Nitroxyl Radical/$PhI(OAc)_2$: One-Pot Oxidative Cleavage of Vicinal Diols to (Di)Carboxylic Acids

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Supporting Information

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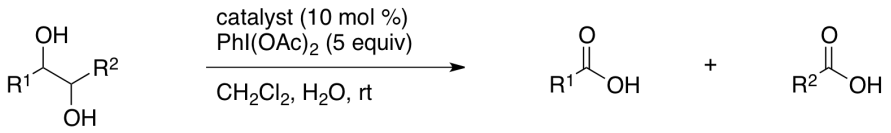
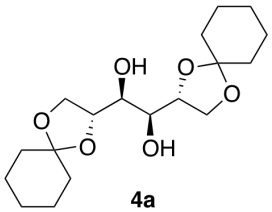
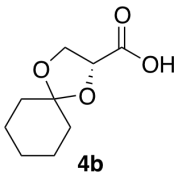
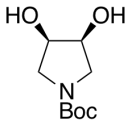
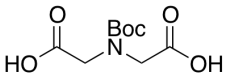
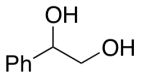
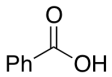
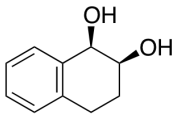
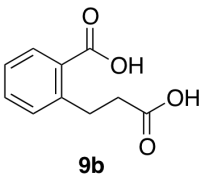
General Experimental Procedures:

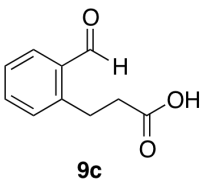
All reactions were stirred magnetically, under an atmosphere of argon, unless otherwise specified. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck silica Kieselgel 60 F_{254}). Flash column chromatography was performed on silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on JEOL JNM-AL400 (400 MHz) and JEOL JNM-ECA600 (600 MHz) spectrometers. Chemical shifts (δ) are given in parts per million (ppm) relative to internal TMS (0.00 ppm) in $CDCl_3$ or residual non-deuterated MeOH peak (3.31 ppm) in CD_3OD. Coupling constants (*J*) are reported in Hz. The following abbreviations are used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet; br d, broad doublet; dd, double doublet; ddd, double double doublet; dddd, double double double doublet; tt, triple triplet. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL JNM-AL400 (100 MHz) and JEOL JNM-ECA600 (150 MHz) spectrometers. Chemical shifts are given in ppm relative to the center line of the triplet of $CDCl_3$ (77.0 ppm) or the center line of the septet of CD_3OD (49.0 ppm). Infrared spectra were recorded on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrometer. Mass spectra were recorded on JMS-DX303, JMS-700 or JMS-T 100 GC using electron impact (EI) or fast atom bombardment (FAB). ESI mass spectra were recorded on a Thermo Fisher SCIENTIFIC Exactive.

Table S1 : Scopes of TEMPO-Catalyzed One-Pot Oxidative Cleavages



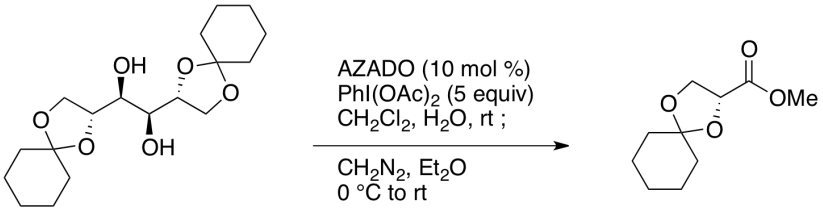
entry	diol	product	yield[a] / time AZADO **TEMPO**
1	 **4a**	 **4b**	90%[b] / 1 h **89%[b] / 1 h**
2	 **8a**	 **8b**	91%[b] / 1 h **91%[b] / 1 h**
3	 **S1a**	 **S1b**	90%[b] / 12 h (95%[b] / 4 h)[c] **10%[b] / 12 h (53%[b] / 4 h)[c]**
4	 **9a**	 **9b**	85%[b,c] / 4 h **17%[b,c,d] / 4 h**

[a] Isolated yield. [b] Carboxylic acids were isolated as methyl esters after treatment with CH_2N_2. [c] Bu_4NBr was added and MeCN was used as a solvent. [d] Methyl ester of **9c** (72%) was isolated as a by-product.



9c

General Procedure for the Oxidative Cleavage of Diols (Method A)

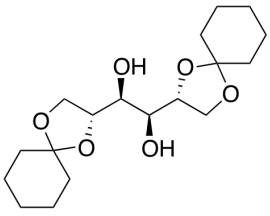


4a **4b'**

To a solution of diol **4a** (30.0 mg, 0.0876 mmol, R_f = 0.63, AcOEt / Hexane = 1 / 1) in CH_2Cl_2 (0.22 mL) and H_2O (0.22 mL) was added AZADO (1.3 mg, 0.00876 mmol) and $PhI(OAc)_2$ (141 mg, 0.438 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. (TLC analysis: At a beginning of the reaction, a tailing spot (R_f = 0.40 – 0.57, AcOEt / Hexane = 1 / 1) was observed, which was presumably a mixture of the corresponding aldehyde and its hydrate. The carboxylic acid **4b** was observed as a tailing spot at R_f = 0 – 0.37, AcOEt / Hexane = 1 / 1) The solvent was removed under reduced pressure, and the residue was added Et_2O. Then, CH_2N_2 in Et_2O was added at 0 °C until yellow color was appeared. The mixture was allowed to warm to room temperature and stirred for 1 h. The solution was concentrated under reduced pressure. Then, water was added to the residue and the resultant solution was extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 10) to give a methyl ester **4b'** (31.4 mg, 0.157 mmol, 90%) as colorless oil.

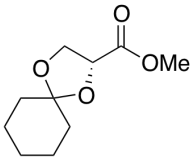
Experimental Data for Compounds

1,2 : 5,6-Di-*O*-cyclohexylidene-D-mannitol (**4a**)[1]



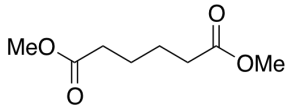
^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.24-4.17 (2H, m), 4.15-4.09 (2H, m), 4.00-3.94 (2H, m), 3.75 (2H, dd, *J* = 6.3 Hz, 6.3 Hz), 2.66 (2H, br d, *J* = 6.3 Hz), 1.71-1.52 (20H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 109.9, 75.6, 71.2, 66.4, 36.4, 34.7, 25.0, 24.0, 23.7. IR (neat, cm^{-1}): 3295, 2935, 2852. MS *m/z*: 342 (M^+), 201 (100%). HRMS (EI): Calcd. for $C_{18}H_{30}O_6$: 342.2042, found: 342.2048.

Methyl (*R*)-1,4-dioxaspiro[4,5]decane-2-carboxylate (**4b'**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.60 (1H, dd, *J* = 7.2 Hz, 5.3 Hz), 4.23 (1H, dd, *J* = 8.7 Hz, 7.2 Hz), 4.10 (1H, dd, *J* = 8.7 Hz, 5.3 Hz), 3.77 (3H, s), 1.79-1.52 (8H, m), 1.50-1.32 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.7, 111.9, 73.7, 66.9, 52.2, 35.2, 34.9, 24.9, 23.8, , 23.7. IR (neat, cm^{-1}): 2937, 2863, 1763, 1737. MS *m/z*: 200 (M^+), 157 (100%). HRMS (EI): Calcd. for $C_{10}H_{16}O_4$: 200.1049, found: 200.1031.

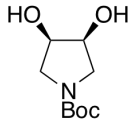
Dimethyl adipate (**6b'**)[2]



6b' was prepared according to the method A. **6b'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 10).

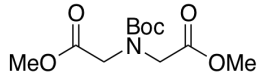
^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.67 (6H, s), 2.37-2.30 (4H, m), 1.71-1.64 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.7, 51.5, 33.6, 24.3. IR (neat, cm^{-1}): 2953, 2872, 1739. MS *m/z*: 175 (M^++H), 114 (100%). HRMS (EI): Calcd. for $C_8H_{15}O_4$: 175.0970, found: 175.0982.

tert-Butyl *cis*-3,4-dihydroxypyrrolidine-1-carboxylate (**8a**)



^{1}H-NMR (400 MHz, $CDCl_3$): mixture of rotamers δ 4.30-4.20 (2H, m), 3.66-3.52 (2H, m), 3.42-3.27 (2H, m), 2.50-2.37 (2H, m), 1.45 (9H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): mixture of rotamers δ 154.8, 79.9, 71.2, 70.5, 50.6, 50.1, 28.4. IR (neat, cm^{-1}): 3395, 2976, 2936, 2887, 1672. MS *m/z*: 203 (M^+), 57 (100%). HRMS (EI): Calcd. for $C_9H_{17}NO_4$: 203.1158, found: 203.1142.

Dimethyl 2,2'-(*tert*-butoxycarbonylazanediyl)diacetate (**8b'**)

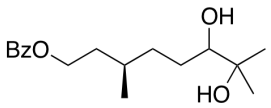


8b' was prepared according to the method A. **8b'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 3).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.12 (2H, s), 4.02 (2H, s), 3.74 (3H, s), 3.37 (3H, s), 1.44 (9H, s).

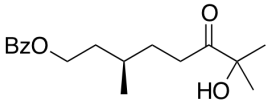
^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 155.0, 81.2, 52.1, 52.0, 49.5, 48.9, 28.1. IR (neat, cm^{-1}): 2978, 2955, 1753, 1706. MS *m/z*: 262 (M^++H), 102 (100%). HRMS (EI): Calcd. for $C_{11}H_{20}NO_6$: 262.1291, found: 262.1268.

(3*R*)-6,7-Dihydroxy-3,7-dimethyloctyl benzoate (**12a**)



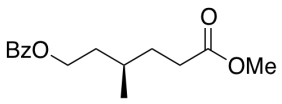
^{1}H-NMR (400 MHz, $CDCl_3$): mixture of diastereomers δ 8.04 (2H, d, *J* = 7.7 Hz), 7.55 (1H, t, *J* = 7.7 Hz), 7.44 (2H, dd, *J* = 7.7, 7.7 Hz), 4.47-4.30 (2H, m), 3.38-3.31 (1H, m), 2.36-2.26 (1H, m), 2.06-1.99 (1H, m), 1.90-1.77 (1H, m), 1.75-1.18 (6H, m), 1.21 (3H, s), 1.16 (3H, s), 1.02-0.94 (3H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): mixture of diastereomers δ 166.73, 166.68, 132.82, 132.80, 130.3, 129.5, 128.3, 78.9, 78.5, 73.09, 73.07, 63.4, 35.7, 35.3, 34.1, 33.7, 30.1, 29.8, 29.0, 28.8, 26.43, 26.42, 23.1, 19.6, 19.3. IR (neat, cm^{-1}): 3424, 2960, 2928, 2872, 1718. MS *m/z*: 277 (M^+−OH), 123 (100%). HRMS (EI): Calcd. for $C_{17}H_{25}O_3$: 277.1804, found: 277.1790.

(*R*)-7-Hydroxy-3,7-dimethyl-6-oxooctyl benzoate (**12c**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (2H, d, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.44 (2H, dd, *J* = 7.5, 7.5 Hz), 4.44-4.32 (2H, m), 3.74 (1H, s), 2.62-2.55 (2H, m), 1.89-1.48 (5H, m), 1.38 (6H, s), 0.99 (3H, d, *J* = 6.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 214.4, 166.6, 132.9, 130.3, 129.5, 128.3, 76.2, 35.4, 33.0, 30.6, 29.6, 26.5, 19.2. IR (neat, cm^{-1}): 3486, 2965, 2931, 1716. MS *m/z*: 293 (M^+), 123 (100%). HRMS (EI): Calcd. for $C_{17}H_{25}O_4$: 293.1753, found: 293.1750.

(*R*)-6-Methoxy-3-methyl-6-oxohexyl benzoate (**12b'**)

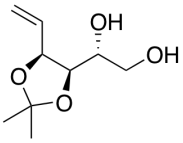


12b' was prepared according to the method A. **12b'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 2).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (2H, d, *J* = 7.6 Hz), 7.56 (1H, t, *J* = 7.6 Hz), 7.44 (2H, dd, *J* = 7.6, 7.6 Hz), 4.43-4.31 (2H, m), 3.66 (3H, s), 2.44-2.28 (2H, m), 1.88-1.49 (5H, m), 0.98 (3H, d, *J* = 6.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 174.1, 166.6, 132.8, 130.4, 129.5, 128.3, 63.1, 51.5, 35.2, 31.8, 31.7, 29.6, 19.1. IR (neat, cm^{-1}): 2955, 1738, 1719. MS *m/z*: 264 (M^+), 142 (100%). HRMS

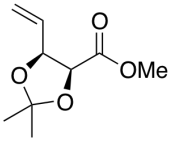
(EI): Calcd. for $C_{15}H_{20}O_4$: 264.1362, found: 264.1346.

(1*R*)-1-((4*R*,5*S*)-2,2-Dimethyl-5-vinyl[1,3]dioxolan-4-yl)ethane-1,2-diol (**13a**)[3]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.01 (1H, ddd, *J* = 17.1, 9.5, 6.9 Hz), 5.47 (1H, d, *J* = 17.1 Hz), 5.34 (1H, d, *J* = 9.8 Hz), 4.71 (1H, t, *J* = 6.9 Hz), 4.11 (1H, dd, *J* = 8.5, 6.5 Hz), 3.85-3.65 (3H, m), 1.48 (3H, s), 1.37 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 133.7, 118.3, 109.0, 78.5, 78.0, 69.8, 64.2, 27.6, 25.2. IR (neat, cm^{-1}): 3407, 2987, 1217, 1059. FAB-MS *m/z*: 189 (M^++H), 189 (100%). HRMS (FAB): Calcd. for $C_9H_{17}O_4$: 189.1127, found:189.1127.

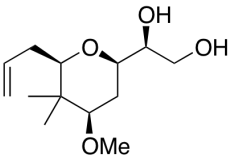
Methyl (*R*,*R*)-2,3-dihydroxy-2,3-*O*-isopropylidene-pent-4-enoate (**13b'**)[4]



13b' was prepared according to the method A. **13b'** was obtained as a colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 10).

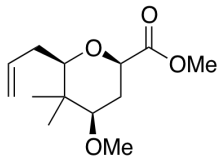
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.73 (1H, ddd, *J* = 17.1, 10.2, 6.8 Hz), 5.43 (1H, d, *J* = 17.1 Hz), 5.28 (1H, d, *J* = 10.2 Hz), 4.81 (1H, t, *J* = 6.8 Hz), 4.70 (1H, d, *J* = 6.8 Hz), 3.71 (3H, s), 1.64 (3H, s), 1.41 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.9, 132.1, 119.4, 111.2, 78.7, 77.7, 51.8, 26.9, 25.5. IR (neat, cm^{-1}): 2988, 1761, 1205, 1098. ESI-MS *m/z*: 209 (M^++Na), 209 (100%). HRMS (ESI): Calcd. for $C_9H_{14}O_4Na$: 209.0790, found:209.0776.

(*S*)-1-((2*R*,4*R*,6*R*)-6-Allyl-4-methoxy-5,5-dimethyltetrahydro-2*H*-pyran-2-yl)ethane-1,2-diol (**14a**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.82 (1H, dddd, *J* = 17.0, 12.5, 6.8, 6.8 Hz), 5.10-5.01 (2H, m), 3.82-3.68 (2H, m), 3.64-3.56 (1H, m), 3.46 (1H, ddd, *J* = 12.6, 5.1, 2.1 Hz), 3.36 (3H, s), 3.01 (1H, dd, *J* = 11.1, 2.2 Hz), 2.89 (1H, dd, *J* = 11.1, 4.4 Hz), 2.53 (1H, br s), 2.36 (1H, br s), 2.25 (1H, dd, *J* = 13.2, 6.8 Hz), 2.15-2.05 (1H, m), 2.01 (1H, ddd, *J* = 12.6, 4.4, 2.4 Hz), 1.42-1.31 (1H, m), 0.95 (3H, s), 0.92 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.3, 116.3, 84.7, 84.2, 78.5, 73.3, 63.9, 57.2, 38.9, 33.4, 28.6, 22.4, 13.2. IR (neat, cm^{-1}): 3404, 2973, 2936, 2878, 2833. MS *m/z*: 244 (M^+), 85 (100%). HRMS (EI): Calcd. for $C_{13}H_{24}O_4$: 244.1675, found: 244.1656.

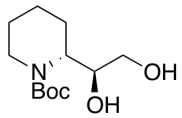
(2*R*,4*R*,6*R*)-Methyl-6-allyl-4-methoxy-5,5-dimethyltetrahydro-2*H*-pyran-2-carboxylate (**14b'**)



14b' was prepared according to the method A. **14b'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 8).

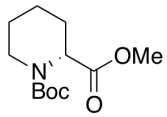
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.99-5.87 (1H, m), 5.08 (1H, ddd, *J* = 17.0, 3.4, 1.6 Hz), 5.05-5.00 (1H, m), 3.97 (1H, dd, *J* = 12.4, 2.8 Hz), 3.76 (3H, s), 3.37 (3H, s), 3.01 (1H, dd, *J* = 9.4, 3.0 Hz), 2.91 (1H, dd, *J* = 11.6, 4.8 Hz), 2.35-2.19 (3H, m), 1.63-1.51 (1H, m), 0.95 (3H, s), 0.88 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 136.5, 116.0, 85.1, 84.5, 75.3, 57.2, 52.2, 38.8, 33.4, 29.5, 22.4, 13.2. IR (neat, cm^{-1}): 3076, 2975, 2827, 1761, 1742, 1642. MS *m/z*: 242 (M^+), 85 (100%). HRMS (EI): Calcd. for $C_{13}H_{22}O_4$: 242.1518, found: 242.1522.

1-(*R*)-*tert*-Butyl 2-((*S*)-1,2-dihydroxylethyl)piperidine-1-carboxylate (**15a**)[5]



^{1}H-NMR (600 MHz, $CDCl_3$): mixture of rotamers δ 4.26-4.16 (1H, m), 4.05-3.88 (2H, m), 3.77-3.63 (1H, m), 3.56-3.46 (1H, m), 3.06-2.57 (2H, m), 1.70-1.51 (6H, m), 1.47 (9H, s). ^{13}C-NMR (150 MHz, $CDCl_3$): mixture of rotamers δ 157.4, 80.2, 71.5, 64.4, 52.1, 40.9, 28.4, 25.9, 25.0, 19.7. IR (neat, cm^{-1}): 3415, 2933, 2873, 1662. MS *m/z*: 246 (M^++H), 128 (100%). HRMS (EI): Calcd. for $C_{12}H_{24}O_4N$: 246.1705, found: 246.1694.

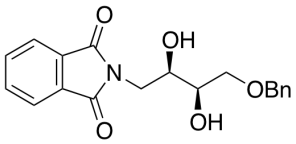
1-(*R*)-*tert*-Butyl 2-methyl piperidine-1,2-dicarboxylate (**15b'**)[6]



15b' was prepared according to the method A. **15b'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 10 to 1 / 4).

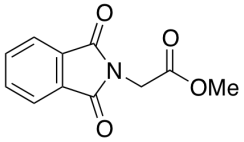
^{1}H-NMR (600 MHz, $CDCl_3$): mixture of rotamers δ 4.88 (0.5H, br s), 4.71 (0.5H, br s), 4.07-3.96 (0.5H, m), 3.96-3.85 (0.5H, m), 3.71 (3H, s), 3.02-2.90 (0.5H, m), 2.90-2.79 (0.5H, m) 2.18 (1H, br s) 1.71-1.55 (3H, m), 1.51-1.33 (10H, m), 1.27-1.16 (1H, m). ^{13}C-NMR (150 MHz, $CDCl_3$): mixture of rotamers δ 172.6, 172.4, 156.0, 155.5, 80.0, 55.0, 53.8, 52.0, 42.1, 41.1, 28.4, 26.8, 24.9, 24.6, 20.9, 20.7. IR (neat, cm^{-1}): 2977, 2942, 2862, 1746, 1698. MS *m/z*: 243 (M^+), 128 (100%). HRMS (EI): Calcd. for $C_{12}H_{21}O_4N$: 243.1471, found: 243.1470.

2-((2*R*,3*R*)-4-(Benzyloxy)-2,3-dihydroxybutyl)isoindoline-1,3-dione (**17a**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.89-7.82 (2H, m), 7.77-7.70 (2H, m), 7.38-7.26 (5H, m), 4.57 (1H, d, *J* = 12.6 Hz), 4.54 (1H, d, *J* = 12.6 Hz), 4.04-3.94 (2H, m), 3.85-3.73 (2H, m), 3.70-3.62 (2H, m), 2.84 (2H, br s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.6, 137.6, 134.0, 131.9, 128.4, 127.74, 127.70, 123.3, 73.5, 72.0, 70.1, 69.8, 41.1. IR (neat, cm^{-1}): 3463, 2923, 2867, 1770, 1709. MS *m/z*: 341 (M^+), 161 (100%). HRMS (EI): Calcd. for $C_{19}H_{19}NO_5$: 341.1263, found: 341.1275.

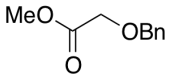
Methyl 2-(1,3-dioxoisoindolin-2-yl)acetate (**17b'**)[7]



17b' was prepared according to the method A. **17b'** was obtained as white solid after silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 6).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93-7.87 (2H, m), 7.79-7.73 (2H, m), 4.46 (2H, s), 3.77 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.7, 167.4, 134.2, 132.0, 123.6, 52.6, 38.8. IR (neat, cm^{-1}): 2987, 2952, 1773, 1742, 1721. MS *m/z*: 219 (M^+), 160 (100%). HRMS (EI): Calcd. for $C_{11}H_9NO_4$: 219.0532, found: 219.0539.

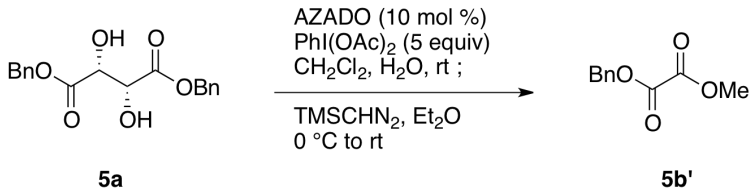
Methyl 2-(benzyloxy)acetate (**17d'**)[8]



17d' was prepared according to the method A. **17d'** was obtained as colorless oil after silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 6).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.27 (5H, m), 4.64 (2H, s), 4.11 (2H, s), 3.77 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.7, 137.0, 128.5, 128.04, 73.3, 67.1, 51.8. IR (neat, cm^{-1}): 3062, 3031, 2952, 2909, 2860, 1755. MS *m/z*: 180 (M^+), 107 (100%). HRMS (EI): Calcd. for $C_{10}H_{12}O_3$: 180.0786, found: 180.0768.

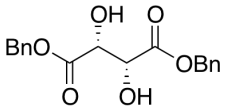
Procedure for the Oxidative Cleavage of the Diol 5a (Method B)



5a **5b'**

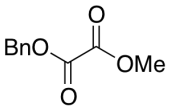
To a solution of diol **5a** (30.0 mg, 0.0908 mmol) in CH_2Cl_2 (0.22 mL) and H_2O (0.22 mL) was added AZADO (1.4 mg, 0.00908 mmol) and $PhI(OAc)_2$ (146 mg, 0.454 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 40 min. Then, buffer (pH = 2.3) was added to the reaction mixture, and the resultant solution was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. To the residue was added Et_2O and cooled at 0 °C. Then, $TMSCHN_2$ in Et_2O was added until yellow color was appeared. The mixture was allowed to warm to room temperature and stirred for 2 h. The solution was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 4) to give a methyl ester **5b'** (30.8 mg, 0.159 mmol, 88%) as colorless oil.

Dibenzyl L-Tartrate (**5a**)[9]



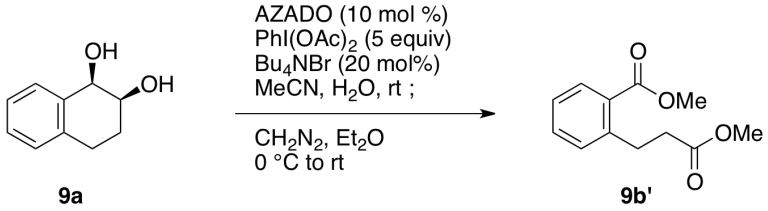
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.31 (10H, m), 5.29 (2H, d, *J* = 12.1 Hz), 5.25 (2H, d, *J* = 12.1 Hz), 4.61 (2H, d, *J* = 6.3 Hz), 3.17 (2H, d, *J* = 6.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 134.8, 128.60, 128.59, 128.3, 72.1, 67.9. IR (neat, cm^{-1}): 3482, 3062, 3033, 2954, 1744. MS *m/z*: 331 (M^++H), 91 (100%). HRMS (EI): Calcd. for $C_{18}H_{19}O_6$: 331.1182, found: 331.1198.

Benzyl methyl oxalate (**5b'**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.35 (5H, m), 5.32 (2H, s), 3.90 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.1, 157.4, 134.1, 128.9, 128.79, 128.75, 68.6, 53.6. IR (neat, cm^{-1}): 3067, 3035, 2957, 1771, 1746. MS *m/z*: 194 (M^+), 91 (100%). HRMS (EI): Calcd. for $C_{10}H_{10}O_4$: 194.0579, found: 194.0584.

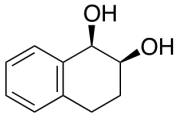
Procedure for the Oxidative Cleavage of the Diol 9a (Method C)



9a **9b'**

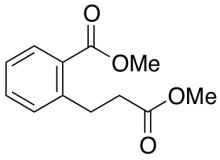
To a solution of diol **9a** (30.0 mg, 0.183 mmol) in MeCN (0.45 mL) and H_2O (0.45 mL) was added AZADO (2.8 mg, 0.0183 mmol), $PhI(OAc)_2$ (295 mg, 0.915 mmol) and Bu_4NBr (12 mg, 0.0366 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed under reduced pressure, and the residue was added Et_2O. Then, CH_2N_2 in Et_2O was added at 0 °C until yellow color was appeared. The mixture was allowed to warm to room temperature and stirred for 1 h. The solution was concentrated under reduced pressure. Then, water was added to the residue and the resultant solution was extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 10) to give a methyl ester **9b'** (34.6 mg, 0.156 mmol, 85%) as colorless oil.

cis-1,2-Dihydroxy-1,2,3,4-tetrahydronaphthalene (**9a**)[10]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (1H, m), 7.25-7.22 (2H, m), 7.15-7.12 (1H, m), 4.74-4.69 (1H, m), 4.07-4.00 (1H, m), 3.02-2.93 (1H, m), 2.85-2.75 (1H, m), 2.29 (1H, d, *J* = 6.8 Hz), 2.24 (1H, d, *J* = 6.0 Hz), 2.11-2.00 (1H, m), 1.98-1.89 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.3, 136.2, 129.9, 128.6, 128.1, 126.4, 69.9, 69.5, 26.9, 26.2. IR (neat, cm^{-1}): 3266, 2937, 2879. MS *m/z*: 164 (M^+), 146 (100%). HRMS (EI): Calcd. for $C_{10}H_{12}O_2$: 164.0837, found: 164.0832.

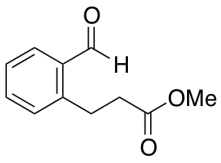
Methyl 2-(3-methoxy-3-oxopropyl)benzoate (**9b'**)[11]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (1H, d, *J* = 8.4 Hz), 7.46-7.41 (1H, m), 7.32-7.25 (2H, m), 3.90 (3H, s), 3.67 (3H, s), 3.28 (2H, t, *J* = 7.8 Hz), 2.67 (2H, t, *J* = 7.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.4, 167.7, 142.4, 132.2, 131.1, 130.9, 129.3, 126.4, 52.0, 51.5, 35.6, 29.9. IR (neat, cm^{-1}): 3067, 3027, 2995, 2952, 1737, 1721. MS *m/z*: 222 (M^+), 162 (100%). HRMS (EI): Calcd. for $C_{12}H_{14}O_4$:

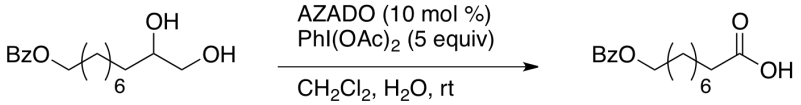
222.0892, found: 222.0880.

Methyl 3-(2-formylphenyl)propanoate (**9c'**)[12]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.21 (1H, s), 7.82 (1H, d, *J* = 7.2 Hz), 7.55-7.49 (1H, m), 7.46-7.39 (1H, m), 7.33 (1H, d, *J* = 7.2 Hz), 3.66 (3H, s), 3.36 (2H, t, *J* = 7.7 Hz), 2.66 (2H, t, *J* = 7.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 192.7, 173.1, 142.8, 133.8, 133.6, 131.2, 127.0, 51.6, 35.3, 28.1. IR (neat, cm^{-1}): 3067, 2995, 2952, 2844, 2743, 1737, 1697. MS *m/z*: 192 (M^+), 132 (100%). HRMS (EI): Calcd. for $C_{11}H_{12}O_3$: 192.0786, found: 192.0786.

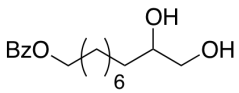
Procedure for the Oxidative Cleavage of the Diol 11a (Method D)



11a **11b**

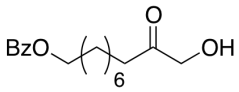
To a solution of diol **11a** (30.0 mg, 0.102 mmol) in CH_2Cl_2 (0.26 mL) and H_2O (0.26 mL) was added AZADO (1.6 mg, 0.0102 mmol) and $PhI(OAc)_2$ (164 mg, 0.510 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. Then, 10% HCl was added to the mixture and the resultant solution was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 8 to only AcOEt) to give a carboxylic acid **11b** (26.8 mg, 0.0963 mmol, 94%) as white solid.

9,10-Dihydroxydecyl benzoate (**11a**)



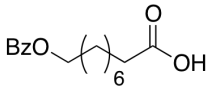
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10-8.02 (2H, m), 7.60-7.53 (1H, m), 7.50-7.41 (2H, m), 4.32 (2H, t, *J* = 6.8 Hz), 3.76-3.62 (2H, m), 3.50-3.39 (1H, m), 2.03 (1H, d, *J* = 4.4 Hz), 1.89 (1H, t, *J* = 5.6 Hz), 1.77 (2H, tt, *J* = 6.8 Hz, 6.8 Hz), 1.51-1.27 (12H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 132.8, 130.4, 129.5, 128.3, 72.3, 66.7, 65.1, 33.1, 29.5, 29.3, 29.1, 28.6, 25.9, 25.4. IR (neat, cm^{-1}): 3391, 2929, 2855, 1719. MS *m/z*: 294 (M^+), 123 (100%). HRMS (EI): Calcd. for $C_{17}H_{26}O_4$: 294.1831, found: 294.1822.

