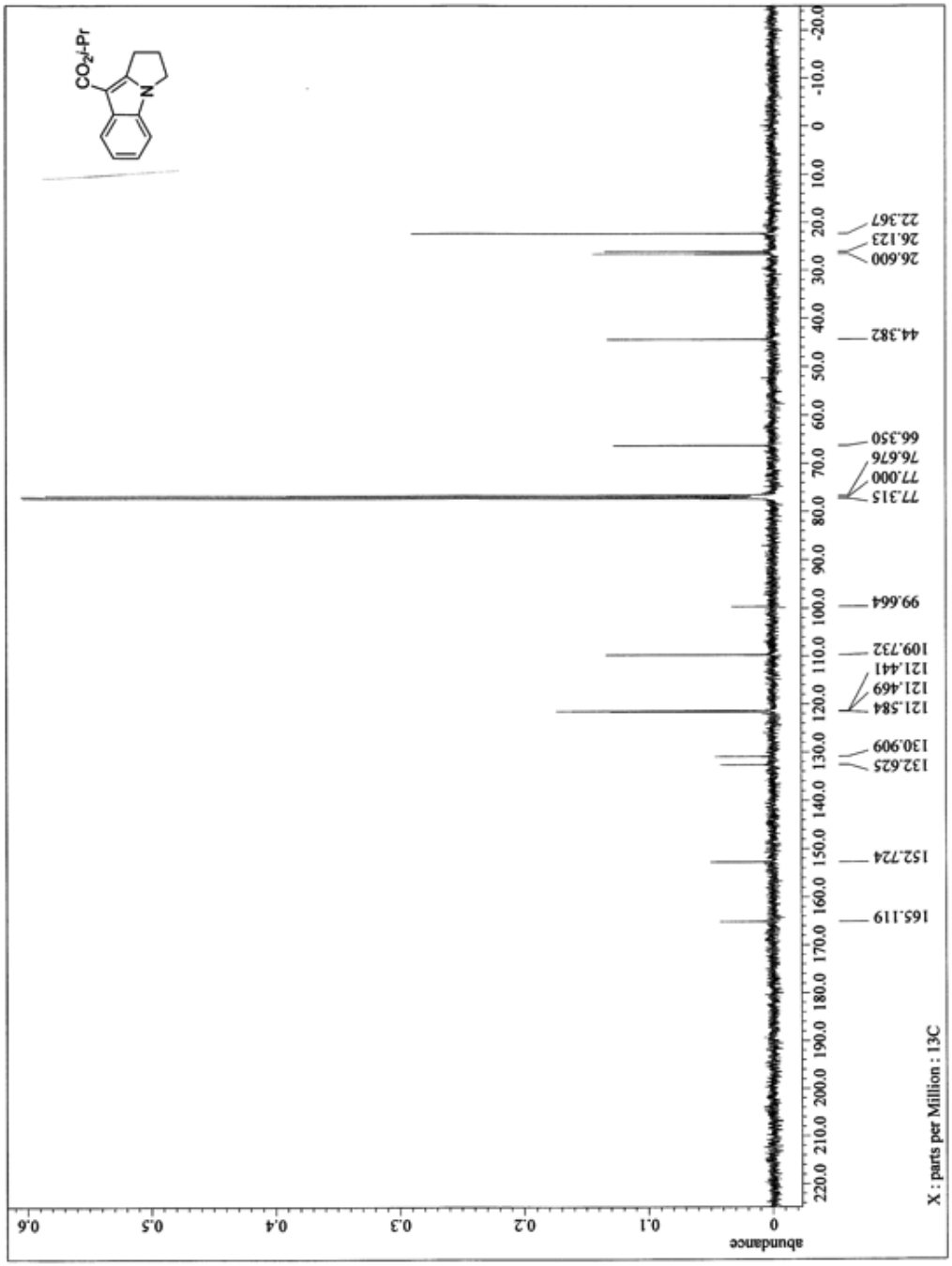
^{13}C NMR spectrum of **4b**.



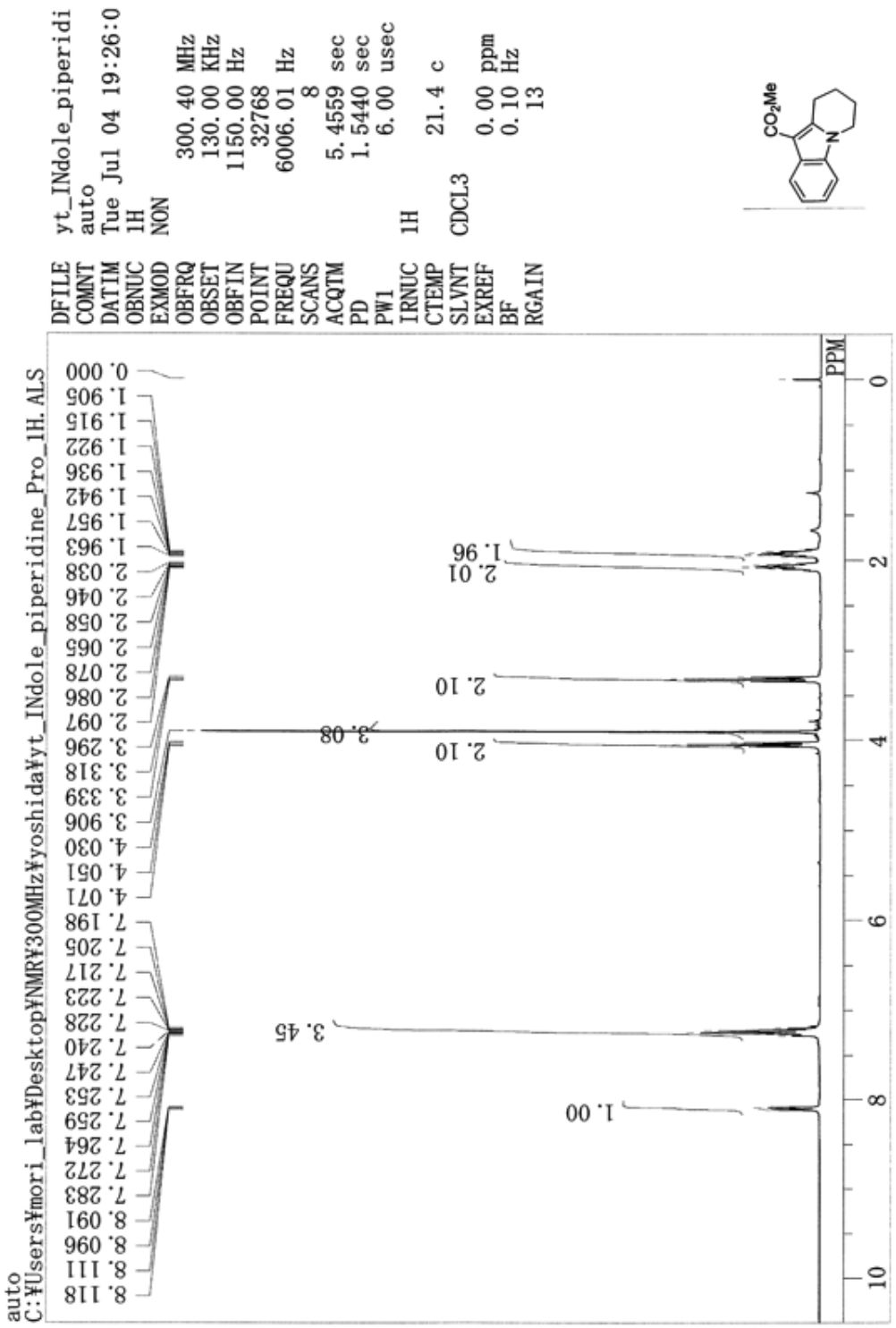
^{1}H NMR spectrum of **4c**.



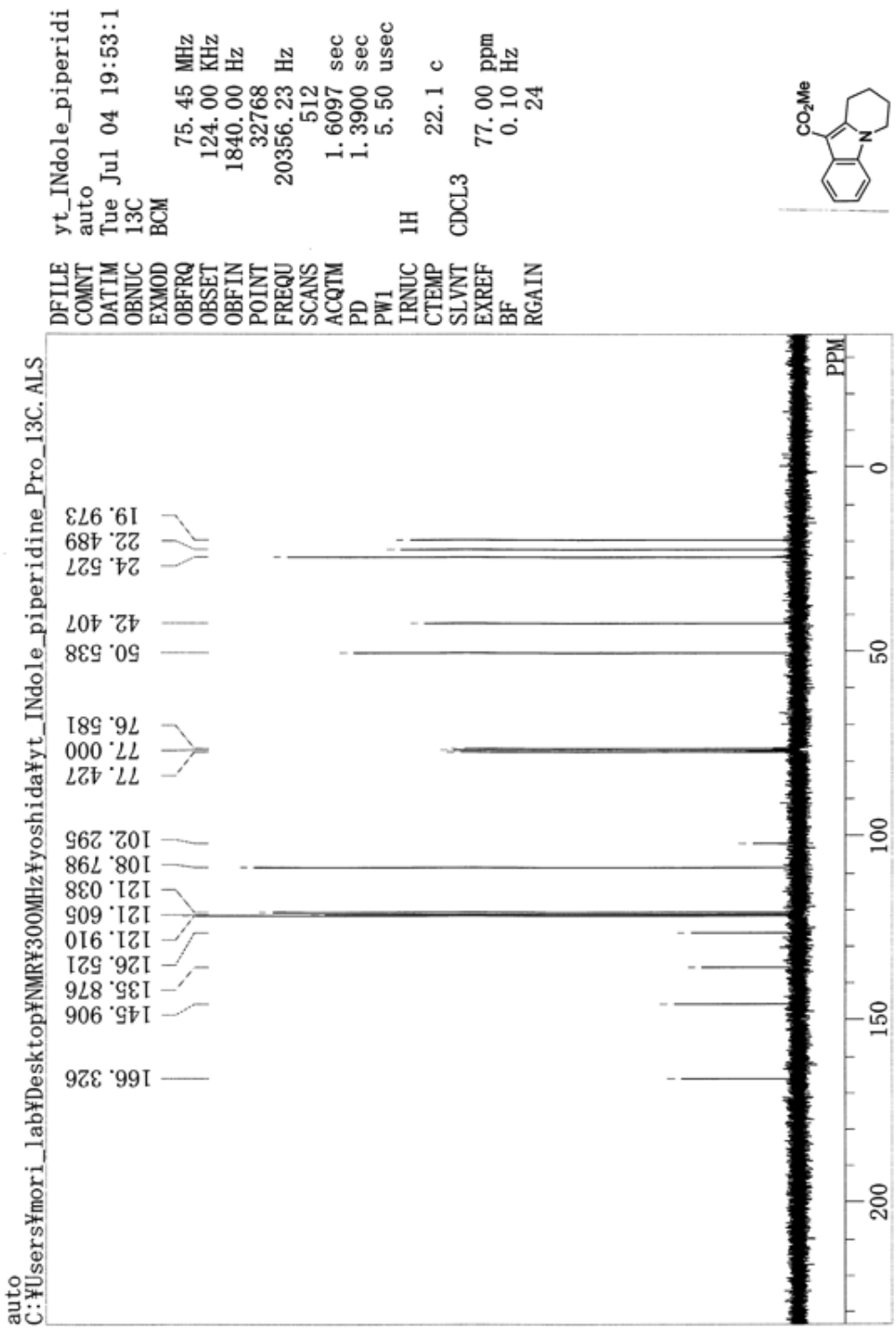
^{13}C NMR spectrum of **4c**.



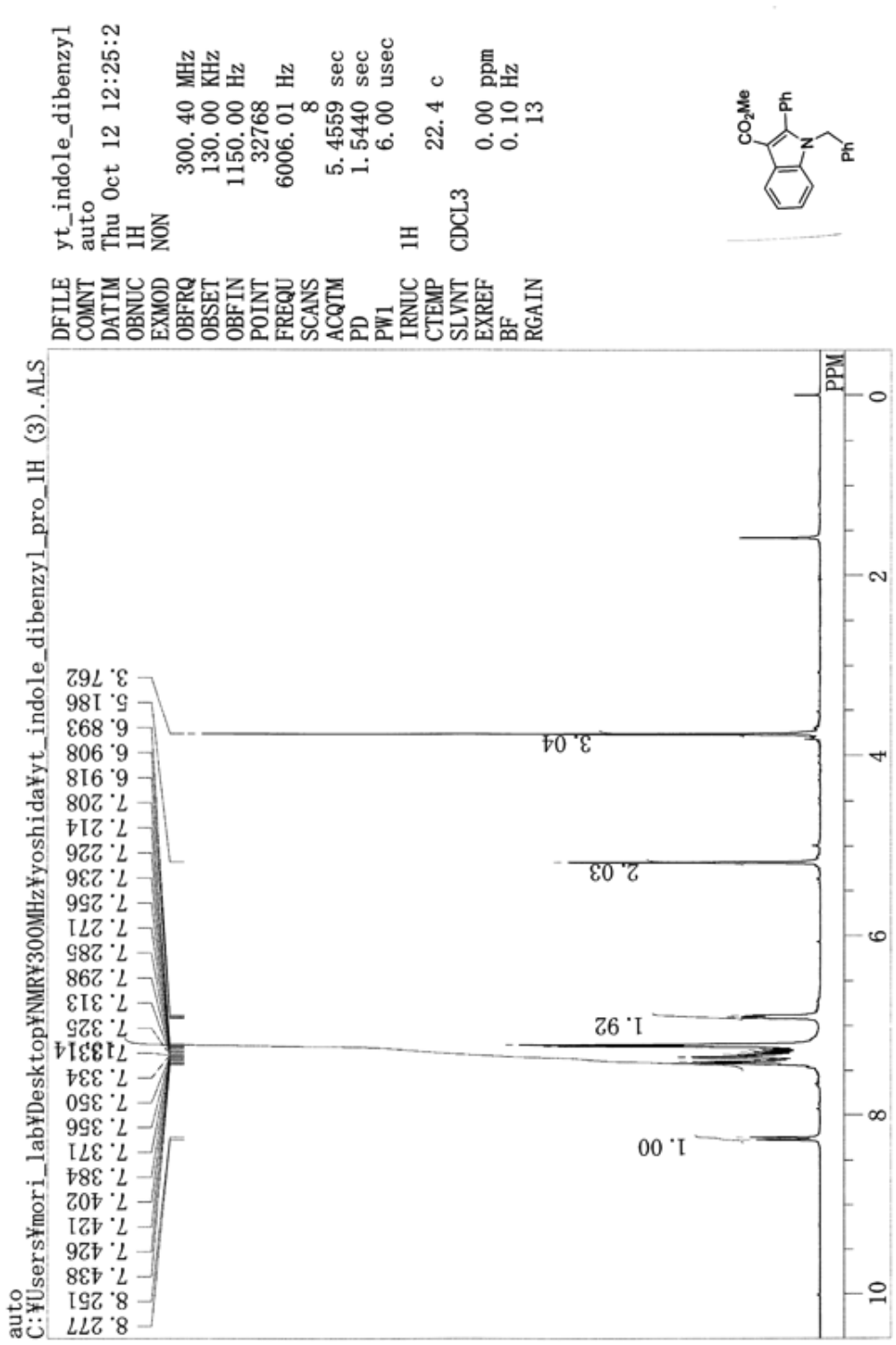
^{1}H NMR spectrum of **4d**.



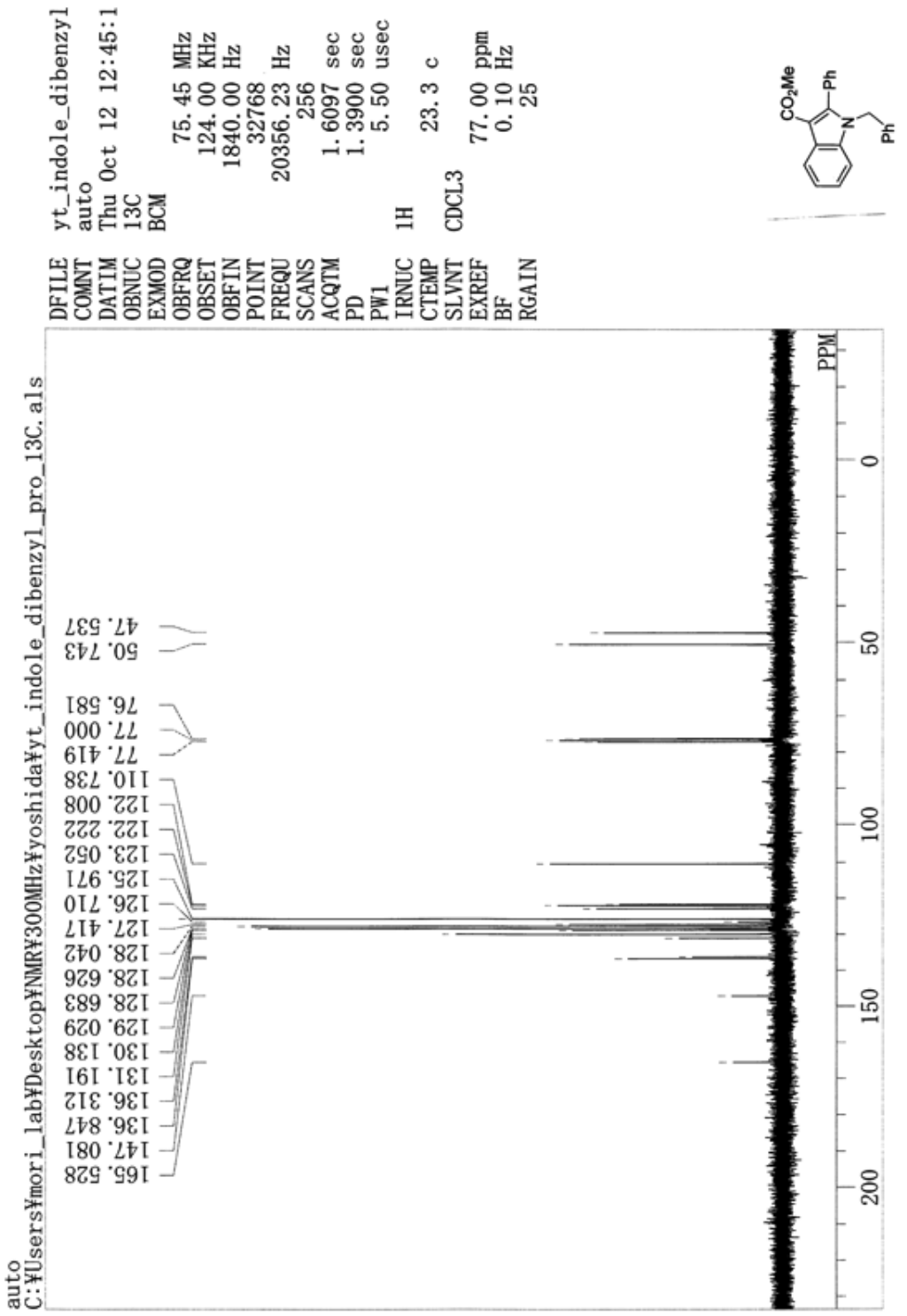
^{13}C NMR spectrum of **4d**.



