N-Heterocyclic Carbene-Catalyzed Decarboxylative Alkylation of Aldehydes

Takuya Ishii, Yuki Kakeno, Kazunori Nagao*, and Hirohisa Ohmiya*

Division of Pharmaceutical Sciences, Graduate School of Medical Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

*E-mail: Kazunori Nagao : nkazunori@p.kanazawa-u.ac.jp

Hirohisa Ohmiya: ohmiya@p.kanazawa-u.ac.jp

Table of Contents

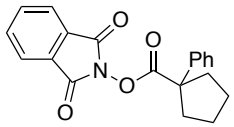
■ Instrumentation and Chemicals■

NMR spectra were recorded on a JNM-ECS400, operating at 400 MHz for ^{1}H NMR and 100.5 MHz for ^{13}C NMR, and JNM-ECA600, operating at 600 MHz for ^{1}H NMR and 150.9 MHz for ^{13}C NMR. Chemical shift values for ^{1}H and ^{13}C are referenced to Me_4Si and the residual solvent resonances, respectively. Chemical shifts are reported in δ ppm. Mass spectra were obtained with JMS-T100TD (DART). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) and aluminum oxide (Nacalai Tesuque, Alumina Activated 200) were used for column chromatography. IR spectra were measured with a Thermo Scientific iD7 ATR Accessory for the Thermo Scientific Nicolet iS5 FT-IR Spectrometer. Melting points were measured on a Yanaco MP-500D apparatus.

All reactions were carried out under nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Li_2CO_3, K_2CO_3, DBU, TMG and iPr_2NEt were purchased from Tokyo Chemical Industry Co., stored under nitrogen, and used as received. Cs_2CO_3 was purchased from Wako Pure Chemical Indusrries, stored under nitrogen, and used as received. DMSO was purchased from Wako Pure Chemical Indusrries, stored under nitrogen, and used as received. Aldehydes **1a**–**1p** were purchased from TCI Chemical Co., stored under nitrogen, and used as received. The redox-active esters were prepared by the reported procedure.[1] The spectra data of **2a**[2], **2b**[1], **2c**[3], **2d**[4], **2g**[4], **2h**[5], **2i**[6], **2l**[6], **2m**[7], **2o**[3], **2p**[8] and **2s**[9] matches that which is previously reported. Thiazolium salt **5** was prepared by the reported procedure.[10]

■ Characterization Data for Redox-Active Esters ■

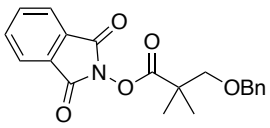
1,3-Dioxoisoindolin-2-yl 1-Phenylcyclopentane-1-carboxylate (2e)



2e

White solid. **M.p.** 81–83 ℃. **IR (neat)** 1066, 1081, 1186, 1366, 1467, 1740, 1778 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.82–1.96 (m, 4H), 2.10–2.18 (m, 2H), 2.76–2.82 (m, 2H), 7.32 (m, 1H), 7.38–7.42 (m, 2H), 7.47–7.50 (m, 2H), 7.73–7.78 (m, 2H), 7.81–7.85 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 23.8, 37.0, 58.0, 123.8, 126.8, 127.4, 128.6, 129.0, 134.6, 141.1, 162.0, 172.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{18}NO_4$, 336.1230; found, 336.1236.

1,3-Dioxoisoindolin-2-yl 3-(Benzyloxy)-2,2-dimethylpropanoate (2f)

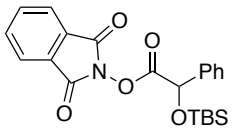


2f

White solid. **M.p.** 63–65 ℃. **IR (neat)** 694, 877, 1052, 1186, 1739 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.44 (s, 6H), 3.63 (s, 2H), 4.64 (s, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H),

7.40 (d, J = 7.2 Hz, 2H), 7.77 (dd, J = 5.5, 3.1 Hz, 2H), 7.88 (dd, J = 5.5, 3.1 Hz, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 22.3, 43.5, 73.5, 76.0, 123.8, 127.5, 127.6, 128.3, 129.0, 134.6, 138.1, 161.9, 172.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{20}NO_5$, 354.1336; found, 354.1323.

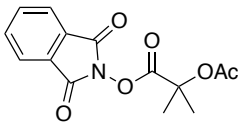
1,3-Dioxoisoindolin-2-yl 2-[(*tert*-Butyldimethylsilyl)oxy]-2-phenylacetate (2j)



2j

White solid. **M.p.** 57–60 ℃. **IR (neat)** 695, 839, 1070, 1186, 1746 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.22 (s, 3H), 0.95 (s, 9H), 5.61 (s, 1H), 7.37–7.45 (m, 3H), 7.59 (d, J = 7.3 Hz, 2H), 7.77 (dd, J = 5.5, 3.2 Hz, 2H), 7.85 (dd, J = 5.5, 3.2 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ –5.2, –5.1, 18.3, 25.6, 72.9, 123.9, 126.6, 128.7, 128.89, 128.92, 134.7, 137.2, 161.6, 168.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{26}NO_5Si$, 412.1575; found, 412.1594.

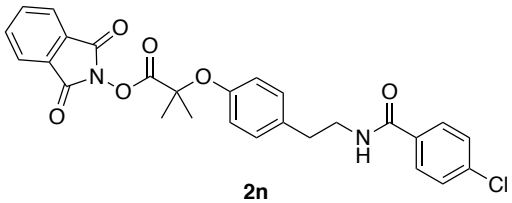
1,3-Dioxoisoindolin-2-yl 2-Acetoxy-2-methylpropanoate (2k)



2k

White solid. **M.p.** 98–100 ℃. **IR (neat)** 696, 1061, 1249, 1369, 1742 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (s, 6H), 2.15 (s, 3H), 7.79 (dd, J = 5.5, 3.2 Hz, 2H), 7.89 (dd, J = 5.5, 3.2 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 20.8, 24.7, 76.8, 123.9, 128.9, 134.7, 161.5, 169.0, 169.7. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{14}NO_6$, 292.0816; found, 292.0831.

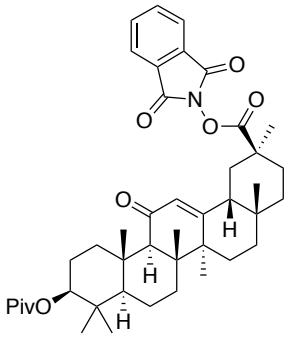
1,3-Dioxoisoindolin-2-yl 2-{4-[2-(4-Chlorobenzamido)ethyl]phenoxy}-2-methylpropanoate (2n)



2n

White solid. **M.p.** 135–137 ℃. **IR (neat)** 1184, 1226, 1485, 1507, 1637, 1741, 1785 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.80 (s, 6H), 2.89 (t, J = 6.4 Hz, 2H), 3.69 (q, J = 6.4 Hz, 2H), 6.19 (brs, 1H), 7.04–7.07 (m, 2H), 7.17–7.20 (m, 2H), 7.33–7.37 (m, 2H), 7.60–7.64 (m, 2H), 7.79–7.82 (m, 2H), 7.84–7.87 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 25.7, 34.8, 41.1, 77.3, 78.7, 120.2, 124.0, 128.3, 128.8, 129.8, 133.0, 133.4, 134.9, 137.5, 153.5, 161.8, 166.4, 170.8. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{24}ClN_2O_6$, 507.1317; found, 507.1344.

1,3-Dioxoisoindolin-2-yl (*2S*,*4aS*,*6aS*,*6bR*,*8aR*,*10S*,*12aS*,*12bR*,*14bR*)-2,4a,6a,6b,9,9,12a-Heptamethyl-13-oxo-10-(pivaloyloxy)-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (2q)



2q

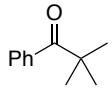
White solid. **M.p.** 250 ℃ (decomposed). **IR (neat)** 1391, 1466, 1655, 1712, 1746, 1780, 2341, 2360, 2970 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 0.82 (m, 1H), 0.87 (s, 3H), 0.90 (s, 3H), 0.91 (s, 3H), 1.03–1.10 (m, 2H), 1.15 (s, 3H), 1.16 (s, 3H), 1.20 (s, 9H), 1.39 (s, 3H), 1.44 (s, 3H), 1.47–1.51 (m, 3H), 1.57–1.70 (m, 7H), 1.78 (t, J = 13.6 Hz, 1H), 1.87 (m, 1H), 2.04–2.10 (m, 2H), 2.12 (m, 1H), 2.37 (s, 1H), 2.46 (m, 1H), 2.80 (m, 1H), 2.46 (m, 1H), 5.77 (s, 1H), 7.78–7.80 (m, 2H), 7.87–7.90 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 16.4, 16.8, 17.3, 18.7, 23.3, 26.4 (× 2C), 27.2, 27.9, 28.0, 28.3, 31.4, 31.8, 32.7, 37.0, 37.2, 38.2, 38.7, 39.0, 41.2, 43.1, 43.9, 45.3, 47.7, 55.0, 61.7, 80.0, 123.9, 127.7, 139.0, 134.7, 162.1, 168.4, 172.6, 178.1, 199.9. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{43}H_{58}NO_7$, 700.4208; found, 700.4120. **[α]$_D^{24}$** +14.4 (*c* 1.00, $CHCl_3$).

■ Procedure for Cross-Coupling of Aldehydes and Redox-Active Esters ■

The reaction in Table 1 entry 1 is representative. Thiazolium salt **N1** (8.3 mg, 0.02 mmol) and redox-active esters **2a** (49.5 mg, 0.2 mmol) were placed in a schlenk tube containing a magnetic stirring bar. The tube was sealed with a rubber septum, and then evacuated and filled with argon. Degassed DMSO (0.4 mL) was added to the tube. Next, benzaldehyde (**1a**) (31.2 μL, 0.3 mmol) were added. Then, Cs_2CO_3 (13.0 mg, 0.04 mmol) was added. After 4 h stirring at 60 ˚C, the reaction mixture was treated with sat. NH_4Claq. (400 μL), then extracted with diethylether (4 times) and dried over sodium sulfate. After filtration, the resulting solution was evaporated under reduced pressure. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–98:2, hexane/EtOAc) gave **3aa** (24.9 mg, 0.15 mmol) in 77% yield.

■ Characterization Data for Aryl alkyl ketones ■

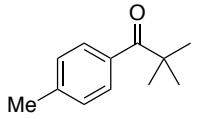
2,2-Dimethyl-1-phenyl-1-propanone (3aa)



3aa

The product **3aa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 1, entry 1; 24.9 mg, 0.15 mmol, 77% isolated yield). The spectrum data of product **3aa** was consistent with the literature.[11]

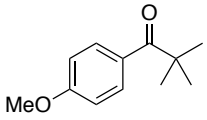
2,2-Dimethyl-1-(*p*-tolyl)propan-1-one (3ba)



3ba

The product **3ba** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 25.0 mg, 0.14 mmol, 71% isolated yield). The spectrum data of product **3ba** was consistent with the literature.[12]

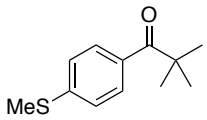
1-(4-Methoxyphenyl)-2,2-dimethylpropan-1-one (3ca)



3ca

The product **3ca** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 27.7 mg, 0.14 mmol, 72% isolated yield). The spectrum data of product **3ca** was consistent with the literature.[13]

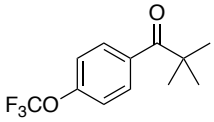
2,2-Dimethyl-1-[4-(methylthio)phenyl]propan-1-one (3da)



3da

The product **3da** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 22.7 mg, 0.11 mmol, 54% isolated yield). The spectrum data of product **3da** was consistent with the literature.[14]

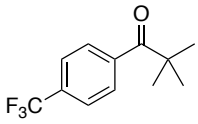
2,2-Dimethyl-1-[4-(trifluoromethoxy)phenyl]propan-1-one (3ea)



3ea

The product **3ea** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 39.9 mg, 0.16 mmol, 81 % isolated yield). Pale yellow oil. **IR** (neat) 1211, 1256, 1368, 1479, 1504, 1602, 1679 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 7.24 (d, J = 8.2 Hz, 2H), 7.76–7.80 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 27.9, 44.2, 120.0, 120.4 (q, J = 257 Hz), 139.9, 136.6, 150.9, 207.5. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{14}F_3O_2$, 247.0940; found, 247.0946.

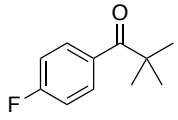
2,2-Dimethyl-1-[4-(trifluoromethyl)phenyl]propan-1-one (3fa)



3fa

The product **3fa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 35.9 mg, 0.16 mmol, 78% isolated yield). The spectrum data of product **3fa** was consistent with the literature.[13]

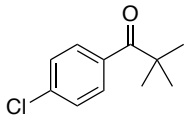
1-(4-Fluorophenyl)-2,2-dimethylpropan-1-one (3ga)



3ga

The product **3ga** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 34.2 mg, 0.19 mmol, 95% isolated yield). The spectrum data of product **3ga** was consistent with the literature.[15]

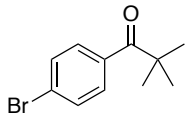
1-(4-Chlorophenyl)-2,2-dimethylpropan-1-one (3ha)



3ha

The product **3ha** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 31.5 mg, 0.16 mmol, 80% isolated yield). The spectrum data of product **3ha** was consistent with the literature.[15]

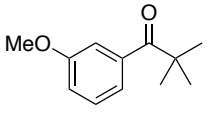
1-(4-Bromophenyl)-2,2-dimethylpropan-1-one (3ia)



3ia

The product **3ia** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 34.2 mg, 0.14 mmol, 71% isolated yield). The spectrum data of product **3ia** was consistent with the literature.[13]

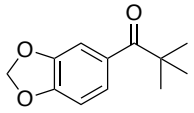
1-(3-Methoxyphenyl)-2,2-dimethylpropan-1-one (3ja)



3ja

The product **3ja** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 31.5 mg, 0.16 mmol, 82% isolated yield). The spectrum data of product **3ja** was consistent with the literature.[16]

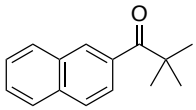
1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2-dimethylpropan-1-one (3ka)



3ka

The product **3ka** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 17.9 mg, 0.09 mmol, 43% isolated yield). Colorless oil. **IR** (neat) 1235, 1260, 1280, 1433, 1488, 1503, 1607, 1666 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.36 (s, 9H), 6.02 (s, 2H), 6.82 (m, 1H), 7.13 (s, 1H), 7.44 (m, 1H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 28.4, 43.9, 101.5, 107.5, 109.0, 124.1, 131.8, 147.5, 150.1, 206.1. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{15}O_3$, 207.1016; found, 207.1011.

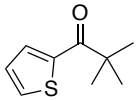
2,2-Dimethyl-1-(naphthalen-2-yl)propan-1-one (3la)



3la

The product **3la** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 23.8 mg, 0.11 mmol, 56% isolated yield). The spectrum data of product **3la** was consistent with the literature.[17]

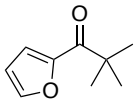
2,2-Dimethyl-1-(thiophen-2-yl)propan-1-one (3ma)



3ma

The product **3ma** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 32.6 mg, 0.19 mmol, 97% isolated yield). The spectrum data of product **3ma** was consistent with the literature.[18]

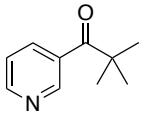
1-(Furan-2-yl)-2,2-dimethylpropan-1-one (3na)



3na

The product **3na** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 20.7 mg, 0.14 mmol, 68% isolated yield). The spectrum data of product **3na** was consistent with the literature.[19]

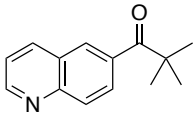
2,2-Dimethyl-1-(pyridin-3-yl)propan-1-one (3oa)



3oa

The product **3oa** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 21.9 mg, 0.13 mmol, 67% isolated yield). The spectrum data of product **3oa** was consistent with the literature.[20]

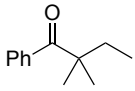
2,2-Dimethyl-1-(quinolin-6-yl)propan-1-one (3pa)



3pa

The product **3pa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 10.2 mg, 0.05 mmol, 24% isolated yield). Pale yellow oil. **IR** (neat) 1322, 1366, 1395, 1458, 1477, 1620, 1674, 2359 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.43 (s, 9H), 7.47 (m, 1H), 8.02 (m, 1H), 8.13 (d, J = 8.9 Hz, 1H), 8.19 (d, J = 2.0 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H), 8.99 (m, 1H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 28.0, 44.4, 121.8, 127.3, 128.2, 128.4, 129.3, 134.5, 137.1, 148.8, 151.9, 208.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{16}NO$, 214.1226; found, 214.1232.

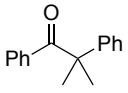
2,2-Dimethyl-1-phenylbutan-1-one (3ab)



3ab

The product **3ab** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 22.6 mg, 0.13 mmol, 64% isolated yield). The spectrum data of product **3ab** was consistent with the literature.[21]

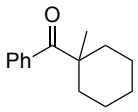
2-Methyl-1,2-diphenylpropan-1-one (3ac)



3ac

The product **3ac** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 34.1 mg, 0.15 mmol, 76% isolated yield). The spectrum data of product **3ac** was consistent with the literature.[21]

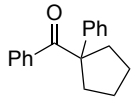
(1-Methylcyclohexyl)(phenyl)methanone (3ad)



3ad

The product **3ad** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 30.3mg, 0.15 mmol, 75% isolated yield). The spectrum data of product **3ad** was consistent with the literature.[22]

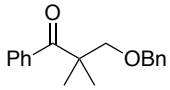
Phenyl(1-phenylcyclopentyl)methanone (3ae)



3ae

The product **3ae** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 18.5 mg, 0.07 mmol, 37% isolated yield). Pale yellow oil. **IR** (neat) 1236, 1447, 1495, 1578, 1597, 1675, 2341, 2360 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.65–1.80 (m, 4H), 2.06–2.13 (m, 2H), 2.48–2.54 (m, 2H), 7.22–7.26 (m, 3H), 7.30–7.38 (m, 5H), 7.61–7.63 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 24.6, 37.4, 63.3, 126.0, 126.5, 127.9, 128.9, 129.8, 131.7, 136.1, 144.5, 202.1. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{19}O$, 251.1430; found, 251.1438.

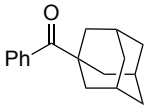
3-(Benzyloxy)-2,2-dimethyl-1-phenylpropan-1-one (3af)



3af

The product **3af** was purified by flash chromatography on silica gel (100:0–92:8, hexane/EtOAc) (Table 2; 27.8 mg, 0.104 mmol, 52% isolated yield). Yellow oil. **IR** (neat) 698, 1099, 1363, 1454, 1677, 2862 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.33 (s, 6H), 3.59 (s, 2H), 4.47 (s, 2H), 7.23–7.32 (m, 5H), 7.36 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ 23.4, 48.9, 73.3, 77.4, 127.2, 127.4, 127.5, 128.0, 128.3, 130.4, 138.2, 139.5, 208.9. **HRMS–DART** (*m/z*): $[M]^+$ calcd for $C_{18}H_{21}O_2$, 269.1536; found, 269.1521.

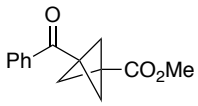
(Adamantan-1-yl)(phenyl)methanone (3ag)



3ag

The product **3ag** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 15.4 mg, 0.06 mmol, 32% isolated yield). The spectrum data of product **3ag** was consistent with the literature.[23]

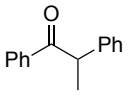
Methyl 3-Benzoylbicyclo[1.1.1]pentane-1-carboxylate (3ah)



3ah

The product **3ah** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 9.2 mg, 0.04 mmol, 20% isolated yield). Colorless oil. **IR** (neat) 1283, 1314, 1437, 1448, 1598, 1664, 1730. cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.56 (s, 6H), 3.72 (s, 3H), 7.45–7.48 (m, 2H), 7.58 (m, 1H), 7.97–7.98 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 38.2, 43.8, 51.9, 54.4, 128.6, 128.8, 133.2, 136.1, 169.9, 196.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{15}O_3$, 231.1016; found, 231.1012.

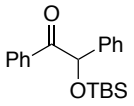
1,2-Diphenylpropan-1-one (3ai)



3ai

The product **3ai** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 26.9 mg, 0.13 mmol, 64% isolated yield). The spectrum data of product **3ai** was consistent with the literature.[24]

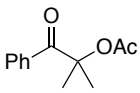
2-[(*tert*-Butyldimethylsilyl)oxy]-1,2-diphenylethan-1-one (3aj)



3aj

The product **3aj** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 22.9 mg, 0.070 mmol, 35% isolated yield). Yellow oil. **IR** (neat) 695, 870, 1118, 1256, 1682, 2955 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 5.74 (s, 1H), 7.23–7.36 (m, 5H), 7.45 (t, J = 7.3 Hz, 1H), 7.52 (d, J = 7.3 Hz, 2H), 8.00 (d, J = 7.3 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$) δ –5.1, –5.0, 18.2, 25.7, 80.4, 125.6, 127.7, 128.0, 128.6, 130.0, 132.8, 134.4, 138.9, 199.0. **HRMS–DART** (*m/z*): $[M]^+$ calcd for $C_{20}H_{27}O_2Si$, 327.1775; found, 327.1765.

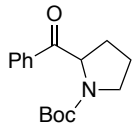
2-Methyl-1-oxo-1-phenylpropan-2-yl Acetate (3ak)



3ak

The product **3ak** was purified by flash chromatography on silica gel (90:10–80:20, hexane/EtOAc) (Table 2; 34.4 mg, 0.167 mmol, 83% isolated yield). The spectrum data of product **3ak** was consistent with the literature.[25]

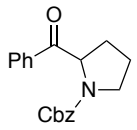
***tert*-Butyl 2-Benzoylpyrrolidine-1-carboxylate (3al)**



3al

The product **3al** was purified by flash chromatography on silica gel (90:10–80:20, hexane/EtOAc) (Table 2; 30.8 mg, 0.112 mmol, 56% isolated yield). The spectrum data of product **3al** was consistent with the literature.[26]

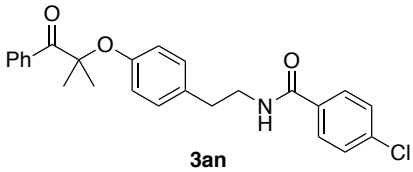
Benzyl 2-Benzoylpyrrolidine-1-carboxylate (3am)



3am

The product **3am** was purified by flash chromatography on silica gel (85:15–70:30, hexane/EtOAc) (Table 2; 42.0 mg, 0.136 mmol, 68% isolated yield). The spectrum data of product **3am** was consistent with the literature.[27]

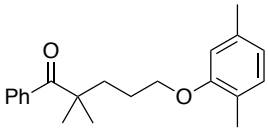
4-Chloro-*N*-{4-[(2-methyl-1-oxo-1-phenylpropan-2-yl)oxy]phenethyl}benzamide (3an)



3an

The product **3an** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 41.3 mg, 0.98 mmol, 49% isolated yield). Colorless oil. **IR** (neat) 1233, 1381, 1486, 1508, 1542, 1596, 1637, 1677 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.68 (s, 6H), 2.78 (t, J = 6.8 Hz, 2H), 3.60 (m, 2H), 6.00 (brs, 1H), 6.71–6.73 (m, 2H), 6.98–7.00 (m, 2H), 7.34–7.36 (m, 2H), 7.38–7.41 (m, 2H), 7.50 (m, 1H), 7.55–7.57 (m, 2H), 8.30–8.32 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 26.0, 34.6, 41.1, 84.9, 118.9, 128.2, 128.4, 128.8, 129.6, 130.1, 132.1, 132.9, 133.0, 134.3, 137.6, 154.2, 166.3, 202.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}ClNO_3$, 422.1517; found, 422.1523.

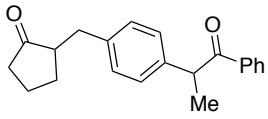
5-(2,5-Dimethylphenoxy)-2,2-dimethyl-1-phenylpentan-1-one (3ao)



3ao

The product **3ao** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Table 2; 41.6 mg, 0.13 mmol, 67% isolated yield). The spectrum data of product **3ao** was consistent with the literature.[28]

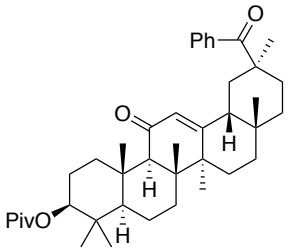
4-Chloro-*N*-{4-[(2-methyl-1-oxo-1-phenylpropan-2-yl)oxy]phenethyl}benzamide (3ap)



3ap

The product **3ap** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 33.1 mg, 0.11 mmol, 54% isolated yield). Colorless oil. **IR** (neat) 1221, 1341, 1448, 1511, 1596, 1681, 1736, 2968 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.51 (m, 1H), 1.51 (d, J = 6.8 Hz, 3H), 1.70 (m, 1H), 1.92 (m, 1H), 2.02–2.10 (m, 2H), 2.26–2.33 (m, 2H), 2.45 (m, 1H), 3.08 (m, 1H), 4.66 (m, 1H), 7.08–7.09 (m, 2H), 7.19–7.20 (m, 2H), 7.37–7.41 (m, 2H), 7.48 (m, 1H), 7.94–7.96 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 19.4, 20.4, 29.2, 35.1, 38.1, 47.3, 50.9, 127.7, 128.4, 128.7, 129.4, 132.7, 136.4, 138.6, 139.1, 200.3, 220.1. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{23}O_2$, 307.1693; found, 307.1683.

(3*S*,4a*R*,6a*R*,6b*S*,8a*S*,11*S*,12a*R*,14a*R*,14b*S*)-11-Benzoyl-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl Pivalate (3aq)



3aq

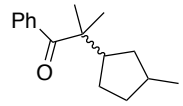
The product **3ar** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Table 2; 67.6 mg, 0.11 mmol, 55% isolated yield). A single diastereomer was observed. Colorless oil. **IR** (neat) 1207, 1285, 1387, 1457, 1662, 1722, 2342, 2359 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 0.80 (m, 1H), 0.87 (s, 3H), 0.89 (s, 3H), 0.90 (s, 3H), 1.01–1.09 (m, 2H), 1.14 (s, 3H), 1.17 (s, 3H), 1.20 (s, 9H), 1.33 (s, 3H), 1.37 (s, 3H), 1.40–1.48 (m, 3H), 1.56–1.70 (m, 8H), 1.79–1.85 (m, 1H), 1.94 (m, 1H), 2.04 (m, 1H), 2.18–2.26 (m, 2H), 2.36 (s, 1H), 2.78 (m, 1H), 4.46 (m, 1H), 5.64 (s, 1H), 7.39–7.41 (m, 2H), 7.46 (m, 1H), 7.61–7.62 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 16.4, 16.8, 17.3, 18.7, 19.8, 23.26, 23.30, 26.3, 26.4, 27.2, 28.0, 28.4, 29.4, 32.2, 32.6, 35.4, 36.9, 38.2, 38.6, 39.0, 39.5, 43.4, 45.4, 46.5, 47.8, 54.9, 61.7, 80.0, 127.7, 128.1, 128.6, 130.8, 138.5, 169.2, 178.1, 200.2, 208.9. **HRMS–DART** (*m/z*): $[M]^+$ calcd for $C_{41}H_{58}O_4$, 614.4330; found, 614.4361. **$[\alpha]_D^{24}$** +3.6 (*c* 0.88, $CHCl_3$).

■ Procedure for Ring-Closing Experiment (Scheme 2A) ■

Thiazolium salt **N1** (41.4 mg, 0.1 mmol) and redox-active esters **2r** (31.5 mg, 0.1 mmol) were placed in a schlenk tube containing a magnetic stirring bar. The tube was sealed with a rubber septum, and then evacuated and filled with argon. Degassed DMSO (0.40 mL) was added to the tube. Next, benzaldehyde (**1a**) (10.4 μL, 0.1 mmol) were added. Then, Cs_2CO_3 (130.3 mg, 0.4 mmol) was added. After 4 h stirring at 60 ˚C, the reaction mixture was treated with sat. NH_4Claq. (400 μL). The reaction mixture was extracted with diethylether (4 times) and dried over sodium sulfate. After filtration, the

resulting solution was evaporated under reduced pressure. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–98:2% EtOAc/hexane) gave **3ar** (3.2 mg, 0.014 mmol, 14% yield) and **3ar'** (3.7 mg, 0.016 mmol, 16% yield).

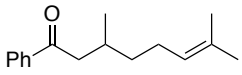
2-Methyl-2-(3-methylcyclopentyl)-1-phenylpropan-1-one (**3ar**)



3ar

The product **3ar** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Scheme 2A; 3.2 mg, 0.014 mmol, 14% isolated yield). The diastereomeric ratio is 1:1 determined by ^{1}H NMR. Pale yellow oil. **IR** (neat)1366, 1387, 1444, 1466, 1673, 1750 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 0.94 (d, J = 6.5Hz, 0.5 × 3H), 0.98 (d, J = 6.5Hz, 0.5 × 3H), 1.02–1.10 (m, 1H), 1.16 (m, 0.5 × 1H), 1.24–1.26 (m, 6H), 1.32 (m, 0.5 × 1H), 1.42 (m, 0.5 × 1H), 1.53–1.58 (m, 0.5 × 2H + 0.5 × 1H), 1.61–1.80 (m, 2H), 1.86 (m, 0.5 × 1H), 1.91 (m, 0.5 × 1H) 2.52 (m, 0.5 × 1H), 2.61 (m, 0.5 × 1H), 7.37–7.39 (m, 2H), 7.44 (m, 1H), 7.58–7.60 (m, 2H). **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 20.4, 20.86, 20.87, 22.4, 22.5, 22.7, 22.8, 26.4, 28.0, 34.0, 34.2, 34.5, 35.2, 35.3, 36.8, 45.4, 46.9, 50.0, 50.3, 127.28, 127.32, 128.0, 130.27, 130.33, 140.0, 140.1, 210.2, 210.3. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{23}O$, 231.1743; found, 231.1751.

3,7-Dimethyl-1-phenyloct-6-en-1-one (**3ar'**)



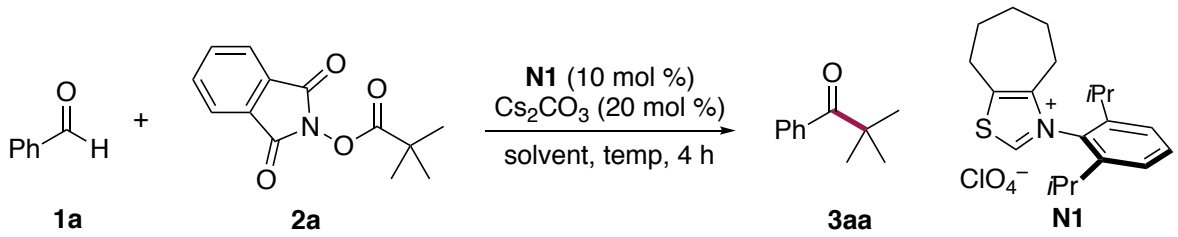
3ar'

The product **3ar'** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Scheme 2A; 3.7 mg, 0.016 mmol, 16% isolated yield). The spectrum data of product **3ar'** was consistent with the literature.[29]

■ Procedure for Stoichiometric Reaction (Scheme 2B) ■

Silylated thiazolium benzyl alcohol **5** (34.9 mg, 0.1 mmol) and redox-active esters **2a** (24.7 mg, 0.1 mmol) were placed in a schlenk containing a magnetic stirring bar. The tube was sealed with a rubber septum, and then evacuated and filled with argon. DMSO (400 μL) was added to the reaction mixture. Next, TBAF in 1.0 M THF solution (100 μL, 0.1 mmol) was added [After stirring for 10 min, Cs_2CO_3 (32.5 mg, 0.1 mmol) was added.]. The reaction mixture was stirred for 1 h at 60 ^{o}C. After 1 h stirring at 60 ˚C, the reaction mixture was treated with sat. NH_4Claq. (400 μL). The reaction mixture was extracted with diethylether (4 times) and dried over sodium sulfate. After filtration, the resulting solution was evaporated under reduced pressure. The yield of the product **3aa** was determined by ^{1}H-NMR analysis (internal standard: tetrachloroethane).

■ Screenings of Solvent and Temperature ■



1a **2a** **3aa** **N1**

solvent	temp (°C)	yield of **3aa** (%)
DMSO	60	99
NMP	60	44
MeCN	60	20
THF	60	10
toluene	60	0
DCE	60	0
DMSO	25	3
DMSO	40	20
DMSO	80	71

Table S1. Screenings of Solvent and Temperature

■ Intermediate Analysis by Theoretical Calculation ■

DFT calculation on the ketyl radical, which is derived from the reaction of benzaldehyde **1a**, a thiazolium salt **N1** and Cs_2CO_3, was carried out. The SOMO of the ketyl radical is shown as Figure S1. The bulky substituent, isopropyl group covers the radical center, and thus might stabilize the radical.

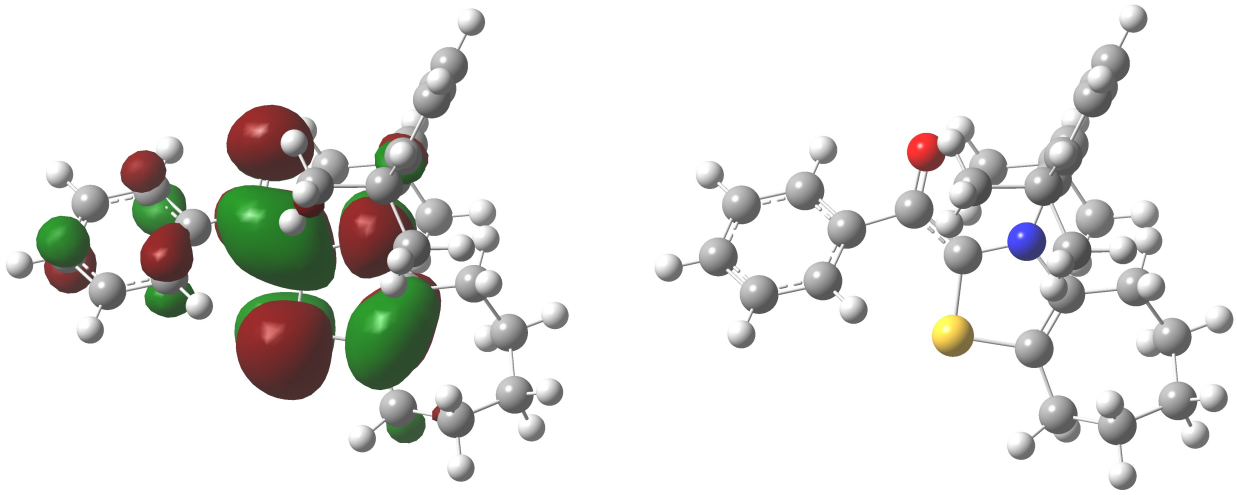


Figure S1. SOMO orbital of the enolate radical of the Breslow intermediate

DFT calculation was conducted using the Gaussian 09 program.[30] Geometry optimizations were conducted using DFT method with UB3LYP functional.[31] The usual 6-31+G(d) basis sets were used for all atoms.[32]

atom	x	y	z
C	-1.17366	0.15267	0
C	-1.92687	-0.73187	-0.77295
C	-3.31199	-0.80324	-0.61079
C	-3.96449	0.00872	0.33053
C	-3.19801	0.91572	1.0821
C	-1.81634	0.98029	0.92638
H	-0.09521	0.20518	-0.12462
H	-1.43926	-1.36118	-1.51307
H	-3.88535	-1.47106	-1.24646
H	-3.71383	1.56649	1.78053
H	-1.23731	1.67955	1.52427
C	-5.44972	0.02947	0.54324
C	-8.1482	-2.51319	0.47899
C	-7.21309	-3.49734	0.48284
C	-6.21741	-1.17376	0.38793
N	-7.60908	-1.21928	0.42785
S	-5.58343	-2.81934	0.40052
C	-9.63879	-2.68435	0.51193
H	-10.08131	-2.17195	1.37316
H	-10.11012	-2.26854	-0.3855
C	-7.37883	-4.98488	0.53789
H	-8.23864	-5.27211	1.15675
H	-6.49253	-5.46926	0.96763
O	-6.00331	1.09818	0.89513
C	-8.46414	-0.07514	0.18219
C	-9.02197	0.61086	1.27333
C	-8.75708	0.26548	-1.14899
C	-9.9176	1.65007	1.00204
C	-9.6526	1.31808	-1.37433
C	-10.23407	2.00191	-0.30924
H	-10.35863	2.19564	1.83233
H	-9.89239	1.59766	-2.39712
H	-10.93071	2.81372	-0.50071
C	-8.61643	0.28823	2.68866
H	-9.23463	0.83524	3.40695
C	-8.1183	-0.46274	-2.30843
H	-8.53582	-0.11664	-3.25856
C	-7.5974	-5.57461	-0.86783
H	-7.09787	-4.96536	-1.59183
H	-7.20136	-6.56798	-0.9034

C	-9.87393	-4.38948	0.33686
H	-9.56225	-4.60289	1.47545
H	-11.07142	-4.2786	0.65672
C	-9.23871	-5.39888	-0.91634
H	-9.73751	-6.01233	-0.19539
H	-9.39027	-5.80382	-1.8951
C	-8.72541	-1.21415	3.00896
H	-9.49972	-1.65058	2.41326
H	-7.79421	-1.69384	2.79064
H	-8.95801	-1.34188	4.04553
C	-7.14567	0.69677	2.89258
H	-6.50754	-0.11256	2.60504
H	-6.92705	1.55435	2.2912
H	-6.98054	0.93236	3.92317
C	-8.32795	-1.98613	-2.22517
H	-7.43676	-2.44915	-1.85597
H	-9.14097	-2.1986	-1.56279
H	-8.55177	-2.36911	-3.19889
C	-6.59747	-0.22337	-2.3452
H	-6.34834	0.58842	-1.69417
H	-6.08927	-1.10804	-2.02273
H	-6.29811	0.01584	-3.34423

■ References■

(1) Qin, T.; Cornella, J.; Li, C.; Malins, L. R.; Edwards, J. T.; Kawamura, S.; Maxwell, B. D.; Eastgate, M. D.; Baran, P. S. *Science* **2016** *352*, 801.

(2) Xu, X.; Sun, J.; Lin, Y.; Cheng, J.; Li, P.; Jiang, X.; Bai, R.; Xie, Y. *Eur. J. Org. Chem.* **2017**, 7160.

(3) Zheng, C.; Wang, Y.; Xu, Y.; Chen, Z.; Chen, G.; Liang S. G. *Org. Lett.* **2018**, *20*, 4824.

(4) Pratsch, G.; Lackner, G. L.; Overman. L. E.; *J. Org. Chem.* **2015**, *80*, 6025.

(5) Toriyama, F.; Cornella, J.; Wimmer, L.; Chen, T-G.; Dixon, D. D.; Creech, G.; Baran, P. S. *J. Am. Chem. Soc.* **2016**, *138*, 11132.

(6) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. *Science* **2017** *357*, 283.

(7) Qin, T.; Malins, L. R.; Edwards, J. T.; Merchant, R. R.; Novak, A. J. E.; Zhong, J. Z.; Mills, R. B.; Yan, M.; Yuan, C.; Eastgate, M. D.; Baran, P. S. *Angew. Chem., Int. Ed.* **2017**, *56*, 260.

(8) Wang, D.; Zhu, N.; Chen, P.; Lin, Z.; Liu, G. *J. Am. Chem. Soc.* **2017,** *139*, 15632.

(9) Yu, L.; Tang, M.-L.; Si, C.-M.; Meng, Z.; Liang, Y.; Han, J.; Sun, X. *Org. Lett.* **2018**, *20*, 4579.

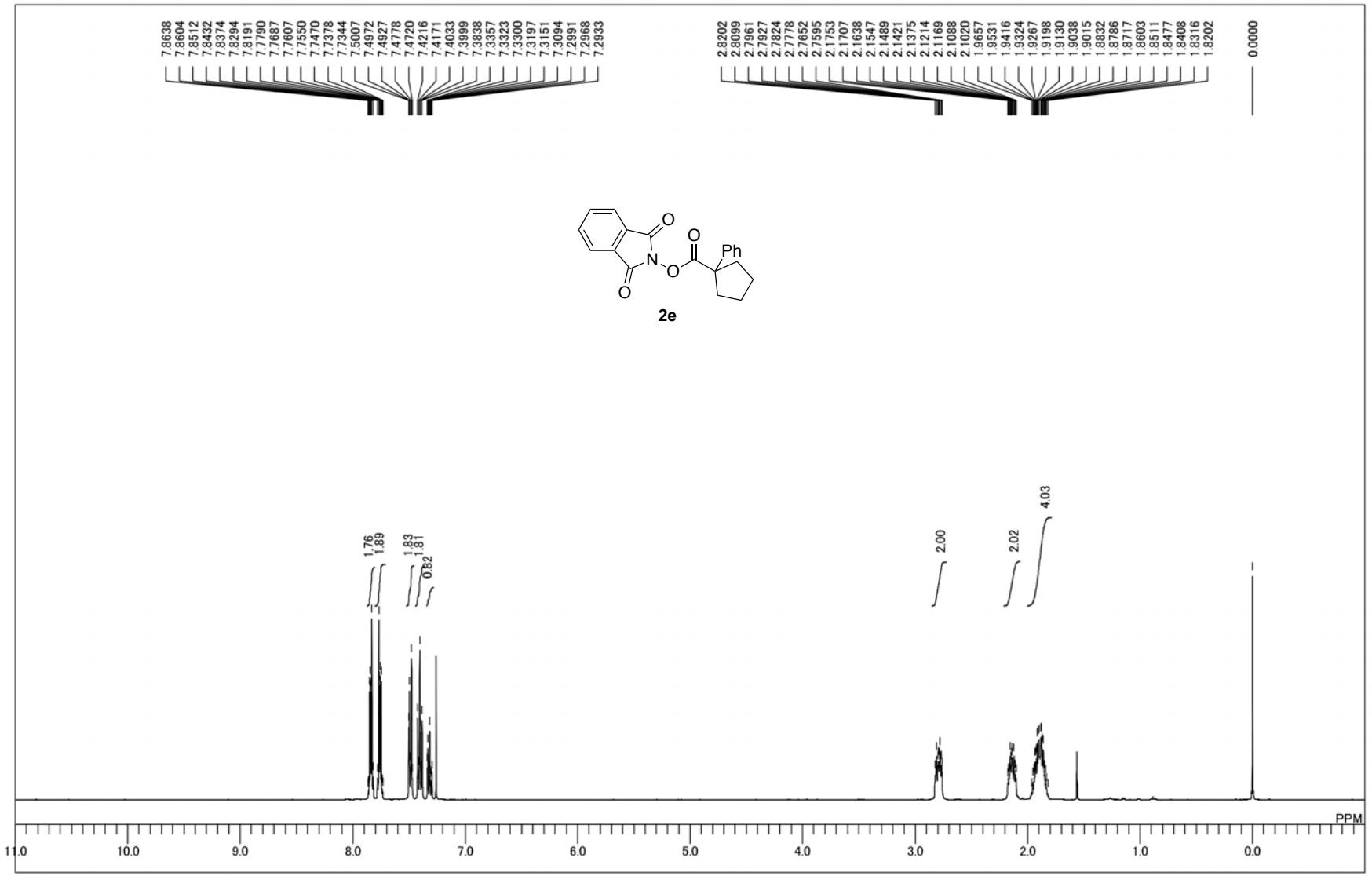
(10) Mattson, A. E.; Zuhl, A. M.; Reynolds, T. E.; Scheidt, K. A. *J. Am. Chem. Soc.* **2006**, *128*, 4932.

(11) Shibuya, M.; Tomizawa, M.; Sasano, Y.; Iwabuchi, Y. *J. Org. Chem.* **2009,** *74*, 4619.

