Supplementary Information

Amine-Tethered Phenylboronic Acid-Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals

Yamato Kanzaki, [‡a] Yuki Hirao, [‡a] Harunobu Mitsunuma, *[a] and Motomu Kanai *[a]

[a]Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

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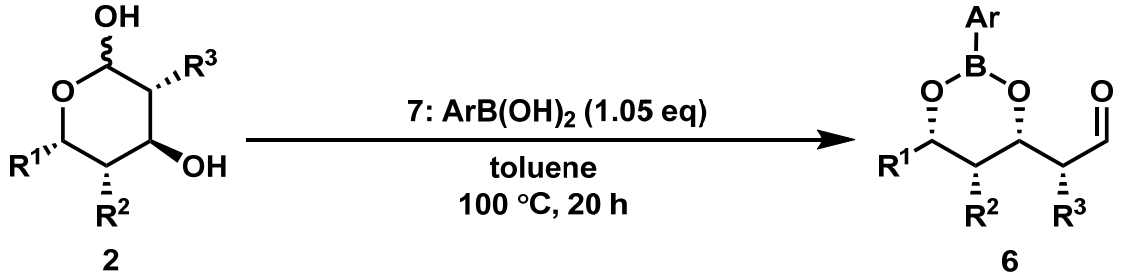
Materials and Methods

Reactions were carried out under argon atmosphere unless otherwise noted. Purified compounds were further dried under high vacuum. Diastereoselectivity of the products was determined by ^{1}H NMR analysis or LC/MS analysis of the crude mixture, comparing authentic samples. Yields refer to the diastereo mixture of compounds. Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 254 μm thickness silica gel 60 F_{254} plates and visualized by fluorescence quenching under UV light and *p*-anisaldehyde stains. Flash chromatography was performed using silica gel 60 (230-400 mesh ASTM) or silica gel 60N (40-100 μm) purchased from Merck or Kanto chemical, respectively. NMR spectra were recorded on either a JEOL ECX 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a JEOL ECS 400 spectrometer operating at 400 MHz, 125 MHz and 100 MHz for ^{1}H, ^{11}B and ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (^{1}H: $CDCl_3$, δ 7.26; CD_3OD, δ 3.31; $(CD_3)_2CO$, δ 2.05), (^{13}C: $CDCl_3$, δ 77.16; CD_3OD, δ 49.00; $(CD_3)_2CO$, δ 29.84). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. All deuterated solvents were purchased from Kanto chemical or Sigma-Aldrich. IR spectra were measured on a JASCO FT/IR 410 spectrophotometer. High-resolution mass spectra were obtained using a JEOL JMS-T100LC AccuTOF spectrometer. LC/MS data were obtained using a Shimazu Prominence-*i* LC-2030/LCMS-2020. Preparative HPLC was performed on a Shimazu SPD-20A/CTO-20AC using 2 cm × 25cm Daicel Chiralpak IA. Optical rotations were measured on a JASCO P-1010 polarimeter.

MesCu was either purchased from Strem or synthesized according to the literature.[1] DTBM-segphos was donated by Takasago International Corporation. Liquid aldehydes, Et_3N and Triisopropyl borate were purified by distillation. All the other chemicals were used as received. THF was deoxidized, stabilizer-free, and organic synthesis grade; acetone was super dehydrated, organic synthesis grade; toluene was JIS special grade. These solvents were purchased from Wako Pure Chemical Industries and used as received without further purification. Compound **2e** was prepared according to the literature.[2]

Experimental Data

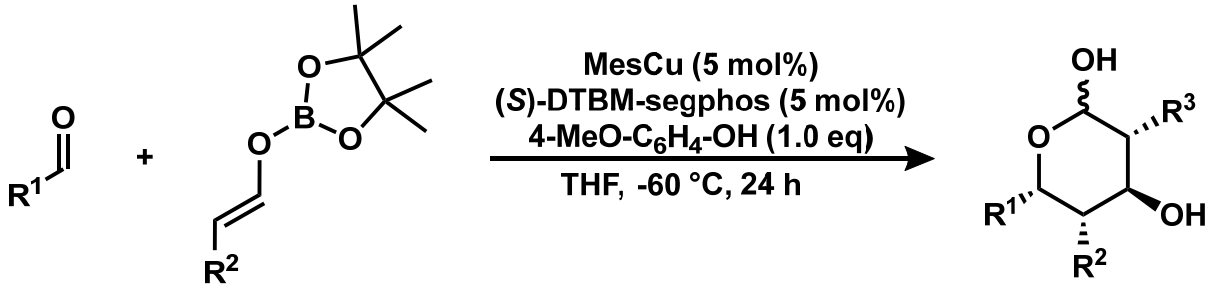
A Representative Procedure of Ring-Opening Reaction



Cyclic hemiacetal **2** (0.1 mmol) and boronic acid **7** (0.105 mmol) were added to a test tube, followed by the addition of toluene (2 mL) at 23 °C. After stirred for 20 hours at 100 °C, the solvent was evaporated.

Deuterated chloroform was added to this crude mixture, followed by the addition of 1,1,2,2-tetrachloroethane as internal standard. The solution was transferred to an NMR tube. The yield was determined by ^{1}H-NMR taken at room temperature.

A Representative Procedure for Synthesis of Cyclic Hemiacetal



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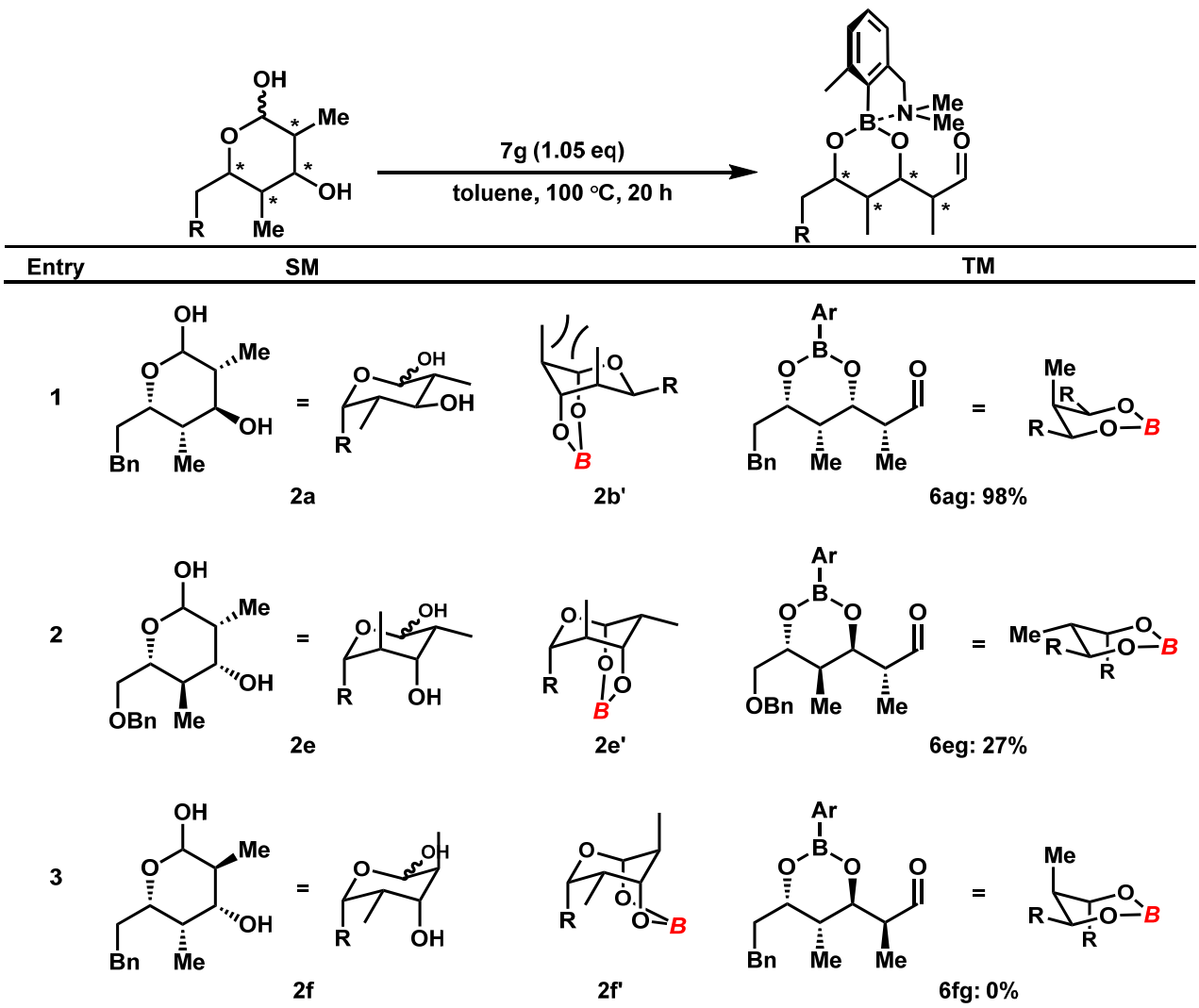
Under an argon atmosphere, mesitylcopper (1.8 mg, 0.01 mmol) and (*S*)-DTBM-segphos (11.8 mg, 0.01 mmol) were added to a round-bottom flask, followed by the addition of THF (0.4 mL) and 4-MeO-C_6H_4-OH (24.8 mg, 0.2 mmol) at 23 °C. After cooled to –60 °C, aldehyde (0.2 mmol) and a solution of boron enolate (0.8 mmol) in THF (0.8 mL), prepared according to the literature[3], were added, and the mixture was stirred for 24 hours at –60 °C. Water was added, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel.

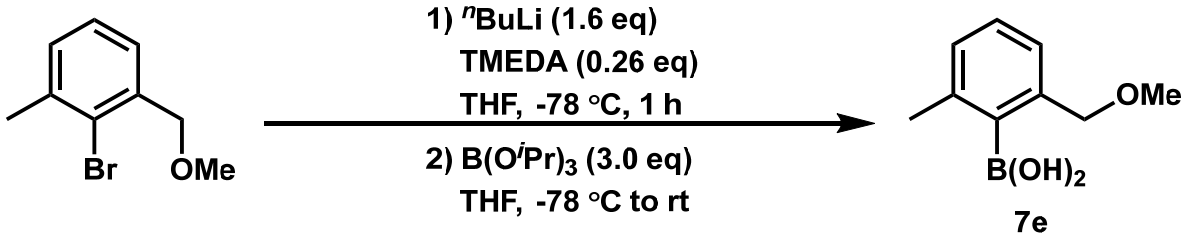
Effects of Stereochemistry of Cyclic Hemiacetal on the Ring-Opening Reaction



Using **7g** as the optimized ring-opening boron reagent, we examined the reactivity of cyclic hemiacetals bearing stereochemistry different from **2a**. **2a** reacted with **7g** to give thermodynamically stable boron ester **6ag** in 98% yield. **2a** and **7g** could afford boron ester **2b'**; however, **2b'** is destabilized by 1,3-diaxial interaction of methyl groups. In the case of **2e**, target product **6eg** was obtained in only 27% yield. We assume that relatively stable boron ester **2e'** is formed, and it disturbed ring-opening process of cyclic hemiacetal. In entry 3, we examined the reactivity of **7g** with cyclic hemiacetal **2f** which could form a similar boron ester **2f'** such as **2e'**. The ring opening reaction did not proceed at all. This result supports our hypothesis.

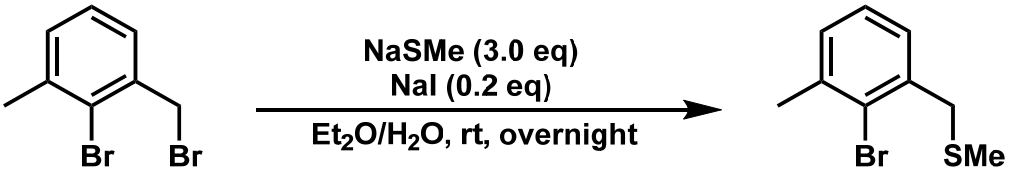
Synthesis of Boronic acids

(2-(methoxymethyl)-6-methylphenyl)boronic acid (7e)



Under an argon atmosphere, tetramethylethylenediamine (96 μL, 0.64 mmol) was added to a solution of 2-bromo-1-(methoxymethyl)-3-methylbenzene[4] (536 mg, 2.49 mmol) in THF (20mL). The mixture was cooled at -78 °C, and buthyllithium (2.65M, 1.46 mL, 3.87 mmol) was slowly added to the solution. The reaction mixture was stirred for an hour. Triisopropyl borate (1.7 mL, 7.41 mmol) was added to the solution. After stirring for 20 hours at room temperature, the solvent was evaporated. The reaction mixture was dissolved in dichloromethane, and insoluble materials were filtrated. Water was added to the filtrate, and the mixture was stirred overnight at room temperature. The solvent was evaporated, and the resulting residue was washed with hexane. The obtained solid was dissolved in dichloromethane and the insoluble solid was removed by filtration. After evaporation of solvent, obtained solid was used for the ring-opening reaction without further purification.

(2-bromo-3-methylbenzyl)(methyl)sulfane (13)



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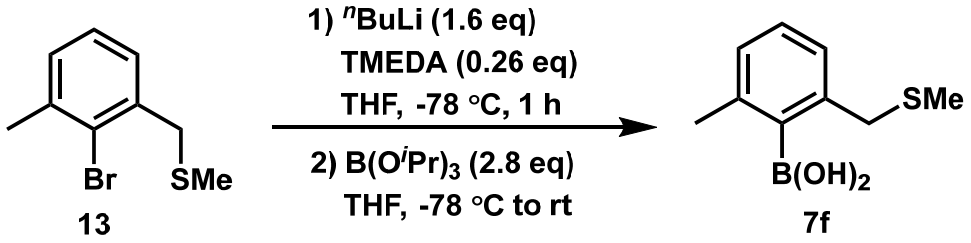
2-Bromo-1-(bromomethyl)-3-methylbenzene[5] (242.8 mg, 0.92 mmol) Et_2O (1.0 mL), H_2O (1.1 mL), sodium methanethiolate (0.193mg, 2.76 mmol), and sodium iodide (27.6 mg, 0.18 mmol) were added to a round bottom flask. After stirring the mixture for overnight at room temperature, the organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane to afford desired product **13** (116.5 mg, 0.50 mmol, 55% yield) as yellow oil.

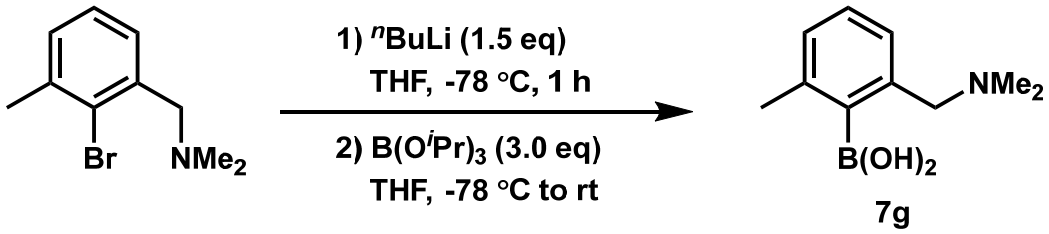
NMR spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17-7.14 (m, 3H), 3.85 (s, 2H), 2.44 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.27, 137.94, 129.66, 128.24, 127.27, 126.77, 39.55, 24.12, 15.42. IR spectroscopy ($CDCl_3$, cm^{-1}): 2909, 2357, 1435, 1026, 786, 738. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_9H_{11}BrS$ $[M+Ag]^+$: 338.8790, found: 338.8794.

(2-methyl-6-((methylthio)methyl)phenyl)boronic acid (7f)



Under an argon atmosphere, tetramethylethylenediamine (118 μL, 0.79 mmol) was added to a solution of (2-bromo-3-methylbenzyl)(methyl)sulfane **13** (706 mg, 3.05 mmol) in THF (25 mL). The mixture was cooled at -78 °C, and buthyllithium (2.65M, 1.46 mL, 4.74 mmol) was slowly added to the solution. The reaction mixture was stirred for an hour. Triisopropyl borate (1.7 mL, 8.63 mmol) was added to the solution. After stirring for 20 hours at room temperature, the solvent was evaporated. The reaction mixture was dissolved in dichloromethane, and insoluble materials were filtrated. Water was added to the filtrate, and the mixture was stirred overnight at room temperature. After evaporation, the residue was collected and washed with hexane. The obtained solid was dissolved in THF and the insoluble solid was removed by filtration. After evaporation, the obtained solid was dissolved in dichloromethane and the insoluble solid was removed by filtration. After evaporation of solvent, obtained solid was used for the ring-opening reaction without further purification.

(2-((dimethylamino)methyl)-6-methylphenyl)boronic acid (7g)

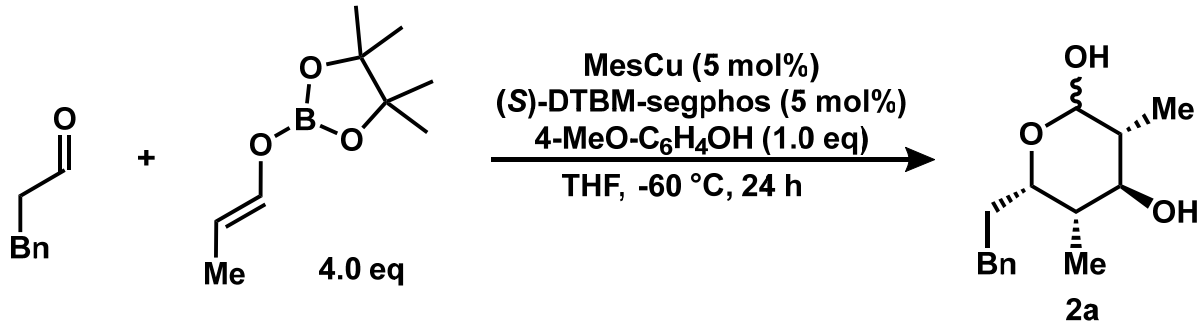


(2-((Dimethylamino)methyl)-6-methylphenyl)boronic acid **7g** was prepared according to the literature[6]. ^{1}H NMR was taken using deuterated acetone and a drop of D_2O.

NMR spectroscopy: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 6.99 (dd, J = 7.8 Hz, 7.3 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 7.3 Hz, 1H), 3.78 (s, 2H), 2.45 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 141.4, 141.1, 128.4, 127.5, 120.8, 64.2, 44.8, 20.4. IR spectroscopy ($CDCl_3$, cm^{-1}): 3281, 2922, 2357, 1457, 1009, 755. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{10}H_{16}BNO_2$ $[M+Na]^+$: 216.1166, found: 216.1171.

