Supporting Information

2,6-Bis(trifluoromethyl)phenylboronic Esters as Protective Groups for Diols: A Protection/Deprotection Protocol for Use under Mild Conditions

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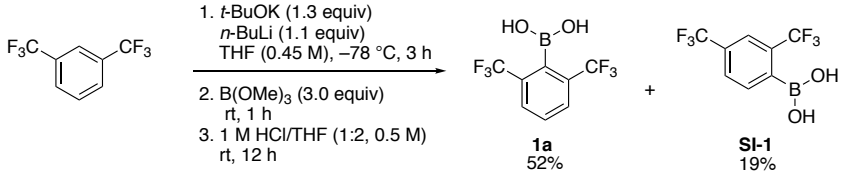
1. General information

NMR spectra were recorded on Agilent Technologies 400-MR DD2 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 377 MHz for ^{19}F), 400-MR (400 MHz for ^{1}H, 100 MHz for ^{13}C, 377 MHz for ^{19}F), NMR DD2 400NB (128 MHz for ^{11}B) spectrometers. ^{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, dt = 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). ^{19}F-NMR chemical shifts are reported in ppm downfield or upfield from C_6H_5F (δ –113.15). ^{11}B-NMR chemical shifts are reported in ppm downfield or upfield from $PhB(OH)_2$ (δ 28.82). Mass spectra were measured with JEOL JMS-AX505HA, JMS-700 MStation, and JEOL JMS-T100LP spectrometers. Melting points (mp) were obtained on Stanford Research Systems MPA100 melting point apparatus. 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 an argon atmosphere using oven-dried glassware. Alcohol **2a**, **2b**, **2f**, **2g**, **2h**, **2i**, **2j**, and **16** were purchased from commercial suppliers and used without further purification. Alcohol **2k**[1] and triyne **19**[2] were synthesized according to the literature.

2. Preparation of 2,6-bis(trifluoromethyl)phenylboronic acid (*o*-FXylB(OH)$_2$, 1a) [3]



To a solution of *t*-BuOK (947 mg, 8.44 mmol, 1.3 equiv)[4] and 1,3-bis(trifluoromethyl)benzene (1.39 g, 6.49 mmol, 1.0 equiv) in THF (14 mL, 0.45 M) at –78 °C was added dropwise a solution of *n*-BuLi in *n*-hexane (1.6 M in *n*-hexane, 4.46 mL, 7.14 mmol, 1.1 equiv). After stirring for 3 h, trimethyl borate (2.18 mL, 19.5 mmol, 3.0 equiv) was added at –78 °C and the mixture was stirred for 1 h at room temperature. The reaction was quenched by adding 1 M aqueous HCl/THF (15 mL, 1 M aqueous HCl : THF = 1 : 2). After stirring 12 h at room temperature, the resulting mixture was extracted with EtOAc (2 x 30 mL). The combined organic layer was washed successively with H_2O (30 mL) and brine (30 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

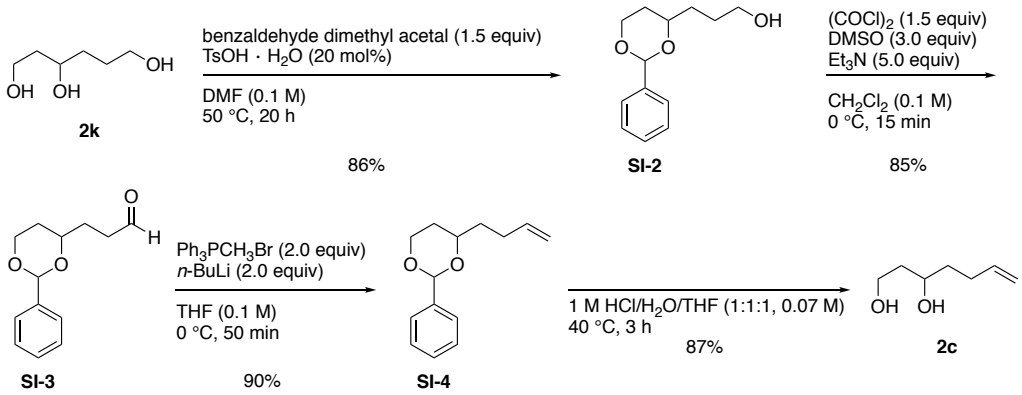
(*n*-hexane : EtOAc = 4 : 1) to give **1a** (881 mg, 3.44 mmol, 52% yield) as a yellow solid and **SI-1** (316 mg, 1.23 mmol, 19% yield) as a yellow solid.

Data for **1a**: R_f 0.34 (4/1 *n*-hexane/EtOAc); mp 171-172 °C; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.90 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 134.4 (q, $^2J_{C\text{-}F}$ = 31.1 Hz), 130.2, 129.9 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 125.7 (q, $^1J_{C\text{-}F}$ = 271.9 Hz); ^{19}F-NMR (377 MHz, $CDCl_3$) δ –8.41; ^{11}B-NMR (128 MHz, $CDCl_3$) δ 29.73; ^{11}B-NMR (128 MHz, CD_3OD/D_2O = 9:1) δ 29.29; IR (KBr) ν = 3346, 1582, 1476, 1350, 1302, 1209, 1186, 1110, 1065, 1010, 839 cm^{-1}; HRMS (EI) m/z Calcd for $C_8H_5{}^{11}BF_6O_2$ $[M]^+$ 258.0287, found 258.028.

Data for **SI-1**: R_f 0.13 (4/1 *n*-hexane/EtOAc); mp 109-110 °C;^{1}H-NMR (400 MHz, CD_3OD) δ 7.95 (s, 1H), 7.91 (d, J = 15.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD) δ 143.1, 141.0 (q, J = 31.3 Hz), 138.6 (q, J = 32.7 Hz), 137.3 (q, J = 3.5 Hz), 133.5 (q, J = 271.9 Hz), 133.1 (q, J = 270.4 Hz), 131.0 (m); ^{19}F-NMR (377 MHz, $CDCl_3$) δ –60.40, –62.38; IR (KBr) ν = 3358, 1344, 1121,849 cm^{-1}; HRMS (EI) m/z Calcd for $C_8H_5{}^{11}BF_6O_2$ $[M]^+$ 258.0287, found 258.028.

3. Preparations of 1,3-diols 2c, 2d, and 2e

Preparation of hept-6-ene-1,3-diol (2c)



To a stirred solution of **2k**[1] (126 mg, 0.940 mmol) and benzaldehyde dimethyl acetal (0.200 mL, 1.41 mmol, 1.5 equiv) in DMF (10 mL, 0.094 M) at room temperature was added *p*-toluenesulfonic acid monohydrate (35.8 mg, 0.188 mmol, 20 mol%). After stirring for 20 h at 50 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc/hexane (4:1, 2 x 10 mL). The combined organic extract was washed with H_2O (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 (*n*-hexane : EtOAc = 3 : 2) to give **SI-2** (181 mg, 0.813 mmol, 86% yield) as a colorless oil.

Data for **SI-2**: R_f= 0.29 (1/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ7.50-7.47 (m, 2H), 7.39-7.30 (m, 3H), 5.52 (s, 1H), 4.28 (ddd, J = 11.6, 5.2, 1.2 Hz, 1H), 3.97 (ddd, J = 12.0, 11.6, 2.4 Hz, 1H), 3.92-3.86 (m, 1H), 3.69-3.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 128.7, 128.2, 126.0, 101.2, 77.2, 67.0, 62.7, 32.5, 31.2, 28.5; IR (neat) ν = 3402, 2923, 2863, 1027 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{13}H_{18}O_3Na$ $[M+Na]^+$ 245.1154, found 245.1156.

To a stirred solution of oxalyl chloride (386 μL, 4.53 mmol, 1.5 equiv) in CH_2Cl_2 (20 mL) at –78 °C was dropwise added DMSO (544 μL, 9.05 mmol, 3.0 equiv) over 5 min. The mixture was stirred for 10 min at –78 °C and a solution of **SI-2** (670 mg, 3.02 mmol) in CH_2Cl_2 (20 mL) was added dropwise. After stirring for 20 min, Et_3N (2.10 mL, 15.1 mmol, 5.0 equiv) was added dropwise at –78 °C. After the mixture was stirred at 0 °C for 15 min, the reaction was quenched by adding saturated aqueous NH_4Cl (30 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layer was washed with brine (40 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 (*n*-hexane : EtOAc = 2 : 1) to give **SI-3** (563 mg, 2.56 mmol, 85% yield) as a colorless oil.

Data for **SI-3**: R_f = 0.30 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.39-7.31 (m, 3H), 5.49 (s, 1H), 4.27 (ddd, *J* = 11.6, 5.2, 1.2 Hz, 1H), 3.95 (ddd, *J* = 12.4, 11.6, 2.4 Hz, 1H), 3.91-3.84 (m, 1H), 2.71-2.58 (m, 2H), 2.01-1.79 (m, 3H), 1.58-1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ202.12, 202.09, 138.54, 138.53, 128.71, 128.70, 128.19, 128.18, 125.9, 101.1, 76.0, 66.8, 39.6, 31.2, 31.2, 28.3; IR (neat) ν = 2925, 2853, 1723, 1364, 1105 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ 243.1000, found 243.1000.

To a solution of methyltriphenylphosphonium bromide (1.82 g, 0.200 mmol, 2.0 equiv) in THF (15 mL) at 0 °C was added dropwise a solution of *n*-BuLi in hexane (1.6 M in hexane, 3.18 mL, 5.09 mmol, 2.0 equiv). After stirring for 20 min at 0 °C, a solution of **SI-3** (560 mg, 2.54 mmol) in THF (10 mL) was added dropwise to the mixture. After stirring for 50 min at 0 °C, the reaction mixture was diluted with Et_2O (2.0 mL). The resulting mixture was filtered through a Celite pad and rinsed with Et_2O (100 mL). Concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 2 : 1) to give **SI-4** (500 mg, 2.29 mmol, 90% yield) as a colorless oil.

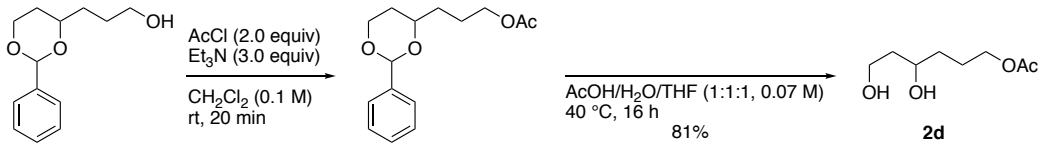
Data for **SI-4**: R_f= 0.38 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.39-7.31 (m, 3H), 5.85 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.51 (s, 1H), 5.05 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.97-5.01 (m, 1H), 4.27 (ddd, *J* = 11.6, 5.2, 1.2 Hz, 1H), 3.96 (ddd, *J* = 12.4, 11.6, 2.8 Hz, 1H), 3.89-3.82 (m, 1H), 2.32-2.15 (m, 2H), 1.88-1.75 (m, 2H), 1.67-1.58 (m, 1H), 1.58-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.2, 128.6, 128.2, 126.0, 114.8, 101.1, 76.4, 67.0, 35.0, 31.3, 29.1; IR (neat) ν = 2925, 2852, 1364, 1105 cm^{-1}; HRMS (FAB) m/z Calcd for $C_{14}H_{19}O_2$ $[M+H]^+$ 219.2385, found 219.1396.

A solution of **SI-4** (500 mg, 2.29 mmol) in 0.5 M aqueous HCl and THF (30 mL, 0.076 M, 0.5 M aqueous HCl : THF = 2 : 1) was stirred for 3 h at 40 °C. The reaction mixture was extracted with $CHCl_3$, (6 x 20 mL). The combined organic layer was dried over Na_2SO_4. Filtration and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (EtOAc) to give **2c** (258 mg, 1.98 mmol, 87% yield) as a colorless oil.

Data for **2c**: R_f = 0.15 (2/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.05 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.00-4.96 (m, 1H), 3.92-3.08 (m, 3H), 2.52 (br,

2H), 2.25-2.01 (m, 2H), 1.76-1.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 145.0, 71.8, 61.8, 38.3, 36.7, 29.9; IR (neat) ν = 3343, 2937, 1058 cm^{-1}; HRMS (ESI) m/z Calcd for $C_7H_{15}O_2$ $[M+H]^+$ 131.1072, found 131.1080.

Preparation of 4,6-dihydroxyhexyl acetate (2d)



SI-2 92% **SI-5** 81% **2d**

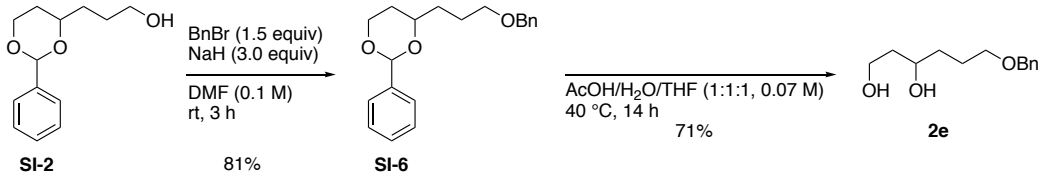
To a stirred solution of **SI-2** (111 mg, 0.500 mmol) and triethyl amine (209 μL, 1.50 mmol, 3.0 equiv) in CH_2Cl_2 (5.0 mL, 0.10 M) at room temperature was added acetyl chloride (71.4 μL, 1.00 mmol, 2.0 equiv). After stirring for 20 min, the reaction was quenched by adding 1 M aqueous HCl (5.0 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with brine (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 (*n*-hexane : EtOAc = 5 : 1) to give **SI-5** (121 mg, 0.458 mmol, 92% yield) as a colorless oil.

Data for **SI-5**: R_f = 0.18 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57-7.47 (m, 2H), 7.38-7.30 (m, 3H), 5.51 (s, 1H), 4.27 (ddd, *J* = 11.4, 5.0, 1.3 Hz, 1H), 4.16-4.06 (m, 2H) 3.96 (ddd, *J* = 12.3, 11.4, 2.6 Hz, 1H), 3.89-3.83 (m, 1H), 2.05 (s, 3H), 1.93-1.50 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.1, 138.7, 128.6, 128.2, 126.0, 101.1, 76.6, 66.9, 64.3, 32.3, 31.3, 24.3, 20.9; IR (neat) ν = 2956, 2853, 1738, 1243, 1108 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{15}H_{20}O_4Na$ $[M+Na]^+$287.1259, found 287.1256.

A solution of **SI-5** (121 mg, 0.458 mmol) in AcOH, H_2O and THF (6.5 mL, 0.070 M, AcOH : H_2O : THF = 1 : 1 : 1) was stirred for 16 h at 40 °C. The reaction mixture was extracted with $CHCl_3$, (4 x 10 mL). The combined organic layer was washed with brine (40 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 ($CHCl_3$: MeOH = 19:1) to give **2d** (65.6 mg, 0.373 mmol, 81% yield) as a colorless oil.

Data for **2d**: R_f = 0.15 (1/2 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.09 (t, *J* = 6.8 Hz, 2H), 3.92-3.79 (m, 3H), 2.87 (br, 1H), 2.60 (br, 1H), 2.04 (s, 3H), 1.84-1.64 (m, 4H), 1.57-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 71.1, 64.4, 61.3, 38.3, 33.8, 24.7, 20.9; IR (neat) ν = 3384, 2940, 1732, 1254, 1050 cm^{-1}; HRMS (EI) m/z Calcd for $C_8H_{17}O_4$ $[M+H]^+$ 177.1127, found 177.1122.

Preparation of 6-(benzyloxy)hexane-1,3-diol (2e)



SI-2 81% **SI-6** **2e**

To a suspension of sodium hydride (44.4 mg, 1.85 mmol, 3.0 equiv) in DMF (2.2 mL) at 0 °C was added dropwise a solution of **SI-2** (137 mg, 0.617 mmol) in DMF (2.0 mL) and the mixture was strried for 10 min at room temperature. Benzyl bromide (110 μL, 0.926 mmol, 1.5 equiv) was added dropwise at 0 °C and the mixture was sirred for 3 h. The reaction was quenched by adding saturated aqueous NH_4Cl (10 mL). The resulting mixture was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (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 (*n*-hexane : EtOAc = 9 : 1) to give **SI-6** (156 mg, 0.500 mmol, 81% yield) as a colorless oil.

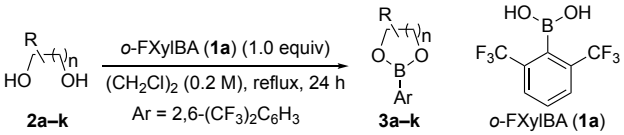
Data for **SI-6**: R_f= 0.28 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.38-7.26 (m, 8H), 5.49 (s, 1H), 4.51 (s, 2H), 4.26 (ddd, *J* = 11.6, 5.2, 1.2 Hz, 1H), 3.95 (ddd, *J* = 12.4, 11.6, 2.4 Hz, 1H), 3.87-3.81 (m, 1H), 3.57-3.47 (m, 2H), 1.90-1.64 (m, 5H), 1.55-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 128.6, 128.3, 128.2, 127.6, 127.5, 126.0, 101.1, 77.0, 72.9, 70.2, 67.1, 32.7, 31.3, 25.3; IR (neat) ν = 3032, 2950, 2853, 1364, 1107 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{20}H_{24}O_3Na$ $[M+Na]^+$ 335.1623, found 335.1610.

A solution of **SI-6** (156 mg, 0.500 mmol) in AcOH / H_2O / THF (7.0 mL, 0.071 M, AcOH : H_2O : THF = 1 : 1 : 1) was stirred for 14 h at 40 °C. The reaction mixture was extracted with $CHCl_3$, (5 x 10 mL). The combined organic layer was washed with brine (40 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 (EtOAc) to give **2e** (80.0 mg, 0.357 mmol, 71% yield) as a colorless oil.

Data for **2e**: R_f = 0.13 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.09 (t, *J* = 6.8 Hz, 2H), 3.92-3.79 (m, 3H), 2.87 (br, 1H), 2.60 (br, 1H), 2.04 (s, 3H), 1.84-1.64 (m, 4H), 1.57-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 71.1, 64.4, 61.3, 38.3, 33.8, 24.7, 20.9; IR (neat) ν = 3372, 2942, 2865, 1278, 1099 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{13}H_{20}O_3Na$ $[M+Na]^+$ 247.1310, found 247.1311.

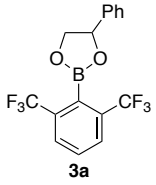
4. General procedure for the formations of boronic esters and characterization data for compounds 3a–k

General procedure for the formation of boronic esters from diols



To a solution of diols **2a-k** (0.200 mmol, 1.0 equiv) in $ClCH_2CH_2Cl$ (1.0 mL, 0.20 M) was added 2,6-bis(trifluoromethyl)phenylboronic acid (**1a**) (0.200 mmol, 1.0 equiv). After stirring for 24 h at reflux, the reaction mixture was concentrated under reduced pressure to give the crude boronic ester, which was purified by silica gel column chromatography.

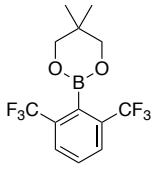
2-(2,6-Bis(trifluoromethyl)phenyl)-4-phenyl-1,3,2-dioxaborolane (3a)



3a

80% yield, Data for **3a**; yellow oil; R_f 0.34 (20/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 8.0 Hz, 1H), 7.43-7.34 (m, 5H), 5.66 (t, J = 8.8 Hz, 1H), 4.80 (t, J = 8.8 Hz, 1H), 4.24 (t, J = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.5, 134.7 (q, $^2J_{C\text{-}F}$ = 31.6 Hz), 130.1, 128.8, 128.7 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 128.4, 125.9, 124.0 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 80.1, 73.9; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.79; IR (neat) ν = 3037, 2912, 1580, 1297, 1132 cm^{-1}; HRMS (FAB) m/z Calcd for $C_{16}H_{12}{}^{11}BF_6O_2$ $[M+H]^+$ 361.0835, found 361.0833.

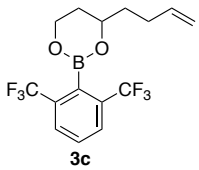
2-(2,6-Bis(trifluoromethyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (3b)



3b

80% yield, Data for **3b**: yellow solid; R_f 0.41 (20/1 *n*-hexane/EtOAc); mp 49-51 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 3.79 (s, 4H), 1.10 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.8 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 72.8, 31.8, 22.4; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.74; IR (KBr) ν = 2921, 1164 cm^{-1}; HRMS (EI) m/z Calcd for $C_{13}H_{13}{}^{11}BF_6O_2$ $[M]^+$ 326.0913, found 326.0919.

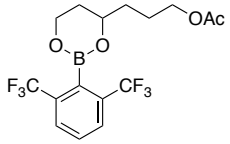
2-(2,6-Bis(trifluoromethyl)phenyl)-4-(but-3-en-1-yl)-1,3,2-dioxaborinane (3c)



3c

99% yield, Data for **3c**: yellow oil; R_f 0.51 (9/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 5.83 (ddt, J = 17.2, 10.4, 6.8 Hz, 1H), 5.04 (dq, J = 17.2, 1.6 Hz, 1H), 5.04-4.96 (m, 1H), 4.22-4.08 (m, 3H), 2.28-2.12 (m, 2H), 2.04 (dq, J = 14.0, 3.6 Hz, 1H), 1.98-1.88 (m, 1H), 1.82-1.73 (m, 1H), 1.68-1.59 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.9, 133.7 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 128.9, 128.6 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 115.0, 71.6, 61.9, 35.6, 31.6, 29.1; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.40; IR (neat) ν = 3080, 2926, 1295, 1132 cm^{-1}; HRMS (EI) m/z Calcd for $C_{15}H_{15}{}^{11}BF_6O_2$ $[M]^+$ 352.1069, found 352.1098.

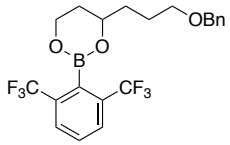
3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propyl acetate (3d)



3d

96% yield, Data for **3d**: colorless oil; R_f 0.81 (2/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0, 1H), 4.21-4.07 (m, 5H), 2.03 (s, 3H), 2.05-2.00 (m, 1H), 1.97-1.60 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 133.7 (q, J_2= 31.1 Hz), 128.9, 128.6 (q, J_3= 3.1 Hz), 124.3 (q, J_1= 272.0 Hz), 71.8, 64.2, 61.9, 33.0, 31.8, 24.2, 20.9; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; IR (neat) ν = 2960, 2923, 2891, 2850, 1740, 1577, 1487, 1433, 1368, 1344, 1296, 1243, 1199, 1177, 1132, 1089, 1069, 818 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{16}H_{17}BF_6O_4Na$ $[M+Na]^+$ 421.1022, found 421.1028.

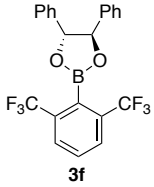
4-(3-(Benzyloxy)propyl)-2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (3e)



3e

97% yield, Data for **3e**: yellow oil; R_f 0.45 (9/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.9 Hz, 1H), 7.37-7.25 (m, 5H), 4.50 (s, 2H), 4.21-4.07 (m, 3H), 3.56-3.47 (m, 2H), 2.04 (dq, J = 14.1, 3.6 Hz, 1H), 1.97-1.88 (m, 1H), 1.86-1.68 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.6, 133.7 (q, $^2J_{C\text{-}F}$ = 31.2 Hz), 128.9, 128.5 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 128.3, 127.6, 127.5, 124.3 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 72.8, 72.1, 70.0, 61.9, 33.2, 31.7, 25.2; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; ^{11}B-NMR (128 MHz, $CDCl_3$) δ 27.94; ^{11}B-NMR (128 MHz, CD_3OD/D_2O = 9:1) δ 27.93; IR (neat) ν = 2922, 1295, 1130 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{21}H_{21}{}^{11}BF_6O_3Na$ $[M+Na]^+$ 469.1386, found 469.1375.

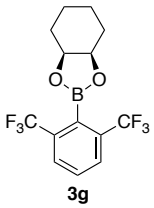
(4*R*,5*R*)-2-(2,6-Bis(trifluoromethyl)phenyl)-4,5-diphenyl-1,3,2-dioxaborolane (3f)



3f

83% yield, Data for **3f**: yellow solid; R_f 0.38 (20/1 *n*-hexane/EtOAc); mp 97-100 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 8.0 Hz, 1H), 7.45-7.35 (m, 10H), 5.40 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.4, 134.7 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 130.2, 128.8, 128.8 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 128.6, 126.2, 124.2 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 88.0; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.42; IR (KBr) ν = 3036, 2908, 1300, 1130 cm^{-1}; HRMS (EI) m/z Calcd for $C_{22}H_{15}BF_6O_2$ $[M]^+$ 436.1069, found 436.1067.

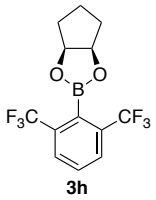
(3a*R*,7a*S*)-2-(2,6-Bis(trifluoromethyl)phenyl)hexahydrobenzo[*d*][1,3,2]dioxaborole (3g)



3g

90% yield, Data for **3g**: yellow oil; R_f 0.31 (20/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 2H), 7.63 (t, J = 7.9 Hz, 1H), 4.61-4.56 (m, 2H), 1.91-1.89 (m, 4H), 1.69-1.58 (m, 2H), 1.43-1.33 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.6 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.7, 128.6 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 76.6, 28.2, 19.7; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.79; IR (neat) ν = 3420, 2942, 1297, 1132 cm^{-1}; HRMS (EI) m/z Calcd for $C_{14}H_{13}{}^{11}BF_6O_2$ $[M]^+$ 338.0913, found 338.0919.

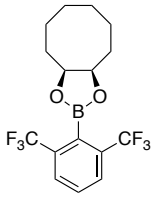
(3a*R*,6a*S*)-2-(2,6-Bis(trifluoromethyl)phenyl)tetrahydro-4*H*-cyclopenta[*d*][1,3,2]dioxaborole (3h)



3h

90% yield, Data for **3h**: yellow oil; R_f 0.44 (20/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 8.0 Hz, 1H), 5.07-5.03 (m, 2H), 2.08-2.02 (m, 2H), 1.96-1.86 (m, 1H), 1.76-1.64 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.6 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.7, 128.6, (q, $^3J_{C\text{-}F}$ = 4.3 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 84.1, 34.1, 21.7; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.84; IR (neat) ν = 2967, 1298, 1132 cm^{-1}; HRMS (EI) m/z Calcd for $C_{13}H_{11}{}^{11}BF_6O_2$ $[M]^+$ 324.0756, found 324.0748.

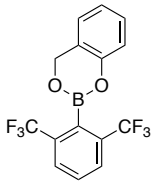
(3a*R*,9a*S*)-2-(2,6-Bis(trifluoromethyl)phenyl)octahydrocycloocta[*d*][1,3,2]dioxaborole (3i)



3i

90%, yield, Data for **3i**: yellow solid; R_f 0.41 (20/1 *n*-hexane/EtOAc); mp 64-66 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 8.0 Hz, 1H), 4.65-4.59 (m, 2H), 2.12-2.02 (m, 2H), 1.96-1.90 (m, 2H), 1.72-1.65 (m, 2H), 1.56-1.26 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.6 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.7, 129.0 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 82.4, 29.0, 27.0, 25.6; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.77; IR (KBr) ν = 2934, 1300, 1133 cm^{-1}; HRMS (EI) m/z Calcd for $C_{16}H_{17}{}^{11}BF_6O_2$ $[M]^+$ 366.1226, found m/z: 366.1239.

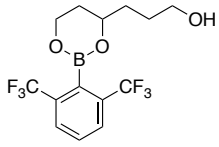
2-(2,6-Bis(trifluoromethyl)phenyl)-4*H*-benzo[*d*][1,3,2]dioxaborinine (3j)



3j

84% yield, Data for **3j**: yellow oil; R_f 0.41 (20/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.10 (dt, J = 7.6, 1.2 Hz, 1H), 7.04-7.01 (m, 2H), 5.26 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.8, 134.1 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.7, 129.0, 128.8 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.9, 124.2 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 123.7, 122.2, 117.9, 63.6; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.74; IR (neat) ν = 3050, 2905, 1297, 1169 cm^{-1}; HRMS (EI) m/z Calcd for $C_{15}H_9{}^{11}BF_6O_2$ $[M]^+$ 346.0600, found 346.0599.

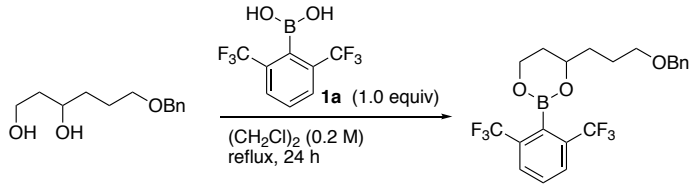
3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-ol (3k)



3k

77% yield, Data for **3k**: yellow oil; R_f 0.16 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 4.21-4.08 (m, 3H), 3.67-3.64 (m, 2H), 2.06-1.89 (m, 2H), 1.78-1.64 (m, 5H) ^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.7 (q, J_2= 31.2 Hz), 128.96, 128.6 (q, J_3= 4.3 Hz), 124.3 (q, J_1= 272.1 Hz), 72.3, 62.6, 62.0, 33.0, 31.8, 28.40; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.38; IR (neat) ν = 2952, 2927, 2872, 2840, 1488, 1431, 1343, 1295, 1197, 1168, 1131, 1088, 1066, 812 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{14}H_{15}{}^{11}BF_6O_3Na$ $[M+Na]^+$ 379.0916, found 379.0918.

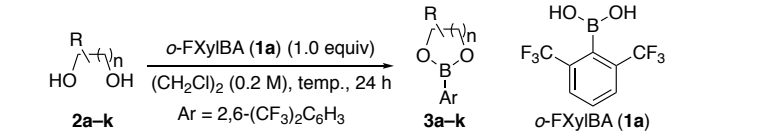
Preparation of 4-(3-(benzyloxy)propyl)-2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (3e) on a 3 mmol scale



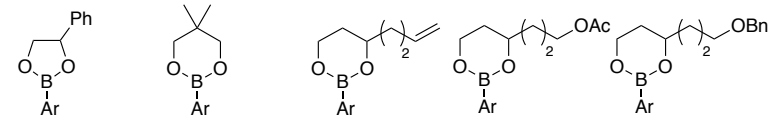
2e 97% **3e**

To a solution of **2e** (674 mg, 3.00 mmol, 1.0 equiv) in $ClCH_2CH_2Cl$ (15 mL, 0.20 M) was added **1a** (776 mg, 3.00 mmol, 1.0 equiv). After stirring for 24 h at reflux, the reaction mixture was concentrated under reduced pressure to furnish the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **3e** (1.30 g, 2.91 mmol, 97% yield) as a yellow oil.

Table S1. Formation of cyclic boronic esters between *o*-FXylB(OH)$_2$ and different diols.



2a–k **3a–k** *o*-FXylBA (**1a**)



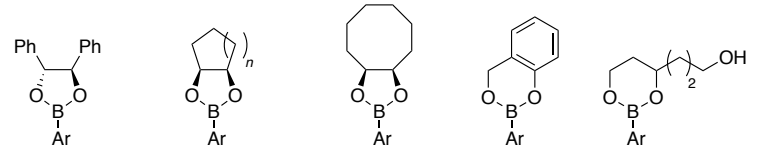
3a
100%[a] (rt)
80%[b] (reflux)

3b
58%[a] (rt)
68%[c] (rt with MS4 Å)
80%[b] (reflux)

3c
89%[a] (rt)
99%[b] (reflux)

3d
91%[a] (rt)
96%[b] (reflux)

3e
84%[a] (rt)
97%[b] (reflux)



3f
4%[a] (rt)
83%[b] (reflux)

n = 2: **3g**
69%[a] (rt)
90%[b] (reflux)
n = 1: **3h**
9%[a] (rt)
90%[b] (reflux)

3i
19%[a] (rt)
90%[b] (reflux)

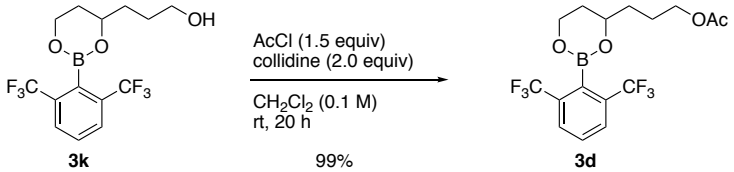
3j
75%[a] (rt)
84%[b] (reflux)

3k
77%[d]

[a] Determined by ^{1}H-NMR analysis of crude mixture.
[b] Isolated yield.
[c] Performed with MS4 Å (1 g/mol)
[d] Reaction time 60 h.

5. Experimental procedures for the chamical transformation of 2,6-bis(trifluoromethyl)-phenylboronic esters

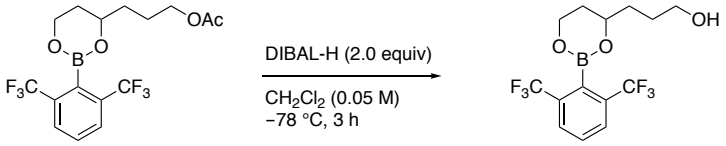
3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propyl acetate (3d)



3k 99% **3d**

To a stirred solution of **3k** (100 mg, 0.280 mmol) and 2,4,6-trimethylpyridine (74.0 μL, 0.560 mmol, 2.0 equiv) in CH_2Cl_2 (3.0 mL, 0.093 M) at room temperature was added acetyl chloride (30.0 μL, 0.420 mmol, 1.5 equiv). After stirring for 20 h, the reaction was quenched by adding 1 M aqueous HCl. The resulting mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with brine (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 (*n*-hexane : EtOAc = 9 : 1) to give **3d** (110 mg, 0.276 mmol, 99% yield) as a colorless oil.

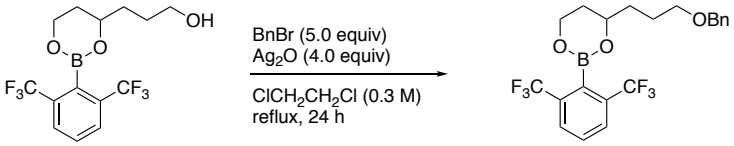
3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-ol (3k)



3d 78% **3k**

To a stirred solution of **3d** (43.8 mg, 0.110 mmol) in CH_2Cl_2 (2.0 mL, 0.055 M) at –78 °C was added dropwise a solution of DIBAL-H in hexane (1.03 M in hexane, 0.22 mL, 0.220 mmol, 2.0 equiv). After stirring for 3 h at –78 °C, the reaction was quenched by adding EtOAc (2.0 mL). A saturated aqueous solution of potassium sodium tartrate (6 mL) was added to the resulting mixture. After stirring for 10 min, saturated aqueous NH_4Cl was added. The resulting mixture was extracted with EtOAc (3 x 15 mL). The combined organic layer was washed successively with H_2O (30 mL) and brine (30 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 (*n*-hexane : EtOAc = 1 : 1) to give **3k** (30.7 mg, 0.0862 mmol, 78% yield) as a yellow oil.

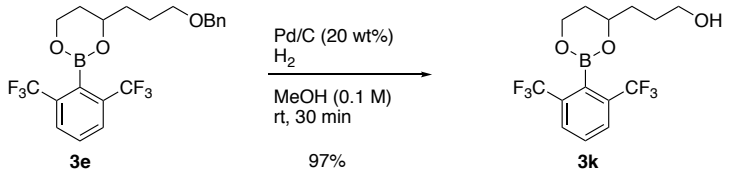
4-(3-(Benzyloxy)propyl)-2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (3e)



3k 81% **3e**

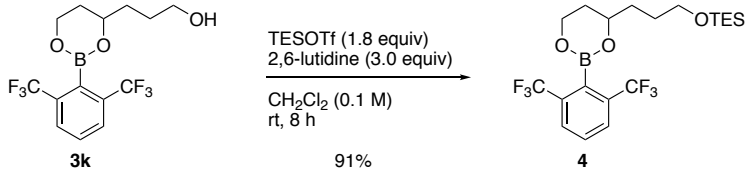
To a stirred suspension of **3k** (356 mg, 1.00 mmol) and Ag_2O (927 mg, 4.00 mmol) in $(CH_2Cl)_2$ (3.0 mL, 0.33 M) at room temperature was added benzyl bromide (0.60 mL, 5.00 mmol, 5.0 equiv). After stirring for 20 h at reflux, the reaction mixture was filtrated through Celite pad and rinsed with CH_2Cl_2 (20 mL). Concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **3e** (362 mg, 0.812 mmol, 81% yield) as a yellow oil.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-ol (3k)



A mixture of 10% Pd/C (16.0 mg, 20 wt%) and **3e** (79.0 mg, 0.180 mmol) in MeOH (2.0 mL, 0.090 M) was stirred for 30 min at room temperature under H_2 atmosphere (balloon). The reaction mixture was filtrated through Celite pad and rinsed with CH_2Cl_2 (20 mL). Concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **3k** (62.2 mg, 0.175 mmol, 97% yield) as a yellow oil.

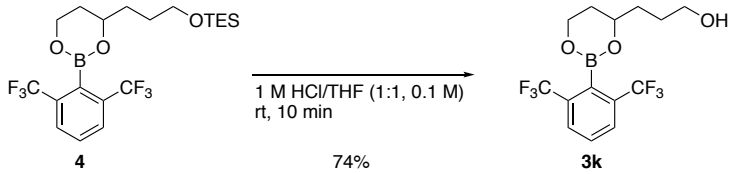
(3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propoxyl)triethylsilane (4)



To a stirred solution of **3k** (71.2 mg, 0.200 mmol) and 2,6-lutidine (47.0 μL, 0.400 mmol, 3.0 equiv) in CH_2Cl_2 (2.0 mL, 0.10 M) at room temperature was added dropwise TESOTf (54.0 μL, 0.240 mmol, 1.8 equiv). After stirring for 8 h, the reaction was quenched by adding saturated aqueous NH_4Cl (2.0 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with brine (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 (*n*-hexane : EtOAc = 19 : 1) to give **4** (85.5 mg, 0.182 mmol, 91% yield) as a colorless oil.

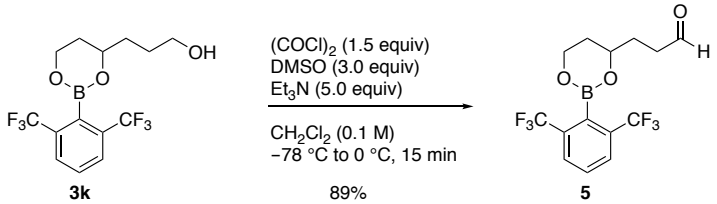
Data for **4**: colorless oil; R_f 0.35 (20/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 4.21-4.08 (m, 3H), 3.69-3.59 (m, 2H), 2.05 (dq, J = 14.2, 3.6 Hz, 1H), 1.97-1.87 (m, 1H), 1.73-1.57 (m, 4H), 0.94 (t, J = 8.1 Hz, 9H), 0.58 (q, J = 8.1 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.7 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 128.9, 128.5 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 72.2, 62.6, 61.9, 32.9, 31.7, 28.3, 6.7, 4.4; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.41; IR (neat) ν = 2956, 1297, 1135 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{30}{}^{11}BO_3F_6Si$ $[M]^+$ 471.1961, found 471.1956.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-ol (3k)



A solution of **4** (47.0 mg, 0.100 mmol) in 1 M aqueous HCl / THF (1.0 mL, 1 M aqueous HCl : THF = 1 : 1) was stirred for 10 min at room temperature. The reaction mixture was extracted with CH_2Cl_2, (2 x 2.0 mL). The combined organic layer was washed with brine (5.0 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 (*n*-hexane : EtOAc = 2 : 1) to give **3k** (26.0 mg, 0.0740 mmol, 74% yield) as a yellow oil.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propanal (5)

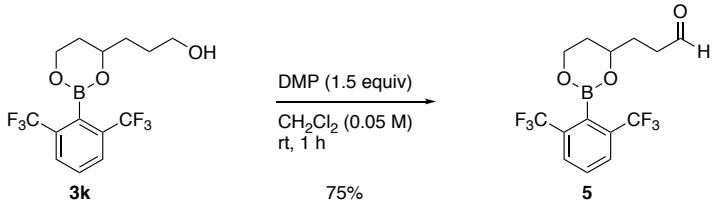


3k 89% **5**

To a stirred solution of oxalyl chloride (128 μL, 1.50 mmol, 1.5 equiv) in CH_2Cl_2 (5.0 mL) at –78 °C was added dropwise DMSO (180 μL, 3.00 mmol, 3.0 equiv) dropwise over 5 min. The mixture was stirred for 10 min at –78 °C and a solution of **3k** (356 mg, 1.00 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise. After stirring for 20 min, Et_3N (696 μL, 5.00 mmol, 5.0 equiv) was added dropwise at –78 °C. After the mixture was stirred at 0 °C for 15 min, the reaction was quenched by adding saturated aqueous NH_4Cl (10 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with brine (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 (*n*-hexane : EtOAc = 2 : 1) to give **5** (85.5 mg, 0.182 mmol, 89% yield) as a colorless oil.

Data for **5**: colorless oil; R_f 0.43 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.79 (t, J = 1.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 4.22-4.09 (m, 3H), 2.72-2.58 (m, 2H), 2.08-1.80 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.8, 133.7 (q, $^2J_{C\text{-}F}$= 31.0 Hz), 129.0, 128.59 (q, $^3J_{C\text{-}F}$= 4.2 Hz), 124.29 (q, $^1J_{C\text{-}F}$= 272.7 Hz), 71.3, 61.9, 39.5, 31.8, 28.7; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.38; IR (neat) ν = 2953, 2927, 1725, 1577, 1487, 1431, 1344, 1295, 1200, 1168, 1131, 1987, 1068, 818 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{13}{}^{11}BF_6O_3Na$ $[M+Na]^+$ 377.0760, found 377.0749.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propanal (5)

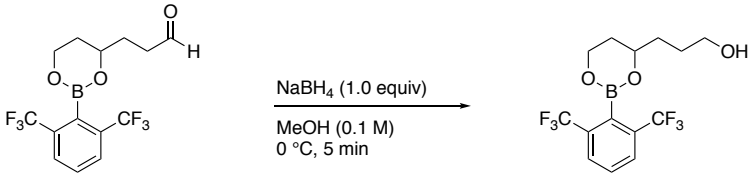


3k 75% **5**

To a stirred solution of Dess–Martin periodinane (68.2 mg, 0.161 mmol, 1.5 equiv) in CH_2Cl_2

(1.0 mL, total 0.050 M) at room temperature was added a solution of **3k** (38.2 mg, 0.107 mmol) in CH_2Cl_2 (1.0 mL). After stirring for 1 h, the reaction was quenched by successively adding saturated aqueous $Na_2S_2O_3$ (1.0 mL) and saturated aqueous $NaHCO_3$ (1.0 mL). After stirring for 30 min, the resulting mixture was extracted with EtOAc (5.0 mL). The combined organic layer was washed with brine (5.0 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 (*n*-hexane : EtOAc = 4 : 1) to give **5** (25.4 mg, 0.0717 mmol, 75% yield) as a colorless oil.

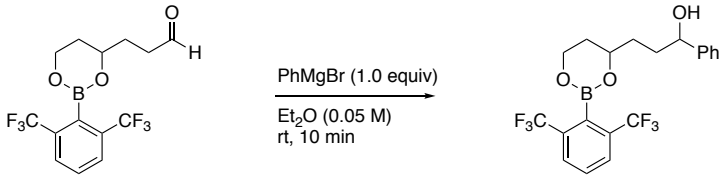
3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-ol (3k)



5 90% **3k**

To a stirred solution of **5** (35.4 mg, 0.100 mmol) in MeOH (1.0 mL, 0.10 M) at 0 °C was added $NaBH_4$ (3.78 mg, 0.100 mmol, 1.0 equiv). After stirring for 5 min, the reaction was quenched by adding saturated aqueous NH_4Cl (1.0 mL). The resulting mixture was extracted with EtOAc (5.0 mL). The organic layer was washed with brine (5.0 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 (*n*-hexane : EtOAc = 2 : 1) to give **3k** (32.0 mg, 0.0900 mmol, 90% yield) as a yellow oil.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)-1-phenylpropan-1-ol (6)



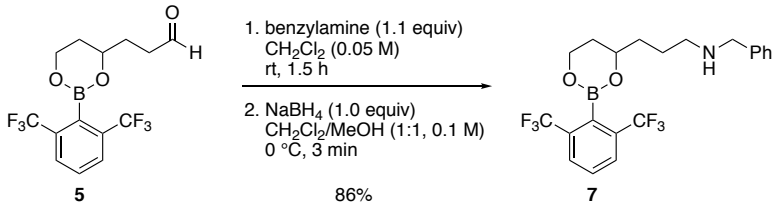
5 70% **6**

To a stirred solution of **5** (35.4 mg, 0.100 mmol) in Et_2O (2.0 mL, 0.050 M) at room temperature was added dropwise a solution of PhMgBr in Et_2O (0.70 M in Et_2O, 140 μL, 0.098 mmol, 1.0 equiv). After stirrng for 10 min, the reaction was quenched by adding saturated aqueous NH_4Cl (2.0 mL). The resulting mixture was extracted with EtOAc (3 x 5.0 mL). The combined organic layer was washed with 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 (*n*-hexane : EtOAc = 5 : 1) to give **6** (30.4 mg, 0.0703 mmol, 70% yield) as a colorless oil.

Data for **6**: colorless oil; R_f 0.51 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.34-7.32 (m, 4H), 7.28-7.23 (m, 1H), 4.72-4.70 (m, 1H), 4.22-4.07 (m, 3H), 2.06-1.57 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.54, 144.51, 133.70 (q,

$^{2}J_{C\text{-}F}$ = 31.0 Hz), 133.69 (q, $^{2}J_{C\text{-}F}$ = 31.0 Hz), 128.94,, 128.93, 128.6 (q, $^{3}J_{C\text{-}F}$ = 4.2 Hz), 128.44,, 128.43, 127.5, 125.79, 125.76, 124.3 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 74.3, 74.1, 72.5, 72.2, 62.0, 61.9, 34.7, 34.5, 32.9, 32.7, 31.9, 31.8; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.37; IR (neat) ν = 3390, 2925, 1296, 1132 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{19}{}^{11}BF_6O_3$ $[M]^+$ 432.1331, found 432.1337.

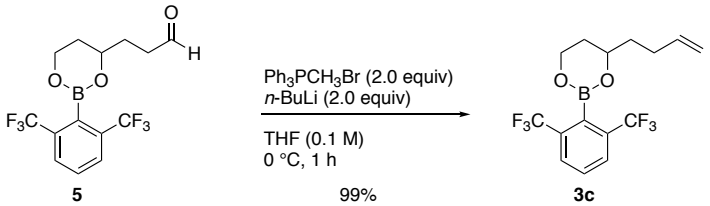
_N_-Benzyl-3-(2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propan-1-amine (7)



To a stirred solution of **5** (35.4 mg, 0.100 mmol) in CH_2Cl_2 (0.50 mL, 0.20 M) at room temperature was added benzylamine (12.0 μL, 0.110 mmol, 1.1 equiv). After stirring for 1 h, a solution of $NaBH_4$ (3.78 mg, 0.100 mmol) in MeOH (0.5 mL) was added to the mixture at 0 °C. After stirring for 3 min, the reaction was quenched by adding saturated aqueous NH_4Cl (2.0 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was washed with 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 ($CHCl_3$: MeOH = 19 : 1) to give **7** (38.2 mg, 0.0858 mmol, 86% yield) as a colorless oil.

Data for **7**: colorless oil; R_f 0.32 (19/1 $CHCl_3$/MeOH); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.22-7.37 (m, 5H), 4.20-4.07 (m, 3H), 3.78 (s, 2H), 3.01 (brs, 1H), 2.69-2.65 (m, 2H), 2.02 (dq, *J* = 14.3, 3.6 Hz, 1H), 1.96-1.86 (m, 1H), 1.74-1.60 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 139.2, 133.7 (q, J_2= 31.0 Hz), 128.9, 128.6 (q, J_3= 4.2 Hz), 128.4, 128.3, 127.1, 124.3 (q, J_1= 272.2 Hz), 72.1, 61.9, 53.4, 48.6, 34.1, 31.7, 25.0; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.38; IR (neat) ν = 3341, 2925, 1296, 1131 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{23}{}^{11}BF_6NO_2$ $[M+H]^+$ 446.1724, found 446.1726.

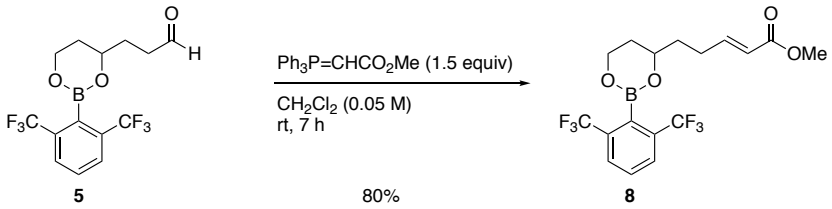
2-(2,6-Bis(trifluoromethyl)phenyl)-4-(but-3-en-1-yl)-1,3,2-dioxaborinane (3c)



To a suspention of methyltriphenylphosphonium bromide (35.7 mg, 0.200 mmol, 2.0 equiv) in THF (0.70 mL) at 0 °C was added dropwise a solution of *n*-BuLi in hexane (1.6 M in hexane, 0.13 mL, 0.200 mmol, 2.0 equiv). After stirring for 20 min at 0 °C, a solution of **5** (35.4 mg, 0.100 mmol) in THF (0.30 mL, total, 0.17 M) was added. After stirring for 1 h at 0 °C, the reaction was diluted by adding Et_2O (2.0 mL). The resulting mixture was filtered through a Celite pad and rised

with Et_2O (20 mL). Concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **3c** (35.2 mg, 0.100 mmol, 99% yield) as a yellow oil.

