(*Z*)-α-Boryl-crotylboron Reagents via *Z*-Selective Alkene Isomerization and Application to Stereoselective Syntheses of (*E*)-δ-Boryl-*syn*-Homoallylic Alcohols

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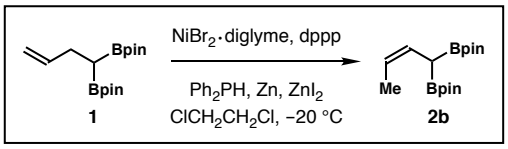
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

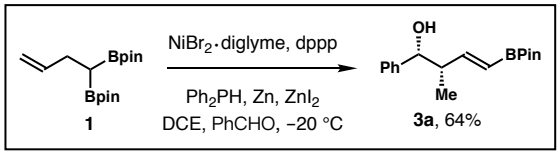
General Experimental Details. All reaction solvents were purified before use. Dichloromethane, 1,2-dichloroethane and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using 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 the removal of residual solvents 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 the 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. 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.

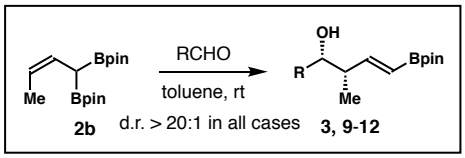


(*Z*)-2,2'-(But-2-ene-1,1-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b): In an Ar-filled glove box, $NiBr_2$·diglyme (7.0 mg, 0.02 mmol, 10 mol %), dppp (8.2 mg, 0.02 mmol, 10 mol %), zinc powder (2.6 mg, 0.04 mmol, 20 mol %), anhydrous zinc iodide (12.6 mg, 0.04 mmol, 20 mol %) and a Teflon-coated magnetic stirring bar were sequentially added into a reaction tube. The tube was capped with a rubber septum and removed from glove box. Anhydrous 1,2-dichloroethane (DCE, 0.3 mL) was added and the mixture was stirred for 10 min. Then Ph_2PH (1.9 mg, 0.01 mmol, 5 mol %) in 0.1 mL DCE were added to the reaction mixture. The reaction tube was placed in a cold bath and cooled to −20 °C and stirred stirring for 5 min. Then homoallylic boronate **1** (61.6 mg, 0.2 mmol, 1.0 equiv) was added and the reaction mixture was stirred at −20 °C for 12 h. After complete consumption of boronate **1**, diethyl ether (5 mL) was added and the resulting mixture was filtered through a pad of silica gel. The solvent was removed under reduced pressure. The *Z*/*E* ratio (> 20:1) was determined by ^{1}H NMR analysis of the crude reaction mixture. Purification of the crude product by flash chromatography (gradient elution with hexane and ethyl acetate) gave product **2b** in 70 % yield (43 mg) as a white solid. When the reaction was run in a 2-mmol scale, **2b** was isolated in 74% yield (456 mg, *Z*/*E* > 20 :1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.63 (ddq, *J* = 10.3, 10.2, 1.3 Hz, 1H), 5.430 (dq, *J* = 10.3, 6.6 Hz, 1H), 1.98 (d, *J* = 9.9 Hz, 1H), 1.53 (dd, *J* = 6.6, 1.4 Hz, 3H), 1.21 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 126.5, 122.5, 83.5, 25.0, 24.9, 13.1, 12.3. HRMS (EI^+): *m*/*z* for $C_{16}H_{30}B_2O_4$ $[M]^+$ calcd. 308.2330, found 308.2335.

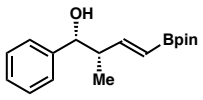


Procedure for one-pot alkene isomerization and crotylboration with benzaldehyde from boronate 1: The procedure for the synthesis of boronate **2b** was adopted. After the addition of homoallylic boronate **1** (92.4 mg, 0.3 mmol, 1.5 equiv), benzaldehyde (0.2 mmol, 1.0 equiv) was added to the reaction vessel and the reaction mixture was stirred at −20 °C for 24 h. After complete consumption of benzaldehyde, diethyl ether (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

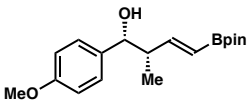
chromatography (gradient elution with n-hexane and ethyl acetate) to give product **3a** in 64 % yield (37 mg) as a colorless oil.



General procedure for crotylboration of aldehydes with reagent 2b: To a reaction flask containing a stirring bar was added freshly distilled aldehydes (0.1 mmol, 1.0 equiv, if it is a liquid). Toluene (0.3 mL) and crotylboronates **2b** (40 mg, 0.13 mmol, 1.3 equiv) were added to the flask. The reaction mixture was kept stirring for 12 h at ambient temperature. After complete consumption of the aldehyde, 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 the homoallylic alcohol product.

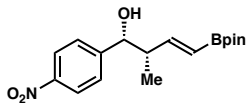


***rac*-(1*R*,2*S*,*E*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3a)**[1] Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 90% yield (24.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.37 (m, 4H), 7.24 – 7.26 (m, 1H), 6.67 (dd, *J* = 18.1, 6.5 Hz, 1H), 5.51 (d, *J* = 18.2 Hz, 1H), 4.77 (d, *J* = 2.6 Hz, 1H), 2.63 – 2.65 (m, 1H), 1.86 (br, 1H), 1.26 (s, 12H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 142.8, 128.4, 127.6, 126.5, 120.0, 83.5, 76.6, 46.6, 25.13, 25.05, 12.8. HRMS (ESI^+): *m*/*z* for $C_{17}H_{25}BO_3Na$ $[M+Na]^+$ calcd. 311.1794, found 311.1806.

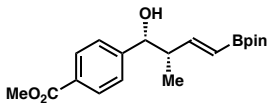


***rac*-(1*R*,2*S*,*E*)-1-(4-Methoxyphenyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3b)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 94% yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.63 (dd, *J* = 18.2, 6.5 Hz, 1H), 5.48 (d, *J* = 18.1 Hz, 1H), 4.69 (d, *J* = 4.9 Hz, 1H), 3.80 (s, 3H), 2.58 – 2.63 (m, 1H), 1.83 (s, 1H), 1.25 (s, 12H), 0.98 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 155.9, 134.9, 127.7, 119.7, 113.7, 83.5, 76.5, 55.6, 46.7, 25.1, 25.0, 13.3. HRMS (EI^+): *m*/*z* for $C_{18}H_{25}BO_3$ $[M–H_2O]^+$ calcd. 300.1897, found 300.1913.

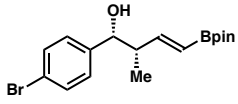
1. T. Miura, J. Nakahashi and M. Murakami, *Angew. Chem., Int. Ed*, 2017, **56**, 6989.



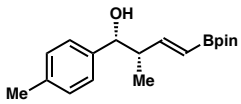
***rac*-(1*R*,2*S*,*E*)-2-Methyl-1-(4-nitrophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3c)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as white solid in 78% yield (26 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 18.1, 6.4 Hz, 1H), 5.53 (d, *J* = 18.2 Hz, 1H), 4.88 (d, *J* = 3.8 Hz, 1H), 2.64 – 2.67 (m, 1H), 2.05 (br, 1H), 1.27 (s, 12H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 150.2, 147.4, 127.4, 123.7, 83.7, 75.7, 46.5, 25.1, 25.0, 12.5. HRMS (ESI^-): *m*/*z* for $C_{17}H_{24}BNO_5Cl$[M+Cl]- calcd. 368.1436, found 368.1453



***rac*-Methyl-4-((1*R*,2*S*,*E*)-1-hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)benzoate (3d)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as white solid in 93% yield (32.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.64 (dd, *J* = 18.1, 6.5 Hz, 1H), 5.51 (d, *J* = 18.1 Hz, 1H), 4.82 (d, *J* = 4.4 Hz, 1H), 3.91 (s, 3H), 2.61 – 2.68 (m, 1H), 1.95 (br, 1H), 1.26 (s, 12H), 0.95 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 155.2, 148.0, 129.8, 129.4, 126.6, 120.2, 83.6, 76.3, 52.4, 46.6, 25.15, 25.08, 12.8. HRMS (ESI^+): *m*/*z* for $C_{19}H_{27}BO_5Na$ $[M+Na]^+$ calcd. 369.1849, found 369.1814.

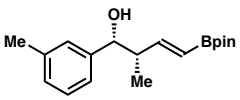


***rac*-(1*R*,2*S*,*E*)-1-(4-Bromophenyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3e)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as white solid in 85% yield (31.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.62 (dd, *J* = 18.2, 6.5 Hz, 1H), 5.50 (dd, *J* = 18.1, 0.8 Hz, 1H), 4.72 (d, *J* = 4.5 Hz, 1H), 2.57 – 2.62 (m, 1H), 1.89 (s, 1H), 1.26 (s, 12H), 0.95 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 141.7, 131.5, 128.3, 121.3, 120.2, 83.6, 76.0, 46.5, 25.13, 25.05, 12.8. HRMS (ESI^+): *m*/*z* for $C_{17}H_{28}BNBrO_3$ $[M+NH_4]^+$ calcd. 384.1346, found 384.1319.

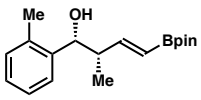


***rac*-(1*R*,2*S*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)but-3-en-1-ol (3f)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 91% yield (27.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.66 (dd, *J*

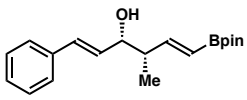
= 18.1, 6.4 Hz, 1H), 5.50 (d, *J* = 18.0 Hz, 1H), 4.73 (d, *J* = 4.5 Hz, 1H), 2.59 – 2.64 (m, 1H), 2.33 (s, 3H), 1.71 (br, 1H), 1.26 (s, 12H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 139.8, 137.2, 129.1, 126.5, 119.6, 83.5, 76.6, 46.6, 25.13, 25.05, 21.5, 12.9. HRMS (ESI^+): *m*/*z* for $C_{18}H_{27}BO_3Na$ $[M+Na]^+$ calcd. 325.1951, found 325.1974.



***rac*-(1*R*,2*S*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*m*-tolyl)but-3-en-1-ol (3g)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 93% yield (28.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.12 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.67 (dd, *J* = 18.2, 6.4 Hz, 1H), 5.50 (dd, *J* = 18.2, 1.0 Hz, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 2.60 – 2.65 (m, 1H), 2.34 (s, 3H), 1.84 (s, 1H), 1.26 (s, 12H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 142.7, 138.0, 128.31, 128.29, 127.2, 123.6, 119.7, 83.5, 76.7, 46.5, 25.1, 25.0, 21.9, 12.8. HRMS (ESI^+): *m*/*z* for $C_{18}H_{27}BO_3Na$ $[M+Na]^+$ calcd. 325.1951, found 325.1963.

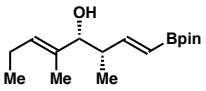


***rac*-(1*R*,2*S*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*o*-tolyl)but-3-en-1-ol (3h)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 94% yield (28.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 1H), 7.22 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.16 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.75 (dd, *J* = 18.2, 6.1 Hz, 1H), 5.55 (d, *J* = 18.2 Hz, 1H), 5.01 (d, *J* = 3.2 Hz, 1H), 2.56 – 2.60 (m, 1H), 2.29 (s, 3H), 1.74 (br, 1H), 1.27 (s, 12H), 1.01 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 141.2, 134.5, 130.6, 127.3, 126.4, 126.2, 119.2, 83.6, 72.8, 44.4, 25.12, 25.07, 19.5, 11.8. HRMS (ESI^+): *m*/*z* for $C_{18}H_{31}BNO_3$ $[M+NH_4]^+$ calcd. 320.2397, found 320.2366.

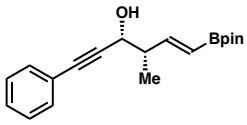


***rac*-(1*E*,3*S*,4*S*,5*E*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-dien-3-ol (3i)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 91% yield (28.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.23 – 7.26 (m, 1H), 6.66 (dd, *J* = 18.1, 7.0 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 6.5 Hz, 1H), 5.57 (d, *J* = 18.1 Hz, 1H), 4.30 (dd, *J* = 4.9, 4.9 Hz, 1H), 2.53 – 2.59 (m, 1H), 1.61 (br, 1H), 1.27 (s, 12H), 1.08 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz,

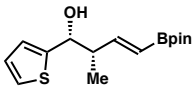
$CDCl_3$) δ 155.2, 137.0, 131.6, 130.1, 128.9, 127.9, 126.8, 120.6, 83.6, 75.7, 45.8, 25.14, 25.10, 14.3. HRMS (EI^+): *m*/*z* for $C_{19}H_{25}BO_2$ $[M-H_2O]^+$ calcd. 296.1948, found 296.1974.



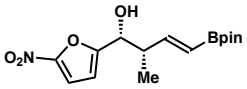
***rac*-(1*E*,3*S*,4*R*,5*E*)-3,5-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,5-dien-4-ol (3j)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 83% yield (23.2 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 6.49 (dd, *J* = 18.1, 7.3 Hz, 1H), 5.44 (d, *J* = 18.0 Hz, 1H), 5.38 (t, *J* = 6.9 Hz, 1H), 3.85 (d, *J* = 6.6 Hz, 1H), 2.42 – 2.47 (m, 1H), 1.96 – 2.05 (m, 2H), 1.56 (s, 3H), 1.48 (br, 1H), 1.252 (s, 6H), 1.245 (s, 6H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 134.9, 129.4, 118.3, 83.4, 80.7, 43.3, 25.2, 25.0, 21.1, 14.7, 14.4, 12.3. HRMS (EI^+): *m*/*z* for $C_{16}H_{27}BO_2$ $[M-H_2O]^+$ calcd. 262.2104, found 262.2097.



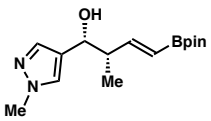
***rac*-(3*R*,4*S*,*E*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yn-3-ol (3k)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 58% yield (18.2 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.44 (m, 2H), 7.31 – 7.32 (m, 3H), 6.69 (dd, *J* = 18.0, 7.5 Hz, 1H), 5.63 (d, *J* = 18.0 Hz, 1H), 4.57 (d, *J* = 4.5 Hz, 1H), 2.62 – 2.67 (m, 1H), 1.90 (br, 1H), 1.27 (s, 12H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 132.1, 128.8, 128.6, 122.8, 121.5, 88.4, 86.4, 83.6, 66.5, 46.5, 25.2, 25.1, 15.3. HRMS (ESI^+): *m*/*z* for $C_{19}H_{25}BO_3Na$ $[M+Na]^+$ calcd. 335.1794, found 335.1810.



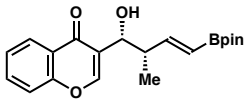
***rac*-(1*R*,2*S*,*E*)-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)but-3-en-1-ol (3l)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 82% yield (24.1 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 4.0 Hz, 1H), 6.94 – 6.96 (m, 2H), 6.64 (dd, *J* = 18.1, 6.7 Hz, 1H), 5.53 (d, *J* = 18.1 Hz, 1H), 4.96 (d, *J* = 4.2 Hz, 1H), 2.69 – 2.72 (m, 1H), 2.05 (s, 1H), 1.26 (s, 12H), 1.07 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 146.7, 126.9, 124.8, 124.4, 120.3, 83.5, 73.6, 47.0, 25.1, 25.0, 13.9. HRMS (EI^+): *m*/*z* for $C_{15}H_{21}BO_2S$ $[M-H_2O]^+$ calcd. 276.1355, found 276.1377.



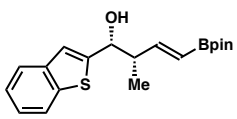
***rac*-(1*R*,2*S*,*E*)-2-Methyl-1-(5-nitrofuran-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3m)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 67% yield (21.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 3.4 Hz, 1H), 6.57 (dd, *J* = 18.1, 6.9 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H), 5.57 (d, *J* = 18.1 Hz, 1H), 4.79 (d, *J* = 3.2 Hz, 1H), 2.83 – 2.88 (m, 1H), 2.16 (s, 1H), 1.27 (s, 12H), 1.06 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 153.1, 151.9, 121.5, 113.0, 110.6, 83.8, 71.0, 44.4, 25.1, 25.0, 13.7. HRMS (ESI$^+$): *m*/*z* for $C_{15}H_{22}BNO_6Na$ $[M+Na]^+$ calcd. 346.1438, found 346.1468.



***rac*-(1*R*,2*S*,*E*)-2-Methyl-1-(1-methyl-1*H*-pyrazol-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3n)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 86% yield (25.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.30 (s, 1H), 6.63 (dd, *J* = 18.1, 6.7 Hz, 1H), 5.53 (d, *J* = 17.4 Hz, 1H), 4.70 (d, *J* = 5.1 Hz, 1H), 3.88 (s, 3H), 2.57 – 2.65 (m, 1H), 1.62 (br, 1H), 1.26 (s, 12H), 1.04 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 137.6, 128.7, 123.9, 120.3, 83.6, 70.2, 46.2, 39.3, 25.14, 25.08, 14.1. HRMS (ESI$^+$): *m*/*z* for $C_{15}H_{26}BN_2O_3$ $[M+H]^+$ calcd. 293.2036, found 293.2029.

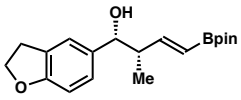


***rac*-3-((1*R*,2*S*,*E*)-1-Hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-4*H*-chromen-4-one (3o)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 89% yield (31.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.69 (ddd, *J* = 7.0, 7.0, 1.4 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.61 (dd, *J* = 18.1, 6.9 Hz, 1H), 5.47 (d, *J* = 18.1 Hz, 1H), 4.56 (d, *J* = 6.2 Hz, 1H), 3.25 (br, 1H), 2.92 – 2.97 (m, 1H), 1.25 (s, 12H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 156.5, 155.8, 153.6, 134.2, 125.9, 125.6, 124.1, 124.0, 120.1, 118.5, 83.6, 72.5, 43.9, 25.1, 25.0, 14.1. HRMS (ESI$^+$): *m*/*z* for $C_{20}H_{25}BO_5Na$ $[M+Na]^+$ calcd. 379.1693, found 379.1711.

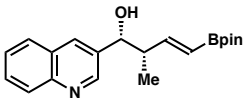


***rac*-(1*R*,2*S*,*E*)-1-(Benzo[*b*]thiophen-2-yl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3p)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 78% yield (26.7

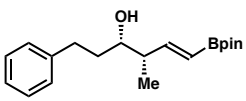
mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.29 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.19 (s, 1H), 6.68 (dd, *J* = 18.1, 6.6 Hz, 1H), 5.57 (d, *J* = 18.1 Hz, 1H), 5.03 (d, *J* = 4.7 Hz, 1H), 2.76 – 2.79 (m, 1H), 1.89 (br, 1H), 1.26 (s, 12H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 147.6, 139.8, 139.6, 124.5, 124.3, 123.7, 122.7, 120.9, 120.5, 83.6, 73.8, 46.7, 25.12, 25.05, 13.6. HRMS (ESI^+): *m*/*z* for $C_{19}H_{25}BO_3SNa$ $[M+Na]^+$ calcd. 367.1515, found 367.1530.



***rac*-(1*R*,2*S*,*E*)-1-(2,3-Dihydrobenzofuran-5-yl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3q)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 91% yield (30.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.00 – 7.03 (m, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.62 (dd, *J* = 18.2, 6.6 Hz, 1H), 5.47 (dd, *J* = 3.2, 1.9 Hz, 1H), 4.65 (dd, *J* = 4.7, 2.9 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 2H), 3.19 (t, *J* = 8.7 Hz, 2H), 2.56 – 2.64 (m, 1H), 1.77 (d, *J* = 3.3 Hz, 1H), 1.26 (s, 12H), 1.01 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 156.0, 135.0, 127.2, 126.5, 123.2, 119.5, 108.9, 83.5, 76.8, 71.6, 46.7, 30.0, 25.1, 25.0, 13.4. HRMS (EI^+): *m*/*z* for $C_{19}H_{25}BO_3$ $[M-H_2O]^+$ calcd. 312.1897, found 312.1915.

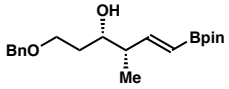


***rac*-(1*R*,2*S*,*E*)-2-Methyl-1-(quinolin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3r)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 91% yield (30.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.14 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.56 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.69 (dd, *J* = 18.1, 6.4 Hz, 1H), 5.54 (d, *J* = 18.1 Hz, 1H), 5.00 (d, *J* = 3.6 Hz, 1H), 2.75 – 2.79 (m, 1H), 2.44 (br, 1H), 1.25 (s, 12H), 1.01 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.7, 149.4, 147.2, 135.6, 134.1, 129.9, 129.0, 128.2, 128.0, 127.3, 120.8, 83.6, 74.6, 46.5, 25.1, 25.0, 12.9. HRMS (ESI^+): *m*/*z* for $C_{20}H_{27}BNO_3$ $[M+H]^+$ calcd. 340.2084, found 340.2103.

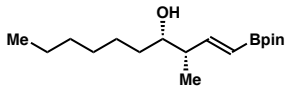


***rac*-(3*S*,4*S*,*E*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-ol (3s)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 72% yield (22.6 mg). ^{1}H

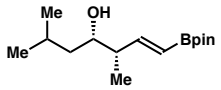
NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.30 (m, 2H), 7.18– 7.21 (m, 3H), 6.57 (dd, *J* = 18.1, 7.0 Hz, 1H), 5.50 (dd, *J* = 18.1, 0.9 Hz, 1H), 3.58 – 3.60 (m, 1H), 2.82 – 2.87 (m, 1H), 2.62 – 2.66 (m, 1H), 2.35 – 2.38 (m, 1H), 1.77 – 1.82 (m, 1H), 1.69 – 1.75 (m, 1H), 1.40 (br, 1H), 1.27 (s, 12H), 1.04 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 142.4, 128.8, 128.7, 126.1, 83.5, 73.9, 45.6, 36.3, 32.8, 25.14, 25.11, 13.8. HRMS (ESI^+): *m*/*z* for $C_{19}H_{29}BO_3Na$ $[M+Na]^+$ calcd. 339.2107, found 339.2135.



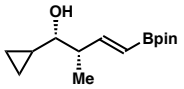
***rac*-(3*S*,4*S*,*E*)-1-(Benzyloxy)-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-ol (3t)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 51% yield (17.8 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.36 (m, 5H), 6.56 (dd, *J* = 18.1, 7.5 Hz, 1H), 5.47 (d, *J* = 18.1 Hz, 1H), 4.51 (s, 2H), 3.71 – 3.74 (m, 2H), 3.62 – 3.65 (m, 1H), 3.01 (s, 1H), 2.30 – 2.35 (m, 1H), 1.69 – 1.79 (m, 2H), 1.26 (s, 12H), 1.07 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 138.1, 128.8, 128.11, 128.05, 120.0, 83.5, 74.8, 73.7, 70.0, 46.2, 34.0, 25.13, 25.11, 15.2. HRMS (ESI^+): *m*/*z* for $C_{20}H_{31}BO_4Na$ $[M+Na]^+$ calcd. 369.2213, found 369.2238.



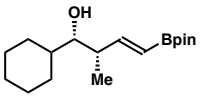
***rac*-(3*S*,4*S*,*E*)-3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-1-en-4-ol (3u)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 72% yield (21.4 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 18.1, 7.0 Hz, 1H), 5.50 (d, *J* = 18.1 Hz, 1H), 3.55 (br, 1H), 2.32 – 2.36 (m, 1H), 1.46 – 1.49 (m, 1H), 1.46 (br, 1H), 1.36 – 1.40 (m, 1H), 1.27 (s, 12H), 1.16 – 1.35 (m, 8H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.86 – 0.88 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 119.5, 83.5, 74.7, 45.4, 34.5, 32.2, 29.6, 26.4, 25.14, 25.11, 23.0, 14.5, 13.7. HRMS (ESI^+): *m*/*z* for $C_{17}H_{37}BNO_3$ $[M+NH_4]^+$ calcd. 314.2866, found 314.2881.



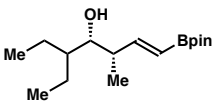
***rac*-(3*S*,4*S*,*E*)-3,6-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-4-ol (3v)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 89% yield (23.8 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 18.1, 6.9 Hz, 1H), 5.50 (d, *J* = 18.1 Hz, 1H), 3.66 – 3.68 (m, 1H), 2.29 – 2.35 (m, 1H), 1.73 – 1.80 (m, 1H), 1.37 (ddd, *J* = 14.3, 10.0, 4.9 Hz, 1H), 1.27 (s, 12H), 1.19 – 1.31 (m, 2H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 83.5, 72.4, 45.7, 43.4, 25.2, 25.1, 25.0, 24.0, 22.0, 13.6. HRMS (ESI^+): *m*/*z* for $C_{15}H_{29}BO_3Na$ $[M+Na]^+$ calcd. 291.2107, found 291.2102.



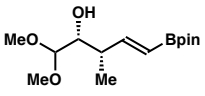
***rac*-(1*S*,2*S*,*E*)-1-Cyclopropyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3w)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 92% yield (23.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 18.1, 6.8 Hz, 1H), 5.53 (d, *J* = 18.1 Hz, 1H), 2.82 (dd, *J* = 8.6, 4.6 Hz, 1H), 2.50 – 2.54 (m, 1H), 1.53 (br, 1H), 1.26 (s, 12H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.91 – 0.97 (m, 1H), 0.47 – 0.56 (m, 2H), 0.21 – 0.29 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 119.4, 83.5, 79.9, 45.7, 25.14, 25.06, 15.5, 14.3, 3.8, 2.8. HRMS (ESI$^+$): *m*/*z* for $C_{14}H_{29}BNO_3$ $[M+NH_4]^+$ calcd. 270.2240, found 270.2245.



***rac*-(1*S*,2*S*,*E*)-1-Cyclohexyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (3x)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 74% yield (21.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 18.2, 6.5 Hz, 1H), 5.50 (dd, *J* = 18.2, 1.0 Hz, 1H), 3.27 (dd, *J* = 6.2, 5.0 Hz, 1H), 2.47 – 2.50 (m, 1H), 1.93 (d, *J* = 12.4 Hz, 1H), 1.73 (d, *J* = 10.3 Hz, 2H), 1.57 – 1.65 (m, 3H), 1.37 – 1.40 (m, 1H), 1.27 (s, 12H), 1.09 – 1.27 (m, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.93 – 1.06 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 119.0, 83.5, 78.5, 41.6, 40.5, 29.8, 28.4, 26.7, 26.5, 26.2, 25.1 (two overlapping carbon signals), 12.6. HRMS (ESI$^+$): *m*/*z* for $C_{17}H_{31}BO_3Na$ $[M+Na]^+$ calcd. 317.2264, found 317.2277.

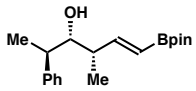


***rac*-(3*S*,4*S*,*E*)-5-Ethyl-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-4-ol (3y)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 68% yield (19.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 (dd, *J* = 18.1, 6.9 Hz, 1H), 5.49 (d, *J* = 18.1 Hz, 1H), 3.48 (dd, *J* = 5.2, 5.2 Hz, 1H), 2.47 – 2.50 (m, 1H), 1.57 – 1.60 (m, 2H), 1.31 – 1.39 (m, 3H), 1.27 (s, 12H), 1.26 (br, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.85 – 0.87 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 83.5, 75.4, 42.8, 42.4, 25.14, 25.08, 21.8, 20.5, 13.5, 11.4, 11.0. HRMS (ESI$^+$): *m*/*z* for $C_{16}H_{31}BO_3Na$ $[M+Na]^+$ calcd. 305.2264, found 305.2291.

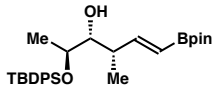


***rac*-(2*R*,3*S*,*E*)-1,1-Dimethoxy-3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-ol (3z)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 81% yield (23.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63 (dd, *J* = 18.1, 7.0 Hz, 1H), 5.51 (dd, *J* = 18.1, 0.8 Hz, 1H), 4.25 (d, *J* = 5.6 Hz, 1H),

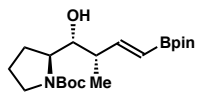
3.60 (*app.* t, J = 5.3 Hz, 1H), 3.44 (s, 3H), 3.39 (s, 3H), 2.47 – 2.53 (m, 1H), 1.66 (br, 1H), 1.27 (s, 12H), 1.08 (d, J = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 118.8, 104.8, 83.5, 73.6, 55.4, 54.9, 41.4, 25.2, 25.1, 13.9. HRMS (EI^+): *m*/*z* for $C_{13}H_{23}BO_4$ $[M-CH_3OH]^+$ calcd. 254.1689, found 254.1669.



***rac*-(3*R*,4*S*,*E*)-4-Methyl-2-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-ol (9)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 78% yield (24.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.31 (m, 2H), 7.19 – 7.22 (m, 3H), 6.60 (dd, J = 18.1, 6.7 Hz, 1H), 5.48 (d, J = 18.1 Hz, 1H), 3.67 – 3.69 (m, 1H), 2.85 – 2.89 (m, 1H), 2.21 – 2.26 (m, 1H), 1.47 (s, 1H), 1.31 (d, J = 6.9 Hz, 3H), 1.27 (s, 12H), 1.02 (d, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 145.0, 128.9, 127.9, 126.7, 83.5, 78.7, 43.1, 42.0, 25.2, 25.1, 16.7, 13.0. HRMS (ESI^+): *m*/*z* for $C_{19}H_{33}BNO_3$ $[M+NH_4]^+$ calcd. 334.2553, found 334.2566.