10-Hydroxy-9-oxodecyl benzoate (**11c**)



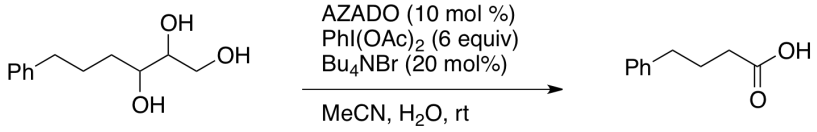
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09-7.98 (2H, m), 7.60-7.52 (1H, m), 7.48-7.39 (2H, m), 4.31 (2H, t, *J* = 6.8 Hz), 4.23 (2H, s), 3.11 (1H, s), 2.40 (2H, t, *J* = 7.5 Hz), 1.76 (2H, tt, *J* = 6.8 Hz, 6.8 Hz), 1.70-1.56 (2H, m), 1.50-1.36 (2H, m), 1.42-1.24 (6H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 209.8, 166.7, 132.8, 130.5, 129.5, 128.3, 68.1, 65.0, 38.4, 29.13, 29.07, 29.0, 28.7, 25.9, 23.6. IR (neat, cm^{-1}): 3479, 2931, 2856, 1716. MS *m/z*: 293 (M^++H), 105 (100%). HRMS (EI): Calcd. for $C_{17}H_{25}O_4$: 293.1753, found: 293.1751.

9-(Benzoyloxy)nonanoic acid (**11b**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07-8.02 (2H, m), 7.58-7.52 (1H, m), 7.47-7.41 (2H, m), 4.31 (2H, t, *J* = 6.8 Hz), 2.35 (2H, t, *J* = 7.6 Hz), 1.77 (2H, tt, *J* = 6.8, 6.8 Hz), 1.69-1.59 (2H, m), 1.50-1.29 (8H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 179.9, 166.7, 132.8, 130.5, 129.5, 128.3, 65.1, 34.0, 29.1, 29.0, 28.9, 28.7, 25.9, 24.6. IR (neat, cm^{-1}): 3063, 3035, 2932, 2857, 1718. MS *m/z*: 279 (M^++H), 123 (100%). HRMS (EI): Calcd. for $C_{16}H_{22}O_4$: 279.1596, found: 279.1583.

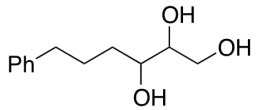
Procedure for the Oxidative Cleavage of the Diol 16a (Method E)



16a **16b**

To a solution of triol **16a** (30.0 mg, 0.143 mmol) in MeCN (0.36 mL) and H_2O (0.36 mL) was added AZADO (2.2 mg, 0.0143 mmol), $PhI(OAc)_2$ (276 mg, 0.858 mmol) and Bu_4NBr (9.2 mg, 0.0286 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the residue was added Et_2O. Then, CH_2N_2 in Et_2O was added at 0 °C until yellow color was appeared. Then, 10% HCl was added to the mixture and the resultant solution was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20 to 1 / 2) to give a carboxylic acid **16b** (23.3 mg, 0.142 mmol, 99%) as white solid.

6-Phenylhexane-1,2,3-triol (**16a**)



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m), 7.20-7.15 (3H, m), 3.74 (1H, m), 3.68 (2H, br s), 3.53 (1H, br s), 2.80-2.60 (2H, m), 2.40-2.20 (2H, m) 1.80-1.50 (2H, m) 1.60-1.50 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.1, 128.40, 128.36, 125.8, 73.4, 72.6, 65.0, 35.7, 33.3, 27.3. IR (neat, cm^{-1}): 3373, 2938, 1080. MS *m/z*: 210 (M^+), 104 (100%). HRMS (EI): Calcd. for $C_{12}H_{18}O_3$: 210.1256, found: 210.1257.

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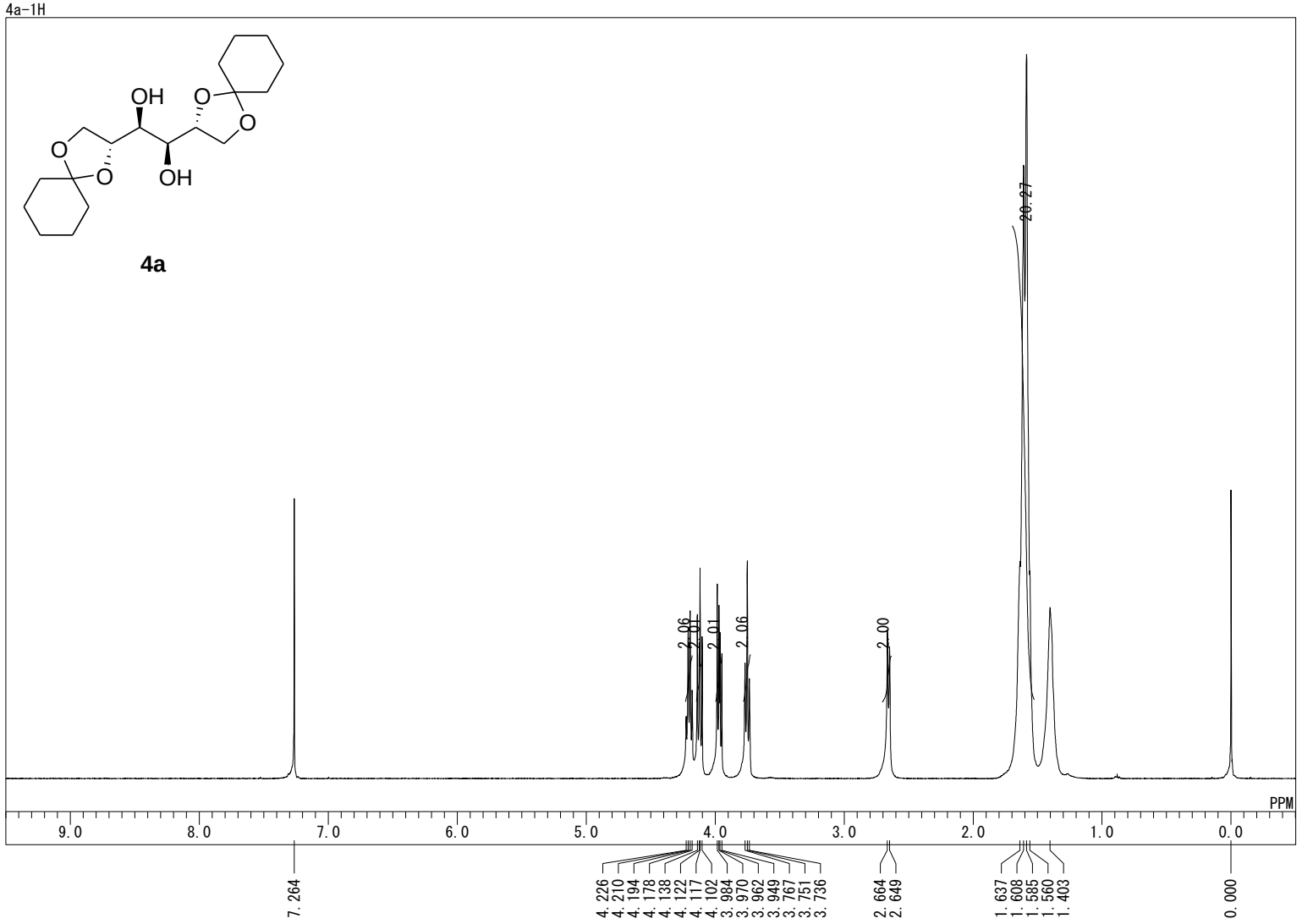
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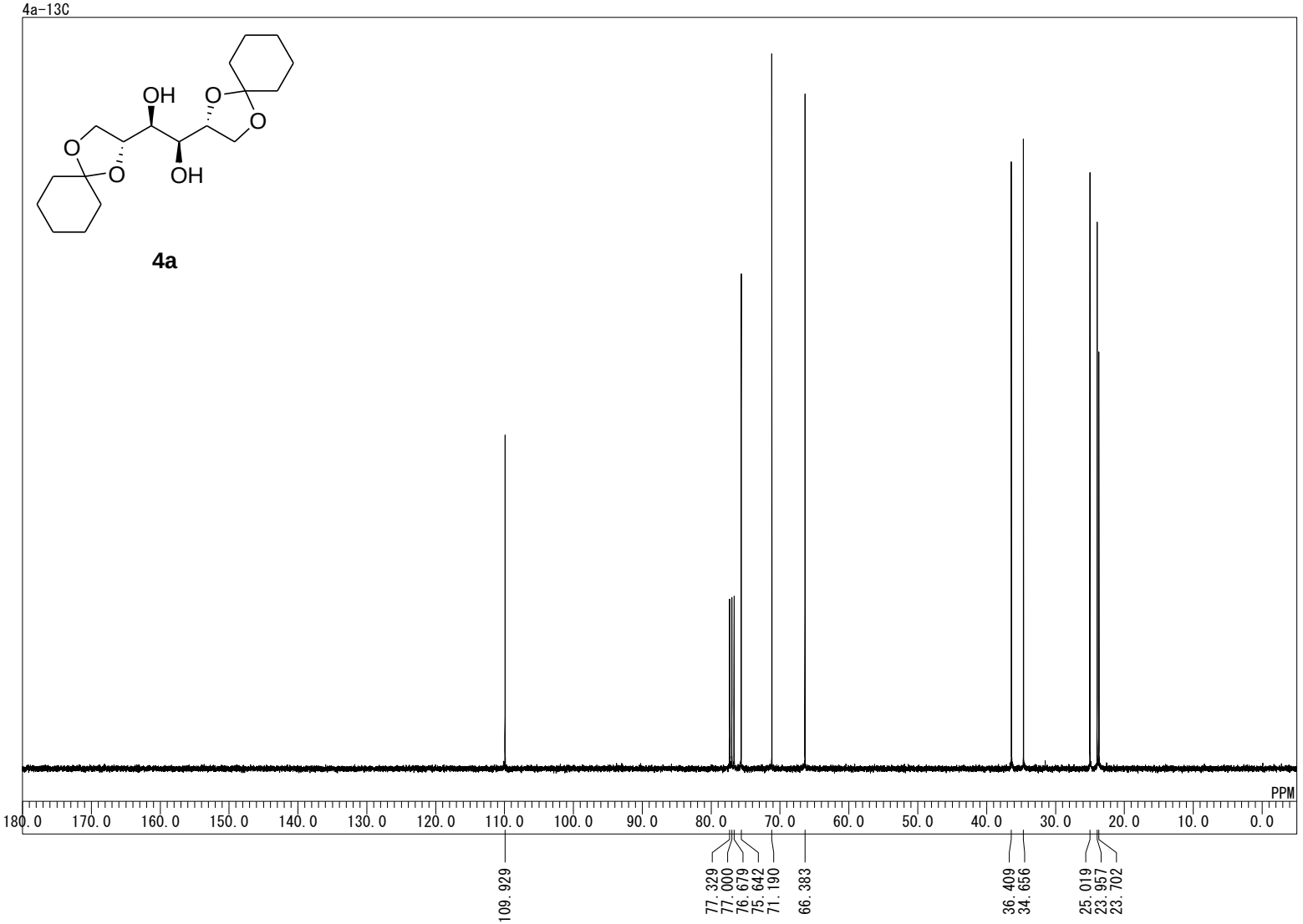
OH
O
O
O
O
OH
4a
20.27
2.06
2.01
2.01
2.06
2.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
4.226
4.210
4.194
4.178
4.138
4.122
4.117
4.102
3.984
3.970
3.962
3.949
3.767
3.751
3.736
2.664
2.649
1.637
1.608
1.585
1.560
1.403
0.000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OH
O
O
O
O
OH
4a
PPM
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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77.000
76.679
75.642
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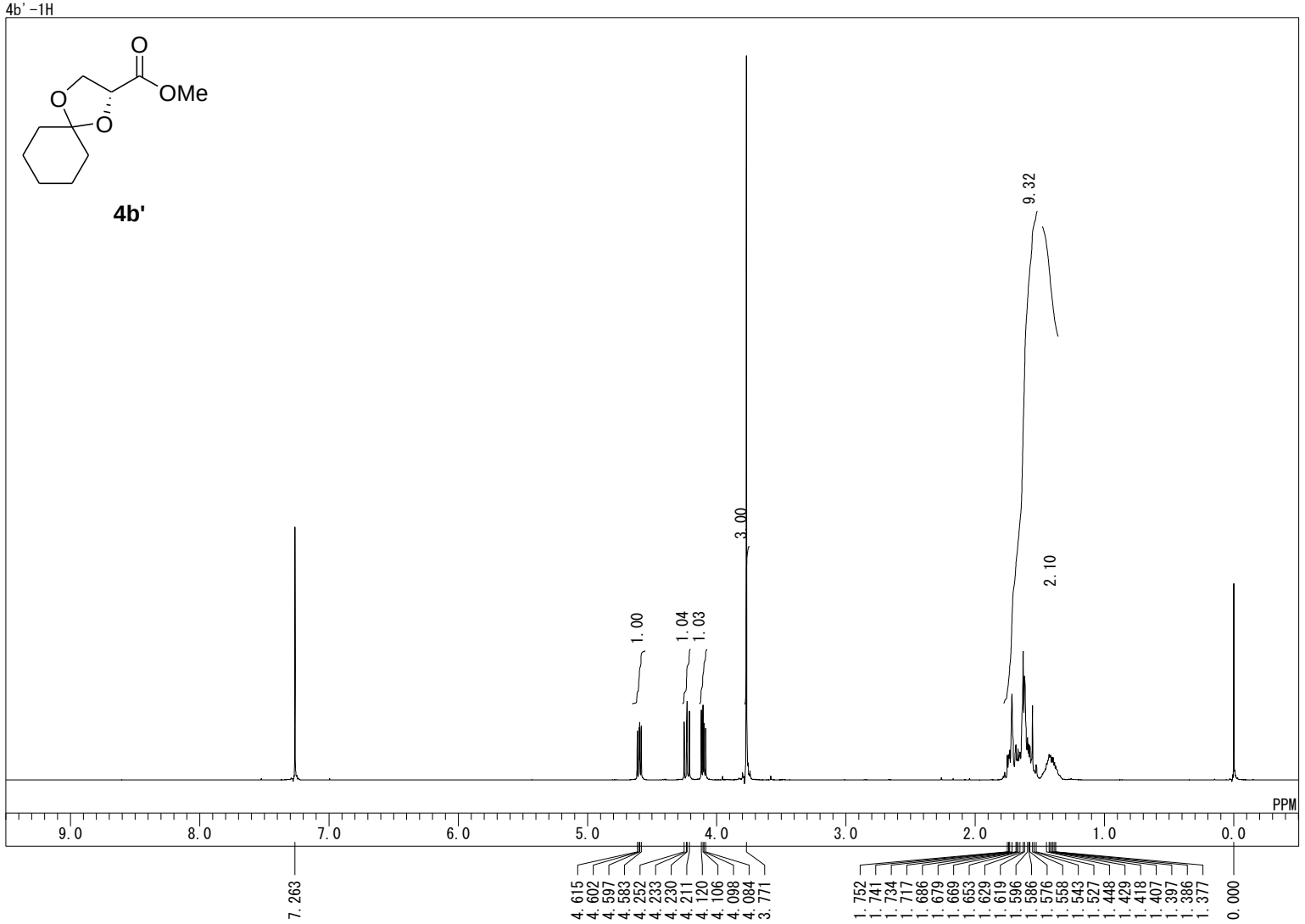
66.383
36.409
34.656
25.019
23.957
23.702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O
OMe
O
O
4b'
9.32
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2.10
1.00
1.04
1.03
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.263
4.615
4.602
4.597
4.583
4.252
4.233
4.230
4.211
4.120
4.106
4.098
4.084
3.771
1.752
1.741
1.734
1.717
1.686
1.679
1.669
1.653
1.629
1.619
1.596
1.586
1.576
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1.543
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1.418
1.407
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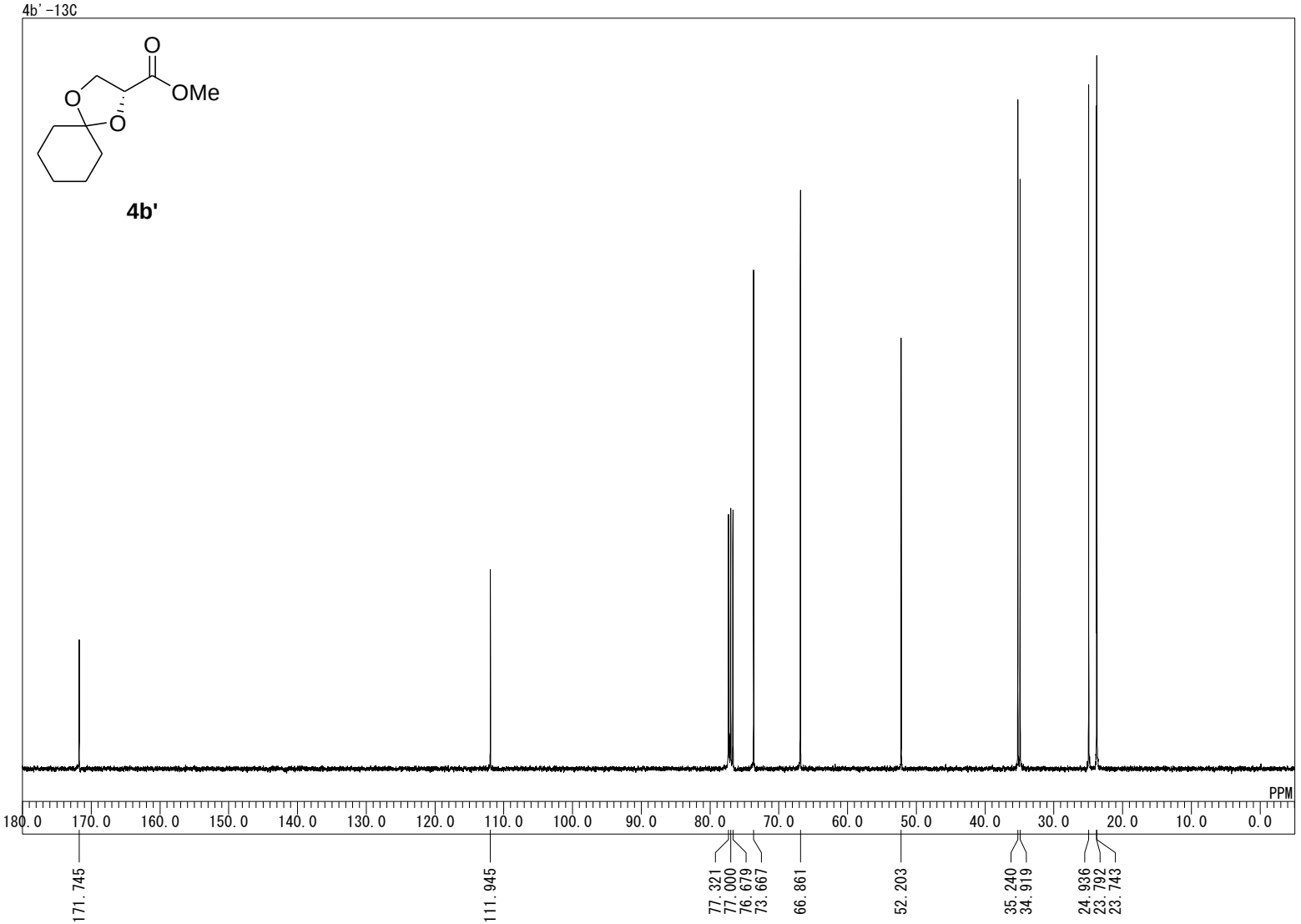
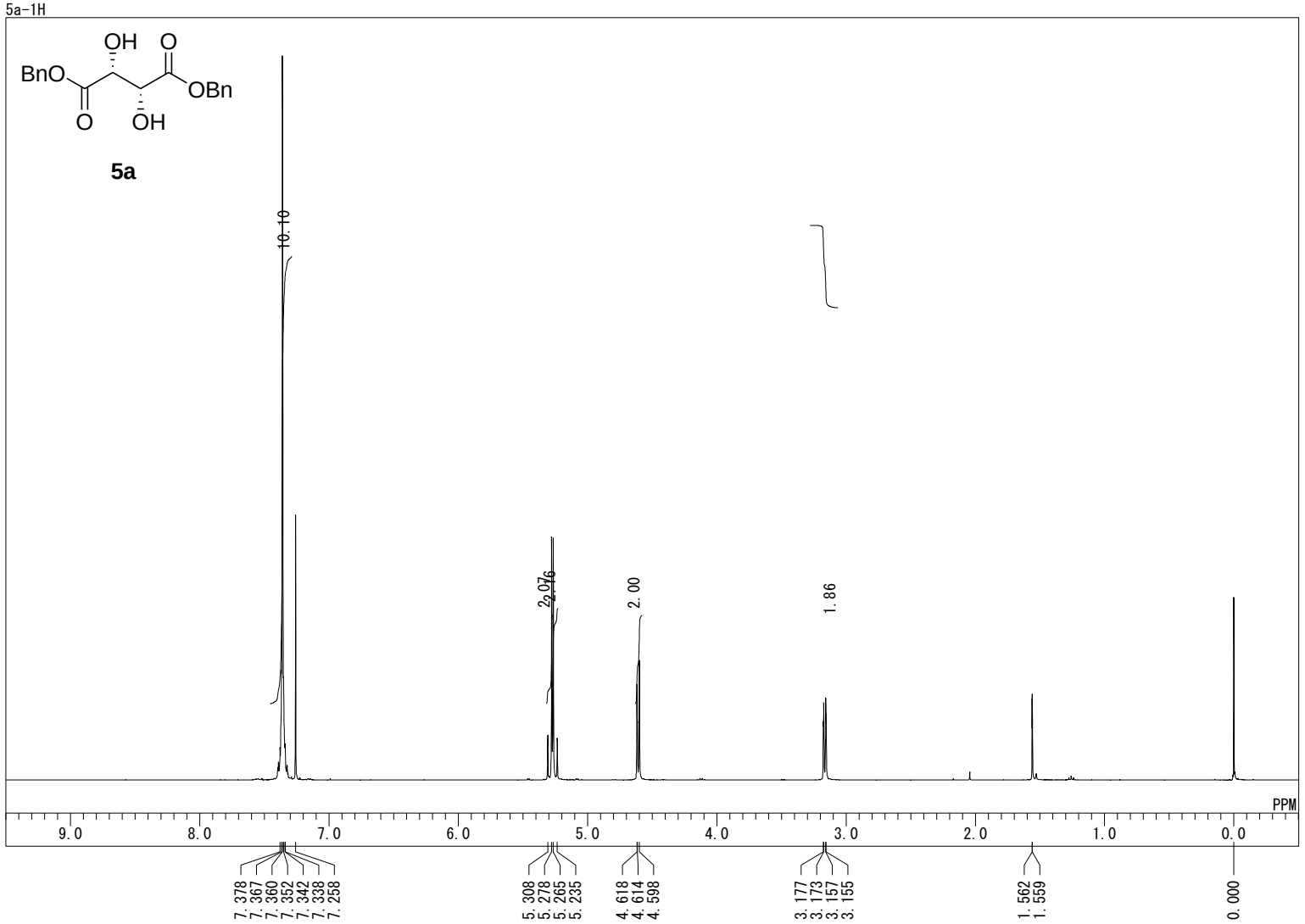

4b'-13C
O
OMe
O
O
4b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
171.745
111.945
77.321
77.000
76.679
73.667
66.861
52.203
35.240
34.919
24.936
23.792
23.743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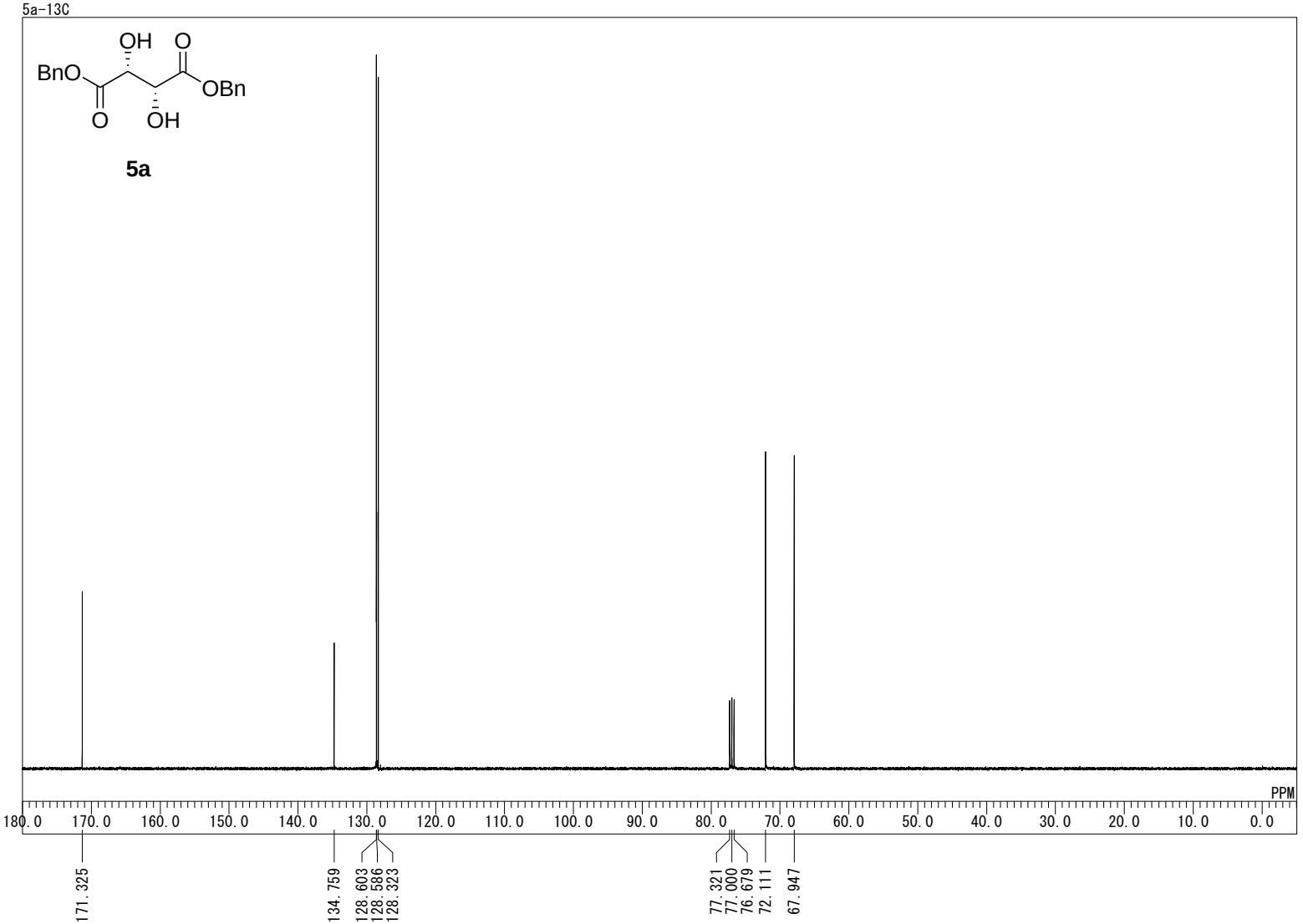
O
BnO
OBn
O
OH
5a
10.10
2.07
2.06
2.00
1.86
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.378
7.367
7.360
7.352
7.342
7.338
7.258
5.308
5.278
5.265
5.235
4.618
4.614
4.598
3.177
3.173
3.157
3.155
1.562
1.559
0.000