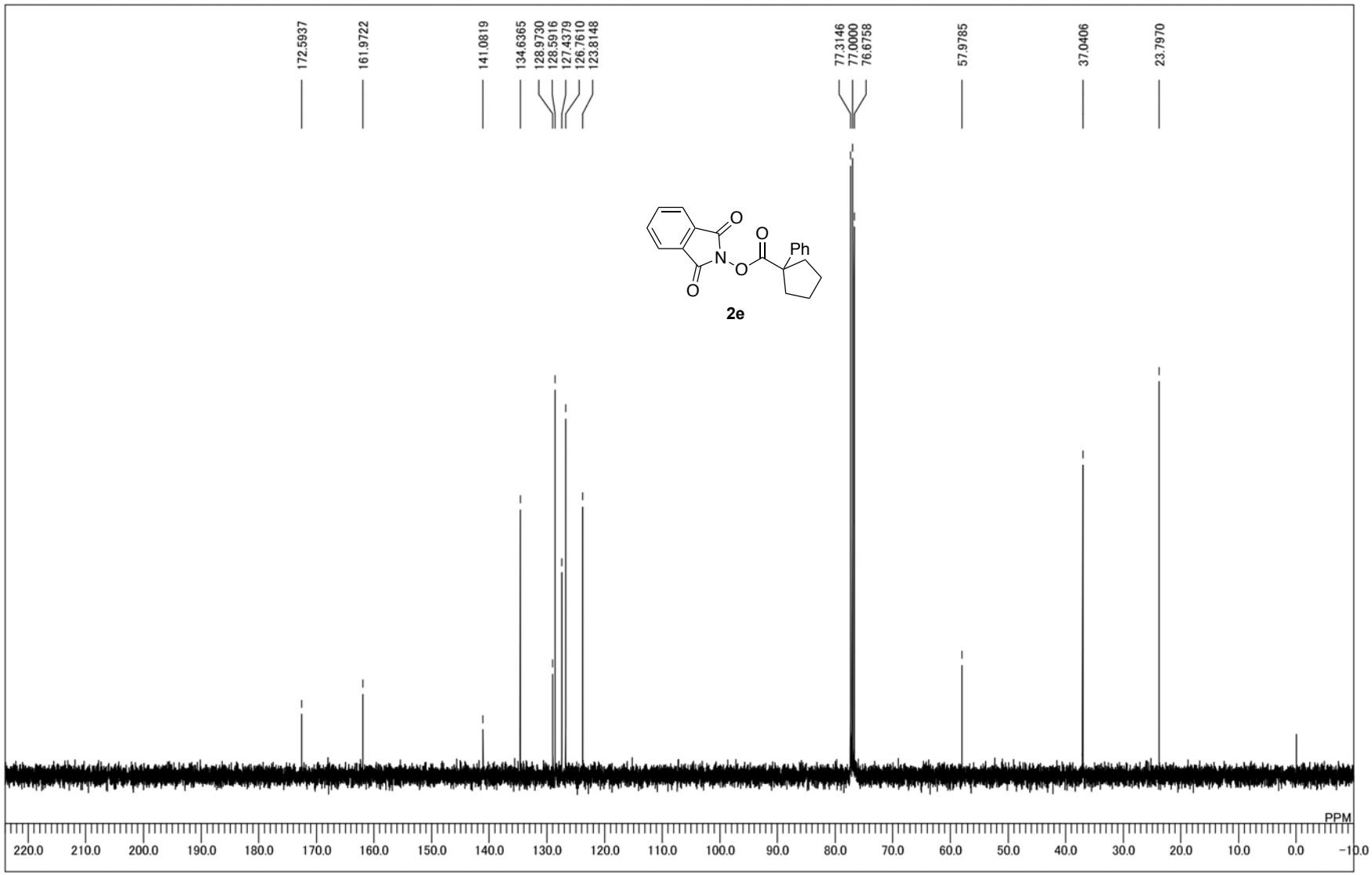
(12) Ushijima, S.; Dohi, S.; Moriyama, K.; Togo, H. *Tetrahedron* **2012,** *68*, 1436.

(13) Fujihara, T.; Semba, K.; Terao, J.; Tsuji, Y. *Angew. Chem. Int. Ed.* **2010***, 49*, 1472.

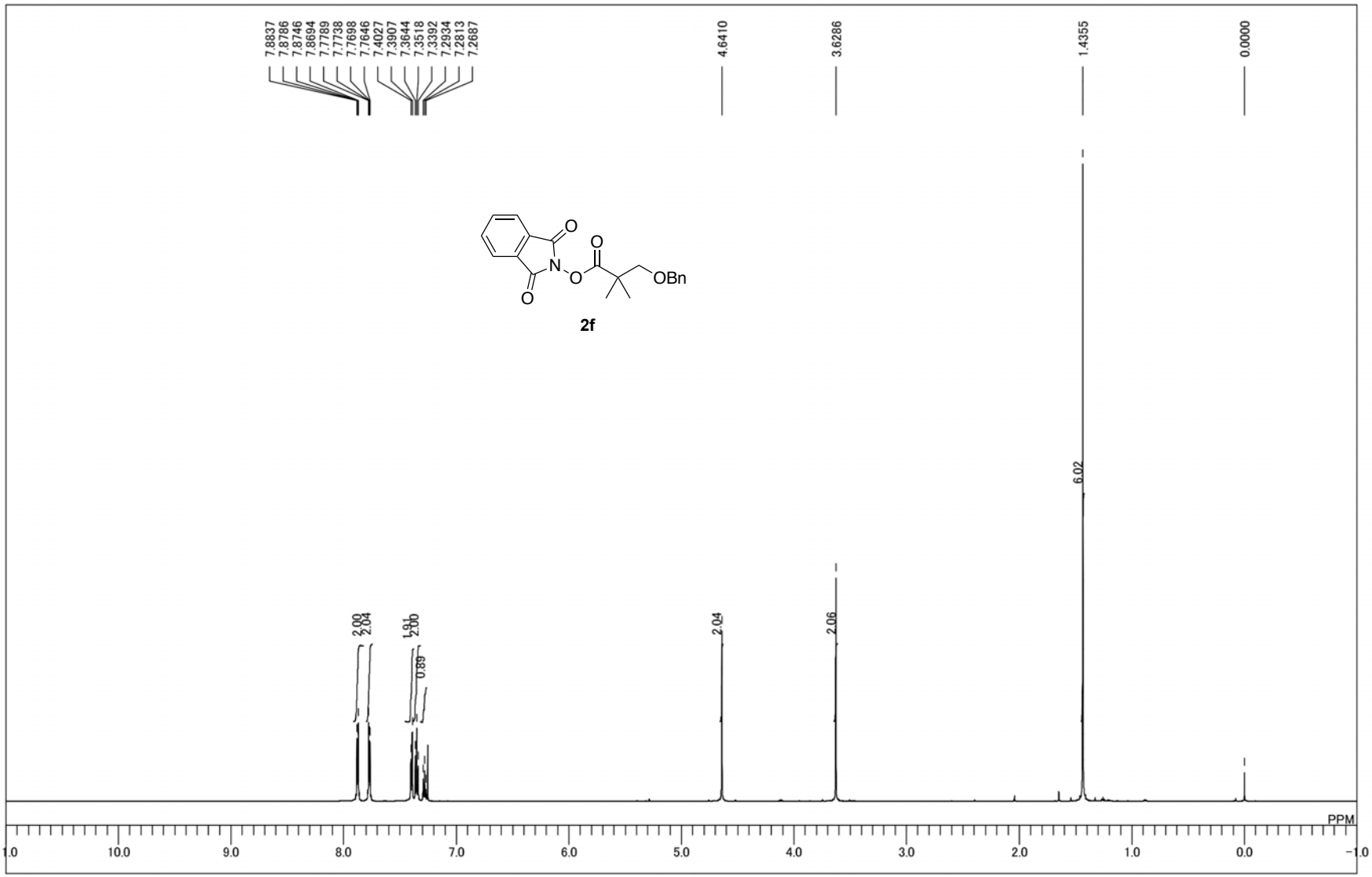
(14) Tsuji, Y.; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 856.
(15) Gohier, F.; Castanet, A.-S.; Mortier, J. *J. Org. Chem.* **2005***, 70,* 1501.
(16) Palmer, B. D.; Boyd, M.; Denny, W. A. *J. Org. Chem.* **1990**, *55*, 438.
(17) Peyman, A.; Hickl, E.; Beckhaus, H.-D. *Chem. Ber.* **1987**, *120*, 713.
(18) Lauber, M. B.; Stahl, S. S. *ACS Catal.* **2013***, 3*, 2612.
(19) Ohkuma, T.; Sandoval, C. A.; Srinivasan, R.; Lin, Q.; Wei, Y.; Muñiz, K.; Noyori, R. *J. Am. Chem. Soc.* **2005,** *127,* 8288.
(20) El Din, M. G.; Knaus, E. E.; Giam, C.-S. *Canadian J. Chem*. **1982**, *60*, 1821.
(21) Díaz-Valenzuela, M.; Phillips, S.; France, M.; Gunn, M.; Clarke, M. *Chem. Eur. J.* **2009**, *15*, 1227.
(22) Kulasekharan, R.; Jayaraj, N.; Porel, M.; Choudhury, R.; Sundaresan, A. K.; Parthasarathy, A.; Ottaviani, M. F.; Jockusch, S.; Turro, N. J.; Ramamurthy V. *Langmuir* **2010** *26*, 6943.
(23) Lo Fiego, M. J.; Lockhart M. T.; Chopa A. B. *J. Organomet. Chem.* **2009**, *694*, 3674.
(24) Šimonyiová S.; Wanner K. T. *Tetrahedron* **2008**, *64,* 5107.
(25) Padwa, A.; Kennedy, G. D. *J. Org. Chem*. **1984**, *49*, 4344.
(26) Kong, C.; Jana, N.; Driver, T. G. *Org. Lett.* **2013**, *15*, 824.
(27) Gribkov, D. V.; Pastine, S. J.; Schnürch, M.; Sames, D. *J. Am. Chem. Soc.* **2007**, *129*, 11750.
(28) Gehrtz, P. H.; Kathe, P.; Fleischer I. *Chem. Eur. J.* **2018**, *24*, 8774.
(29) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 627.
(30) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
(31) (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
(32) (a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys*. **1971**, *54*, 724. (b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys*. **1972**, *56*, 2257. (c) P. C. Hariharan, J. A. Pople, *Theor. Chem. Acc.* **1973**, *28*, 213.



