$Hf(OTf)_4$-catalyzed highly diastereoselective synthesis of 1,3-disubstituted tetralin derivatives by benzylic $C(sp^3)$–H bond functionalization

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Supporting Information

General experimental procedures

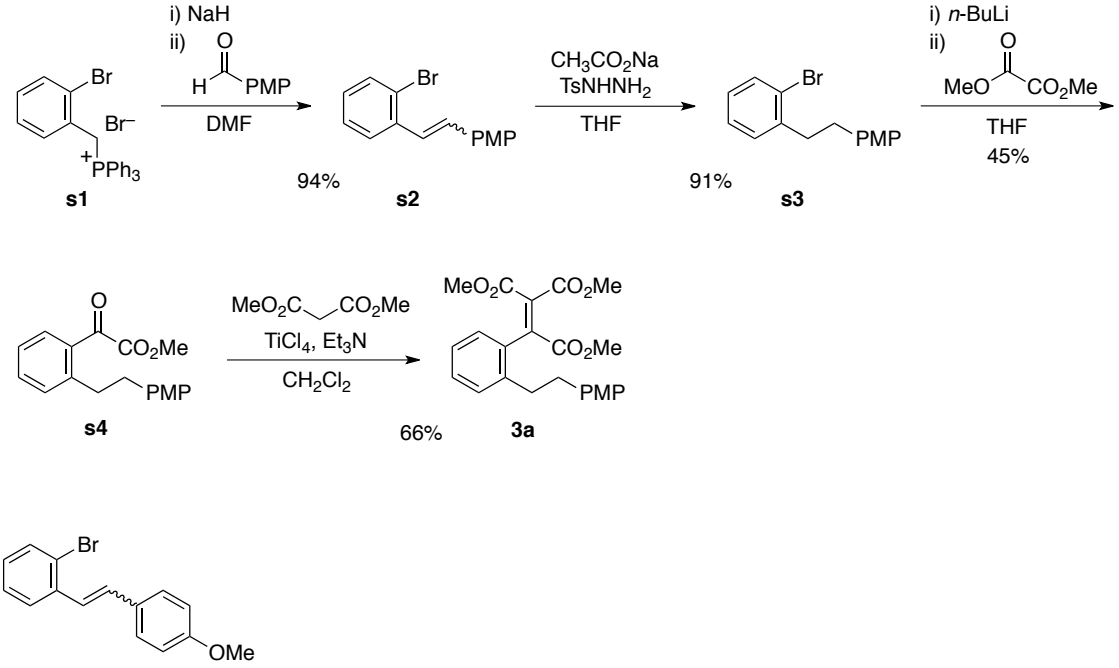
All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry nitrogen. Ethereal solvents (THF, Et_2O) were distilled from benzophenone ketyl. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2. Benzene and toluene were distilled 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 PSQ 60B, Fuji Silysia 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 1. General synthetic route to triester **3**. Preparation of **3a** is shown as a representative example via modified procedure of the reported method.[1]



Synthesis of 1-bromo-2-(4-methoxystyryl)benzene (s2):

To a solution of **s1** (2.30 g, 4.49 mmol) in DMF (11.5 mL) was added NaH (60% oil, 206 mg, 5.15 mmol) at 0 °C. After being stirred for 20 min at 0 °C, p-anisaldehyde (0.42 mL, 3.45 mmol) was added to the reaction mixture. After being stirred for 1 h at room temperature, 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 1 M aqueous HCl (x6), brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give **s2** (935 mg, 94%, *E*/*Z* = 3/2) as a colorless oil.

* shows the peaks of *Z*-isomer.

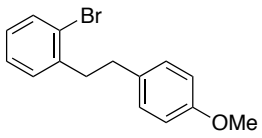
IR (neat) 3005, 2957, 2933, 2838, 1605, 1511, 1465, 1436, 1252, 1175, 1114, 1025, 958, 832 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.75* (s, 3H), 6.42 (d, 1H, *J* = 12.0 Hz), 6.53 (d, 1H, *J* = 12.0 Hz), 6.63 (d, 2H, *J* = 8.4 Hz), 6.83* (d, 2H, *J* = 8.4 Hz) 6.88–7.65 (m, 6+8*H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 55.1, 76.6, 113.5, 114.1, 123.9, 125.2, 126.4, 127.0, 127.5,

127.6, 128.1, 128.4, 128.5, 128.8, 129.8, 130.3, 130.8, 130.9, 132.6, 133.0, 137.3, 138.2, 158.7, 159.6.

Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53. Found: C, 62.16; H, 4.75.



Synthesis of 1-bromo-2-(4-methoxyphenethyl)benzene (s3):

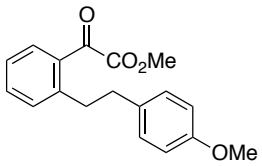
The mixture of **s2** (935 mg, 3.24 mmol), $TsNHNH_2$ (3.08 g, 16.5 mmol), CH_3CO_2Na (2.84 g, 34.6 mmol), and THF (17.2 mL) were heated at reflux for 24 h. After cooling to room temperature, the reaction was stopped by adding H_2O. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give **s3** (858 mg, 91%) as a colorless oil.

IR (neat) 3001, 2931, 2833, 1611, 1512, 1469, 1436, 1301, 1246, 1177, 1037, 822 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.65–2.79 (m, 2H), 2.82–2.95 (m, 2H), 3.67 (s, 3H), 6.73 (d, 2H, J = 8.1 Hz), 6.90–7.15 (m, 5H), 7.44 (dd, 1H, J = 1.5, 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 35.2, 38.6, 55.2, 113.7, 124.4, 127.3, 127.6, 129.3, 130.5, 132.7, 133.5, 140.9, 157.8.

Anal. Calcd for $C_{15}H_{15}BrO$: C, 61.87; H, 5.19. Found: C, 61.62; H, 5.01.



Synthesis of methyl 2-(2-(4-methoxyphenethyl)phenyl)-2-oxoacetate (s4):

To a solution of **s3** (858 mg, 2.95 mmol) in THF (12.0 mL) was added *n*-BuLi (1.60 M in hexane, 2.20 mL, 3.52 mmol) at –78 °C. After being stirred for 15 min, a solution of dimethyl oxalate (503 mg, 4.26 mmol) in THF (2.70 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

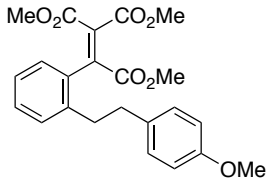
products were extracted with ether (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give **s4** (398 mg, 45%) as a pale yellow oil.

IR (neat) 2954, 2836, 1749, 1611, 1571, 1513, 1454, 1302, 1252, 1205, 1117, 989, 914, 858 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.73–2.90 (m, 2H), 3.10–3.25 (m, 2H), 3.77 (s, 3H), 3.95 (s, 3H), 6.82 (d, 2H, *J* = 8.1 Hz), 7.16 (d, 2H, *J* = 8.1 Hz), 7.25 (d, 1H, *J* = 7.8 Hz), 7.32 (dd, 1H, *J* = 7.8, 7.8 Hz), 7.49 (dd, 1H, *J* = 7.8, 7.8 Hz), 7.68 (d, 1H, *J* = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 36.7, 36.9, 52.8, 55.2, 113.6, 126.1, 129.4, 130.8, 131.9, 132.5, 133.6, 133.7, 145.0, 157.8, 164.6, 188.3.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.71; H, 5.96.



Synthesis of trimethyl 2-(2-(4-methoxyphenethyl)phenyl)ethene-1,1,2-tricarboxylate (3a):

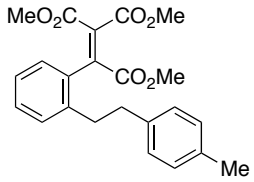
To a solution of **s4** (396 mg, 1.33 mmol) in CH_2Cl_2 (16.5 mL) were successively added dimethyl malonate (0,16 mL, 1.33 mmol) and $TiCl_4$ (1.0 M solution in CH_2Cl_2, 1.35 mL, 1.35 mmol) at 0 °C. After being stirred for 2 h at 0 °C, the reaction was stopped by adding 1 M aqueous HCl at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with 1 M aqueous HCl (x6), brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 6/1) to give **3a** (363 mg, 66%) as a Yellow amorphous.

IR (neat) 3061, 3005, 2953, 2838, 1732, 1673, 1635, 1611, 1584, 1513, 1484, 1435, 1301, 1247, 1179, 1096, 1083, 1021, 988, 949, 910, 857, 823, 761, 735 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.77–2.93 (m, 4H), 3.52 (s, 3H), 3.78 (s, 6H), 3.87 (s, 3H), 6.84 (d, 2H, *J* = 8.4 Hz), 7.10–7.35 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 35.9, 52.4, 53.0, 55.2, 113.7, 126.0, 128.5, 129.3, 129.3, 130.9, 132.5, 133.7, 139.7, 146.4, 157.8, 163.6, 163.8, 166.5.

Anal. Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.71; H, 5.99.



Trimethyl 2-(2-(4-methylphenethyl)phenyl)ethene-1,1,2-tricarboxylate (**3b**).

Yellow Solid.

Yield: 82%.

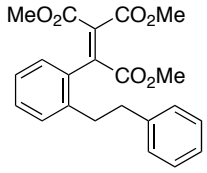
Mp. 80–82 °C.

IR (KBr) 3019, 2952, 2925, 2864, 1736, 1636, 1515, 1485, 1435, 1243, 1097, 1082, 1020, 904, 806, 762 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.74–2.94 (m, 4H), 3.50 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 7.01-7.27 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 29.7, 35.4, 36.4, 52.5, 53.0, 126.0, 128.3, 128.5, 129.0, 129.3, 129.3, 130.9, 132.5, 135.3, 138.6, 139.8, 146.5, 163.6, 163.9, 166.6.

Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.42; H, 6.32.



Trimethyl 2-(2-phenethylphenyl)ethene-1,1,2-tricarboxylate (**3c**).

Yellow solid.

Yield 60%.

Mp. 73–76 °C.

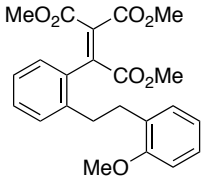
IR (KBr) 3026, 2953, 1735, 1636, 1495, 1435, 1243, 1084, 1020, 906, 757, 701, 658 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.76–2.88 (m, 4H), 3.45 (s 3H), 3.72 (s, 3H), 3.80 (s, 3H), 7.10–7.25 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 35.3, 36.8, 52.5, 53.0, 125.9, 126.1, 128.4, 128.5, 128.6,

129.3, 129.4, 131.0, 132.6, 139.7, 141.7, 146.5, 163.6, 163.9, 166.6.

Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 68.85; H, 5.71.



Trimethyl 2-(2-(2-methoxyphenethyl)phenyl)ethene-1,1,2-tricarboxylate (**3d**).

Colorless oil.

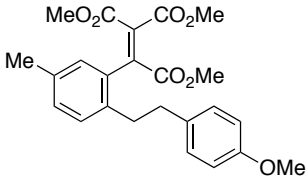
Yield: 46%.

IR (neat) 3062, 3005, 2952, 2838, 1736, 1637, 1601, 1587, 1495, 1436, 1244, 1095, 1082, 1051, 1022, 907, 755 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.89 (m, 4H), 3.52 (s, 3H), 3.78 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 6.85–6.92 (m, 2H), 7.16–7.33 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5, 33.3, 52.3, 52.8, 55.0, 110.0, 120.2, 125.7, 127.1, 128.2, 129.1, 129.2, 129.8, 129.9, 131.3, 132.6, 140.2, 146.1, 157.4, 163.7, 163.8, 166.4.

Anal. Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 67.26; H, 5.98.



Trimethyl 2-(2-(4-methoxyphenethyl)-5-methylphenyl)ethene-1,1,2-tricarboxylate (**3e**).

Orange solid.

Yield: 67%.

Mp. 76–79 °C.

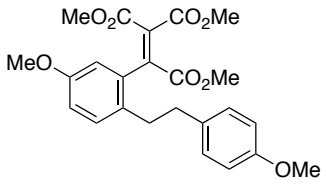
IR (KBr) 3005, 2952, 2828, 1736, 1612, 1513, 1435, 1297, 1243, 1179, 1082, 1028, 828, cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.70–2.85 (m, 4H), 3.51 (s, 3H), 3.77 (s, 3H), 3.77 (s, 3H), 3.84 (s, 3H), 6.81 (d, 2H, J = 8.4 Hz), 6.96 (s, 1H), 7.06–7.15(m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 35.1, 36.0, 52.4, 52.9, 52.9, 55.2, 113.7, 128.8, 129.2, 129.3, 130.1, 130.6, 132.3, 133.9, 135.5, 136.6, 146.8, 157.8, 163.6, 163.9,

166.7.

Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.40; H, 6.04.



Trimethyl 2-(5-methoxy-2-(4-methoxyphenethyl)phenyl)ethene-1,1,2-tricarboxylate (**3f**).

Yellow solid.

Yield: 54%.

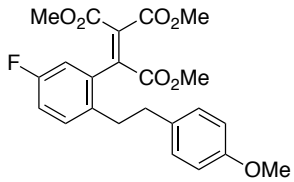
Mp. 88–90 °C.

IR (KBr) 3005, 2955, 2832, 1734, 1610, 1512, 1434, 1242, 1023, 828 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.70–2.84 (m, 4H), 3.53 (s, 3H), 3.75 (s, 3H), 3.77 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 6.70 (d, 1H, *J* = 3.0 Hz), 6.78–6.86 (m, 3H), 7.06–7.15 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 34.7, 36.1, 52.5, 53.0, 53.0, 55.2, 55.3, 113.4, 113.7, 115.3, 129.3, 130.4, 130.9, 131.7, 133.2, 133.9, 146.2, 157.5, 157.8, 163.6, 163.8, 166.5.

Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 64.89; H, 6.21.



Trimethyl 2-(5-fluoro-2-(4-methoxyphenethyl)phenyl)ethene-1,1,2-tricarboxylate (**3g**).

Yellow solid.

Yield: 60%.

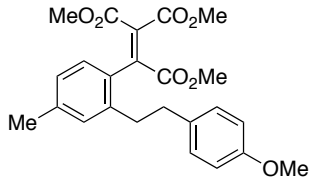
Mp. 76–80 °C.

IR (KBr) 3008, 2954, 2838, 1736, 1609, 1513, 1493, 1435, 1243, 1077, 1027, 829, 724 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.68–2.91 (m, 4H), 3.55 (s, 3H), 3.77 (s, 6H), 3.86 (s, 3H), 6.78–7.20 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 34.8, 35.9, 52.6, 53.1, 53.1, 55.2, 113.8, 115.5 (d, *J* = 22.2 Hz), 116.1 (d, *J* = 20.1 Hz), 129.4, 130.9 (d, *J* = 8.0 Hz), 131.8, 133.4, 133.9 (d, *J* = 8.0 Hz), 135.5 (d, *J* = 3.7 Hz), 144.6, 157.9, 159.0 (d, *J* = 244.2 Hz), 163.4, 163.6, 166.0.

Anal. Calcd for $C_{23}H_{23}FO_7$: C, 64.18; H, 5.39. Found: C, 63.91; H, 5.17.



Trimethyl 2-(2-(4-methoxyphenethyl)-4-methylphenyl)ethene-1,1,2-tricarboxylate (**3h**).

Yellow solid.

Yield: 60%.

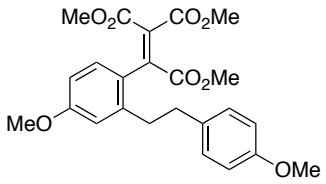
Mp. 82–85 °C.

IR (KBr) 3005, 2952, 2837, 1736, 1610, 1513, 1435, 1244, 1171, 1081, 1021, 822 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.75–2.90 (m, 4H), 3.52 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 3.85 (s, 3H), 6.83 (d, 2H, *J* = 8.7 Hz), 6.95-7.07 (m, 3H), 7.13 (d, 2H, *J* = 8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 35.7, 36.1, 52.5, 52.9, 55.2, 113.7, 126.8, 128.5, 129.3, 129.7, 130.2, 130.8, 133.9, 139.3, 139.6, 146.8, 157.8, 163.7, 164.0, 166.8.

Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.73; H, 6.35.



Trimethyl 2-(4-methoxy-2-(4-methoxyphenethyl)phenyl)ethene-1,1,2-tricarboxylate (**3i**).

Yellow oil

Yield 46%

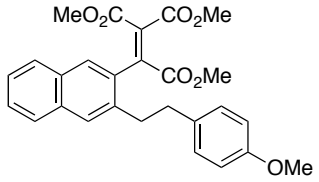
IR (neat) 3008, 2952, 2917, 2833, 1734, 1603, 1512, 1440, 1304, 1241, 1180, 1109, 1077, 1038, 1013, 985, 818 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.74–2.86 (m, 4H), 3.53 (s 3H), 3.74 (s, 3H), 3.77 (s, 3H),

3.84 (s, 3H), 6.69–6.81 (m, 2H), 6.81 (d, 2H, J = 6.6 Hz), 7.06–7.14 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 35.8, 52.5, 52.9, 55.1, 55.2, 111.4, 113.7, 115.0, 124.9, 129.4, 130.0, 130.8, 133.7, 141.6, 146.6, 157.8, 160.2, 163.6, 164.2, 166.9.

Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.41; H, 5.75.



Trimethyl 2-(3-(4-methoxyphenethyl)naphthalen-2-yl)ethene-1,1,2-tricarboxylate (**3j**).

Yellow solid.

Yield: 70%.

Mp. 128–130 °C.

IR (KBr) 3005, 2952, 1735, 1612, 1513, 1435, 1245, 1179, 1115, 1072, 1020, 982, 902, 822, 752, cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.85–3.07 (m, 4H), 3.45 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 6.83 (d, 2H, J = 8.7 Hz), 7.16 (d, 2H, J = 8.7 Hz), 7.38–7.49 (m, 2H), 7.64–7.80 (m, 4H).

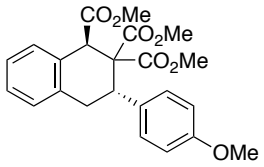
^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 35.8, 52.6, 53.1, 53.1, 55.3, 113.8, 125.9, 126.9, 127.3, 127.7, 127.9, 128.1, 129.4, 131.4, 131.8, 133.6, 133.8, 137.1, 146.1, 157.9, 163.8, 163.9, 166.5.

Anal. Calcd for $C_{27}H_{26}O_7$: C, 70.12; H, 5.67. Found: C, 70.36; H, 5.48.

2. Synthesis of 1,3-disubstituted tetralin derivatives.

General Procedure of the formation of 1,3-disubstituted tetralin derivatives.

To a solution of triester **3** (0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added $Hf(OTf)_4$ (0.0025 mmol, 2.5 mol%), and the mixture was heated at reflux. After completion of the reaction, the reaction was stopped by adding saturated aqueous $NaHCO_3$. 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 preparative TLC to give 1,3-disubstituted tetralin derivatives **4**.



Trimethyl 3-(4-methoxyphenyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4a**).

White solid.

Yield: 85%.

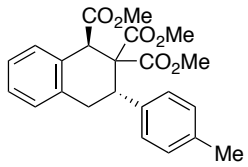
Mp. 120–125 °C

IR (KBr) 3001, 2952, 2838, 1734, 1610, 1513, 1433, 1252, 1034, 836, 753 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.25 (dd, 1H, *J* = 6.6, 16.8 Hz), 3.37 (dd, 1H, *J* = 9.0, 16.8 Hz), 3.43 (s, 3H), 3.51 (s, 3H), 3.72 (s, 3H), 3.75 (s, 3H), 4.53 (dd, 1H, *J* = 6.6, 9.0 Hz), 4.62 (s, 1H), 6.76 (d, 2H, *J* = 8.8 Hz), 7.11–7.34 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 33.7, 40.6, 50.9, 52.2, 52.4, 52.5, 55.1, 60.8, 113.0, 126.3, 127.6, 128.7, 129.0, 130.6, 131.4, 133.1, 136.3, 158.4, 169.3, 170.4, 172.4.

Anal. Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.71; H, 5.99.



Trimethyl 3-(*p*-tolyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4b**).

Yellow solid.

Yield: 65%.

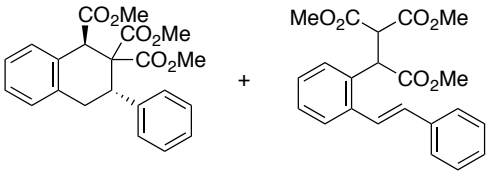
Mp. 115–120 °C

IR (KBr) 3023, 2952, 2922, 2848, 1735, 1514, 1433, 1257, 1239, 1216, 1159, 1113, 1062, 1021, 972, 826, 752 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.26 (dd, 1H, *J* = 6.6, 17.1 Hz), 3.32–3.46 (m, 1H), 3.44 (s, 3H), 3.52 (s, 3H), 3.72 (s, 3H), 4.50–4.54 (m, 1H), 4.64 (s, 1H), 7.04 (d, 2H, *J* = 8.1 Hz), 7.10–7.35 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 33.7, 41.0, 50.9, 52.1, 52.4, 52.4, 60.7, 126.3, 127.6, 128.4, 128.6, 128.9, 129.4, 131.4, 136.3, 136.5, 138.1, 169.2, 170.3, 172.4.

Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.39; H, 6.32.



Trimethyl 3-phenyl-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4c**) and (*E*)-trimethyl 2-(2-styrylphenyl)ethane-1,1,2-tricarboxylate (**6**).

These compounds were difficult to separate with silica-gel Chromatography and also GPC.

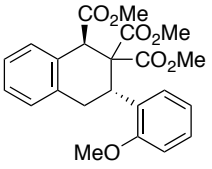
White solid.

Yield: 30% for **4c** and 30% for **6**.

* shows the peaks of **6**.

IR (neat) 3061, 3029, 2952, 2848, 1735, 1496, 1434, 1233, 1158, 1113, 1005, 966, 763, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.27 (dd, 1H, *J* = 6.3, 17.1 Hz), 3.35–3.48 (m, 1H), 3.38* (s, 3H), 3.40 (s, 3H), 3.50 (s, 3H), 3.64* (s, 3H), 3.72 (s, 3H), 3.77* (s, 3H), 4.29* (d, 1H, *J* = 11.7 Hz), 4.58 (dd, 1H, *J* = 6.3, 9.0 Hz), 4.63 (s, 1H), 4.79* (d, 1H, *J* = 11.7 Hz), 5.17* (d, 1H, *J* = 16.2 Hz), 7.10–7.65 (m, 9+10*H).



Trimethyl 3-(2-methoxyphenyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4d**).

Colorless oil.

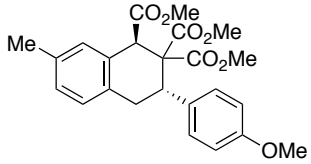
Yield: 52%.

IR (neat) 3062, 2997, 2949, 2839, 1736, 1600, 1493, 1459, 1433, 1333, 1291, 1243, 1202, 1155, 1114, 1030, 912, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.10 (dd, 1H, *J* = 6.3, 17.1 Hz), 3.38–3.45 (m, 7H), 3.66 (s, 3H), 3.72 (s 3H), 4.58 (s, 1H), 5.17 (dd, 1H, *J* = 6.3, 9.9 Hz), 6.73–6.83 (m, 2H), 7.02–7.32 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.0, 33.3, 50.9, 52.2, 55.6, 59.9, 60.3, 109.9, 120.1, 126.1, 127.5, 127.6, 128.8, 128.9, 129.2, 130.2, 131.0, 136.8, 169.4, 170.2, 171.1, 172.3.

Anal. Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.71; H, 5.99.



Trimethyl

3-(4-methoxyphenyl)-7-methyl-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4e**).

White solid.

Yield: 69%.

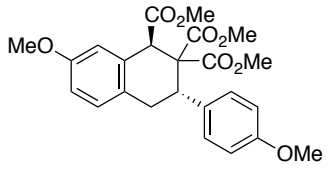
Mp. 159–162 °C

IR (KBr) 3001, 2952, 2838, 1734, 1610, 1582, 1513, 1433, 1335, 1252, 1208, 1180, 1167, 1034, 1009, 914, 836, 812, 737 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.14 (dd, 1H, *J* = 6.3, 16.8 Hz), 3.28 (dd, 1H, *J* = 6.3, 9.0 Hz), 3.39 (s, 3H), 3.44 (s, 3H), 3.67 (s, 3H), 3.70 (s, 3H), 4.30 (dd, 1H, *J* = 6.3, 9.0 Hz), 4.51 (s, 1H), 6.71 (d, 2H, *J* = 8.7 Hz), 6.90–7.05 (m, 3H), 7.10–7.20 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 33.3, 40.7, 50.9, 52.2, 52.4, 52.5, 55.1, 61.0, 113.0, 128.6, 128.8, 129.1, 130.7, 131.1, 133.2, 133.2, 135.8, 158.4, 169.3, 170.4, 172.5.

Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.43; H, 5.88.



Trimethyl

7-methoxy-3-(4-methoxyphenyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4f**).

Yellow oil.

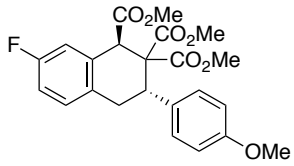
Yield: 71%.

IR (neat) 3005, 2952, 2838, 1735, 1612, 1512, 1434, 1251, 1209, 1181, 1122, 1035, 917, 836 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.16 (dd, 1H, *J* = 6.3, 16.8 Hz), 3.31 (dd, 1H, *J* = 9.3, 16.5 Hz), 3.35 (s, 3H), 3.45 (s, 3H), 3.72 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 4.48 (dd, 1H, *J* = 6.6, 9.3 Hz), 4.57 (s, 1H), 6.72–6.82 (m, 4H), 7.04 (d, 1H, *J* = 8.1 Hz), 7.21 (d, 2H, *J* = 8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 32.9, 40.8, 51.1, 52.2, 52.4, 52.5, 55.1, 55.2, 60.9, 113.0, 113.4, 113.9, 128.3, 129.9, 130.7, 132.3, 133.2, 157.9, 158.5, 169.3, 170.3, 172.3.

Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.26; H, 6.06.