5a-13C
OH
O
BnO
OBn
O
OH
5a
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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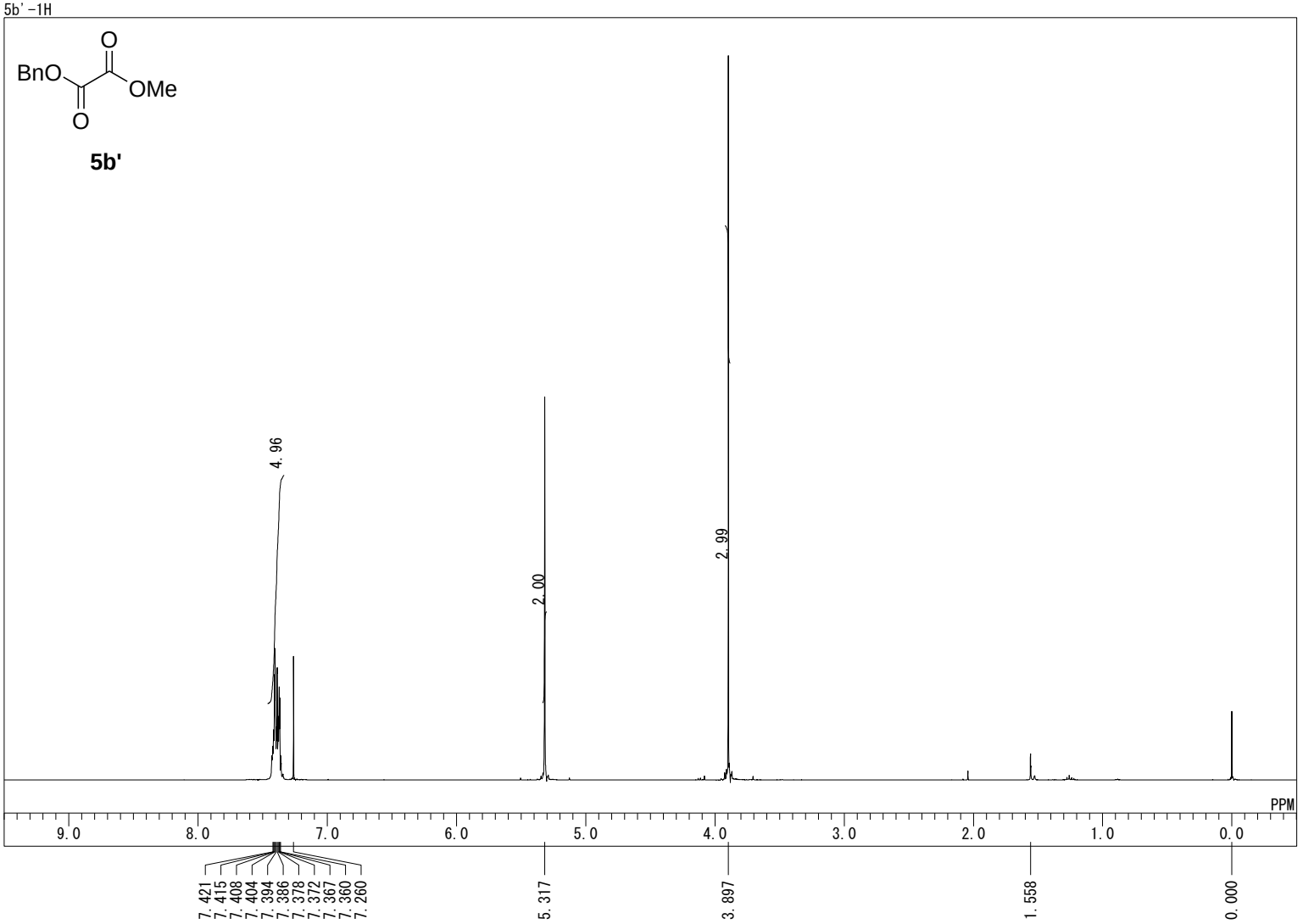
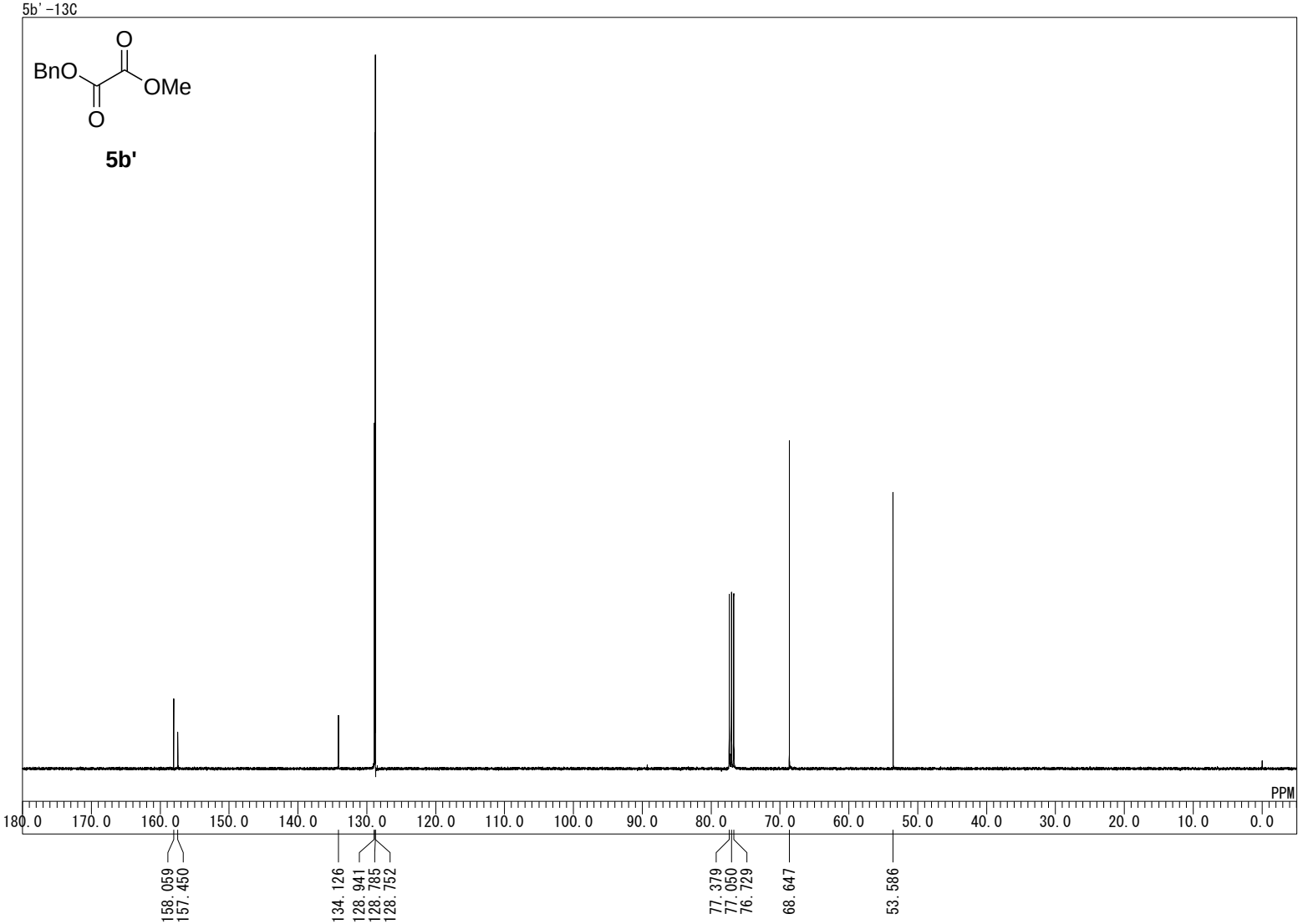
128.603
128.586
128.323
77.321
77.000
76.679
72.111
67.947


5b'-1H
BnO
O
O
OMe
O
5b'
4.96
2.00
2.99
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.421
7.415
7.408
7.404
7.394
7.386
7.378
7.372
7.367
7.360
7.260
5.317
3.897
1.558
0.000


5b'-13C
BnO
O
O
OMe
O
5b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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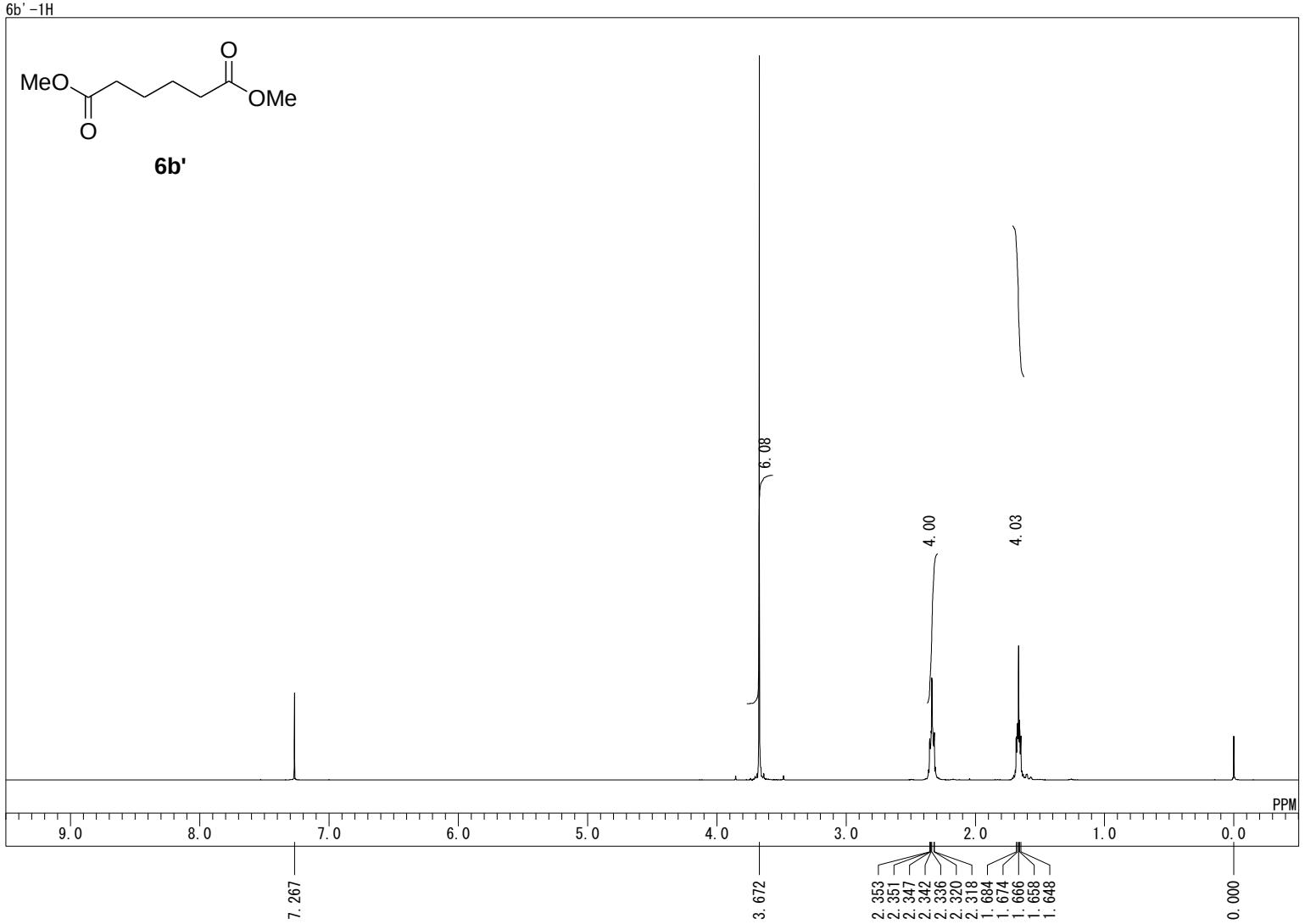
157.450
134.126
128.941
128.785
128.752
77.379
77.050
76.729
68.647
53.586


6b'-1H
MeO
O
O
OMe
O
6b'
6.08
4.00
4.03
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.267
3.672
2.353
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2.336
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2.318
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1.674
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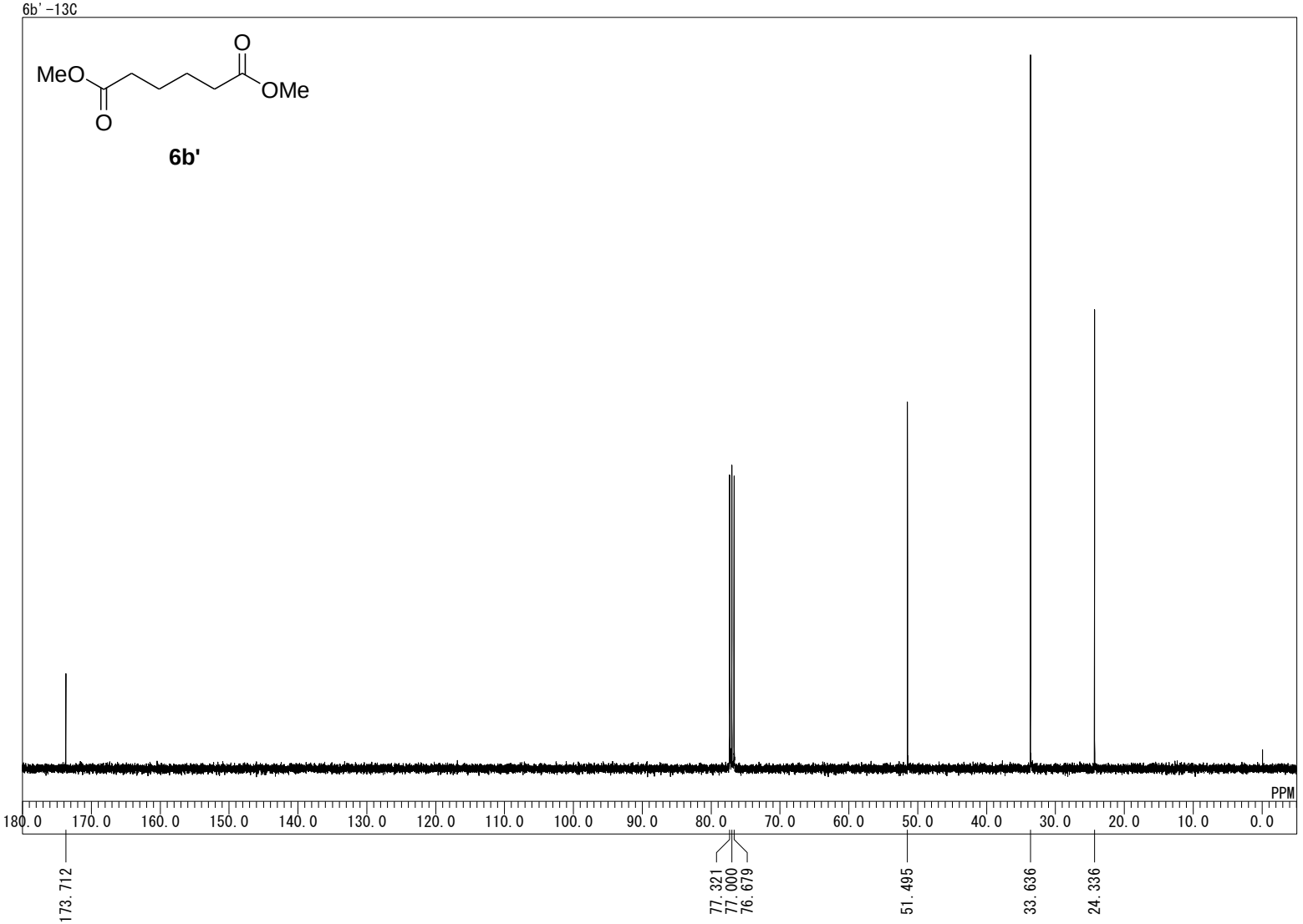
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O
O
OMe
6b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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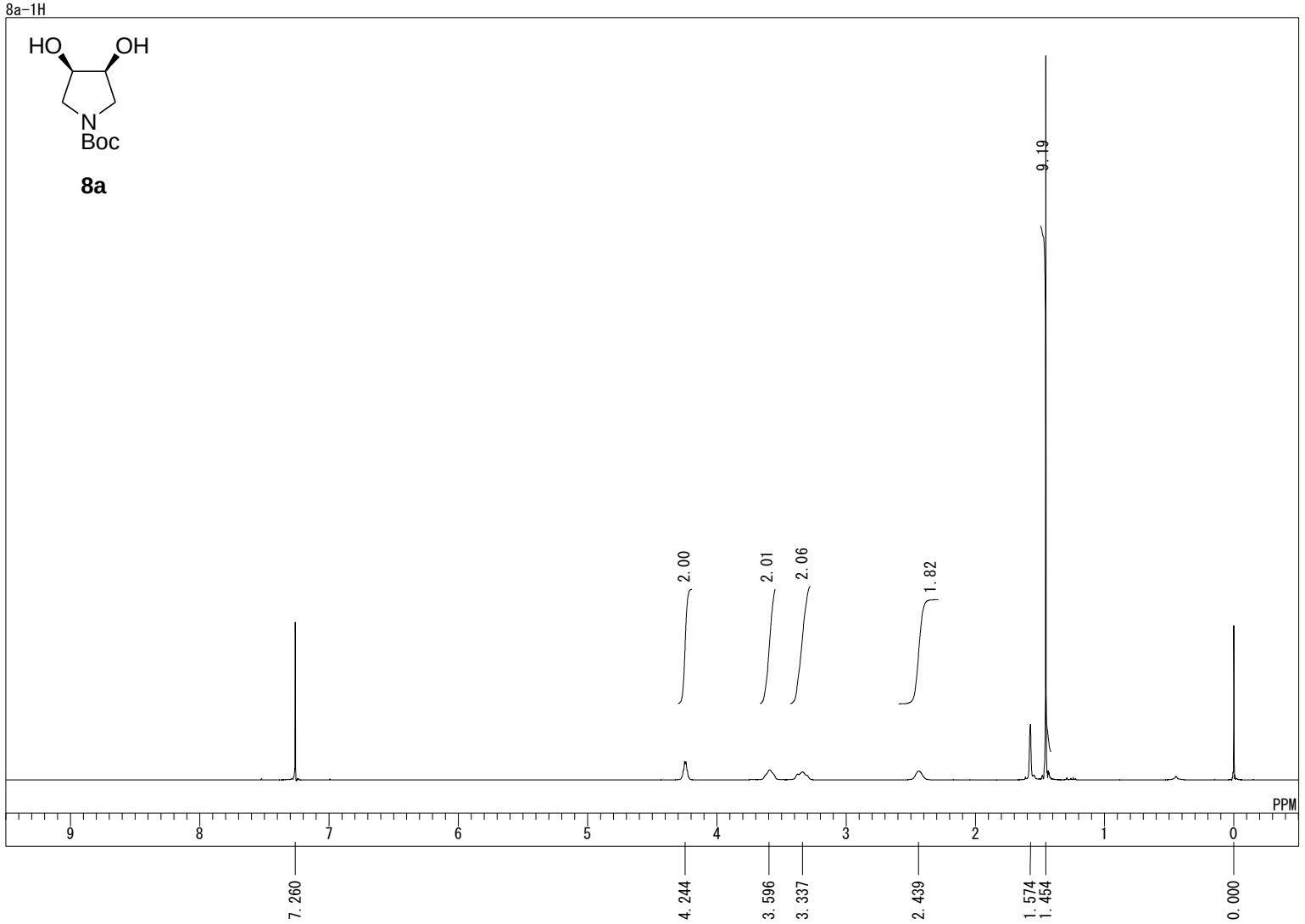
77.000
76.679
51.495
33.636
24.336


8a-1H
HO
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N
Boc
8a
9.19
2.00
2.01
2.06
1.82
PPM
9
8
7
6
5
4
3
2
1
0
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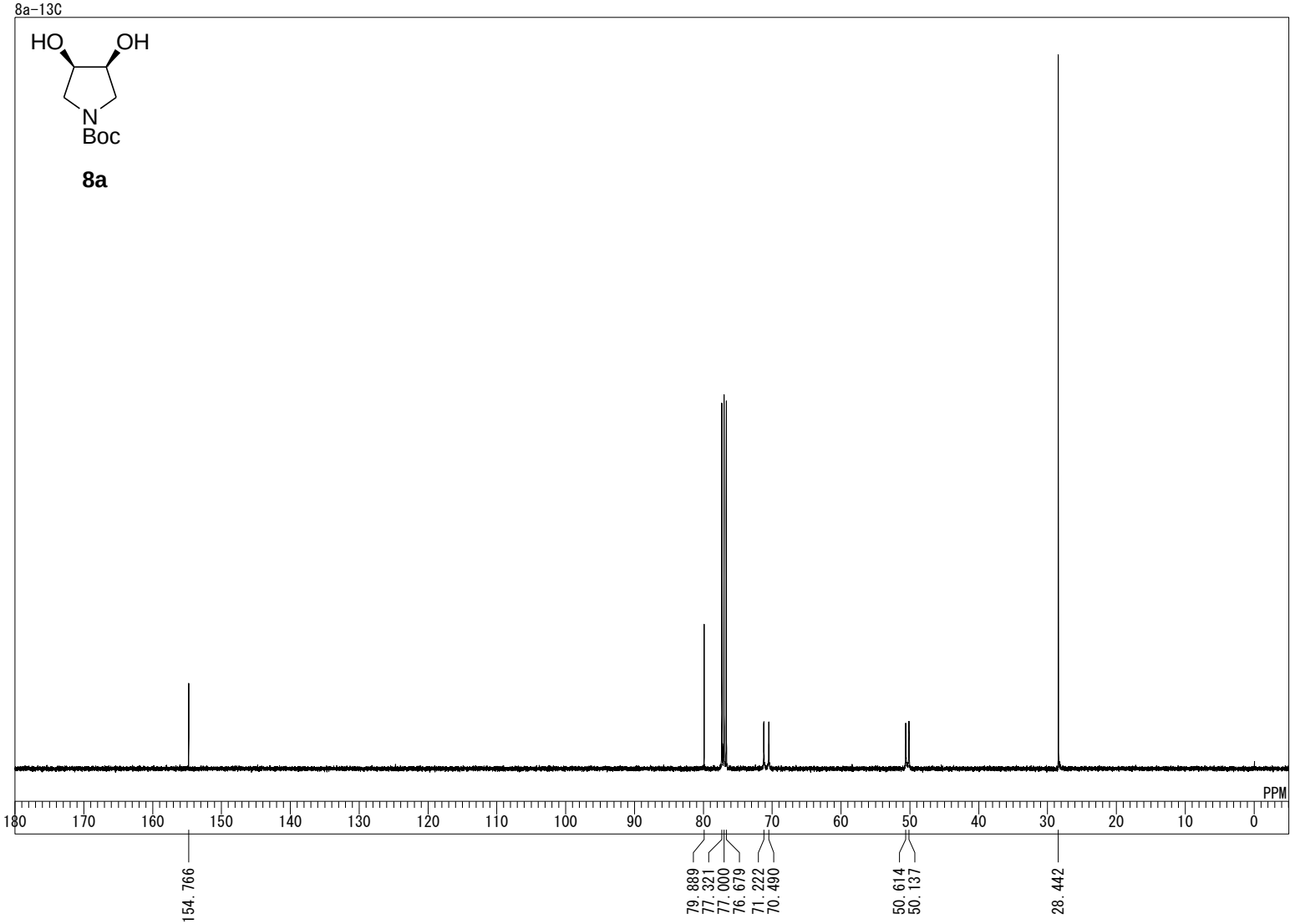
4.244
3.596
3.337
2.439
1.574
1.454
0.000


8a-13C
HO
OH
N
Boc
8a
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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79.889
77.321
77.000
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71.222
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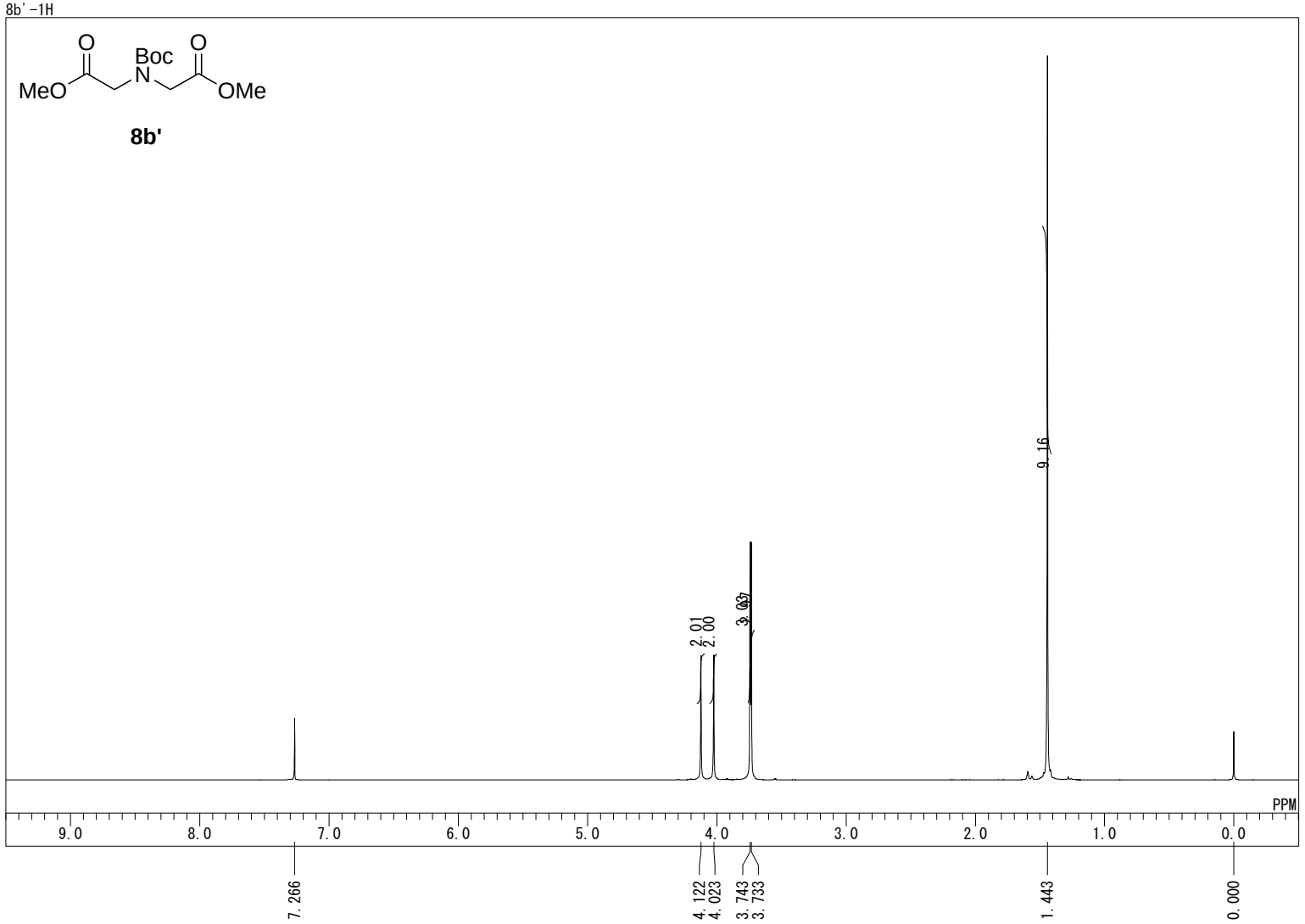
50.614
50.137
28.442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O
Boc
N
O
OMe
8b'
9.16
2.01
2.00
PPM
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8.0
7.0
6.0
5.0
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1.443
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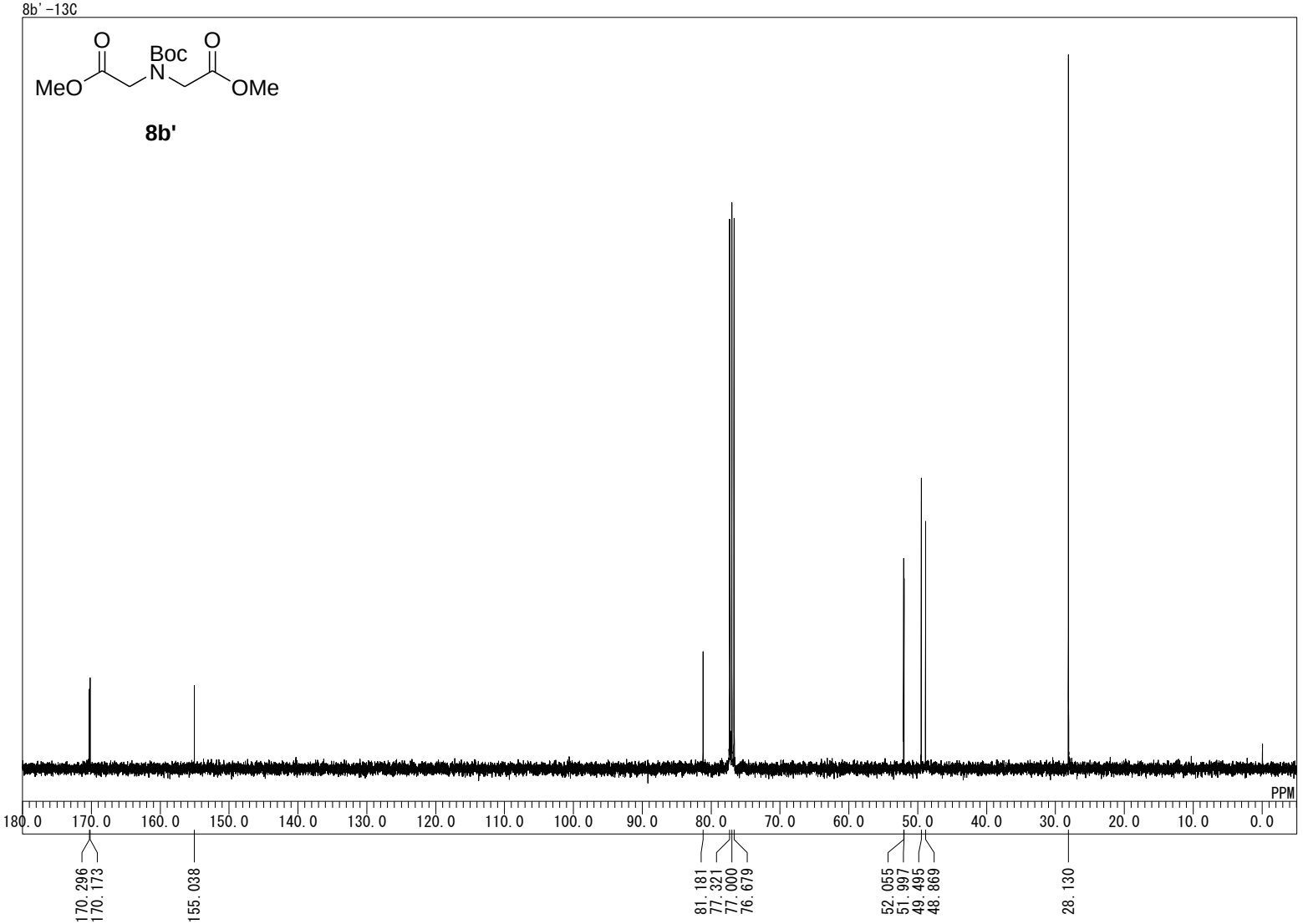
8b'-13C
O
Boc
O
MeO
N
OMe
8b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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155.038
81.181
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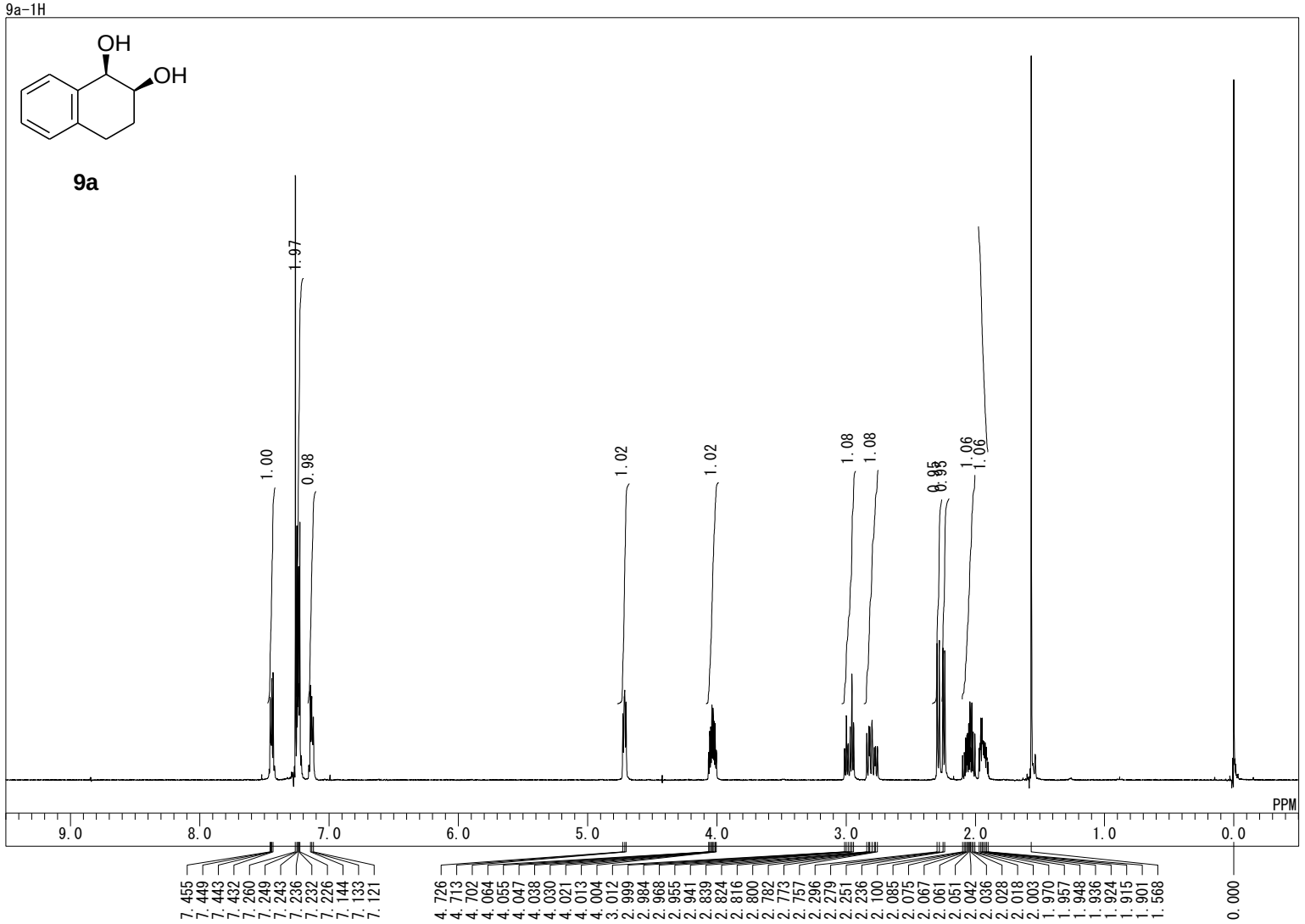
77.000
76.679
52.055
51.997
49.495
48.869
28.130