Synthesis of Cyclic Hemiacetals

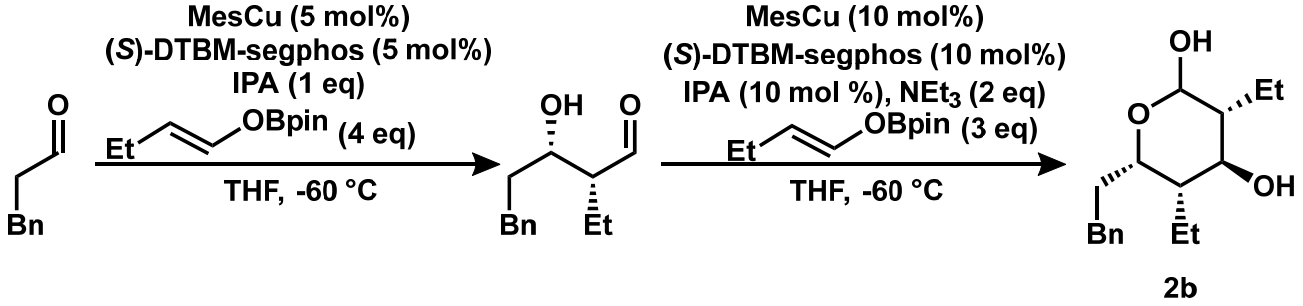
(3*R*,4*S*,5*S*,6*S*)-3,5-dimethyl-6-phenethyltetrahydro-2H-pyran-2,4-diol (2a)



Under an argon atmosphere, mesitylcopper (82.2 mg, 0.45 mmol) and (*S*)-DTBM-segphos (530.8 mg, 0.45 mmol) were added to a round bottom flask, followed by the addition of THF (8 mL) and 4-MeO-C_6H_4OH (1117 mg, 9 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (36 mmol) in THF (30 mL) and aldehyde (4 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 4:1 to 1:1 to afford desired product (1.5g, 6.0 mmol, 67% yield) as a white solid (**2a** : anomer = 1 : 0.15).

NMR spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 2H), 7.23-7.18 (m, 3H), 4.80 (dd, *J* = 6.5, 4.6 Hz, 1H), 4.17 (dt, *J* = 10.9, 4.3 Hz, 1H), 3.44 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.03 (d, *J* = 6.5 Hz, 1H), 2.86-2.80 (m, 1H), 2.68-2.62 (m, 1H), 2.00 (d, *J* = 6.0 Hz, 1H), 1.89-1.79 (m, 2H), 1.77-1.64 (m, 2H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.2, 128.7, 128.5, 126.1, 96.0, 75.8, 69.9, 42.6, 39.9, 32.4, 31.4, 14.6, 13.1. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{15}H_{22}O_3$ $[M+Na]^+$: 273.1461, found 273.1460.

(3*R*,4*S*,5*S*,6*S*)-3,5-diethyl-6-phenethyltetrahydro-2H-pyran-2,4-diol (2b)



Under an argon atmosphere, mesitylcopper (36 mg, 0.2 mmol) and (*S*)-DTBM-segphos (236 mg, 0.2 mmol) were added to a round bottom flask, followed by the addition of THF (4 mL) and isopropanol (304 μL, 4 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (16 mmol) in THF (16 mL) and aldehyde (4.0 mmol) were added, and the mixture was stirred for 24

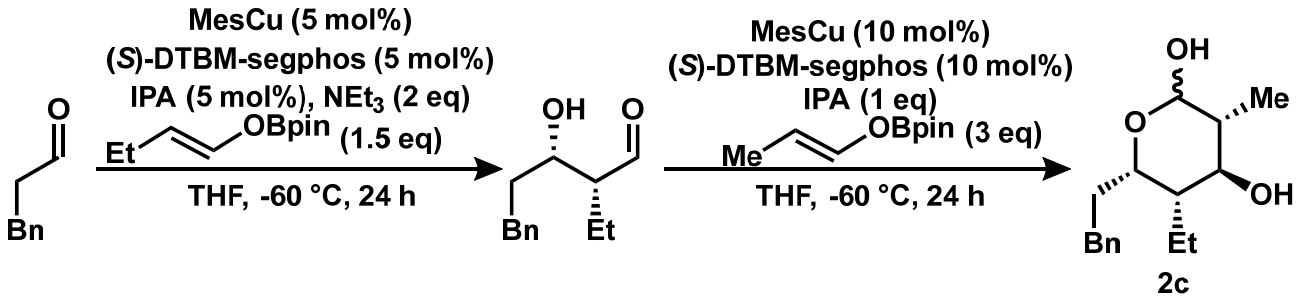
hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 3:1 to 1:1 to afford (2*S*,3*S*)-2-ethyl-3-hydroxy-5-phenylpentanal (770.3 mg, 3.7 mmol, 93% yield) as a white solid.

Under an argon atmosphere, mesitylcopper (18 mg, 0.1 mmol) and (*S*)-DTBM-segphos (118 mg, 0.1 mmol) were added to a round bottom flask, followed by the addition of THF (2 mL), isopropanol (7.7 μL, 0.1 mmol), and triethylamine (279 μL, 2 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (3.0 mmol) in THF (3.0 mL) and (2*S*,3*S*)-2-ethyl-3-hydroxy-5-phenylpentanal (1.0 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 3:1 to 1:1 to afford desired product (108.3 mg, 0.39 mmol, 39% yield) as a white solid (**2b** : anomer = 1 : 0.11).

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 7.23-7.18 (m, 3H), 4.98 (dd, *J* = 6.5 Hz, 2.6 Hz, 1H), 4.29 (dt, *J* = 10.3 Hz, 3.6 Hz, 1H), 3.83-3.79 (m, 1H), 3.29 (d, *J* = 6.5 Hz, 1H), 2.88-2.82 (m, 1H), 2.67-2.66 (m, 1H), 2.20 (d, *J* = 5.7 Hz, 1H), 1.92-1.84 (m, 1H), 1.70-1.63 (m, 1H), 1.61-1.38 (m, 6H), 0.99 (t, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.2, 128.7, 128.5, 126.0, 94.7, 71.6, 67.6, 48.4, 46.8, 32.6, 32.1, 22.0, 19.6, 13.0, 12.6.

Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{17}H_{26}O_3$ $[M+Na]^+$: 301.1774, found: 301.1773.

(3*R*,4*S*,5*S*,6*S*)-5-ethyl-3-methyl-6-phenethyltetrahydro-2H-pyran-2,4-diol (2c)

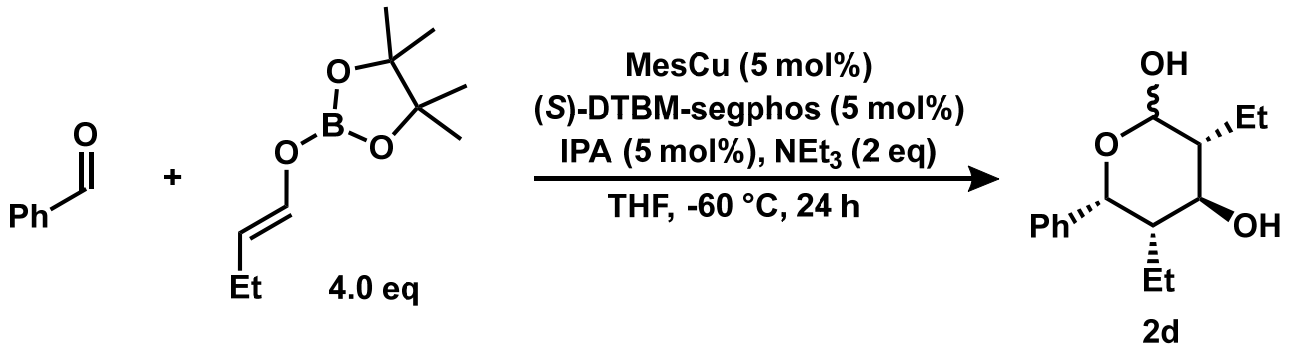


Under an argon atmosphere, mesitylcopper (27 mg, 0.2 mmol) and (*S*)-DTBM-segphos (177 mg, 0.2 mmol) were added to a round bottom flask, followed by the addition of THF (2 mL) and isopropanol (152 μL, 2.0 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (6.0 mmol) in THF (6.0 mL) and (2*S*,3*S*)-2-ethyl-3-hydroxy-5-phenylpentanal (2.0 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the

aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 3:1 to 1:1 to afford desired product (228.9 mg, 0.86 mmol, 43% yield) as a white solid (**2c** : anomer = 1 : 0.09).

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.26 (m, 2H), 7.23-7.18 (m, 3H), 4.72 (dd, *J* = 6.6 Hz, 6.3 Hz, 1H), 4.17 (dt, *J* = 11.5, 4.0 Hz, 1H), 3.45-3.41 (m, 1H), 3.17 (d, *J* = 6.6 Hz, 1H), 2.85-2.83 (m, 1H), 2.66-2.64 (m, 1H), 1.96 (d, *J* = 6.6 Hz, 1H), 1.86-1.82 (m, 1H), 1.72-1.58 (m, 4H), 1.29-1.23 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H) , 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.0, 128.6, 128.5, 126.1, 95.2, 73.6, 70.9, 47.1, 44.4, 32.4, 29.8, 20.4, 13.9, 12.1. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{16}H_{24}O_3$ $[M+Na]^+$: 287.1618, found 287.1620.

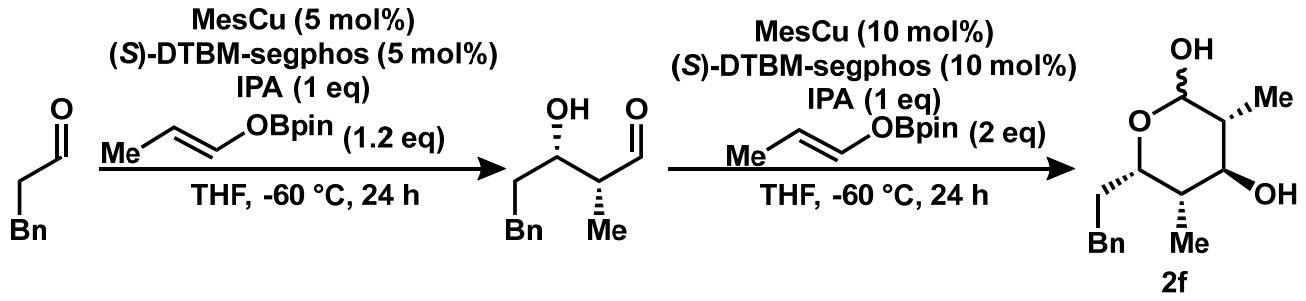
(3*R*,4*S*,5*S*,6*R*)-3,5-diethyl-6-phenyltetrahydro-2H-pyran-2,4-diol (2d)



Under an argon atmosphere, mesitylcopper (46 mg, 0.25 mmol) and (*S*)-DTBM-segphos (295 mg, 0.25 mmol) were added to a round bottom flask, followed by the addition of THF (5 mL), isopropanol (19 μL, 0.25 mmol) and triethylamine (1.4 mL, 10 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (20 mmol) in THF (20 mL) and aldehyde (5 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 4:1 to 1:1 to afford desired product (402.8 mg, 1.6 mmol, 32% yield) as a white solid (**2d** : aldehyde form = 1 : 0.08).

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.32 (m, 4H), 7.26-7.22 (m, 1H), 5.62 (d, *J* = 3.4 Hz, 1H), 5.28 (d, *J* = 5.2 Hz, 1H), 4.08-4.01 (m, 1H), 3.70 (brs, 1H), 3.01 (brs, 1H), 1.81-1.77 (m, 2H), 1.67-1.60 (m, 1H), 1.54-1.46 (m, 1H), 1.28-1.13 (m, 2H), 1.03 (t, *J* = 5.7 Hz, 3H), 0.58 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =140.8, 128.2, 126.9, 126.0, 96.3, 72.0, 67.1, 48.2, 46.3, 23.0, 19.4, 13.4, 13.3. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{15}H_{22}O_3$ $[M+Na]^+$: 273.1461, found 273.1462.

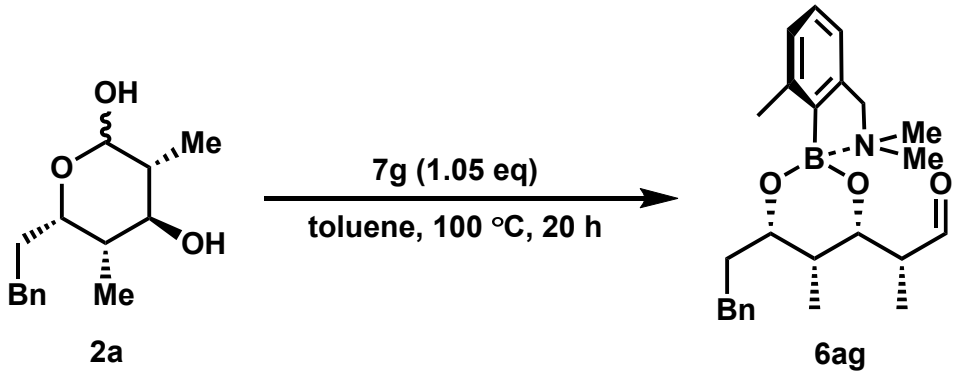
(3*S*,4*R*,5*S*,6*S*)-3,5-dimethyl-6-phenethyltetrahydro-2H-pyran-2,4-diol (2f)



Under an argon atmosphere, mesitylcopper (36 mg, 0.2 mmol) and (*S*)-DTBM-segphos (236 mg, 0.2 mmol) were added to a round bottom flask, followed by the addition of THF (4 mL) and isopropanol (304 μL, 4 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (4.8 mmol) in THF (4.8 mL) and aldehyde (4 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 2:1 to afford desired product (607.5 mg, 3.16 mmol, 79% yield) as a colorless oil. Under an argon atmosphere, mesitylcopper (30 mg, 0.16 mmol) and (*R*)-DTBM-segphos (194 mg, 0.16 mmol) were added to a round bottom flask, followed by the addition of THF (3 mL) and isopropanol (125 μL, 1.6 mmol) at 23 °C. After cooled to –60 °C, a solution of boron enolate (3.2 mmol) in THF (3.2 mL) and aldehyde (1.6 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution was added water, and the mixture was allowed to warm up to room temperature. The organic layer was separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 4:1 to 1:1 to afford desired product (102.6 mg, 0.41 mmol, 26% yield) as a white solid (**2f** : anomer = 1 : 0.5).

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 7.21-7.18 (m, 3H), 4.30 (dd, *J* = 8.0, 6.3 Hz, 1H), 3.43-3.39 (m, 2H), 3.21 (d, *J* = 6.3 Hz, 1H), 2.80-2.71 (m, 1H), 2.67-2.57 (m, 1H), 2.10-1.85 (m, 2H), 1.73-1.53 (m, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.9, 128.6, 128.5, 126.0, 99.7, 74.2, 71.6, 40.2, 38.2, 34.1, 32.3, 12.7, 5.7. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{15}H_{22}O_3$ $[M+Na]^+$: 273.1461, found 273.1461.

Ring-Opening Reaction of 2a

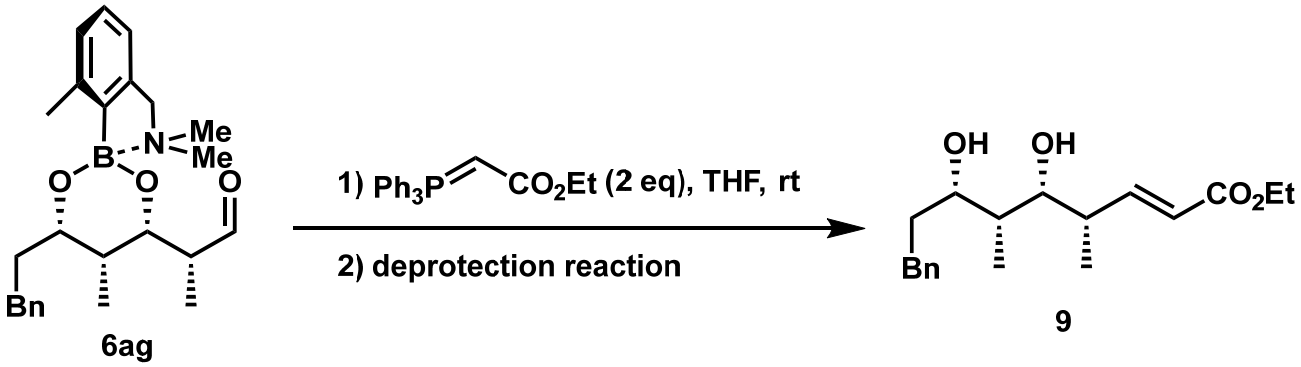


2a **6ag**

Cyclic hemiacetal **2a** (12.5 mg, 0.05 mmol) and **7g** (10.1 mg, 0.053 mmol) were added to a test tube, followed by the addition of toluene (1 mL) at 23 °C. After stirred for 20 hours at 100 °C, the solvent was evaporated. Deuterated chloroform was added to this crude mixture, followed by the addition of 1,1,2,2-tetrachloroethane (10.6 μL, 0.1 mmol) as an internal standard. The solution was transferred to an NMR tube. ^{1}H-NMR and ^{11}B-NMR were taken at room temperature. The yield was determined by ^{1}H NMR using the internal standard.

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (d, *J* = 2.3 Hz, 1H), 7.30-7.27 (m, 2H), 7.25-7.15 (m, 3H), 7.10 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 4.20 (dd, *J* = 8.9 Hz, 2.5Hz, 1H), 4.11-4.07 (m, 1H), 3.74 (d, *J* = 13.7 Hz, 1H), 3.70 (d, *J* = 13.7 Hz, 1H), 2.90-2.83 (m, 1H), 2.77-2.69 (m, 1H), 2.67-2.59 (m, 1H), 2.53 (s, 6H), 2.47 (s, 3H), 2.01-1.92 (m, 1H), 1.80-1.68 (m, 2H), 1.22 (d, *J* = 7.3 Hz, 3H), 1.07 (d, *J* = 7.3 Hz, 3H). ^{11}B NMR (125 MHz, $CDCl_3$): δ =13.7.

ethyl (4*S*,5*R*,6*R*,7*S*,*E*)-5,7-dihydroxy-4,6-dimethyl-9-phenylnon-2-enoate (9)



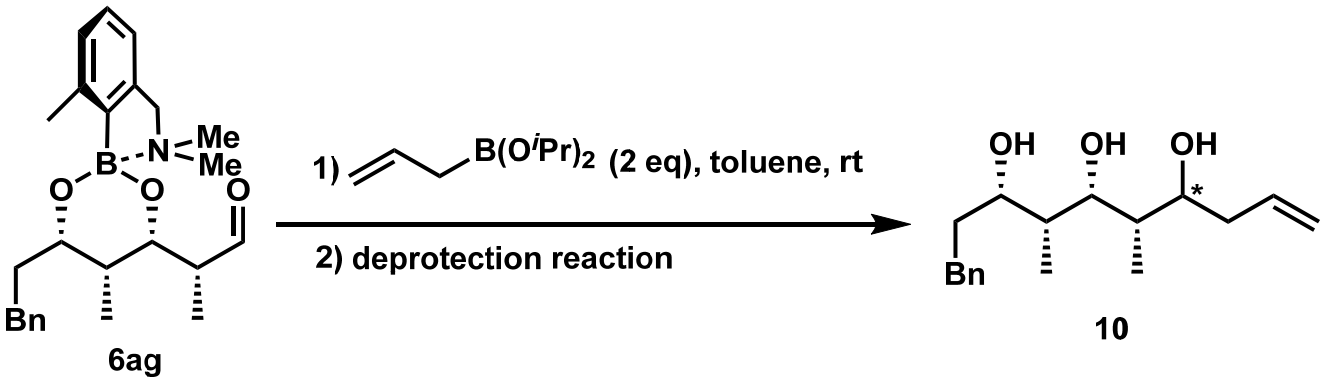
6ag **9**

To a solution of **6ag** (0.05 mmol) in THF (1.0 mL) was added ethyl(triphenylphosphoranylidene) acetate (34.8 mg, 0.10 mmol) at room temperature. After stirring for 5 hours, the solvent was removed by evaporation. To this residue, MeOH (1.0 mL) and 2-amino-2-methyl-1,3-propanediol (15.8 mg, 015 mmol) were added. After stirring for 24 hours at 50 °C, the reaction mixture was concentrated under reduced pressure. The resulting mixture was diluted with EtOAc and washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 2:1 to afford desired product **9** (12.1

mg, 0.037 mmol, 76% yield) as a colorless oil.

