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Divergent Synthesis of CF_3-Substituted Polycyclic Skeletons Based on Control of Activation Site of Acid Catalysts

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Supporting Information

General experimental procedures

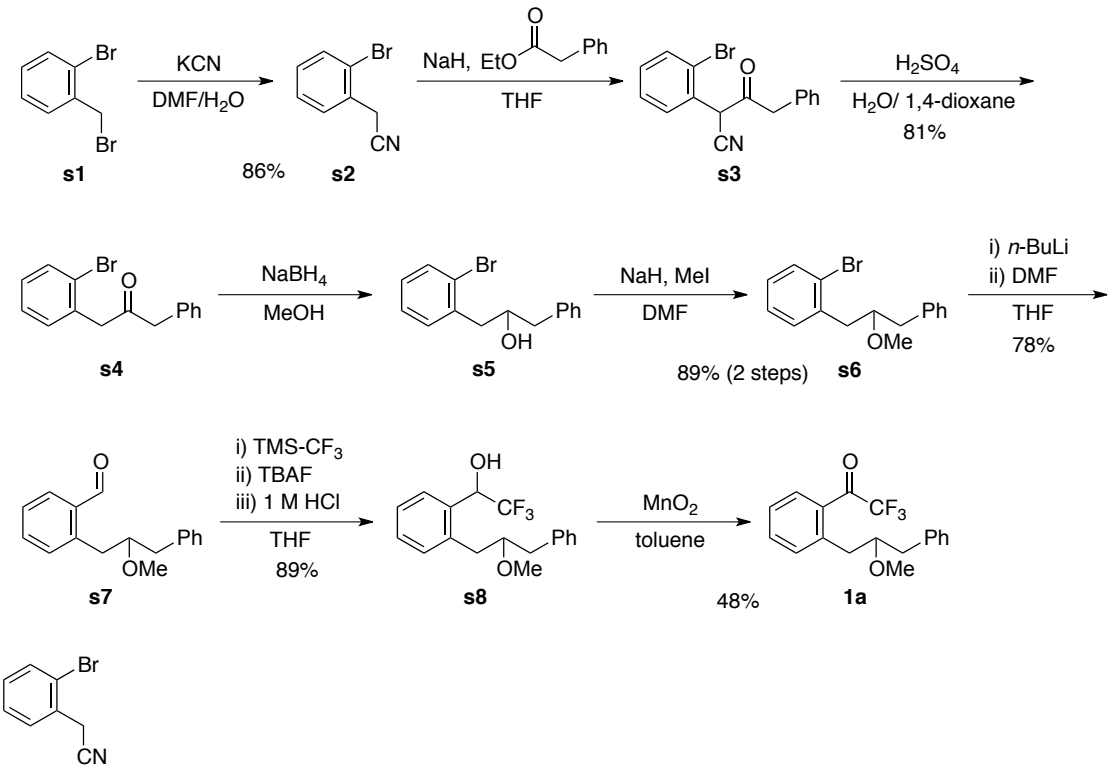
All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry nitrogen. Anhydrous ethereal solvents (THF, Et_2O) were purchased from Kanto Chemical Co., INC., and used directly. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2. 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, C_6F_6 for ^{19}F, 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.).

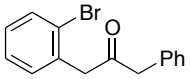
1. Preparation of starting materials.

Scheme 1. Preparation of starting materials **1**. Preparation of **1a** was shown as a representative example.



Synthesis of 2-(2-bromophenyl)acetonitrile (s2):

To a solution of 2-bormobenzyl bromide (**s1**) (1.57 g, 6.26 mmol) in DMF (2.5 mL) and H_2O (1.6 mL) was added KCN (612 mg, 9.39 mmol) at room temperature. After being stirred for 5 min, the reaction temperature was suddenly warmed up to room temperature. After being stirred for 2 h at room temperature, the reaction was stopped by adding H_2O. 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 = 10/1) to give **s2** (1.05 g, 86%, commercially available) as colorless oil.



Synthesis of 1-(2-bromophenyl)-3-phenylpropan-2-one (s4):

To a suspension of NaH (60% oil, 428 mg, 10.7 mmol) in THF (3.0 mL) was added a solution of **s2** (1.68 g, 8.53 mmol) in THF (1.9 mL) at 0 °C. After being stirred for 2 h,

a solution of 1-phenethyl acetate (3.60 mL, 22.5 mmol) was added to the reaction mixture, and then heated at 70 °C. After being stirred for 16 h at 70 °C, the reaction was stopped by adding H_2O. After separation of organic and aqueous layer, the aqueous layer acidified with 1 M HCl. 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 = 6/1) to give **s3** (2.36 g, 88%) as yellow oil.

A solution of **s3** (3.09 g, 9.82 mmol) in 1,4-dioxane (5.5 mL) and 80% H_2SO_4 (16.4 mL) was heated at 105 °C. After being stirred for 17 h at 105 °C, the reaction was stopped by adding H_2O. The crude products were extracted with EtOAc (x5) 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 = 4/1) to give **s4** (2.30 g, 81%) as yellow solid.

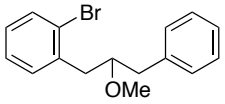
Mp. 44–46 °C.

IR (KBr) 3086, 3061, 3029, 2904, 1719, 1602, 1584, 1568, 1496, 1472, 1454, 1441, 1409, 1330, 1277, 1210, 1187, 1160, 1118, 1090, 1058, 1047, 1027, 1003, 947 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (2H), 3.88 (s, 2H), 7.10–7.42 (m, 8H), 7.55 (d, 1H, J = 8.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 49.1, 49.6, 124.9, 127.0, 127.4, 128.6, 128.7, 129.4, 131.7, 132.6, 133.7, 134.4, 204.2.

Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53. Found: C, 62.54; H, 4.31.



Synthesis of 1-bromo-2-(2-methoxy-3-phenylpropyl)benzene (s6):

To a stirred solution of **s4** (289 mg, 1.00 mmol) in MeOH (10.0 mL) was added $NaBH_4$ (366 mg, 9.68 mmol) at 0 °C. After being stirred for 11 h, the reaction was quenched by addition of H_2O at 0 °C. The crude mixture was extracted with EtOAc (x4) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo to give crude **s5** (225 mg) as yellow oil. This crude material was used for next reaction without further purification.

To a solution of **s5** in DMF (5.0 mL) were successively added NaH (60 % oil, 87.2 mg,

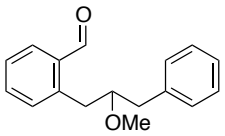
2.18 mmol), and MeI (112 μL, 1.90 mmol) at 0 °C. After being stirred for 14 h at room temperature, the reaction was quenched by addition of 1 M HCl at 0 °C. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 40/1) to give **s6** (270 mg, 89% from **s4**) as yellow oil.

IR (neat) 3058, 3019, 2924, 2816, 1596, 1561, 1469, 1439, 1362, 1181, 1099, 1023, 749 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.77–3.00 (m, 4H), 3.18 (s, 3H), 3.67–3.75 (m, 1H), 7.07 (d, 1H, *J* = 8.0, 8.0 Hz), 7.17–7.34 (m, 7H), 7.52 (d, 1H, *J* = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.6, 41.0, 57.8, 81.8, 124.6, 126.1, 127.2, 127.9, 128.2, 129.4, 132.0, 132.7, 138.4, 138.8.

Anal. Calcd for $C_{16}H_{17}BrO$: C, 62.96; H, 5.61. Found: C, 63.26; H, 5.85.



Synthesis of 2-(2-methoxy-3-phenylpropyl)benzaldehyde (s7):

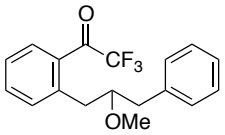
To a solution of **s6** (885 mg, 2.90 mmol) in THF (11.3 mL) was added *n*-BuLi (1.55 M in hexane, 2.52 mL, 3.90 mmol) at –78 °C. The reaction mixture was stirred for 10 min at –78 °C, to which DMF (0.45 mL, 5.73 mmol) was added. The reaction was quenched by addition of 1 M HCl at –78 °C. The crude mixture 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 afford aldehyde **s7** (576 mg, 78%) as colorless oil.

IR (neat) 3061, 3023, 2930, 2827, 2742, 1692, 1600, 1574, 1494, 1453, 1396, 1360, 1284, 1209, 1099, 1027, 884 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.60–3.31 (m, 4H), 3.10 (s, 3H), 3.45–3.54 (m, 1H), 7.15–7.55 (m, 8H), 7.84 (d, 1H, *J* = 7.8 Hz), 10.17 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.3, 40.6, 57.9, 83.4, 126.2, 126.8, 128.3, 129.4, 131.3, 132.2, 133.4, 134.4, 138.6, 141.8, 192.6.

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.11; H, 6.94.



Synthesis of 2,2,2-Trifluoro-1-(2-(2-methoxy-3-phenylpropyl)phenyl)ethanone (1a):

To a solution of aldehyde **s7** (803 mg, 3.16 mmol) in THF (15.8mL) was added $TMSCF_3$ (0.93 mL, 6.3 mmol). After being stirred for 5 min, TBAF (1.0 M in THF, 0.16 mL, 0.16 mmol) was added to the reaction mixture. After the mixture was stirred for 11 h at room temperature, the reaction was quenched by addition of 1 M HCl (7.9 mL, 7.9 mmol) at 0 °C. After being stirred for 1 h, 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 = 6/1) to afford aldohol **s8** (909 mg, 89% from **s1**) as yellow oil.

To a solution of **s8** (1.65 g, 5.09 mmol) in toluene (33.9 mL) was added MnO_2 (4.42 g, 50.9 mmol) at room temperature. After the reaction mixture was heated to reflux for 20 h, the crude material was filtered through Celite® pad and the resulting filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give **1a** (780g, 48%) as colorless oil.

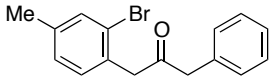
IR (neat) 3064, 3029, 2984, 2934, 2830, 1733, 1716, 1602, 1573, 1495, 1452, 1360, 1324, 1287, 1201, 1185, 1142, 1097, 1063, 1031, 953, 936, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.72 (dd, 1H, J = 6.4, 13.6 Hz), 2.86 (dd, 1H, J = 6.4, 13.6 Hz), 2.96–3.10 (m, 2H), 3.07 (s, 3H), 3.45–3.54 (m, 1H), 7.16–7.34 (m, 6H), 7.36 (dd, 1H, J = 8.0, 8.0 Hz), 7.50 (dd, 1H, J = 8.0, 8.0 Hz), 7.76 (d, 1H, J = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9, 40.4, 57.6, 83.1, 116.3 (q, J_{C-F} = 290.8 Hz), 126.2, 126.3, 128.3, 128.9 (q, J_{C-F} = 3.8 Hz), 129.4, 131.2, 132.9, 133.1, 138.6, 141.4, 183.6 (q, J_{C-F} = 34.4 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 89.9 (s, 3F).

Anal. Calcd for $C_{18}H_{17}F_3O_2$: C, 67.07; H, 5.32. Found: C, 66.93; H, 5.15.



1-(2-Bromo-4-methylphenyl)-3-phenylpropan-2-one (**s9**).

Yellow solid.

Yield: 65% (synthesized from (synthesized from 2-bromo-1-(bromomethyl)-4-methylbenzene[1]).

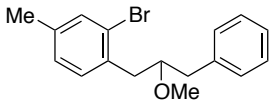
Mp. 53–56 °C.

IR (KBr) 3087, 3061, 3027, 2945, 2919, 1715, 1679, 1607, 1565, 1497, 1453, 1411, 1342, 1324, 1307, 1215, 1154, 1058, 1039, 948, 866 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.76 (s, 2H), 3.83 (2H), 6.98–7.10 (m, 2H), 7.18–7.38 (m, 5H), 7.39 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 48.8, 49.6, 124.7, 127.0, 128.4, 128.6, 129.5, 131.3, 131.4, 133.2, 133.9, 138.9, 204.7.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.21; H, 5.24.



2-Bromo-1-(2-methoxy-3-phenylpropyl)-4-methylbenzene (**s10**).

Colorless oil.

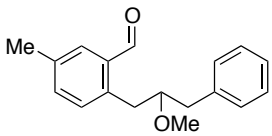
Yield: 99% (synthesized from **s9**).

IR (neat) 3085, 3062, 3027, 2976, 2925, 2824, 1606, 1561, 1492, 1454, 1389, 1360, 1210, 1181, 1101, 1079, 1041, 991, 910 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.75–2.95 (m, 4H), 3.19 (s, 3H), 3.66–3.75 (m, 1H), 7.02 (d, 1H, J = 8.0 Hz), 7.14 (d, 1H, J = 8.0 Hz), 7.15–7.31 (m, 5H), 7.35 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 40.4, 40.5, 57.8, 81.9, 124.3, 126.0, 128.0, 128.2, 129.4, 131.6, 133.1, 135.2, 137.8, 138.9.

Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.96; H, 6.00. Found: C, 63.75; H, 6.27.



2-(2-Methoxy-3-phenylpropyl)-5-methylbenzaldehyde (**s11**).

Colorless oil.

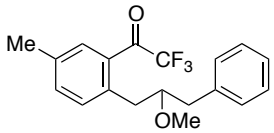
Yield: 73% (synthesized from **s10**).

IR (neat) 3085, 3061, 3028, 2873, 2827, 2733, 1687, 1610, 1569, 1496, 1454, 1400, 1380, 1360, 1311, 1283, 1246, 1199, 1181, 1157, 1099, 1079, 1065, 1031, 964 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.79 (dd, 1H, J = 5.6, 14.0 Hz), 2.88 (dd, 1H, J = 6.4, 14.0 Hz), 3.11 (3H), 3.09–3.14 (m, 2H), 3.48–3.57 (m, 1H), 7.15 (d, 1H, J = 8.0 Hz), 7.18–7.35 (m, 6H), 7.64 (s, 1H), 10.14 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 36.8, 40.5, 57.8, 83.5, 126.2, 128.2, 129.4, 131.6, 132.1, 134.2, 134.3, 136.5, 138.6, 138.8, 192.7.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.41; H, 7.34.



2,2,2-Trifluoro-1-(2-(2-methoxy-3-phenylpropyl)-5-methylphenyl)ethanone (**1b**).

Colorless oil.

Yield: 53% (synthesized from **s11**).

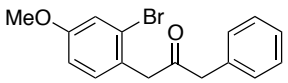
IR (neat) 3087, 3063, 3028, 2983, 2931, 2830, 1734, 1604, 1571, 1496, 1455, 1444, 1382, 1360, 1328, 1283, 1236, 1202, 1144, 1099, 1079, 1064, 1031, 065, 911 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.71 (dd, 1H, J = 6.0, 13.2 Hz), 2.83 (dd, 1H, J = 6.8, 13.2 Hz), 2.92–3.08 (m, 2H), 3.08 (s, 3H), 3.42–3.50 (m, 1H), 7.17–7.35 (m, 7H), 7.54 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 37.5, 40.4, 114.3, 116.3 (q, J_{C-F} = 291.8 Hz), 126.1, 128.3, 129.3 (q, J_{C-F} = 2.5 Hz), 129.4, 131.1, 132.8, 133.9, 136.0, 138.3, 138.7, 183.7 (q, J_{C-F} = 34.3 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 90.0 (s, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_2$: C, 67.85; H, 5.69. Found: C, 67.53; H, 5.62.



1-(2-Bromo-4-methoxyphenyl)-3-phenylpropan-2-one (**s12**).

Yellow solid.

Yield: 60% (synthesized from 2-bromo-1-(bromomethyl)-4-methoxybenzene[2]).

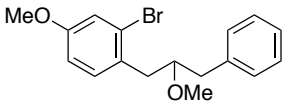
Mp. 52–54 °C.

IR (KBr) 3087, 3062, 3028, 3005, 2961, 2941, 2904, 2836, 1718, 1607, 1585, 1569, 1541, 1454, 1412, 1283, 1198, 1183, 1131, 1057, 1003, 969, 948 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2H), 3.78 (s, 3H), 3.81 (2H), 6.81 (dd, 1H, *J* = 2.8, 8.4 Hz), 7.03 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 2.8 Hz), 7.18–7.36 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 48.2, 49.3, 55.3, 113.5, 117.7, 125.0, 126.3, 126.9, 128.5, 129.4, 131.9, 133.8, 159.0, 204.7.

Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.14; H, 4.99.



2-Bromo-4-methoxy-1-(2-methoxy-3-phenylpropyl)benzene (**s13**).

Yellow oil.

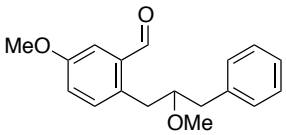
Yield: 91% (synthesized from **s12**).

IR (neat) 3061, 3019, 2927, 2823, 1604, 1565, 1494, 1454, 1358, 1308, 1282, 1243, 1181, 1100, 1030, 865 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.70–2.92 (m, 4H), 3.19 (s, 3H), 3.60–3.72 (m, 1H), 3.77 (s, 3H), 6.79 (dd, 1H, *J* = 2.4, 8.4 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 7.12–7.39 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 39.9, 40.5, 55.4, 57.8, 82.1, 113.4, 117.7, 124.6, 126.0, 128.2, 129.4, 130.3, 132.2, 138.9, 158.5.

Anal. Calcd for $C_{17}H_{19}BrO_2$: C, 60.91; H, 5.71. Found: C, 60.76; H, 5.61.



5-Methoxy-2-(2-methoxy-3-phenylpropyl)benzaldehyde (**s14**).

Colorless oil.

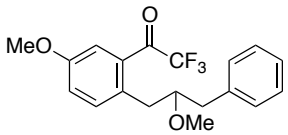
Yield: 92% (synthesized from **s13**).

IR (neat) 3058, 3023, 2931, 2827, 1686, 1607, 1569, 1497, 1454, 1404, 1358, 1327, 1284, 1261, 1193, 1163, 1100, 1038, 934, 873 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.77 (dd, 1H, *J* = 5.7, 13.5 Hz), 2.89 (dd, 1H, *J* = 6.6, 13.5 Hz), 3.02–3.15 (m, 2H), 3.11 (s, 3H), 3.38–3.55 (m, 1H), 3.85 (s, 3H), 7.06 (dd, 1H, *J* = 2.7, 8.7 Hz), 7.12–7.39 (m, 7H), 10.1 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 36.0, 40.5, 55.4, 57.9, 83.7, 113.0, 120.7, 126.2, 128.3, 129.4, 133.2, 134.2, 135.2, 138.5, 158.3, 191.9.

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.24; H, 6.88.



2,2,2-Trifluoro-1-(5-methoxy-2-(2-methoxy-3-phenylpropyl)phenyl)ethanone (**1c**).

Colorless oil.

Yield: 51% (synthesized from **s14**).

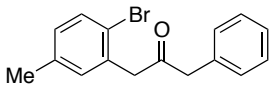
IR (neat) 3060, 3029, 2936, 2831, 1736, 1610, 1573, 1504, 1455, 1410, 1339, 1286, 1243, 1203, 1142, 1096, 1043, 963, 854 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 (dd, 1H, J = 5.7, 13.8 Hz), 2.83 (dd, 1H, J = 6.6, 13.8 Hz), 2.87–3.01 (m, 2H), 3.08 (s, 3H), 3.38–3.50 (m, 1H), 3.83 (s, 3H), 7.04 (dd, 1H, J = 2.4, 7.8 Hz), 7.13–7.38 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 36.9, 40.3, 55.4, 57.6, 83.2, 114.3, 116.5 (q, J_{C-F} = 290.4 Hz), 118.4, 126.1, 128.2, 129.4, 131.9, 132.9, 133.8, 138.6, 157.5, 183.3 (q, J_{C-F} = 34.1 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 89.8(s, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_3$: C, 64.77; H, 5.44. Found: C, 64.86; H, 5.19.



1-(2-Bromo-5-methylphenyl)-3-phenylpropan-2-one (**s15**).

White solid.

Yield: 59% (synthesized from 1-bromo-2-(bromomethyl)-4-methylbenzene[3]).

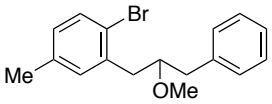
Mp. 58–60 °C.

IR (KBr) 3087, 3062, 3028, 2945, 2920, 1714, 1497, 1454, 1412, 1343, 1335, 1324, 1306, 1281, 1234, 1061, 1025, 896 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 3.78 (s, 2H), 3.84 (s, 2H), 6.94 (brs, 2H), 7.17–7.37 (m, 6H), 7.42 (d, 1H, J = 8.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 49.3, 49.8, 121.6, 127.1, 128.7, 129.6, 129.8, 132.5, 132.6, 133.9, 134.1, 137.5, 204.7.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.53; H, 5.15.



1-Bromo-2-(2-methoxy-3-phenylpropyl)-4-methylbenzene (**s16**).

Colorless oil.

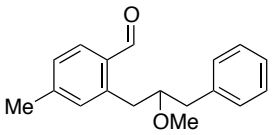
Yield: 89% (synthesized from **s15**).

IR (neat) 3085, 3060, 3027, 2976, 2925, 2824, 1602, 1495, 1473,1354, 1399, 1360, 1233, 1182, 1163, 1132, 1101, 1079, 1025, 807 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.77–2.95 (m, 4H), 3.19 (s, 3H), 3.68–3.78 (m, 1H), 6.89 (dd, 1H, *J* = 2.0, 8.4 Hz), 7.07 (d, 1H, *J* = 2.0 Hz), 7.18–7.33 (m, 5H), 7.39 (d, 1H, *J* = 8.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 40.6, 40.9, 57.8, 81.8, 121.2, 126.1, 128.2, 128.7, 129.4, 132.4, 132.8, 137.0, 138.0, 138.9.

Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.96; H, 6.00. Found: C, 64.17; H, 5.87.



2-(2-Methoxy-3-phenylpropyl)-4-methylbenzaldehyde (**s17**).

Colorless oil.

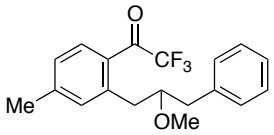
Yield: 70% (synthesized from **s16**).

IR (neat) 3085, 3061, 3027, 2975, 2929, 2874, 2827, 2734, 1691, 1608, 1584, 1569, 1496, 1454, 1400, 1360, 1304, 1292, 1259, 1234, 1211, 1200, 1099, 1079, 1065, 1031, 1019, 1002, 950 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.81 (dd, 1H, *J* = 5.6, 14.0 Hz), 2.88 (dd, 1H, *J* = 6.4, 14.0 Hz), 3.11 (3H), 3.09–3.16 (m, 2H), 3.52–3.62 (m, 1H), 7.06 (s, 1H), 7.15–7.35 (m, 6H), 7.73 (d, 1H, *J* = 8.0 Hz), 10.11 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 37.4, 40.6, 57.9, 83.3, 126.2, 127.6, 128.2, 129.4, 131.9, 132.1, 132.9, 138.7, 141.7, 144.3, 192.2.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.67; H, 7.74.



2,2,2-Trifluoro-1-(2-(2-methoxy-3-phenylpropyl)-4-methylphenyl)ethanone (**1d**).

Colorless oil.

Yield: 70% (synthesized from **s17**).

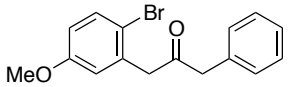
IR (neat) 3028, 2931, 2829, 2718, 1711, 1610, 1564, 1496, 1454, 1360, 1324, 1193, 1141, 1120, 1098, 961 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.77 (dd, 1H, J = 5.6, 13.6 Hz), 2.84 (dd, 1H, J = 6.8, 13.6 Hz), 2.95–3.08 (m, 2H), 3.07 (s, 3H), 3.47–3.56 (m, 1H), 7.08–7.32 (m, 7H), 7.54 (d, 1H, J = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 38.5, 40.6, 57.8, 83.0, 116.4 (q, J_{C-F} = 291.7 Hz), 126.1, 127.0, 127.8, 128.2, 129.4, 129.8 (q, J_{C-F} = 3.8 Hz), 134.0, 138.7, 142.3, 144.5, 182.7 (q, J_{C-F} = 33.4 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 90.4 (s, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_2$: C, 67.85; H, 5.69. Found: C, 67.91; H, 5.46.



1-(2-Bromo-5-methoxyphenyl)-3-phenylpropan-2-one (**s18**).

Yellow oil.

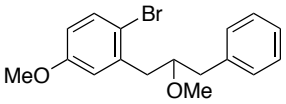
Yield: 53% (synthesized from commercially available, 1-bromo-2-(bromomethyl)-4-methoxybenzene).

IR (neat) 3081, 3031, 3000, 2038, 2839, 1715, 1596, 1573, 1473, 1404, 1338, 1306, 1251, 1161, 1065, 1015, 919, 865, 818 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.79 (s, 2H), 3.84 (s, 2H), 6.66–6.74 (m, 2H), 7.17–7.36 (m, 5H), 7.44 (d, 1H, J = 8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 49.4, 49.7, 55.4, 114.7, 115.3, 117.2, 127.1, 128.7, 129.5, 133.3, 133.8, 135.3, 158.9, 204.4.

Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.54; H, 4.95.



1-Bromo-4-methoxy-2-(2-methoxy-3-phenylpropyl)benzene (**s19**).

Yellow oil.

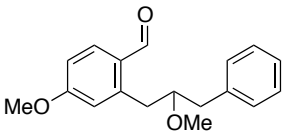
Yield: 99% (synthesized from **s18**).

IR (neat) 3031, 2930, 2831, 1592, 1565, 1473, 1288, 1241, 1166, 1100, 1027, 1008, 796 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.78–2.99 (m, 4H), 3.20 (s, 3H), 3.61–3.80 (m, 1H), 3.77 (s, 3H), 6.65 (d, 1H, *J* = 2.7, 8.7 Hz), 6.83 (d, 1H, *J* = 2.7 Hz), 7.19–7.32 (m, 5H), 7.40 (d, 1H, *J* = 8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 41.2, 55.4, 57.8, 81.8, 113.7, 115.1, 117.4, 126.1, 128.2, 129.4, 133.1, 138.8, 139.4, 158.6.

Anal. Calcd for $C_{17}H_{19}BrO_2$: C, 60.91; H, 5.71. Found: C, 61.17; H, 5.46.



4-Methoxy-2-(2-methoxy-3-phenylpropyl)benzaldehyde (**s20**).

Yellow oil.

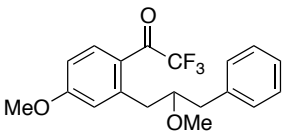
Yield: 78% (synthesized from **s19**).

IR (neat) 3085, 3058, 3027, 2931, 2835, 1685, 1600, 1567, 1496, 1455, 1408, 1358, 1327, 1292, 1249, 1207, 1162, 1101, 1031, 938 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.78–2.95 (m, 2H), 3.07–3.24 (m, 2H), 3.12 (s, 3H), 3.55–3.68 (m, 1H), 3.85 (s, 3H), 6.76 (d, 1H, *J* = 2.4Hz), 6.87 (dd, 1H, *J* = 2.4, 8.0 Hz), 7.17–7.36 (m, 5H), 7.79 (d, 1H, *J* = 8.0 Hz), 10.00 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.7, 40.6, 55.4, 57.9, 83.2, 112.0, 117.4, 126.2, 127.9, 128.2, 129.4, 134.6, 138.6, 144.4, 163.4, 191.1.

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.93; H, 7.09. Found: C, 76.78; H, 6.92.



2,2,2-Trifluoro-1-(4-methoxy-2-(2-methoxy-3-phenylpropyl)phenyl)ethanone (**1e**).

Colorless oil.

Yield: 53% (synthesized from **s20**).

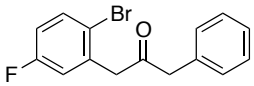
IR (neat) 3088, 3063, 3029, 2935, 2831, 1701, 1605, 1564, 1496, 1456, 1427, 1338, 1314, 1260, 1192, 1141, 1119, 1104, 956, 917, 822 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.78–2.92 (m, 2H), 3.02 (dd, 1H, J = 8.0, 13.2 Hz), 3.08 (s, 3H), 3.15 (dd, 1H, J = 3.6, 13.2 Hz), 3.54–3.62 (m, 1H), 3.84 (s, 3H), 6.82–6.88 (m, 2H), 7.18–7.33 (m, 5H), 7.87 (d, 1H, J = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 40.7, 55.5, 58.0, 82.6, 111.6, 116.7 (q, J_{C-F} = 290.8 Hz), 119.0, 122.2, 126.1, 128.2, 129.5, 133.2 (q, J_{C-F} = 3.8 Hz), 146.5, 163.5, 180.8 (q, J_{C-F} = 32.4 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 90.3 (s, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_3$: C, 64.77; H, 5.44. Found: C, 64.53; H, 5.71.



1-(2-Bromo-5-fluorophenyl)-3-phenylpropan-2-one (**s21**).

White solid.

Yield: 49% (synthesized from commercially available, 1-bromo-2-(bromomethyl)-4-fluorobenzene).

Mp. 69–71 °C.

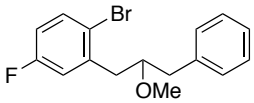
IR (KBr) 3080, 3061, 3029, 2923, 1712, 1603, 1580, 1498, 1472, 1454, 1418, 1406, 1335, 1306, 1267, 1236, 1154, 1104, 1059, 1031, 862 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 2H), 3.86 (s, 2H), 6.82–6.93 (m, 2H), 7.17–7.39 (m, 5H), 7.45–7.55 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 49.0, 50.0, 116.0 (d, J_{C-F} = 21.9 Hz), 118.7 (d, J_{C-F} = 22.9 Hz), 119.1, 127.3, 128.8, 129.5, 133.6, 133.9 (d, J_{C-F} = 7.6 Hz), 136.5 (d, J_{C-F} = 2.3 Hz), 161.8 (d, J_{C-F} = 246.0 Hz), 203.6.

^{19}F NMR (283 MHz, $CDCl_3$) δ 46.9 (m, 1F).

Anal. Calcd for $C_{15}H_{12}BrFO$: C, 58.65; H, 3.95. Found: C, 58.86; H, 4.16.



1-Bromo-4-fluoro-2-(2-methoxy-3-phenylpropyl)benzene (**s22**).

Yellow oil.

Yield: 94% (synthesized from **s21**).

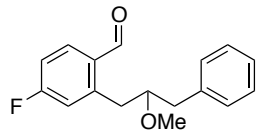
IR (neat) 3086, 3063, 3028, 2979, 2929, 2826, 1605, 1579, 1496, 1470, 1455, 1437, 1409, 1361, 1274, 1237, 1180, 1154, 1100, 1080, 1066, 1031, 955 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.74–2.98 (m, 4H), 3.20 (s, 3H), 3.62–3.73 (m, 1H), 6.81 (ddd, 1H, J = 2.8, 8.4, 8.4 Hz), 7.01 (d, 1H, J = 2.8, 9.2 Hz), 7.18–7.33 (m, 5H), 7.40 (dd, 1H, J = 5.6, 8.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.5, 40.9, 57.8, 81.6, 115.0 (d, J_{C-F} = 21.9 Hz), 118.7 (d, J_{C-F} = 22.0 Hz), 126.2, 128.3, 129.4, 133.6 (d, J_{C-F} = 8.6 Hz), 138.5, 140.7 (d, J_{C-F} = 6.7 Hz), 161.7 (d, J_{C-F} = 245.0 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 46.2 (m, 1F).

Anal. Calcd for $C_{16}H_{16}BrFO$: C, 59.46; H, 4.99. Found: C, 59.63; H, 5.27.



4-Fluoro-2-(2-methoxy-3-phenylpropyl)benzaldehyde (**s23**).

Yellow oil.

Yield: 79% (synthesized from **s22**).

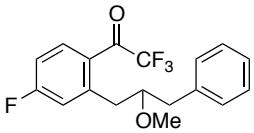
IR (neat) 3086, 3062, 3028, 2978, 2932, 2878, 2829, 1582, 1493, 1454, 1400, 1360, 1314, 1281, 1244, 1195, 1153, 1101, 1064, 1031, 1007, 966 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.81 (dd, 1H, J = 6.0, 14.0 Hz), 2.93 (dd, 1H, J = 6.0, 14.0 Hz), 3.05–3.22 (m, 2H), 3.12 (s, 3H), 3.52–3.60 (m, 1H), 6.96 (dd, 1H, J = 2.0, 9.6 Hz), 7.05 (ddd, 1H, J = 2.4, 8.4, 8.4 Hz), 7.18–7.35 (m, 5H), 7.85 (dd, 1H, J = 6.0, 8.4 Hz), 10.07 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.1, 40.5, 57.8, 83.1, 114.0 (d, J_{C-F} = 21.9 Hz), 118.8 (d, J_{C-F} = 22.0 Hz), 126.4, 128.4, 129.4, 131.1 (d, J_{C-F} = 2.0 Hz), 133.9 (d, J_{C-F} = 9.5 Hz), 138.2, 145.3 (d, J_{C-F} = 9.5 Hz), 165.4 (d, J_{C-F} = 254.6 Hz), 190.8.

^{19}F NMR (283 MHz, $CDCl_3$) δ 57.4 (m, 1F).

Anal. Calcd for $C_{17}H_{17}FO_2$: C, 74.98; H, 6.29. Found: C, 74.75; H, 6.07.



2,2,2-Trifluoro-1-(4-fluoro-2-(2-methoxy-3-phenylpropyl)phenyl)ethanone (**1f**).

Yellow oil.

Yield: 57% (synthesized from **s23**).

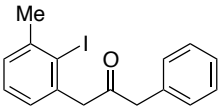
IR (neat) 3087, 3064, 3029, 2932, 2831, 1733, 1716, 1607, 1583, 1496, 1455, 1417, 1328, 1295, 1202, 1185, 1144, 1102, 974, 919, 883, 825, 776, 740 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (dd, 1H, J = 6.4, 13.6 Hz), 2.89 (dd, 1H, J = 6.4, 13.6 Hz), 3.01–3.07 (m, 2H), 3.09 (s, 3H), 3.46–3.55 (m, 1H), 7.01–7.09 (m, 2H), 7.18–7.36 (m, 5H), 7.78–7.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 38.2, 40.3, 57.7, 82.7, 113.5 (d, J_{C-F} = 21.9 Hz), 116.3 (q, J_{C-F} = 290.8 Hz), 120.1 (d, J_{C-F} = 21.9 Hz), 126.3, 127.2 (d, J_{C-F} = 2.9 Hz), 128.4, 129.3, 132.0 (m), 138.2, 146.1 (d, J_{C-F} = 9.5 Hz), 165.0 (d, J_{C-F} = 255.5 Hz), 182.0 (q, J_{C-F} = 34.3 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 58.2 (m, 1F), 90.1 (s, 3F).

Anal. Calcd for $C_{18}H_{16}F_4O_2$: C, 63.53; H, 4.74. Found: C, 64.46; H, 4.56.



1-(2-Iodo-3-methylphenyl)-3-phenylpropan-2-one (**s24**).

Brown solid.

Yield: 51% (synthesized from 1-(bromomethyl)-2-iodo-3-methylbenzene[4]).

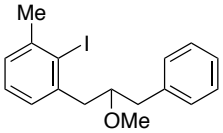
Mp. 49–51 °C.

IR (neat) 3061, 3028, 1718, 1600, 1577, 1496, 1455, 1404, 1381, 1327, 1162, 1089, 1057, 1008, 761 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.79 (s, 2H), 3.96 (s, 2H), 6.92 (d, 1H, J = 7.2 Hz), 7.05–7.42 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 29.9, 50.0, 55.0, 108.5, 127.0, 127.8, 128.2, 128.4, 128.6, 129.6, 133.8, 138.9, 142.6, 204.6.

Anal. Calcd for $C_{16}H_{15}IO$: C, 54.88; H, 4.32. Found: C, 54.71; H, 4.61.



2-Iodo-1-(2-methoxy-3-phenylpropyl)-3-methylbenzene (**s25**).

Yellow oil.

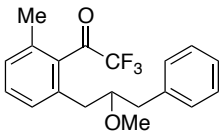
Yield: 96% (synthesized from **s24**).

IR (neat) 3058, 3027, 2973, 2925, 2819, 1596, 1565, 1493, 1456, 1400, 1358, 1177, 1100, 1023, 1008, 780 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 2.75–2.90 (m, 2H), 2.98–3.06 (m, 2H), 3.17 (s, 3H), 3.67–3.89 (m, 1H), 7.02–7.17 (m, 3H), 7.18–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 40.6, 46.5, 57.9, 81.9, 108.2, 126.1, 127.4, 127.7, 128.2, 128.4, 129.5, 138.9, 142.2, 142.4.

Anal. Calcd for $C_{17}H_{19}IO$: C, 55.75; H, 5.23. Found: C, 55.53; H, 5.11.



2,2,2-Trifluoro-1-(2-(2-methoxy-3-phenylpropyl)-6-methylphenyl)ethanone (**1g**).

Colorless oil.

Yield: 33% (synthesized from **s25**).

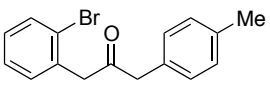
IR (neat) 3064, 3028, 2932, 2829, 1739, 1594, 1496, 1455, 1361, 1306, 1245, 1205, 1179, 1152, 1104, 1032, 930, 787 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.52–2.77 (m, 3H), 2.83 (dd, 1H, J = 6.4, 13.6 Hz), 3.12 (s, 3H), 3.42–3.51 (m, 1H), 7.08–7.35 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 38.1, 40.4, 57.5, 83.2, 115.4 (q, J_{C-F} = 290.8 Hz), 126.2, 128.3, 128.5, 129.3, 130.5, 134.6, 135.0, 136.9, 138.3, 191.0 (q, J_{C-F} = 36.2 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 85.7 (m, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_2$: C, 67.85; H, 5.69. Found: C, 67.69; H, 5.76.



1-(2-Bromophenyl)-3-(*p*-tolyl)propan-2-one (**s26**).

Yellow solid.

Yield: 46% (synthesized from **s2** and methyl 2-(*p*-tolyl)acetate).

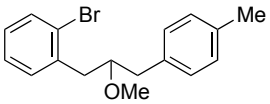
Mp. 41–43 °C.

IR (KBr) 3052, 3021, 2920, 1720, 1569, 1515, 1471, 1441, 1409, 1328, 1210, 1186, 1161, 1118, 1058, 1028 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.73 (s, 2H), 3.87 (s, 2H), 7.05–7.20 (m, 6H), 7.25 (dd, 1H, J = 7.5, 7.5 Hz), 7.55 (d, 1H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 49.1, 49.3, 125.0, 127.5, 128.7, 129.4, 129.4, 130.7, 131.8, 132.8, 134.6, 136.7, 204.6.

Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.17; H, 4.84.



1-Bromo-2-(2-methoxy-3-(*p*-tolyl)propyl)benzene (**s27**).

Yellow oil.

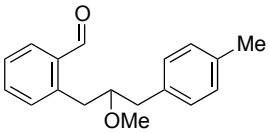
Yield: 78% (synthesized from **s26**).

IR (neat) 3051, 3019, 3004, 2976, 2925, 2825, 1566, 1515, 1471, 1439, 1361, 1204, 1182, 1159, 1099, 1066, 1045, 1026 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.71–2.85 (m, 2H), 2.86–3.00 (m, 2H), 3.19 (s, 3H), 3.65–3.76 (m, 1H), 7.02–7.15 (m, 5H), 7.17–7.32 (m, 2H), 7.27 (dd, 1H, J = 1.2, 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 40.1, 40.9, 81.9, 124.7, 127.2, 127.8, 128.9, 129.3, 132.0, 132.7, 135.5, 135.7, 138.6.

Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.96; H, 6.00. Found: C, 63.75; H, 6.24.



2-(2-Methoxy-3-(*p*-tolyl)propyl)benzaldehyde (**s28**).

Colorless oil.

Yield: 84% (synthesized from **s27**).

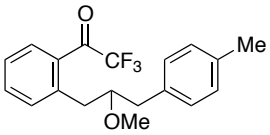
IR (neat) 3048, 3021, 3004, 2929, 2827, 2734, 1695, 1600, 1574, 1515, 1486, 1452, 1402, 1360, 1290, 1208, 1160, 1097, 1023, 957, 883 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.76 (dd, 1H, J = 5.7, 14.4 Hz), 2.86 (dd,

1H, *J* = 6.3, 14.4 Hz), 3.10 (s, 3H), 3.10–3.18 (m, 2H), 3.47–3.59 (m, 1H), 7.05–7.17 (m, 4H), 7.27 (d, 1H, *J* = 7.5 Hz), 7.38 (ddd, 1H, *J* = 1.2, 7.5, 7.5 Hz), 7.49 (ddd, 1H, *J* = 1.6, 7.5, 7.5 Hz), 7.84 (dd, 1H, *J* = 1.6, 7.5 Hz), 10.2 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 37.1, 40.1, 57.8, 83.5, 126.8, 129.0, 129.3, 131.1, 132.1, 133.4, 134.4, 135.4, 135.7, 141.9, 192.5.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.76; H, 7.79.



2,2,2-Trifluoro-1-(2-(2-methoxy-3-(*p*-tolyl)propyl)phenyl)ethanone (**1h**).

Colorless oil.

Yield: 35% (synthesized from **s28**).

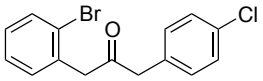
IR (neat) 3048, 3022, 3003, 2982, 2930, 2830, 1734, 1717, 1602, 1572, 1516, 1492, 1448, 1360, 1323, 1288, 1186, 1143, 1098, 1065, 952 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.67 (dd, 1H, *J* = 6.0, 13.6 Hz), 2.82 (dd, 1H, *J* = 6.8, 13.6 Hz), 2.95–3.09 (m, 2H), 3.08 (s, 3H), 3.39–3.49 (m, 1H), 7.05–7.13 (m, 4H), 7.30 (d, 1H, *J* = 8.0 Hz), 7.35 (ddd, 1H, *J* = 1.6, 8.0, 8.0 Hz), 7.50 (ddd, 1H, *J* = 1.6, 8.0, 8.0 Hz), 7.72–7.79 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 38.1, 40.4, 57.5, 83.2, 115.4 (q, J_{C-F} = 290.8 Hz), 126.2, 128.3, 128.5, 129.3, 130.5, 134.6, 135.0, 136.9, 138.3, 191.0 (q, J_{C-F} = 36.2 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 89.9 (s, 3F).

Anal. Calcd for $C_{19}H_{19}F_3O_2$: C, 67.85; H, 5.69. Found: C, 67.95; H, 5.47.



1-(2-Bromophenyl)-3-(4-chlorophenyl)propan-2-one (**s29**).

White solid.

Yield: 31% (synthesized from **s2** and methyl 2-(4-chlorophenyl)acetate).

Mp. 69–71 °C.

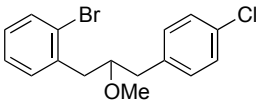
IR (KBr) 3088, 3063, 3044, 3029, 2930, 2906, 1889, 1726, 1491, 1473, 1446, 1420, 1401, 1338, 1317, 1301, 1295, 1093, 1055, 1027, 1016 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 2H), 3.89 (s, 2H), 7.08–7.19 (m, 3H), 7.23–7.34

(m, 4H), 7.57 (d, 1H, J = 8.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 48.7, 49.5, 125.0, 127.6, 128.8, 129.0, 130.9, 131.8, 132.2, 132.9, 133.1, 134.3, 203.8.

Anal. Calcd for $C_{15}H_{12}BrClO$: C, 55.67; H, 3.74. Found: C, 55.39; H, 3.63.



1-Bromo-2-(3-(4-chlorophenyl)-2-methoxypropyl)benzene (**s30**).

Yellow oil.

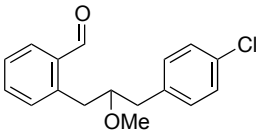
Yield: 95% (synthesized from **s29**).

IR (neat) 3056, 3026, 2978, 2927, 2826, 1596, 1567, 1492, 1472, 1440, 1407, 1361, 1180, 1100, 1067, 1045, 1026, 1016, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (d, 2H, J = 6.4 Hz), 2.88 (dd, 1H, J = 5.6, 14.0 Hz), 2.95 (dd, 1H, J = 7.6, 14.0 Hz), 3.18 (s, 3H), 3.65–3.73 (m, 1H), 7.14 (d, 1H, J = 8.0 Hz), 7.21–7.27 (m, 6H), 7.53 (d, 1H, J = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 40.9, 57.9, 81.6, 124.6, 127.2, 128.0, 128.3, 130.8, 131.9, 132.0, 132.8, 137.3, 138.2.

Anal. Calcd for $C_{16}H_{16}BrClO$: C, 56.58; H, 4.75. Found: C, 56.41; H, 4.85.



2-(3-(4-Chlorophenyl)-2-methoxypropyl)benzaldehyde (**s31**).

Colorless oil.

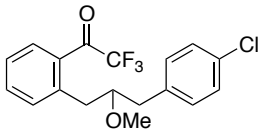
Yield: 82% (synthesized from **s30**).

IR (neat) 3065, 3027, 2977, 2930, 2828, 2736, 1696, 1600, 1574, 1492, 1452, 1407, 1361, 1290, 1209, 1192, 1160, 1091, 1016, 885 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (d, 2H, J = 6.0 Hz), 3.08 (s, 3H), 3.08–3.19 (m, 2H), 3.48–3.57 (m, 1H), 7.15 (d, 2H, J = 8.4 Hz), 7.22–7.32 (m, 3H), 7.41 (dd, 1H, J = 7.6, 7.6 Hz), 7.51 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.83 (dd, 1H, J = 1.2, 7.6 Hz), 10.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 40.0, 58.0, 83.0, 126.9, 128.3, 130.8, 130.8, 132.1, 132.3, 133.4, 134.4, 137.1, 141.4, 192.7.

Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.71; H, 5.93. Found: C, 70.85; H, 6.14.



1-(2-(3-(4-Chlorophenyl)-2-methoxypropyl)phenyl)-2,2,2-trifluoroethanone (**1i**).

Colorless oil.

Yield: 28% (synthesized from **s31**).

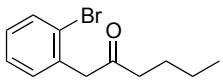
IR (neat) 3067, 3029, 2986, 2934, 2831, 1734, 1717, 1602, 1572, 1492, 1448, 1408, 1361, 1324, 1288, 1256, 1186, 1142, 1091, 1066, 1016, 953 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.72 (dd, 1H, J = 5.2, 14.0 Hz), 2.78 (dd, 1H, J = 6.8, 14.0 Hz), 2.93–3.09 (m, 2H), 3.05 (s, 3H), 3.42–3.52 (m, 1H), 7.14 (d, 2H, J = 8.0 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.31 (d, 1H, J = 8.0 Hz), 7.38 (dd, 1H, J = 8.0, 8.0 Hz), 7.52 (dd, 1H, J = 8.0, 8.0 Hz), 7.79 (d, 1H, J = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 38.1, 39.8, 57.8, 82.9, 116.3 (q, J_{C-F} = 290.8 Hz), 126.4, 128.4, 129.1 (q, J_{C-F} = 3.8 Hz), 130.8, 131.0, 132.0, 133.0, 133.2, 137.1, 141.4, 183.4 (q, J_{C-F} = 34.4 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 90.0 (s, 3F).

Anal. Calcd for $C_{18}H_{16}ClF_3O_2$: C, 60.60; H, 4.52. Found: C, 60.38; H, 4.79.



1-(2-Bromophenyl)hexan-2-one (**s32**).

Yellow oil.

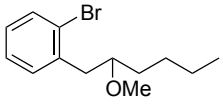
Yield: 63% (synthesized from **s2** and methyl pentanoate).

IR (neat) 3058, 3017, 2957, 2932, 2872, 1718, 1593, 1569, 1471, 1441, 1411, 1379, 1365, 1343, 1329, 1277, 1125, 1091, 1053, 1026, 945 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7.2 Hz), 1.22–1.40 (m, 2H), 1.50–1.67 (m, 2H), 2.50 (t, 2H, J = 7.2 Hz), 3.85 (s, 2H), 7.13 (ddd, 1H, J = 2.1, 7.8, 7.8 Hz), 7.18–7.33 (m, 2H), 7.57 (d, 1H, J = 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.2, 25.8, 42.2, 49.9, 125.0, 127.5, 128.7, 131.7, 132.8, 134.8, 207.1.

Anal. Calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93. Found: C, 56.37; H, 6.16.



1-Bromo-2-(2-methoxyhexyl)benzene (**s33**).

Red oil.

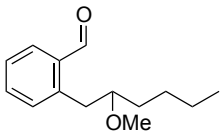
Yield: 88% (synthesized from **s32**).

IR (neat) 3057, 2956, 2930, 2871, 2860, 2823, 1567, 1471, 1439, 1378, 1362, 1181, 1132, 1093, 1046, 1026, 976 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.8 Hz), 1.25–1.57 (m, 6H), 2.84 (dd, 1H, *J* = 5.6, 14.0 Hz), 2.98 (dd, 1H, *J* = 6.8, 14.0 Hz), 3.29 (s, 3H), 3.42–3.50 (m, 1H), 7.07 (ddd, 1H, *J* = 1.6, 8.0, 8.0 Hz), 3.20–3.29 (m, 2H), 7.53 (d, 1H, *J* = 8.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.8, 27.5, 33.6, 40.8, 57.2, 80.5, 124.7, 127.1, 127.8, 132.0, 132.7, 138.7.

Anal. Calcd for $C_{13}H_{19}BrO$: C, 57.57; H, 7.06. Found: C, 57.81; H, 6.87.



2-(2-Methoxyhexyl)benzaldehyde (**s34**).

Colorless oil.

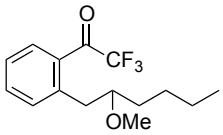
Yield: 84% (synthesized from **s33**).

IR (neat) 3067, 3022, 2931, 2860, 2826, 2732, 1701, 1601, 1574, 1478, 1453, 1401, 1378, 1360, 1129, 1209, 1193, 1160, 1129, 1093, 987 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, *J* = 7.2 Hz), 1.26–1.68 (m, 6H), 3.12 (dd, 1H, *J* = 4.8, 13.2 Hz), 3.19 (s, 3H), 3.17–3.28 (m, 1H), 3.29–3.37 (m, 1H), 7.31 (d, 1H, *J* = 8.0 Hz), 7.39 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.51 (ddd, 1H, *J* = 1.2, 8.0, 8.0 Hz), 7.85 (dd, 1H, *J* = 1.2, 8.0 Hz), 10.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.8, 27.4, 33.8, 37.2, 57.4, 57.7, 126.7, 131.5, 132.2, 133.4, 134.4, 141.9, 192.5.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.04; H, 9.38.



2,2,2-Trifluoro-1-(2-(2-methoxyhexyl)phenyl)ethanone (**1j**).

Colorless oil.

Yield: 62% (synthesized from **s34**).

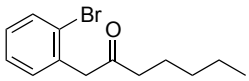
IR (neat) 3068, 3028, 2958, 2934, 2874, 2862, 2830, 1734, 1817, 1602, 1572, 1492, 1467, 1449, 1379, 1360, 1323, 1289, 1186, 1146, 1089, 991 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.2 Hz), 1.22–1.58 (m, 6H), 2.95–3.15 (m, 2H), 3.15 (s, 3H), 3.17–3.28 (m, 1H), 7.33–7.41 (m, 2H), 7.53 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.77 (d, 1H, J = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.8, 27.3, 33.5, 38.0, 57.2, 81.8, 116.3 (q, J_{C-F} = 290.8 Hz), 126.2, 129.0 (q, J_{C-F} = 2.8 Hz), 131.0, 133.1, 133.1, 141.9, 183.4 (q, J_{C-F} = 34.3 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 90.0 (s, 3F).

Anal. Calcd for $C_{15}H_{19}F_3O_2$: C, 62.49; H, 6.64. Found: C, 62.22; H, 6.73.



1-(2-Bromophenyl)heptan-2-one (**s35**).

Yellow oil.

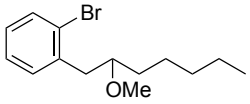
Yield: 49% (synthesized from **s2** and methyl hexanoate).

IR (neat) 3058, 2956, 2930, 2871, 2859, 1718, 1569, 1470, 1441, 1411, 1362, 1324, 1125, 1059, 1026 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.2 Hz), 1.21–1.33 (m, 4H), 1.55–1.68 (m, 2H), 2.49 (t, 2H, J = 7.2 Hz), 3.85 (s, 2H), 7.14 (ddd, 1H, J = 1.5, 8.1, 8.1 Hz), 7.18 (dd, 1H, J = 1.5, 8.1 Hz), 7.29 (ddd, 1H, J = 1.5, 8.1, 8.1 Hz), 7.57 (dd, 1H, J = 1.5, 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.4, 23.4, 31.3, 42.5, 50.0, 125.0, 127.5, 128.7, 131.7, 132.8, 134.8, 207.2.

Anal. Calcd for $C_{13}H_{17}BrO$: C, 58.01; H, 6.37. Found: C, 57.94; H, 6.33.



1-Bromo-2-(2-methoxyheptyl)benzene (**s36**).

Colorless oil.

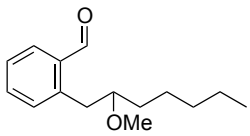
Yield: 97% (synthesized from **s35**).

IR (neat) 3057, 2955, 2930, 2871, 2858, 2823, 1736, 1567, 1471, 1440, 1377, 1360, 1297, 1239, 1184, 1132, 1096, 1046, 1026, 942 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.2 Hz), 1.21–1.35 (m, 4H), 1.41–1.54 (m, 4H), 2.83 (dd, 1H, *J* = 6.0, 13.5 Hz), 3.00 (dd, 1H, *J* = 6.9, 13.5 Hz), 3.29 (s, 3H), 3.41–3.53 (m, 1H), 7.03–7.12 (m, 1H), 7.18–7.30 (m, 2H), 7.53 (dd, 1H, *J* = 8.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.0, 32.0, 33.9, 40.8, 57.2, 80.6, 124.7, 127.1, 127.8, 132.0, 132.7, 138.6.

Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42. Found: C, 59.11; H, 7.56.



2-(2-Methoxyheptyl)benzaldehyde (**s37**).

Colorless oil.

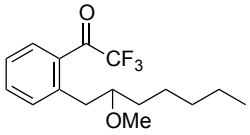
Yield: 68% (synthesized from **s36**).

IR (neat) 3067, 3022, 2954, 2931, 2871, 2859, 2826, 2730, 1699, 1601, 1574, 1488, 1453, 1401, 1377, 1359, 1290, 1209, 1192, 1160, 1129, 1097 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.2 Hz), 1.20–1.62 (m, 8H), 3.10 (dd, 1H, *J* = 4.8, 12.8 Hz), 3.17–3.28 (m, 1H), 3.20 (s, 3H), 3.28–3.38 (m, 1H), 7.31 (d, 1H, *J* = 8.0 Hz), 7.39 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.51 (dd, 1H, *J* = 1.2, 8.0, 8.0 Hz), 7.85 (dd, 1H, *J* = 1.2, 8.0 Hz), 12.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.0, 31.9, 34.1, 37.2, 57.4, 82.2, 126.7, 131.5, 132.3, 133.4, 134.4, 142.0, 192.6.

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.75; H, 9.62.



2,2,2-Trifluoro-1-(2-(2-methoxyheptyl)phenyl)ethanone (**1k**).

Colorless oil.

Yield: 55% (synthesized from **s37**).

IR (neat) 3068, 2956, 2933, 2861, 2830, 1734, 1718, 1602, 1572, 1492, 1449, 1378, 1360, 1323, 1288, 1201, 1186, 1144, 1091, 938 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7.2 Hz), 1.18–1.58 (m, 8H), 2.95–3.18 (m, 2H), 3.15 (s, 3H), 3.18–3.28 (m, 1H), 7.33–7.41 (m, 2H), 7.53 (dd, 1H, J = 7.6, 7.6 Hz), 7.77 (d, 1H, J = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.8, 24.9, 32.0, 33.8, 38.0, 57.2, 81.8, 116.3 (q, J_{C-F} = 291.8 Hz), 126.2, 129.1, 131.0, 133.1, 133.1, 141.9, 183.5 (q, J_{C-F} = 34.3 Hz).

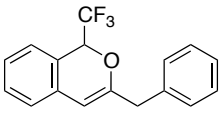
^{19}F NMR (283 MHz, $CDCl_3$) δ 90.0 (s, 3F).

Anal. Calcd for $C_{16}H_{21}F_3O_2$: C, 63.56; H, 7.00. Found: C, 63.74; H, 7.17.

2. Synthesis of CF_3-substituted isochromene and bicyclo[3.3.1]nonane derivatives.

General Procedure of the formation of CF_3-substituted isochromene and bicyclo[3.3.1]nonane derivatives.

To a solution of CF_3-ketone **1** (0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added $Sc(OTf)_3$ (0.005 mmol, 5 mol%) or Tf_2NH (0.010 mmol, 10 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 CF_3-substituted isochromene **2** and bicyclo[3.3.1]nonane derivatives **3**.



3-Benzyl-1-(trifluoromethyl)-1*H*-isochromene (**2a**).

Colorless amorphous.

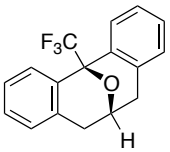
IR (neat) 3067, 3029, 2920, 1663, 1604, 1495, 1456, 1375, 1352, 1265, 1174, 1132, 1112, 1065, 925, 872 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (s, 2H), 5.46 (q, 1H, J = 7.6 Hz), 5.56 (s, 1H), 6.95 (d, 1H, J = 7.6 Hz), 7.08 (d, 1H, J = 7.6 Hz), 7.16 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.23–7.37 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 74.9 (q, J_{C-F} = 32.4 Hz), 120.3, 123.5 (q, J_{C-F} = 285.1 Hz), 123.9, 126.5, 126.6, 126.7, 128.4, 129.2, 129.9, 131.0, 136.5, 154.4.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.8 (d, J = 6.8 Hz).

Anal. Calcd for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.15; H, 4.77.



12-(Trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulene (**3a**).

Colorless crystal (recrystallized from hexane/ether), which was subjected to X-ray analysis.

Mp. 159–161 °C.

IR (KBr) 3061, 2980, 2930, 2904, 2839, 1604, 1493, 1454, 1342, 1311, 1288, 1265, 1211, 1185, 1170, 1156, 1123, 1082, 1042, 1023, 984, 954, 938 cm^{-1}.

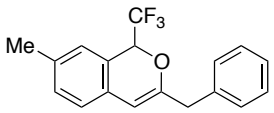
^1H NMR (400 MHz, $CDCl_3$) δ 2.52 (dd, 2H, J = 1.2, 16.8 Hz), 2.46 (dd, 2H, J = 8.0, 16.8 Hz), 4.86–4.95 (m, 1H), 7.08–7.25 (m, 6H), 7.52–7.60 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5, 65.5, 124.0 (q, J_{C-F} = 2.9 Hz), 126.5 (q, J_{C-F} = 290.1 Hz), 126.4, 127.7, 129.7, 133.1, 134.7.

^{13}C NMR (100 MHz, acetone-d6) δ 34.0, 66.2, 77.3 (q, J_{C-F} = 28.6 Hz), 124.6 (q, J_{C-F} = 2.9 Hz), 126.2 (q, J_{C-F} = 282.2 Hz), 127.1, 128.6, 130.7, 134.5, 135.7.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.4 (s, 3F).

Anal. Calcd for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.06; H, 4.44.



3-Benzyl-7-methyl-1-(trifluoromethyl)-1*H*-isochromene (**2b**).

Colorless amorphous.

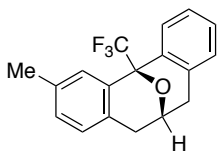
IR (neat) 3087, 3064, 3030, 2924, 2860, 1663, 1604, 1507, 1496, 1455, 1427, 1373, 1347, 1291, 1266, 1248, 1231, 1173, 1153, 1132, 1078, 1071, 1030, 958 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.53 (s, 2H), 5.41 (q, 1H, J = 7.2 Hz), 5.53 (s, 1H), 6.86 (d, 1H, J = 8.0 Hz), 6.90 (s, 1H), 6.99 (d, 1H, J = 8.0 Hz), 7.22–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 39.8, 74.9 (q, J_{C-F} = 32.4 Hz), 100.9, 120.4, 123.5 (q, J_{C-F} = 286.0 Hz), 123.8, 126.7, 127.2, 128.2, 128.4, 129.2, 130.5, 136.4, 136.7, 153.5.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.8 (d, J = 6.8 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 70.93; H, 5.05.



2-Methyl-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulene (**3b**).

White solid.

Mp. 177–179 °C.

IR (KBr) 3065, 3025, 2955, 2925, 2907, 2853, 2837, 1504, 1490, 1453, 1436, 1315, 1288, 1276, 1262, 1220, 1207, 1184, 1167, 1160, 1129, 1118, 1092, 1047, 994 cm^{-1}.

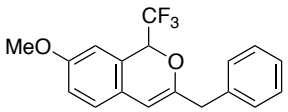
^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.45–2.57 (m, 2H), 3.38–3.59 (m, 2H), 4.85–4.94 (m, 1H), 7.01 (s, 2H), 7.10–7.24 (m, 3H), 7.33 (s, 1H), 7.53–7.62 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 33.4, 65.5, 123.8 (q, J_{C-F} = 2.8 Hz), 124.7 (q, J_{C-F} = 2.9 Hz), 125.0 (q, J_{C-F} = 282.2 Hz), 126.3, 127.7, 128.6, 129.5, 129.6, 129.9, 133.2, 134.2, 135.1, 136.0.

^{13}C NMR (100 MHz, acetone-d6) δ 21.2, 33.8, 33.8, 66.2, 77.3 (q, J_{C-F} = 28.6 Hz), 124.5 (q, J_{C-F} = 2.9 Hz), 125.2 (q, J_{C-F} = 2.9 Hz), 126.2 (q, J_{C-F} = 282.2 Hz), 127.0, 128.5, 129.4, 130.6, 130.6, 131.3, 134.5, 135.3, 136.1, 136.6.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.5 (s, 3F).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 71.28; H, 5.11.



3-Benzyl-7-methoxy-1-(trifluoromethyl)-1*H*-isochromene (**2c**).

Colorless amorphous.

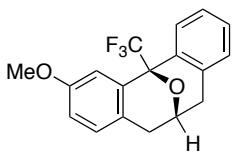
IR (neat) 3064, 3030, 3005, 2919, 1665, 1615, 1578, 1506, 1366, 1455, 1431, 1373, 1347, 1323, 1304, 1293, 1267, 1228, 1172, 1150, 1130, 1037, 953 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 2H), 3.78 (s, 3H), 5.41 (q, 1H, *J* = 7.2 Hz), 5.52 (s, 1H), 6.66 (s, 1H), 6.83 (dd, 1H, *J* = 7.2 Hz), 6.90 (d, 1H, *J* = 2.0, 8.0 Hz), 7.22–7.38 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 55.4, 74.8 (q, J_{C-F} = 31.5 Hz), 100.5, 112.6, 115.0, 121.7, 123.5 (q, J_{C-F} = 285.1 Hz), 125.0, 126.7, 128.4, 129.2, 129.4, 136.8, 152.3, 158.3.

^{19}F NMR (283 MHz, $CDCl_3$) δ 83.1 (d, *J* = 6.8 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.41; H, 4.89.



2-Methoxy-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulen

e (**3c**).

White solid.

Mp. 120–122 °C.

IR (KBr) 3061, 3007, 2953, 2835, 1614, 1584, 1504, 1454, 1435, 1314, 1292, 1242, 1173, 1116, 1087, 1029, 993, 954, 862 cm^{-1}.

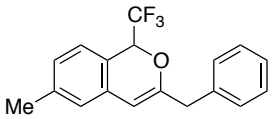
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (dd, 1H, J = 2.0, 16.0 Hz), 2.52 (dd, 1H, J = 2.0, 16.0 Hz), 3.36–3.50 (m, 2H), 3.77 (s, 3H), 4.86–4.95 (m, 1H), 6.77 (dd, 1H, J = 2.4, 8.0 Hz), 7.05 (d, 1H, J = 8.0 Hz), 7.08–7.25 (m, 4H), 7.52–7.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9, 33.4, 55.3, 65.6, 110.2, 113.3, 123.8 (q, J_{C-F} = 2.9 Hz), 124.9, 125.0 (q, J_{C-F} = 290.1 Hz), 126.4, 127.8, 129.6, 130.5, 133.2, 134.7, 135.2, 157.9.

^{13}C NMR (100 MHz, acetone-d6) δ 33.3, 33.8, 55.5, 66.3, 77.3 (q, J_{C-F} = 28.6 Hz), 110.8 (q, J_{C-F} = 2.8 Hz), 113.9, 124.5 (q, J_{C-F} = 2.9 Hz), 126.0, 126.2 (q, J_{C-F} = 282.2 Hz), 127.1, 128.6, 130.6, 131.6, 134.5, 135.8, 136.3, 158.9.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.5 (s, 3F).

Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.74; H, 4.51.



3-Benzyl-6-methyl-1-(trifluoromethyl)-1*H*-isochromene (**2d**).

Colorless amorphous.

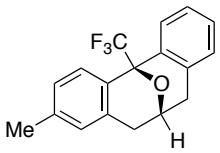
IR (neat) 3030, 2925, 2858, 1664, 1614, 1502, 1455, 1424, 1373, 1348, 1268, 1215, 1173, 1131, 1065, 1030, 939, 884 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.53 (s, 2H), 5.43 (q, 1H, J = 7.2 Hz), 5.51 (s, 1H), 6.78 (s, 1H), 6.81 (s, 2H), 7.23–7.39 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 39.9, 74.8 (q, J_{C-F} = 31.5 Hz), 101.0, 117.5, 123.6 (q, J_{C-F} = 285.1 Hz), 124.6, 126.5, 126.7, 127.2, 128.4, 129.2, 130.8, 136.6, 139.8, 154.4.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.6 (d, J = 7.1 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 71.27; H, 5.21.



3-Methyl-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulene (**3d**).

White solid.

Mp. 53–55 °C.

IR (KBr) 3025, 2925, 2854, 1616, 1490, 1455, 1435, 1316, 1289, 1273, 1172, 1157, 1131, 1086, 1031, 991, 970, 943, 908 cm^{-1}.

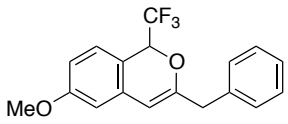
^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.46 (dd, 1H, J = 1.6, 6.4 Hz), 2.52 (dd, 1H, J = 1.6, 6.4 Hz), 3.38–3.52 (m, 2H), 4.85–4.96 (m, 1H), 6.95 (s, 1H), 6.99 (d, 1H, J = 8.4 Hz), 7.08–7.25 (m, 3H), 7.42 (d, 1H, J = 8.4 Hz), 7.53–7.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 33.4, 33.7, 65.5, 123.7 (q, J_{C-F} = 2.9 Hz), 124.1 (q, J_{C-F} = 2.9 Hz), 125.0 (q, J_{C-F} = 290.6 Hz), 126.3, 127.2, 127.6, 129.6, 130.3, 131.5, 132.9, 133.1, 135.2, 137.5.

^{13}C NMR (100 MHz, acetone-d6) δ 20.8, 30.2, 34.1, 66.2, 77.3 (q, J_{C-F} = 28.6 Hz), 124.3 (q, J_{C-F} = 3.9 Hz), 124.7 (q, J_{C-F} = 2.9 Hz), 126.3 (q, J_{C-F} = 282.3 Hz), 127.0, 127.9, 128.5, 130.6, 131.1, 132.6, 134.2, 134.4, 136.2, 138.3.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.4 (s, 3F).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 71.16; H, 4.76.



3-Benzyl-6-methoxy-1-(trifluoromethyl)-1*H*-isochromene (**2e**).

Colorless amorphous.

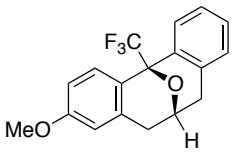
IR (neat) 3064, 3030, 3006, 2934, 2838, 1664, 1606, 1578, 1505, 1496, 1466, 1455, 1433, 1423, 1374, 1349, 1269, 1196, 1170, 1131, 1112, 1065, 1037, 1004, 960 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (s, 2H), 3.78 (s, 3H), 5.42 (q, 1H, J = 7.2 Hz), 5.50 (s, 1H), 6.49 (d, 1H, J = 2.4 Hz), 6.71 (dd, 1H, J = 2.4, 8.4 Hz), 7.01 (d, 1H, J = 7.2 Hz), 7.23–7.38 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 55.2, 77.2 (q, J_{C-F} = 32.4 Hz), 101.0, 109.0, 123.5 (q, J_{C-F} = 285.0 Hz), 126.7, 127.8, 128.4, 129.2, 132.4, 136.5, 154.8, 160.8.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.3 (d, J = 6.8 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.64; H, 4.56.



3-Methoxy-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulen e (**3e**).

Colorless oil.

IR (neat) 3067, 3005, 2954, 2838, 1710, 1578, 1502, 1466, 1455, 1433, 1356, 1326, 1305, 1280, 1255, 1171, 1124, 1111, 1086, 1043, 1029, 991, 969, 941, 897 cm^{-1}.

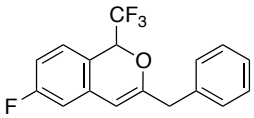
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47–2.57 (m, 2H), 2.46 (dd, 2H, J = 7.2, 16.8 Hz), 3.75 (s, 3H), 4.85–4.95 (m, 1H), 6.66 (s, 1H), 6.73 (dd, 1H, J = 2.4, 8.4 Hz), 7.10–7.25 (m, 3H), 7.43 (d, 1H, J = 8.4 Hz), 7.52–7.59 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 33.2, 34.2, 55.2, 63.3, 113.2, 114.5, 123.5 (q, J_{C-F} = 2.6 Hz), 125.6 (q, J_{C-F} = 2.6 Hz), 125.0 (q, J_{C-F} = 290.0 Hz), 126.5, 126.6, 127.6, 129.6, 133.0, 134.6, 135.5, 158.8.

^{13}C NMR (100 MHz, acetone-d6) δ 33.6, 34.6, 55.5, 66.1, 77.2 (q, J_{C-F} = 28.6 Hz), 113.2, 115.3, 124.1 (q, J_{C-F} = 2.9 Hz), 126.2 (q, J_{C-F} = 2.9 Hz), 126.3 (q, J_{C-F} = 282.2 Hz), 127.0, 127.4, 128.4, 130.6, 134.4, 136.0, 136.7, 159.9.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.2 (s, 3F).

Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.35; H, 4.56.



3-Benzyl-6-fluoro-1-(trifluoromethyl)-1*H*-isochromene (**2f**).

Colorless amorphous.

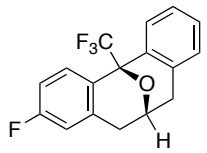
IR (neat) 3087, 3065, 3031, 2925, 2850, 1664, 1614, 1586, 1500, 1455, 1435, 1425, 1375, 1350, 1290, 1269, 1167, 1136, 1107, 1065, 972 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (s, 2H), 5.43 (q, 1H, J = 7.2 Hz), 5.51 (s, 1H), 6.65 (dd, 1H, J = 2.4, 8.4 Hz), 6.85 (ddd, 1H, J = 2.4, 8.4, 8.4 Hz), 7.01–7.11 (m, 1H), 7.21–7.42 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 74.6 (q, J_{C-F} = 32.4 Hz), 100.4, 110.7 (d, J_{C-F} = 21.9 Hz), 113.2 (d, J_{C-F} = 22.9 Hz), 115.9, 123.3 (q, J_{C-F} = 286.0 Hz), 126.9, 128.2 (d, J_{C-F} = 9.6 Hz), 128.5, 129.2, 133.4 (d, J_{C-F} = 8.6 Hz), 136.1, 155.7, 163.7 (d, J_{C-F} = 246.0 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 50.0 (m, 1F), 82.5 (d, J = 7.1 Hz).

Anal. Calcd for $C_{17}H_{12}F_4O$: C, 66.23; H, 3.92. Found: C, 66.04; H, 4.05.



3-Fluoro-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulene (**3f**).

White solid.

Mp. 77–79 °C.

IR (KBr) 3073, 3028, 2957, 2917, 2848, 1617, 1593, 1496, 1455, 1435, 1323, 1311, 1291, 1268, 1250, 1142, 1224, 1172, 1150, 1119, 1107, 1088, 1047, 1029, 993 cm^{-1}.

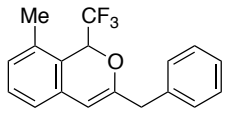
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (d, 2H, J = 17.2 Hz), 3.33–3.55 (m, 2H), 4.81–4.97 (m, 1H), 6.87–6.95 (m, 2H), 7.08–7.29 (m, 3H), 7.45–7.60 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 33.4, 33.7, 65.2, 113.5 (d, J_{C-F} = 21.0 Hz), 116.2 (d, J_{C-F} = 21.0 Hz), 123.9 (d, J_{C-F} = 2.9 Hz), 124.9 (q, J_{C-F} = 282.2 Hz), 125.9 (m), 126.5, 127.9, 129.7, 130.6 (d, J_{C-F} = 1.5 Hz), 132.9, 134.5, 135.9 (d, J_{C-F} = 8.6 Hz), 161.8 (d, J_{C-F} = 246.0 Hz).

^{13}C NMR (100 MHz, acetone-d6) δ 33.8, 34.1, 65.9, 77.2 (q, J_{C-F} = 28.6 Hz), 114.1 (d, J_{C-F} = 21.9 Hz), 117.0 (d, J_{C-F} = 22.0 Hz), 124.5 (q, J_{C-F} = 2.8 Hz), 126.1 (q, J_{C-F} = 282.2 Hz), 126.8 (qd, J_{C-F} = 2.9, 5.7 Hz), 127.2, 130.3, 130.7, 131.9 (d, J_{C-F} = 1.5 Hz), 134.2, 135.5, 137.6 (d, J_{C-F} = 7.6 Hz), 162.7 (d, J_{C-F} = 245.0 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ 47.4 (m, 1F), 83.4 (s, 3F).

Anal. Calcd for $C_{17}H_{12}F_4O$: C, 66.23; H, 3.92. Found: C, 66.47; H, 3.73.



3-Benzyl-8-methyl-1-(trifluoromethyl)-1*H*-isochromene (**2g**).

Colorless amorphous.

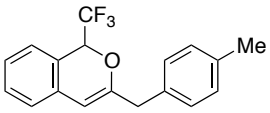
IR (neat) 3065, 3030, 2957, 2925, 2854, 1665, 1591, 1496, 1469, 1455, 1426, 1373, 1345, 1290, 1263, 1229, 1199, 1172, 1148, 1133, 1076, 1029, 969 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.54 (s, 2H), 5.59 (s, 1H), 5.68 (q, 1H, J = 7.2 Hz), 6.81 (d, 1H, J = 8.0 Hz), 7.02 (d, 1H, J = 8.0 Hz), 7.18 (dd, 1H, J = 8.0, 8.0 Hz), 7.23–7.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 39.7, 72.1 (q, J_{C-F} = 32.4 Hz), 102.1, 118.7, 121.8, 124.3 (q, J_{C-F} = 287.0 Hz), 126.7, 128.4, 129.2, 129.2, 129.5, 131.5, 135.5, 136.5, 153.9.

^{19}F NMR (283 MHz, $CDCl_3$) δ 84.4 (d, J = 6.8 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 71.27; H, 5.21.



3-(4-Methylbenzyl)-1-(trifluoromethyl)-1*H*-isochromene (**2h**).

Colorless amorphous.

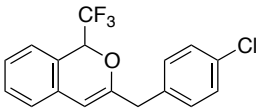
IR (neat) 3050, 3027, 3007, 2924, 2859, 1662, 1605, 1579, 1516, 1494, 1457, 1427, 1375, 1348, 1298, 1265, 1204, 1174, 1132, 1112, 1067, 1034, 1023, 946 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.50 (s, 2H), 5.46 (q, 1H, J = 7.6 Hz), 5.54 (s, 1H), 6.94 (d, 1H, J = 7.2 Hz), 7.05–7.21 (m, 6H), 7.27 (dd, 1H, J = 7.6, 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 39.4, 74.9 (q, J_{C-F} = 32.5 Hz), 100.8, 120.3, 123.5 (q, J_{C-F} = 285.1 Hz), 123.8, 126.4, 126.6, 129.1, 129.1, 129.8, 131.1, 133.4, 136.3, 154.7.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.9 (d, J = 7.1 Hz).

Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 70.87; H, 5.05.



3-(4-Chlorobenzyl)-1-(trifluoromethyl)-1*H*-isochromene (**2i**).

Colorless amorphous.

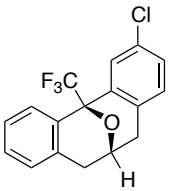
IR (neat) 3069, 3030, 2926, 1664, 1605, 1580, 1492, 1457, 1427, 1409, 1375, 1348, 1298, 1146, 1132, 1112, 1092, 1067, 1017, 946 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 2H), 5.45 (q, 1H, J = 7.2 Hz), 5.57 (s, 1H), 6.97 (d, 1H, J = 7.6 Hz), 7.09 (d, 1H, J = 7.6 Hz), 7.14–7.33 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 74.9 (q, J_{C-F} = 32.4 Hz), 101.2, 120.3, 123.4 (q, J_{C-F} = 286.0 Hz), 123.9, 126.6, 126.7, 128.5, 129.9, 130.5, 130.8, 132.6, 135.0, 153.8.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.8 (d, J = 6.8 Hz).

Anal. Calcd for $C_{17}H_{12}ClF_3O$: C, 62.88; H, 3.72. Found: C, 62.59; H, 3.83.



2-Chloro-12-(trifluoromethyl)-5,6,7,12-tetrahydro-6,12-epoxydibenzo[*a*,*d*][8]annulene (**3i**).

White solid.

Mp. 174–176 °C.

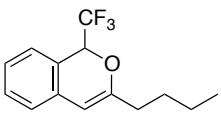
IR (KBr) 2959, 2849, 1492, 1453, 1435, 1313, 1290, 1271, 1169, 1159, 1129, 1118, 1101, 1091, 1048, 1035, 989 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d6) δ 2.46 (ddd, 2H, J = 2.0, 8.0, 17.2 Hz), 2.52 (dd, 2H, J = 8.0, 8.0, 17.2 Hz), 3.38–3.52 (m, 2H), 4.88–4.91 (m, 1H), 7.17–7.32 (m, 5H), 7.51–7.63 (m, 2H).

^{13}C NMR (100 MHz, acetone-d6) δ 33.3, 33.9, 66.2, 77.1 (q, J_{C-F} = 28.6 Hz), 124.5 (q, J_{C-F} = 2.8 Hz), 124.7 (q, J_{C-F} = 2.8 Hz), 126.0 (q, J_{C-F} = 281.9 Hz), 127.4, 128.8, 129.0 130.8, 132.3, 132.5, 133.6, 134.4, 134.8, 137.6.

^{19}F NMR (283 MHz, $CDCl_3$) δ 88.4 (s, 3F).

Anal. Calcd for $C_{17}H_{12}ClF_3O$: C, 62.88; H, 3.72. Found: C, 62.97; H, 3.58.



3-Butyl-1-(trifluoromethyl)-1*H*-isochromene (**2j**).

Colorless oil.

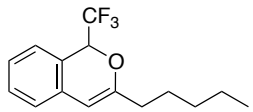
IR (neat) 3072, 3030, 2959, 2933, 2874, 1665, 1606, 1580, 1494, 1468, 1457, 1430, 1376, 1348, 1322, 1299, 1267, 1174, 1155, 1133, 1114, 1064, 1034, 944 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz), 1.31–1.46 (m, 2H), 1.47–1.66 (m, 2H), 2.14–2.30 (m, 2H), 5.47 (q, 1H, J = 7.6 Hz), 5.59 (s, 1H), 6.97 (d, 1H, J = 7.6 Hz), 7.10 (d, 1H, J = 7.6 Hz), 7.16 (dd, 1H, J = 7.6, 7.6 Hz), 7.29 (dd, 1H, J = 7.6, 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.1, 28.7, 33.2, 74.8 (q, J_{C-F} = 31.4 Hz), 99.6, 120.3, 123.5, 123.7 (q, J_{C-F} = 285.1 Hz), 126.1, 126.6, 129.8, 131.3, 155.8.

^{9}F NMR (283 MHz, $CDCl_3$) δ 82.9 (d, J = 9.3 Hz).

Anal. Calcd for $C_{14}H_{15}F_3O$: C, 65.62; H, 5.90. Found: C, 65.48; H, 6.05.



3-Pentyl-1-(trifluoromethyl)-1*H*-isochromene (**2k**).

Colorless oil.

IR (neat) 2957, 2932, 2862, 1664, 1606, 1494, 1468, 1457, 1376, 1348, 1300, 1265, 1206, 1174, 1155, 1133, 1114, 1064, 1034, 925 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81–0.98 (m, 3H), 1.22–1.42 (m, 4H), 1.46–1.69 (m, 2H), 2.11–2.32 (m, 2H), 5.47 (q, 1H, J = 7.2 Hz), 5.59 (s, 1H), 6.97 (d, 1H, J = 7.6 Hz), 7.10 (d, 1H, J = 7.6 Hz), 7.16 (dd, 1H, J = 7.6, 7.6 Hz), 7.28 (dd, 1H, J = 7.6, 7.6 Hz).

^{13}C NMR (100 MHz, CDCl3) δ 14.0, 22.4, 26.3, 31.2, 33.4, 74.8 (q, J_{C-F} = 32.5 Hz), 99.7, 120.3, 123.6, 123.7 (q, J_{C-F} = 284.1 Hz), 126.2, 126.6, 129.8, 131.3, 155.8.

^{19}F NMR (283 MHz, $CDCl_3$) δ 82.9 (d, J = 6.8 Hz).

Anal. Calcd for $C_{15}H_{17}F_3O$: C, 66.65; H, 6.34. Found: C, 66.76; H, 6.58.

3. NMR experiments (^{13}C NMR mixing with SM and catalyst)

Figure S1 shows the ^{13}C NMR spectra of **1a** and mixture of **1a** and Tf_2NH (**1a**:Tf_2NH = 1:1), especially focusing on the peaks of carbonyl carbon and the carbon adjacent to methoxy group.

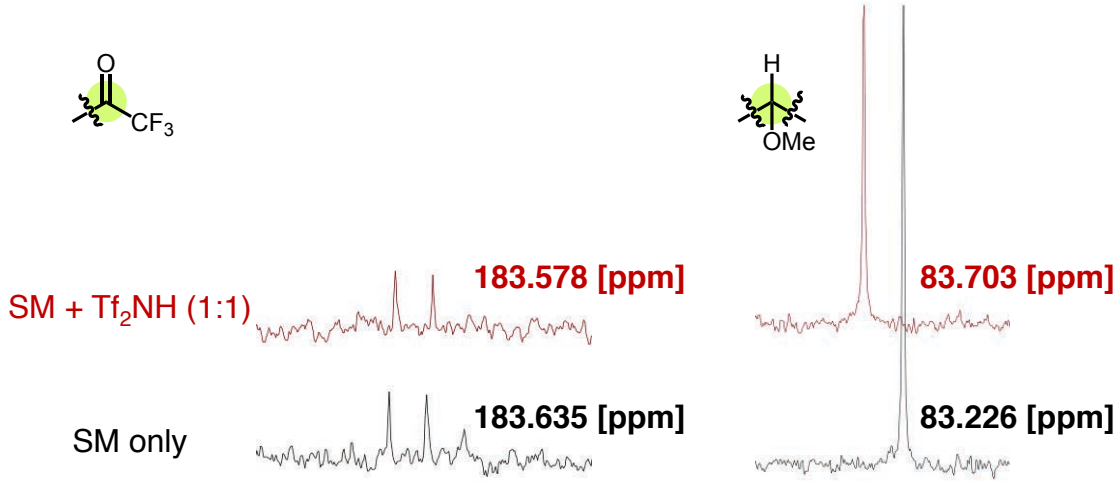


Figure S1. ^{13}C NMR spectra of **1a** and mixture of **1a** and Tf_2NH (**1a**:Tf_2NH = 1:1).

References

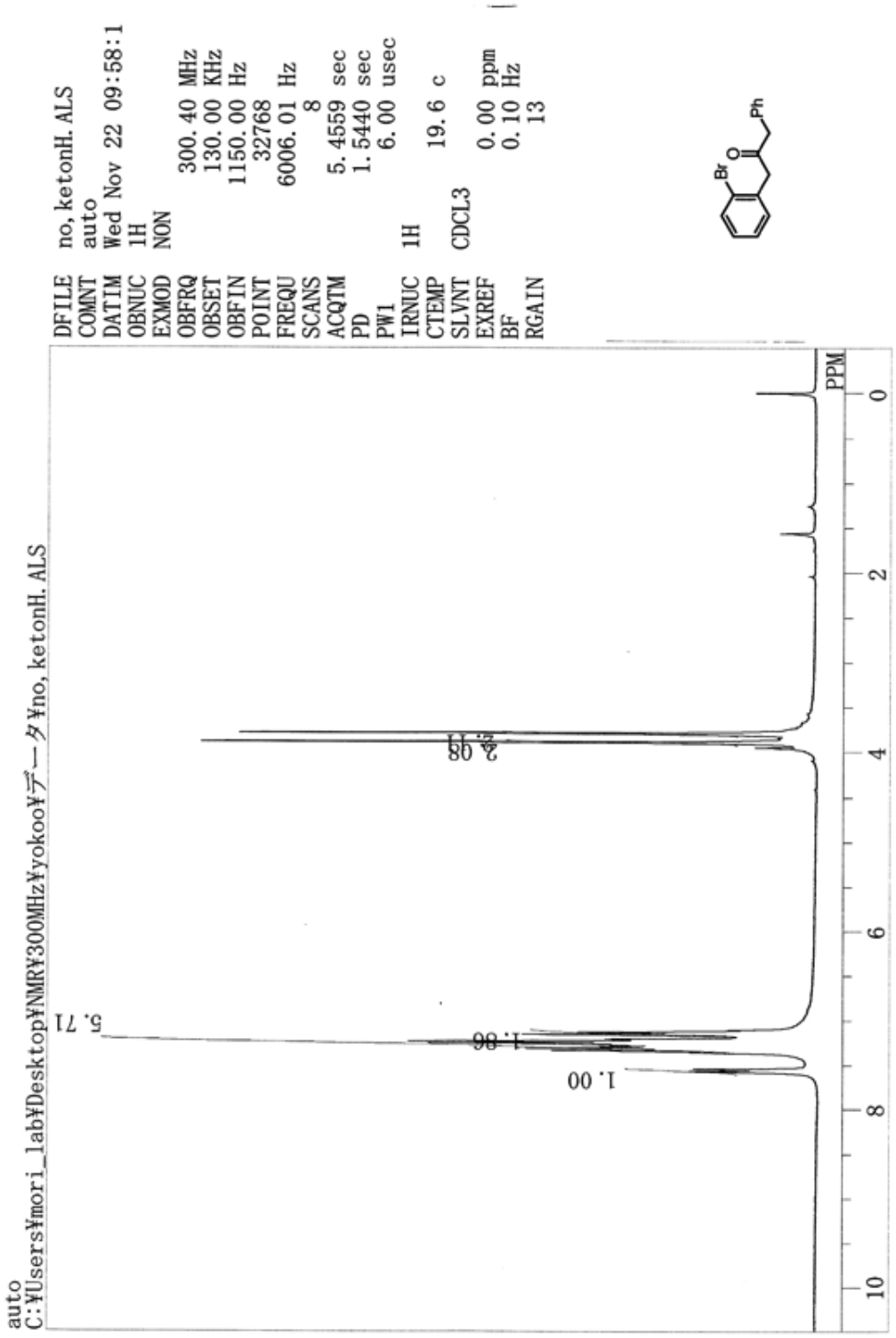
1) Dai, Y.; Feng, X.; Liu, H,; Jiang, H.; Bao, M. *J. Org. Chem*. **2011**, *76*, 10068.

