Efficient Boron-Copper Additions to Aryl-Substituted Alkenes Promoted by NHC-Based Catalysts. Enantioselective Cu-Catalyzed Hydroboration Reactions

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SUPPORTING INFORMATION

General. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by high-performance liquid chromatography (HPLC) with a Shimadzu chromatograph (Chiral Technologies Chiralcel OD-R (4.6 x 250 mm) or Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm)) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 ºC) or flame-dried glassware with standard dry box or vacuum-line techniques. Toluene (Fisher Scientific) was purified by being passed through two alumina columns under a positive pressure of dry argon by a modified Innovative Technologies purification system. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketal immediately prior to use unless otherwise specified. Methanol (Aldrich Chemical Co.) was distilled over CaH_2. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Doe & Ingalls) under air.

■ Reagents and ligands:

***trans*-Anethole ((*E*)-1-methoxy-4-(prop-1-enyl)benzene):** purchased from Aldrich Chemical Co. and purified by flash silica gel column chromatography (100% hexanes).

1,2-Bis(diphenylphosphino)ethane: purchased from Strem Chemicals Inc. and recrystallized from EtOH.

Bis(pinacolato)diboron: purchased from CombiPhos Catalysts, Inc. and recrystallized from pentane.

2*H*-Chromene: prepared according to a known literature procedure.[1]

Cinnamyl acetate: purchased from Aldrich Chemical Co. and purified by Kugelrohr distillation under reduced pressure.

Cinnamyl alcohol: purchased from Aldrich Chemical Co. and recrystallized from ethyl ether and pentane.

Copper (I) chloride: purchased from Aldrich Chemical Co. and used as received.

Cu-NHC (2, 3, 4): prepared according to known literature procedures.[2]

1,2-Dihydronaphthalene: purchased from Aldrich Chemical Co. and purified by flash silica gel column chromatography (100% hexanes).

Hydrogen peroxide (35 wt. % solution in water): purchased from Aldrich Chemical Co. and used as received.

Imidazolinium salt 13: prepared according to known literature procedures.[3]

Imidazolinium salt 19: prepared according to known literature procedures.[4]

Indene: purchased from Aldrich Chemical Co. and purified by flash silica gel column chromatography (100% hexanes).

***trans*-β-Methylstyrene:** purchased from Aldrich Chemical Co. and purified by distillation over powdered NaOH under reduced pressure and passed through activated neutral alumina prior to use.

***cis*-β-Methylstyrene:** purchased from TCI America and purified by distillation over powdered NaOH under under reduced pressure and passed through activated neutral alumina prior to use.

Potassium *tert*-butoxide: purchased from Strem Chemicals Inc. and used as received.

Sodium *tert*-butoxide (98%)**:** purchased from Strem Chemicals Inc. and used as received.

Substituted aryl alkenes (entries 5-7 in Table 2): prepared according to known literature procedures.[5]

Tricyclohexylphosphine: purchased from Strem Chemicals Inc. and used as received.

Triphenylphosphine: purchased from Aldrich Chemical Co. and recrystallized from hexanes.

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(3) (a) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1097-1100. (b) May, T. L.; Brown, M. K.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 7468-7472.
(4) (a) Chaulagain, M. R.; Sormunen, G. J.; Montgomery, J. *J. Am. Chem. Soc.* **2007**, *129*, 9568-9569. (b) Lillo, V.; Prieto, A.; Bonet, A.; Díaz-Requejo, M. M.; Ramírez, J.; Pérez, P. J.; Fernández, E. *Organometallics*, **2009**, ASAP.
(5) (a) Schlosser, M.; Schaub, B. *J. Am. Chem. Soc.* **1982**, *104*, 5821-5823. (b) Jang, Y.-J.; Yan, M.-C.; Lin, Y.-F.; Yao, C.-F. *J. Org. Chem.* **2004**, *69*, 3961-3963.

■ **Representative experimental procedure for Cu-catalyzed hydroboration of (*E*)-*β*-methylstyrene with bis(pinacolato)diboron:**[6]

In an N_2-filled glovebox, an oven-dried vial (8 mL, 17 x 60 mm) with magnetic stir bar was charged with NHC-CuCl complex **2** (2.00 mg, 5.00 x 10^{-3} mmol, 0.5 mol %), NaO*t*Bu (0.480 mg, 5.00 x 10^{-3} mmol, 0.5 mol %), and toluene (0.5 mL). The mixture was sealed with a septum and allowed to stir for 5 min. Bis(pinacolato)diboron **1** (279 mg, 1.10 mmol, 1.10 equiv) and toluene (1 mL) were added to the mixture. The vial was sealed with a septum and wrapped with parafilm before removal from the glove box. The solution turned dark brown immediately. After 10 min, to the reaction mixture under an N_2 atmosphere were added (*E*)-*β*-methylstyrene (127 μL, 1.00 mmol, 1.00 equiv) and MeOH (81.0 μL, 2.00 mmol, 2.00 equiv) by syringes. The resulting solution was allowed to stir at 22 °C for 10 min (Caution: reaction is exothermic). At this time, the solution was passed through a short plug of celite and silica gel and washed with Et_2O (3 x 2 mL). The filtrate was concentrated *in vacuo* to provide dark brown oil, which was purified by silica gel column chromatography (hexanes:Et_2O=10:1) to afford the desired product **5** as colorless oil (239 mg, 0.973 mmol, 97.3% yield).

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (5, This compound has been previously reported and spectra data match those described**).**[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.12 (5H, m, Ar**H**), 2.81 (1H, dd, *J* = 13.6, 7.6 Hz, PhC**H**$_2$), 2.54 (1H, dd, *J* = 13.6, 8.0 Hz, PhC**H**$_2$), 1.37 (1H, m, C**H**Bpin), 1.19 (6H, s, B**pin**), 1.18 (6H, s, B**pin**), 0.96 (3H, d, *J* = 7.6 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 129.1, 128.2, 125.7, 83.2, 39.1, 24.9, 15.4.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (5-*d*$_1$ from (*E*)-*β*-methyl styrene). IR (neat): 2977 (w), 2929 (w), 1458 (w), 1379 (m), 1361 (m), 1316 (s), 1212 (m), 1142 (s), 967 (w), 855 (m), 698 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.14 (5H, m, Ar**H**), 2.55 (1H, d, *J* = 8.4 Hz, PhC**H**D), 1.39 (1H, m, C**H**Bpin), 1.21 (6H, s, B**pin**), 1.20 (6H, s, B**pin**), 0.99 (3H, d, *J* = 7.2 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 129.0, 128.1, 125.7, 83.1, 38.8 (t, *J* = 19.3 Hz, Ph**C**HD), 24.8, 15.3; HRMS (ESI+): Calcd for$C_{15}H_{23}D_1B_1O_2$ [M+H]: 248.19321, Found: 248.19411.

Proof of Stereochemistry of 5-*d*$_1$: To obtain an authentic sample of the diastereomer obtained from reaction of (*E*)-*β*-methylstyrene, the Cu-catalyzed process was carried out with the (*Z*)-*β*-methylstyrene under identical conditions and quenched with MeOD in the same manner. The stereochemical identity of the deuterated product (**5-*d*$_1$**) is established by analysis and comparison of the ^{1}H NMR and ^{13}C NMR spectra of the derived diastereomeric alcohols (obtained through oxidation with H_2O_2) with those previously reported for (1*S*, 2*R*)-1-phenyl(1-D)propan-2-ol[8] (see the underlined spectral values in Page S4 for specific points of comparison).

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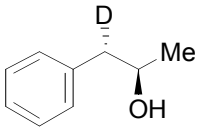
(6) Cu-Catalyzed hydroboration reactions of disubstituted olefins with NHC-Cu complex **2** were carried out in toluene except for allylic carbonate **6** (THF was used).

(7) Moran, W. J.; Morken, J. P. *Org. Lett.* **2006**, *8*, 2413-2415.

(8) Moufid, N.; Renaud, P.; Hassler, C.; Giese, B. *Helv. Chim. Acta*, **1995**, *78*, 1006-1012.

(1*S*, 2*R*)-1-Phenyl(1-D)propan-2-ol.[8] 

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-19 (5H, m, Ar**H**), 4.01(1H, dq, *J* = 8.0, 6.0 Hz, C**H**OH), 2.67 (1H, dt, ^2J(D,H) = 2.0 Hz, ^3J(H,H) = 8.0 Hz, PhC**H**D), 1.59 (1H, br s, O**H**), 1.24 (3H, d, *J* = 6.2 Hz, C**H**$_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 138.5, 129.2, 128.3, 126.2, 68.6, 45.2 (dt, ^1J(C,D) = 19.4 Hz), 22.5.

1-Phenyl(1-D)propan-2-ol (Oxidation of 5-d_1 from (*E*)-β-methyl styrene). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (2H, m, Ar**H**), 7.24-7.18 (3H, m, Ar**H**), 4.00 (1H, m, C**H**OH), 2.76-2.74 (1H, m, ArC**H**D), 1.60 (1H, br s, O**H**), 1.21 (2H, d, *J* = 6.0 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 129.5, 128.6, 126.6, 68.9, 45.5 (t, *J* = 19.4 Hz, Ph**C**HD), 22.8.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (5-d_1 from (*Z*)-β-methyl styrene). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.12 (5H, m, Ar**H**), 2.78 (1H, d, *J* = 7.6 Hz, PhC**H**D), 1.35 (1H, m, C**H**Bpin), 1.18 (6H, s, B**pin**), 1.17 (6H, s, B**pin**), 0.95 (3H, d, *J* = 7.2 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 129.1, 128.2, 125.7, 83.2, 38.8 (t, *J* = 19.3 Hz, Ph**C**HD), 24.9, 15.3.

1-Phenyl(1-D)propan-2-ol (Oxidation of 5-d_1 from (*Z*)-β-methyl styrene, Spectra data of this diastereomer match those described**).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (2H, m, Ar**H**), 7.24-7.19 (3H, m, Ar**H**), 4.04-3.97 (1H, m, C**H**OH), 2.66 (1H, d, *J* = 8.0 Hz, ArC**H**D), 1.50 (1H, d, *J* = 3.2 Hz, O**H**), 1.23 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 129.5, 128.7, 126.6, 68.9, 45.5(t, *J* = 19.4 Hz, Ph**C**HD), 22.9.

2-(2,3-Dihydro-1*H*-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 2). IR (neat): 2976 (w), 2932 (w), 2845 (w), 1414 (w), 1371 (s), 1314 (s), 1261 (m), 1226 (m), 1140 (s), 1108 (w), 970 (m), 856 (s), 740 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (2H, m, Ar**H**), 7.15-7.11 (2H, m, Ar**H**), 3.08 (2H, dd, *J* = 15.2, 9.2 Hz, C**H**$_2$CHBpin), 3.01 (2H, dd, *J* = 15.2, 10.4 Hz, C**H**$_2$CHBpin), 1.90 (1H, *pseudo*-tt, *J* = 10.4, 9.6 Hz, C**H**Bpin), 1.28 (12H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 126.1, 124.4, 83.4, 35.3, 24.9; HRMS (ESI+): Calcd for $C_{15}H_{22}B_1O_2$ [M+H]: 245.17128, Found: 245.17257.

4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (Table 2, entry 3). IR (neat): 2976 (w), 2919 (w), 1412 (w), 1381(s), 1314 (s), 1224 (m), 1141 (s), 1004 (m), 886 (m), 739 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.03 (4H, m, Ar**H**), 2.88-2.72 (4H, m, Ar(C**H**$_2$)$_2$), 2.05-1.98 (1H, m, C**H**$_2$CHBpin), 1.70-1.59 (1H, m, C**H**$_2$CHBpin), 1.37-1.30 (1H, m, C**H**Bpin), 1.25 (6H, s, B**pin**), 1.25 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.9, 129.1, 129.0, 125.3, 83.1, 30.7, 29.7, 24.8, 24.8, 24.7; HRMS (ESI+): Calcd for $C_{16}H_{24}B_1O_2$ [M+H]: 259.18693, Found: 259.18675.

2-(1-(4-Methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 4). IR (neat): 2976 (w), 2952 (w), 1611 (w), 1510 (s), 1460 (m), 1379 (s), 1369 (s), 1315 (s), 1244 (s), 1166 (m), 1141 (s), 1110 (m), 1037 (m), 967 (m), 856 (m), 834 (m), 804 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.12-7.10 (2H, m, Ar**H**), 6.80-6.78 (2H, m, Ar**H**), 3.77 (3H, s, ArOC**H**$_3$), 2.74 (1H, dd, *J* = 13.6, 7.6 Hz, ArC**H**$_2$CH), 2.48 (1H, dd, *J* = 13.6, 8.4 Hz, ArC**H**$_2$CH), 1.32 (1H, m, C**H**Bpin), 1.19 (6H, s, B**pin**), 1.18 (6H, s, B**pin**), 0.95 (3H, d, *J* = 7.6 Hz, CHBpinC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 134.6, 129.9, 113.6, 83.1, 55.4, 38.2, 24.9, 24.9, 15.3; HRMS (ESI+): Calcd for $C_{16}H_{26}B_1O_3$ [M+H]: 277.19750, Found: 277.19846.

4,4,5,5-Tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)propan-2-yl)-1,3,2-dioxaborolane (Table 2, entry 5). IR (neat): 2979 (w), 1617 (w), 1381 (m), 1370 (m), 1320 (s), 1215 (m), 1161 (s), 1142 (s), 1113 (w), 1087 (s), 848 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.30 (2H, d, *J* = 8.0 Hz, Ar**H**), 2.85 (1H, dd, *J* = 13.6, 7.6 Hz, ArC**H**$_2$CH), 2.59 (1H, d, *J* = 13.6, 8.0 Hz, ArC**H**$_2$CH), 1.36 (1H, m, C**H**Bpin), 1.18 (6H, s, B**pin**), 1.17 (6H, s, B**pin**), 0.97 (3H, d, *J* = 7.6 Hz, CHBpinC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 129.3, 128.1 (q, *J* = 31.9 Hz), 125.1, 125.1, 124.7 (q, *J* = 270.2 Hz), 83.3, 39.0, 24.9, 24.8, 15.3; HRMS (ESI+): Calcd for $C_{16}H_{23}B_1F_3O_2$ [M+H]: 315.17432, Found: 315.17504.

4,4,5,5-Tetramethyl-2-(1-*o*-tolylpropan-2-yl)-1,3,2-dioxaborolane (Table 2, entry 6). IR (neat): 2976 (w), 2954 (w), 2929 (w), 1459 (m), 1378 (s), 1369 (s), 1315 (s), 1269 (w), 1232 (w), 1214 (w), 1142 (s), 966 (w), 857 (m), 833 (w), 739 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.05 (4H, m, Ar**H**), 2.81 (1H, dd, *J* = 14.0, 8.0 Hz, ArC**H**$_2$CH), 2.52 (1H, dd, *J* = 14.0, 8.0 Hz, ArC**H**$_2$CH), 2.32 (3H, s, ArC**H**$_3$), 1.38 (1H, m, C**H**Bpin), 1.02 (6H, s, B**pin**), 1.00 (6H, s, B**pin**), 1.01 (3H, d, *J* = 7.6 Hz, CHBPinC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 136.4, 130.2, 129.5, 125.8, 125.6, 83.1, 36.2, 24.9, 24.9, 19.7, 15.7; HRMS (ESI+): Calcd for $C_{16}H_{26}B_1O_2$ [M+H]: 261.20258, Found: 261.20339.