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

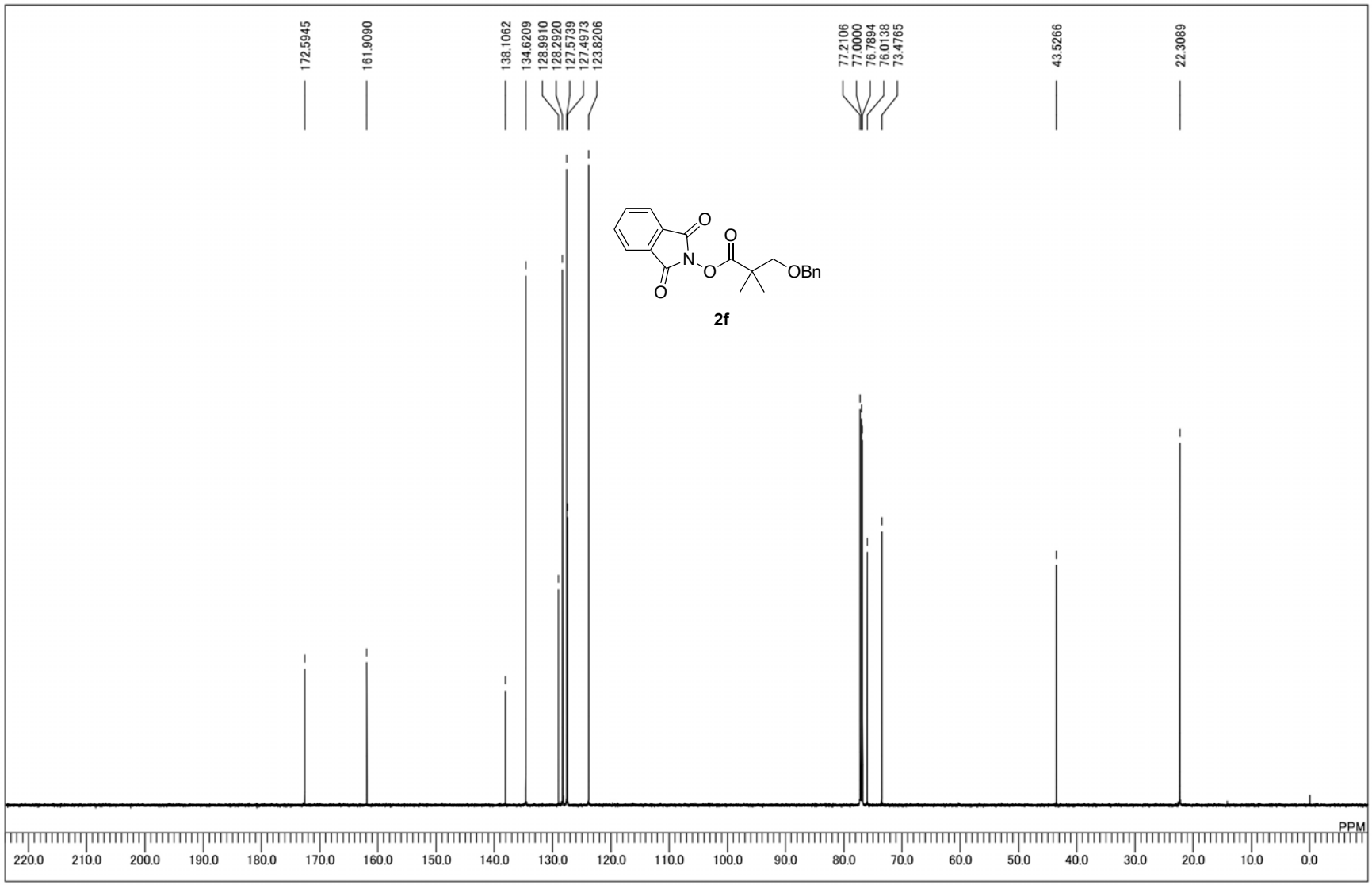


^{13}C NMR spectrum of **2e**

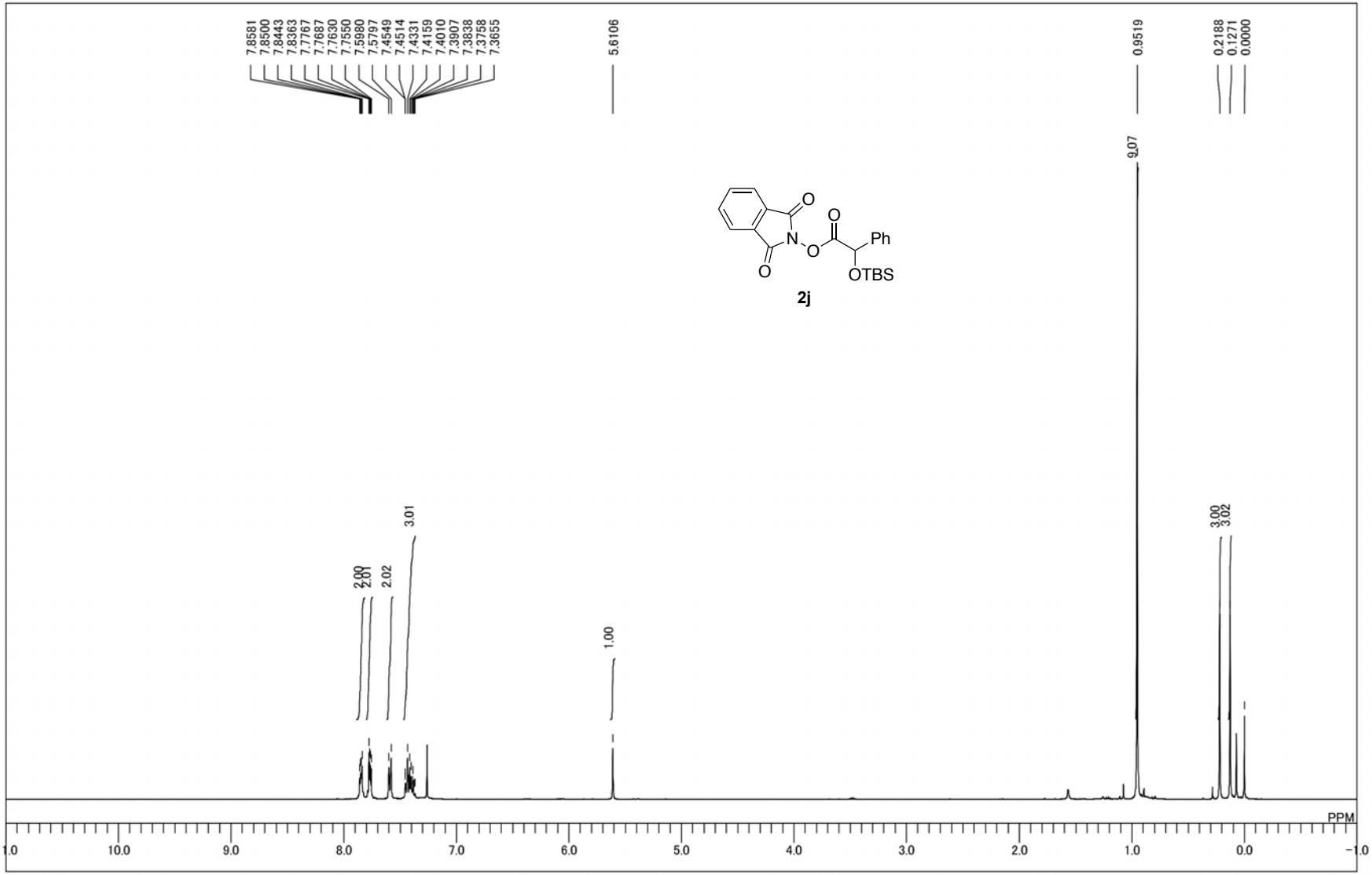


2f

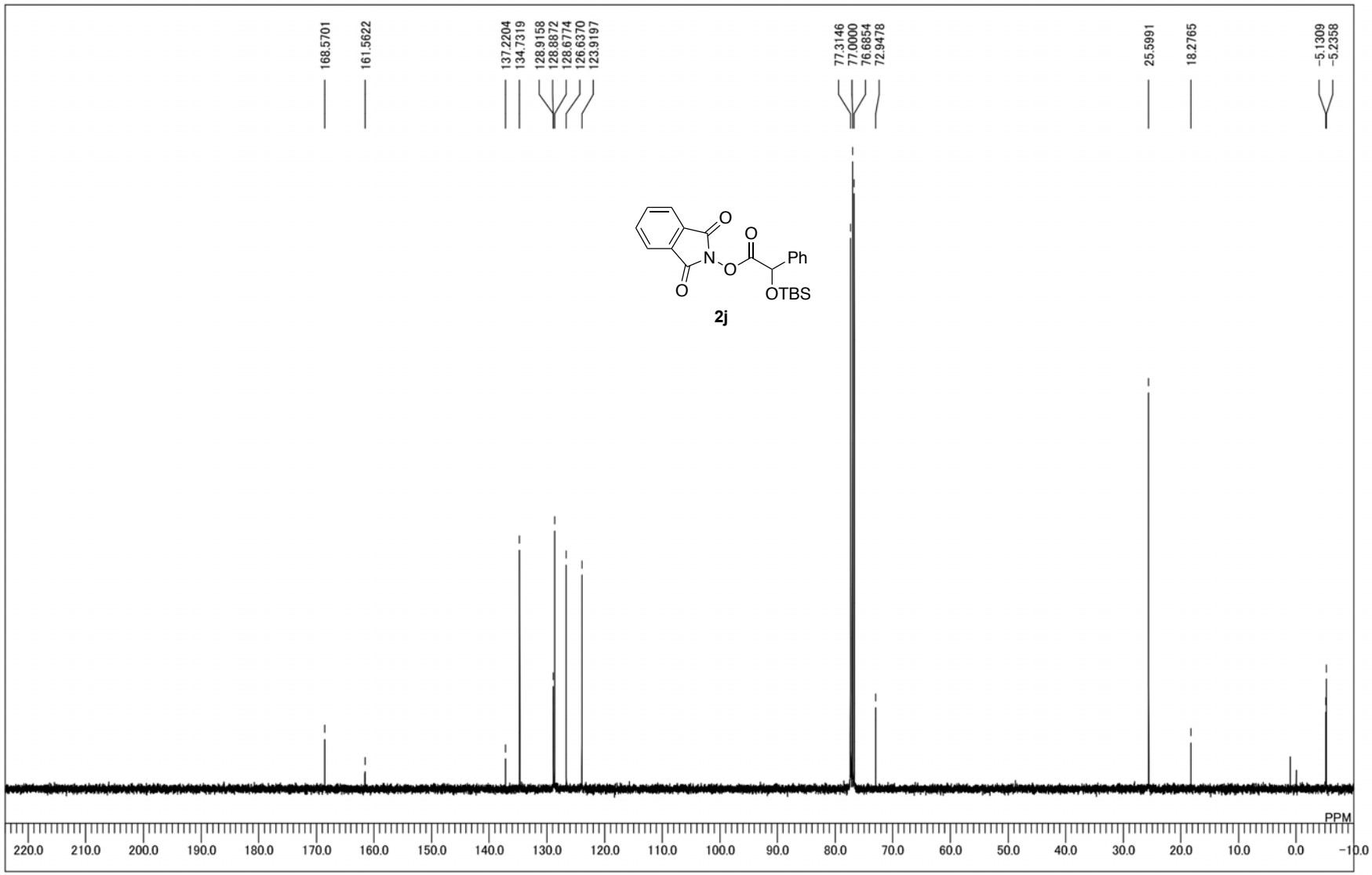
^{1}H NMR spectrum of **2f**



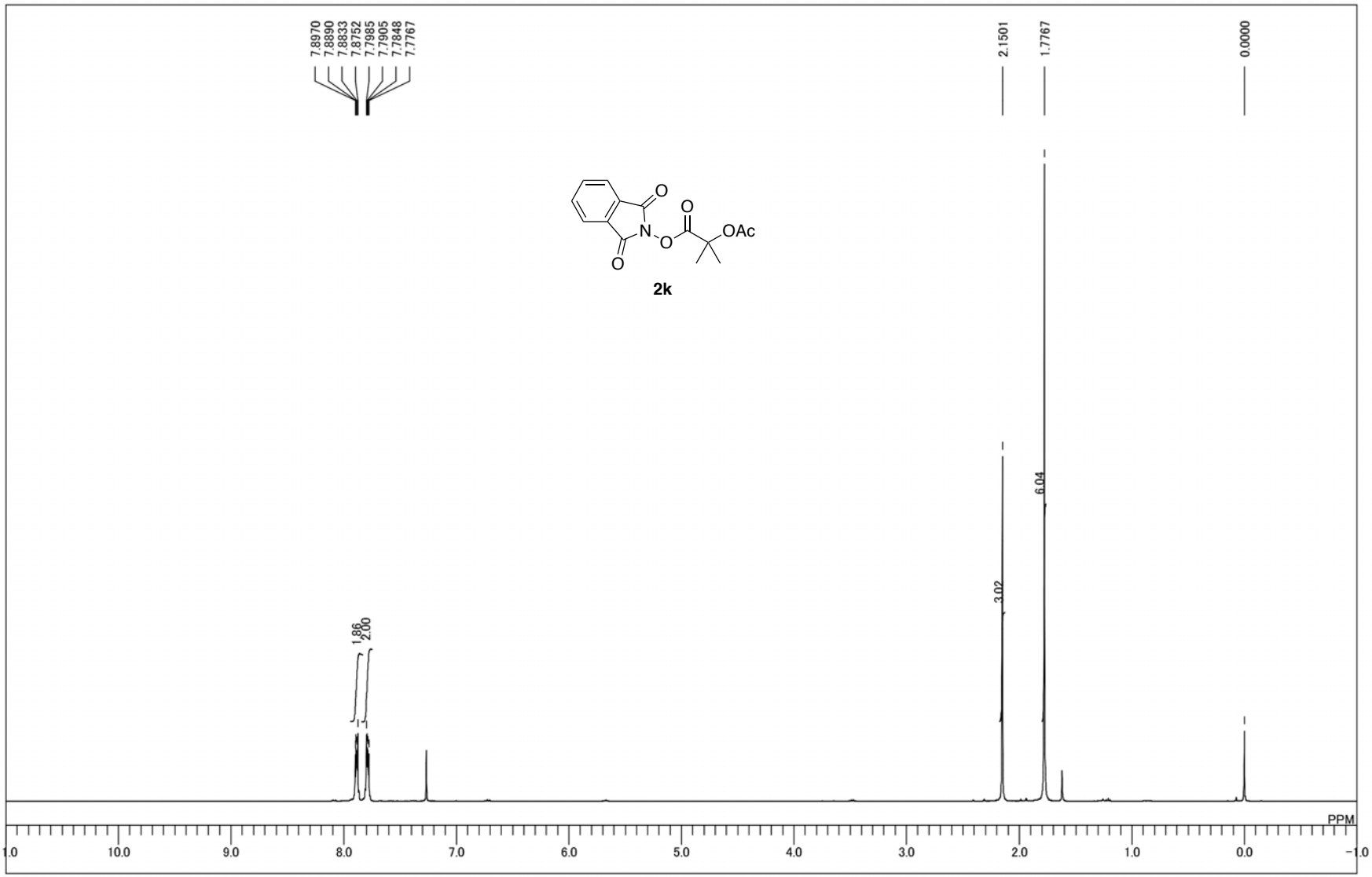
^{13}C NMR spectrum of **2f**



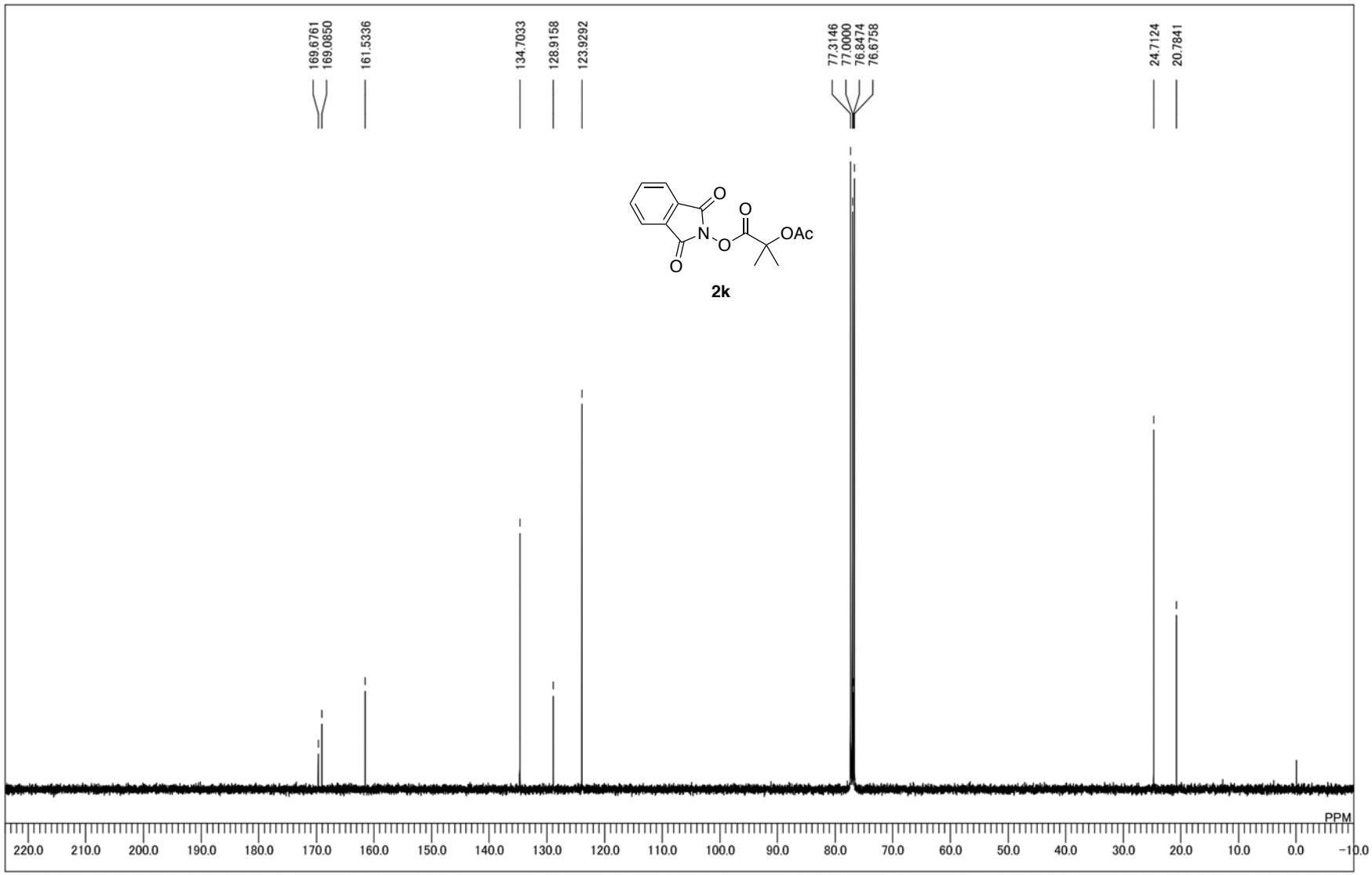
^{1}H NMR spectrum of **2j**



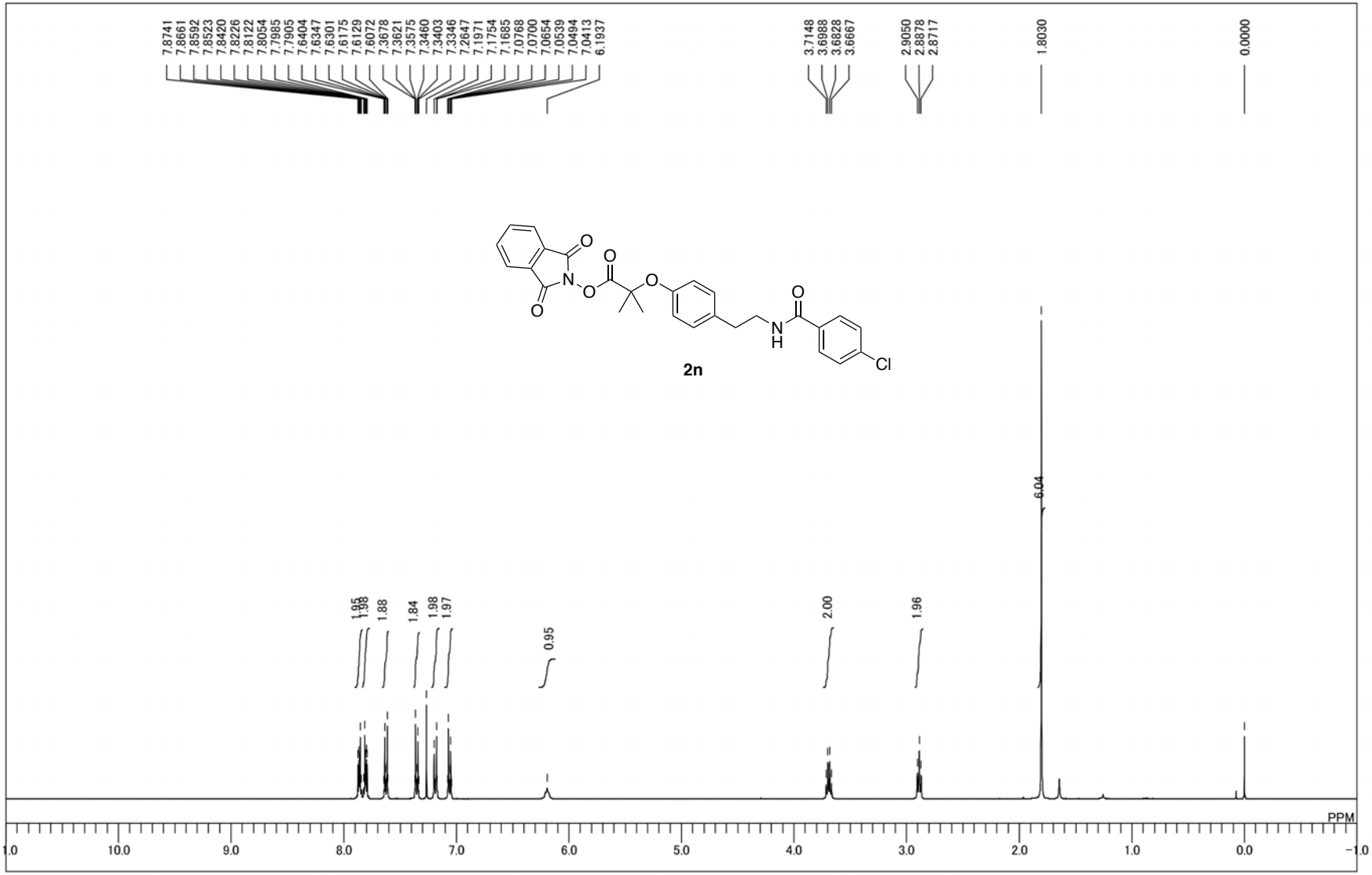
^{13}C NMR spectrum of **2j**



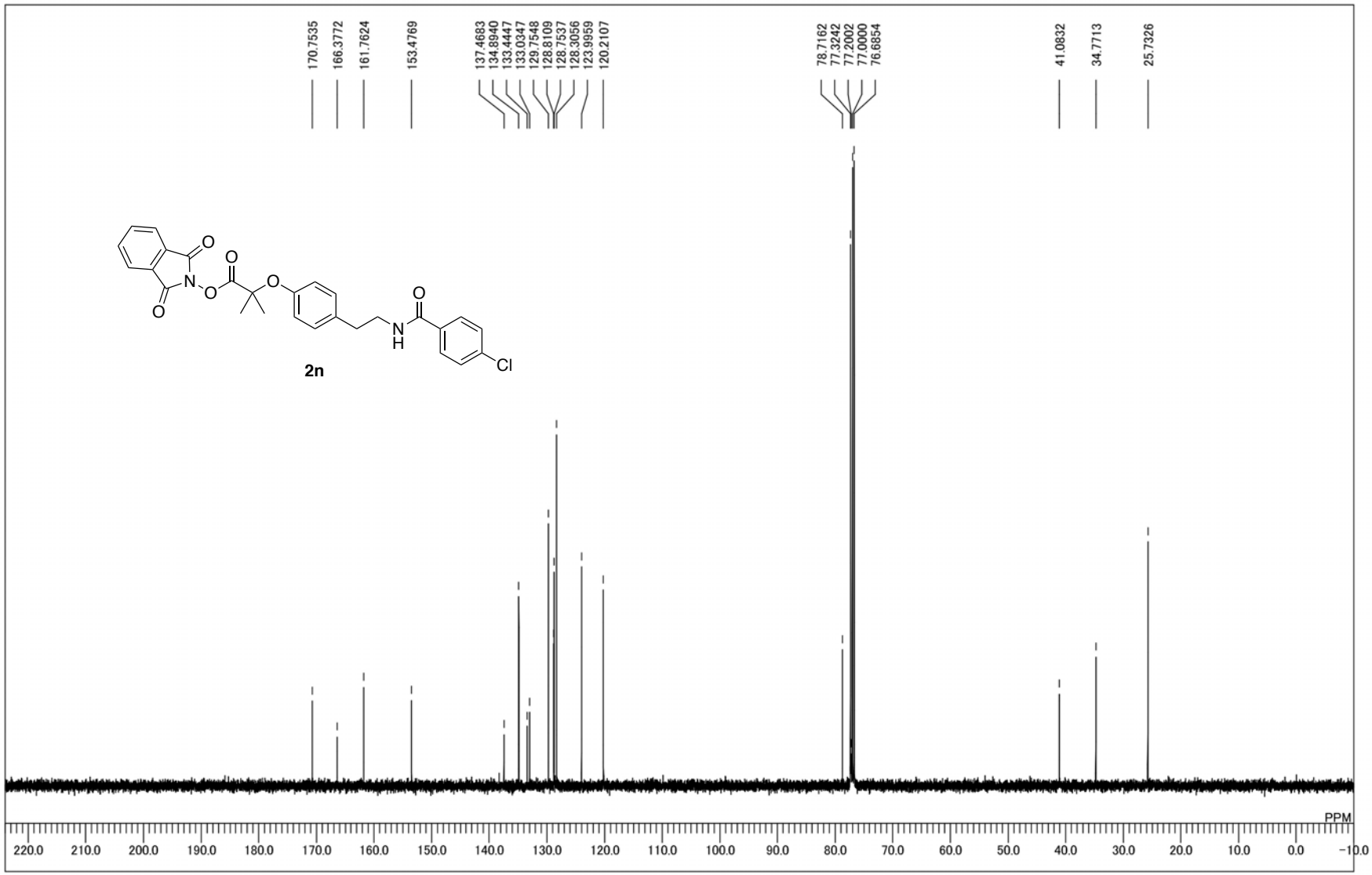
^{1}H NMR spectrum of **2k**



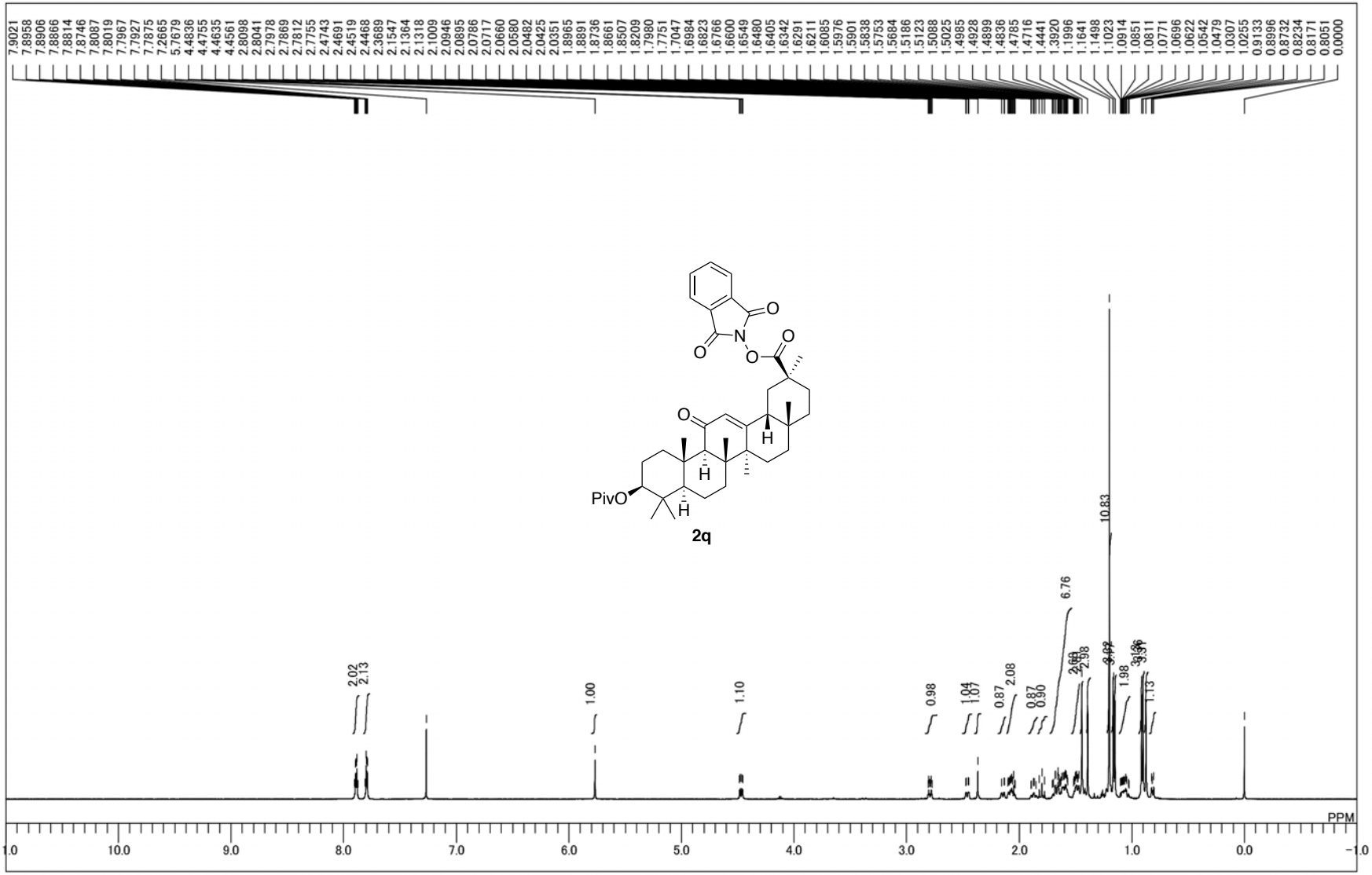
^{13}C NMR spectrum of **2k**



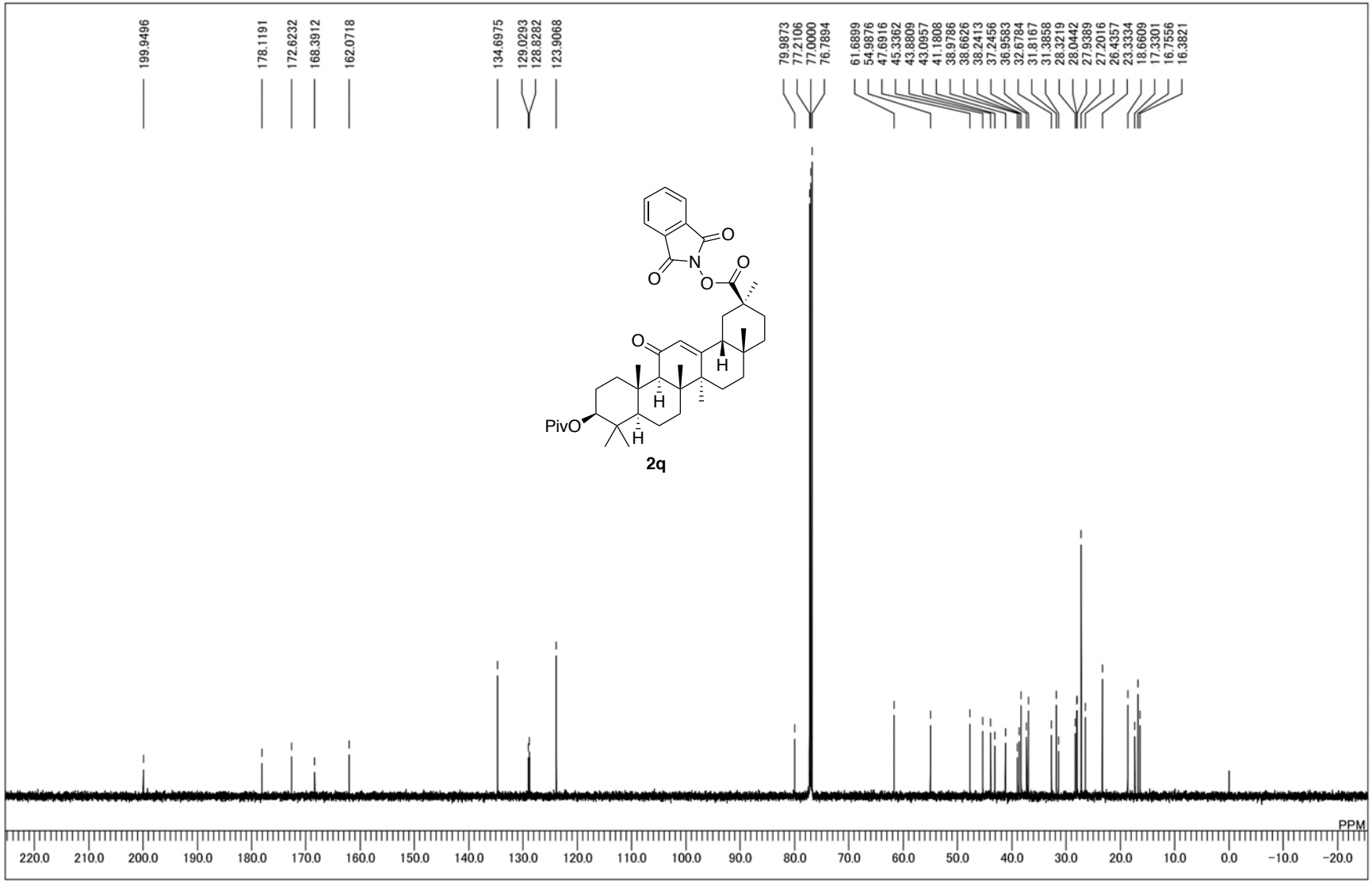
^{1}H NMR spectrum of **2n**



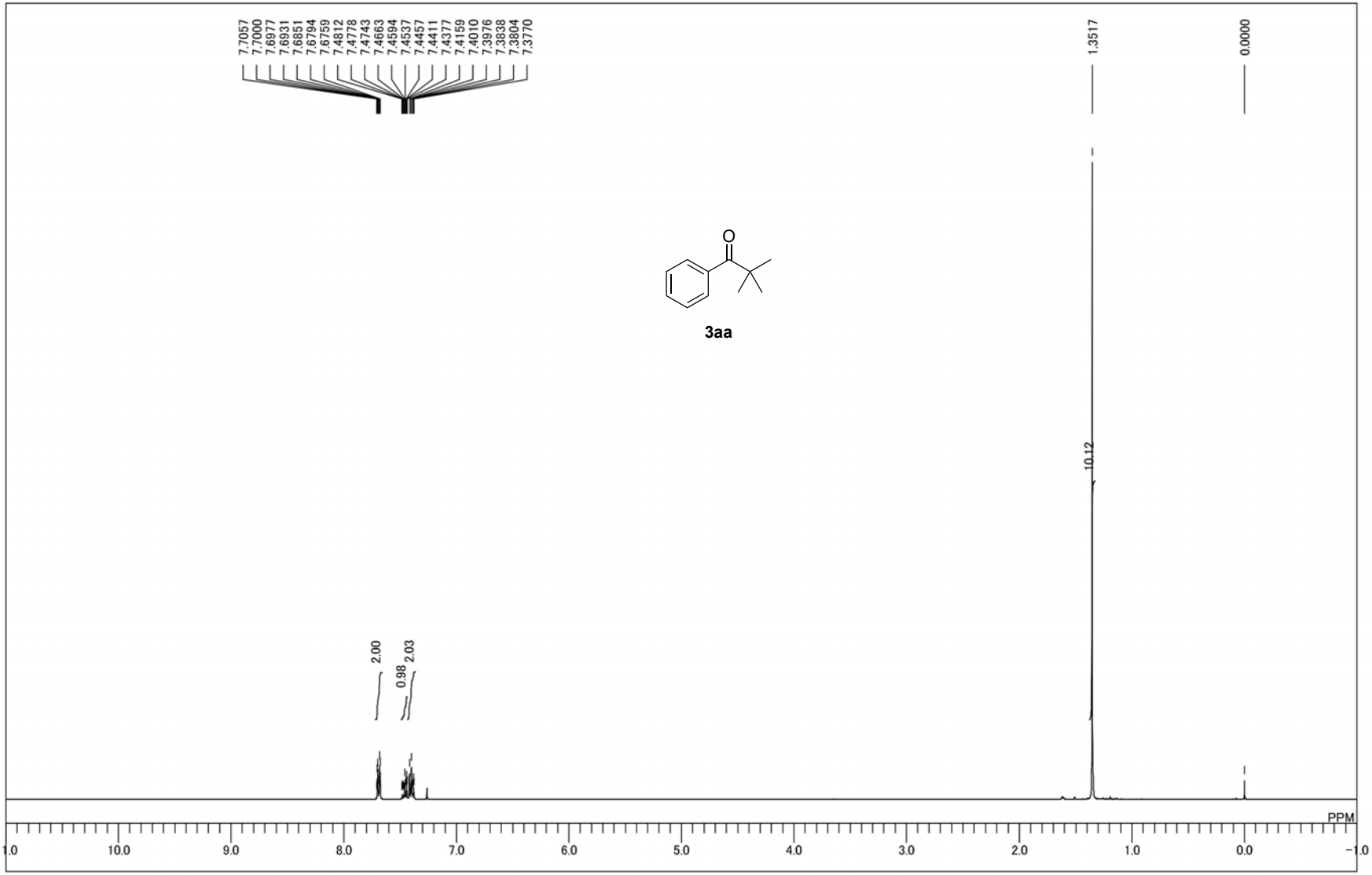
^{13}C NMR spectrum of **2n**



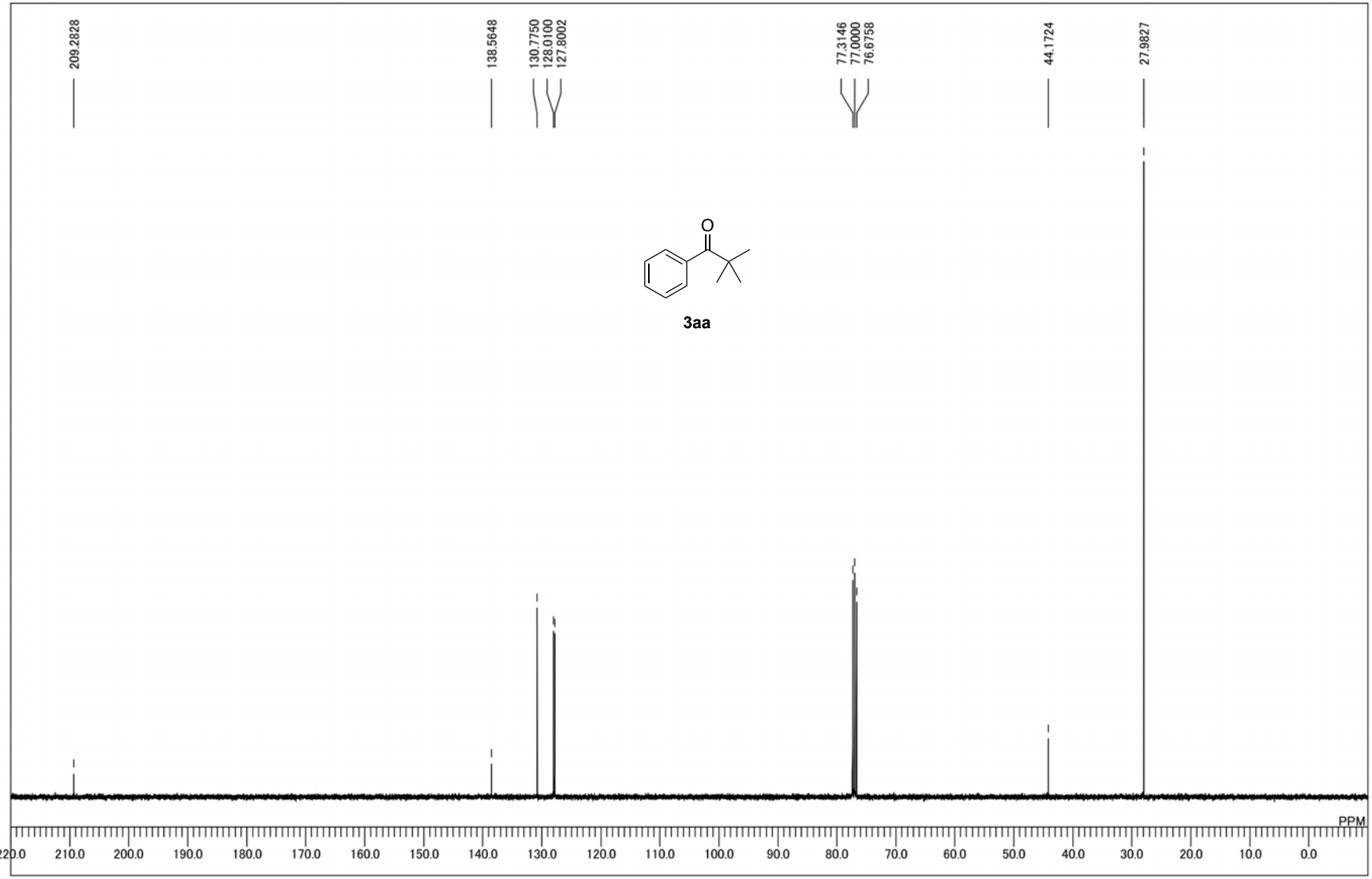
^{1}H NMR spectrum of **2q**



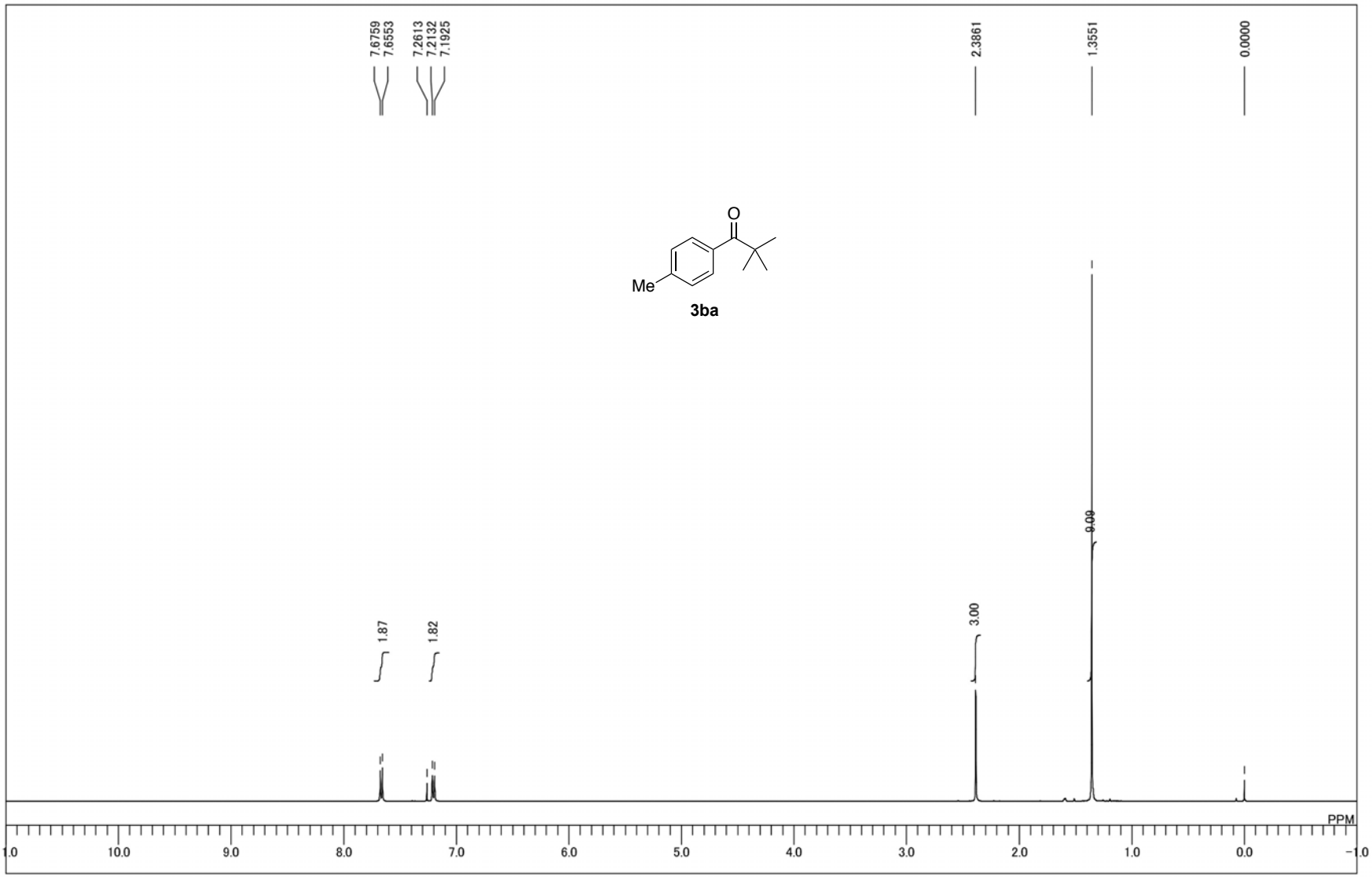
^{13}C NMR spectrum of **2q**



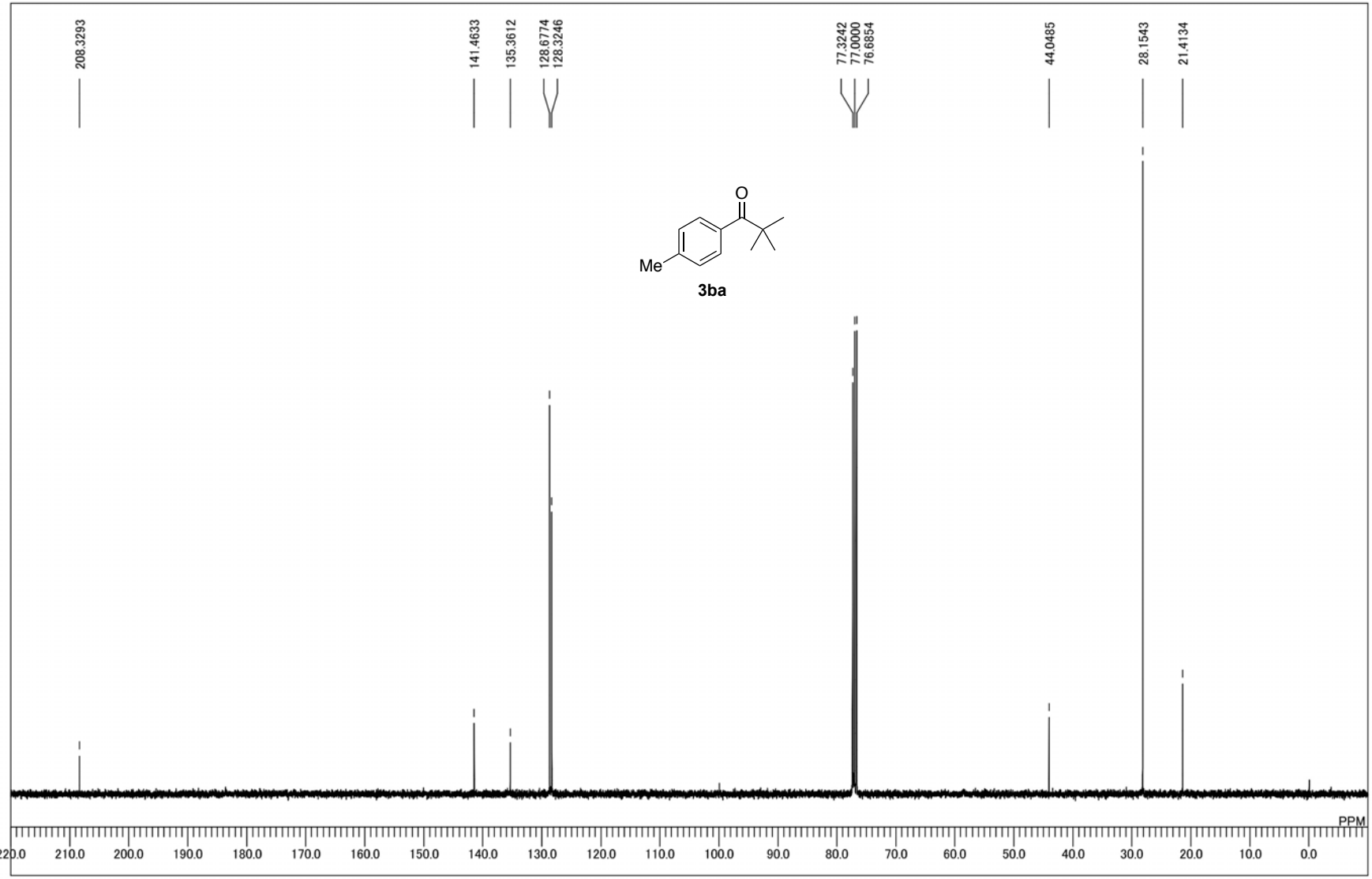
^{1}H NMR spectrum of **3aa**



