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Catalytic Carboboration of Dienylboronate for Stereoselective Synthesis of (*E*)-γ',δ-Bisboryl-*anti*-Homoallylic Alcohols

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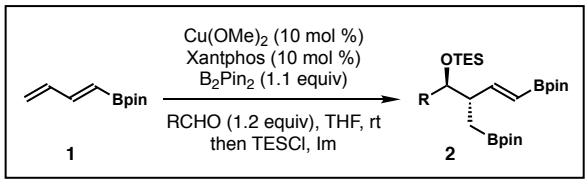
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

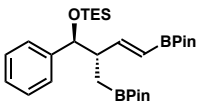
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of 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 100 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.

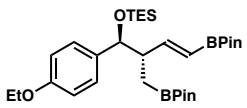
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$.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



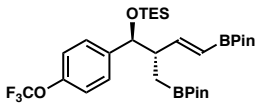
General procedure for the syntheses of TES protected homoallylic alcohols 2: In an Ar-filled glove box, $Cu(OMe)_2$ (1.3 mg, 0.01 mmol, 10 mol %), Xantphos (5.6 mg, 0.01 mmol, 10 mol %), a Teflon-coated magnetic stir bar, and THF (0.3 mL) were sequentially added to a 1-dram vial. And the mixture was stirred for 15 min at ambient temperature in the glove box. B_2Pin_2 (28 mg, 0.11 mmol, 1.1 equiv) was added and the mixture was stirred for 5 min. Dienylboronate **1** (0.10 mmol, 1.0 equiv) and aldehyde (0.12 mmol, 1.2 equiv) were added to the mixture sequentially and the mixture was kept stirring at ambient temperature. After complete consumption of diene **1**, imidazole (0.2 mmol, 2.0 equiv) and TESCl (0.2 mmol, 2.0 equiv) were added to the vial, and the reaction was stirred vigorously for another 4 h at ambient temperature. The resulting mixture was filtered through a pad of silica gel. H_2O (2 mL) and Et_2O (0.5 mL) were added to the obtained solution, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 3 mL). The combined organic extracts were concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and ethyl acetate) to give the product **2**.



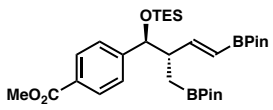
***rac*-Triethyl(((1*S*,2*S*,*E*)-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)silane (2a)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2a** as white solid in 72% yield (38 mg, *dr* > 20:1). A 1 mmol-scale reaction was also conducted and **2a** was isolated in 87% yield (460 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.29 (m, 4H), 7.20 – 7.22 (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), 0.75 (dd, J = 15.5, 5.1 Hz, 1H), 0.70 (dd, J = 15.5, 11.0 Hz, 1H), 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, 24.9, 13.1, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{29}H_{50}B_2O_5SiNa$ $[M+Na]^+$ calcd. 551.3511, found 551.3522.



***rac*-(((1*S*,2*S*,*E*)-1-(4-Ethoxyphenyl)-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)triethylsilane (2b)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2b** as white solid in 89% yield (51 mg, *dr* >20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.61 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.39 (d, *J* = 18.0 Hz, 1H), 4.38 (d, *J* = 7.1 Hz, 1H), 3.99 (q, *J* = 6.9 Hz, 2H), 2.57–2.61 (m, 1H), 1.40 (t, *J* = 6.9 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 1.15 (s, 6H), 1.13 (s, 6H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.69 (dd, *J* = 15.8, 5.3 Hz, 1H), 0.66 (dd, *J* = 15.4, 10.6 Hz, 1H), 0.37 – 0.47 (m, *J* = 7.5 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 157.3, 136.2, 128.5, 119.2, 113.7, 83.2, 83.1, 79.2, 63.5, 50.4, 25.3, 25.04, 24.97, 24.9, 15.3, 13.2, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{31}H_{54}B_2O_6SiNa$ $[M+Na]^+$ calcd. 595.3773, found 595.3815.

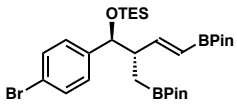


***rac*-Triethyl(((1*S*,2*S*,*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-(4-(trifluoromethoxy)phenyl) but-3-en-1-yl)oxy)silane (2c)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2c** as white solid in 70% yield (43 mg, *dr* =16:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.30 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.57 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.37 (d, *J* = 17.9 Hz, 1H), 4.53 (d, *J* = 6.5 Hz, 1H), 2.26 – 2.64 (m, 1H), 1.23 (s, 12H), 1.17 (s, 6H), 1.16 (s, 6H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.76 (dd, *J* = 15.4, 5.0 Hz, 1H), 0.68 (dd, *J* = 15.4, 10.0 Hz, 1H), 0.39 – 0.53 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 148.3, 142.8, 128.6, 120.7 (q, *J* = 257 Hz), 120.4, 120.0, 83.3, 83.2, 78.6, 50.2, 25.3, 25.02, 24.96, 24.9, 13.0, 7.1, 5.0. HRMS (ESI^+): *m*/*z* for $C_{30}H_{49}B_2O_6F_3SiNa$ $[M+Na]^+$ calcd. 635.3334, found 635.3342.

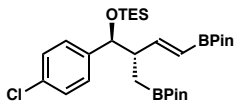


***rac*-Methyl-4-((1*S*,2*S*,*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-((triethylsilyl)oxy)but-3-en-1-yl)benzoate (2d)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2d** as white solid in 72% yield (42 mg, *dr* =12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.57 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 4.56 (d, *J* = 6.1 Hz, 1H), 3.89 (s, 3H), 2.59 – 2.63 (m, 1H), 1.22 (s, 12H), 1.16 (s, 6H), 1.15 (s, 6H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.76 (dd, *J* = 15.7, 5.0 Hz, 1H), 0.71 (dd, *J* = 15.3, 10.2 Hz, 1H), 0.40 – 0.50 (m, 6H). ^{13}C NMR

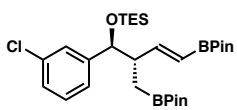
(151 MHz, $CDCl_3$) δ 167.6, 155.9, 149.5, 129.3, 129.0, 127.3, 120.0, 83.3, 83.2, 78.9, 52.4, 50.2, 25.2, 25.04, 24.98, 24.9, 13.1, 7.1, 5.0. HRMS (ESI^+): *m*/*z* for $C_{31}H_{52}B_2O_7SiNa$ $[M+Na]^+$ calcd. 609.3566, found 609.3524.



***rac*-(((1*S*,2*S*,*E*)-1-(4-bromophenyl)-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)triethylsilane (2e)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2e** as white solid in 72% yield (44 mg, *dr* > 20:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.56 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.36 (d, *J* = 18.0 Hz, 1H), 4.45 (d, *J* = 6.4 Hz, 1H), 2.54–2.59 (m, 1H), 1.229 (s, 6H), 1.226 (s, 6H), 1.16 (s, 6H), 1.15 (s, 6H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.74 (dd, *J* = 15.4, 4.8 Hz, 1H), 0.68 (dd, *J* = 15.3, 10.1 Hz, 1H), 0.39 – 0.49 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 143.2, 131.0, 129.0, 121.0, 83.3, 83.2, 78.7, 50.2, 25.3, 25.04, 24.98, 24.9, 13.0, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{29}H_{49}B_2O_5SiBrNa$ $[M+Na]^+$ calcd. 629.2616, found 629.2617.

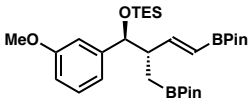


***rac*-(((1*S*,2*S*,*E*)-1-(4-Chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (2f)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2f** as white solid in 91% yield (51 mg, *dr* = 17:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.56 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.35 (d, *J* = 17.9 Hz, 1H), 4.46 (d, *J* = 6.4 Hz, 1H), 2.55 – 2.59 (m, 1H), 1.229 (s, 6H), 1.226 (s, 6H), 1.16 (s, 6H), 1.15 (s, 6H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.74 (dd, *J* = 15.4, 4.8 Hz, 1H), 0.68 (dd, *J* = 15.3, 10.2 Hz, 1H), 0.39 – 0.49 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 142.7, 132.7, 128.7, 128.1, 83.3, 83.1, 78.7, 50.3, 25.3, 25.04, 24.98, 24.9, 13.1, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{29}H_{49}B_2O_5SiClNa$ $[M+Na]^+$ calcd. 585.3122, found 585.3090.

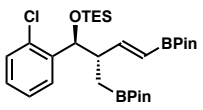


***rac*-(((1*S*,2*S*,*E*)-1-(3-Chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (2g)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2g** as white solid in 75% yield (42 mg, *dr* = 15:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.11–7.19 (m, 3H), 6.57 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.35 (d, *J* =

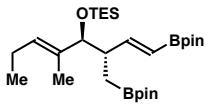
18.0 Hz, 1H), 4.50 (d, *J* = 6.3 Hz, 1H), 2.55 – 2.62 (m, 1H), 1.23 (*app* s, 12H), 1.17 (s, 6H), 1.16 (s, 6H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.79 (dd, *J* = 15.5, 7.5 Hz, 1H), 0.70 (dd, *J* = 15.5, 9.9 Hz, 1H), 0.42 – 0.54 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 146.2, 133.8, 129.2, 127.4 (2C), 125.5, 120.0, 83.3, 83.2, 78.7, 50.2, 25.3, 25.04, 24.97, 24.9, 13.0, 7.1, 5.0. HRMS (ESI$^+$): *m*/*z* for $C_{29}H_{49}B_2O_5SiClNa$ $[M+Na]^+$ calcd. 585.3122, found 585.3122.



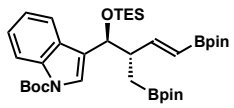
***rac*-Triethyl(((1*S*,2*S*,*E*)-1-(3-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)silane (2h)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2h** as white solid in 82% yield (46 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 18.0, 8.2 Hz, 1H), 5.38 (d, *J* = 18.0 Hz, 1H), 4.46 (d, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 2.59 – 2.63 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.16 (s, 6H), 1.15 (s, 6H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.76 (dd, *J* = 15.5, 4.8 Hz, 1H), 0.71 (dd, *J* = 15.4, 10.1Hz, 1H), 0.42 – 0.50 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 156.9, 145.8, 128.8, 119.9, 113.2, 112.2, 83.2, 83.1, 79.4, 55.4, 50.2, 25.3, 25.05, 24.98, 24.9, 7.2, 5.1. HRMS (ESI$^+$): *m*/*z* for $C_{30}H_{52}B_2O_6SiNa$ $[M+Na]^+$ calcd. 581.3617, found 581.3583.



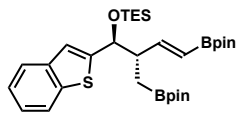
***rac*-(((1*S*,2*S*,*E*)-1-(2-Chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (2i)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2i** as colorless oil in 73% yield (41 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.12 (dd, *J* = 7.5, 7.4 Hz, 1H), 6.63 (dd, *J* = 17.9, 8.5 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 5.01 (d, *J* = 6.4 Hz, 1H), 2.61 – 2.66 (m, 1H), 1.22 (*app.* s, 12H), 1.16 (s, 6H), 1.14 (s, 6H), 0.95 (dd, *J* = 15.3, 11.2 Hz, 1H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.71 (dd, *J* = 15.3, 4.4 Hz, 1H), 0.40 – 0.51 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 142.0, 132.4, 129.6, 128.9, 128.3, 126.8, 83.3, 83.1, 74.7, 49.8, 25.3, 25.03, 24.96, 24.9, 13.2, 7.1, 4.9. HRMS (ESI$^+$): *m*/*z* for $C_{29}H_{49}B_2O_5SiClNa$ $[M+Na]^+$ calcd. 585.3122, found 585.3110.



***rac*-Triethyl(((1*E*,3*S*,4*S*,5*E*)-5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)octa-1,5-dien-4-yl)oxy)silane (2j)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2j** as colorless oil in 67% yield (35 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 (dd, *J* = 17.9, 8.2 Hz, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 5.23 (t, *J* = 6.6 Hz, 1H), 3.70 (d, *J* = 8.3 Hz, 1H), 2.46 – 2.52 (m, 1H), 1.91 – 2.04 (m, 2H), 1.53 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 8.0 Hz, 9H), 0.72 (dd, *J* = 15.5, 4.1 Hz, 1H), 0.62 (dd, *J* = 15.4, 10.4 Hz, 1H), 0.48 – 0.52 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 135.6, 129.8, 118.8, 83.6, 83.2, 83.0, 45.8, 25.3, 25.0 (2C), 24.9, 21.1, 14.3, 13.6, 11.2, 7.3, 5.1. HRMS (ESI$^+$): *m*/*z* for $C_{28}H_{54}B_2O_5SiNa$ $[M+Na]^+$ calcd. 543.3835, found 543.3824.

