Supporting Information

Total syntheses of seminalipid and its analogues by using 2,6-bis(trifluoromethyl)phenylboronic acid as protective reagent

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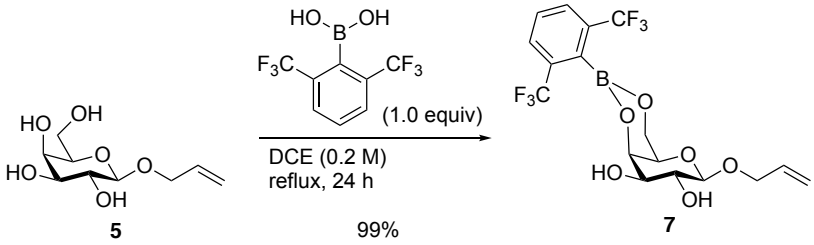
1. General information

NMR spectra were recorded on Agilent Technologies 400-MR DD2 (400 MHz for ^{1}H, 100 MHz for ^{13}C), 400-MR (400 MHz for ^{1}H, 100 MHz for ^{13}C). ^{1}H-NMR data are reported as follows; chemical shift in parts per million (ppm) downfield or upfield from $CDCl_3$ (δ 7.26), CD_3OD (δ 3.31) integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, dd = double doublet, ddd = double double doublet, dddd = double double double doublet, dt = double triplet, ddt = double double triplet, dq = double qualtet, and m = multiplet), and coupling constants (Hz). ^{13}C-NMR chemical shifts are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.0) or CD_3OD (δ 49.0). Mass spectra were measured with JEOL JMS-AX505HA, JMS-700 MStation, and JEOL JMS-T100LP spectrometers. Thin-layer chromatography (TLC) was carried out on Merck 60F-254 precoated silica gel plates and were visualized by fluorescence quenching under UV light. Column chromatography was performed using Silica Gel 60N (spherical, neutral, 63-210 μm) (Kanto Chemical Co., Inc.). Air- and/or moisture-sensitive reactions were carried out under nitrogen atmosphere using oven-dried glassware. Allyl *β*-D-galactopyranoside (**5**)[1] was synthesized according to the literature.

Allyl β-D-galactopyranoside 2,3-[2,6-bis(trifluoromethyl)phenyl]boronate ester (**7**)



2,6-Bis(trifluoromethyl)phenylboronic acid (264 mg, 1.00 mmol, 1.0 equiv) was added to a stirred solution of allyl *β*-D-galactopyranoside (**5**) (225 mg, 1.00 mmol)[1] in DCE (5.1 mL, 0.2 M). After stirring for 24 h under reflux, the reaction mixture was concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 1 : 2) to give **7** (649 mg, 0.99 mmol, 99%) as a yellow amorphous material.

TLC

R_f 0.33 (hexane / EtOAc = 1 : 2).

Optical rotation

$[\alpha]_D^{23}$ −23.3 (*c* 1.56, $CHCl_3$).

IR(neat)

3476, 3424, 3099, 2915, 2879, 1578, 1473, 1433, 1348, 1296, 1204, 1185, 1146, 1076, 1035, 982, 896, 872, 822, 756, 748, 705, 679, 622, 541 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 5.97 (dddd, *J* = 17.2, 10.4, 6.4, 5.2 Hz, 1H, C*H*=CH_2), 5.35 (dq, *J* = 17.2, 1.6 Hz, 1H, CH=CH*H*, *trans*), 5.24-5.22 (m, 1H, CH=CH*H*, *cis*), 4.45-4.37 (m, 3H, H-1, H-4, CH*H*CH=CH_2), 4.31-4.23 (m, 2H, H-6), 4.17 (ddt, *J* = 12.8, 6.4, 1.2 Hz, 1H, CH*H*CH=CH_2), 3.88-3.87 (m, 1H, H-3), 3.72-3.65 (m, 2H, H-2, H-5), 2.55 (br s, 2H, 2-OH, 3-OH).

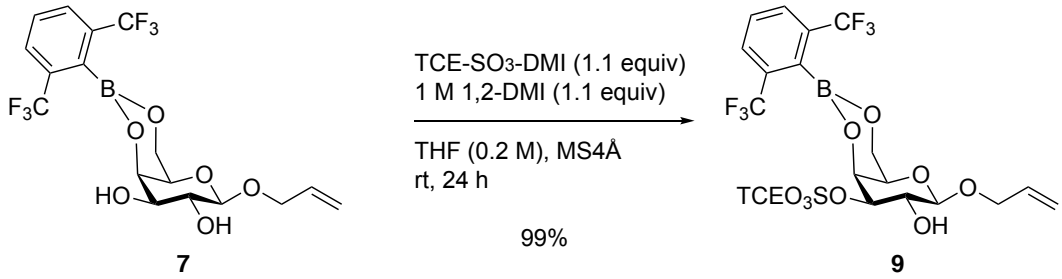
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 134.0, 133.8 (q, $^{2}J_{C\text{-}F}$ = 31.1 Hz), 129.3, 128.6 (q, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 274.2 Hz), 117.7, 101.6, 72.9, 71.1, 70.8, 69.9, 68.3, 65.2.

ESI-HRMS

HRMS (ESI) m/z Calcd for $C_{17}H_{17}{}^{11}B^{19}F_6NaO_6$ $[M+Na]^+$ 465.0920, found 465.0903.

Allyl 3-*O*-(2,2,2-trichloroethyl)sulfo-*β*-D-galactopyranoside 4,6-[2,6-bis(trifuluoromethyl)phenyl]boronic ester (**9**)



TCE-SO_3-DMI (516 mg, 1.10 mmol, 1.1 equiv) was added to a stirred mixture of **7** (442 mg, 1.00 mmol), MS4Å (1.00 g, 1.00 g/1.00 mmol) and 1,2-dimethylimidazole (1.0 M in DCM solution, 1.10 mL, 1.10 mmol, 1.1 equiv) in THF (5.1 mL, 0.2 M) at 0 °C under N_2 atmosphere. After stirring for 24 h at room temperature, the reaction mixture was filtered through a pad of Celite® rinsing with DCM (50 mL). The organic layer was washed successively with aqueous 1 M HCl (25 mL) and H_2O (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1) to give **9** (649 mg, 0.99 mmol, 99%) as a yellow oil.

TLC

R_f 0.53 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{27}$ +33.8 (*c* 1.00, $CHCl_3$).

IR (neat)

3436, 2959, 2920, 2848, 1579, 1472, 1413, 1345, 1296, 1271, 1201, 1178, 1132, 1092, 1048, 1011, 988, 907, 887, 834, 818, 775, 747, 727, 705, 679, 617, 542 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 5.96 (dddd, *J* = 17.2, 10.4, 6.4, 4.8 Hz, 1H, C*H*=CH_2), 5.36 (dq, *J* = 17.2, 1.6 Hz, 1H, CH=CH*H*, *trans*), 5.27 (dq, *J* = 10.4, 1.6 Hz, 1H, CH=CH*H*, *cis*), 4.95 (d, *J* = 10.8 Hz, 1H, CH_2), 4.75 (brd, *J* = 3.6 Hz, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, CH_2), 4.67 (dd, *J* = 10.0, 3.6 Hz, 1H, H-3), 4.47-4.42 (m, 2H, H-1, CH*H*CH=CH_2, H-1), 4.32 (dd, *J* = 12.8, 1.2 Hz, 1H, H-6), 4.26 (dd, *J* = 12.8, 2.4 Hz, 1H, H-6'), 4.19 (ddt, *J* = 12.4, 6.4, 1.6 Hz, 1H, CH*H*CH=CH_2), 3.97 (dd, *J* = 10.0, 7.6 Hz, 1H, H-2), 3.92-3.91 (m, 1H, H-5), 2.54 (brs, 1H, OH).

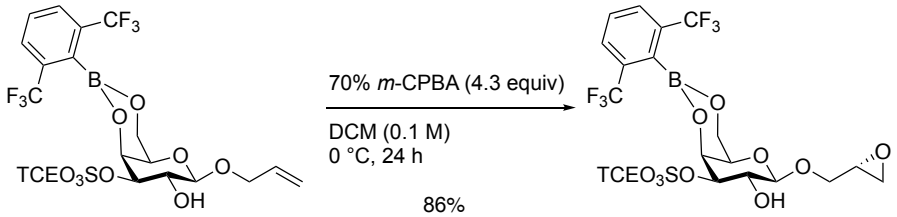
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 133.9 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 133.5, 129.5, 128.7 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 118.3, 101.4, 92.6, 83.7, 79.8, 70.3, 68.8, 67.9, 67.6, 64.9.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}{}^{11}B^{35}Cl_3F_6NaO_9S$ $[M+Na]^+$ 674.9632, found 674.9620.

(4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-(2,6-bis(trifluoromethyl)phenyl-7-hydroxy-6-((*R*)-oxiran-2-ylmethoxy)hexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-8-yl (2,2,2-trichloroethyl) sulfate (**10**)



70% *m*-CPBA (380 mg, 2.20 mmol, 4.3 equiv) was added to a stirred solution of **9** (327 mg, 0.50 mmol) in DCM (5.0 mL, 0.1 M) at 0 °C. After stirring for 24 h, the reaction was quenched by adding saturated aqueous $Na_2S_2O_3$ (10 mL). After stirring for 2 h at room temperature, the resulting mixture was extracted with EtOAc (2 x 20 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (20 mL), saturated aqueous $Na_2S_2O_3$, (2 x 20 mL), H_2O (2 x 20 mL) and brine (2 x 20 mL) and dried over Na_2SO_4. Filtration and concentration under reduced

pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 2) to give **10** (288 mg, 0.43 mmol, 86%, 93:7 dr) as a white powder.

TLC

R_f 0.42 (hexane / EtOAc = 3 : 2).

Optical rotation

$[\alpha]_D^{23}$ +35.2 (*c* 1.00, $CHCl_3$).

IR (neat)

3422, 2962, 1628, 1578, 1474, 1413, 1376, 1346, 1298, 1202, 1178, 1092, 1049, 889, 727, 544 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H, CH_2), 4.75-4.74 (m, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, CH_2), 4.65 (dd, *J* = 10.4, 3.2 Hz, 1H, H-3) 4.46 (d, *J* = 7.6 Hz, 1H, H-1), 4.33-4.25 (m, 2H, H-6), 4.04-3.92 (m, 4H, H-2, H-5, $OC\underline{H_2}CHCH_2$), 3.28-3.25 (m, 1H, $OCH_2C\underline{H}CH_2$), 3.14 (brs, 1H, OH), 2.88-2.82 (m, 2H, $OCH_2CHC\underline{H_2}$).

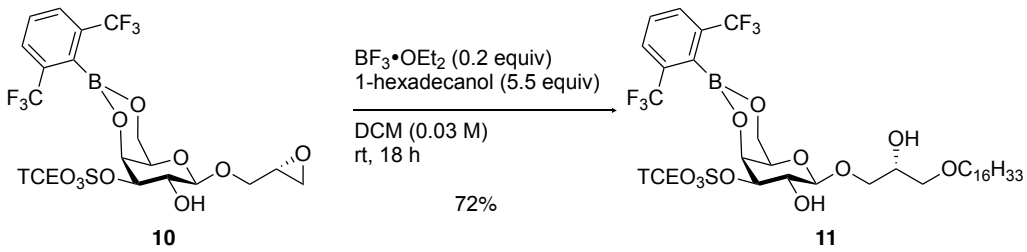
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 133.8 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.5, 128.7 (q, $^3J_{C\text{-}F}$ = 4.3 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 102.7, 92.6, 83.9, 79.8, 68.8, 68.5, 67.8, 67.7, 64.9, 50.8, 44.4.

ESI-HRMS

HRMS (ESI) m/z Caicd for $C_{19}H_{18}{}^{11}B^{35}Cl_3{}^{19}F_6NaO_{10}S$ $[M+Na]^+$ 690.9581, found 690.9581.

(4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-[2,6-bis(trifluoromethyl)phenyl]-6-[(*R*)-3-(hexadecyloxy)-2-hydroxypropoxy]-7-hydroxyhexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-8-yl (2,2,2-trichloroethyl) sulfate (**11**)



BF_3•OEt_2 (2.50 μL, 0.02 mmol, 0.2 equiv) was added to a stirred solution of **10** (67.0 mg, 0.100 mmol) and 1-hexadecanol (133 mg, 0.550 mmol, 5.5 equiv) in DCM (3.3 mL, total 0.03 M) at room temperature under N_2. After stirring for 18 h, the reaction

was quenched by adding saturated aqueous $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc (2 x 20 mL). The combined organic extract was washed with H_2O (2 x 20 mL) and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1) to give **11** (56.8 mg, 0.072 mmol, 72%) as a colorless oil.

TLC

R_f 0.30 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{27}$ +31.3 (*c* 1.00, $CHCl_3$).

IR (neat)

3751, 3375, 2925, 2854, 1735, 1718, 1467, 1413, 1345, 1296, 1200, 1178, 1134, 1089, 1046, 1011, 975, 872, 834, 817, 775, 746, 726, 678, 542, 448, 438 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}$CCl$_3$), 4.75 (brd, *J* = 3.2 Hz, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}$CCl$_3$), 4.68 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3), 4.48 (d, *J* = 7.6 Hz, 1H, H-1), 4.31-4.23 (m, 2H, H-6), 4.05-3.99 (m, 1H, OCH$_2$C$\underline{H}$CH$_2$O) 3.98-3.91 (m, 3H, H-2, H-5, OC$\underline{H_2}$CHCH$_2$O), 3.84 (dd, *J* = 10.8, 3.6 Hz,1H, OC$\underline{H_2}$CHCH$_2$O), 3.57 (dd, *J* = 9.6, 6.4 Hz ,1H, OCH$_2$CHC$\underline{H_2}$O), 3.53 (dd, *J* = 9.6, 4.4 Hz, 1H, OCH$_2$CHC$\underline{H_2}$O), 3.51-3.45 (m, 3H, OC$\underline{H_2}$CH$_2$C$_{14}$H$_{29}$), 1.62-1.54 (m, 3H, OCH$_2$C$\underline{H_2}$C$_{14}$H$_{29}$, OH), 1.25 (m, 26H,), 0.87 (m, 3H, OC$_{15}$H$_{30}$C$\underline{H_3}$).

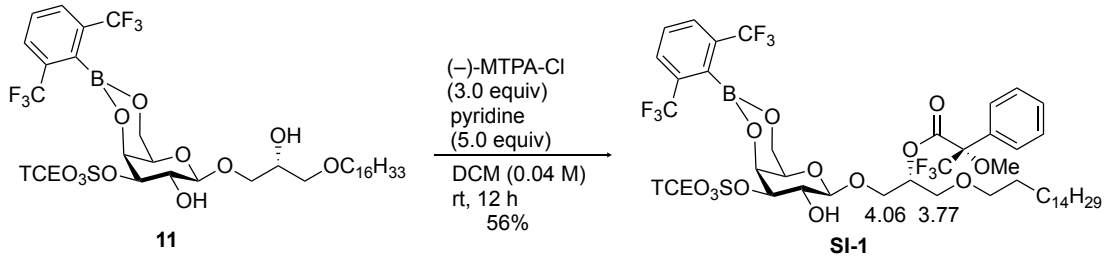
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 133.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.4, 128.7 (q, $^3J_{C\text{-}F}$ = 4.8 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.0 Hz), 102.7, 92.6, 84.0, 79.8, 71.8, 71.5, 70.4, 69.6, 68.8, 67.6, 65.0, 31.9, 29.7, 29.65, 29.63, 29.61, 29.59, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{35}H_{52}{}^{11}B^{35}Cl_3F_6NaO_{11}S$ $[M+Na]^+$933.2190, found 933.2192.

(*R*)-1-(((4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-(2,6-bis(trifluoromethyl)phenyl)-7-hydroxy-8-(((2,2,2-trichloroethoxy)sulfonyl)oxy)hexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-6-yl)oxy)-3-(hexadecyloxy)propan-2-yl (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**SI-1**)



(–)-MTPA-Cl (75.8 mg, 0.300 mmol, 3.0 equiv)[2] was added to a stirred solution of **11** (91.0 mg, 0.100 mmol) and pyridine (40.4 μL, 0.500 mmol, 5.0 equiv) in DCM (2.50 mL, 0.04 M) at room temperature under N_2. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1) to give (*S*)-ester (63.1 mg, 0.056 mmol, 56%) as a colorless oil.

TLC

R_f 0.49 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{25}$ +12.3 (*c* 1.00, $CHCl_3$).

IR (neat)

3578, 2929, 2856, 1750, 1471, 1416, 1345, 1297, 1270, 1202, 1178, 1134, 1010, 977, 889, 816, 721, 543, 451, 436, 427, 412 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.64-7.57 (m, 3H), 7.43-7.40 (m, 3H), 5.49-5.43 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.92 (d, *J* = 10.8 Hz, 1H, $C\underline{H}_2CCl_3$), 4.71 (d, *J* = 10.8 Hz, 1H, $C\underline{H}_2CCl_3$), 4.70 (brd, *J* = 4.0 Hz, 1H, H-4), 4.55 (dd, *J* = 10.0, 3.6 Hz, 1H, H-3), 4.28-4.21 (m, 3H, H-1, H-6), 4.06 (dd, *J* = 12.0, 4.8 Hz ,1H, $OC\underline{H}_2CHCH_2O$) 3.86-3.80 (m, 3H, H-2, H-5, $OC\underline{H}_2CHCH_2O$), 3.77 (dd, *J* = 10.8, 6.8 Hz, 1H, $OCH_2CHC\underline{H}_2O$), 3.68 (dd, *J* = 10.8, 4.0 Hz, 1H, $OCH_2CHC\underline{H}_2O$), 3.60 (s, 3H, OCH_3), 3.52-3.42 (m, 2H, $OC\underline{H}_2CH_2C_{14}H_{29}$), 2.75 (brs, 1H, OH) 1.62-1.54 (m, 2H,

$OCH_2C\underline{H_2}C_{14}H_{29}$), 1.25 (m, 26H), 0.87 (t, J = 6.8Hz, 3H, $OC_{15}H_{30}C\underline{H_3}$).

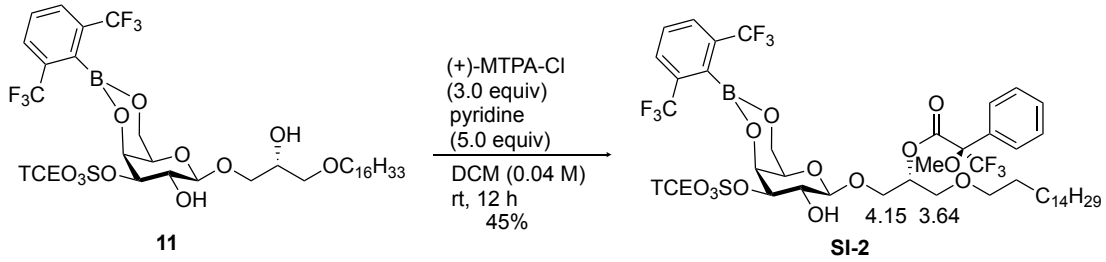
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 166.4, 133.8 (q, $^2J_{C\text{-}F}$ = 31.3 Hz), 132.4, 129.7, 129.5, 128.7 (q, $^3J_{C\text{-}F}$ = 5.1 Hz), 128.4, 127.4, 124.1 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 123.2 (q, $^1J_{C\text{-}F}$ = 287.2 Hz), 103.0, 92.6, 83.5, 79.8, 73.9, 71.8, 68.8, 68.7, 68.4, 67.7, 67.6, 64.9, 55.5, 31.9, 29.69, 29.67, 29.66, 29.64, 29.60, 29.59, 29.58, 29.45, 29.4, 26.0, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m/z* calcd for $C_{45}H_{59}{}^{11}B^{35}Cl_3F_9NaO_{13}S$ $[M+Na]^+$ 1149.2589, found 1149.2572.

(*R*)-1-(((4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-(2,6-bis(trifluoromethyl)phenyl)-7-hydroxy-8-(((2,2,2-trichloroethoxy)sulfonyl)oxy)hexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-6-yl)oxy)-3-(hexadecyloxy)propan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**SI-2**)



(+)-MTPA-Cl (75.8 mg, 0.300 mmol, 3.0 equiv)[2] was added to a stirred solution of **11** (91.0 mg, 0.100 mmol) and pyridine (40.4 μL, 0.500 mmol, 5.0 equiv) in DCM (2.50 mL, 0.04 M) at room temperature under N_2. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1) to give (*R*)-ester (50.7 mg, 0.045 mmol, 45%) as a colorless oil.

TLC

R_f 0.49 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{25}$ +26.5 (*c* 1.00, $CHCl_3$).

IR (neat)

3850, 3747, 3686, 3666, 3646, 3626, 2928, 2856, 1748, 1731, 1579, 1470, 1416, 1381, 1345, 1297, 1201, 1177, 1133, 1013, 975, 888, 721, 543, 507, 447, 435, 425, 411 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.64-7.55 (m, 3H), 7.42-7.39 (m, 3H), 5.51-5.44 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.92 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.74 (brd, *J* = 3.2 Hz, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl$), 4.64 (dd, *J* = 10.8, 3.2 Hz, 1H, H-3), 4.44 (d, *J* = 7.6 Hz, 1H, H-1,), 4.32-4.24 (m, 2H, H-6), 4.15 (dd, *J* = 12.0, 6.8 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.94-3.87 (m, 3H, H-2, H-5, $OC\underline{H_2}CHCH_2O$), 3.64 (dd, *J* = 10.8, 6.0 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.59 (s, 3H, OCH_3), 3.55 (dd, *J* = 10.8, 6.0 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.41-3.11 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 3.06 (brs, 1H, OH), 1.50-1.46 (m, 2H, $OCH_2C\underline{H_2}C_{14}H_{29}$), 1.25 (m, 26H,), 0.87 (t, *J* = 6.8Hz, 3H, $OC_{15}H_{30}C\underline{H_3}$).

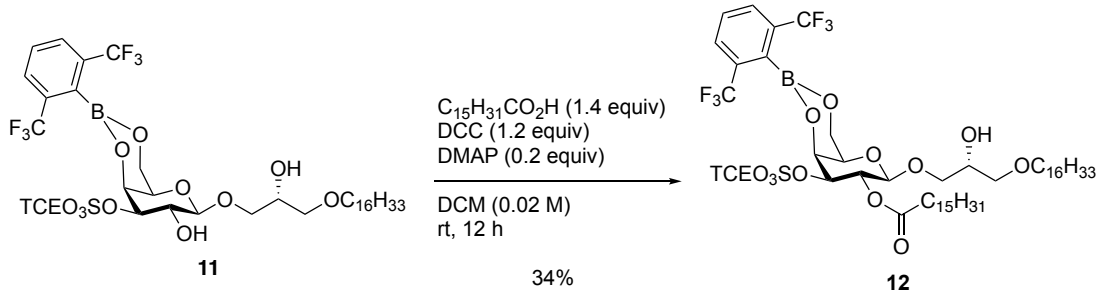
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 166.7, 133.8 (q, $^{2}J_{C\text{-}F}$ = 31.2 Hz), 132.1, 129.7, 129.5, 128.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 128.4, 127.4, 124.1 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 123.2 (q, $^{1}J_{C\text{-}F}$ = 286.6 Hz), 103.4, 92.6, 83.5, 79.8, 73.8, 71.9, 69.0, 68.7, 68.5, 67.8, 67.6, 64.9, 55.5, 31.9, 29.69, 29.66, 29.65, 29.62, 29.58, 29.49, 29.42, 29.4, 25.9, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m/z* calcd for $C_{45}H_{59}{}^{11}B^{35}Cl_3F_9NaO_{13}S$ $[M+Na]^+$ 1149.2589, found 1149.2567.

(4a*R*,6*R*,7*R*,8*S*,8a*S*)-2-(2,6-bis(trifluoromethyl)phenyl)-6-((*R*)-3-(hexadecyloxy)-2-hydroxypropoxy)-8-(((2,2,2-trichloroethoxy)sulfonyl)oxy)hexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-7-yl palmitate (**12**)



Palmitic acid (38.5 mg, 0.15 mmol, 1.4 equiv) was added to a stirred solution of **11** (95.6 mg, 0.110 mmol, 1.0 equiv), DCC (26.8 mg, 0.130 mmol, 1.2 equiv) and DMAP (2.7 mg, 0.022 mmol, 0.2 equiv) in DCM (5.5 mL, 0.02 M) at room temperature. After stirring for 12 h, the reaction was quenched by adding H_2O (5.0 mL). The resulting mixture was extracted with DCM (2 x 10 mL). The combined organic layer was washed successively with aqueous 1 M HCl (10 mL), H_2O (10 mL) and brine (10 mL),

and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 4 : 1) to give **12** (42.7 mg, 0.037 mmol, 34%) as a colorless oil.

TLC

R_f 0.29 (hexane / EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{23}$ +5.6 (*c* 1.0, $CHCl_3$).

IR (neat)

3414, 2919, 2850, 1747, 1469, 1417, 1346, 1298, 1202, 1177, 1135, 1092, 1049, 887, 834, 776, 724, 679, 543, 446 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.65 (t, *J* = 7.9 Hz, 1H), 5.36 (dd, *J* = 10.1, 8.0 Hz, 1H, $OCH_2C\underline{H}CH_2$), 4.83 (dd, *J* = 10.1, 3.3 Hz, 1H, H-2), 4.79-4.78 (m, 1H, H-4), 4.68 (d, *J* = 10.9 Hz, 1H, $C\underline{H_2}CCl_3$), 4.63 (d, *J* = 8.0 Hz, 1H, H-1), 4.61 (d, *J* = 10.9 Hz, 1H, $C\underline{H_2}CCl_3$), 4.35-4.32 (m, 1H, H-6), 4.30-4.26 (m, 1H, H-6'), 3.99-3.95 (m, 2H, H-3, H-5) 3.82 (d, *J* = 5.2 Hz, 2H, $OC\underline{H_2}CHCH_2O$, $COC\underline{H_2}C_{14}H_{29}$), 3.52-3.41 (m, 4H, $OCH_2CHC\underline{H_2}O$), 2.37 (dd, *J* = 8.0, 7.0 Hz, 2H, $COC\underline{H_2}C_{14}H_{29}$), 1.66-1.54 (m, 4H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{14}H_{29}$), 1.38-1.25 (m, 50H), 0.90-0.86 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

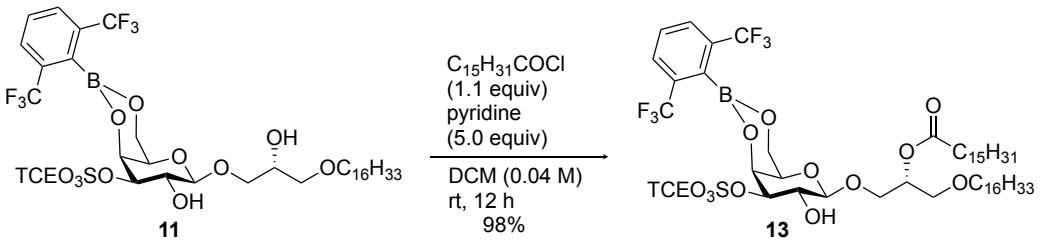
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 172.2, 134.1 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.8, 128.9 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 101.2, 92.5, 82.3, 80.2, 72.0, 71.7, 71.5, 69.6, 68.9, 67.8, 67.4, 65.1, 34.3, 32.1, 29.92, 29.88, 29.87, 29.85, 29.84, 29.73, 29.67, 29.6, 29.5, 29.3, 26.3, 25.0, 22.9, 14.3.

ESI-HRMS

HRMS (ESI) m/z Calcd for $C_{51}H_{82}{}^{11}B^{35}Cl_3{}^{19}F_6NaO_{12}S$ $[M+Na]^+$ 1171.4488, found 1171.4489.

(*R*)-1-(((4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-(2,6-bis(trifluoromethyl)phenyl)-7-hydroxy-8-(((2,2,2-trichloroethoxy)sulfonyl)oxy)hexahydropyrano[3,2-d][1,3,2]dioxaborinin-6-yl)oxy)-3-(hexadecyloxy)propan-2-yl palmitate (**13**)



Palmitoyl chloride (33.2 μL, 0.110 mmol, 1.1 equiv) was added to a stirred solution of **11** (91.0 mg, 0.100 mmol) and pyridine (40.4 μL, 0.500 mmol, 5.0 equiv) in DCM (2.50 mL, 0.04 M) at room temperature. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (toluene only to toluene : EtOAc = 15 : 1) to give **13** (113 mg, 0.098 mmol, 98%) as a colorless oil.

TLC

R_f 0.74 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{23}$ +20.0 (*c* 1.00, $CHCl_3$).

IR (neat)

3798, 3742, 3666, 2922, 2852, 2252, 1730, 1681, 1644, 1633, 1556, 1537, 1469, 1415, 1345, 1296, 1270, 1201, 1178, 1136, 1091 1048, 1010, 971, 906, 888, 833, 819, 784, 725, 677, 543, 433, 418 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 5.26-5.21 (m, 1H, $OCH_2C\underline{H}CH_2$), 4.95 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.74-4.70 (m, 2H, H-4, $C\underline{H_2}CCl_3$), 4.64 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3), 4.42 (d, *J* = 7.6 Hz, 1H, H-1), 4.32-4.24 (m, 2H, H-6), 4.04 (dd, *J* = 11.2, 6.4 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.93-3.84 (m, 3H, H-2, H-5, $OC\underline{H_2}CHCH_2O$), 3.64 (dd, *J* = 10.4, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.58 (dd, *J* = 10.8, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.49-3.41 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 2.36 (t, *J* = 7.6 Hz, 2H, $COC\underline{H_2}C_{14}H_{29}$), 1.67-1.52 (m, 5H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{14}H_{29}$, OH), 1.28-1.25 (m, 50H), 0.90-0.86 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

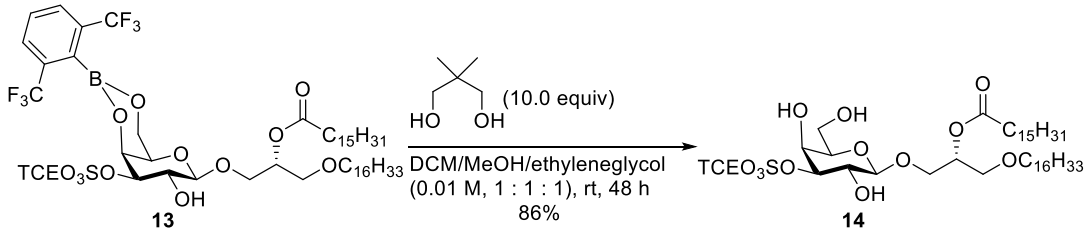
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 173.9, 133.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.4, 128.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 103.1, 92.6, 83.9, 79.8, 71.8, 71.1, 69.2, 69.0, 68.8, 67.7, 67.5, 64.9, 34.3, 31.9, 29.7, 29.62, 29.61, 29.60, 29.5, 29.45, 29.42, 29.3, 29.2, 29.0, 26.0, 24.9, 22.6, 14.1.