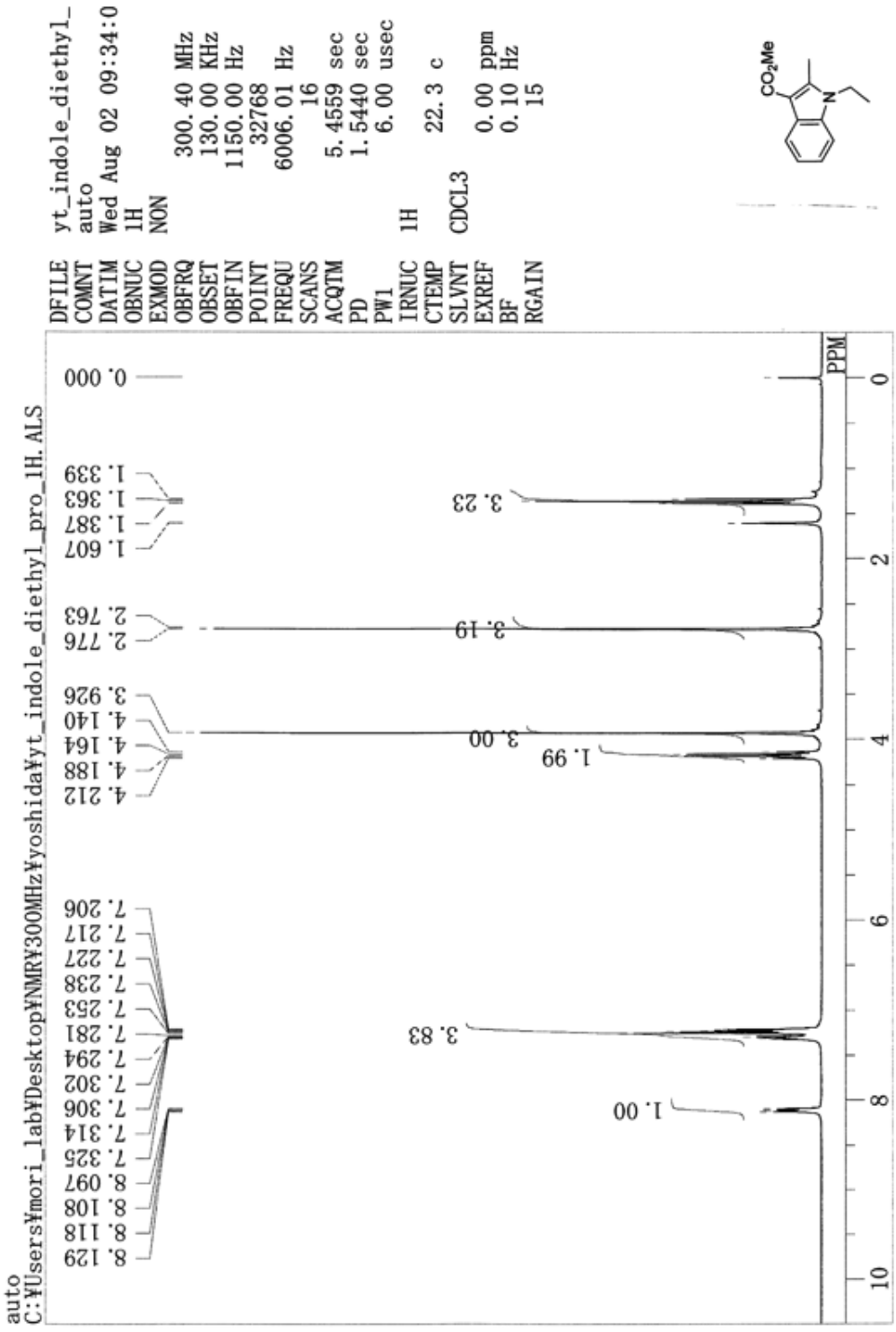
^{1}H NMR spectrum of **4e**.



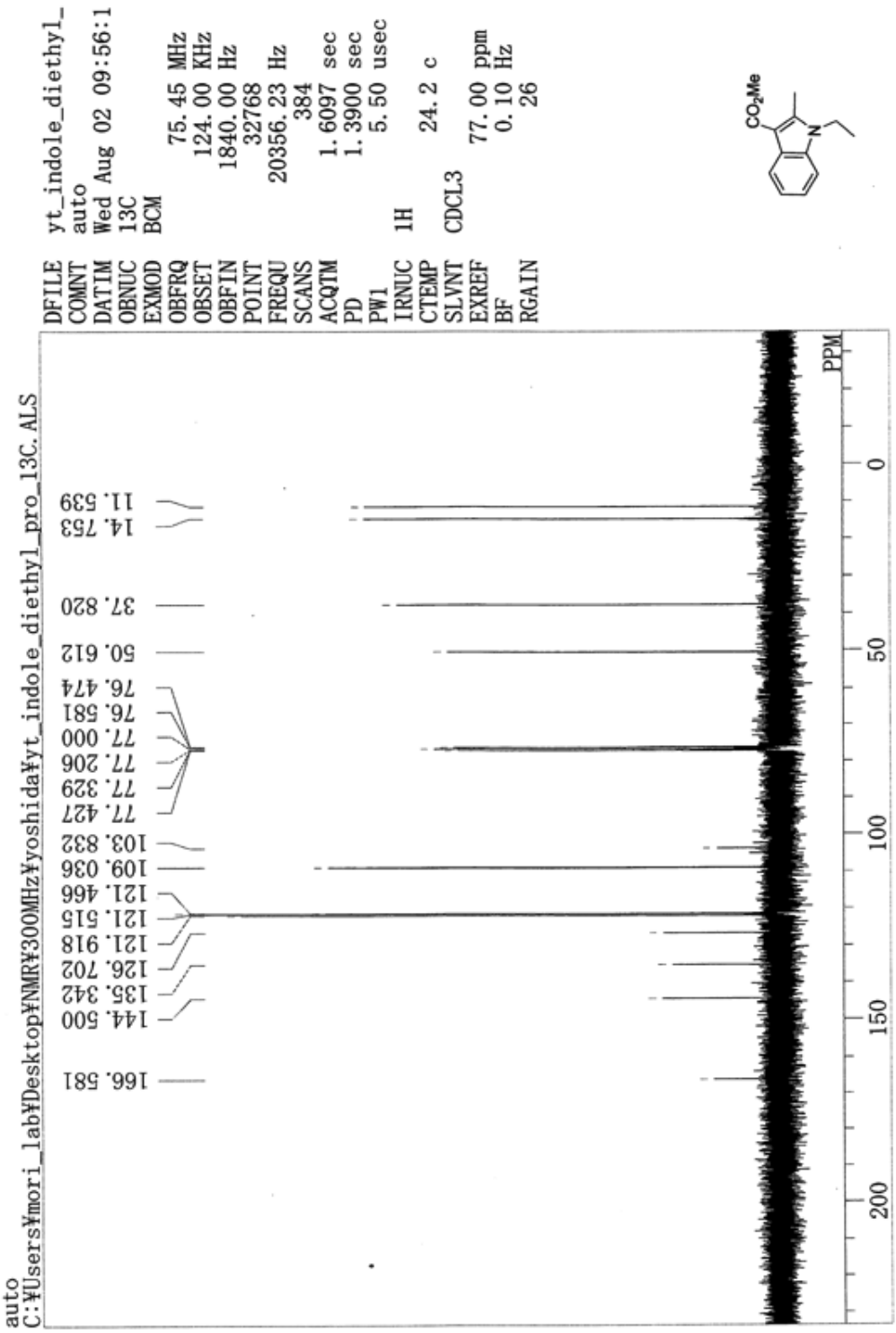
^{13}C NMR spectrum of **4e**.



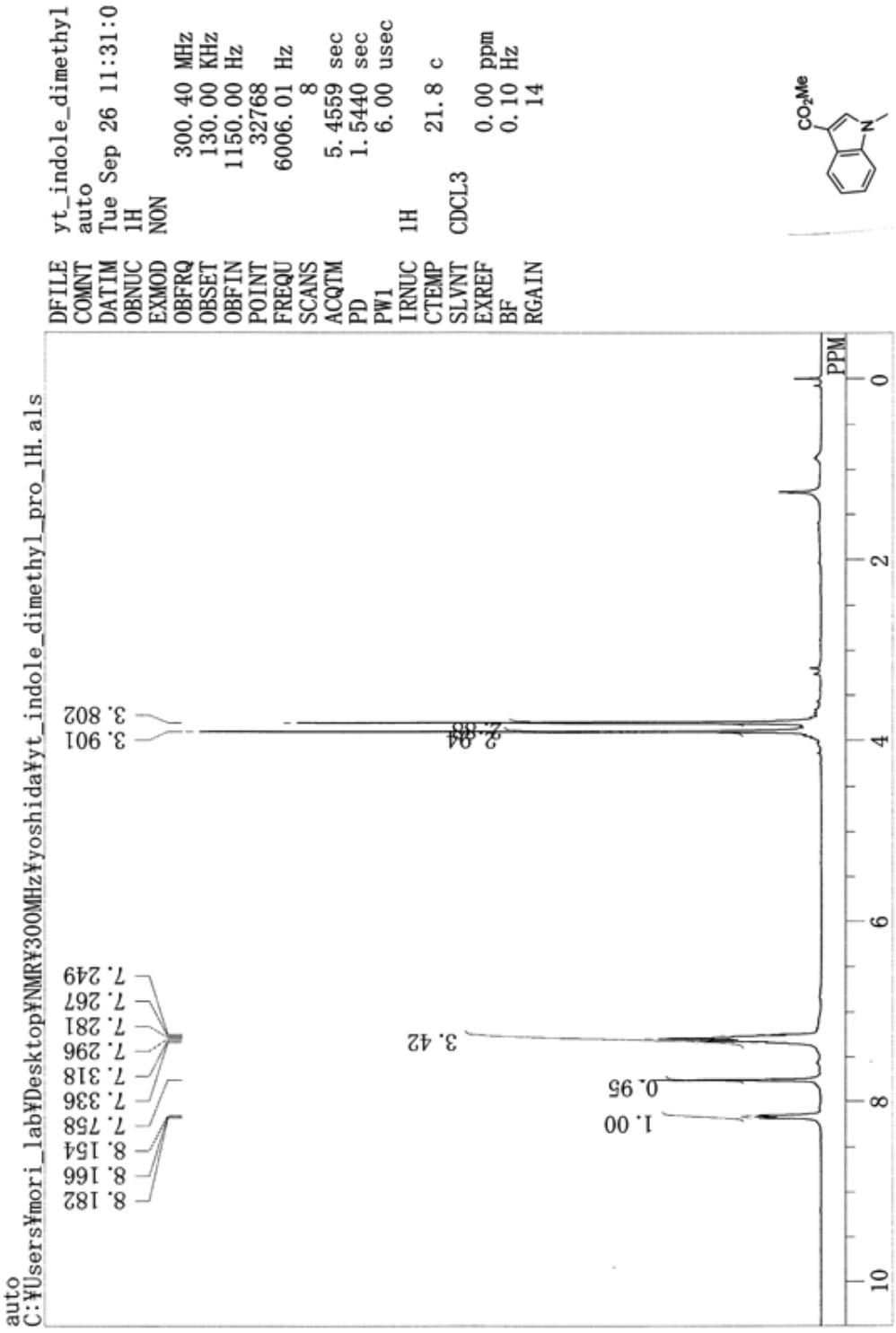
^{1}H NMR spectrum of **4f**.



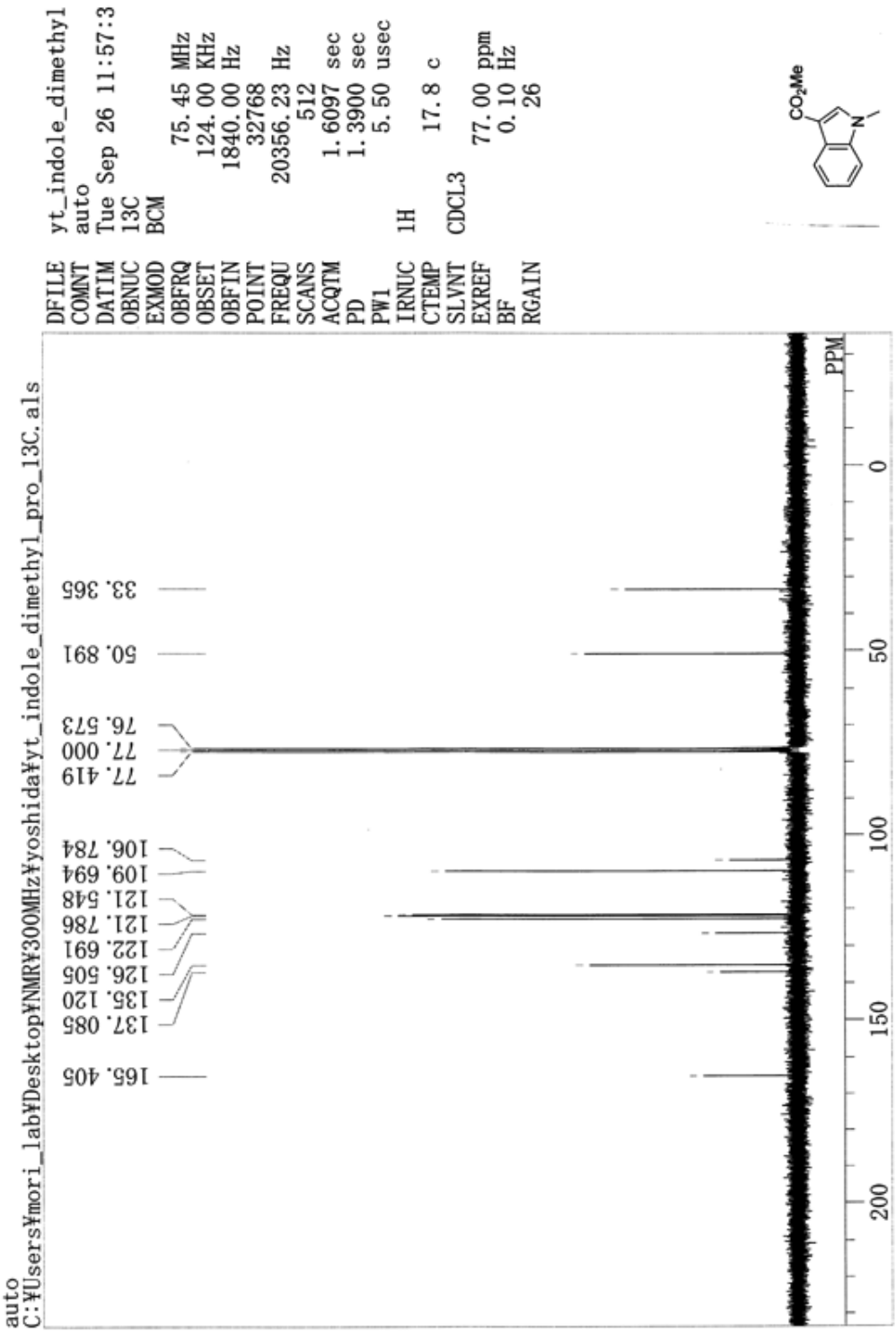
^{13}C NMR spectrum of **4f**.



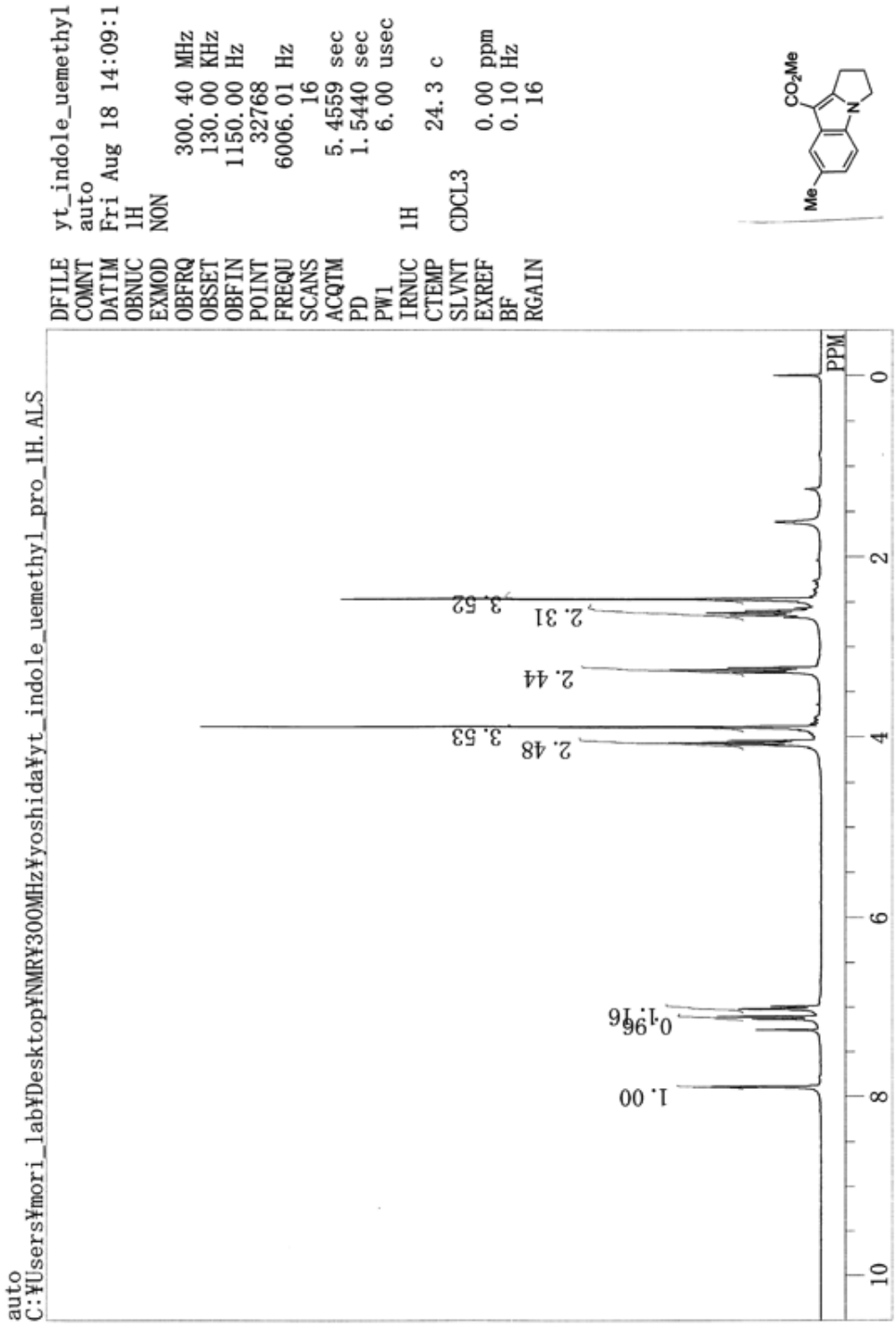
^{1}H NMR spectrum of **4g**.



