Chemoselective Catalytic Oxidation of 1,2-Diols to α-Hydroxy Acids Controlled by TEMPO-ClO_2 Charge-Transfer Complex

Keisuke Furukawa, Masatoshi Shibuya* and Yoshihiko Yamamoto

Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8601, Japan

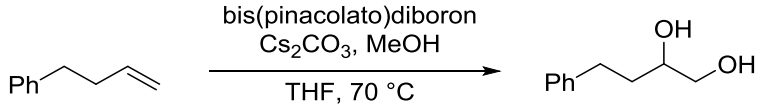
Supporting Information

1. General considerations

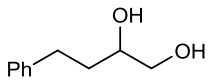
Reagents were purchased from commercial suppliers and used without purification. Column chromatography was performed on SO_3H silicagel (CHROMATOREX®, Fuji Silysia Chemical LTD) for α-hydroxy acids and neutral silicagel (Cica silica gel 60N) for others with solvents specified below. ^1H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ or CD_3CN solutions at 25 ˚C. ^1H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 0.00 ppm for tetramethylsilane as an internal standard substance. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$.

2. Preparation of diols

Typical procedure for syntheses of the 1,2-diols[1]

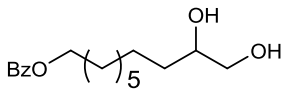


To a solution of the 4-phenyl1-butene (220 mg, 1.67 mmol), bis(pinacolato)diboron (847 mg, 3.34 mmol), Cs_2CO_3 (163 mg, 0.501 mmol) in THF (6.7 mL) were added MeOH (338 µL, 8.34 mmol) and stirred for 6 h at 70 °C. The mixture was allowed to cool until 0 °C, followed by the dropwise addition of 30% H_2O_2 (aq) (927 µL, 8.34 mmol) and 2.5 M NaOH (aq) (3.30 mL, 8.34 mmol). After 1 h stirring, the reaction was carefully quenched with sat. $Na_2S_2O_3$ (aq) and H_2O. The aqueous layer was extracted with AcOEt. The extracted organic layer was combined, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude compounds were purified by column chromatography on silica gel (hexane:AcOEt = 2:1 to 1:1) to afford 4-phenyl-butane-1,2-diol (**1a**) (262 mg, 94%) as a colorless oil.



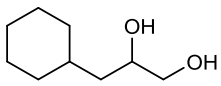
1a

^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.17 (m, 3H), 3.77-3.70 (m, 2H), 3.66 (dd, *J* = 10.8, 2.8 Hz, 2H), 3.47 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.81 (ddd, *J* = 13.6, 8.8, 6.4 Hz, 1H), 2.70 (dt, *J* = 13.6, 8.8 Hz, 1H), 2.11 (br s, 1H), 1.87 (br s, 1H), 1.85-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.5, 128.4, 126.0, 71.5, 66.7, 34.6, 31.8; IR (neat, cm^{-1}); 3700-3200, 2930; HRMS (ESI, m/z) Calcd. for $C_{10}H_{14}O_2$•Na: 189.0892 ($[M+Na]^+$), found 189.0887 ($[M+Na]^+$).



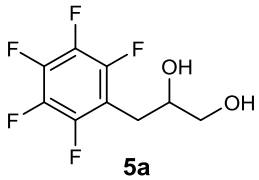
2a

10-(Benzoyloxy)-decane-1,2-diol (**2a**) was isolated by flash chromatography on silica gel (hexane:AcOEt = 2:1) as a colorless oil (590 mg, 90%). mp: 44-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.00 (m, 2H), 7.60-7.51 (m, 1H), 7.49-7.40 (m, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.77-3.60 (m, 2H), 3.44 (dd, *J* = 10.4, 7.6 Hz, 1H), 2.05 (br s, 1H), 1.91 (br s, 1H), 1.77 (quint, *J* = 7.0 Hz, 2H), 1.53-1.27 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 132.8, 130.5, 129.5, 128.3, 72.2, 66.8, 65.1, 33.1, 29.5, 29.3, 29.1, 28.7, 26.0, 25.5; IR (neat, cm^{-1}); 3700-3200, 2929, 2855, 1717, 1276; HRMS (DART, m/z) Calcd. for $C_{17}H_{26}O_4$•NH_4: 312.2175 ($[M+NH_4]^+$), found 312.2164 ($[M+NH_4]^+$).



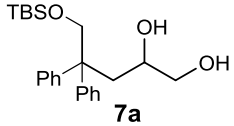
4a

3-Cyclohexylpropane-1,2-diol (**4a**) was isolated by flash chromatography on silica gel (hexane:EtOAc= 2:1) as a colorless oil (300 mg, 94%). ^{1}H NMR(400 MHz, $CDCl_3$) δ 3.90-3.78 (m, 1H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.41 (dd, *J* = 10.4, 9.2 Hz, 1H), 2.05-1.89 (m, 2H), 1.79 (d, *J* = 12.4 Hz, 1H), 1.75-1.56 (m, 4H), 1.53-1.33 (m, 2H), 1.32-1.09 (m, 4H), 1.04-0.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.8, 67.2, 40.6, 34.1, 33.8, 32.9, 26.5, 26.3, 26.1; IR (neat, cm^{-1}): 3600-3100, 2921; HRMS (ESI, m/z) Calcd. for $C_9H_{18}O_2$•Na: 181.1205 ($[M+Na]^+$), found 181.1208 ($[M+Na]^+$).



5a

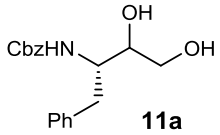
3-(2,3,4,5,6-Pentafluorophenyl)propane-1,2-diol (**5a**) [2] was purified by recrystallization, after temporary acetonide-protection and removed an impurity from bronate, as a white solid (357 mg, 61%). mp: 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02-3.90 (m, 1H), 3.74 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.56 (dd, *J* = 10.8, 6.4 Hz, 1H), 2.93 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.85 (dd, *J* = 14.0, 4.8Hz, 1H), 2.15 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 (dm, *J* = 245 Hz), 140.0 (dm, *J* = 253 Hz), 137.5 (dm, *J* = 251 Hz), 111.4 (t, *J* = 19.0 Hz), 70.9, 65.9, 26.3 ; IR (KBr, cm^{-1}): 3600-3250, 3250-3000, 2944, 1505; HRMS (ESI, m/z) Calcd. for $C_9H_7F_5O_2$•Na: 265.0264 ($[M+Na]^+$), found 265.0259 ($[M+Na]^+$).



7a

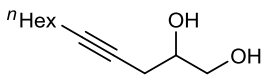
5-((*tert*-Butyldimethylsillyl)oxy)-4,4-diphenylpentane-1,2-diol (**7a**) was isolated by flash chromatography on silica gel (hexane:AcOEt = 2:1) as a colorless oil (374 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.12 (m, 10H), 4.37 (d, *J* = 10.0 Hz, 1H), 4.13 (d, *J* = 10.0 Hz, 1H), 3.63-3.58 (m, 1H), 3.51-3.38 (m, 2H), 3.23 (dd, *J* = 15.0, 2.8 Hz, 1H), 2.51 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.37 (dd, *J* = 14.6,

1.4 Hz, 1H), 2.15-2.00 (m, 1H), 0.83 (s, 9H), -0.10 (s, 3H), -0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.3, 128.2, 128.1, 128.0(0), 127.9(7), 126.3(3), 126.2(8), 69.7, 68.6, 67.5, 60.4, 51.0, 41.3, 25.7, 21.0, 18.1, 14.2, -5.8(9), -5.9(2); IR (neat, cm^{-1}); 3700-3200, 3058, 2928, 1600; HRMS (ESI, m/z) Calcd. for $C_{23}H_{34}O_3Si$•Na: 409.2175 ($[M+Na]^+$), found 409.2177 ($[M+Na]^+$).



11a

(3*S*)-*N*-(Benzyloxycarbonyl)-3-amino-4-phenylbutane-1,2-diol (**11a**) was isolated by flash chromatography on silica gel (hexane:EtOAc= 1.5:1 to 1:1) as a colorless oil (32 mg, 49%). mp: 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.12 (m, 10H), 5.21 (d, 9.2 Hz, 0.4H), 5.12-5.96 (m, 2H), 4.89 (d, *J* = 8.4 Hz, 0.6H), 4.04-3.96 (m, 1H), 3.74-3.20 (m, 3H), 3.19-2.79 (m, 3H), 1.81 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.30, 157.0, 137.7, 137.1, 136.2, 136.0, 129.4, 129.2, 128.7, 128.6, 128.5 (2C), 128.2(5), 128.1(5), 127.9 (2C), 126.7, 126.6, 72.9, 71.4, 67.1, 67.0, 64.0, 62.9, 53.2, 53.1, 38.2, 36.5; IR (neat, cm^{-1}): 3600-3100, 1692, 1261; HRMS (ESI, m/z) Calcd. for $C_{18}H_{21}NO_4$•Na: 338.1368 ($[M+Na]^+$), found 338.1376 ($[M+Na]^+$)

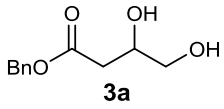


13a

Undec-4-yne-1,2-diol (**13a**) was isolated by flash chromatography on silica gel (hexane:EtOAc= 2:1), after separation of impurities by temporal protection as the acetonide, as a colorless oil (112 mg, 25%). ^{1}H NMR(400 MHz, $CDCl_3$) δ 3.92-3.79 (m, 1H), 3.74 (d, *J* = 10.6 Hz, 1H), 3.58 (dd, *J* = 10.6, 6.8 Hz, 1H), 2.48 (d, *J* = 3.6 Hz, 1H), 2.45-2.36 (m, 2H), 2.26-2.08 (m, 3H), 1.49 (quint, *J* = 6.8 Hz, 2H), 1.41-1.20 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.5, 75.2, 70.4, 65.6, 31.3, 28.9, 28.6, 23.8, 22.5, 18.7, 14.0; IR (neat, cm^{-1}): 3700-3100, 2930, 2858; HRMS (ESI, m/z) Calcd. for $C_{11}H_{20}O_2$•Na: 207.1361 ($[M+Na]^+$), found 207.1357 ($[M+Na]^+$).

The other diols were prepared by known method or the procedures shown below.

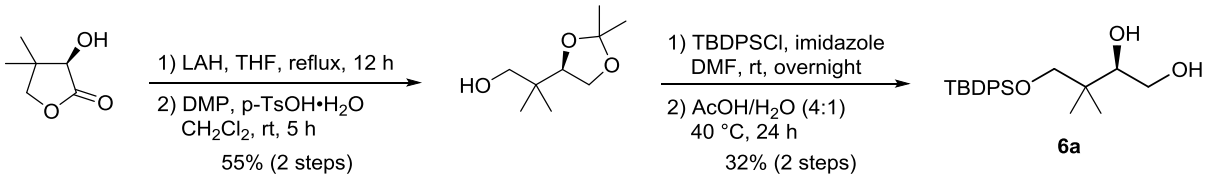
Benzyl 3,4-dihydroxybutanoate (**3a**)[3]

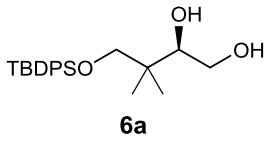


3a

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 5H), 5.17 (s, 2H), 4.20-4.09 (m, 1H), 3.74-3.64 (m, 1H), 3.53 (dt, *J* = 11.6, 5.8 Hz, 1H), 3.21 (br s, 1H), 2.62 (dd, *J* = 16.6, 8.8 Hz, 1H), 2.55 (dd, *J* = 16.6, 4.4 Hz, 1H), 2.11 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 135.4, 128.6, 128.4, 128.3, 68.4, 66.7, 65.7, 37.6; IR (neat, cm^{-1}): 3700-3200, 1731; HRMS (DART, m/z) Calcd. for $C_{11}H_{14}O_4$•NH_4: 228.1236 ($[M+NH_4]^+$), found 228.1240 ($[M+NH_4]^+$).

(*R*)-4-((*tert*-Butyldiphenylsilyl)oxy)-3,3-dimethylbutane-1,2-diol (**6a**)

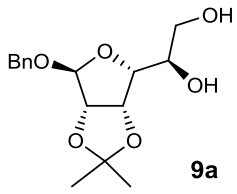




6a

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.62 (m, 4H), 7.49-7.36 (m, 6H), 3.74-3.57 (m, 3H), 3.47 (dd, *J* = 12.2, 10.2 Hz, 2H), 2.41 (br s, 1H), 1.08 (s, 9H), 0.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.6, 132.5, 132.4, 130.0(0), 129.9(6), 127.8, 78.4, 72.5, 63.1, 37.9, 26.9, 22.4, 19.8, 19.2; IR (neat, cm^{-1}): 3700-3200, 2960, 1589; HRMS (ESI, m/z) Calcd. for $C_{22}H_{32}O_3Si$•Na: 395.2018 ($[M+Na]^+$), found 395.2026 ($[M+Na]^+$).

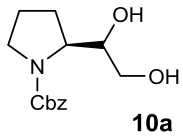
Benzyl 2,3-*O*-isopropylidene-α-D-mannofuranose (**9a**)[4]



9a

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 5.11 (s, 1H), 4.86 (dd, *J* = 5.6, 4.0 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.10-3.98 (m, 1H), 3.96 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.82 (dd, *J* = 11.2, 1.6 Hz, 1H), 3.66 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.02 (br s, 1H), 2.35 (br s, 1H), 1.47 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.4, 128.0, 127.8, 112.6, 105.4, 84.8, 80.0, 79.2, 70.3, 69.1, 64.4, 25.9, 24.6; IR (neat, cm^{-1}): 3700-3250, 2938; HRMS (ESI, m/z) Calcd. for $C_{16}H_{22}O_6$•Na: 333.1314 ($[M+Na]^+$), found 333.1311 ($[M+Na]^+$).

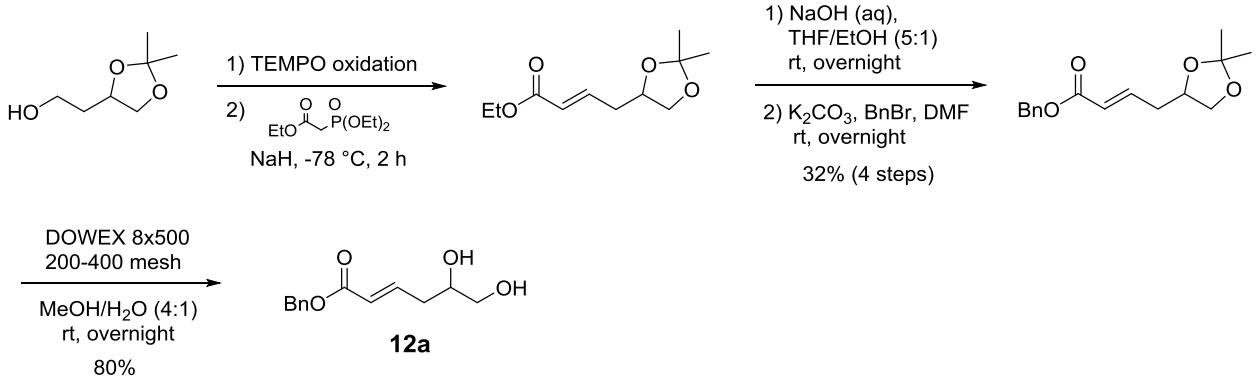
(2*S*)-*N*-Benzyloxycarbonyl-2-(1,2-dihydroxyethyl)pyrrolidine **(10a)**[5]



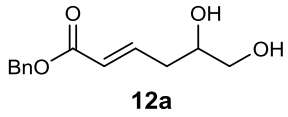
10a

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 4.13-4.00 (m, 0.3H), 3.99-3.87 (m, 0.7H), 3.75-3.27 (m, 5H), 2.20-1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.1, 136.3, 136.2, 132.1, 132.0, 128.5 (2C), 128.4, 128.1, 127.9, 127.1, 75.8, 72.6, 67.6, 67.4, 64.3, 62.6, 60.2, 59.3, 47.4, 47.0, 28.7, 27.7, 24.2, 23.3; IR (neat, cm^{-1}): 3700-3200, 1680, 1418, 1359; HRMS (ESI, m/z) Calcd. for $C_{14}H_{19}NO_4$•Na: 288.1212 ($[M+Na]^+$), found 288.1207 ($[M+Na]^+$).

Benzyl (*E*)-5,6-dihydroxyhexe-2-enoate (**12a**)



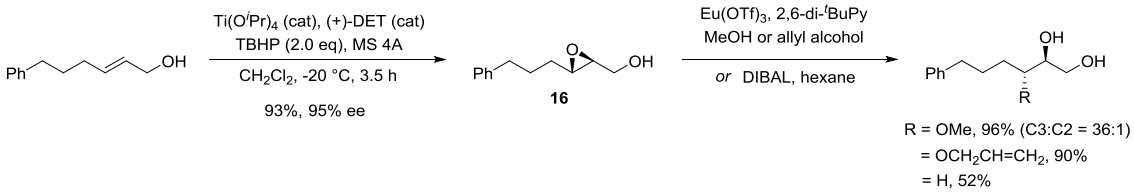
12a



12a

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.01 (dt, *J* = 15.8, 7.6 Hz, 1H), 5.96 (dt, *J* = 15.8, 1.6 Hz, 1H), 5.16 (s, 2H), 3.86-3.78 (m, 1H), 3.62 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.45 (dd, *J* = 11.4, 7.0 Hz, 1H), 2.97 (br s, 2 H), 2.35 (td, *J* = 7.2, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 145.4, 135.8, 128.5, 128.2, 123.5, 70.7, 66.3, 66.1, 36.0; IR (neat, cm^{-1}): 3700-3200, 3033, 1715, 1587, 1497; HRMS (DART, m/z) Calcd. for $C_{13}H_{16}O_4$•NH_4: 254.1392 ($[M+NH_4]^+$), found 254.1385 ($[M+NH_4]^+$).

3. Preparation of chiral 1,2-diols utilizing Sharpless asymmetric epoxidation



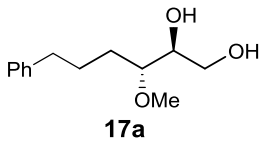
Sharpless asymmetric epoxidation

To preactivated 4Å molecular sieves (200 mg) in CH_2Cl_2 (3.6 mL) was added (+)-DET (38.9 µL, 0.228 mmol) and Ti(O^{i}Pr)$_4$ (67.6 µL, 0.228 mmol) at -20 °C. The suspension was stirred for 5 min and then TBHP (1.06 M solution in CH_2Cl_2, 2.15 mL, 2.28 mmol) was added using dropping funnel over 5 min. After reaction mixture was stirred for 30 min, 6-phenyl-hex-2-ene-1-ol (201 mg, 1.14 mmol) in CH_2Cl_2 (2 mL) was added, the reaction mixture was stirred for 3.5 h. H_2O (1 mL), 10% NaOH (aq) (3 mL) and NaCl was added, then it was stirred for additional 1 h at room temperature. The mixture was extracted AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography on silica gel (hexane:AcOEt = 3:1) afforded epoxy alcohol **16** (204 mg, 93%) as a colorless oil. Its optical purity was determined by HPLC analysis (see chapter 7).

Ring opening of 2,3-epoxy alcohol by MeOH[6]

To a solution of 2,3-epoxy alcohol **16** (103 mg, 0.534 mmol) in MeOH (2.7 mL, 0.2 M) was added 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 24.0 µL, 0.107 mmol) followed by Eu(OTf)$_3$ (63.9 mg, 0.107 mmol). The reaction mixture was stirred for 5 h at 50 °C and then cooled to room temperature and quenched with sat. $NaHCO_3$ (aq). The mixture was extracted AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography on silica gel (hexane:AcOEt = 1:1 to AcOEt only) gave desired diol **17a** (115 mg, 96%) as a white solid.

(2*S*,3*R*)-3-methoxy-6-phenylhexane-1,2-diol (**17a**) [9]



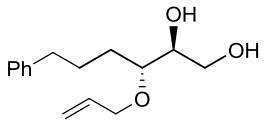
17a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 3.75-3.61 (m, 3H), 3.40 (s, 3H), 3.35-3.29 (m, 1H), 2.87-2.57 (m, 3H), 2.50 (br s, 1H), 1.94-1.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.3, 128.2, 125.7, 82.8, 72.3, 63.3, 58.3, 35.9, 29.6, 27.1; IR (neat, cm^{-1}): 3700-3200, 2936; HRMS (ESI, m/z) Calcd. for $C_{13}H_{20}O_3$•Na: 247.1310 ([M+Na]$^+$), found 247.1312 ([M+Na]$^+$).

Ring opening of 2,3-epoxy alcohol by allyl alcohol[6]

To a solution of 2,3-epoxy alcohol **16** (215 mg, 1.12 mmol) in allyl alcohol (5.6 mL, 0.2 M) was added 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 50.3 μL, 0.223 mmol) followed by $Eu(OTf)_3$ (134 mg, 0.223 mmol). The reaction mixture was stirred for 3 h at 60 °C and then cooled to room temperature and quenched with sat. $NaHCO_3$ (aq). The mixture was extracted AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography on silica gel (hexane:AcOEt = 1.5:1 to 1:1) gave desired diol **18a** (231 mg, 83%) as a colorless oil.

(2*R*,3*R*)- 3-Allyloxy-6-phenylhexane-1,2-diol (**18a**)



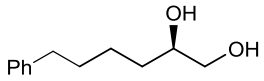
18a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.24-7.12 (m, 3H), 5.99-5.82 (m, 1H), 5.25 (ddd, *J* = 17.2, 2.8, 1.6 Hz, 1H), 5.17 (ddd, *J* = 10.6, 2.8, 1.2 Hz, 1H), 4.13-3.99 (m, 2H), 3.82-3.61 (m, 3H), 3.55-3.44 (m, 1H), 2.73-2.58 (m, 2H), 2.56-2.46 (m, 1H), 2.33-2.18 (m, 1H), 1.91-1.73 (m, 1H), 1.72-1.59 (m, 2H), 1.58-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 134.6, 128.4 (2C), 125.8, 117.2, 81.2, 72.4, 71.8, 63.3, 35.9, 30.1, 27.1; IR (neat, cm^{-1}): 3700-3200, 2926, 1603, 1423, 1086; HRMS (ESI, m/z) Calcd. for $C_{15}H_{22}O_3$•Na: 273.1467 ($[M+Na]^+$), found 273.1461 ($[M+Na]^+$).

Ring opening of 2,3-epoxy alcohol by DIBAL[7]

To a solution of 2,3-epoxy alcohol **16** (72 mg, 0.374 mmol) in hexane (600 μL, 0.6 M) was added DIBAL (1.01 M, hexane solution, 1.11 mL, 1.12 mmol) at 0 °C. After 2 h stirring, additional DIBAL (1.11 mL, 1.12 mmol) was added to the reaction mixture and it was stirred for 2 h at 0 °C. The reaction mixture was added sat. Rochell sat (aq) and violently stirred for 30 min. The mixture was extracted AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography (hexane:AcOEt = 1.5:1 to 1:1) gave the desired diol (68 mg, 94%, as regioisomeric mixture C3-H:C2-H = 4:1). 1,2-Diol **19a** was isolated by column chromatography on silica gel (hexane:EtOAc= 2:1), after separation of regioisomer by temporal protection as the acetonide, as a colorless oil (50%, 3 steps including separation from regioisomer).

(*R*)- 6-Phenylhexane-1,2-diol (**19a**)[8]



19a

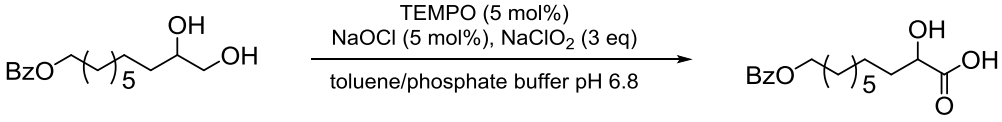
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20-7.15 (m, 3H), 3.74-3.65 (m, 1H), 3.64 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.42 (dd, *J* = 10.8, 7.6 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.17 (br s, 2H), 1.69-1.58 (m, 2H),

1.55-1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.4, 128.3, 125.7, 76.7, 72.2, 66.8, 35.8, 33.0, 31.4, 25.2; IR (neat, cm^{-1}): 3700-3200, 2933; HRMS (ESI, m/z) Calcd. for $C_{12}H_{18}O_2$•Na: 217.1205 ($[M+Na]^+$), found 217.1208 ($[M+Na]^+$).

4. Oxidation of 1,2-diols to α-hydroxycarboxylic acids

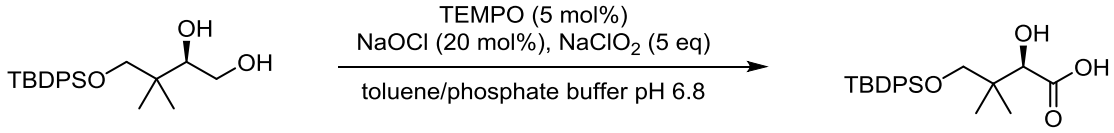
General procedure for syntheses of the 1,2-diols

Method A



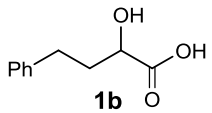
A mixture of 10-(Benzoyloxy)-decane-1,2-diol (**2a**) (38.9 mg, 0.132 mmol) and TEMPO (100 mM, 66.1 µL, 6.61 µmol) in toluene (660 µL) and 1 M sodium phosphate buffer (pH = 6.8, 470 µL) was stirred at 25 °C. Then $NaClO_2$ (80%, 44.8 mg, 0.396 mmol) as 3.5 M aqueous solution and dilute bleach (0.168 M, 39.3 µL, 6.61 µmmol) were added simultaneously over 1 minute. The mixture was stirred at 50 °C for 1.5 h. The reaction mixture was quenched with 1 M sodium phosphate buffer (pH = 2.1), added NaCl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude materials were purified by column chromatography on silica gel (SO_3H) to give 9-(benzoyloxy)-2-hydroxydecanoic acid (**2b**) (34.4 mg, 85%).

Method B



A mixture of (*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-3,3-dimethylbutane-1,2-diol (**6a**) (57.5 mg, 0.154 mmol) and TEMPO (100 mM toluene soln., 77.2 µL, 7.72 µmol) in toluene (770 µL) and 1 M sodium phosphate buffer (pH = 6.8, 550 µL) was stirred at 25 °C. Then $NaClO_2$ (80%, 87.2 mg, 0.772 mmol) as 3.5 M aqueous solution was added, and dilute bleach (0.206 M, 150 µL, 30.9 µmol) were added over 1 h using syringe driver. The mixture was stirred at 25 °C for additional 3 h. The reaction mixture was quenched with 1 M sodium phosphate buffer (pH = 2.1), added NaCl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude materials were purified by column chromatography on silica gel (SO_3H) to give (*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-2-hydroxy-3,3-dimethylbutanoic acid (**6b**) (52.3 mg, 88%).

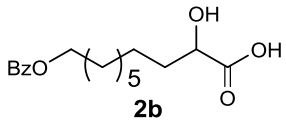
2-Hydroxy-4-phenylbutanoic acid (**1b**)



1b

Hydroxy acid **1b** was isolated by column chromatography (SO_3H, hexane:Et_2O= 1:2) in 86% yield (26.9 mg). White solid; mp: 171-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.25-7.16 (m, 2H), 4.27 (dd, *J* = 7.6, 4.0 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.29-2.12 (m, 1H), 2.02 (quint, *J* = 7.6 Hz, 1H), 2.09-1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 140.7, 128.6, 128.5, 126.2, 69.4, 35.7, 31.0; IR (KBr, cm^{-1}): 3600-3400, 2930, 1719; HRMS (ESI, m/z) Calcd. for $C_{10}H_{12}O_3$•Na: 198.1130 ($[M+Na]^+$), found 198.1131 ($[M+Na]^+$).

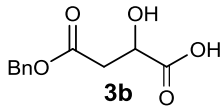
9-(Benzoyloxy)-2-hydroxydecanoic acid (**2b**)[9]



2b

Hydroxy acid **2b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 1:1) in 85% yield (34.4 mg). Colorless oil; mp: 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.59-7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 4.28 (dd, *J* = 12.0, 4.0 Hz, 1H), 1.92-1.65 (m, 4H), 1.53-1.29 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 166.9, 132.9, 130.4, 129.5, 128.3, 70.2, 65.1, 34.1, 29.2, 29.1, 28.6, 25.9, 24.6; IR (neat, cm^{-1}); 3700-3450, 3450-3200, 2929, 1718,; HRMS (DART, m/z) Calcd. for-$C_{17}H_{24}O_5$•NH_4: 326.1968 ($[M+NH_4]^+$), found 326.1966 ($[M+NH_4]^+$).

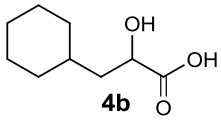
4-(Benzyloxy)-2-hydroxy-4-oxobutanoic acid (**3b**)[10]



3b

Hydroxy acid **3b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 1:1) in 87% yield (32.1 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.41-7.32 (m, 5H), 6.38 (br s, 2H), 5.17 (d, *J* =12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 4.58 (dd, *J* = 6.2, 4.4 Hz, 1H), 2.97 (dd, *J* = 17.2, 4.4 Hz, 1H), 2.89 (dd, *J* = 17.2, 6.2 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.9, 135.1, 128.6, 128.4, 128.3, 67.1, 66.9, 38.3; IR (neat, cm^{-1}): 3700-3200, 1739; HRMS (DART, m/z) Calcd. for $C_{11}H_{12}O_5$•NH_4: 242.1029 ($[M+NH_4]^+$), found 242.1021 ($[M+NH_4]^+$).

3-Cyclohexyl-2-hydroxypropanoic acid (**4b**)[11]

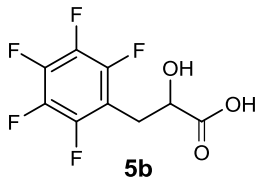


4b

Hydroxy acid **4b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 5:1) in 92% yield (65.5 mg). White solid;.mp: 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (dd, *J* = 9.0, 3.4 Hz, 1H), 1.85 (d, *J* = 12.4 Hz, 1H), 1.77-1.63 (m, 5H), 1.62-1.47 (m, 2H), 1.38-1.09 (m, 3H), 1.07-0.85 (m,

2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 68.3, 41.6, 33.9, 33.6, 32.0, 26.4, 26.2, 25.9; IR (neat, cm^{-1}): 3600-3400, 2925, 1739, 1447; HRMS (ESI, m/z) Calcd. for $C_9H_{16}O_3$•Na: 195.0997 ($[M+Na]^+$), found 195.0098 ($[M+Na]^+$).

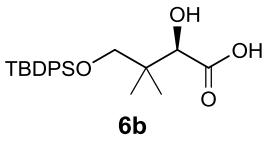
2-Hydroxy-3-(2,3,4,5,6-pentafluorophenyl)propanoic acid (**5b**)[12]



5b

Hydroxy acid **5b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 5:1 to 4:1) in 84% yield (46.6 mg). White solid; mp: 136-138 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 4.33 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.18 (d, *J* = 13.8 Hz, 1H), 3.01 (dd, *J* = 13.8, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 174.3, 146.6 (dm., *J* = 242 Hz), 140.9 (dm, *J* = 259 Hz), 138.3 (dm, *J* = 247 Hz), 112.4 (td, *J* = 19.1, 3.8 Hz), 69.5, 28.3; IR (KBr, cm^{-1}): 3700-3400, 3300-3050, 1717, 1506; HRMS (ESI^-, m/z) Calcd. for $C_9H_4F_5O_3$: 255.0086 ($[M-H]^-$), found 255.0086 ($[M-H]^-$).

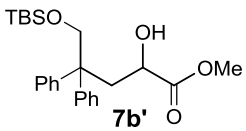
(*R*)-4-((*tert*-Butyldiphenylsilyl)oxy)-2-hydroxy-3,3-dimethylbutanoic acid (**6b**)



6b

Hydroxy acid **6b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 10:1 to 8:1) in 88% yield (52.3 mg). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.61 (m, 4H), 7.49-7.38 (m, 6H), 4.23 (s, 1H), 3.57 (d, *J* = 10.0 Hz, 1H), 3.54 (d, *J* = 10.4 Hz, 1H), 1.08 (s, 9H), 1.04 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 135.7, 135.6, 132.3, 132.2, 130.0(3), 130.0(0), 127.8, 77.2, 72.0, 39.1, 26.8, 21.8, 19.8, 19.2; IR (neat, cm^{-1}): 3700-3200, 2961, 1714; HRMS (ESI, m/z) Calcd. for $C_{22}H_{30}O_4Si$•Na: 409.1811 ($[M+Na]^+$), found 409.1811 ($[M+Na]^+$).

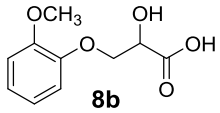
Methyl 5-(*tert*-butyldimethylsillyloxy)-2-hydroxy-4,4-diphenylpentanoate (**7b'**)



7b'

Crude material was treated with CH_2N_2 and then purified. Ester **7b'** was isolated by column chromatography (hexane:EtOAc= 10:1) in 78% yield (65.6 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 7.27-7.07 (m, 8H), 4.38 (d, *J* = 9.6 Hz, 1H), 4.21 (d, *J* = 9.6 Hz, 1H), 4.01-3.94 (m, 1H), 3.70 (s, 3H), 3.27 (d, *J* = 4.8 Hz, 1H), 2.77-2.61 (m, 2H), 0.79 (s, 9H), -0.14 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 147.1, 144.5, 128.5, 128.2 (2C), 127.7, 126.4, 126.2, 69.2, 68.8, 52.4, 51.5, 41.9, 25.8, 18.2, -5.8(6), -5.9(3); IR (neat, cm^{-1}); 3600-3300, 2953, 1738; HRMS (ESI, m/z) Calcd. for $C_{24}H_{34}O_4Si$•Na: 437.2124 ($[M+Na]^+$), found 437.2127 ($[M+Na]^+$).

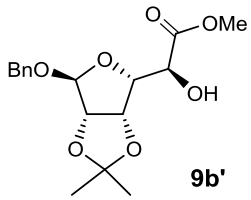
2-Hydroxyl-3-(2-methoxyphenoxy)propionic acid (**8b**)[13]



8b

Hydroxy acid **8b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 2:1) in 73% yield (38.8 mg). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.94 (m, 2H), 6.93-6.84 (m, 2H), 4.54 (dd, *J* = 4.4, 3.6 Hz, 1H), 4.35 (d, *J* = 10.0, 4.4 Hz, 1H), 4.27 (d, *J* = 10.0, 3.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 149.6, 147.3, 123.3, 121.2, 116.2, 112.1, 71.5, 69.6, 55.8; IR (neat, cm^{-1}): 3700-3200, 2839, 1741; HRMS (ESI, m/z) Calcd. for $C_{10}H_{12}O_5$•Na: 235.0582 ($[M+Na]^+$), found 235.0583 ($[M+Na]^+$).