4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylbutan-2-yl)-1,3,2-dioxaborolane (Table 2, entry 7). IR (neat): 3027 (w), 2976 (m), 2955 (w), 2869 (w), 1494 (w), 1454 (w), 1409 (s), 1378 (s), 1317 (s), 1258 (m), 1214 (m), 1141 (s), 975 (m), 865 (m), 852 (m), 743 (m), 696 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.10 (5H, m, Ar**H**), 2.75 (1H, dd, *J* = 13.2, 6.4 Hz, PhC**H**$_2$), 2.65 (1H, dd, *J* = 13.2, 10.4 Hz, PhC**H**$_2$), 1.74 (1H, m, C**H**$(CH_3)_2$), 1.28 (1H, *pseudo*-dt, *J* = 10.4, 6.4 Hz, C**H**Bpin), 1.11 (6H, s, B**pin**), 1.06 (6H, s, B**pin**), 0.99 (3H, d, *J* = 6.4 Hz, CH(C**H**$_3)_2$), 0.97 (3H, d, *J* = 6.8 Hz, CH(C**H**$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 129.1, 128.2, 125.7, 83.0, 35.6, 30.0, 25.07, 24.9, 22.8, 21.6; HRMS (ESI+): Calcd for $C_{17}H_{28}B_1O_2$ [M+H]: 275.21823, Found: 275.21700.

Methyl 3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl carbonate (7). IR (neat): 2978 (w), 1746 (s), 1495 (m), 1441 (m), 1370 (m), 1326 (m), 1258 (s), 1214 (m), 1140 (s), 945 (m), 856 (m), 792 (m), 746 (m), 699 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.13 (5H, m, Ar**H**), 4.20 (2H, d, *J* = 6.8 Hz, C**H**$_2$OCO$_2$CH$_3$), 3.76 (3H, s, CH$_2$OCO$_2$C**H**$_3$), 2.80 (2H, d, *J* =

7.6 Hz, PhC**H**$_2$), 1.79 (1H, *pseudo*-tt, *J* = 7.2, 7.2 Hz, C**H**Bpin), 1.16 (6H, s, B**pin**), 1.16 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 140.6, 128.8, 128.1, 125.8, 83.4, 68.7, 54.5, 33.1, 24.6, 24.6; HRMS (ESI+): Calcd for $C_{17}H_{26}B_1O_5$ [M+H]: 321.18733, Found: 321.18769.

3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl acetate (8). IR (neat): 3027 (w), 2977 (w), 1736 (s), 1454 (w), 1370 (s),1324 (s), 1233 (s), 1140 (s), 1026 (m), 966 (m), 856 (m), 745 (m), 698 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.13 (5H, m, Ar**H**), 4.15 (1H, dd, *J* = 10.8, 7.2 Hz, C**H**$_2$OAc), 4.11 (1H, dd, *J* = 10.8, 6.8 Hz, C**H**$_2$OAc), 2.80 (1H, dd, *J* = 14.0, 8.0 Hz, PhC**H**$_2$CH), 2.75 (1H, dd, *J* = 14.0, 7.6 Hz, PhC**H**$_2$CH), 2.01 (3H, s, OCOC**H**$_3$), 1.75 (1H, *pseudo*-tt, *J* = 7.2, 7.2 Hz, C**H**Bpin), 1.17 (6H, s, B**pin**), 1.16 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ171.2, 141.2, 129.1, 128.4, 126.1, 83.6, 65.6, 33.7, 24.9, 24.9, 21.1; HRMS (ESI+): Calcd for $C_{17}H_{26}B_1O_4$ [M+H]: 305.19241, Found: 305.19315.

2-(1-Methoxy-3-o-tolylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). IR (neat): 2978 (w), 1746 (s), 1495 (m), 1441 (m), 1370 (m), 1326 (m), 1258 (s), 1214 (m), 1140 (s), 945 (m), 856 (m), 792 (m), 746 (m), 699 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.04 (4H, m, Ar**H**), 3.48 (1H, dd, *J* = 8.8, 6.8 Hz, C**H**$_2$OCH$_3$), 3.43 (1H, dd, *J* = 8.8, 6.4 Hz, C**H**$_2$OCH$_3$), 3.32 (3H, s, CH$_2$OC**H**$_3$), 2.78 (1H, dd, *J* = 14.0, 7.6 Hz, ArC**H**$_2$CH), 2.74 (1H, dd, *J* = 14.0, 8.4 Hz, ArC**H**$_2$CH), 2.32 (3H, s, ArC**H**$_3$), 1.69 (1H, *pseudo*-tt, *J* = 7.6, 6.8 Hz, C**H**Bpin), 1.20 (6H, s, B**pin**), 1.17 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 136.4, 130.2, 129.5, 125.9, 125.7, 83.4, 74.2, 58.7, 30.9, 24.8, 24.8, 19.6; HRMS (ESI+): Calcd for $C_{17}H_{28}B_1O_3$ [M+H]: 291.21315, Found: 291.21354.

2-(Chroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10). IR (neat): 2977 (w), 2930 (w), 1582 (w), 1489 (m), 1411 (m), 1361 (s), 1323 (s), 1310 (s), 1227 (s), 1140 (s), 1114 (m), 1005 (m), 968 (m), 853 (m), 750 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.01 (2H, m, ArH), 6.83-6.77 (2H, m, ArH), 4.41 (1H, m, OC**H**$_2$), 4.02 (1H, dd, *J* = 11.2, 10.8 Hz, OC**H**$_2$), 2.81 (2H, d, *J* = 8.4 Hz, ArC**H**$_2$), 1.75-1.67 (1H, m, C**H**Bpin), 1.25 (6H, s, B**pin**), 1.25 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 129.7, 127.2, 122.8, 120.0, 116.8, 83.7, 67.8, 26.7, 24.9, 24.9; HRMS (ESI+): Calcd for $C_{15}H_{22}B_1O_3$ [M+H]: 261.16620, Found: 261.16594.

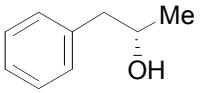
3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-ol (12). IR (neat): 3443 (br), 3026 (w), 2978 (w), 2928 (w), 2976 (w), 1453 (w), 1372 (s), 1317 (s), 1140 (s), 966 (m), 855 (m), 731 (s), 698 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27- 7.13 (5H, m, Ar**H**), 3.68 (1H, dd, *J* = 10.4, 5.6 Hz, C**H**$_2$OH), 3.61 (1H, dd, *J* = 10.4, 6.4 Hz, C**H**$_2$OH), 2.83 (1H, dd, *J* = 13.6, 7.2 Hz, PhC**H**$_2$), 2.73 (1H, dd, *J* = 13.6, 8.4 Hz, PhC**H**$_2$), 2.05 (1H, s, CH$_2$O**H**), 1.60 (1H, *pseudo*-tt, *J* = 6.8, 6.8 Hz, C**H**Bpin), 1.21 (6H, s, B**pin**), 1.19 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 129.0, 128.3, 125.9, 83.6, 63.4, 33.4, 25.0, 24.9, 24.9; HRMS (ESI+): Calcd for $C_{15}H_{24}B_1O_3$ [M+H]: 263.18185, Found: 263.18207.

■ **Representative experimental procedure for enantioselective Cu-catalyzed hydroboration of (*E*)-(3-methoxyprop-1-enyl)benzene with bis(pinacolato)diboron:**

In an N_2-filled glovebox, an oven-dried vial (4 mL, 17 x 38 mm) with magnetic stir bar was charged with imidazolinium salt **13** (8.70 mg, 0.0150 mmol, 7.5 mol %), CuCl (1.50 mg, 0.0150 mmol, 7.5 mol %), KO*t*Bu (6.70 mg, 0.0600 mmol, 30 mol %) and THF (0.4 mL). The mixture was sealed with cap (phenolic open topcap) and allowed to stir for 20 min. Bis(pinacolato)diboron (55.8 mg, 0.220 mmol, 1.10 equiv) was added to the solution. The vial was sealed with cap and removed from glovebox. After stirring for 30 min, the solution turned dark brown. The reaction mixture was allowed to cool to -78 °C (dry ice/acetone bath). A solution of (*E*)-(3-methoxyprop-1-enyl)benzene (29.6 mg, 0.200 mmol, 1.00 equiv) in THF (0.2 mL) and MeOH (16.0 μL, 0.400 mmol, 2.00 equiv) were added by syringes. The resulting brown solution transferred to a -15 °C cryocool. After 48 h, the solution was allowed to cool to -78 °C and passed through a short plug of celite and silica gel and washed with Et_2O (3 x 2 mL). The filtrate was concentrated *in vacuo* to provide dark brown oil, which was oxidized without further purification. To a solution of unpurified dark brown oil in THF (1 mL) at 0 °C (ice bath) were added H_2O_2 (97.0 μL, 1.00 mmol, 5.00 equiv) and 2 N NaOH (500 μL, 1.00 mmol, 5.00 equiv). The resulting solution was allowed to stir for 20 min. After this time, the mixture was diluted with water (2 mL), washed with Et_2O (3 x 1 mL), and filtered through a plug of $MgSO_4$. The filtrate was concentrated *in vacuo* to provide colorless oil, which was purified by silica gel column chromatography (hexanes:Et_2O=3:1) to afford the desired product **14** as colorless oil (24.9 mg, 0.149 mmol, 75% yield).

Imidazolinium salt (13, prepared similar to reported procedures**).**[3] IR (neat): 2962 (w), 2928 (w), 1614 (s), 1586 (m), 1573 (m), 1497 (m), 1198 (s), 1141 (s), 1089 (m), 1021 (m), 880 (w), 758 (m), 732 (s), 715 (s), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (1H, s), 8.25 (1H, dd, *J* = 7.6, 1.6 Hz), 7.64-7.62 (2H, m), 7.46-7.39 (5H, m), 7.39-7.31 (4H, m), 7.10 (1H, dt, *J* = 7.6, 1.6 Hz), 7.04 (1H, d, *J* = 2.0 Hz), 6.85 (1H, d, *J* = 2.0 Hz), 6.71 (1H, dt, *J* = 8.0, 1.2 Hz), 6.51 (1H, d, *J* = 11.6 Hz), 5.32 (1H, d, *J* = 12.0 Hz), 3.20 (2H, m), 2.83 (1H, m), 1.50 (3H, d, *J* = 7.2 Hz), 1.40 (3H, d, *J* = 6.8 Hz), 1.19 (3H, d, *J* = 6.8 Hz), 1.18 (3H, d, *J* = 6.8 Hz), 1.11 (3H, d, *J* = 6.8 Hz), 0.25 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 152.0, 149.2, 145.5, 144.0, 135.1, 131.5, 130.9, 130.7, 130.6, 130.4, 130.1, 129.9, 129.8, 129.5, 129.0, 127.3, 126.2, 123.6, 122.5, 78.6, 74.8, 34.3, 29.4, 28.7, 26.5, 25.4, 25.0, 23.9, 22.9; HRMS (ESI+): Calcd for $C_{36}H_{41}N_2O_3S_1$ [M+H]: 581.28379, Found: 581.28176; Optical Rotation: $[\alpha]_D^{20}$ +34.7 (*c* = 1.00, $CHCl_3$).

(*S*)-1-Phenylpropan-2-ol (Oxidation of 5, This compound has been previously reported and spectra data match those described**)**.[9] ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (2H, m, Ar**H**), 7.25-7.20 (3H, m, Ar**H**), 4.01 (1H, m, C**H**OH), 2.78 (1H, dd, *J*

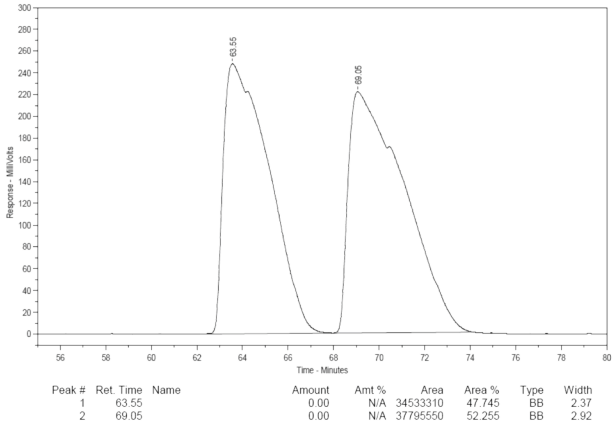


(9) (a) Musa, M. M.; Ziegelmann-Fjeld, K. I.; Vieille, C.; Zeikus, J. G.; Phillips, R. S. *J. Org. Chem.* **2007**, *72*, 30-34. (b) Erdélyi, B.; Szabó, A.; Seres, G.; Birincsik, L.; Ivanics, J.; Szatzker, G.; Poppe, L. *Tetrahedron: Asymmetry* **2006**, *17*, 268-274.

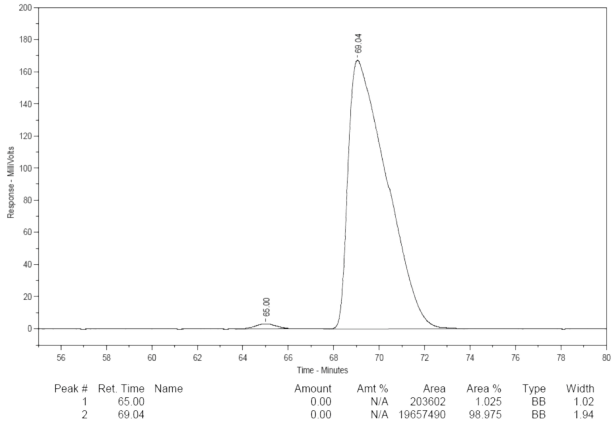
= 13.6, 4.8 Hz, PhC**H**$_2$), 2.70 (1H, dd, *J* = 13.6, 7.6 Hz, PhC**H**$_2$), 1.76 (1H, s, CHO**H**), 1.24 (3H, d, *J* = 6.4 Hz, CHOHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 129.5, 128.7, 126.6, 69.0, 45.9, 22.9; Optical Rotation: $[\alpha]_D^{20}$ +48.2 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er (98% ee).