FAB-HRMS

HRMS (FAB) *m*/*z* calcd for $C_{51}H_{82}{}^{11}B^{35}Cl_3F_6NaO_{12}S$ $[M+Na]^+$ 1171.4589, found 1171.4519.

(*R*)-1-(((2*R*,3*R*,4*S*,5*S*,6*R*)-4-((((2-(2*l*3-trichloran-2-yl)acetyl)peroxy)thio)oxy)-3,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3-(hexadecyloxy)propan-2-yl palmitate (**14**)



2,2-Dimethyl-1,3-propanediol (52.1 mg, 0.500 mmol, 10.0 equiv) was added to a stirred solution of **13** (60.2 mg, 0.0500 mmol) in DCM/MeOH/ethyleneglycol (5.0 mL, 0.01 M, 1 : 1 : 1) at room temperature. After stirring for 48 h, the resulting mixture was diluted with DCM (50 mL). The combined organic layer was washed successively with H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 2 : 1) to give **14** (40.0 mg, 0.043 mmol, 86%) as a colorless oil.

TLC

R_f 0.25 (hexane : EtOAc = 2 : 1).

Optical rotation

$[\alpha]_D^{22}$ +14.7 (*c* 1.00, $CHCl_3$).

IR (neat)

3393, 3184, 2923, 2853, 1710, 1666, 1466, 1405, 1377, 1296, 1267, 1199, 1167, 1122, 1093, 1072, 1040, 1015, 963, 947, 895, 856, 786, 727, 702, 620, 544, 426, 414 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 5.21-5.19 (m, 1H, $OCH_2C\underline{H}CH_2O$), 5.00 (d, J = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.85 (d, J = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.58 (dd, J = 10.0, 3.2 Hz, 1H, H-3), 4.41 (brd, J = 2.8 Hz 1H, H-4), 4.36 (d, J = 7.6 Hz, 1H, H-1), 4.01-3.82 (m, 5H), 3.58-3.54 (m, 3H), 3.48-3.42 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 2.36-2.32 (m, 3H, $COC\underline{H_2}C_{14}H_{29}$, OH), 1.63-1.54 (m, 6H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{14}H_{29}$, OHx2), 1.26 (m, 50H), 0.90-0.86 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

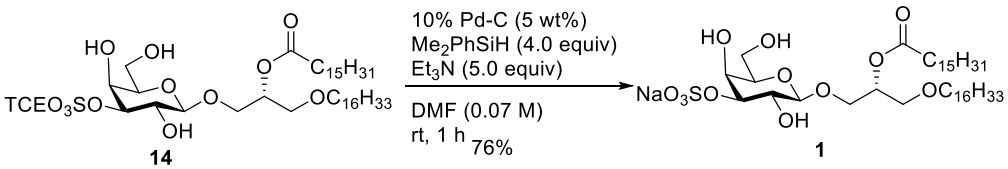
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 174.1, 104.1, 92.7, 85.8, 79.9, 73.6, 72.0, 71.2, 69.9, 69.0, 68.6, 68.1, 62.6, 34.5, 31.9, 29.70, 29.65, 29.64, 29.63, 29.50, 29.49, 29.45, 29.35, 29.27, 29.1, 26.0, 24.9, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) calcd for $C_{43}H_{81}{}^{35}Cl_3NaO_{12}S$ $[M+Na]^+$ 949.4412, found m/z: 949.4425.

Seminolipid sodium salt (**1**)



Dimethylphenylsilane (34.6 μL, 0.226 mmol, 2.0 equiv) was added to a stirred mixture of **14** (105 mg, 0.113 mmol, 1.0 equiv), 10% Pd-C (5 w/w%, 5.2 mg) and Et_3N (78.7 μL, 0.565 mmol, 5.0 equiv) in DMF (1.60 mL, 0.07 M) at room temperature. After stirring for 30 minutes, dimethylphenylsilane (34.6 μL, 0.226 mmol, 2.0 equiv) was added again. After stirring for additional 0.5 h, the reaction mixture was filtered through a Celite pad rinsing with DMF (10 mL). The filtrate was lyophilized. The resulting residue was dissolved in MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1), and loaded onto a cation exchange resin column (DOWEX^{TM}HCR-S Na^+ form), eluting with MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1). The obtained fractions were lyophilized to give seminolipid sodium salt **1** (70.2 mg, 0.086 mmol, 76%) as an amorphous material.

Optical rotation

$[\alpha]_D{}^{27}$ +2.3 (*c* 0.10, $CHCl_3$ / MeOH = 1 : 1).

^{1}H-NMR (400 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 5.22-5.16 (m, 1H, $OCH_2C\underline{H}CH_2$), 4.31 (d, J = 8.0 Hz, 1H, H-1), 4.25-4.19 (m, 2H), 3.92(dd, J = 10.8, 6.0 Hz, 1H) 3.81-3.66 (m, 4H), 3.61-3.37 (m, 5H), 2.31 (t, J = 8.0 Hz, 2H, $COC\underline{H_2}C_{14}H_{29}$), 1.63-1.48 (m, 4H), 1.24 (m, 50H), 0.87-0.83 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

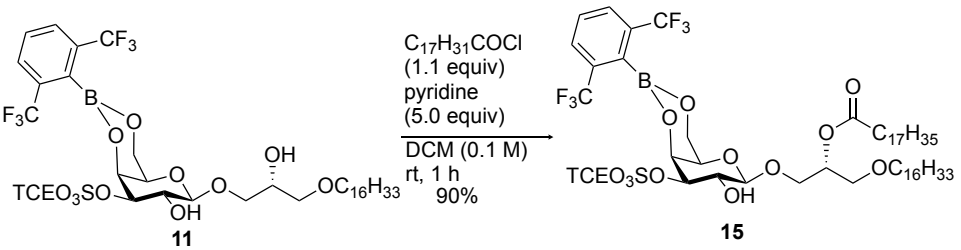
^{13}C-NMR (100 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 174.8, 104.2, 81.0, 75.3, 72.3, 72.2, 70.0, 69.8, 68.7, 67.8, 61.8, 34.9, 32.4, 30.19, 30.17, 30.16, 30.15, 30.07, 30.01, 29.9, 29.8, 29.6, 26.6, 25.5, 23.2, 14.3.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{41}H_{79}O_{12}S$ $[M-Na]^-$ 795.5292, found 795.5267.

(*R*)-1-(((4a*R*,6*R*,7*R*,8*R*,8a*S*)-8-((((2-(2l3-trichloran-2-yl)acetyl)peroxy)thio)oxy)-2-(2,6-bis(trifluoromethyl)phenyl)-7-hydroxyhexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-6-yl)oxy)-3-(hexadecyloxy)propan-2-yl stearate (**15**)



Stearoyl chloride (37.2 μL, 0.110 mmol, 1.1 equiv) was added to a stirred solution of **11** (91.0 mg, 0.100 mmol) and pyridine (40.4 μL, 0.500 mmol, 5.0 equiv) in DCM (2.50 mL, 0.1 M) at room temperature under N_2. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (toluene only to toluene : EtOAc = 15 : 1) to give **15** (105.8 mg, 0.090 mmol, 90%) as a colorless oil.

TLC

R_f 0.74 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{23}$ +16.1 (*c* 1.00, $CHCl_3$).

IR (neat)

3743, 3645, 3479, 2917, 2851, 2685, 1746, 1714, 1697, 1642, 1614, 1596, 1582, 1469, 1412, 1381, 1345, 1297, 1202, 1178, 1006, 975, 947, 906, 885, 864, 836, 815, 771, 722, 701, 670, 550, 436, 414 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 5.27-5.21 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.95 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.74 (brd, *J* = 3.2 Hz, 1H, H-4), 4.72 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.65 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.43 (d, *J* = 7.6 Hz 1H, H-1), 4.33-4.23(m, 2H, H-6), 4.04 (dd, *J* = 11.2, 6.4 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.93-3.88 (m, 2H, H-2, H-5), 3.86 (dd, *J* = 11.2, 4.0 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.64 (dd, *J*= 10.4, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.58 (dd, *J*= 10.4, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.51-3.42 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 2.38-2.34 (m, 2H, $COC\underline{H_2}C_{16}H_{33}$), 1.65-1.54 (m, 5H, $COCH_2C\underline{H_2}C_{15}H_{31}$, $OCH_2C\underline{H_2}C_{14}H_{29}$, OH), 1.26 (m, 54H), 0.90-0.86 (m, 6H, $COCH_2C_{15}H_{30}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

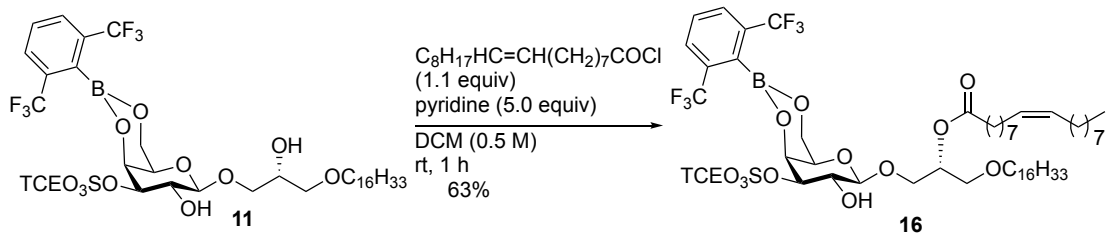
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 173.9, 133.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.4, 128.6 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 103.2, 92.6, 83.8, 79.8, 71.9, 71.0, 69.2, 68.9, 68.8, 67.7, 67.5, 64.9, 34.4, 31.9, 29.69, 29.66, 29.65, 29.64, 29.62, 29.61, 29.50, 29.47, 29.44, 29.34, 29.2, 29.1, 26.0, 24.9, 22.7, 14.1.

FAB-HRMS

HRMS (FAB) *m/z* calcd for $C_{53}H_{86}{}^{11}B^{35}Cl_3F_6NaO_{12}S$ $[M+Na]^+$ 1199.4795, found 1199.4803.

(*R*)-1-(((4a*R*,6*R*,7*R*,8*R*,8a*S*)-8-((((2-(2l3-trichloran-2-yl)acetyl)peroxy)thio)oxy)-2-(2,6-bis(trifluoromethyl)phenyl)-7-hydroxyhexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-6-yl)oxy)-3-(hexadecyloxy)propan-2-yl oleate (**16**)



Oleyl chloride (36.3 μL, 0.11 mmol, 1.1 equiv) was added to a stirred solution of **11** (91.0 mg, 0.100 mmol) and pyridine (40.4 μL, 0.500 mmol, 5.0 equiv) in DCM (2.50 mL, 0.5 M) at room temperature under N_2. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (toluene only to toluene : EtOAc = 15 : 1) to give **16** (74.0 mg, 0.063 mmol, 63%) as a colorless oil.

TLC

R_f 0.74 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{27}$ +15.3 (*c* 1.00, $CHCl_3$).

IR (neat)

2924, 2854, 1730, 1579, 1416, 1344, 1296, 1201, 1178, 1135, 1010, 975, 906, 889, 867, 836, 812, 774, 724, 673, 423, 407 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 5.37-5.31 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}CH_2$), 5.27-5.21 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.95 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.74 (brd, *J* = 3.2 Hz, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.65 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H, H-3), 4.43 (d, *J* = 7.6 Hz, 1H, H-1), 4.33-4.23 (m, 2H, H-6), 4.04 (dd, *J* = 11.2, 6.4 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.93-3.88 (m, 2H, H-2, H-5), 3.85 (dd, *J* = 11.2, 4.4 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.64 (dd, *J*= 10.8, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.57 (dd, *J*= 10.8, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.51-3.41 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 2.36 (t, *J* = 7.6 Hz, 2H, $COC\underline{H_2}C_{17}H_{33}$), 2.03-1.98 (m, 4H, $C\underline{H_2}CH$=CH$C\underline{H_2}$), 1.65-1.53 (m, 5H, $COCH_2C\underline{H_2}C_{16}H_{33}$, $OCH_2C\underline{H_2}C_{14}H_{29}$, OH), 1.30-1.24 (m, 46H), 0.89-0.86 (m, 6H, $COCH_2C_{16}H_{30}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

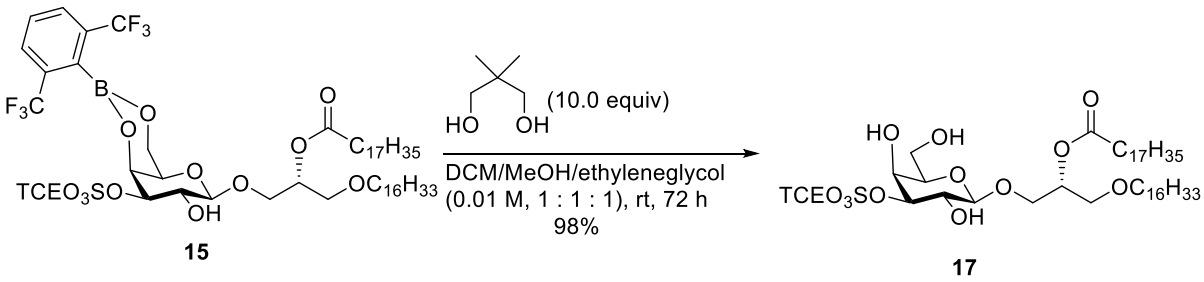
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 173.9, 133.9 (q, $^2J_{C\text{-}F}$ = 31.3 Hz), 130.0, 129.7, 129.4, 128.7 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 103.2, 92.6, 83.7, 79.8, 71.9, 71.0, 69.2, 68.9, 68.8, 67.8, 67.5, 64.9, 34.4, 31.91 31.89, 29.8, 29.69, 29.67, 29.65, 29.63, 29.62, 29.51, 29.45, 29.4, 29.31, 29.30, 29.15, 29.11, 29.0, 27.21, 27.16, 26.0, 24.90, 22.68, 22.67, 14.1.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{53}H_{84}{}^{11}B^{35}Cl_3F_6NaO_{12}S$ $[M+Na]^+$ 1197.4644, found 1197.4649.

(*R*)-1-(((2*R*,3*R*,4*S*,5*S*,6*R*)-4-((((2-(2*l*3-trichloran-2-yl)acetyl)peroxy)thio)oxy)-3,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3-(hexadecyloxy)propan-2-yl stearate (**17**)



2,2-Dimethyl-1,3-propanediol (71.8 mg, 0.680 mmol, 10.0 equiv) was added to a stirred solution of **15** (80.0 mg, 0.0680 mmol) in DCM/MeOH/ethyleneglycol (6.8 mL, 0.01 M, 1 : 1 : 1) at room temperature. After stirring for 48 h, the resulting mixture was diluted with DCM (50 mL). The combined organic layer was washed successively with H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 2 : 1) to give **17** (63.7 mg, 0.066 mmol, 98%) as a colorless oil.

TLC

R_f 0.25 (hexane : EtOAc = 2 : 1).

Optical rotation

$[\alpha]_D^{27}$ +18.6 (*c* 1.00, $CHCl_3$).

IR (neat)

3708, 3645, 3382, 2924, 2857, 2057, 1742, 1725, 1713, 1469, 1405, 1381, 1345, 1294, 1277, 1263, 1199, 1072, 1015, 963, 947, 896, 854, 786, 767, 727, 701, 673, 546, 447, 433, 423, 414 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 5.22-5.17 (m, 1H, $OCH_2C\underline{H}CH_2O$), 5.00 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.85 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.55 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H, H-3), 4.40 (brd, *J* = 2.8 Hz, 1H, H-4), 4.36 (d, *J* = 7.6 Hz, 1H, H-1), 4.01-3.81 (m, 5H), 3.58-3.54 (m, 3H), 3.49-3.40 (m, 2H, $OC\underline{H_2}CH_2C_{14}H_{29}$), 2.35-2.32 (m, 3H, $COC\underline{H_2}C_{14}H_{33}$, OH), 1.63-1.52 (m, 6H, $COCH_2C\underline{H_2}C_{14}H_{29}$, $OCH_2C\underline{H_2}C_{14}H_{29}$, OHx2), 1.25 (m, 54H,), 0.89-0.86 (m, 6H, $COCH_2C_{15}H_{30}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

^{13}C-NMR (100 MHz, $CDCl_3$)

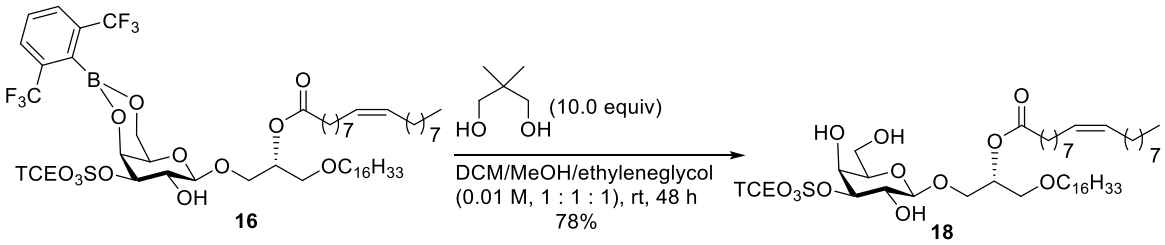
δ 174.1, 104.0, 92.7, 85.8, 79.9, 73.6, 72.0, 71.2, 69.8, 69.1, 68.6, 68.0, 62.4, 34.5, 31.9,

29.70, 29.66, 29.65, 29.63, 29.49, 29.45, 29.35, 29.27, 29.1, 26.0, 24.9, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{45}H_{85}{}^{35}Cl_3NaO_{12}S$ $[M+Na]^+$ 977.4720, found 977.4753.

(*R*)-1-(((2*R*,3*R*,4*S*,5*S*,6*R*)-4-((((2-(2*l*3-trichloran-2-yl)acetyl)peroxy)thio)oxy)-3,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3-(hexadecyloxy)propan-2-yl oleate (**18**)



2,2-Dimethyl-1,3-propanediol (266.2 mg, 2.55 mmol, 10.0 equiv) was added to a stirred solution of **16** (300 mg, 0.255 mmol) in DCM/MeOH/ethyleneglycol (25.5 mL, 0.01 M, 1 : 1 : 1) at room temperature. After stirring for 48 h, the resulting mixture was diluted with DCM (100 mL). The combined organic layer was washed successively with H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 2 : 1) to give **18** (189.4 mg, 0.199 mmol, 78%) as a colorless oil.

TLC

R_f 0.23 (hexane : EtOAc = 2 : 1).

Optical rotation

$[\alpha]_D^{22}$ +20.1 (*c* 1.00, $CHCl_3$).

IR (neat)

3731, 3381, 2923, 2853, 2248, 1713, 1464, 1405, 1375, 1347, 1296, 1267, 1232, 1169, 1136, 1072, 963, 947, 895, 861, 843, 787, 727, 543, 462, 439, 420 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 5.37-5.31 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}CH_2$), 5.22-5.17 (m, 1H, $OCH_2C\underline{H}CH_2O$), 5.00 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}CCl_3$), 4.84 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}CCl_3$), 4.54 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H, H-3) 4.40 (brd, *J* = 2.8 Hz 1H, H-4), 4.35 (d, *J* = 7.6 Hz, 1H, H-1), 4.00-3.80 (m, 5H), 3.58-3.54 (m, 3H), 3.49-3.40 (m, 2H, OC$\underline{H_2}CH_2C_{14}H_{29}$), 2.35-2.32 (m, 3H,

$COCH_2C_{14}H_{33}$, OH), 2.01-2.00 (m, 4H, $CH_2CH{=}CHCH_2$), 1.63-1.53 (m, 6H, $COCH_2CH_2C_{16}H_{33}$, $OCH_2CH_2C_{14}H_{29}$, OHx2), 1.30-1.24 (m, 46H), 0.89-0.86 (m, 6H, $COCH_2C_{16}H_{30}CH_3$, $OC_{15}H_{30}CH_3$).

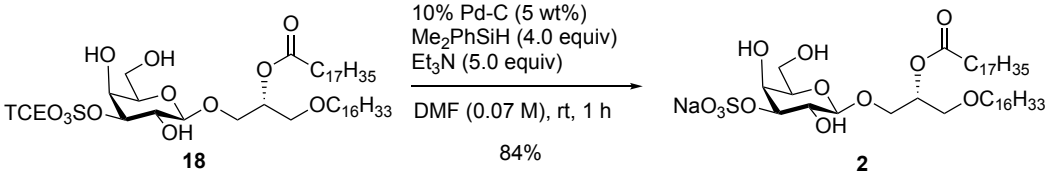
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 174.1, 130.0, 129.7, 104.0, 92.7, 85.8, 79.9, 73.6, 72.0, 71.2, 69.7, 69.0, 68.6, 68.0, 62.4, 34.4, 31.91, 31.88, 29.8, 29.7, 29.64, 29.62, 29.51, 29.48, 29.44, 29.34, 29.31, 29.30, 29.2, 29.1, 29.0, 27.21, 27.16, 26.0, 24.9, 22.67, 22.66, 14.1.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{45}H_{83}{}^{35}Cl_3NaO_{12}S$ $[M+Na]^+$ 975.45685, found 975.45880.

Seminolipid stearoyl ester analogue sodium salt (**2**)



Dimethylphenylsilane (20.8 μL, 0.136 mmol, 2.0 equiv) was added to a stirred mixture of **19** (65.2 mg, 0.0683 mmol, 1.0 equiv), 10% Pd-C (5 w/w%, 3.2 mg) and Et_3N (47.7μL, 0.342 mmol, 5.0 equiv) in DMF (0.9 mL, 0.07 M) at room temperature. After stirring for 0.5 h, dimethylphenylsilane (18.6 mg, 0.136 mmol, 2.0 equiv) was added again. After stirring for additional 0.5 h, the reaction mixture was filtered through a Celite pad rinsing with DMF (20 mL). The filtrate was lyophilized. The resulting residue was dissolved in MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1), and loaded onto a cation exchange resin column (DOWEX^{TM}HCR-S Na^+ form), eluting with MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1). The obtained fractions were lyophilized to give seminolipid stearoyl ester analogue sodium salt **2** (48.5 mg, 0.0573 mmol, 84%) as an amorphous material.

Optical rotation

$[\alpha]_D{}^{28}$ +2.3 (*c* 0.10, $CHCl_3$ / MeOH = 1 : 1).

^{1}H-NMR (400 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 5.22-5.16 (m, 1H, OCH_2CHCH_2O), 4.31 (d, *J* = 8.0 Hz, 1H, H-1), 4.25-4.19 (m, 2H), 3.93(dd, *J* = 10.8, 6.0 Hz, 1H) 3.81-3.67 (m, 4H), 3.61-3.39 (m, 5H), 2.32 (t, *J* = 7.6 Hz, 2H, $COCH_2C_{16}H_{33}$), 1.62-1.51 (m, 4H, $COCH_2CH_2C_{15}H_{31}$, $OCH_2CH_2C_{14}H_{29}$), 1.24 (m, 54H), 0.88-0.84 (m, 6H, $COCH_2C_{15}H_{30}CH_3$, $OC_{15}H_{30}CH_3$).

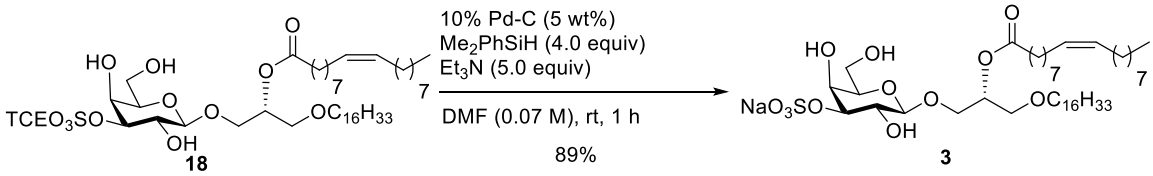
^{13}C-NMR (100 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 174.9, 104.3, 81.1, 75.5, 72.4, 72.3, 70.1, 69.9, 68.8, 67.9, 61.9, 35.0, 32.5, 30.29, 30.25, 30.2, 30.12, 30.11, 30.07, 29.96, 29.93, 29.9, 29.7, 26.7, 25.6, 23.2, 14.3.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{43}H_{83}O_{12}S$ $[M-Na]^-$ 823.5605, found 823.5586.

Seminolipid oleoyl ester analogue sodium salt (**3**)



Dimethylphenylsilane (50.8 μL, 0.332 mmol, 2.0 equiv) was added to a stirred mixture of **19** (158 mg, 0.166 mmol), 10% Pd-C (5 w/w%, 7.9 mg) and Et_3N (115 μL, 0.828 mmol, 5.0 equiv) in DMF (2.3 mL, 0.07 M) at room temperature. After stirring for 0.5 h, dimethylphenylsilane (45.2 mg, 0.332mmol, 2.0 equiv) was added again. After stirring for additional 0.5 h, the reaction mixture was filtered through a Celite pad rinsing with DMF (20 mL). The filtrate was lyophilized. The resulting residue was dissolved in MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1), and loaded onto a cation exchange resin column (DOWEX^{TM}HCR-S Na^+ form), eluting with MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1). The obtained fractions were lyophilized to give seminolipid oleoyl ester analogue sodium salt **3** (125 mg, 0.148 mmol, 89%) as an amorphous material.

Optical rotation

$[\alpha]_D^{28}$ +1.4 (*c* 0.10, $CHCl_3$ / MeOH = 1 : 1).

^{1}H-NMR (400 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 5.35-5.27 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}CH_2$), 5.22-5.16 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.31 (d, *J* = 7.6 Hz, 1H, H-1), 4.25-4.18 (m, 2H), 3.92 (dd, *J* = 11.2, 6.0 Hz, 1H) 3.81-3.67 (m, 4H), 3.61-3.38 (m, 5H), 2.32 (t, *J* = 7.2 Hz, 2H, $COC\underline{H_2}C_{14}H_{33}$), 2.01-1.97 (m, 4H, $C\underline{H_2}CH$=CH$C\underline{H_2}$), 1.62-1.50 (m, 4H, $COCH_2C\underline{H_2}C_{15}H_{31}$, $OCH_2C\underline{H_2}C_{14}H_{29}$), 1.28-1.24 (m, 46H), 0.87-0.83 (m, 6H, $COCH_2C_{15}H_{28}C\underline{H_3}$, $OC_{15}H_{30}C\underline{H_3}$).

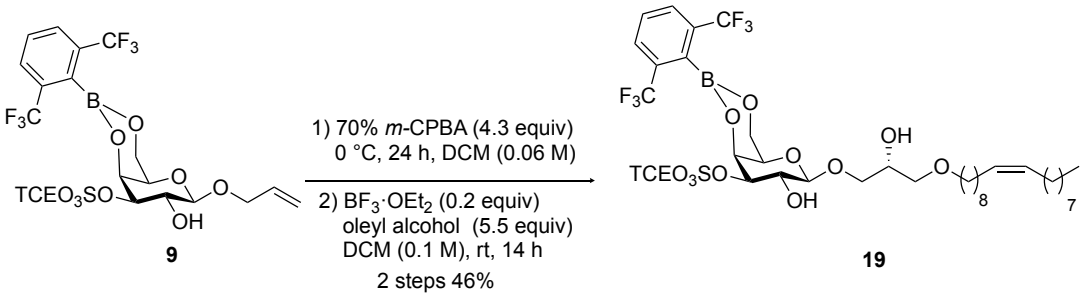
^{13}C-NMR (100 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 174.8, 130.4, 130.2, 104.2, 80.9, 75.3, 72.3, 72.2, 70.0, 69.8, 68.8, 67.8, 61.8, 34.9, 32.46, 32.44, 30.273, 30.26, 30.22, 30.20, 30.18, 30.11, 30.04, 29.9, 29.84, 29.81, 29.77, 29.67, 29.62, 27.69, 27.68, 26.59, 25.5, 23.2, 14.3.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{43}H_{81}O_{12}S$ $[M-Na]^-$ 821.5448, found 821.5447.

(4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-[2,6-bis(trifluoromethyl)phenyl]-6-[(*R*)-3-(hexadecyloxy)-2-hydroxypropoxy]-7-hydroxyhexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-8-yl (2,2,2-trichloroethyl) sulfate (**19**)



70% *m*-CPBA (965 mg, 5.59 mmol, 4.3 equiv) was added to a stirred solution of **9** (848 mg, 1.30 mmol) in DCM (21.0 mL, 0.06 M) at 0 °C. After stirring for 24 h, the reaction was quenched by adding saturated aqueous $Na_2S_2O_3$ (10 mL). After stirring for 2 h at room temperature, the resulting mixture was extracted with EtOAc (2 x 100 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (50 mL), saturated aqueous $Na_2S_2O_3$, (2 x 50 mL), H_2O (2 x 50 mL) and brine (2 x 50 mL) and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude epoxide, which was used without further purification to the next step. BF_3•OEt_2 (32.0 μL, 0.260 mmol, 0.2 equiv) was added to a stirred solution of the crude product and oleyl alcohol (1.92 g, 7.15 mmol, 5.5 equiv) in DCM (13.0 mL, total 0.1 M) at room temperature under N_2. After stirring for 14 h, the reaction was quenched by adding saturated aqueous $NaHCO_3$ (50 mL). The resulting mixture was extracted with EtOAc (2 x 100 mL). The combined organic extract was washed with H_2O (2 x 50 mL) and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1) to give **19** (569.1 mg, 0.60 mmol, 46%) as a colorless oil.

TLC

R_f 0.30 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{27}$ +27.3 (*c* 1.00, $CHCl_3$).

IR (neat)

3850, 3645, 3415, 2925, 2854, 1727, 1414, 1345, 1296, 1200, 1178, 1134, 1089, 1046,

873, 726, 666, 542, 429, 409 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 5.38-5.32 (m, 2H, $CH_2C\underline{H}{=}C\underline{H}CH_2$), 4.93 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.74 (brd, *J* = 3.2 Hz, 1H, H-4), 4.71 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.69 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.48 (d, *J* = 8.0 Hz, 1H, H-1), 4.30-4.23 (m, 2H, H-6), 4.05-4.00 (m, 1H, $OCH_2C\underline{H}CH_2O$) 3.98-3.92 (m, 3H, H-2, H-5, $OC\underline{H_2}CHCH_2O$), 3.84 (dd, *J* = 11.2, 3.6 Hz, 1H, $OC\underline{H_2}CHCH_2O$), 3.62-3.51 (m, 2H, $OCH_2CHC\underline{H_2}O$), 3.48 (t, *J* = 6.8 Hz, 2H, $OC\underline{H_2}CH_2C_{16}H_{33}$), 3.31 (brs, 1H, OH) 2.03-1.98 (m, 4H, $C\underline{H_2}CH{=}CHC\underline{H_2}$) 1.61-1.54 (m, 2H, $OCH_2C\underline{H_2}C_{16}H_{33}$), 1.28-1.26 (m, 22H), 0.86 (m, 3H, $OC_{17}H_{32}C\underline{H_3}$).