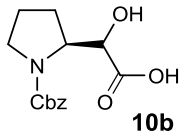
Methyl (benzyl 2,3-*O*-isopropylidene-α-D-mannofuranosid)uronate (**9b'**)[9]



9b'

Crude material was treated with CH_2N_2 and then purified. Ester **9b'** was isolated by column chromatography (hexane:EtOAc= 4:1) in 96% yield (57.0 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 5H), 5.19 (s, 1H), 4.87 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.65 (d, *J* = 10.4 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.58 (dd, *J* = 8.6, 7.2 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.17 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.82 (s, 3H), 3.44 (d, *J* = 8.8 Hz, 1H), 1.48 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 137.0, 128.4, 128.0, 127.9, 113.0, 105.5, 84.7, 80.3, 78.7, 69.8, 69.1, 52.6, 25.8, 24.3; IR (neat, cm^{-1}): 3600-3200, 2951, 1744; HRMS (ESI, m/z) Calcd. for $C_{17}H_{22}O_7$•Na: 361.1263 ($[M+Na]^+$), found 361.1258 ($[M+Na]^+$).

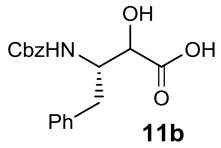
Hydroxy acid **10b**



10b

Hydroxy acid **10b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 2:1 to 1:1) in 82% yield (47.0 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 5H), 5.27-4.98 (m, 2H), 4.69 (br s, 0.3H), 4.62 (br s, 0.7H), 4.33-4.12 (m, 1H), 3.63-3.49 (m, 1H), 3.48-3.32 (m, 1H), 2.25-1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 174.7, 156.7, 155.1, 136.1 (2C), 128.5 (2C), 128.1, 128.4, 128.0, 127.8 (2C), 72.2, 71.2, 67.6, 67.3, 61.0, 59.5, 47.6 (2C), 27.1, 26.4, 24.2, 23.7; IR (neat, cm^{-1}): 3700-3200, 2958, 1732, 1681; HRMS (DART, m/z) Calcd. for $C_{14}H_{18}NO_5$: 280.1185 ($[M+H]^+$), found 280.1186 ($[M+H]^+$).

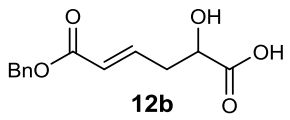
(*3S*)-*N*-(Benzyloxycarbonyl)-3-amino-2-hydroxy-4-phenylbutanoic acid (**11b**)[14]



11b

Hydroxy acid **11b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 1:1) in 85% yield (29.1 mg). White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42-7.10 (m, 10H), 5.04-4.79 (m, 2H), 4.15-3.96 (m, 1.4H), 3.93 (d, *J* = 2.8 Hz, 0.6H), 2.92-2.79 (m, 0.6H), 2.78-2.63 (m, 1.4H); ^{113}C NMR (100 MHz, DMSO-d_6): 173.7(6), 173.7(2), 155.4 (2C), 138.9, 138.4, 129.0, 128.9, 128.1, 128.0 (2C), 127.8, 127.4(2), 127.3(6), 127.1(4), 127.0(6), 126.0, 125.7, 72.5, 70.4, 64.8, 55.1, 37.1, 34.6; IR (neat, cm^{-1}): 3600-3400, 3400-3200, 2923, 1739, 1702; HRMS (ESI, m/z) Calcd. for $C_{18}H_{19}NO_5$•Na: 352.1161 ([M+Na]$^+$), found 352.1168 ([M+Na]$^+$).

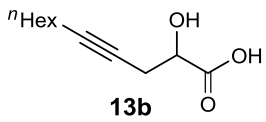
(*E*)-6-(Benzyloxy)-2-hydroxy-6-oxohex-4-enoic acid (**12b**)



12b

Hydroxy acid **12b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 2:1 to 1:1) in 81% yield (22.6 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 7.00 (dt, *J* = 15.4, 7.0 Hz, 1H), 6.02 (dt, *J* = 15.4, 1.4 Hz, 1H), 5.68 (br s, 2H), 5.17 (s, 2H), 4.39 (dd, *J* = 7.0, 4.4 Hz, 1H), 2.76 (dddd, *J* = 15.0, 7.0, 4.6, 1.6 Hz, 1H), 2.62 (dtd, *J* = 15.0, 7.0, 1.6 Hz, 1H; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 166.4, 143.5, 135.7, 128.6, 128.3, 128.2, 124.4, 69.0, 66.5, 36.5; IR (neat, cm^{-1}): 3700-3200, 1715 (br); HRMS (DART, m/z) Calcd. for $C_{13}H_{14}O_5$•NH_4: 268.1185 ([M+NH_4]$^+$), found 268.1179 ([M+NH_4]$^+$).

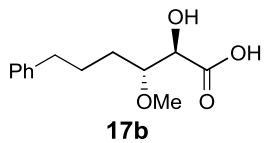
2-Hydroxyundec-4-ynoic acid (**13b**)



13b

Hydroxy acid **13b** was isolated by column chromatography (SO_3H, hexane:EtOAc=5:1) in 80% yield (44.1 mg). White solid; mp: 82-84 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 4.37 (t, *J* = 4.8 Hz, 1H), 2.83-2.65 (m, 2H), 2.23-2.10 (m, 2H), 1.48 (quint, *J* = 7.2 Hz, 2H), 1.41-1.19 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 84.6, 73.1, 68.9, 31.3, 28.7, 28.5, 25.1, 22.5, 18.6, 14.0; IR (KBr, cm^{-1}): 3700-3400, 2931, 1721; HRMS (ESI, m/z) Calcd. for $C_{11}H_{18}O_3$•Na: 221.1154 ([M+Na]$^+$), found 221.1151 ([M+Na]$^+$).

(2*R*,3*R*)-2-Hydroxy-3-methoxy-6-phenylhexanoic acid (**17b**)

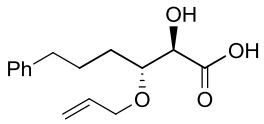


17b

Hydroxy acid **17b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 1.5:1) in 94% yield (58.5 mg). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.22-7.12 (m, 3H), 4.40 (d, *J* = 3.6 Hz,

1H), 3.56 (quint, *J* = 3.6 Hz, 1H), 3.44 (s, 3H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.90-1.62 (m, 3H), 1.60-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 142.0, 128.3(3), 128.3(1), 125.8, 82.4, 70.9, 58.0, 35.7, 28.8, 27.0; IR (neat, cm^{-1}): 3700-3200, 1731; HRMS (DART, m/z) Calcd. for $C_{13}H_{18}O_4 \bullet NH_4$: 256.1549 ($[M+NH_4]^+$), found 256.1556 ($[M+NH_4]^+$).

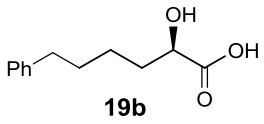
(2*R*,3*R*)- 3-Allyloxy-2-hydroxy-6-phenylhexanoic acid (**18b**)



18b

Hydroxy acid **18b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 3:1) in 76% yield (40.4 mg). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.23-7.11 (m, 3H), 5.97-5.80 (m, 1H), 5.29 (ddd, *J* = 17.1, 3.0, 1.2 Hz, 1H), 5.21 (ddd, *J* = 10.3, 3.0, 1.2 Hz, 1H), 4.38 (d, *J* = 3.6 Hz, 1H), 4.16-4.03 (m, 2H), 3.73 (dt, *J* = 8.0, 3.6 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.92-1.61 (m, 3H), 1.60-1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 142.0, 133.8, 128.3 (2C), 125.8, 118.3, 80.0, 71.3 (2C), 35.7, 29.1, 27.0; IR (neat, cm^{-1}): 3700-3400, 2941, 1730, 1347, 1218; HRMS (ESI, m/z) Calcd. for $C_{15}H_{20}O_4 \bullet Na$: 287.1259 ($[M+Na]^+$), found 287.1264 ($[M+Na]^+$).

(*R*)-2-Hydroxy-6-phenylhexanoic acid (**19b**)[15]



19b

Hydroxy acid **19b** was isolated by column chromatography (SO_3H, hexane:EtOAc= 4:1) in 85% yield (23.1 mg). White solid; mp: 82-83 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.23-7.12 (m, 3H), 4.27 (dd, *J* = 7.4, 4.4 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.00-1.82 (m, 1H), 1.81-1.61 (m, 3H), 1.60-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 142.3, 128.3(4), 128.2(9), 125.7, 70.2, 35.7, 34.0, 31.1, 24.5; IR (neat, cm^{-1}): 3600-3300, 1739, 1496; HRMS (ESI, m/z) Calcd. for $C_{12}H_{16}O_3 \bullet Na$: 231.0997 ($[M+Na]^+$), found 231.1000 ($[M+Na]^+$

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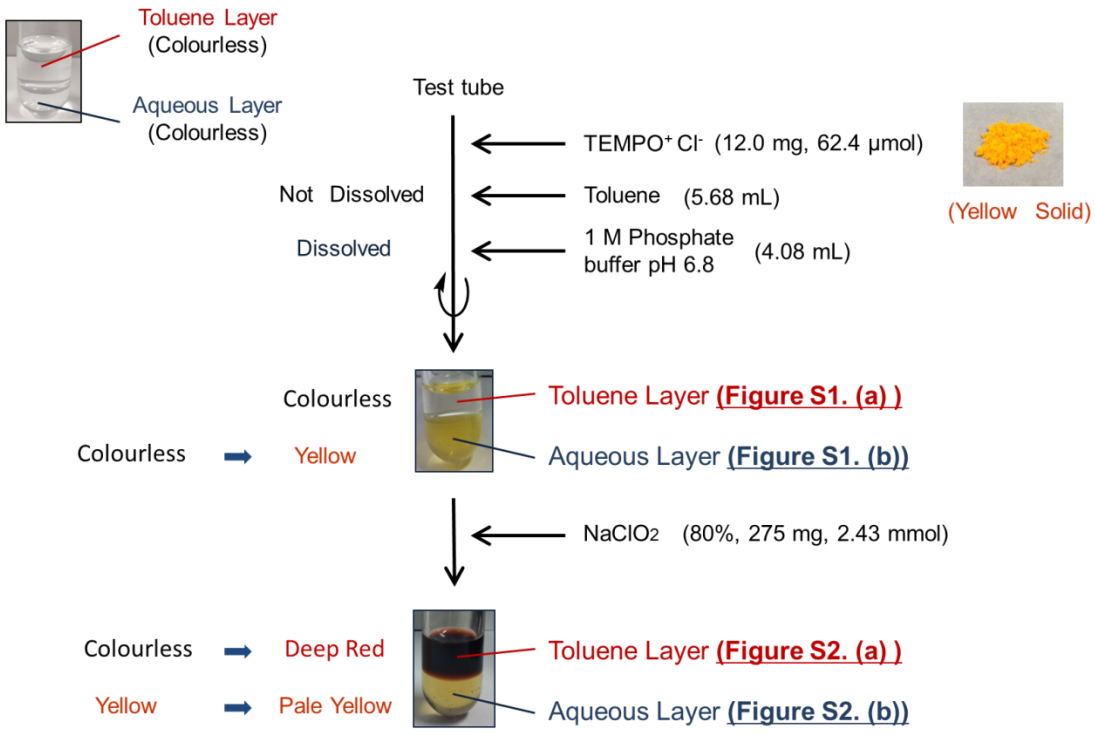
5. Photophysical studies



Blank spectra

Figure S1

(a) Toluene layer : toluene

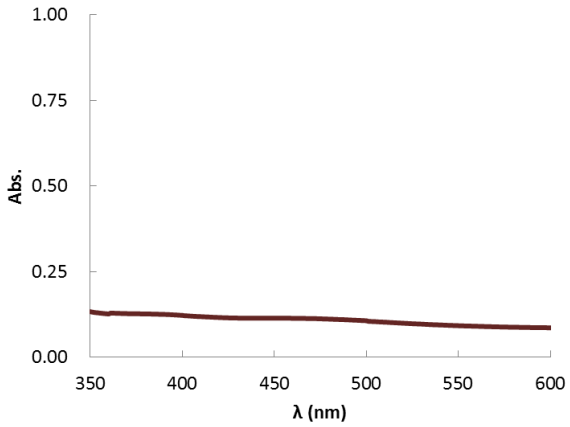
(b) Aqueous layer: 1M sodium phosphate buffer (pH 6.8)

Figure S2

(a) Toluene layer : toluene

(b) Aqueous layer: 1M sodium phosphate buffer (pH 6.8) in $NaClO_2$ (80%, 275 mg, 2.43 mmol)

(a) toluene layer



(b) aqueous layer

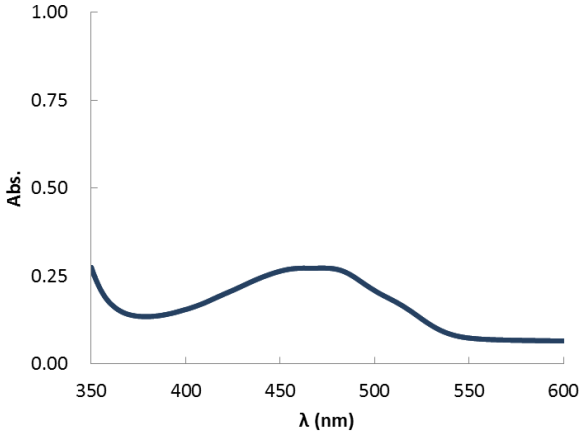
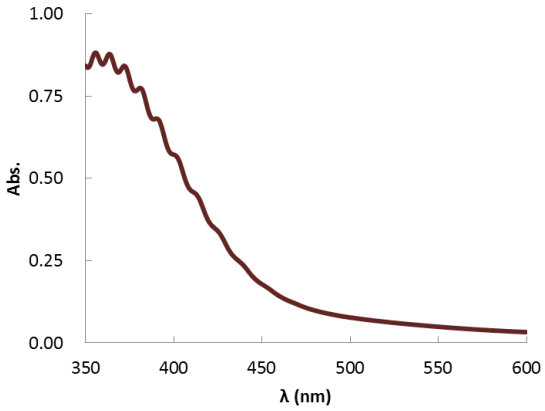


Figure S1. UV-Vis absorption spectra of $TEMPO^{+}Cl^{-}$ in toluene/phosphate buffer. (a) toluene layer, (b) aqueous layer.

(a) toluene layer



(b) aqueous layer

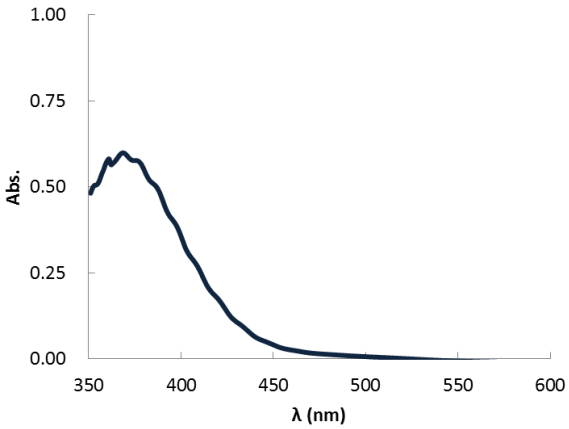


Figure S2. UV-Vis absorption spectra after the addition of $NaClO_2$. (a) toluene layer (b) aqueous layer.

UV-Vis spectra of TEMPO and CT-complex

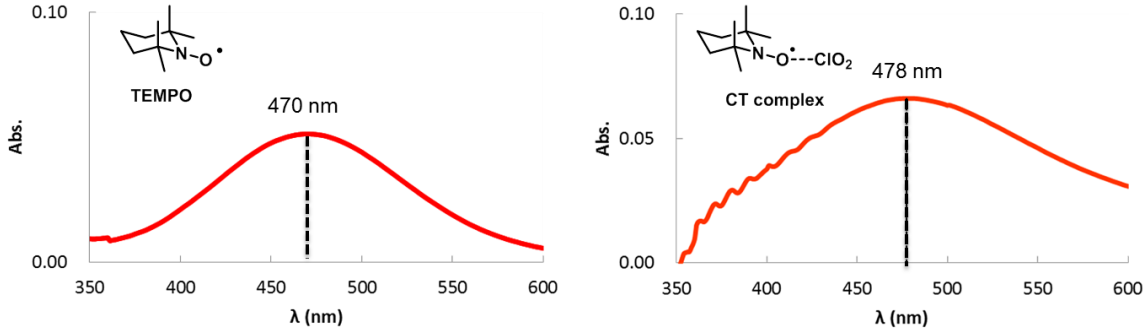


Figure S3. (a) UV-Vis absorption spectra of TEMPO in toluene. (b) Subtraction spectra of ClO_2 from toluene layer after addition of $NaClO_2$.

Preparation of ClO_2 solution in toluene

$$2\ KClO_3 + (COOH)_2 + 2\ H_2SO_4 \longrightarrow 2\ ClO_2 + CO_2 + 2\ H_2O + 2\ KHSO_3$$

To a suspension of $KClO_3$ (150 mg, 1.22 mmol) and $(COOH)_2$ (105 mg, 1.17 mmol) in H_2O (400 μL) was added cooled conc. H_2SO_4 (110 μL) at room temperature. The reaction mixture was gently warmed to 30-40 °C, and then generated yellow gas was flowed and collected in toluene. And then UV-Vis spectra was measured (**Figure S4**).

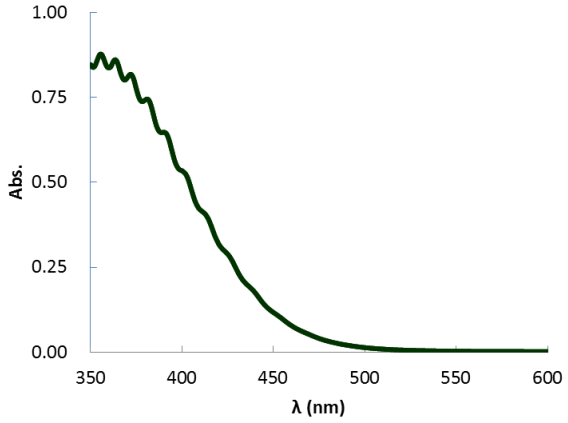
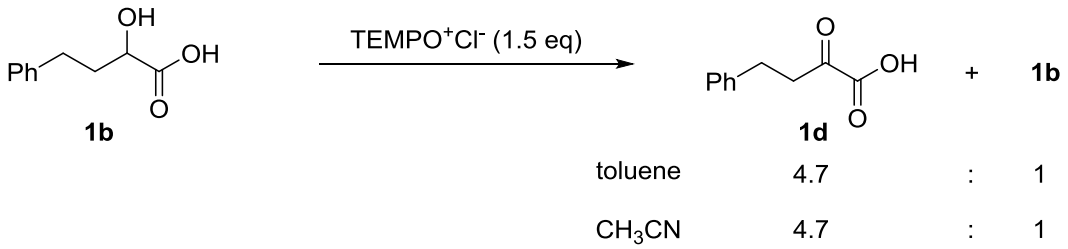


Figure S4. UV-Vis absorption spectra of ClO_2 in toluene.

6. Mechanistic studies

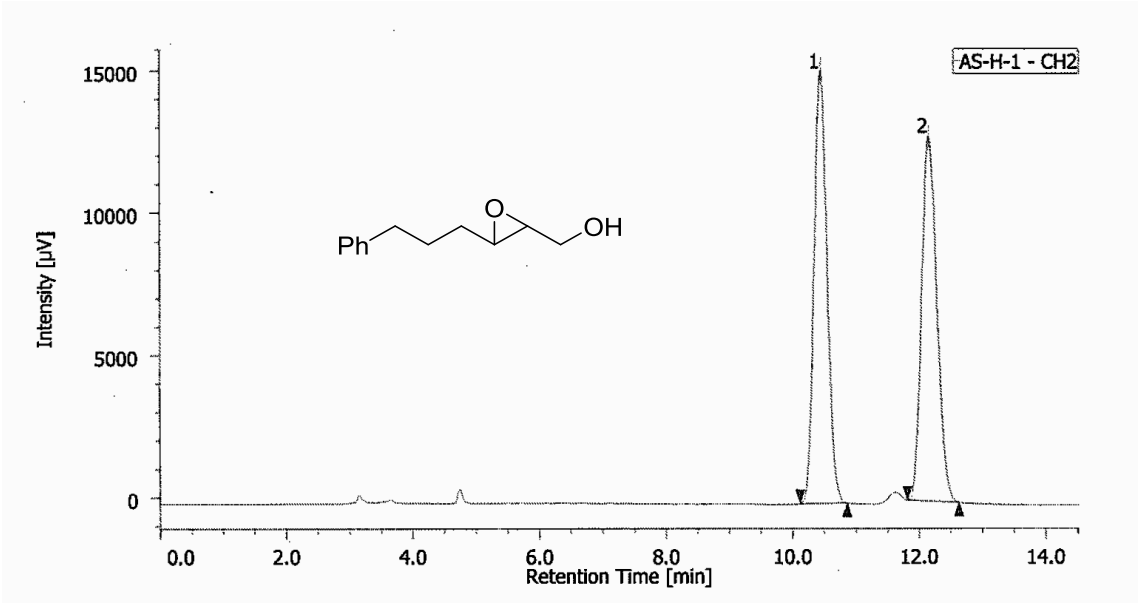
Oxidation of hydroxylic acid by oxoammonium species.

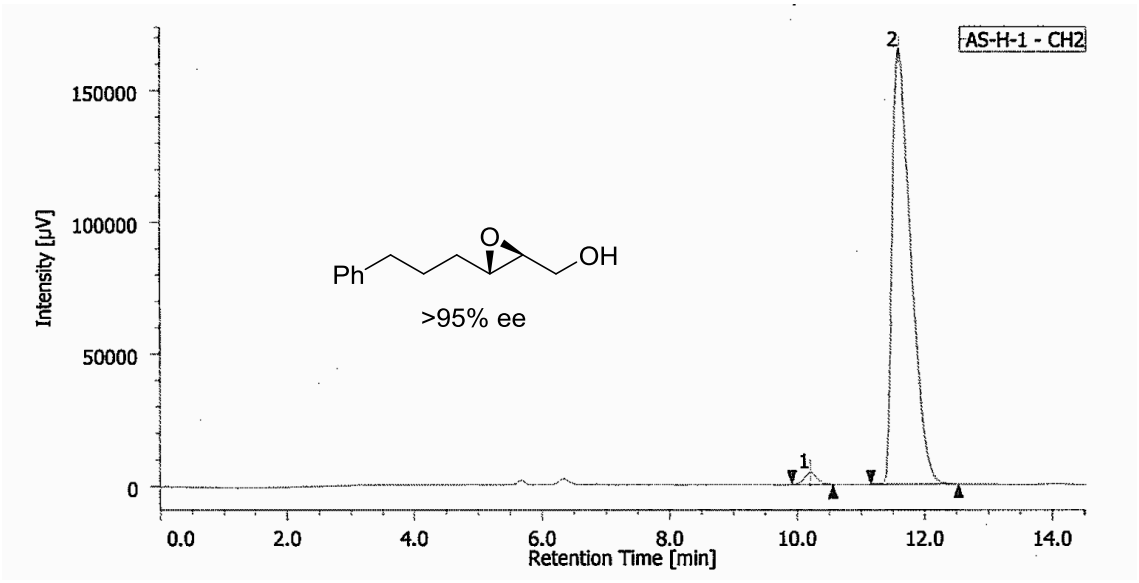


To a solution of hydroxylic acid **1b** (25.6 mg, 0.142 mmol) in toluene (710 µL, 0.20 M) and 1 M sodium phosphate buffer (510 µL, 0.28 M, pH = 6.8) was stirred at 25 °C. Then $TEMPO^{+}Cl^{-}$ (41.0 mg, 0.214 mmol) was added to the mixture and simultaneously stirred for 1 h. It was quenched with 1 M phosphate buffer (pH = 2.1), added NaCl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The product ratio was determined by NMR measurement of its crude material

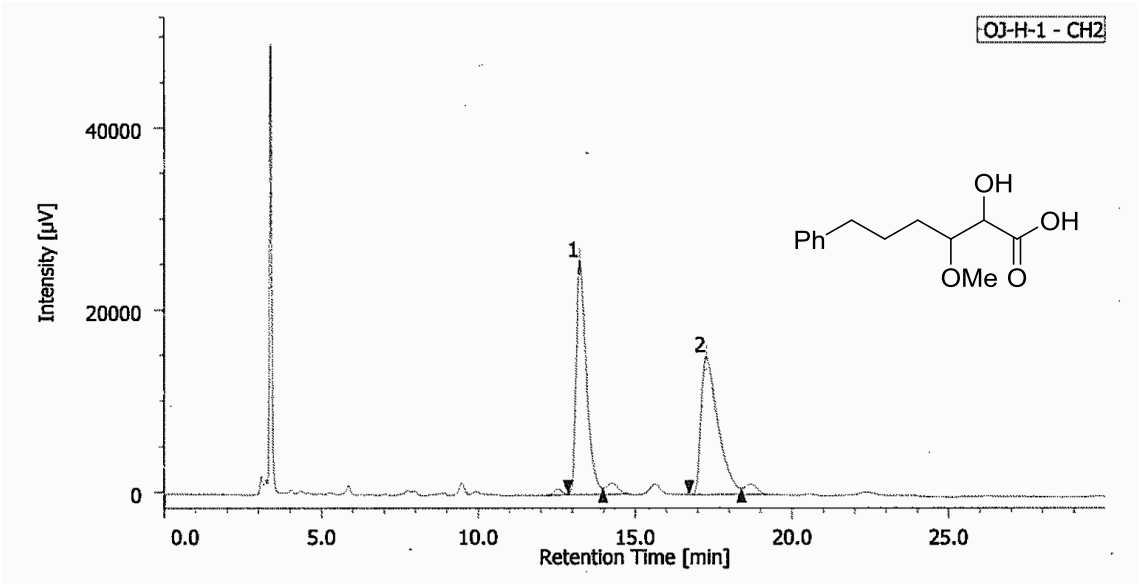
7. HPLC charts

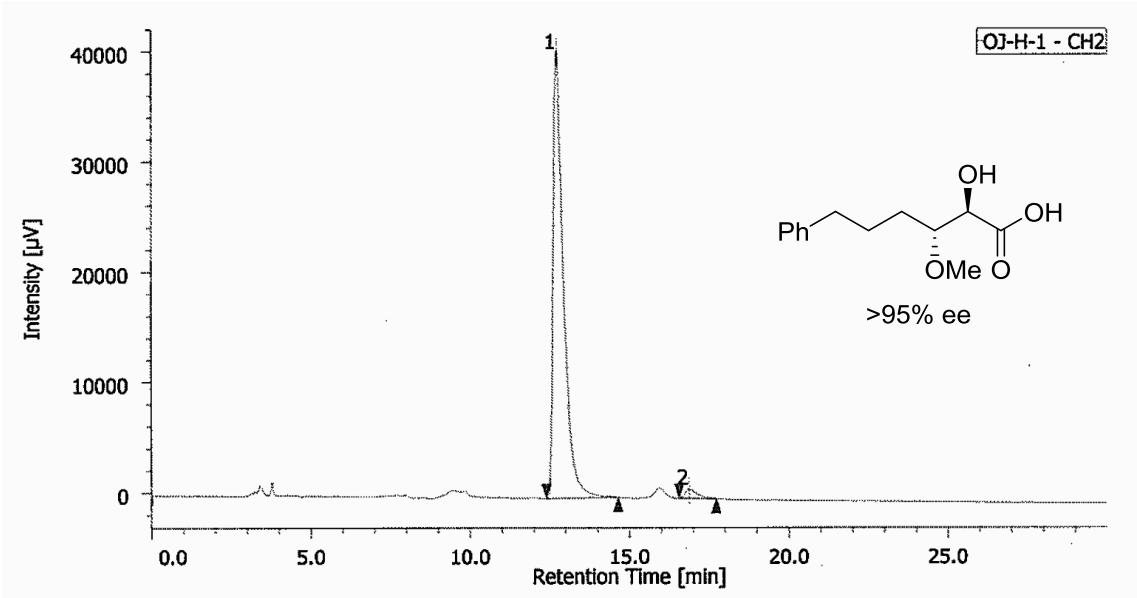
The enantiometric purity of **16** was determined to be >95% ee by chiral HPLC analysis using DAICEL CHIRALPAK AS-H. The conditions used for the analysis were as follow; Solvent: ^{i}PrOH-hexane (1:9 v/v). Flow rate: 1.0 mL/min. Retention time: major enantiomer (2*S*,3*S*)-**16**: 11.6 min, minor enentiomer (2*R*,3*R*)-**16**: 10.2 min.



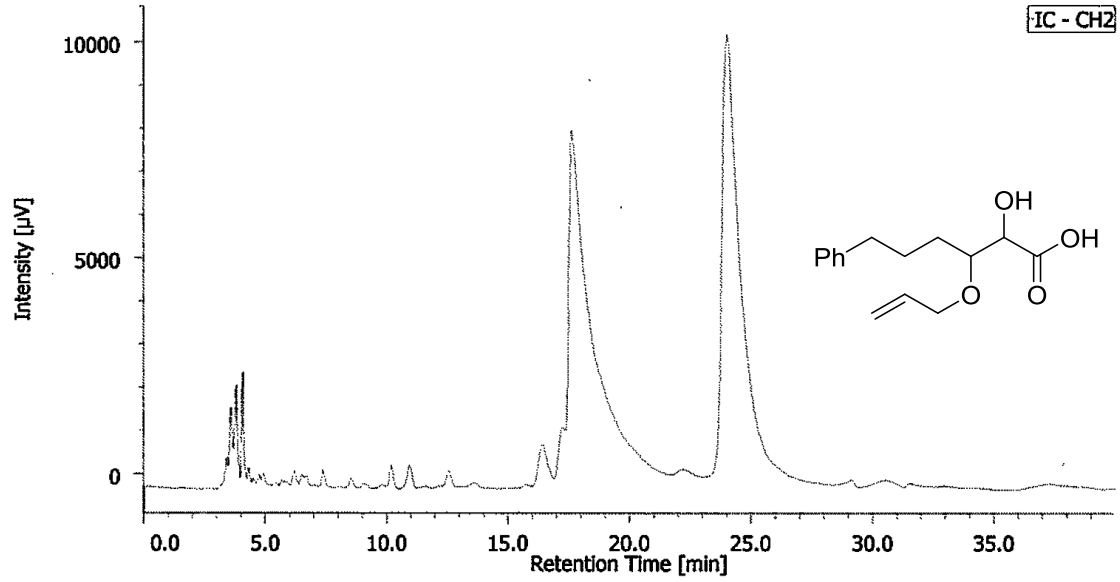


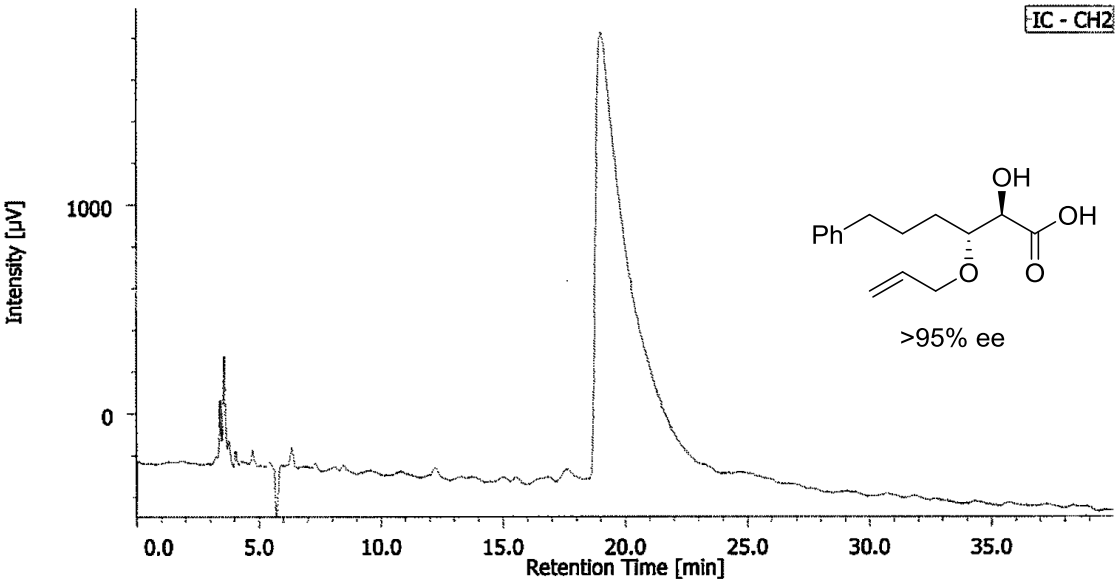
The enantiometric purity of **17b** was determined to be >95% ee by chiral HPLC analysis using DAICEL CHIRALCEL OJ-H. The conditions used for the analysis were as follow; Solvent: ^{i}PrOH-hexane-AcOH (1:9:0.01 v/v/v). Flow rate: 1.0 mL/min. Retention time: major enantiomer (2*R*,3*R*)-**17b**: 12.7 min, minor enentiomer (2*S*,3*S*)-**17b**: 16.9 min.



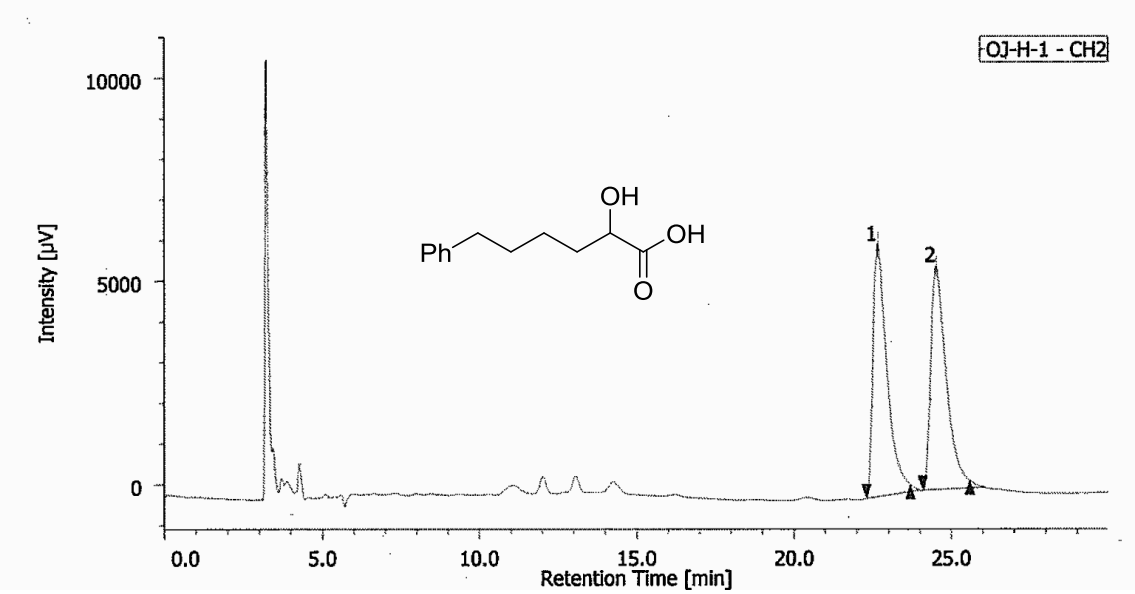


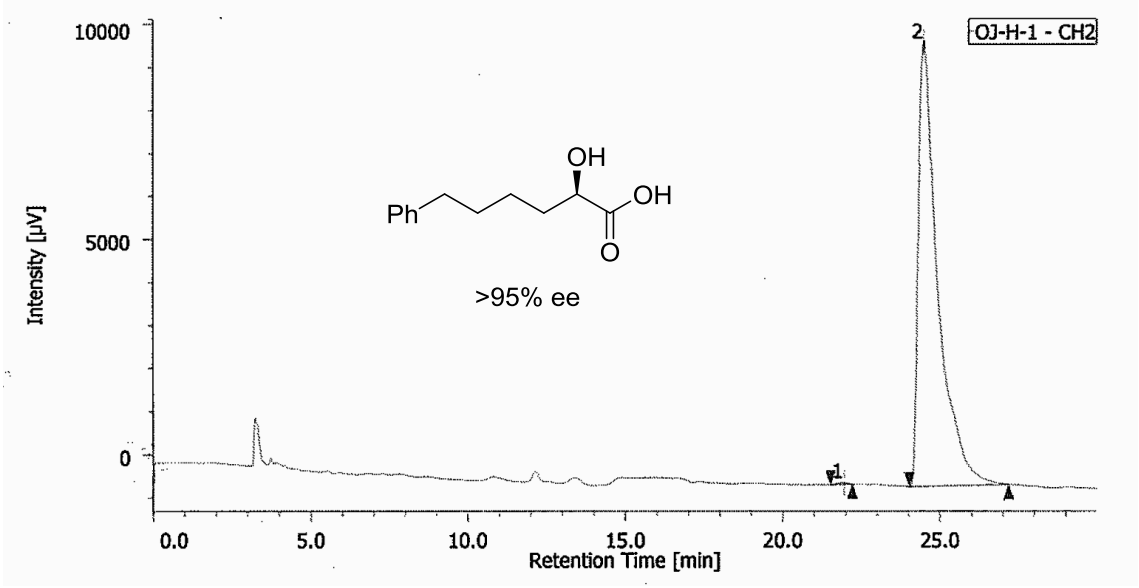
The enantiometric purity of **18b** was determined to be >95% ee by chiral HPLC analysis using DAICEL CHIRALPAK IC. The conditions used for the analysis were as follow; Solvent: ^{i}PrOH-hexane-AcOH (5:95:0.01 v/v/v). Flow rate: 1.0 mL/min. Retention time: major enantiomer (2*R*,3*R*)-**18b**: 19.0 min, minor enentiomer (2*S*,3*S*)-**18b**: 24.0 min.