2) Viswanathan, R.; Pranhakaran, E. N.; Plotkin, M. A.; Johnston, J. N. *J. Am. Chem. Soc*. **2003**, *125*, 163.

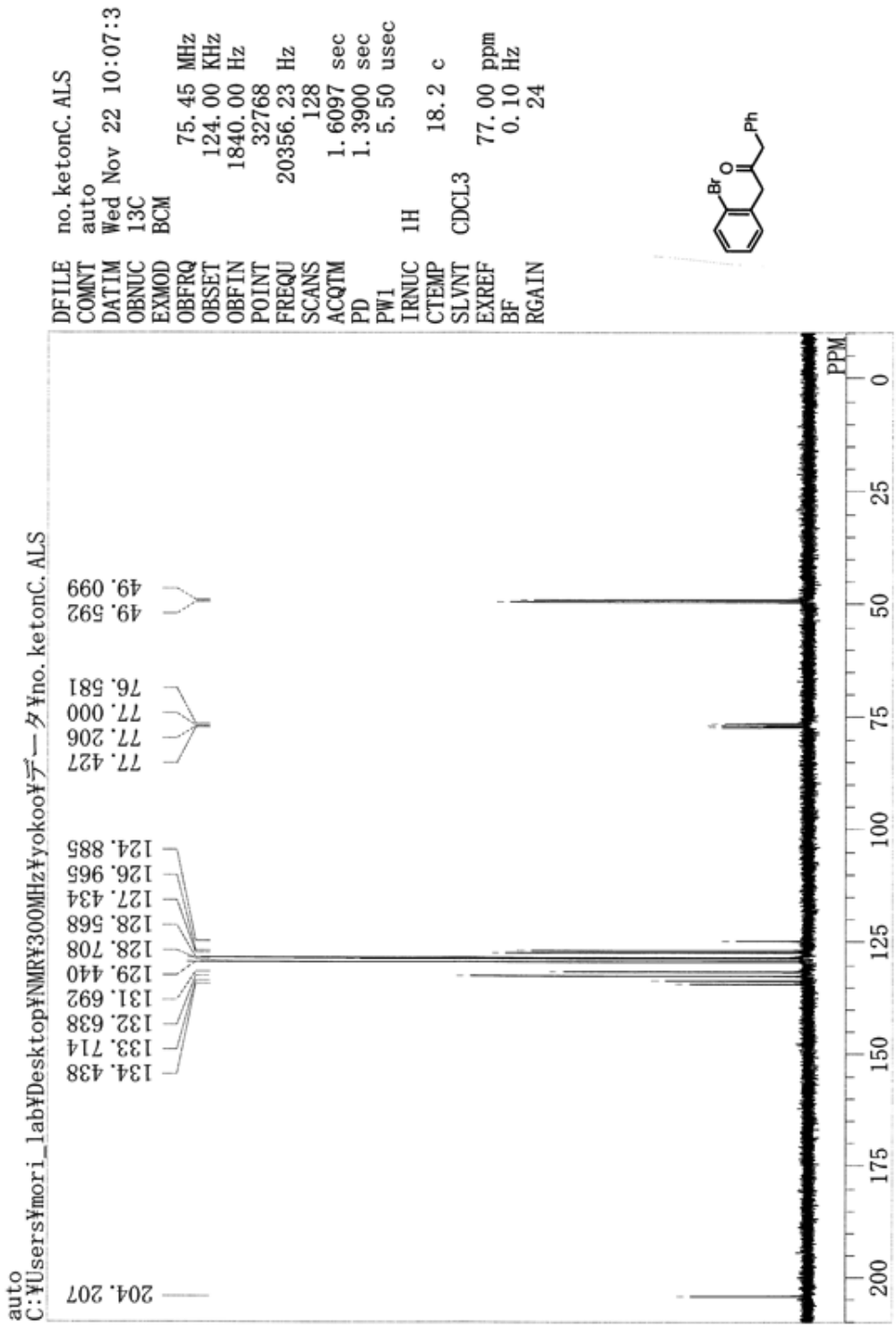
3) Watanabe, K.; Mino, T.; Hatta, C.; Ito, S.; Sakamoto, M. *Org. Biomol. Chem*. **2015**, *13*, 11645.

4) Konishi, H.; Tanaka, H.; Manabe, K. *Org. Lett*. **2017**, *19*, 1578

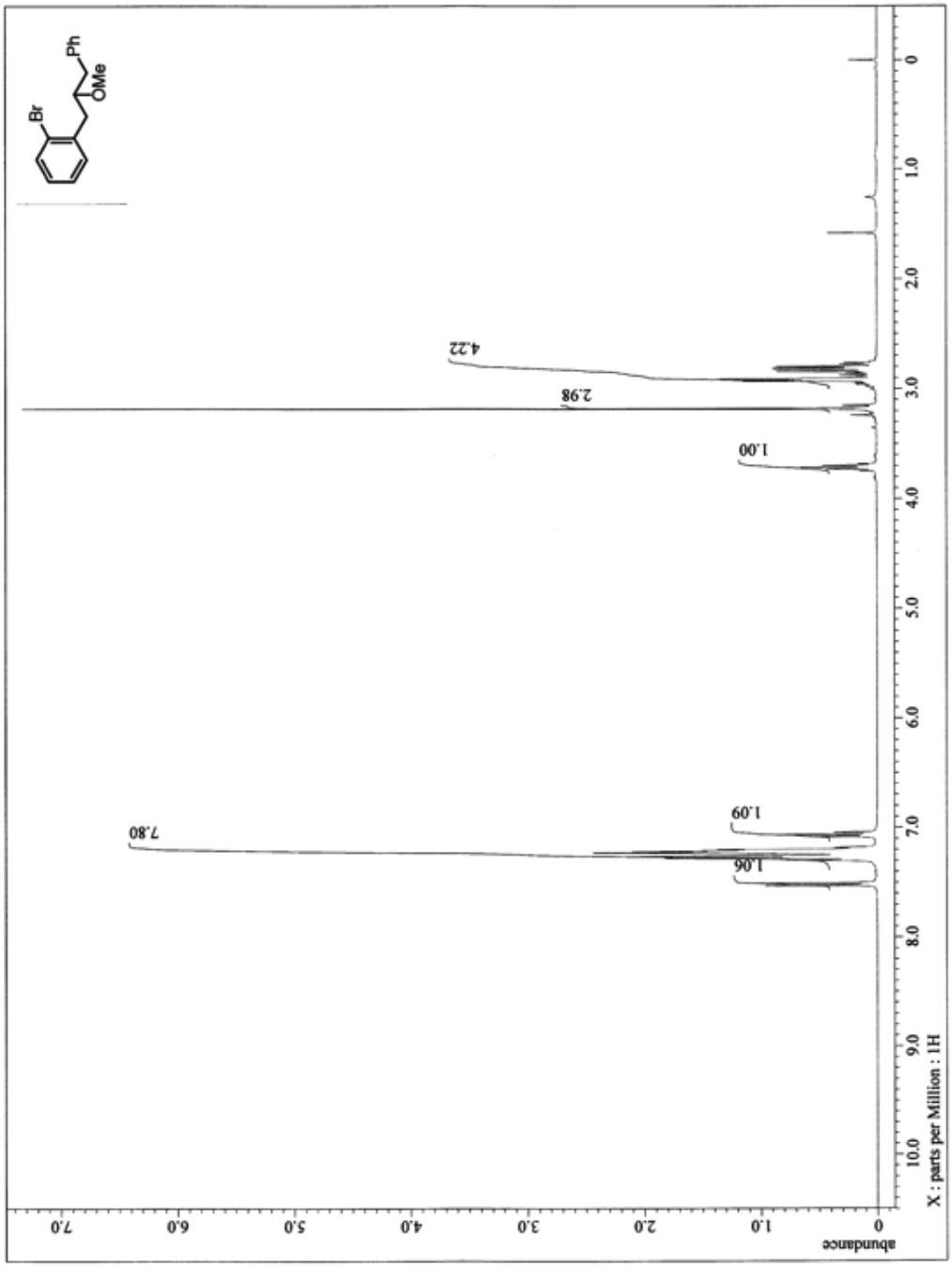
^{1}H NMR spectrum of **s4**.



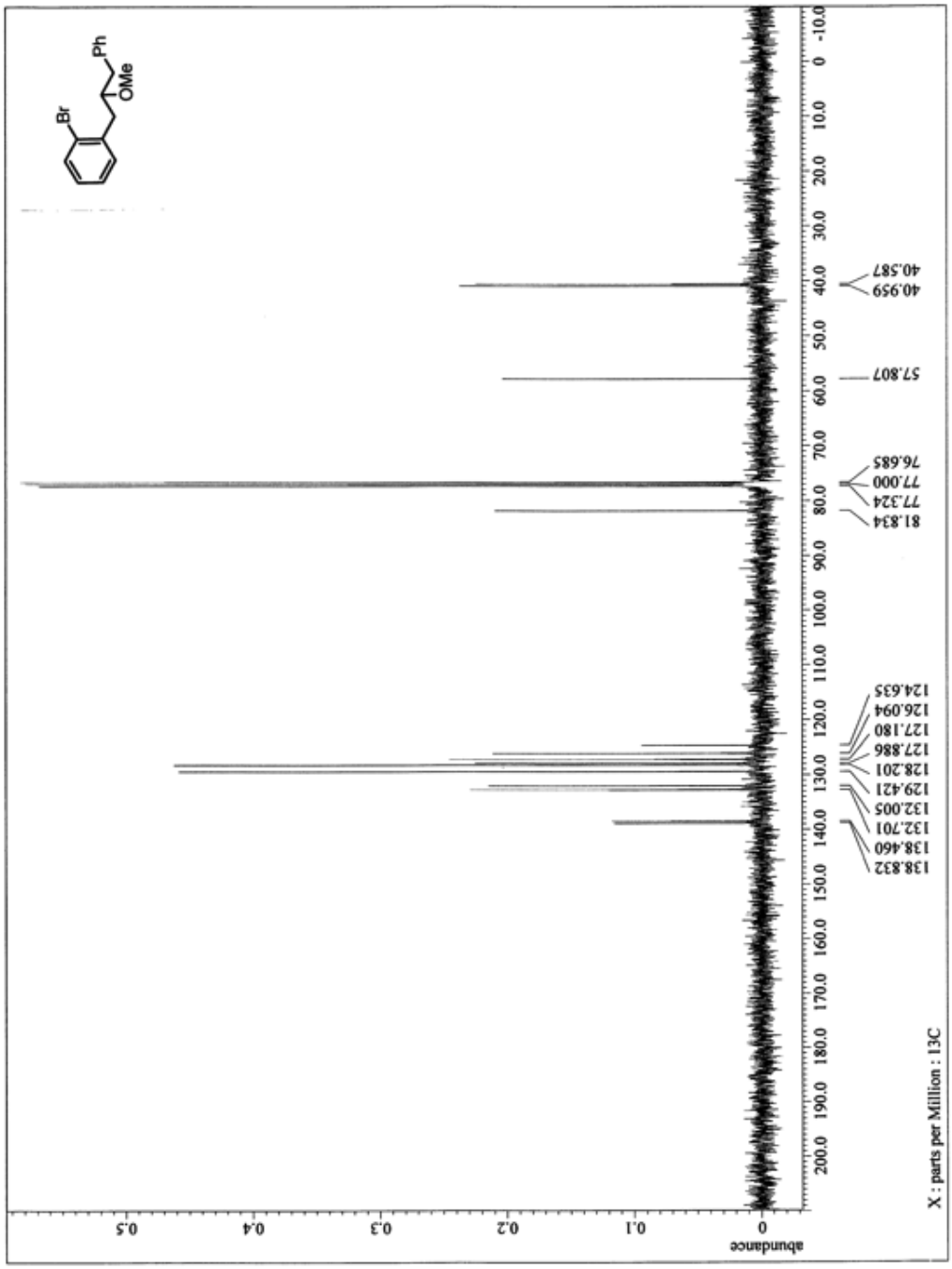
^{13}C NMR spectrum of **s4**.



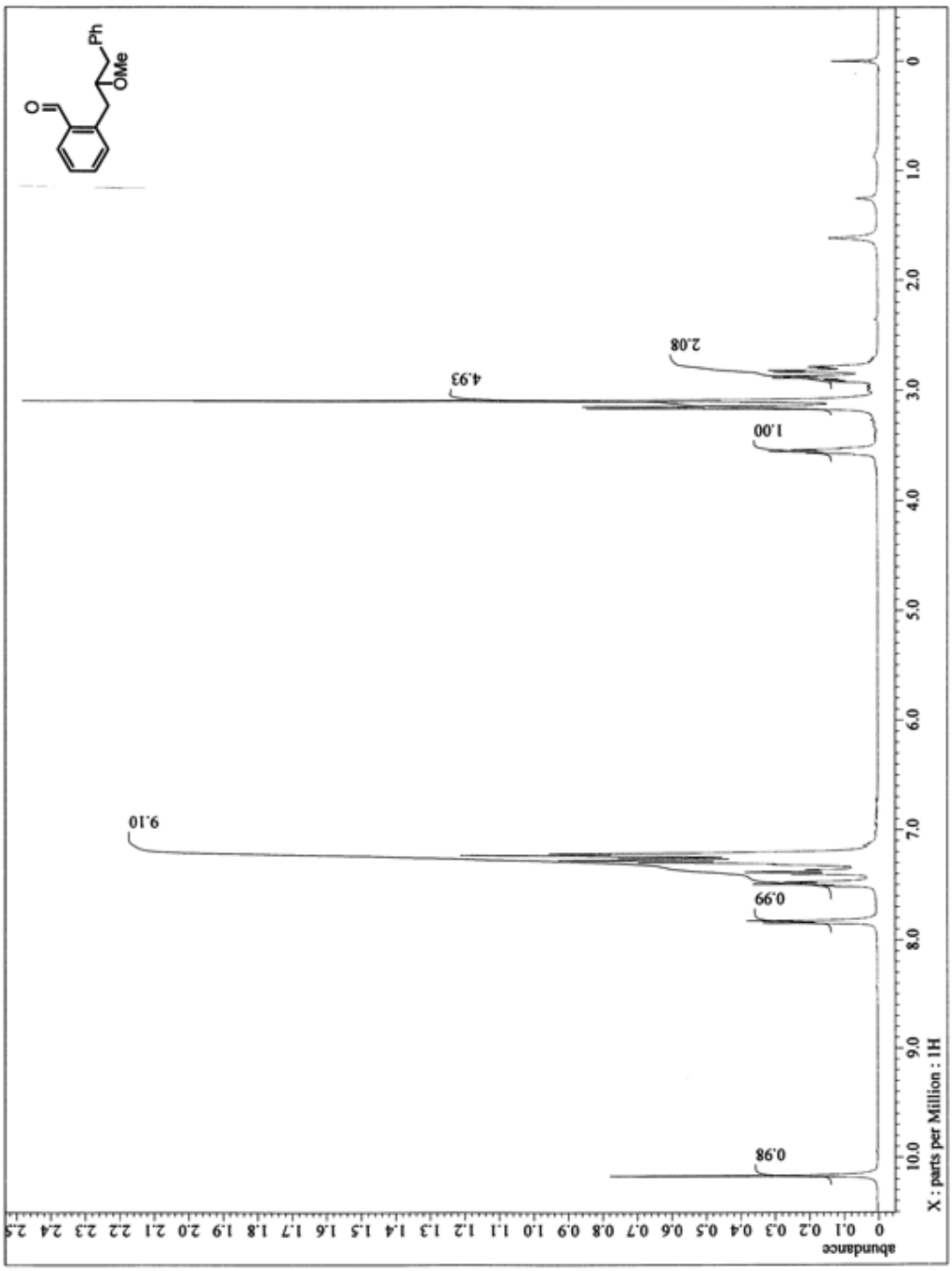
^{1}H NMR spectrum of **s6**.



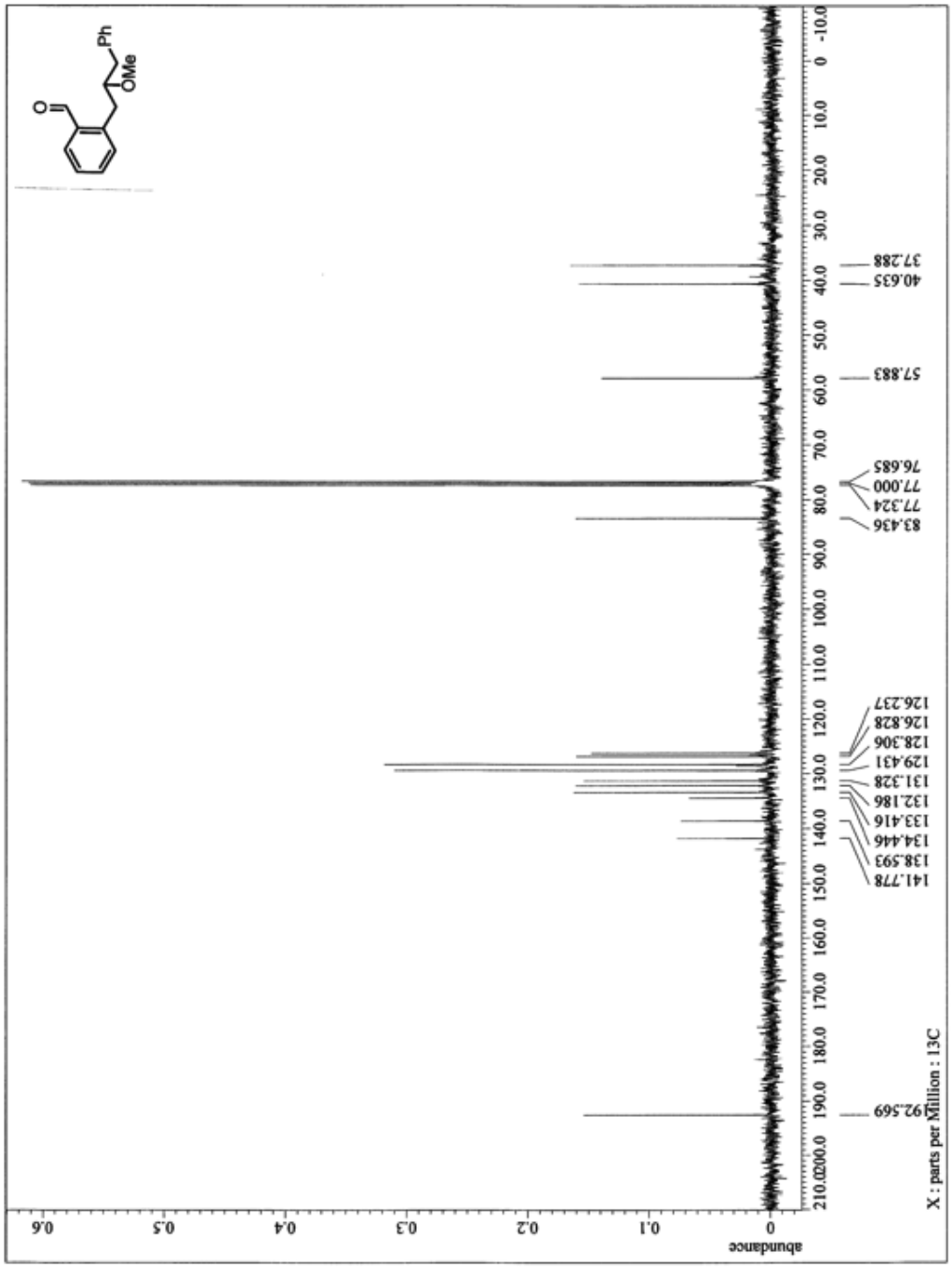
^{13}C NMR spectrum of **s6**.



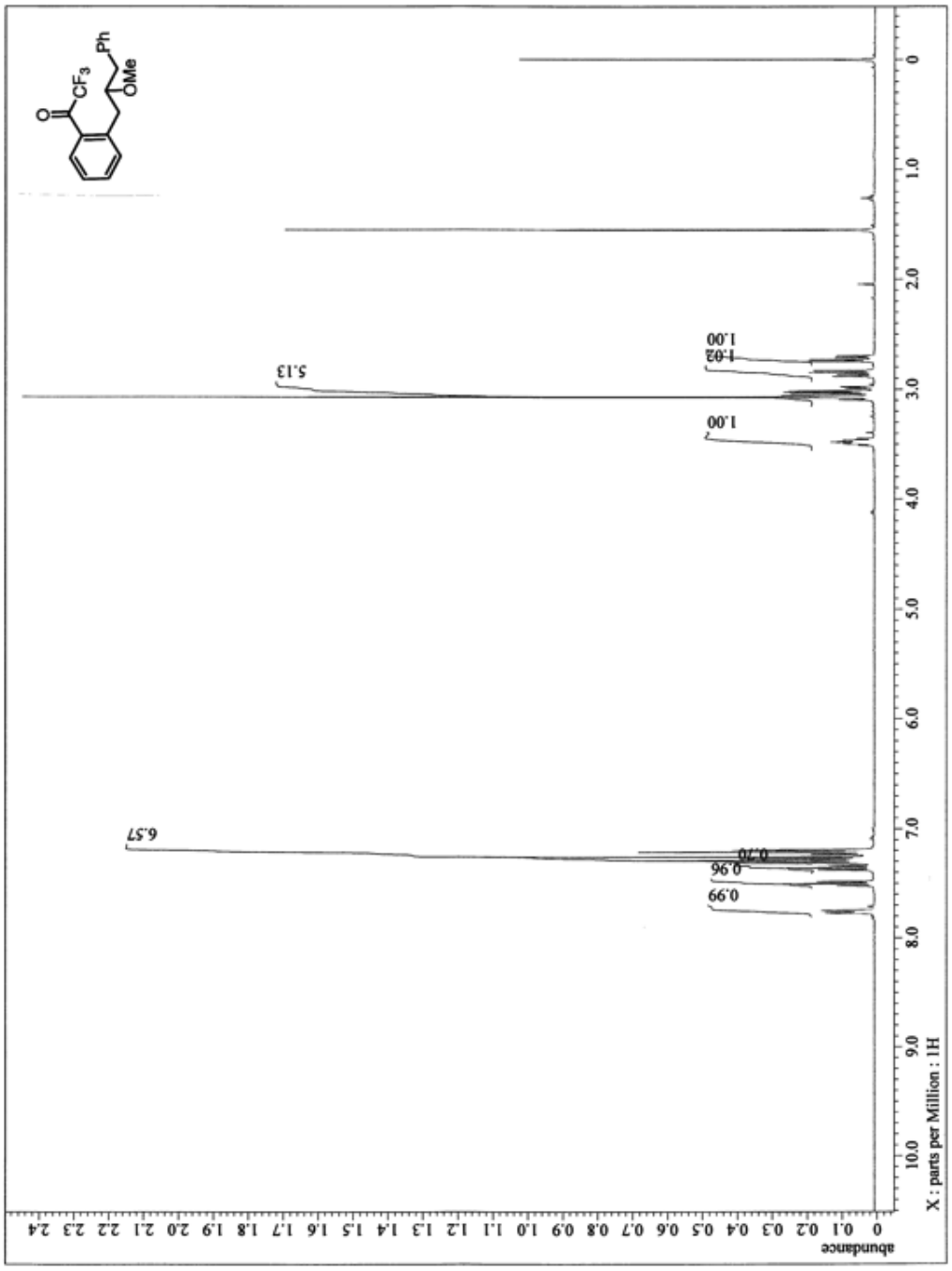
^{1}H NMR spectrum of **s7**.



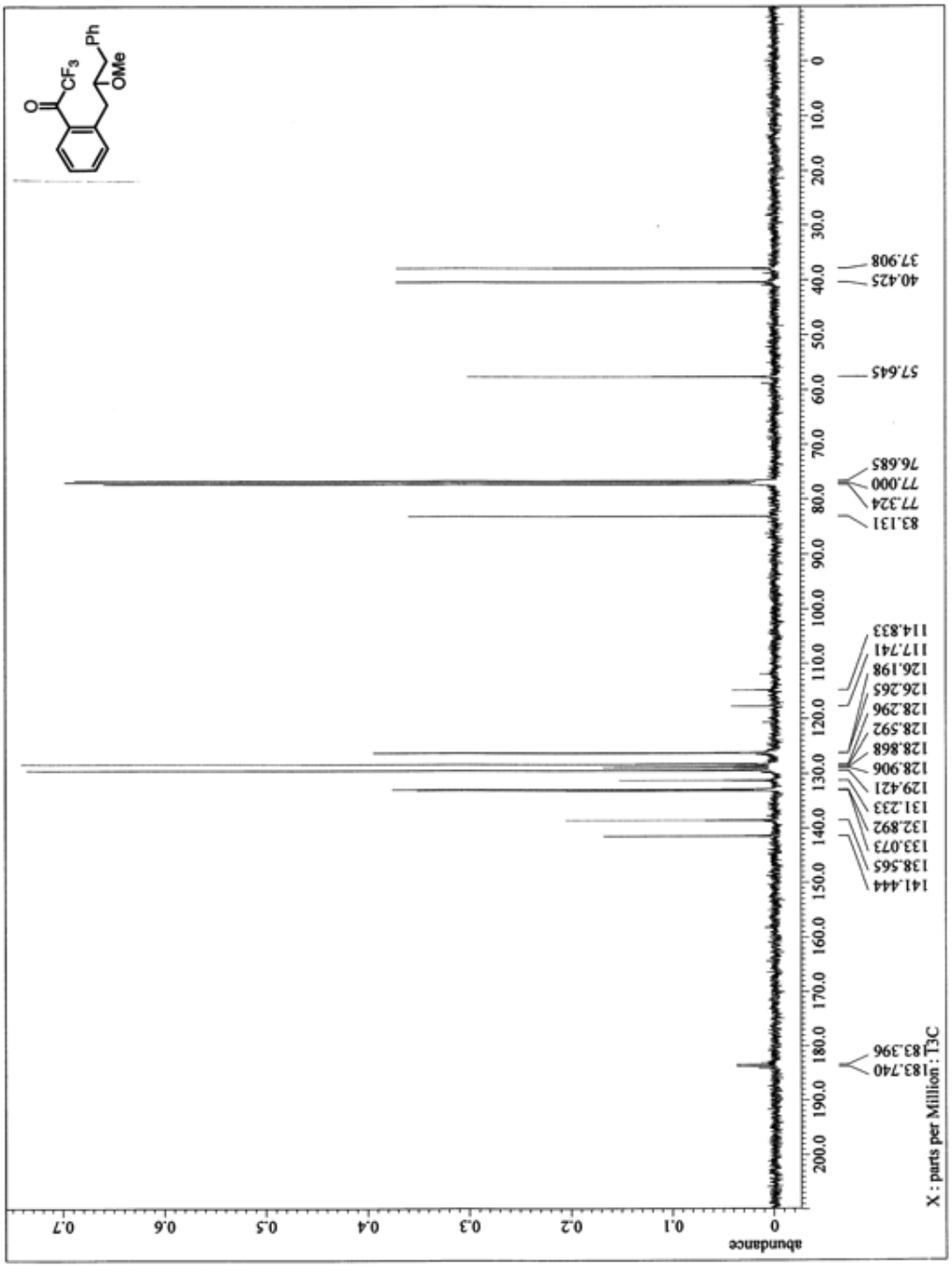
^{13}C NMR spectrum of **s7**.



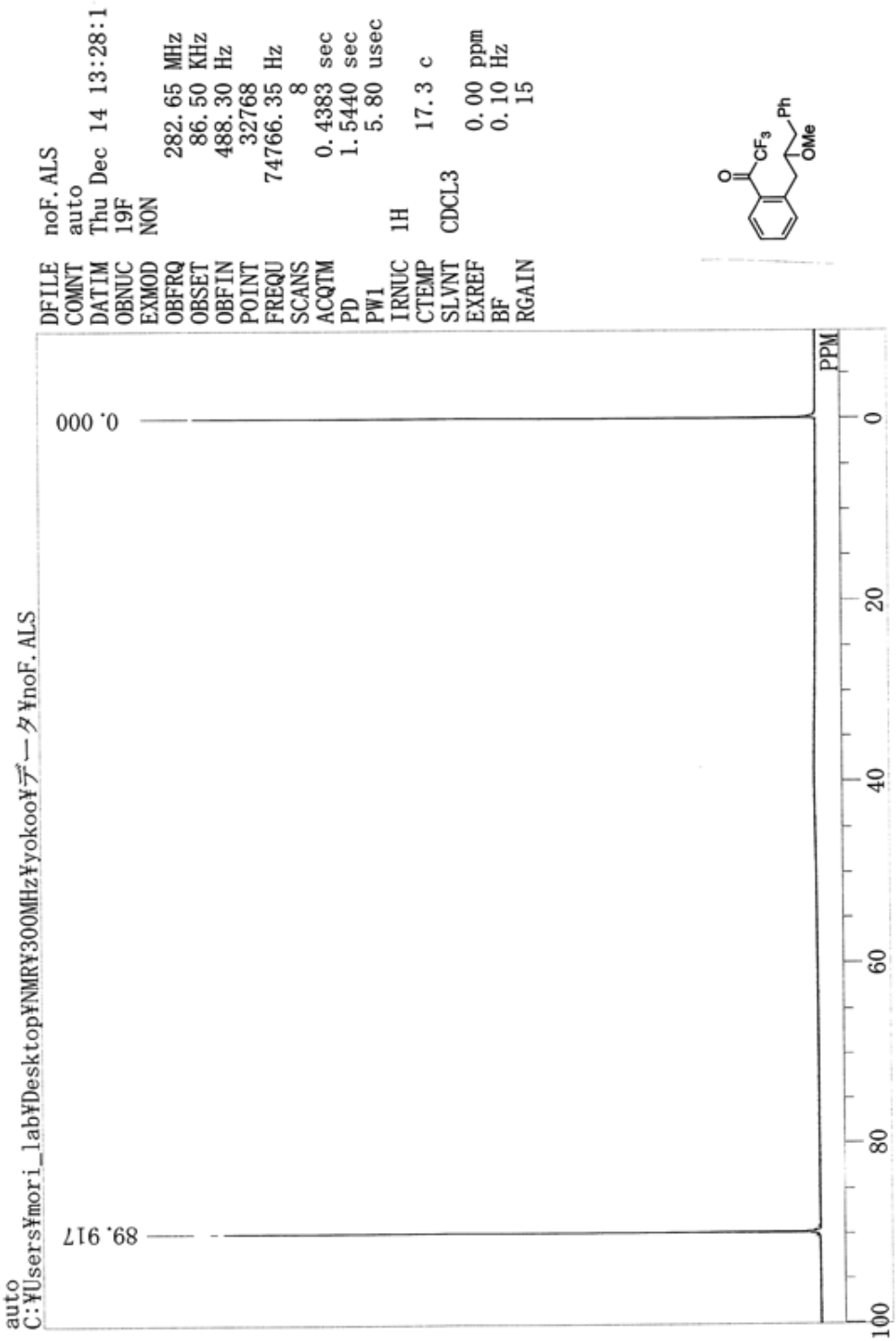
^{1}H NMR spectrum of **1a**.



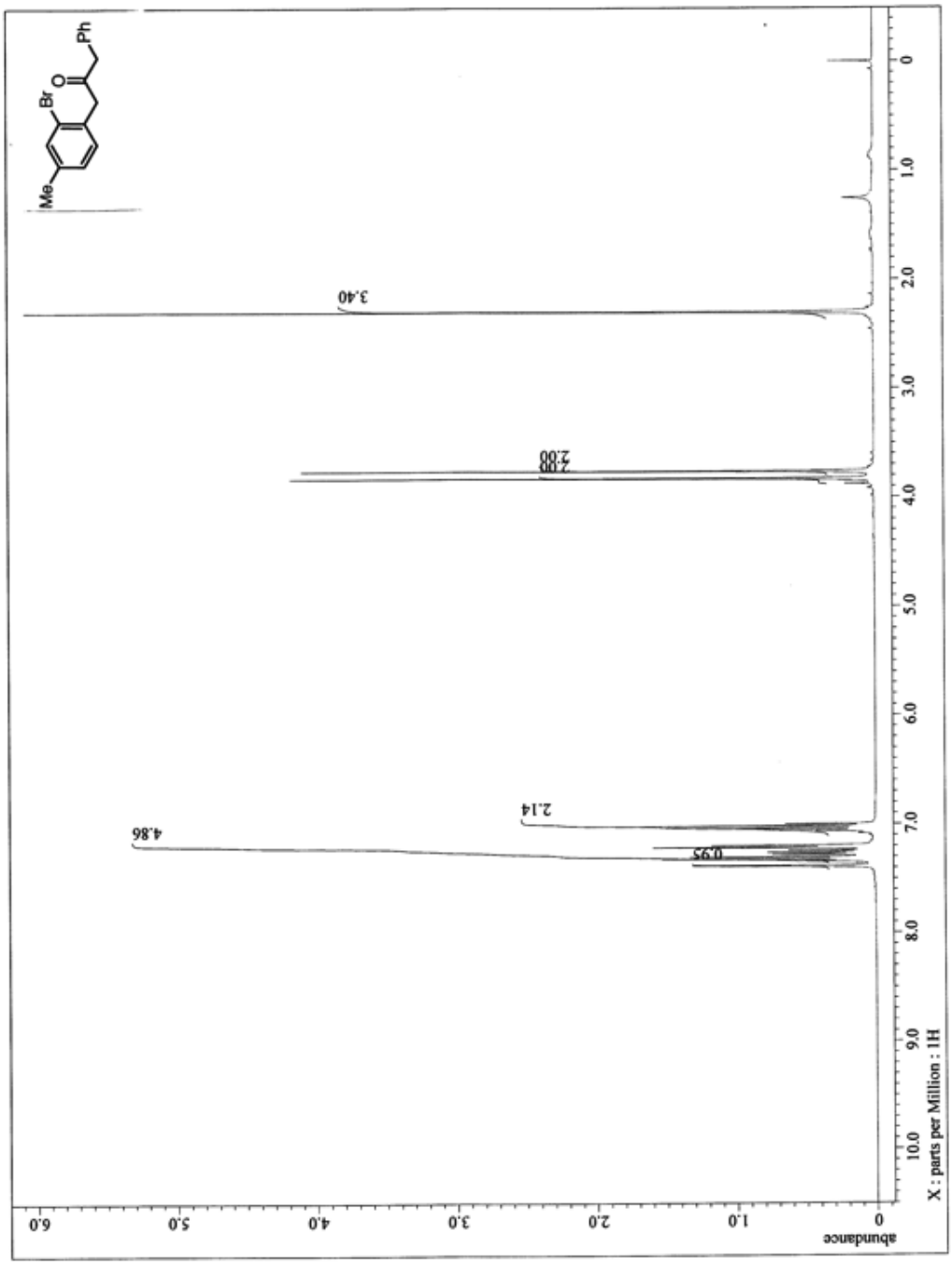
^{13}C NMR spectrum of **1a**.



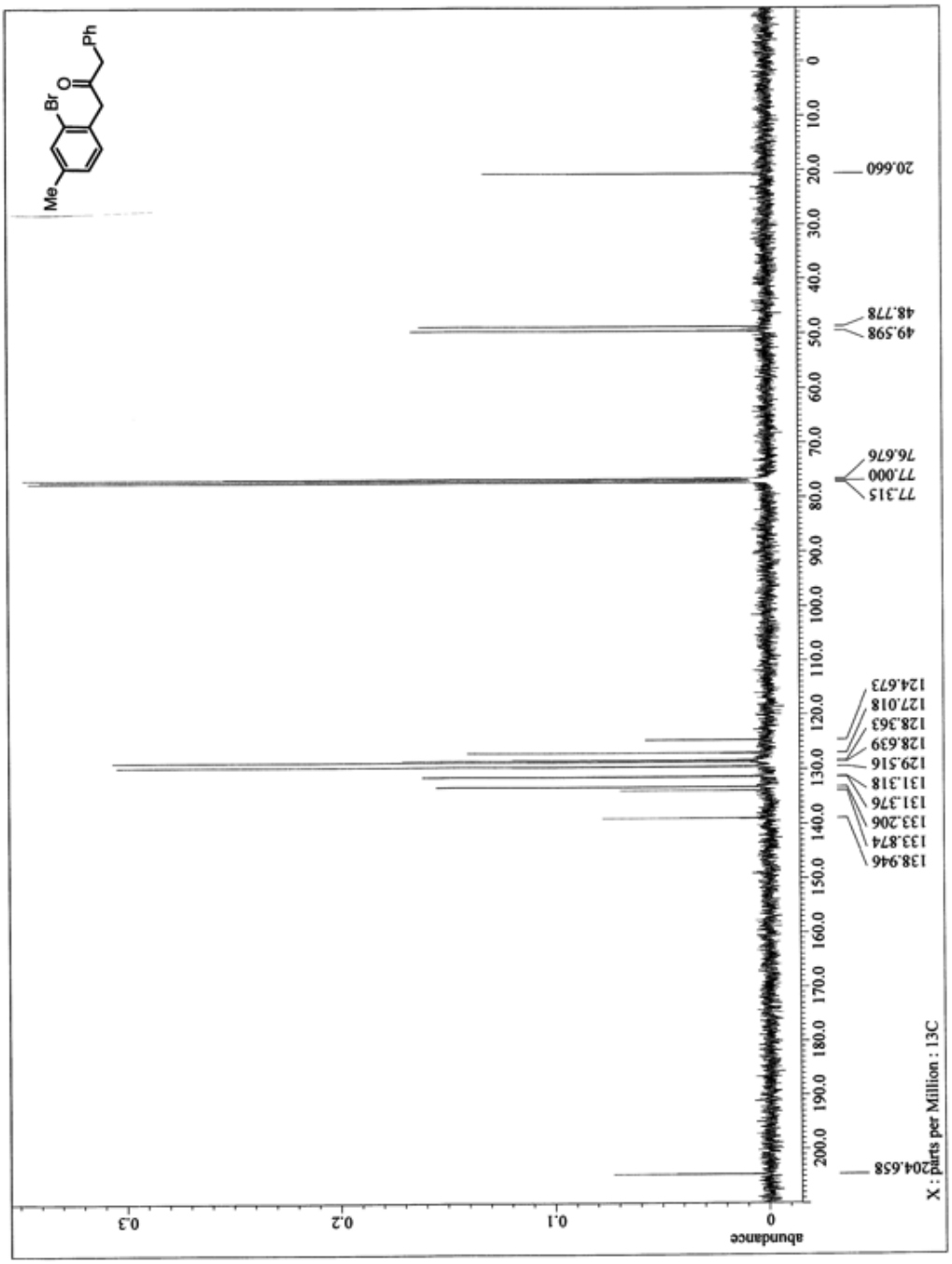
^{19}F NMR spectrum of **1a**.



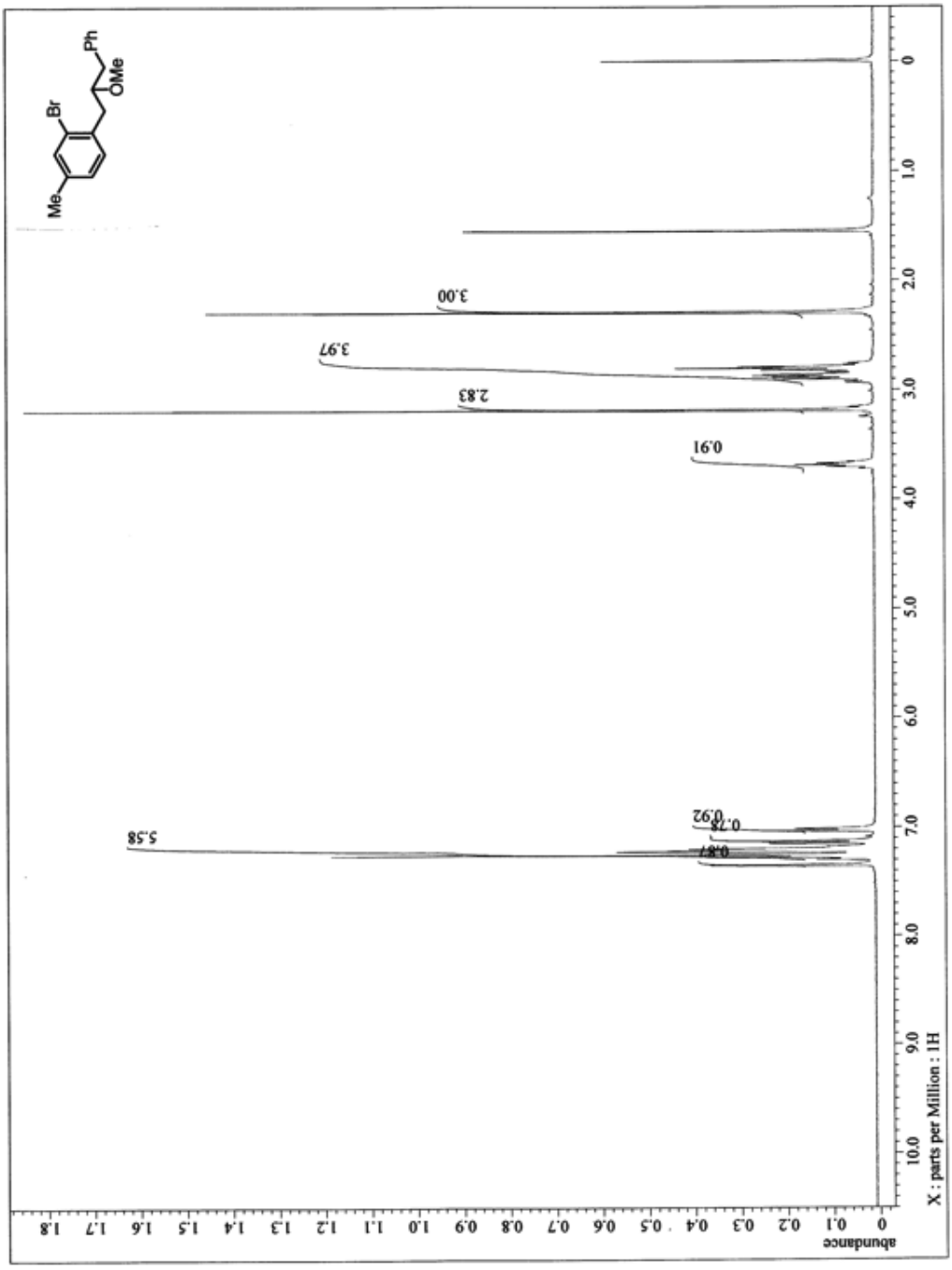
^{1}H NMR spectrum of **s9**.



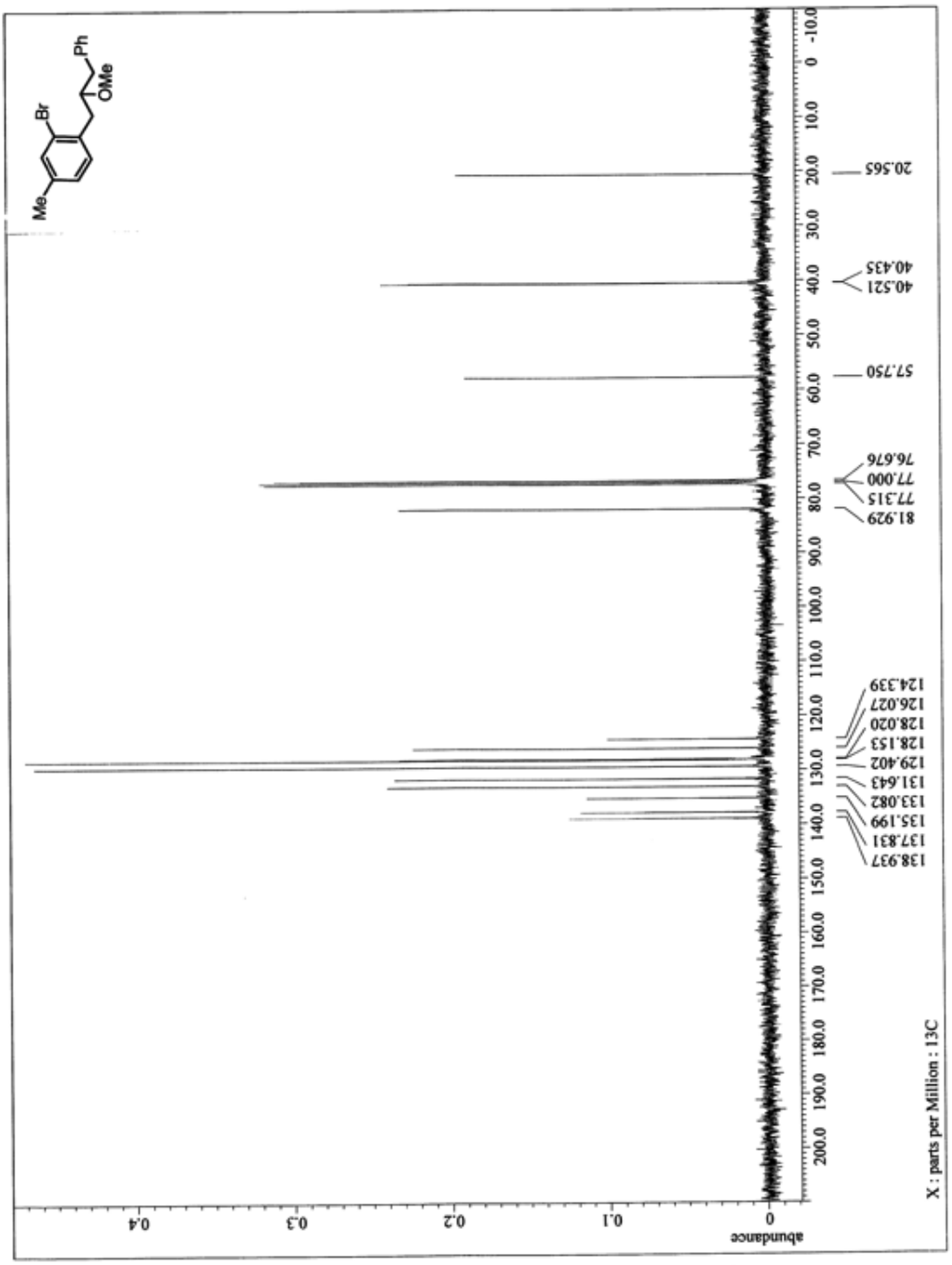
^{13}C NMR spectrum of **s9**.



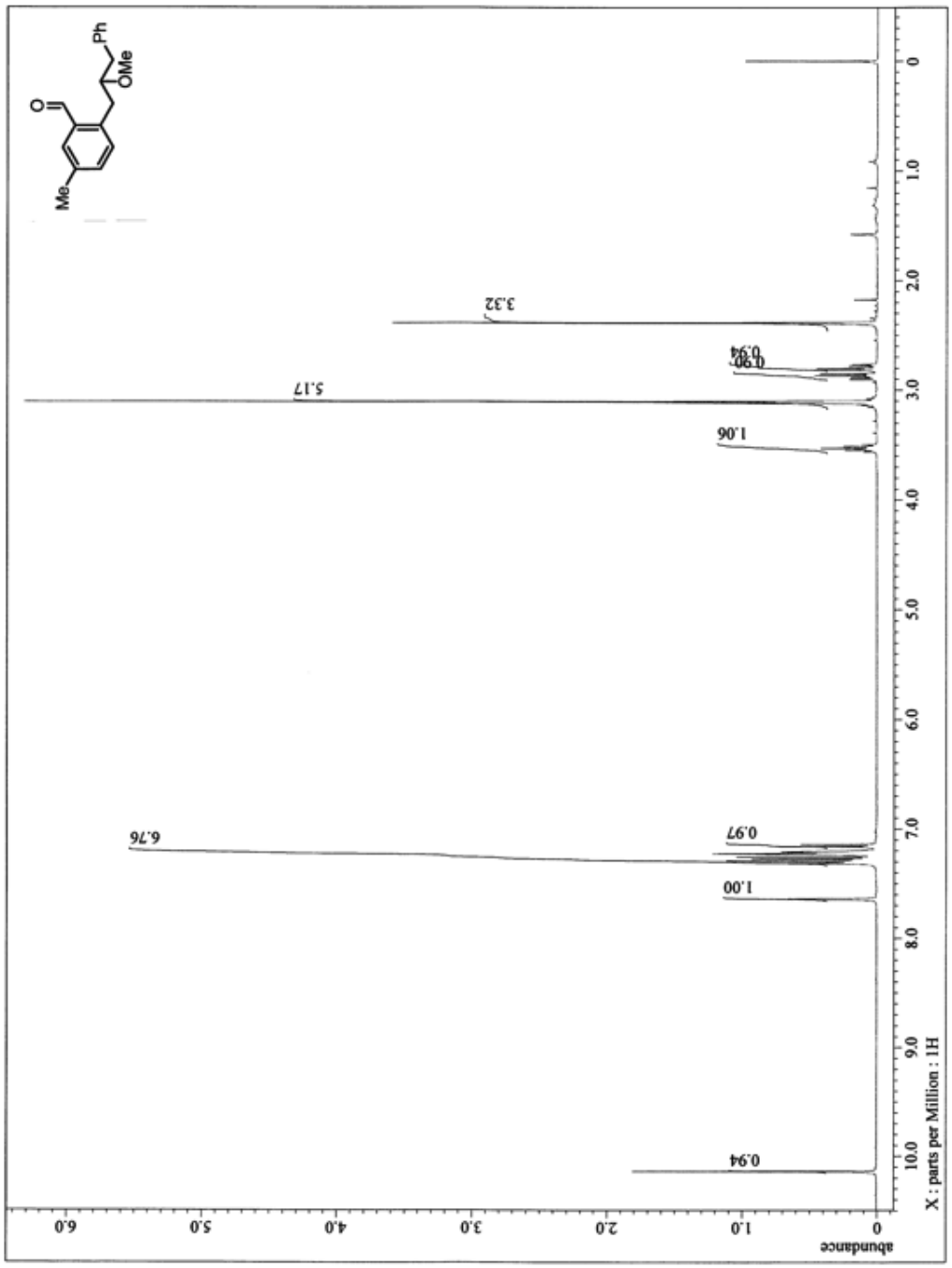
^{1}H NMR spectrum of **s10**.



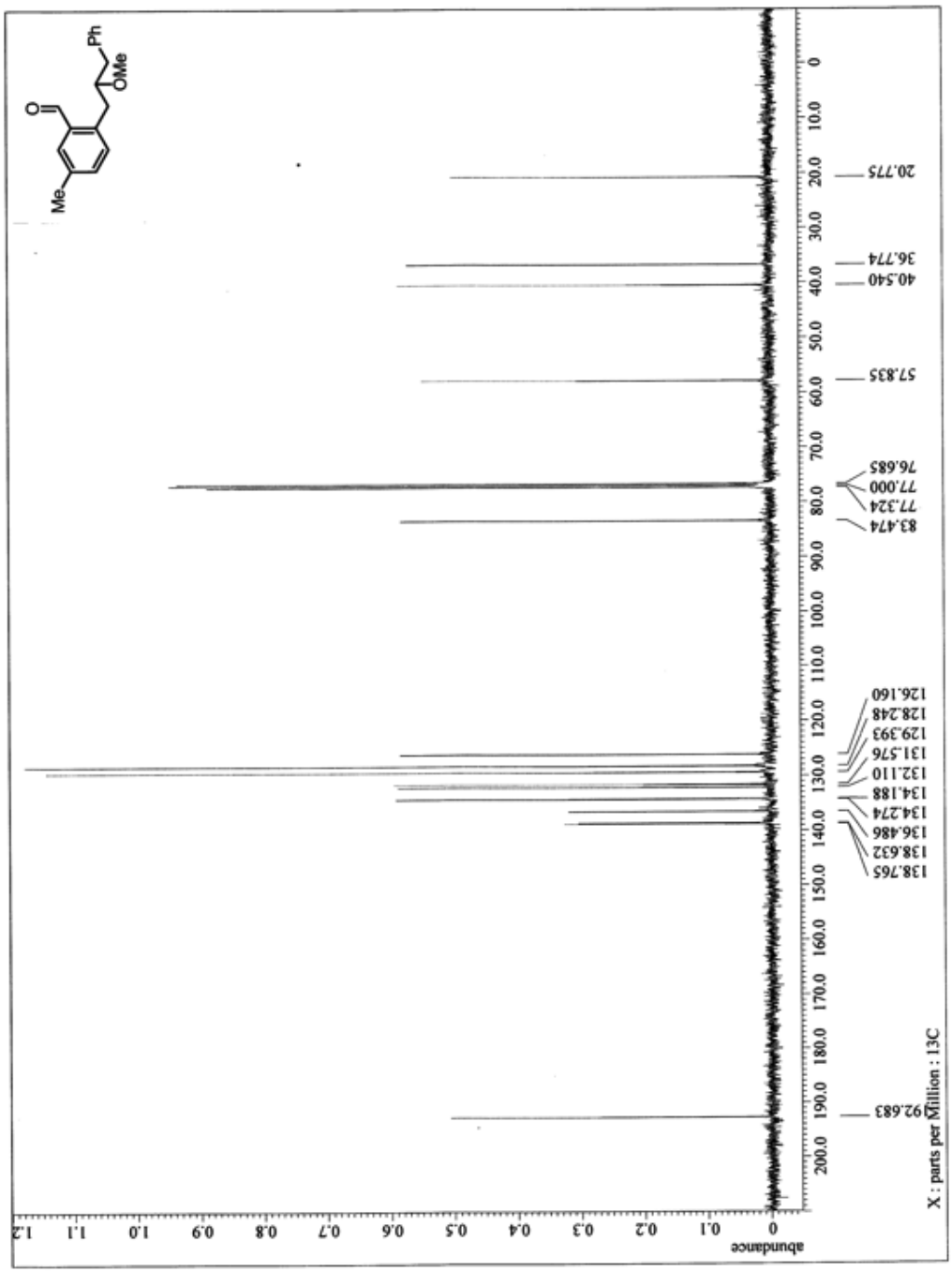
^{13}C NMR spectrum of **s10**.



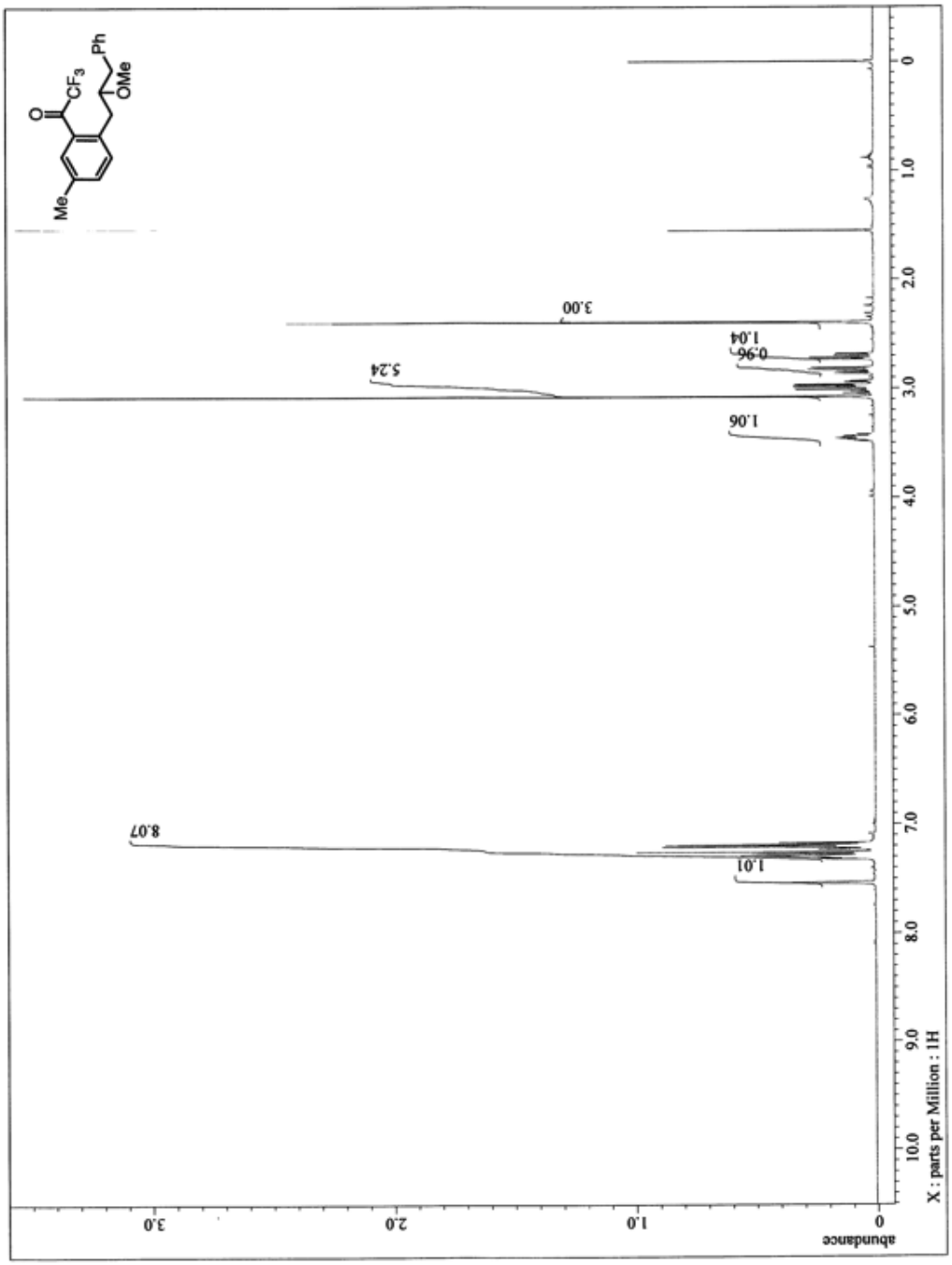
^{1}H NMR spectrum of **s11**.



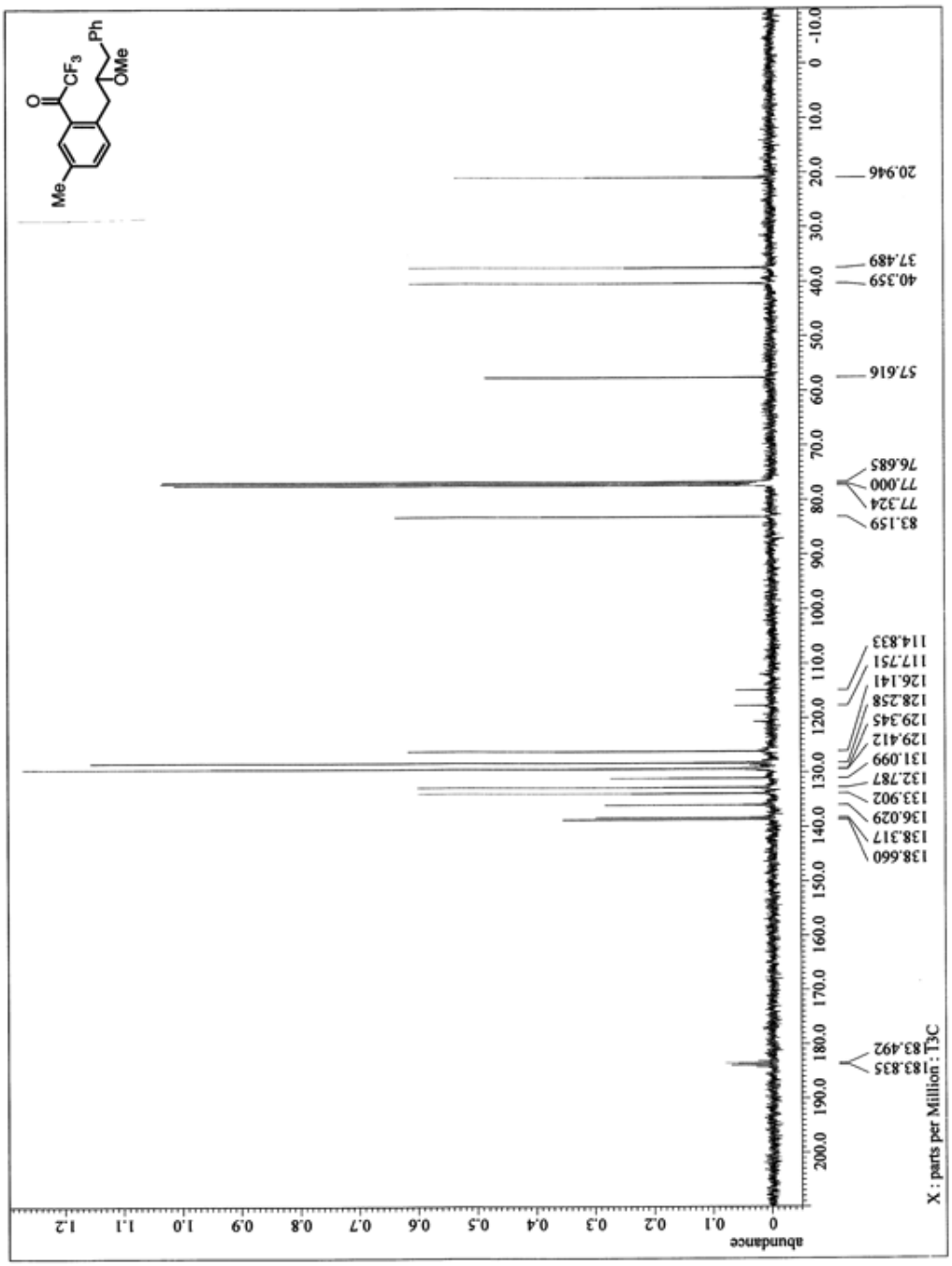
^{13}C NMR spectrum of **s11**.



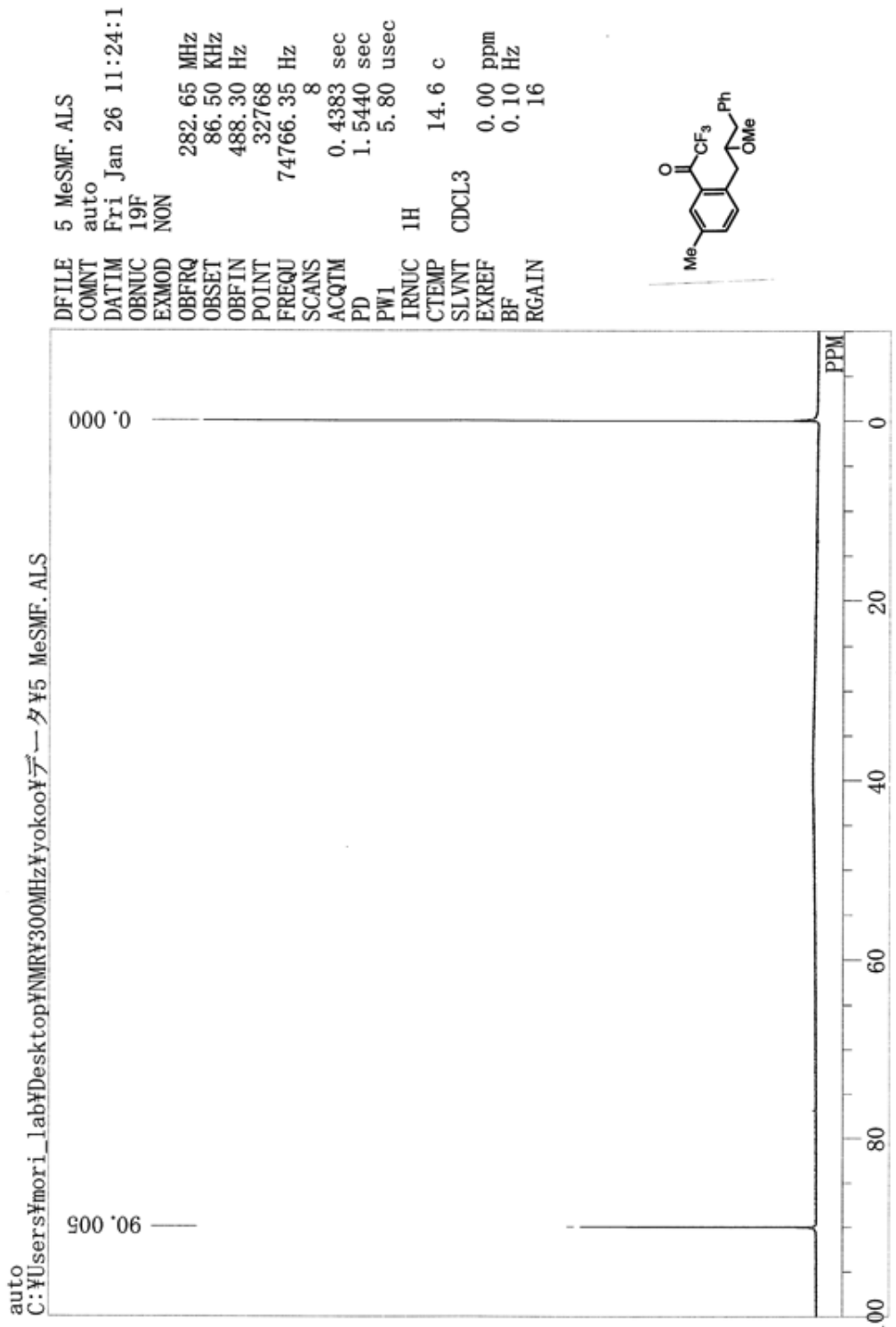
^{1}H NMR spectrum of **1b**.



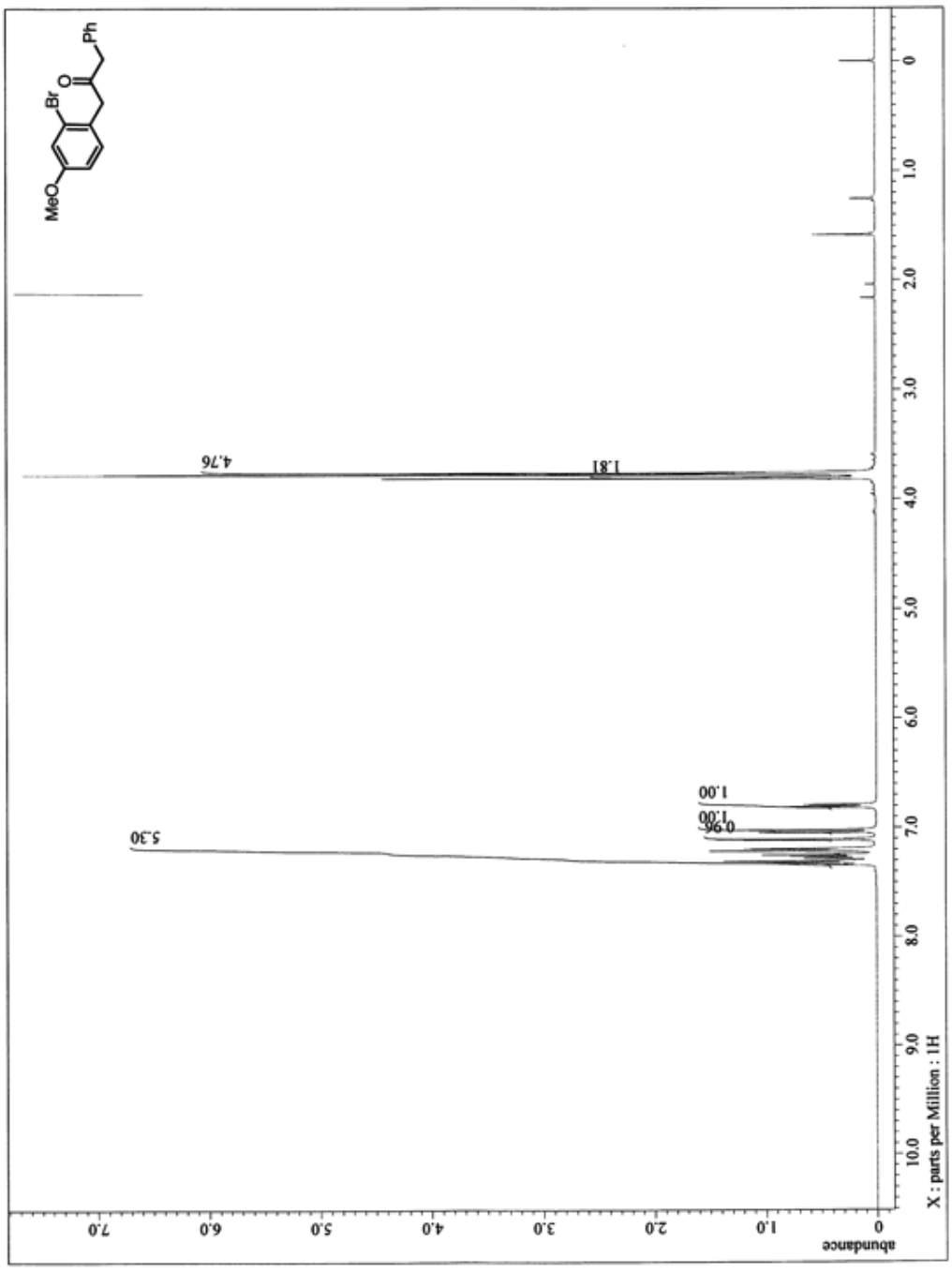
^{13}C NMR spectrum of **1b**.



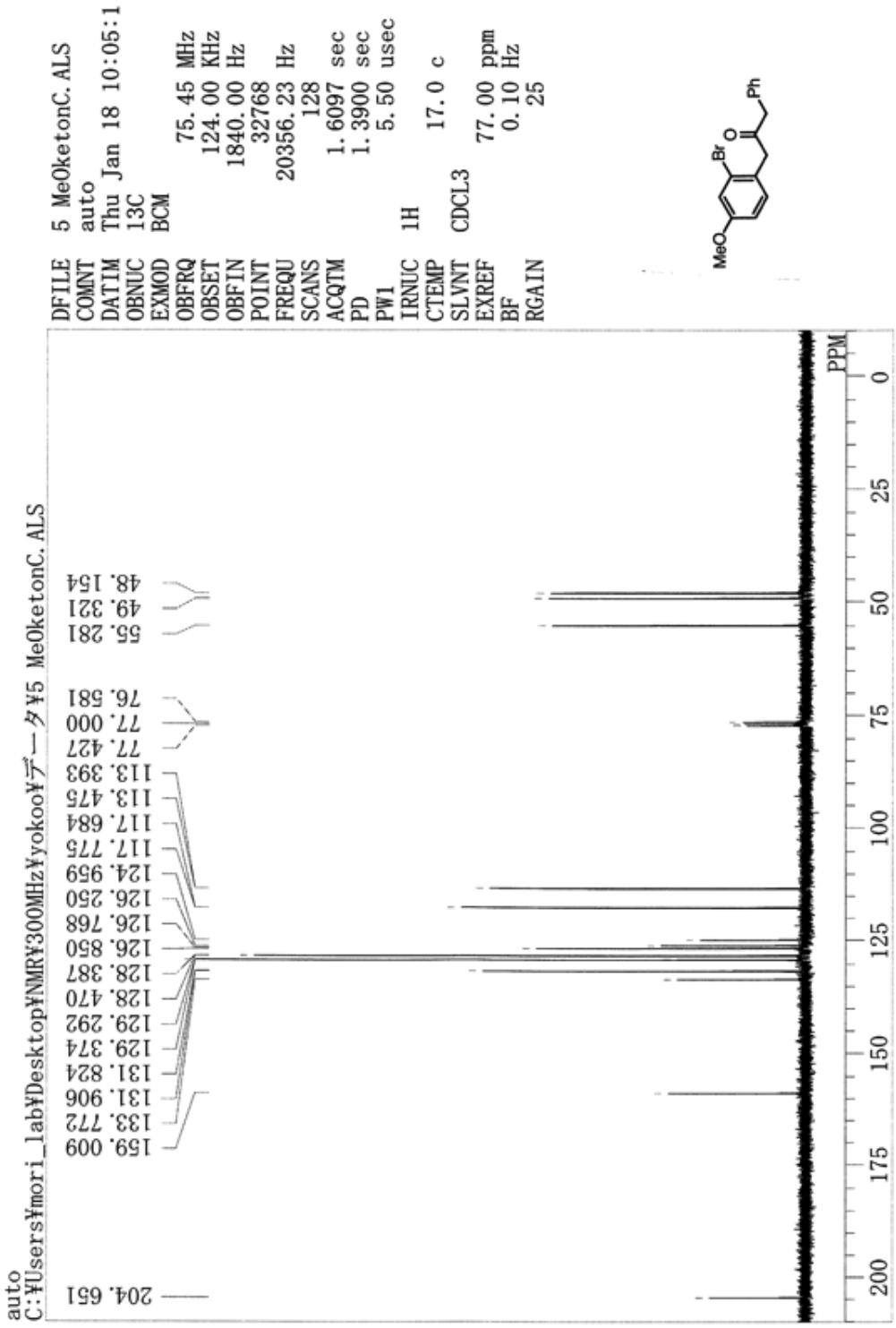
^{19}F NMR spectrum of **1b**.



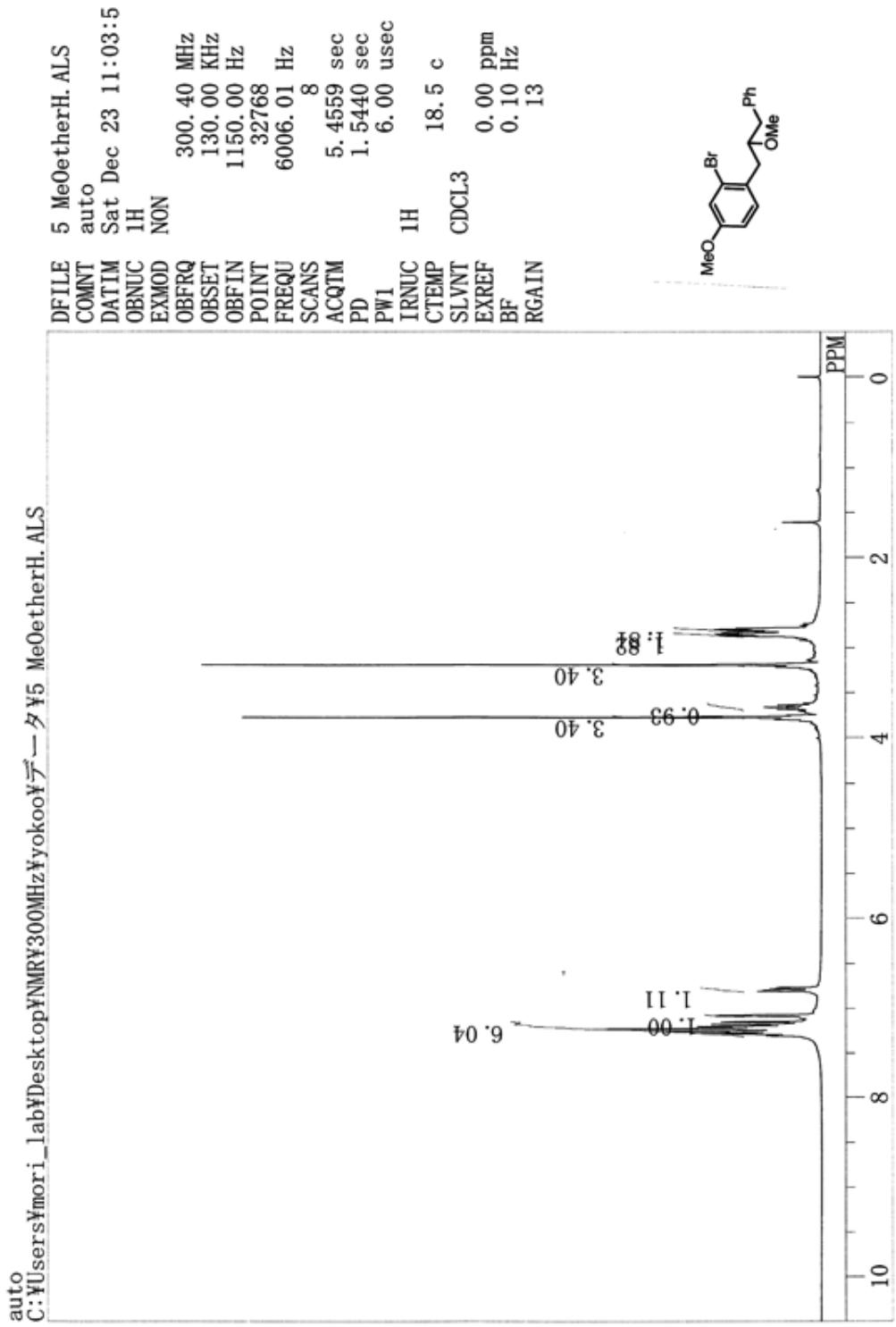
^{1}H NMR spectrum of **s12**.



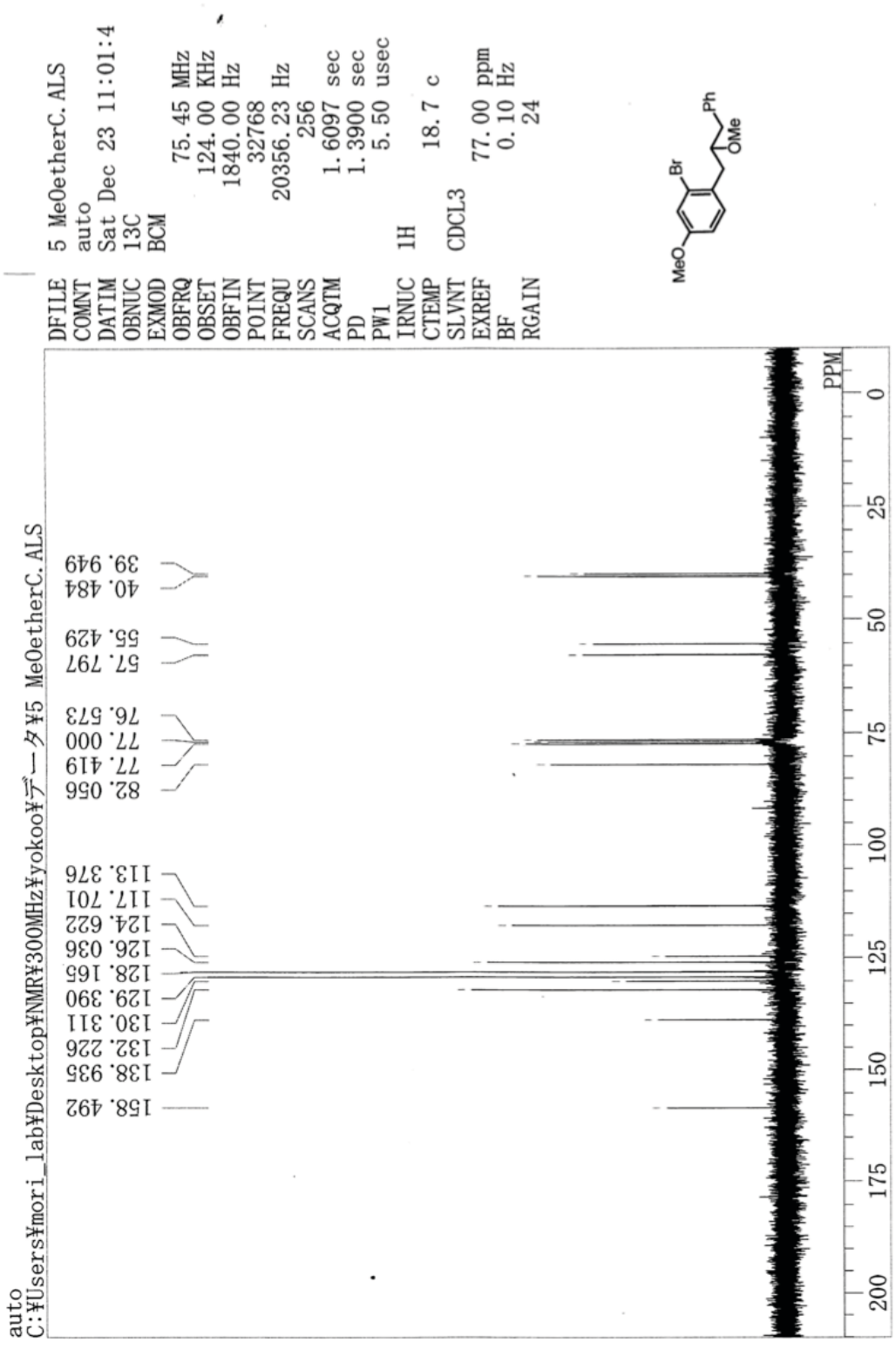
^{13}C NMR spectrum of **s12**.



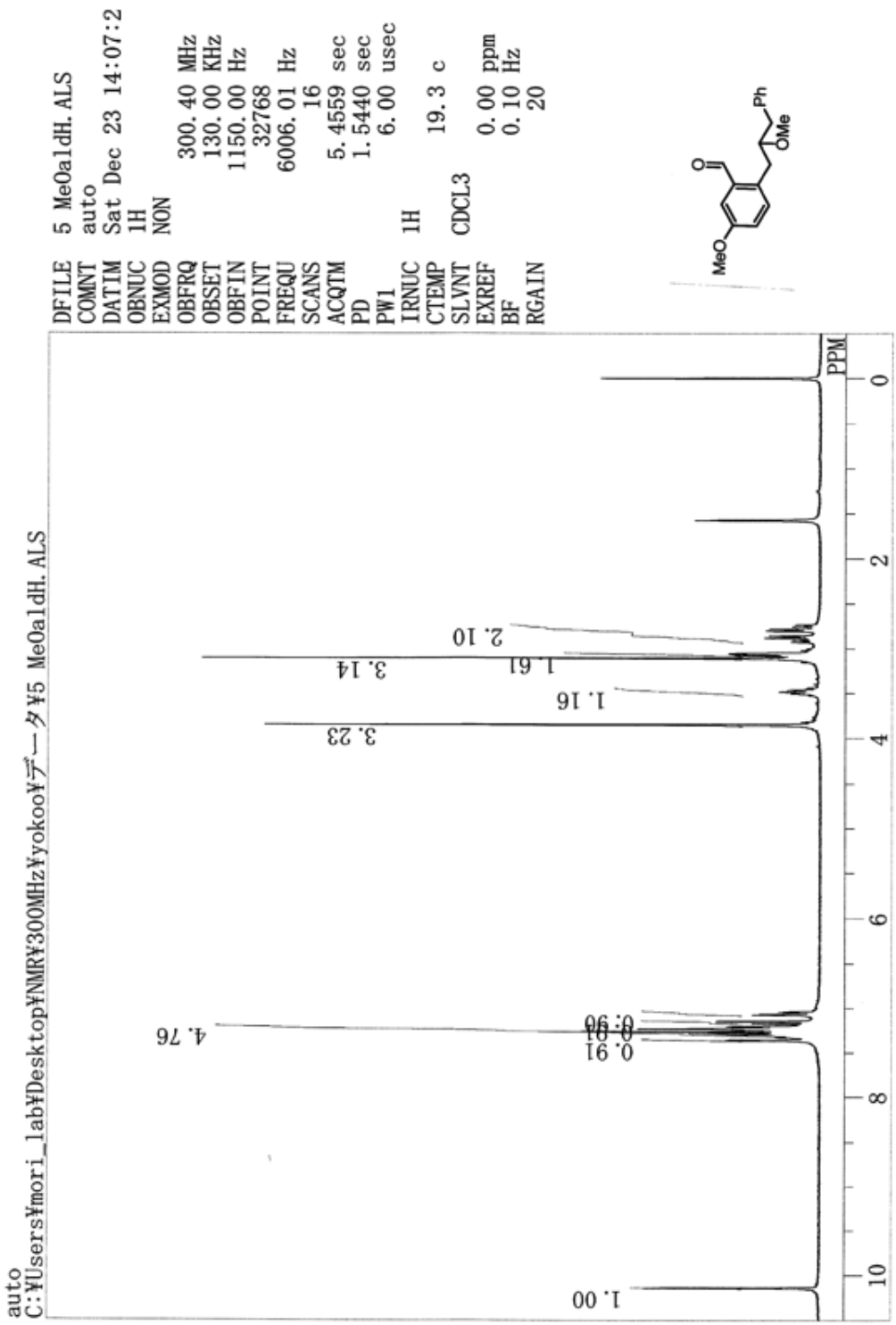
^{1}H NMR spectrum of **s13**.