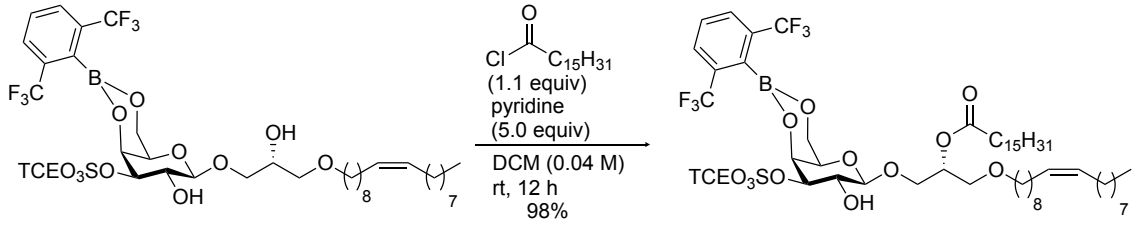
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 133.8 (q, $^{2}J_{C\text{-}F}$ = 31.2 Hz), 129.9, 129.7, 129.4, 128.6 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 102.8, 92.6, 83.8, 79.8, 71.8, 71.4, 70.6, 69.6, 68.8, 67.7, 67.6, 65.0, 31.9, 29.74, 29.68, 29.51, 29.48, 29.42, 29.297, 29.290, 29.25, 27.2, 26.0, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m/z* calcd for $C_{37}H_{54}{}^{11}B^{35}Cl_3F_6NaO_{11}S$ $[M+Na]^+$959.2347, found 959.2381.

(4a*R*,6*R*,7*R*,8*R*,8a*S*)-2-[2,6-bis(trifluoromethyl)phenyl]-6-[(*R*)-3-(hexadecyloxy)-2-hydroxypropoxy]-7-hydroxyhexahydropyrano[3,2-*d*][1,3,2]dioxaborinin-8-yl (2,2,2-trichloroethyl) sulfate (**20**)



19 **20**

Palmitoyl chloride (75.2 μL, 0.250 mmol, 1.1 equiv) was added to a stirred solution of **19** (213.5 mg, 0.228 mmol) and pyridine (92.0 μL, 1.14 mmol, 5.0 equiv) in DCM (0.46 mL, 0.5 M) at room temperature. After stirring for 12 h, the reaction was quenched by adding aqueous 1 M HCl (10 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (25 mL), H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (toluene only to toluene : EtOAc = 15 : 1) to give **20** (147 mg, 0.125 mmol, 55%) as a colorless oil.

TLC

R_f 0.30 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{24}$ +20.4 (*c* 1.00, $CHCl_3$).

IR (neat)

3722, 3694, 3438, 2925, 2854, 1731, 1467, 1416, 1345, 1296, 1270, 1201, 1178, 1136, 1091, 1048, 1011, 978, 888, 775, 726, 678, 540, 458, 426 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 5.37-5.31 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}CH_2$), 5.26-5.21 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.95 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}CCl_3$), 4.74 (brd, *J* = 3.2 Hz, 1H, H-4), 4.72 (d, *J* = 10.8 Hz, 1H, C$\underline{H_2}CCl_3$), 4.65(dd, *J* = 10.0 Hz, 3.6 Hz, 1H, H-3), 4.43 (d, *J* = 7.6 Hz, 1H, H-1), 4.32-4.24 (m, 2H, H-6), 4.04 (dd, *J* = 11.6, 6.4 Hz, 1H, OC$\underline{H_2}CHCH_2O$), 3.94-3.90 (m, 2H, H-2, H-5), 3.86 (dd, *J* = 11.2, 4.0 Hz, 1H, OC$\underline{H_2}CHCH_2O$), 3.64 (dd, *J*= 10.8, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.58 (dd, *J*= 10.8, 5.2 Hz, 1H, $OCH_2CHC\underline{H_2}O$), 3.46 (ddd, *J*= 23.2, 9.2, 6.8 Hz, 2H, OC$\underline{H_2}CH_2C_{16}H_{32}$), 2.36 (t, *J* = 7.6 Hz, 2H, COC$\underline{H_2}C_{14}H_{29}$), 2.04-1.99 (m, 4H, C$\underline{H_2}$CH=CHC$\underline{H_2}$), 1.65-1.52 (m, 5H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{16}H_{31}$, OH), 1.28-1.25 (m, 46H), 0.89-0.86 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{17}H_{32}C\underline{H_3}$).

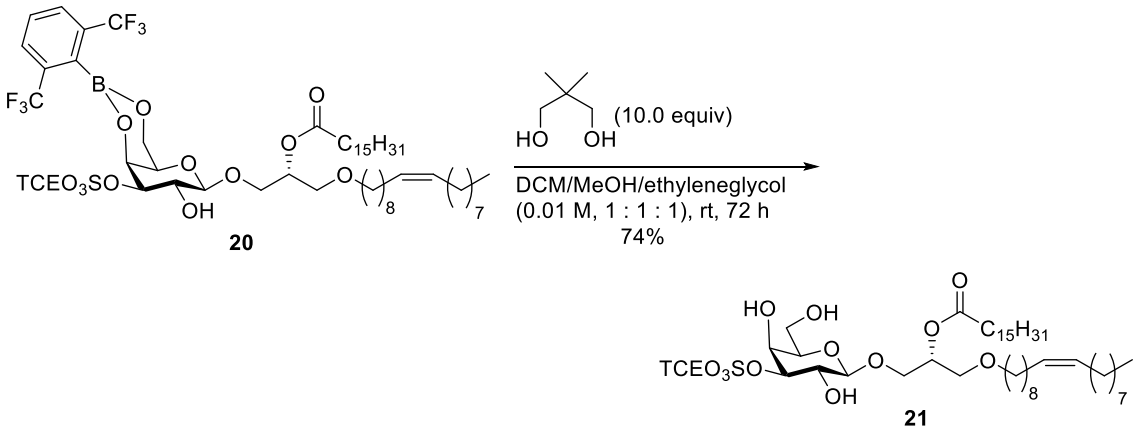
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 173.9, 133.8 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 129.93, 129.89, 129.77, 128.6 (q, $^3J_{C\text{-}F}$ = 3.1 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 103.2, 92.6, 83.7, 79.8, 71.9, 71.0, 69.2, 68.9, 68.8, 67.8, 67.5, 65.0, 34.4, 31.90, 31.88, 29.74, 29.68, 29.64, 29.61, 29.5, 29.46, 29.40, 29.33, 29.29, 29.25, 29.23, 29.1, 27.2, 26.0, 24.9, 14.1.

ESI-HRMS

HRMS (FAB) *m/z* calcd for $C_{53}H_{84}{}^{11}B^{35}Cl_3F_6NaO_{12}S$ $[M+Na]^+$1197.4746, found 1197.4663.

(*R*)-1-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,5-dihydroxy-6-(hydroxymethyl)-4-(((2,2,2-trichloroethoxy)sulfonyl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-3-(((*Z*)-octadec-9-en-1-yl)oxy)propan-2-yl palmitate (**21**)



2,2-Dimethyl-1,3-propanediol (69.7 mg, 0. 669 mmol, 10.0 equiv) was added to a stirred solution of **20** (78.6 mg, 0.0669 mmol) in DCM/MeOH/ethyleneglycol (6.7 mL, 0.01 M, 1 : 1 : 1) at room temperature. After stirring for 72 h, the resulting mixture was diluted with DCM (50 mL). The combined organic layer was washed successively with H_2O (25 mL) and brine (25 mL), and dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (hexane : EtOAc = 2 : 1) to give **21** (47.6 mg, 0.0499 mmol, 74%) as a colorless oil.

TLC

R_f 0.30 (hexane : EtOAc = 3 : 1).

Optical rotation

$[\alpha]_D^{23}$ +20.6 (*c* 1.00, $CHCl_3$).

IR (neat)

3387, 3190, 2924, 2853, 1711, 1465, 1405, 1378, 1296, 1199, 1168, 1122, 1072, 1041, 1015, 963, 895, 856, 786, 727, 619, 544, 421, 410 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ 5.37-5.30 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}CH_2$), 5.23-5.16 (m, 1H, $OCH_2C\underline{H}CH_2O$), 5.00 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.85 (d, *J* = 10.8 Hz, 1H, $C\underline{H_2}CCl_3$), 4.54(dd, *J* = 9.6 Hz, 3.2 Hz, 1H, H-3) 4.40 (brd, *J* = 2.8 Hz 1H, H-4), 4.35 (d, *J* = 7.6 Hz, 1H, H-1), 4.01-3.78 (m, 5H), 3.58-3.53 (m, 3H), 3.44 (ddd, *J*= 22.4, 9.2, 6.8 Hz , 2H, $OC\underline{H_2}CH_2C_{16}H_{31}$), 2.35-2.32 (m, 3H, $COC\underline{H_2}C_{14}H_{29}$, OH), 2.03-1.98 (m, 4H, $C\underline{H_2}CH$=CH$C\underline{H_2}$), 1.63-1.50 (m, 6H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{16}H_{31}$, OHx2), 1.28-1.25 (m, 46H), 0.89-0.85

(m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{17}H_{32}C\underline{H_3}$).

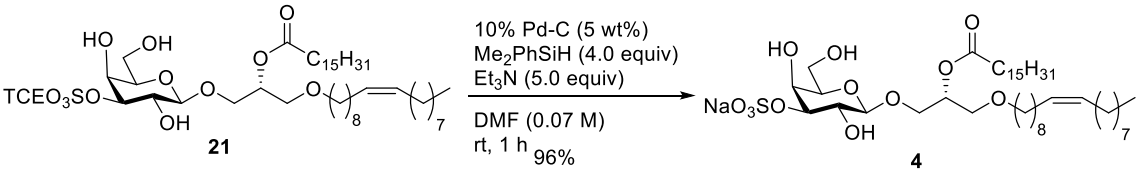
^{13}C-NMR (100 MHz, $CDCl_3$)

δ 174.1, 130.0, 129.8, 104.0, 92.7, 85.9, 79.9, 73.6, 71.9, 71.2, 69.7, 69.1, 68.6, 67.8, 62.3, 34.4, 31.90, 31.88, 29.74, 29.68, 29.65, 29.63, 29.61, 29.50, 29.47, 29.40, 29.33, 29.30, 29.29, 29.26, 29.25, 29.1, 27.19, 27.18, 26.0, 24.9, 22.7, 14.1.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{45}H_{83}{}^{35}Cl_3NaO_{12}S$ $[M+Na]^+$975.4670, found 975.4570.

Seminolipid oleyl ether analogue sodium salt (**4**)



Dimethylphenylsilane (15.3 μL, 0.100 mmol, 2.0 equiv) was added to a stirred mixture of **21** (47.6 mg, 0.0499 mmol), 10% Pd-C (5 w/w%, 2.4 mg) and Et_3N (34.7 μL, 0.250mmol, 5.0 equiv) in DMF (0.7 mL, 0.07 M) at room temperature. After stirring for 0.5 h, dimethylphenylsilane (13.7 mg, 0.100 mmol, 2.0 equiv) was added again. After stirring for additional 0.5 h, the reaction mixture was filtered through a Celite pad rinsing with DMF (20 mL). The filtrate was lyophilized. The resulting residue was dissolved in MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1), and loaded onto a cation exchange resin column (DOWEX^{TM}HCR-S Na^+ form), eluting with MeCN/MeOH/H_2O/DMF (4 : 2 : 2 : 1). The obtained fractions were lyophilized to give seminolipid oleyl ether analogue sodium salt **4** (40.8 mg, 0.0483 mmol, 96%) as an amorphous material.

Optical rotation

$[\alpha]_D{}^{28}$ +1.1 (*c* 0.10, $CHCl_3$ / MeOH = 1 : 1).

^{1}H-NMR (400 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 5.35-5.27 (m, 2H, $CH_2C\underline{H}$=$C\underline{H}CH_2$), 5.22-5.16 (m, 1H, $OCH_2C\underline{H}CH_2O$), 4.31 (d, *J* = 7.6 Hz, 1H, H-1), 4.25-4.19 (m, 2H), 3.92 (dd, *J* = 11.2, 6.0 Hz, 1H) 3.81-3.67 (m, 4H), 3.61-3.37 (m, 5H), 2.32 (t, *J* = 7.6 Hz, 2H, $COC\underline{H_2}C_{14}H_{29}$), 2.02-1.96 (m, 4H, $C\underline{H_2}CH$=$CHC\underline{H_2}$), 1.61-1.50 (m, 4H, $COCH_2C\underline{H_2}C_{13}H_{27}$, $OCH_2C\underline{H_2}C_{16}H_{31}$), 1.28-1.24 (m, 46H), 0.87-0.83 (m, 6H, $COCH_2C_{13}H_{26}C\underline{H_3}$, $OC_{17}H_{32}C\underline{H_3}$).

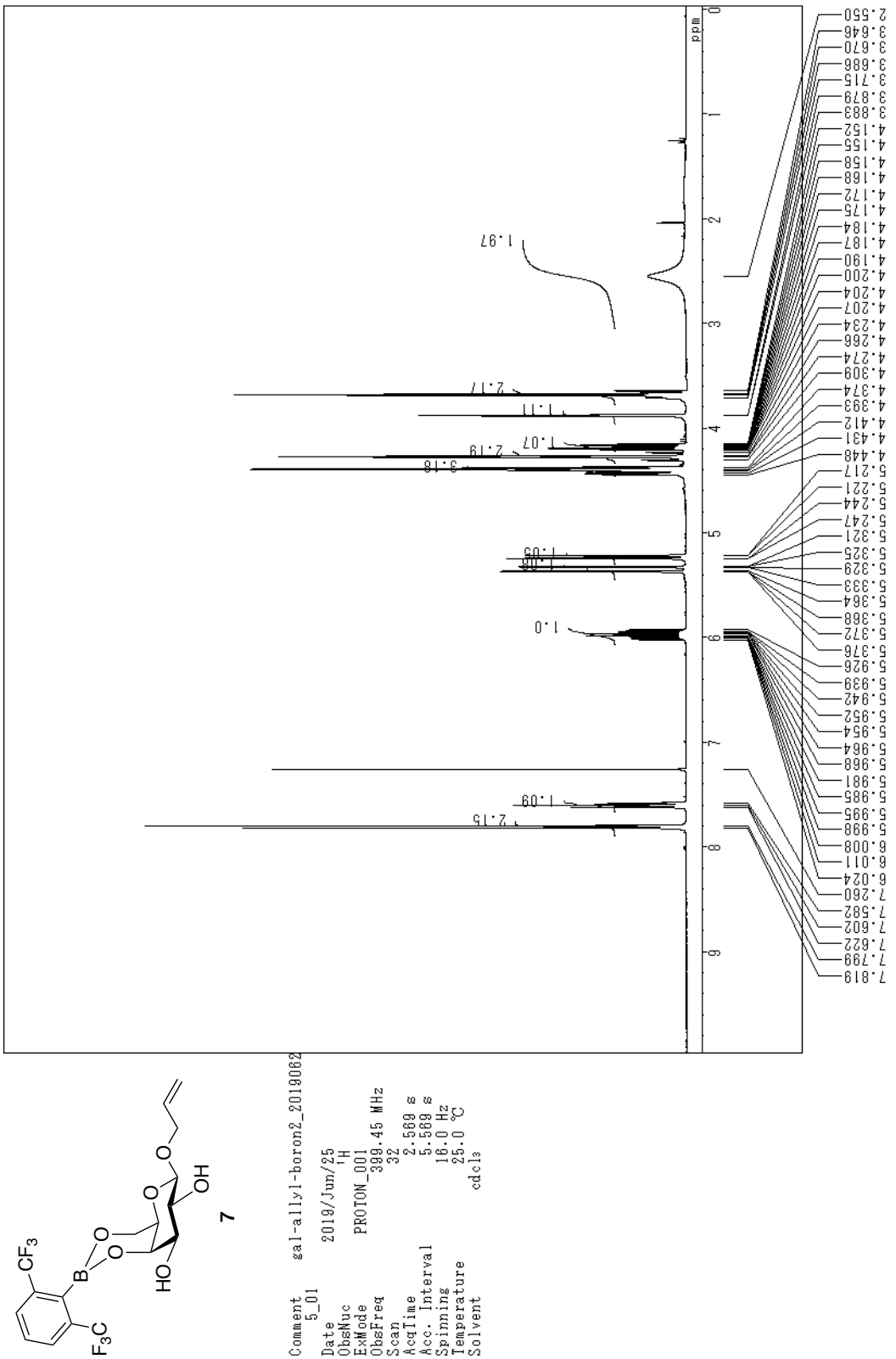
^{13}C-NMR (100 MHz, $CDCl_3$ / CD_3OD = 1 : 1)

δ 174.8, 130.4, 130.3, 104.2, 81.1, 75.4, 72.3, 72.2, 70.0, 69.9, 68.8, 67.9, 61.9, 34.9,

32.47, 32.46, 30.31, 30.28, 30.22, 30.20, 30.18, 30.11, 30.08, 30.04, 30.02, 29.89, 29.85, 29.80, 29.64, 27.69, 27.68, 26.6, 25.5, 23.2, 14.3.

ESI-HRMS

HRMS (ESI) *m*/*z* calcd for $C_{43}H_{81}O_{12}S$ $[M-Na]^-$ 821.5448, found 821.5408.


7
Comment gal-allyl-boron2_20190628
5_01
Date 2019/Jun/25
ObsNuc 1H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 32
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
1.97
2.17
1.11
1.07
2.19
3.18
1.03
1.0
1.09
2.15
7.819
7.799
7.622
7.602
7.582
7.260
6.024
6.011
6.008
5.998
5.985
5.981
5.968
5.964
5.954
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5.942
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4.274
4.266
4.234
4.207
4.204
4.200
4.190
4.187
4.184
4.175
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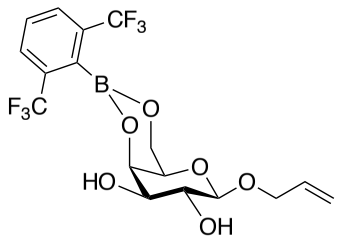
3.715
3.686
3.670
3.646
2.550



7

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    0626_01
Date          2019/Jun/26
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.66 MHz
Scan                  512
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature        40.0 ℃
Solvent            cdcl3
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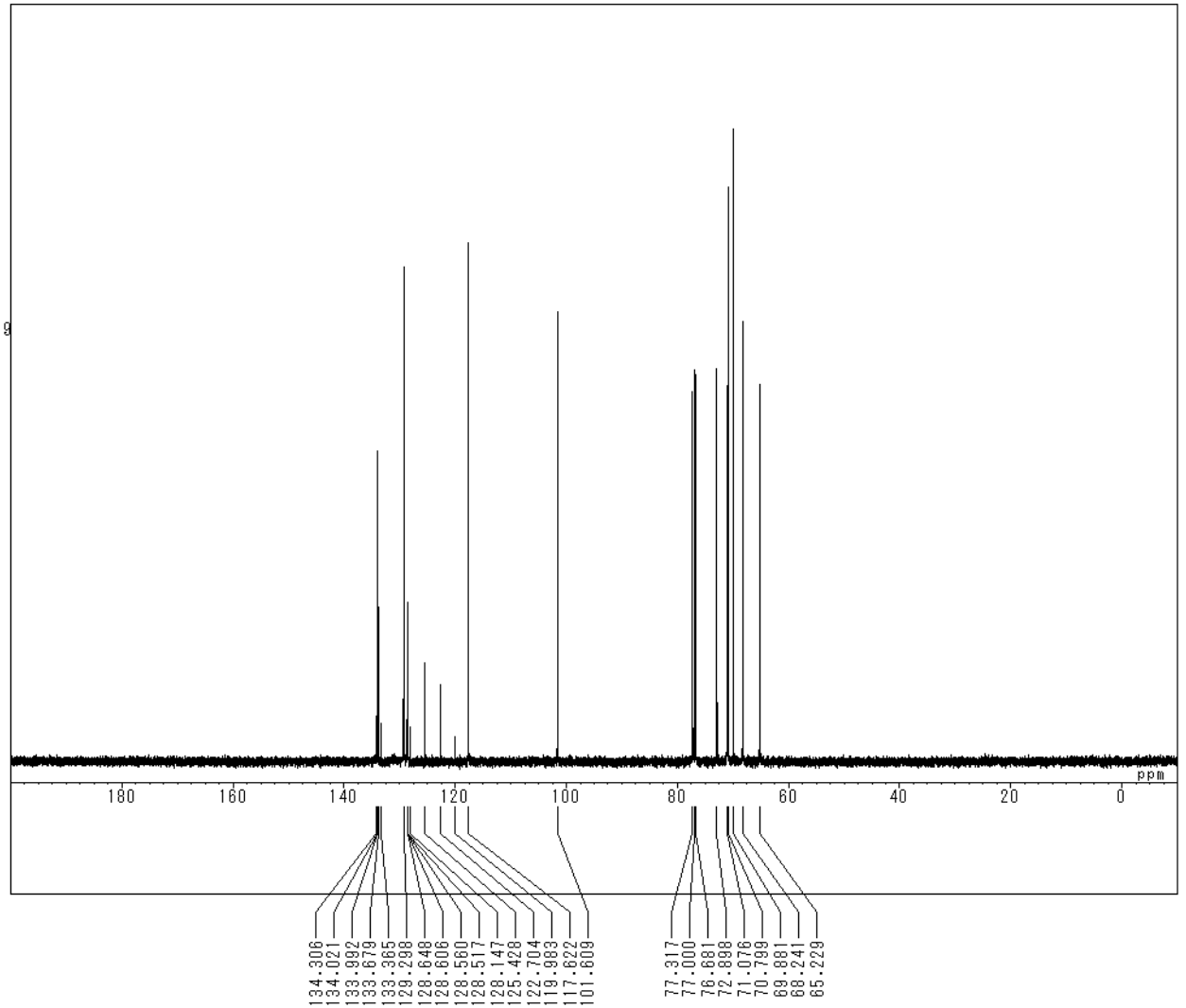
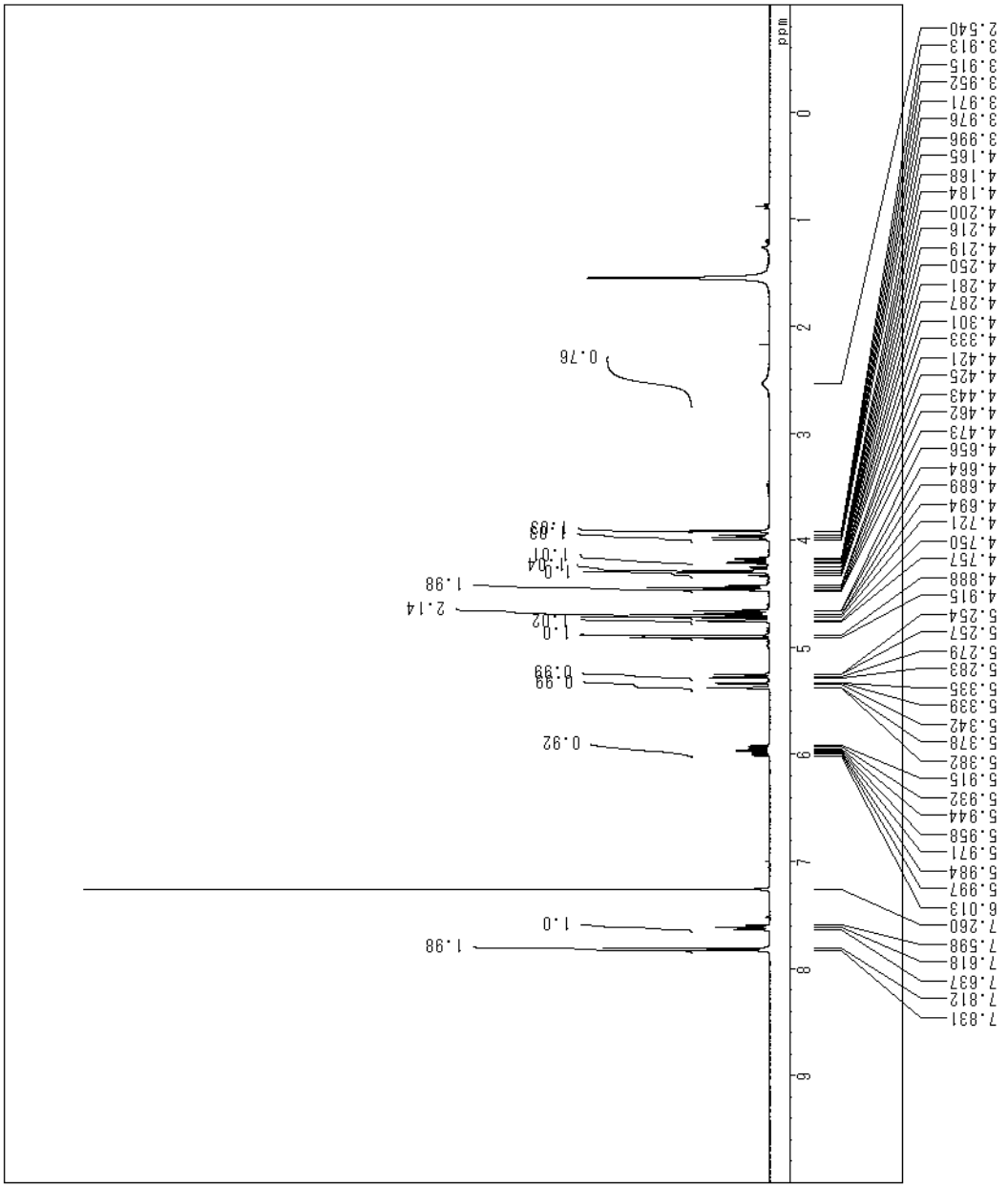
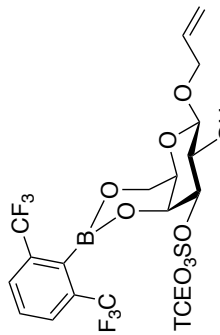
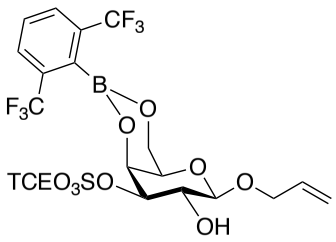






9

Comment su34017-5_20190717_01
Date 2019/Jul/17
ObsNuc 1H
ExMode PROTON_001
ObsFreq 400.27 MHz
Scan 16
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 40.0 ℃
Solvent cdcl3



9

Comment	TRS-02-29-C_20150412_01
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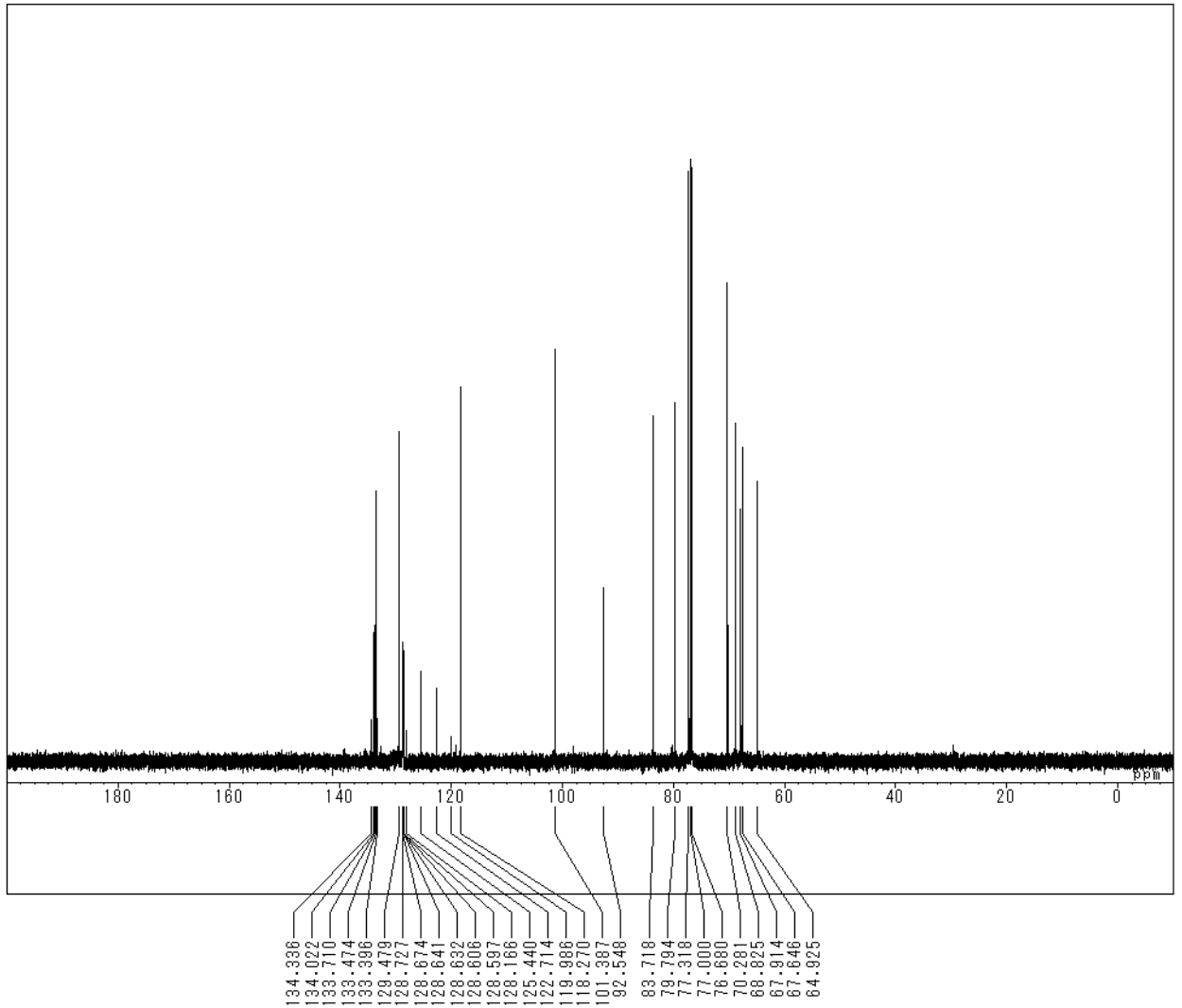
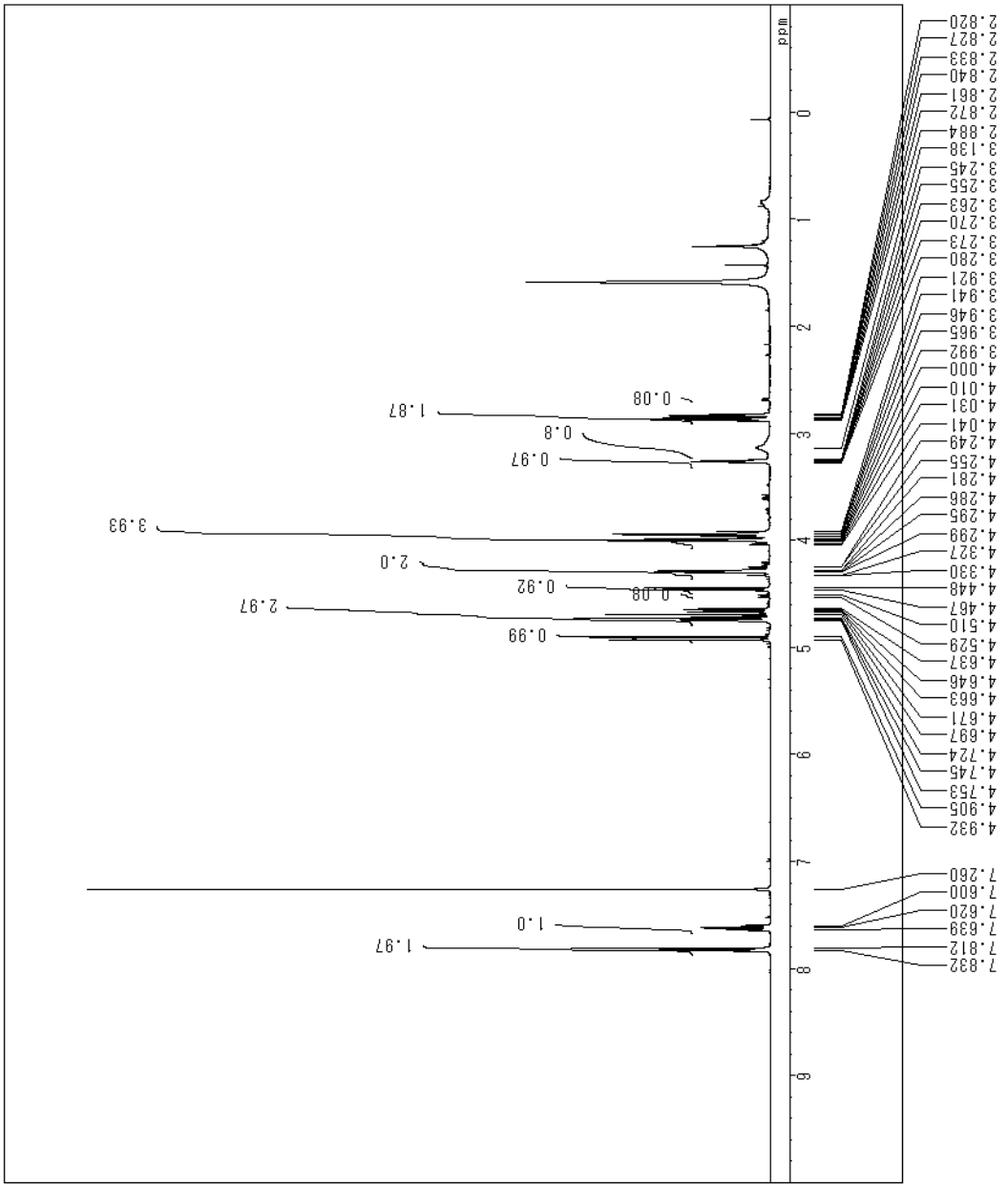
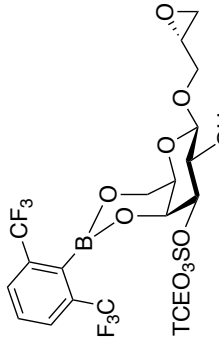
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	3.0 ℃
Solvent	cdcl3