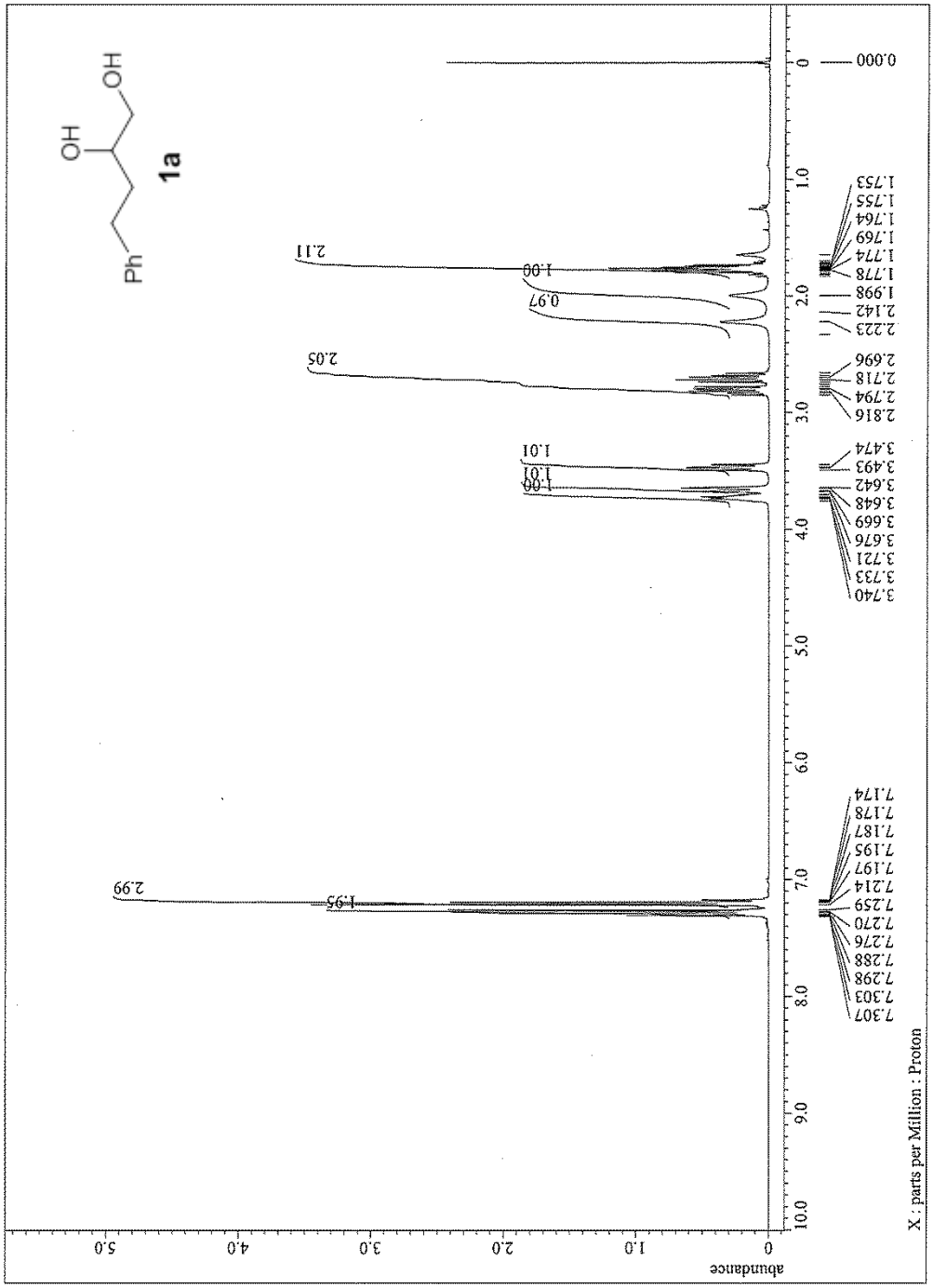


The enantiometric purity of **19b** was determined to be >95% ee by chiral HPLC analysis using DAICEL CHIRALCEL OJ-H. The conditions used for the analysis were as follow; Solvent: ^{i}PrOH-hexane-AcOH (1:9:0.01 v/v/v). Flow rate: 1.0 mL/min. Retention time: major enantiomer (2*R*)-**19b**: 24.5 min, minor enentiomer (2*S*)-**19b**: 21.9min.





8. NMR charts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OH
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1.755
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1.769
1.774
1.778
1.998
2.142
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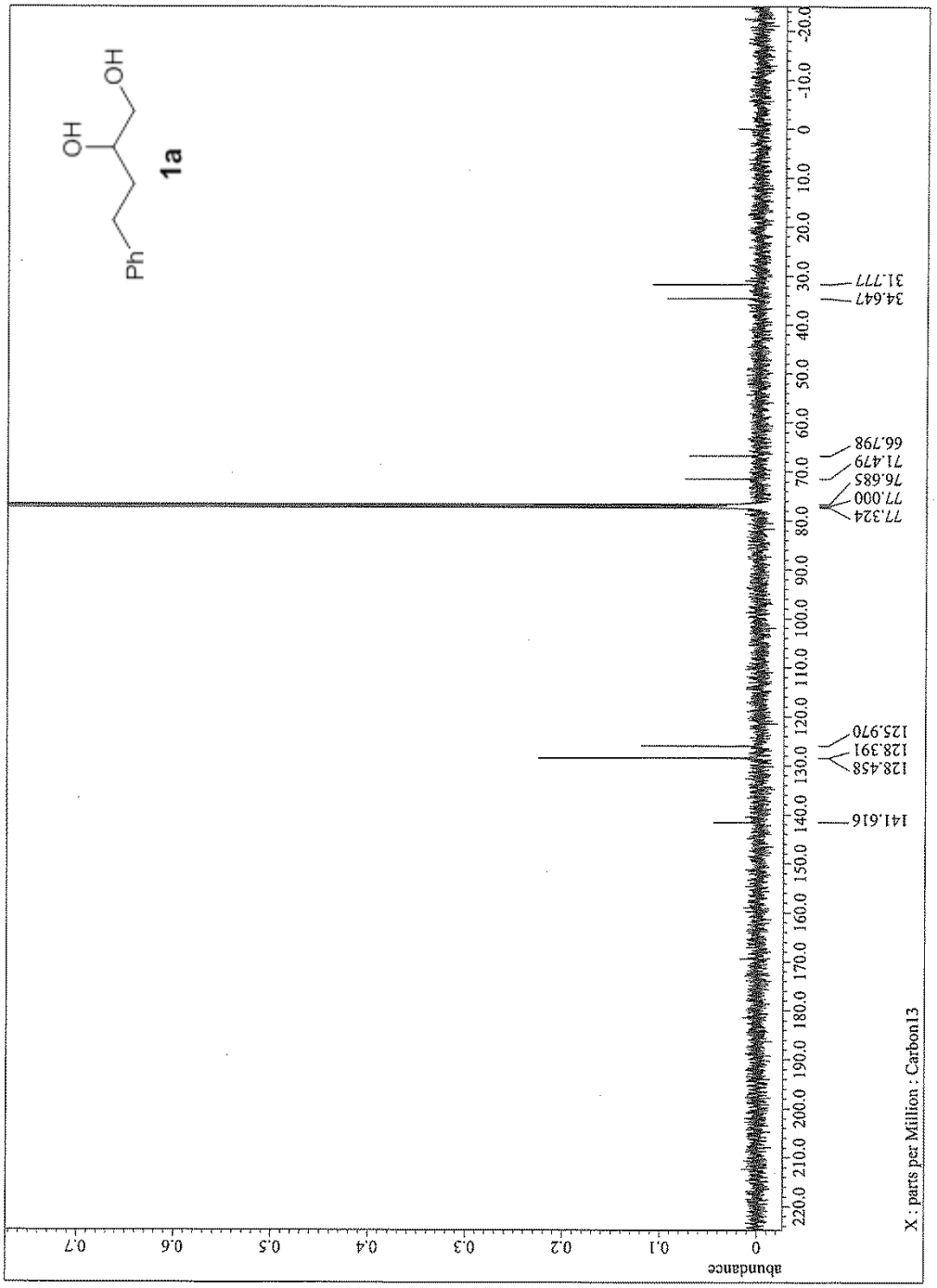
2.696
2.718
2.794
2.816
3.474
3.493
3.642
3.648
3.669
3.676
3.721
3.733
3.740
7.174
7.178
7.187
7.195
7.197
7.214
7.259
7.270
7.276
7.288
7.298
7.303
7.307
2.99
1.95
2.11
1.00
0.97
2.05
1.00
1.01
1.01
abundance
X : parts per Million : Proton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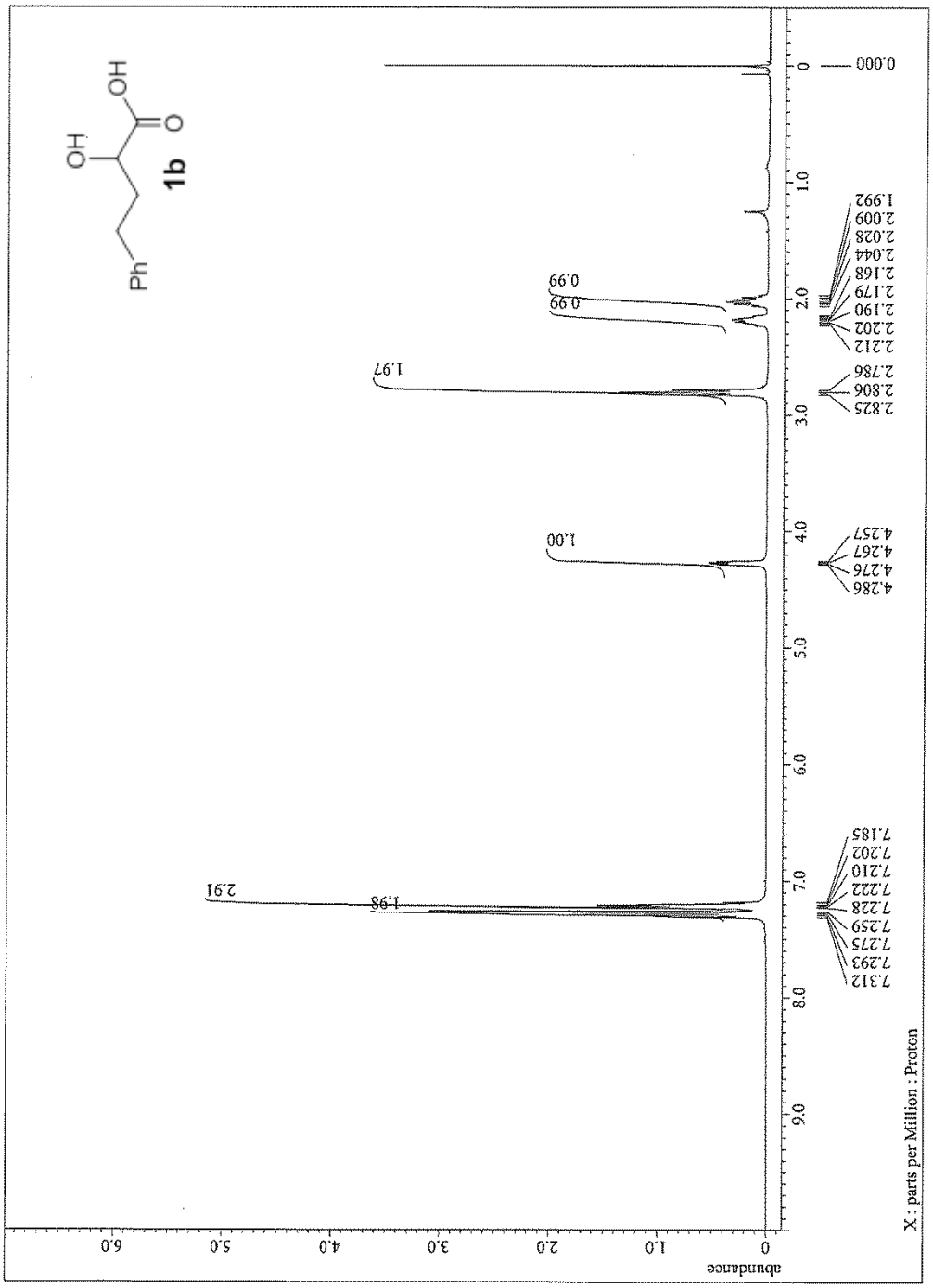
X : parts per Million : Carbon13
abundance


1b
OH
OH
O
Ph
X : parts per Million : Proton
abundance
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2.009
2.028
2.044
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2.179
2.190
2.202
2.212
2.786
2.806
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4.267
4.276
4.286
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7.202
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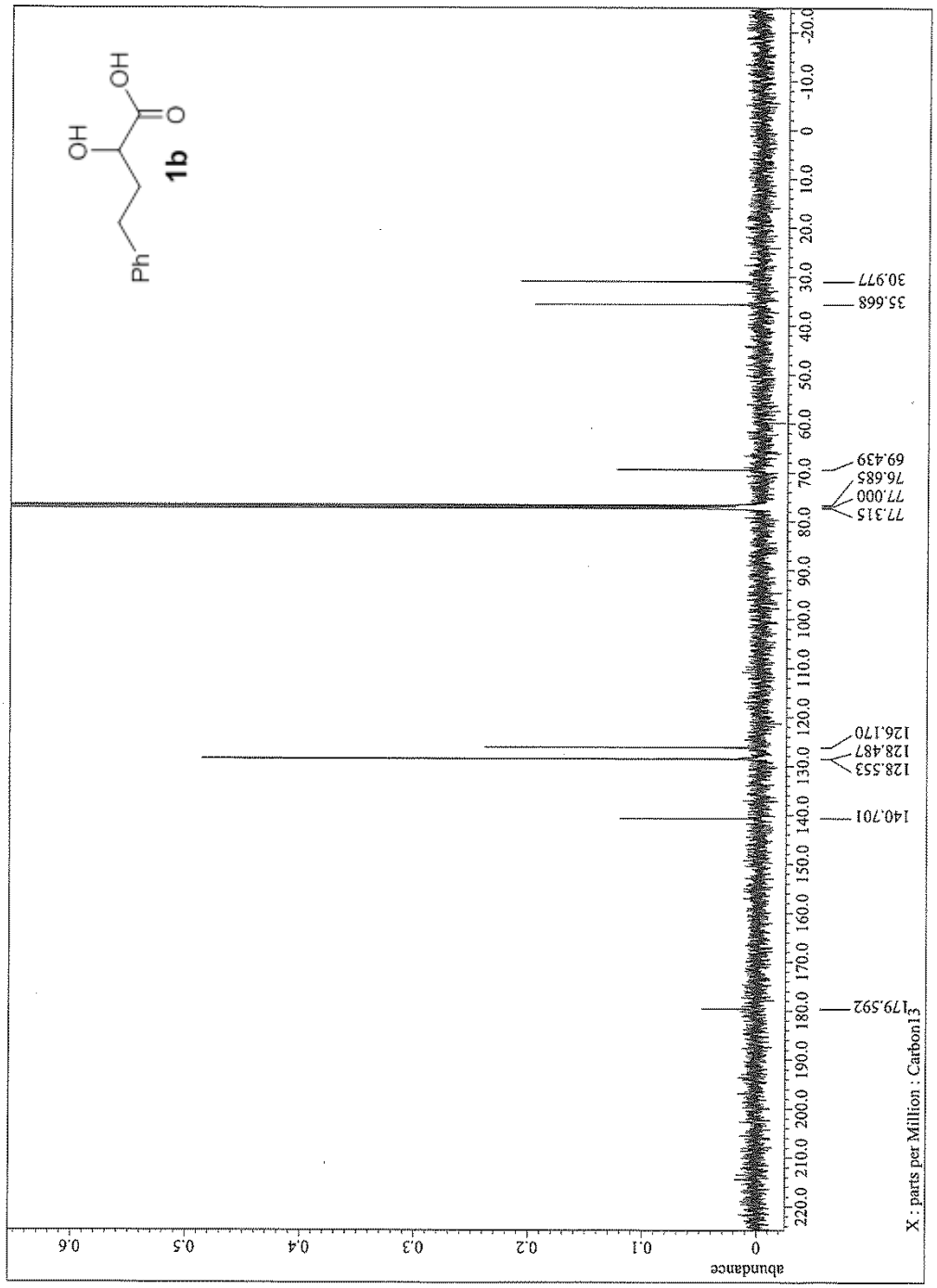
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O
Ph
1b
abundance
X : parts per Million : Carbon13
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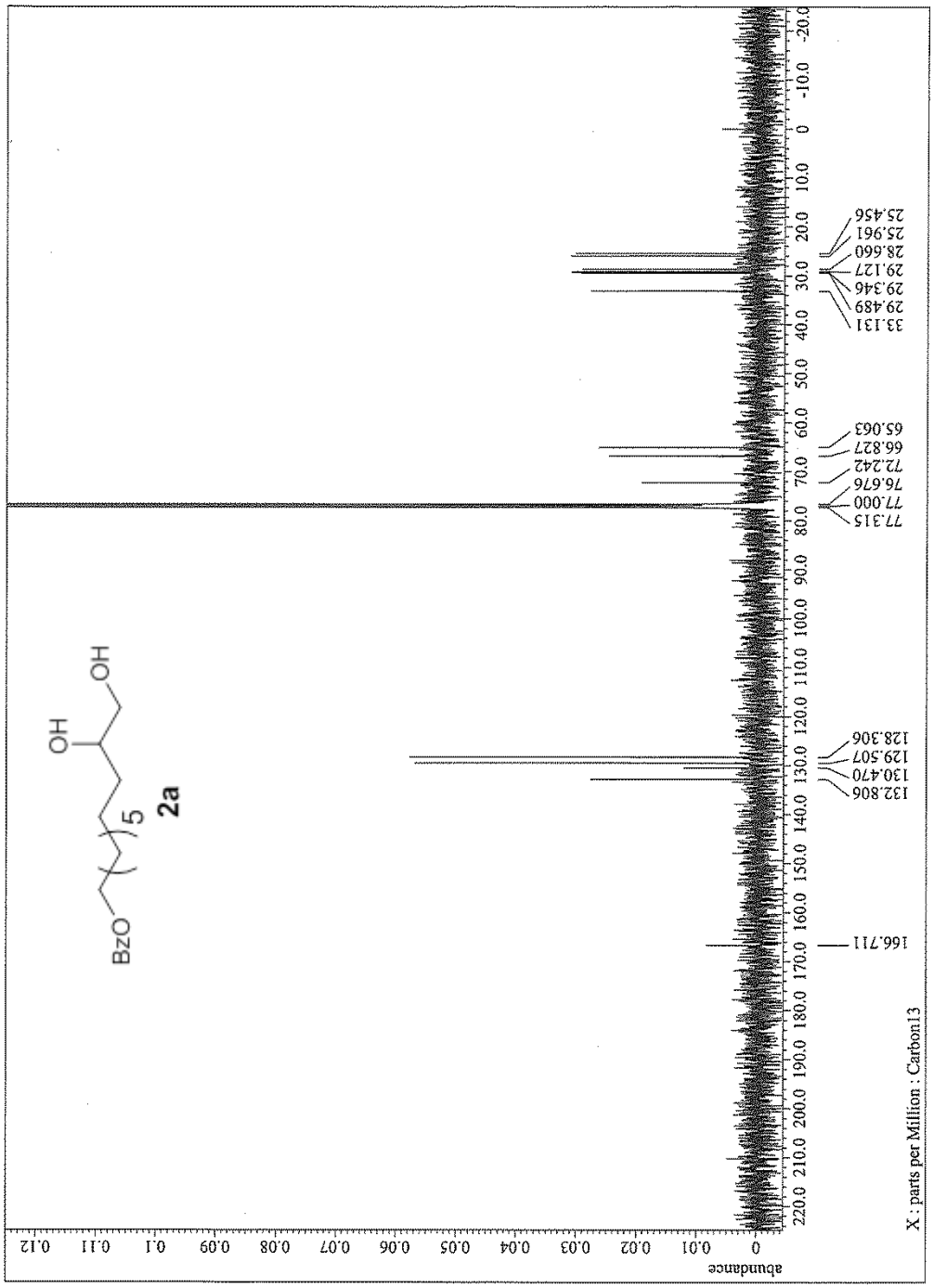
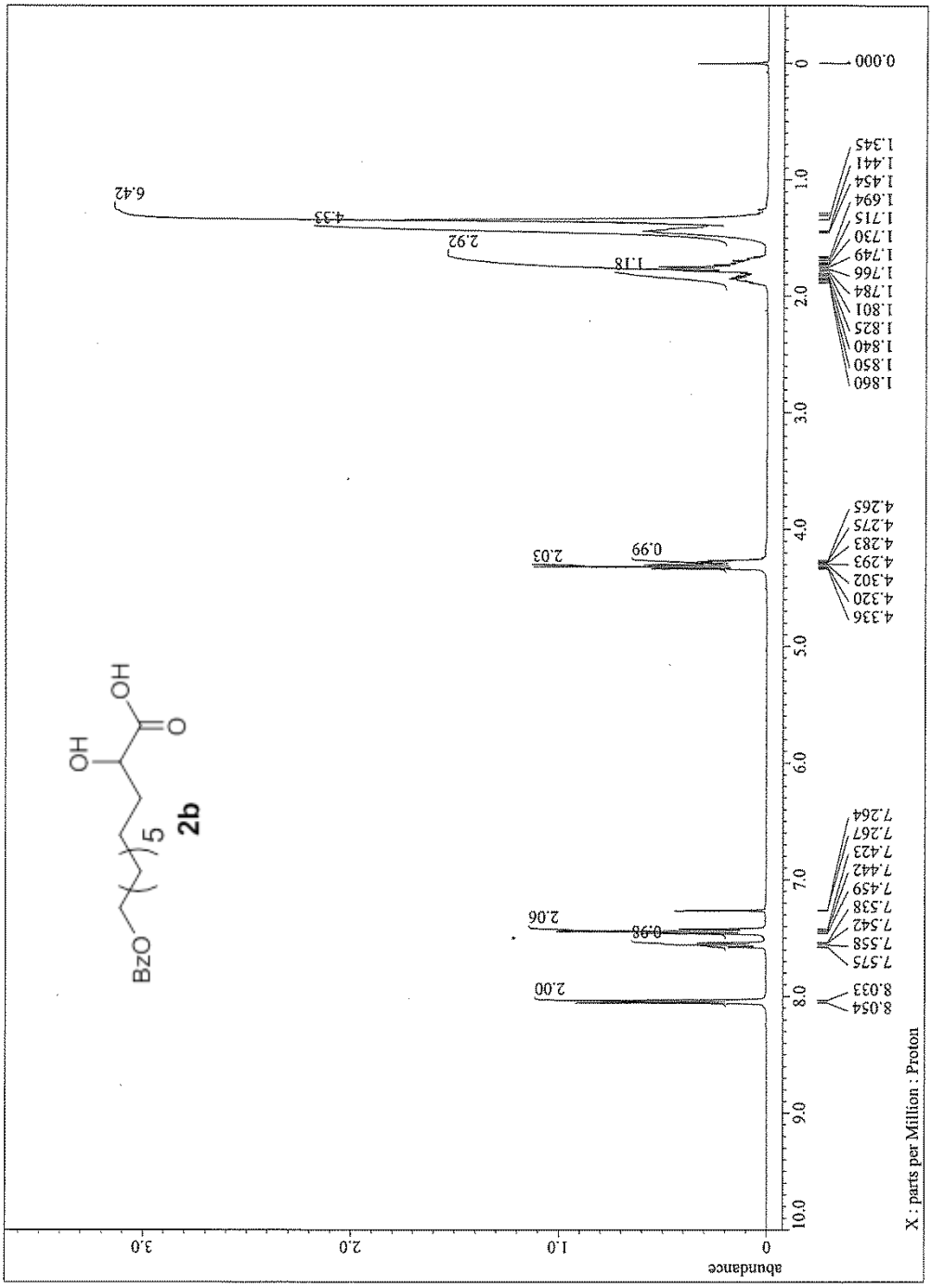
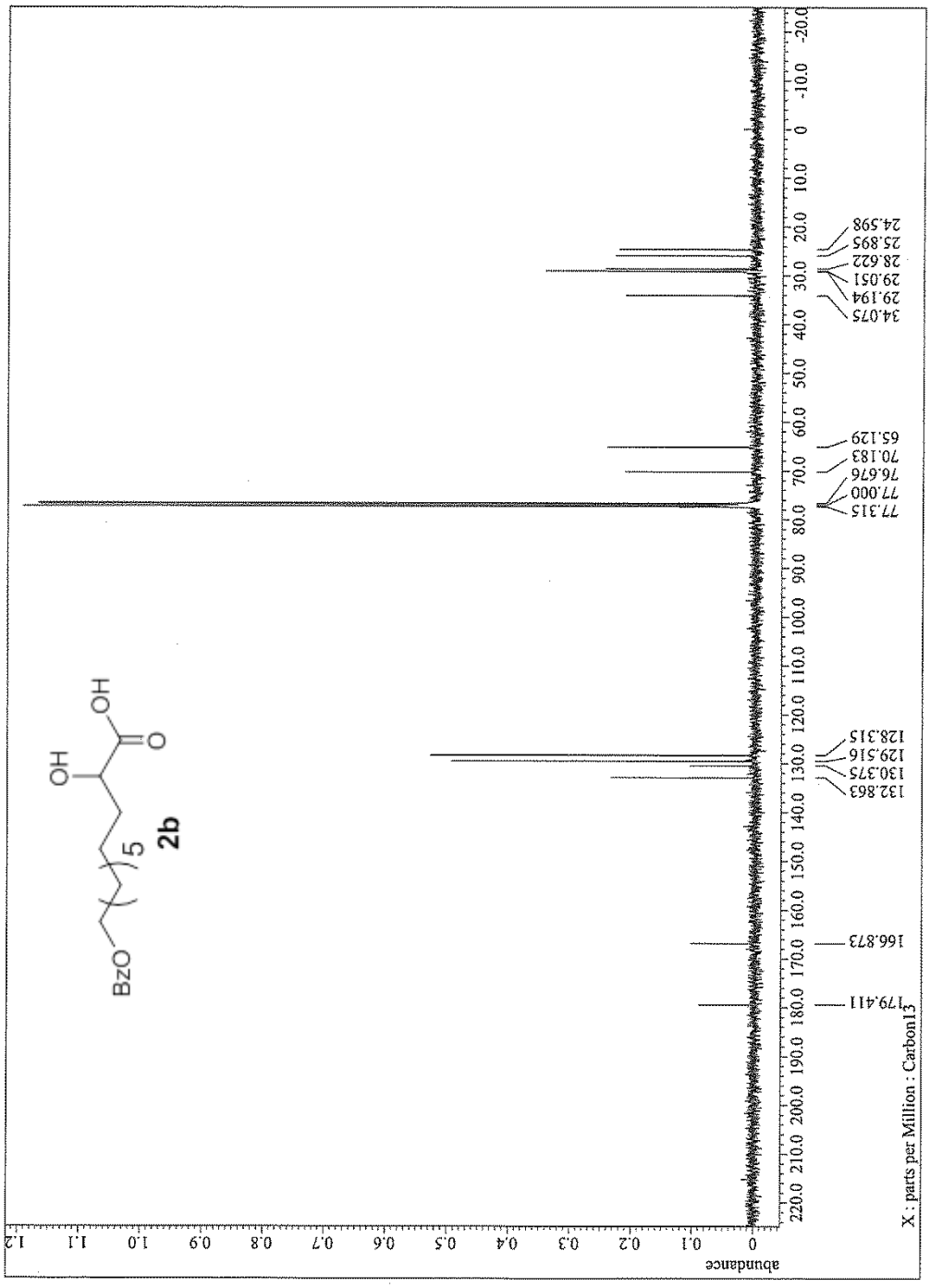
128.487
126.170
77.315
77.000
76.685
69.439
35.668
30.977

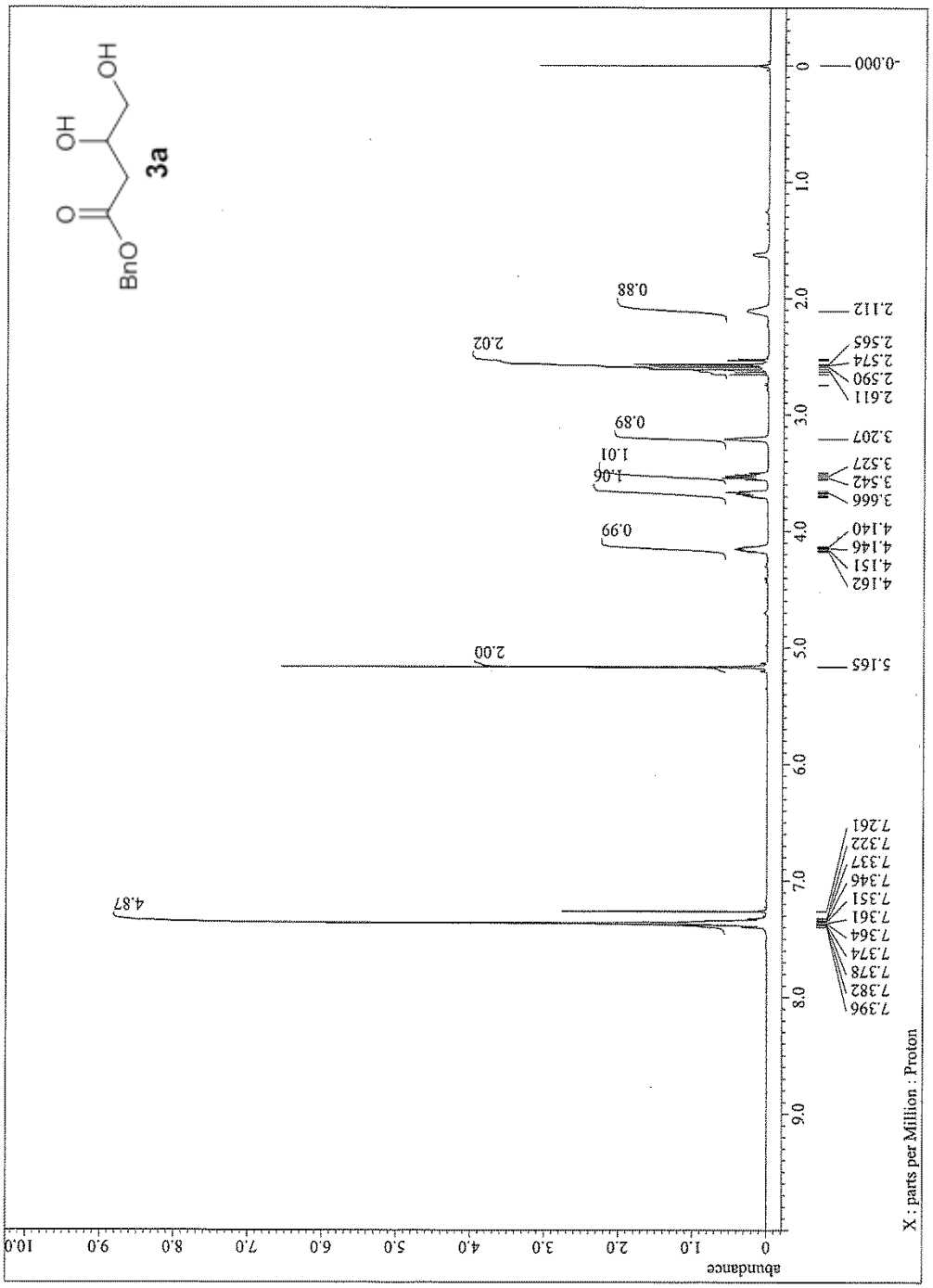
2a
BzO
OH
OH
5
X : parts per Million : Proton
abundance
12.49
2.08
2.05
2.00
2.00
1.97
1.00
0.99
0.97
0.93
0.87
-0.000

