Electronic Supplementary Material (ESI) for ChemComm.

Highly Stereoselective Syntheses of (*E*)-δ-Boryl-*anti*-homoallylic Alcohols via Allylation with α-Boryl-(*E*)-crotylboronate

*Jiaming Liu and Ming Chen**

Department of Chemistry and Biochemistry

Auburn University

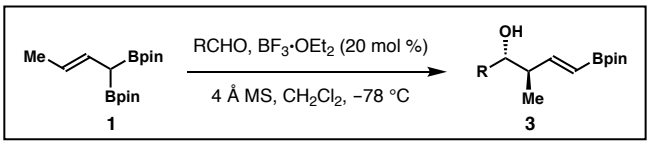
E-mail: mzc0102@auburn.edu

Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

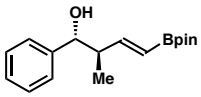
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using flame-dried or oven-dried (120 ˚C) glassware. The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 30 ˚C, followed by removal of residual solvent at high vacuum (< 0.2 mbar).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (400 and 600 MHz) at Auburn University NMR facility. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 101 and 151 MHz. The proton signal for residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry and Biochemistry, Auburn University.

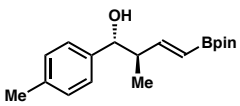
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$. Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product.



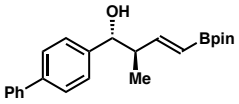
General procedure for syntheses of homoallylic alcohols 3: Allylboronate **1**[1] (40 mg, 0.13 mmol, 1.3 equiv), freshly activated 4 Å MS (50 mg), a Teflon-coated magnetic stirring bar and dichloromethane (1 mL) were sequentially added into a reaction flask. The flask was placed into a −78 °C acetone/dry ice bath. BF_3•Et_2O (20 mol %) was added to the flask *via* a microliter syringe, and the resulting mixture was stirred for 10 min at −78 °C. Then freshly distilled aldehyde (0.1 mmol, 1.0 equiv, if it is a liquid) was added, and the reaction mixture was kept stirring at −78 °C. After complete consumption of the aldehyde (3-5 h for aromatic aldehydes, 12 h for aliphatic aldehydes), saturated $NaHCO_3$ solution (1.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by column (gradient elution with hexane and ethyl acetate) to give product **3**.



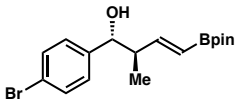
***rac*-(1*R*,2*R*,*E*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3a)** Prepared according to the general procedure to give compound **3a** in 97% yield (28 mg) as colorless oil. ^{1}H NMR (600 MHz, CDCl3) δ 7.26 – 7.35 (m, 5H), 6.62 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.62 (d, *J* = 18.0 Hz, 1H), 4.37 (d, *J* = 8.5 Hz, 1H), 2.51 – 2.57 (m, 1H), 2.23 (brs, 1H), 1.27 (s, 12H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 142.5, 128.6, 128.1, 127.3, 121.2, 83.6, 78.1, 48.6, 25.1, 16.7. HRMS (ESI^+): m/z for $C_{17}H_{25}BO_3Na$ $[M+Na]^+$ calcd. 311.1794, found: 311.1805.



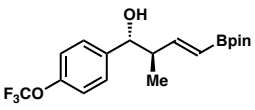
***rac*-(1*R*,2*R*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)but-3-en-1-ol (3b)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3b** in 89% yield (27 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.62 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.62 (d, *J* = 18.0 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 2.50 – 2.56 (m, 1H), 2.34 (s, 3H), 2.08 (s, 1H), 1.28 (s, 12H), 0.81 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 139.5, 137.8, 129.3, 127.2, 83.6, 78.0, 48.6, 25.14, 25.13, 21.5, 16.8. HRMS (ESI^+): m/z for $C_{18}H_{27}BO_3Na$ $[M+Na]^+$ calcd. 325.1951, found: 325.1959.



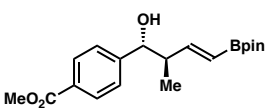
***rac*-(1*R*,2*R*,*E*)-1-([1,1'-biphenyl]-4-yl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3c)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3c** in 96% yield (35 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.64 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.66 (d, *J* = 18.0 Hz, 1H), 4.42 (d, *J* = 8.2 Hz, 1H), 2.56 – 2.62 (m, 1H), 2.16 (d, *J* = 1.9 Hz, 1H), 1.29 (s, 12H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 141.5, 141.1, 140.9, 129.1, 127.7, 127.6, 127.41, 127.39, 83.6, 77.9, 48.7, 25.1, 16.8. HRMS (ESI^+): m/z for $C_{23}H_{29}BO_3Na$ $[M+Na]^+$ calcd. 387.2107, found: 387.2092.



***rac*-(1*R*,2*R*,*E*)-1-(4-Bromophenyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3d)** Prepared according to the general procedure. The crude mixture was purified by column to give compound **3d** in 71% yield (26 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.56 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.61 (d, *J* = 18.0 Hz, 1H), 4.35 (d, *J* = 8.3 Hz, 1H), 2.46 – 2.52 (m, 1H), 1.74 (brs, 1H), 1.28 (s, 12H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 141.4, 131.7, 129.0, 121.9, 83.7, 77.4, 48.7, 25.1, 16.5. HRMS (ESI^+): m/z for $C_{17}H_{24}BO_3NaBr$ $[M+Na]^+$ calcd. 389.0900, found: 389.0903; $[M+2+Na]^+$ found: 391.0882.

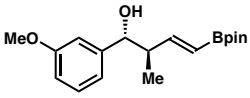


***rac*-(1*R*,2*R*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethoxy)phenyl)but-3-en-1-ol (3e)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3e** in 94% yield (35 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.57 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.63 (d, *J* = 18.0 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 2.47 – 2.53 (m, 1H), 2.20 (s, 1H), 1.28 (s, 12H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 148.9, 141.1, 128.7, 121.9, 121.2, 120.7 (q, *J* = 257 Hz), 83.7, 77.3, 48.8, 25.1, 16.6. HRMS (ESI^+): m/z for $C_{18}H_{24}BO_4F_3Na$ $[M+Na]^+$ calcd. 395.1617, found: 395.1614. ^{19}F NMR (471 MHz, $CDCl_3$) δ − 57.87.

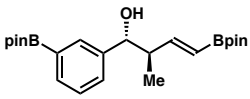


***rac*-Methyl-4-((1*R*,2*R*,*E*)-1-hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)benzoate (3f)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3f** in 78% yield (27 mg) as

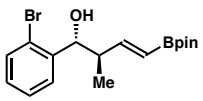
colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 6.56 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.61 (d, *J* = 18.0 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 2.50 – 2.56 (m, 1H), 2.25 (s, 1H), 1.28 (s, 12H), 0.83 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 155.2, 147.6, 129.9, 129.7, 127.3, 121.9, 83.7, 77.6, 52.5, 48.6, 25.1, 16.5. HRMS (ESI$^+$): m/z for $C_{19}H_{27}BO_5Na$ $[M+Na]^+$ calcd. 369.1849, found: 369.1835.



***rac*-(1*R*,2*R*,*E*)-1-(3-methoxyphenyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3g)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3g** in 75% yield (24 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.26 (m, 1H), 6.87 – 6.91 (m, 2H), 6.82 (dd, , *J* = 8.2, 1.7 Hz, 1H), 6.61 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.62 (d, *J* = 18.0 Hz, 1H), 4.35 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.51 – 2.57 (m, 1H), 2.12 (brs, 1H), 1.28 (s, 12H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 156.0, 144.1, 129.6, 119.7, 113.7, 112.4, 83.6, 78.1, 55.6, 48.5, 25.1, 16.7. HRMS (EI$^+$): m/z for $C_{18}H_{27}BO_4$ $[M]^+$ calcd. 318.2002, found: 318.2008.

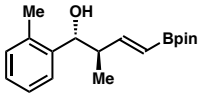


***rac*-(1*R*,2*R*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-1-ol (3h)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3h** in 87% yield (36 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.61 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.63 (d, *J* = 18.0 Hz, 1H), 4.38 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.56 – 2.62 (m, 1H), 2.10 (d, *J* = 2.3 Hz, 1H), 1.34 (s, 12H), 1.28 (s, 12H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 141.8, 134.7, 133.6, 130.3, 128.2, 84.2, 83.6, 78.2, 48.6, 25.21, 25.17, 25.14, 16.9. HRMS (ESI$^+$): m/z for $C_{23}H_{36}B_2O_5Na$ $[M+Na]^+$ calcd. 437.2647, found: 437.2667.

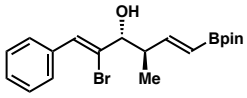


***rac*-(1*R*,2*R*,*E*)-1-(2-Bromophenyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3i)** Prepared according to the general procedure. The crude mixture was purified by column to give compound **3i** in 93% yield (34 mg) as colorless oil^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.33 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.12 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.65 (dd, *J* = 18.0, 7.8 Hz, 1H), 5.57 (d, *J* = 18.0 Hz, 1H), 4.97 (dd, *J* = 7.3,

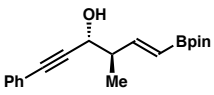
2.9 Hz, 1H), 2.60 – 2.66 (m, 1H), 2.23 (d, *J* = 2.7 Hz, 1H), 1.27 (s, 12H), 0.97 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 141.8, 132.8, 129.3, 128.7, 128.0, 123.5, 121.4, 83.6, 75.7, 47.9, 25.11, 25.10, 16.5. HRMS (ESI^+): m/z for $C_{17}H_{24}BO_3NaBr$ $[M+Na]^+$ calcd. 389.0900, found: 389.0897; $[M+2+Na]^+$ found: 391.0895.



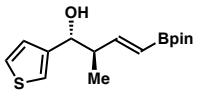
***rac*-(1*R*,2*R*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*o*-tolyl)but-3-en-1-ol (3j)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3j** in 83% yield (25 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.17 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.67 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.64 (d, *J* = 18.0 Hz, 1H), 4.72 (dd, *J* = 8.5, 1.9 Hz, 1H), 2.59 – 2.65 (m, 1H), 2.35 (s, 3H), 2.02 (d, *J* = 2.1 Hz, 1H), 1.28 (s, 12H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 140.7, 135.9, 130.6, 127.7, 126.7, 126.6, 121.4, 83.6, 73.5, 48.5, 25.1, 20.0, 16.5. HRMS (ESI^+): m/z for $C_{18}H_{27}BO_3Na$ $[M+Na]^+$ calcd. 325.1951, found: 325.1964.



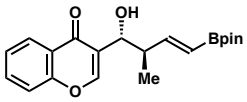
***rac*-(1*Z*,3*R*,4*R*,5*E*)-2-Bromo-4-methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dien-3-ol (3k)** Prepared according to the general procedure. The crude mixture was purified to give compound **3k** in 84% yield (33 mg) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.32 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.02 (s, 1H), 6.64 (dd, *J* = 18.0, 7.9 Hz, 1H), 5.64 (d, *J* = 18.0 Hz, 1H), 3.97 (dd, *J* = 8.3, 5.4 Hz, 1H), 2.69 – 2.75 (m, 1H), 2.13 (d, *J* = 5.3 Hz, 1H), 1.28 (s, 12H), 1.02 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 135.2, 130.6, 129.5, 128.6, 128.52, 128.49, 121.5, 83.6, 81.2, 45.0, 25.1, 16.7. HRMS (ESI^+): m/z for $C_{19}H_{26}BO_3NaBr$ $[M+Na]^+$ calcd. 415.1056, found: 415.1045; $[M+2+Na]^+$ found: 417.1033.



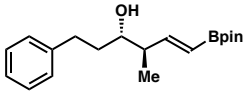
***rac*-(3*R*,4*R*,*E*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yn-3-ol (3l)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3l** in 90% yield (28 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.44 (m, 2H), 7.30 – 7.35 (m, 3H), 6.63 (dd, *J* = 18.1, 7.3 Hz, 1H), 5.62 (d, *J* = 18.1 Hz, 1H), 4.48 (dd, *J* = 6.0, 6.0 Hz, 1H), 2.59 – 2.67 (m, 1H), 1.98 (d, *J* = 5.4 Hz, 1H), 1.28 (s, 12H), 1.22 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 132.1, 128.8, 128.6, 123.0, 88.7, 86.4, 83.6, 66.8, 46.8, 25.2, 25.1, 15.6. HRMS (ESI^+): m/z for $C_{19}H_{25}BO_3Na$ $[M+Na]^+$ calcd. 335.1794, found: 335.1779.



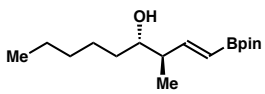
***rac*-(1*R*,2*R*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-3-yl)but-3-en-1-ol (3m)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3m** in 75% yield (22 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.61 (dd, *J* = 18.0, 7.8 Hz, 1H), 5.61 (d, *J* = 18.0 Hz, 1H), 4.55 (dd, *J* = 7.9, 2.6 Hz, 1H), 2.56 – 2.62 (m, 1H), 2.04 (d, *J* = 3.0 Hz, 1H), 1.28 (s, 12H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 144.1, 126.3, 126.2, 122.2, 83.6, 74.2, 47.9, 25.2, 16.5. HRMS (EI^+): m/z for $C_{15}H_{23}BO_3S$ $[M]^+$ calcd. 294.1461, found: 294.1455.



***rac*-3-((1*R*,2*R*,*E*)-1-Hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-4*H*-chromen-4-one (3n)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3n** in 98% yield (35 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.87 (s, 1H), 7.69 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.68 (dd, *J* = 18.1, 7.4 Hz, 1H), 5.54 (d, *J* = 18.1 Hz, 1H), 4.46 (dd, *J* = 7.3, 7.3 Hz, 1H), 3.43 (d, *J* = 7.5 Hz, 1H), 2.84 – 2.89 (m, 1H), 1.26 (s, 12H), 1.02 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 156.4, 155.2, 153.7, 134.2, 126.0, 125.6, 124.2, 124.1, 120.7, 118.5, 83.5, 73.3, 45.3, 25.13, 25.08, 17.1. HRMS (ESI^+): m/z for $C_{20}H_{25}BO_5Na$ $[M+Na]^+$ calcd. 379.1693, found: 379.1676

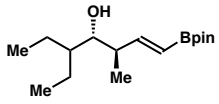


***rac*-(3*S*,4*R*,*E*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-ol (3o)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **3o** in 79% yield (25 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.29 (m, 2H), 7.17 – 7.21 (m, 3H), 6.53 (dd, *J* = 18.0, 7.9 Hz, 1H), 5.52 (d, *J* = 18.0 Hz, 1H), 3.45 – 3.48 (m, 1H), 2.82 – 2.86 (m, 1H), 2.64 – 2.69 (m, 1H), 2.29 – 2.34 (m, 1H), 1.80 – 1.85 (m, 1H), 1.66 – 1.73 (m, 1H), 1.57 (d, *J* = 4.4 Hz, 1H), 1.27 (s, 12H), 1.03 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 142.5, 128.8, 128.7, 126.1, 83.6, 74.2, 46.5, 36.3, 32.5, 25.14, 25.10, 16.1. HRMS (EI^+): m/z for $C_{19}H_{27}BO_2$ $[M–H_2O]^+$ calcd. 298.2104, found: 298.2116.

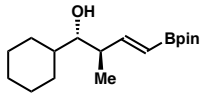


***rac*-(3*R*,4*S*,*E*)-3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-1-en-4-ol (3p)** Prepared according to the general

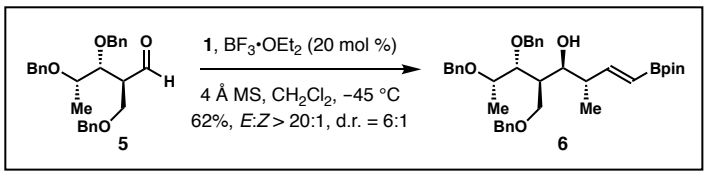
procedure. The crude mixture was purified by flash column chromatography to give compound **3p** in 81% yield (23 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.55 (dd, *J* = 18.1, 7.8 Hz, 1H), 5.51 (d, *J* = 18.1 Hz, 1H), 3.43 – 3.46 (m, 1H), 2.27 – 2.32 (m, 1H), 1.44 – 1.52 (m, 3H), 1.27 – 1.39 (m, 18H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 120.7, 83.5, 75.0, 46.2, 34.4, 32.2, 25.8, 25.2, 25.1, 23.0, 16.1, 14.5. HRMS (EI^+): m/z for $C_{16}H_{29}BO_2$ $[M–H_2O]^+$ calcd. 264.2261, found: 264.2256.



***rac*-(3*R*,4*S*,*E*)-5-Ethyl-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-4-ol (3q)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3q** in 81% yield (23 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.53 (d, *J* = 18.0 Hz, 1H), 3.36 – 3.39 (m, 1H), 2.41 – 2.47 (m, 1H), 1.51 – 1.55 (m, 1H), 1.42 – 1.48 (m, 1H), 1.36 – 1.40 (m, 1H), 1.34 (d, *J* = 4.8 Hz, 1H), 1.27 (s, 12H), 1.22 – 1.26 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.86 – 0.90 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 83.5, 75.6, 43.6, 42.9, 25.14, 25.11, 22.4, 20.4, 17.0, 12.0, 11.6. HRMS (EI^+): m/z for $C_{16}H_{29}BO_2$ $[M–H_2O]^+$ calcd. 264.2261, found: 264.2257.

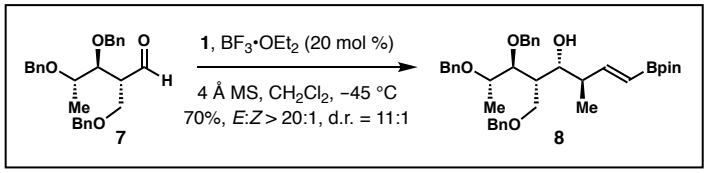


***rac*-(1*S*,2*R*,*E*)-1-Cyclohexyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3r)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3r** in 95% yield (28 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 18.1, 8.0 Hz, 1H), 5.51 (d, *J* = 18.1 Hz, 1H), 3.12 – 3.15 (m, 1H), 2.43 – 2.47 (m, 1H), 1.70 – 1.81 (m, 3H), 1.60 – 1.65 (m, 2H), 1.37 – 1.43 (m, 2H), 1.09 – 1.26 (m, 16H), 1.01 – 1.07 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 120.7, 83.5, 79.3, 42.7, 40.5, 30.3, 27.3, 26.8, 26.7, 26.4, 25.2, 25.1, 17.0. HRMS (EI^+): m/z for $C_{17}H_{29}BO_2$ $[M–H_2O]^+$ calcd. 276.2261, found: 276.2250.

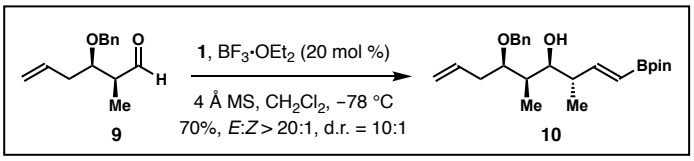


Synthesis of homoallylic alcohol 6: Prepared according to the general procedure from aldehyde **5** at −45 °C for about 12 h. The crude mixture was purified by flash column

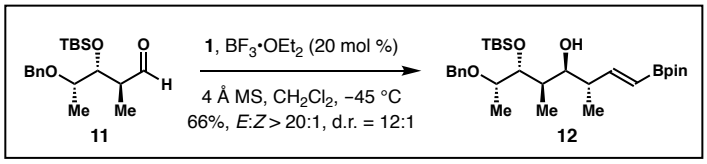
chromatography to give compound **6** in 62% yield (37 mg, *E*:*Z* > 20:1, dr = 6:1) as a colorless oil. $[\alpha]_D^{20}$ = − 0.04 (c 1.35, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.34 (m, 13H), 7.19 – 7.21 (m, 2H), 6.67 (dd, *J* = 18.0, 7.6 Hz, 1H), 5.48 (d, *J* = 18.1, 1H), 4.83 (d, J_{AB} = 11.0 Hz, 1H), 4.63 (d, J_{AB} = 11.6 Hz, 1H), 4.53 (d, J_{AB} = 11.6 Hz, 1H), 4.49 (d, J_{AB} = 10.9 Hz, 1H), 4.45 (d, J_{AB} = 11.9 Hz, 1H), 4.36 (d, J_{AB} = 12.1 Hz, 1H), 3.94 (dd, *J* = 7.1, 3.5 Hz, 1H), 3.77 – 3.81 (m, 1H), 3.74 (app. d, *J* = 8.9 Hz, 1H), 3.69 (d, *J* = 2.4 Hz, 1H), 3.67 (dd, *J* = 9.7, 7.9 Hz, 1H), 3.63 (dd, *J* = 9.7, 4.3 Hz, 1H), 2.36 – 2.42 (m, 1H), 2.05 – 2.08 (m, 1H), 1.24 (s, 12H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 138.9, 138.7, 138.4, 128.8, 128.73, 128.72, 128.4, 128.22, 128.20, 128.1, 128.0, 127.9, 83.5, 83.3, 77.6 (assigned via DEPT 135), 76.2, 74.3, 73.6, 72.1, 67.0, 43.7, 41.3, 25.2, 17.0, 16.8. HRMS (ESI^+): m/z for $C_{37}H_{49}BO_6Na$ $[M+Na]^+$ calcd. 623.3520, found: 623.3494.



Synthesis of homoallylic alcohol 8: Prepared according to the general procedure from aldehyde **7** at −45 °C for about 12 h. The crude mixture was purified by flash column chromatography to give compound **8** in 70% yield (42 mg, *E*:*Z* > 20:1, dr = 11:1) as a colorless oil. $[\alpha]_D^{20}$ = + 0.3 (c 2.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.34 (m, 8H), 7.24 – 7.30 (m, 7H), 6.67 (dd, *J* = 18.0, 7.8 Hz, 1H), 5.47 (d, *J* = 18.0 Hz, 1H), 4.67 (d, J_{AB} = 11.0 Hz, 1H), 4.61 (d, J_{AB} = 11.7 Hz, 1H), 4.47 – 4.50 (m, 2H), 4.45 (d, J_{AB} = 11.7 Hz, 1H), 4.39 (d, J_{AB} = 11.8 Hz, 1H), 3.94 (dd, *J* = 5.6, 4.0 Hz, 1H), 3.91 – 3.93 (m, 1H), 3.73 – 3.77 (m, 1H), 3.64 – 3.71 (m, 2H), 3.34 (d, *J* = 2.6 Hz, 1H), 2.35 – 2.41 (m, 1H), 2.21–2.24 (m, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.24 (s, 12H), 0.92 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 138.9, 138.5, 138.4, 128.8 (two overlapping carbon signals), 128.7, 128.3, 128.2, 128.09, 128.05, 128.0, 127.9, 83.3, 82.6, 75.6, 75.0, 74.3, 73.6, 71.0, 67.5, 43.9, 41.4, 25.2, 17.2, 16.4. HRMS (ESI^+): m/z for $C_{37}H_{49}BO_6Na$ $[M+Na]^+$ calcd. 623.3520, found: 623.3533.

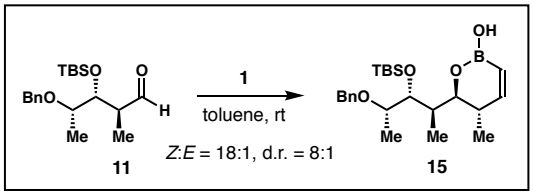


Synthesis of homoallylic alcohol 10: Prepared according to the general procedure from aldehyde **9** at −45 °C for about 12 h. The crude mixture was purified by flash column chromatography to give compound **10** in 70% yield (28 mg, *E*:*Z* > 20:1, dr = 10:1) as colorless oil. $[\alpha]_D^{20}$ = − 3.6 (c 0.15, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.28 (m, 2H), 7.21 – 7.25 (m, 3H), 6.55 (dd, *J* = 18.0, 8.0 Hz, 1H), 5.72 – 5.77 (m, 1H), 5.44 (d, *J* = 18.0 Hz, 1H), 5.07 (dd, d, *J* = 17.1, 1.5 Hz 1H), 5.02 (d, *J* = 9.6 Hz, 1H), 4.61 (d, J_{AB} = 11.3 Hz, 1H), 4.39 (d, J_{AB} = 11.3 Hz, 1H), 3.55 – 3.57 (m, 1H), 3.47 – 3.49 (m, 1H), 2.63 (d, *J* = 1.9 Hz, 1H), 2.44 – 2.47 (m, 1H), 2.31 – 2.35 (m, 1H), 2.27 – 2.31 (m, 1H), 1.76 – 1.79 (m, 1H), 1.20 (s, 12H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3, 138.5, 134.9, 128.8, 128.1, 128.0, 117.7, 83.43, 83.36, 77.5, 71.8, 44.2, 37.2, 35.7, 25.18, 25.15, 16.6, 7.0. HRMS (ESI^+): m/z for $C_{24}H_{37}BO_4Na$ $[M+Na]^+$ calcd. 423.2683, found: 423.2694.

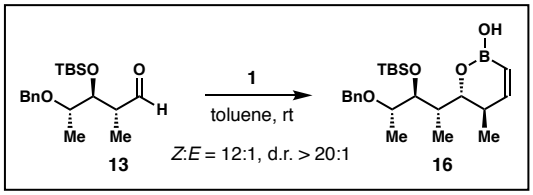


Synthesis of homoallylic alcohol 12: Prepared according to the general procedure from aldehyde **11** at −45 °C for about 12 h. The crude mixture was purified by flash column chromatography to give compound **12** in 66% yield (34 mg, *E*:*Z* > 20:1, dr = 12:1) as colorless oil. $[\alpha]_D^{20}$ = + 0.5 (c 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.34 (m, 4H), 7.27 – 7.29 (m, 1H), 6.68 (dd, *J* = 18.0, 7.5 Hz, 1H), 5.51 (d, *J* = 18.0 Hz, 1H), 4.58 (d, J_{AB} = 11.6 Hz, 1H), 4.46 (d, J_{AB} = 11.6 Hz, 1H), 3.80 (*app*. d, *J* = 8.8 Hz, 1H), 3.74 (dd, *J* = 4.9, 4.4 Hz, 1H), 3.60 – 3.64 (m, 1H), 2.93 (s, 1H), 2.31 – 2.37 (m, 1H), 1.90 – 1.95 (m, 1H), 1.26 (s, 12H), 1.22 (d, *J* = 6.2 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 138.7, 128.7, 128.1, 127.9, 83.3, 80.6, 76.7, 74.8, 71.1, 43.6, 37.2, 26.5, 25.2, 18.6, 16.6, 16.2, 10.6, −3.6, −3.7. HRMS (ESI^+): m/z for $C_{29}H_{51}BO_5NaSi$ $[M+Na]^+$ calcd. 541.3497, found: 541.3521.

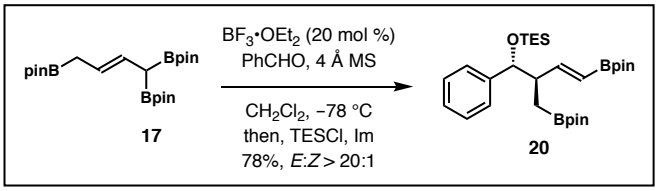
Synthesis of homoallylic alcohol 14: Prepared according to the general procedure from aldehyde **13** at −45 °C for about 12 h. The crude mixture was purified by flash column chromatography to give compound **14** in 64% yield (33 mg, *E*:*Z* > 20:1, dr > 20:1) as colorless oil. $[\alpha]_D^{20}$ = + 0.5 (c 0.70, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.36 (m, 4H), 7.27 – 7.30 (m, 1H), 6.74 (dd, *J* = 18.1, 7.3 Hz, 1H), 5.53 (dd, *J* = 18.1, 0.8 Hz, 1H), 4.59 (d, J_{AB} = 11.9 Hz, 1H), 4.50 (d, J_{AB} = 11.9 Hz, 1H), 3.72 – 3.74 (m, 2H), 3.64 – 3.69 (m, 1H), 3.55 (s, 1H), 2.33 – 2.39 (m, 1H), 1.90 – 1.93 (m, 1H), 1.27 (s, 12H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.05 (d, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.08 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 139.2, 128.6, 127.9, 127.7, 83.3, 81.7, 78.4, 74.9, 71.3, 43.3, 35.1, 26.5, 25.2, 18.7, 16.4, 15.9, 11.6, –3.7, –4.4. HRMS (ESI^+): m/z for $C_{29}H_{51}BO_5NaSi$ $[M+Na]^+$ calcd. 541.3497, found: 541.3513.