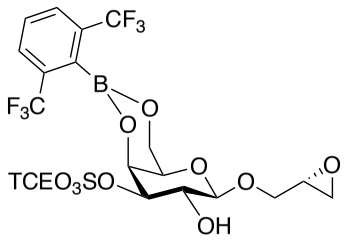




10

93/7 dr

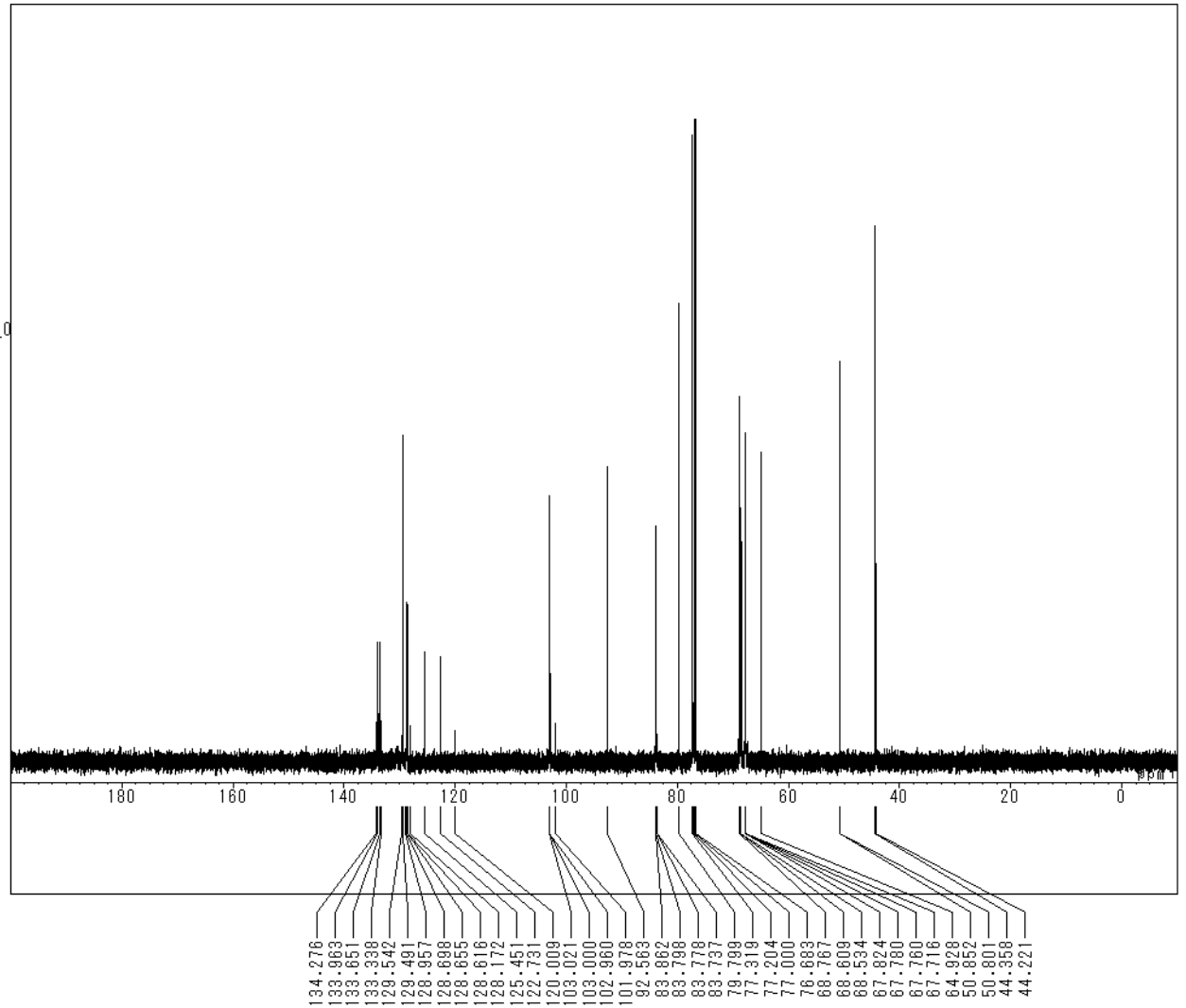
Comment	su34018-3_20190717_01
Date	2019/Jul/17
ObsNuc	1H
ExMode	PROTON_001
ObsFreq	400.27 MHz
Scan	32
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	40.0 ℃
Solvent	cdcl3

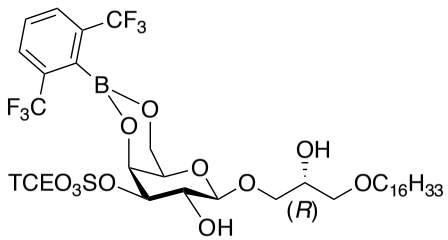


10

93/7 dr

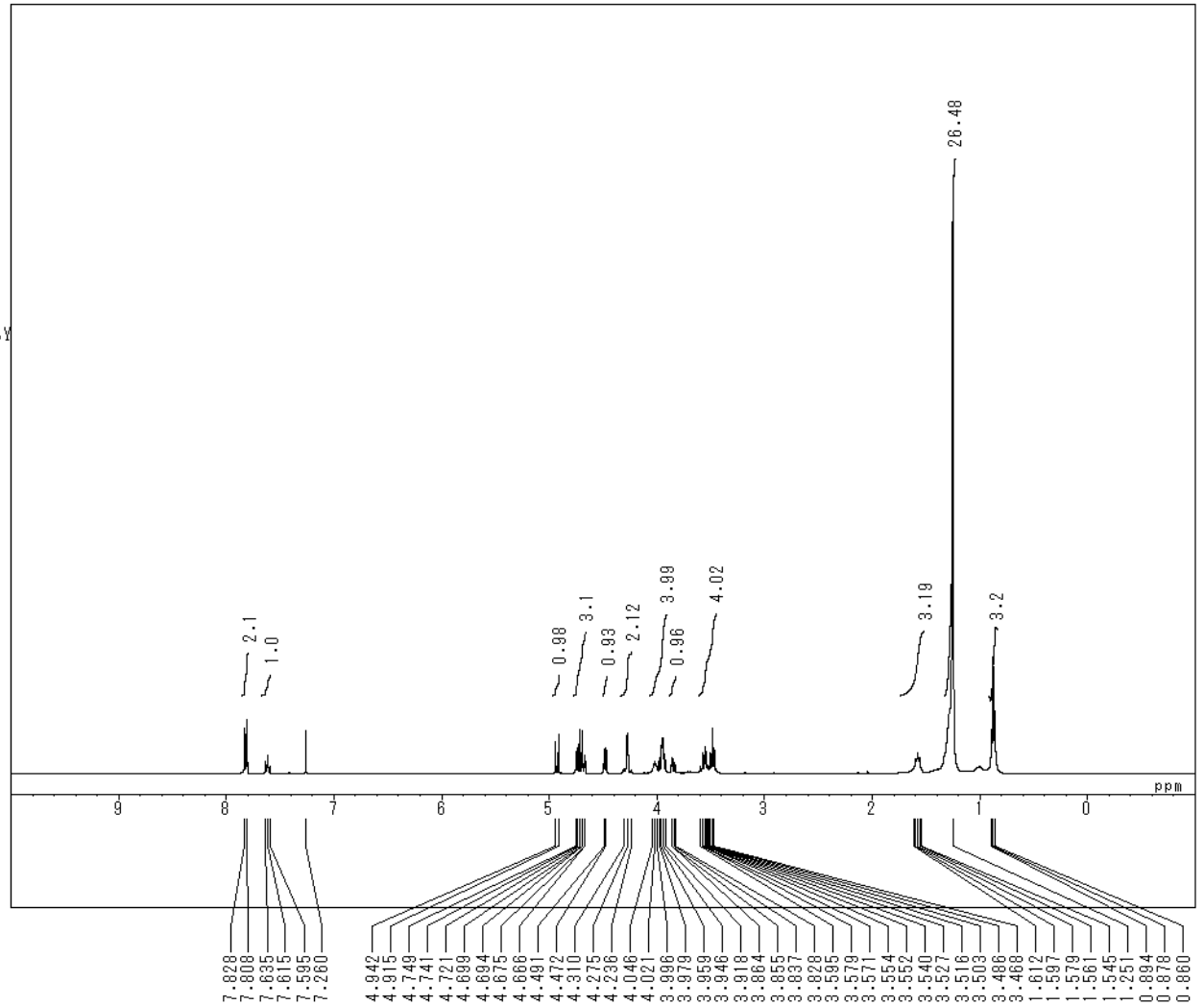
Comment	gal-boron-epo_20160729_0
	1
Date	2016/Jul/29
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

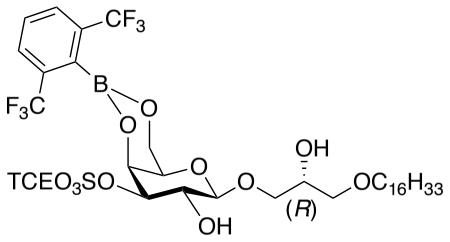




11

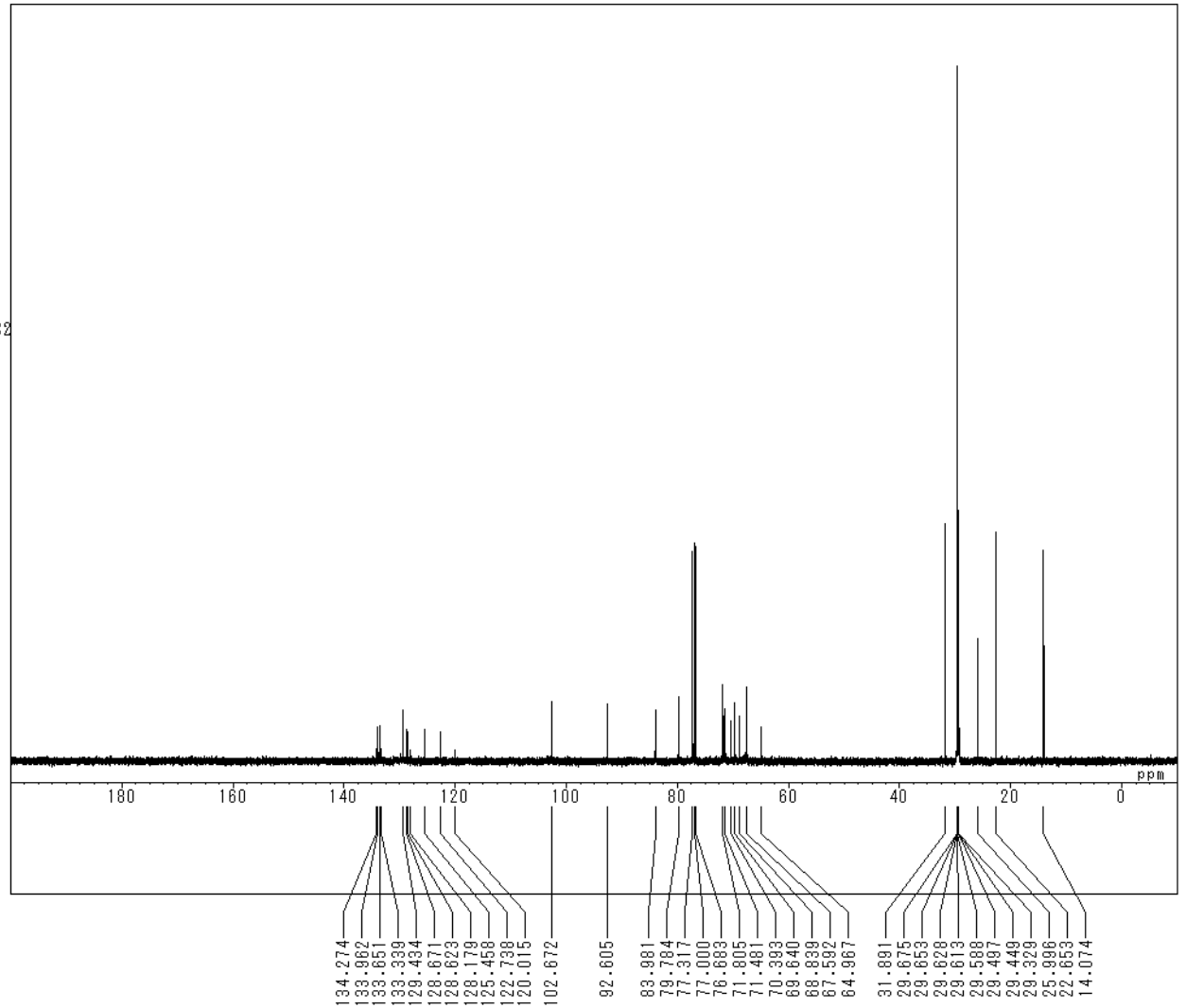
Comment KF-TCE-S-decanol-SM-COSY_20150529_01
Date 2015/May/29
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 8
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

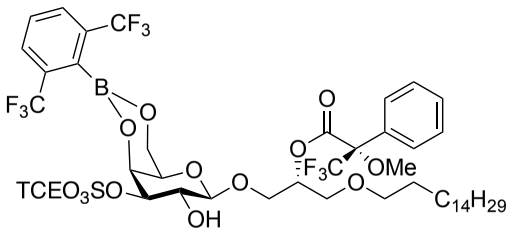




11

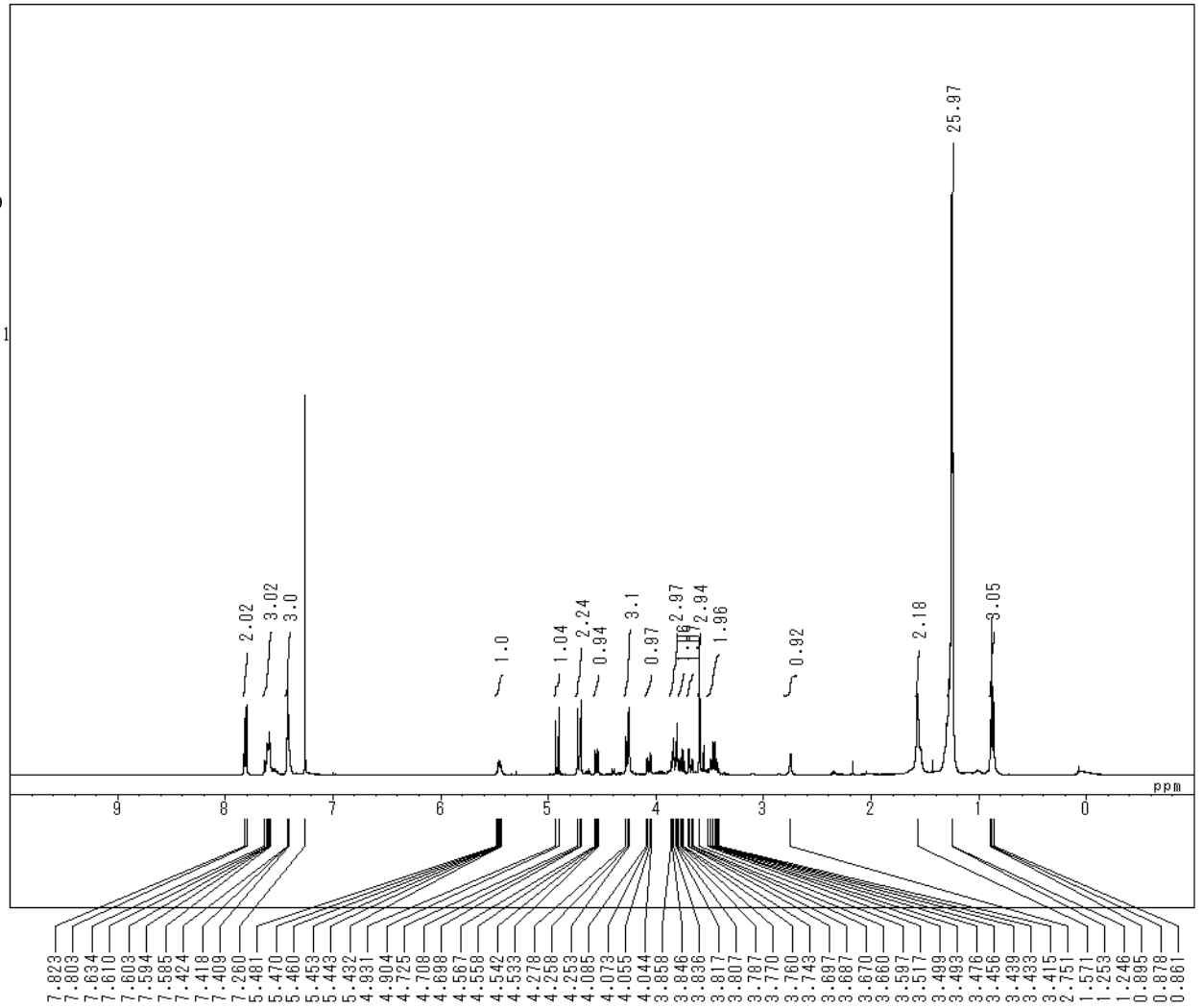
Comment KF-decanol-TCE-C_2015082 1_02
Date 2015/Aug/21
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 256
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

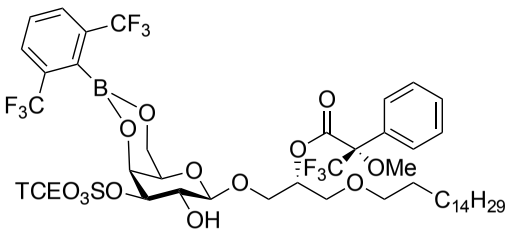




SI-1

Comment	KF-decanol-S_20151208_01
Date	2015/Dec/08
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3





SI-1

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ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 2048
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Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature        25.0 ℃
Solvent            cdcl3
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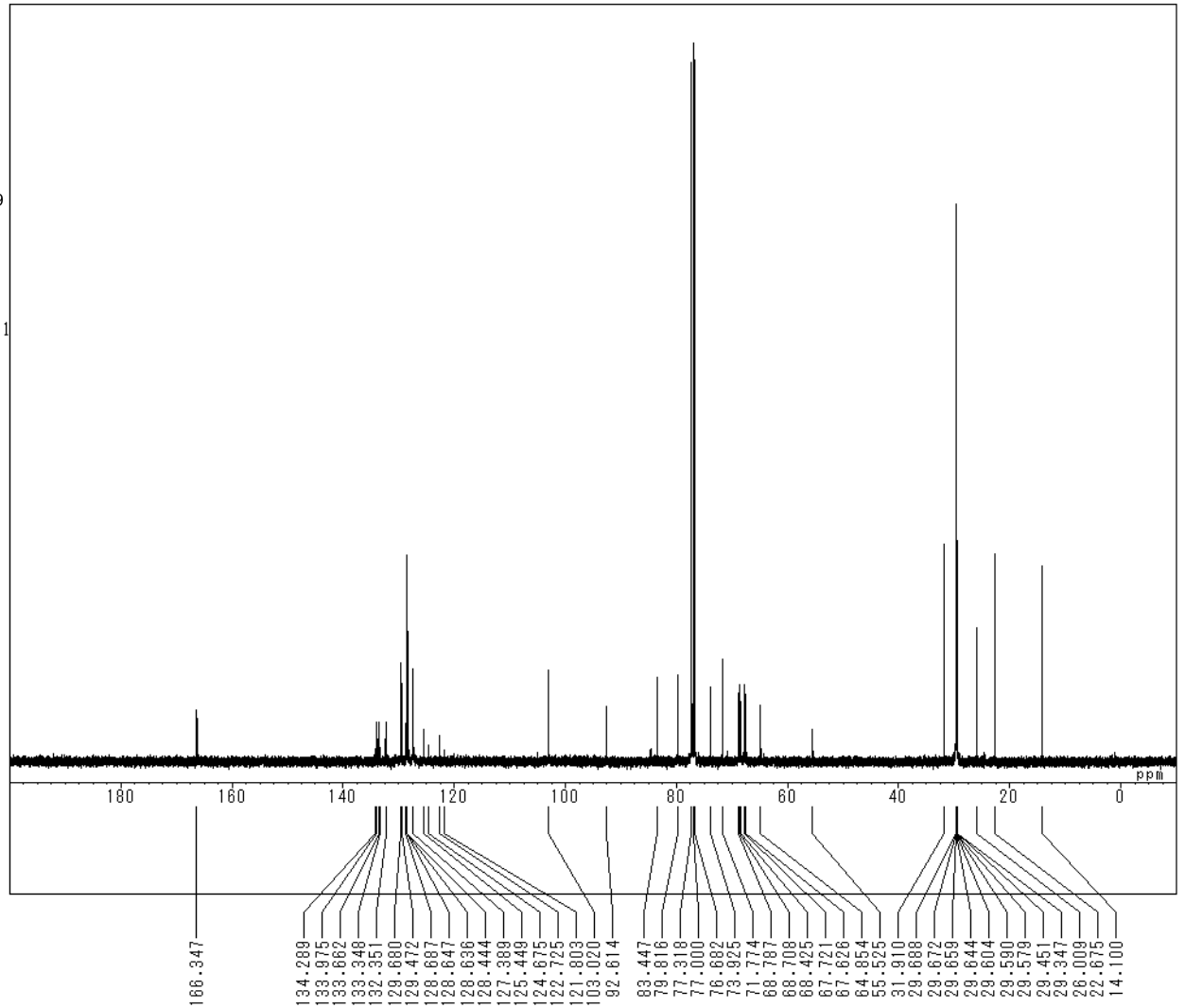

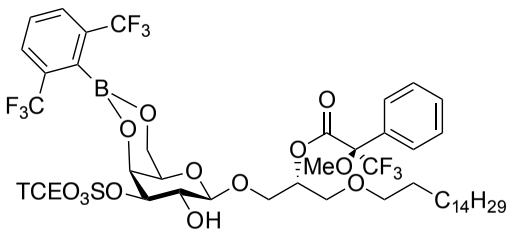

SI-2

Comment	KF-decanol-R-__20150607_01
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ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
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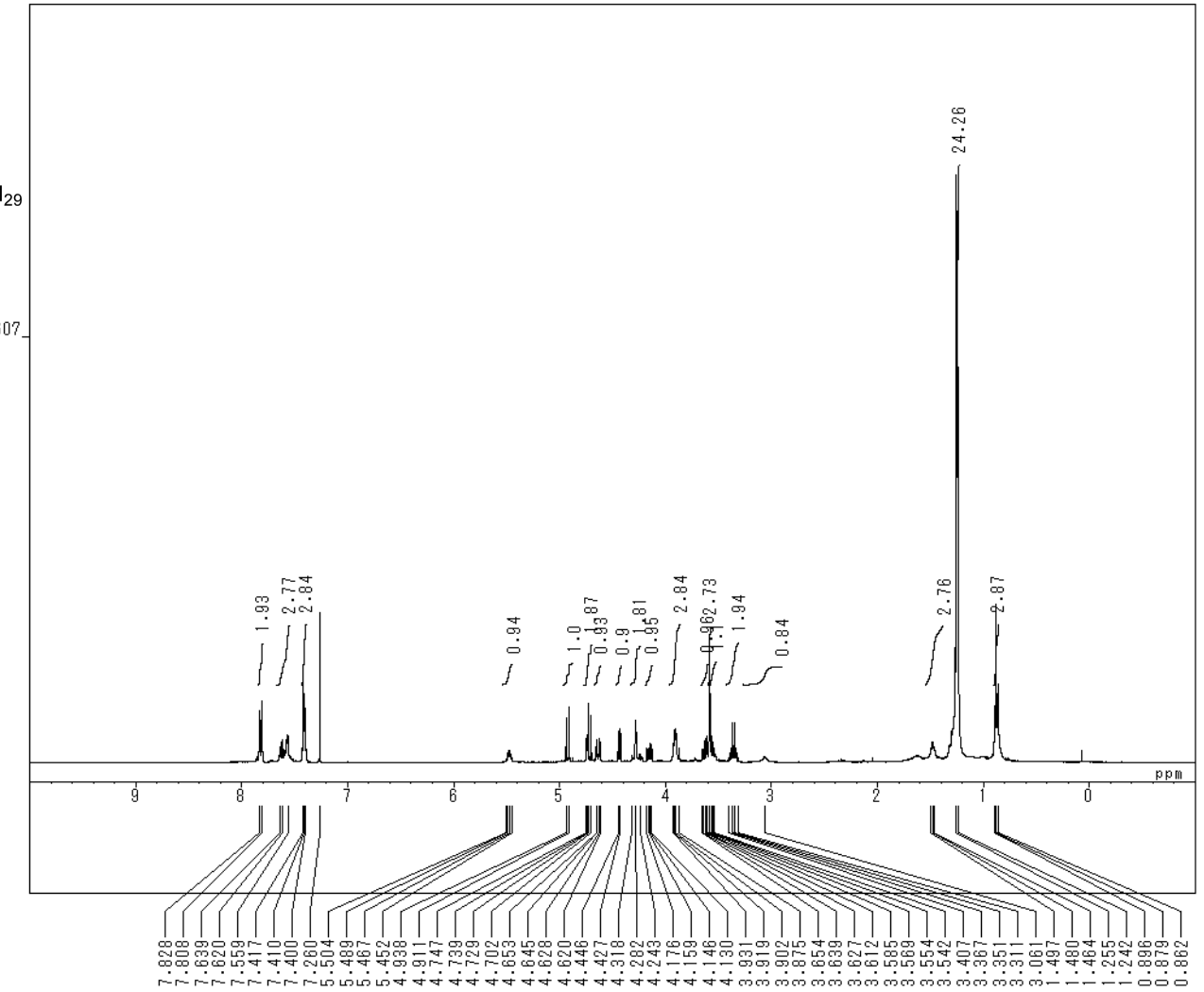
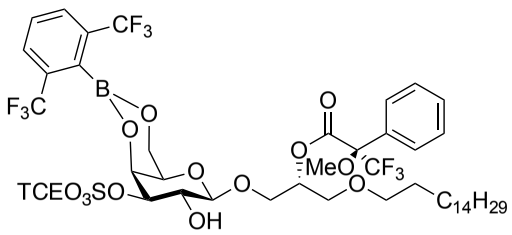
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3