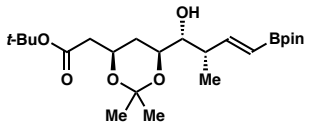


(2*S*,3*R*,4*S*,*E*)-2-((*tert*-Butyldiphenylsilyl)oxy)-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-ol (10) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 93% yield (45.8 mg). $[\alpha]_D^{25}$ = –4.1° (c 1.94, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.68 (m, 4H), 7.36 – 7.44 (m, 6H), 6.20 (dd, J = 18.0, 8.2 Hz, 1H), 5.32 (d, J = 18.0 Hz, 1H), 3.78 – 3.81 (m, 1H), 3.38 – 3.39 (m, 1H), 2.36 (s, 1H), 2.23 – 2.29 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.05 (s, 9H), 1.02 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 136.10, 136.05, 134.2, 133.7, 130.1, 130.0, 128.0, 127.9, 119.2, 83.4, 78.0, 71.0, 42.4, 27.3, 25.2, 25.0, 19.5, 16.6, 16.3. HRMS (ESI^+): *m*/*z* for $C_{29}H_{43}BO_4SiNa$ $[M+Na]^+$ calcd. 517.2921, found 517.2892.

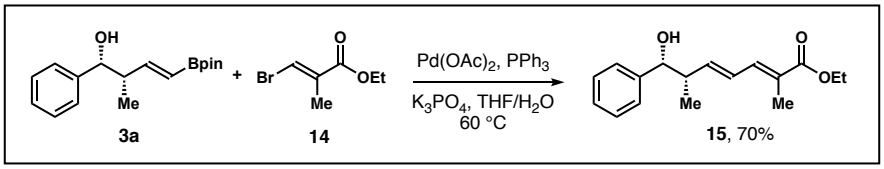


***tert*-Butyl-(*S*)-2-((1*R*,2*S*,*E*)-1-hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)pyrrolidine-1-carboxylate (11)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as white solid in 74% yield (28.3 mg). $[\alpha]_D^{25}$ = –18.1° (c 1.07, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.50 (dd, J = 17.7, 8.2 Hz, 1H), 5.44 (d, J = 17.9 Hz, 1H), 3.85 (br, 2H), 3.54 (br, 1H), 3.19 – 3.23 (m, 1H), 2.25 – 2.28 (m, 1H), 1.92 (br, 1H), 1.85 (br, 2H), 1.67 – 1.72 (m, 1H), 1.45 (s, 9H), 1.26 (s, 6H), 1.25 (s, 6H), 1.11 (d, J = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

156.1, 155.6, 119.2, 83.5, 80.0, 75.0, 61.1, 48.0, 43.9, 28.9, 25.6, 25.3, 25.0, 24.7, 17.1. HRMS (ESI$^+$): *m*/*z* for $C_{20}H_{36}BNO_5Na$ $[M+Na]^+$ calcd. 404.2584, found 404.2563.

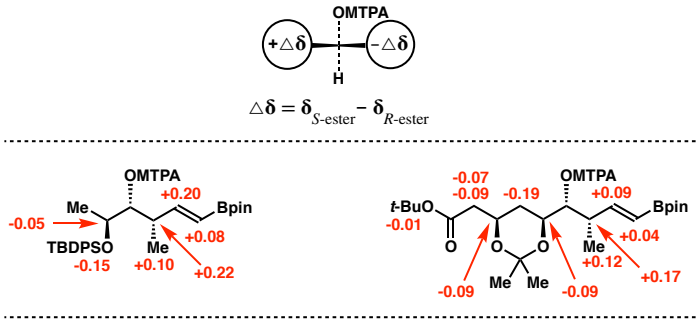


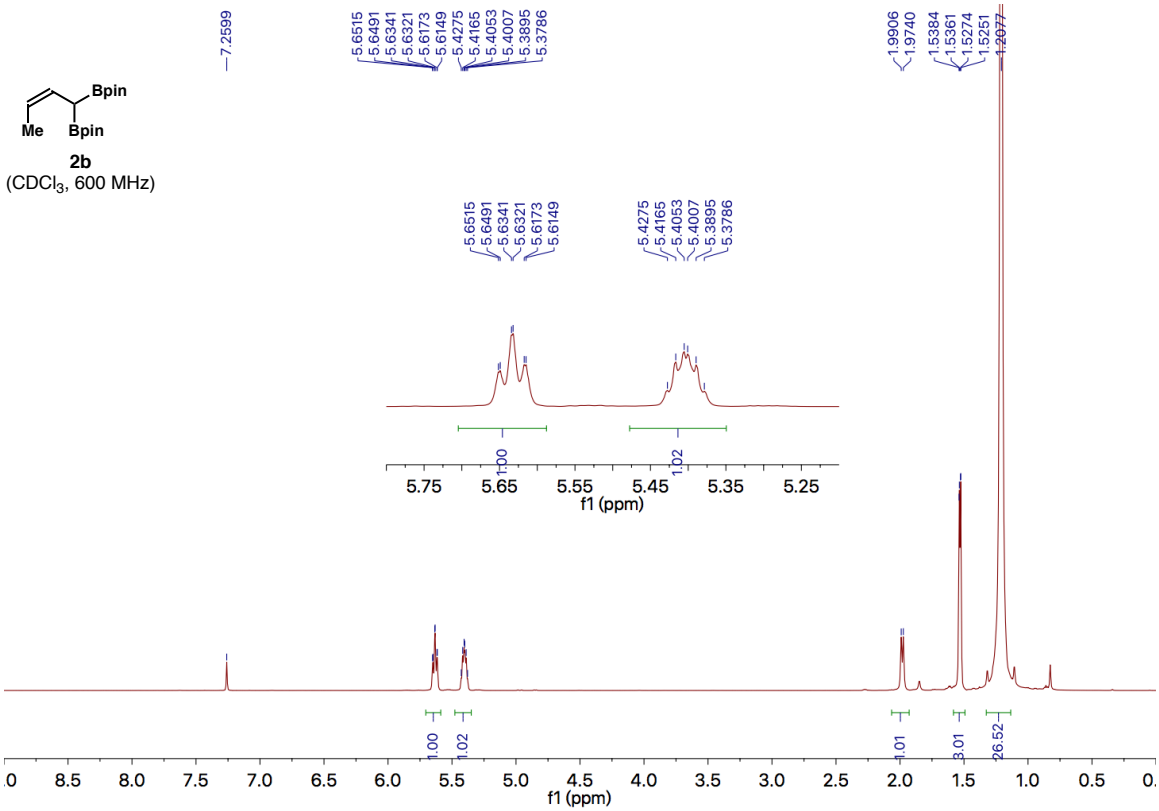
***tert*-Butyl-2-((4*R*,6*S*)-6-((1*R*,2*S*,*E*)-1-hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (12)** Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as white solid in 82% yield (36.2 mg). $[\alpha]_D^{25}$ = −19.7° (c 1.46, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.48 (dd, *J* = 18.0, 8.0 Hz, 1H), 5.46 (d, *J* = 18.0 Hz, 1H), 4.22 – 4.25 (m, 1H), 3.83 – 3.85 (m, 1H), 3.48 (dd, *J* = 7.4, 4.1 Hz, 1H), 2.36 – 2.42 (m, 2H), 2.32 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.13 (s, 1H), 1.51 (*app.* d, *J* = 12.8 Hz, 1H), 1.44 (s, 9H), 1.42 (s, 3H), 1.38 – 1.41 (m, 1H), 1.35 (s, 3H), 1.28 (s, 12H), 1.09 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 155.3, 119.6, 99.0, 83.6, 81.0, 75.6, 70.0, 66.1, 43.1, 41.4, 30.2, 29.4, 28.4, 25.1 (two overlapping carbon signals), 20.2, 16.0. HRMS (ESI$^+$): *m*/*z* for $C_{23}H_{41}BO_7Na$ $[M+Na]^+$ calcd. 463.2843, found 463.2822.

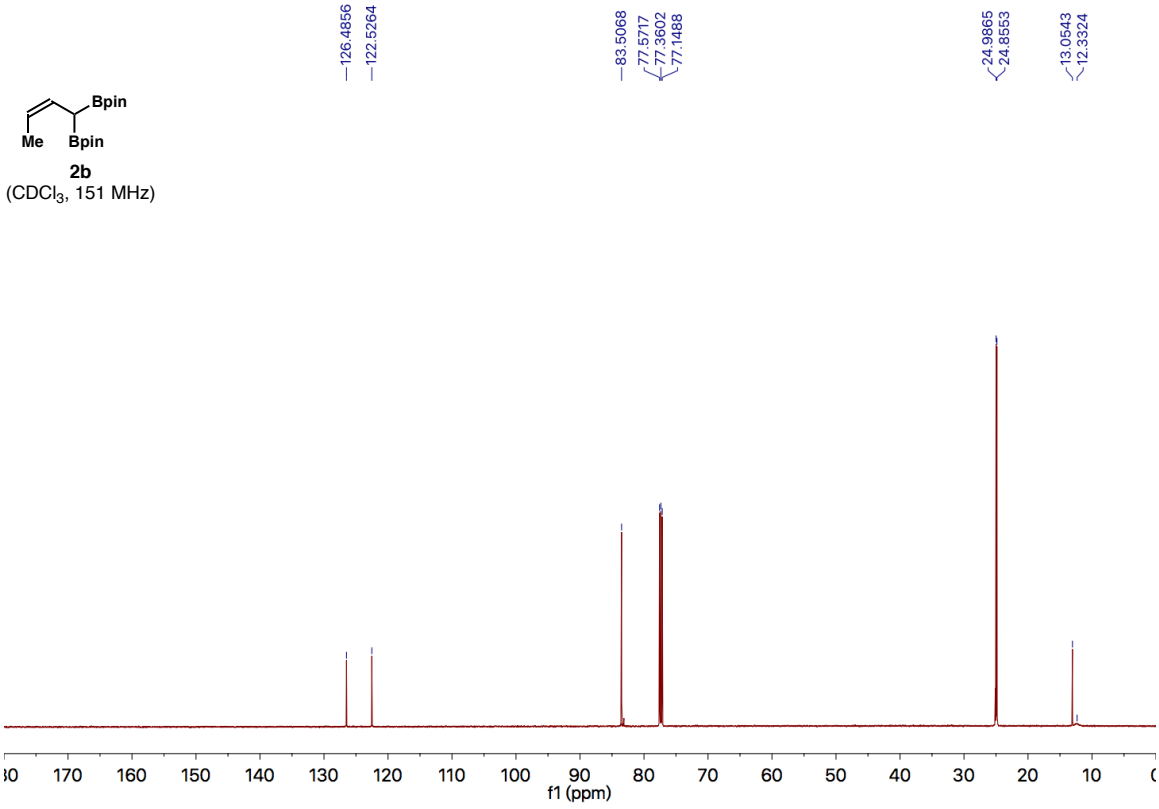


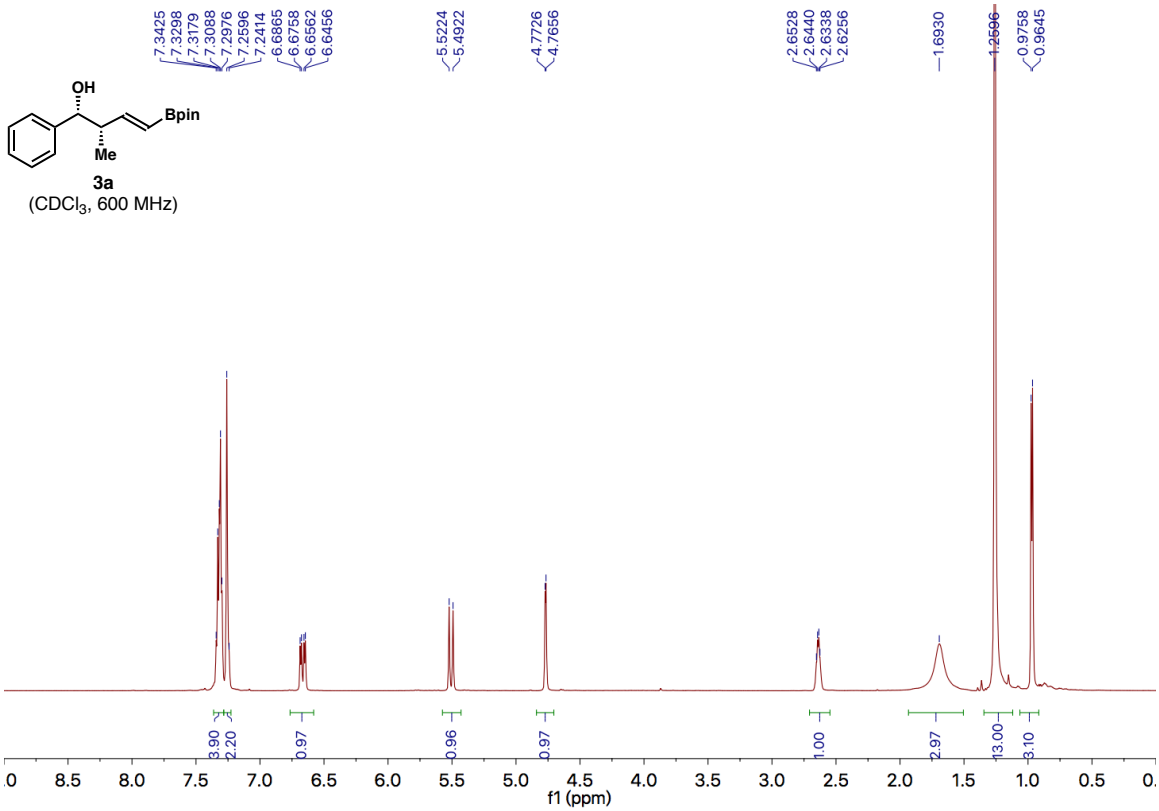
Ethyl (2*E*,4*E*,6*S*,7*R*)-7-hydroxy-2,6-dimethyl-7-phenylhepta -2,4-dienoate (15) An oven-dried 1-dram vial equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.01 mmol, 10 mol %), PPh_3 (0.02 mmol, 20 mol %) and K_3PO_4 (0.2 mmol, 2.0 equiv). A solution of **3a** (29 mg, 0.1 mmol) in THF (0.5 mL) was added followed by the addition of ester **14** (39 mg, 0.2 mmol, 2.0 equiv) and H_2O (0.05 mL). The reaction mixture was stirred at 60 °C for 12 h. After complete consumption of alcohol **3a**, 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** (19.3 mg, 70% yield) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.36 (m, 2H), 7.26 – 7.30 (m, 3H), 7.11 (d, *J* = 11.2 Hz, 1H), 6.31 (dd, *J* = 14.5, 11.9 Hz, 1H), 5.97 (dd, *J* = 15.1, 7.6 Hz, 1H), 4.65 (d, *J* = 4.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.70 – 2.75 (m, 1H), 1.94 (s, 1H), 1.89 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 143.9, 142.5, 138.4, 128.5, 128.0, 126.82, 126.79, 126.4, 77.9, 60.9, 44.7, 15.1, 14.7, 13.0. HRMS (ESI$^+$): *m*/*z* for $C_{17}H_{23}O_3$ $[M+H]^+$ calcd. 275.1647, found 275.1628.

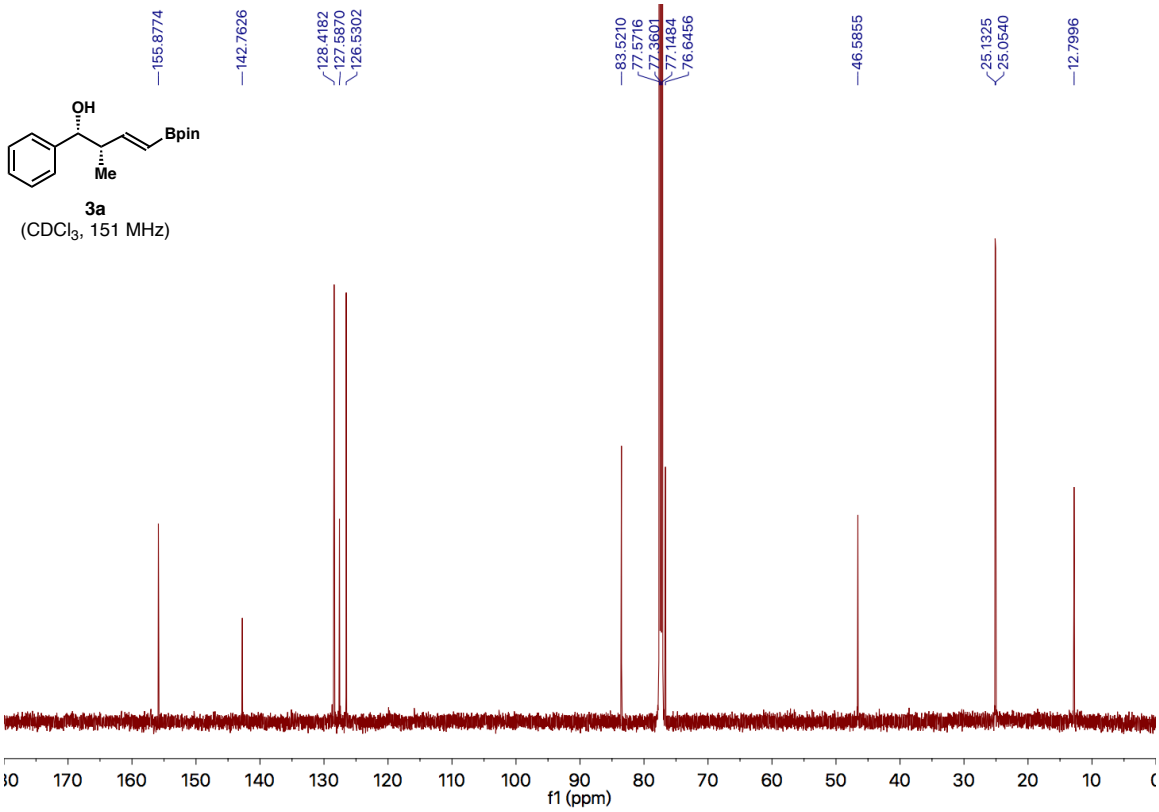
Assignment of the absolute configuration of 10 and 12 using Mosher ester analysis:

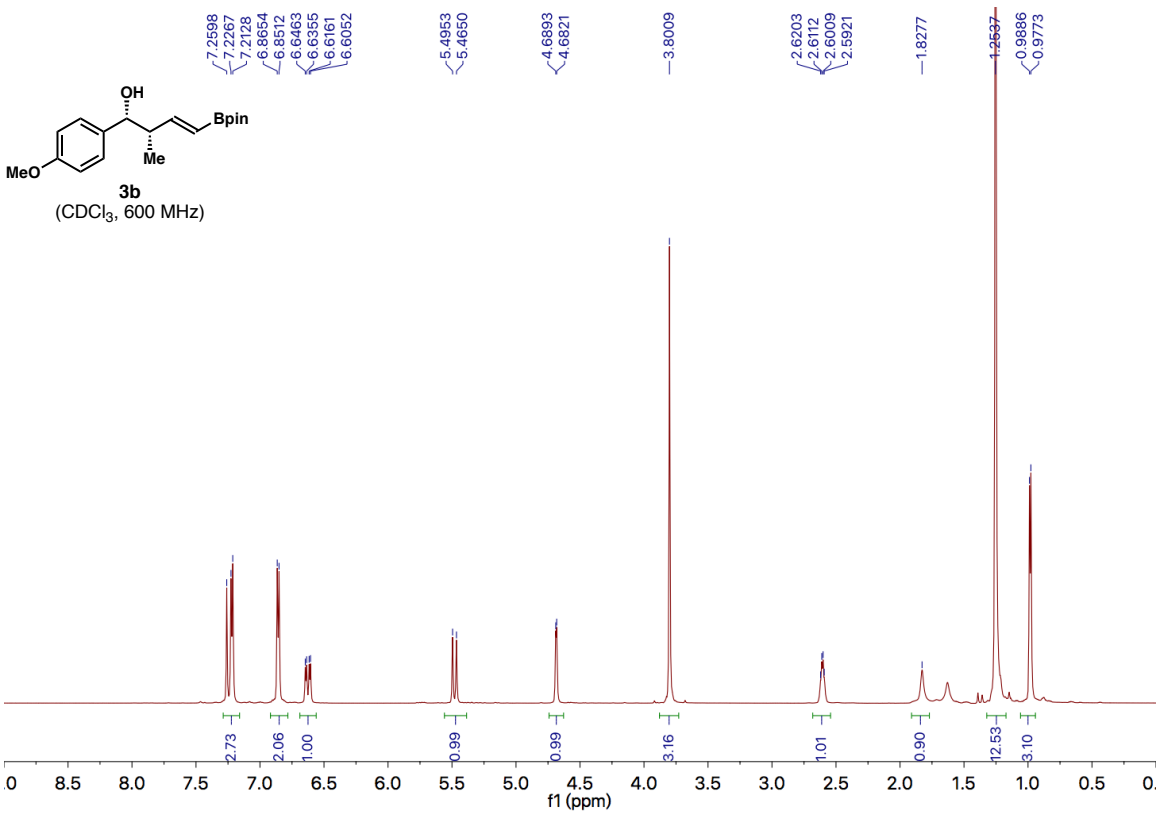



Bpin
Me
Bpin
2b
(CDCl3, 600 MHz)
7.2599
5.6515
5.6491
5.6341
5.6321
5.6173
5.6149
5.4275
5.4165
5.4053
5.4007
5.3895
5.3786
1.9906
1.9740
1.5384
1.5361
1.5274
1.5251
1.2077
1.00
1.02
1.01
3.01
26.52
f1 (ppm)

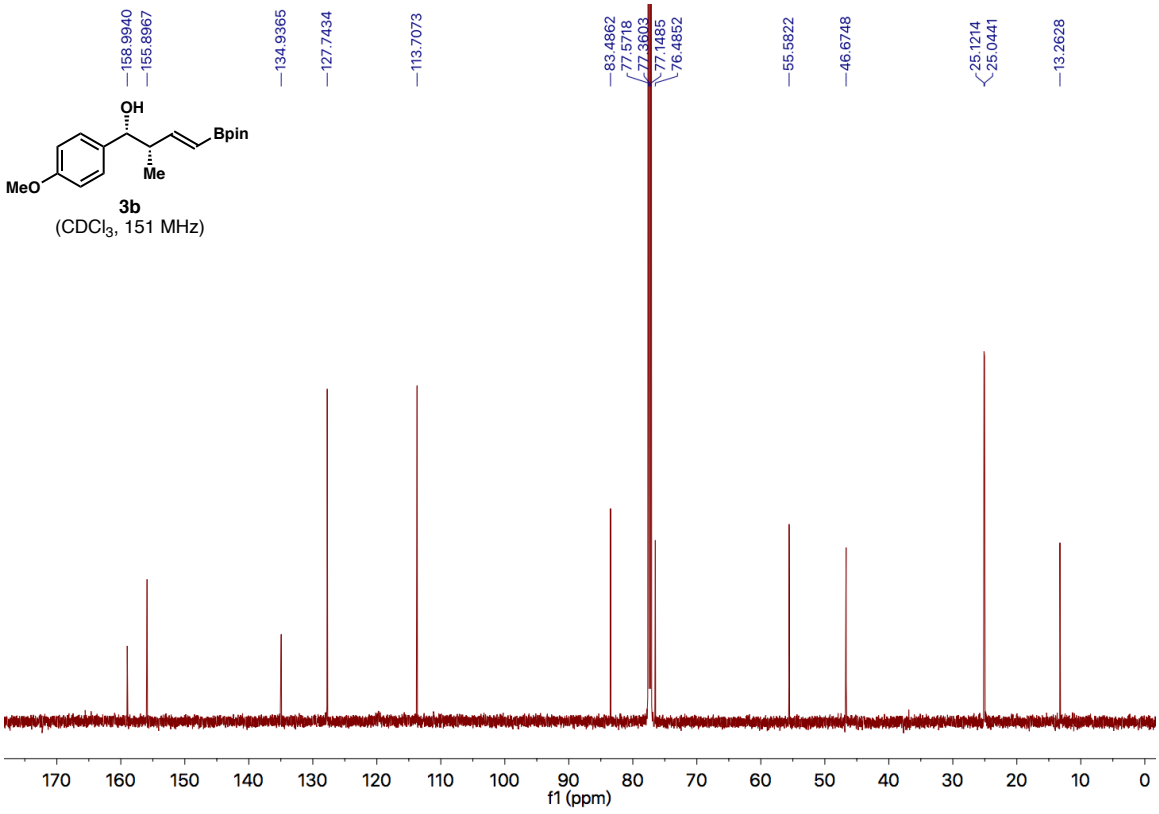

Bpin
Me
Bpin
2b
(CDCl3, 151 MHz)
126.4856
122.5264
83.5068
77.5717
77.3602
77.1488
24.9865
24.8553
13.0543
12.3324
f1 (ppm)


7.3425
7.3298
7.3179
7.3088
7.2976
7.2596
7.2414
6.6865
6.6758
6.6562
6.6456
5.5224
5.4922
4.7726
4.7656
2.6528
2.6440
2.6338
2.6256
1.6930
1.2596
0.9758
0.9645
OH
Bpin
Me
3a
(CDCl3, 600 MHz)
3.90
2.20
0.97
0.96
0.97
1.00
2.97
13.00
3.10
f1 (ppm)

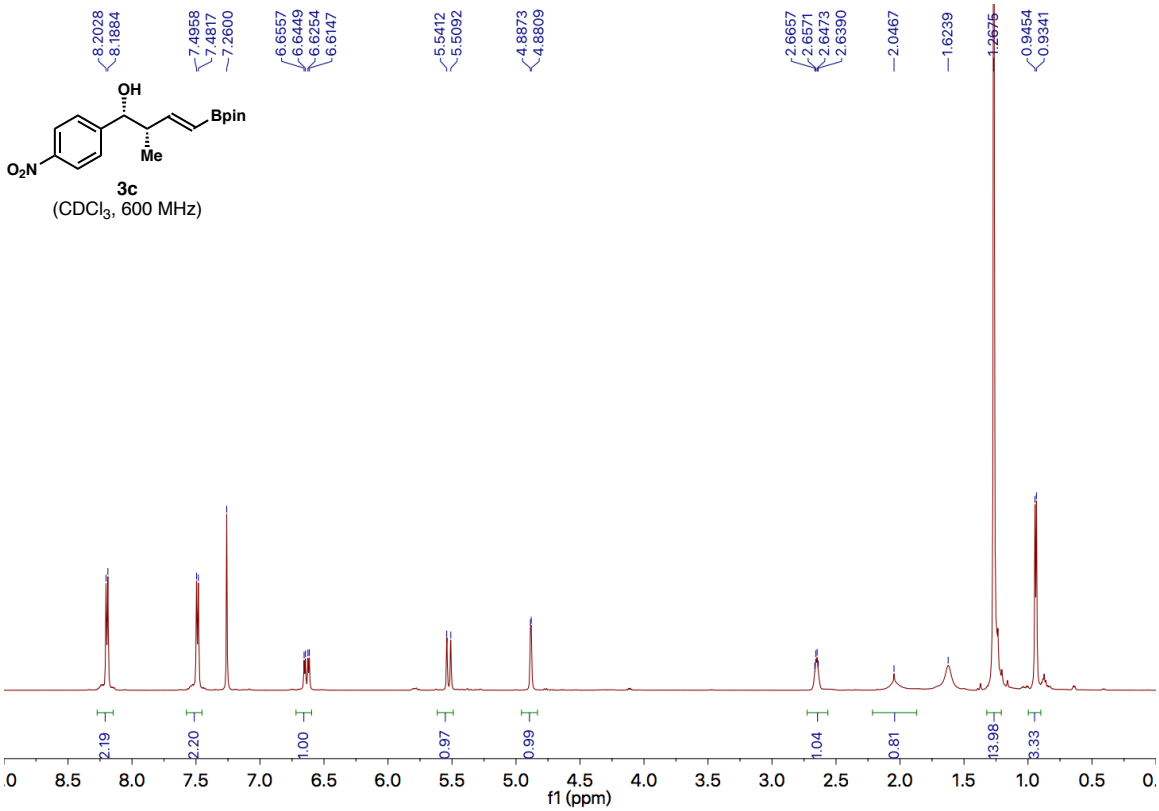

155.8774
142.7626
128.4182
127.5870
126.5302
83.5210
77.5716
77.3601
77.1484
76.6456
46.5855
25.1325
25.0540
12.7996
OH
Bpin
Me
3a
(CDCl3, 151 MHz)
f1 (ppm)



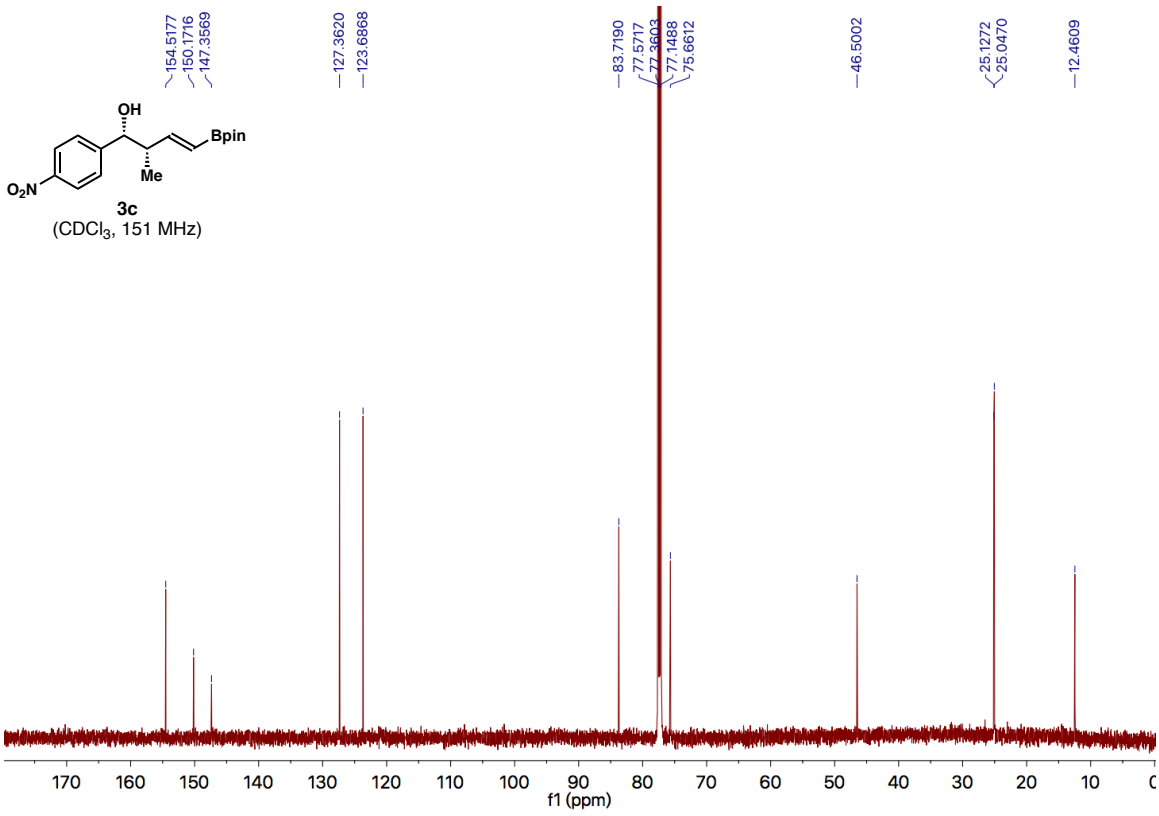
3b
($CDCl_3$, 600 MHz)