9a-1H
OH
OH
9a
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1.97
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1.02
1.02
1.08
1.08
0.95
0.95
1.06
1.06
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.455
7.449
7.443
7.432
7.260
7.249
7.243
7.236
7.232
7.226
7.144
7.133
7.121
4.726
4.713
4.702
4.064
4.055
4.047
4.038
4.030
4.021
4.013
4.004
3.012
2.999
2.984
2.968
2.955
2.941
2.839
2.824
2.816
2.800
2.782
2.773
2.757
2.296
2.279
2.251
2.236
2.100
2.085
2.075
2.067
2.061
2.051
2.042
2.036
2.028
2.018
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1.936
1.924
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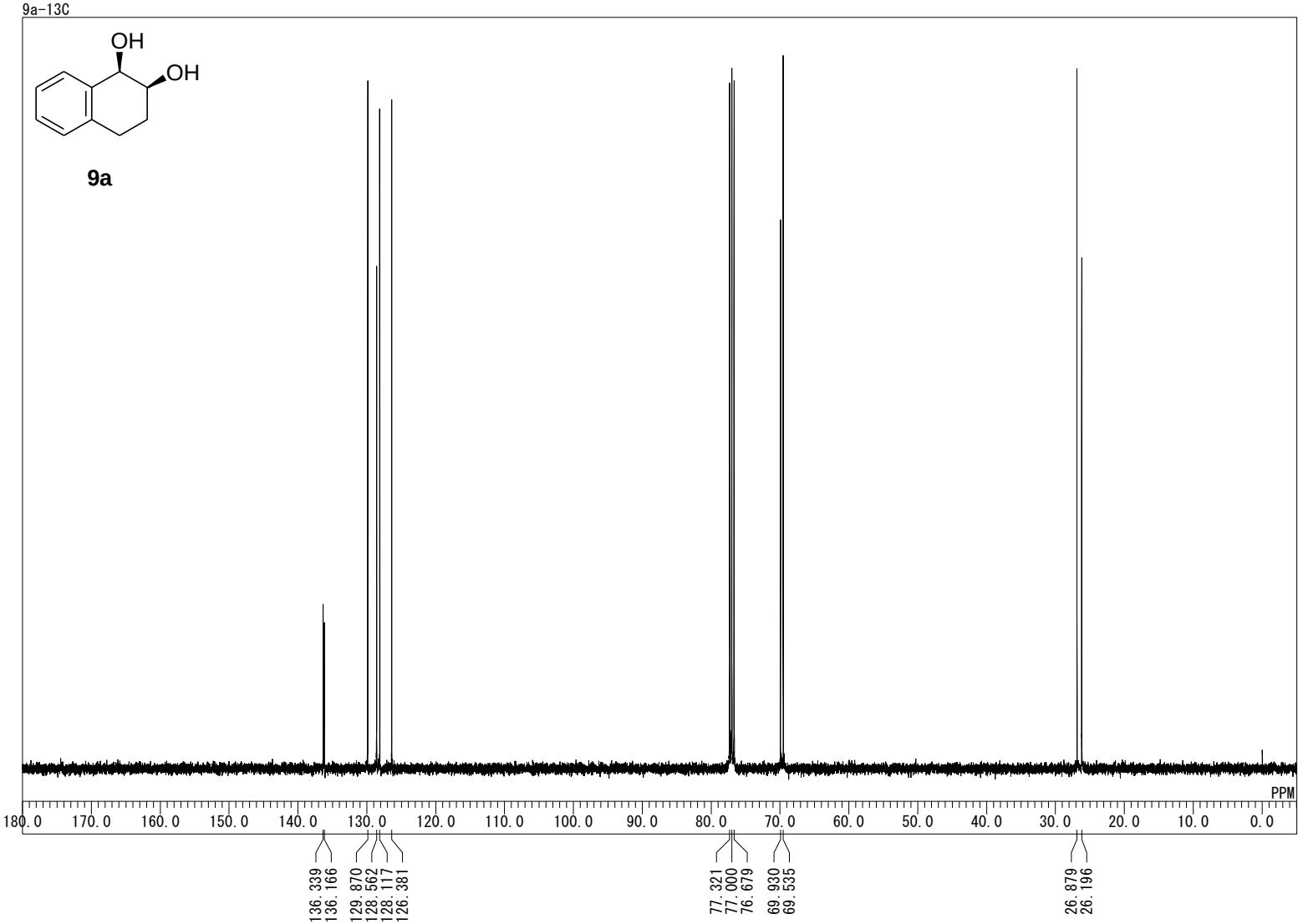
1.901
1.568
0.000


9a-13C
OH
OH
9a
PPM
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
136.339
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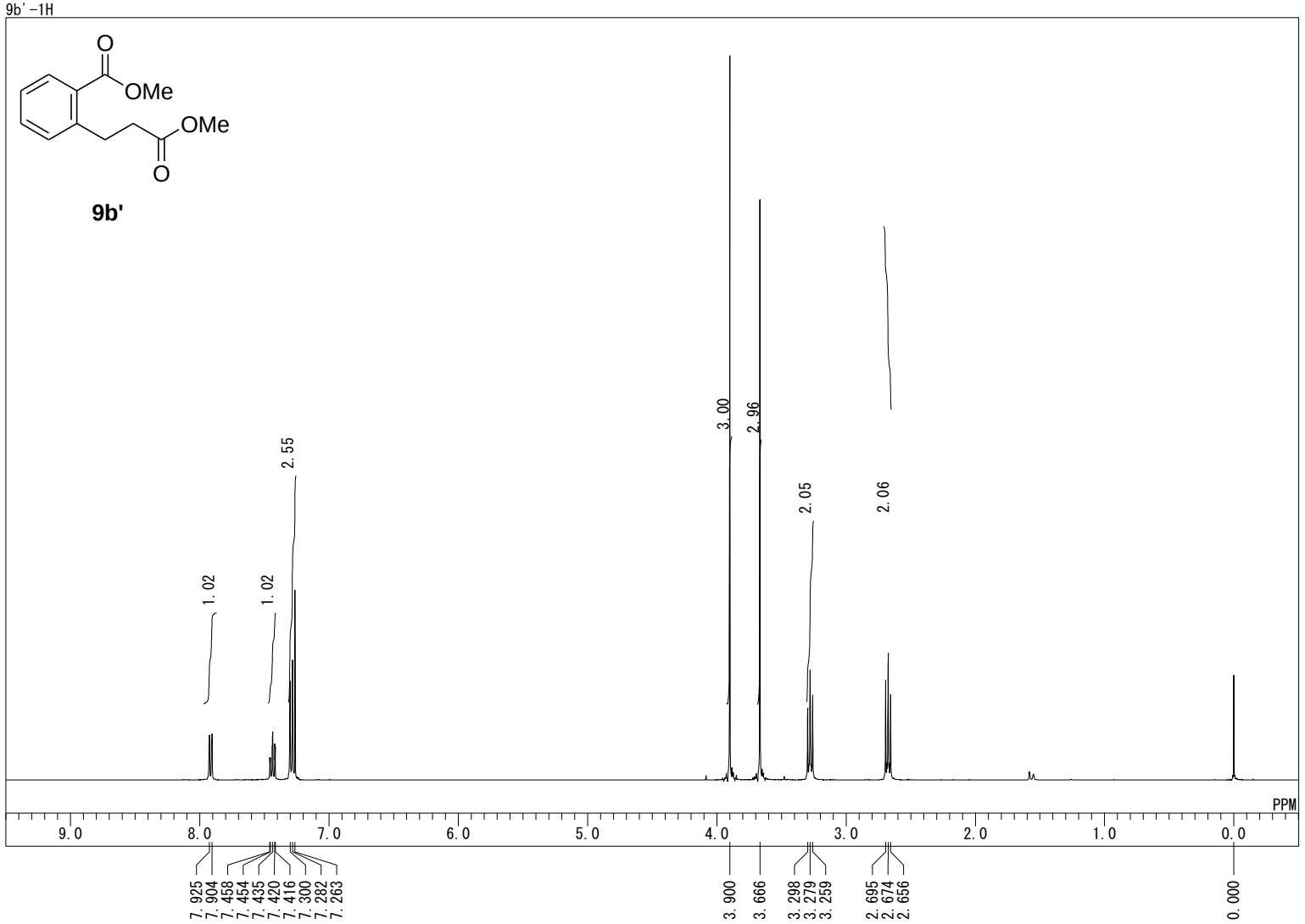
77.321
77.000
76.679
69.930
69.535
26.879
26.196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O
OMe
OMe
O
9b'
1.02
1.02
2.55
3.00
2.96
2.05
2.06
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.925
7.904
7.458
7.454
7.435
7.420
7.416
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7.263
3.900
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3.259
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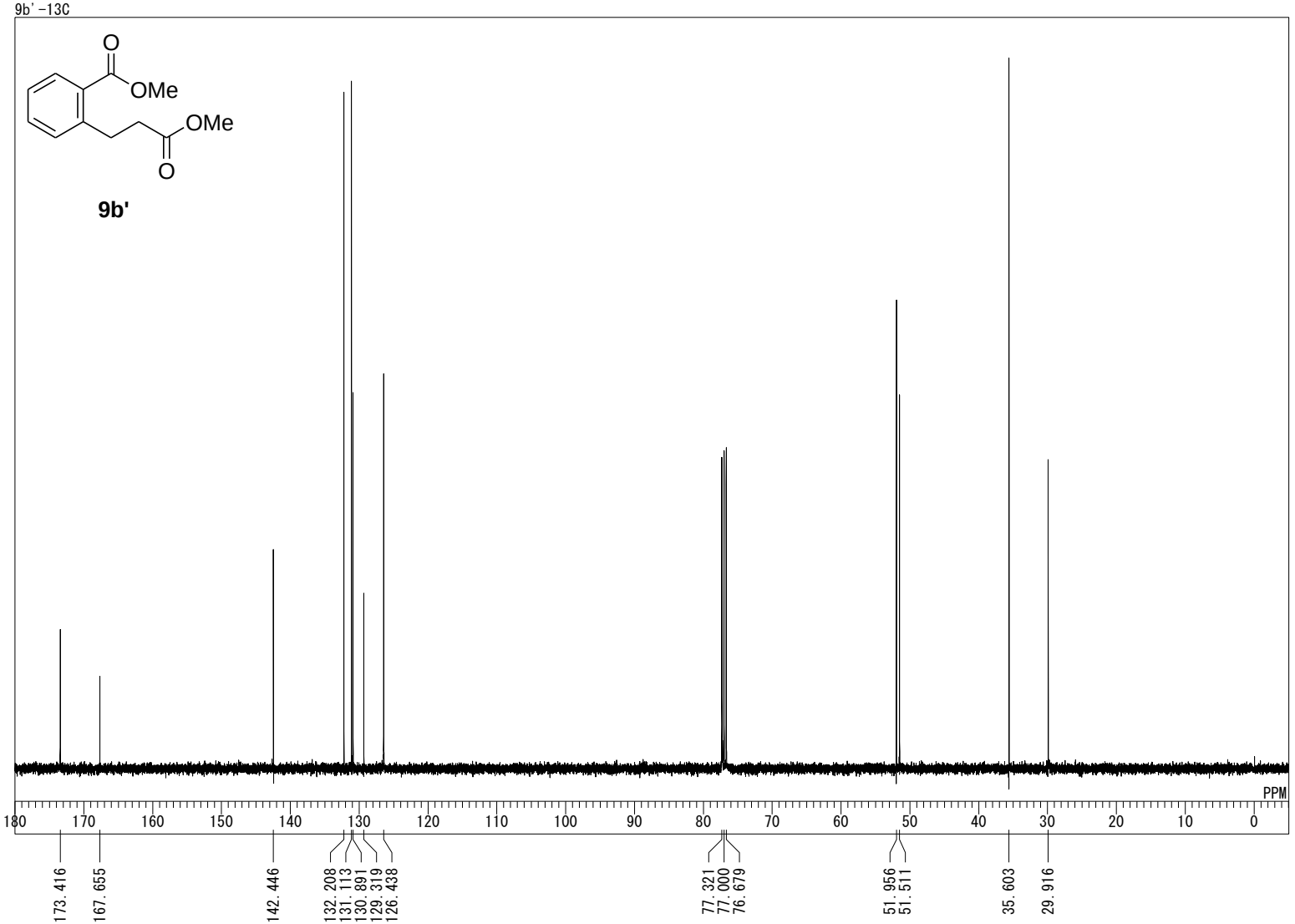
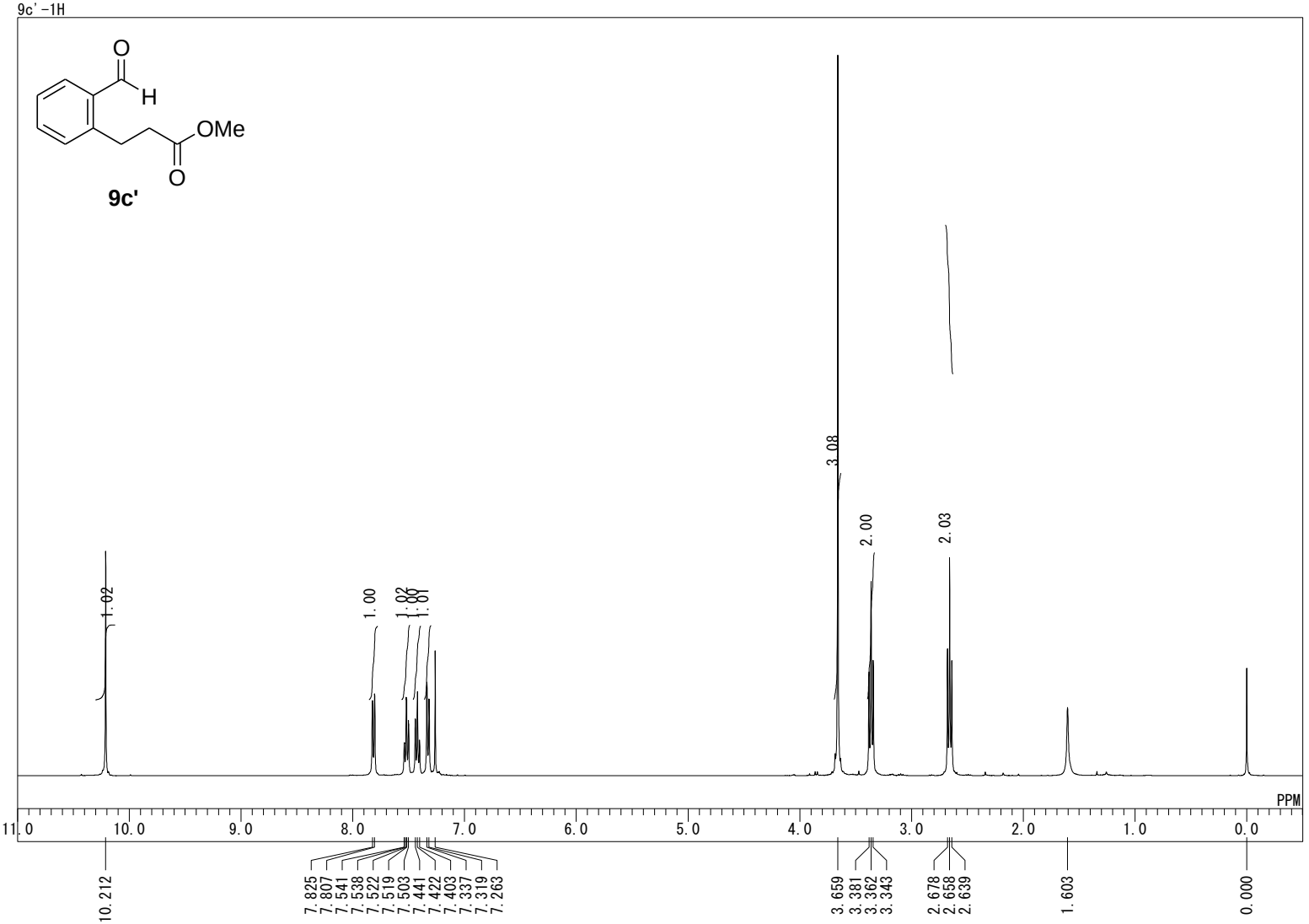
2.674
2.656
0.000