SI-2

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Date	2015/Jun/08
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
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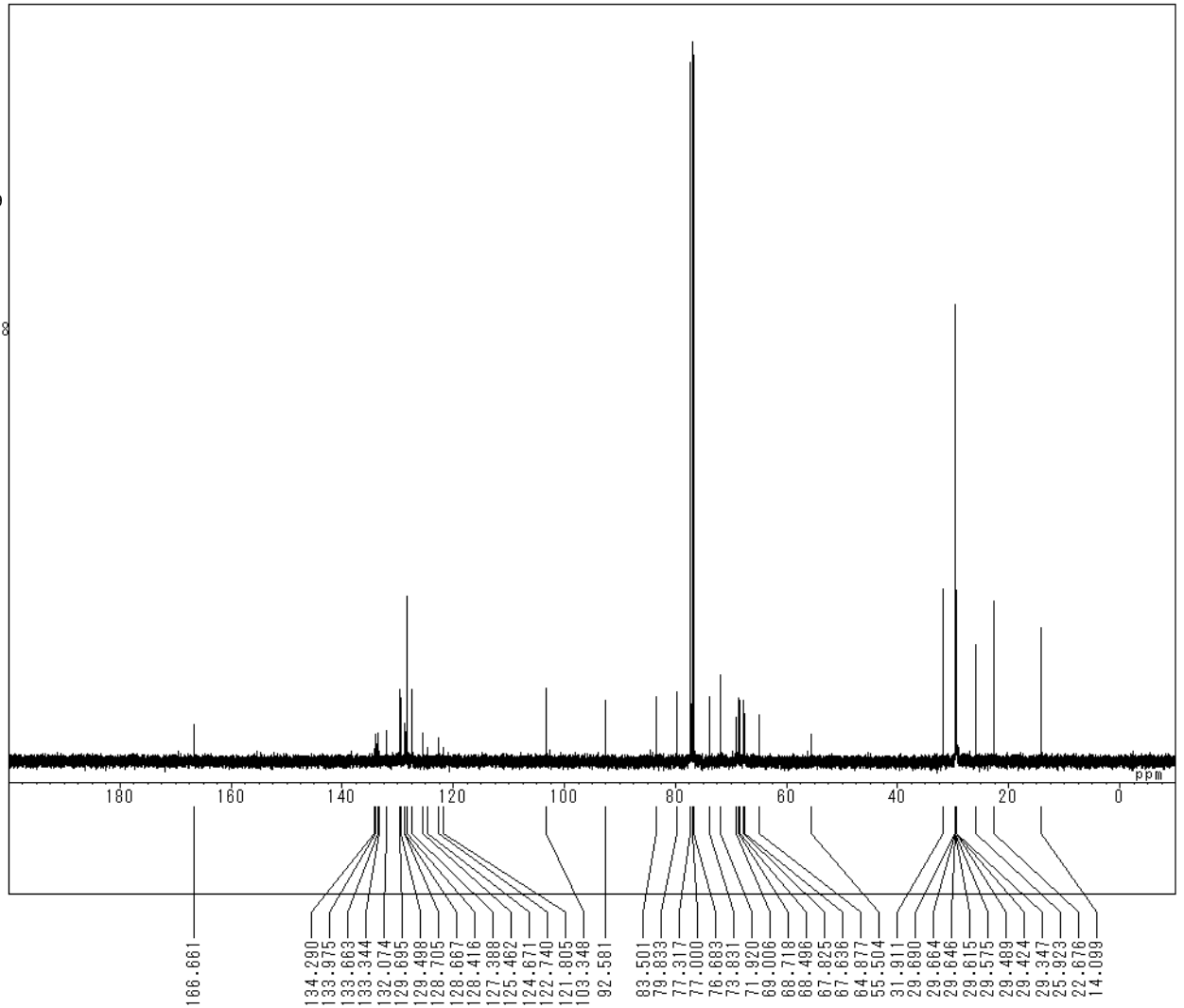
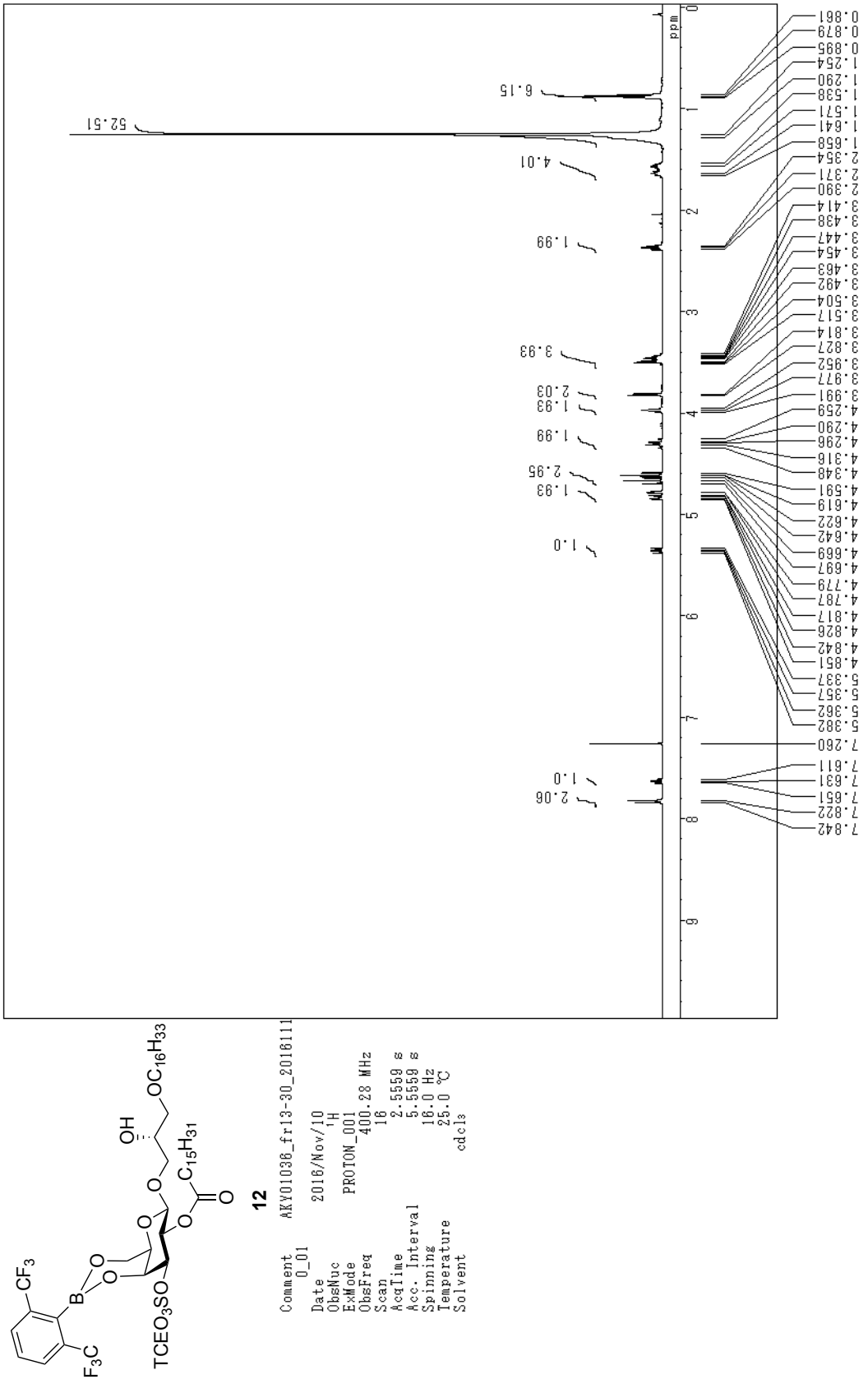
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3




12
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0_01
Date 2016/Nov/10
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ExMode PROTON_001
ObsFreq 400.28 MHz
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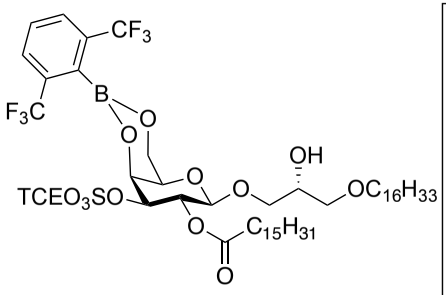
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm



12

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ObsFreq 100.45 MHz
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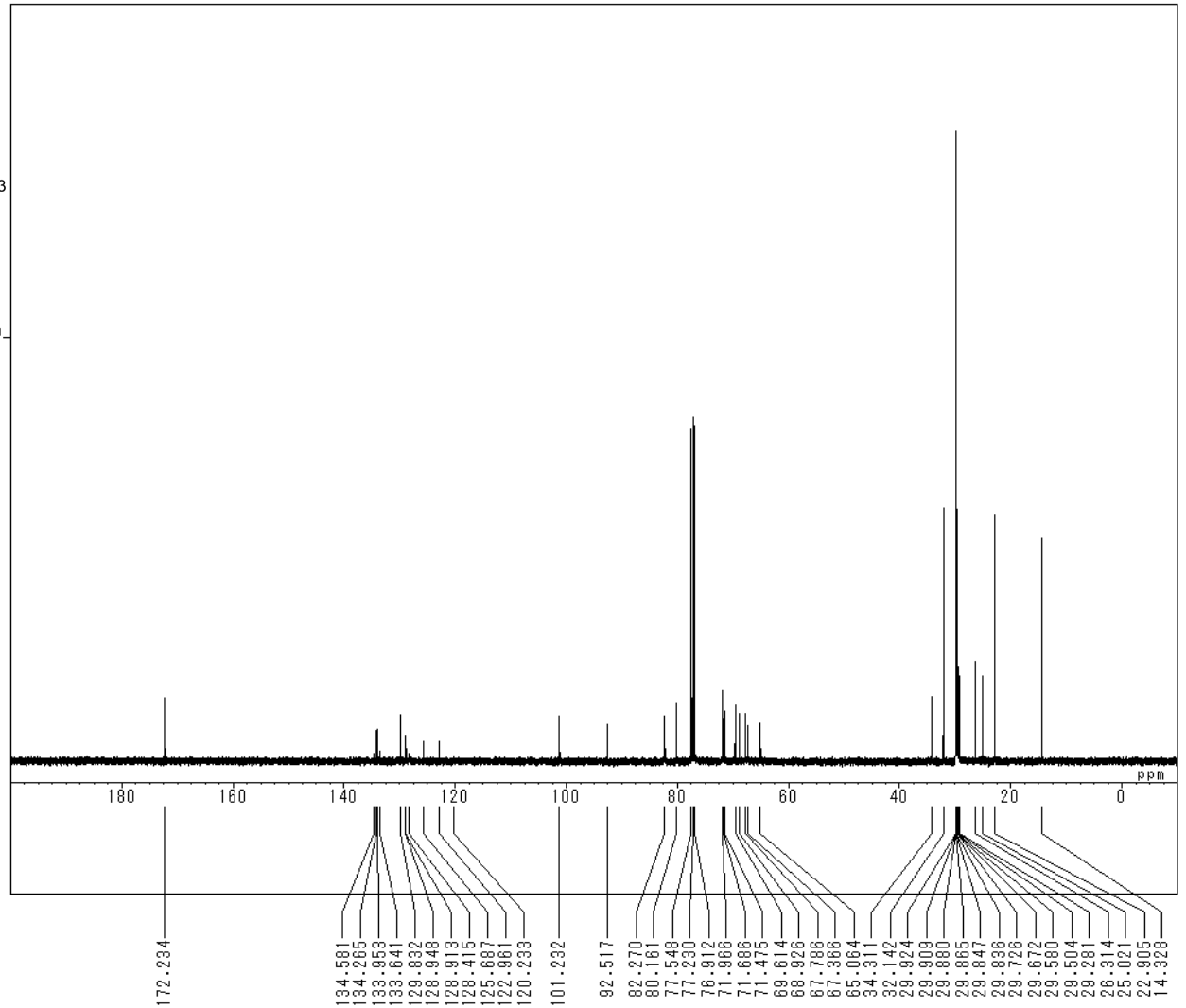
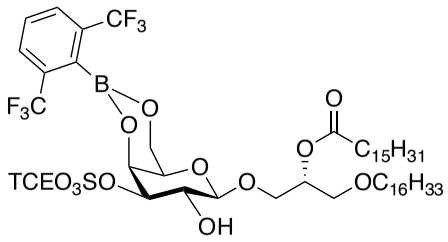
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3





13

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ObsNuc	^{1}H
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ObsFreq	399.45 MHz
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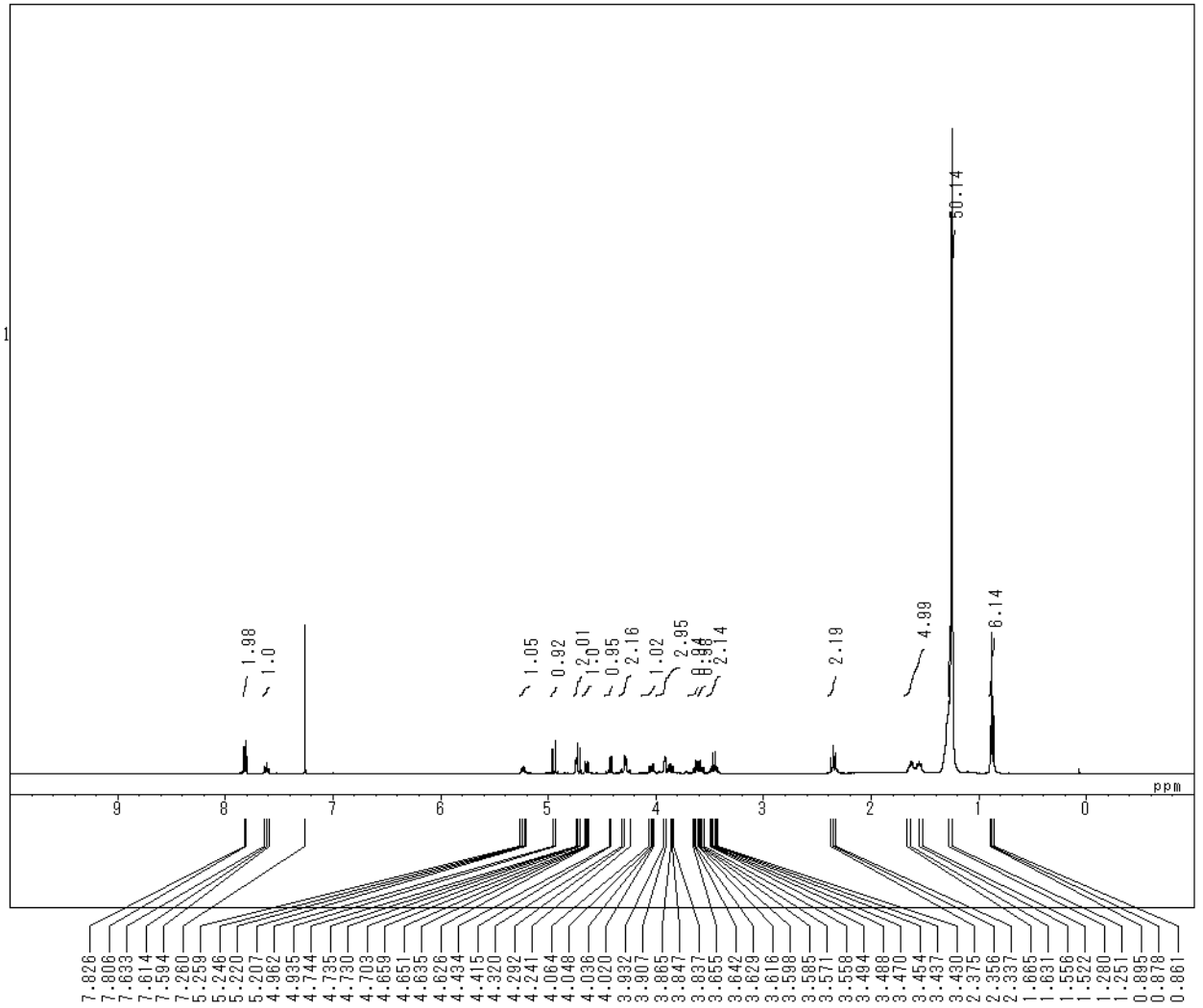
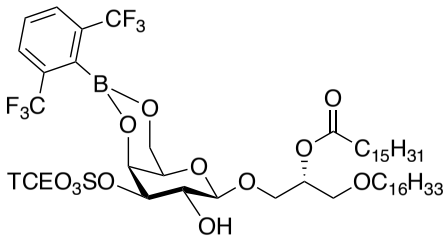
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3





13

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Comment    KF-S-TCE-pal-boron-C_201
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ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 1024
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Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature         3.0 ℃
Solvent            cdcl3
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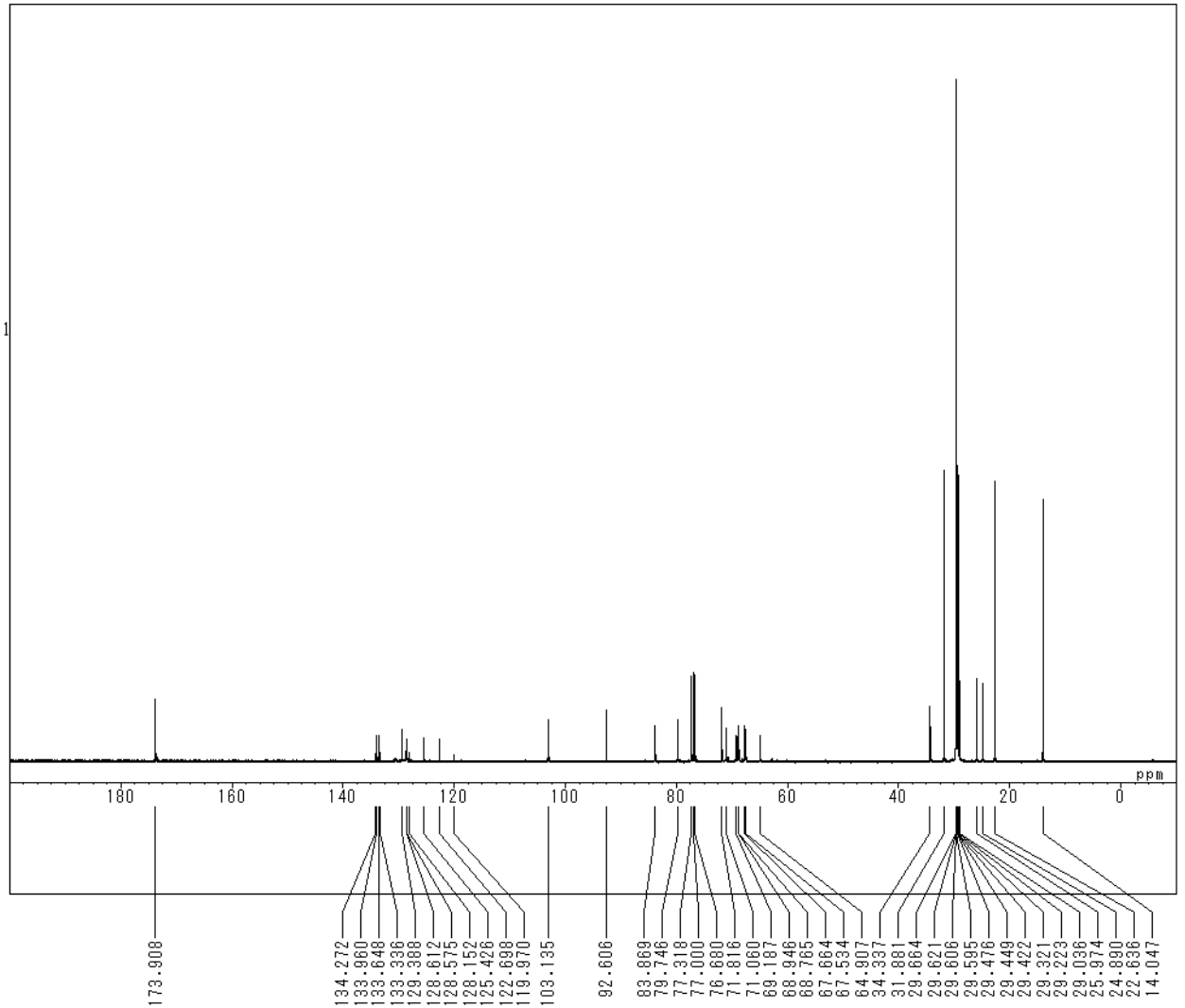
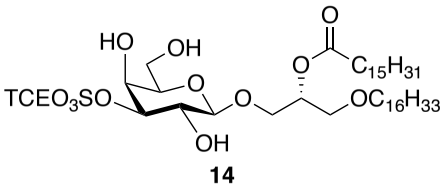
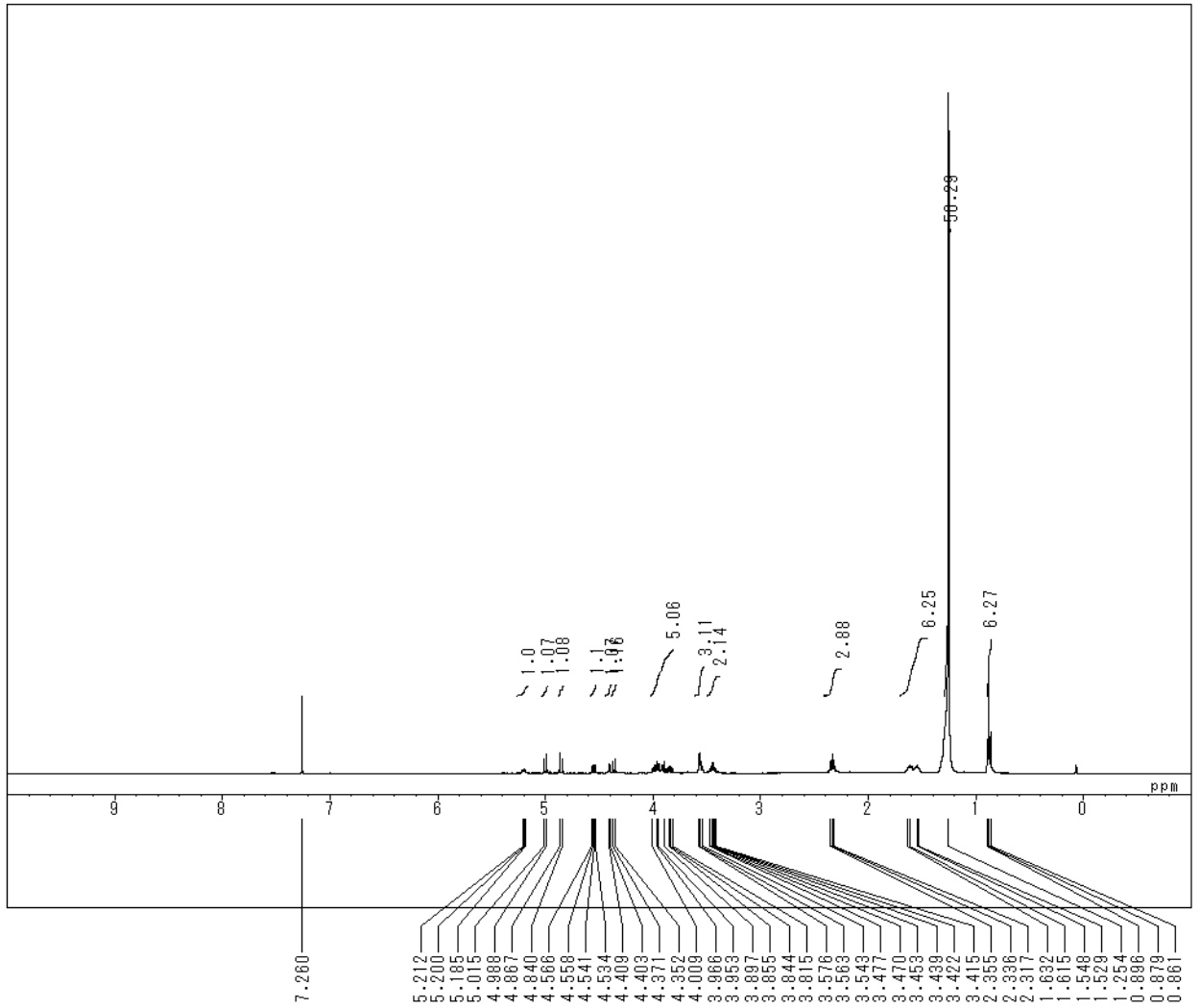
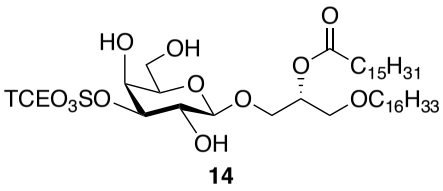




14

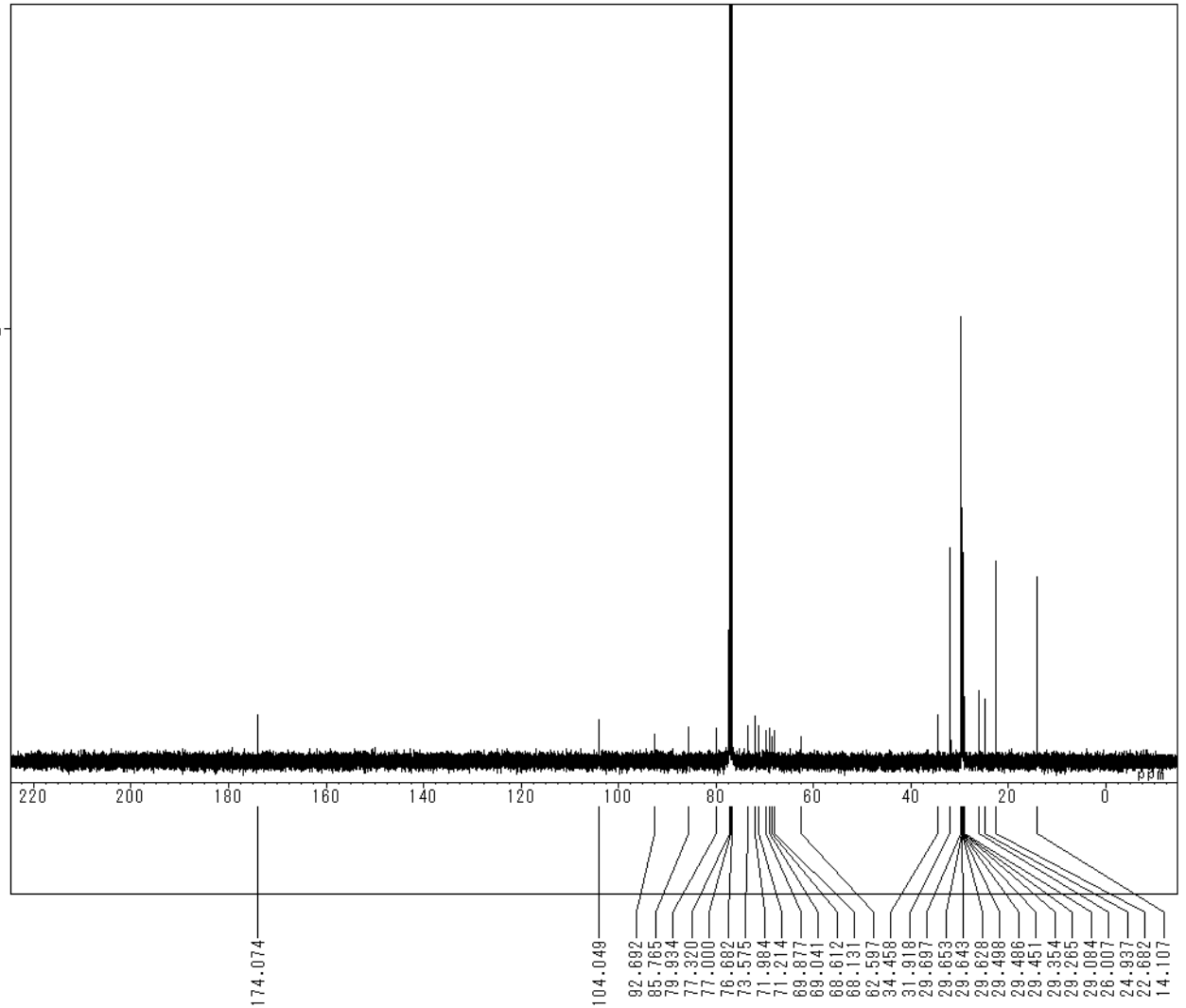
Comment	su34024pure_20190721_01
Date	2019/Jul/21
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	16
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

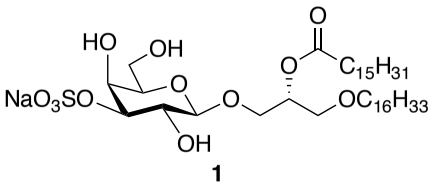




14

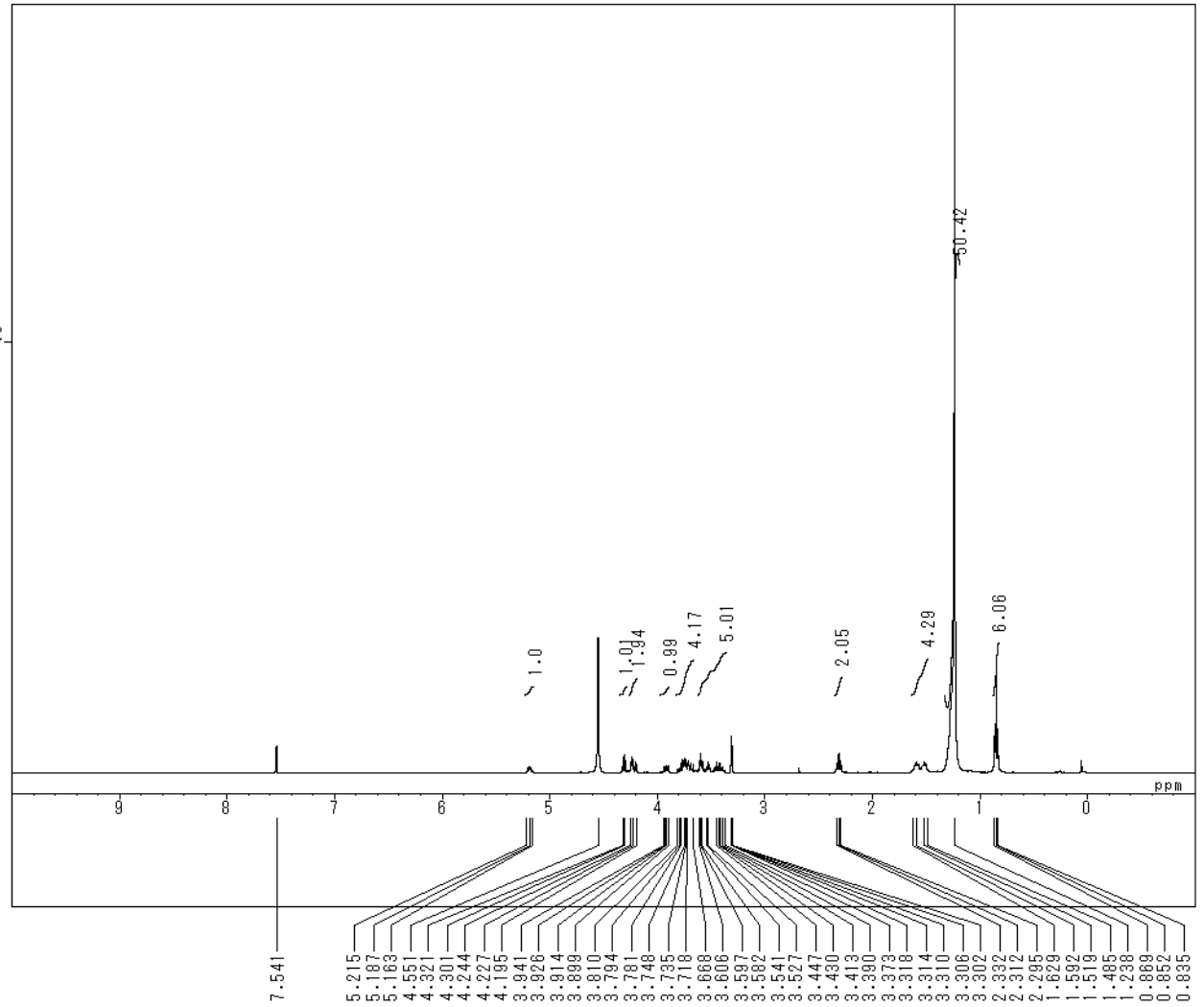
Comment KF-TCE-pal-deprotection-C_20151215_01
Date 2015/Dec/15
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 1024
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