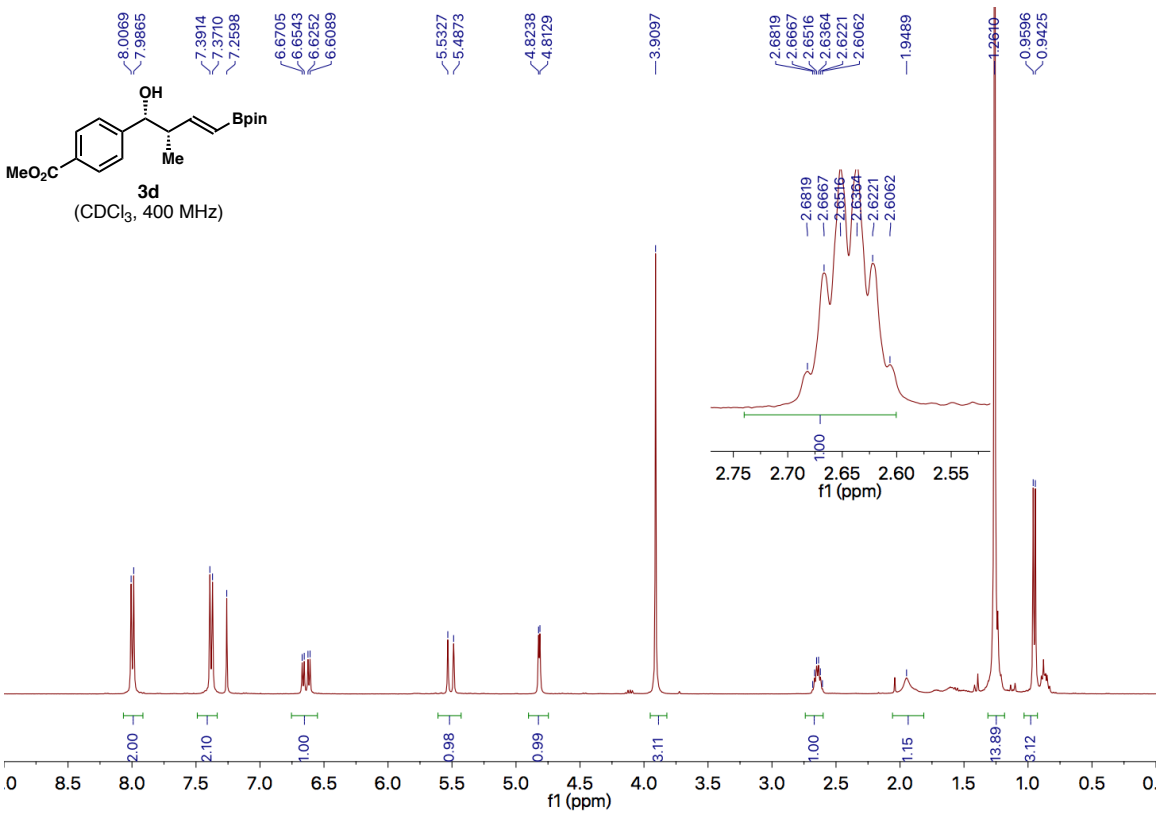
3b
($CDCl_3$, 151 MHz)

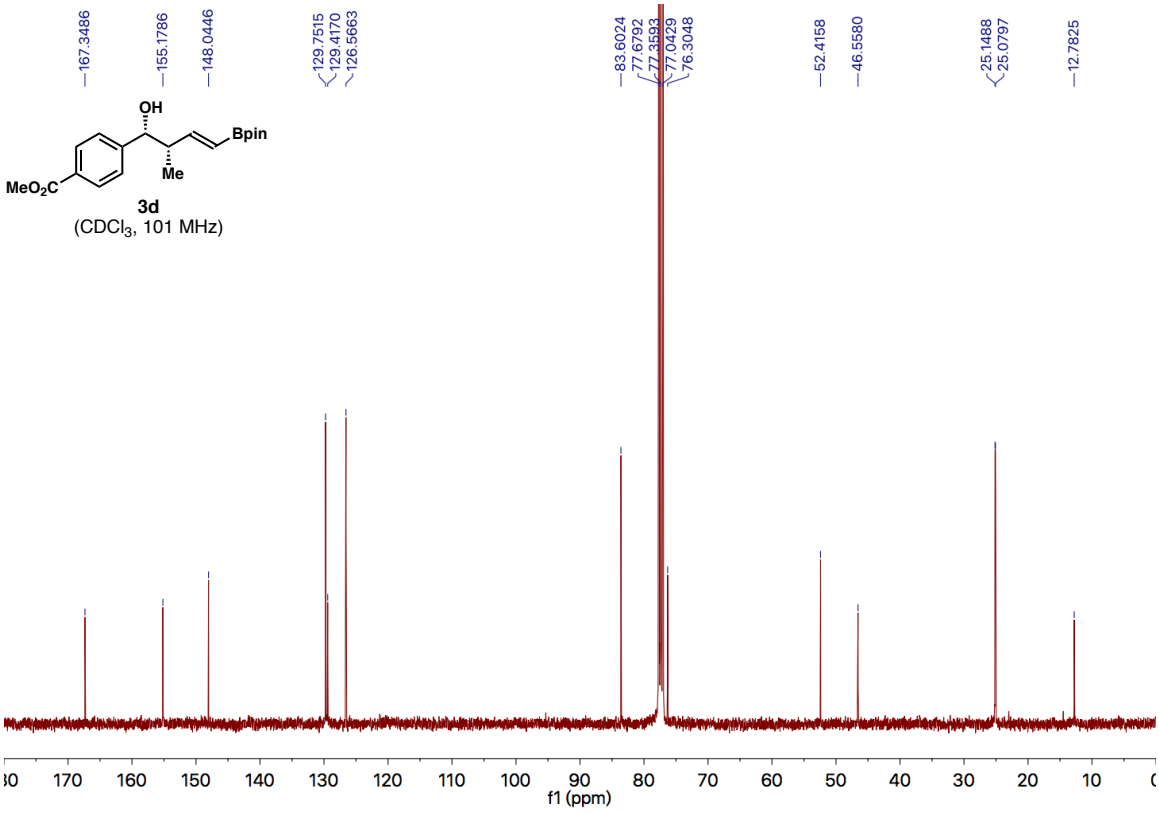


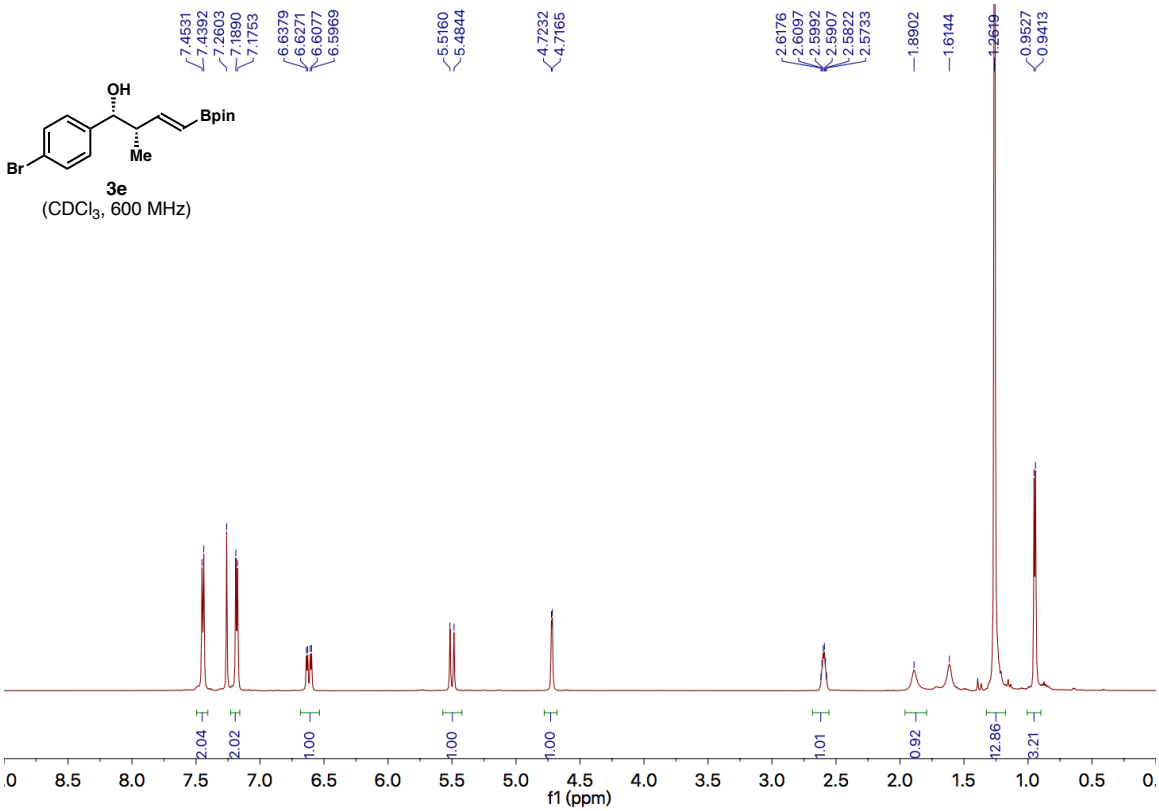
3c
($CDCl_3$, 600 MHz)



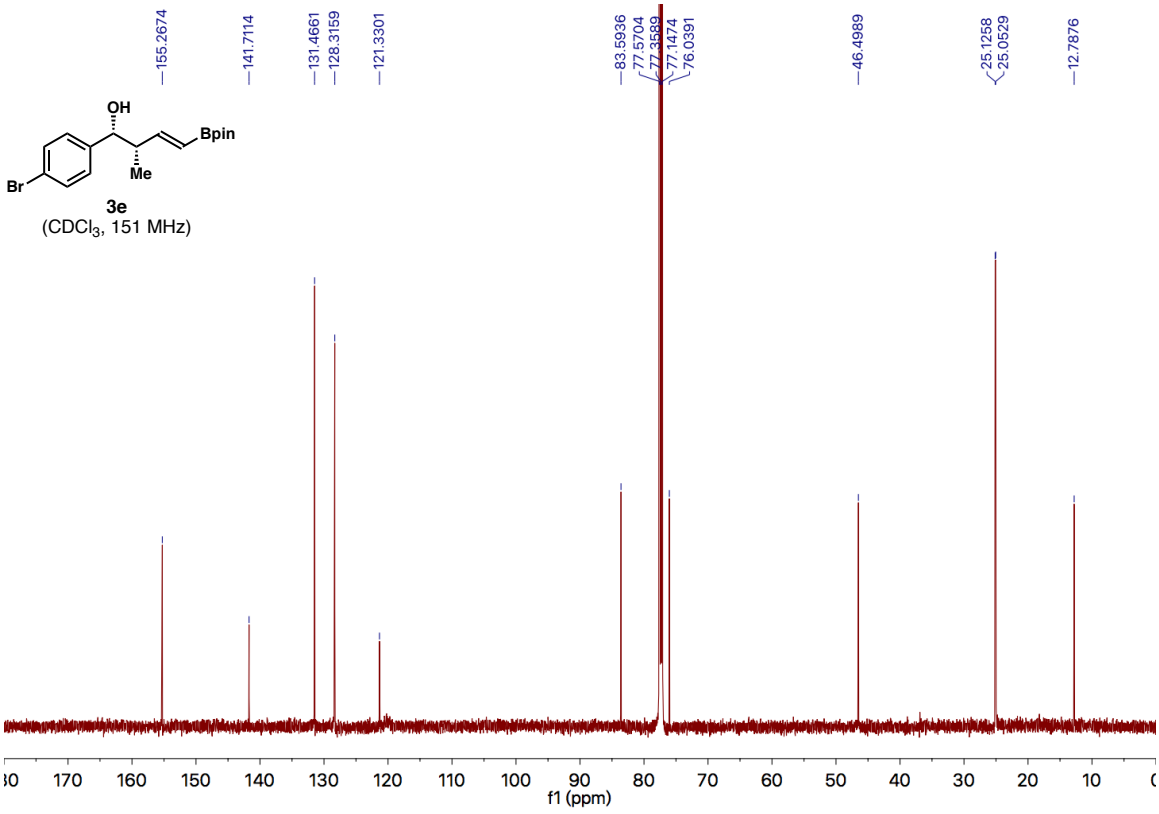
3c
($CDCl_3$, 151 MHz)


8.0069
7.9865
7.3914
7.3710
7.2598
6.6705
6.6543
6.6252
6.6089
5.5327
5.4873
4.8238
4.8129
3.9097
2.6819
2.6667
2.6516
2.6364
2.6221
2.6062
1.9489
1.2610
0.9596
0.9425
OH
Bpin
Me
MeO2C
3d
(CDCl3, 400 MHz)
2.00
2.10
1.00
0.98
0.99
3.11
1.00
1.15
13.89
3.12
f1 (ppm)

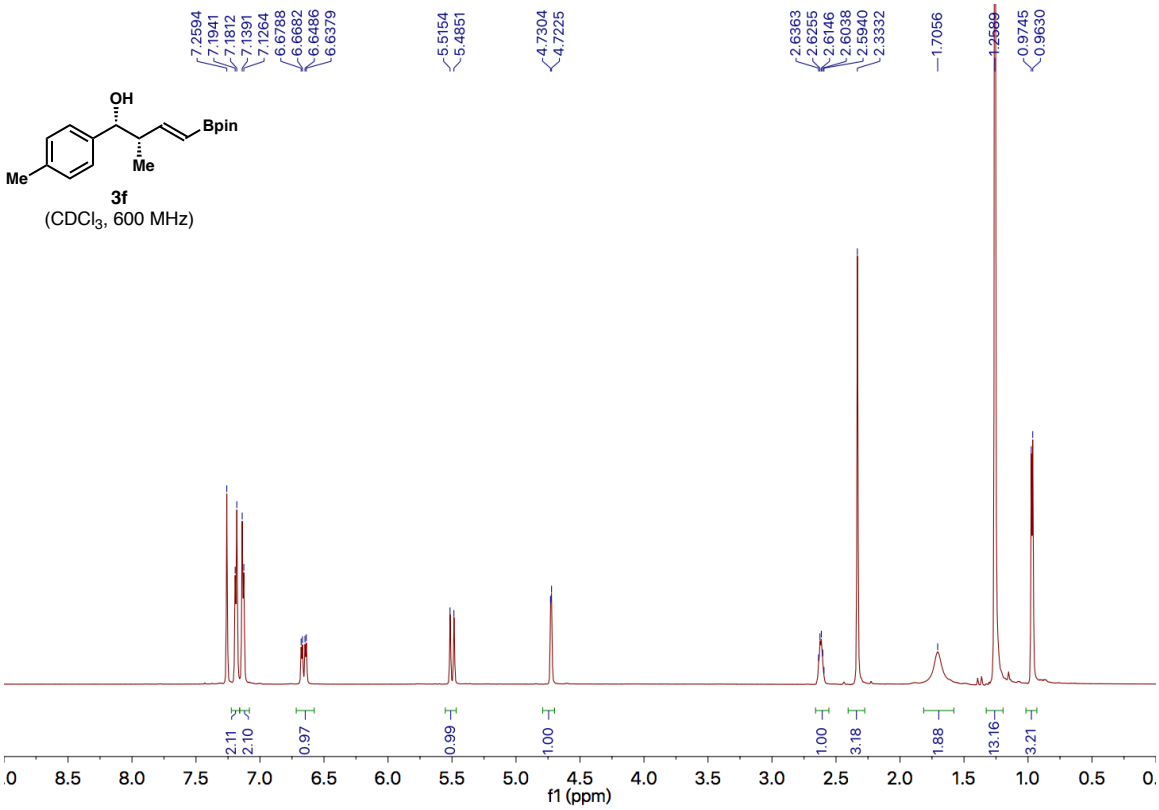

167.3486
155.1786
148.0446
129.7515
129.4170
126.5663
83.6024
77.6792
77.3593
77.0429
76.3048
52.4158
46.5580
25.1488
25.0797
12.7825
OH
Bpin
Me
MeO2C
3d
(CDCl3, 101 MHz)
f1 (ppm)

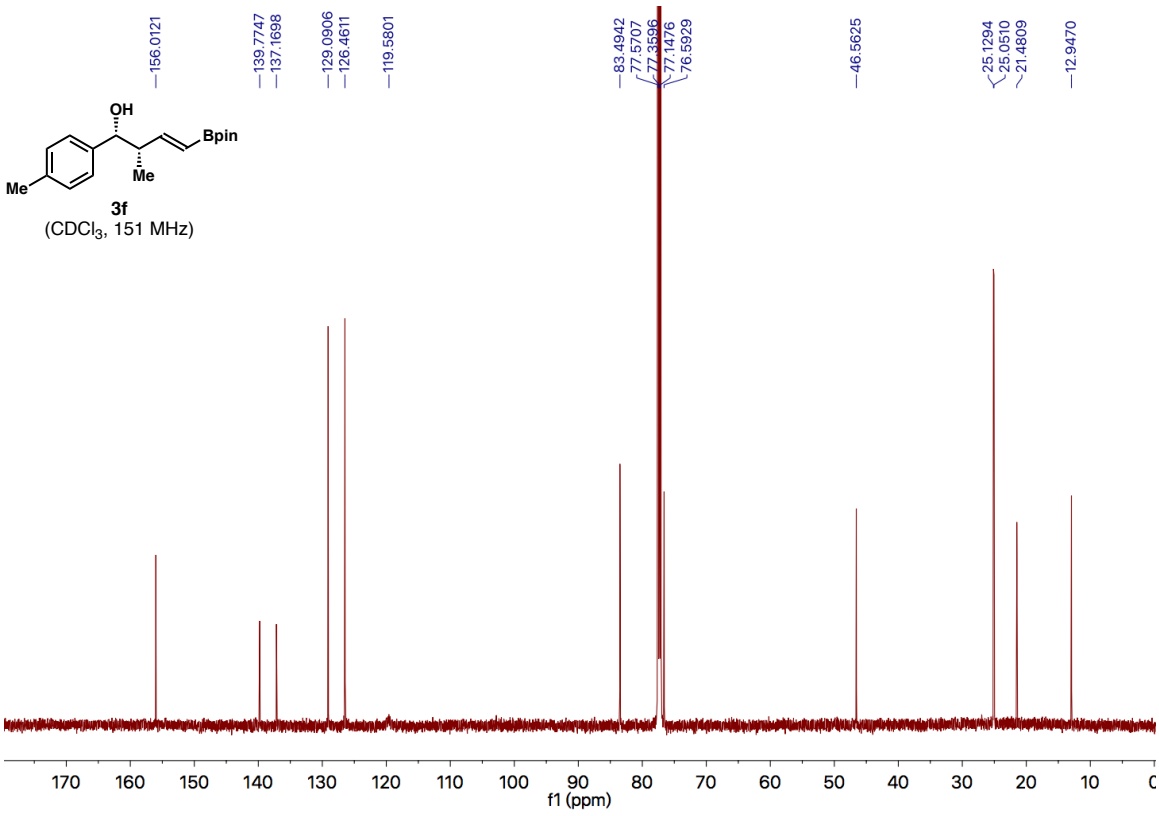


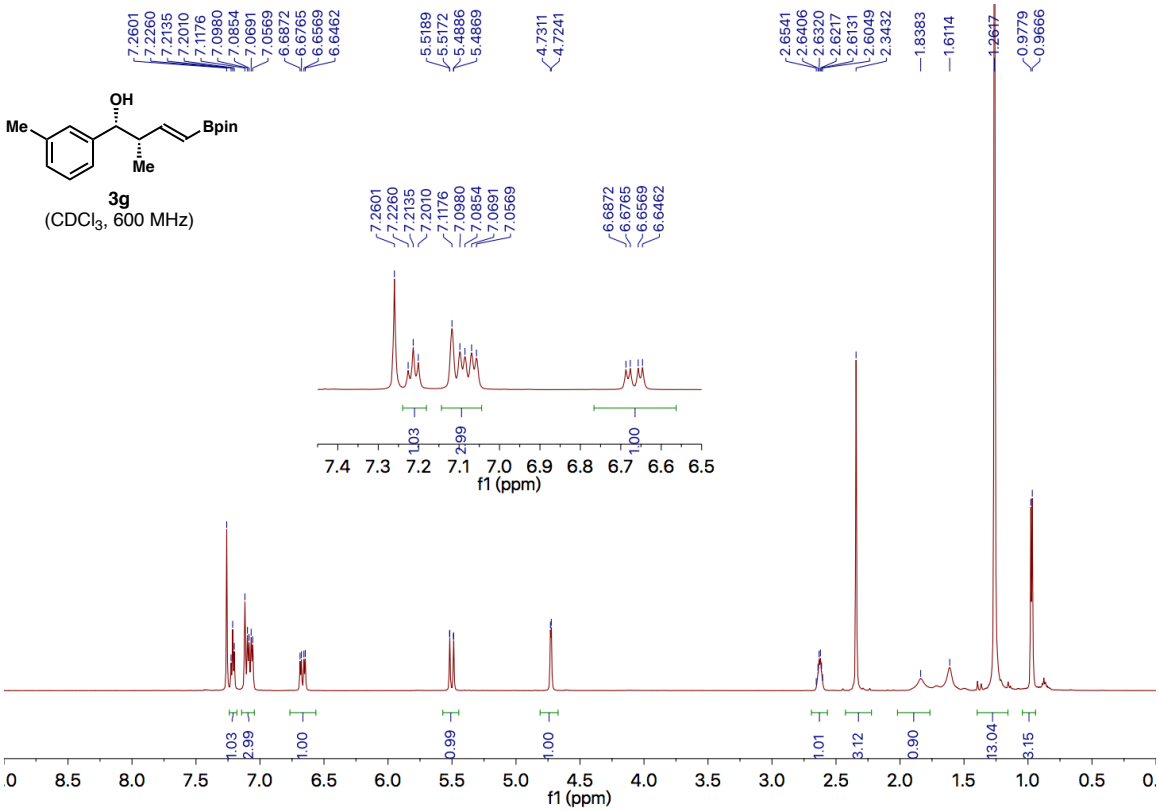
3e
($CDCl_3$, 600 MHz)

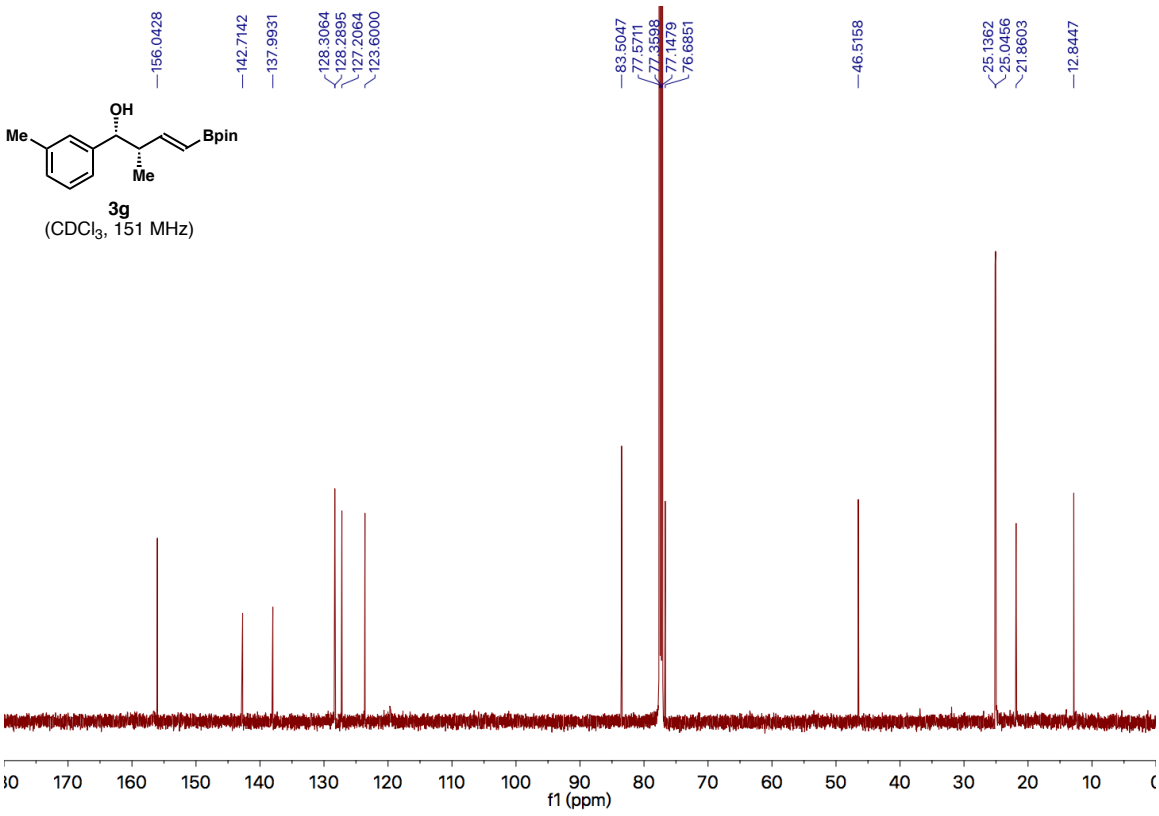


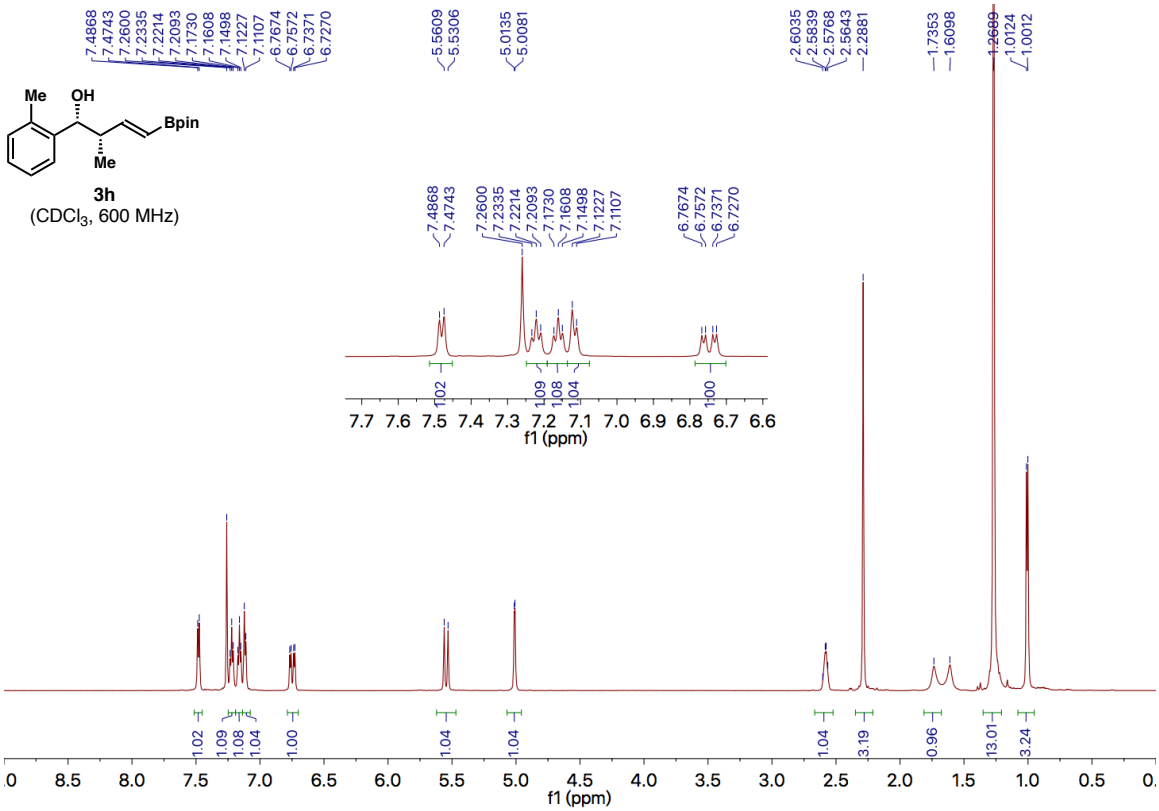
3e
($CDCl_3$, 151 MHz)