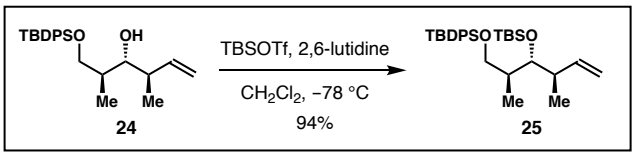
Synthesis of vinyl boronate 15: To a solution of aldehyde **11** (34 mg, 0.1 mmol, 1.0 equiv) in toluene (0.3 mL) was added allylic boronate **1** (40 mg, 0.13 mmol, 1.3 equiv). The reaction mixture was kept stirring at ambient temperature (~12 h). After complete consumption of aldehyde **11**, Et_2O (2 mL) was added and the resulting mixture was filtered through a pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate) to give product **15** (37 mg, 88% yield, *Z*:*E* = 18:1, dr = 8:1). $[\alpha]_D^{20}$ = + 1.0 (c 1.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.36 (m, 4H), 7.25 – 7.28 (m, 1H), 6.68 (dd, *J* = 12.0, 1.6 Hz, 1H), 5.62 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.55 (d, J_{AB} = 12.3 Hz, 1H), 4.52 (d, J_{AB} = 12.2 Hz, 1H), 4.16 (dd, *J* = 10.7, 1.8 Hz, 1H), 3.96 (dd, *J* = 9.3, 1.6 Hz, 1H), 3.81 (s, 1H), 3.61 (qd, *J* = 6.3, 1.6 Hz, 1H), 2.39 – 2.45 (m, 1H), 1.53 – 1.59 (m, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.87 (s, 9H), 0.78 (d, *J* = 6.9 Hz, 3H), 0.08 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 139.4, 128.6, 128.0, 127.6, 78.0, 76.6, 74.6, 70.8, 38.8, 34.7, 26.6, 18.9, 17.7, 13.0, 10.2, −3.2, −4.7. HRMS (ESI^+): m/z for $C_{23}H_{39}BO_4NaSi$ $[M+Na]^+$ calcd. 441.2608, found: 441.2591.



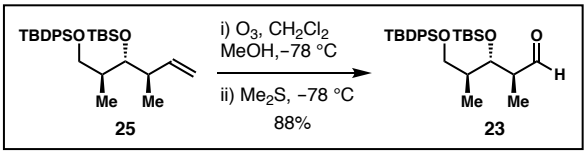
Synthesis of vinyl boronate 16: To a solution of aldehyde **13** (34 mg, 0.1 mmol, 1.0 equiv) in toluene (0.3 mL), was added allylic boronate **1** (40 mg, 0.13 mmol, 1.3 equiv). The reaction mixture was kept stirring at ambient temperature (~12 h). After complete consumption of aldehyde **13**, Et_2O (2 mL) was added and the resulting mixture was filtered through a pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate) to give product **16** (33 mg, 79% yield, *Z*:*E* = 12:1, dr > 20:1) as a colorless oil. $[\alpha]_D^{20} = -1.6$ (c 0.50, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.35 (m, 4H), 7.26 – 7.28 (m, 1H), 6.69 (dd, *J* = 12.1, 1.3 Hz, 1H), 5.61 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.59 (d, J_{AB} = 12.0 Hz, 1H), 4.57 (d, J_{AB} = 12.0 Hz, 1H), 4.04 (dd, *J* = 11.0, 1.6 Hz, 1H), 3.90 (dd, *J* = 9.4, 2.9 Hz, 1H), 3.79 (s, 1H), 3.65 (qd, *J* = 6.5, 2.9 Hz, 1H), 2.44 – 2.50 (m, 1H), 1.81 – 1.86 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 7.2 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 139.4, 128.6, 127.73, 127.68, 78.5, 78.4, 72.5, 71.1, 37.4, 34.5, 26.3, 18.5, 17.7, 14.1, 9.4, −3.9, −4.2. HRMS (ESI^+): m/z for $C_{23}H_{39}BO_4NaSi$ $[M+Na]^+$ calcd. 441.2608, found: 441.2588.



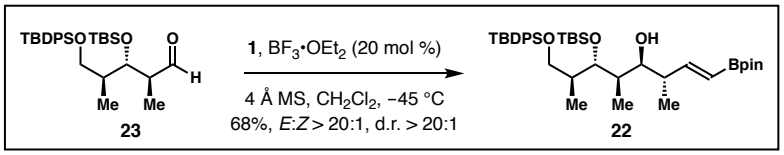
Triethyl(((1*S*,2*S*,*E*)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) but-3-en-1-yl)oxy)silane Prepared according to the general procedure from allylboron reagent **17**.[2] The crude mixture was purified by flash column chromatography to give compound **20** in 78% yield (41 mg, *E*:*Z* > 20:1) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.29 (m, 4H), 7.20 – 7.23 (m, 1H), 6.65 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 4.48 (d, *J* = 6.8 Hz, 1H), 2.63 – 2.68 (m, 1H), 1.26 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.69 – 0.77 (m, 2H), 0.42 – 0.52 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 144.1, 127.9, 127.4, 127.2, 83.2, 83.1, 79.5, 50.3, 25.3, 25.04, 24.97, 24.90, 7.2, 5.1. HRMS (ESI^+): m/z for $C_{29}H_{50}B_2O_5NaSi$ $[M+Na]^+$ calcd. 551.3511, found: 551.3522.



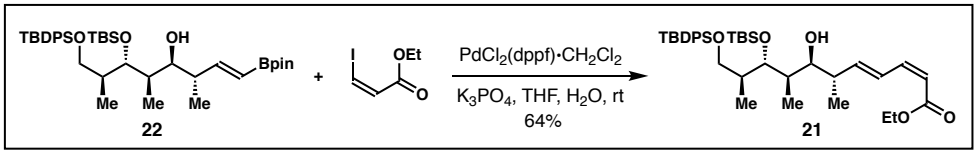
Synthesis of TBS ether 25: A 25-mL, pear-shaped flask equipped with a stir bar and rubber septum was charged with alcohol **24**[3] (191 mg, 0.5 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (10 mL). The solution was cooled to −78 °C, and 2,6-lutidine (134 mg, 1.25 mmol, 2.5 equiv) was added under an argon atmosphere. After stirring for 10 min, TBSOTf (264 mg, 1.0 mmol, 2.0 equiv) was added via a microliter syringe. The reaction mixture was kept stirring at –78 °C for 1 h. After complete consumption of alcohol **24**, Et_2O (5 mL) was added and the resulting mixture was filtered through a pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (*n*-hexane/ethyl acetate) to give TBS ether **25** (234 mg, 94% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.66 (m, 4H), 7.39 – 7.42 (m, 2H), 7.35 – 7.38 (m, 4H), 5.84 – 5.90 (m, 1H), 4.88 – 4.91 (m, 2H), 3.76 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.55 (dd, *J* = 5.6, 3.3 Hz, 1H), 3.42 (dd, *J* = 9.9, 7.9 Hz, 1H), 2.32 – 2.37 (m, 1H), 1.90 – 1.97 (m, 1H), 1.06 (s, 9H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.82 (s, 9H), 0.00 (s, 3H), –0.10 (s, 3H).



Synthesis of aldehyde 23: A stream of ozone in air was bubbled through a solution (initially light red, with Sudan III as the indicator) of TBS ether **25** (149 mg, 0.3 mmol) in dichloromethane (4 mL) and MeOH (1 mL) at −78 °C until the light red solution became colorless. The solution was bubbled with nitrogen for 5 min to remove any excess ozone, and then Me_2S (5 mL) was added at −78 °C. The reaction was allowed to warm to ambient temperature and stirred for 5 h. The reaction mixture was filtrated through a pad of Celite. The solution was concentrated under reduced pressure. Purification of the crude product was performed by column chromatography (*n*-hexane/ethyl acetate) to provide aldehyde **23** (132 mg, 88% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (d, *J* = 2.6 Hz, 1H), 7.64 – 7.66 (m, 4H), 7.41 – 7.45 (m, 2H), 7.37 – 7.40 (m, 4H), 4.05 (dd, *J* = 4.9, 3.5 Hz, 1H), 3.68 (dd, *J* = 10.2, 7.3 Hz, 1H), 3.52 (dd, *J* = 10.3, 6.5 Hz, 1H), 2.52 – 2.57 (m, 1H), 2.01 – 2.07 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.07 (s, 9H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.85 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H).



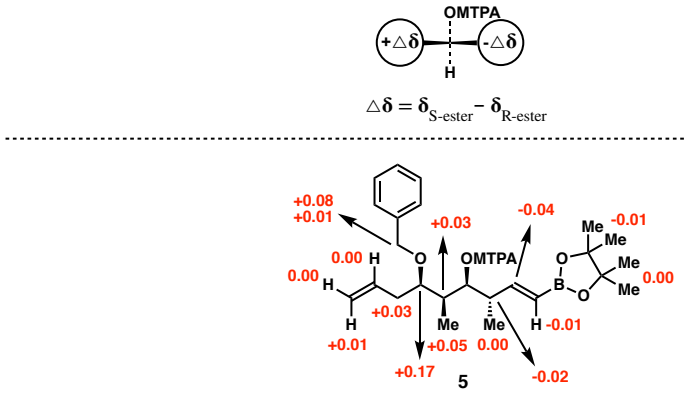
Synthesis of vinyl boronate 22: Prepared according to the general procedure from aldehyde **23** at −45 °C for about 12 h. The crude mixture was purified by flash column chromatography to give compound **22** in 68% yield (46 mg, *E*:*Z* > 20:1, dr > 20:1) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.65 (m, 4H), 7.41 – 7.44 (m, 2H), 7.36 – 7.39 (m, 4H), 6.69 (dd, *J* = 18.1, 7.4 Hz, 1H), 5.50 (d, *J* = 18.1 Hz, 1H), 3.79 (d, *J* = 9.3 Hz, 2H), 3.71 (dd, *J* = 9.9, 6.3 Hz, 1H), 3.45 (dd, *J* = 9.9, 7.4 Hz, 1H), 3.29 (s, 1H), 2.26 – 2.33 (m, 1H), 2.07 – 2.15 (m, 1H), 1.81 – 1.85 (m, 1H), 1.25 (s, 12H), 1.06 (s, 9H), 0.97 (d, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.81 (s, 9H), 0.06 (s, 3H), –0.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 136.0 (two overlapping carbon signals), 134.1, 134.0, 130.02, 129.96, 128.02, 127.99, 83.3, 80.3, 74.9, 66.7, 43.4, 41.0, 35.0, 27.3, 26.5, 25.21, 25.18, 19.6, 18.5, 16.6, 13.9, 12.3, –3.5, –4.0. HRMS (ESI^+): m/z for $C_{39}H_{66}BO_5Si_2$ $[M+H]^+$ calcd. 681.4542, found: 681.4532.



Synthesis of compound 21: In an Ar-filled glove box, $PdCl_2(dppf)\cdot CH_2Cl_2$ (4 mg, 0.005 mmol, 10 mol %), K_3PO_4 (28 mg, 0.13 mmol, 2.6 equiv), THF (0.5 mL), vinylboronate **22** (34 mg, 0.05 mmol, 1.0 equiv), and a Teflon-coated magnetic stirring bar were sequentially added into a 1-dram vial. The vial was sealed with a rubber septum and removed from the glove box. Then vinyl iodide (16 mg, 0.07 mmol, 1.4 equiv) and 50 µL H_2O were added to the mixture under argon. The reaction was kept stirring at ambient temperature for 48 h. After complete consumption of boronate **22**, Et_2O (2 mL) was added and the resulting mixture was filtered through a short pad of Celite. Brine (5 mL) and Et_2O (1 mL) were added to the filtrate, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography to provide product **21** in 64% yield (21 mg) as colorless oil. $[\alpha]_D^{20}$ = − 2.9 (c 1.15, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.65 (m, 4H), 7.40 – 7.44 (m, 3H), 7.35 – 7.39 (m, 4H), 6.59 (dd, *J* = 11.8, 11.3 Hz, 1H), 6.22 (dd, *J* = 15.5, 7.4 Hz, 1H), 5.56 (d, *J* = 11.4

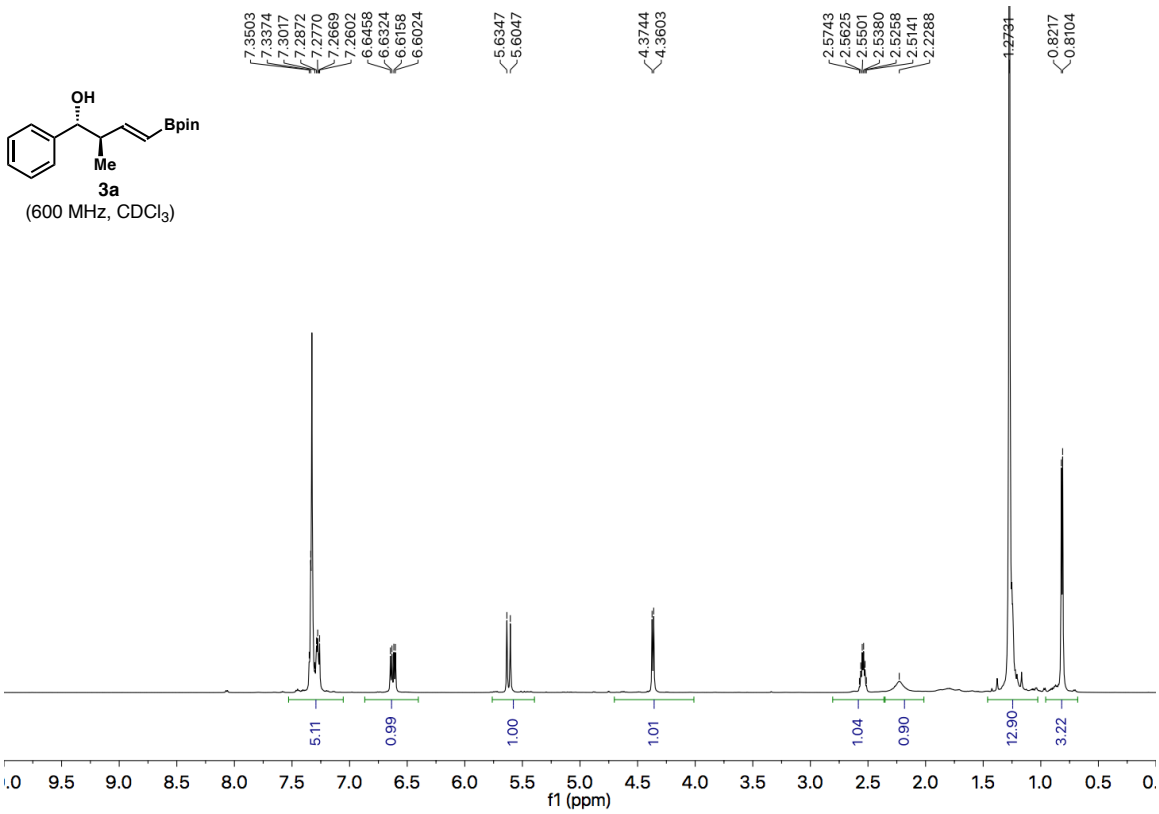
Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.81 (dd, J = 6.8, 2.5 Hz, 1H), 3.76 (dd, J = 9.2, 1.2 Hz, 1H), 3.72 (dd, J = 10.0, 6.4 Hz, 1H), 3.45 – 3.48 (m, 2H), 2.38 – 2.44 (m, 1H), 2.09 – 2.16 (m, 1H), 1.84 – 1.88 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.06 (s, 9H), 0.99 (d, J = 7.1 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.82 (s, 9H), 0.07 (s, 3H), –0.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 149.3, 145.9, 136.0 (two overlapping carbon signals), 134.01, 133.99, 130.04, 130.00, 128.02, 128.00, 126.6, 116.1, 80.5, 75.7, 66.7, 60.1, 41.0, 40.8, 35.0, 27.3, 26.4, 19.6, 18.5, 16.4, 14.7, 13.9, 12.4, –3.5, –4.0. HRMS (ESI$^+$): m/z for $C_{38}H_{61}O_5Si_2$ $[M+H]^+$ calcd. 653.4058, found: 653.4080.

Assignment of the absolute configuration of 10 using Mosher ester analysis:[4]



Reference:

1. Reagent **1** was prepared according to the reported procedure: Park, J.; Choi, S.; Lee, Y.; Cho, S. H. *Org. Lett.* **2017**, *19*, 4054.
2. Reagent **17** was prepared according to the reported procedure: Chen, J.; Chen, M. *Org. Lett.* **2020**, *22*, 7321.
3. Alcohol **24** was prepared according to the reported procedures: (a) Hale, K. J.; Dimopoulos, P.; Cheung, M. L. F.; Frigerio, M.; Steed, J. W.; Levett, P. C. *Org. Lett.* **2002**, *4*, 897. (b) Pasqua, A. E.; Ferrari, F. D.; Hamman, C.; Liu, Y.; Crawford, J. J.; Marquez, R. *J. Org. Chem.* **2012**, *77*, 6989. (c) Tokairin, Y.; Konno, H. *Tetrahedron* **2017**, *73*, 39.
4. (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc*. **1991**, *113*, 4092. (c) Hoye, T. R.; Jeffrey; C. S.; Shao, F. *Nat. Protoc.* **2007**, *2*, 2451.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4.3603
2.5743
2.5625
2.5501
2.5380
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2.5141
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0.8104
OH
Bpin
Me
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(600 MHz, CDCl3)
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1.00
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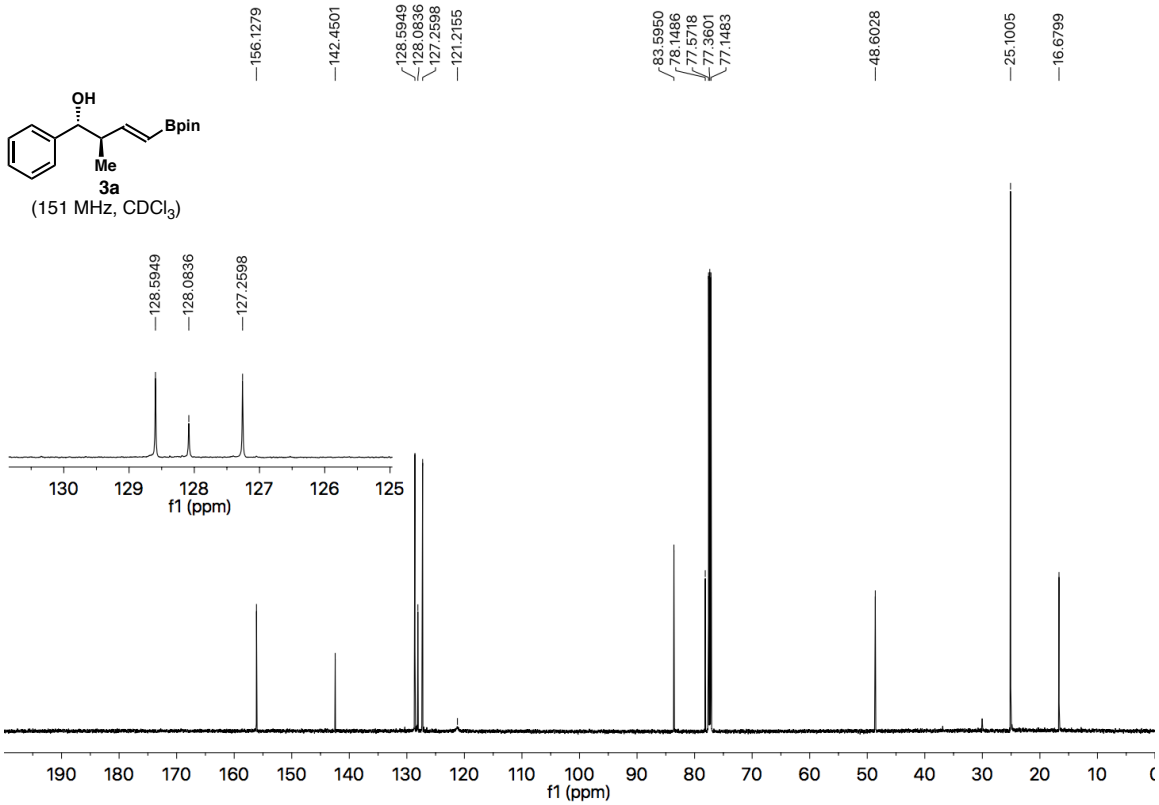
f1 (ppm)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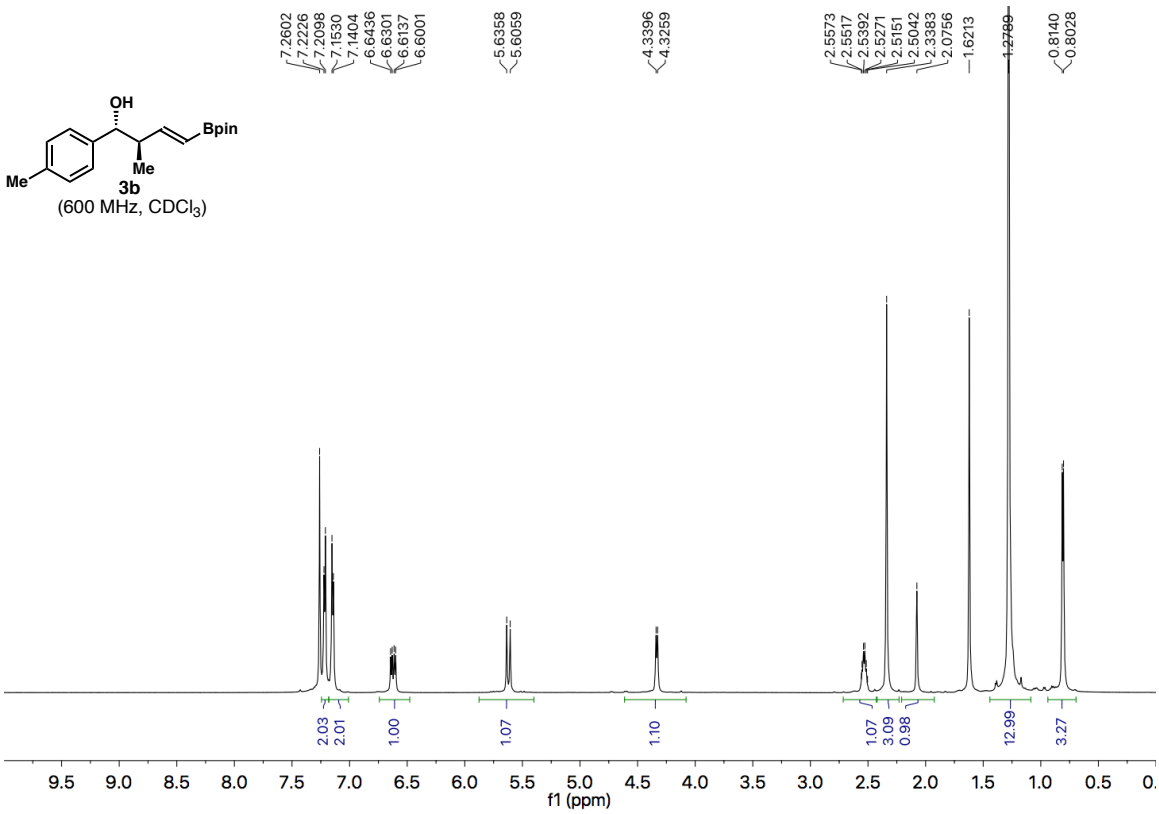
(151 MHz, CDCl3)
f1 (ppm)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Me
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3b
(600 MHz, CDCl3)
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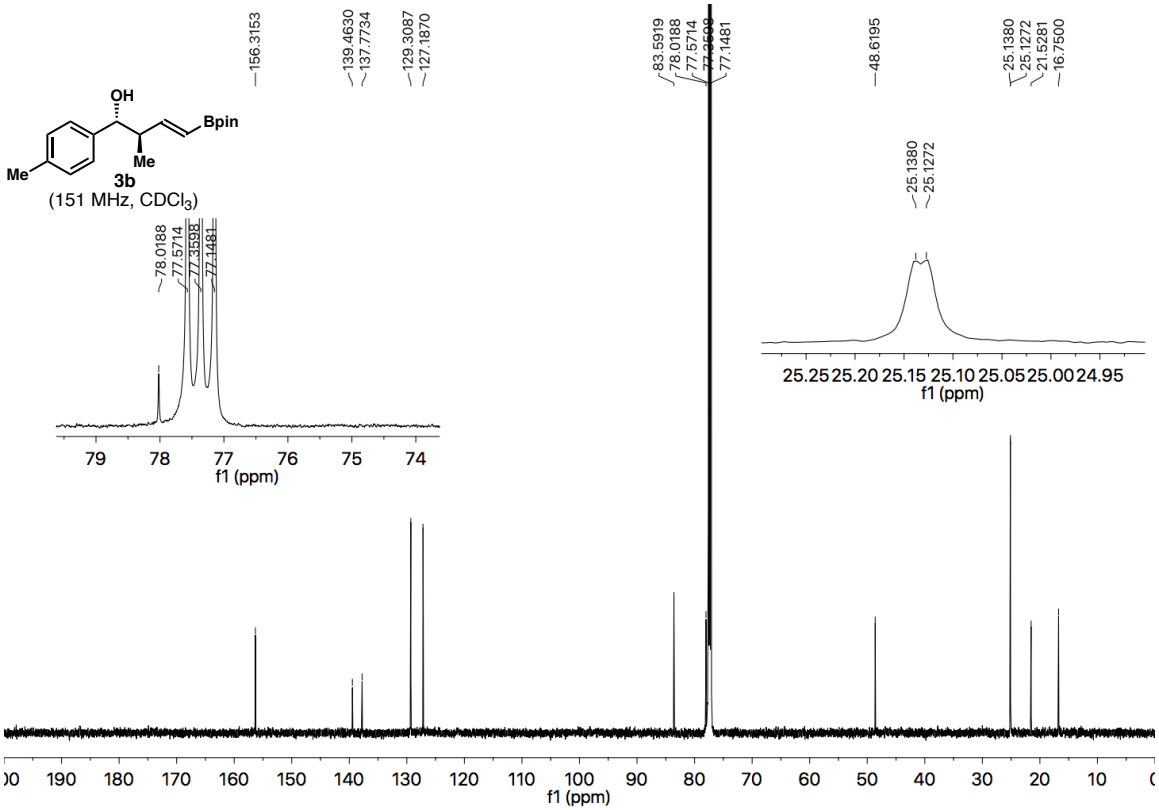
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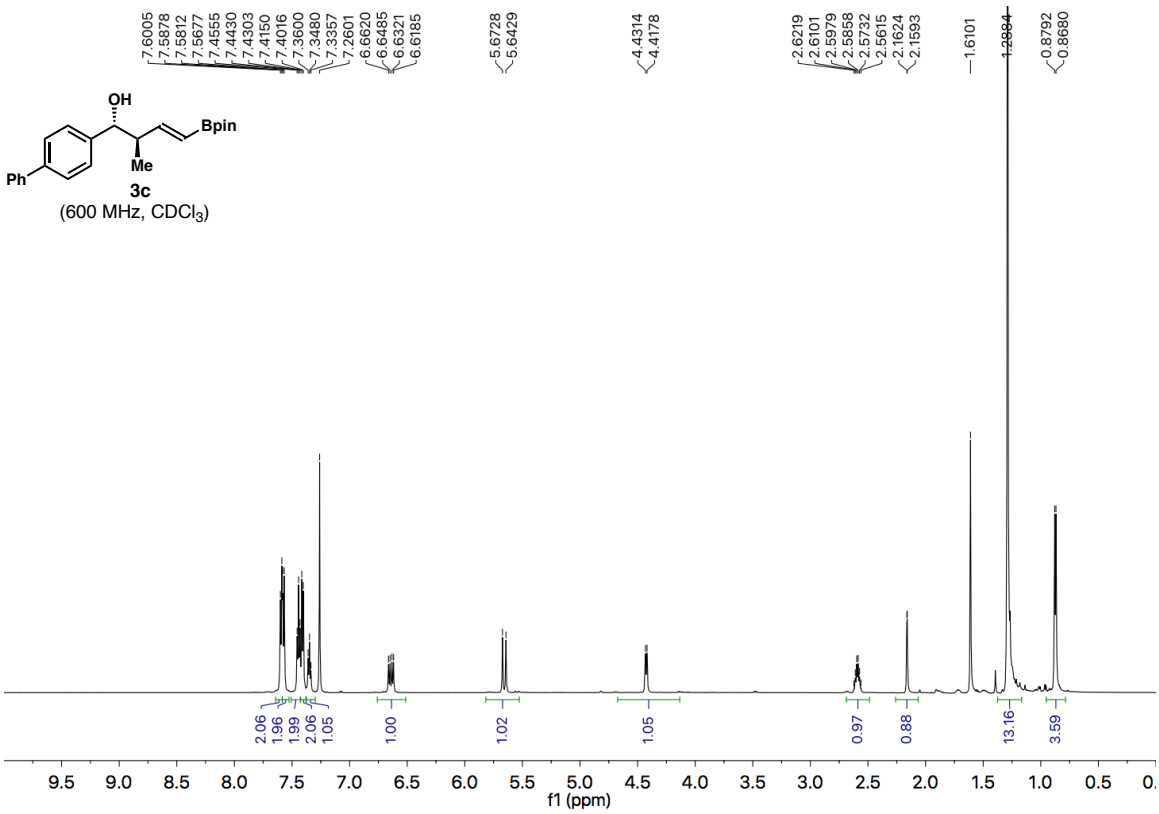
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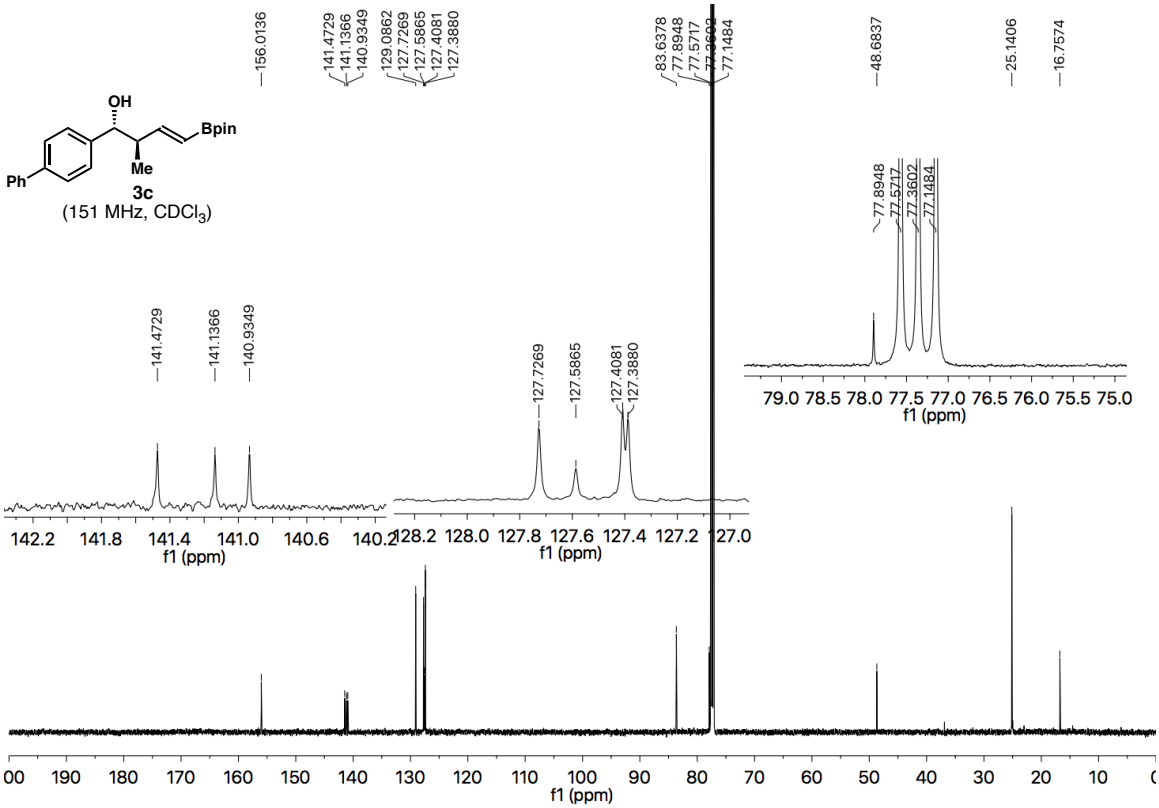
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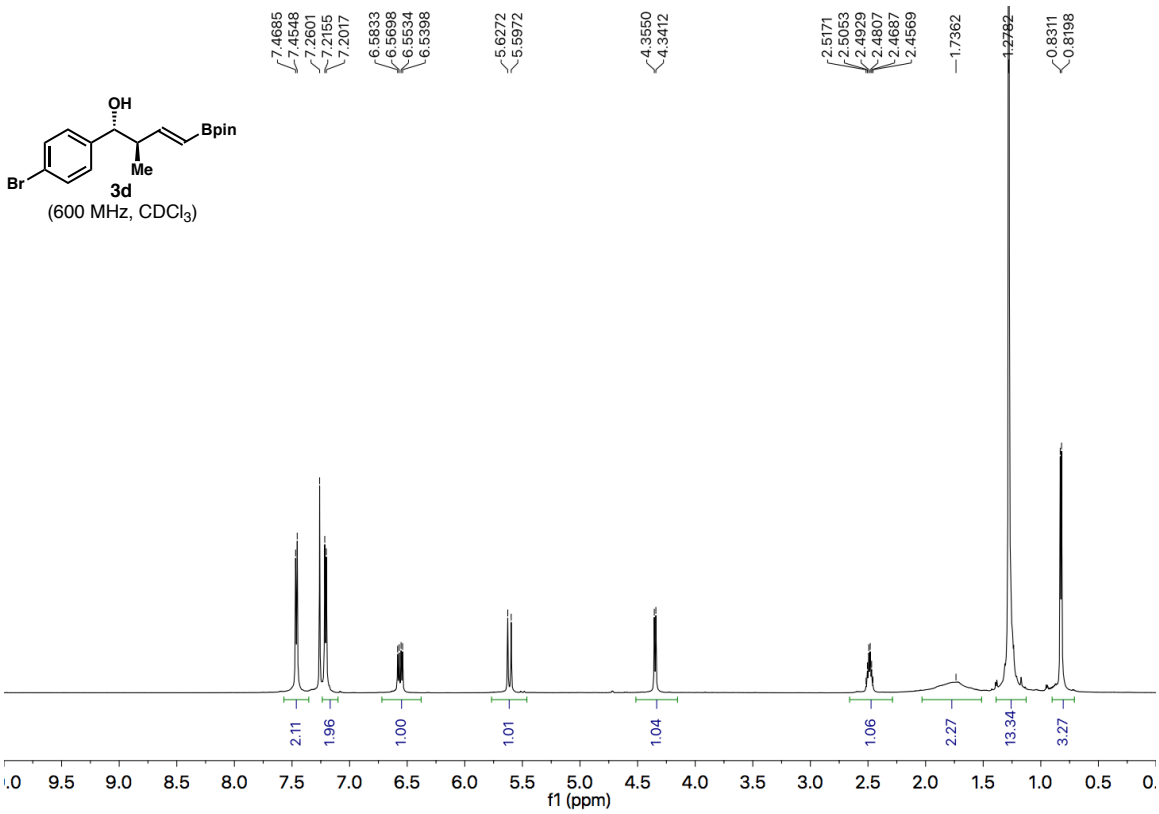
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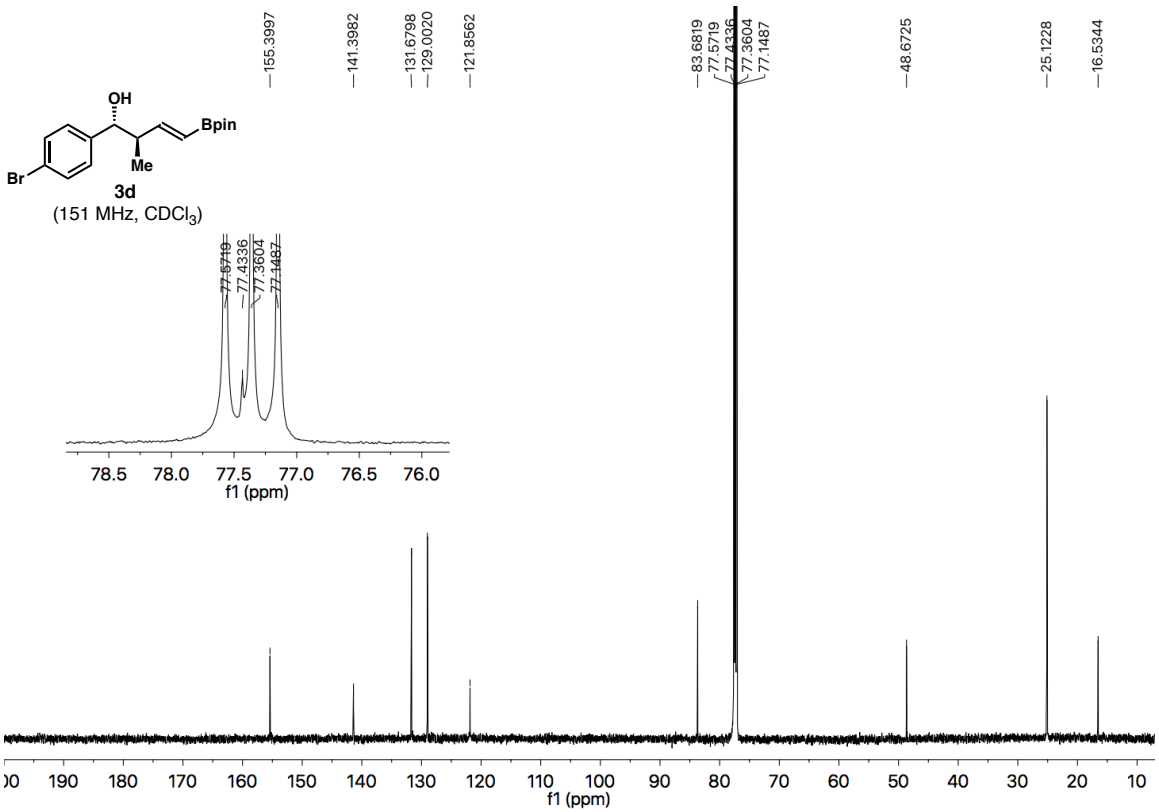
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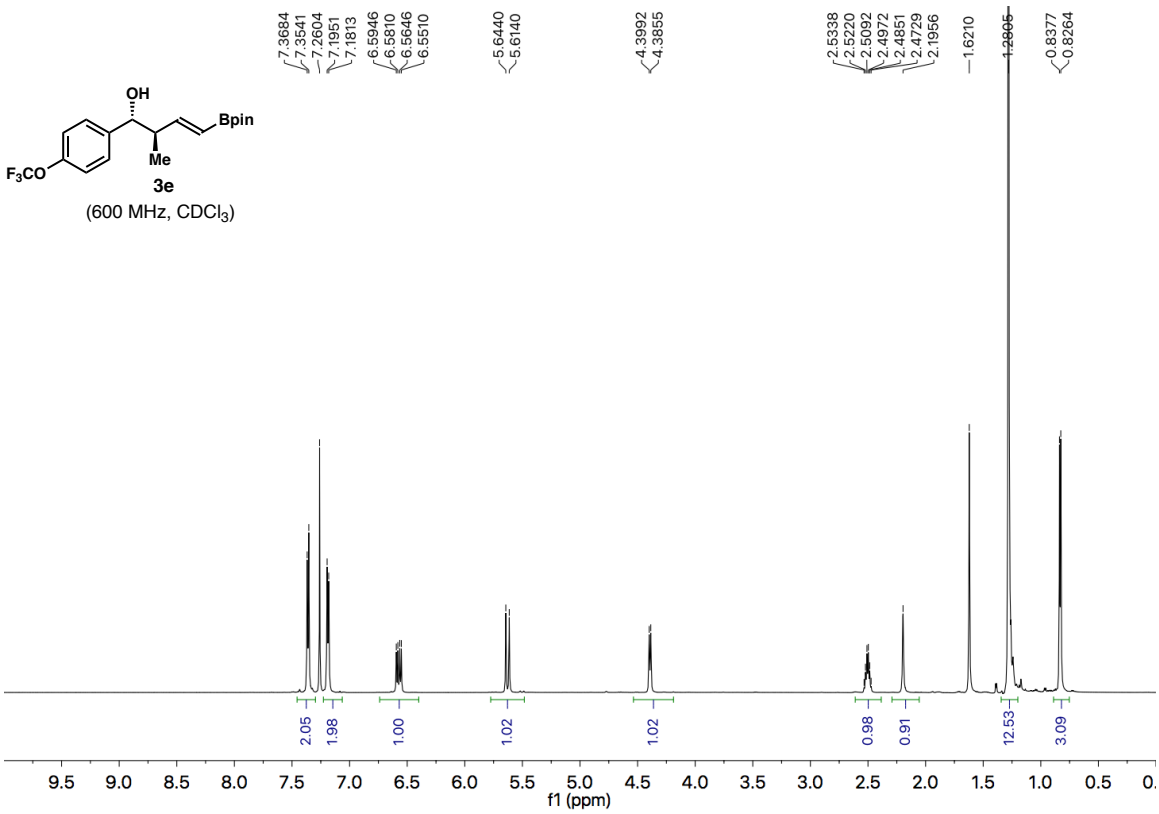
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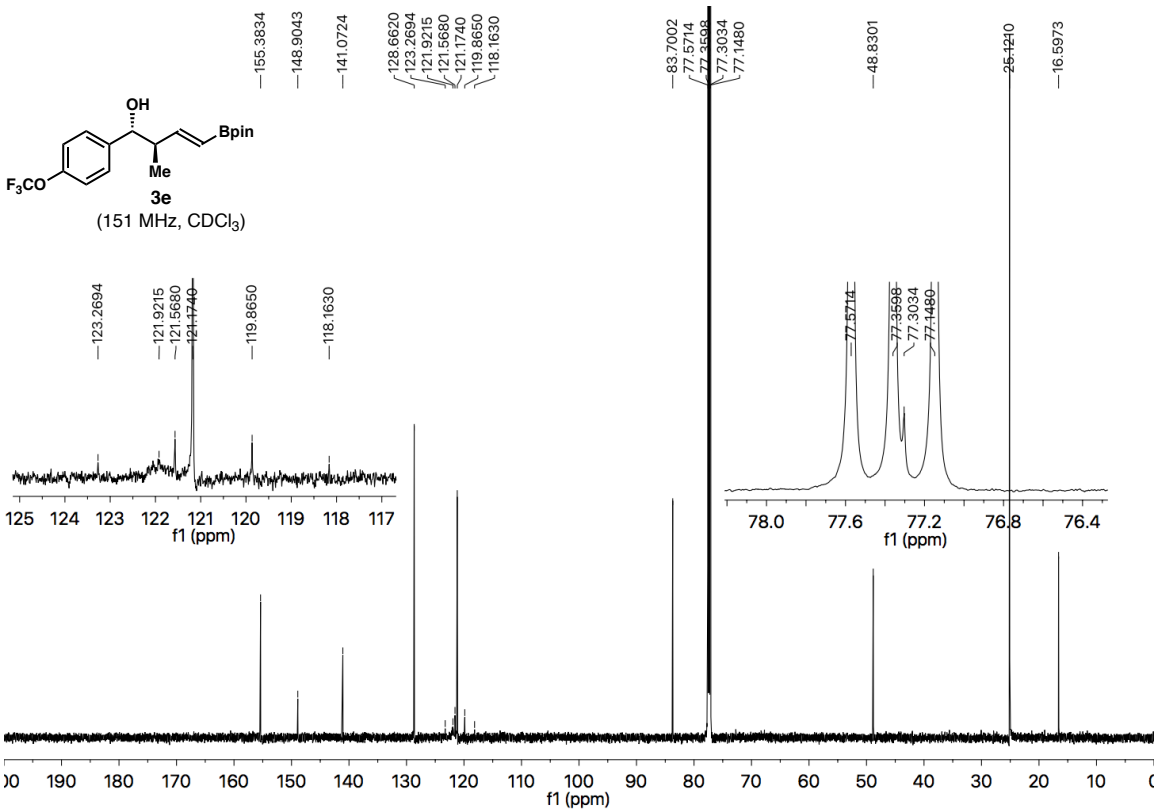
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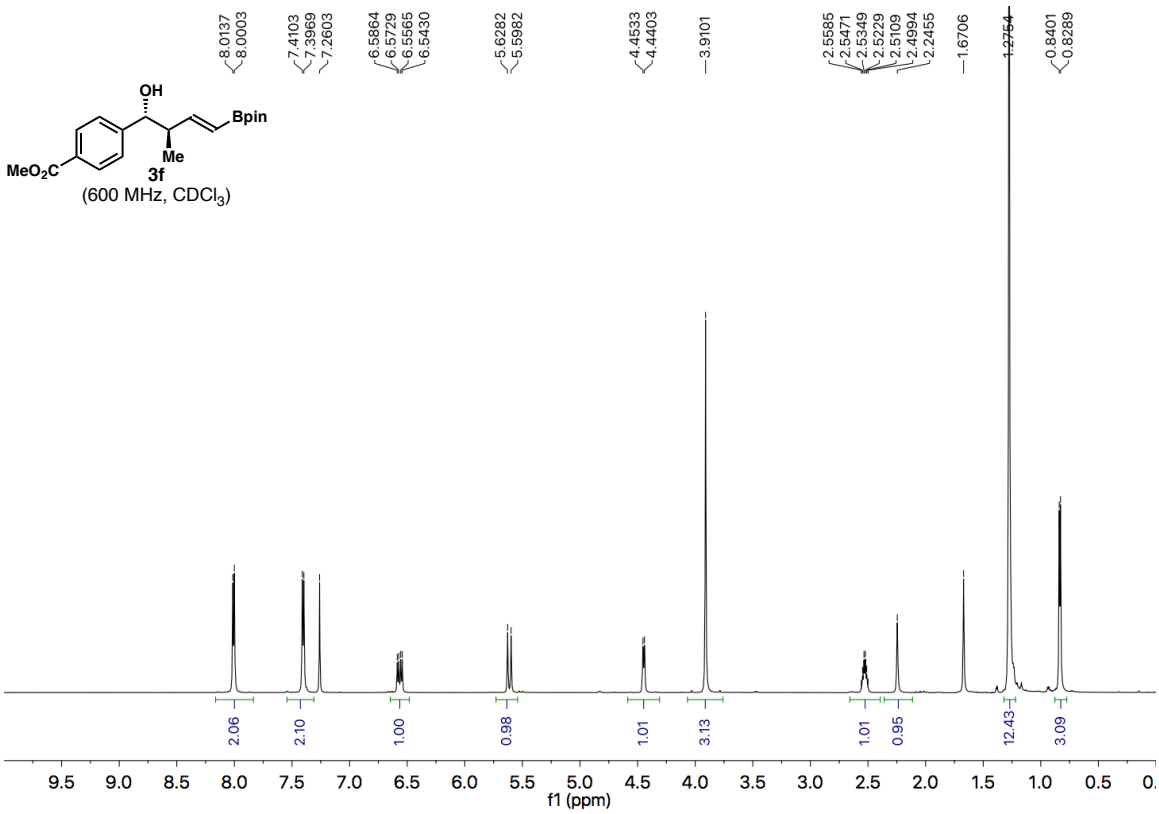
f1 (ppm)
f1 (ppm)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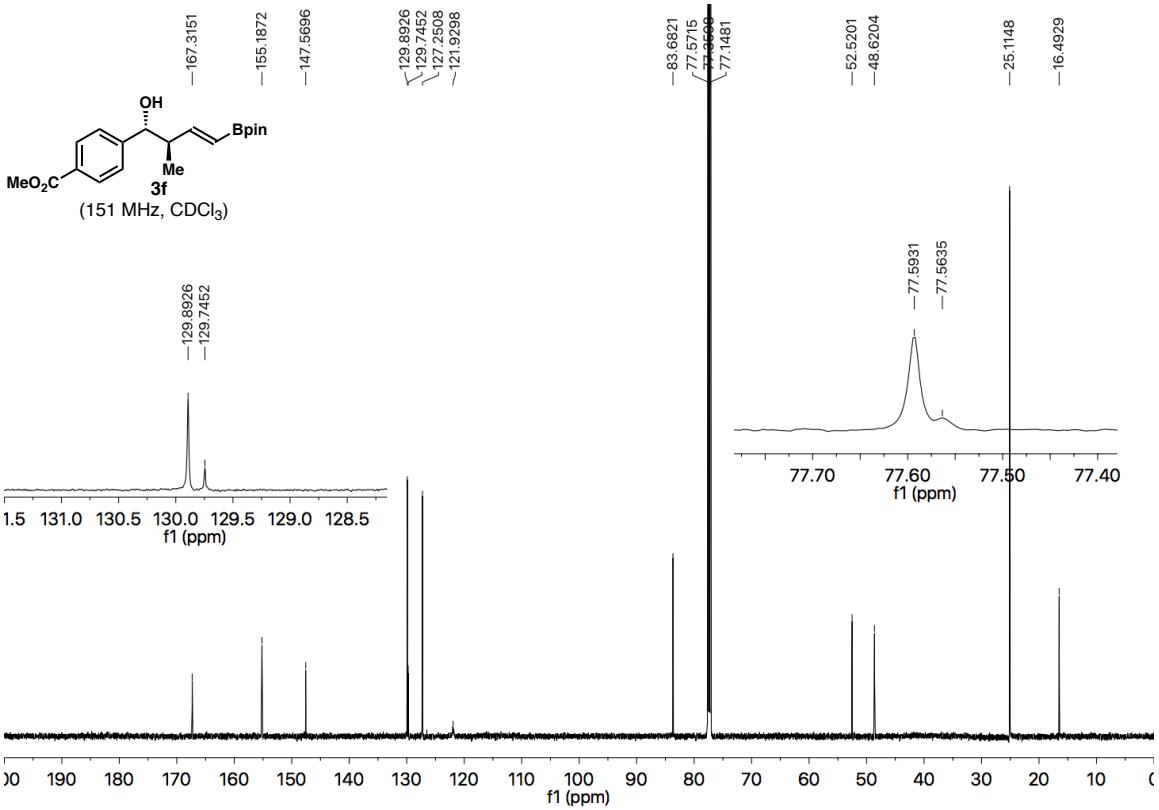
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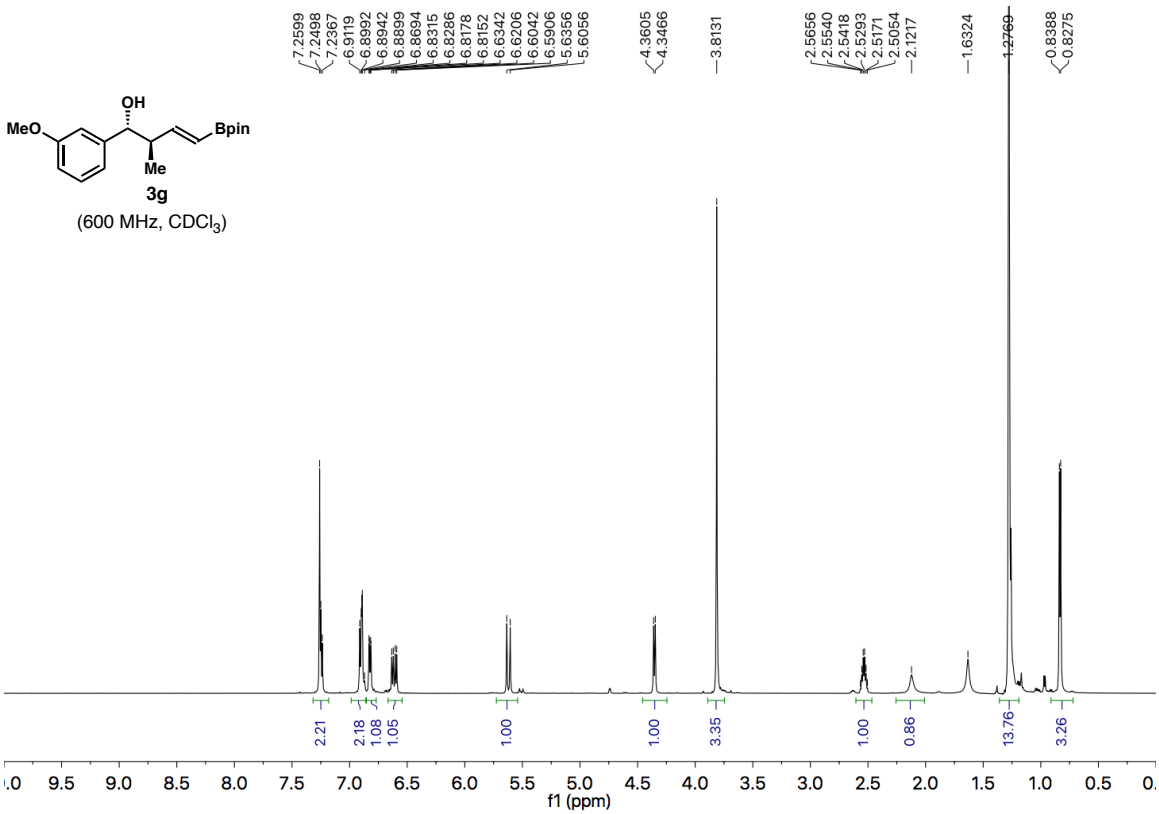
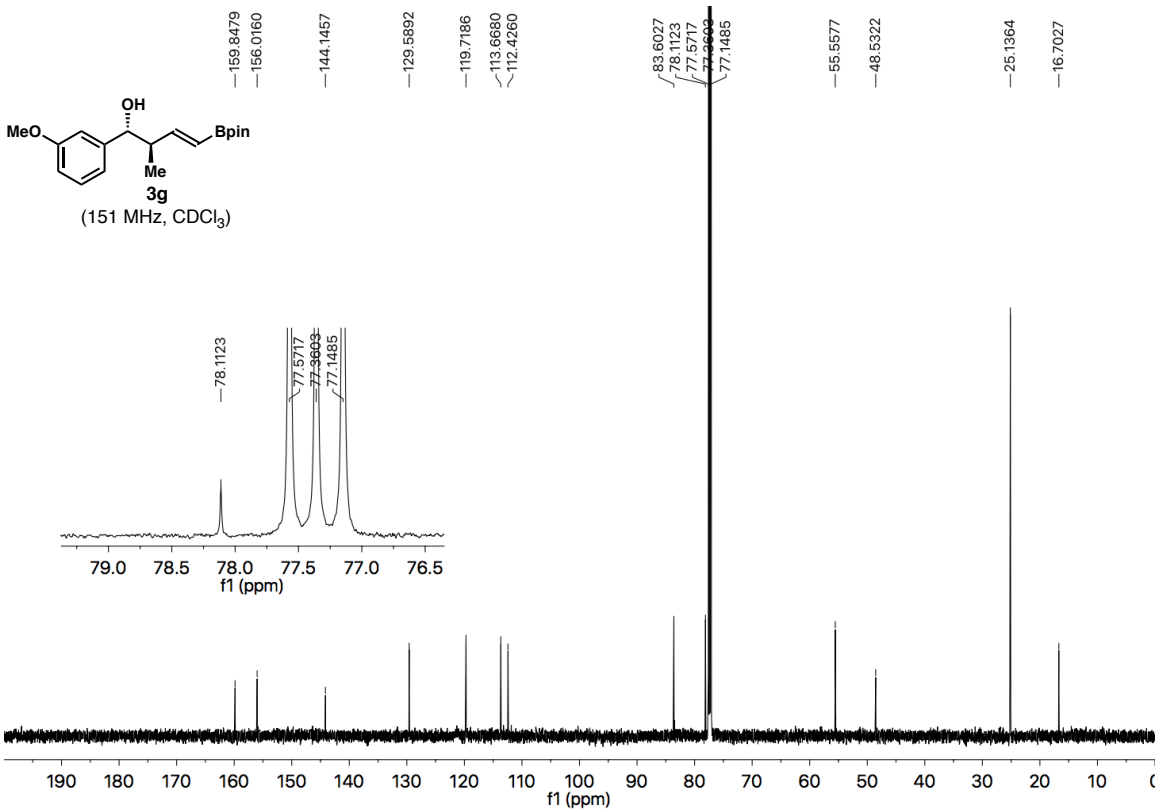
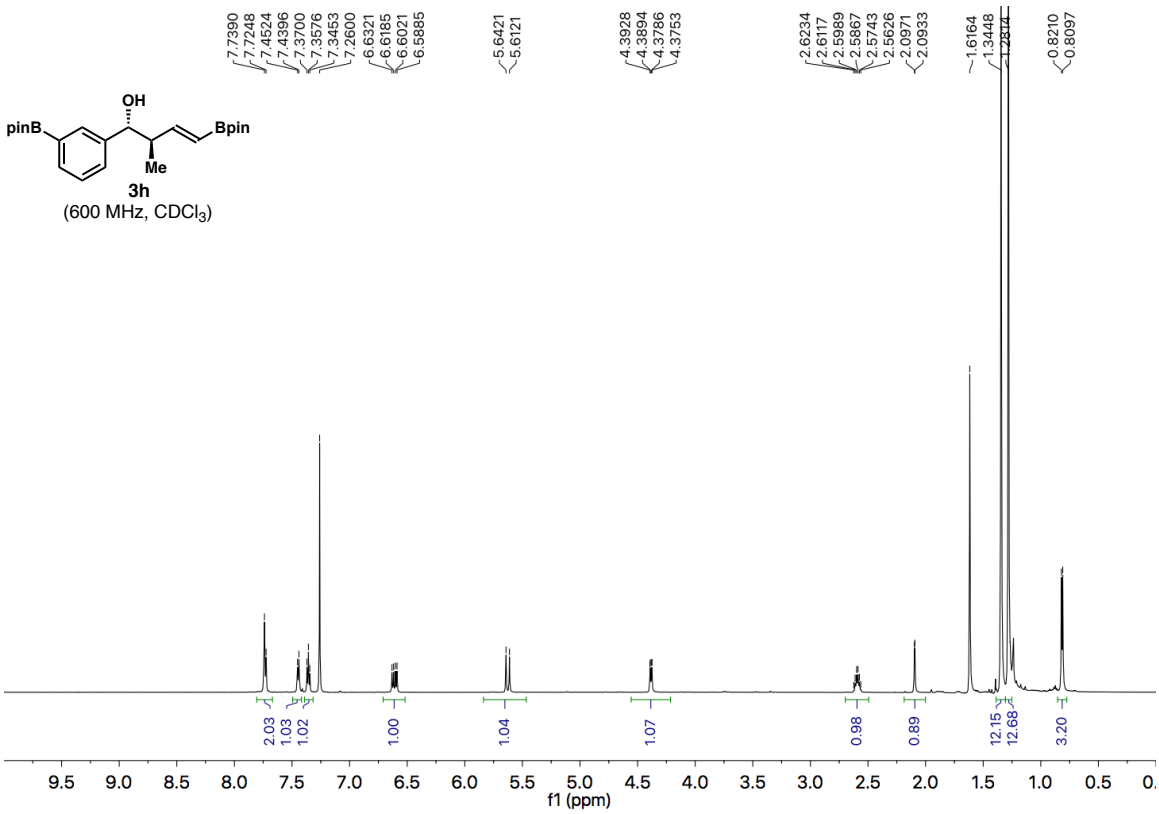
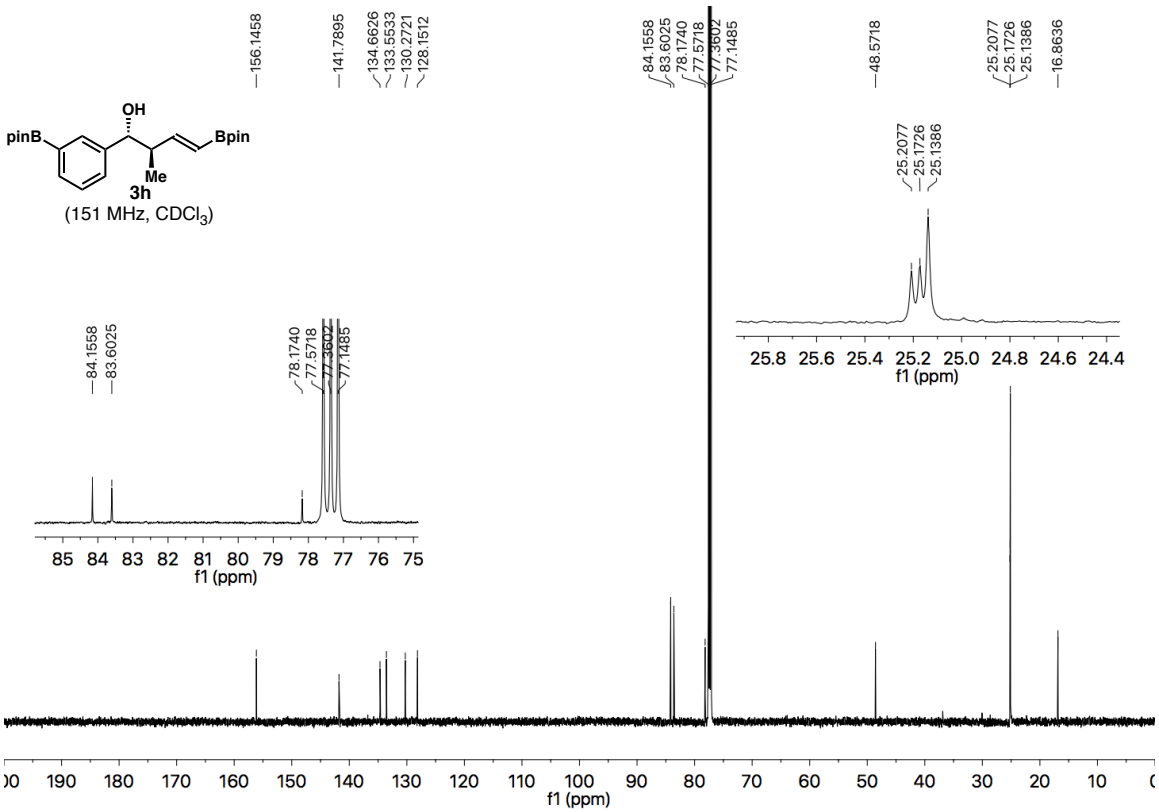
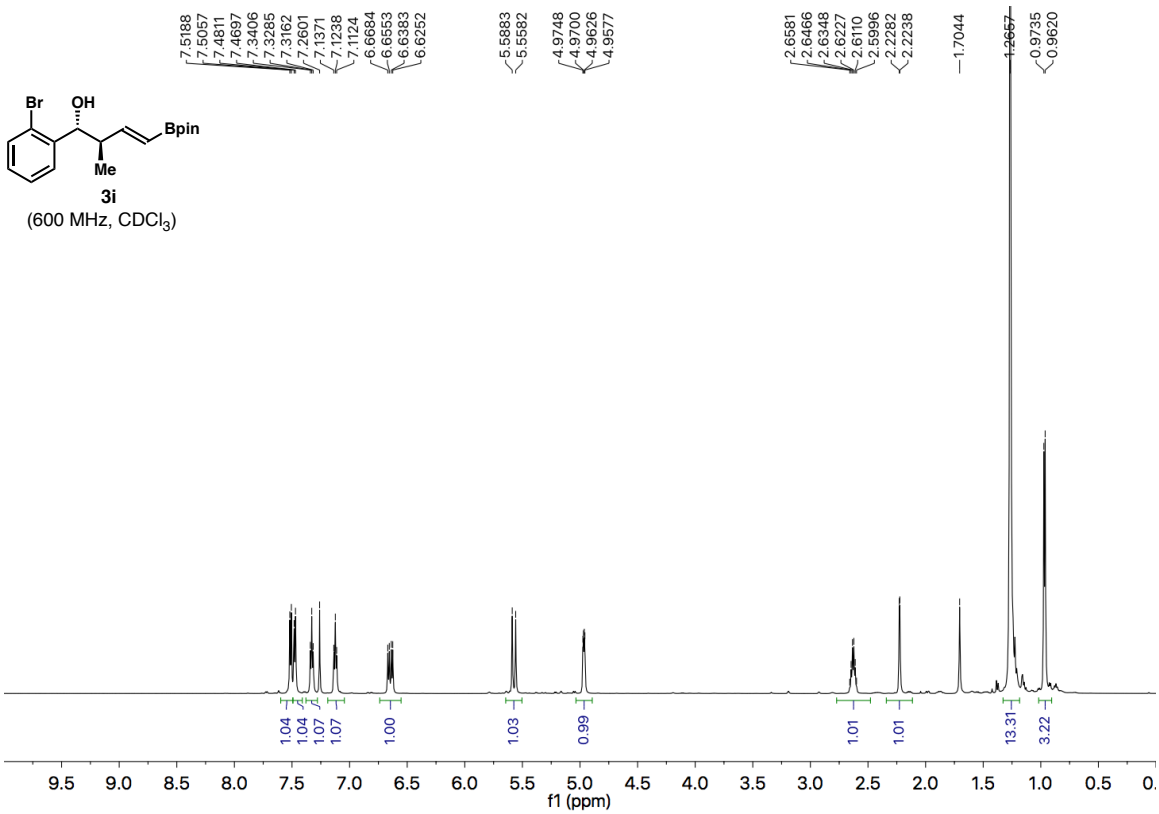
f1 (ppm)
f1 (ppm)