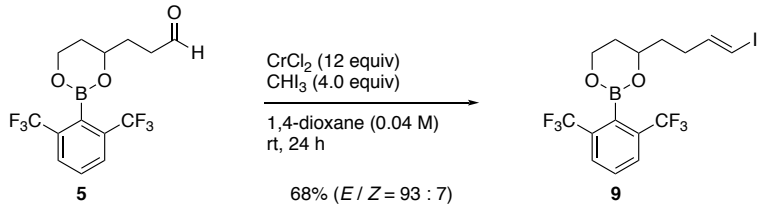
Methyl (*E*)-5-(2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)pent-2- enoate (8)



To a stirred solution of **5** (30.6 mg, 0.0864 mmol) in CH_2Cl_2 (2.0 mL, 0.043 M) at 0 °C was added methyl (triphenylphosphoranylidene)acetate (50.4 mg, 0.130 mmol, 1.5 equiv). After stirring for 10 min at room temperature, the reaction was quenched by adding saturated aqueous NH_4Cl (2.5 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 5.0 mL). The combined organic layer was washed with brine (5.0 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 (*n*-hexane : EtOAc = 4 : 1) give **8** (28.0 mg, 0.0757 mmol, 80% yield) as a colorless oil.

Data for **8**: colorless oil; R_f 0.52 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 6.97 (dt, J = 15.6, 7.2 Hz, 1H), 5.84 (dt, J = 15.6, 1.6 Hz, 2H), 4.21-4.08 (m, 3H), 3.71 (s, 3H), 2.46-2.28 (m, 2H), 2.06-1.86 (m, 2H), 1.84-1.66 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.0, 148.4, 133.7 (q, $^2J_{C\text{-}F}$= 31.0 Hz), 128.6 (q, $^3J_{C\text{-}F}$= 4.2 Hz), 124.30 (q, $^1J_{C\text{-}F}$= 272.0 Hz), 121.5, 71.3, 61.8, 51.4, 34.8, 31.7, 27.6; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.37; IR (neat) ν = 2952, 2920, 2847, 1725, 1652, 1578, 1488, 1436, 1343, 1295, 1199, 1167, 1131, 1081, 986, 819 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{17}H_{17}{}^{11}BF_6O_4Na$ $[M+Na]^+$ 433.1022, found 433.1015.

(*E*)-2-(2,6-Bis(trifluoromethyl)phenyl)-4-(4-iodobut-3-en-1-yl)-1,3,2-dioxaborinane (9)

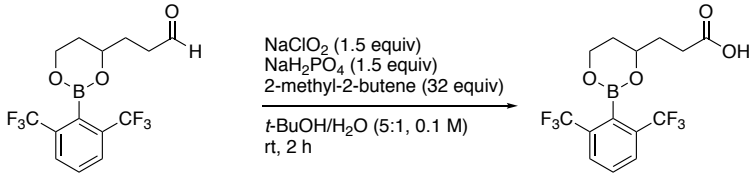


To a stirred solution of chromium (II) chloride (73.7 mg, 0.600 mmol, 6.0 equiv) in 1,4-dioxane (1.3 mL, total 0.40 M) at room temperature was added a solution of iodoform (78.7 mg, 0.200 mmol, 2.0 equiv) and **5** (35.4 mg, 0.100 mmol) in 1,4-dioxane (1.3 mL). After stirring for 5 h, chromium (II) chloride (73.7 mg, 0.600 mmol, 6.0 equiv) and iodoform (78.7 mg, 0.200 mmol, 2.0 equiv) were added to the reaction mixture. After stirring for 19 h, the reaction was quenched by

adding H_2O (3.0 mL). The resulting mixture was extracted with EtOAc (2 x 5.0 mL). The combined organic layer was washed successively with saturated aqueous $Na_2S_2O_3$ (5 x 15 mL) and brine (10 mL), and dried over Na_2SO_4. Filteration and concentration under reduced pressure furnished the crude product, which was pureified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **9** (32.5 mg, 0.0680 mmol, 68% yield, *E*/*Z* = 93 : 7) as a colorless oil.

Data for (*E*)-**9**: colorless oil; R_f 0.41 (2/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 4.21-4.09 (m, 3H), 2.64-2.47 (m, 2H), 2.05 (dq, *J* = 14.2, 3.5 Hz, 1H), 1.99-1.82 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.4, 133.7 (q, $^2J_{C\text{-}F}$ = 31.1 Hz), 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 71.1, 61.8, 31.7, 31.2, 29.3; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; IR (neat) ν = 2953, 1296, 1132 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{13}{}^{11}BF_6O_4$ $[M]^+$ 370.0811, found 370.0803.

3-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propanoic acid (10)

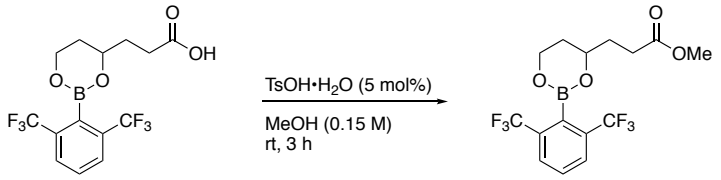


5 86% **10**

To a stirred solution of **5** (35.4 mg, 0.100 mmol) and 2-methyl-2-butene (0.340 mL, 3.20 mmol, 32 equiv) in *t*-BuOH / H_2O (1.5 mL, *t*-BuOH : H_2O = 5 : 1, 0.067 M) at 0 °C was added NaH_2PO_4 (23.4 mg, 0.150 mmol, 1.5 equiv) and $NaClO_2$ (13.6 mg, 0.150 mmol, 1.5 equiv). After stirring for 2 h at room temperature, the reaction was quenched by adding 1 M aqueous HCl (2.0 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was washed with 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 ($CHCl_3$: MeOH = 9 : 1) to give **10** (30.0 mg, 0.0811 mmol, 86% yield) as a white solid.

Data for **10**: white solid; R_f 0.41 (2/1 *n*-hexane/EtOAc); mp 119-124 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 4.21-4.09 (m, 3H), 2.64-2.47 (m, 2H), 2.05 (dq, *J* = 14.2, 3.5 Hz, 1H), 1.99-1.82 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 179.4, 133.7 (q, $^2J_{C\text{-}F}$ = 31.1 Hz), 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 71.1, 61.8, 31.7, 31.2, 29.3l; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; IR (KBr) ν = 2969, 2934, 1712, 1294, 1135 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{13}{}^{11}BF_6O_4$ $[M]^+$ 370.0811, found 370.0803.

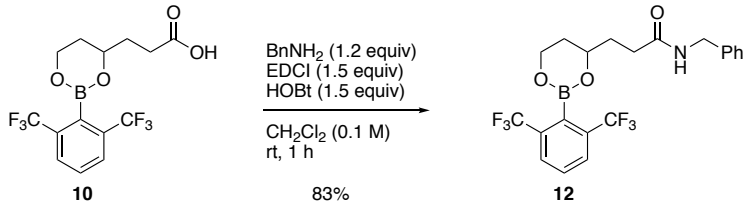
Methyl 3-(2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propanoate (11)



To a stirred solution of **10** (74.0 mg, 0.200 mmol) in MeOH (1.3 mL, 0.15 M) at room remperature was added *p*-toluenesulfonic acid monohydrate (1.90 mg, 0.0100 mmol, 5 mol%). After stirring for 3 h, the reaction was quenched by adding saturated aqueous $NaHCO_3$ (2.0 mL). The resulting mixture was extracted with EtOAc (2 x 5.0 mL). The combined organic layer was washed successively with saturated aqueous $Na_2S_2O_3$ (10 mL) and brine (10 mL), and dried over Na_2SO_4. Filteration and concention under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **11** (56.9 mg, 0.148 mmol, 74% yield) as a colorless oil.

Data for **11**: colorless oil; R_f 0.33 (9/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 4.21-4.09 (m, 3H), 3.65 (s, 3H), 2.55-2.43 (m, 2H), 2.04 (dq, J = 14.0, 3.6 Hz, 1H), 2.00-1.85 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.8, 133.7 (q, $^2J_{C\text{-}F}$ = 36.9 Hz), 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.0 Hz), 71.2, 61.9, 51.6, 31.7, 31.5, 29.4; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; IR (neat) ν = 2957, 1740, 1296, 1131 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{15}{}^{11}BF_6O_4$ $[M]^+$ 384.0968, found 384.0973.

***N*-Benzyl-3-(2-(2,6-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)propanamide (12)**

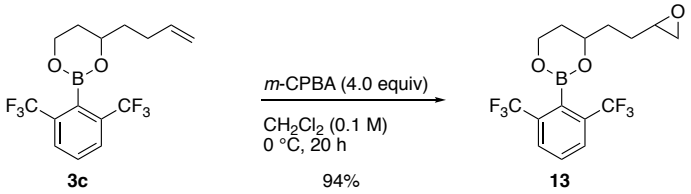


To a stirred solution of **10** (37.0 mg, 0.100 mmol) and benzylamine (13.1 μL, 0.120 mmol, 1.2 equiv) in CH_2Cl_2 (1.0 mL, 0.10 M) at 0 °C was added EDCI (28.7 mg, 0.150 mmol, 1.5 equiv) and HOBt (20.3 mg, 0.150 mmol, 1.5 equiv). After stirring for 1 h at room temperature, the reaction was quenched by adding H_2O (2.0 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 5.0 mL). The combined organic layer washed with 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 (*n*-hexane : EtOAc = 2 : 1) to give **12** (56.9 mg, 0.0828 mmol, 83% yield) as a colorless oil.

Data for **12**: colorless oil; R_f 0.31 (2/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.33-7.23 (m, 5H), 5.85 (br, 1H), 4.41 (d, J = 5.6 Hz, 2H), 4.20-4.07 (m, 3H), 2.45-2.33 (m, 2H), 2.11-1.78 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3,

138.2, 133.7 (q, $^{2}J_{C\text{-}F}$ = 31.0 Hz), 129.0, 128.65, 128.56 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 127.7, 127.4, 124.3 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 71.4, 62.0, 43.6, 32.1, 31.9, 31.8; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.35; IR (neat) ν = 3299, 2925, 1650, 1296, 1130 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{20}{}^{11}BF_6NO_3$ $[M]^+$ 459.1440, found 459.1433.

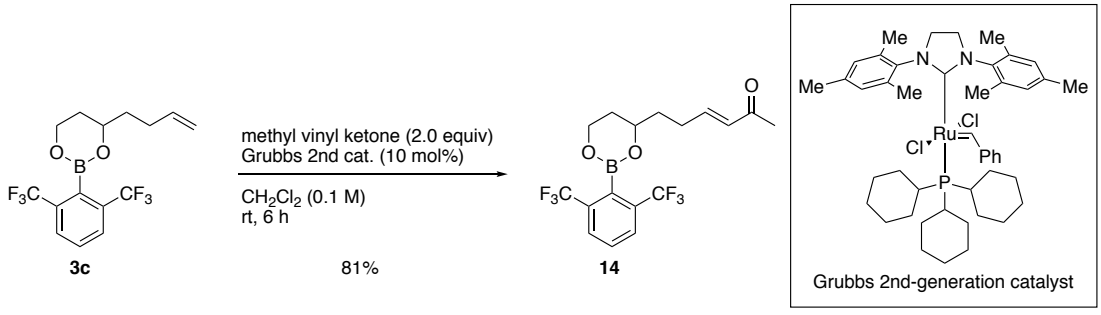
2-(2,6-Bis(trifluoromethyl)phenyl)-4-(2-(oxiran-2-yl)ethyl)-1,3,2-dioxaborinane (13)



To a stirred solution of **3c** (45.0 mg, 0.130 mmol) in CH_2Cl_2 (1.3 mL, 0.10 M) at 0 °C was added 70% *m*-CPBA (126 mg, 0.520 mmol, 4.0 equiv). After stirring for 20 h at 0 °C, the reaction was quenched by adding saturated aqueous $Na_2S_2O_3$ (2.0 mL). The resulting mixture was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layer was washed successively with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), and dried over Na_2SO_4. Filtered and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 4 : 1) to give **13** (45.0 mg, 0.122 mmol, 94% yield) as a colorless oil.

Data for **13**: colorless oil; R_f 0.49 (4/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 4.25-4.09 (m, 3H), 2.91-2.98 (m, 1H), 2.75-2.72 (m, 1H), 2.50-2.45 (m, 1H), 2.08-2.01 (m, 1H), 1.99-1.64 (m, 4H), 1.59-1.51 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 133.7 (q, $^{2}J_{C\text{-}F}$ = 31.0 Hz), 128.9, 128.6 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 124.3 (q, $^{1}J_{C\text{-}F}$ = 271.9 Hz), 72.1, 71.5, 61.9, 61.8, 52.2, 51.7, 47.1, 47.0, 33.0, 32.5, 31.8, 31.7, 28.4, 27.6; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.37, -59.38; IR (neat) ν = 2926, 1433, 1296, 1131 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{15}{}^{11}BF_6O_3$ $[M]^+$ 368.1018, found 368.1017.

(*E*)-6-(2-(2,6-Bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-4-yl)hex-3-en-2-one (14)

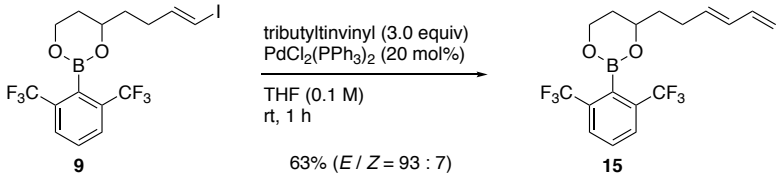


To a stirred solution of **3c** (35.2 mg, 0.100 mmol) and methyl vinyl ketone (16.0 μL, 0.200 mmol, 2.0 equiv) in CH_2Cl_2 (1.0 mL, 0.10 M) at room temperature was added Grubbs 2nd catalyst (4.24 mg, 0.00500 mmol, 10 mol%) was added. After stirring for 6 h, the reaction mixture was

concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 9 : 1) to give **14** (32.1 mg, 0.0814 mmol, 81% yield) as a colorless oil.

Data for **14**: colorless oil; R_f 0.24 (9/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1 H), 6.81 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.09 (dt, *J* = 16.0, 1.6 Hz, 1H), 4.21-4.09 (m, 3H), 2.49-2.30 (m, 2H), 2.20 (s, 3H), 2.03 (dq, *J* = 14.0, 3.6 Hz, 1H), 2.06-1.89 (m, 1H), 1.85-1.68 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.6, 147.3, 133.7 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 131.6, 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 71.4, 61.8, 34.8, 31.7, 27.9, 26.9; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.37; IR (neat) ν = 3343, 2925, 1676, 1296, 1129 cm^{-1}; HRMS (EI) m/z Calcd for $C_{17}H_{17}{}^{11}BF_6O_3$ $[M]^+$ 394.1175, found 394.1173.

(*E*)-2-(2,6-Bis(trifluoromethyl)phenyl)-4-(hexa-3,5-dien-1-yl)-1,3,2-dioxaborinane (15)



9 **15**

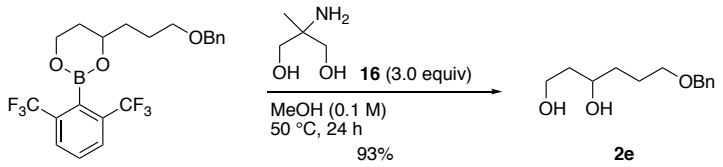
To a stirred solution of **9** (47.8 mg, 0.100 mmol) in THF (1.0 mL, 0.10 M) at room temperature was added tributylvinyltin (87.3 μL, 0.300 mmol, 3.0 equiv). After stirring for 10 min, bis(triphenylphosphine)palladium dichloride (14.0 mg, 0.0200 mmol, 20 mol%) was added to the mixture. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (silica / K_2CO_3 = 9:1, *n*-hexane : EtOAc = 19 : 1) to give **15** (23.8 mg, 0.0629 mmol, 63% yield, *E*/*Z* = 93 : 7) as a colorless oil.

Data for **15**: colorless oil; R_f 0.29 (19/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 1H), 6.31 (dt, *J* = 17.0, 10.2 Hz, 1H), 6.08 (dd, *J* = 15.2, 10.2 Hz, 1H), 5.70 (dt, *J* = 15.2, 7.0 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 4.21-4.08 (m, 3H), 2.35-2.16 (m, 2H), 2.03 (dq, *J* = 14.2, 3.6 Hz, 1H), 1.97-1.88 (m, 1H), 1.82-1.73 (m, 1H), 1.68-1.06 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.1, 134.1, 134.7 (q, $^2J_{C\text{-}F}$ = 31.1 Hz), 131.6, 128.9, 128.6 (q, $^3J_{C\text{-}F}$ = 4.3 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 115.1, 71.5, 61.9, 35.9, 31.6, 27.9; ^{19}F-NMR (377 MHz, $CDCl_3$) δ –59.39; IR (neat) ν = 3327, 2921, 1644, 1296, 1069 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{17}{}^{11}BF_6O_3$ $[M]^+$ 378.1226, found 378.1233.

6. Experimental procedures for the deprotection of 2,6-bis(trifluoromethyl)phenylboronic ester 3e and the formation of *o*-FXylB(OH)$_2$ from potassium trifluoroborate 17

Deprotection of boronic ester 3e by transesterification

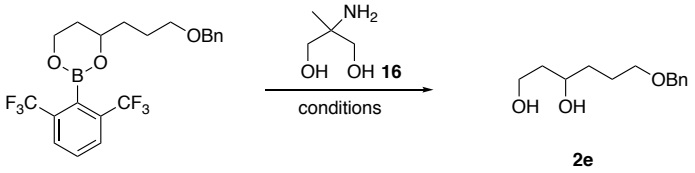
6-(Benzyloxy)hexane-1,3-diol (2e)



3e **2e**

To a stirred solution of **3e** (44.6 mg, 0.100 mmol, 1.0 equiv) in MeOH (1.0 mL, 0.10 M) at room temperature was added 2-amino-2-methyl-1,3-propanediol (**16**) (31.5 mg, 0.300 mmol, 3.0 equiv). After stirring for 24 h at 50 °C, the reaction mixture was concentrated under reduced pressure. The resulting mixture was diluted EtOAc (5.0 mL), and washed successively with 1 M aqueous HCl (3.0 mL) and brine (3.0 mL), and dried over Na_2SO_4. Filtered and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (EtOAc) to give **2e** (20.8 mg, 0.0927 mmol, 93% yield) as a colorless oil.

Table S2. Optimization of deprotection conditions by transesterification using diol **16**

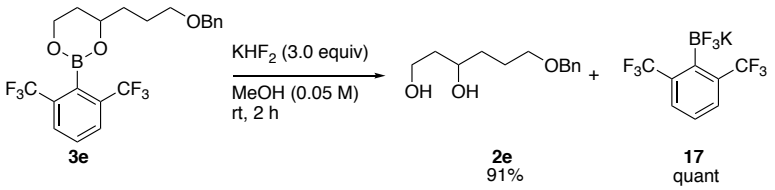


3e **2e**

entry	**16** (equiv)	solvent	temp.	time	ratio **3e/2e**	isolated yield **2e**
1	10	MeOH (0.1 M)	rt	24 h	0:100	90%
2	3	MeOH (0.1 M)	rt	24 h	25:75	ND
3	**3**	**MeOH (0.1 M)**	**50 °C**	**24 h**	**0:100**	**93%**
4	1.2	MeOH (0.1 M)	50 °C	36 h	12:88	ND

Deprotection and recovering method of *o*-FXylB(OH)$_2$ (1a)

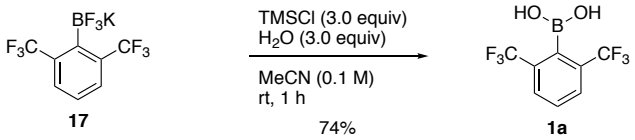
6-(Benzyloxy)hexane-1,3-diol (2e) and (2,6-bis(trifluoromethyl)phenyl)trifluoro-λ^4-borane, potassium salt (17)



To a stirred solution of **3e** (22.3 mg, 0.0500 mmol, 1.0 equiv) in MeOH (1.0 mL, 0.050 M) at room temperature was added a aqueous solution of potassium bifluoride (4.5 M in H_2O, 33.3 μL, 0.150 mmol, 3.0 equiv). After stirring for 2 h, the reaction mixture was concentrated under reduced pressure to remove MeOH. The resulting mixture was filtrated and rinsed with CH_2Cl_2 (20 mL). Trifluoroborate **17** (18.3 mg, 0.0500 mmol, quant) was obtained as a white solid after drying. Concentration of the filtrate under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (EtOAc) to give **2e** (10.2 mg, 0.0460 mmol, 91% yield) as a colorless oil.

Data for **17**: white solid; R_f 0.60 (4/1 $CHCl_3$/MeOH); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.6 (q, $^2J_{C\text{-}F}$ = 30.7 Hz), 129.8 (q, $^3J_{C\text{-}F}$ = 5.6 Hz), 127.4, 126.6 (q, $^1J_{C\text{-}F}$ = 272.5 Hz); ^{19}F-NMR (377 MHz, $CDCl_3$) δ –56.3 (q, J = 23.8 Hz, 6F), –134.3 (m, 3F); IR (neat) ν = 3367, 1293, 1120 cm^{-1}; HRMS (FAB) m/z Calcd for $C_8H_3{}^{11}BF_9$ $[M\text{-}K]^+$ 281.0184, found 281.0188.

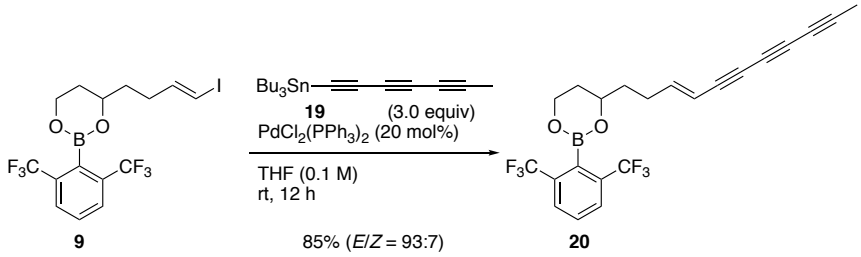
2,6-Bis(trifluoromethyl)phenylboronic acid (1a)



To a stirred solution of **17** (16.0 mg, 0.0500 mmol) in MeCN (0.50 mL, 0.10 M) at room temperature was added trimethylsilylchloride (18.5 μL, 0.150 mmol, 3.0 equiv) and H_2O (2.70 μL, 0.150 mmol, 3.0 quiv) were added. After stirring for 1 h, the reaction was quenched by adding saturated aqueous $NaHCO_3$ (0.5 mL). The resulting mixture was extracted with EtOAc (2 x 2 mL). The combined organic layer was washed with brine (3.0 mL), and dried over Na_2SO_4. Filtered and concentration under reduced pressure furnished the crude product, which was purified by silicagel column chromatography (*n*-hexane : EtOAc = 2 : 1) to give **1a** (9.50 mg, 0.0368 mmol, 74% yield) as a white solid.

7. Experimental procedures for the synthsis of enetriyne natural product 18

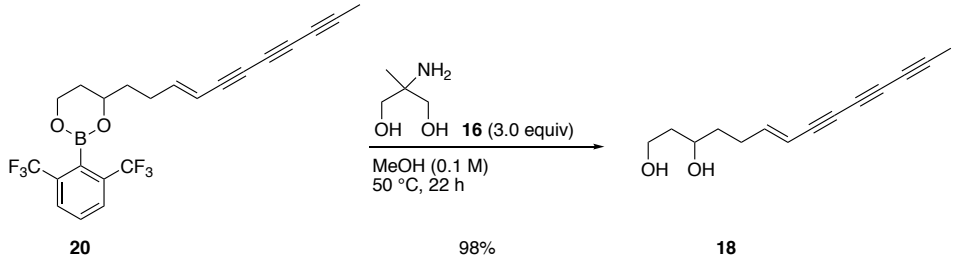
(*E*)-2-(2,6-Bis(trifluoromethyl)phenyl)-4-(undeca-3-en-5,7,9-triyn-1-yl)-1,3,2-dioxaborinane (20)



To a stirred solution of **9** (62.1 mg, 0.130 mmol) in THF (1.3 mL, 0.10 M) at room temperature was added **19**[2] (147 mg, 0.390 mmol, 3.0 equiv). After stirring for 10 min, bis(triphenylphosphine)palladium dichloride (18.2 mg, 0.0260 mmol, 20 mol%) was added to the mixture. After stirring for 12 h, the reaction mixture was concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography (silica / K_2CO_3 = 9:1, *n*-hexane : EtOAc = 19 : 1) to give **20** (48.5 mg, 0.110 mmol, 85% yield, *E*/*Z* = 93 : 7) as a colorless oil.

Data for **20**: colorless oil; R_f 0.32 (9/1 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 1H), 6.37 (dt, *J* = 15.8, 3.2 Hz, 1H), 5.53(d, *J* = 15.8 Hz, 1H), 4.21-4.08 (m, 3H), 2.39-2.22 (m, 2H), 2.04-1.87 (m, 2H), 1.98 (s, 3H), 1.78-1.59 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.1, 133.7 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 129.0, 128.6 (q, $^3J_{C\text{-}F}$ = 4.3 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 108.9, 77.7, 74.3, 73.5, 71.2, 66.5, 64.9, 61.9, 59.2, 35.2, 31.7, 28.7, 4.6; IR (neat) ν = 2927, 2223, 1295, 1130 cm^{-1}; HRMS (FAB) m/z Calcd for $C_{22}H_{17}{}^{11}BF_6O_2Na$ $[M+Na]^+$ 461.1123, found 461.1139.

(*E*)-tetradeca-6-en-8,10,12-triyne-1,3-diol (18)



To a stirred solution of **20** (20.3 mg, 0.0460 mmol, 1.0 equiv) in MeOH (0.46 mL, 0.10 M) at room temperature was added 2-amino-2-methyl-1,3-propanediol (**16**) (14.6 mg, 0.140 mmol, 3.0 equiv). After stirring for 22 h at 50 °C, the reaction mixture was concentrated under reduced pressure. The resulting mixture was diluted with EtOAc (3.0 mL), washed successively with 1 M aqueous HCl (2.0 mL) and brine (2.0 mL), and dried over Na_2SO_4. Filtered and concentration under reduced pressure furnished the crude product, which was purified by silica gel column chromatography (*n*-hexane : EtOAc = 1 : 4) to give **18** (9.8 mg, 0.045 mmol, 98% yield) as a white

solid.

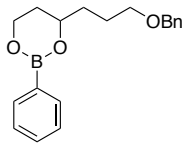
Data for **18**: white solid; R_f 0.29 (1/4 *n*-hexane/EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.39 (dt, *J* = 15.9, 7.2 Hz, 1H), 5.54 (d, *J* = 15.9 Hz, 1H), 3.93-3.80 (m, 3H), 2.34-2.21 (m, 2H), 1.98 (S, 3H), 1.71-1.53 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ149.5, 108.7, 77.8, 74.3, 73.5, 71.2, 66.6, 64.9, 61.8, 59.2, 38.3, 36.3, 29.4, 4.6; IR (neat) ν = 3326, 2932, 2222, 1054 cm^{-1}; HRMS (FAB) m/z Calcd for $C_{14}H_{16}O_2$ [M] 216.1150, found 216.1149.

8. Estimation of the half-lives of boronic esters 3e, 3l–n

General procedure for the formation of boronic esters 3l–n of diol 2e

To a solution of **2e** (0.200 mmol, 1.0 equiv) in $ClCH_2CH_2Cl$ (1.0 mL, 0.20 M) at room temperature was added boronic acid **1b–d** (0.200 mmol, 1.0 equiv), respectively. After stirring for 24 h under reflux, the reaction mixture was concentrated under reduced pressure to give the boronic ester **3l–n**, respectively.

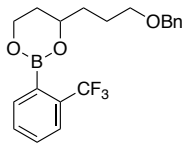
4-(3-(Benzyloxy)propyl)-2-phenyl-1,3,2-dioxaborinane (3l)



3l

Data for **3l**: colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.43-7.72 (m, 8H), 4.54 (s, 2H), 4.22-4.07 (m, 3H), 3.63-3.53 (m, 2H), 2.00 (dq, *J* = 14.0, 3.4 Hz, 1H), 2.03-1.92 (m, 1H), 1.87-1.69 (m, 4H).

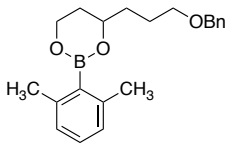
4-(3-(Benzyloxy)propyl)-2-(2-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (3m)



3m

Data for **3m**: colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ7.67-7.62 (m, 2H), 7.50-7.43 (m, 2H), 7.35-7.27 (m, 5H), 4.52 (s, 2H), 4.22-4.09 (m, 3H), 3.59-3.49 (m, 3H), 2.03 (dq, *J* = 14.2, 3.4 Hz, 1H), 1.92-1.68 (m, 5H).

4-(3-(Benzyloxy)propyl)-2-(2,6-dimethylphenyl)-1,3,2-dioxaborinane (3n)



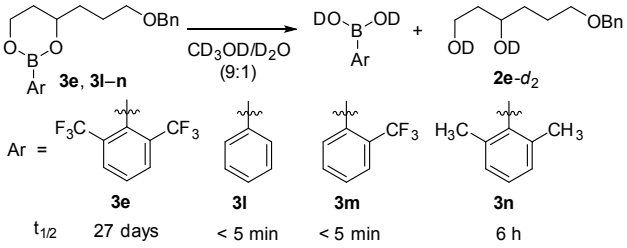
3n

Data for **3n**: yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 2H), 4.51 (s, 2H), 4.10-4.21 (m, 3H), 3.57-3.48 (m, 2H), 2.36 (s, 6 H), 2.06 (dq, *J* = 14.1, 3.4 Hz, 1H), 1.92-1.69 (m, 5H).

Estimation of half-lives of boronic esters 3l–n by ^{1}H NMR in CD_3OD/D_2O (9:1)

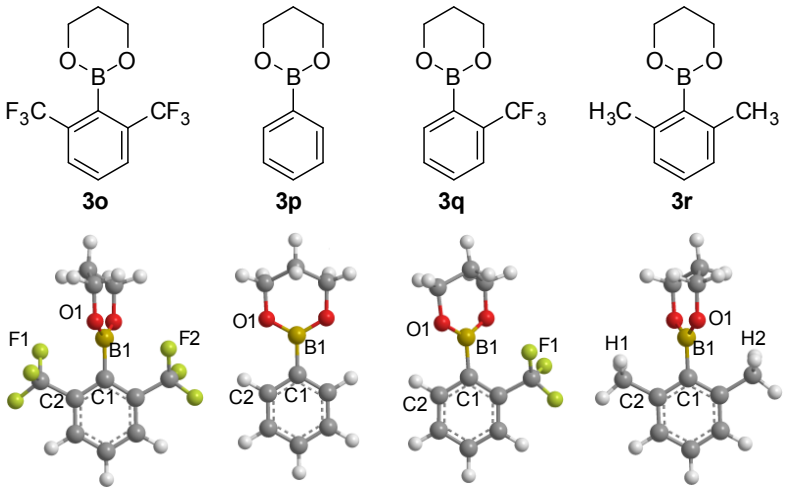
A 5-mm NMR tube was charged with the boronic ester (0.050 mmol), CD_3OD (540 μL) and D_2O (60.0 μL). The tube was capped with a septum, shaken, and left at room temperature. Conversion of boronic ester to diol **2e** was monitored by ^{1}H NMR spectroscopy.

Scheme S1. Stabilities of arylboronic esters **3a,l–n** in aqueous media



9. DFT calculations of boronic esters 3o–r

The geometric optimizations of four boronic esters **3o–r** were performed by the long-range correction[5a] for Becke 1988 exchange[6] and one-parameter progressive correlation[5b] functional (LC-BOP) with the cc-pVTZ basis set on the development version of Gaussian 09 program (Figure S1).



	3o	3p	3q	3r
dihedral angle (deg)				
O1—B1—C1—C2	71.3	0.1	45.9	114.4
bond distance (Å)				
B1—C1	1.584	1.557	1.570	1.567
B1—O1	1.350	1.360	1.357	1.360
B1—O2	1.350	1.360	1.352	1.360
B1—F1	2.623	——	2.806	——
B1—F2	2.597	——	——	——
B1—H1	——	——	——	2.965
B1—H2	——	——	——	2.820

Figure S1. Optimized structures of boronic esters **3o–r**

Incorporating a bulky trifluoromethyl group to both the ortho positions is considered to sterically shield the boron atom of the 1,3,2-dioxaborinane ring from the attacks of water and oxygen molecules and other nucleophiles coming from the perpendicular to the 1,3,2-dioxaborinane ring. In the optimized structure of 2,6-bis(trifluoromethyl)phenyl boronic ester **3o**, both B-F distances (B1-F1:2.623 Å, B1-F2:2.597 Å) are shorter than the sum of the van der Waals radii (3.3 Å). We therefore performed the atoms-in-molecules (AIM) analysis[7] for the optimized structure of 2,6-bis(triflulromethyl)phenylboronic ester **3o** to investigate the possibility of the penta-coordination of boron atom *via* three-center four-electron (3c–4e) F-B-F bond.[8] As a result, we found no bond path between the boron atom and the two fluorine atoms.

We also compared the electronic structures of these esters **3o**–**3r** to analyze a significant difference in the stability of the boronic esters (Table S2 and Figure S2). Calculated results showed that the trifluoromethylations at the both *ortho* positions of benzene ring remarkably increased LUMO energy by 2.544 eV and decreased HOMO energy by 1.008 eV, from those of phenylboronic ester **3p**. Consequently, the 2,6-bis(triflulromethyl)phenylboronic ester **3o** replaces LUMO with the LUMO+1, compared to those of other boronic ester **3p**, **3q** and **3r**. In terms of LUMO distribution, the each LUMO of **3p**, **3q** and **3r** mainly delocalized on benzene ring and 1,3,2-dioxaborinane ring containing boron atom. In contrast, the LUMO of **3o** is well distributed on benzene ring, but not localized on boron atom. These differences may cause the high stability of boronic ester **3o** against nucleophiles such as water and alcohols.

Table S3. Molecular orbital energy levels (eV) of **3o**–**3r**

	3o	3p	3q	3r
LUMO+5	5.439	4.110	4.126	4.043
LUMO+4	5.087	3.862	3.754	3.771
LUMO+3	4.809	3.825	3.616	3.481
LUMO+2	4.727	3.038	3.000	2.882
LUMO+1	4.370	2.590	1.993	2.822
LUMO	4.218	1.826	1.521	2.228
HOMO	−10.530	−9.522	−10.010	−9.035
HOMO−1	−10.700	−9.561	−10.169	−9.195
HOMO−2	−11.518	−11.339	−11.410	−11.344
HOMO−3	−11.776	−11.571	−11.743	−11.429
HOMO−4	−12.282	−11.792	−12.159	−11.611
HOMO−5	−12.483	−12.307	−12.381	−12.029

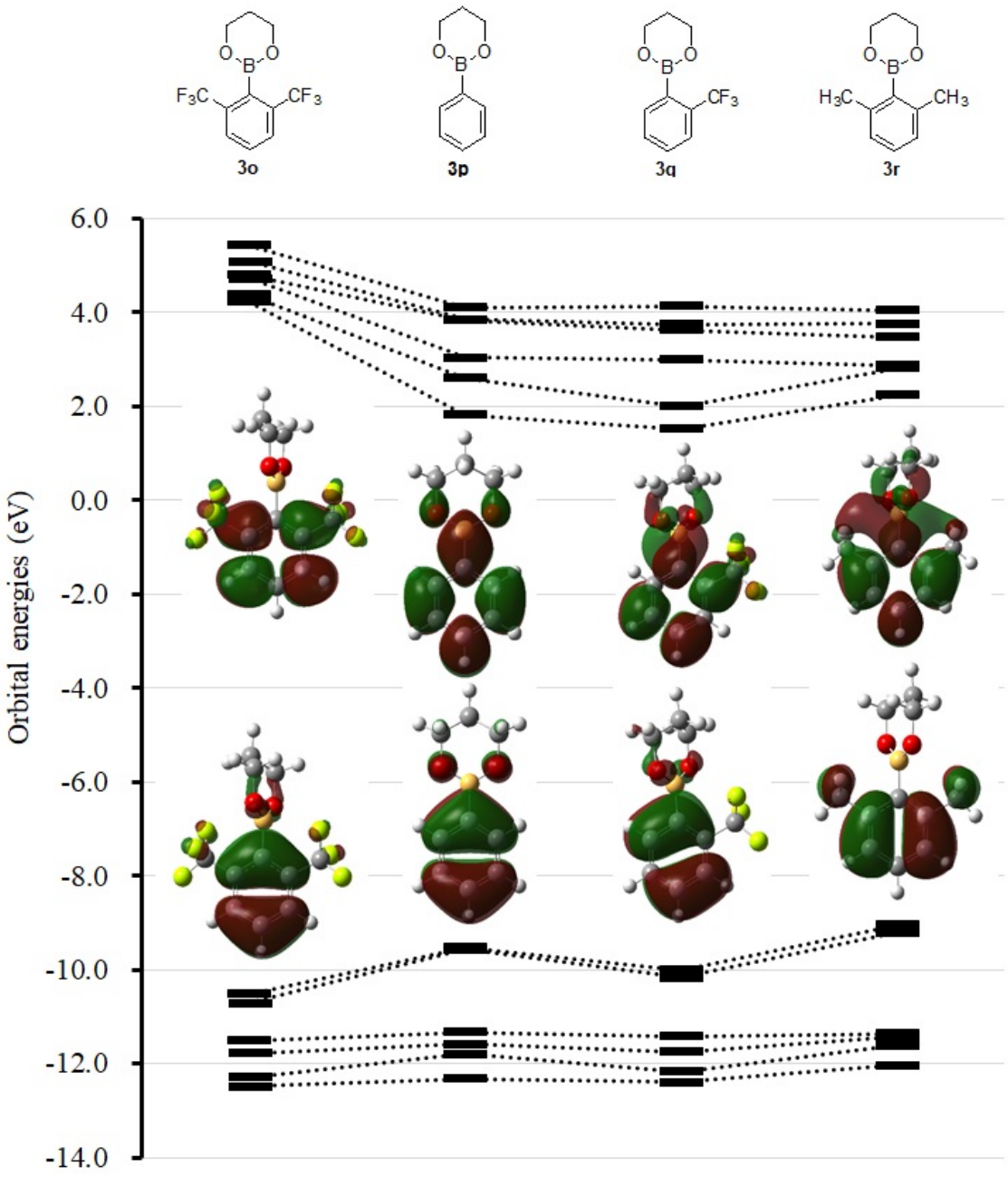


Figure S2. Comparison of molecular orbital surfaces and their energy levels (eV) of **3o**–**3r**

Cartesian coordinates of the optimized structures of boronic esters 3o–r

Boronic ester **3o**

C	0.2563970	-0.5319190	0.0019310
C	-0.5411680	-1.6647470	-0.0532260
C	-0.0033980	-2.9328920	-0.0678880
C	1.3587090	-3.1031030	-0.0277490
C	2.1750630	-2.0005130	0.0270150
C	1.6269390	-0.7366430	0.0415800
B	-0.3600000	0.9266680	0.0232200
C	-2.0372440	-1.5418980	-0.0670970
C	2.5703660	0.4307740	0.0708930
O	-0.9931190	1.3349470	1.1431650
O	-0.2232070	1.6941960	-1.0791190
F	-2.5427840	-1.4445760	1.1633970
F	-2.6192940	-2.5983860	-0.6397160
F	-2.4478260	-0.4631260	-0.7451790
F	2.0713160	1.4650580	0.7594800
F	2.8519750	0.8773240	-1.1537840
F	3.7350380	0.1159500	0.6431620
C	-1.5737130	2.6248790	1.2054260
C	-0.7346830	3.0141440	-1.0824630
C	-1.9324430	3.1231280	-0.1724570
H	-0.6570510	-3.7910470	-0.1166590
H	1.7841100	-4.0960650	-0.0390030
H	3.2477080	-2.1192810	0.0649450
H	-0.8617780	3.2973180	1.6874740
H	-2.4521490	2.5534780	1.8430100
H	-0.9925530	3.2584180	-2.1104280
H	0.0592560	3.6925840	-0.7641450
H	-2.7491950	2.5243100	-0.5759050
H	-2.2725160	4.1563300	-0.1197790

Boronic ester **3p**

C	0.9019610	0.0000200	-0.0296440
C	1.6124560	1.1891860	-0.0059050
C	2.9884280	1.1930140	0.0410500
C	3.6777930	-0.0000070	0.0646540
C	2.9884060	-1.1930150	0.0411140
C	1.6124310	-1.1891630	-0.0057950
B	-0.6537980	-0.0000040	-0.0838750
H	1.0705660	2.1252650	-0.0249640
H	1.0705170	-2.1252290	-0.0247000
O	-1.3151320	1.1879880	-0.1059930
O	-1.3150850	-1.1880410	-0.1058560
C	-2.7257820	1.2316260	-0.1514050
C	-2.7257290	-1.2315530	-0.1517270
C	-3.3238780	-0.0000600	0.4799890
H	3.5279080	2.1303360	0.0591270
H	4.7590150	-0.0000120	0.1013590
H	3.5278650	-2.1303470	0.0592610
H	-3.0398540	1.3192900	-1.1939180
H	-3.0419570	2.1351410	0.3664170
H	-3.0421200	-2.1352460	0.3656450
H	-3.0395210	-1.3187640	-1.1943660
H	-3.1121800	-0.0002140	1.5498960
H	-4.4060150	-0.0000680	0.3564090

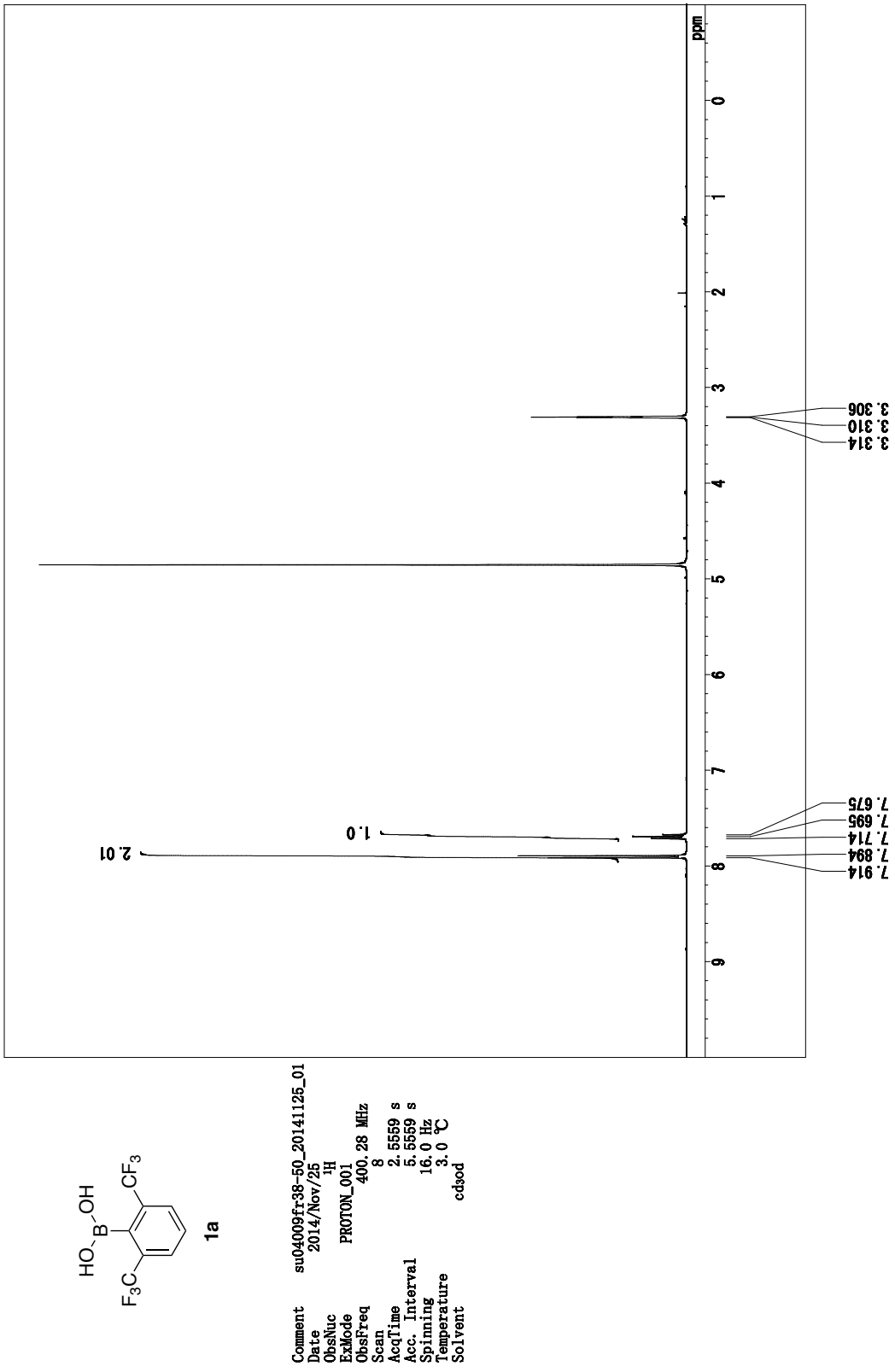
Boronic ester **3q**

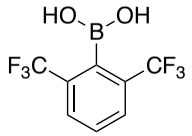
C	0.4980280	0.8668970	0.0765080
C	1.4980880	-0.0920760	-0.0176630
C	2.8289850	0.2603780	0.0069940
C	3.1926690	1.5823110	0.1298600
C	2.2202530	2.5501660	0.2078060
C	0.8912360	2.1901890	0.1719570
B	-1.0445970	0.5755410	0.1090340
C	1.1555910	-1.5458430	-0.1668180
H	0.1317550	2.9589360	0.2160180
O	-1.5359500	-0.3639600	0.9475010
O	-1.8466820	1.3493550	-0.6650180
F	0.8485900	-2.1219460	0.9959840
F	2.1717500	-2.2479350	-0.6811460
F	0.1142750	-1.7329190	-0.9883600
C	-2.9168200	-0.6649240	0.9800370
C	-3.2482700	1.1570700	-0.6455740
C	-3.5852790	-0.2745140	-0.3140080
H	3.5872120	-0.5029750	-0.0815100
H	4.2389650	1.8531030	0.1517180
H	2.4956670	3.5926320	0.2906730
H	-3.3655120	-0.1341540	1.8219980
H	-3.0118180	-1.7320490	1.1700660
H	-3.6273680	1.4377750	-1.6258830
H	-3.6850080	1.8368940	0.0892480
H	-3.2342610	-0.9236140	-1.1168920
H	-4.6640130	-0.4001330	-0.2333510

Boronic ester **3r**

H	3.8364470	-0.3083310	-0.0020180
C	-0.5825010	2.7218090	-0.1976470
H	1.9287890	3.4621390	-0.3584380
C	3.0124820	1.6385910	-0.1940010
C	2.9289790	0.2777130	-0.0494440
C	1.6982380	-0.3458180	0.0325860
C	0.5288990	0.4085240	-0.0398270
C	0.6155940	1.7958950	-0.1715890
C	1.8609310	2.3872860	-0.2497510
H	3.9780610	2.1216010	-0.2621380
C	1.6525040	-1.8513170	0.1874980
B	-0.8223830	-0.3918690	0.0154870
O	-1.2179570	-1.0821760	-1.0892080
O	-1.5399470	-0.4395410	1.1707730
C	-2.3722800	-1.8958110	-1.0689890
C	-2.7156550	-1.2179420	1.2739000
C	-3.3794490	-1.3865460	-0.0691620
H	-2.7833940	-1.9037230	-2.0765510
H	-2.0741270	-2.9182850	-0.8249400
H	-3.3748580	-0.7199280	1.9824010
H	-2.4505860	-2.1899930	1.6953480
H	-4.2156130	-2.0799320	0.0100900
H	-3.7782470	-0.4294310	-0.4056660
C	2.5031630	-2.3431830	1.3476250
C	2.0359900	-2.5466580	-1.1090820
H	0.6259380	-2.1388170	0.4155310
H	1.9678350	-3.6293000	-1.0039850
H	3.0600860	-2.3033520	-1.3904830
H	1.3822280	-2.2383940	-1.9221570
H	2.3689720	-3.4151220	1.4883590
H	2.2330150	-1.8418180	2.2751480
H	3.5632240	-2.1696110	1.1714490
C	-1.6929110	2.3003920	-1.1444590
C	-1.1196050	2.9676170	1.2054220
H	-0.2082270	3.6766460	-0.5687810
H	-1.9382150	3.6870730	1.1825020
H	-0.3415000	3.3620960	1.8564790
H	-1.4869190	2.0442080	1.6481950
H	-2.4043470	3.1162560	-1.2666040
H	-1.3054450	2.0359900	-2.1261980
H	-2.2542470	1.4498010	-0.7659860