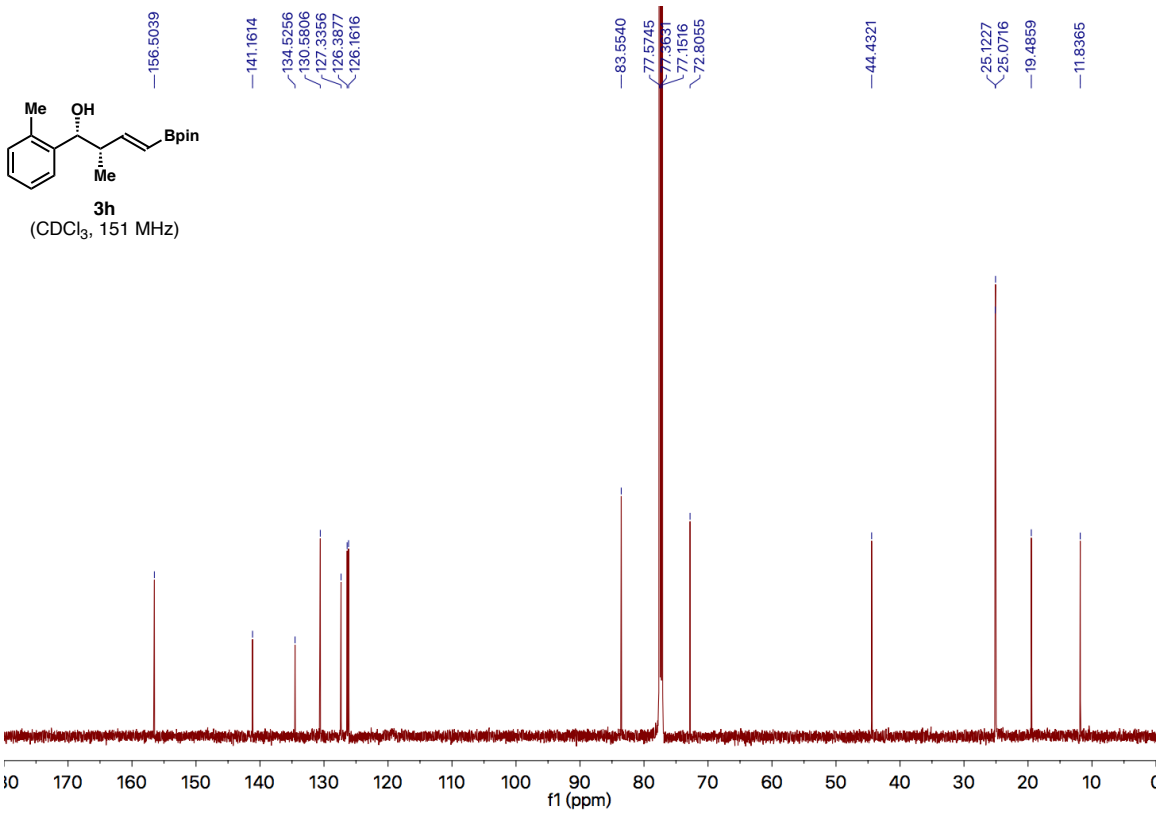

7.2594
7.1941
7.1812
7.1391
7.1264
6.6788
6.6682
6.6486
6.6379
5.5154
5.4851
4.7304
4.7225
2.6363
2.6255
2.6146
2.6038
2.5940
2.3332
1.7056
1.2589
0.9745
0.9630
OH
Bpin
Me
Me
3f
(CDCl3, 600 MHz)
2.11
2.10
0.97
0.99
1.00
1.00
3.18
1.88
13.16
3.21
f1 (ppm)

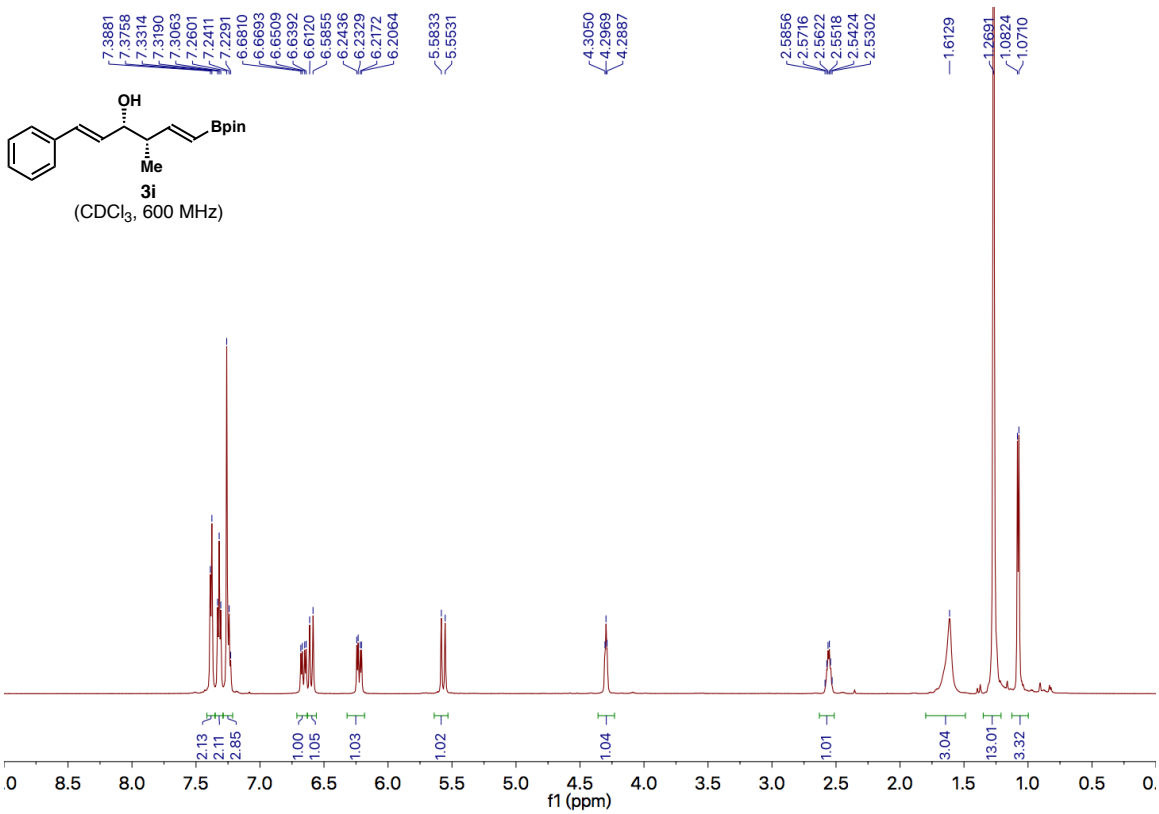

156.0121
139.7747
137.1698
129.0906
126.4611
119.5801
83.4942
77.5707
77.3596
77.1476
76.5929
46.5625
25.1294
25.0510
21.4809
12.9470
OH
Bpin
Me
Me
3f
(CDCl3, 151 MHz)
f1 (ppm)

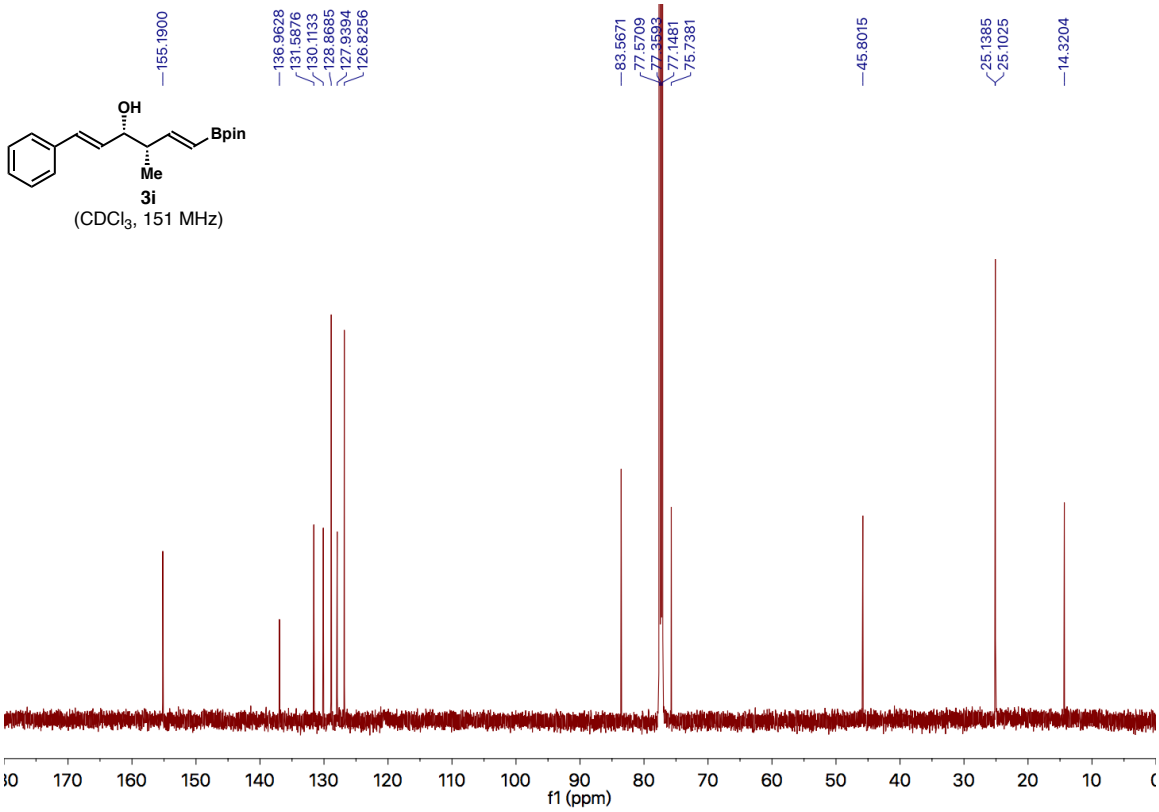

OH
Me
Bpin
Me
3g
(CDCl3, 600 MHz)
f1 (ppm)

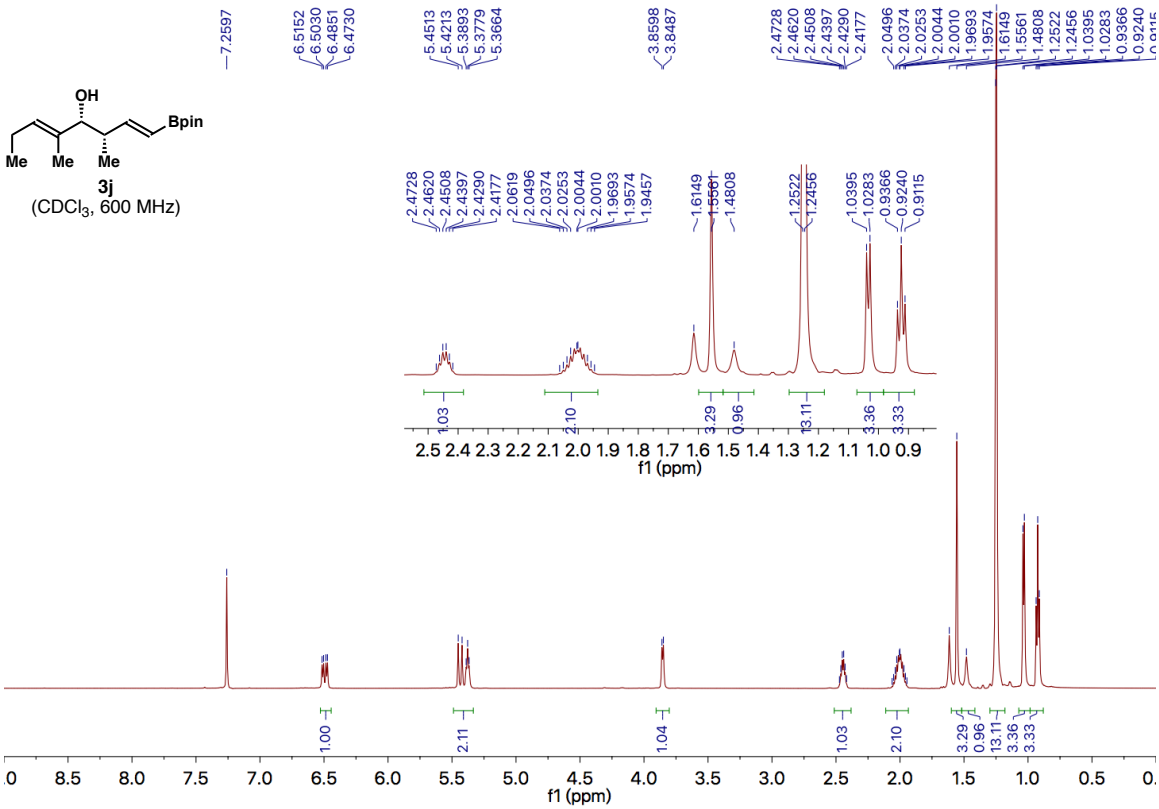

OH
Me
Bpin
Me
3g
(CDCl3, 151 MHz)
f1 (ppm)

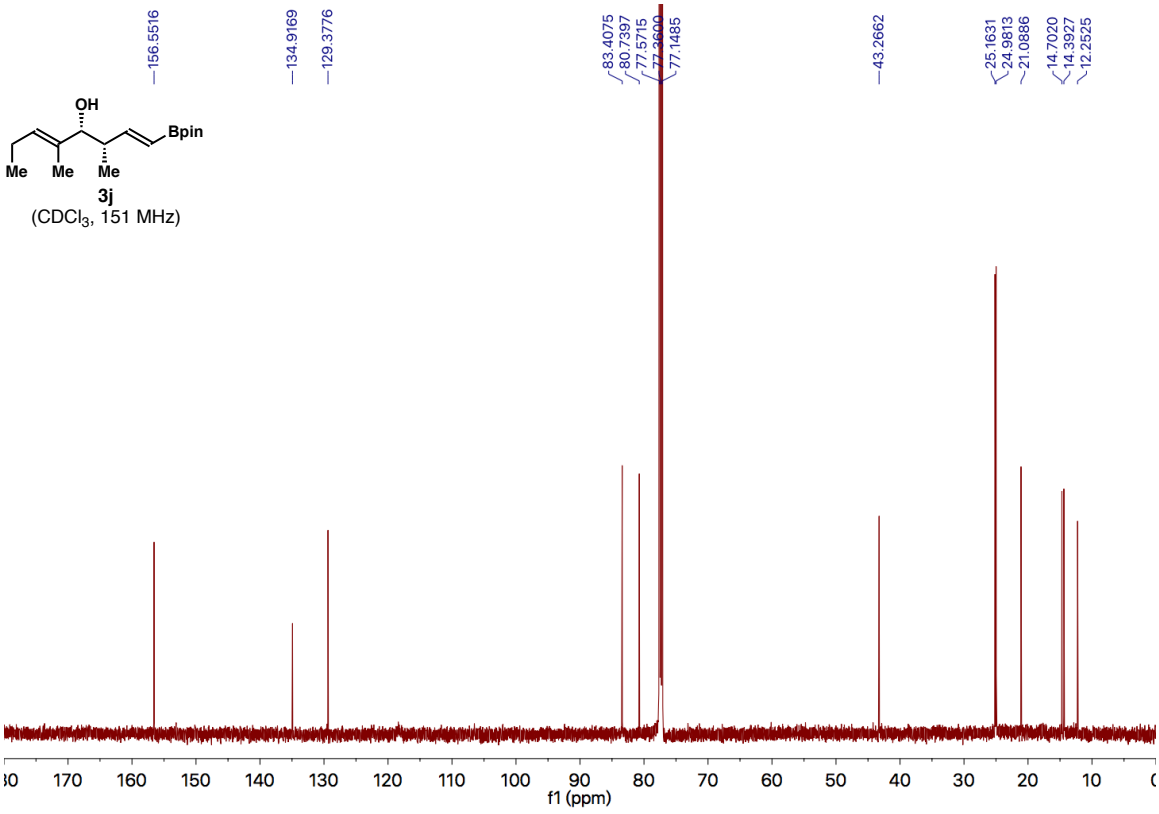

Me
OH
Bpin
Me
3h
(CDCl3, 600 MHz)
f1 (ppm)

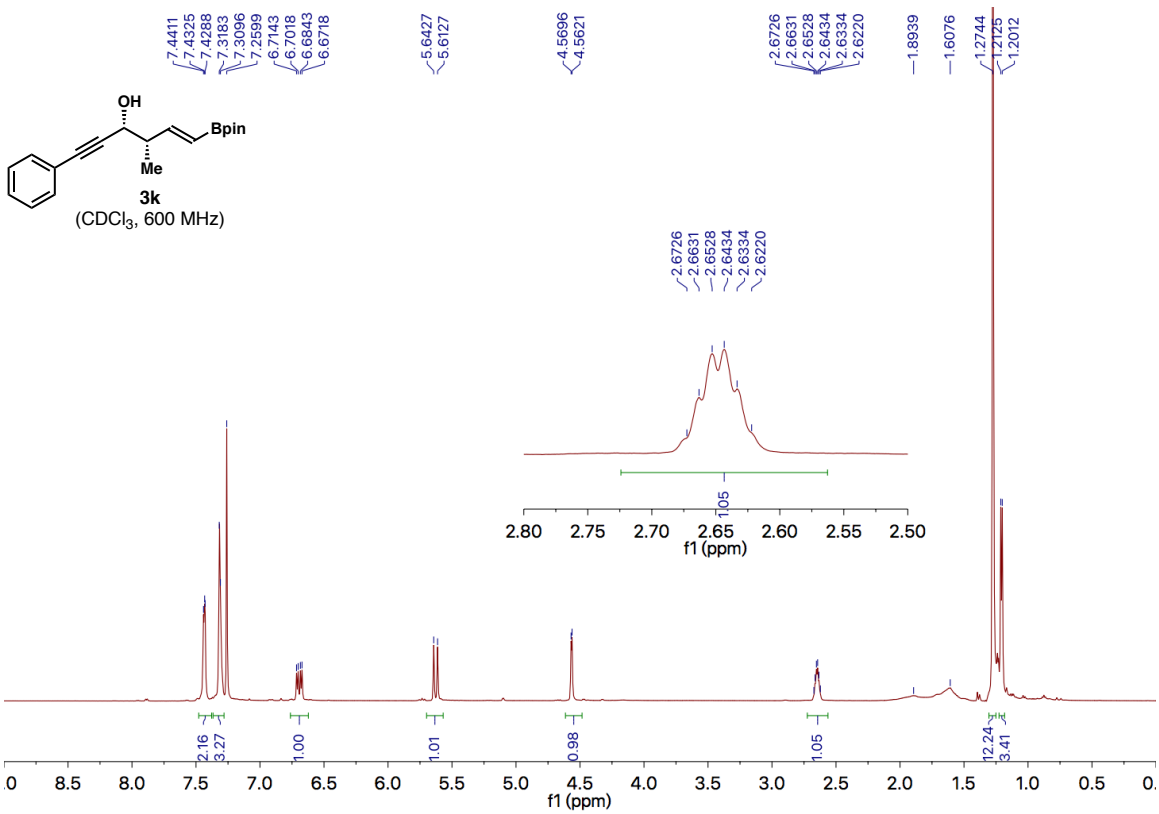

Me
OH
Bpin
Me
3h
(CDCl3, 151 MHz)
f1 (ppm)

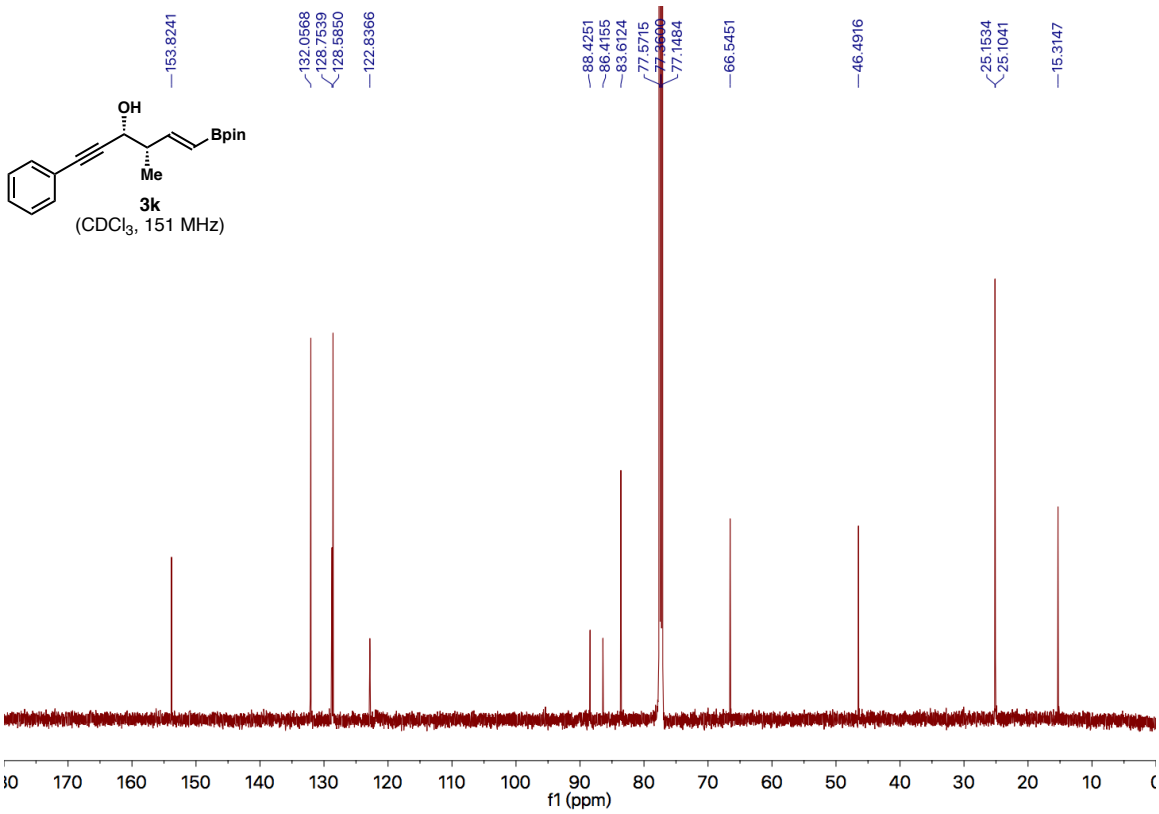

7.3881
7.3758
7.3314
7.3190
7.3063
7.2601
7.2411
7.2291
6.6810
6.6693
6.6509
6.6392
6.6120
6.5855
6.2436
6.2329
6.2172
6.2064
5.5833
5.5531
4.3050
4.2969
4.2887
2.5856
2.5716
2.5622
2.5518
2.5424
2.5302
1.6129
1.2691
1.0824
1.0710
OH
Bpin
Me
3i
(CDCl3, 600 MHz)
2.13
2.11
2.85
1.00
1.05
1.03
1.02
1.04
1.01
3.04
13.01
3.32
f1 (ppm)

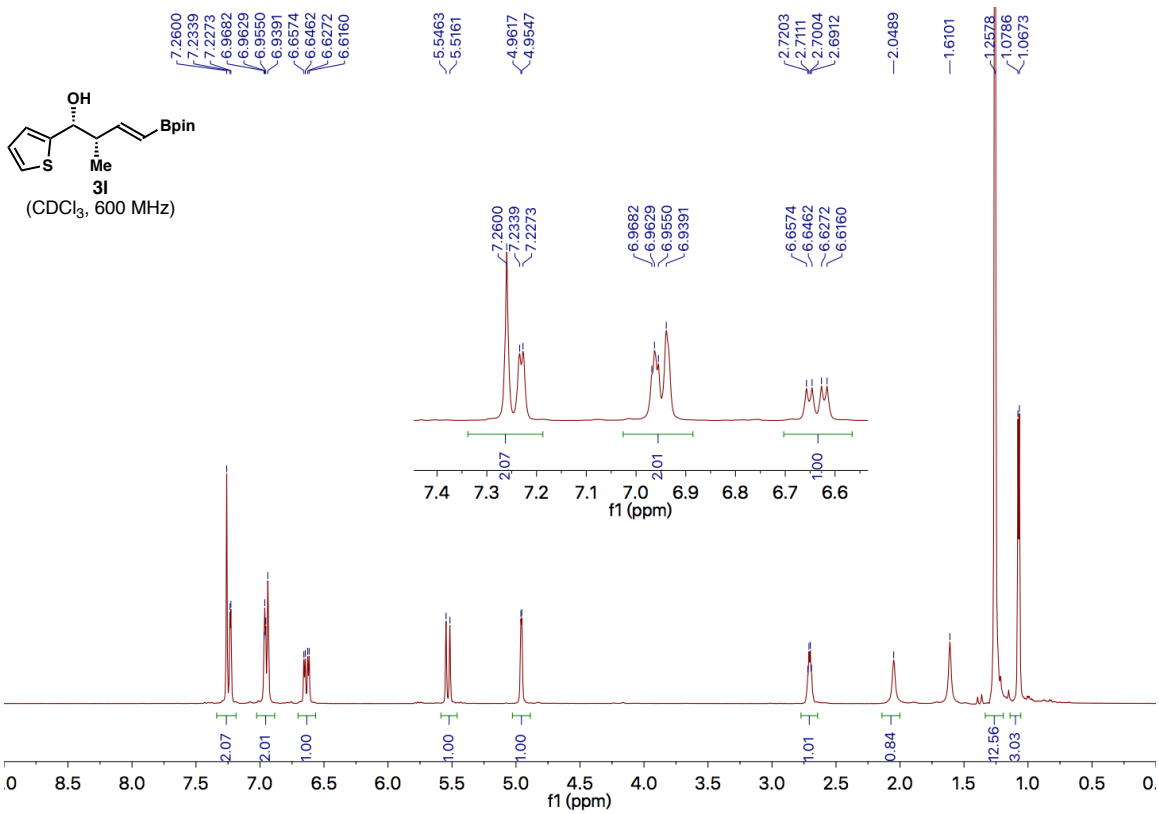

155.1900
136.9628
131.5876
130.1133
128.8685
127.9394
126.8256
83.5671
77.5709
77.3593
77.1481
75.7381
45.8015
25.1385
25.1025
14.3204
OH
Bpin
Me
3i
(CDCl3, 151 MHz)
f1 (ppm)

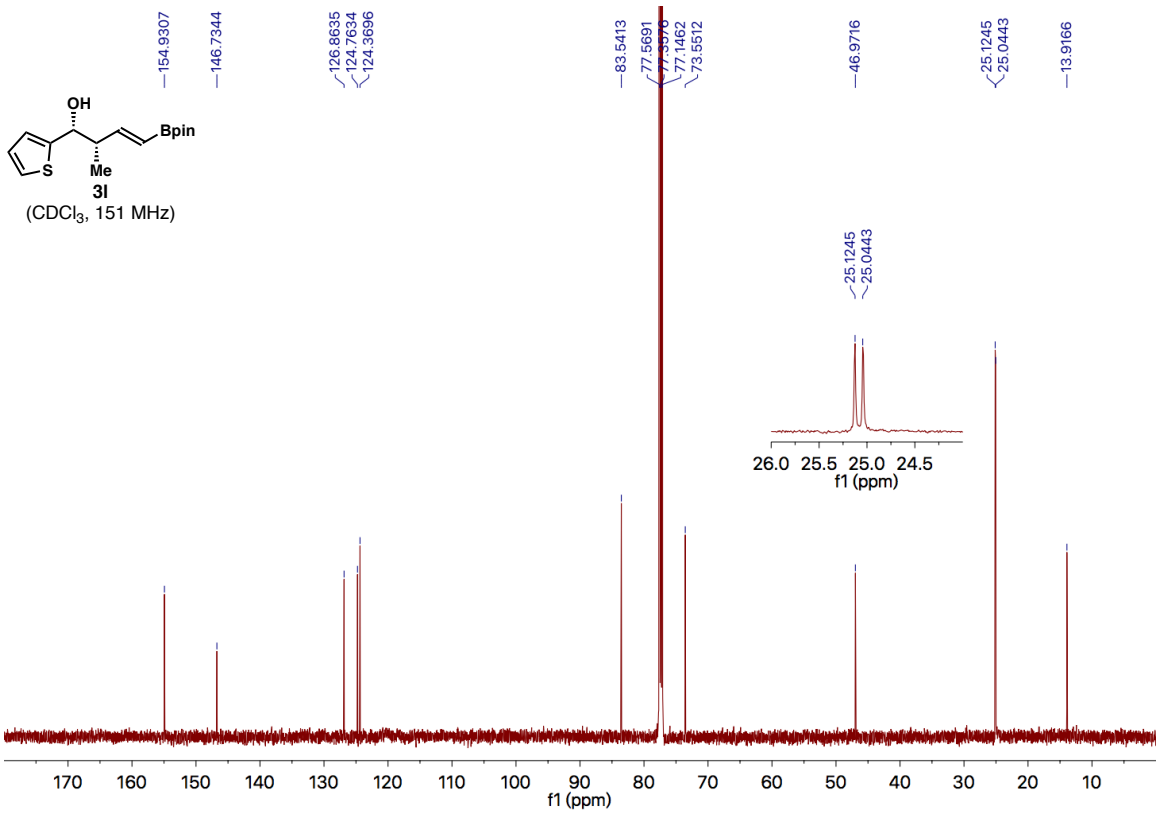

OH
Bpin
Me
Me
Me
3j
(CDCl3, 600 MHz)
f1 (ppm)