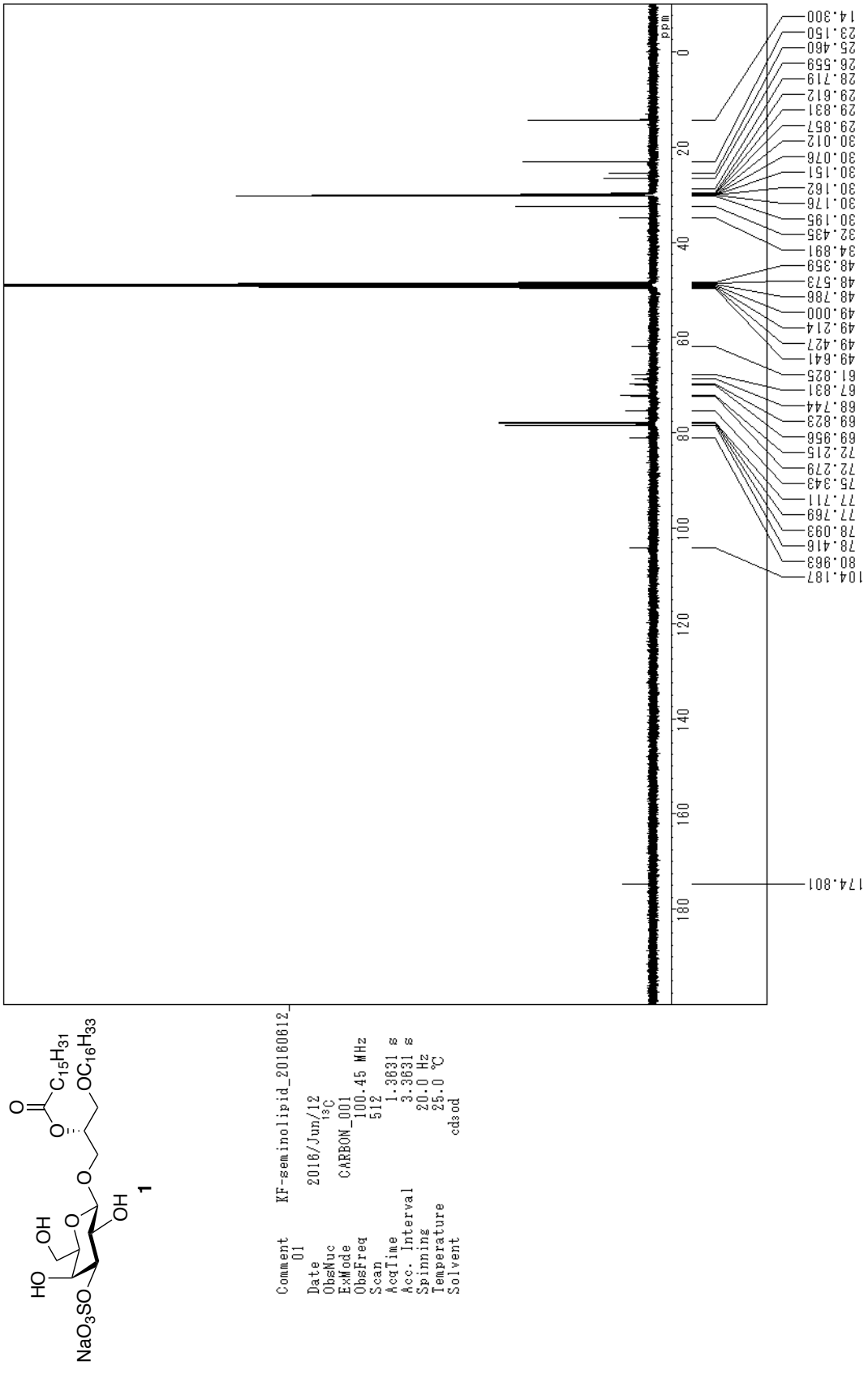




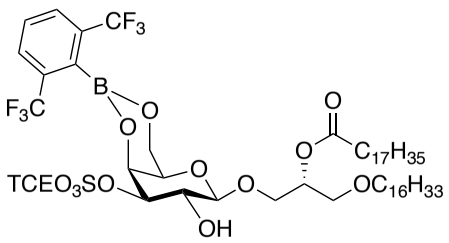
1

Comment	KF-seminolipid_20160612_01
Date	2016/Jun/12
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdsod



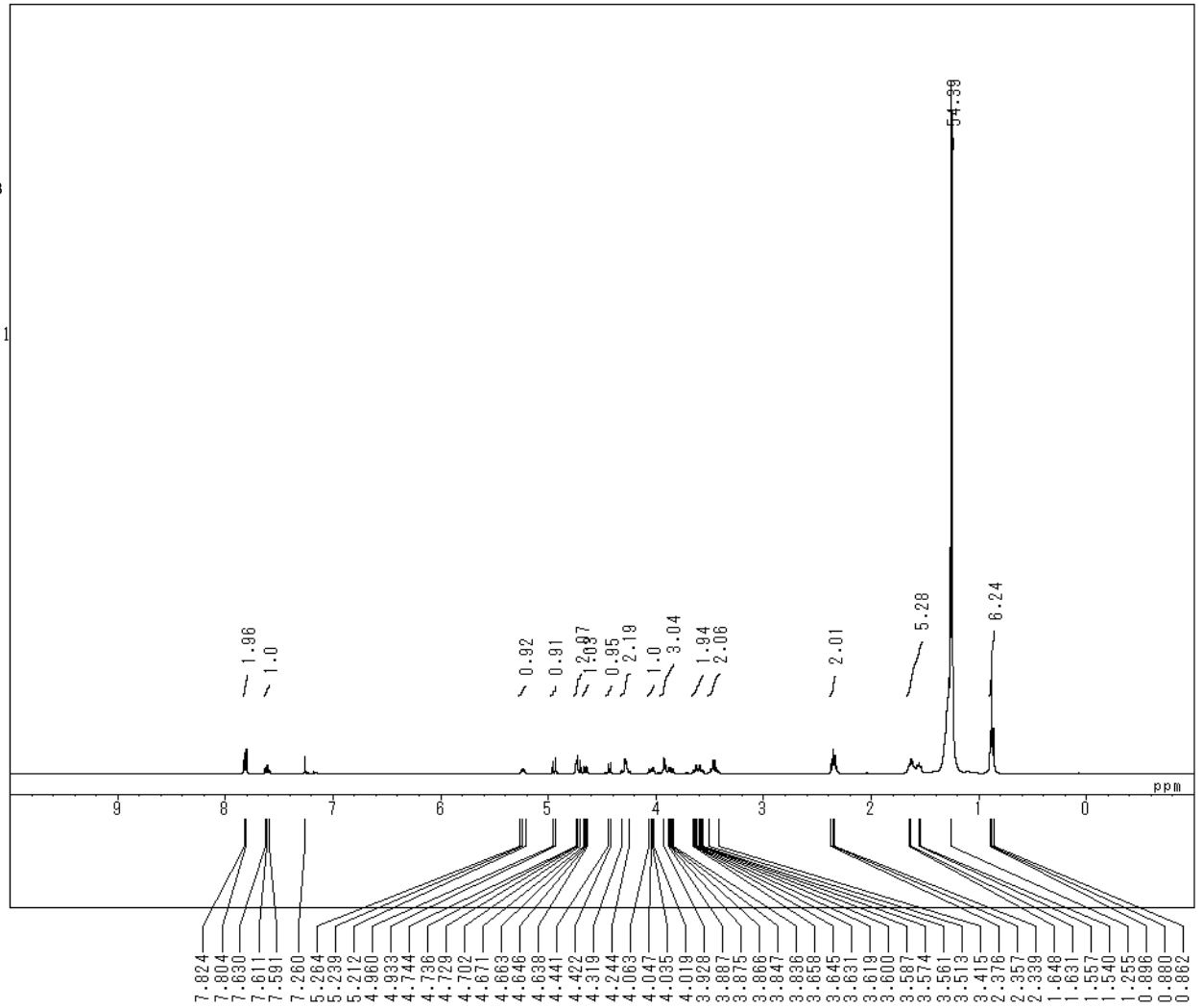

Comment KF-seminolipid_20160612_01
Date 2016/Jun/12
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 512
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cd3od
ppm
0
20
40
60
80
100
120
140
160
180
14.300
23.150
25.460
26.559
28.719
29.612
29.831
29.857
30.012
30.076
30.151
30.162
30.176
30.195
32.435
34.891
48.359
48.573
48.786
49.000
49.214
49.427
49.641
61.825
67.831
68.744
69.823
69.956
72.215
72.279
75.343
77.711
77.769
78.093
78.416
80.963
104.187
174.801

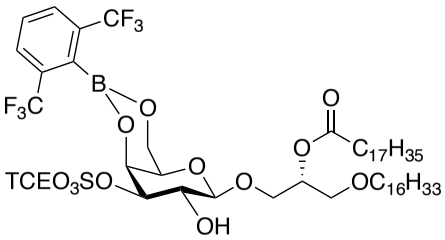
O
O
C15H31
OC16H33
O
O
OH
HO
OH
NaO3SO
1



15

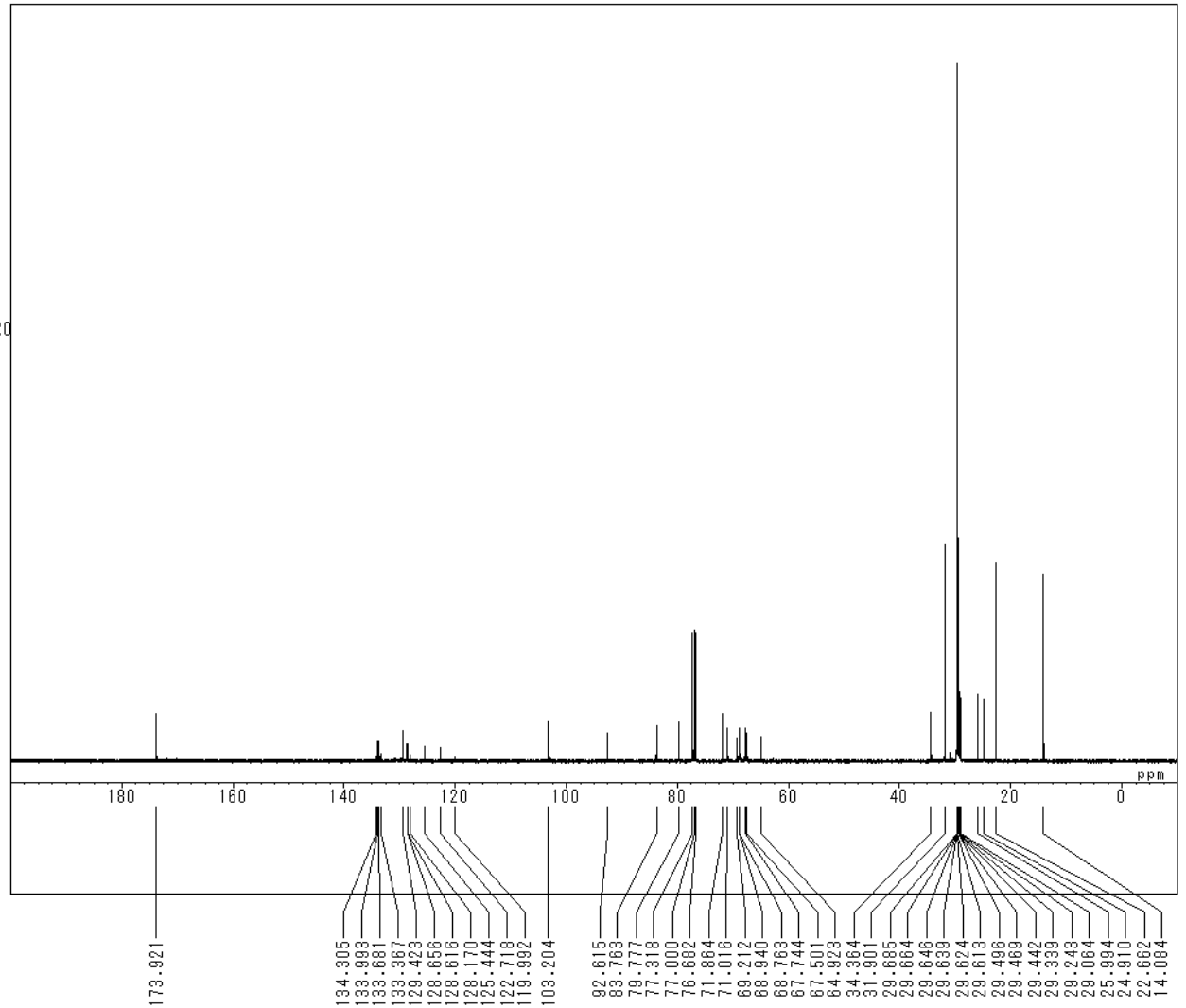
```
Comment     AI-01-014_ste-pure_20151
    007_01
Date          2015/Oct/07
ObsNuc                1H
ExMode         PROTON_001
ObsFreq          400.28 MHz
Scan                   8
AcqTime           2.5559 s
Acc. Interval     5.5559 s
Spinning           16.0 Hz
Temperature        25.0 ℃
Solvent            cdcl3
```

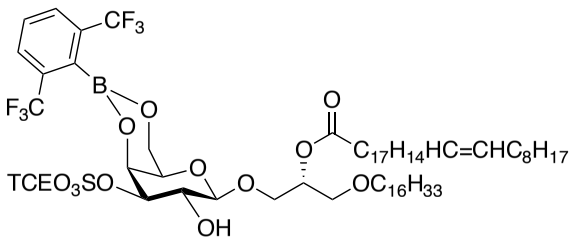




15

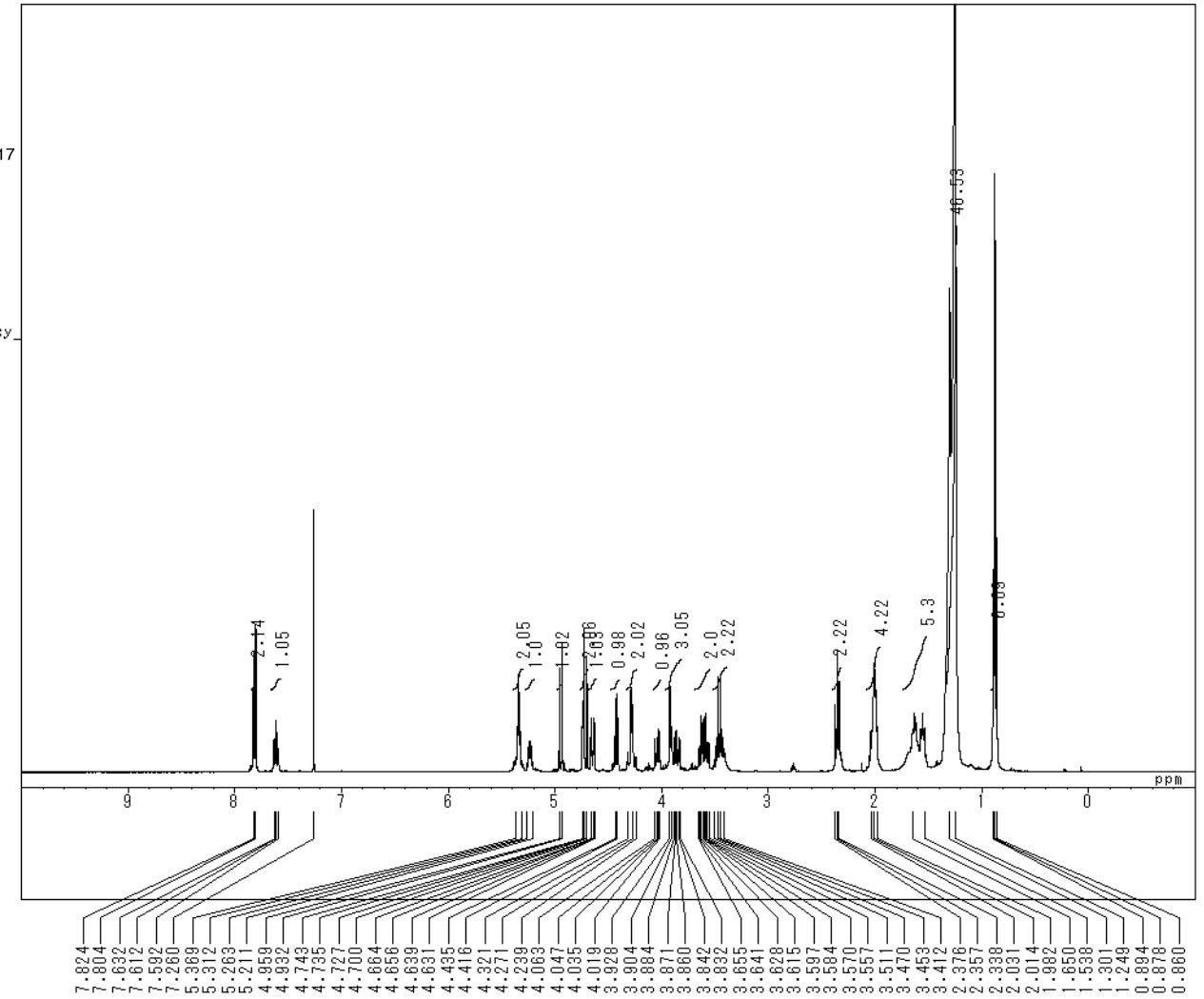
```
Comment    KF-S-TCE-stea-boron-C_20
    151021_01
Date          2015/Oct/21
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 1024
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature         3.0 ℃
Solvent            cdcl3
```

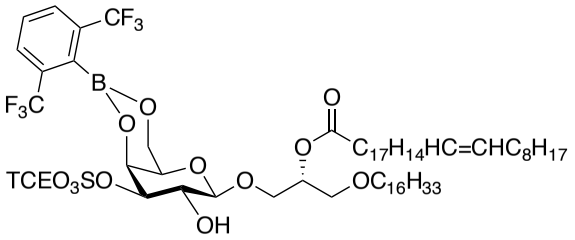




16

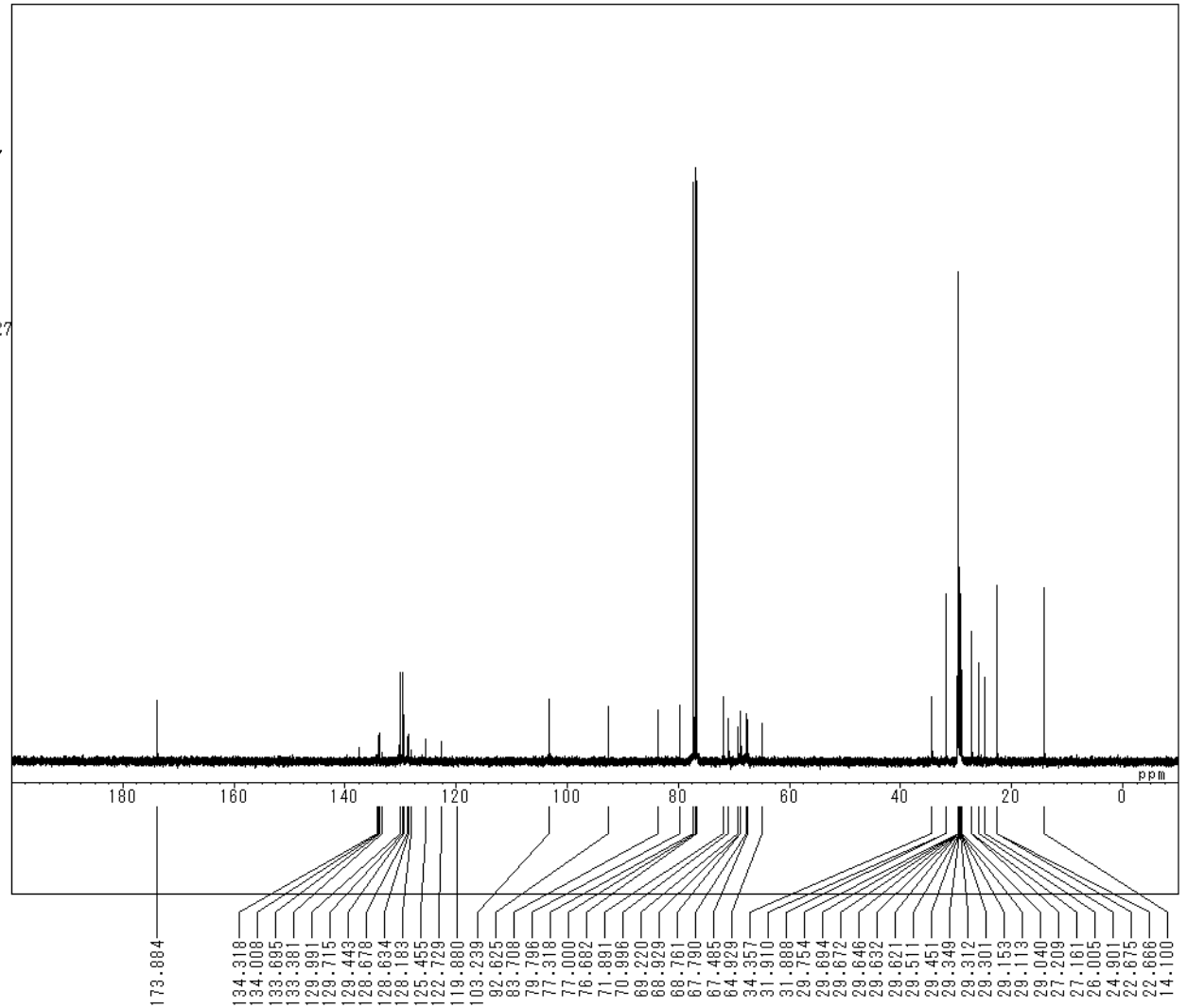
Comment KF-TCE-S-boron-Ole-cosy_20151012_01
Date 2015/Oct/12
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 8
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 3.0 ℃
Solvent cdcl3

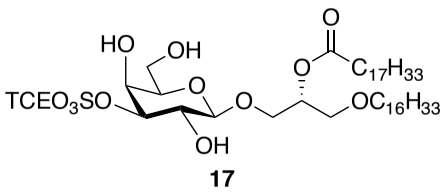




16

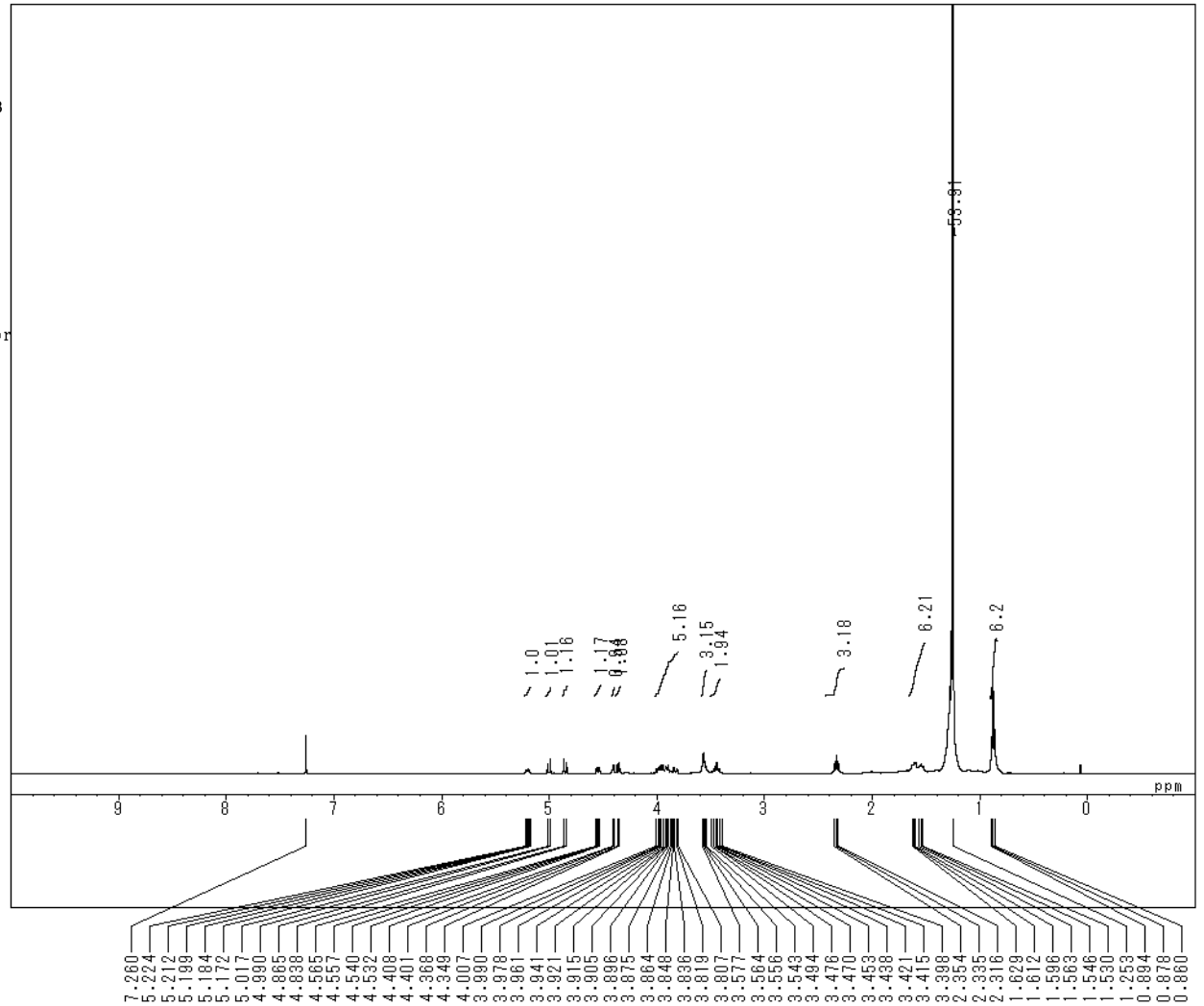
Comment MMY-S-TCE-Ole-C_20150827_01
Date 2015/Aug/27
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 2048
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 3.0 ℃
Solvent cdcl3

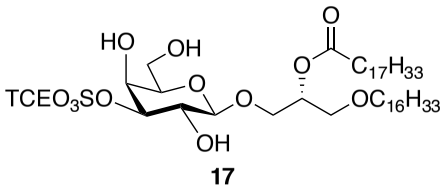




17

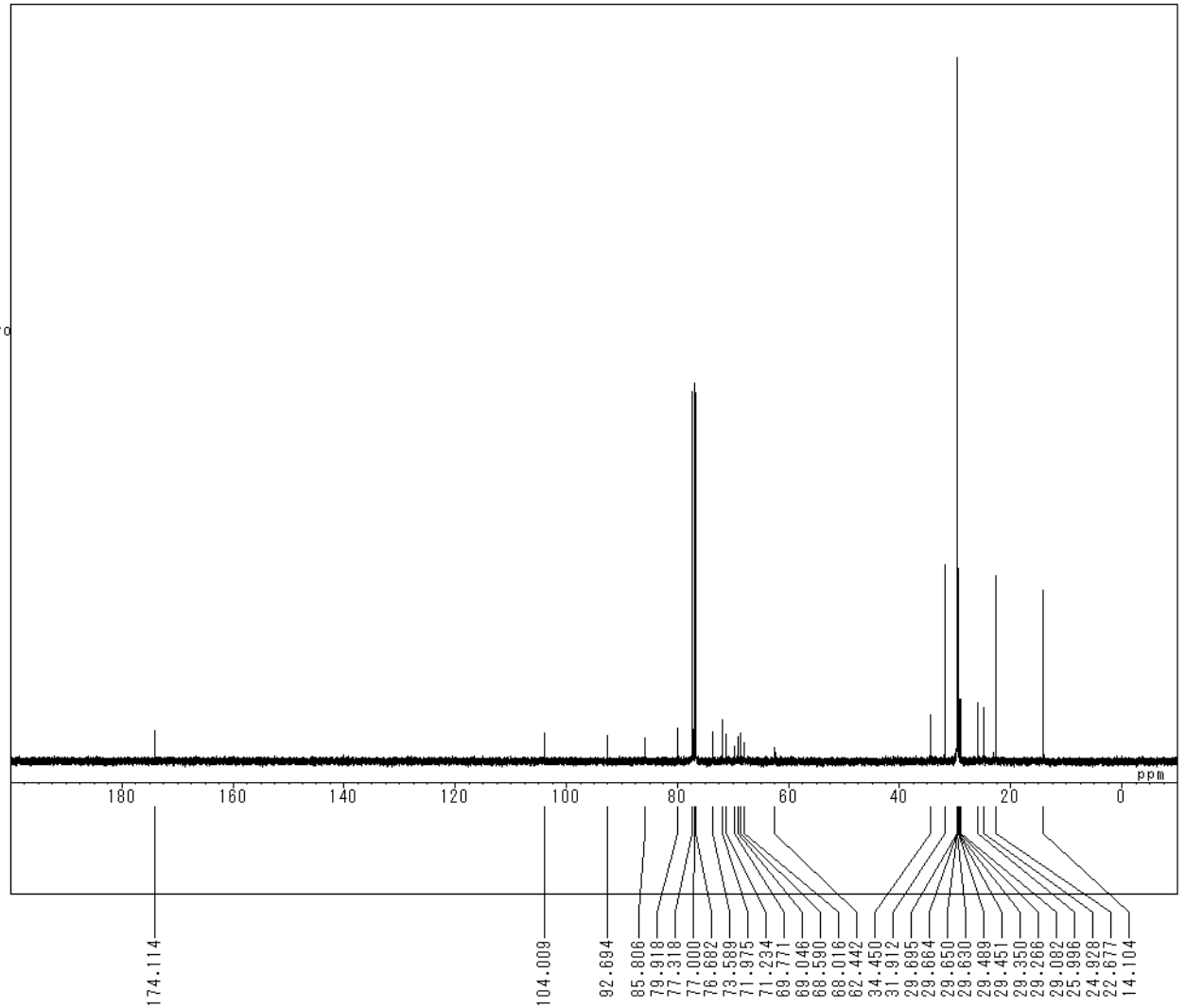
```
Comment    KF-TCE-S-Stea-boron-depr
    otection_20150912_01
Date          2015/Sep/12
ObsNuc                1H
ExMode         PROTON_001
ObsFreq         399.45 MHz
Scan                   8
AcqTime            2.569 s
Acc. Interval      5.569 s
Spinning          16.0 Hz
Temperature        3.0 ℃
Solvent           cdcl3
```