9b'-13C
O
OMe
OMe
O
9b'
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
173.416
167.655
142.446
132.208
131.113
130.891
129.319
126.438
77.321
77.000
76.679
51.956
51.511
35.603
29.916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O
H
OMe
O
9c'
1.02
1.00
1.02
1.01
1.01
3.08
2.00
2.03
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10.212
7.825
7.807
7.541
7.538
7.522
7.519
7.503
7.441
7.422
7.403
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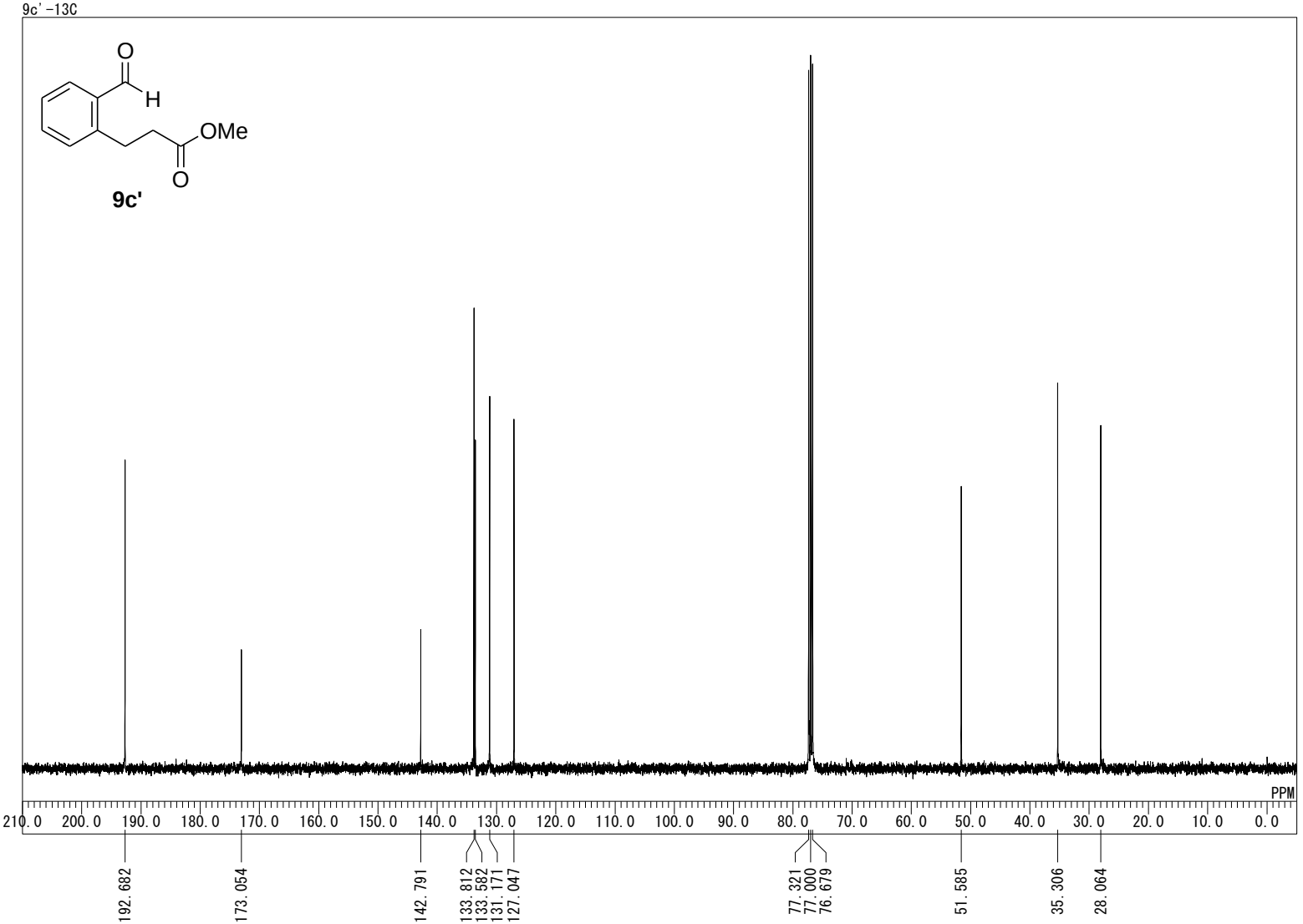
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O
H
OMe
O
9c'
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
192.682
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133.582
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127.047
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77.000
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35.306
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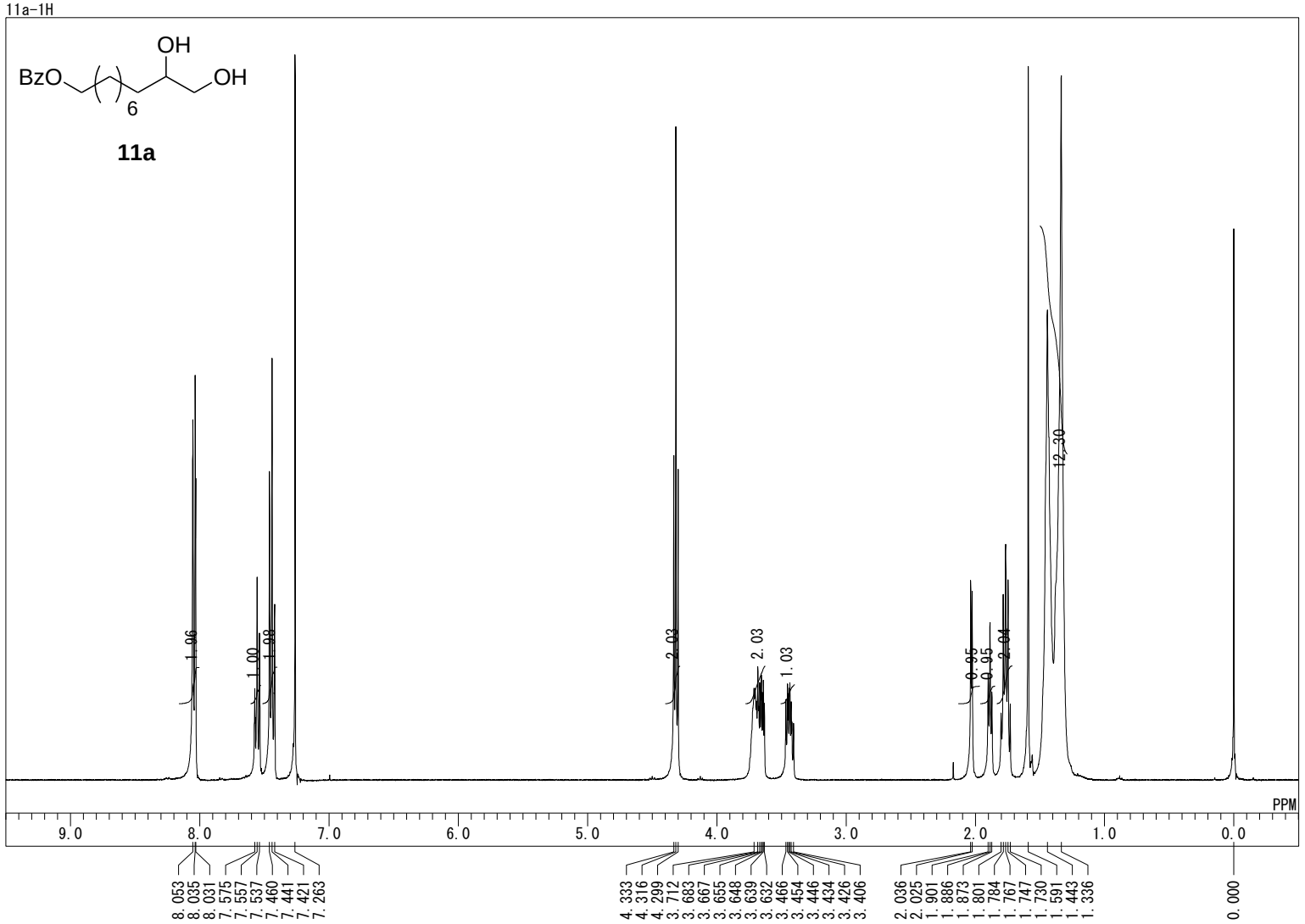
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BzO
OH
6
11a
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1.00
1.08
2.03
2.03
1.03
0.95
0.95
2.04
12.30
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.053
8.035
8.031
7.575
7.557
7.537
7.460
7.441
7.421
7.263
4.333
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4.299
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3.655
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3.639
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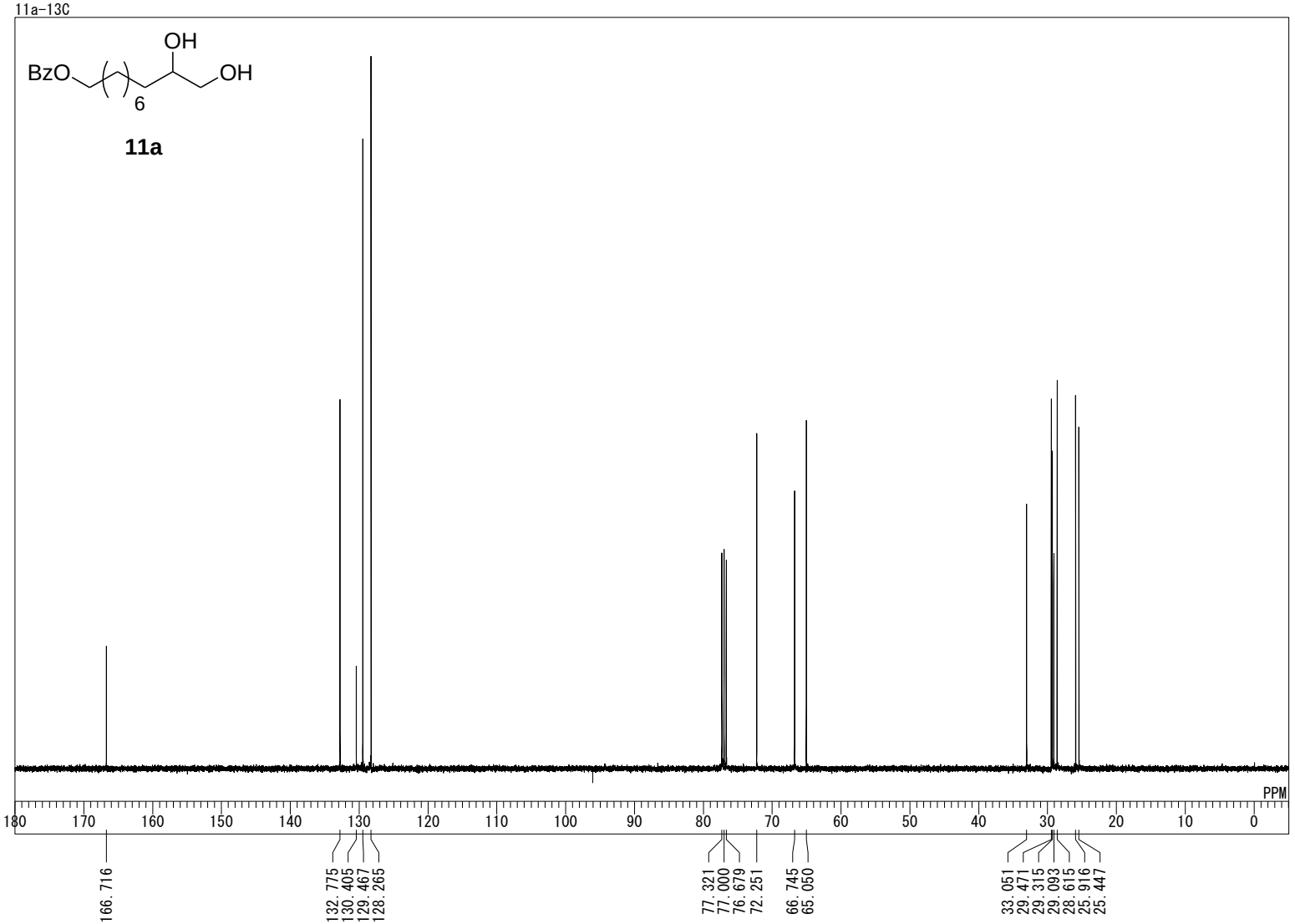
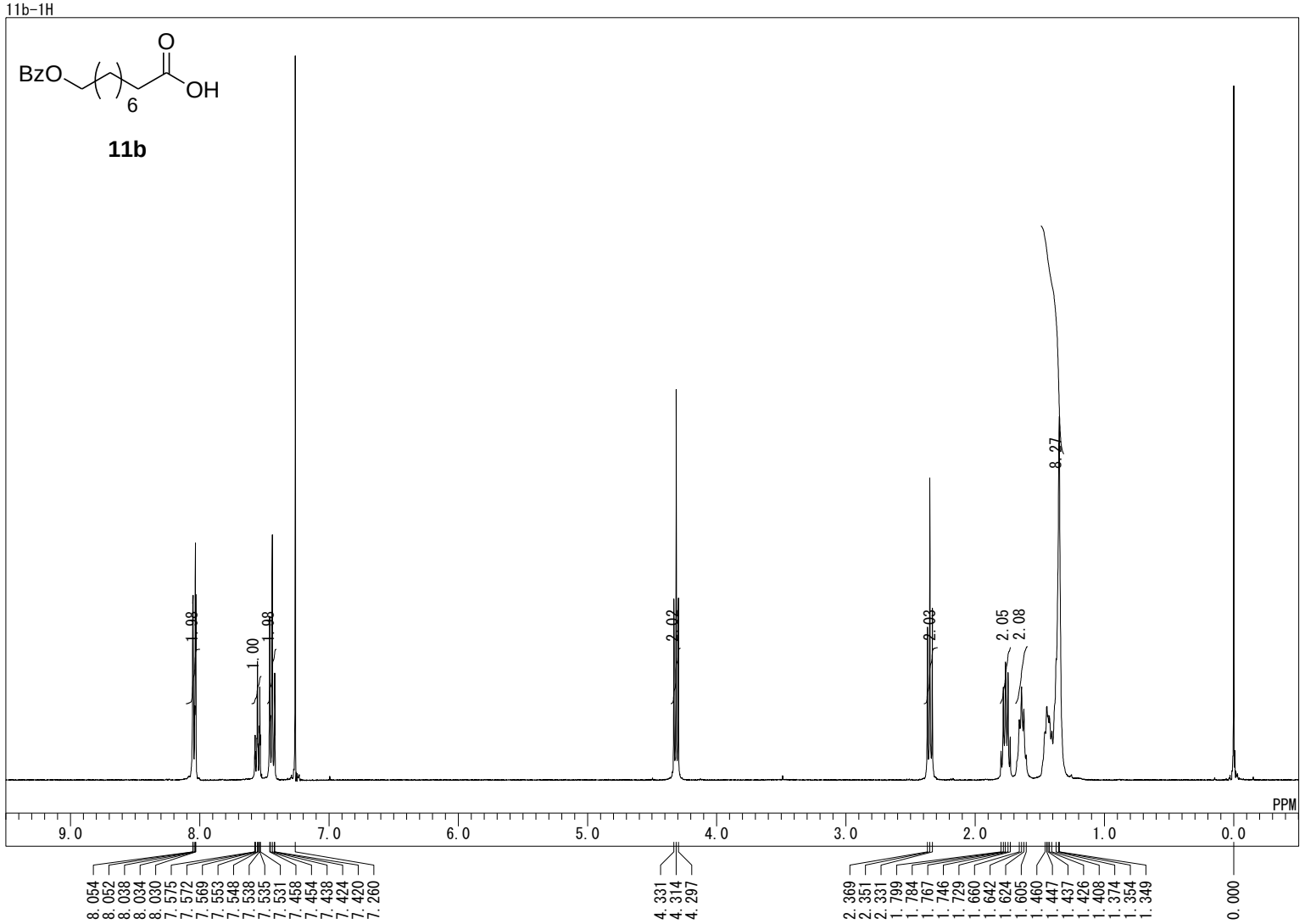
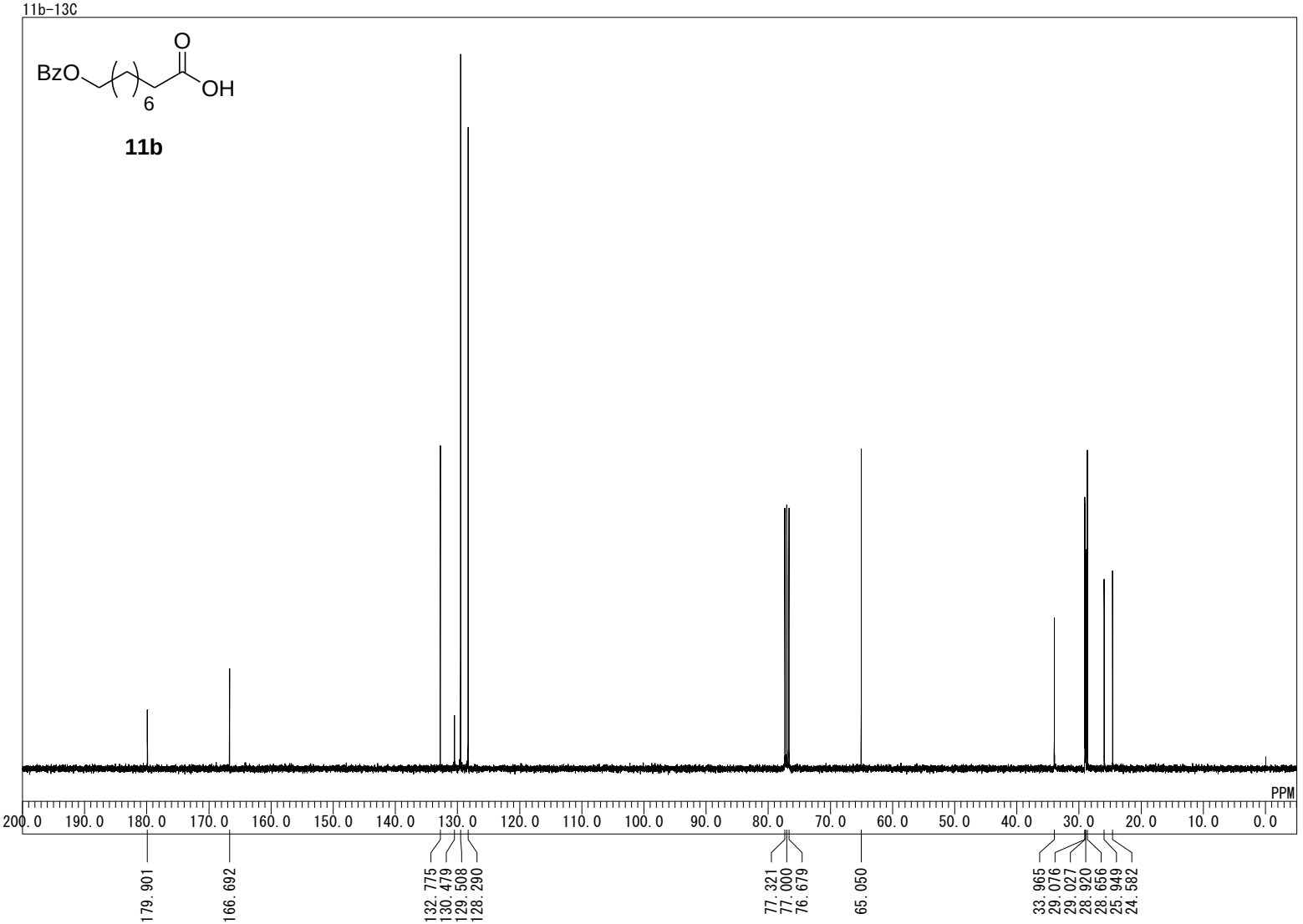
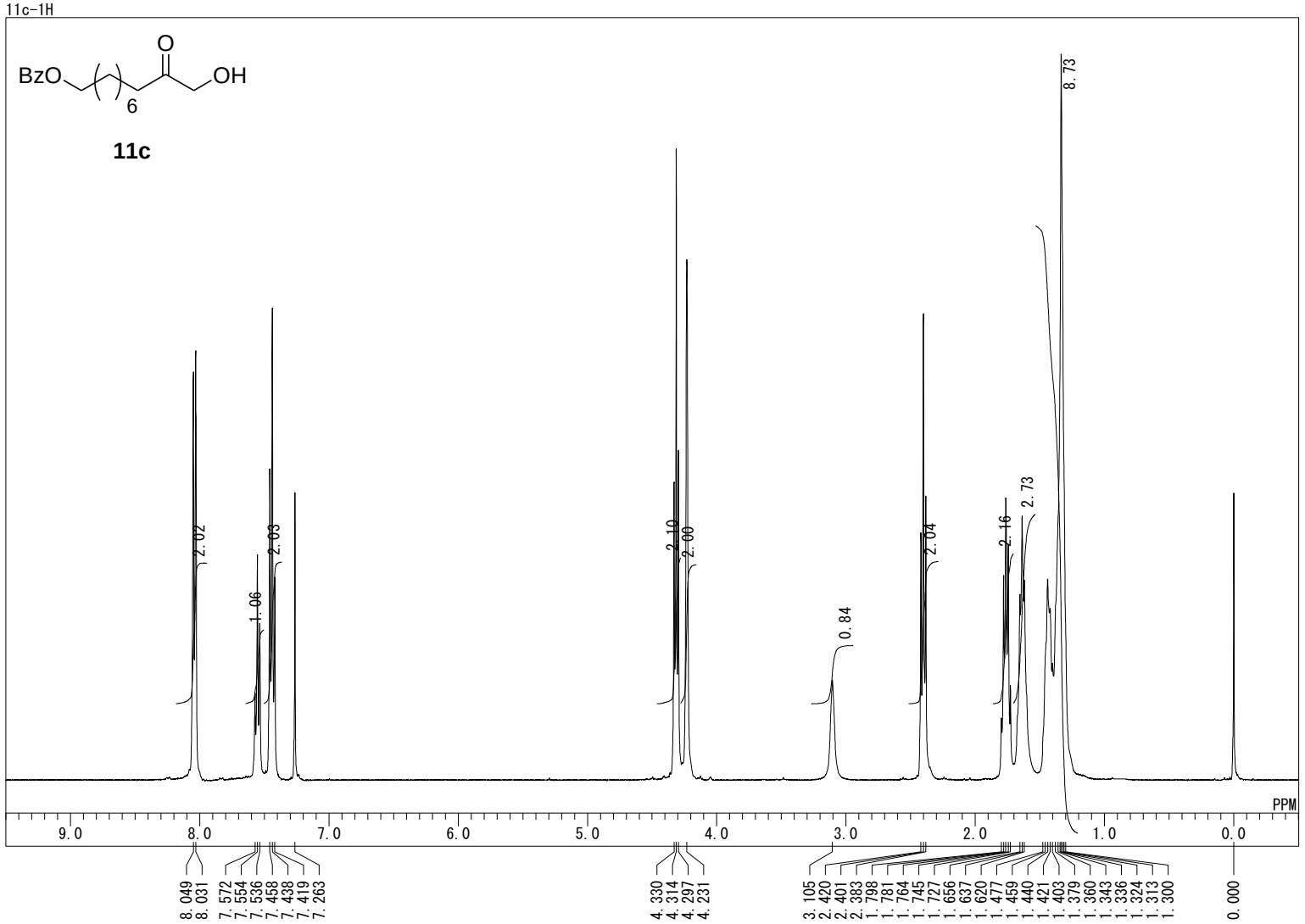
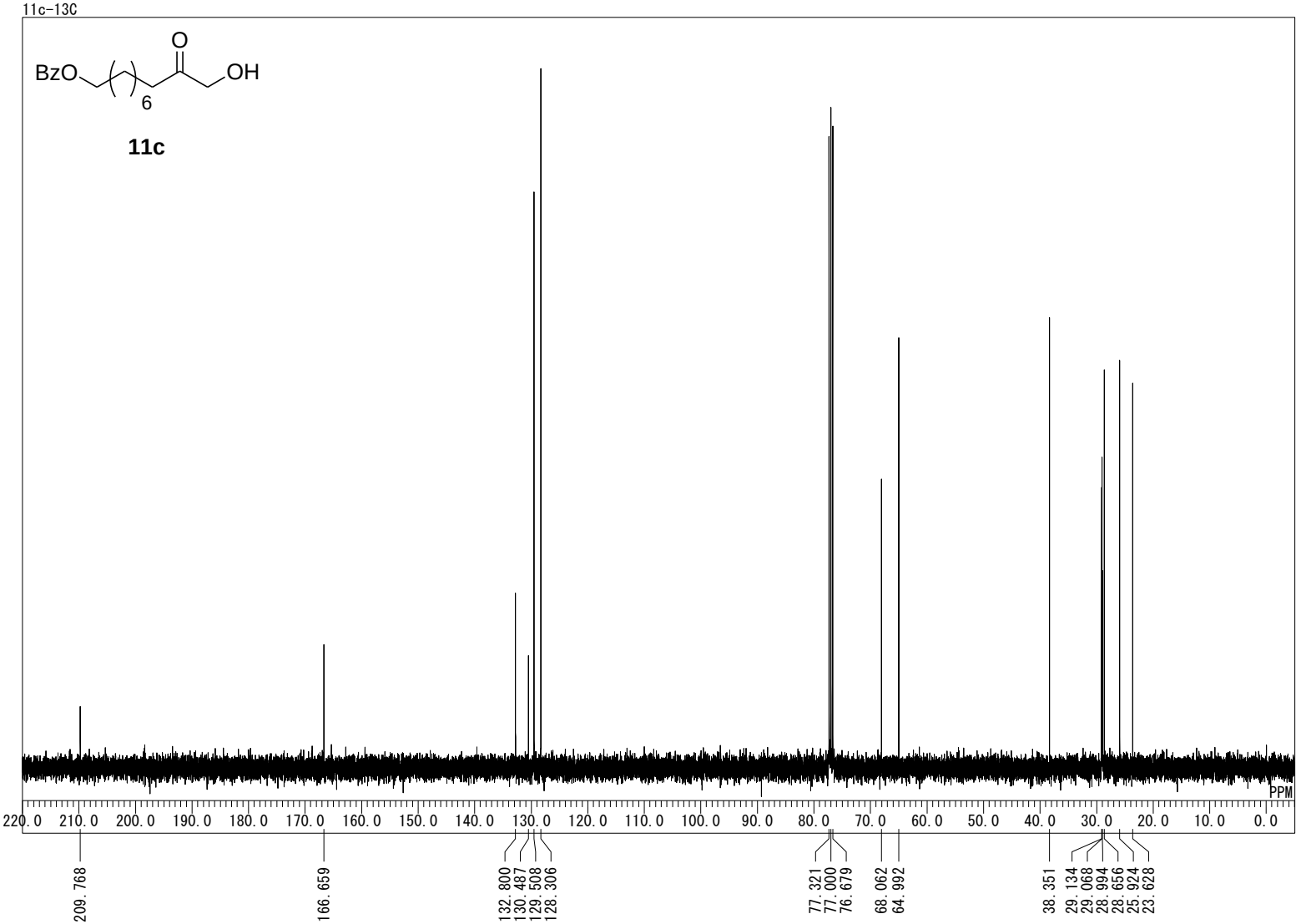
1.901
1.886
1.873
1.801
1.784
1.767
1.747
1.730
1.591
1.443
1.336
0.000

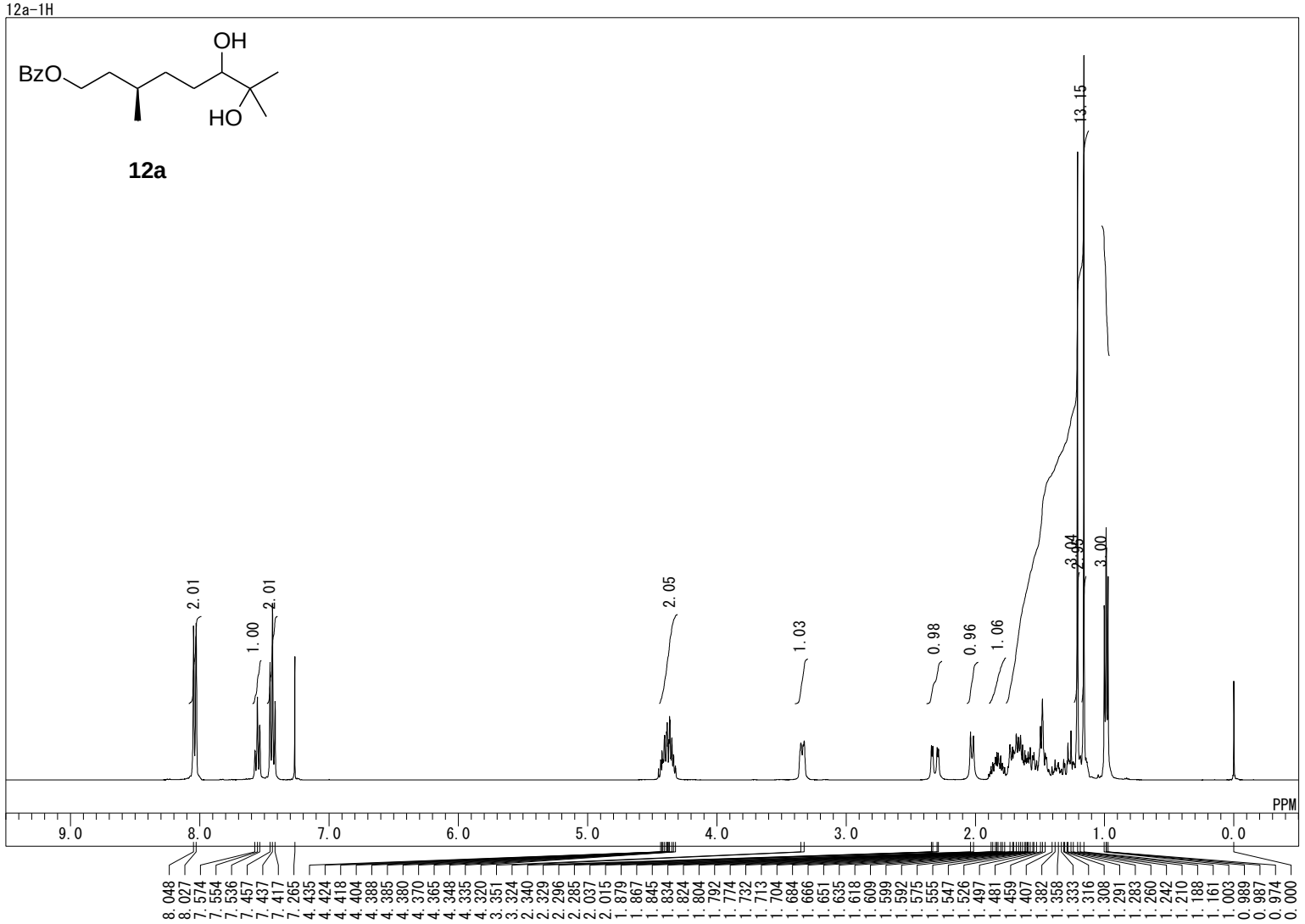

11a-13C
OH
BzO
OH
6
11a
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
166.716
132.775
130.405
129.467
128.265
77.321
77.000
76.679
72.251
66.745
65.050
33.051
29.471
29.315
29.093
28.615
25.916
25.447

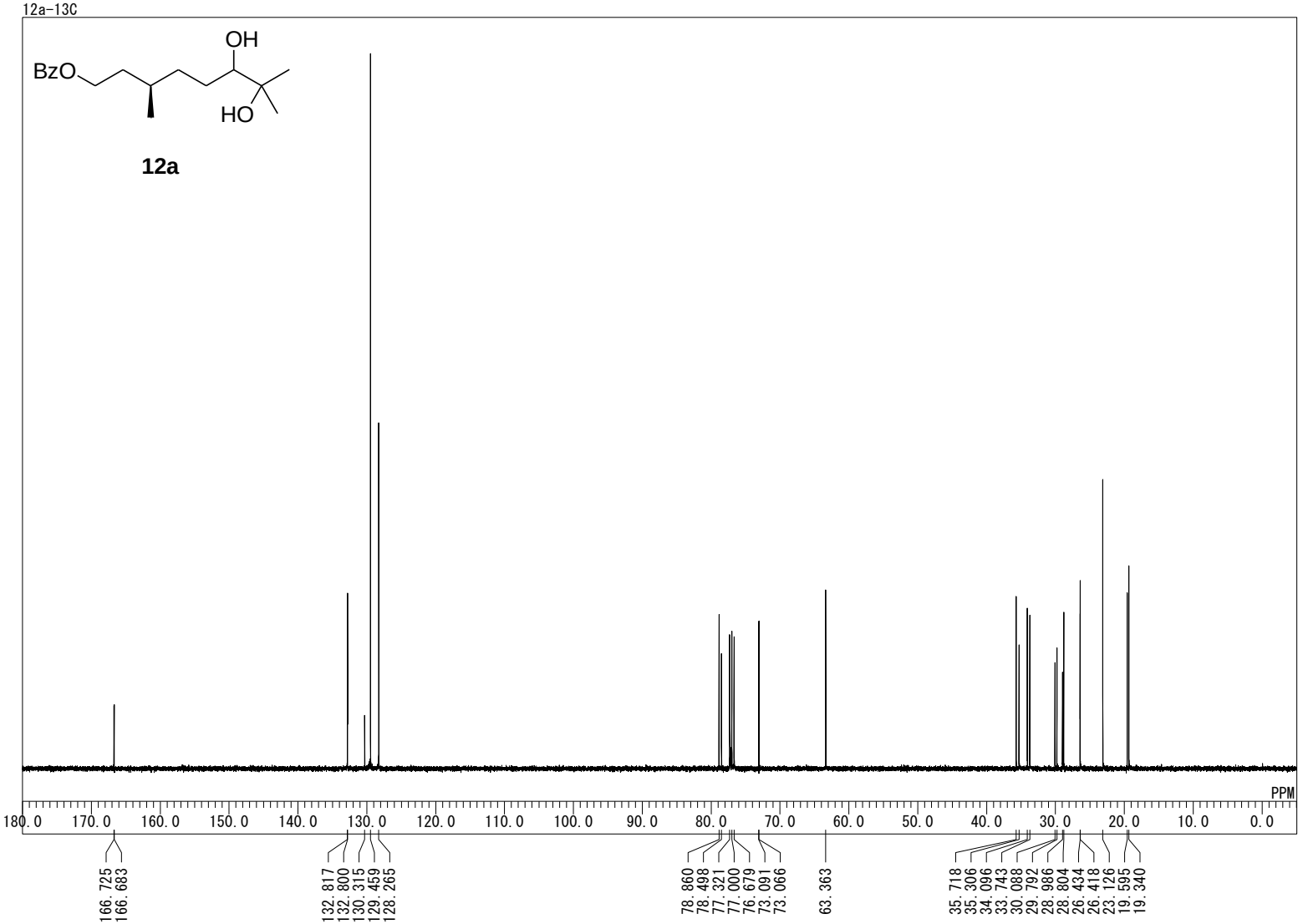

11b-1H
BzO
O
OH
6
11b
1.98
1.00
1.98
2.02
2.03
2.05
2.08
8.27
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.054
8.052
8.038
8.034
8.030
7.575
7.572
7.569
7.553
7.548
7.538
7.535
7.531
7.458
7.454
7.438
7.424
7.420
7.260
4.331
4.314
4.297
2.369
2.351
2.331
1.799
1.784
1.767
1.746
1.729
1.660
1.642
1.624
1.605
1.460
1.447
1.437
1.426
1.408
1.374
1.354
1.349
0.000

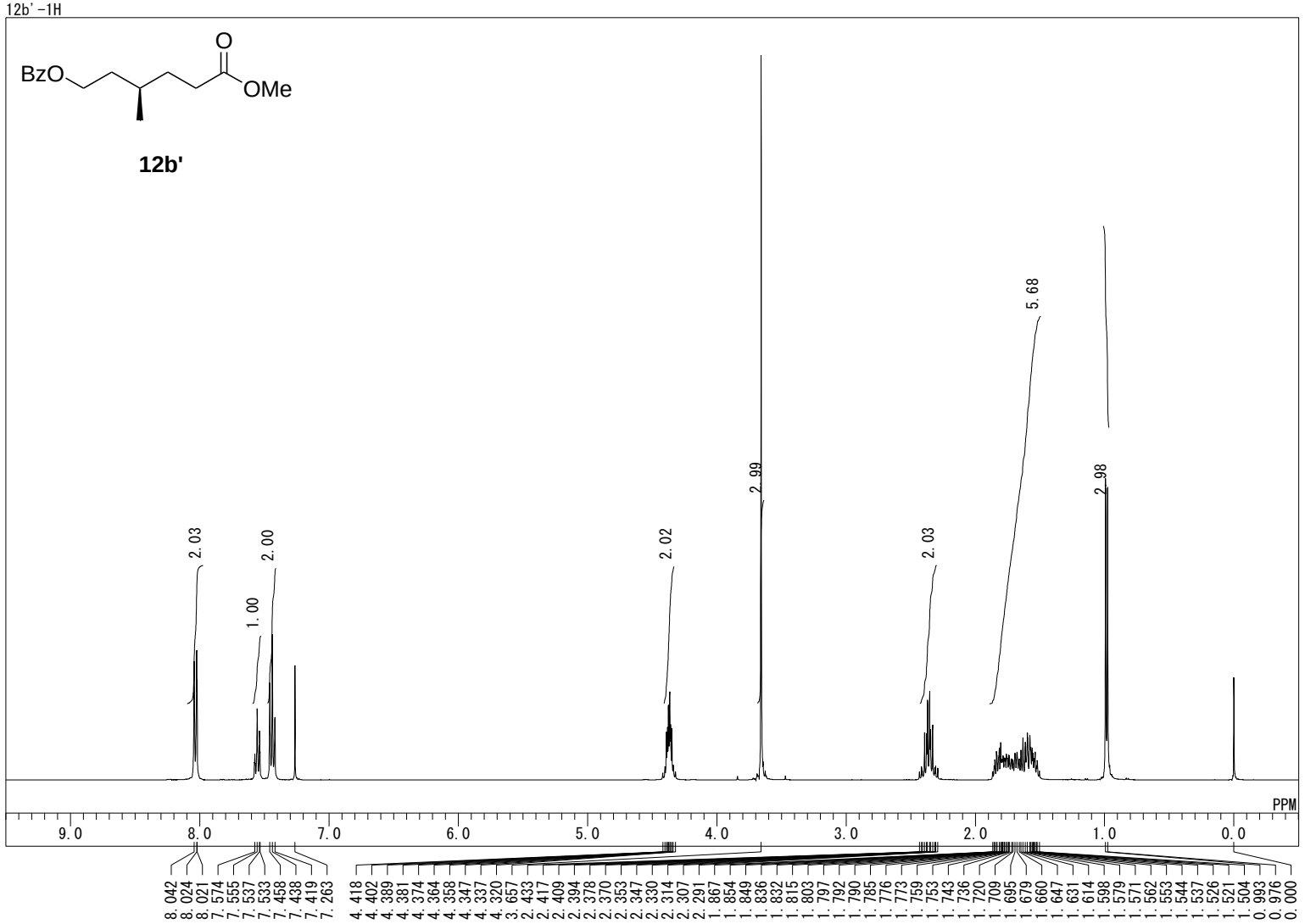

11b-13C
BzO
O
OH
6
11b
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
179.901
166.692
132.775
130.479
129.508
128.290
77.321
77.000
76.679
65.050
33.965
29.076
29.027
28.920
28.656
25.949
24.582

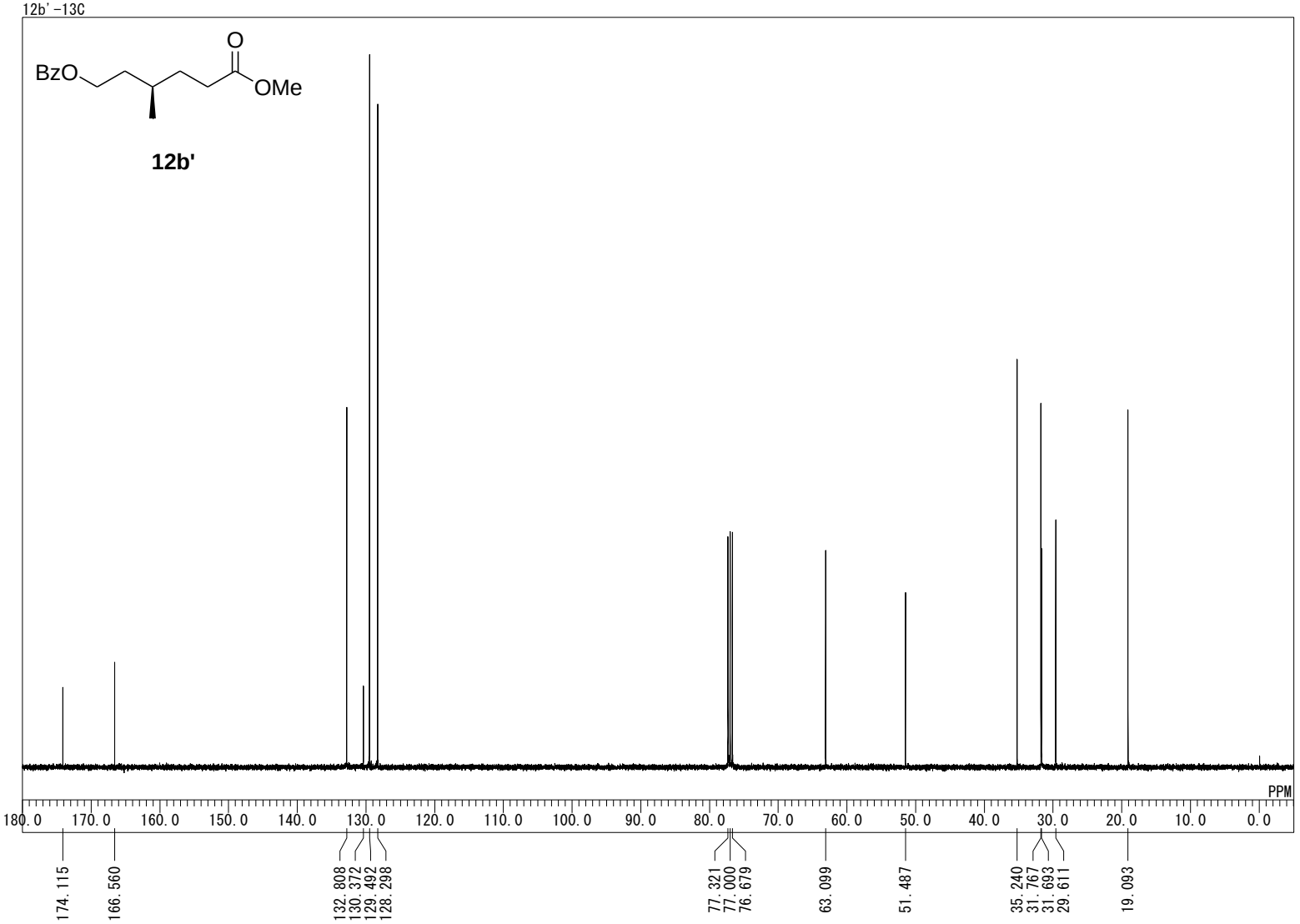

11c-1H
BzO
O
OH
6
11c
2.02
1.06
2.03
2.10
2.00
0.84
2.04
2.16
2.73
8.73
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.049
8.031
7.572
7.554
7.536
7.458
7.438
7.419
7.263
4.330
4.314
4.297
4.231
3.105
2.420
2.401
2.383
1.798
1.781
1.764
1.745
1.727
1.656
1.637
1.620
1.477
1.459
1.440
1.421
1.403
1.379
1.360
1.343
1.336
1.324
1.313
1.300
0.000