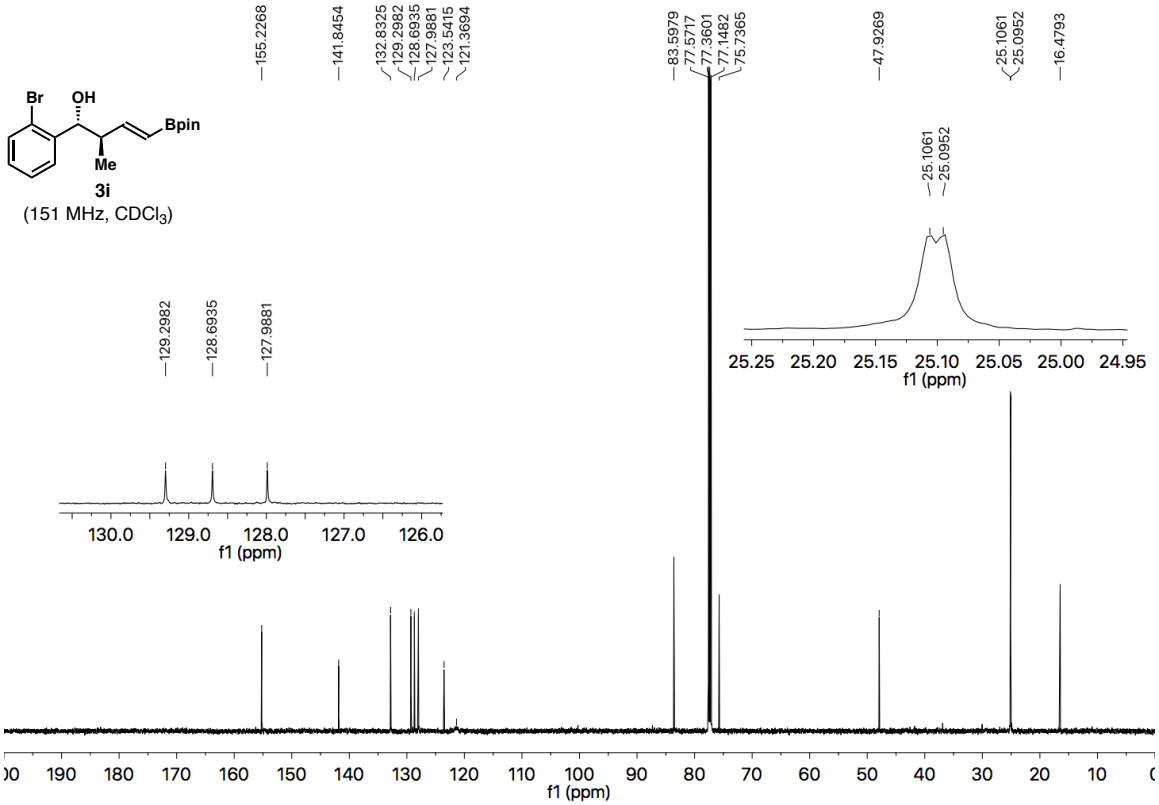

OH
MeO
Bpin
Me
3g
(600 MHz, CDCl3)
7.2599
7.2498
7.2367
6.9119
6.8992
6.8942
6.8899
6.8694
6.8315
6.8286
6.8178
6.8152
6.6342
6.6206
6.6042
6.5906
6.5356
6.5056
4.3605
4.3466
3.8131
2.5656
2.5540
2.5418
2.5293
2.5171
2.5054
2.1217
1.6324
1.2760
0.8388
0.8275
2.21
2.18
1.08
1.05
1.00
1.00
3.35
1.00
0.86
13.76
3.26
f1 (ppm)

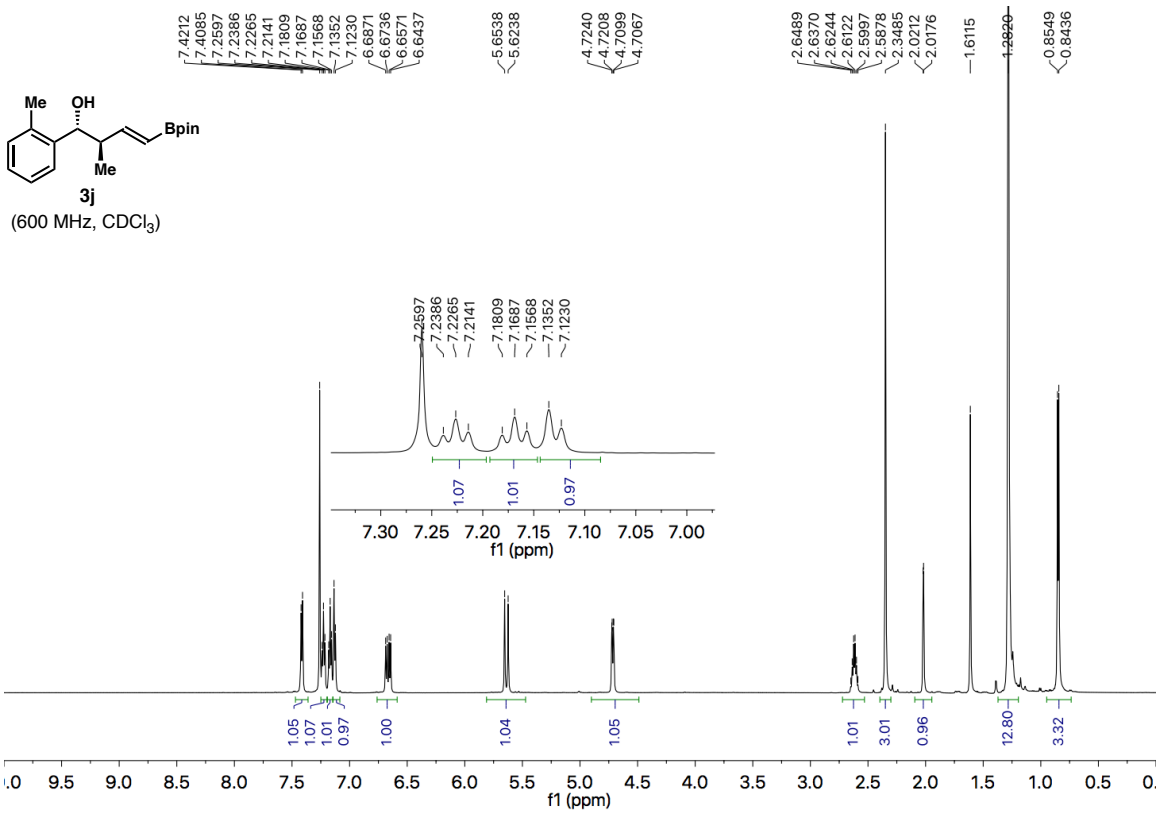

OH
MeO
Bpin
Me
3g
(151 MHz, CDCl3)
159.8479
156.0160
144.1457
129.5892
119.7186
113.6680
112.4260
83.6027
78.1123
77.5717
77.3603
77.1485
55.5577
48.5322
25.1364
16.7027
f1 (ppm)

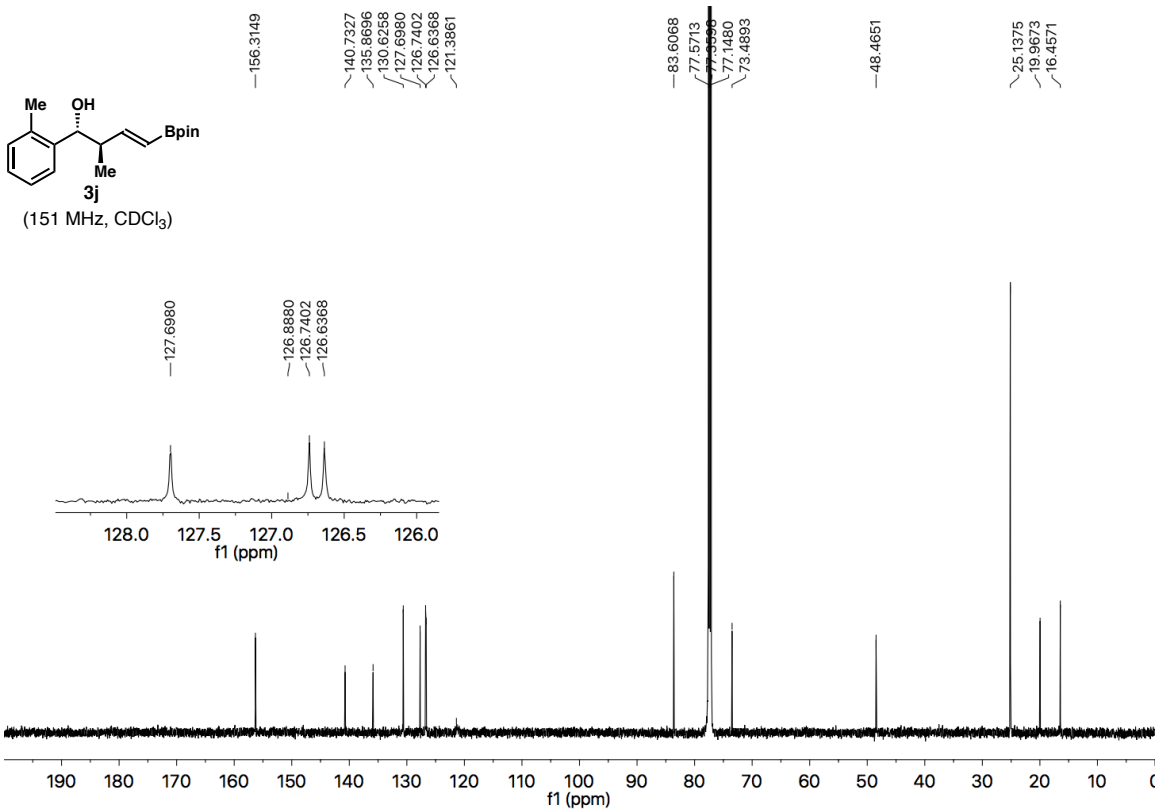

OH
pinB
Bpin
Me
3h
(600 MHz, CDCl3)
f1 (ppm)

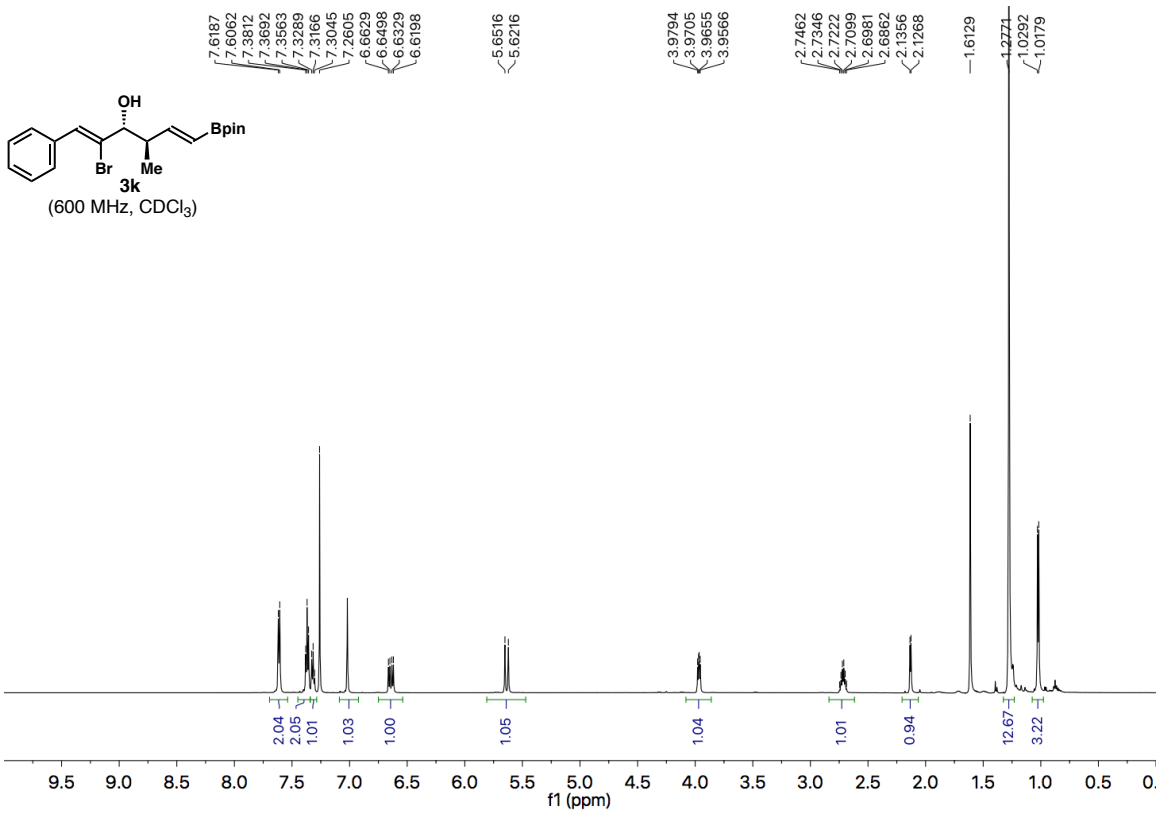

OH
pinB
Bpin
Me
3h
(151 MHz, CDCl3)
f1 (ppm)

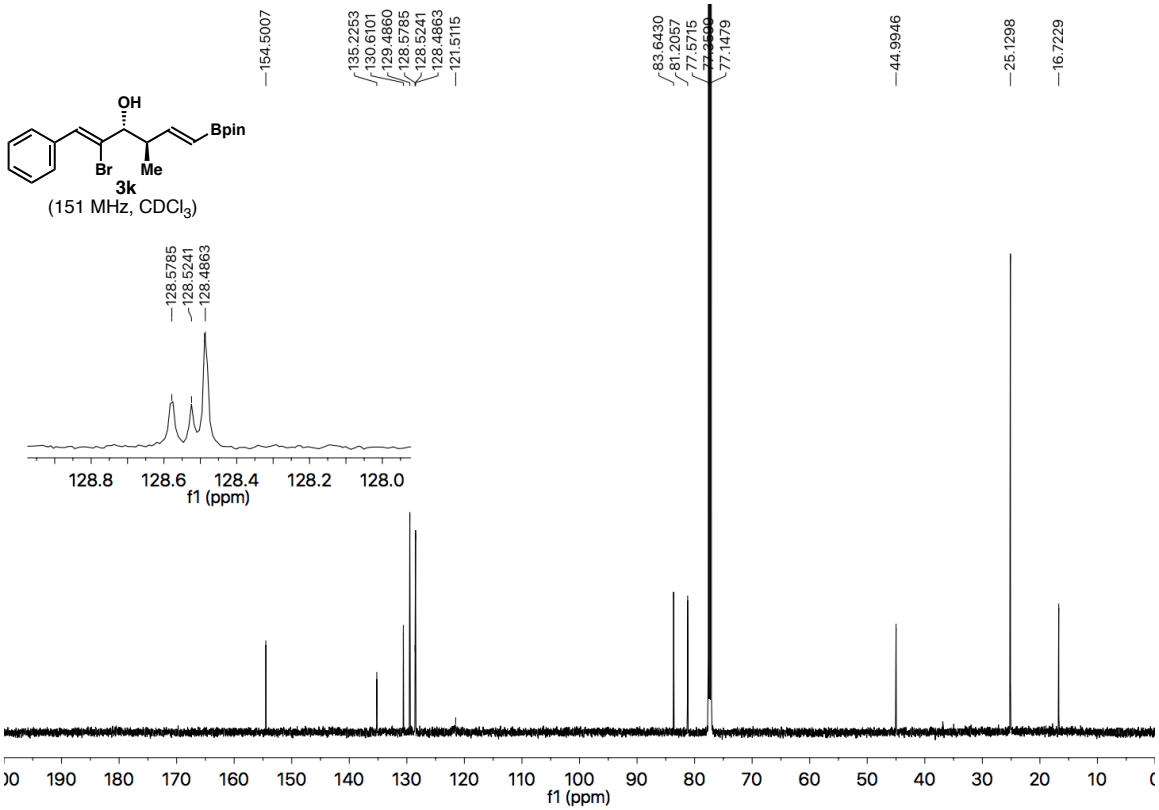

Br
OH
Bpin
Me
3i
(600 MHz, CDCl3)
7.5188
7.5057
7.4811
7.4697
7.3406
7.3285
7.3162
7.2601
7.1371
7.1238
7.1124
6.6684
6.6553
6.6383
6.6252
5.5883
5.5582
4.9748
4.9700
4.9626
4.9577
2.6581
2.6466
2.6348
2.6227
2.6110
2.5996
2.2282
2.2238
1.7044
1.2657
0.9735
0.9620
1.04
1.04
1.07
1.07
1.00
1.03
0.99
1.01
1.01
13.31
3.22
f1 (ppm)

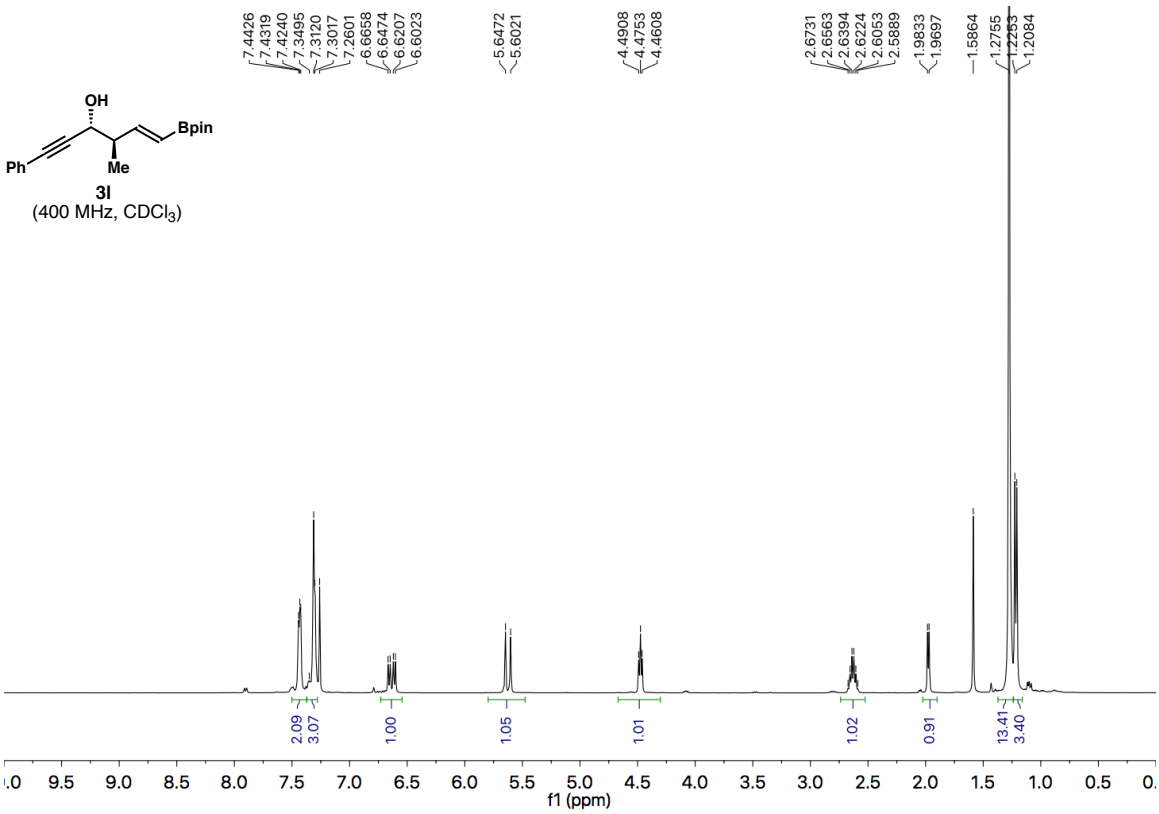

Br
OH
Bpin
Me
3i
(151 MHz, CDCl3)
155.2268
141.8454
132.8325
129.2982
128.6935
127.9881
123.5415
121.3694
83.5979
77.5717
77.3601
77.1482
75.7365
47.9269
25.1061
25.0952
16.4793
129.2982
128.6935
127.9881
f1 (ppm)