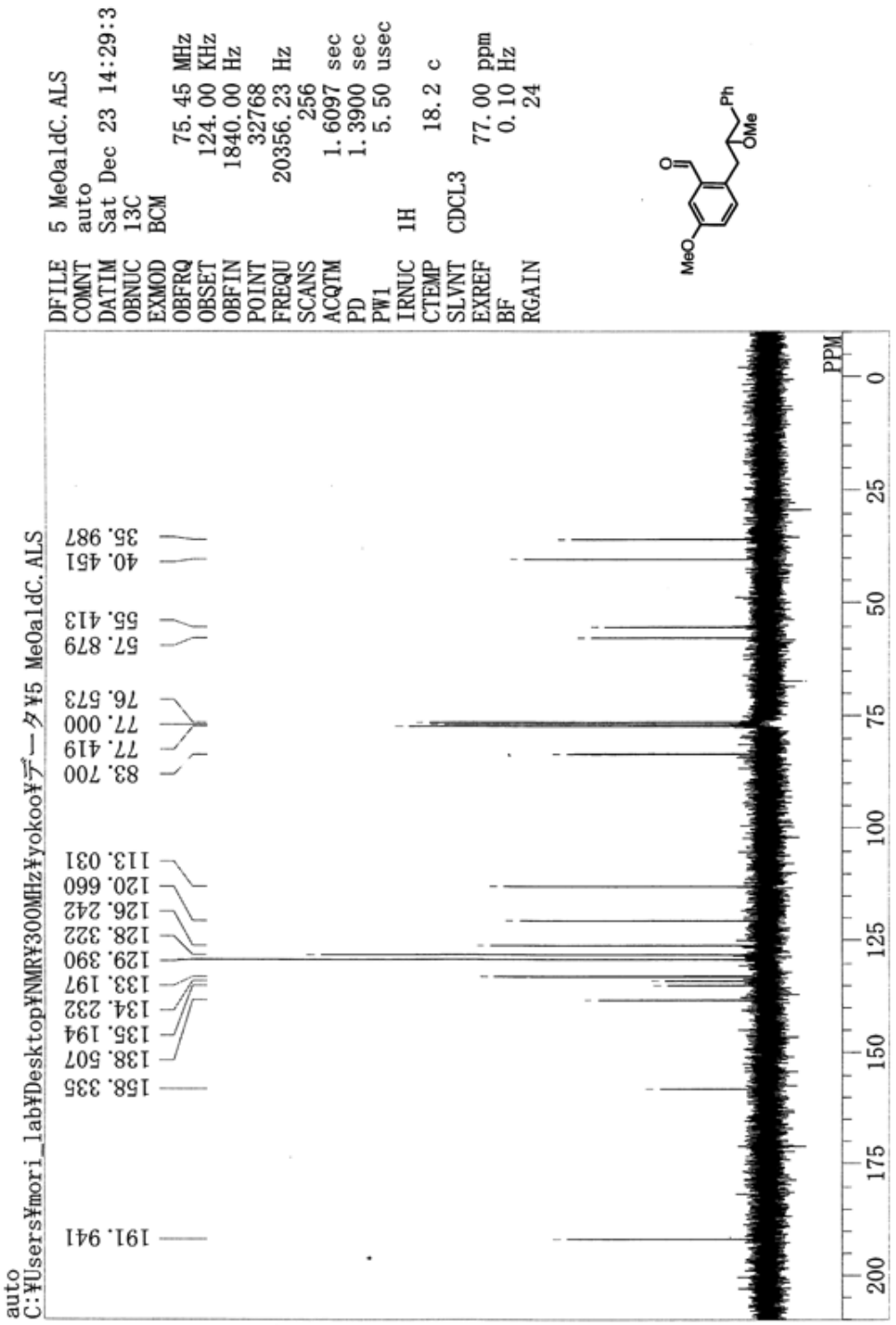
^{13}C NMR spectrum of **s13**.



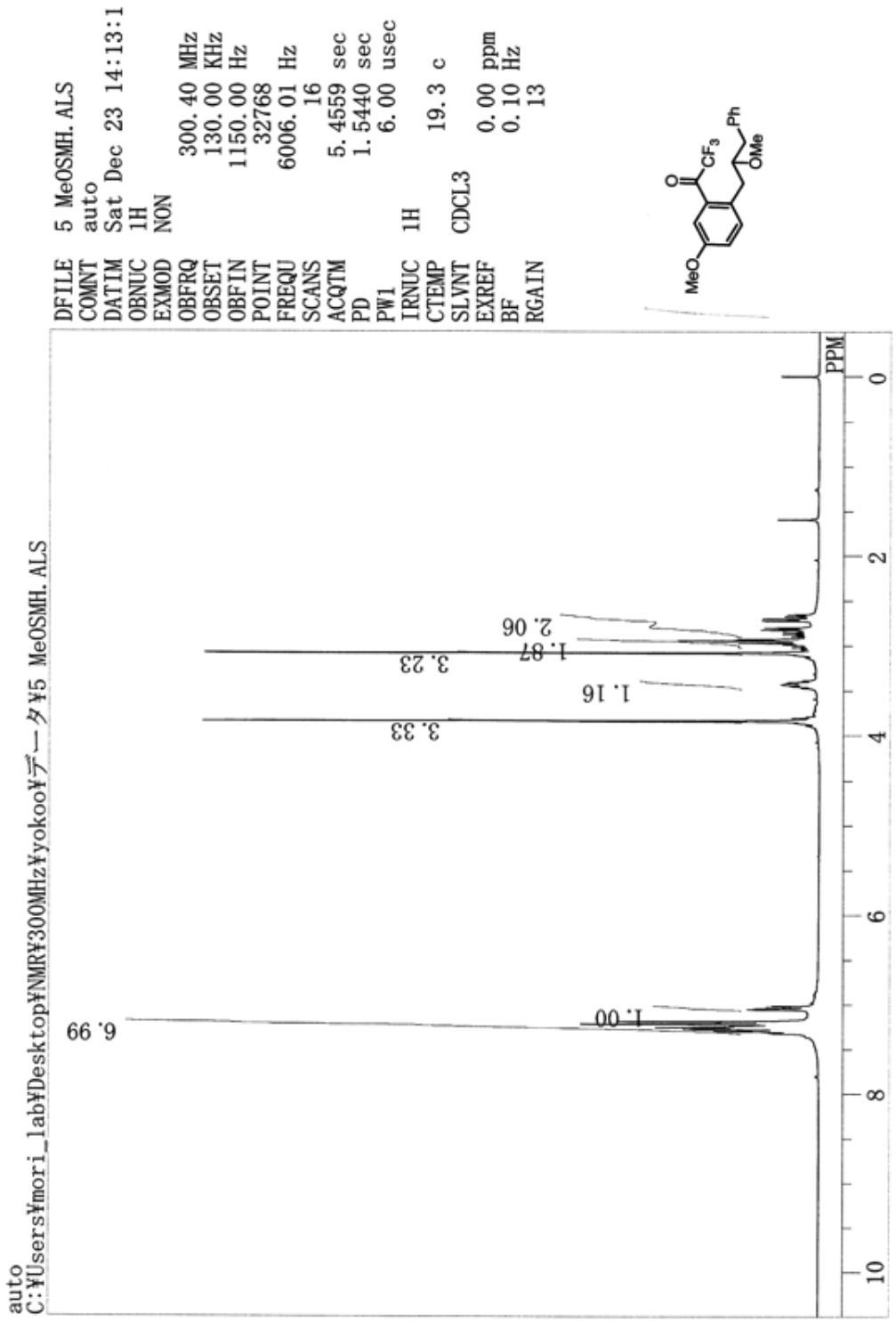
^{1}H NMR spectrum of **s14**.



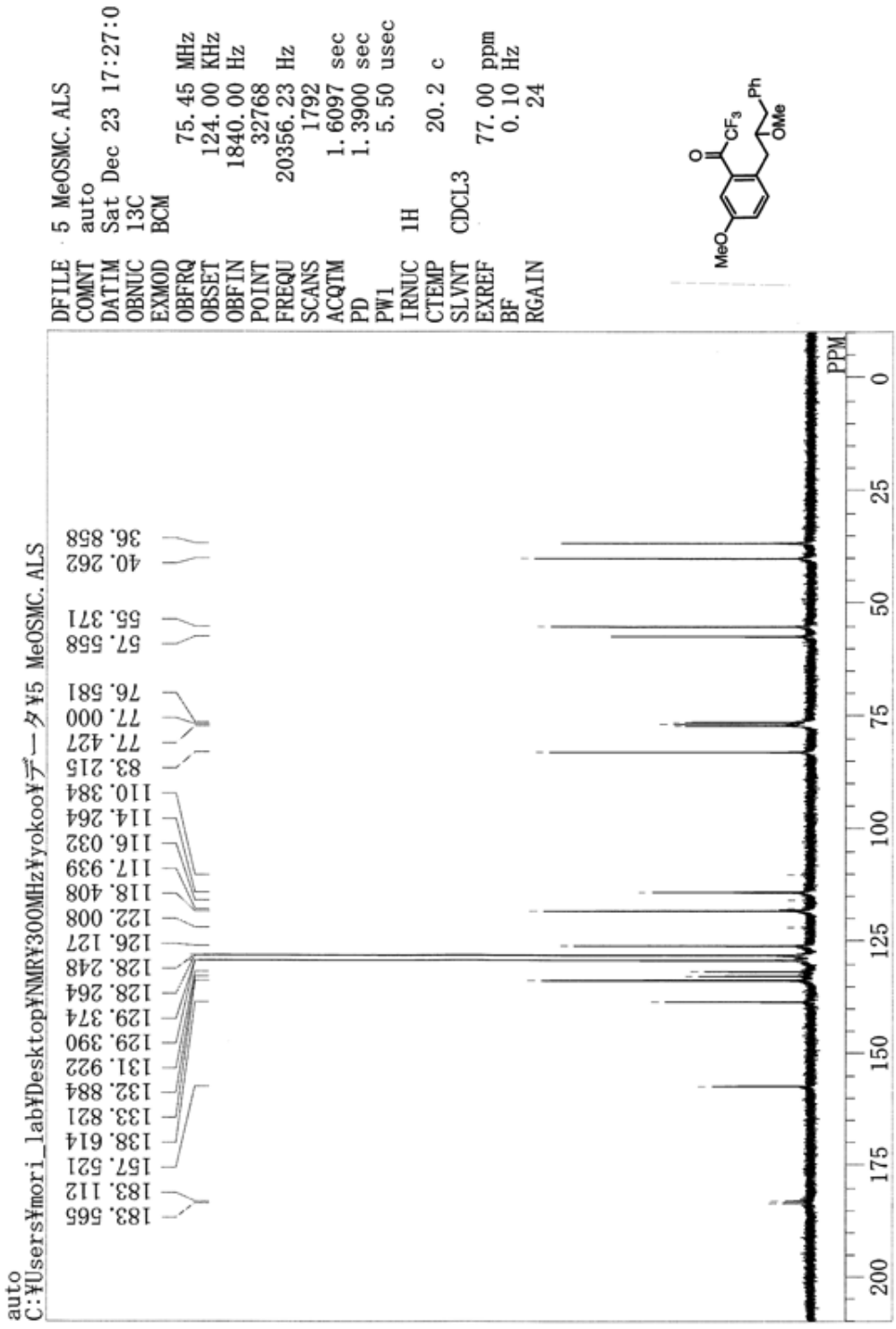
^{13}C NMR spectrum of **s14**.



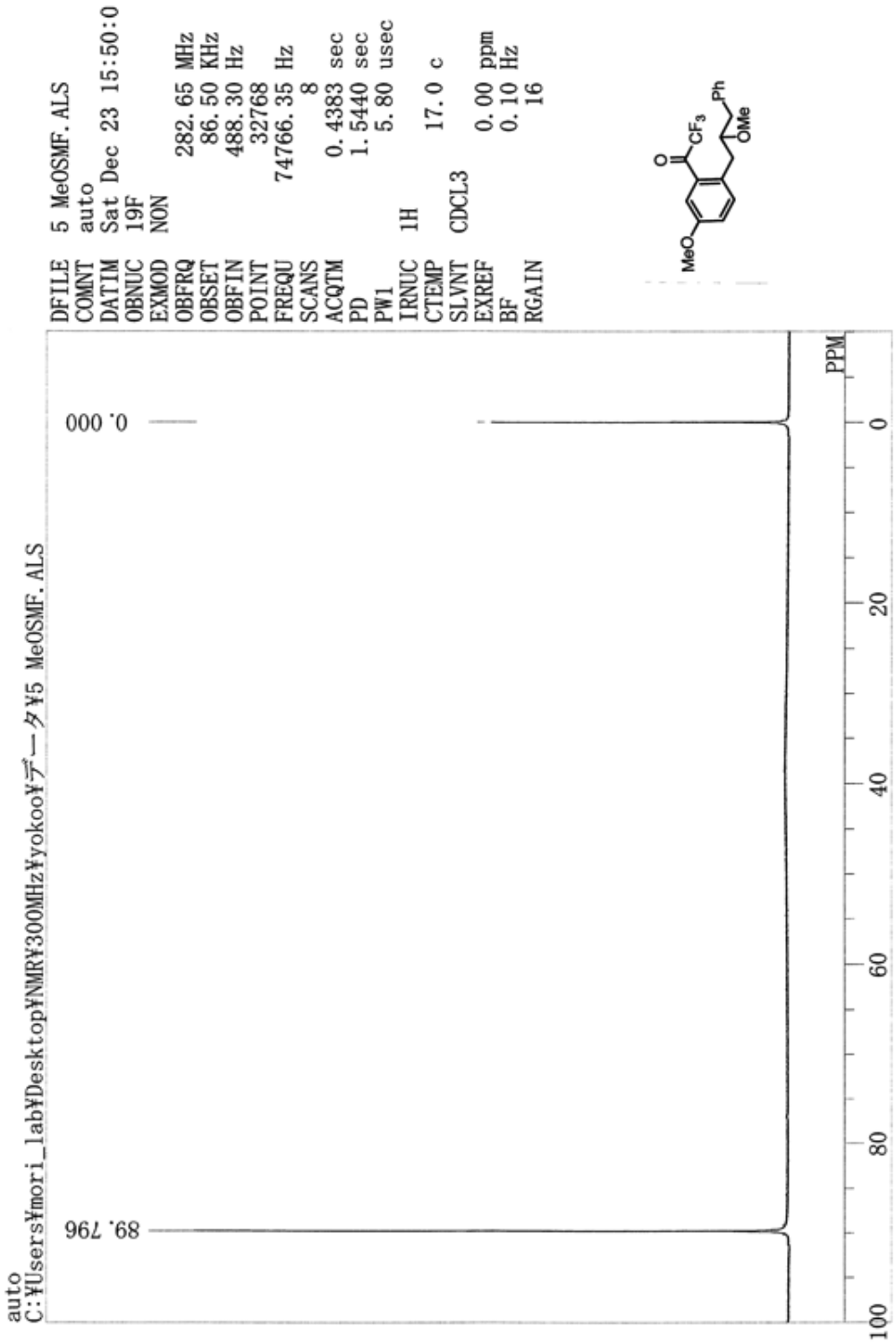
^{1}H NMR spectrum of **1c**.



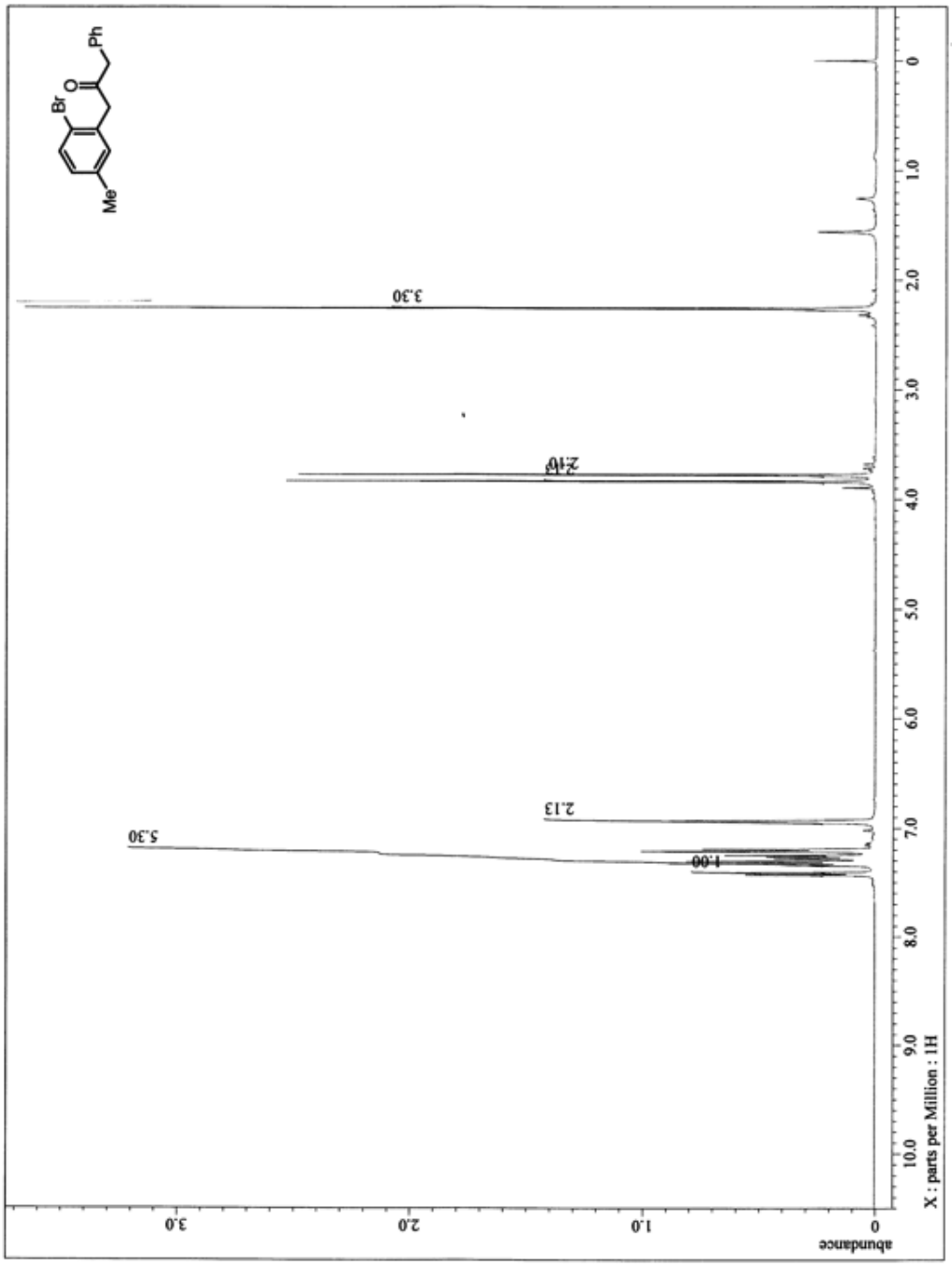
^{13}C NMR spectrum of **1c**.



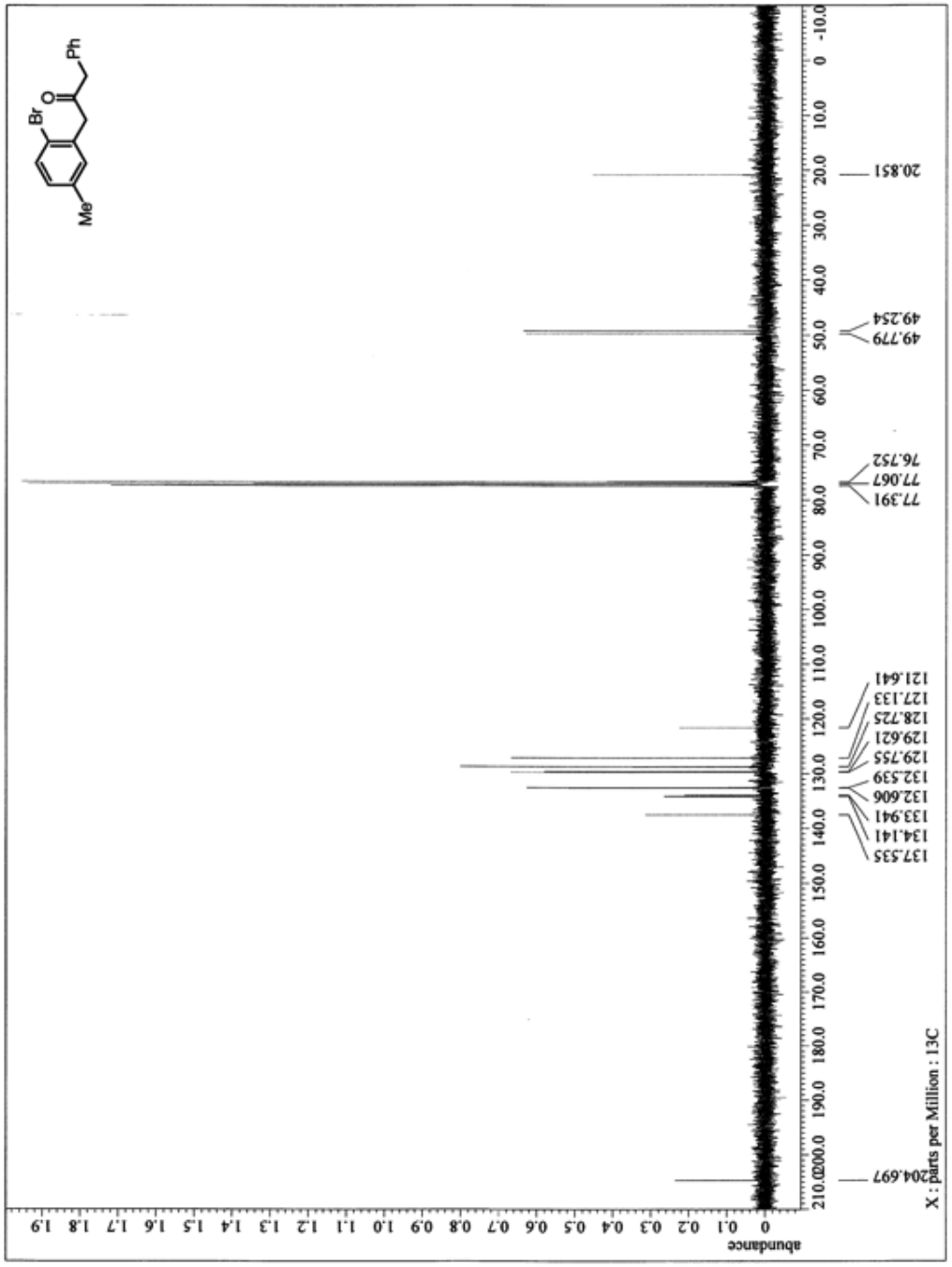
^{19}F NMR spectrum of **1c**.



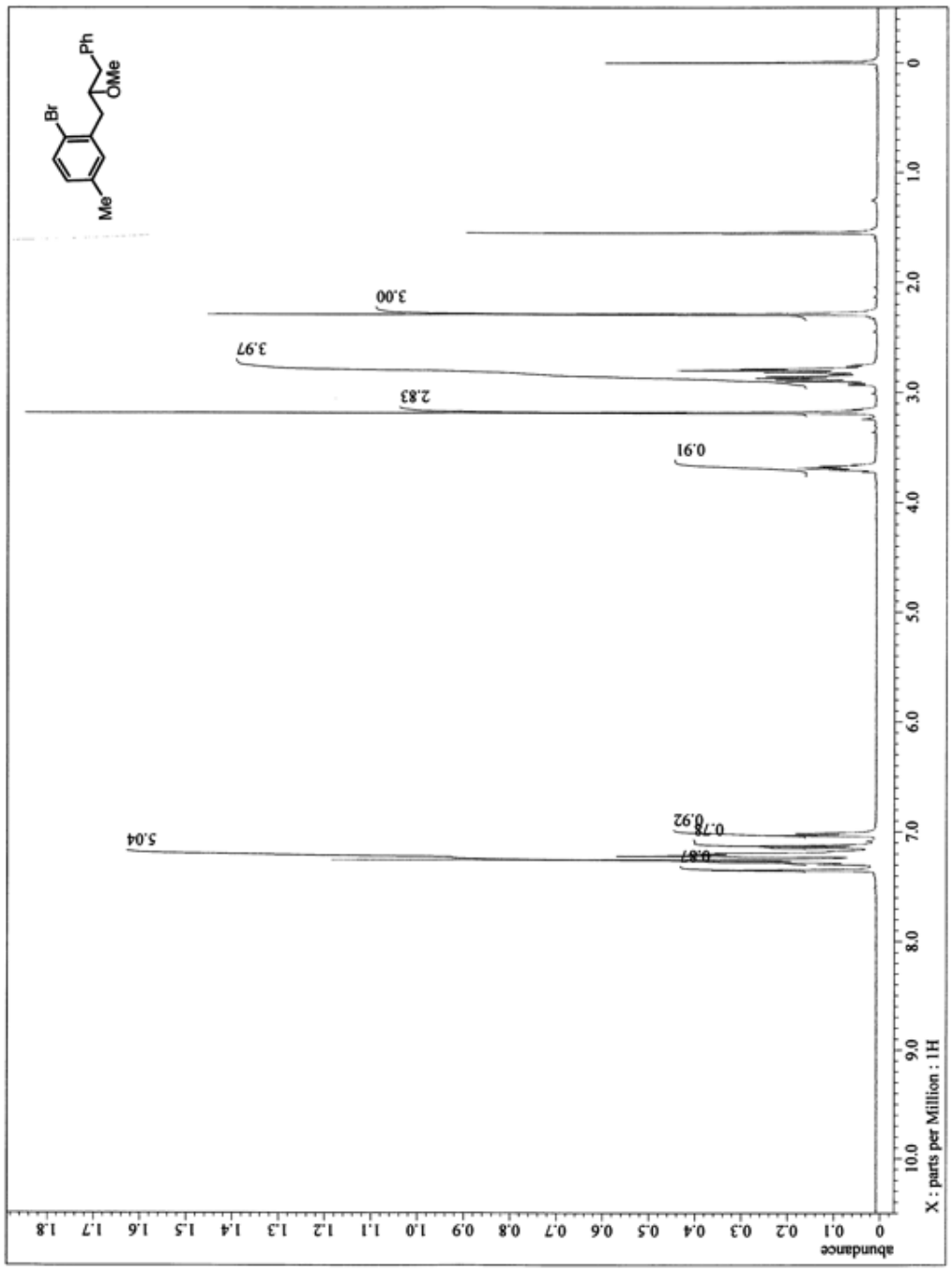
^{1}H NMR spectrum of **s15**.



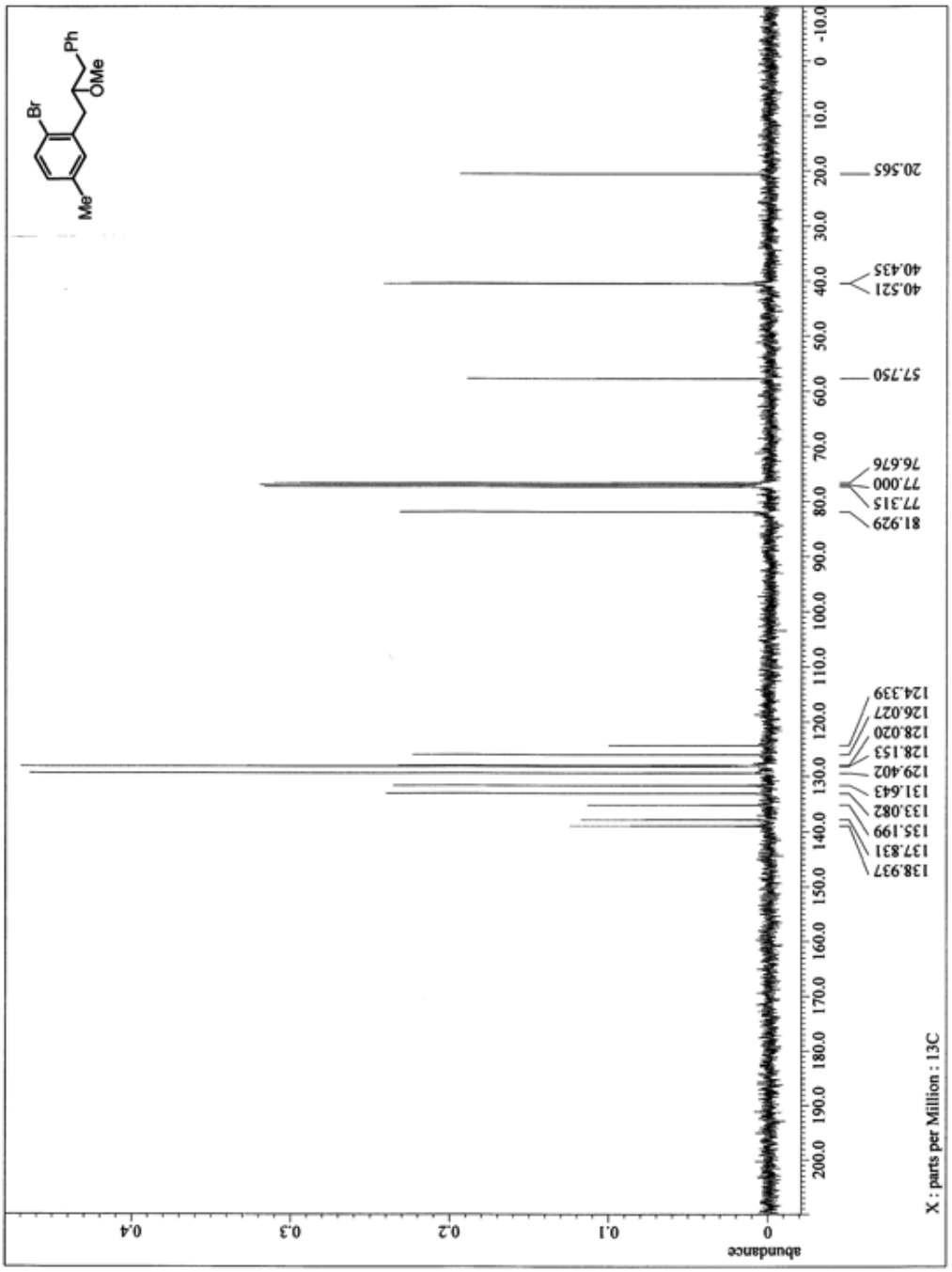
^{13}C NMR spectrum of **s15**.



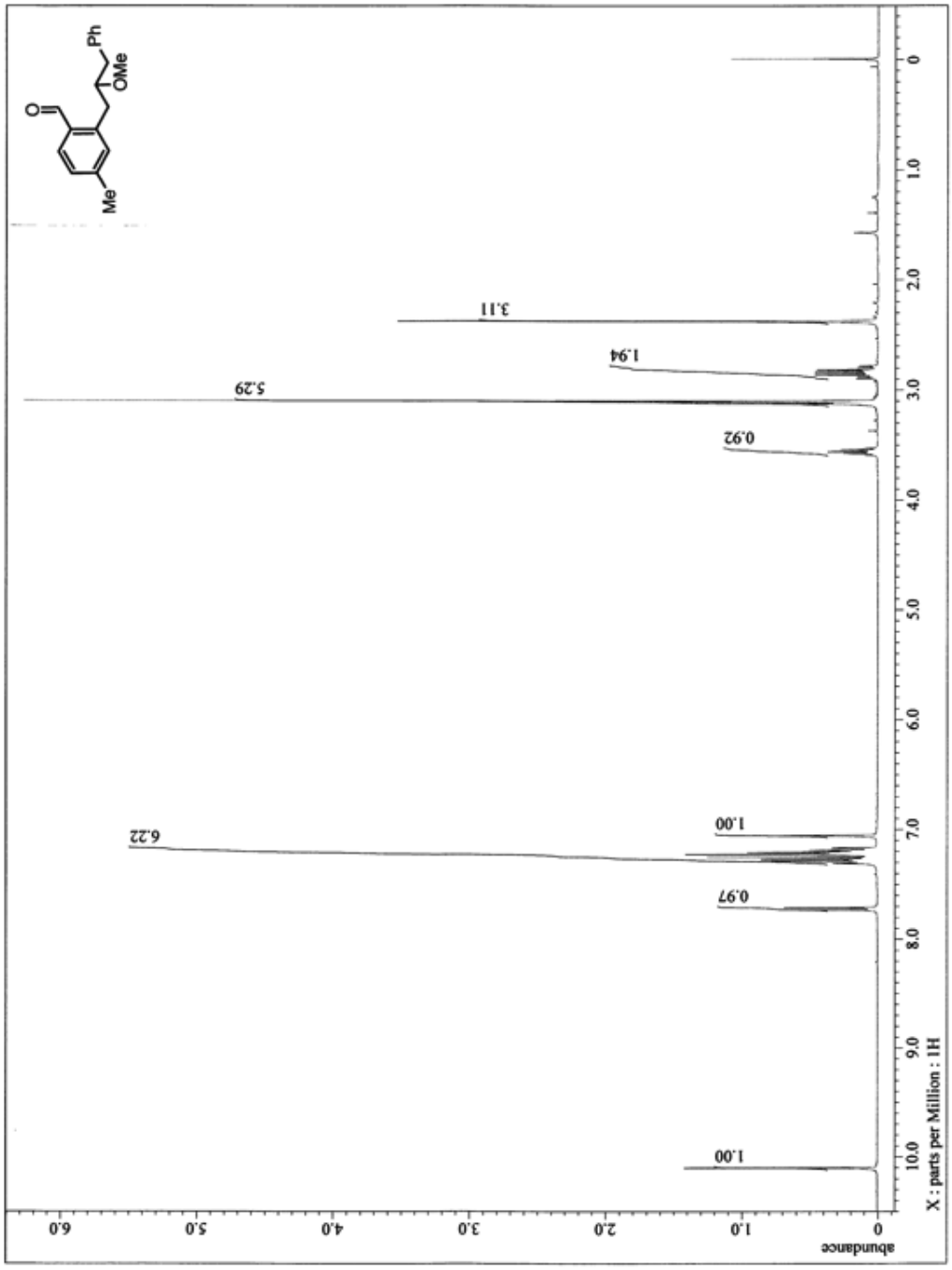
^{1}H NMR spectrum of **s16**.



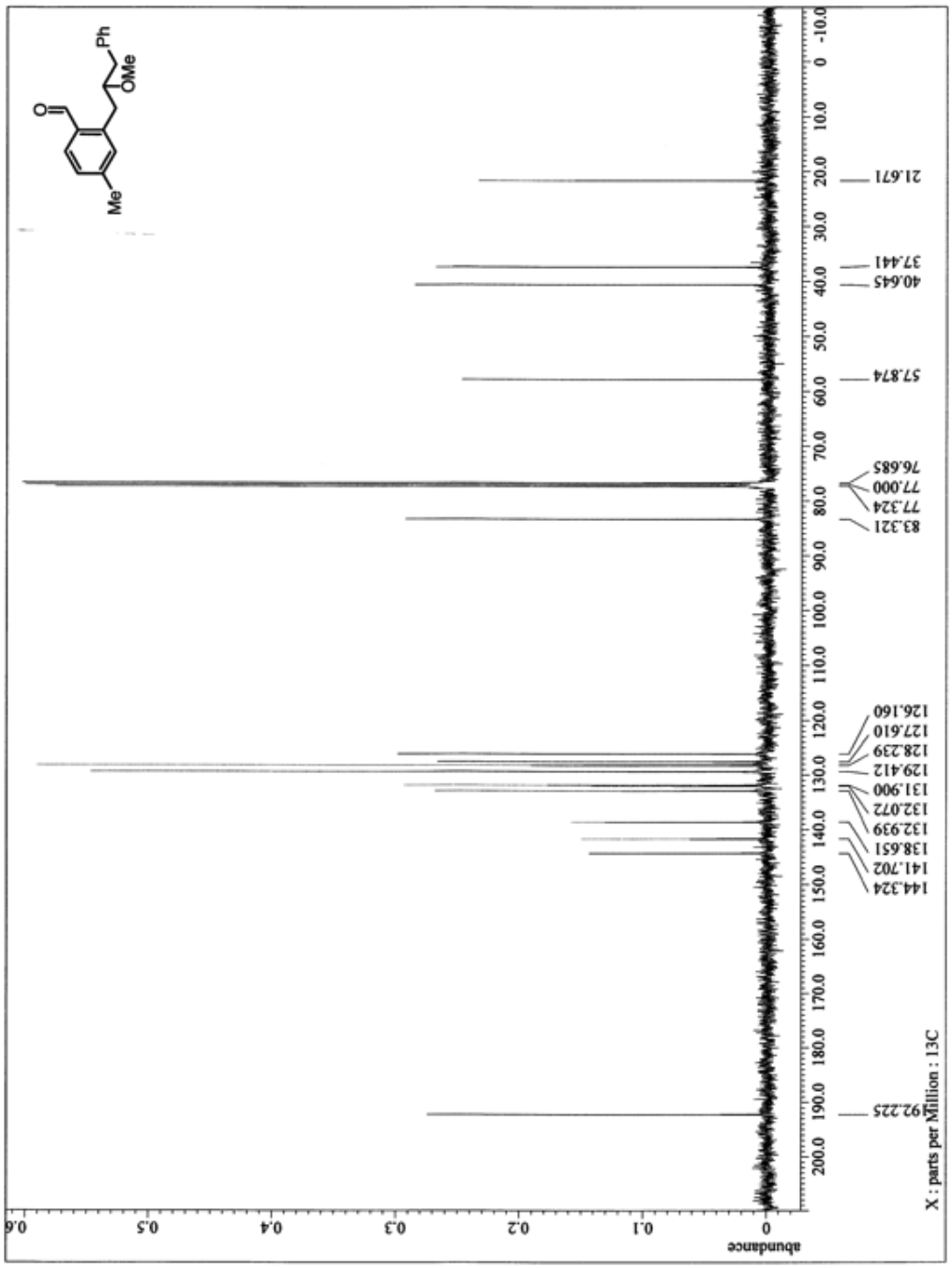
^{13}C NMR spectrum of **s16**.



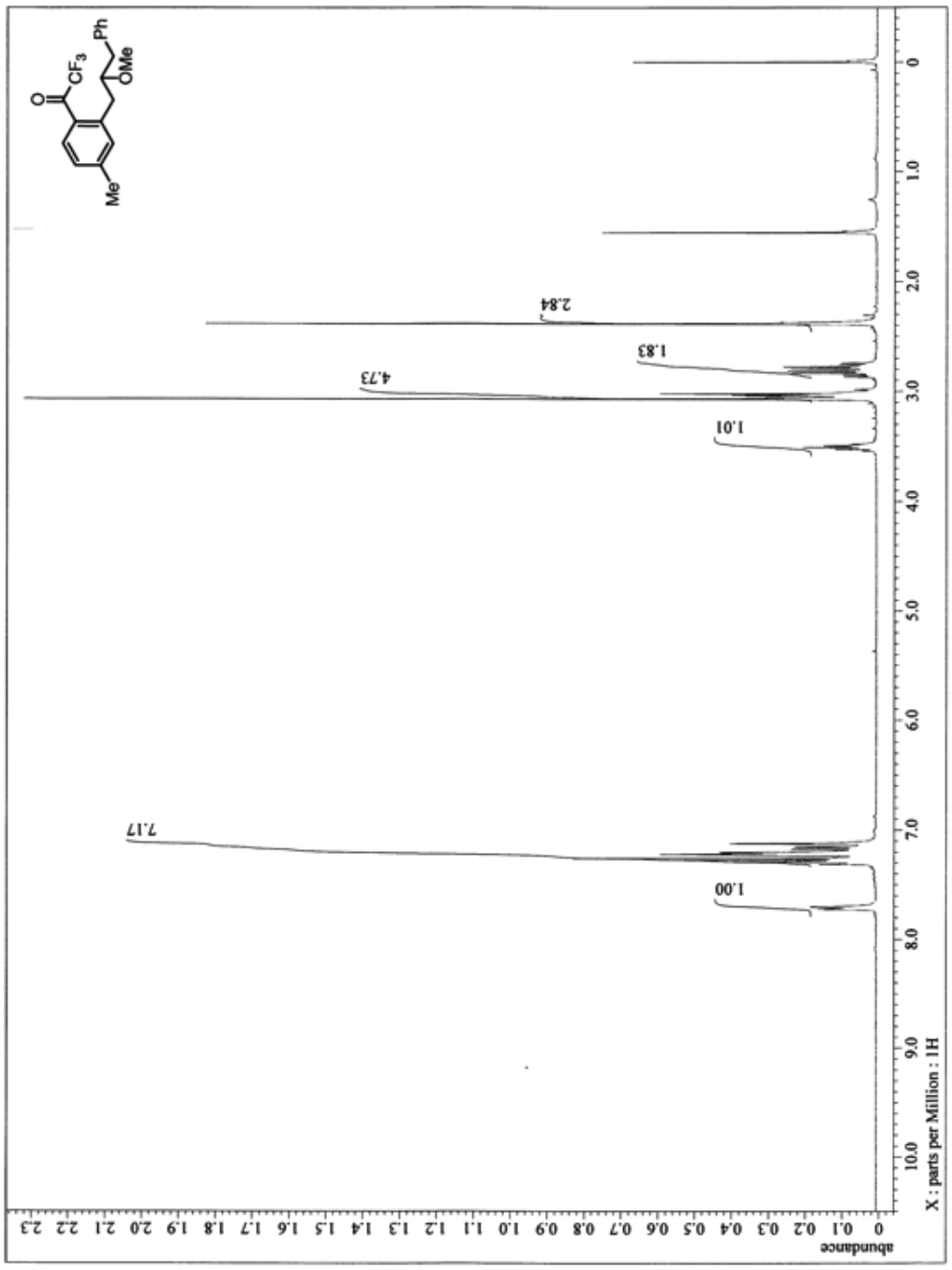
^{1}H NMR spectrum of **s17**.



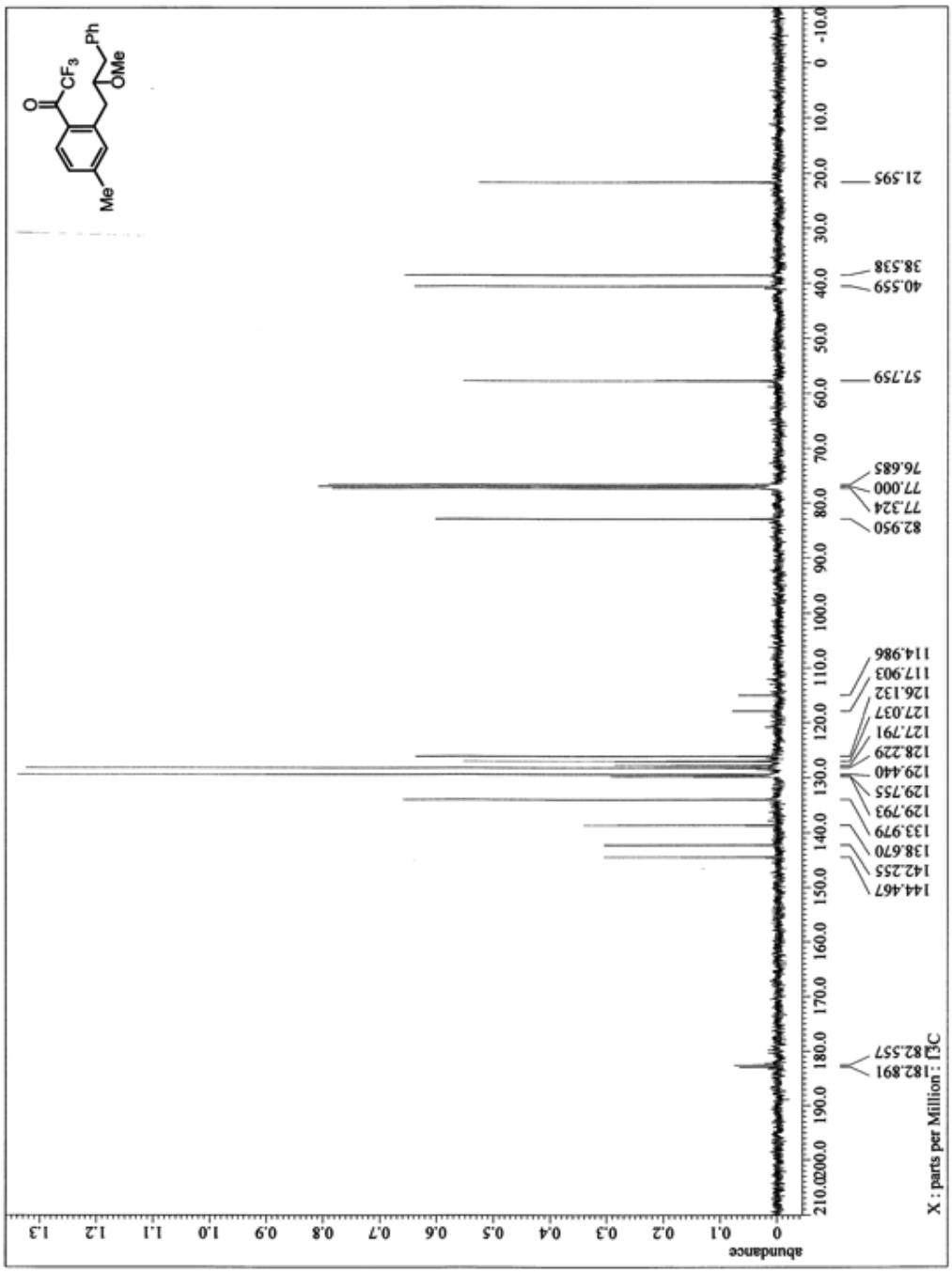
^{13}C NMR spectrum of **s17**.



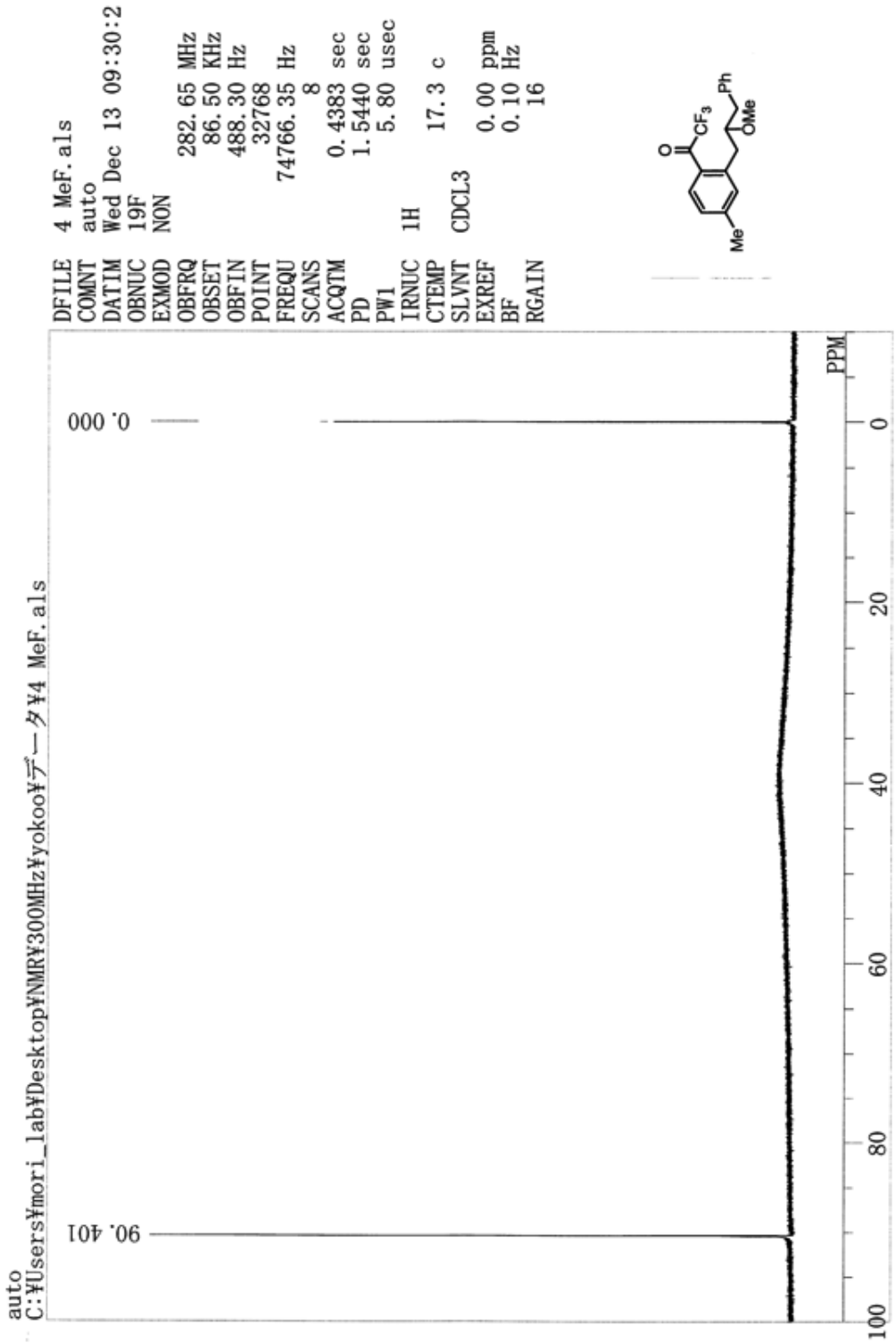
^{1}H NMR spectrum of **1d**.



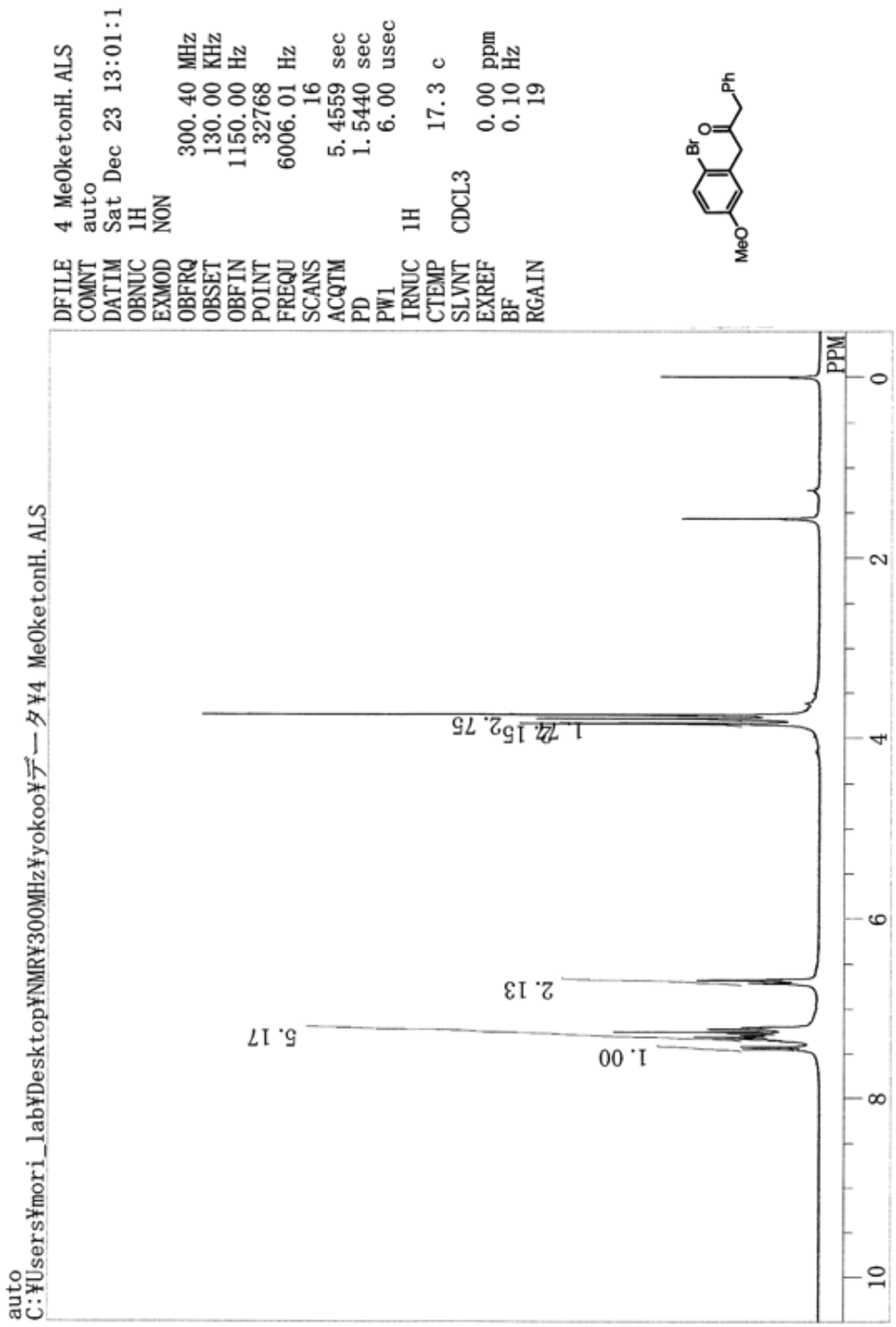
^{13}C NMR spectrum of **1d**.



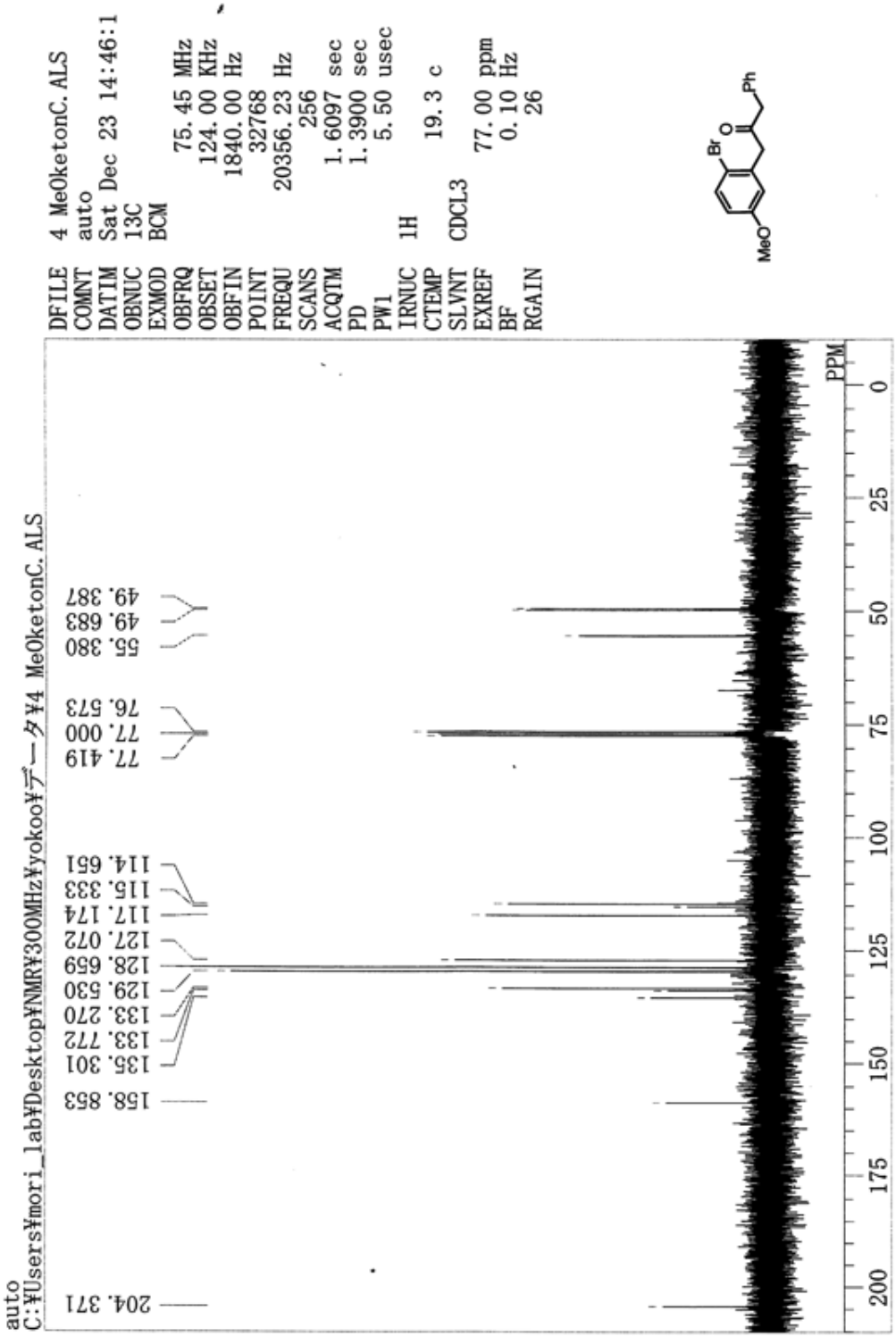
^{19}F NMR spectrum of **1d**.



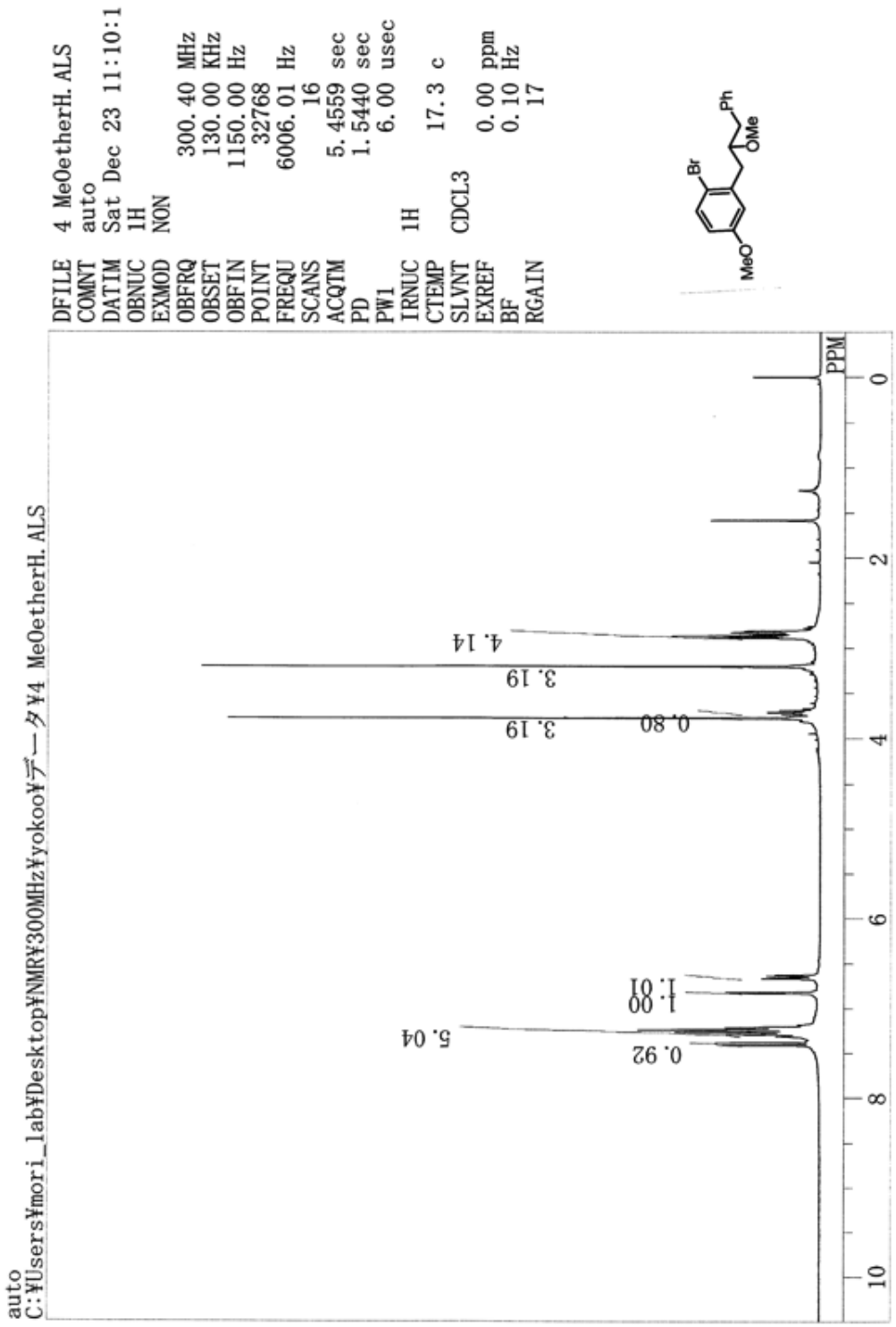
^{1}H NMR spectrum of **s18**.



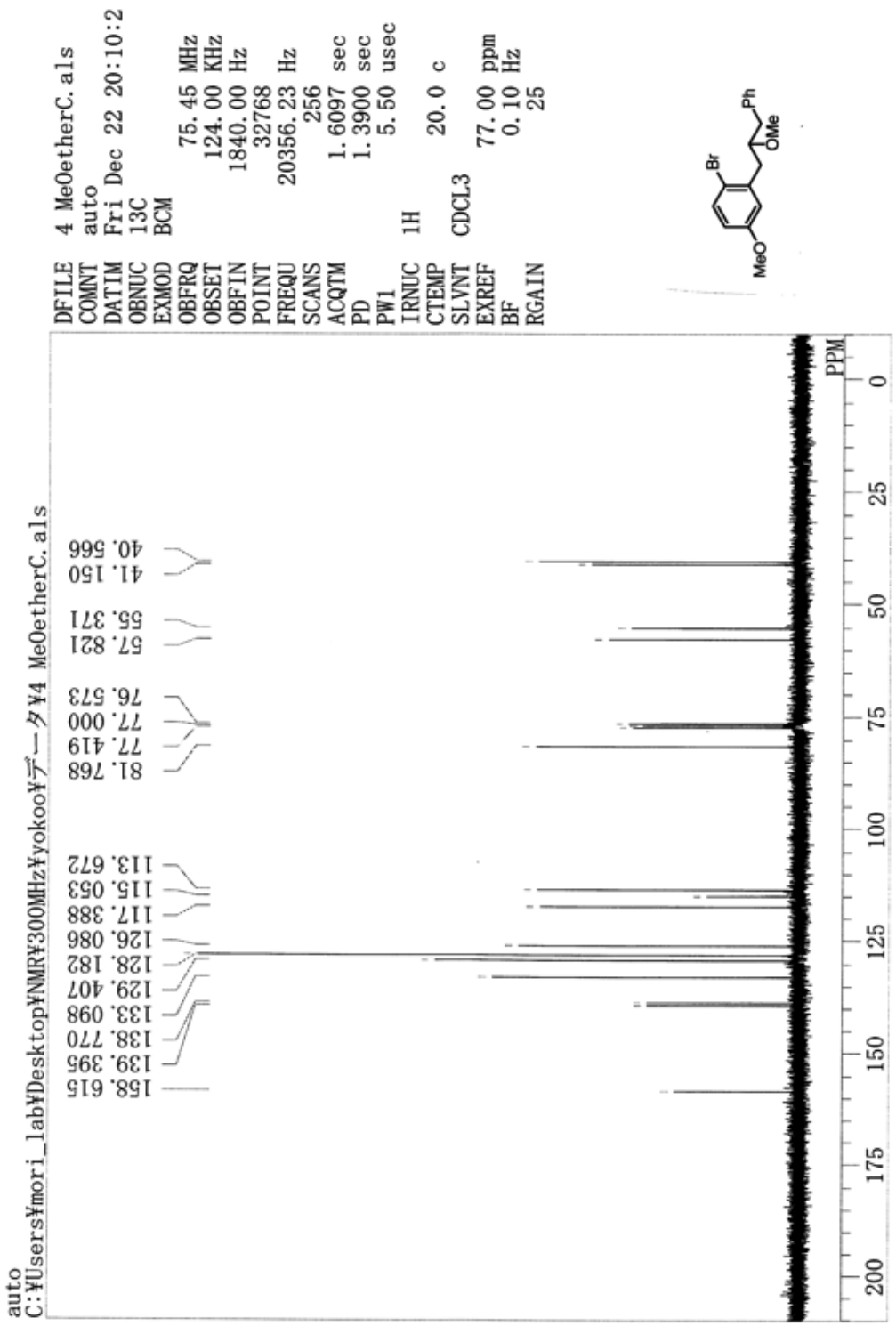
^{13}C NMR spectrum of **s18**.



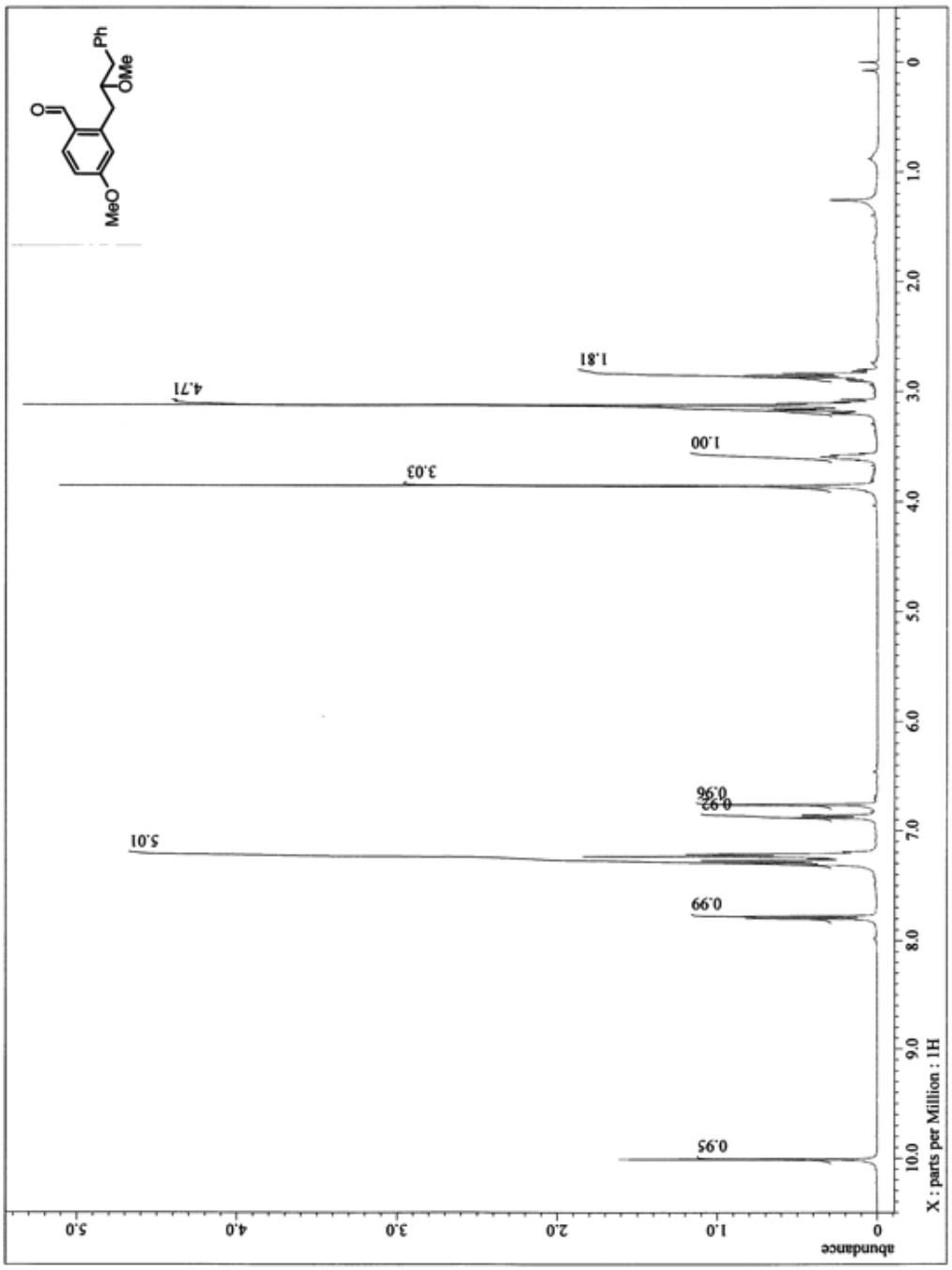
^{1}H NMR spectrum of **s19**.



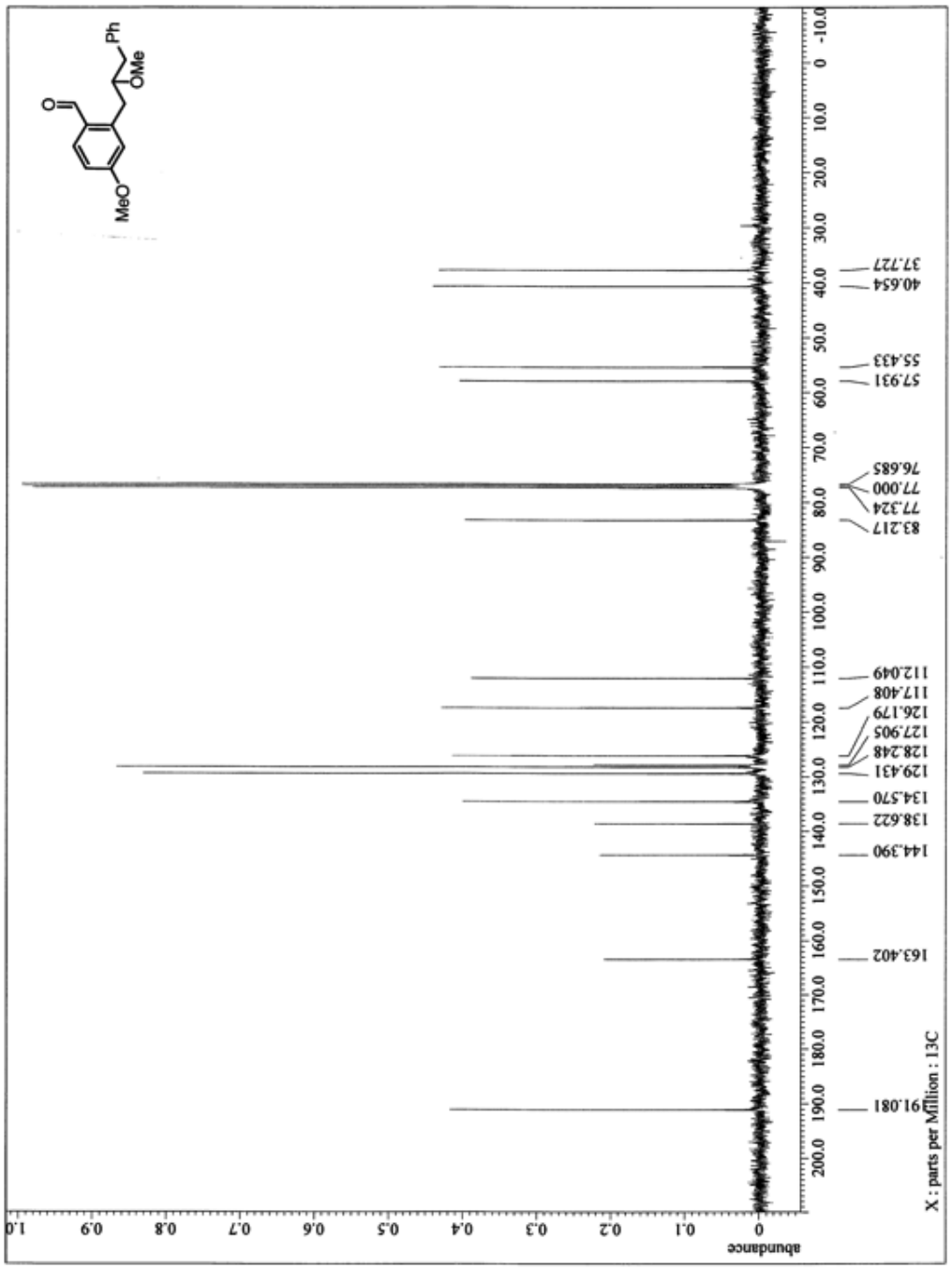
^{13}C NMR spectrum of **s19**.



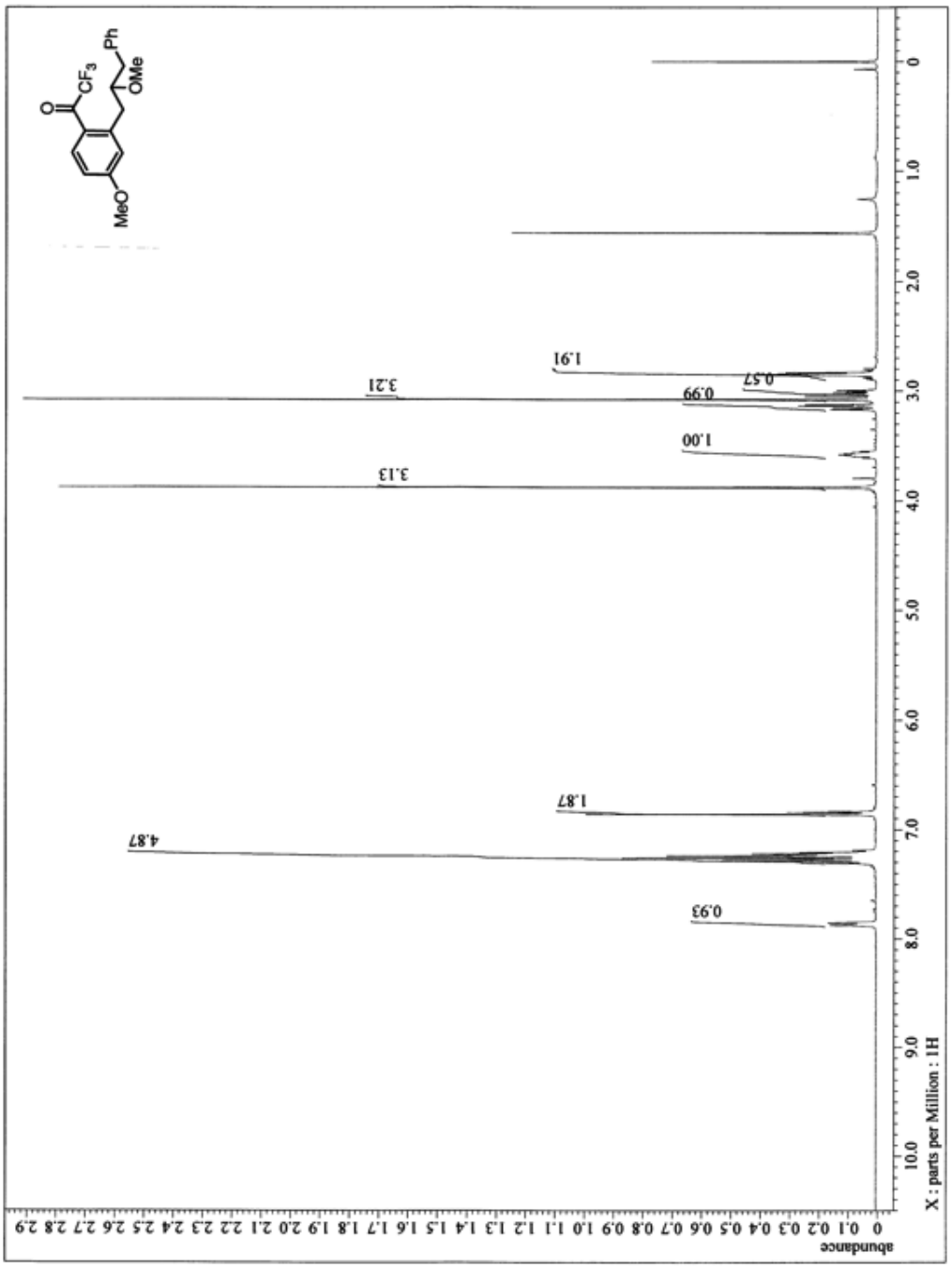
^{1}H NMR spectrum of **s20**.



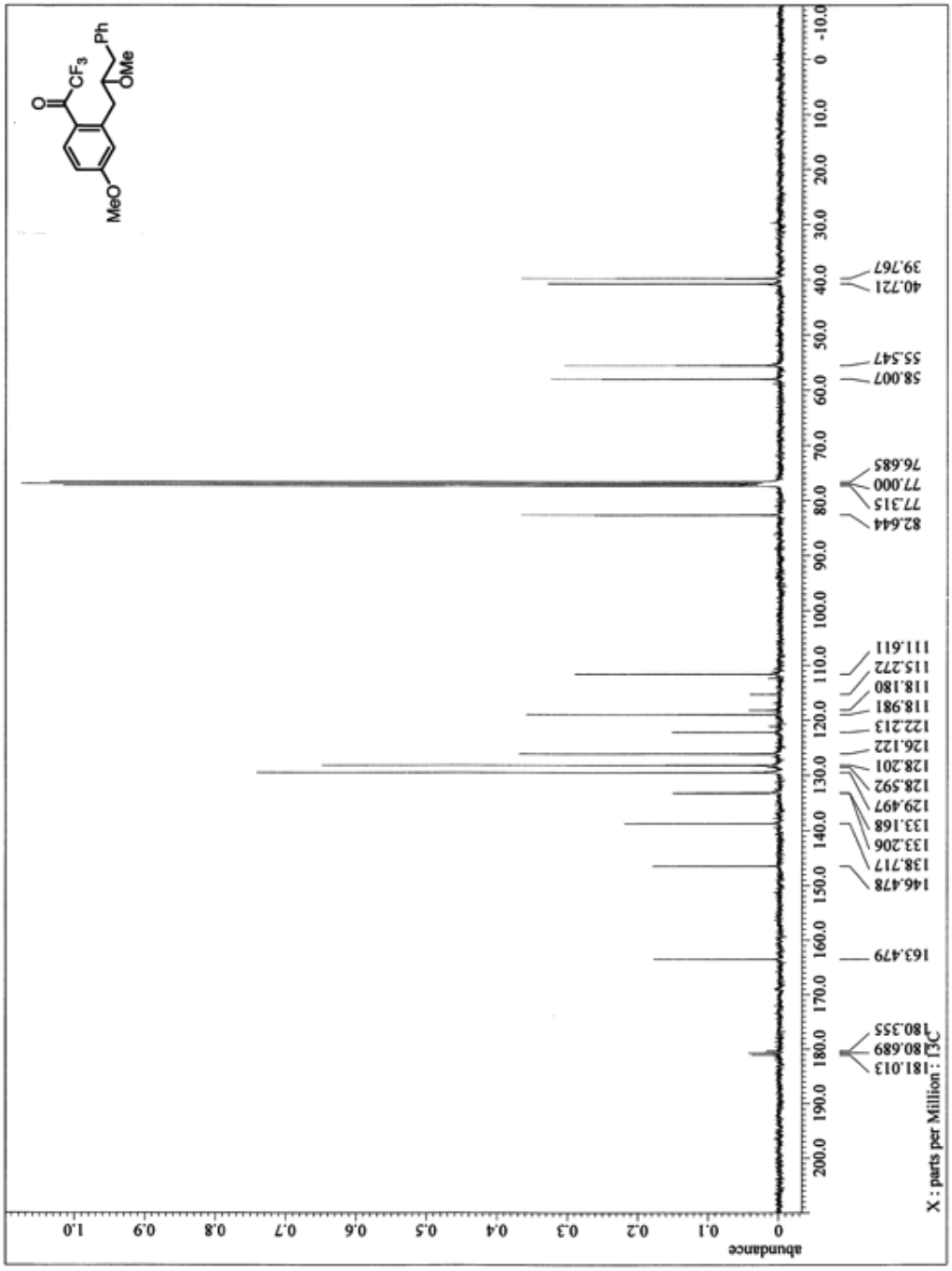
^{13}C NMR spectrum of **s20**.



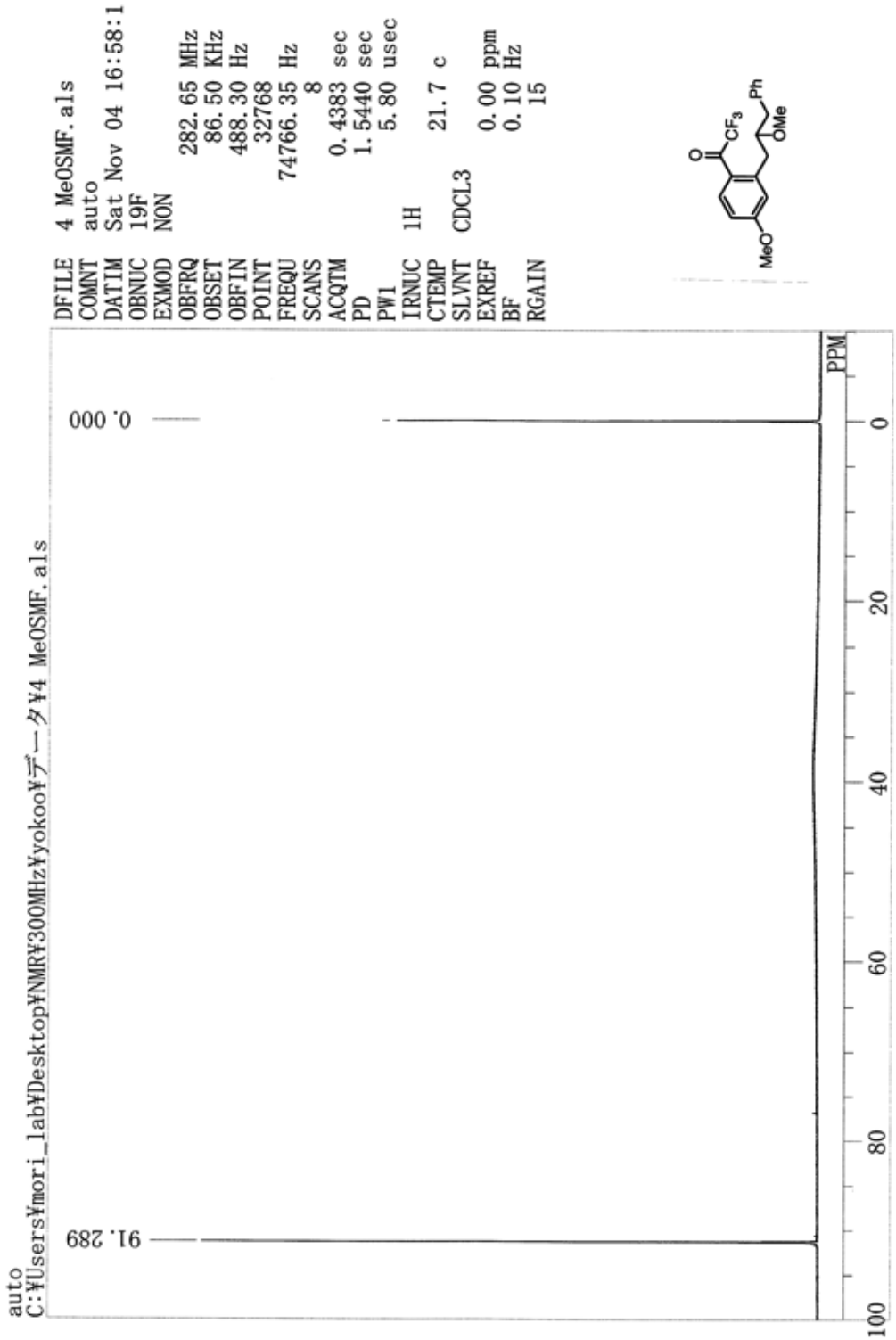
^{1}H NMR spectrum of **1e**.



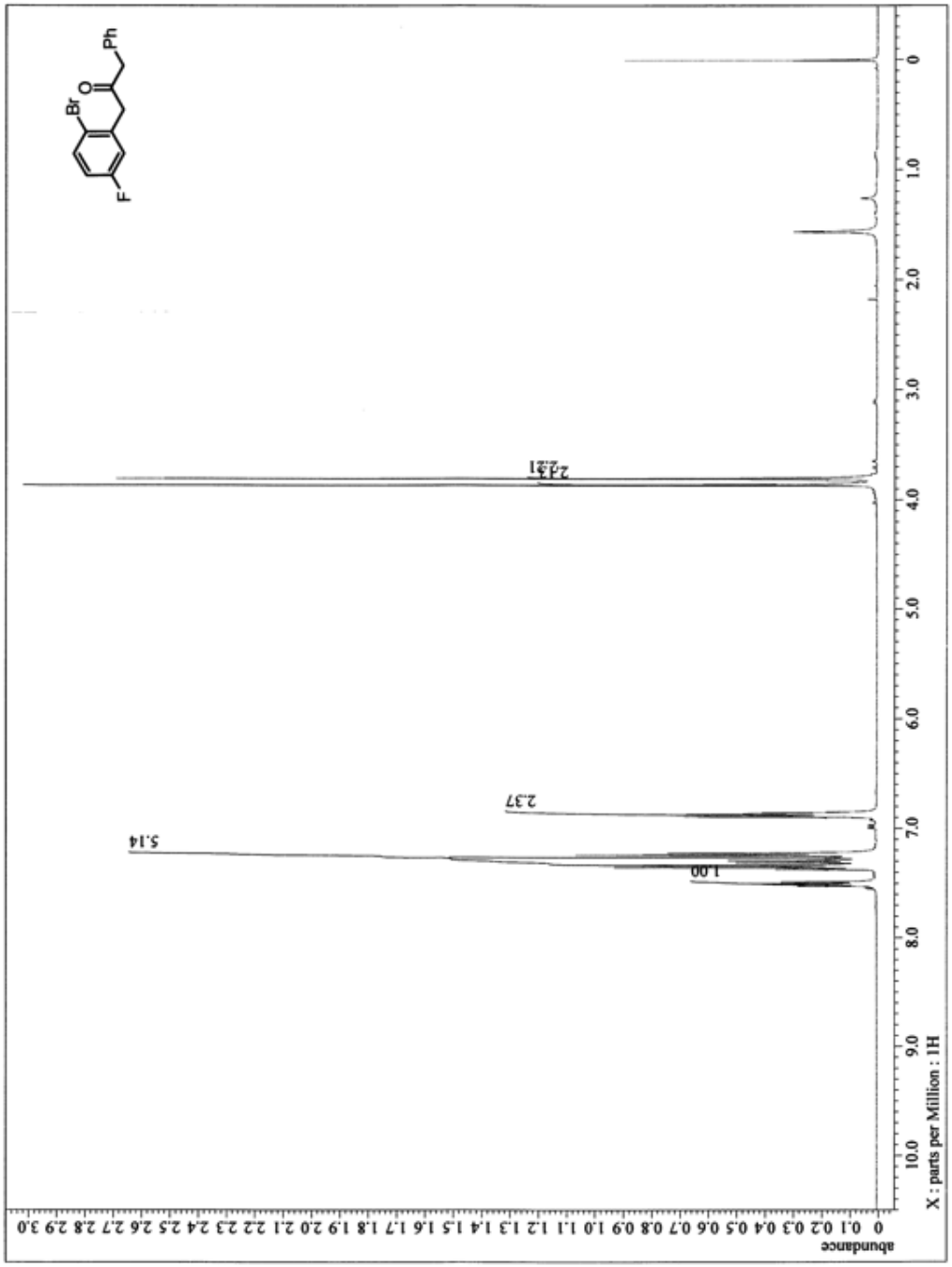
^{13}C NMR spectrum of **1e**.