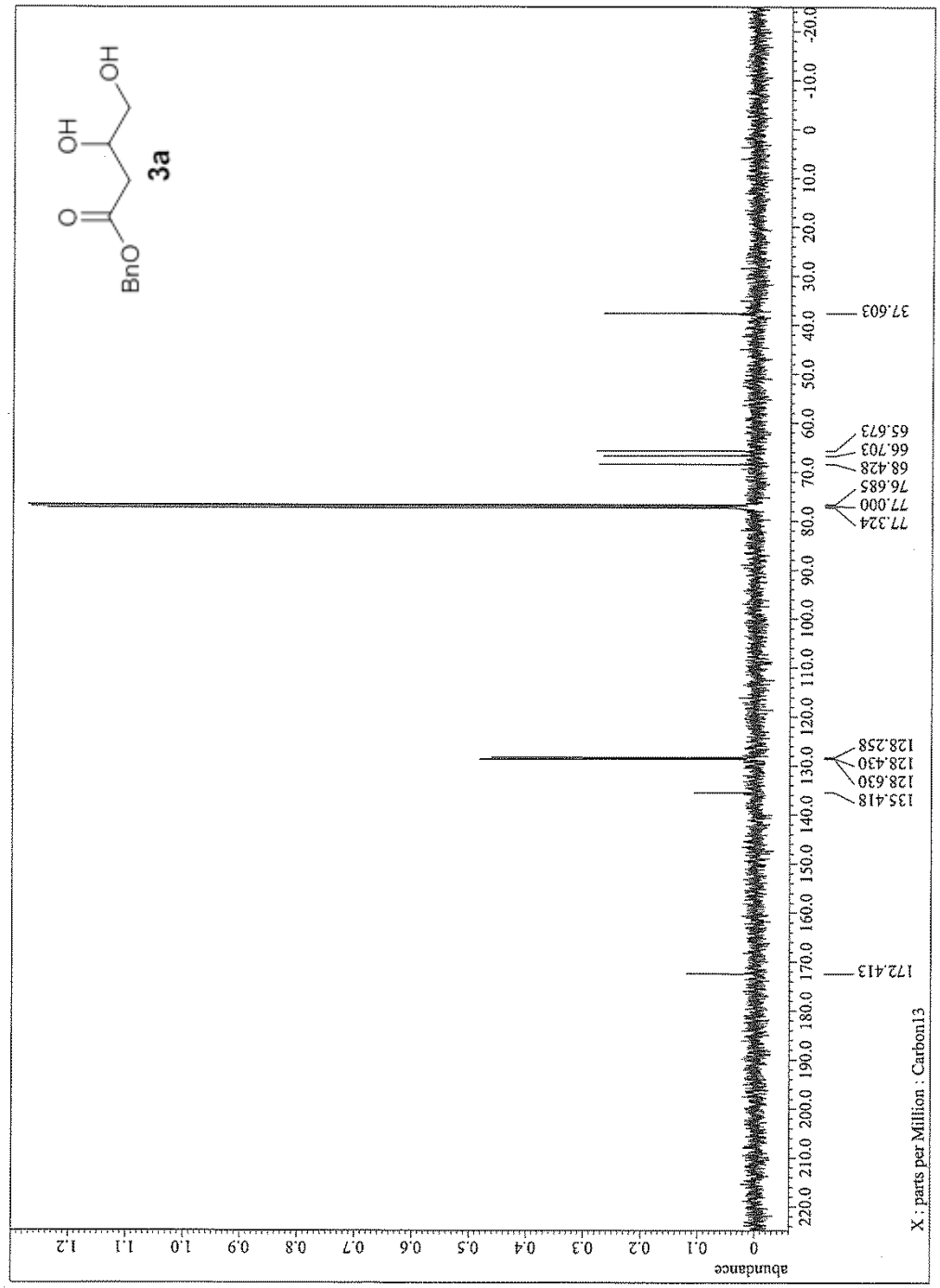

BzO
OH
OH
5
2a
X : parts per Million : Carbon13
abundance
166.711
132.806
130.470
129.507
128.306
77.315
77.000
76.676
72.242
66.827
65.063
33.131
29.489
29.346
29.127
28.660
25.961
25.456


2b
X : parts per Million : Proton
abundance
0.000
8.054
8.033
7.575
7.558
7.542
7.538
7.459
7.442
7.423
7.267
7.264
4.336
4.320
4.302
4.293
4.283
4.275
4.265
1.860
1.850
1.840
1.825
1.801
1.784
1.766
1.749
1.730
1.715
1.694
1.454
1.441
1.345
6.42
4.33
2.92
1.18
0.99
2.03
0.98
2.06
2.00
OH
OH
O
BzO
5
2b

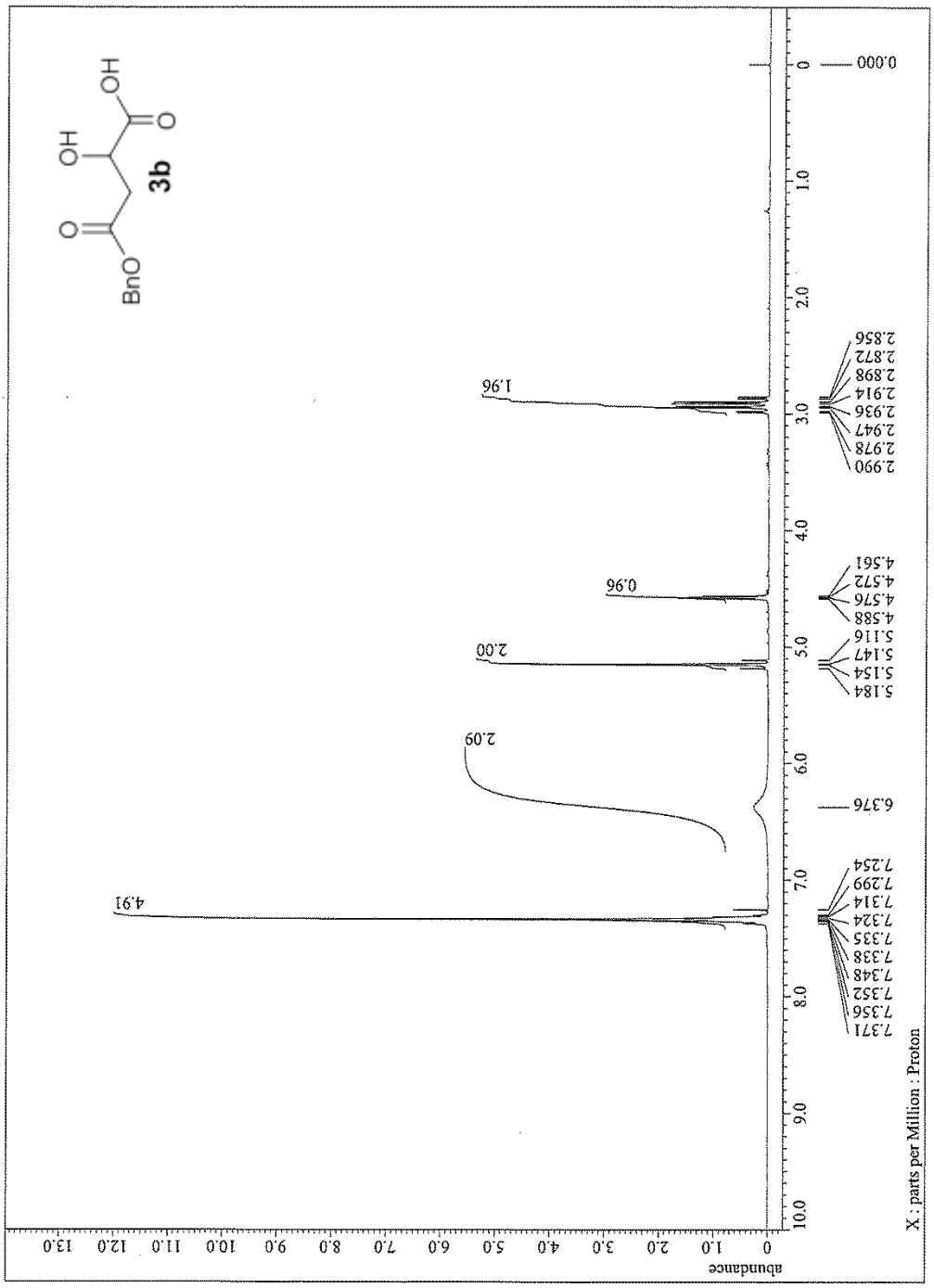

2b
BzO
OH
OH
O
5
X : parts per Million : Carbon13
179.411
166.873
132.863
130.375
129.516
128.315
77.315
77.000
76.676
70.183
65.129
34.075
29.194
29.051
28.622
25.895
24.598
abundance

2b


3a
OH
OH
O
BnO
X : parts per Million : Proton
abundance
-0.000
0.88
2.02
0.89
1.01
1.06
0.99
2.00
4.87
2.112
2.565
2.574
2.590
2.611
3.207
3.527
3.542
3.666
4.140
4.146
4.151
4.162
5.165
7.261
7.322
7.337
7.346
7.351
7.361
7.364
7.374
7.378
7.382
7.396


3a
OH
OH
O
BnO
172.413
135.418
128.258
128.430
128.630
77.324
77.000
76.685
68.428
66.703
65.673
37.603
X : parts per Million : Carbon13
abundance

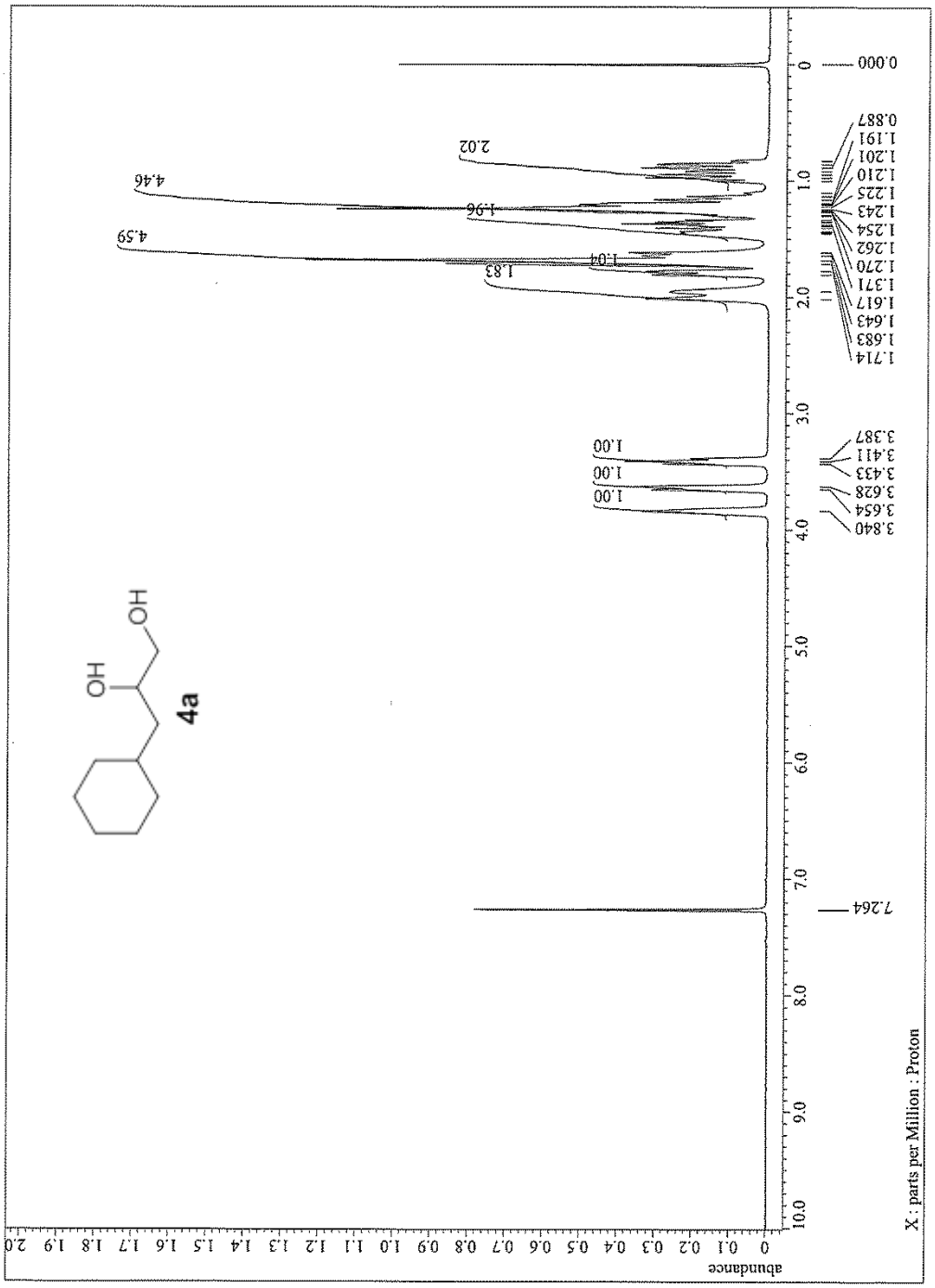
3c

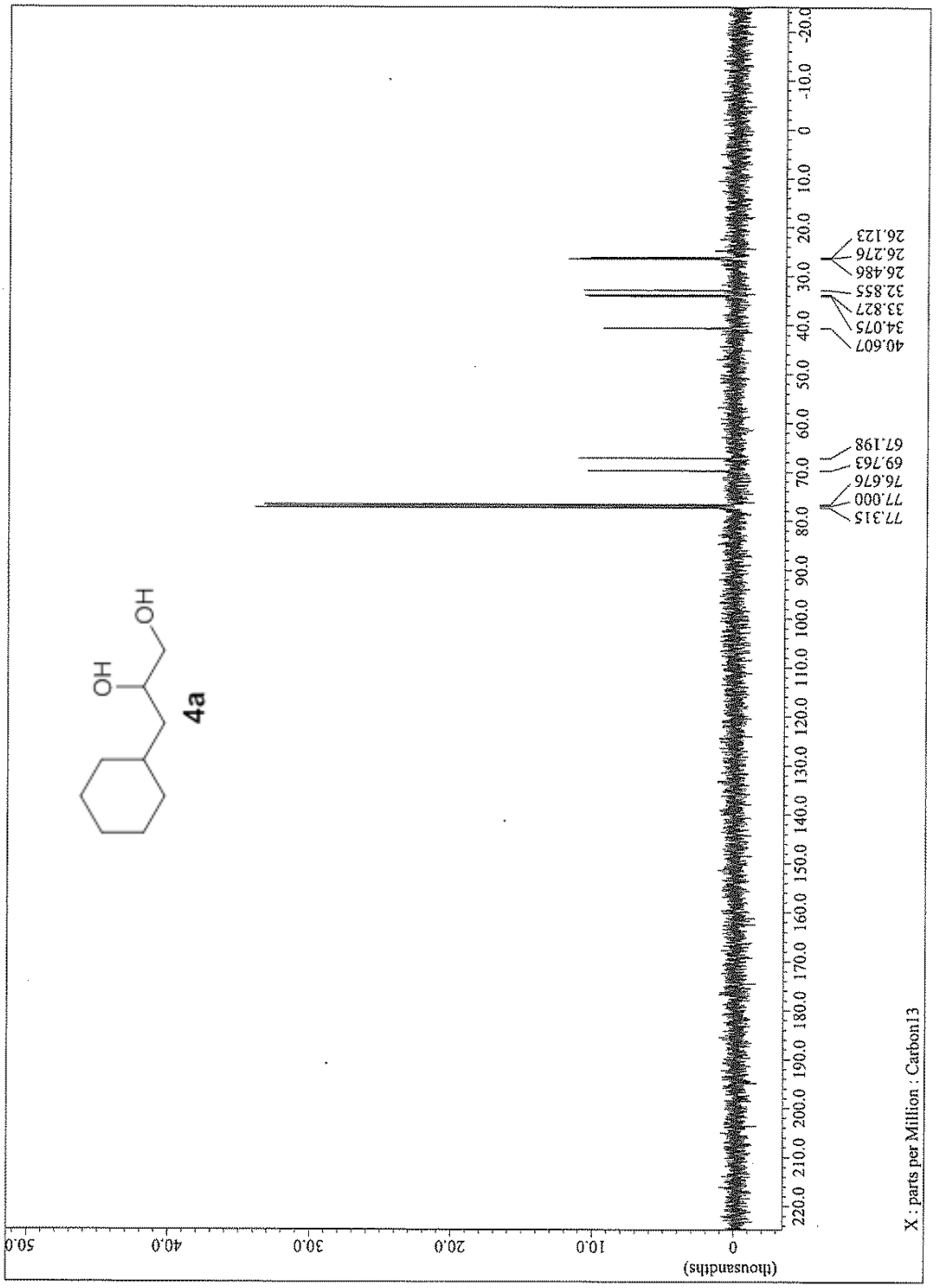

3b
BnO
OH
OH
O
O
O
4.91
2.09
2.00
0.96
1.96
0.000
6.376
7.371
7.356
7.352
7.348
7.338
7.335
7.324
7.314
7.299
7.254
5.184
5.154
5.147
5.116
4.588
4.576
4.572
4.561
2.990
2.978
2.947
2.936
2.914
2.898
2.872
2.856
abundance
X : parts per Million : Proton

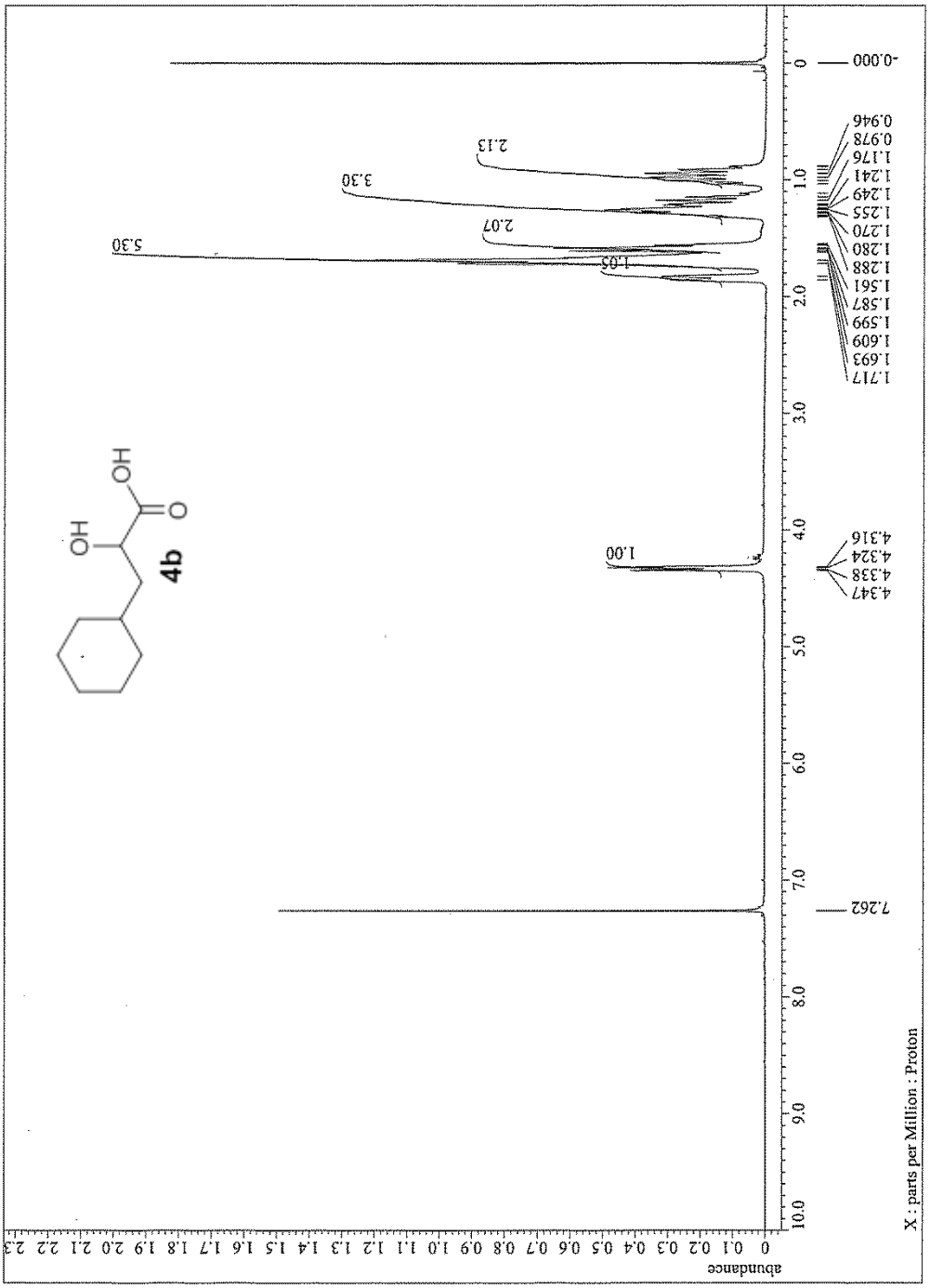
3b

3b
BnO
OH
OH
O
O
O
38.280
66.903
67.103
76.676
77.000
77.315
128.258
128.439
128.582
135.123
170.916
176.713
X : parts per Million : Carbon13
abundance

3b

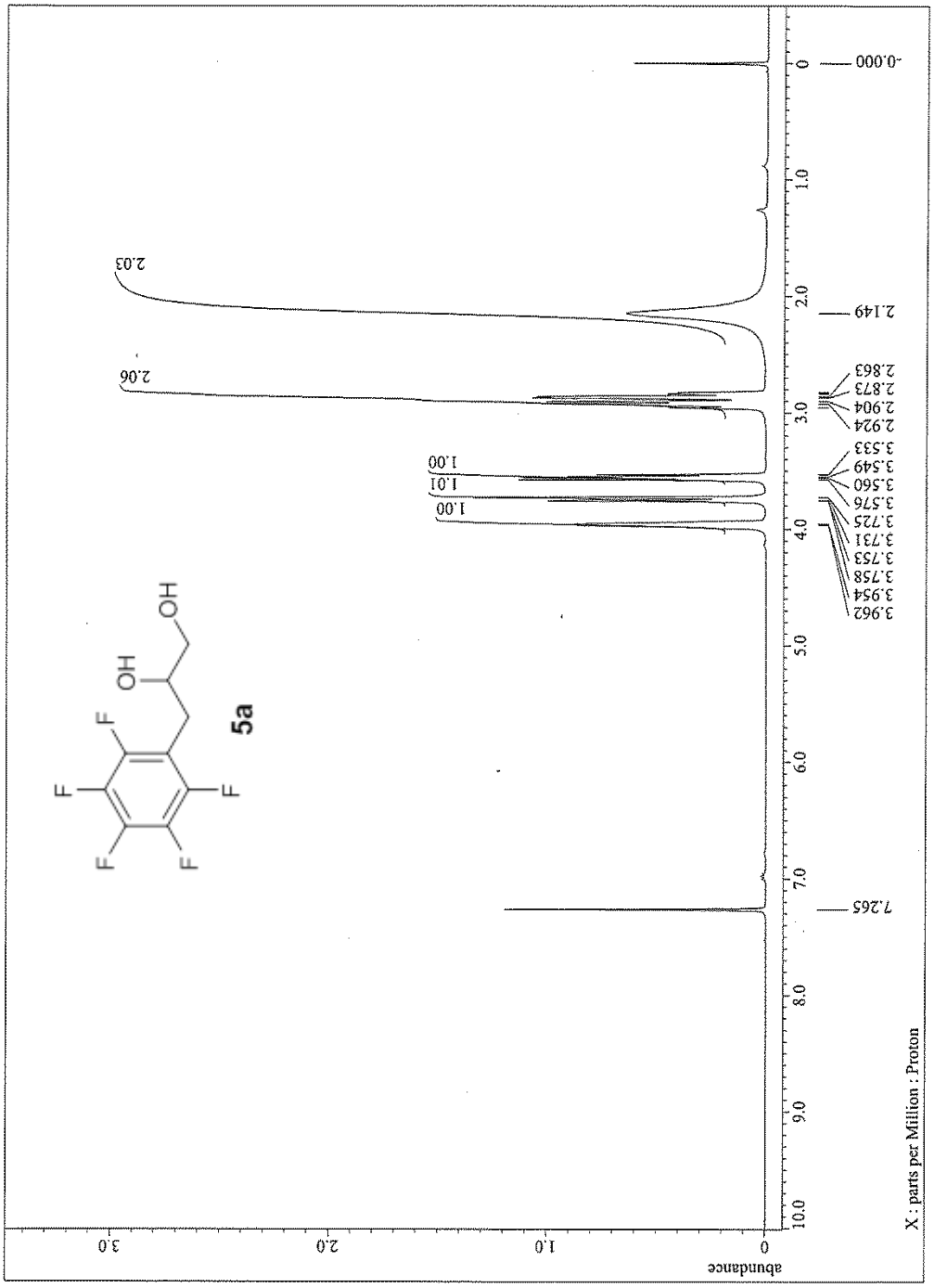

4a
OH
OH
7.264
3.840
3.654
3.628
3.433
3.411
3.387
1.714
1.683
1.643
1.617
1.371
1.270
1.262
1.254
1.243
1.225
1.210
1.201
1.191
0.887
0.000
4.59
4.46
2.02
1.96
1.83
1.04
1.00
1.00
1.00
X : parts per Million : Proton
abundance

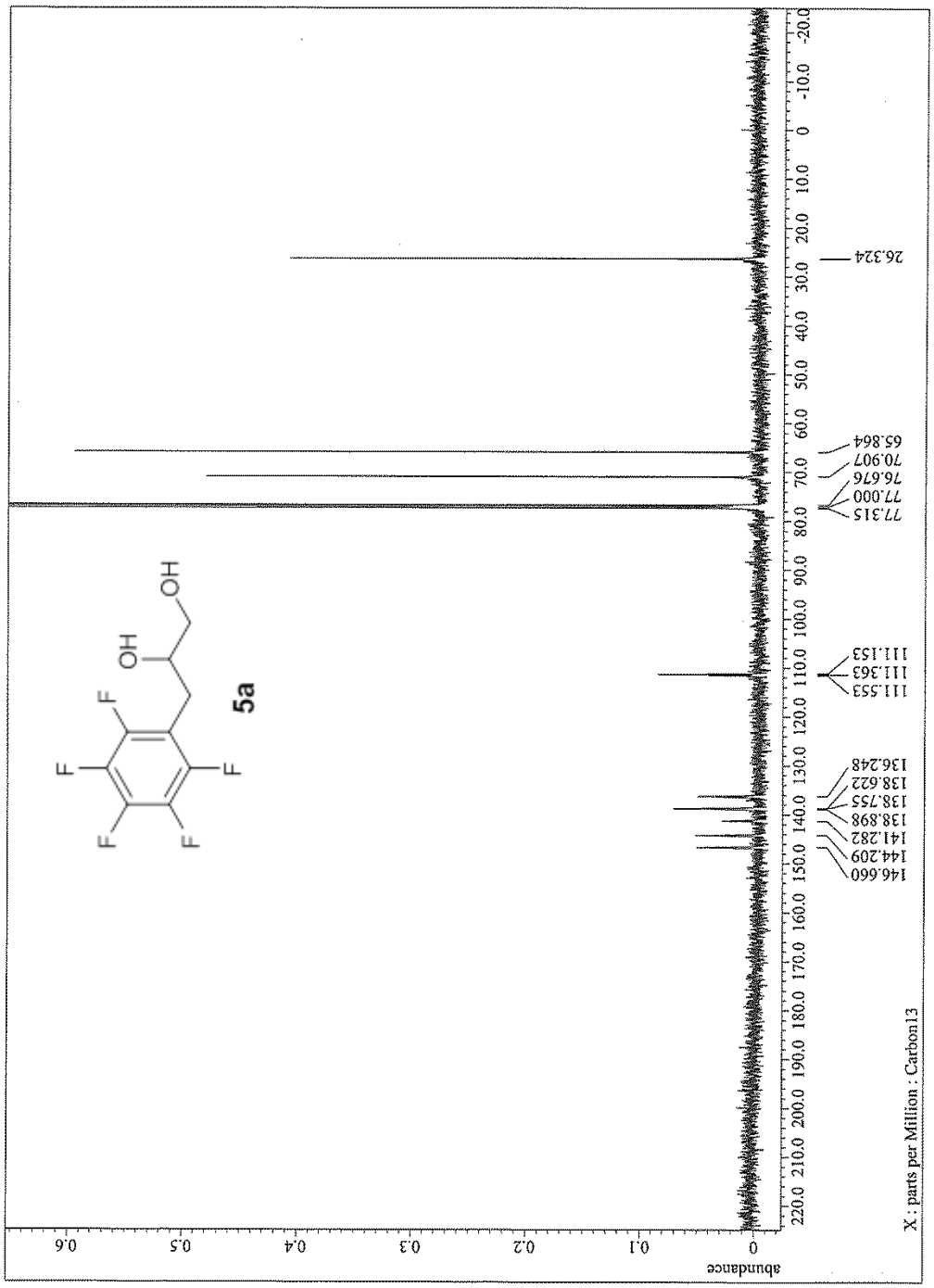

OH
OH
4a
(thousandths)
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13
77.315
77.000
76.676
69.763
67.198
40.607
34.075
33.827
32.855
26.486
26.276
26.123

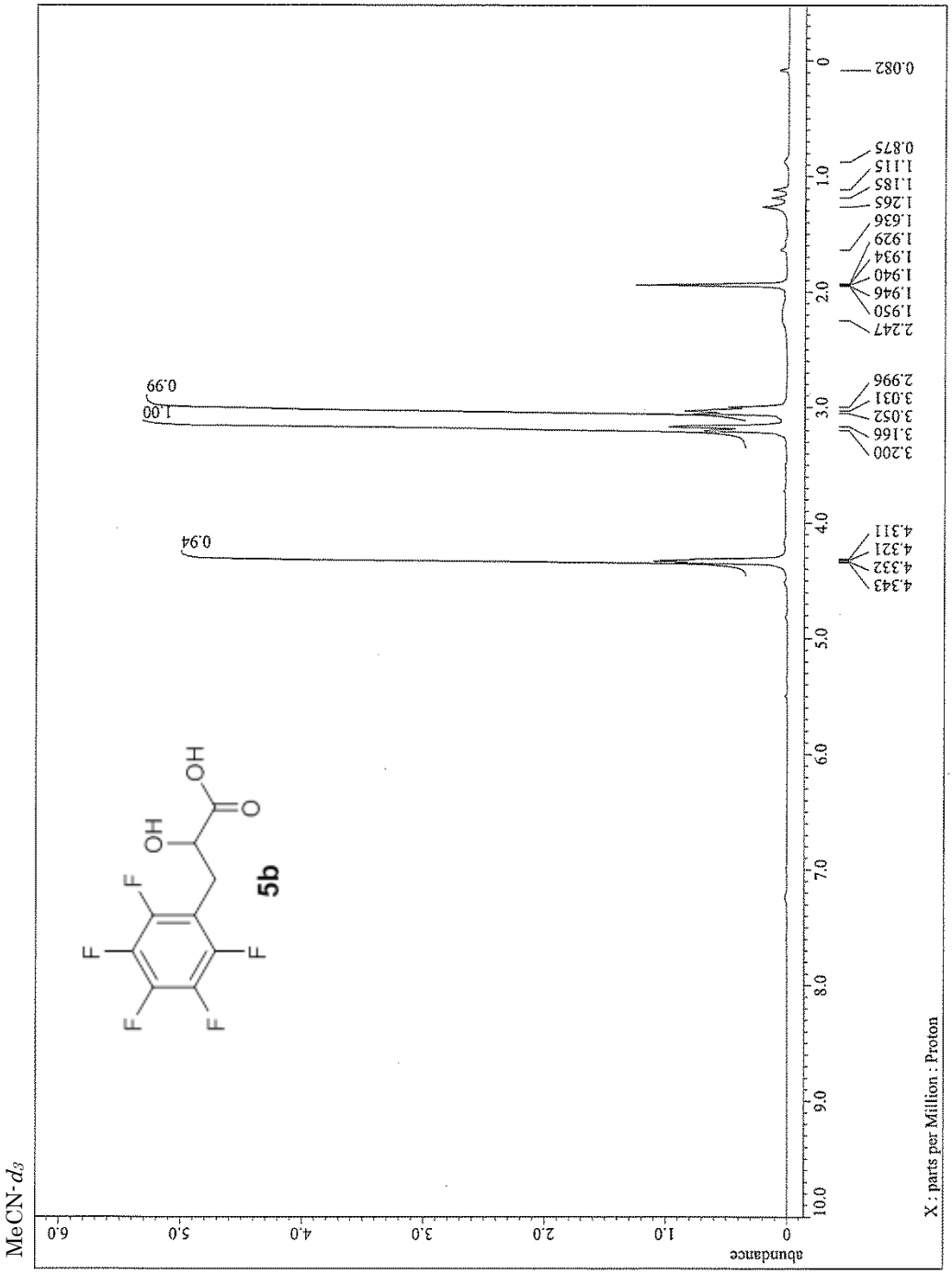

4b
7.262
4.347
4.338
4.324
4.316
1.717
1.693
1.609
1.599
1.587
1.561
1.288
1.280
1.270
1.255
1.249
1.241
1.176
0.978
0.946
-0.000
1.00
1.05
5.30
2.07
3.30
2.13
X : parts per Million : Proton
abundance

4b
OH
OH
O
abundance
0
0.1
0.2
0.3
X : parts per Million : Carbon13
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 -10.0 -20.0
179.964
77.315
77.000
76.685
68.276
41.636
33.856
33.570
32.016
26.362
26.162
25.923

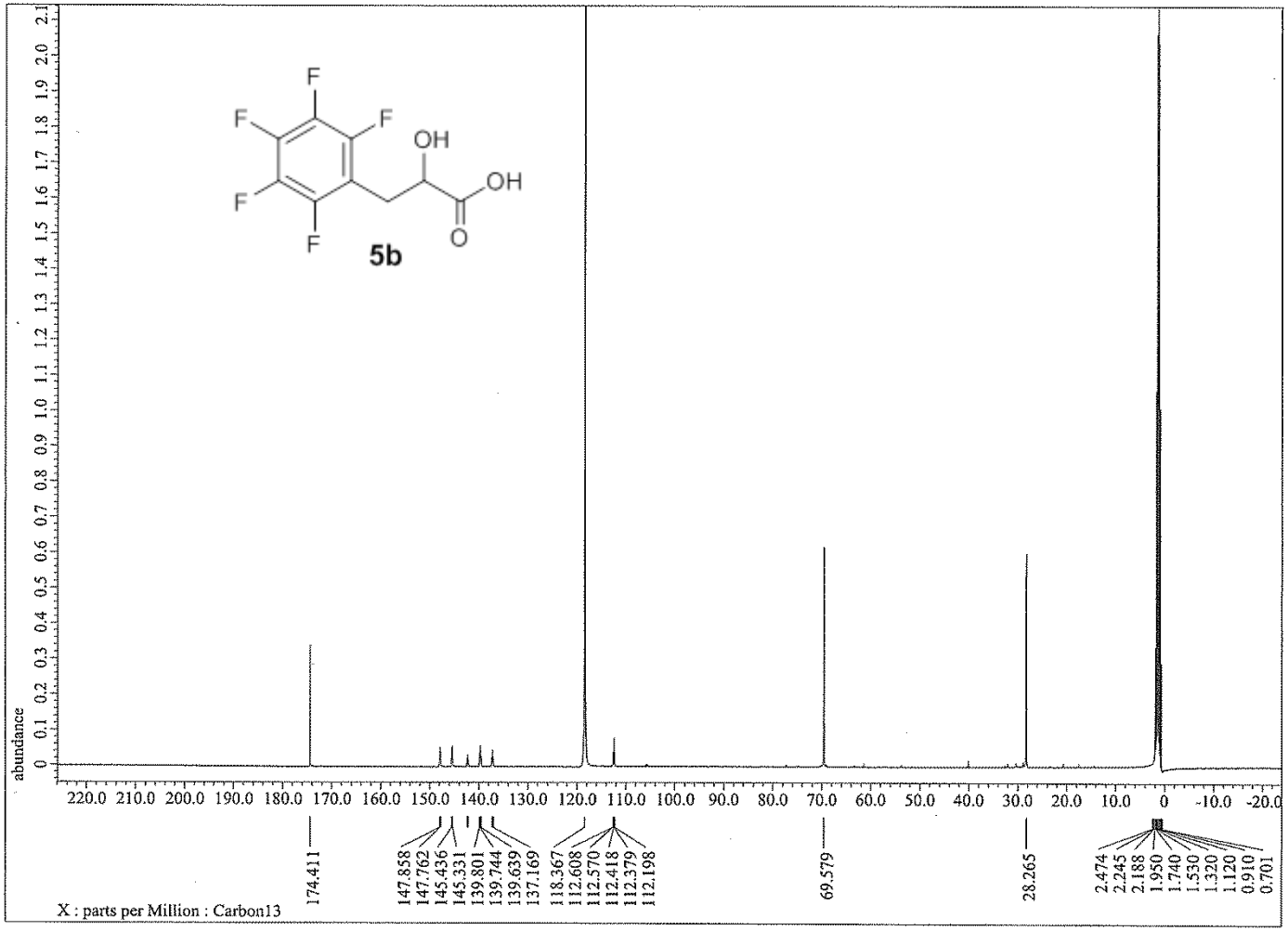
4b


5a
F
F
F
F
F
OH
OH
7.265
3.962
3.954
3.758
3.753
3.731
3.725
3.576
3.560
3.549
3.533
2.924
2.904
2.873
2.863
2.149
2.06
2.03
1.00
1.01
1.00
-0.000
X : parts per Million : Proton
abundance