10. ^{1}H and ^{13}C NMR spectra





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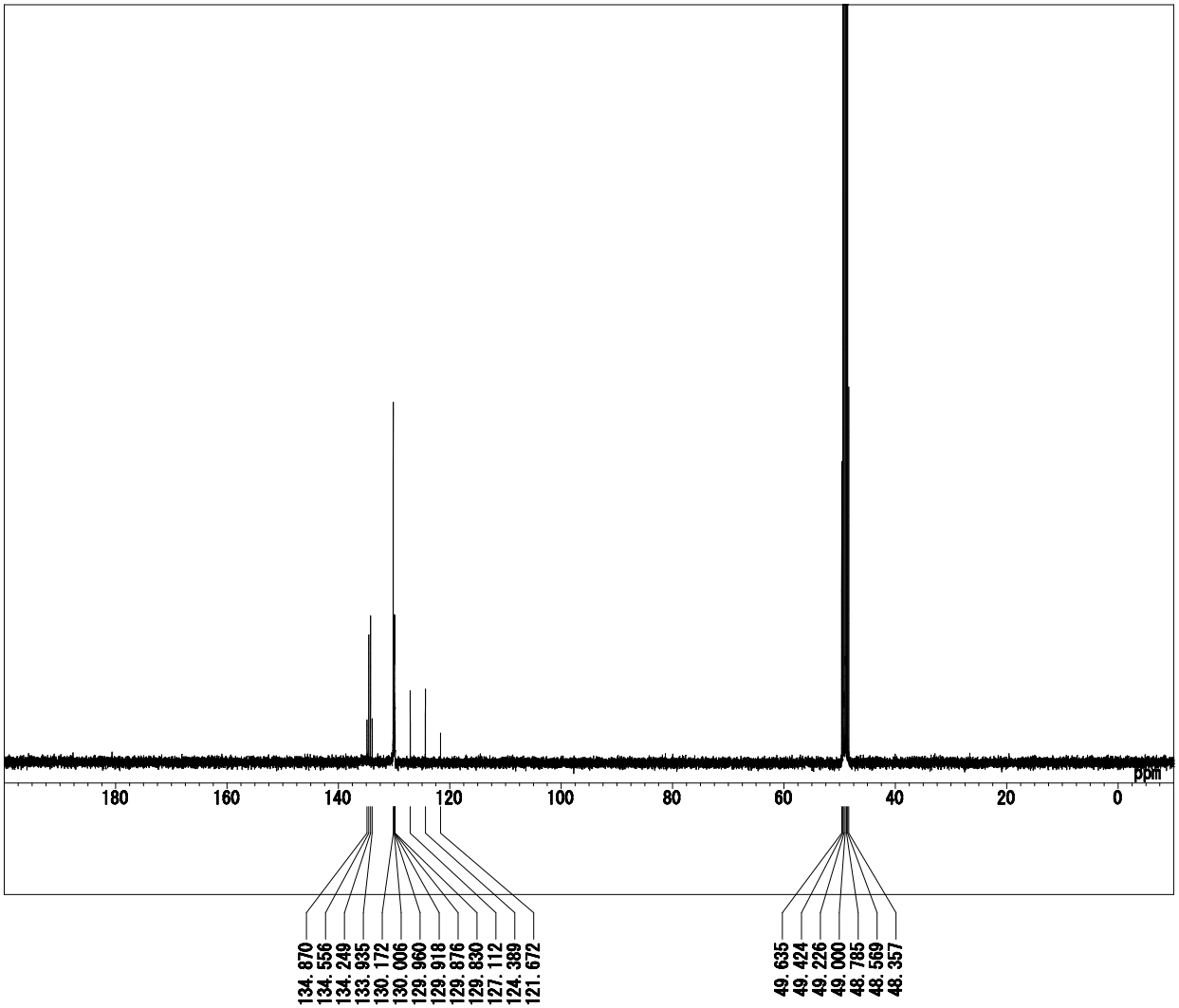

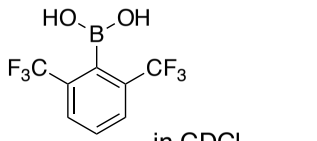

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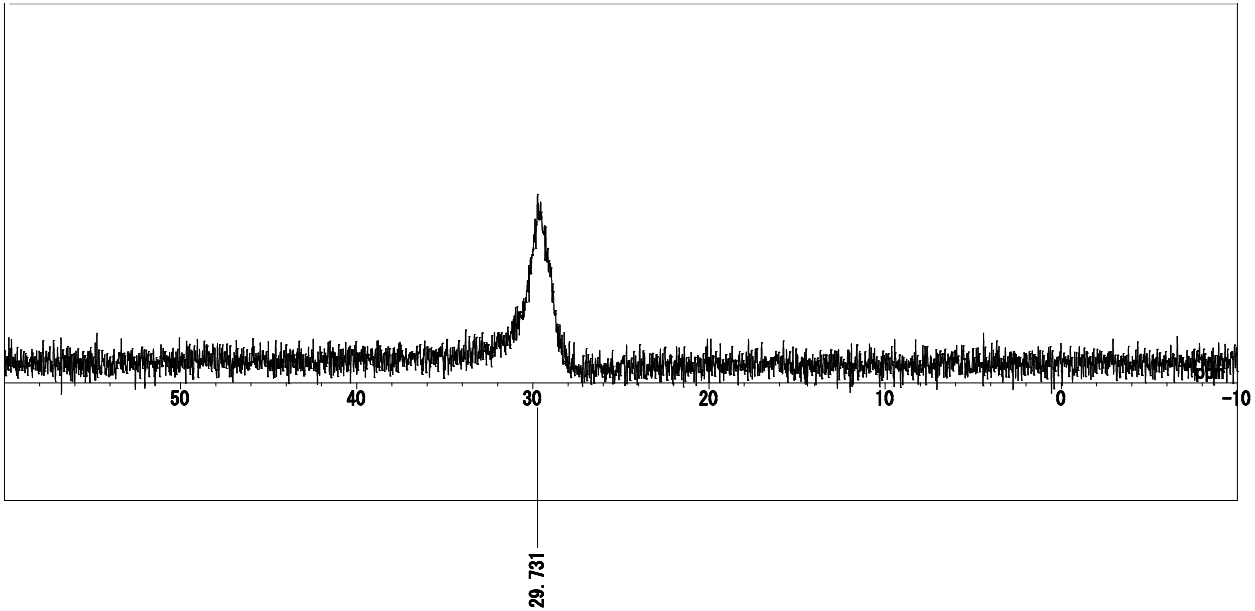

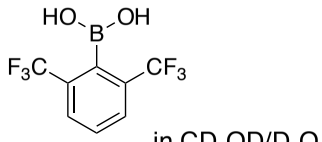

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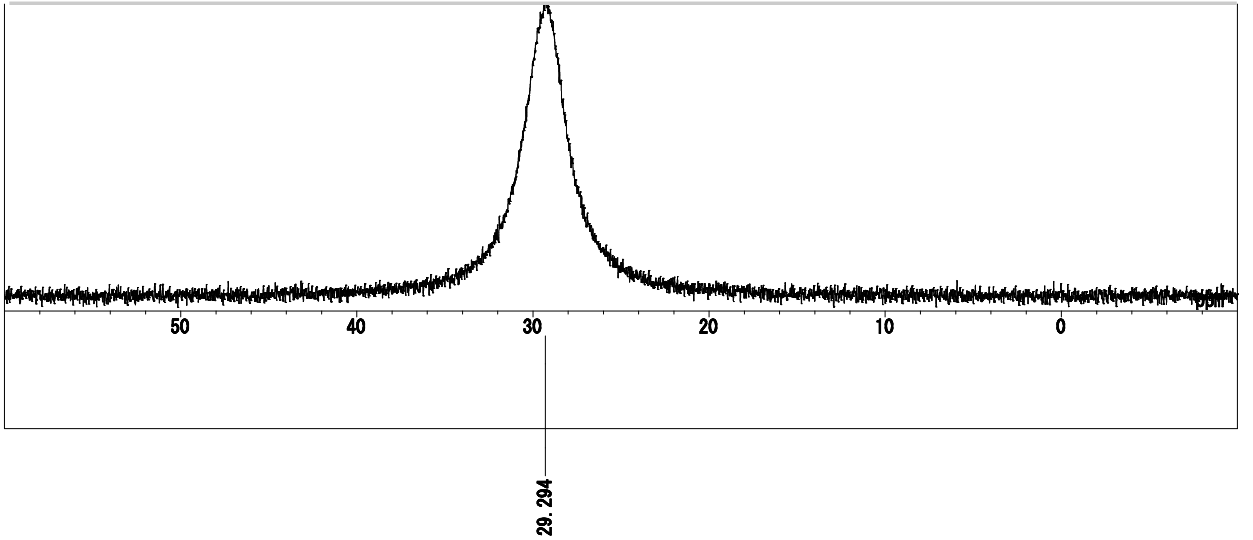

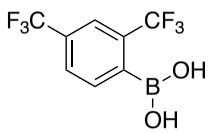

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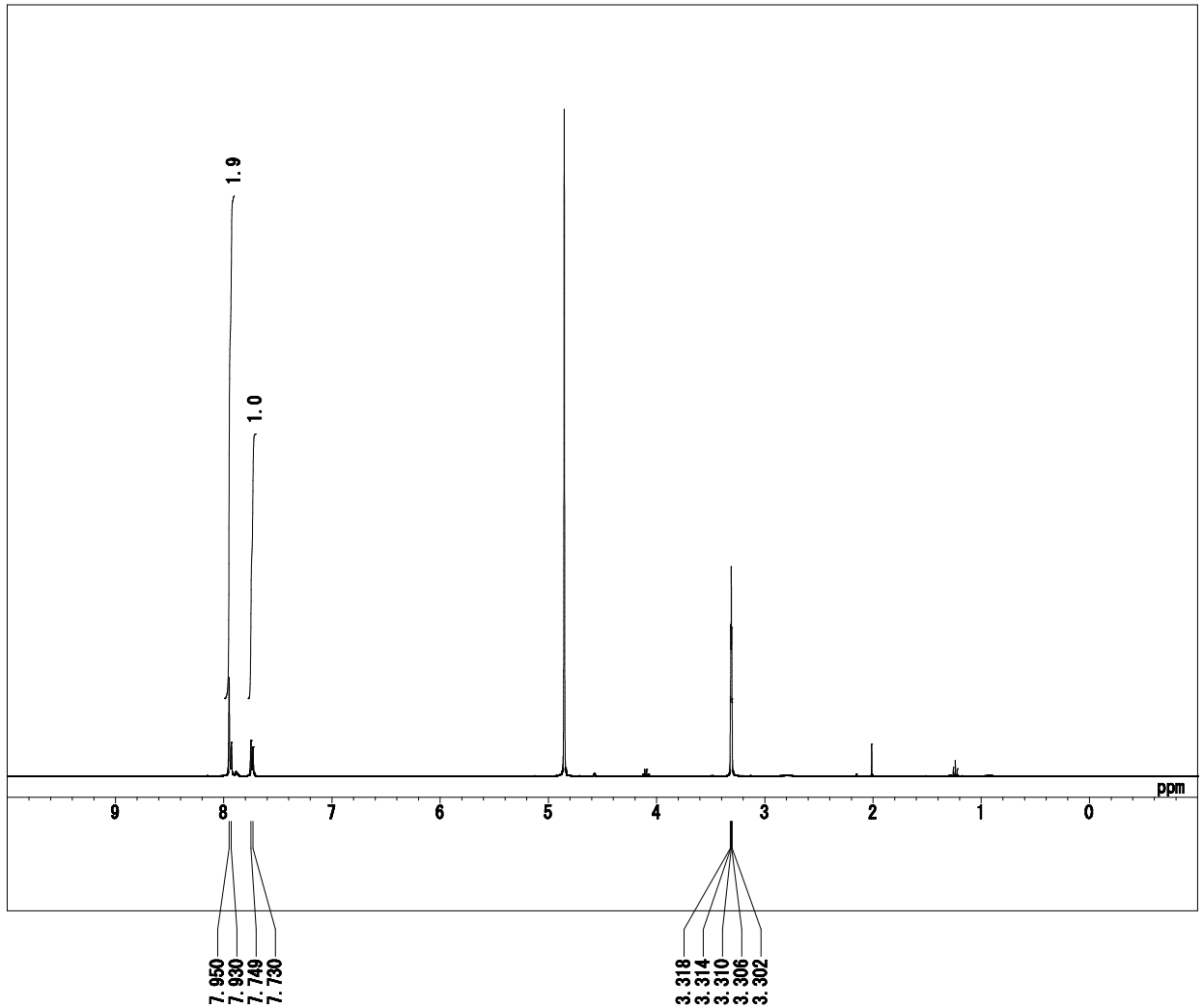

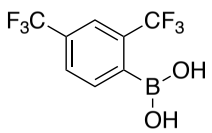

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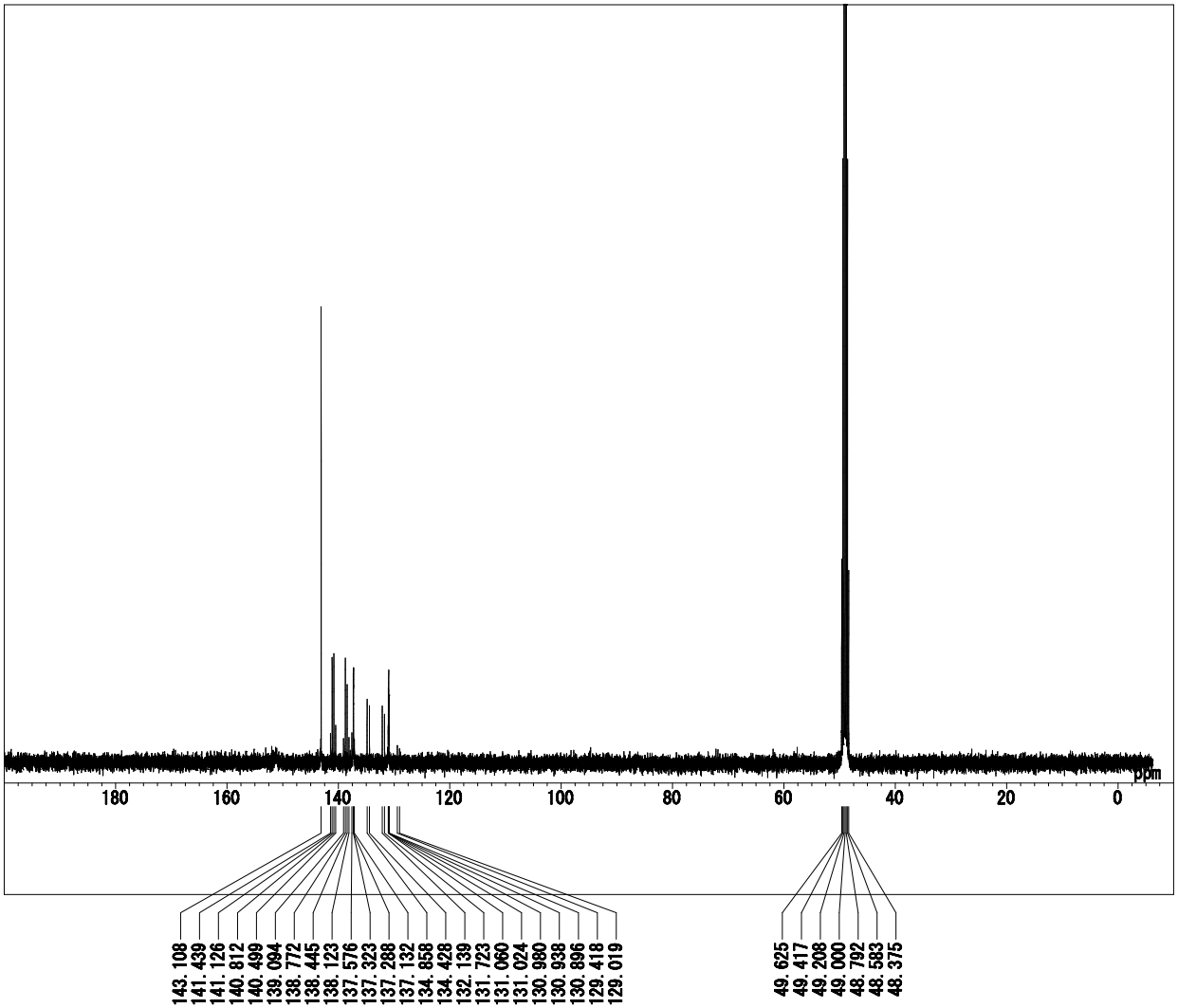

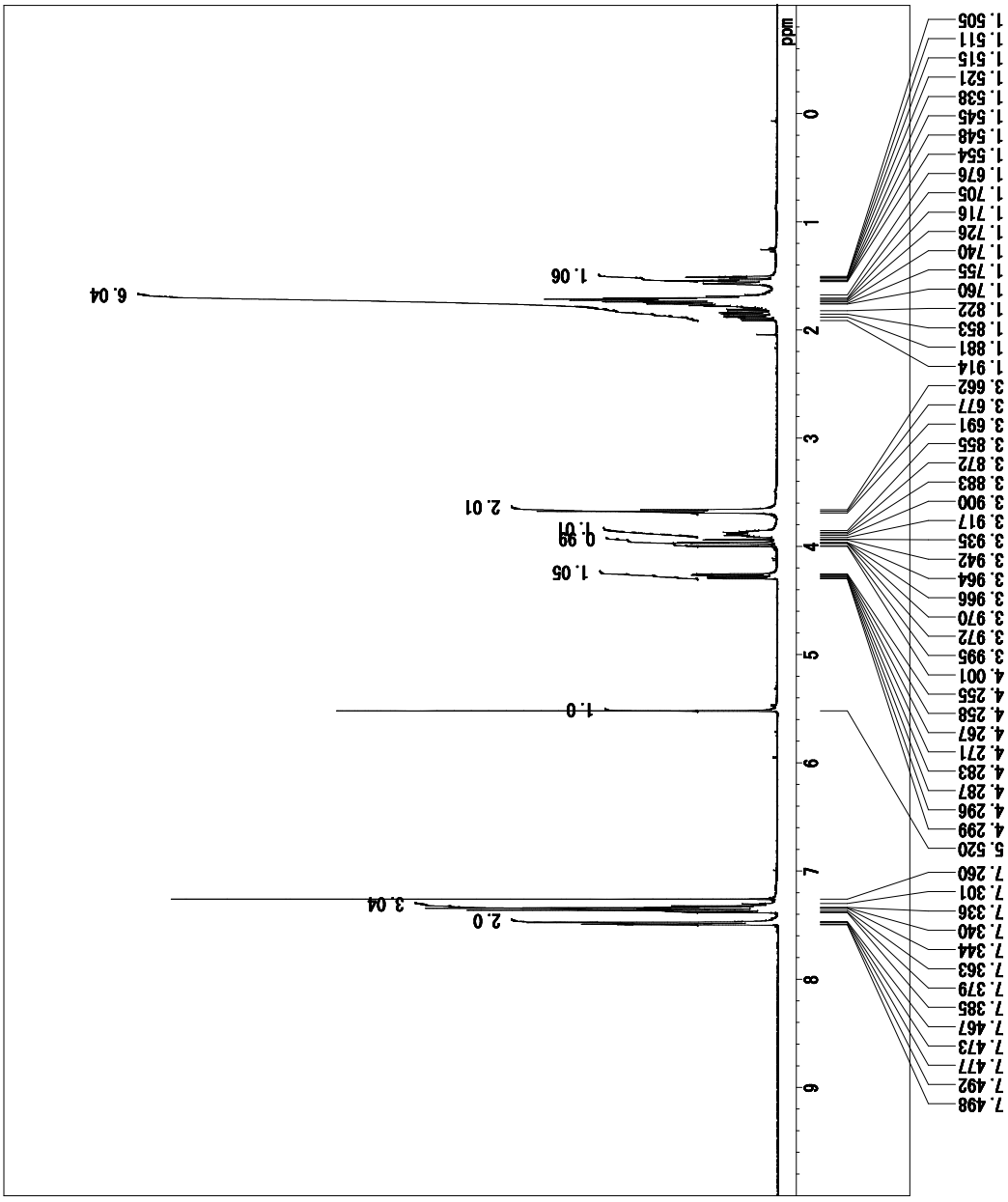

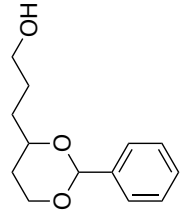

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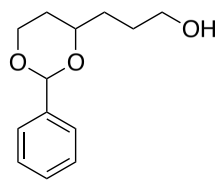

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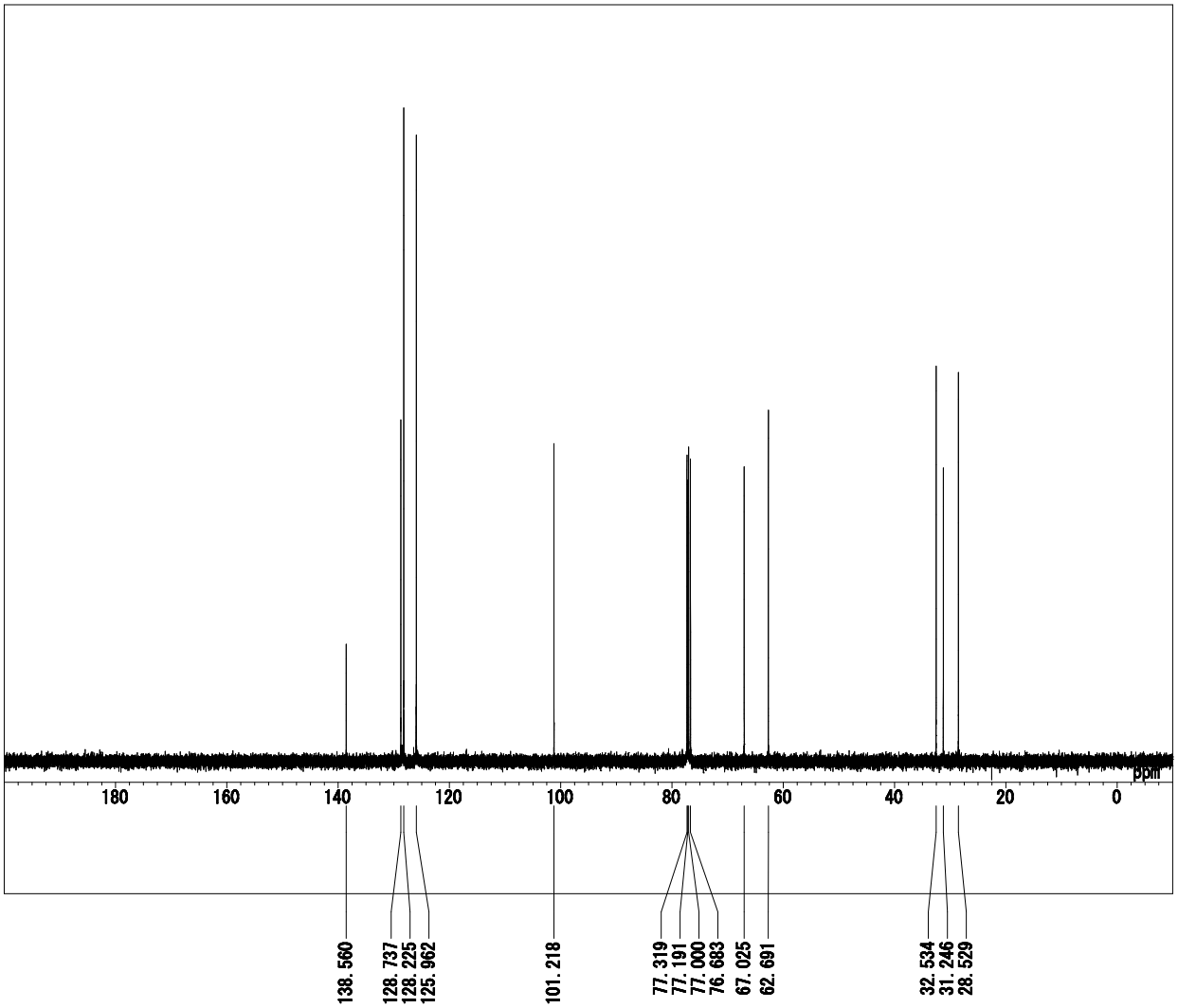

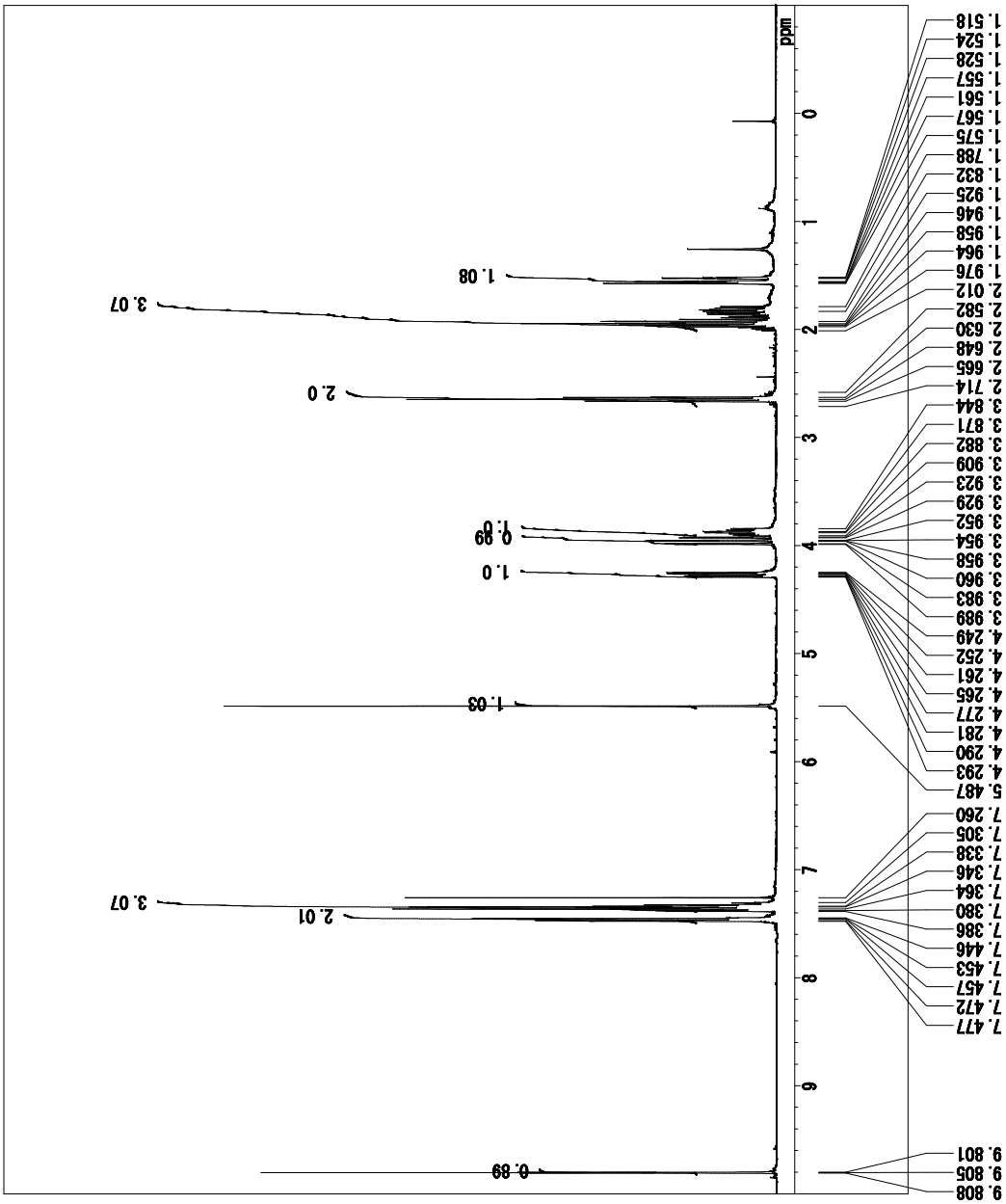

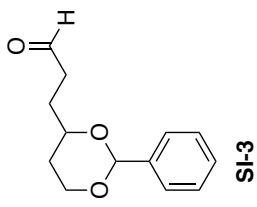

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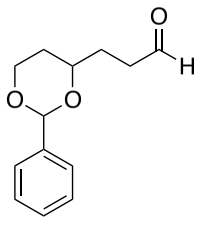

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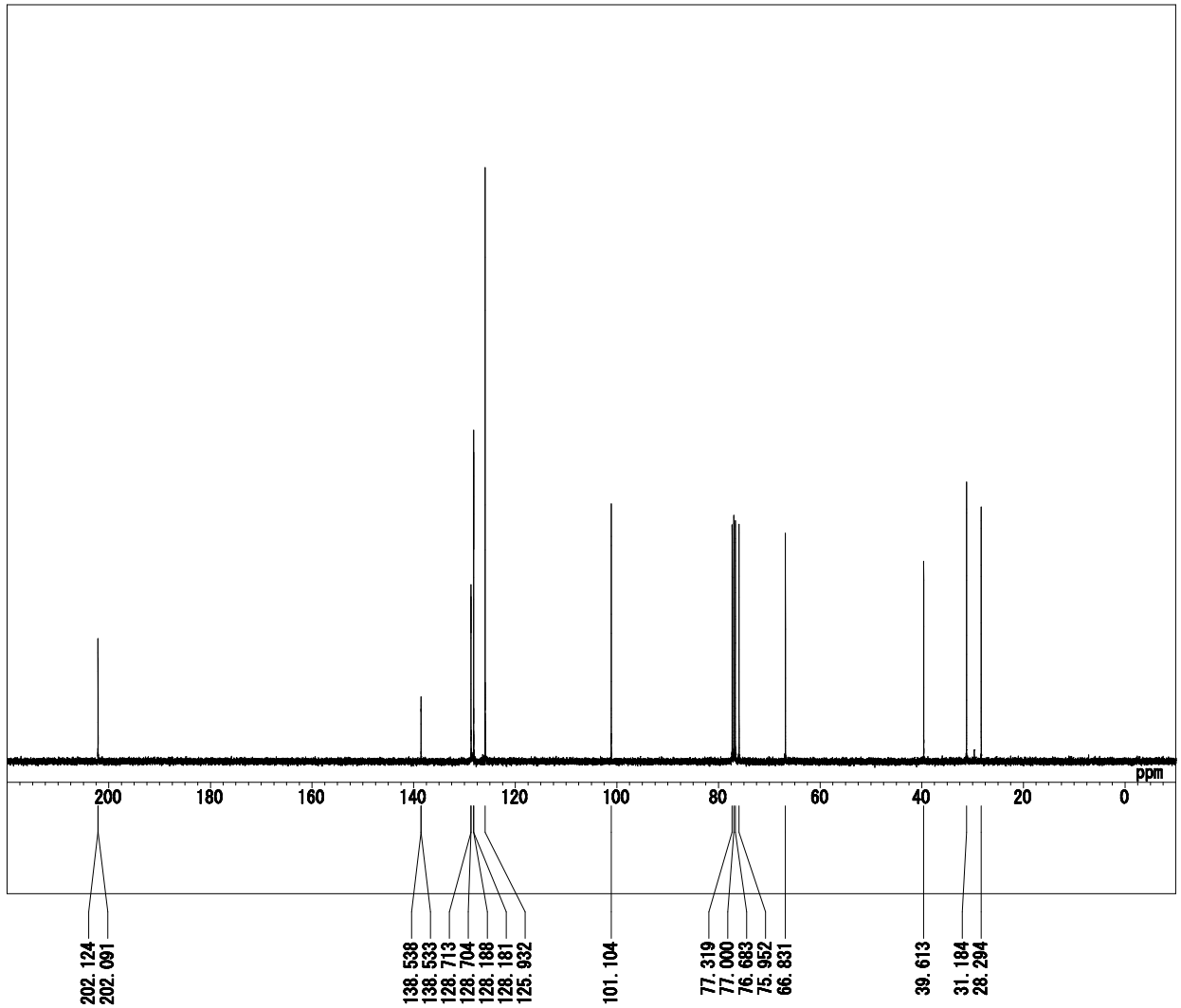
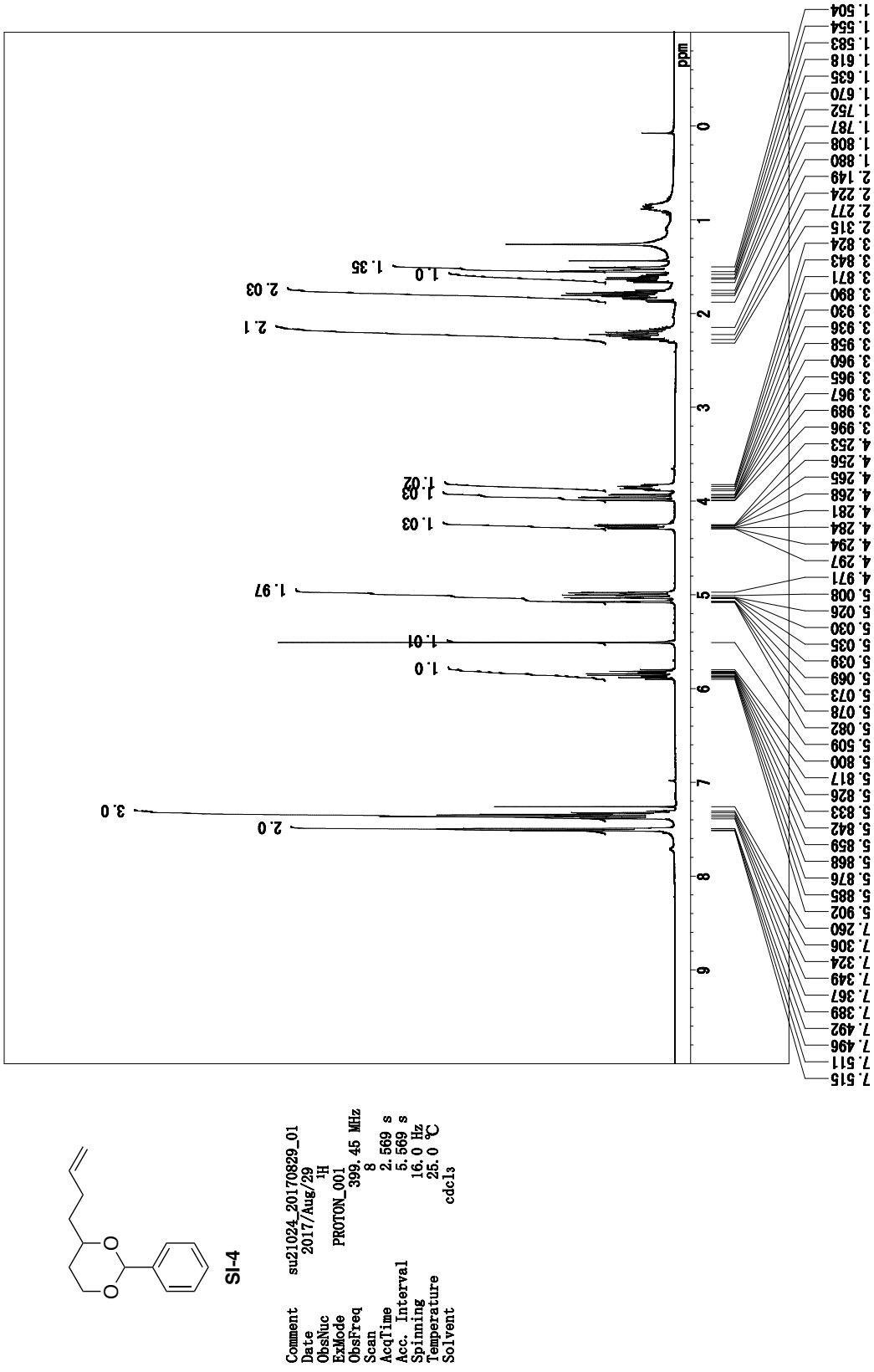
Solvent	cdcl3

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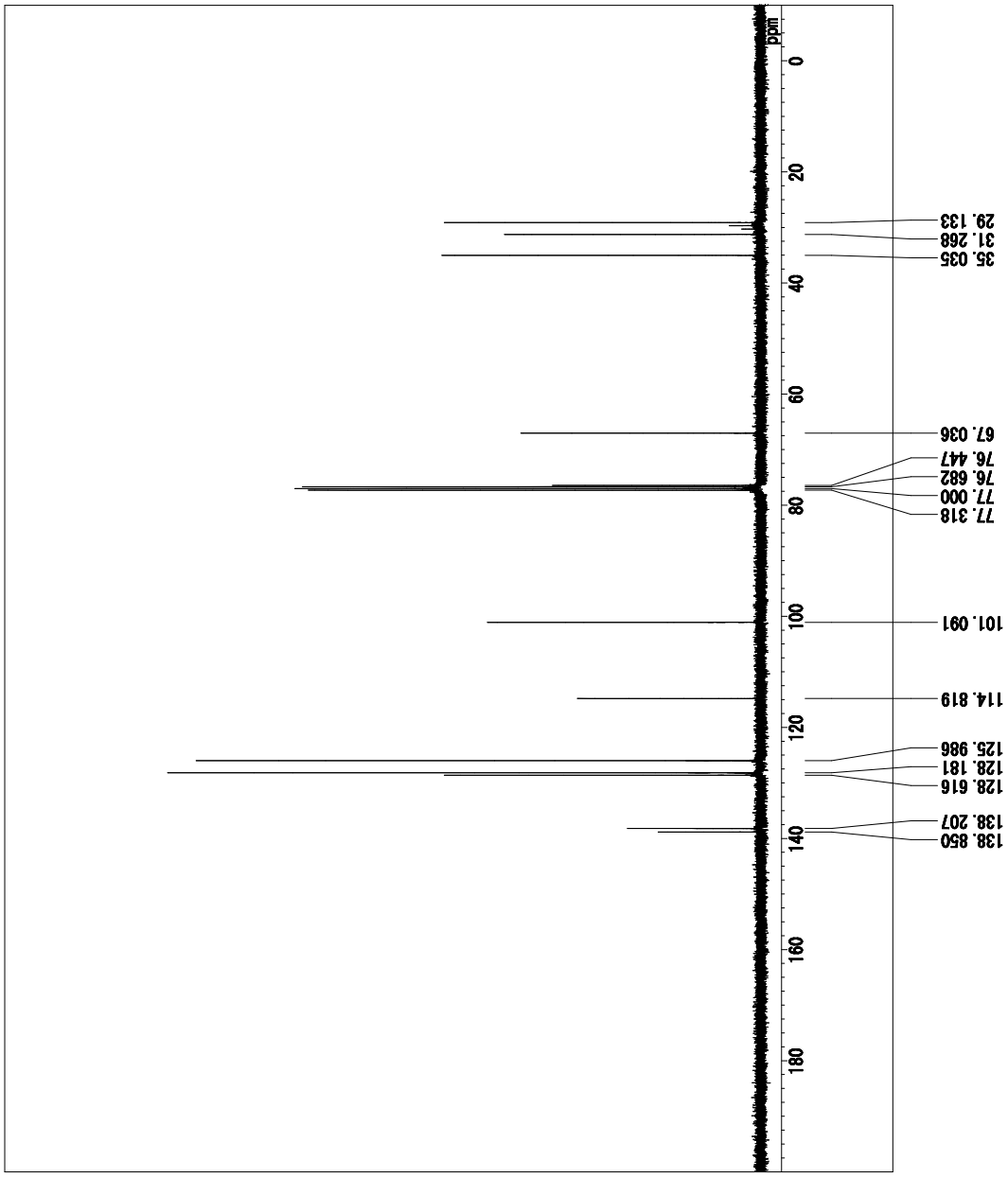
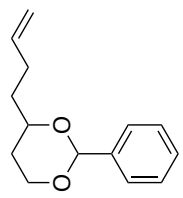
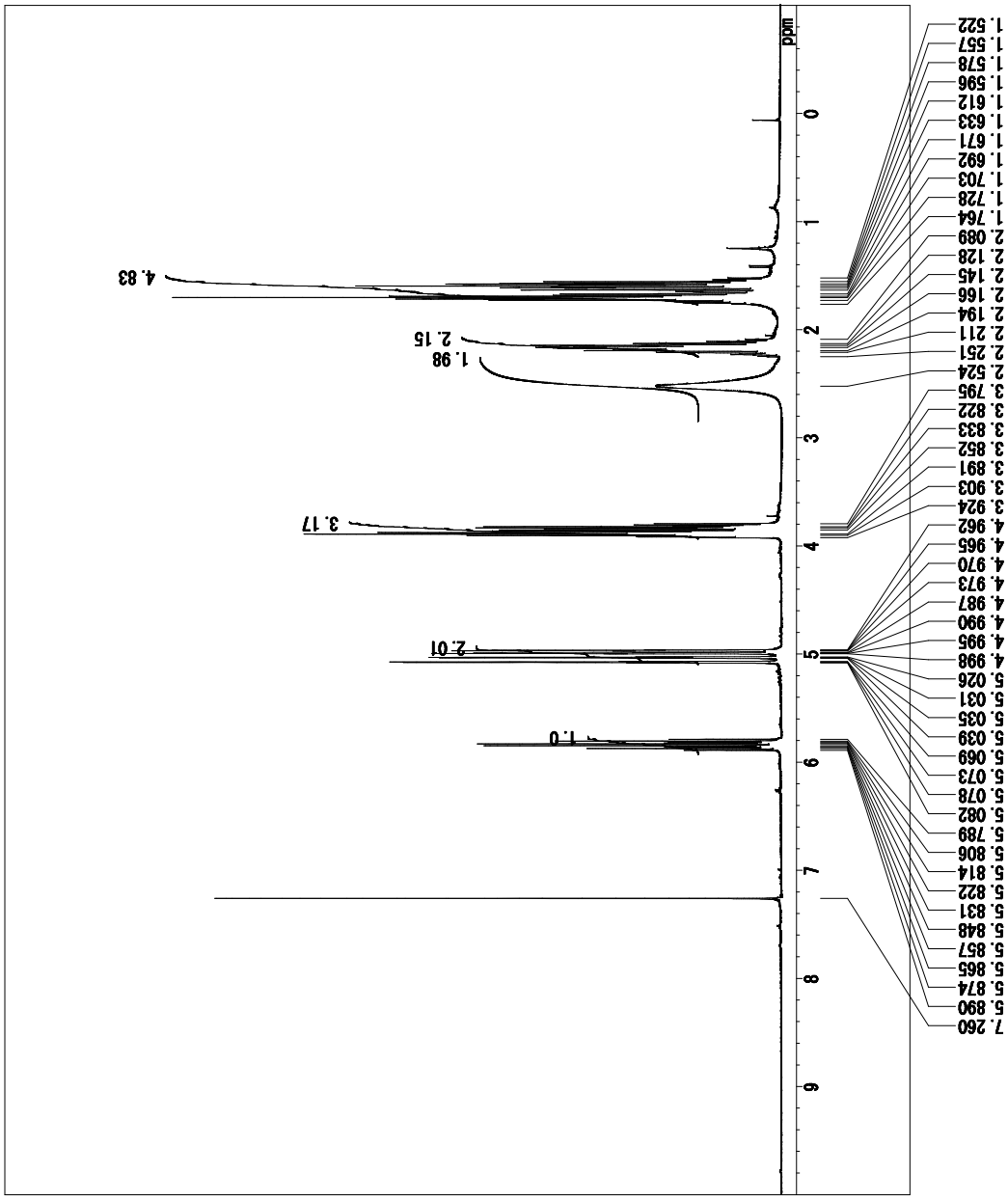
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
3.0
2.0
1.0
1.01
1.97
1.03
1.03
1.02
2.1
2.03
1.0
1.35

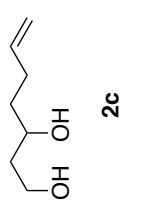




SI-4

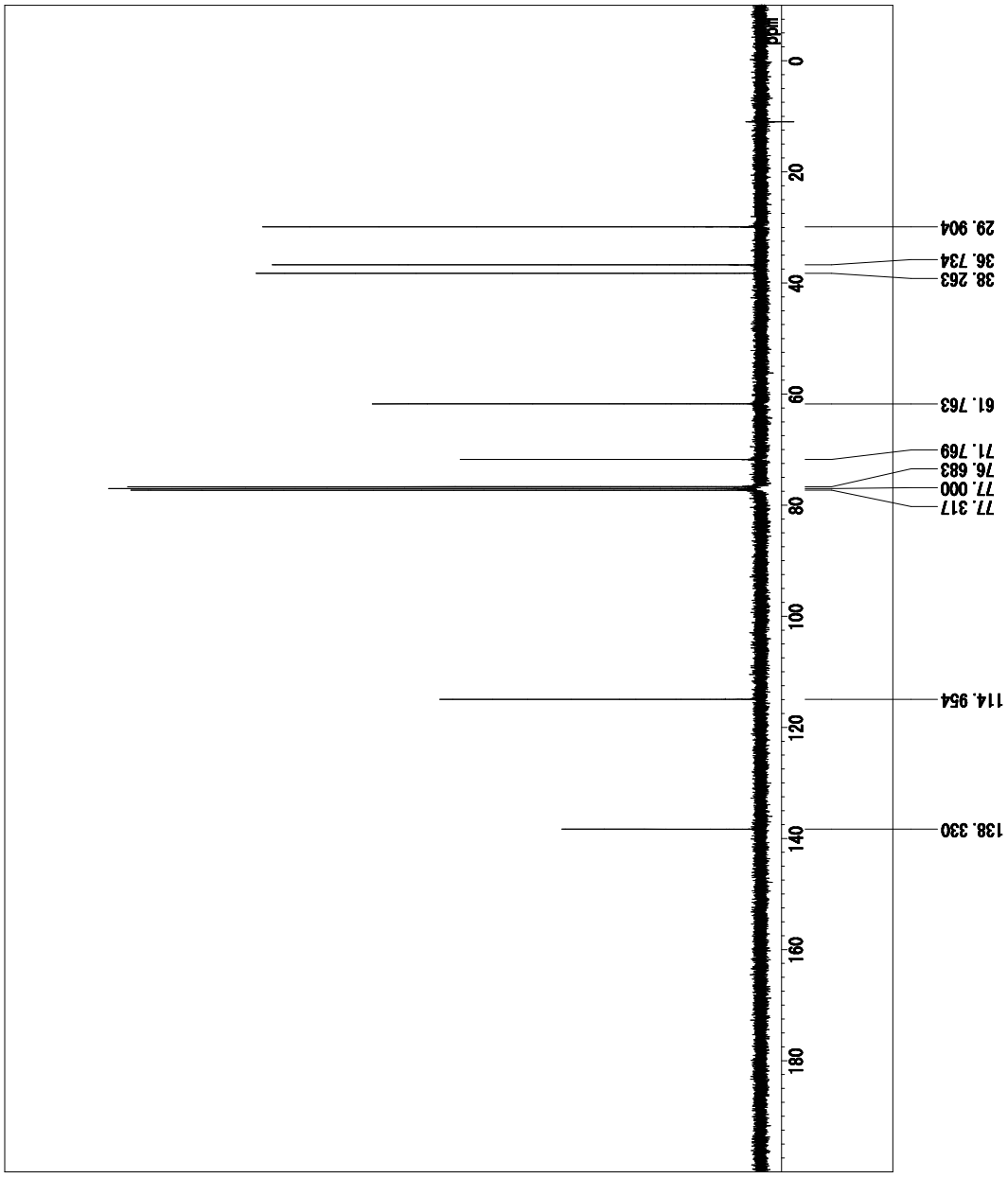
Comment su210124_20170829_01
Date 2017/Aug/29
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 704
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

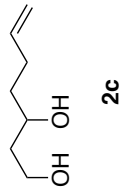




2c

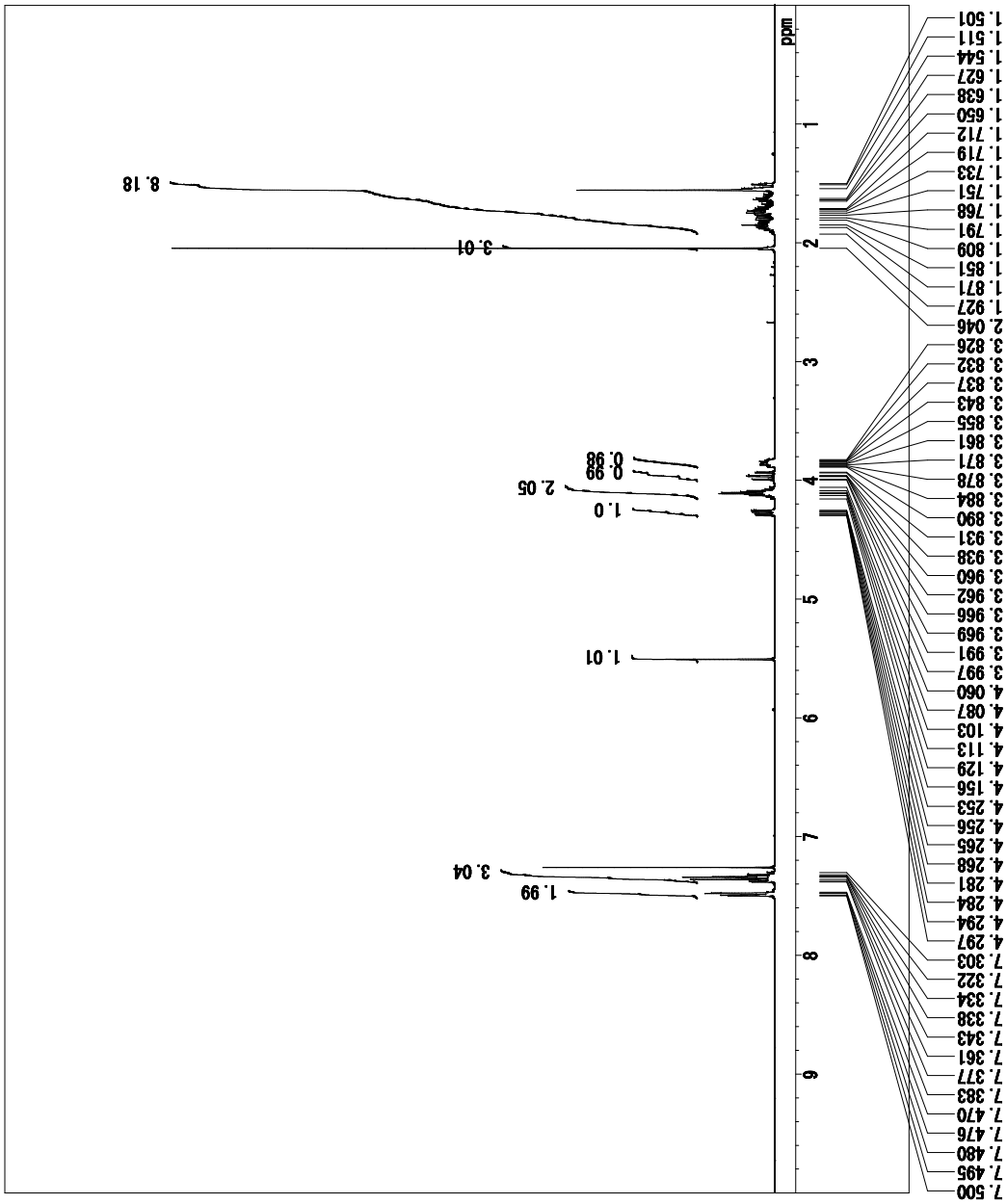
Comment su21025_20170830_01
Date 2017/Aug/30
ObsNuc 1H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 8
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