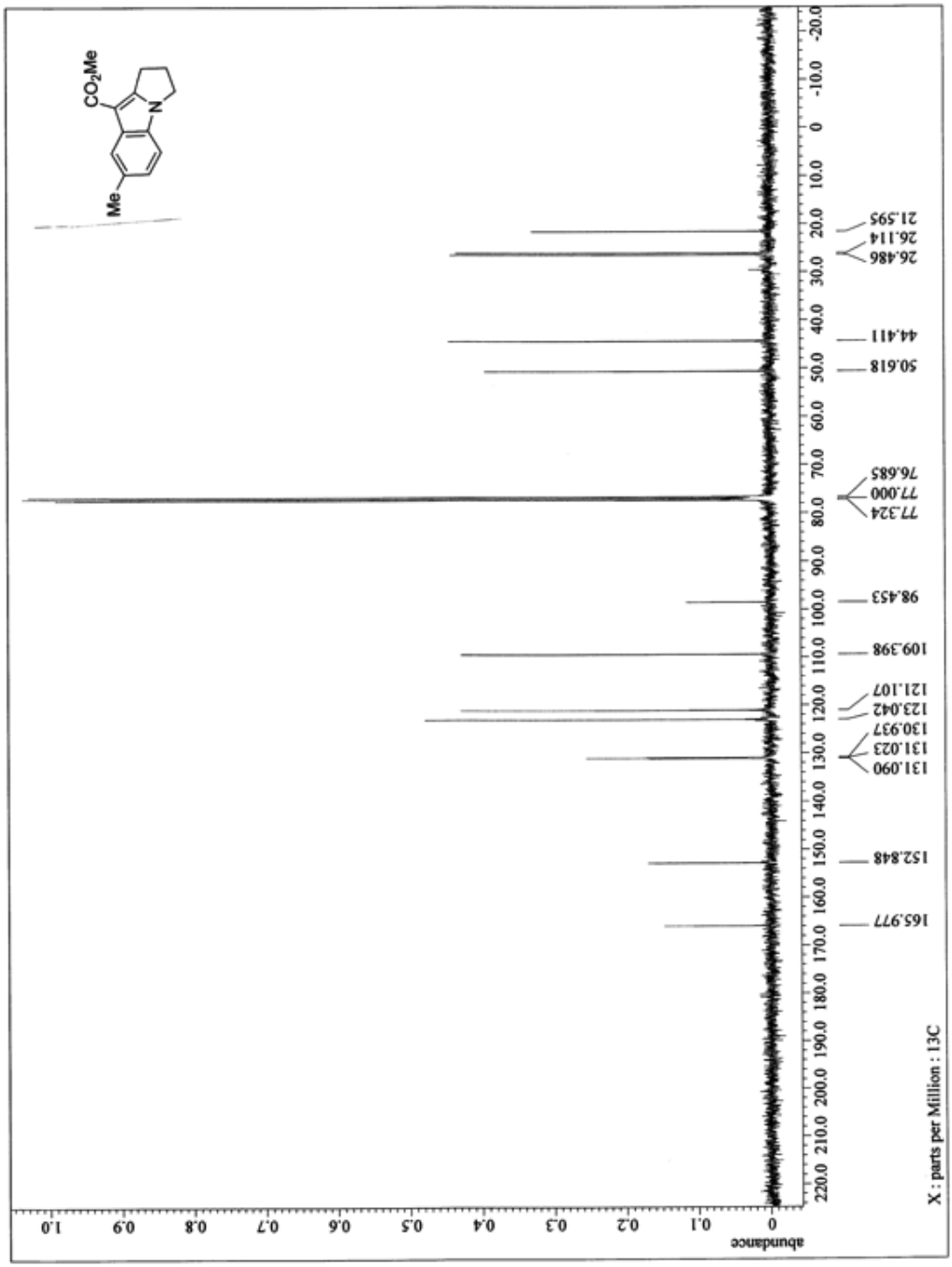
^{13}C NMR spectrum of **4g**.



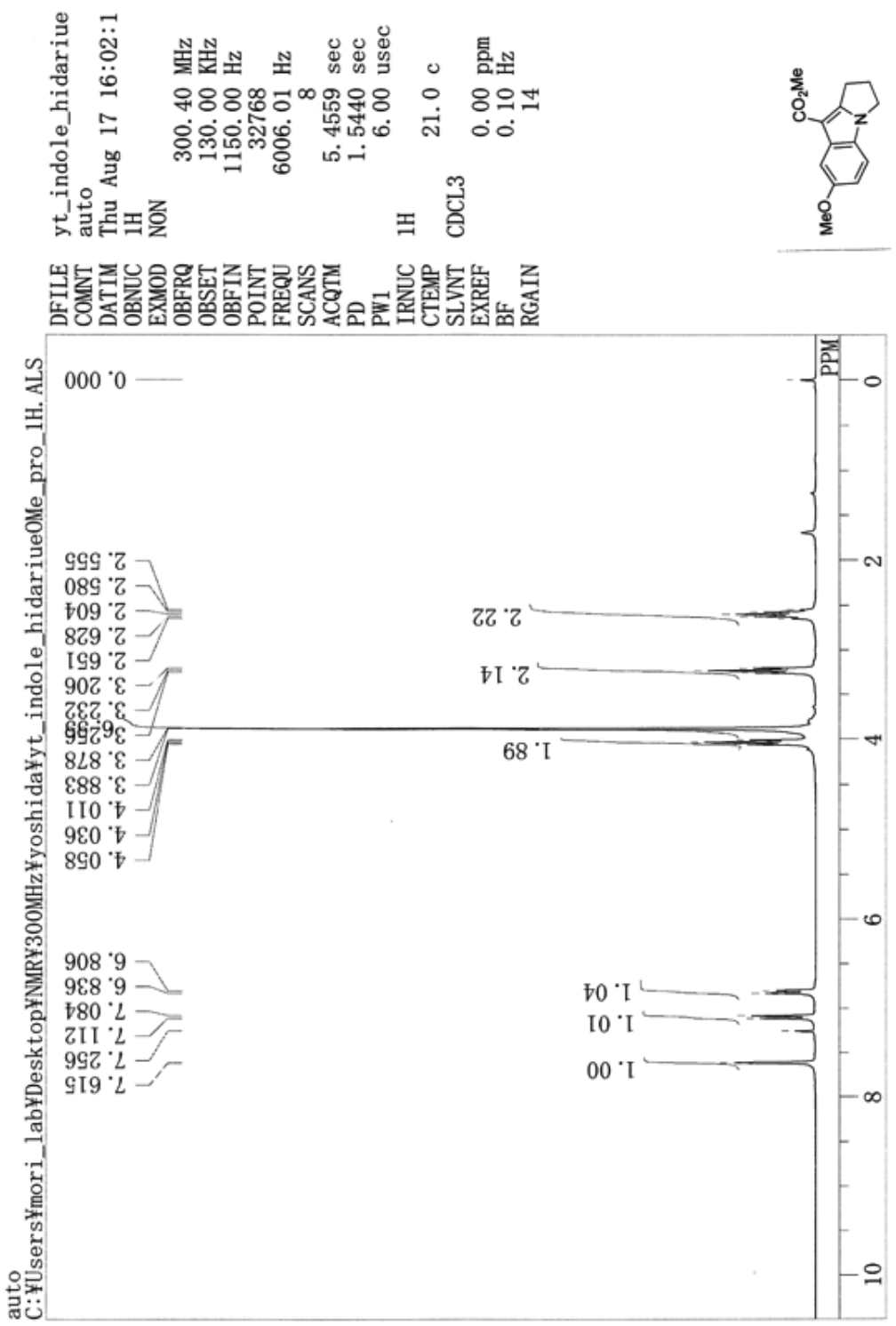
^{1}H NMR spectrum of **4h**.



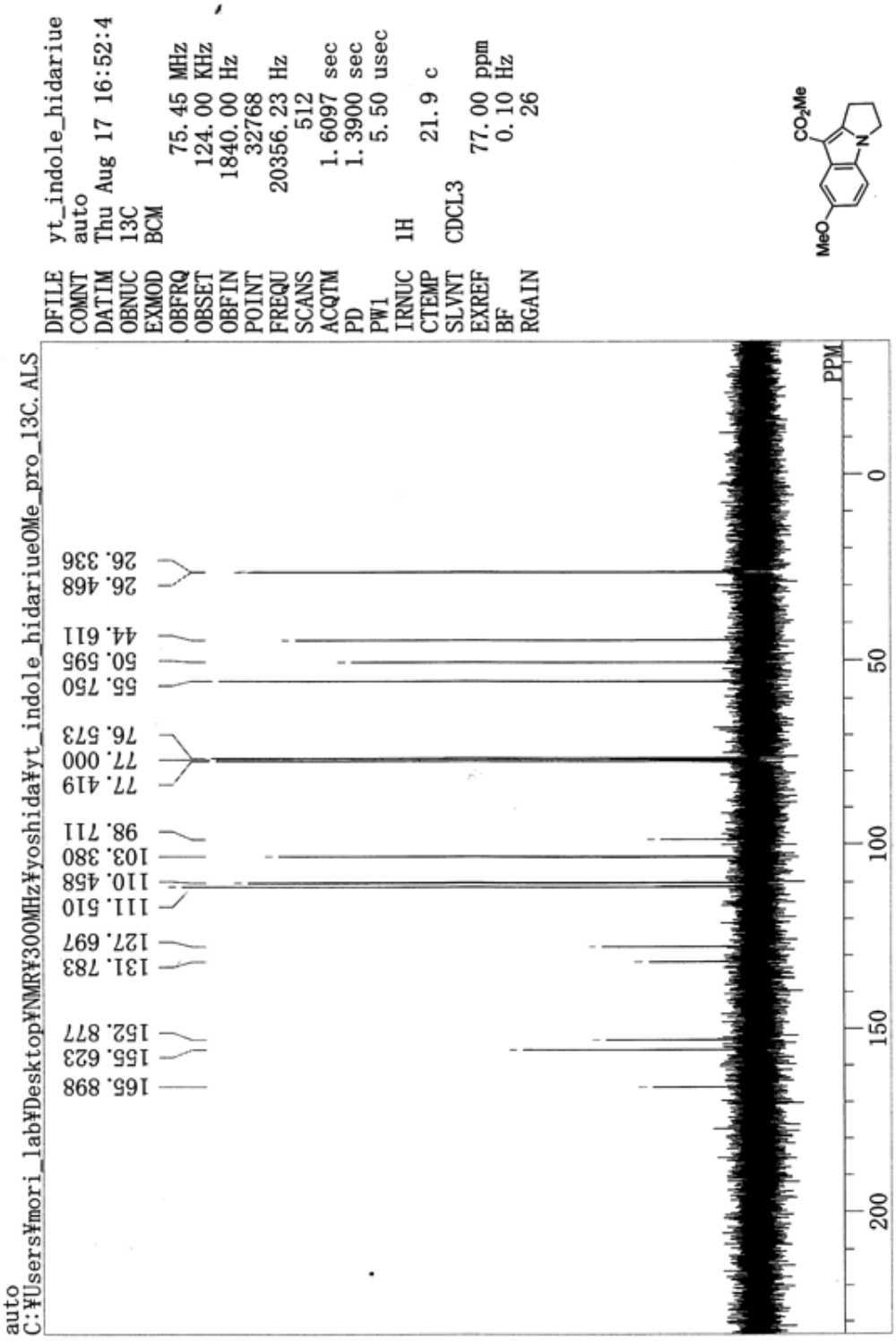
^{13}C NMR spectrum of **4h**.



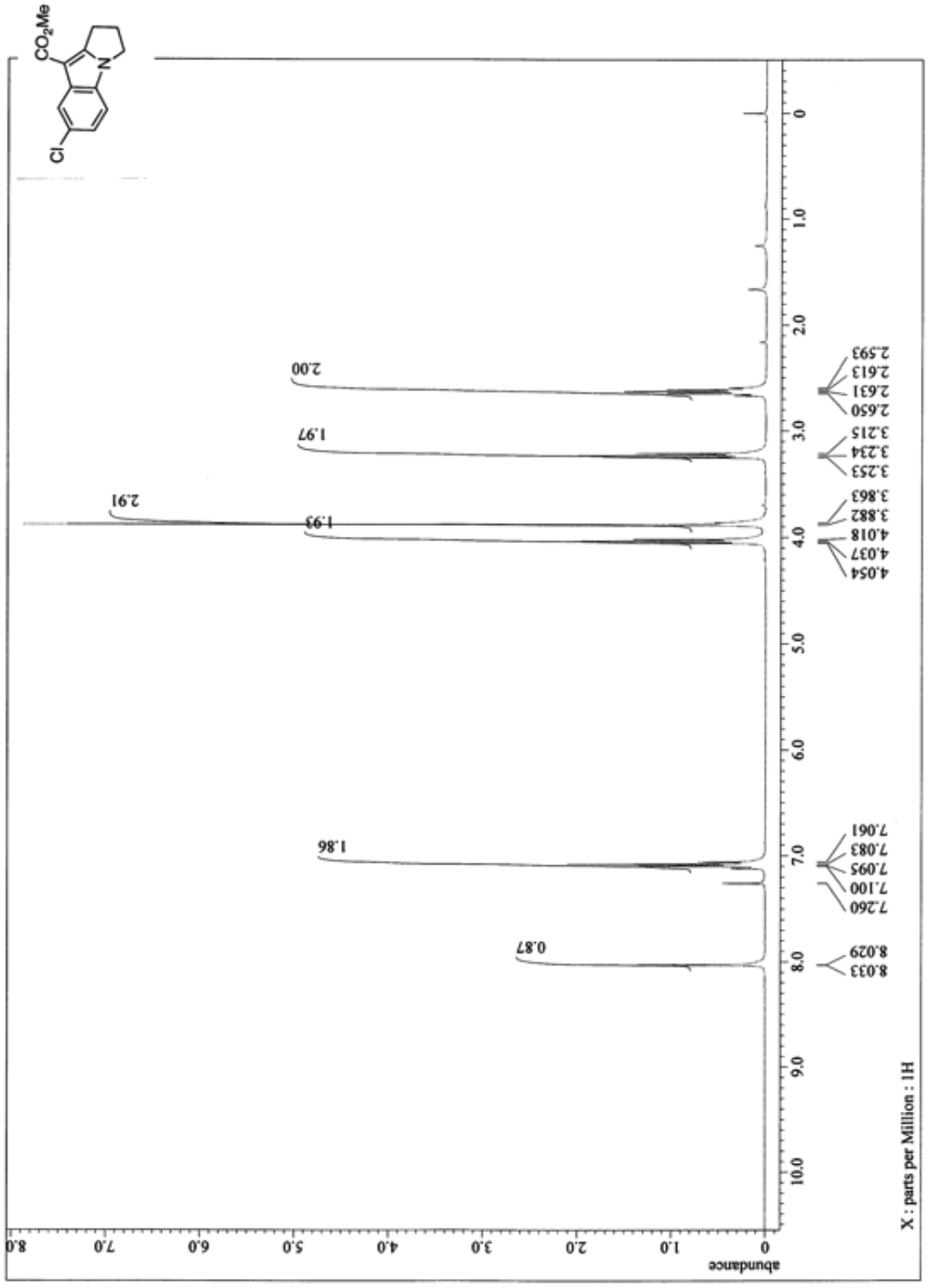
^{1}H NMR spectrum of **4i**.



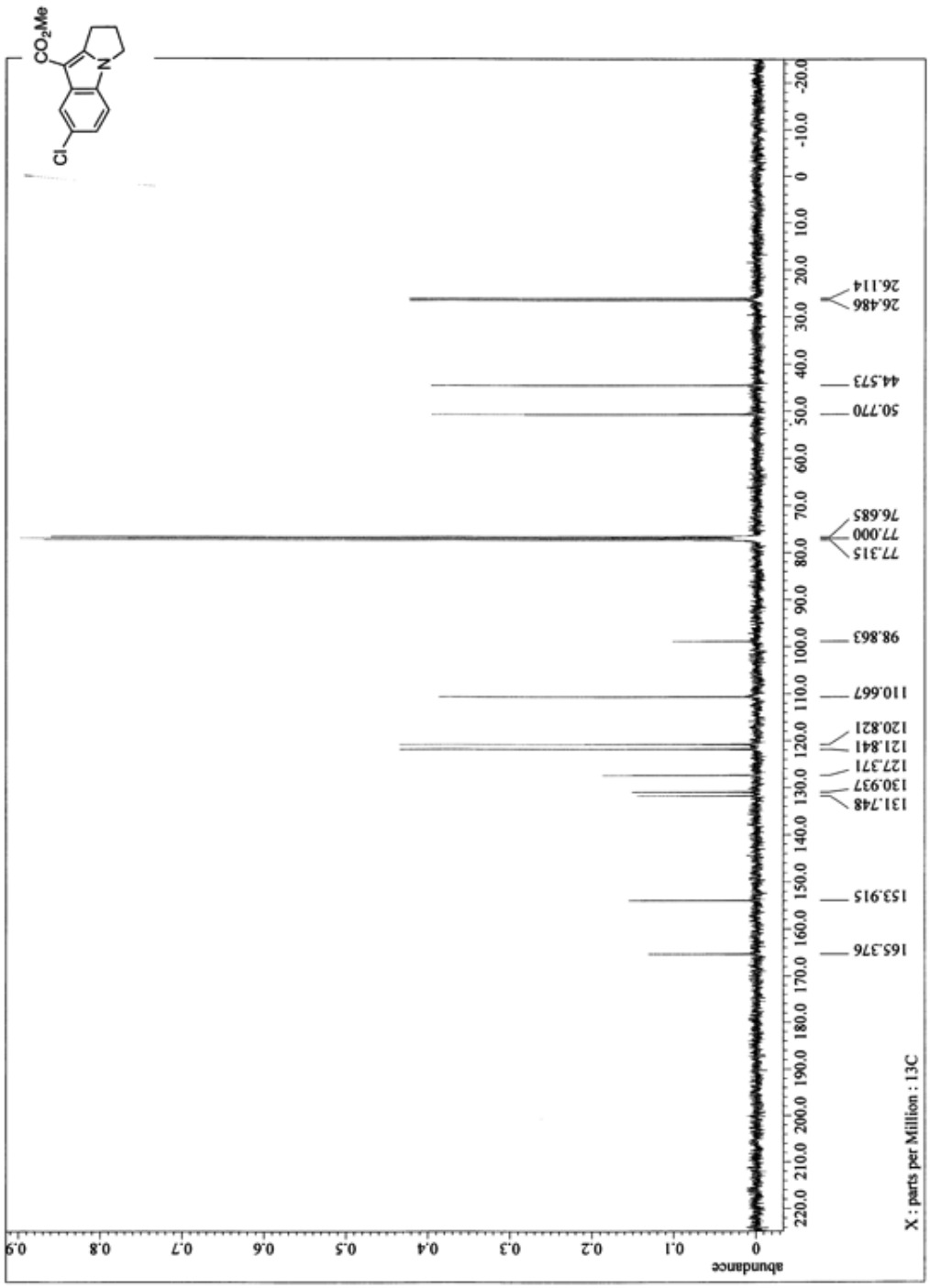
^{13}C NMR spectrum of **4i**.