Proof of Stereochemistry: literature value ($[\alpha]_D^{25}$ +42.2 (*c* = 1.0, $CHCl_3$), >99% ee) is assigned to the (*S*) enantiomer.[9b]

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).:



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	63.55		0.00	N/A	34533310	47.745	BB	2.37
2	69.05		0.00	N/A	37795550	52.255	BB	2.92

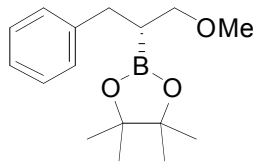


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	65.00		0.00	N/A	203602	1.025	BB	1.02
2	69.04		0.00	N/A	19657490	98.975	BB	1.94

Peak #	Ret. Time	Area	Area %
1	63.55	34533310	47.745
2	69.05	37795550	52.255

Peak #	Ret. Time	Area	Area %
1	65.00	203602	1.025
2	69.04	19657490	98.975

2-(1-Methoxy-3-phenylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. IR (neat): 2977



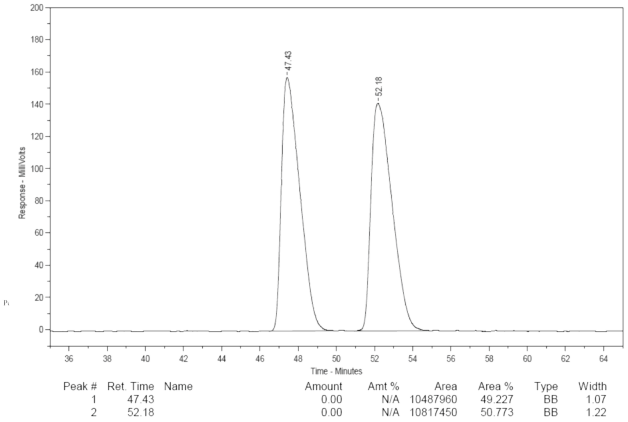
(w), 2926 (w), 2870 (w), 1495 (w), 1387 (m), 1369 (s), 1318 (s), 1247 (w), 1142 (s), 1109 (s), 1086 (m), 965 (m), 859 (m), 745 (m), 698 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.20 (4H, m, Ar**H**), 7.16-7.13 (1H, m, Ar**H**), 3.42 (2H, d, *J* = 7.2 Hz, C**H**$_2$OCH$_3$), 3.31 (3H, s, CH$_2$OC**H**$_3$), 2.79 (1H, dd, *J* = 13.6, 7.6 Hz, PhC**H**$_2$), 2.75 (1H, dd, *J* = 13.6, 8.0 Hz, PhC**H**$_2$), 1.70 (1H, *pseudo*-tt, *J* = 7.2, 7.2 Hz, C**H**Bpin), 1.17 (6H, s, B**pin**), 1.16 (6H, s, B**pin**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 129.2, 128.2, 125.8, 83.4, 73.6, 58.7, 33.7, 24.9, 24.8; HRMS (ESI+): Calcd for $C_{16}H_{26}B_1O_3$ [M+H]: 277.19750, Found: 277.19794.

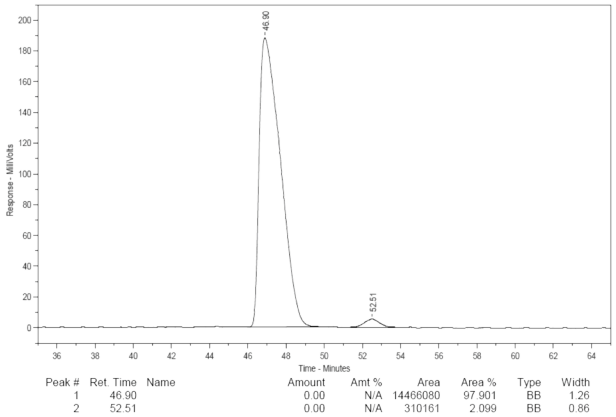
(*R*)-1-Methoxy-3-phenylpropan-2-ol (**14**, This compound has been previously reported and spectra data match those described**).**[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.20 (5H, m, Ar**H**), 4.00 (1H, m, C**H**OH), 3.39 (1H, dd, *J* = 9.6, 3.6 Hz, C**H**$_2$OCH$_3$), 3.36 (3H, s, CH$_2$OC**H**$_3$), 3.28 (1H, dd, *J* = 9.6, 6.8 Hz, C**H**$_2$OCH$_3$), 2.80 (1H, dd, *J* = 13.6, 6.8 Hz, PhC**H**$_2$), 2.76 (1H, dd, *J* = 13.6, 6.4 Hz, PhC**H**$_2$), 2.29 (1H, d, *J* = 3.6 Hz, CHO**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 129.5, 128.7, 126.7, 76.1, 71.4, 59.2, 40.1; Optical Rotation: $[\alpha]_D^{20}$ □2.71 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (96% ee).

(10) Jungen, M.; Gais, H-J. *Tetrahedron: Asymmetry* **1999**, *10*, 3747-3758.

Proof of Stereochemistry: literature value ($[\alpha]_D^{22}$ □0.7 (*c* = 1.21, $CHCl_3$), 90% ee) is assigned to the (*R*) enantiomer.[10]

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H column, 98/2 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).:



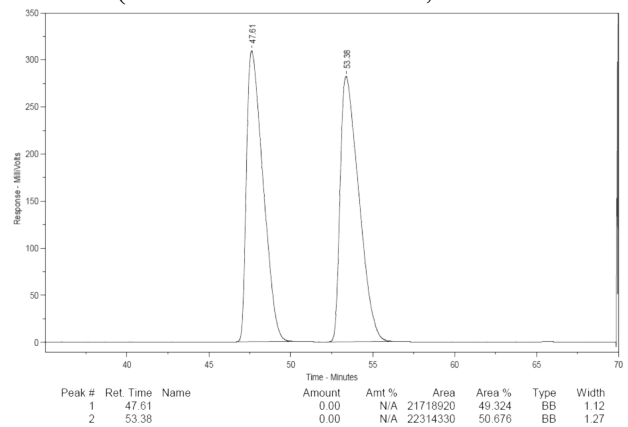


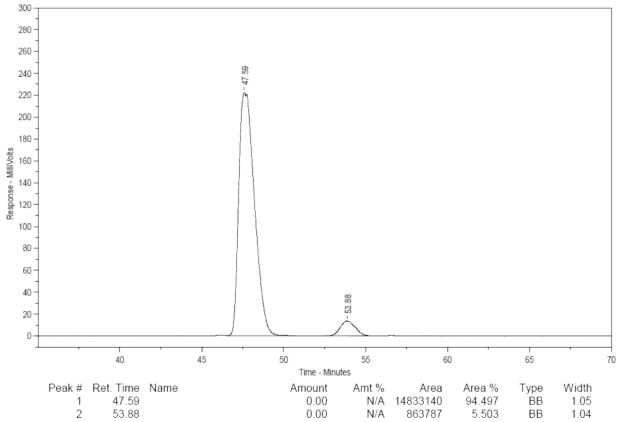
Peak #	Ret. Time	Area	Area %
1	47.43	10487960	49.227
2	52.18	10817450	50.773

Peak #	Ret. Time	Area	Area %
1	46.90	14466080	97.901
2	52.51	310161	2.099

(*R*)-1-Methoxy-3-o-tolylpropan-2-ol (15). IR (neat): 3428 (br), 2924 (w), 2889 (w), 1493 (w), 1455 (w), 1124 (s), 1111 (s), 1082 (s), 961 (m), 761 (m), 741 (s), 720 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.11 (4H, m, Ar**H**), 4.00 (1H, m, C**H**OH), 3.41 (1H, dd, *J* = 9.6, 3.6 Hz, C$\mathbf{H}_2$OCH$_3$), 3.38 (3H, s, CH$_2$OC$\mathbf{H}_3$), 3.32 (1H, dd, *J* = 7.2, 3.6 Hz, C$\mathbf{H}_2$OCH$_3$), 2.82 (1H, dd, *J* = 13.6, 7.2 Hz, ArC$\mathbf{H}_2$), 2.70 (1H, dd, *J* = 13.6, 6.4 Hz, ArC$\mathbf{H}_2$), 2.32 (3H, s, ArC$\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 136.4, 130.6, 130.2, 126.8, 126.2, 76.2, 70.6, 59.2, 37.2, 19.7; HRMS (ESI+): Calcd for $C_{11}H_{20}N_1O_2$ [M+NH_4]: 198.14940, Found: 198.15009; Optical Rotation: $[\alpha]_D^{20}$ □1.76 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94.5:5.5 er (89% ee).

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).:



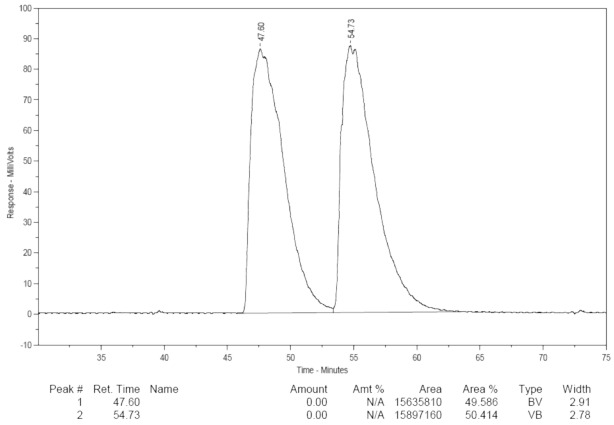


Peak #	Ret. Time	Area	Area %	Peak #	Ret. Time	Area	Area %
1	47.61	21718920	49.324	1	47.59	14833140	94.497
2	53.38	22314330	50.676	2	53.88	863787	5.503

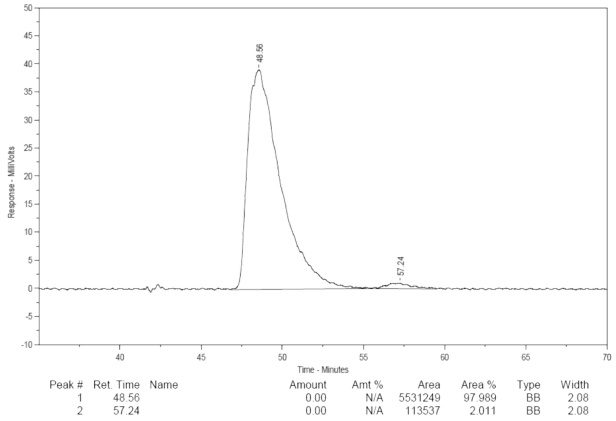
(*R*)-3-Phenylpropane-1,2-diol (16, This compound has been previously reported and spectra data match those described**).**[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.19 (5H, m, Ar**H**), 3.91 (1H, m, C**H**OHCH$_2$OH), 3.65 (1H, d, *J* = 10.8 Hz, C**H**$_2$OH), 3.48 (1H, dd, *J* = 10.8, 7.2 Hz, C**H**$_2$OH), 2.76 (1H, dd, *J* = 13.6, 5.6 Hz, PhC**H**$_2$), 2.71 (1H, dd, *J* = 13.6, 7.6 Hz, PhC**H**$_2$), 2.39 (1H, s, CH$_2$O**H**), 2.35 (1H, s, CH$_2$O**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 129.5, 128.8, 126.8, 73.2, 66.2, 40.0; Optical Rotation: $[\alpha]_D^{20}$ +25.6 (*c* = 1.00, EtOH) for an enantiomerically enriched sample of 98:2 er (96% ee).

Proof of Stereochemistry: literature value ($[\alpha]_D^{22}$ +33.2 (*c* = 1.00, EtOH), 95% ee) is assigned to the (*R*) enantiomer.[11]

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OD-R column, 98:2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).:



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	47.60		0.00	N/A	15635810	49.586	BV	2.91
2	54.73		0.00	N/A	15897160	50.414	VB	2.78



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	48.56		0.00	N/A	5531249	97.989	BB	2.08
2	57.24		0.00	N/A	113537	2.011	BB	2.08

Peak #	Ret. Time	Area	Area %	Peak #	Ret. Time	Area	Area %
1	47.60	15635810	49.586	1	48.56	5531249	97.989
2	54.73	15897160	50.414	2	57.24	113537	2.011

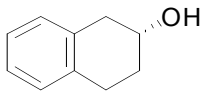
■ Representative experimental procedure for enantioselective Cu-catalyzed hydroboration of cyclic olefins with bis(pinacolato)diboron:

In an N_2-filled glovebox, an oven-dried vial (4 mL, 17 x 38 mm) with magnetic stir bar was charged with imidazolinium salt **19** (9.20 mg, 0.0150 mmol, 7.5 mol %), CuCl (1.50 mg, 0.0150 mmol, 7.5 mol %), NaO*t*-Bu (5.80 mg, 0.0600 mmol, 30 mol %) and THF (0.4 mL). The mixture was sealed with cap (phenolic open topcap) and allowed to stir for 20 min. Bis(pinacolato)diboron (55.8 mg, 0.220 mmol, 1.10 equiv) was added to the solution. The vial was sealed with cap and removed from glovebox. After stirring for 30 min, the solution turned dark brown. The reaction mixture was allowed to cool to -78 °C (dry ice/acetone bath). A solution of *2H*-chromene (26.4 mg, 0.200 mmol, 1.00 equiv) in THF (0.2 mL) and MeOH (16.0

(11) Cardillo, G.; Orena, M.; Romero, M. *Tetrahedron* **1989**, *45*, 1501-1508.

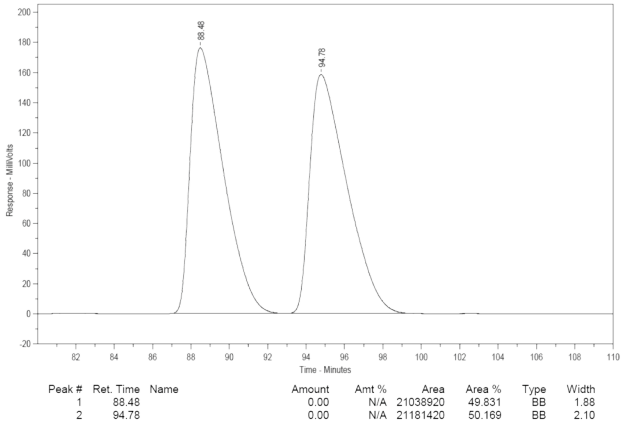
μL, 0.400 mmol, 2.00 equiv) were added by syringes. The resulting brown solution transferred to a -50 °C cryocool. After 48 h, the solution was allowed to cool to -78 °C and passed through a short plug of celite and silica gel and washed with Et_2O (3 x 2 mL). The filtrate was concentrated *in vacuo* to provide dark brown oil, which was purified by silica gel column chromatography (hexanes:Et_2O=10:1) to afford the desired product **18** as colorless oil (51.0 mg, 0.196 mmol, 98% yield).

(*R*)-1,2,3,4-Tetrahydronaphthalen-2-ol (Oxidation of 17, This compound has been previously reported and spectra data match those described**)**.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.06 (4H, m, Ar**H**), 4.16 (1H, m, C**H**OHCH$_2$), 3.04 (1H, dd, *J* = 15.6, 4.4 Hz, ArC**H**$_2$CHOH), 2.96 (1H, dt, *J* = 16.8, 5.6 Hz, ArC**H**$_2$), 2.88-2.74 (2H, m, ArC**H**$_2$), 2.10-2.03 (1H, m, C**H**$_2$CHOH), 1.87-1.78 (1H, m, C**H**$_2$CHOH), 1.70 (1H, br s, CHO**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 134.4, 129.7, 128.8, 126.2, 126.1, 67.4, 38.6, 31.7, 27.2; Optical Rotation: $[\alpha]_D^{20}$ +54.1 (*c* = 1.00, EtOH) for an enantiomerically enriched sample of 86:14 er (72% ee).