NMR spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 2H), 7.21-7.18 (m, 3H), 6.75 (dd, *J* = 15.6, 9.5 Hz, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.83-3.82 (m, 1H), 3.60 (d, *J* = 8.6 Hz, 1H), 3.07 (brs, 1H), 2.75-2.71 (m, 1H), 2.67-2.63 (m, 1H), 2.51-2.46 (m, 1H), 2.29 (brs, 1H), 1.88-1.82 (m, 1H), 1.74-1.70 (m, 1H), 1.56-1.53 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H) , 1.13 (d, *J* = 6.7 Hz, 3H) , 0.90 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 150.3, 141.7, 128.7, 128.6, 126.2, 121.7, 80.2, 77.0, 60.6, 41.1, 39.1, 37.2, 32.6, 17.0, 14.4, 4.4. IR spectroscopy ($CDCl_3$, cm^{-1}): 3413, 2932, 1717, 1651, 700. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{19}H_{28}O_4$ $[M+Na]^+$: 343.1880, found 343.1881. Optical rotation: $[\alpha]_D^{25.6}$ = -28.5 (*c* = 0.23, MeOH).

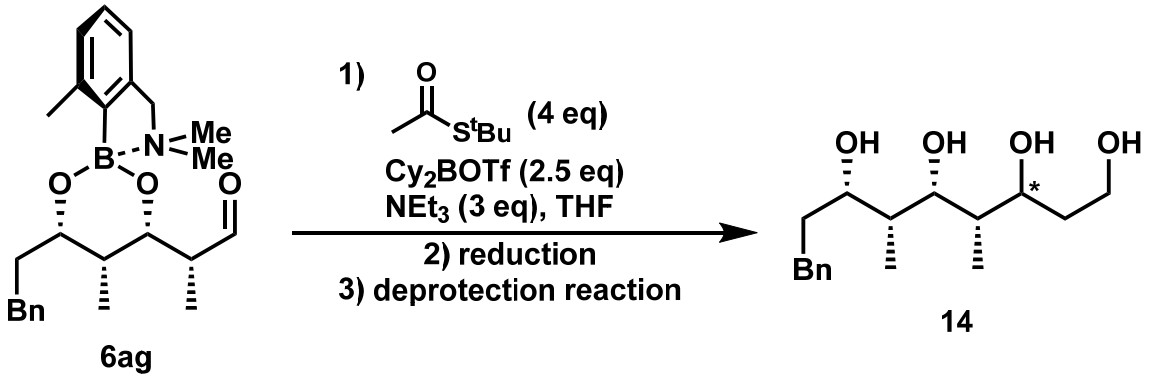
(3*S*,4*R*,5*S*,6*S*)-4,6-dimethyl-1-phenyldec-9-ene-3,5,7-triol (10)



To a solution of **6ag** (0.05 mmol) in toluene (1.0 mL) was added diisopropyl allylboronate (20.8 μL, 0.10 mmol) at room temperature. After stirring for 2 hours, the solvent was removed by evaporation. To this residue, MeOH (1.0 mL) and 2-amino-2-methyl-1,3-propanediol (15.8 mg, 015 mmol) were added. After stirring for 24 hours at 50 °C, the reaction mixture was concentrated under reduced pressure. The resulting mixture was diluted with EtOAc and washed with brine, dried over Na_2SO_4, filtered and concentrated. After the determination of diastereoselectivity by ^{1}H NMR, the residue was purified by column chromatography on silica gel eluting with hexane/EtOAc = 1:1 to afford desired product **10** (10.7 mg, 0.036 mmol, 73% yield, 2.6/1 dr) as a colorless oil.

NMR spectroscopy: Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 5.83-5.74 (m, 1H), 5.16 (d, *J* = 5.7 Hz, 1H), 5.13 (s, 1H), 3.87 (dd, *J* = 4.6 Hz, 4.6Hz, 1H), 3.84-3.79 (m, 2H), 2.75 (m, 1H), 2.64 (m, 1H), 2.23 (m, 1H), 2.17 (brs, 1H), 2.04 (brs, 1H), 1.87 (m, 1H), 1.71 (m, 2H), 0.98 (d, *J* = 7.4 Hz, 3H) , 0.96 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.0, 135.0, 128.6, 128.6, 126.1, 118.5, 79.7, 75.1, 74.0, 40.1, 40.0, 39.7, 37.3, 32.7, 6.9, 6.7. IR spectroscopy ($CDCl_3$, cm^{-1}): 3383, 2924, 1716, 1456, 699. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{17}H_{28}O_3$ $[M+Na]^+$: 315.1931, found 315.1931.

(4*S*,5*S*,6*R*,7*S*)-4,6-dimethyl-9-phenylnonane-1,3,5,7-tetraol (14)

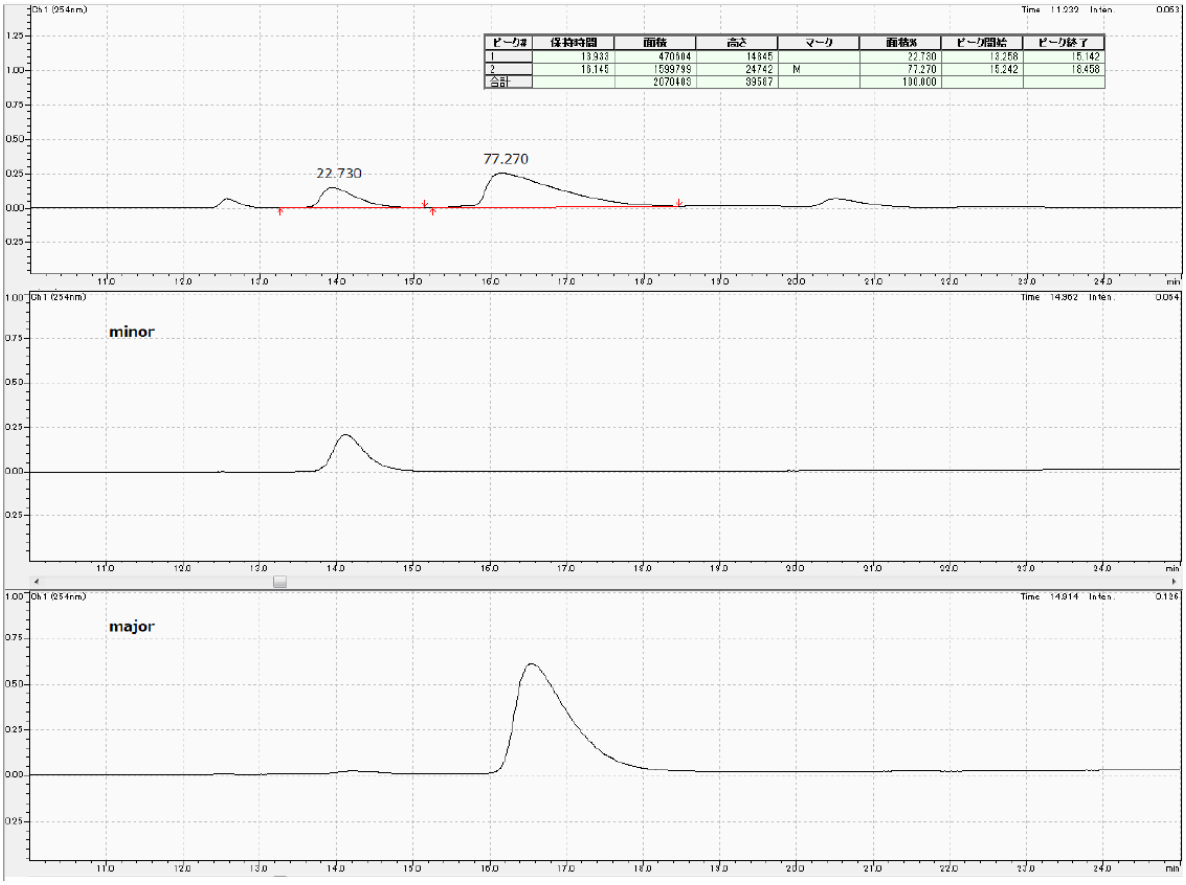


6ag **14**

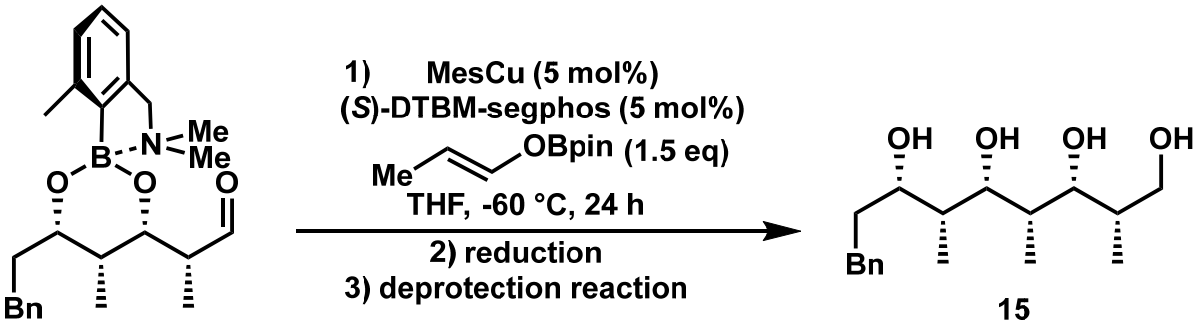
To a solution of dicyclohexylboron trifluoromethanesulfonate (122.4 mg, 0.38 mmol) in hexane (0.85 mL), triethylamine (62.8 μL, 0.45 mmol) and S-t-butyl phenylthiothioacetate (85.6 μL, 0.6 mmol) were added at 0 °C under an argon atmosphere. After stirring for 2 hours, this boron-enolate solution (0.5 mL) was transferred to a solution of **6ag** (0.1 mmol) in dichloromethane (0.33 mL) at –78 °C. The mixture was allowed to stir for 2 hours. To this solution, a solution of $LiBH_4$ (0.5 mmol) in THF (0.25 mL) was added. The mixture was allowed to warm up to room temperature, and stirred for overnight. To this mixture was added HCl (1 M). The organic layer was separated, and the aqueous phase was extracted with Et_2O. To the combined organic layers, water and an excess of H_2O_2 and NaOH were added. After stirring for overnight at 23 °C, Na_2SO_3 was added to the solution. The layers were separated, and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. After the determination of diastereoselectivity by LC/MS analysis, the residue was purified by column chromatography on silica gel eluting with EtOAc to afford the title compound **14** (18.0 mg, 0.061 mmol, 61%, 3.4/1 dr) as colorless oil. Stereoisomers were separated by preparative HPLC using Daicel Chiralpak IA.

NMR spectroscopy: Major isomer: ^{1}H NMR (500 MHz, CD_3OD): δ = 7.27-7.20 (m, 4H), 7.14 (t, J = 7.16 Hz, 1H), 3.79-3.64 (m, 5H), 2.77-2.72 (m, 1H), 2.65-2.59 (m, 1H), 1.85-1.59 (m, 6H), 1.00 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ = 143.5, 129.4, 129.4, 126.8, 75.2, 73.0, 72.3, 60.6, 41.4, 41.3, 38.1, 37.3, 33.5, 10.5, 8.7. IR spectroscopy ($CDCl_3$, cm^{-1}): 3375, 2924, 1681, 1455, 1203. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{17}H_{28}O_4$ $[M+Na]^+$: 319.1880, found: 319.1880. Optical rotation: $[\alpha]_D^{29.4}$ = -61.5 (c = 0.26, $CHCl_3$).

Minor isomer: ^{1}H NMR (500 MHz, CD_3OD): δ = 7.27-7.20 (m, 4H), 7.14 (t, J = 7.16 Hz, 1H), 3.88-3.84 (m, 1H), 3.72-3.63 (m, 4H), 2.80-2.74 (m, 1H), 2.65-2.59 (m, 1H), 1.86-1.62 (m, 6H), 0.96 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ = 143.6, 129.5, 129.4, 126.8, 78.2, 73.9, 71.8, 60.4, 41.0, 40.7, 38.7, 38.3, 33.4, 8.1, 8.1. IR spectroscopy ($CDCl_3$, cm^{-1}): 3381, 2924, 1682, 1455. Mass spectroscopy: HRMS-ESI (m/z): calcd for $C_{17}H_{28}O_4$ $[M+Na]^+$: 319.1880, found: 319.1880. Optical rotation: $[\alpha]_D^{29.4}$ = -138.5 (c = 0.13, $CHCl_3$).



(2*S*,3*R*,4*S*,5*S*,6*R*,7*S*)-2,4,6-trimethyl-9-phenylnonane-1,3,5,7-tetraol (15)

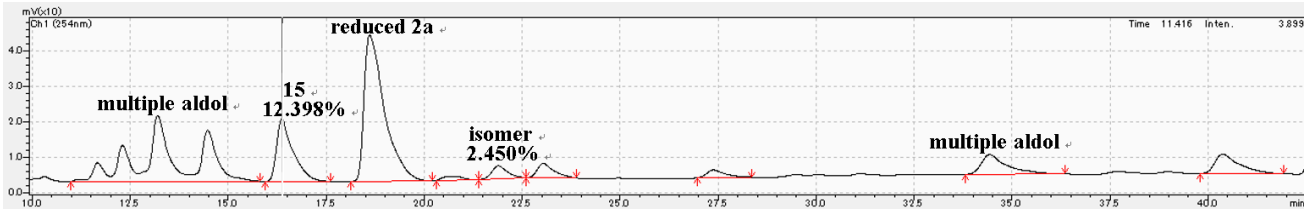


6ag

15

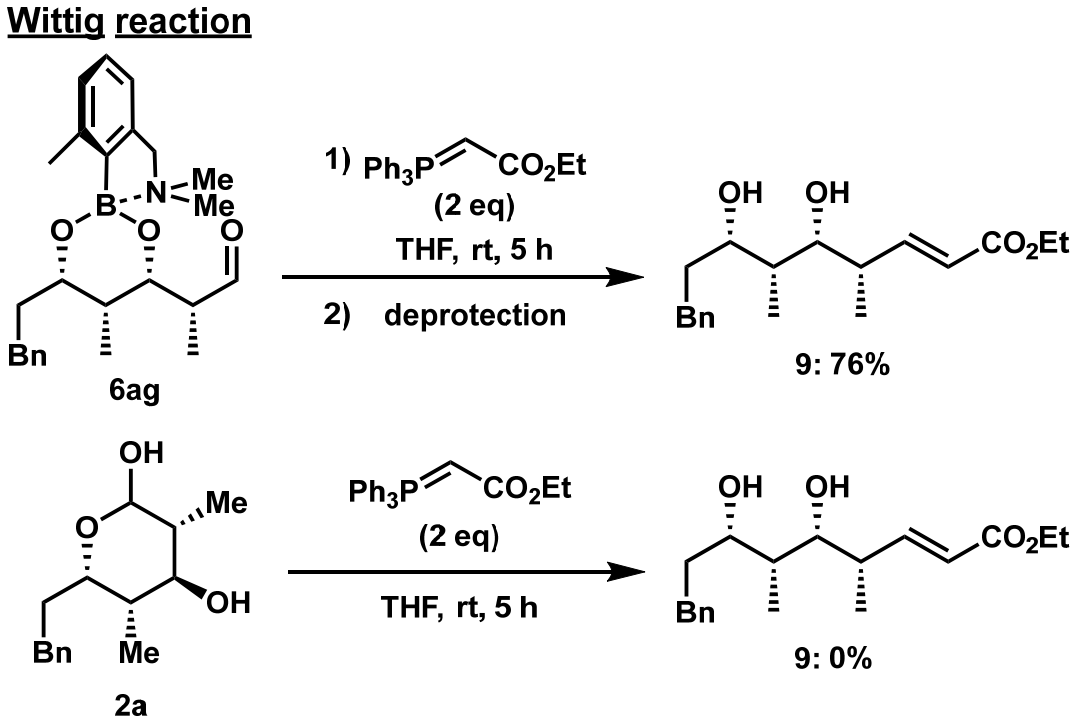
Under an argon atmosphere, mesitylcopper (0.9 mg, 0.005 mmol) and (*S*)-DTBM-segphos (5.9 mg, 0.005 mmol) were dissolved in THF (0.2 mL) at 23 °C. After cooled to –60 °C, a solution of boron enolate (0.15 mmol) in THF (0.15 mL) and **6ag** (0.1 mmol) were added, and the mixture was stirred for 24 hours at –60 °C. To this solution, a solution of $LiBH_4$ (0.5 mmol) in THF (0.25 mL) was added. The mixture was allowed to warm up to room temperature, and stirred for overnight. To this mixture was added HCl (1 M). The layers were separated, and the aqueous phase was extracted with Et_2O. To the combined organic layers, water and an excess of H_2O_2 and NaOH were added. After stirring for overnight at 23 °C, Na_2SO_3 was added to the solution. The organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine,

dried over Na_2SO_4, filtered and concentrated. Yield and diastereoselectivity was determined by LC/MS analysis according to the literature[3].



ピーク#	保持時間	面積	高さ	マーク	面積%	ピーク開始	ピーク終了
1	13.199	1285338	18596	M	31.266	10.983	15.800
2	16.368	509697	17665	M	12.398	15.933	17.600
3	18.610	1494996	41237	M	36.366	18.125	20.200
4	20.830	34946	989	M	0.850	20.317	21.400
5	21.890	100707	3685	M	2.450	21.400	22.600
6	23.041	118833	4027	M	2.891	22.600	23.883
7	27.378	69271	2167	M	1.685	26.975	28.350
8	34.428	253882	5539	M	6.176	33.817	36.358
9	40.377	243336	5541	M	5.919	39.808	41.942
合計		4111006	99446		100.000		

Control Experiments of Transformation of Ring-Opened Aldehyde 6ag



In order to demonstrate that ring-opening of hemiacetal **2a** by amine-tethered phenylboronic acid **7g** is critical for the transformations of **2a**, control experiments were conducted using **2a** without the ring-opening procedure. In the Wittig reaction, the desired product **9** was not obtained, and the starting material was recovered quantitatively. The allylation reaction afforded the desired product **10** in 1% yield. The starting material was recovered mainly.