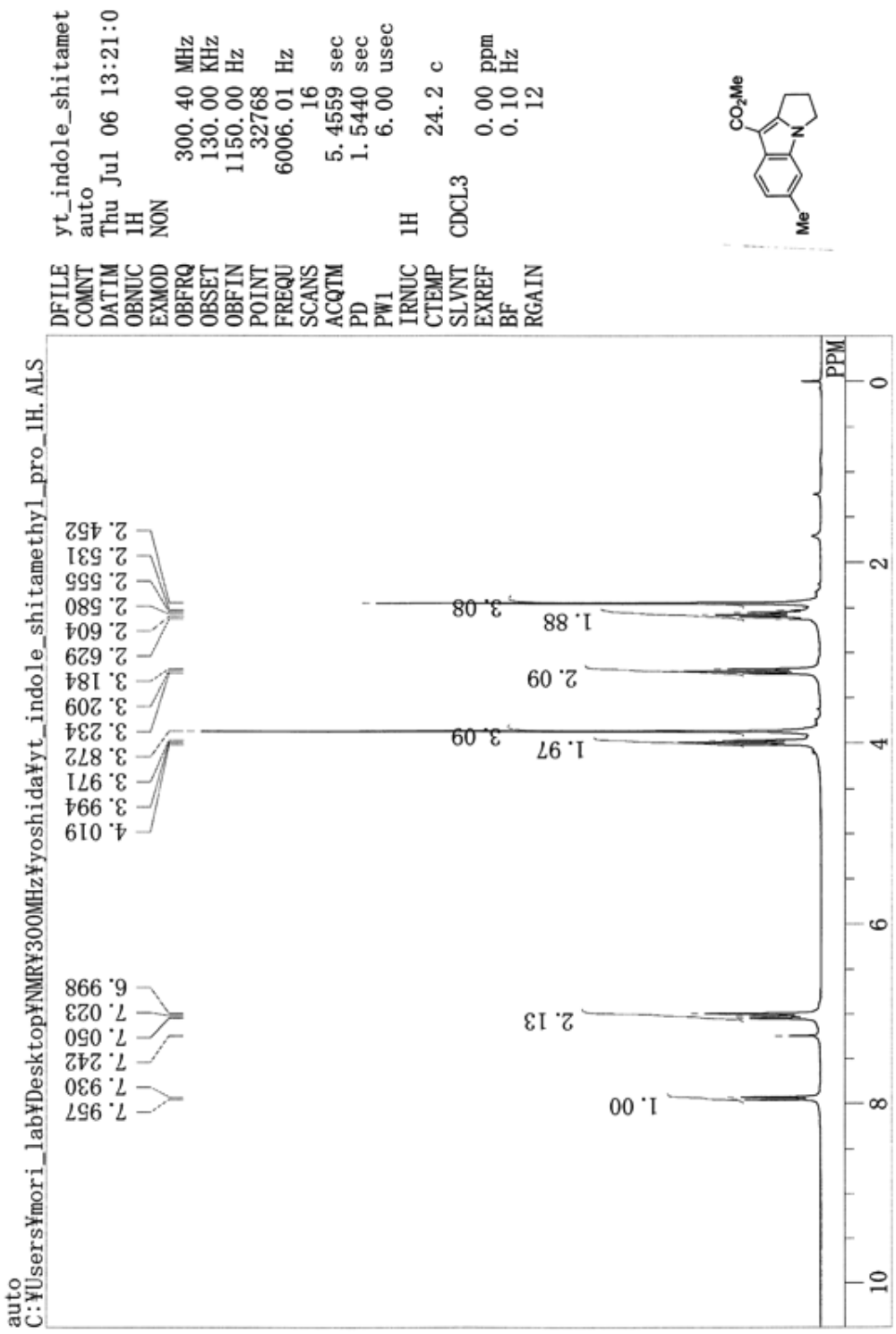
^{1}H NMR spectrum of **4j**.



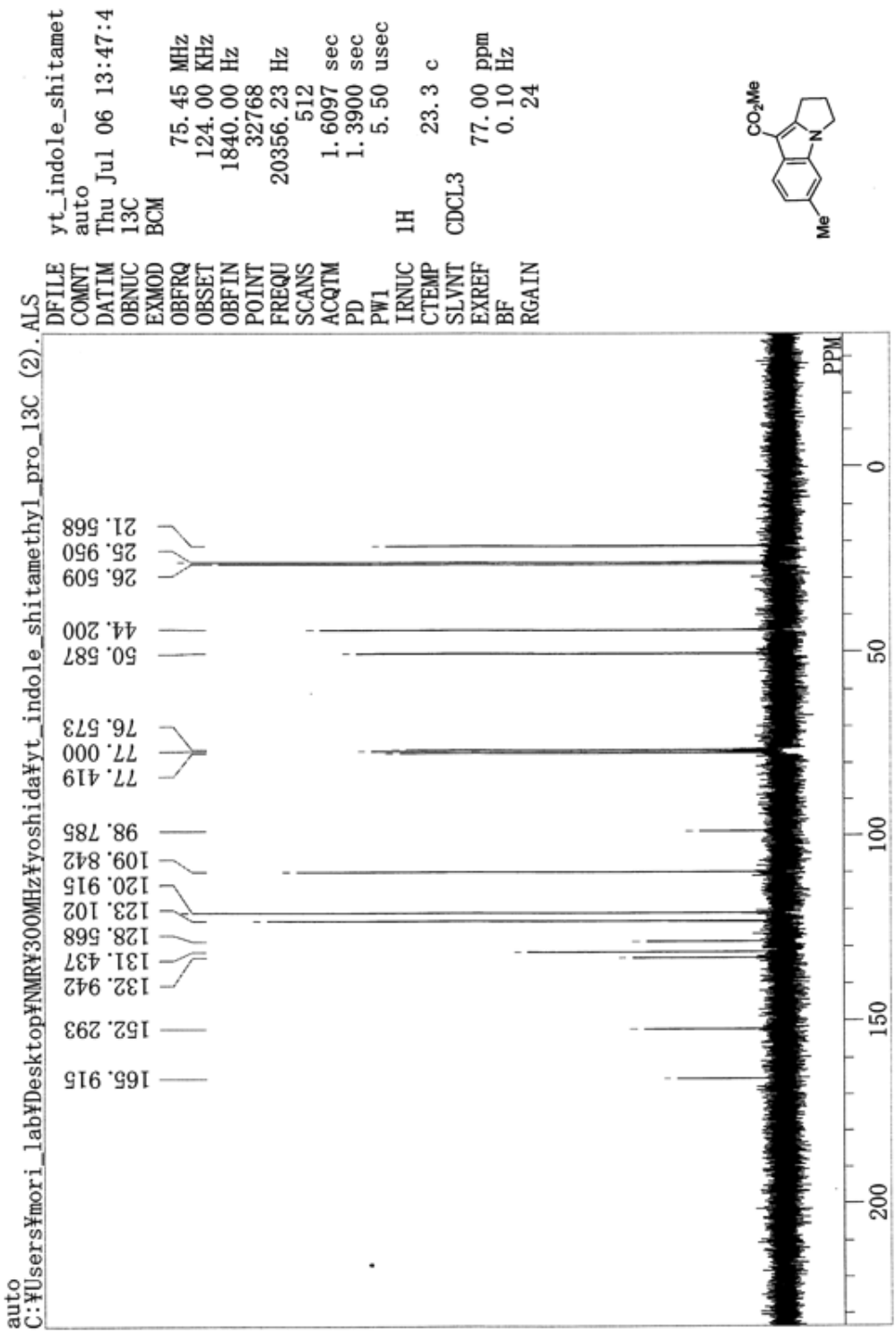
^{13}C NMR spectrum of **4j**.



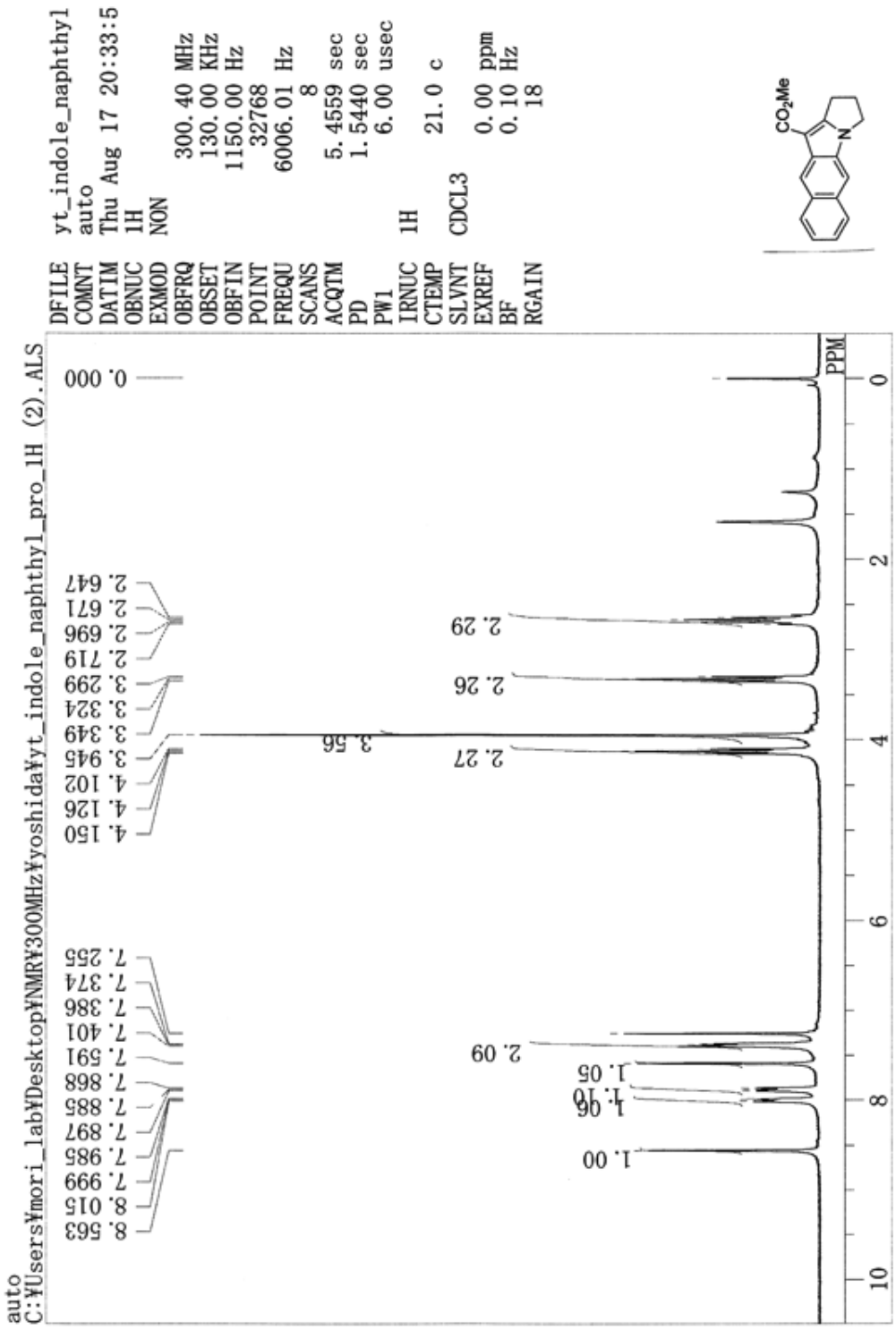
^{1}H NMR spectrum of **4k**.



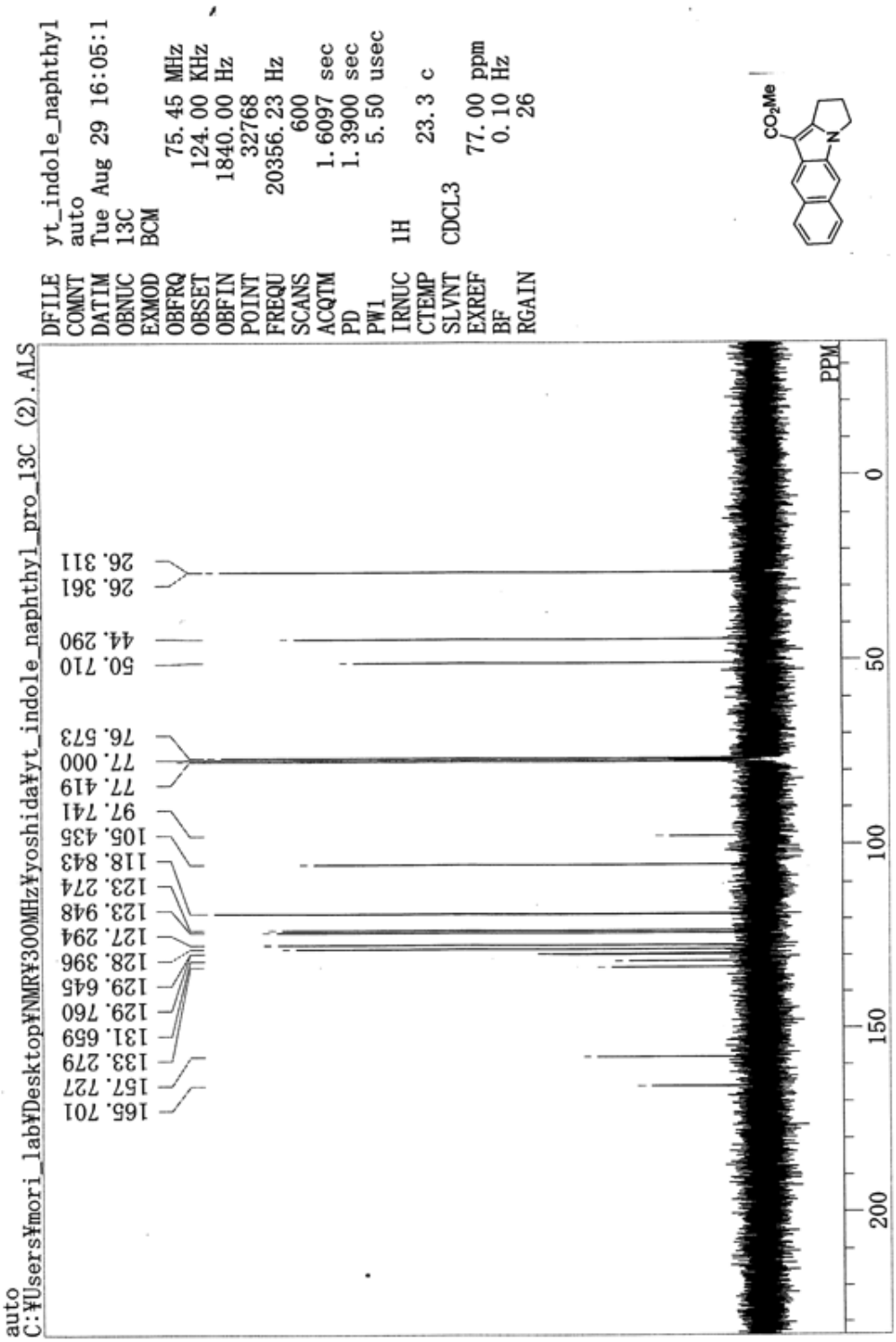
^{13}C NMR spectrum of **4k**.



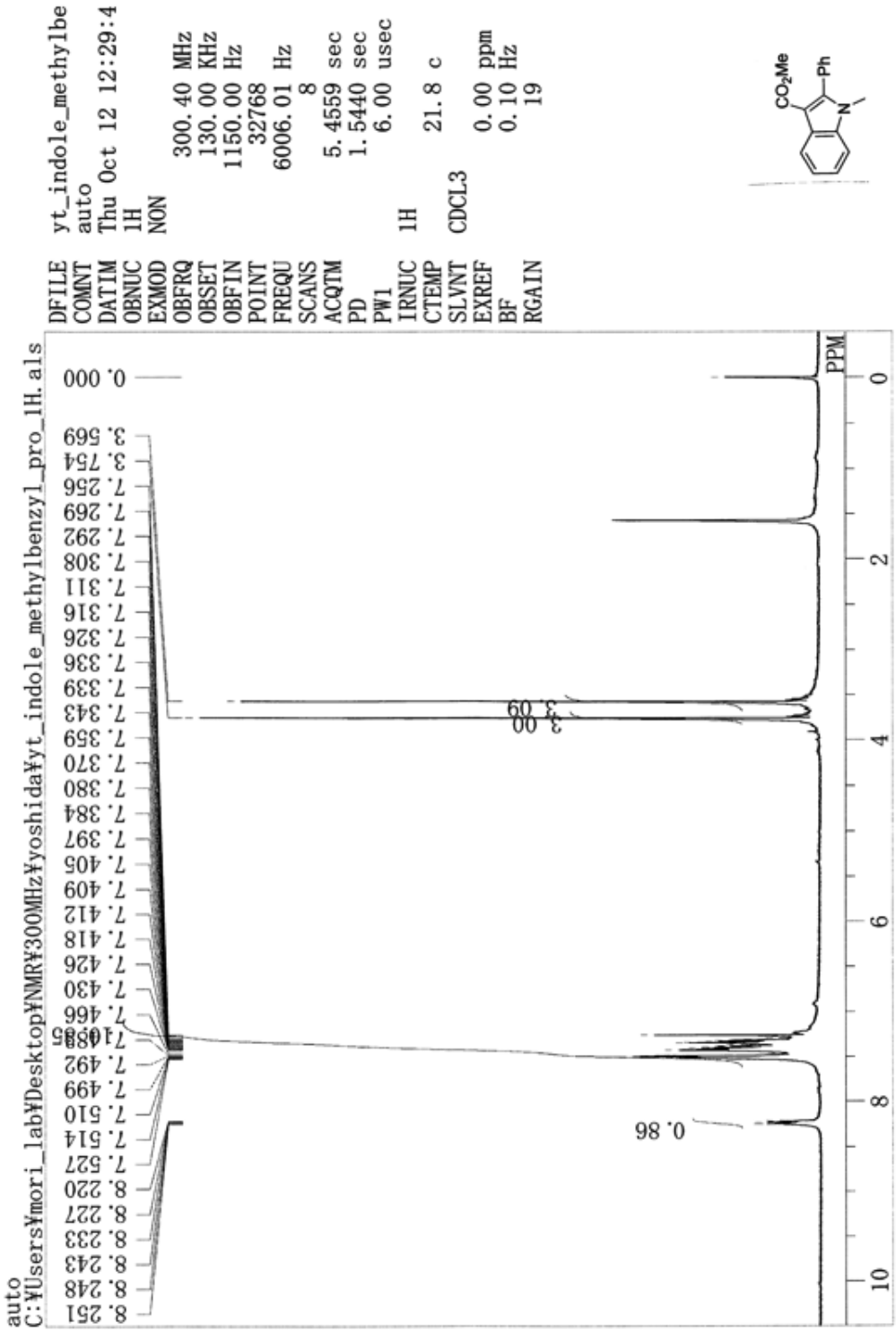
^{1}H NMR spectrum of **4l**.