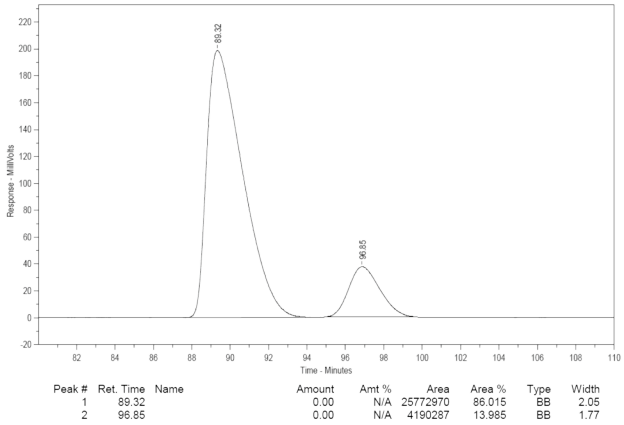


Proof of Stereochemistry: literature value ($[\alpha]_D^{19}$ +68.0 (*c* = 1.61, EtOH), 93% ee) is assigned to the (*R*) enantiomer.[13]

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H column, 99.5:0.5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).:



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	88.48		0.00	N/A	21038920	49.831	BB	1.88
2	94.78		0.00	N/A	21181420	50.169	BB	2.10

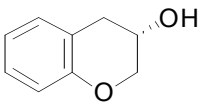


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	89.32		0.00	N/A	25772970	86.015	BB	2.05
2	96.85		0.00	N/A	4190287	13.985	BB	1.77

Peak #	Ret. Time	Area	Area %
1	88.48	21038920	49.831
2	94.78	21181420	50.169

Peak #	Ret. Time	Area	Area %
1	89.32	25772970	86.015
2	96.85	4190287	13.985

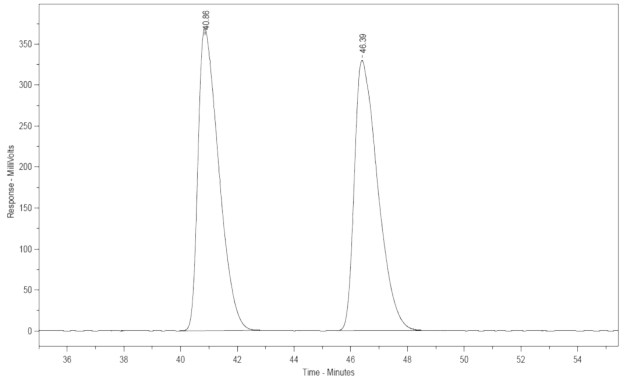
(*S*)- Chroman-3-ol (Oxidation of 18, This compound has been previously reported and spectra data match those described**)**.[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (1H, t, *J* = 8.0 Hz, Ar**H**), 7.05 (1H, d, *J* = 7.6 Hz, Ar**H**), 7.04-6.83 (2H, m, Ar**H**), 4.25-



(12) Elings, J. A.; Downing, R. S.; Sheldon, R. A. *Eur. J. Org. Chem.* **1999**, 837-846.
(13) (a) Arakawa, H.; Torimoto, N.; Nasui, Y. *Tetrahedron Lett.* **1968**, *9*, 4115-4117. (b) Kawasaki, M.; Suzuki, Y.; Terashima, S. *Chem. Lett.* **1984**, 239-242.
(14) (a) Rieke, R. D.; Stack. D. E.; Dawson, B. T.; Wu, T-C. *J. Org. Chem.* **1993**, *58*, 2483-2491. (b) Still, W. C., Jr.; Goldsmith, D. J. *J. Org. Chem.* **1970**, *35*, 2282-2286.

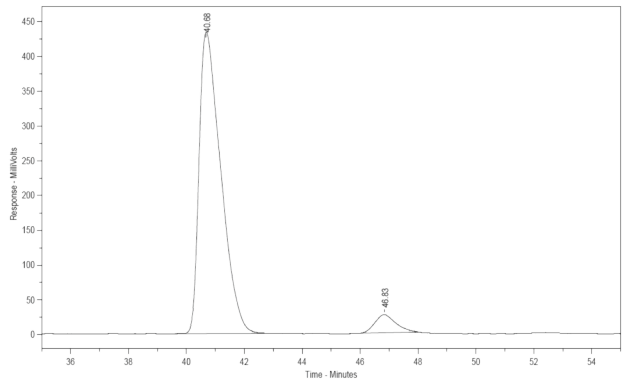
4.20 (1H, m, C**H**OH), 4.12-4.03 (2H, m, CHC**H**$_2$O), 3.08 (1H, dd, J = 16.4, 4.8 Hz, ArC**H**$_2$CHOH), 2.78 (1H, dd, J = 16.4, 4.4 Hz, ArC**H**$_2$CHOH), 2.28 (1H, d, J = 6.8 Hz, CHO**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 130.5, 127.7, 121.2, 119.4, 116.6, 69.7, 63.3, 33.6; Optical Rotation: $[\alpha]_D^{20}$ +28.8 (c = 0.82, EtOH) for an enantiomerically enriched sample of 94.5:5.5 er (89% ee).

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (Chiralcel OJ-H column, 96:4 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).:



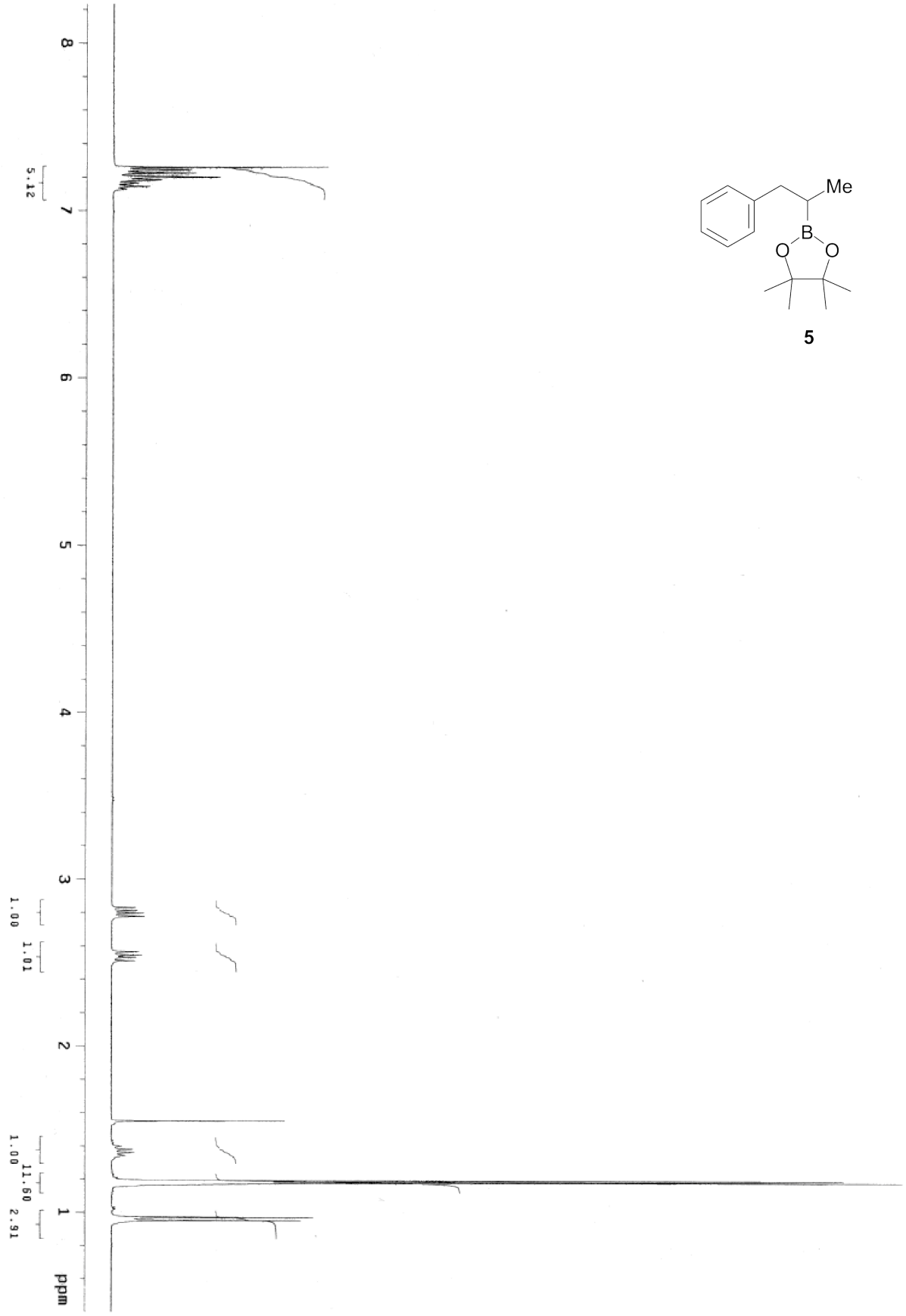
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	40.86		0.00	N/A	18717470	49.802	BB	0.79
2	46.39		0.00	N/A	18866580	50.198	BB	0.88

Peak #	Ret. Time	Area	Area %
1	40.86	18717470	49.802
2	46.39	18866580	50.198



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	40.68		0.00	N/A	22532750	94.480	BB	0.82
2	46.83		0.00	N/A	1316467	5.520	BB	0.80