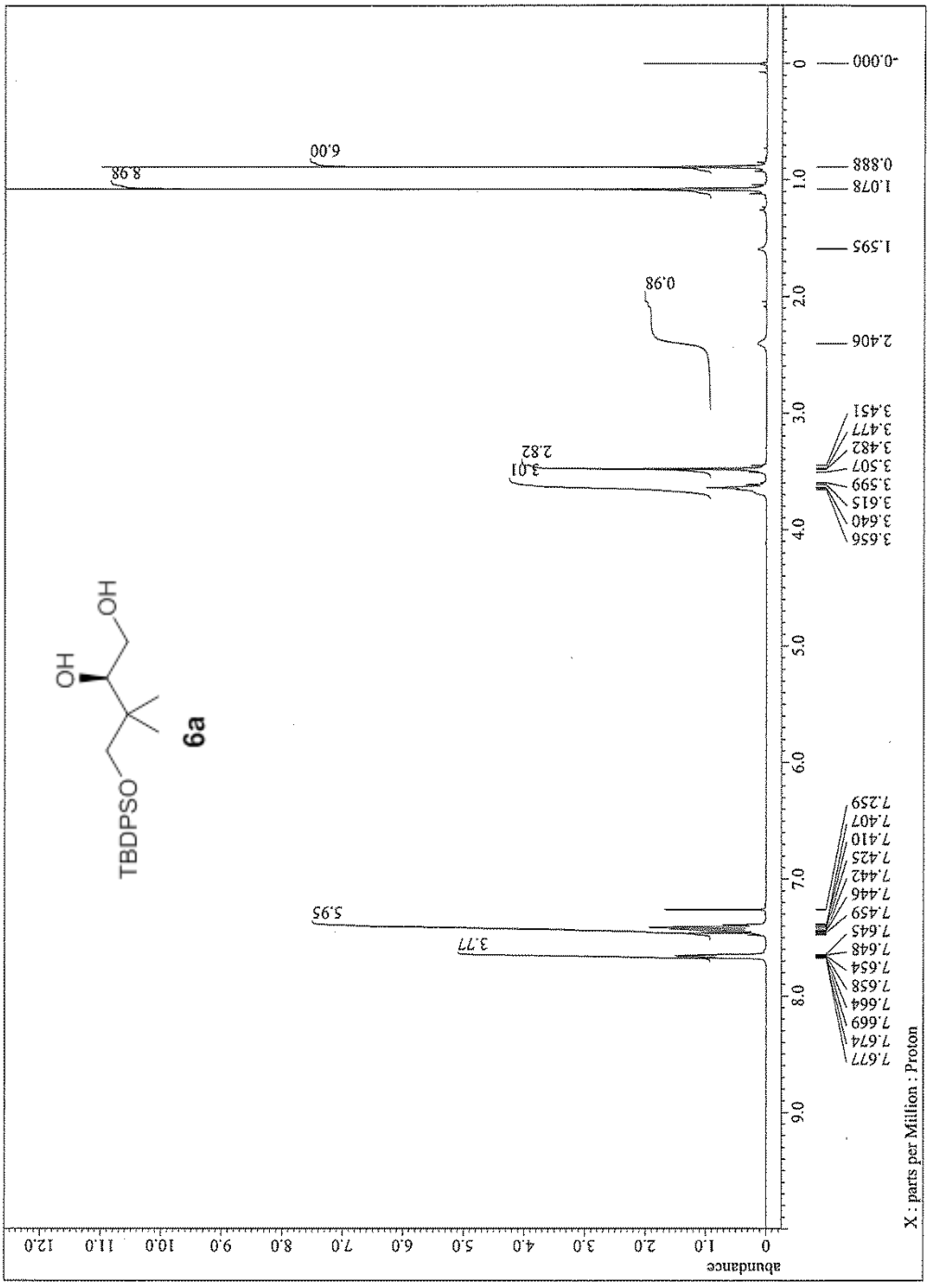

5a
OH
OH
F
F
F
F
F
abundance
X : parts per Million : Carbon13
146.660
144.209
141.282
138.898
138.755
138.622
136.248
111.553
111.363
111.153
77.315
77.000
76.676
70.907
65.864
26.324

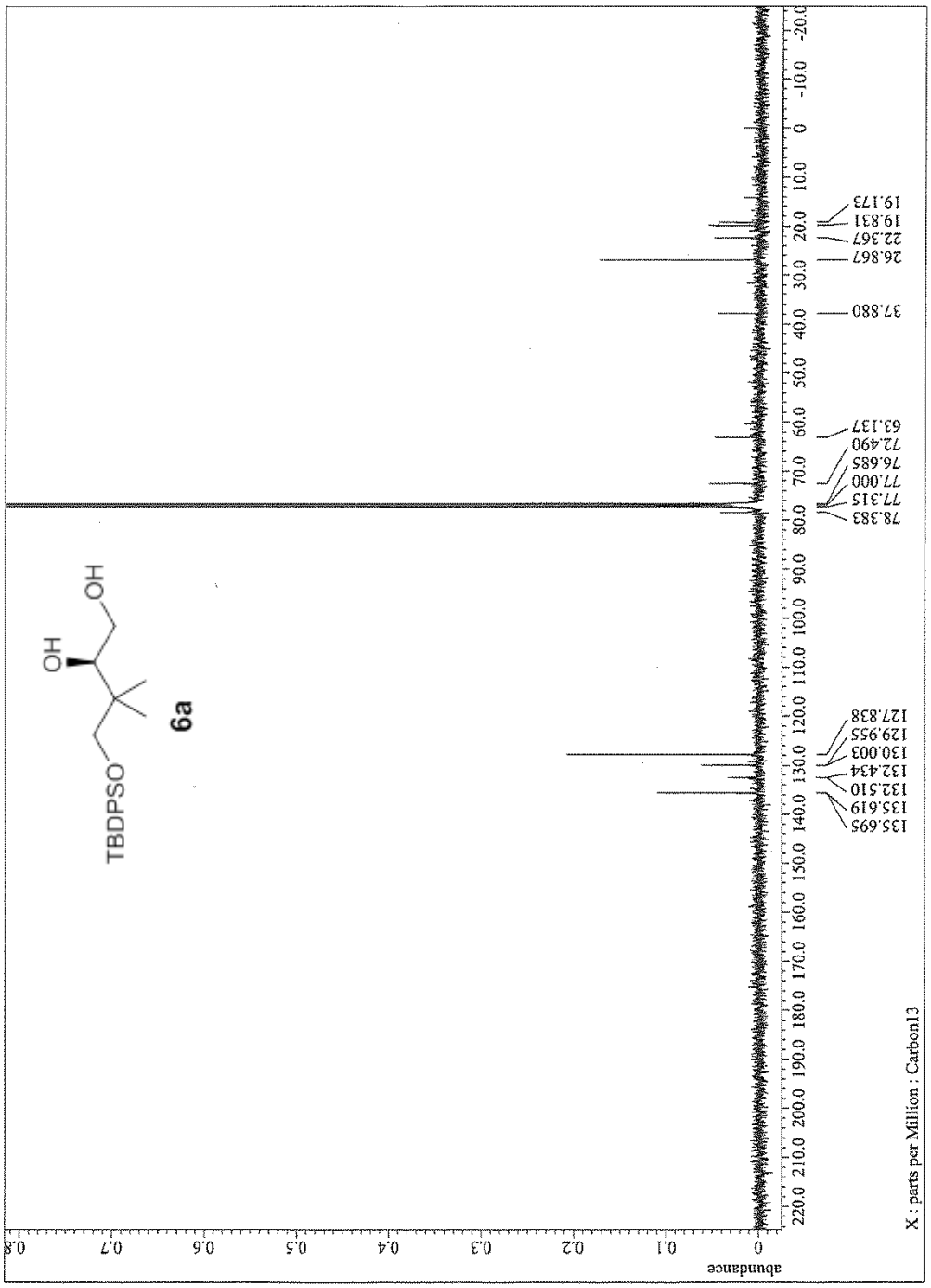

5b
(MeCN-d3)
MeCN-d3
abundance
X : parts per Million : Proton
0.082
0.875
1.115
1.185
1.265
1.636
1.929
1.934
1.940
1.946
1.950
2.247
2.996
3.031
3.052
3.166
3.200
4.311
4.321
4.332
4.343
0.94
1.00
0.99
OH
OH
O
F
F
F
F
F

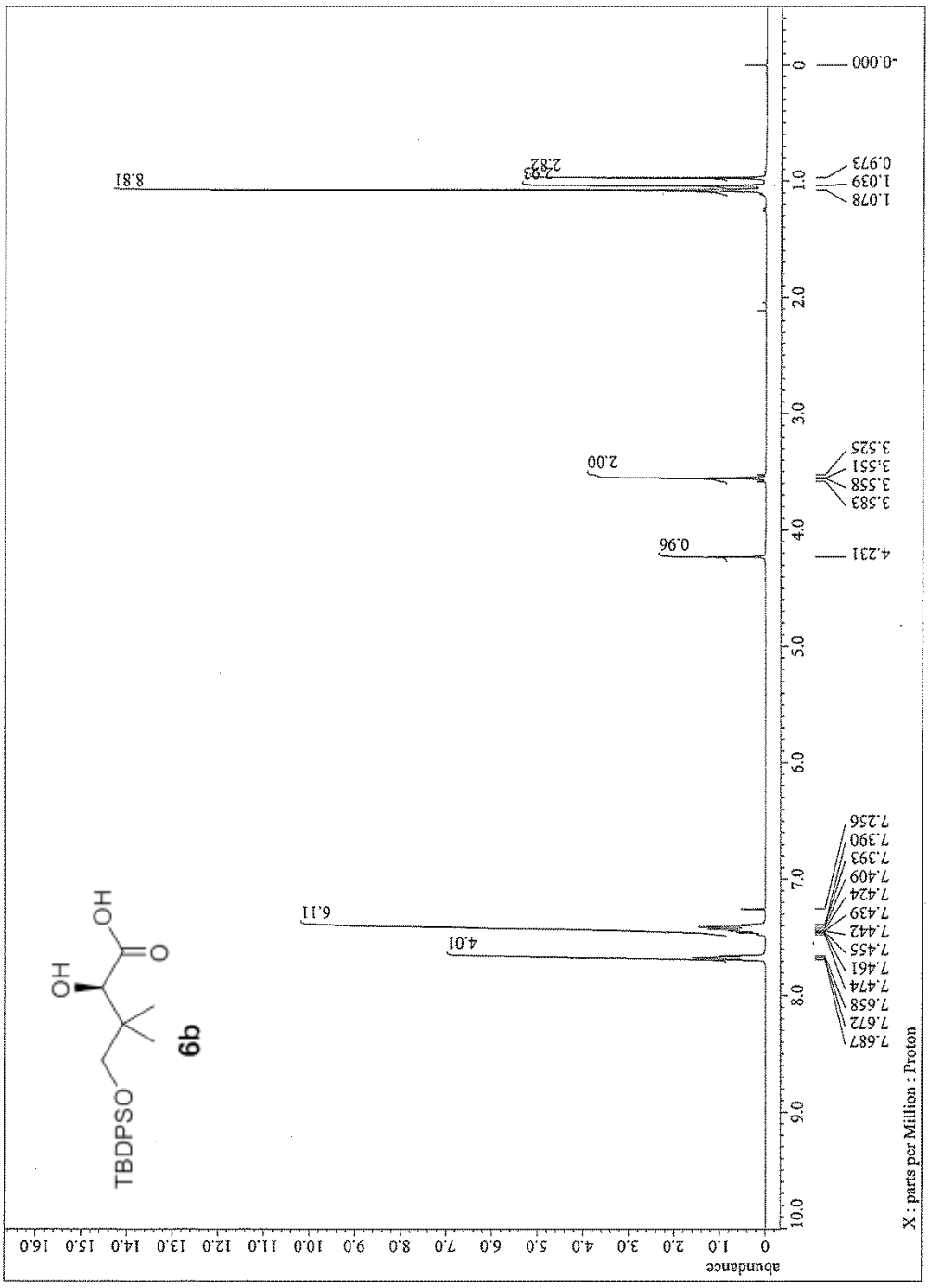
MeCN-d_3



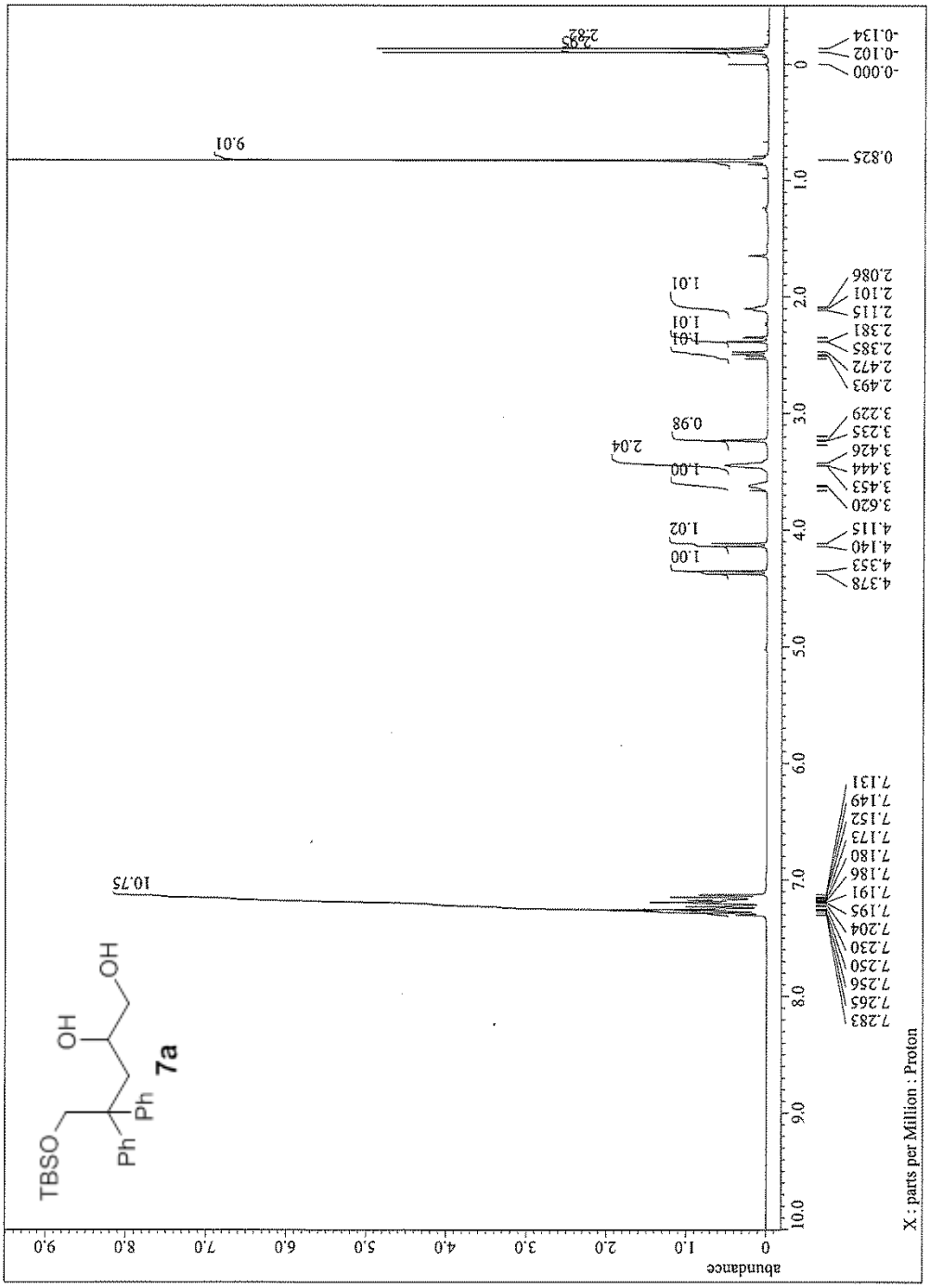
5b
(MeCN-d_3)

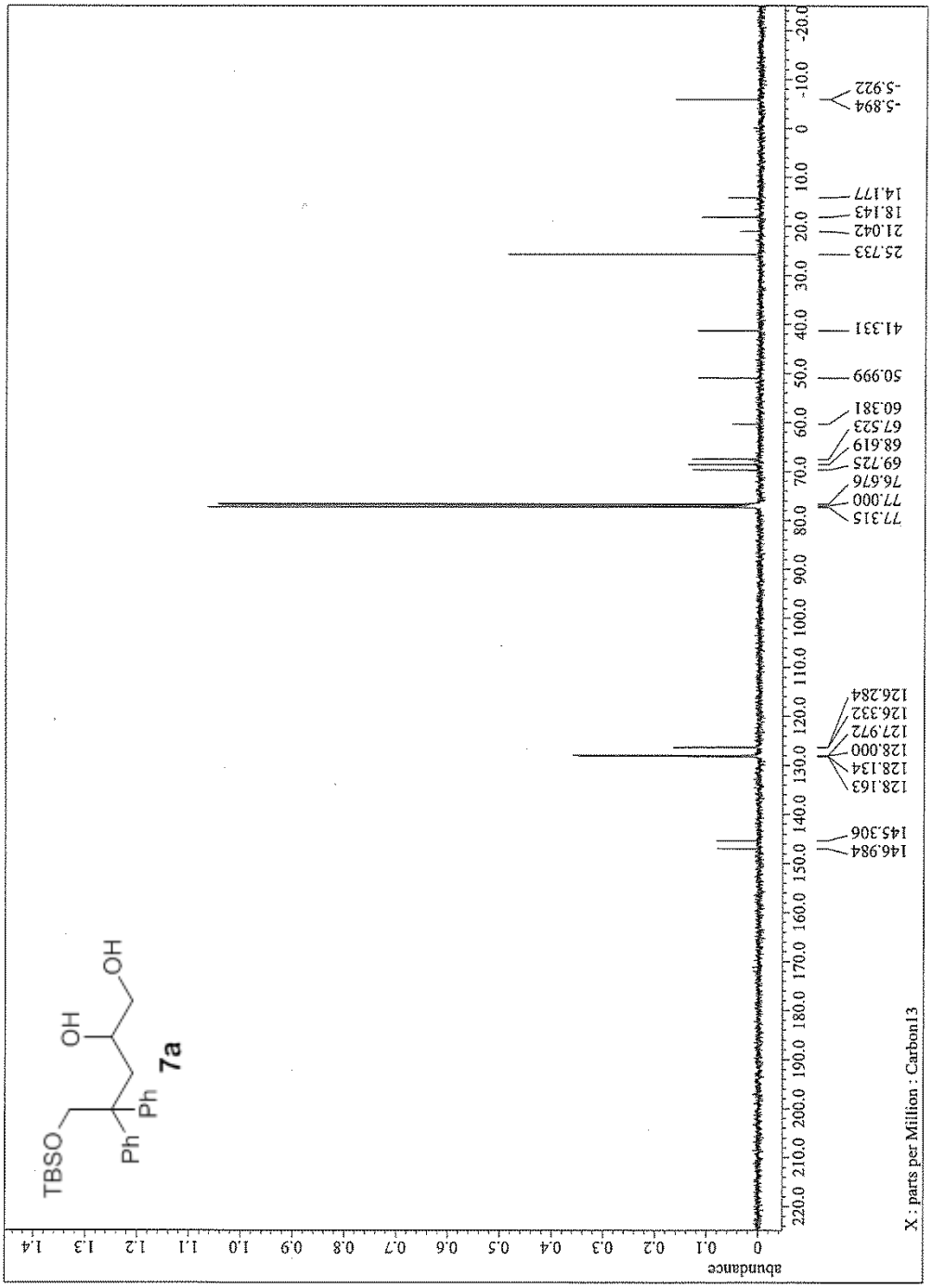

6a
TBDPSO
OH
OH
X : parts per Million : Proton
abundance
-0.000
0.888
1.078
1.595
2.406
3.451
3.477
3.482
3.507
3.599
3.615
3.640
3.656
7.259
7.407
7.410
7.425
7.442
7.446
7.459
7.645
7.648
7.654
7.658
7.664
7.669
7.674
7.677
0.98
2.82
3.01
3.77
5.95
6.00
8.98

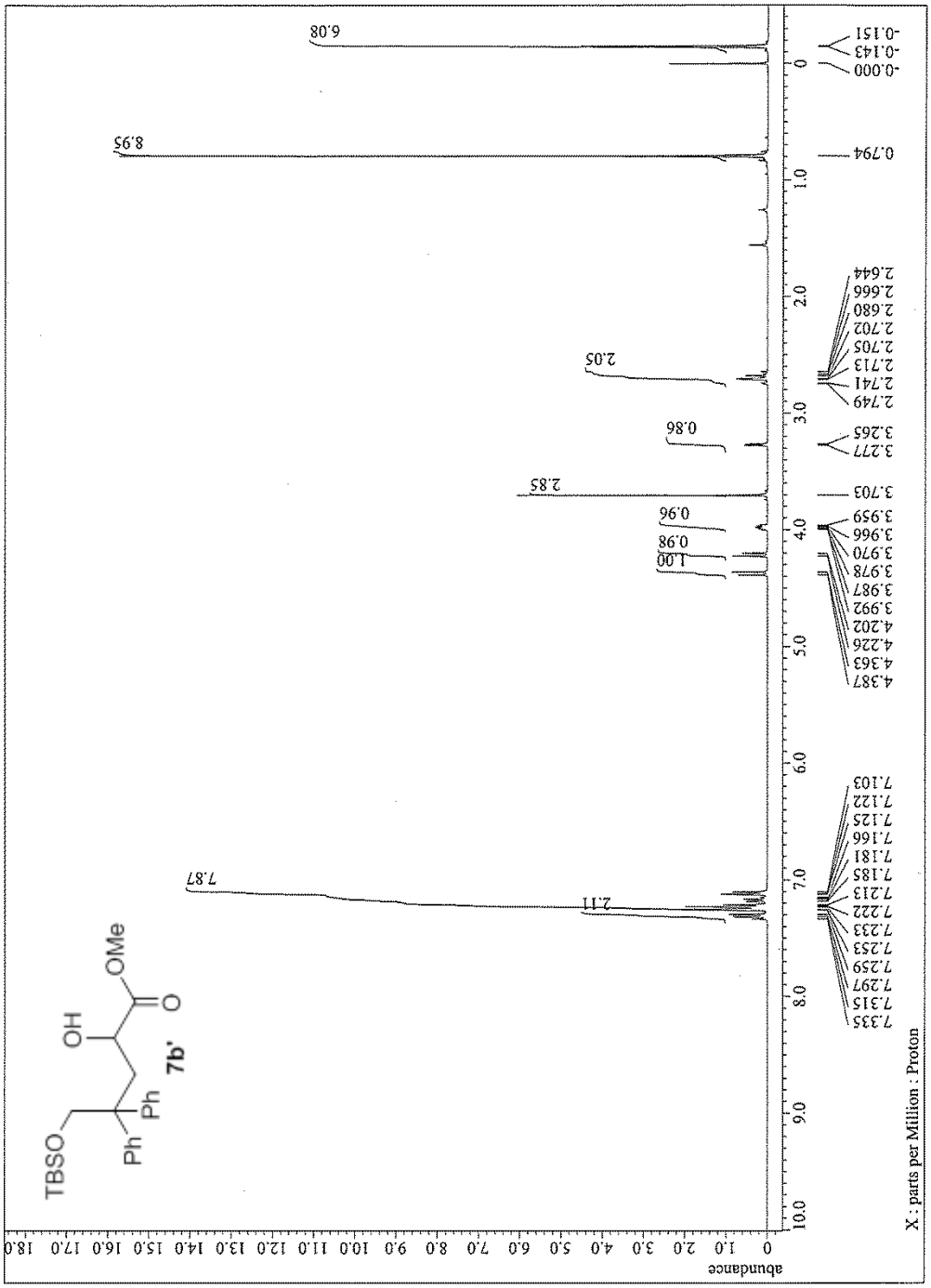

6a
OH
OH
TBDPSO
X : parts per Million : Carbon13
abundance
135.695
135.619
132.510
132.434
130.003
129.955
127.838
78.383
77.315
77.000
76.685
72.490
63.137
37.880
26.867
22.367
19.831
19.173

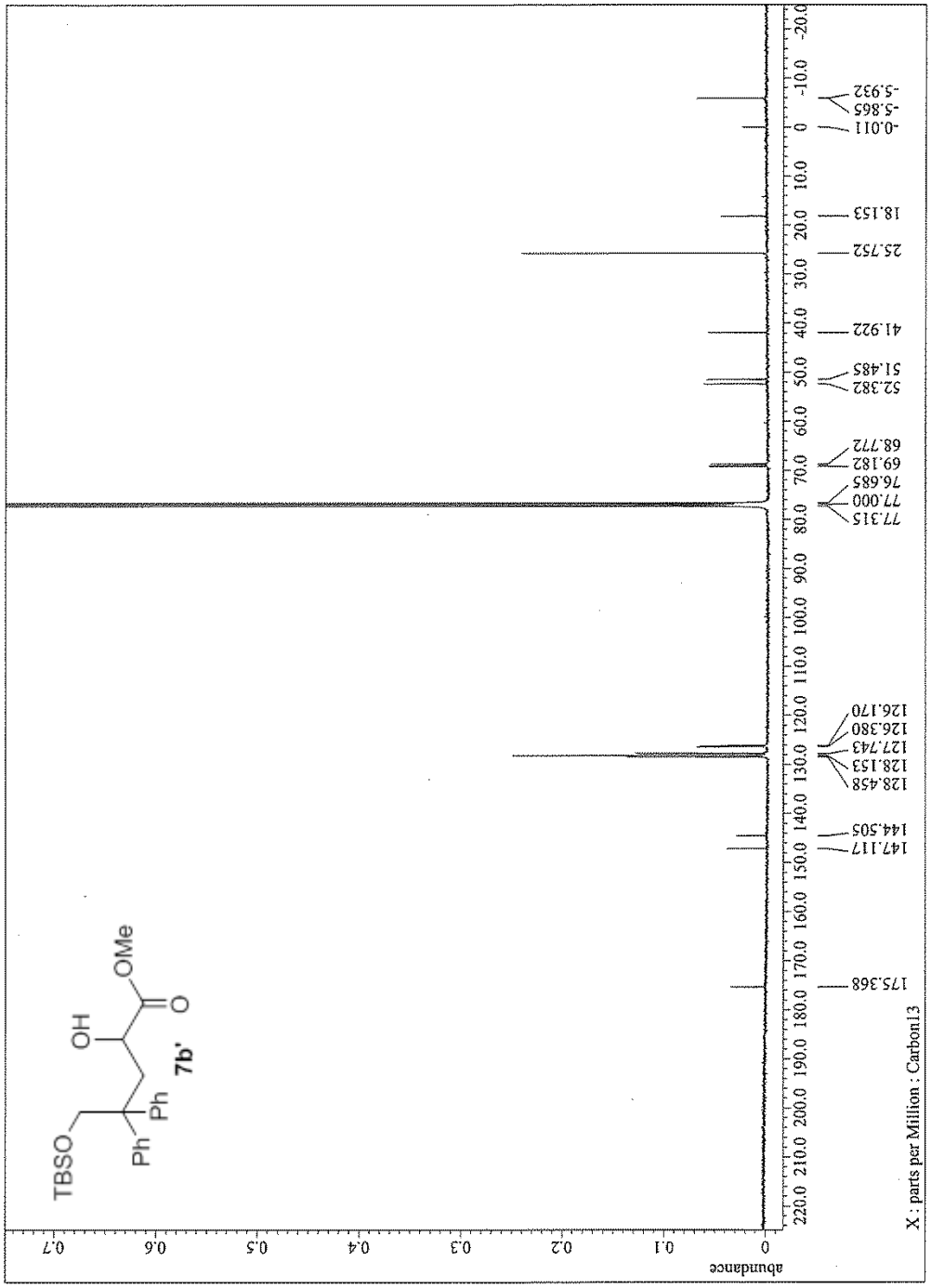

6b
TBDPSO
OH
OH
O
6b
X : parts per Million : Proton
abundance
-0.000
0.973
1.039
1.078
2.83
2.93
8.81
2.00
0.96
3.525
3.551
3.558
3.583
4.231
4.01
6.11
7.256
7.390
7.393
7.409
7.424
7.439
7.442
7.455
7.461
7.474
7.658
7.672
7.687

6b
TBDPSO
OH
O
OH
abundance
X : parts per Million : Carbon13
175.816
135.666
135.600
132.301
132.177
130.031
130.003
127.848
77.315
77.200
77.000
76.676
71.985
39.110
26.781
21.757
19.783
19.173


TBSO
Ph
Ph
OH
OH
7a
10.75
9.01
2.83
1.01
1.01
1.01
0.98
2.04
1.00
1.02
1.00
abundance
X : parts per Million : Proton

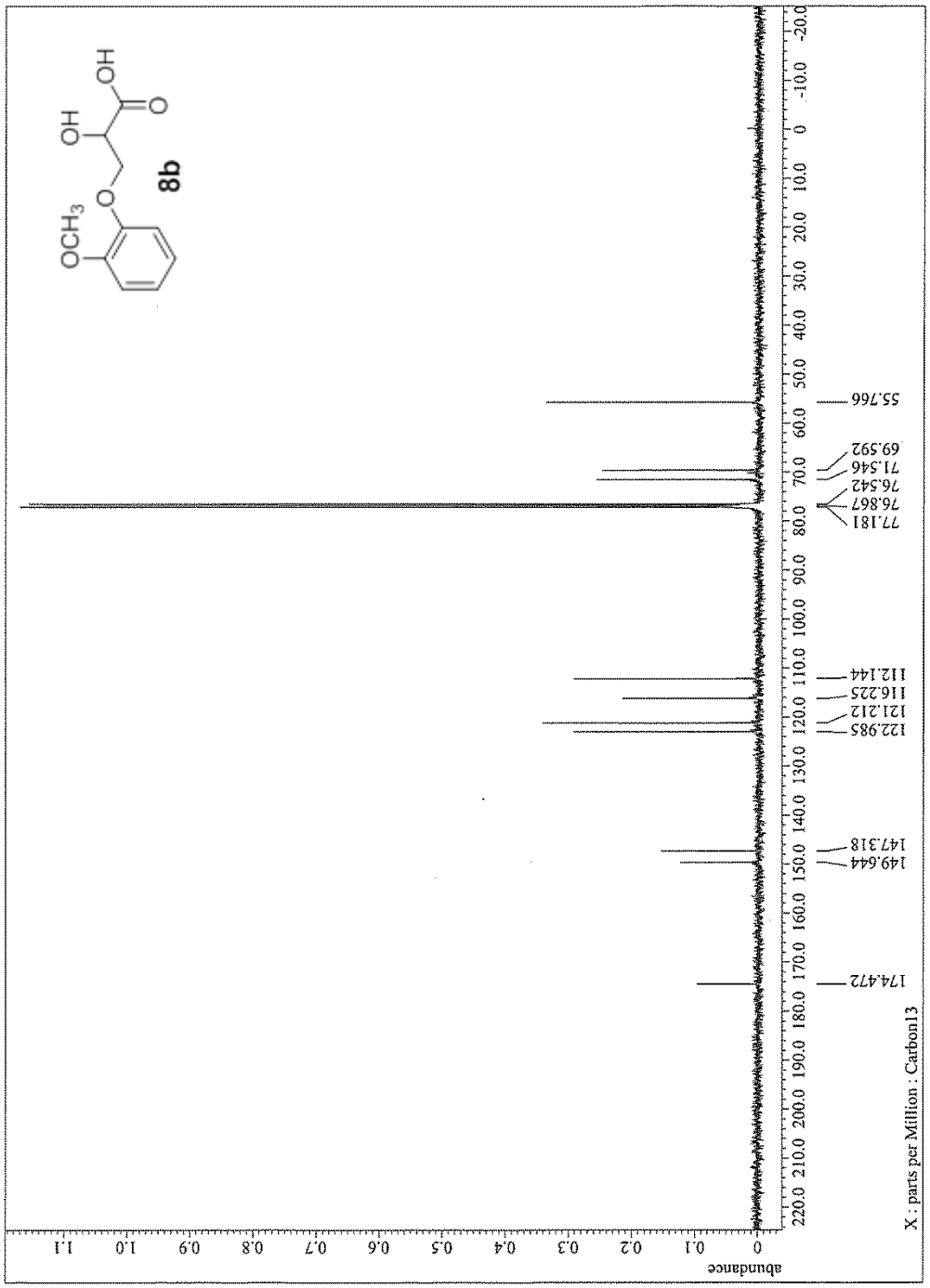

TBSO
Ph
Ph
OH
OH
7a
abundance
X : parts per Million : Carbon13
-5.894
-5.922
14.177
18.143
21.042
25.733
41.331
50.999
60.381
67.523
68.619
69.725
76.676
77.000
77.315
126.284
126.332
127.972
128.000
128.134
128.163
145.306
146.984