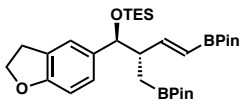


***rac-tert*-Butyl-3-((1*S*,2*S*,*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-((triethylsilyl)oxy)but-3-en-1-yl)-1*H*-indole-1-carboxylate (2k)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2k** as white solid in 90% yield (60 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (br, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.40 (br, 1H), 7.24 – 7.26 (m, 1H), 7.17 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.66 (dd, *J* = 18.0, 8.1 Hz, 1H), 5.40 (d, *J* = 18.0 Hz, 1H), 4.79 (d, *J* = 6.5 Hz, 1H), 2.80 – 2.85 (m, 1H), 1.66 (s, 9H), 1.23 (s, 6H), 1.22 (s, 6H), 1.15 (*app.* s, 12H), 0.90 (dd, *J* = 15.8, 5.3 Hz, 1H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.78 (dd, *J* = 15.8, 9.5 Hz, 1H), 0.42 – 0.53 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 150.1, 135.8, 129.5, 124.3, 123.9, 123.4, 122.5, 121.3, 119.5, 115.2, 83.6, 83.3, 83.1, 73.3, 49.1, 28.5, 25.3, 25.1, 25.0, 24.9, 13.3, 7.2, 5.0. HRMS (ESI$^+$): *m*/*z* for $C_{36}H_{59}B_2NO_7SiNa$ $[M+Na]^+$ calcd. 690.4145, found 690.4169.

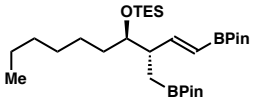


***rac*-(((1*S*,2*S*,*E*)-1-(Benzo[*b*]thiophen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethyl silane (2l)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2l** as white solid in 84% yield (49 mg, *dr* = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.23–7.31 (m, 2H), 7.08 (s, 1H), 6.67 (dd, *J* = 18.0, 7.9 Hz, 1H), 5.49 (d, *J* = 18.0 Hz, 1H), 4.84 (d, *J* = 7.1 Hz, 1H), 2.71 – 2.78 (m, 1H), 1.24 (s, 12H), 1.15 (s, 6H), 1.14 (s, 6H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.85 – 0.89 (m, 1H), 0.75 (dd, *J* = 15.6, 10.0 Hz, 1H), 0.49 – 0.61 (m, 6H).

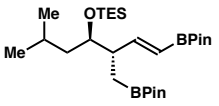
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 149.7, 139.9, 139.6, 124.1, 123.9, 123.5, 122.7, 120.6, 120.1, 83.3, 83.2, 76.0, 50.4, 25.2, 25.1, 24.95, 24.92, 13.1, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{31}H_{50}B_2O_5SiSNa$ $[M+Na]^+$ calcd. 607.3232, found 607.3215.



***rac*-(((1*S*,2*S*,*E*)-1-(2,3-Dihydrobenzofuran-5-yl)-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)trimethyl silane (2m)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2m** as colorless oil in 91% yield (52 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.61 (dd, *J* = 18.1, 8.2 Hz), 5.40 (d, *J* = 18.0 Hz, 1H), 4.54 (t, *J* = 8.6 Hz, 2H), 4.36 (d, *J* = 7.1 Hz, 1H), 3.16 (t, *J* = 8.3 Hz, 2H), 2.55 – 2.60 (m, 1H), 1.231 (s, 6H), 1.226 (s, 6H), 1.15 (s, 6H), 1.14 (s, 6H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.70 (dd, *J* = 15.4, 4.7 Hz, 1H), 0.65 (dd, *J* = 15.3, 10.3 Hz, 1H), 0.38 – 0.48 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 157.4, 136.4, 127.2, 126.5, 123.9, 119.2, 108.3, 83.2, 83.1, 79.5, 71.5, 50.5, 30.0, 25.3, 25.04, 24.96, 24.9, 13.3, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{31}H_{52}B_2O_6SiNa$ $[M+Na]^+$ calcd. 593.3617, found 593.3594.

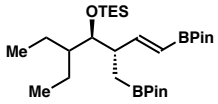


***rac*-Triethyl(((3*S*,4*R*,*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)dec-1-en-4-yl)oxy)silane (2n)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2n** as colorless oil in 73% yield (39 mg, *dr* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, *J* = 18.0, 7.9 Hz, 1H), 5.41 (d, *J* = 18.0 Hz, 1H), 3.60 (dt, *J* = 5.4, 4.1 Hz, 1H), 2.50 (*app* tt, *J* = 8.8, 4.3 Hz, 1H), 1.19–1.39 (m, 10H), 1.24 (*app.* s, 12H), 1.20 (s, 6H), 1.19 (s, 6H), 0.94 – 1.01 (m, 1H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.83 – 0.89 (m, 1H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.59 (*app.* q, *J* = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 119.3, 83.21, 83.17, 76.3, 47.3, 34.6, 32.2, 29.8, 26.0, 25.2, 25.1, 25.03, 24.99, 23.0, 14.5, 12.2, 7.4, 5.5. HRMS (ESI^+): *m*/*z* for $C_{29}H_{58}B_2O_5SiNa$ $[M+Na]^+$ calcd. 559.4137, found 559.4150.

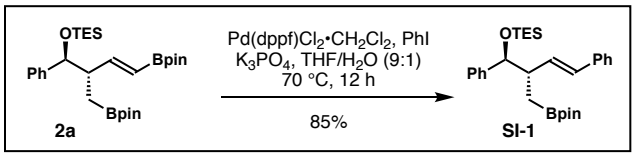


***rac*-Triethyl(((3*S*,4*R*,*E*)-6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hept-1-en-4-yl)oxy)silane (2o)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2o** as colorless oil in 76% yield (39 mg, *dr* > 20:1). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.54 (dd, *J* = 18.1, 7.9 Hz, 1H), 5.40 (d, *J* = 18.1 Hz, 1H), 3.73 (td, *J* = 6.5, 3.6 Hz, 1H), 2.46 – 2.52 (m, 1H), 1.61 – 1.70 (m, 1H), 1.24 (*app* s, 12H), 1.20 (s, 6H), 1.19 (s, 6H), 1.02 (dd, *J* = 15.7, 5.2 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.86 – 0.90 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.59 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 119.3, 83.21, 83.18, 74.1, 47.4, 43.8, 25.2, 25.1 (2C), 25.0, 24.5, 23.4, 23.1, 12.3, 7.5, 5.5. HRMS (ESI$^+$): *m*/*z* for $C_{27}H_{54}B_2O_5SiNa$ $[M+Na]^+$ calcd. 531.3824, found 531.3839.

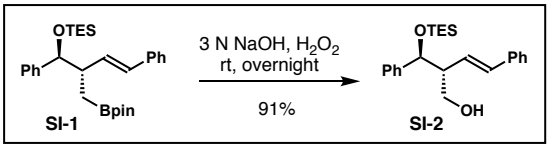


***rac*-Triethyl(((3*S*,4*R*,*E*)-5-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hept-1-en-4-yl)oxy)silane (2p)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **2p** as colorless oil in 84% yield (44 mg, *dr* > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 18.0, 8.5 Hz, 1H), 5.40 (d, *J* = 18.0 Hz, 1H), 3.59 – 3.60 (m, 1H), 2.52 – 2.57 (m, 1H), 1.43–1.50 (m, 1H), 1.234 (s, 6H), 1.225 (s, 6H), 1.194 (s, 6H), 1.189 (s, 6H), 1.19 – 1.35 (m, 4H), 0.91 – 0.94 (m, 10H), 0.80 – 0.86 (m, 7H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 83.3, 83.1, 78.2, 45.9, 45.6, 25.3, 25.1(2C), 24.9, 22.8, 21.9, 14.5, 12.5, 12.3, 7.6, 5.8. HRMS (ESI$^+$): *m*/*z* for $C_{28}H_{56}B_2O_5SiNa$ $[M+Na]^+$ calcd. 545.3990, found 545.3981.

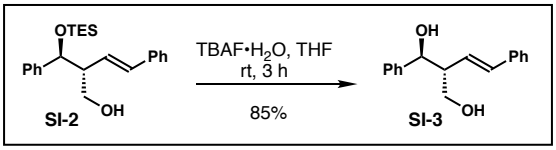


***rac*-(((1*S*,2*S*,*E*)-1,4-Diphenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (SI-1)** In an Ar-filled glove box, vinylboronate **2a** (79 mg, 0.15 mmol, 1.0 equiv), iodobenzene (41 mg, 0.20 mmol, 1.3 equiv), $PdCl_2(dppf)•CH_2Cl_2$ (12 mg, 0.015 mmol, 10 mol %), K_3PO_4 (84 mg, 0.4 mmol, 2.6 equiv), THF (0.9 mL), H_2O (0.1 mL) and a Teflon-coated magnetic stirring bar were sequentially added into a 1-dram vial. The vial was sealed with a cap containing a PTFE-lined silicone septum and removed from glove box. The reaction mixture was stirred at 70 ˚C for 12 h. After complete consumption of boronate **2a**, Et_2O (2 mL) was added and the resulting mixture was filtered through a short pad of silica gel. The solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography to give compound **SI-1** in 85% yield (61 mg)

as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.29 (m, 10H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 8.2 Hz, 1H), 4.64 (d, *J* = 5.5 Hz, 1H), 2.68 – 2.76 (m, 1H), 1.160 (s, 6 H), 1.158 (s, 6H), 0.98 (dd, *J* = 15.3, 4.6 Hz, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.82 – 0.90 (m, 1H), 0.44 – 0.52 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 138.4, 132.9, 130.7, 128.7, 127.9, 127.3, 127.2, 126.9, 126.4, 83.3, 79.7, 47.8, 25.4, 25.0, 7.1, 5.2. HRMS (ESI^+): *m*/*z* for $C_{29}H_{43}BO_3SiNa$ $[M+Na]^+$ calcd. 501.2972, found 501.3006.

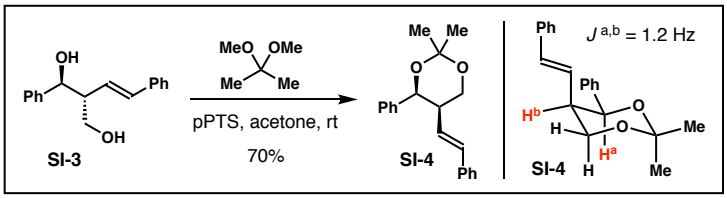


***rac*-(*R*,*E*)-4-Phenyl-2-((*S*)-phenyl((triethylsilyl)oxy)methyl)but-3-en-1-ol (SI-2)** To a solution of compound **4** (59 mg, 0.12 mmol) in Et_2O (2 mL) was added 3 N NaOH (1.0 mL), followed by slow addition of 30% H_2O_2 (0.5 mL). The reaction was stirred vigorously at ambient temperature for 12 h. Then brine (2 mL) and Et_2O (2 mL) were added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography to give compound **SI-2** in 91% yield (41 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.32 (m, 10H), 6.39 (d, *J* = 16.0 Hz, 1H), 5.95 (dd, *J* = 15.9, 9.3 Hz, 1H), 4.93 (d, *J* = 4.2 Hz, 1H), 3.78 (dd, *J* = 10.2, 7.7 Hz, 1H), 3.57 (dd, *J* = 10.4, 6.1 Hz, 1H), 2.79 – 2.83 (m, 1H), 2.55 (br, 1H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.48 – 0.57 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 137.4, 133.6, 128.8, 128.2, 127.7 (2C), 127.08, 127.05, 126.5, 77.5, 64.0, 53.4, 7.1, 4.9. HRMS (ESI^+): *m*/*z* for $C_{23}H_{32}O_2SiNa$ $[M+Na]^+$ calcd. 391.2069, found 391.2053.

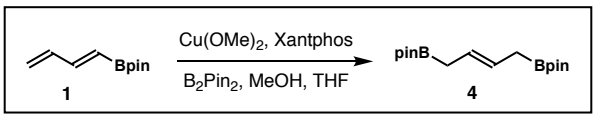


***rac*-(1*S*,2*R*)-1-Phenyl-2-((*E*)-styryl)propane-1,3-diol (SI-3)** To a solution of compound **SI-2** (40 mg, 0.11 mmol) in THF (2 mL) was added TBAF·H_2O (46 mg, 0.16 mmol, 1.5 equiv) and water (0.1 mL). The reaction mixture was stirred at ambient temperature for 3 h. EtOAc (2 mL) were added to the reaction mixture and filtered through a pad of silica gel. The obtained solution was concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and

ethyl acetate) afforded diol **SI-3** in 85% yield (23.5 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.36 (m, 6H), 7.30 – 7.32 (m, 3H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.93 (d, *J* = 5.4 Hz, 1H), 3.74 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.71 (dd, *J* = 10.6, 5.9 Hz, 1H), 2.75 – 2.79 (m, 1H), 2.58 (s, 1H), 1.91 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 137.0, 134.9, 128.9, 128.7, 128.1, 128.0, 126.8, 126.6, 126.5, 75.9, 64.5, 53.1. HRMS (ESI^+): *m*/*z* for $C_{17}H_{18}O_2Na$ $[M+Na]^+$ calcd. 277.1204, found 277.1187.