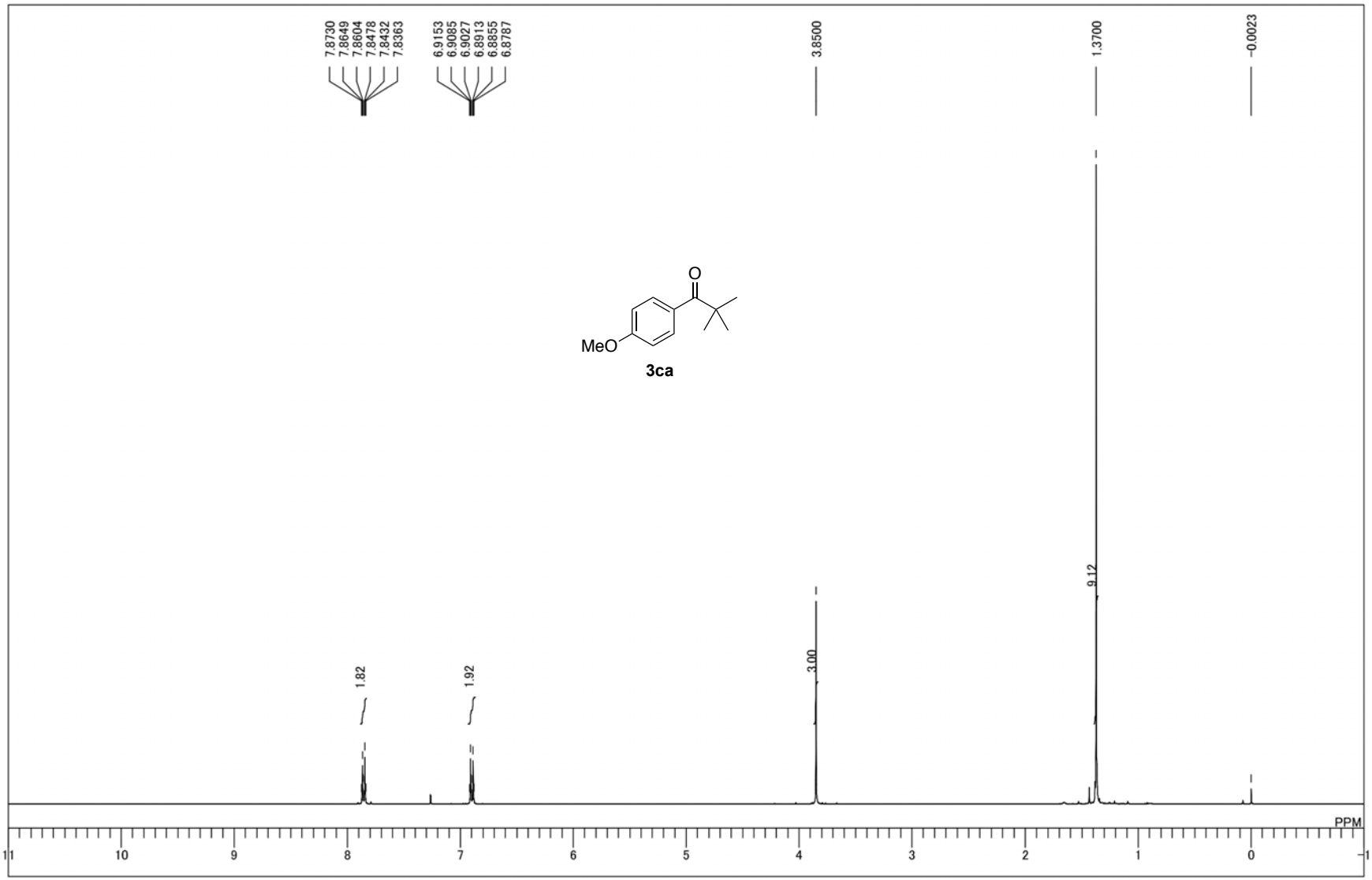
^{13}C NMR spectrum of **3aa**



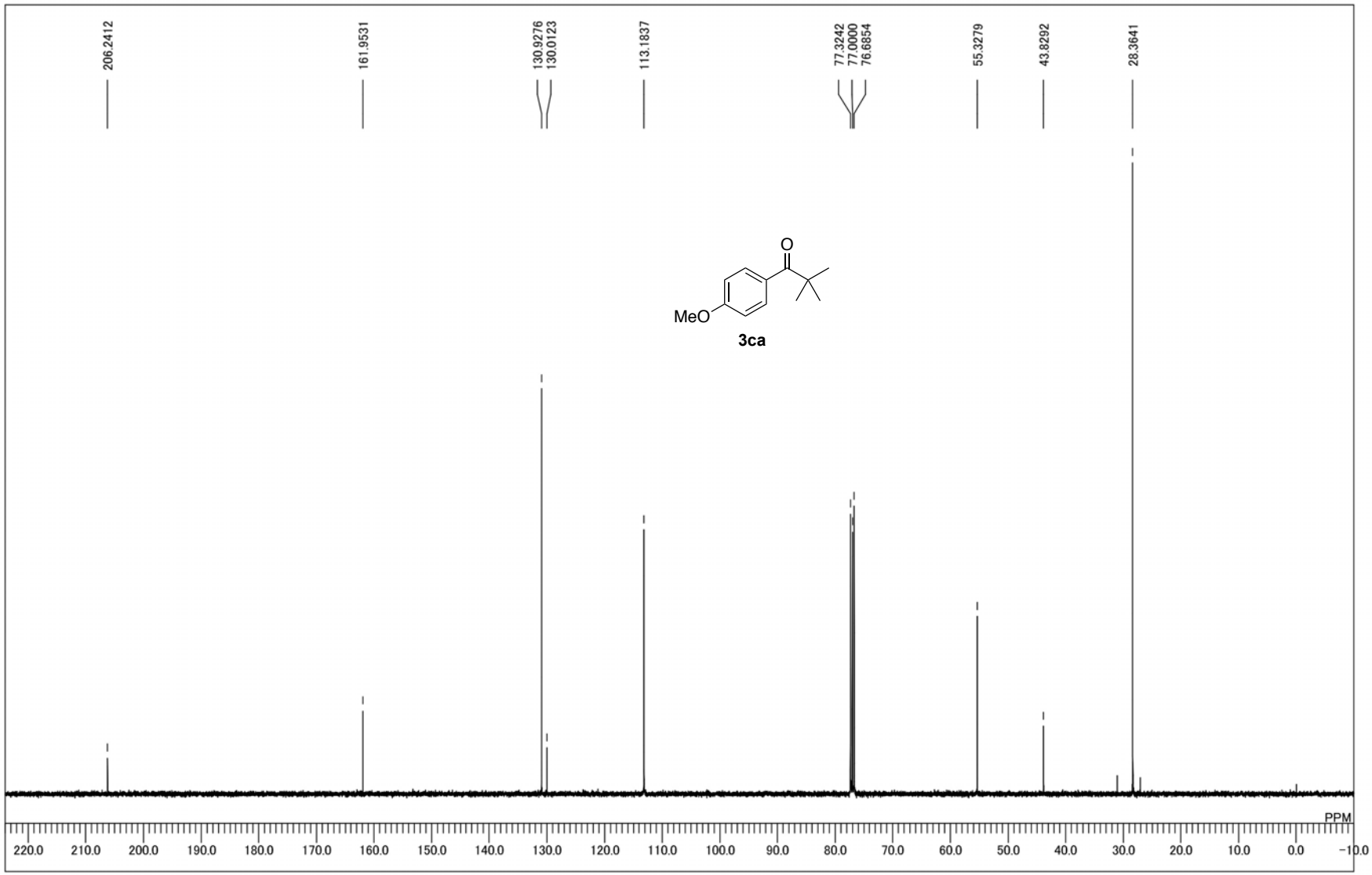
^{1}H NMR spectrum of **3ba**



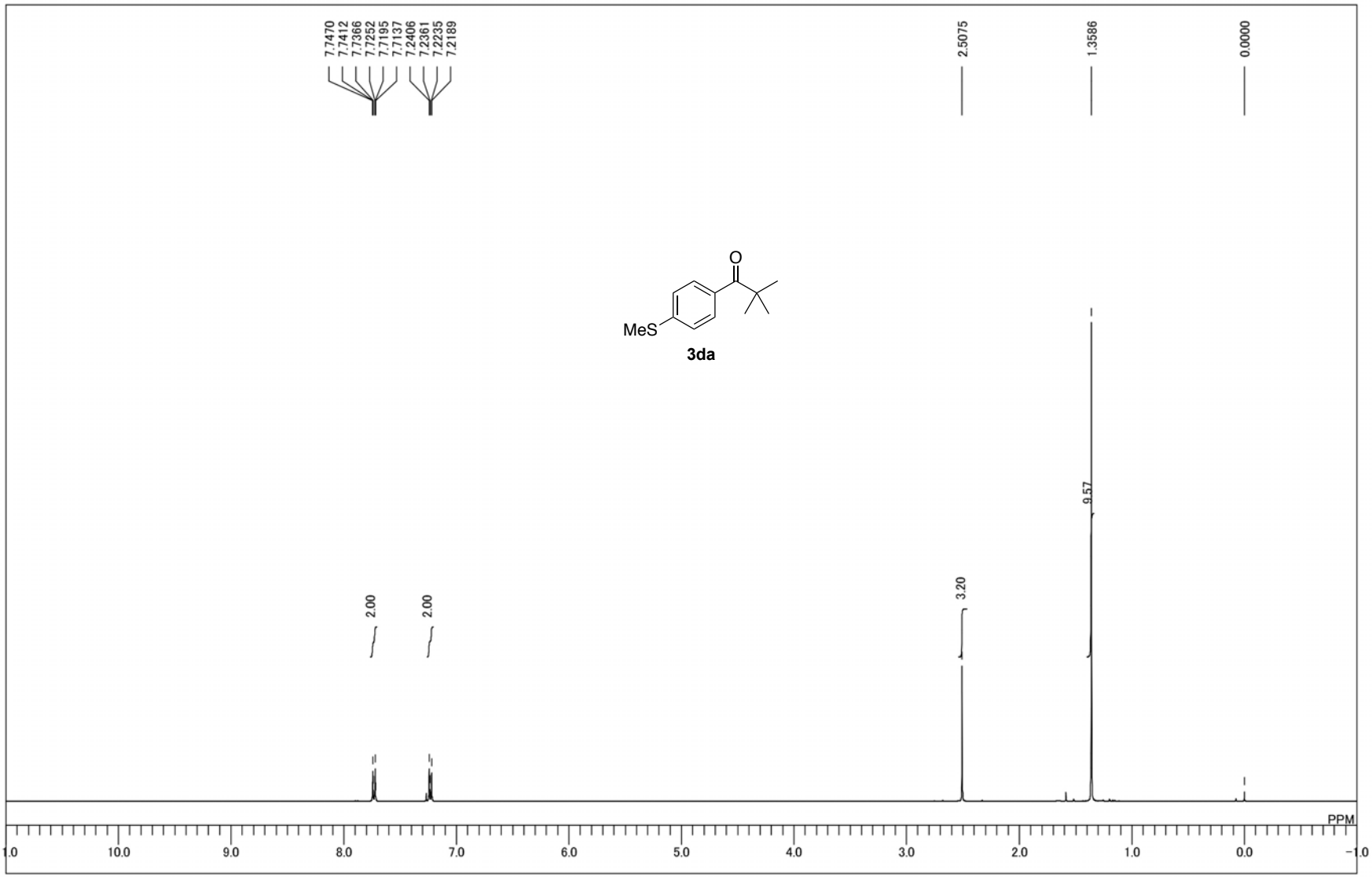
^{13}C NMR spectrum of **3ba**



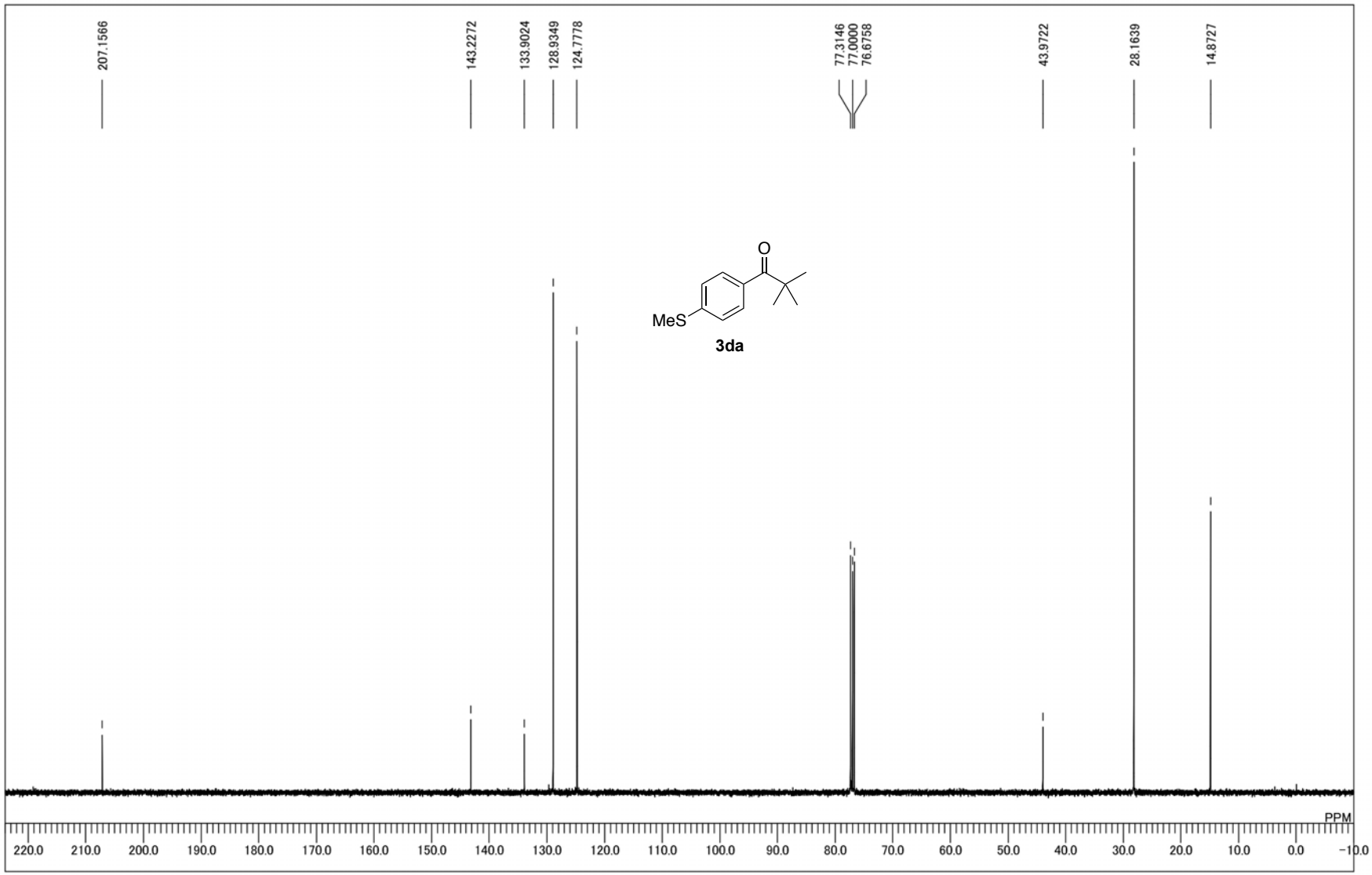
^{1}H NMR spectrum of **3ca**



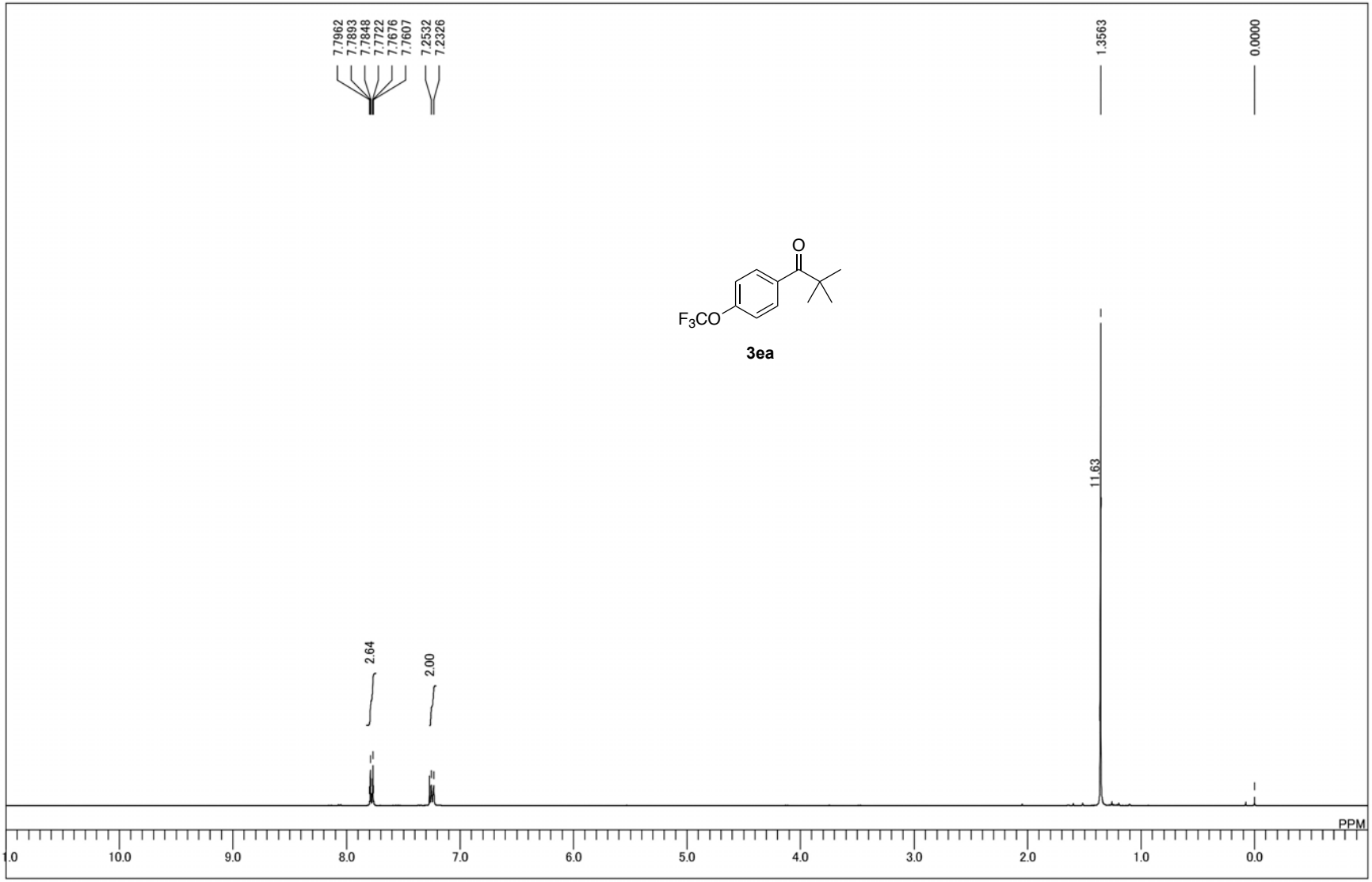
^{13}C NMR spectrum of **3ca**



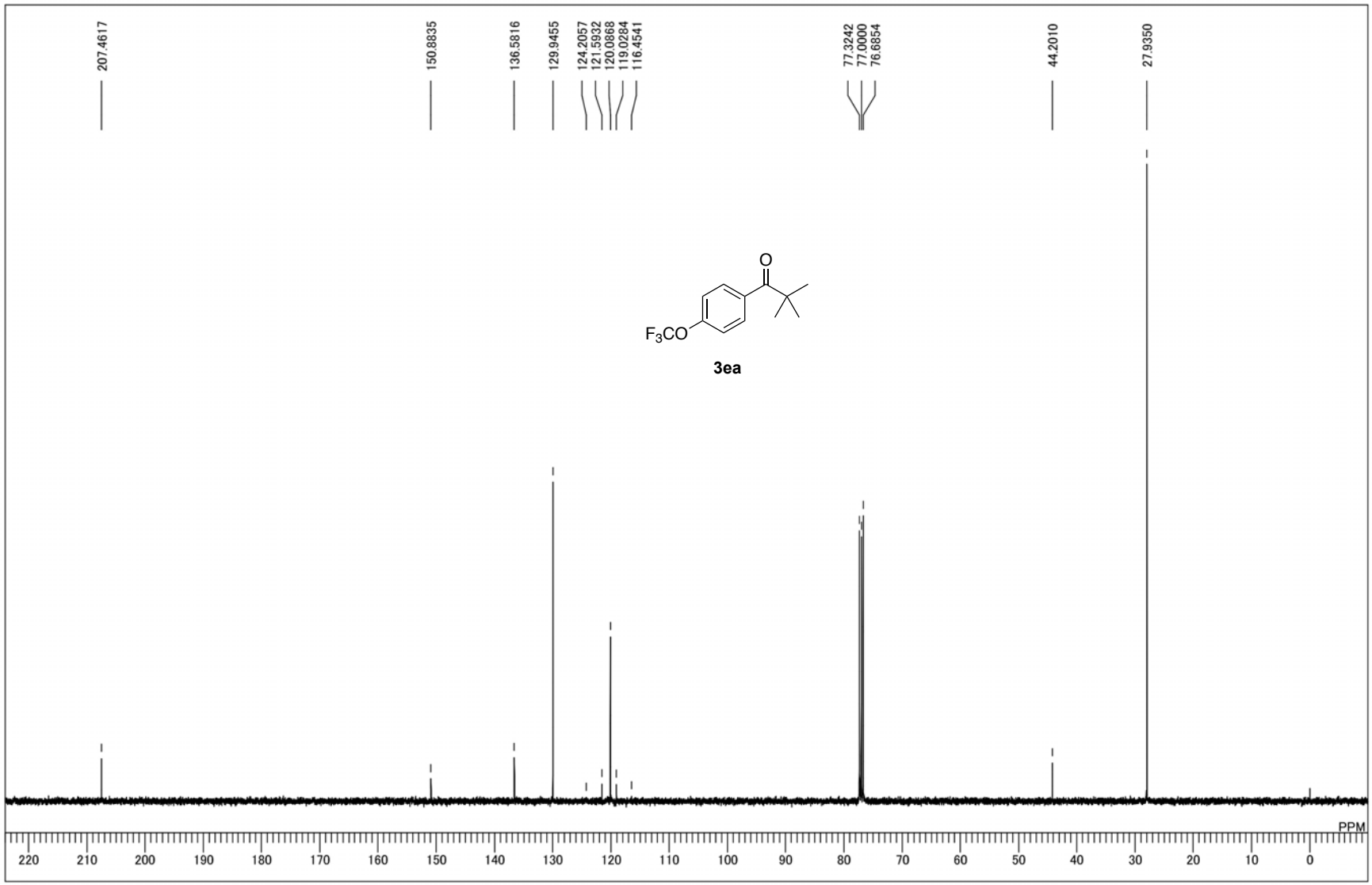
^{1}H NMR spectrum of **3da**



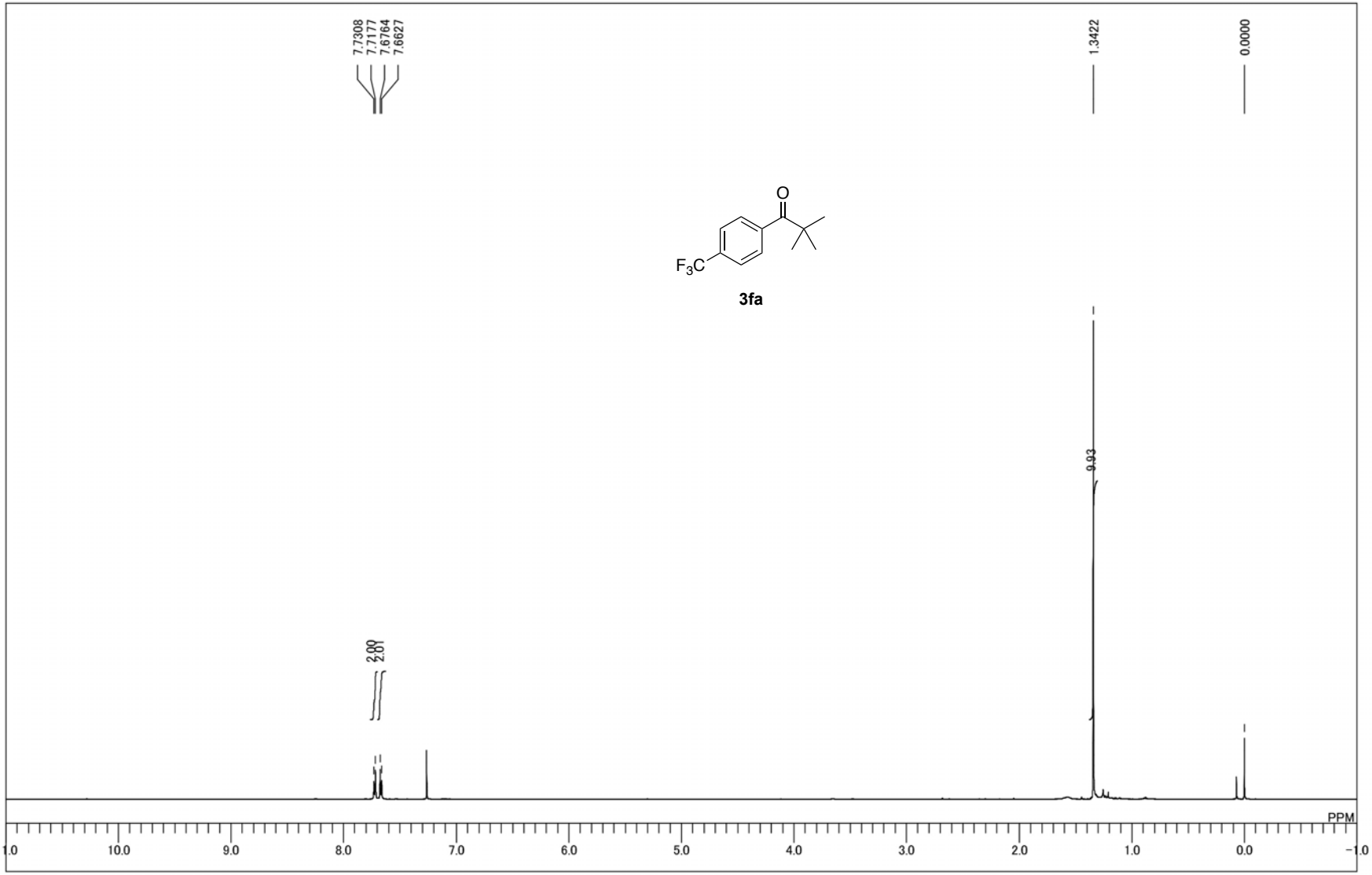
^{13}C NMR spectrum of **3da**



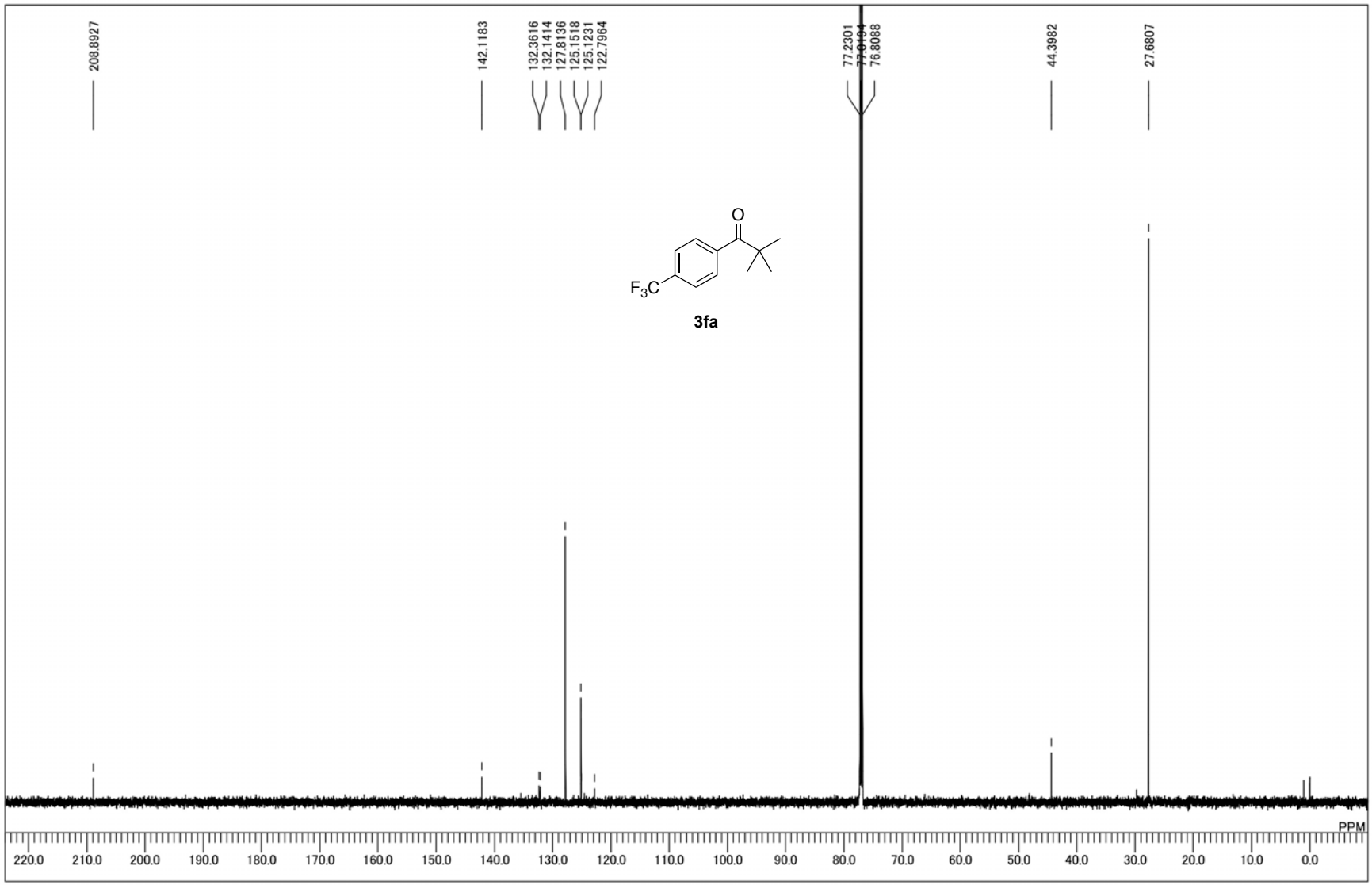
^{1}H NMR spectrum of **3ea**



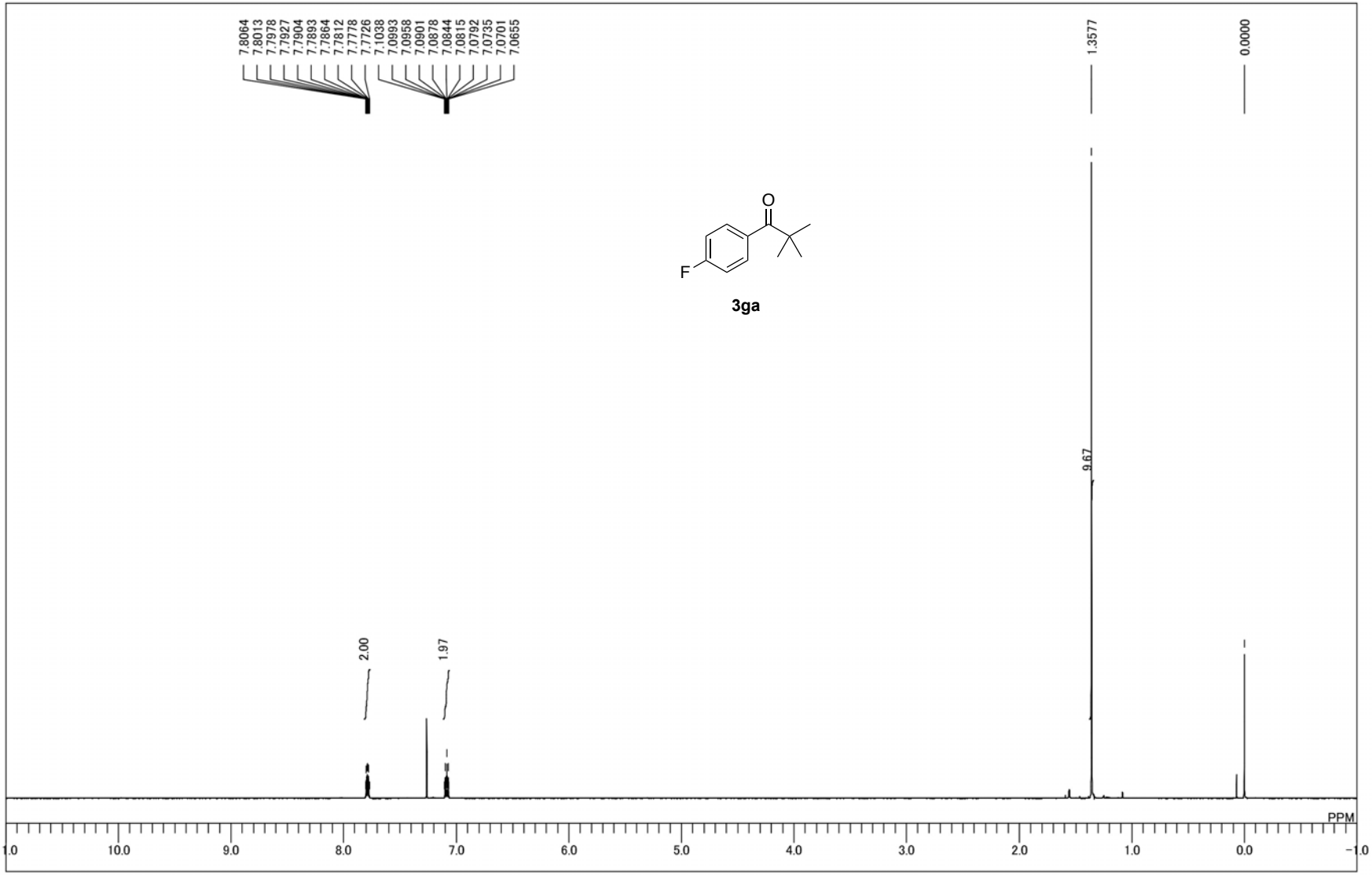
^{13}C NMR spectrum of **3ea**



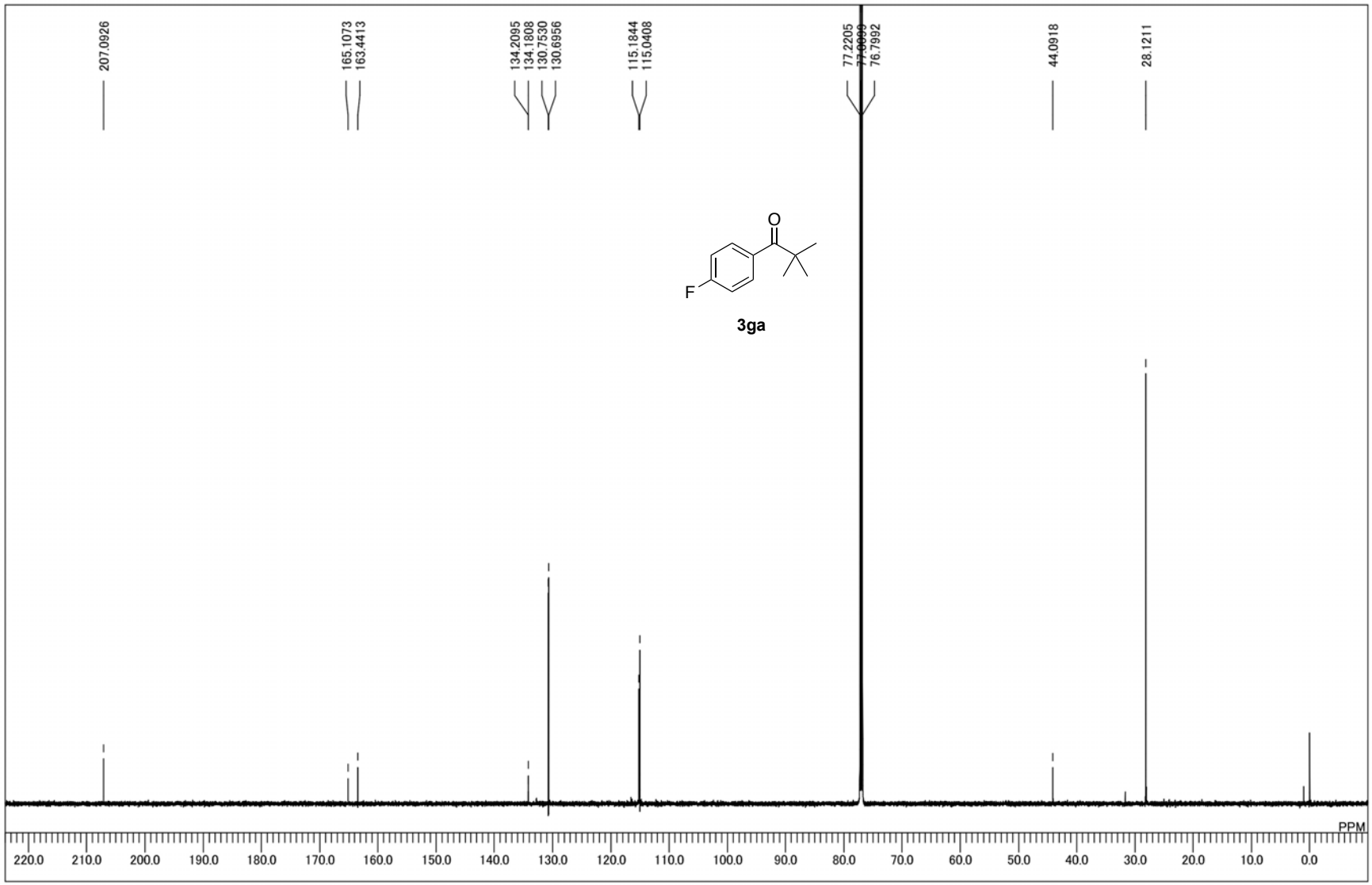
^{1}H NMR spectrum of **3fa**



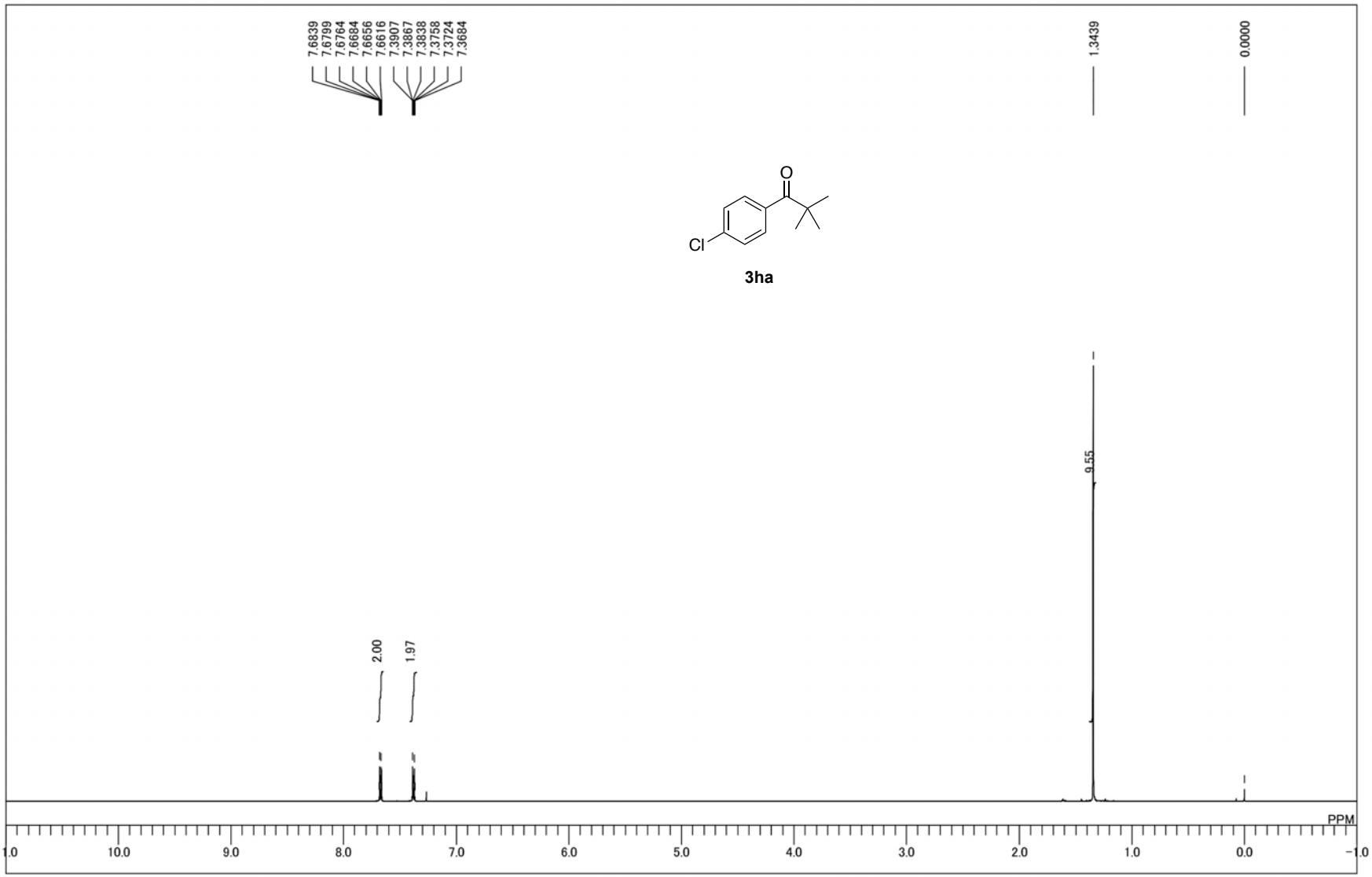
^{13}C NMR spectrum of **3fa**



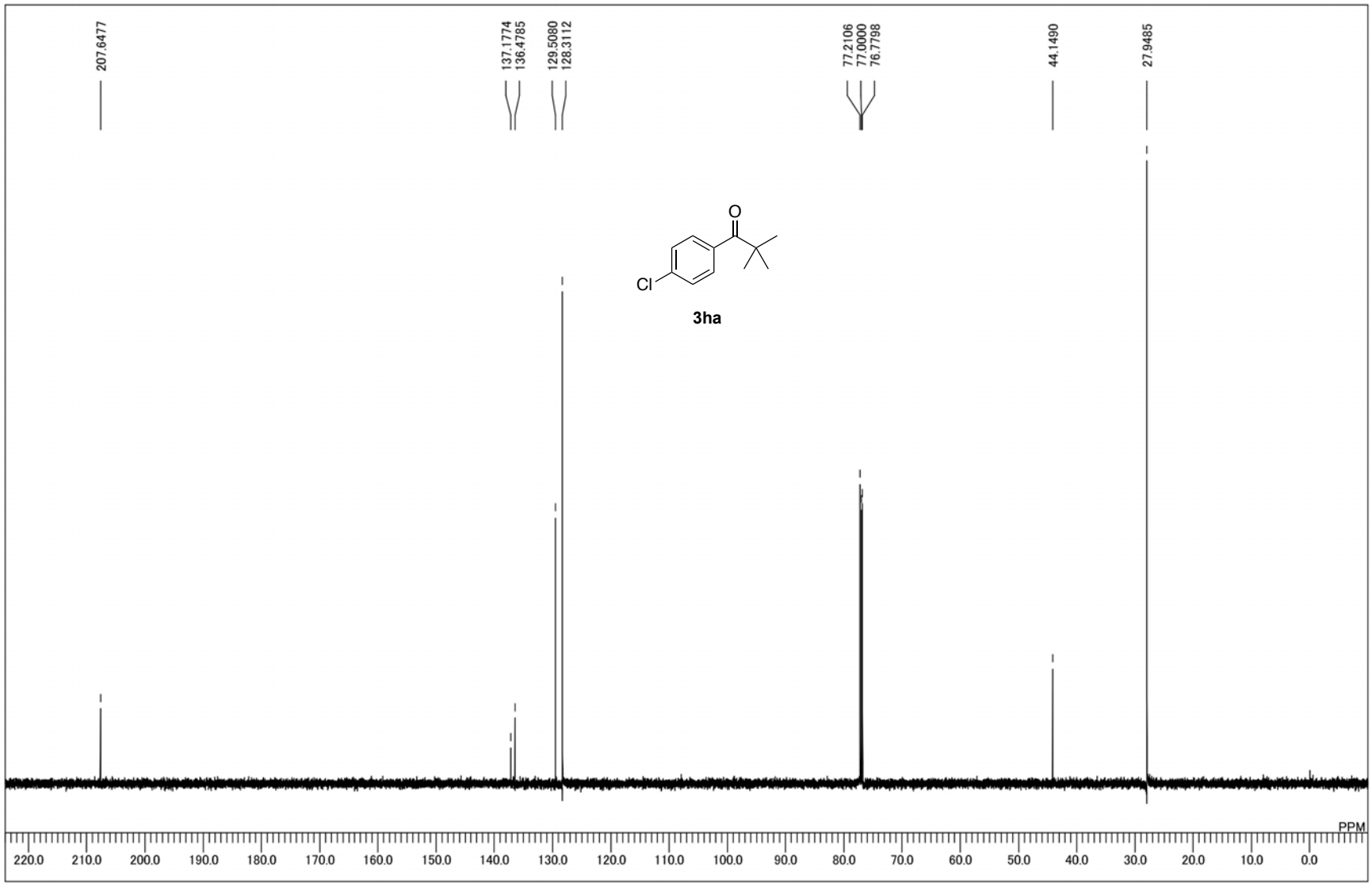
^{1}H NMR spectrum of **3ga**



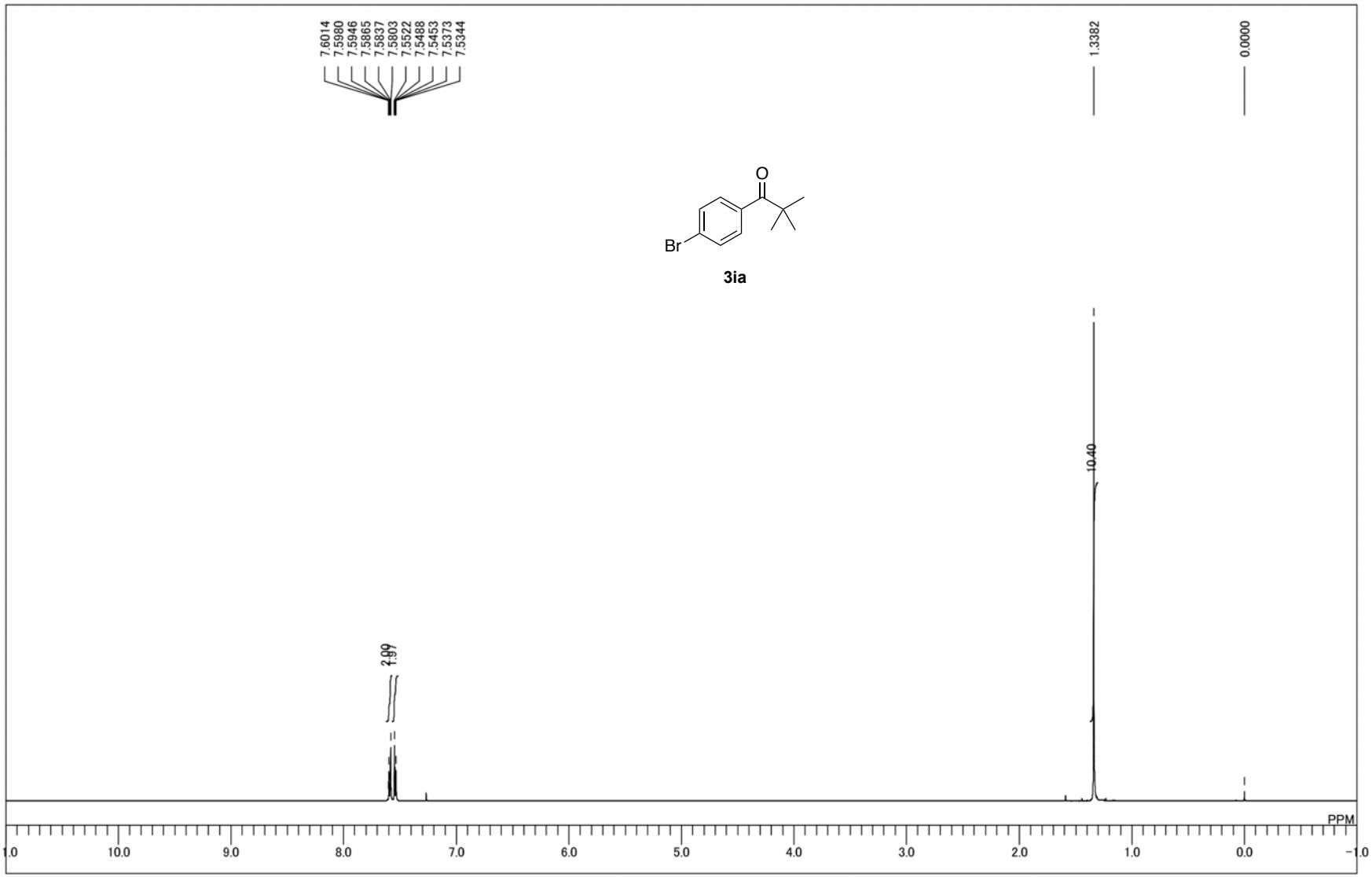
^{13}C NMR spectrum of **3ga**