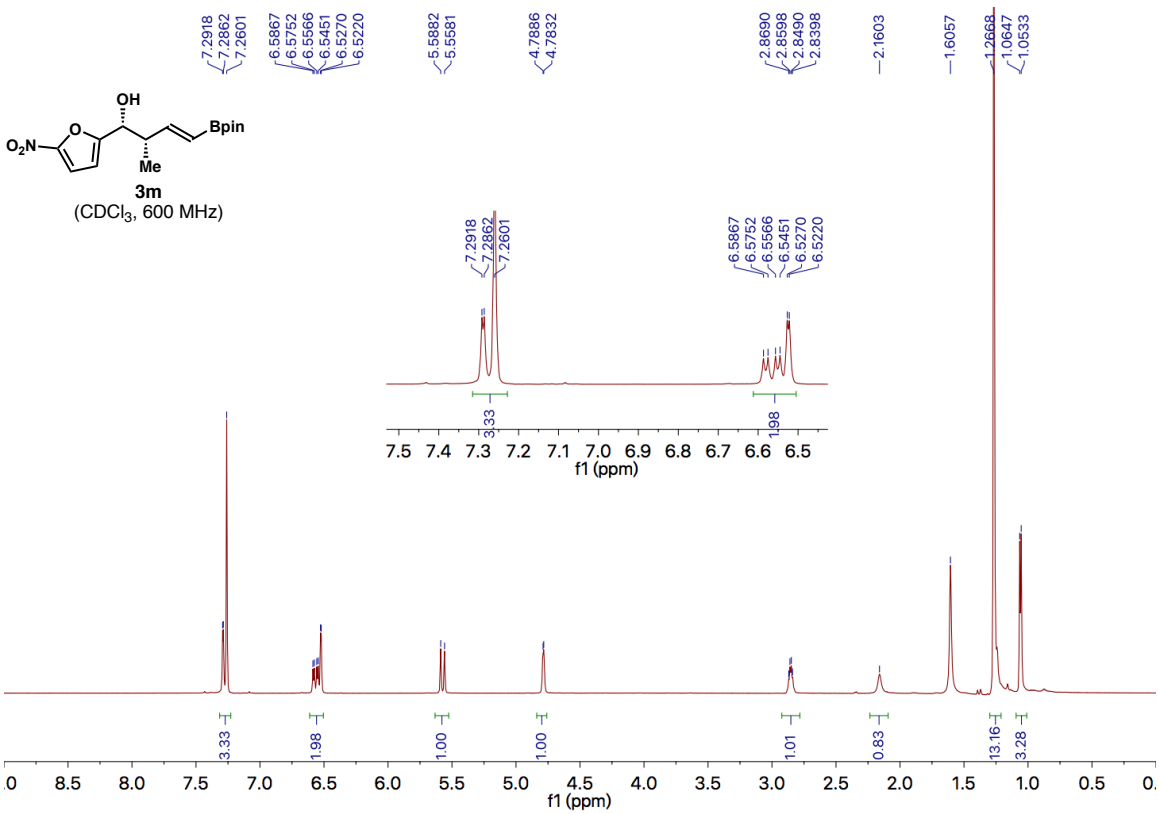

OH
Bpin
Me
Me
Me
3j
(CDCl3, 151 MHz)
f1 (ppm)

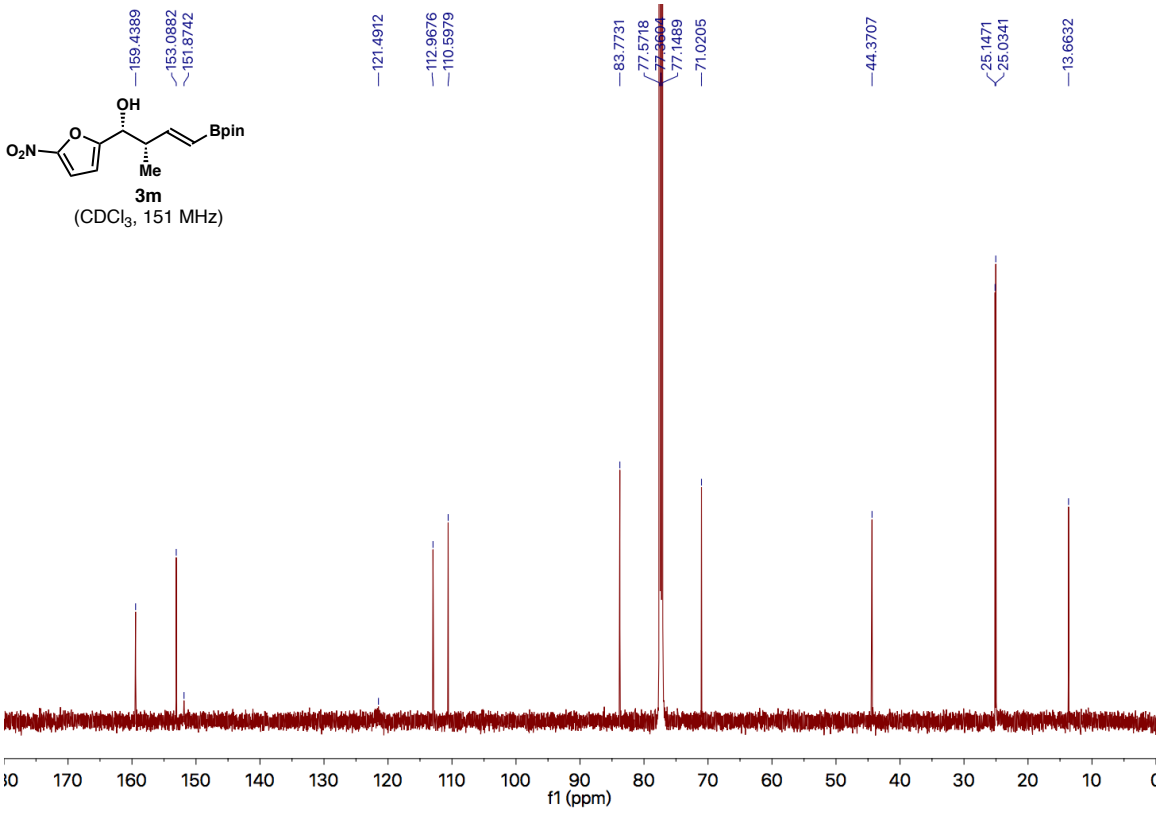

OH
Bpin
Me
3k
(CDCl3, 600 MHz)
f1 (ppm)

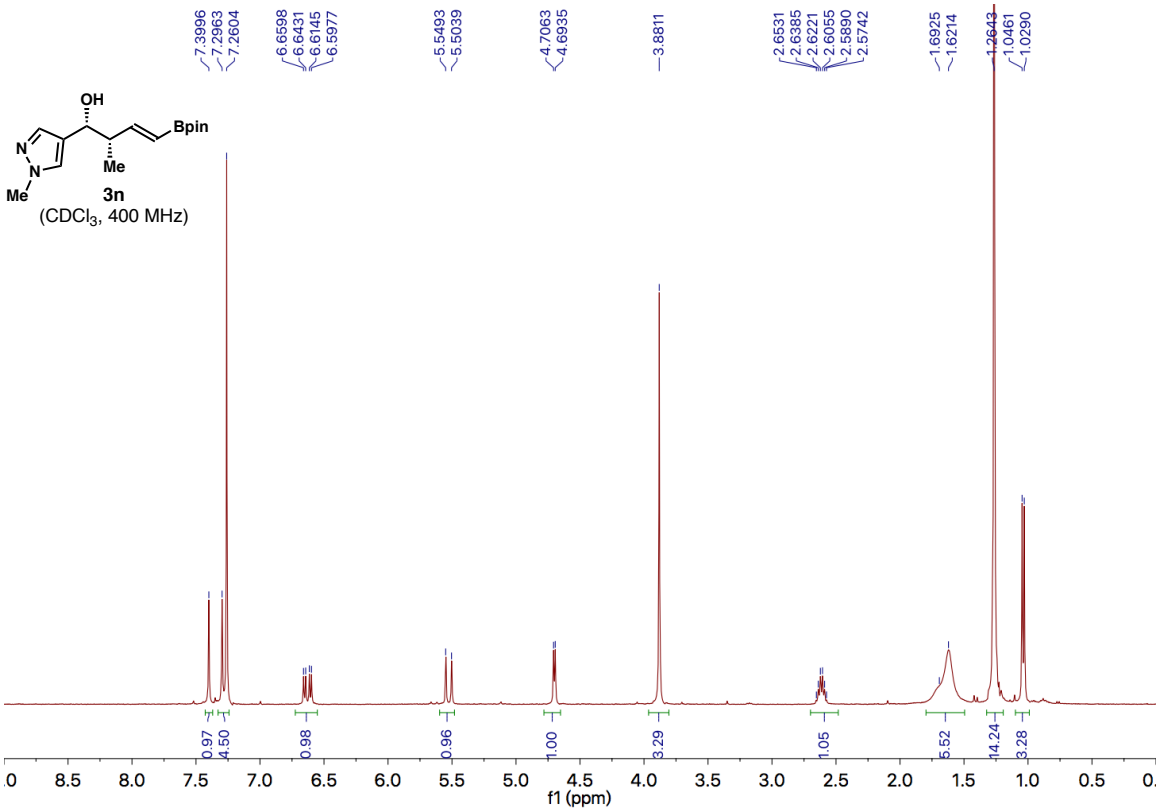

OH
Bpin
Me
3k
(CDCl3, 151 MHz)
f1 (ppm)

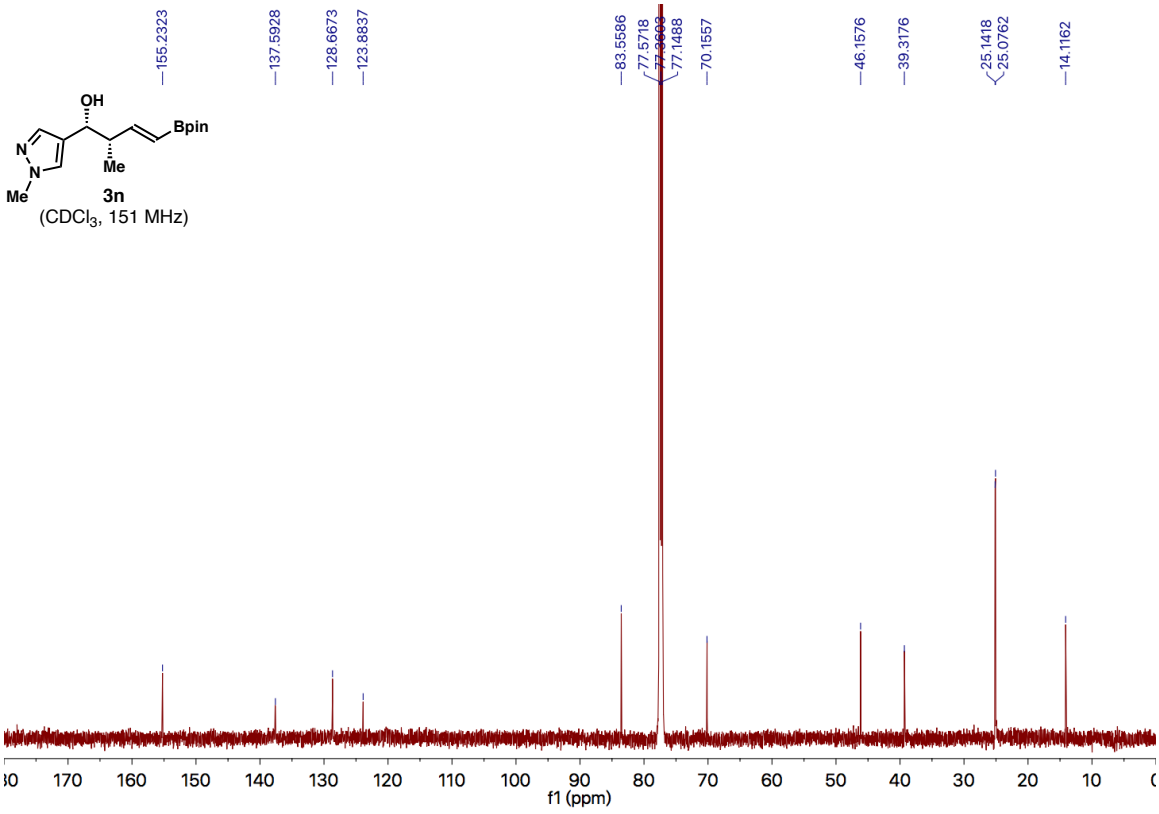

OH
Bpin
S
Me
3l
(CDCl3, 600 MHz)
f1 (ppm)

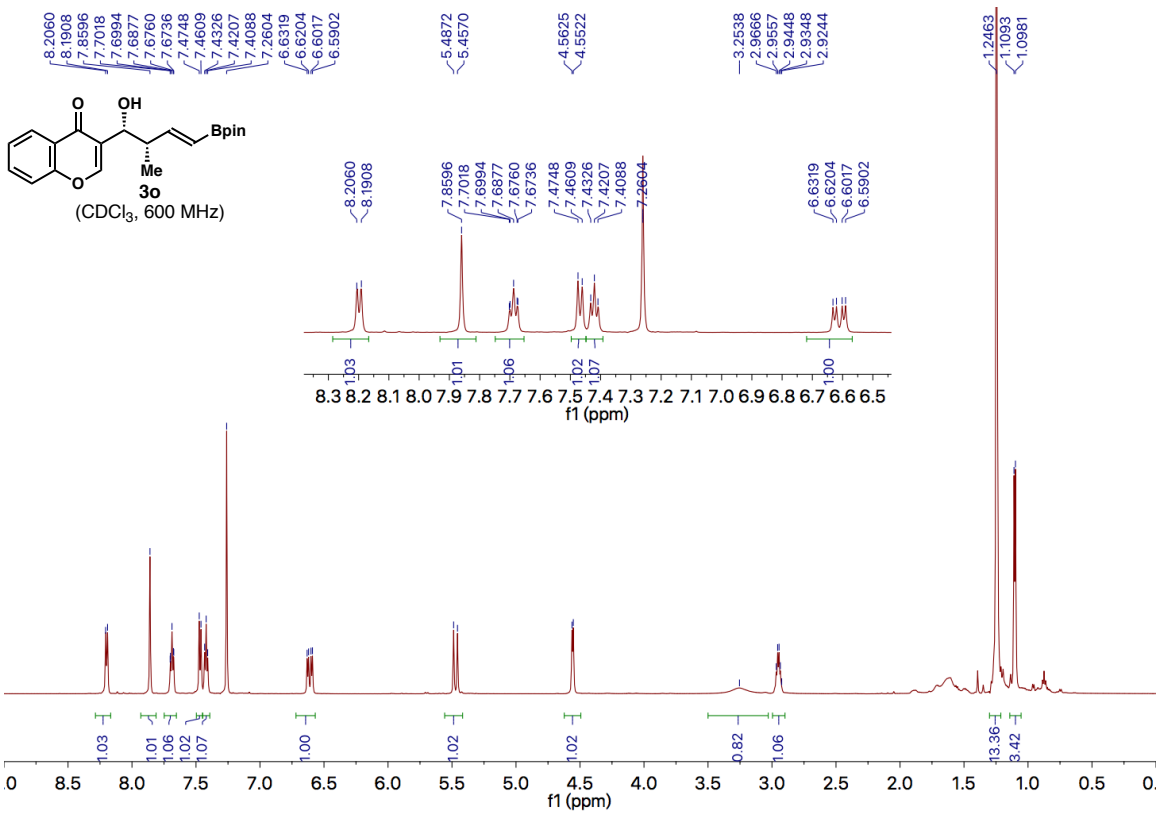

OH
Bpin
S
Me
3l
(CDCl3, 151 MHz)
f1 (ppm)

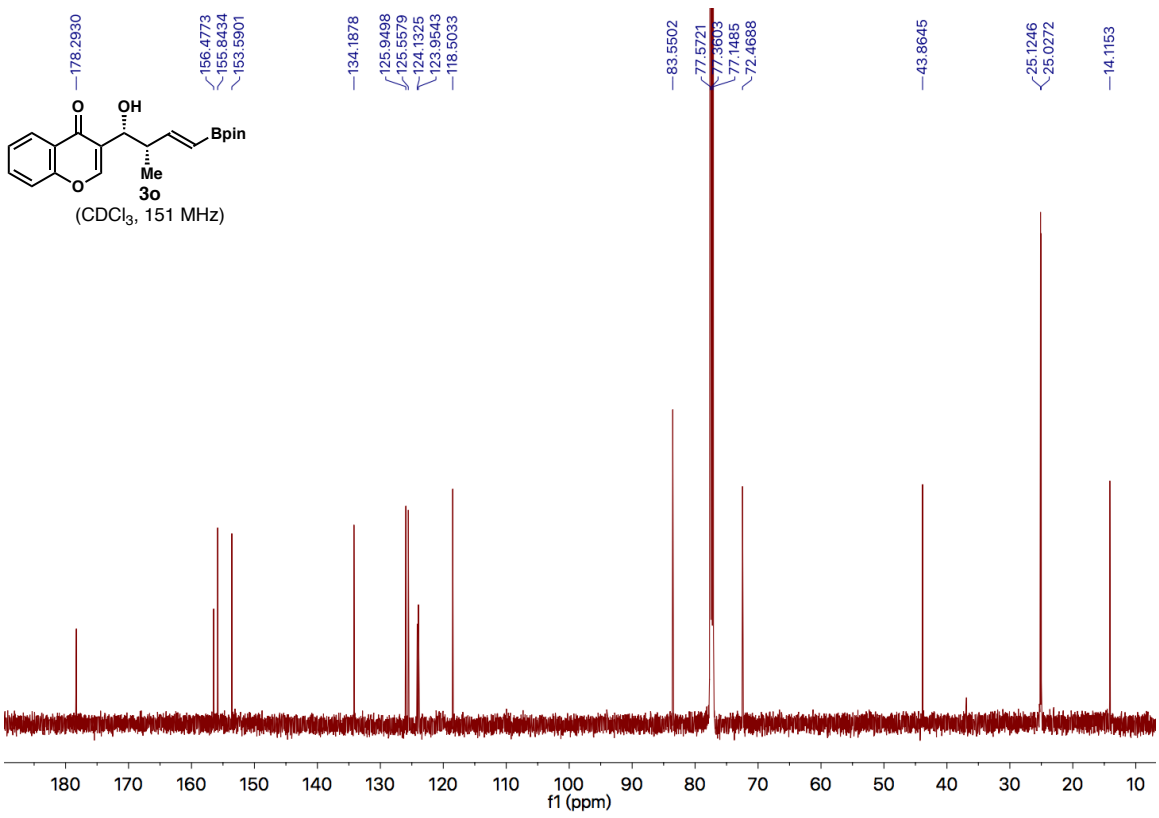

7.2918
7.2862
7.2601
6.5867
6.5752
6.5566
6.5451
6.5270
6.5220
5.5882
5.5581
4.7886
4.7832
2.8690
2.8598
2.8490
2.8398
2.1603
1.6057
1.2668
1.0647
1.0533
OH
O2N
O
Bpin
Me
3m
(CDCl3, 600 MHz)
3.33
1.98
1.00
1.00
1.01
0.83
13.16
3.28
f1 (ppm)

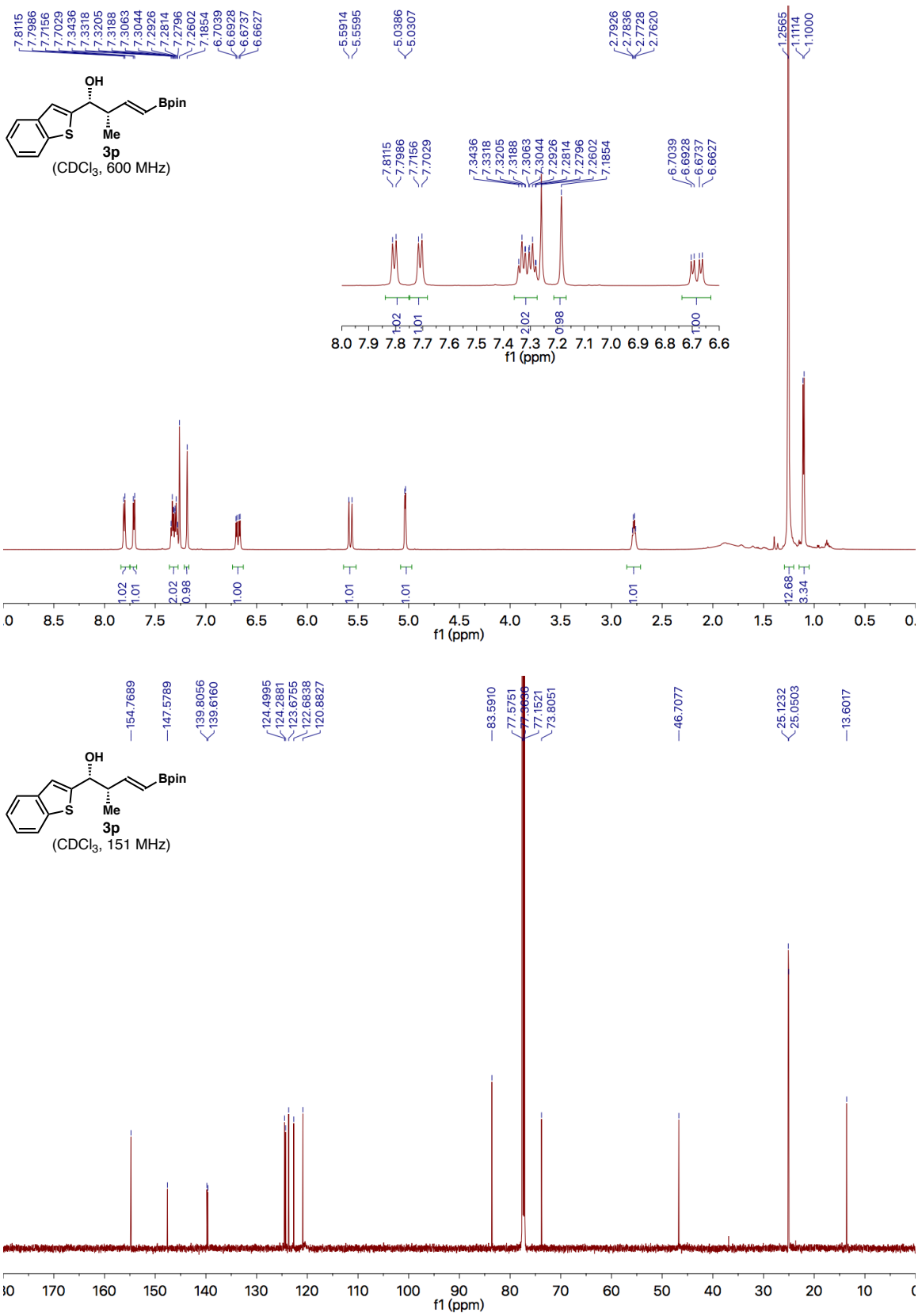

159.4389
153.0882
151.8742
121.4912
112.9676
110.5979
83.7731
77.5718
77.1489
71.0205
44.3707
25.1471
25.0341
13.6632
OH
O2N
O
Bpin
Me
3m
(CDCl3, 151 MHz)
f1 (ppm)

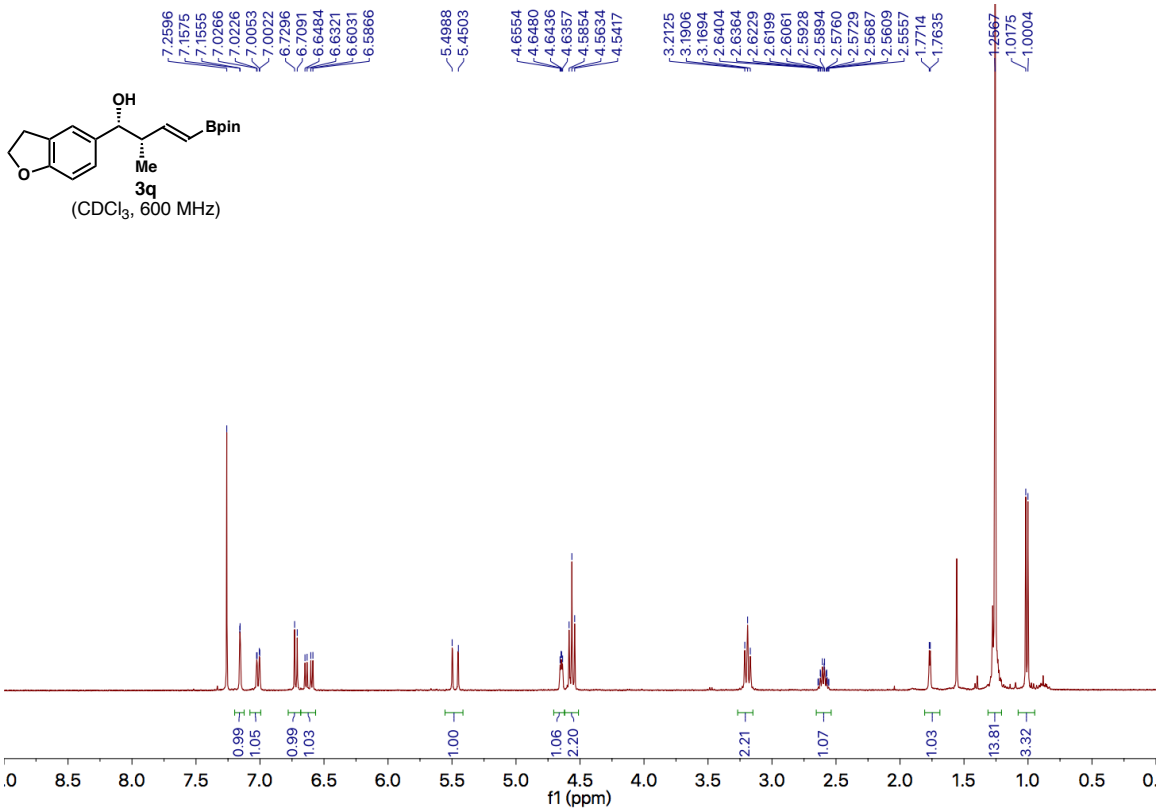

7.3996
7.2963
7.2604
6.6598
6.6431
6.6145
6.5977
5.5493
5.5039
4.7063
4.6935
3.8811
2.6531
2.6385
2.6221
2.6055
2.5890
2.5742
1.6925
1.6214
1.2643
1.0461
1.0290
OH
Bpin
N
N
Me
Me
3n
(CDCl3, 400 MHz)
0.97
4.50
0.98
0.96
1.00
3.29
1.05
5.52
14.24
3.28
f1 (ppm)

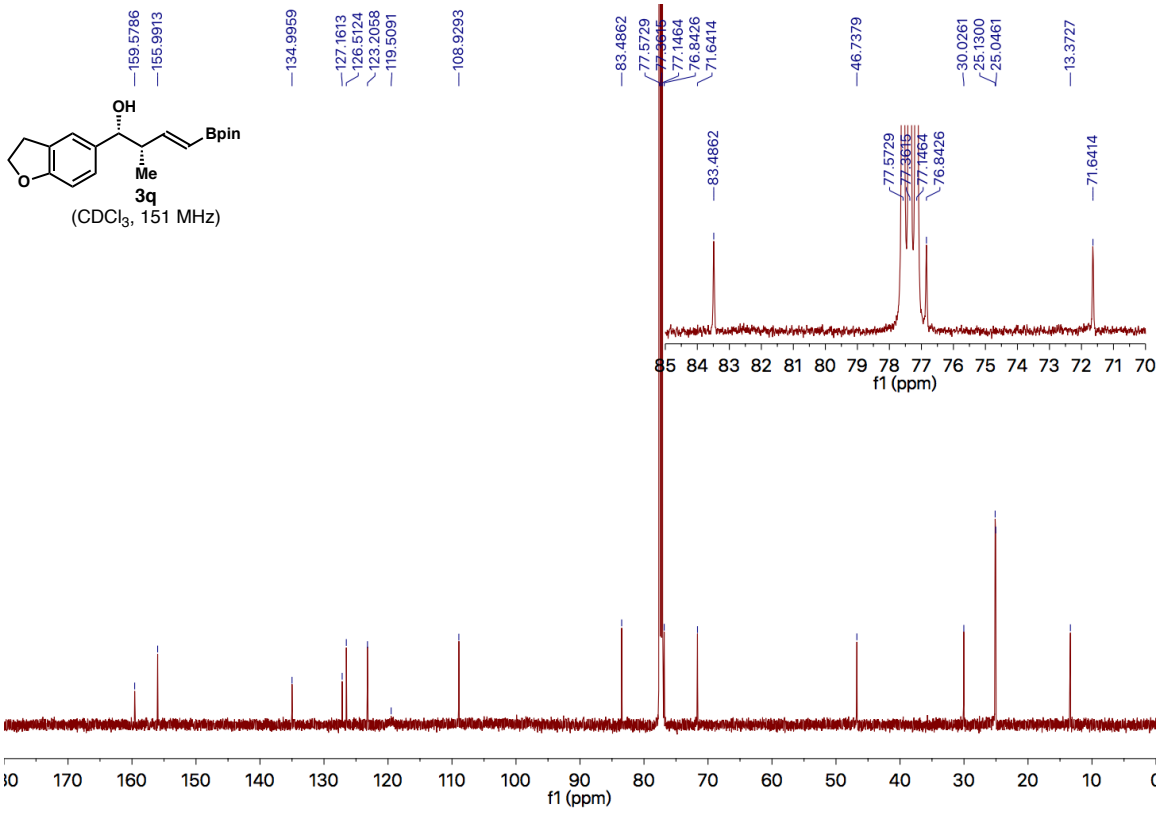

155.2323
137.5928
128.6673
123.8837
83.5586
77.5718
77.1488
70.1557
46.1576
39.3176
25.1418
25.0762
14.1162
OH
Bpin
N
N
Me
Me
3n
(CDCl3, 151 MHz)
f1 (ppm)