Trimethyl

7-fluoro-3-(4-methoxyphenyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4g**).

Yellow solid

Yield 75%.

Mp. 117–121 °C

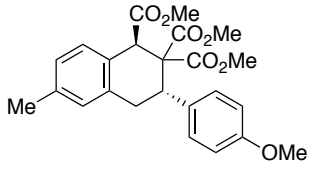
IR (KBr) 3000, 2953, 2841, 1736, 1611, 1513, 1434, 1245, 1106, 1034, 923, 835, 733 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.22 (dd, 1H, *J* = 6.6, 17.1 Hz), 3.34 (dd, 1H, *J* = 8.7, 16.8 Hz), 3.48 (s, 3H), 3.54 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 4.49 (dd, 1H, *J* = 6.6, 9.0 Hz), 4.59 (s, 1H), 6.79 (d, 2H, *J* = 8.4 Hz), 6.90–7.33 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 33.1, 40.7, 50.8, 52.3, 52.6, 55.1, 60.5, 113.0, 115.0 (d, *J*

= 21.6 Hz), 115.1 (d, *J* = 21.6 Hz), 130.4 (d, *J* = 8.0 Hz), 130.6, 130.7, 131.9 (d, *J* = 3.2 Hz), 132.9, 158.5, 161.1 (d, *J* = 242.3 Hz), 169.2, 170.1, 171.9.

Anal. Calcd for $C_{23}H_{23}FO_7$: C, 64.18; H, 5.39. Found: C, 64.24; H, 5.09.



Trimethyl

3-(4-methoxyphenyl)-6-methyl-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4h**).

Colorless oil

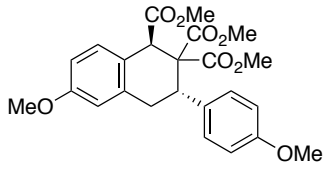
Yield: 63%.

IR (neat) 3002, 2952, 2838, 1611, 1513, 1434, 1253, 1206, 1035, 834, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.20 (dd, 1H, *J* = 6.6, 16.8 Hz), 3.35 (dd, 1H, *J* = 9.3, 16.8 Hz), 3.45 (s, 3H), 3.49 (s, 3H), 3.71 (s, 3H), 3.76 (s, 3H), 4.49 (dd, 1H, *J* = 6.6, 9.3 Hz), 4.57 (s, 1H), 6.77 (d, 2H *J* = 8.4 Hz), 6.95 (s, 1H), 6.97 (d, 1H, *J* = 8.4 Hz) 7.15 (d, 1H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 33.6, 40.6, 50.6, 52.2, 52.4, 52.5, 55.1, 60.9, 113.1, 127.3, 128.4, 128.5, 129.5, 130.7, 133.2, 136.1, 137.3, 158.4, 169.3, 170.4, 172.6.

Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.43; H, 5.88.



Trimethyl

6-methoxy-3-(4-methoxyphenyl)-3,4-dihydronaphthalene-1,2,2(1*H*)-tricarboxylate (**4i**).

Yellow solid.

Yield: 54%.

Mp. 123–127 °C

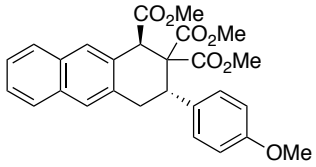
IR (KBr) 3000, 2952, 2838, 1734, 1610, 1583, 1513, 1462, 1433, 1332, 1305, 1252, 1229, 1212, 1180, 1159, 1113, 1090, 1062, 1037, 969, 916, 835, 814, 786, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.17 (dd, 1H, *J* = 6.6, 16.8 Hz), 3.32 (dd, 1H, *J* = 9.3,

16.8 Hz), 3.39 (s, 3H), 3.44 (s, 3H), 3.66 (s, 3H), 3.70 (s, 6H), 4.45 (dd, 1H, J = 6.6, 9.3 Hz), 4.50 (s, 1H), 6.55–6.75 (m, 4H), 7.08–7.21 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 34.0, 40.5, 50.1, 52.2, 52.4, 52.5, 55.1, 55.2, 60.9, 112.9, 113.1, 113.4, 123.6, 129.7, 130.7, 133.1, 137.7, 158.5, 158.9, 169.3, 170.4, 172.7.

Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.03; H, 5.75.



Trimethyl 3-(4-methoxyphenyl)-3,4-dihydroanthracene-1,2,2(1*H*)-tricarboxylate (**4j**).

Colorless solid (recrystallized from Hexane/EtOAc), which was subjected to X-ray crystal analysis.

Yield: 76%.

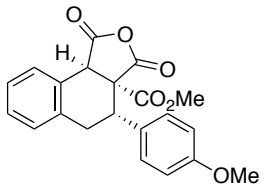
Mp. 179–182 °C

IR (KBr) 3055, 3002, 2952, 2838, 1735, 1610, 1582, 1513, 1459, 1434, 1328, 1252, 1207, 1181, 1155, 1115, 1035, 1017, 869, 911, 879, 834 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.31 (s, 3H), 3.35–3.55 (m, 2H), 3.60 (s, 3H), 3.70 (s, 3H), 3.73 (s, 3H), 4.62–4.67 (m, 1H), 4.88 (s, 1H), 6.67–6.75 (m, 2H), 7.06–7.15 (m, 2H), 7.35–7.48 (m, 3H), 7.61 (m, 1H), 7.68–7.85 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 34.1, 41.1, 51.2, 52.2, 52.5, 52.7, 55.1, 61.2, 113.1, 125.4, 126.0, 127.0, 127.2, 127.6, 127.8, 130.4, 130.7, 132.3, 133.0, 133.7, 134.2, 158.4, 169.5, 170.6, 172.3.

Anal. Calcd for $C_{27}H_{26}O_7$: C, 70.12; H, 5.67. Found: C, 69.98; H, 5.44.



Methyl

4-(4-methoxyphenyl)-1,3-dioxo-1,3,3a,4,5,9b-hexahydronaphtho[1,2-*c*]furan-3a-carboxylate (**5**).

Colorless solid (recrystallized from Hexane/Et_2O), which was subjected to X-ray crystal

analysis.

Mp. 179–182 °C

IR (KBr) 2953, 2933, 2925, 2847, 2840, 1789, 1737, 1610, 1583, 1514, 1499, 1452, 1439, 1254, 1232, 1205, 1184, 1119, 1087, 1034, 992 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (dd, 1H, *J* = 3.2, 16.4 Hz), 3.20 (dd, 1H, *J* = 5.6, 16.4 Hz), 3.60 (s, 3H), 3.70 (s, 3H), 4.20 (dd, 1H, *J* = 3.2, 5.6 Hz), 5.07 (s, 1H), 6.62–6.68 (m, 2H), 6.76–6.83 (m, 2H), 7.04 (d, 1H, *J* = 7.6 Hz), 7.23–7.28 (m, 1H), 7.34 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.68 (d, 1H, *J* = 7.6 Hz)).

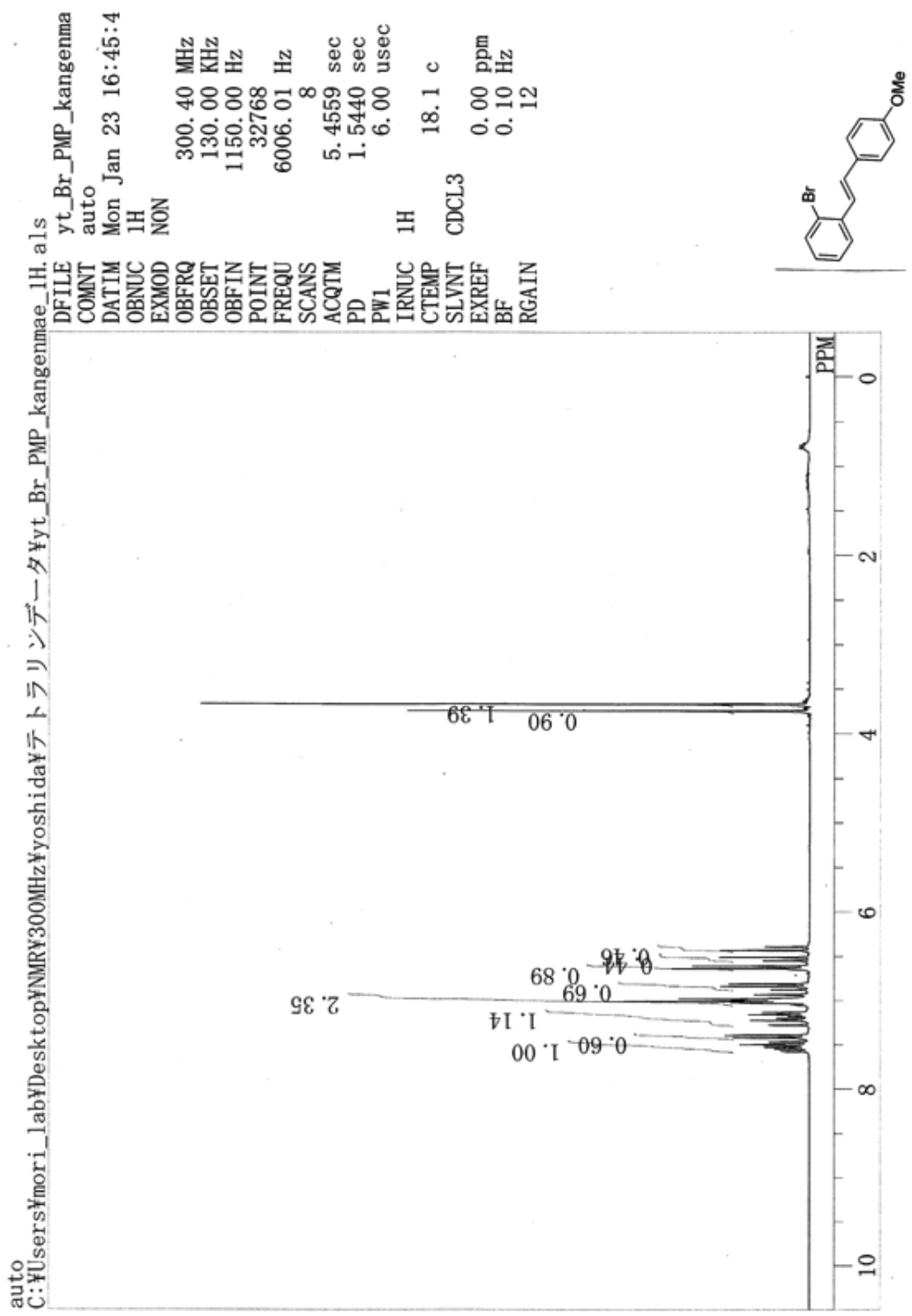
^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 33.9, 41.5, 46.6, 54.0, 55.1, 61.9, 113.9, 127.1, 127.8, 128.9, 128.9, 129.0, 129.8, 130.8, 133.1, 158.8, 166.4, 168.8, 169.5.

Anal. Calcd for $C_{27}H_{26}O_7$: C, 68.85; H, 4.95. Found: C, 68.68; H, 5.11.

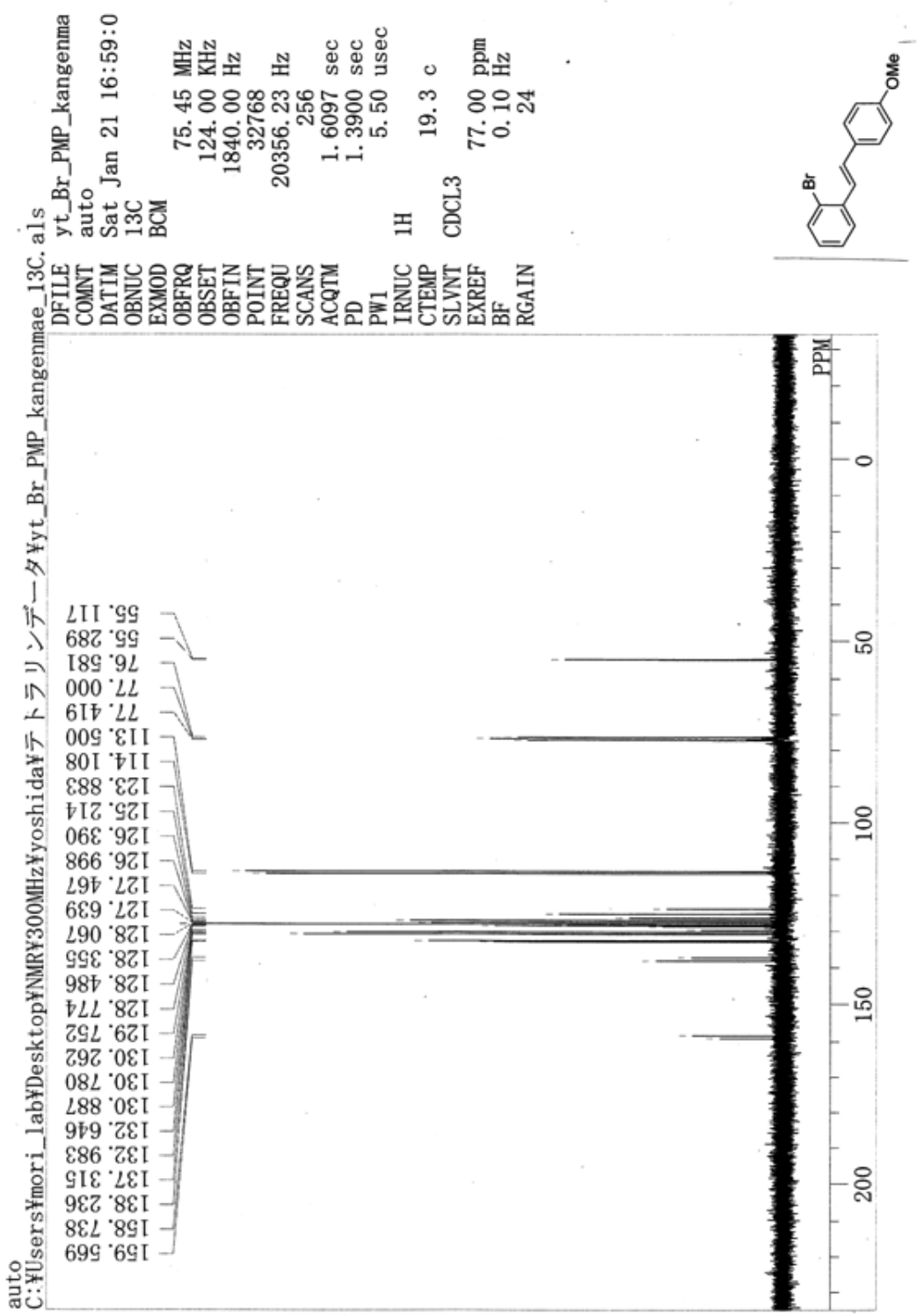
References

1) J. Yu, N. Li, D.-F. Chen, S.-W. Luo, *Tetrahedron Lett*. **2014**, *55*, 2859.

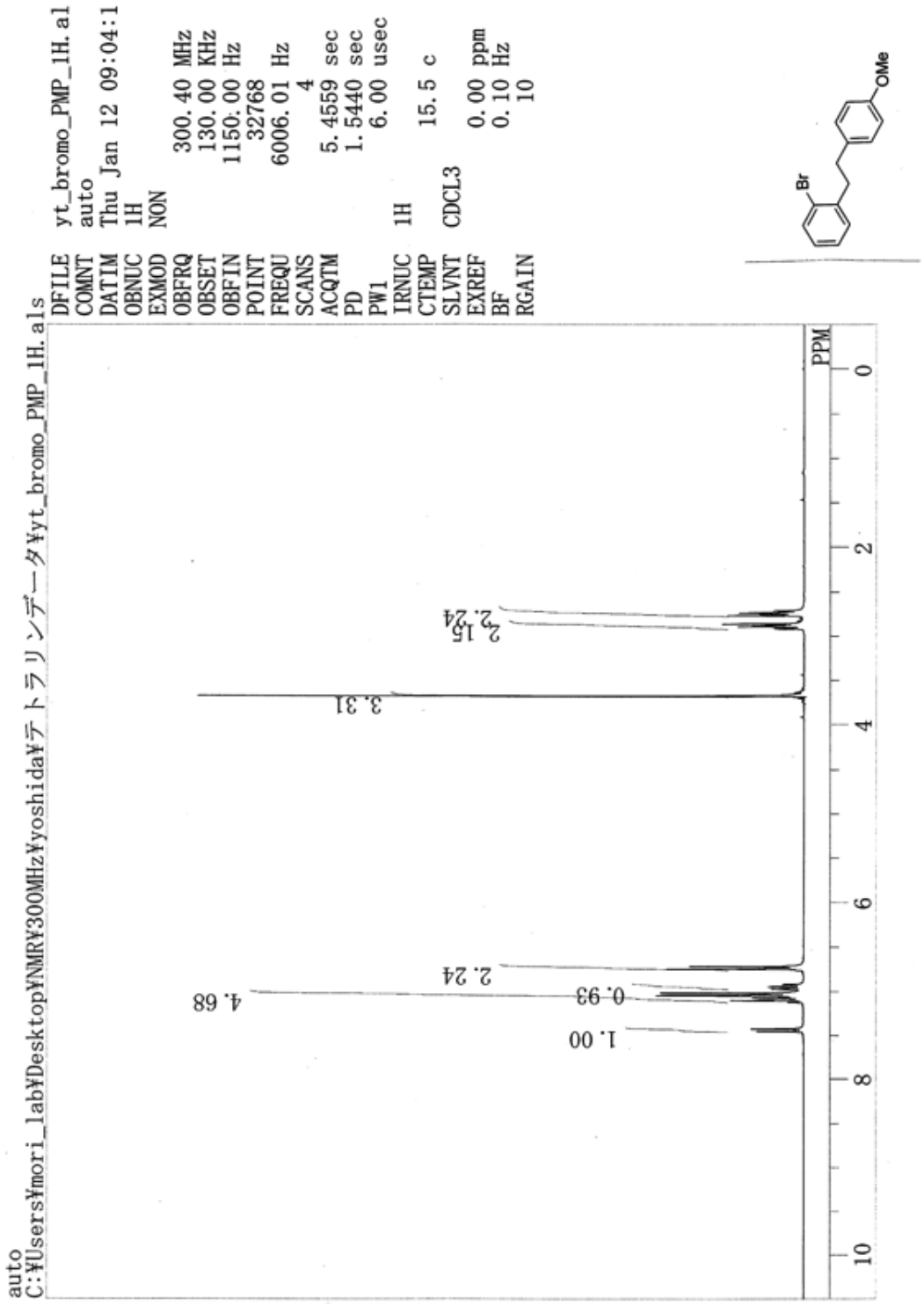
[1]H NMR spectrum of **s2**.



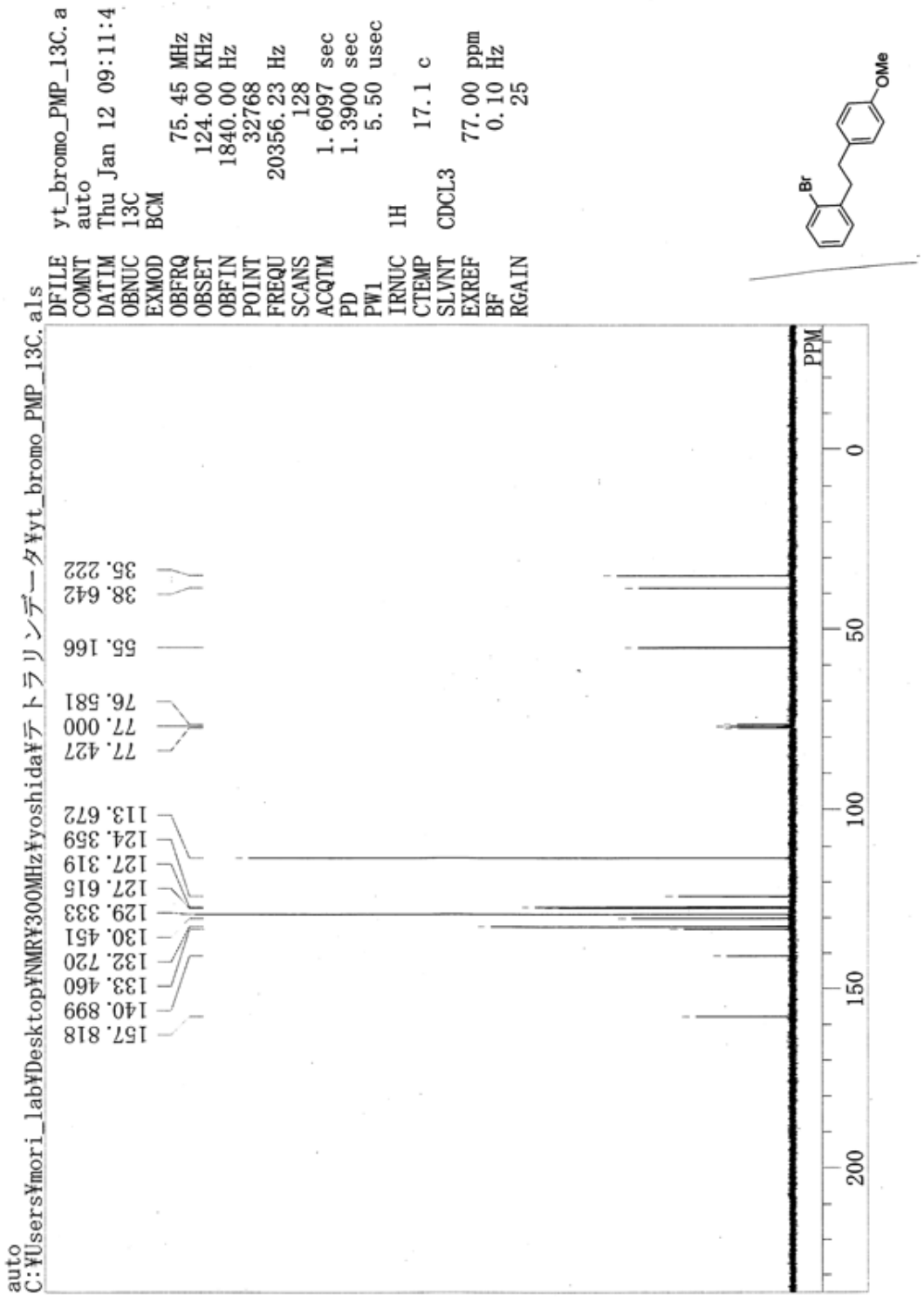
^{13}C NMR spectrum of **s2**.



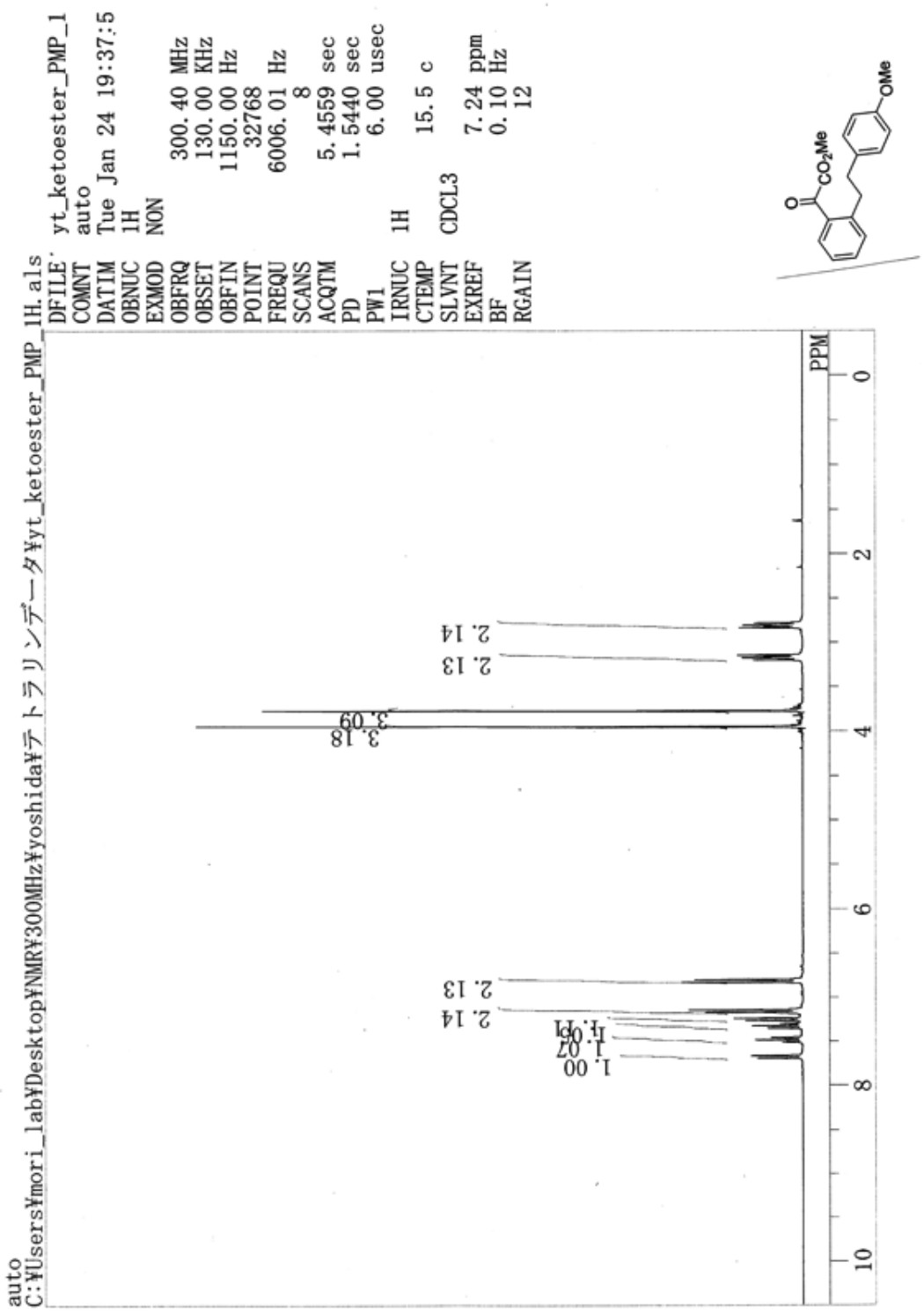
^{1}H NMR spectrum of **s3**.