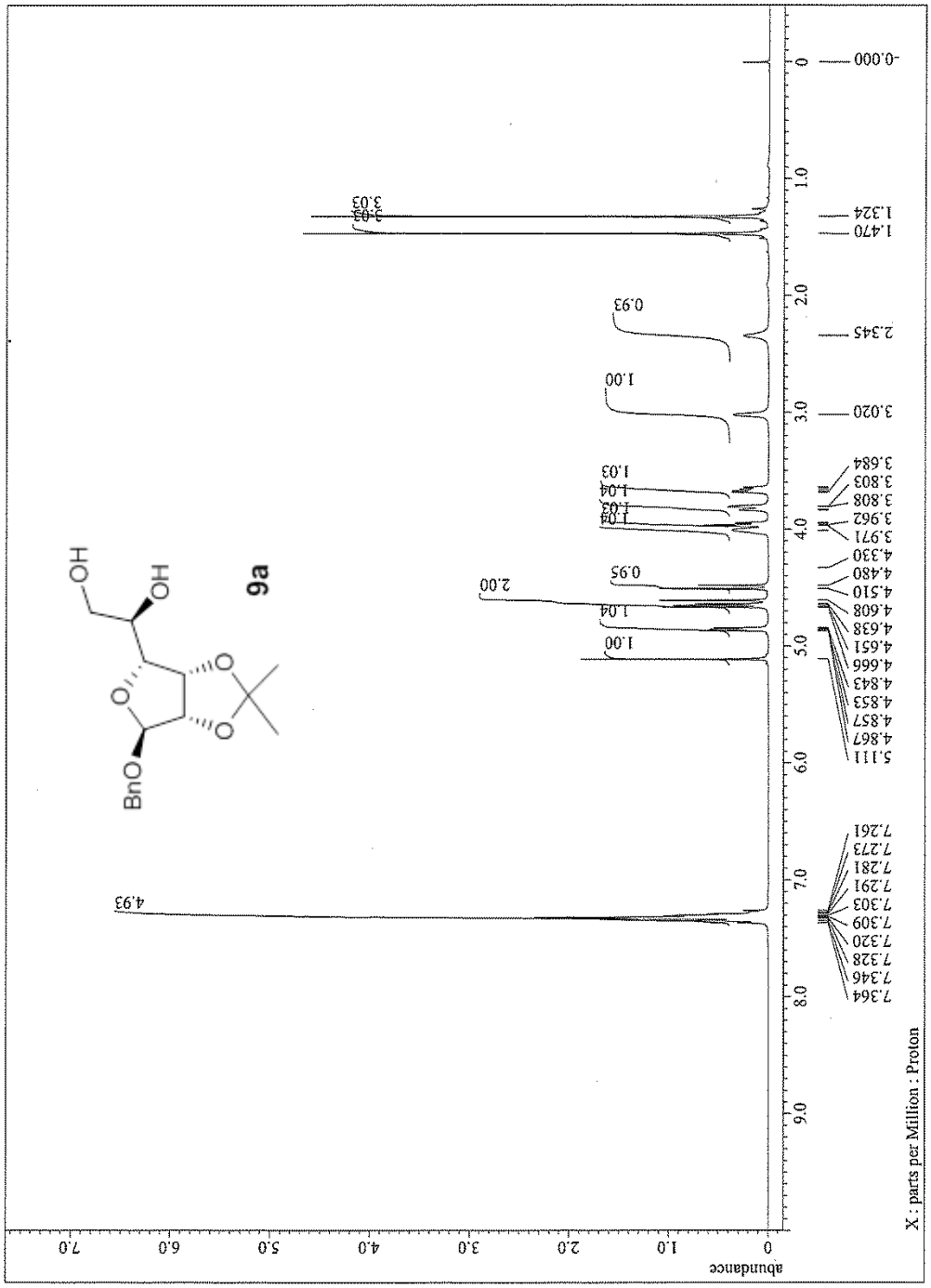

7b'
TBSO
Ph
Ph
OH
OMe
O
7b'
X : parts per Million : Proton
abundance


TBSO
Ph
Ph
OH
OMe
O
7b'
abundance
X : parts per Million : Carbon13
175.368
147.117
144.505
128.458
128.153
127.743
126.380
126.170
77.315
77.000
76.685
69.182
68.772
52.382
51.485
41.922
25.752
18.153
-0.011
-5.865
-5.932

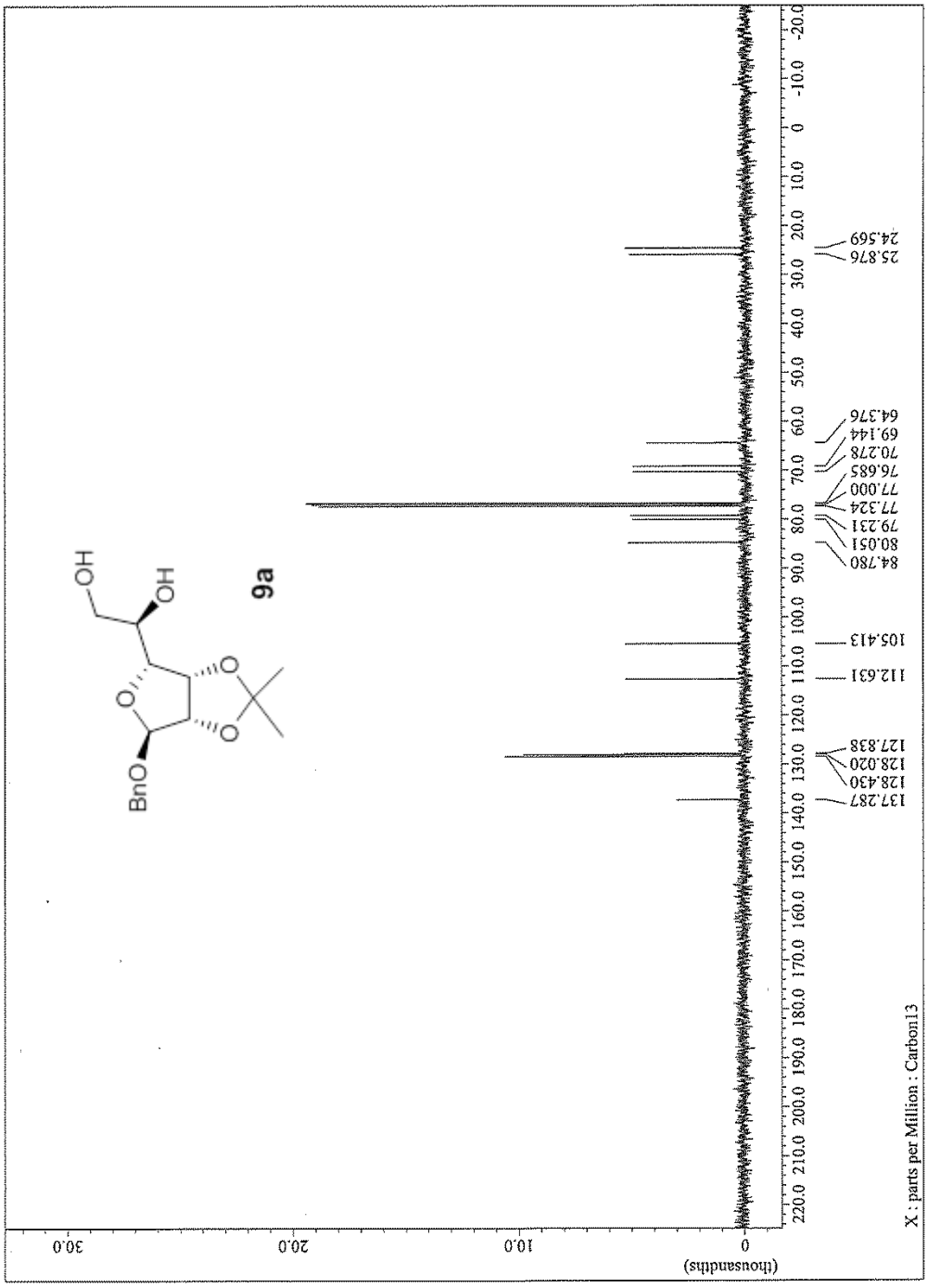
7b'

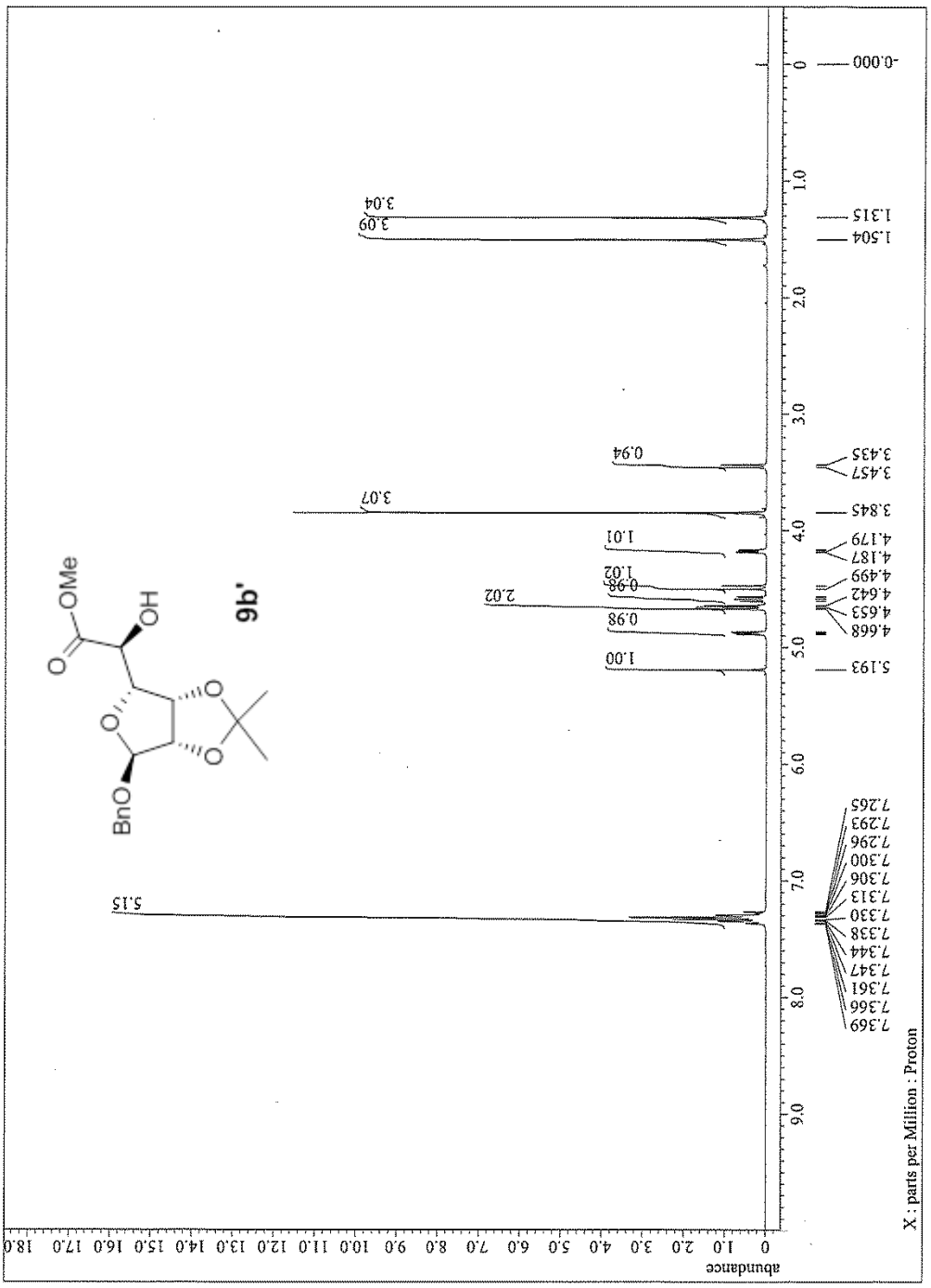
8b
OCH3
OH
OH
O
2.97
1.11
0.97
1.00
2.32
2.16
7.261
7.021
7.004
7.000
6.979
6.976
6.955
6.927
6.908
6.890
6.860
4.560
4.550
4.541
4.400
4.377
4.365
4.352
4.340
4.310
4.301
4.285
4.276
4.245
4.029
3.850
3.817
3.794
3.667
3.394
3.380
0.000
X : parts per Million : Proton
abundance


8b
OCH3
OH
OH
O
X : parts per Million : Carbon13
abundance
174.472
149.644
147.318
122.985
121.212
116.225
112.144
77.181
76.867
76.542
71.546
69.592
55.766

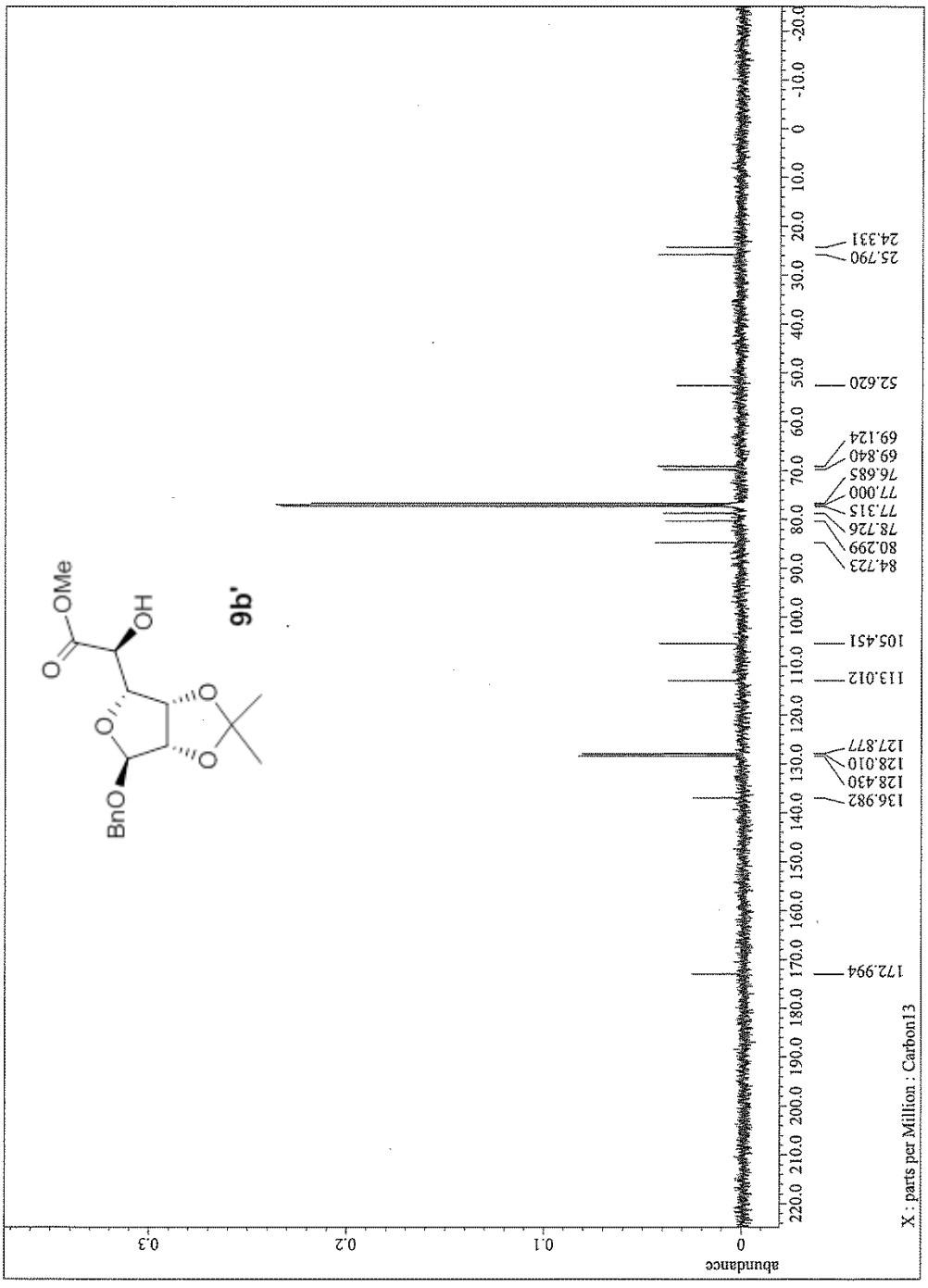

9a
BnO
OH
OH
X : parts per Million : Proton
abundance
-0.000
1.324
1.470
2.345
3.020
3.684
3.803
3.808
3.962
3.971
4.330
4.480
4.510
4.608
4.638
4.651
4.666
4.843
4.853
4.857
4.867
5.111
7.261
7.273
7.281
7.291
7.303
7.309
7.320
7.328
7.346
7.364
4.93
2.00
1.00
0.95
1.04
1.00
0.93
3.03

9c.

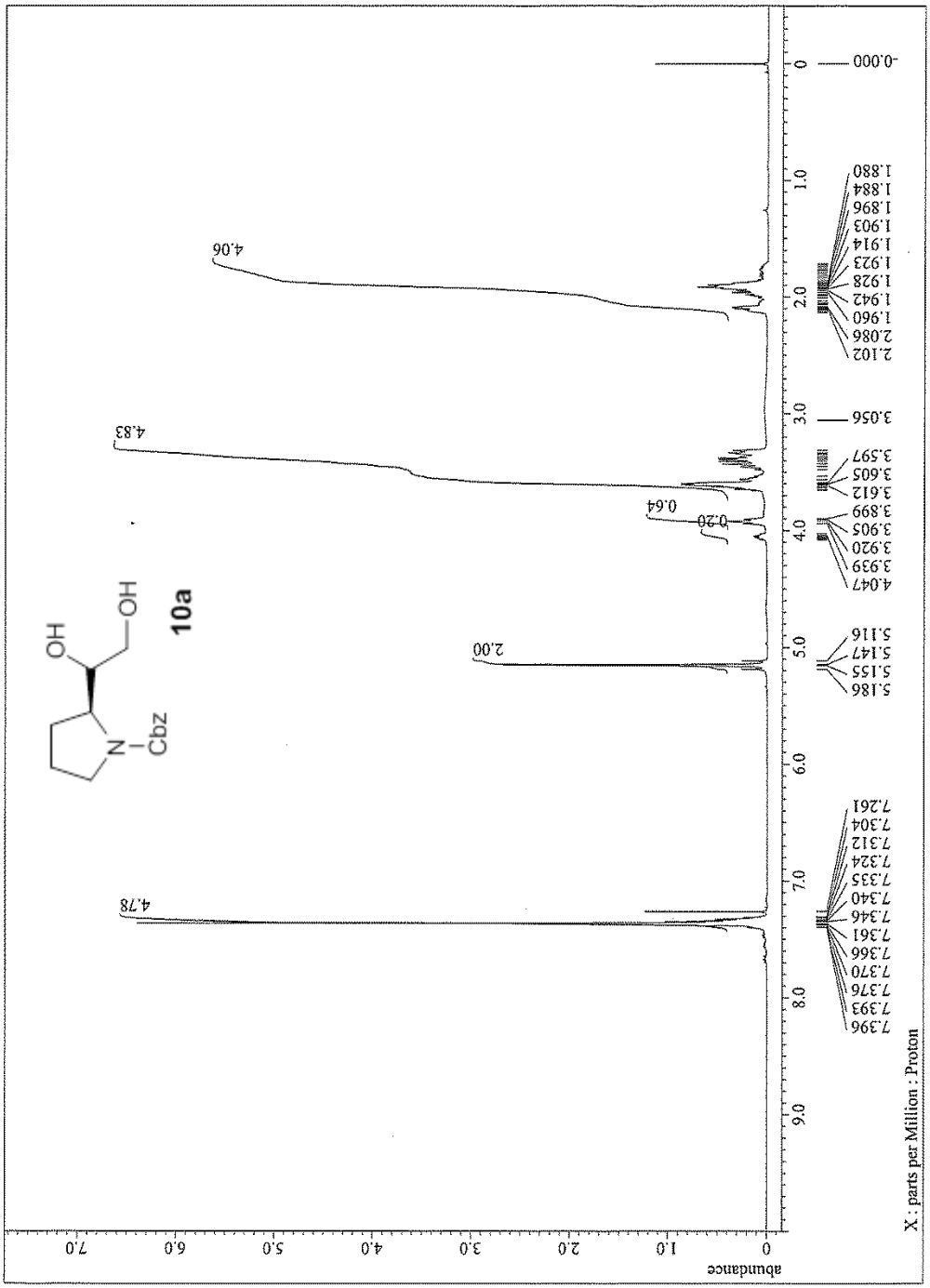

9a
BnO
OH
OH
(thousandths)
30.0
20.0
10.0
0
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.287
128.430
128.020
127.838
112.631
105.413
84.780
80.051
79.231
77.324
77.000
76.685
70.278
69.144
64.376
25.876
24.569

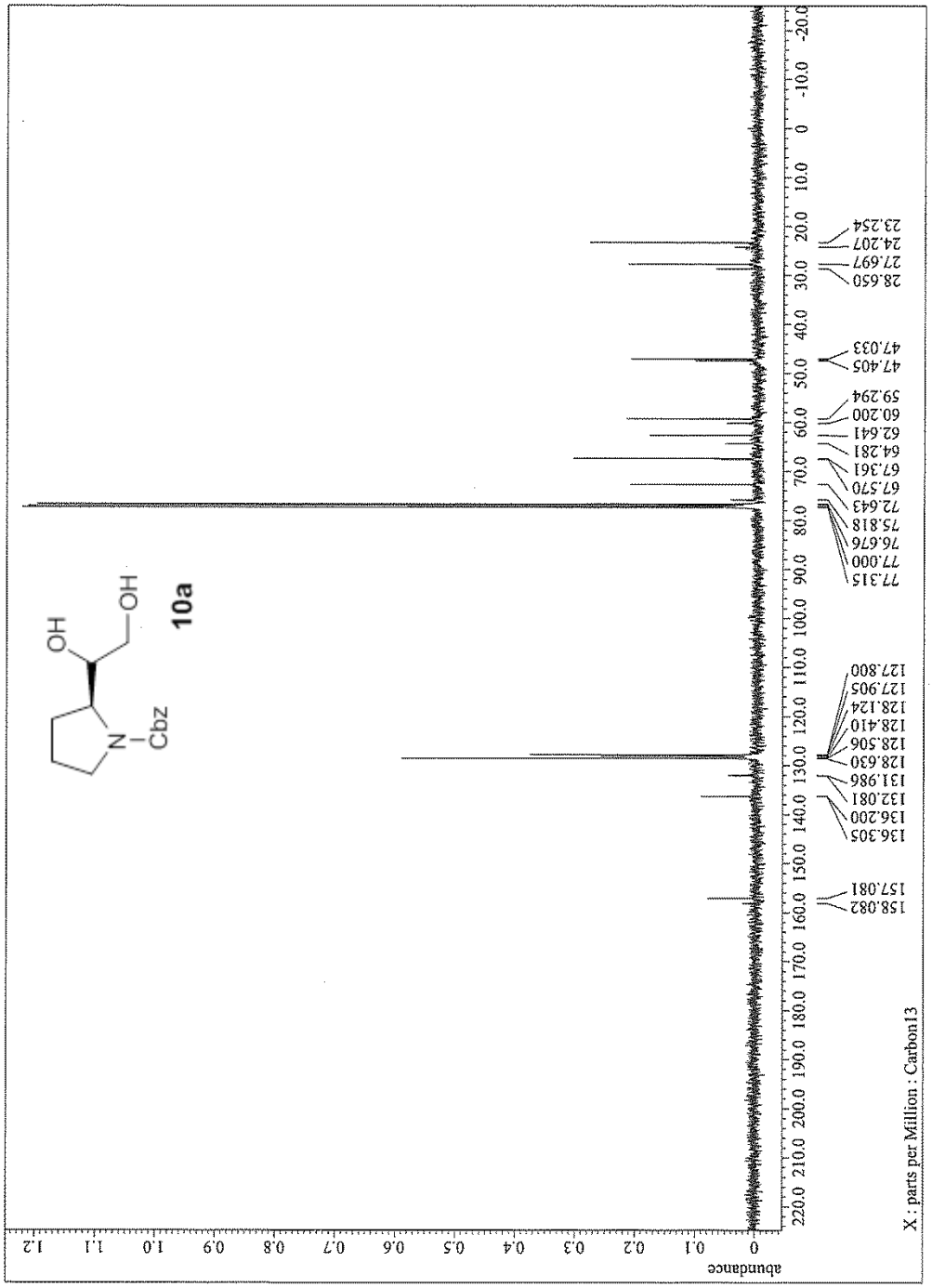

9b'
OMe
OH
BnO
O
O
O
O
5.15
3.09
3.04
3.07
2.02
1.01
1.02
0.98
0.94
1.00
7.369
7.366
7.361
7.347
7.344
7.338
7.330
7.313
7.306
7.300
7.296
7.293
7.265
5.193
4.668
4.653
4.642
4.499
4.187
4.179
3.845
3.457
3.435
1.504
1.315
-0.000
abundance
X : parts per Million : Proton

9b'


9b'
OMe
OH
BnO
O
O
O
O
abundance
0
0.1
0.2
0.3
X : parts per Million : Carbon13
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 -10.0 -20.0
172.994
136.982
128.430
128.010
127.877
113.012
105.451
84.723
80.299
78.726
77.315
77.000
76.685
69.840
69.124
52.620
25.790
24.331

9b'

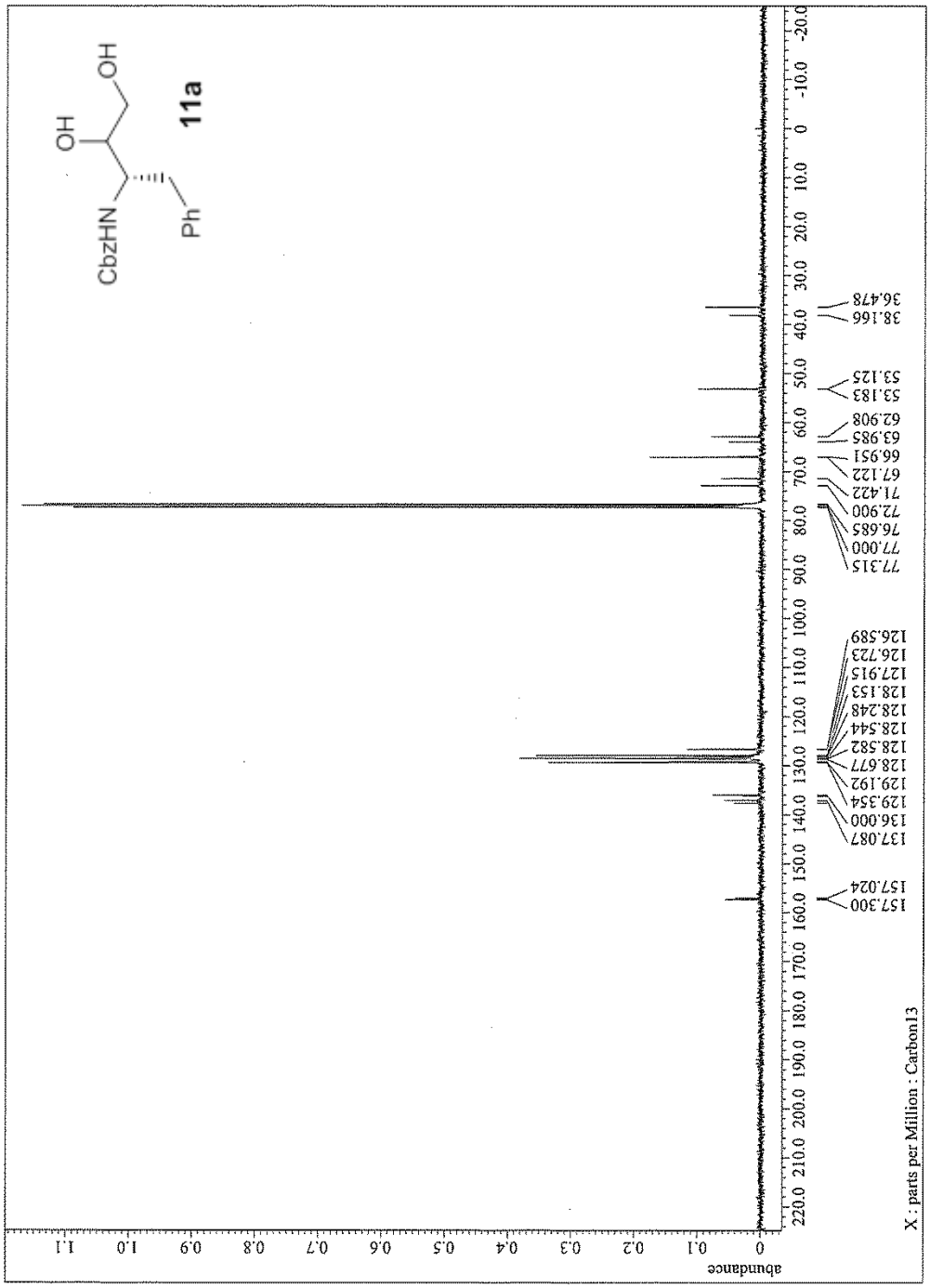

10a
OH
OH
N
Cbz
4.78
2.00
4.83
0.64
0.20
4.06
3.056
-0.000
7.396
7.393
7.376
7.370
7.366
7.361
7.346
7.340
7.335
7.324
7.312
7.304
7.261
5.186
5.155
5.147
5.116
4.047
3.939
3.920
3.905
3.899
3.612
3.605
3.597
2.102
2.086
1.960
1.942
1.928
1.923
1.914
1.903
1.896
1.884
1.880
abundance
X : parts per Million : Proton


OH
OH
N
Cbz
10a
abundance
X : parts per Million : Carbon13
158.082
157.081
136.305
136.200
132.081
131.986
128.630
128.506
128.410
128.124
127.905
127.800
77.315
77.000
76.676
75.818
72.643
67.570
67.361
64.281
62.641
60.200
59.294
47.405
47.033
28.650
27.697
24.207
23.254

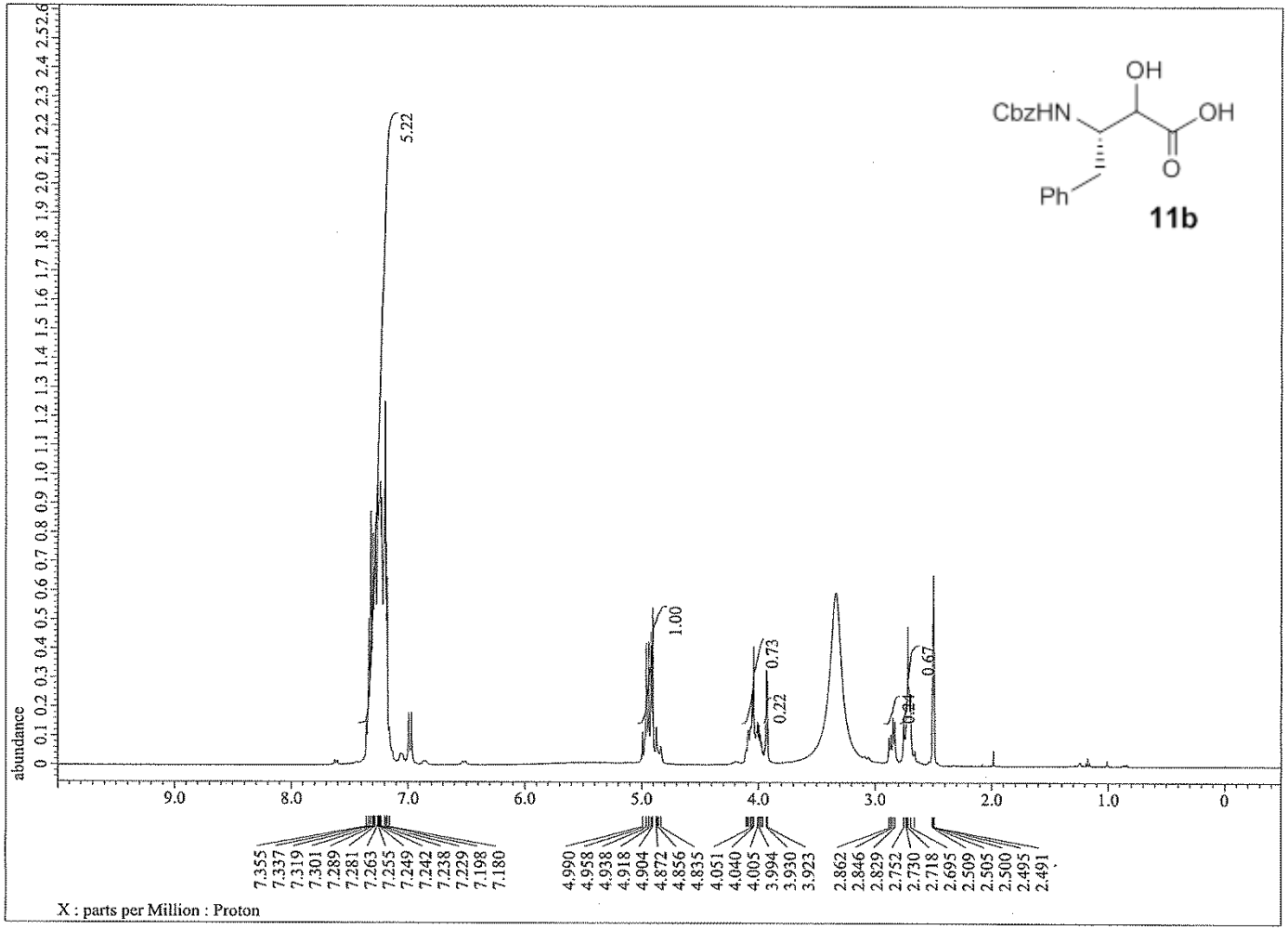
10b
X : parts per Million : Proton
abundance
-0.000
7.260
7.344
5.181
5.151
5.117
5.086
4.690
4.615
4.252
4.233
4.217
3.562
3.549
3.533
3.431
3.414
3.398
3.388
2.107
2.086
2.048
2.031
2.015
1.999
1.984
1.968
1.776
1.758
1.746
5.17
4.26
2.00
1.16
0.60
0.18
1.01
1.07
OH
OH
O
N
Cbz

10b
OH
OH
O
N
Cbz
abundance
X : parts per Million : Carbon13
175.101
174.691
156.738
155.069
136.057
128.506
128.143
127.810
77.315
77.000
76.676
72.156
71.203
67.580
67.275
61.001
59.456
47.586
27.096
26.448
24.150
23.683

11a
OH
OH
CbzHN
Ph
10.78
2.00
0.52
0.34
0.98
3.30
3.22
0.79
1.806
0.000
7.332
7.316
7.294
7.277
7.253
7.231
7.212
7.194
5.217
5.194
5.078
5.052
5.021
4.990
4.900
4.879
3.922
3.684
3.671
3.645
3.544
3.512
3.073
3.063
2.922
2.904
2.885
2.871
2.850
abundance
X : parts per Million : Proton