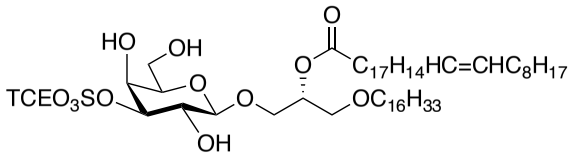




17

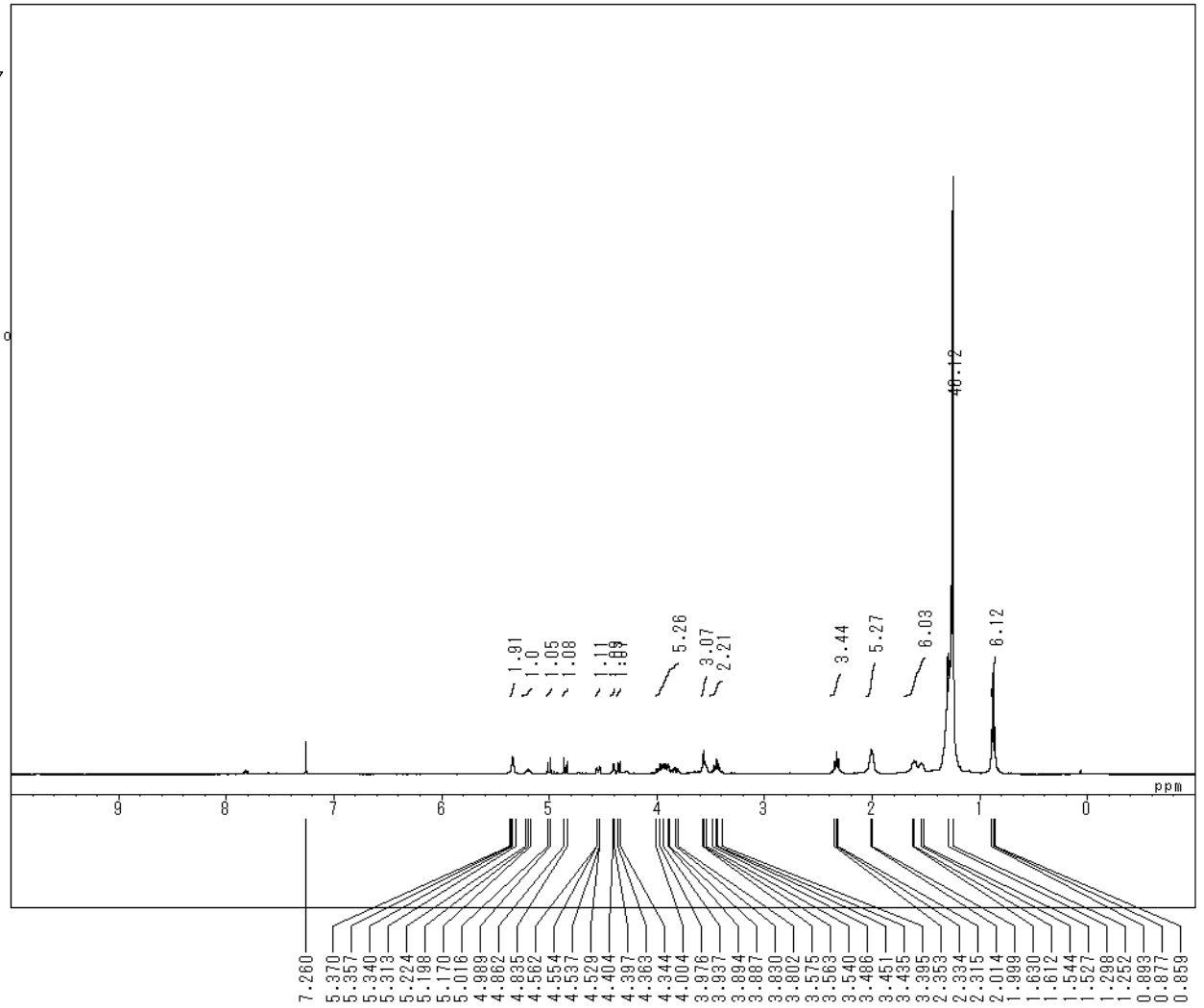
```
Comment    KF-TCE-S-Ste-boron-depro
    tection-C_20150913_01
Date          2015/Sep/13
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 1024
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature         3.0 ℃
Solvent            cdcl3
```

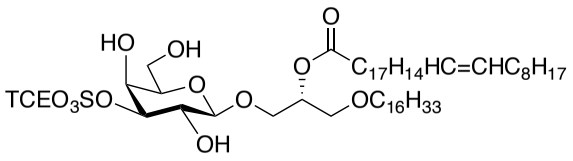




18

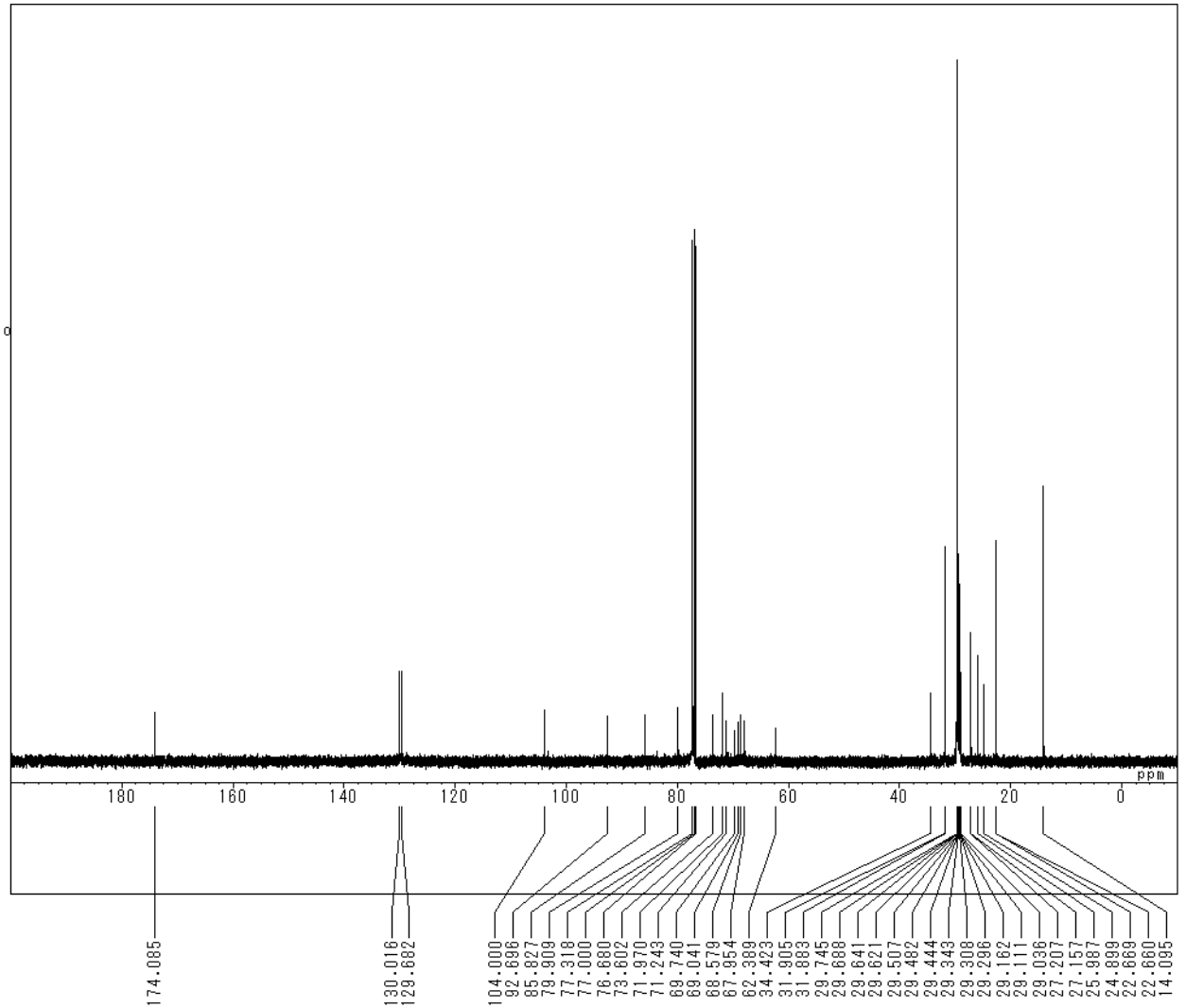
```
Comment     KF-Ole-boron-deprotectio
    n_20150915_01
Date          2015/Sep/15
ObsNuc                1H
ExMode         PROTON_001
ObsFreq         399.45 MHz
Scan                   8
AcqTime            2.569 s
Acc. Interval      5.569 s
Spinning          16.0 Hz
Temperature        3.0 ℃
Solvent           cdcl3
```

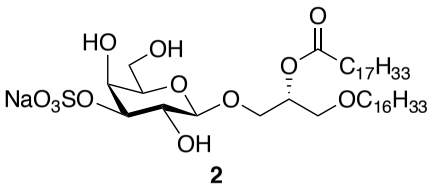




18

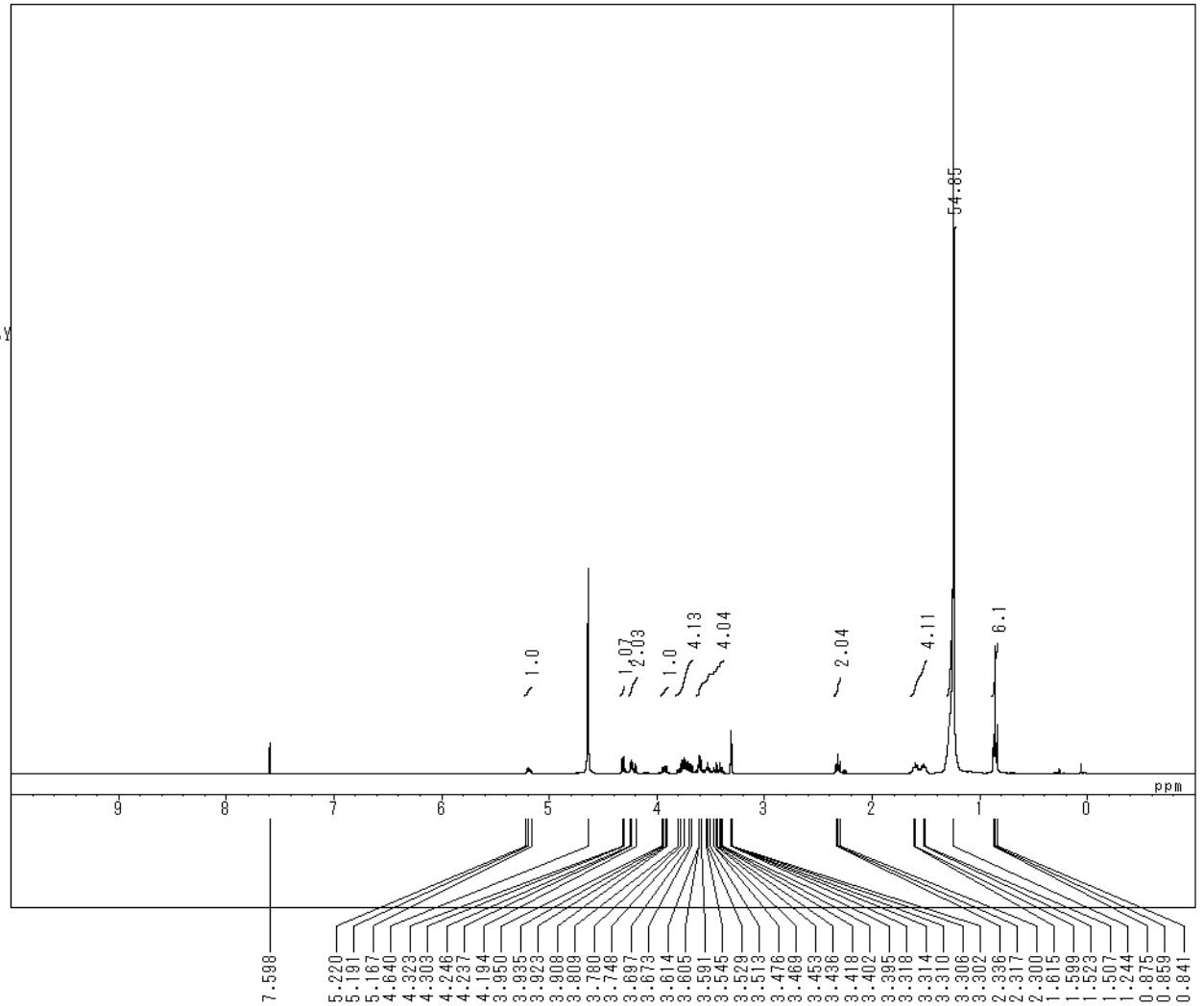
```
Comment    KF-Ole-boron-deprotectio
    n-C_20150915_01
Date          2015/Sep/15
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 1024
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature         3.0 ℃
Solvent            cdcl3
```

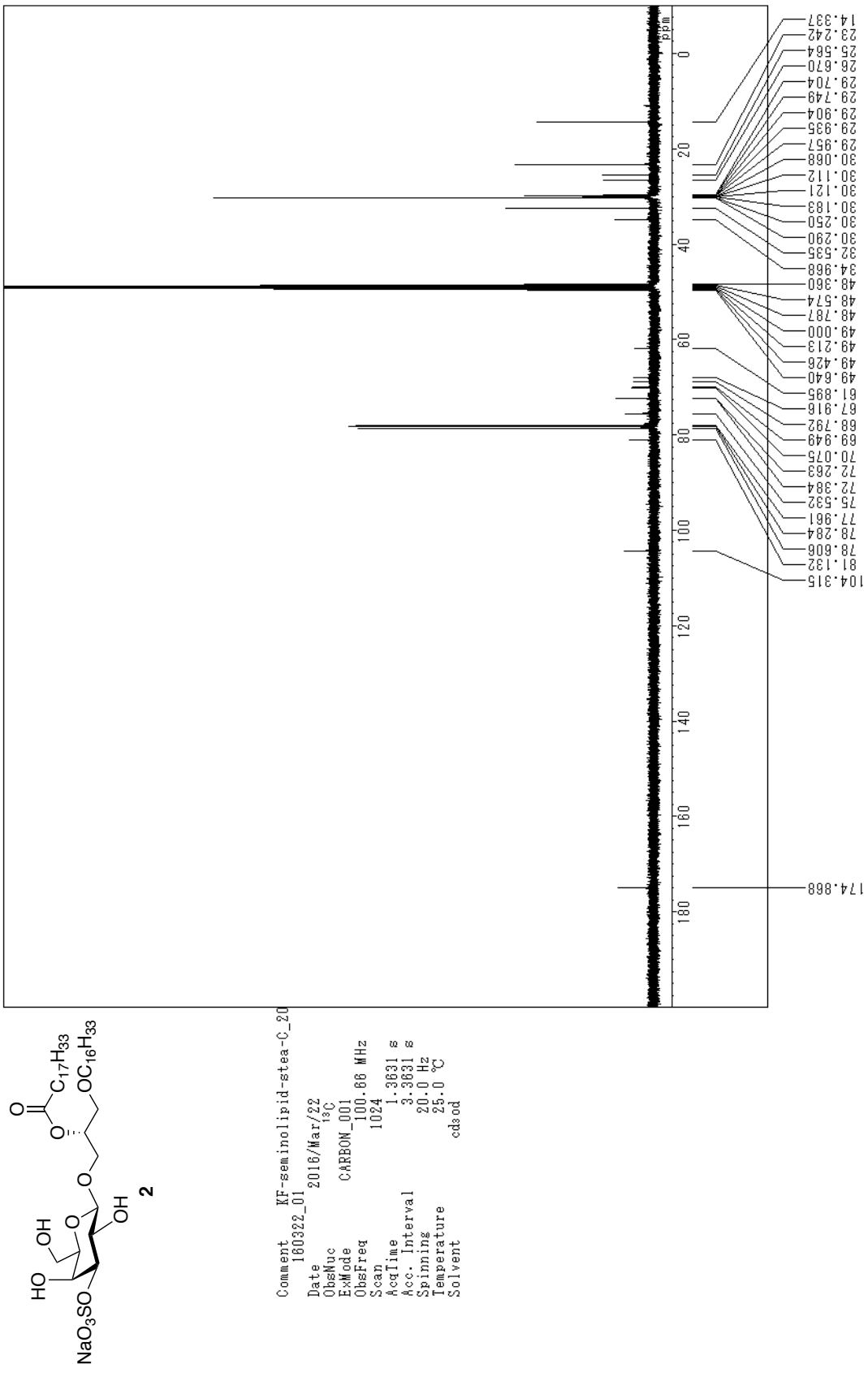


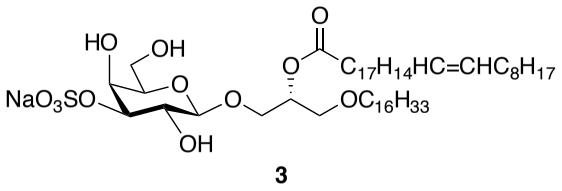


2

Comment KF-seminolipid-stea-COSY_20160322_01
Date 2016/Mar/22
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 8
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdsod

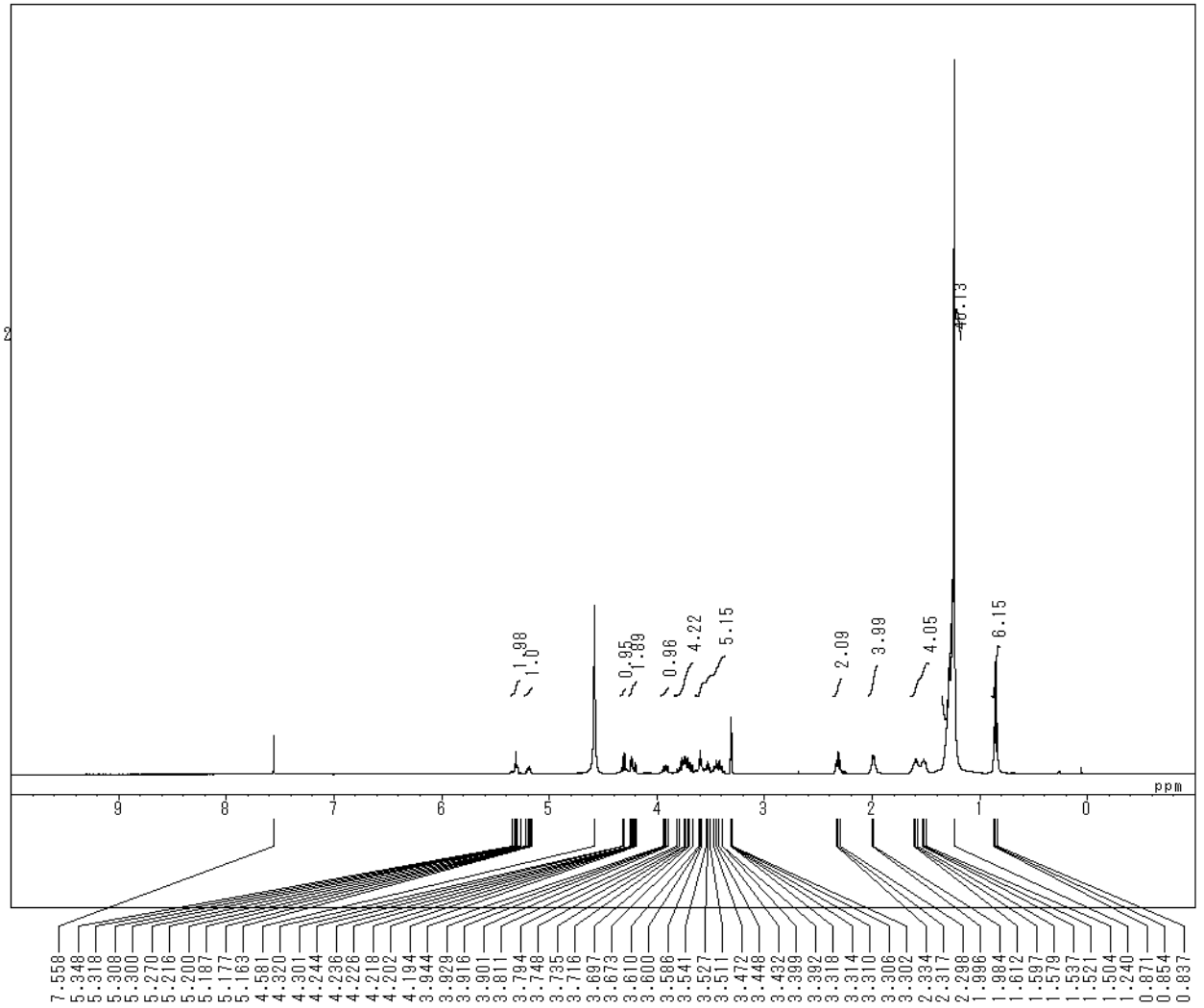


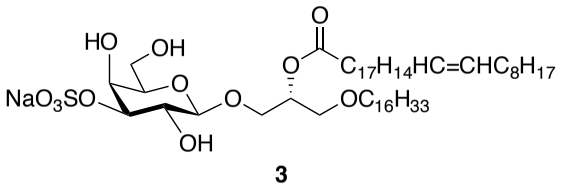

NaO3SO
HO
OH
O
OH
O
O
C17H33
OC16H33
2
Comment KF-seminolipid-stea-C_20
160322_01
Date 2016/Mar/22
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 1024
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cd3od
ppm
0
20
40
60
80
100
120
140
160
180
14.337
23.242
25.564
26.670
29.704
29.749
29.904
29.935
29.957
30.088
30.112
30.121
30.183
30.250
30.290
32.535
34.968
48.360
48.574
48.787
49.000
49.213
49.426
49.640
61.895
67.916
68.792
69.949
70.075
72.263
72.384
75.532
77.961
78.284
78.606
81.132
104.315
174.868



3

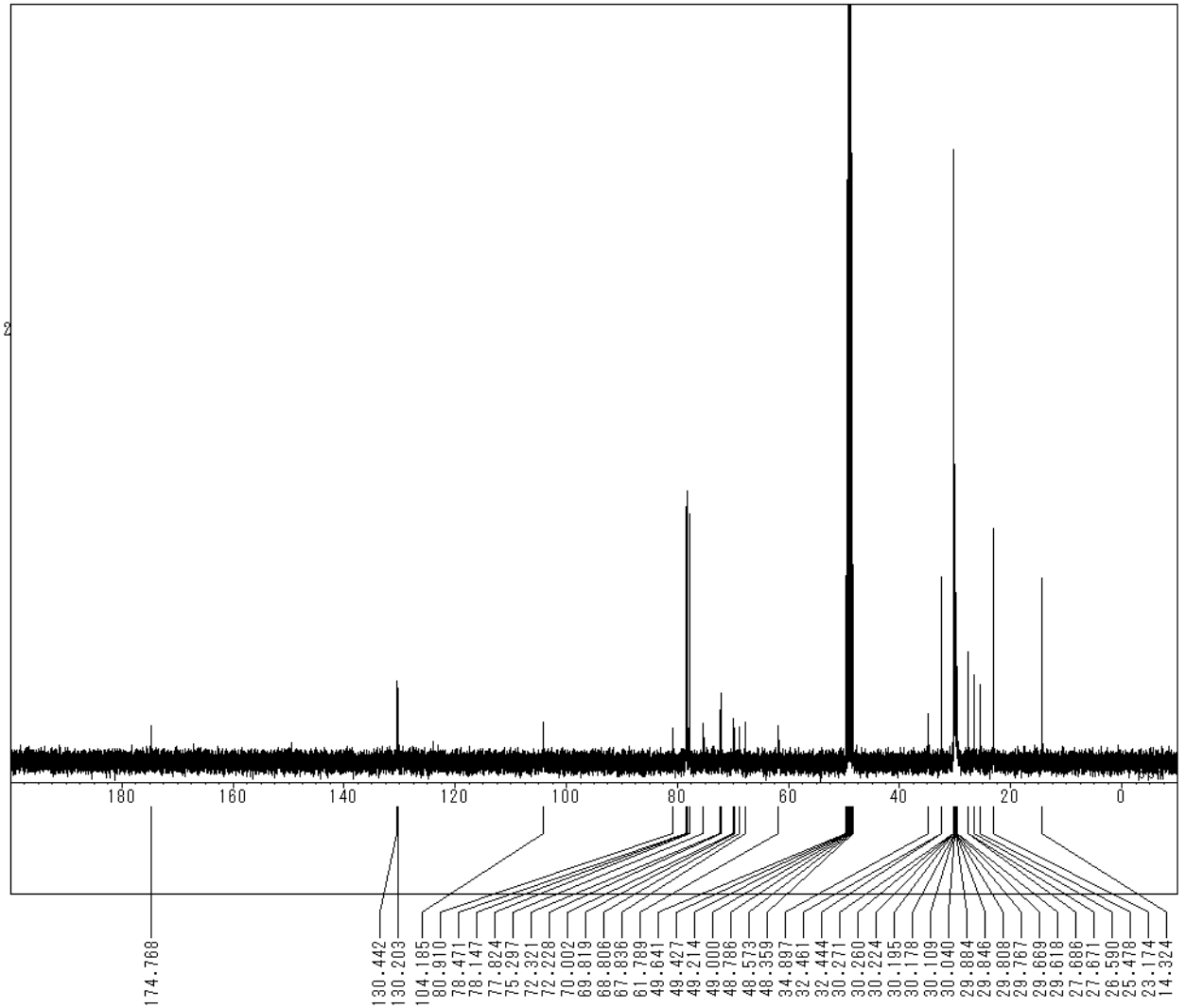
Comment	KF-semino-ole-H_20160612_01
Date	2016/Jun/12
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdsod

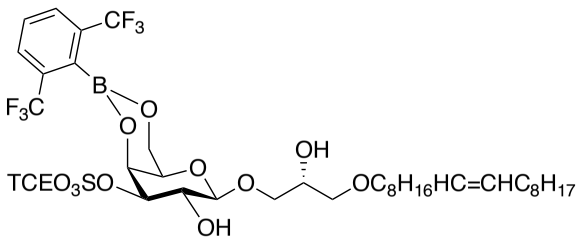




3

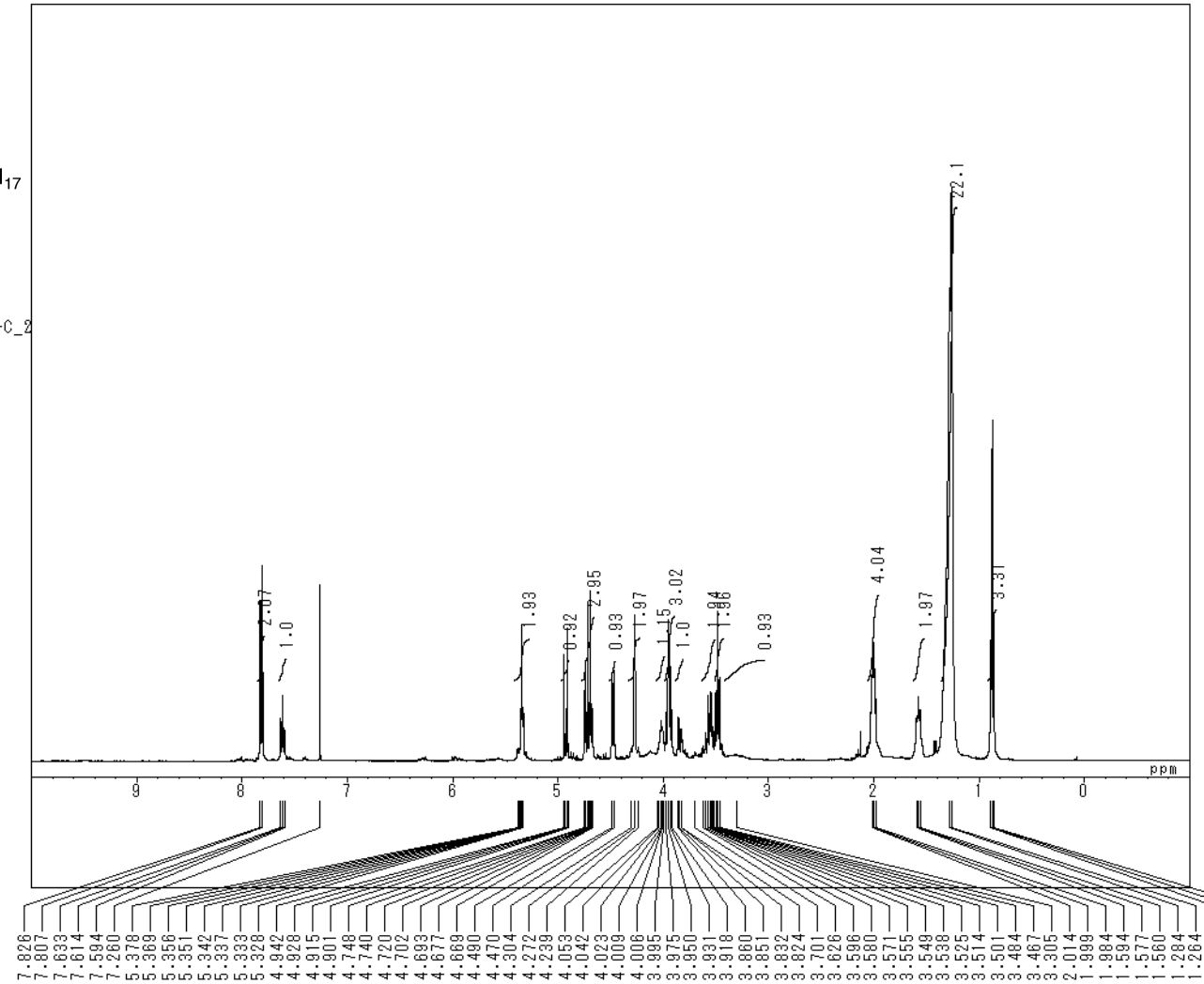
Comment KF-semino-ole-C_20160612_01
Date 2016/Jun/12
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 256
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdsod