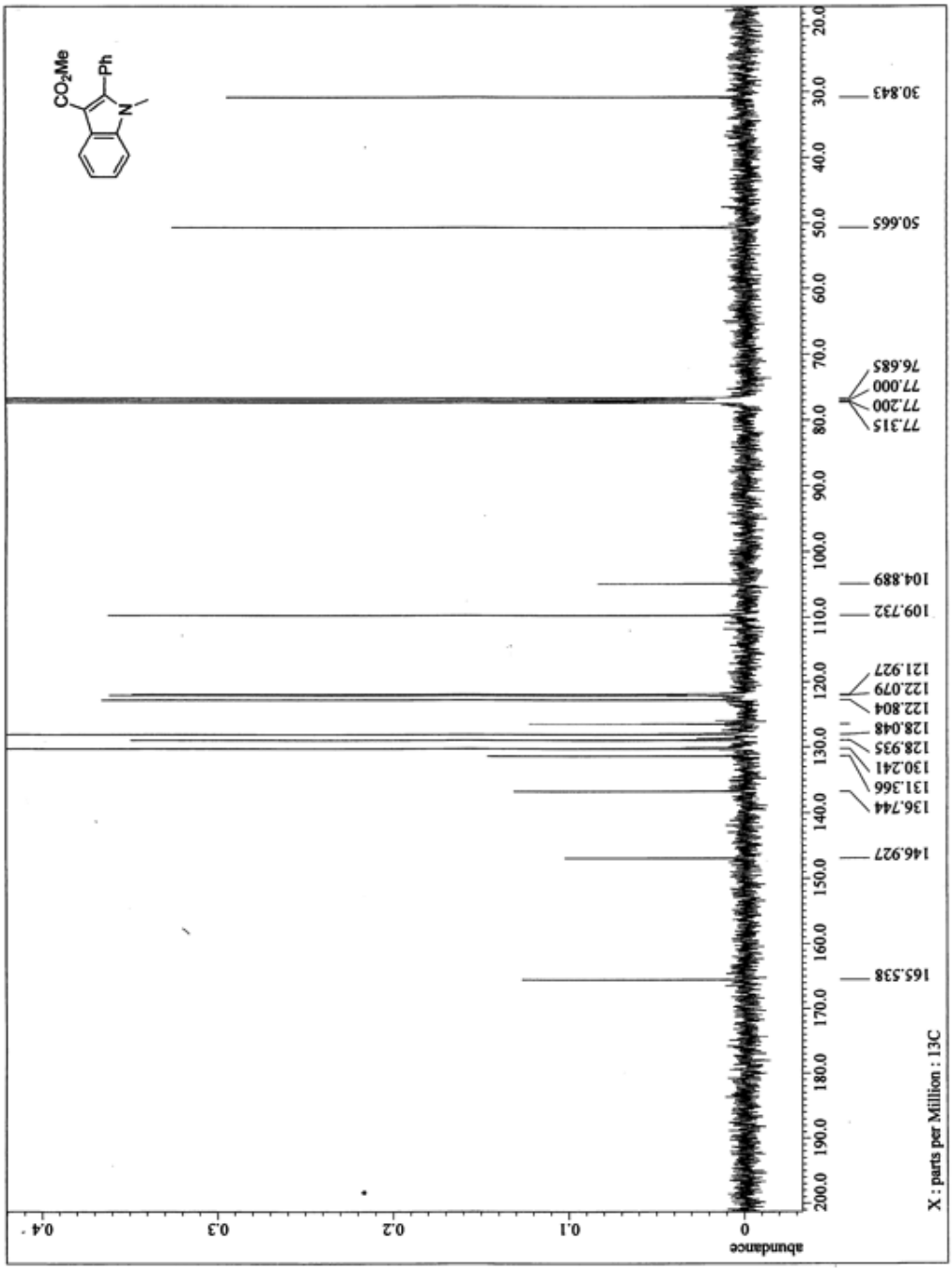
^{13}C NMR spectrum of **4l**.



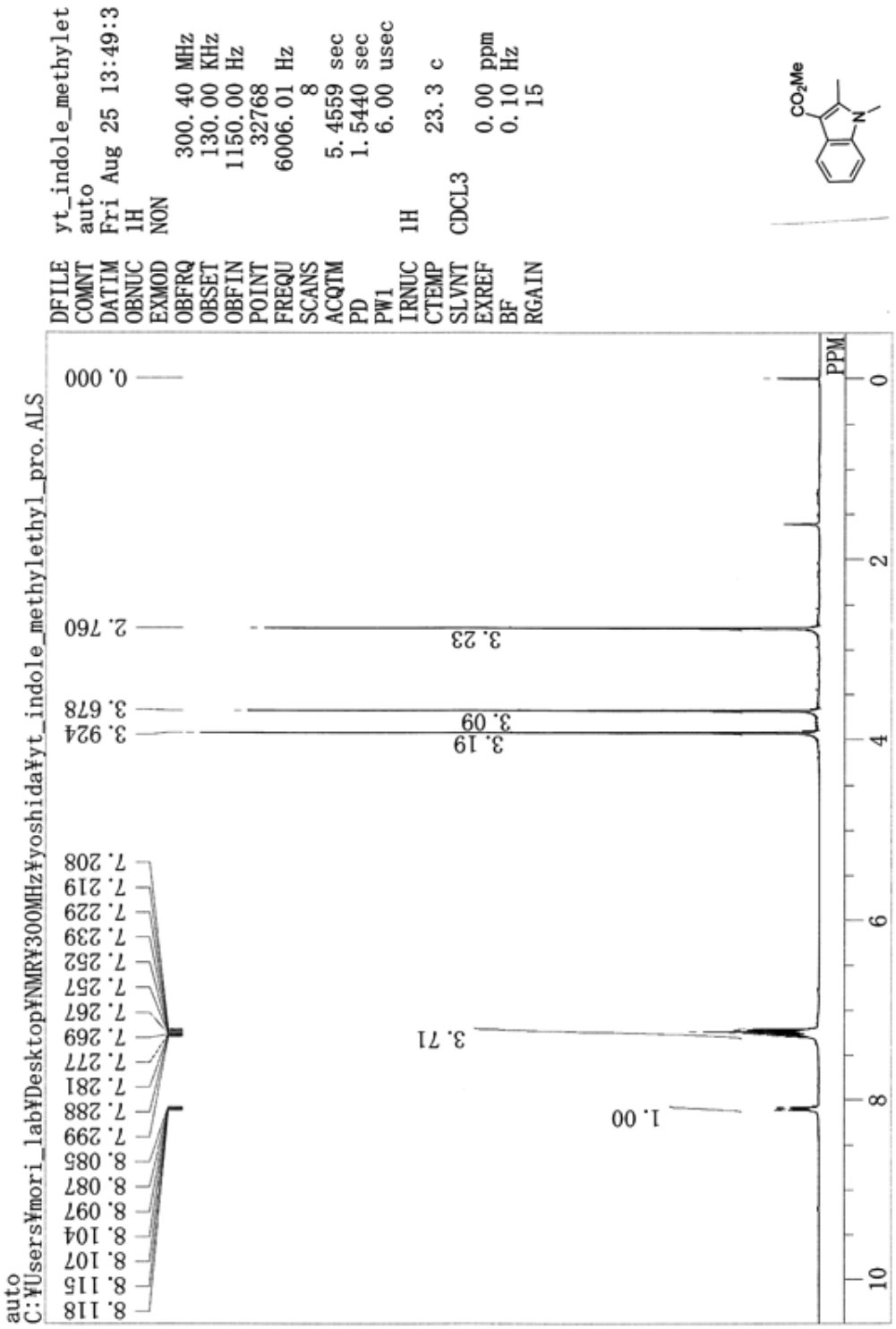
^{1}H NMR spectrum of **4m**.



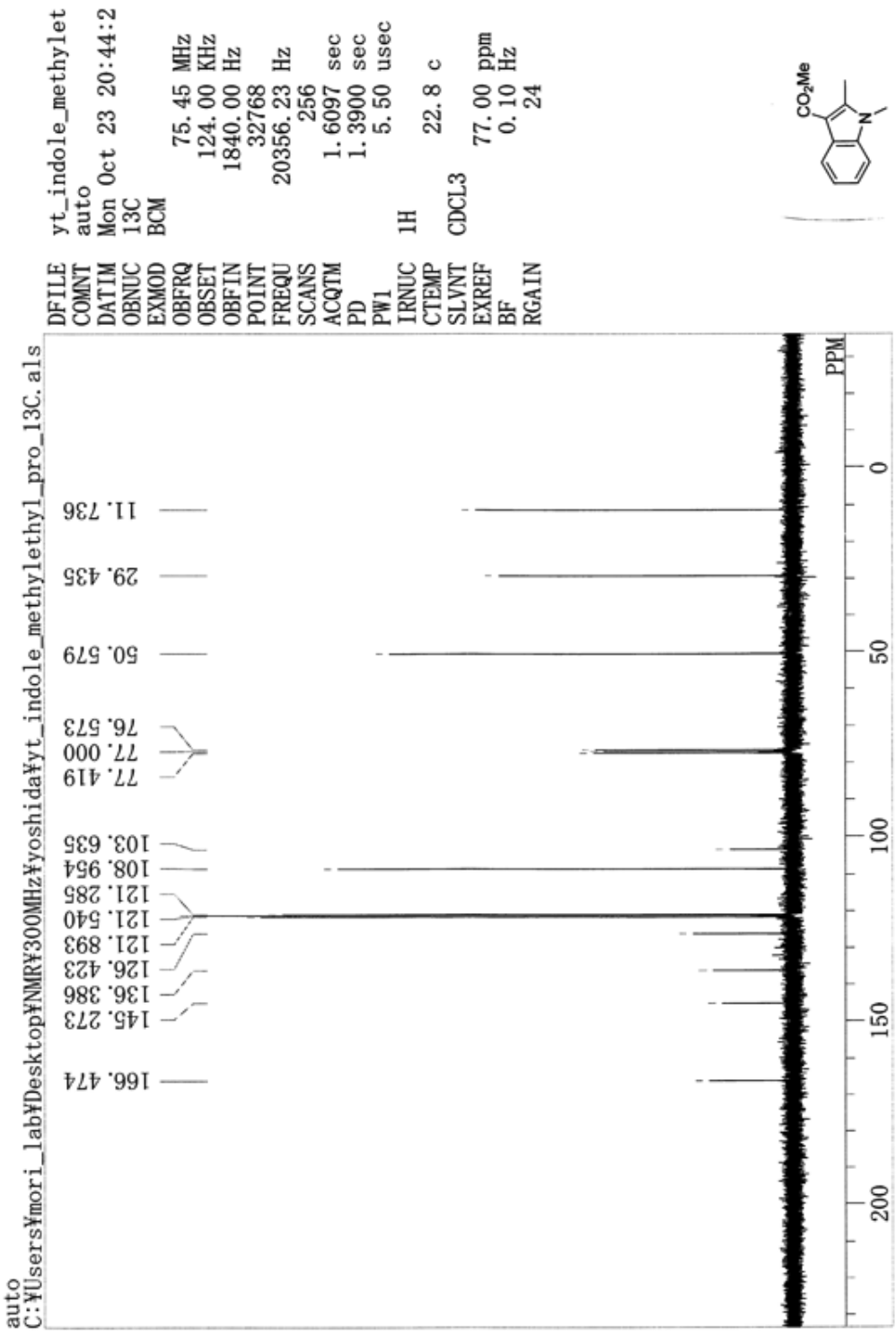
^{13}C NMR spectrum of **4m**.



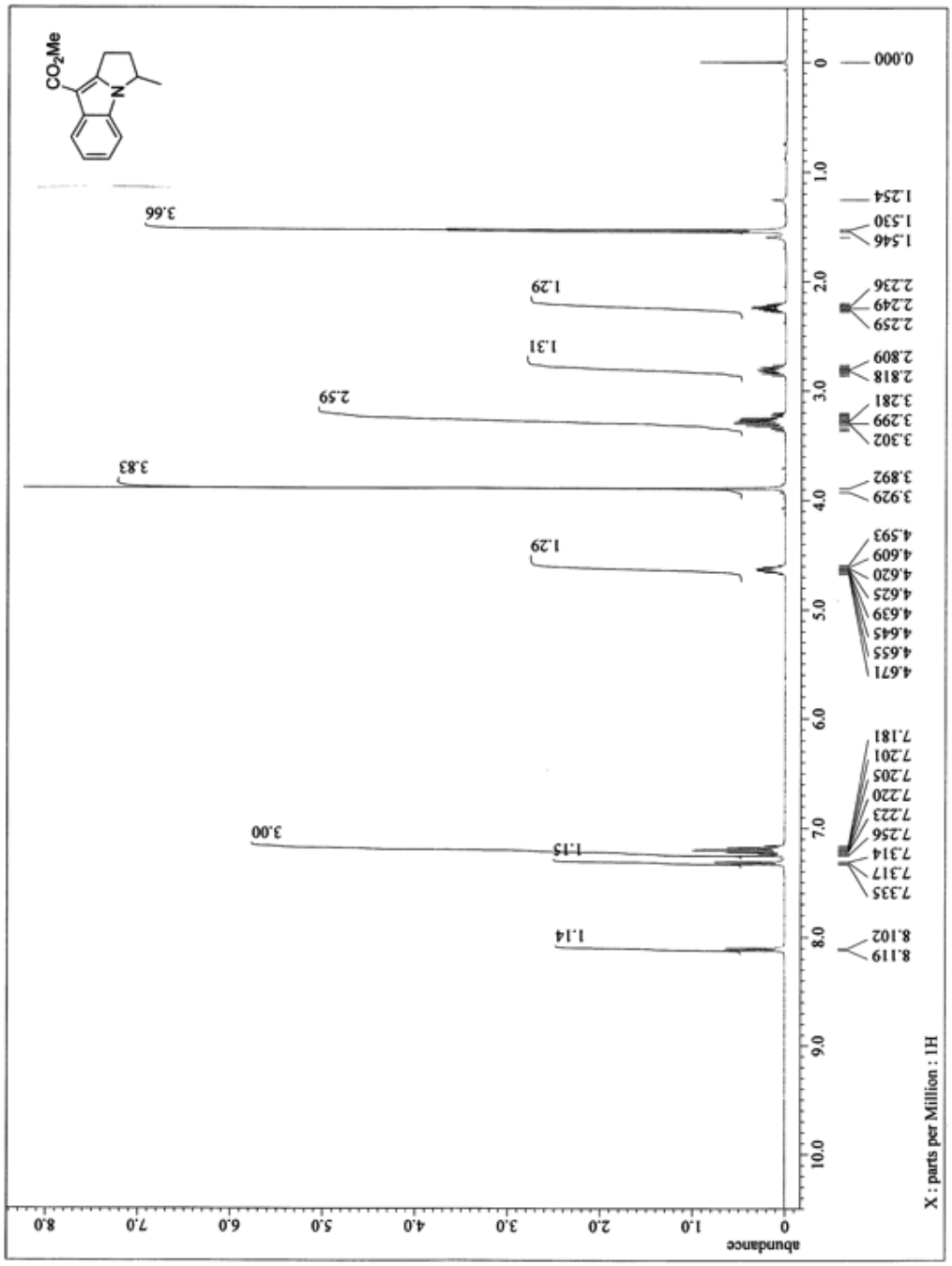
^{1}H NMR spectrum of **4n**.



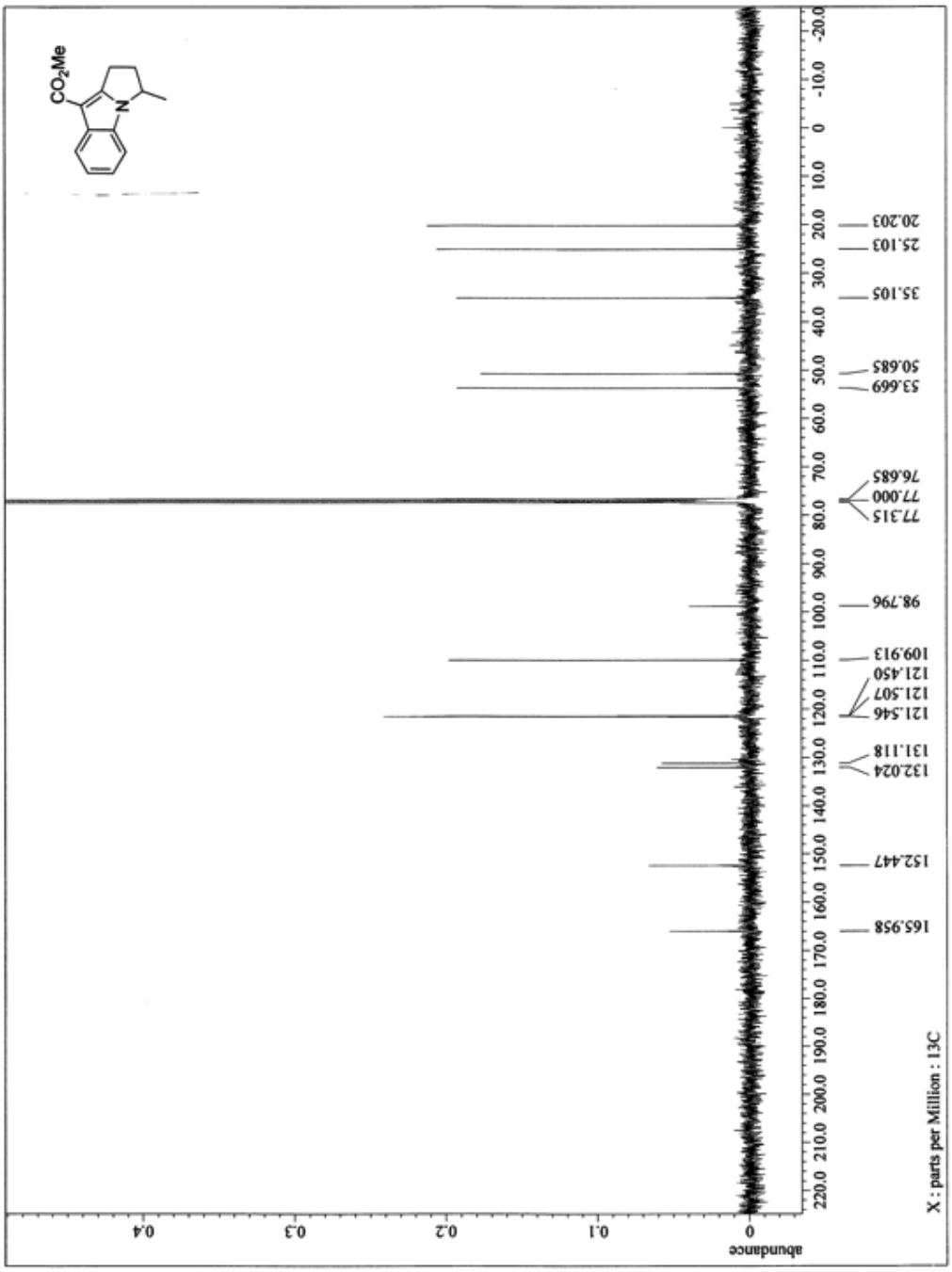
^{13}C NMR spectrum of **4n**.