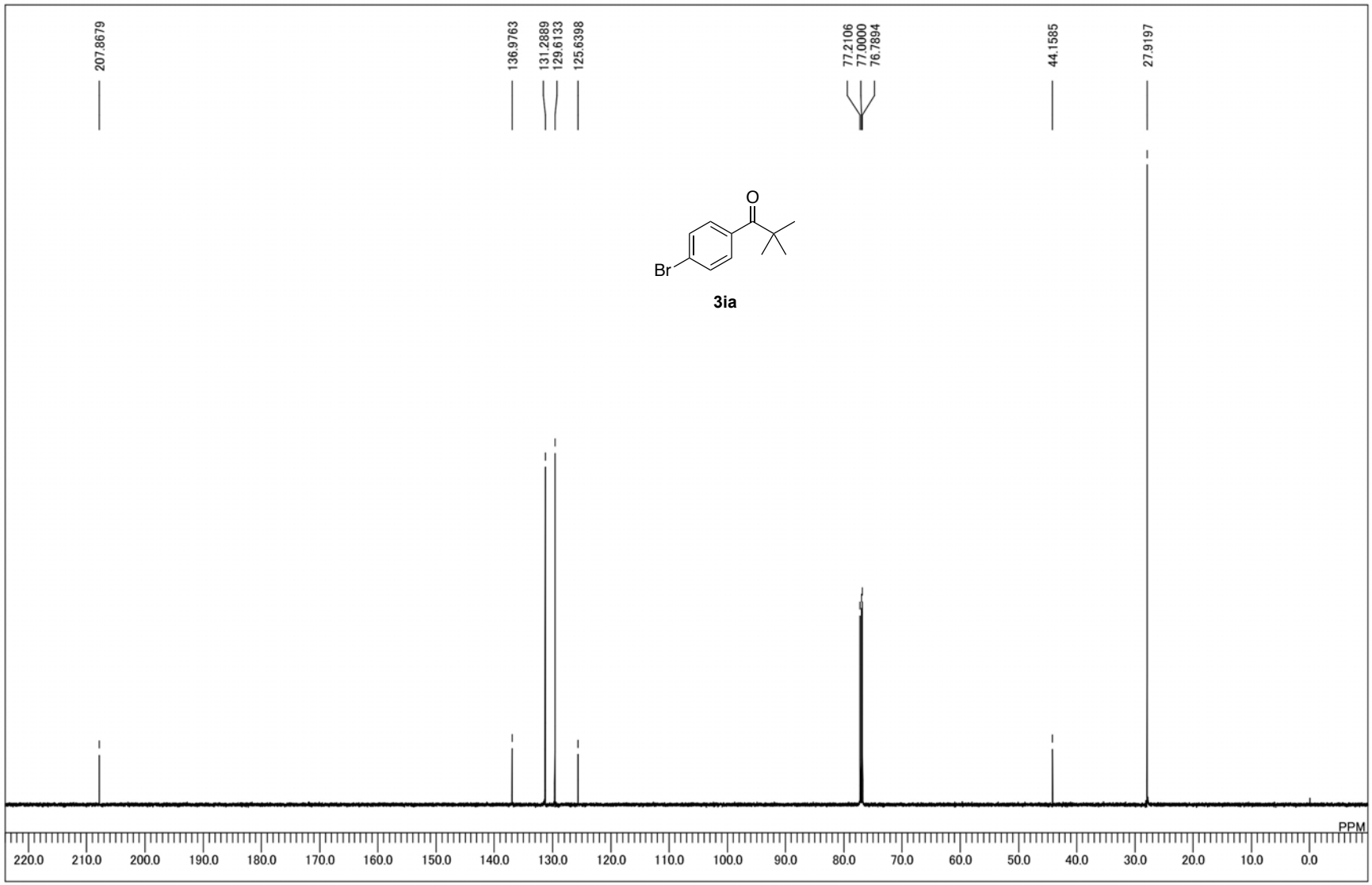
^{1}H NMR spectrum of **3ha**



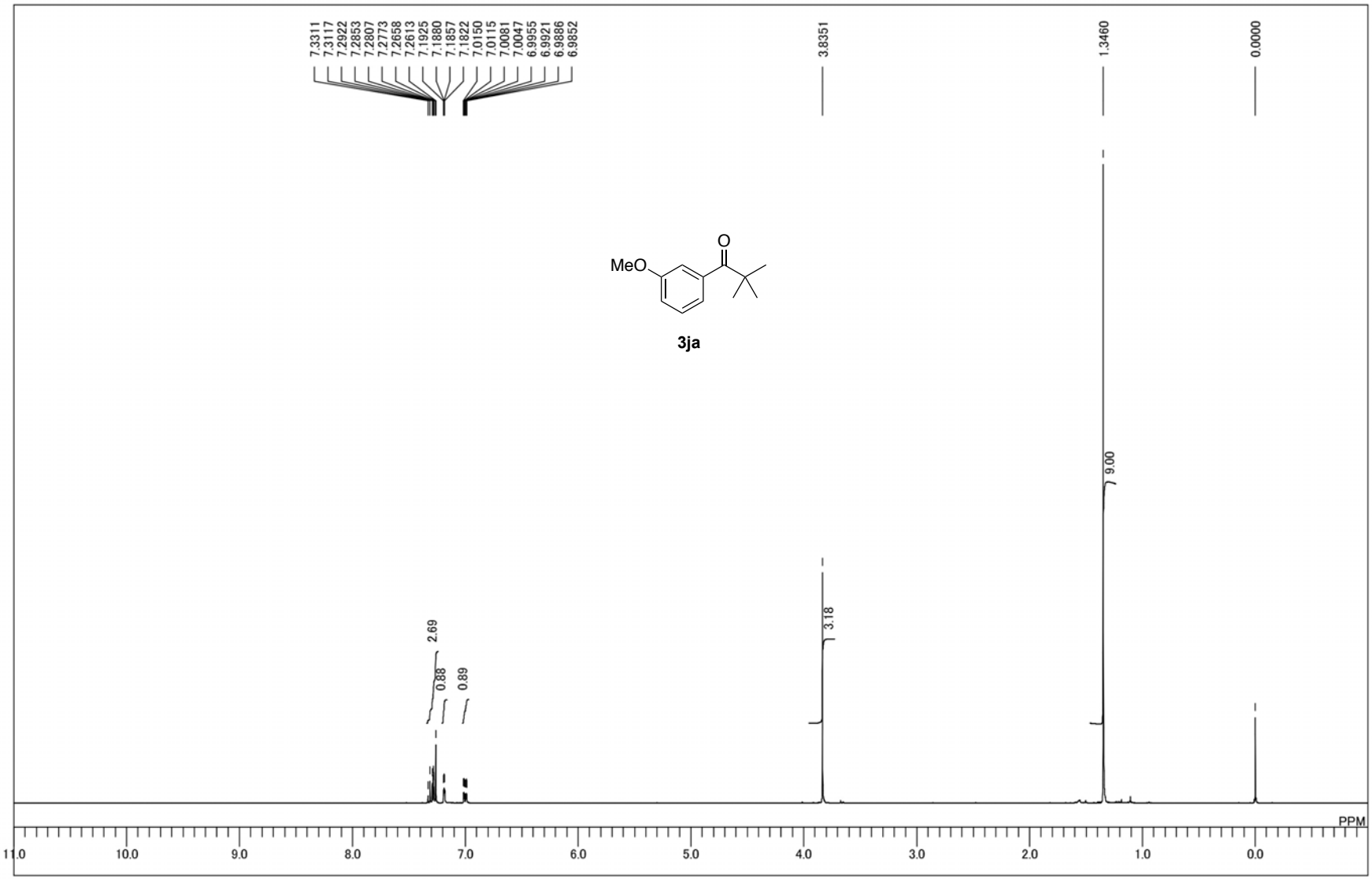
^{13}C NMR spectrum of **3ha**



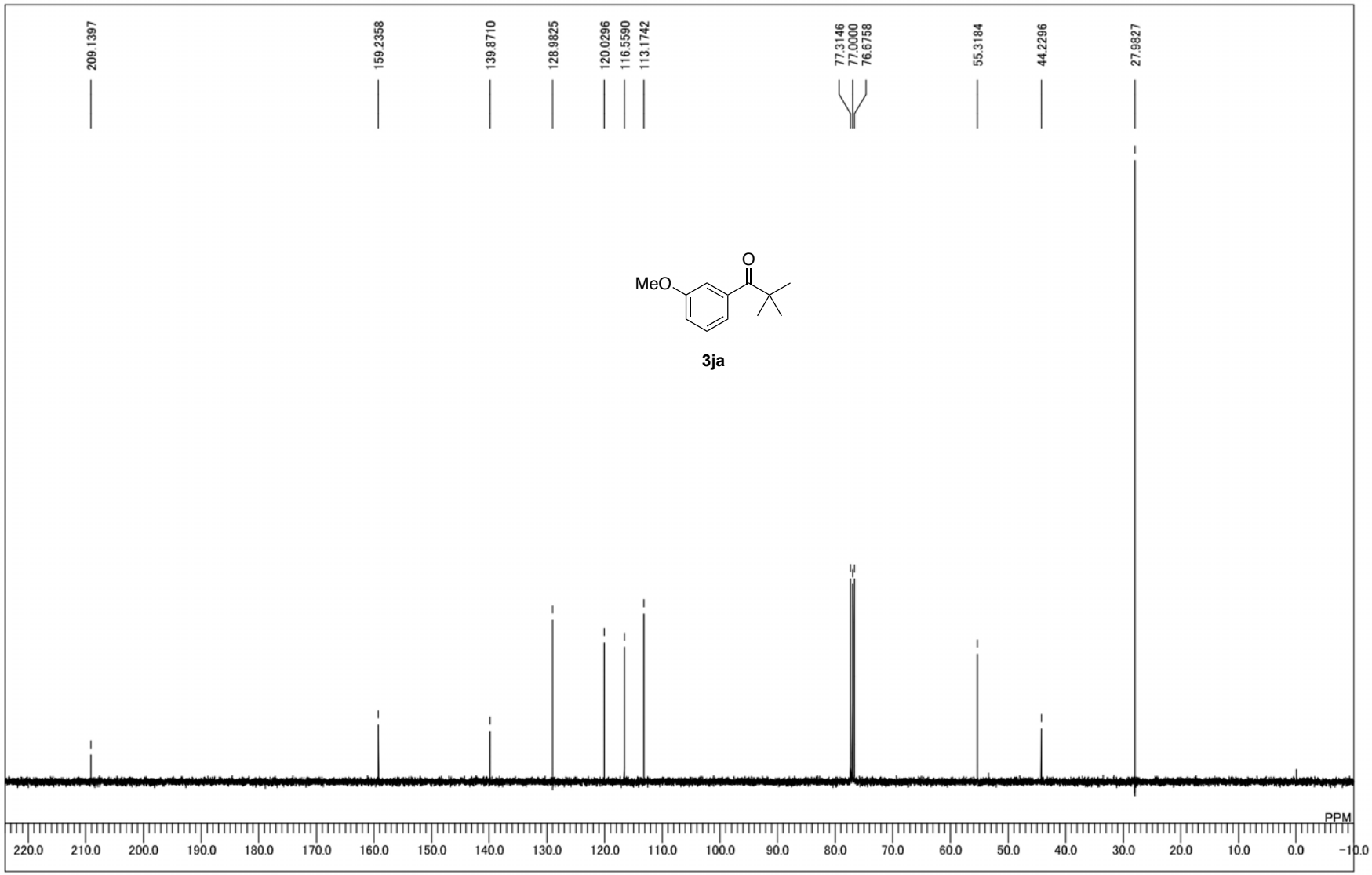
^{1}H NMR spectrum of **3ia**



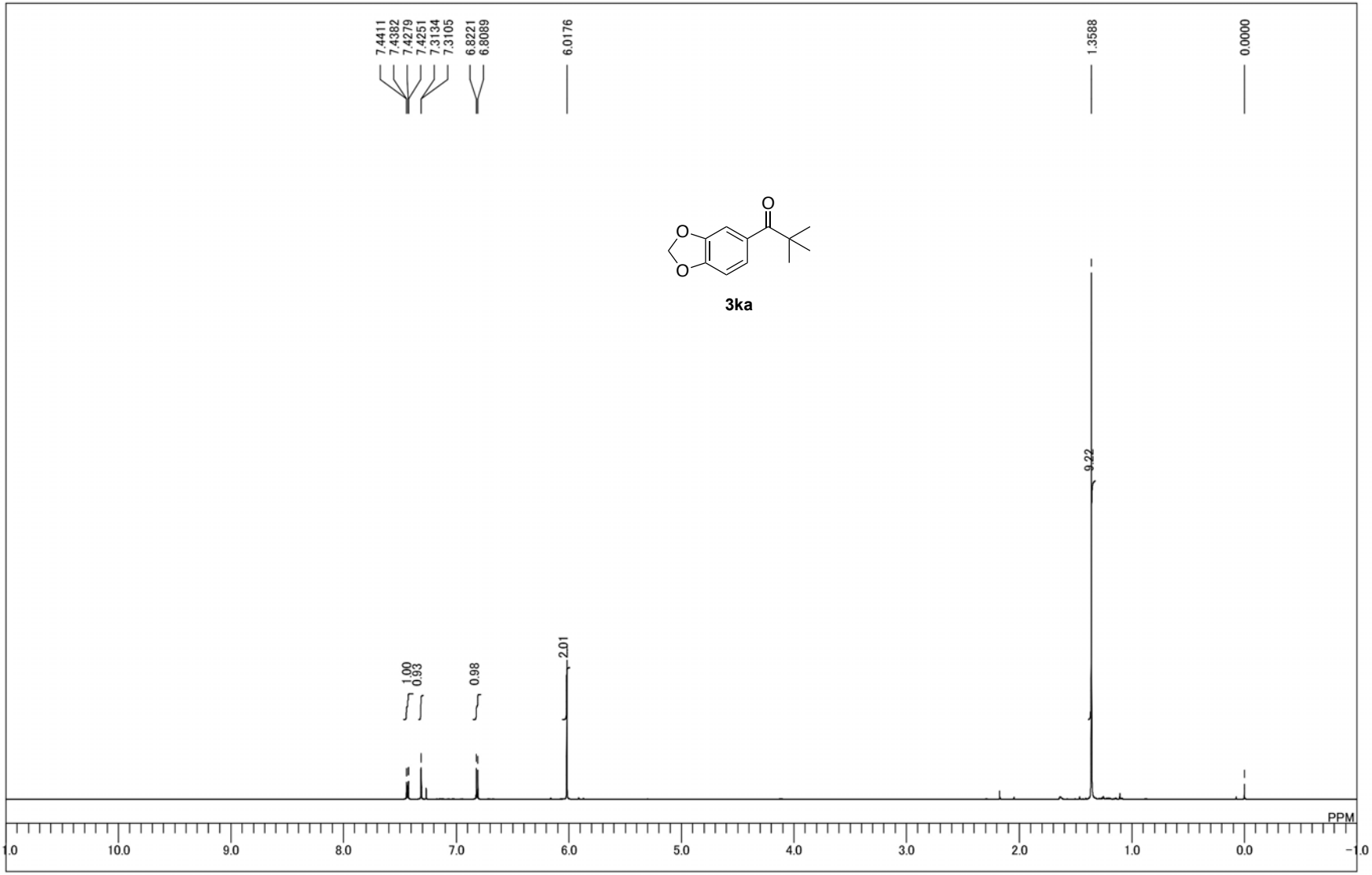
^{13}C NMR spectrum of **3ia**



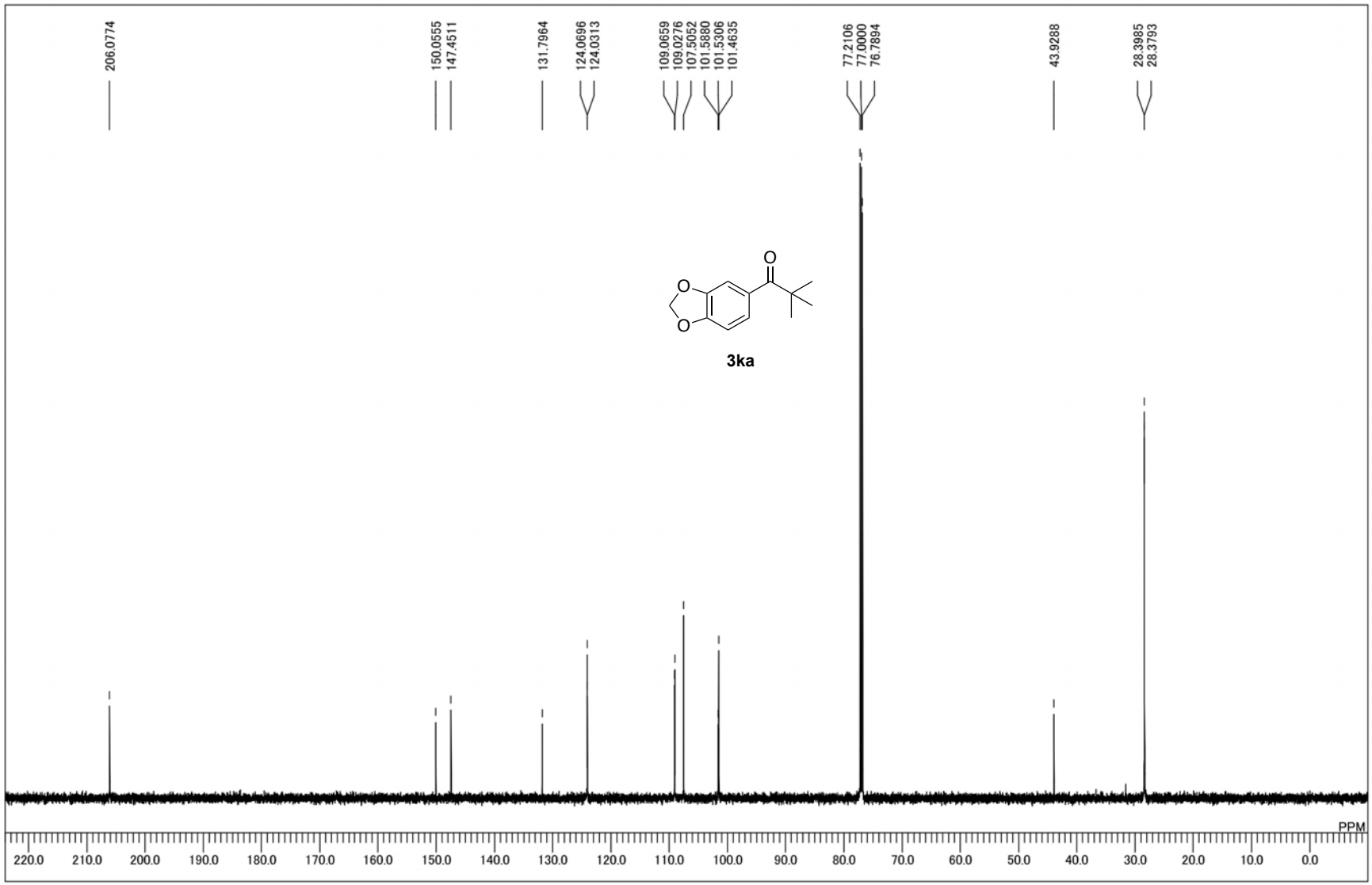
^{1}H NMR spectrum of **3ja**



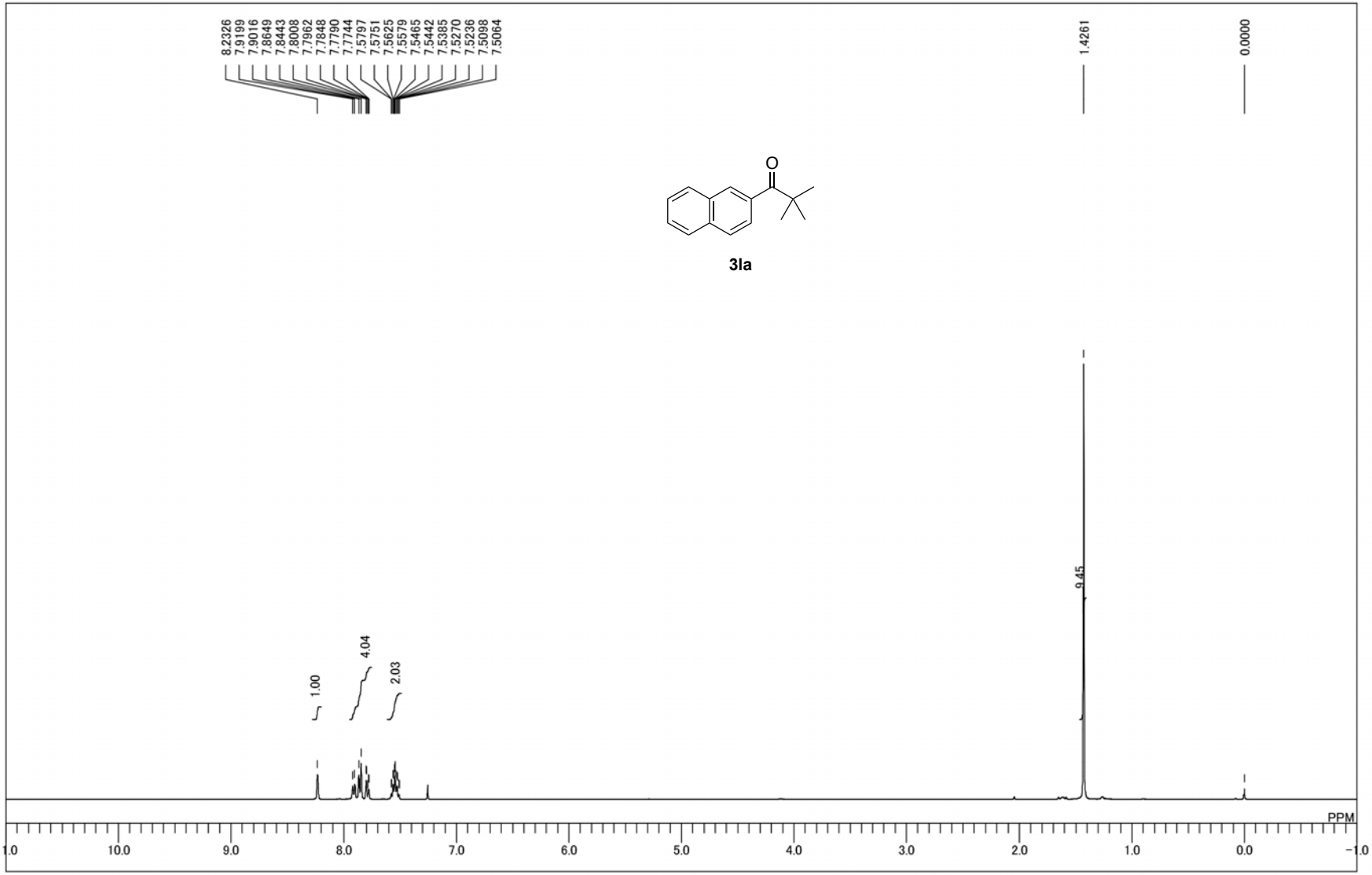
^{13}C NMR spectrum of **3ja**



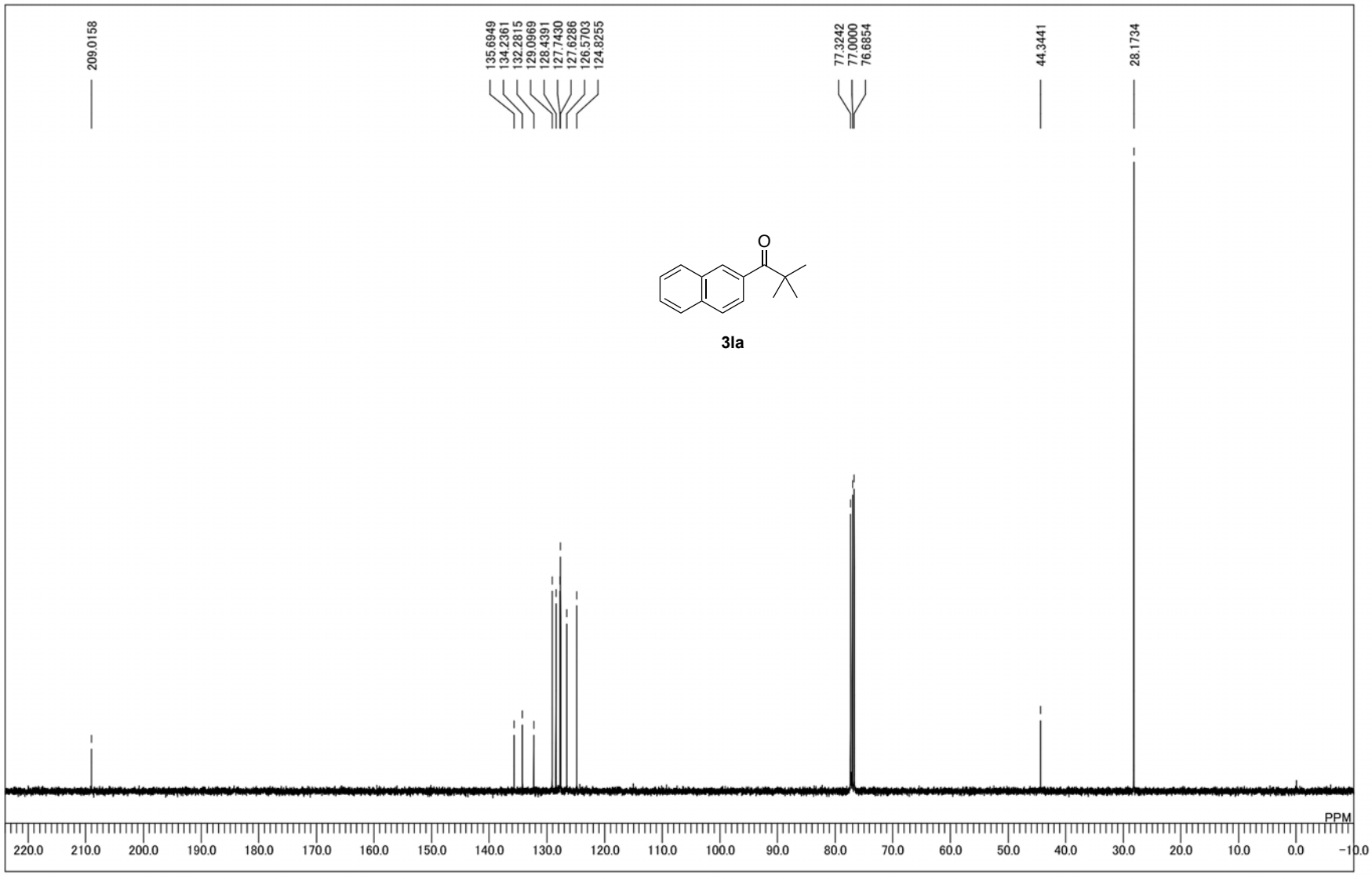
^{1}H NMR spectrum of **3ka**



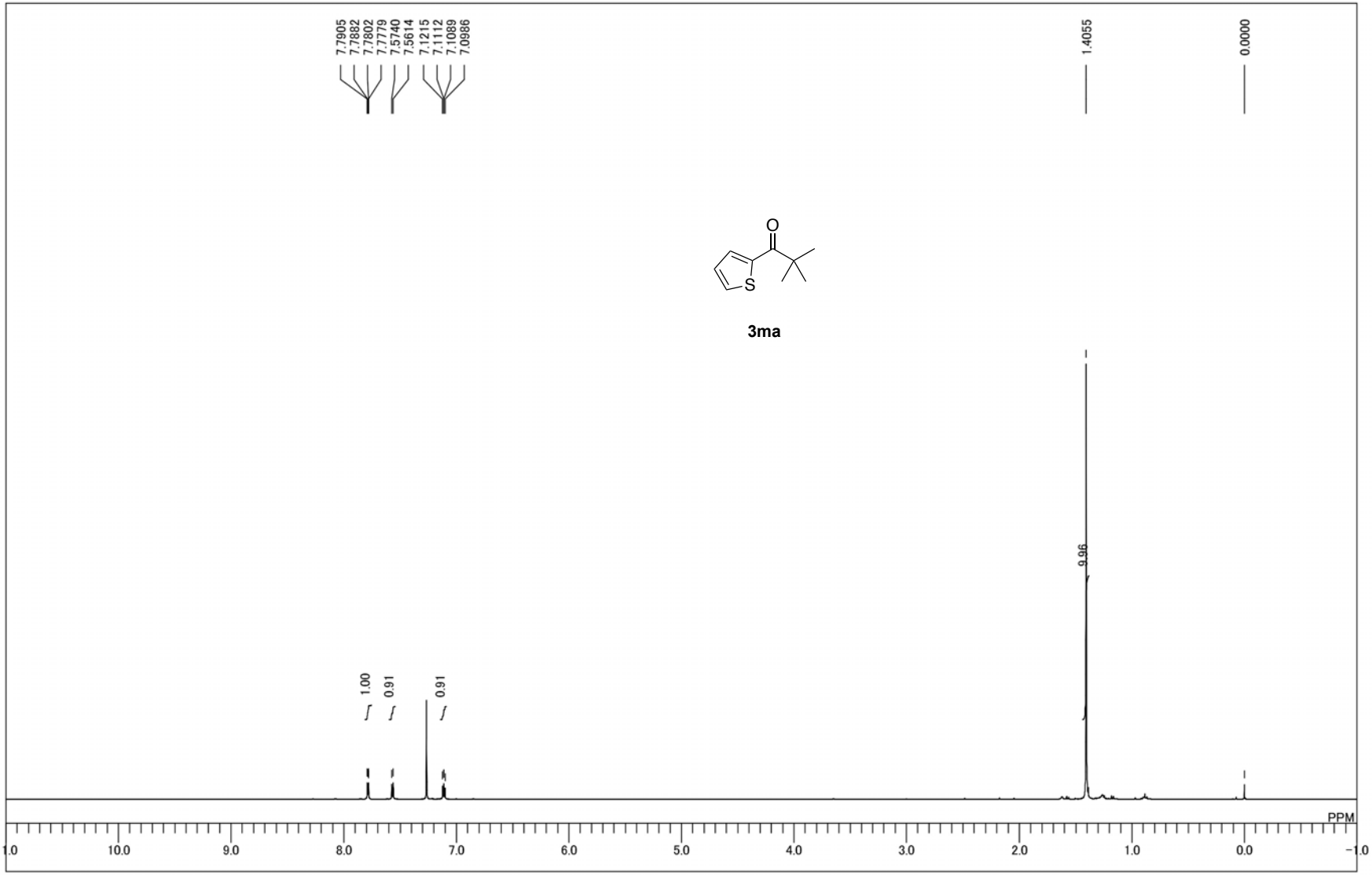
^{13}C NMR spectrum of **3ka**



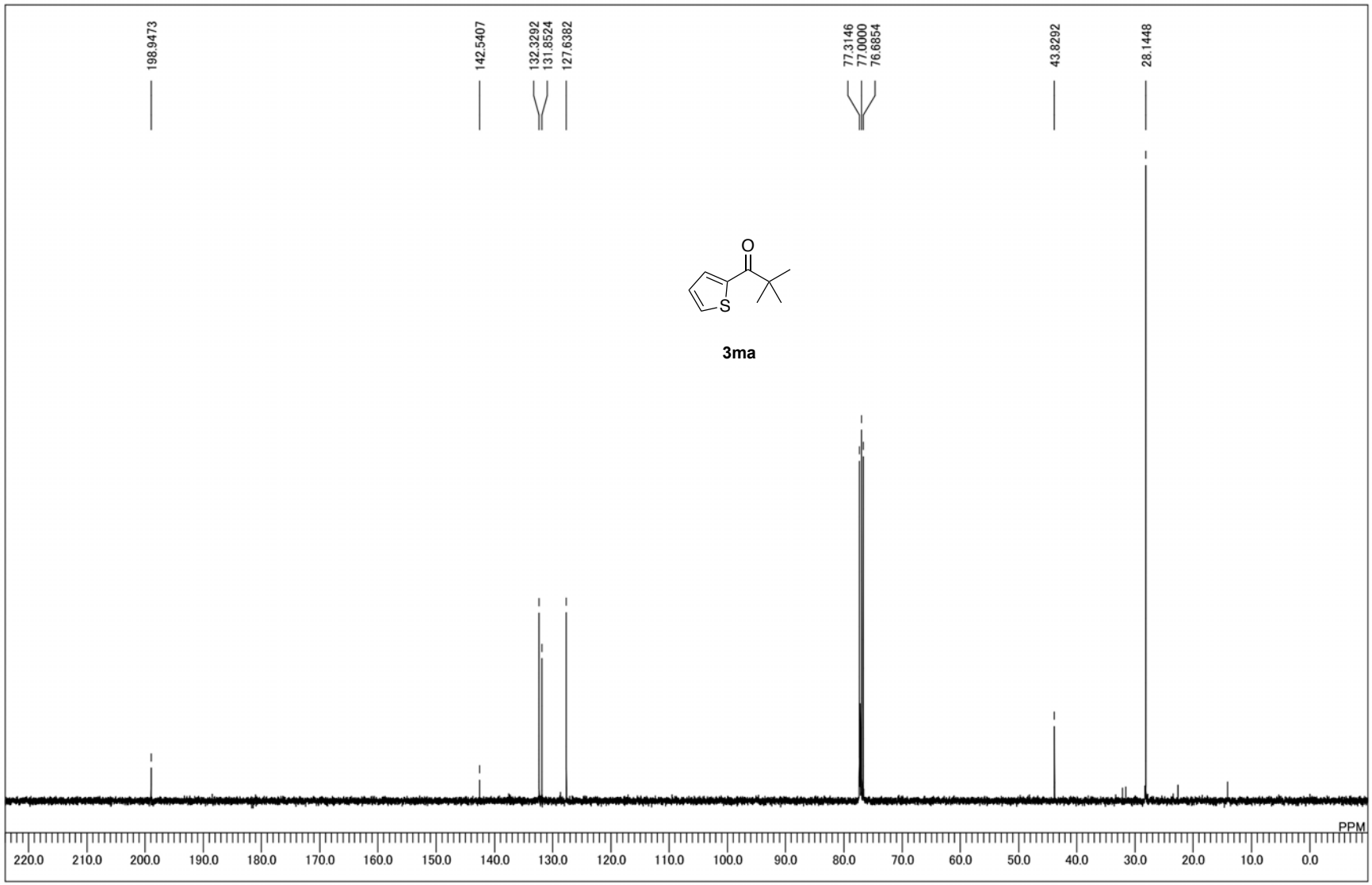
^{1}H NMR spectrum of **3la**



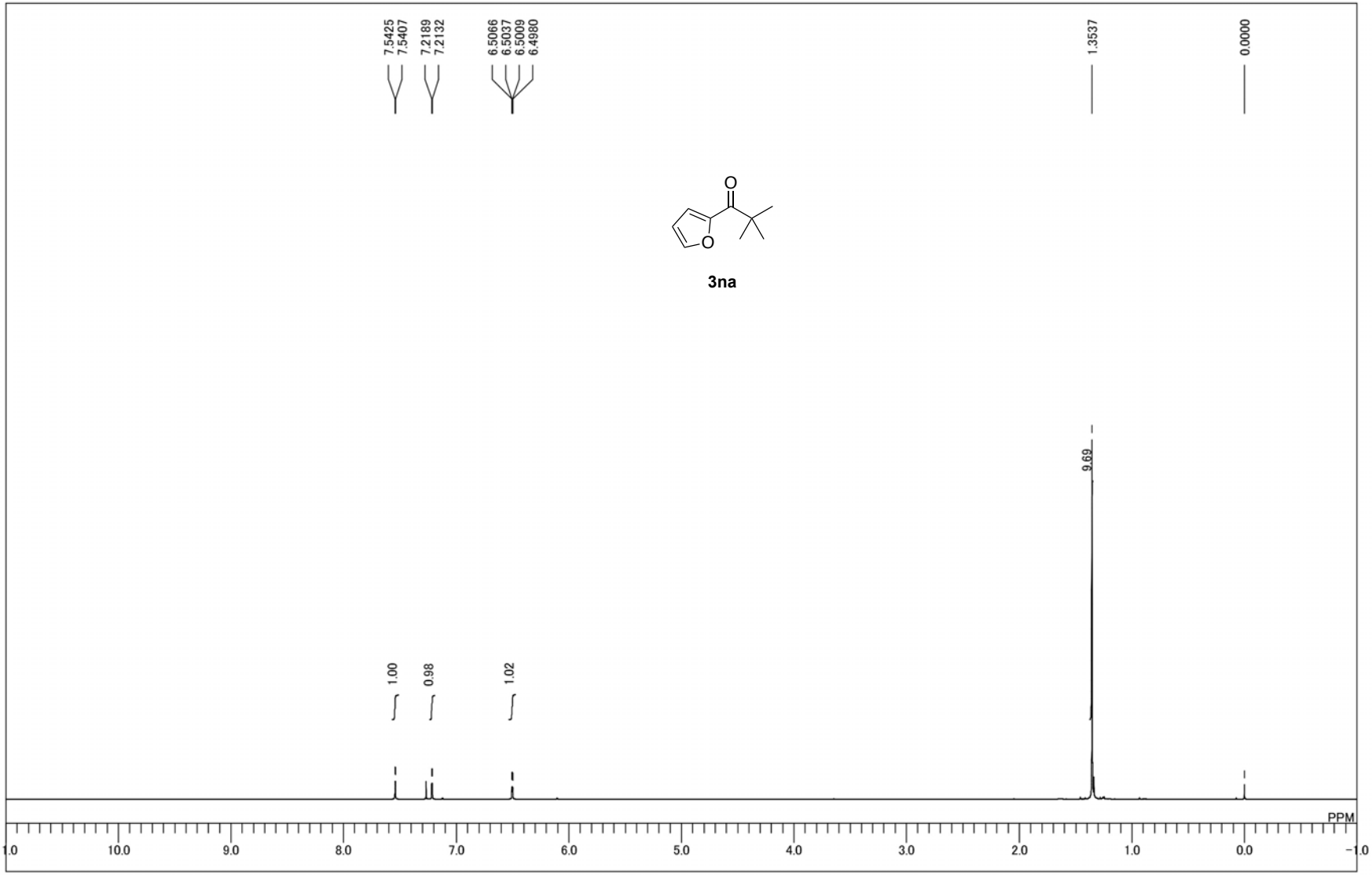
^{13}C NMR spectrum of **3la**



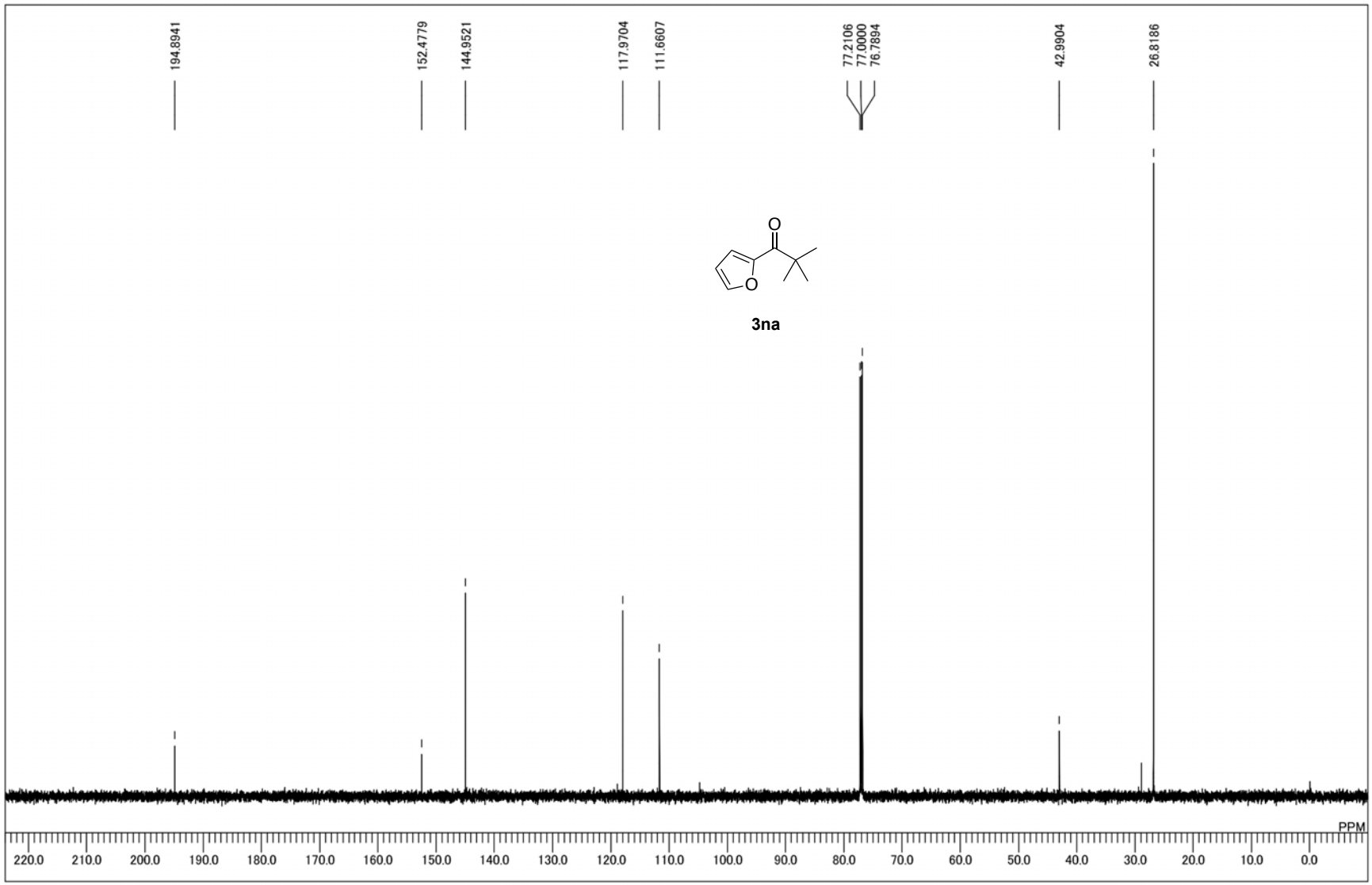
^{1}H NMR spectrum of **3ma**



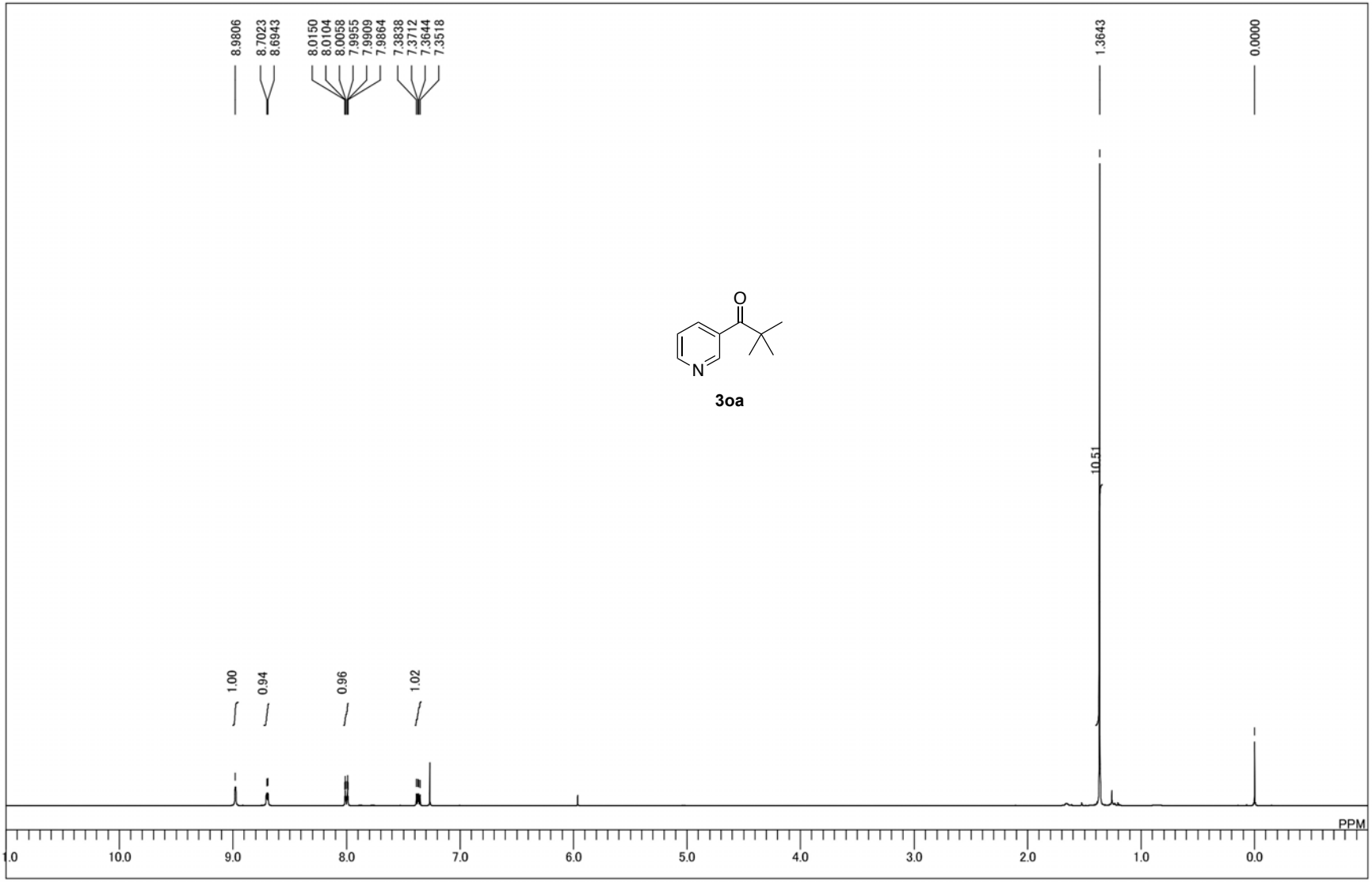
^{13}C NMR spectrum of **3ma**



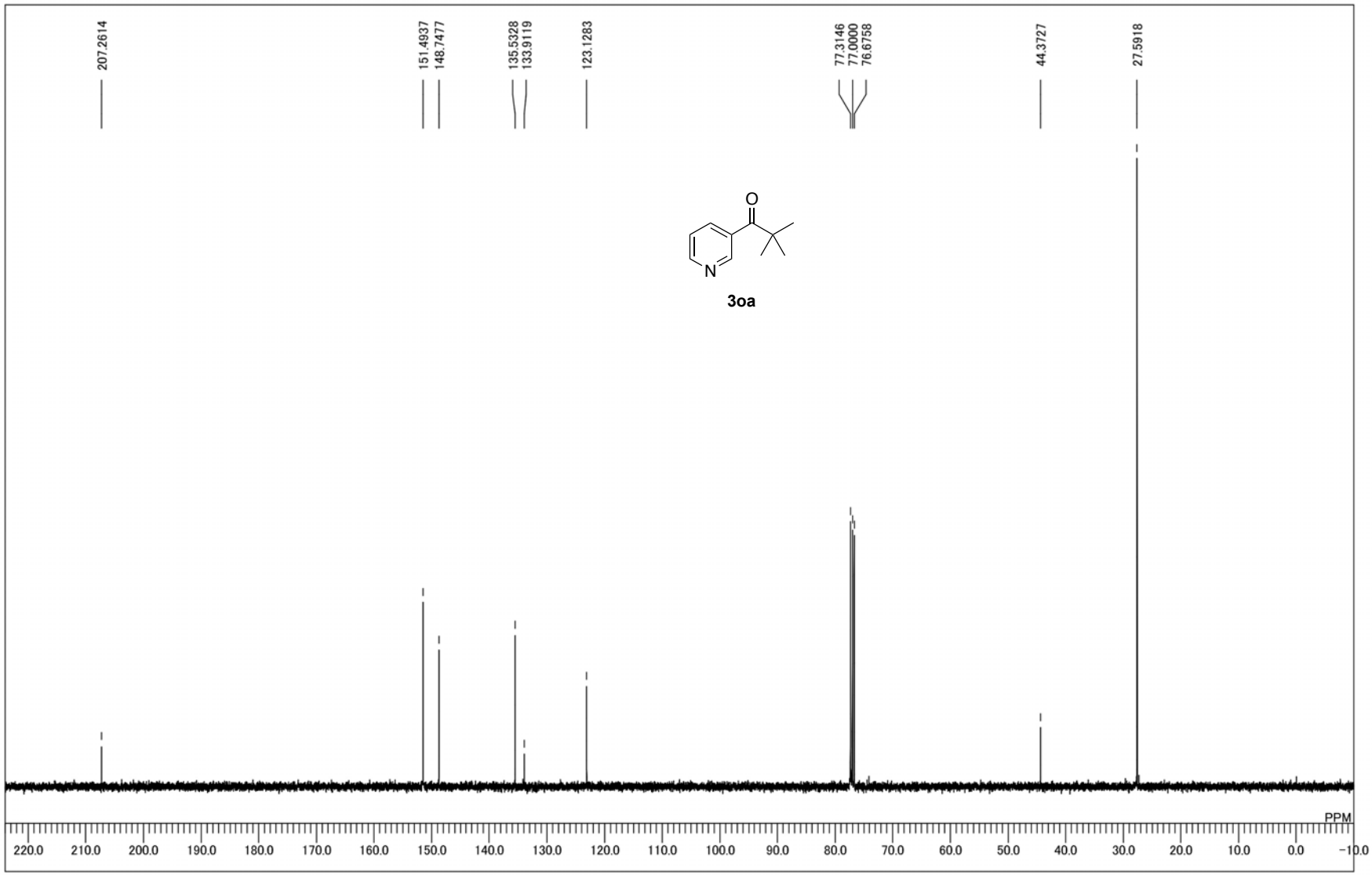
^{1}H NMR spectrum of **3na**