References

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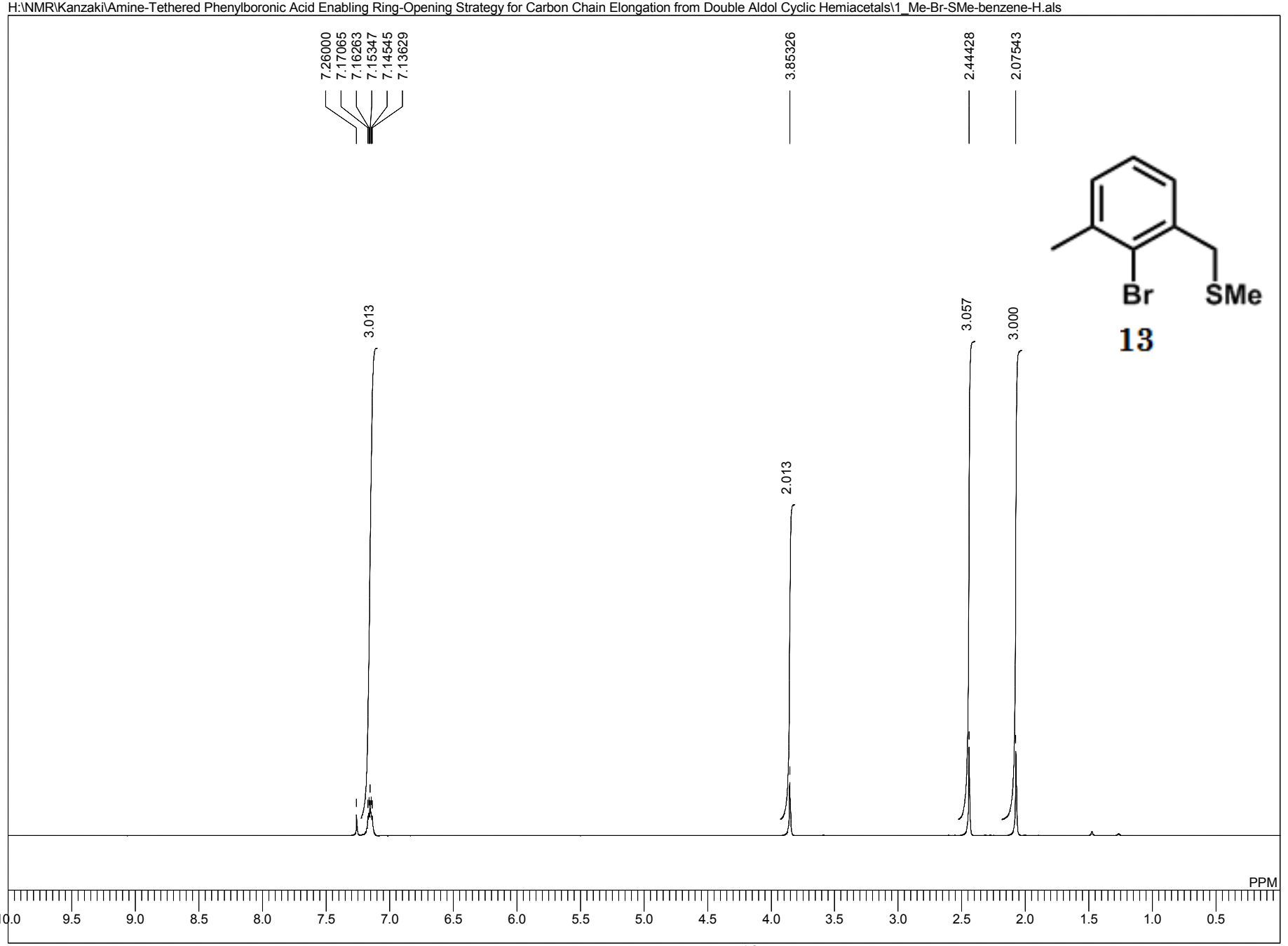
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\1_Me-Br-SMe-benzene-H.als



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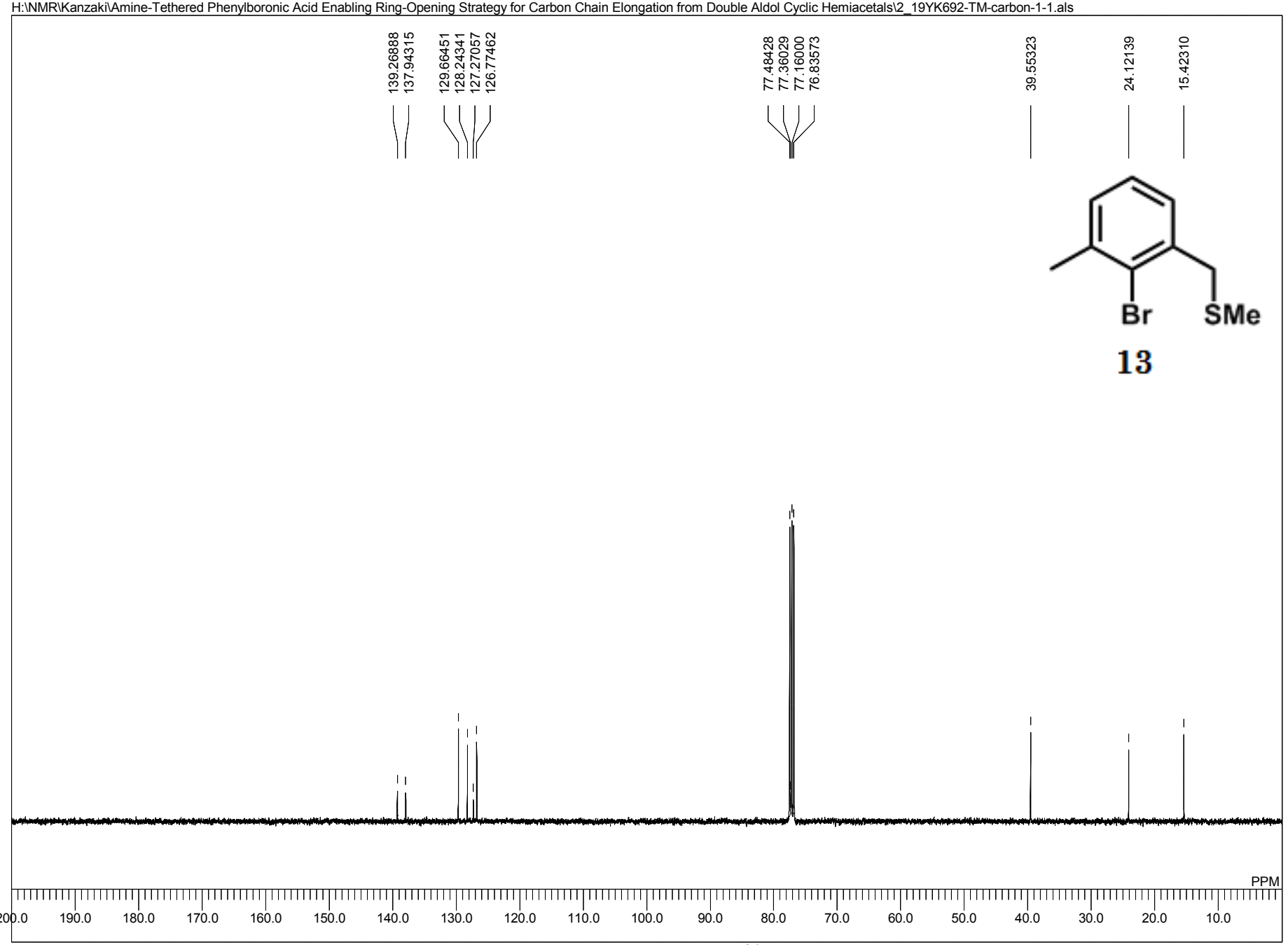
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\2_19YK692-TM-carbon-1-1.als



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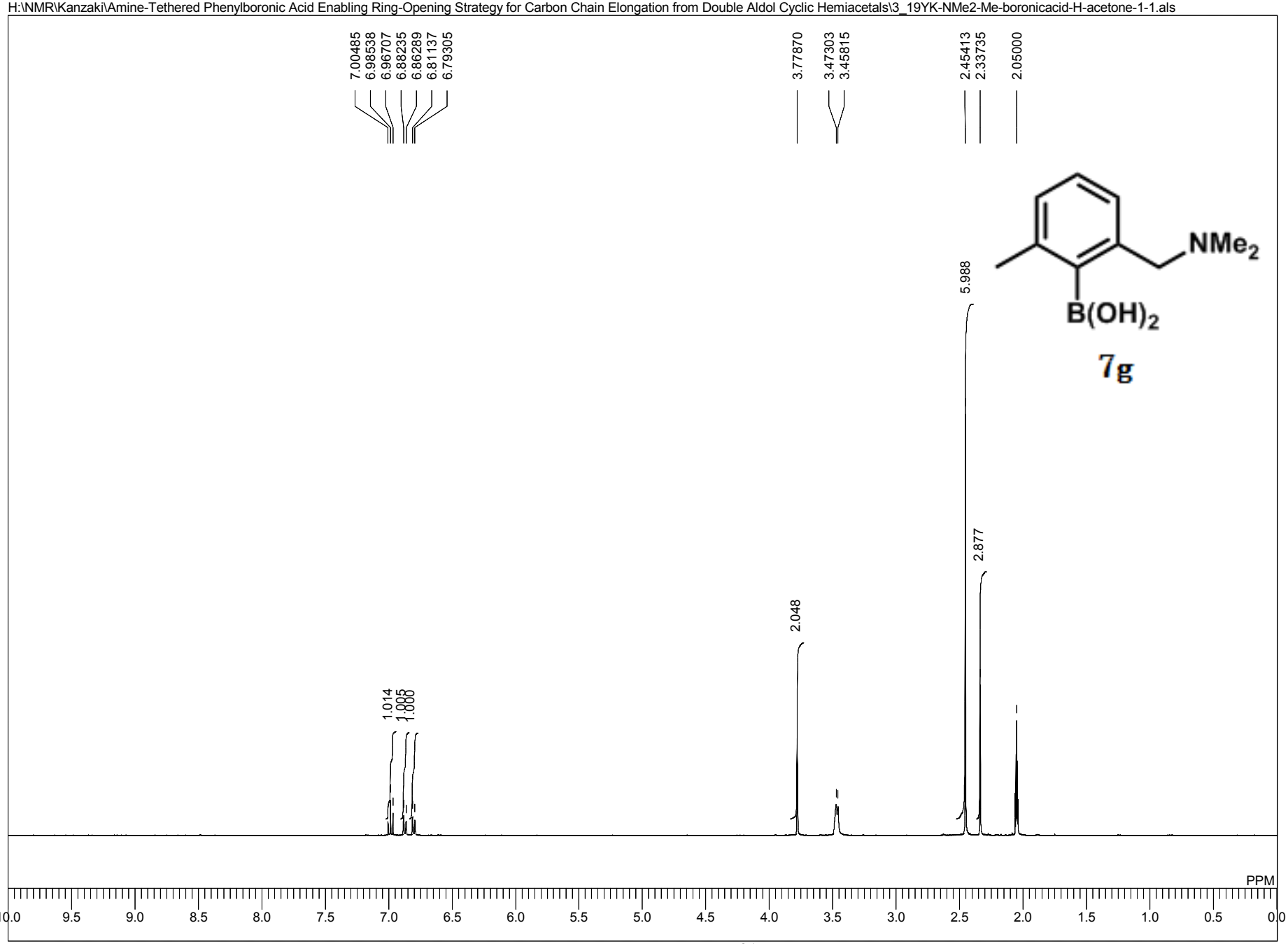
RGAIN	60

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\3_19YK-NMe2-Me-boronicacid-H-acetone-1-1.als



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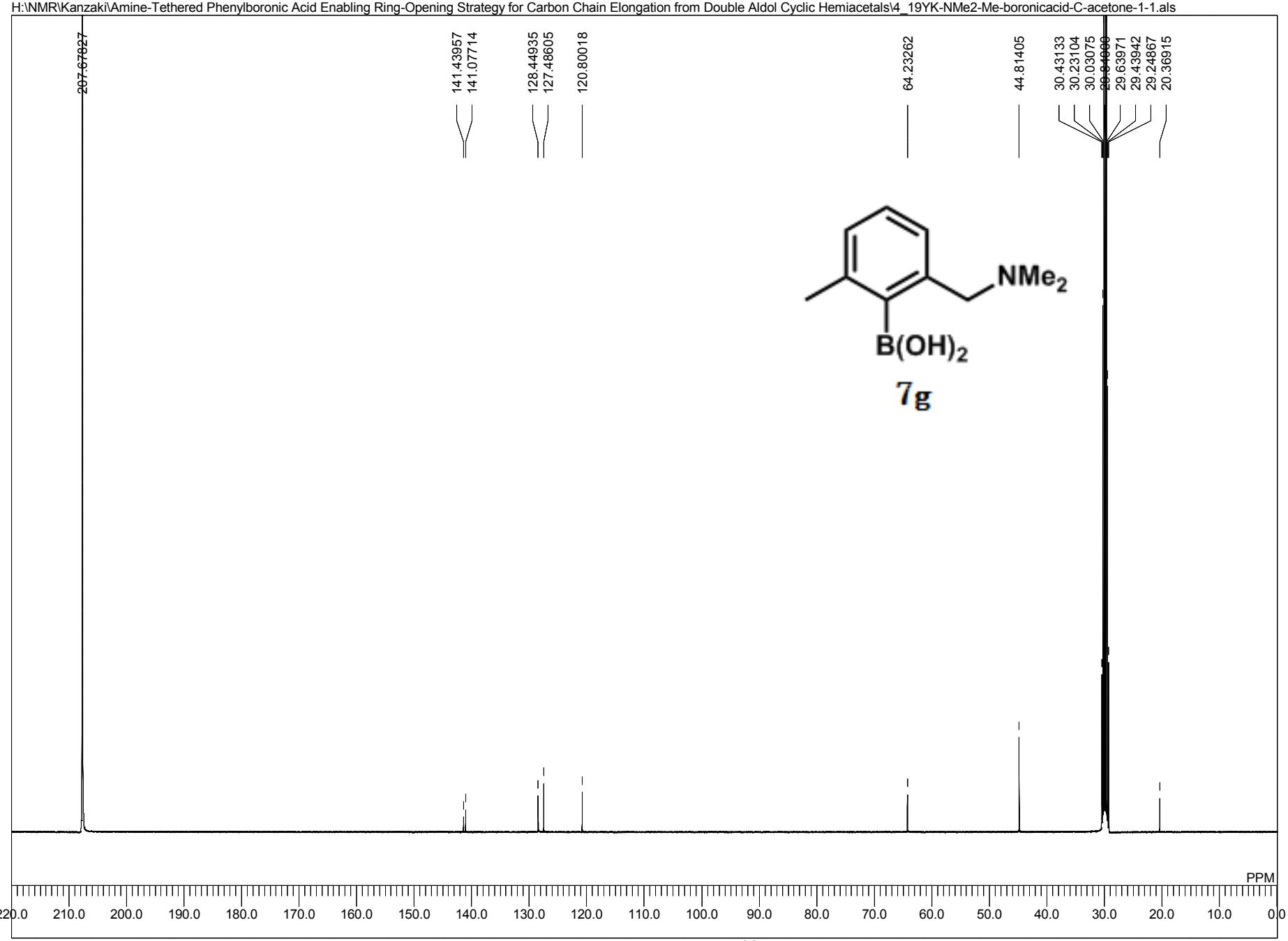
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\4_19YK-NMe2-Me-boronicacid-C-acetone-1-1.als
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EXREF 29.84 ppm
BF 1.20 Hz
RGAIN 60
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\5_synsynsynMeMe-1-1.als

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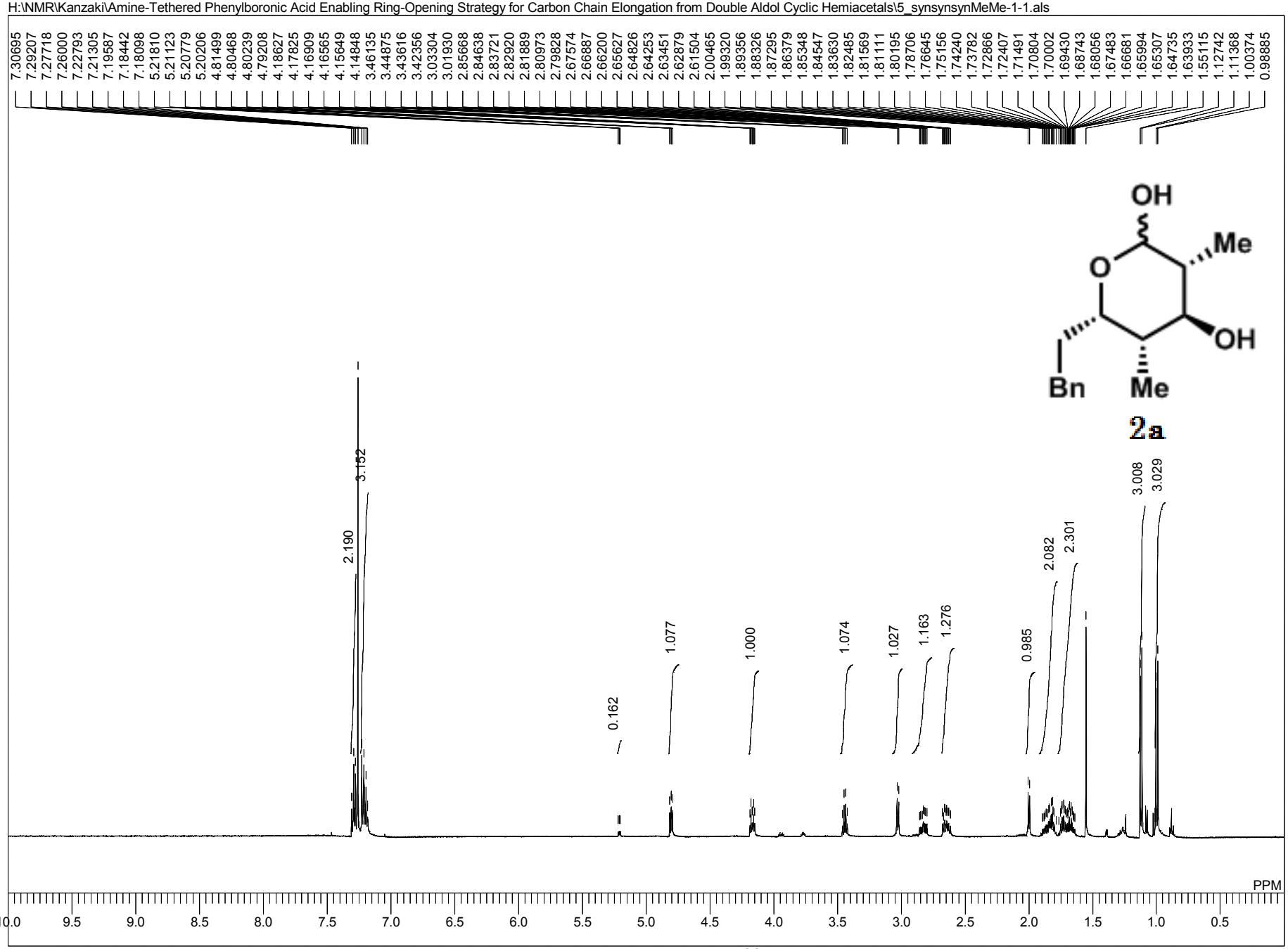