Peak #	Ret. Time	Area	Area %
1	40.68	22532750	94.480
2	46.83	1316467	5.520



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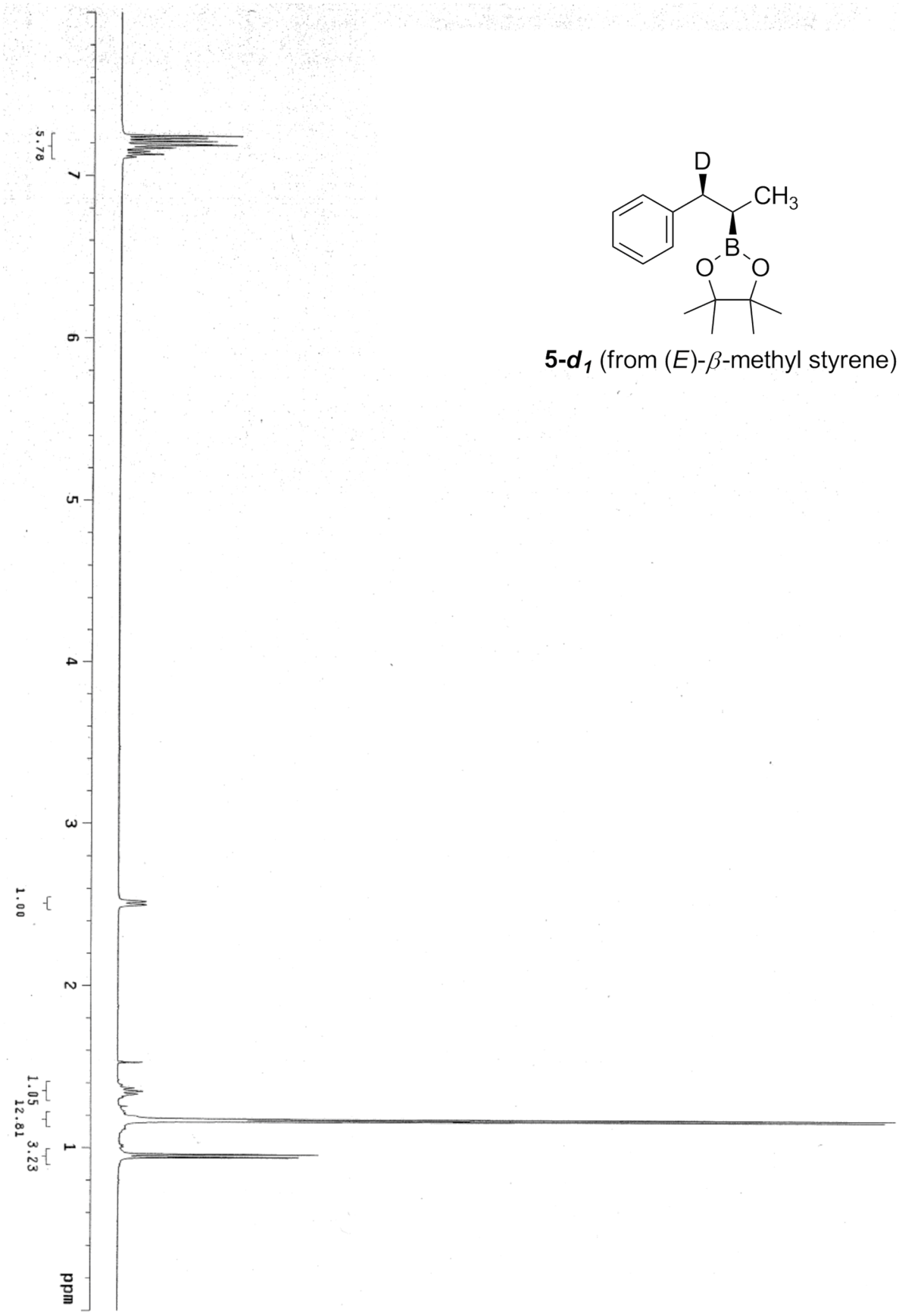
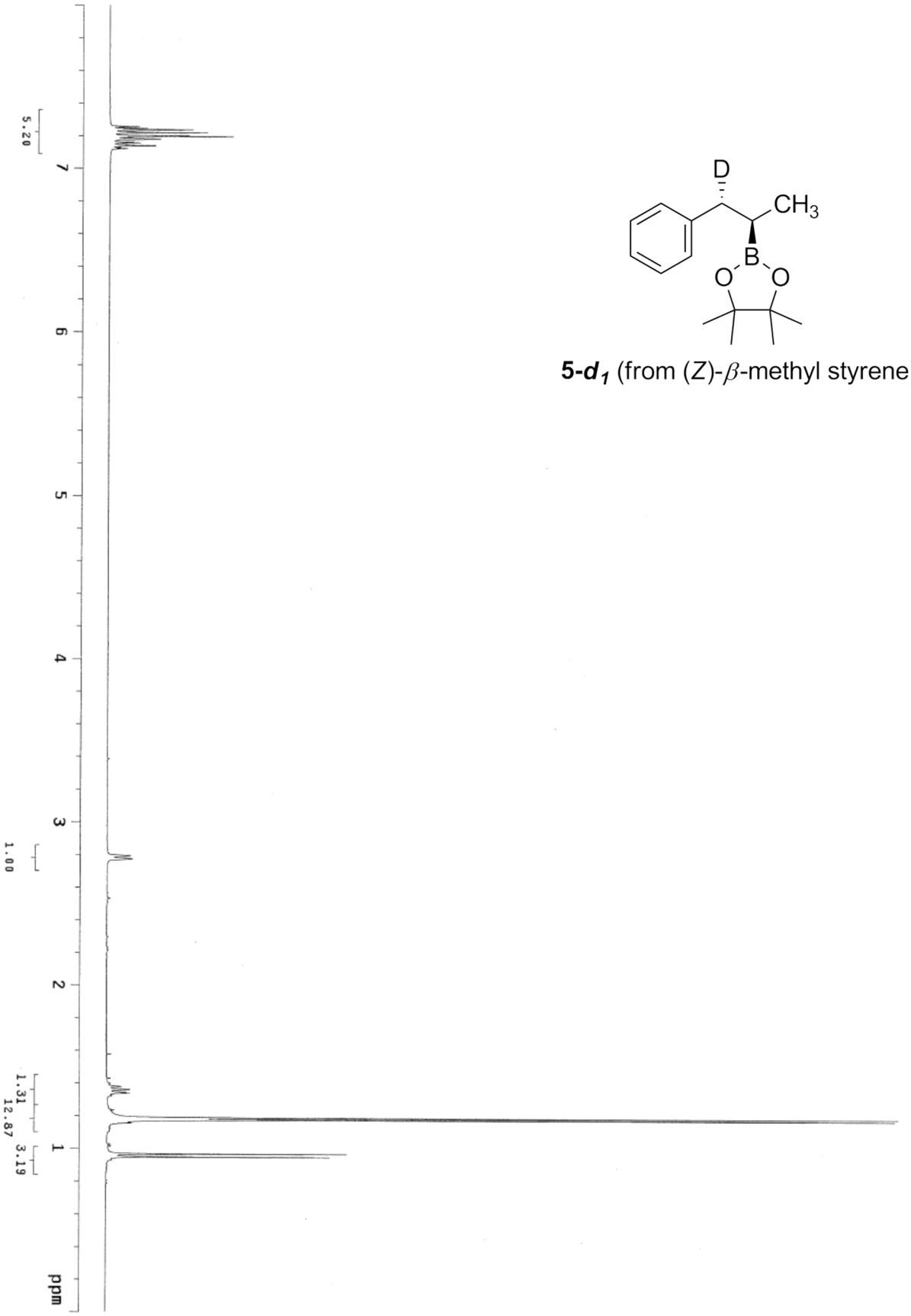
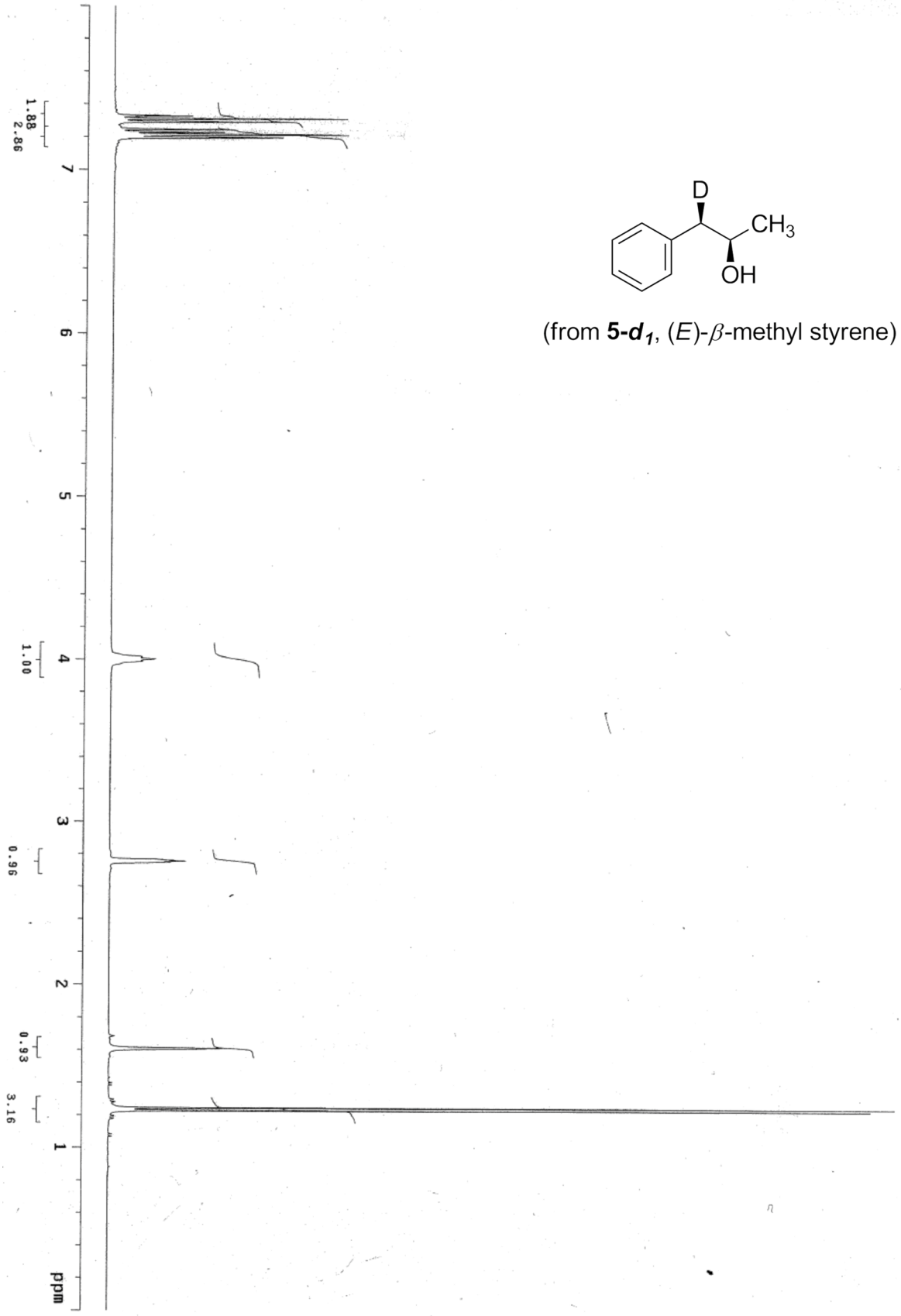


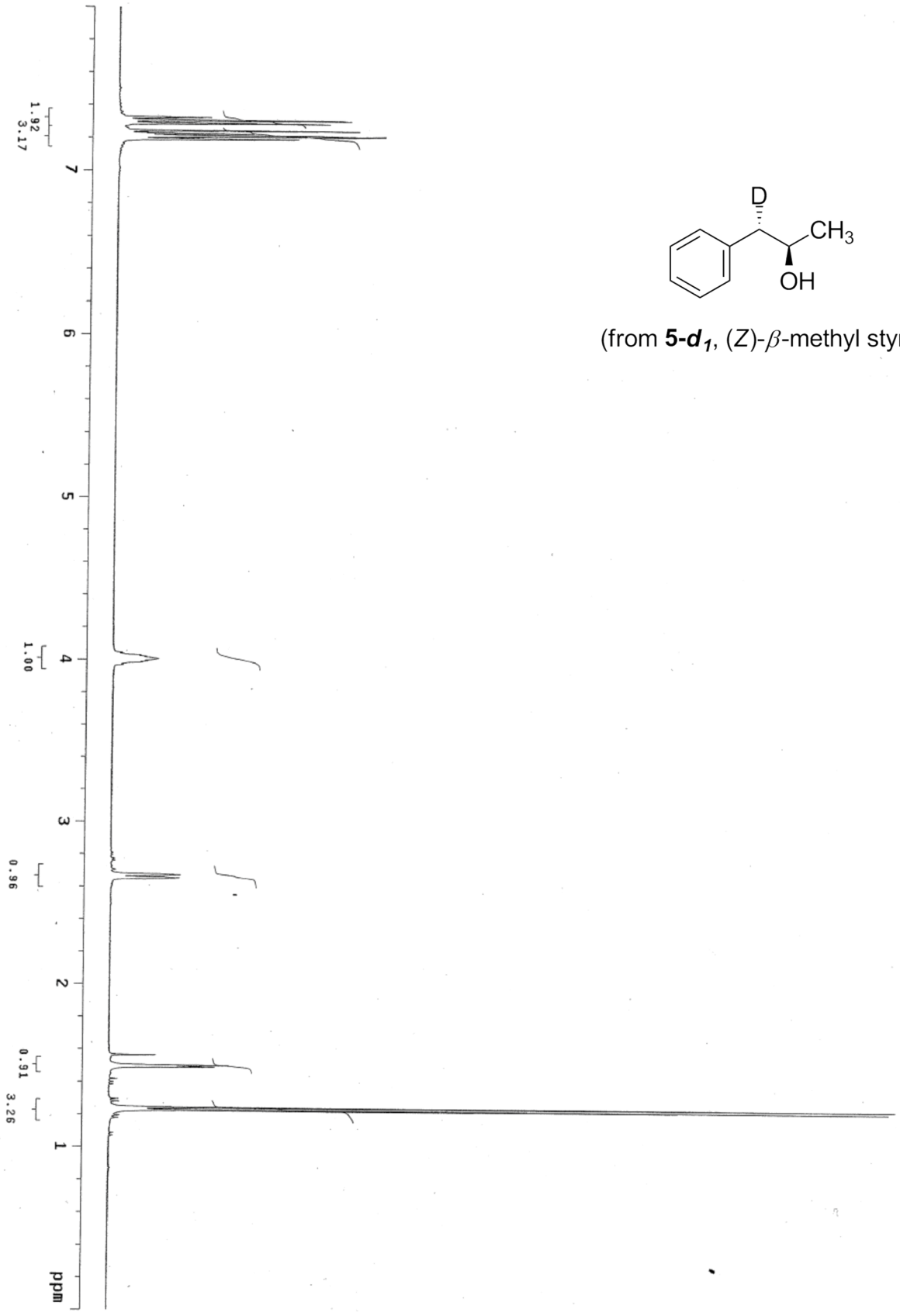
5-*d*$_1$ (from (*E*)-β-methyl styrene)



5-*d*$_1$ (from (*Z*)-β-methyl styrene)



(from **5-*d*$_1$**, (*E*)-β-methyl styrene)



(from **5-*d*$_1$**, (*Z*)-β-methyl styrene)

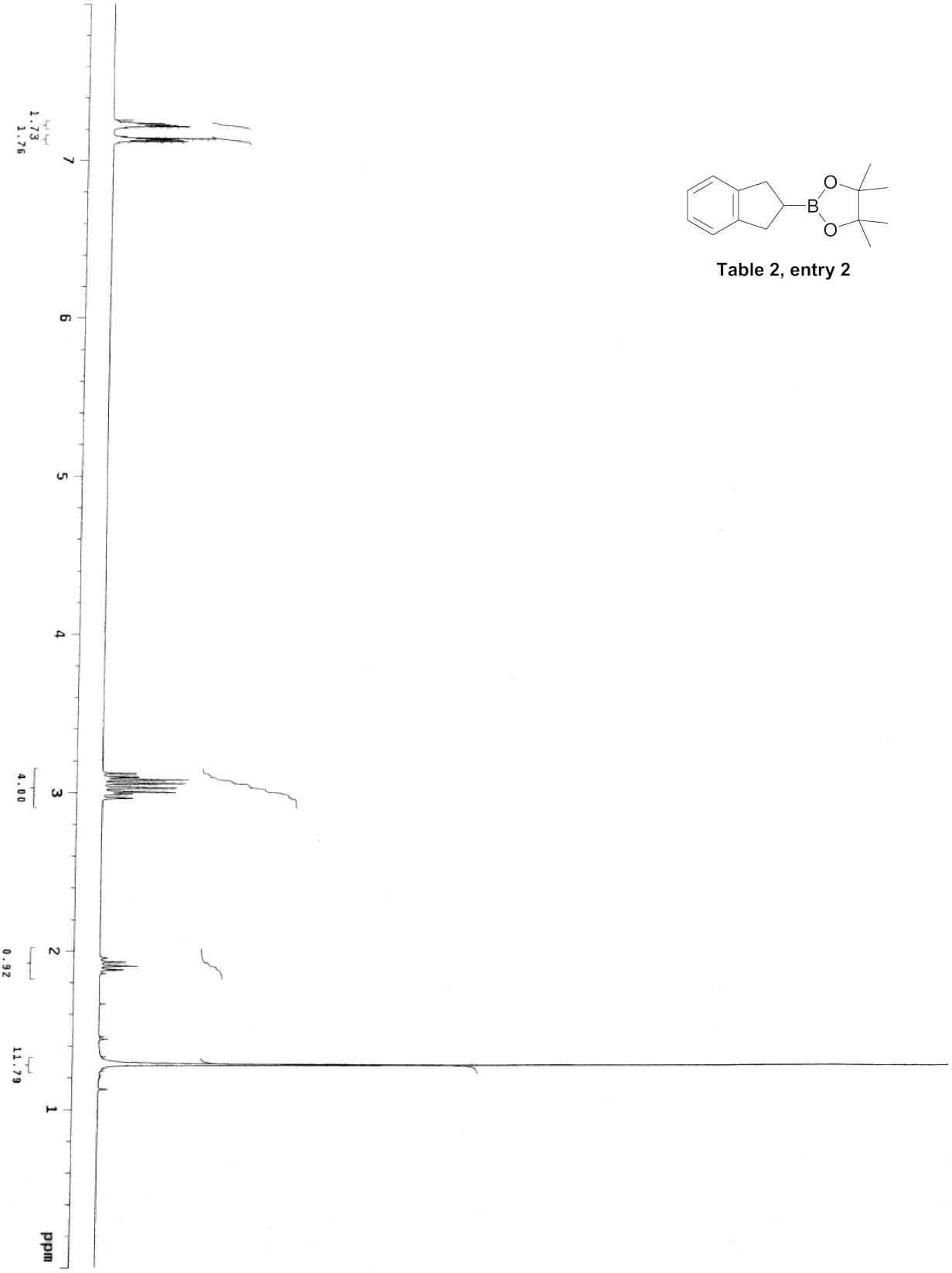
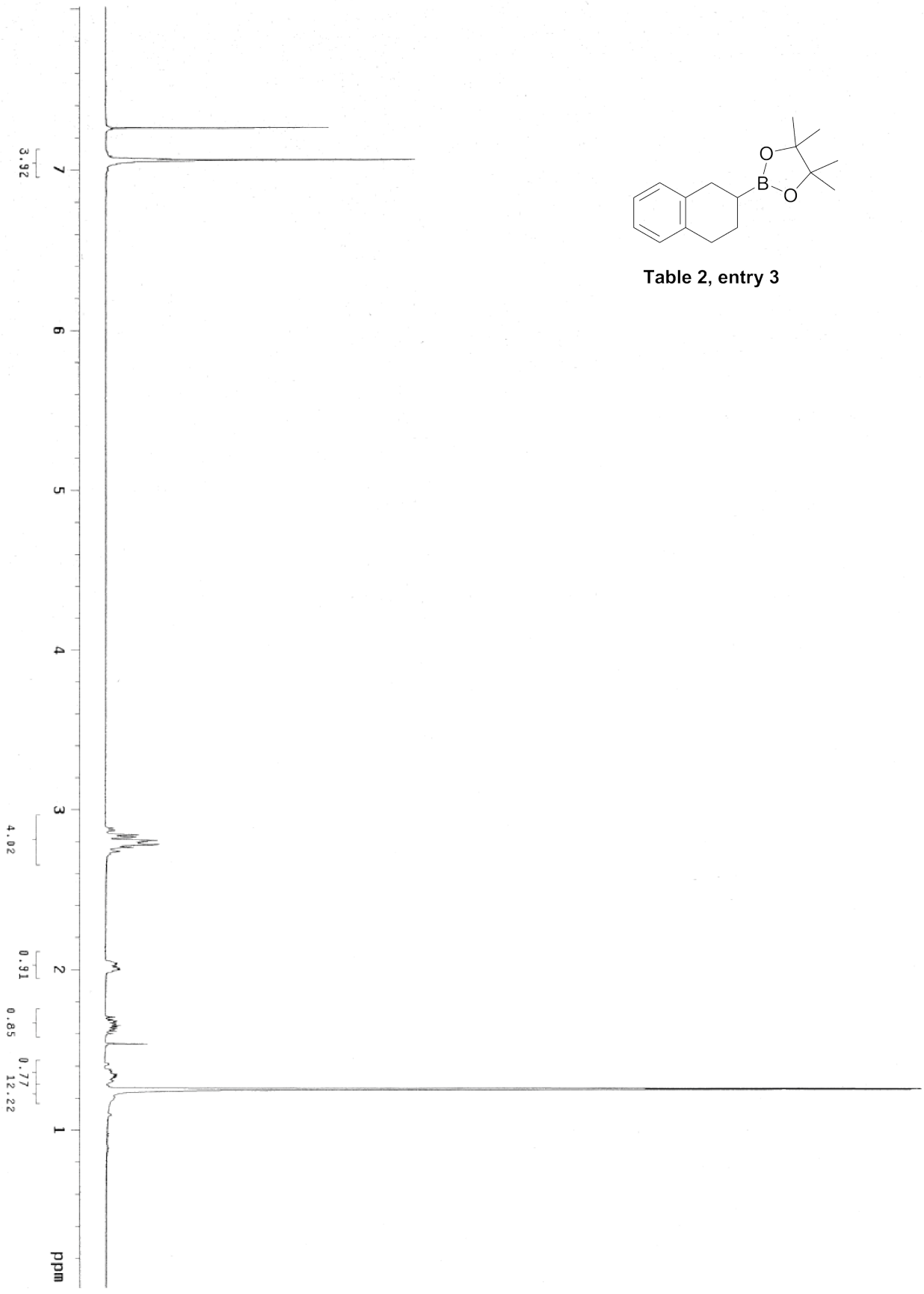