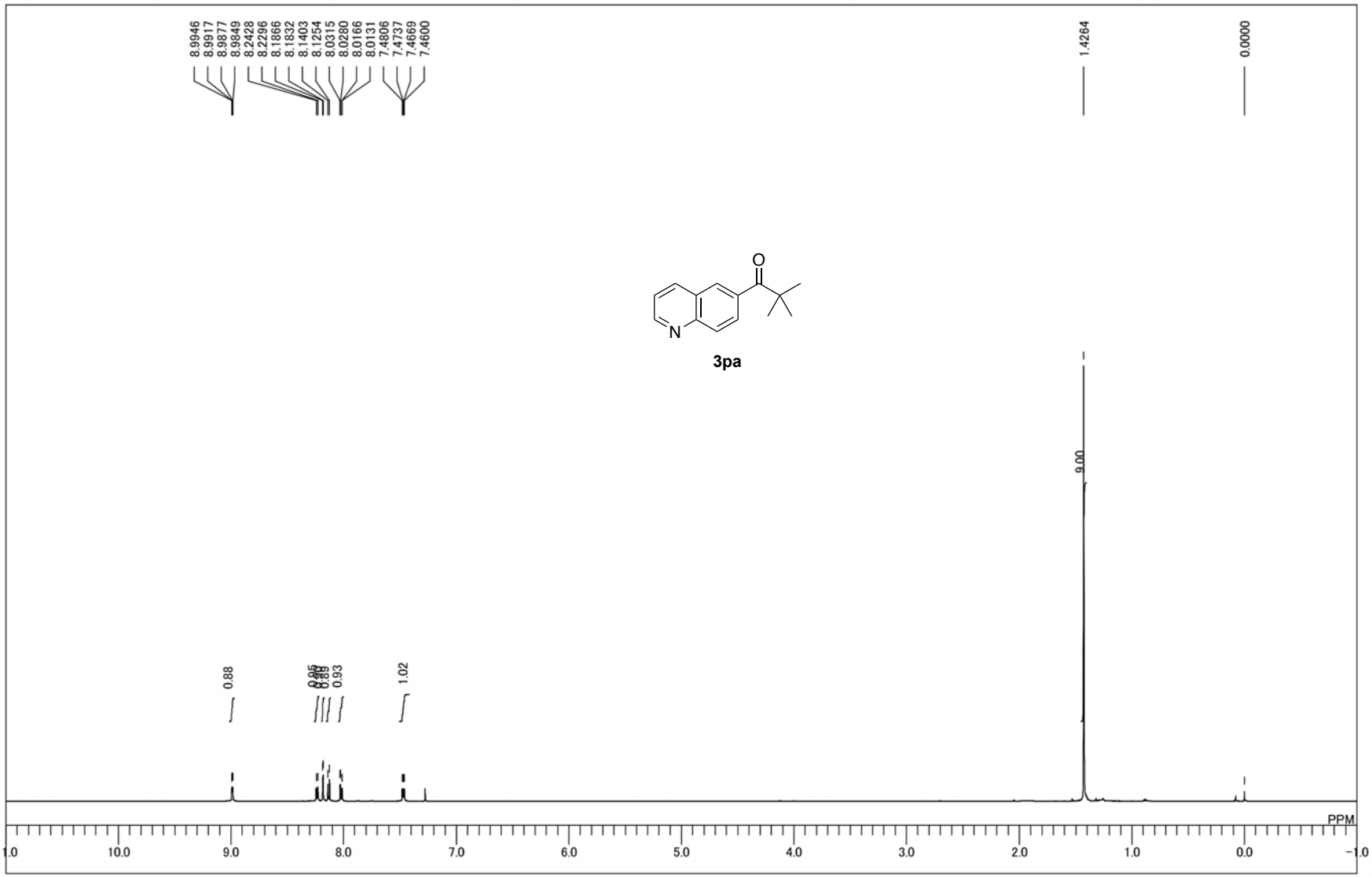
^{13}C NMR spectrum of **3na**



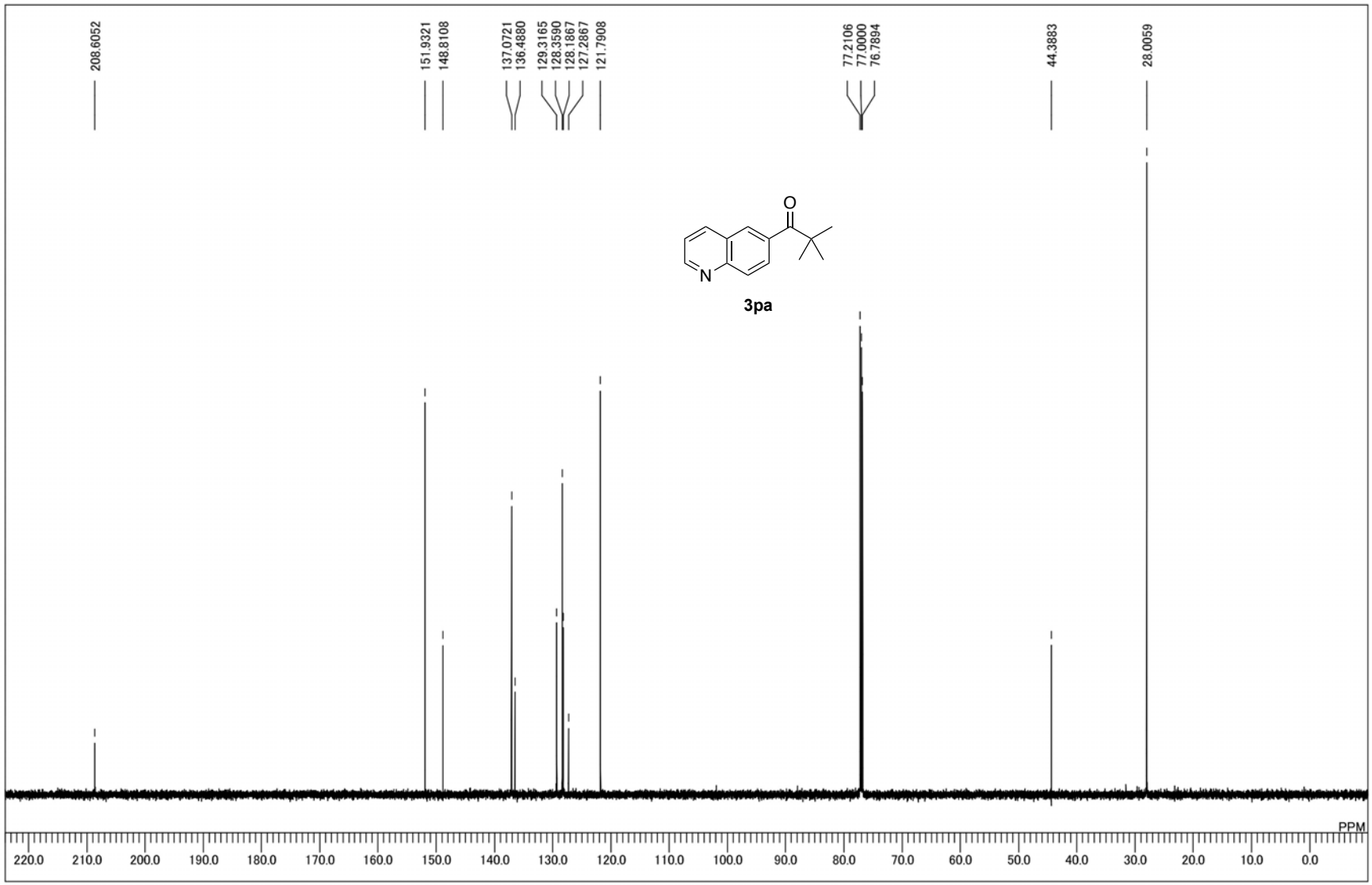
^{1}H NMR spectrum of **3oa**



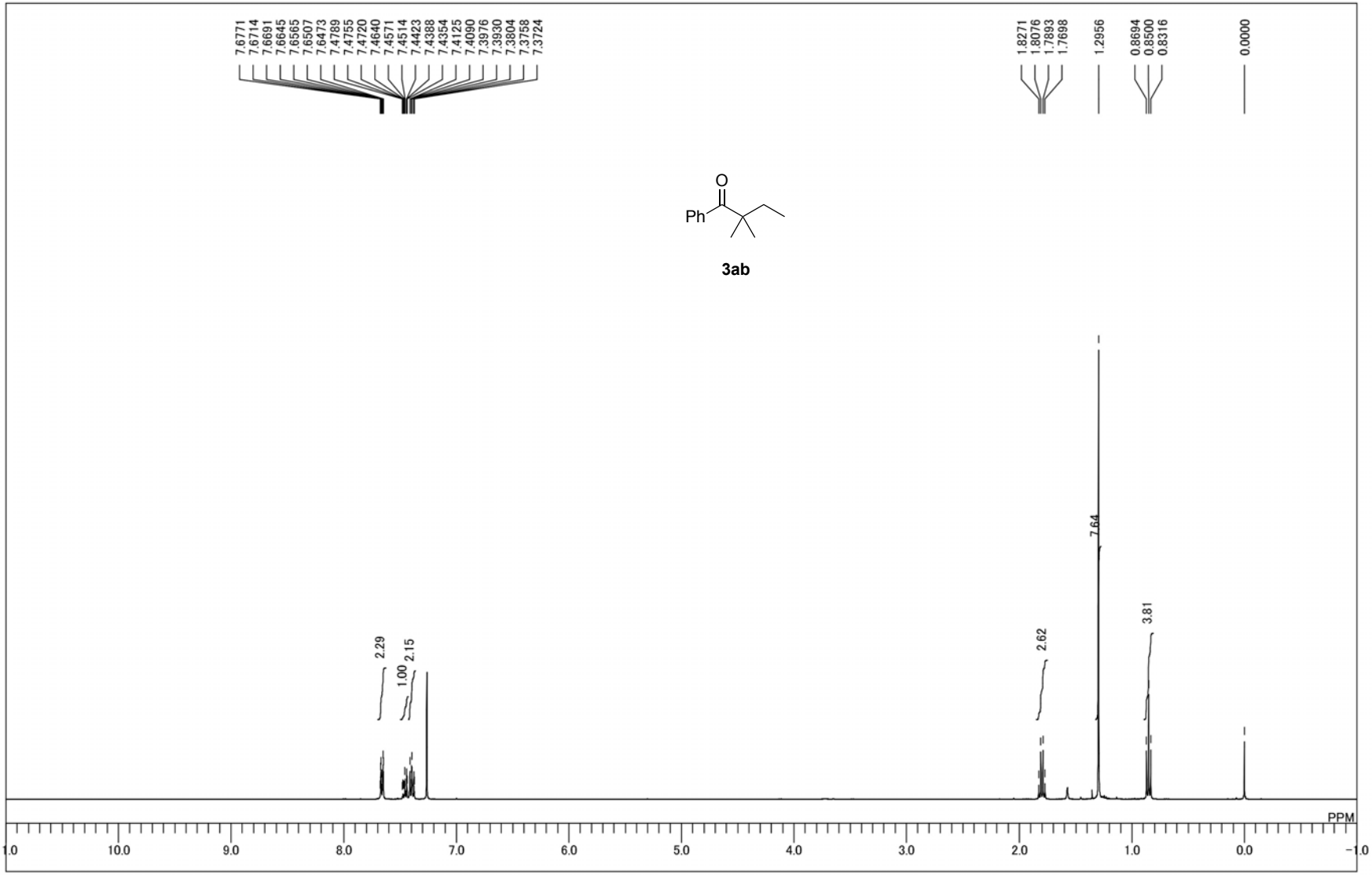
^{13}C NMR spectrum of **3oa**



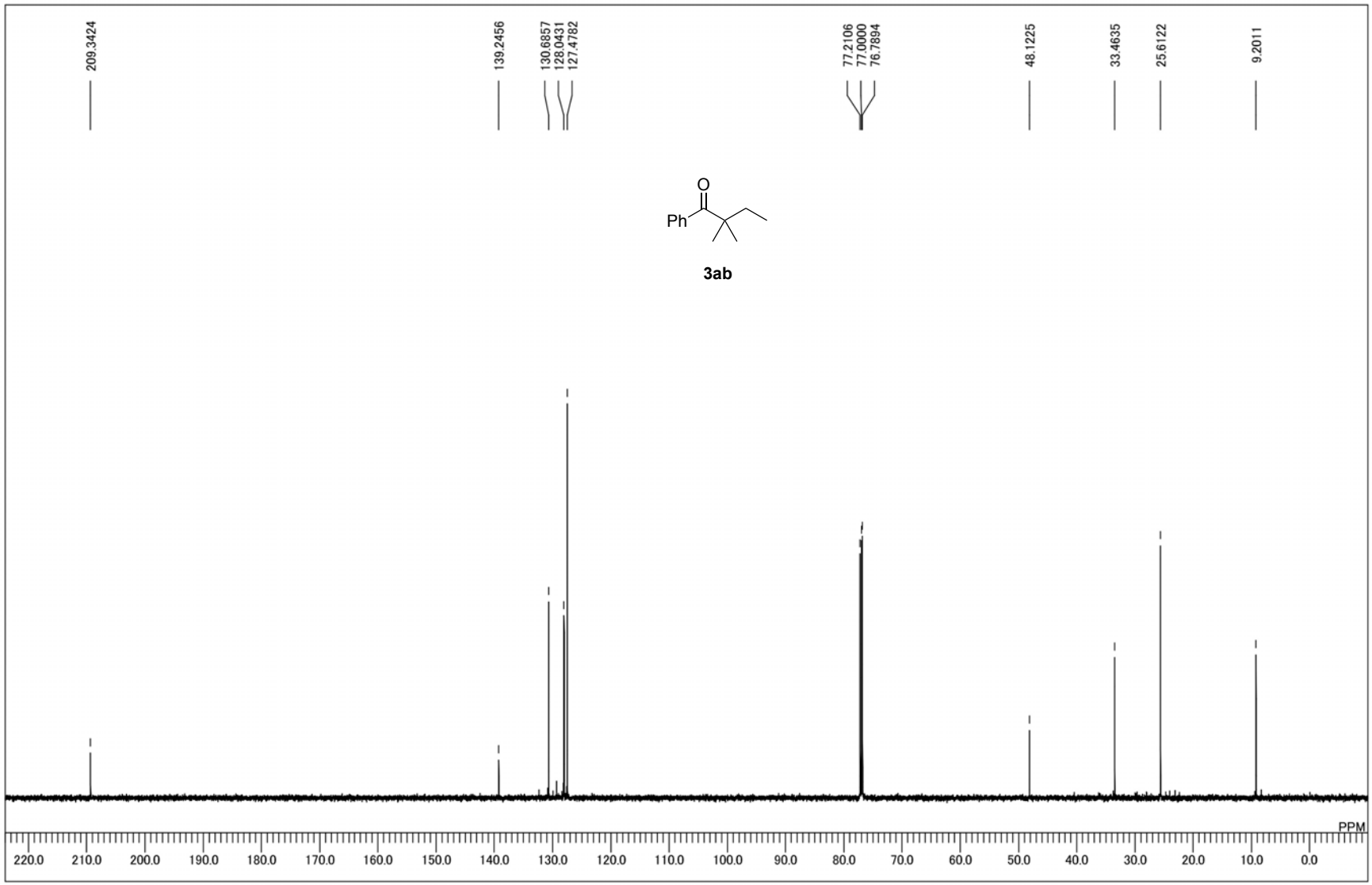
^{1}H NMR spectrum of **3pa**



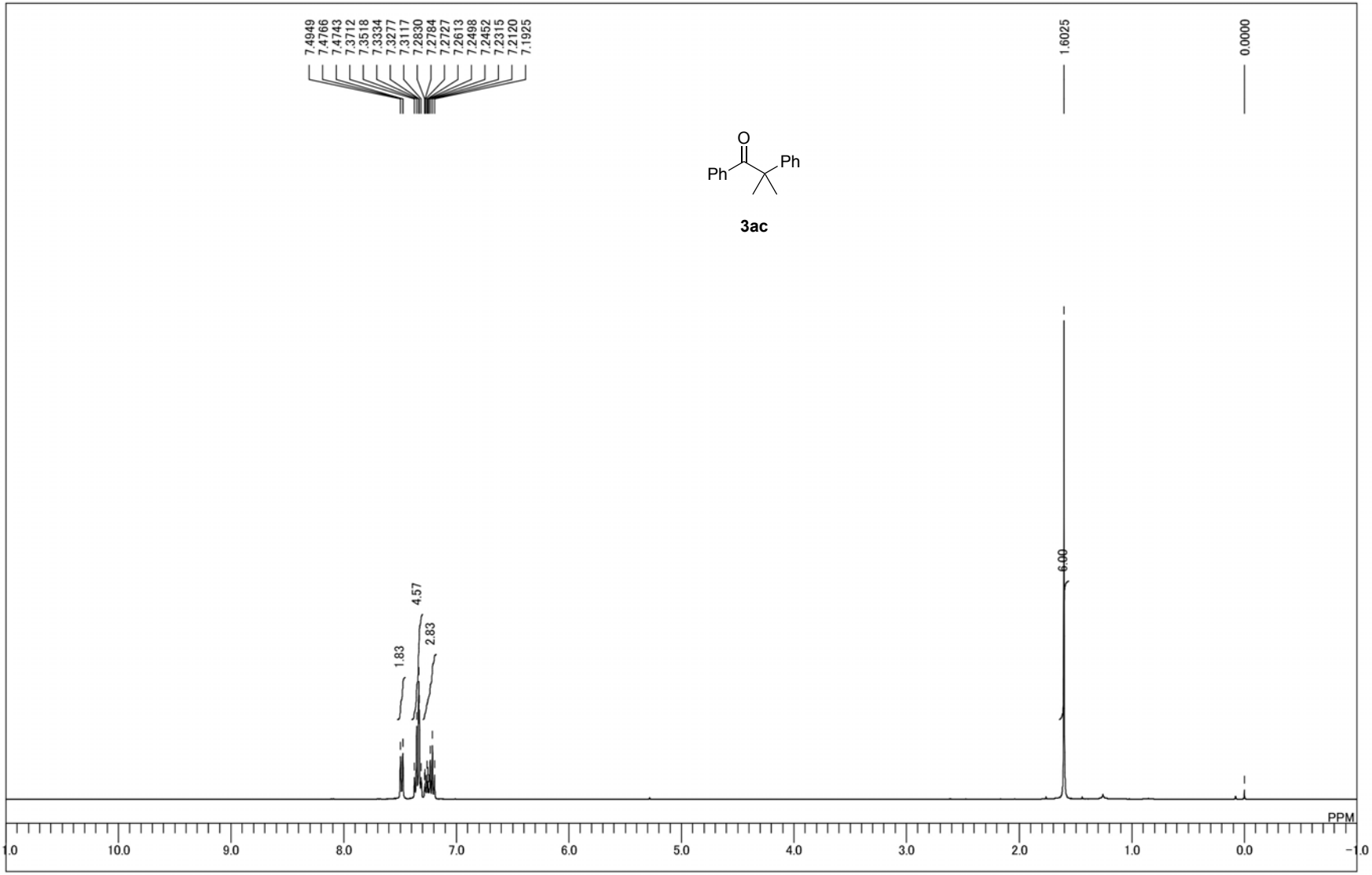
^{13}C NMR spectrum of **3pa**



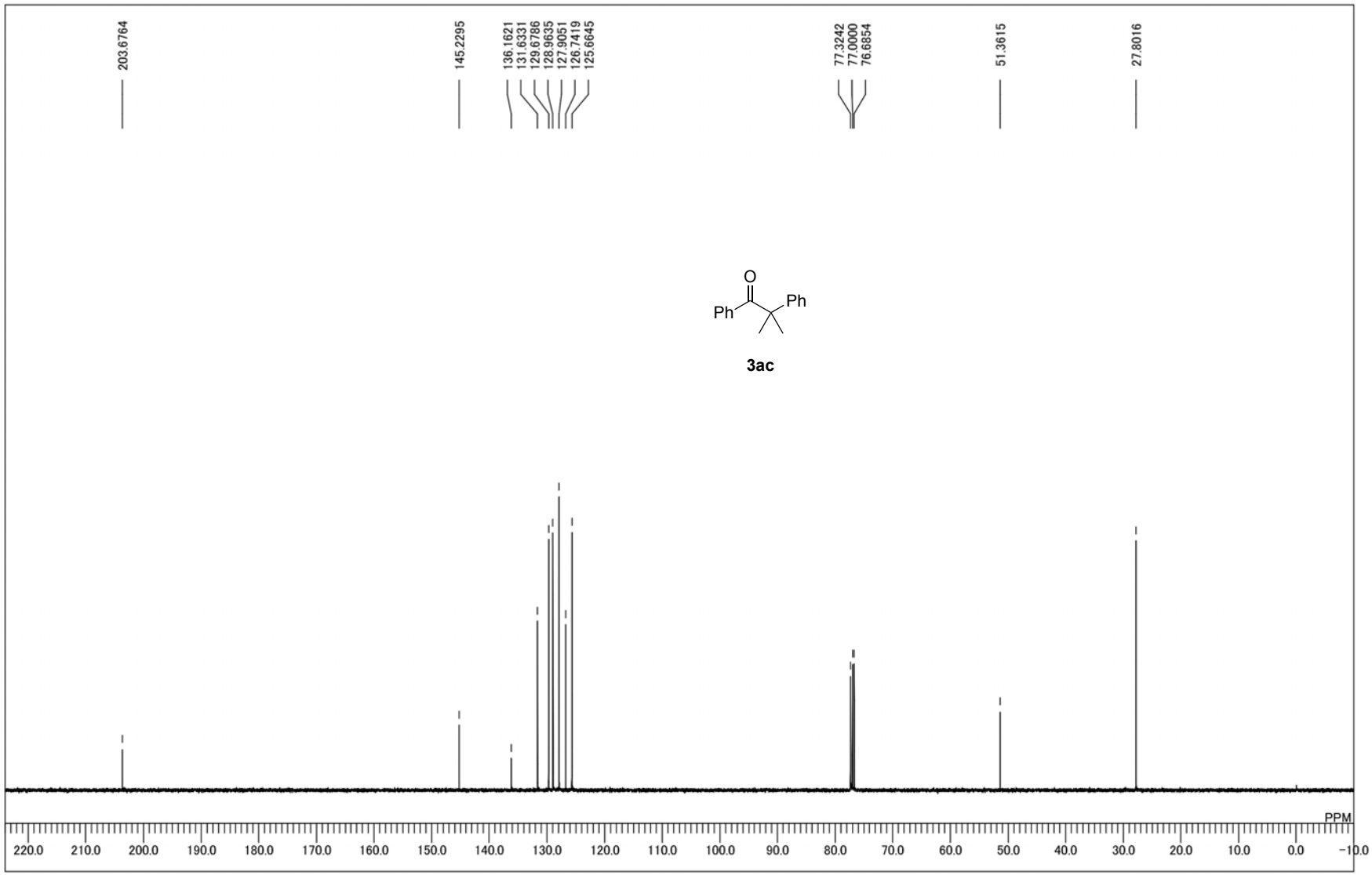
^{1}H NMR spectrum of **3ab**



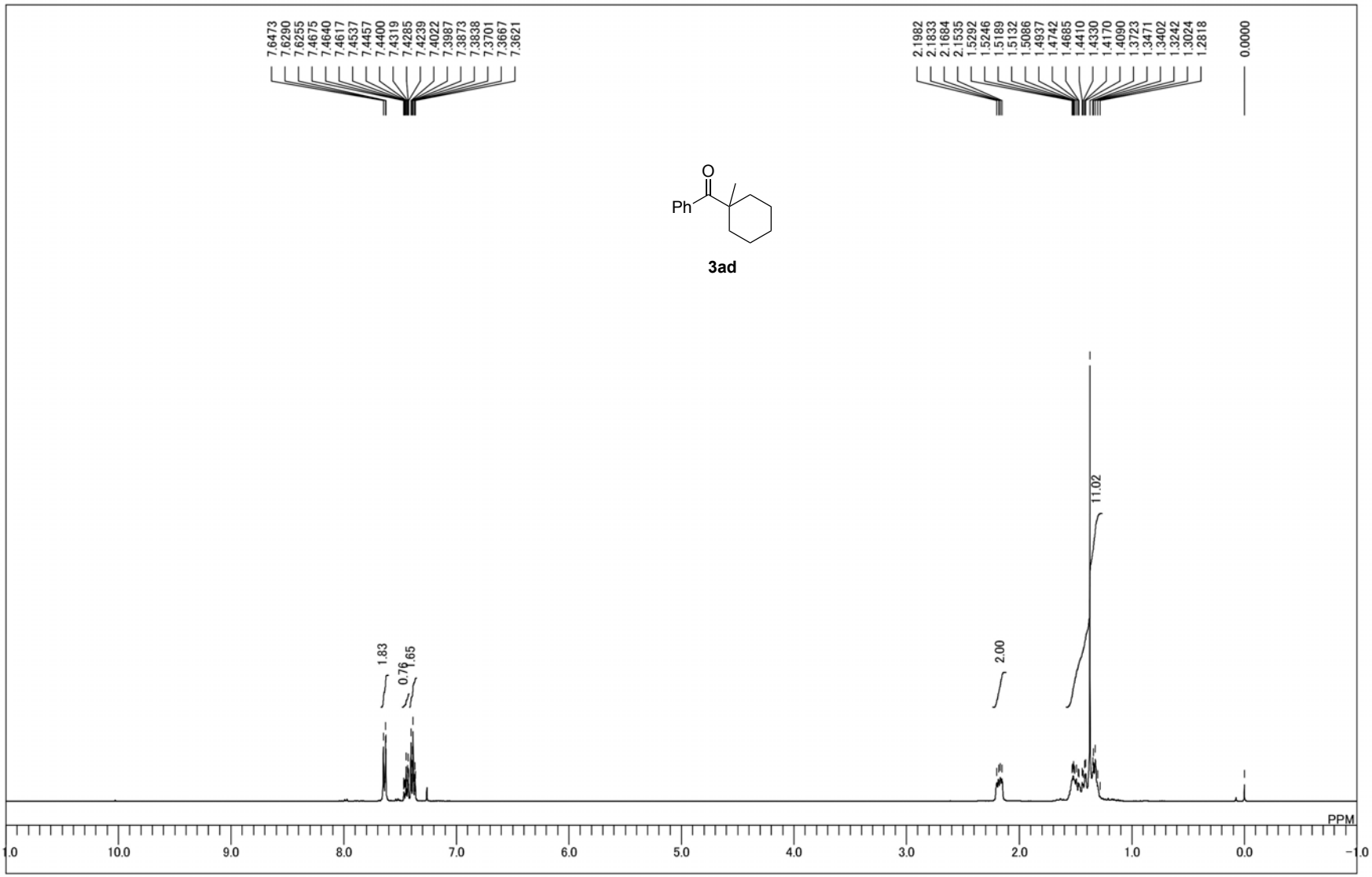
^{13}C NMR spectrum of **3ab**



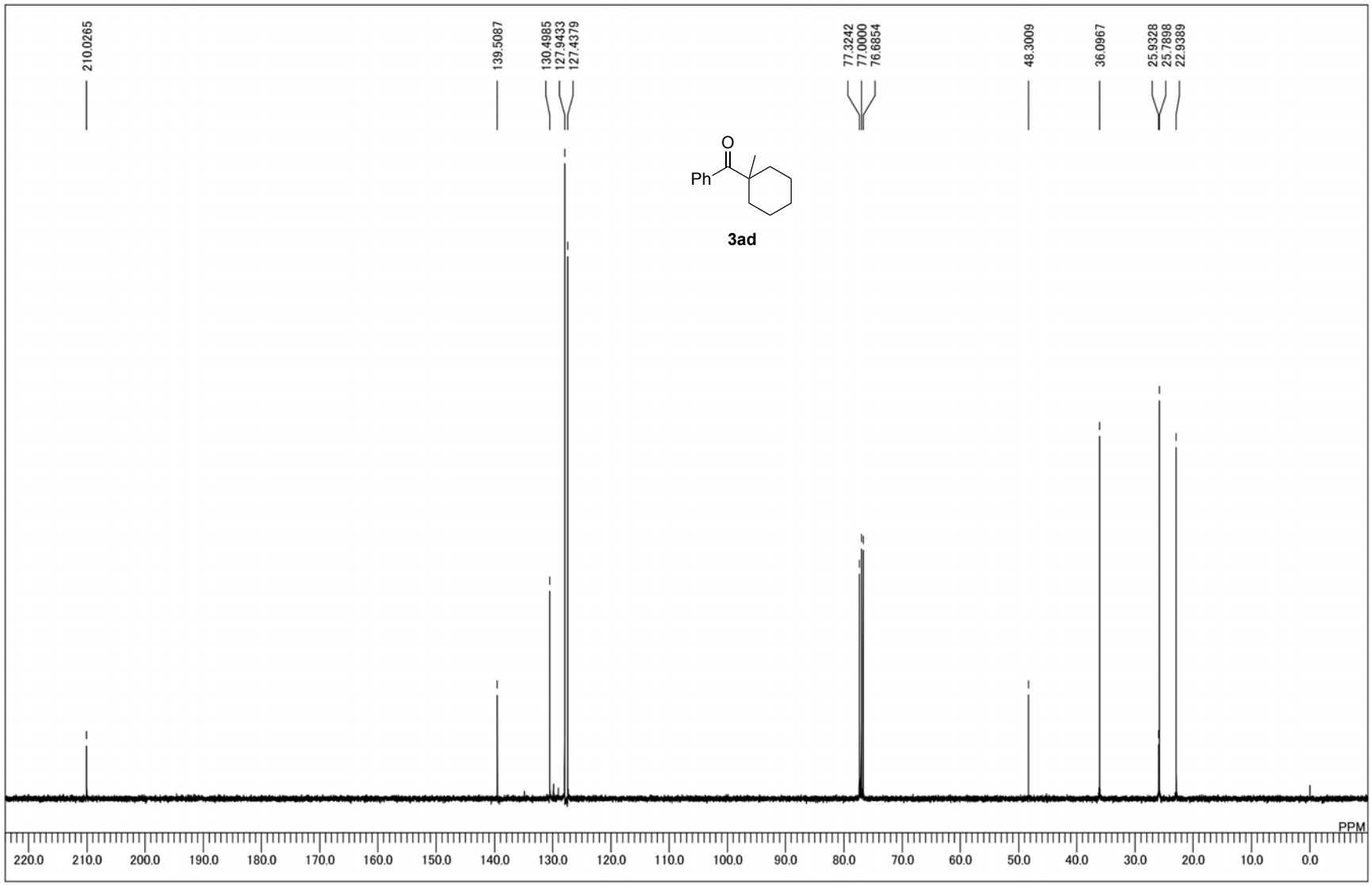
^{1}H NMR spectrum of **3ac**



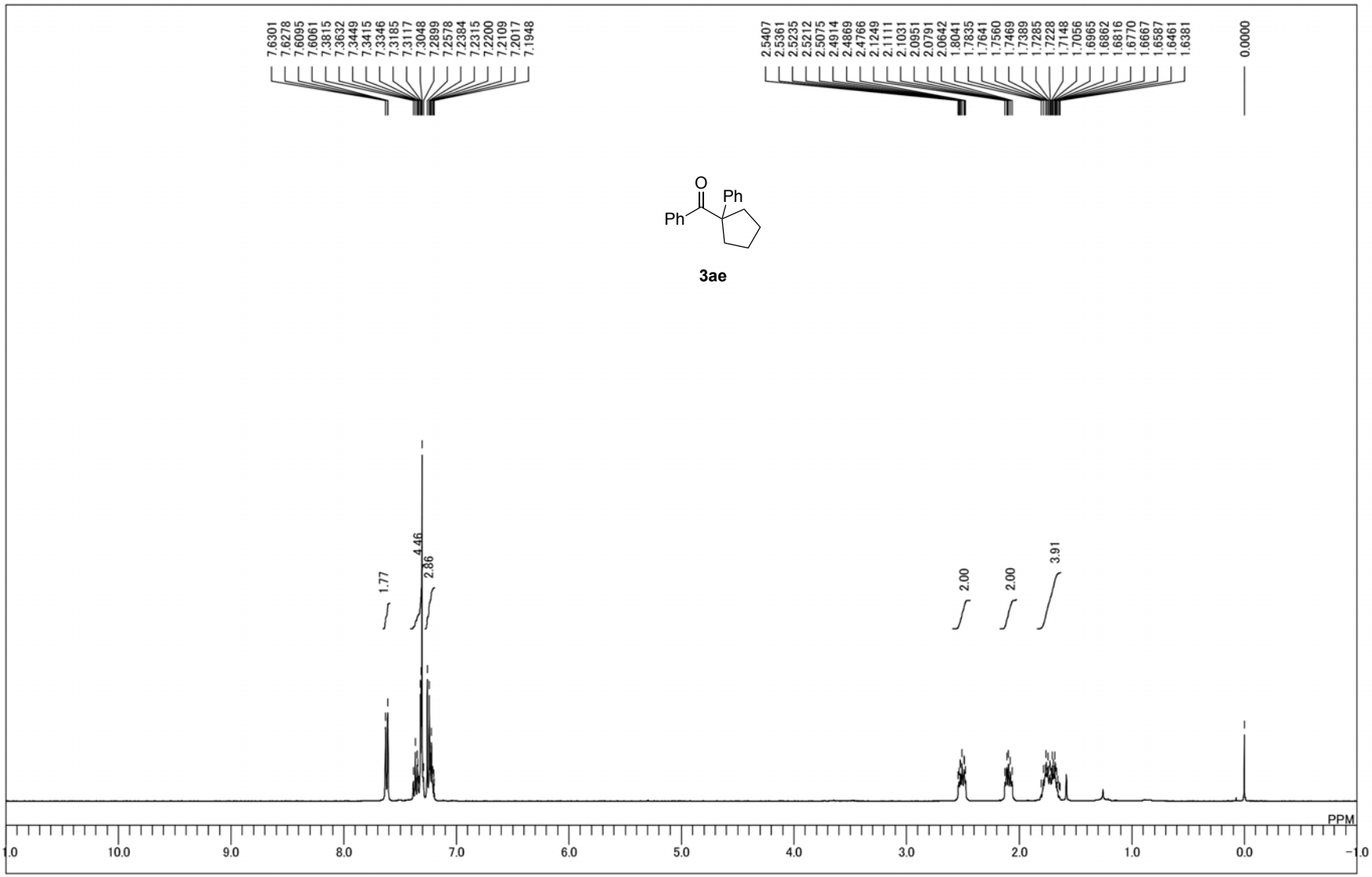
^{13}C NMR spectrum of **3ac**



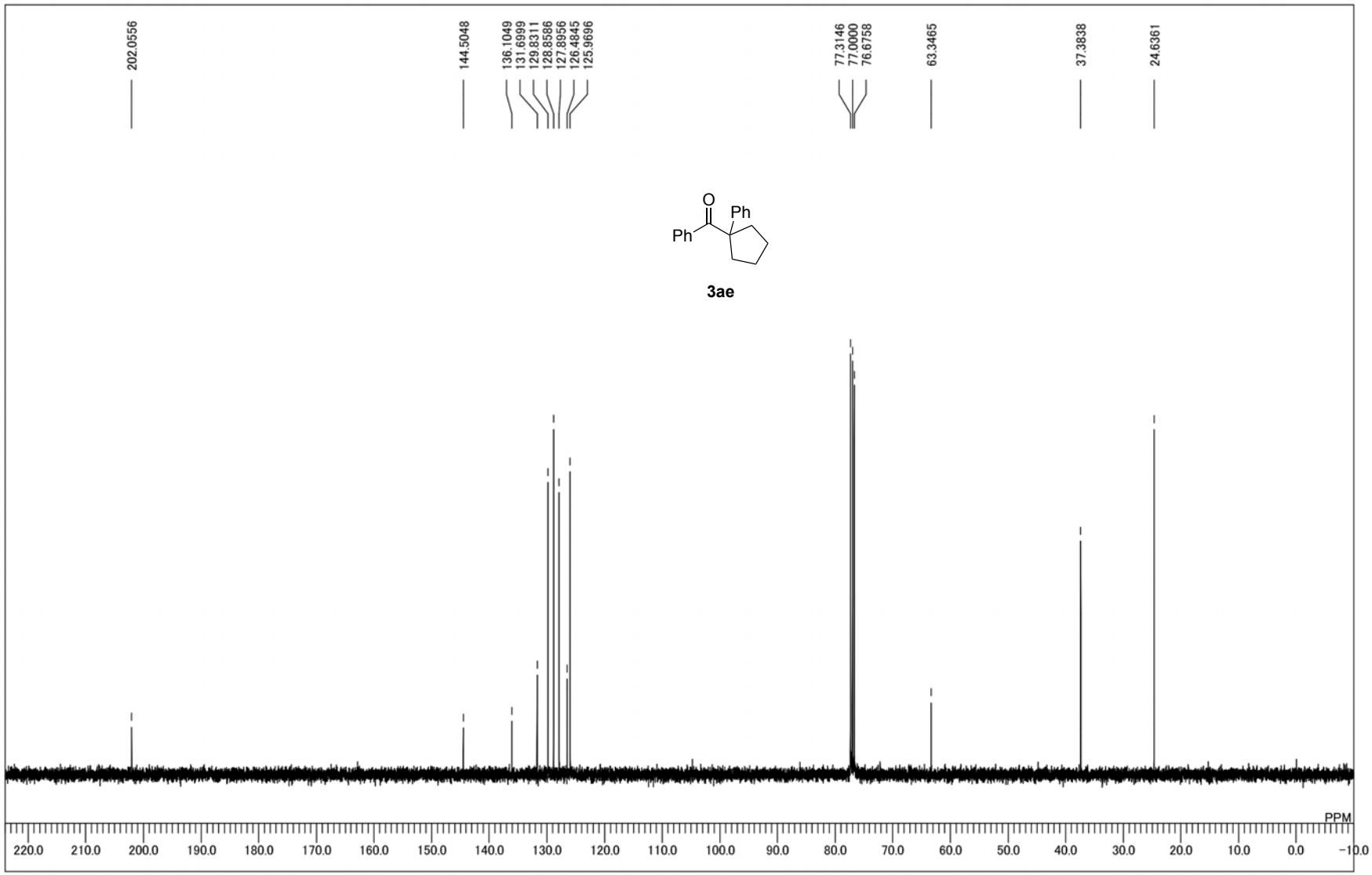
^{1}H NMR spectrum of **3ad**



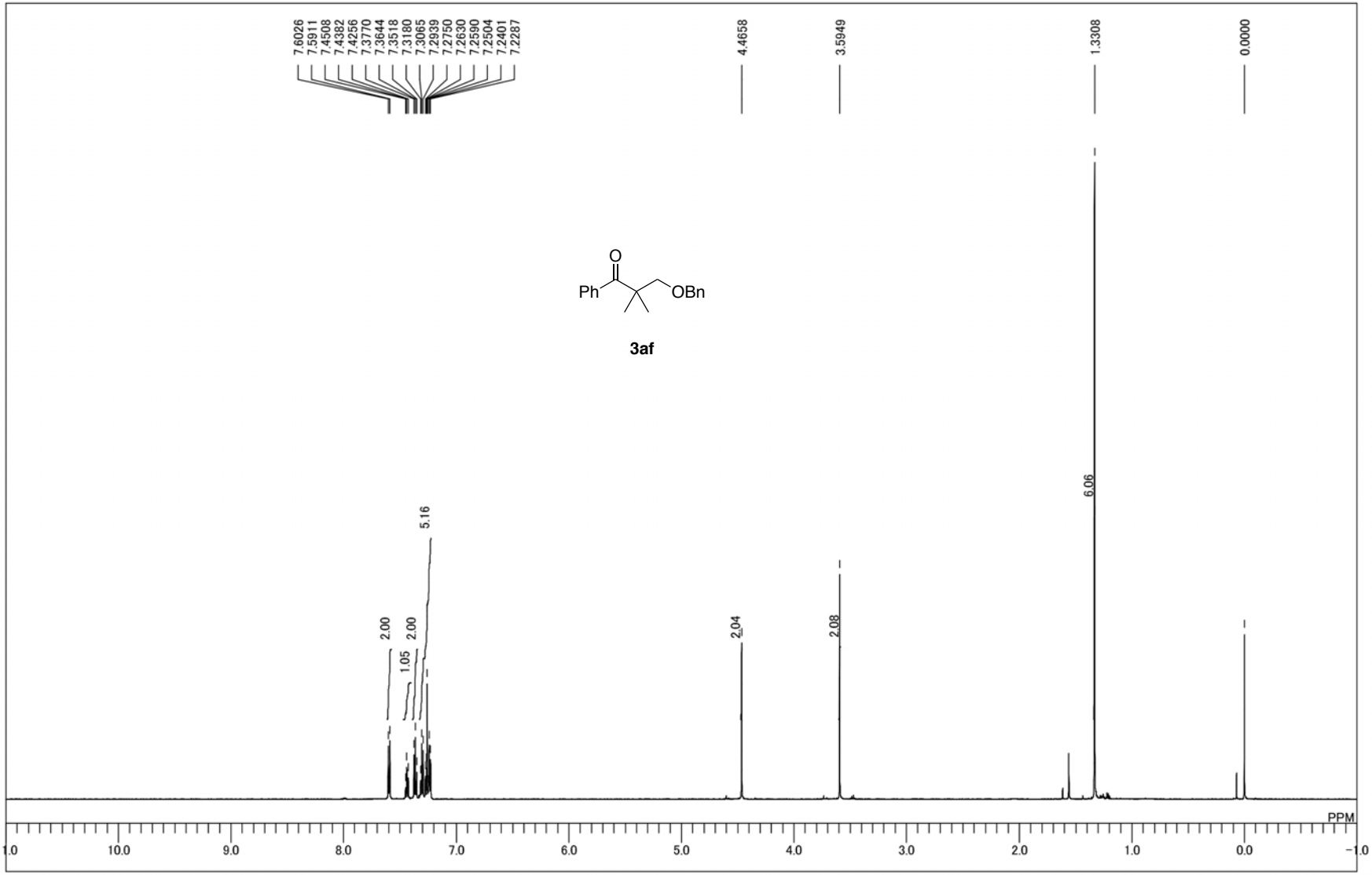
^{13}C NMR spectrum of **3ad**



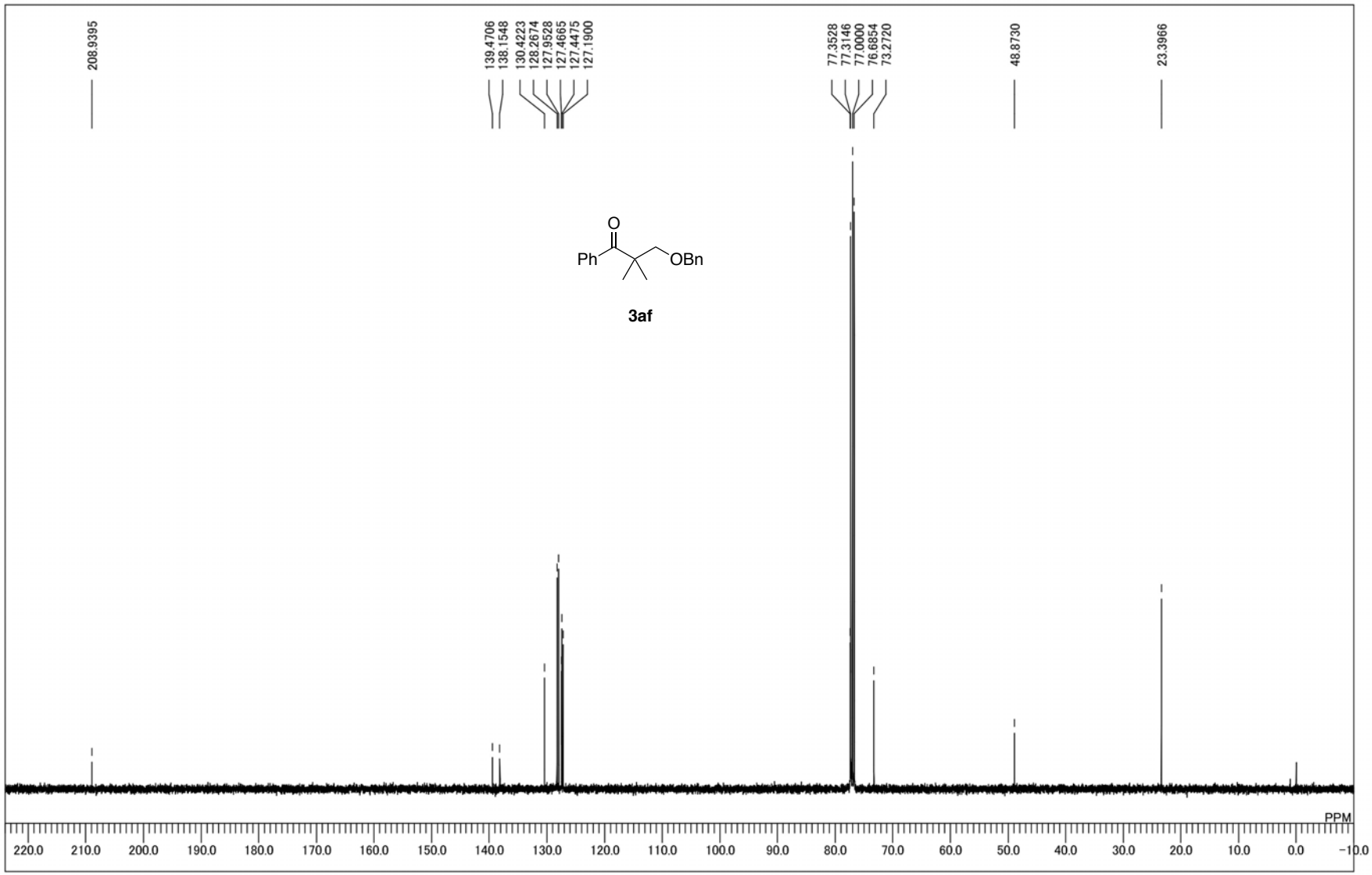
^{1}H NMR spectrum of **3ae**



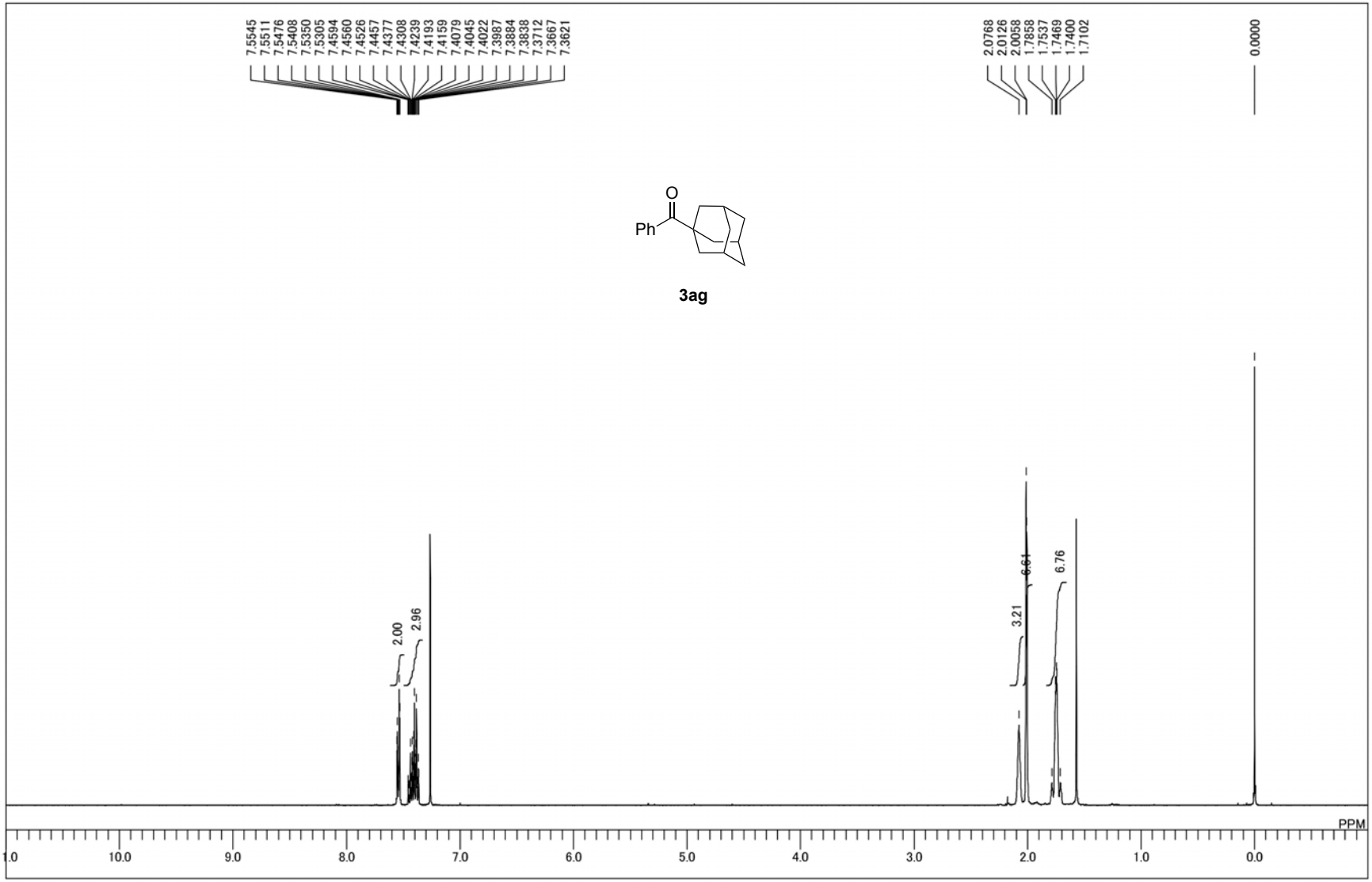
^{13}C NMR spectrum of **3ae**