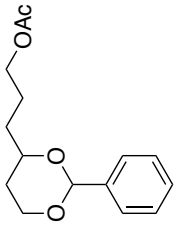




2c

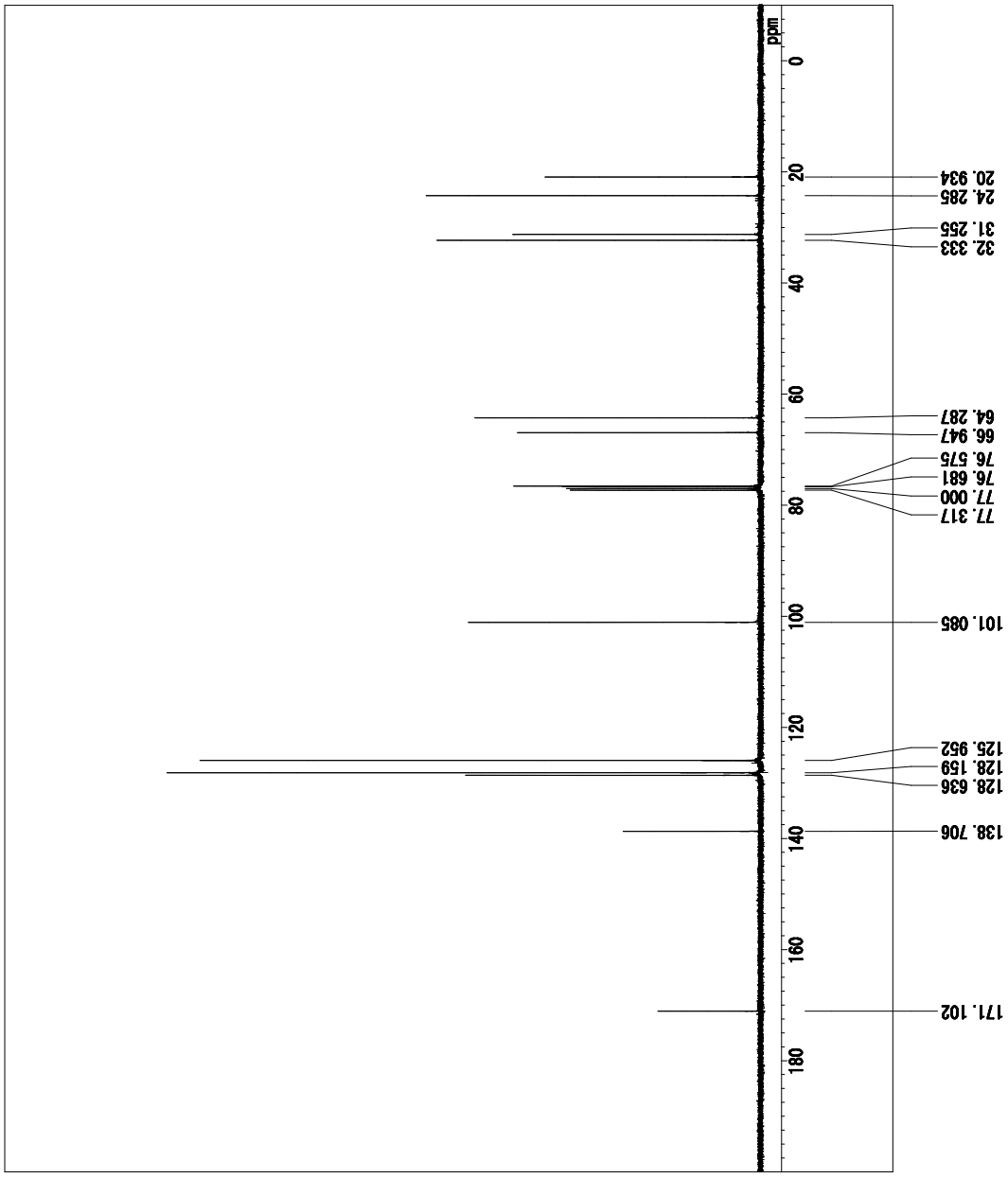
Comment su21025_20170830_01
Date 2017/Aug/30
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 704
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

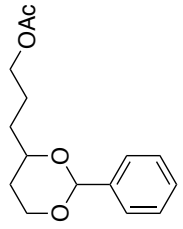




SI-5

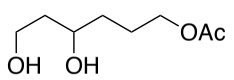
Comment su20037pure_20170717_01
Date 2017/Jul/17
ObsNuc 1H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 32
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3





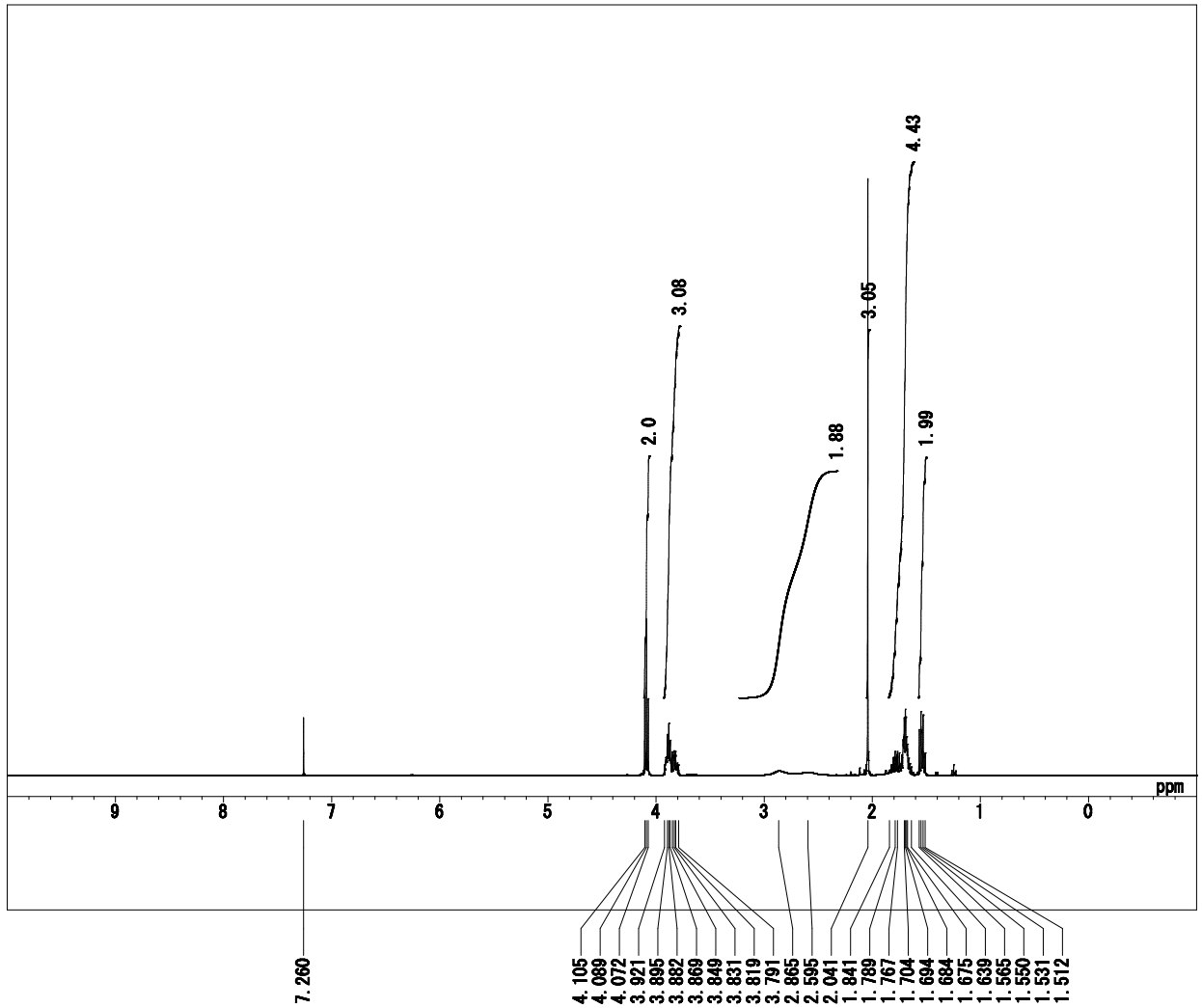
SI-5

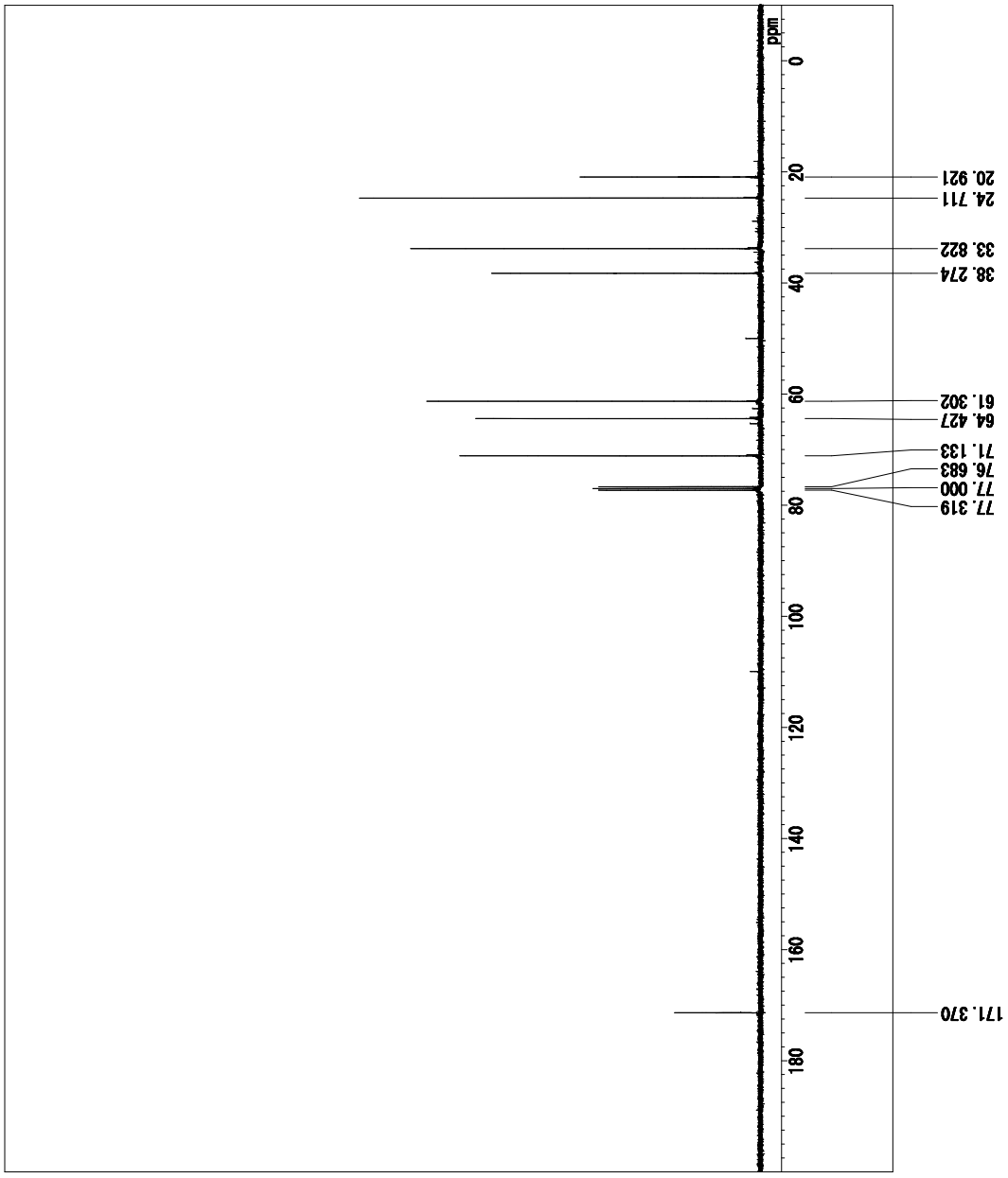
Comment su210226-13C_20170830_01
Date 2017/Aug/30
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 480
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

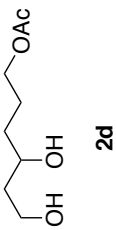


2d

Comment	su20038pure-2_20170719_01
Date	2017/Jul/19
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

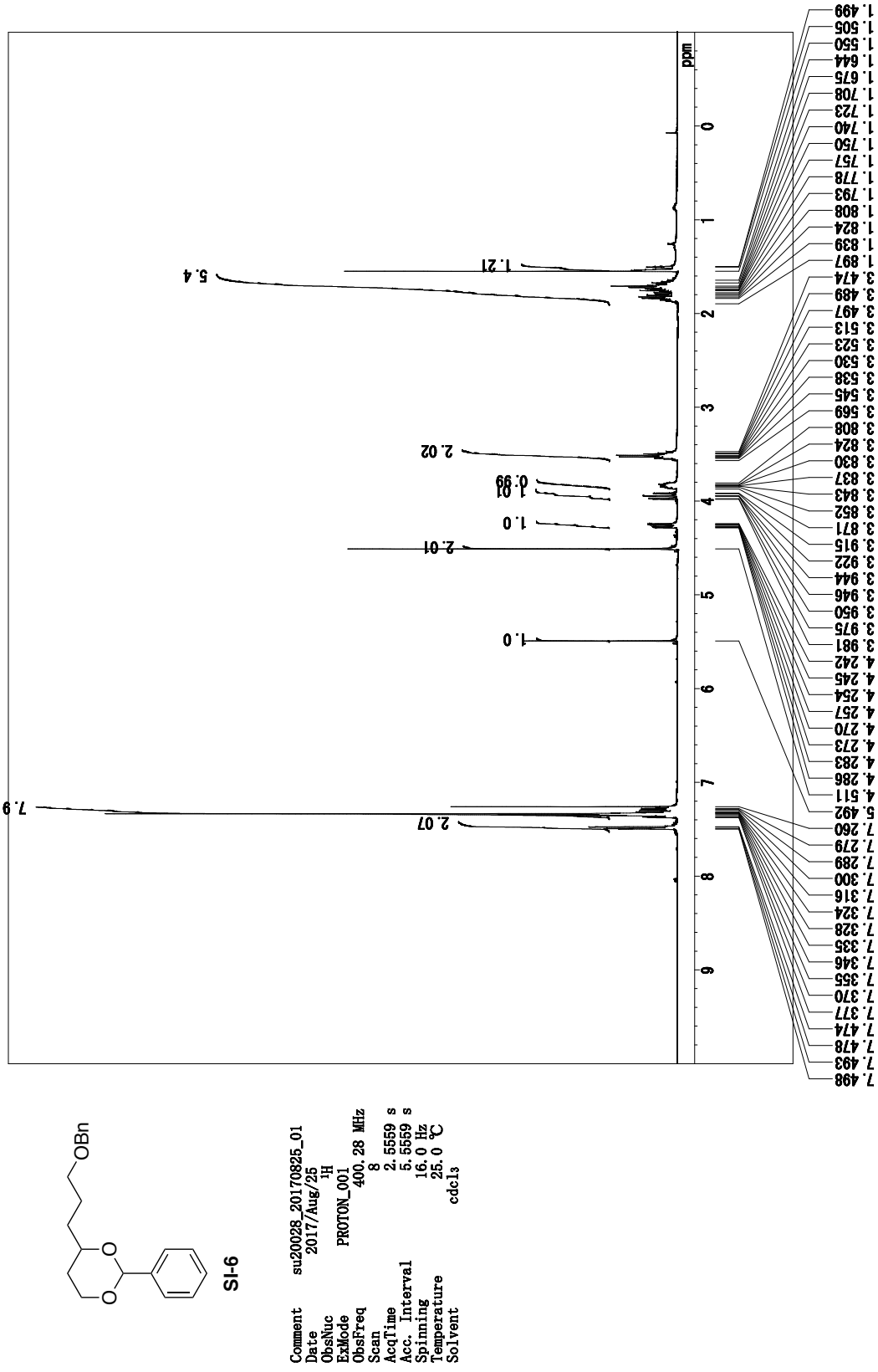


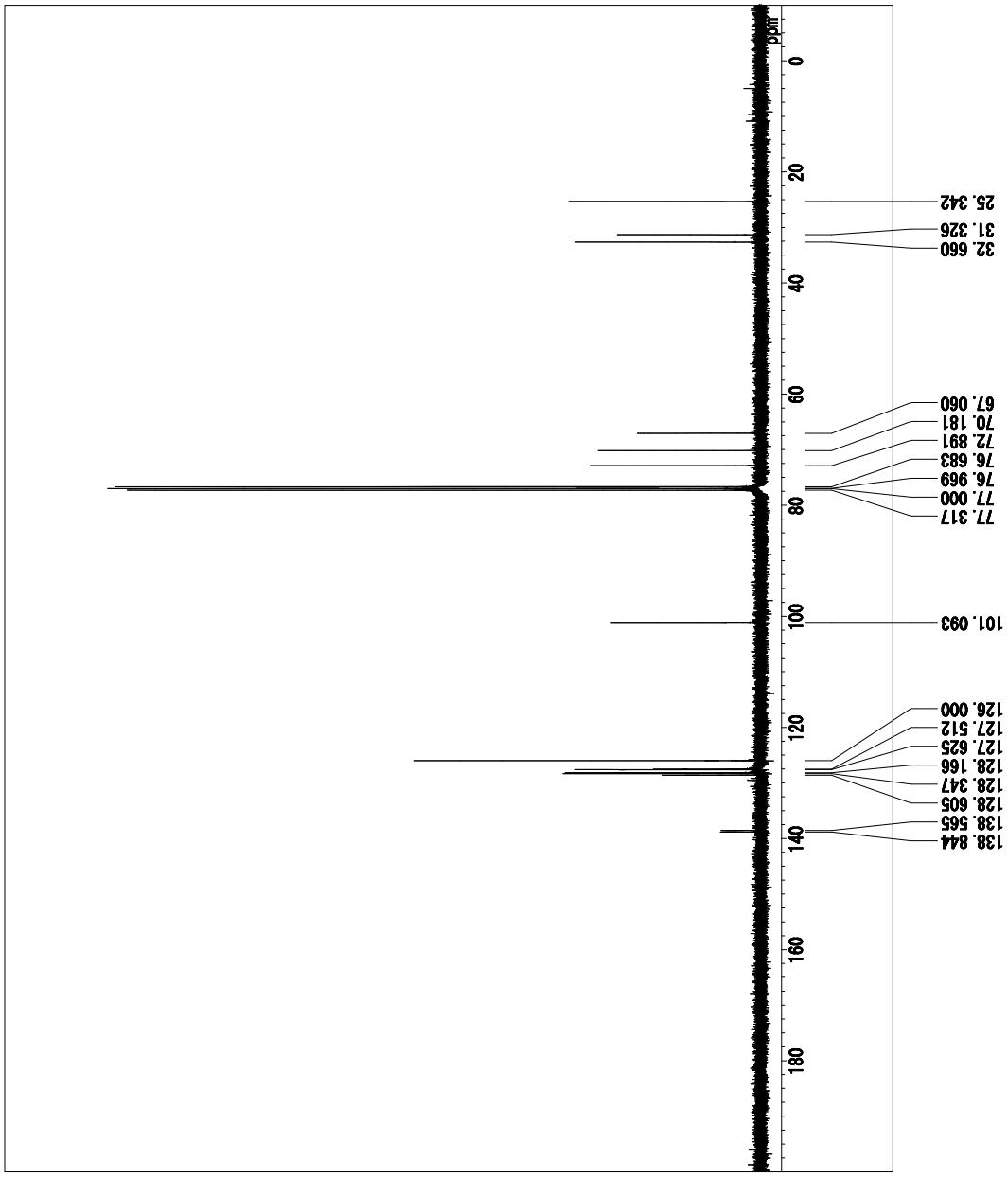


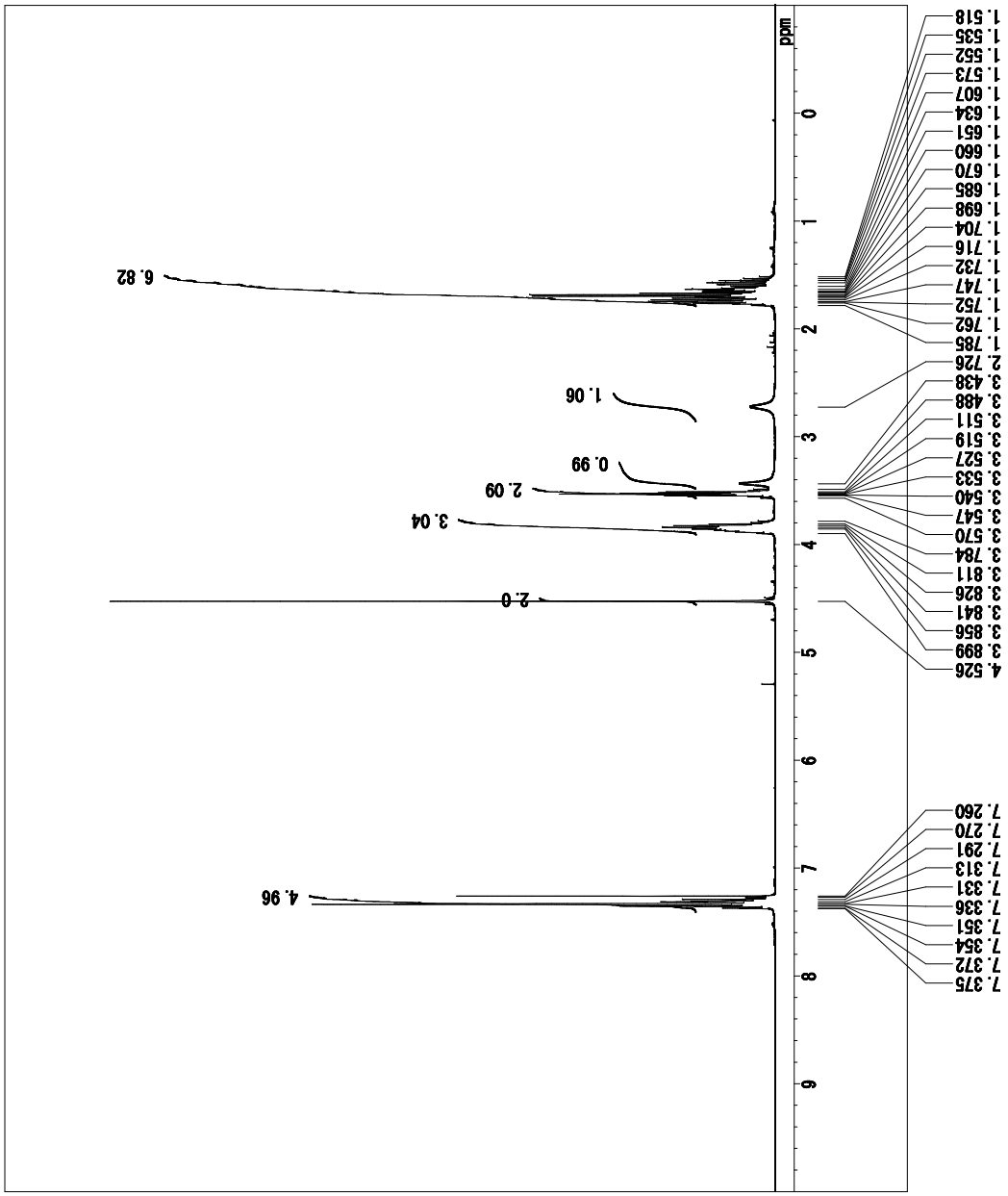


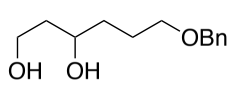
2d

Comment su20037-13C_20170802_01
Date 2017/Aug/02
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 464
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3


OBn
O
O
SI-6
Comment su20028_20170825_01
Date 2017/Aug/25
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
ppm
7.9
2.07
1.0
2.01
1.0
1.01
0.99
2.02
1.21
5.4
7.498
7.493
7.478
7.474
7.377
7.370
7.355
7.346
7.335
7.328
7.324
7.316
7.300
7.289
7.279
7.260
5.492
4.511
4.286
4.283
4.273
4.270
4.257
4.254
4.245
4.242
3.981
3.975
3.950
3.946
3.944
3.922
3.915
3.871
3.852
3.843
3.837
3.830
3.824
3.808
3.569
3.545
3.538
3.530
3.523
3.513
3.497
3.489
3.474
1.897
1.839
1.824
1.808
1.793
1.778
1.757
1.750
1.740
1.723
1.708
1.675
1.644
1.550
1.505
1.499

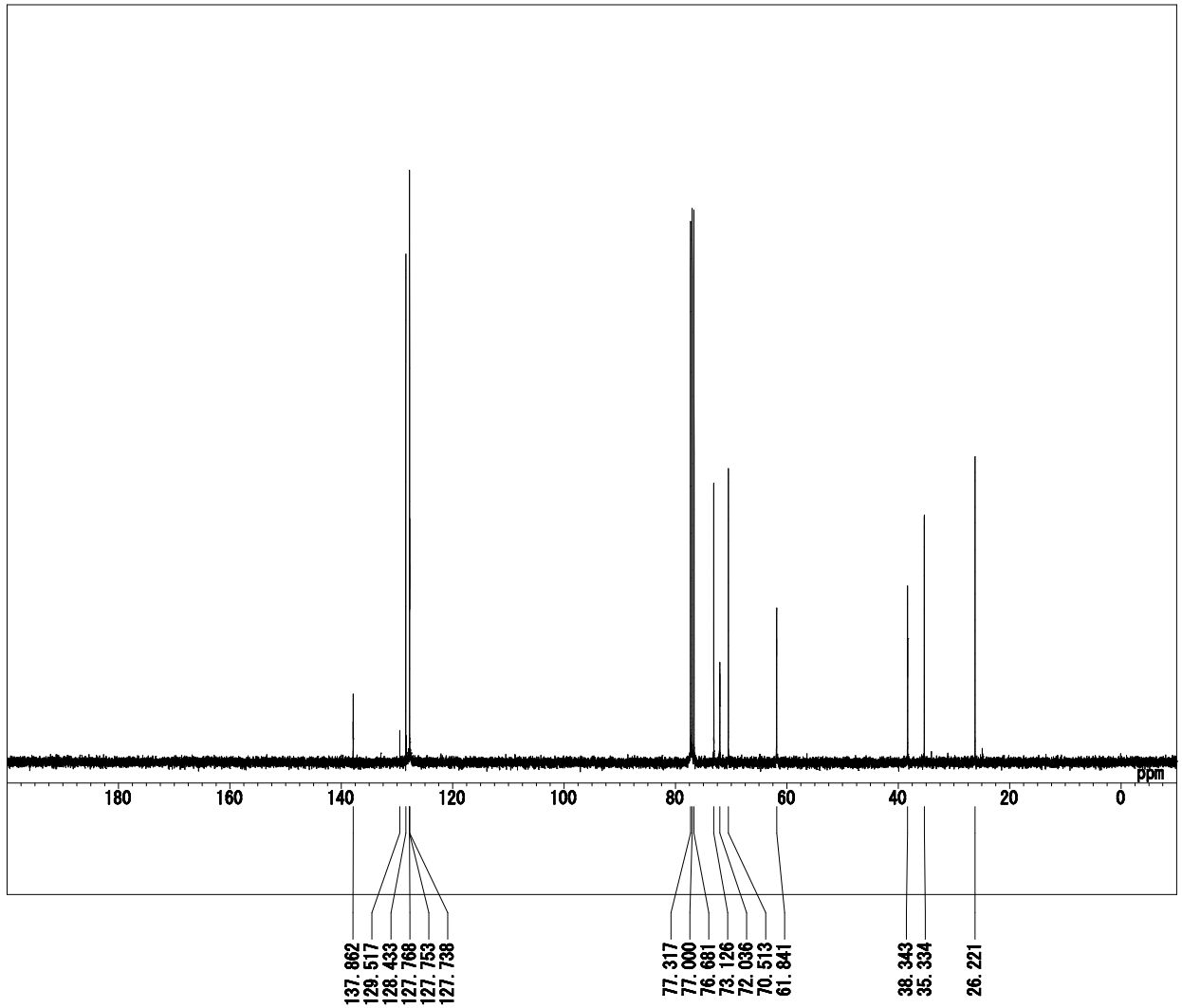

OBn
O
O
SI-6
Comment su20028-13C_20170825_01
Date 2017/Aug/25
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 832
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
0
20
40
60
80
100
120
140
160
180
25.342
31.326
32.660
67.060
70.181
72.891
76.683
76.969
77.000
77.317
101.093
126.000
127.512
127.625
128.166
128.347
128.605
138.565
138.844

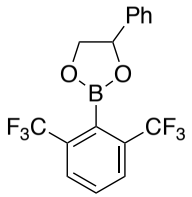

OBn
OH
OH
2e
Comment HRS03-20_pure_20170224_01
Date 2017/Feb/24
ObsNuc 1H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 8
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
6.82
4.96
3.04
2.09
2.00
1.06
0.99
ppm
0
1
2
3
4
5
6
7
8
9
1.518
1.535
1.552
1.573
1.607
1.634
1.651
1.660
1.670
1.685
1.698
1.704
1.716
1.732
1.747
1.752
1.762
1.785
2.726
3.438
3.488
3.511
3.519
3.527
3.533
3.540
3.547
3.570
3.784
3.811
3.826
3.841
3.856
3.899
4.526
7.260
7.270
7.291
7.313
7.331
7.336
7.351
7.354
7.372
7.375



2e

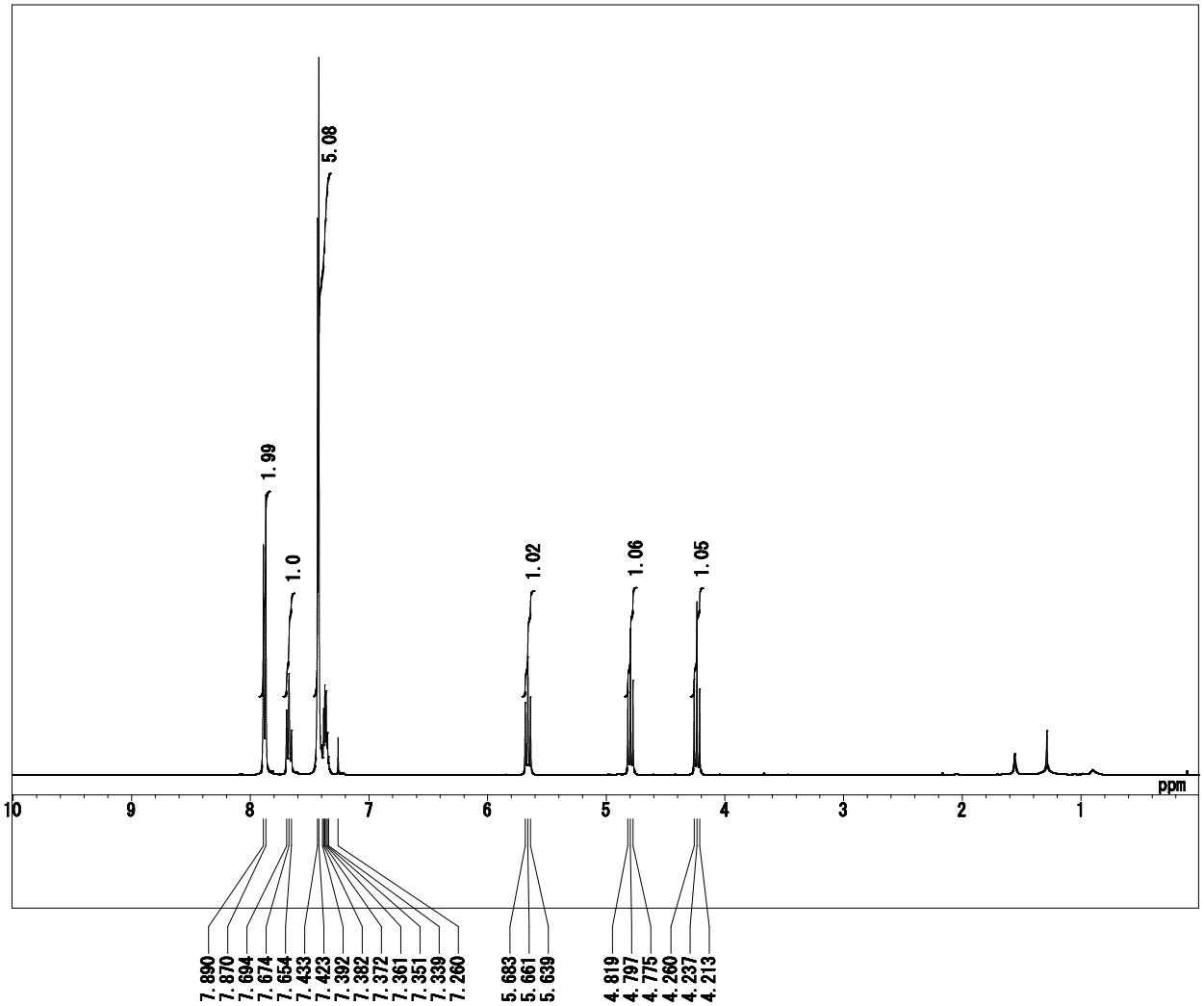
Comment	su-diol0Bn-13C_20170919_01
Date	2017/Sep/19
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	864
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

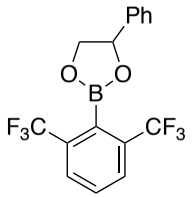




3a

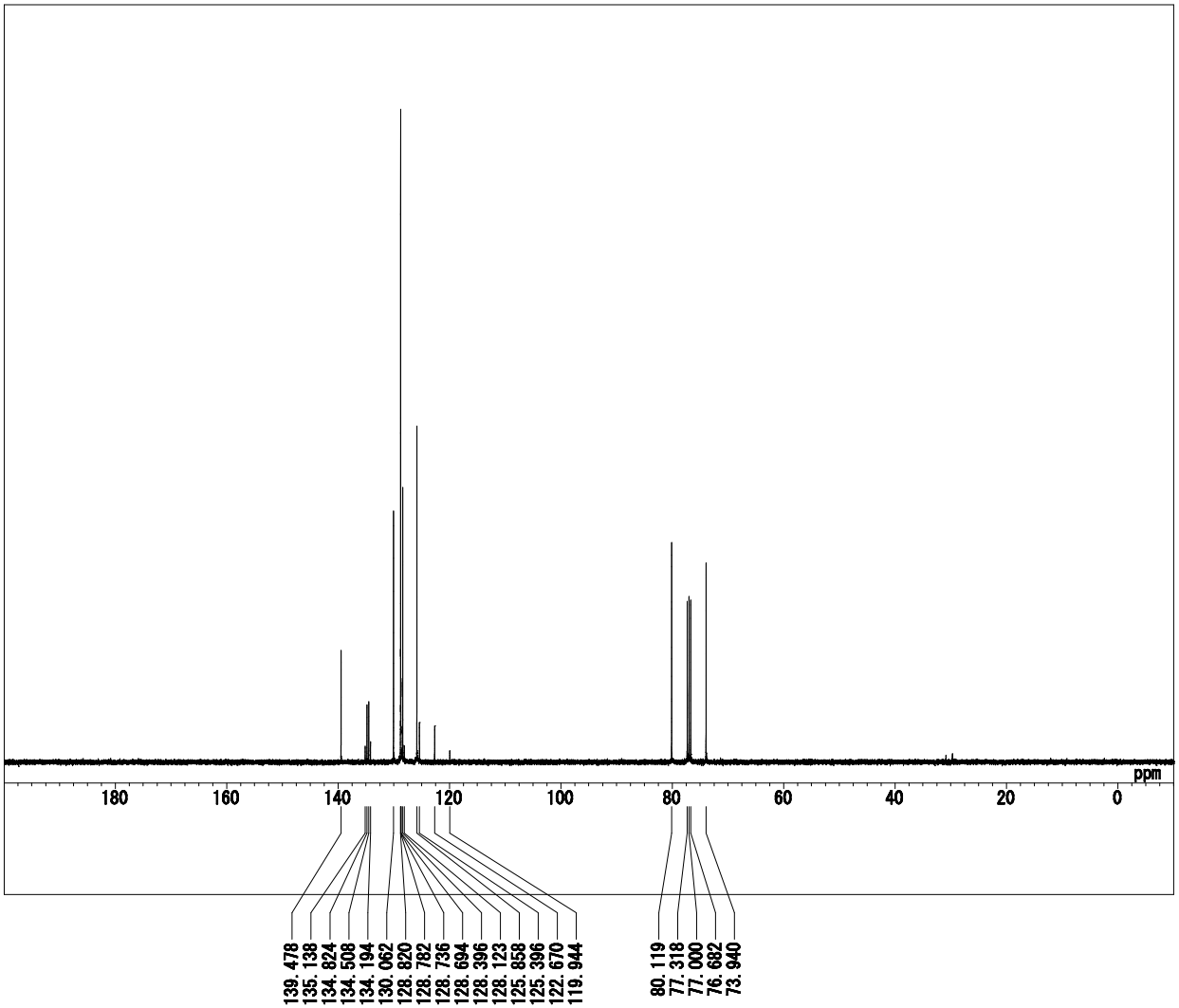
Comment	HRS02-10_pure_20160831_01
Date	2016/Aug/31
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

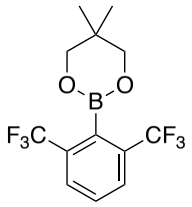




3a

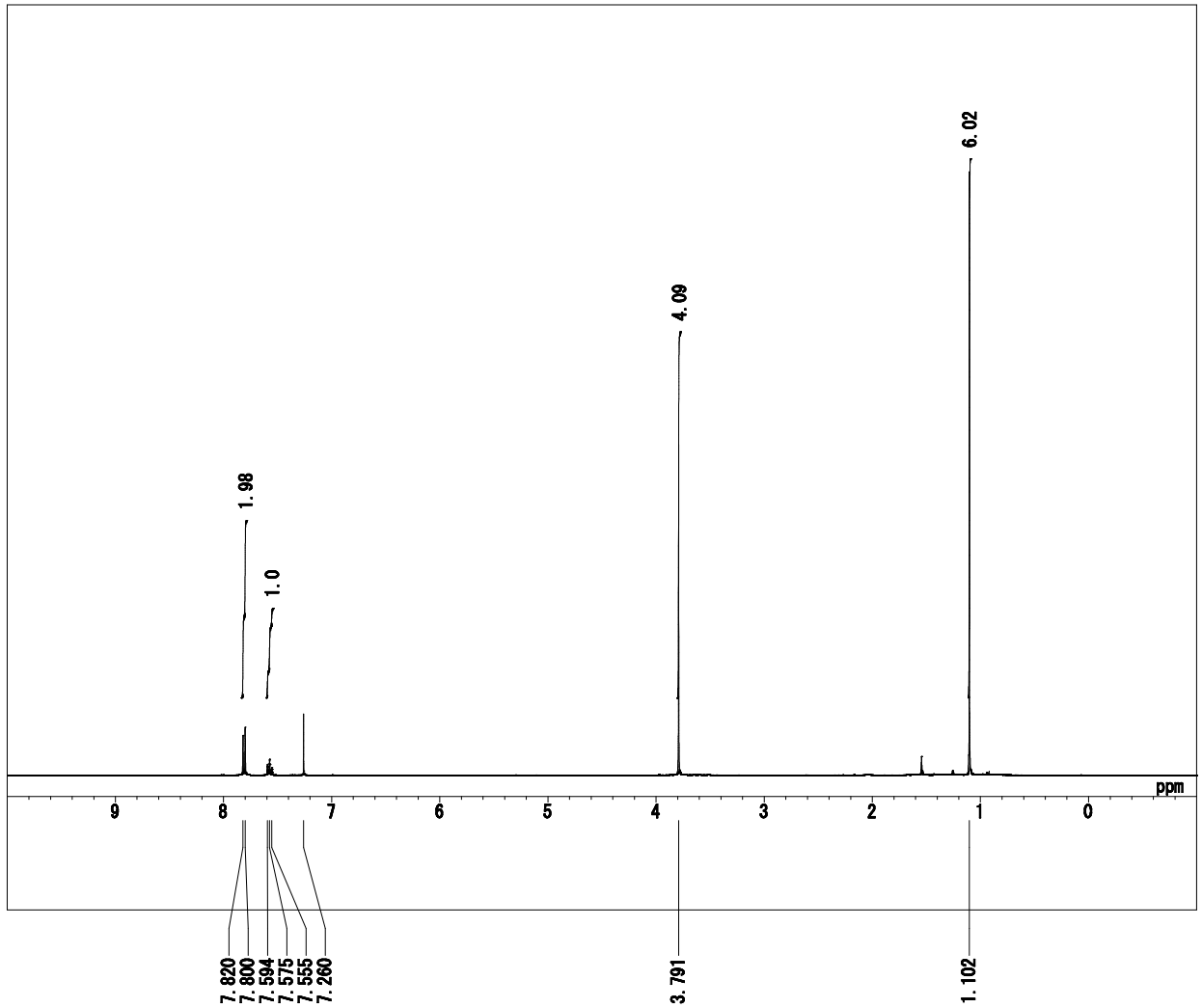
Comment	HRS02-10_C_20160831_01
Date	2016/Aug/31
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

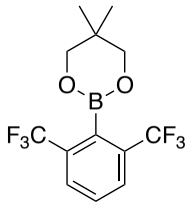




3b

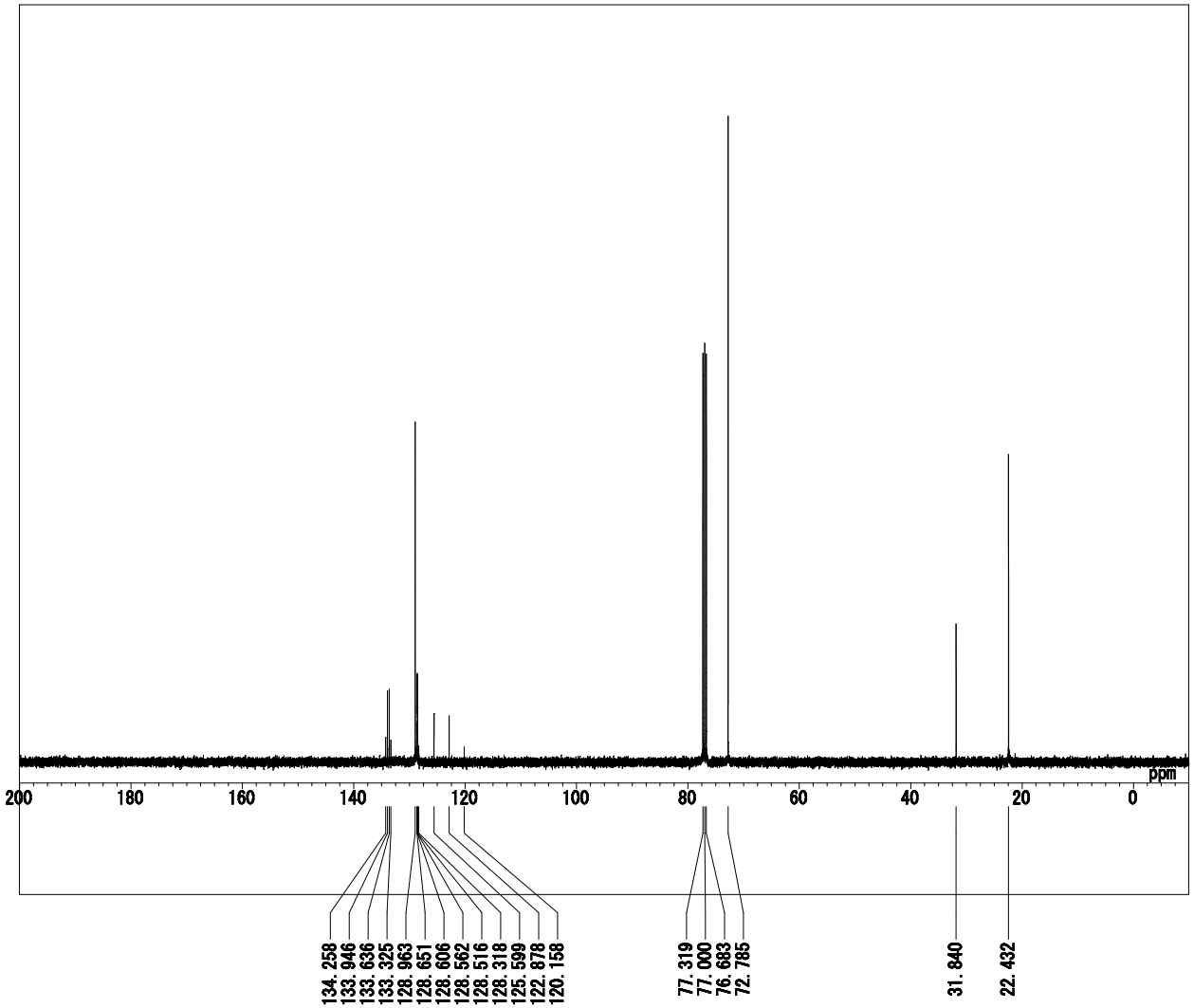
Comment	hrs01040_20160804_01
Date	2016/Aug/04
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl$_3$

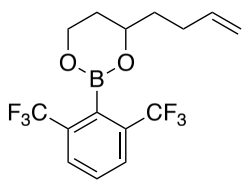




3b

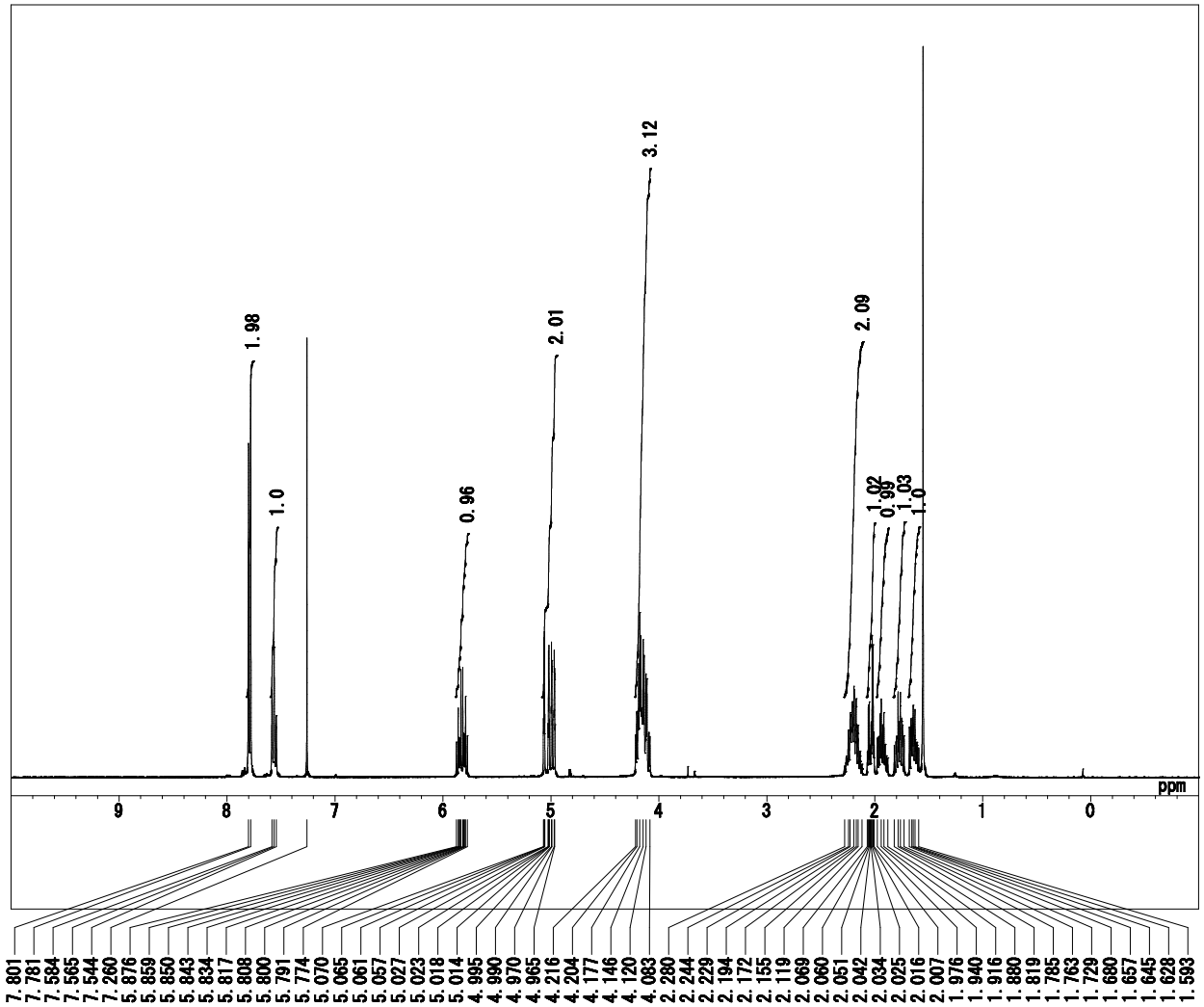
Comment	hrs01040-13C_20160804_01
Date	2016/Aug/04
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