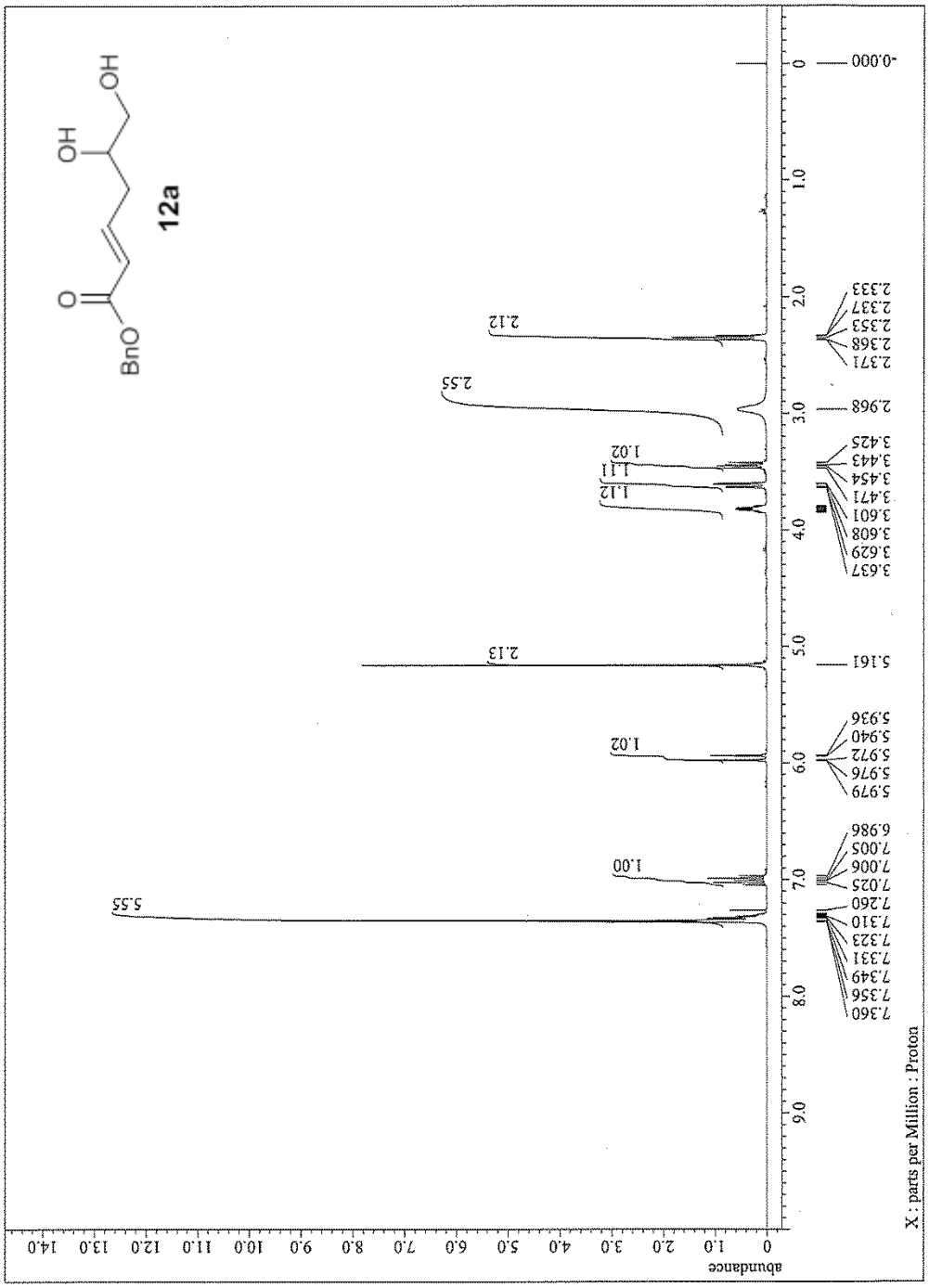

11a
OH
OH
CbzHN
Ph
abundance
X : parts per Million : Carbon13
157.300
157.024
137.087
136.000
129.354
129.192
128.677
128.582
128.544
128.248
128.153
127.915
126.723
126.589
77.315
77.000
76.685
72.900
71.422
67.122
66.951
63.985
62.908
53.183
53.125
38.166
36.478

DMSO-d_6

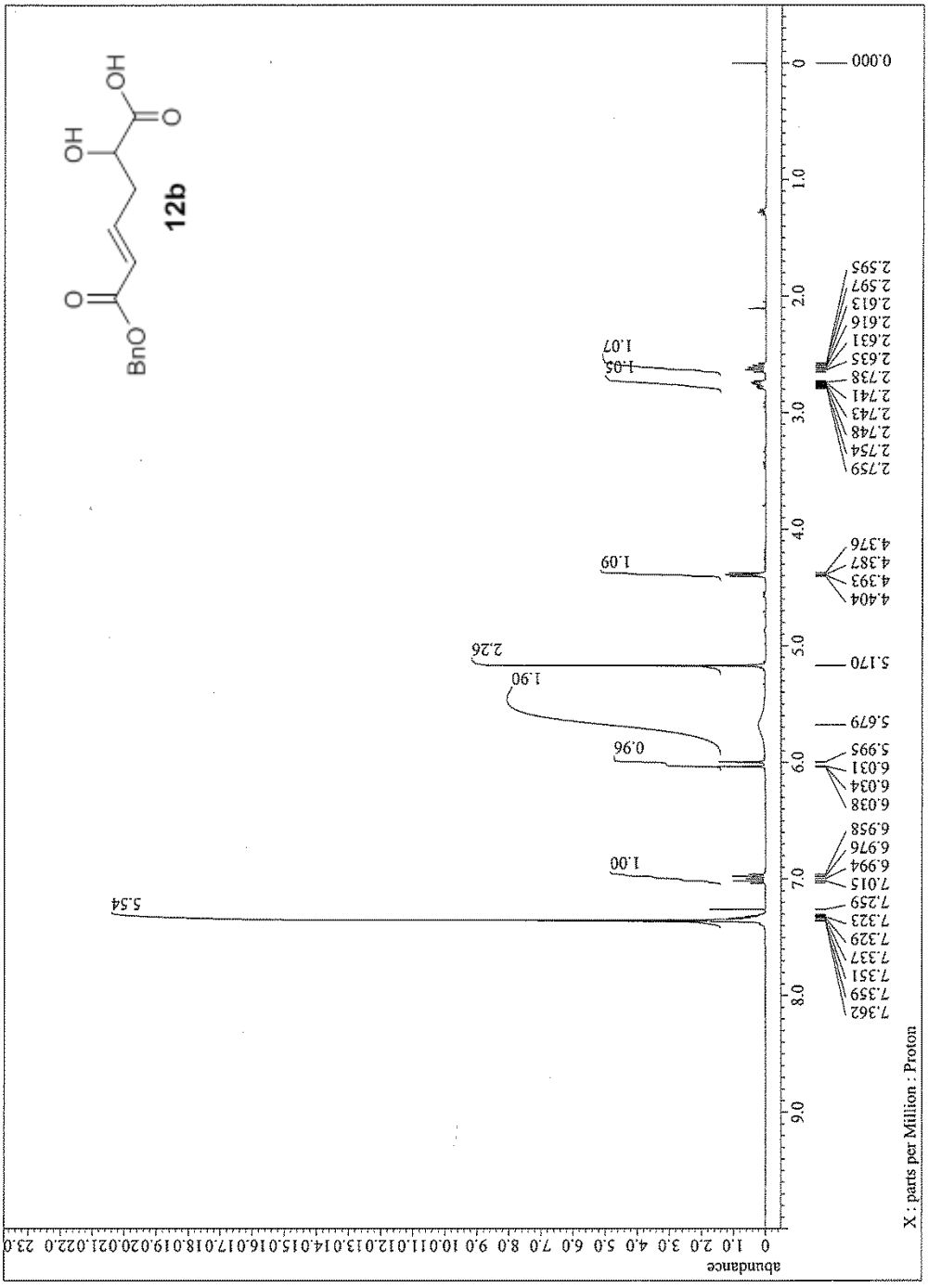

OH
CbzHN
OH
O
Ph
11b
abundance
5.22
1.00
0.73
0.22
0.84
0.67
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.355
7.337
7.319
7.301
7.289
7.281
7.263
7.255
7.249
7.242
7.238
7.229
7.198
7.180
4.990
4.958
4.938
4.918
4.904
4.872
4.856
4.835
4.051
4.040
4.005
3.994
3.930
3.923
2.862
2.846
2.829
2.752
2.730
2.718
2.695
2.509
2.505
2.500
2.495
2.491
X : parts per Million : Proton

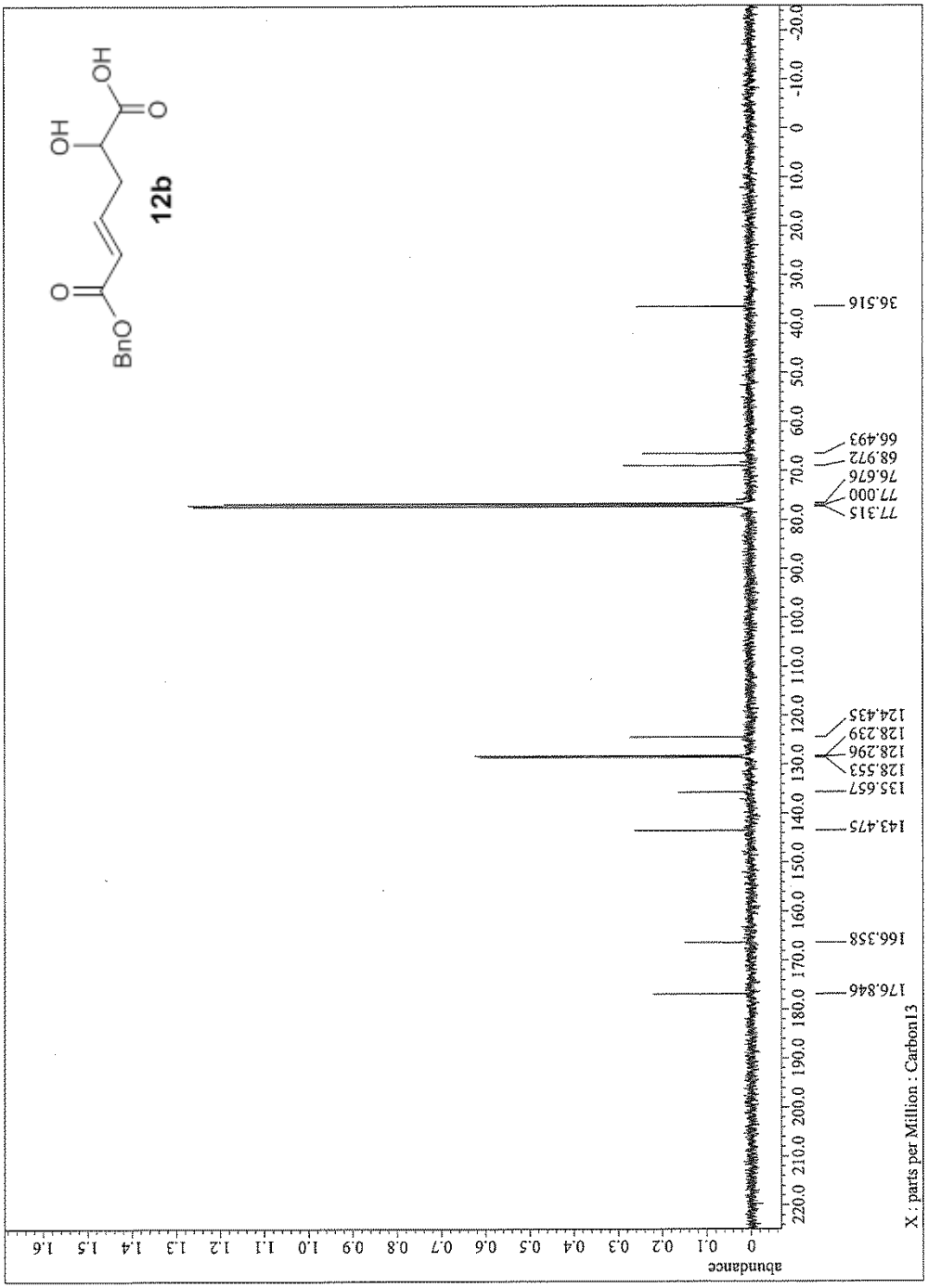
11b

DMSO-d_6
11b
CbzHN
OH
OH
O
Ph
abundance
X : parts per Million : Carbon13
173.762
173.724
155.351
138.885
138.389
136.949
128.969
128.854
128.092
128.035
127.834
127.358
127.138
127.062
72.486
70.427
64.849
64.668
55.105
39.964
39.754
39.544
39.334
39.125
38.924
38.715
37.103
34.596

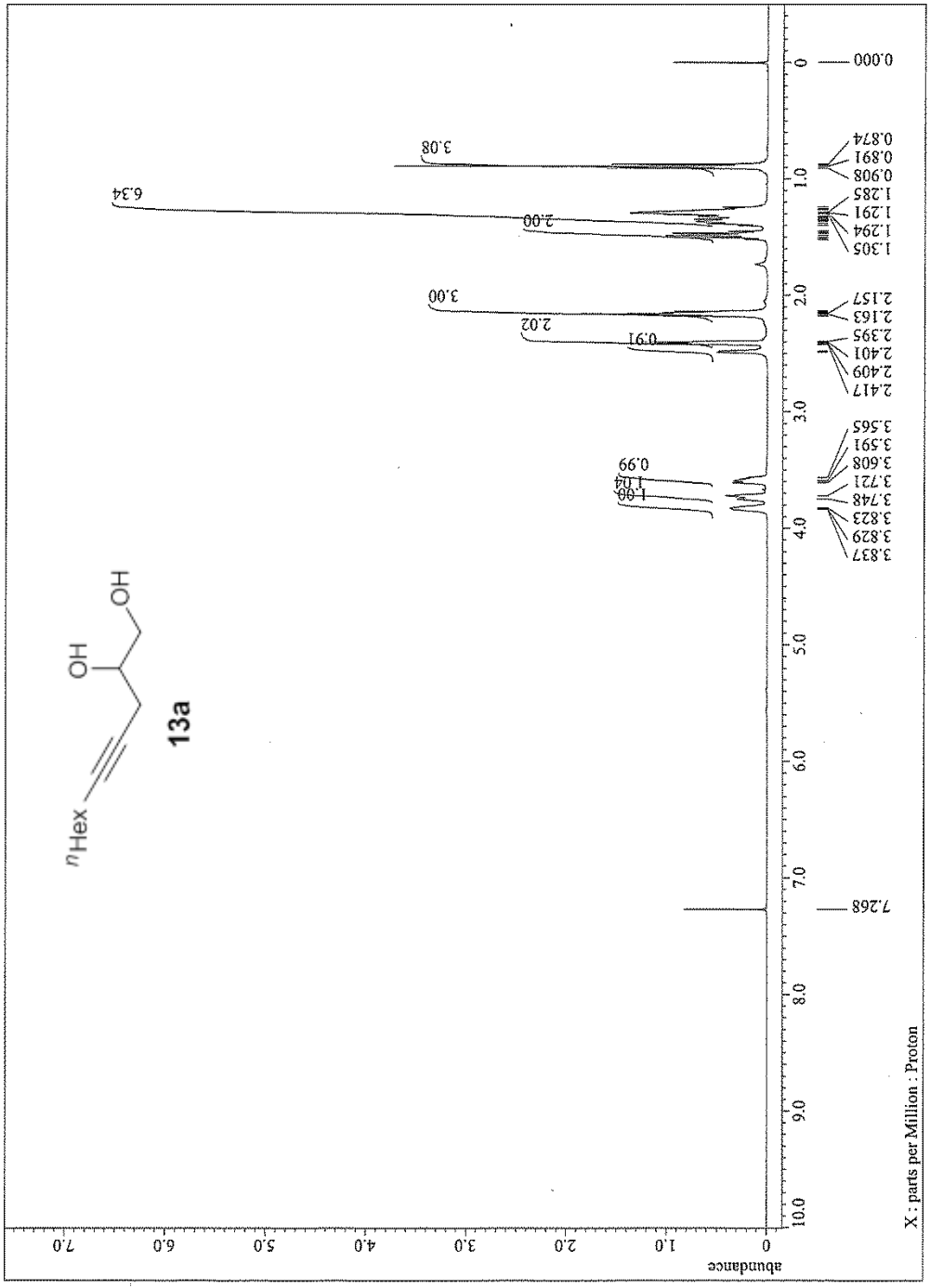

12a
OH
OH
O
BnO
5.55
1.00
1.02
2.13
1.02
1.11
1.12
2.55
2.12
7.360
7.356
7.349
7.331
7.323
7.310
7.260
7.025
7.006
7.005
6.986
5.979
5.976
5.972
5.940
5.936
5.161
3.637
3.629
3.608
3.601
3.471
3.454
3.443
3.425
2.968
2.371
2.368
2.353
2.337
2.333
-0.000
abundance
X : parts per Million : Proton

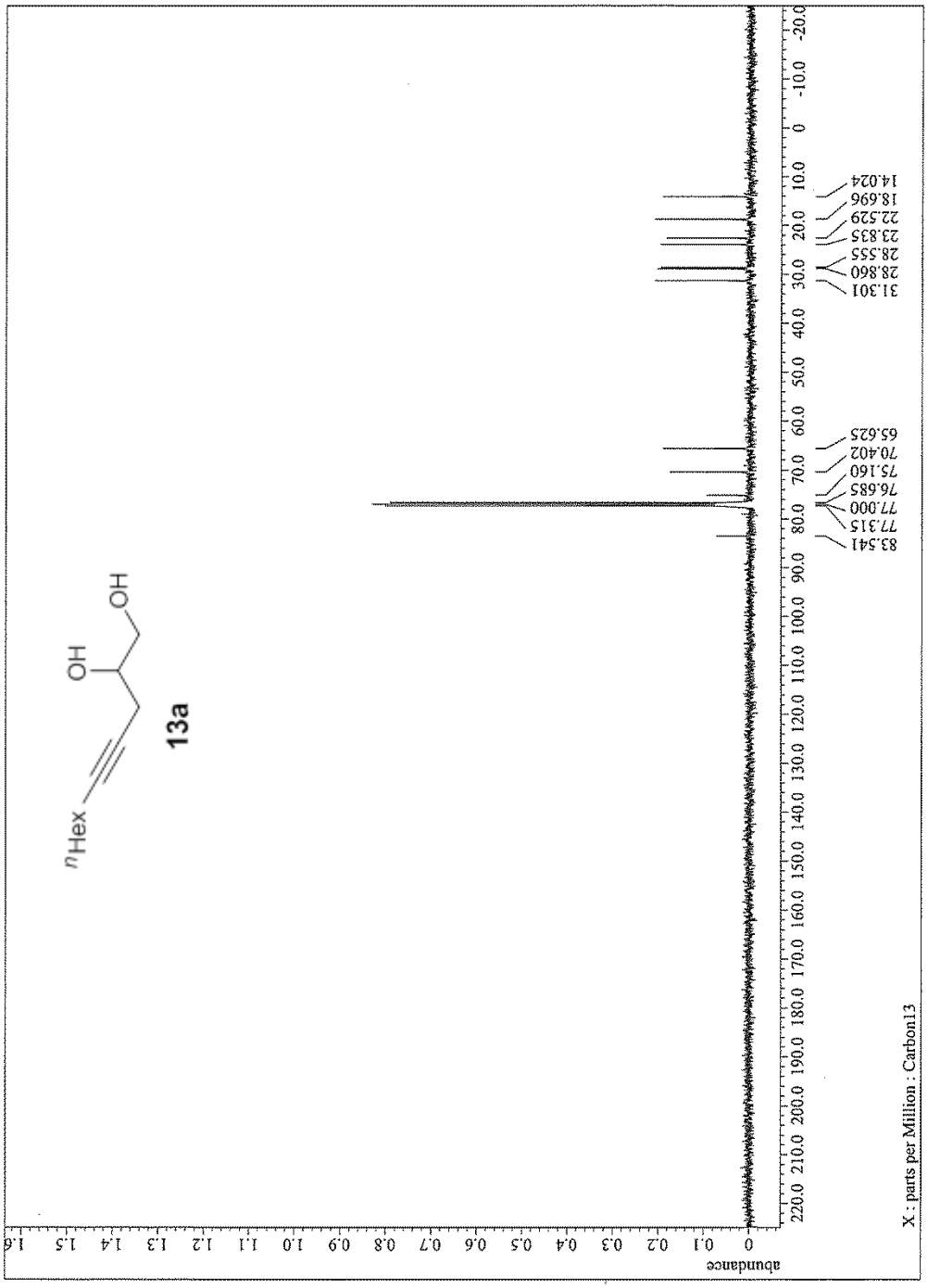
12a
OH
OH
O
BnO
36.030
66.102
66.255
70.698
76.685
77.000
77.324
123.462
128.210
128.525
135.819
145.372
166.272
X : parts per Million : Carbon13
abundance

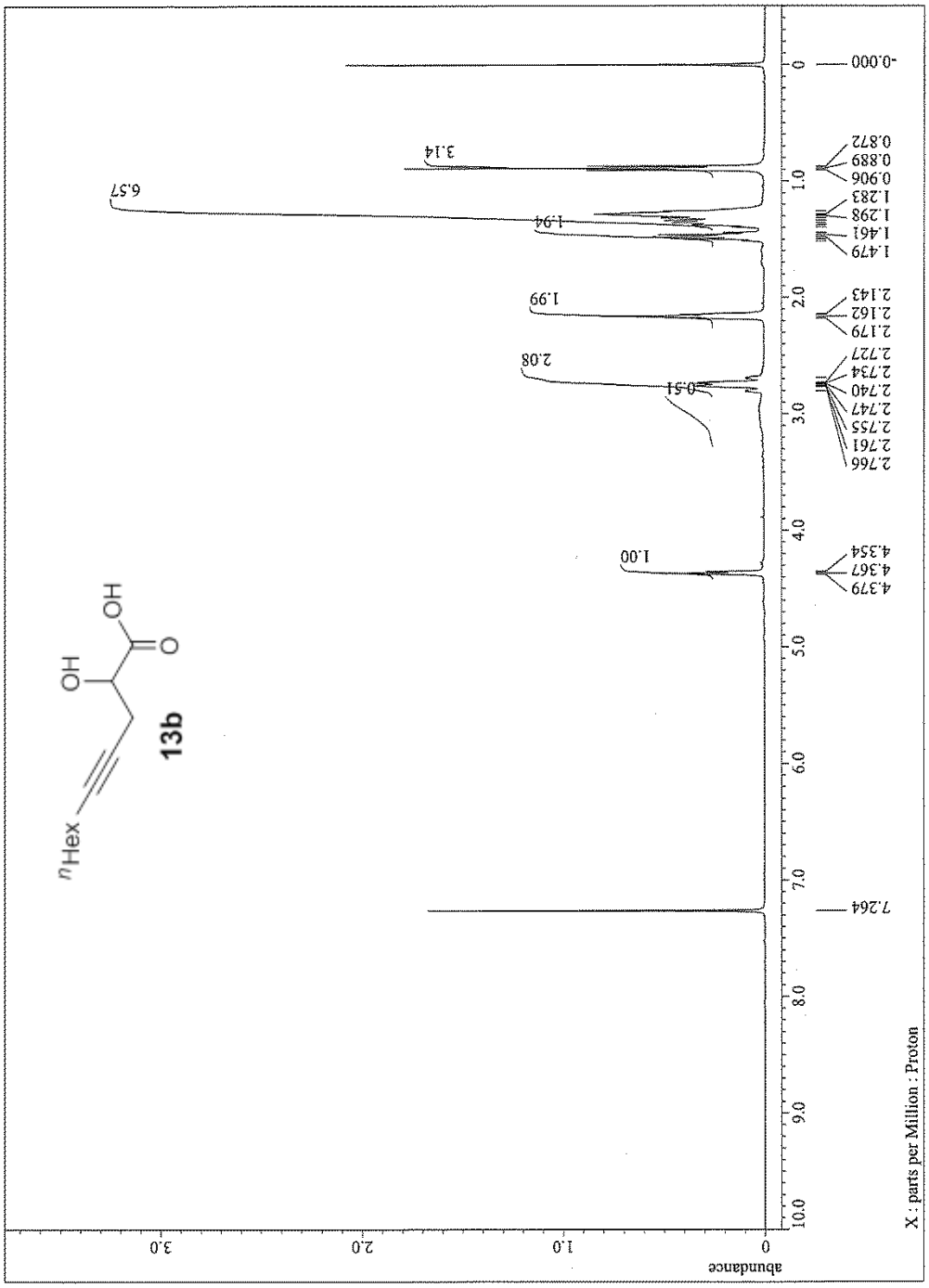

12b
BnO
OH
OH
O
O
X : parts per Million : Proton
abundance
0.000
5.54
1.00
0.96
1.90
2.26
1.09
1.05
1.07
5.170
5.679
7.362
7.359
7.351
7.337
7.329
7.323
7.259
7.015
6.994
6.976
6.958
6.038
6.034
6.031
5.995
4.404
4.393
4.387
4.376
2.759
2.754
2.748
2.743
2.741
2.738
2.635
2.631
2.616
2.613
2.597
2.595


12b
BnO
O
OH
O
OH
X : parts per Million : Carbon13
abundance
176.846
166.358
143.475
135.657
128.553
128.296
128.239
124.435
77.315
77.000
76.676
68.972
66.493
36.516

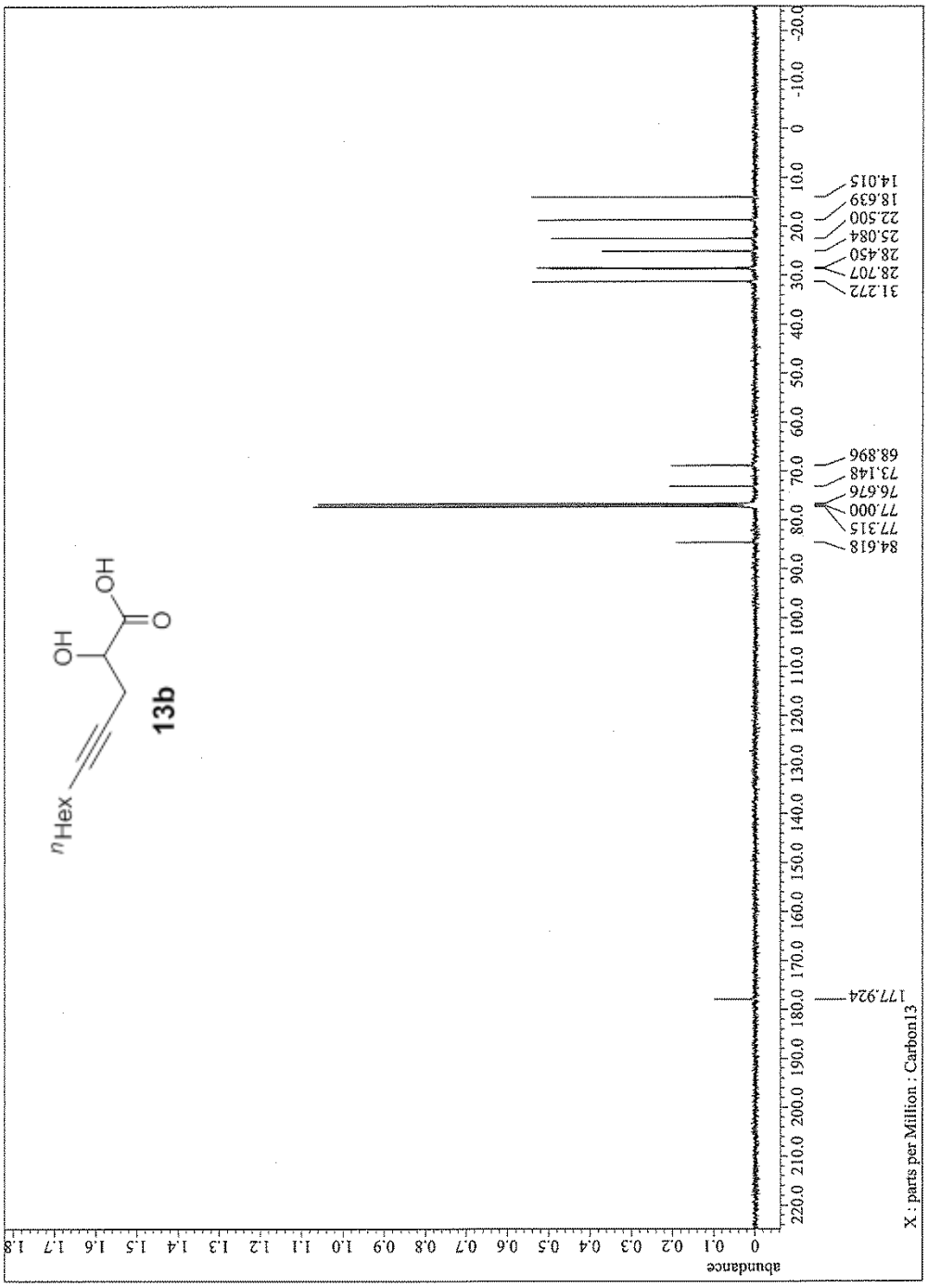
12b


13a
OH
OH
^{n}Hex
X : parts per Million : Proton
abundance
0.000
7.268
6.34
3.08
3.00
2.02
2.00
0.99
0.91
1.00
1.04
3.837
3.829
3.823
3.748
3.721
3.608
3.591
3.565
2.417
2.409
2.401
2.395
2.163
2.157
1.305
1.294
1.291
1.285
0.908
0.891
0.874

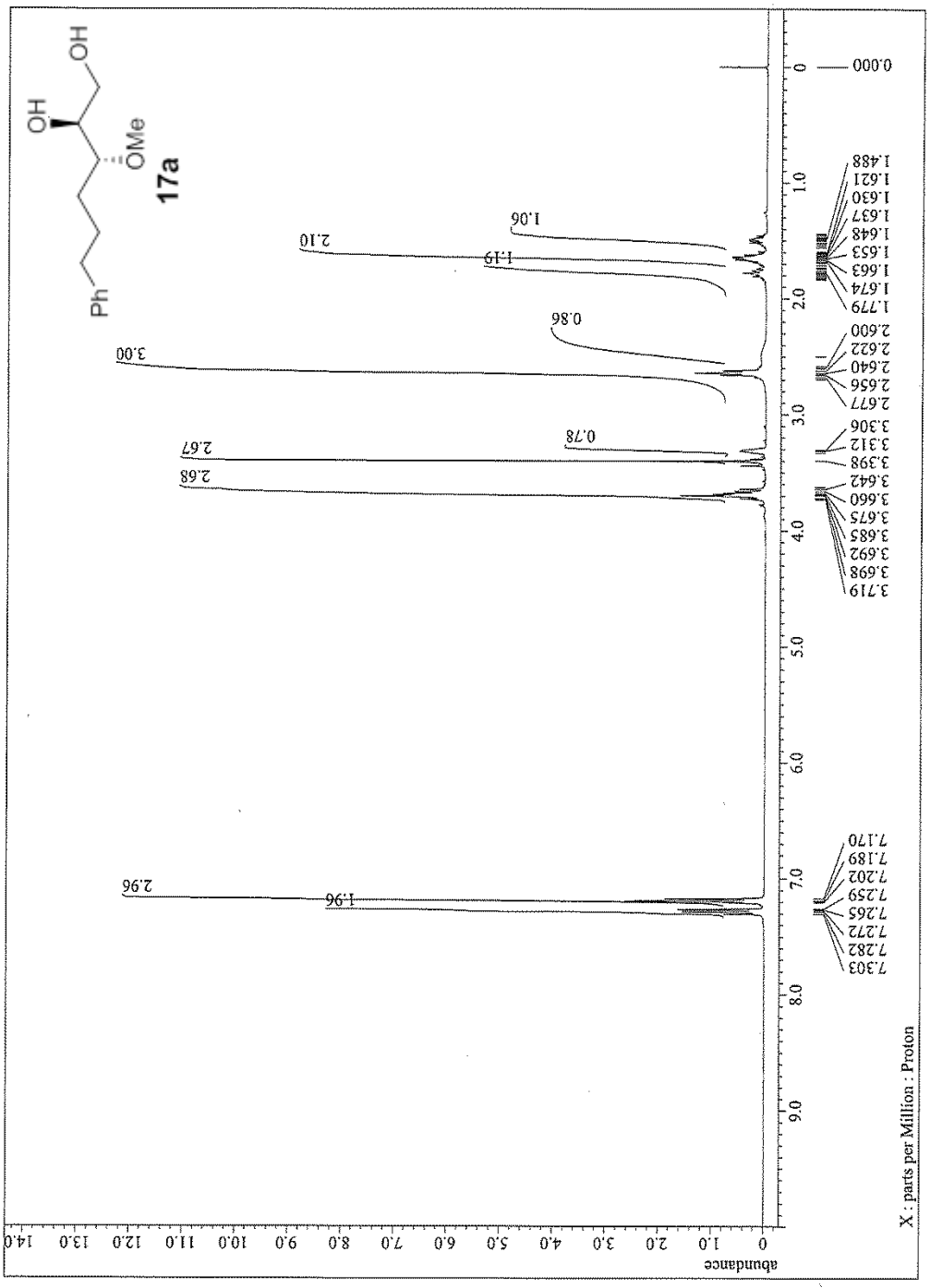

13a
OH
OH
nHex
abundance
X : parts per Million : Carbon13
83.541
77.315
77.000
76.685
75.160
70.402
65.625
31.301
28.860
28.555
23.835
22.529
18.696
14.024

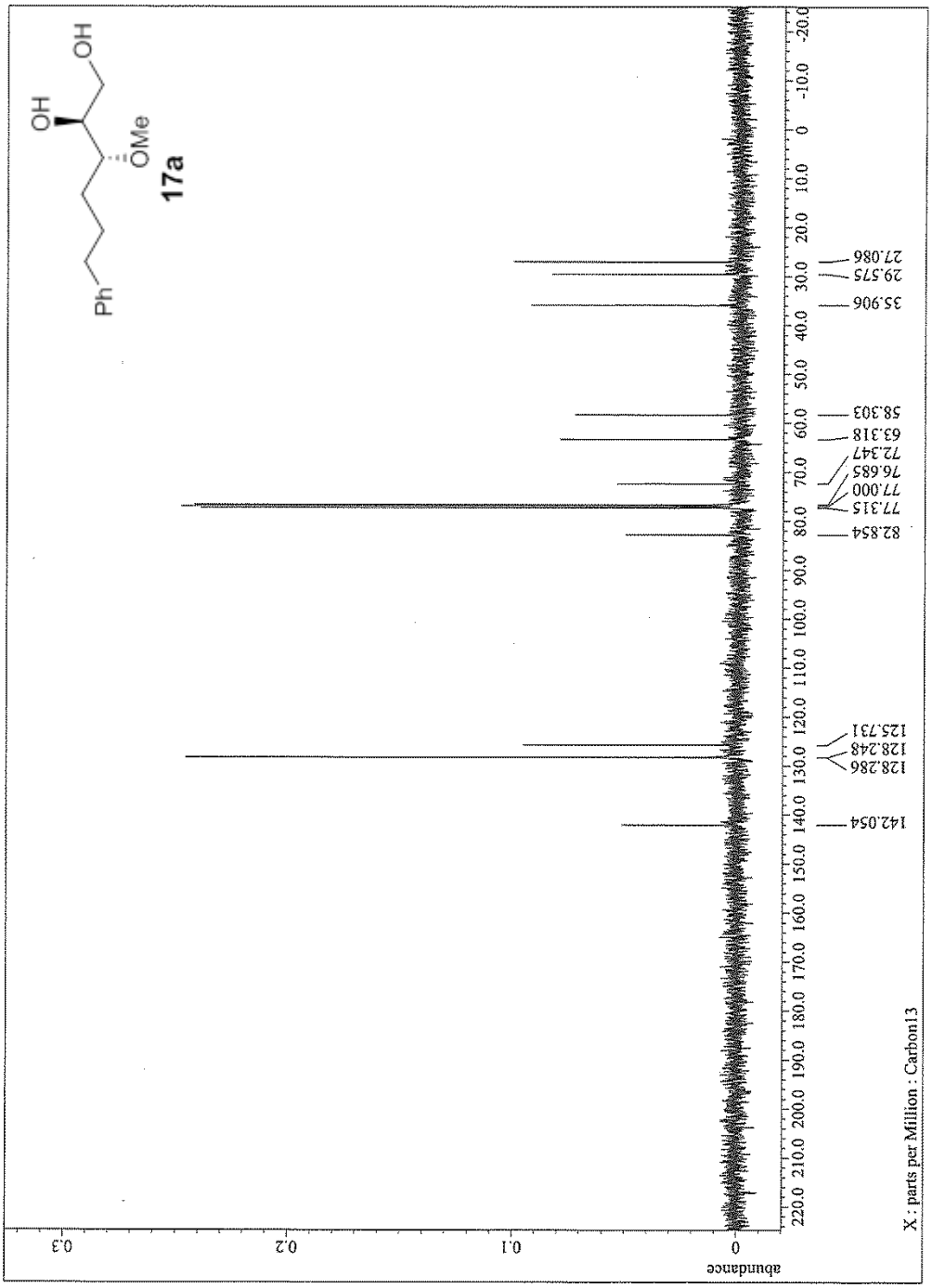

13b
nHex
OH
OH
O
-0.000
0.872
0.889
0.906
1.283
1.298
1.461
1.479
2.143
2.162
2.179
2.727
2.734
2.740
2.747
2.755
2.761
2.766
4.354
4.367
4.379
7.264
1.00
0.51
2.08
1.99
1.94
6.57
3.14
X : parts per Million : Proton
abundance