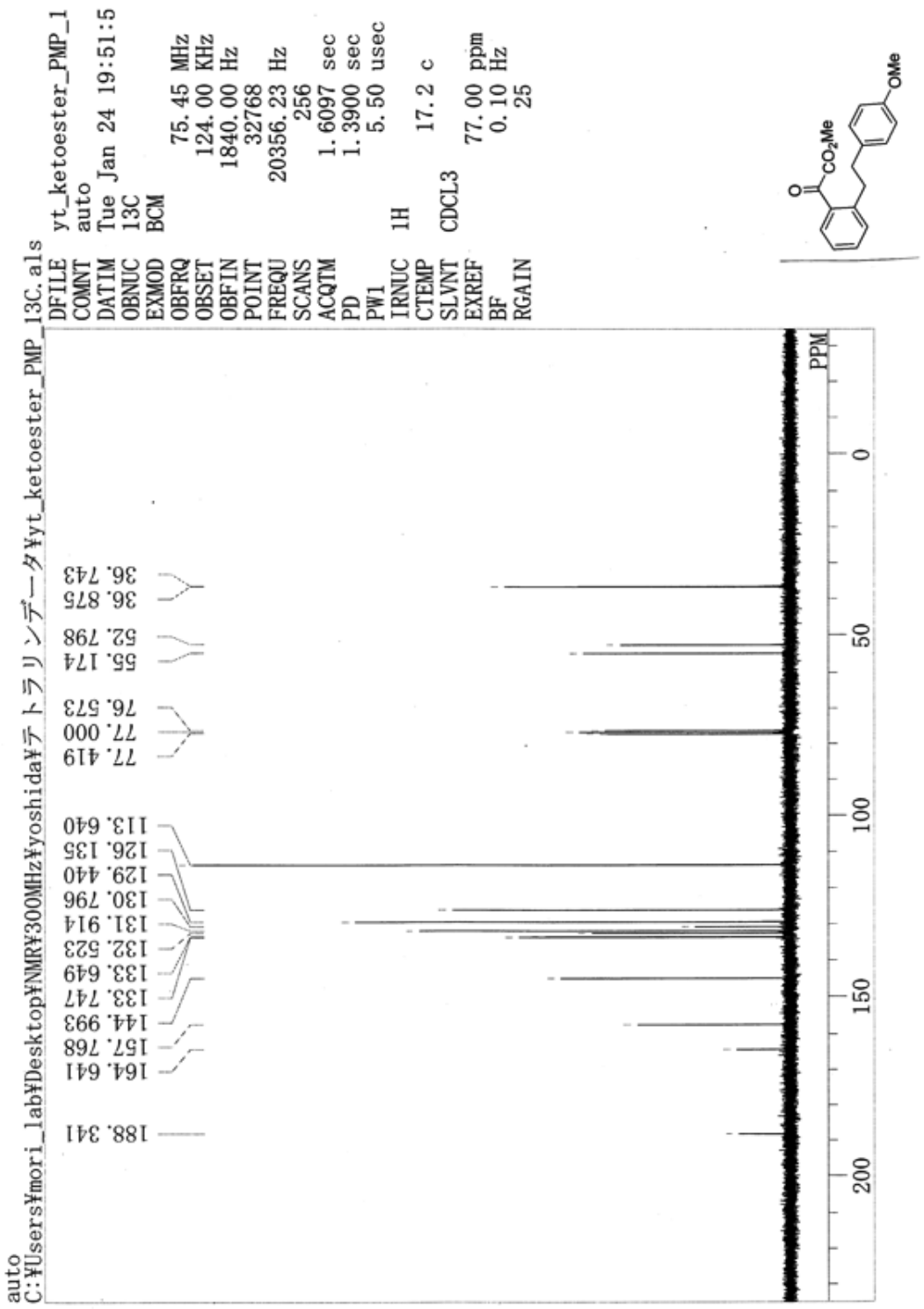
^{13}C NMR spectrum of **s3**.



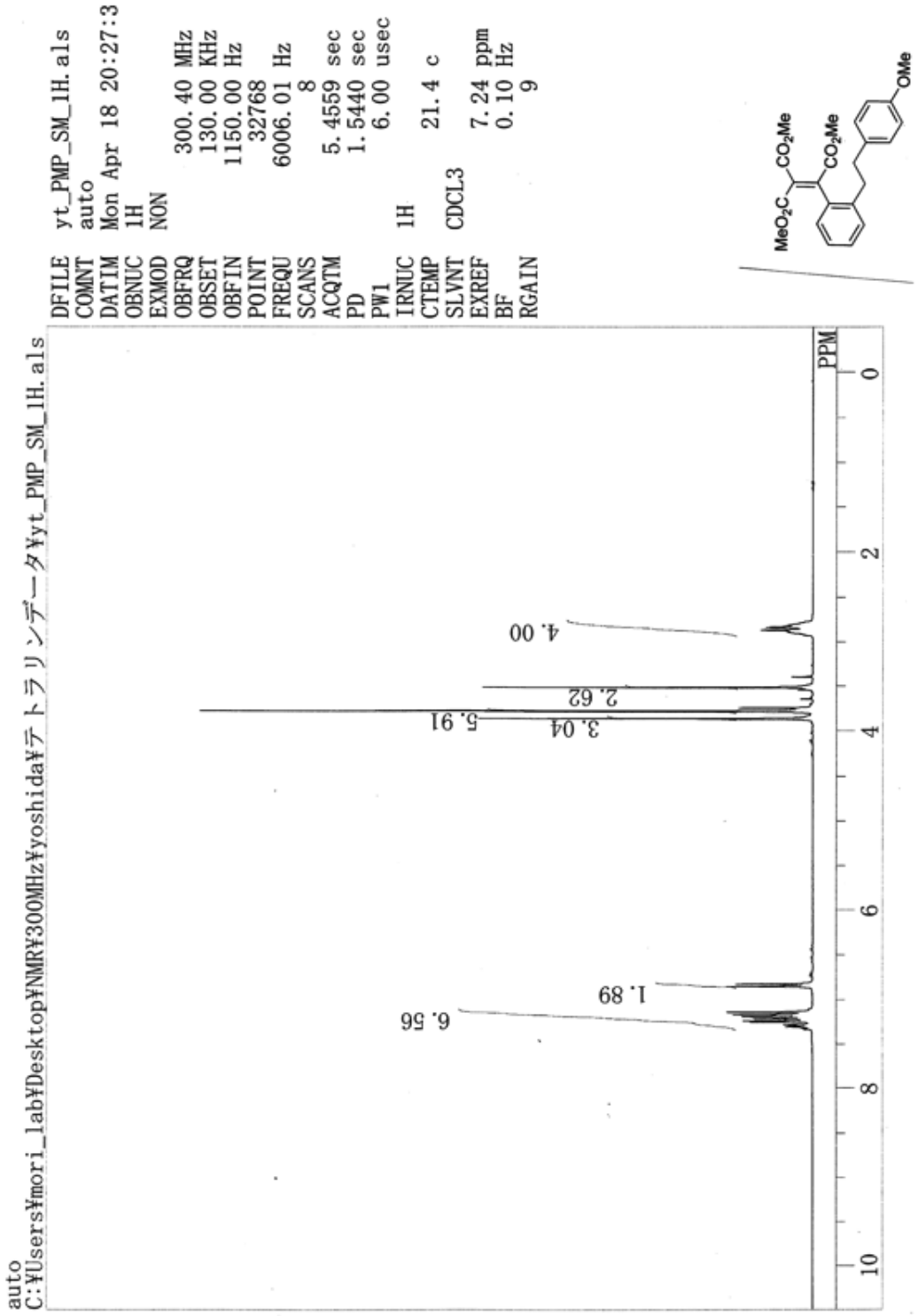
^{1}H NMR spectrum of **s4**.



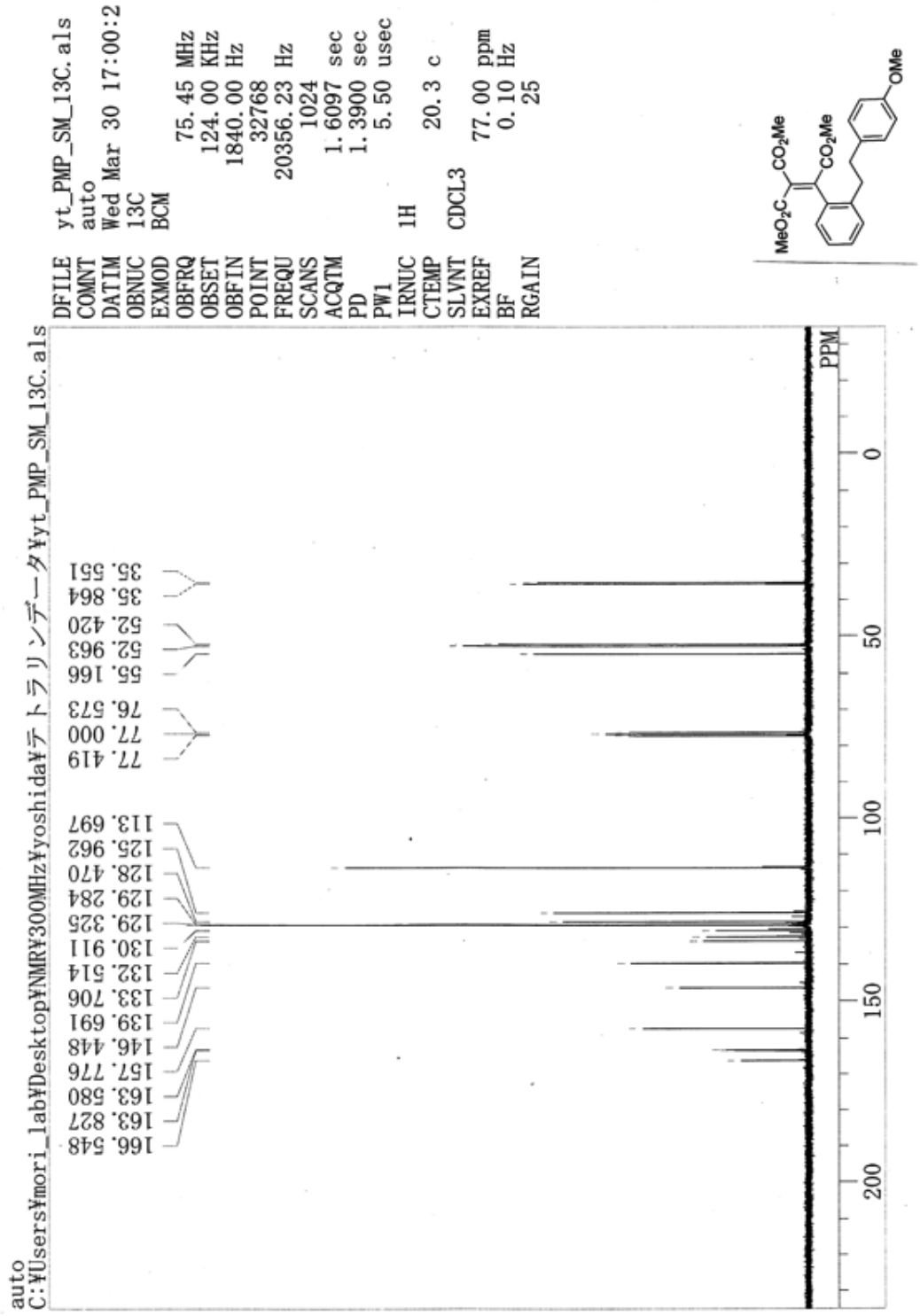
^{13}C NMR spectrum of **s4**.



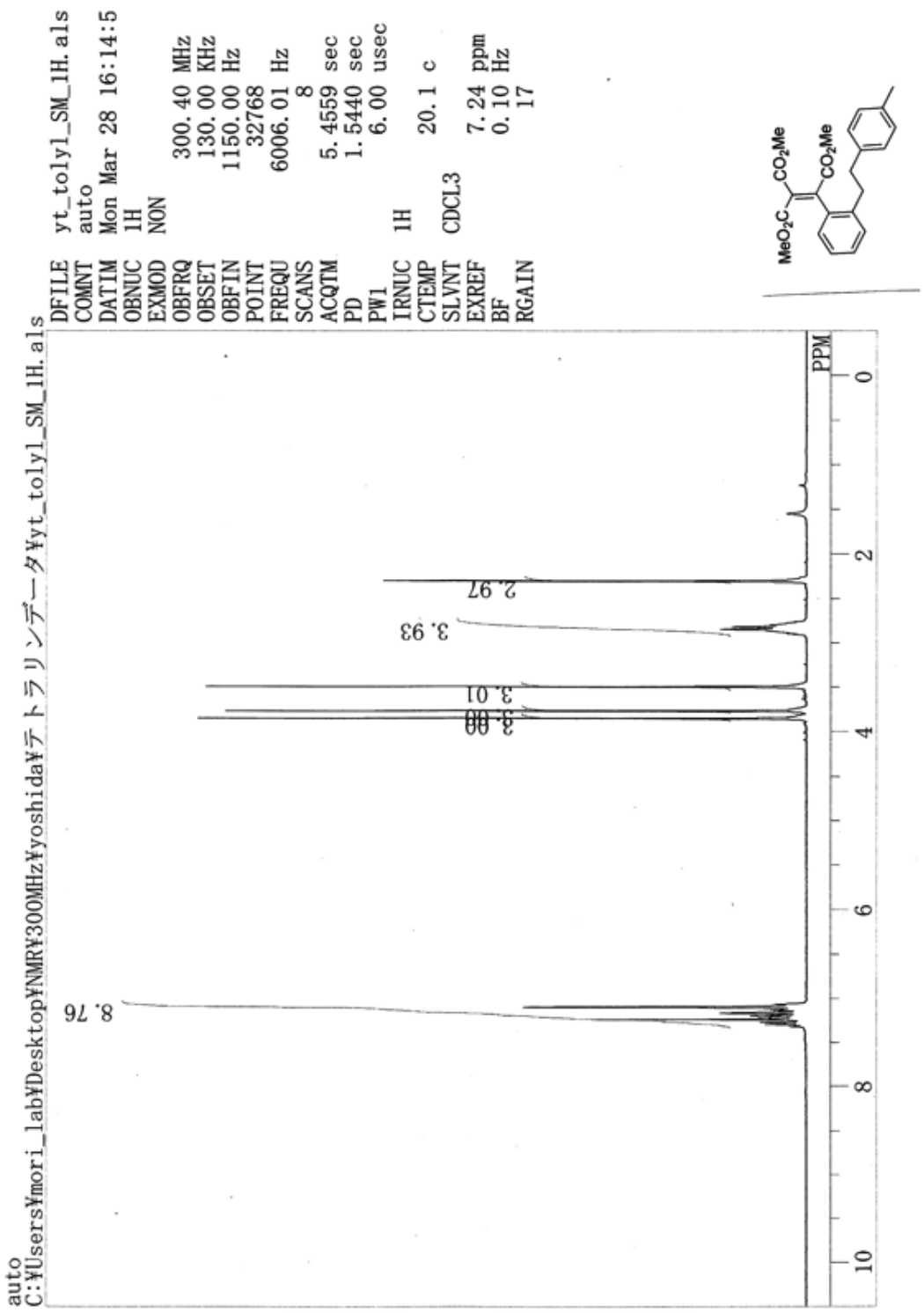
^{1}H NMR spectrum of **3a**.



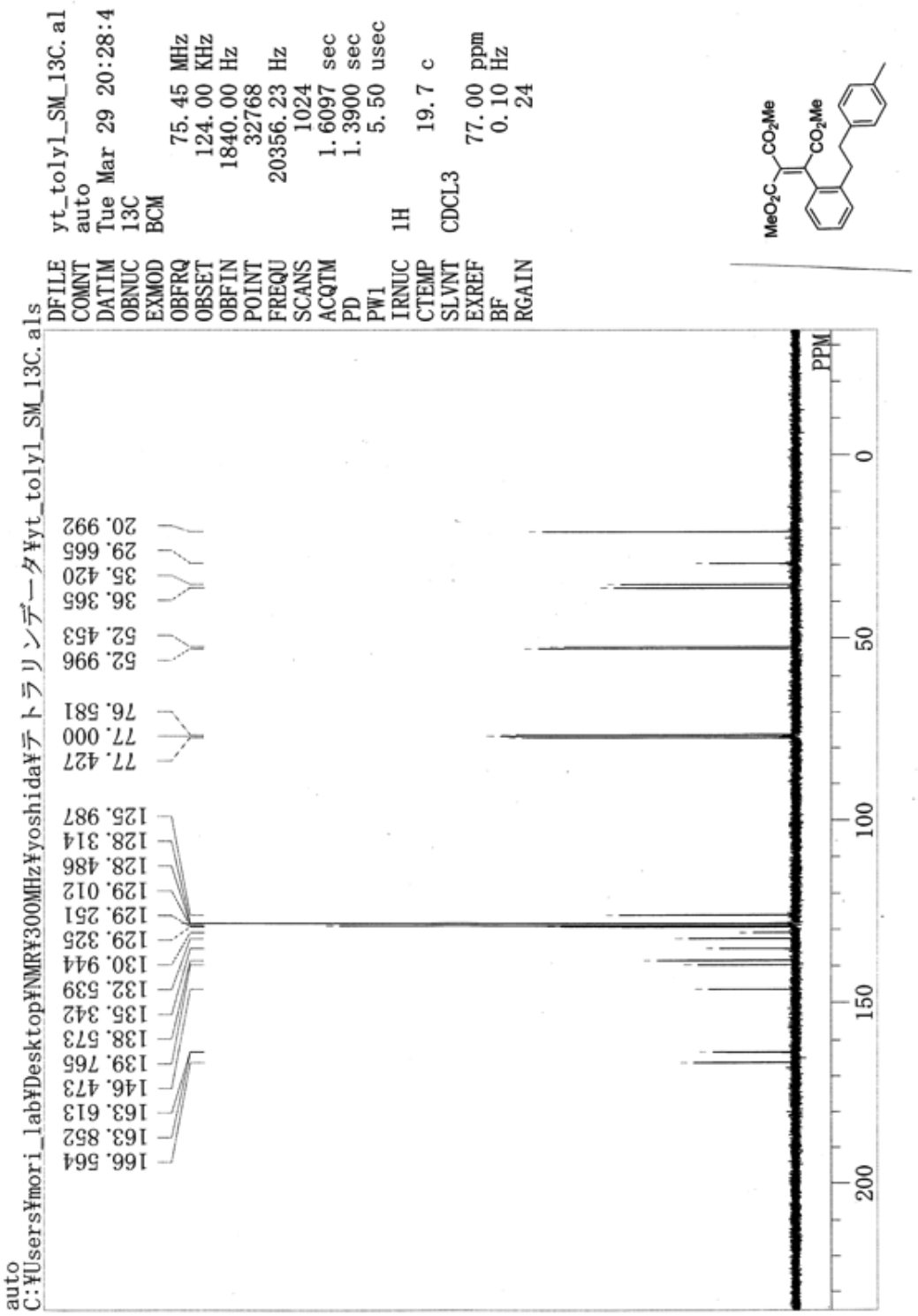
^{13}C NMR spectrum of **3a**.



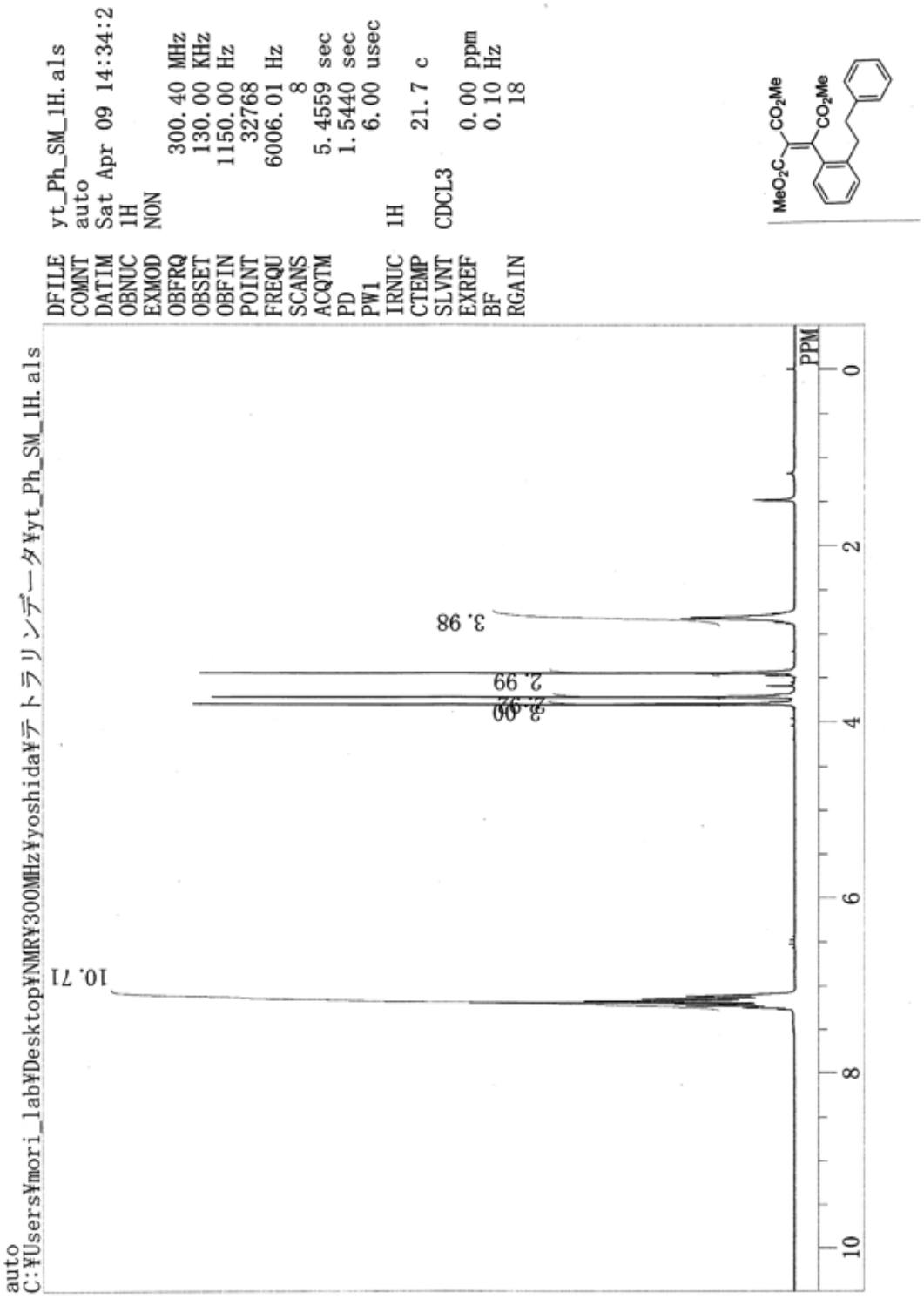
^{1}H NMR spectrum of **3b**.



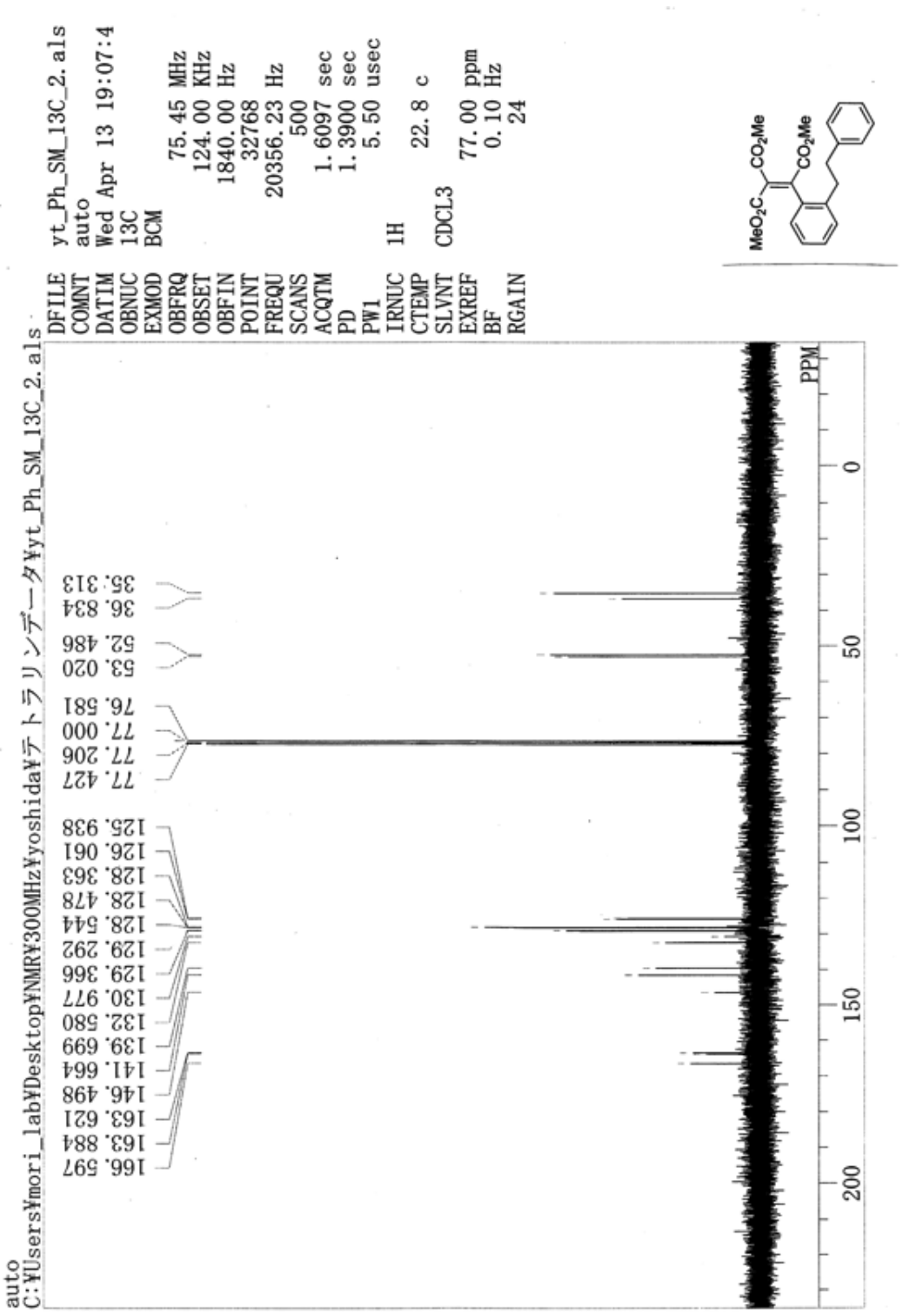
^{13}C NMR spectrum of **3b**.