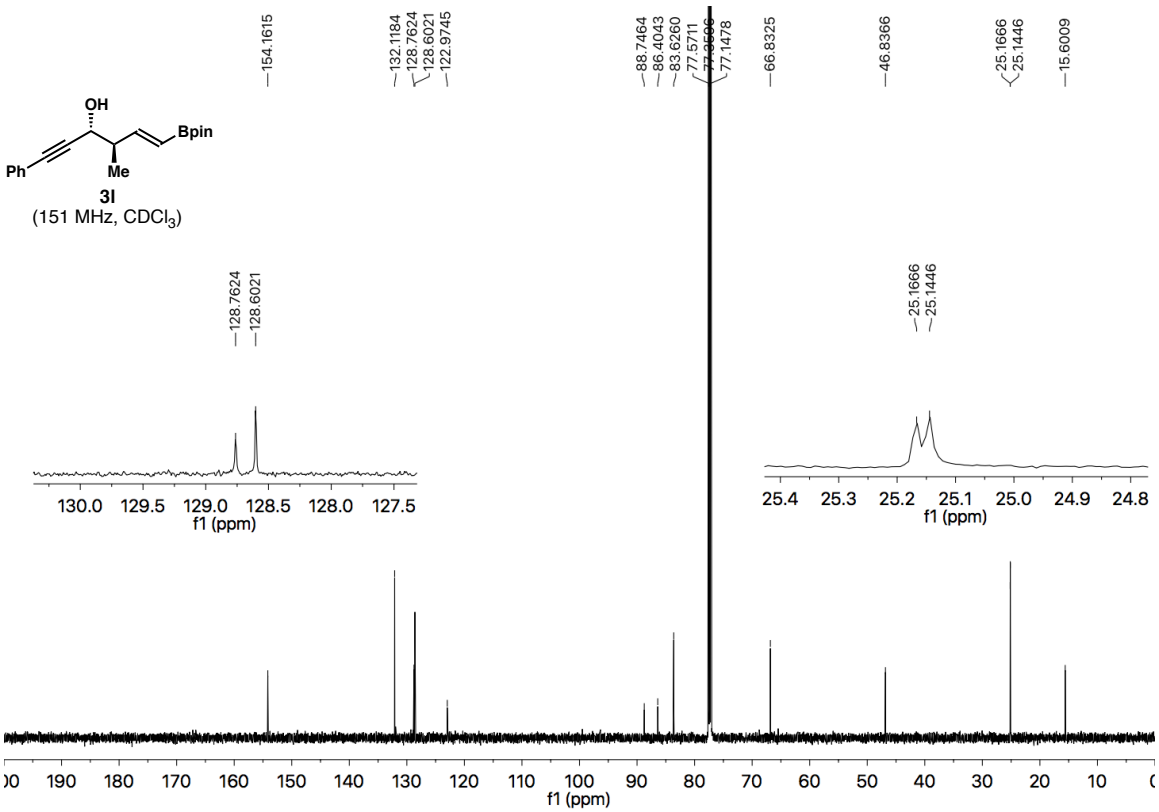

Me
OH
Bpin
Me
3j
(600 MHz, CDCl3)
7.4212
7.4085
7.2597
7.2386
7.2265
7.2141
7.1809
7.1687
7.1568
7.1352
7.1230
6.6871
6.6736
6.6571
6.6437
5.6538
5.6238
4.7240
4.7208
4.7099
4.7067
2.6489
2.6370
2.6244
2.6122
2.5997
2.5878
2.3485
2.0212
2.0176
1.6115
1.2920
0.8549
0.8436
1.05
1.07
1.01
0.97
1.00
1.04
1.05
1.01
3.01
0.96
12.80
3.32
f1 (ppm)

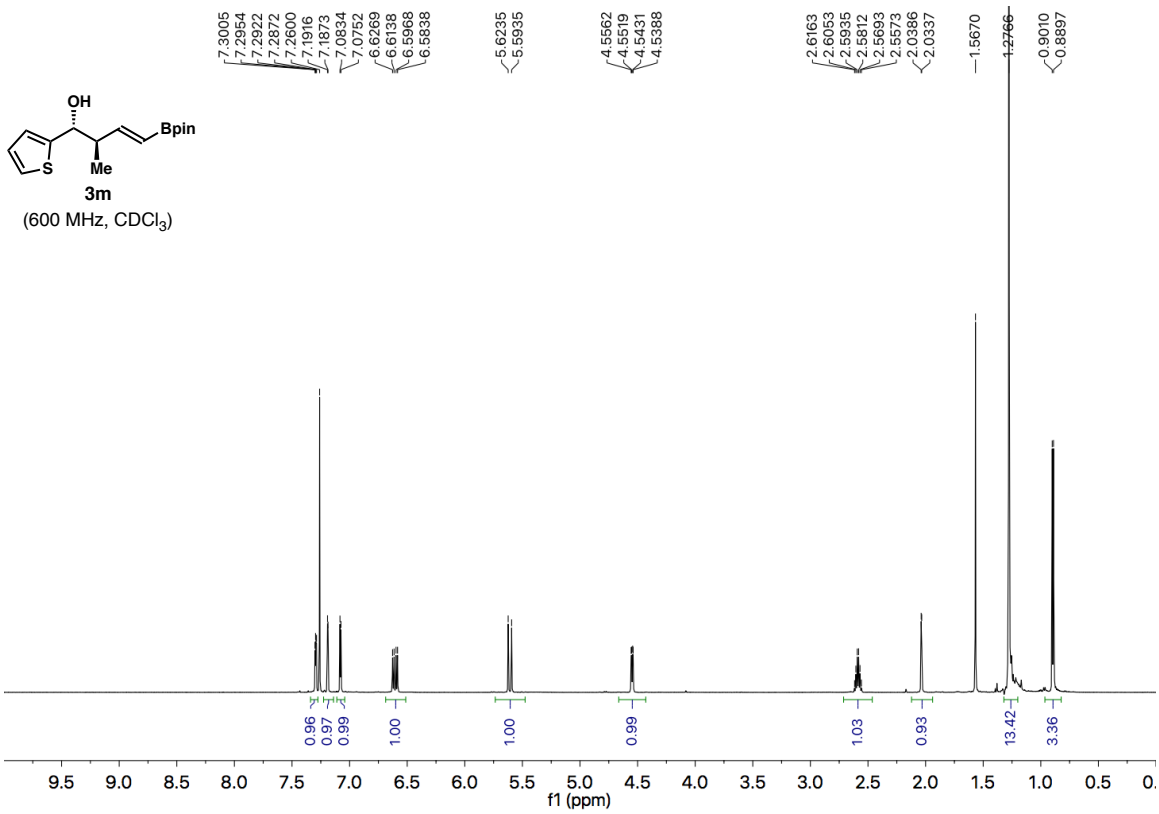

Me
OH
Bpin
Me
3j
(151 MHz, CDCl3)
156.3149
140.7327
135.8696
130.6258
127.6980
126.7402
126.6368
121.3861
83.6068
77.5713
77.1480
73.4893
48.4651
25.1375
19.9673
16.4571
f1 (ppm)

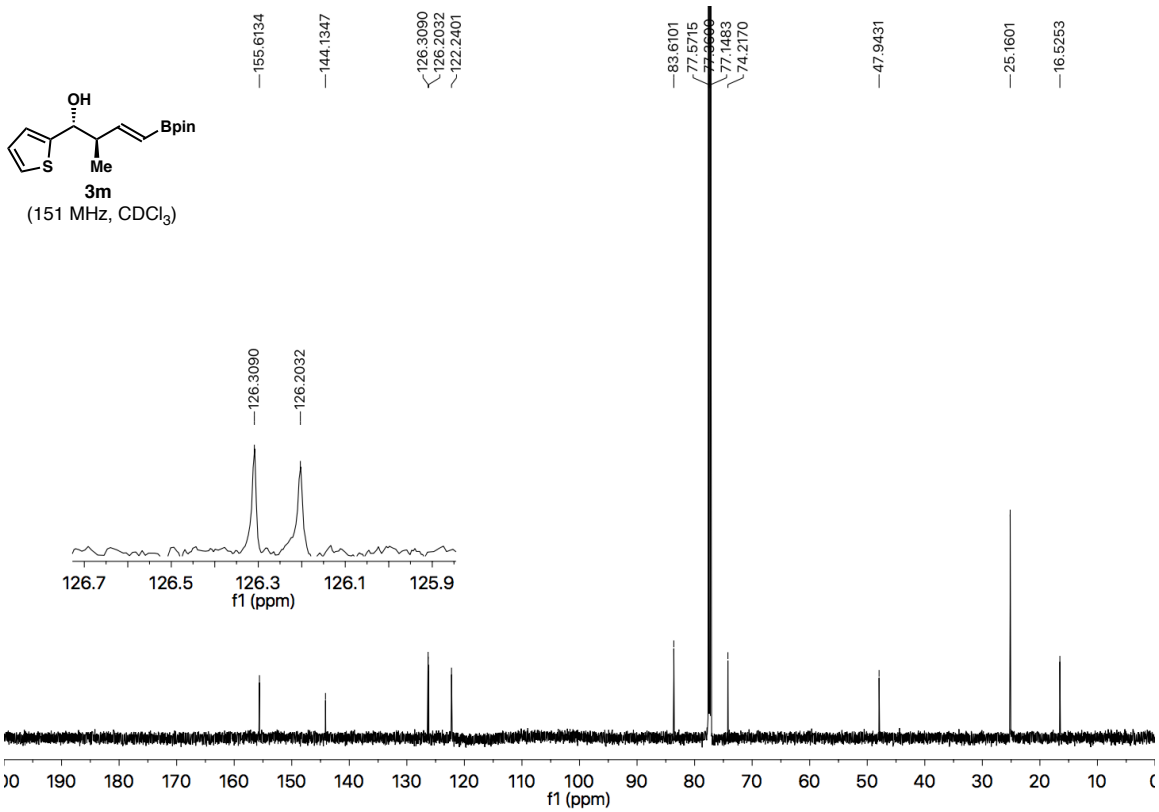

7.6187
7.6062
7.3812
7.3692
7.3563
7.3289
7.3166
7.3045
7.2605
6.6629
6.6498
6.6329
6.6198
5.6516
5.6216
3.9794
3.9705
3.9655
3.9566
2.7462
2.7346
2.7222
2.7099
2.6981
2.6862
2.1356
2.1268
1.6129
1.2771
1.0292
1.0179
OH
Bpin
Br
Me
3k
(600 MHz, CDCl3)
2.04
2.05
1.01
1.03
1.00
1.05
1.04
1.01
0.94
12.67
3.22
f1 (ppm)

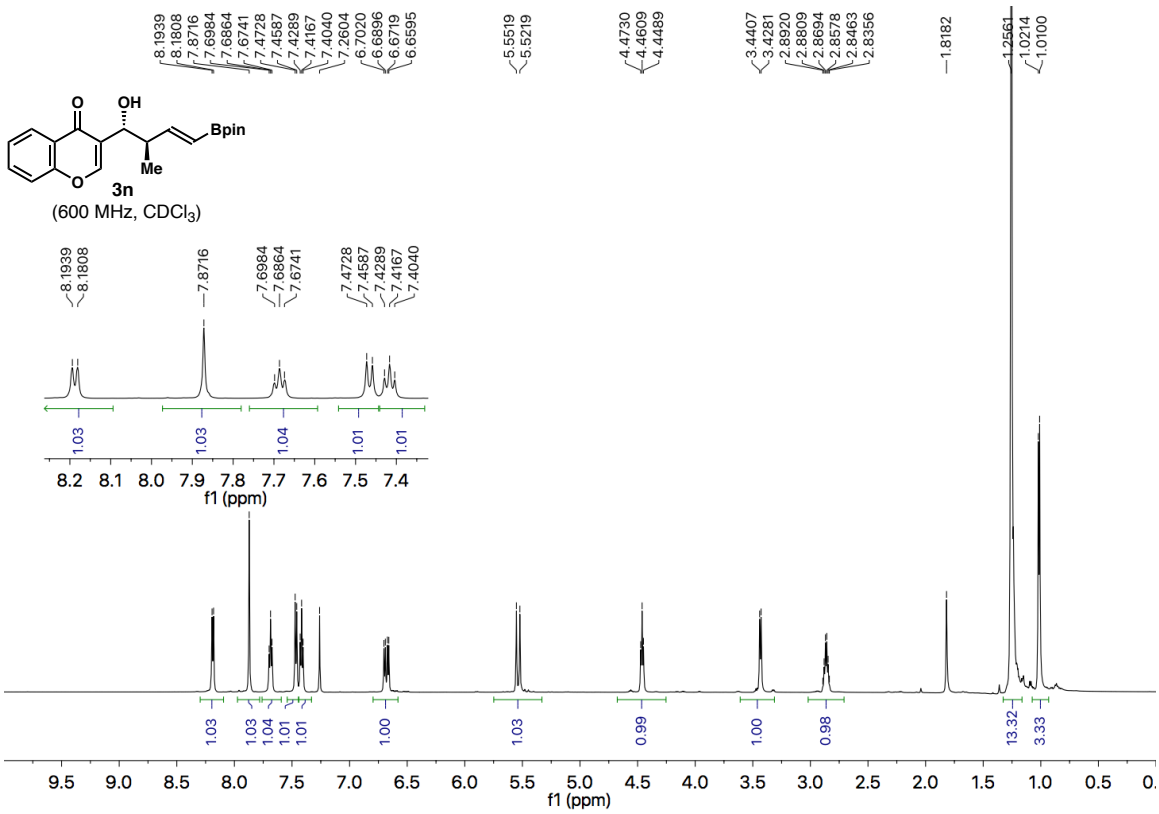

154.5007
135.2253
130.6101
129.4860
128.5785
128.5241
128.4863
121.5115
83.6430
81.2057
77.5715
77.1479
44.9946
25.1298
16.7229
OH
Bpin
Br
Me
3k
(151 MHz, CDCl3)
128.5785
128.5241
128.4863
f1 (ppm)

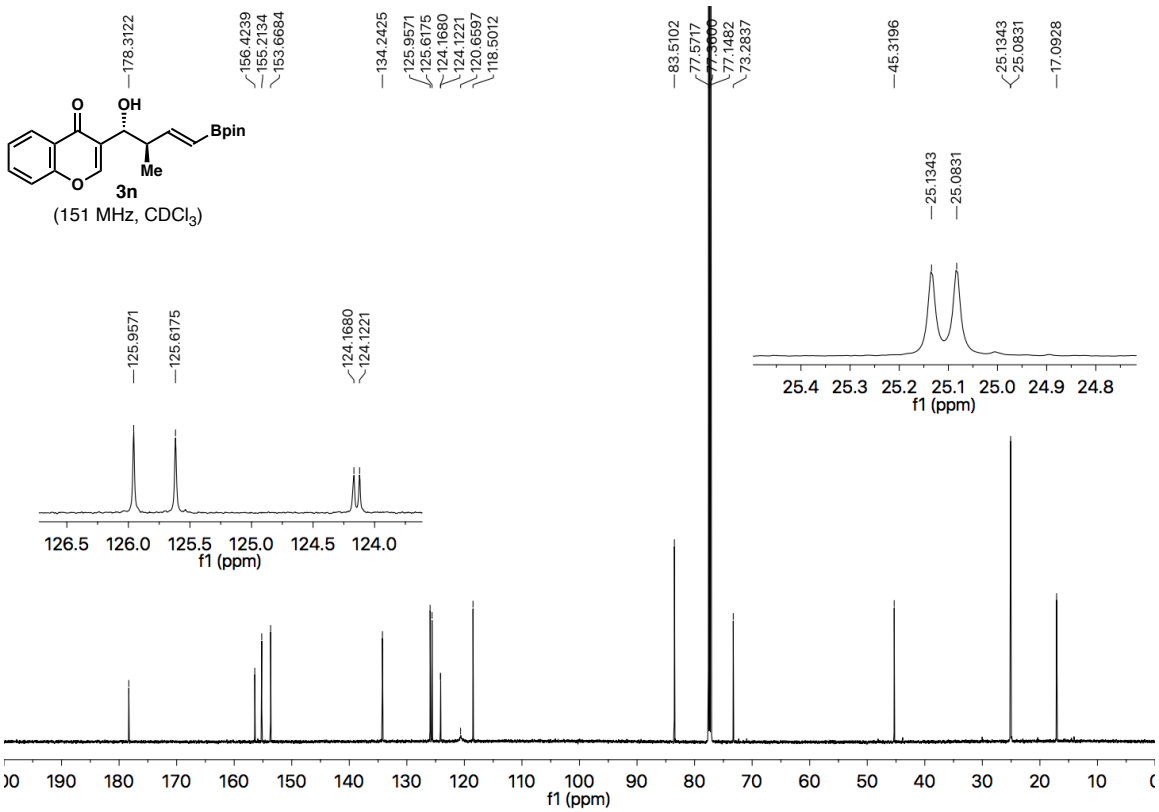

OH
Bpin
Ph
Me
3l
(400 MHz, CDCl3)
7.4426
7.4319
7.4240
7.3495
7.3120
7.3017
7.2601
6.6658
6.6474
6.6207
6.6023
5.6472
5.6021
4.4908
4.4753
4.4608
2.6731
2.6563
2.6394
2.6224
2.6053
2.5889
1.9833
1.9697
1.5864
1.2755
1.2253
1.2084
2.09
3.07
1.00
1.05
1.01
1.02
0.91
13.41
3.40
f1 (ppm)

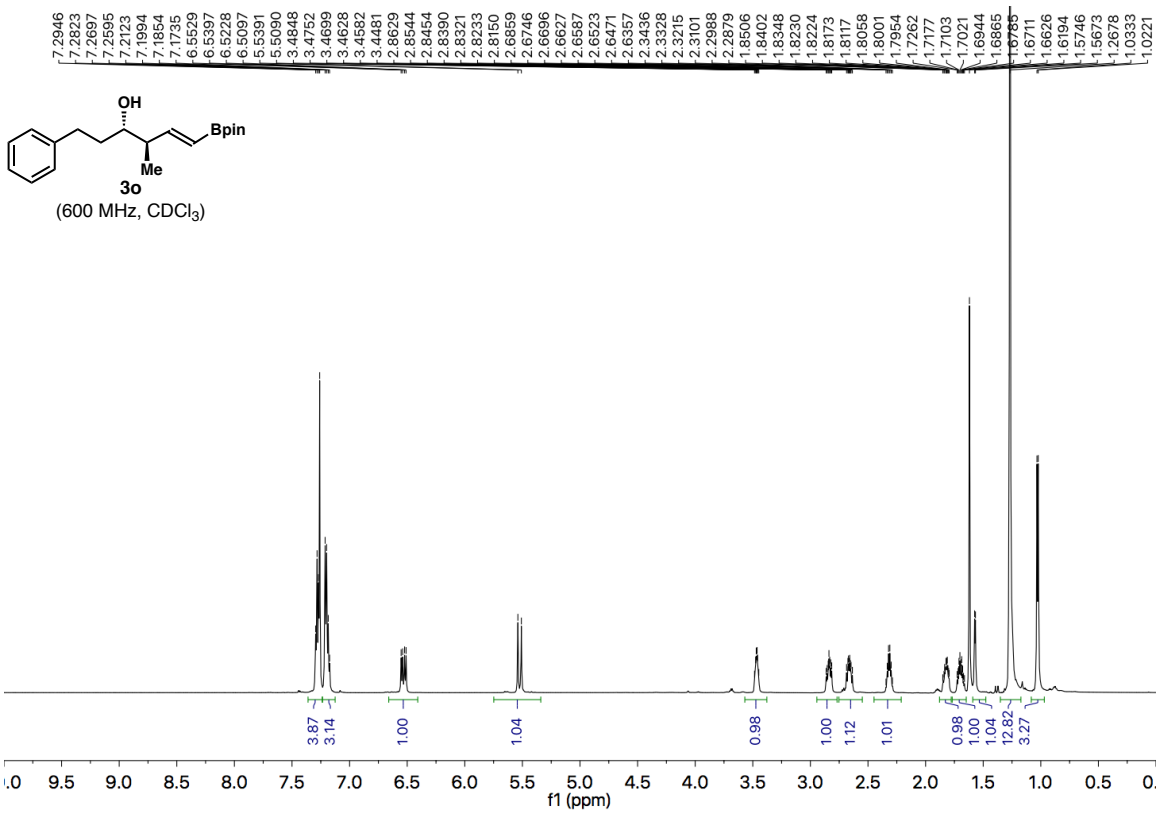

OH
Bpin
Ph
Me
3l
(151 MHz, CDCl3)
154.1615
132.1184
128.7624
128.6021
122.9745
88.7464
86.4043
83.6260
77.5711
77.1478
66.8325
46.8366
25.1666
25.1446
15.6009
128.7624
128.6021
25.1666
25.1446
f1 (ppm)
f1 (ppm)
f1 (ppm)

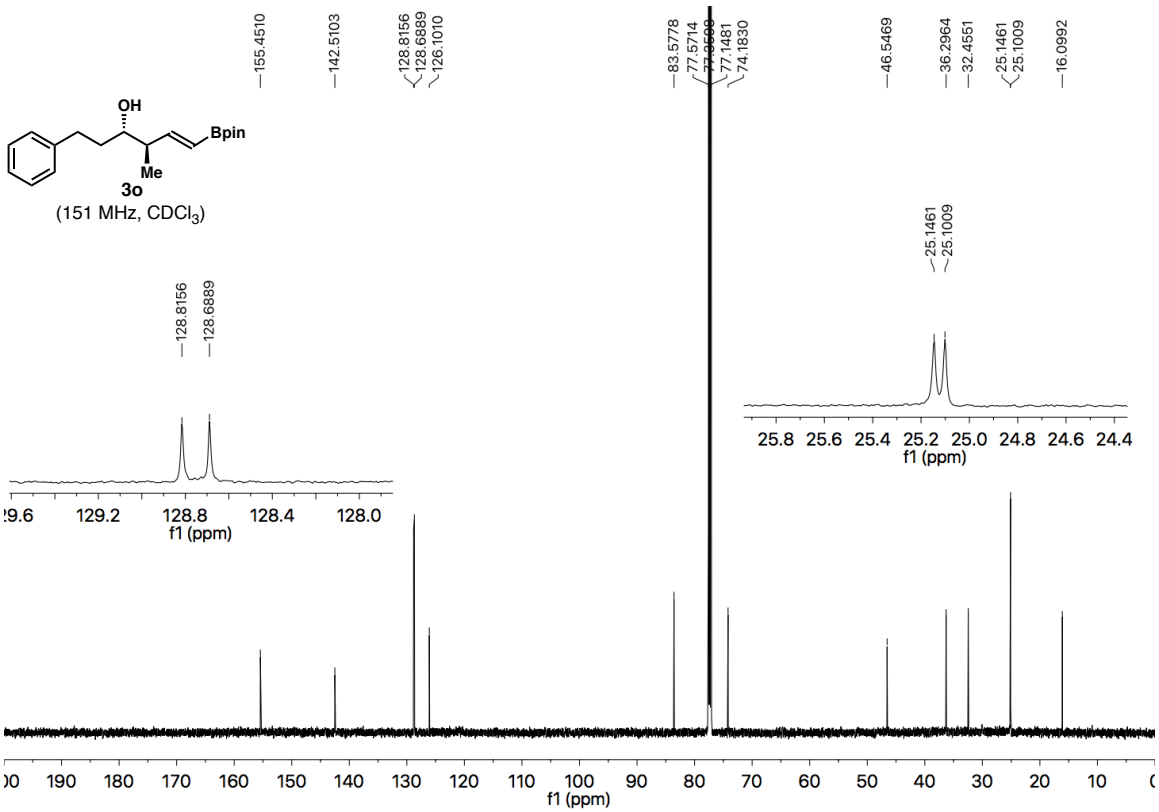

7.3005
7.2954
7.2922
7.2872
7.2600
7.1916
7.1873
7.0834
7.0752
6.6269
6.6138
6.5968
6.5838
5.6235
5.5935
4.5562
4.5519
4.5431
4.5388
2.6163
2.6053
2.5935
2.5812
2.5693
2.5573
2.0386
2.0337
1.5670
1.2766
0.9010
0.8897
OH
Bpin
S
Me
3m
(600 MHz, CDCl3)
0.96
0.97
0.99
1.00
1.00
0.99
1.03
0.93
13.42
3.36
f1 (ppm)

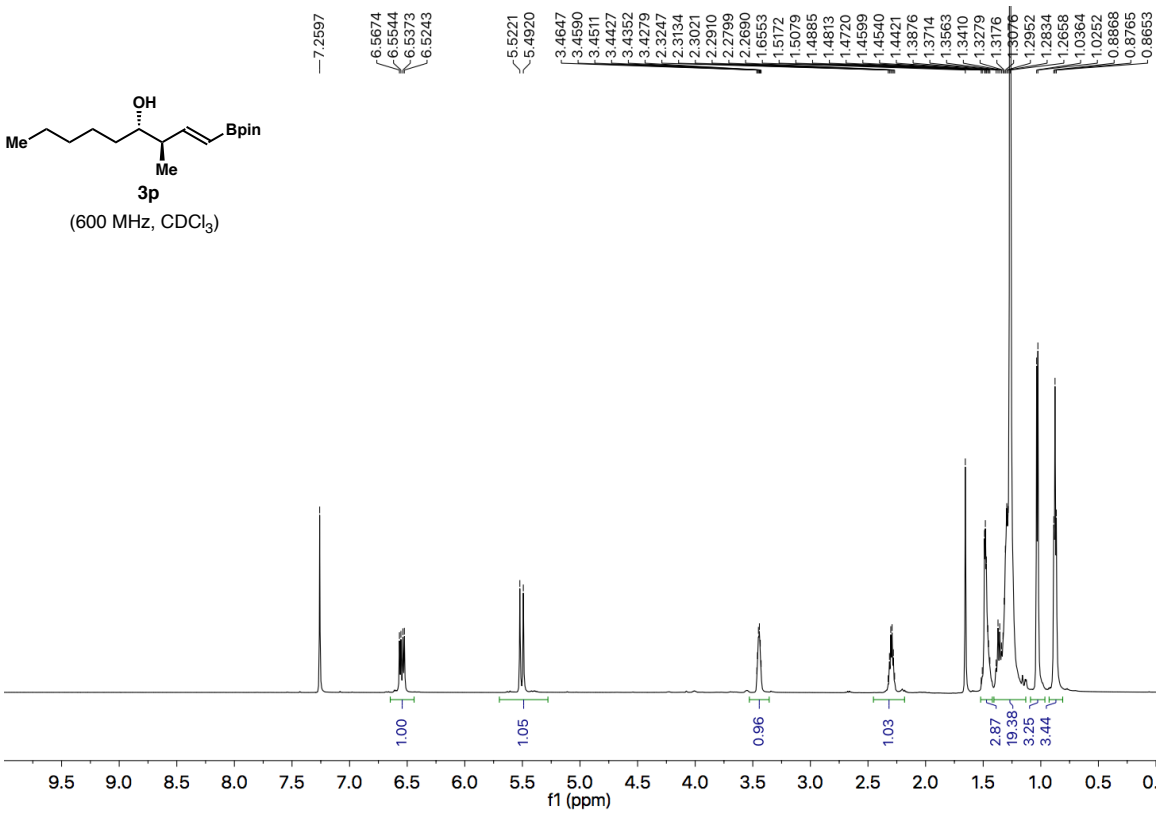

155.6134
144.1347
126.3090
126.2032
122.2401
83.6101
77.5715
77.1483
74.2170
47.9431
25.1601
16.5253
OH
Bpin
S
Me
3m
(151 MHz, CDCl3)
126.3090
126.2032
f1 (ppm)
f1 (ppm)