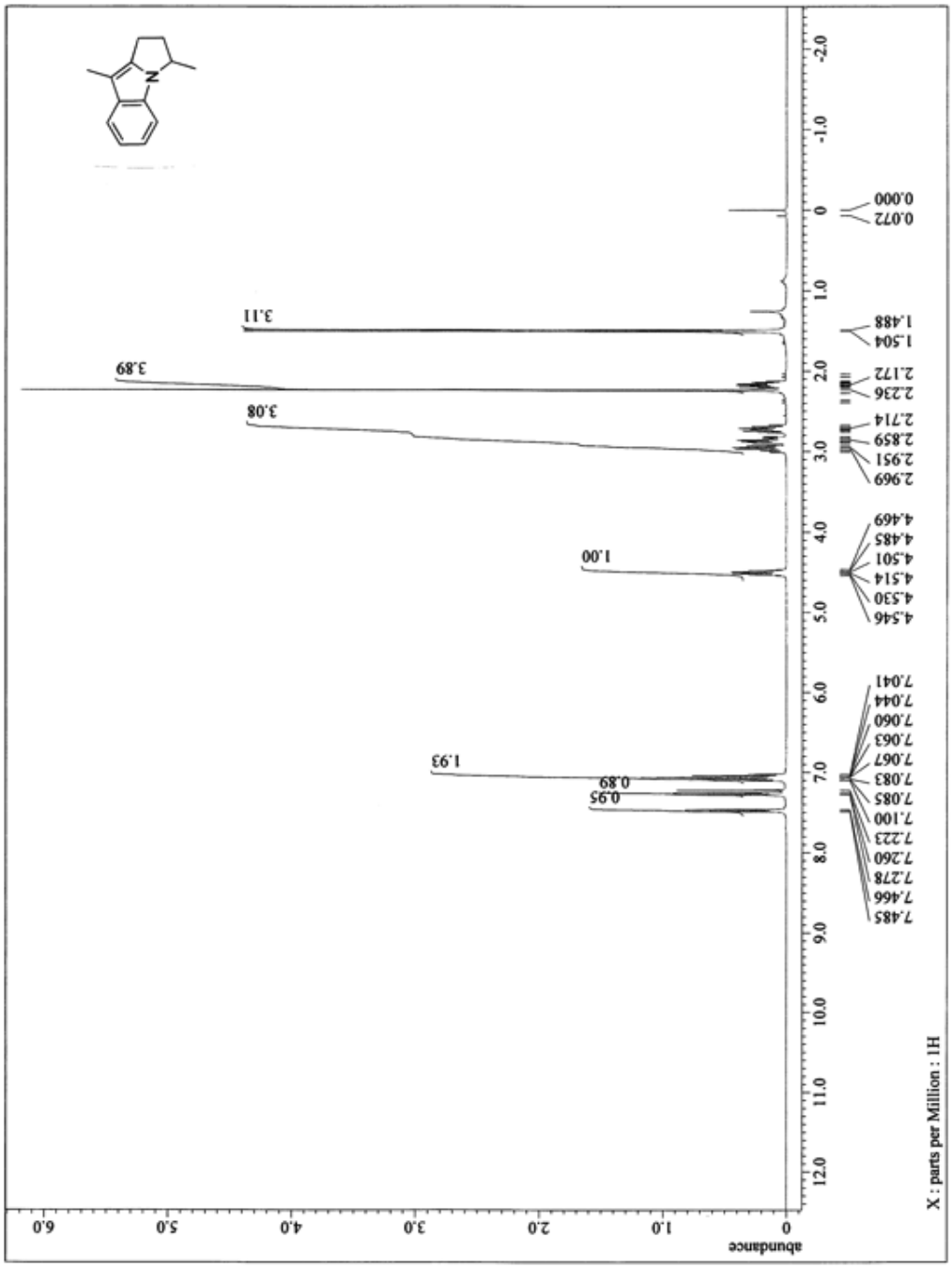
^{1}H NMR spectrum of **4o**.



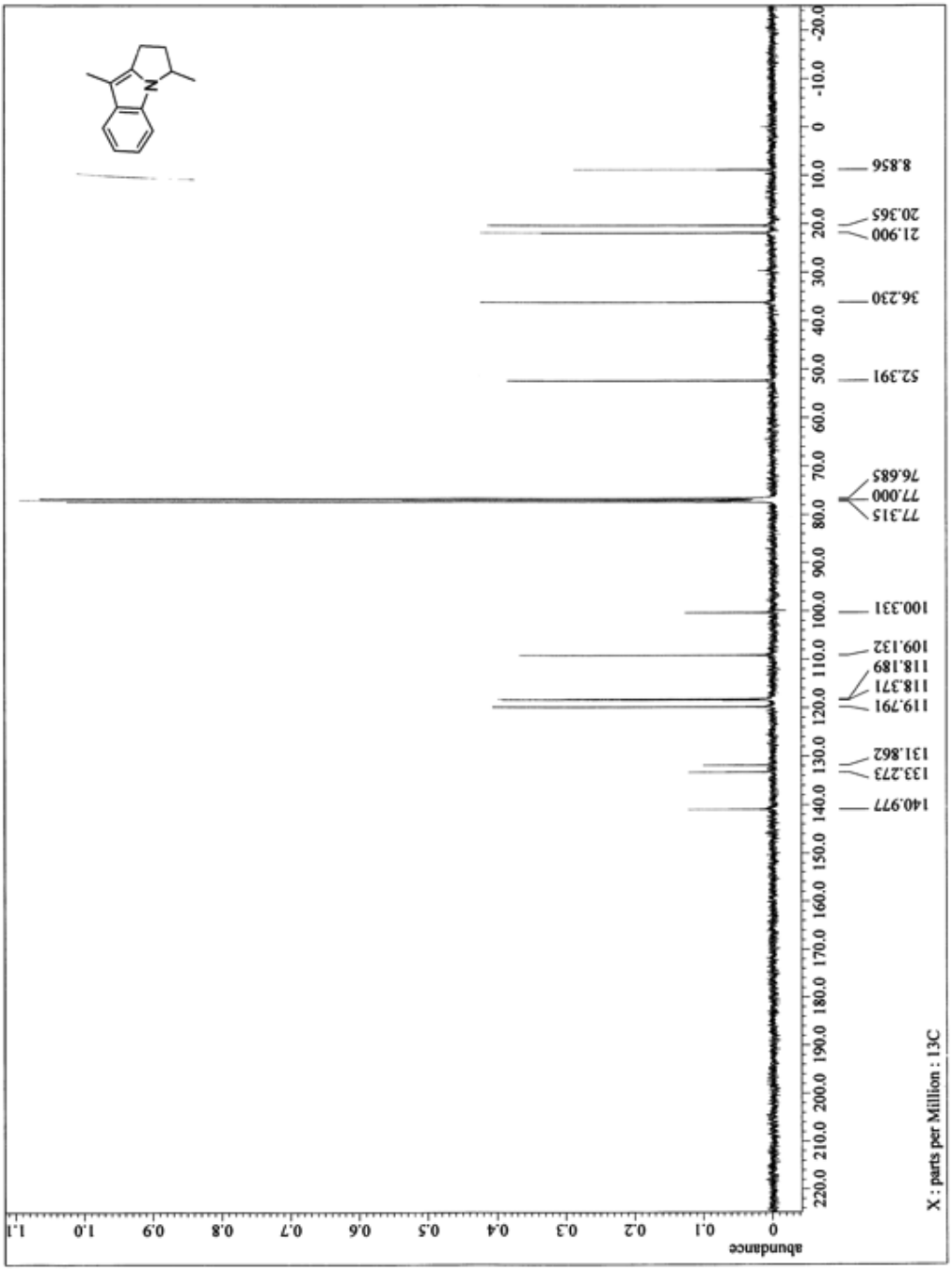
^{13}C NMR spectrum of **4o**.



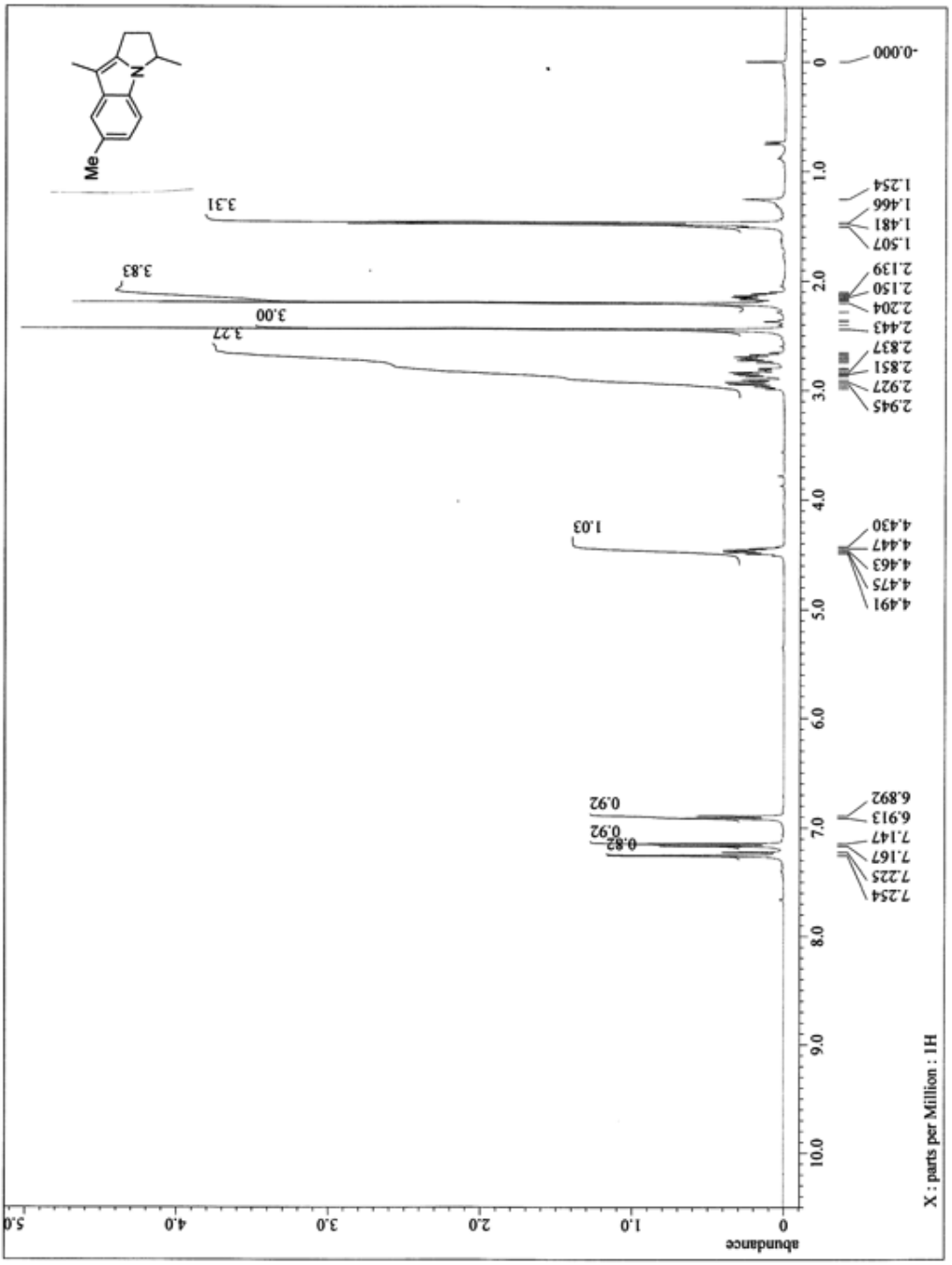
^{1}H NMR spectrum of **8a**.



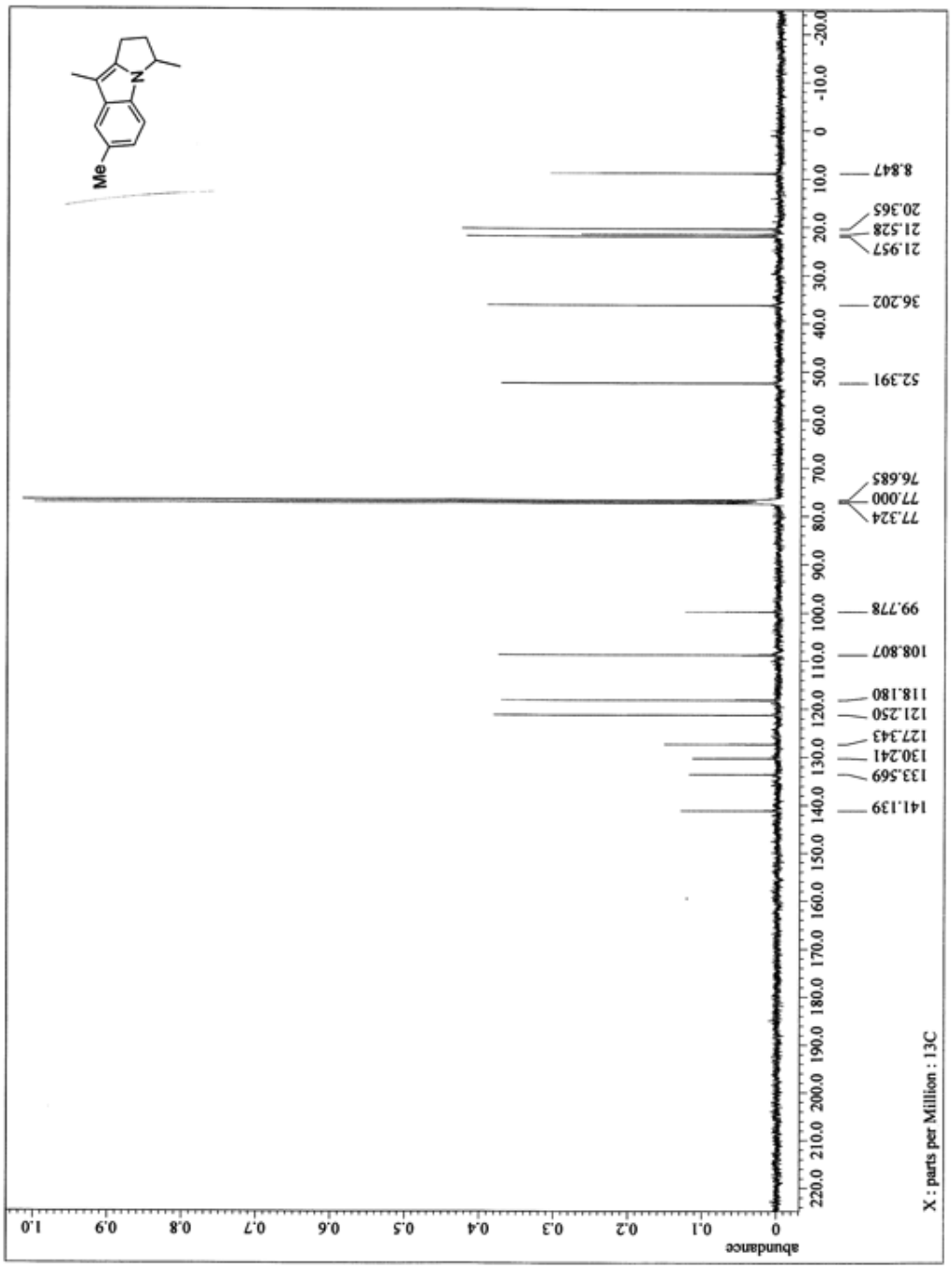
^{13}C NMR spectrum of **8a**.



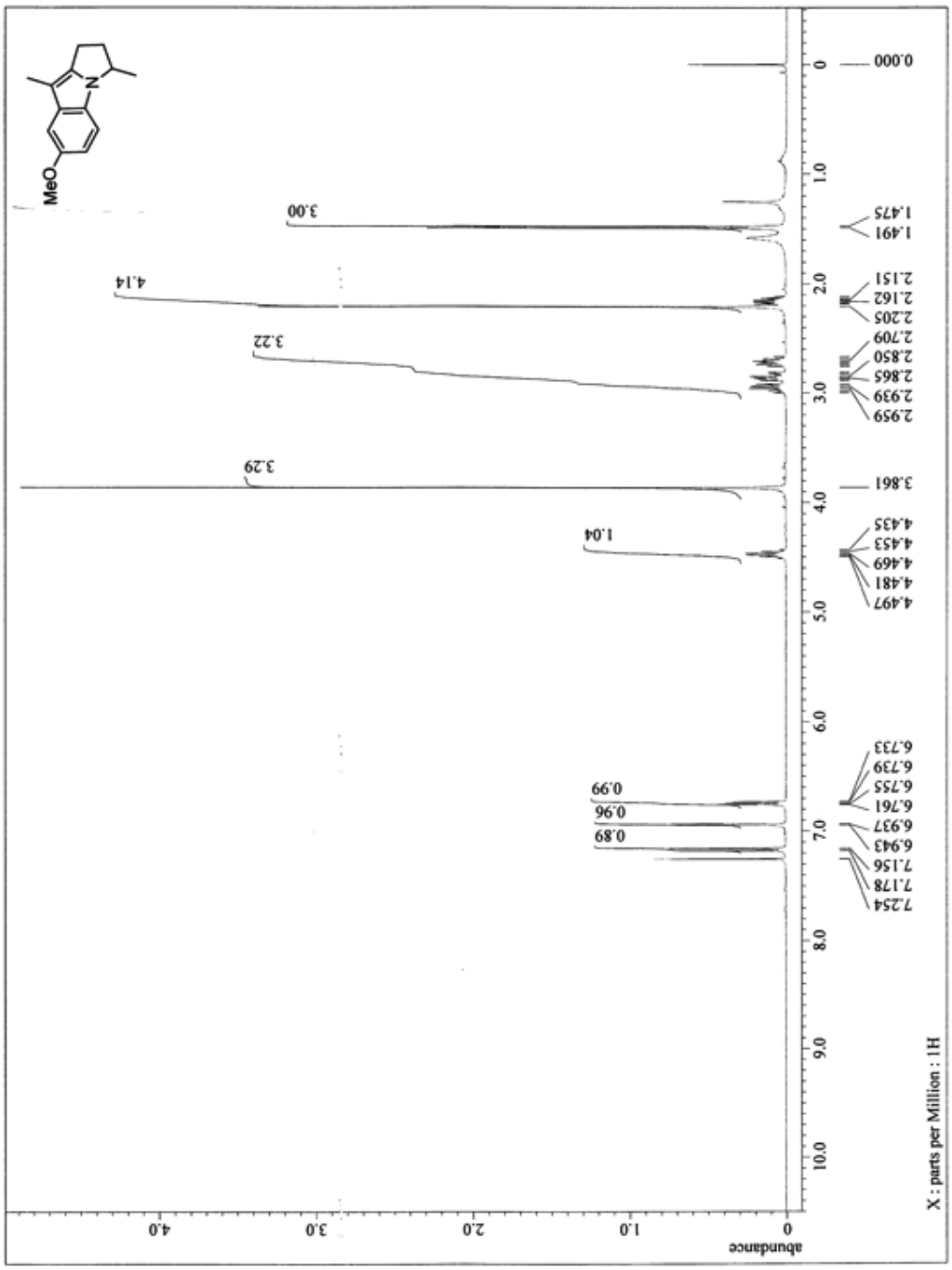
^{1}H NMR spectrum of **8b**.