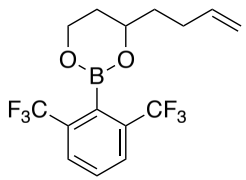




3c

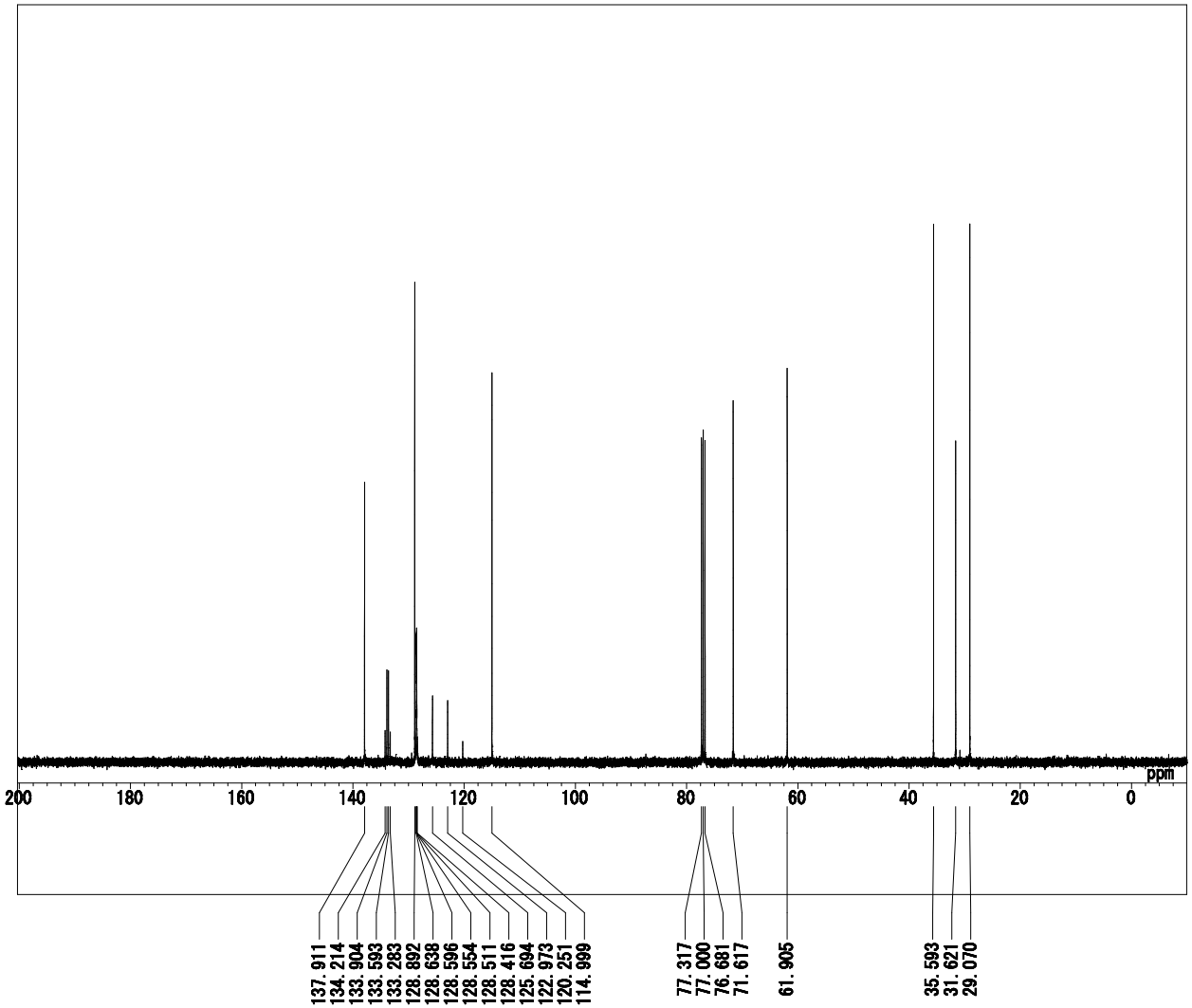
Comment	su14007crude_20160910_01
Date	2016/Sep/10
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

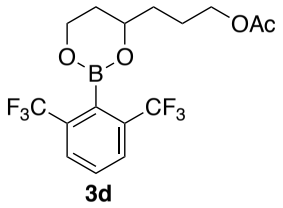




3c

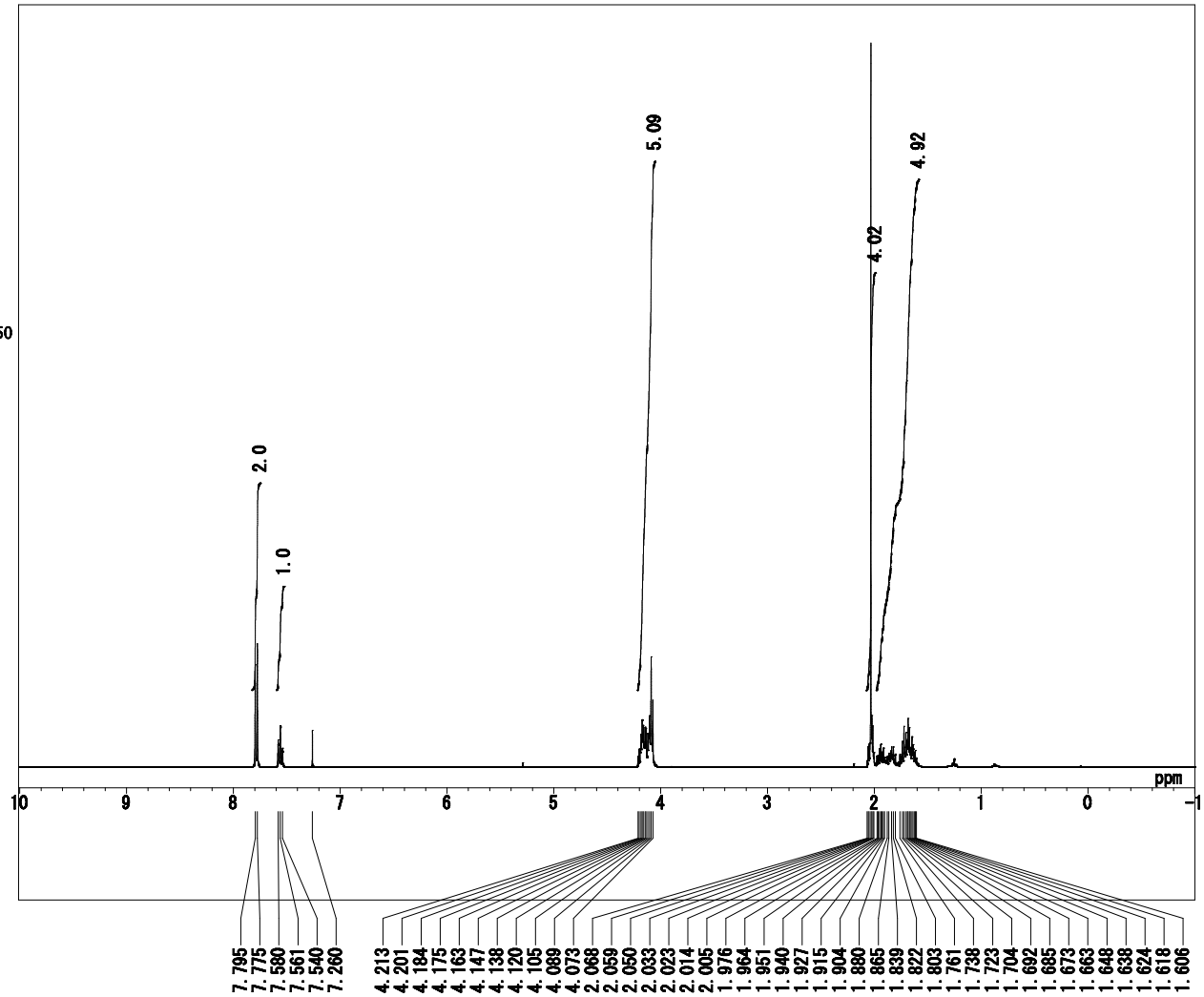
Comment	su14007-13C_20160911_01
Date	2016/Sep/11
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

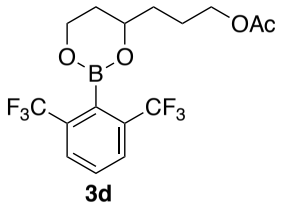




3d

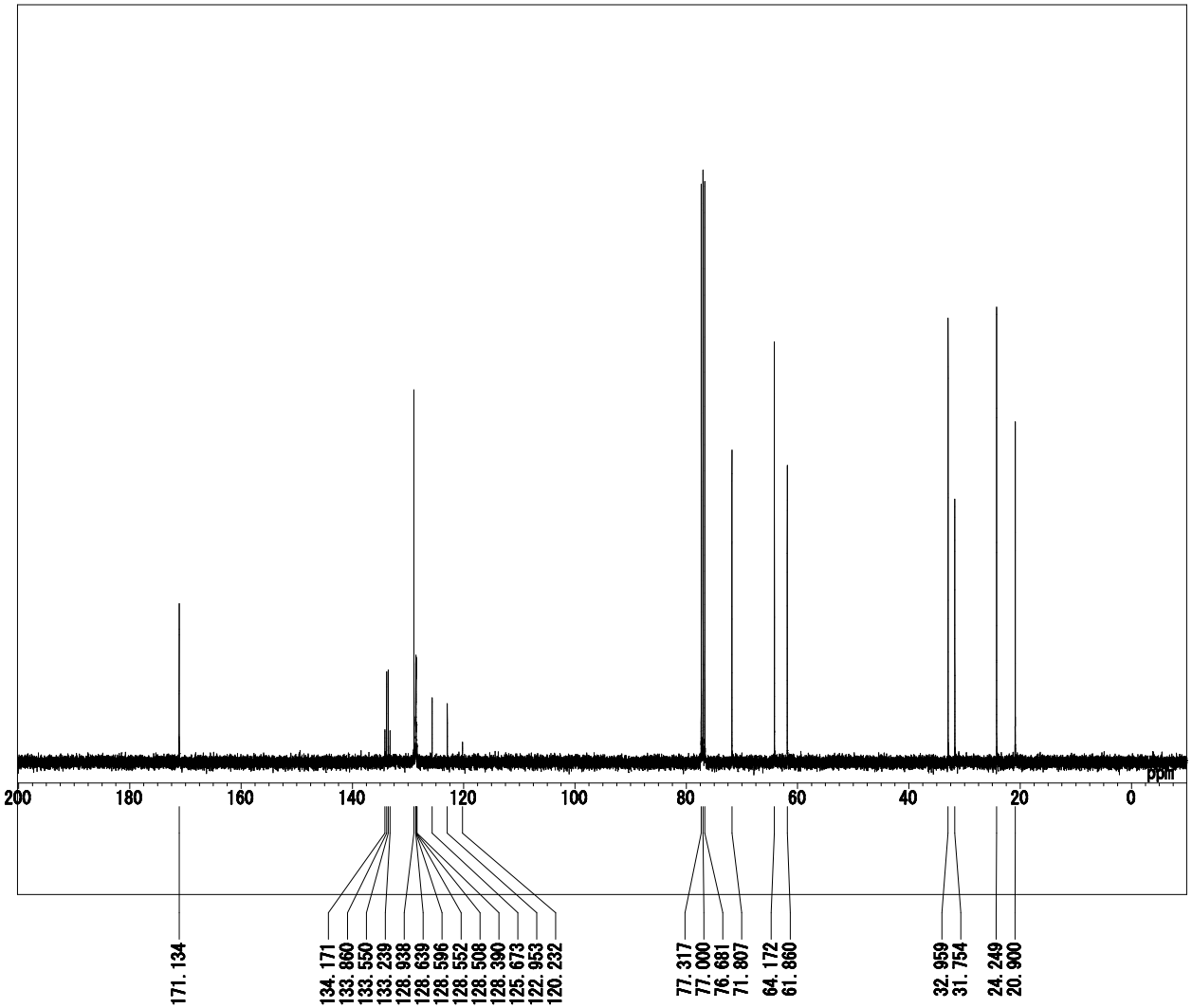
Comment NO-02-34pure-Ac-5_28_20150528_01
Date 2015/May/28
ObsNuc ^{1}H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 16
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 3.0 ℃
Solvent cdcl3

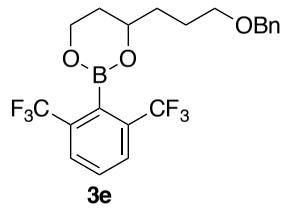




3d

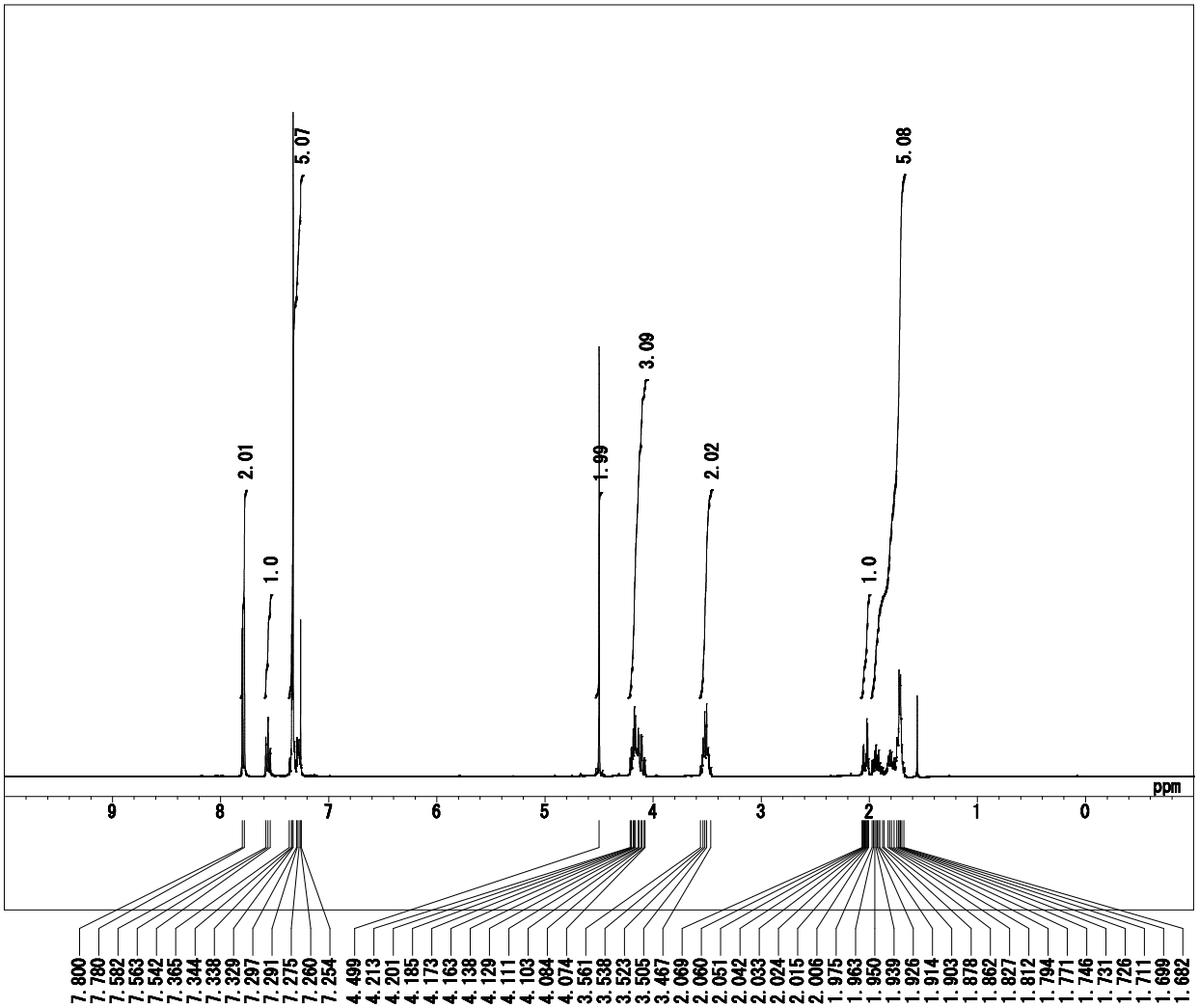
Comment	NO-Ac-C_20150419_03
Date	2015/Apr/19
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

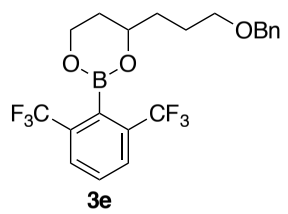




3e

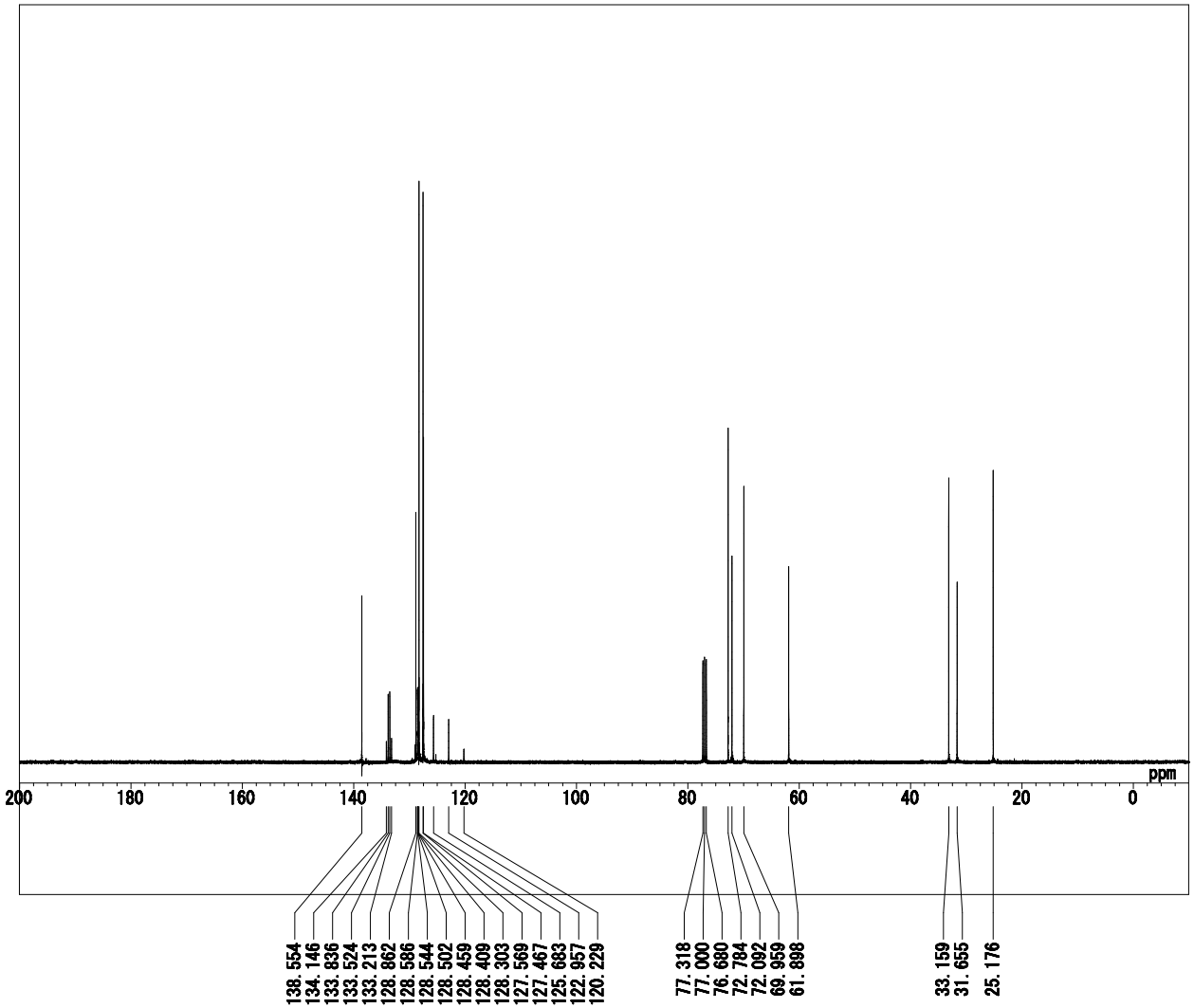
Comment	su10001pure-2
Date	2016/Aug/01
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

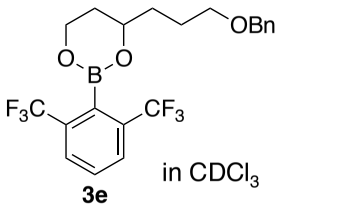




3e

Comment	su10001pure_20160730_01
Date	2016/Jul/30
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	25.0 ℃
Solvent	cdcl3

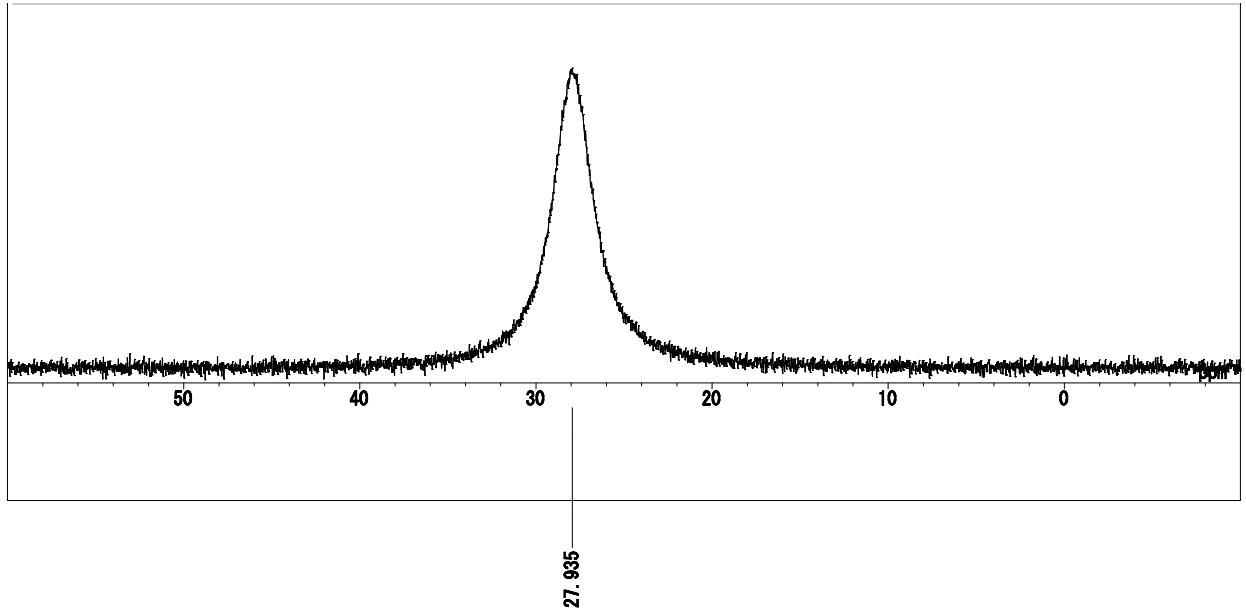


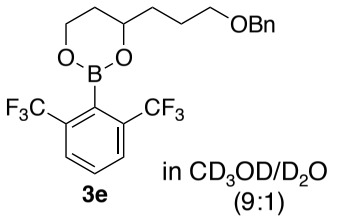


in $CDCl_3$

3e

Comment	
Date	2018/Aug/31
ObsNuc	^{11}B
ExMode	s2pul
ObsFreq	128.31 MHz
Scan	80
AcqTime	0.3211 s
Acc. Interval	2.0 s
Spinning	20.0 Hz
Temperature	50.0 ℃
Solvent	cdcl3

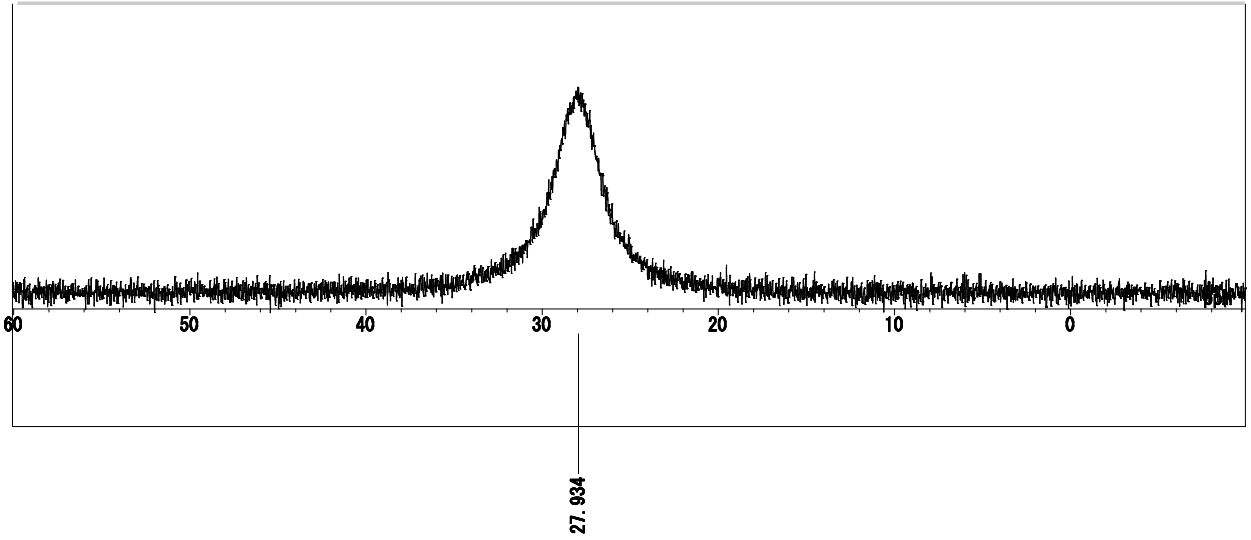


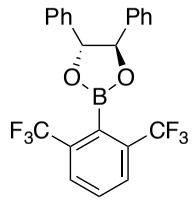


in CD_3OD/D_2O (9:1)

3e

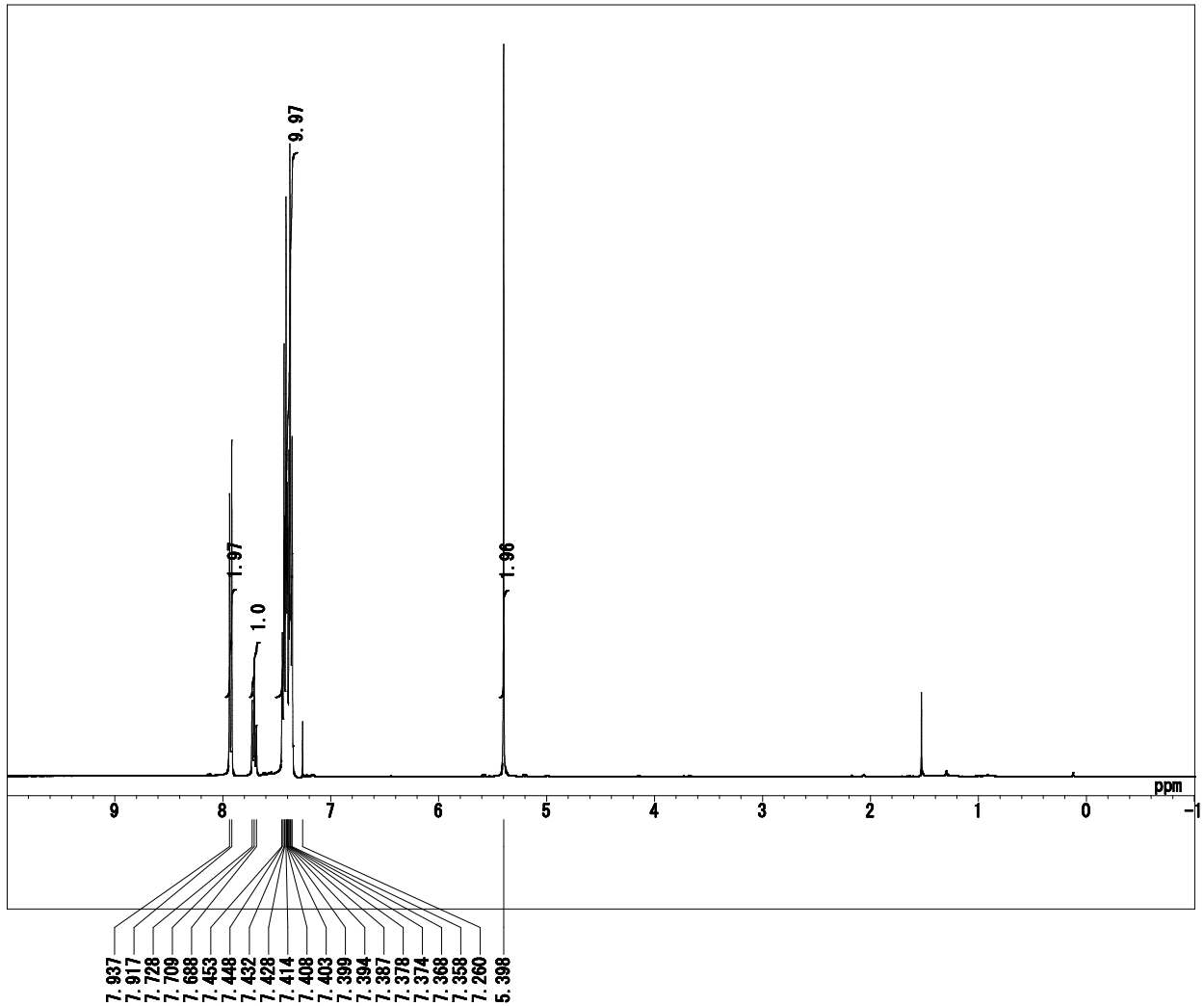
Comment	
Date	2018/Sep/01
ObsNuc	^{11}B
ExMode	s2pul
ObsFreq	128.31 MHz
Scan	80
AcqTime	0.3211 s
Acc. Interval	2.0 s
Spinning	20.0 Hz
Temperature	50.0 ℃
Solvent	cd3od

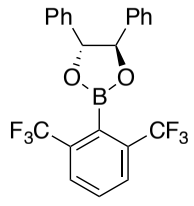




3f

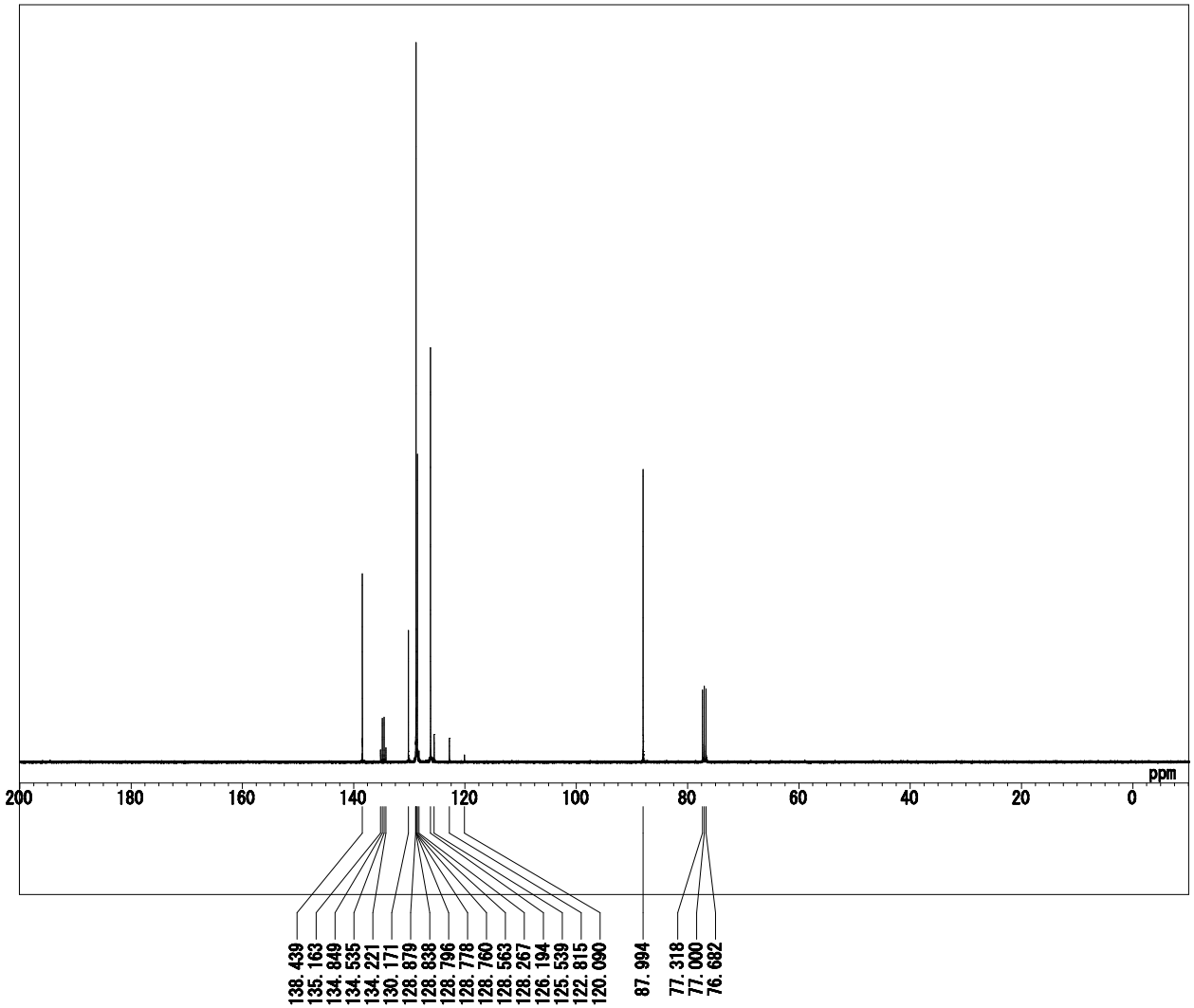
Comment	HRS02-09_pure_20160901_01
Date	2016/Sep/01
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

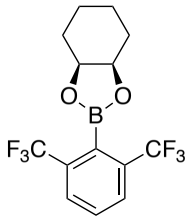




3f

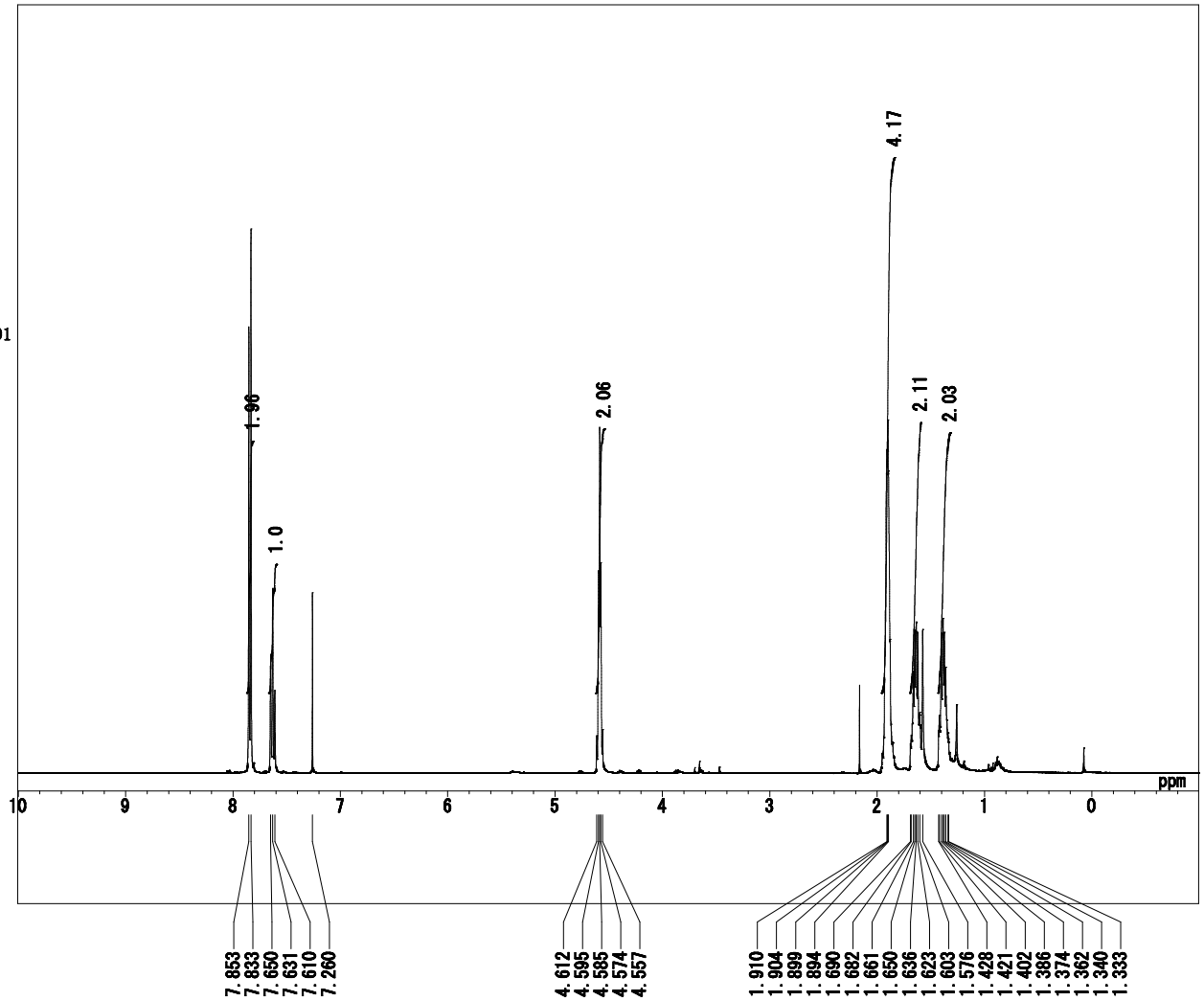
Comment	HRS02-09_C_20160905_01
Date	2016/Sep/05
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

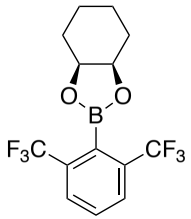




3g

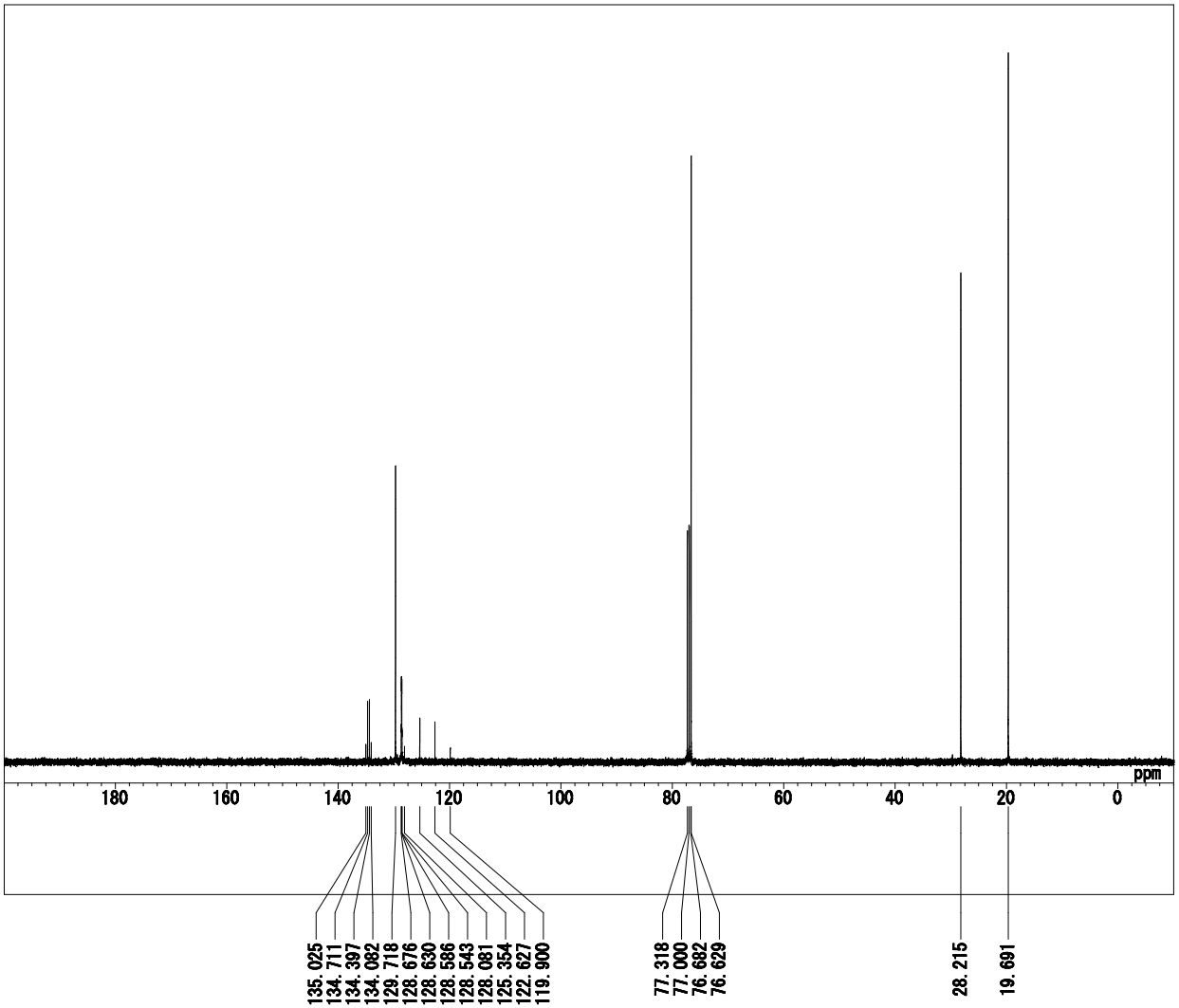
Comment	HRS01-35_pure2_20160906_01
Date	2016/Sep/06
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

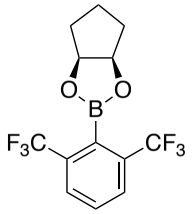




3g

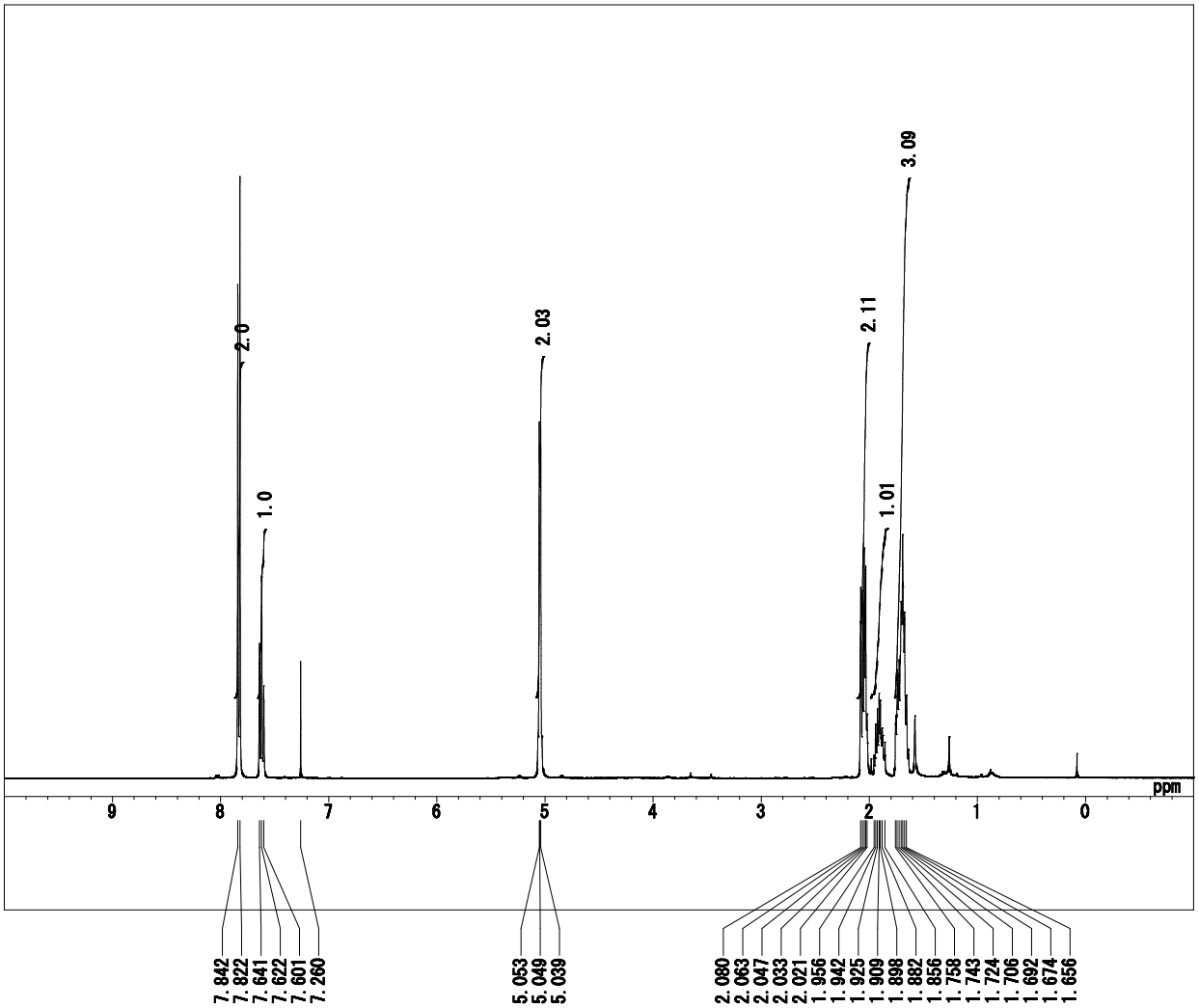
Comment	HRS01-35_C_20160907_01
Date	2016/Sep/07
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

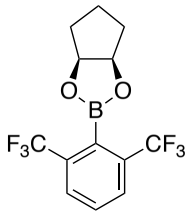




3h

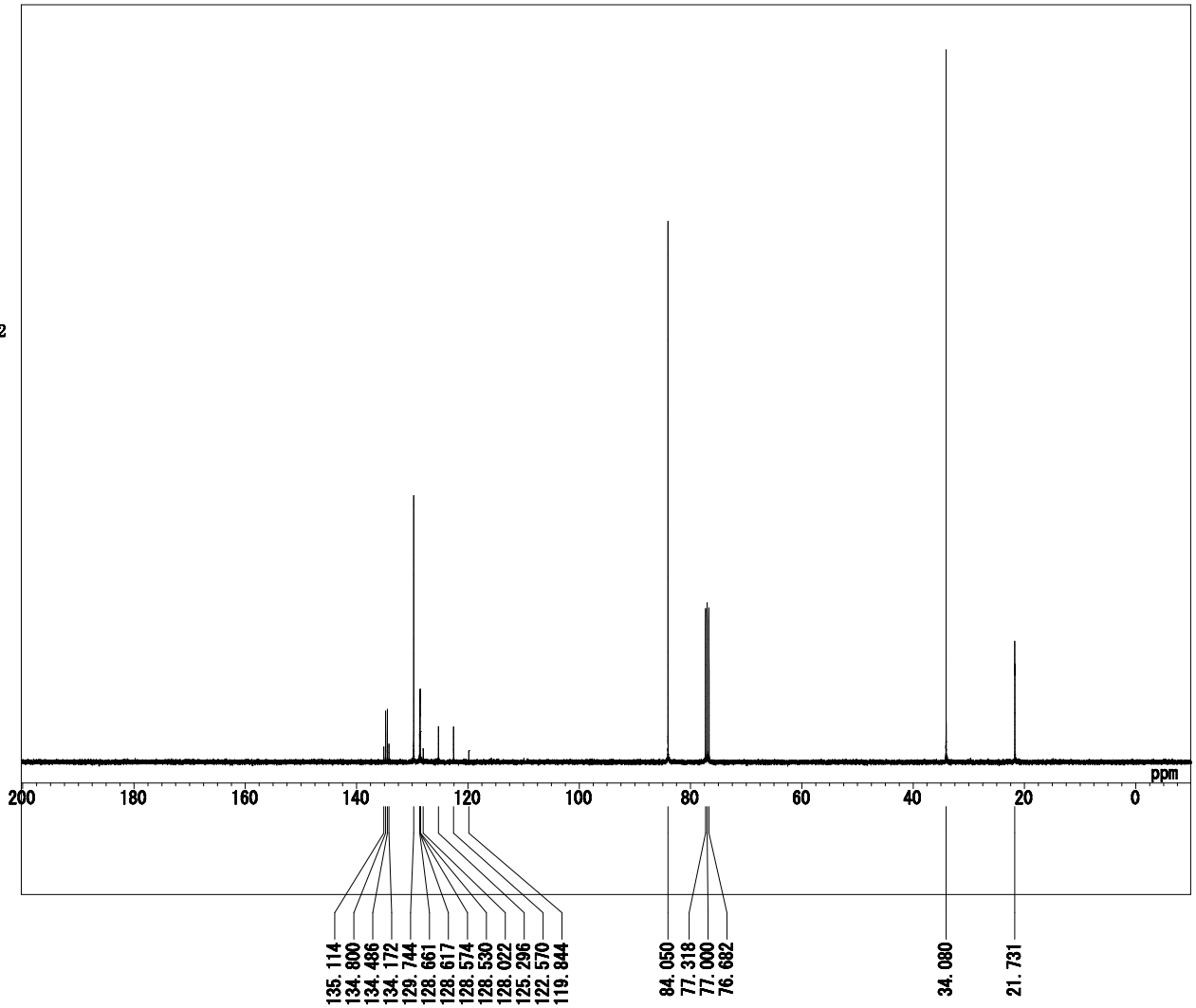
Comment	HRS01-34_pure_20160905_01
Date	2016/Sep/05
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