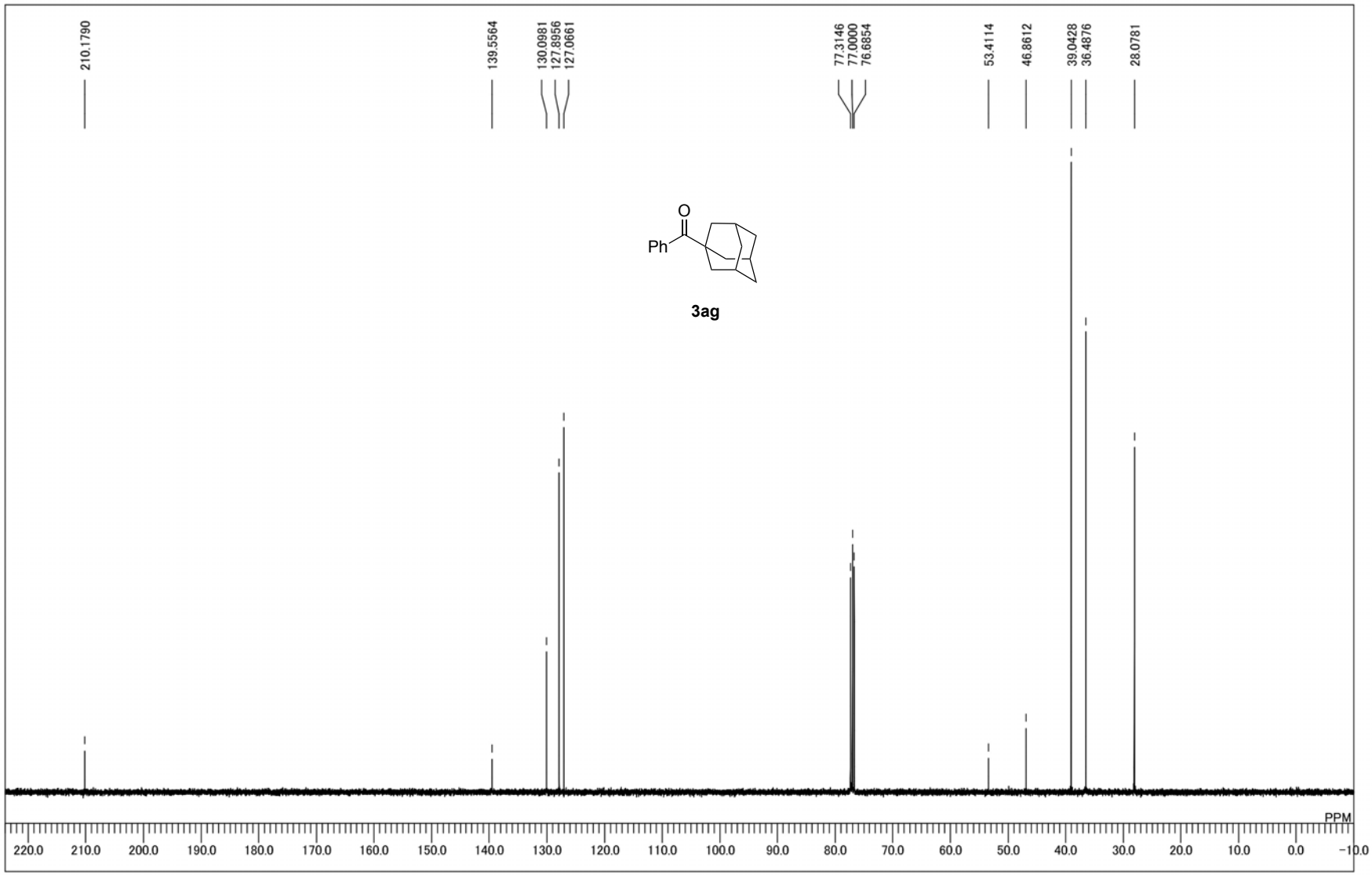
^{1}H NMR spectrum of **3af**



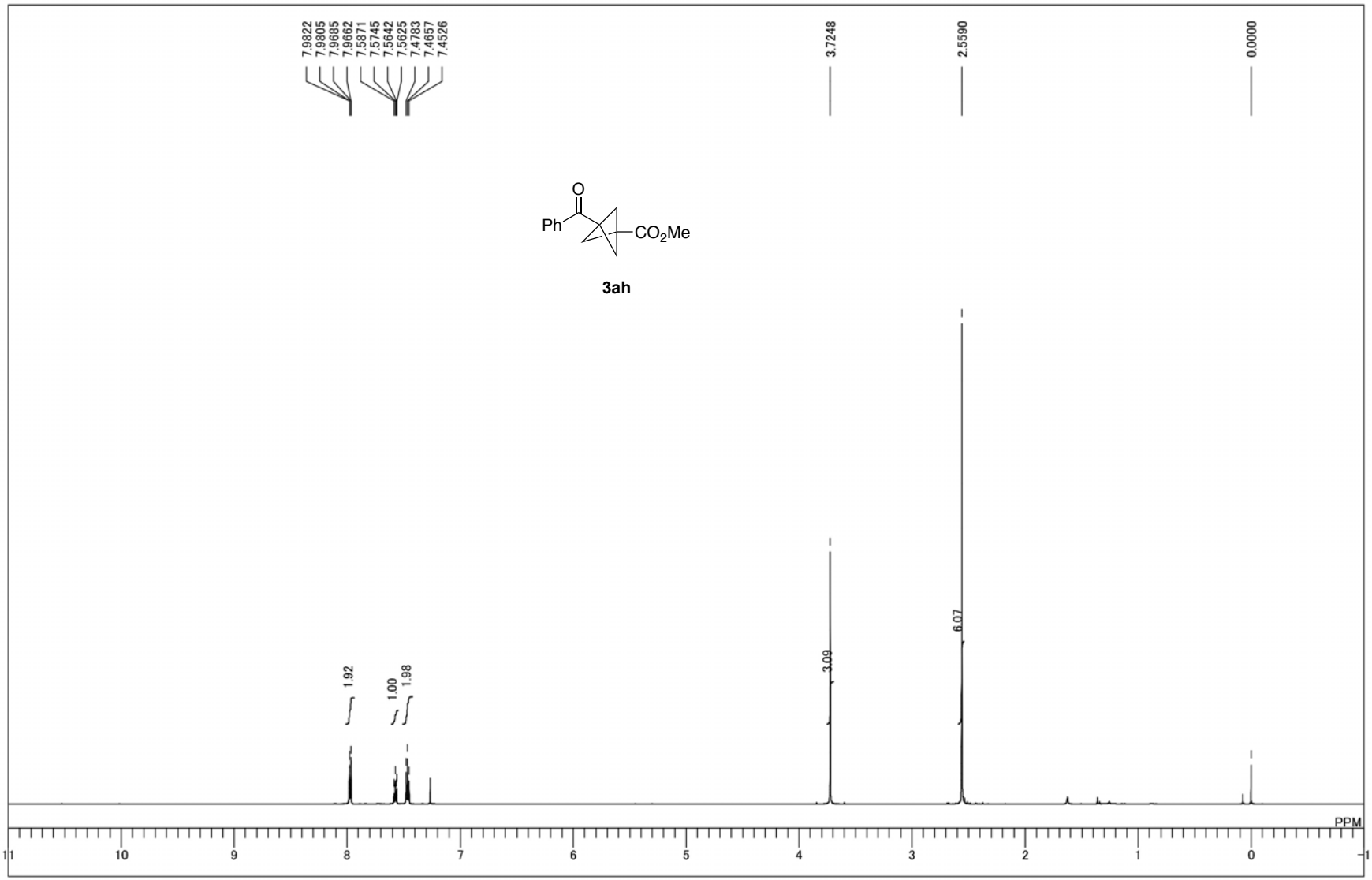
^{13}C NMR spectrum of **3af**



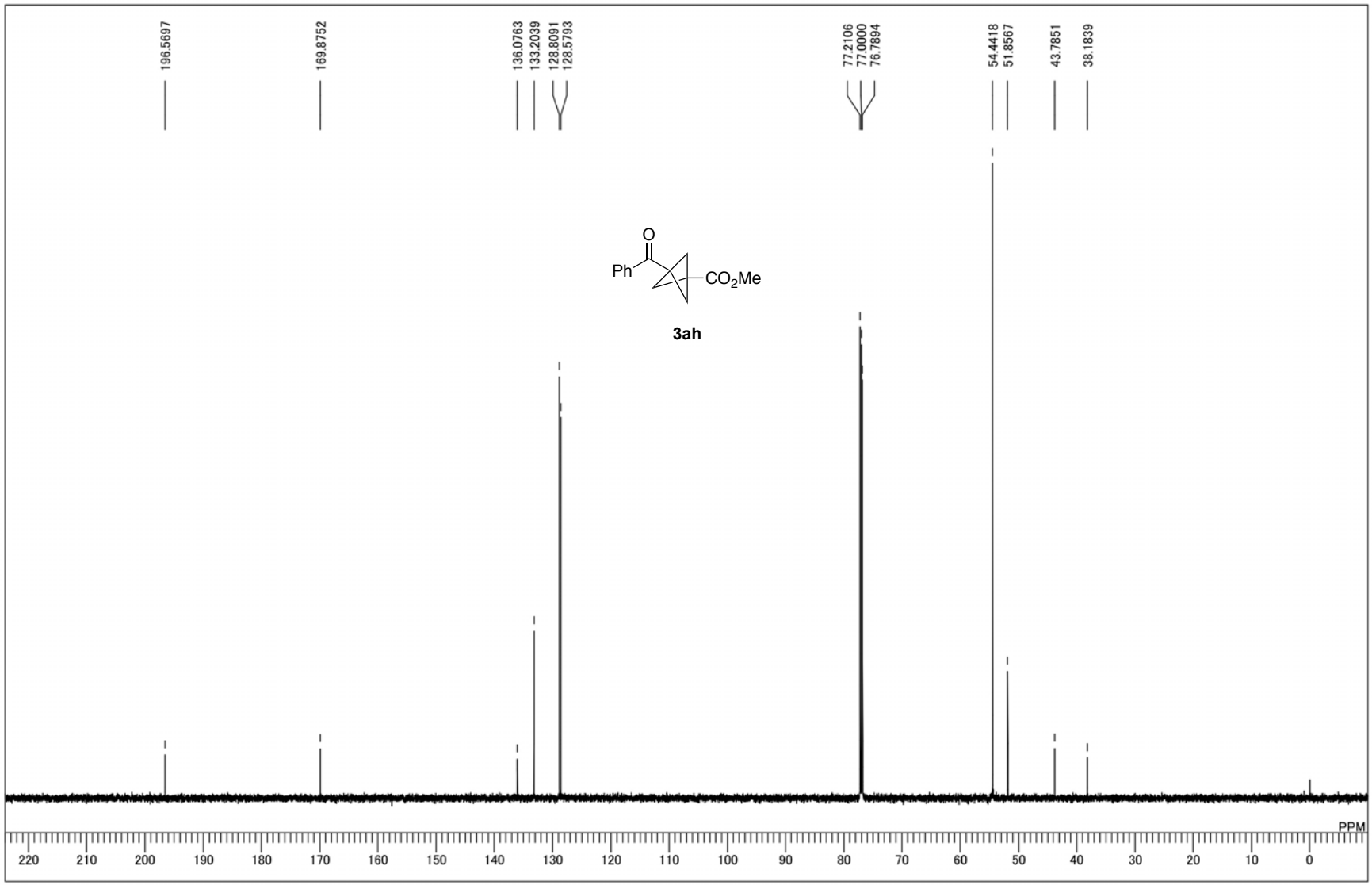
^{1}H NMR spectrum of **3ag**



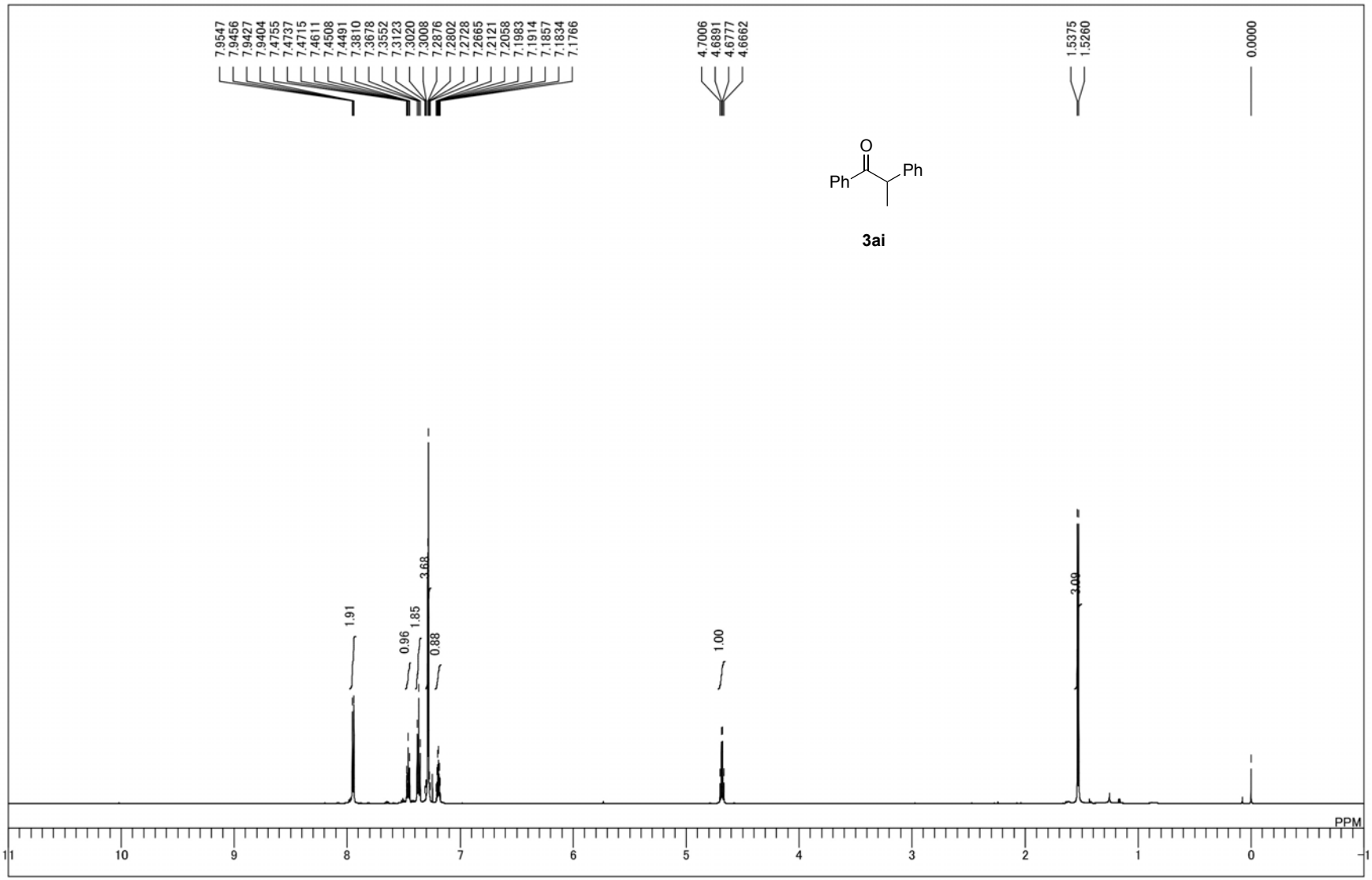
^{13}C NMR spectrum of **3ag**



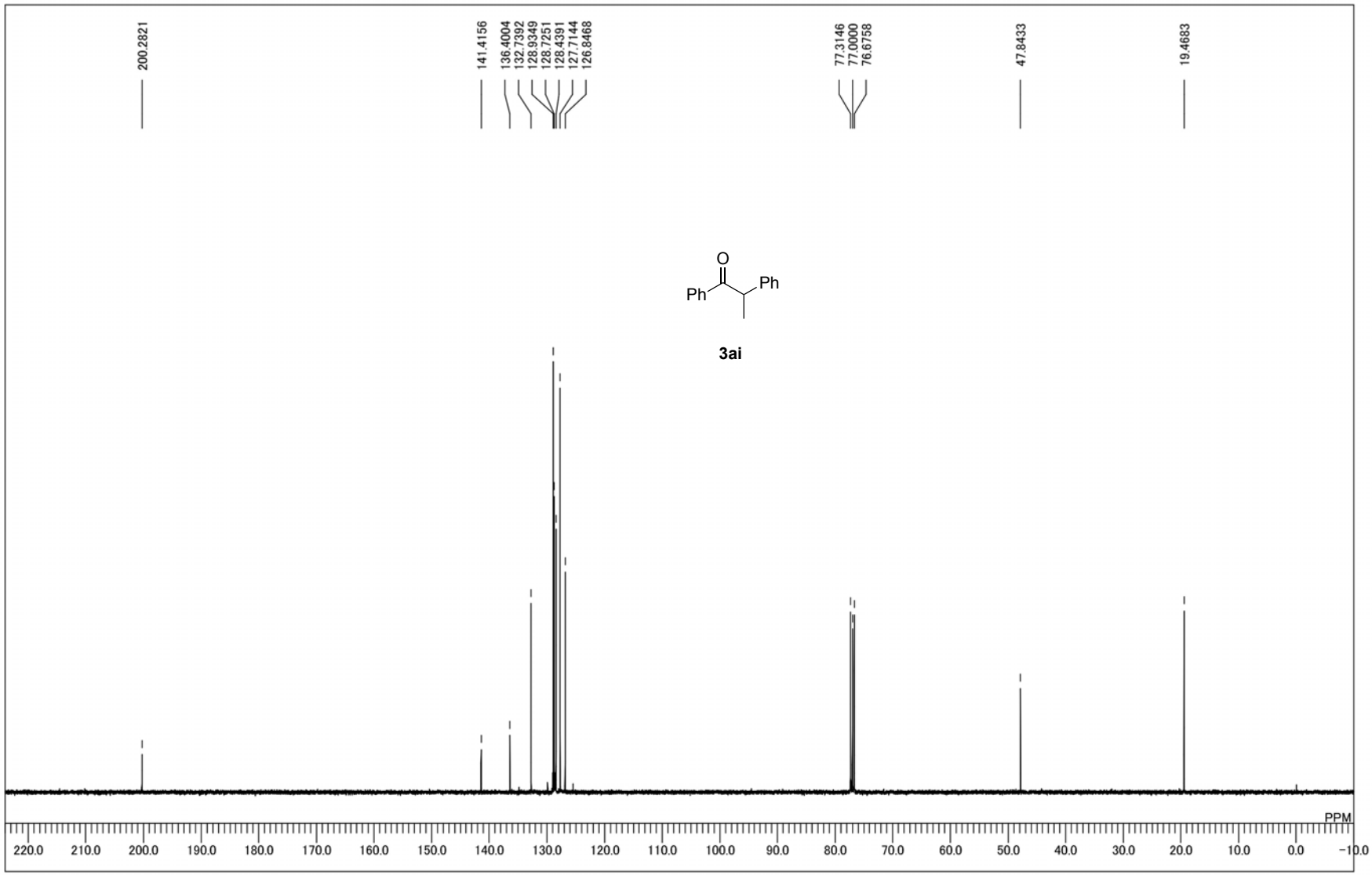
^{1}H NMR spectrum of **3ah**



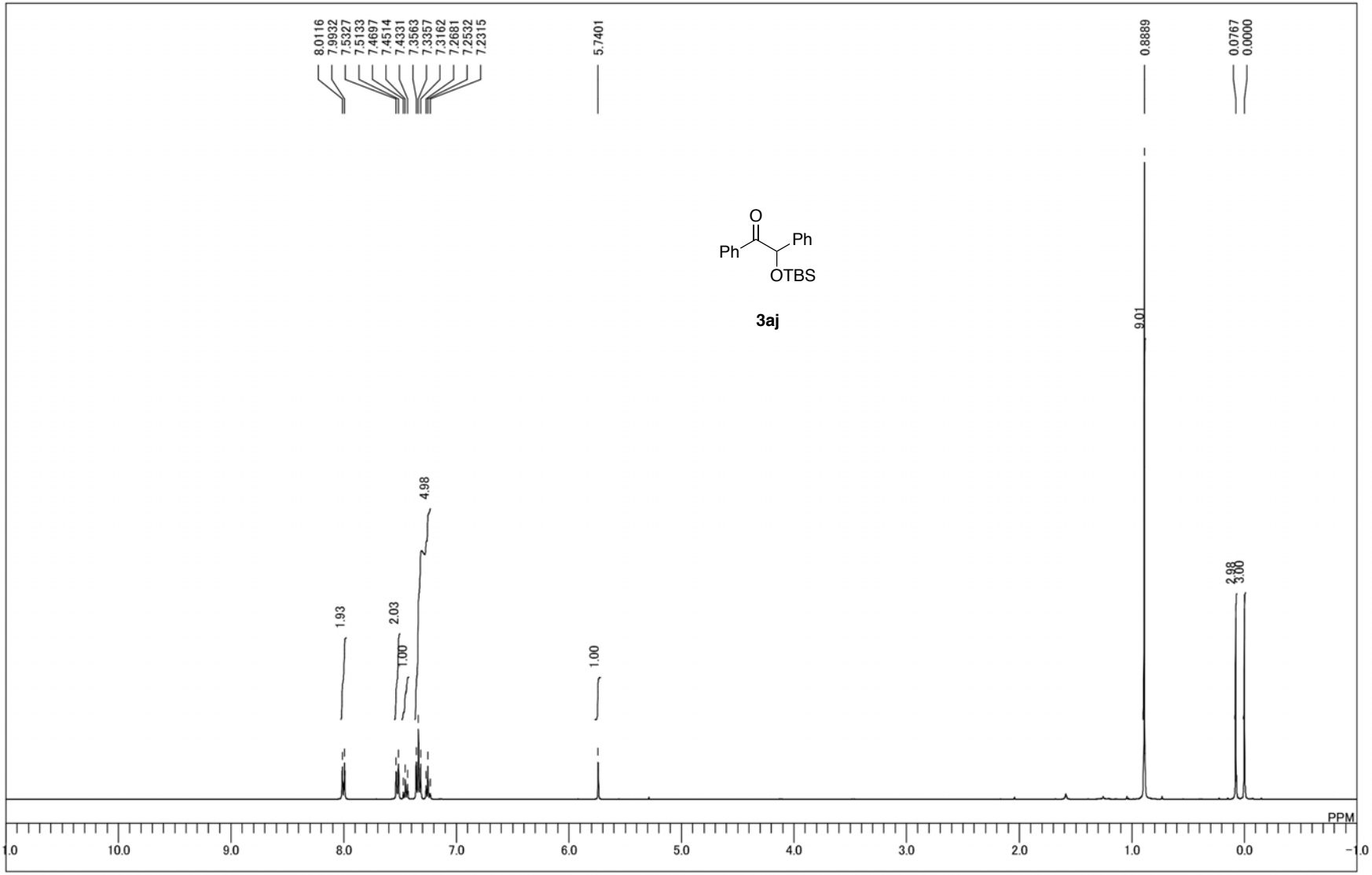
^{13}C NMR spectrum of **3ah**



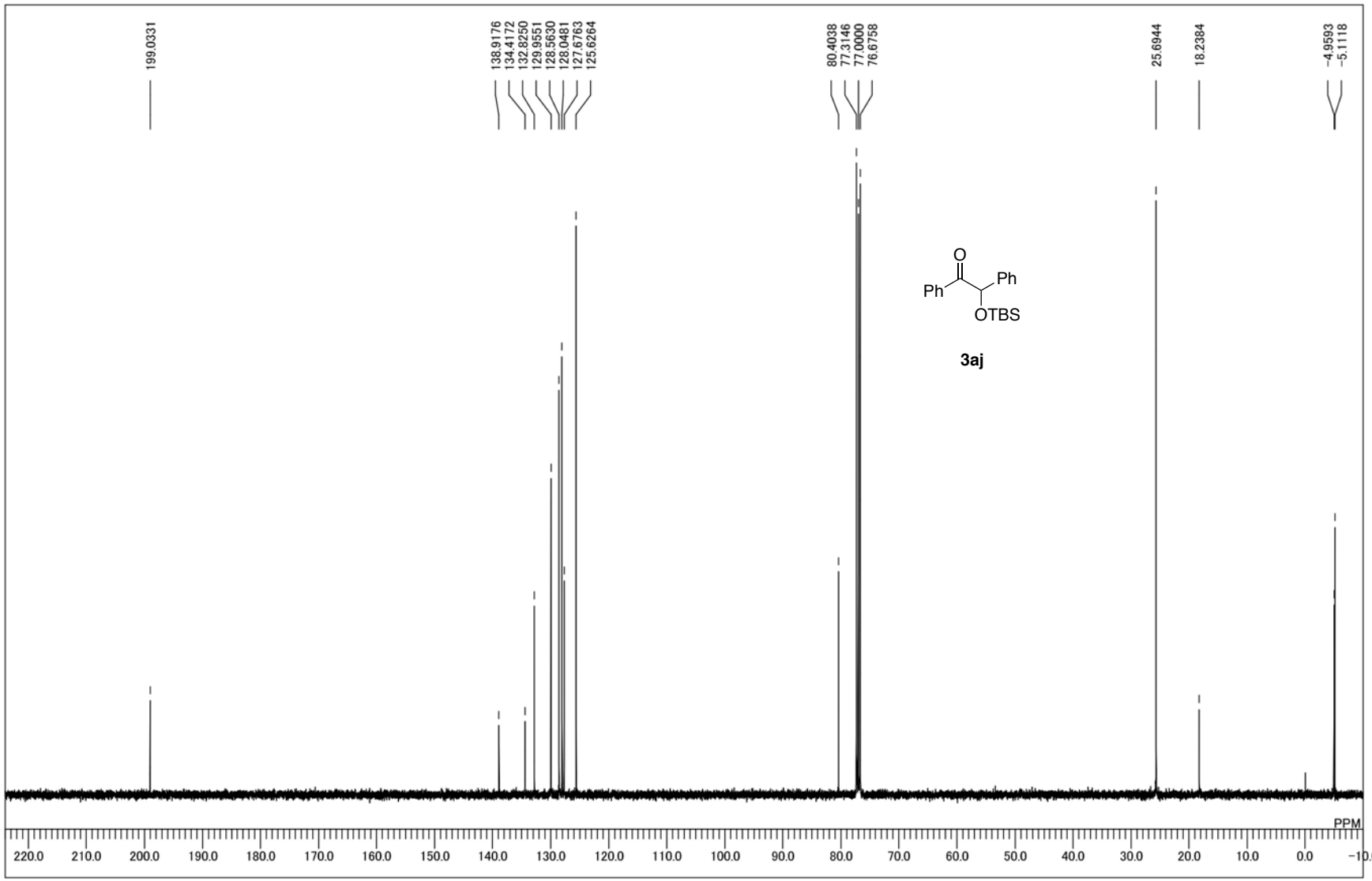
^{1}H NMR spectrum of **3ai**



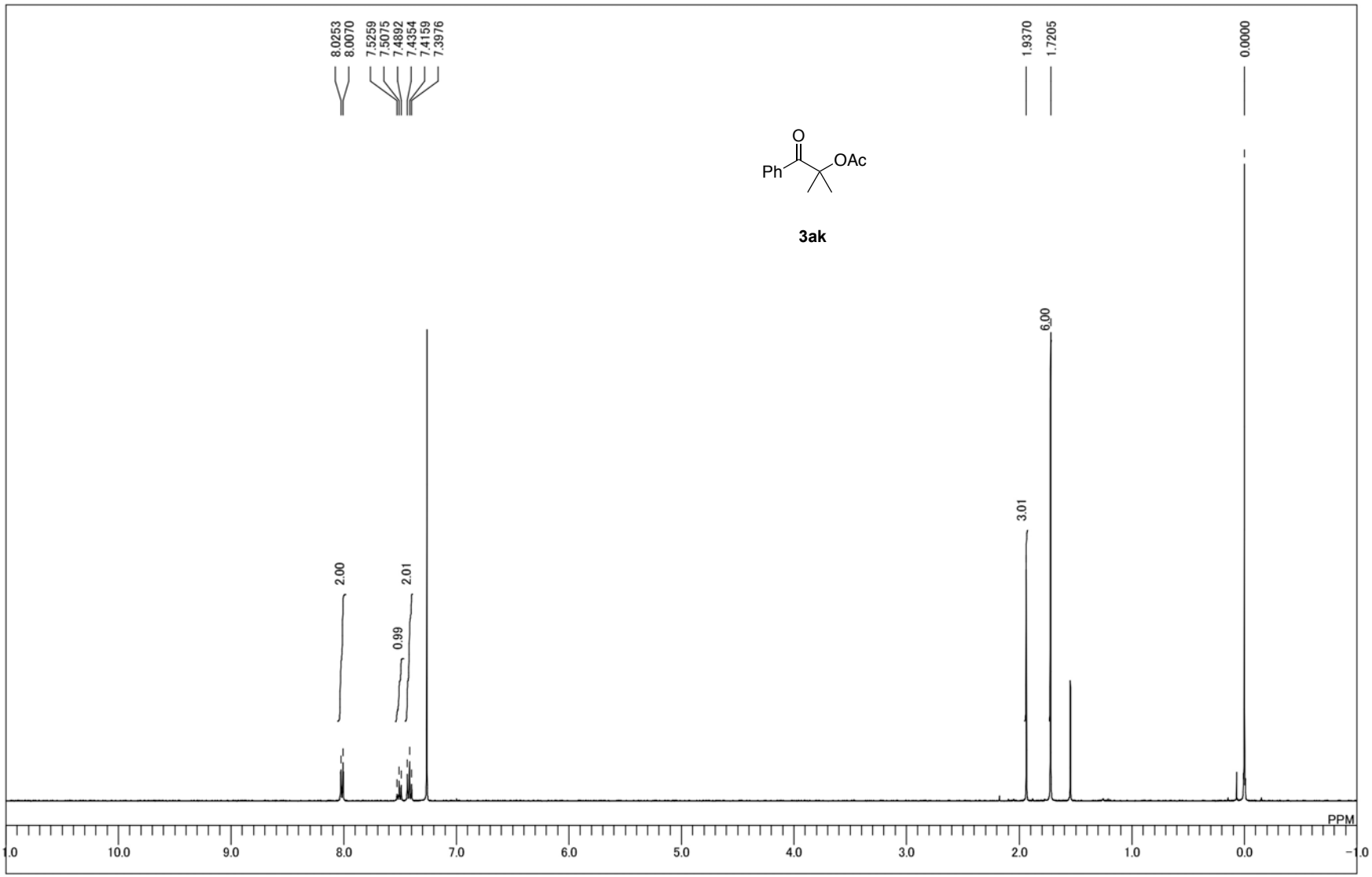
^{13}C NMR spectrum of **3ai**



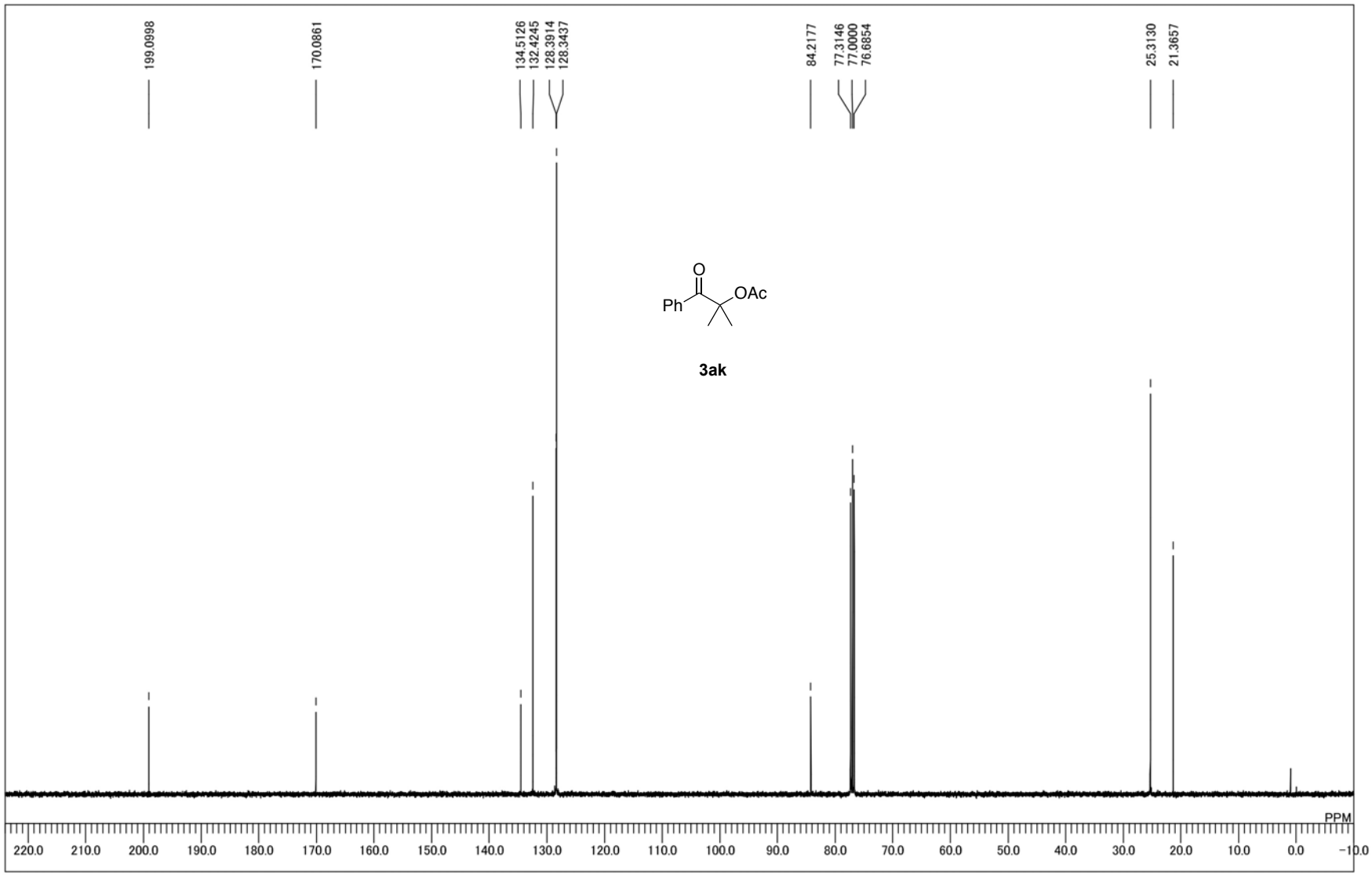
^{1}H NMR spectrum of **3aj**



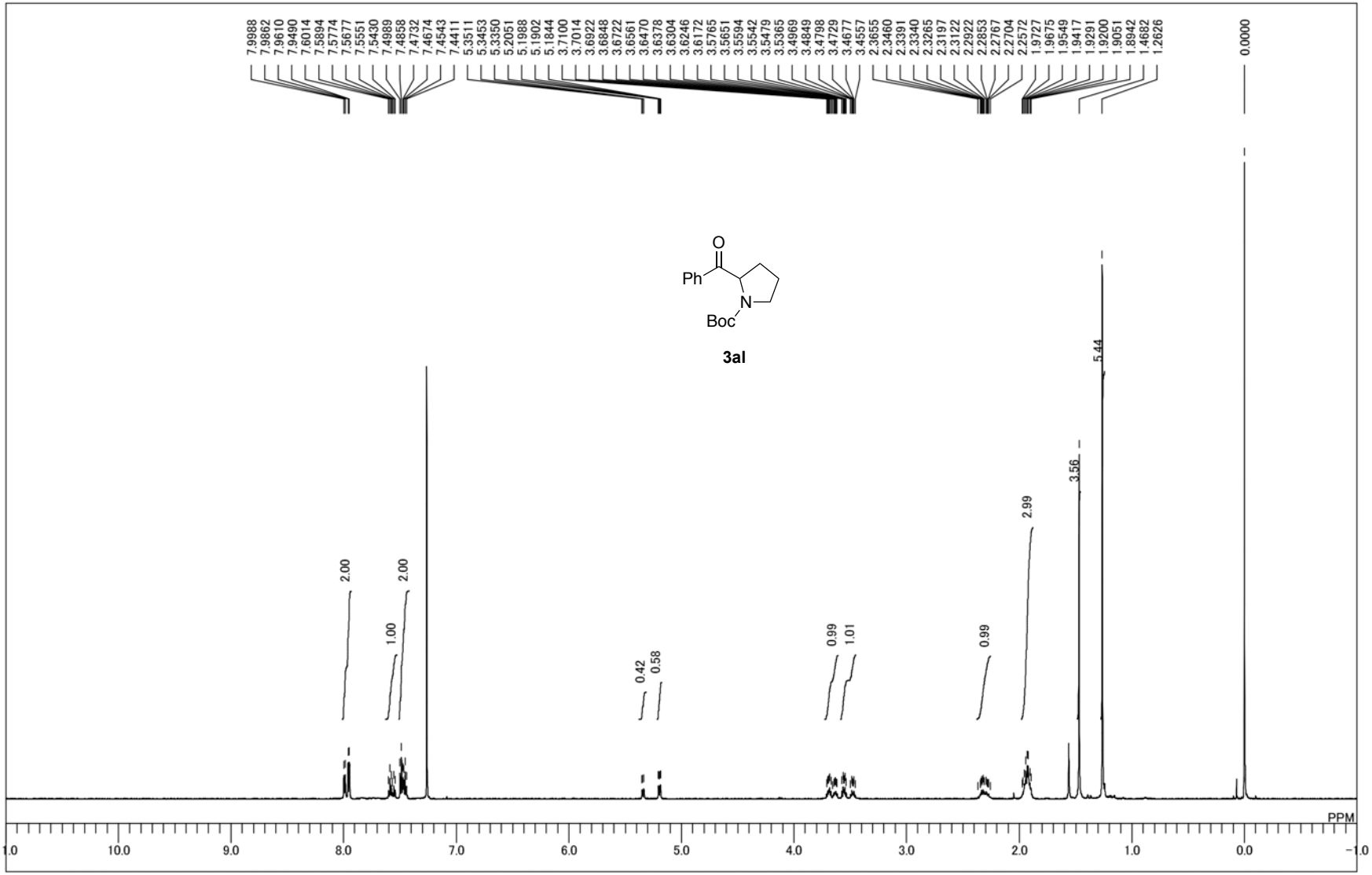
^{13}C NMR spectrum of **3aj**



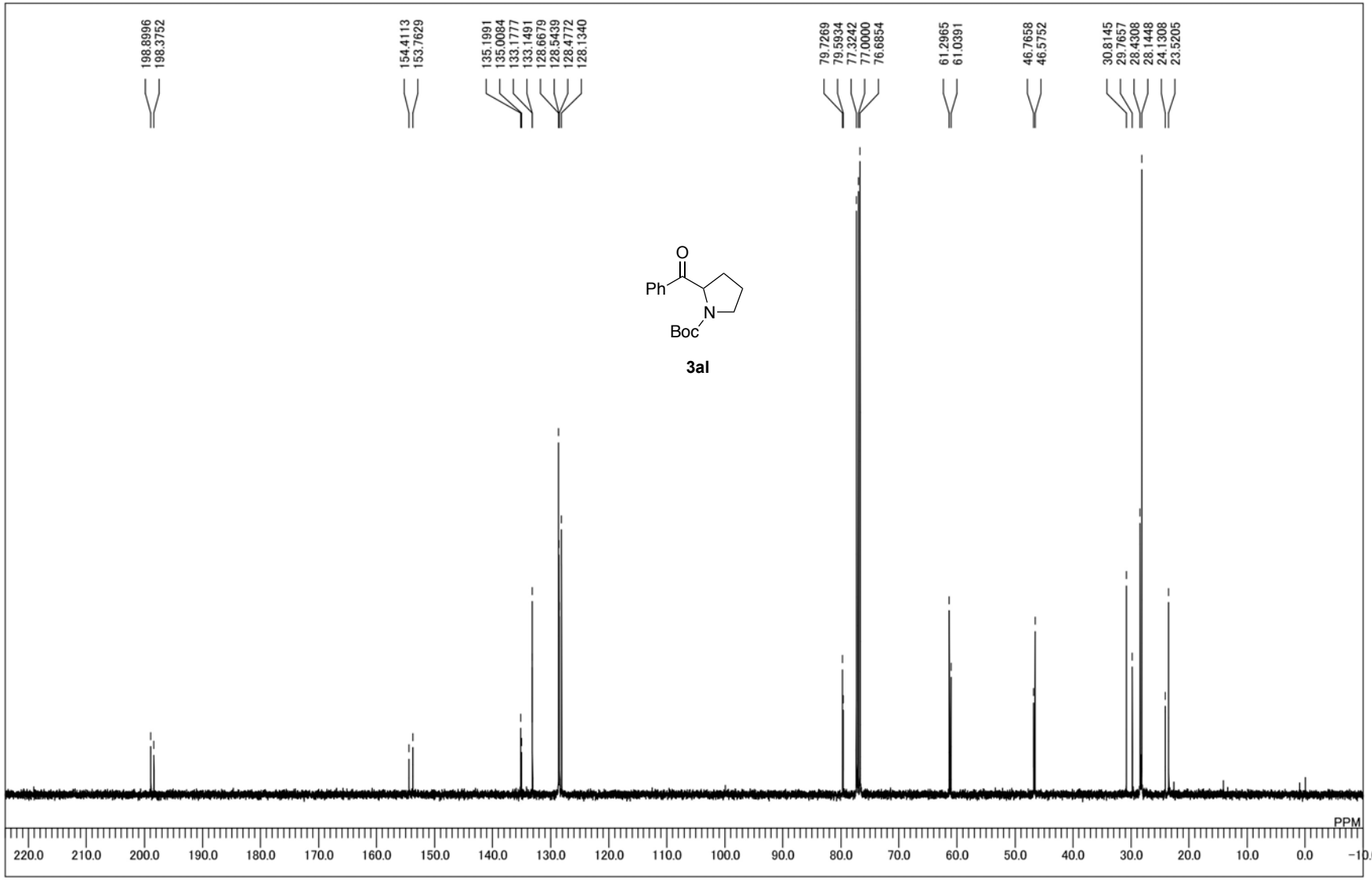
^{1}H NMR spectrum of **3ak**



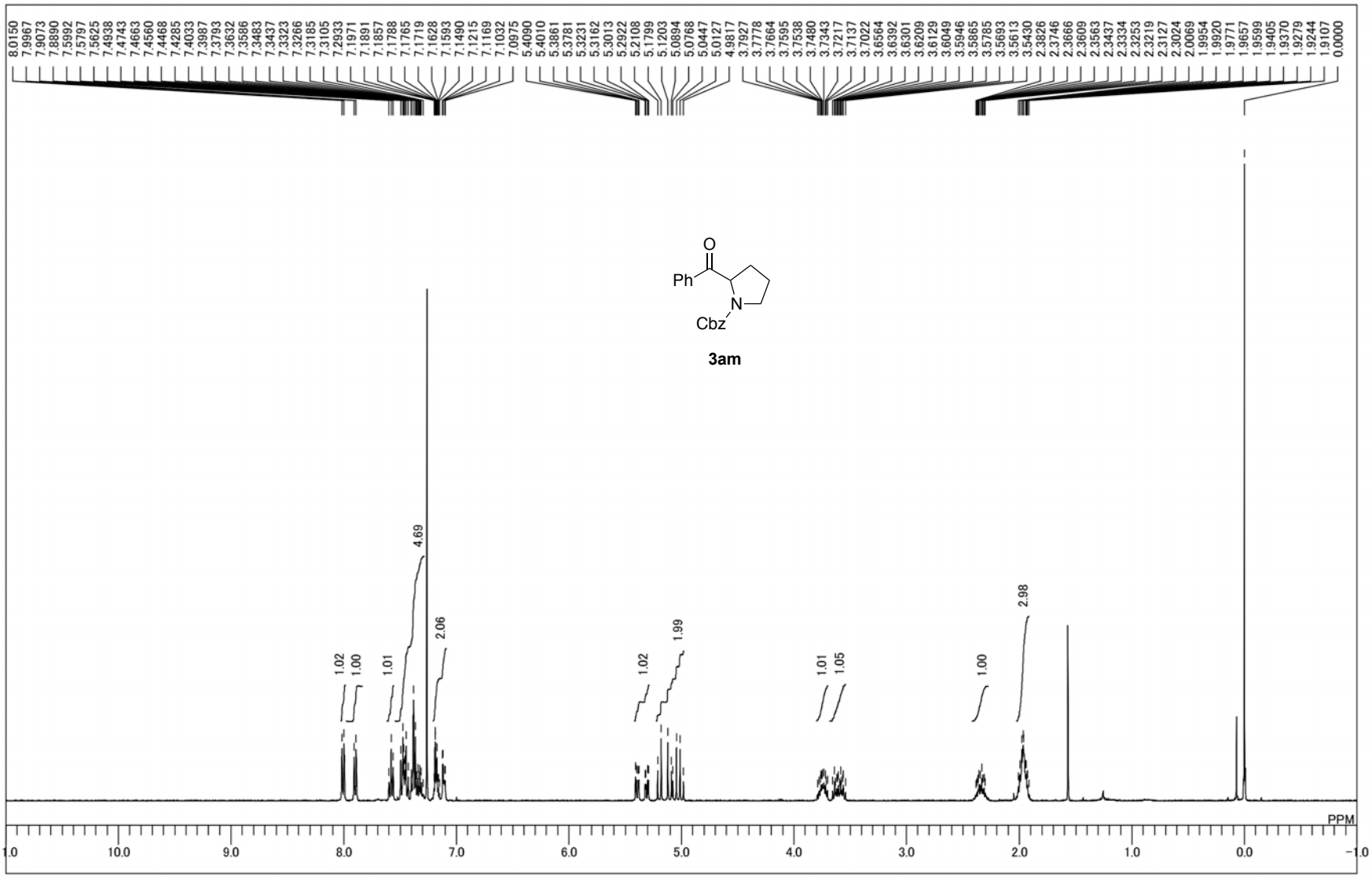
^{13}C NMR spectrum of **3ak**



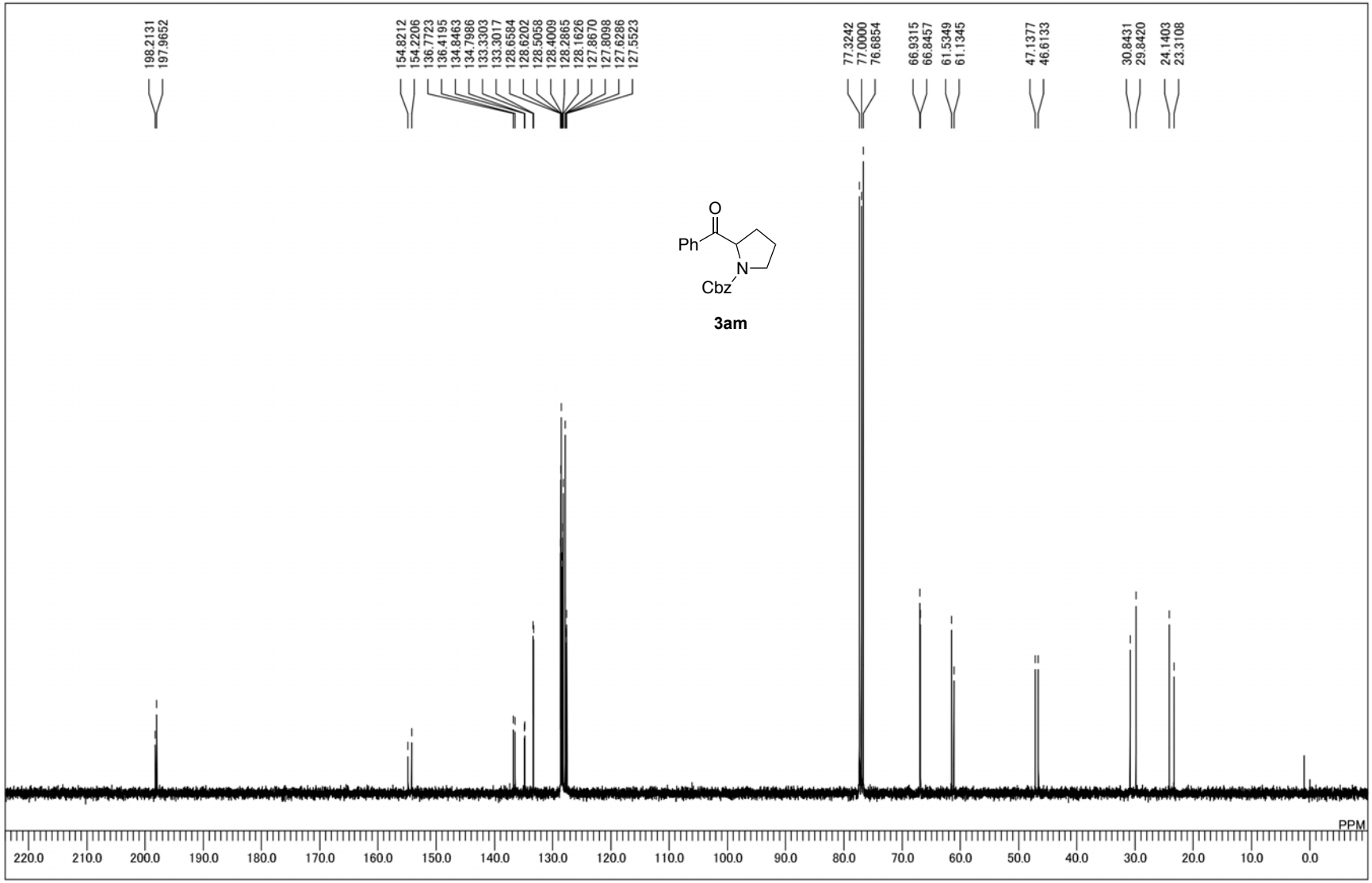
^{1}H NMR spectrum of **3al**