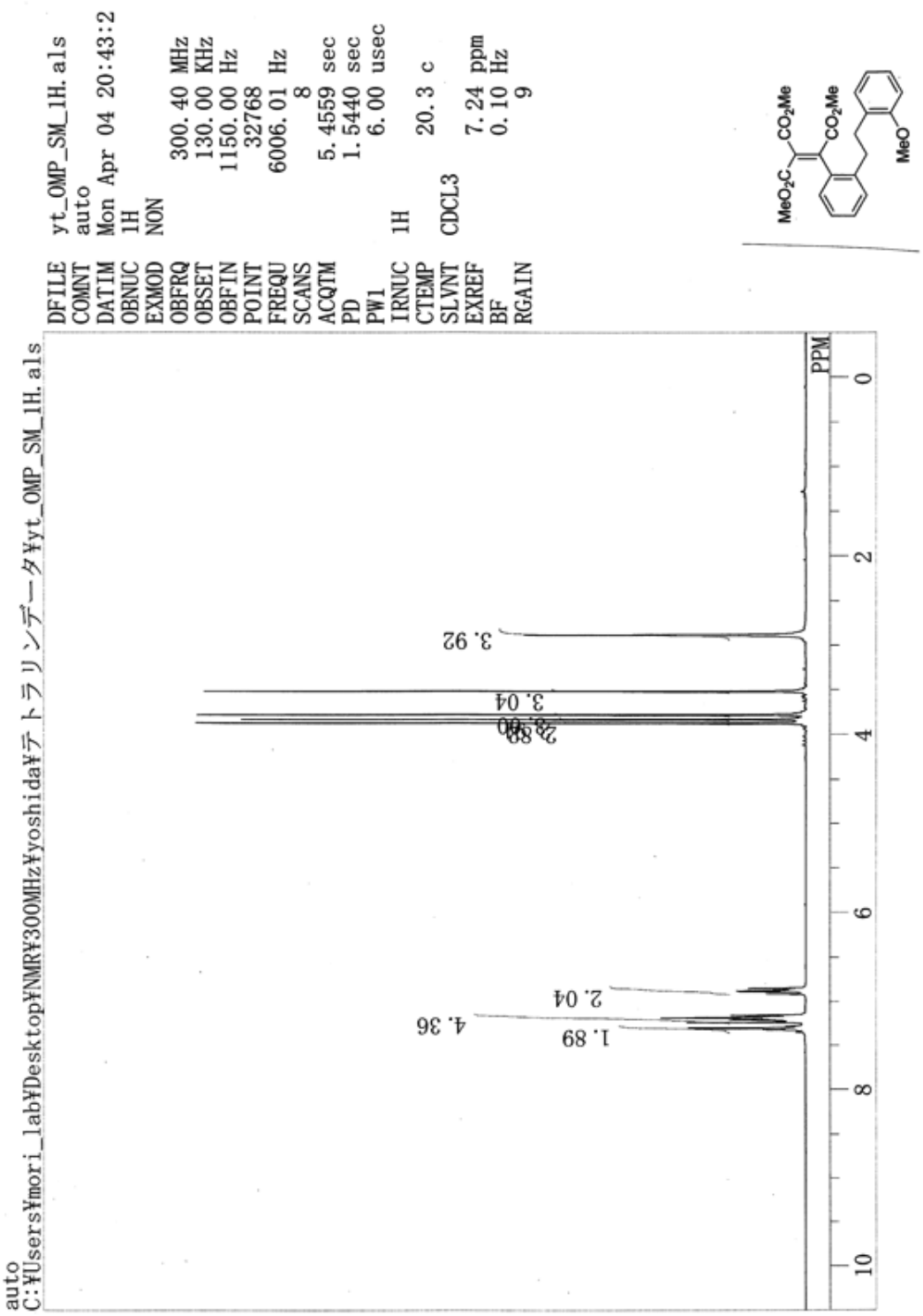
^{1}H NMR spectrum of **3c**.



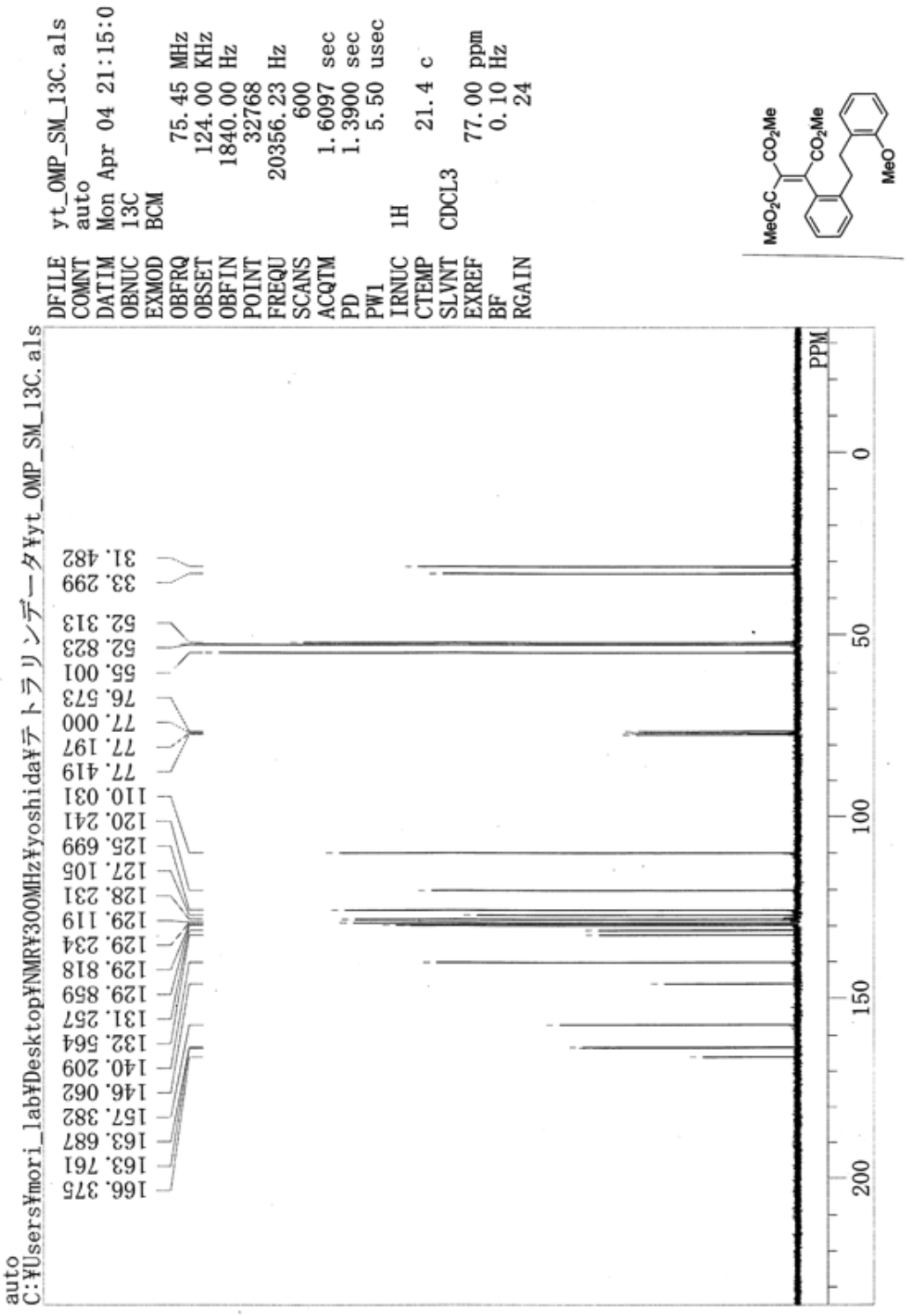
^{13}C NMR spectrum of **3c**.



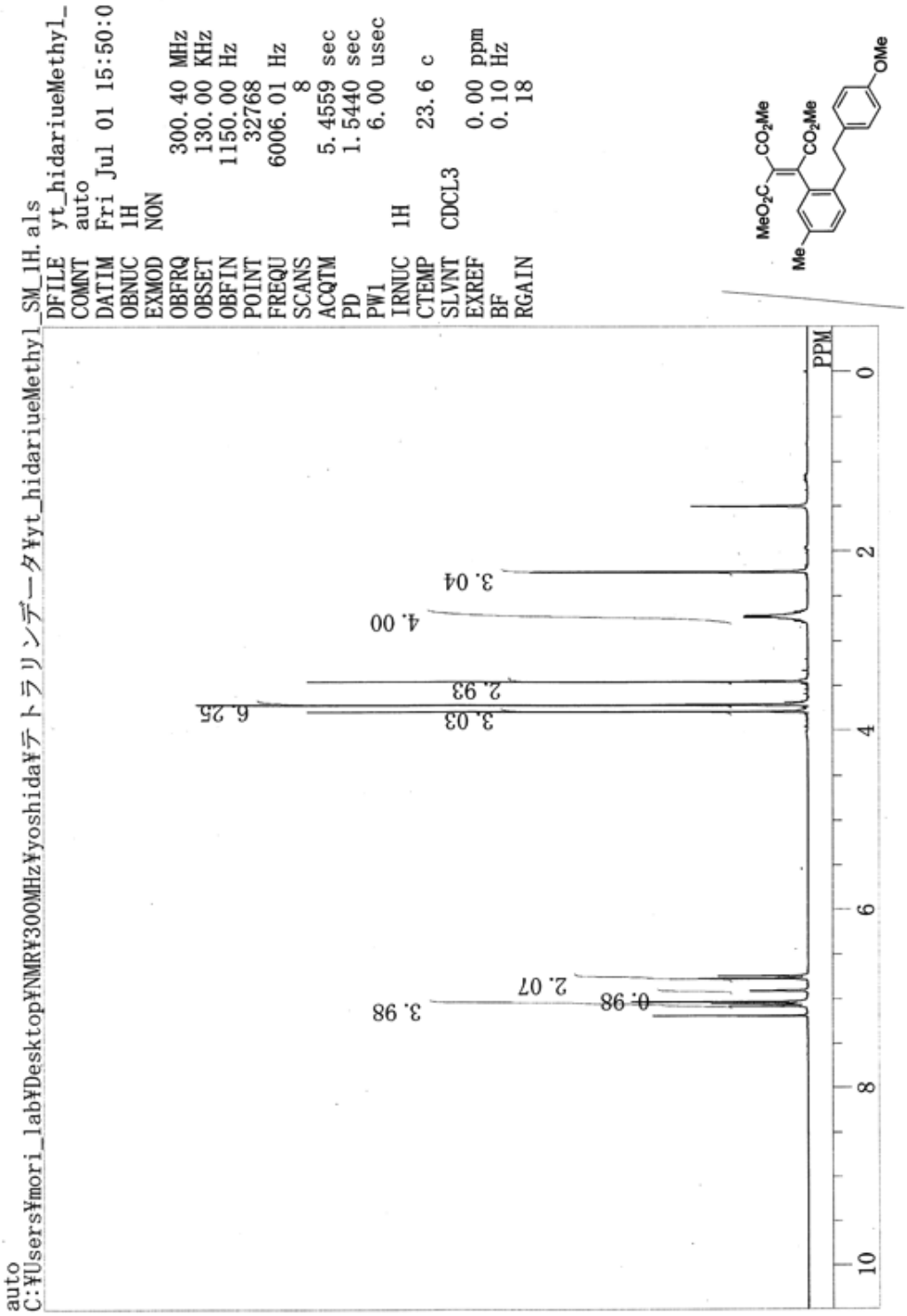
^{1}H NMR spectrum of **3d**.



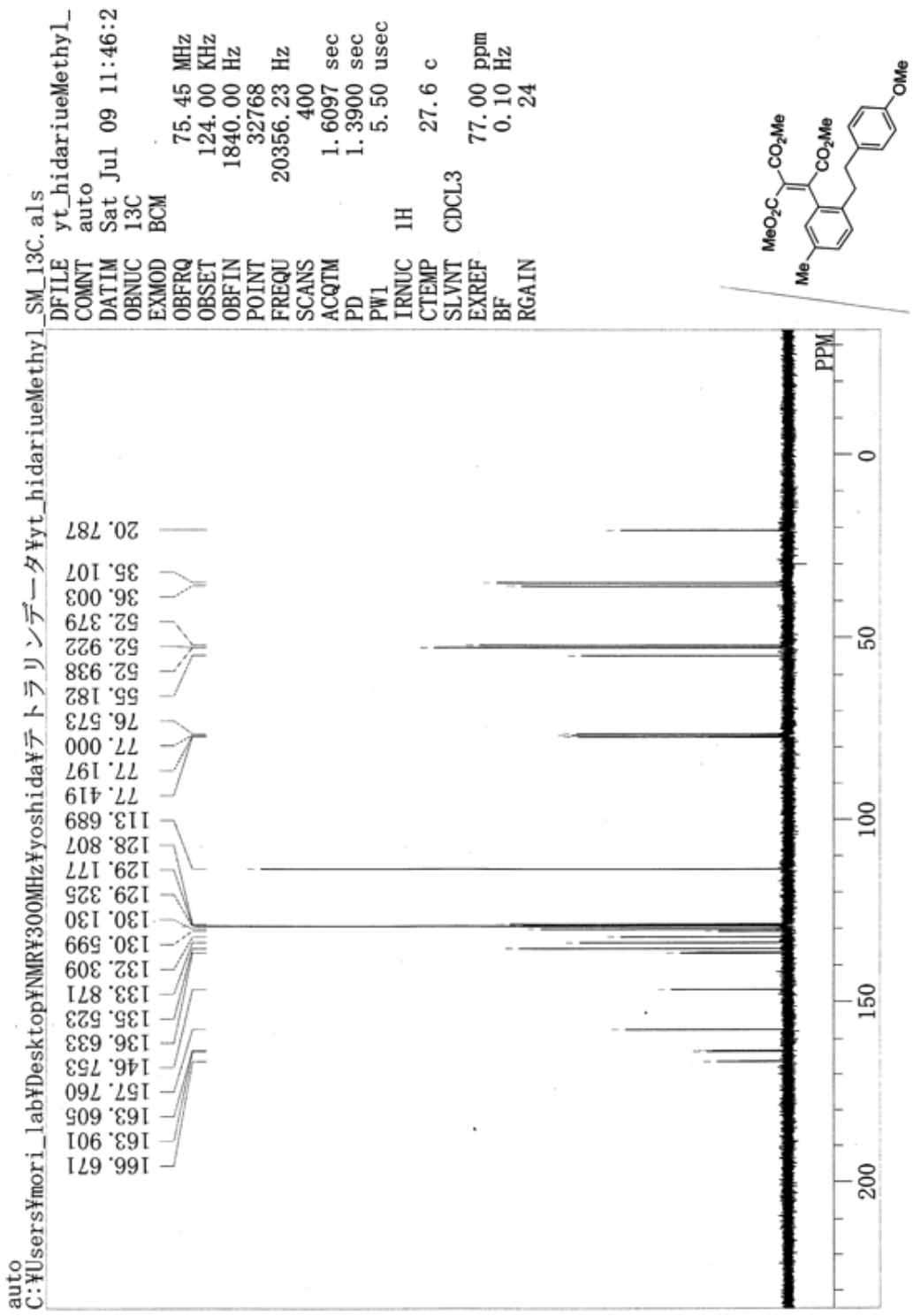
^{13}C NMR spectrum of **3d**.



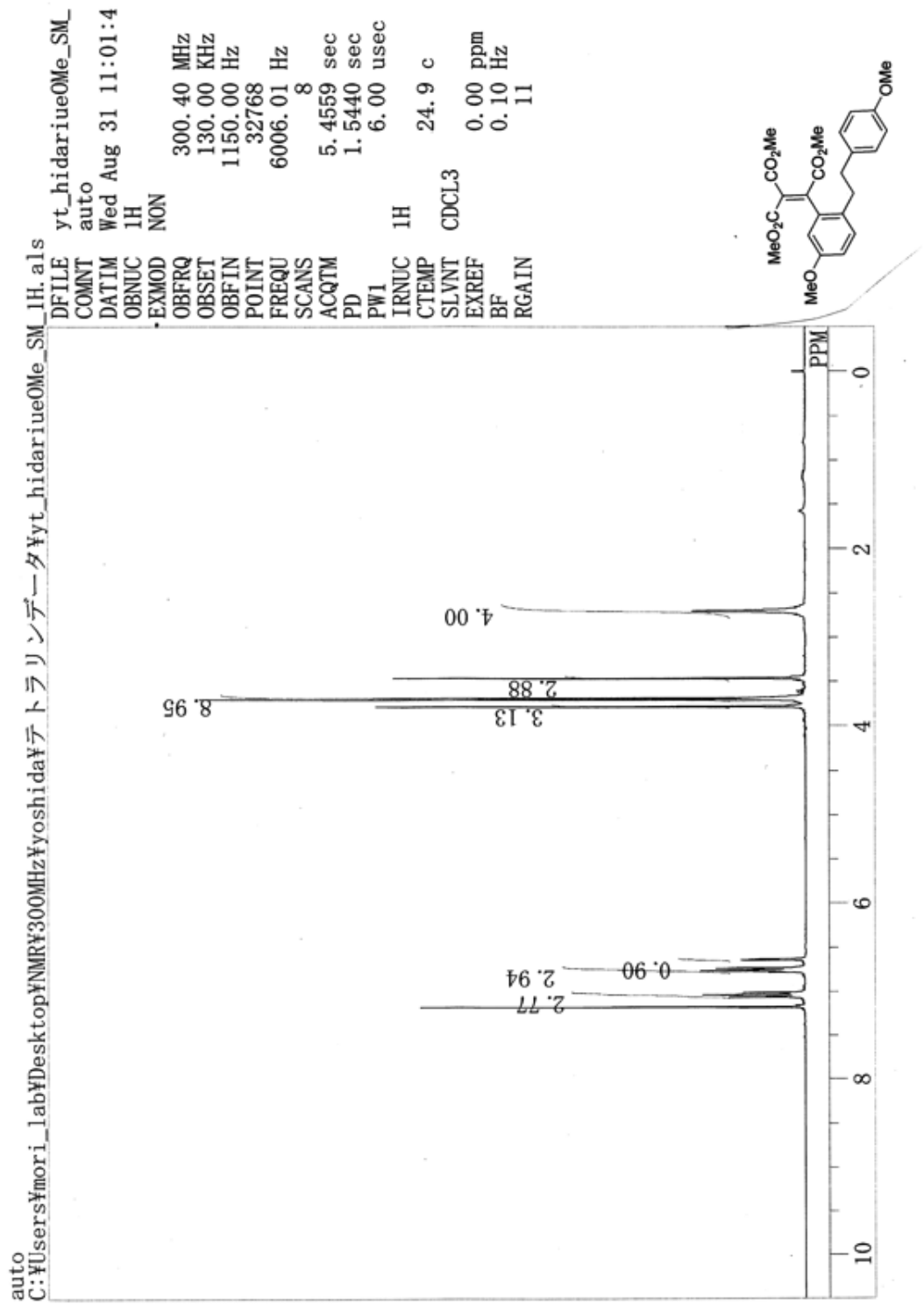
^{1}H NMR spectrum of **3e**.



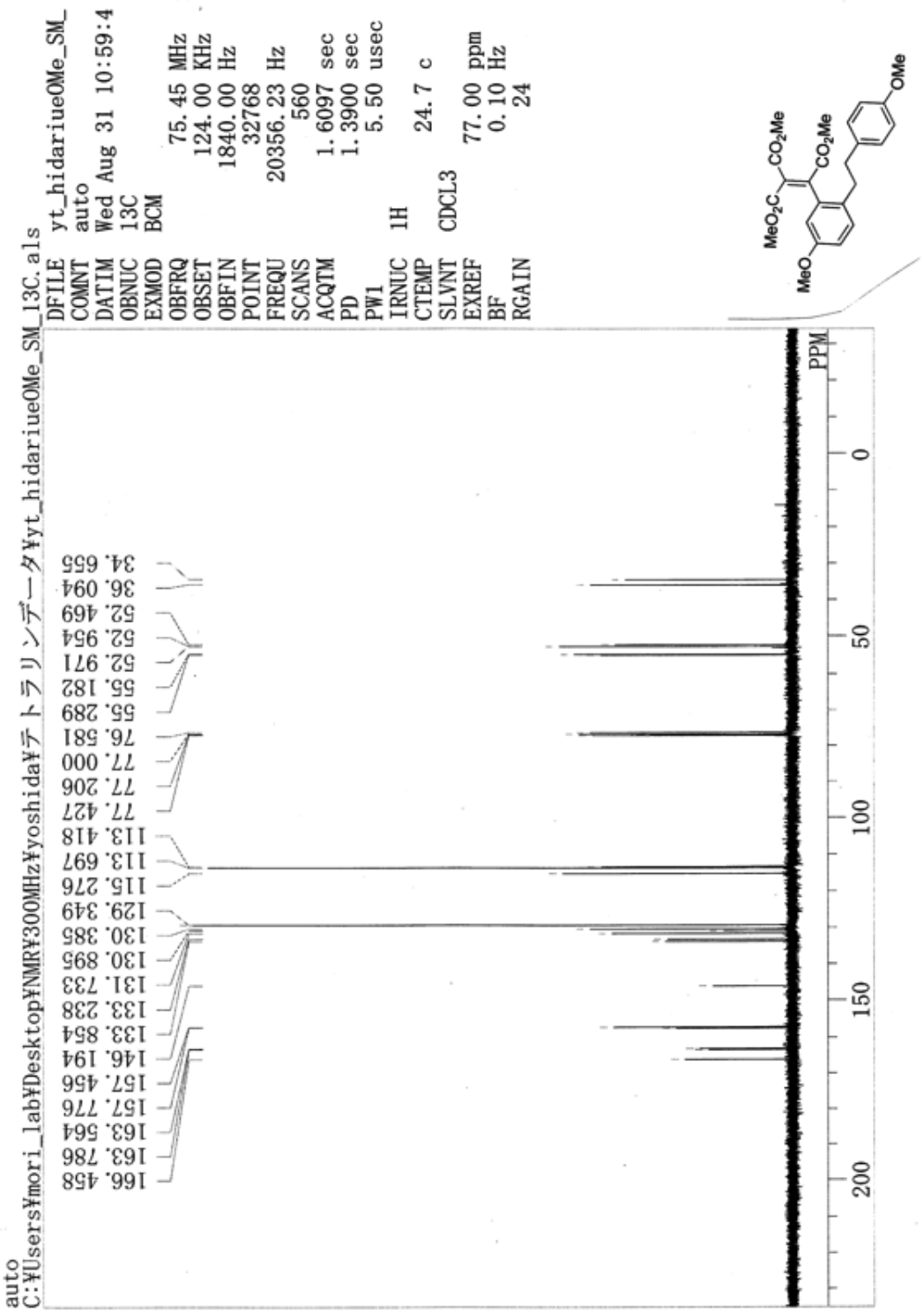
^{13}C NMR spectrum of **3e**.



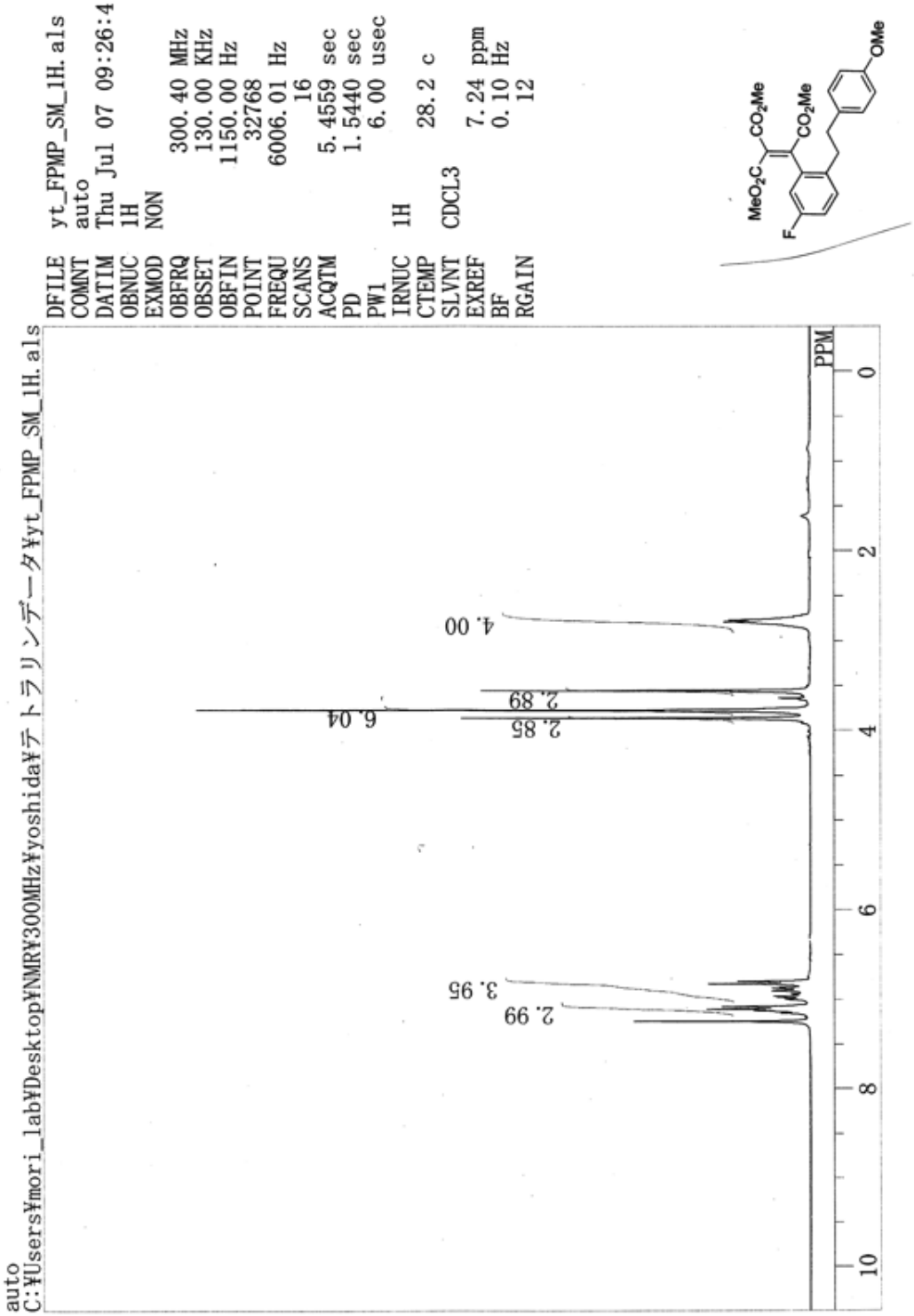
^{1}H NMR spectrum of **3f**.