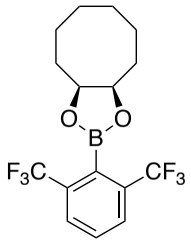




3h

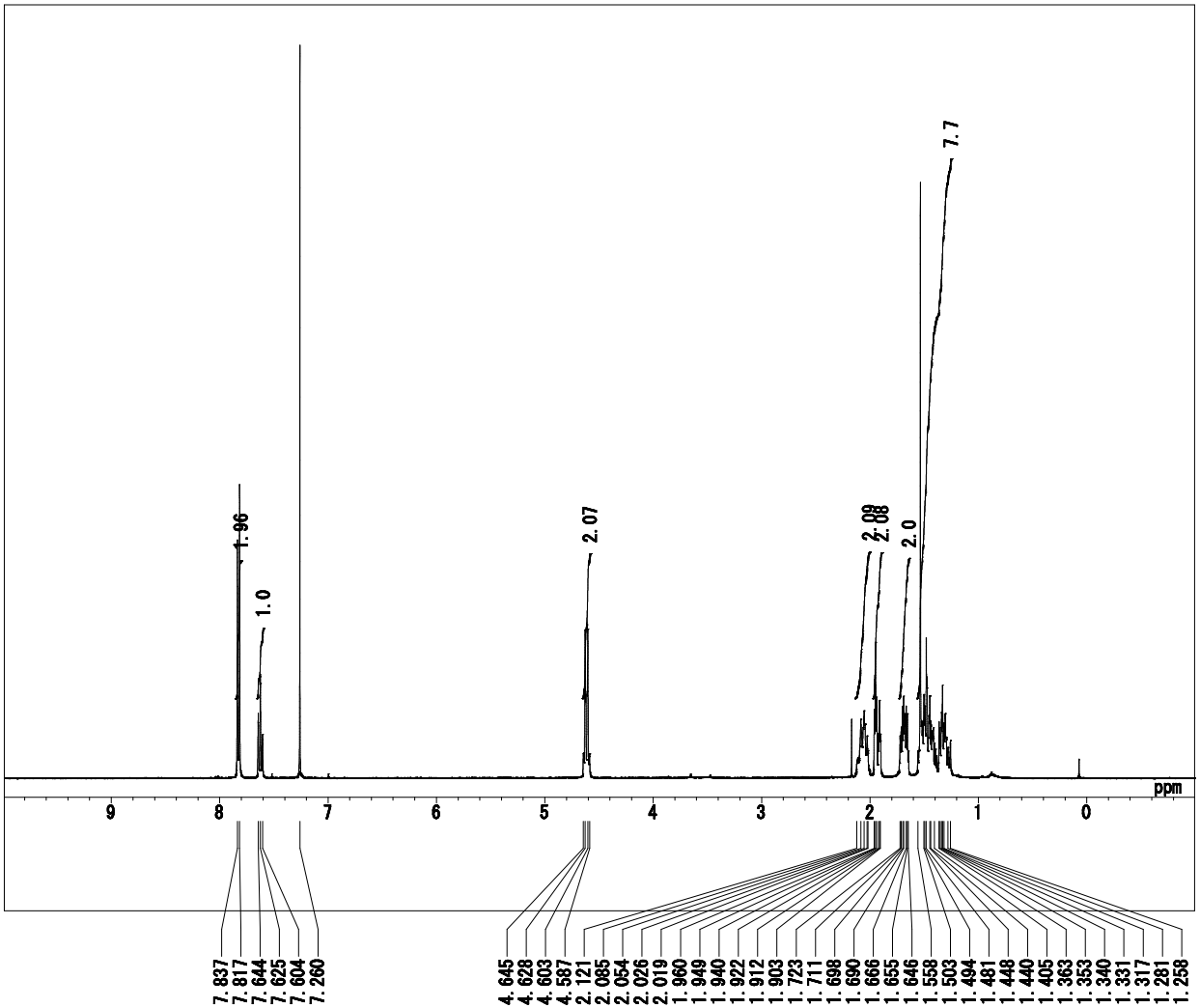
Comment	HRS01-34_pure_20160905_02
Date	2016/Sep/05
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

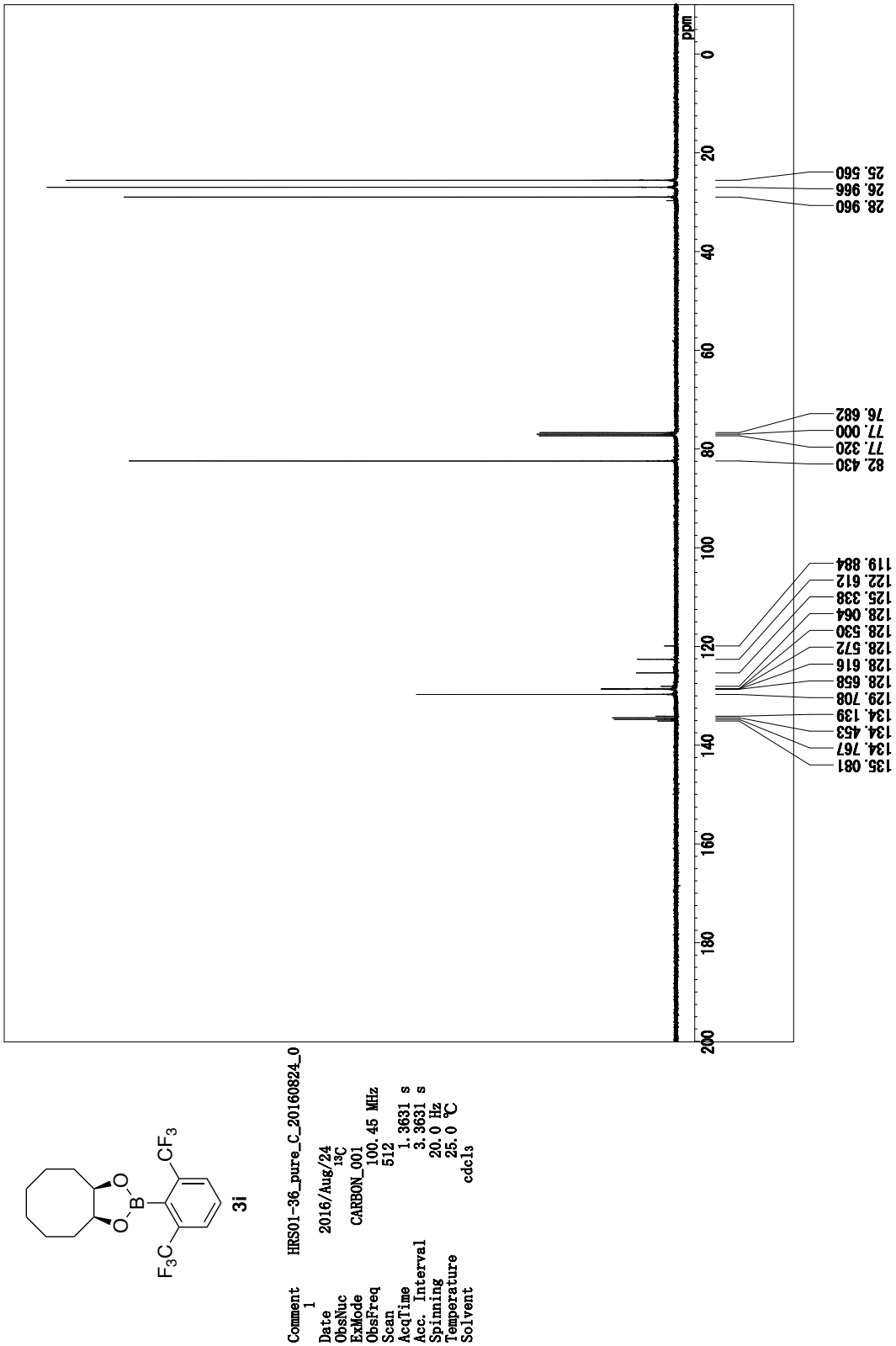


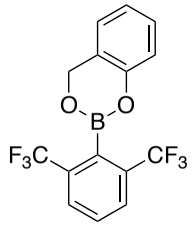


3i

Comment	HRS01-36_pure2_20160824_01
Date	2016/Aug/24
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	30.0 ℃
Solvent	cdcl3

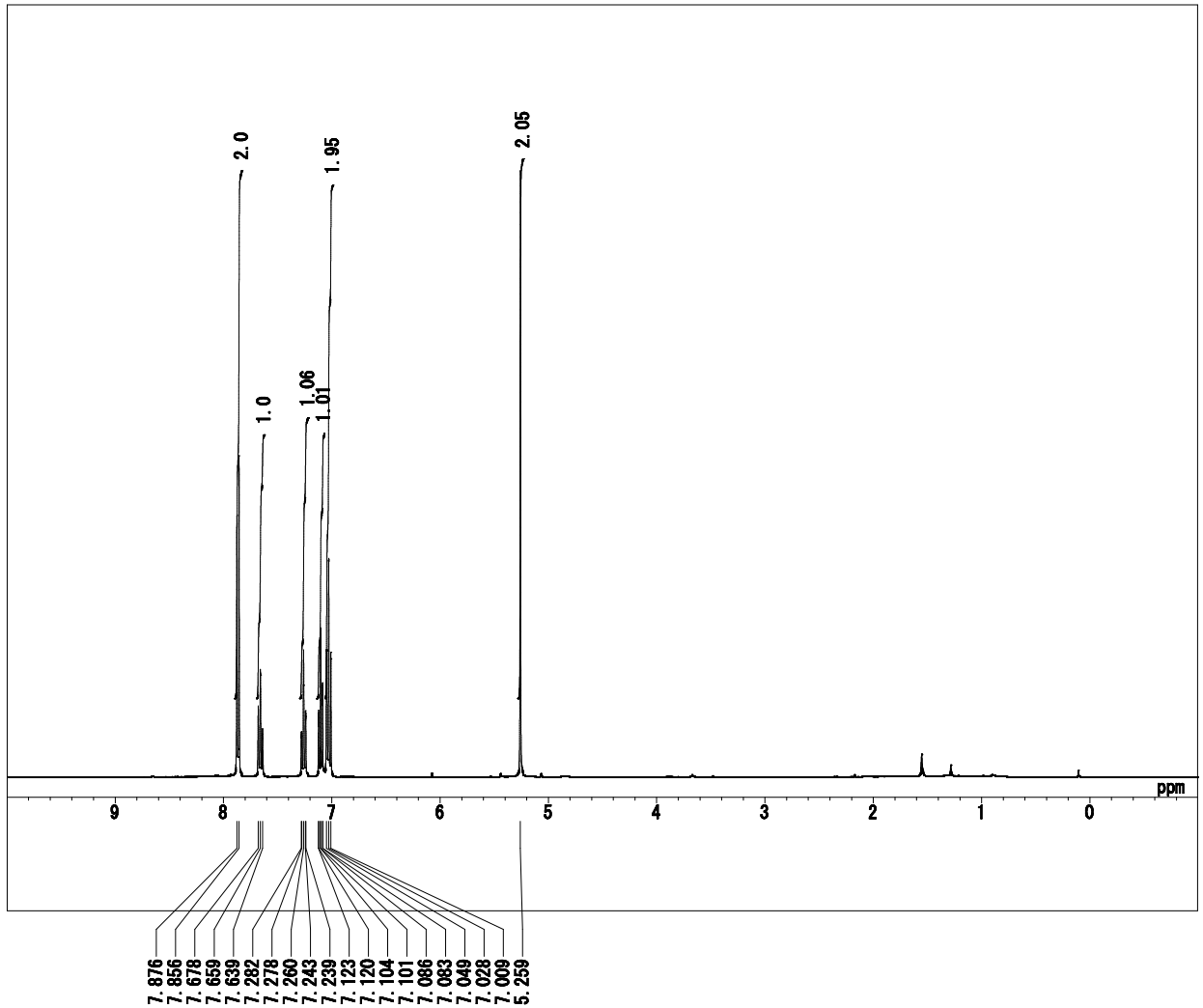


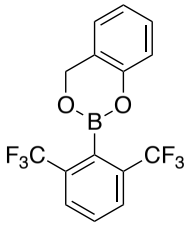

3i
Comment HRS01-36_pure_C_20160824_0
1
Date 2016/Aug/24
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 512
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
0
20
40
60
80
100
120
140
160
180
200
25.560
26.966
28.960
76.682
77.000
77.320
82.430
119.884
122.612
125.338
128.064
128.530
128.572
128.616
128.658
129.708
134.139
134.453
134.767
135.081



3j

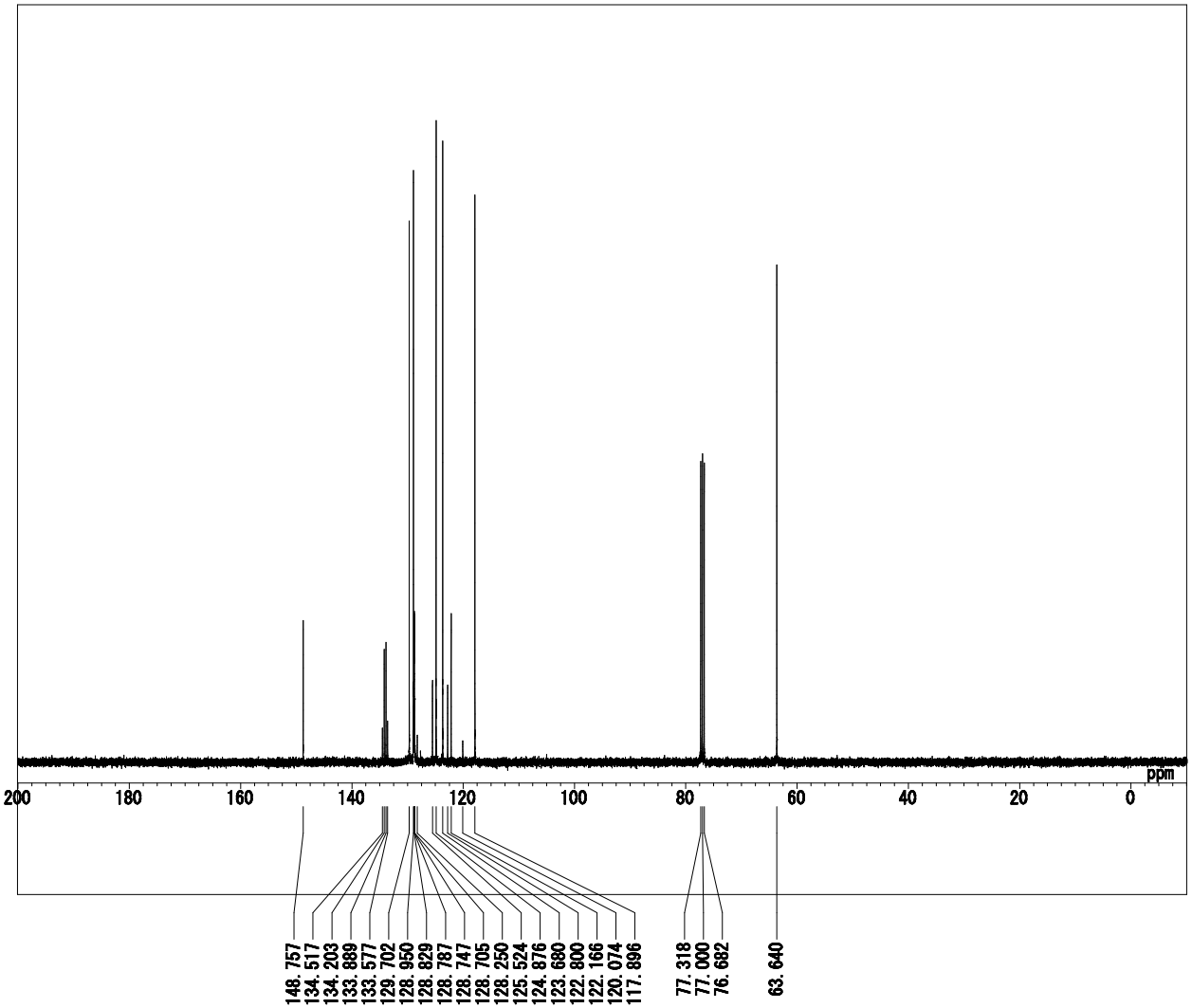
Comment	HRS02-24_pure_20160916_01
Date	2016/Sep/16
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl$_3$

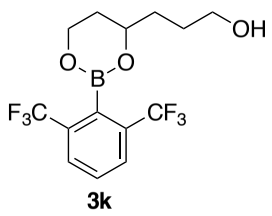




3j

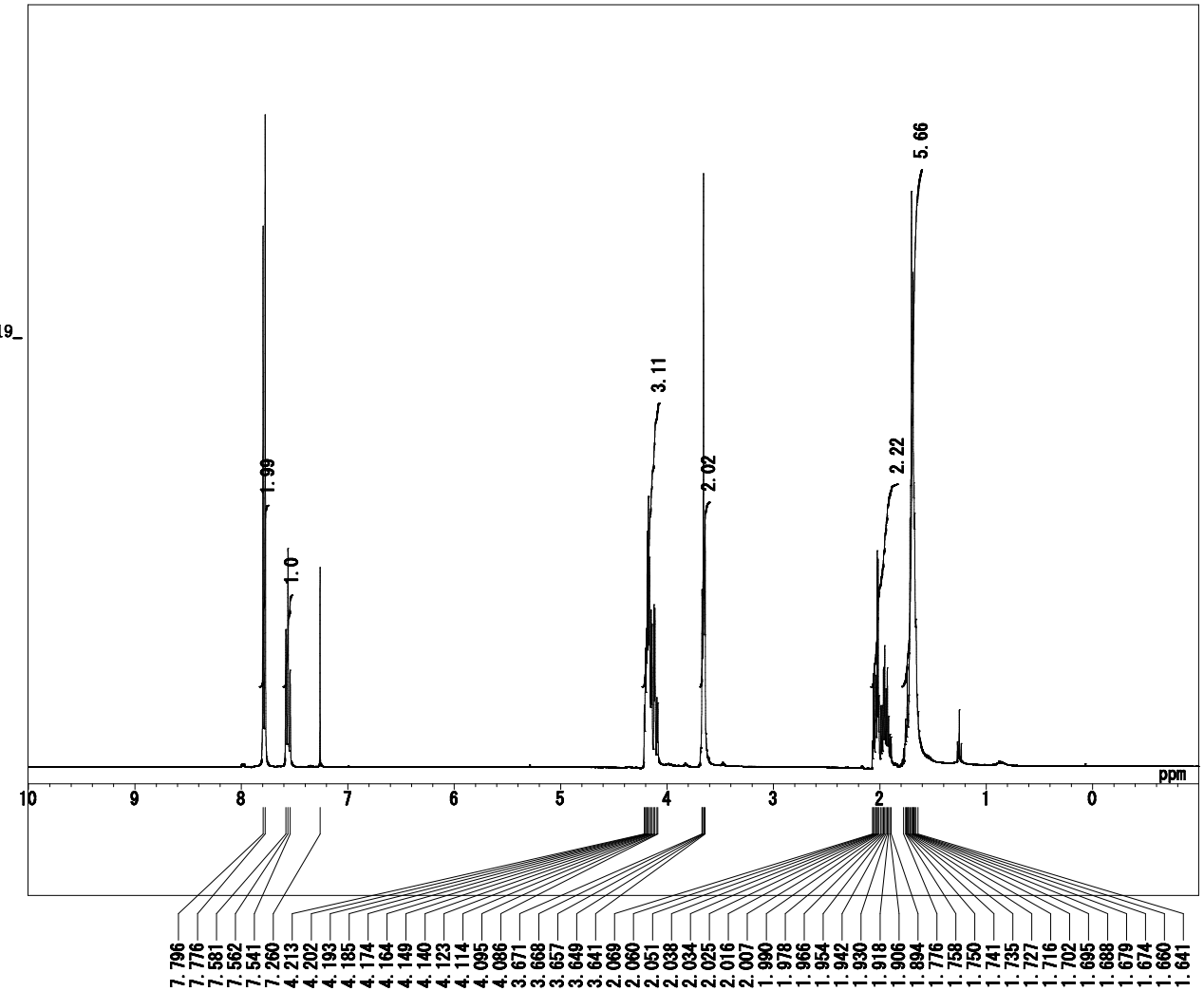
Comment	HRS02-24_C_20160920_01
Date	2016/Sep/20
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

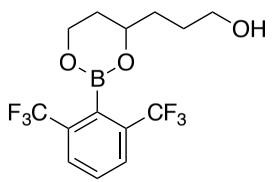




3k

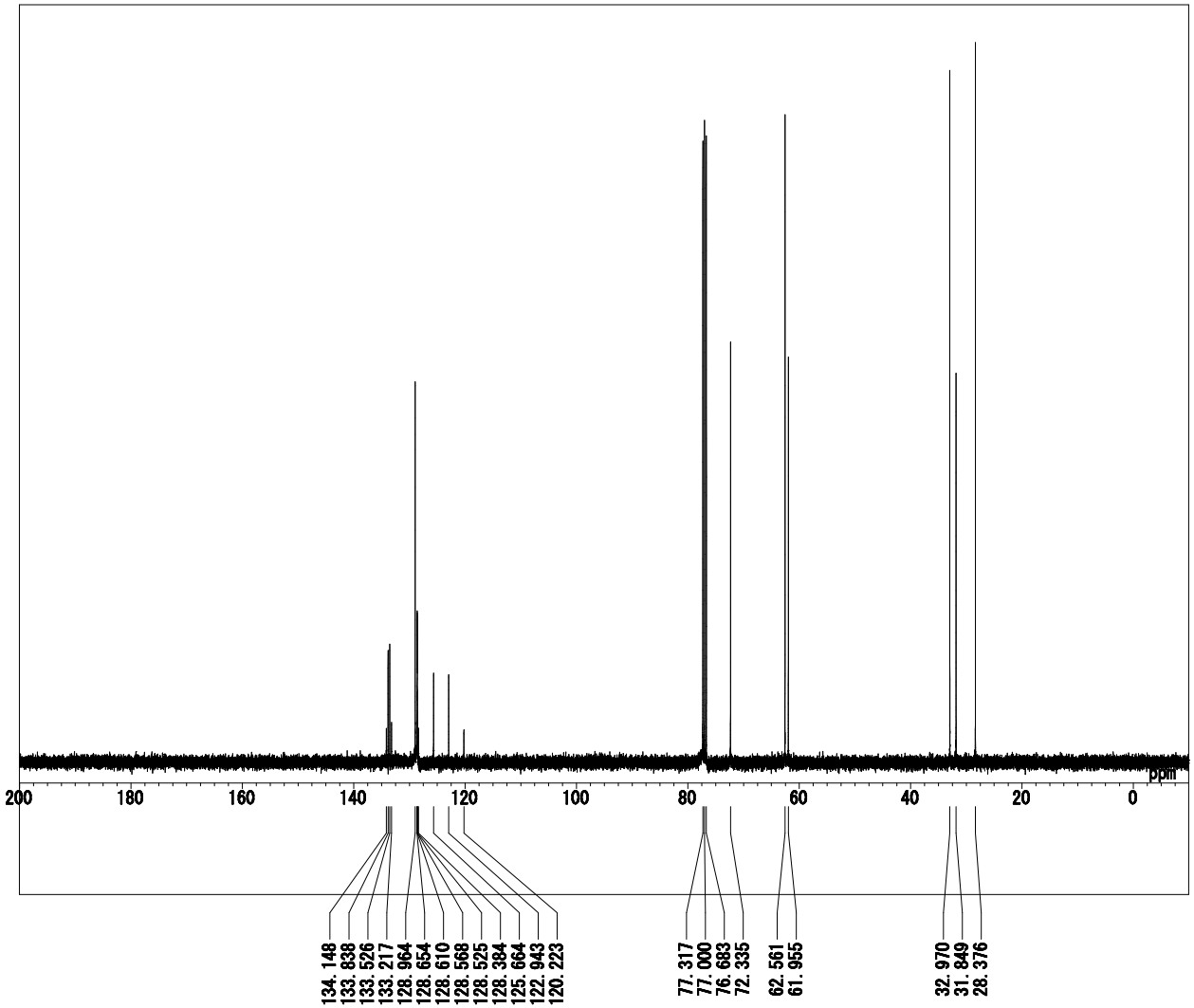
Comment	NO-03-02-fr16-27_20150519_01
Date	2015/May/19
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

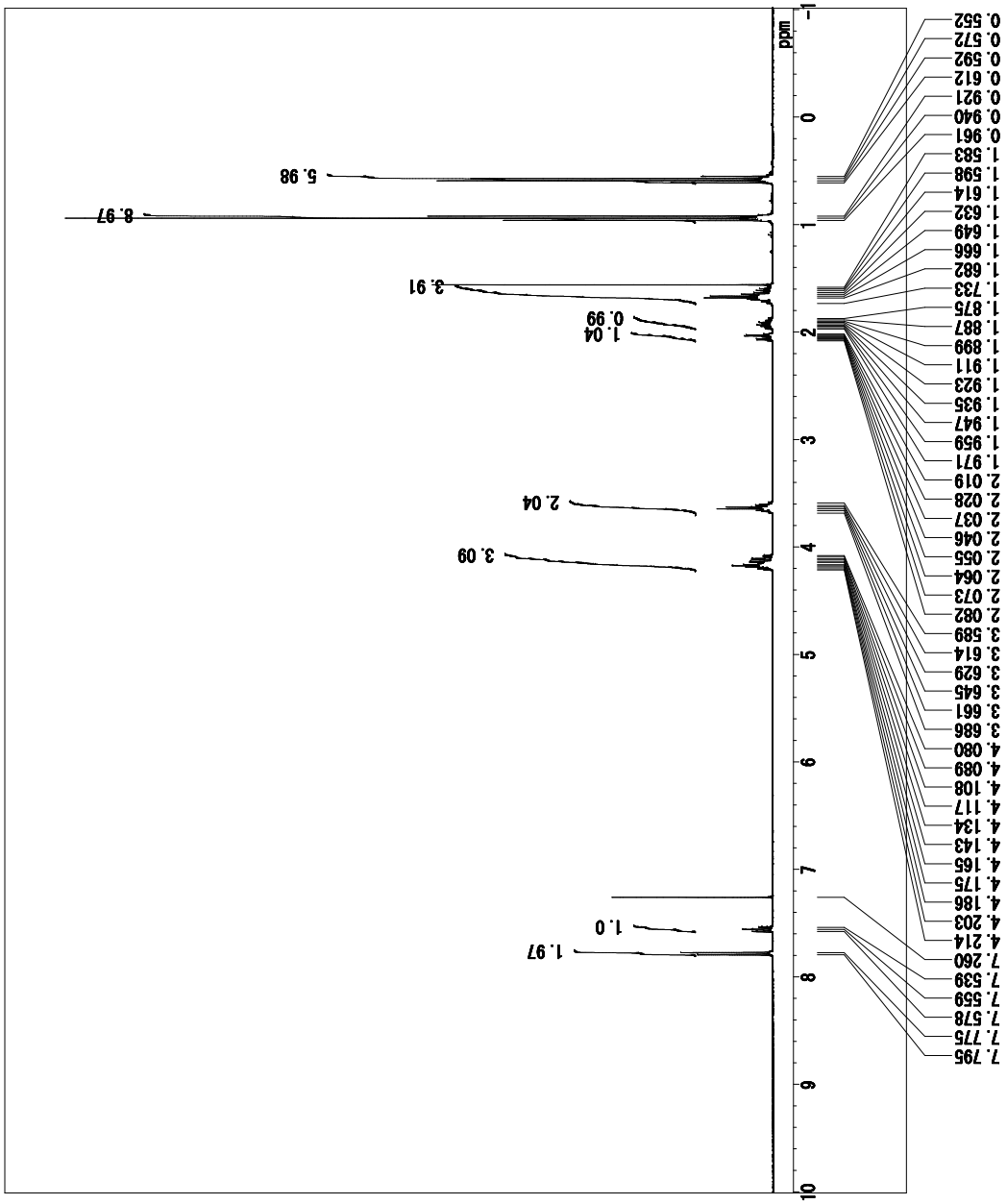


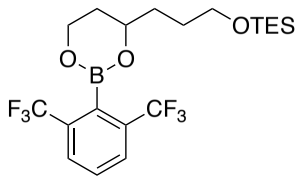


3k

Comment	NO-03-02-C_20150519_01
Date	2015/May/19
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

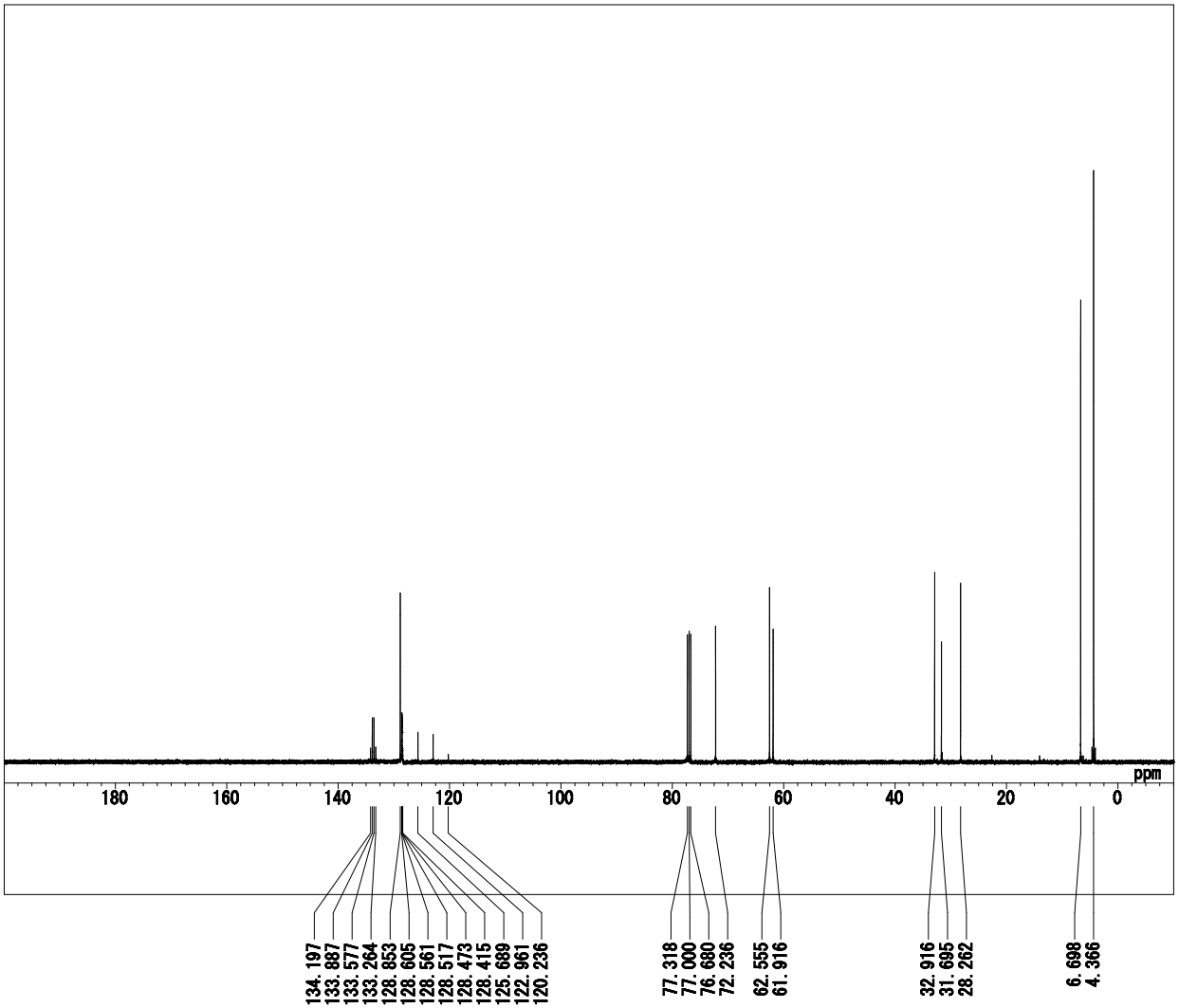


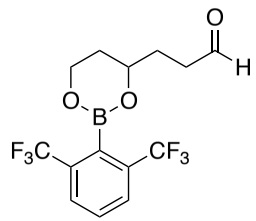

OTES
B
O
O
CF3
F3C
4
Comment su-TES_20160816_01
Date 2016/Aug/16
ObsNuc 1H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 8
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
8.97
5.98
3.91
1.04
0.99
2.04
3.09
1.97
1.0
7.795
7.775
7.578
7.559
7.539
7.260
4.214
4.203
4.186
4.175
4.165
4.143
4.134
4.117
4.108
4.089
4.080
3.686
3.661
3.645
3.629
3.614
3.589
2.082
2.073
2.064
2.055
2.046
2.037
2.028
2.019
1.971
1.959
1.947
1.935
1.923
1.911
1.899
1.887
1.875
1.733
1.682
1.666
1.649
1.632
1.614
1.598
1.583
0.961
0.940
0.921
0.612
0.592
0.572
0.552



4

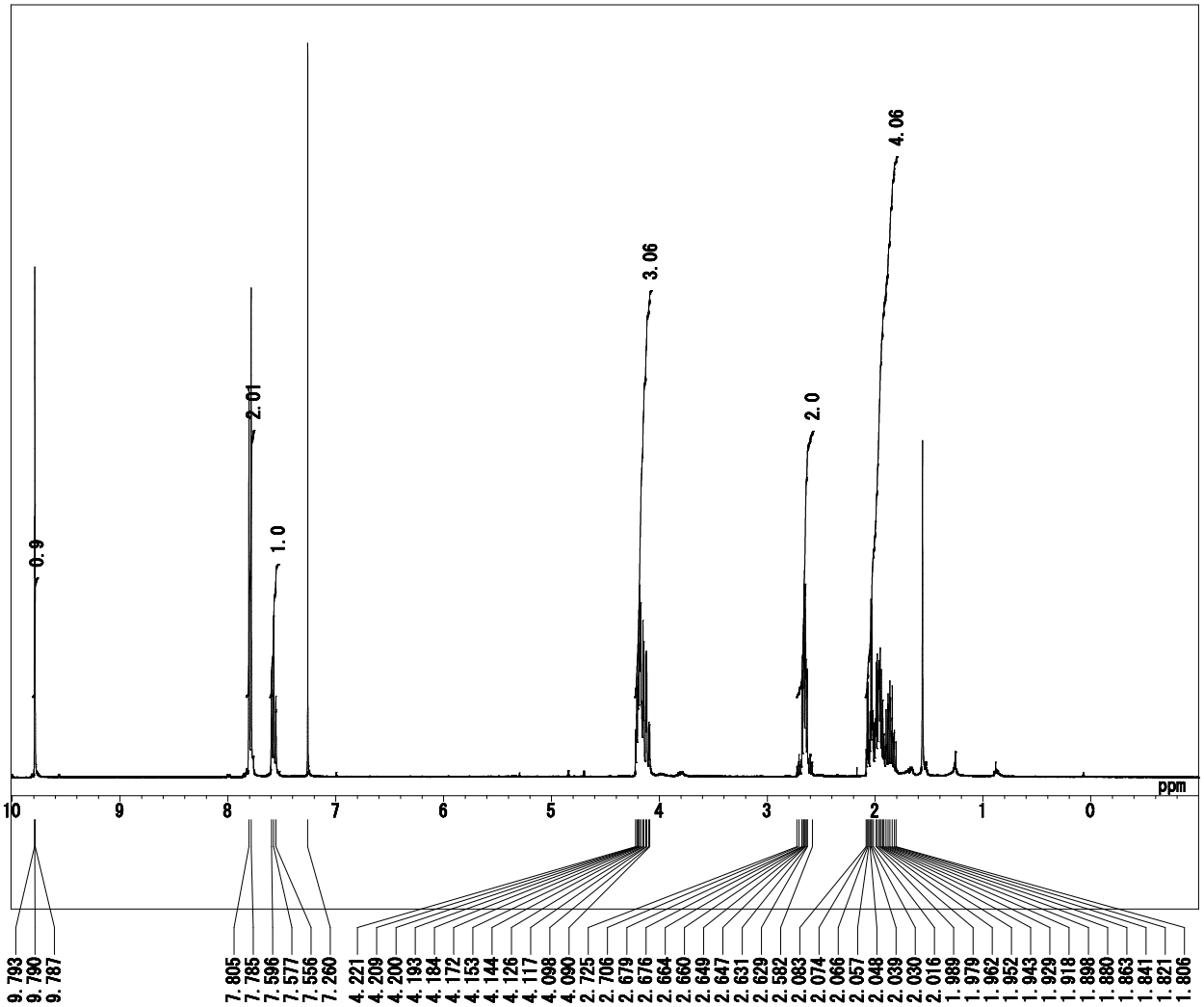
Comment	su-TES-13C_20160816_02
Date	2016/Aug/16
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

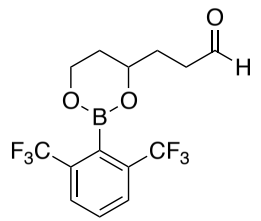




5

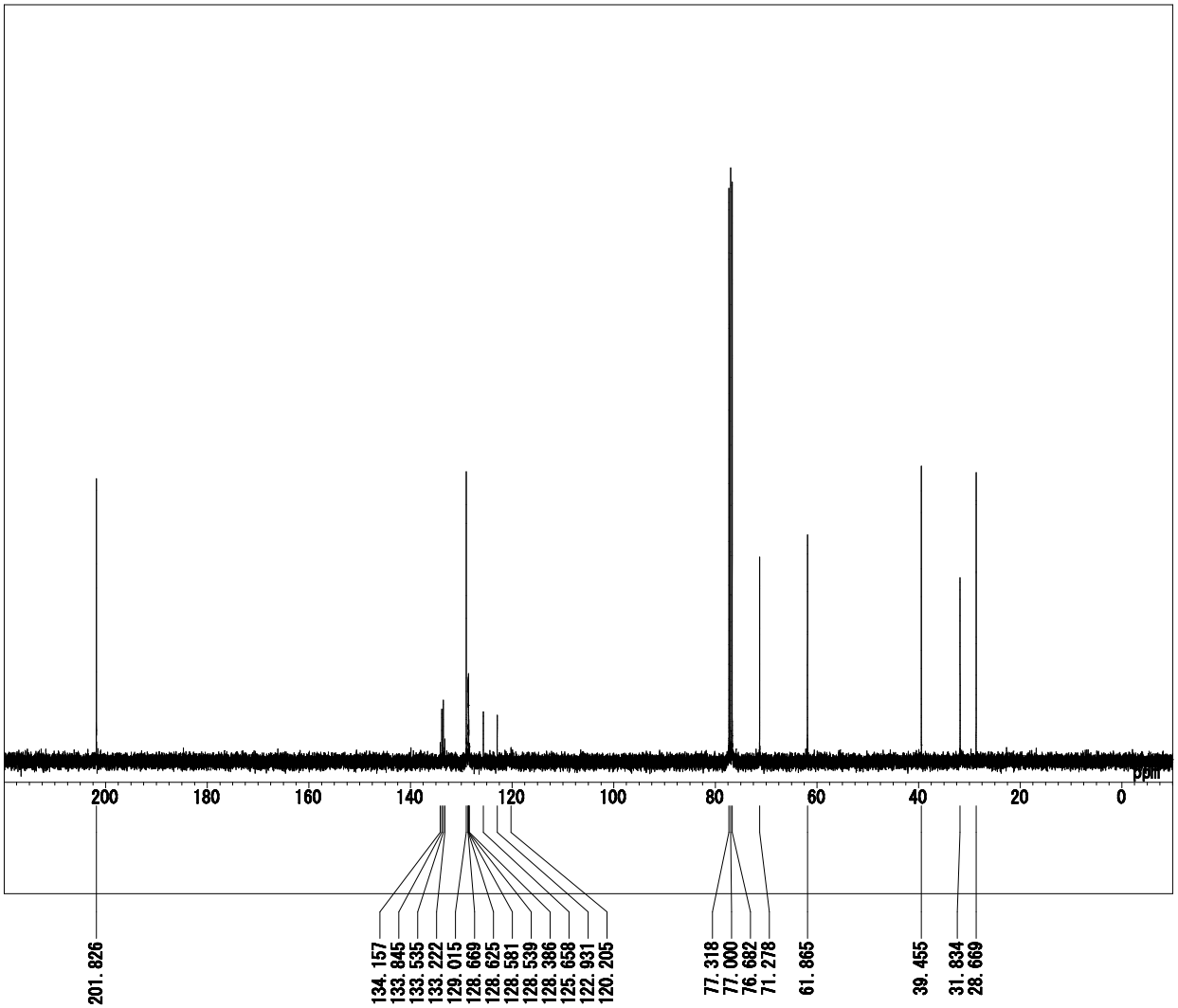
Comment	hrs01-01pure_20160407_01
Date	2016/Apr/07
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

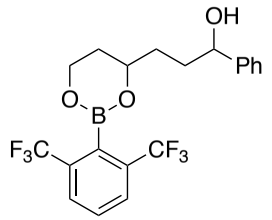




5

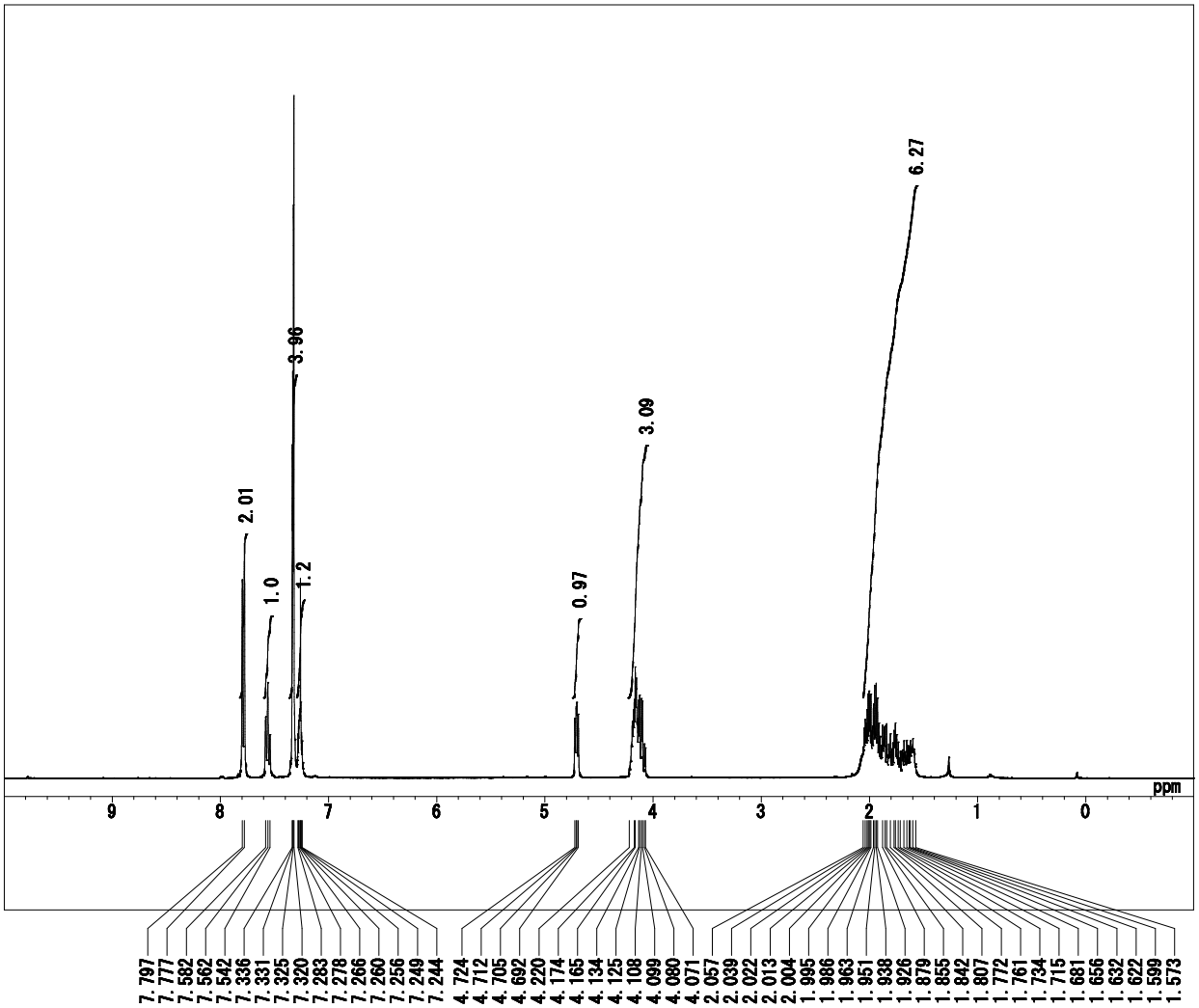
Comment	NO-03-03-C_20150522_01
Date	2015/May/22
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	3.0 ℃
Solvent	cdcl3

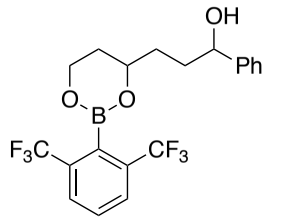




6

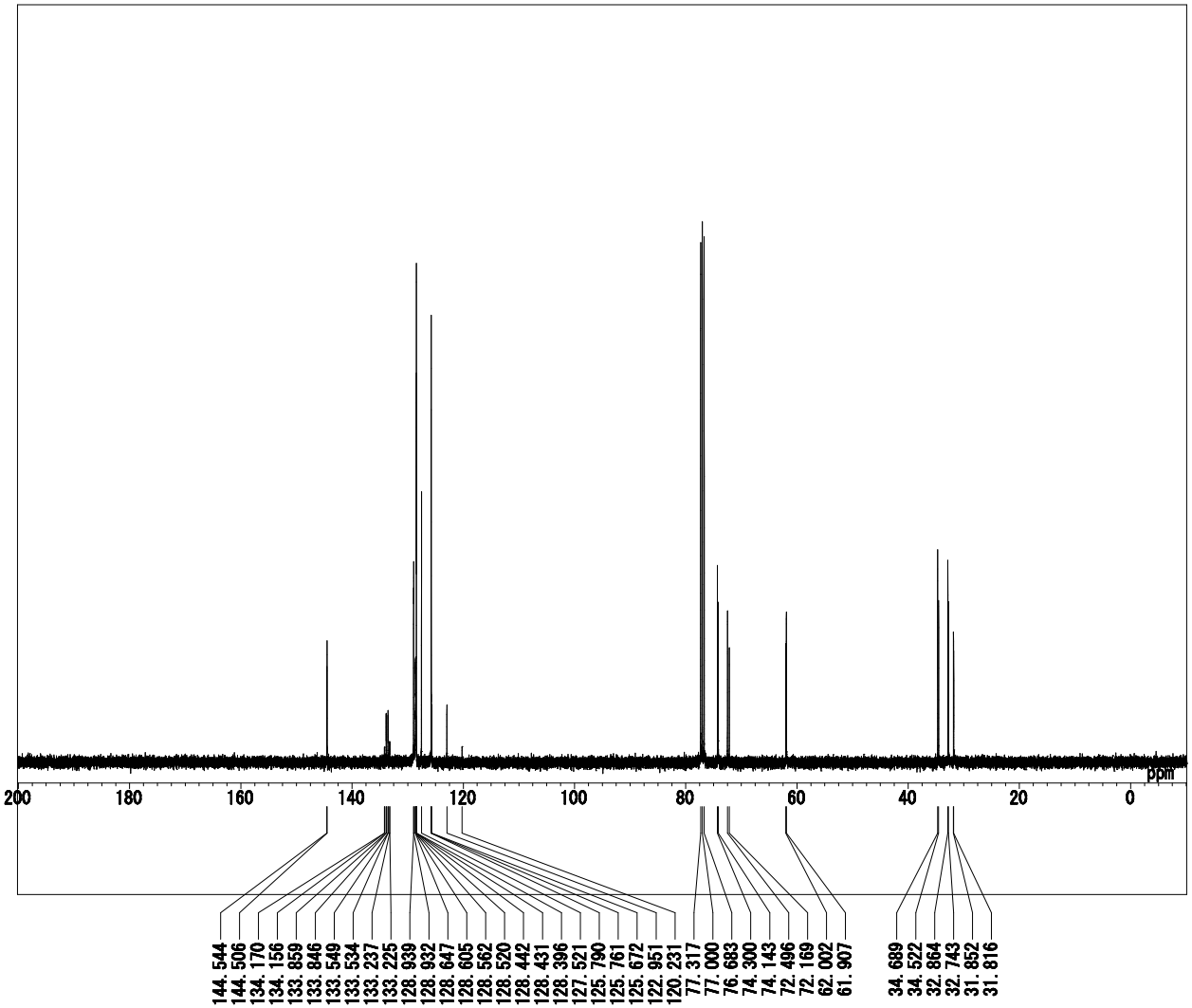
Comment	su13007pure_20160805_01
Date	2016/Aug/05
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