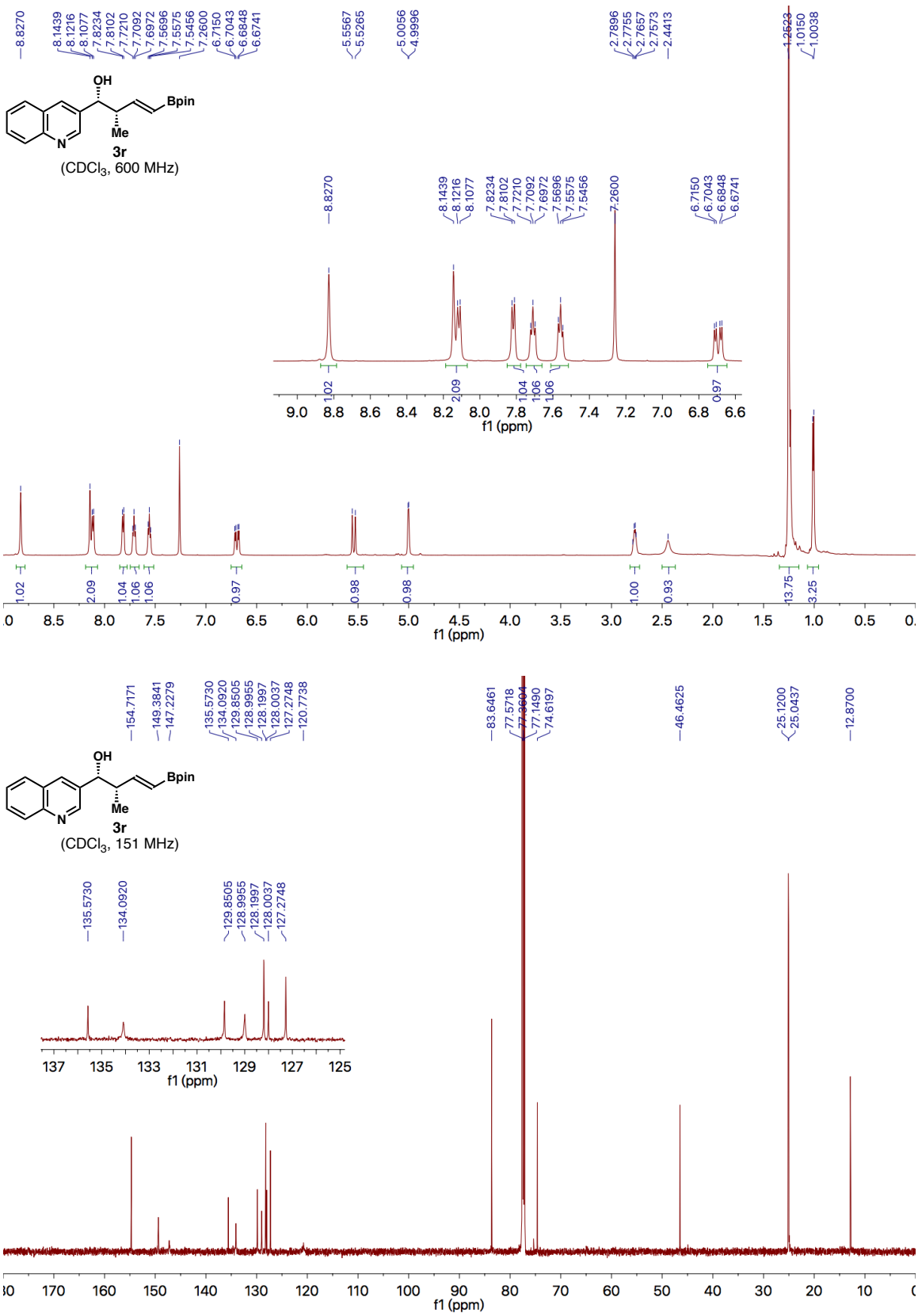

8.2060
8.1908
7.8596
7.7018
7.6994
7.6877
7.6760
7.6736
7.4748
7.4609
7.4326
7.4207
7.4088
7.2604
6.6319
6.6204
6.6017
6.5902
5.4872
5.4570
4.5625
4.5522
3.2538
2.9666
2.9557
2.9448
2.9348
2.9244
1.2463
1.1093
1.0981
O
OH
Bpin
Me
3o
(CDCl3, 600 MHz)
f1 (ppm)

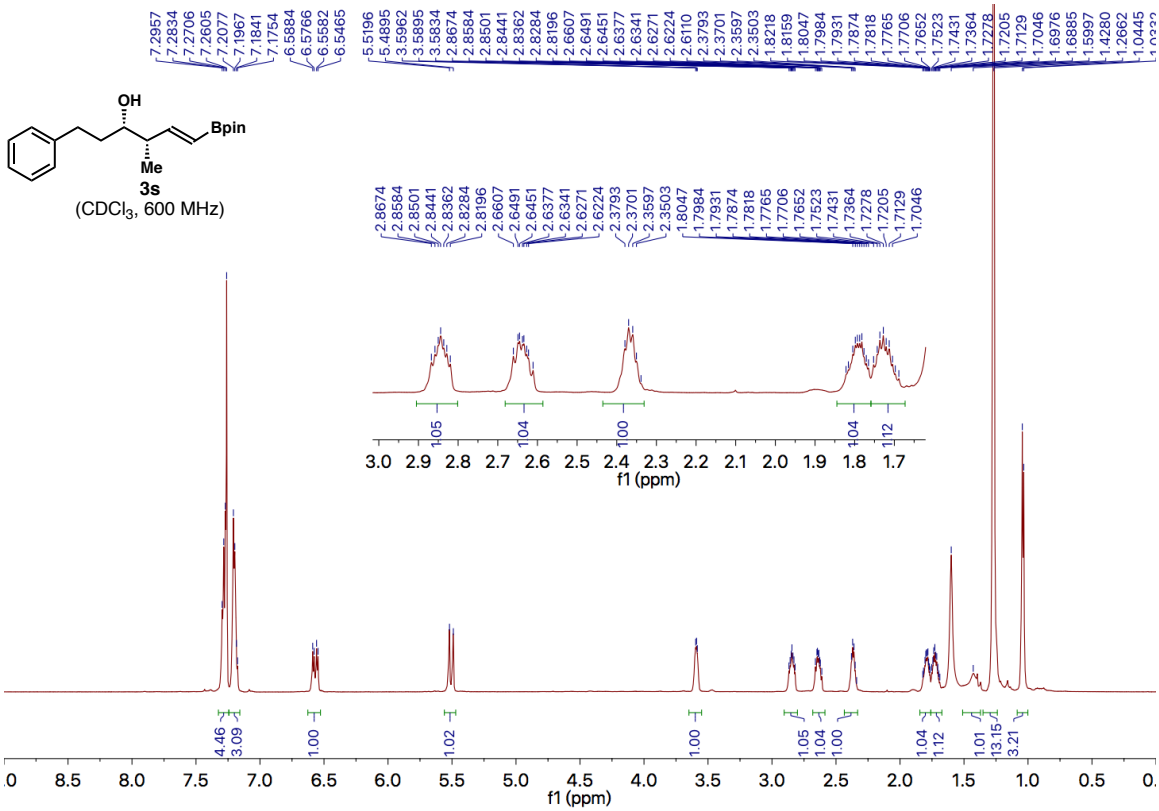

178.2930
156.4773
155.8434
153.5901
134.1878
125.9498
125.5579
124.1325
123.9543
118.5033
83.5502
77.5721
77.3603
77.1485
72.4688
43.8645
25.1246
25.0272
14.1153
O
OH
Bpin
Me
3o
(CDCl3, 151 MHz)
f1 (ppm)

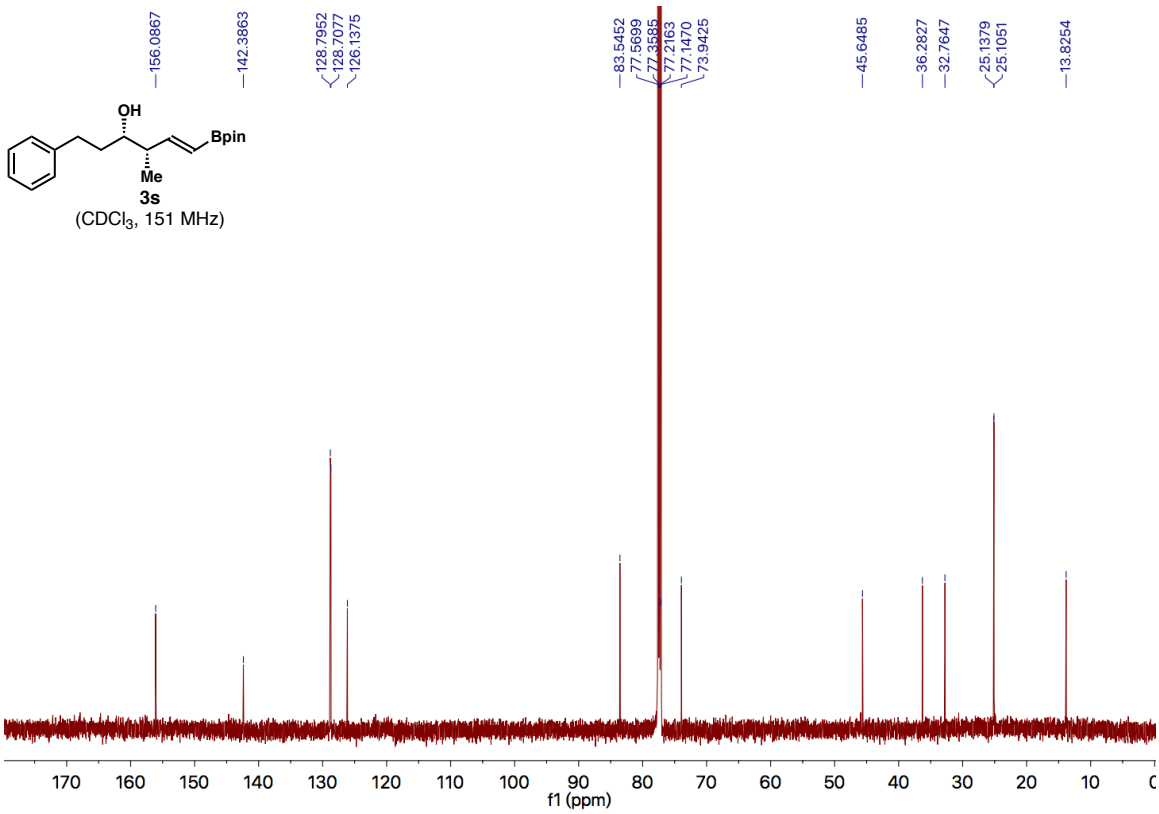

OH
Bpin
S
Me
3p
(CDCl3, 600 MHz)
f1 (ppm)
OH
Bpin
S
Me
3p
(CDCl3, 151 MHz)
f1 (ppm)

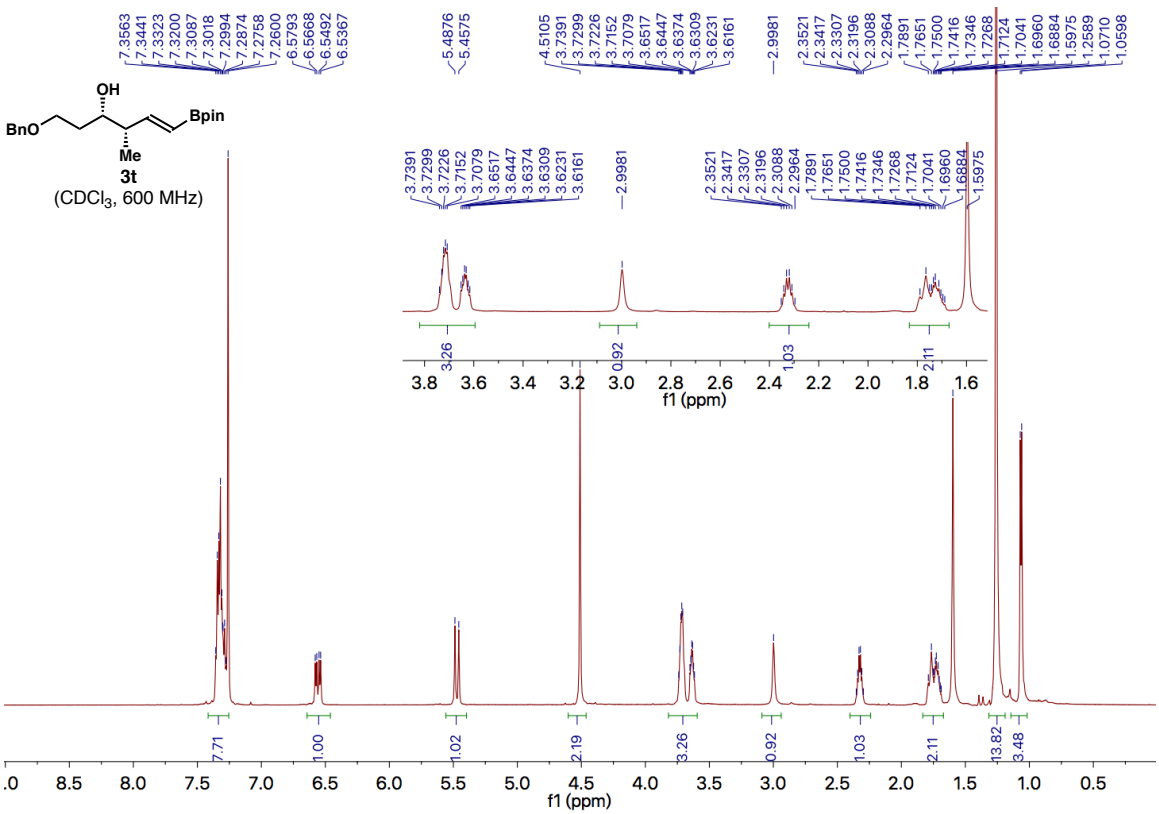

OH
Bpin
Me
O
3q
(CDCl3, 600 MHz)
f1 (ppm)

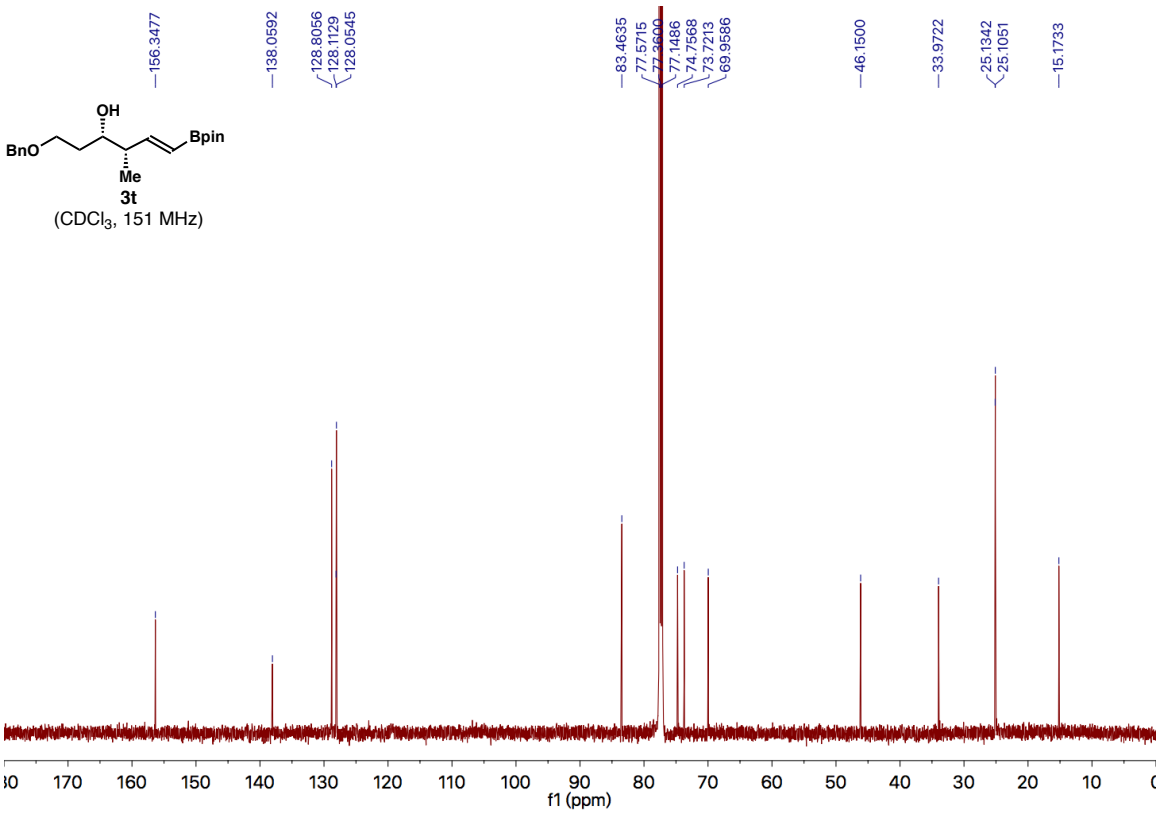

OH
Bpin
Me
O
3q
(CDCl3, 151 MHz)
f1 (ppm)

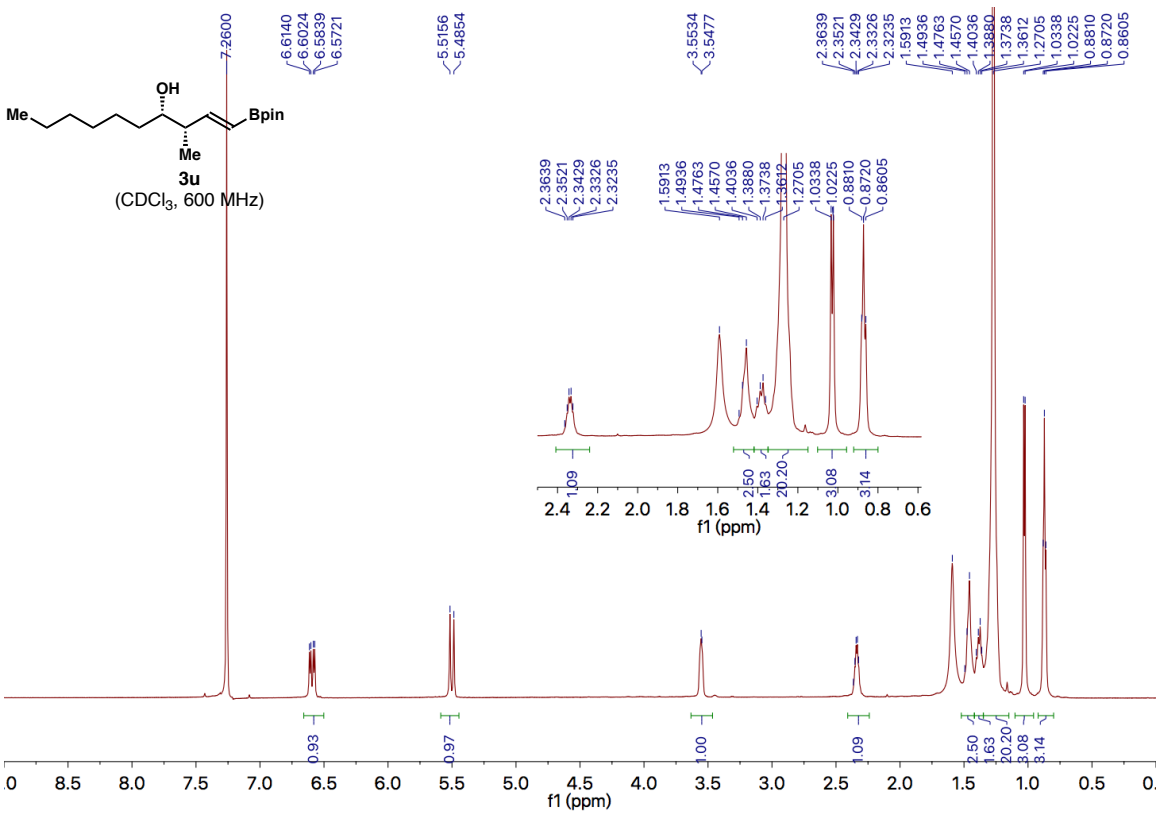

OH
Bpin
Me
N
3r
(CDCl3, 600 MHz)
f1 (ppm)
(CDCl3, 151 MHz)

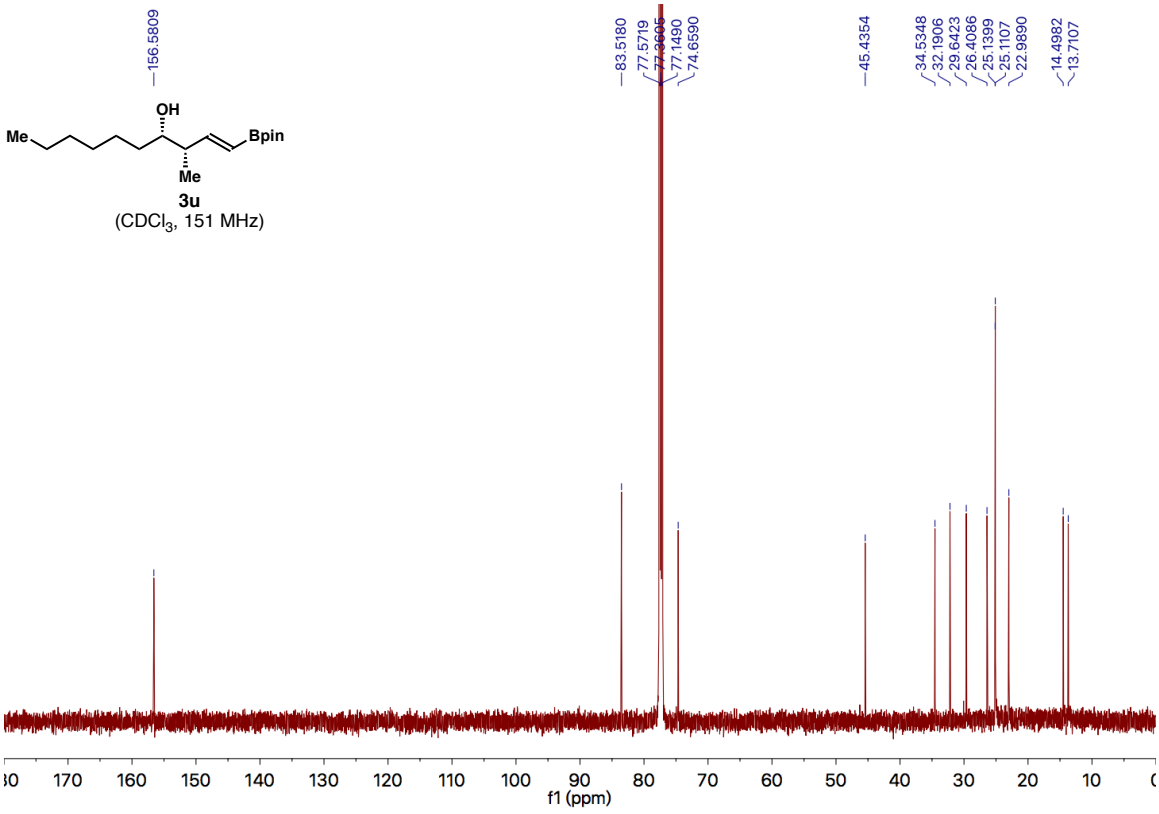

OH
Bpin
Me
3s
(CDCl3, 600 MHz)
f1 (ppm)

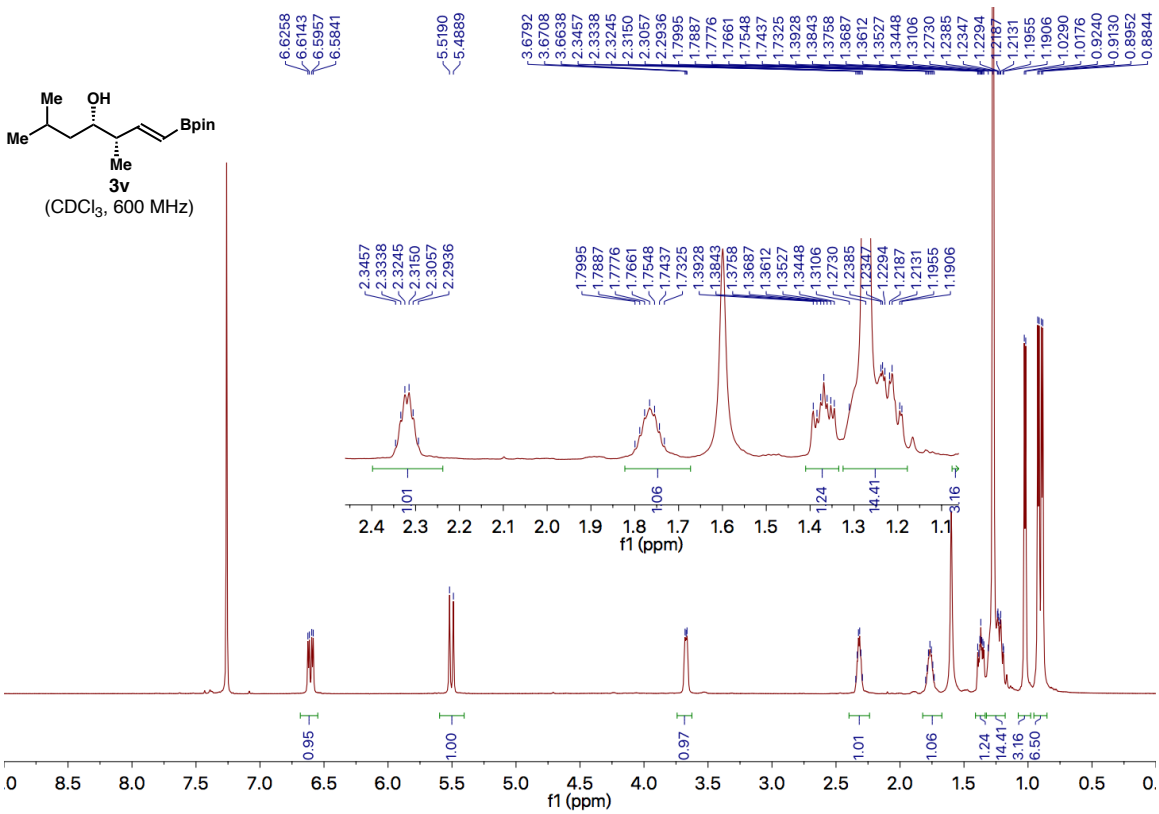

OH
Bpin
Me
3s
(CDCl3, 151 MHz)
f1 (ppm)

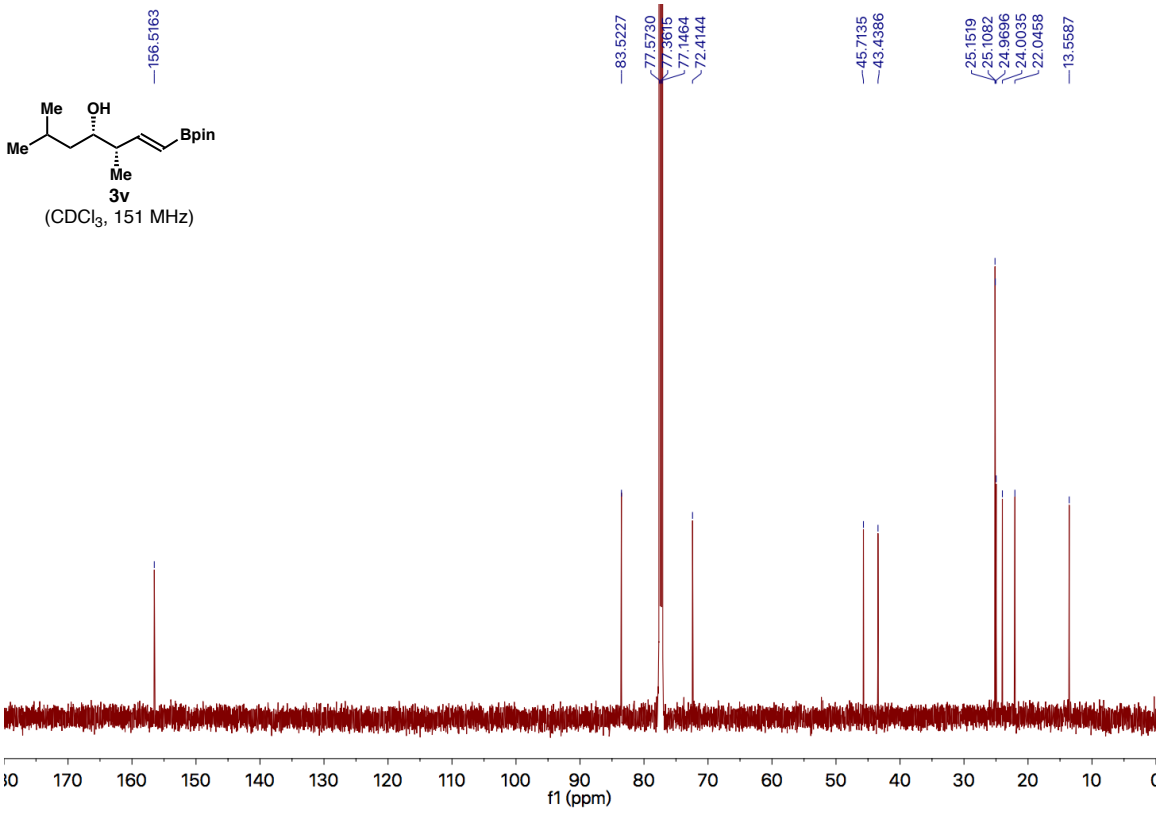

OH
BnO
Bpin
Me
3t
(CDCl3, 600 MHz)
f1 (ppm)