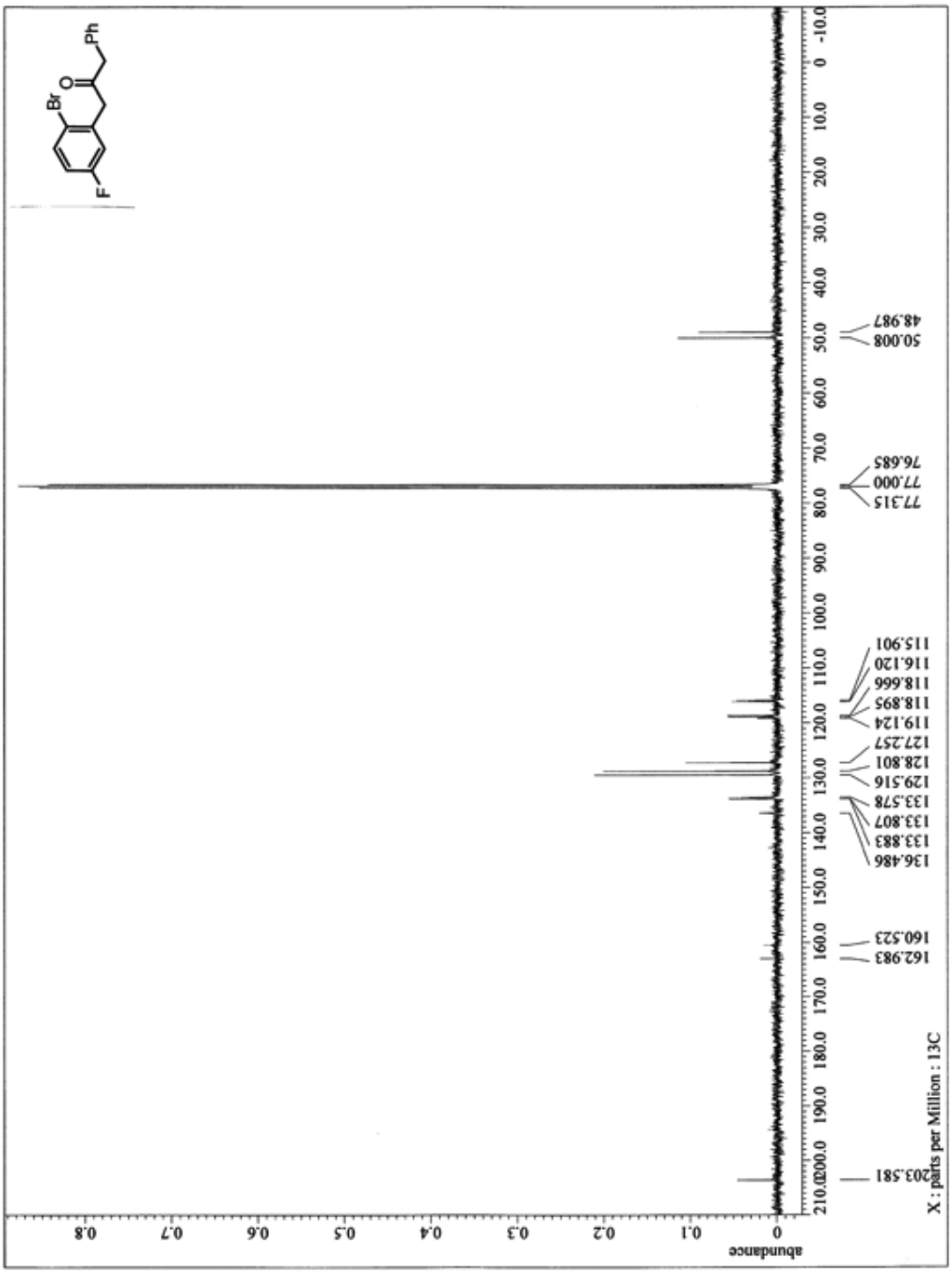
^{19}F NMR spectrum of **1e**.



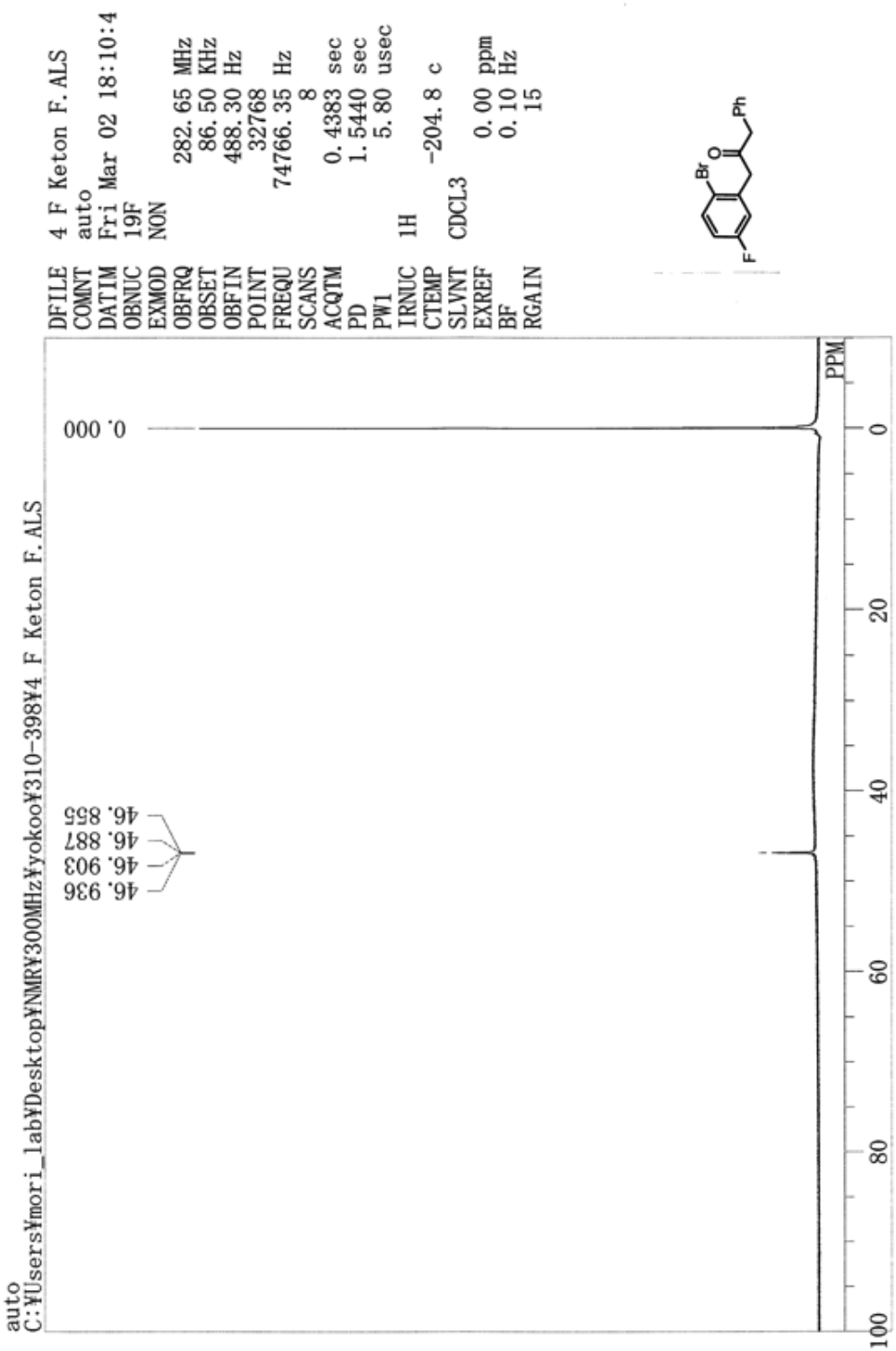
^{1}H NMR spectrum of **s21**.



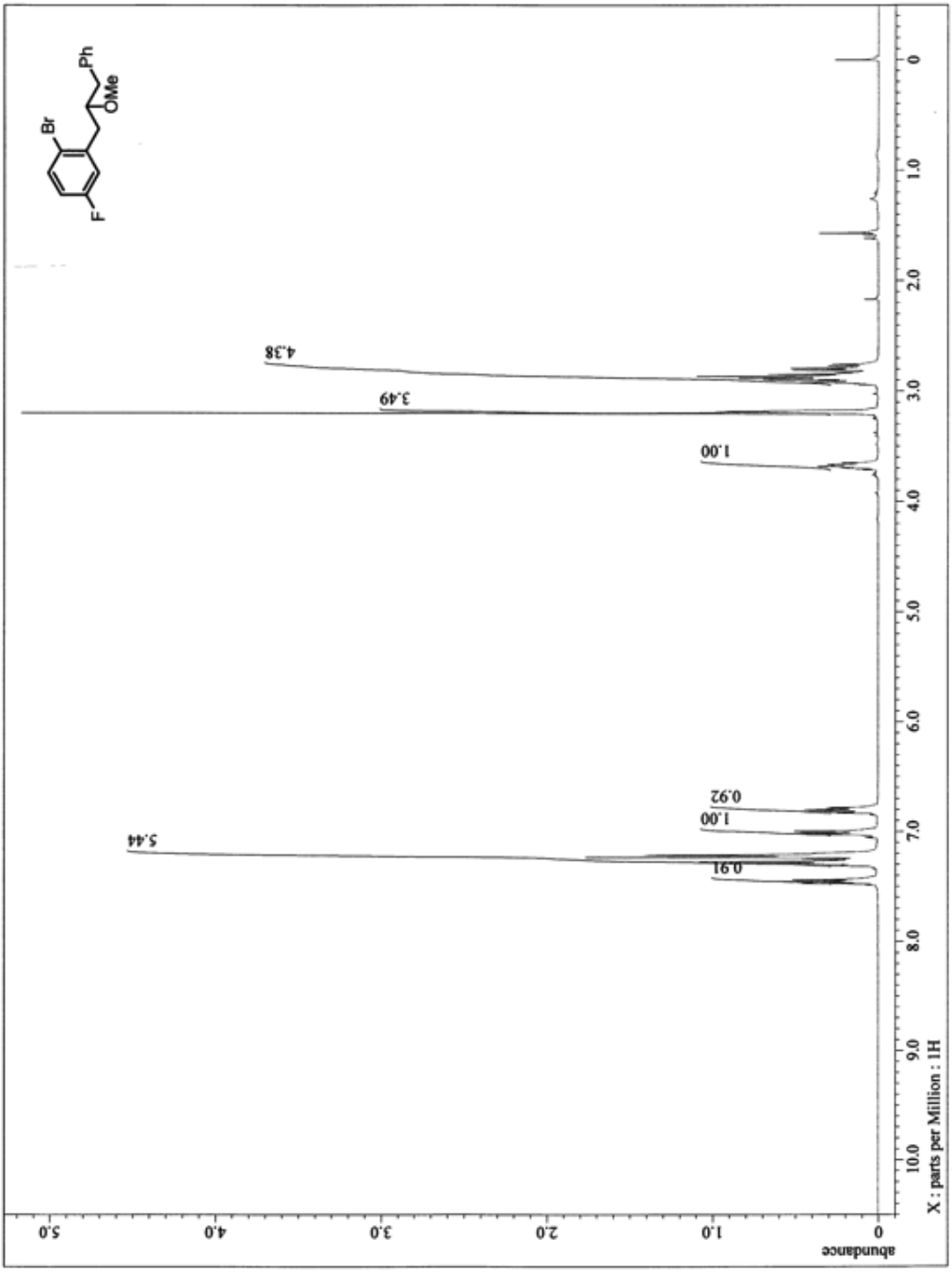
^{13}C NMR spectrum of **s21**.



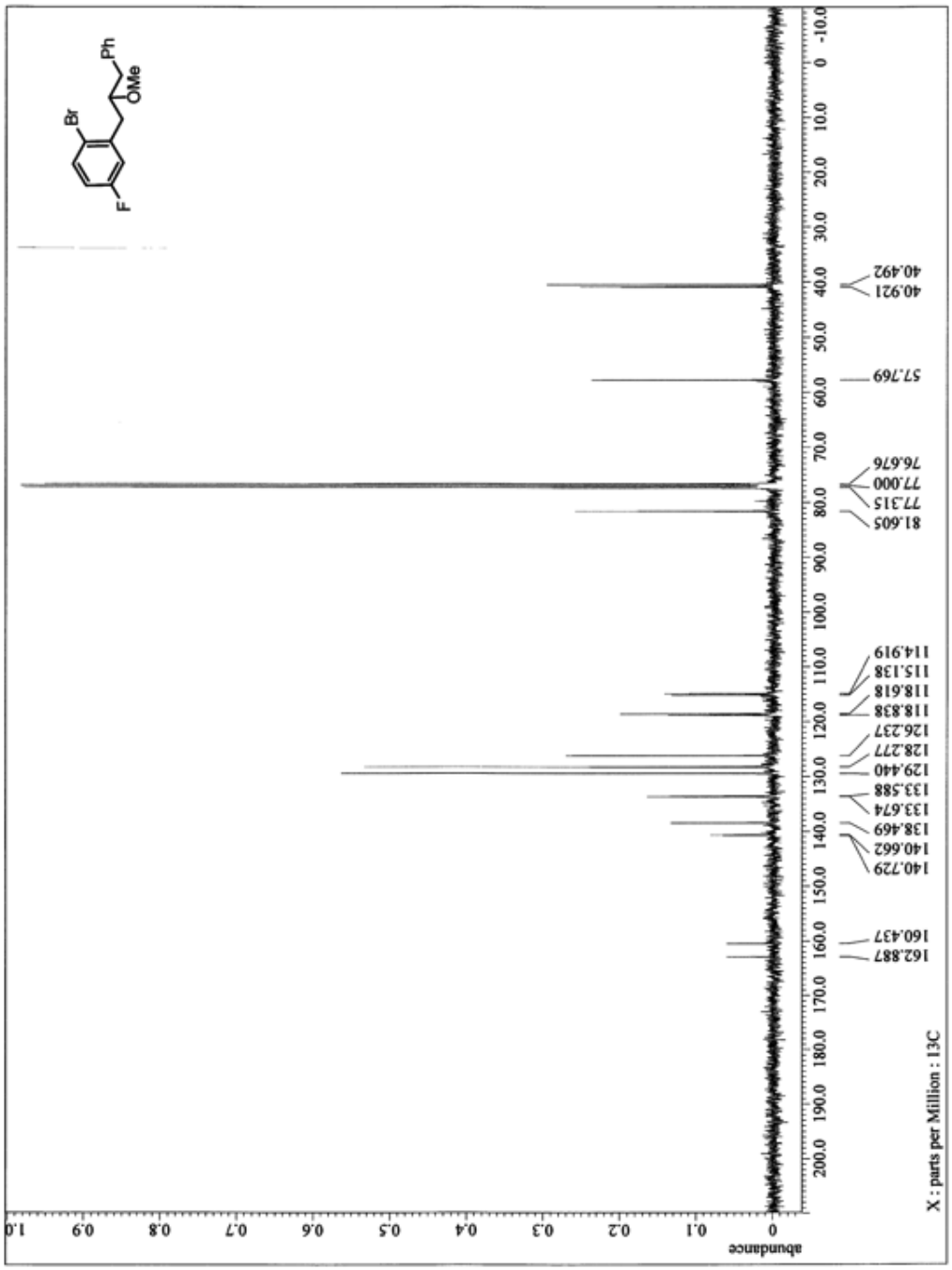
^{19}F NMR spectrum of **s21**.



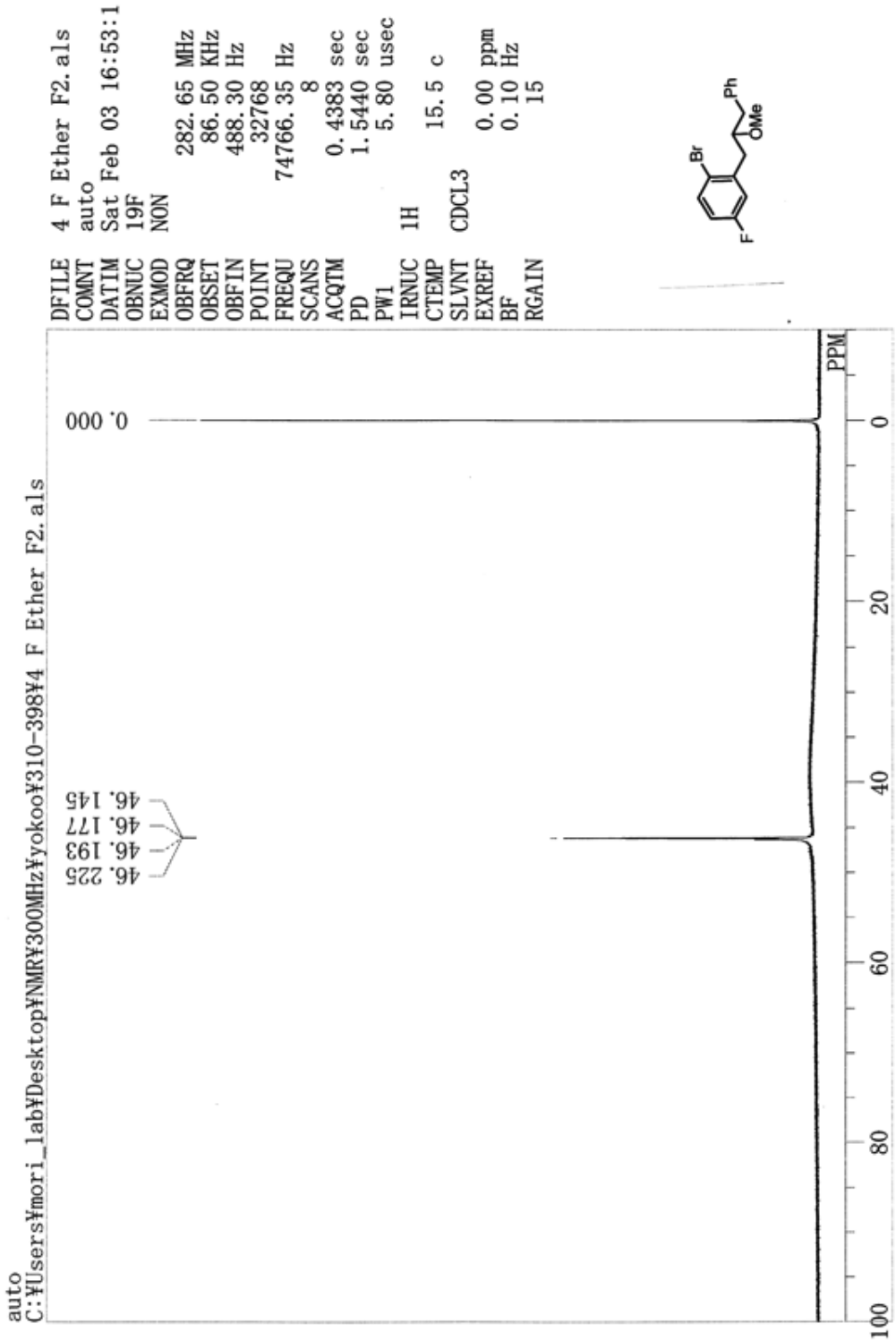
^{1}H NMR spectrum of **s22**.



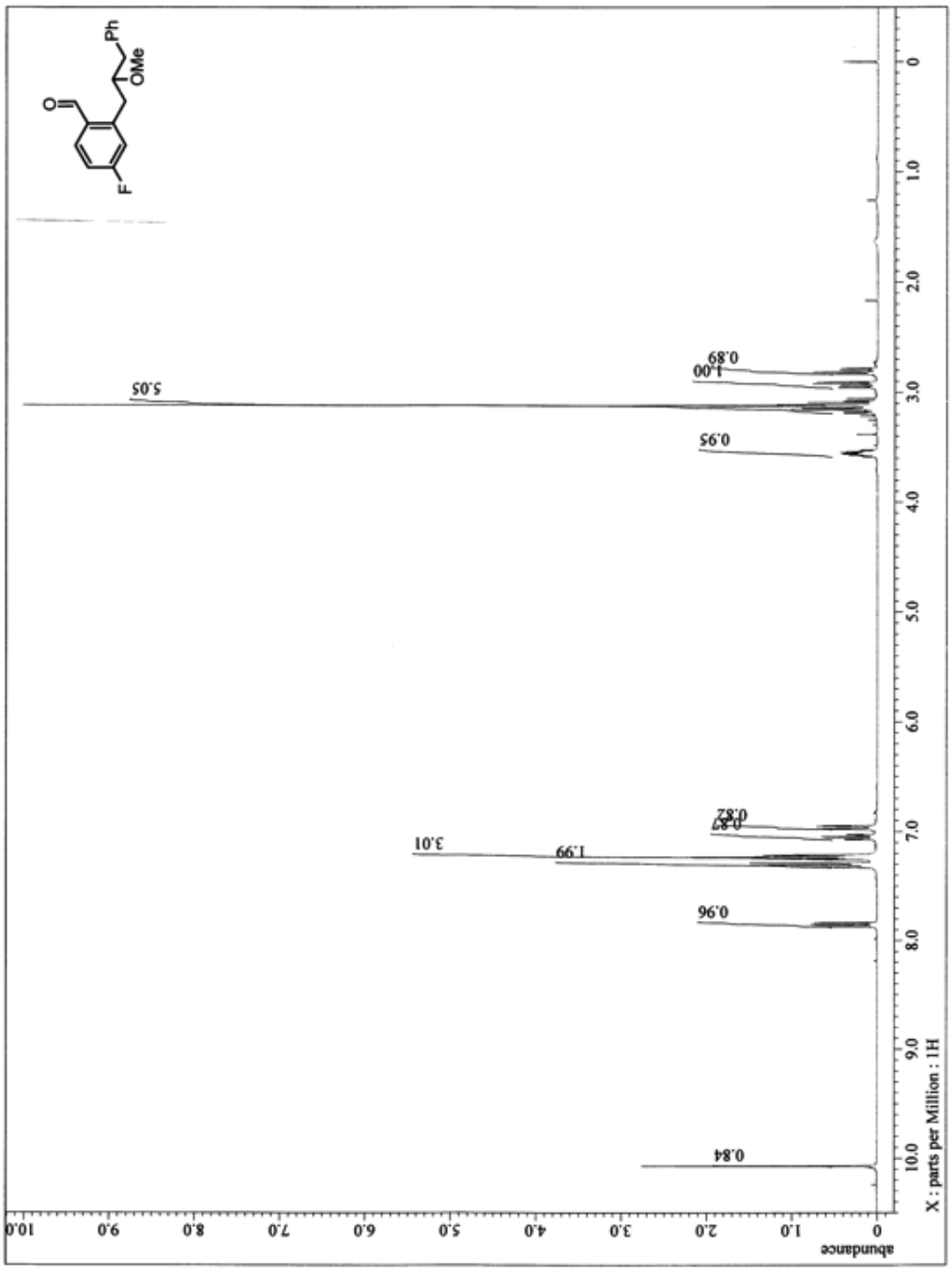
^{13}C NMR spectrum of **s22**.



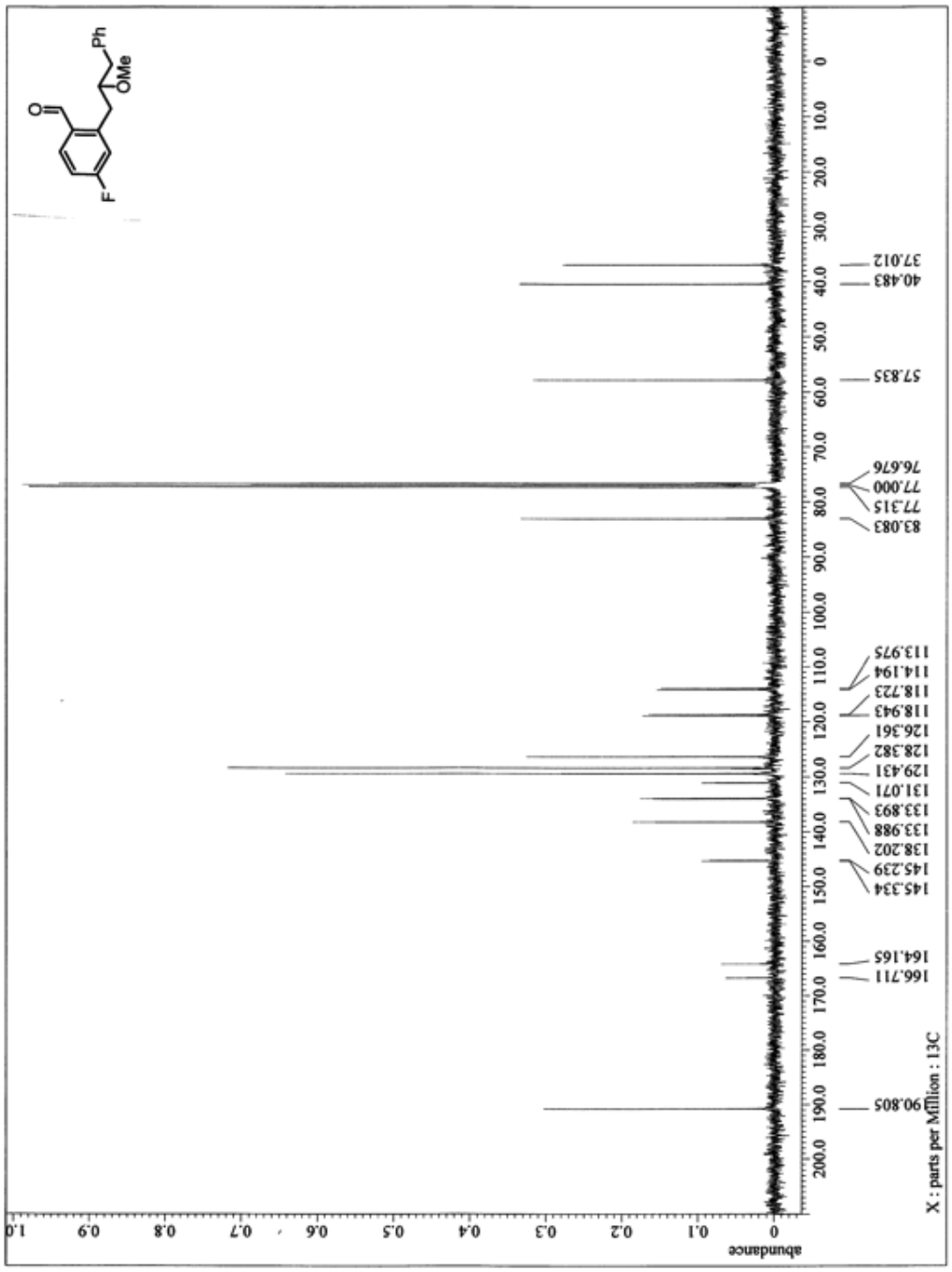
^{19}F NMR spectrum of **s22**.



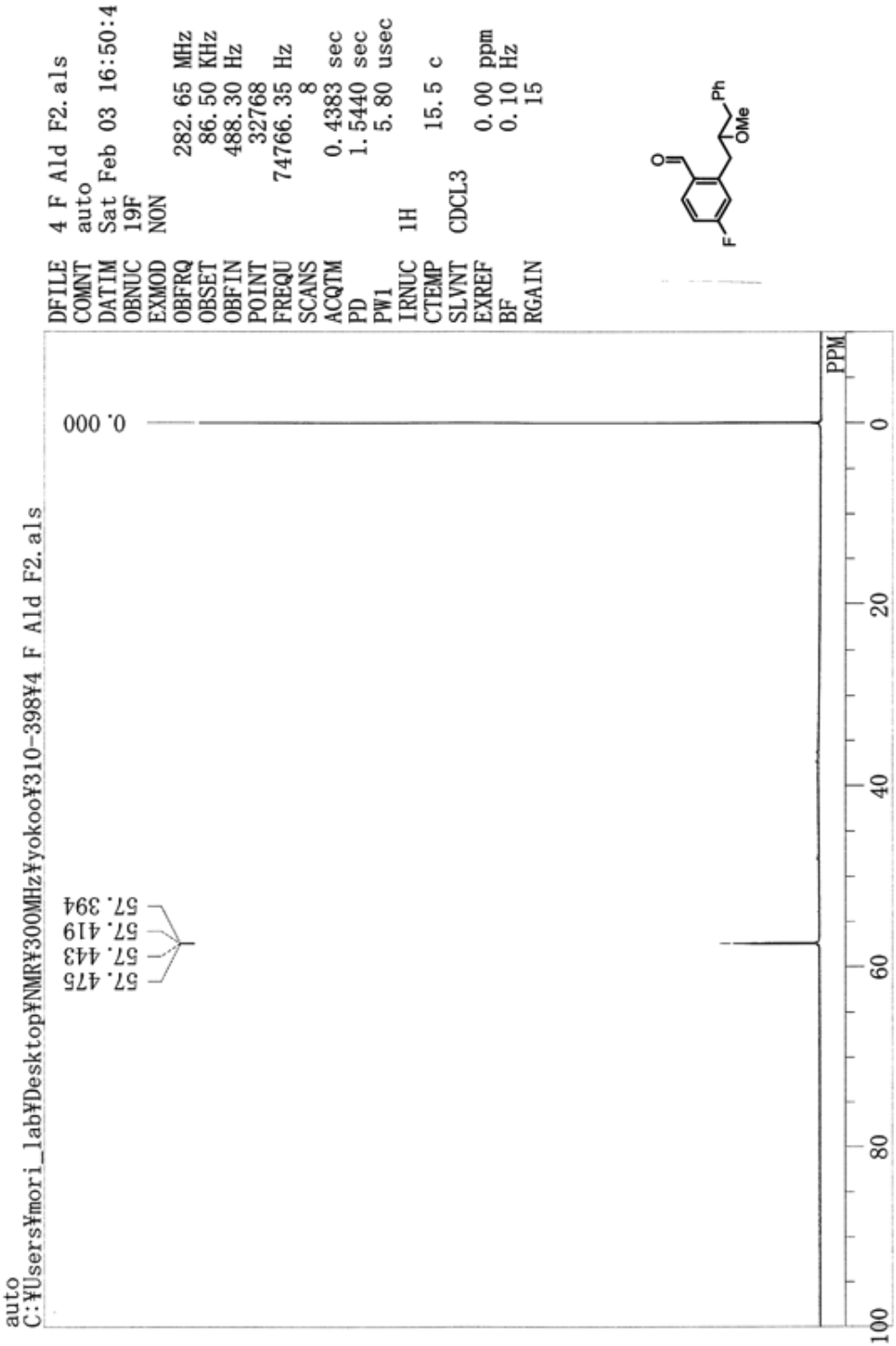
^{1}H NMR spectrum of **s23**.



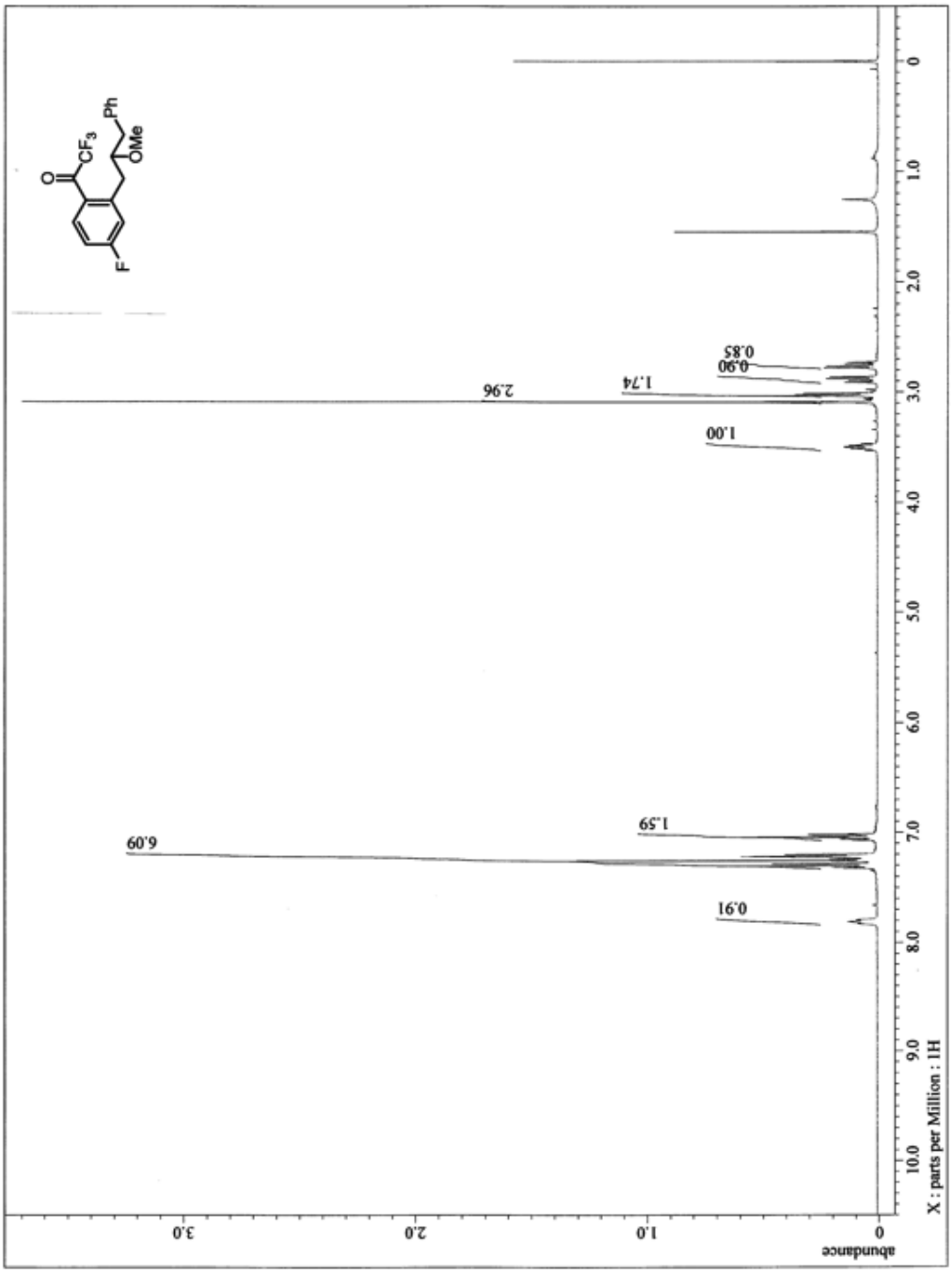
^{13}C NMR spectrum of **s23**.



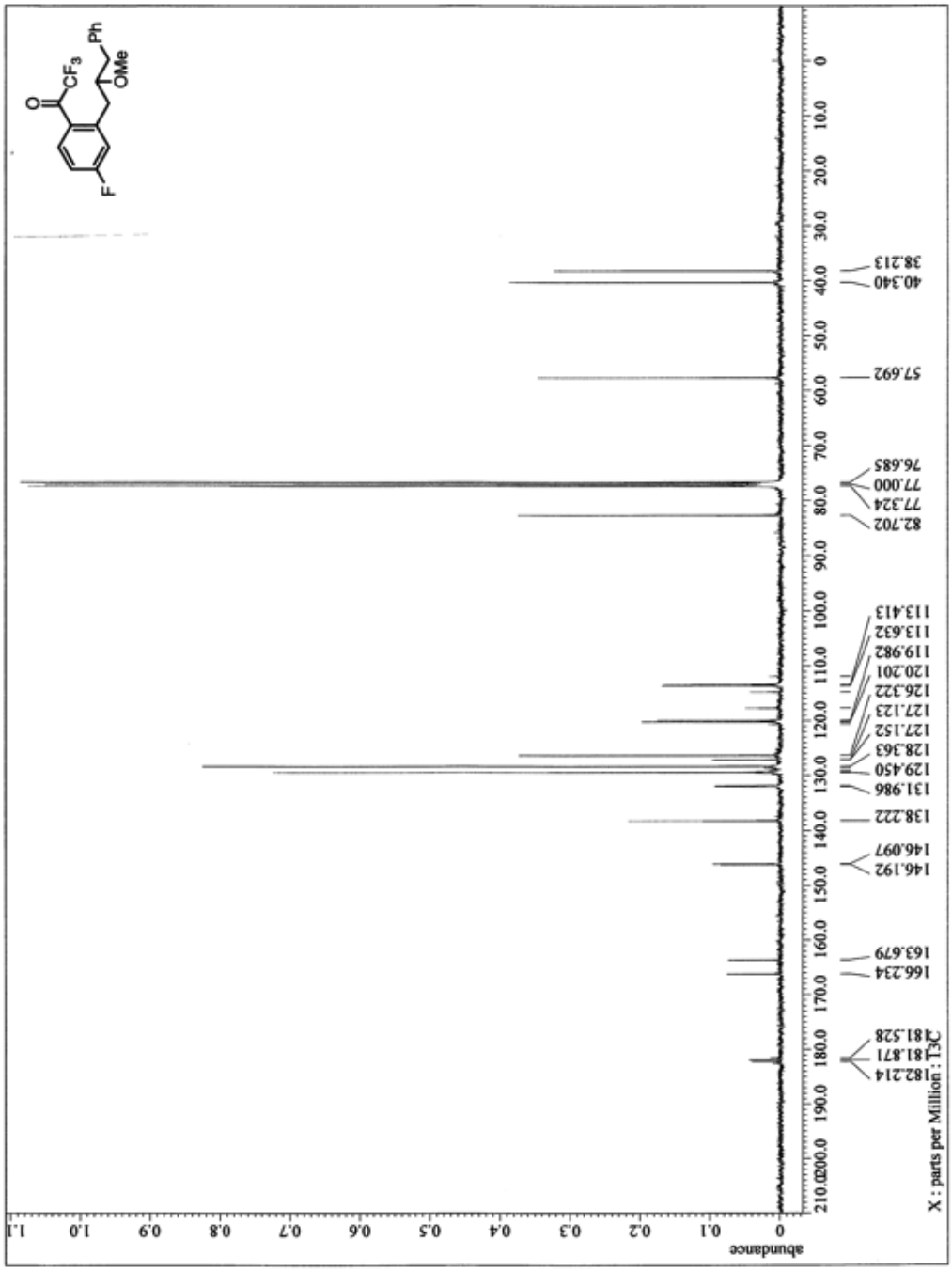
^{19}F NMR spectrum of **s23**.



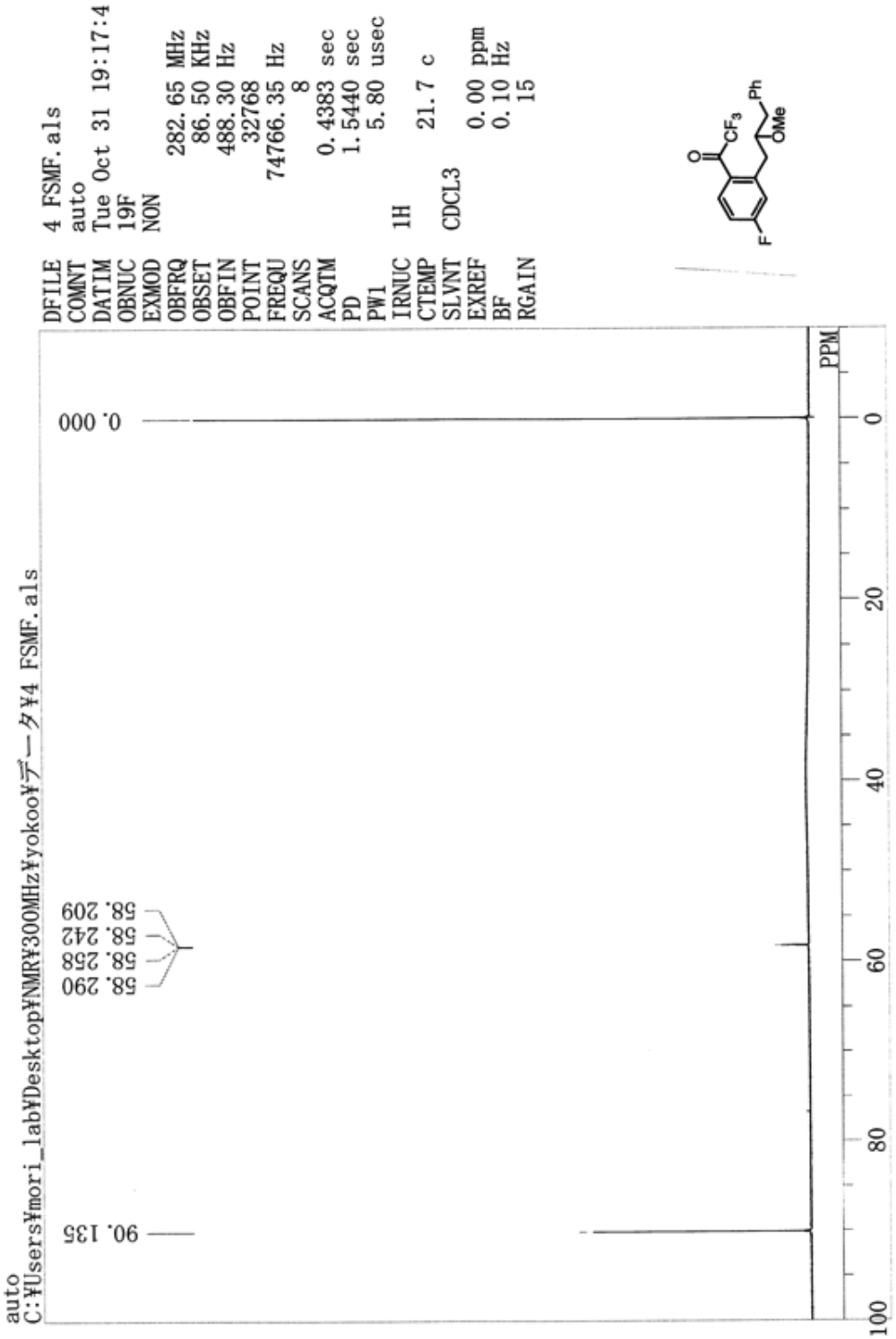
^{1}H NMR spectrum of **1f**.



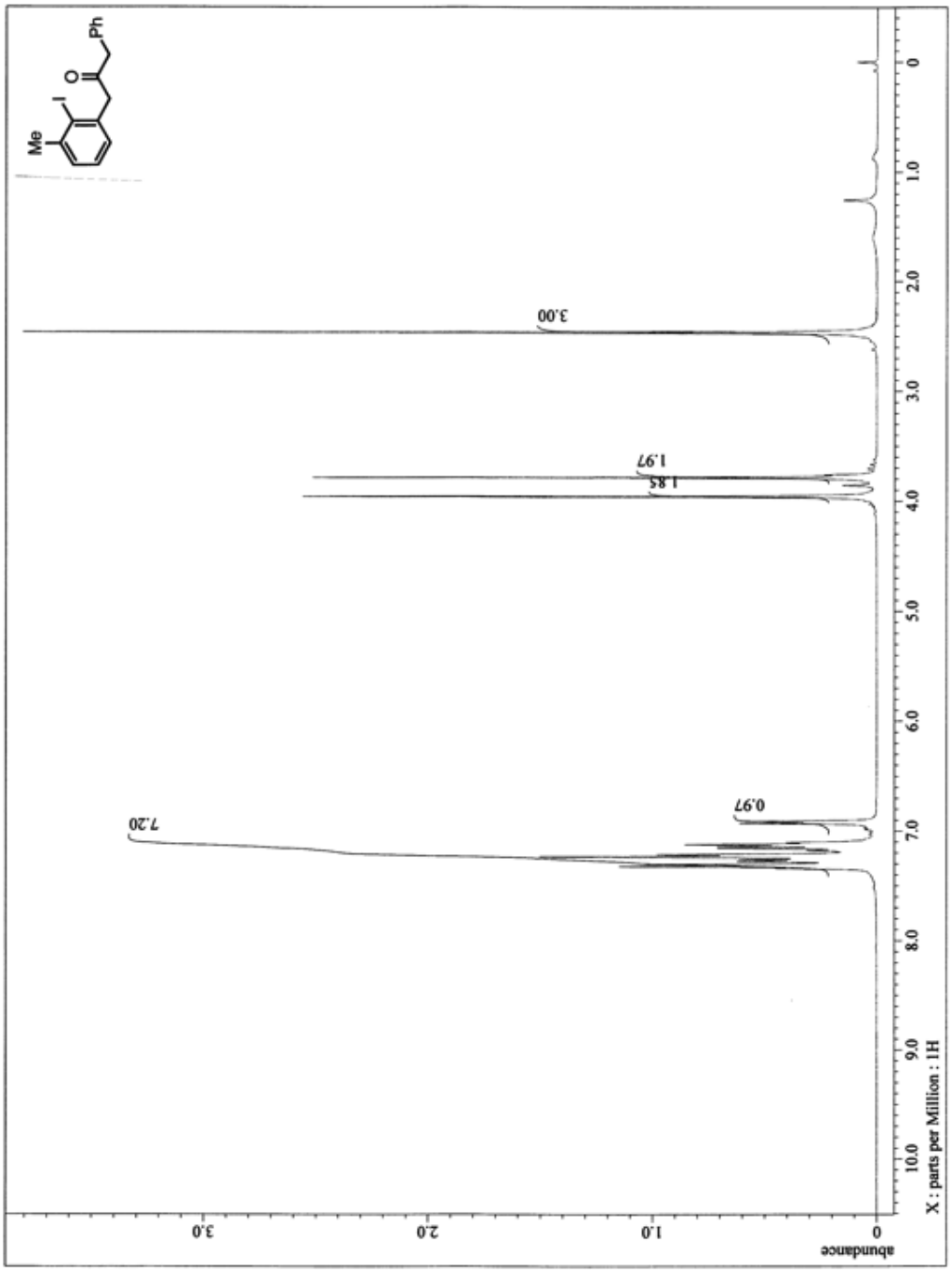
^{13}C NMR spectrum of **1f**.



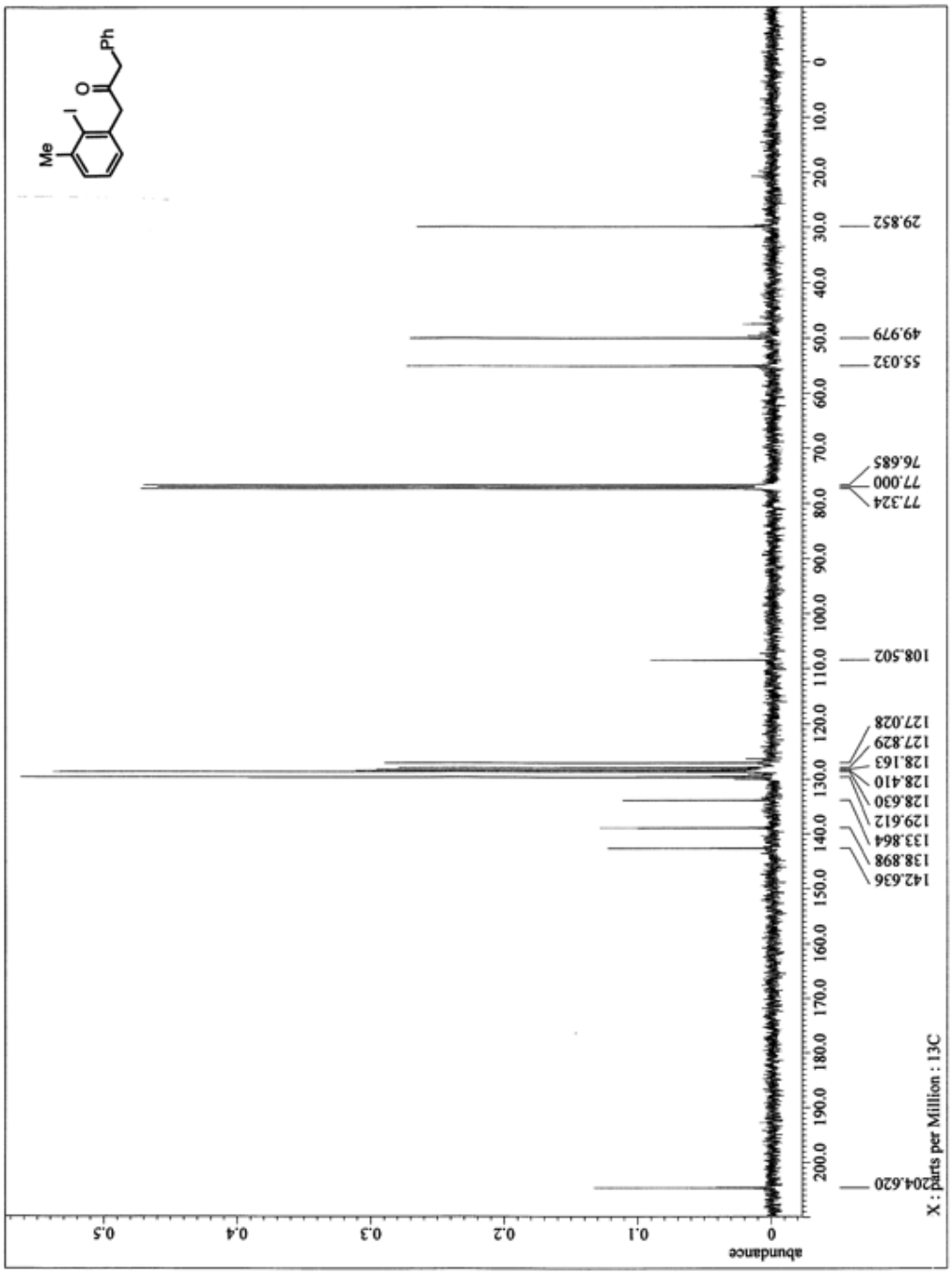
^{19}F NMR spectrum of **1f**.



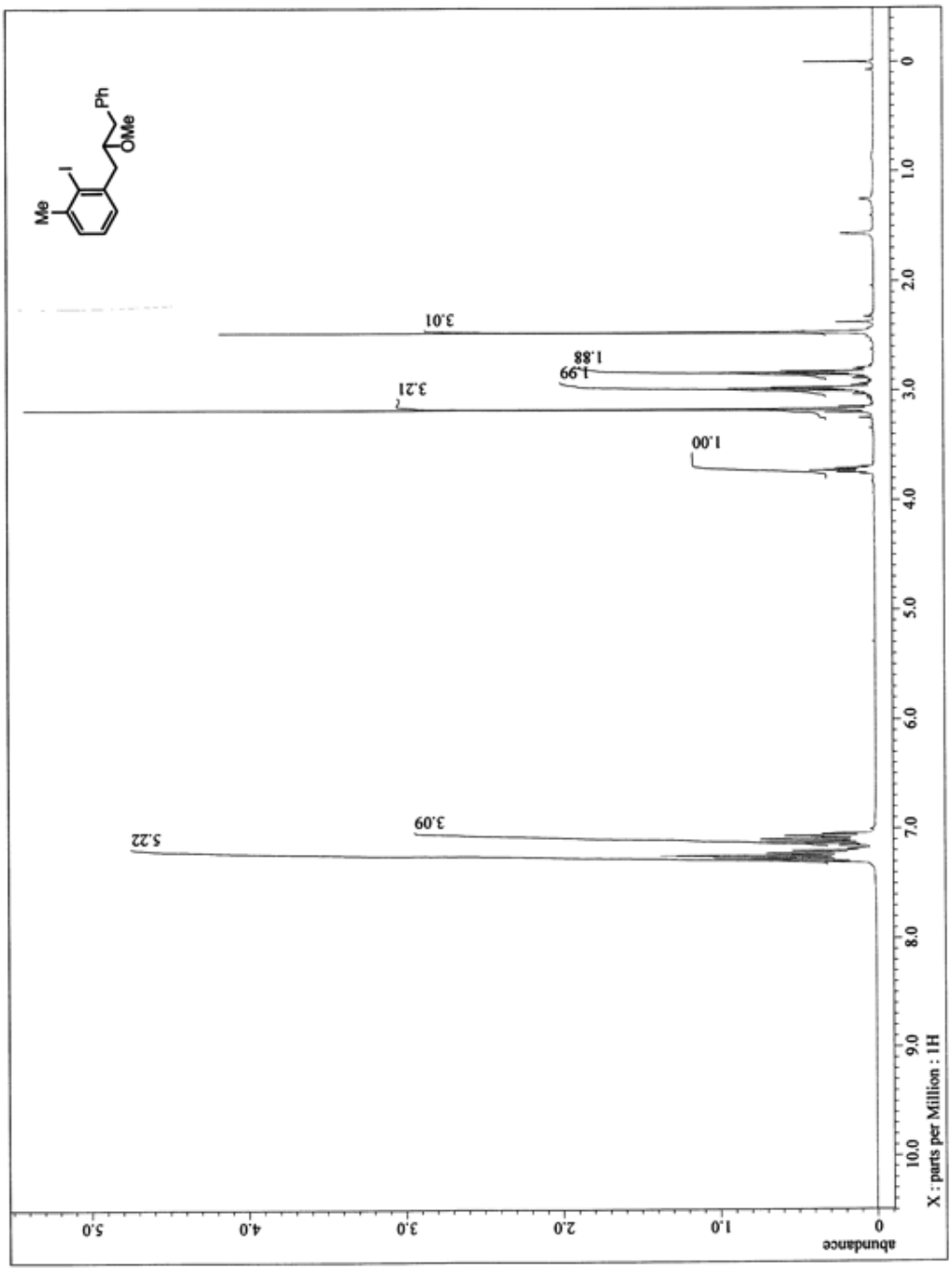
^{1}H NMR spectrum of **s24**.



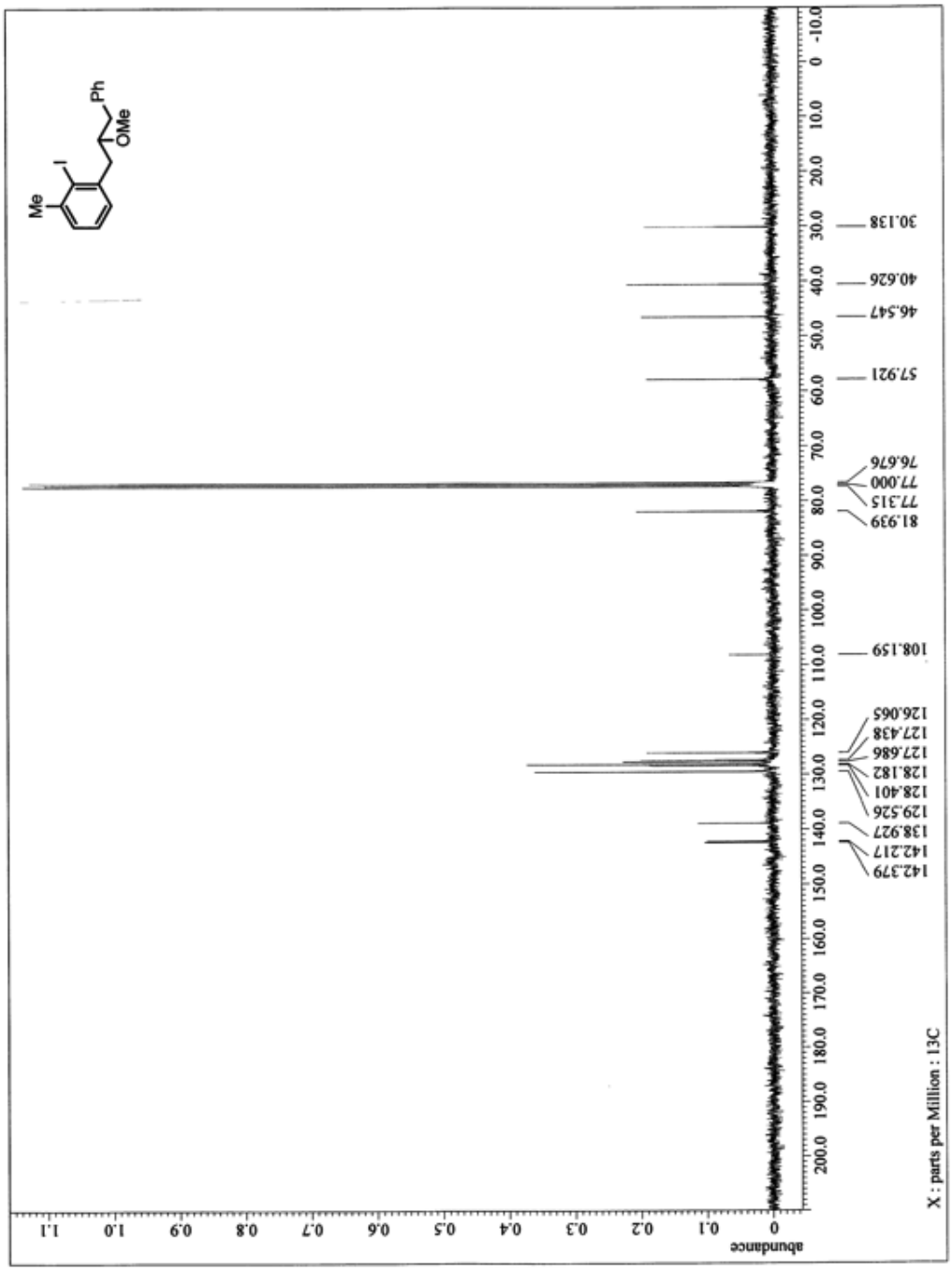
^{13}C NMR spectrum of **s24**.



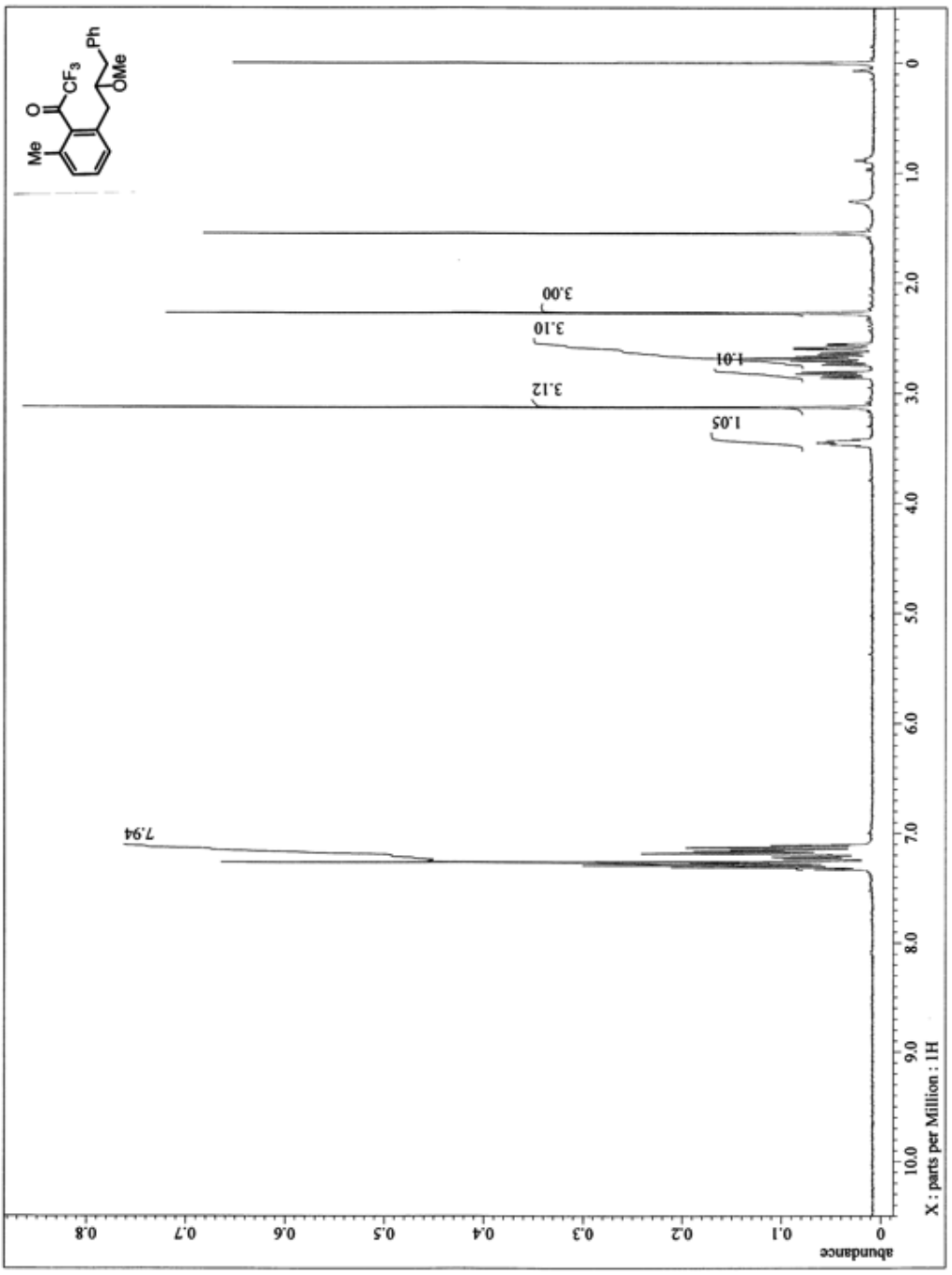
^{1}H NMR spectrum of **s25**.



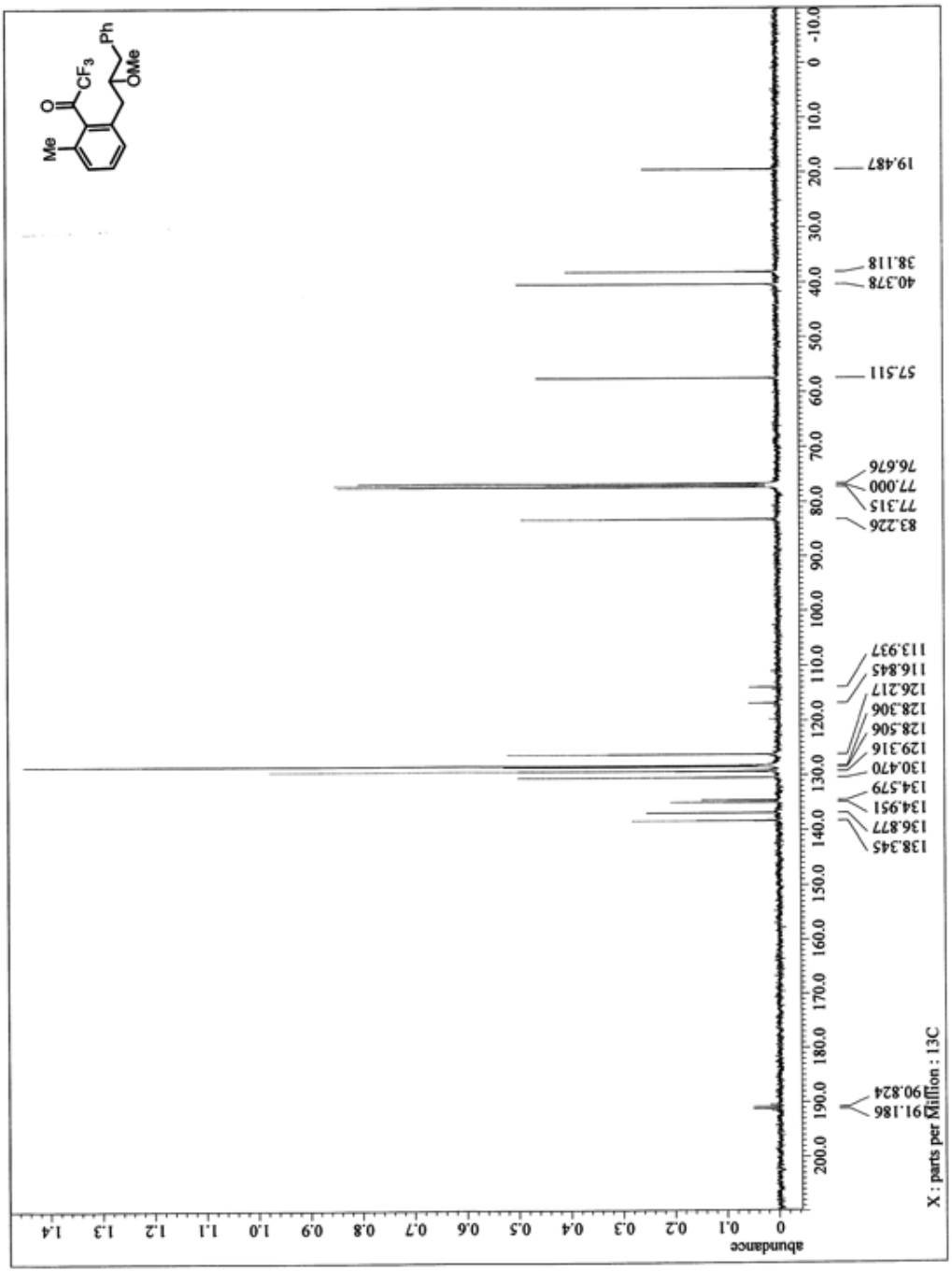
^{13}C NMR spectrum of **s25**.



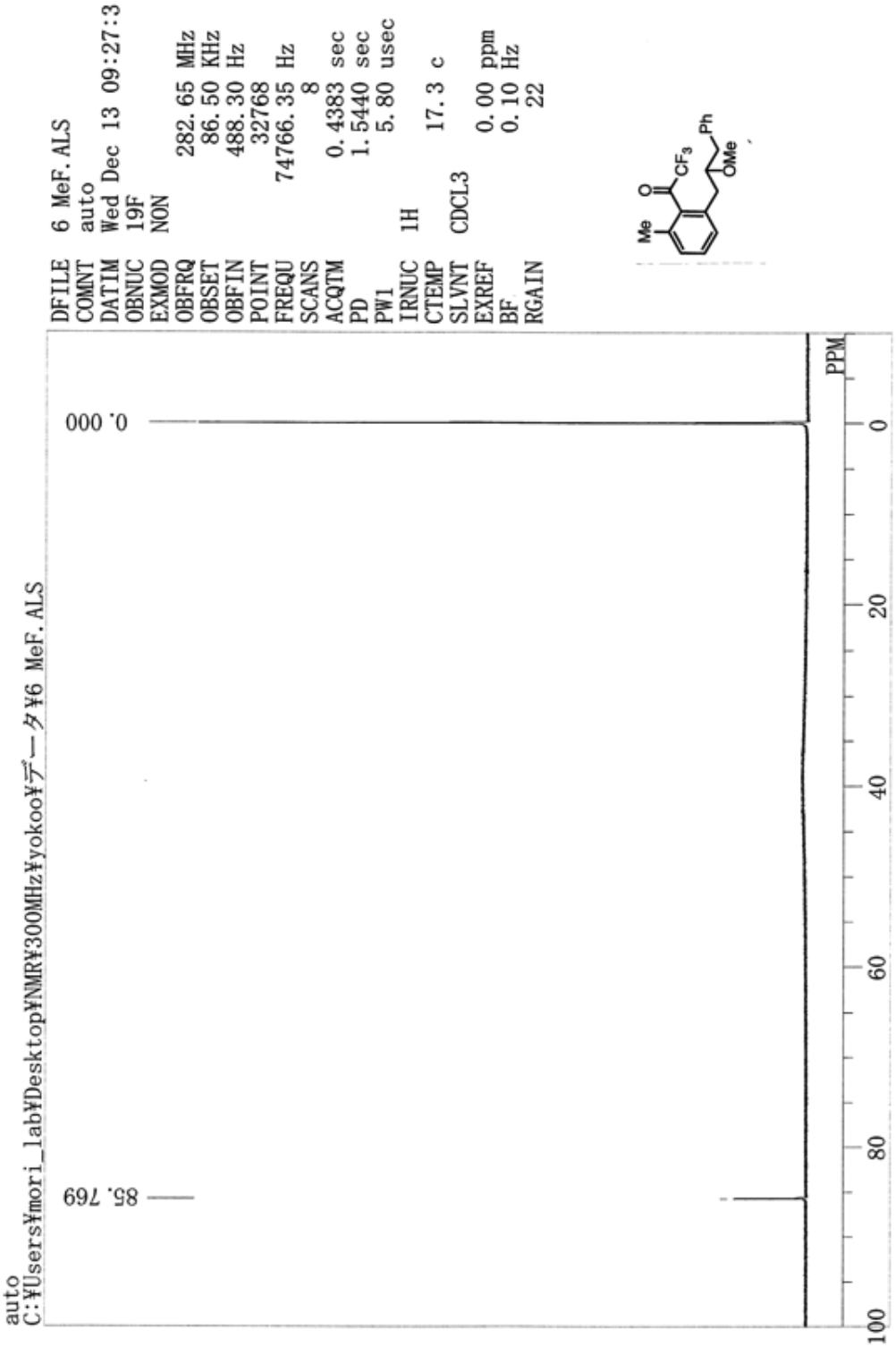
^{1}H NMR spectrum of **1g**.



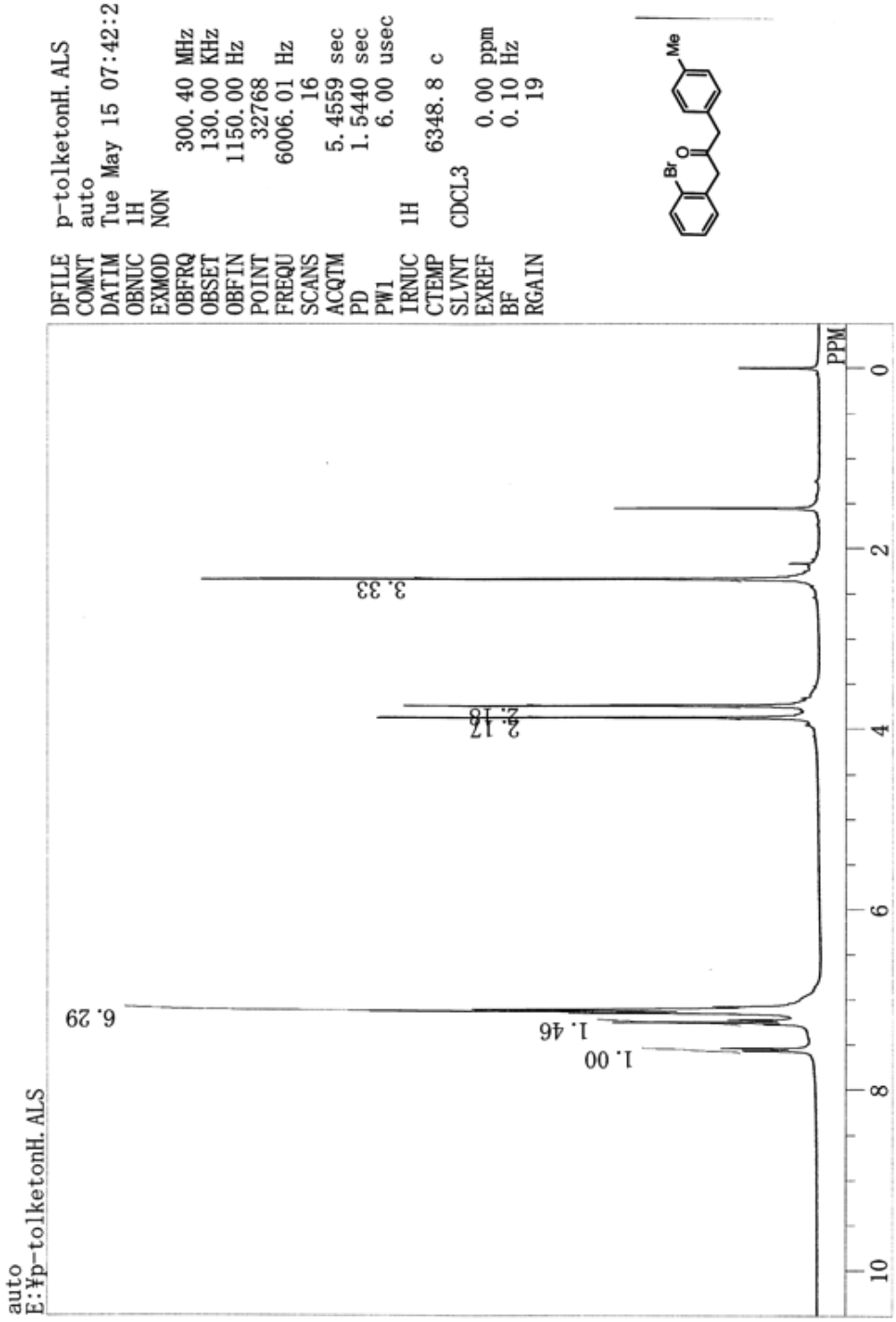
^{13}C NMR spectrum of **1g**.



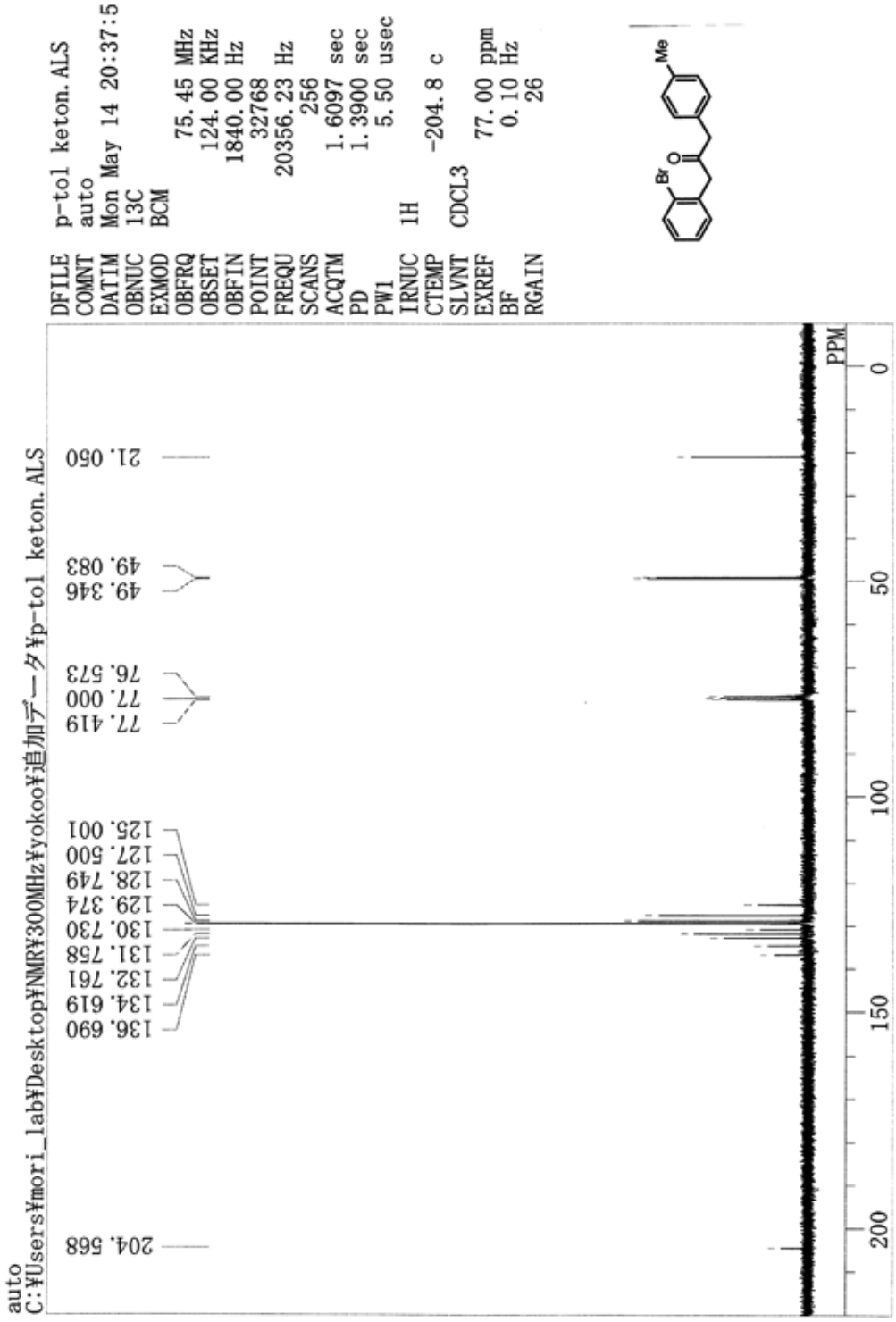
^{19}F NMR spectrum of **1g**.



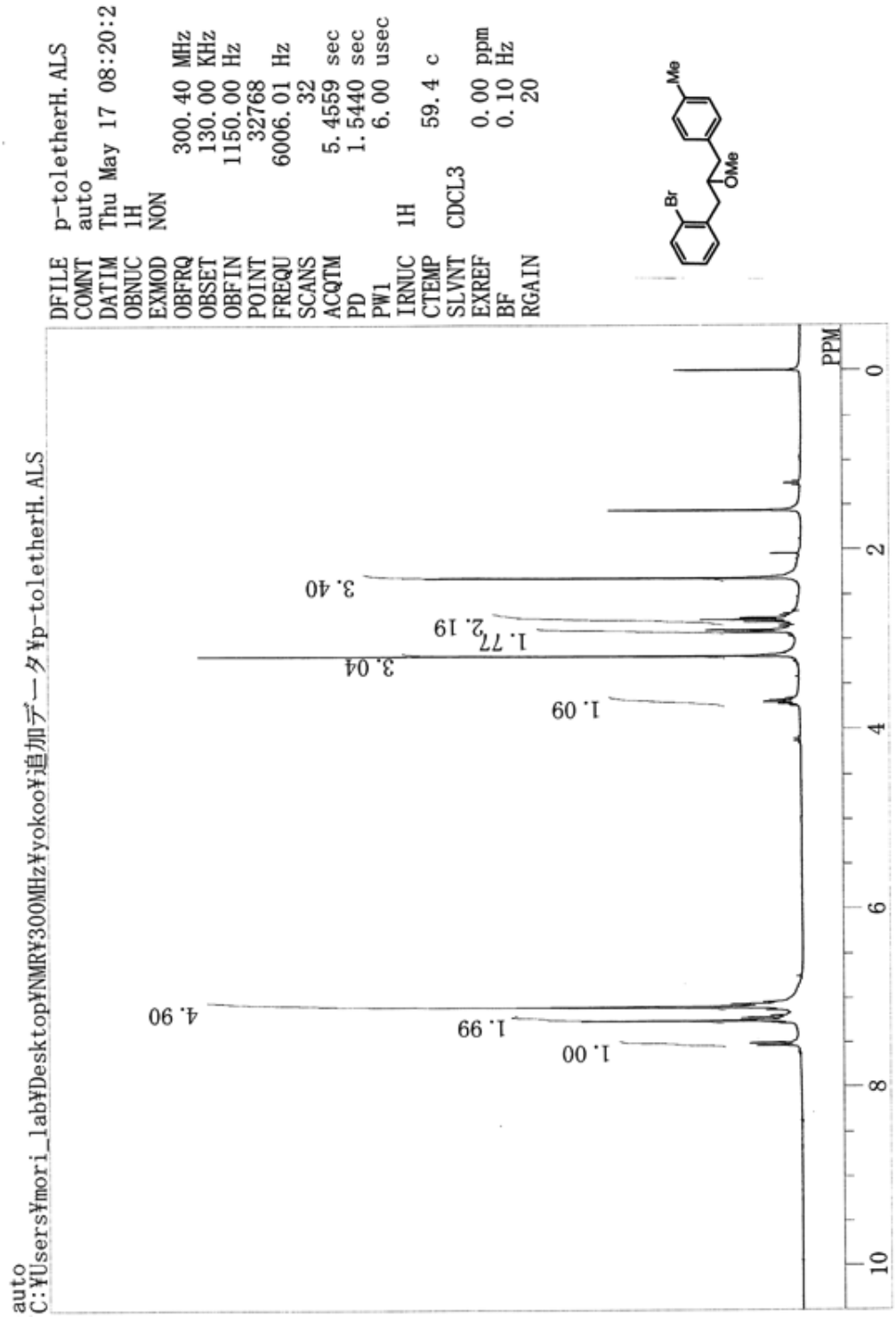
^{1}H NMR spectrum of **s26**.



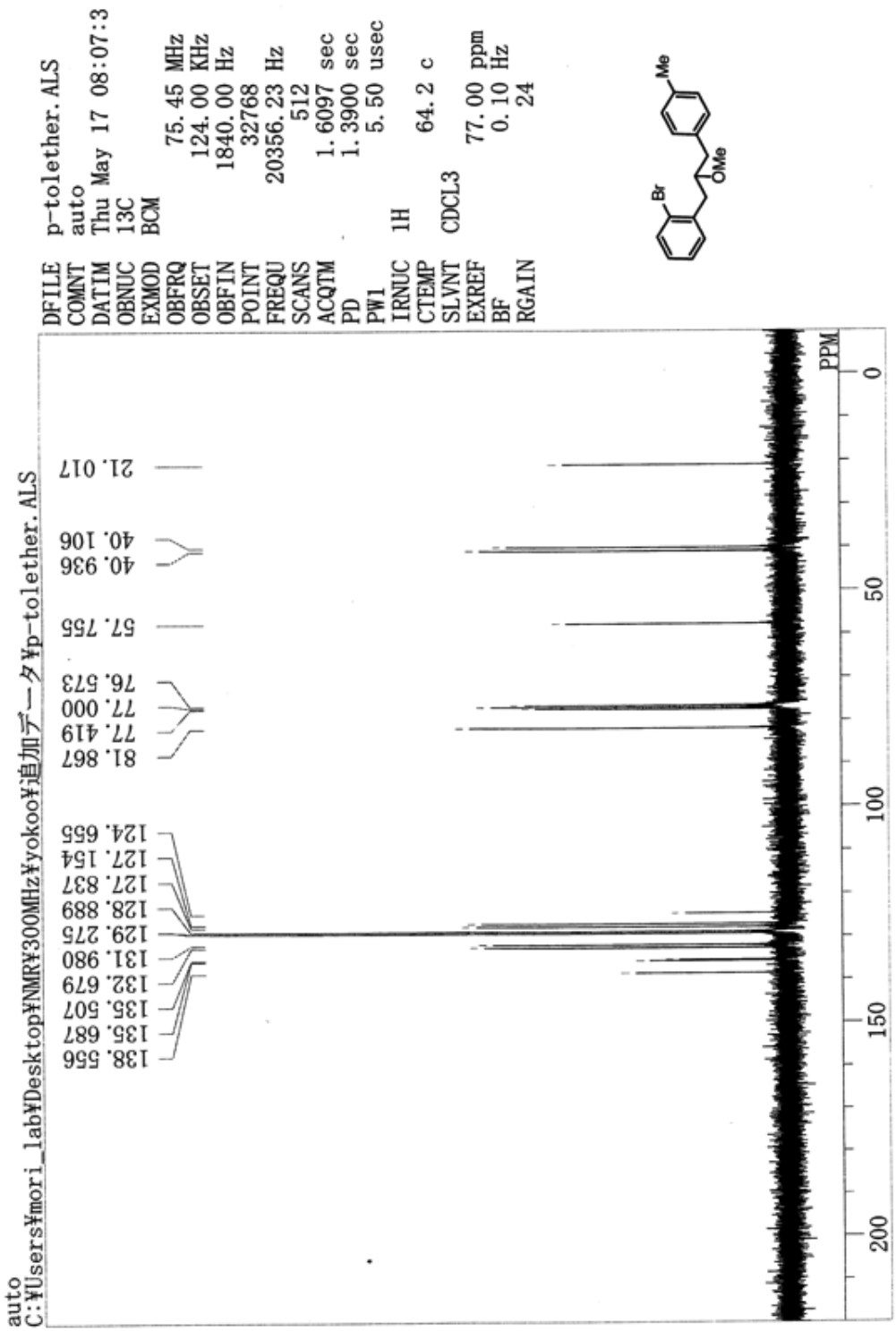
^{13}C NMR spectrum of **s26**.