(13b)

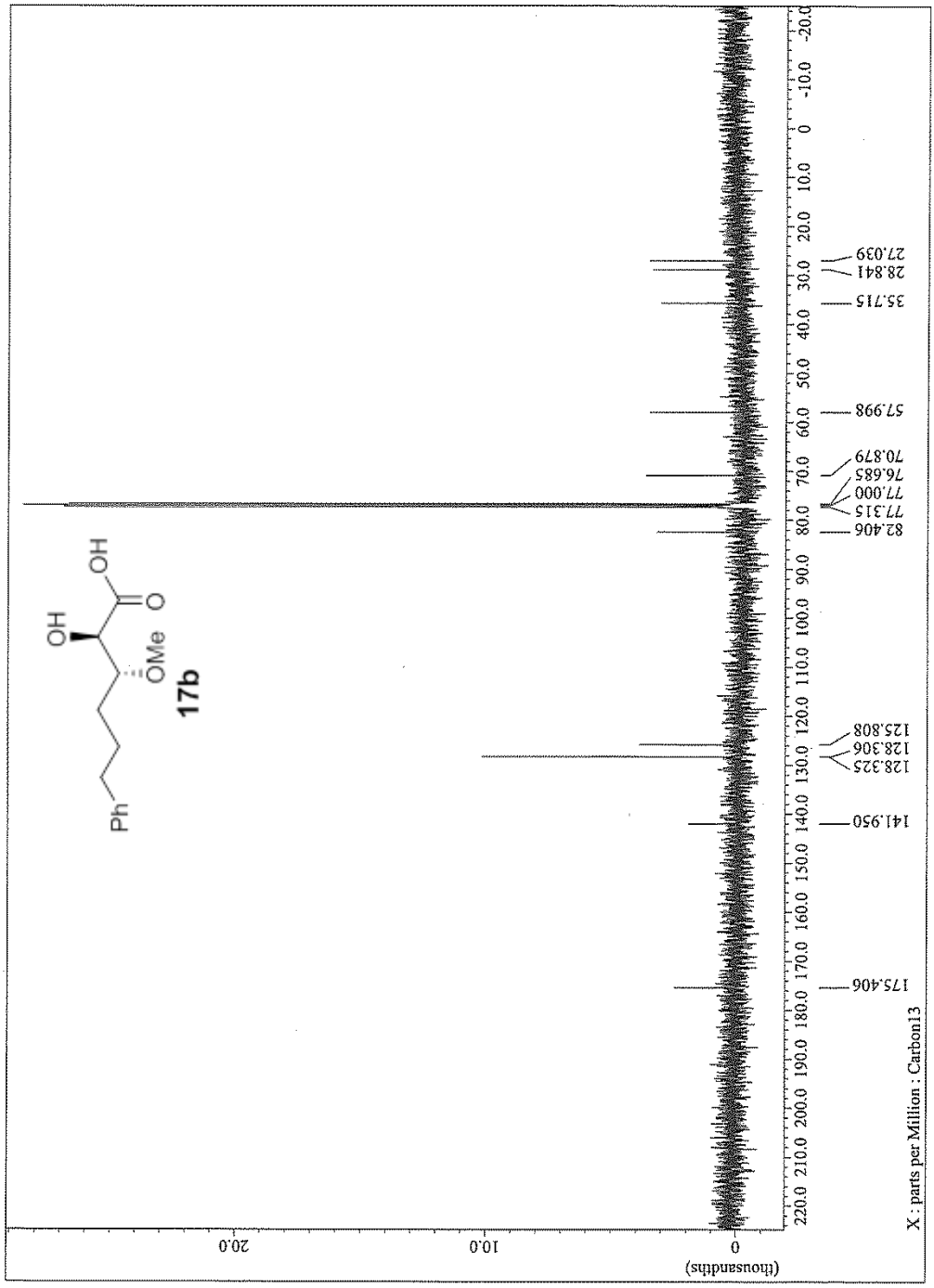

13b
OH
O
OH
nHex
abundance
X : parts per Million : Carbon13
177.924
84.618
77.315
77.000
76.676
73.148
68.896
31.272
28.707
28.450
25.084
22.500
18.639
14.015

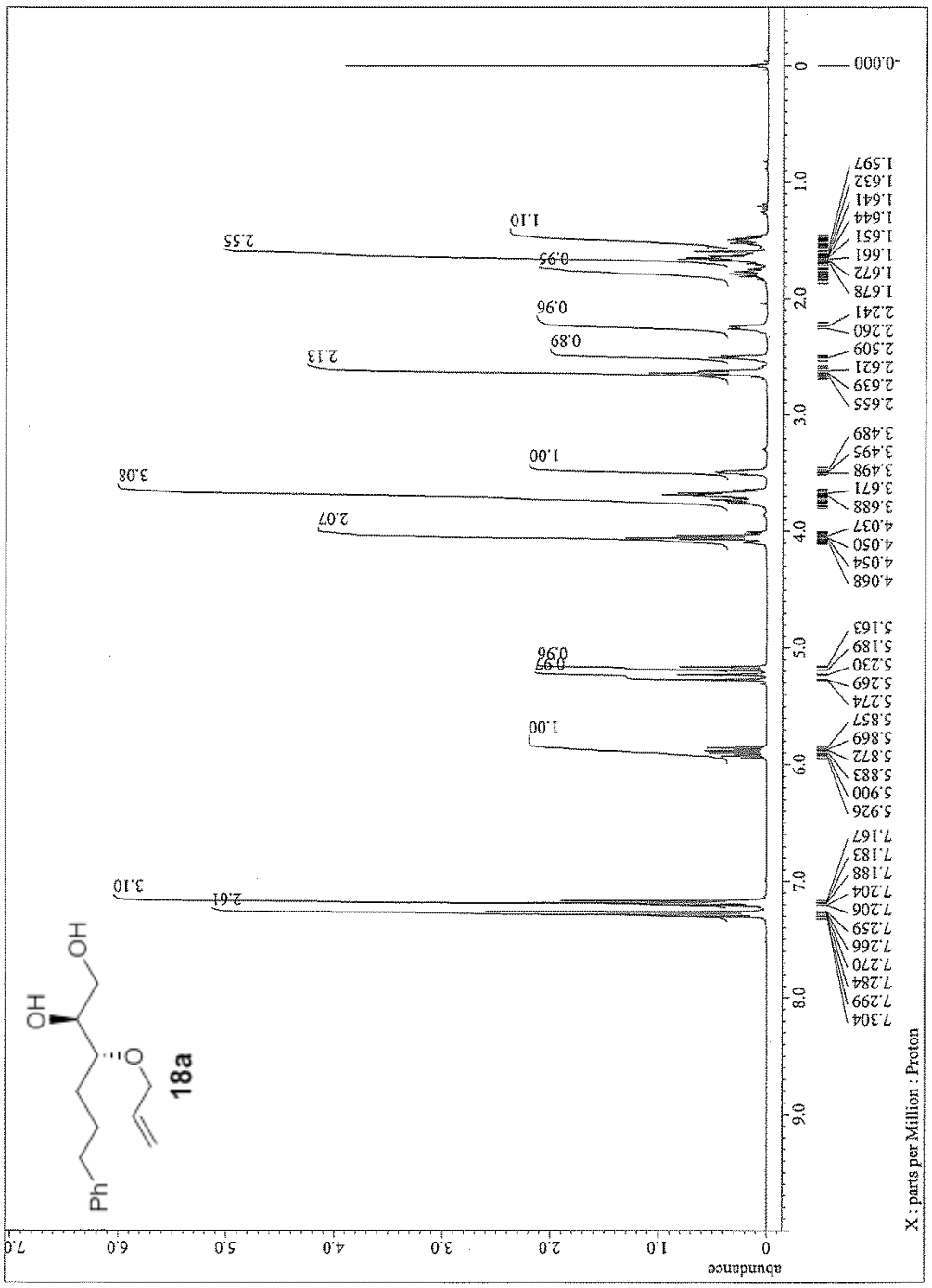
[3b]

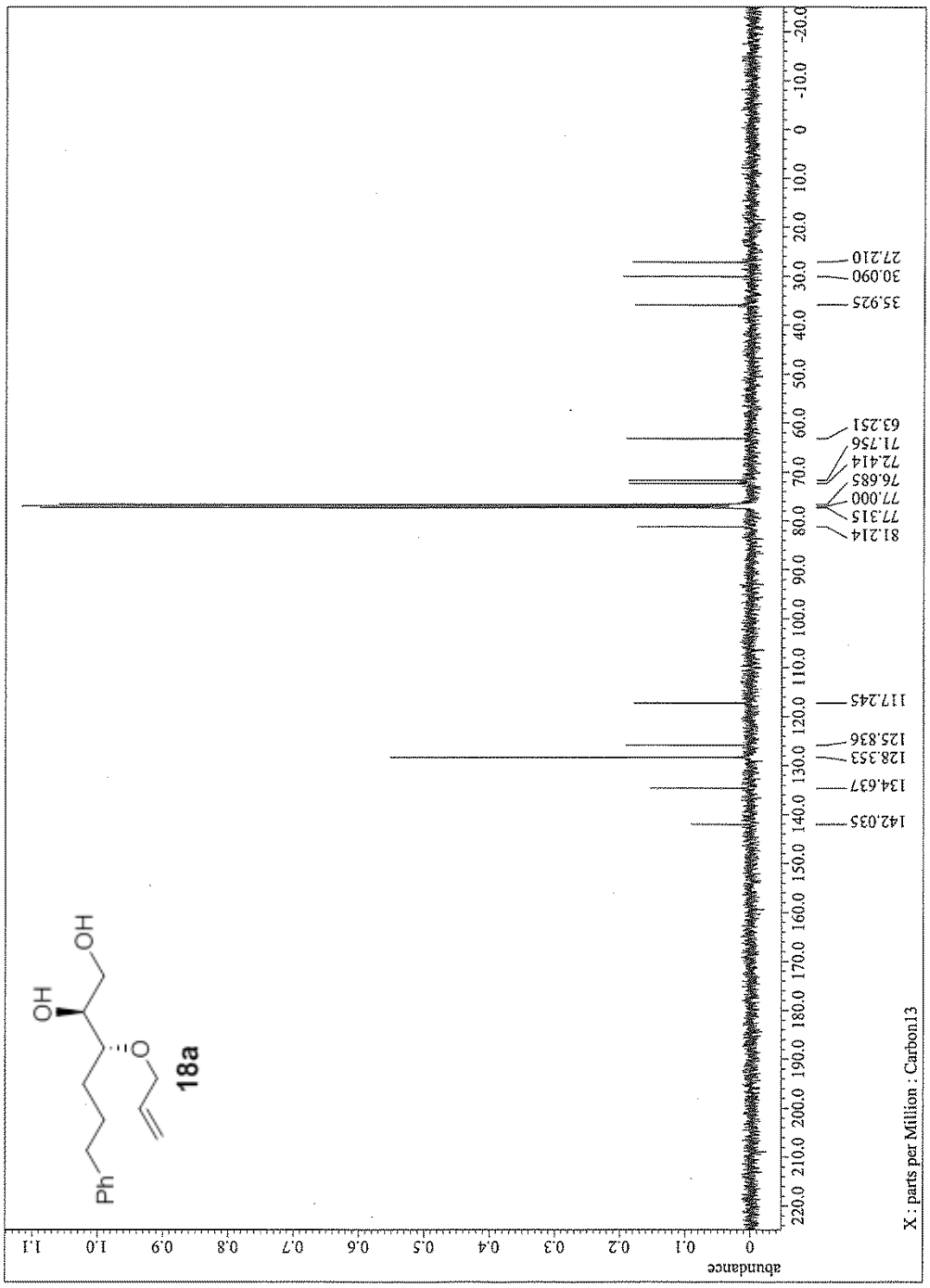

OH
OH
OMe
Ph
17a
0.000
1.06
2.10
1.19
0.86
3.00
0.78
2.67
2.68
2.96
1.96
abundance
X : parts per Million : Proton


OH
OH
OMe
Ph
17a
abundance
0
0.1
0.2
0.3
X : parts per Million : Carbon13
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 -10.0 -20.0
142.054
128.286
128.248
125.731
82.854
77.315
77.000
76.685
72.347
63.318
58.303
35.906
29.575
27.086

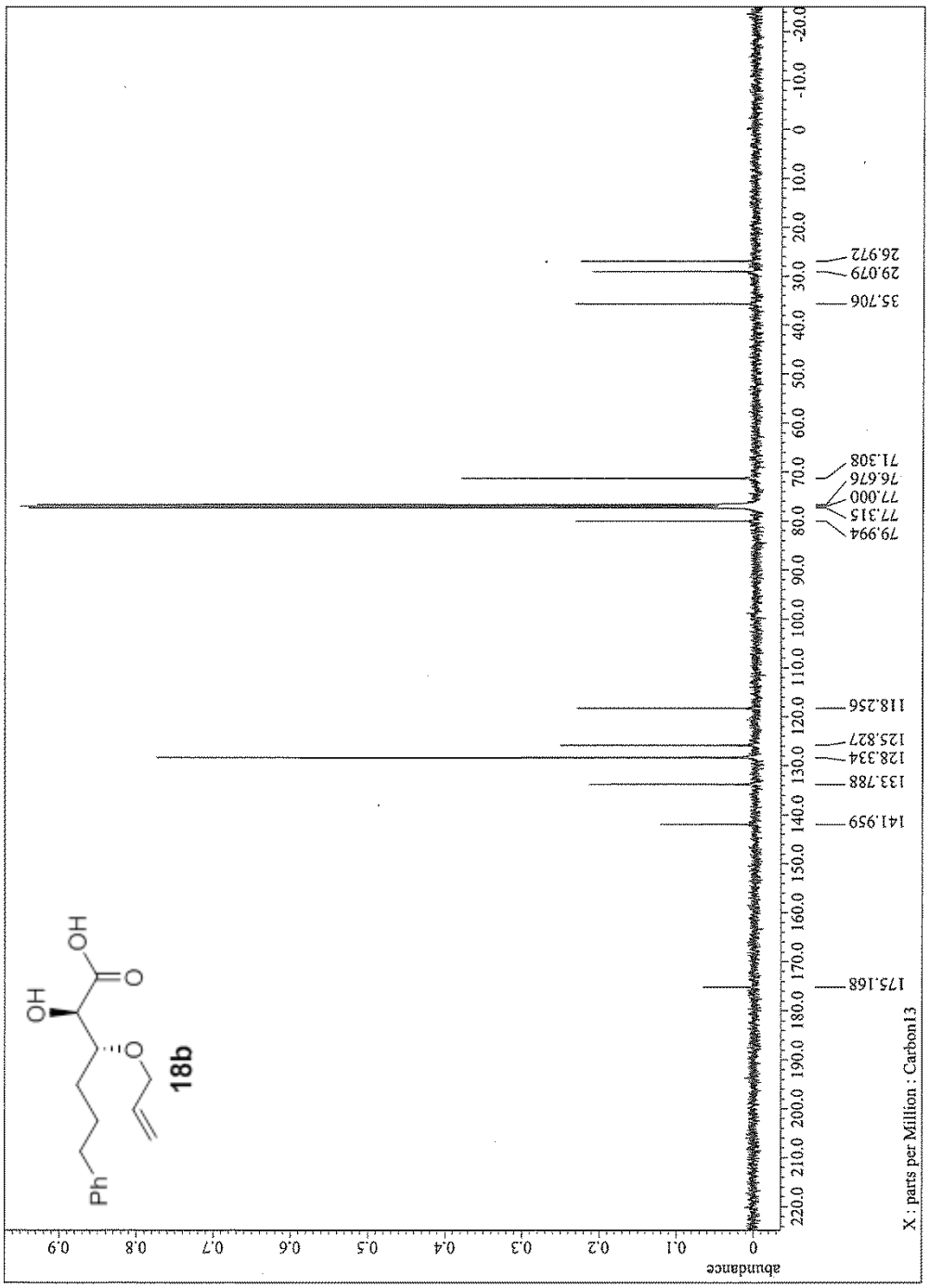
17b
OH
OH
O
OMe
Ph
3.09
2.16
2.06
3.19
1.03
3.20
1.01
1.00
0.000
5.725
7.291
7.272
7.253
7.190
7.180
7.174
7.160
4.401
4.392
3.575
3.566
3.557
3.546
3.438
2.647
2.628
2.609
1.800
1.781
1.772
1.763
1.749
1.729
1.710
1.685
1.518
abundance
X : parts per Million : Proton

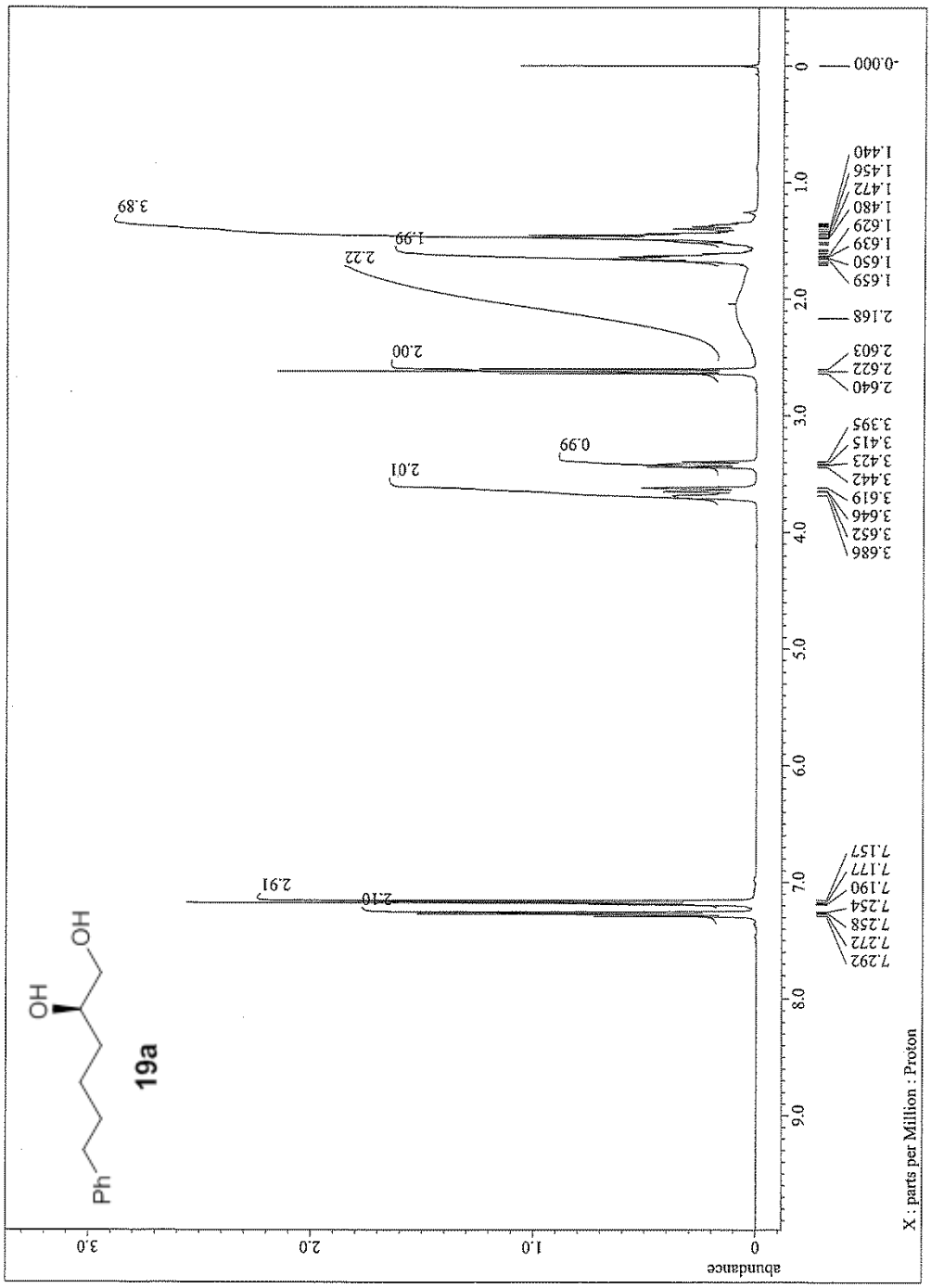

17b
OH
OH
OMe
O
Ph
(thousandths)
20.0
10.0
0
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
175.406
141.950
128.325
128.306
125.808
82.406
77.315
77.000
76.685
70.879
57.998
35.715
28.841
27.039

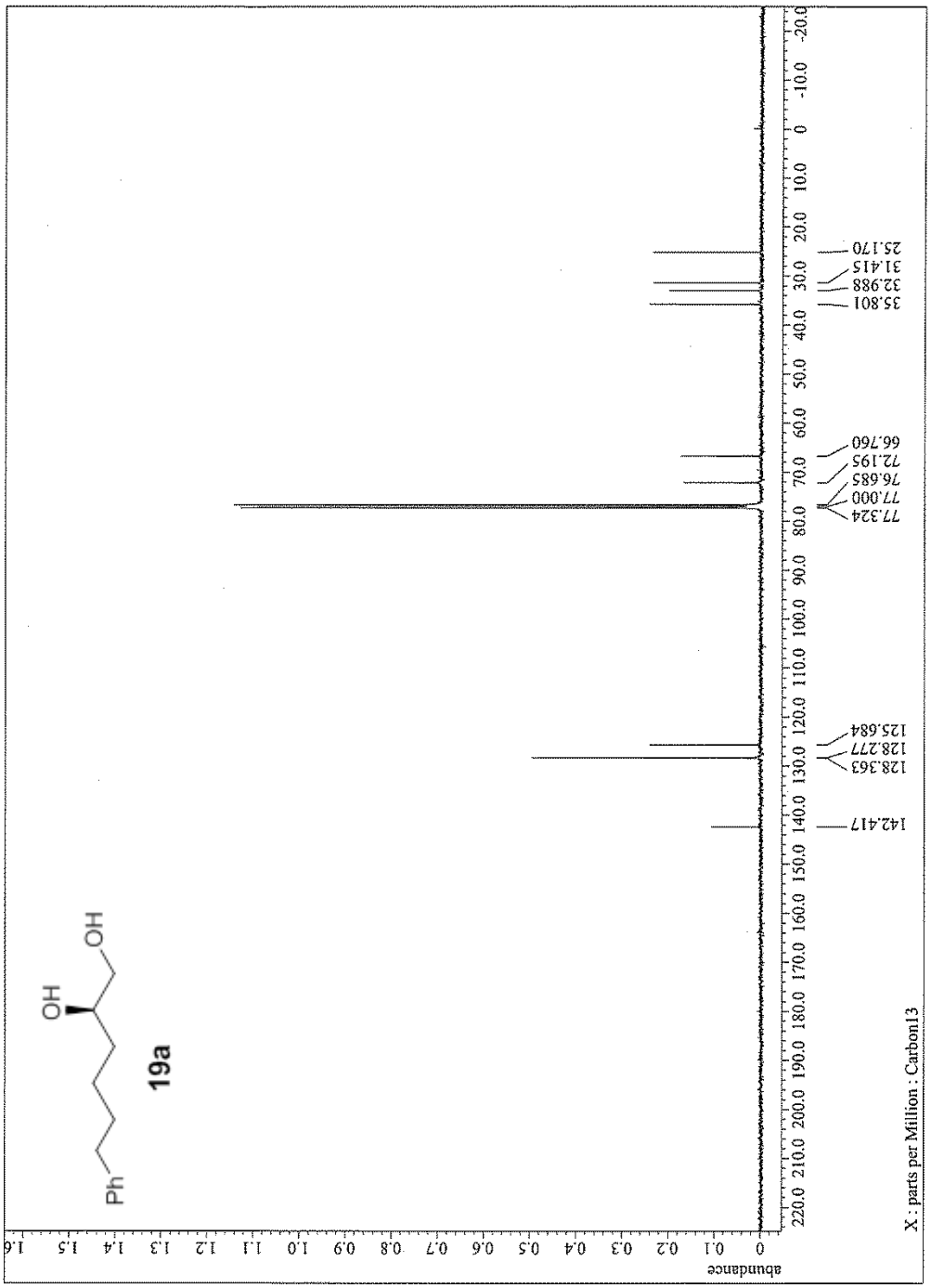

18a
OH
OH
O
Ph
abundance
X : parts per Million : Proton
7.304
7.299
7.284
7.270
7.266
7.259
7.206
7.204
7.188
7.183
7.167
5.926
5.900
5.883
5.872
5.869
5.857
5.274
5.269
5.230
5.189
5.163
4.068
4.054
4.050
4.037
3.688
3.671
3.498
3.495
3.489
2.655
2.639
2.621
2.509
2.260
2.241
1.678
1.672
1.661
1.651
1.644
1.641
1.632
1.597
-0.000
3.10
2.61
1.00
0.97
0.96
2.07
3.08
1.00
2.13
0.89
0.96
0.95
2.55
1.10


18a
OH
OH
O
Ph
abundance
X : parts per Million : Carbon13
142.035
134.637
128.353
125.836
117.245
81.214
77.315
77.000
76.685
72.414
71.756
63.251
35.925
30.090
27.210

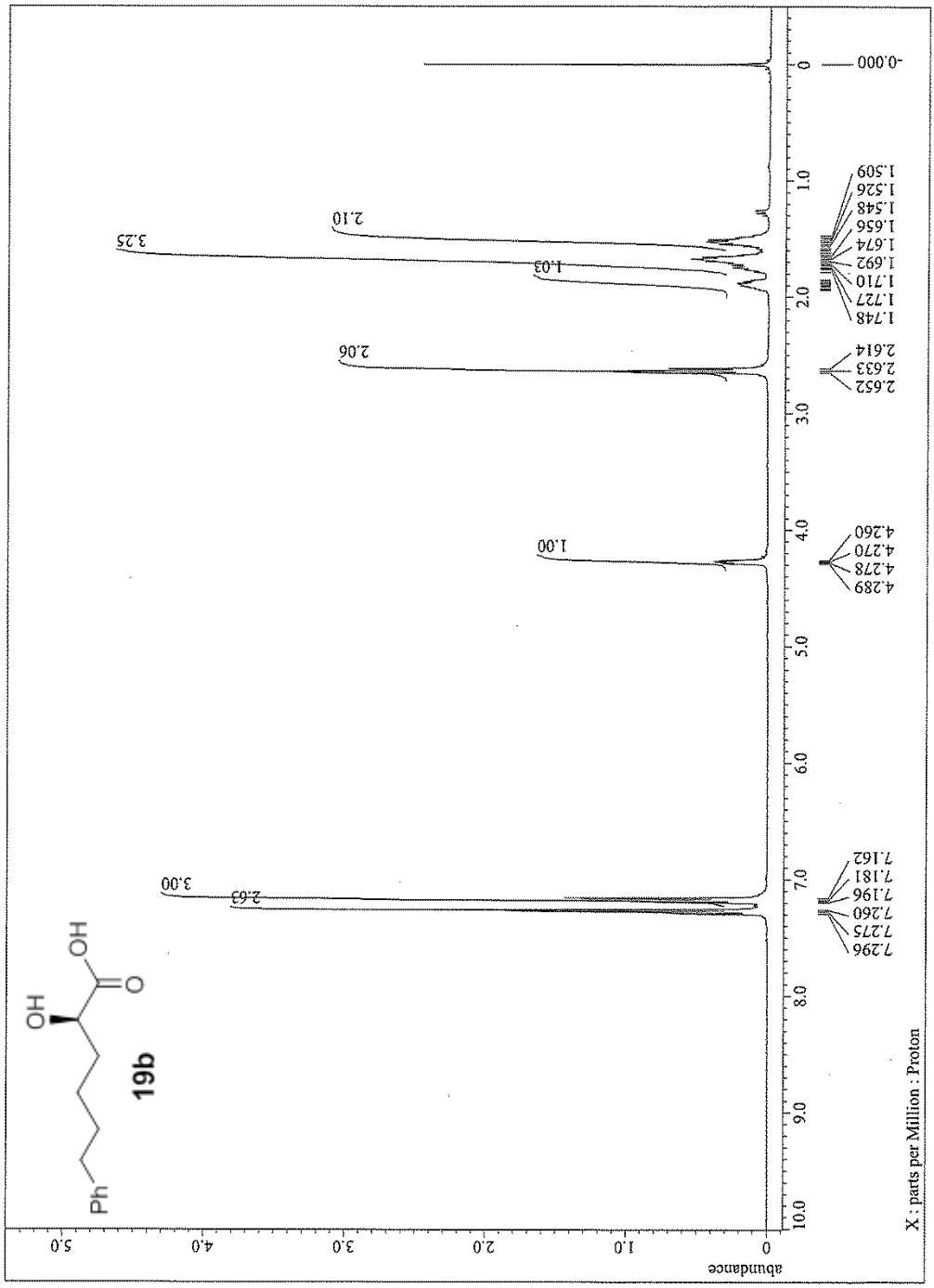
18b
Ph
OH
O
OH
3.06
2.27
2.21
2.09
2.05
2.00
1.01
1.00
0.99
1.02
0.98
7.294
7.275
7.264
7.258
7.256
7.198
7.195
7.181
7.162
5.924
5.899
5.882
5.871
5.867
5.856
5.310
5.307
5.228
5.203
4.415
4.387
4.378
4.091
4.088
3.747
3.738
3.727
3.718
2.646
2.627
2.608
1.819
1.810
1.803
1.789
1.784
1.771
1.758
1.703
1.532
-0.000
abundance
X : parts per Million : Proton


18b
OH
OH
O
O
Ph
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
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 -10.0 -20.0
X : parts per Million : Carbon13
175.168
141.959
133.788
128.334
125.827
118.256
79.994
77.315
77.000
76.676
71.308
35.706
29.079
26.972

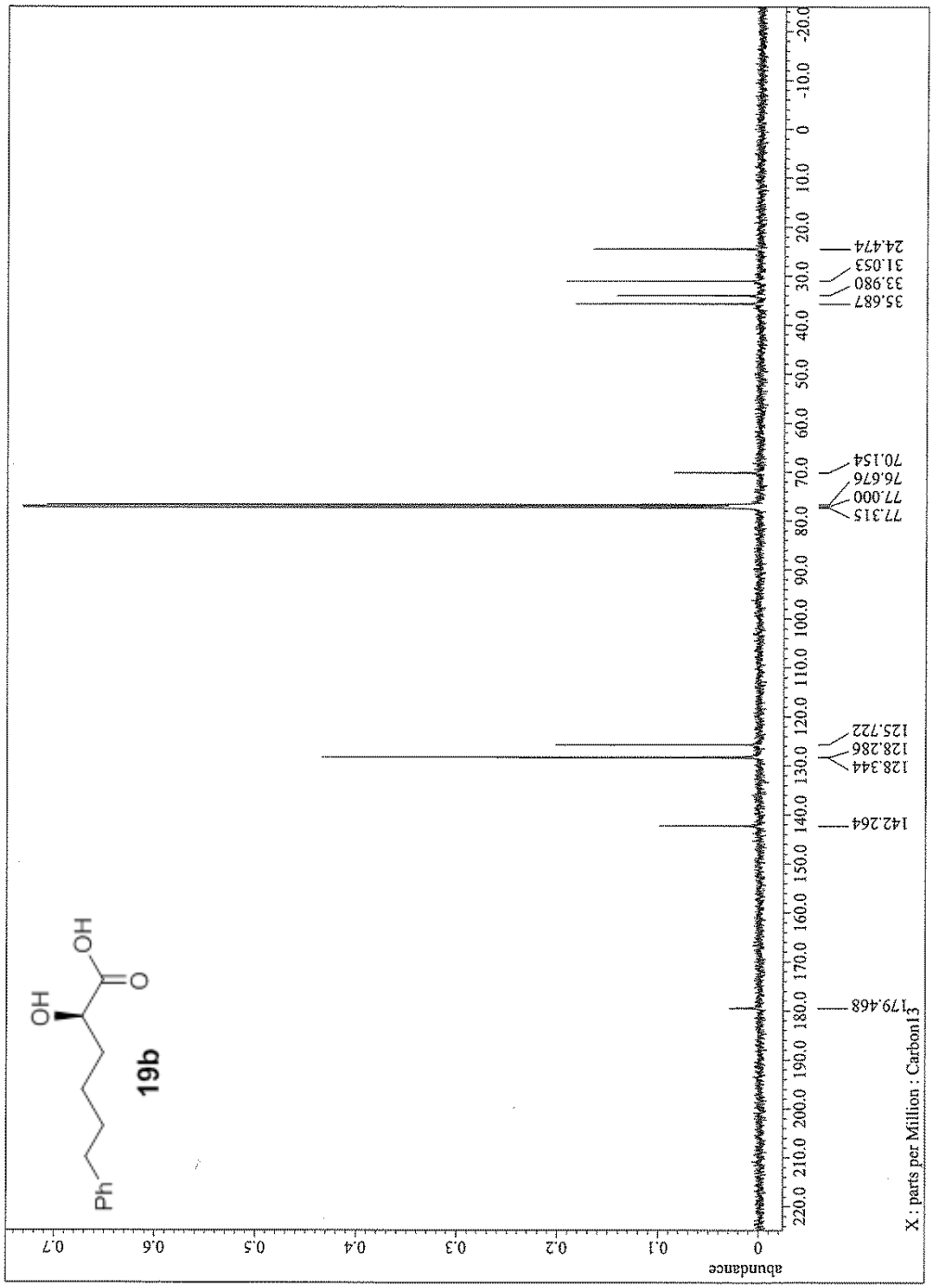

19a
Ph
OH
OH
X : parts per Million : Proton
abundance
7.292
7.272
7.258
7.254
7.190
7.177
7.157
3.686
3.652
3.646
3.619
3.442
3.423
3.415
3.395
2.640
2.622
2.603
2.168
1.659
1.650
1.639
1.629
1.480
1.472
1.456
1.440
-0.000
3.89
2.91
2.10
2.22
1.99
2.00
0.99
2.01


19a
OH
OH
Ph
142.417
128.363
128.277
125.684
77.324
77.000
76.685
72.195
66.760
35.801
32.988
31.415
25.170
X : parts per Million : Carbon13
abundance

19a


19b
OH
OH
O
Ph
X : parts per Million : Proton
abundance
7.296
7.275
7.260
7.196
7.181
7.162
4.289
4.278
4.270
4.260
2.652
2.633
2.614
1.748
1.727
1.710
1.692
1.674
1.656
1.548
1.526
1.509
-0.000
3.00
2.63
1.00
2.06
1.03
3.25
2.10

19b


19b
OH
OH
O
Ph
179.468
142.264
128.344
128.286
125.722
77.315
77.000
76.676
70.154
35.687
33.980
31.053
24.474
X : parts per Million : Carbon13
abundance

(19)