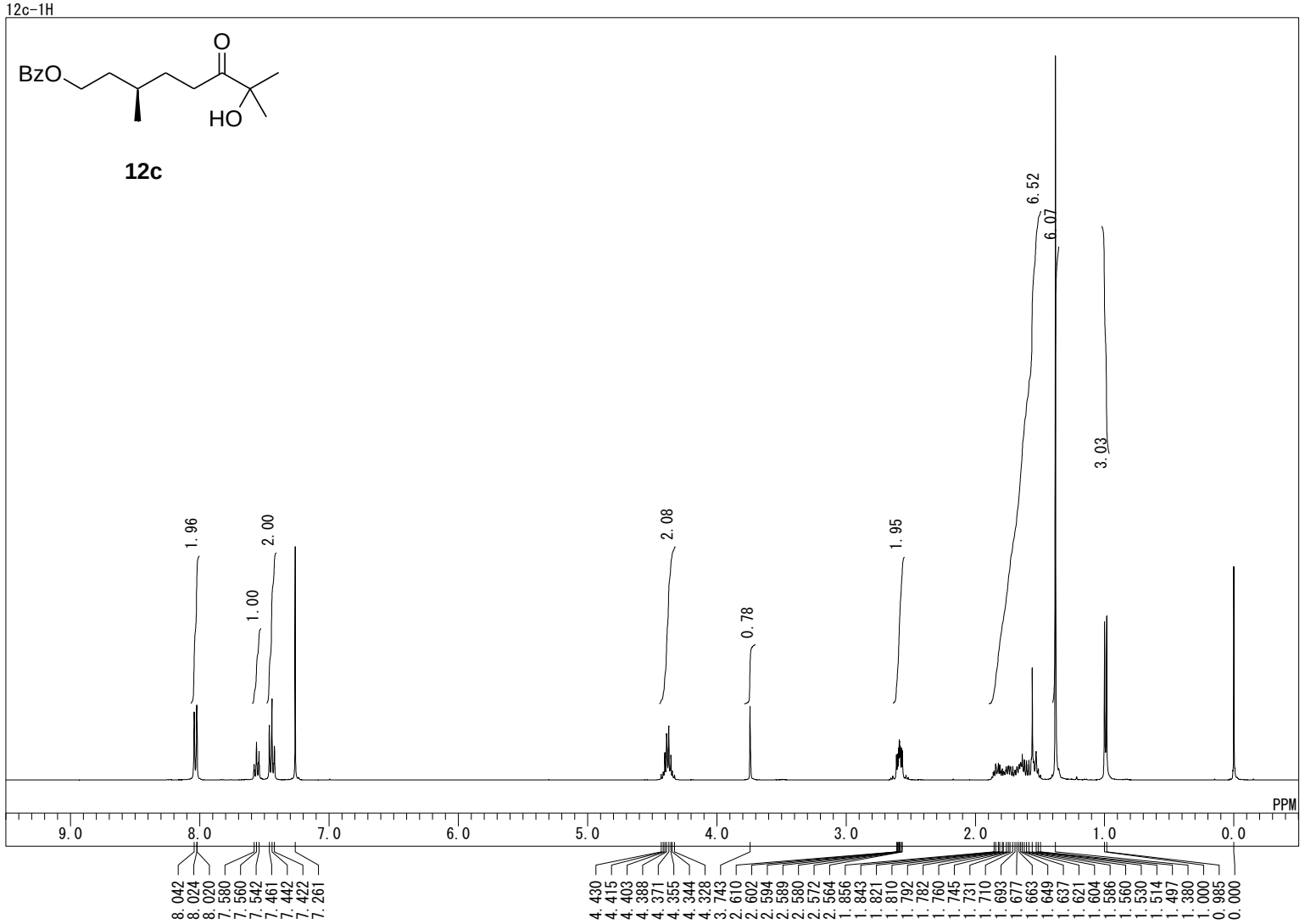

11c-13C
O
BzO
OH
6
11c
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
209.768
166.659
132.800
130.487
129.508
128.306
77.321
77.000
76.679
68.062
64.992
38.351
29.134
29.068
28.994
28.656
25.924
23.628

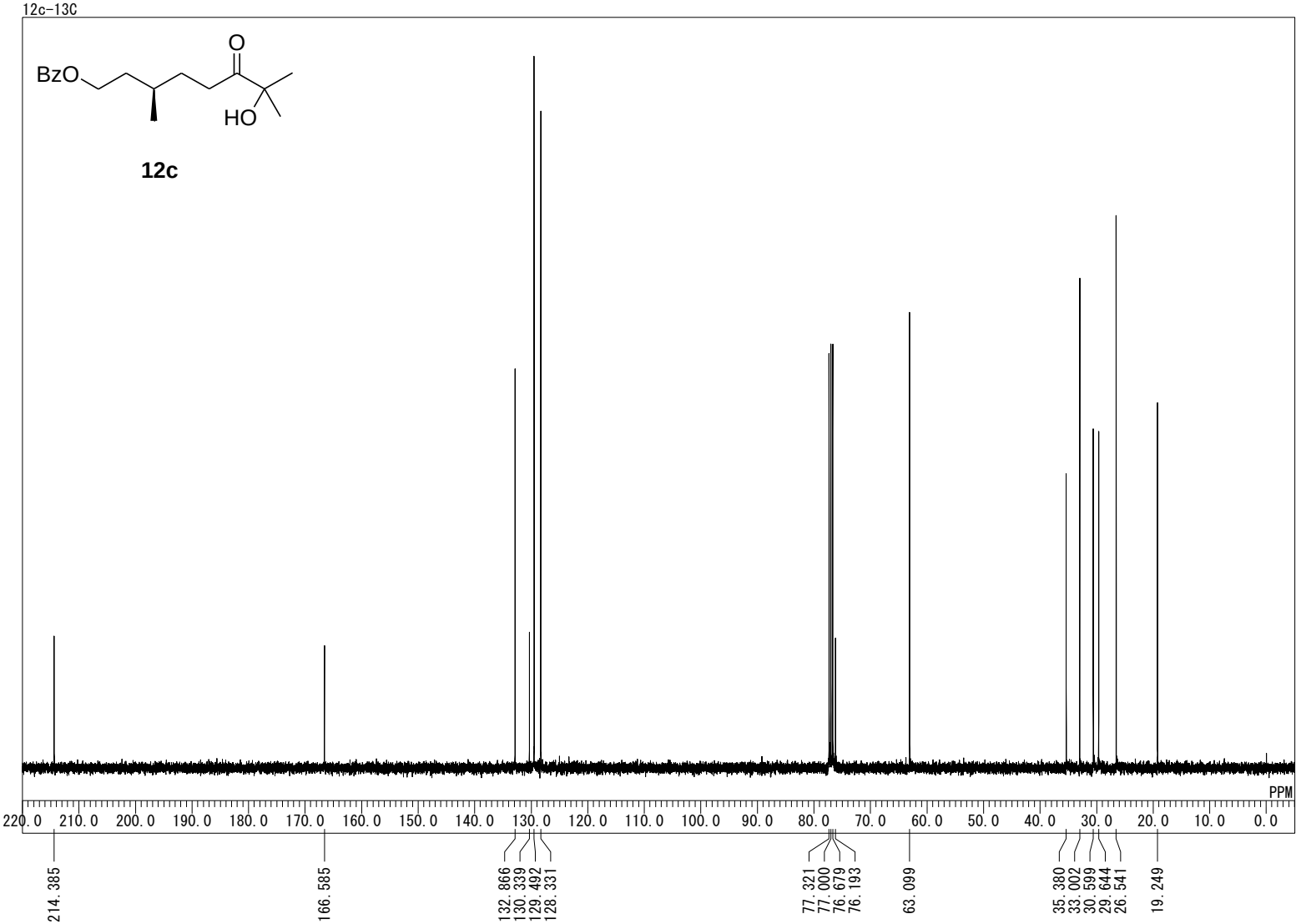

12a-1H
OH
BzO
HO
12a
13.15
3.04
2.99
3.00
2.01
1.00
2.01
2.05
1.03
0.98
0.96
1.06
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

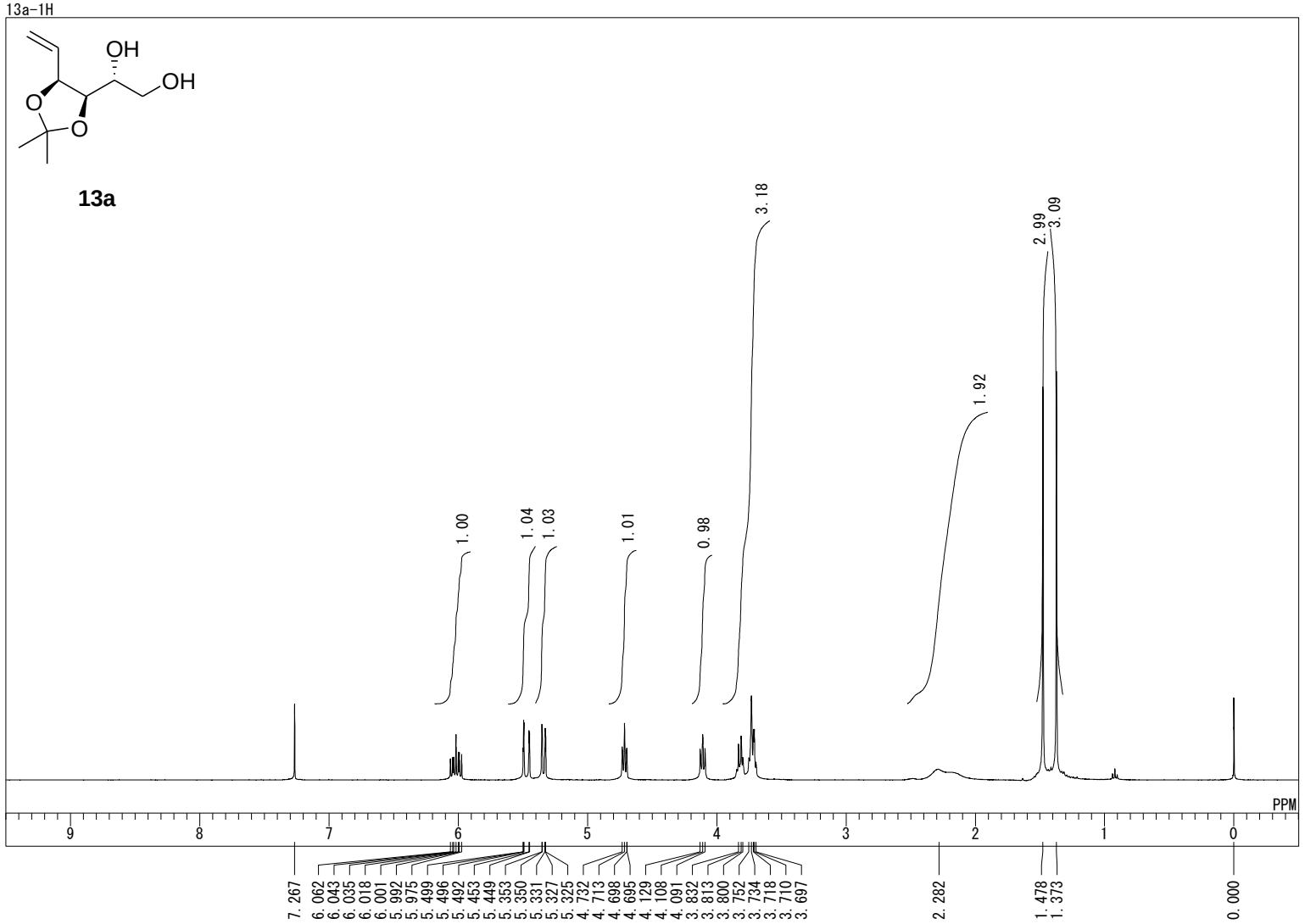

12a-13C
OH
BzO
HO
12a
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
166.725
166.683
132.817
132.800
130.315
129.459
128.265
78.860
78.498
77.321
77.000
76.679
73.091
73.066
63.363
35.718
35.306
34.096
33.743
30.088
29.792
28.986
28.804
26.434
26.418
23.126
19.595
19.340

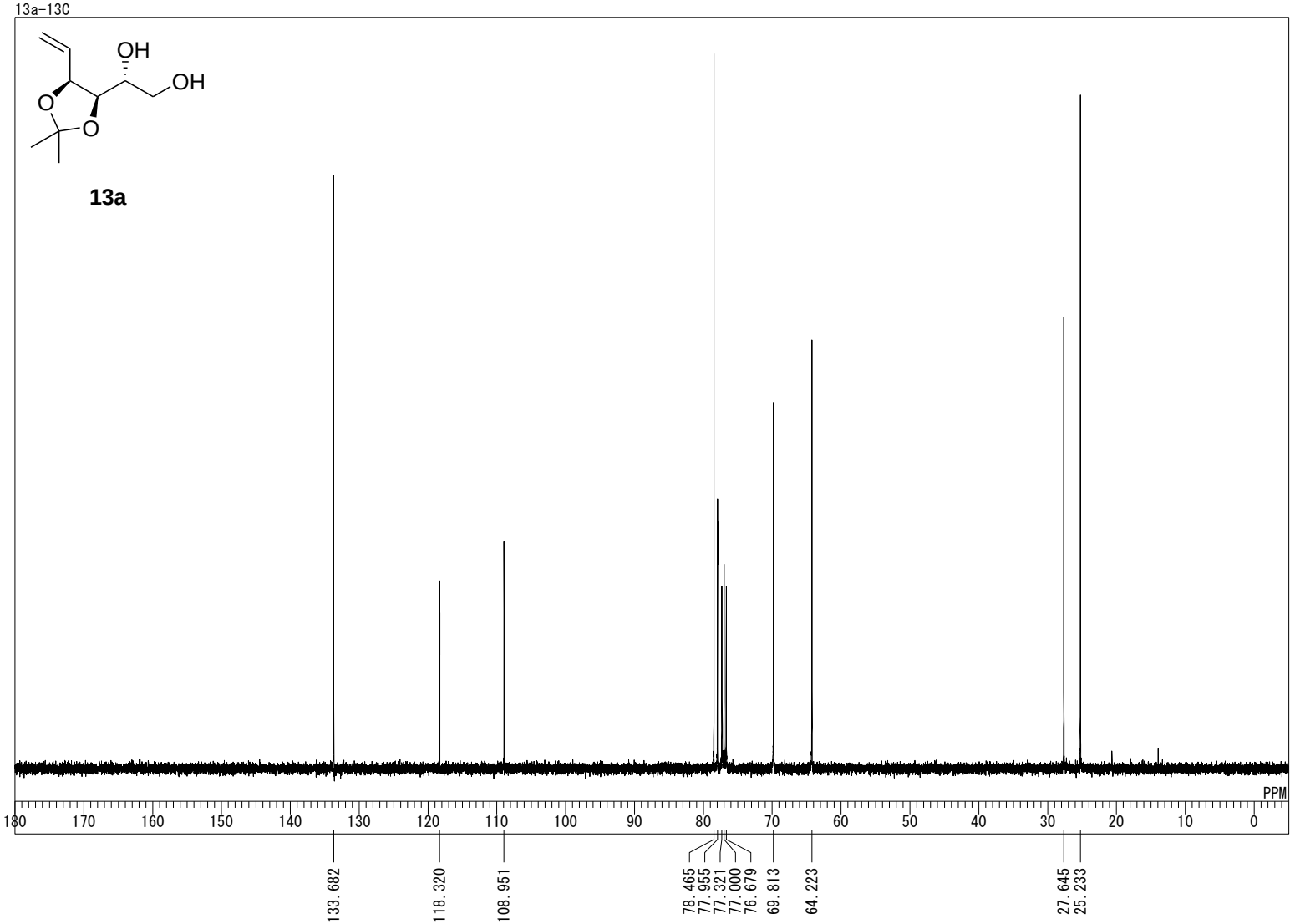

12b'-1H
BzO
O
OMe
12b'
2.03
2.00
1.00
2.02
2.99
2.03
5.68
2.98
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.042
8.024
8.021
7.574
7.555
7.537
7.533
7.458
7.438
7.419
7.263
4.418
4.402
4.389
4.381
4.374
4.364
4.358
4.347
4.337
4.320
3.657
2.433
2.417
2.409
2.394
2.378
2.370
2.353
2.347
2.330
2.314
2.307
2.291
1.867
1.854
1.849
1.836
1.832
1.815
1.803
1.797
1.792
1.790
1.785
1.776
1.773
1.759
1.753
1.743
1.736
1.720
1.709
1.695
1.679
1.660
1.647
1.631
1.614
1.598
1.579
1.571
1.562
1.553
1.544
1.537
1.526
1.521
1.504
0.993
0.976
0.000

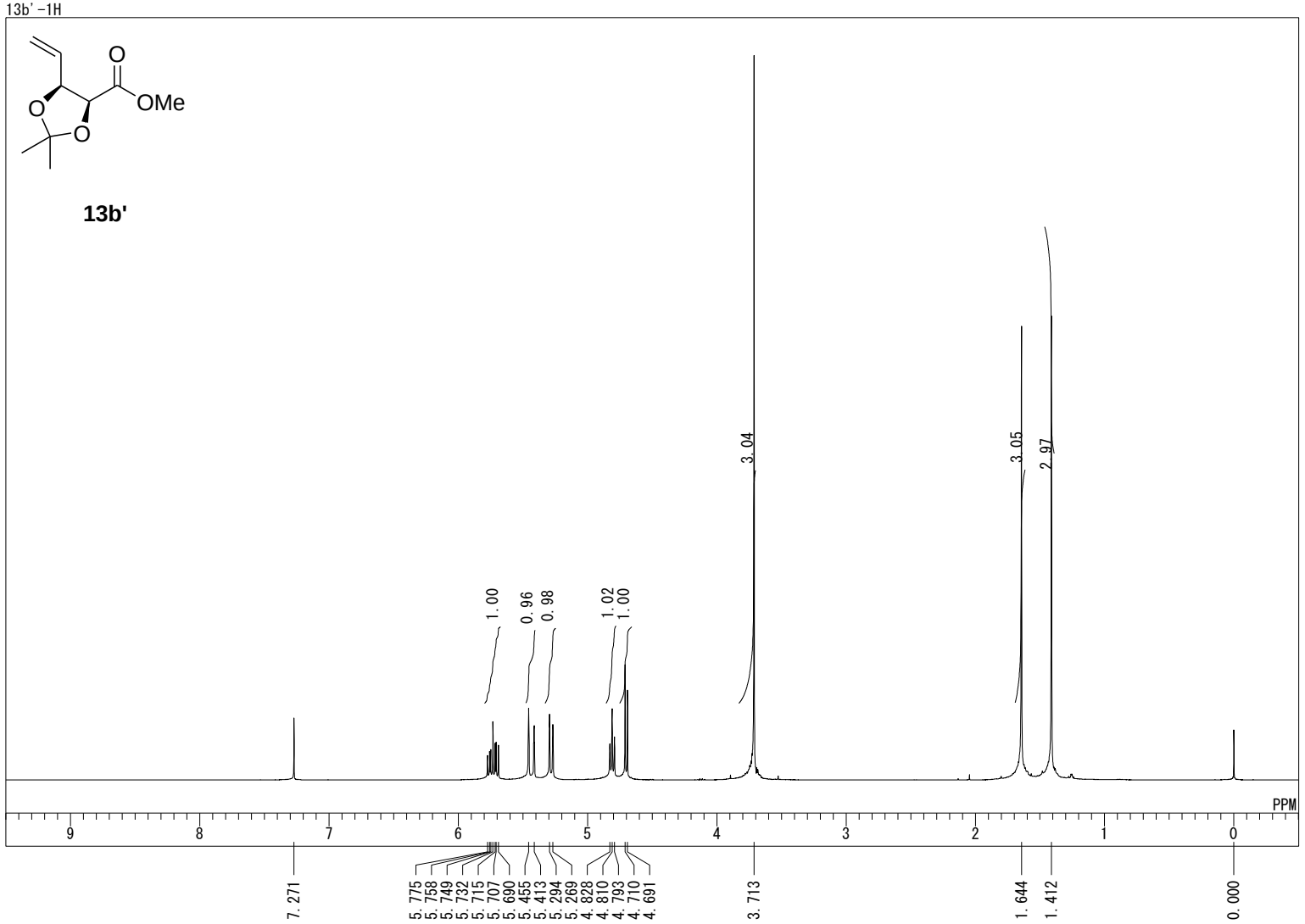

12b'-13C
BzO
O
OMe
12b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
174.115
166.560
132.808
130.372
129.492
128.298
77.321
77.000
76.679
63.099
51.487
35.240
31.767
31.693
29.611
19.093

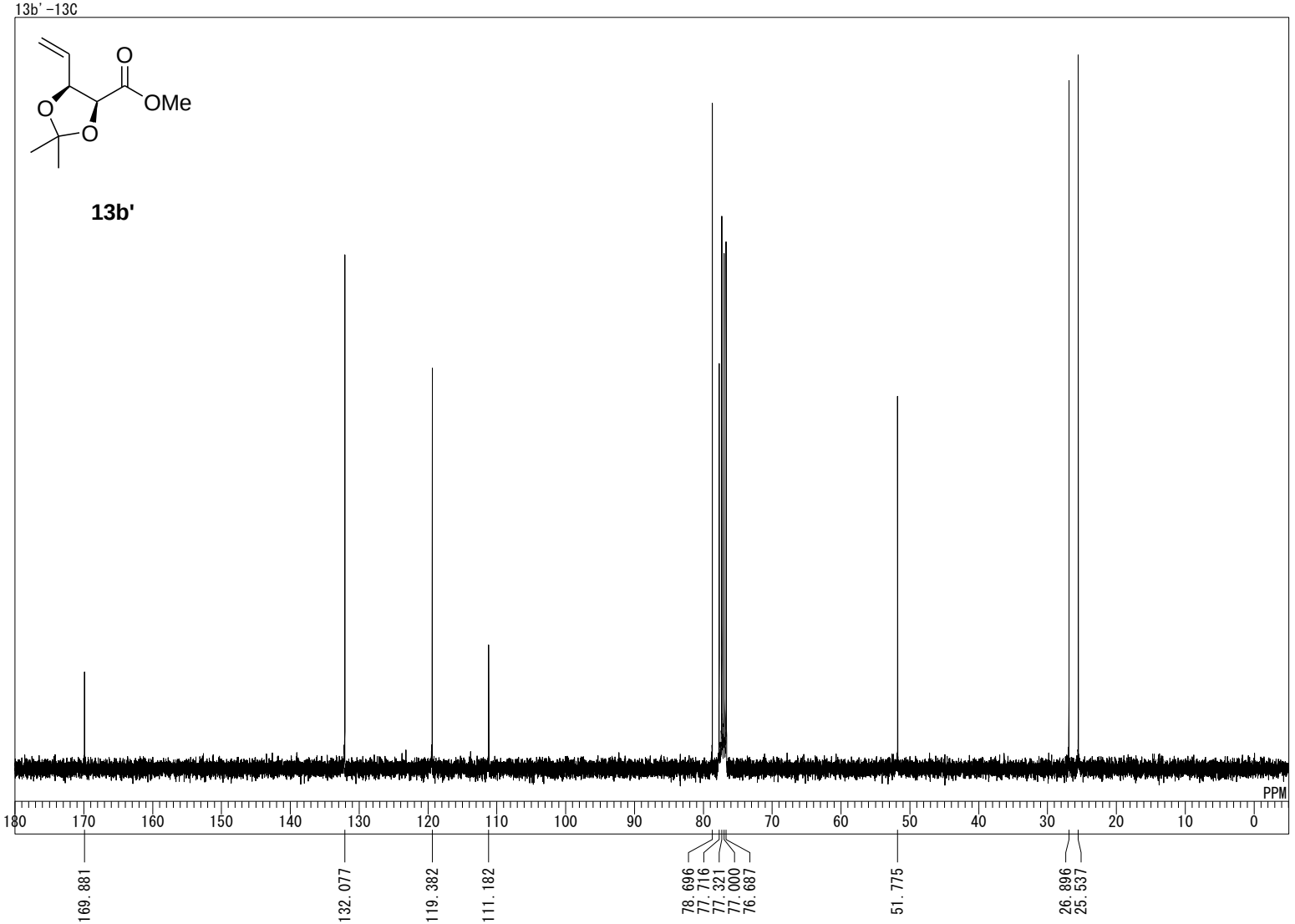

12c-1H
BzO
O
HO
12c
6.52
6.07
3.03
1.96
1.00
2.00
2.08
0.78
1.95
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.042
8.024
8.020
7.580
7.560
7.542
7.461
7.442
7.422
7.261
4.430
4.415
4.403
4.388
4.371
4.355
4.344
4.328
3.743
2.610
2.602
2.594
2.589
2.580
2.572
2.564
1.856
1.843
1.821
1.810
1.792
1.782
1.760
1.745
1.731
1.710
1.693
1.677
1.663
1.649
1.637
1.621
1.604
1.586
1.560
1.530
1.514
1.497
1.380
1.000
0.985
0.000

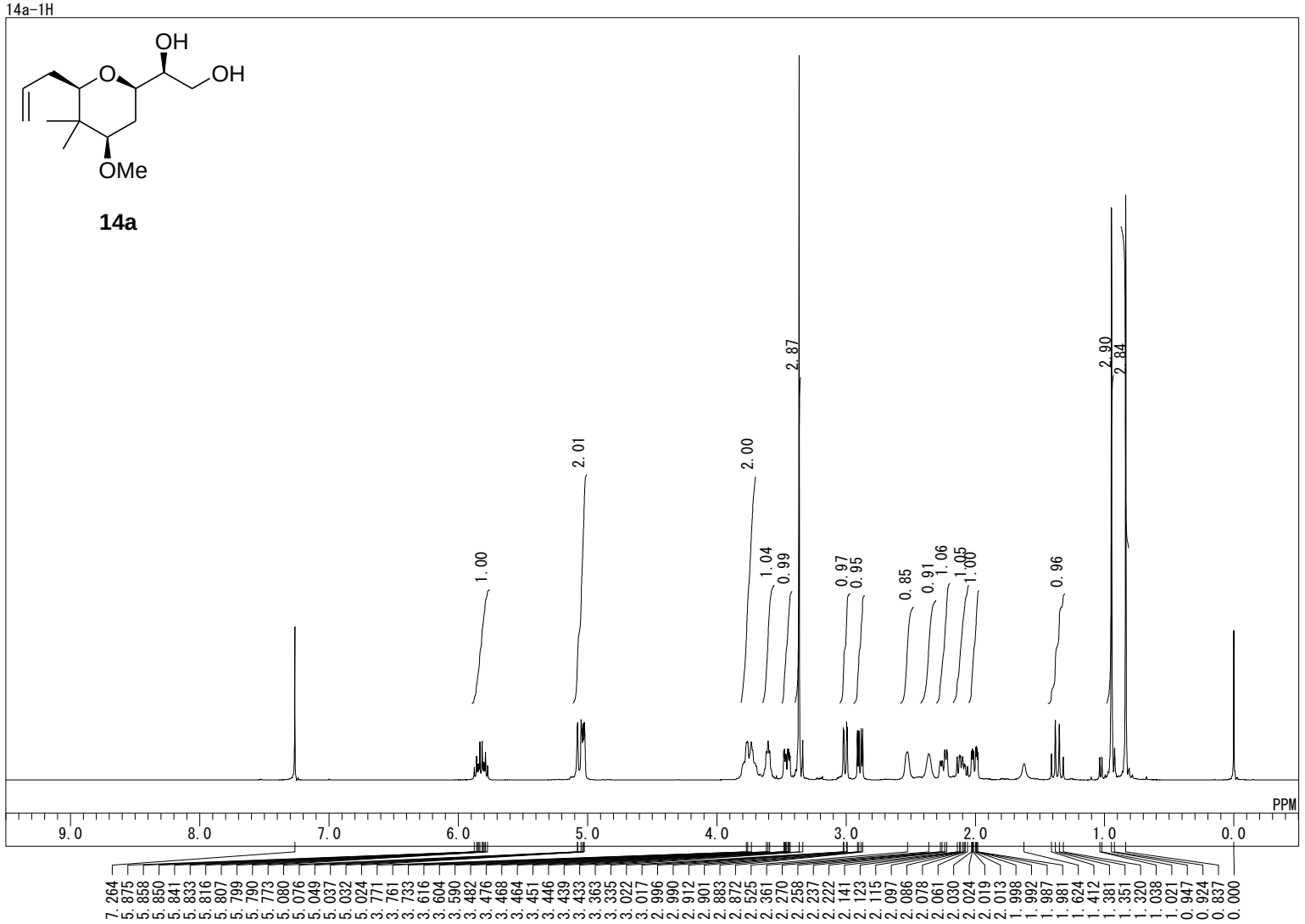

12c-13C
BzO
O
HO
12c
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
214.385
166.585
132.866
130.339
129.492
128.331
77.321
77.000
76.679
76.193
63.099
35.380
33.002
30.599
29.644
26.541
19.249