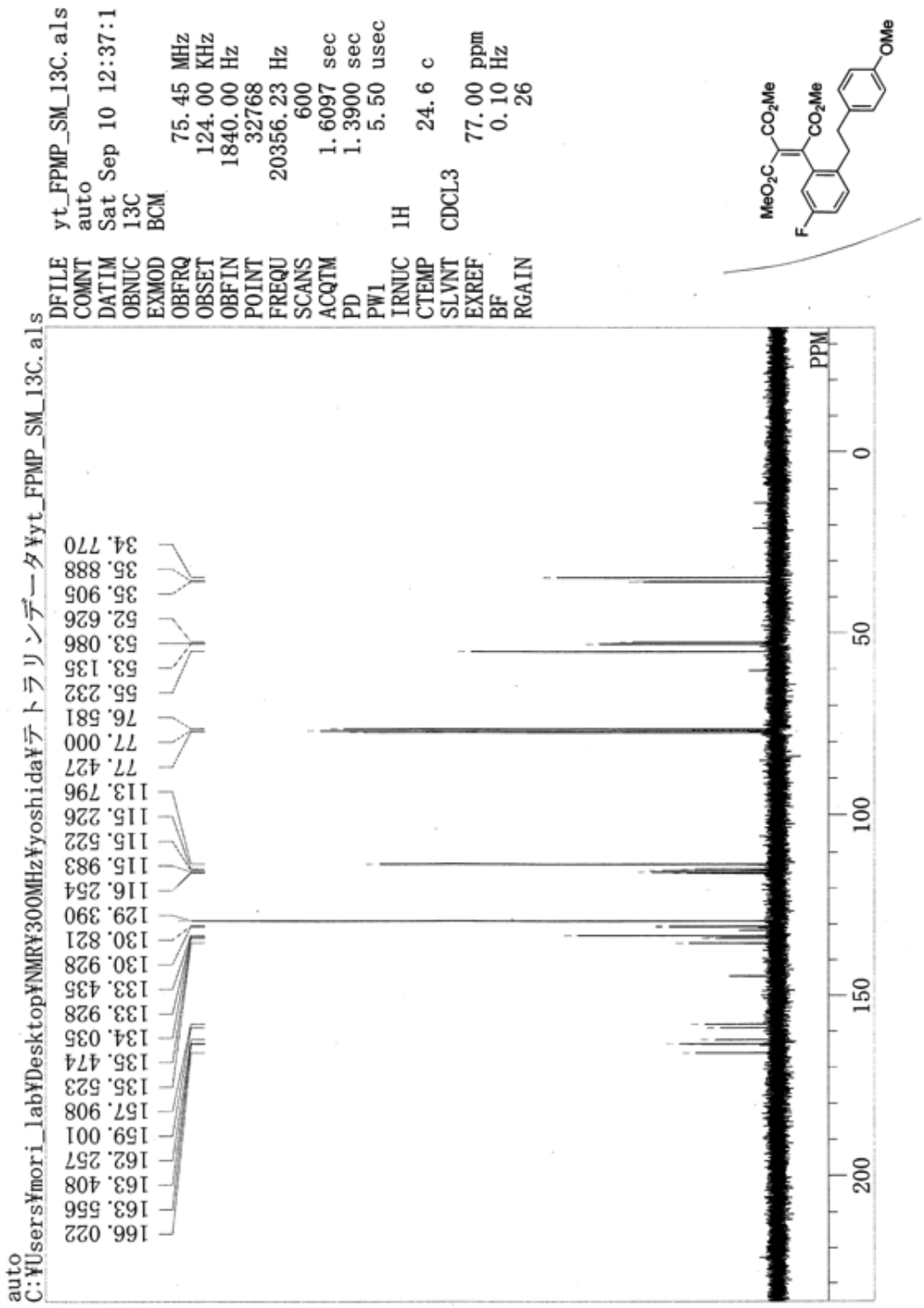
^{13}C NMR spectrum of **3f**.



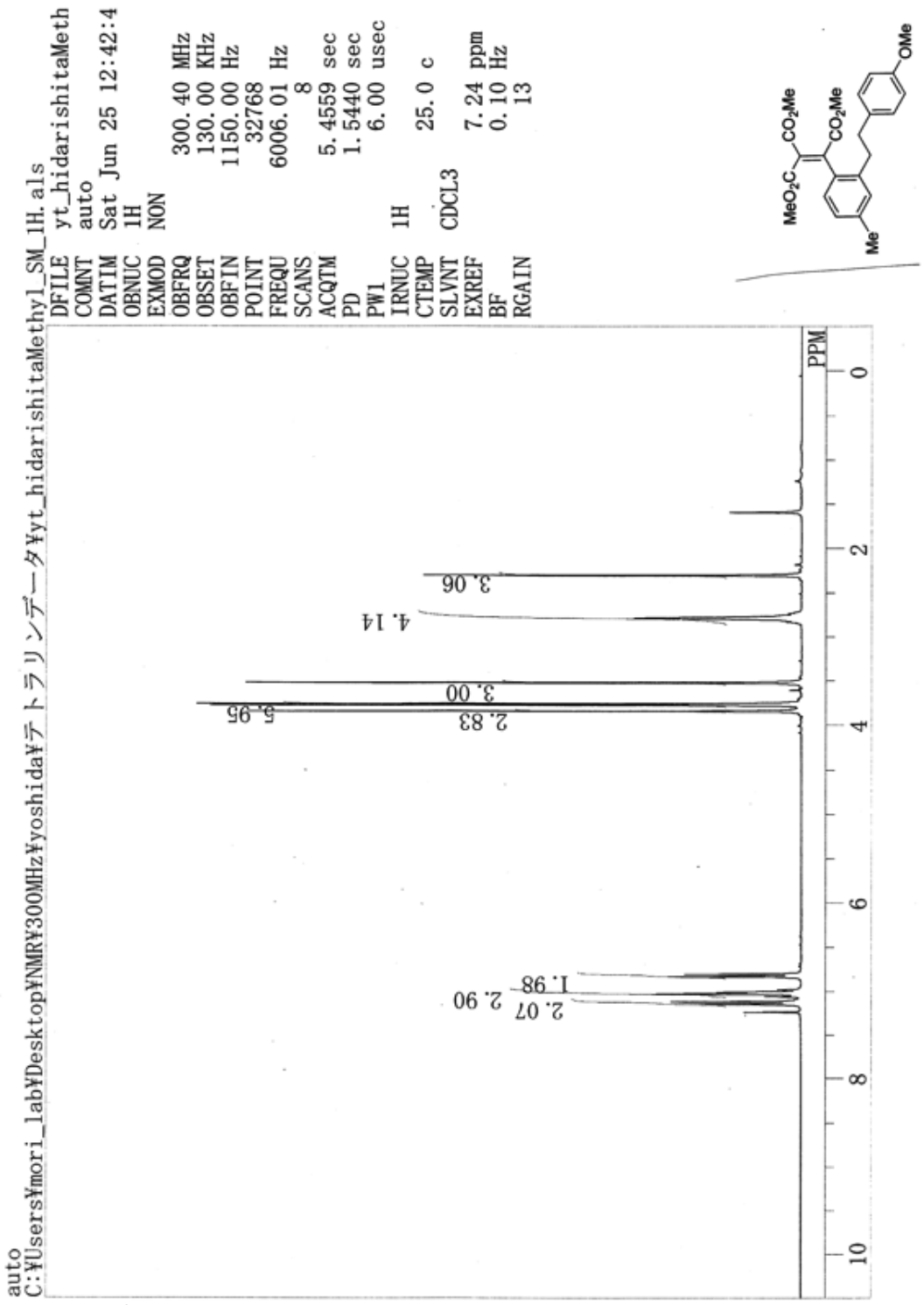
^{1}H NMR spectrum of **3g**.



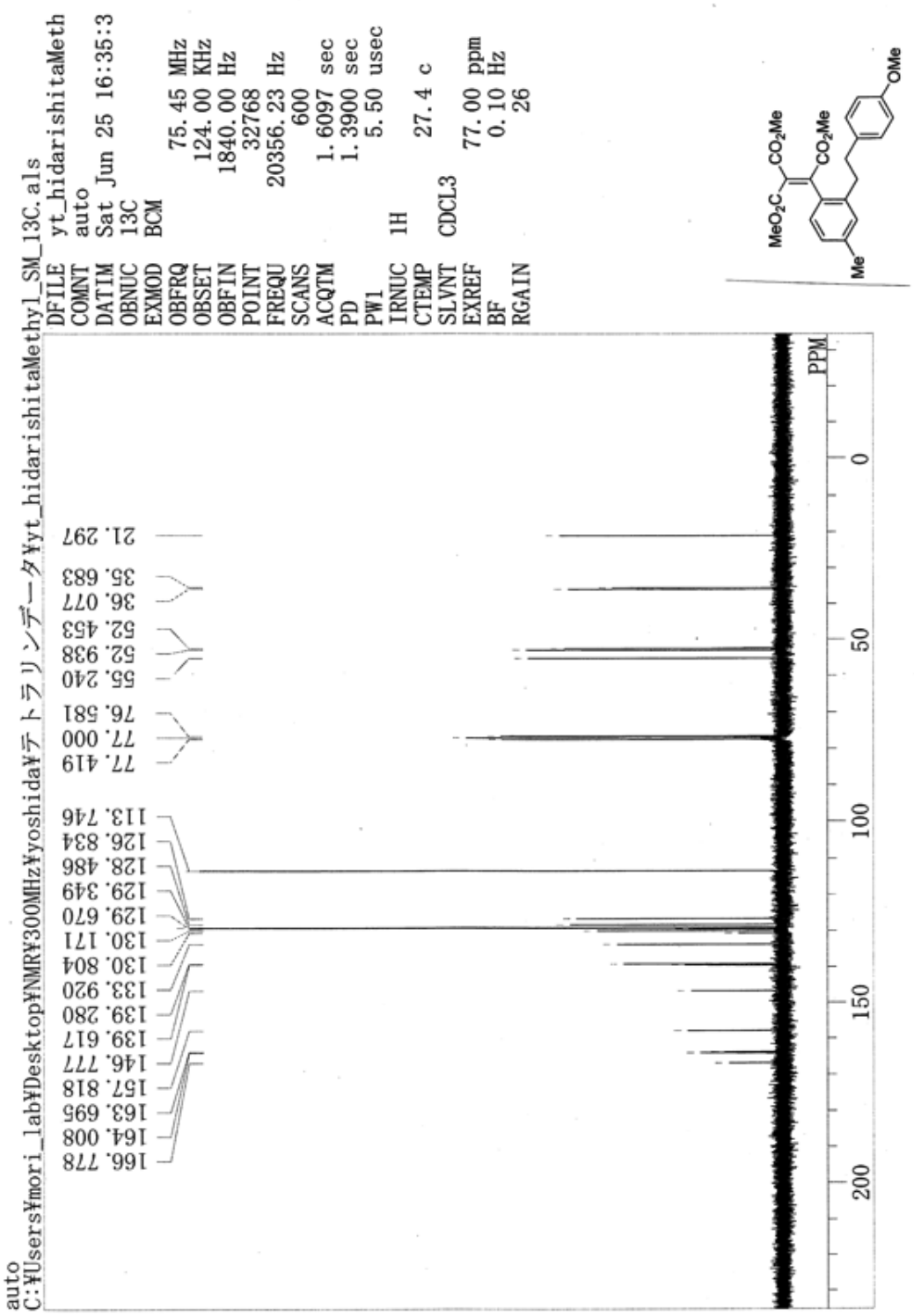
^{13}C NMR spectrum of **3g**.



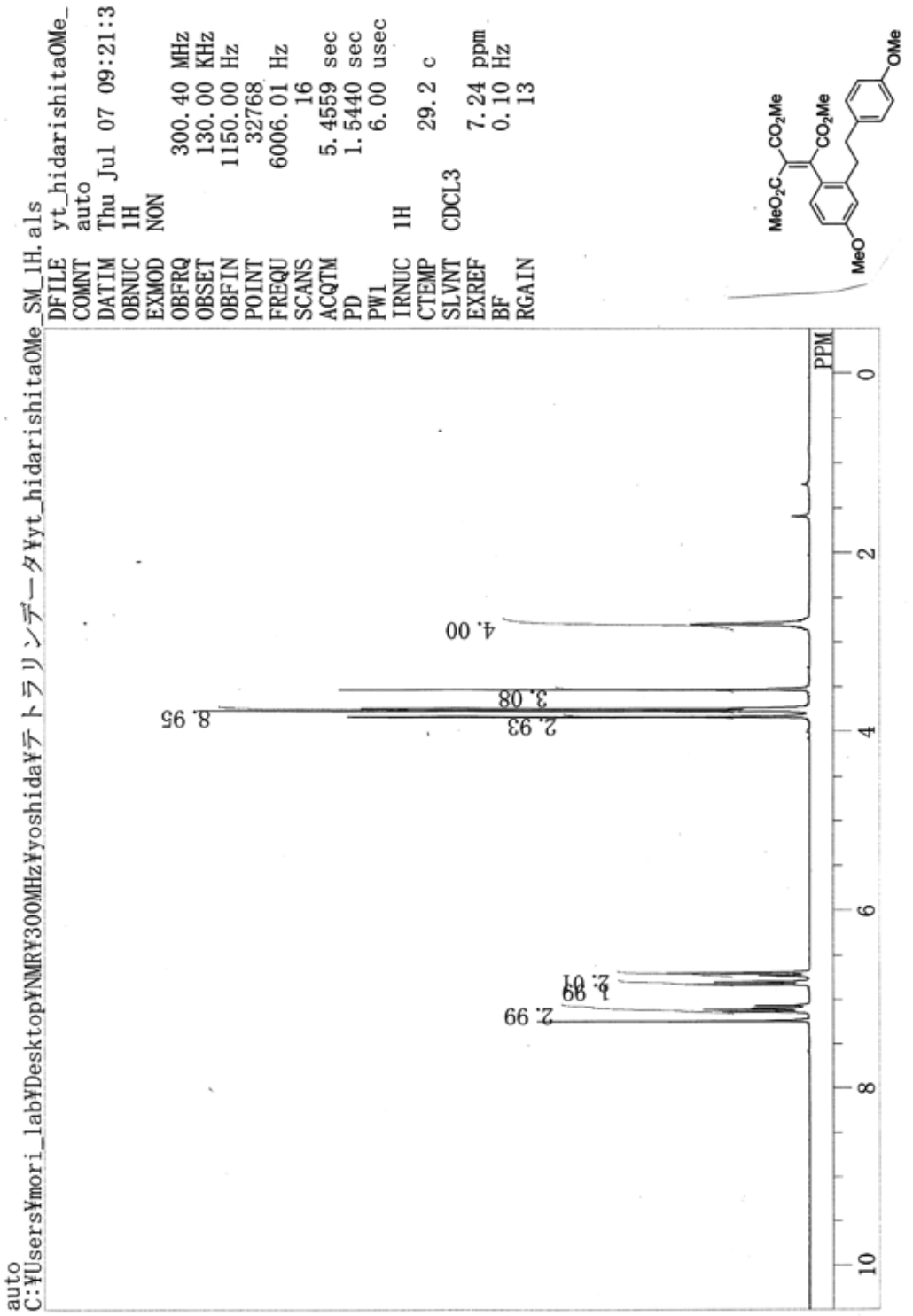
^{1}H NMR spectrum of **3h**.



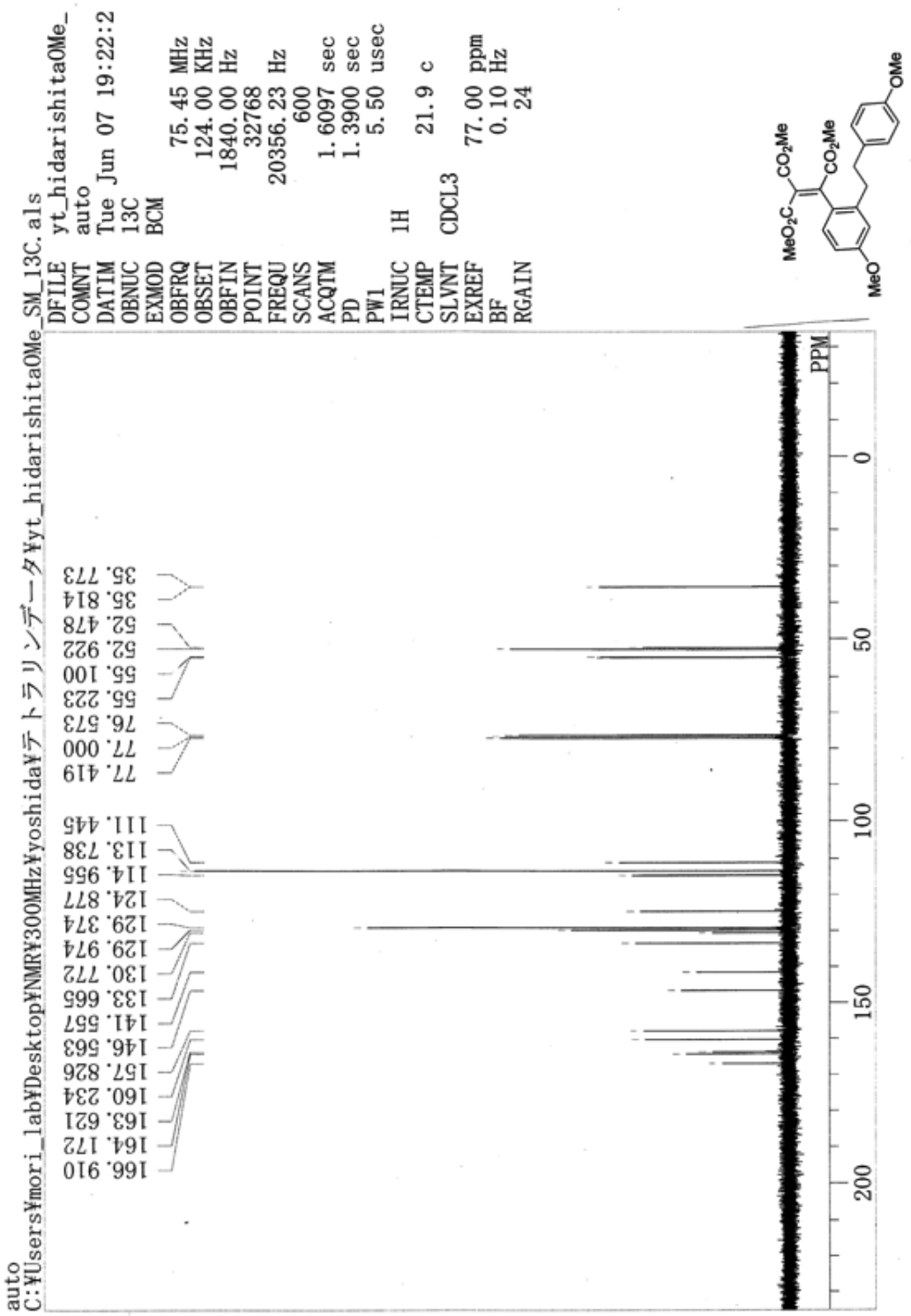
^{13}C NMR spectrum of **3h**.



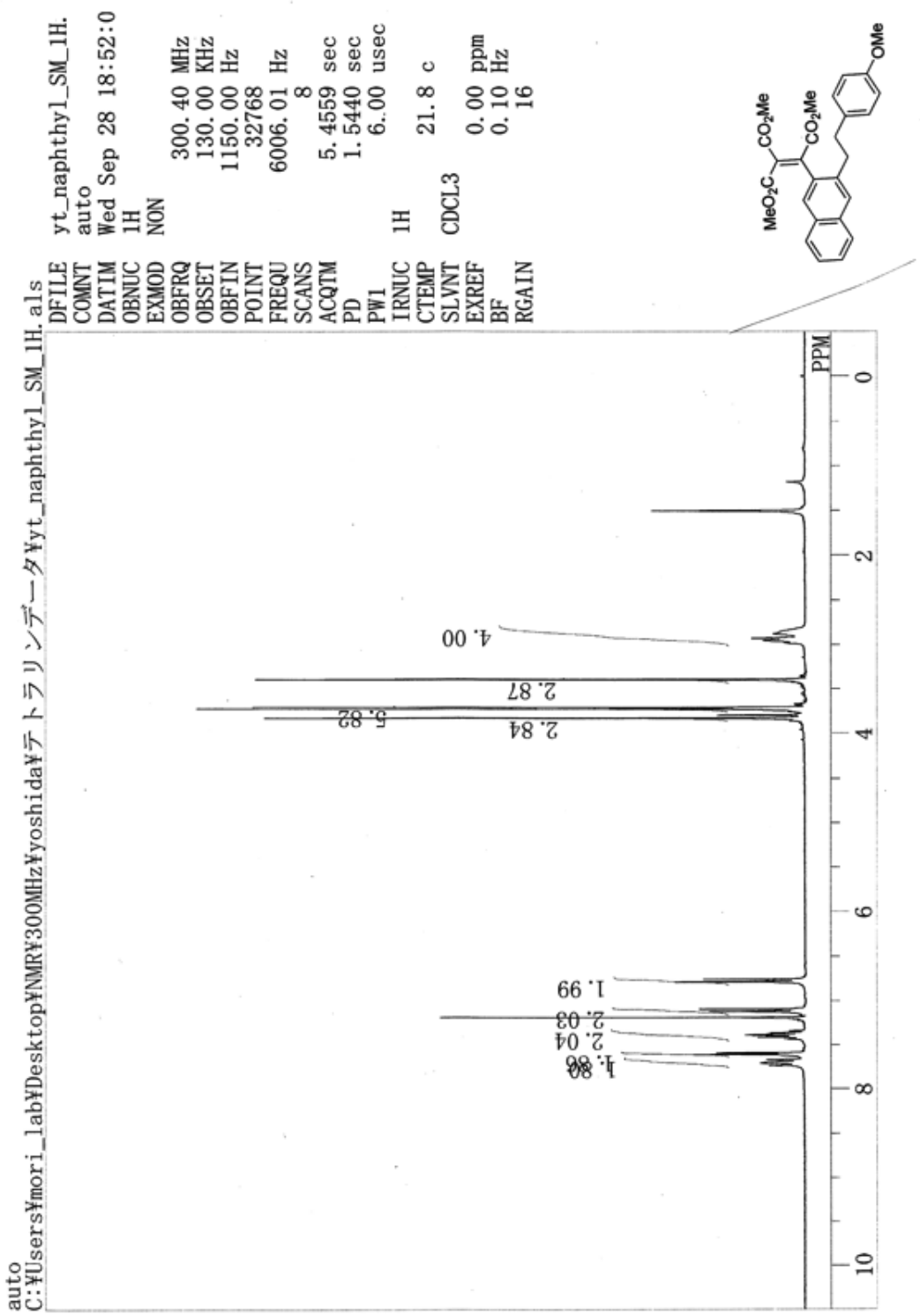
^{1}H NMR spectrum of **3i**.