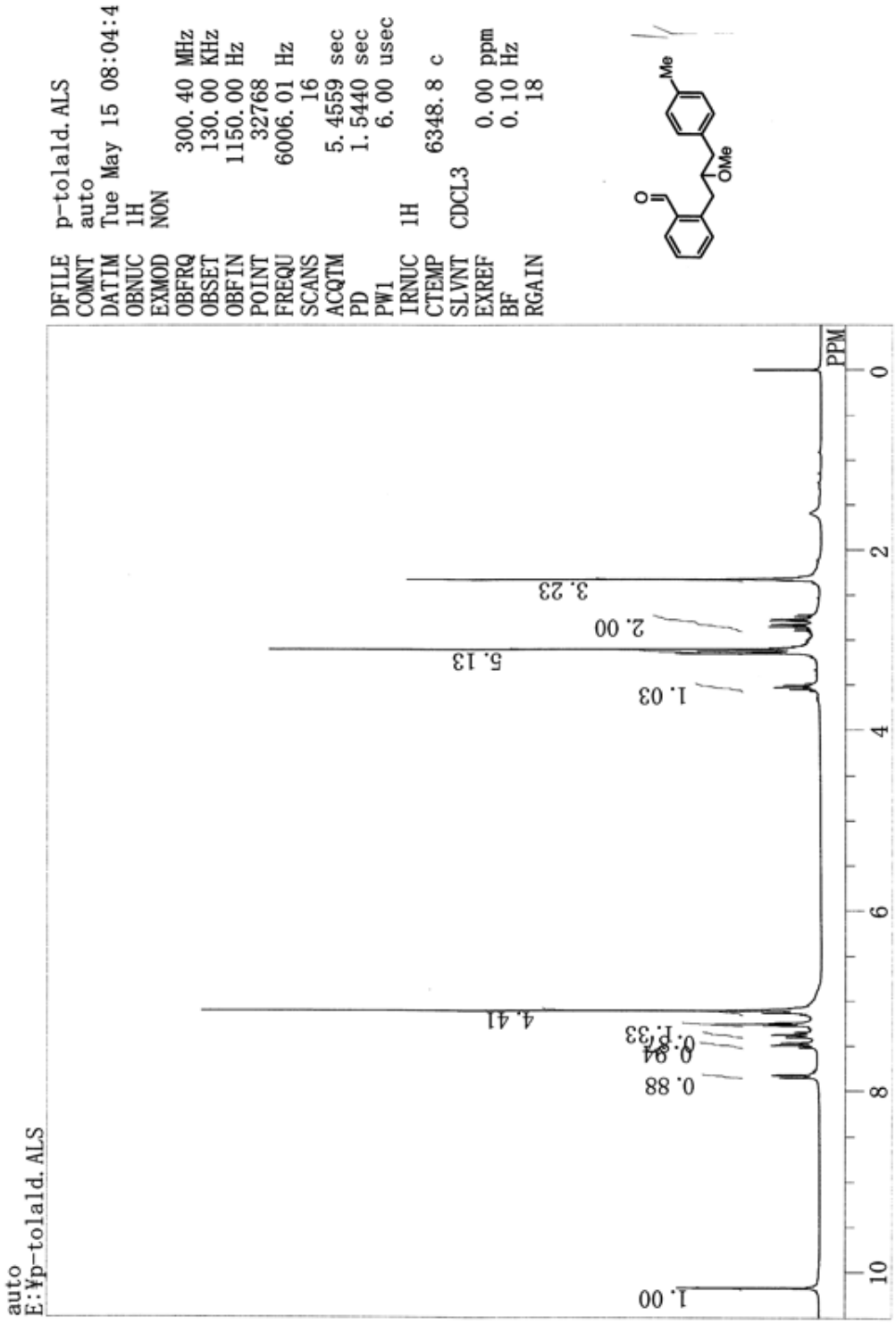
^{1}H NMR spectrum of **s27**.



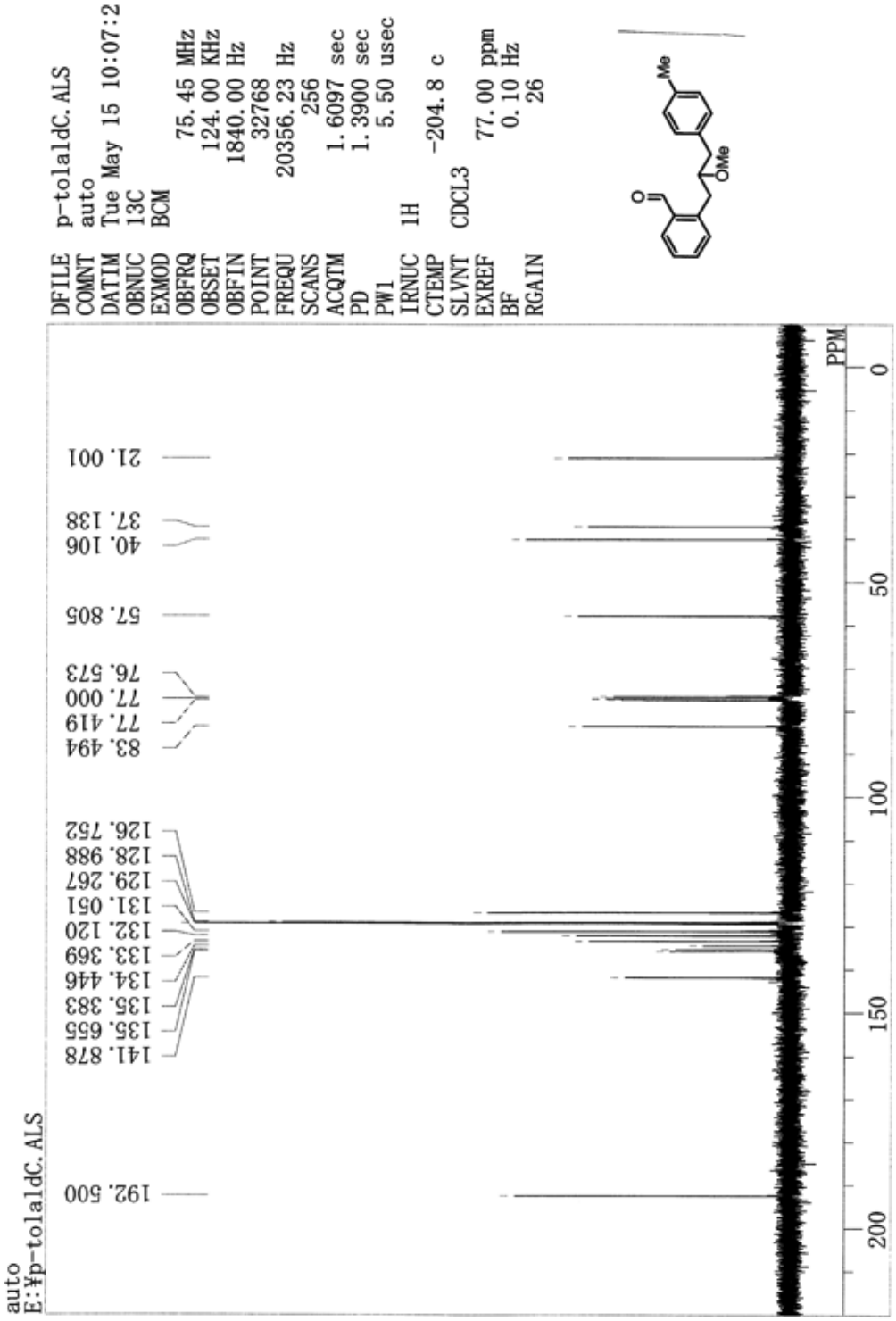
^{13}C NMR spectrum of **s27**.



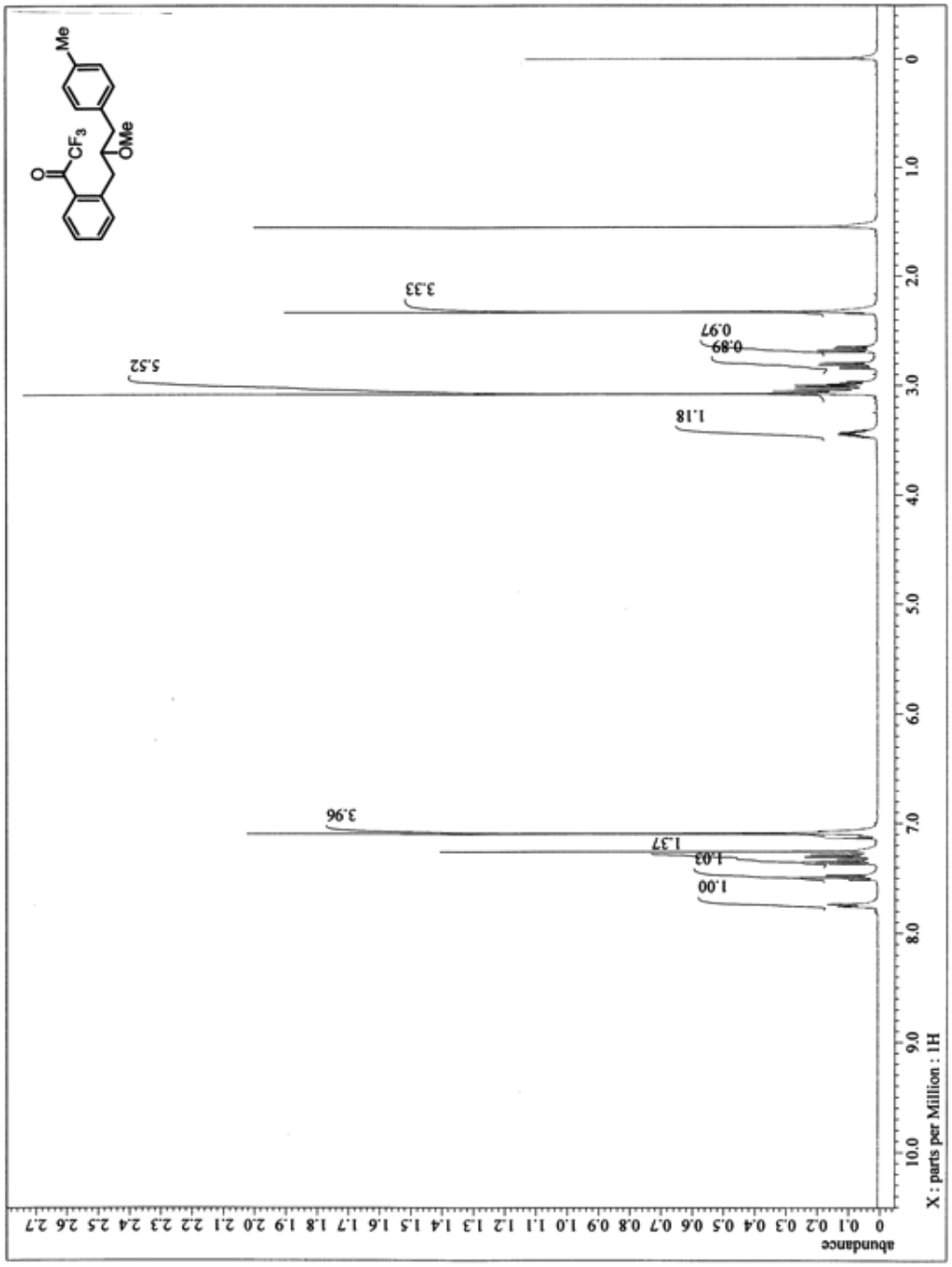
^{1}H NMR spectrum of **s28**.



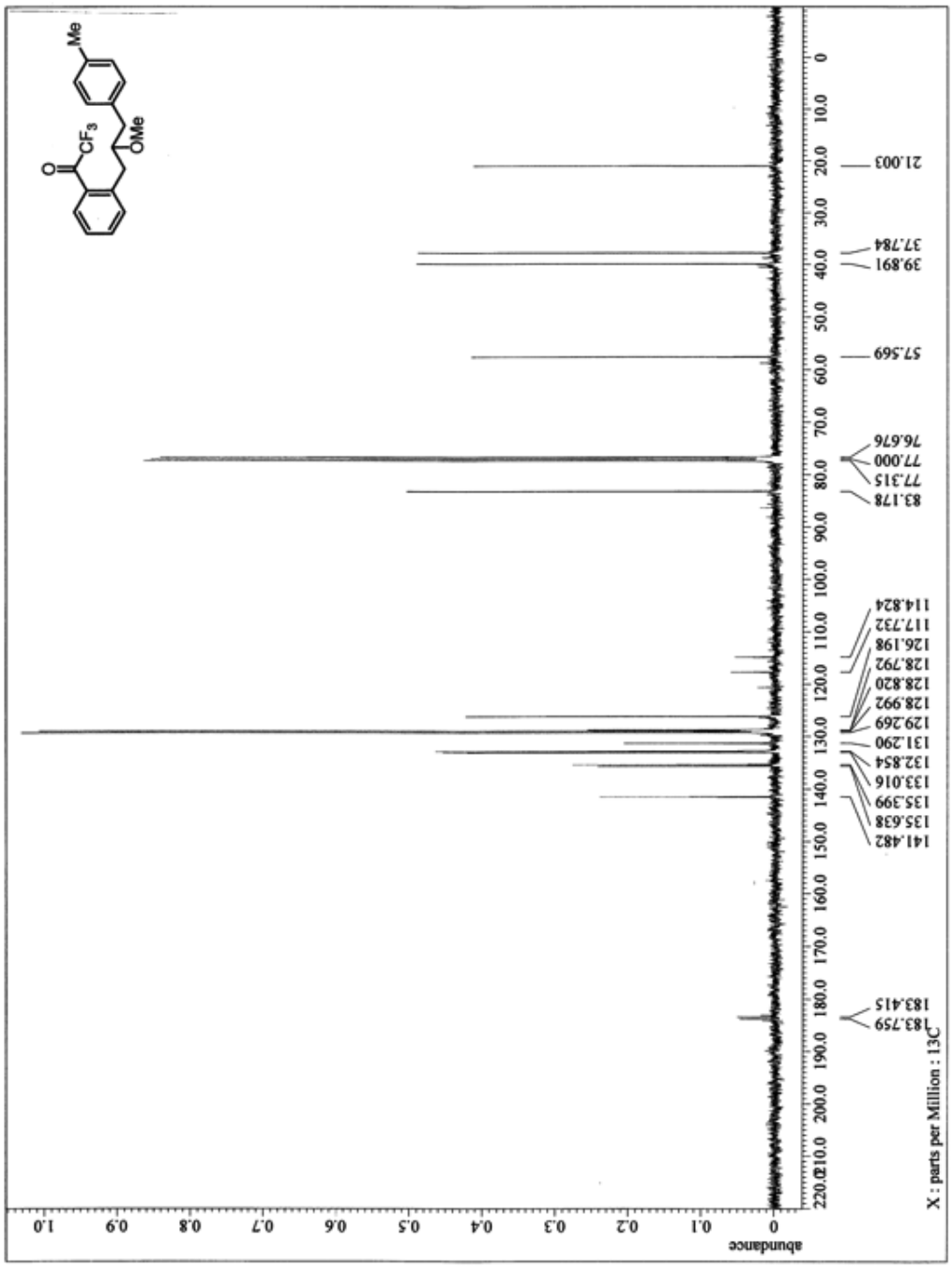
^{13}C NMR spectrum of **s28**.



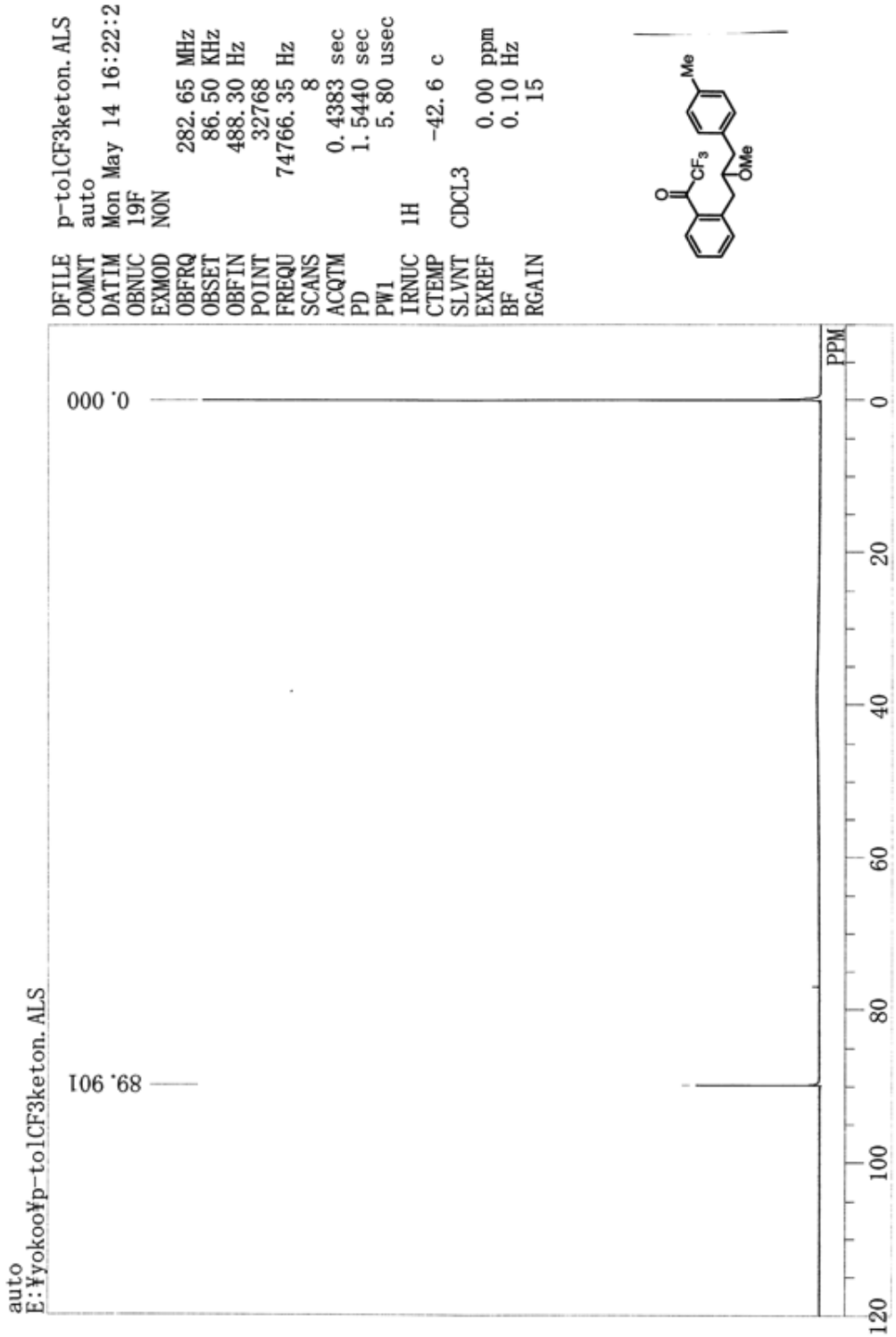
^{1}H NMR spectrum of **1h**.



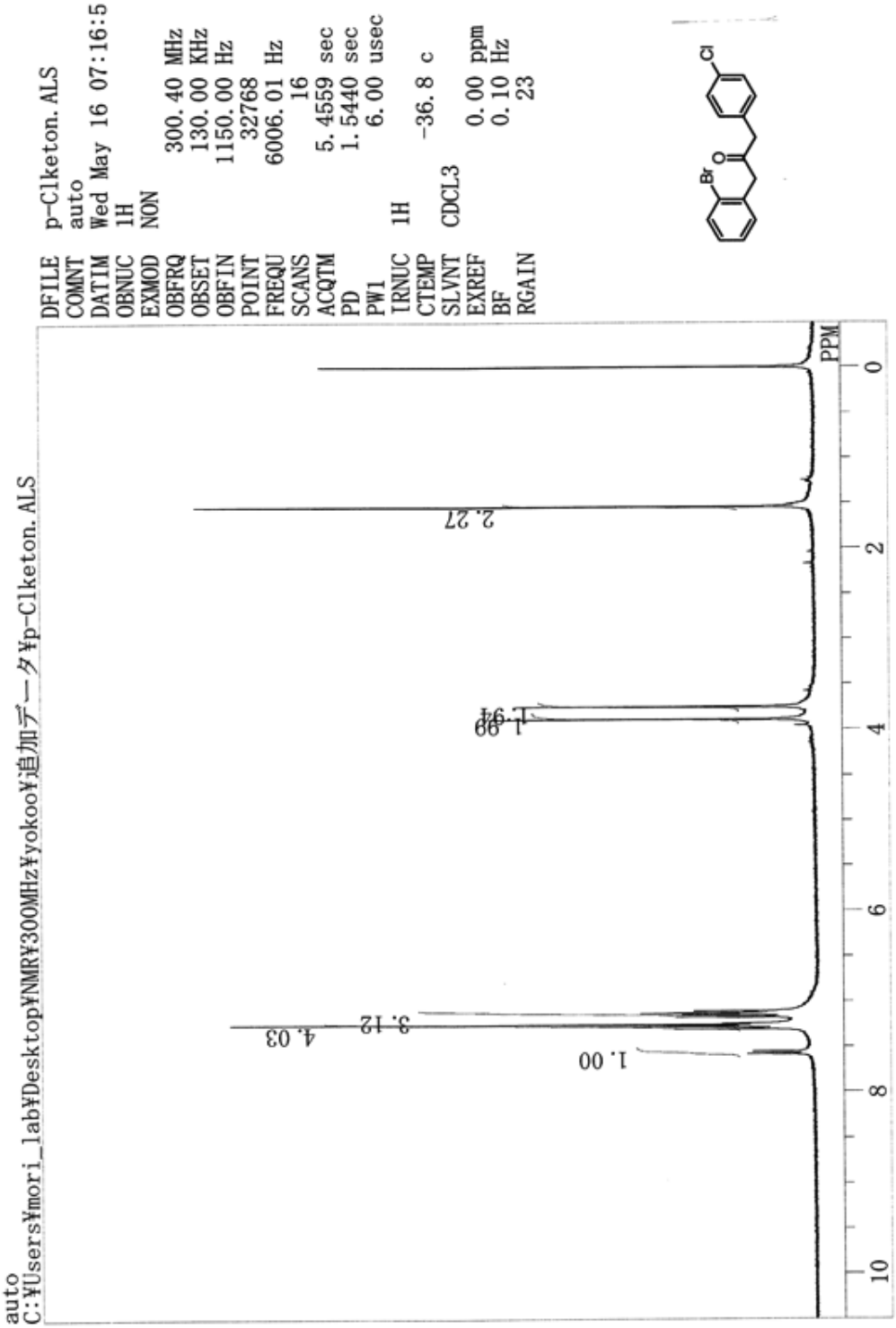
^{13}C NMR spectrum of **1h**.



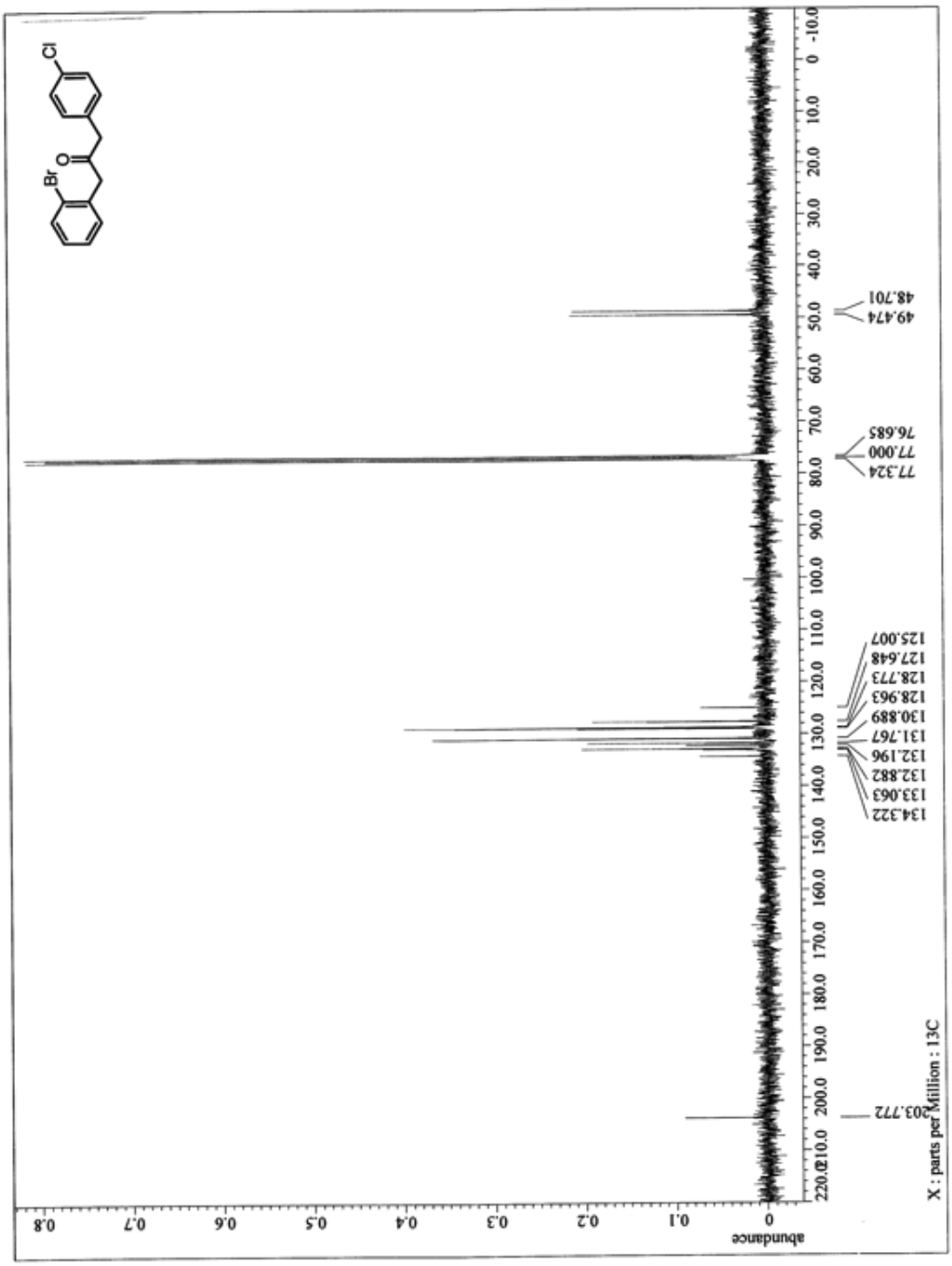
^{19}F NMR spectrum of **1h**.



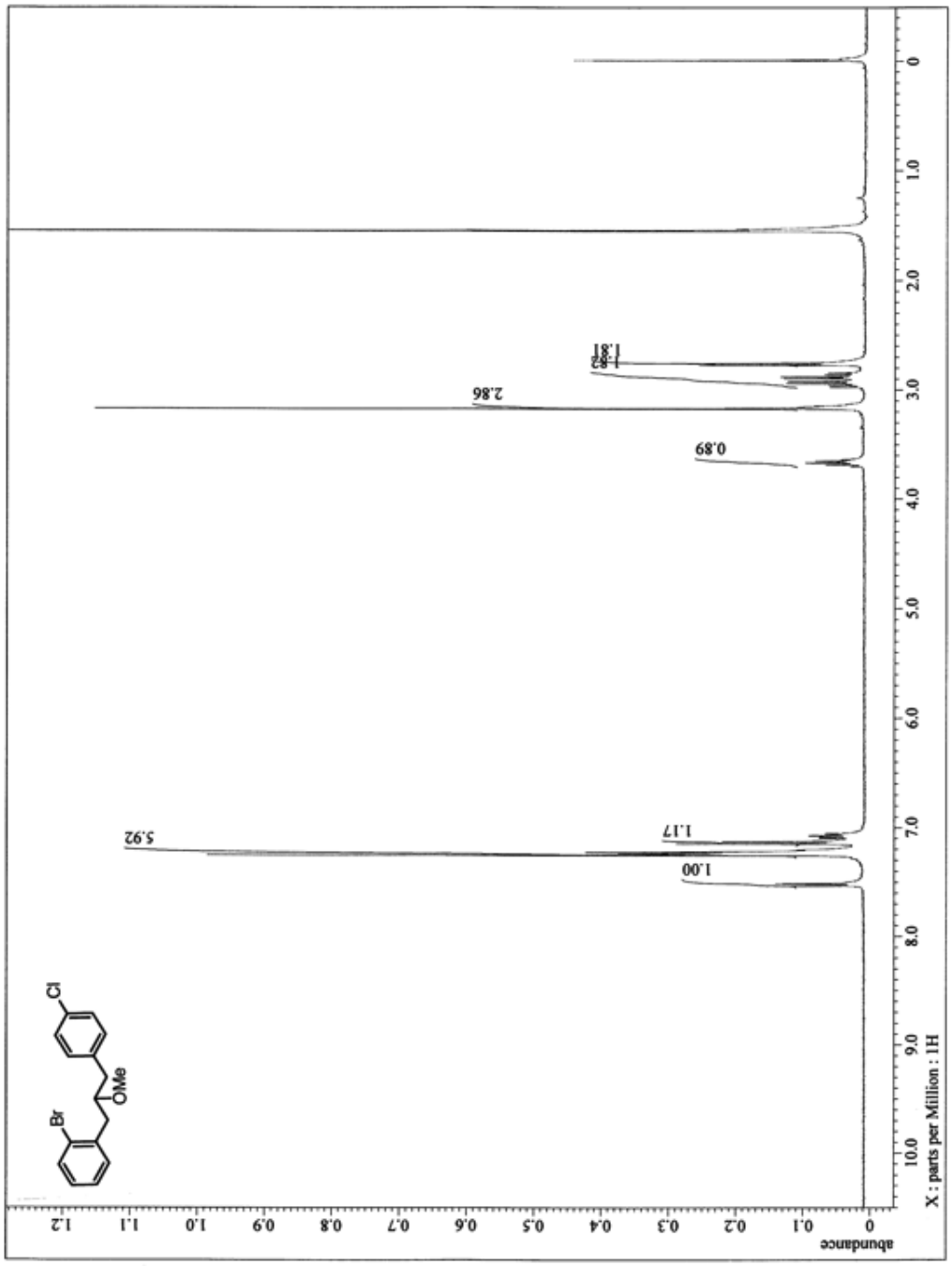
^{1}H NMR spectrum of **s29**.



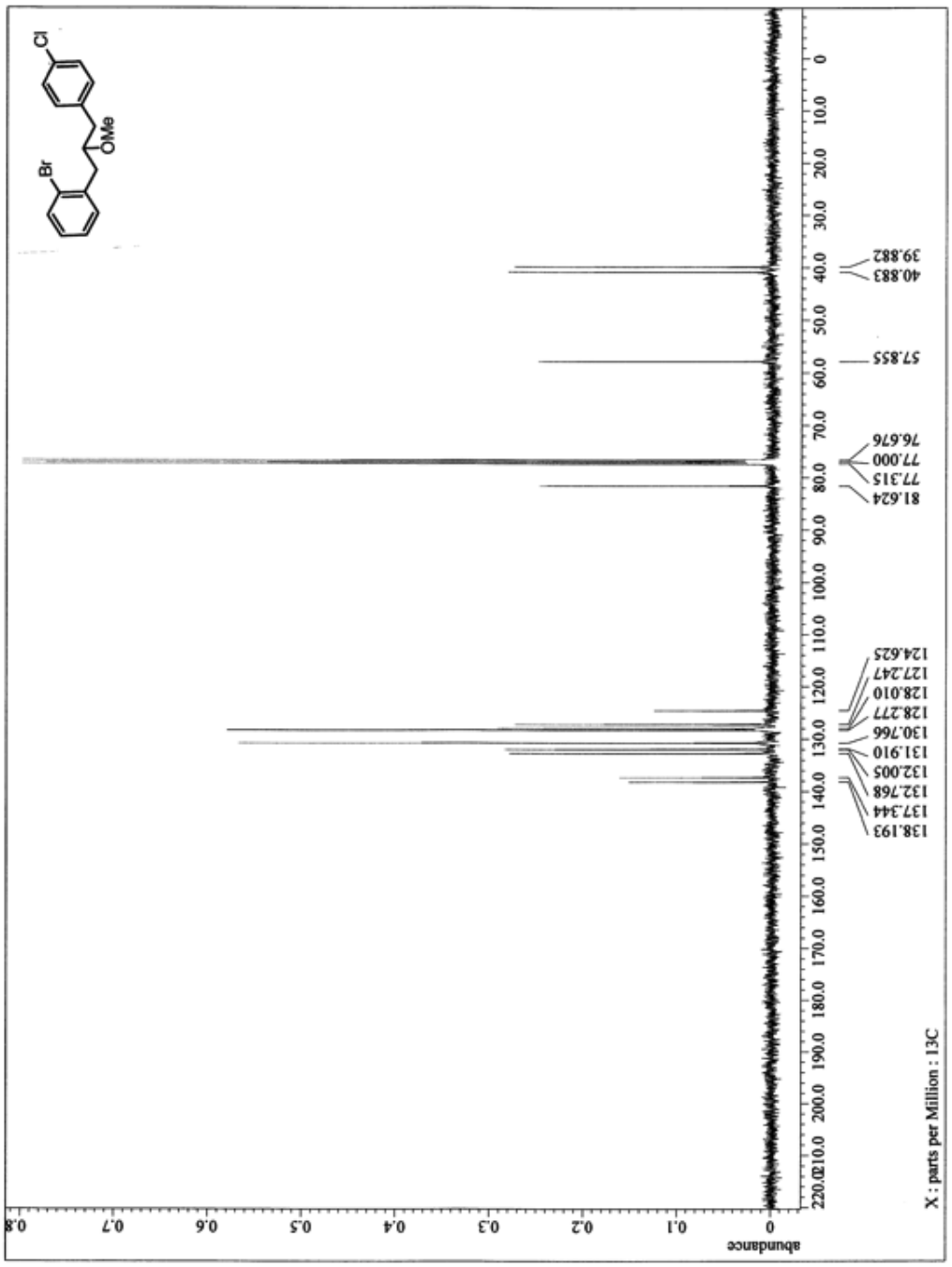
^{13}C NMR spectrum of **s29**



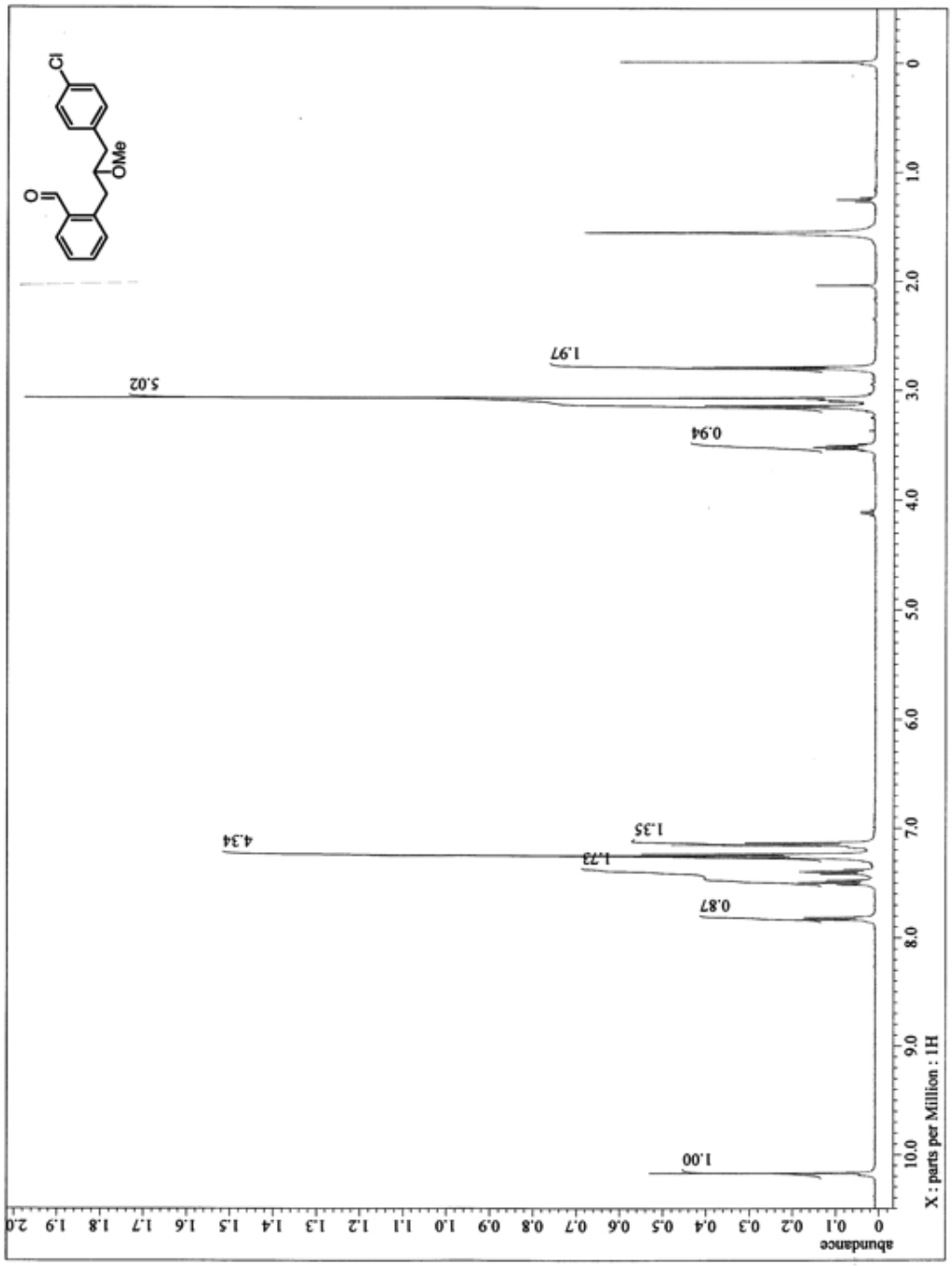
^{1}H NMR spectrum of **s30**.



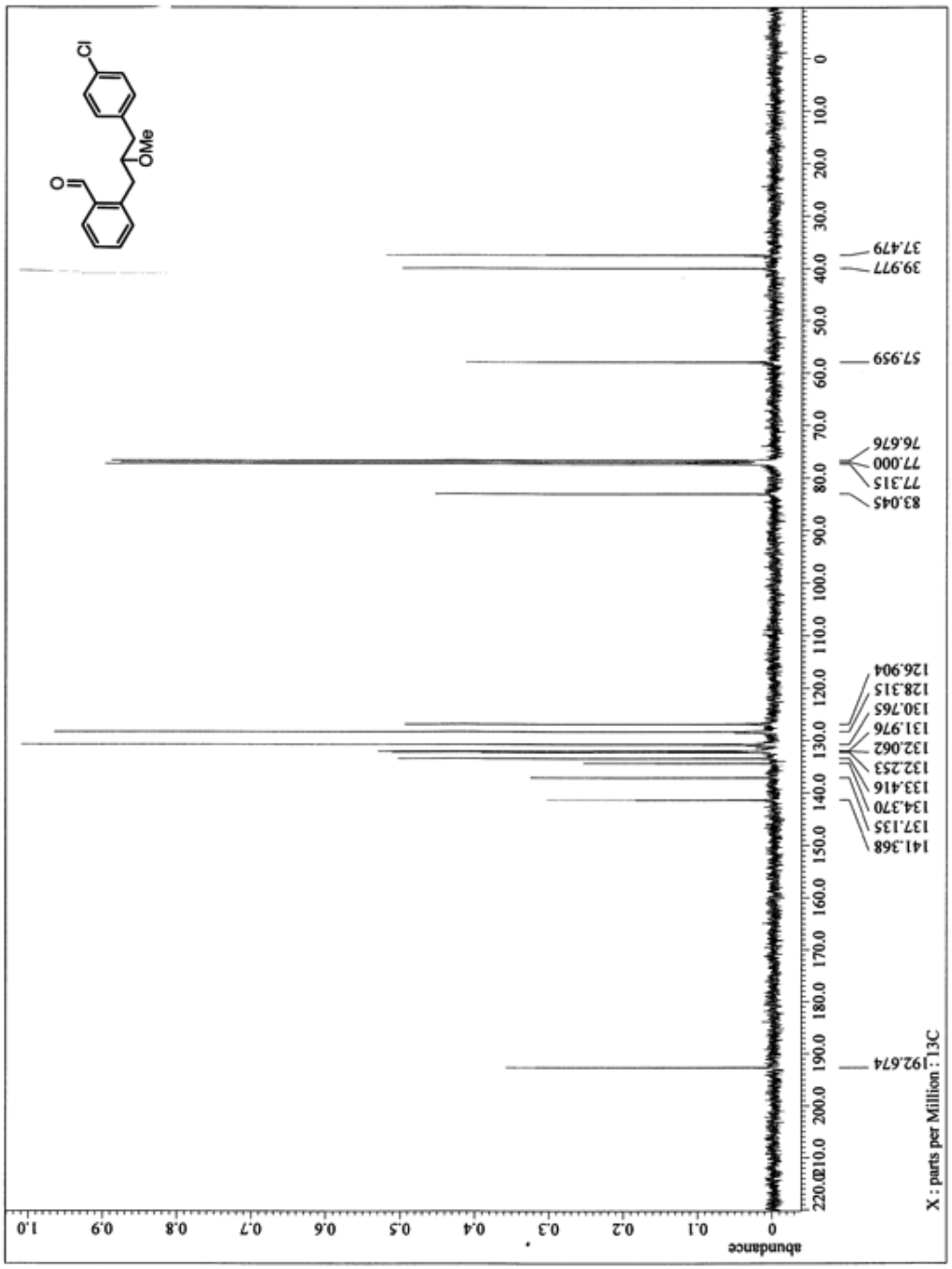
^{13}C NMR spectrum of **s30**.



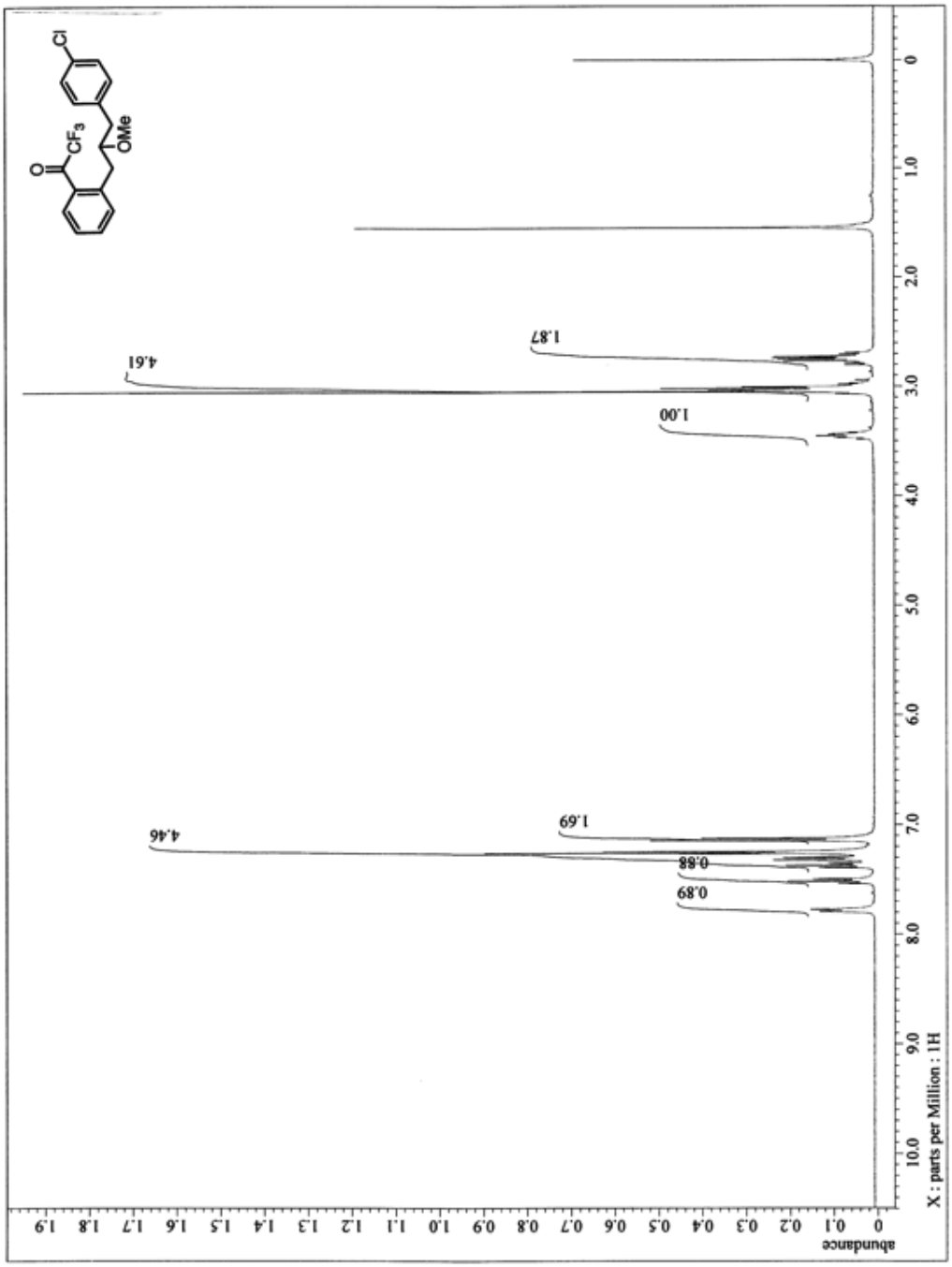
^{1}H NMR spectrum of **s31**.



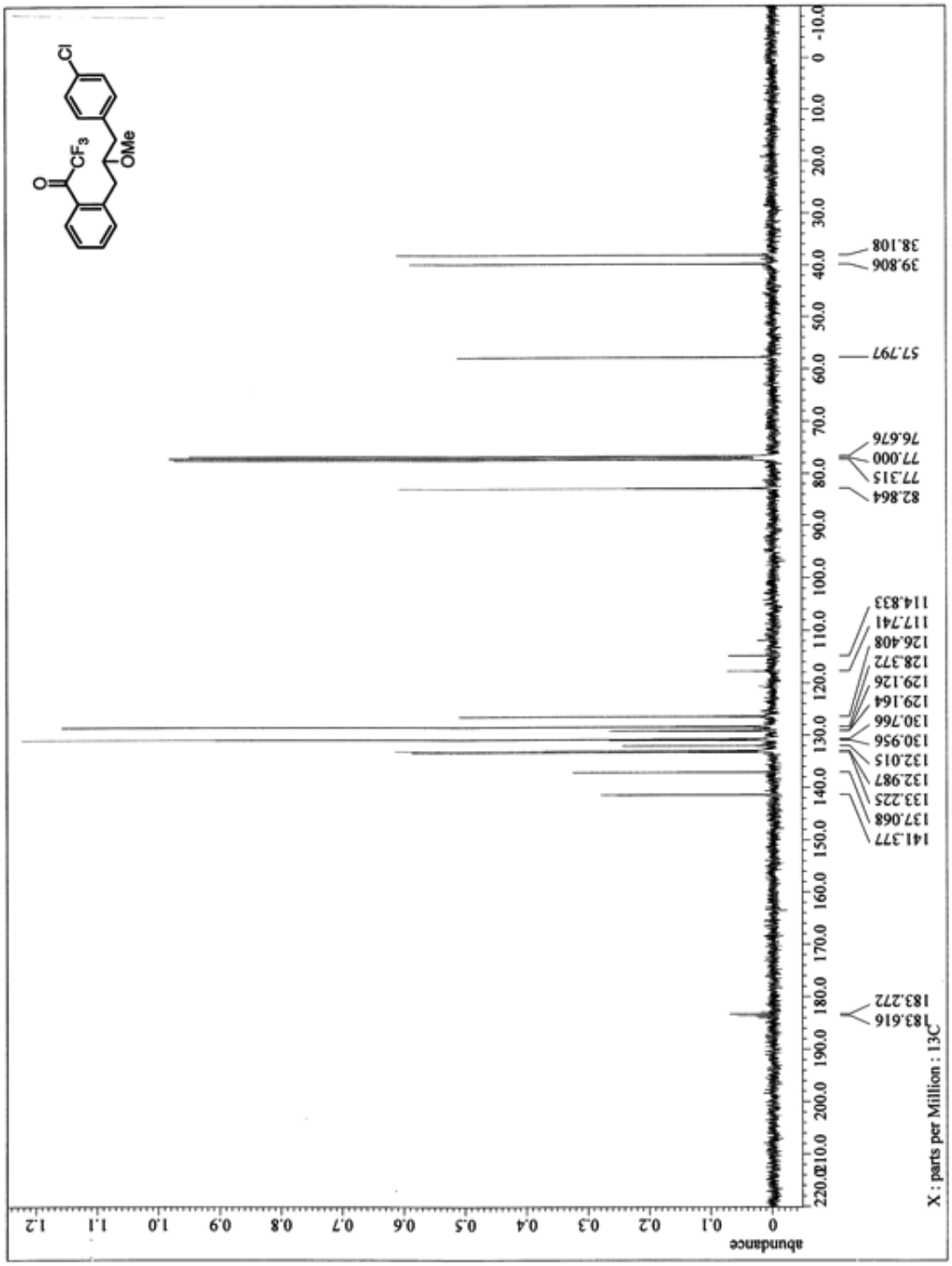
^{13}C NMR spectrum of **s31**.



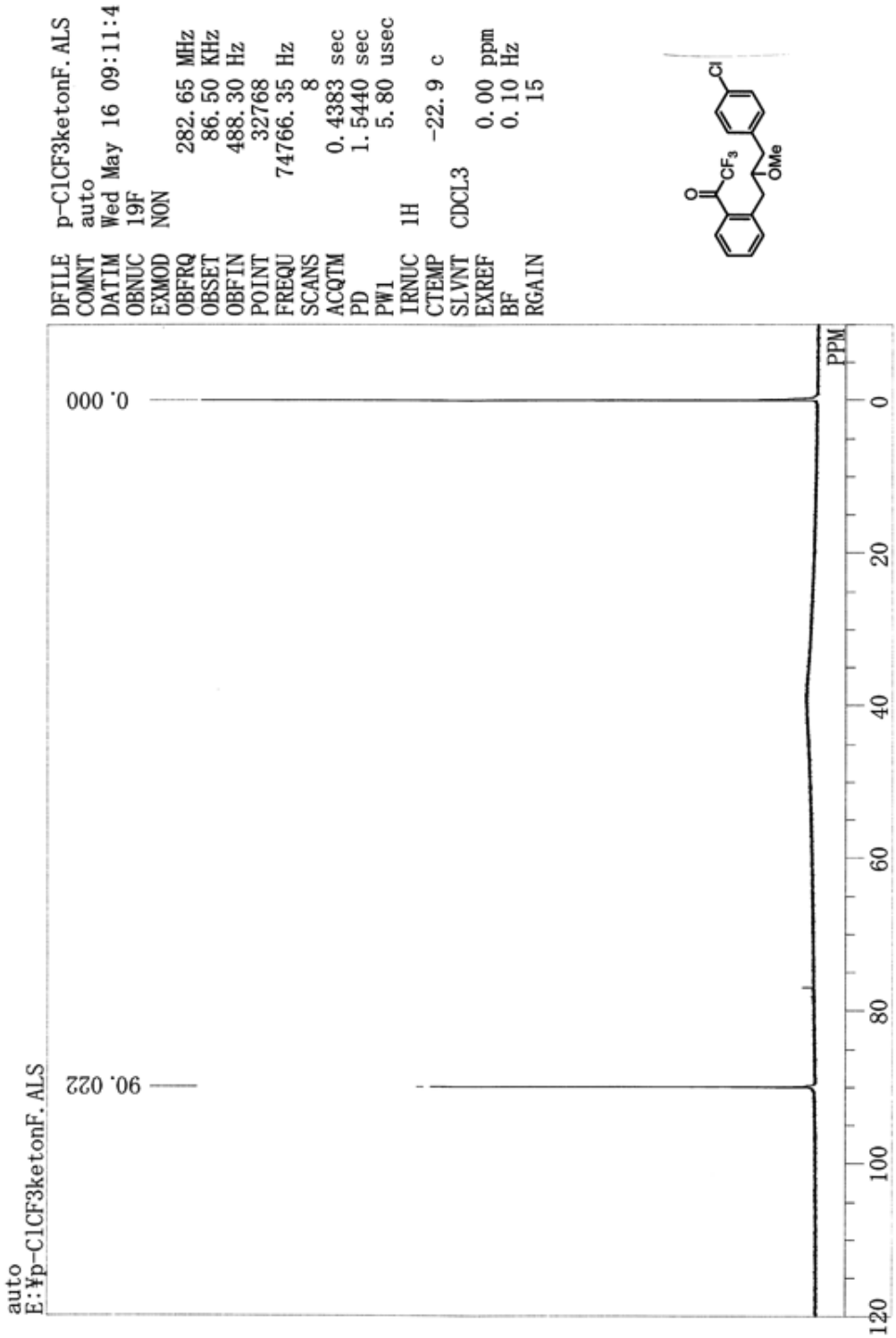
^{1}H NMR spectrum of **1i**.



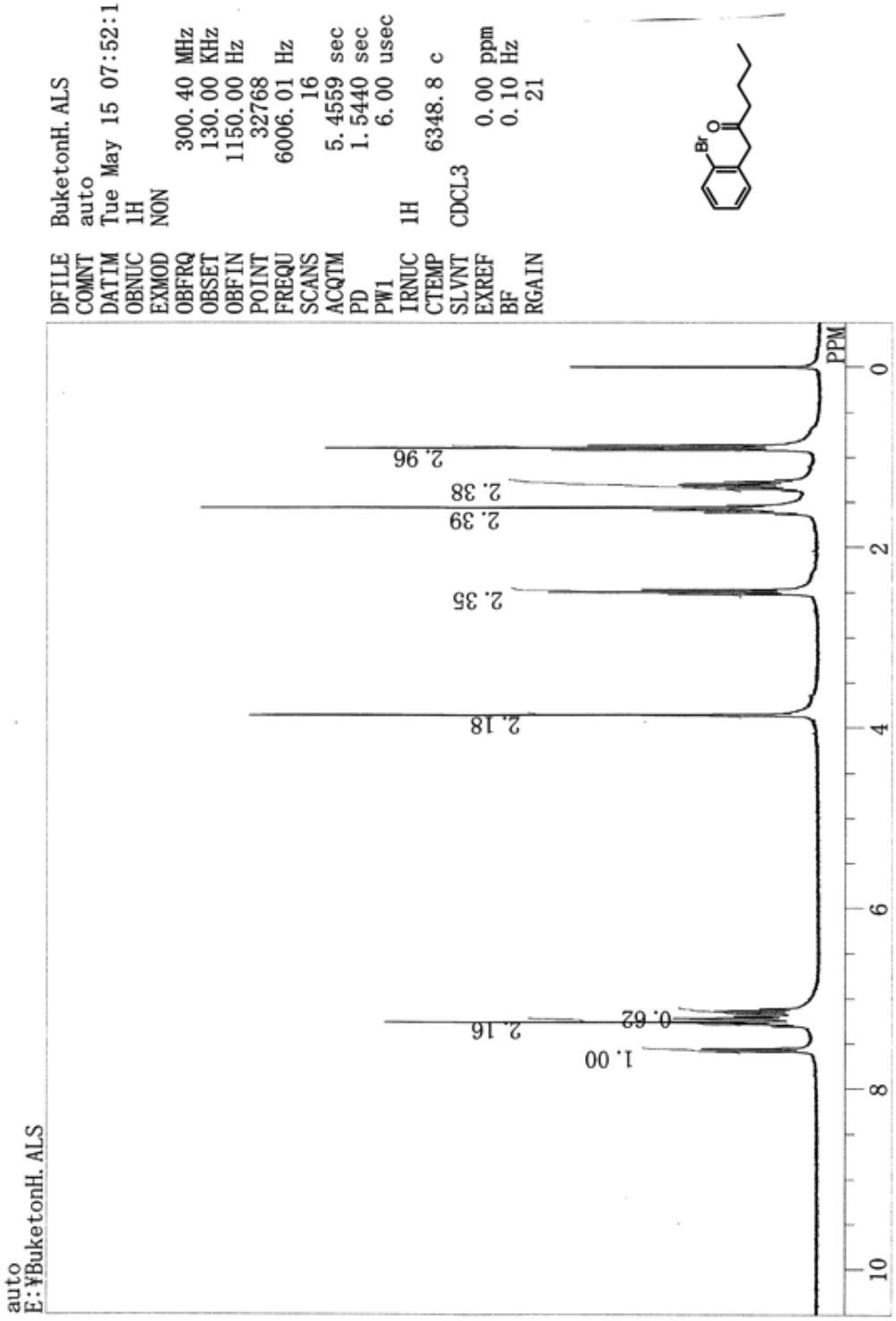
^{13}C NMR spectrum of **1i**.



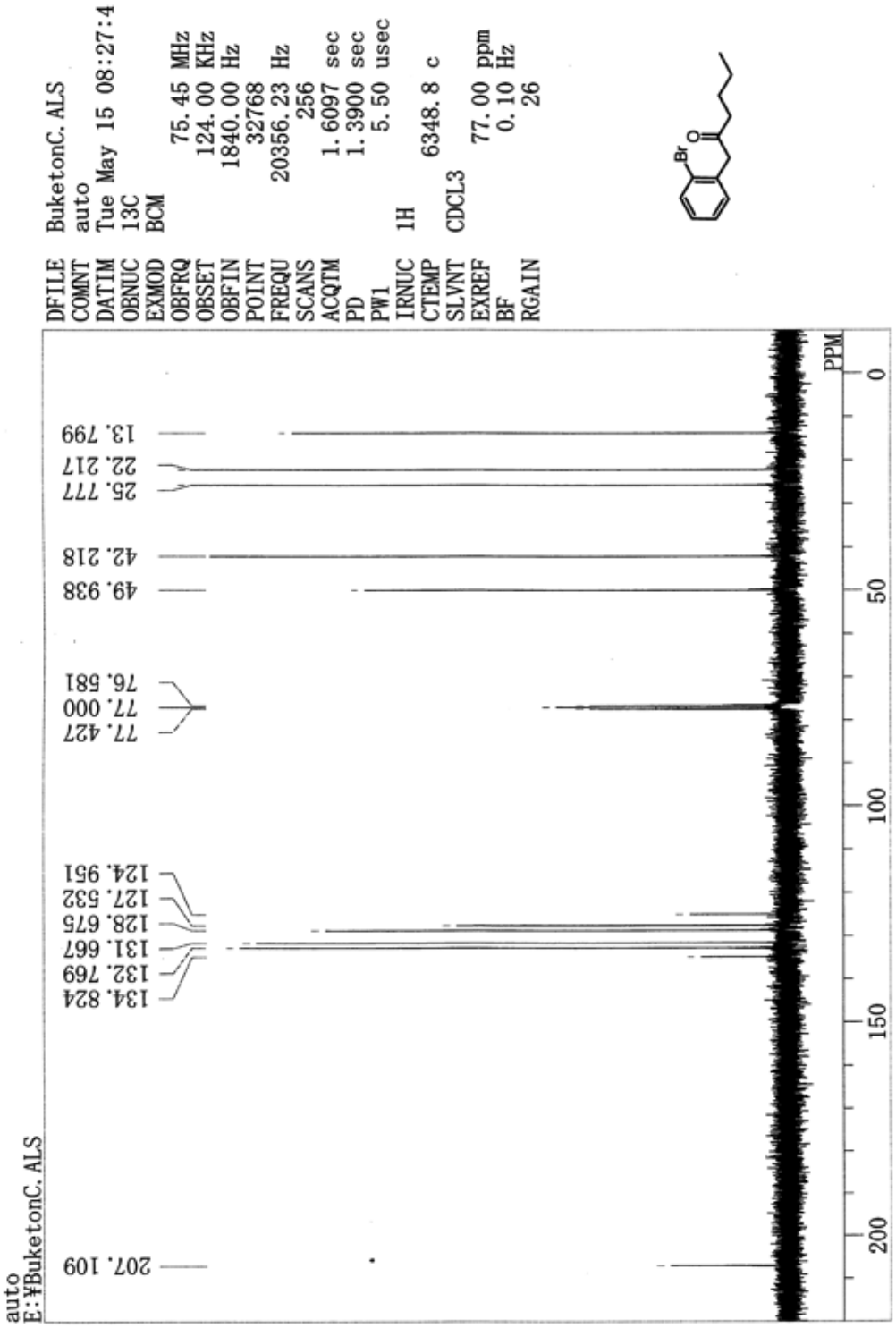
^{19}F NMR spectrum of **1i**.



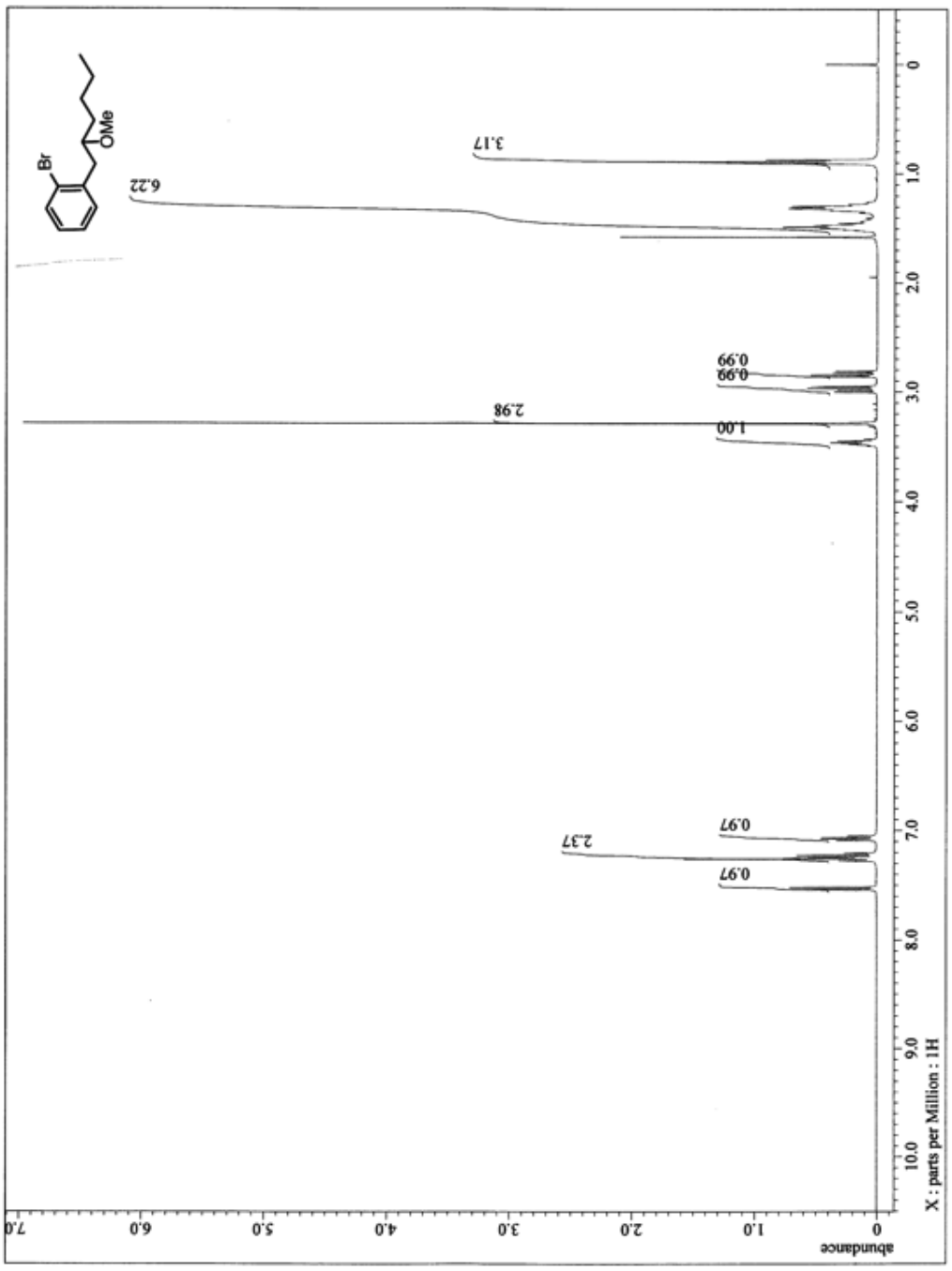
^{1}H NMR spectrum of **s32**.



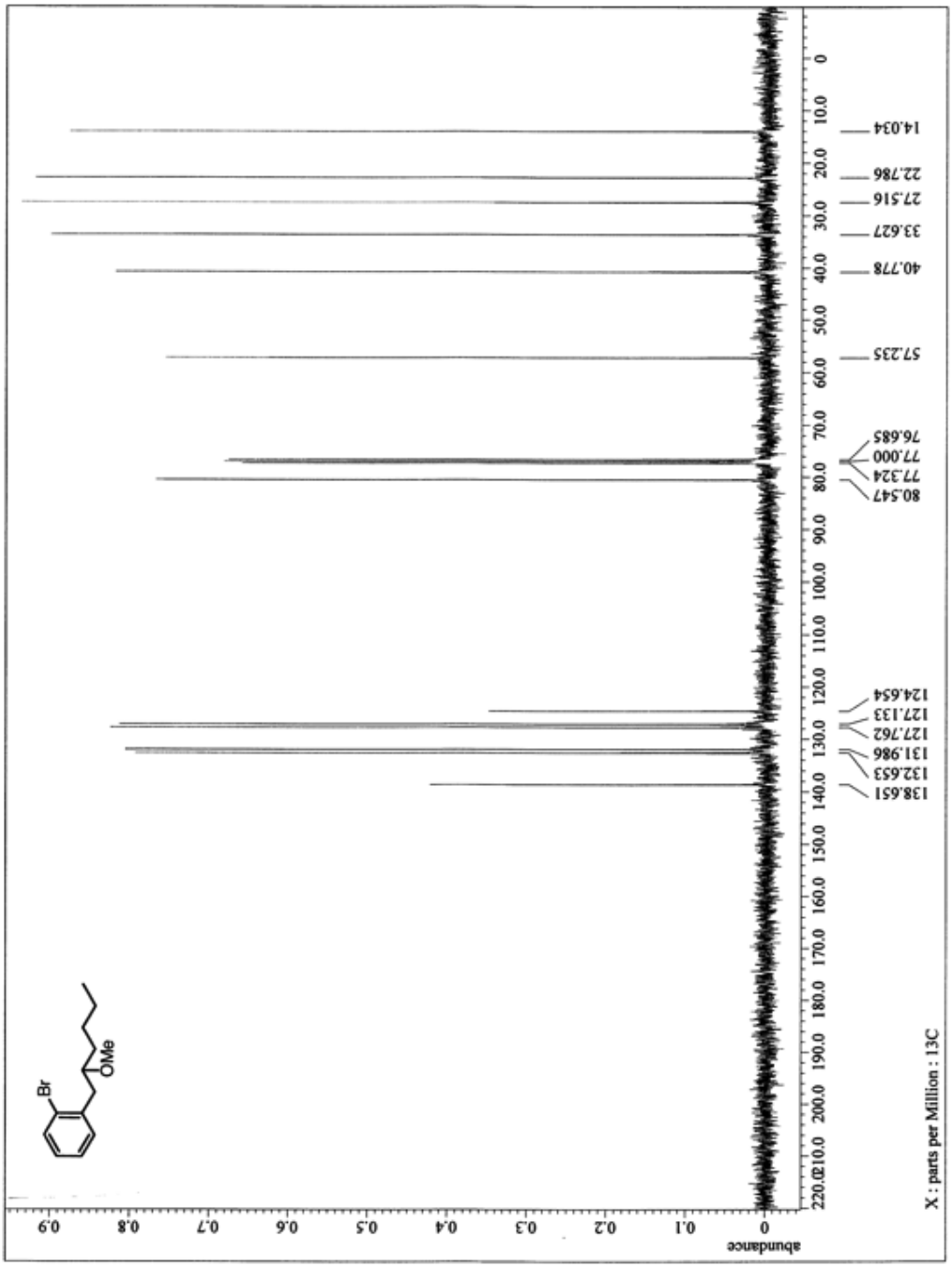
^{13}C NMR spectrum of **s32**.



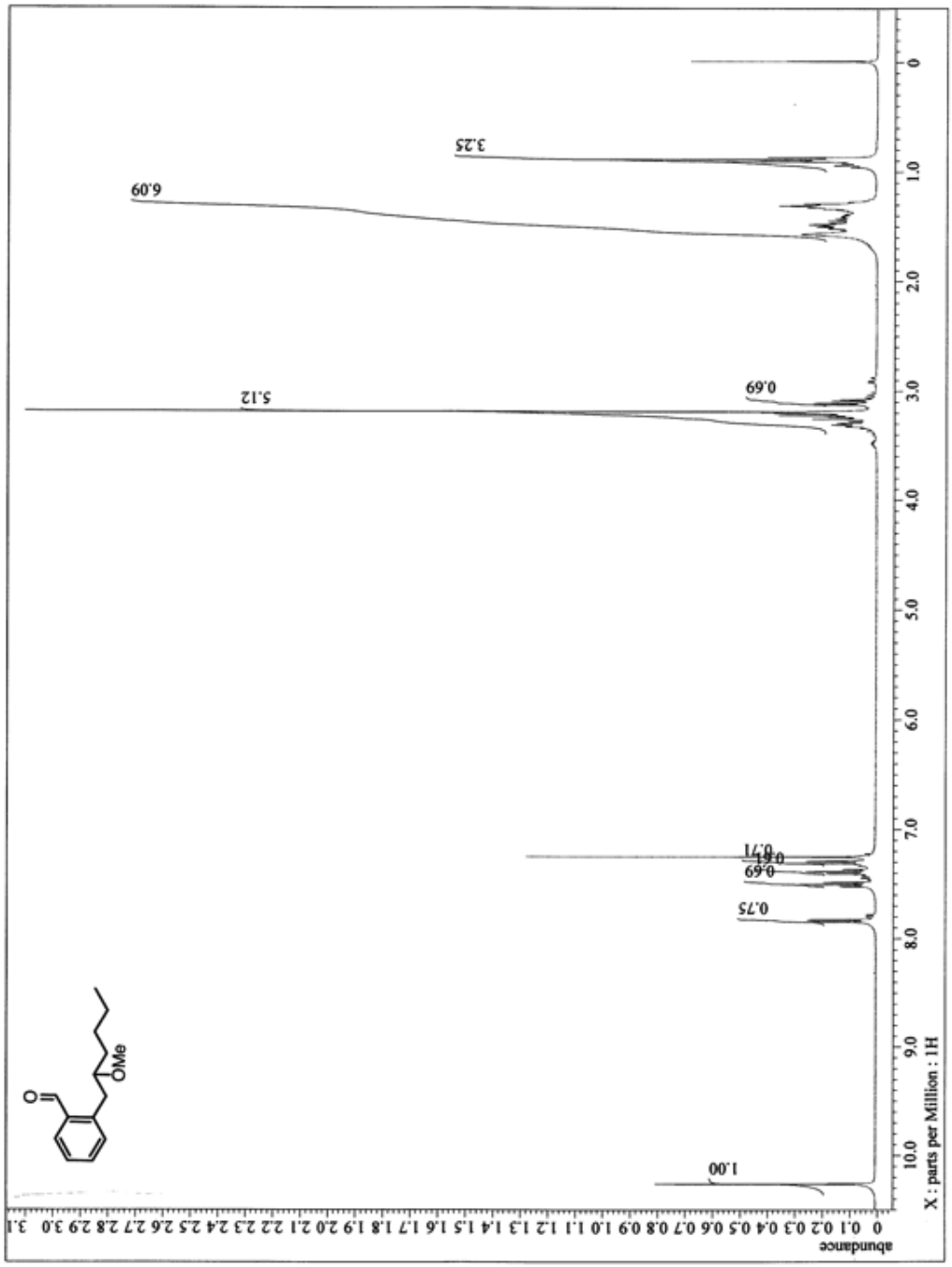
^{1}H NMR spectrum of **s33**.



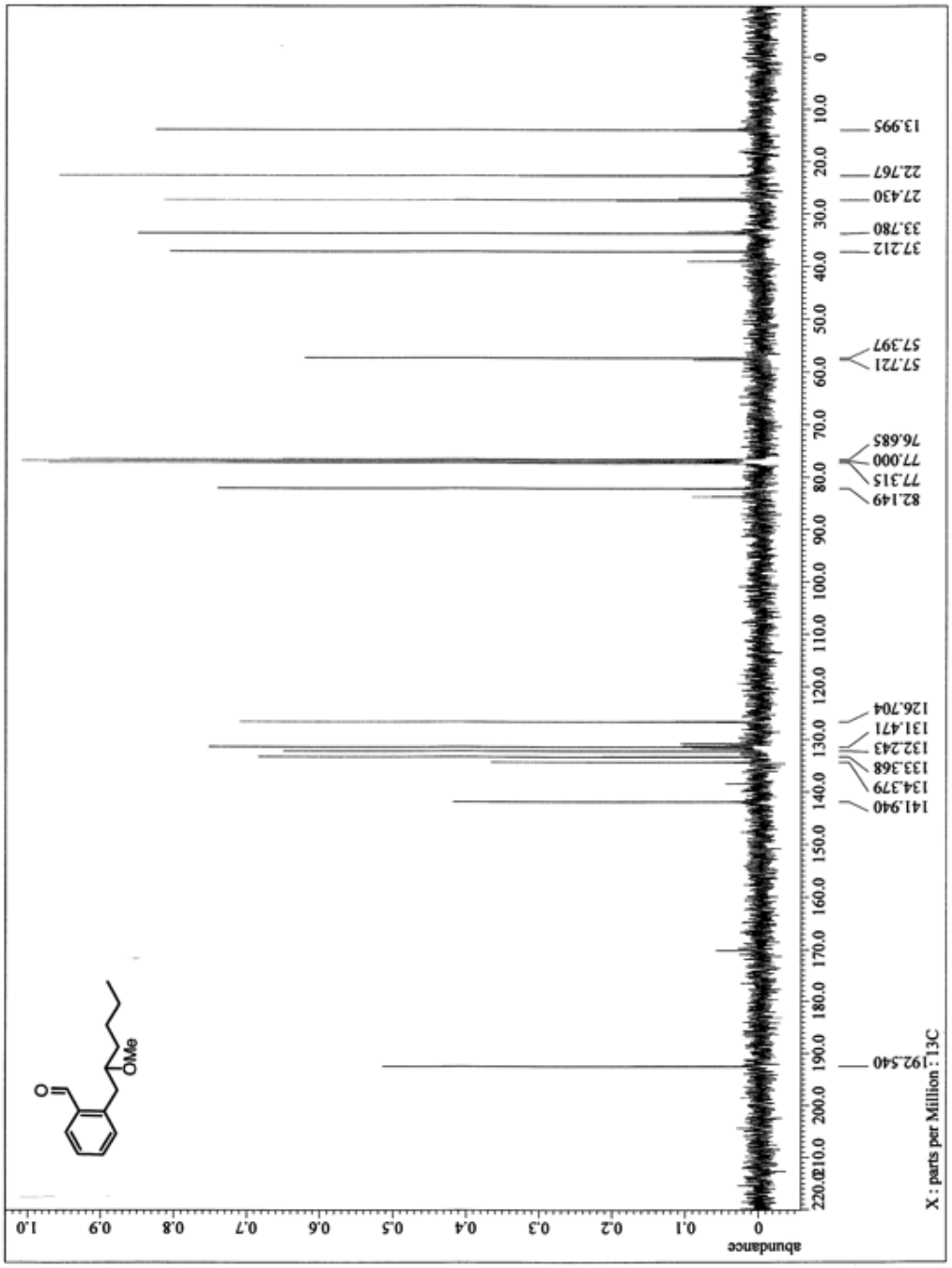
^{13}C NMR spectrum of **s33**.



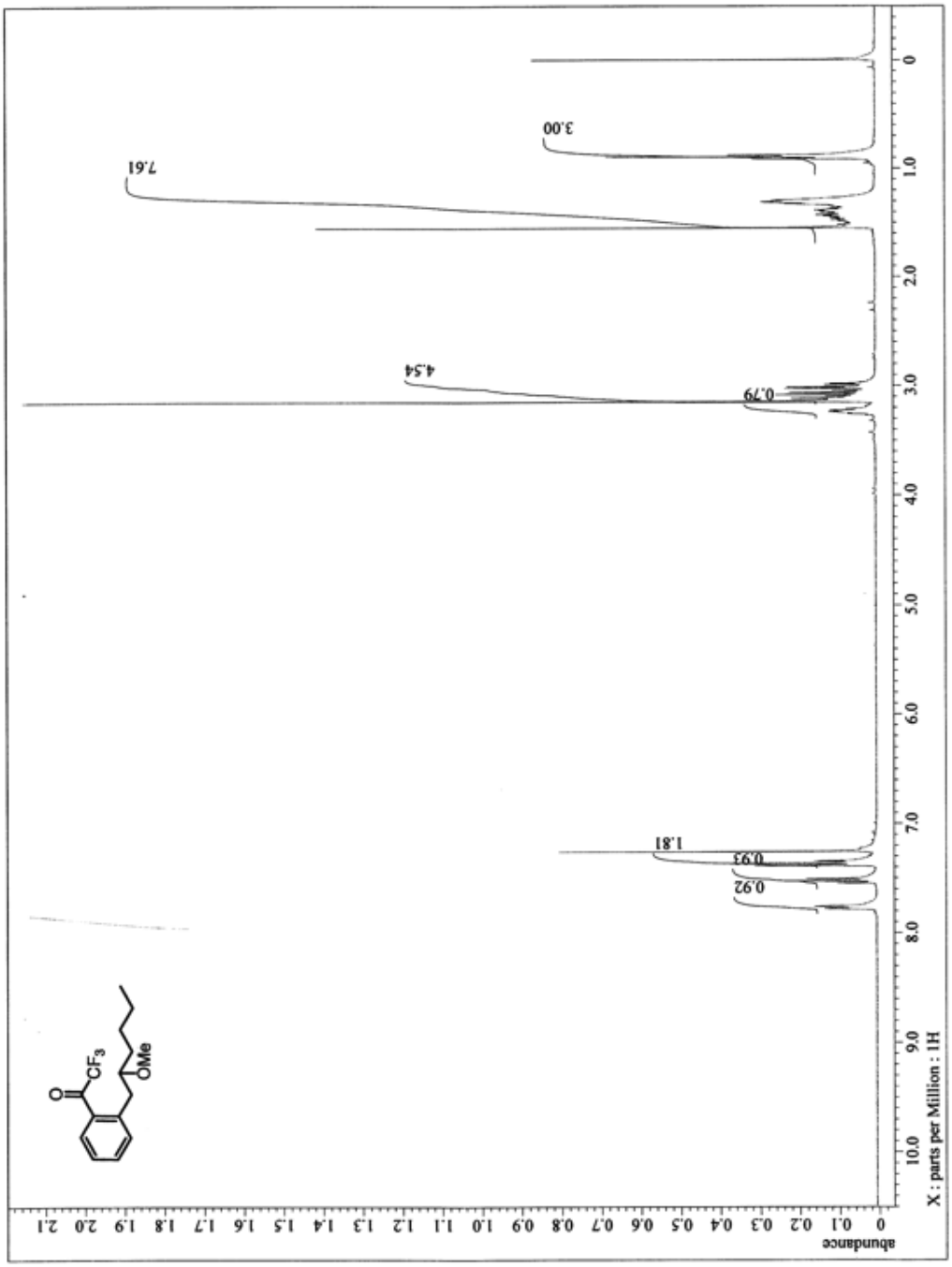
^{1}H NMR spectrum of **s34**.



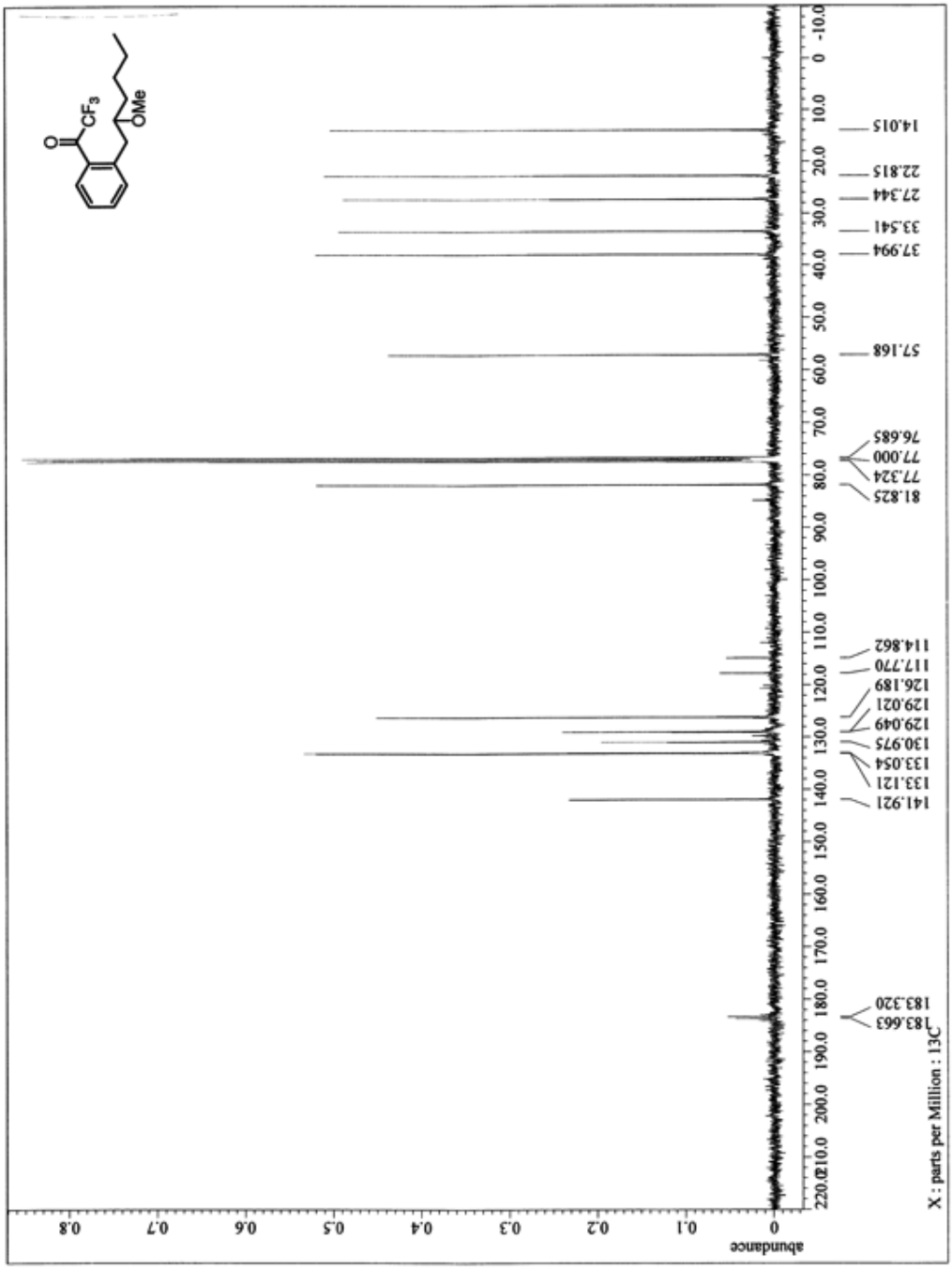
^{13}C NMR spectrum of **s34.**



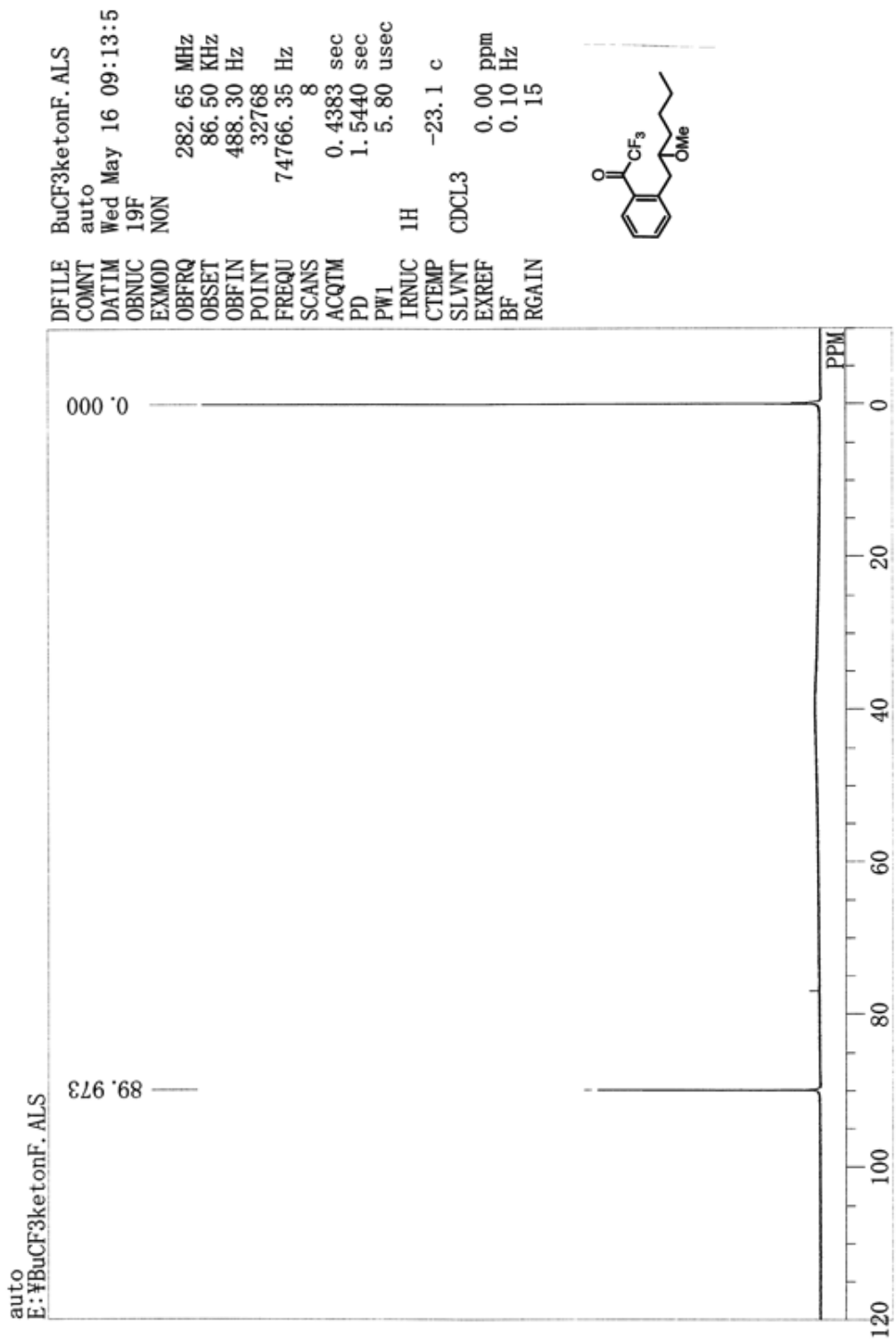
^{1}H NMR spectrum of **1j**.