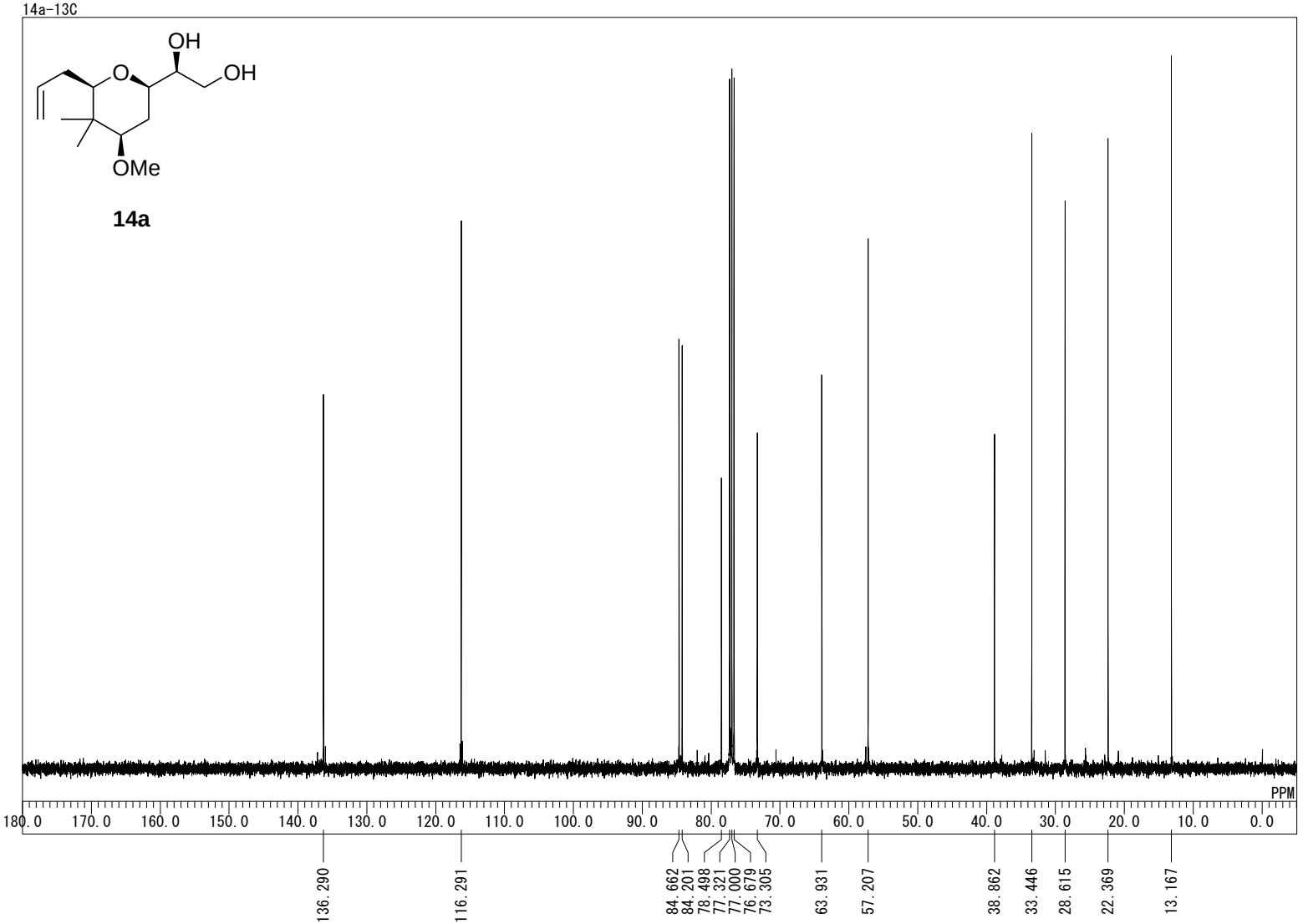

13a-1H
OH
OH
O
O
13a
3.18
2.99
3.09
1.92
1.00
1.04
1.03
1.01
0.98
PPM
9
8
7
6
5
4
3
2
1
0
7.267
6.062
6.043
6.035
6.018
6.001
5.992
5.975
5.499
5.496
5.492
5.453
5.449
5.353
5.350
5.331
5.327
5.325
4.732
4.713
4.698
4.695
4.129
4.108
4.091
3.832
3.813
3.800
3.752
3.734
3.718
3.710
3.697
2.282
1.478
1.373
0.000

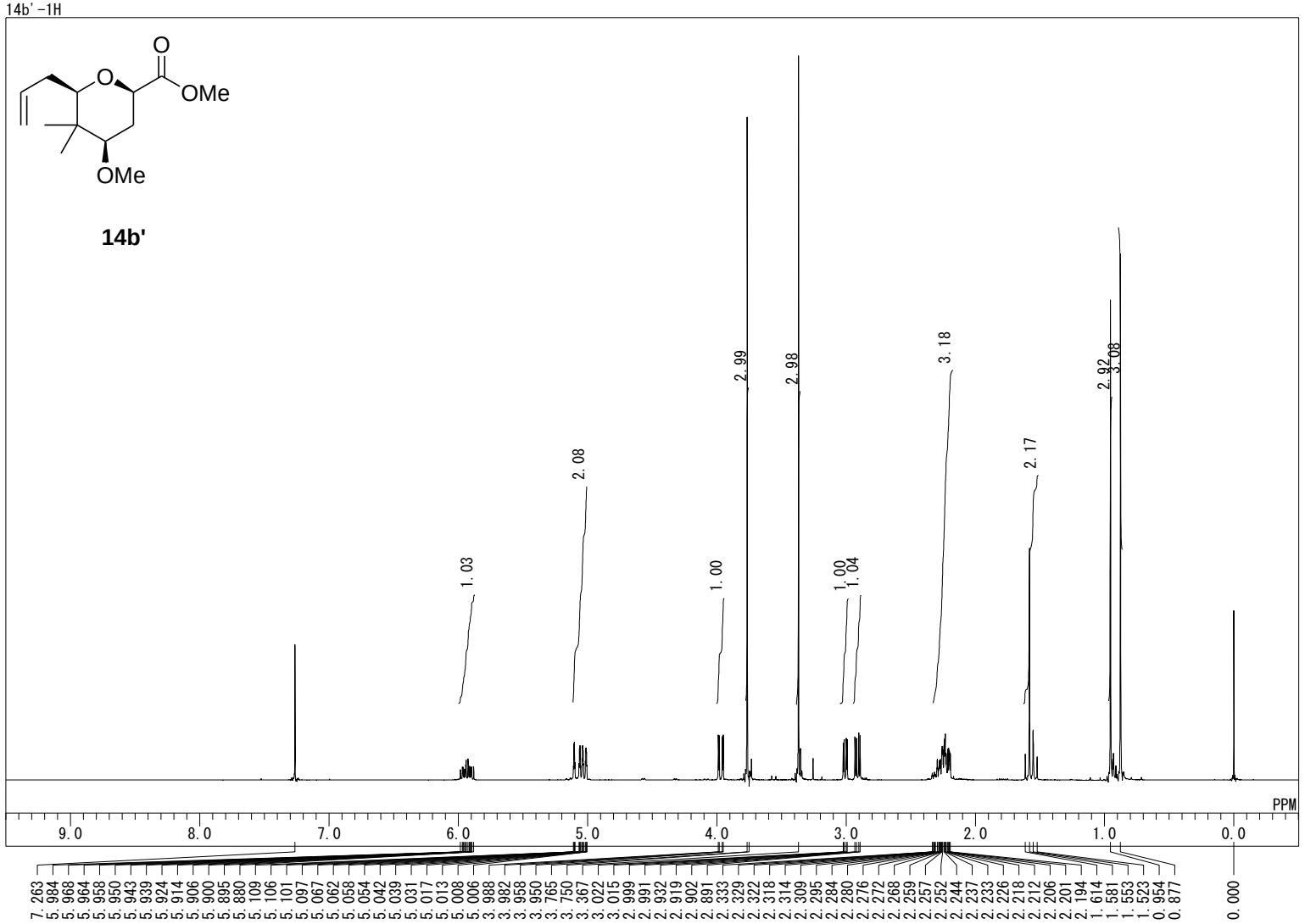

13a-13C
OH
OH
O
O
13a
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
133.682
118.320
108.951
78.465
77.955
77.321
77.000
76.679
69.813
64.223
27.645
25.233

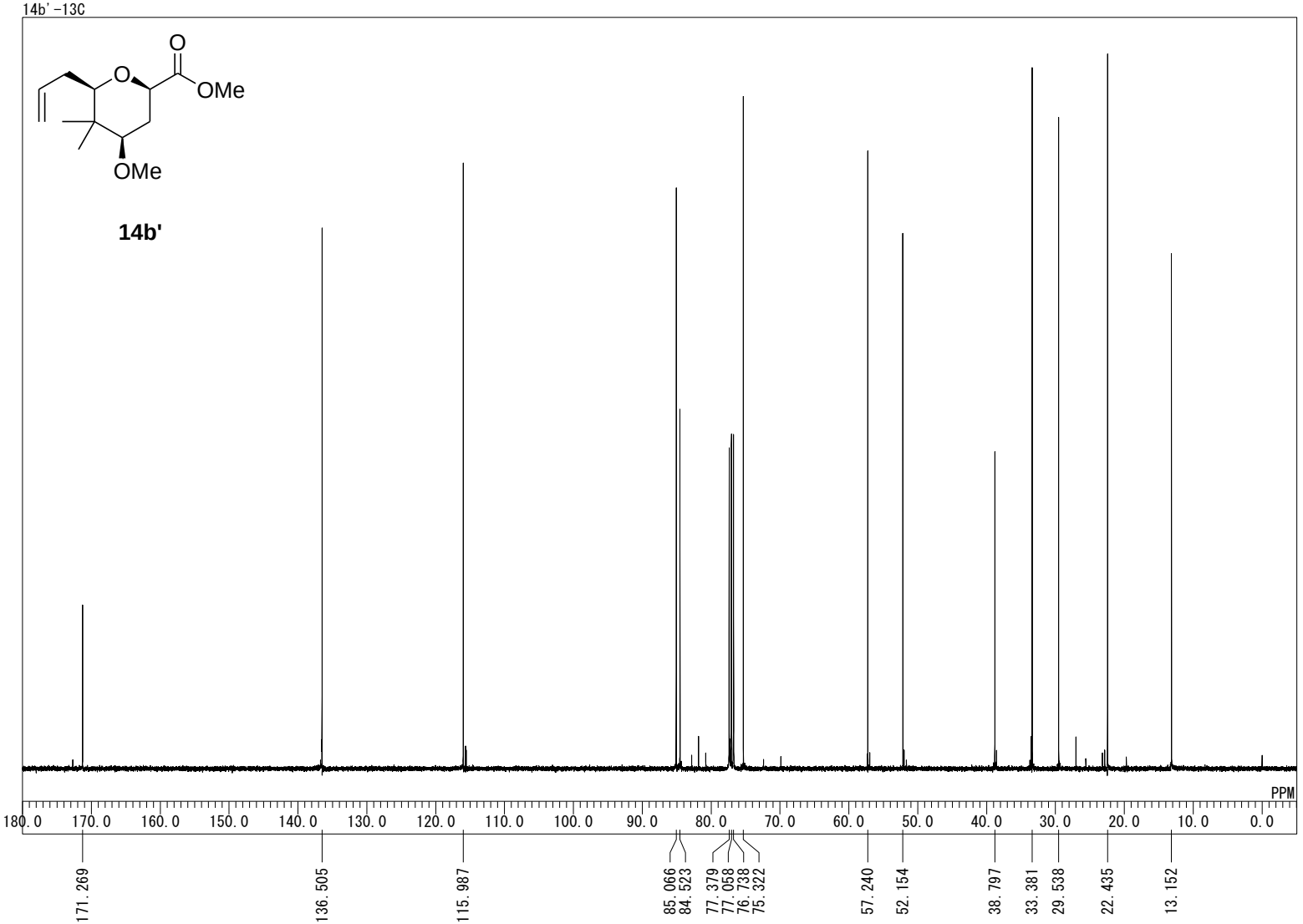

13b'-1H
O
OMe
O
O
13b'
1.00
0.96
0.98
1.02
1.00
3.04
3.05
2.97
PPM
9
8
7
6
5
4
3
2
1
0
7.271
5.775
5.758
5.749
5.732
5.715
5.707
5.690
5.455
5.413
5.294
5.269
4.828
4.810
4.793
4.710
4.691
3.713
1.644
1.412
0.000

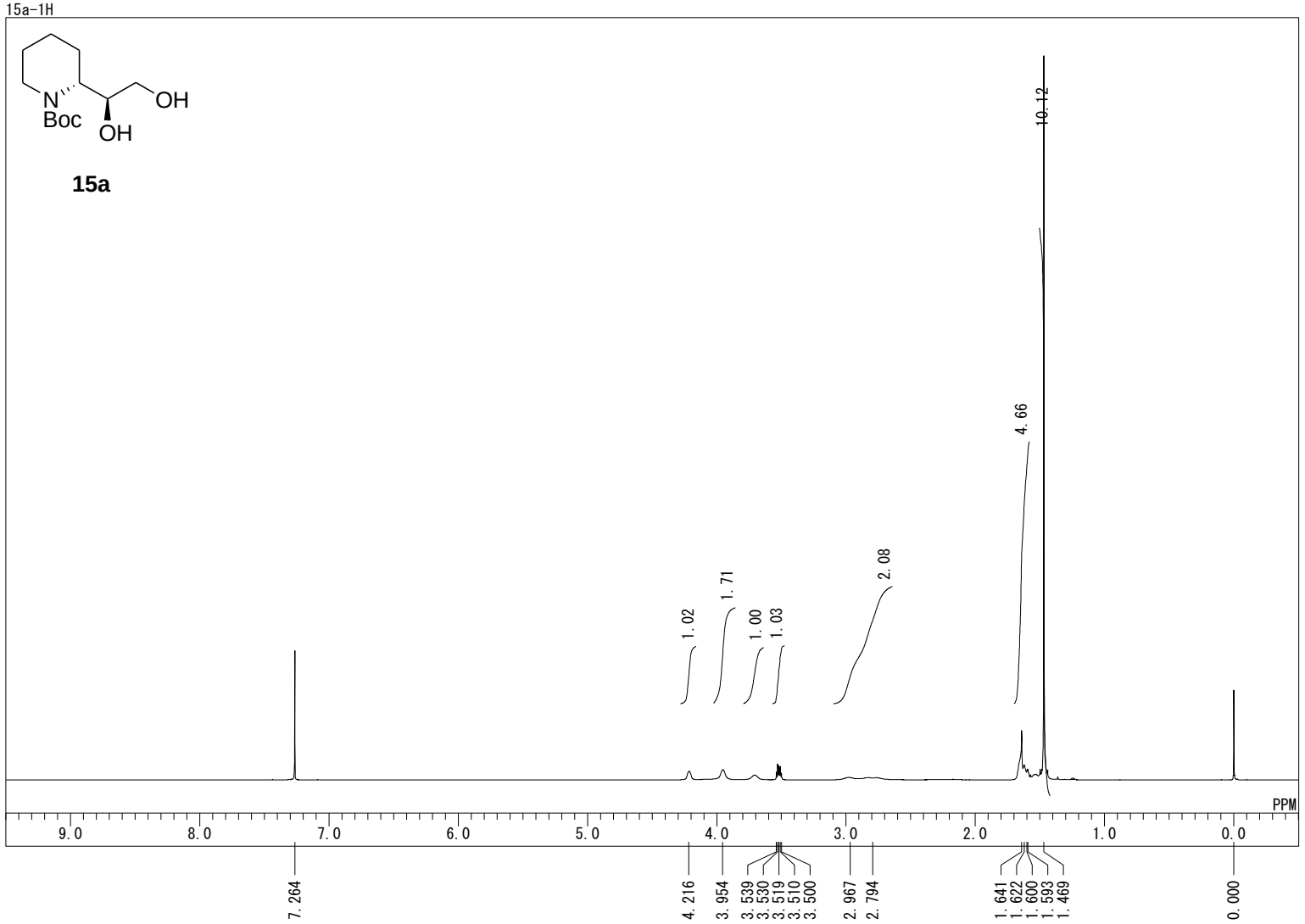

13b'-13C
O
OMe
O
O
13b'
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
169.881
132.077
119.382
111.182
78.696
77.716
77.321
77.000
76.687
51.775
26.896
25.537

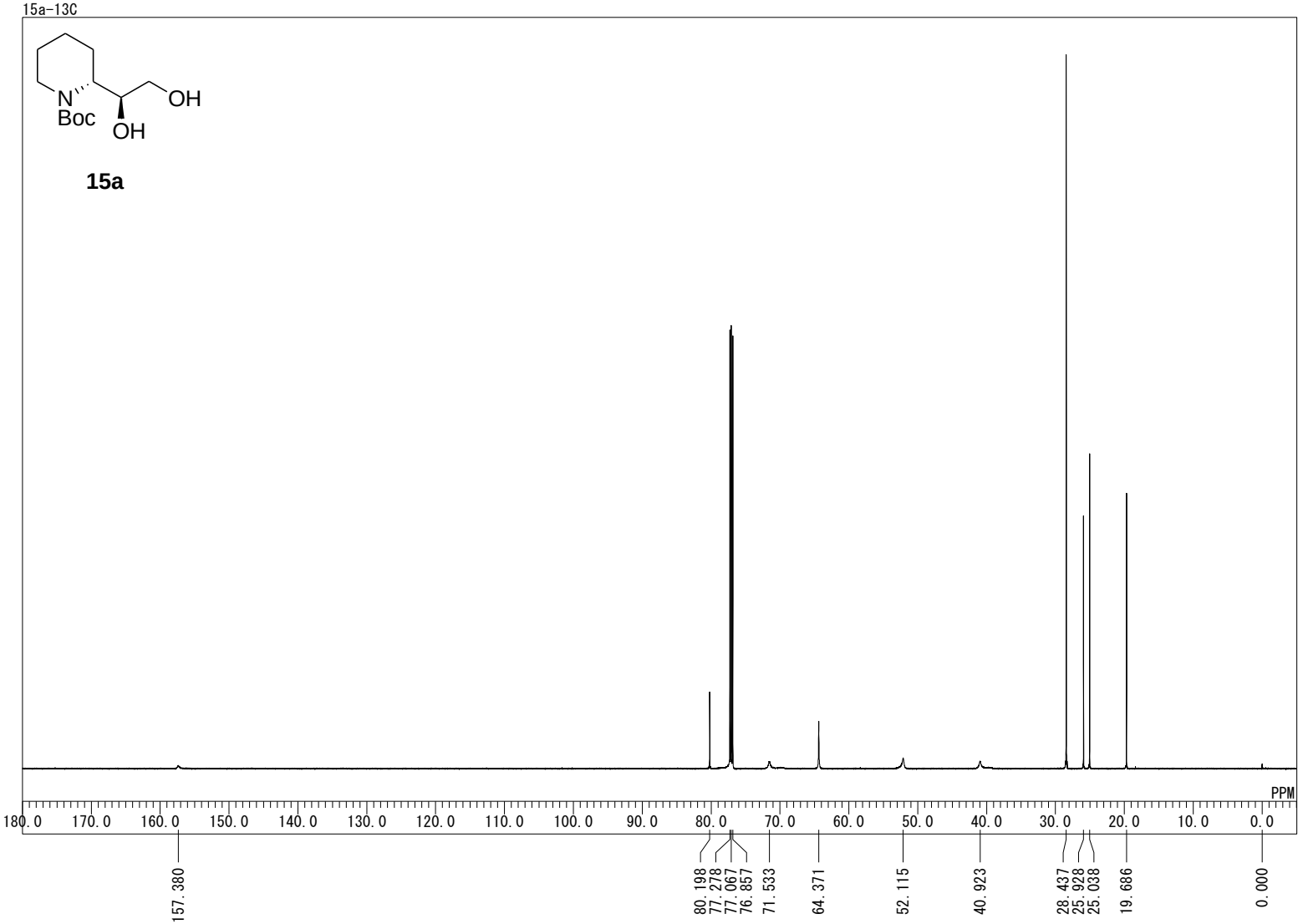

14a-1H
OH
O
OH
OMe
14a
1.00
2.01
2.00
1.04
0.99
2.87
0.97
0.95
0.85
0.91
1.06
1.05
1.00
0.96
2.90
2.84
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

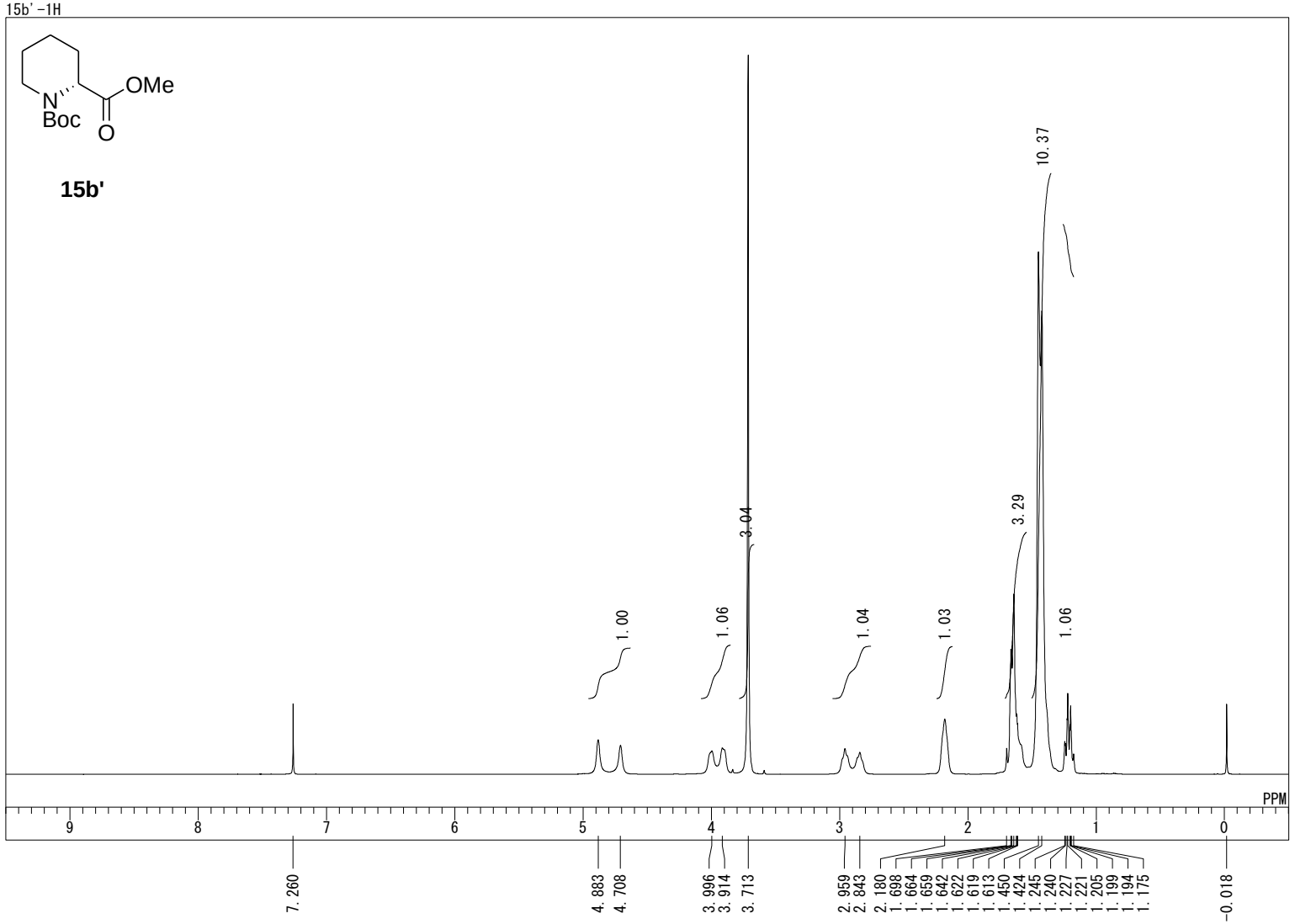

14a-13C
OH
O
OH
OMe
14a
PPM
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
136.290
116.291
84.662
84.201
78.498
77.321
77.000
76.679
73.305
63.931
57.207
38.862
33.446
28.615
22.369
13.167

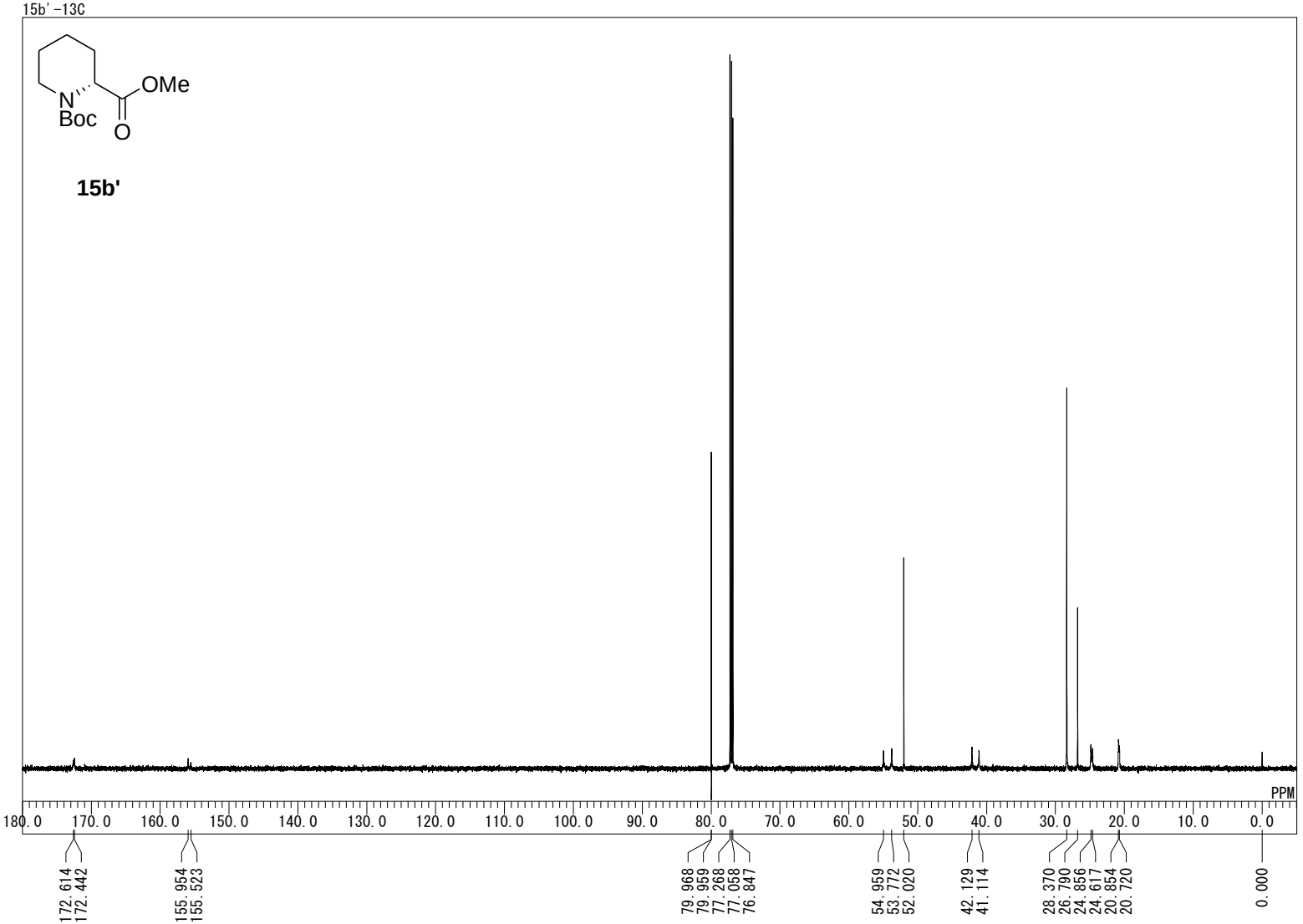

14b'-1H
O
O
OMe
OMe
14b'
1.03
2.08
1.00
2.99
2.98
1.00
1.04
3.18
2.17
2.92
3.08
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

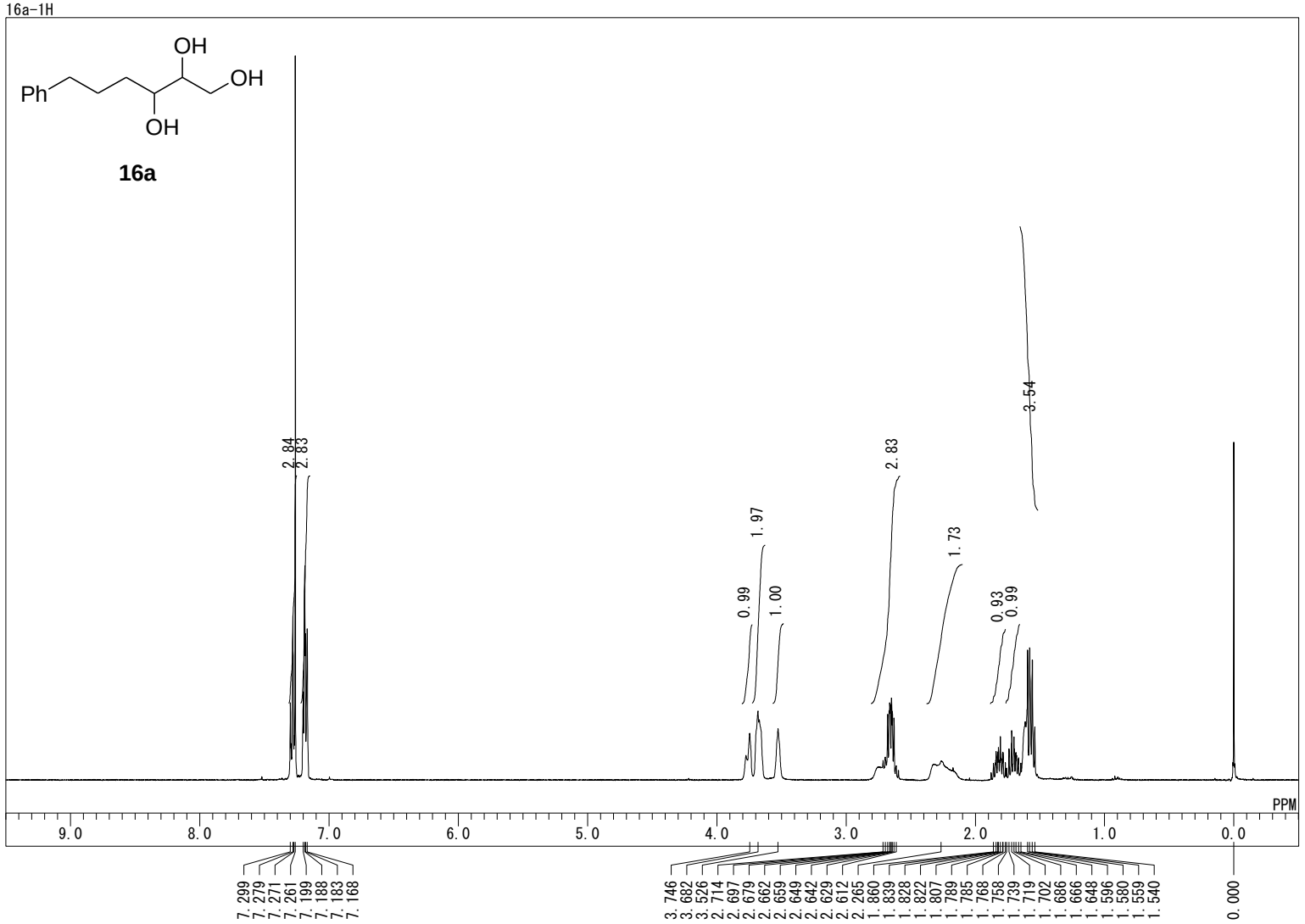

14b'-13C
O
O
OMe
OMe
14b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
171.269
136.505
115.987
85.066
84.523
77.379
77.058
76.738
75.322
57.240
52.154
38.797
33.381
29.538
22.435
13.152