Table 2, entry 2



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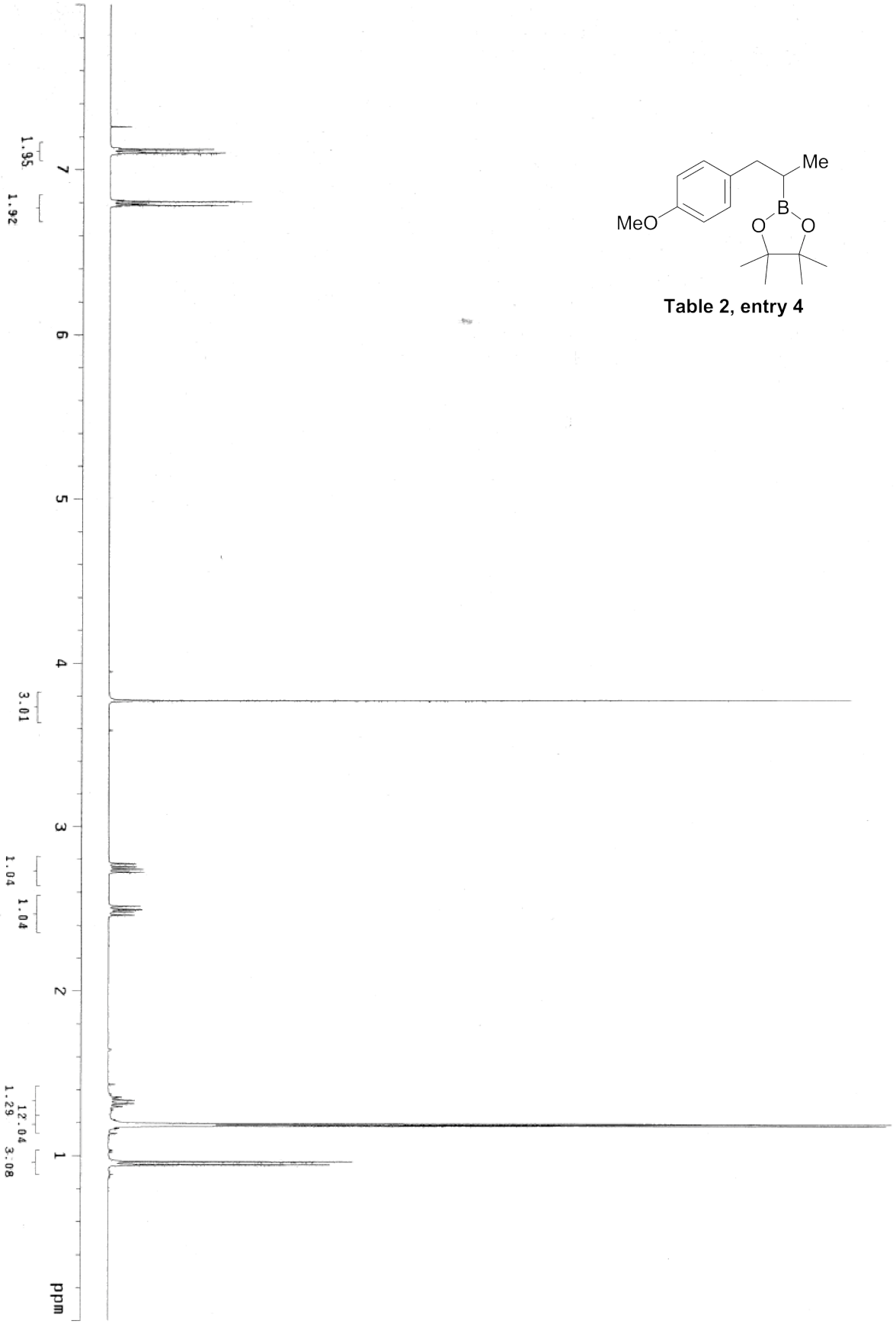

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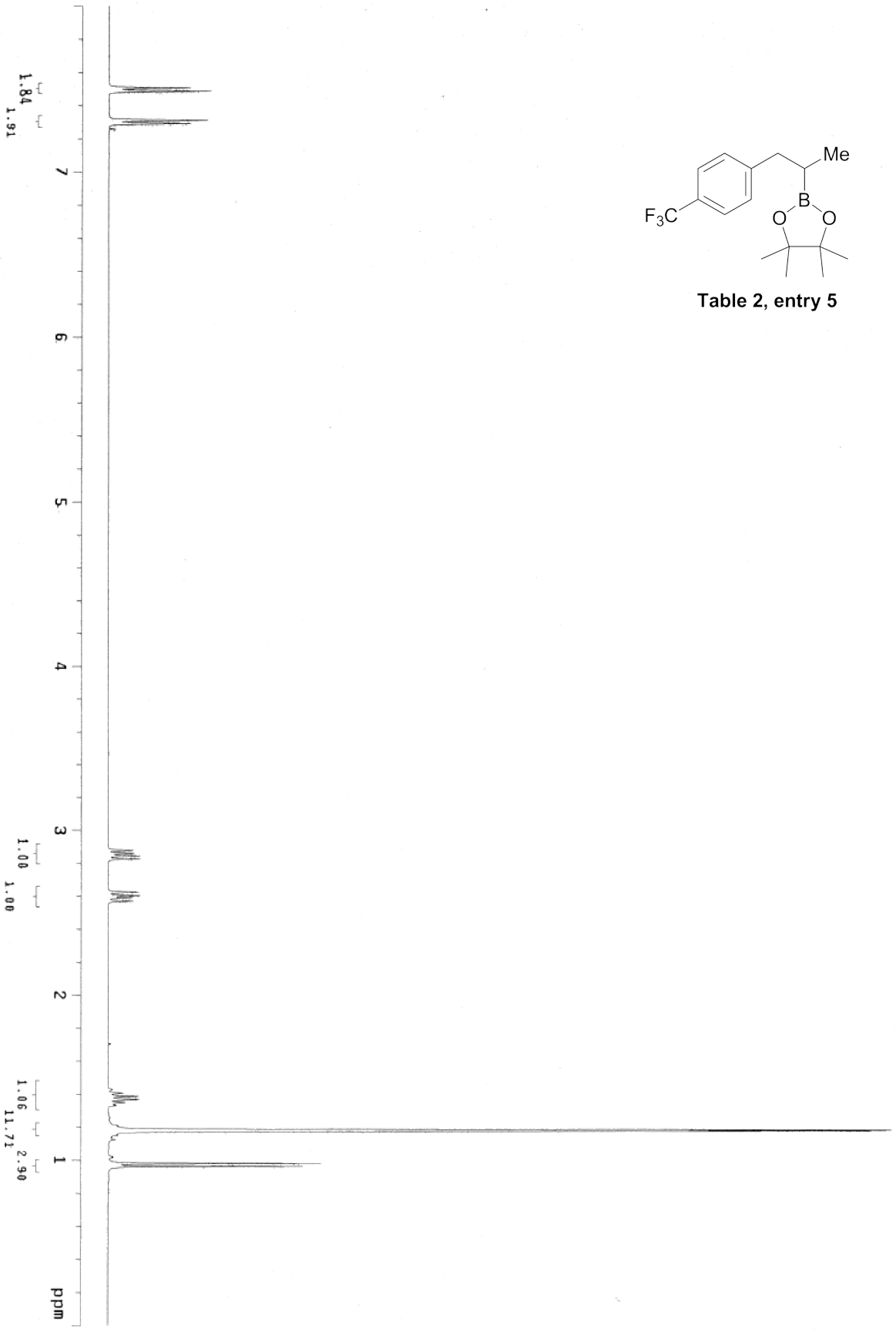

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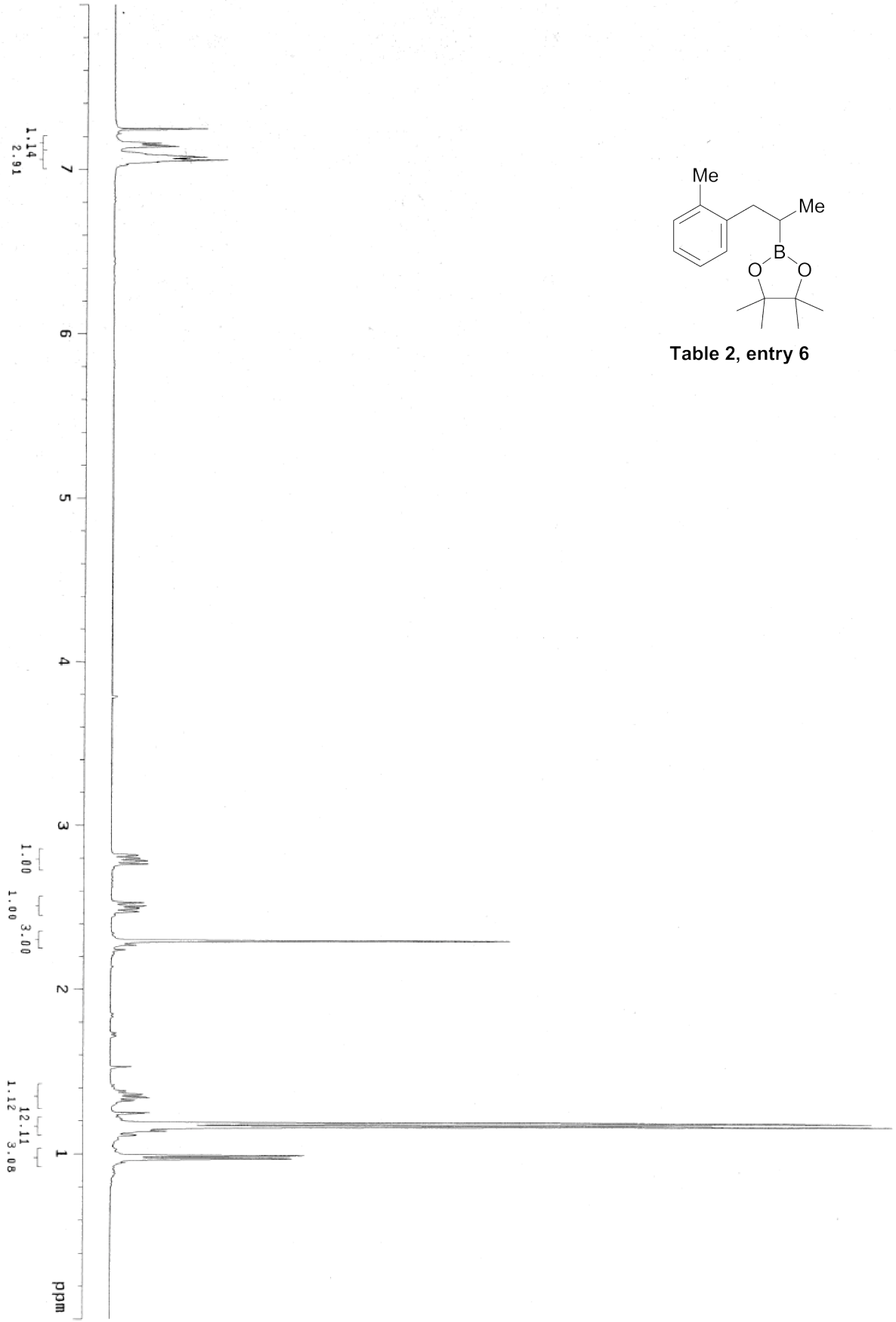