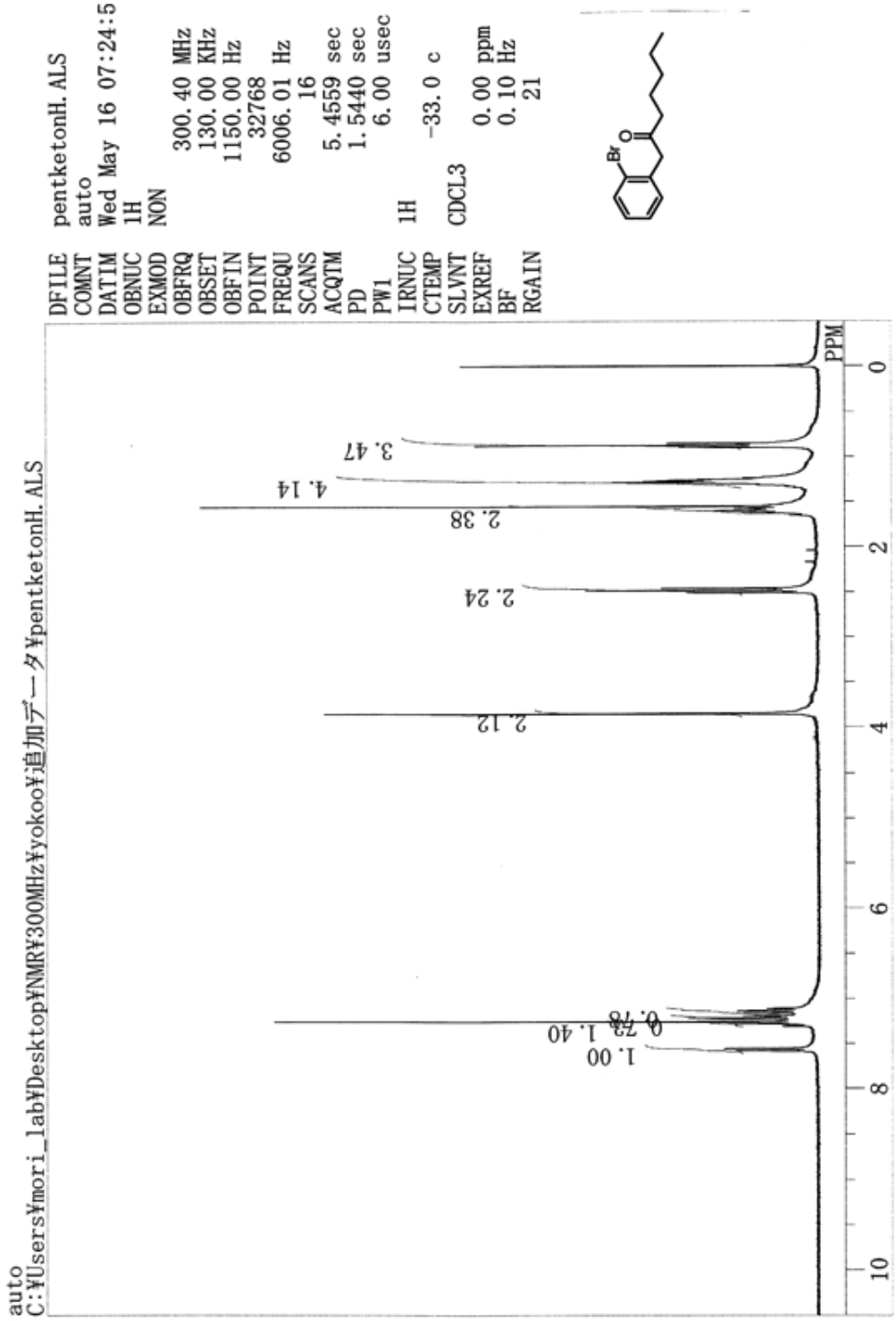
^{13}C NMR spectrum of **1j**.



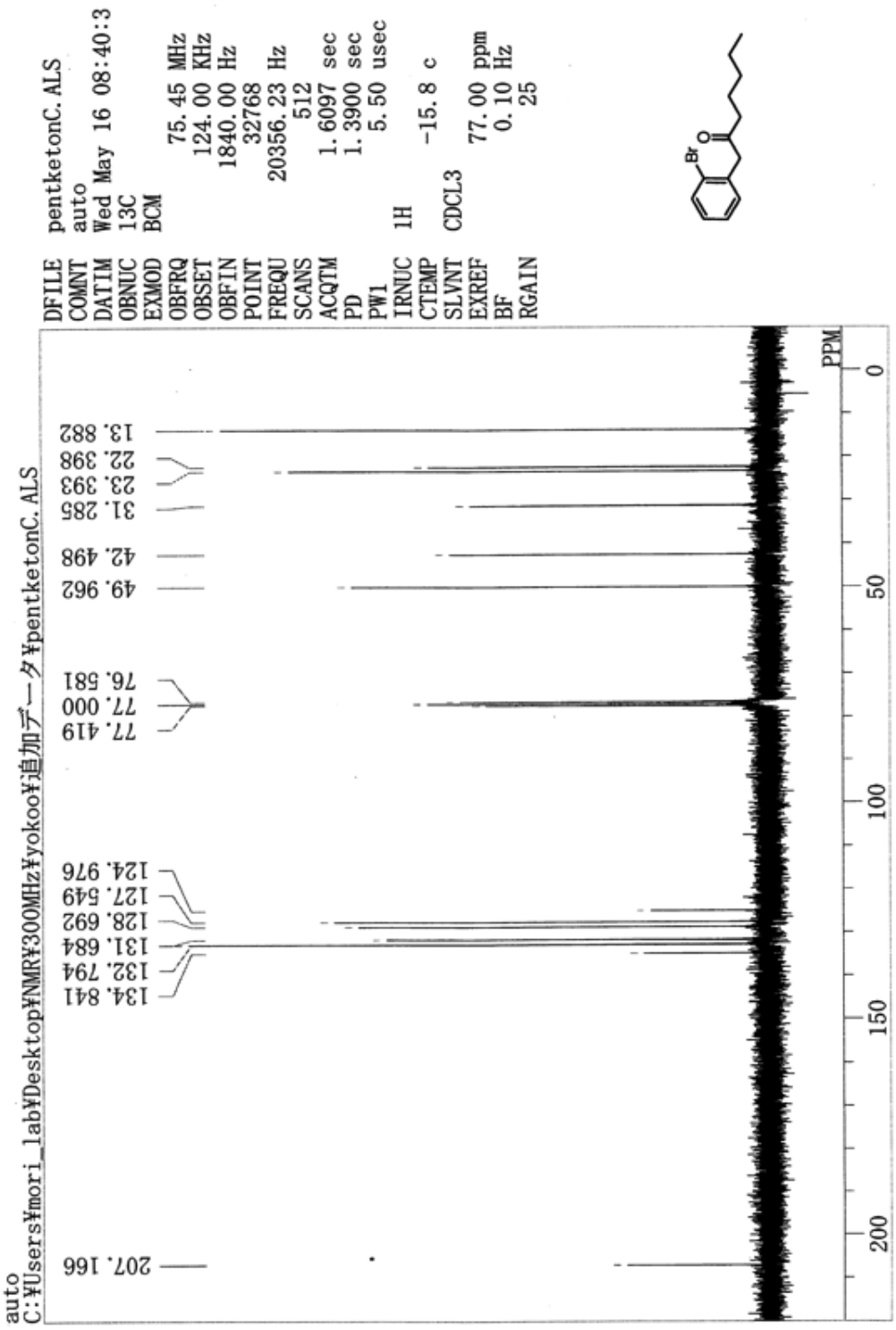
^{19}F NMR spectrum of **1j**.



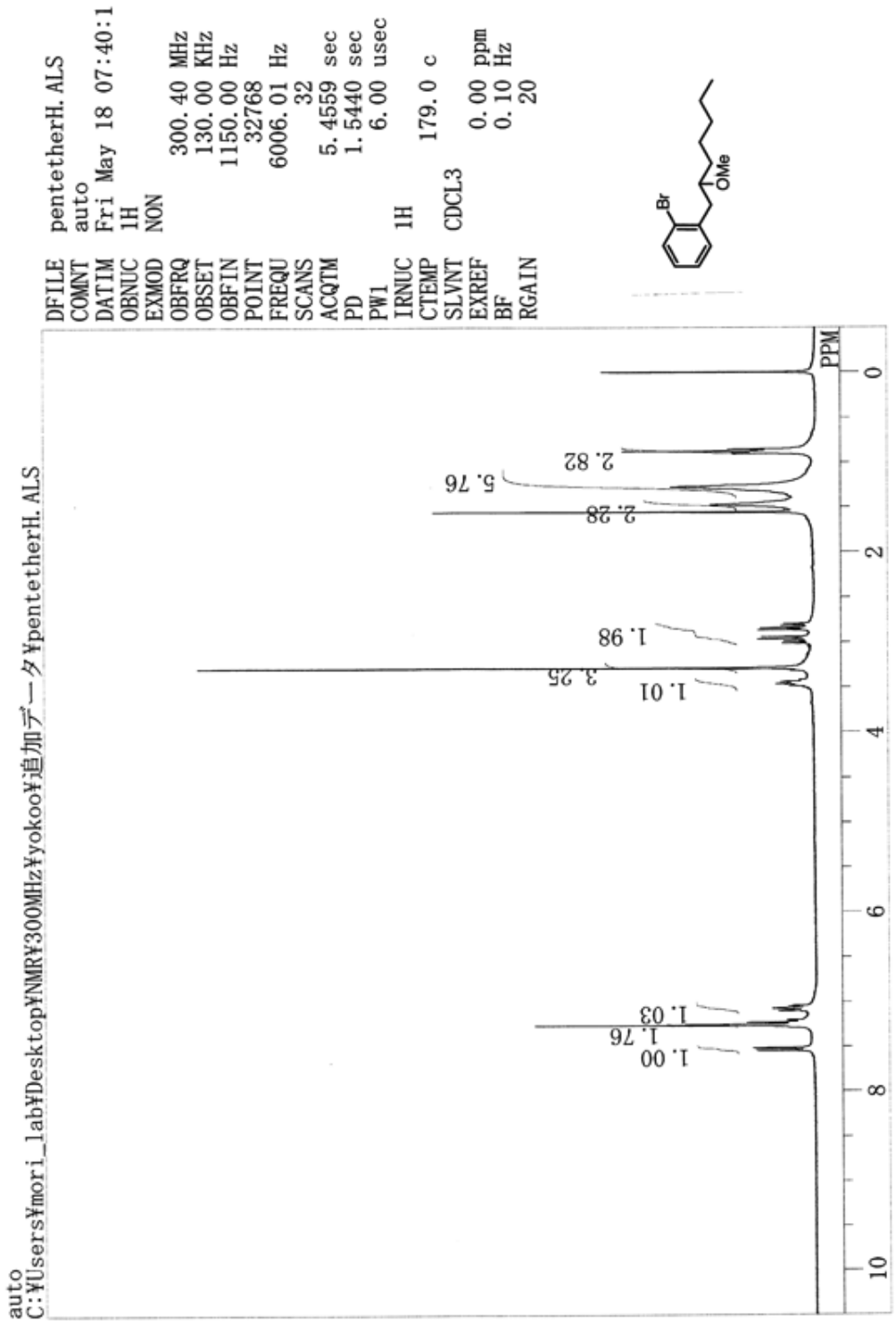
^{1}H NMR spectrum of **s35**.



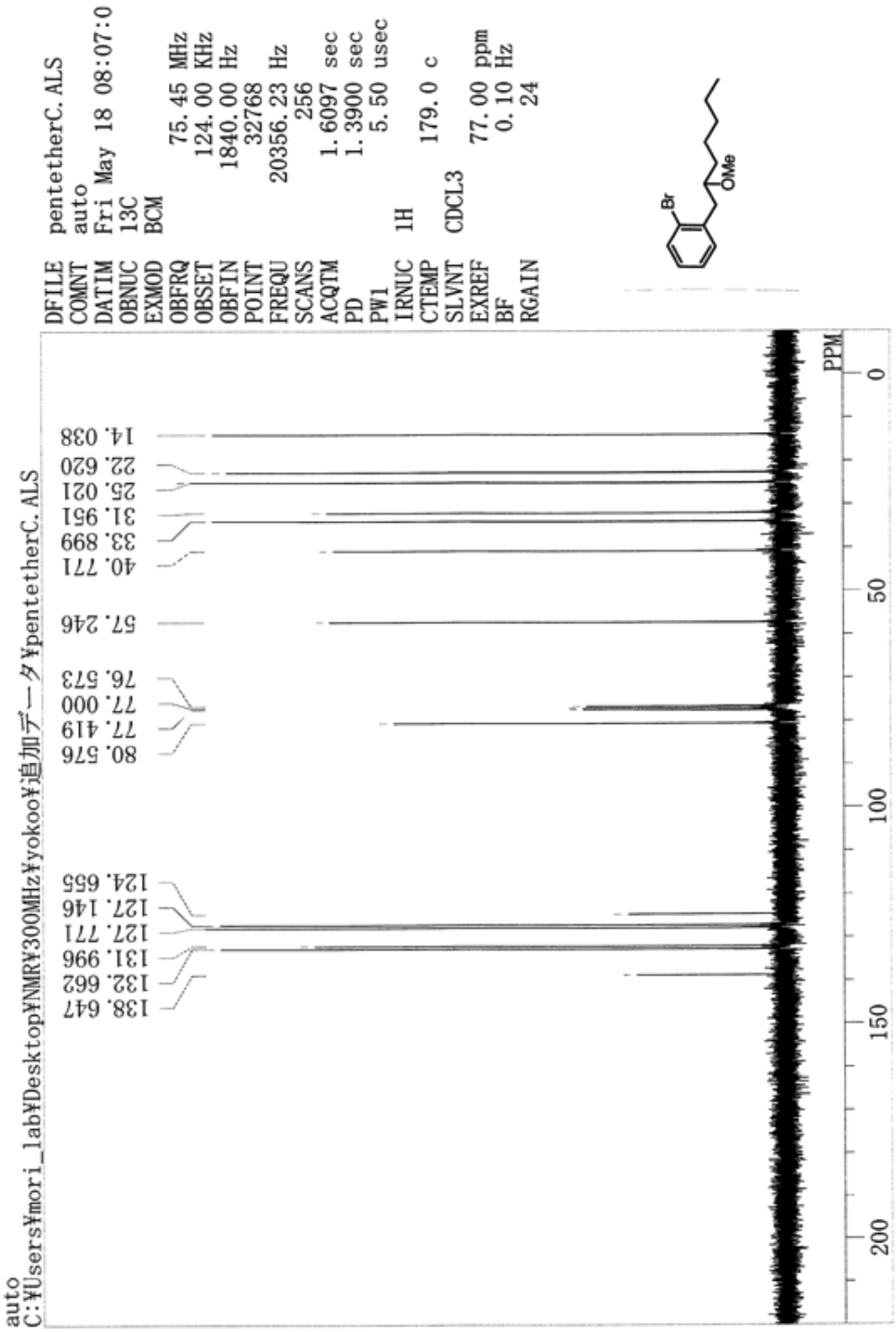
^{13}C NMR spectrum of **s35**.



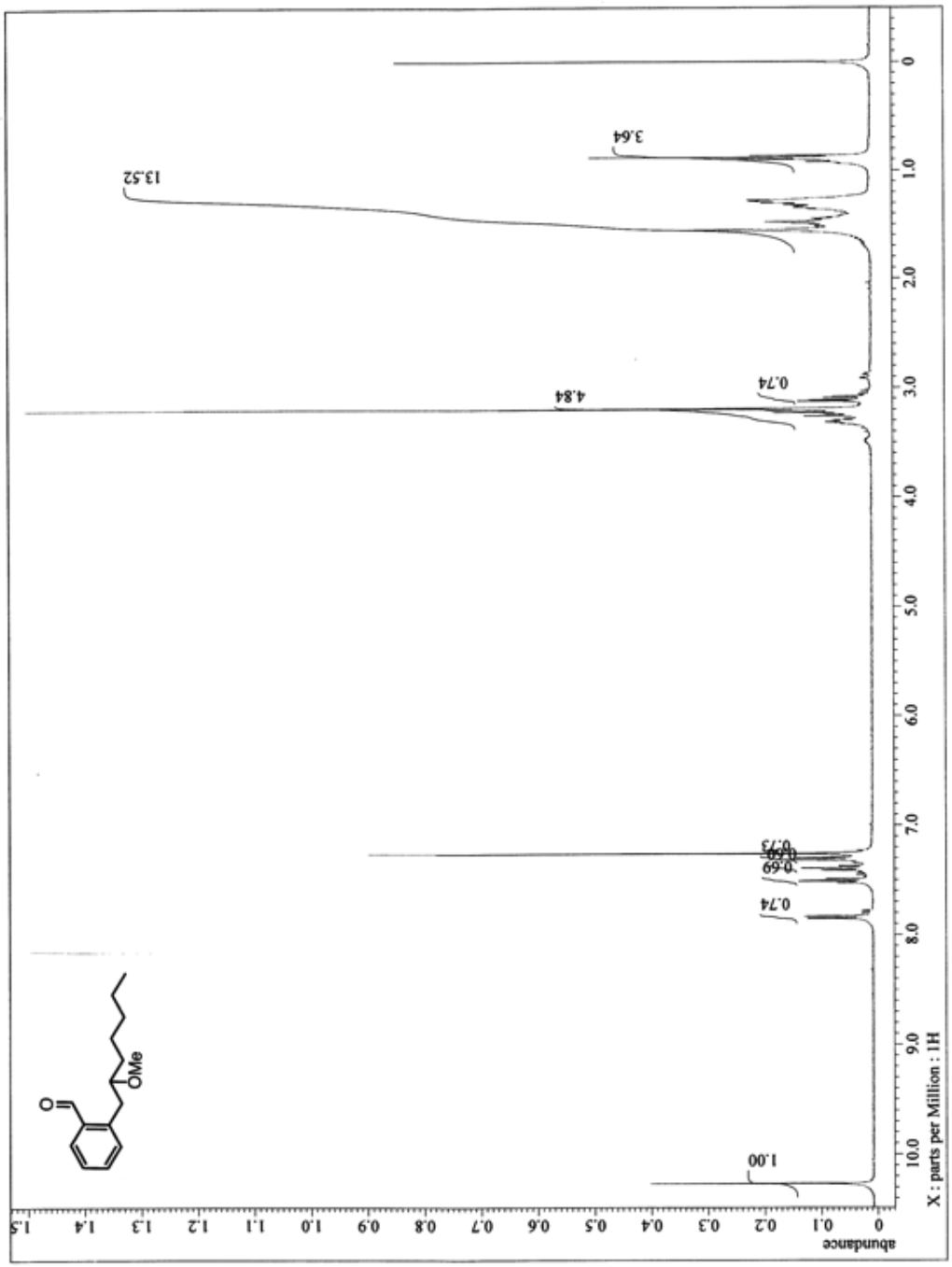
^{1}H NMR spectrum of **s36**.



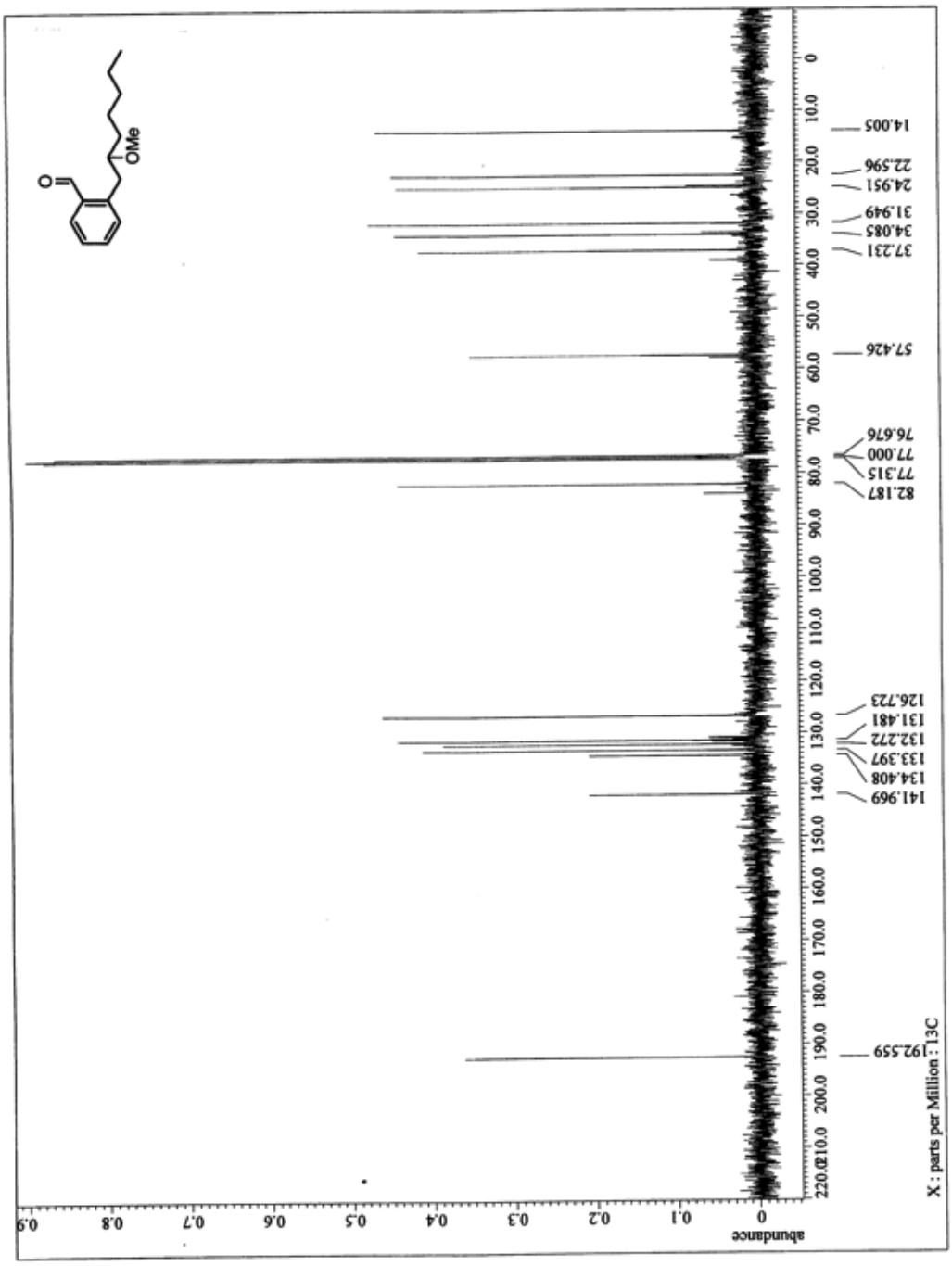
^{13}C NMR spectrum of **s36**.



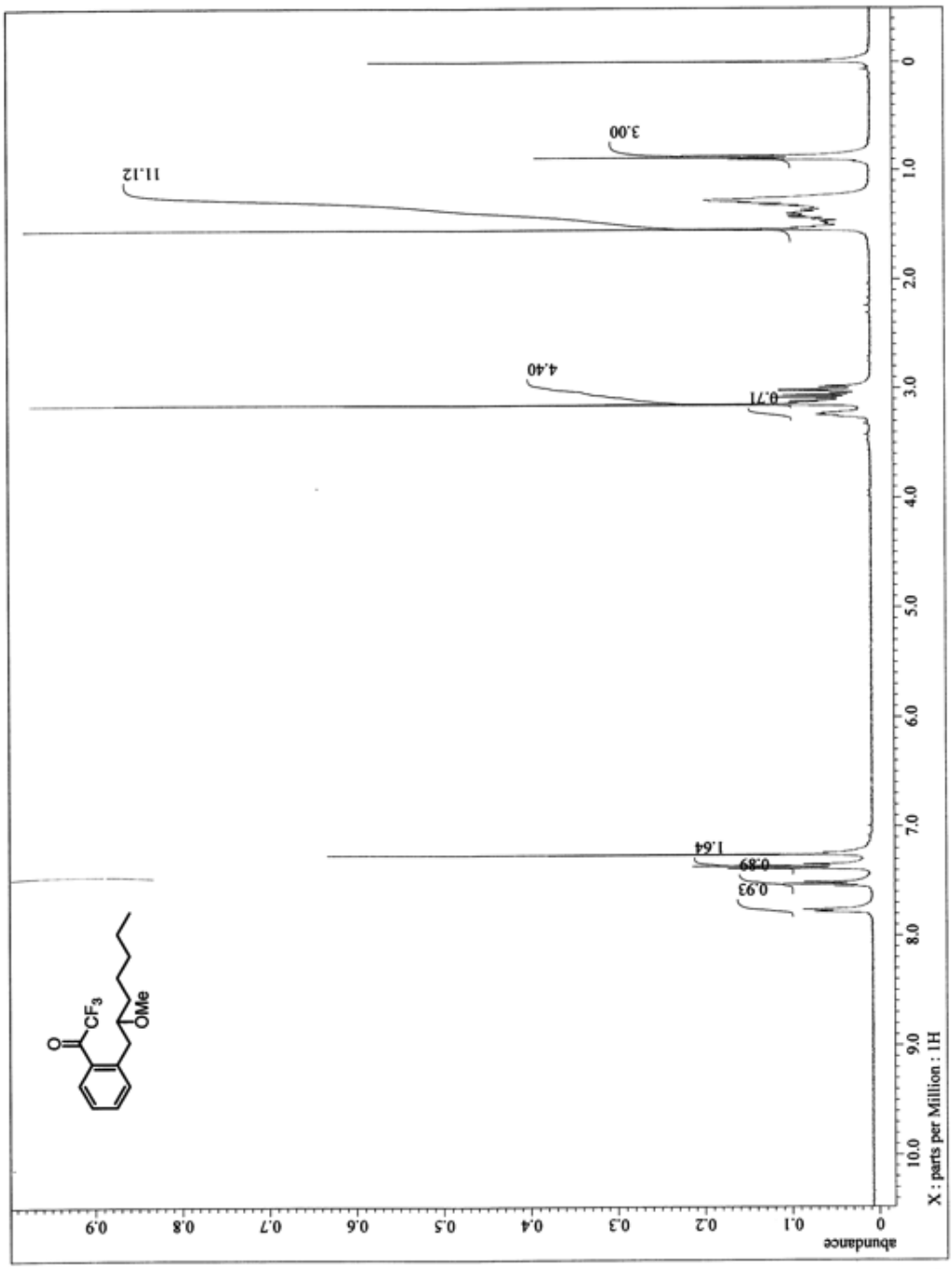
^{1}H NMR spectrum of **s37**.



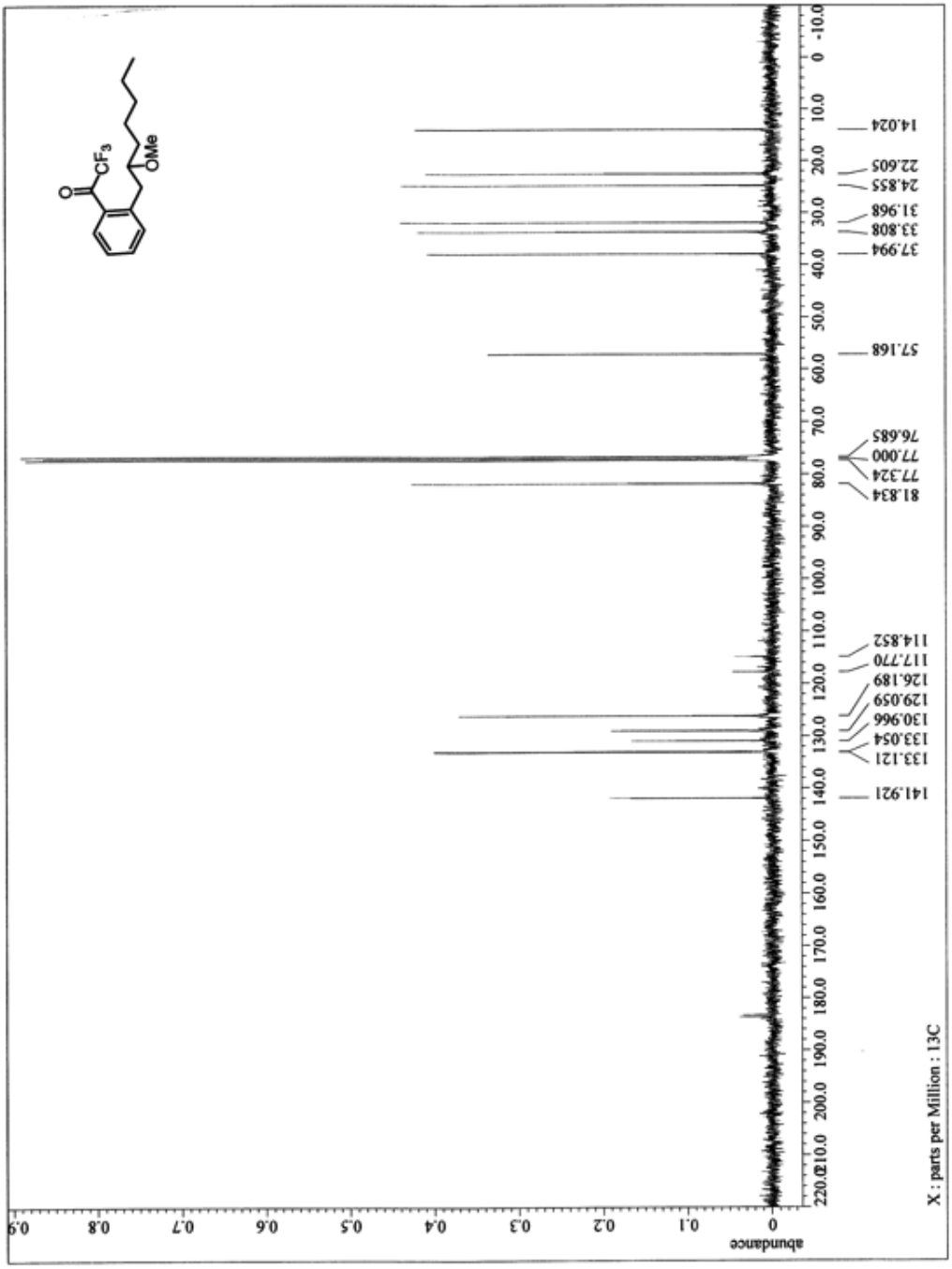
^{13}C NMR spectrum of **s37**.



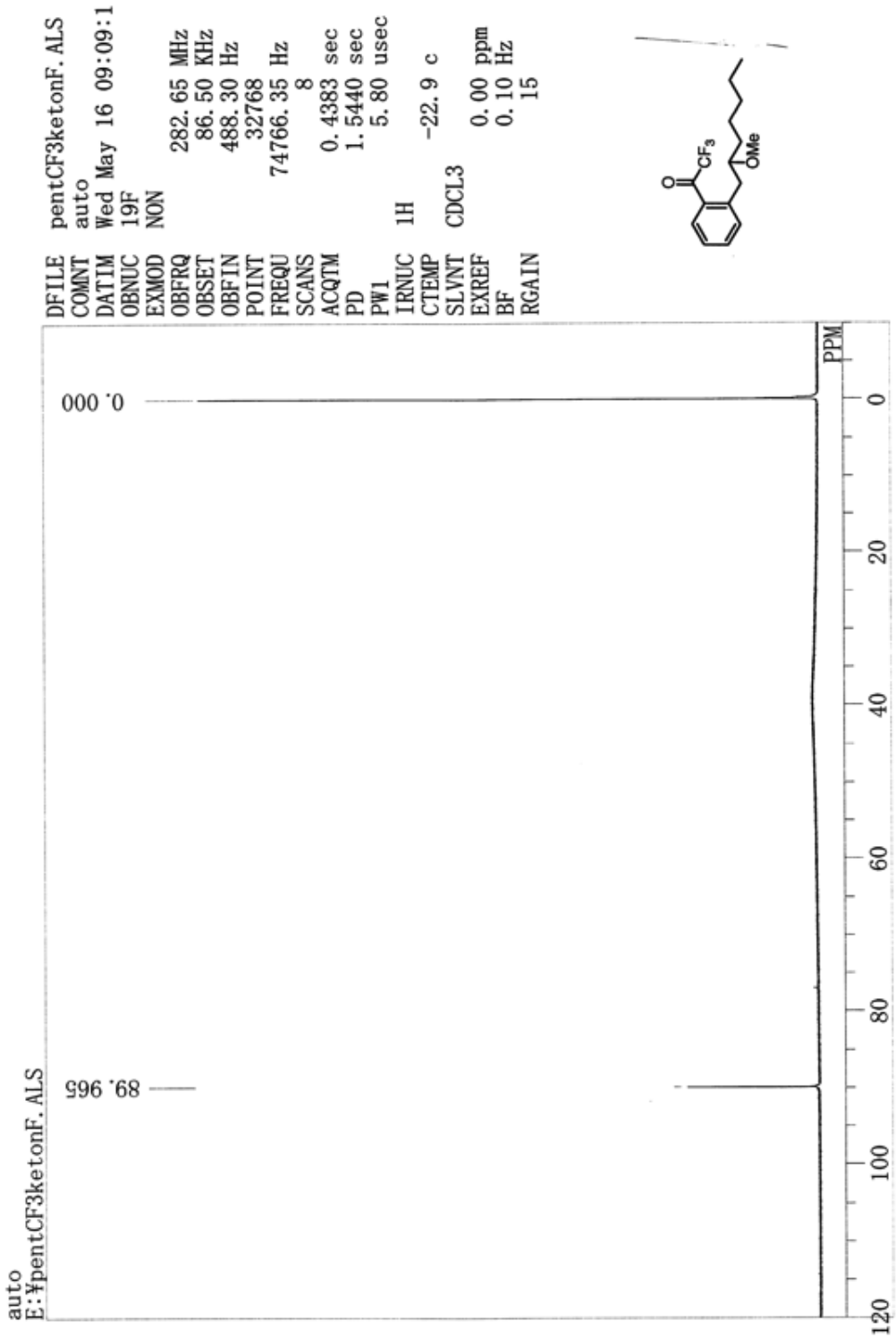
^{1}H NMR spectrum of **1k**.



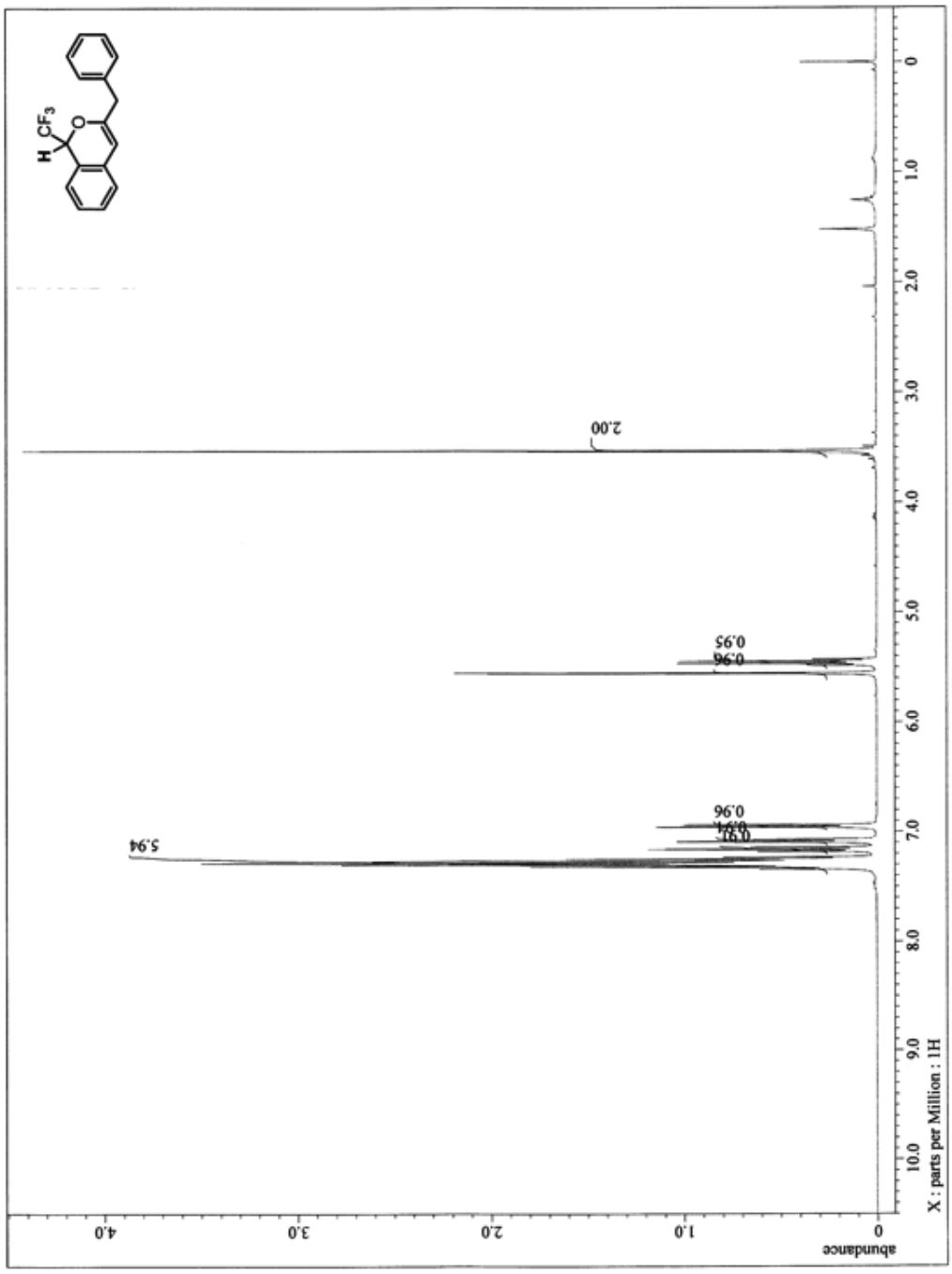
^{13}C NMR spectrum of **1k**.



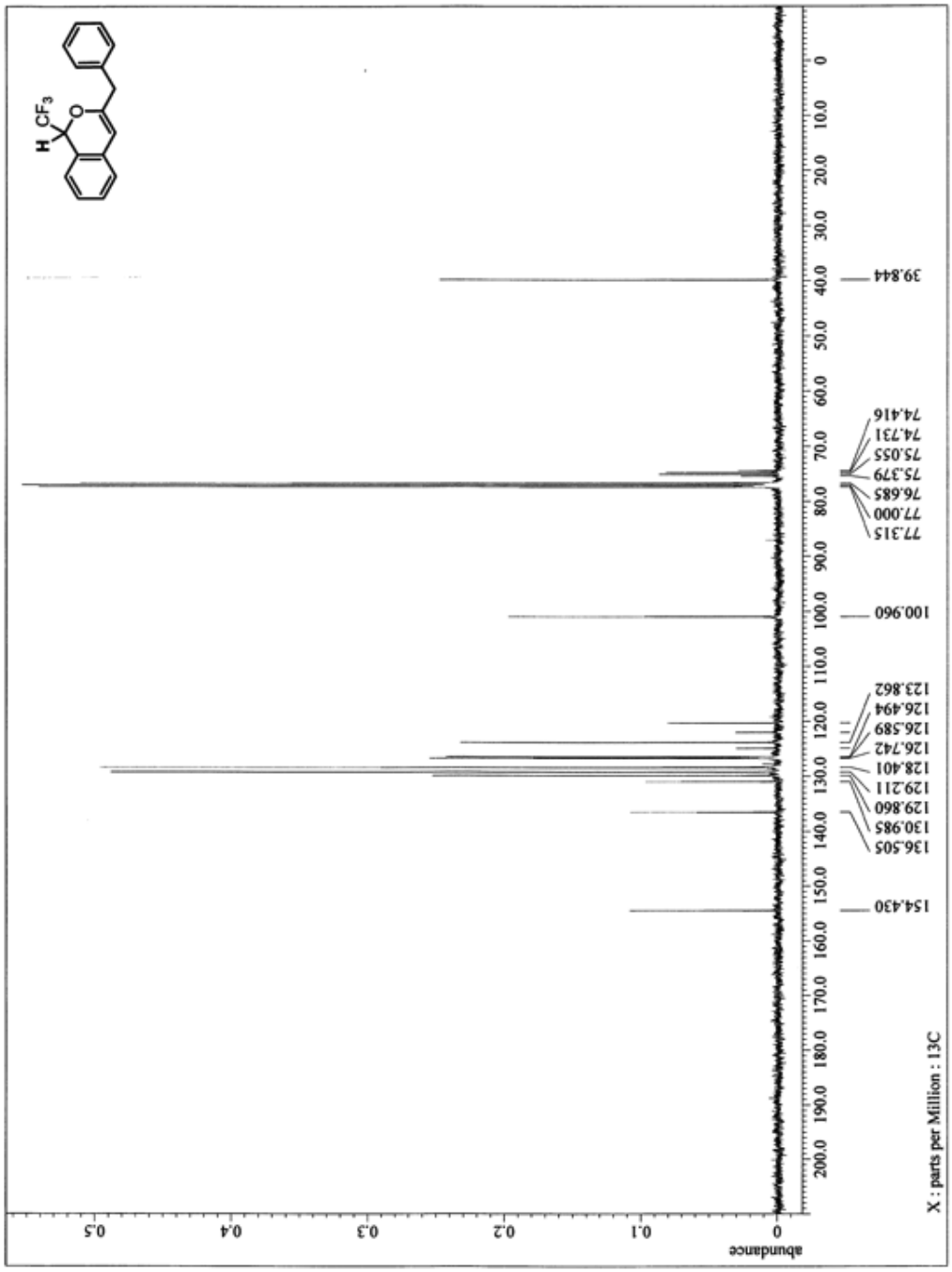
^{19}F NMR spectrum of **1k**.



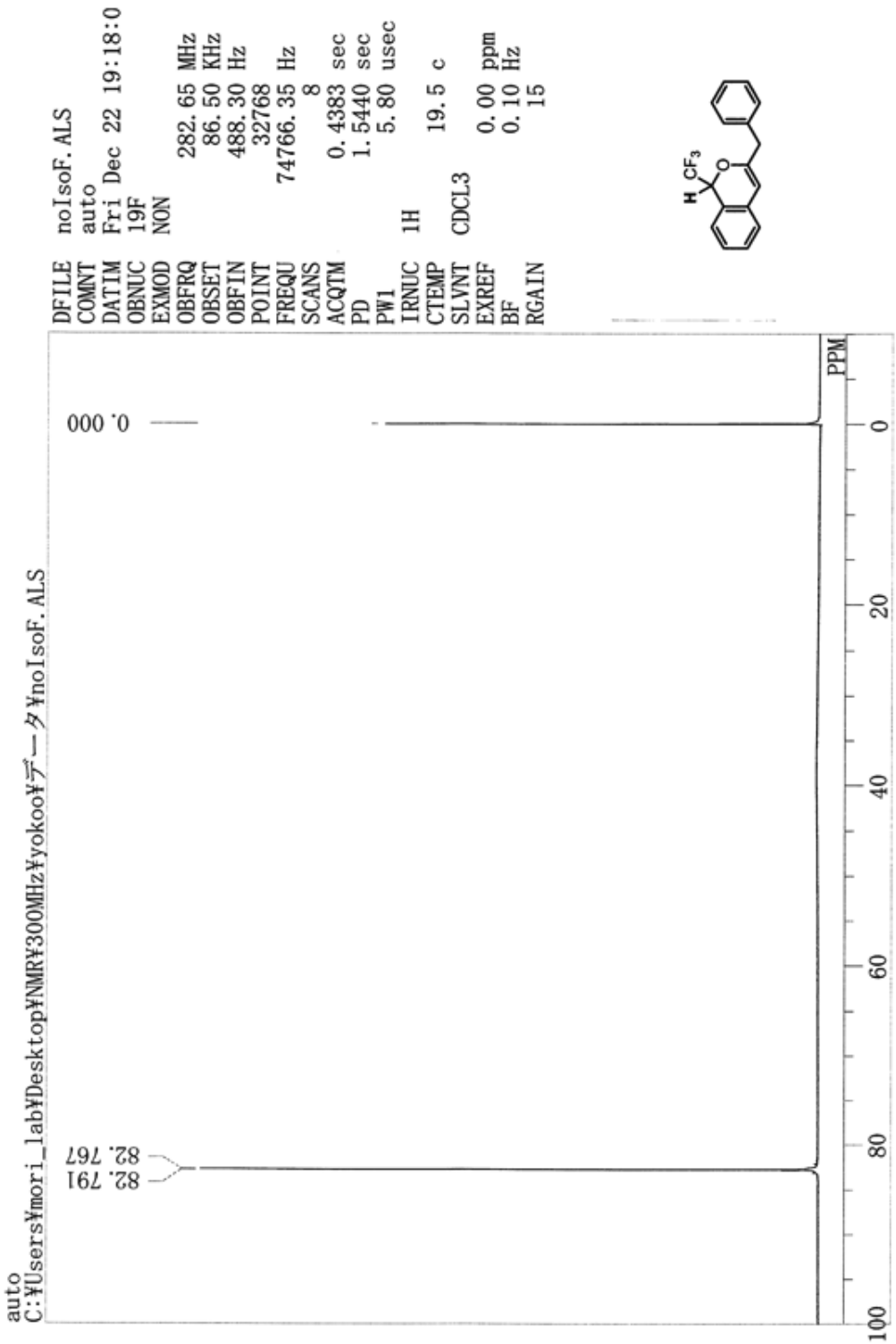
^{1}H NMR spectrum of **2a**.



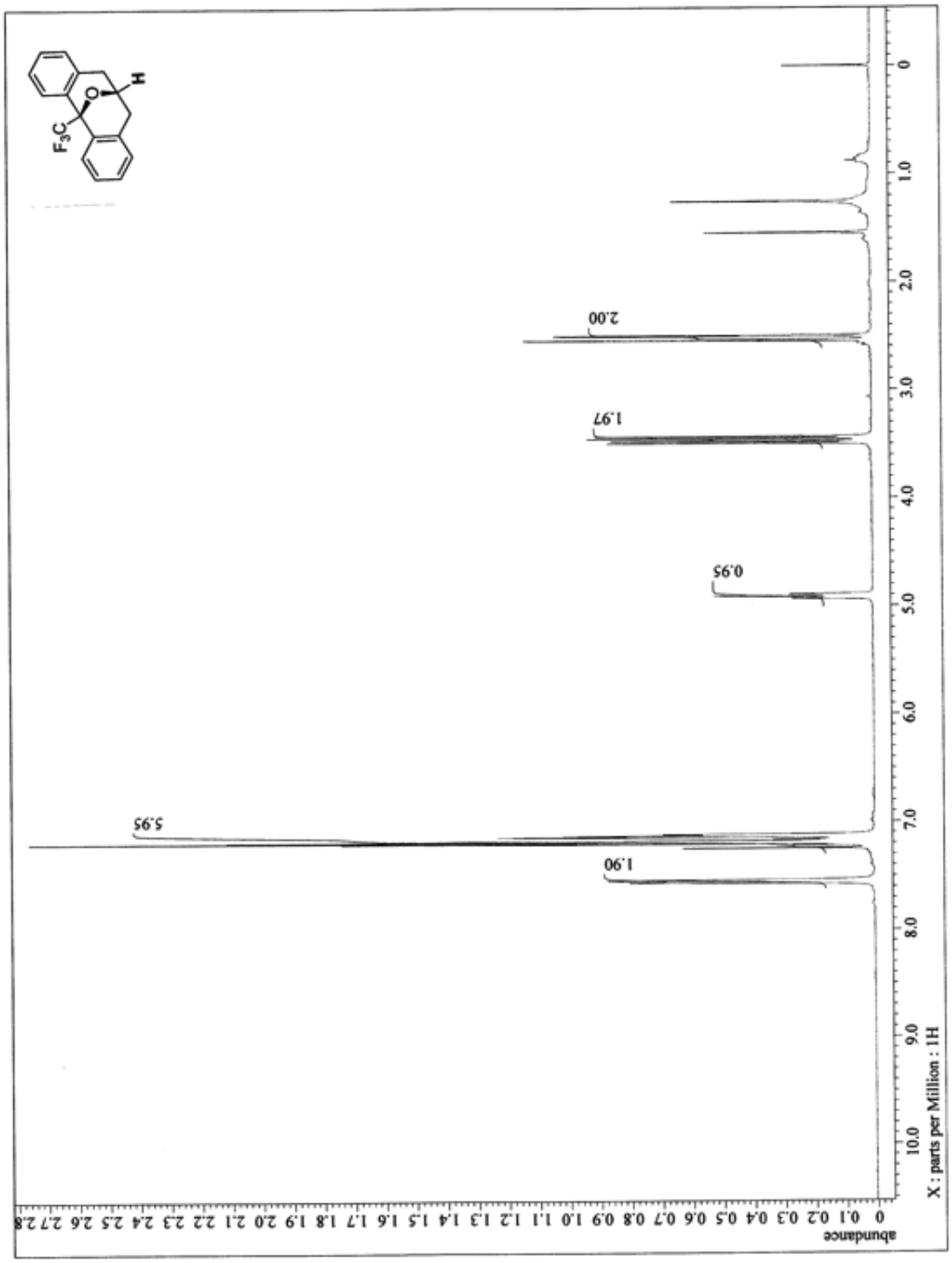
^{13}C NMR spectrum of **2a**.



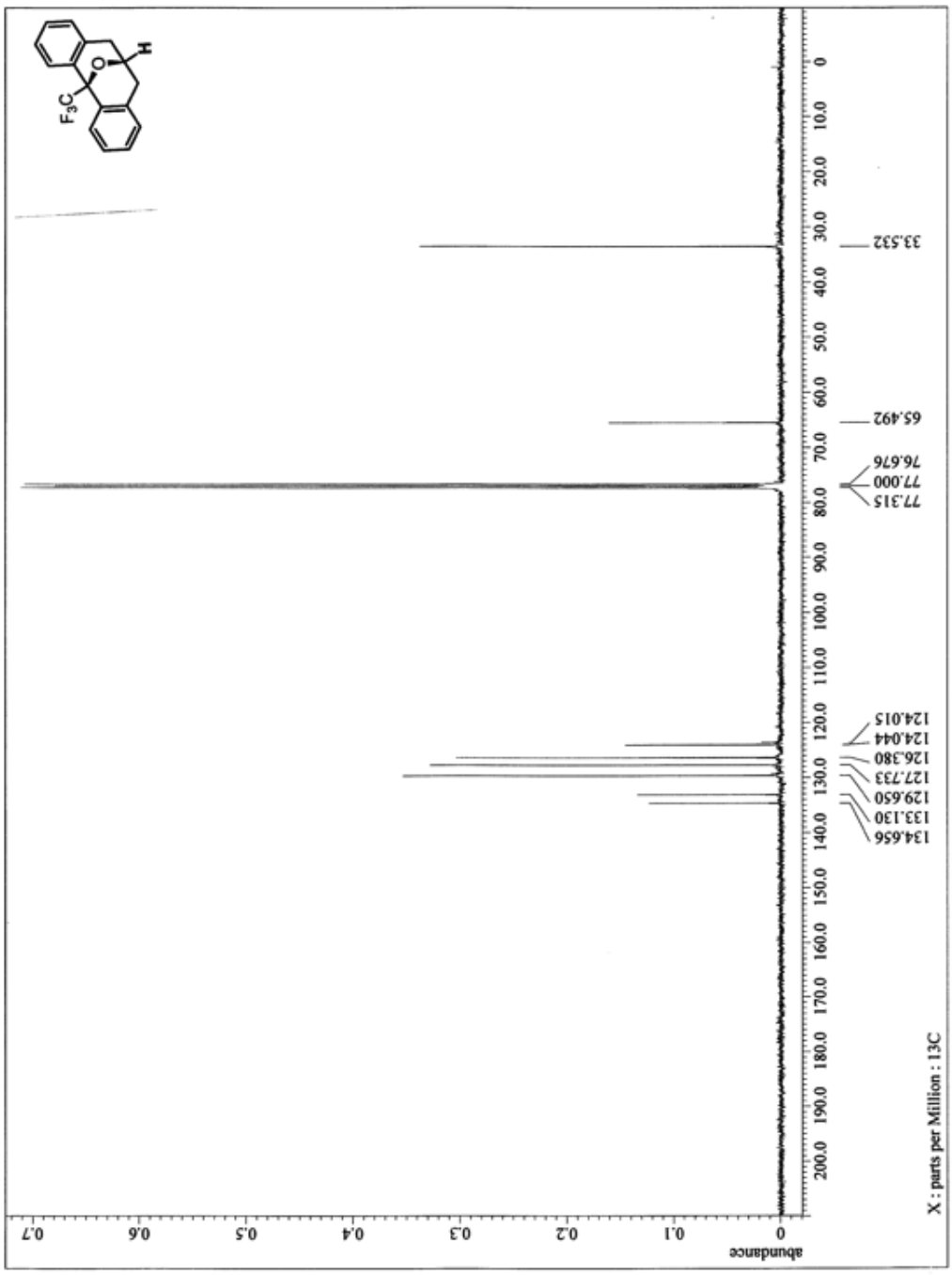
^{19}F NMR spectrum of **2a**.



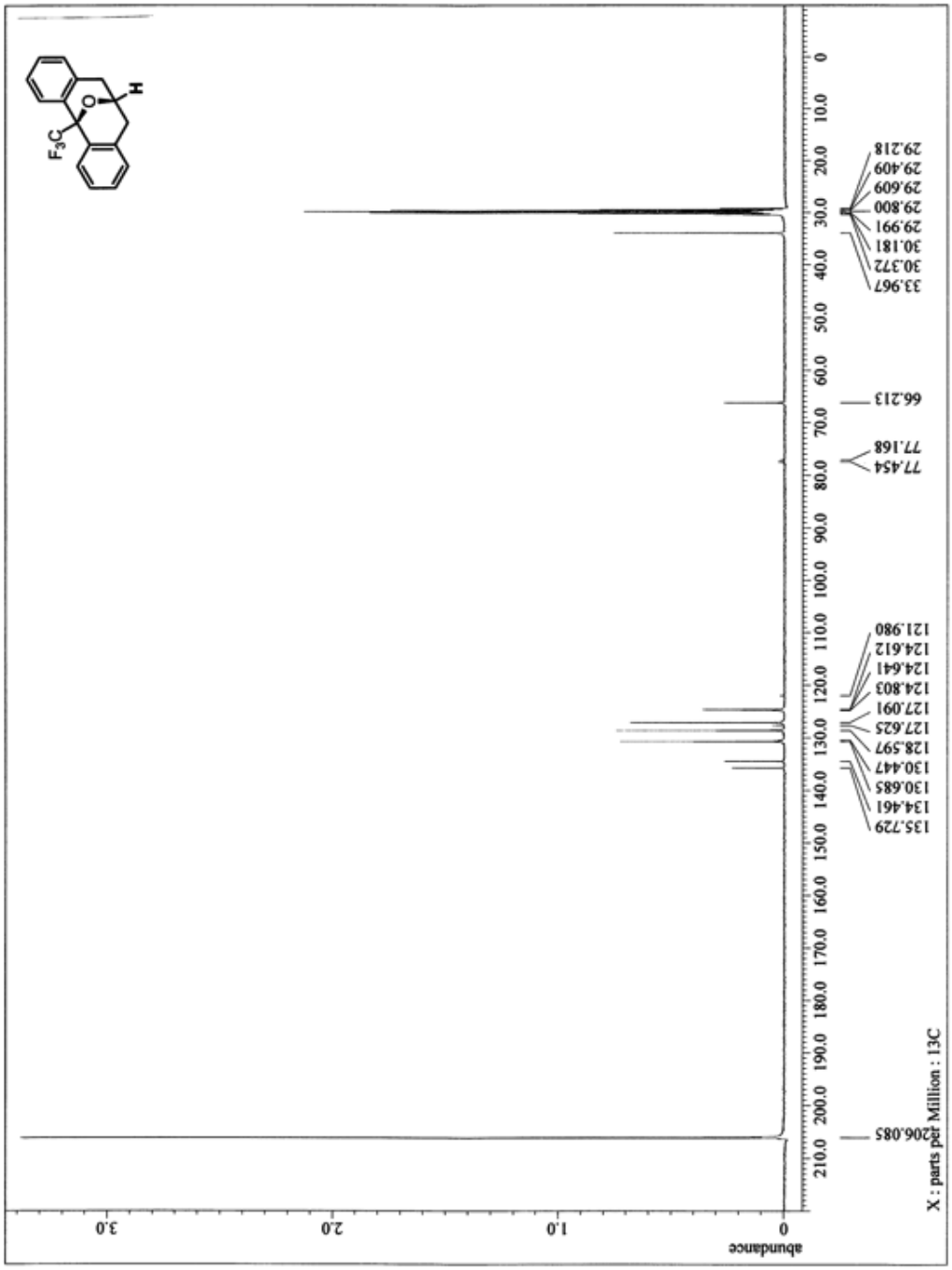
^{1}H NMR spectrum of **3a**.



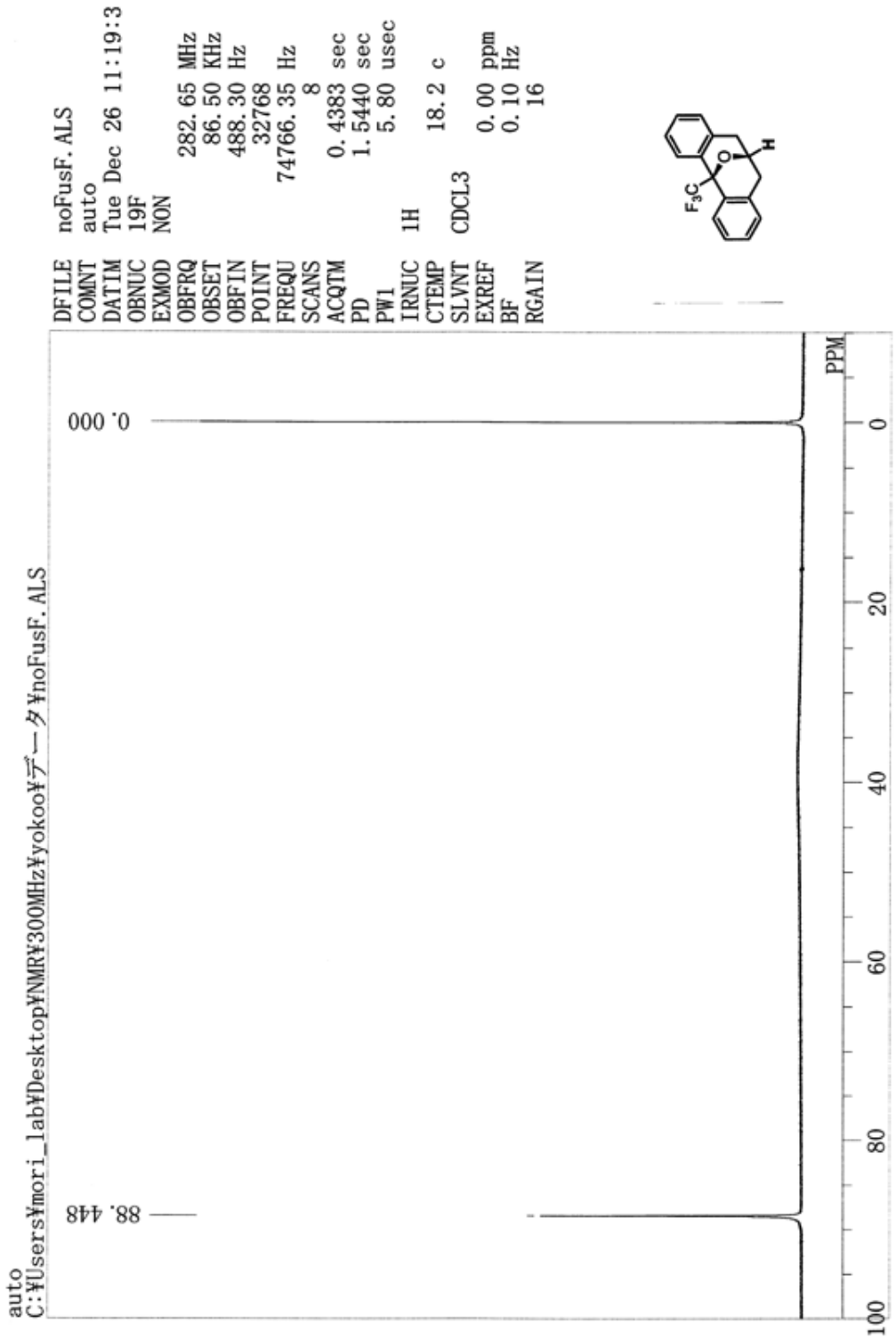
^{13}C NMR spectrum of **3a**.



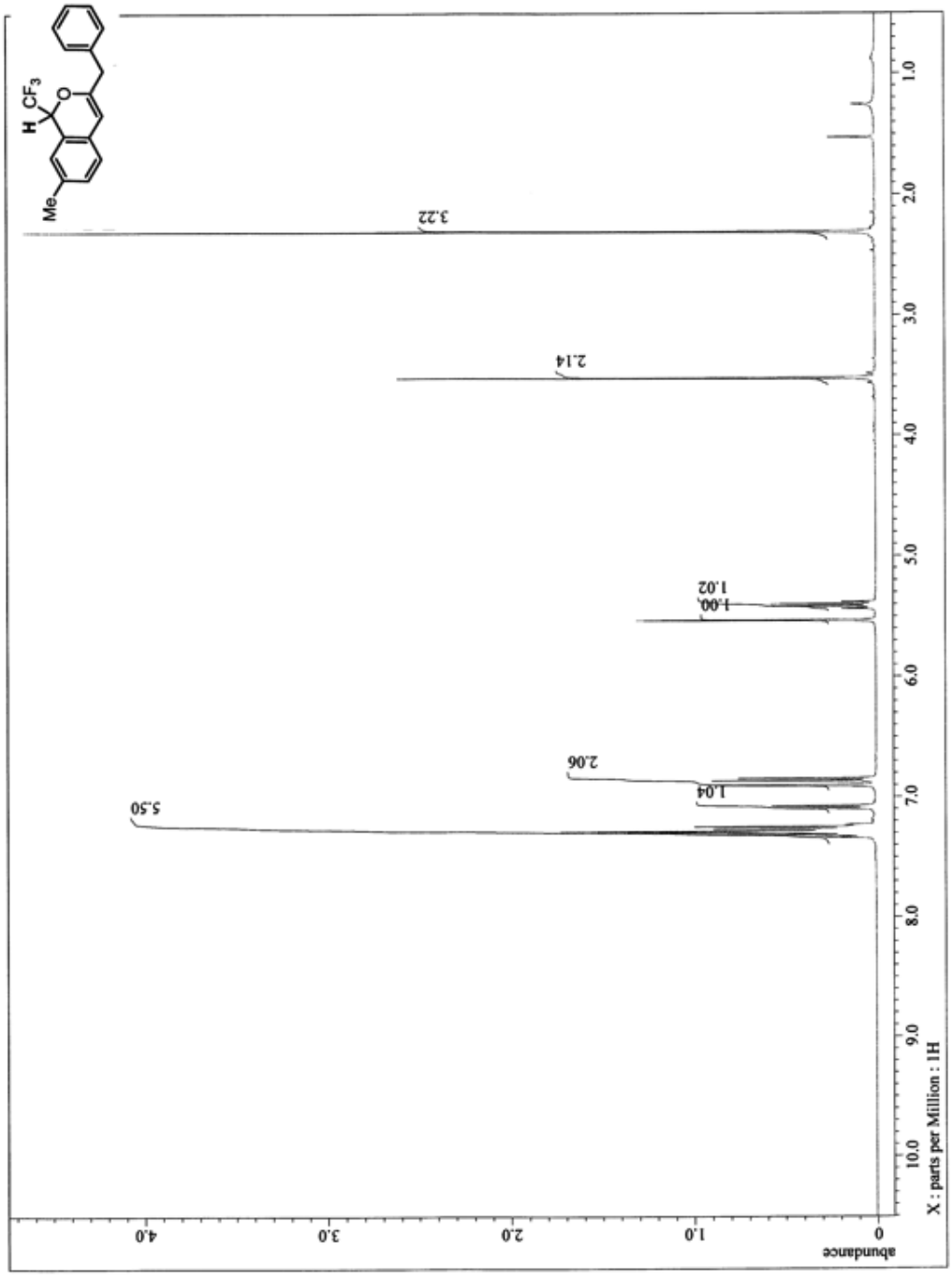
^{13}C NMR spectrum of **3a** (acetone-d6).



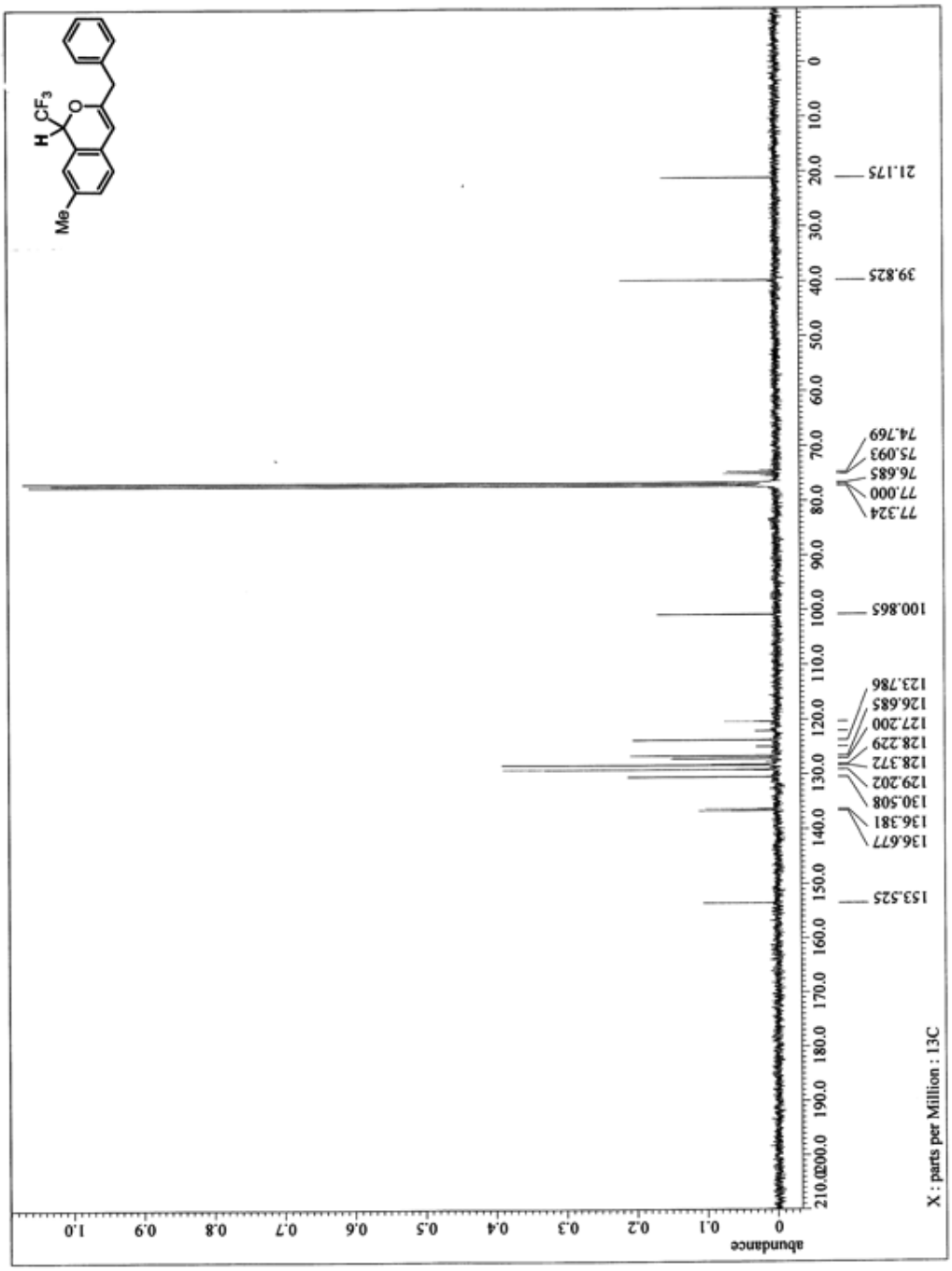
^{19}F NMR spectrum of **3a**.



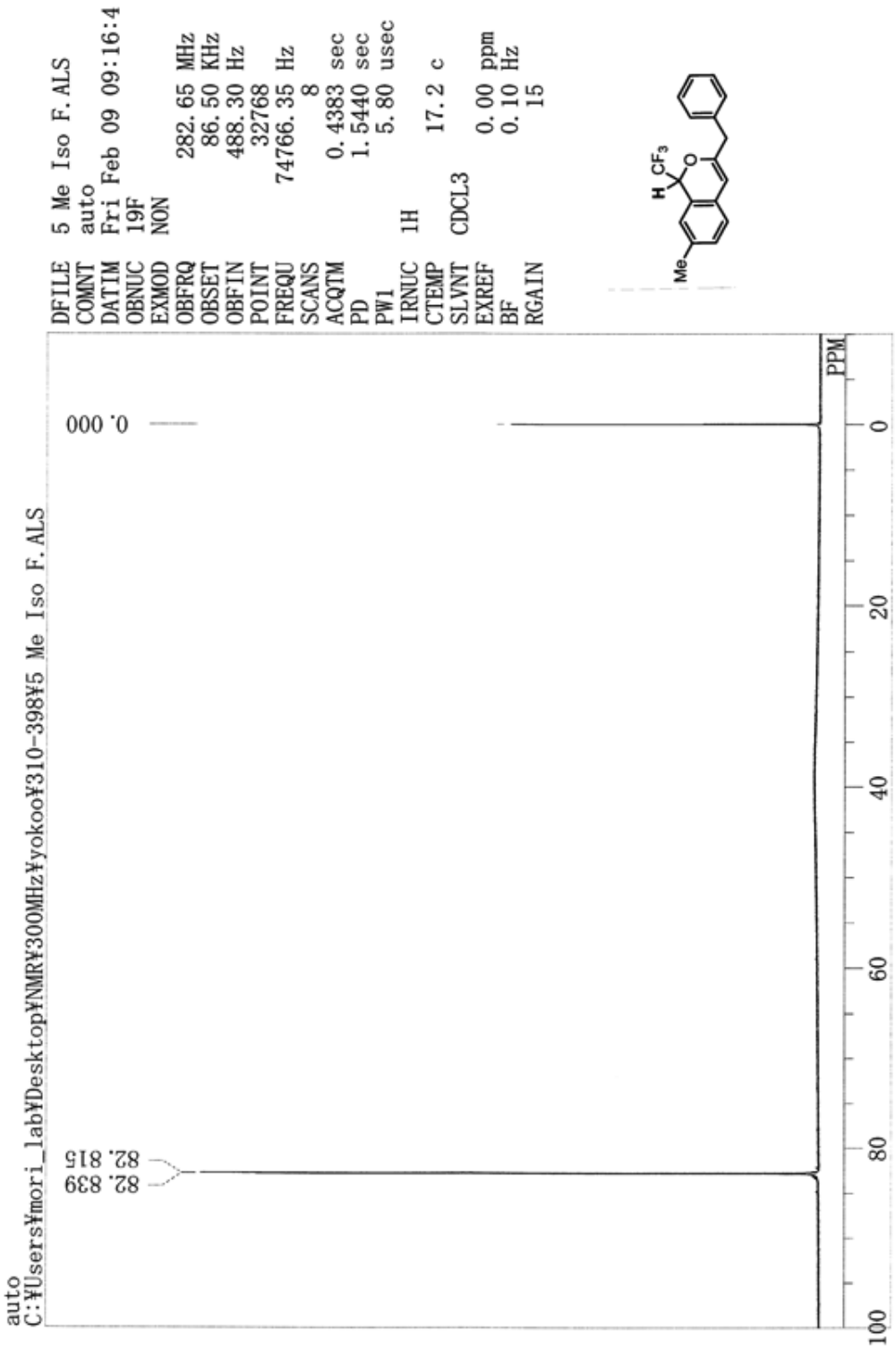
^{1}H NMR spectrum of **2b**.



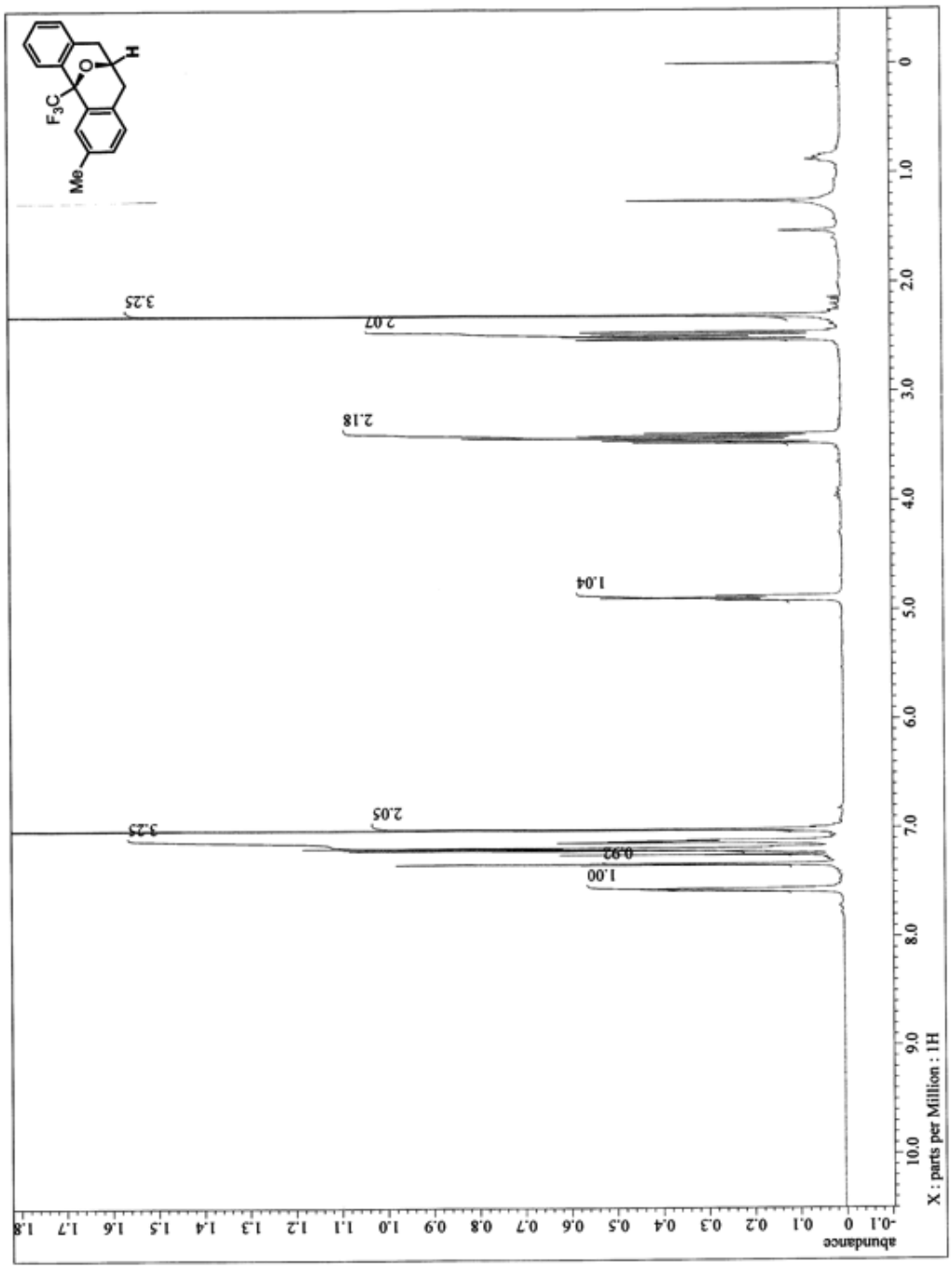
^{13}C NMR spectrum of **2b**.



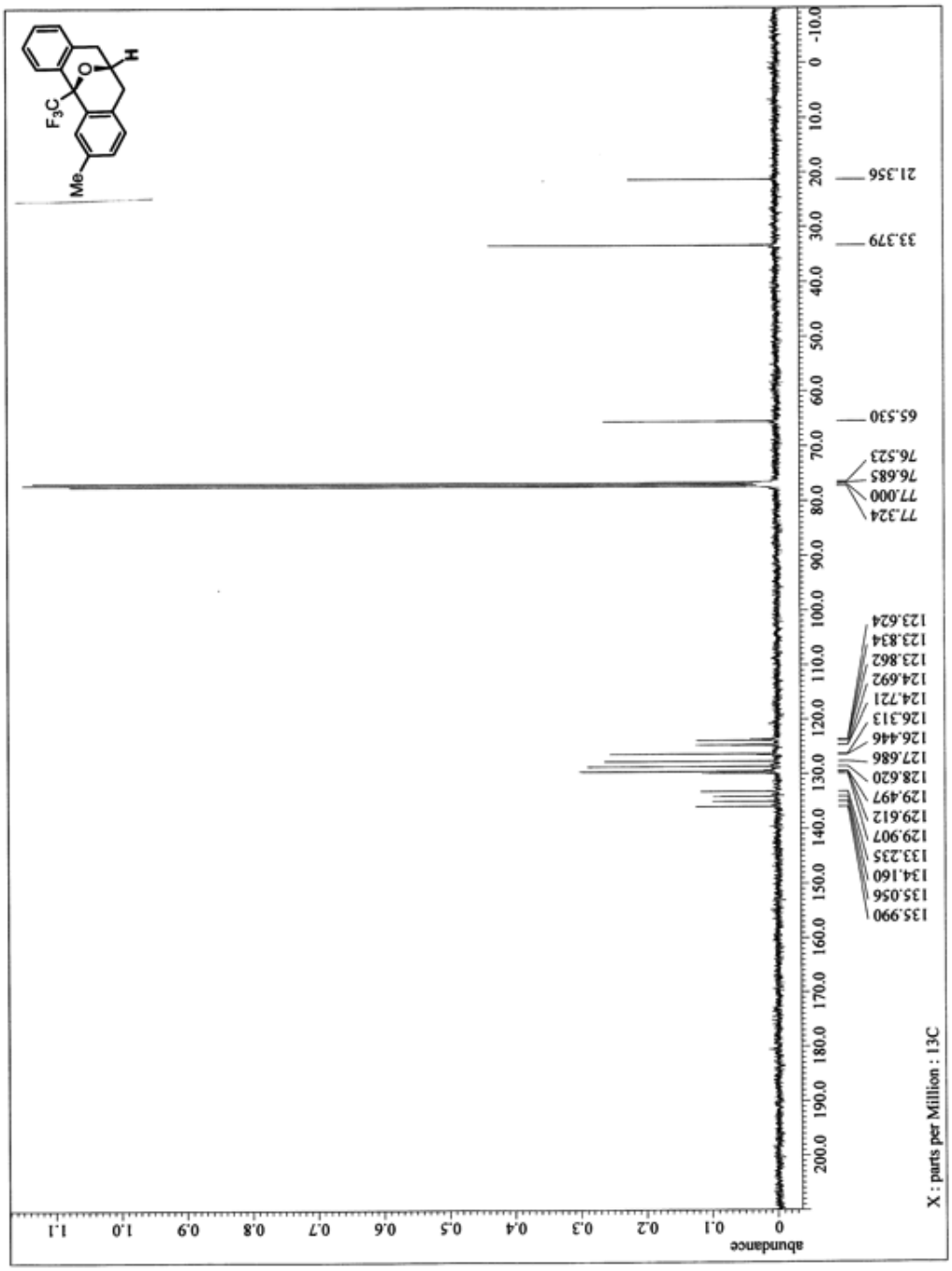
^{19}F NMR spectrum of **2b**.



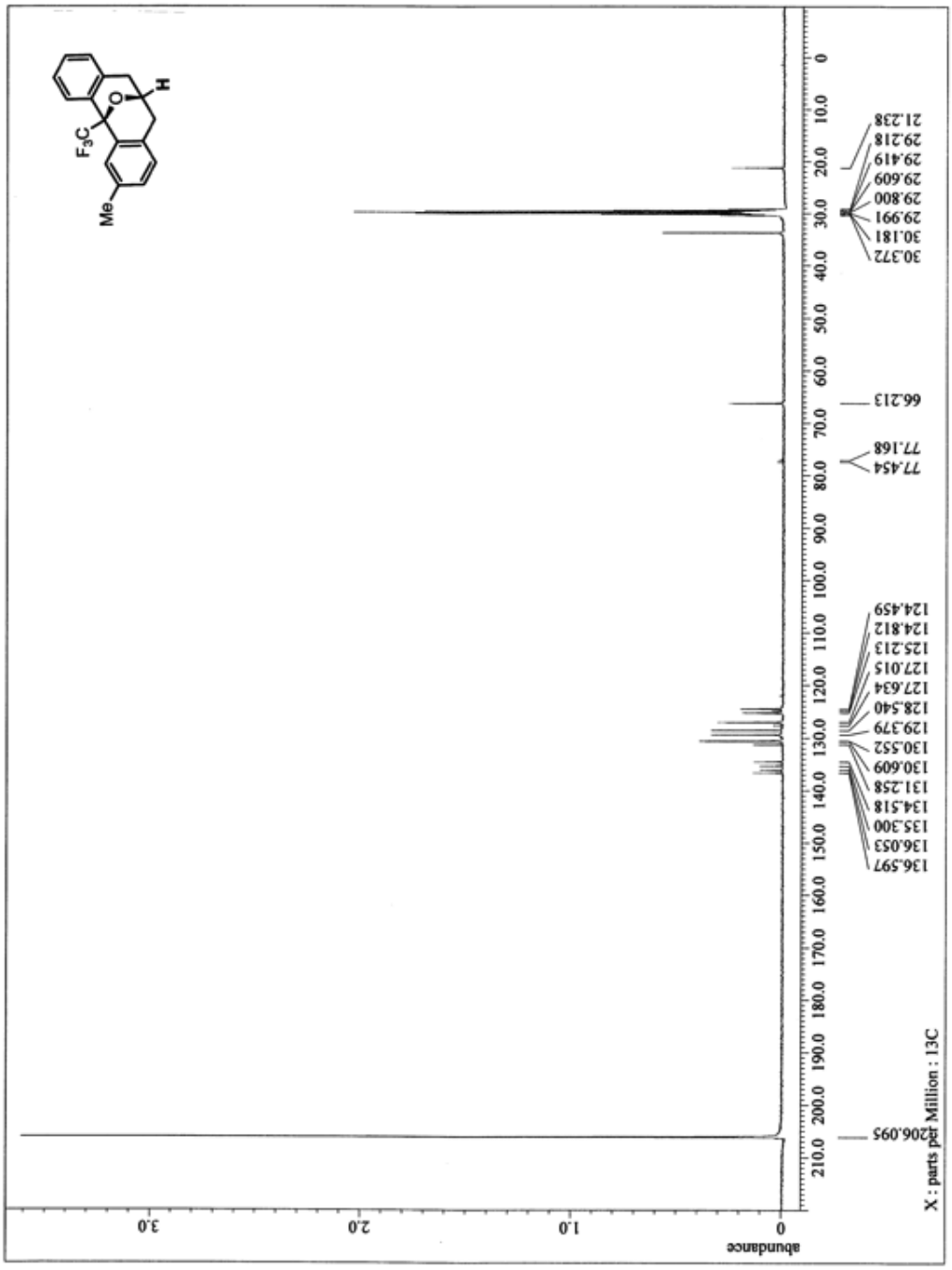
^{1}H NMR spectrum of **3b**.



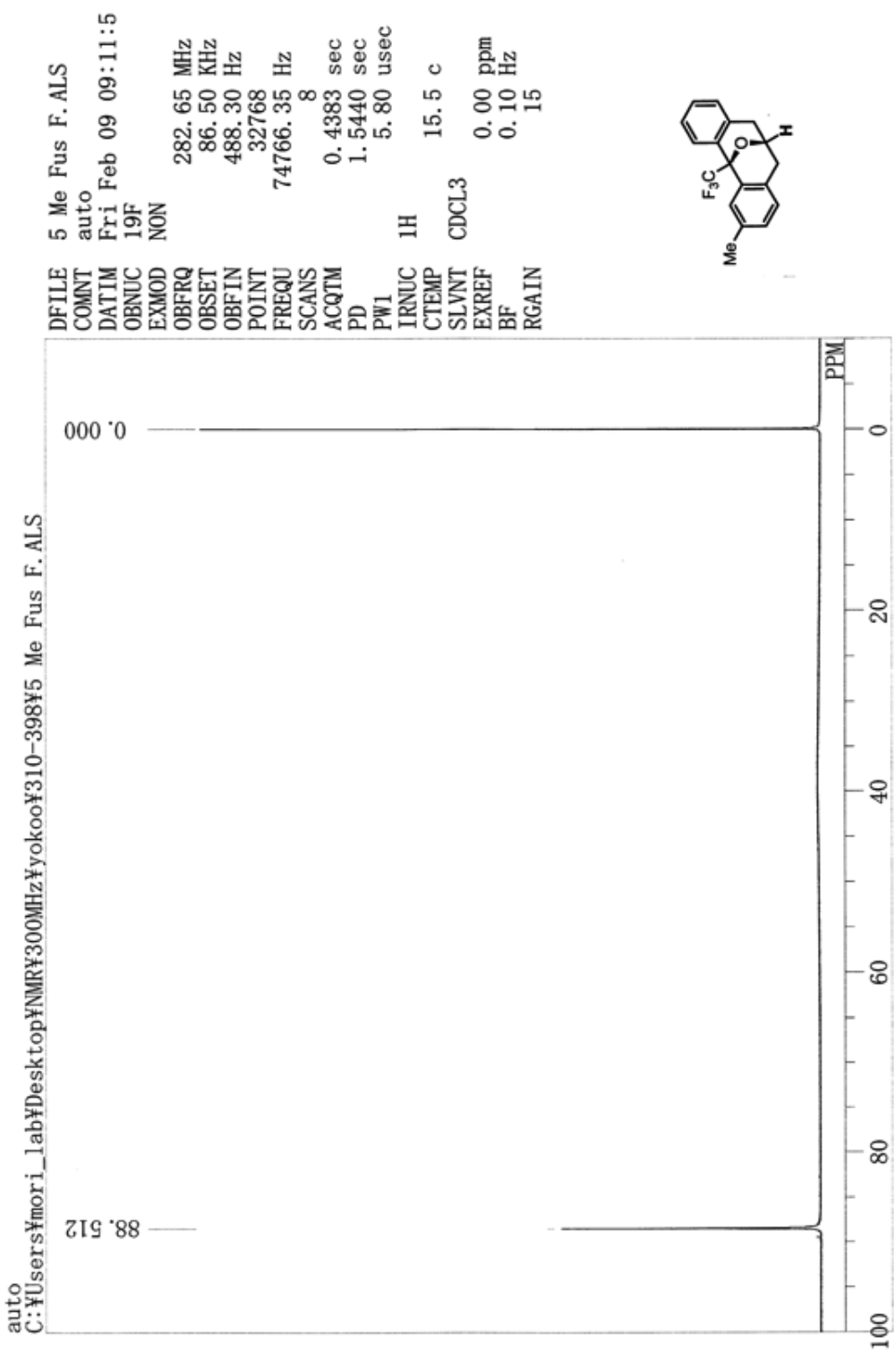
^{13}C NMR spectrum of **3b**.