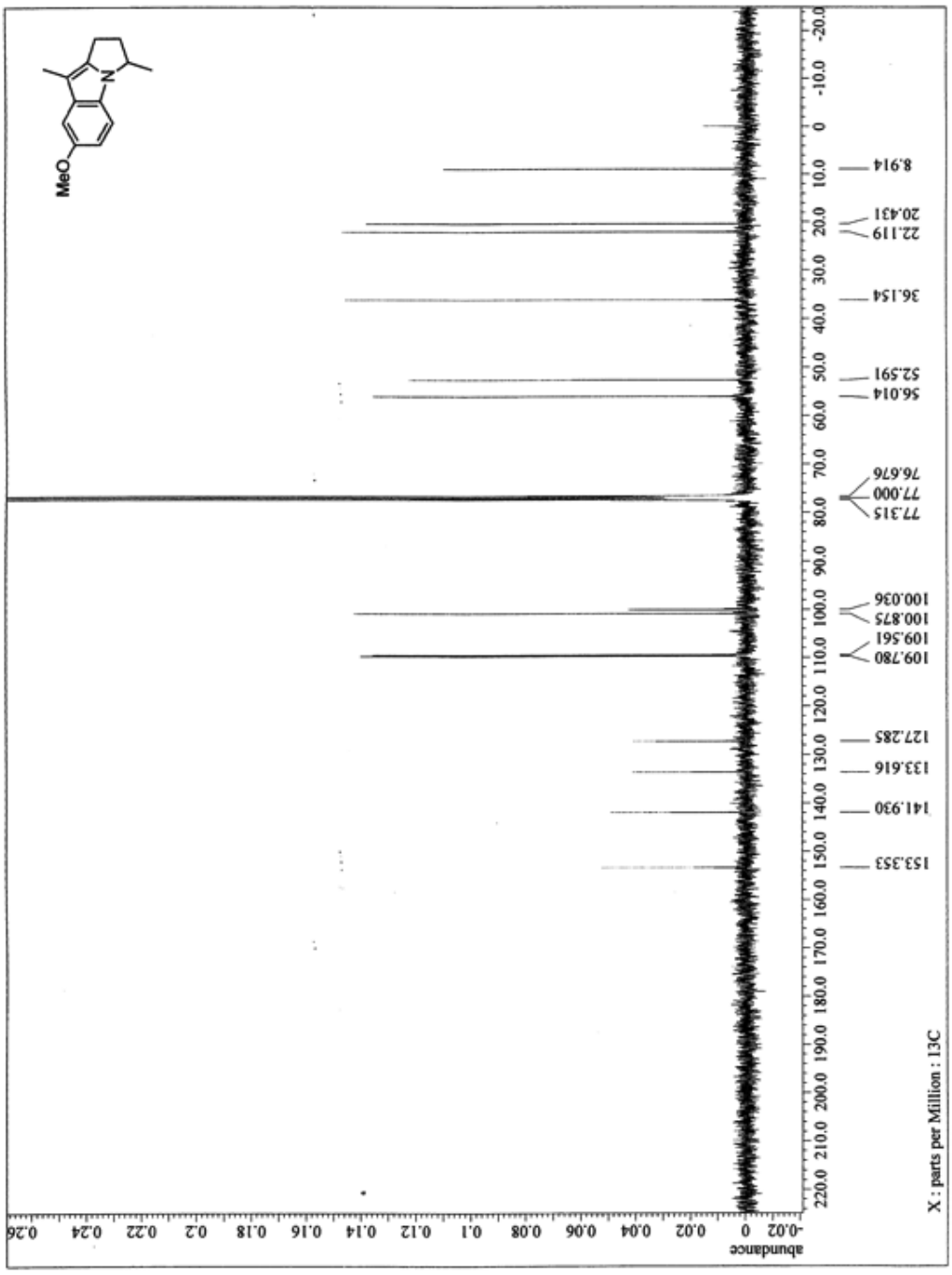
^{13}C NMR spectrum of **8b**.



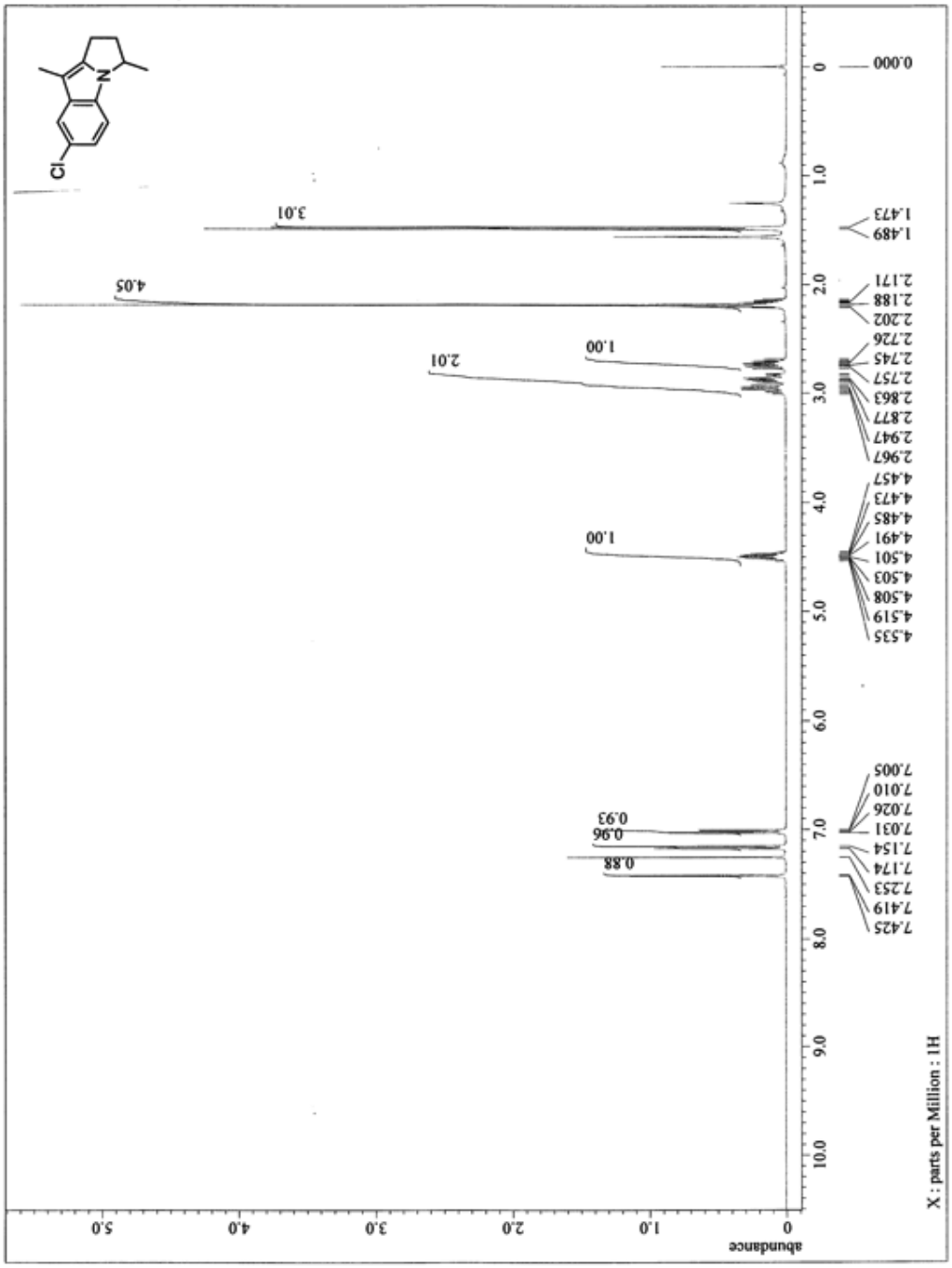
^{1}H NMR spectrum of **8c**.



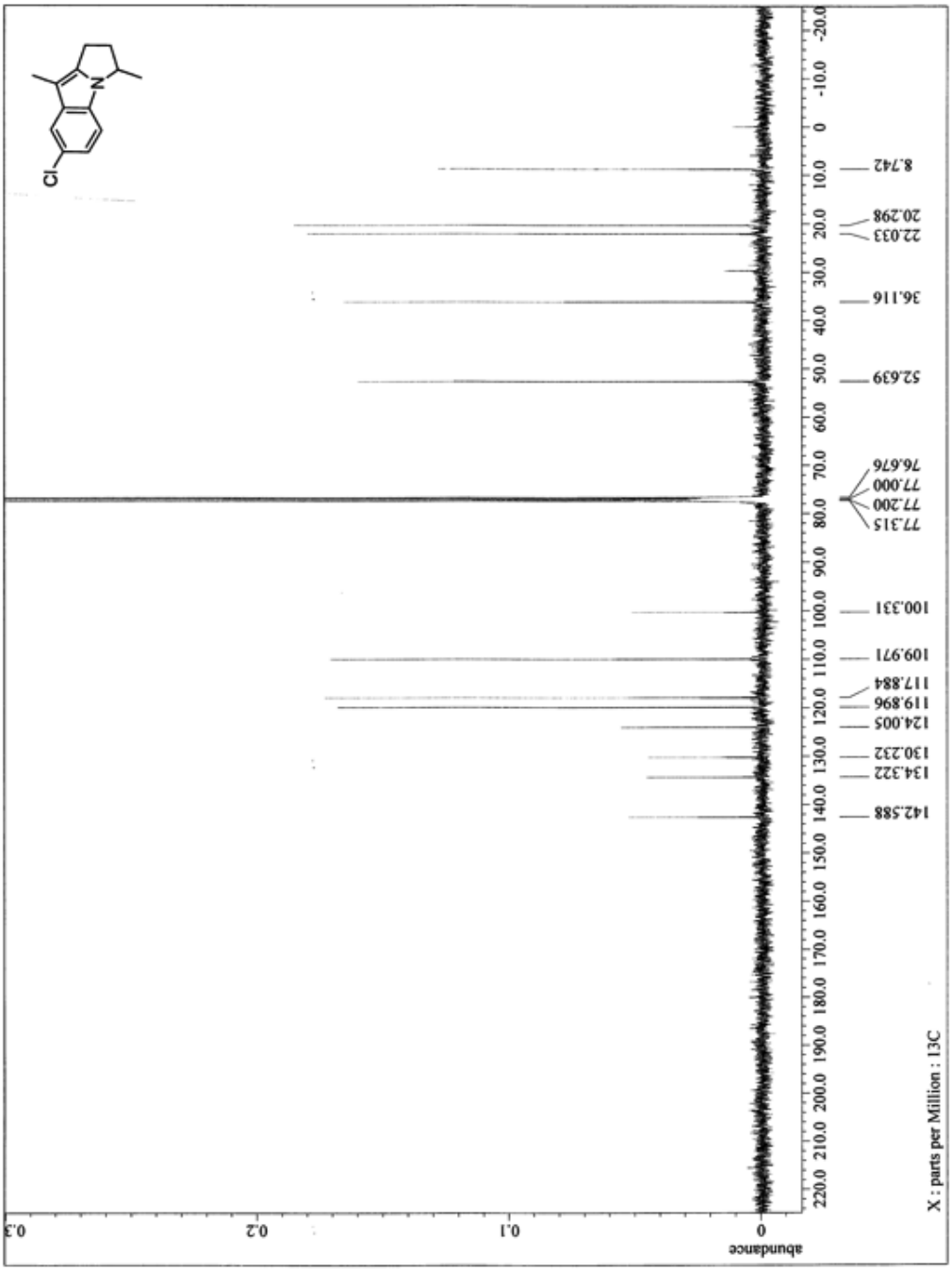
^{13}C NMR spectrum of **8c**.



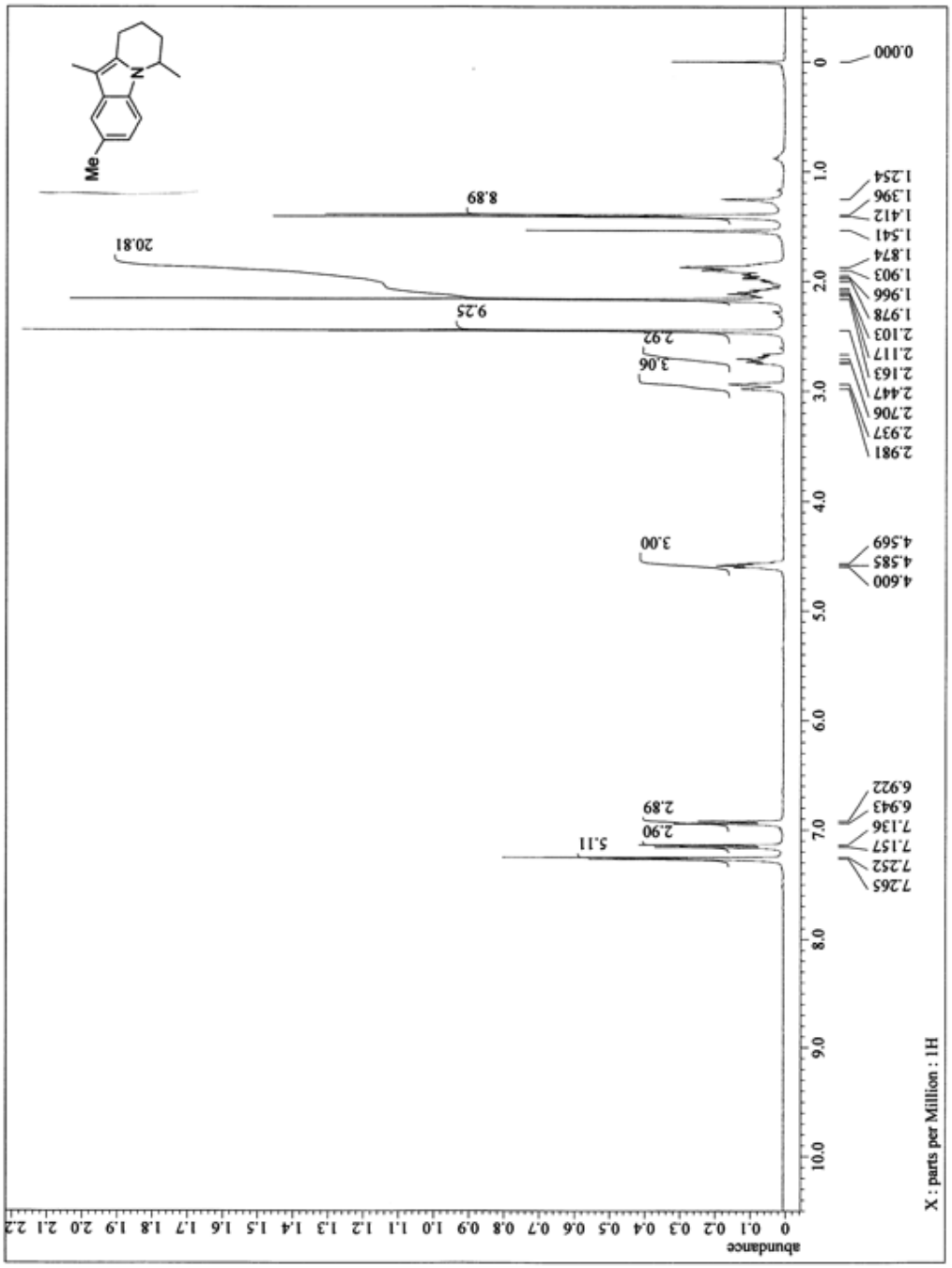
^{1}H NMR spectrum of **8d**.



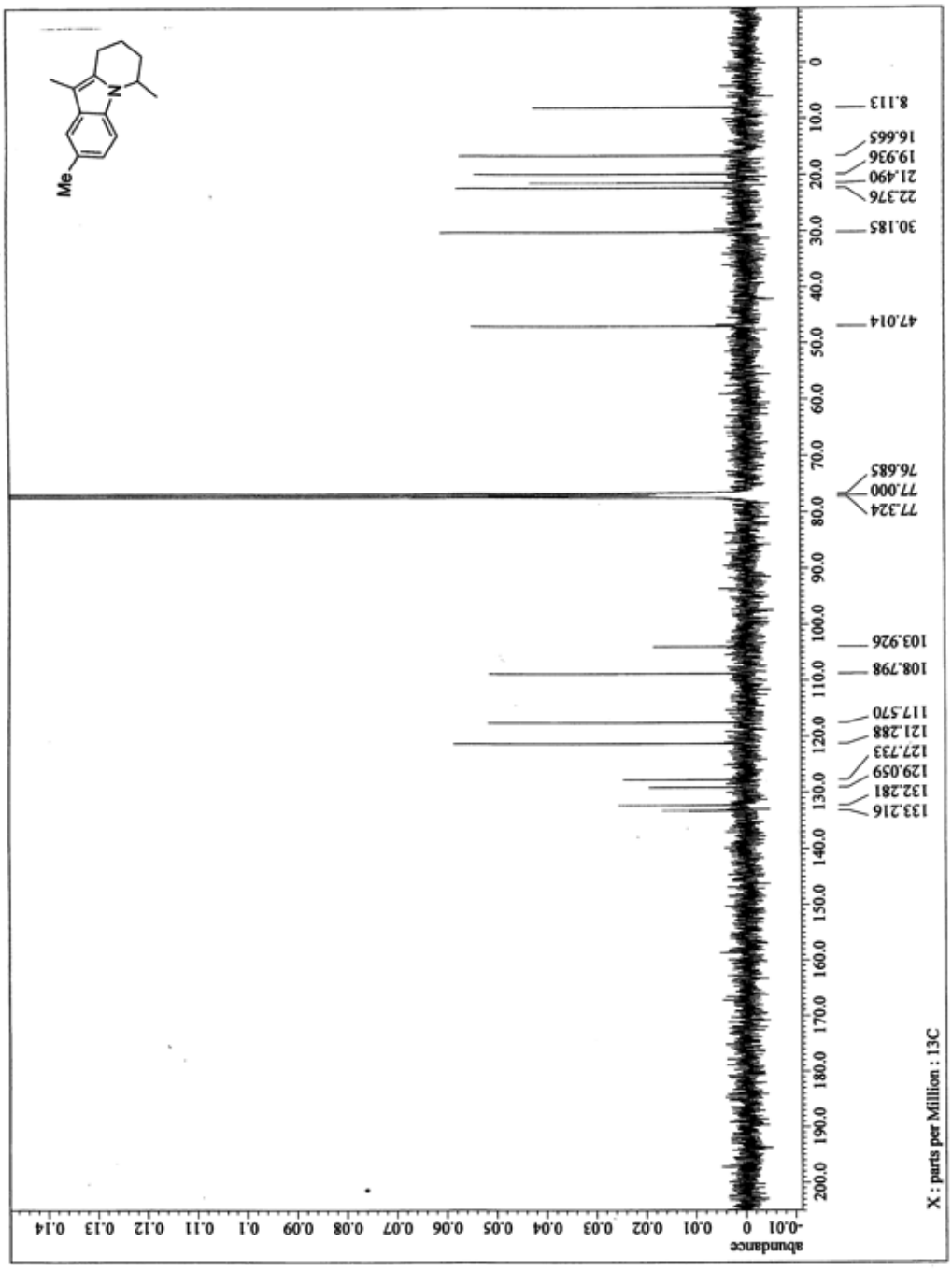
^{13}C NMR spectrum of **8d**.