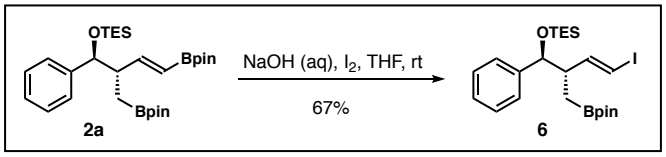


***rac*-(4*S*,5*R*)-2,2-Dimethyl-4-phenyl-5-((*E*)-styryl)-1,3-dioxane (SI-4)** To a solution of diol **SI-3** (21 mg, 0.083 mmol) in 2, 2-dimethoxypropane (1 mL) was added *p*PTS (2 mg) and acetone (0.2 mL). The reaction mixture was stirred at ambient temperature for 48 h. After complete consumption of the diol intermediate, the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give acetonide **SI-4** in 70% yield (17 mg) as a colorless oil. The small *J* value is consistent with the *syn* stereochemistry in compound **SI-4**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 – 7.31 (m, 10H), 6.50 (dd, *J* = 16.1, 9.1 Hz, 1H), 6.14 (d, *J* = 16.1 Hz, 1H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.47 (dd, *J* = 11.3, 1.4 Hz,1H), 3.97 (d, *J* = 11.4 Hz, 1H), 2.48 (d, *J* = 8.5 Hz, 1H), 1.64 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.7, 137.9, 132.4, 128.6, 128.3, 127.44, 127.39, 127.2, 126.4, 126.2, 99.7, 74.0, 66.1, 44.4, 30.1, 19.3. HRMS (ESI^+): *m*/*z* for $C_{20}H_{22}O_2Na$ $[M-+Na]^+$ calcd. 317.1519, found 317.1517.

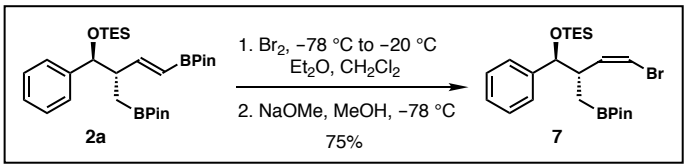


(*E*)-1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-ene (4): In an Ar-filled glove box, $Cu(OMe)_2$ (2.5 mg, 0.02 mmol, 10 mol %), Xantphos (12 mg, 0.02 mmol, 10 mol %), THF (0.5 mL) and a Teflon-coated magnetic stirring bar were sequentially added

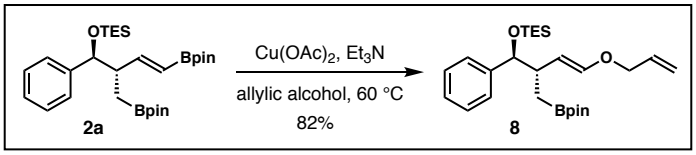
into a 1-dram vial. The mixture was stirred for 15 min in glove box and B_2Pin_2 (56 mg, 0.22 mmol, 1.1 equiv) was added. After stirring for 5 min, dienylboronate **1** (0.20 mmol, 1.0 equiv) and methanol (0.20 mmol, 1.0 equiv) were added sequentially, and the reaction mixture was stirred at ambient temperature for 10 min. After complete consumption of boronate **1**, the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. The *Z*/*E* ratio was determined by ^{1}H NMR analysis of crude reaction mixture. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl ether) to give product **4** as a white solid (50 mg, *E*/*Z* > 20:1, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.39 – 5.45 (m, 2H), 1.64 (*app.* s, 4H), 1.23 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 125.6, 83.4, 25.1, 16.5. HRMS (ESI$^+$): *m*/*z* for $C_{16}H_{31}B_2O_4$ $[M+H]^+$ calcd. 309.2413, found 309.2408.



***rac*-Triethyl(((1*S*,2*S*,*E*)-4-iodo-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)silane (6)** To a solution of boronate **2a** (26.4 mg, 0.05 mmol) in THF (0.5 mL) was added an aqueous solution of 3N NaOH (35 µL, 2.0 equiv). The reaction mixture was stirred for 10 min at ambient temperature. Then a solution of I_2 (25 mg, 0.1 mmol, 2.0 equiv) in THF (0.5 mL) was added. The reaction mixture was stirred for 1 h at ambient temperature and a saturated aqueous $Na_2S_2O_3$ solution (3 mL) was added to the mixture. After stirring for 15 min, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 2 mL). The combined organic extracts were washed with saturated $NaHCO_3$ and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and Et_2O) to give product **6** in 67% yield (17.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.30 (m, 5H), 6.49 (dd, *J* = 14.4, 9.1 Hz, 1H), 5.90 (d, *J* = 14.4 Hz, 1H), 4.50 (d, *J* = 5.7 Hz, 1H), 2.53 – 2.59 (m, 1H), 1.24 (s, 6H), 1.29 (s, 6H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.80 – 0.82 (m, 2H), 0.44 – 0.54 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 143.8, 128.0, 127.4, 127.1, 83.5, 78.9, 76.4, 51.3, 25.5, 25.0, 13.5, 7.2, 5.1. HRMS (ESI$^+$): *m*/*z* for $C_{23}H_{38}BO_3SiINa$ $[M+Na]^+$ calcd. 551.1626, found 551.1581.

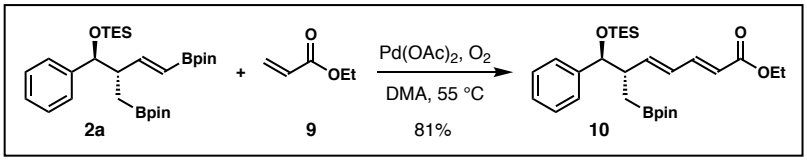


***rac*-(((1*S*,2*S*,*Z*)-4-Bromo-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (7)** To a solution of boronate **2a** (53 mg, 0.1 mmol) in Et_2O (2.0 mL) was added a solution of Br_2 in dichloromethane (1 N, 0.09 mmol, 0.9 equiv) over 2 min at −78 °C. After stirring at −78 °C for 10 min, the solution was warmed to −20 °C and kept stirring for 20 min. Then the reaction was cooled to −78 °C, a solution of 3.0 M sodium methoxide in methanol (2.2 equiv) was added and the reaction mixture was stirred at −78 °C for 30 min. Et_2O (5 mL) was added next and the reaction was allowed to warm to ambient temperature. The reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and Et_2O) to give product **7** in 75% yield (36 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.26 (m, 5H), 6.10 (d, *J* = 7.0 Hz, 1H), 5.98 (dd, *J* = 9.5, 7.2 Hz, 1H), 4.72 (d, *J* = 4.6 Hz, 1H), 3.10 (ddt, *J* = 9.4, 9.3, 5.0 Hz, 1H), 1.22 (s, 12H), 1.06 (dd, *J* = 15.2, 5.3 Hz, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.77 (dd, *J* = 15.2, 9.3 Hz, 1H), 0.45 – 0.56 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 136.7, 127.8, 127.2, 127.0, 108.3, 83.5, 77.9, 44.9, 25.2, 25.1, 13.2, 7.2, 5.1. HRMS (ESI^+): *m*/*z* for $C_{23}H_{38}BBrO_3Na$ $[M+Na]^+$ calcd. 503.1755, found 503.1764.

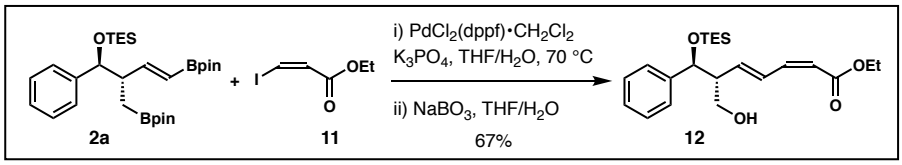


***rac*-(((1*S*,2*S*,*E*)-4-(Allyloxy)-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)triethylsilane (8)** To an oven-dried 1-dram vial equipped with a Teflon-coated magnetic stirring bar was added vinyl boronic ester **2a** (26.4 mg, 0.05 mmol, 1.0 equiv), copper (II) acetate (27 mg, 0.15 mmol, 3.0 equiv), triethylamine (14 μL, 0.1 mmol, 2.0 equiv), allyl alcohol (200 μL) and . The vial was sealed with a cap containing a PTFE-lined silicone septum and the reaction mixture was stirred for 12 h at 60 °C. Then Et_2O (2 mL) was added to the vial and the reaction mixture was filtered through a pad of silica gel. The solution was concentrated under reduced pressure.

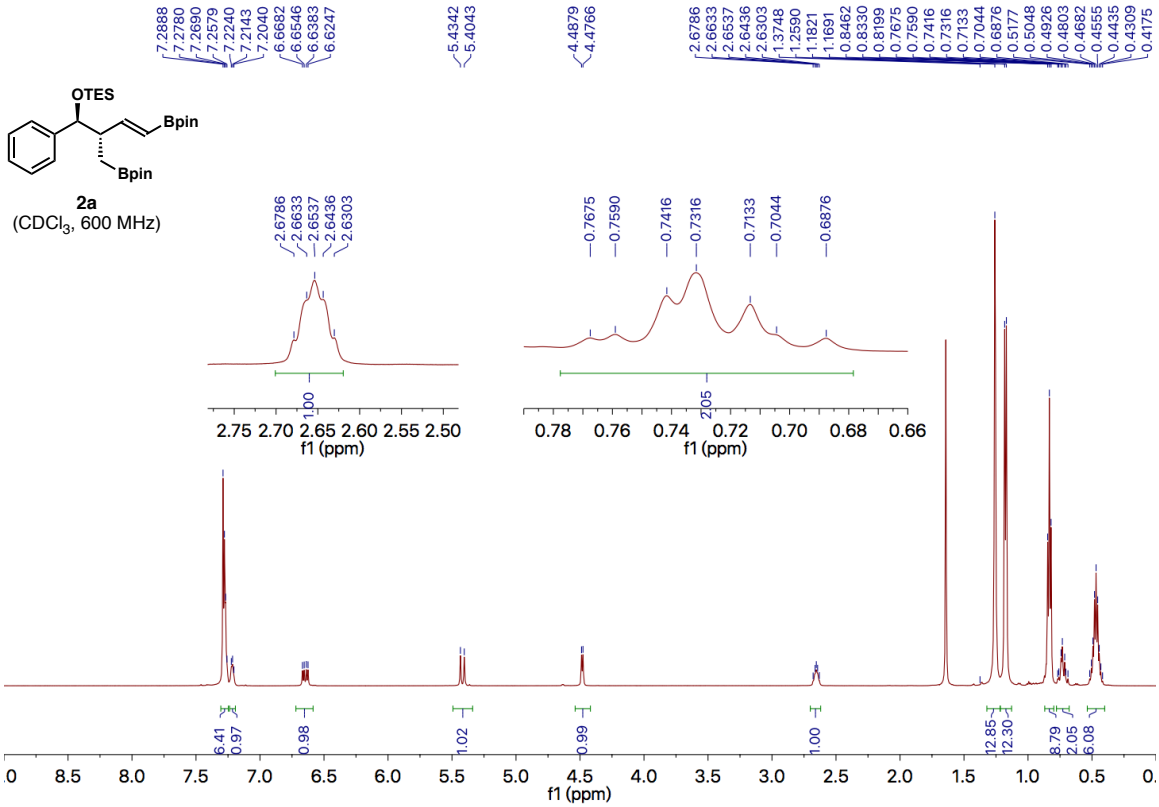
Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **8** in 82% yield (18.8 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.24 (m, 4H), 7.16 – 7.18 (m, 1H), 6.07 (d, *J* = 12.7 Hz, 1H), 5.90 (ddt, *J* = 17.1, 10.7, 5.4 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.64 (dd, *J* = 12.4, 9.8 Hz, 1H), 4.52 (d, *J* = 4.7 Hz, 1H), 4.12 (d, *J* = 4.8 Hz, 2H), 2.35 – 2.40 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 0.93 (dd, *J* = 15.1, 4.1 Hz, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.78 (dd, *J* = 15.0, 11.0 Hz, 1H), 0.42 – 0.52 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.5, 144.3, 134.0, 127.7, 127.2, 127.0, 117.6, 105.7, 83.2, 79.7, 69.8, 43.6, 25.4, 25.1, 7.2, 5.1. HRMS (EI$^+$): *m*/*z* for $C_{26}H_{43}BO_4Si$ $[M]^+$ calcd. 458.3024, found 458.3039.