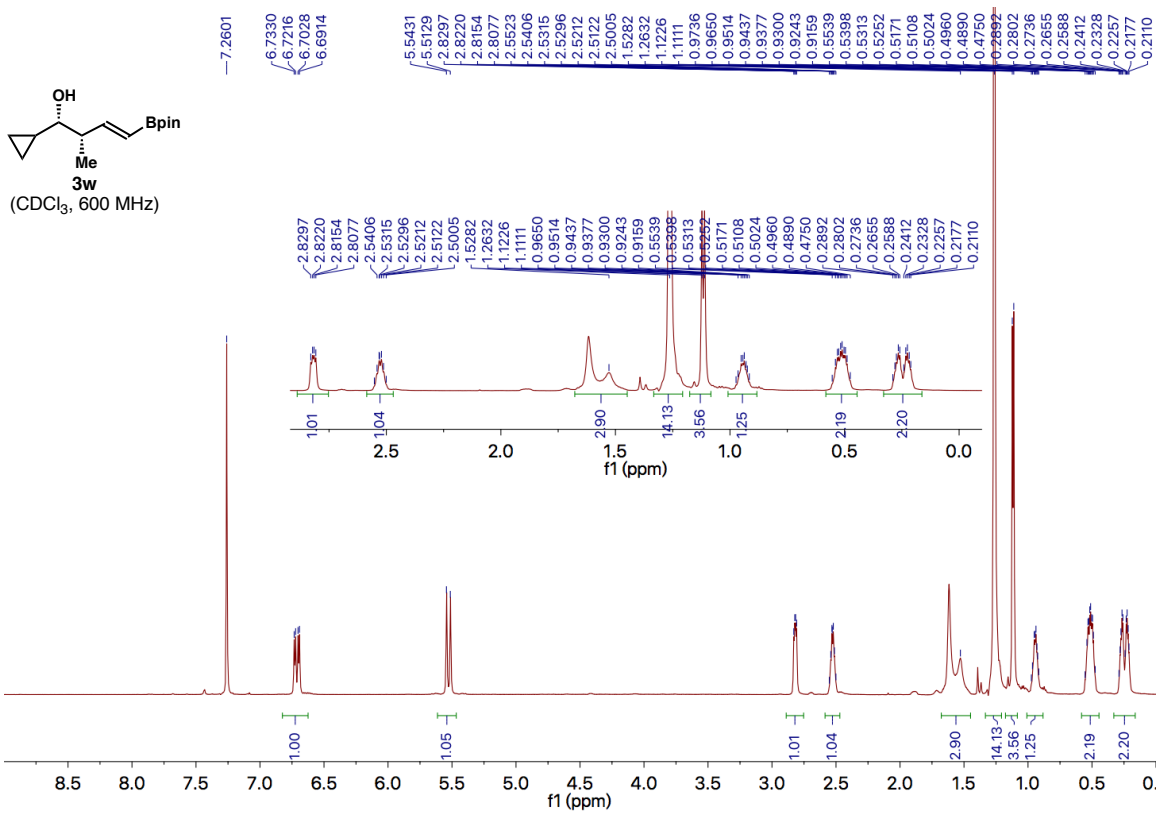

OH
BnO
Bpin
Me
3t
(CDCl3, 151 MHz)
f1 (ppm)

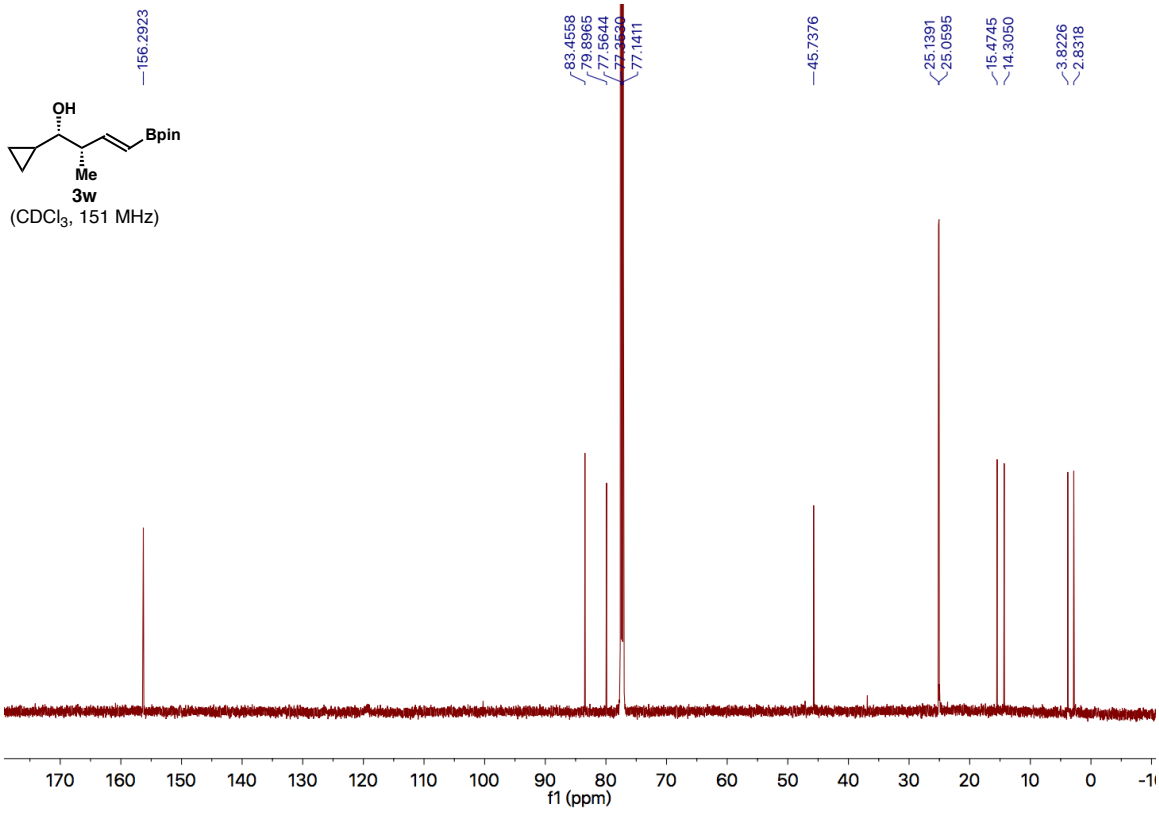

OH
Me
Bpin
Me
3u
(CDCl3, 600 MHz)
7.2600
6.6140
6.6024
6.5839
6.5721
5.5156
5.4854
3.5534
3.5477
2.3639
2.3521
2.3429
2.3326
2.3235
1.5913
1.4936
1.4763
1.4570
1.4036
1.3880
1.3738
1.3612
1.2705
1.0338
1.0225
0.8810
0.8720
0.8605
0.93
0.97
1.00
1.09
2.50
1.63
20.20
3.08
3.14
f1 (ppm)

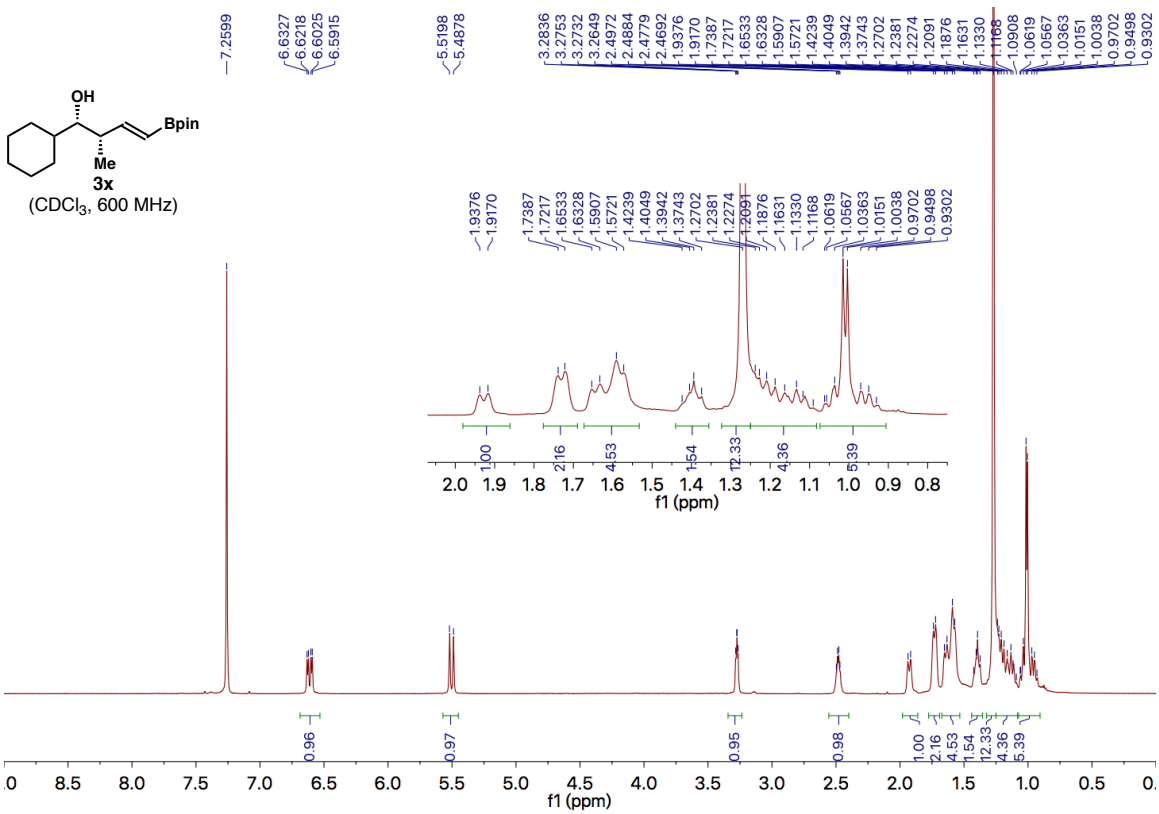

OH
Me
Bpin
Me
3u
(CDCl3, 151 MHz)
156.5809
83.5180
77.5719
77.3605
77.1490
74.6590
45.4354
34.5348
32.1906
29.6423
26.4086
25.1399
25.1107
22.9890
14.4982
13.7107
f1 (ppm)

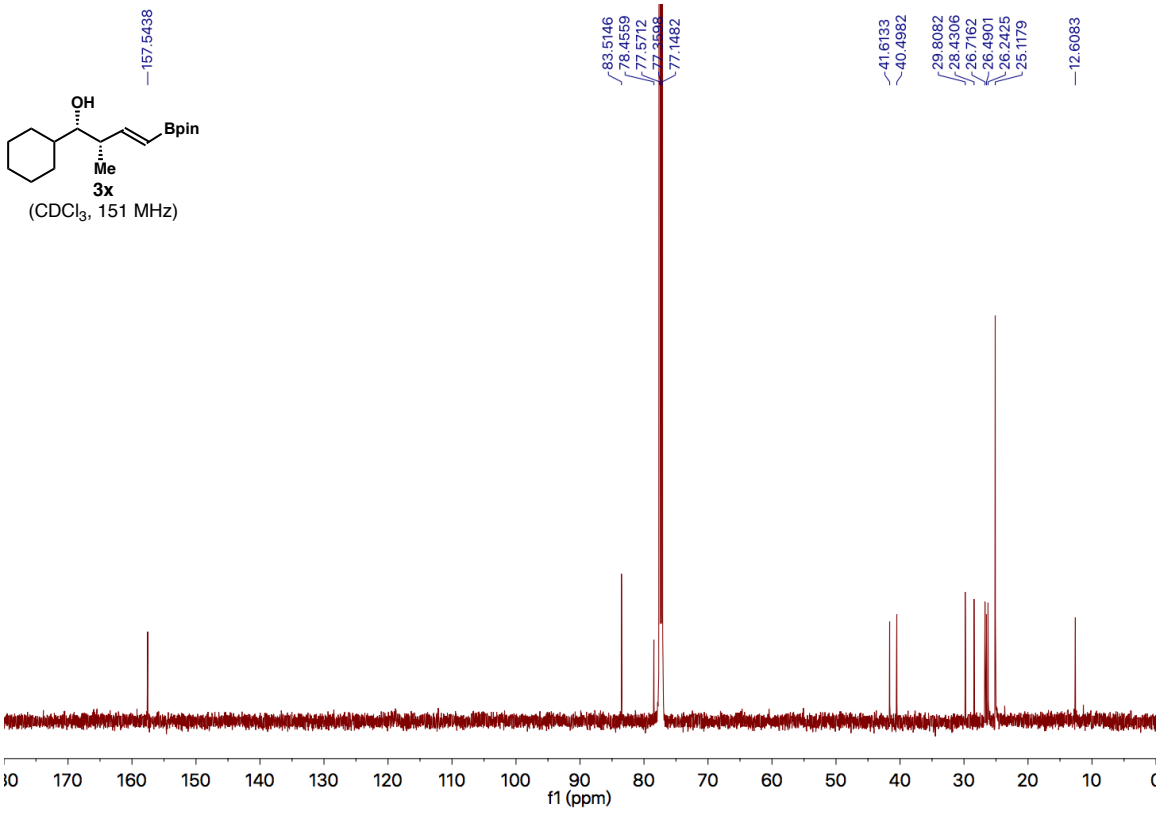

Me
OH
Me
Bpin
Me
3v
(CDCl3, 600 MHz)
f1 (ppm)

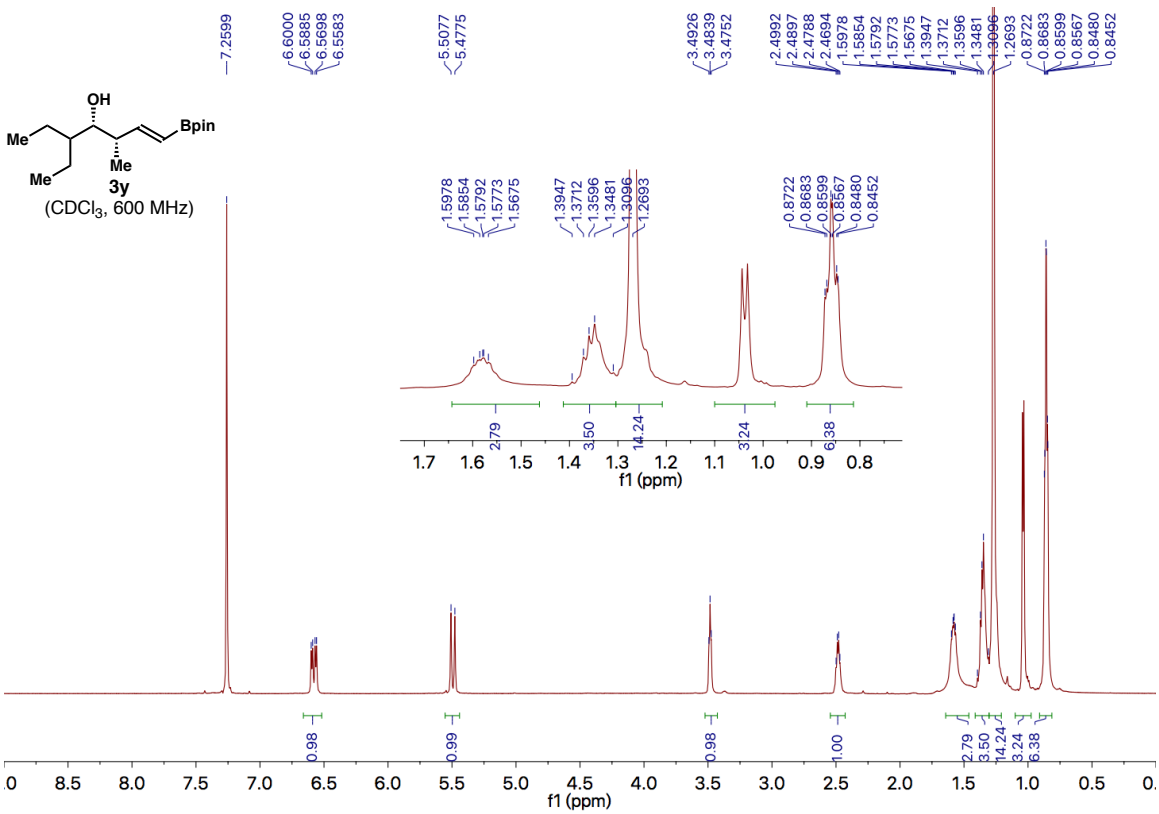

Me
OH
Me
Bpin
Me
3v
(CDCl3, 151 MHz)
f1 (ppm)

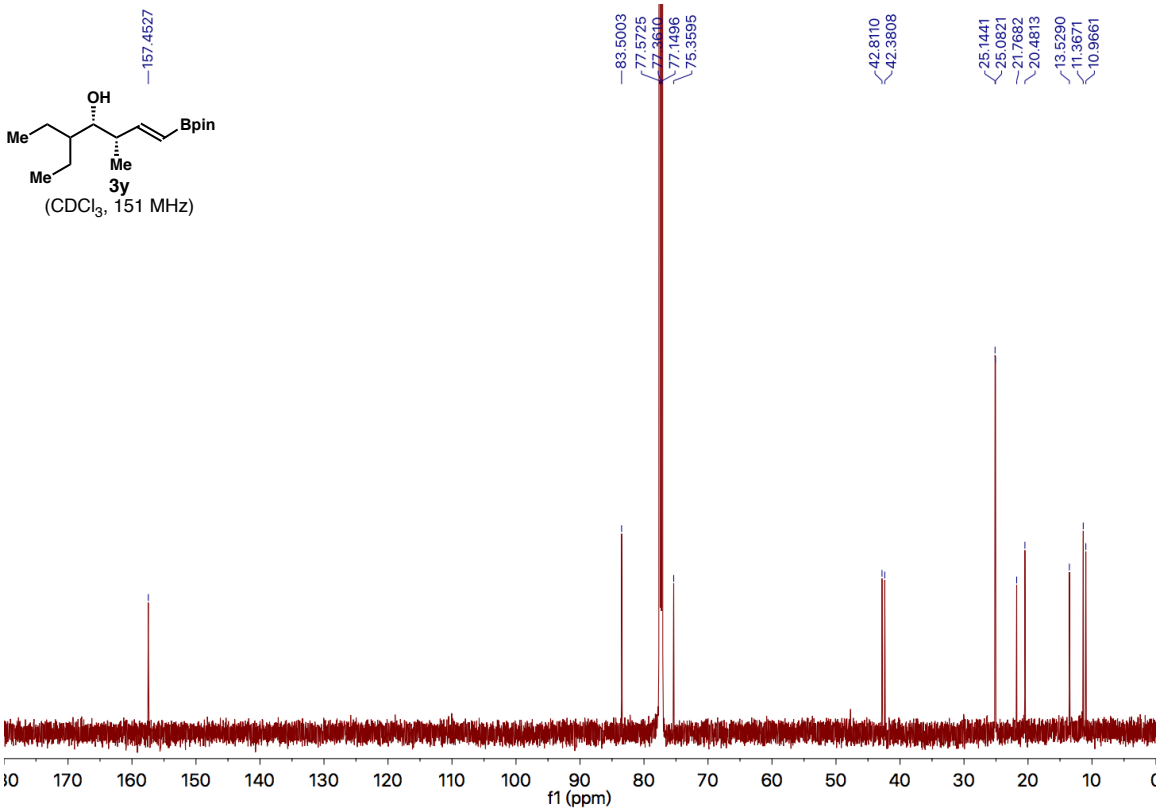

OH
Bpin
Me
3w
(CDCl3, 600 MHz)
f1 (ppm)

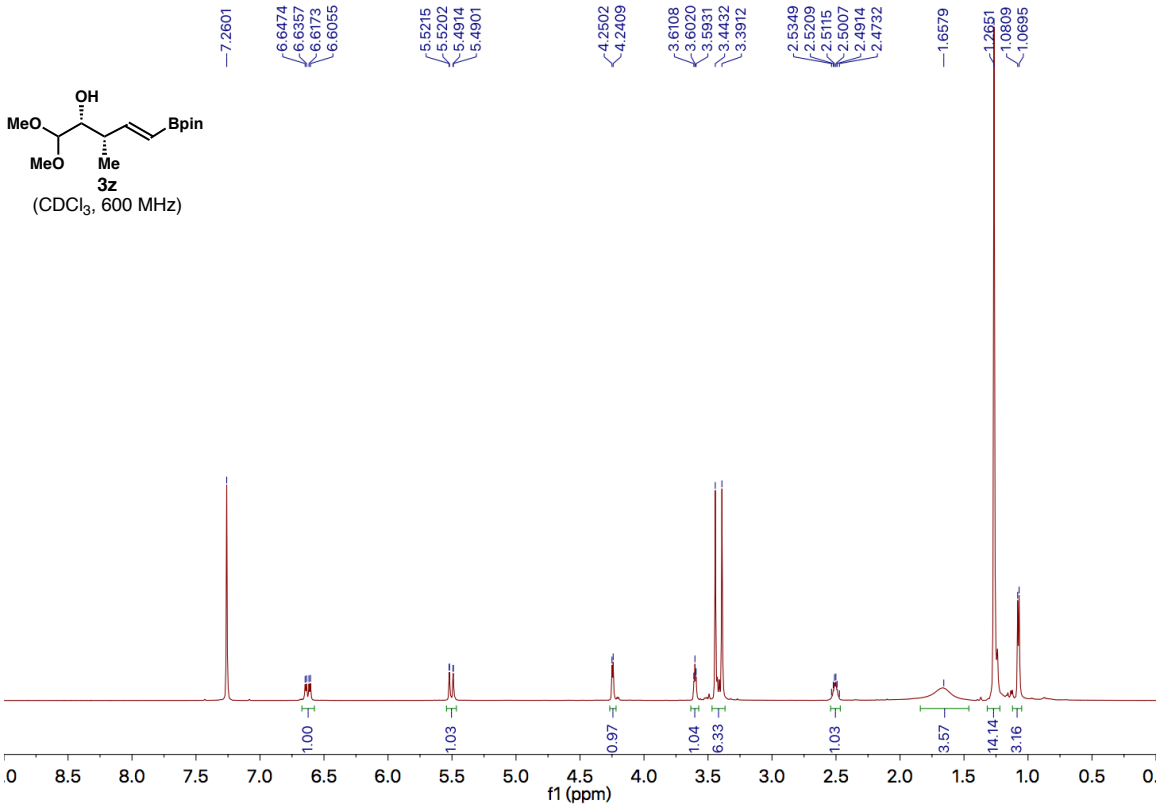

OH
Bpin
Me
3w
(CDCl3, 151 MHz)
f1 (ppm)

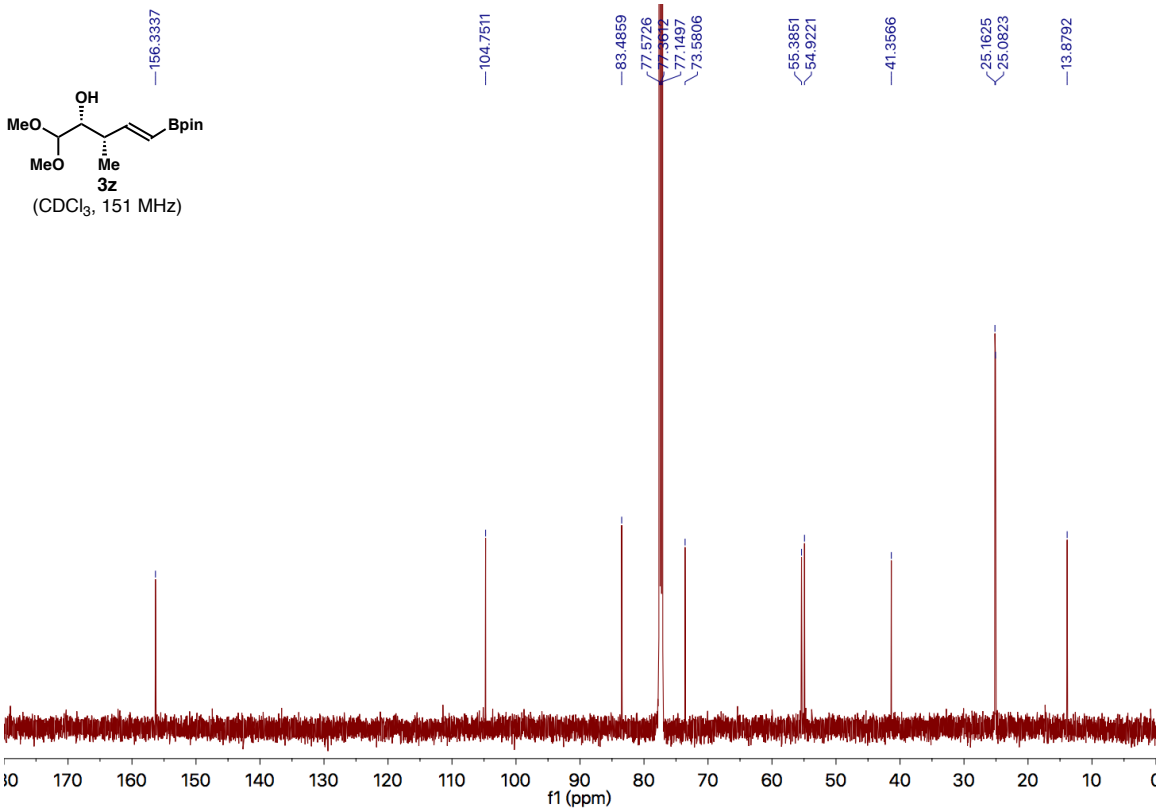

OH
Bpin
Me
3x
(CDCl3, 600 MHz)
f1 (ppm)

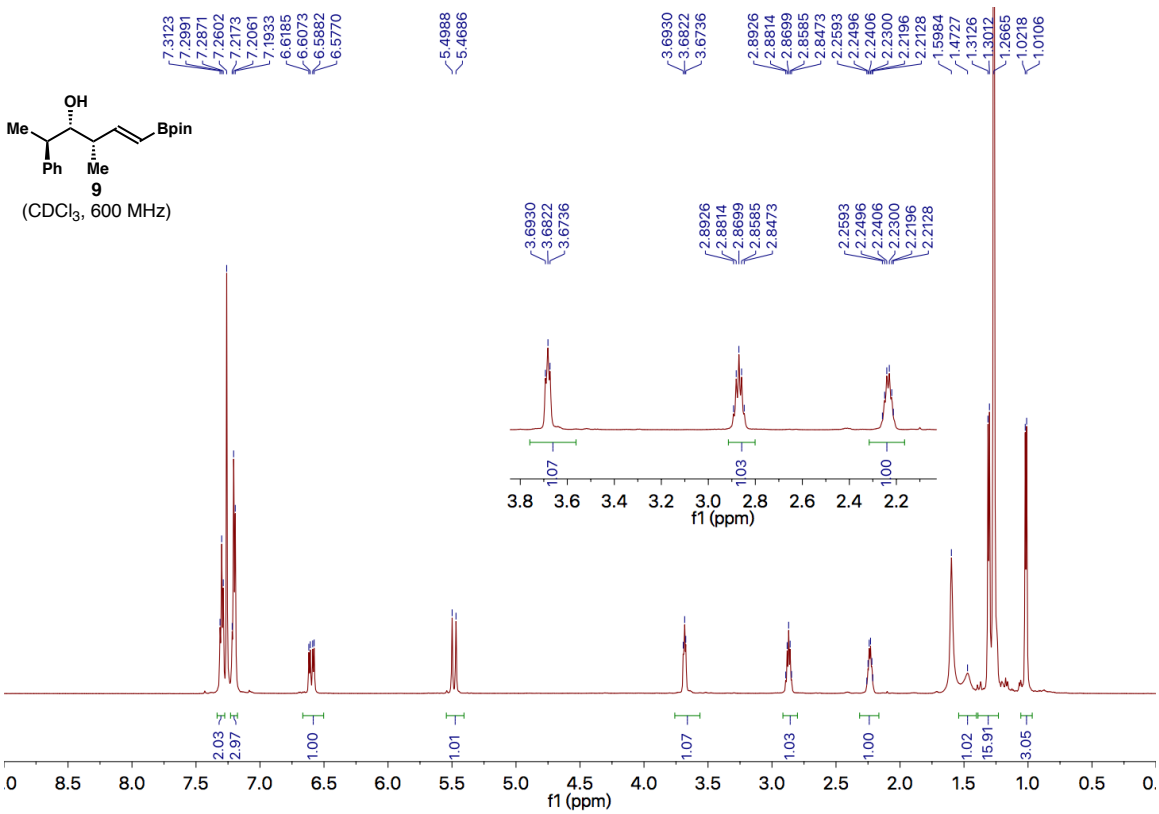

OH
Bpin
Me
3x
(CDCl3, 151 MHz)
f1 (ppm)