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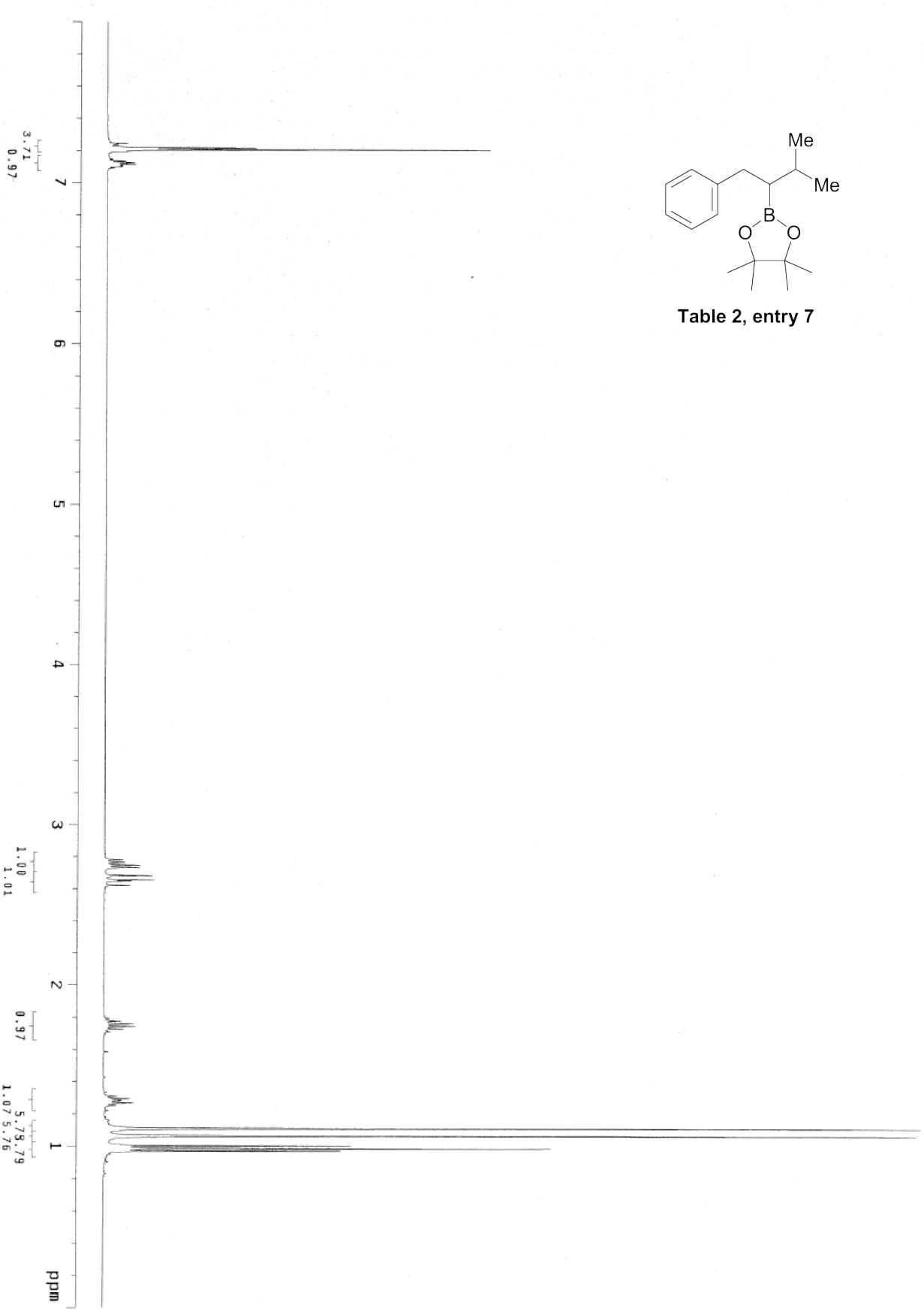
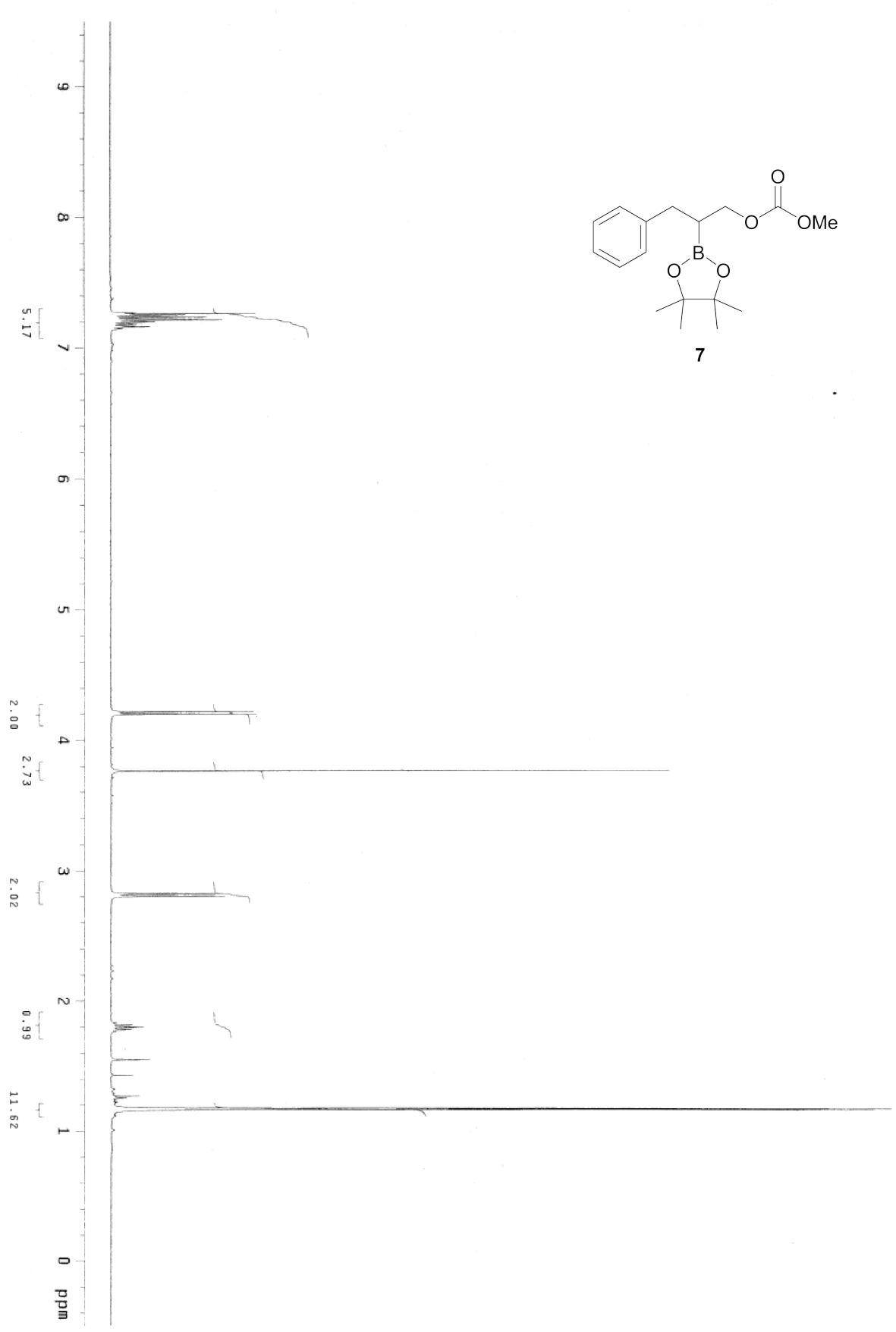
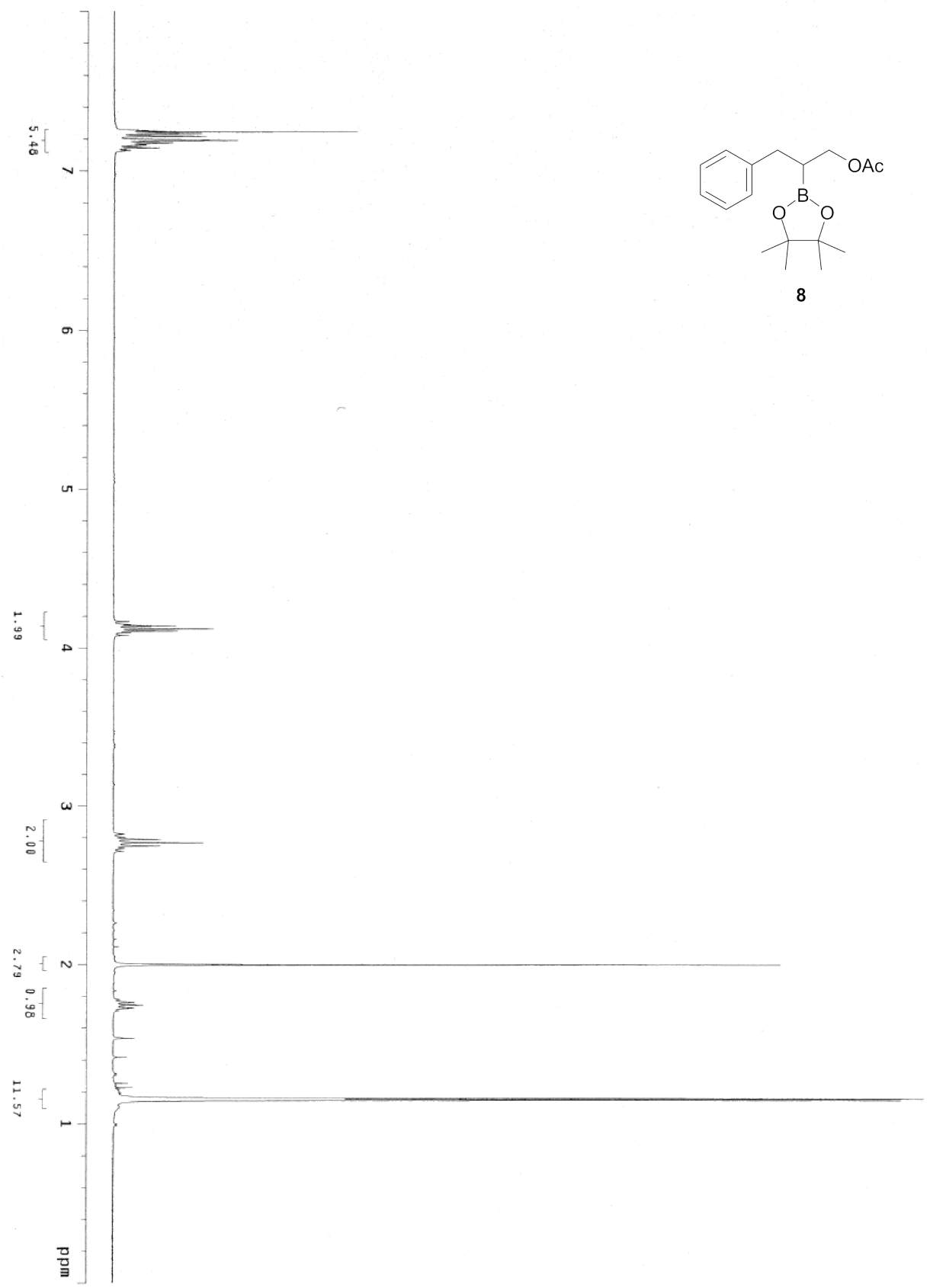