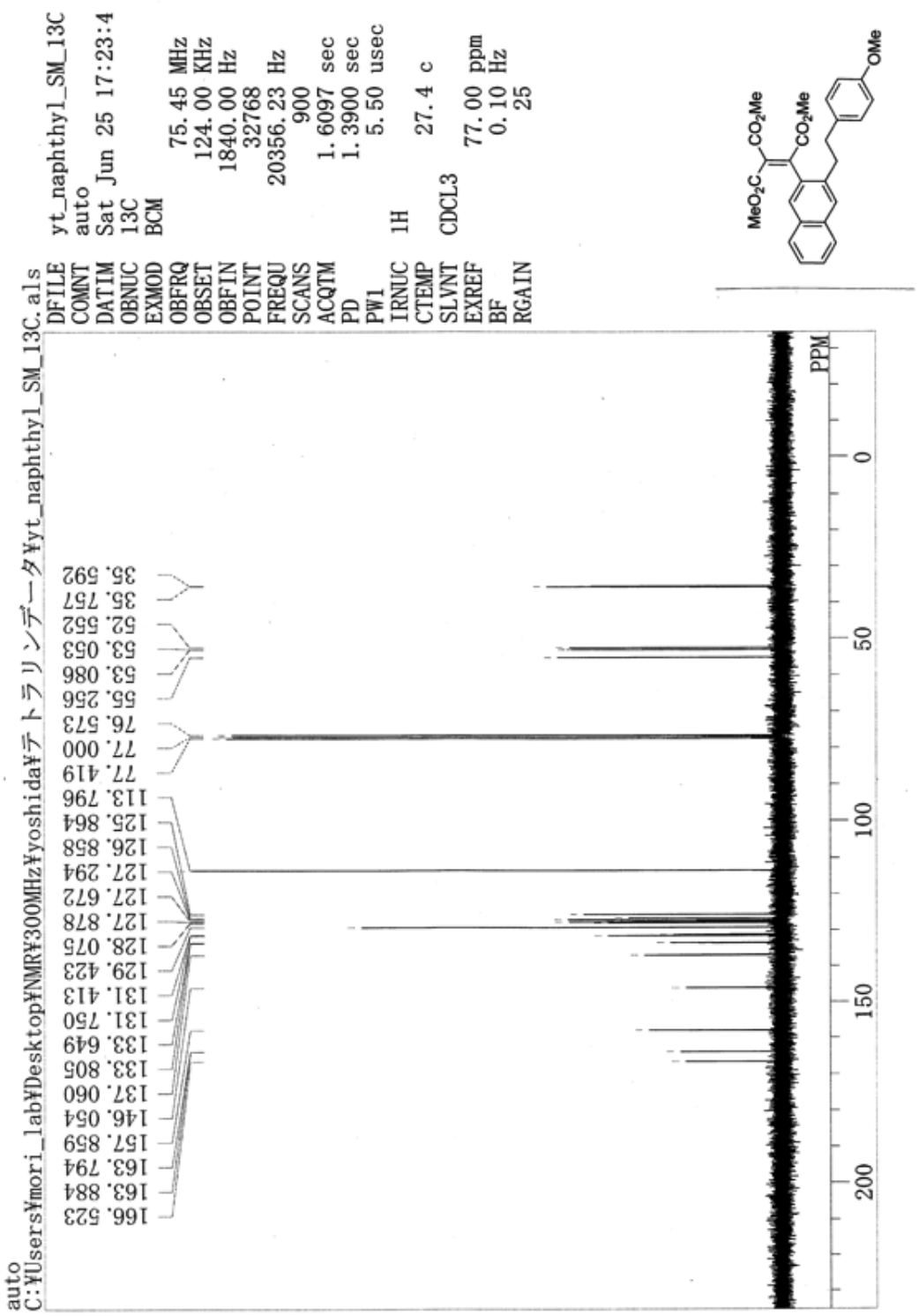
^{13}C NMR spectrum of **3i**.



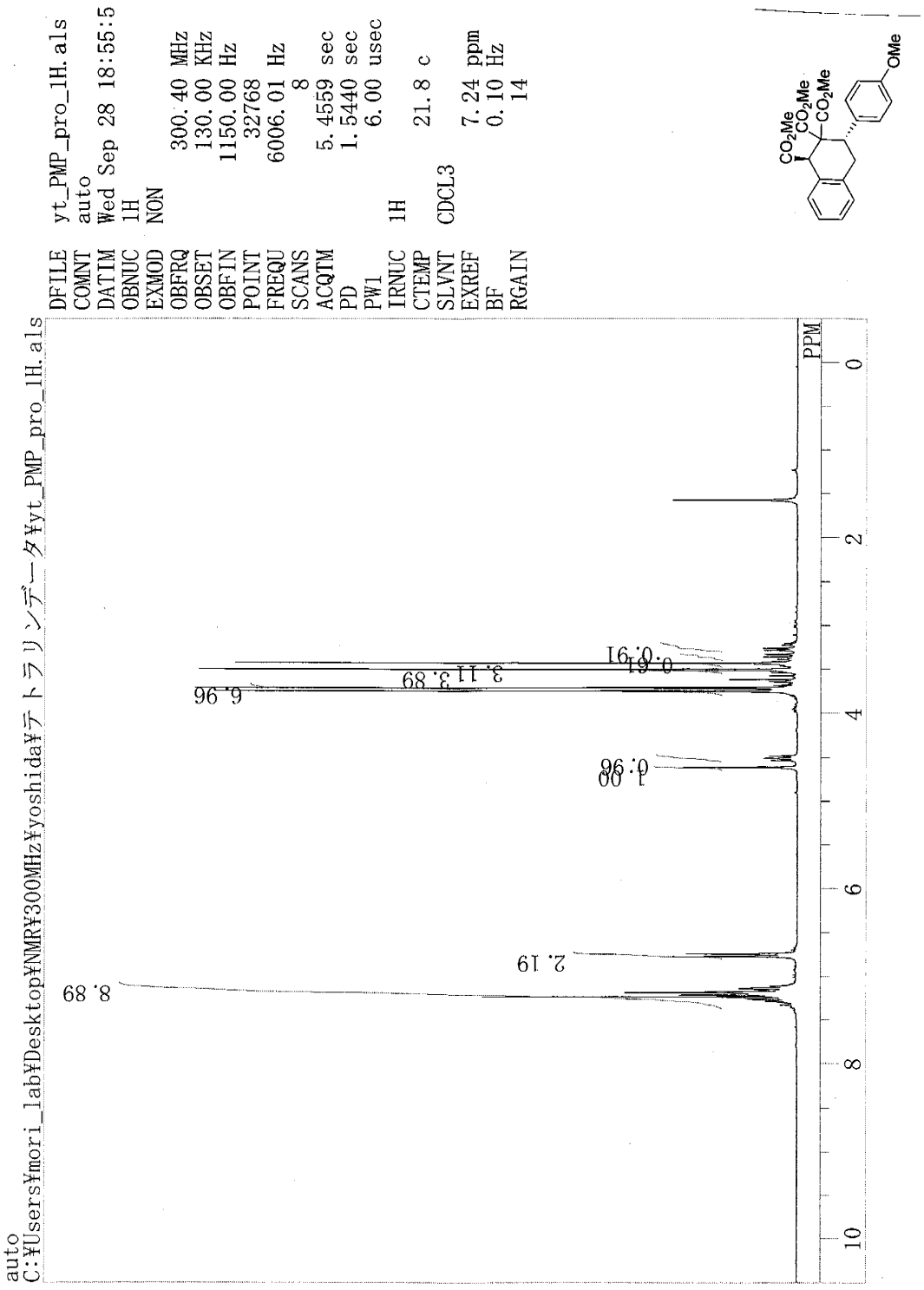
^{1}H NMR spectrum of **3j**.



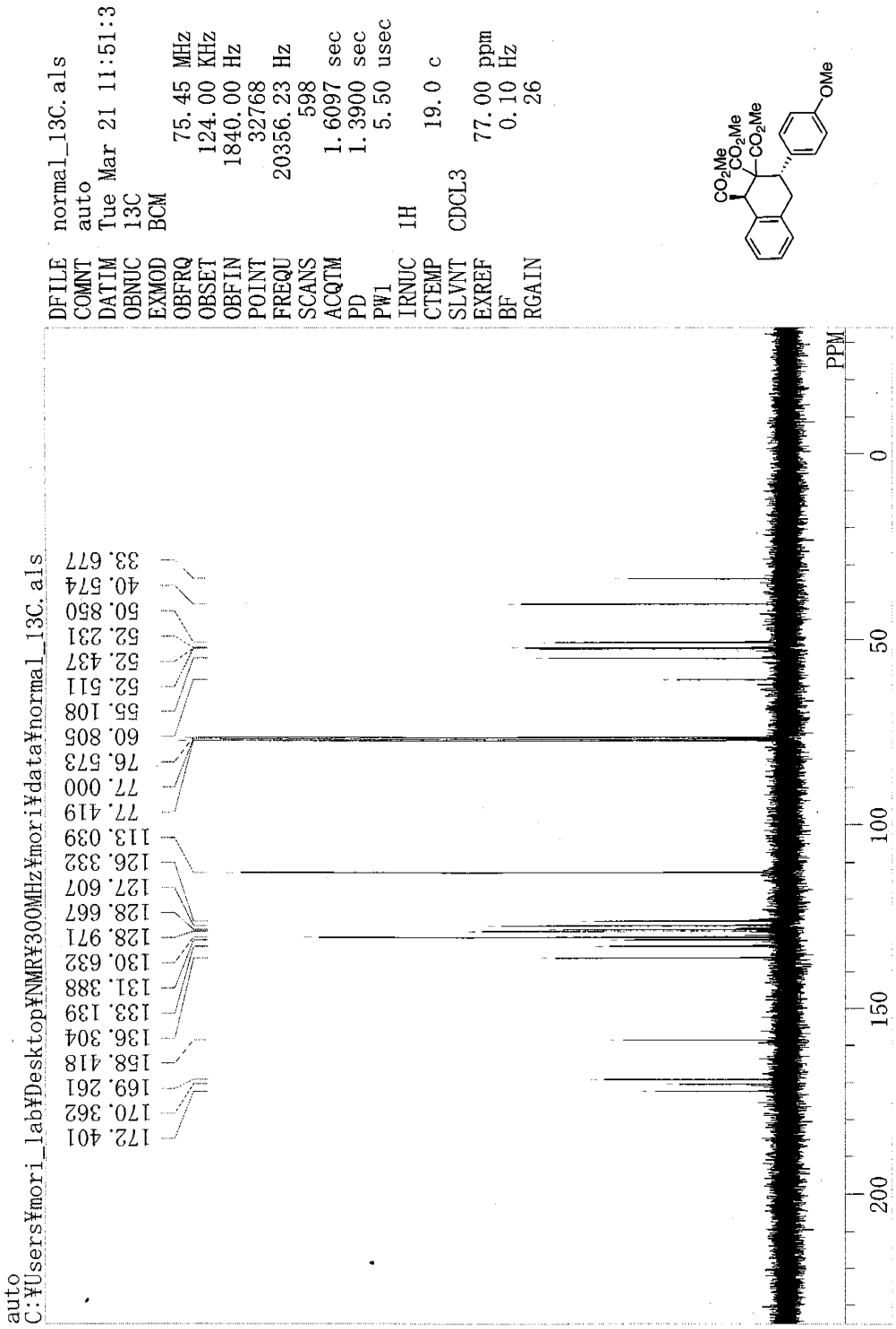
^{13}C NMR spectrum of **3j**.



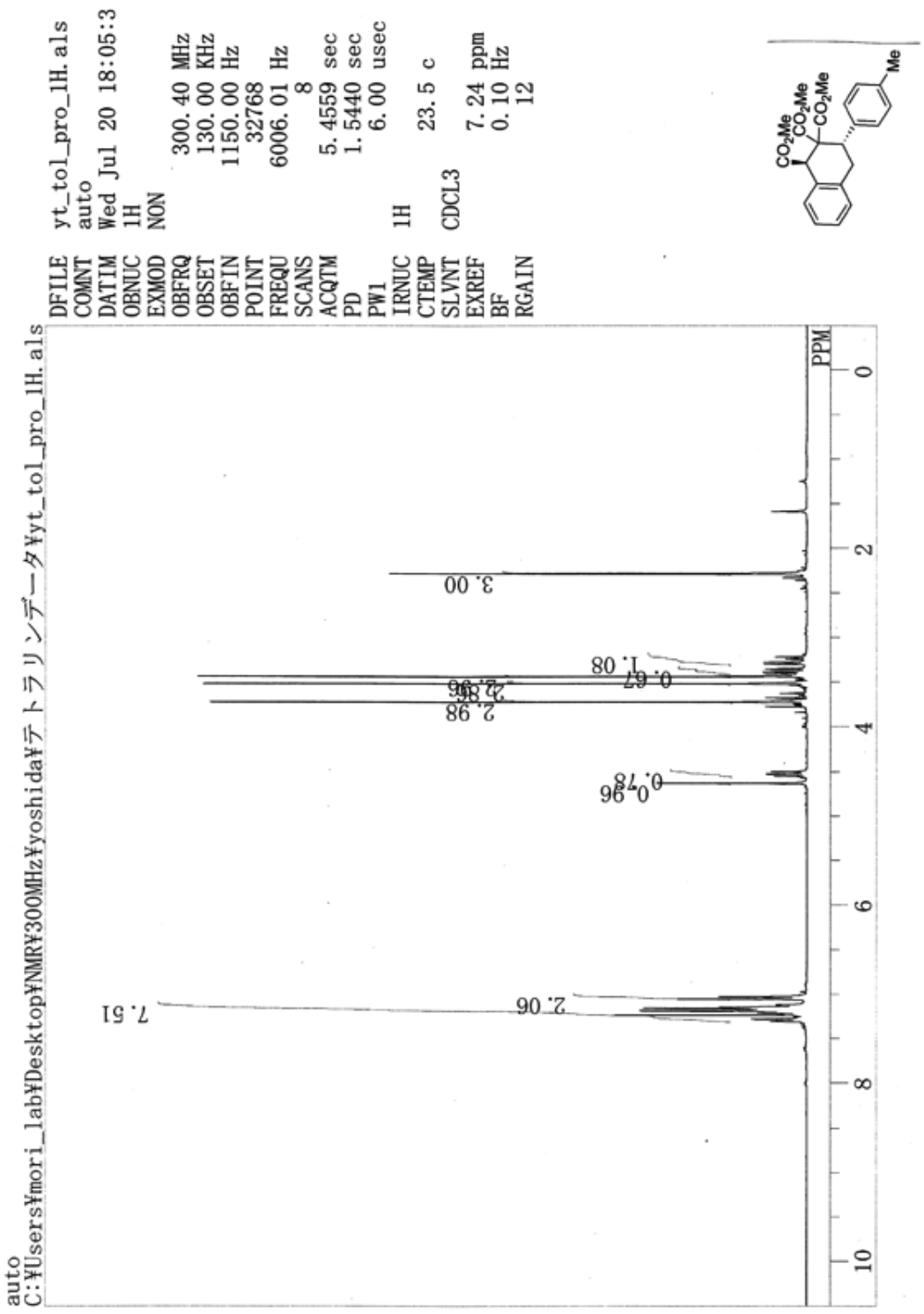
^{1}H NMR spectrum of **4a**.



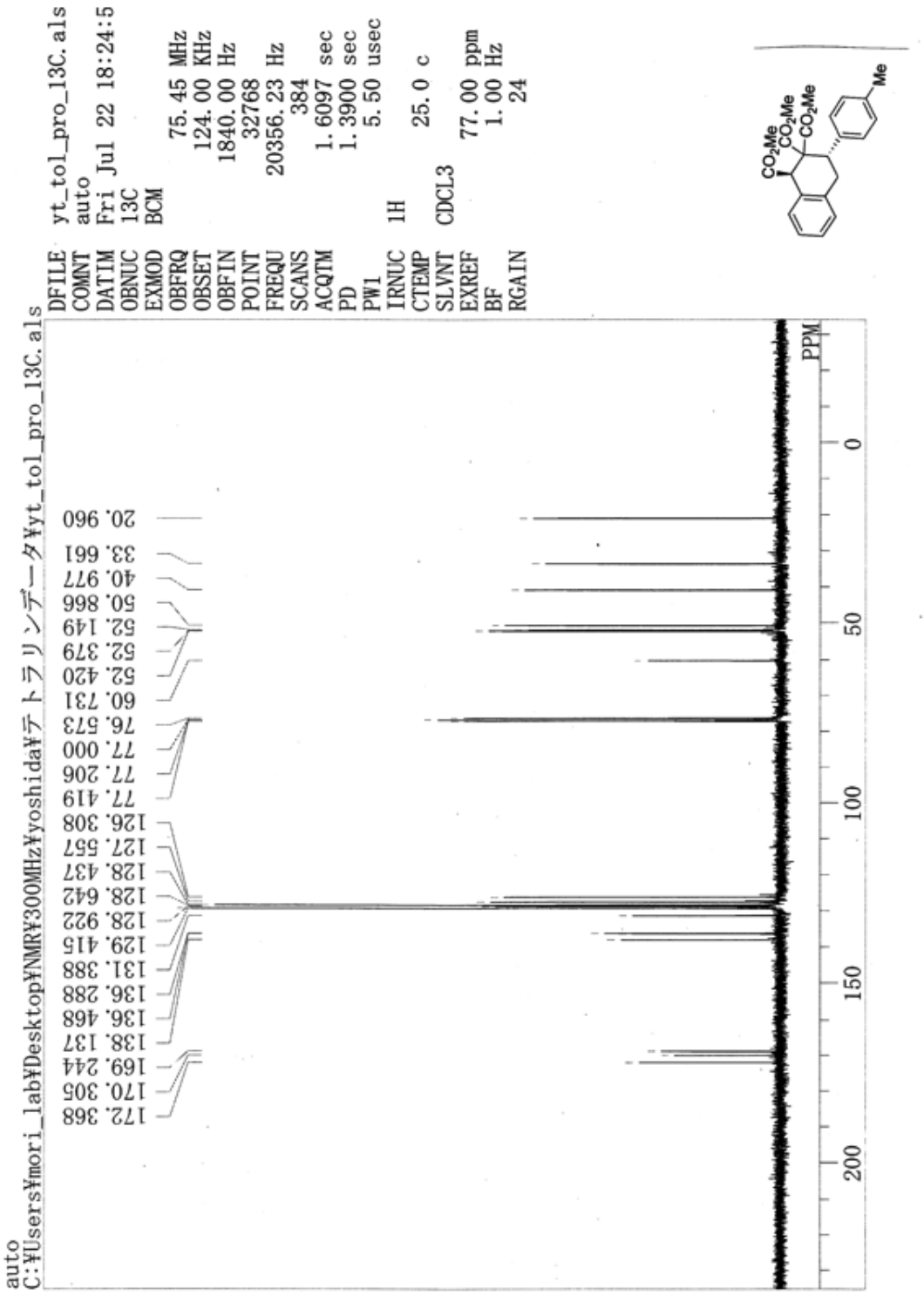
^{13}C NMR spectrum of **4a**.



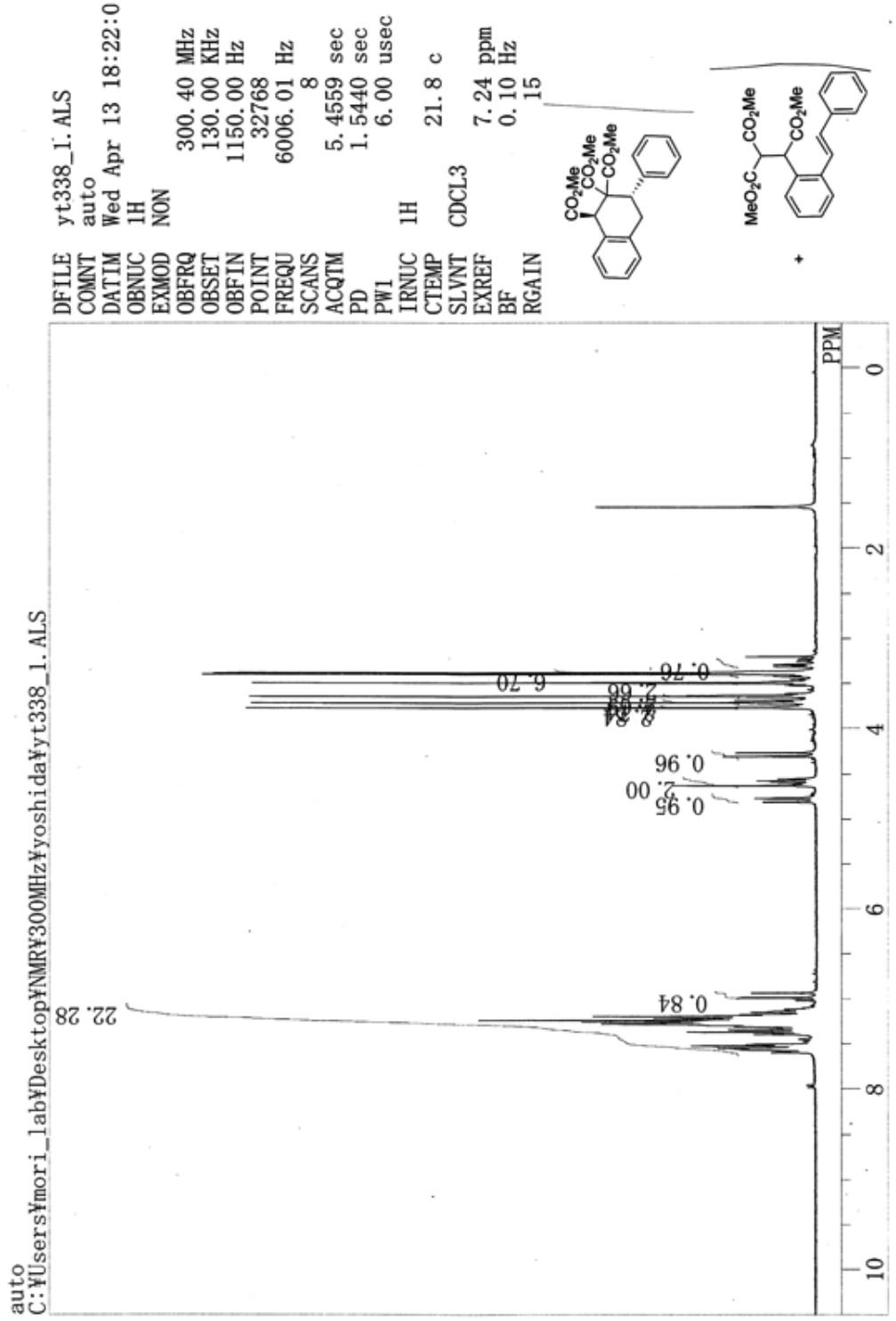
^{1}H NMR spectrum of **4b**.



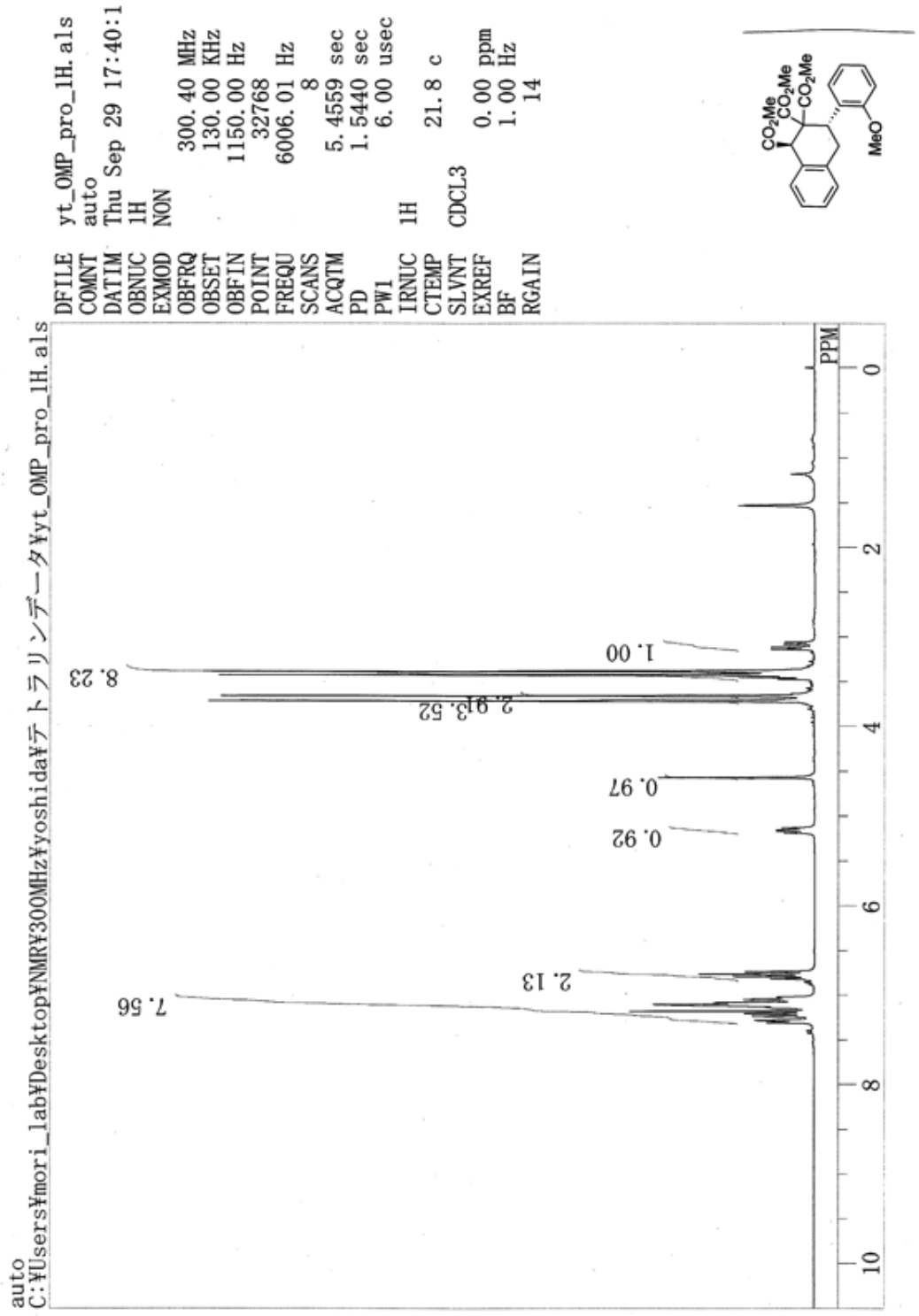
^{13}C NMR spectrum of **4b**.