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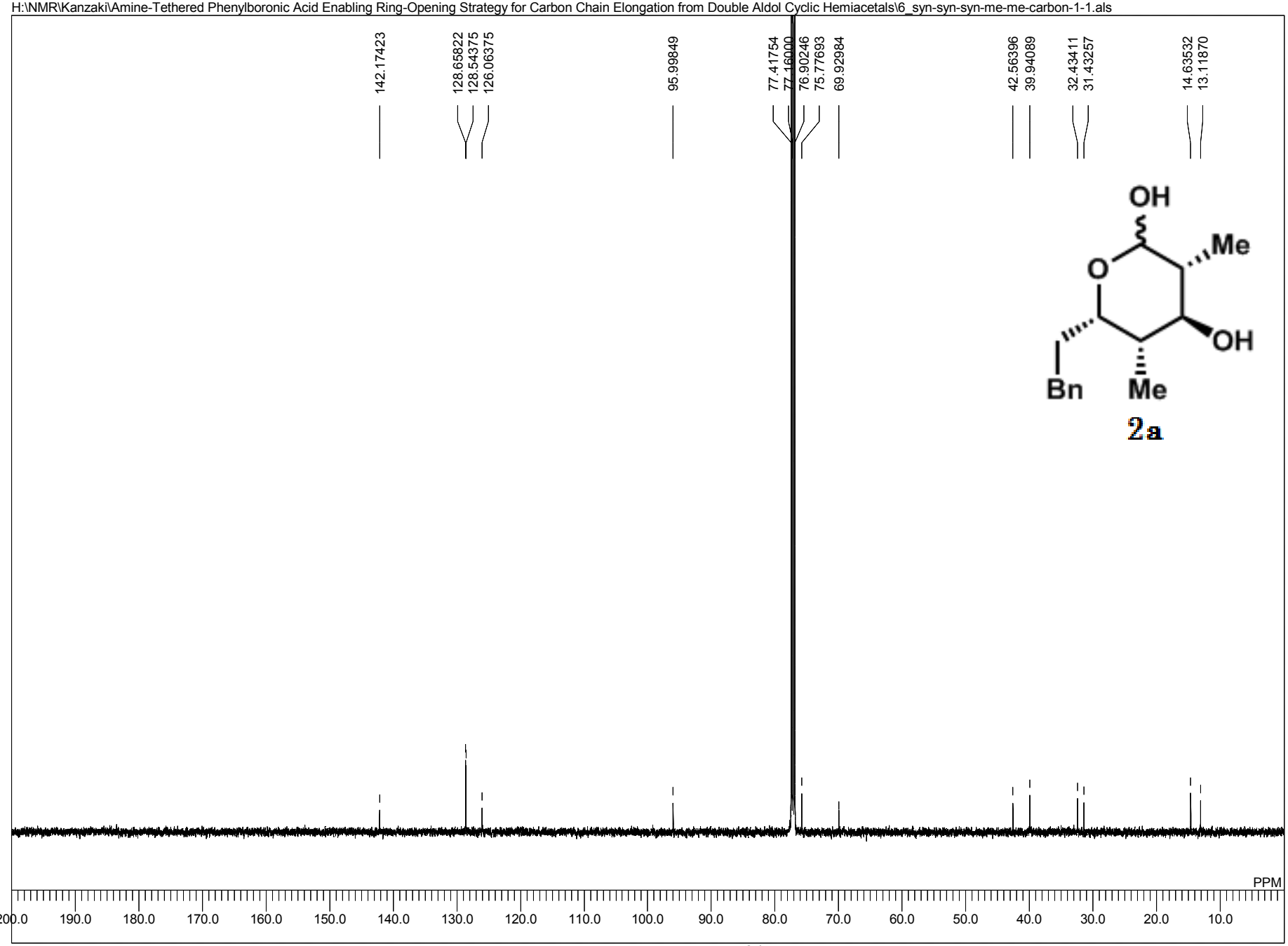

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EXREF	77.16 ppm
BF	1.20 Hz
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H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\7_YH133-fra17-19-1-1.als

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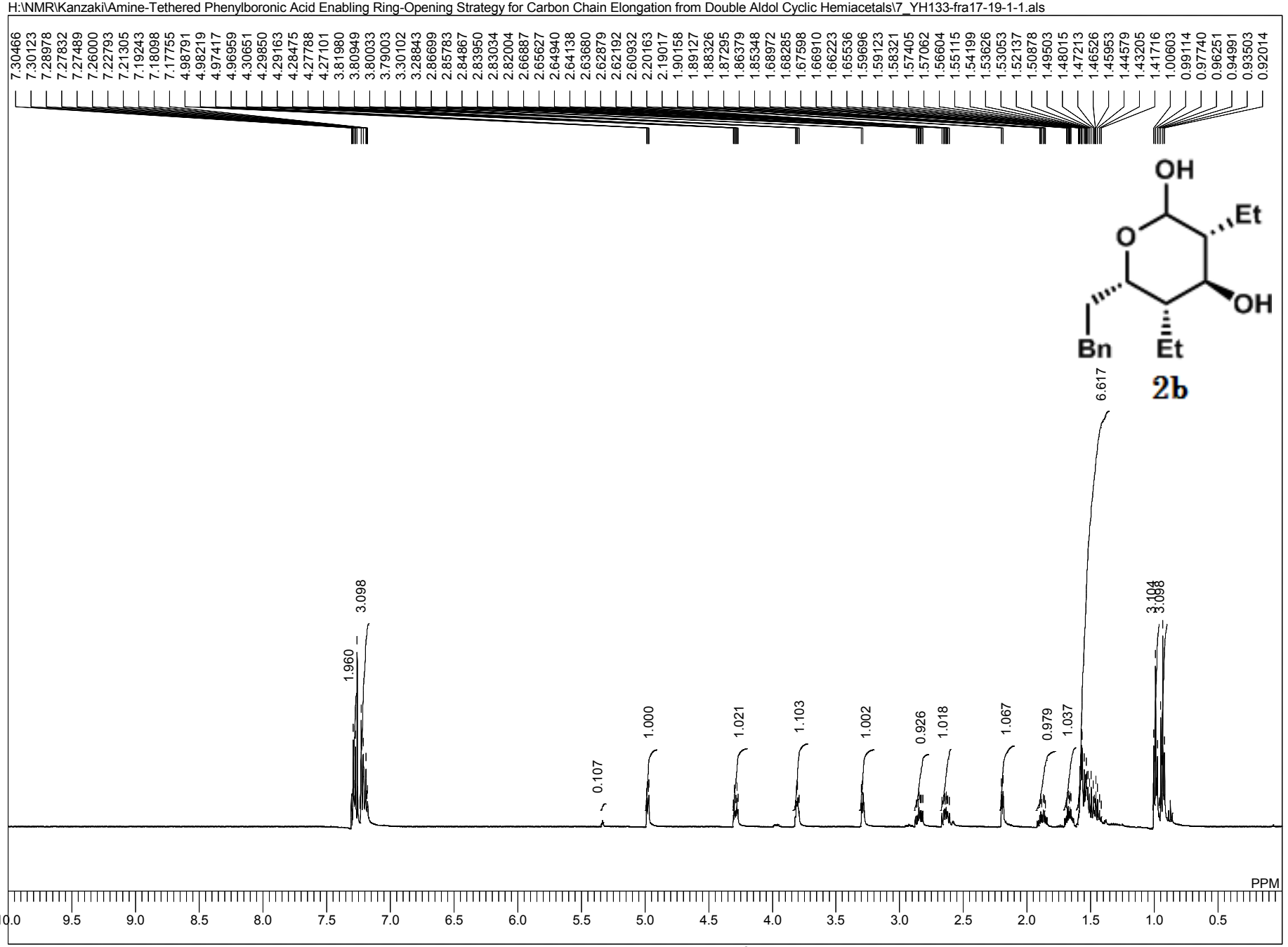
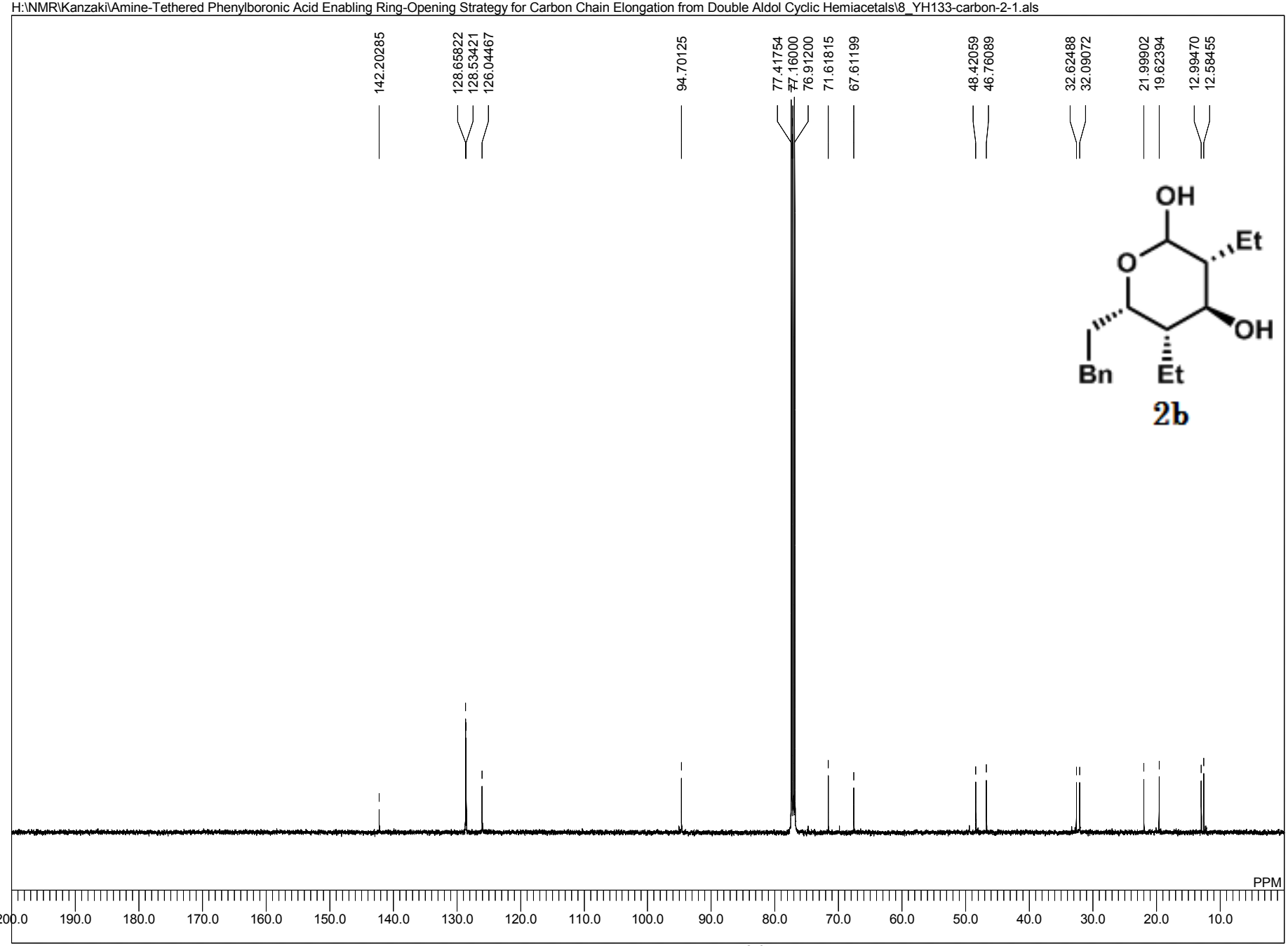
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 40



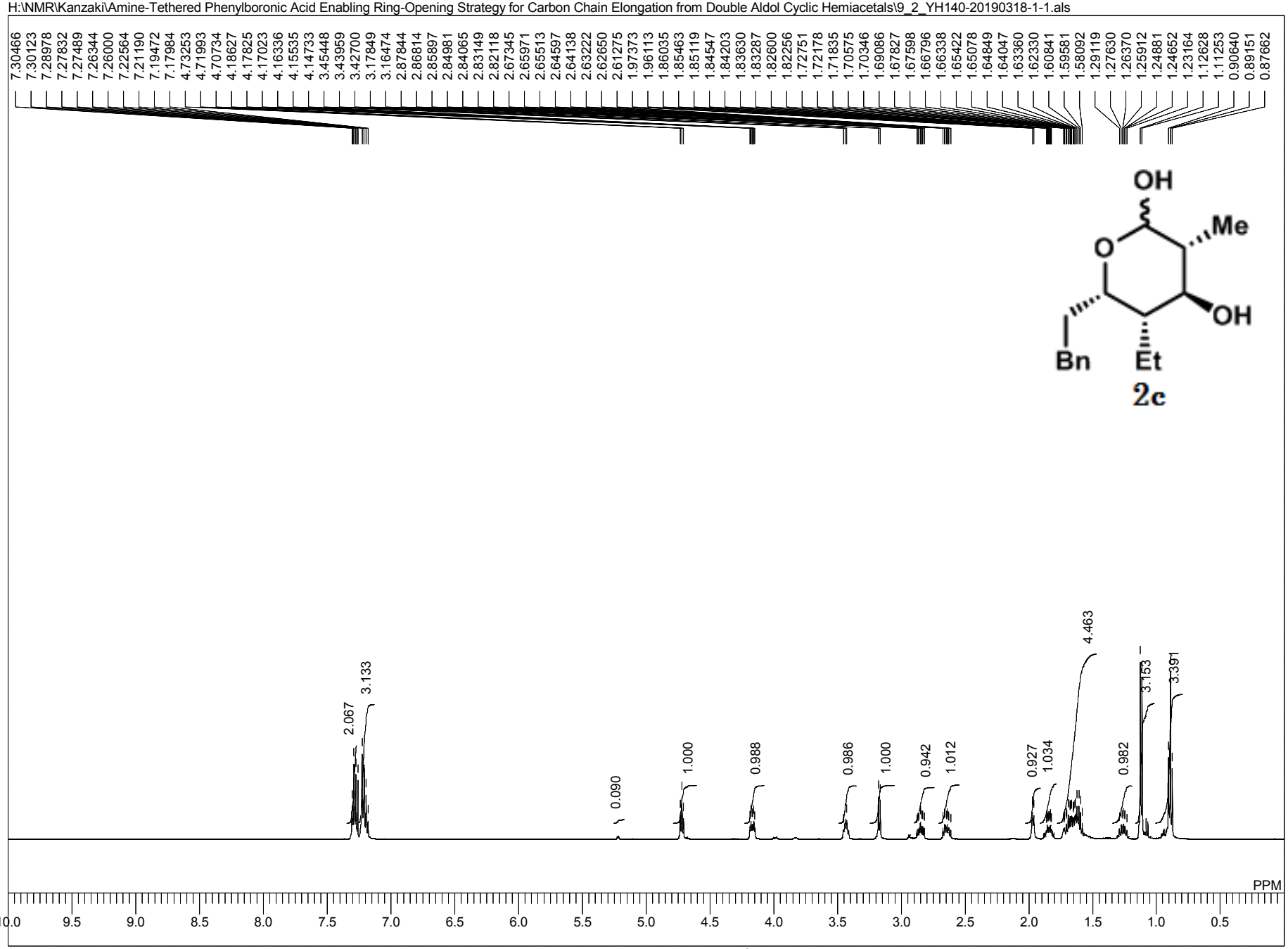
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\8_YH133-carbon-2-1.als



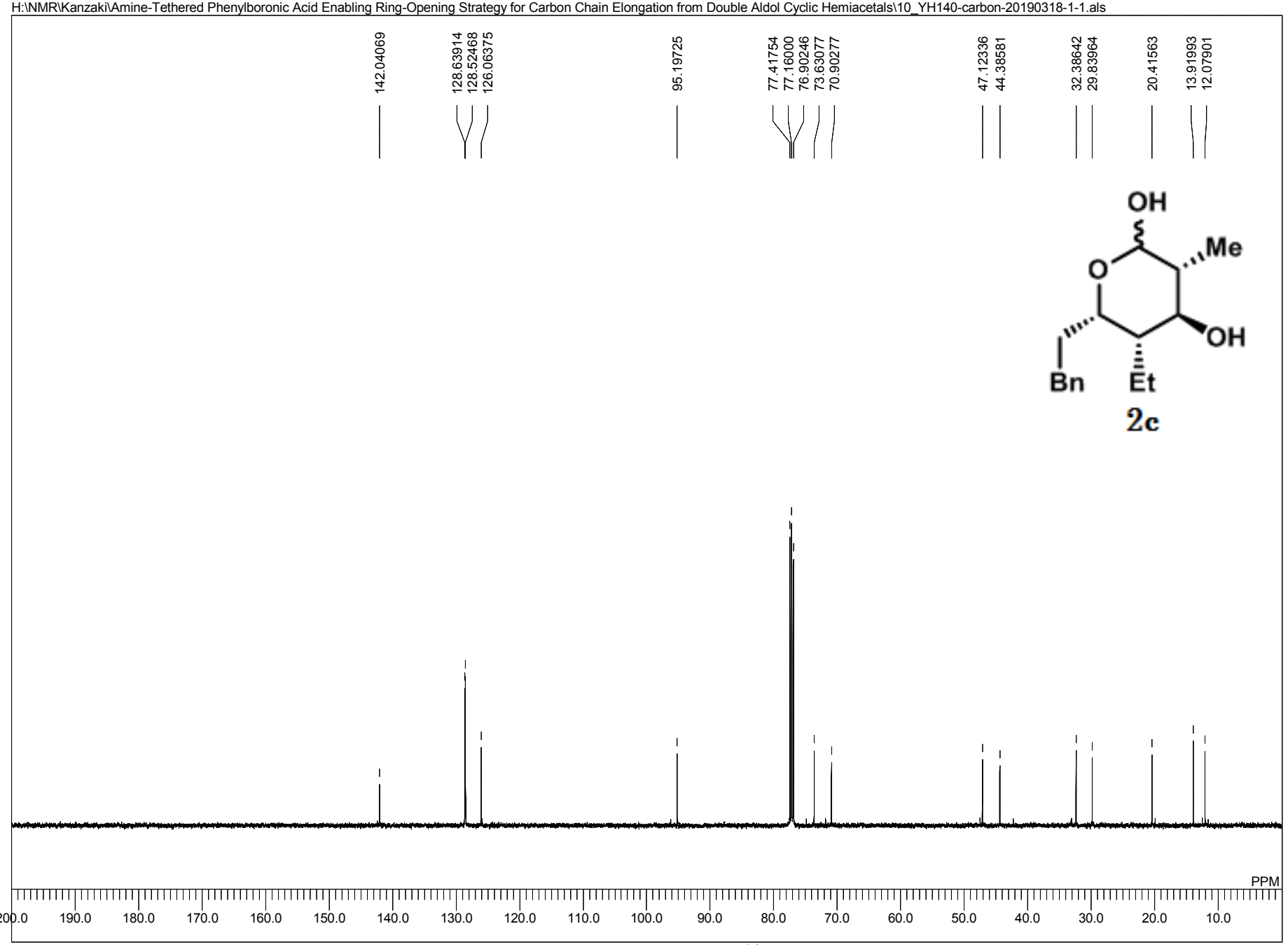
DFILE	8_YH133-carbon-2-1.als
COMNT	
DATIM	2019-03-14 17:05:56
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	3000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\9_2_YH140-20190318-1-1.als