***rac*-Ethyl-(2*E*,4*E*,6*S*,7*S*)-7-phenyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-7-((triethylsilyl)oxy)hepta-2,4-dienoate (10)** To a solution of ethyl acrylate (16 μL, 0.15 mmol, 3.0 equiv) in *N*,*N*-dimethylacetamide (0.25 mL) was added vinyl boronic ester **2a** (26.4 mg, 0.05 mmol, 1.0 equiv) and $Pd(OAc)_2$ (1 mg, 0.005 mmol, 10 mol %). The reaction flask was fitted with an oxygen balloon and the reaction mixture was stirred for 6 h at 55 °C. Then ethyl acetate (20 mL) was added to the reaction flask, and the resulting solution was washed with water (2 × 10 mL). The separated organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **10** in 81% yield (20.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.28 (m, 6H), 6.14 (dd, *J* = 15.3, 8.2 Hz, 1H), 6.06 (dd, *J* = 15.3, 10.4 Hz, 1H), 5.73 (d, *J* = 15.3 Hz, 1H), 4.60 (d, *J* = 5.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.62 – 2.70 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H), 0.94 (dd, *J* = 15.6, 4.9 Hz, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.80 (dd, *J* = 15.6, 7.9 Hz, 1H), 0.48 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 146.5, 145.6, 143.9, 129.3, 128.0, 127.4, 127.0, 119.4, 83.4, 79.2, 60.6, 48.0, 25.4, 25.0, 14.6, 14.1, 7.1, 5.1. HRMS (ESI$^+$): *m*/*z* for $C_{28}H_{46}BO_5Si$ $[M+H]^+$ calcd. 501.3205, found 501.3208.