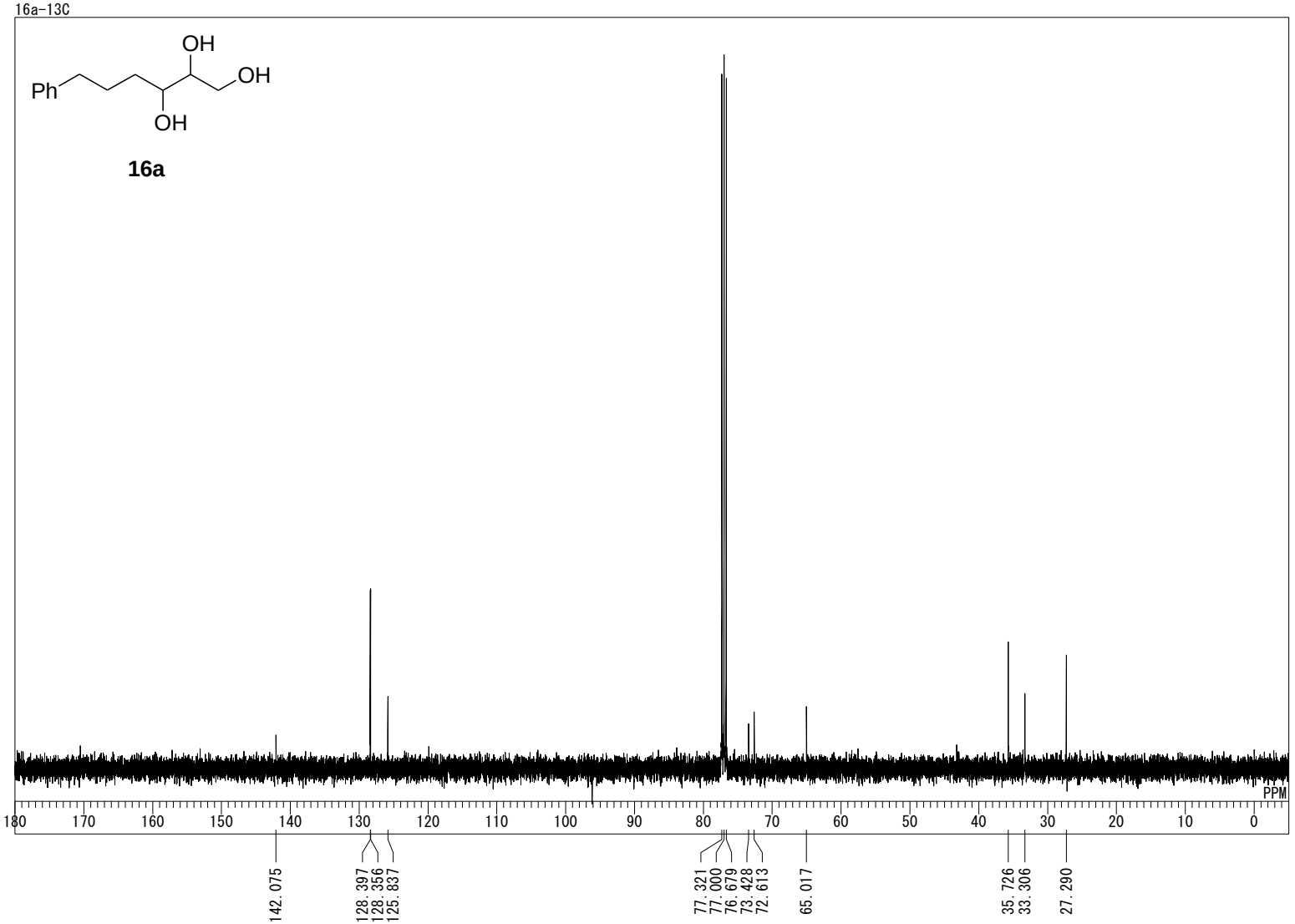

15a-1H
N
Boc
OH
OH
15a
10.12
4.66
2.08
1.71
1.02
1.00
1.03
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
4.216
3.954
3.539
3.530
3.519
3.510
3.500
2.967
2.794
1.641
1.622
1.600
1.593
1.469
0.000

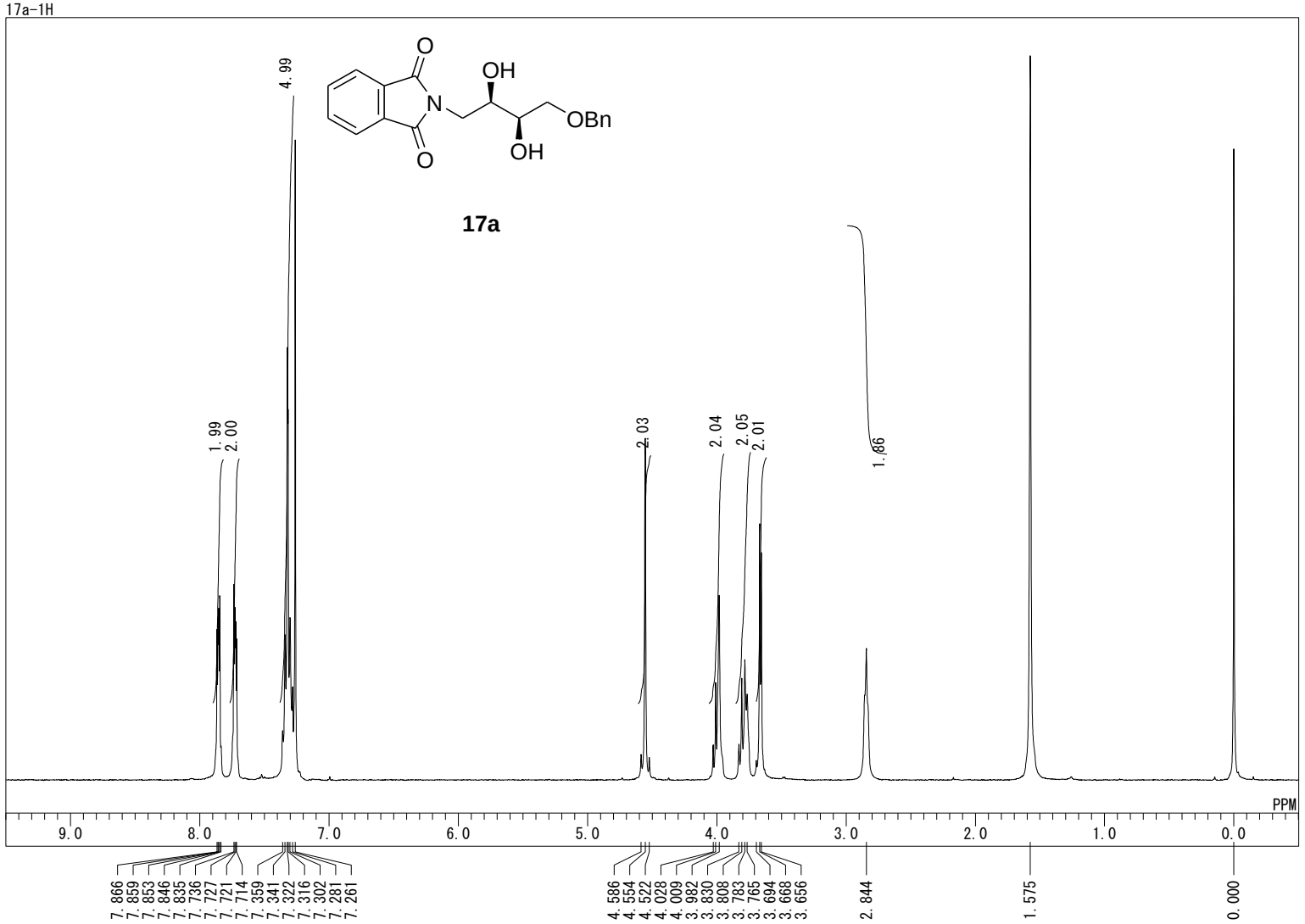

15a-13C
N
Boc
OH
OH
15a
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
157.380
80.198
77.278
77.067
76.857
71.533
64.371
52.115
40.923
28.437
25.928
25.038
19.686
0.000

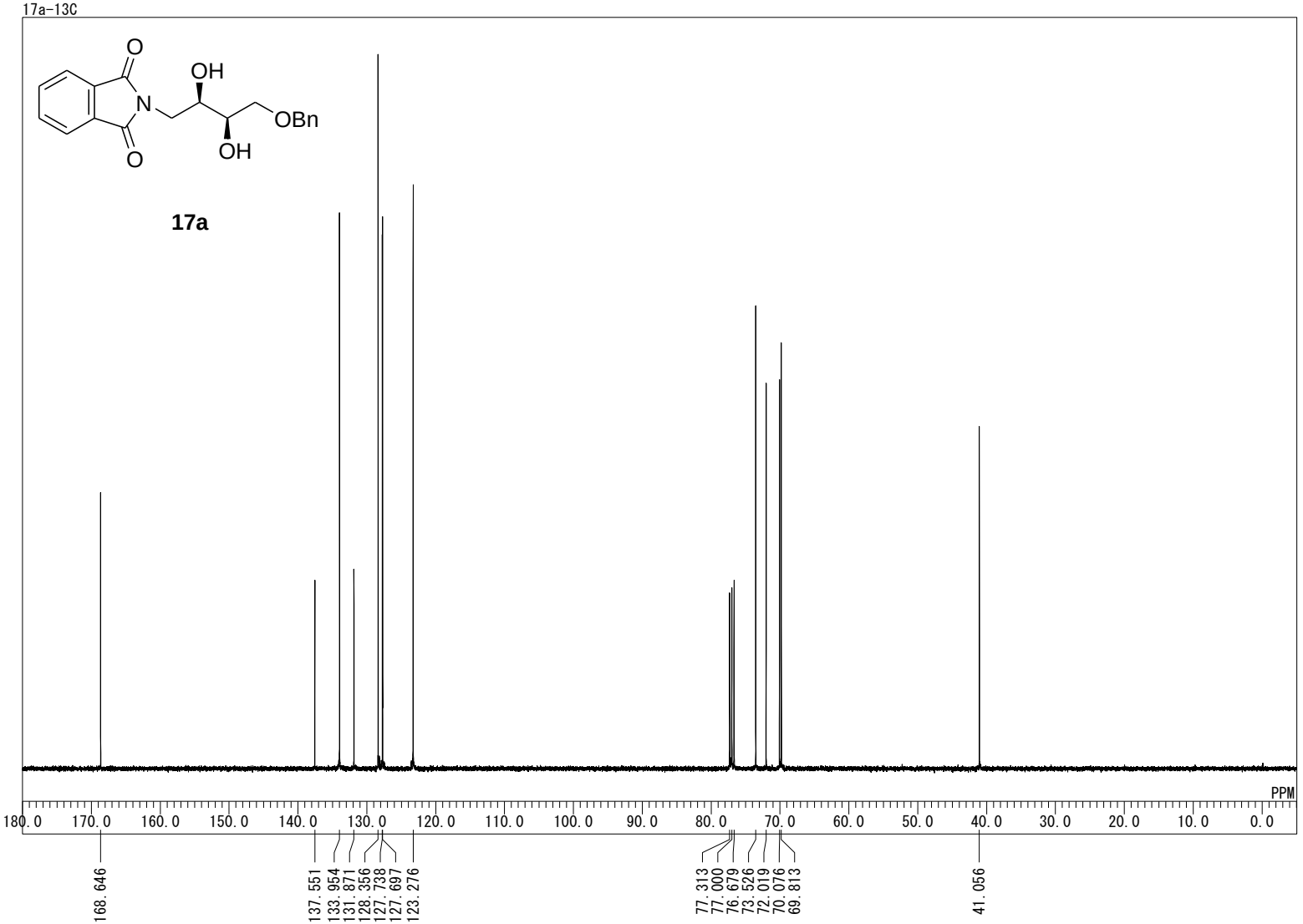

15b'-1H
OMe
N
Boc
O
15b'
10.37
3.29
3.04
1.00
1.06
1.04
1.03
1.06
PPM
9
8
7
6
5
4
3
2
1
0
7.260
4.883
4.708
3.996
3.914
3.713
2.959
2.843
2.180
1.698
1.664
1.659
1.642
1.622
1.619
1.613
1.450
1.424
1.245
1.240
1.227
1.221
1.205
1.199
1.194
1.175
-0.018

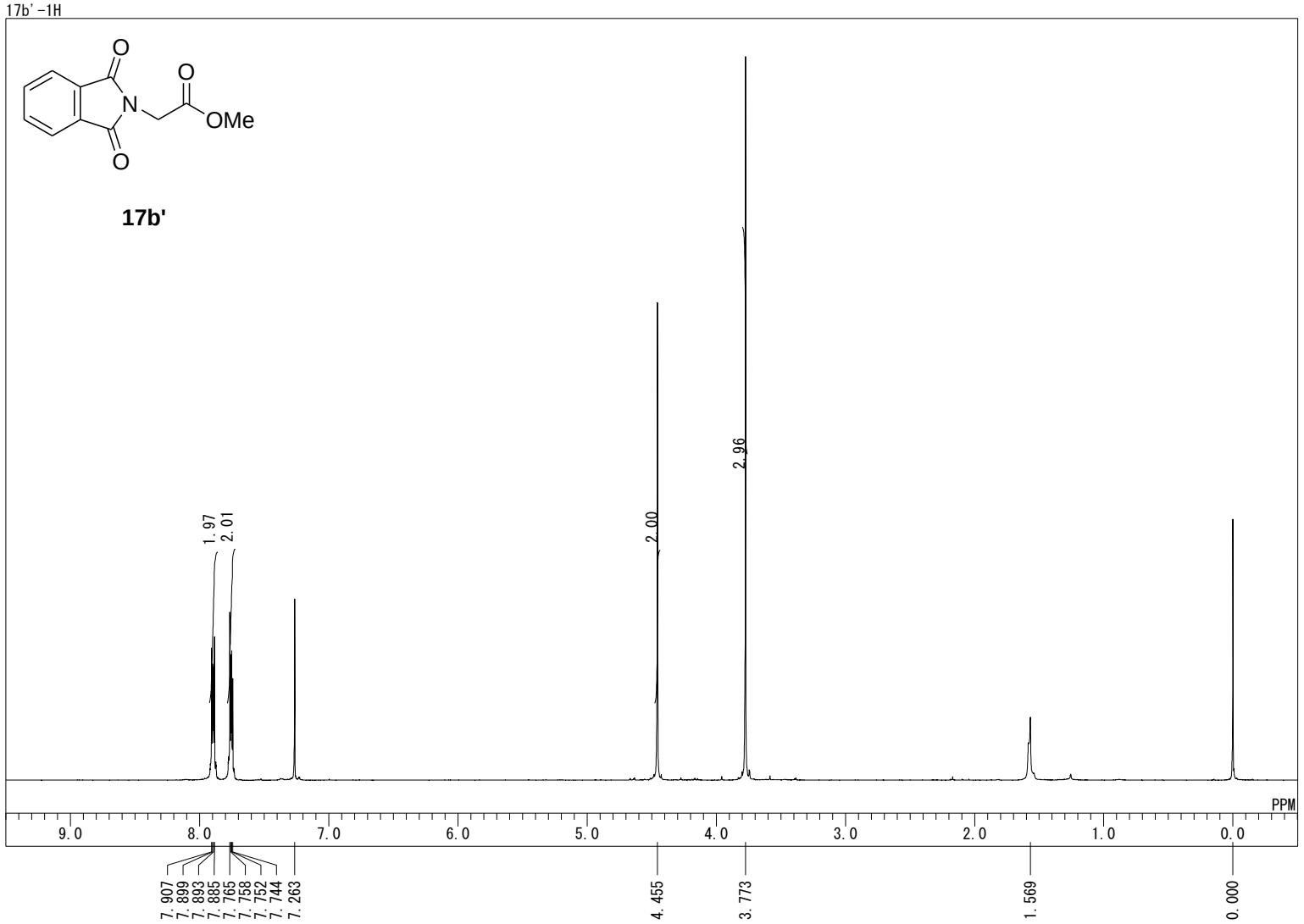

15b'-13C
N
Boc
OMe
O
15b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
172.614
172.442
155.954
155.523
79.968
79.959
77.268
77.058
76.847
54.959
53.772
52.020
42.129
41.114
28.370
26.790
24.856
24.617
20.854
20.720
0.000

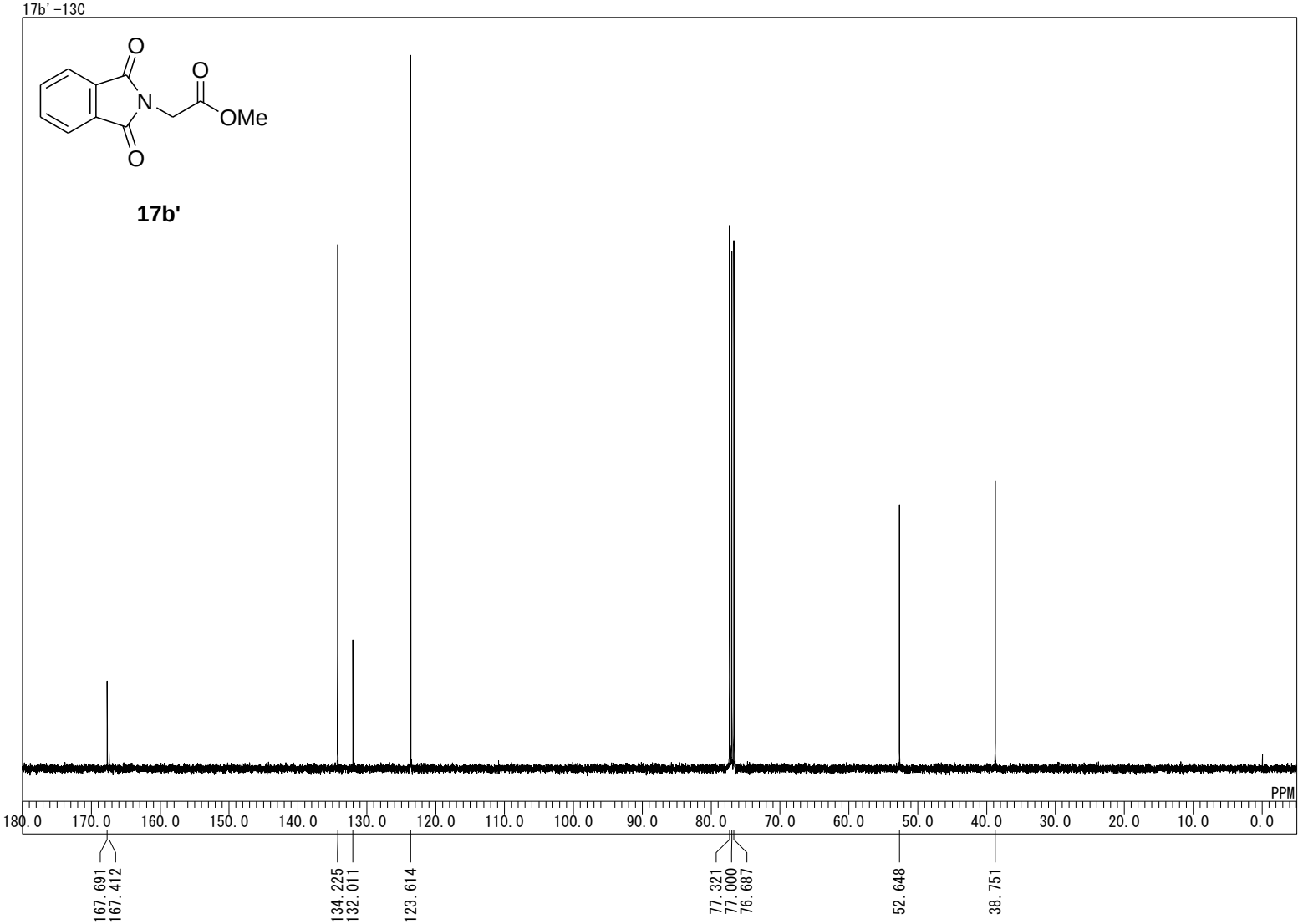

16a-1H
OH
OH
Ph
OH
16a
2.84
2.83
0.99
1.97
1.00
2.83
1.73
0.93
0.99
3.54
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.299
7.279
7.271
7.261
7.199
7.188
7.183
7.168
3.746
3.682
3.526
2.714
2.697
2.679
2.662
2.659
2.649
2.642
2.629
2.612
2.265
1.860
1.839
1.828
1.822
1.807
1.789
1.785
1.768
1.758
1.739
1.719
1.702
1.686
1.666
1.648
1.596
1.580
1.559
1.540
0.000

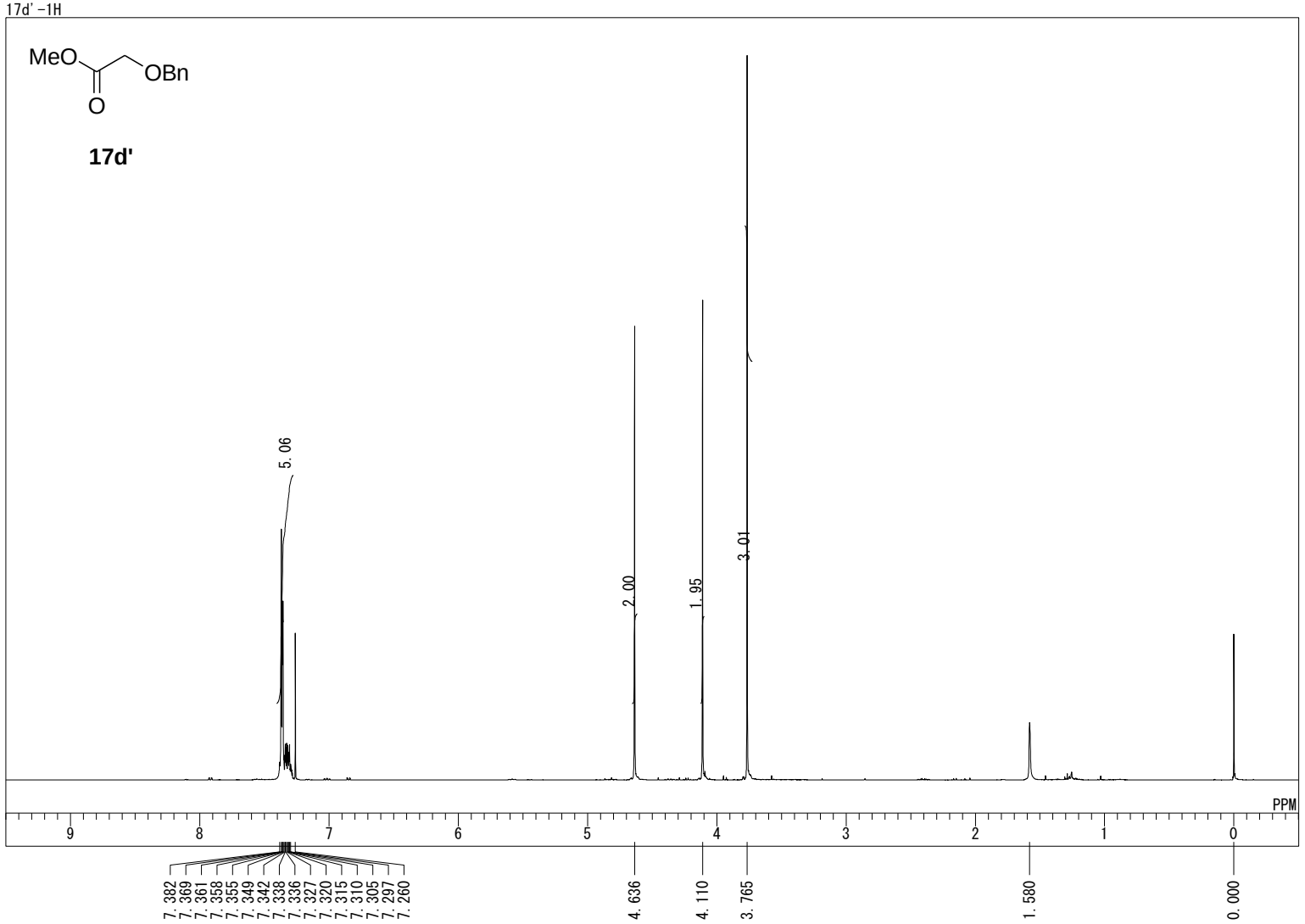

16a-13C
OH
OH
Ph
OH
16a
PPM
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
142.075
128.397
128.356
125.837
77.321
77.000
76.679
73.428
72.613
65.017
35.726
33.306
27.290

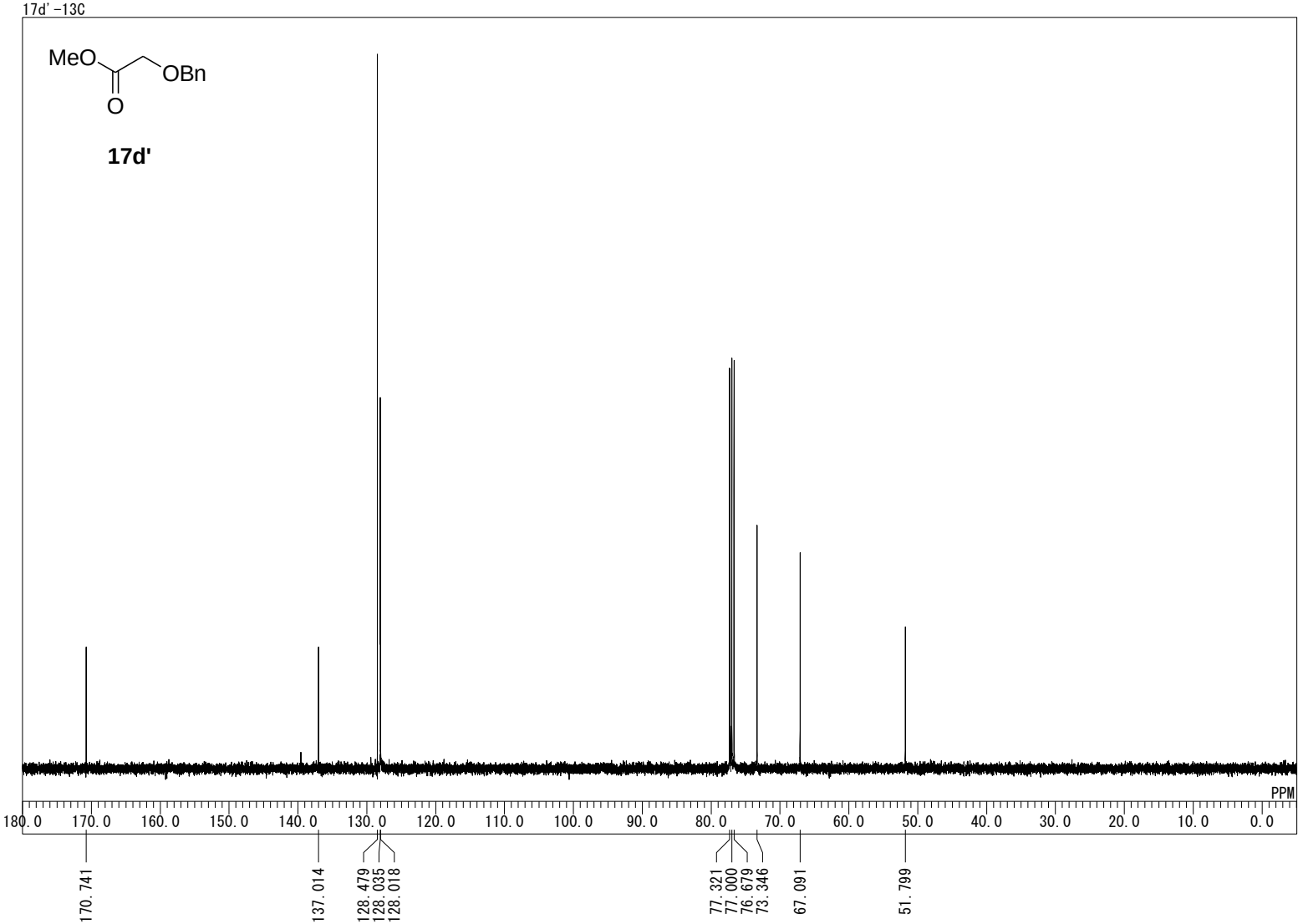

17a-1H
O
OH
N
OBn
OH
O
17a
4.99
1.99
2.00
2.03
2.04
2.05
2.01
1.66
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.866
7.859
7.853
7.846
7.835
7.736
7.727
7.721
7.714
7.359
7.341
7.322
7.316
7.302
7.281
7.261
4.586
4.554
4.522
4.028
4.009
3.982
3.830
3.808
3.783
3.765
3.694
3.668
3.656
2.844
1.575
0.000


17a-13C
O
OH
N
OBn
OH
O
17a
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
168.646
137.551
133.954
131.871
128.356
127.738
127.697
123.276
77.313
77.000
76.679
73.526
72.019
70.076
69.813
41.056


17b'-1H
O
O
N
OMe
O
17b'
1.97
2.01
2.00
2.96
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.907
7.899
7.893
7.885
7.765
7.758
7.752
7.744
7.263
4.455
3.773
1.569
0.000


17b'-13C
O
O
N
OMe
O
17b'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
167.691
167.412
134.225
132.011
123.614
77.321
77.000
76.687
52.648
38.751


17d'-1H
MeO
OBn
O
17d'
5.06
2.00
1.95
3.01
PPM
9
8
7
6
5
4
3
2
1
0
7.382
7.369
7.361
7.358
7.355
7.349
7.342
7.338
7.336
7.327
7.320
7.315
7.310
7.305
7.297
7.260
4.636
4.110
3.765
1.580
0.000


17d'-13C
MeO
OBn
O
17d'
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
170.741
137.014
128.479
128.035
128.018
77.321
77.000
76.679
73.346
67.091
51.799