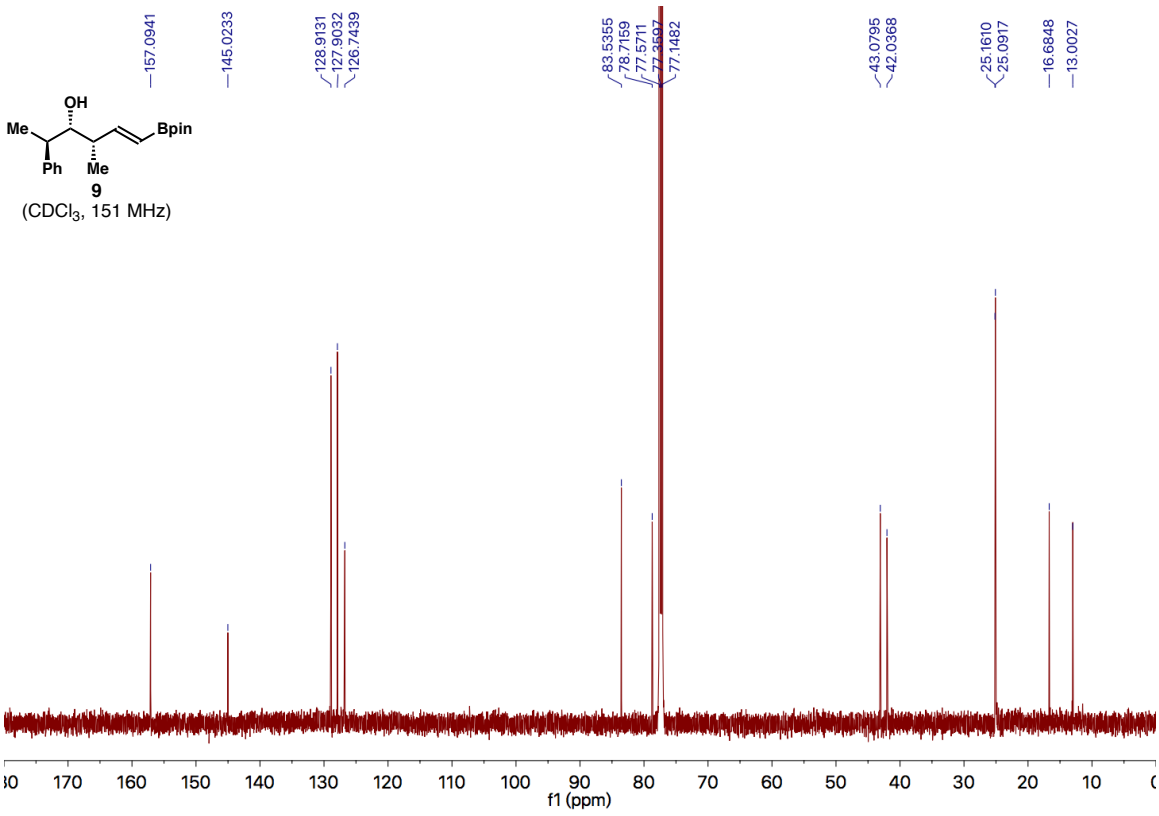

OH
Bpin
Me
Me
Me
3y
(CDCl3, 600 MHz)
7.2599
6.6000
6.5885
6.5698
6.5583
5.5077
5.4775
3.4926
3.4839
3.4752
2.4992
2.4897
2.4788
2.4694
1.5978
1.5854
1.5792
1.5773
1.5675
1.3947
1.3712
1.3596
1.3481
1.3096
1.2693
0.8722
0.8683
0.8599
0.8567
0.8480
0.8452
0.98
0.99
0.98
1.00
2.79
3.50
14.24
3.24
6.38
f1 (ppm)

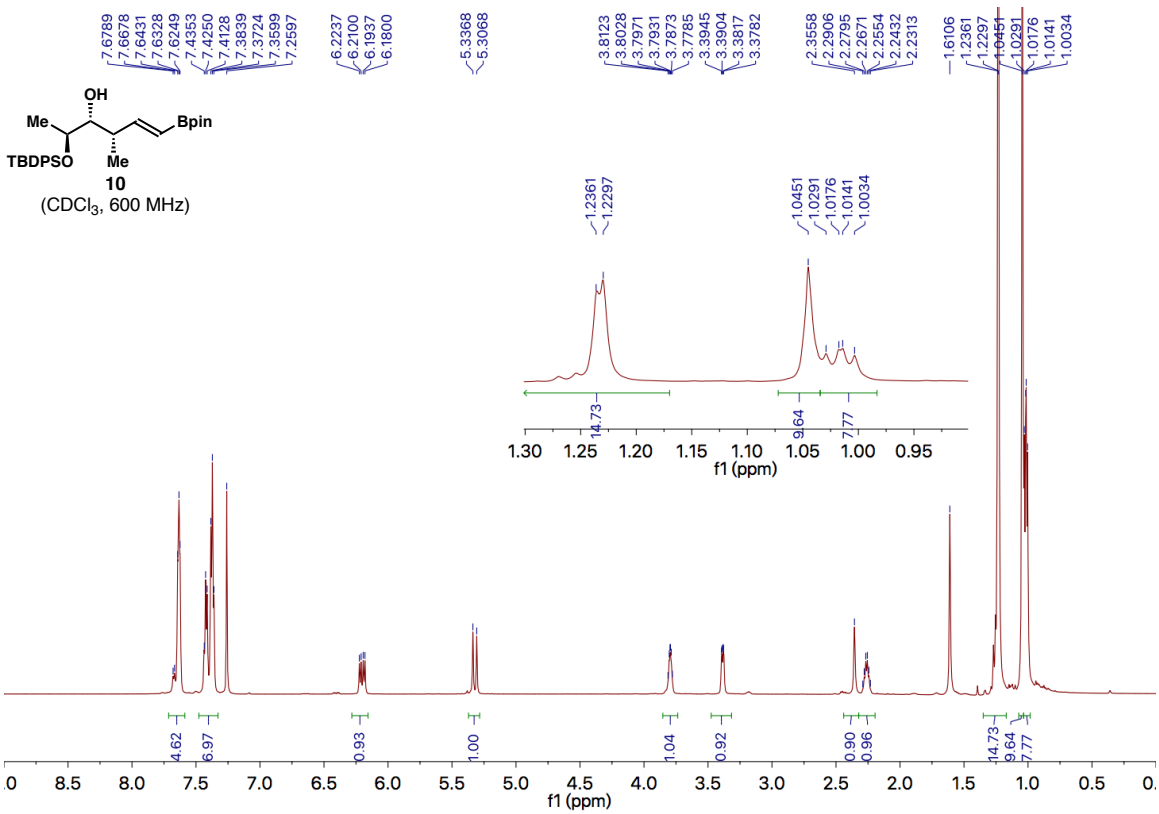

OH
Bpin
Me
Me
Me
3y
(CDCl3, 151 MHz)
157.4527
83.5003
77.5725
77.3610
77.1496
75.3595
42.8110
42.3808
25.1441
25.0821
21.7682
20.4813
13.5290
11.3671
10.9661
f1 (ppm)

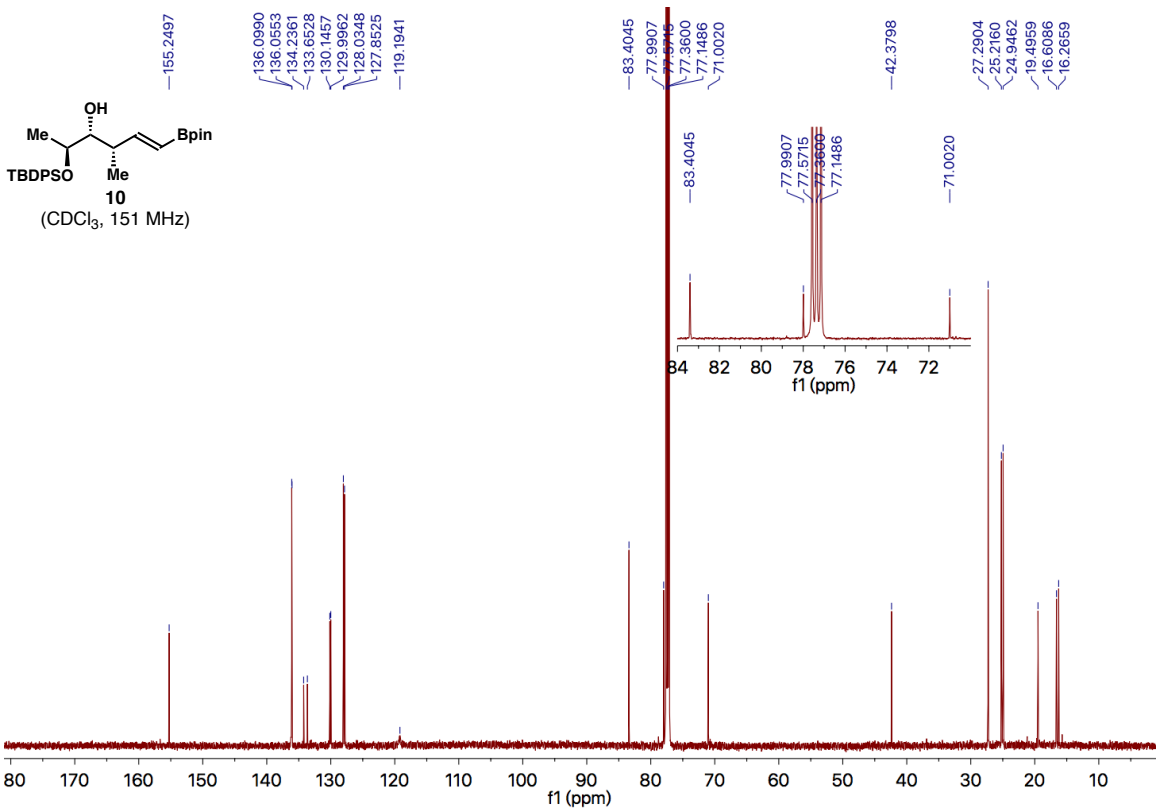

OH
MeO
MeO
Me
Bpin
3z
(CDCl3, 600 MHz)
7.2601
6.6474
6.6357
6.6173
6.6055
5.5215
5.5202
5.4914
5.4901
4.2502
4.2409
3.6108
3.6020
3.5931
3.4432
3.3912
2.5349
2.5209
2.5115
2.5007
2.4914
2.4732
1.6579
1.2651
1.0809
1.0695
1.00
1.03
0.97
1.04
6.33
1.03
3.57
14.14
3.16
f1 (ppm)

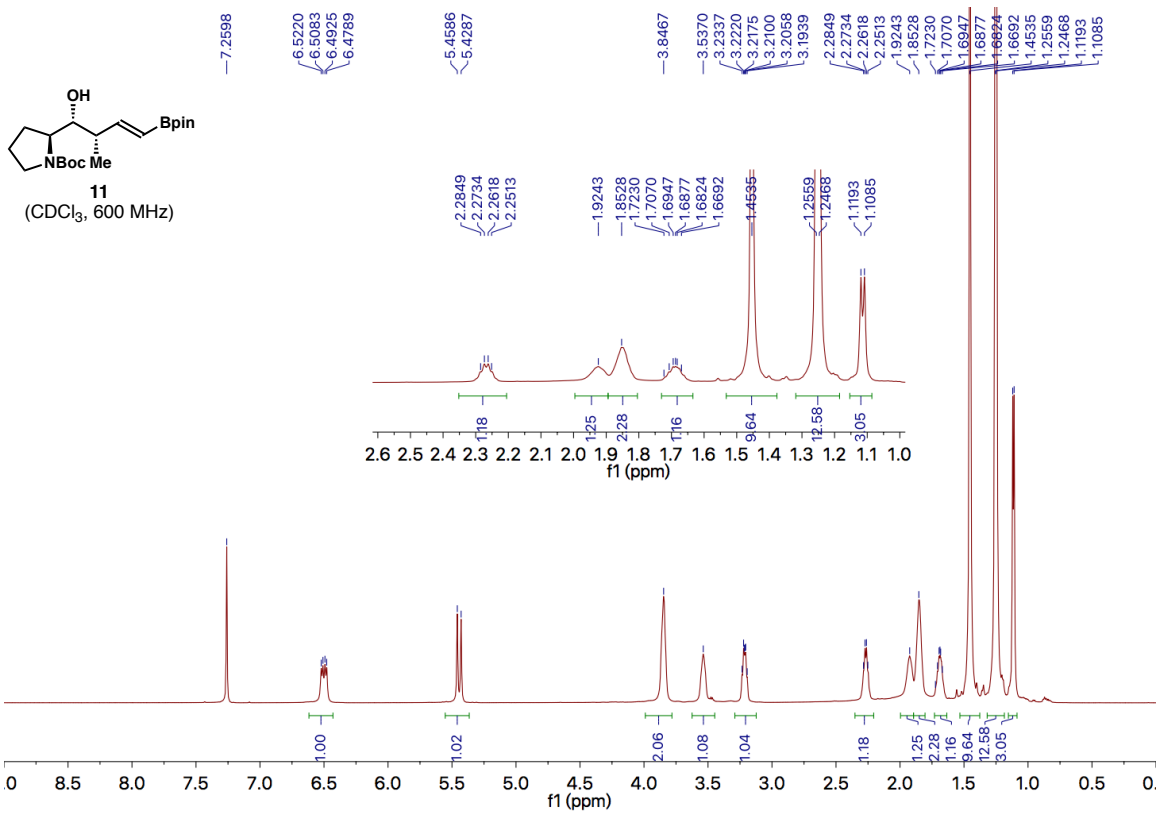

OH
MeO
MeO
Me
Bpin
3z
(CDCl3, 151 MHz)
156.3337
104.7511
83.4859
77.5726
77.3012
77.1497
73.5806
55.3851
54.9221
41.3566
25.1625
25.0823
13.8792
f1 (ppm)

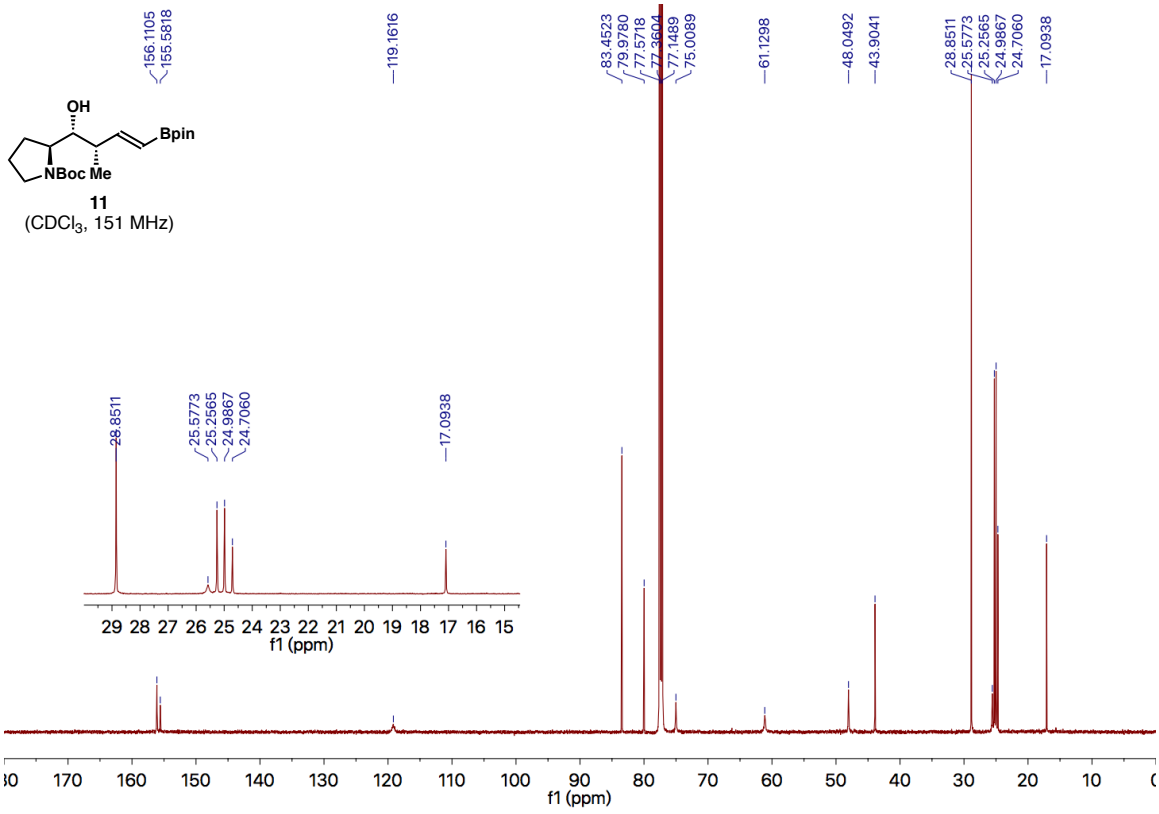

OH
Me
Bpin
Ph
Me
9
(CDCl3, 600 MHz)
f1 (ppm)

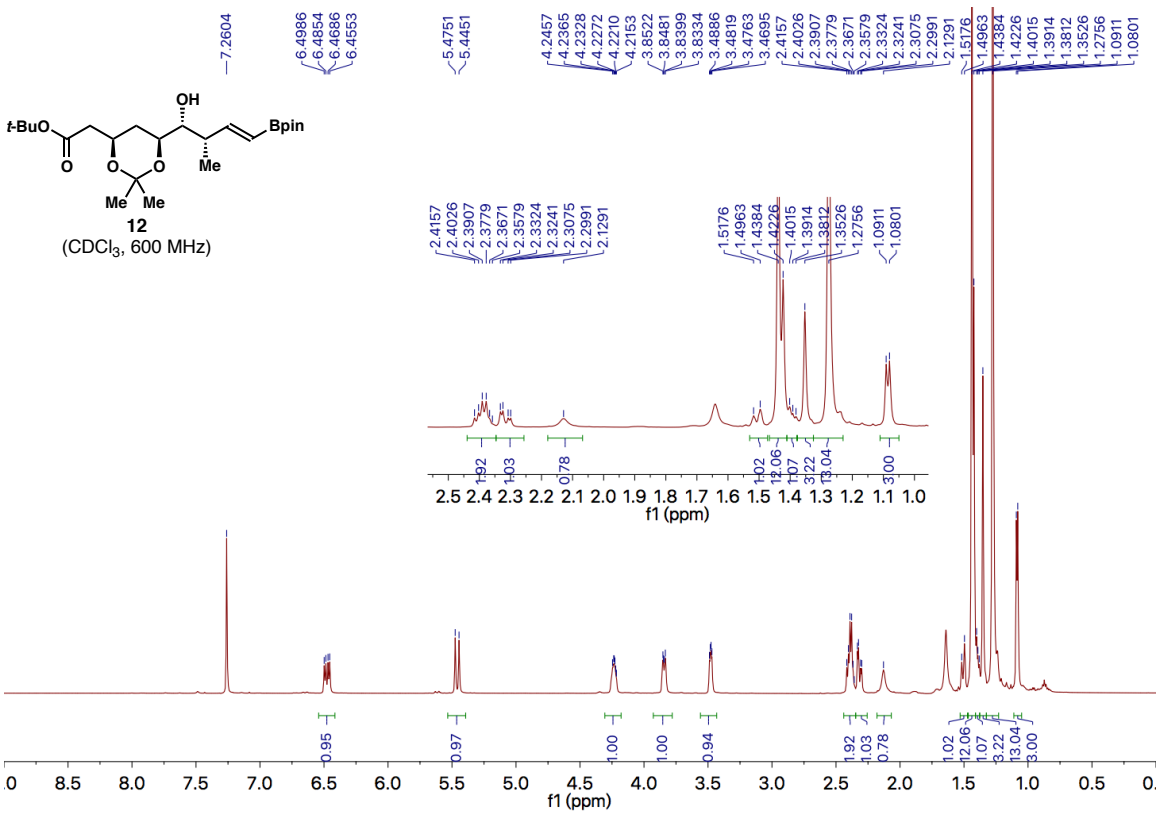

OH
Me
Bpin
Ph
Me
9
(CDCl3, 151 MHz)
f1 (ppm)

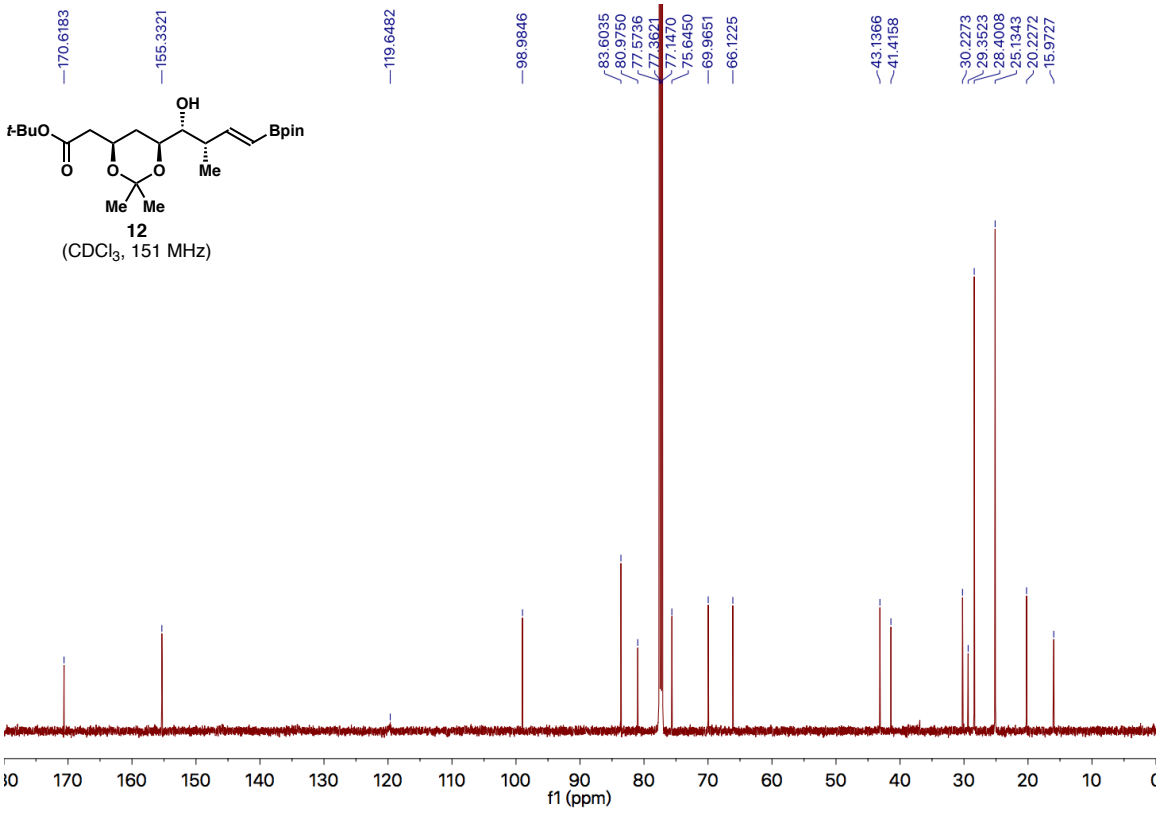

OH
Me
Bpin
TBDPSO
Me
10
(CDCl3, 600 MHz)
f1 (ppm)

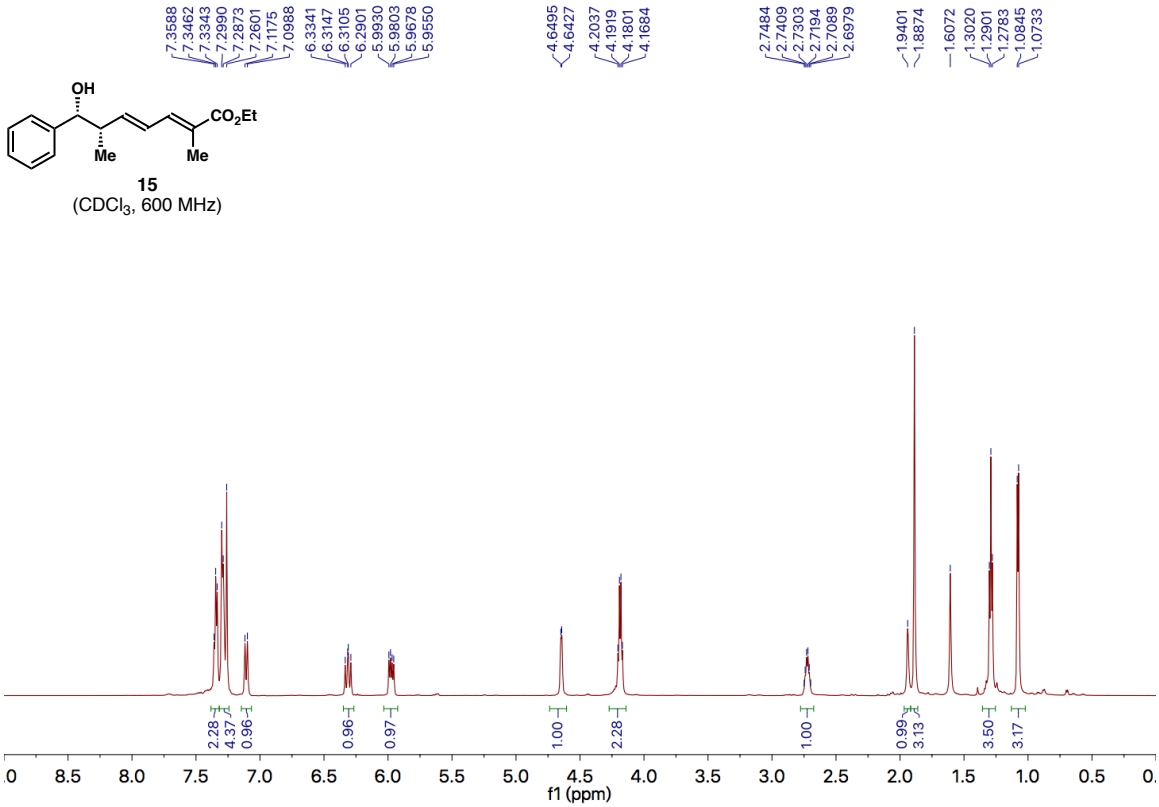

OH
Me
Bpin
TBDPSO
Me
10
(CDCl3, 151 MHz)
f1 (ppm)

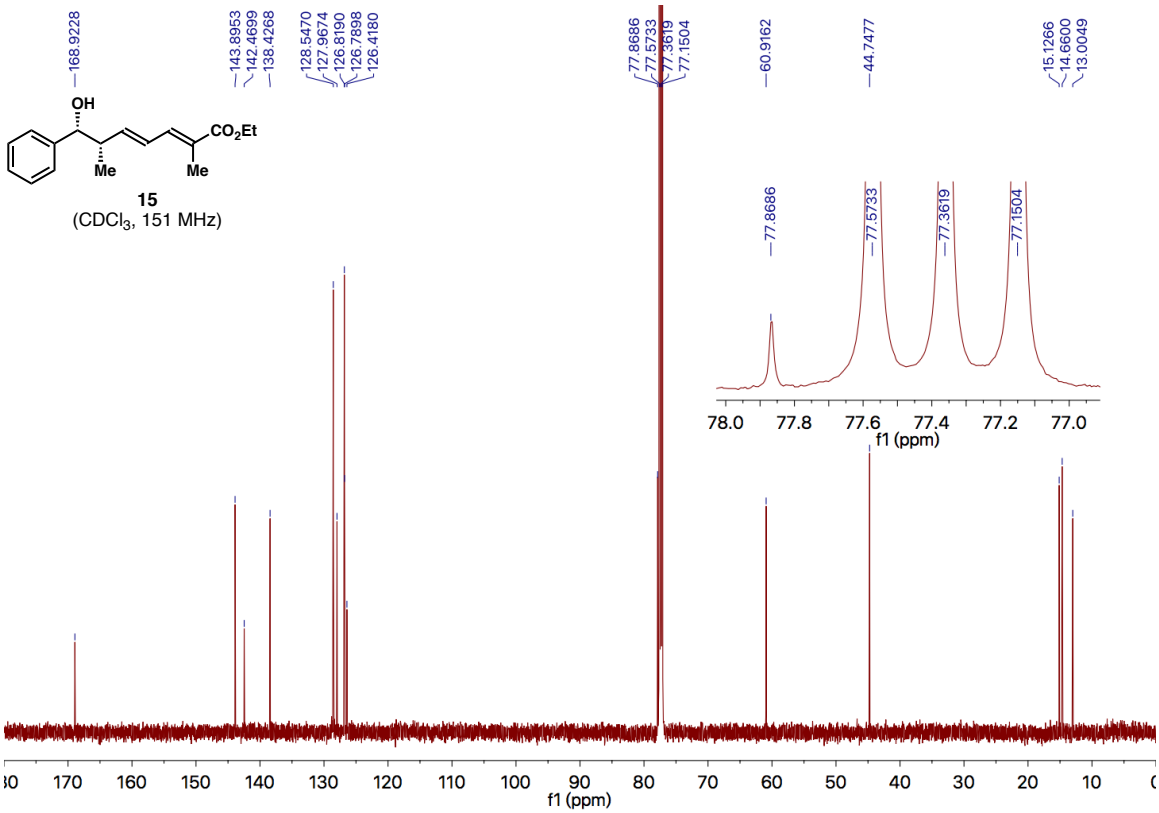

OH
Bpin
NBoc Me
11
(CDCl3, 600 MHz)
f1 (ppm)


OH
Bpin
NBoc Me
11
(CDCl3, 151 MHz)
f1 (ppm)


t-BuO
OH
Bpin
Me
Me Me
12
(CDCl3, 600 MHz)
f1 (ppm)


t-BuO
OH
Bpin
Me
Me Me
12
(CDCl3, 151 MHz)
f1 (ppm)


7.3588
7.3462
7.3343
7.2990
7.2873
7.2601
7.1175
7.0988
6.3341
6.3147
6.3105
6.2901
5.9930
5.9803
5.9678
5.9550
4.6495
4.6427
4.2037
4.1919
4.1801
4.1684
2.7484
2.7409
2.7303
2.7194
2.7089
2.6979
1.9401
1.8874
1.6072
1.3020
1.2901
1.2783
1.0845
1.0733
OH
CO2Et
Me
Me
15
(CDCl3, 600 MHz)
2.28
4.37
0.96
0.96
0.97
1.00
2.28
1.00
0.99
3.13
3.50
3.17
f1 (ppm)


168.9228
143.8953
142.4699
138.4268
128.5470
127.9674
126.8190
126.7898
126.4180
77.8686
77.5733
77.3619
77.1504
60.9162
44.7477
15.1266
14.6600
13.0049
OH
CO2Et
Me
Me
15
(CDCl3, 151 MHz)
f1 (ppm)