***rac*-Ethyl-(2*Z*,4*E*,6*R*,7*S*)-6-(hydroxymethyl)-7-phenyl-7-((triethylsilyl)oxy)hepta-2,4-dienoate (12)** In an Ar-filled glove box, $PdCl_2(dppf)•CH_2Cl_2$ (4 mg, 10 mol %), K_3PO_4 (28 mg, 0.13 mmol, 2.6 equiv), THF (0.45 mL), vinylboronate **2a** (26.4 mg, 0.05 mmol, 1.0 equiv), and a Teflon-coated magnetic stirring bar were sequentially added into a 1-dram vial. Then vinyl iodide **11** (15 mg, 0.065 mmol, 1.3 equiv) and 50 μL H_2O were added to the mixture. The vial was sealed with a cap containing a PTFE-lined silicone septum and removed from glove box. The reaction was kept stirring at 70 °C for 12 h. After complete consumption of boronate **2a**, 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 extracts were concentrated under reduced pressure. The crude product was dissolved in THF (1.0 mL); $NaBO_3•4H_2O$ (15 mg, 0.1 mmol, 2.0 equiv) and 0.5 mL water were added to the solution. The reaction mixture was stirred at ambient temperature for 4 h. Then Et_2O (0.5 mL) were added, 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 **12** in 67% yield (13 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 15.2, 11.5 Hz, 1H), 7.29 – 7.31 (m, 2H), 7.23 – 7.26 (m, 3H), 6.50 (*app.* t, *J* = 11.3 Hz, 1H), 5.82 (dd, *J* = 15.4, 9.2 Hz, 1H), 5.59 (d, *J* = 11.3 Hz, 1H), 4.90 (d, *J* = 4.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 10.0, 7.7 Hz, 1H), 3.54 (dd, *J* = 10.2, 5.3 Hz, 1H), 2.79 – 2.83 (m, 1H), 2.42 (br, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.45 – 0.55 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 144.8, 142.1, 141.4, 129.9, 128.3, 127.8, 126.9, 117.1, 76.8, 63.7, 60.3, 53.2, 14.6, 7.1, 4.9. HRMS (ESI^+): *m*/*z* for $C_{22}H_{34}O_4SiNa$ $[M+Na]^+$ calcd. 413.2124, found 413.2091.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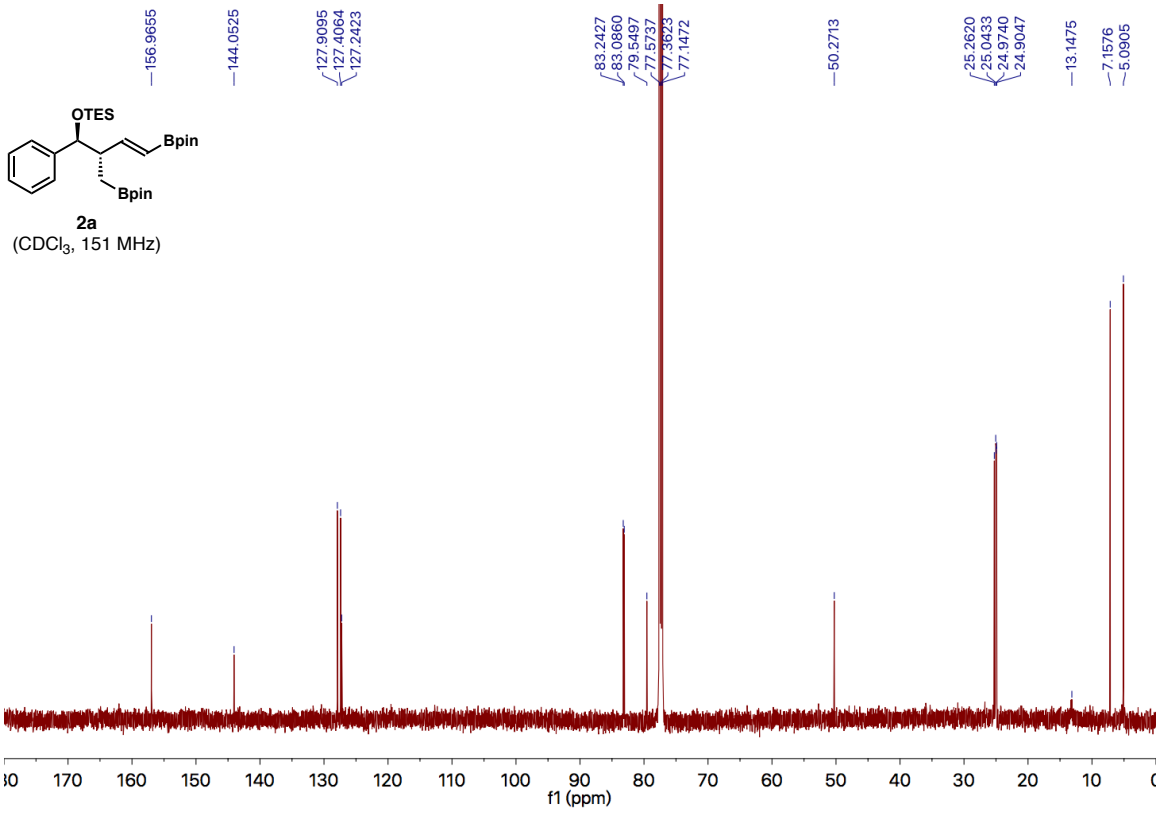
f1 (ppm)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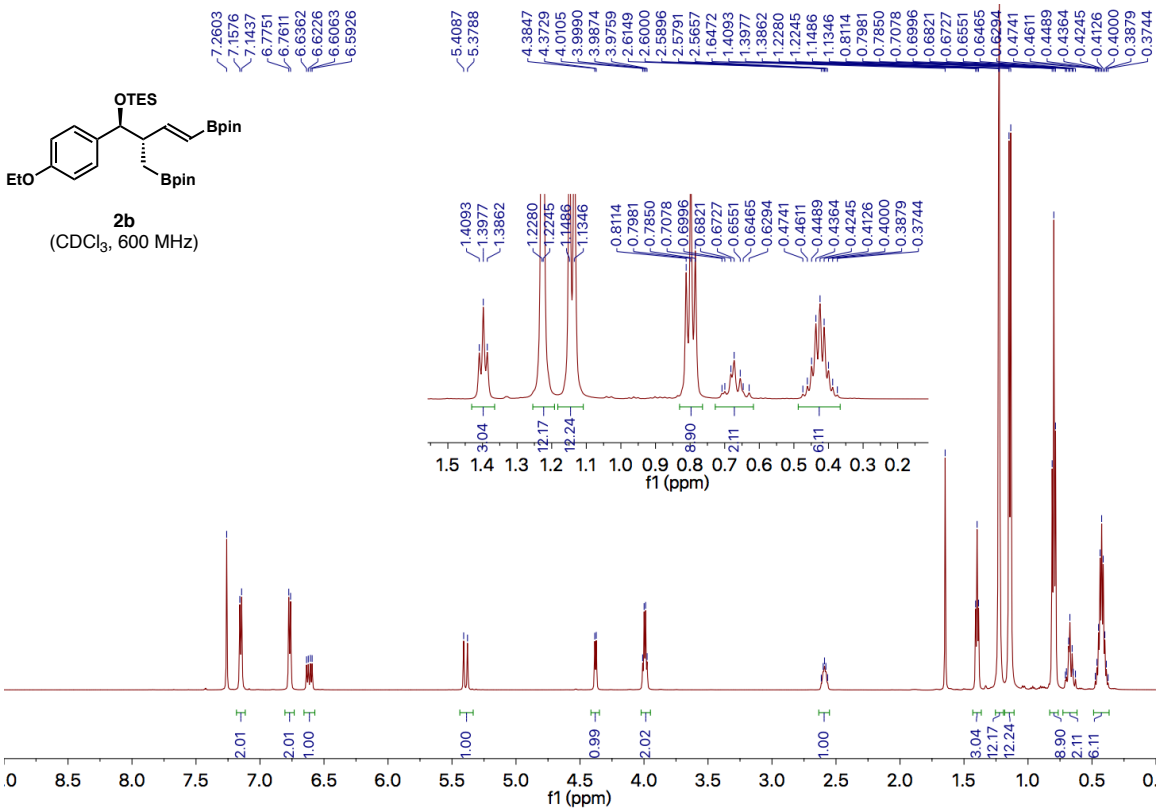