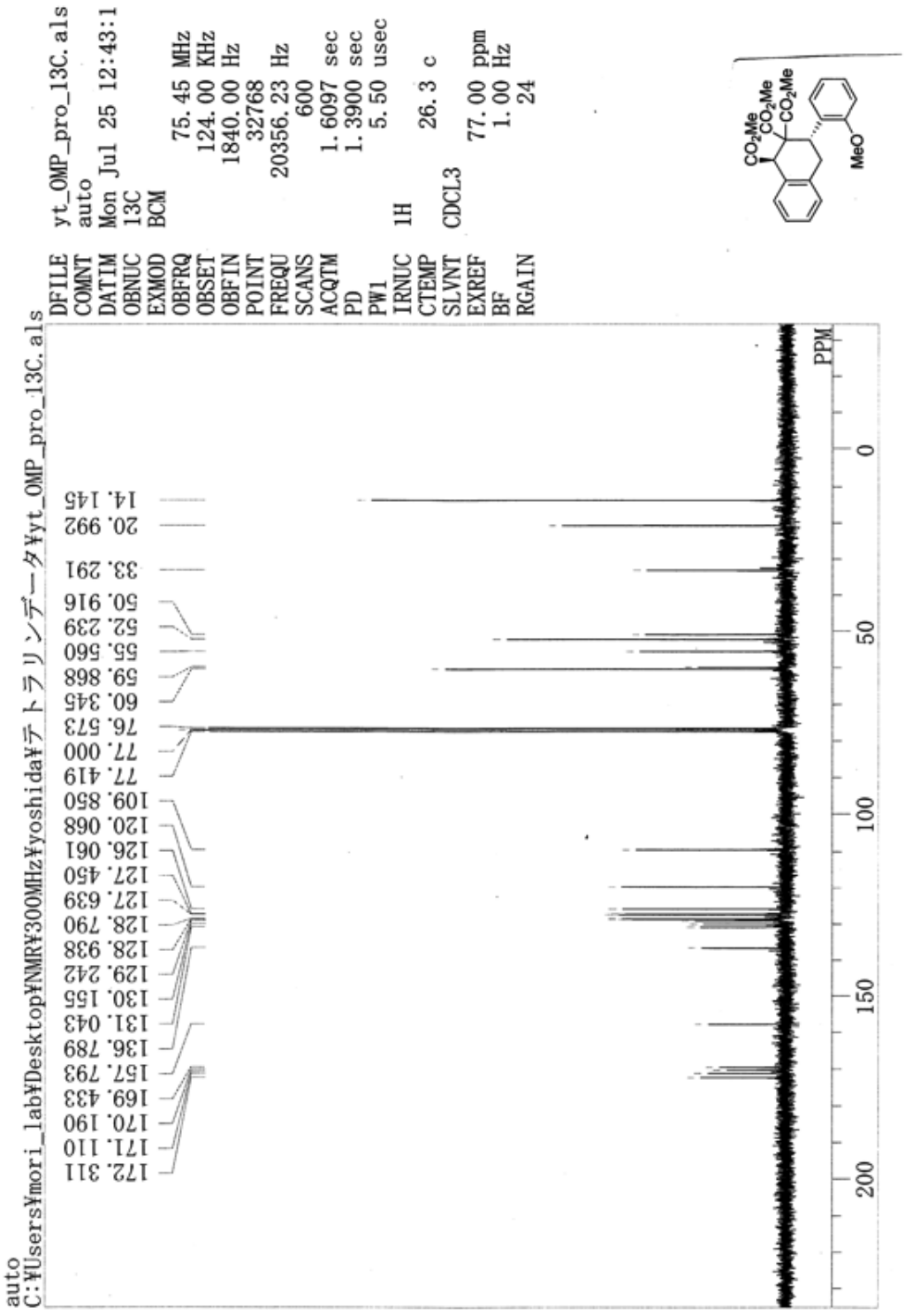
^{1}H NMR spectrum of **4c** and **6**.



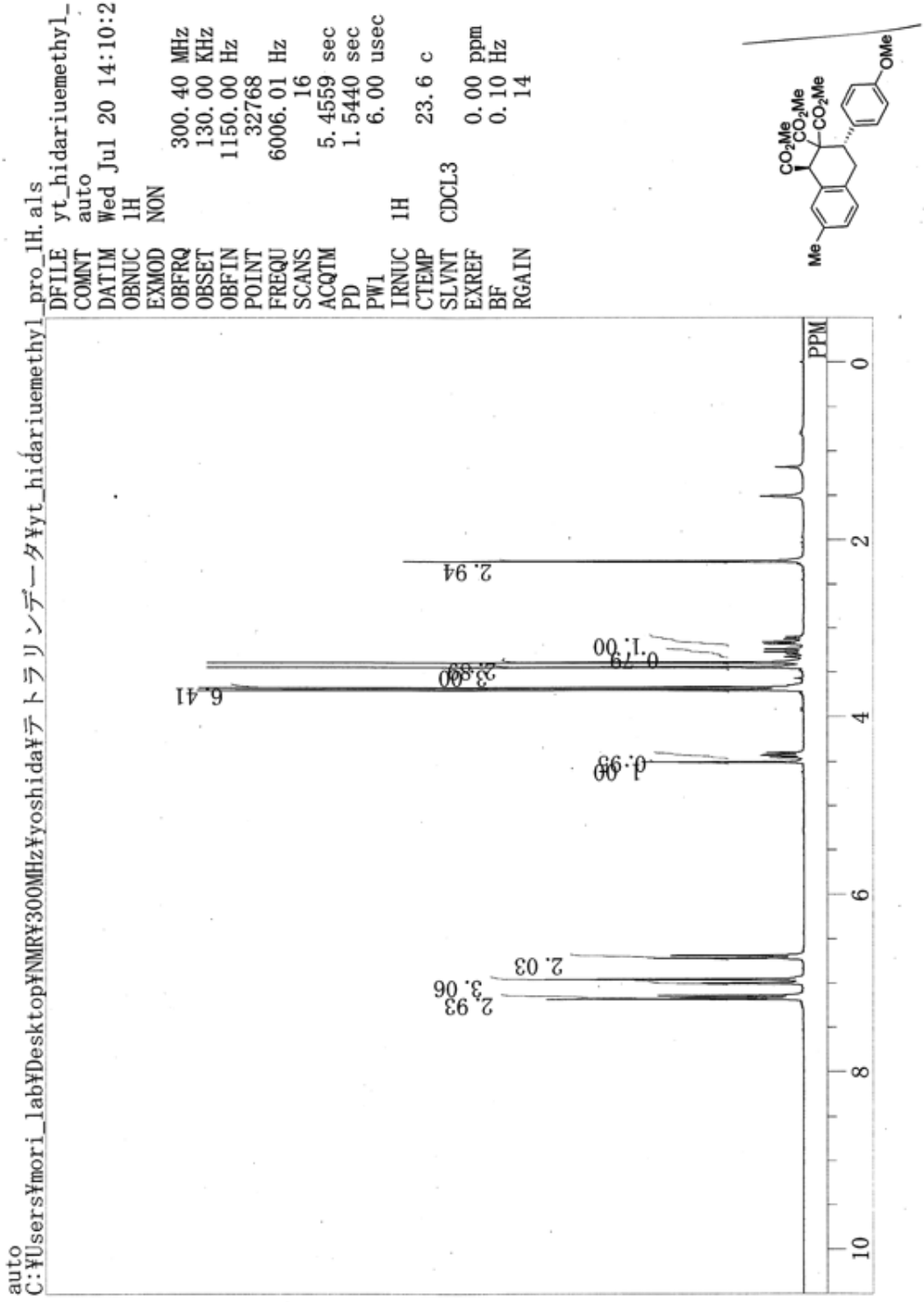
^{1}H NMR spectrum of **4d**.



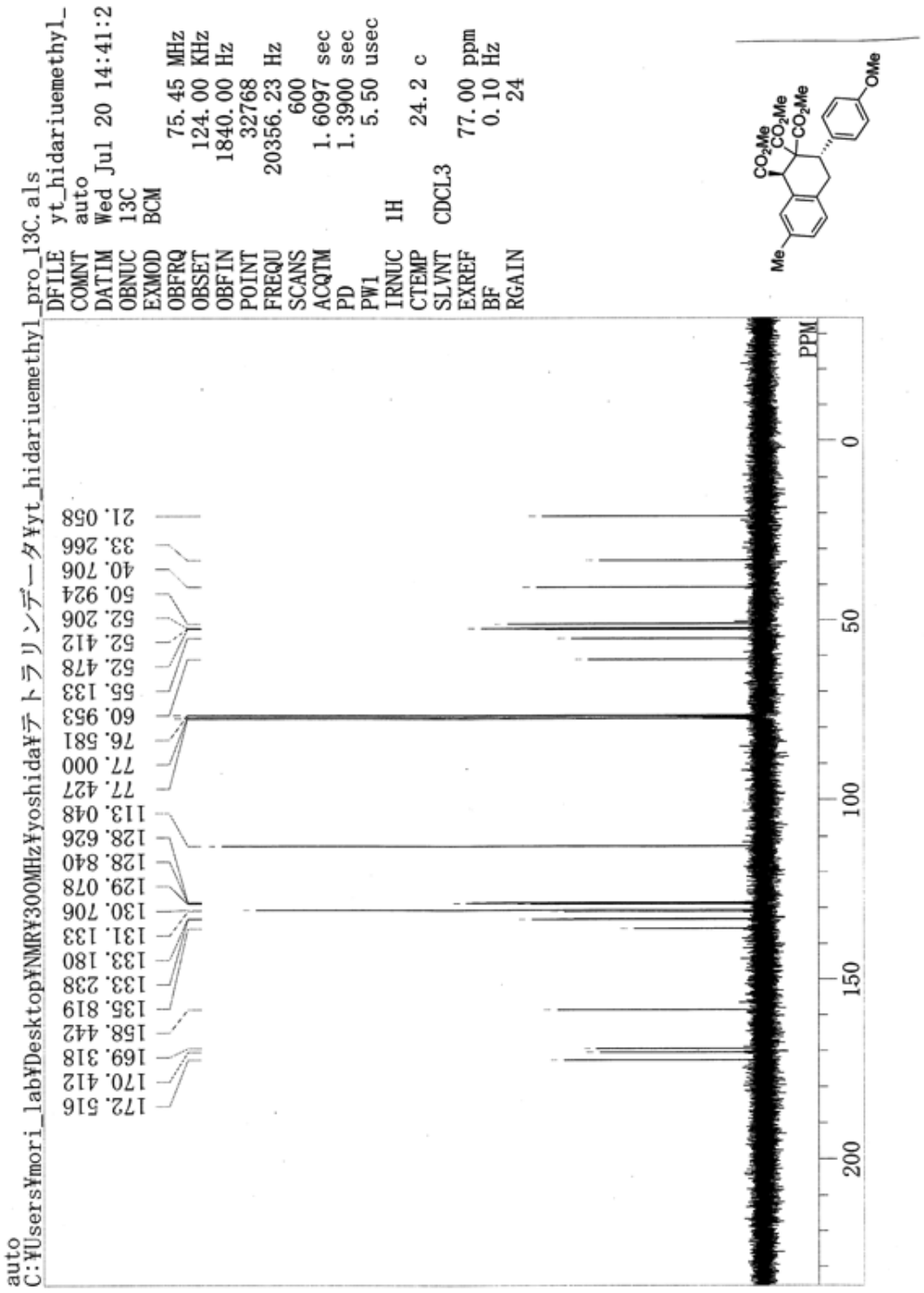
^{13}C NMR spectrum of **4d**.



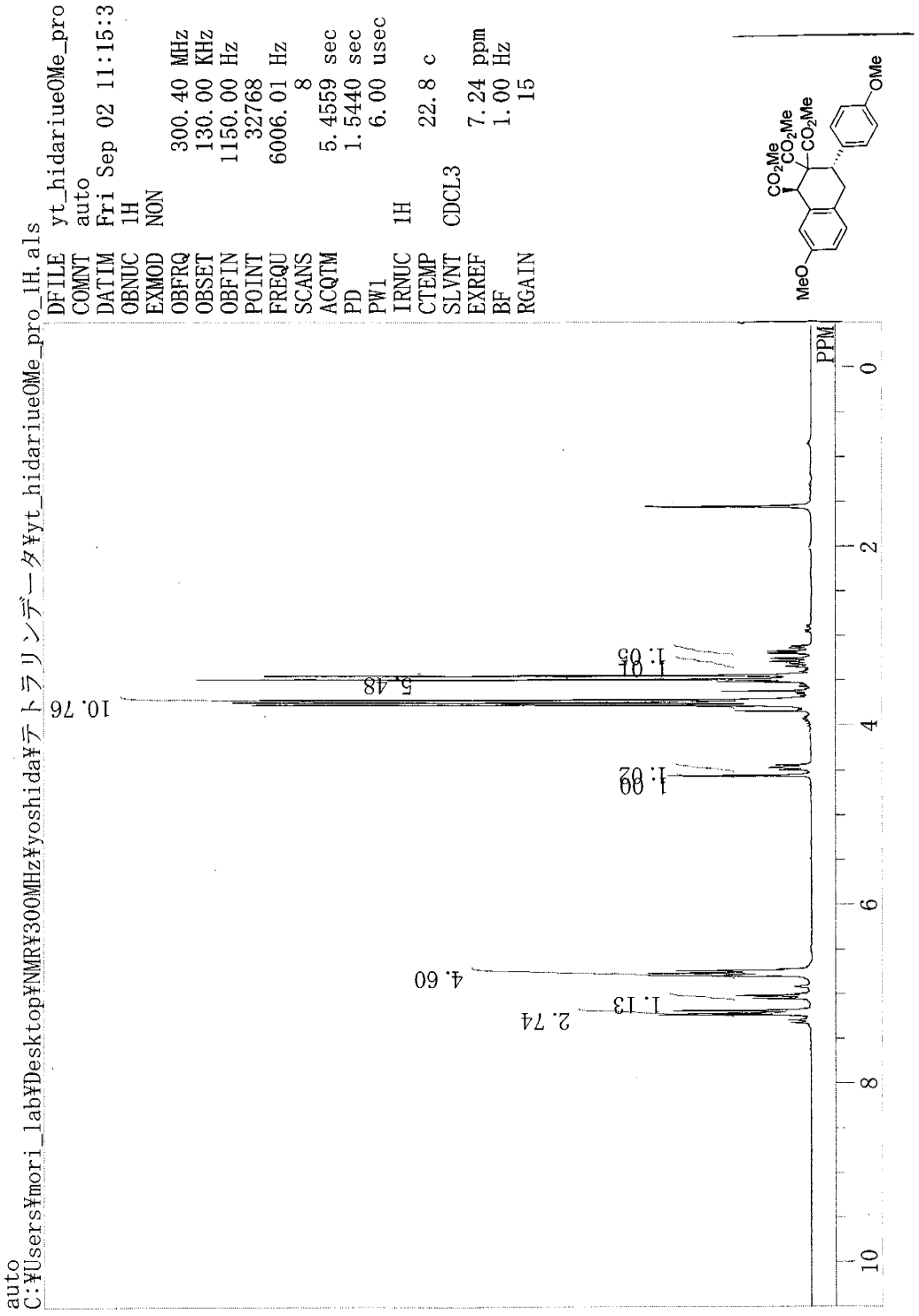
^{1}H NMR spectrum of **4e**.



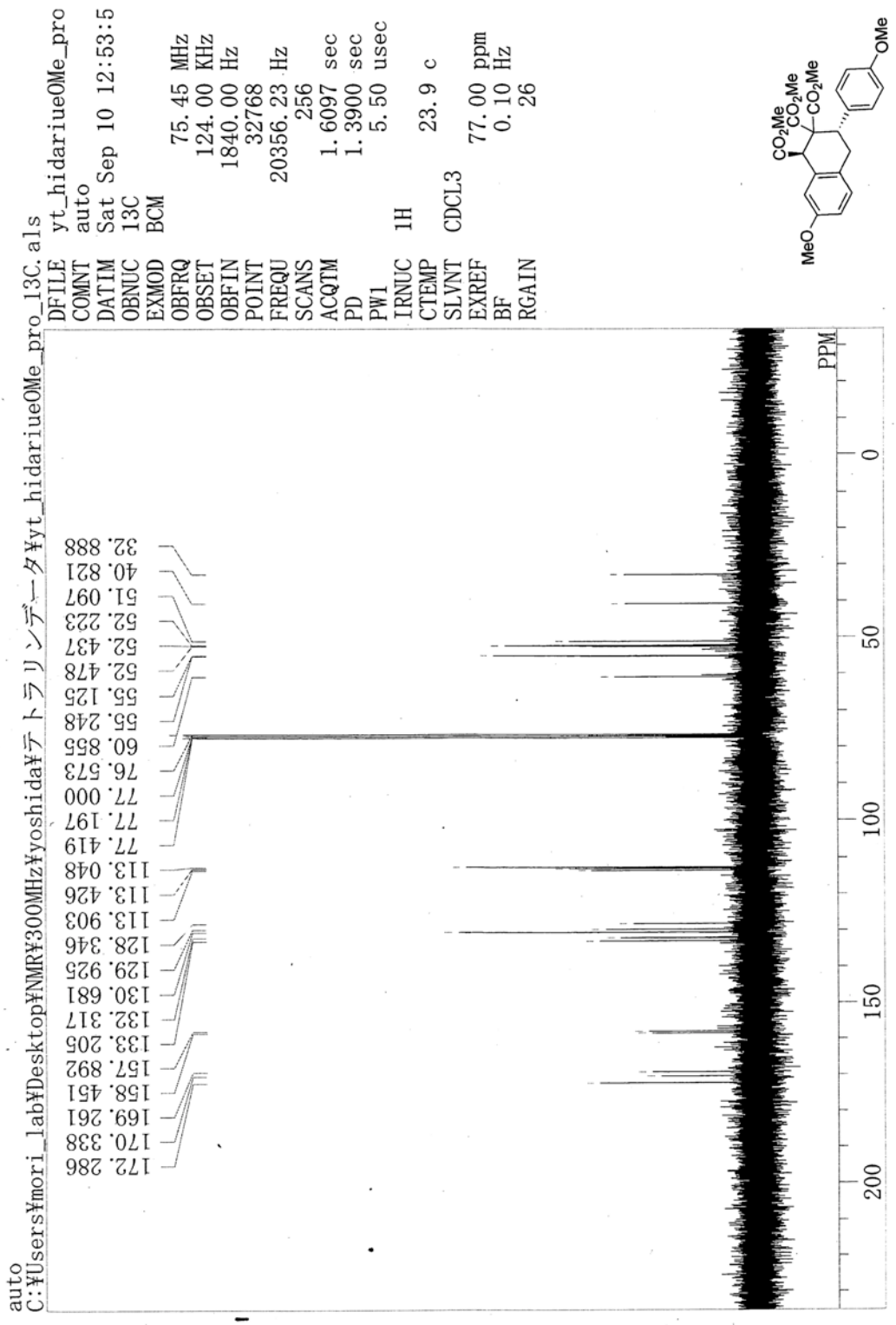
^{13}C NMR spectrum of **4e**.



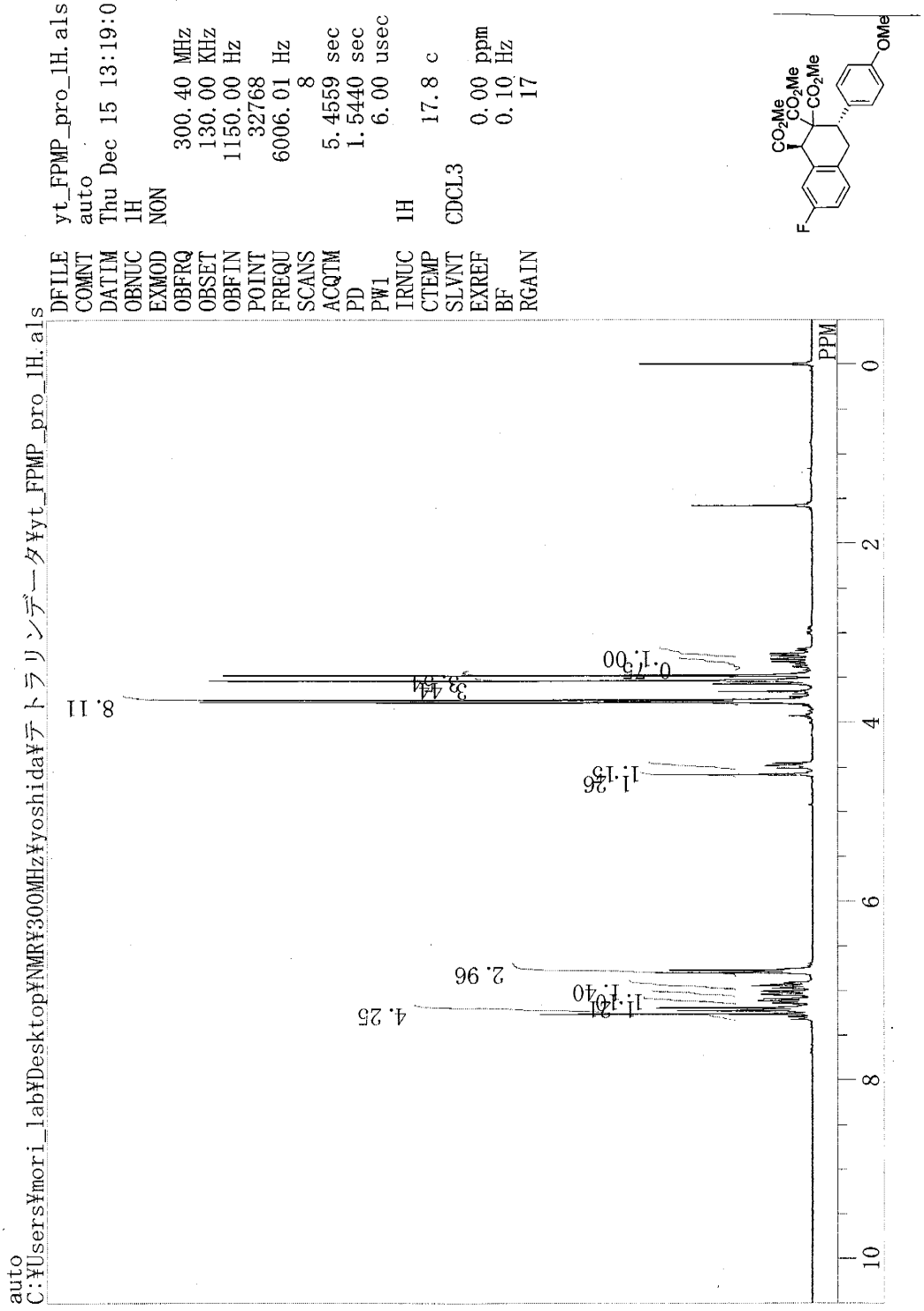
^{1}H NMR spectrum of **4f**.



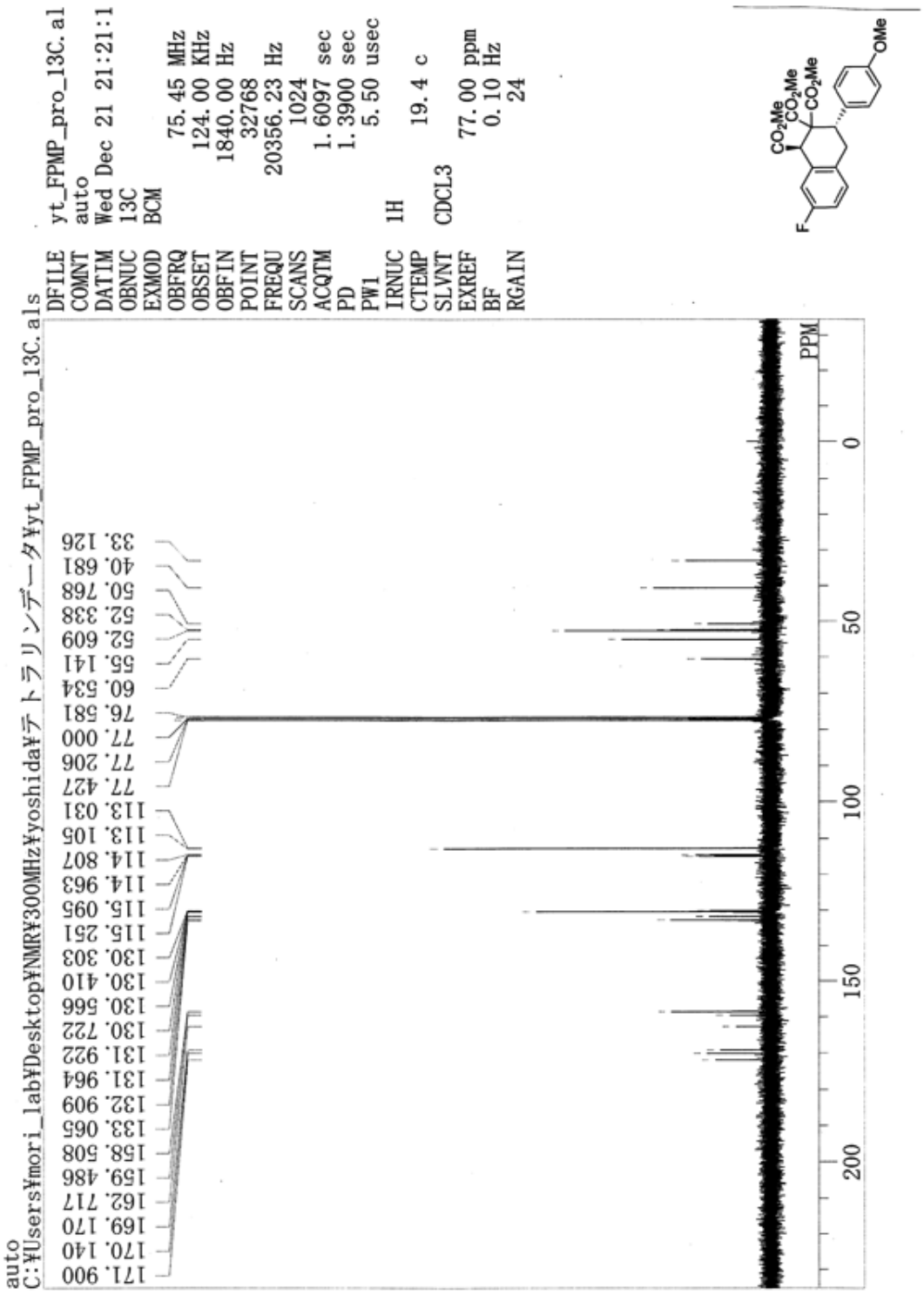
^{13}C NMR spectrum of **4f**.