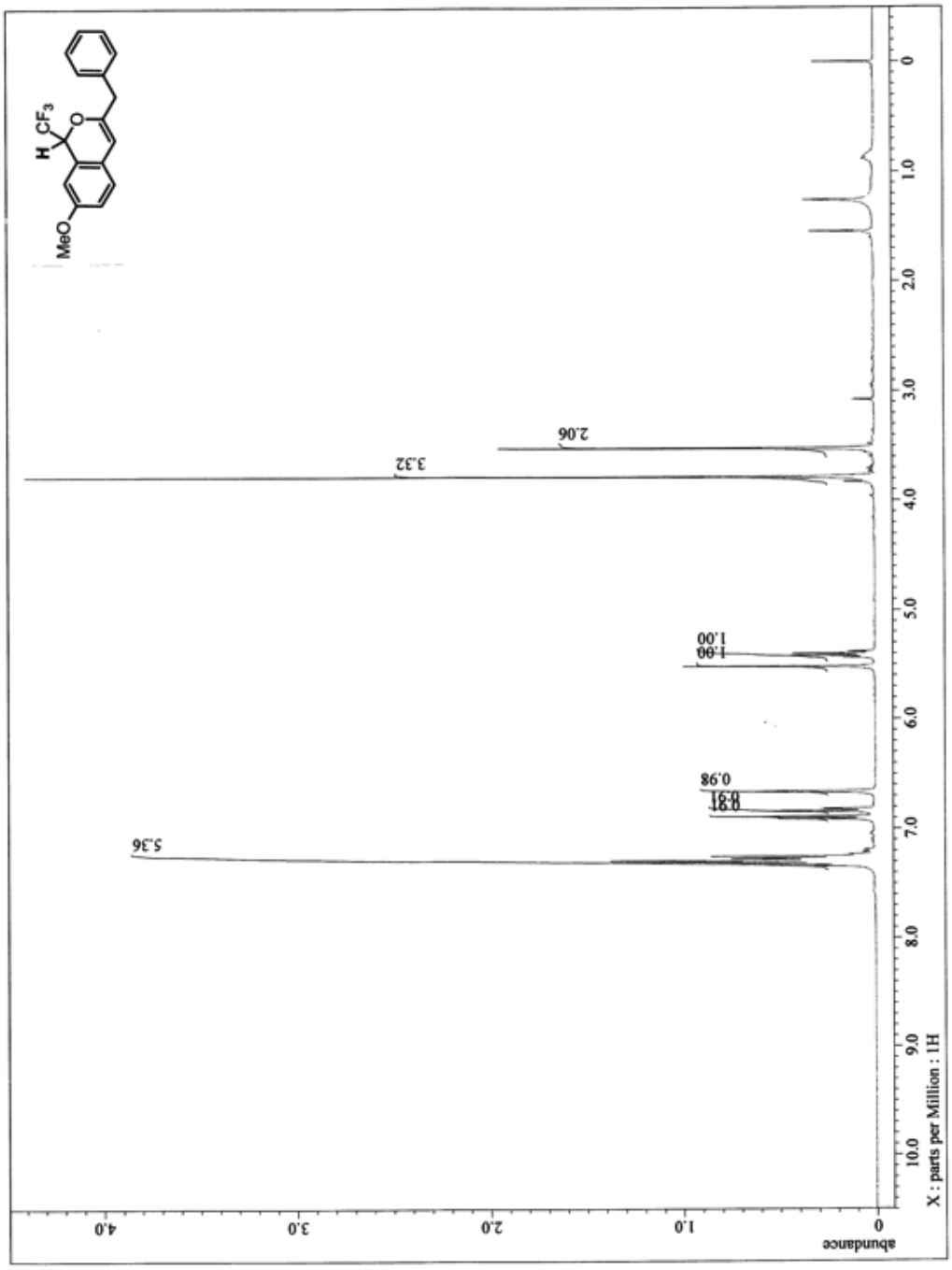
^{13}C NMR spectrum of **3b** (acetone-d6).



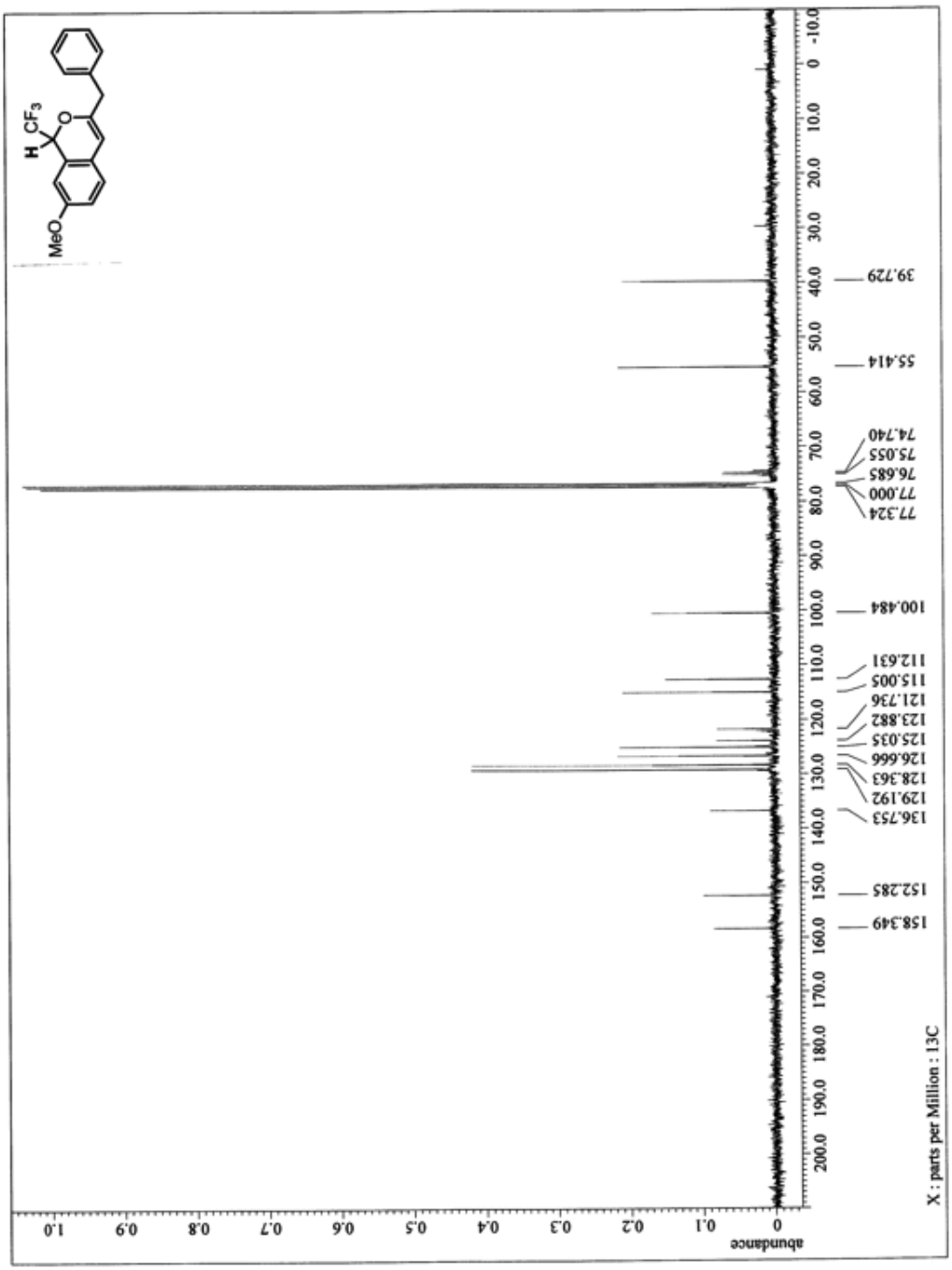
^{19}F NMR spectrum of **3b**.



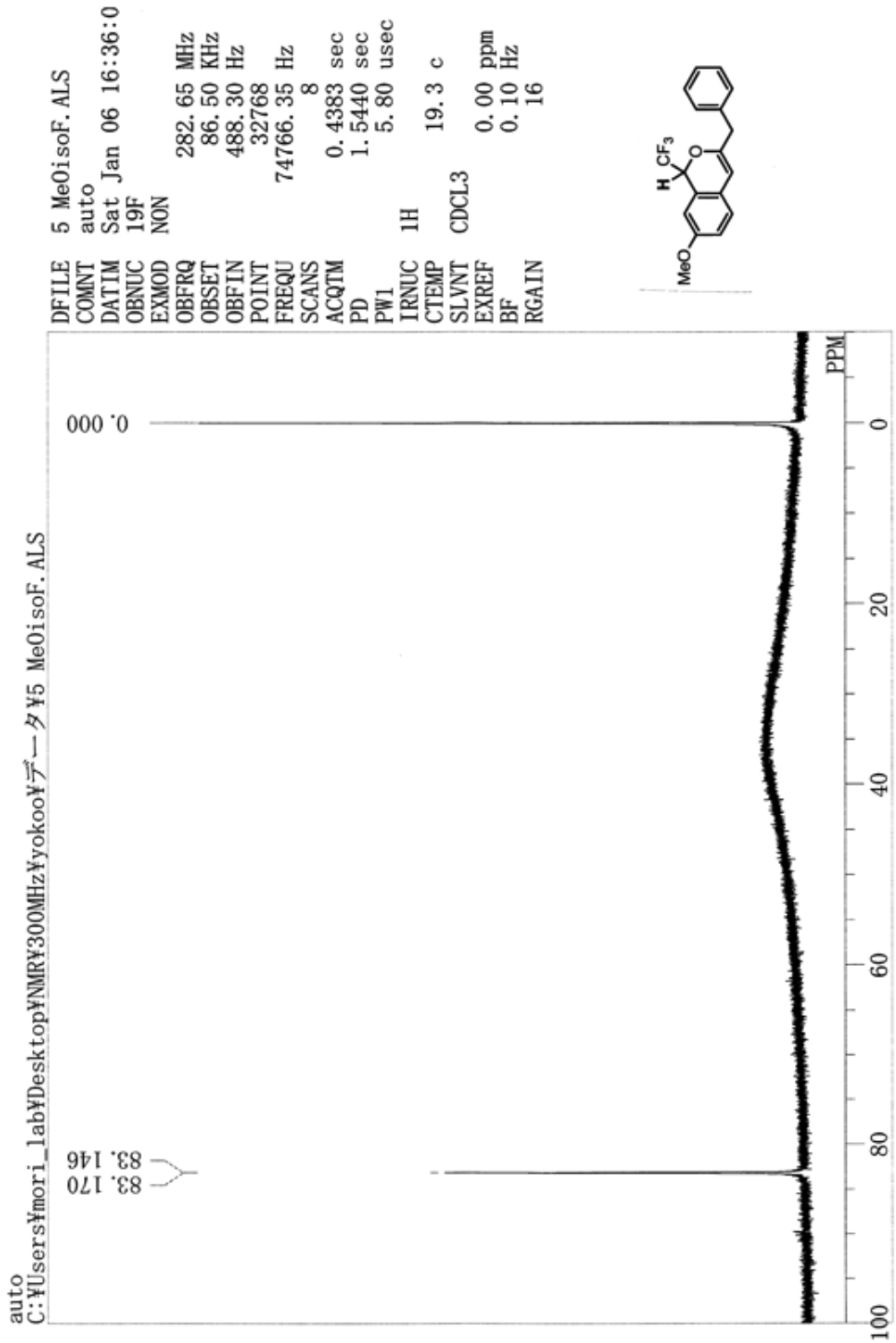
^{1}H NMR spectrum of **2c**.



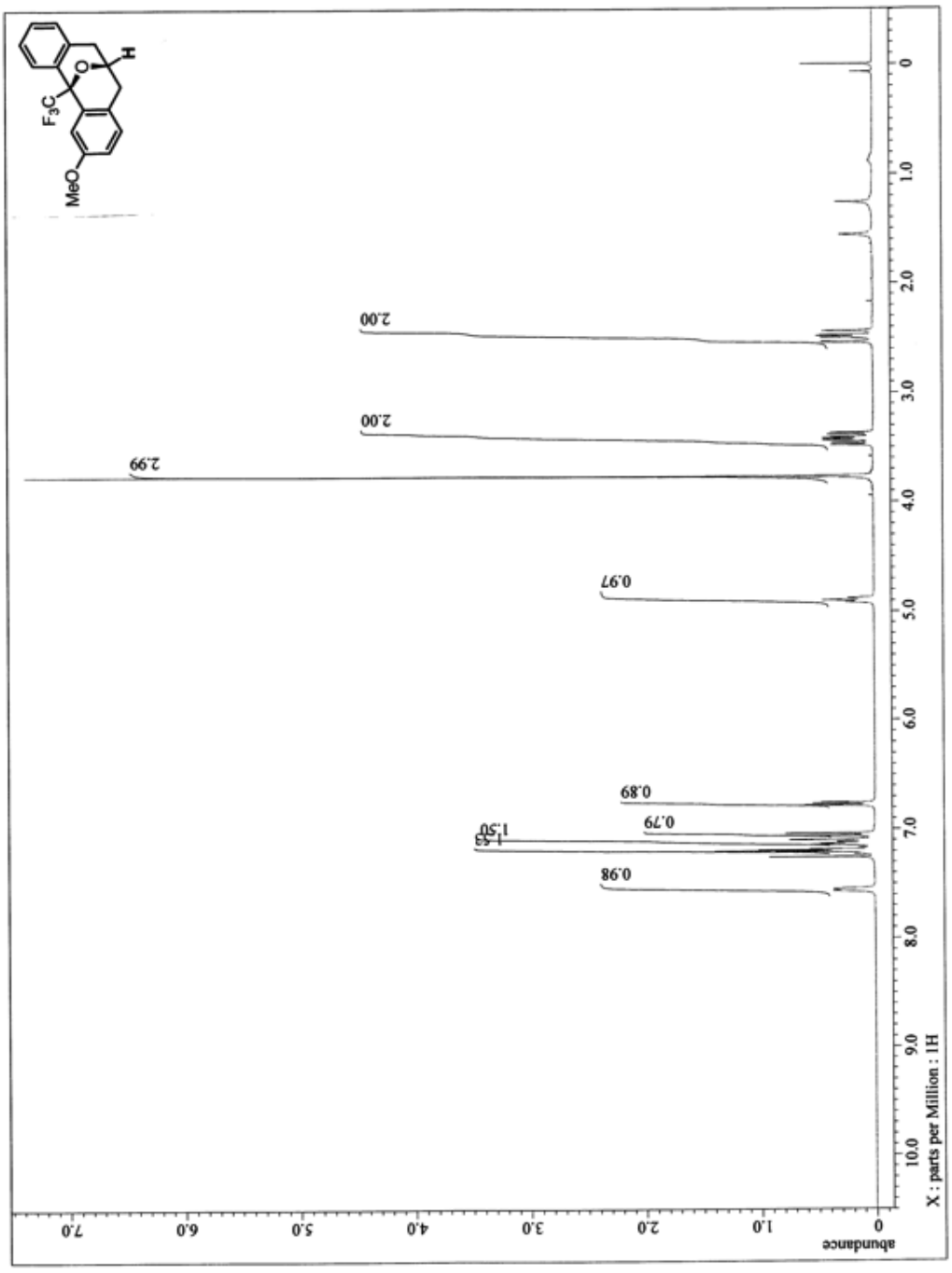
^{13}C NMR spectrum of **2c**.



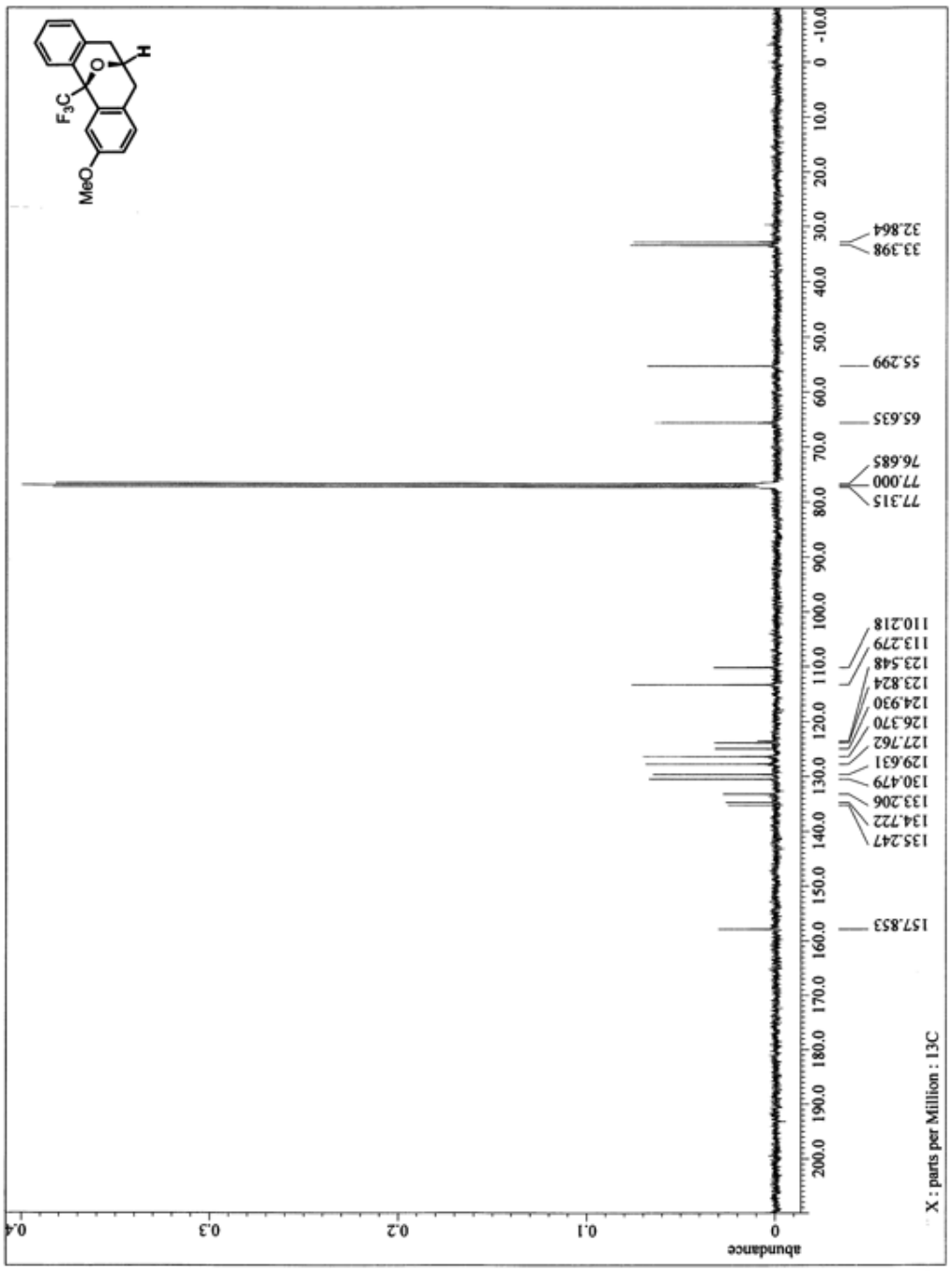
^{19}F NMR spectrum of **2c**.



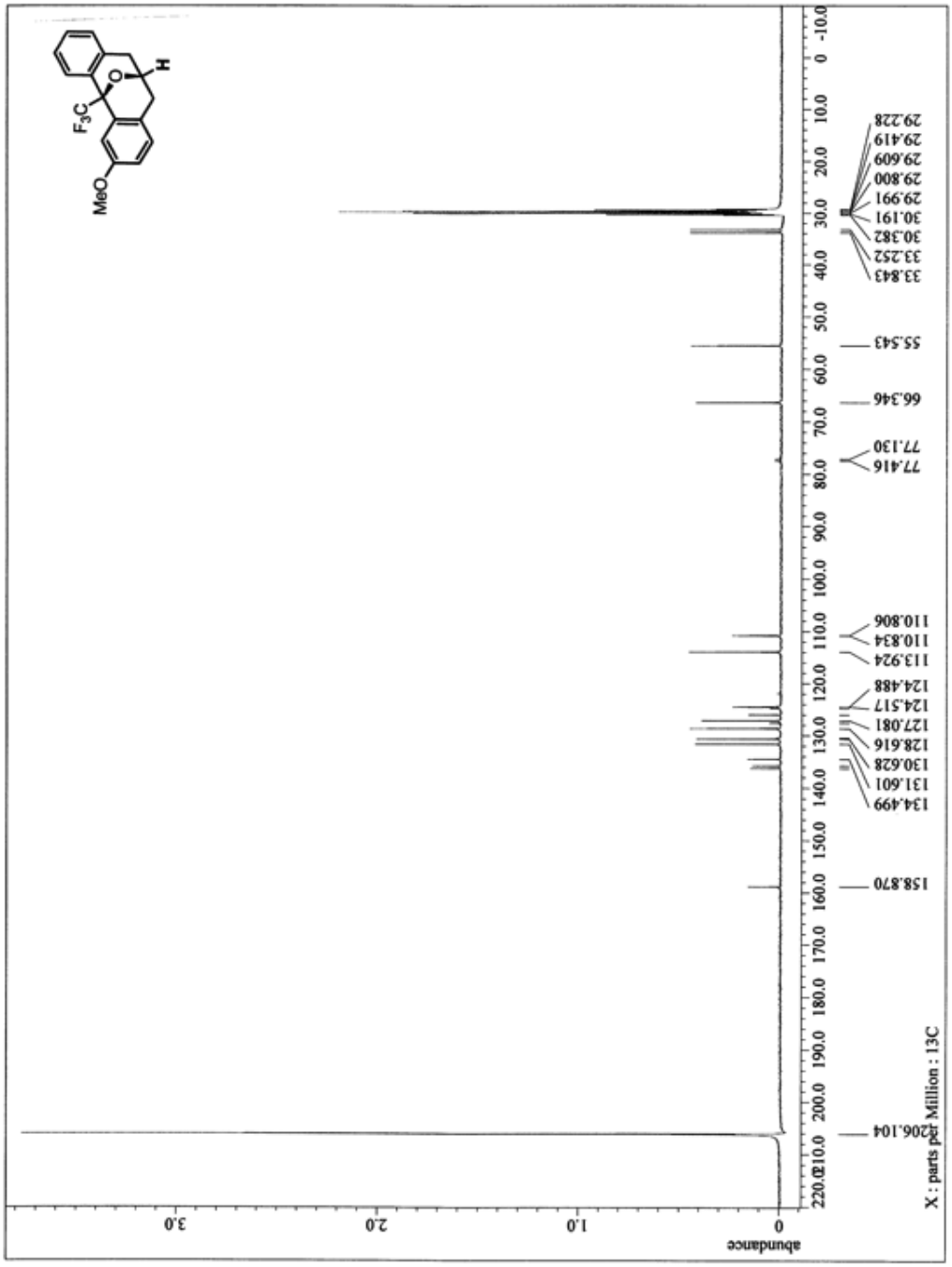
^{1}H NMR spectrum of **3c**.



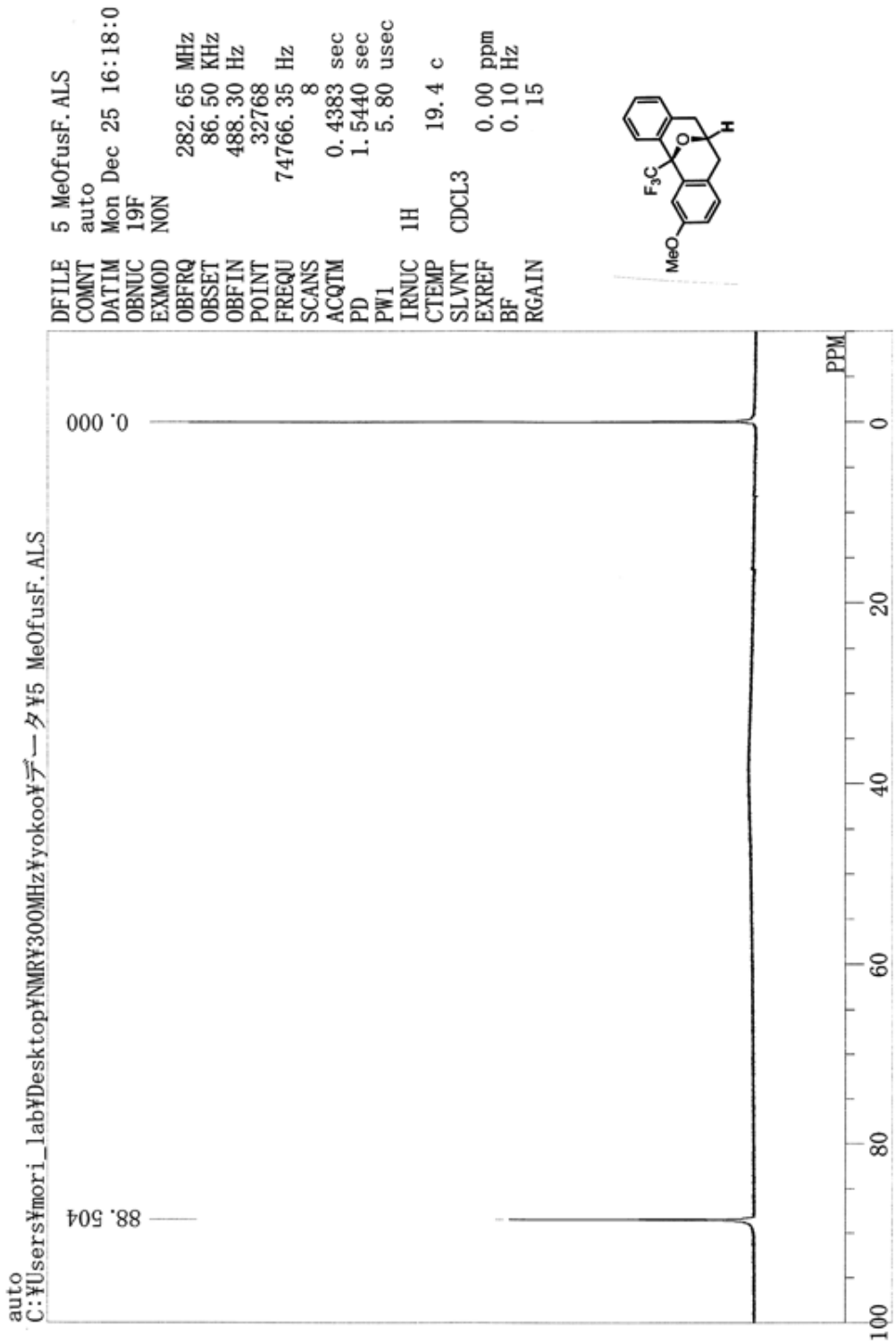
^{13}C NMR spectrum of **3c**.



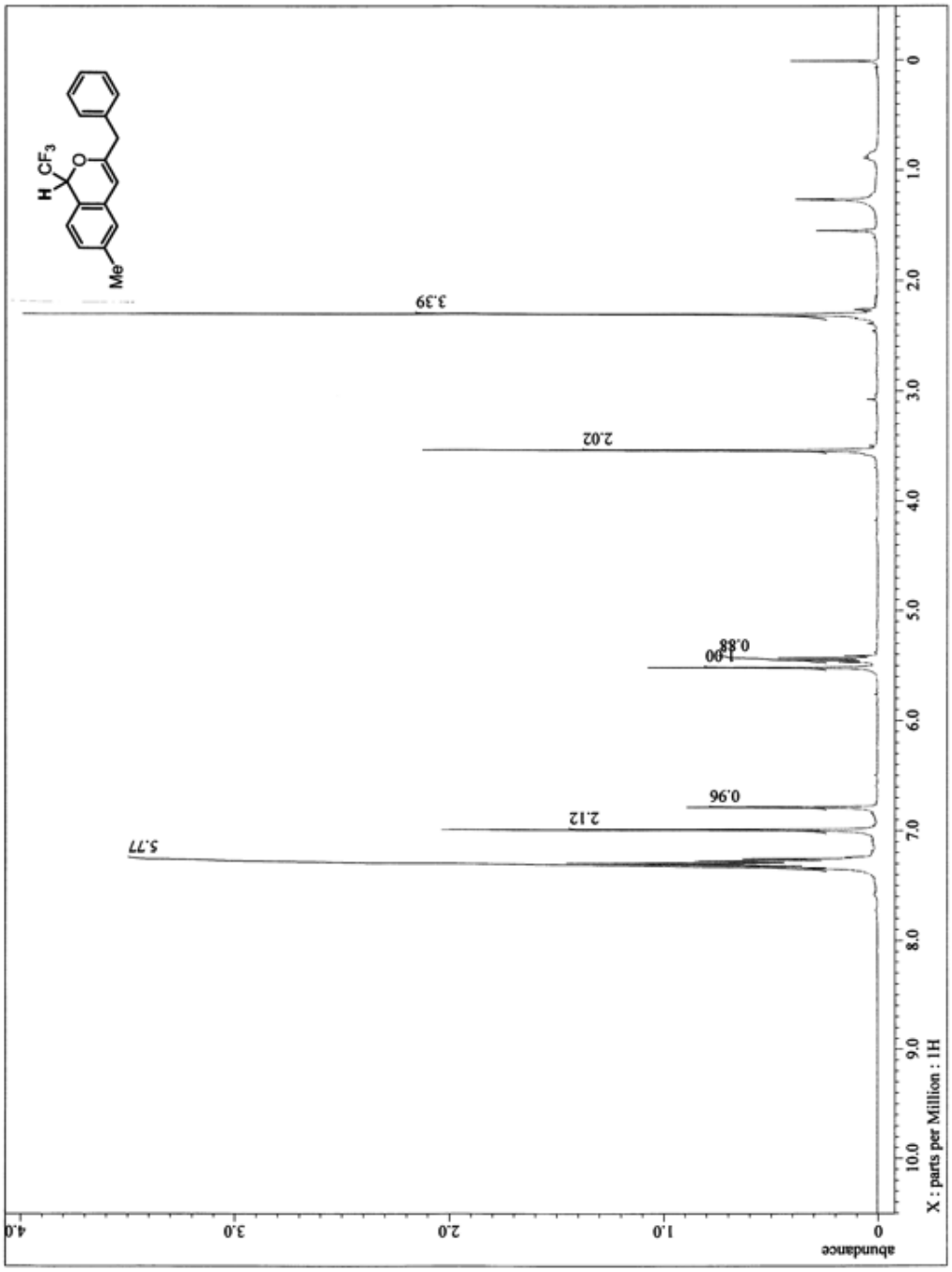
^{13}C NMR spectrum of **3c** (acetone-d6).



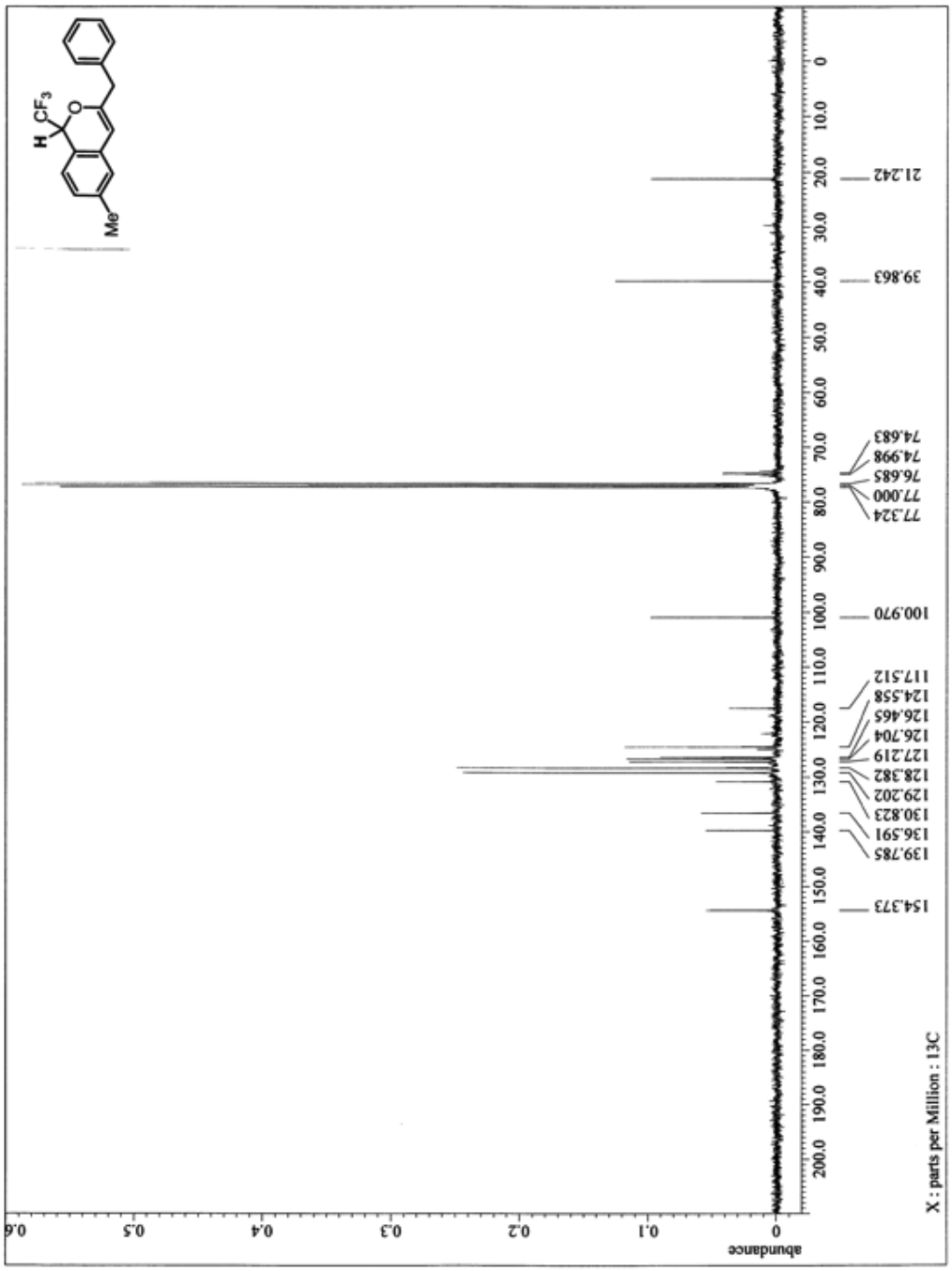
^{19}F NMR spectrum of **3c**.



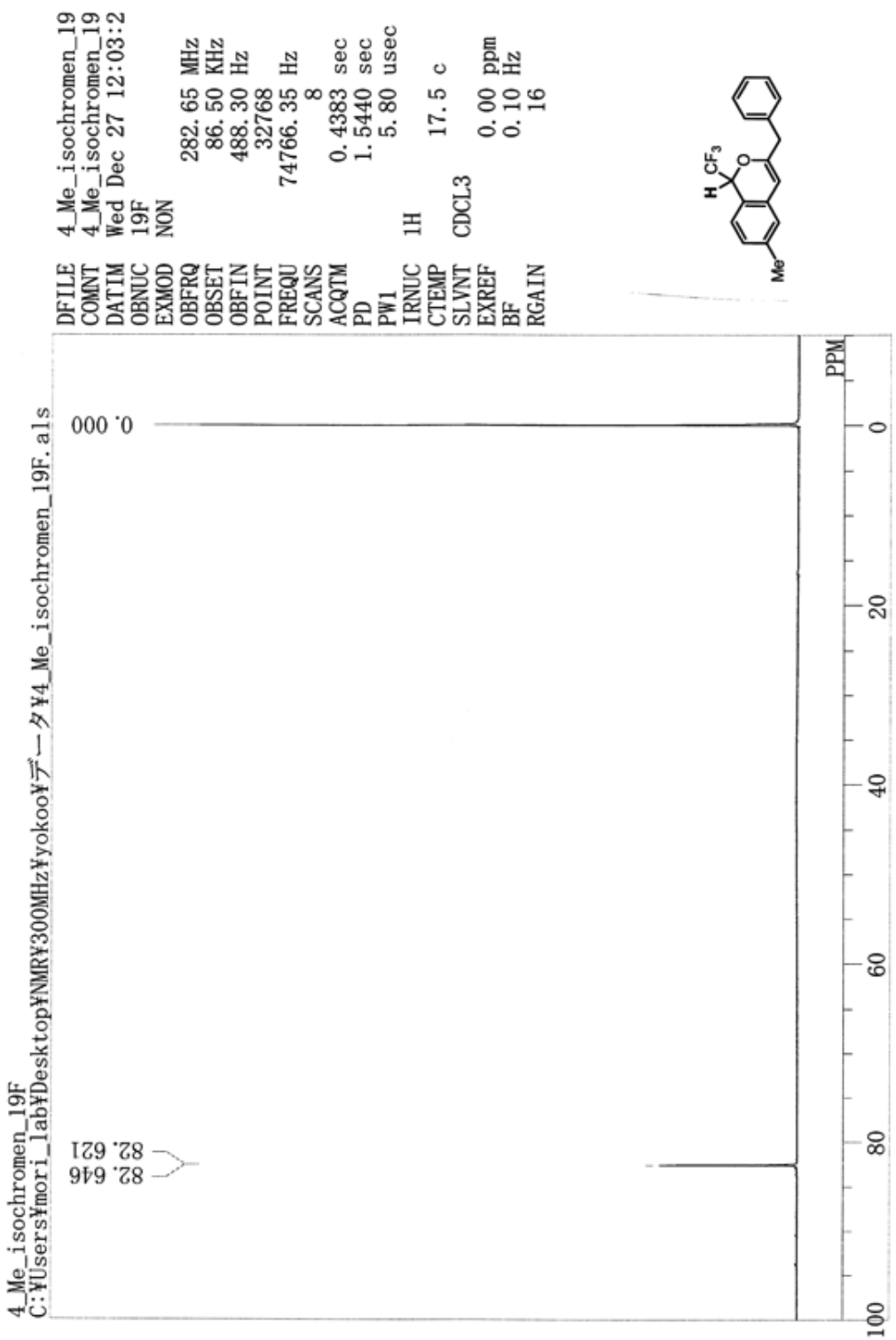
^{1}H NMR spectrum of **2d**.



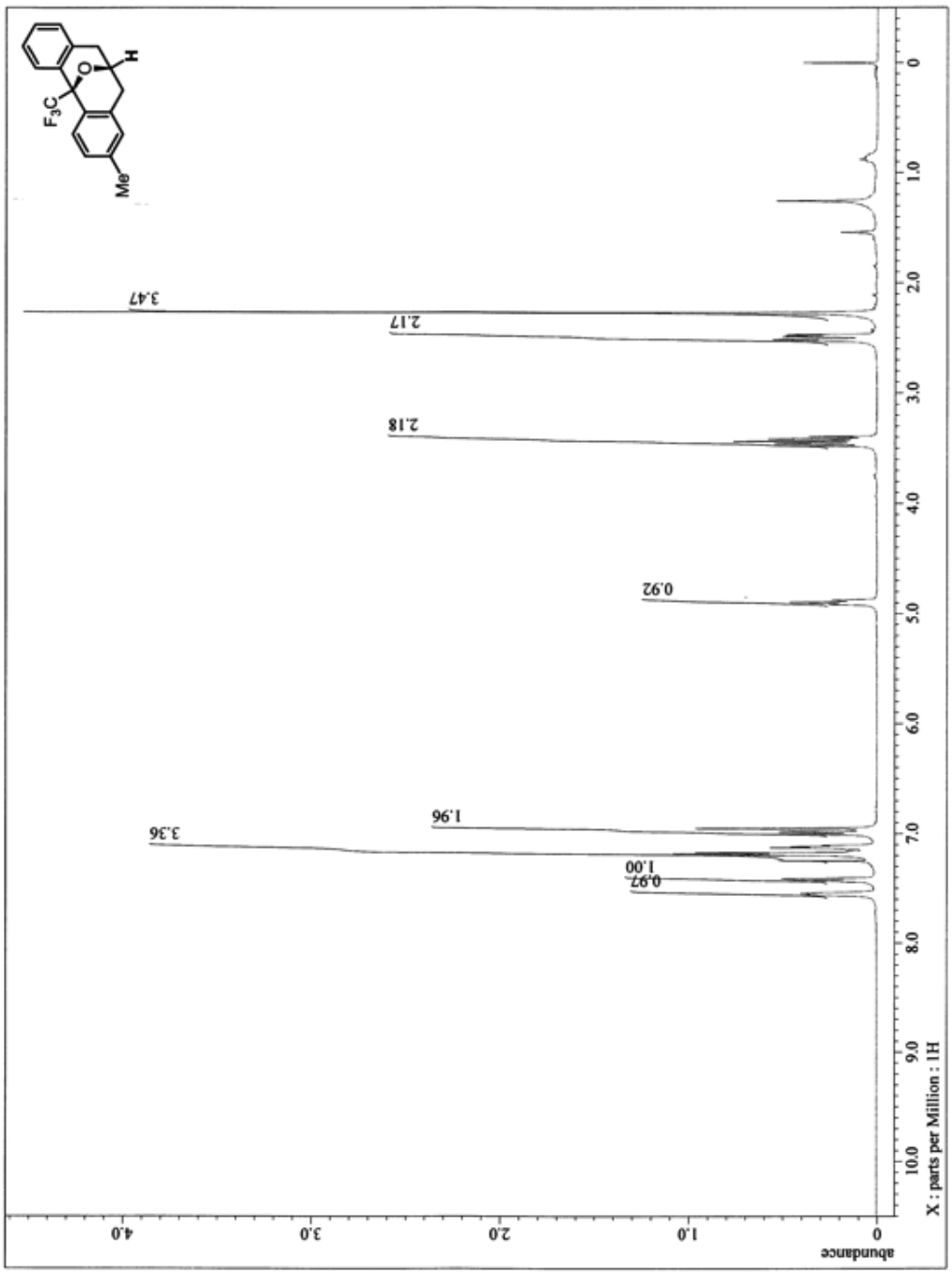
^{13}C NMR spectrum of **2d**.



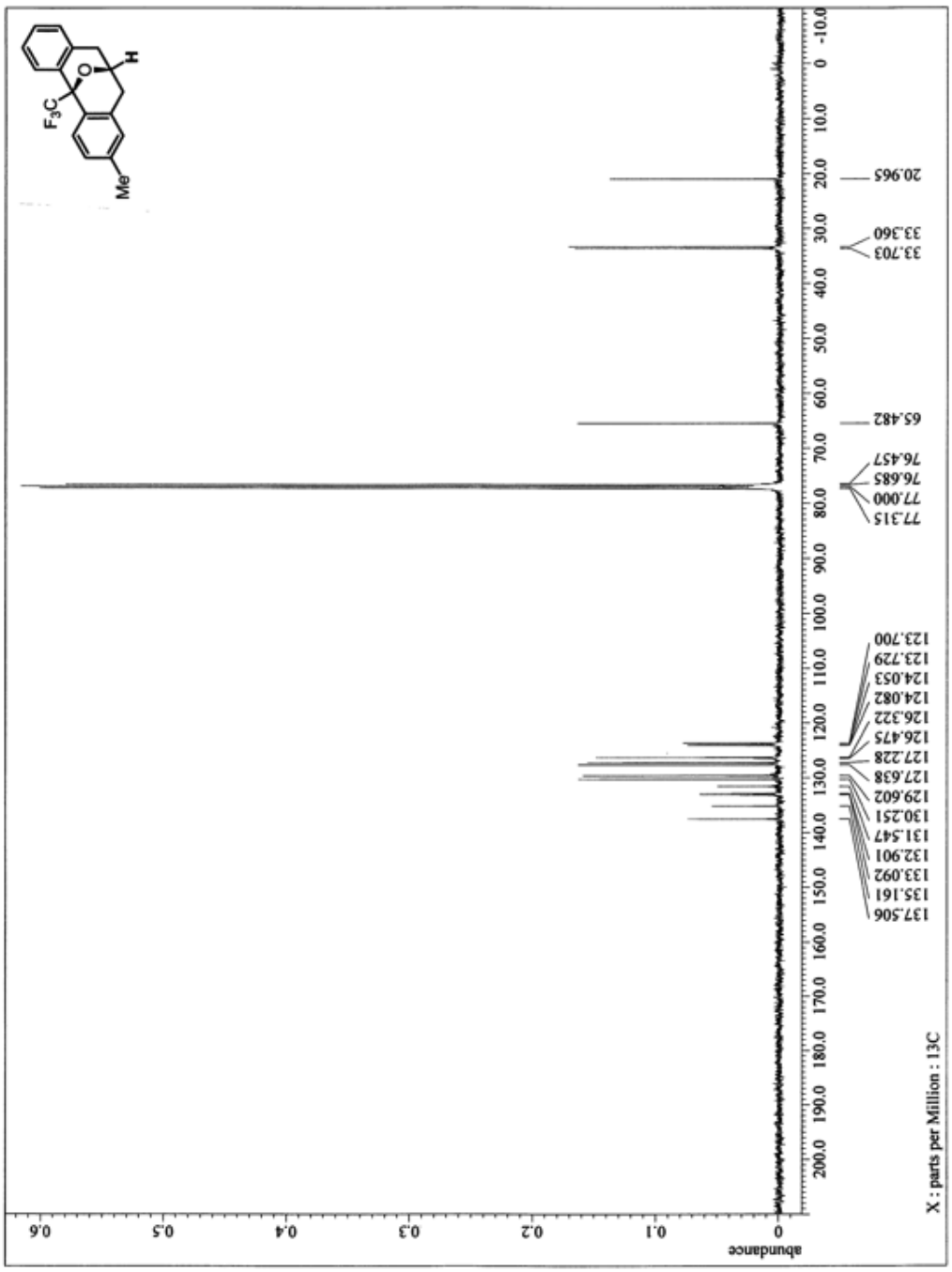
^{19}F NMR spectrum of **2d**.



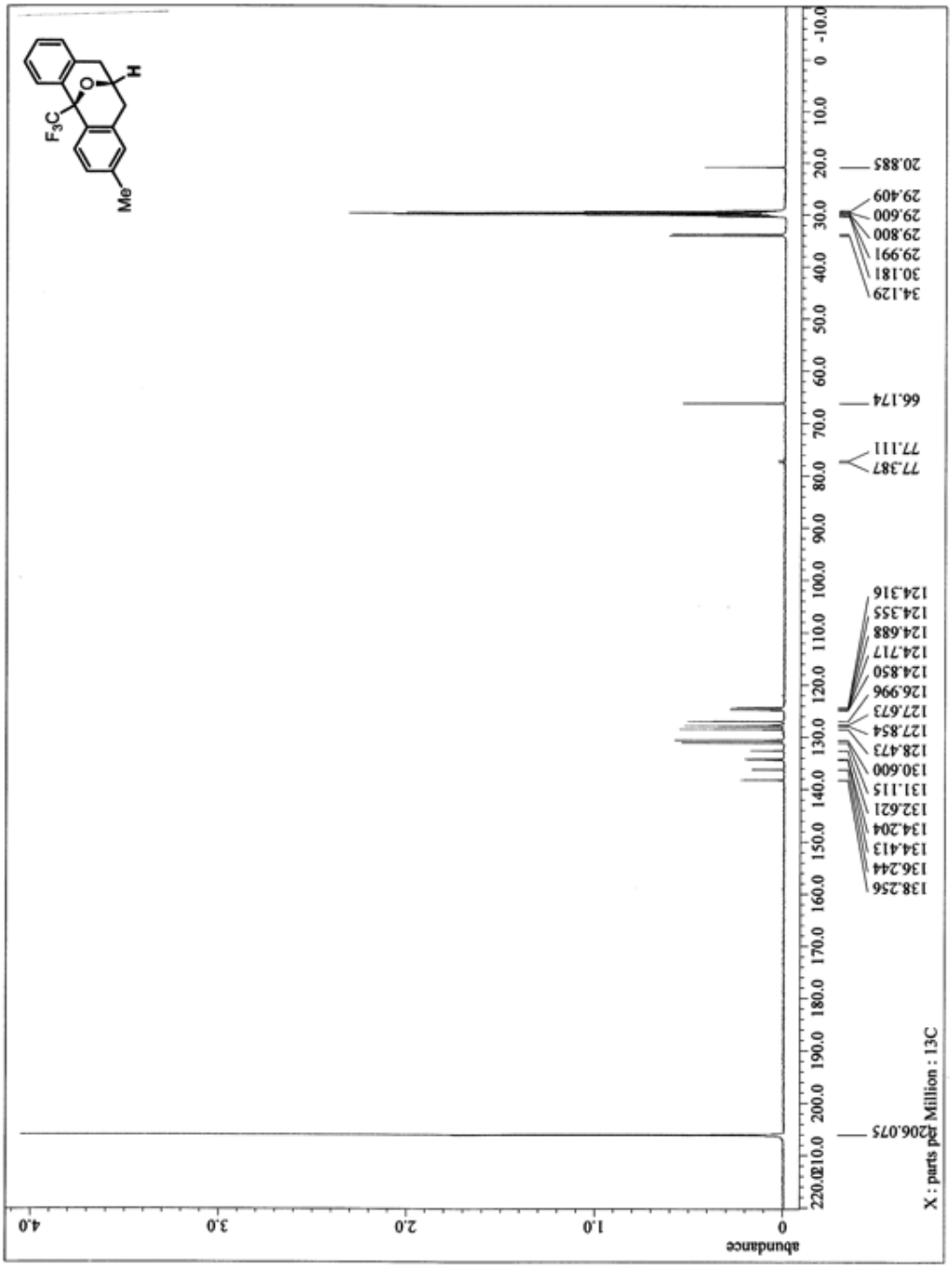
^{1}H NMR spectrum of **3d**.



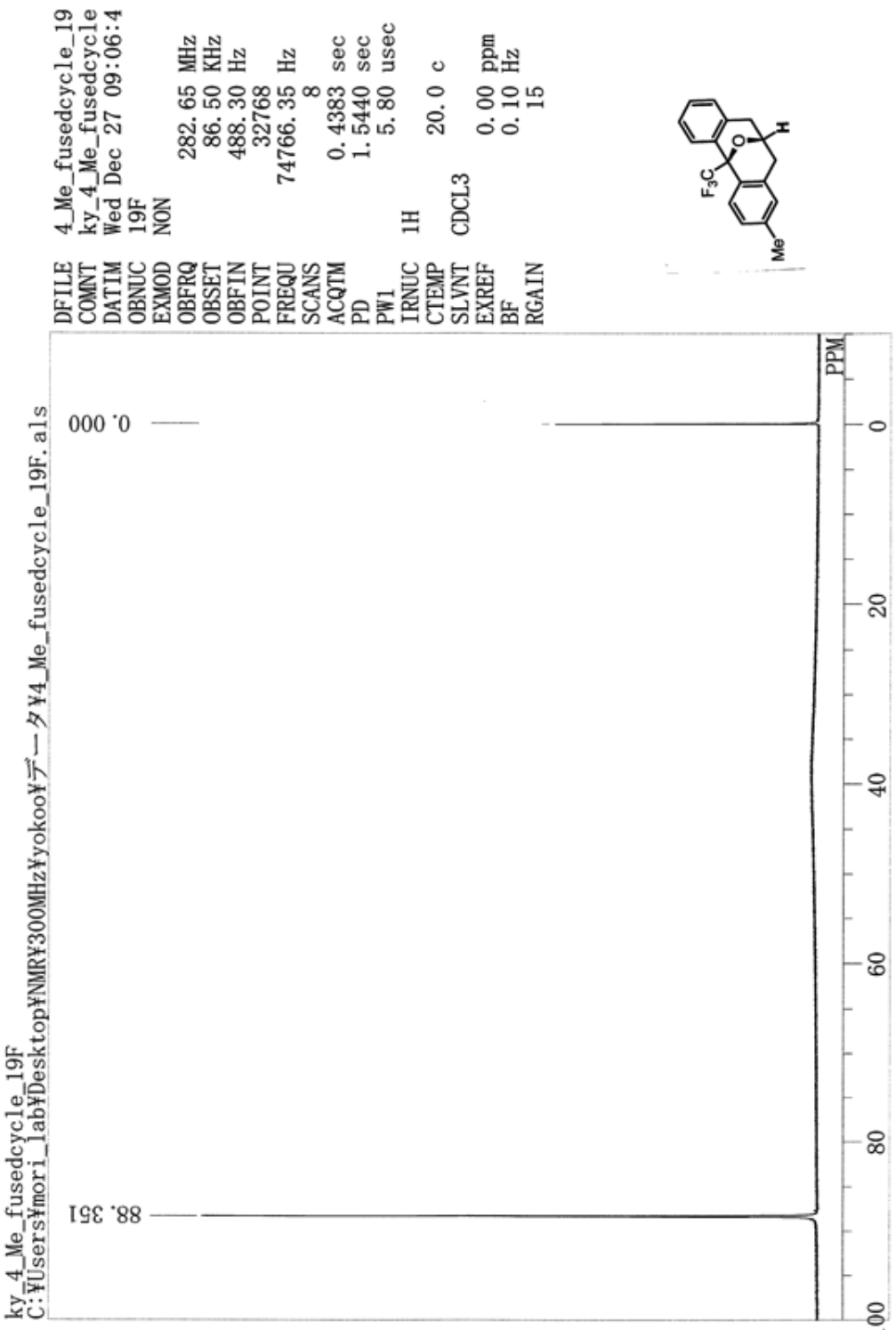
^{13}C NMR spectrum of **3d**.



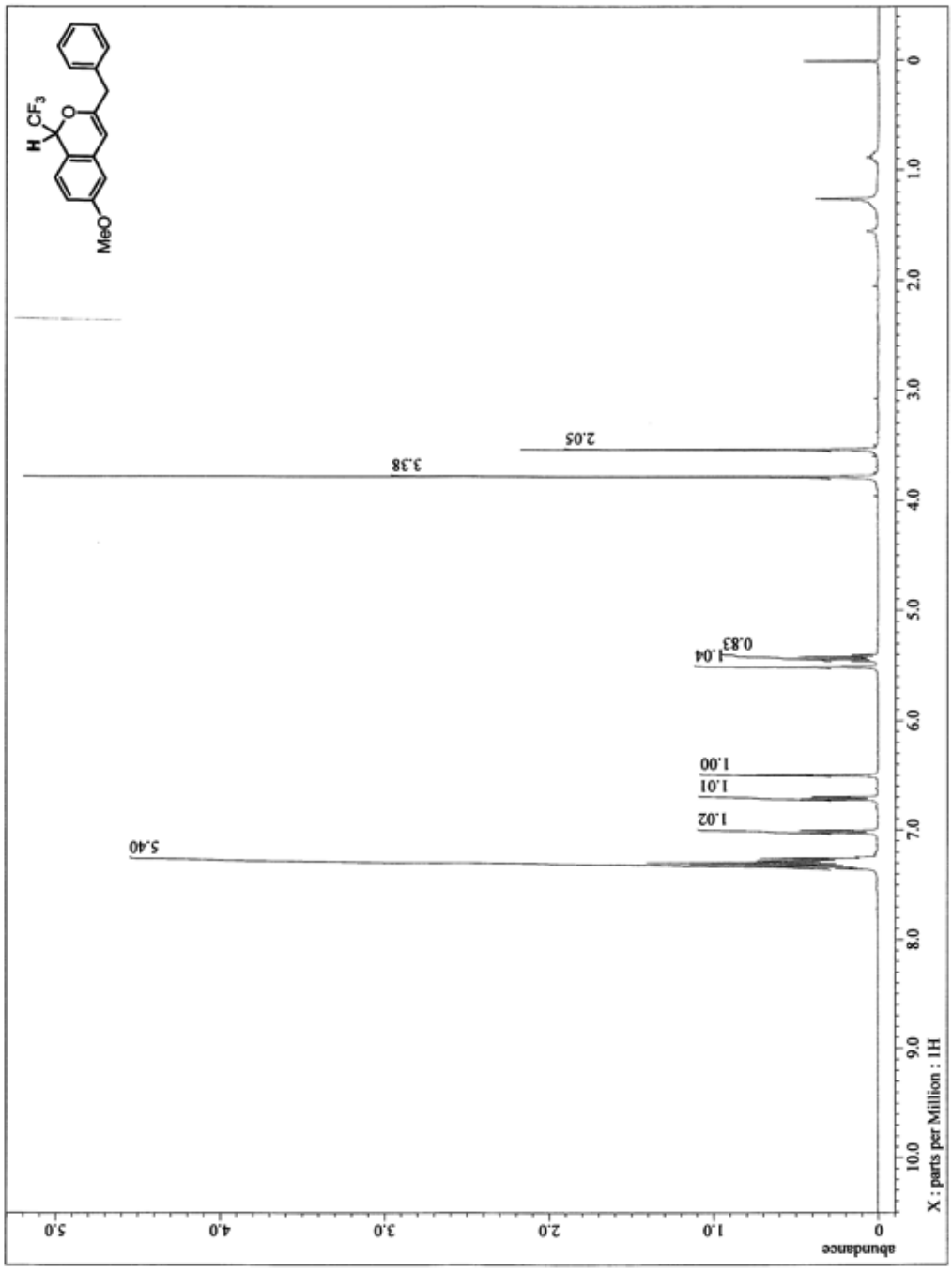
^{13}C NMR spectrum of **3d** (acetone-d6).



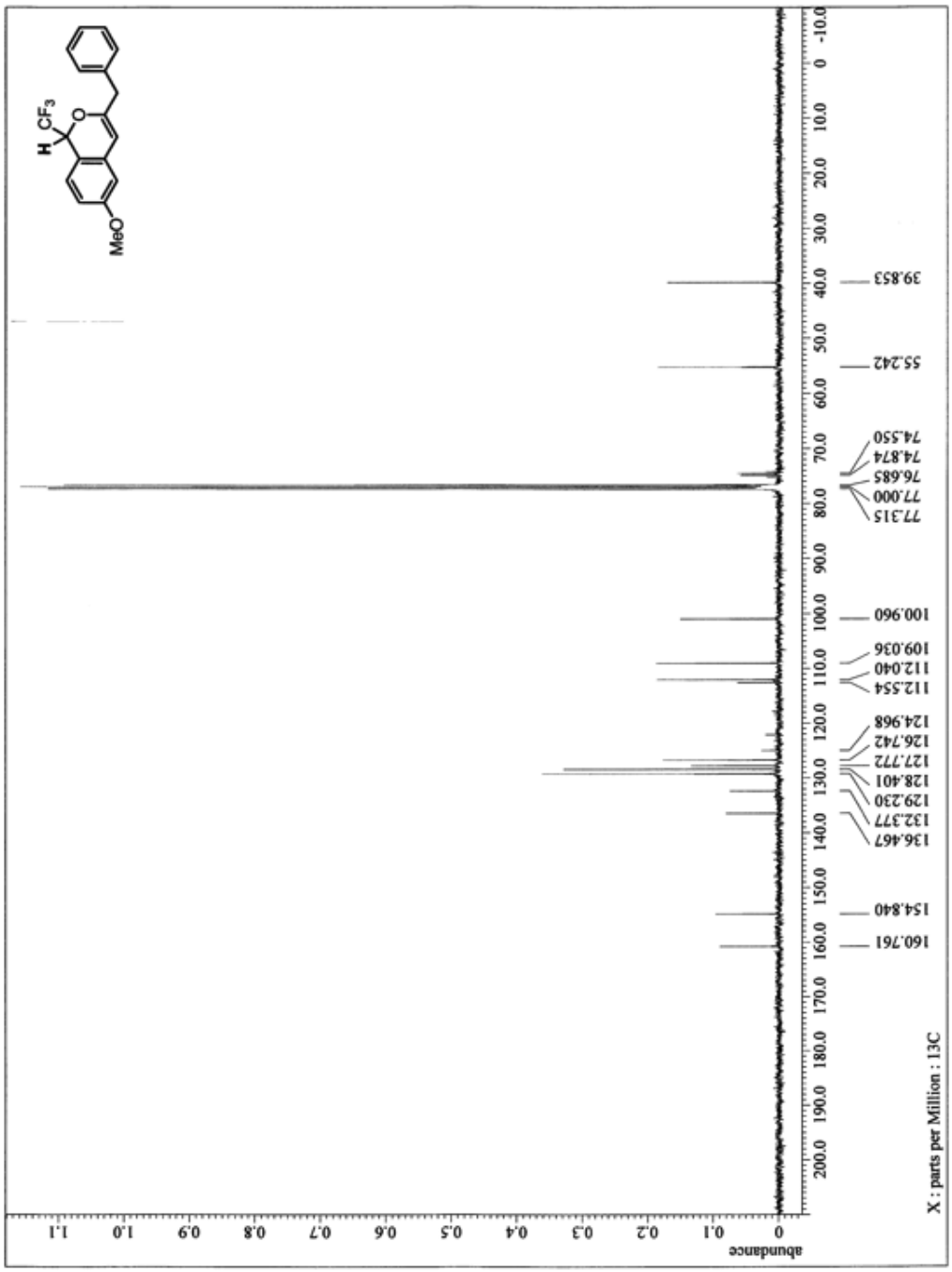
^{19}F NMR spectrum of **3d**.



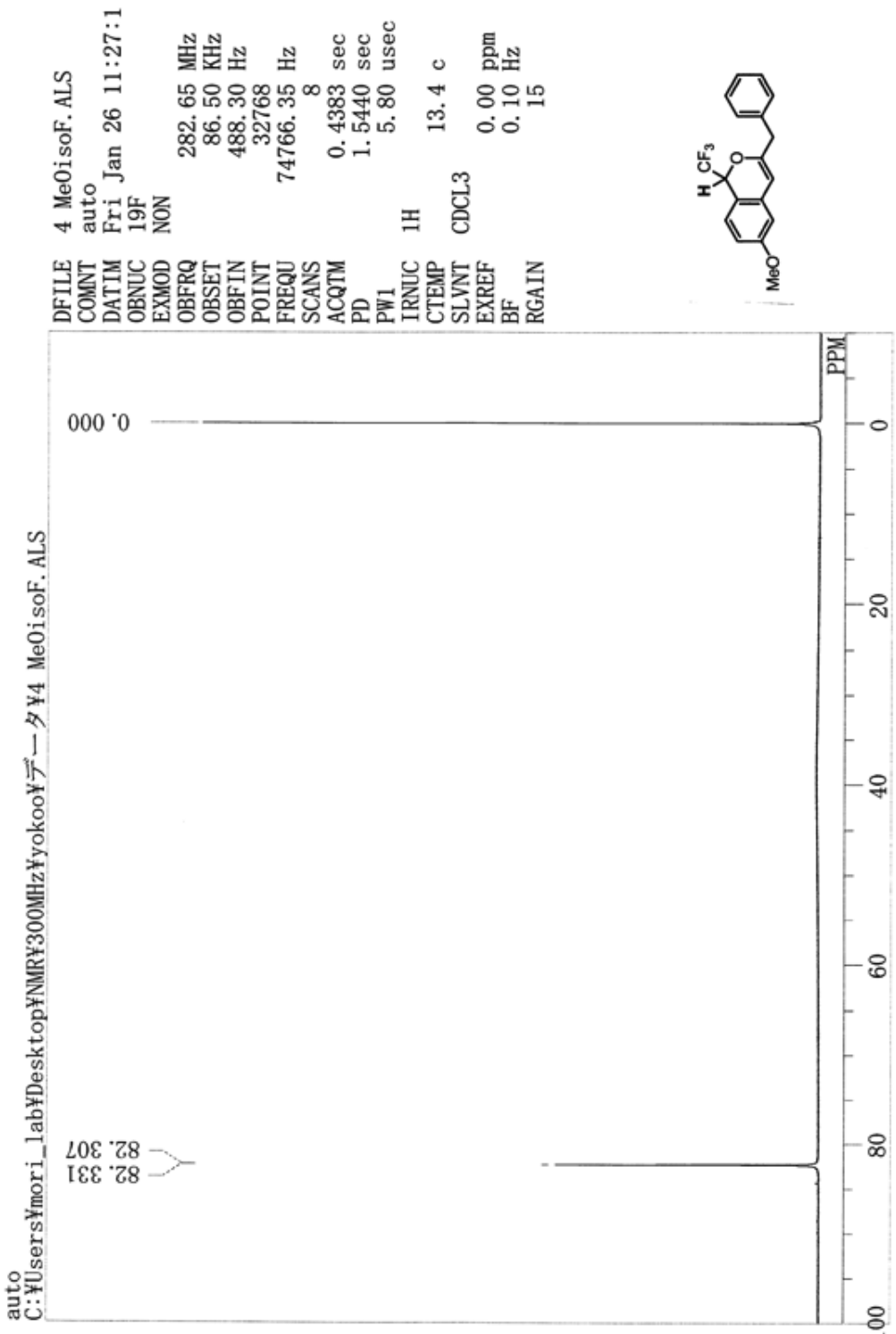
^{1}H NMR spectrum of **2e**.



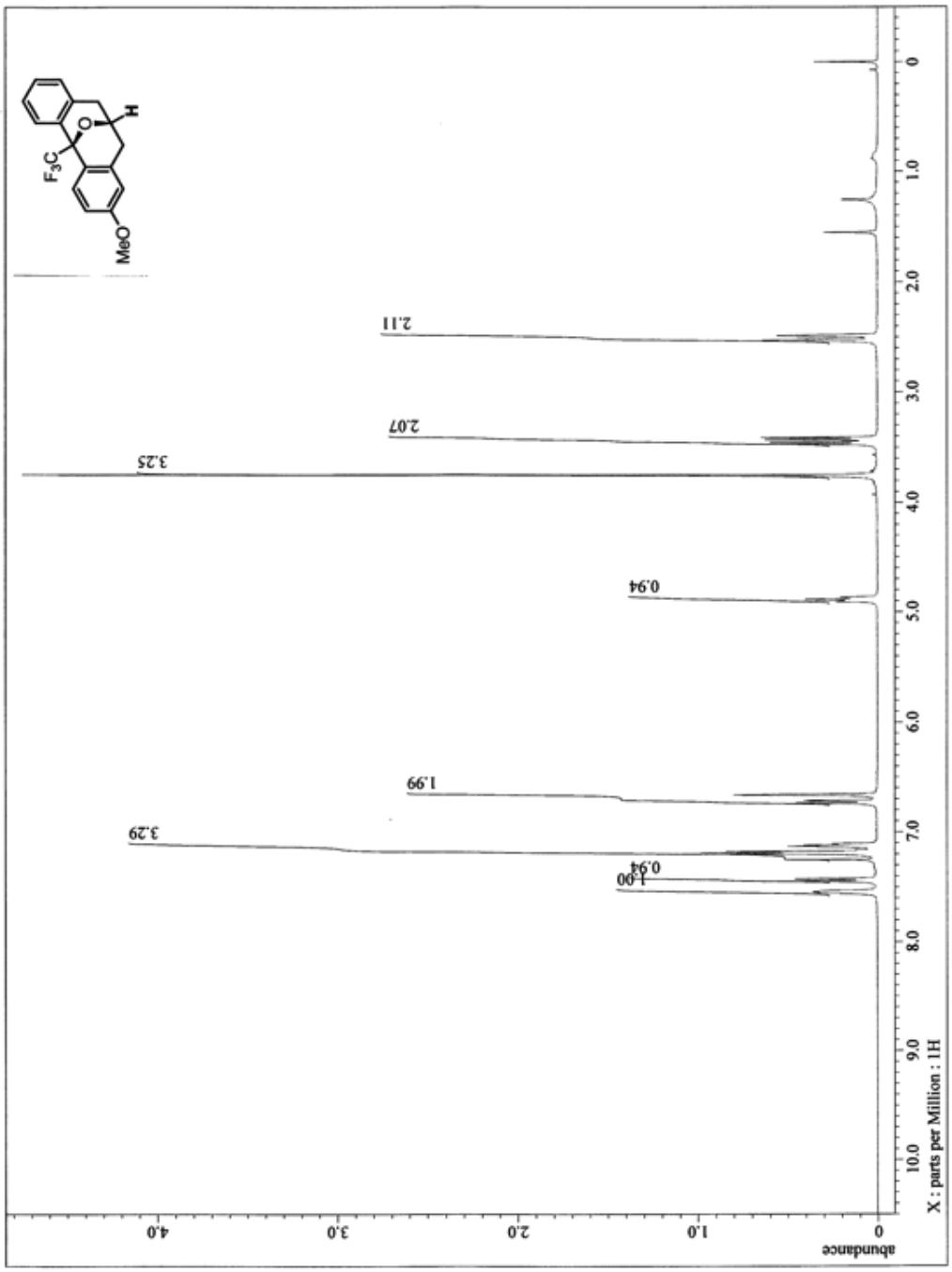
^{13}C NMR spectrum of **2e**.



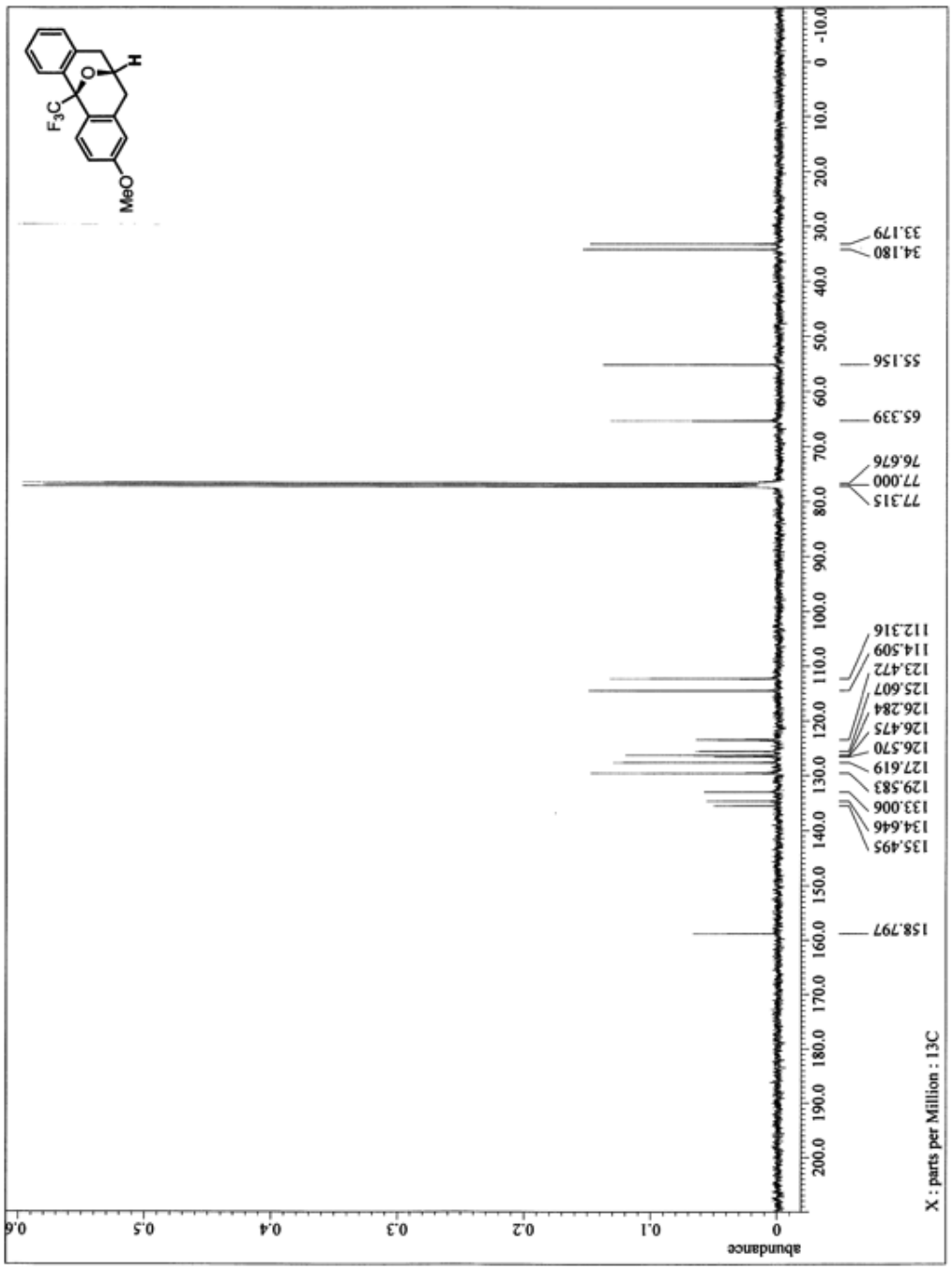
^{19}F NMR spectrum of **2e**.



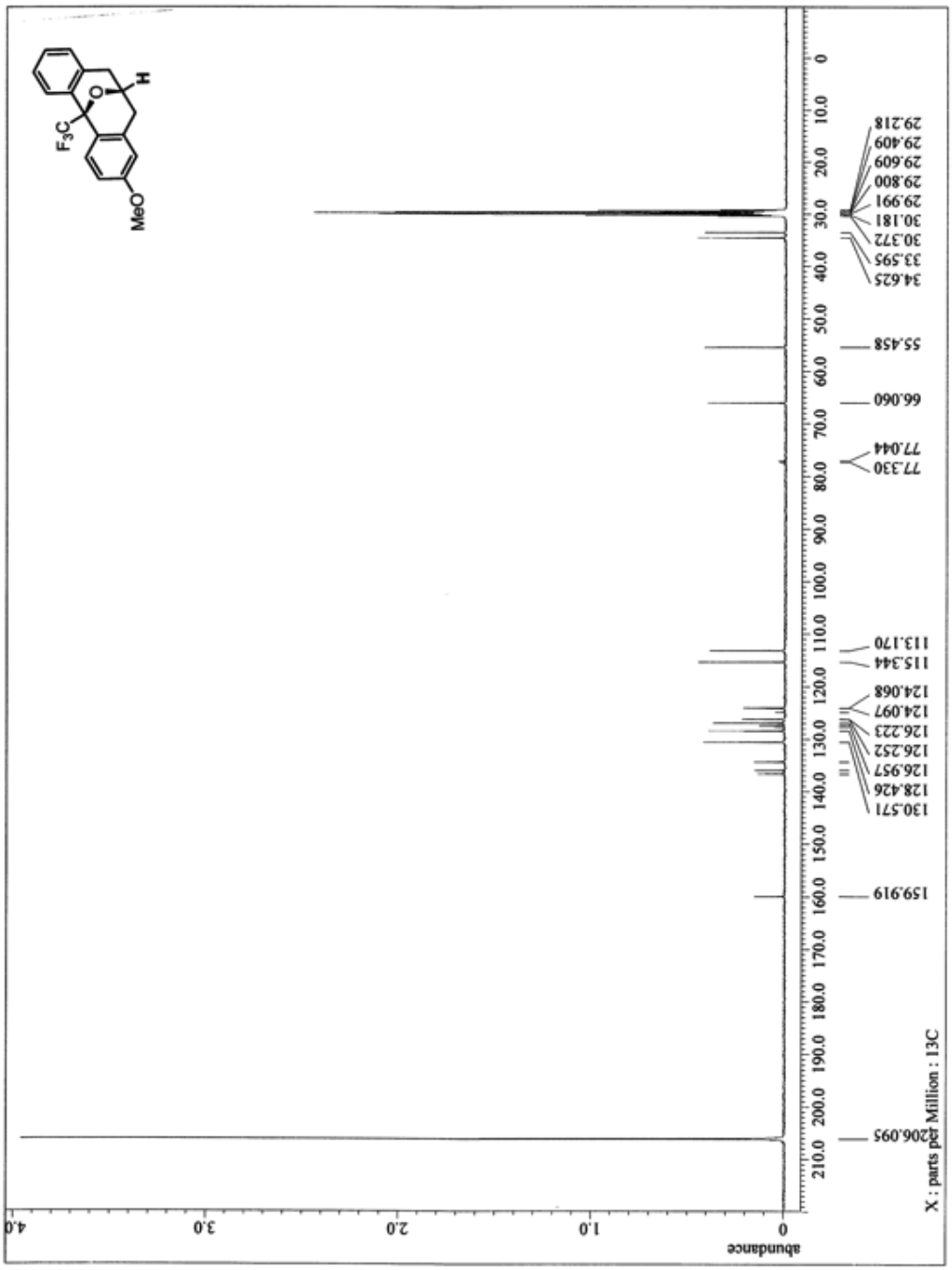
^{1}H NMR spectrum of **3e**.



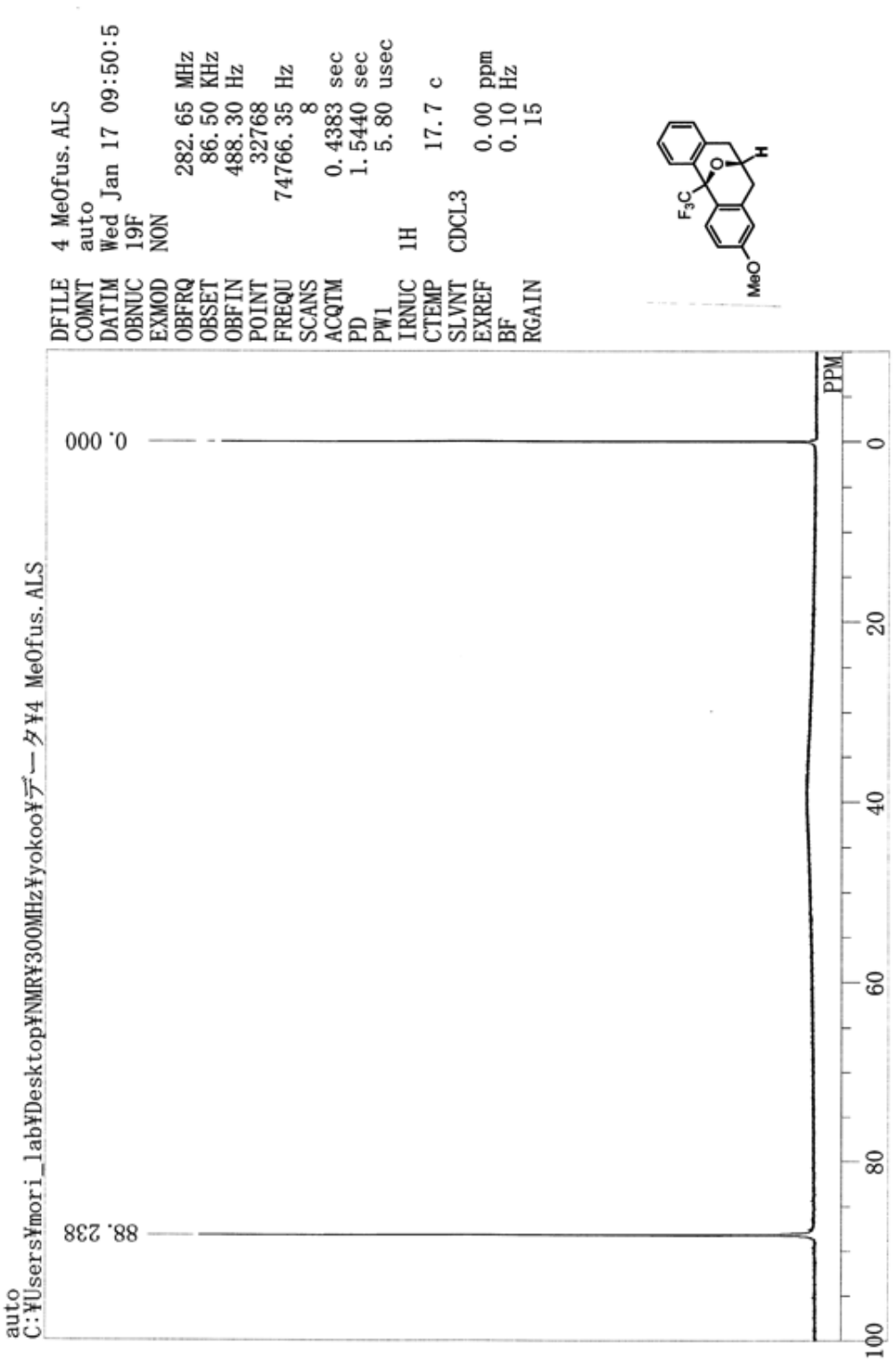
^{13}C NMR spectrum of **3e**.



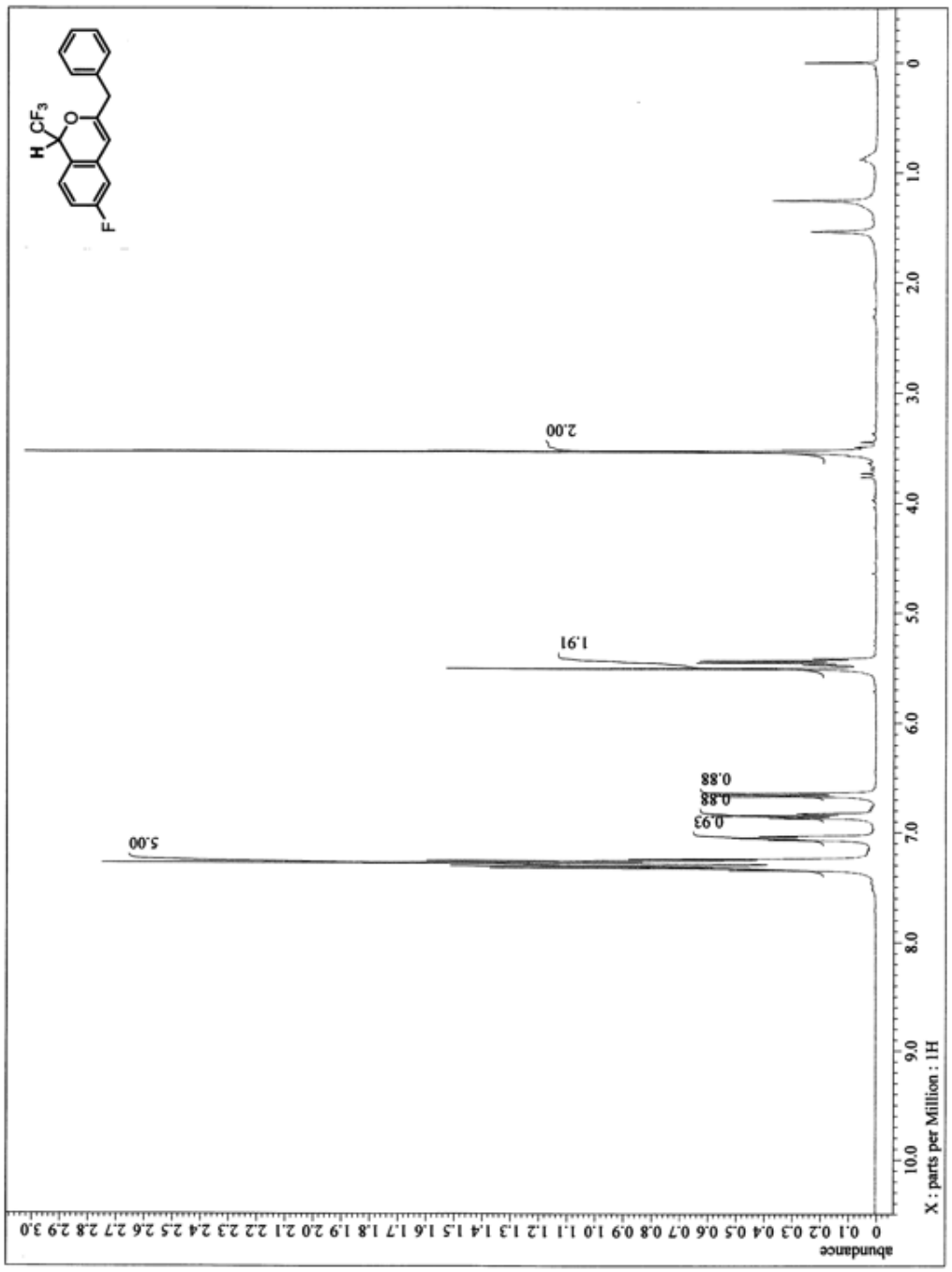
^{13}C NMR spectrum of **3e** (acetone-d6).