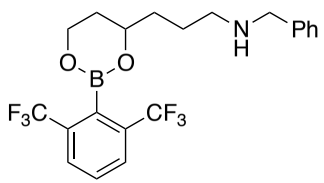




6

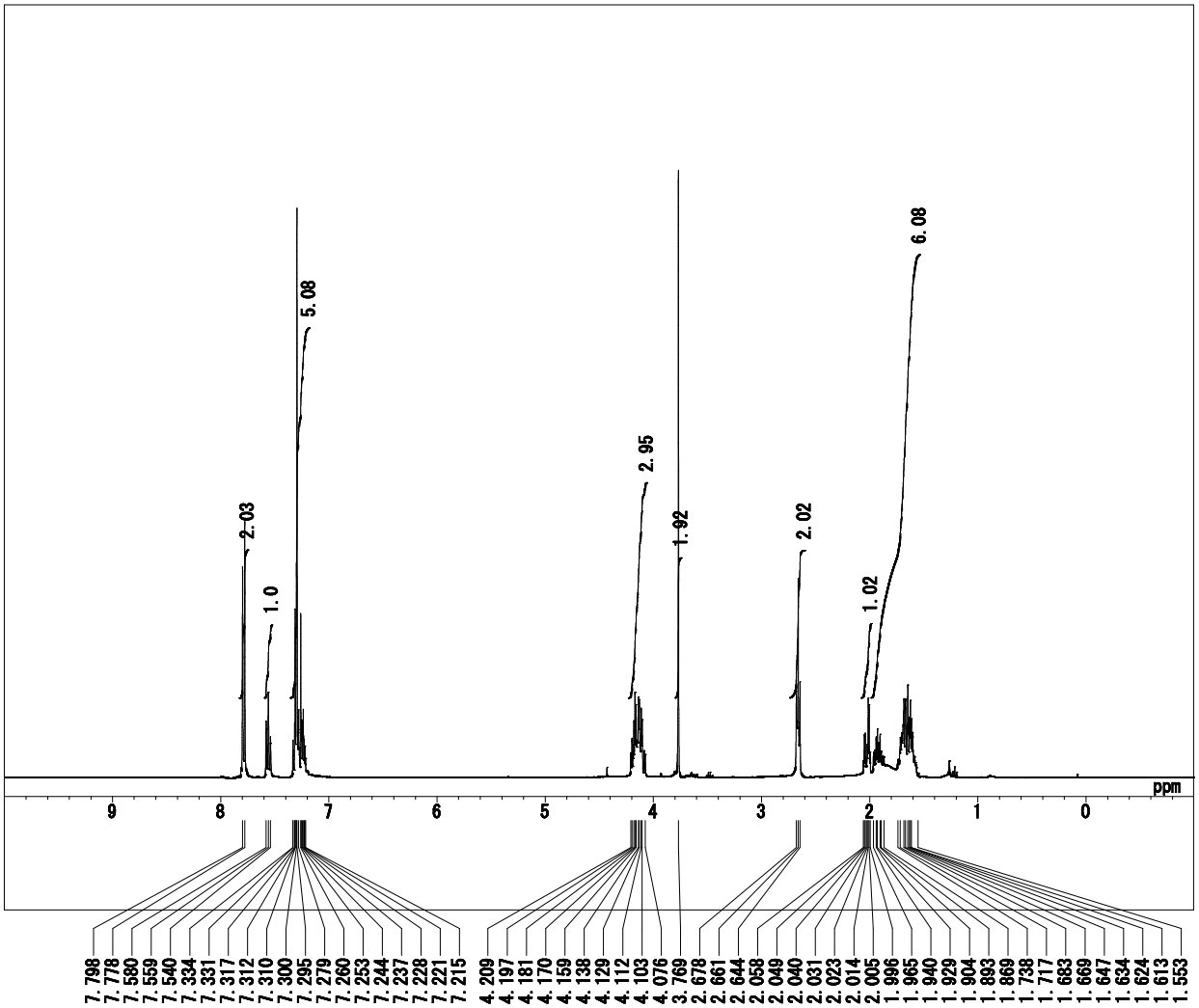
Comment	su13007pure_20160805_01
Date	2016/Aug/05
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

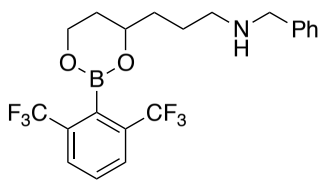




7

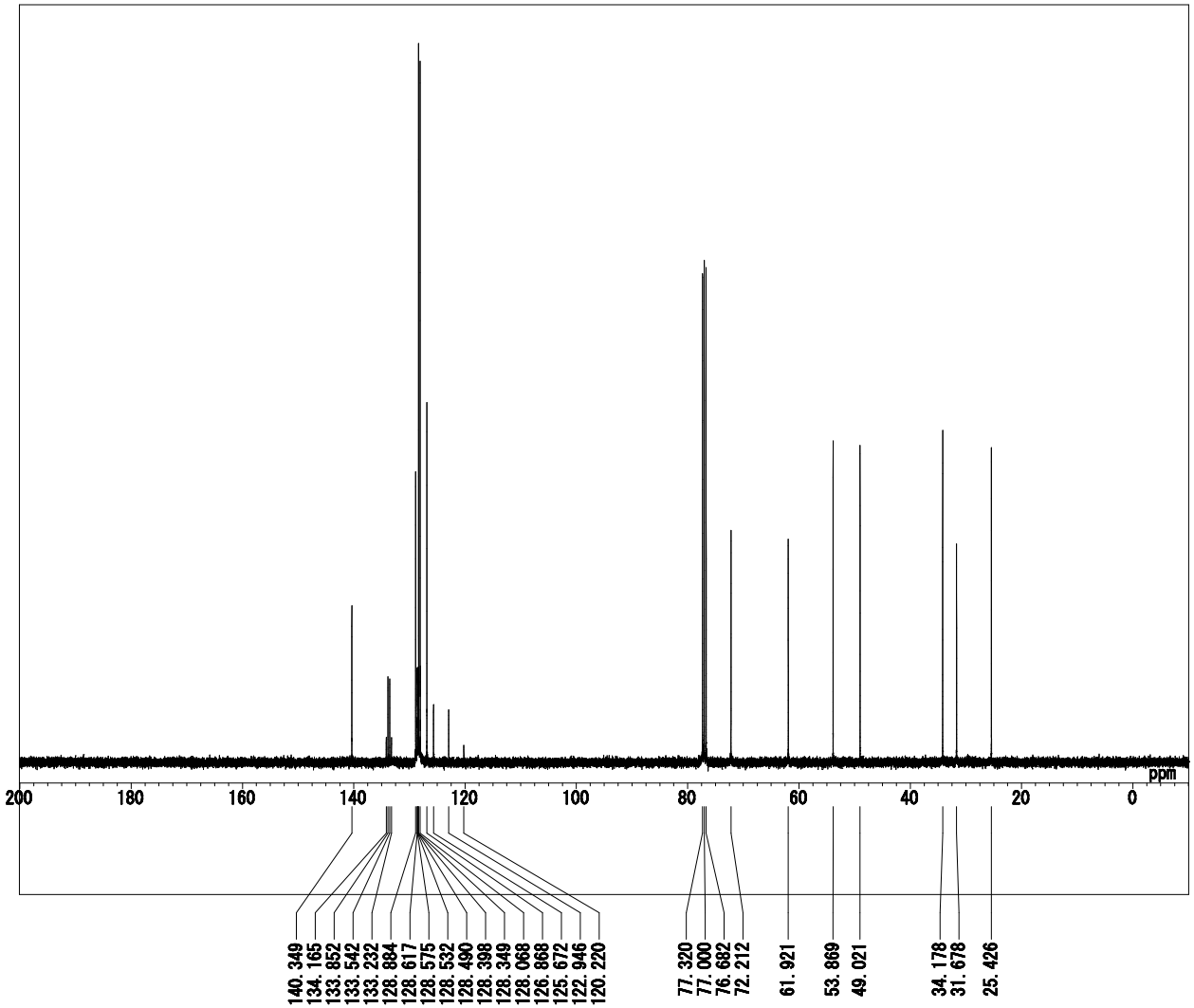
Comment	su15023_20170825_01
Date	2017/Aug/25
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

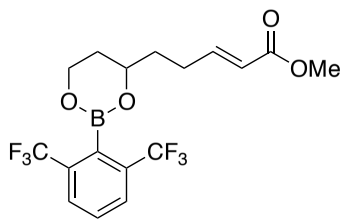




7

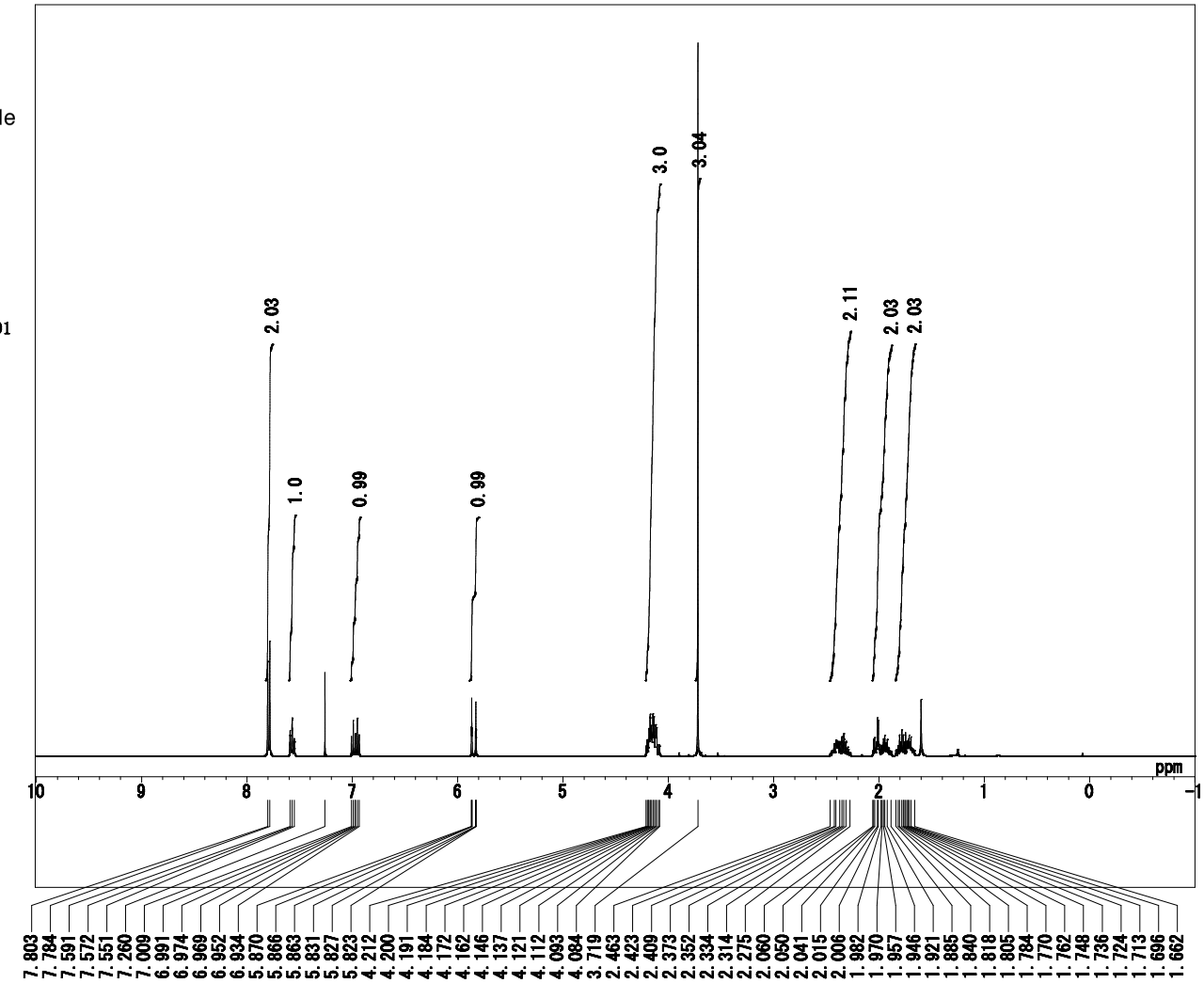
Comment	su15023_20170825_01
Date	2017/Aug/25
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	1024
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

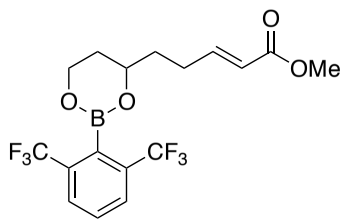




8

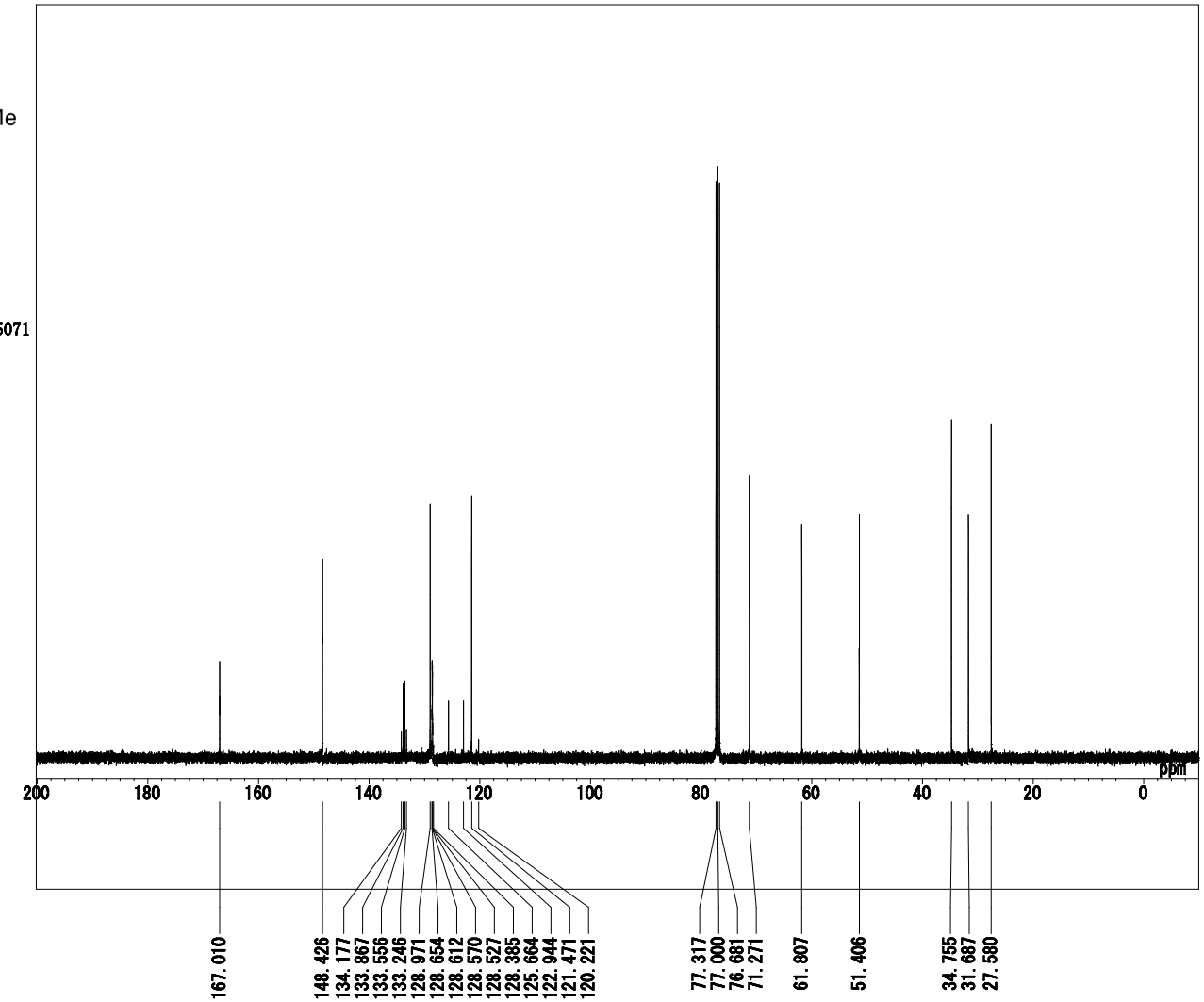
Comment	NO-03-20pure_20150713_01
Date	2015/Jul/13
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	16
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	3.0 ℃
Solvent	cdcl3

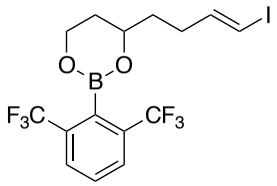




8

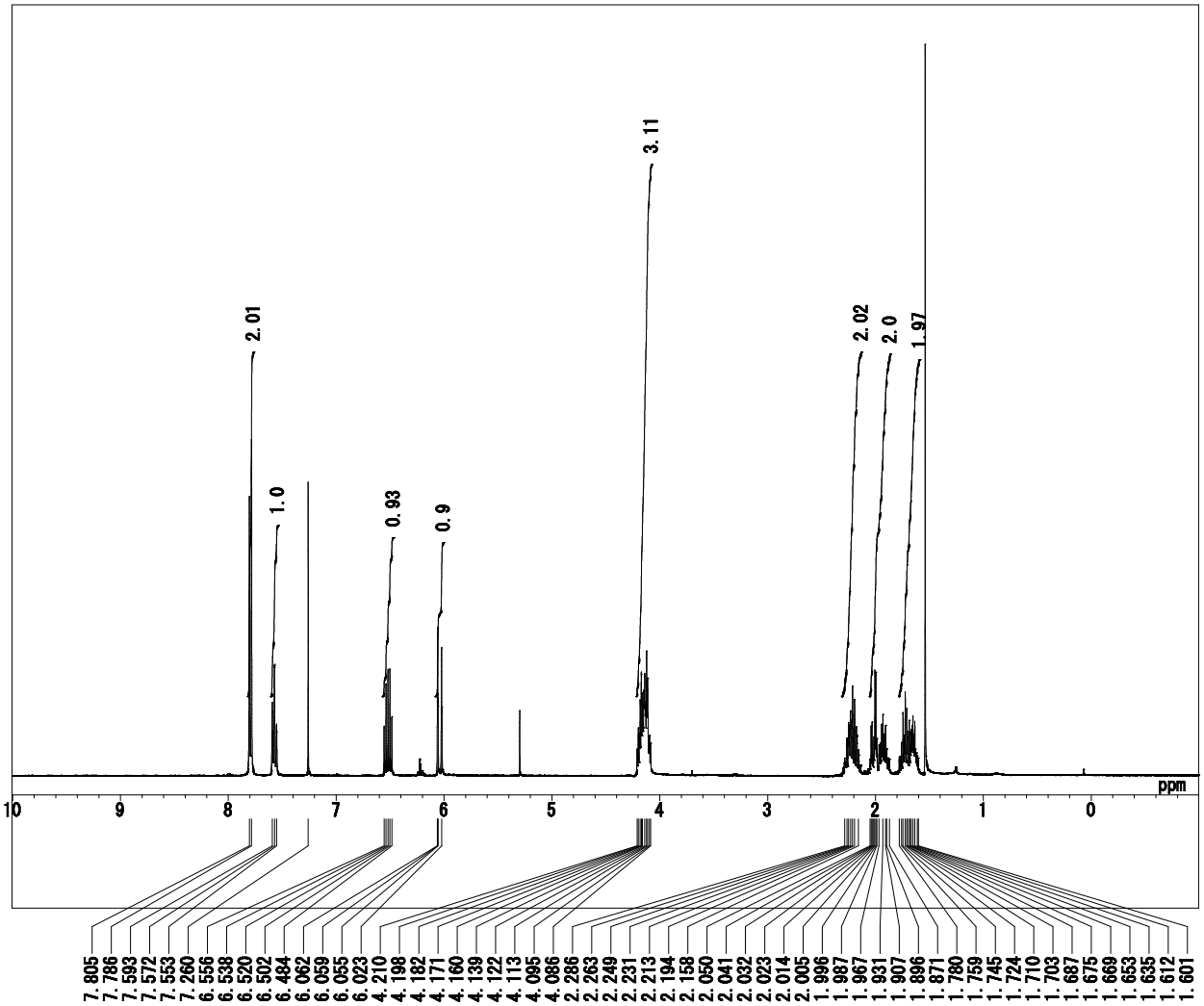
Comment NO-03-20-witting-C_2015071 3_01
Date 2015/Jul/13
ObsNuc ^{13}C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 1024
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3

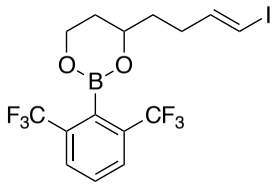




9

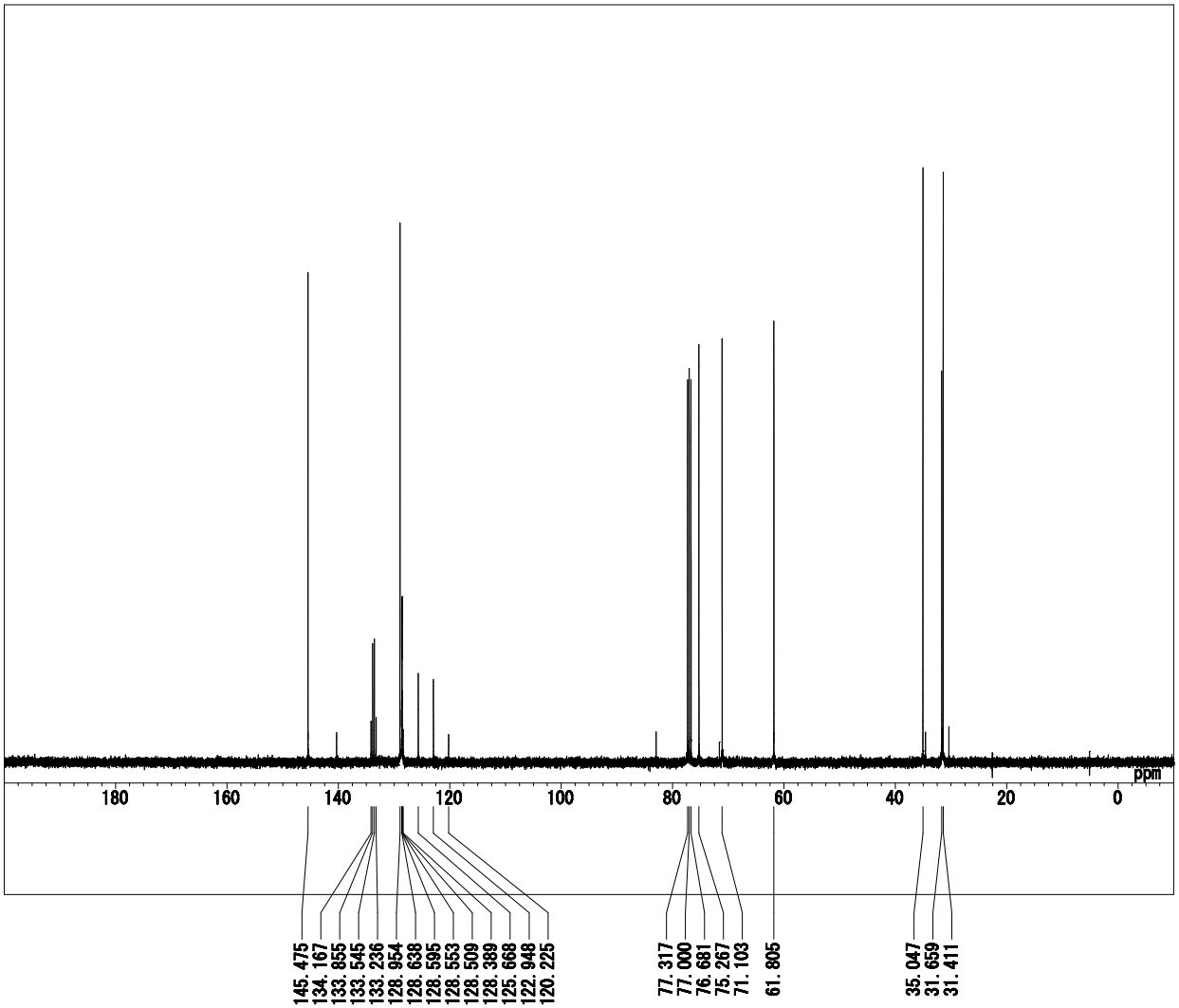
Comment	su15016pure_20161116_01
Date	2016/Nov/16
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

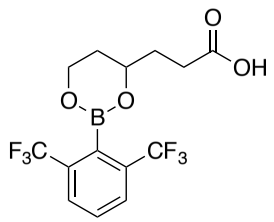




9

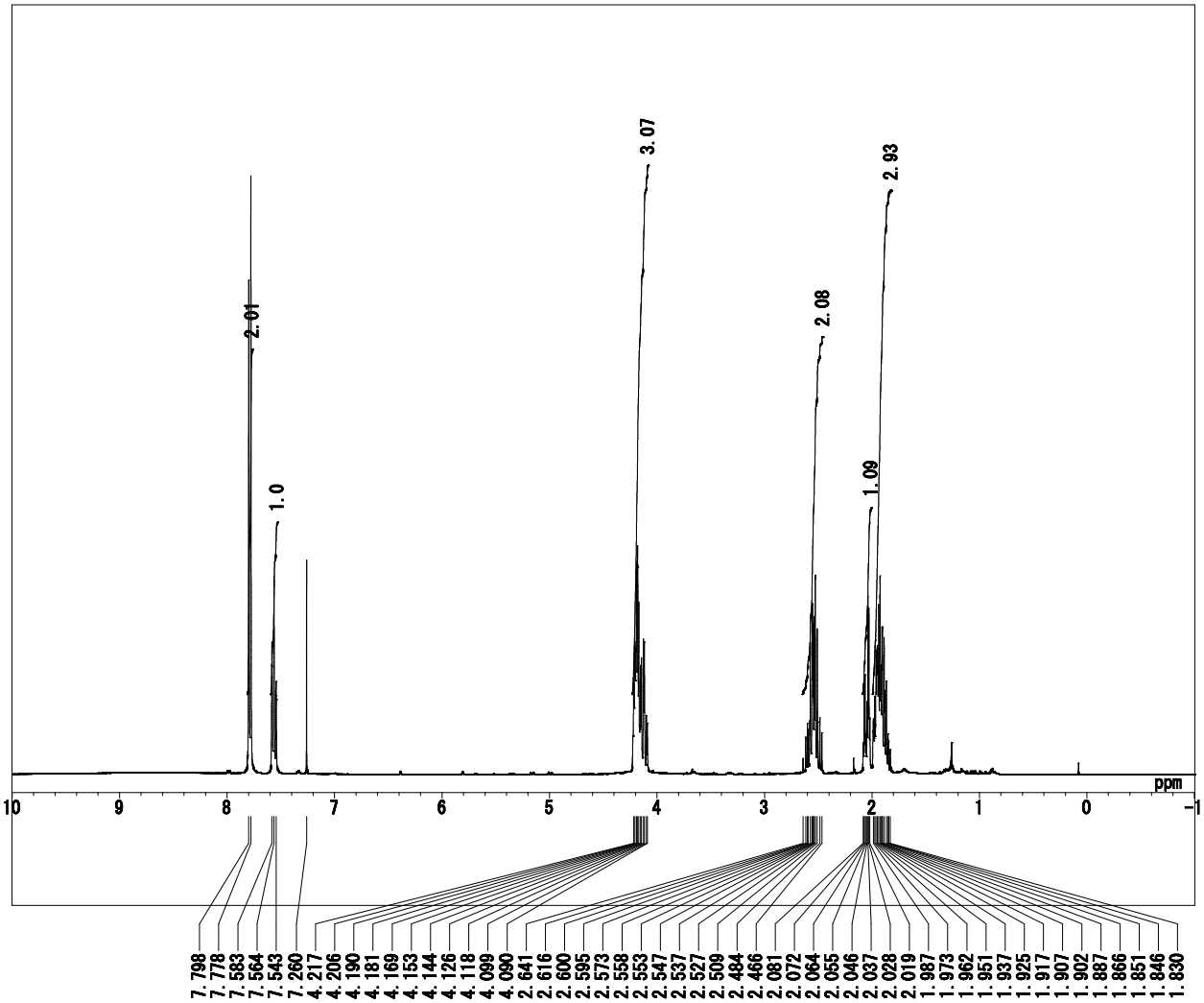
Comment	su15016pure-13C_20161116_0 1
Date	2016/Nov/16
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

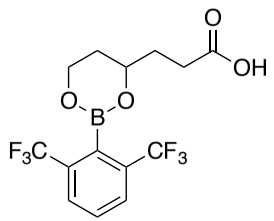




10

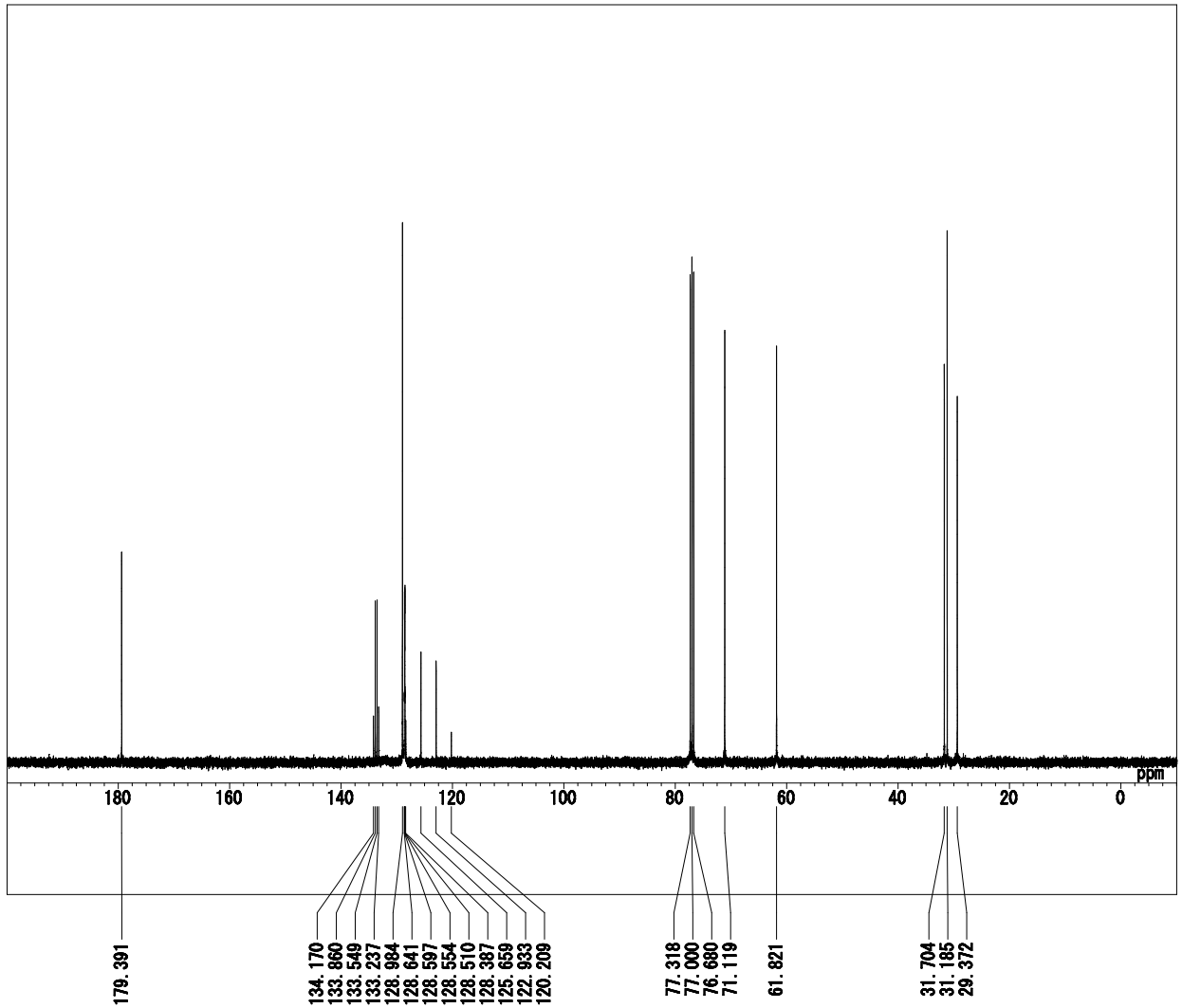
Comment	su13002pure2_20160803_01
Date	2016/Aug/03
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	399.45 MHz
Scan	8
AcqTime	2.569 s
Acc. Interval	5.569 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

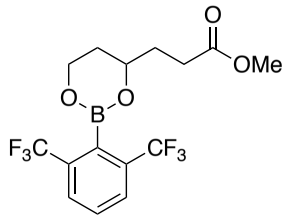




10

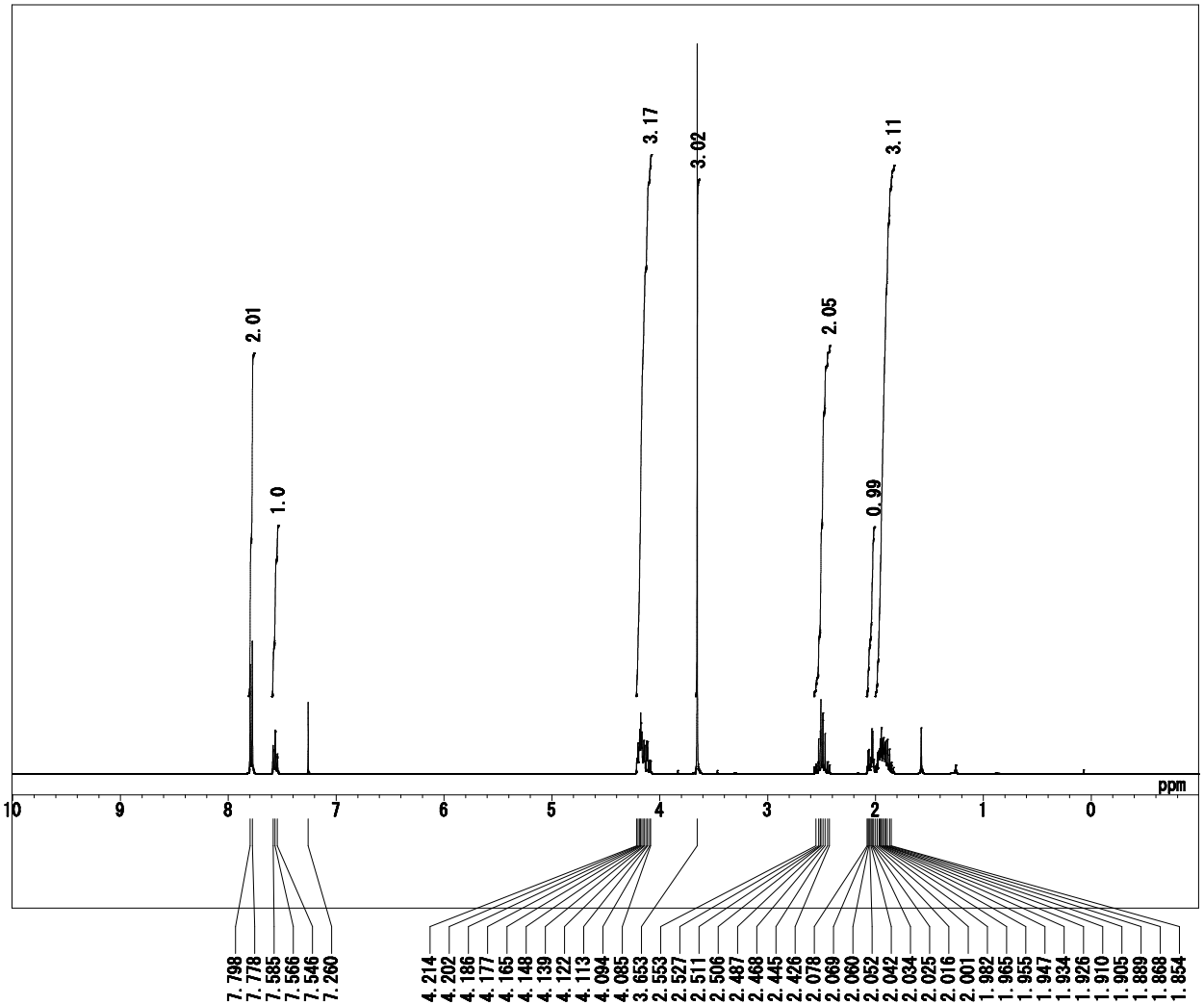
Comment	su13002pure2_20160803_01
Date	2016/Aug/03
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	1024
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

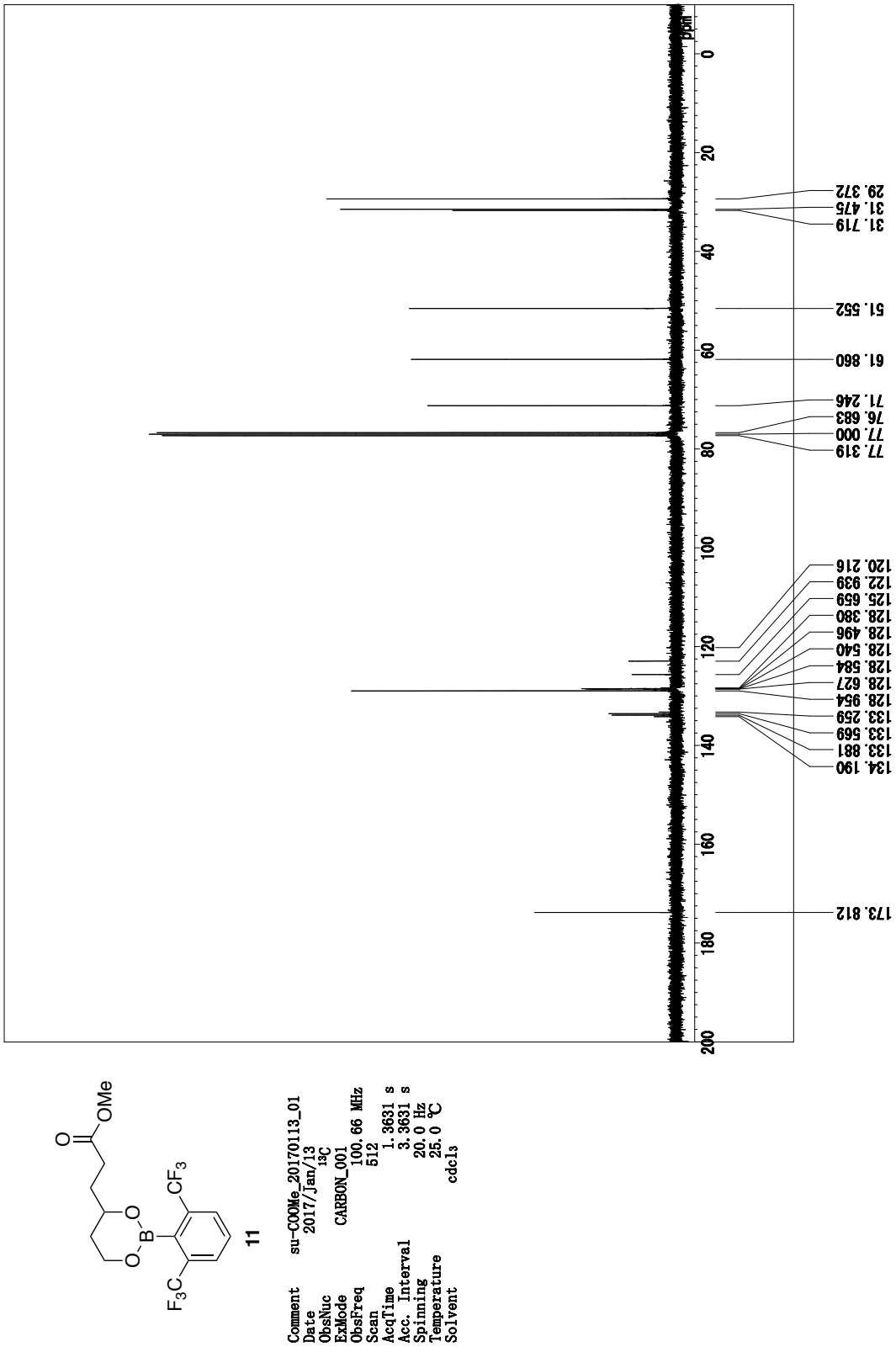


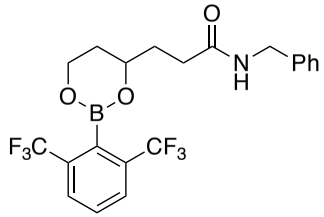


11

Comment	su13032pure_20160902_01
Date	2016/Sep/02
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	30.0 ℃
Solvent	cdcl3

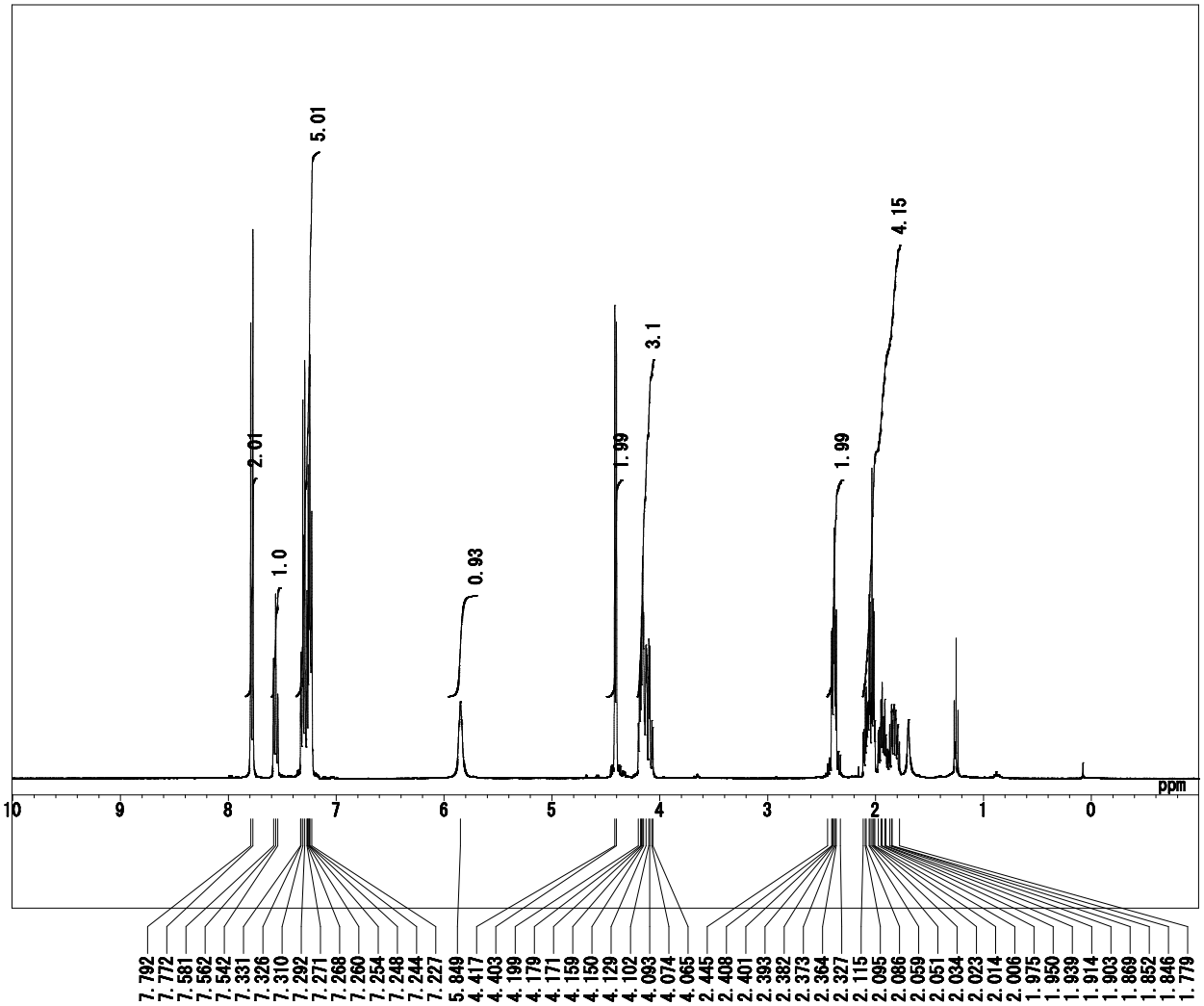


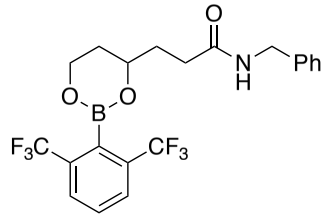

ppm
0
20
40
60
80
100
120
140
160
180
200
29.372
31.475
31.719
51.552
61.860
71.246
76.683
77.000
77.319
120.216
122.939
125.659
128.380
128.496
128.540
128.584
128.627
128.954
133.259
133.569
133.881
134.190
173.812
OMe
O
O
O
B
CF3
F3C
11
Comment su-COOMe_20170113_01
Date 2017/Jan/13
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 512
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3



12

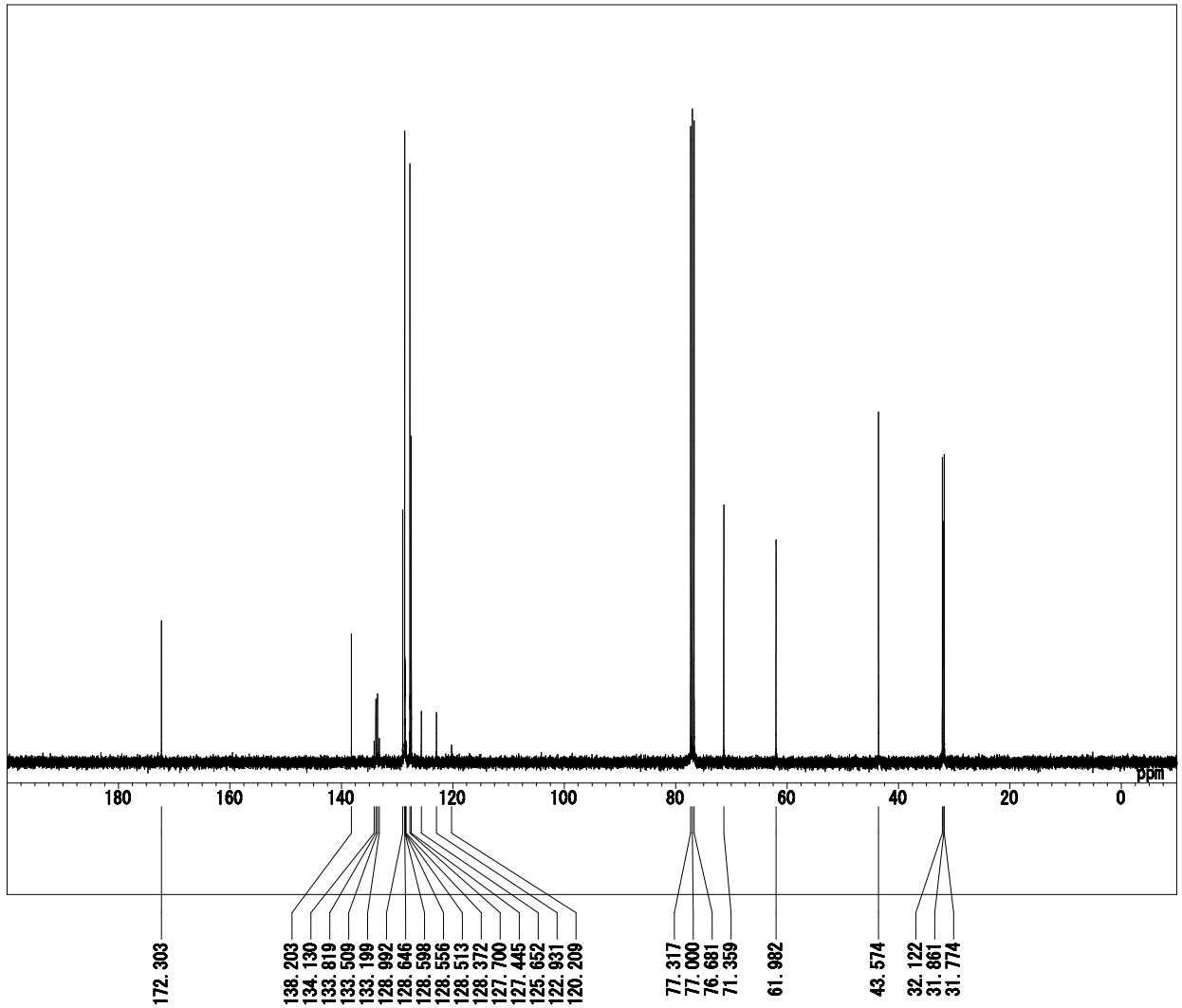
Comment	su13031pure_20160902_01
Date	2016/Sep/02
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