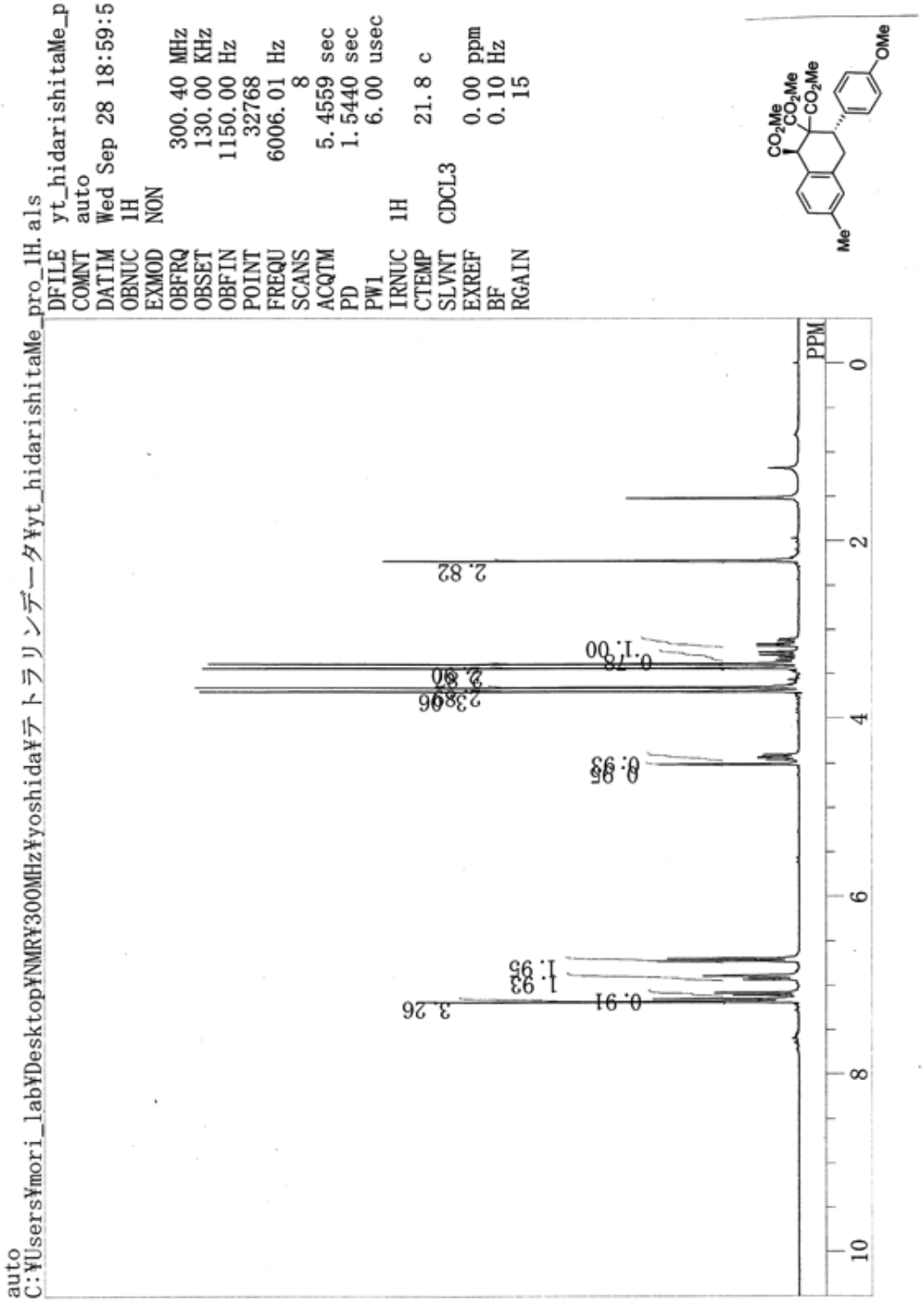
^{1}H NMR spectrum of **4g**.



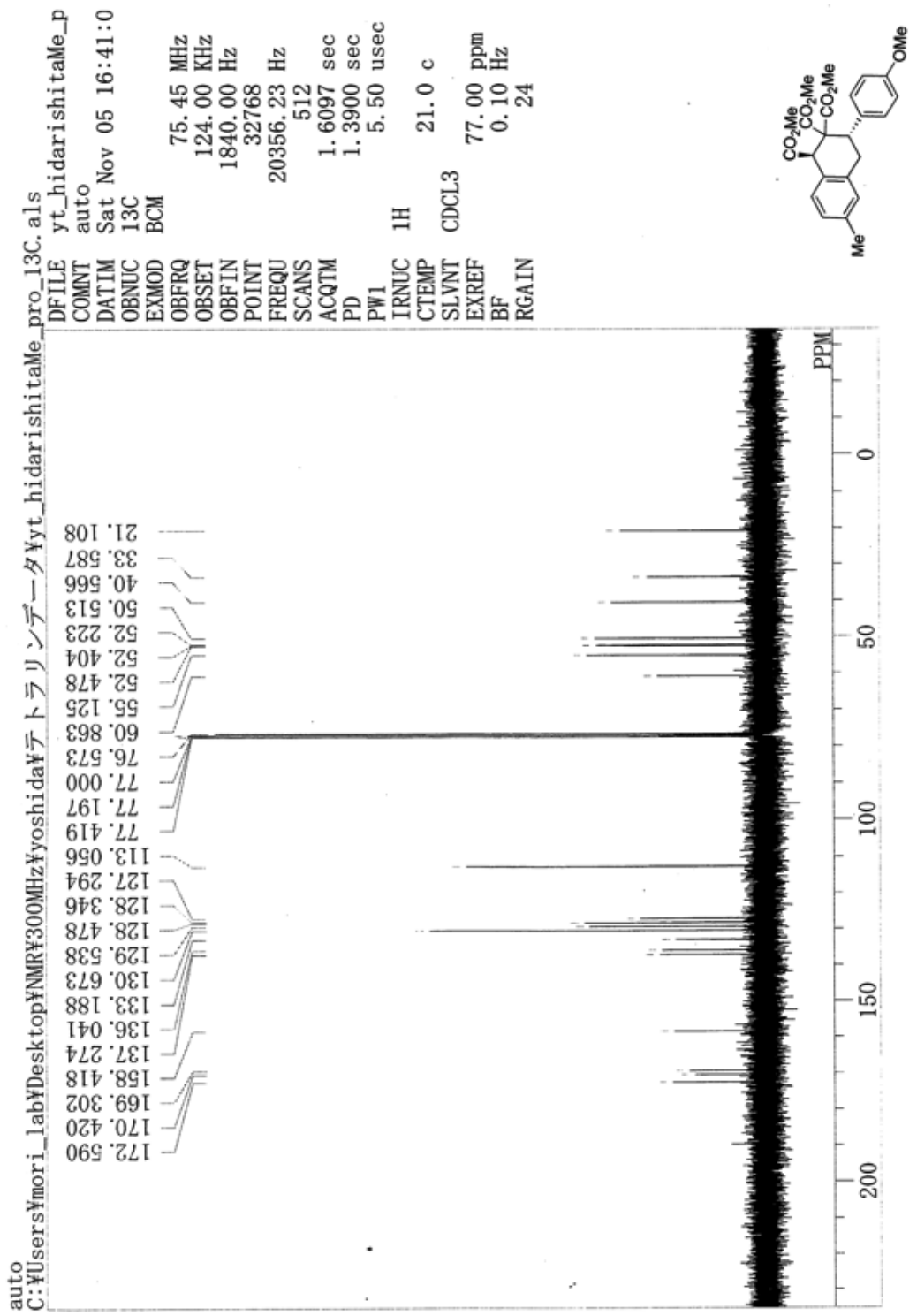
^{13}C NMR spectrum of **4g**.



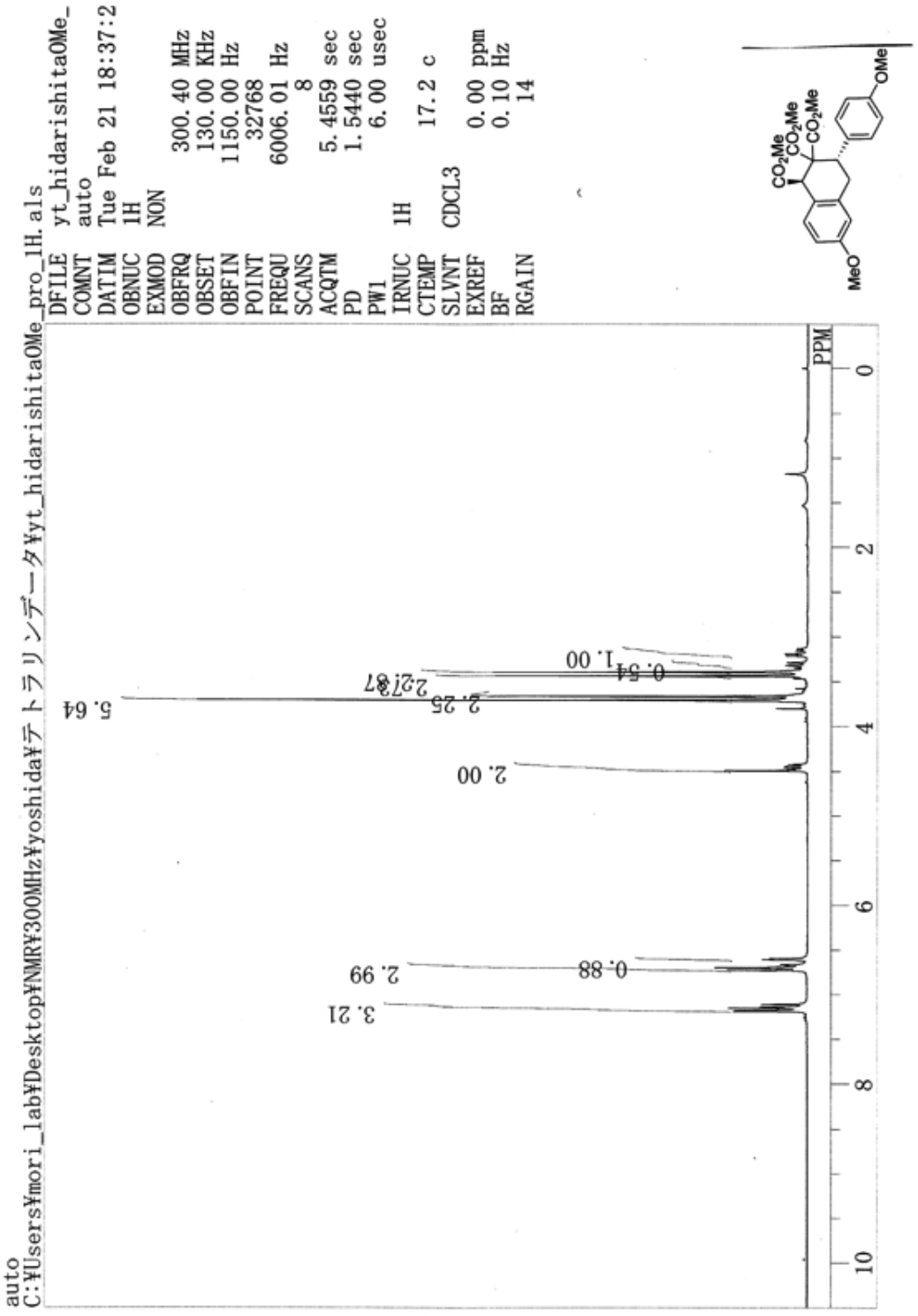
^{1}H NMR spectrum of **4h**.



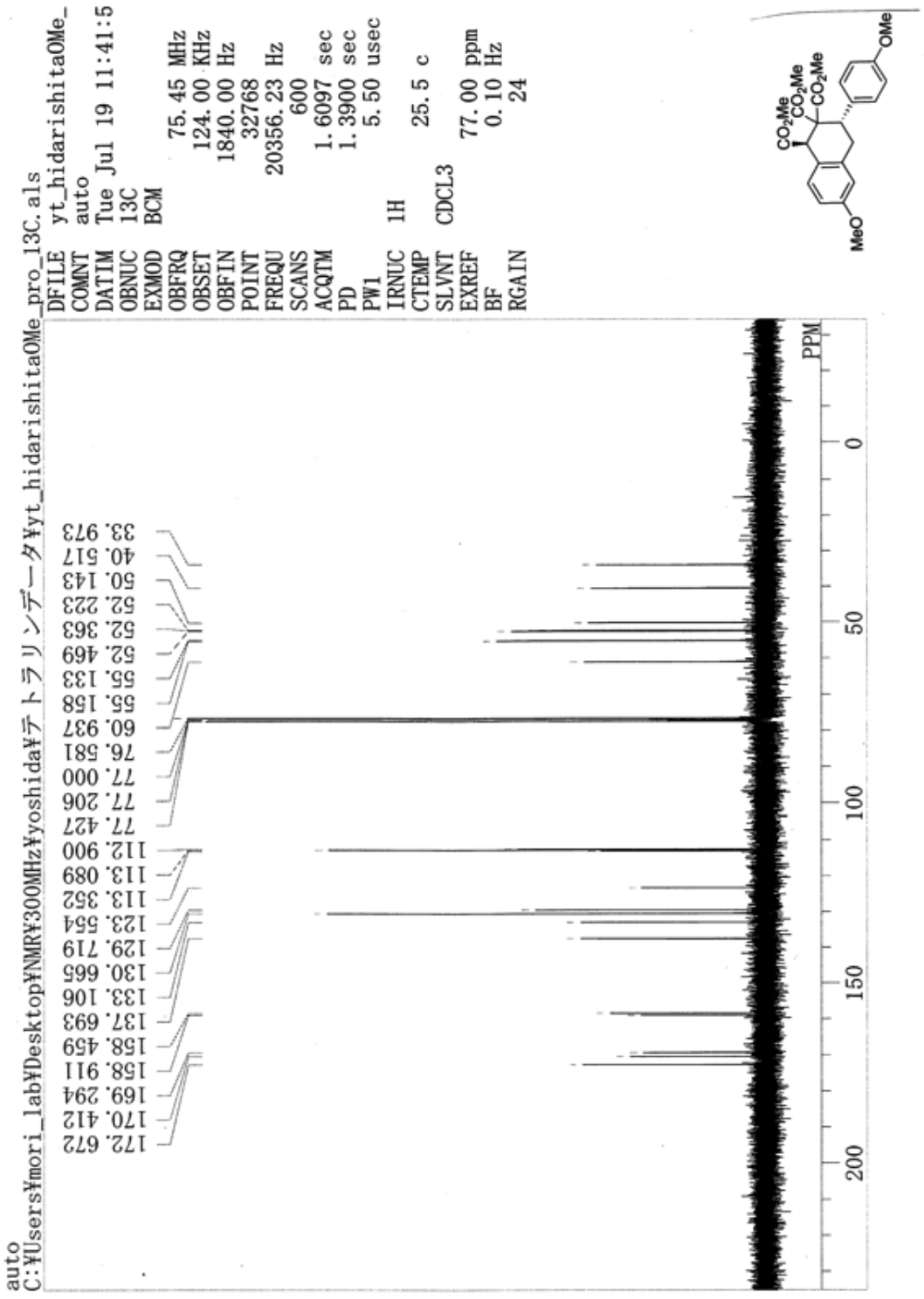
^{13}C NMR spectrum of **4h**.



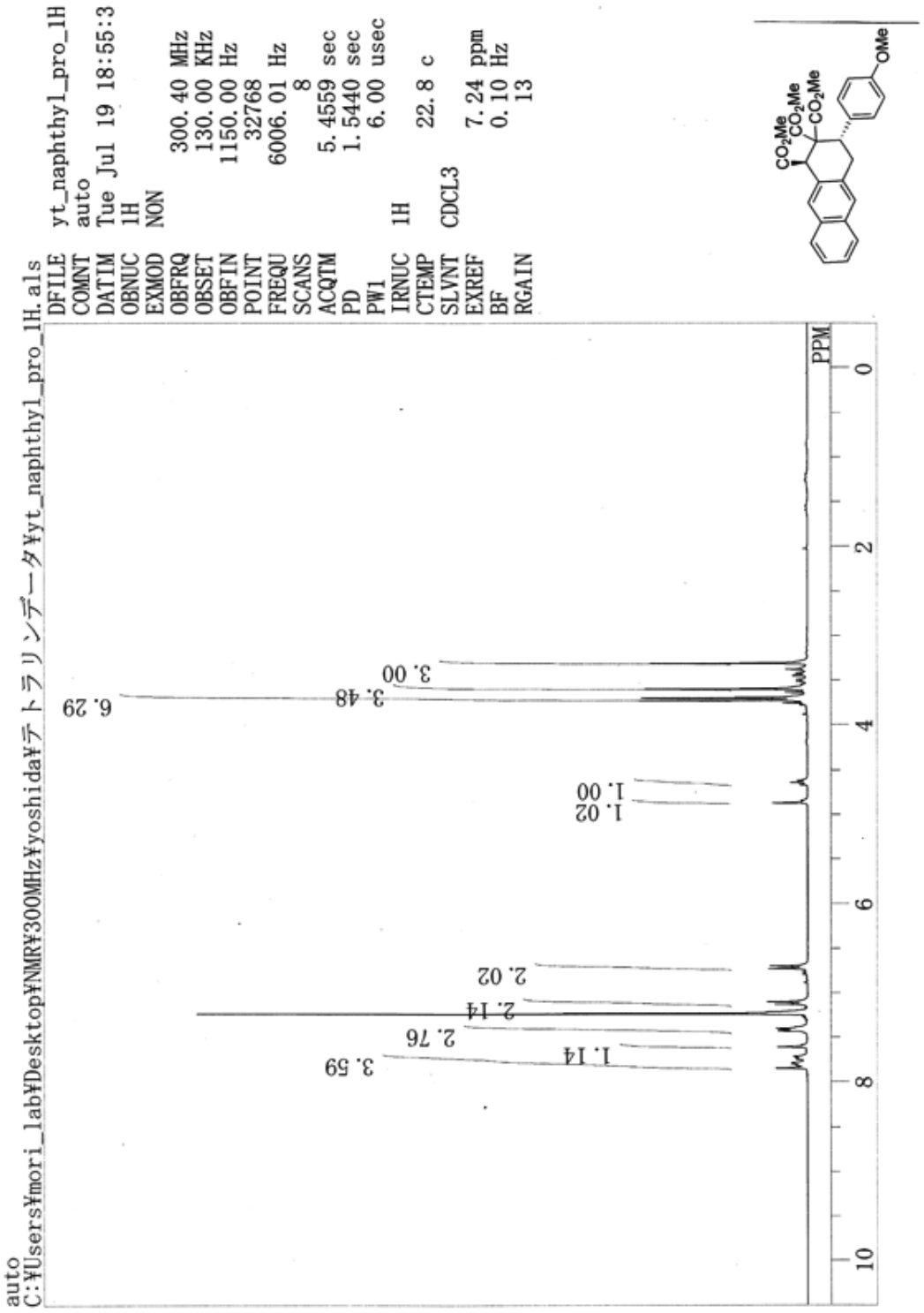
^{1}H NMR spectrum of **4i**.



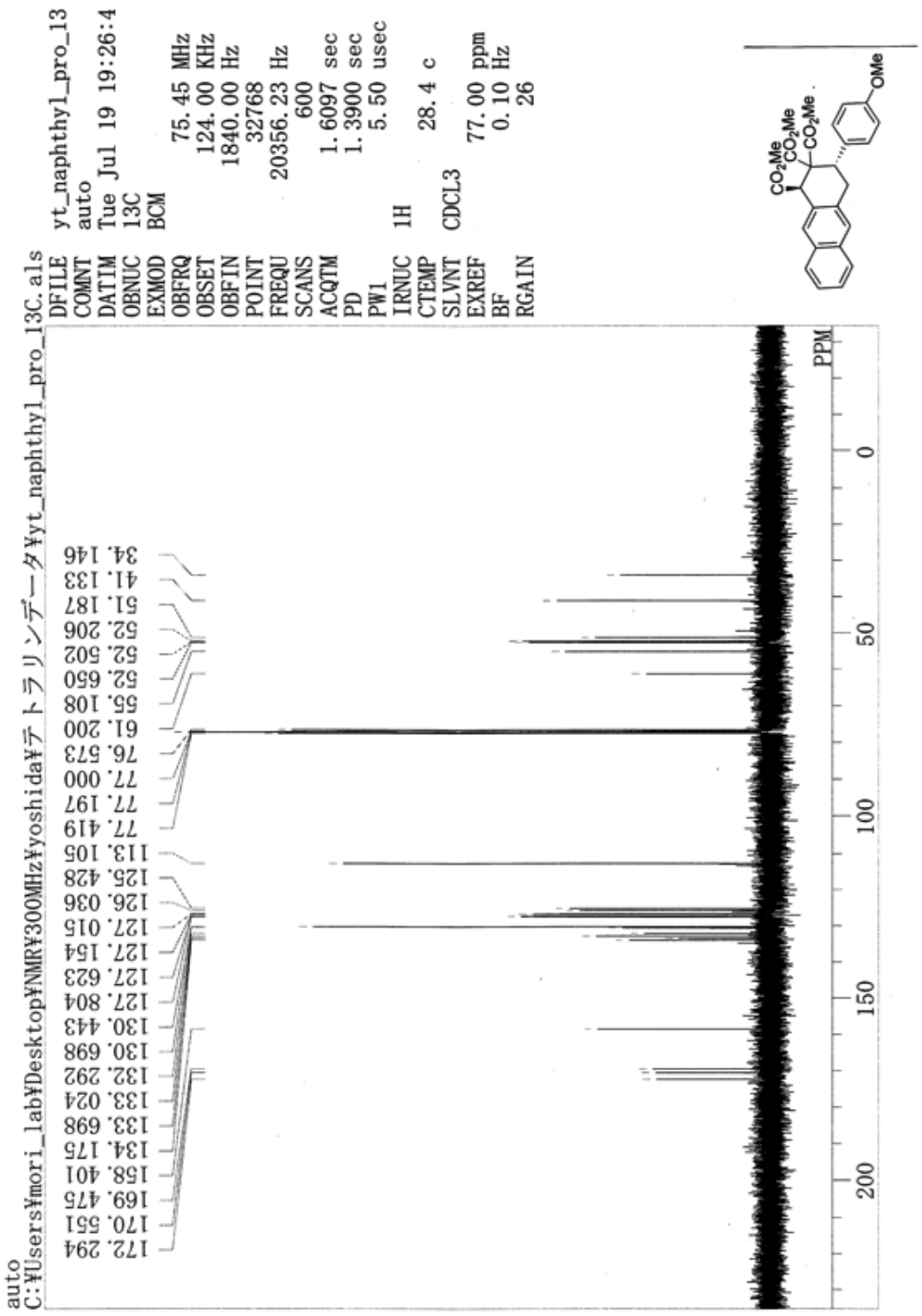
^{13}C NMR spectrum of **4i**.



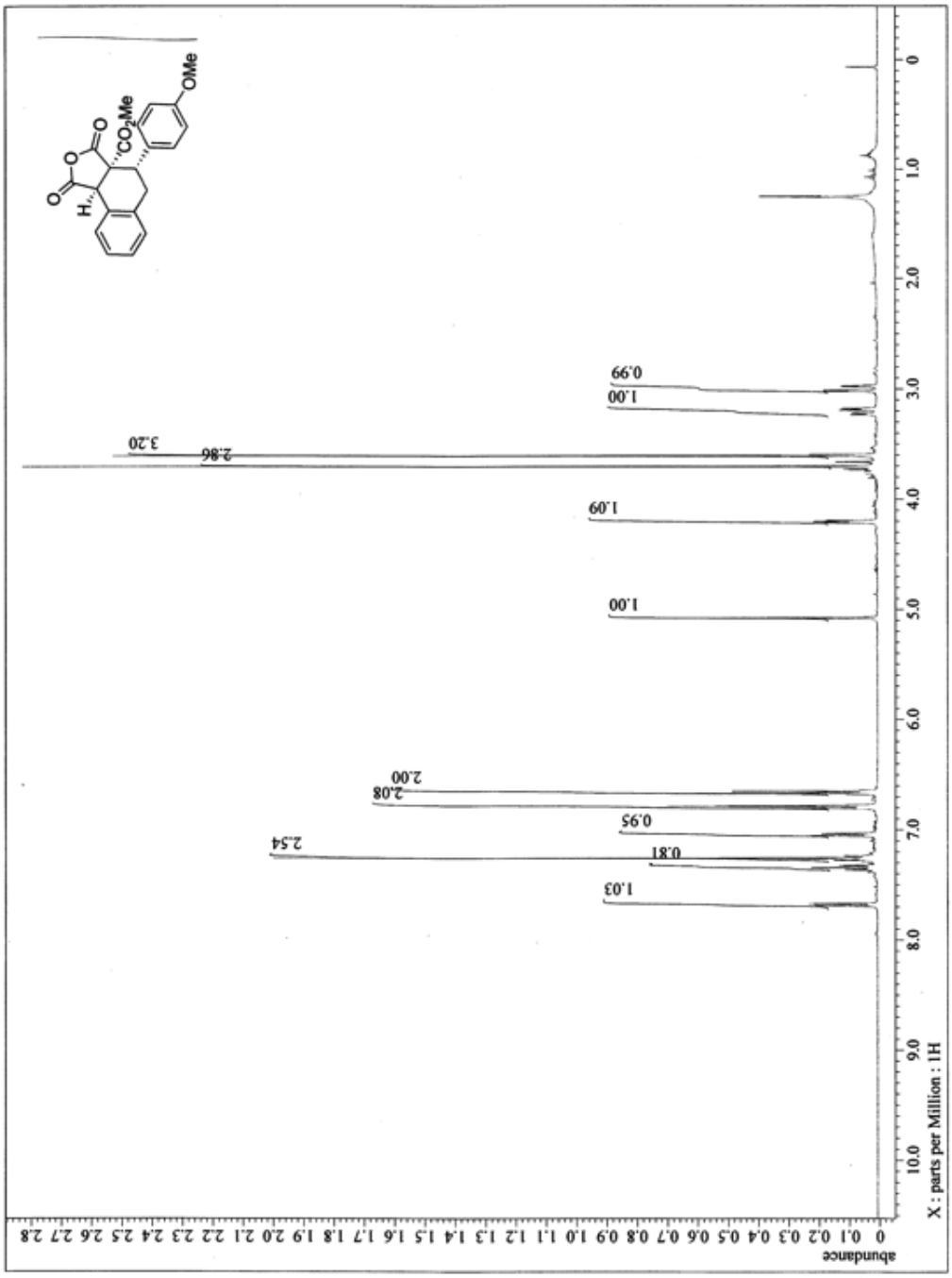
^{1}H NMR spectrum of **4j**.



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



^{1}H NMR spectrum of **5**.



^{13}C NMR spectrum of **5**.