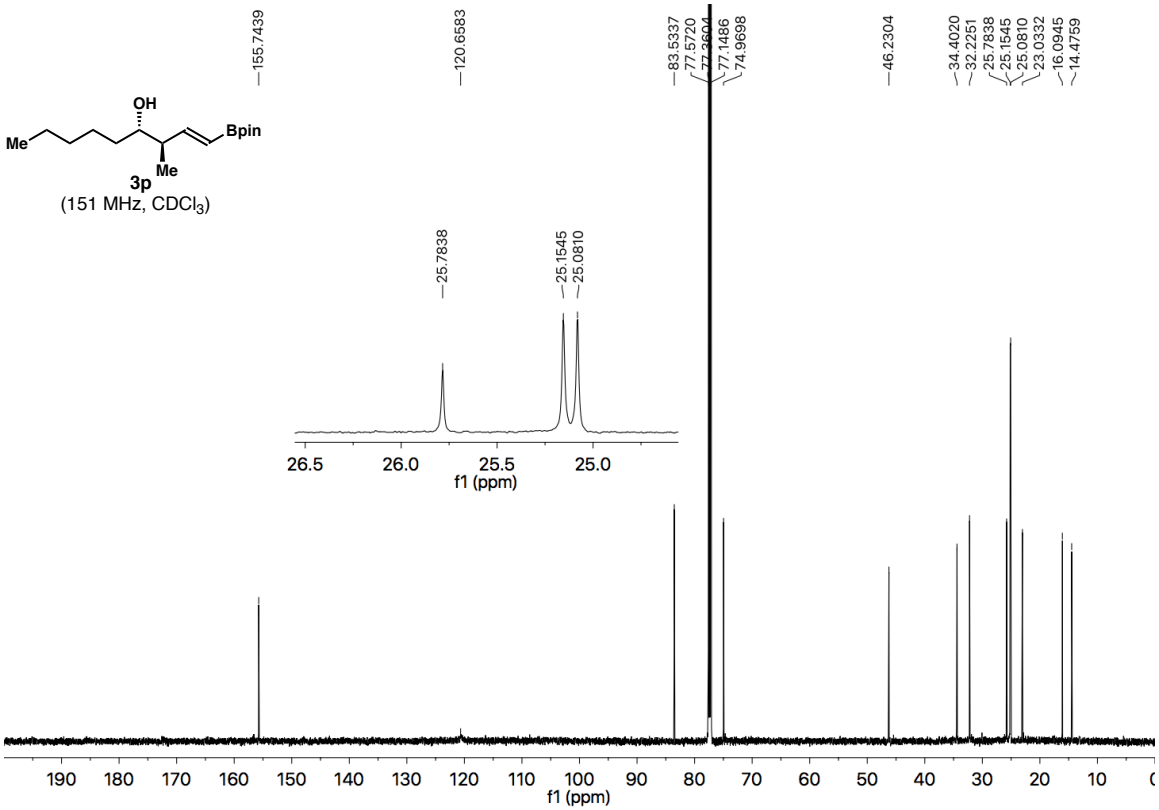

8.1939
8.1808
7.8716
7.6984
7.6864
7.6741
7.4728
7.4587
7.4289
7.4167
7.4040
7.2604
6.7020
6.6896
6.6719
6.6595
5.5519
5.5219
4.4730
4.4609
4.4489
3.4407
3.4281
2.8920
2.8809
2.8694
2.8578
2.8463
2.8356
1.8182
1.2561
1.0214
1.0100
O
OH
Bpin
Me
O
3n
(600 MHz, CDCl3)
1.03
1.03
1.04
1.01
1.01
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
1.03
1.03
1.04
1.01
1.01
1.00
1.03
0.99
1.00
0.98
13.32
3.33
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
f1 (ppm)

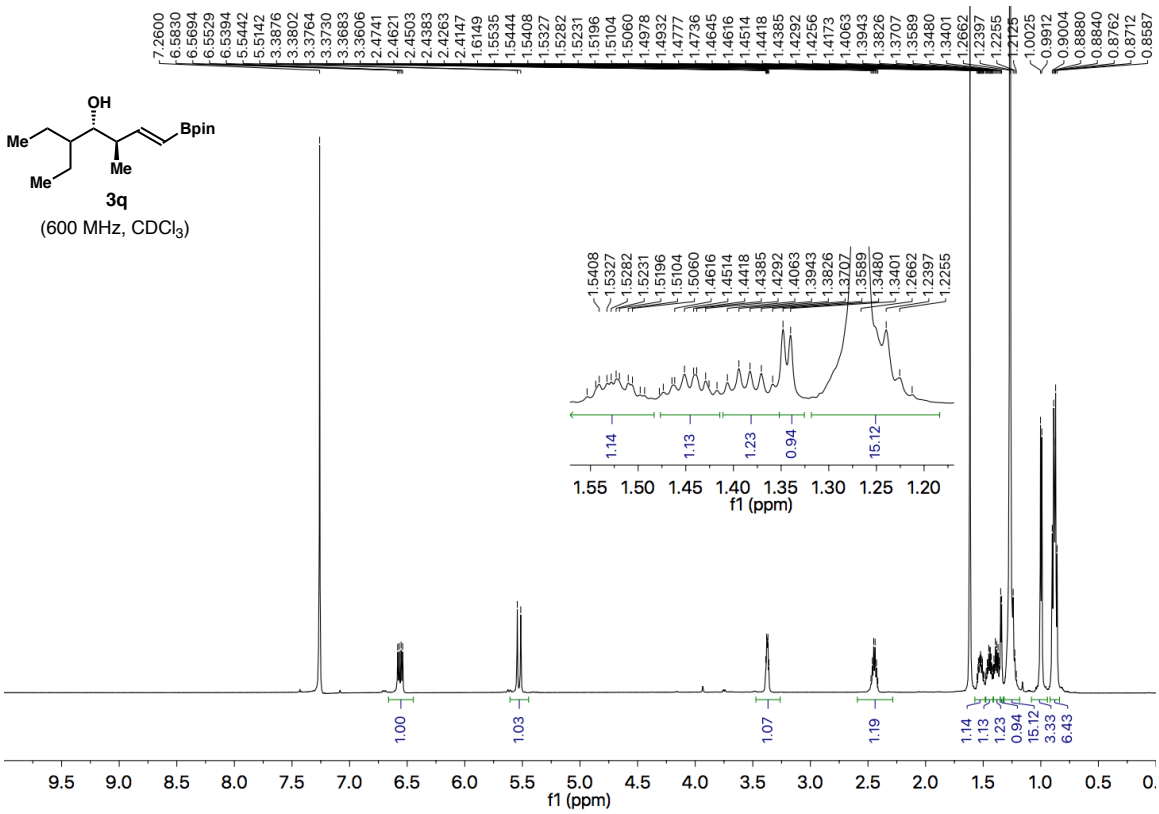

178.3122
156.4239
155.2134
153.6684
134.2425
125.9571
125.6175
124.1680
124.1221
120.6597
118.5012
83.5102
77.5717
77.3000
77.1482
73.2837
45.3196
25.1343
25.0831
17.0928
O
OH
Bpin
Me
O
3n
(151 MHz, CDCl3)
125.9571
125.6175
124.1680
124.1221
126.5 126.0 125.5 125.0 124.5 124.0
f1 (ppm)
25.1343
25.0831
25.4 25.3 25.2 25.1 25.0 24.9 24.8
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

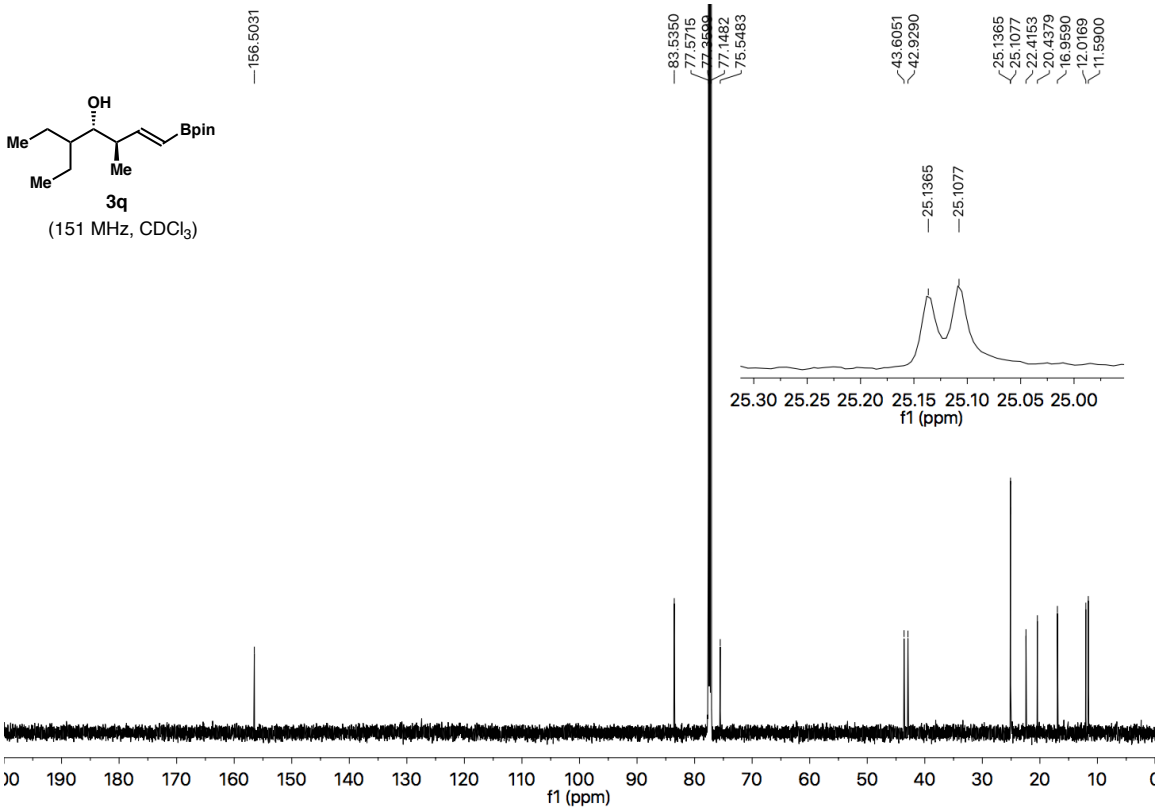

OH
Bpin
Me
3o
(600 MHz, CDCl3)
f1 (ppm)

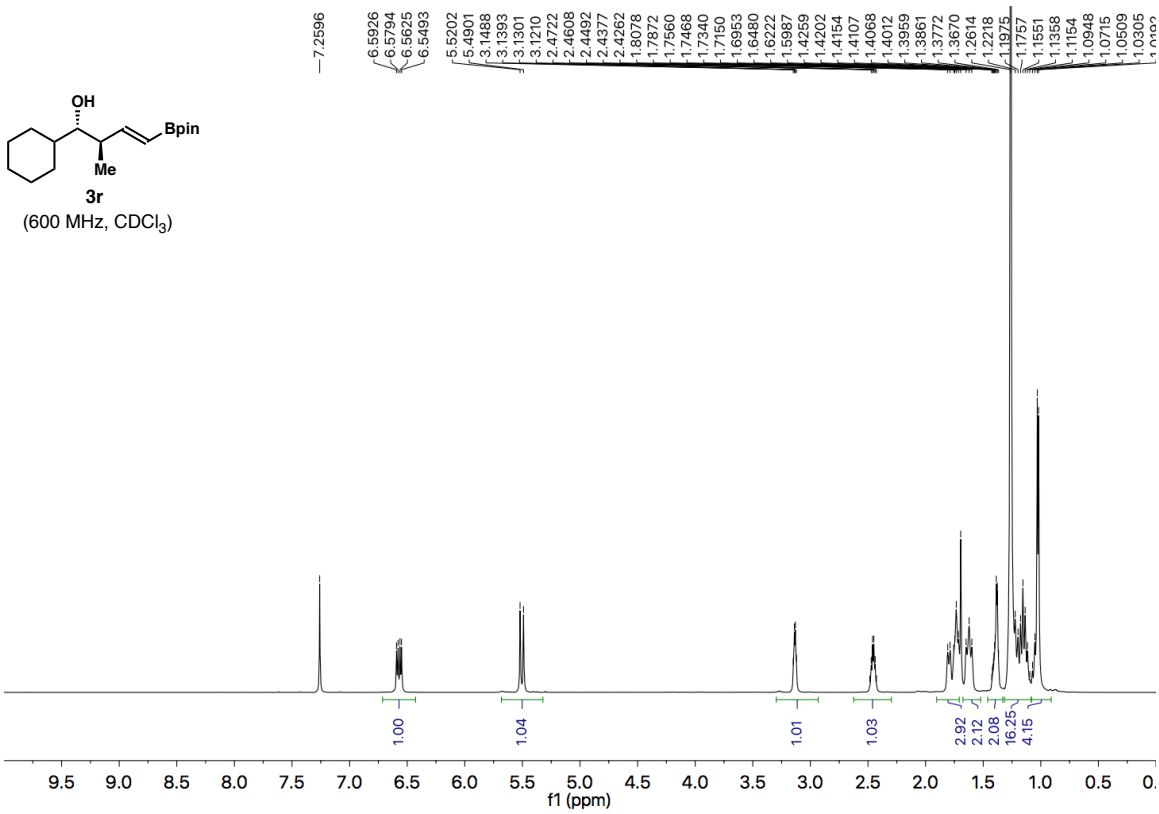

OH
Bpin
Me
3o
(151 MHz, CDCl3)
f1 (ppm)

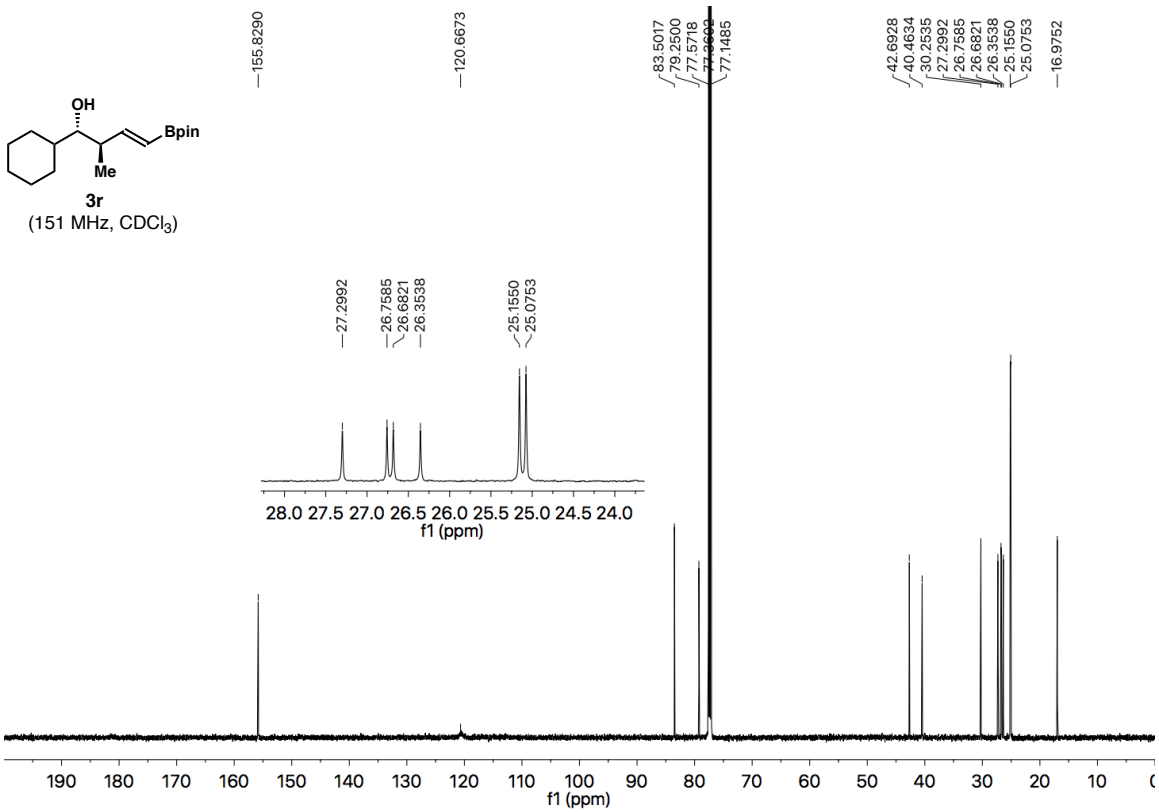

OH
Me
Bpin
Me
3p
(600 MHz, CDCl3)
7.2597
6.5674
6.5544
6.5373
6.5243
5.5221
5.4920
3.4647
3.4590
3.4511
3.4427
3.4352
3.4279
3.3247
2.3134
2.3021
2.2910
2.2799
2.2690
1.6553
1.5172
1.5079
1.4885
1.4813
1.4720
1.4599
1.4540
1.4421
1.3876
1.3714
1.3563
1.3410
1.3279
1.3176
1.3076
1.2952
1.2834
1.2658
1.0364
1.0252
0.8868
0.8765
0.8653
1.00
1.05
0.96
1.03
2.87
19.38
3.25
3.44
f1 (ppm)

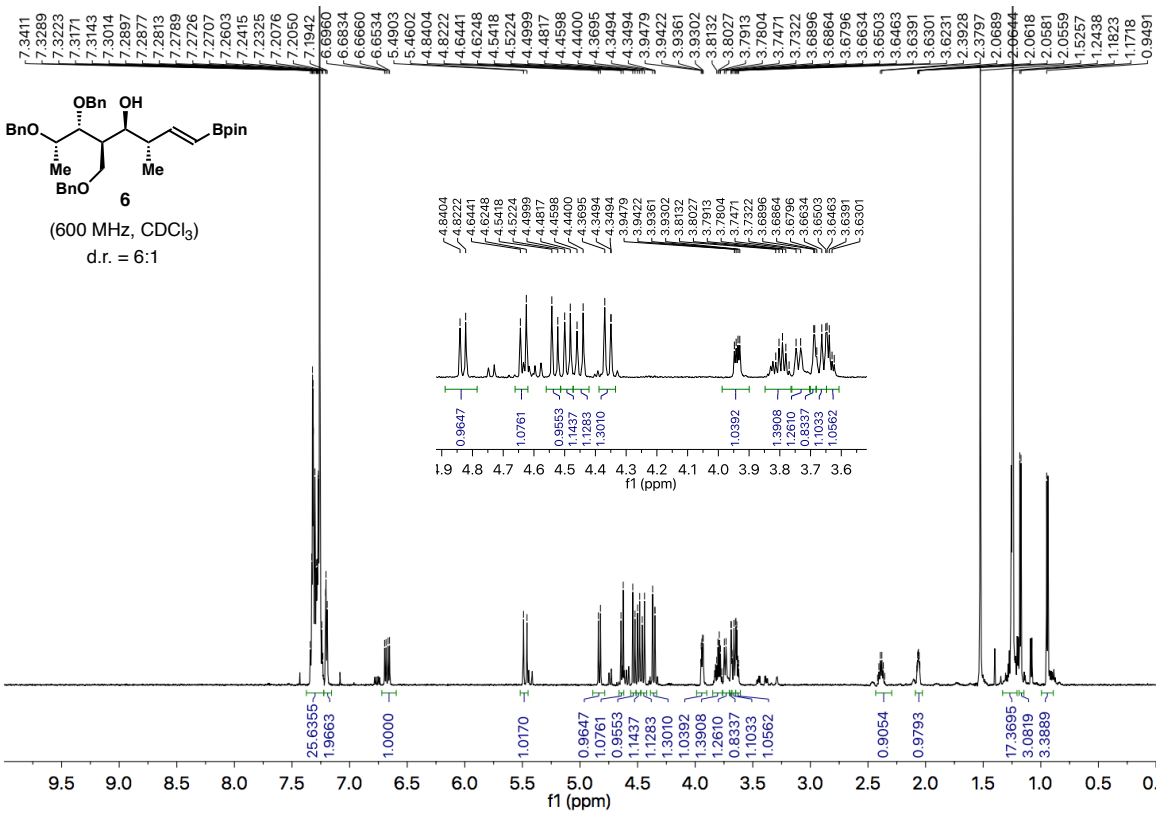

OH
Me
Bpin
Me
3p
(151 MHz, CDCl3)
155.7439
120.6583
83.5337
77.5720
77.1486
74.9698
46.2304
34.4020
32.2251
25.7838
25.1545
25.0810
23.0332
16.0945
14.4759
25.7838
25.1545
25.0810
26.5
26.0
25.5
25.0
f1 (ppm)
f1 (ppm)

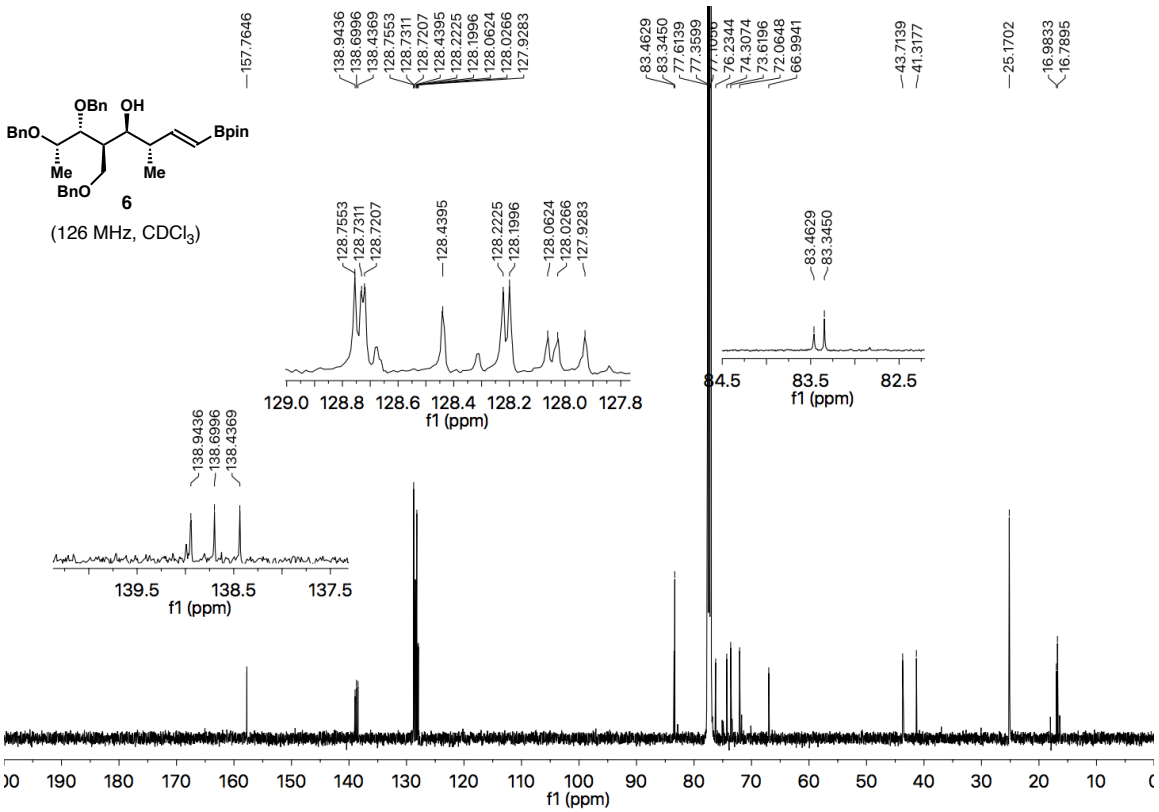

OH
Bpin
Me
Me
Me
3q
(600 MHz, CDCl3)
f1 (ppm)

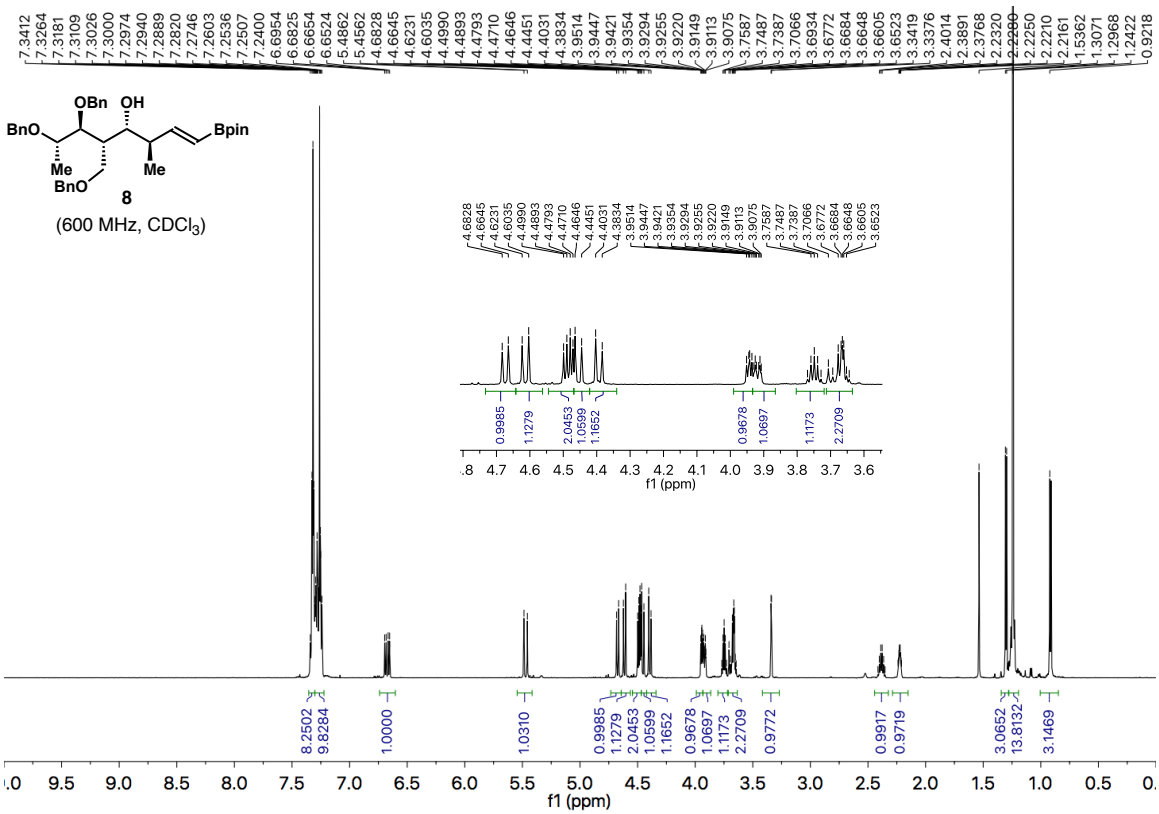

OH
Bpin
Me
Me
Me
3q
(151 MHz, CDCl3)
f1 (ppm)

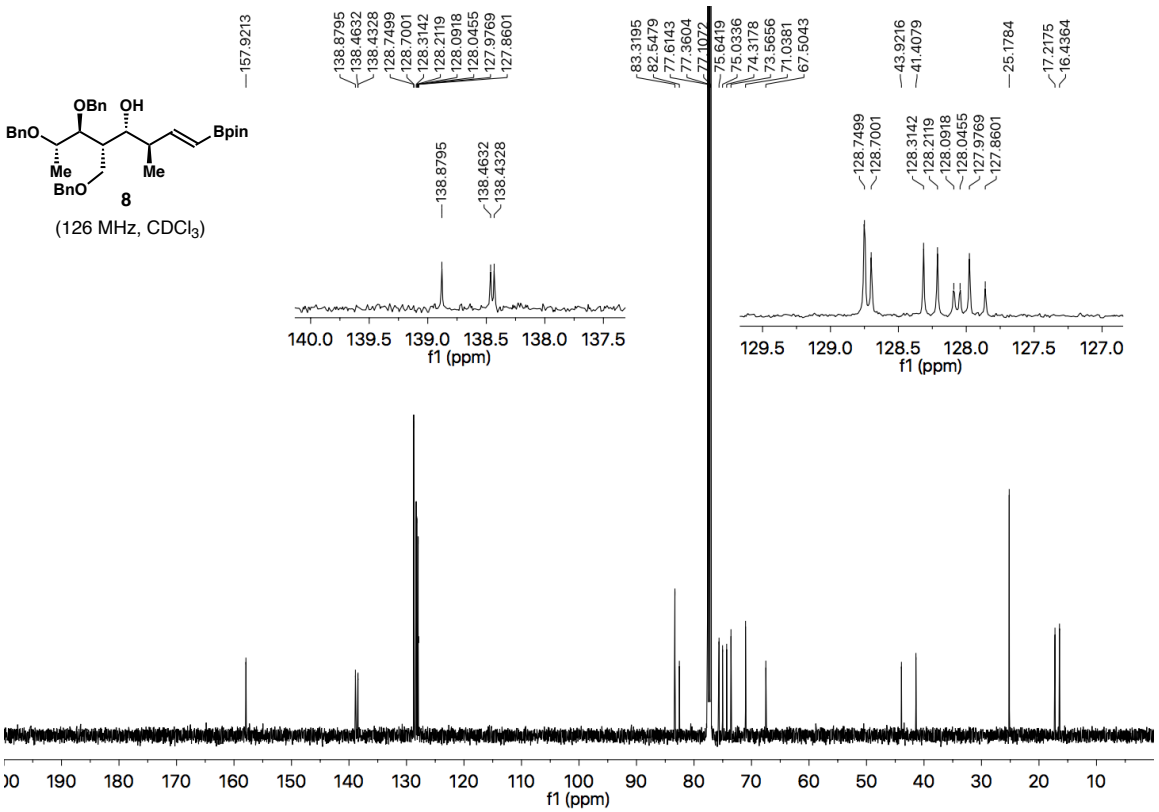

OH
Bpin
Me
3r
(600 MHz, CDCl3)
7.2596
6.5926
6.5794
6.5625
6.5493
5.5202
5.4901
3.1488
3.1393
3.1301
3.1210
2.4722
2.4608
2.4492
2.4377
2.4262
1.8078
1.7872
1.7560
1.7468
1.7340
1.7150
1.6953
1.6480
1.6222
1.5987
1.4259
1.4202
1.4154
1.4107
1.4068
1.4012
1.3959
1.3861
1.3772
1.3670
1.2614
1.2218
1.1975
1.1757
1.1551
1.1358
1.1154
1.0948
1.0715
1.0509
1.0305
1.00
1.04
1.01
1.03
2.92
2.12
2.08
16.25
4.15
f1 (ppm)