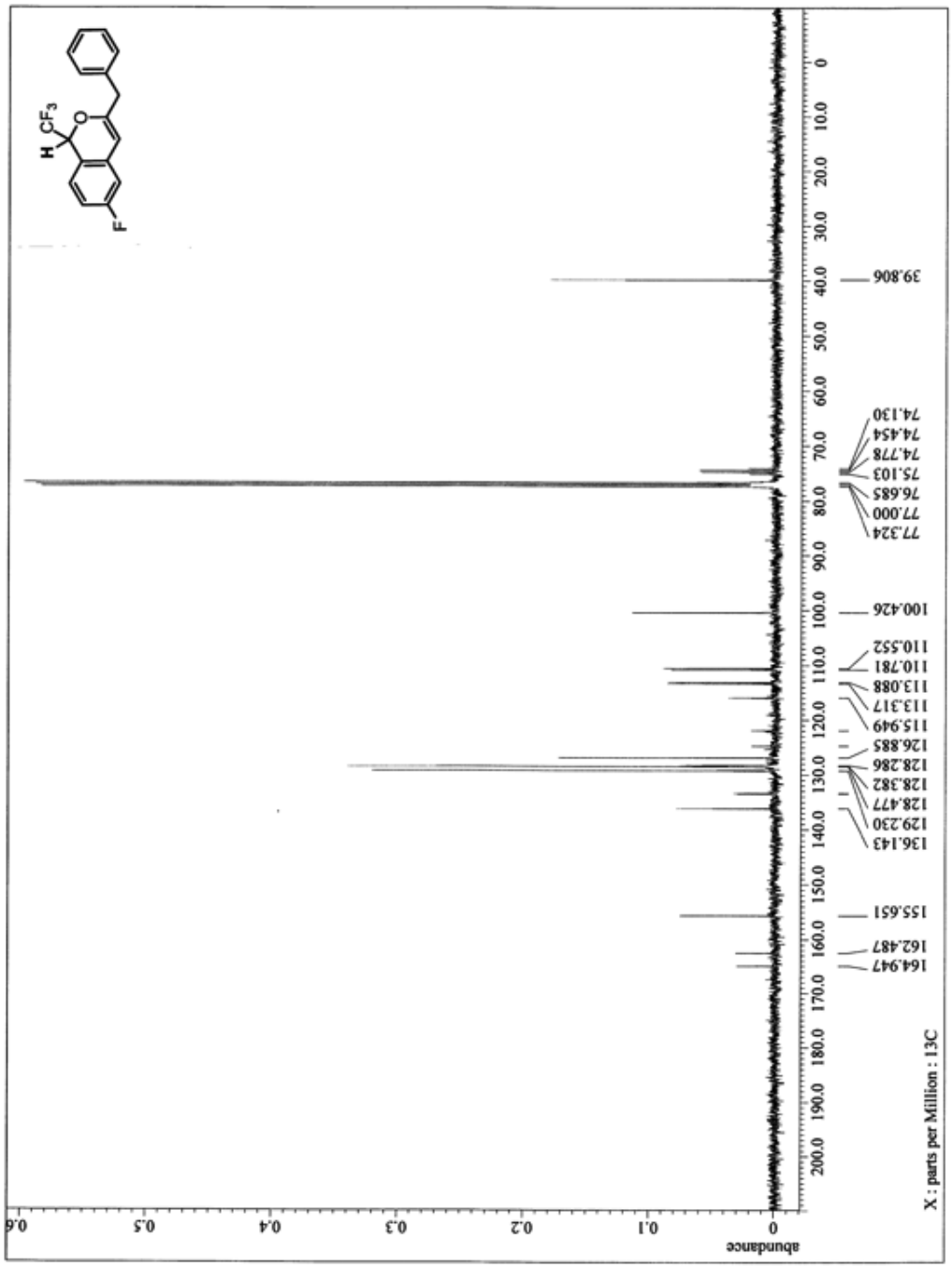
^{19}F NMR spectrum of **3e**.



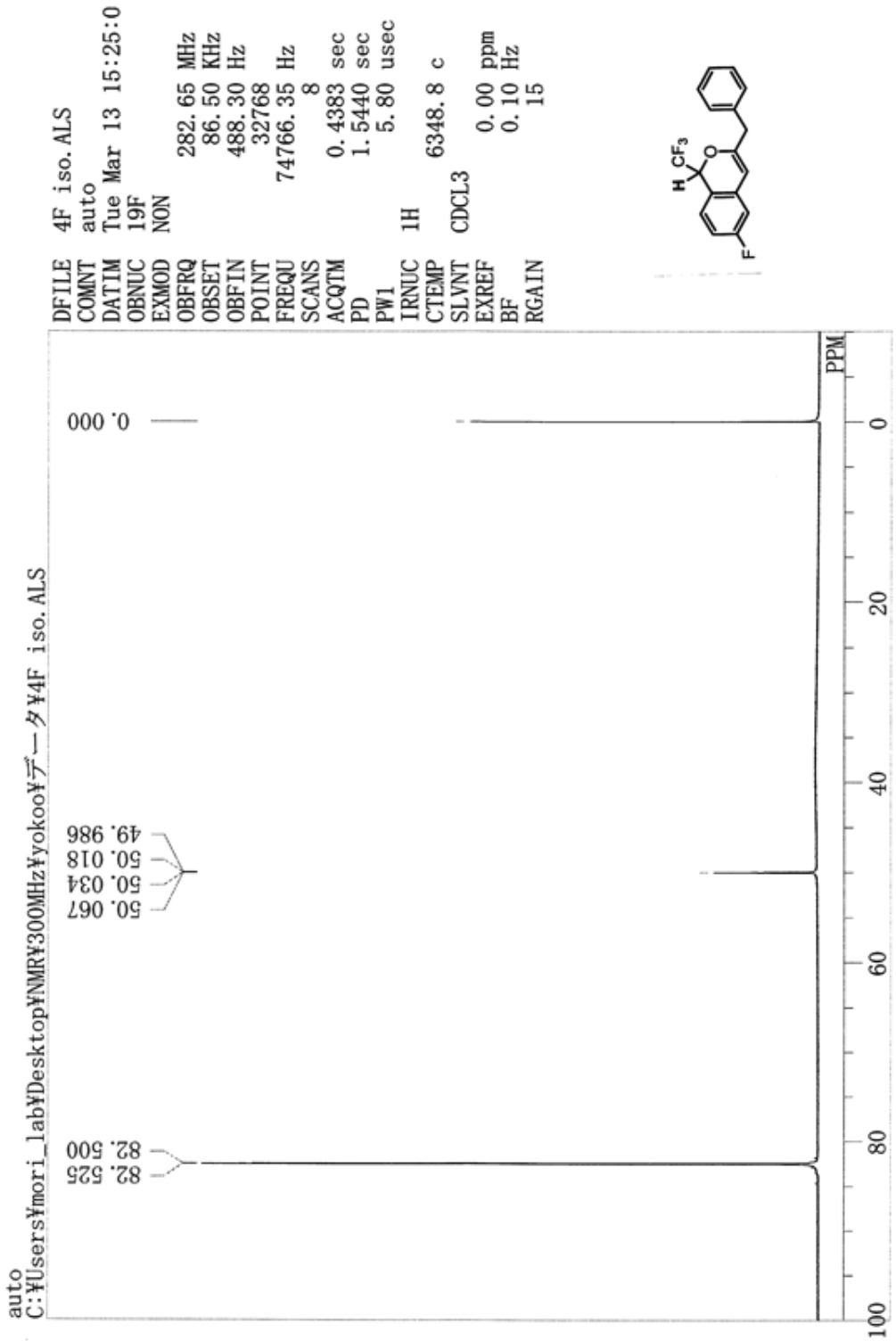
^{1}H NMR spectrum of **2f**.



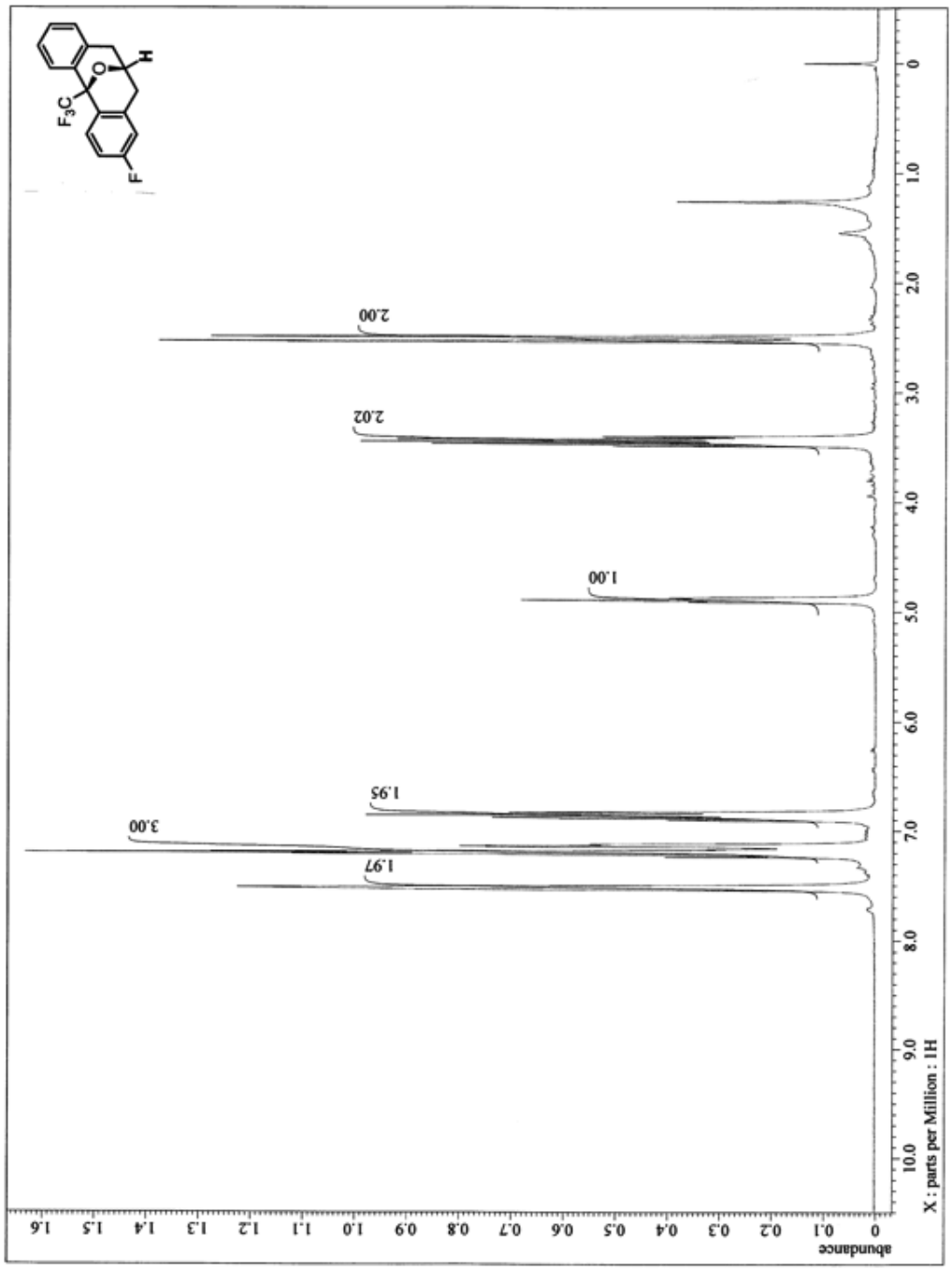
^{13}C NMR spectrum of **2f**.



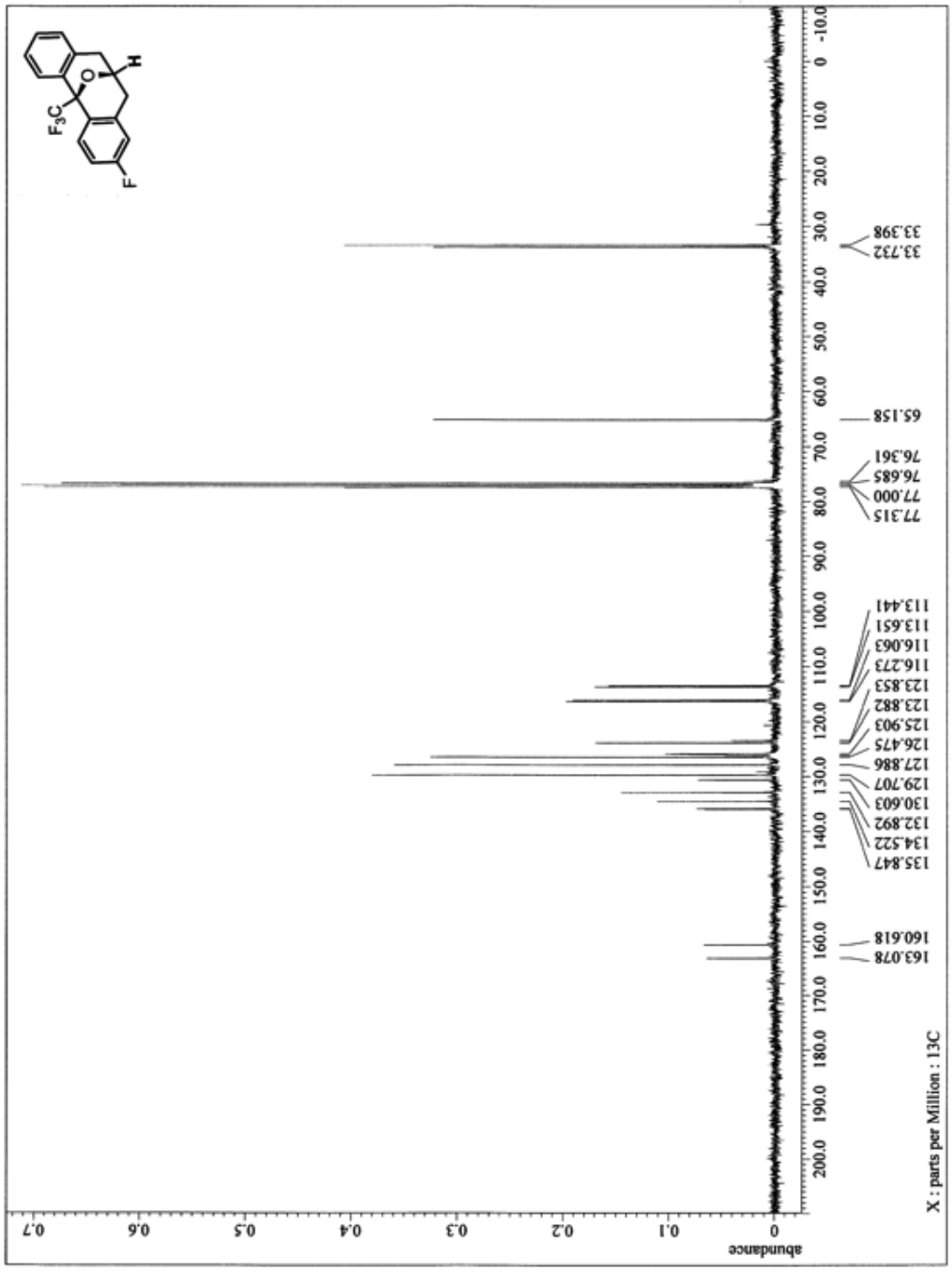
^{19}F NMR spectrum of **2f**.



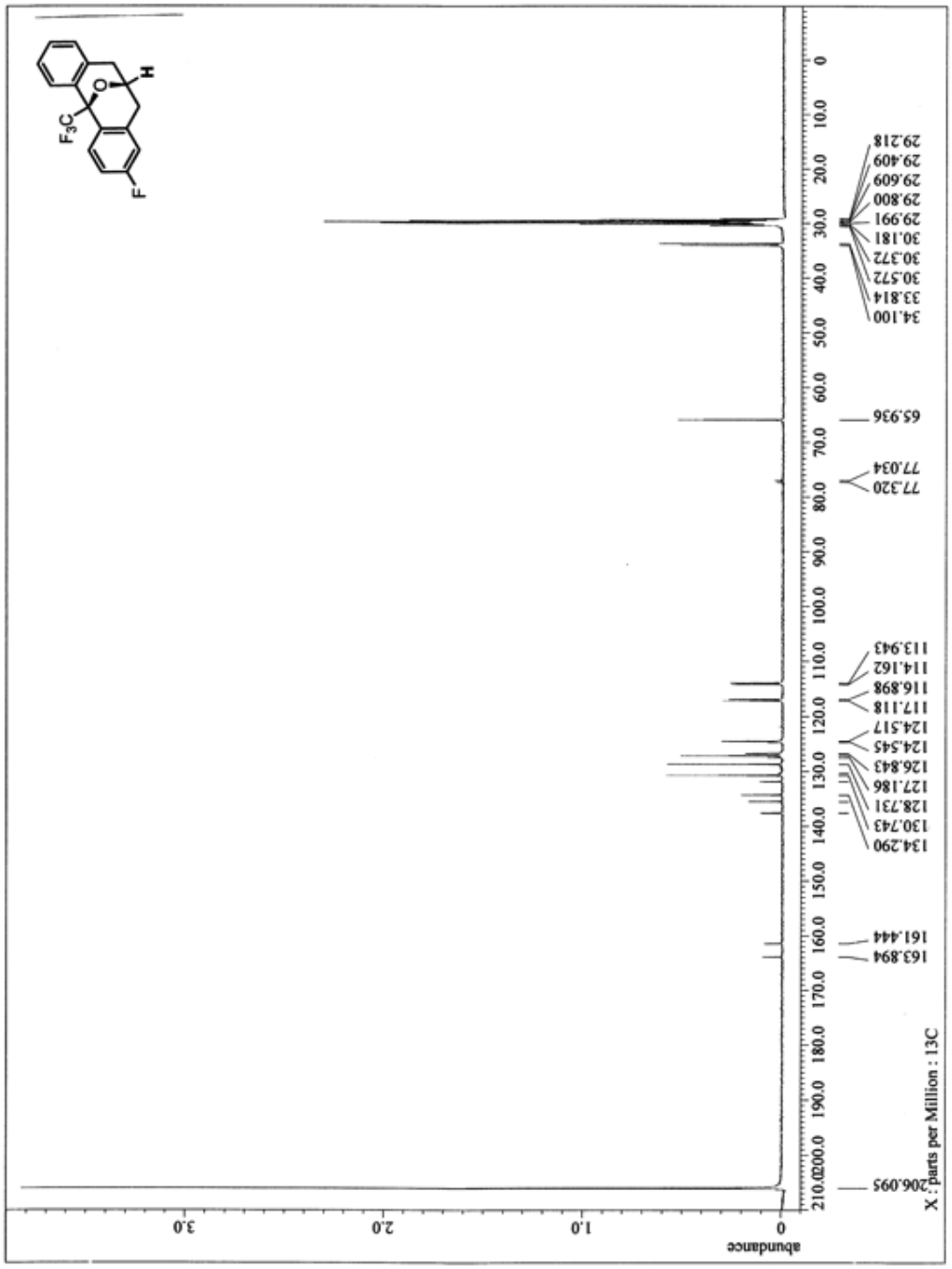
^{1}H NMR spectrum of **3f**.



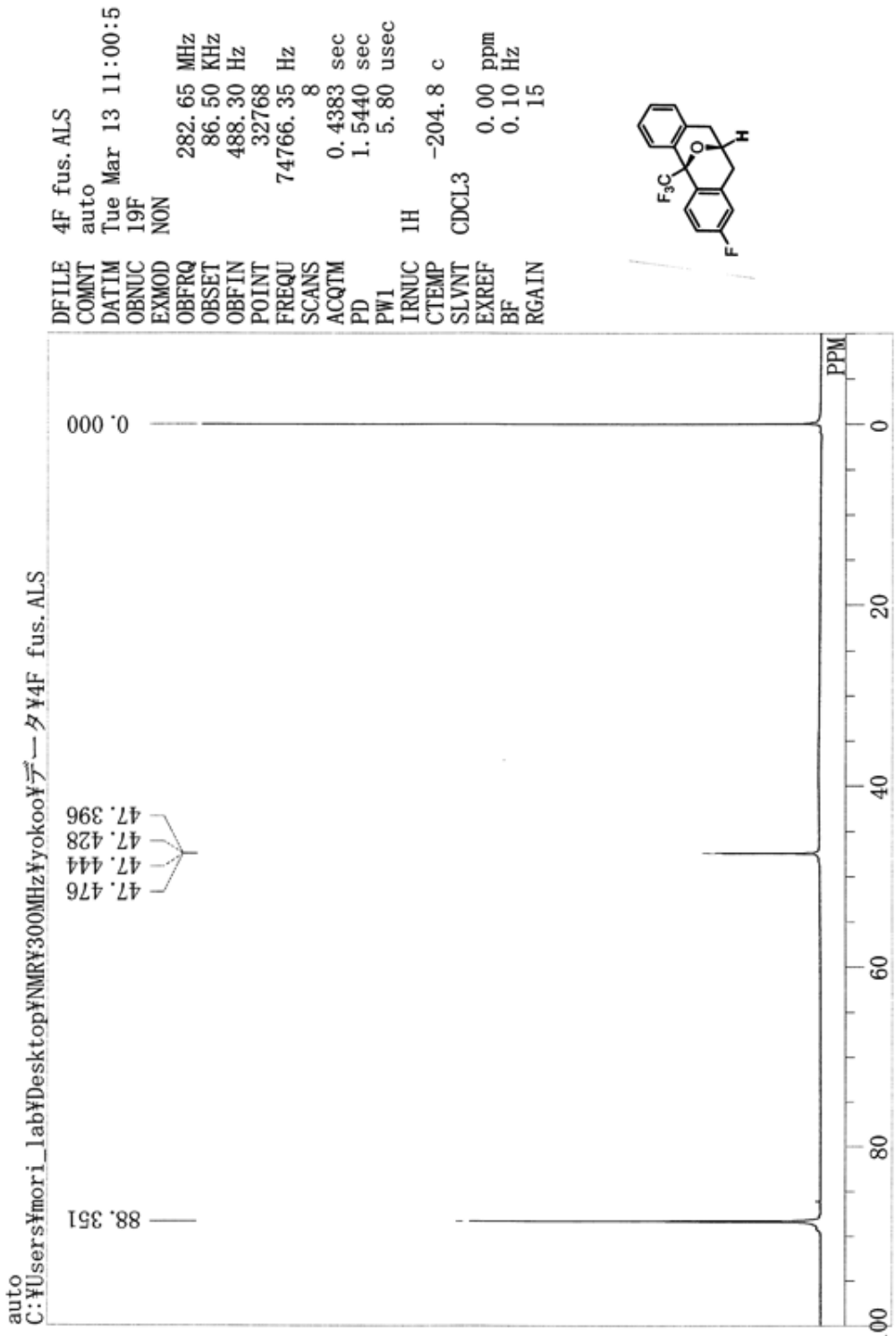
^{13}C NMR spectrum of **3f**.



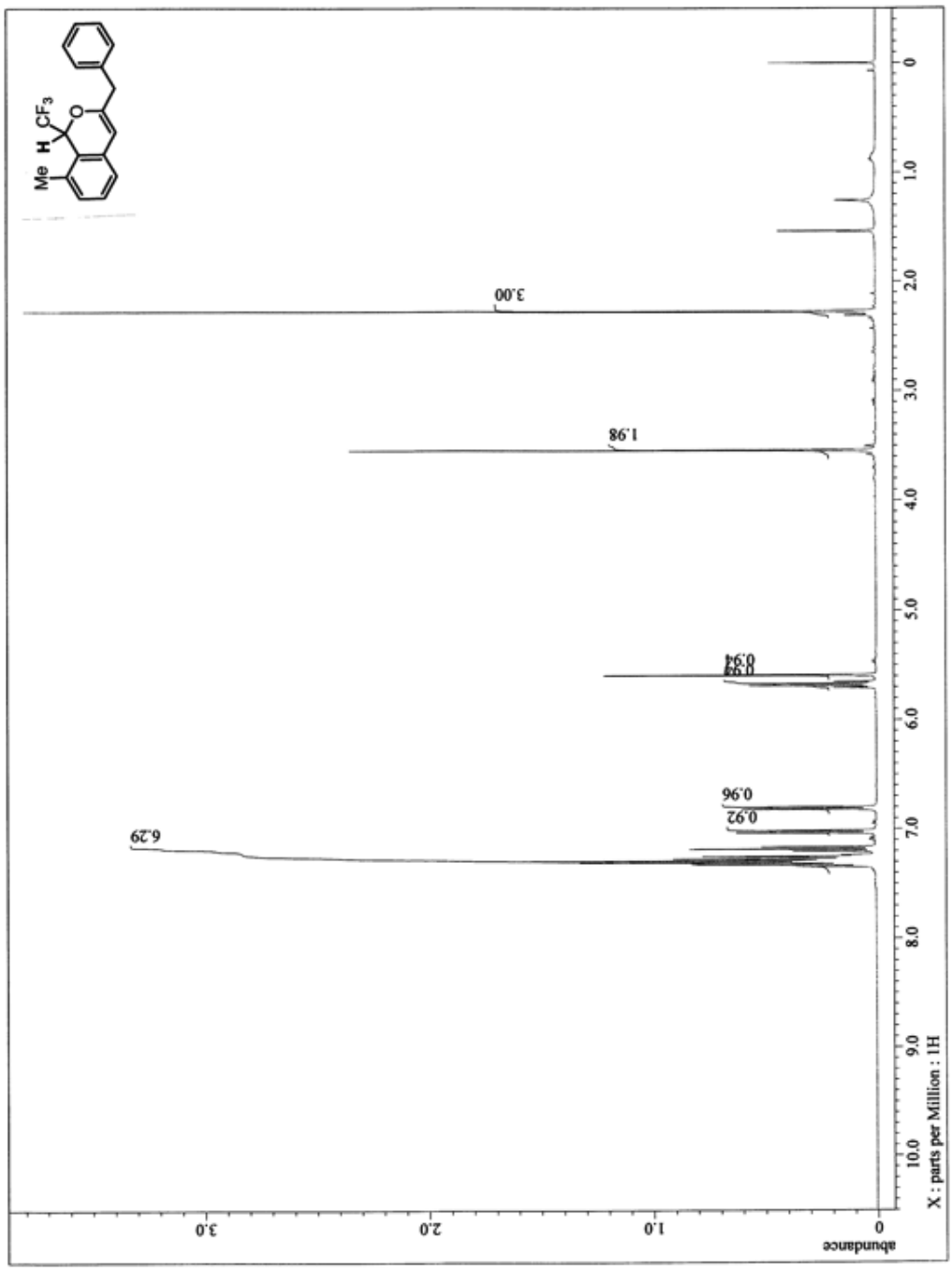
^{13}C NMR spectrum of **3f** (acetone-d6).



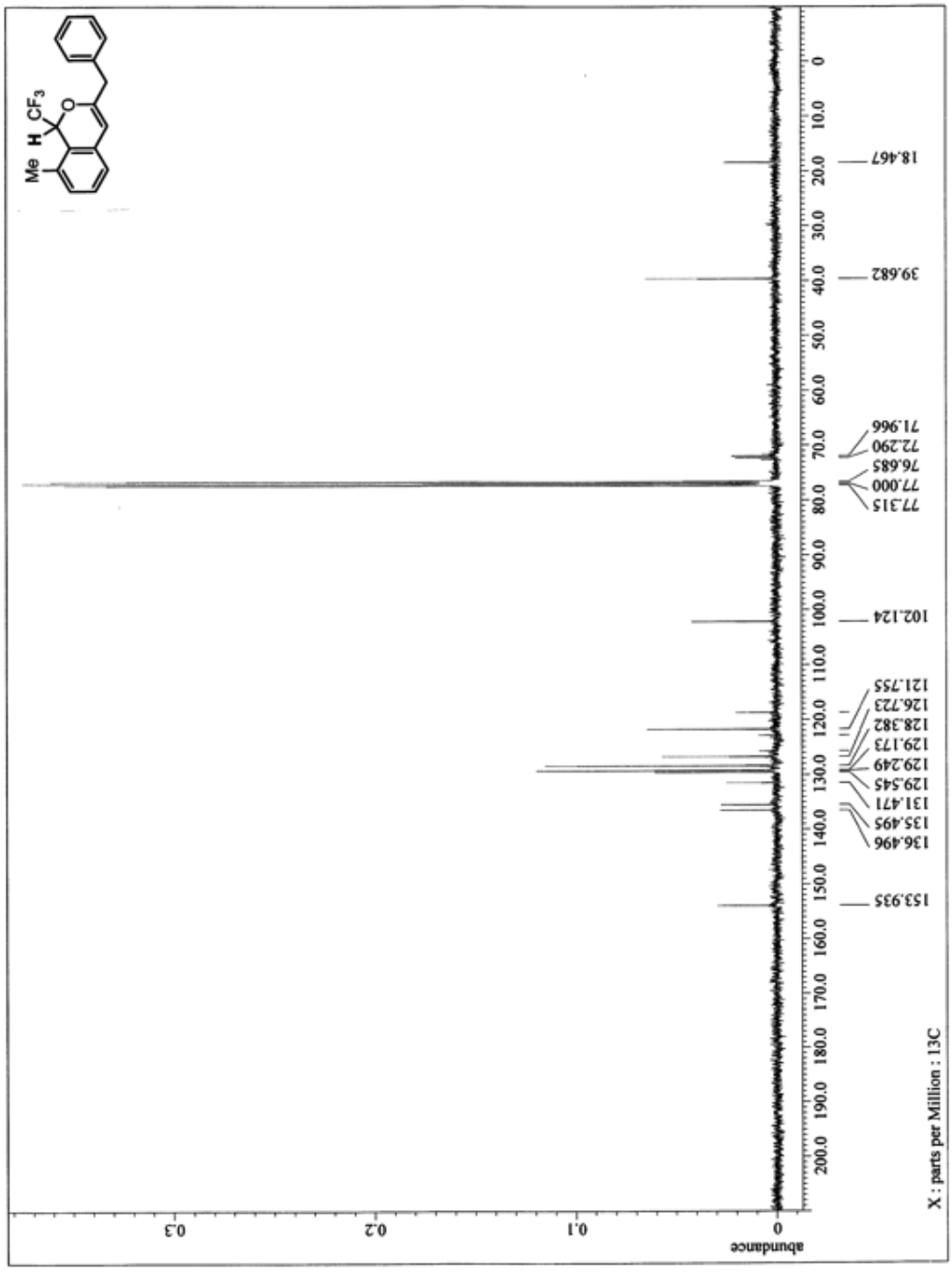
^{19}F NMR spectrum of **3f**.



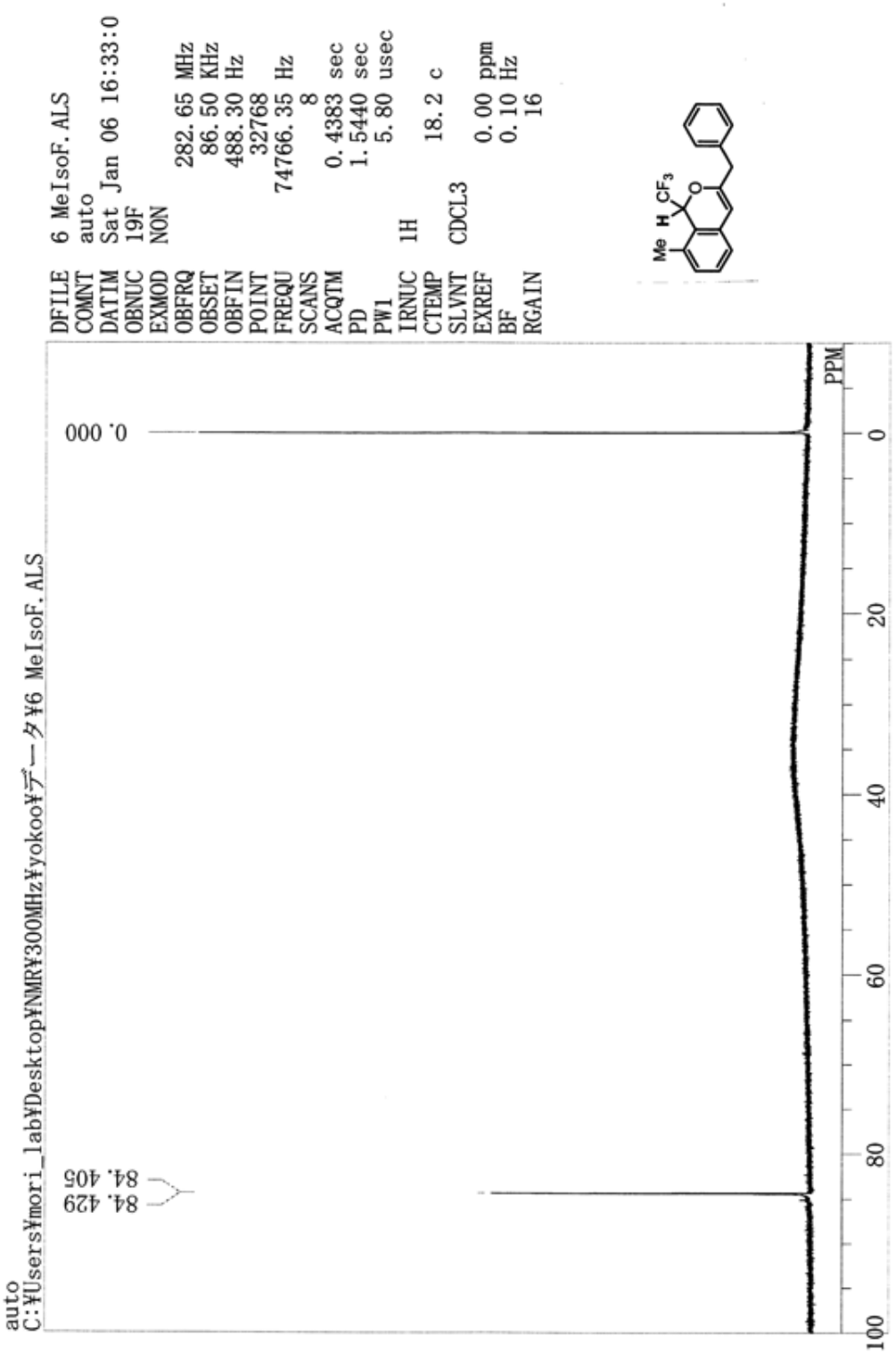
^{1}H NMR spectrum of **3g**.



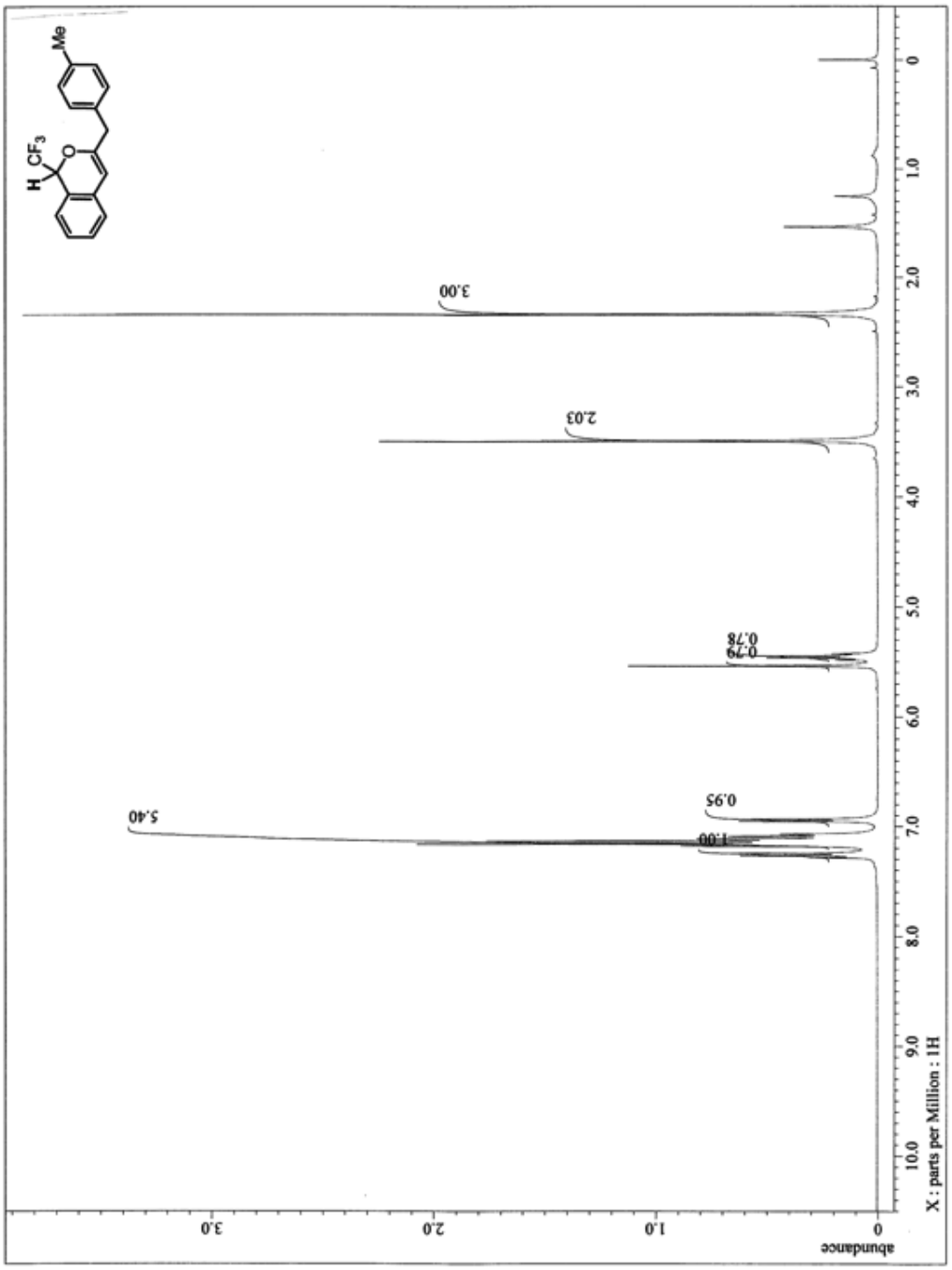
^{13}C NMR spectrum of **3g**.



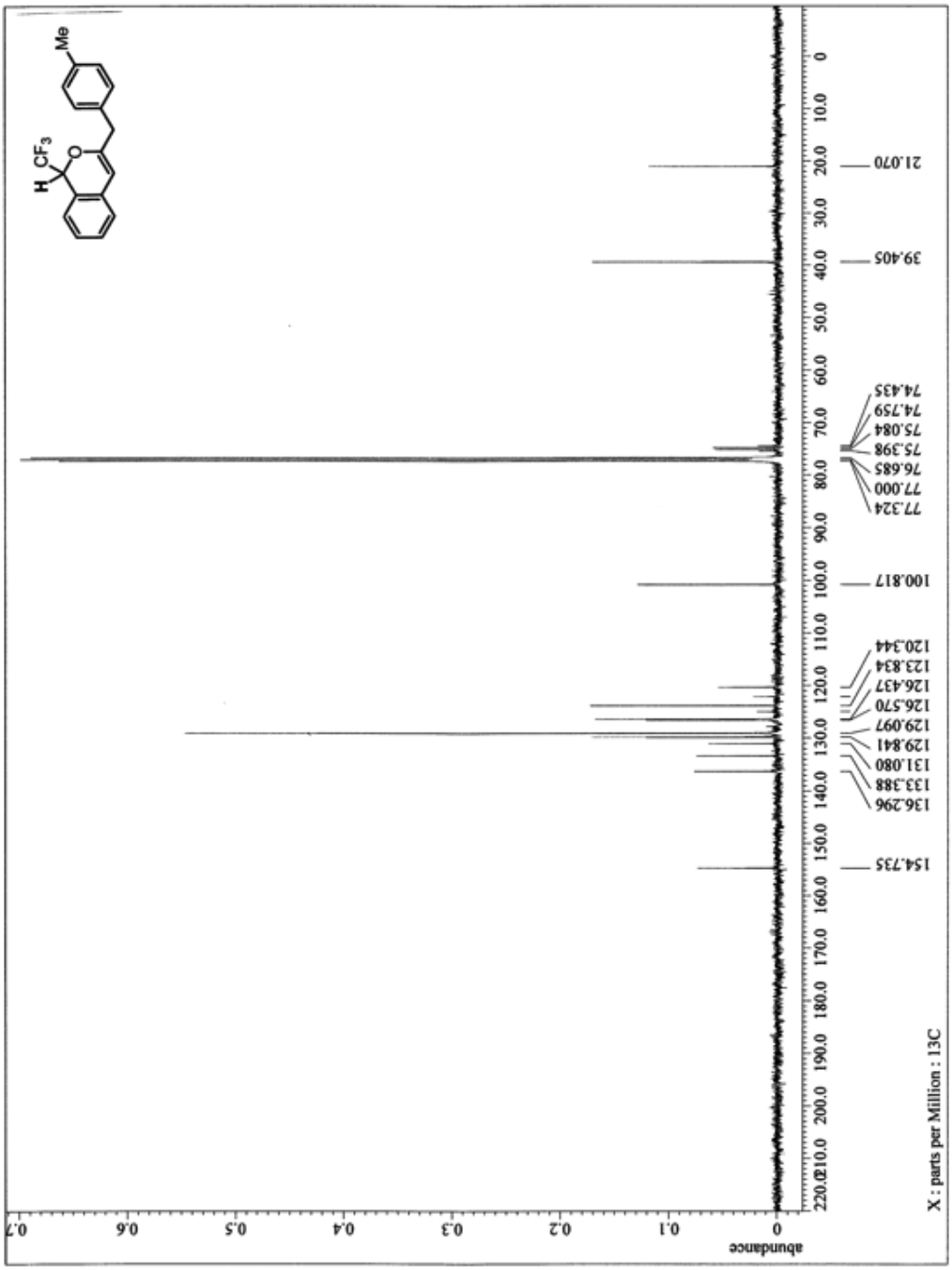
^{19}F NMR spectrum of **3g**.



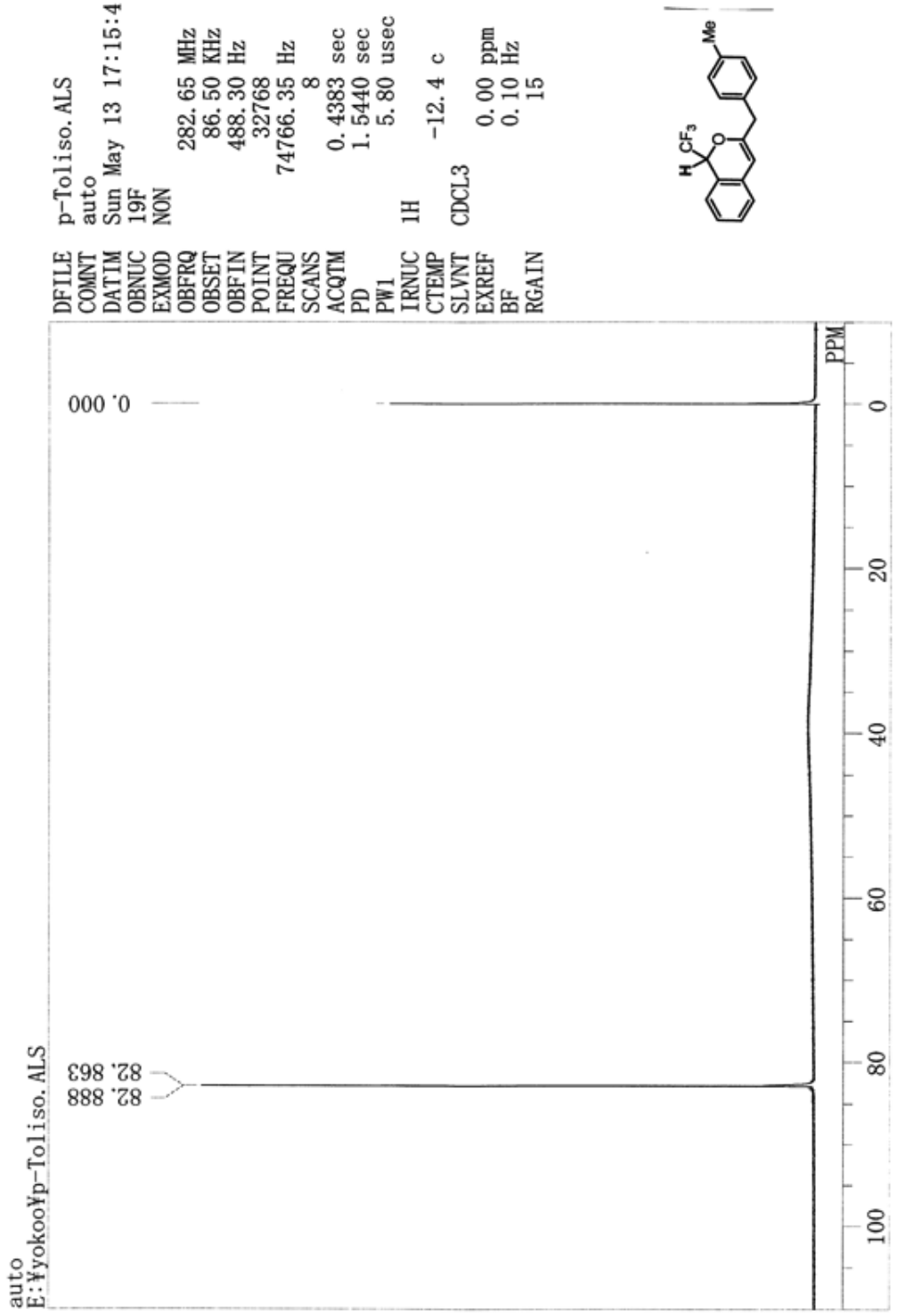
^{1}H NMR spectrum of **2h**.



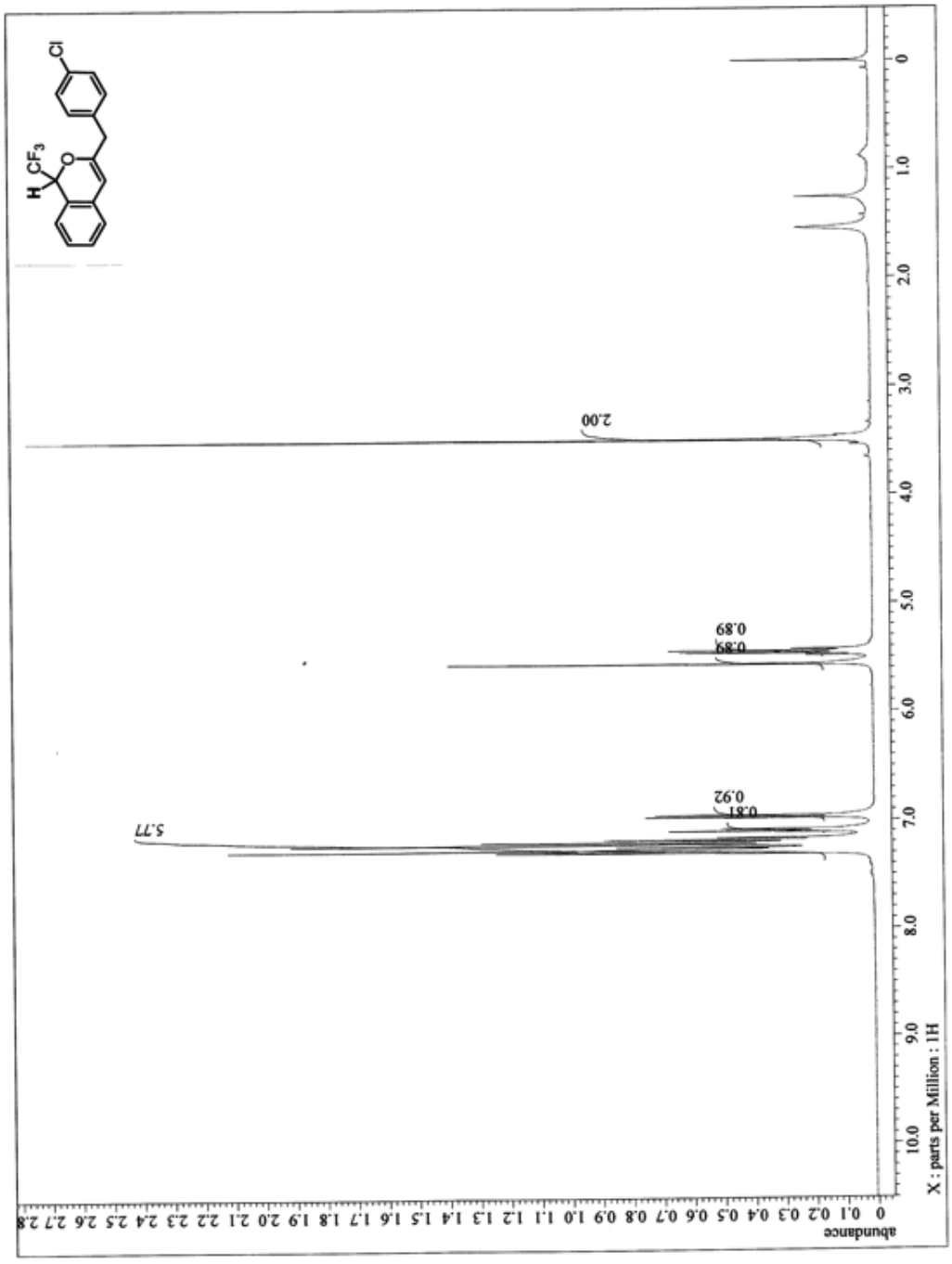
^{13}C NMR spectrum of **2h**.



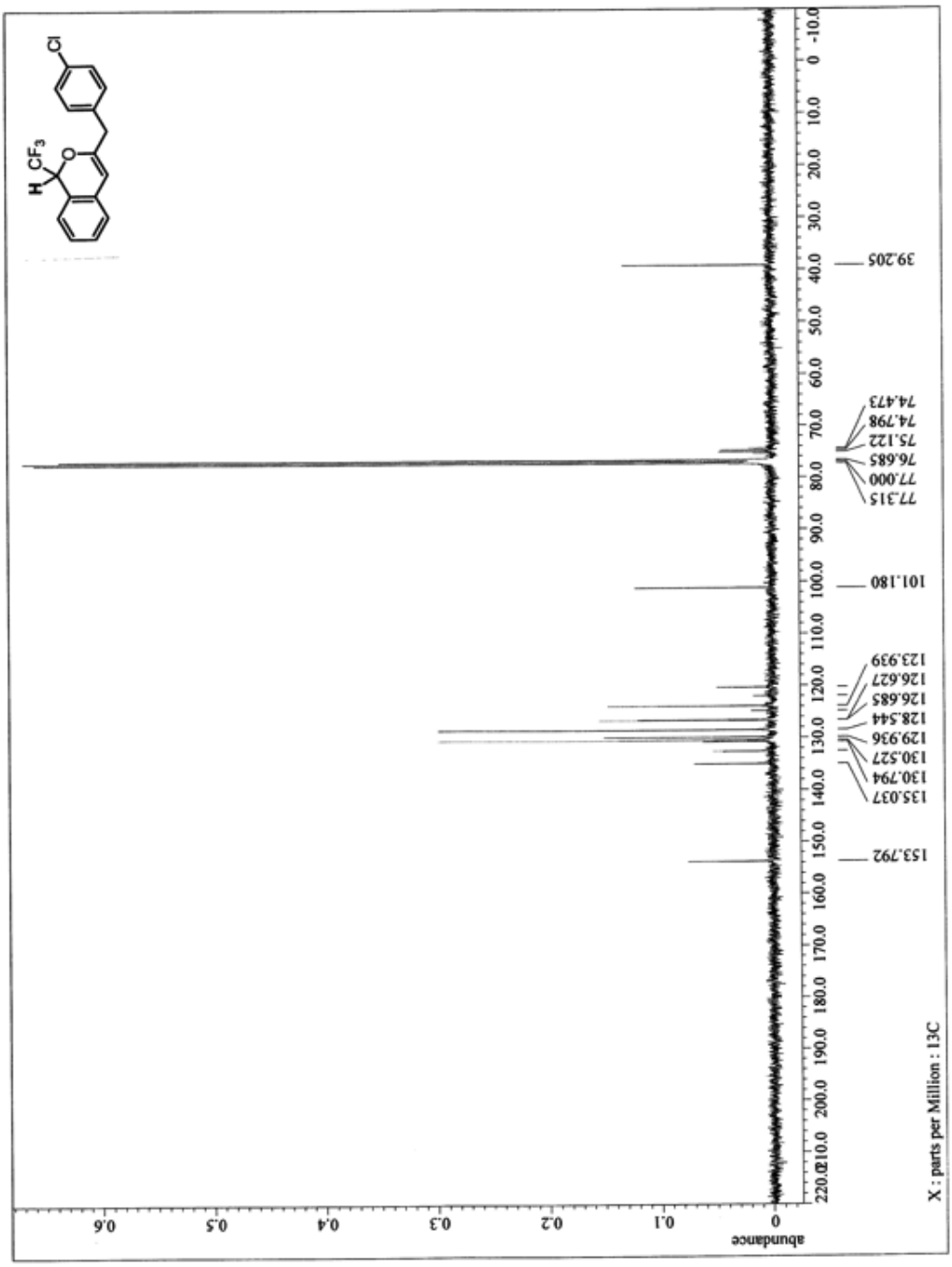
^{19}F NMR spectrum of **2h**.



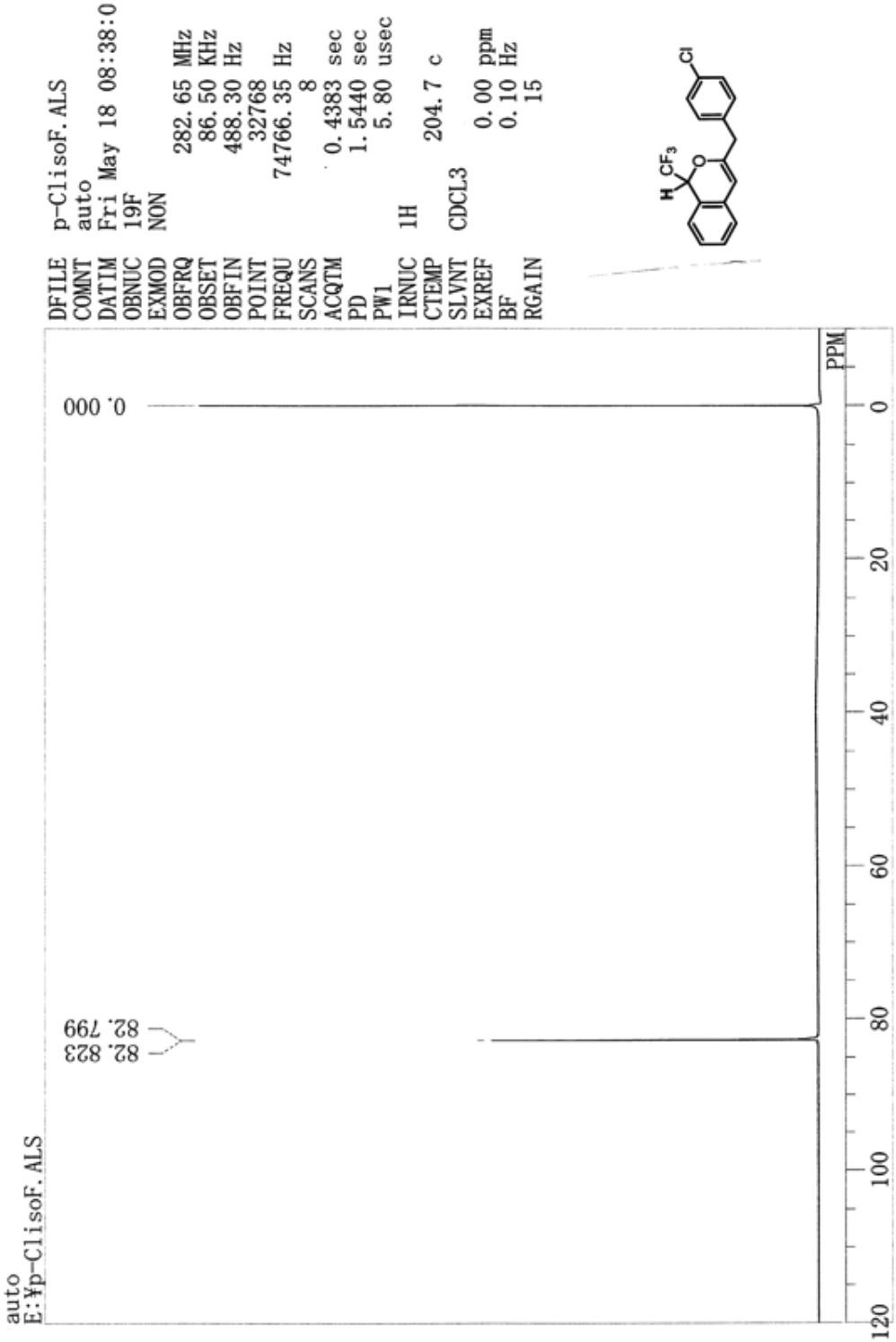
^{1}H NMR spectrum of **2i**.



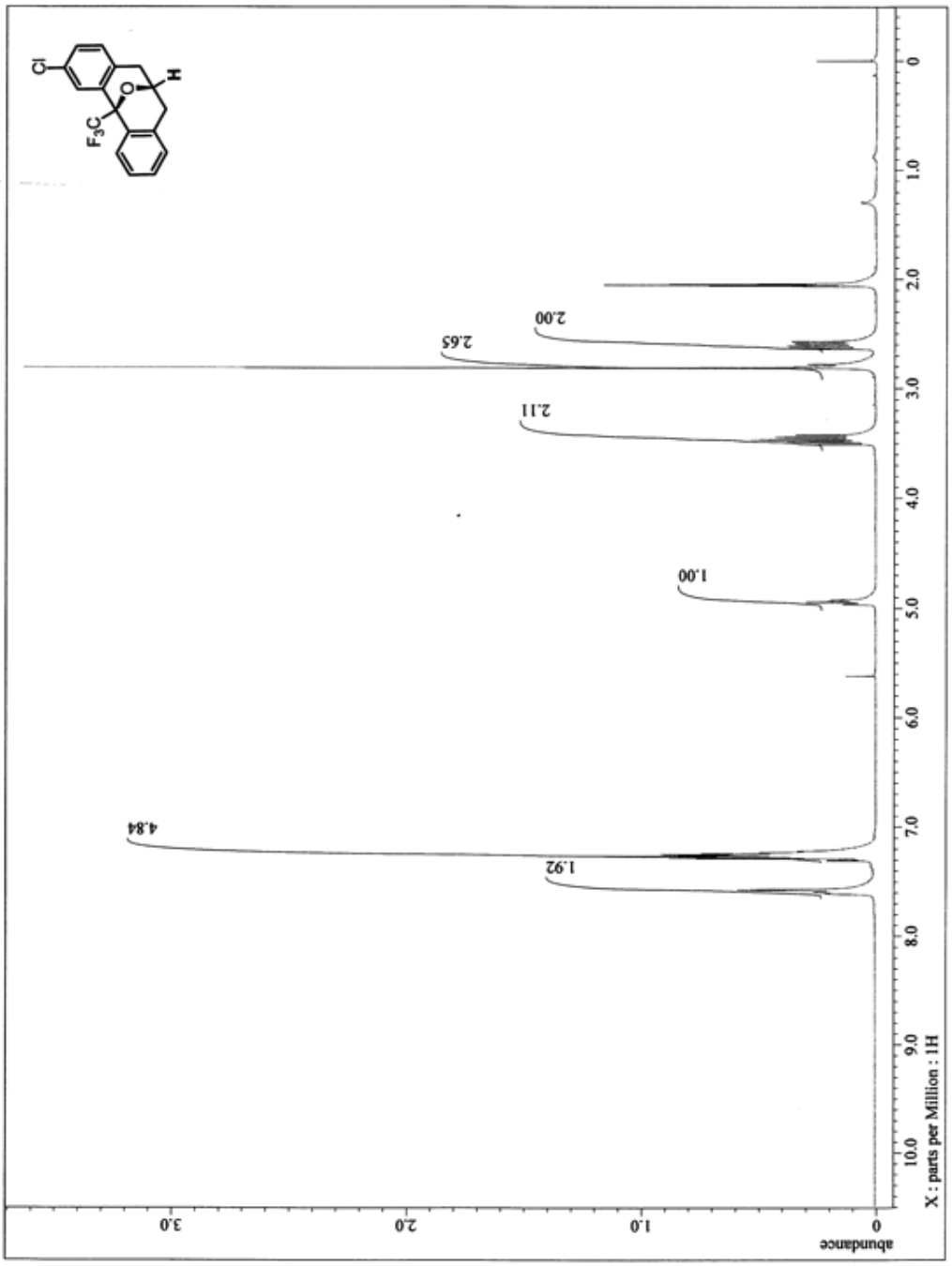
^{13}C NMR spectrum of **2i**.



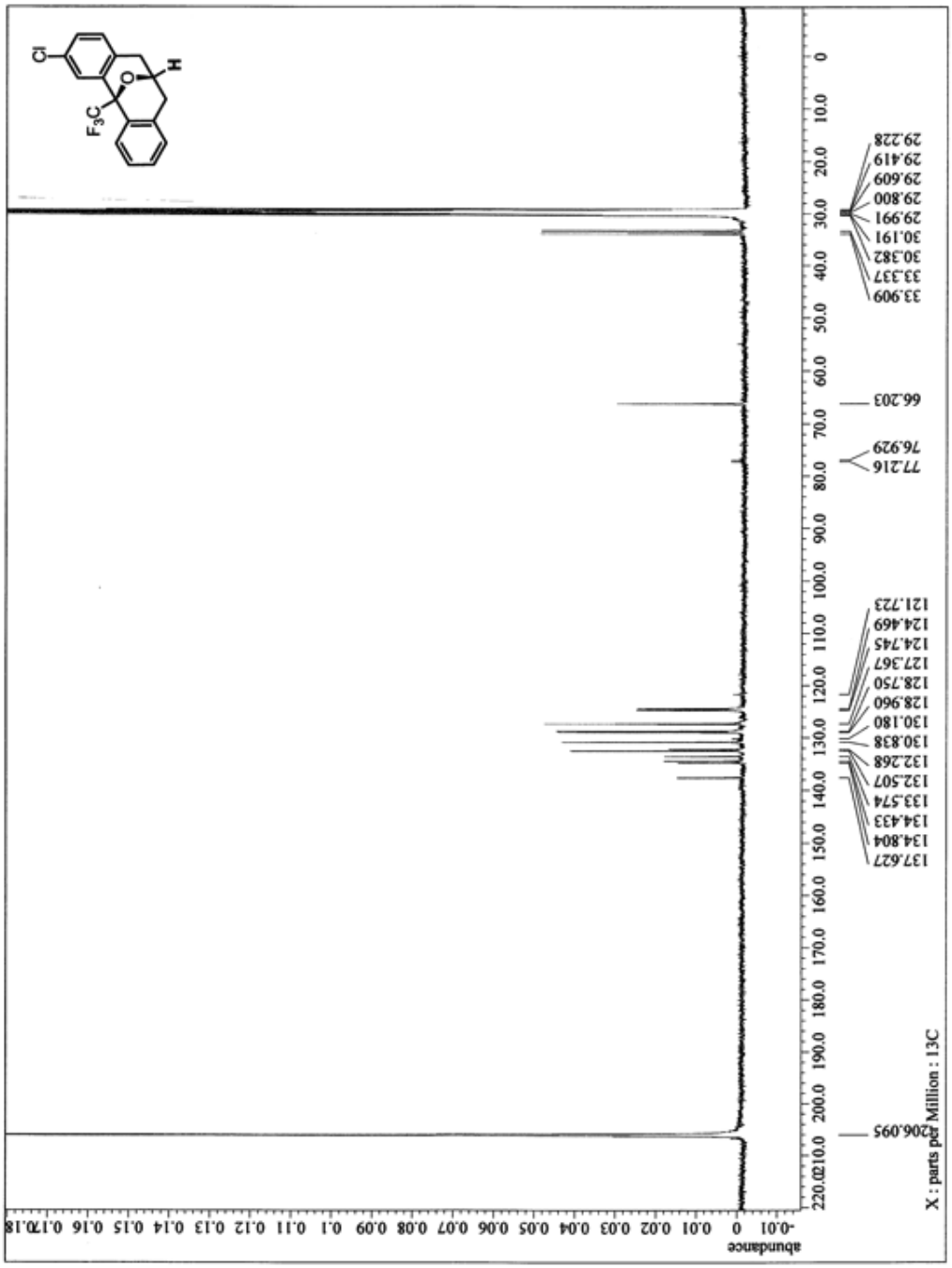
^{19}F NMR spectrum of **2i**.



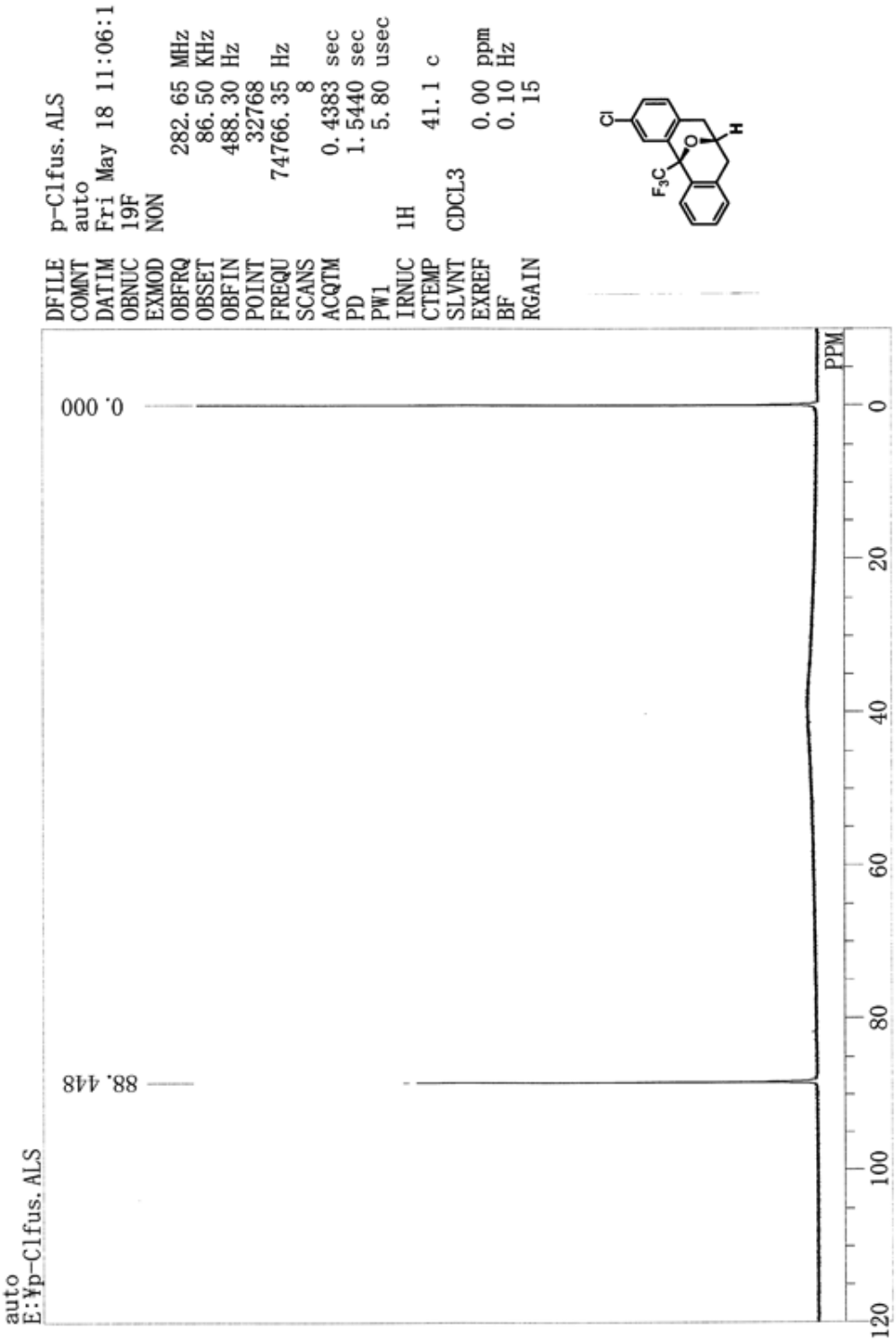
^{1}H NMR spectrum of **3i**.



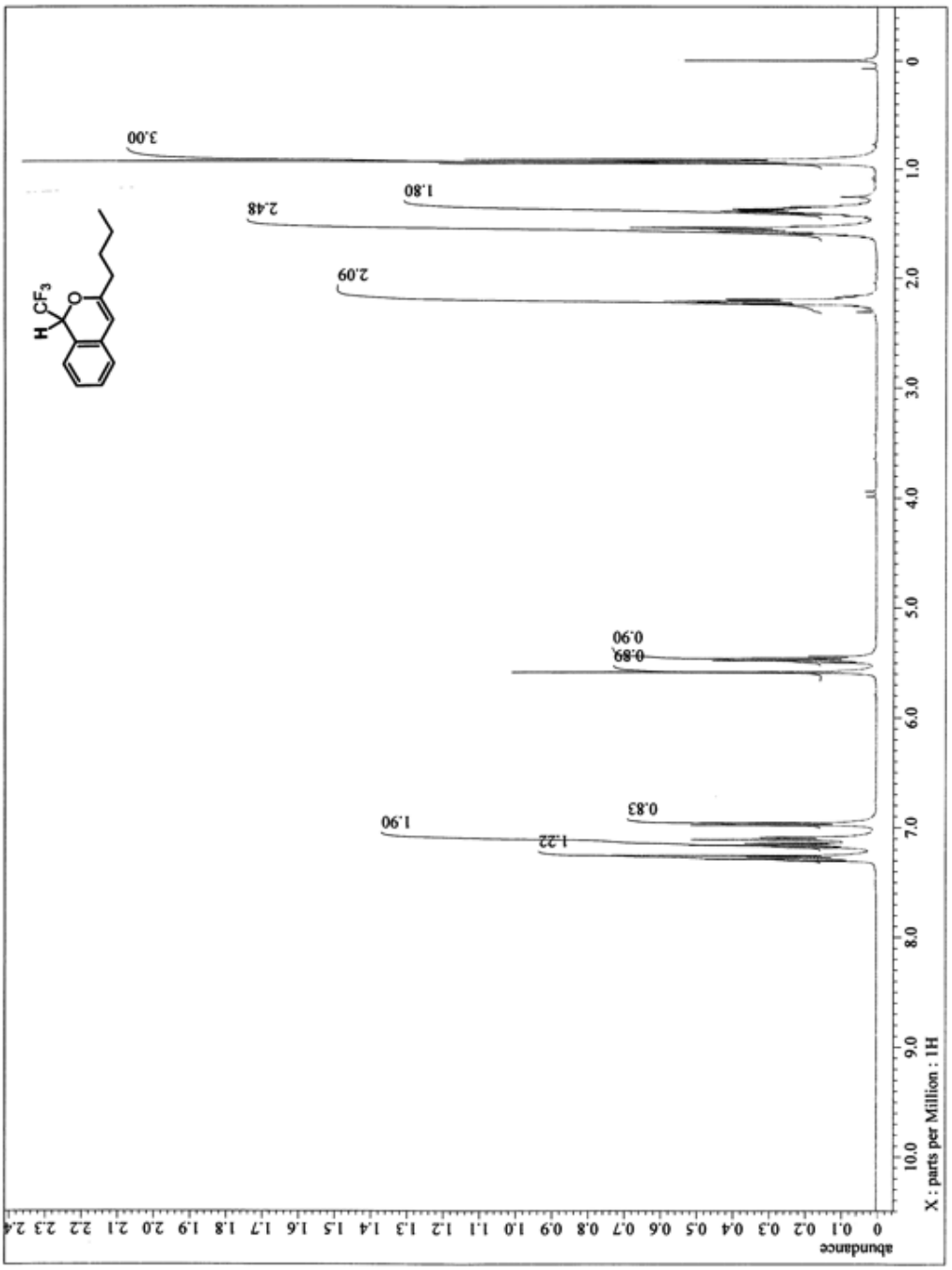
^{13}C NMR spectrum of **3i**.



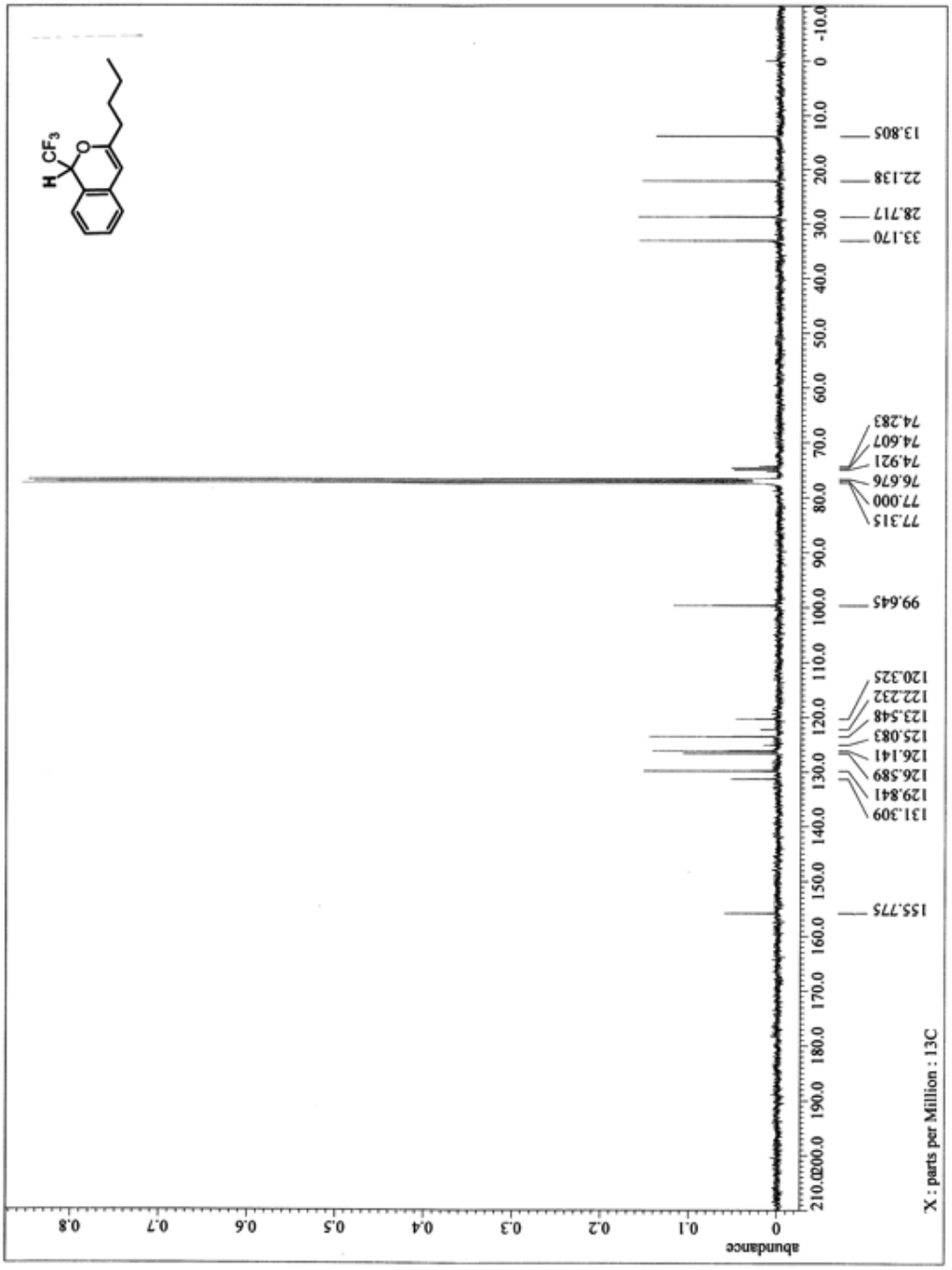
^{19}F NMR spectrum of **3i**.



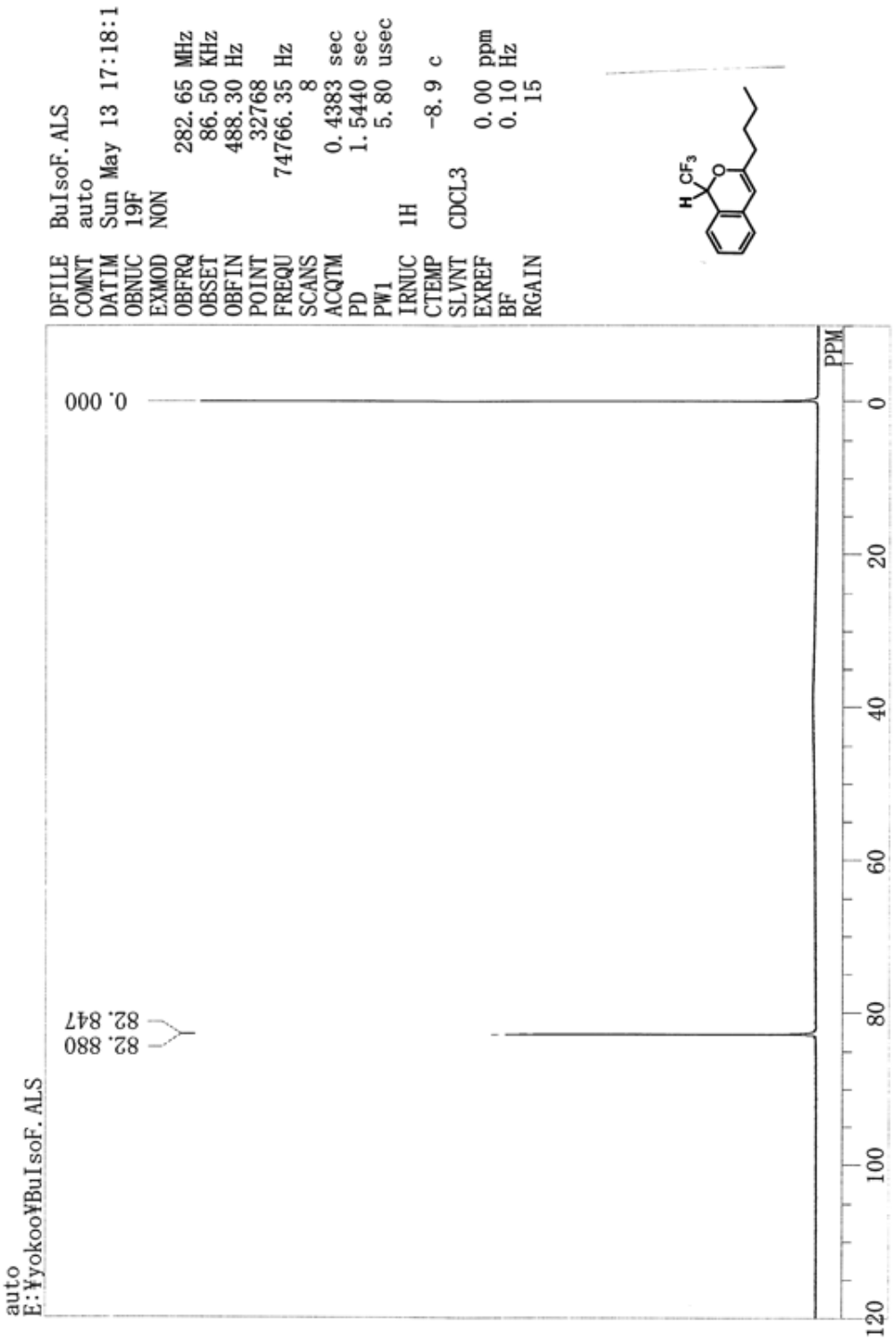
^{1}H NMR spectrum of **2j**.



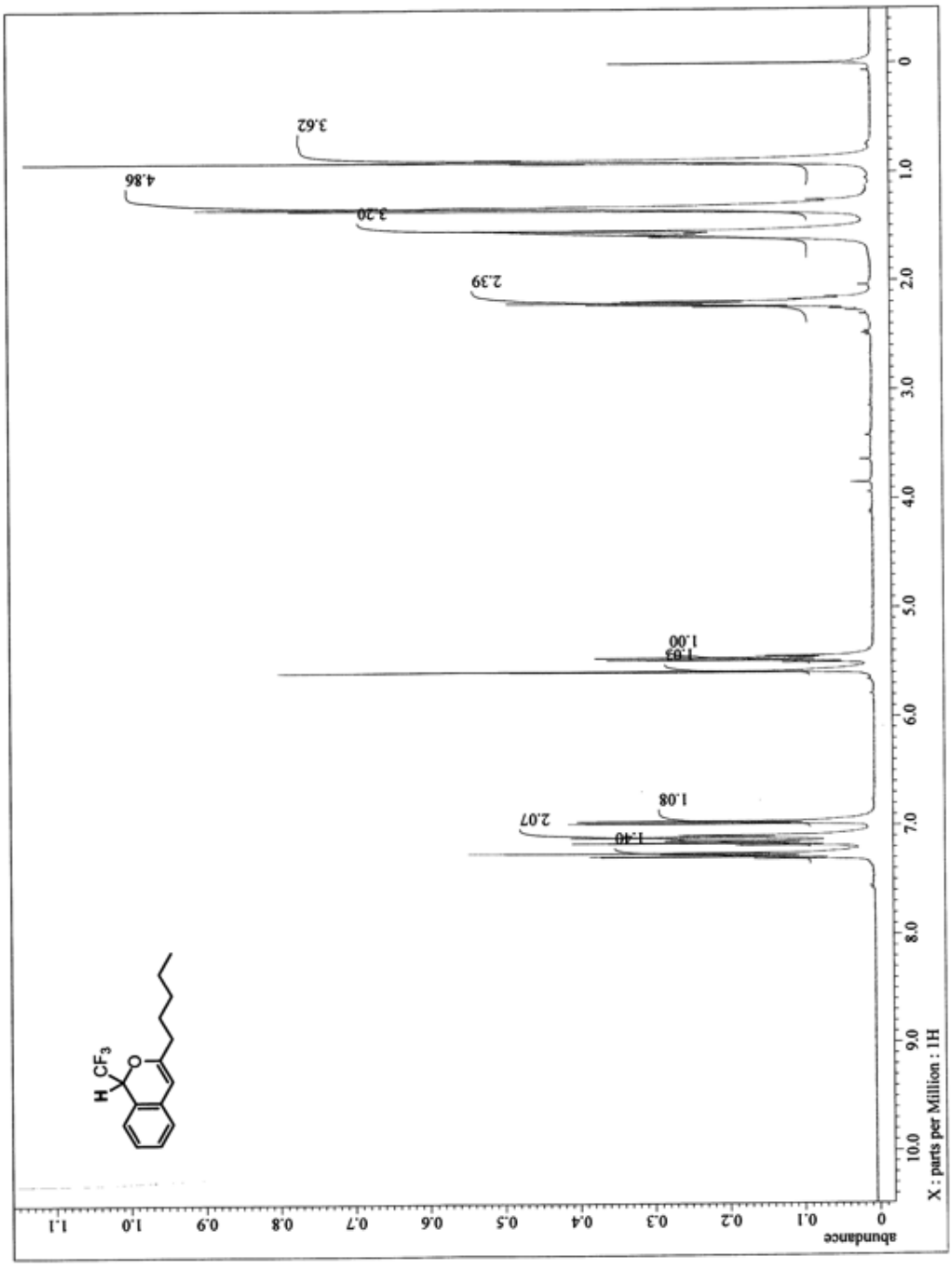
^{13}C NMR spectrum of **2j**.



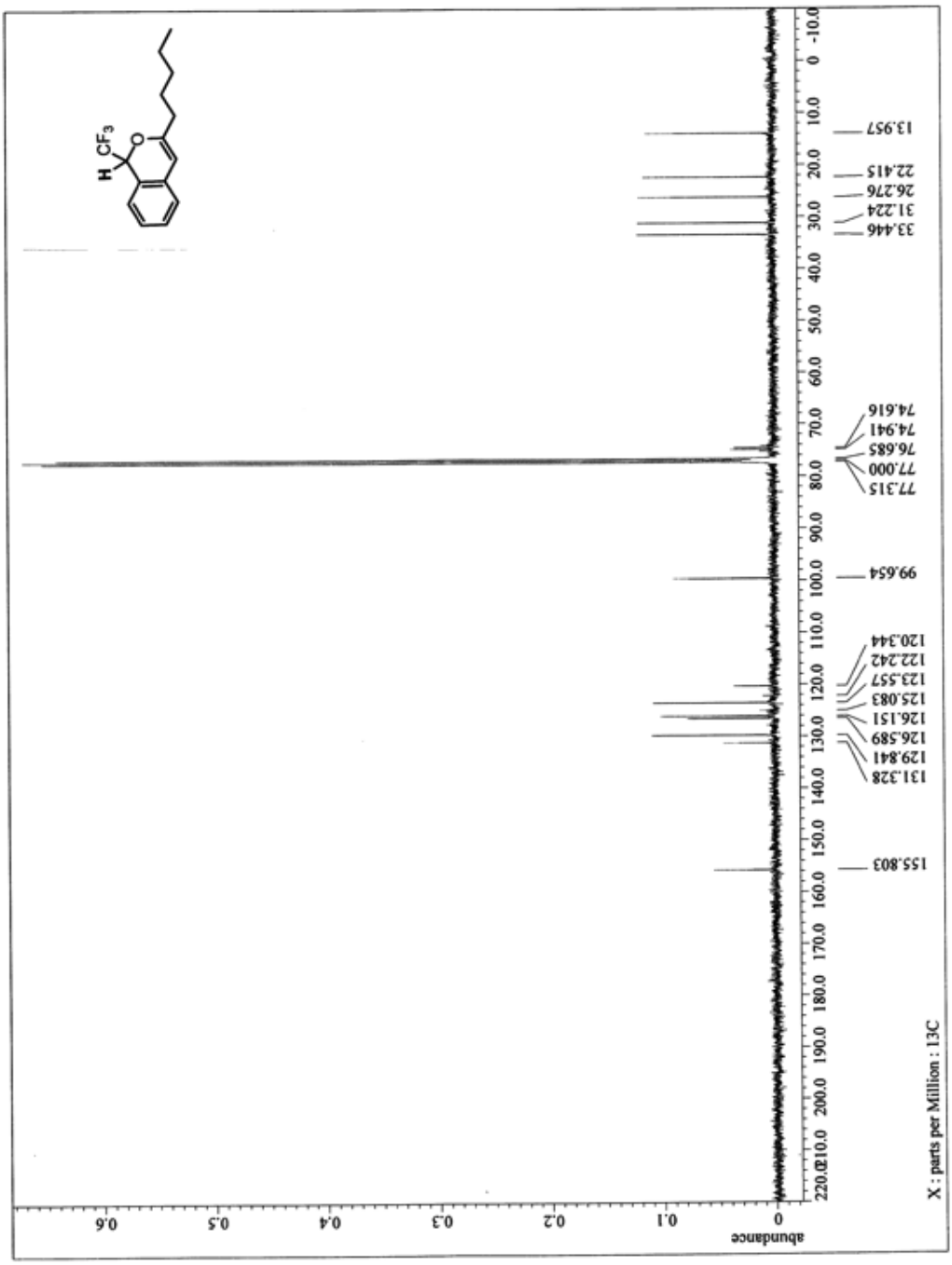
^{19}F NMR spectrum of **2j**.



^{1}H NMR spectrum of **2k**.



^{13}C NMR spectrum of **2k**.



^{19}F NMR spectrum of **2k**.