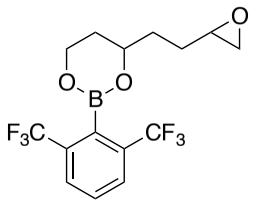




12

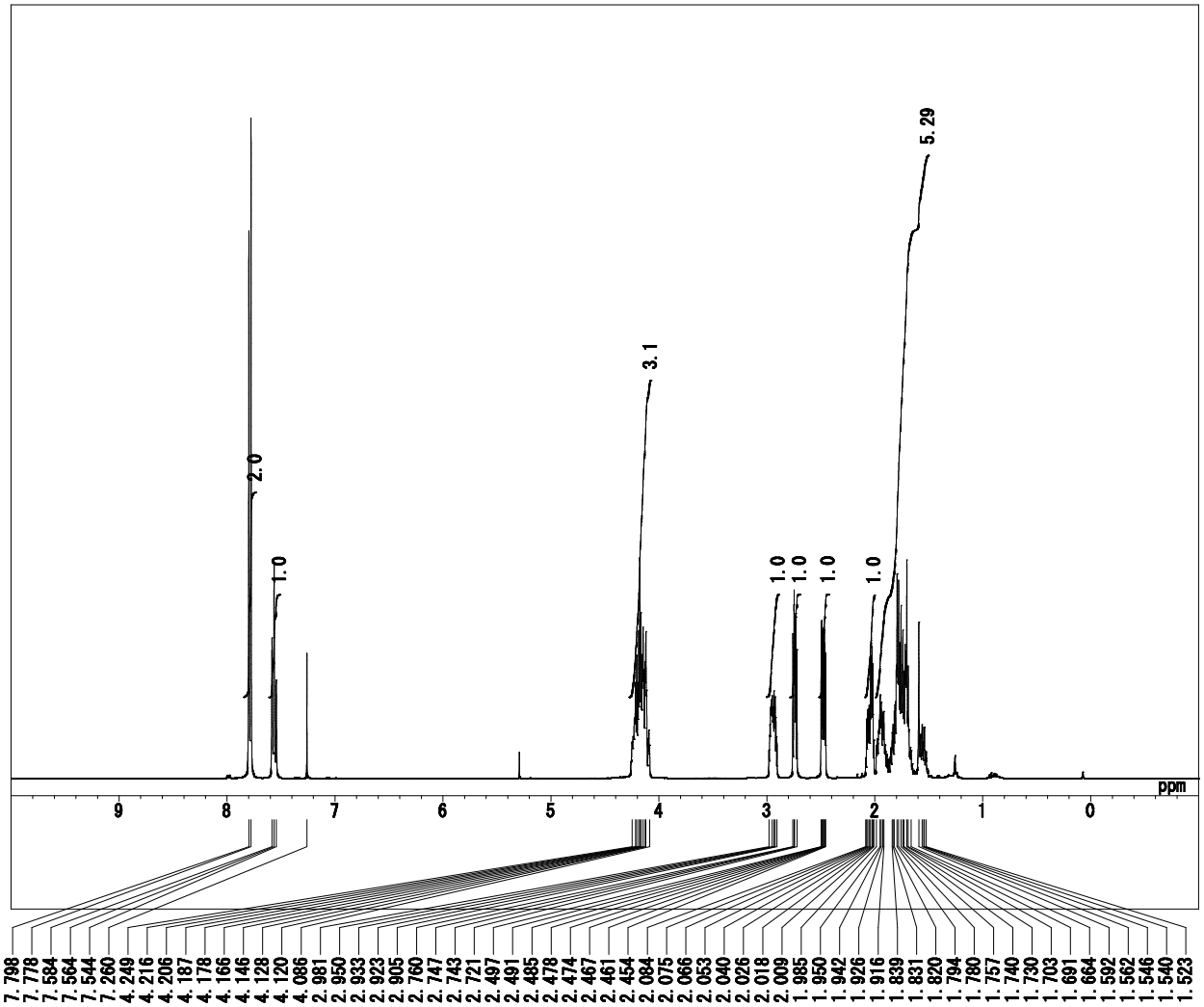
Comment	su13031-13C_20170113_01
Date	2017/Jan/13
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	1024
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

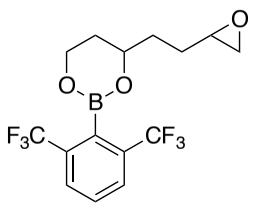




13

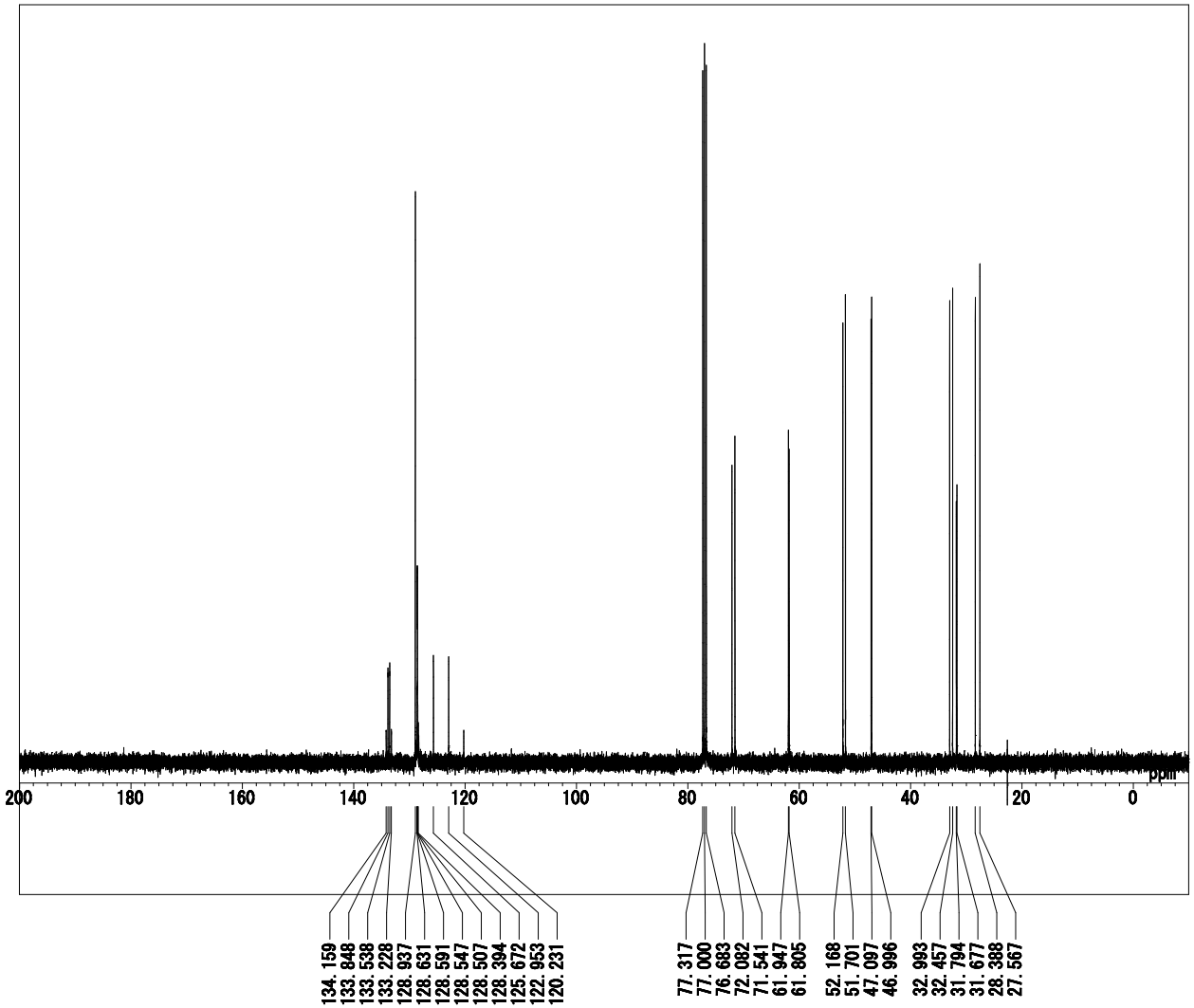
Comment	su11025pure2_20161111_01
Date	2016/Nov/11
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

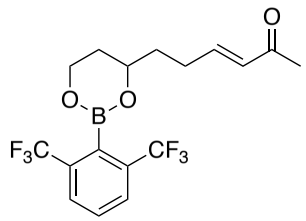




13

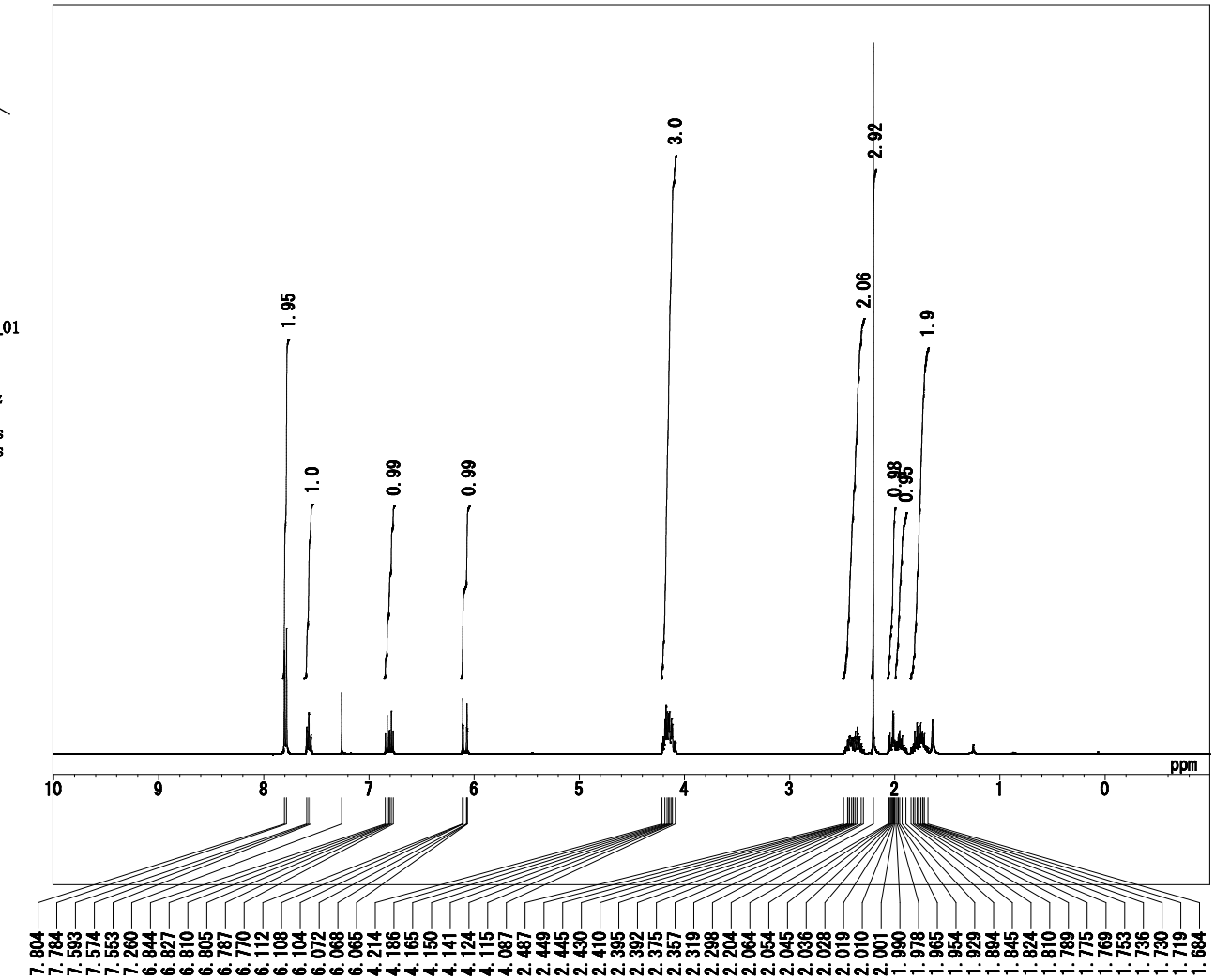
Comment	su11025pure2_20161111_01
Date	2016/Nov/11
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

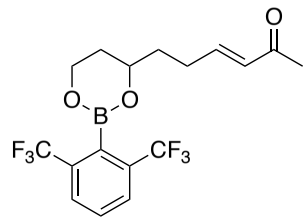




14

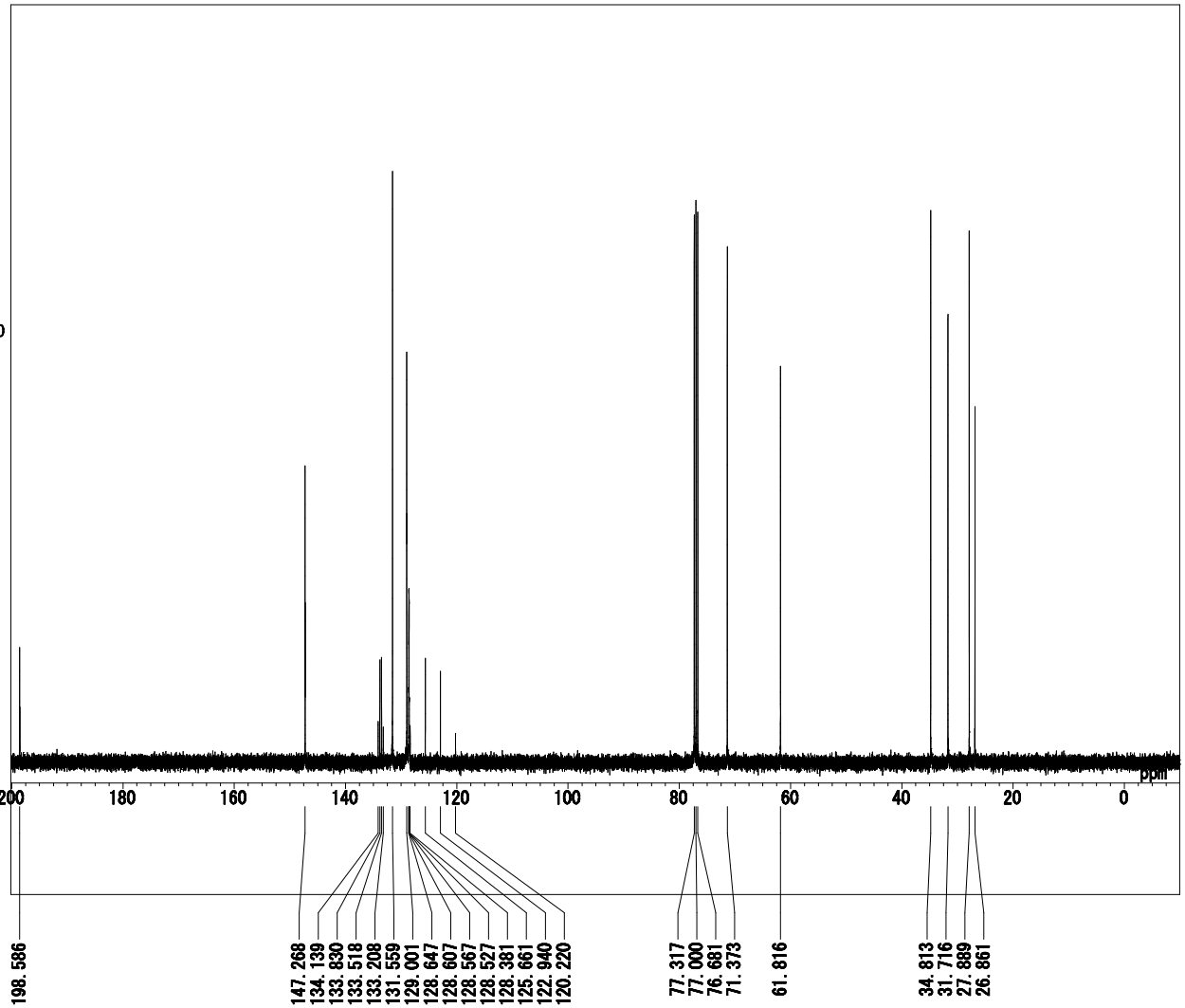
Comment	su14009pure_20160912_01
Date	2016/Sep/12
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	8
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

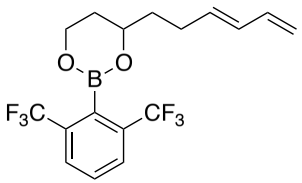




14

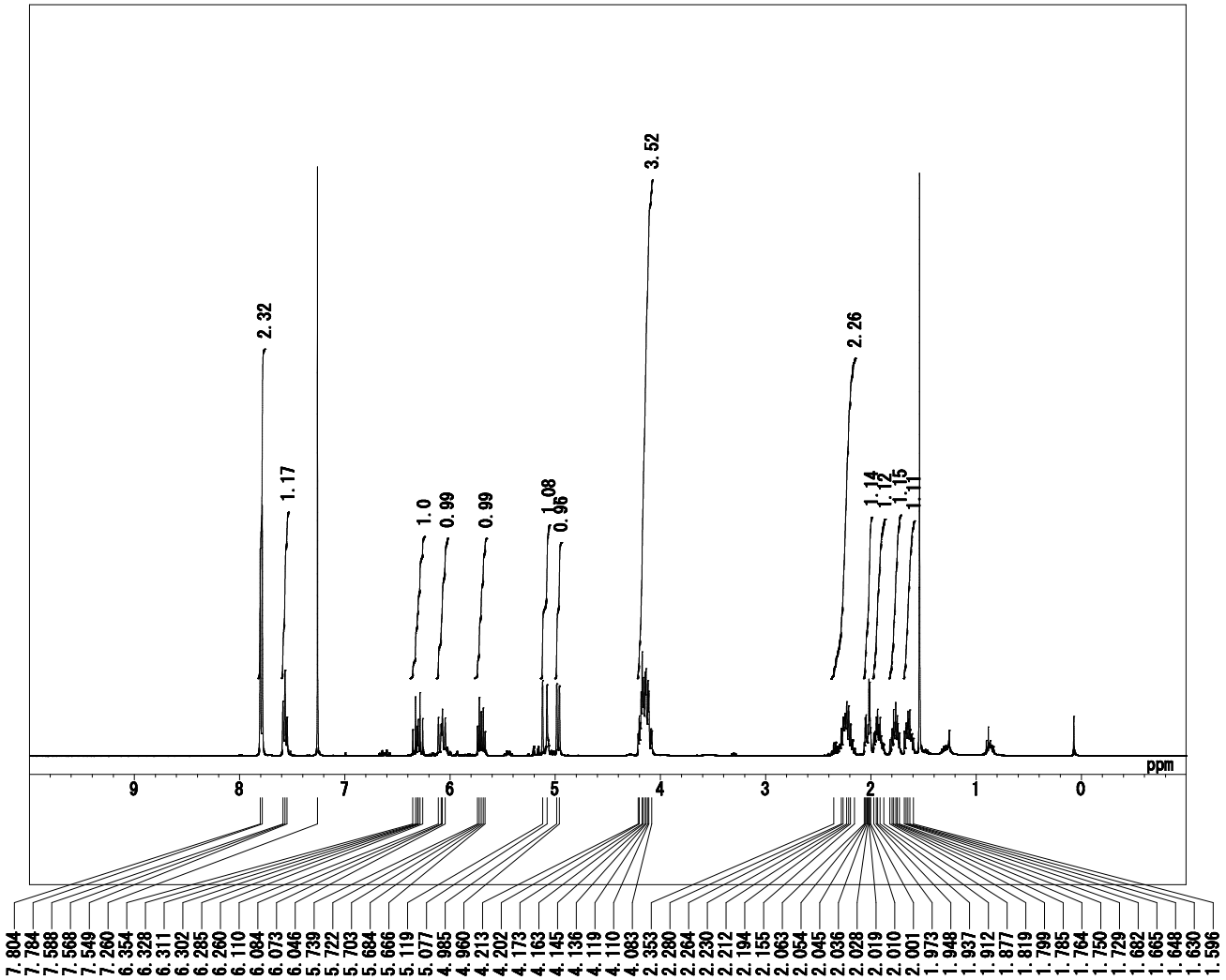
Comment	su14008pure-13C_20160912_01
Date	2016/Sep/12
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	512
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	30.0 ℃
Solvent	cdcl3

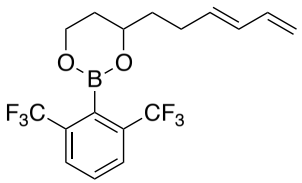




15

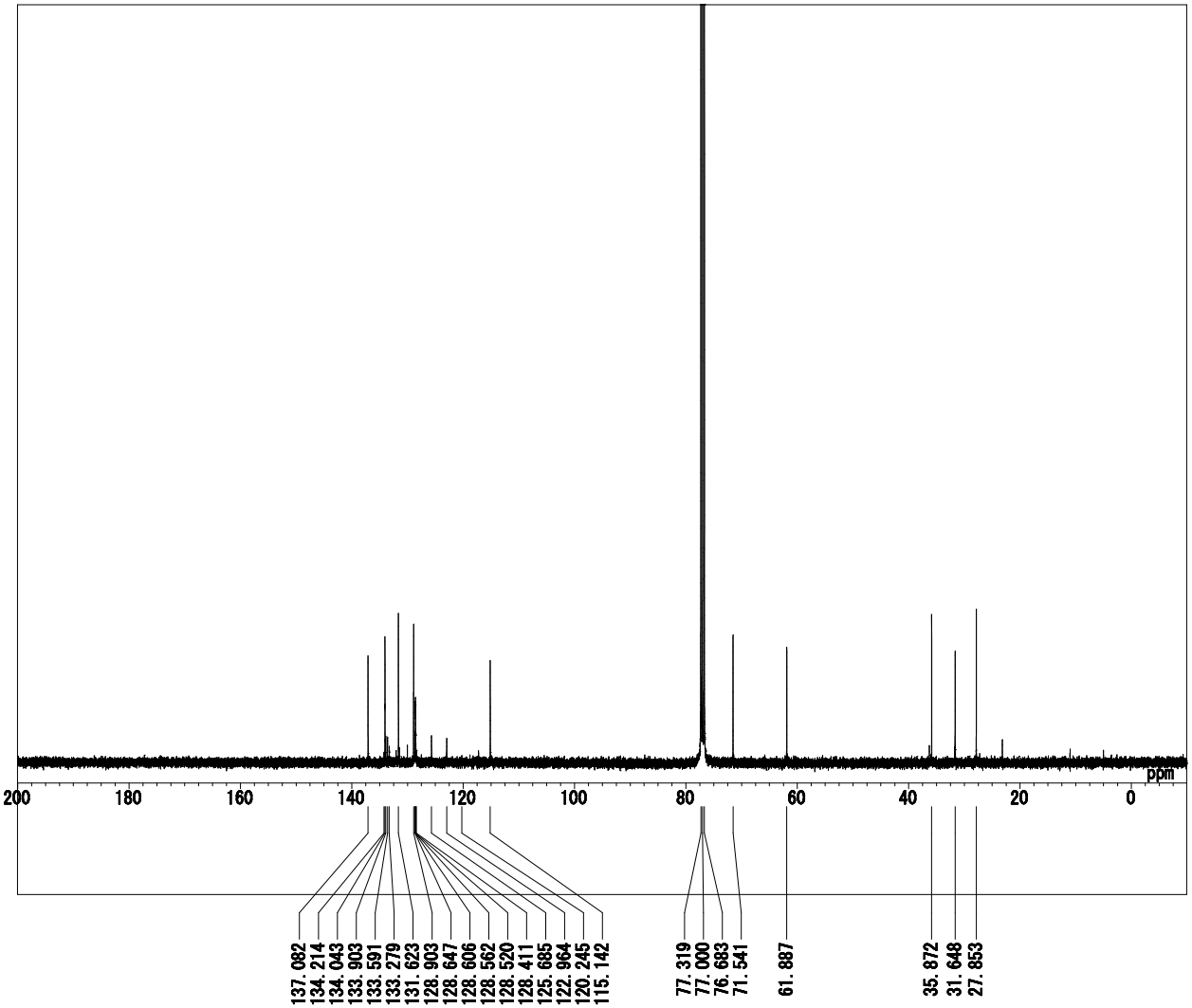
Comment	su15024pure_20170821_01
Date	2017/Aug/21
ObsNuc	^{1}H
ExMode	PROTON_001
ObsFreq	400.28 MHz
Scan	160
AcqTime	2.5559 s
Acc. Interval	5.5559 s
Spinning	16.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

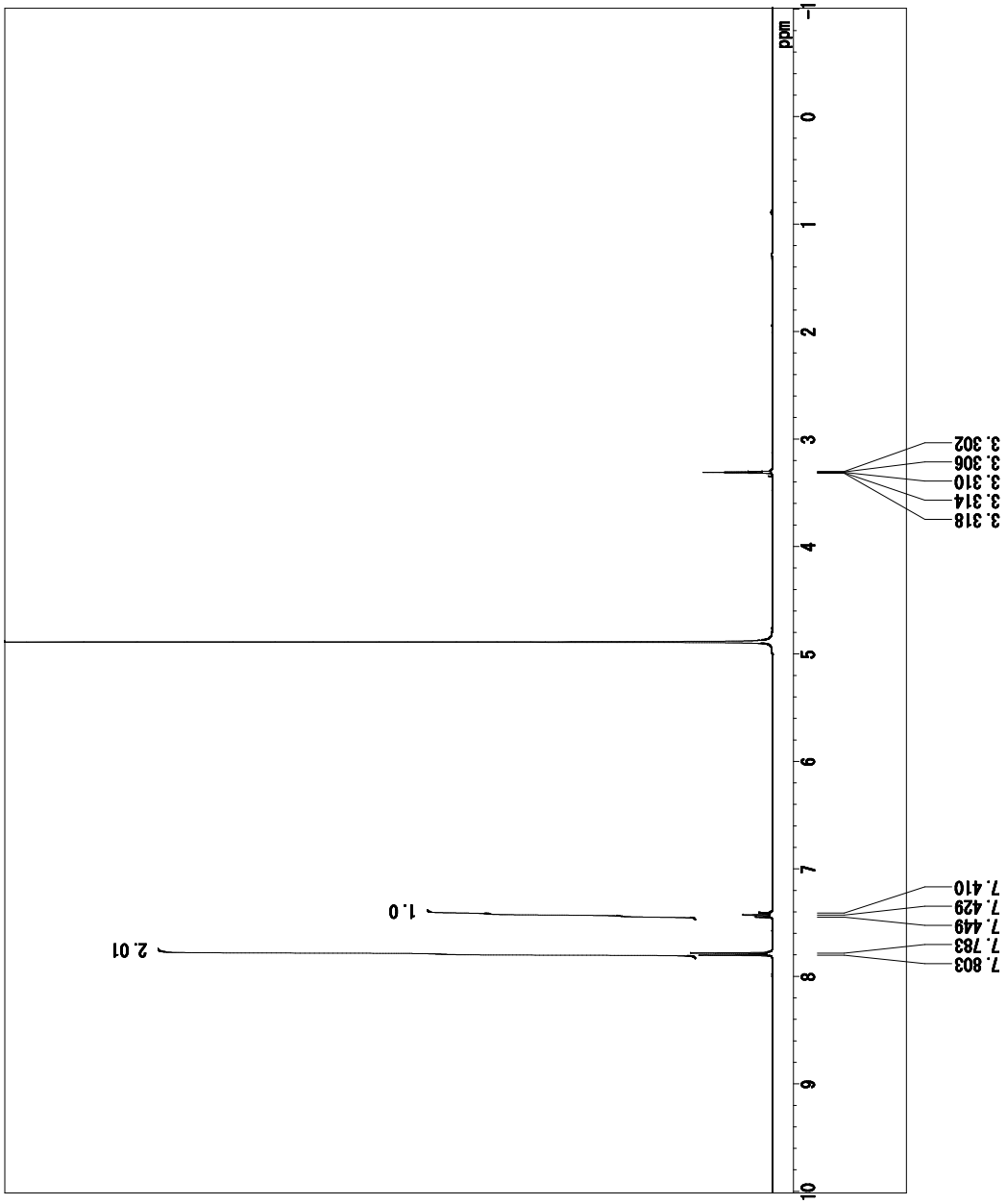


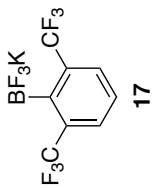


15

Comment	su15024-13C_20170821_01
Date	2017/Aug/21
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.66 MHz
Scan	10000
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cdcl3

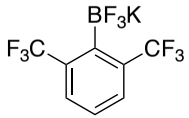






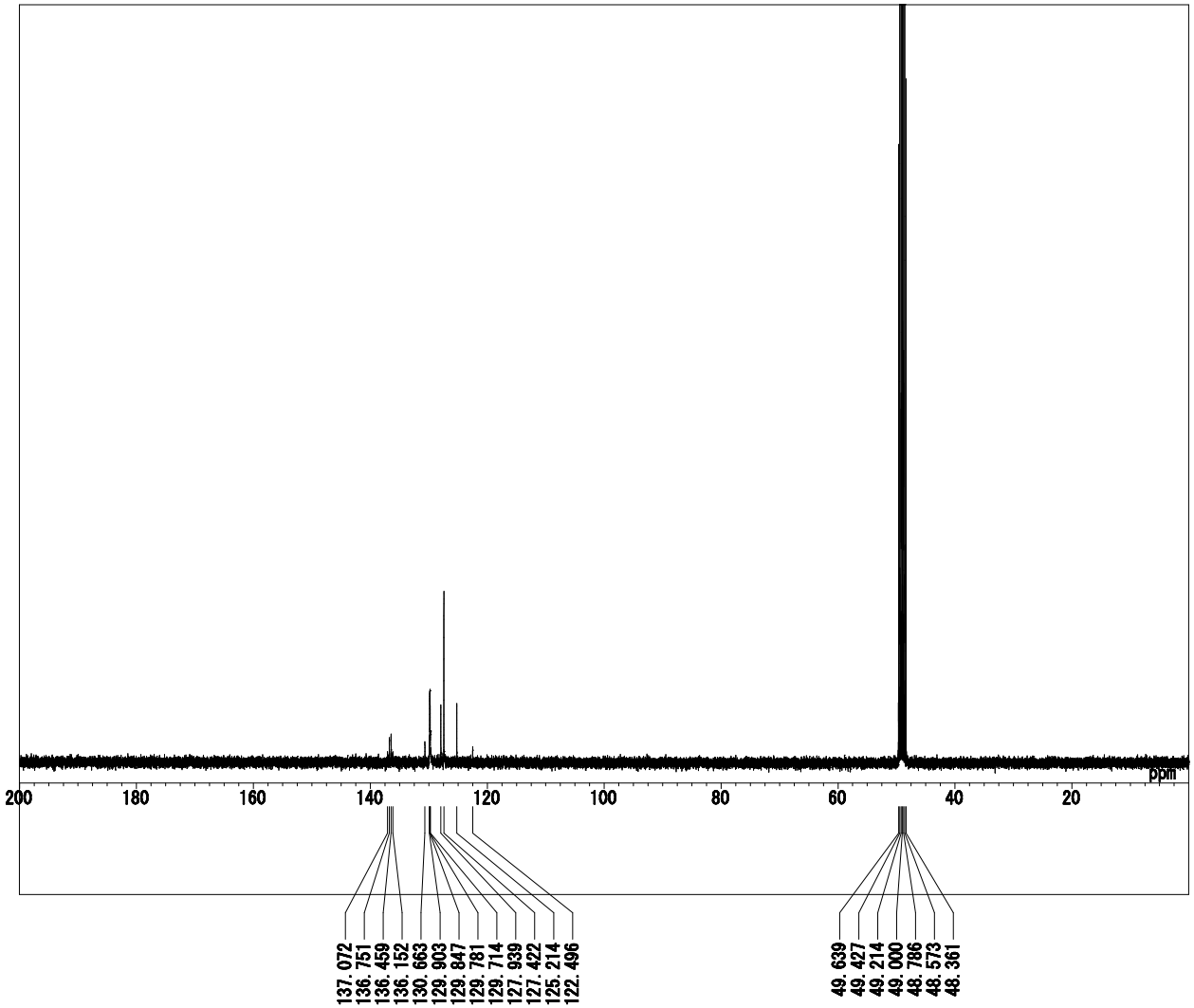
17

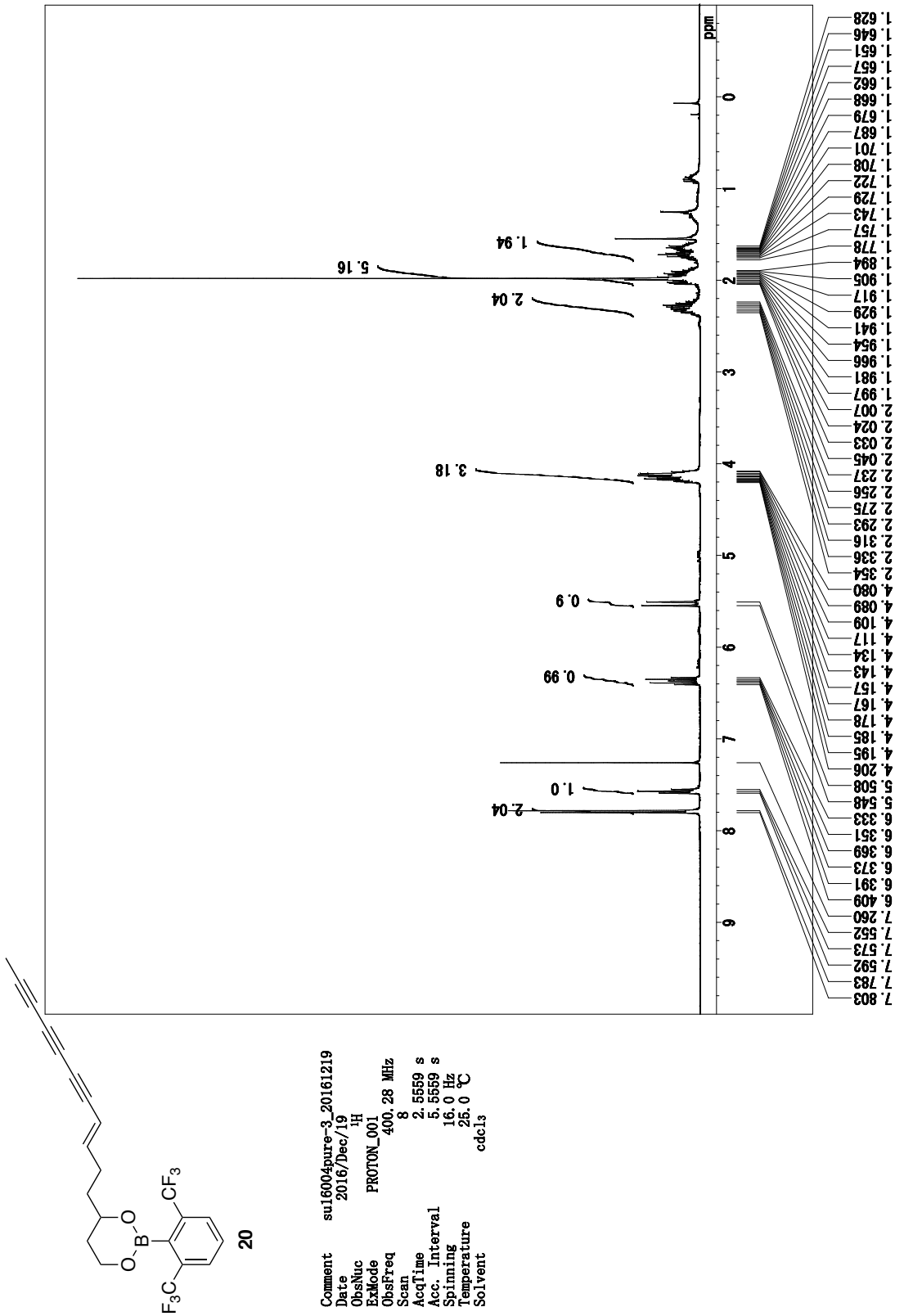
Comment su21018_20170808_01
Date 2017/Aug/08
ObsNuc 1H
ExMode PROTON_001
ObsFreq 399.45 MHz
Scan 8
AcqTime 2.569 s
Acc. Interval 5.569 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdsod

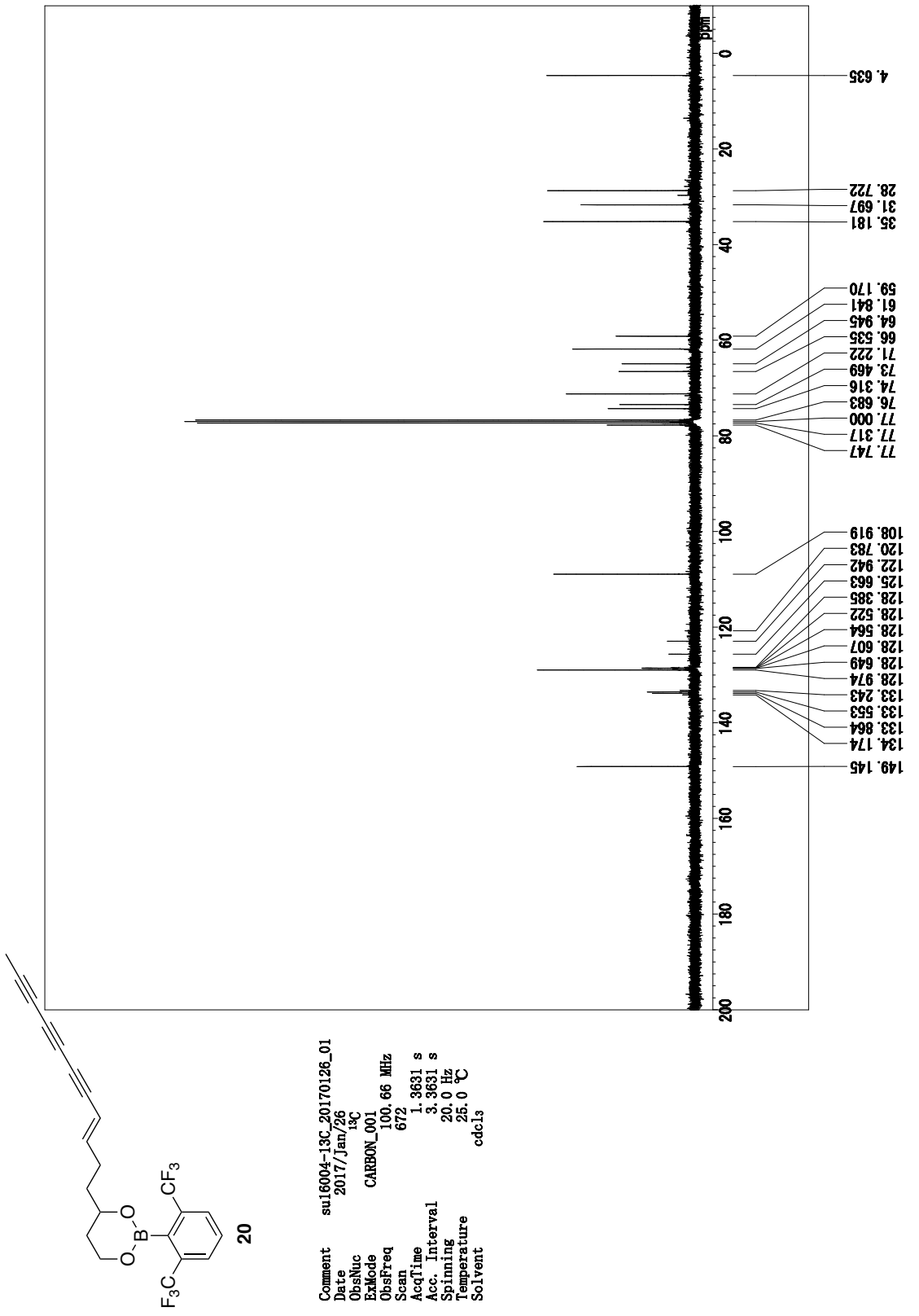


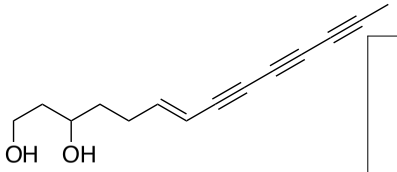
17

Comment	su21018-13C_20170808_01
Date	2017/Aug/08
ObsNuc	^{13}C
ExMode	CARBON_001
ObsFreq	100.45 MHz
Scan	912
AcqTime	1.3631 s
Acc. Interval	3.3631 s
Spinning	20.0 Hz
Temperature	25.0 ℃
Solvent	cd3od



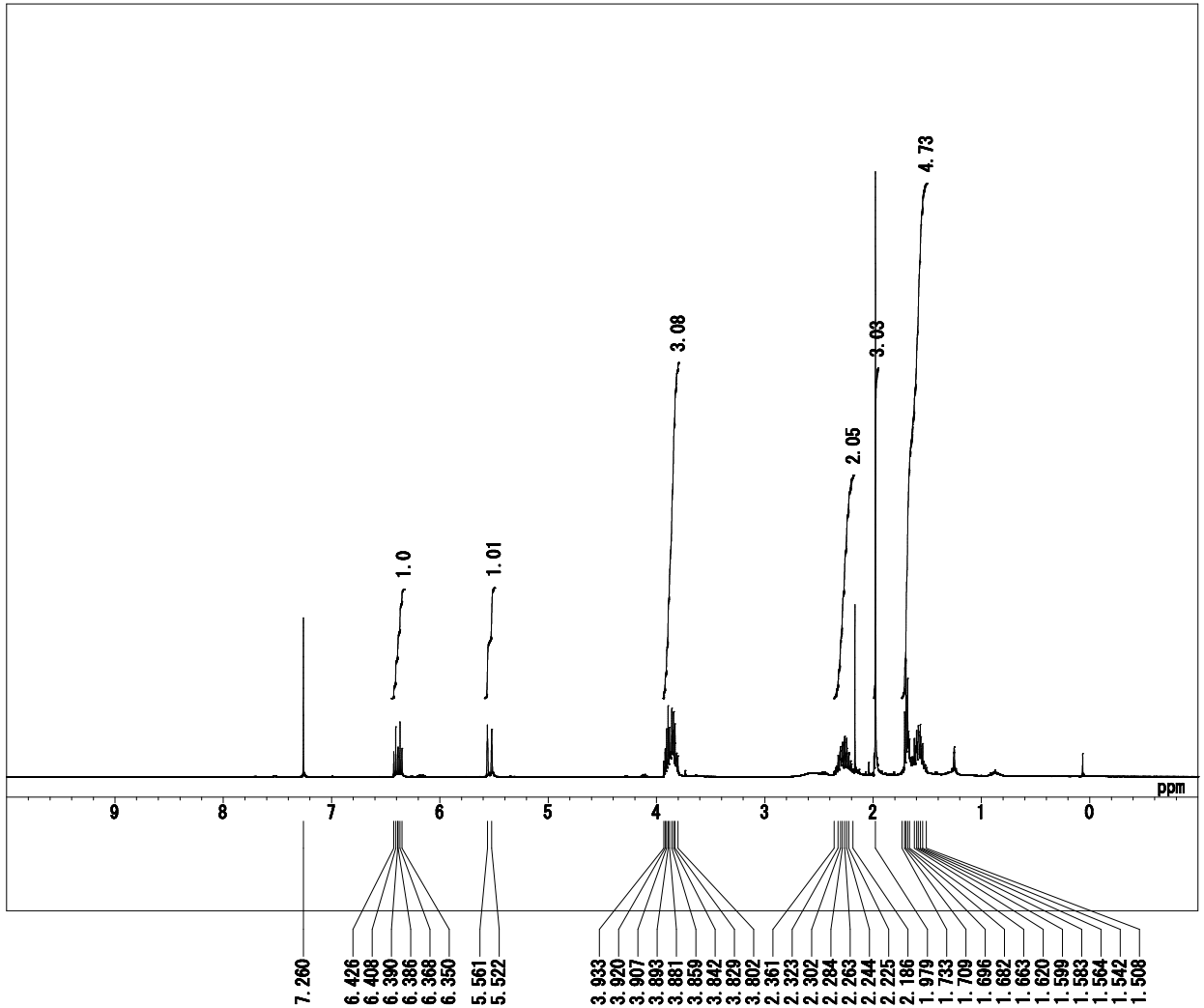

20
Comment su16004pure-3_20161219
Date 2016/Dec/19
ObsNuc 1H
ExMode PROTON_001
ObsFreq 400.28 MHz
Scan 8
AcqTime 2.5559 s
Acc. Interval 5.5559 s
Spinning 16.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
2.04
1.0
0.99
0.9
3.18
2.04
5.16
1.94

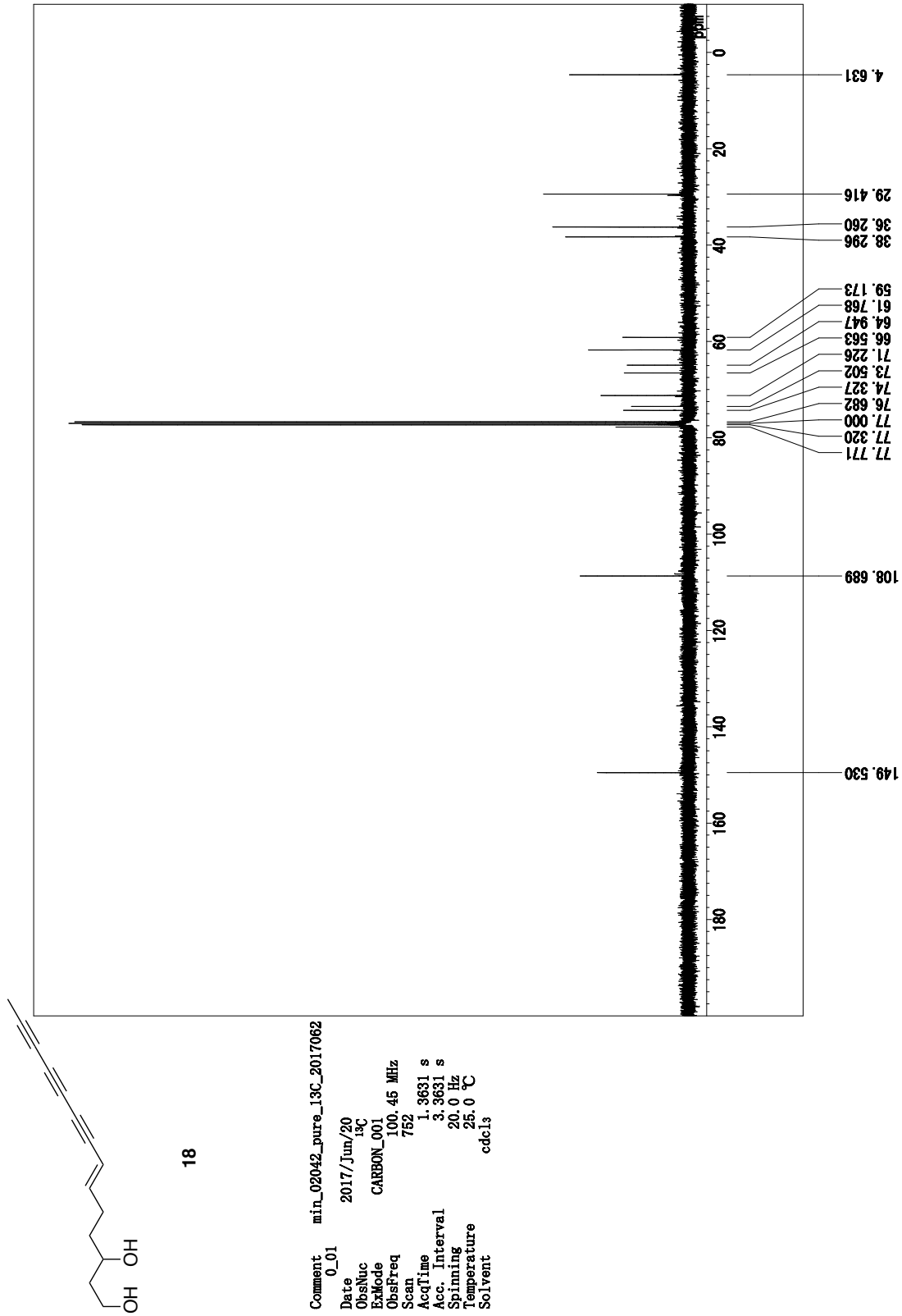

20
Comment su16004-13C_20170126_01
Date 2017/Jan/26
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.66 MHz
Scan 672
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
4.635
28.722
31.697
35.181
59.170
61.841
64.945
66.535
71.222
73.469
74.316
76.683
77.000
77.317
77.747
108.919
120.783
122.942
125.663
128.385
128.522
128.564
128.607
128.649
128.974
133.243
133.553
133.864
134.174
149.145



18

Comment	su20019pure_20170705_01
Date	2017/Jul/05
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




OH
OH
18
Comment min_02042_pure_13C_2017062
0_01
Date 2017/Jun/20
ObsNuc 13C
ExMode CARBON_001
ObsFreq 100.45 MHz
Scan 752
AcqTime 1.3631 s
Acc. Interval 3.3631 s
Spinning 20.0 Hz
Temperature 25.0 ℃
Solvent cdcl3
ppm
0
20
40
60
80
100
120
140
160
180
4.631
29.416
36.260
38.296
59.173
61.768
64.947
66.563
71.226
73.502
74.327
76.682
77.000
77.320
77.771
108.689
149.530

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