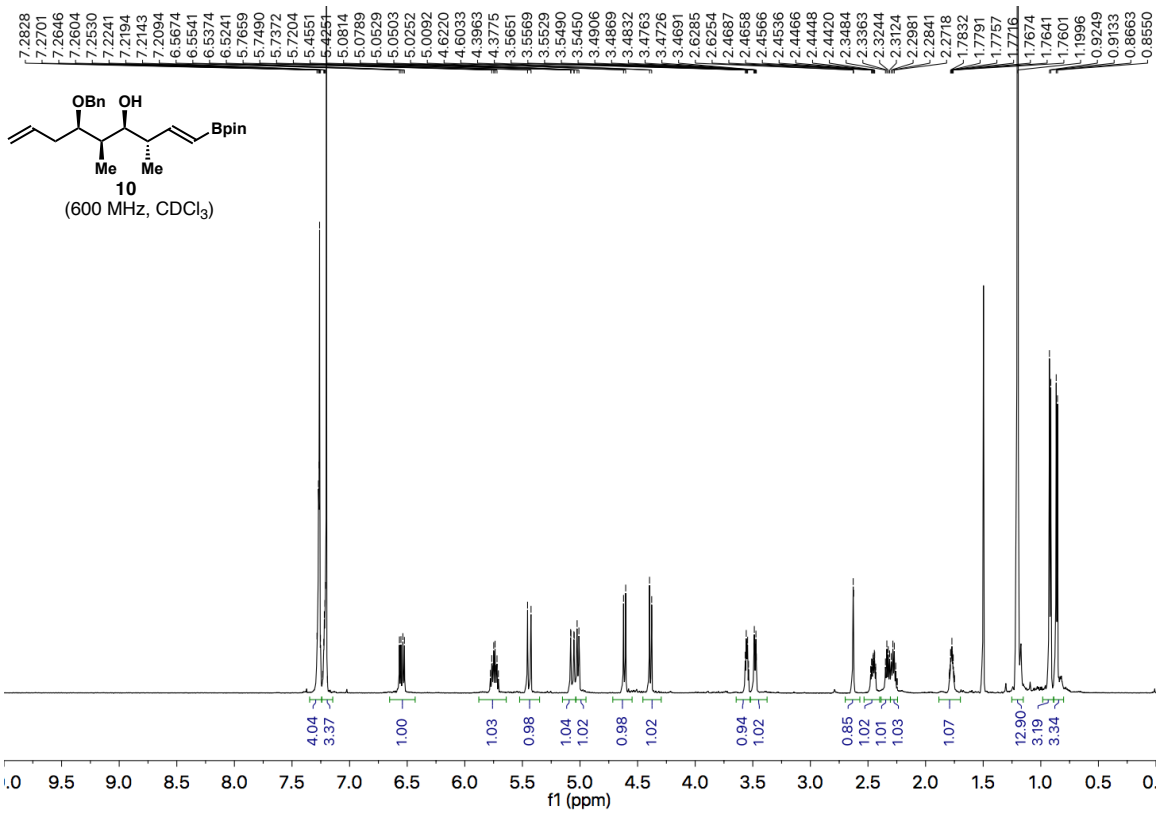

OH
Bpin
Me
3r
(151 MHz, CDCl3)
155.8290
120.6673
83.5017
79.2500
77.5718
77.3600
77.1485
42.6928
40.4634
30.2535
27.2992
26.7585
26.6821
26.3538
25.1550
25.0753
16.9752
27.2992
26.7585
26.6821
26.3538
25.1550
25.0753
28.0 27.5 27.0 26.5 26.0 25.5 25.0 24.5 24.0
f1 (ppm)
f1 (ppm)

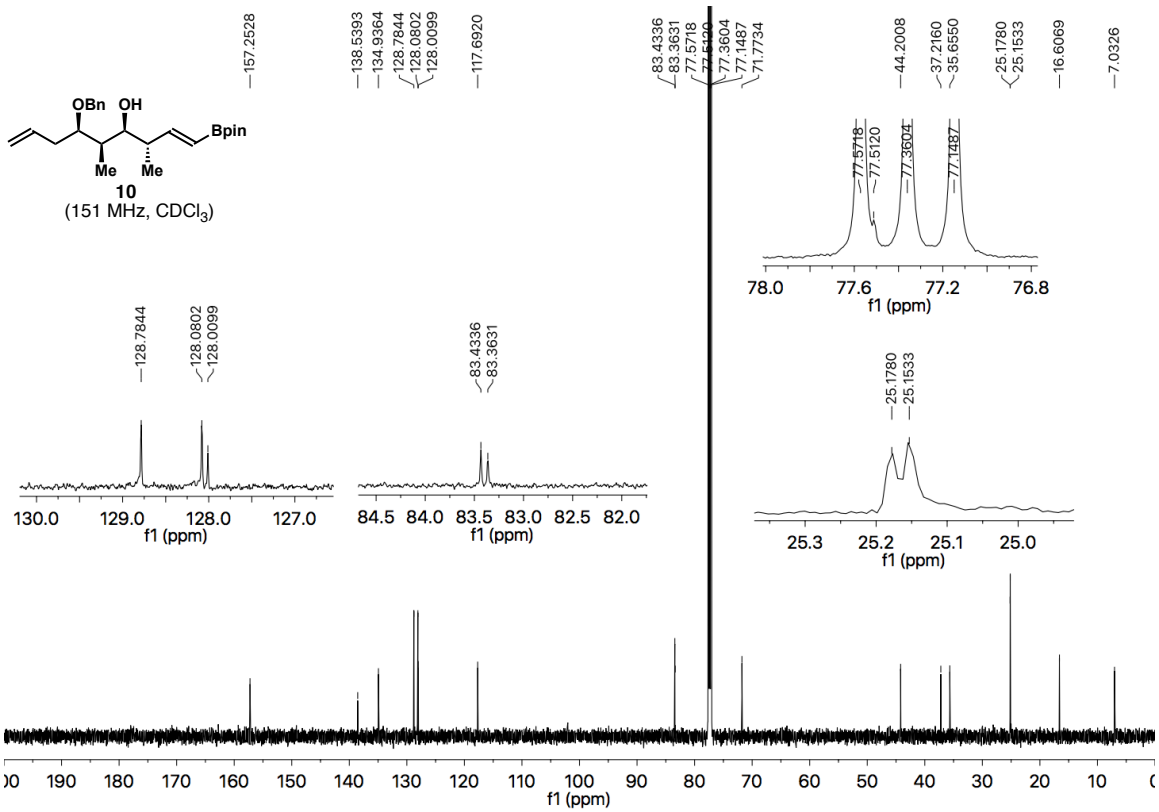

OBn
OH
BnO
Bpin
Me
Me
BnO
6
(600 MHz, CDCl3)
d.r. = 6:1
f1 (ppm)

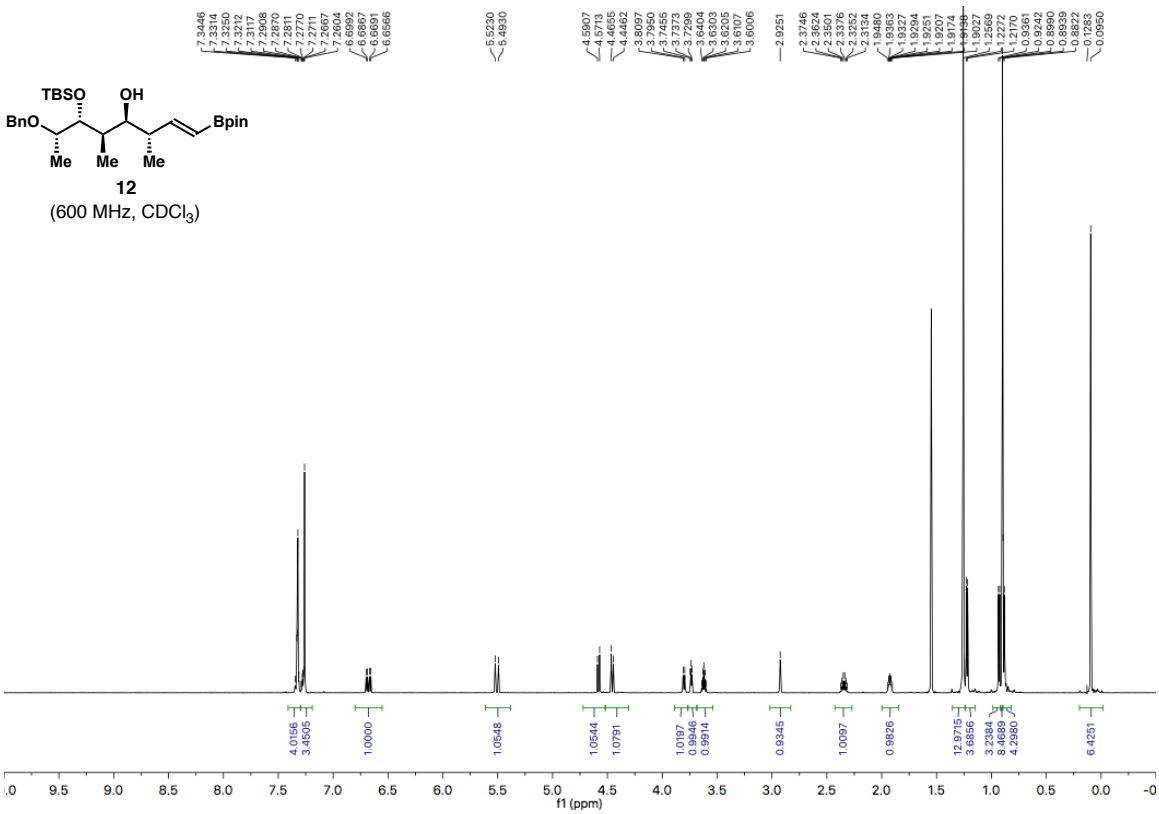

OBn
OH
BnO
Bpin
Me
Me
BnO
6
(126 MHz, CDCl3)
f1 (ppm)

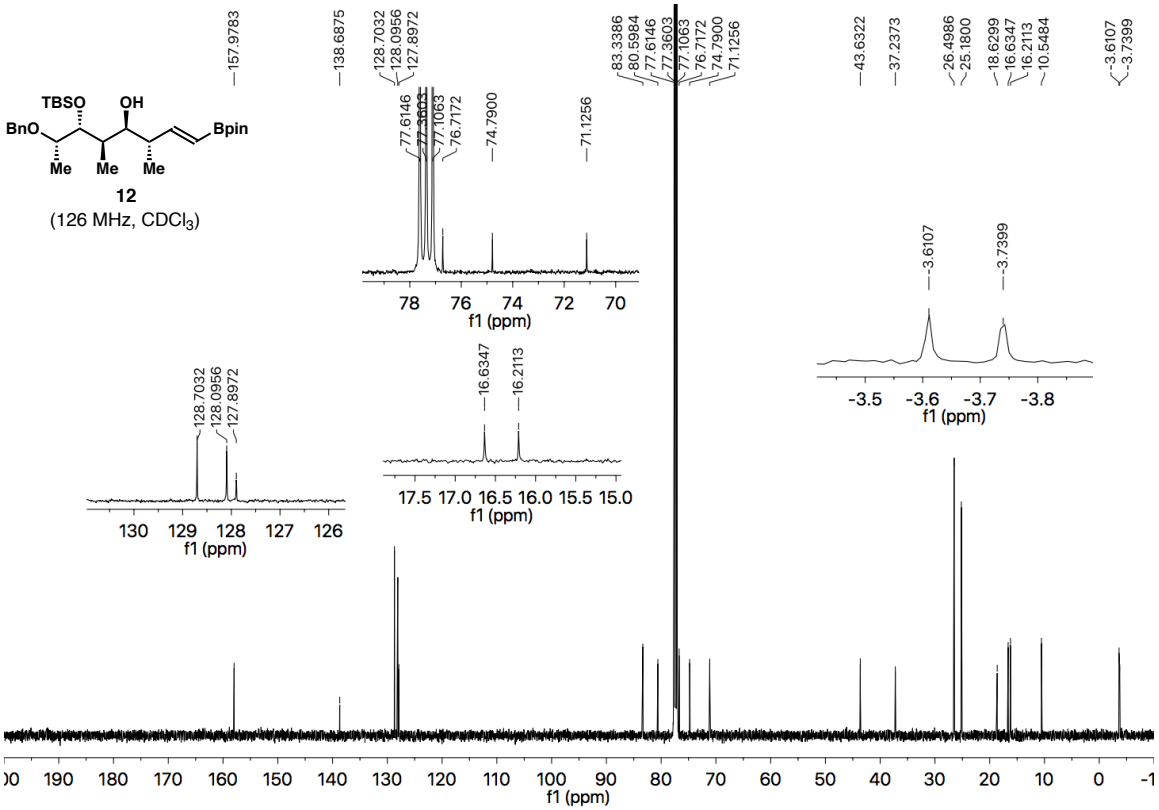

OBn
OH
BnO
Bpin
Me
Me
BnO
8
(600 MHz, CDCl3)
f1 (ppm)

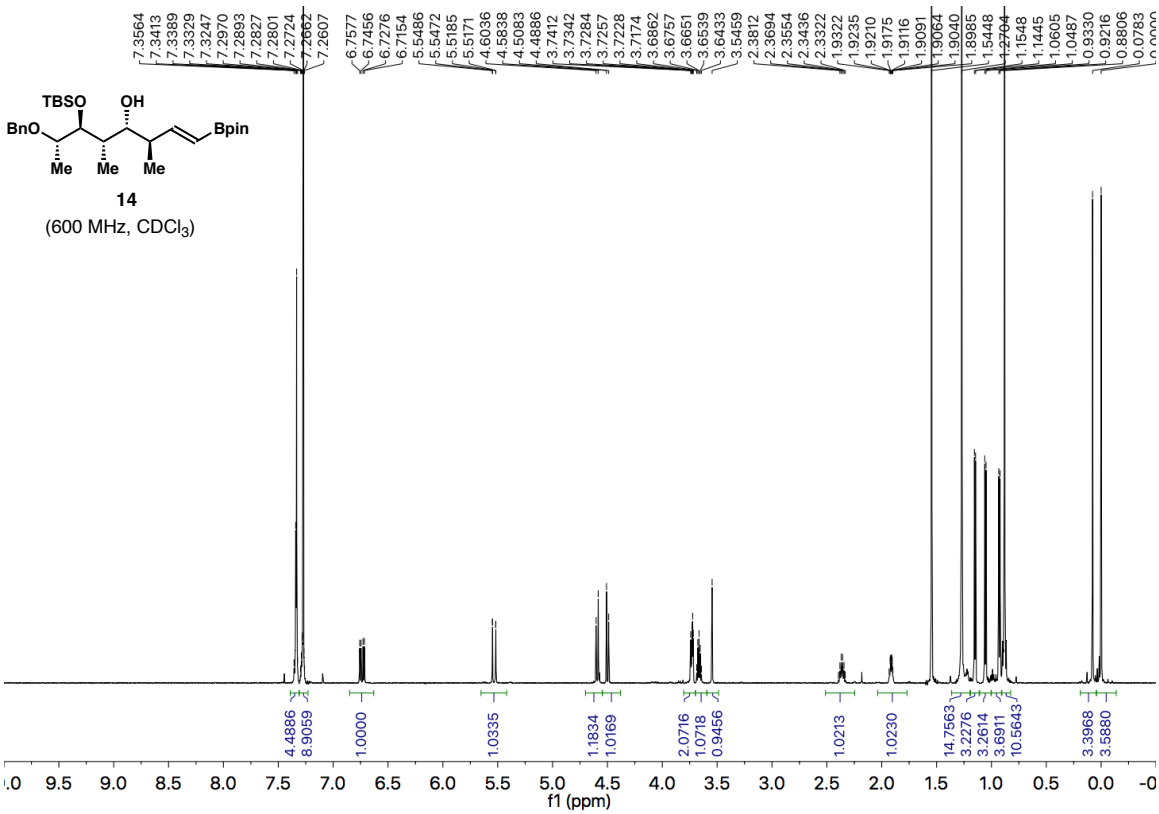

OBn
OH
BnO
Bpin
Me
Me
BnO
8
(126 MHz, CDCl3)
f1 (ppm)

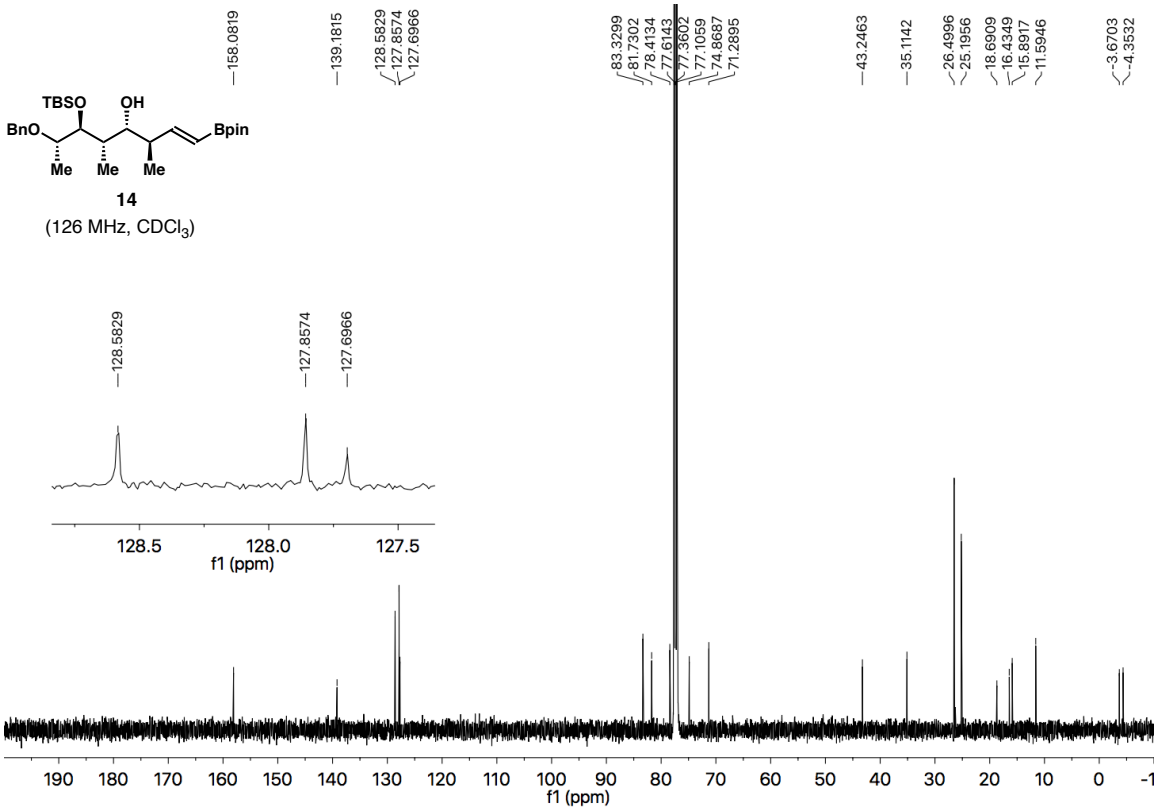

OBn OH
Bpin
Me Me
10
(600 MHz, CDCl3)
f1 (ppm)

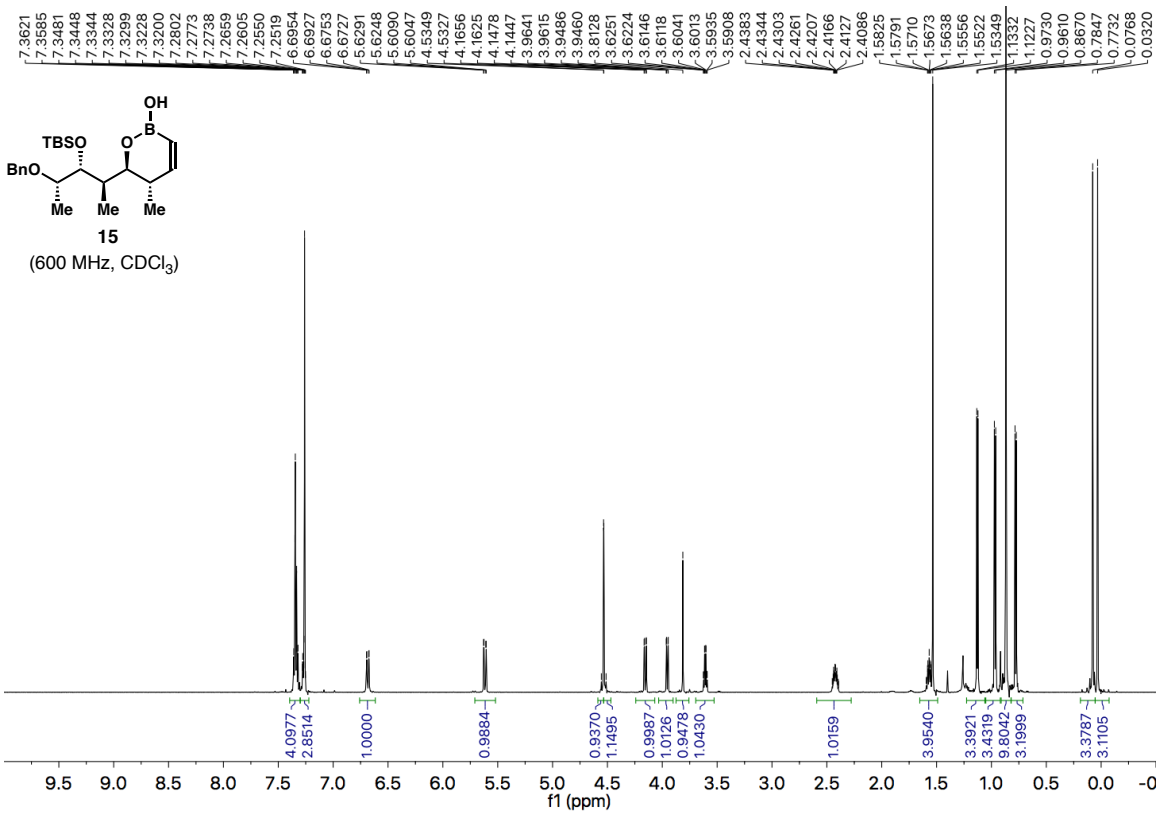

OBn OH
Bpin
Me Me
10
(151 MHz, CDCl3)
f1 (ppm)

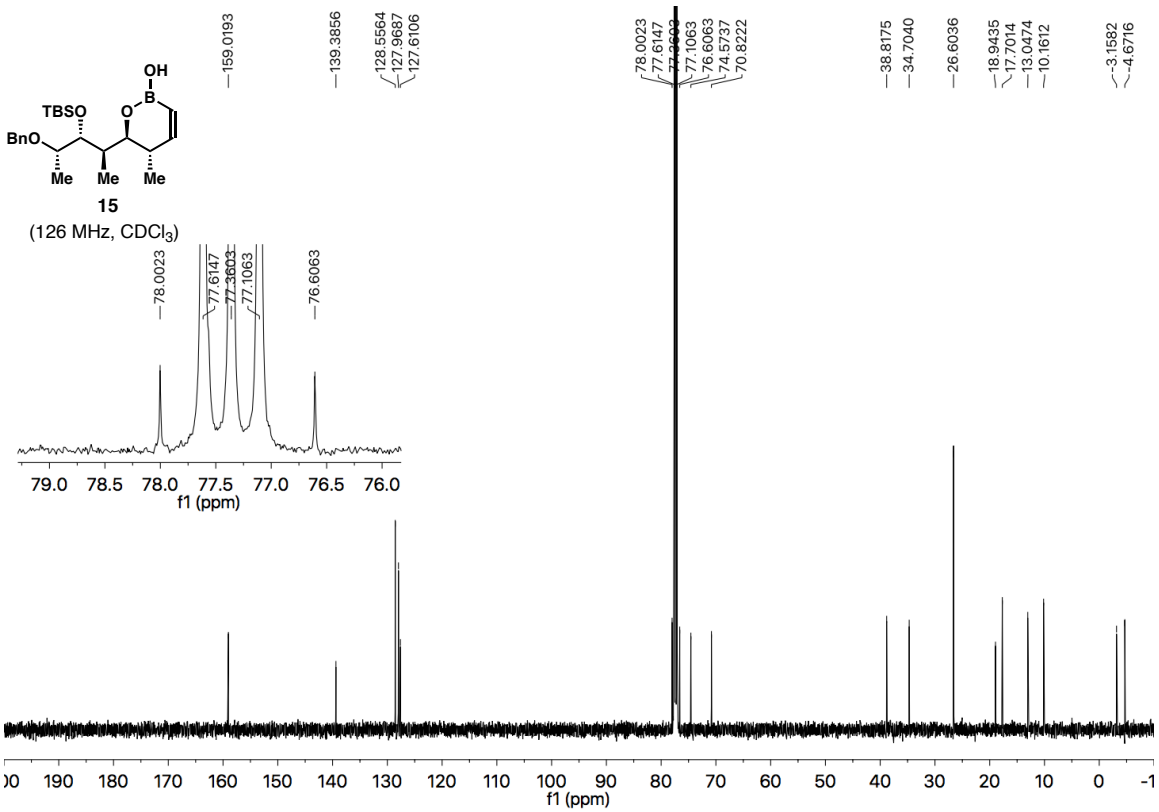

TBSO
OH
BnO
Bpin
Me
Me
Me
12
(600 MHz, CDCl3)
f1 (ppm)

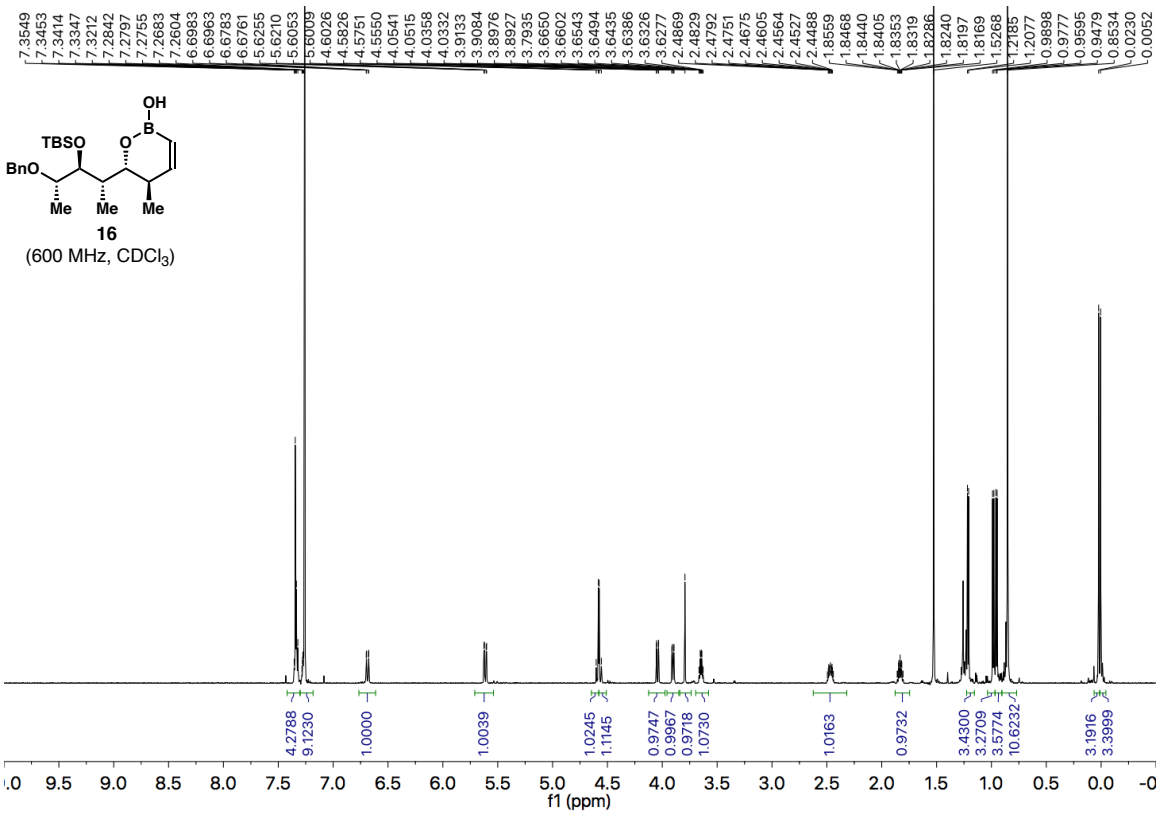

TBSO
OH
BnO
Bpin
Me
Me
Me
12
(126 MHz, CDCl3)
f1 (ppm)