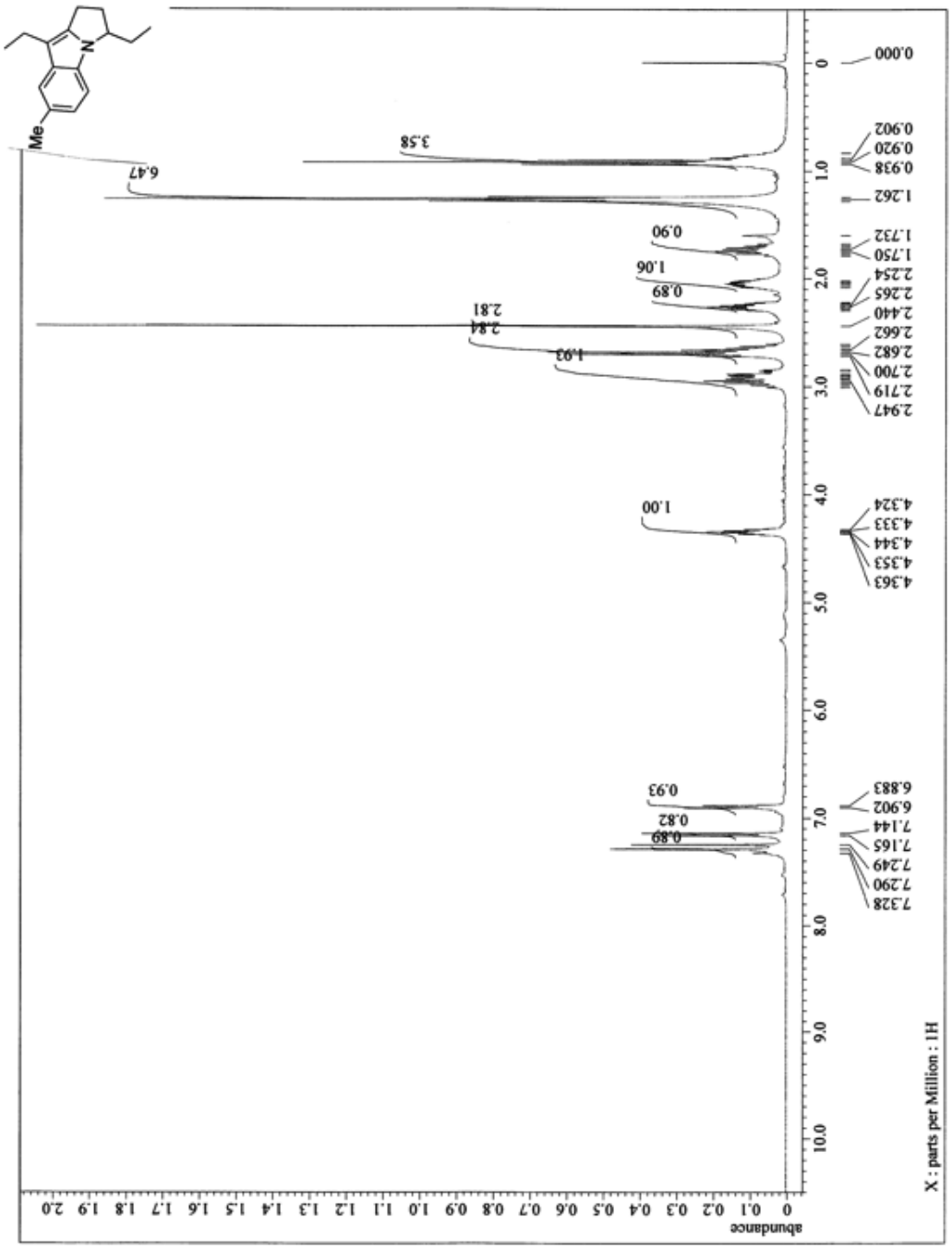
^{1}H NMR spectrum of **8e**.



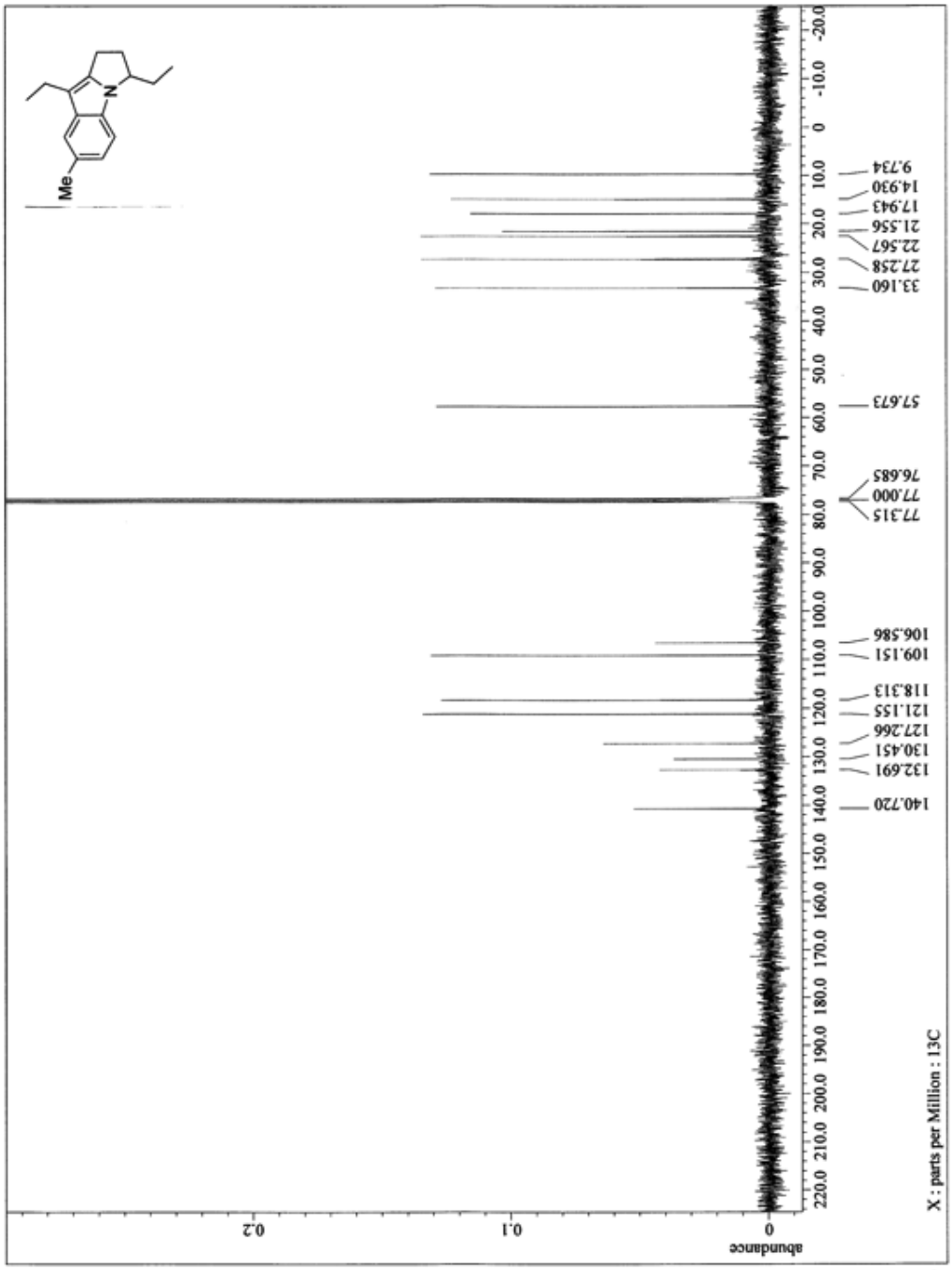
^{13}C NMR spectrum of **8e**.



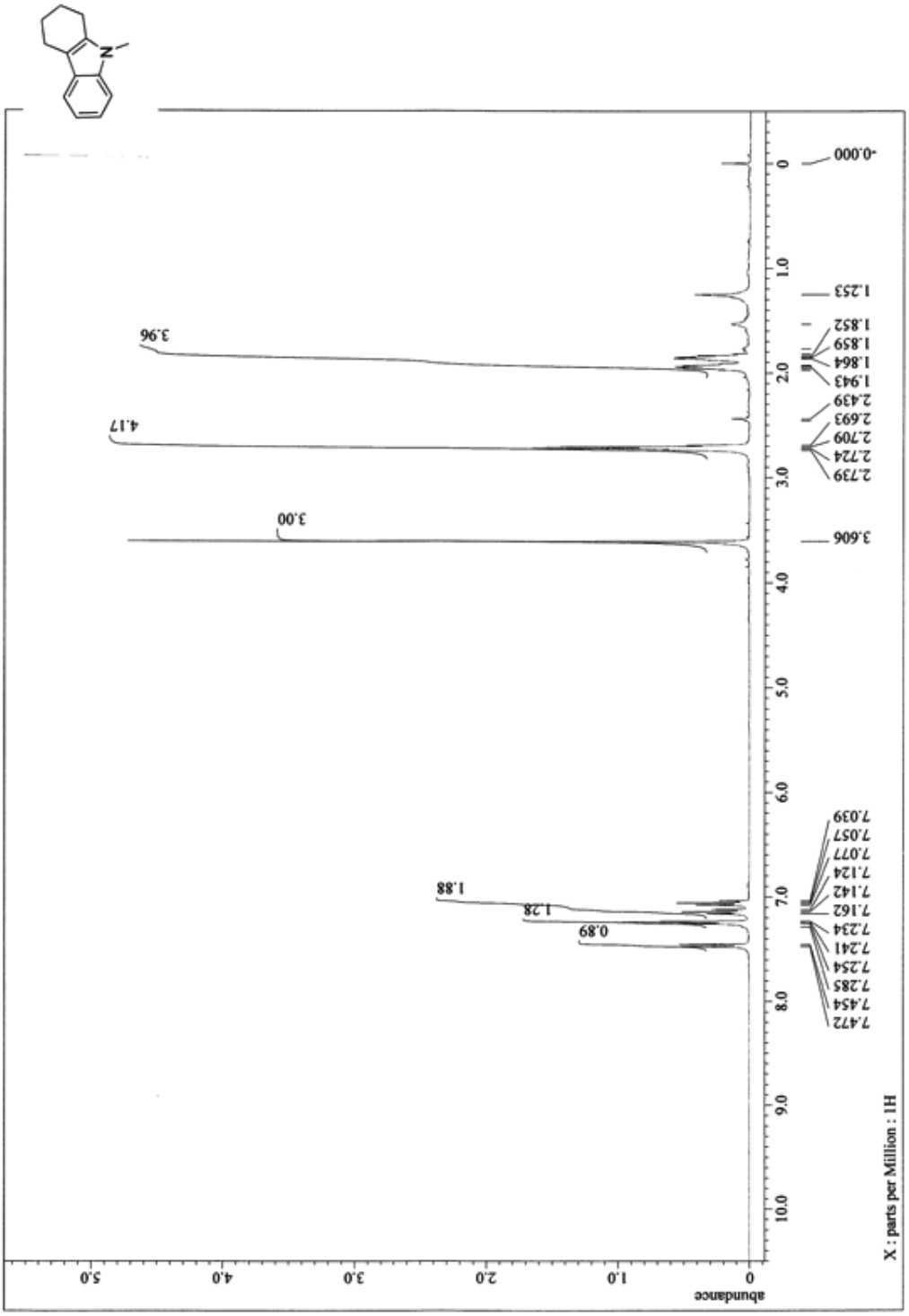
^{1}H NMR spectrum of **8f**.



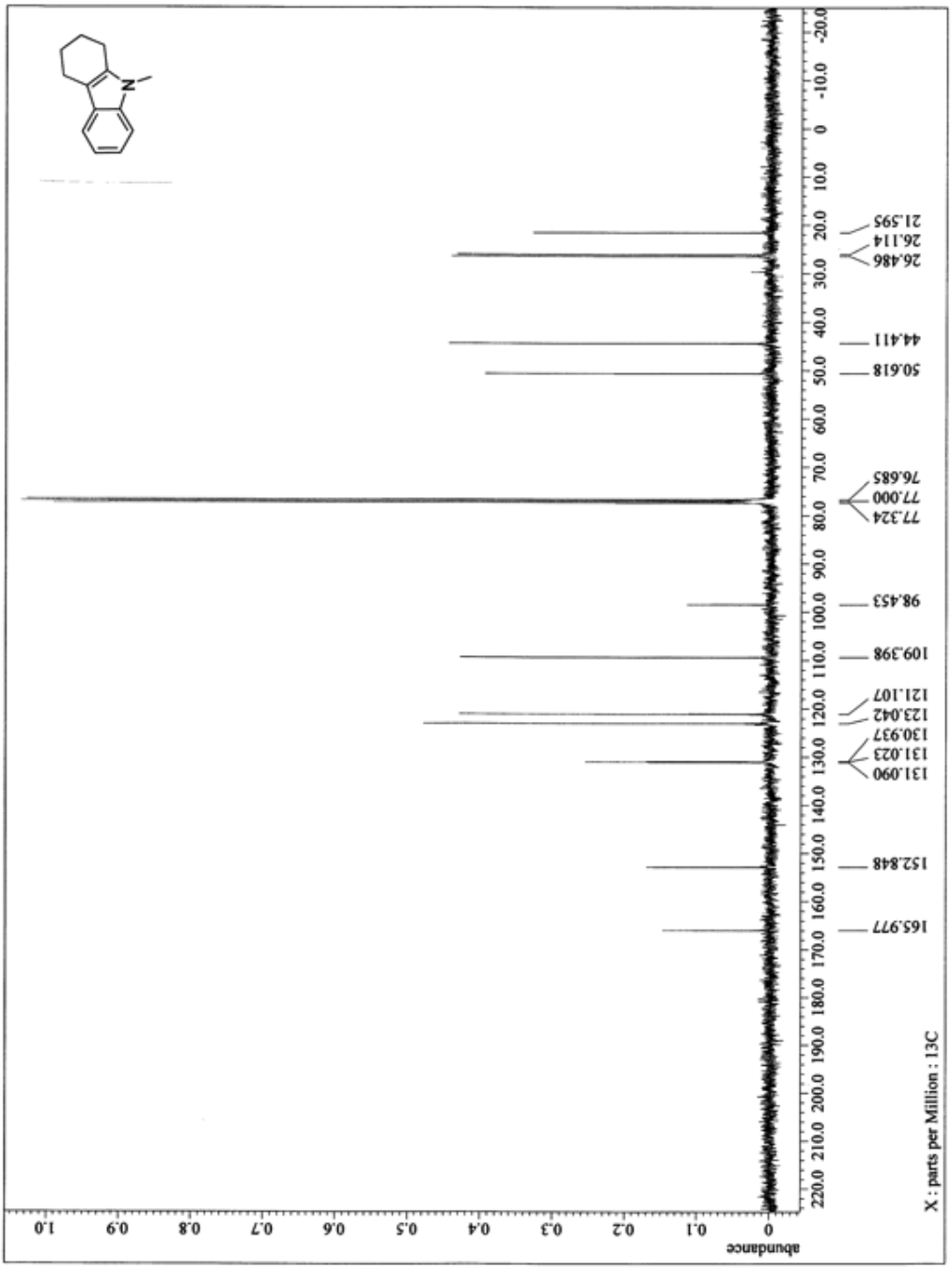
^{13}C NMR spectrum of **8f**.



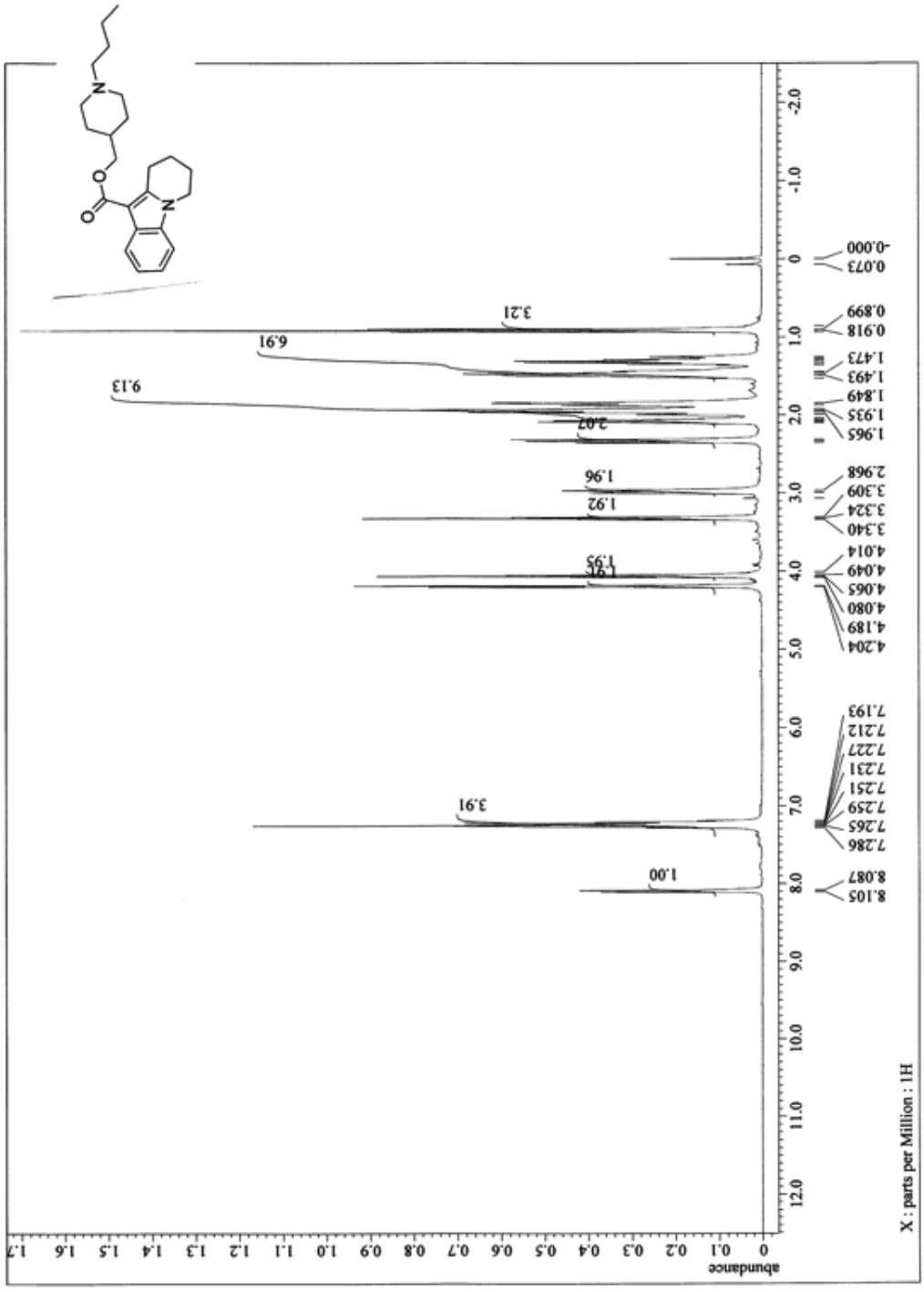
^{1}H NMR spectrum of **8g**.



^{13}C NMR spectrum of **8g**.



^{1}H NMR spectrum of **11**.



^{13}C NMR spectrum of **11**.