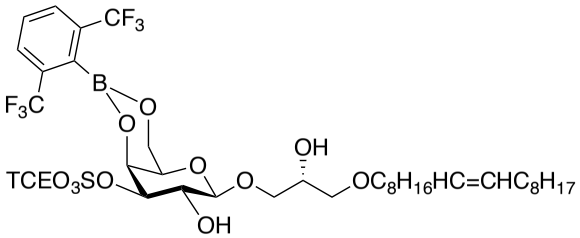




19

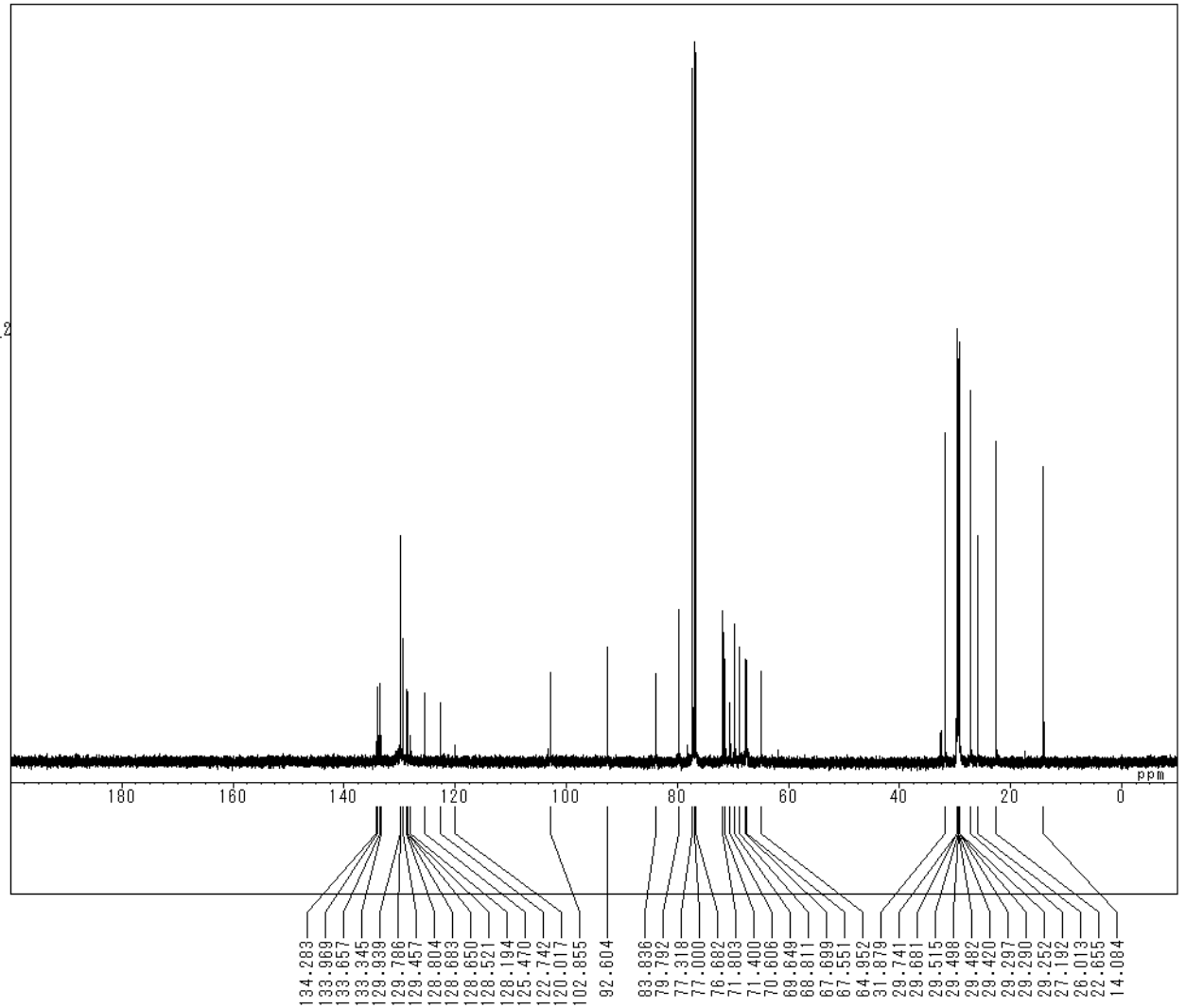
Comment KF-TCE-oleyl-alcohol-C_2
0160221_01
Date 2016/Feb/21
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 8
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

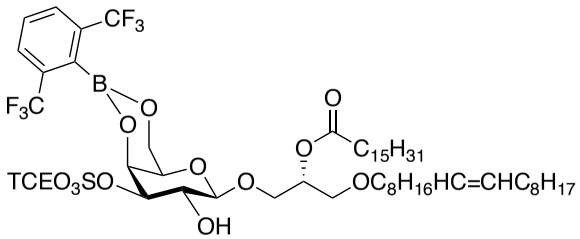




19

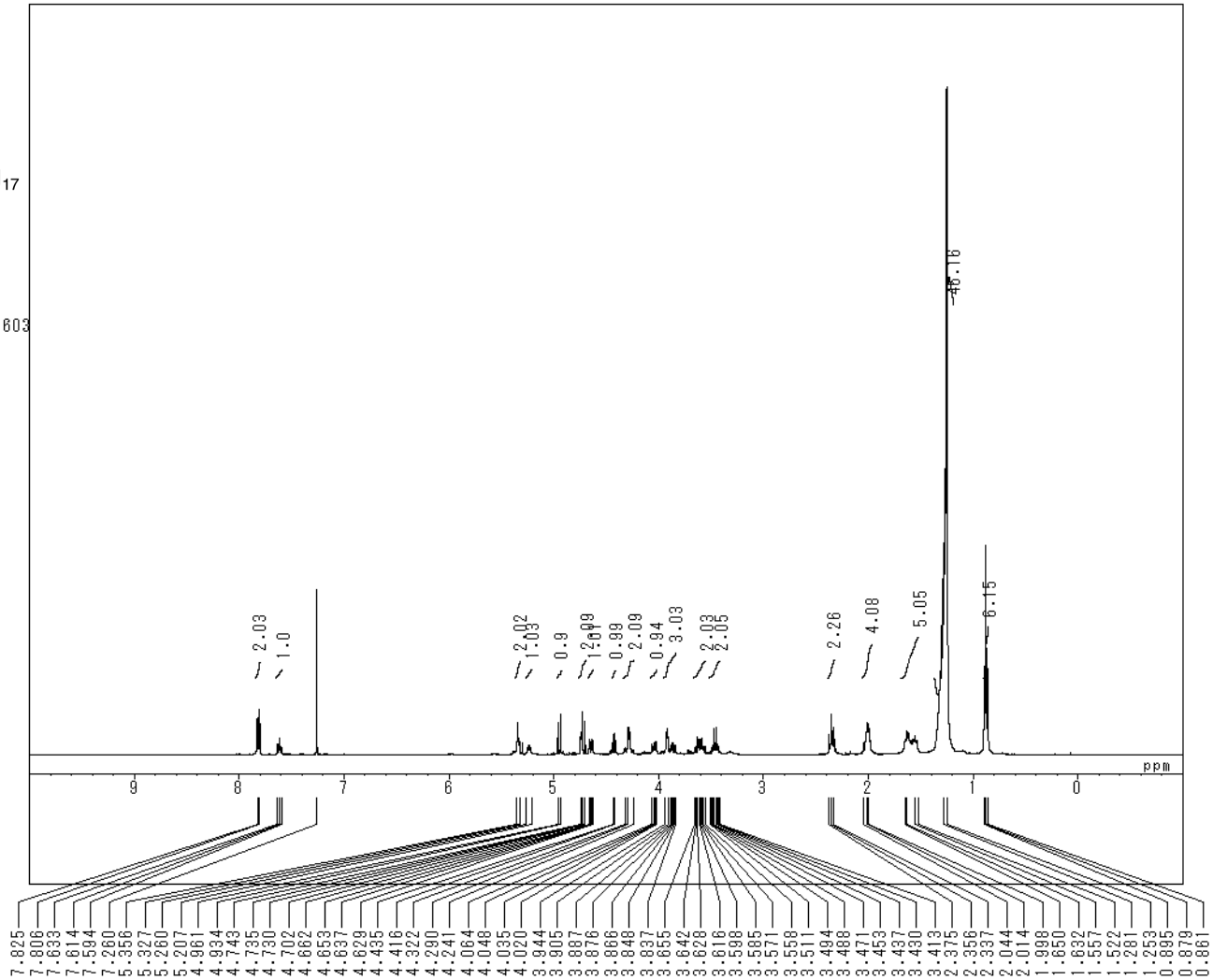
Comment KF-TCE-oleyl-alcohol-C_2
0160221_01
Date 2016/Feb/21
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 2048
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

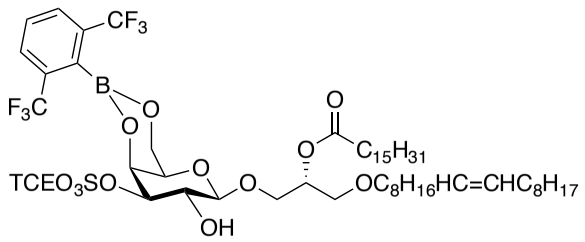




20

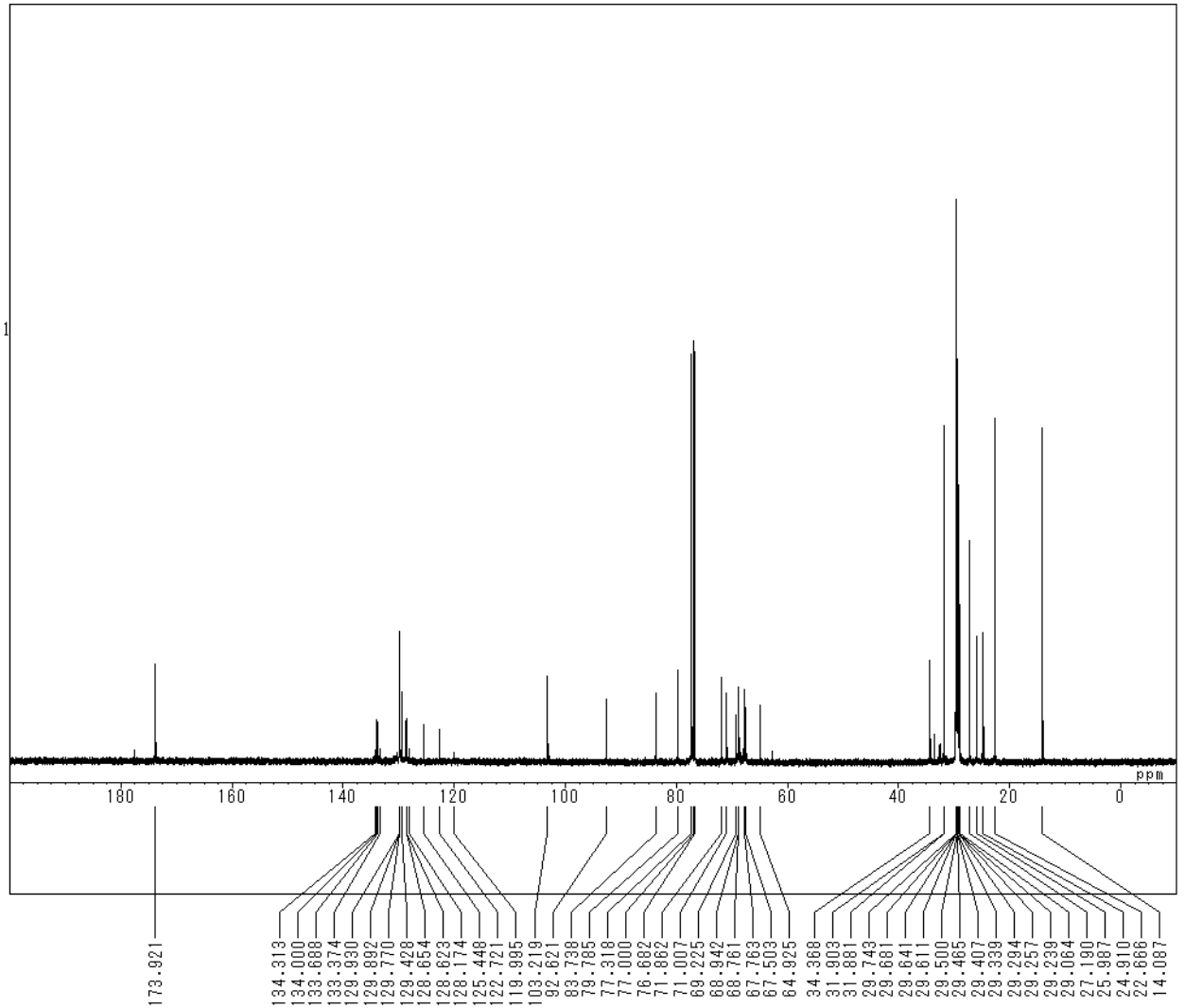
Comment KF-oleal-pal-COSY_20160302_01
Date 2016/Mar/02
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 4
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

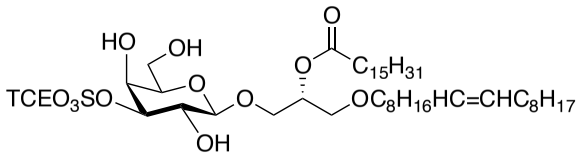




20

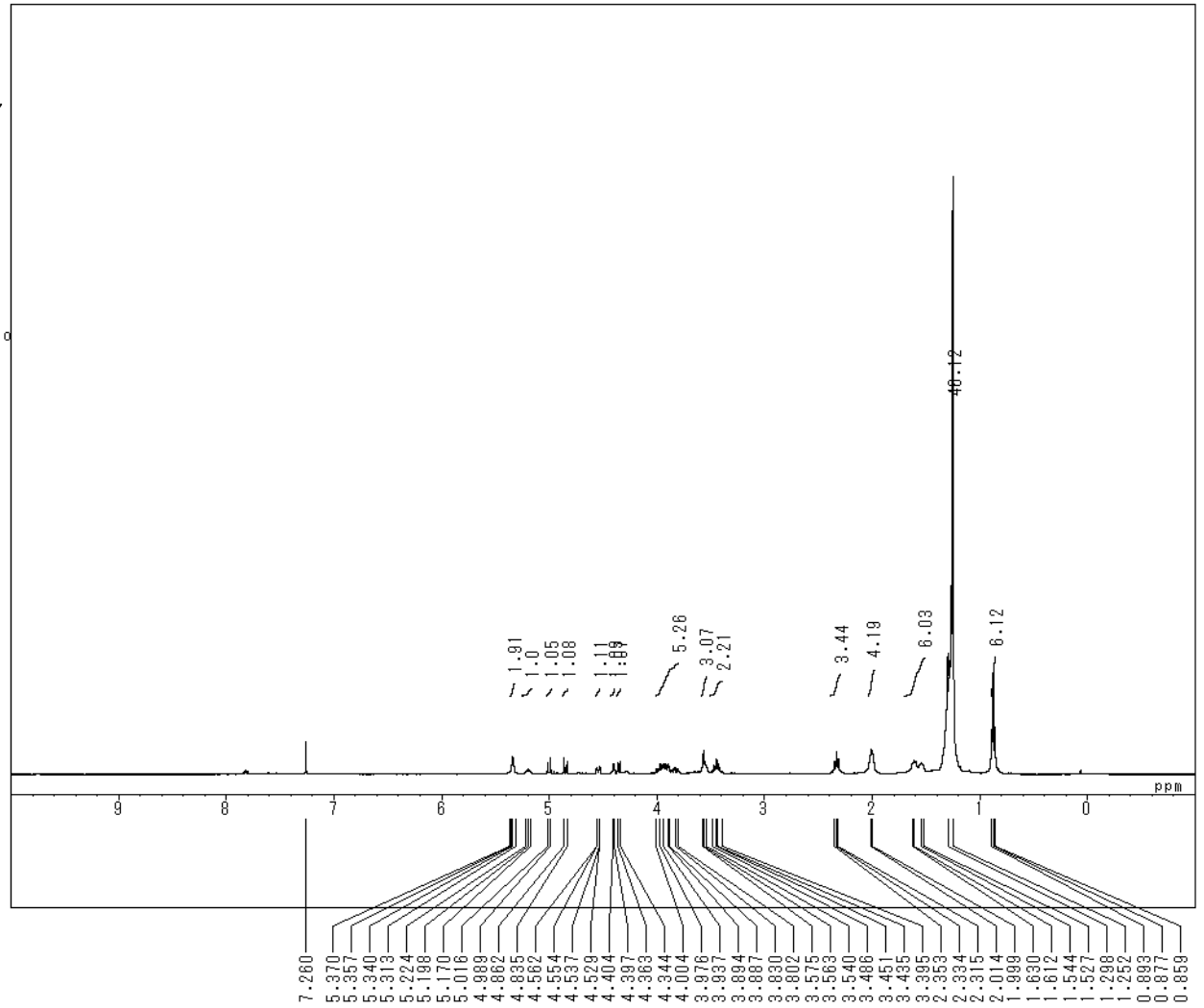
```
Comment    KF-oleal-pal-boron-C_201
    60229_01
Date          2016/Feb/29
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                 2048
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature        25.0 ℃
Solvent            cdcl3
```

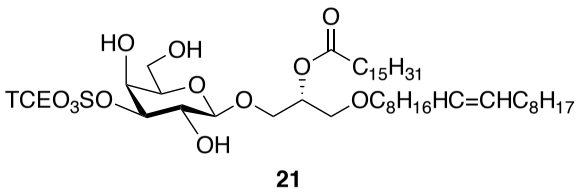




21

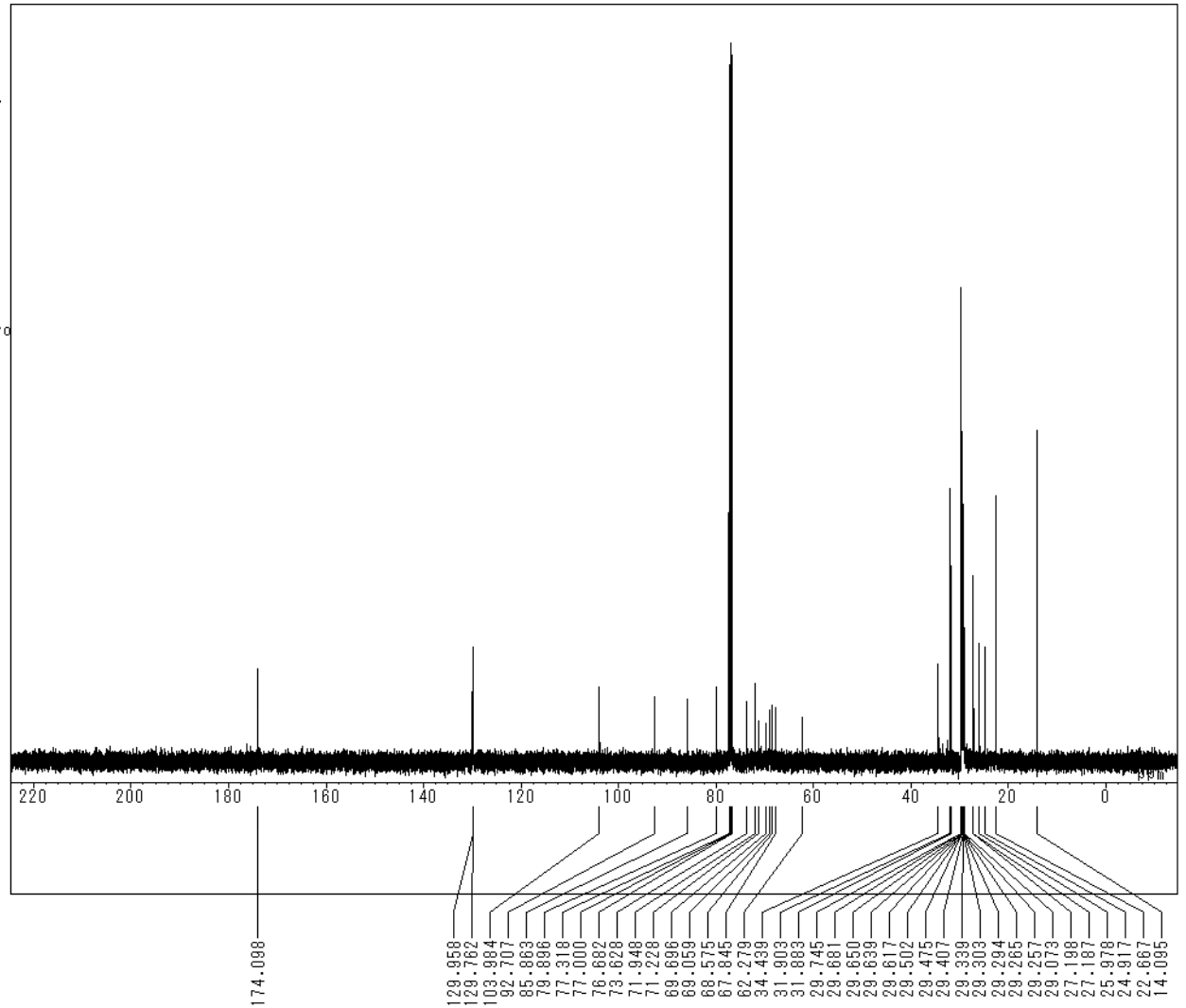
Comment KF-Ole-boron-deprotection_20150915_01
Date 2015/Sep/15
ObsNuc ^1H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 8
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 3.0 ℃
Solvent cdcl3

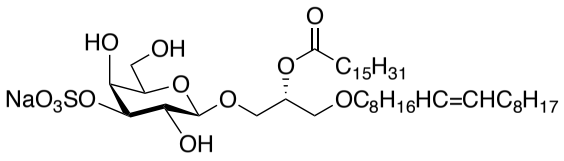




21

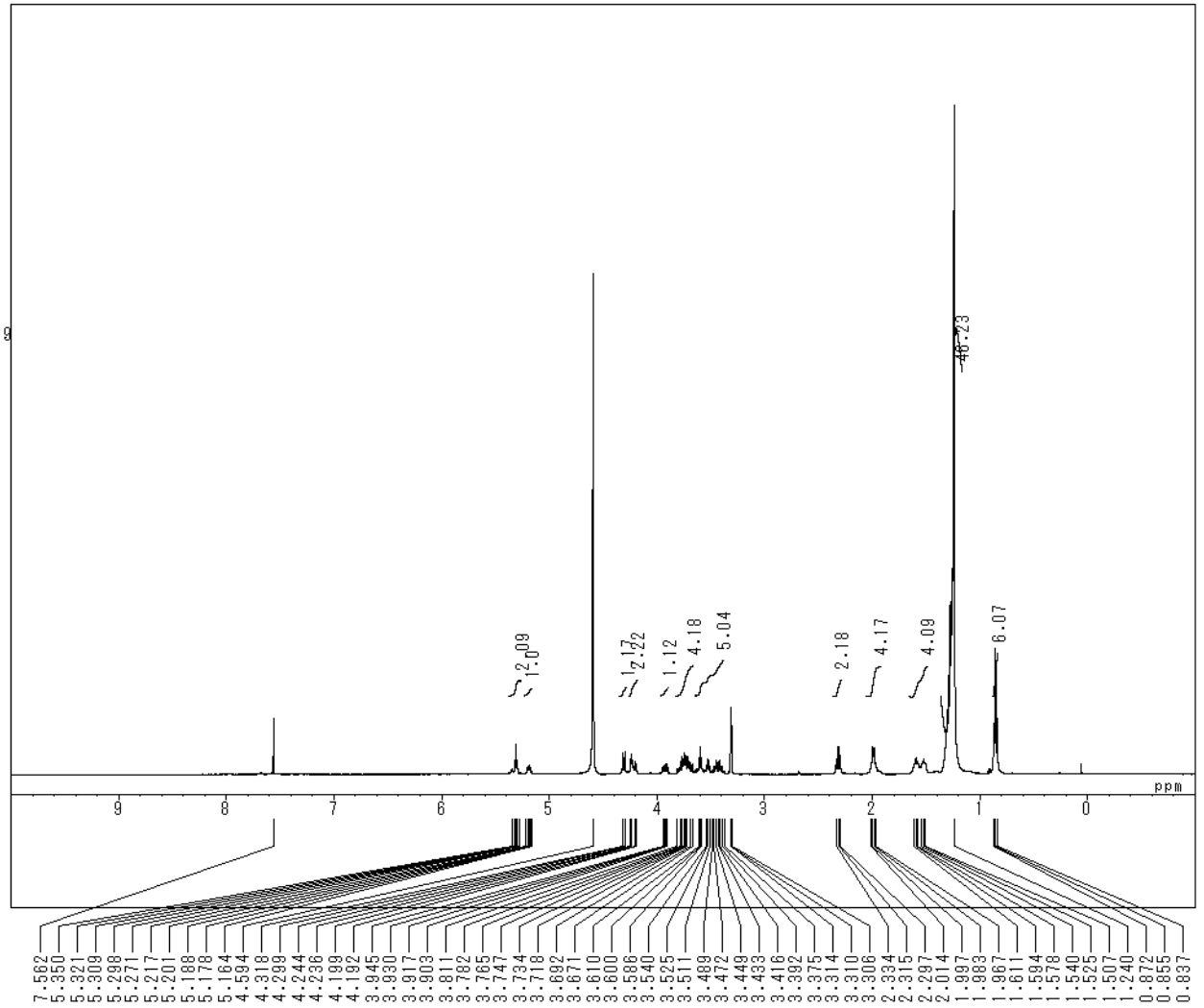
```
Comment    KF-oleal-pal-boron-depro
    tection-C_20160307_01
Date          2016/Mar/07
ObsNuc                13C
ExMode         CARBON_001
ObsFreq          100.45 MHz
Scan                  512
AcqTime             1.3631 s
Acc. Interval       3.3631 s
Spinning           20.0 Hz
Temperature        25.0 ℃
Solvent            cdcl3
```

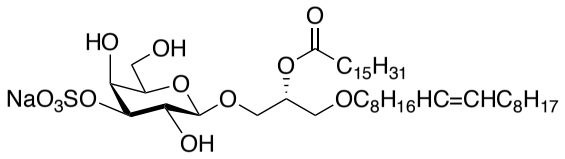




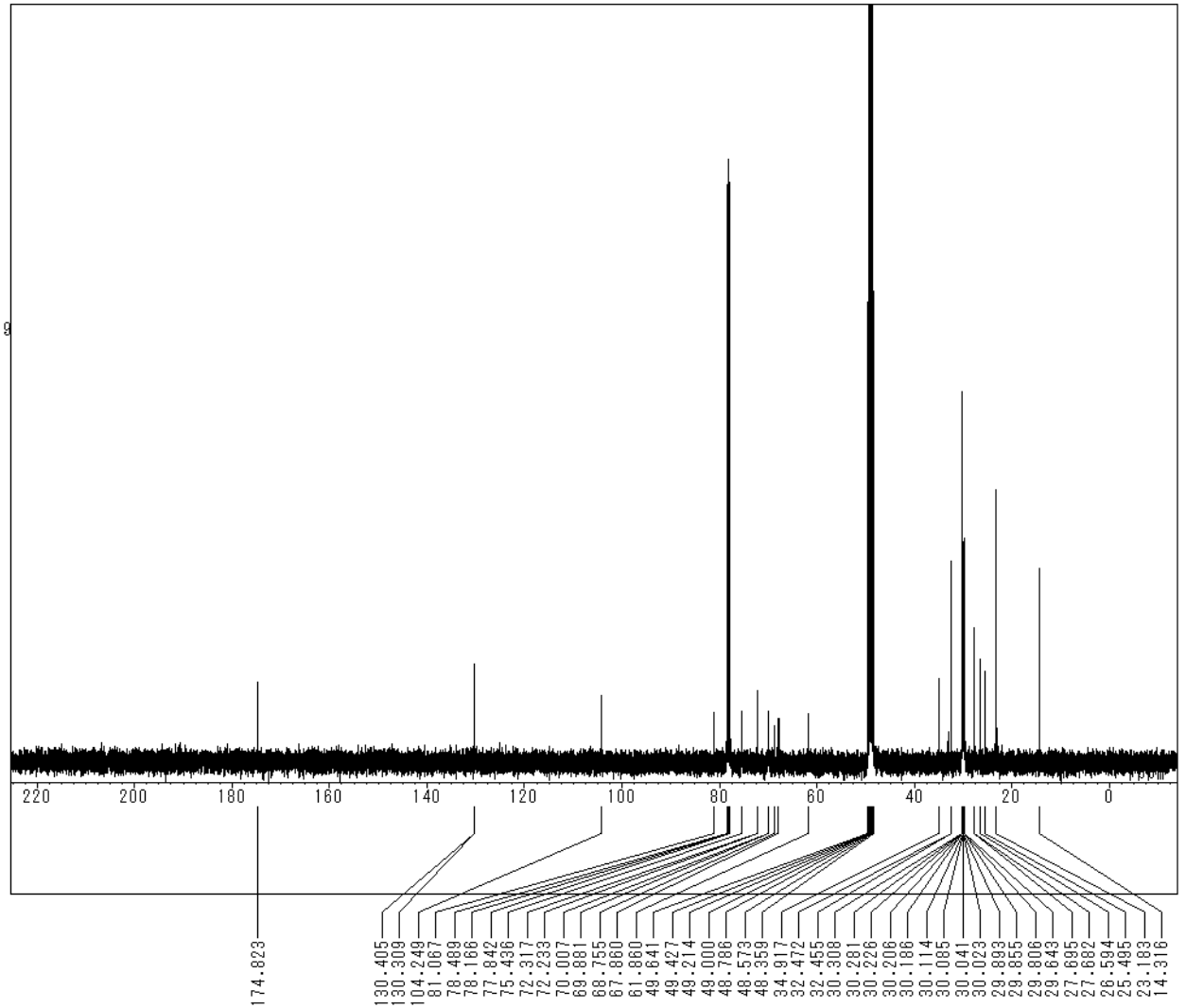
4

Comment	KF-oleal-pal-Na_20160619_01
Date	2016/Jun/19
ObsNuc	^1H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdsod





4



Comment KF-oleal-pal-Na_20160619_01
Date 2016/Jun/19
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 1024
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdsod

References

(1) A. L. Yuya, M. C. Justin and G. D. Benjamin, *J. Am. Chem. Soc.* 2010, **132**, 16805–16811.

(2) (a) I. Ohtani, T. Kusumi, Y. Kashaman and H. Kakisawa, *J. Am. Chem. Soc.* 1991, **113**, 16805–16811; (b) T. R. Hoye, C. S. Jeffrey and F. Shao, *Nat*. *Protoc*. 2007, **2**, 2451–2458.