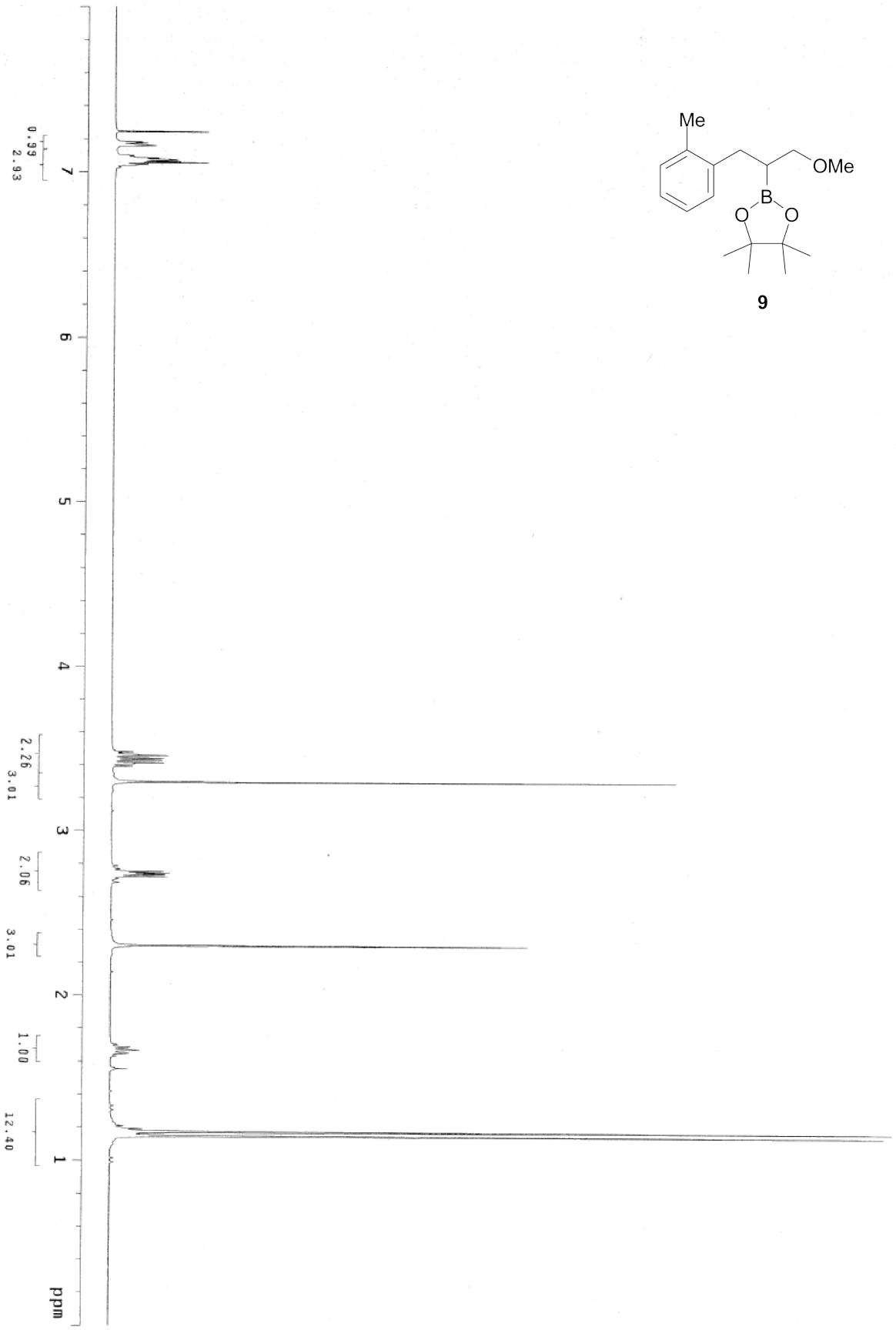
Table 2, entry 7



7



8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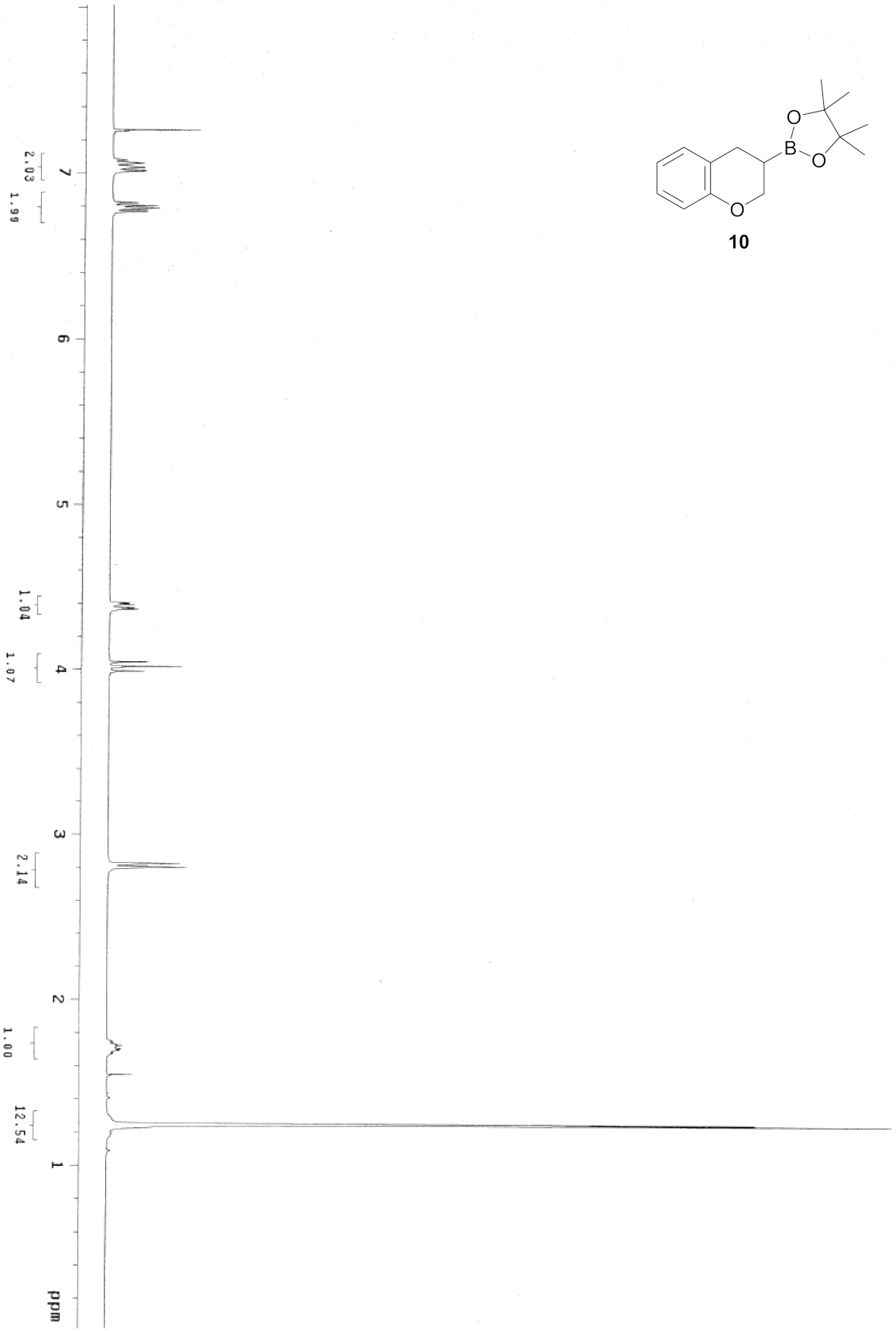
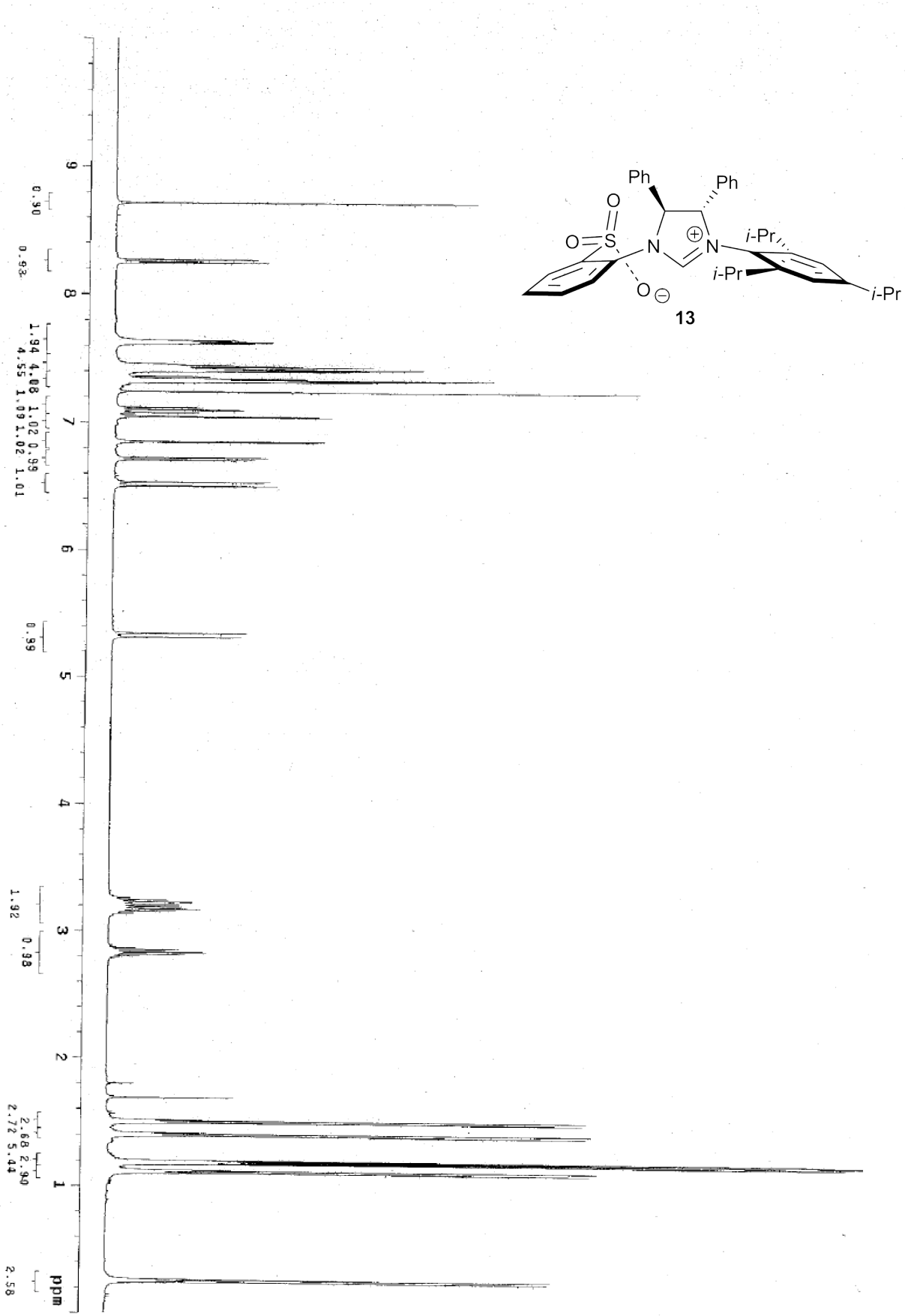
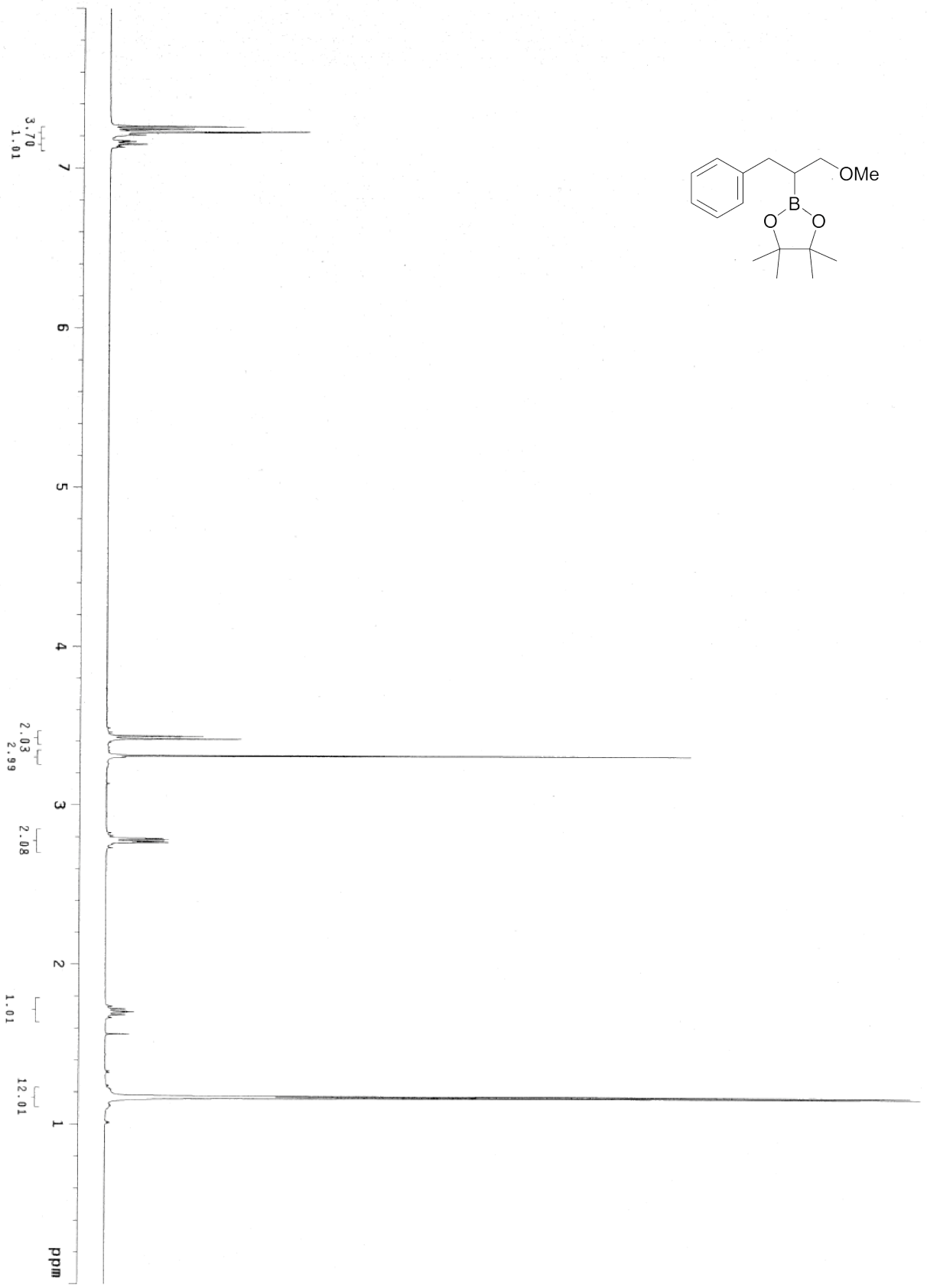
3.01
2.06
3.01
1.00
12.40
7
6
5
4
3
2
1
ppm



10

12


Ph
Ph
O
O=S
N
N
i-Pr
i-Pr
i-Pr
O
13
0.90
0.93
1.94 4.08 1.02 0.99
4.55 1.09 1.02 1.01
0.99
1.92
0.98
2.68 2.90
2.72 5.44
2.58
ppm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2.08
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12.01
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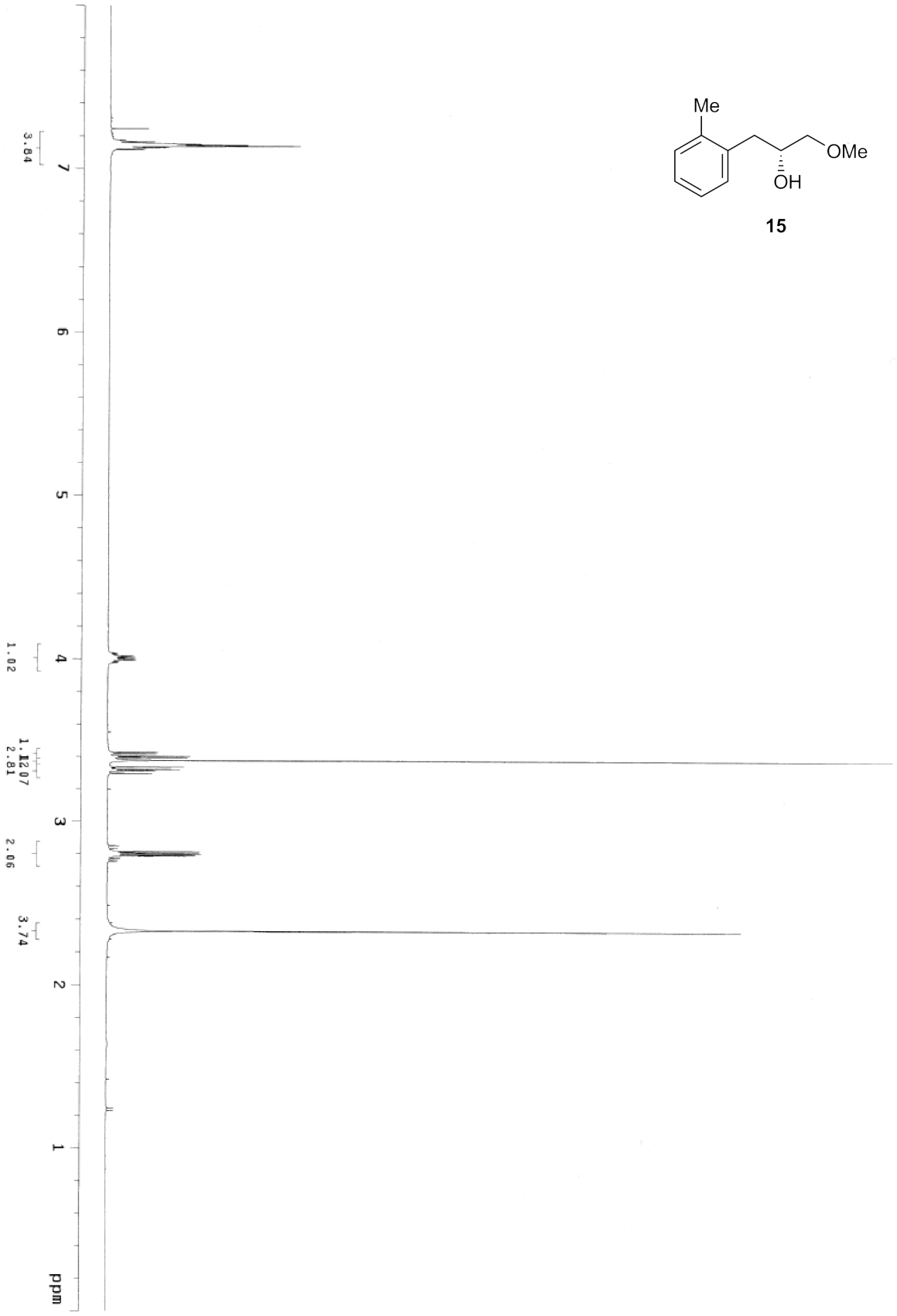
5
4
3
2
1
ppm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4
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2
1
ppm