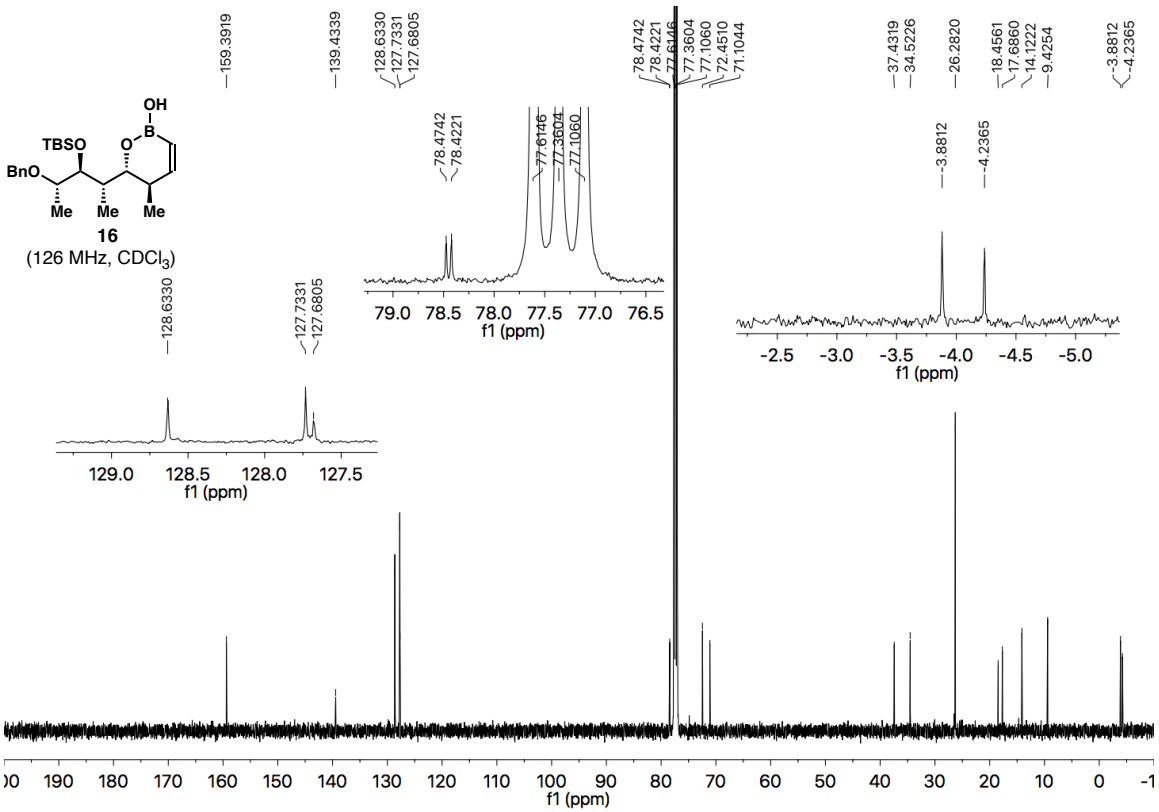

TBSO
OH
BnO
Bpin
Me
Me
Me
14
(600 MHz, CDCl3)
f1 (ppm)

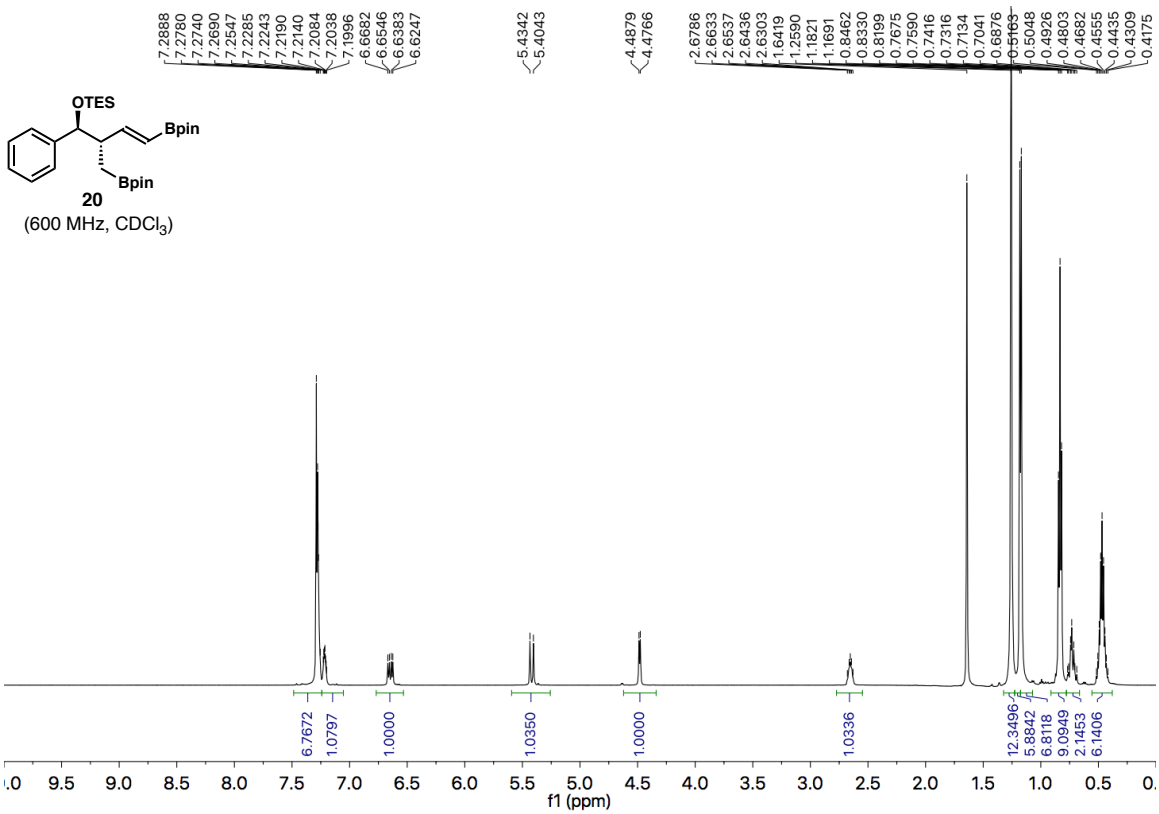

TBSO
OH
BnO
Bpin
Me
Me
Me
14
(126 MHz, CDCl3)
f1 (ppm)

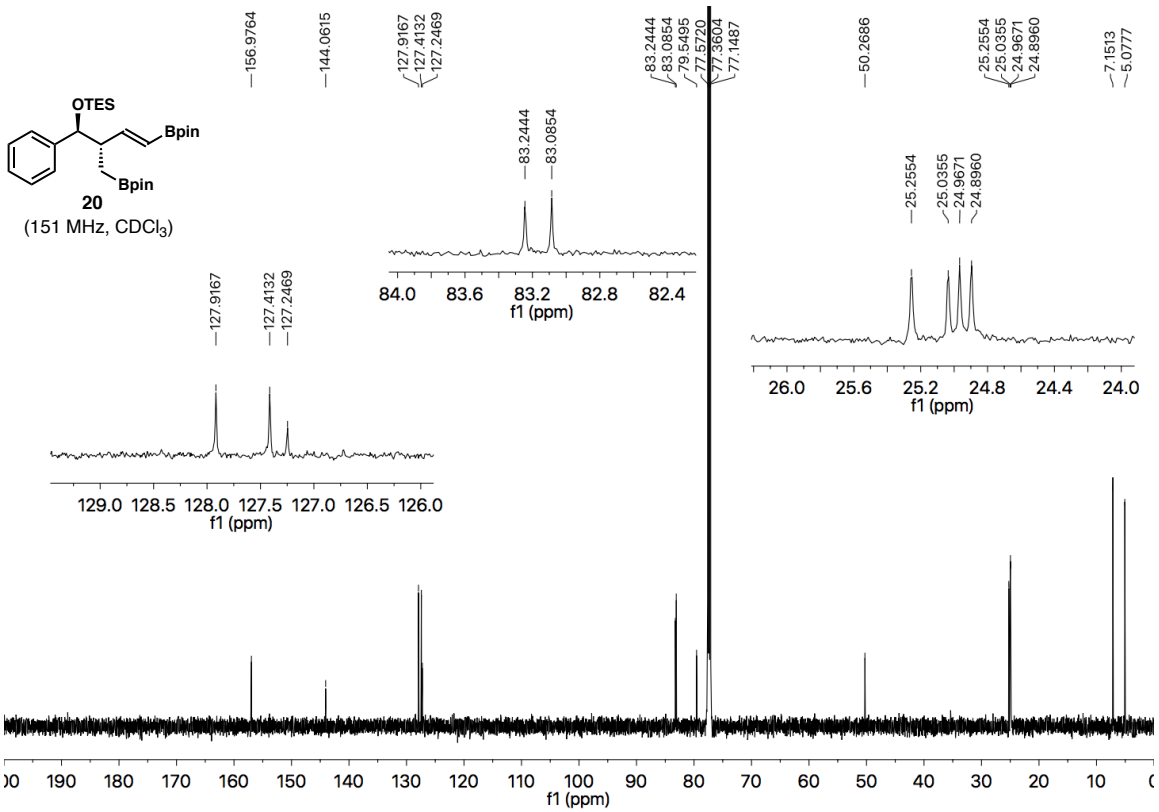

OH
B
O
TBSO
BnO
Me
Me
Me
15
(600 MHz, CDCl3)
f1 (ppm)

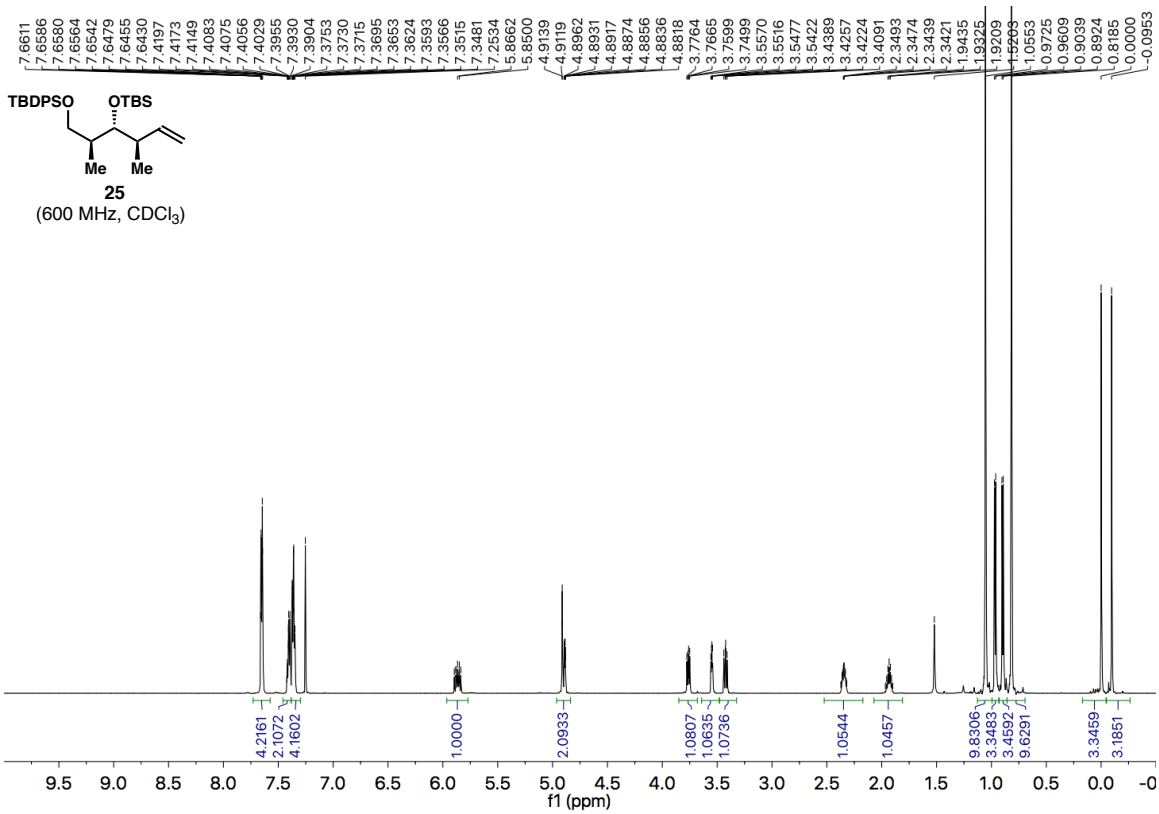

OH
B
O
TBSO
BnO
Me
Me
Me
15
(126 MHz, CDCl3)
f1 (ppm)

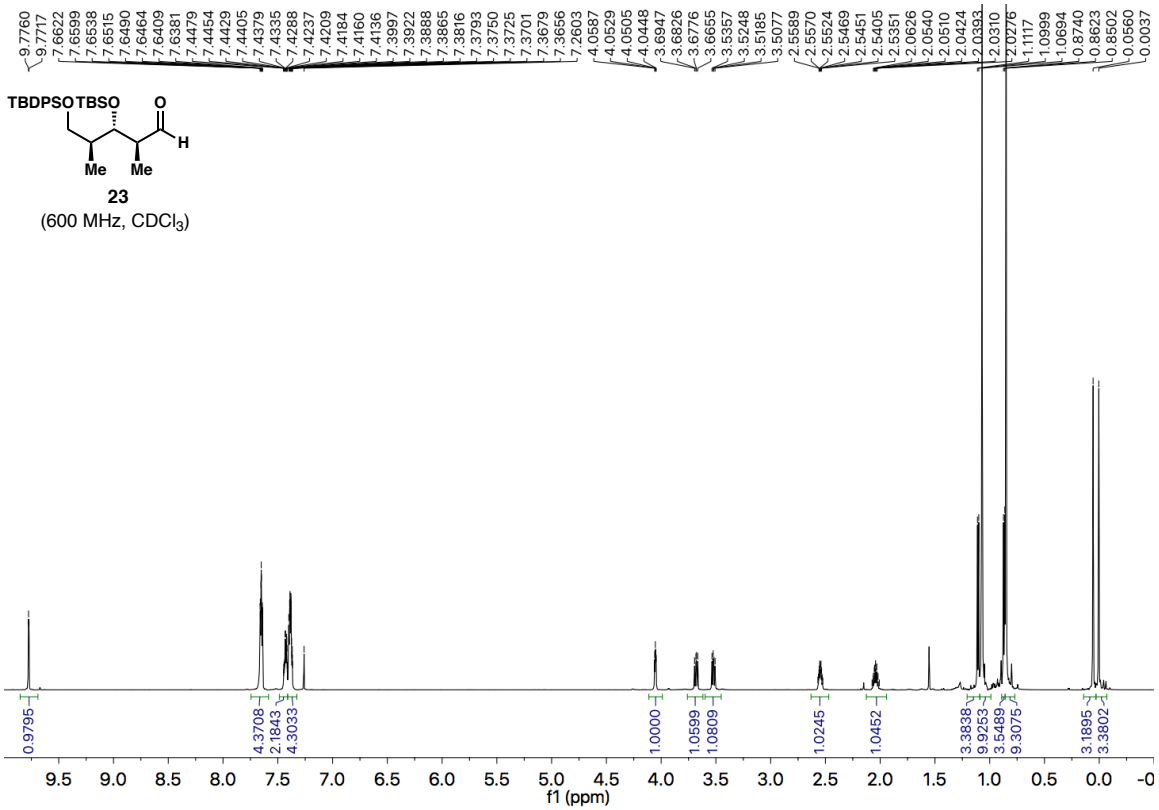

OH
B
O
TBSO
BnO
Me
Me
Me
16
(600 MHz, CDCl3)
f1 (ppm)

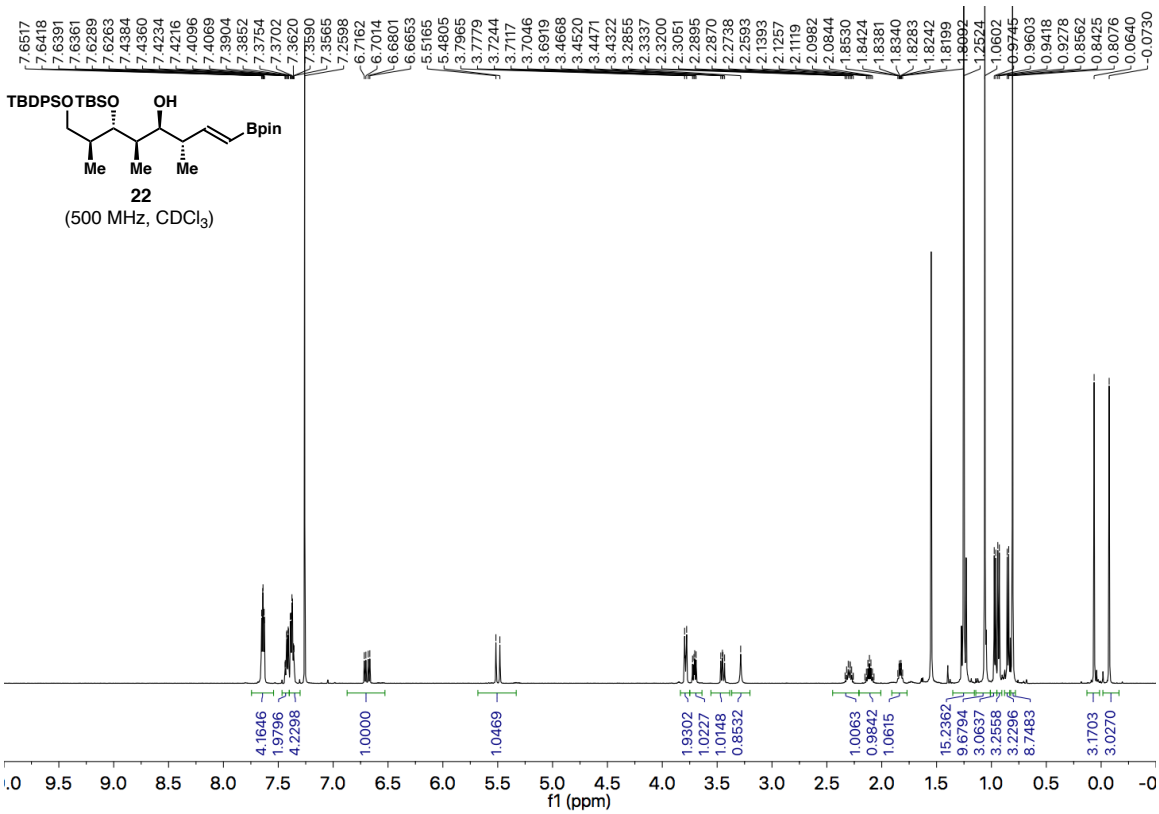

OH
B
O
TBSO
BnO
Me
Me
Me
16
(126 MHz, CDCl3)
f1 (ppm)

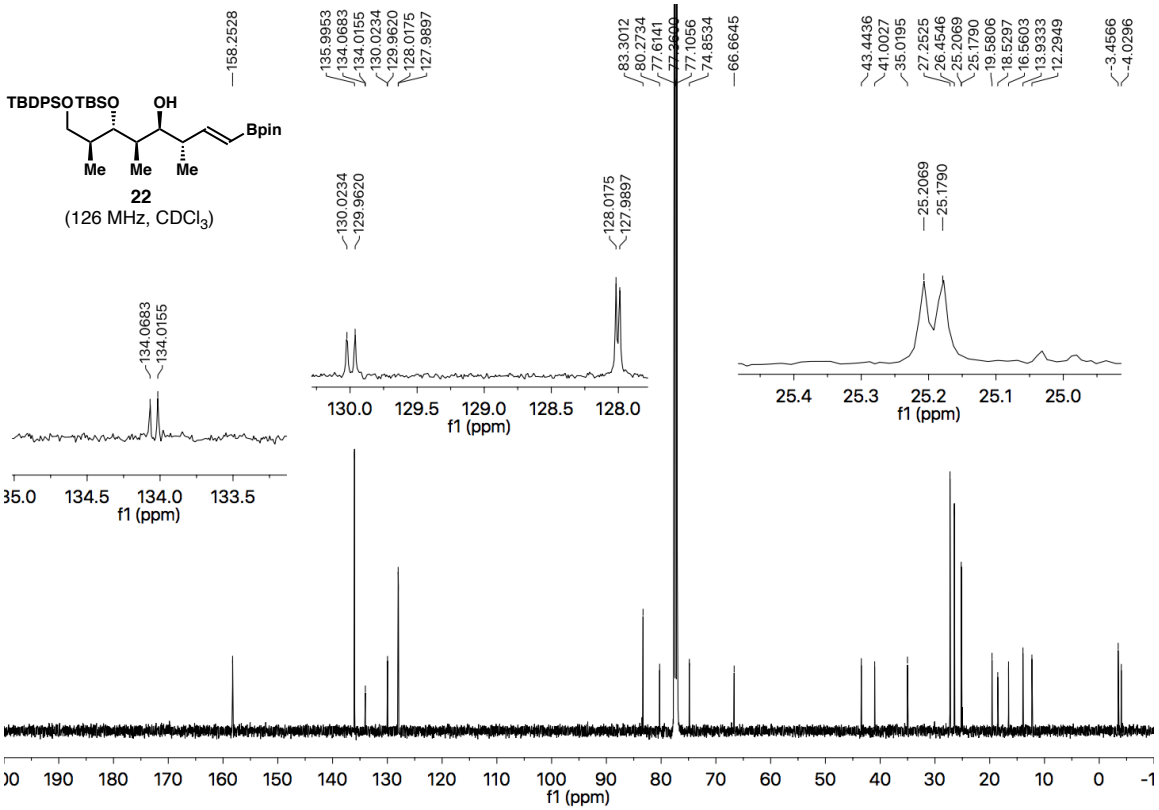

OTES
Bpin
Bpin
20
(600 MHz, CDCl3)
f1 (ppm)

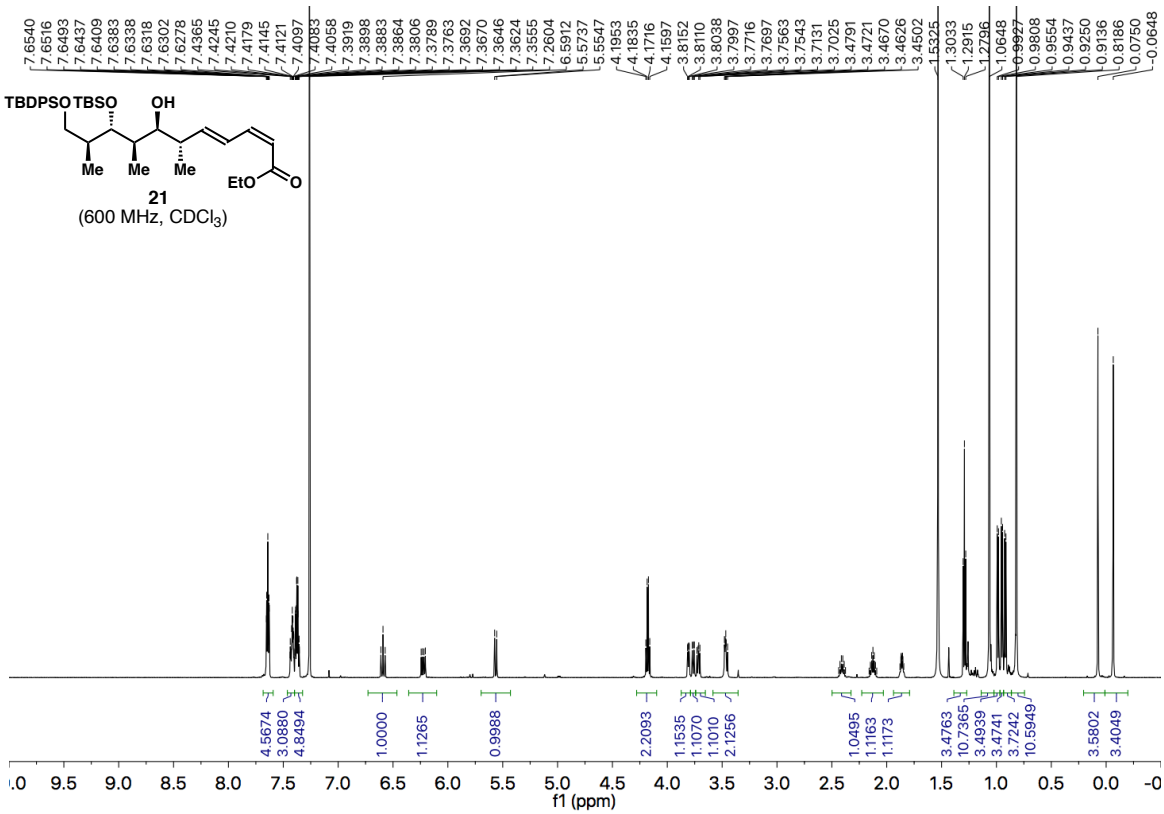

OTES
Bpin
Bpin
20
(151 MHz, CDCl3)
f1 (ppm)

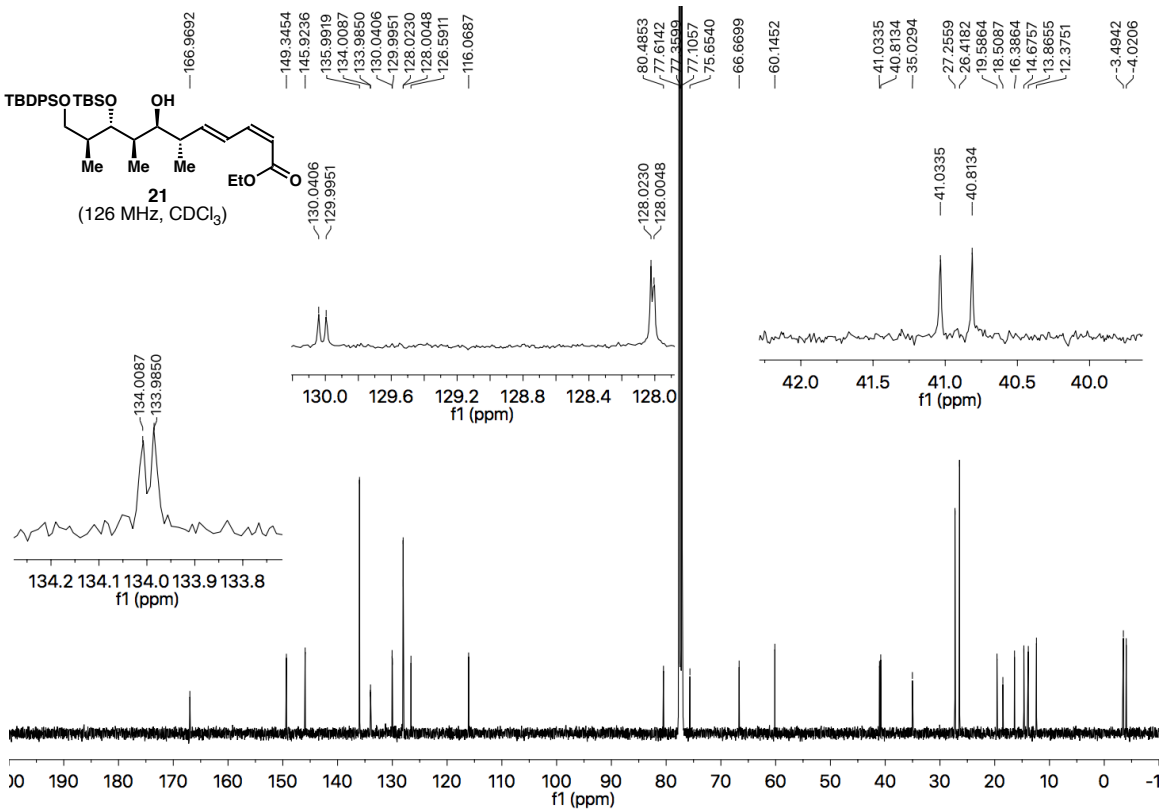

TBDPSO
OTBS
Me
Me
25
(600 MHz, CDCl3)
f1 (ppm)


TBDPSO
TBSO
O
H
Me
Me
23
(600 MHz, CDCl3)
f1 (ppm)

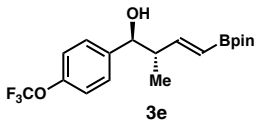

TBDPSO TBSO OH
Bpin
Me Me Me
22
(500 MHz, CDCl3)
f1 (ppm)


TBDPSO TBSO OH
Bpin
Me Me Me
22
(126 MHz, CDCl3)
f1 (ppm)


TBDPSO TBSO OH
Me Me Me
EtO O
21
(600 MHz, CDCl3)
f1 (ppm)


TBDPSO TBSO OH
Me Me Me
EtO O
21
(126 MHz, CDCl3)
f1 (ppm)

^{19}F NMR of compound 3e:



3e

(^{19}F NMR, 471 MHz)