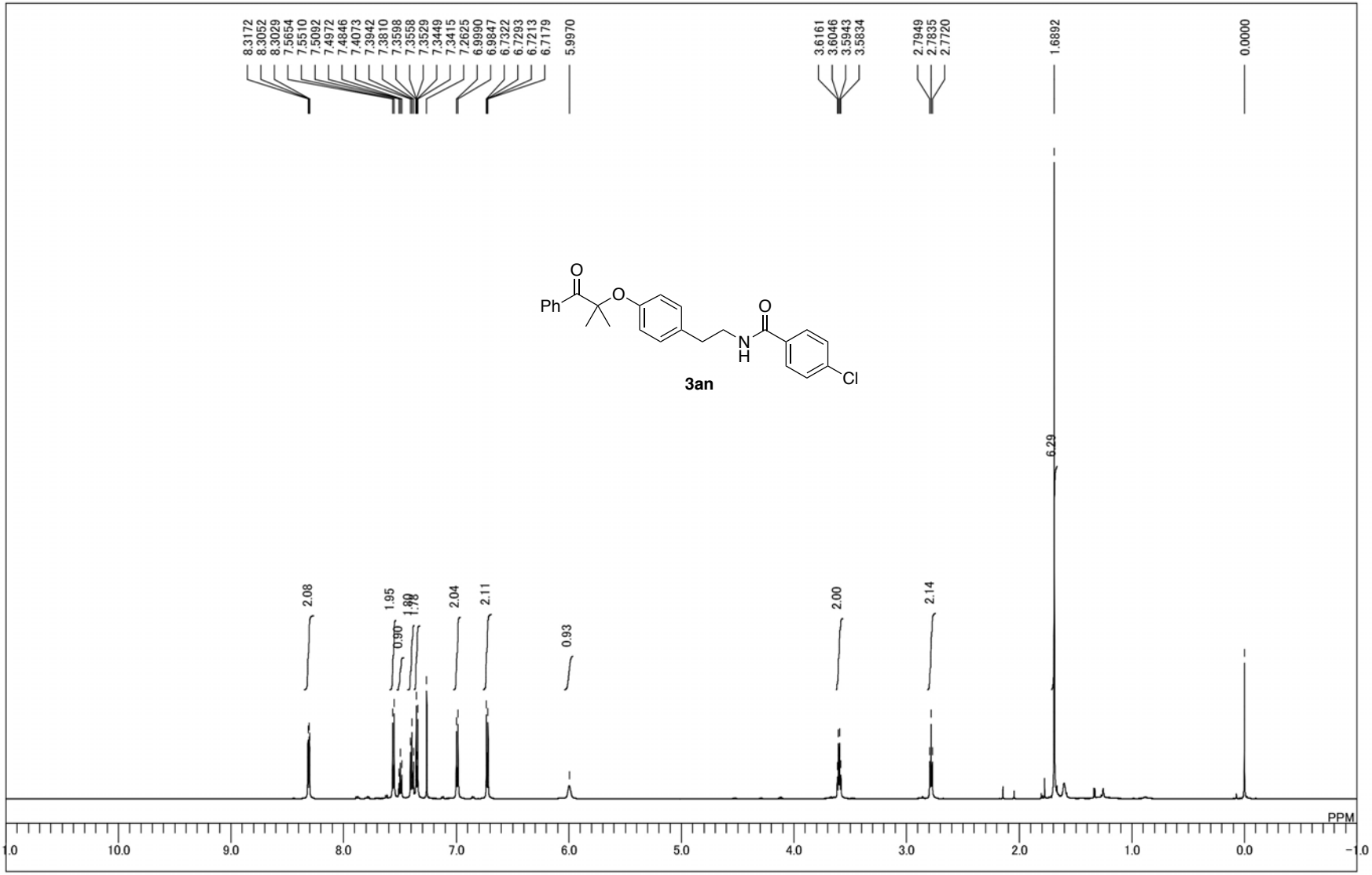
^{13}C NMR spectrum of **3al**



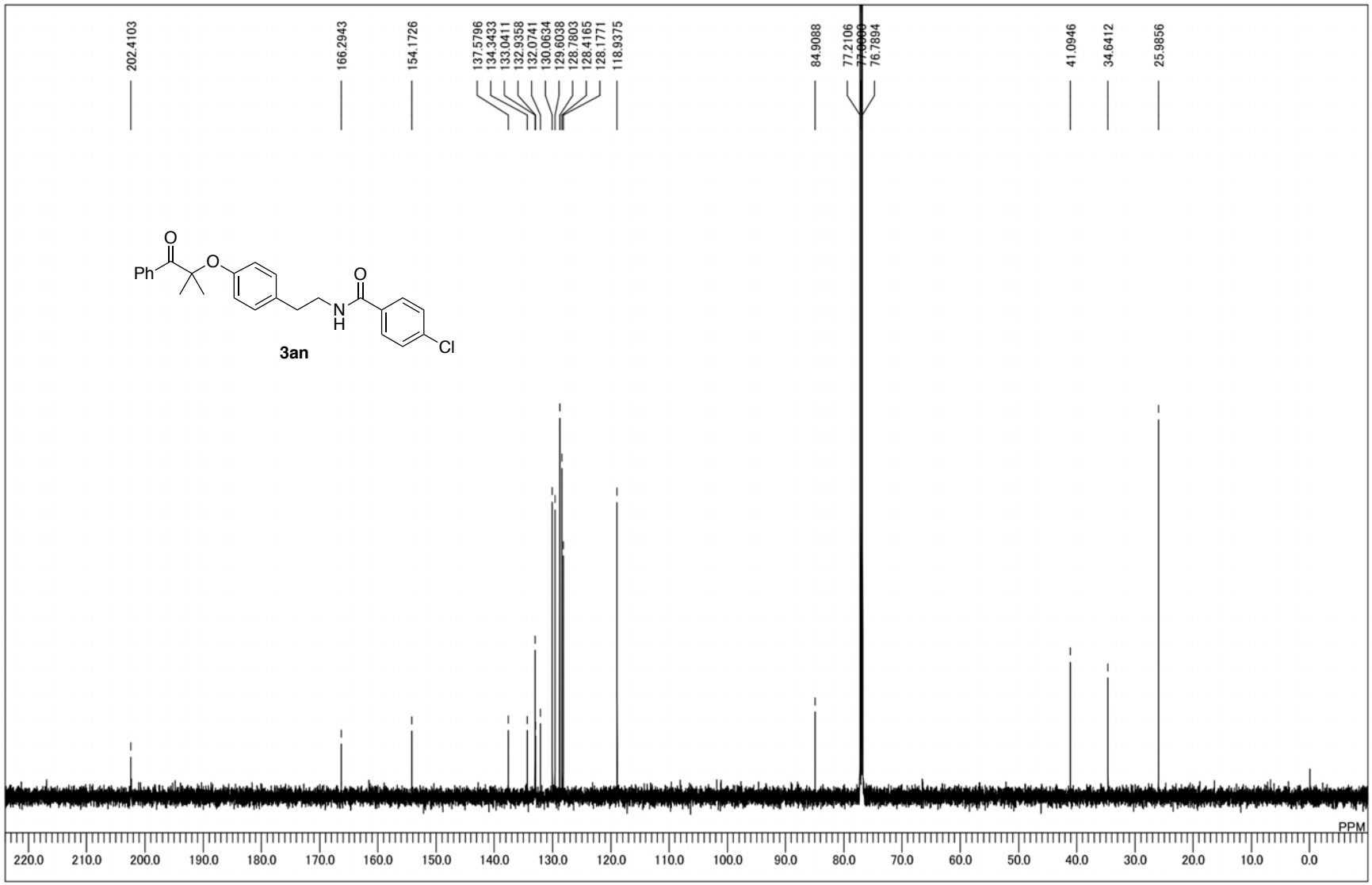
^{1}H NMR spectrum of **3am**



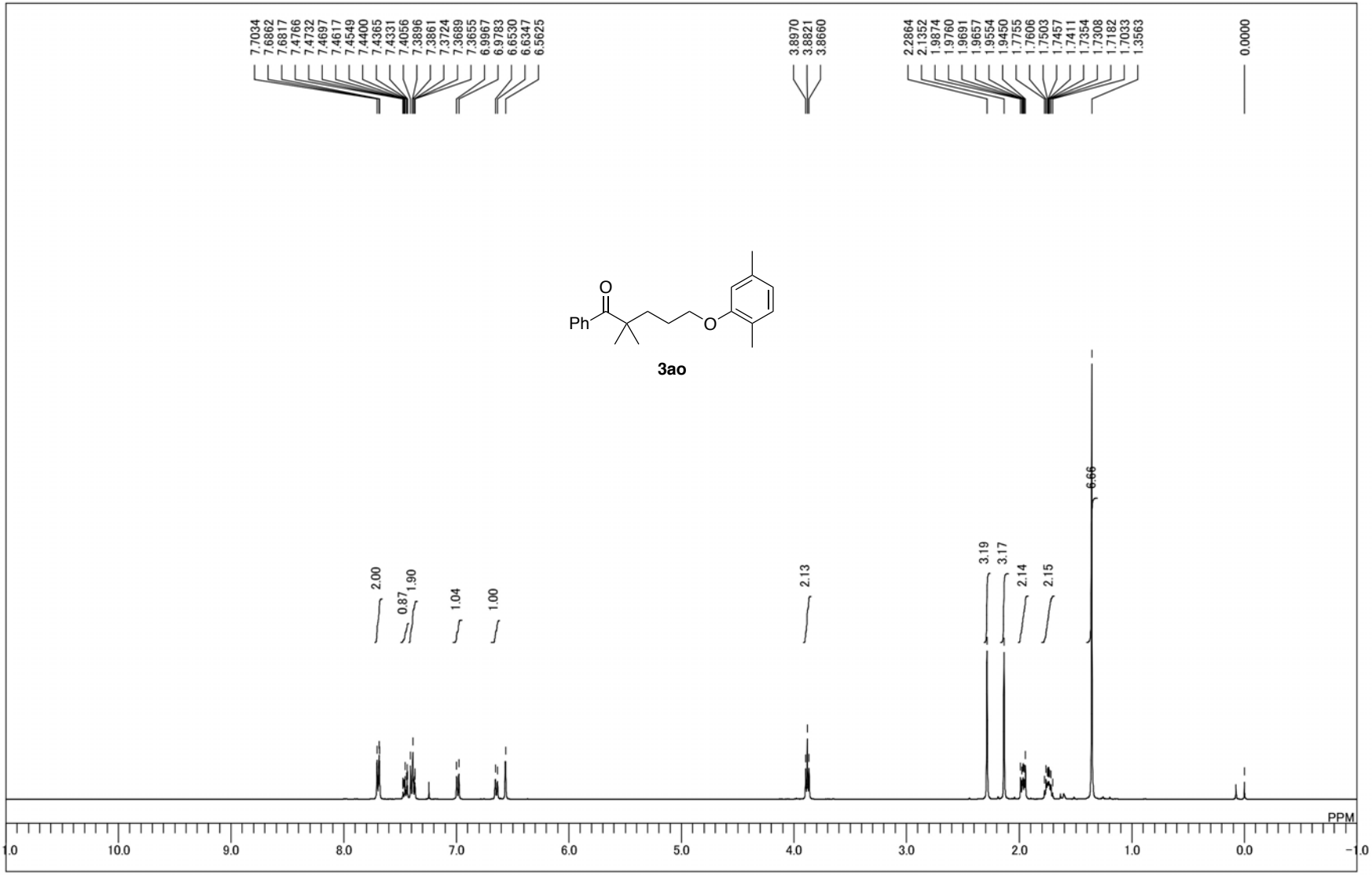
^{13}C NMR spectrum of **3am**



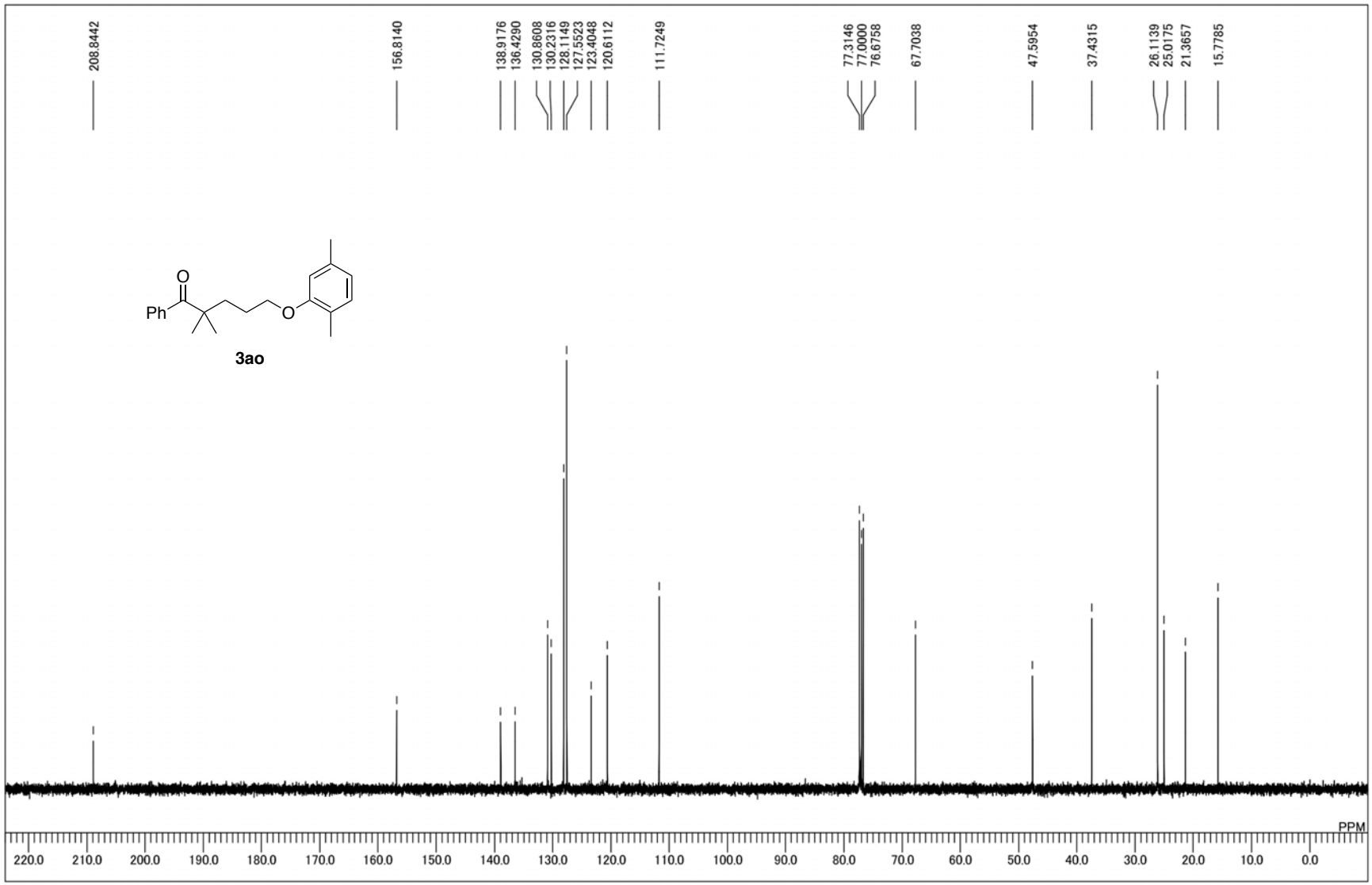
^{1}H NMR spectrum of **3an**



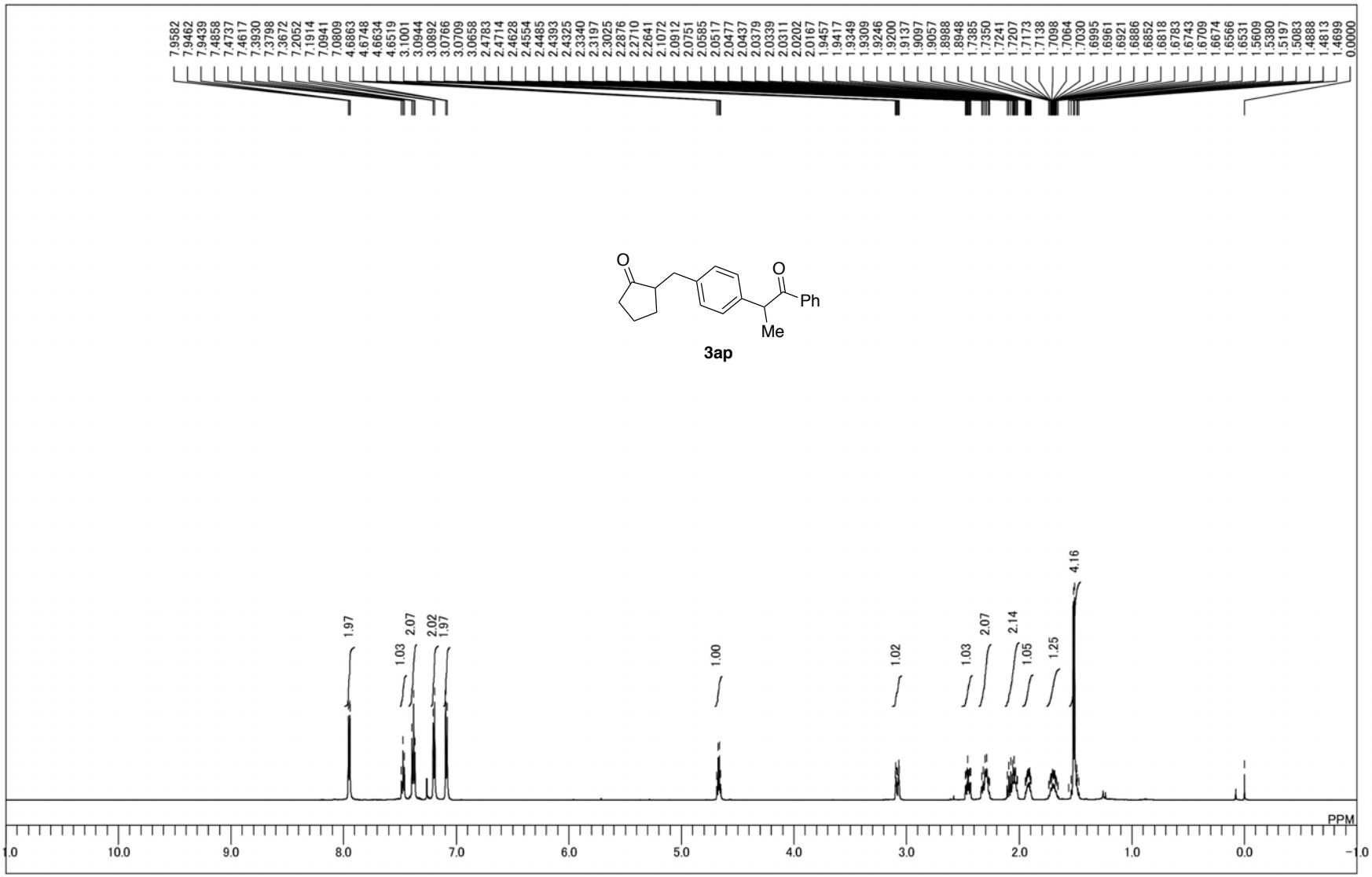
^{13}C NMR spectrum of **3an**



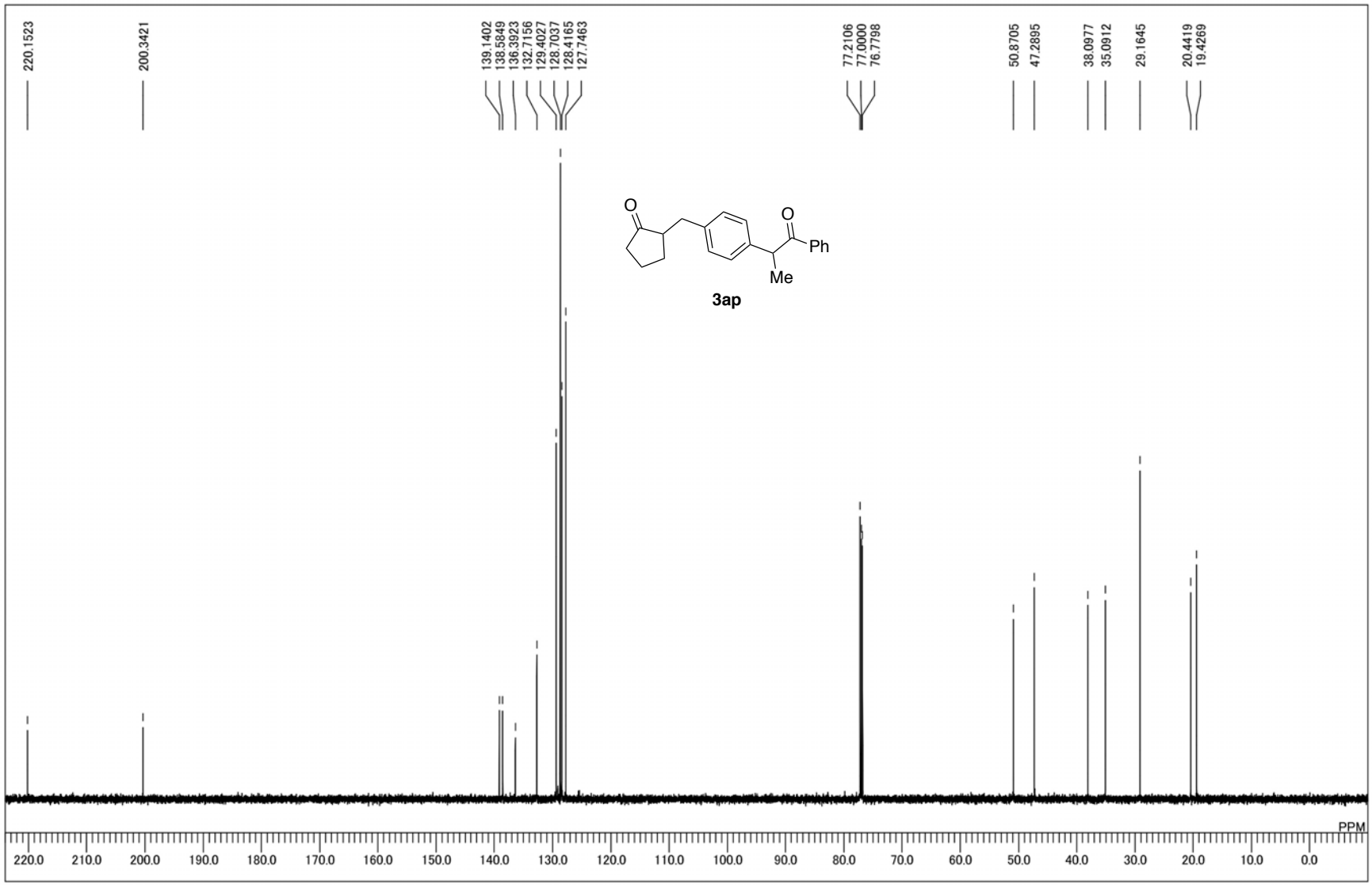
^{1}H NMR spectrum of **3ao**



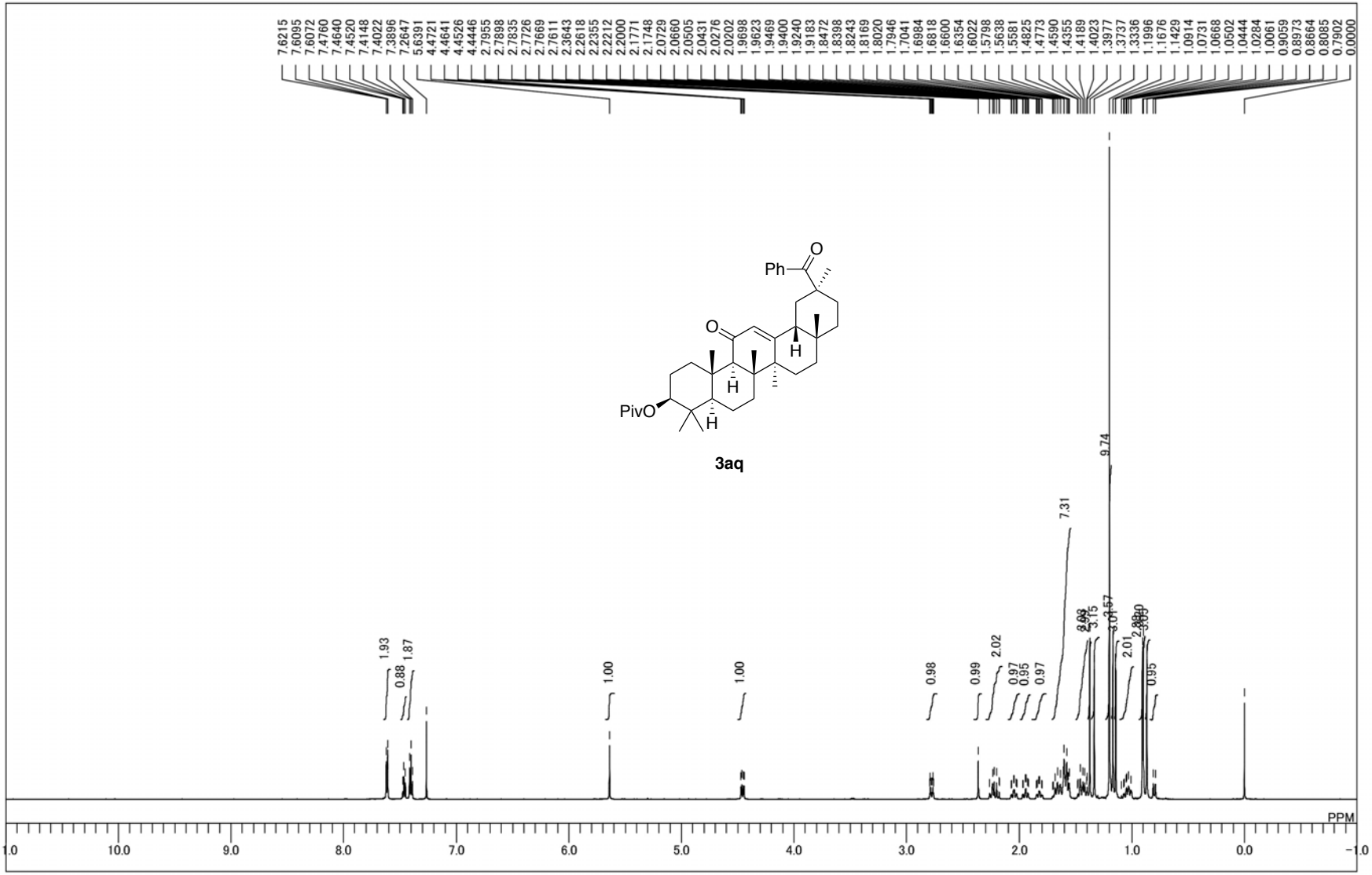
^{13}C NMR spectrum of **3ao**



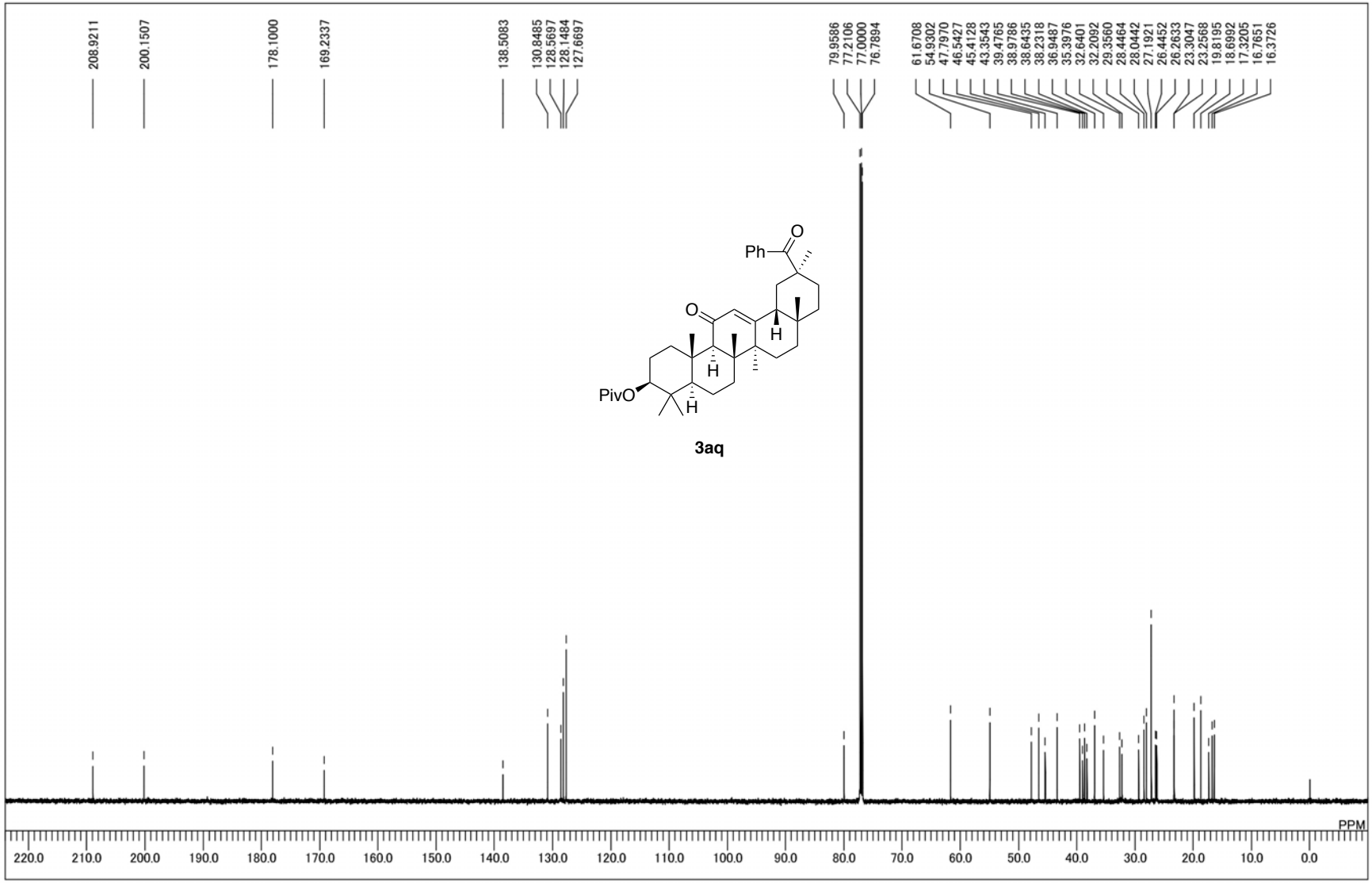
^{1}H NMR spectrum of **3ap**



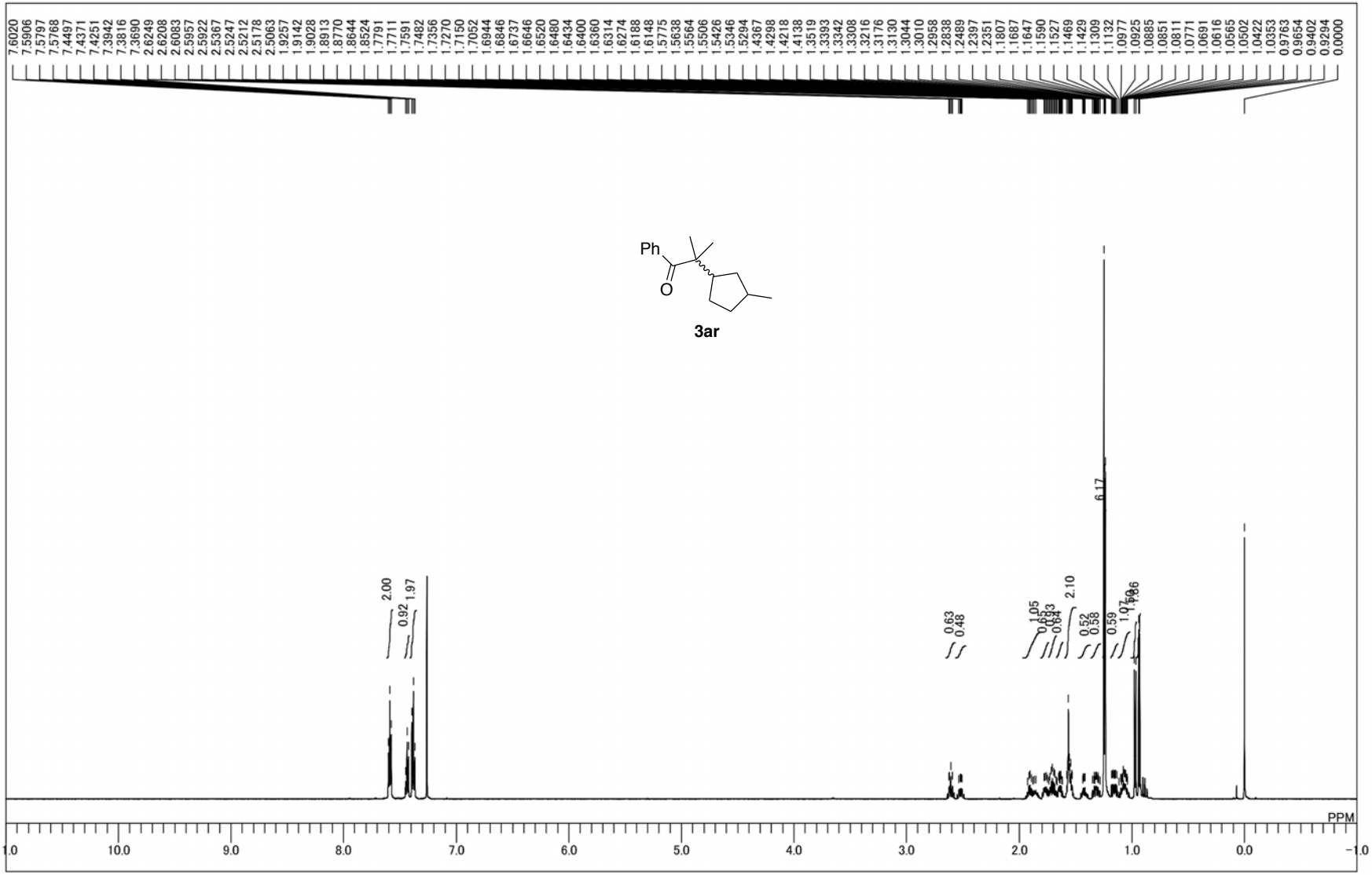
^{13}C NMR spectrum of **3ap**



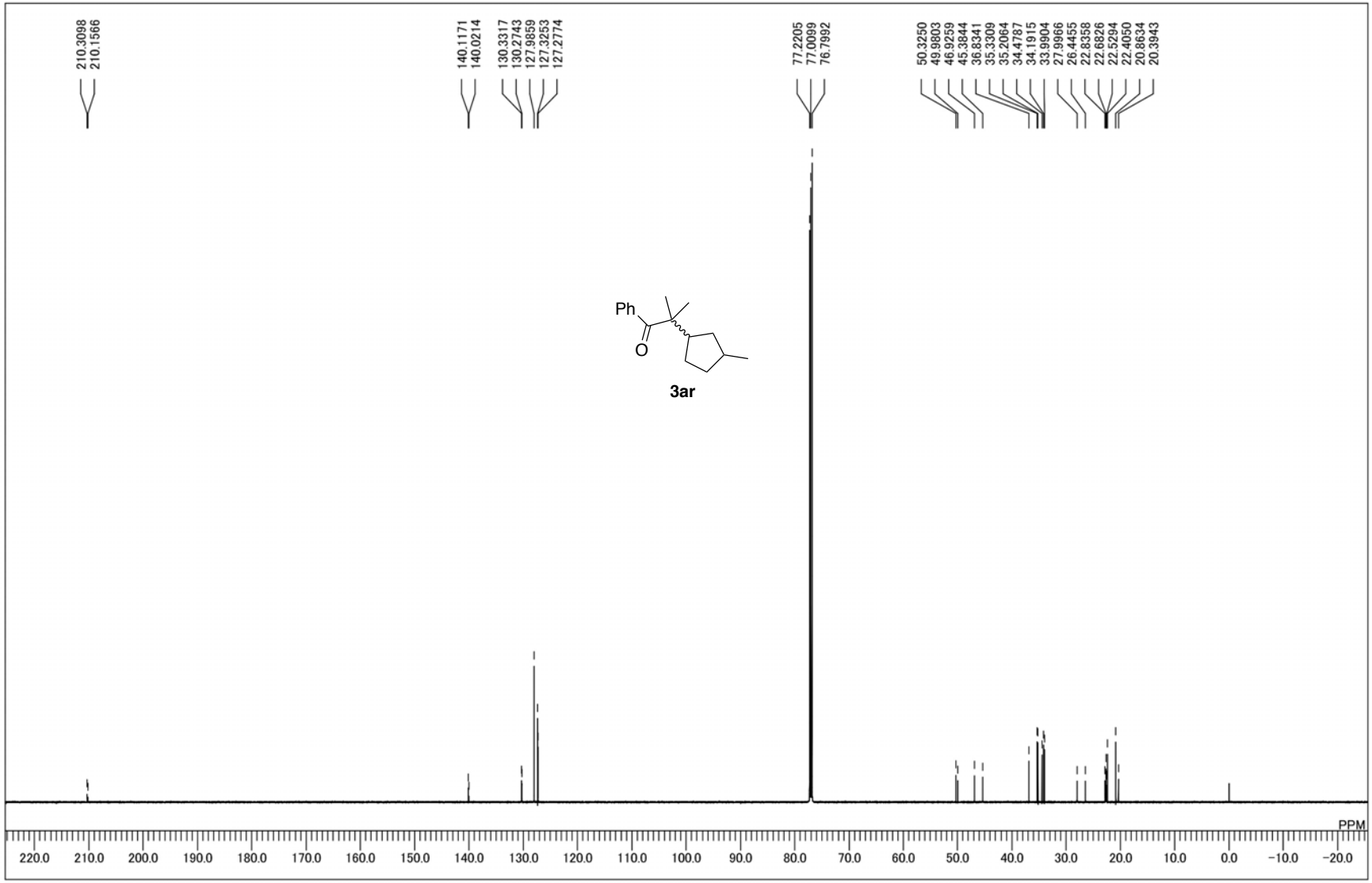
^{1}H NMR spectrum of **3aq**



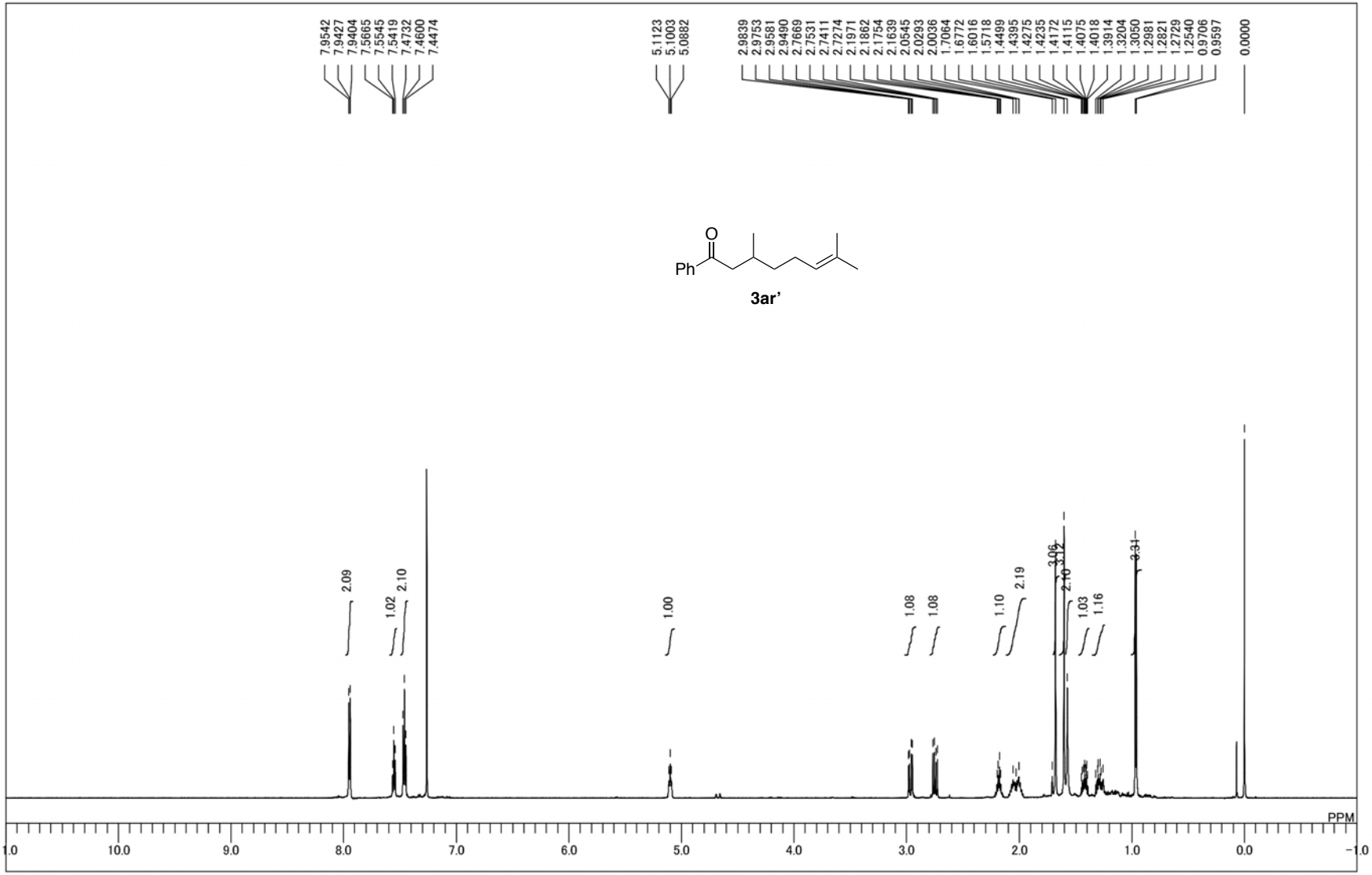
^{13}C NMR spectrum of **3aq**



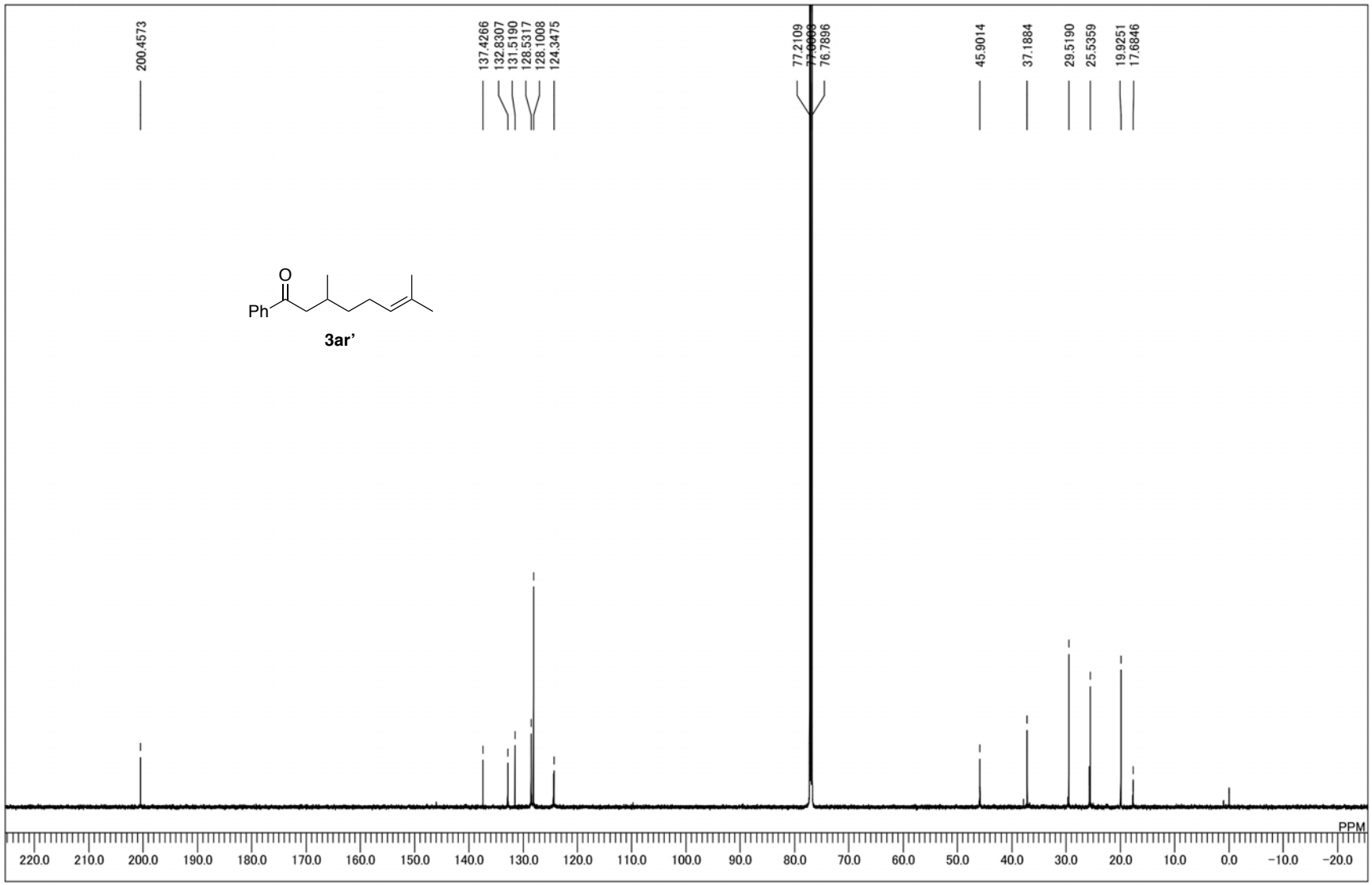
^{1}H NMR spectrum of **3ar**



^{13}C NMR spectrum of **3ar**



^{1}H NMR spectrum of **3ar'**



^{13}C NMR spectrum of **3ar'**