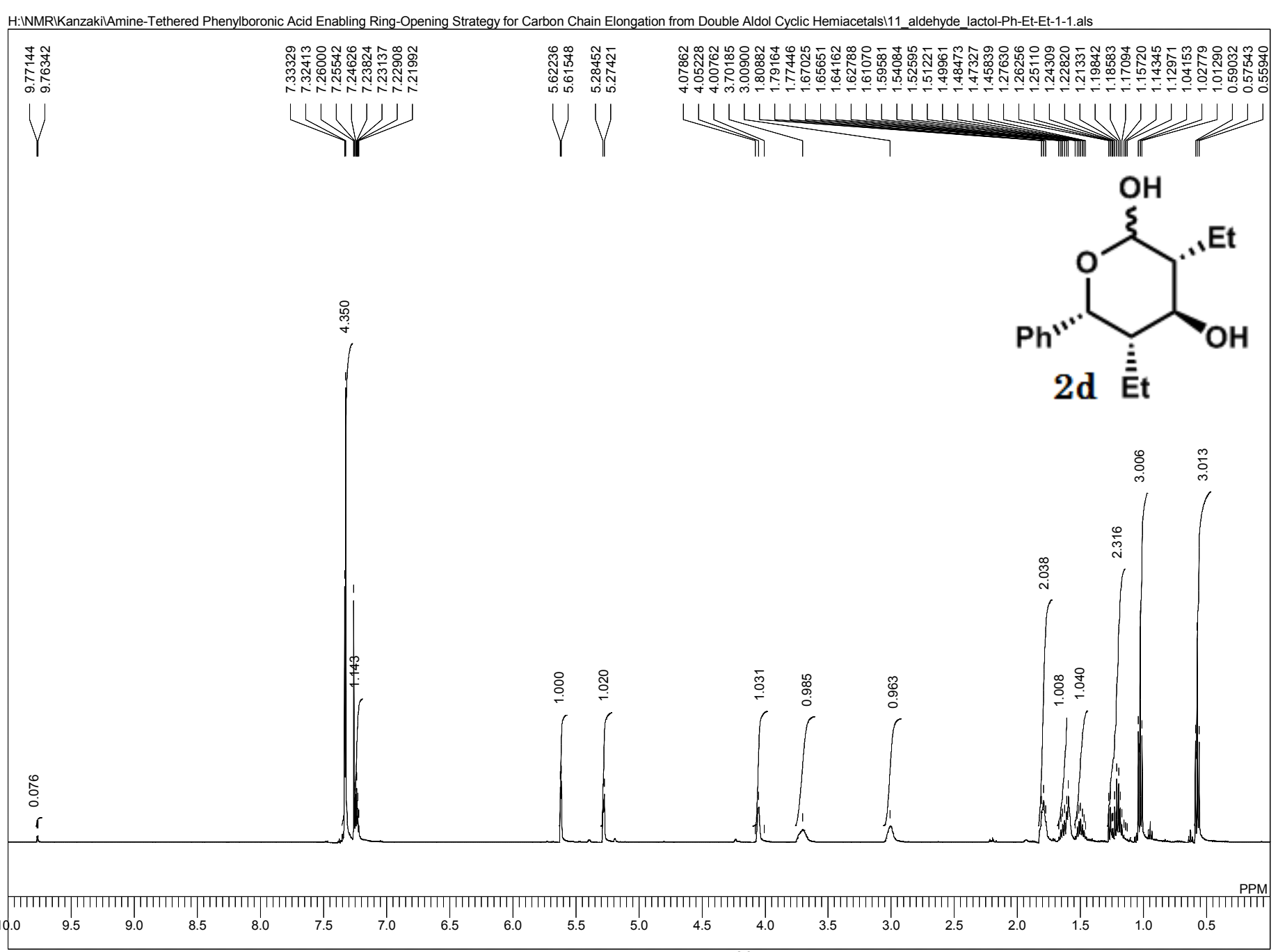
DFILE	9_2_YH140-20190318-1-1.al
COMNT	
DATIM	2019-03-18 19:04:04
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	6.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\10_YH140-carbon-20190318-1-1.als

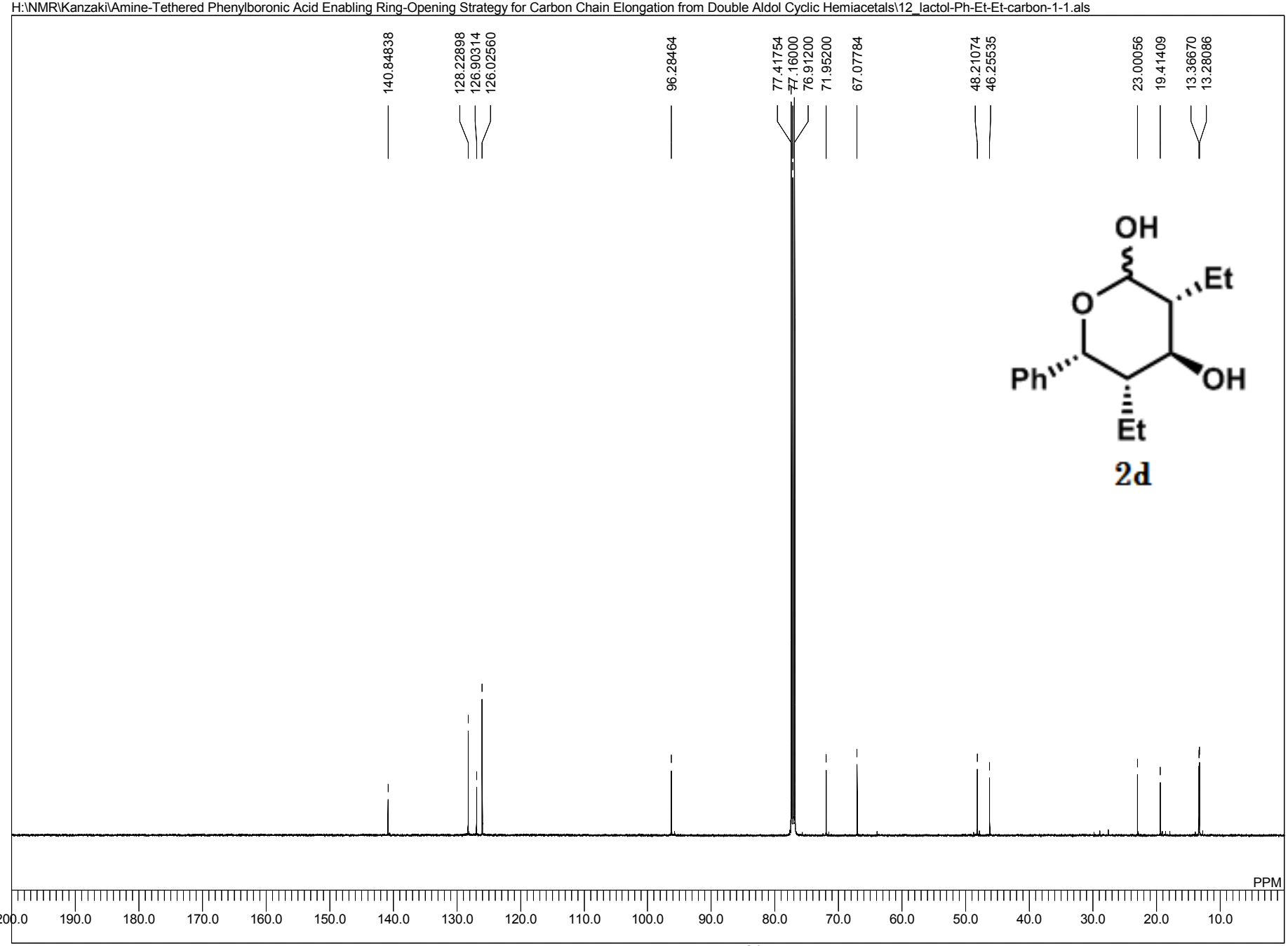


DFILE	10_YH140-carbon-20190318
COMNT	
DATIM	2019-03-18 19:07:10
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	272
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60



DFILE 11_aldehyde_lactol-Ph-Et-Et
COMNT
DATIM 2019-05-20 21:57:43
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 6.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 38

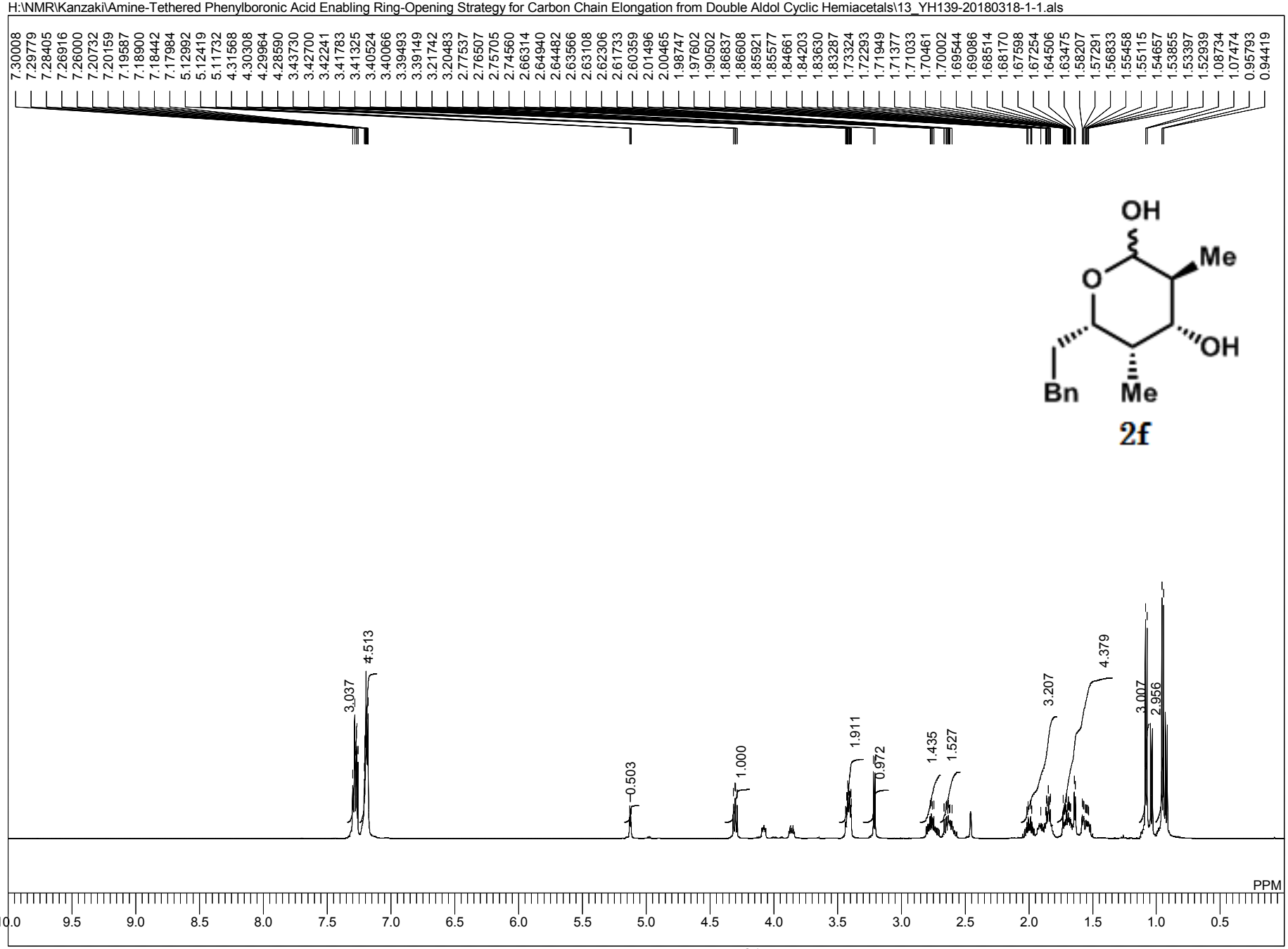
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\12_lactol-Ph-Et-Et-carbon-1-1.als



DFILE	12_lactol-Ph-Et-Et-carbon-1-
COMNT	
DATIM	2019-05-20 22:07:21
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	13000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60

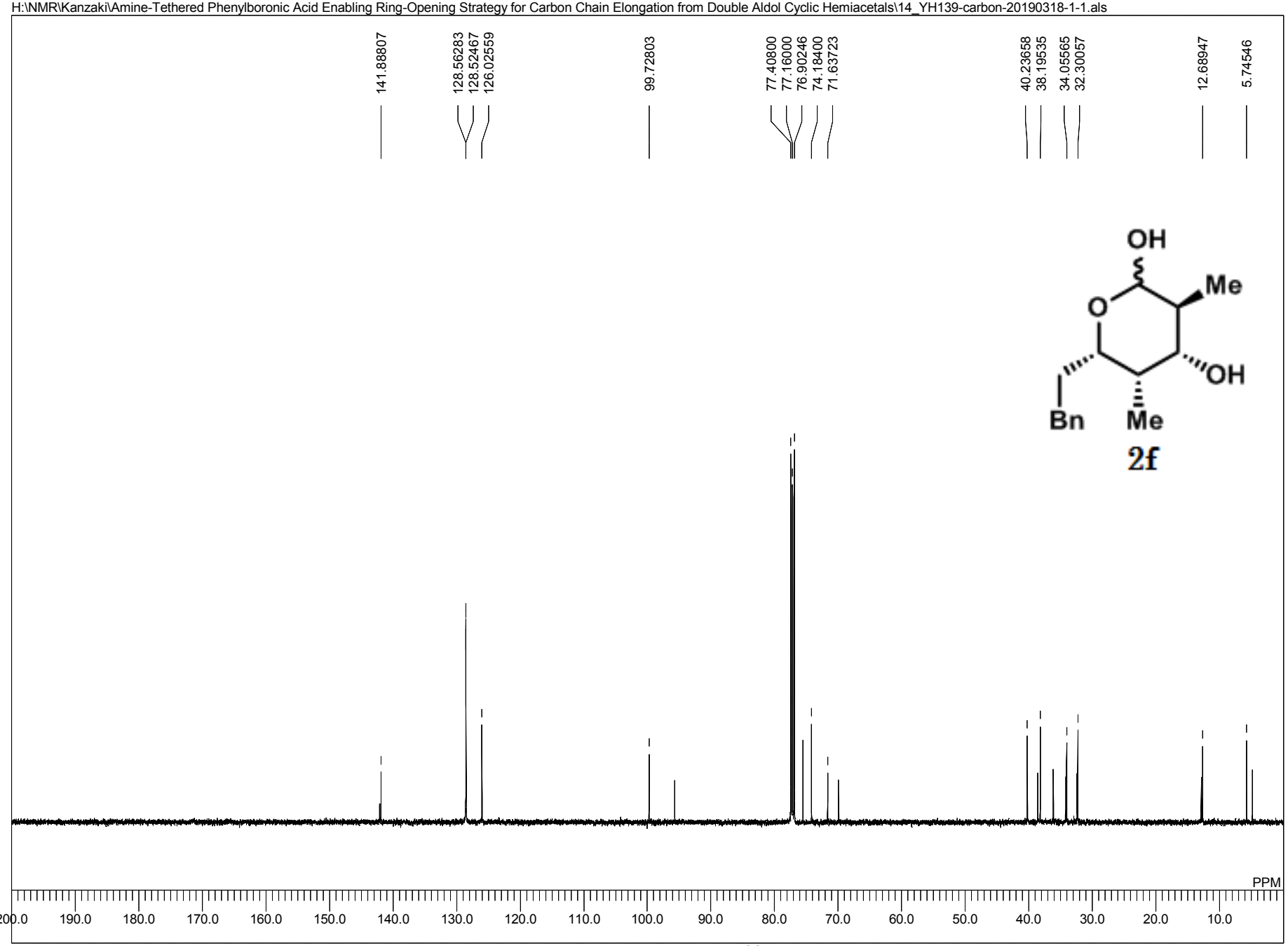
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\13_YH139-20180318-1-1.als

DFILE	13_YH139-20180318-1-1.als
COMNT	
DATIM	2019-03-18 20:10:57
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	6.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



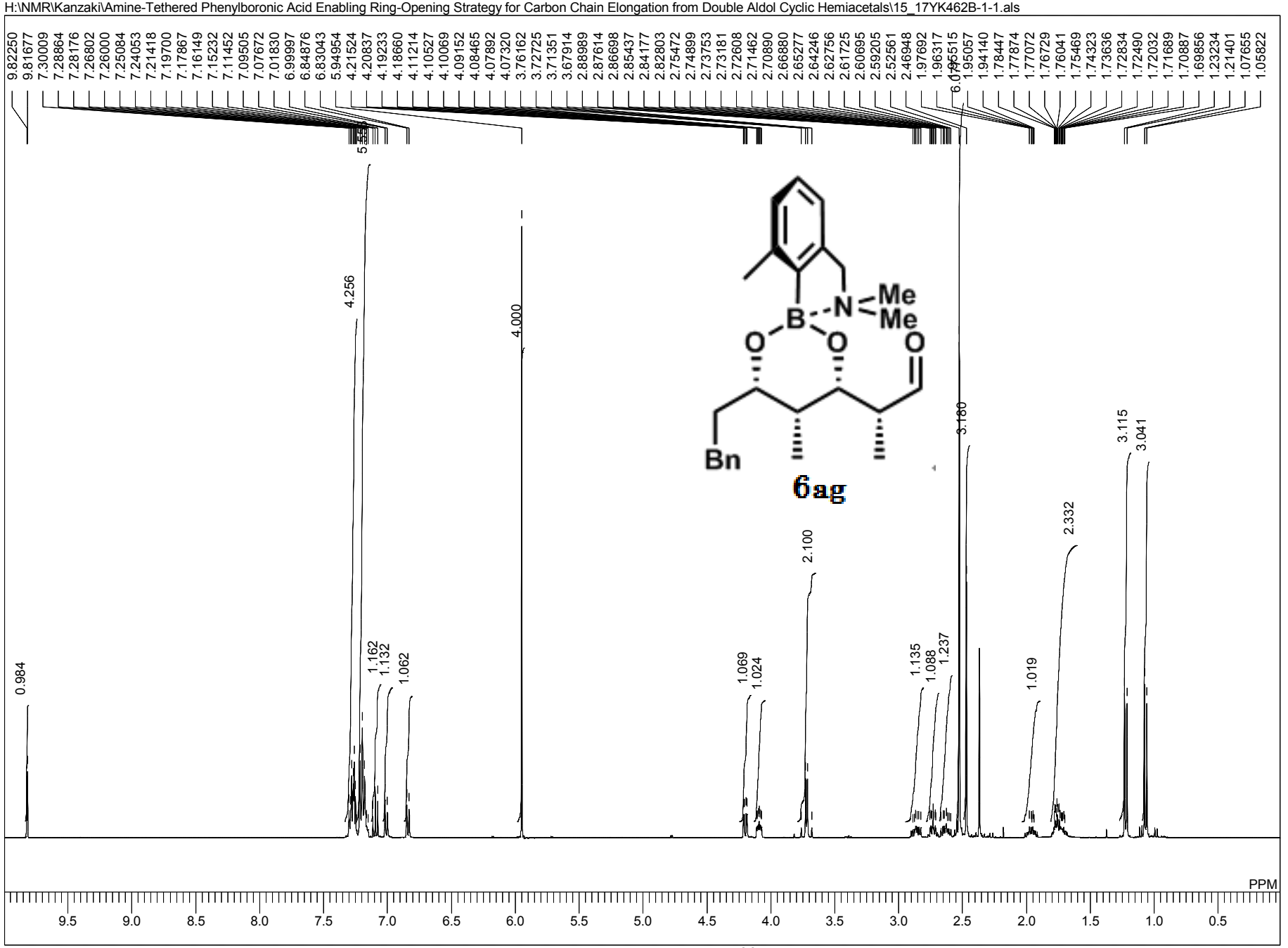
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\14_YH139-carbon-20190318-1-1.als