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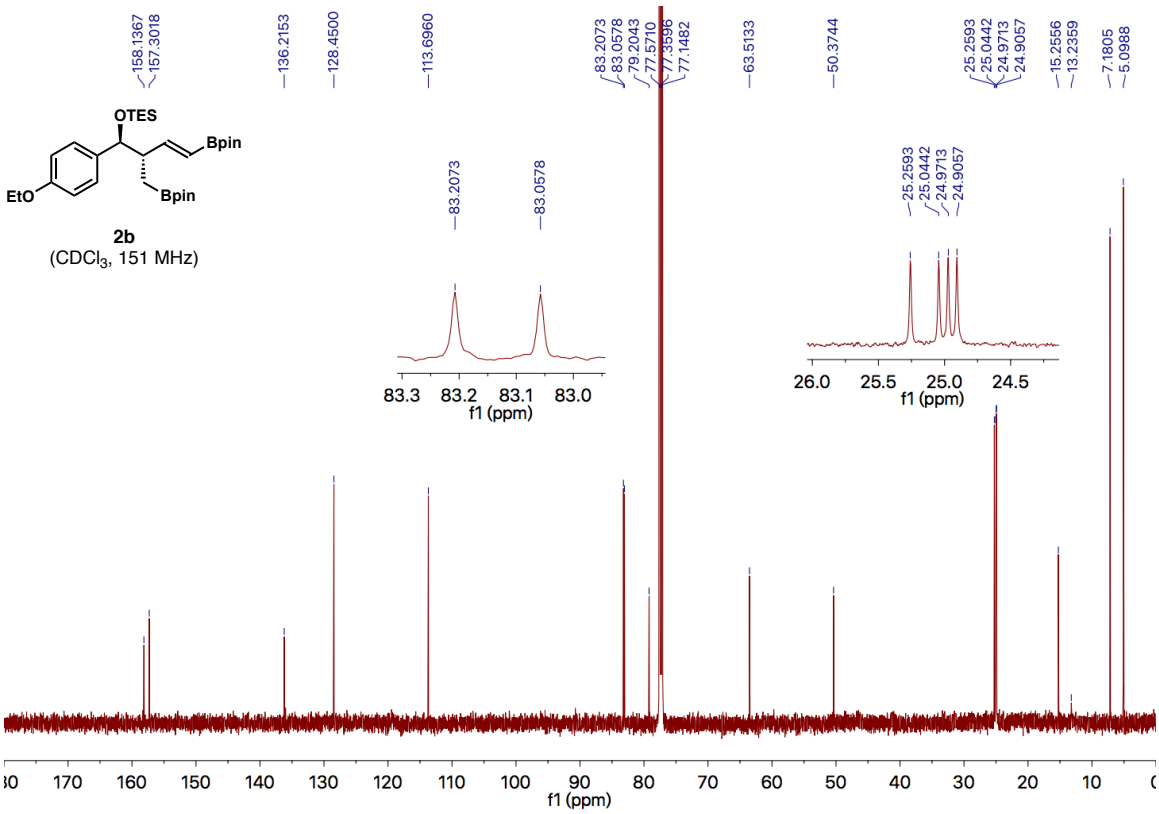
f1 (ppm)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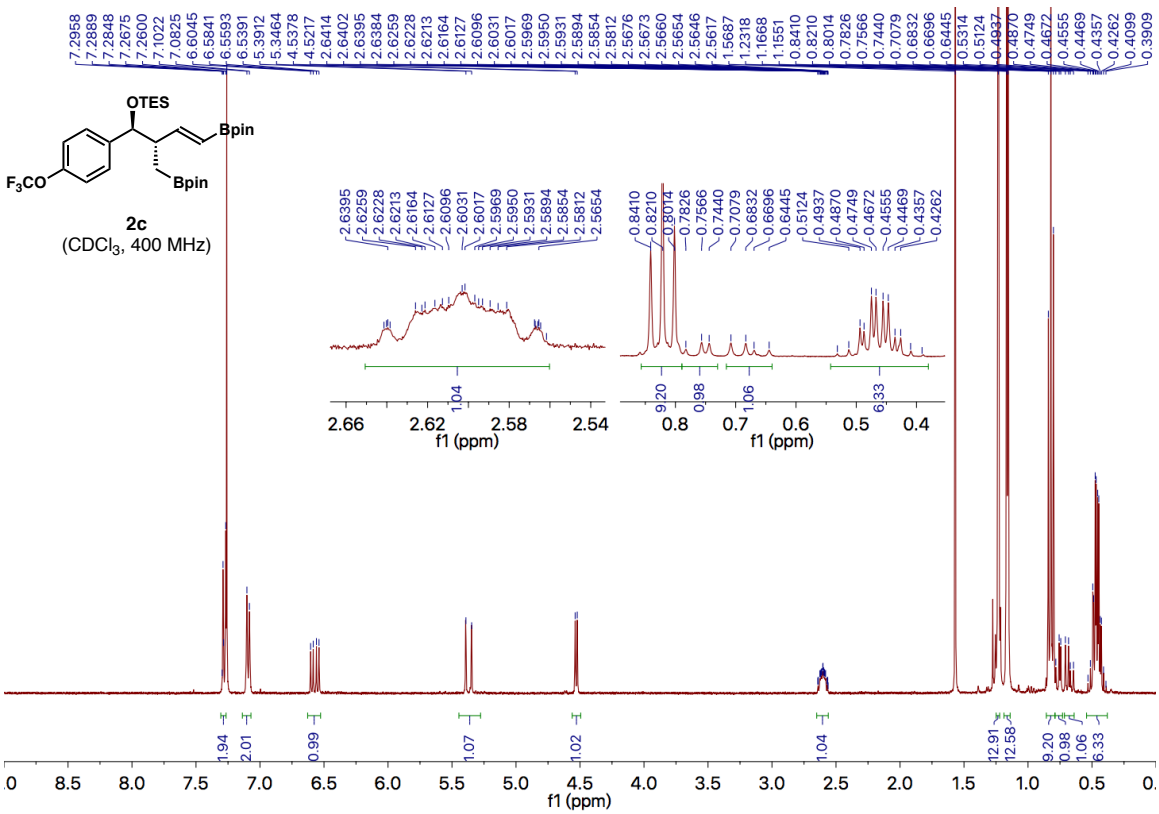
f1 (ppm)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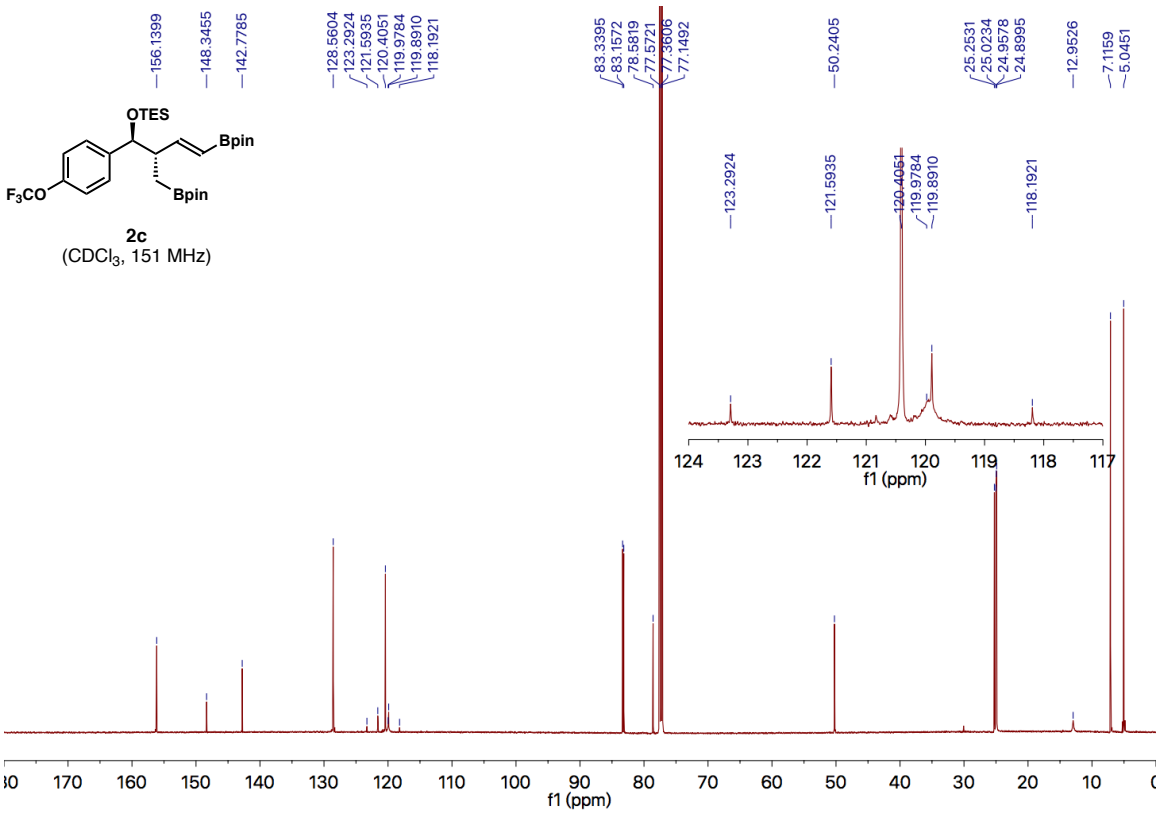
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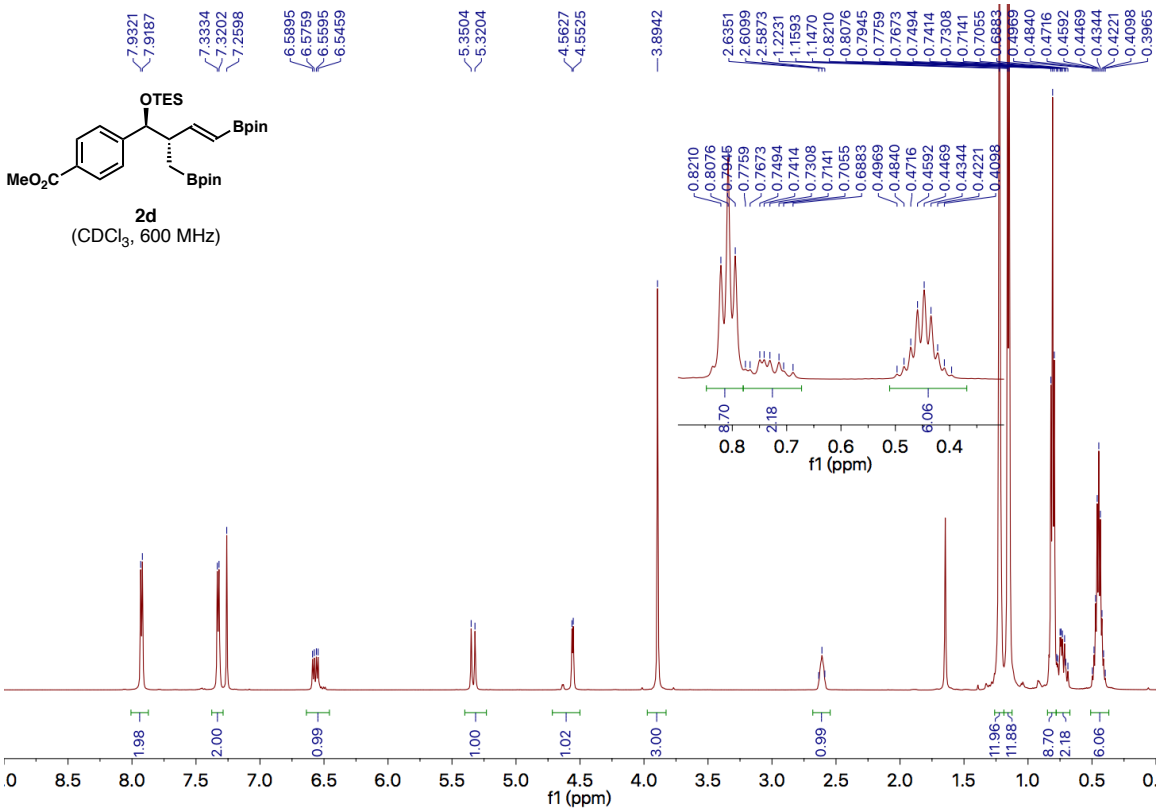
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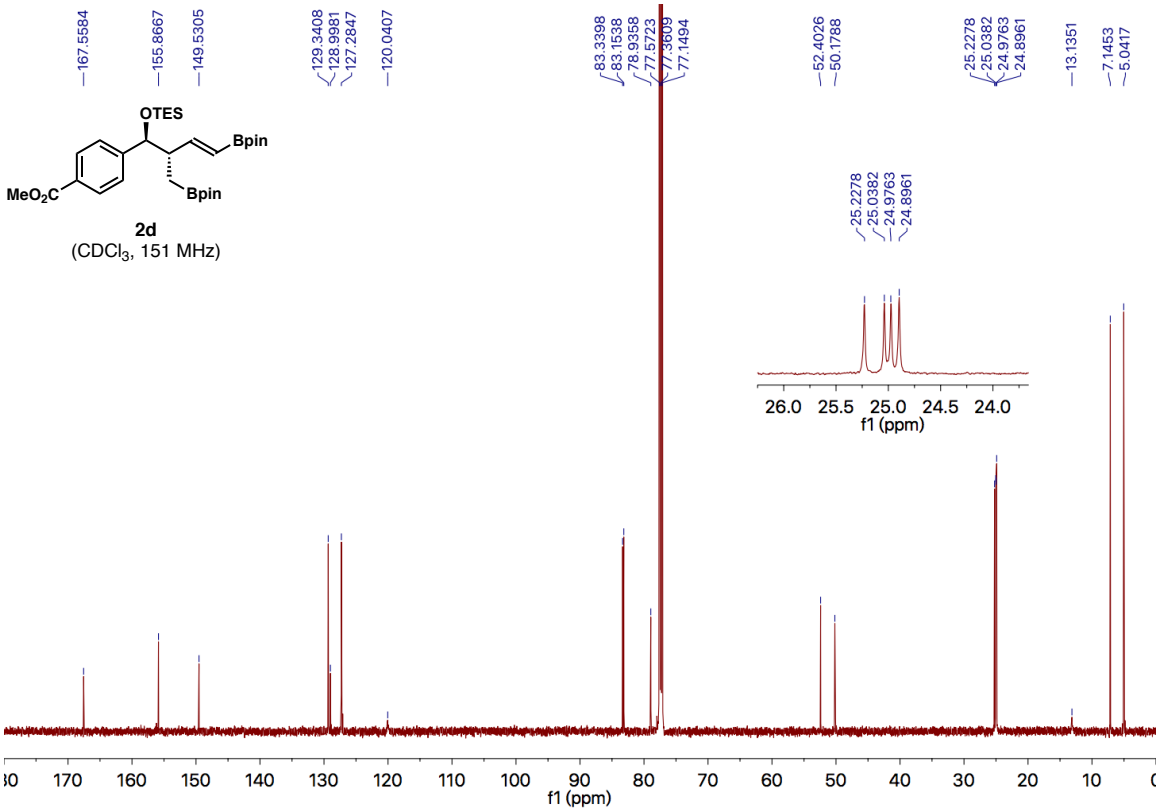
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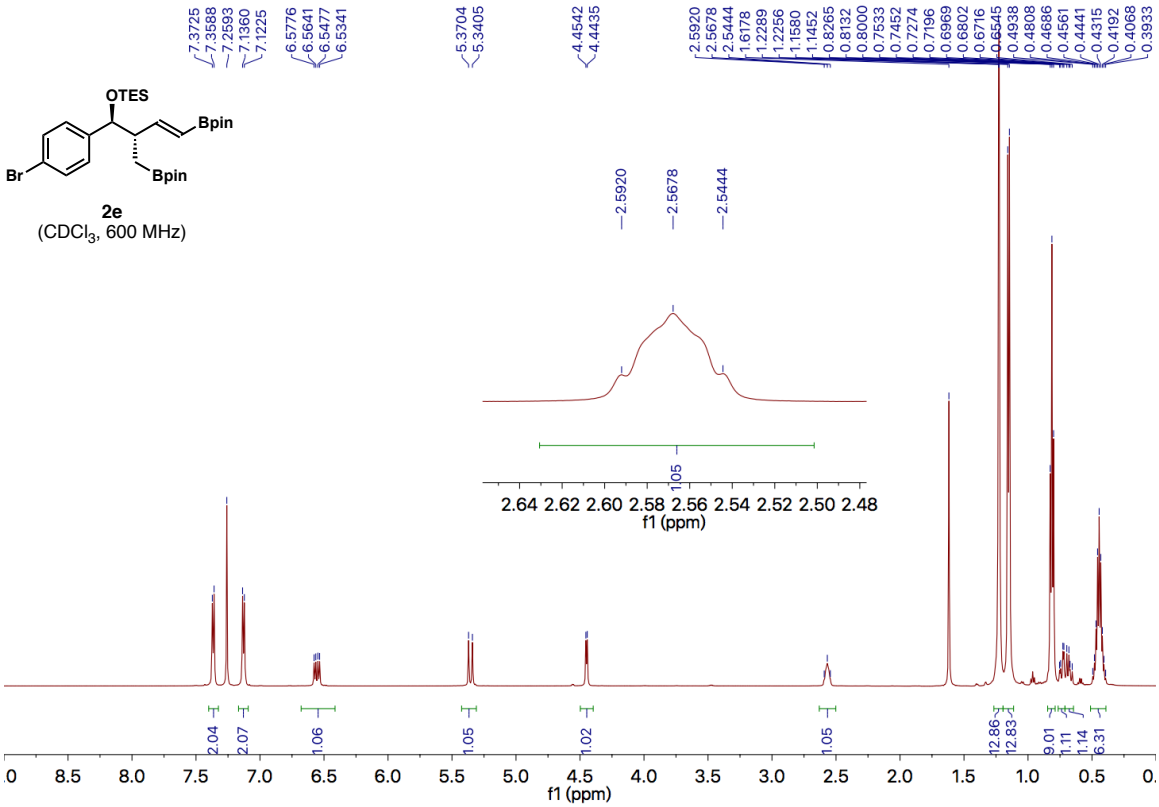
f1 (ppm)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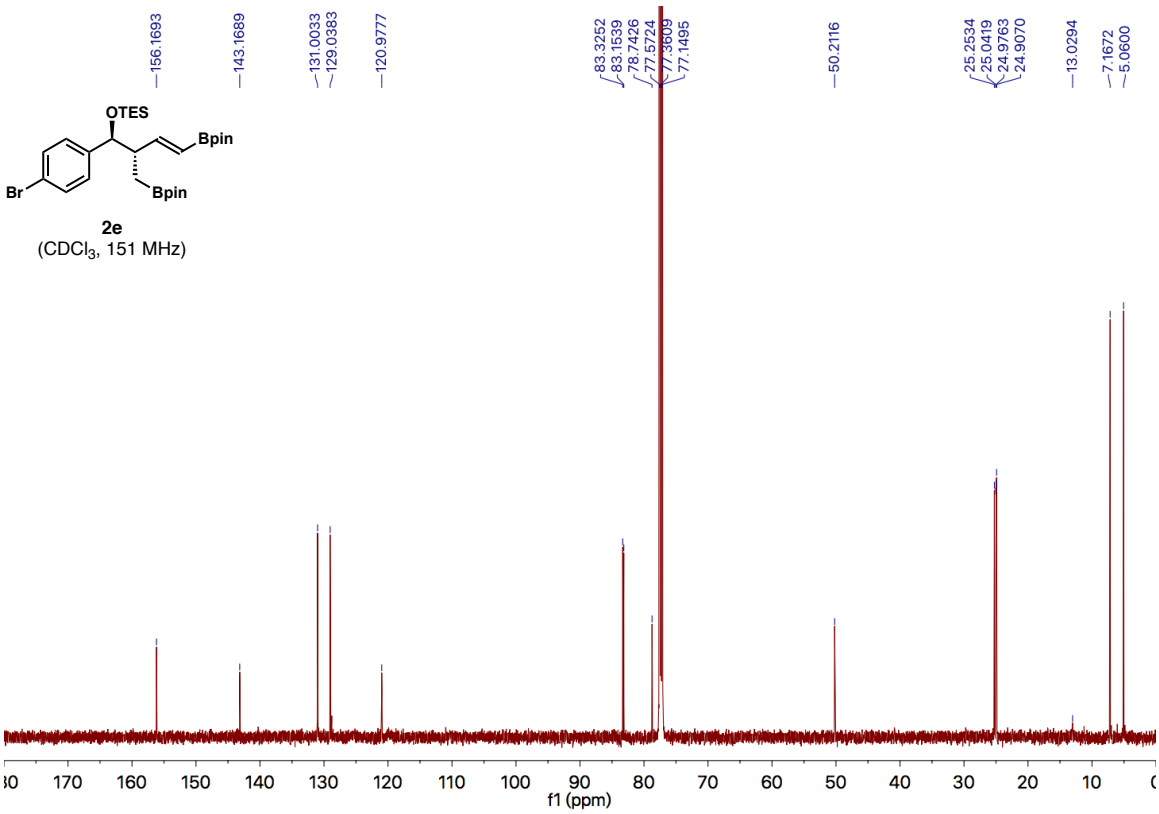
f1 (ppm)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Br
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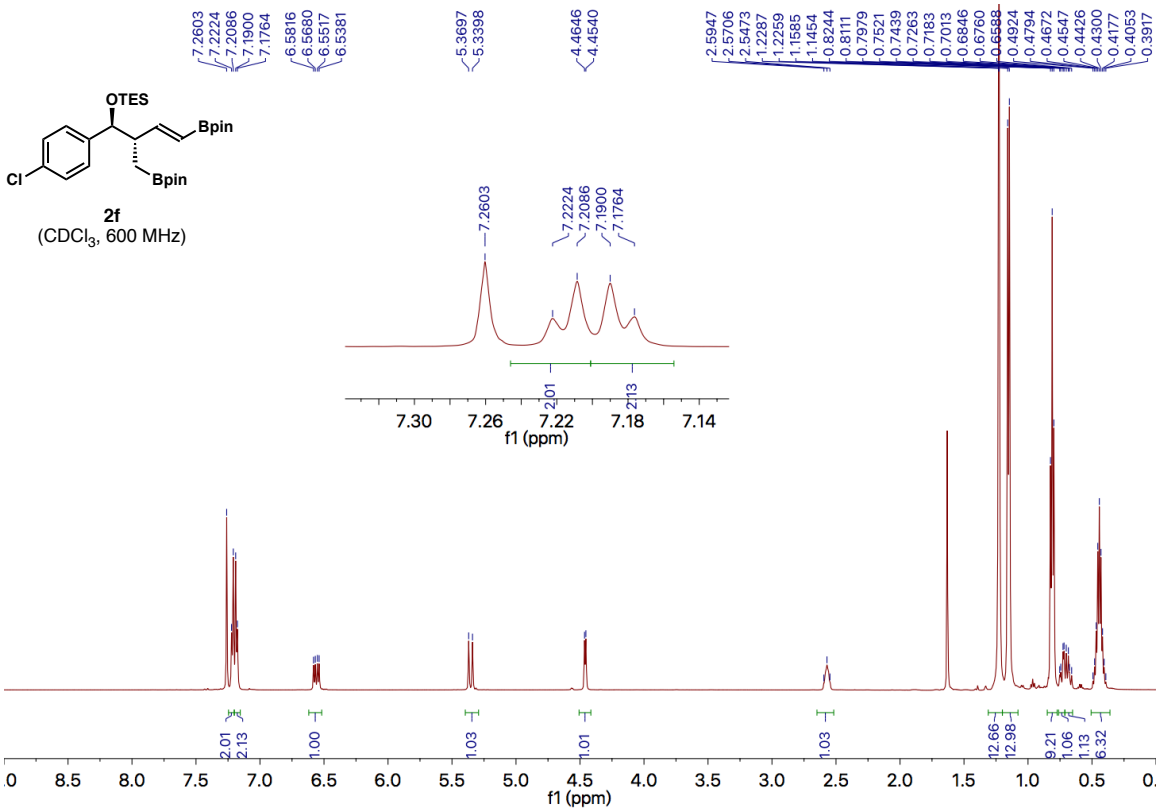
f1 (ppm)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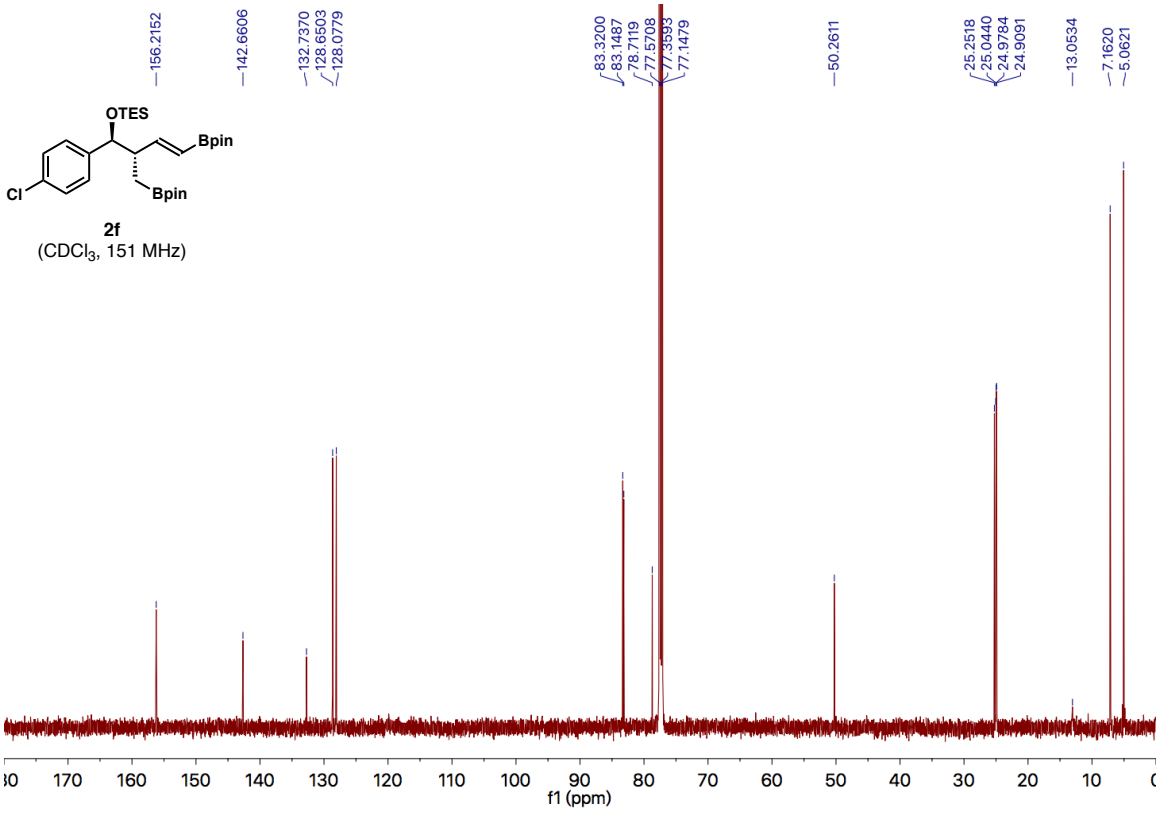