DFILE	14_YH139-carbon-20190318
COMNT	
DATIM	2019-03-18 20:12:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	345
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60

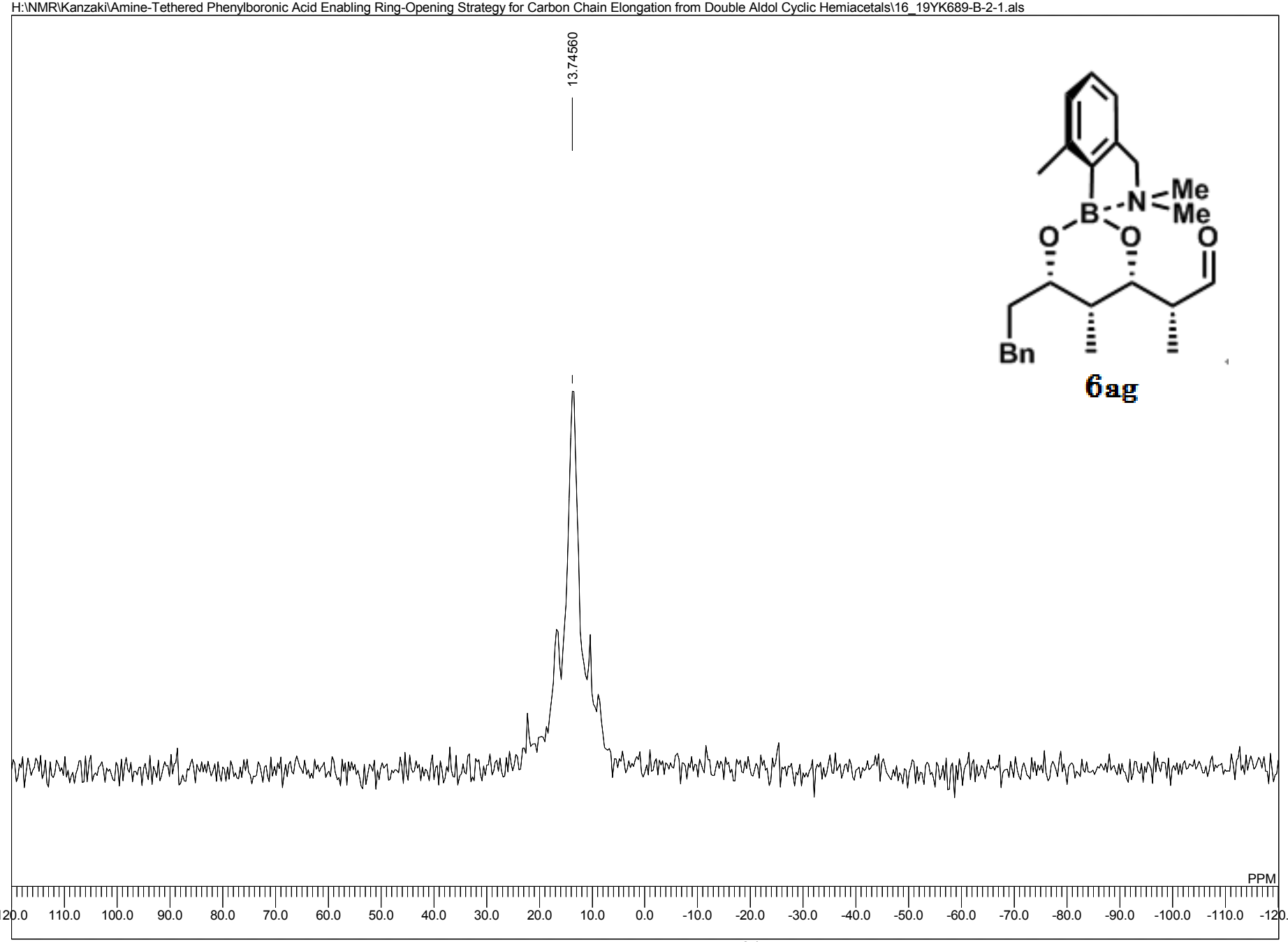


H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\15_17YK462B-1-1.als

DFILE	15_17YK462B-1-1.als
COMNT	
DATIM	15-11-2017 20:32:33
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	391.78 MHz
OBSET	8.51 KHz
OBFIN	3.34 Hz
POINT	13107
FREQU	5882.35 Hz
SCANS	8
ACQTM	2.2282 sec
PD	5.0000 sec
PW1	5.22 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	30



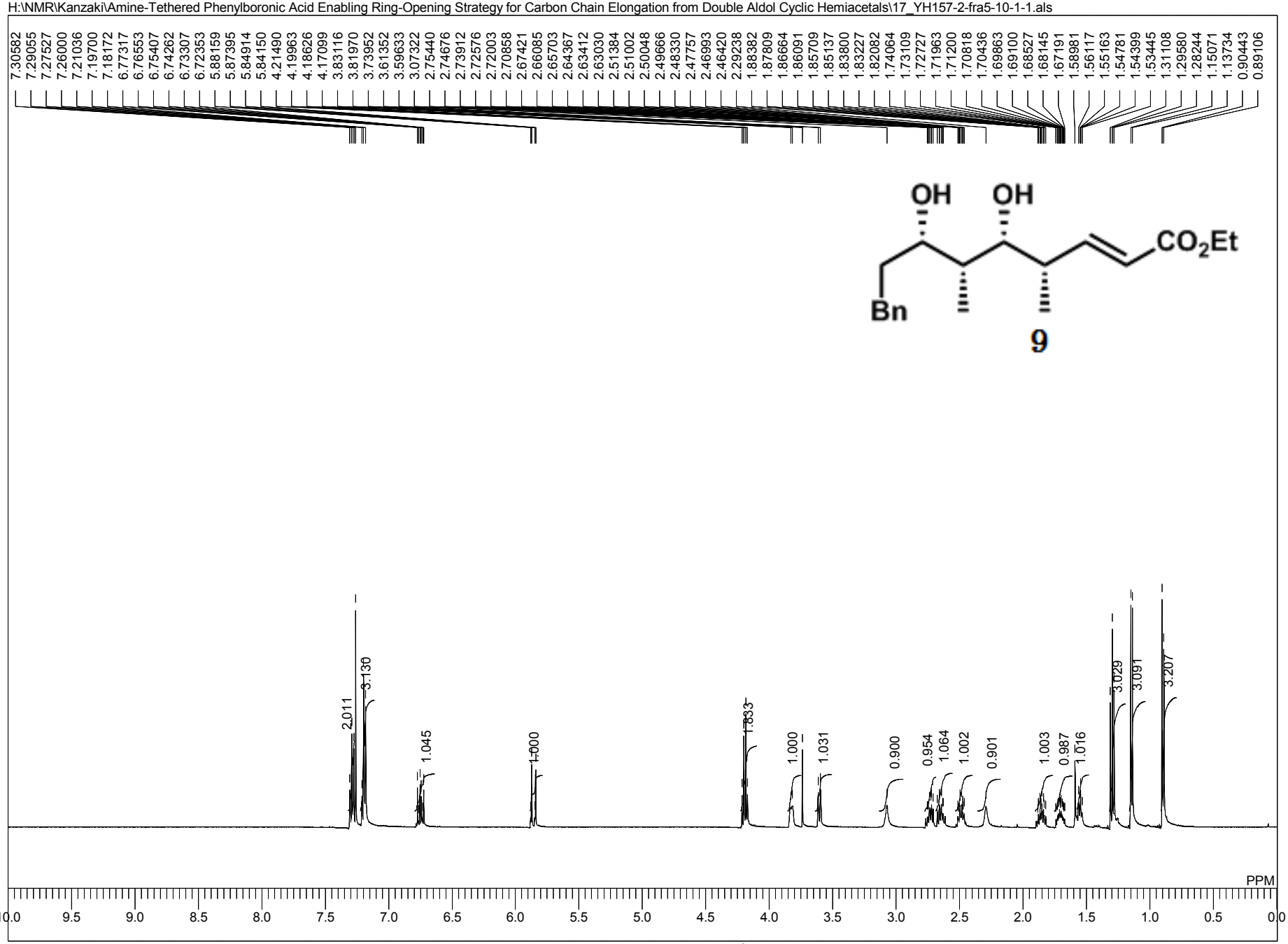
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\16_19YK689-B-2-1.als



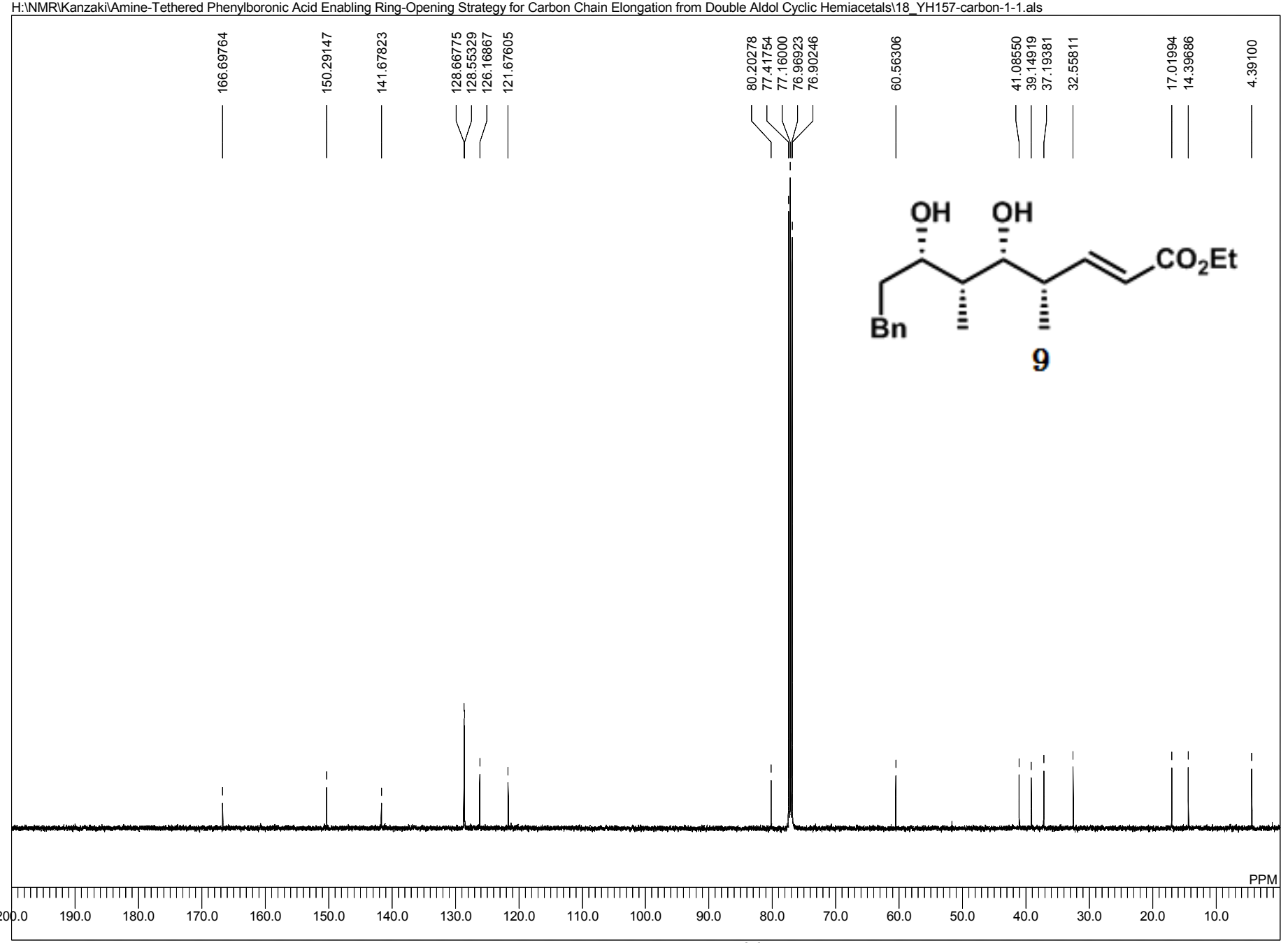
DFILE	16_19YK689-B-2-1.als
COMNT	
DATIM	25-04-2019 13:56:07
OBNUC	11B
EXMOD	carbon.jxp
OBFRQ	125.70 MHz
OBSET	0.81 KHz
OBFIN	3.25 Hz
POINT	819
FREQU	31446.54 Hz
SCANS	8096
ACQTM	0.0261 sec
PD	80.0000 sec
PW1	3.98 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	60

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\17_YH157-2-fra5-10-1-1.als

DFILE 17_YH157-2-fra5-10-1-1.als
COMNT
DATIM 2019-04-09 09:12:56
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 12515.64 Hz
SCANS 8
ACQTM 1.0473 sec
PD 6.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 34



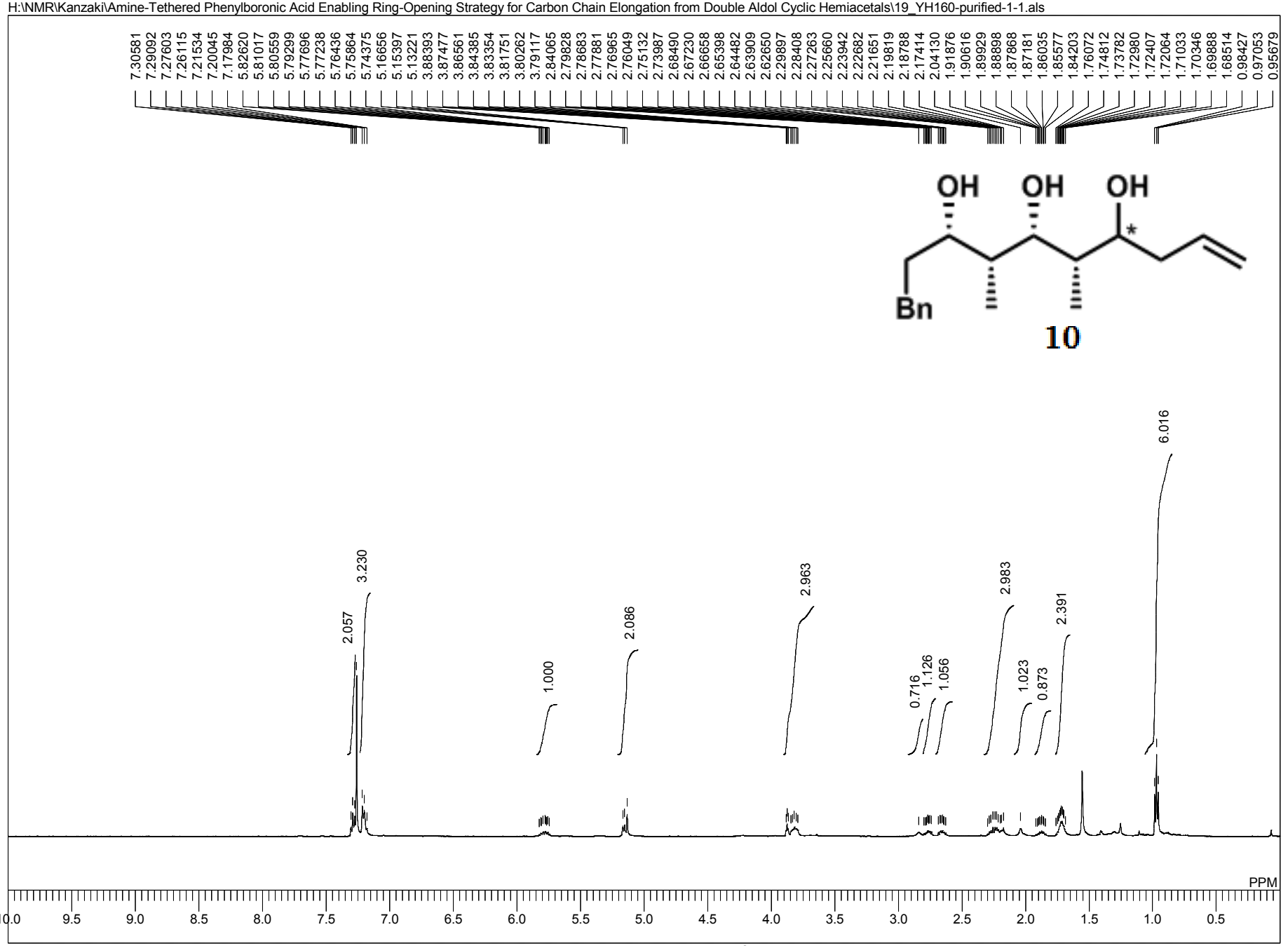
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\18_YH157-carbon-1-1.als



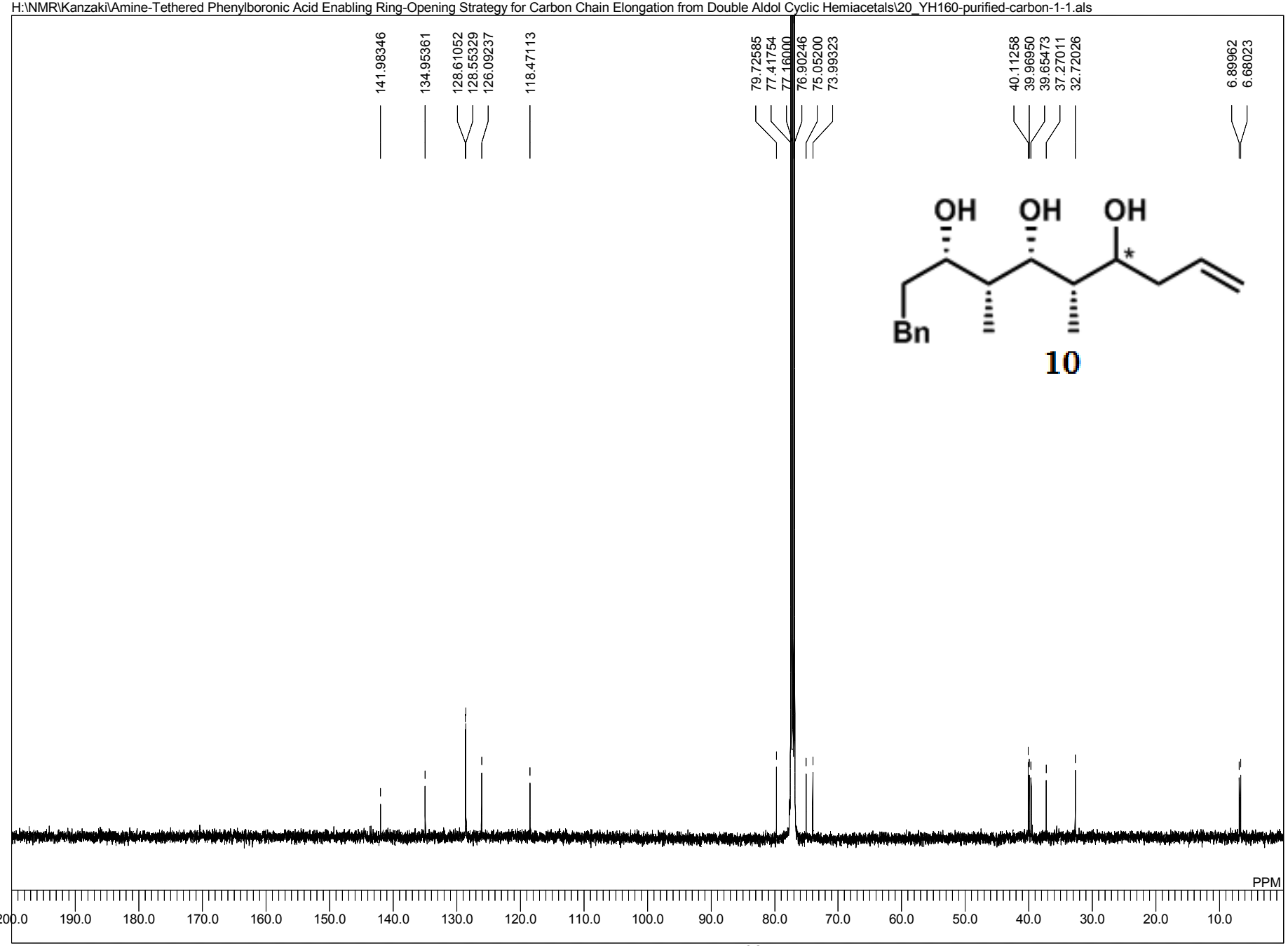
DFILE	18_YH157-carbon-1-1.als
COMNT	
DATIM	2019-04-15 11:02:09
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1200
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\19_YH160-purified-1-1.als

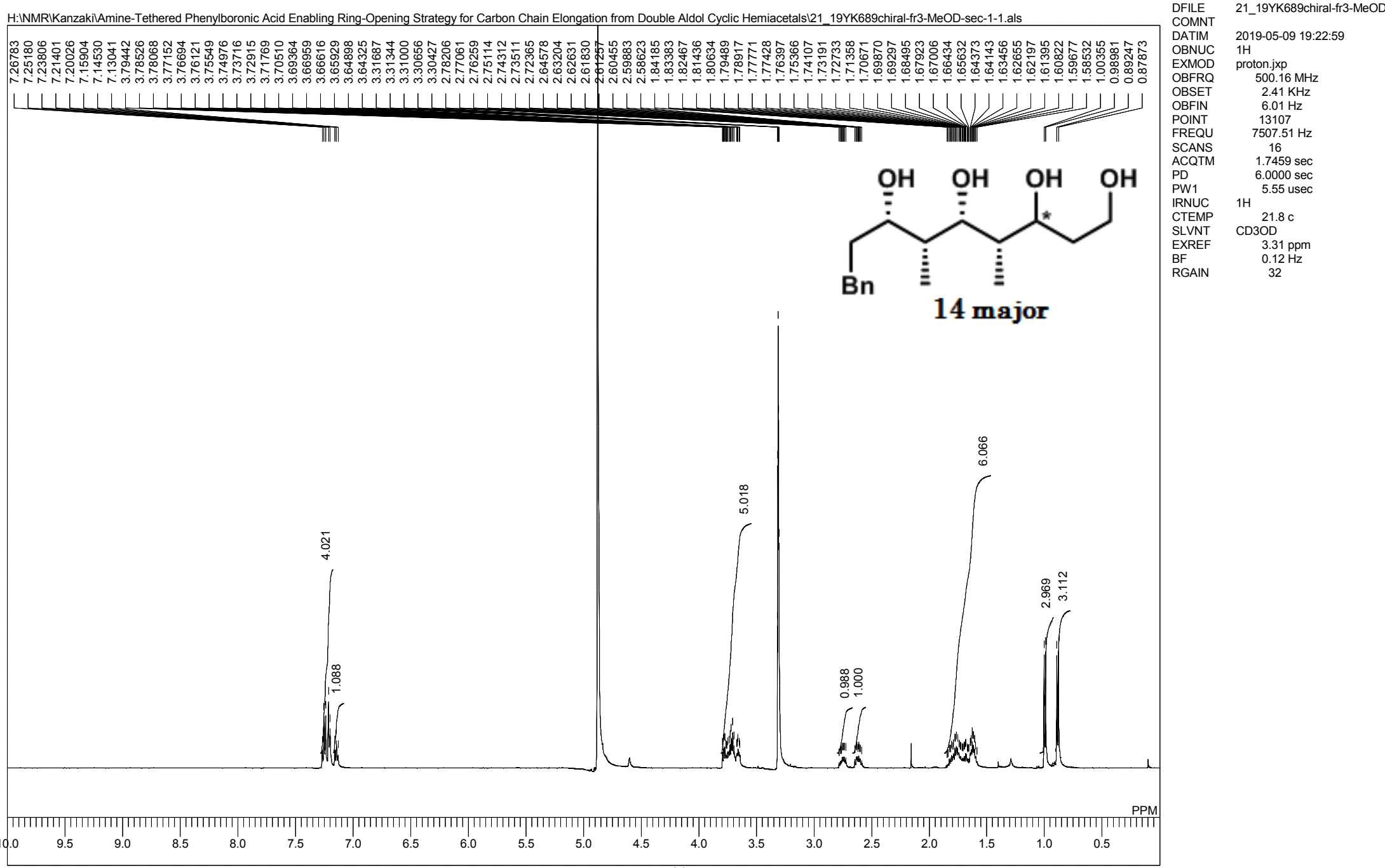
DFILE	19_YH160-purified-1-1.als
COMNT	
DATIM	2019-04-12 20:44:20
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	32
ACQTM	1.7459 sec
PD	6.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	40



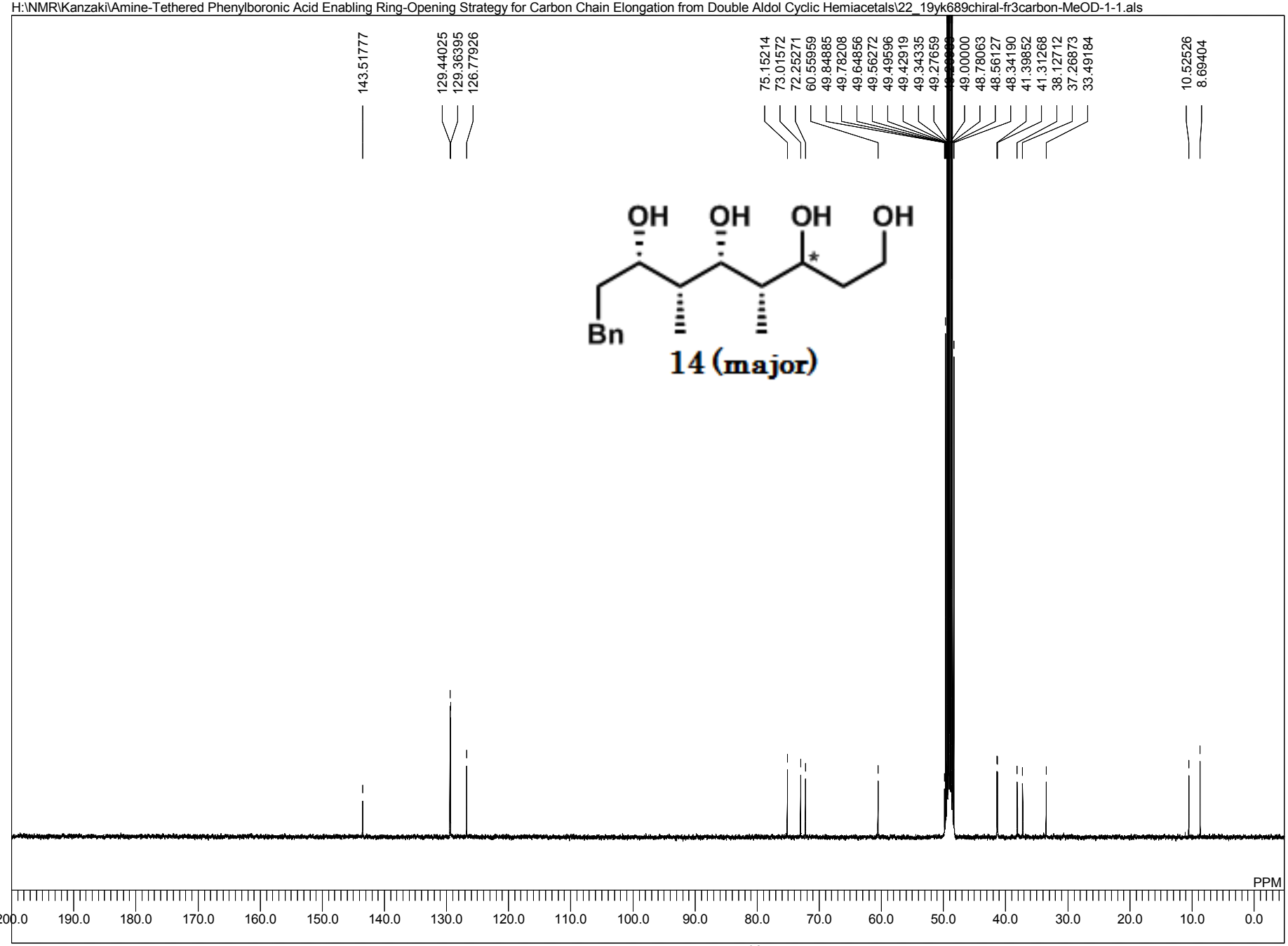
H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\20_YH160-purified-carbon-1-1.als



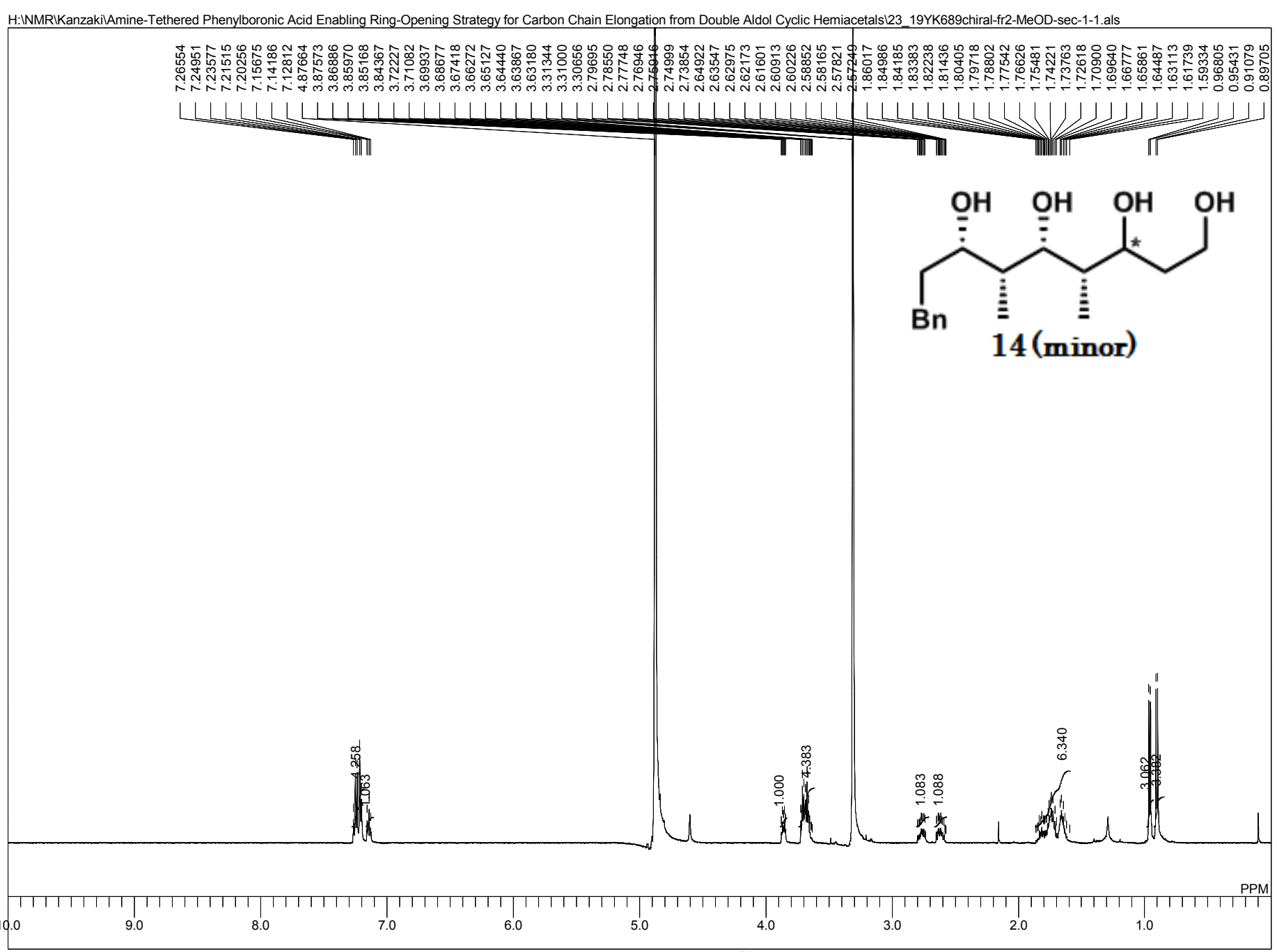
DFILE	20_YH160-purified-carbon-1-
COMNT	
DATIM	2019-04-12 23:40:42
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	12000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	60


H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\21_19YK689chiral-fr3-MeOD-sec-1-1.als
DFILE 21_19YK689chiral-fr3-MeOD
COMNT
DATIM 2019-05-09 19:22:59
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 16
ACQTM 1.7459 sec
PD 6.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CD3OD
EXREF 3.31 ppm
BF 0.12 Hz
RGAIN 32
OH
OH
OH
OH
Bn
14 major
4.021
1.088
5.018
0.988
1.000
6.066
2.969
3.112
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\22_19yk689chiral-fr3carbon-MeOD-1-1.als

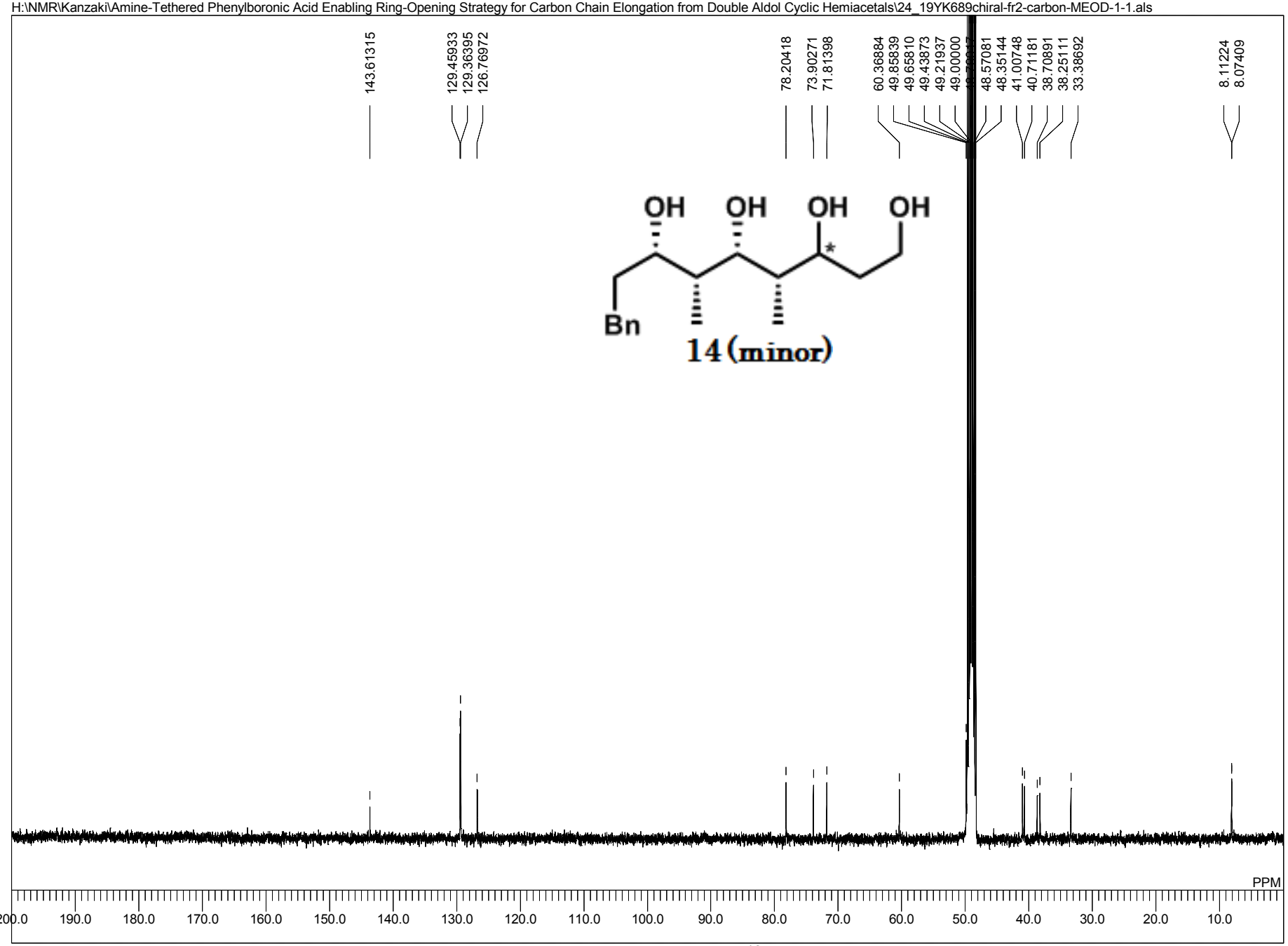


DFILE	22_19yk689chiral-fr3carbon-
COMNT	
DATIM	10-05-2019 22:34:59
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	98.52 MHz
OBSET	4.64 KHz
OBFIN	8.74 Hz
POINT	26214
FREQU	24630.54 Hz
SCANS	13000
ACQTM	1.0643 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	CD3OD
EXREF	49.00 ppm
BF	1.20 Hz
RGAIN	60



DFILE 23_19YK689chiral-fr2-MeOD
COMNT
DATIM 2019-05-09 19:17:43
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 16
ACQTM 1.7459 sec
PD 6.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CD3OD
EXREF 3.31 ppm
BF 0.12 Hz
RGAIN 32

H:\NMR\Kanzaki\Amine-Tethered Phenylboronic Acid Enabling Ring-Opening Strategy for Carbon Chain Elongation from Double Aldol Cyclic Hemiacetals\24_19YK689chiral-fr2-carbon-MEOD-1-1.als



DFILE	24_19YK689chiral-fr2-carbon
COMNT	
DATIM	09-05-2019 20:16:57
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	98.52 MHz
OBSET	4.64 KHz
OBFIN	8.74 Hz
POINT	26214
FREQU	24630.54 Hz
SCANS	16384
ACQTM	1.0643 sec
PD	2.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CD3OD
EXREF	49.00 ppm
BF	1.20 Hz
RGAIN	60