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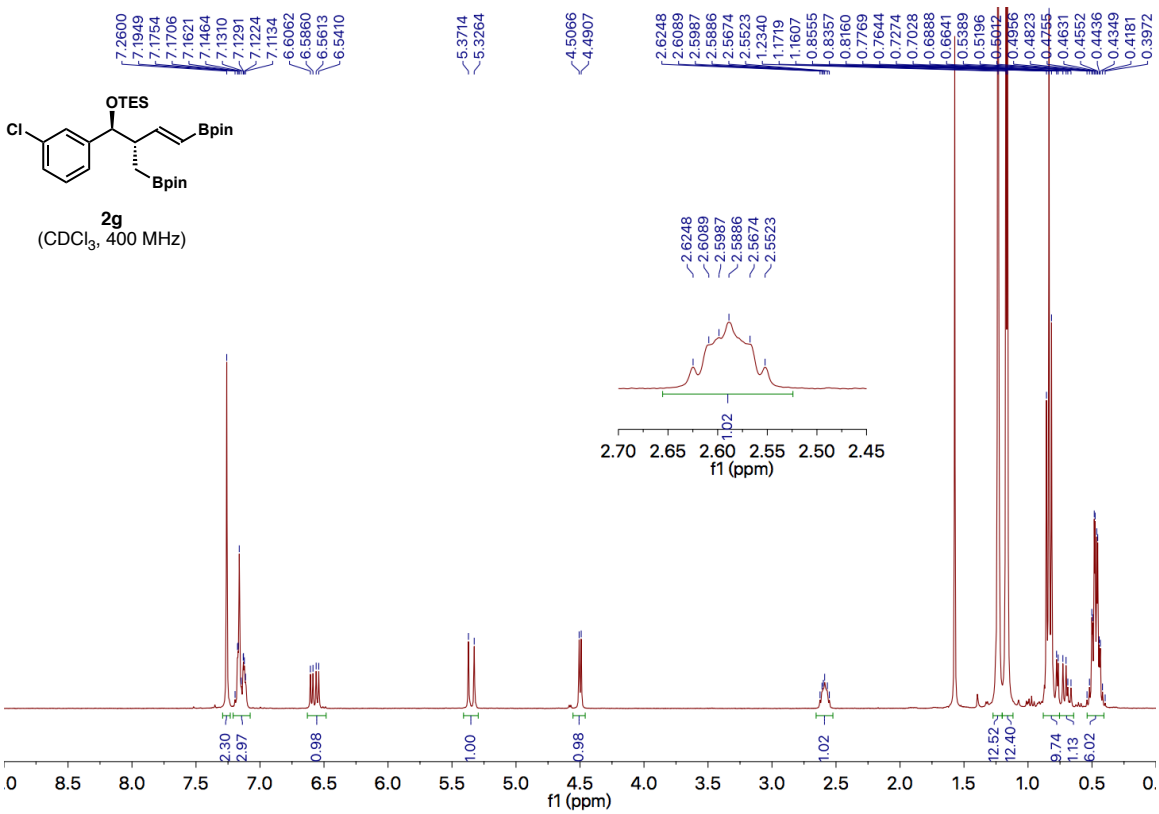
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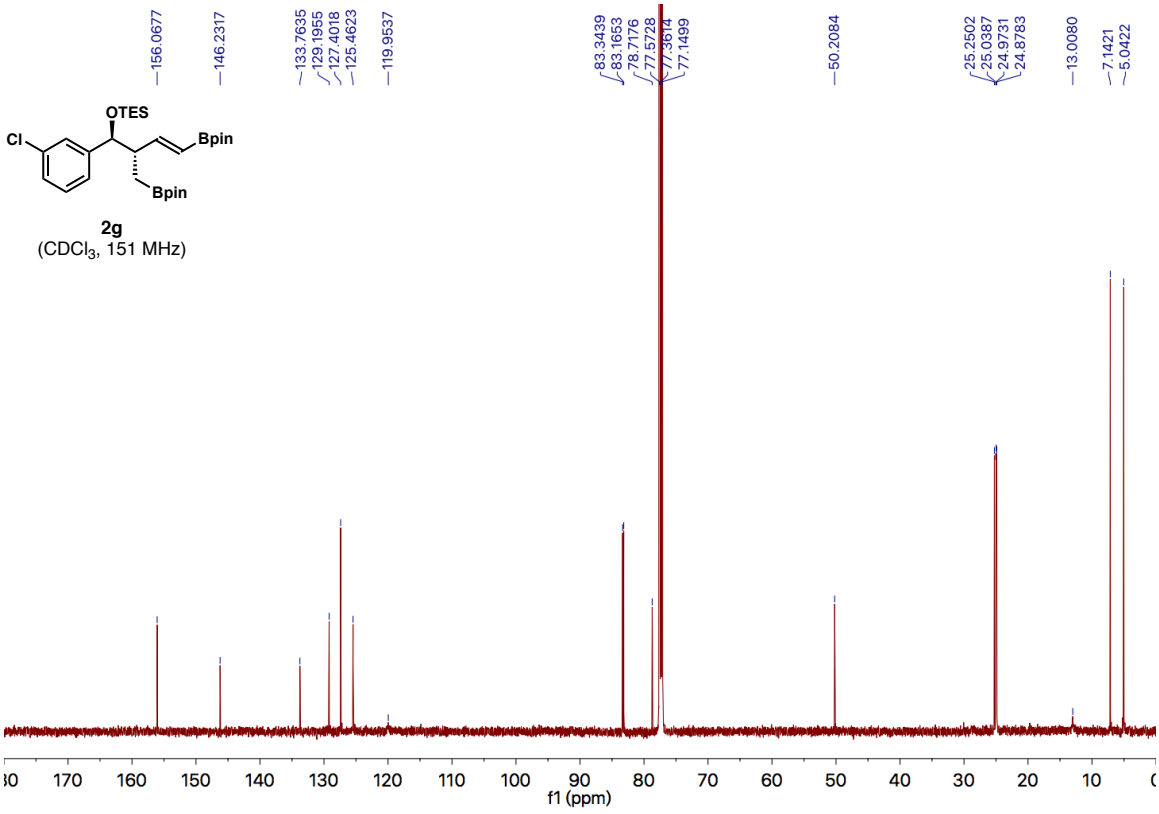
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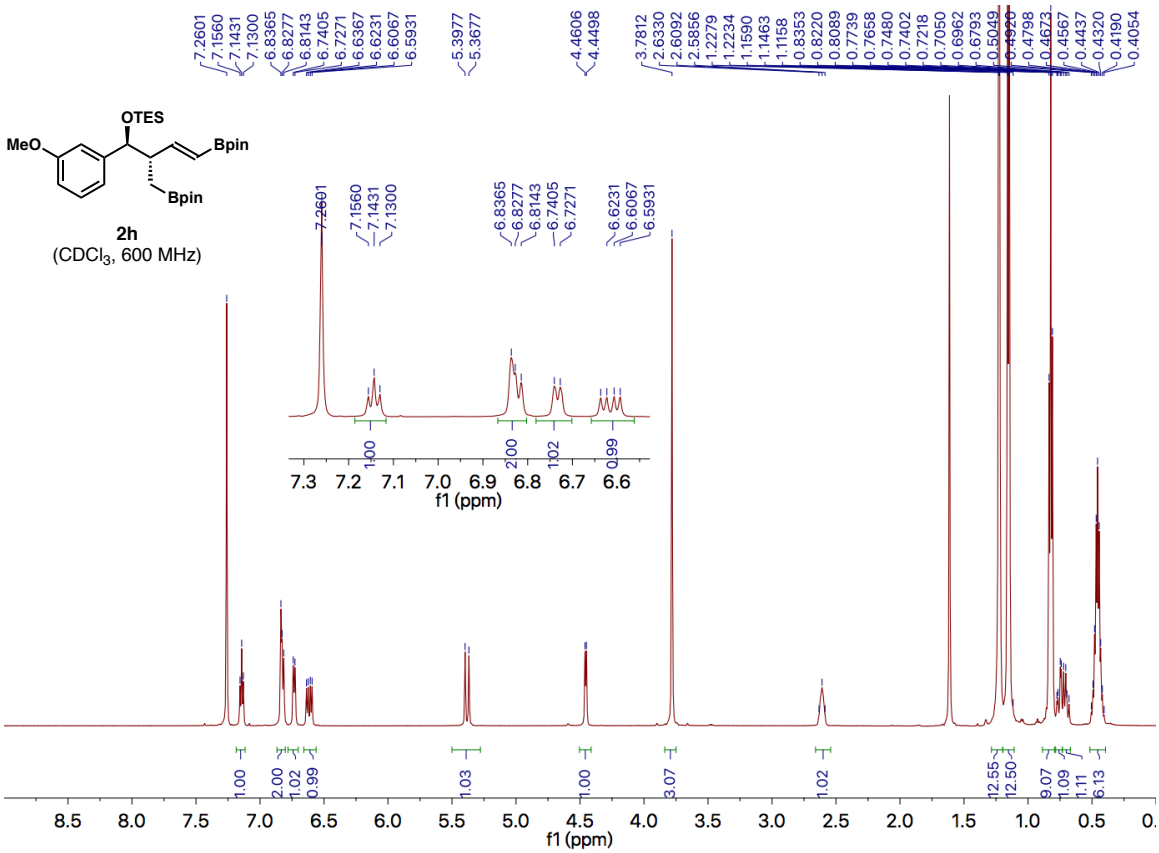
f1 (ppm)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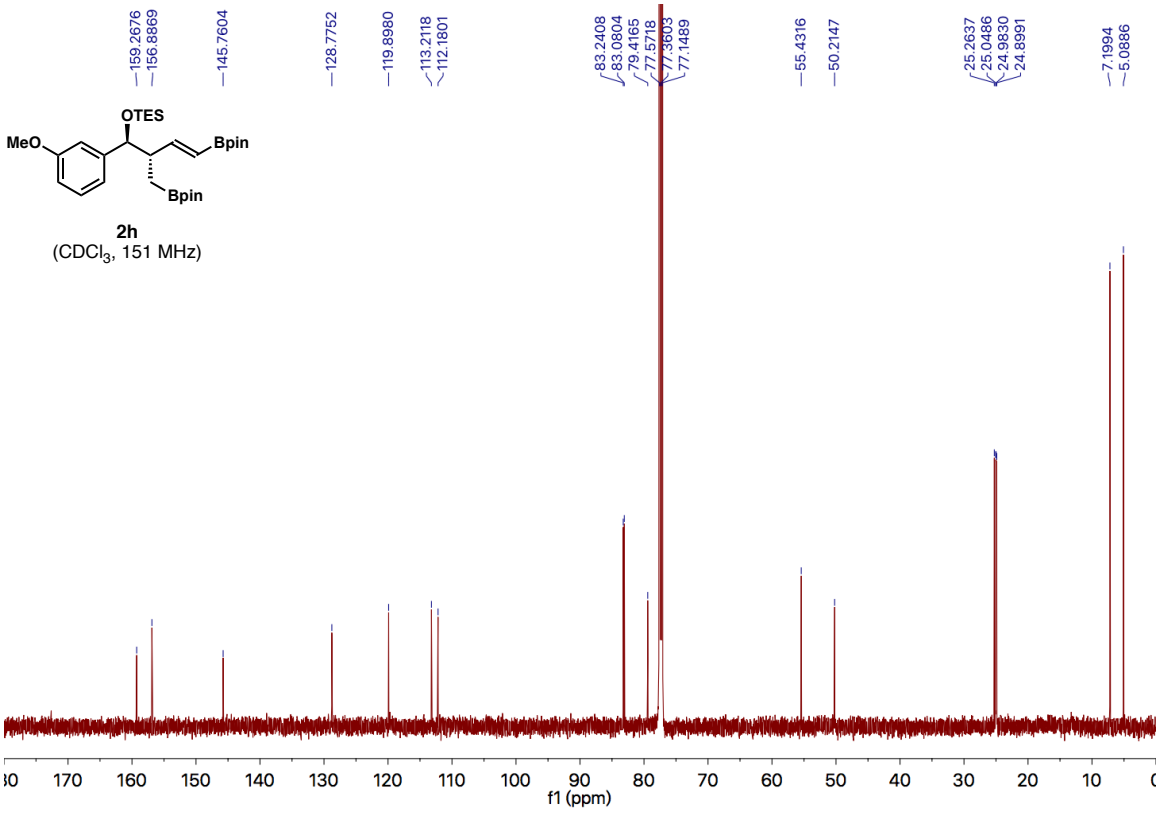
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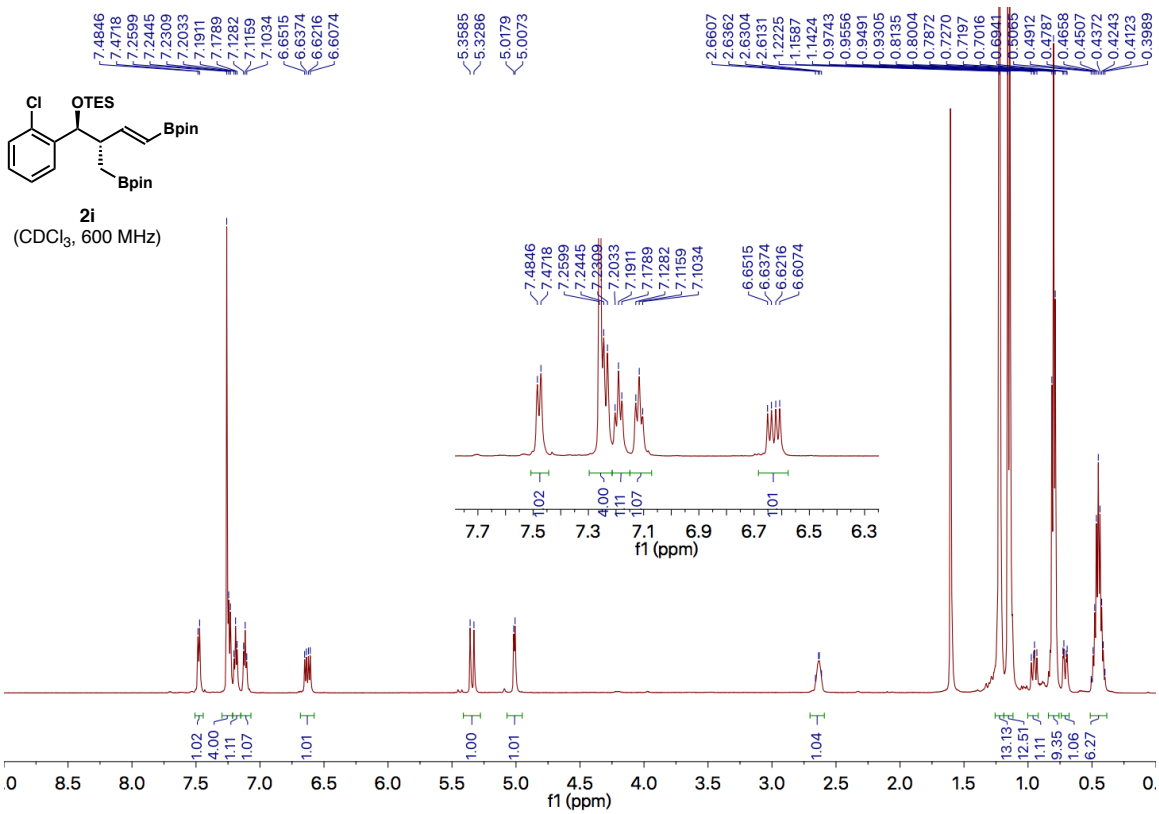
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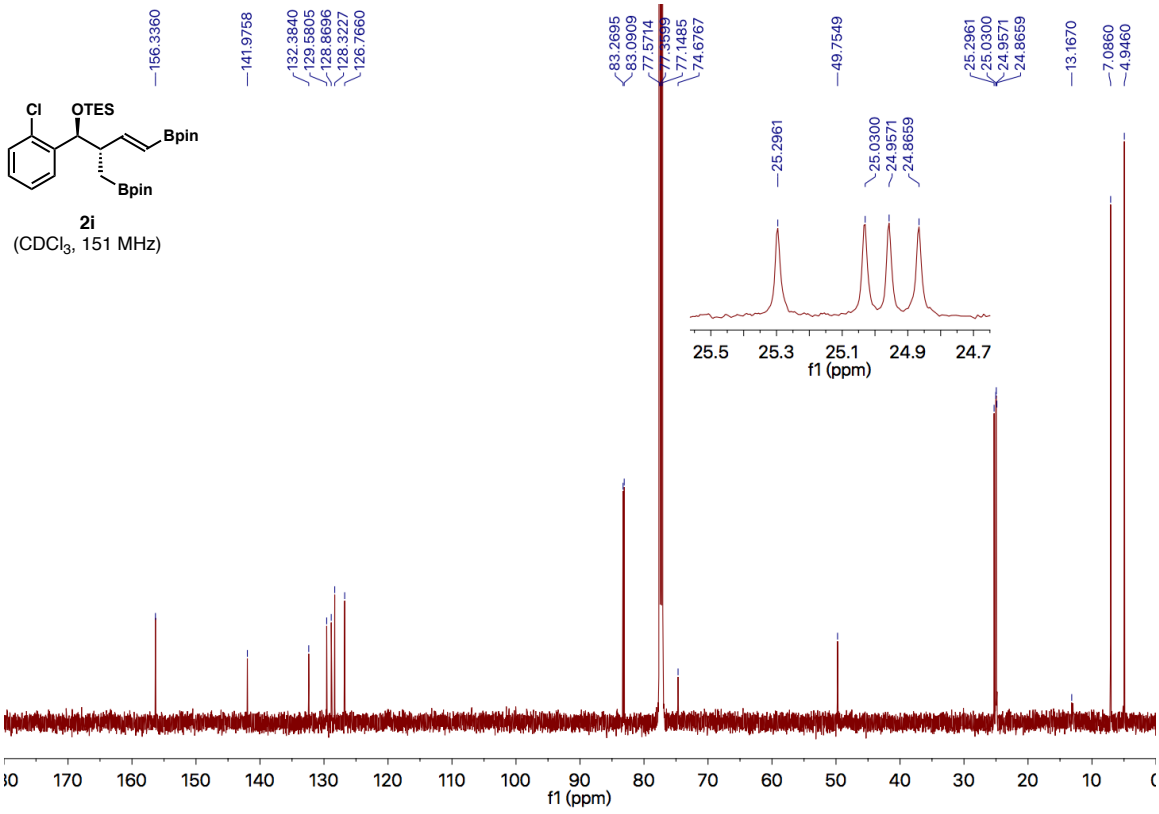
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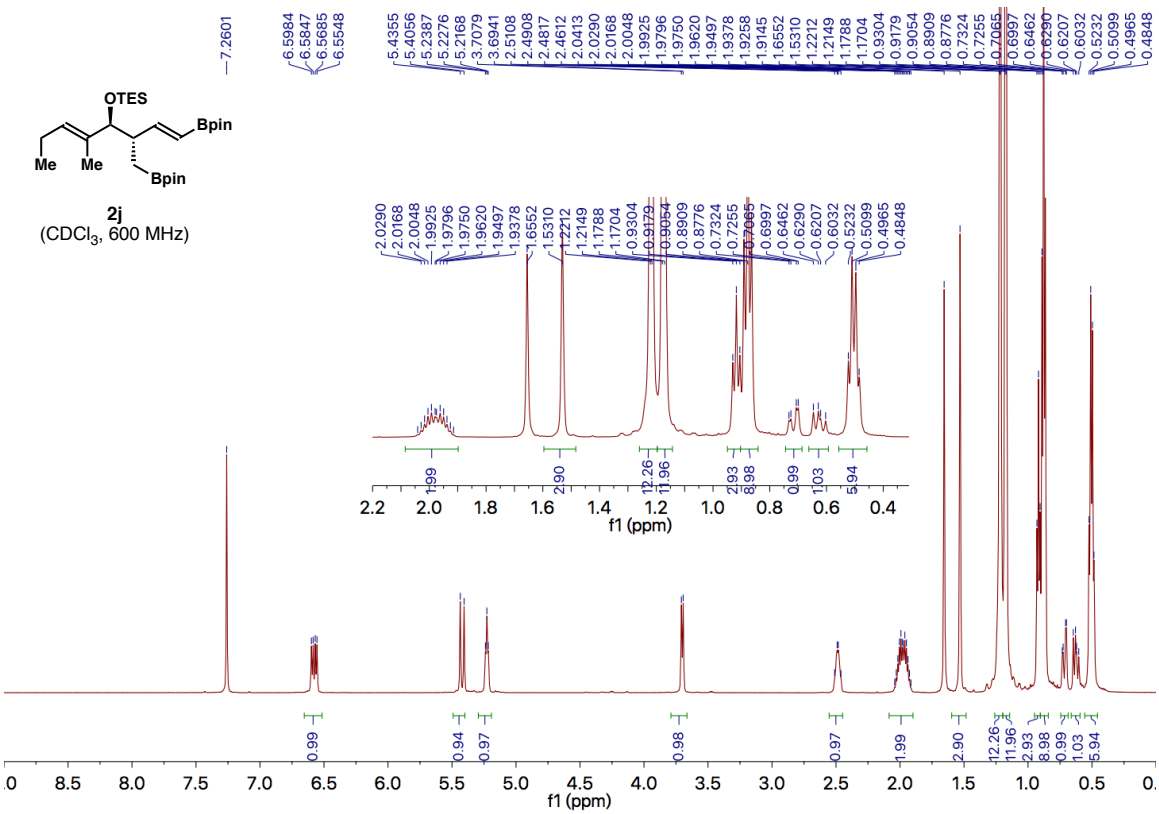
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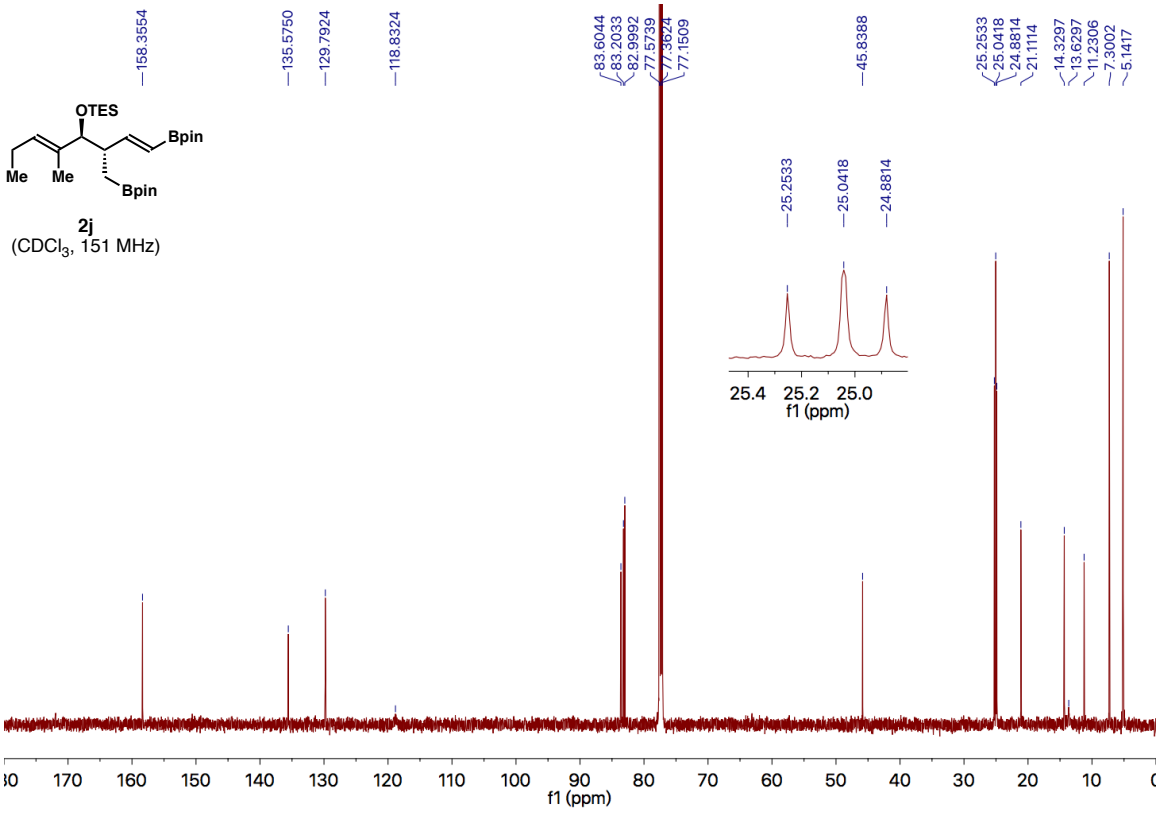
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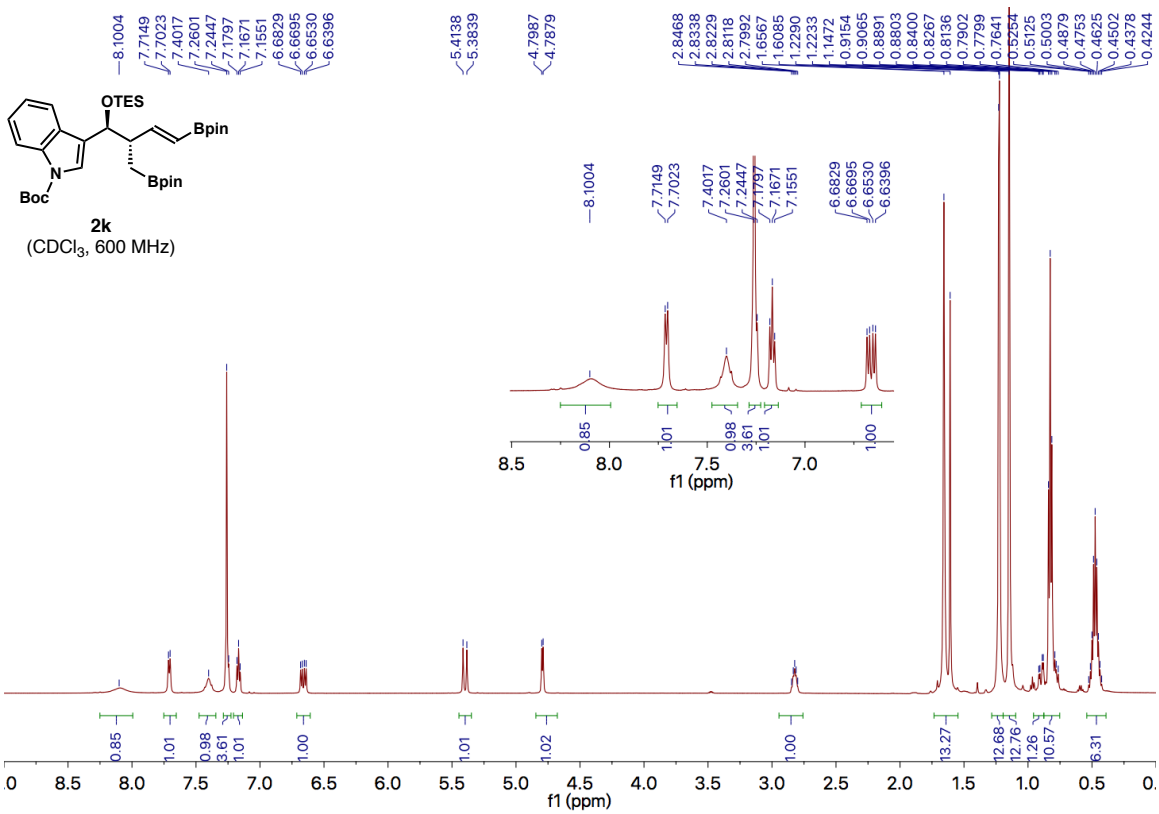
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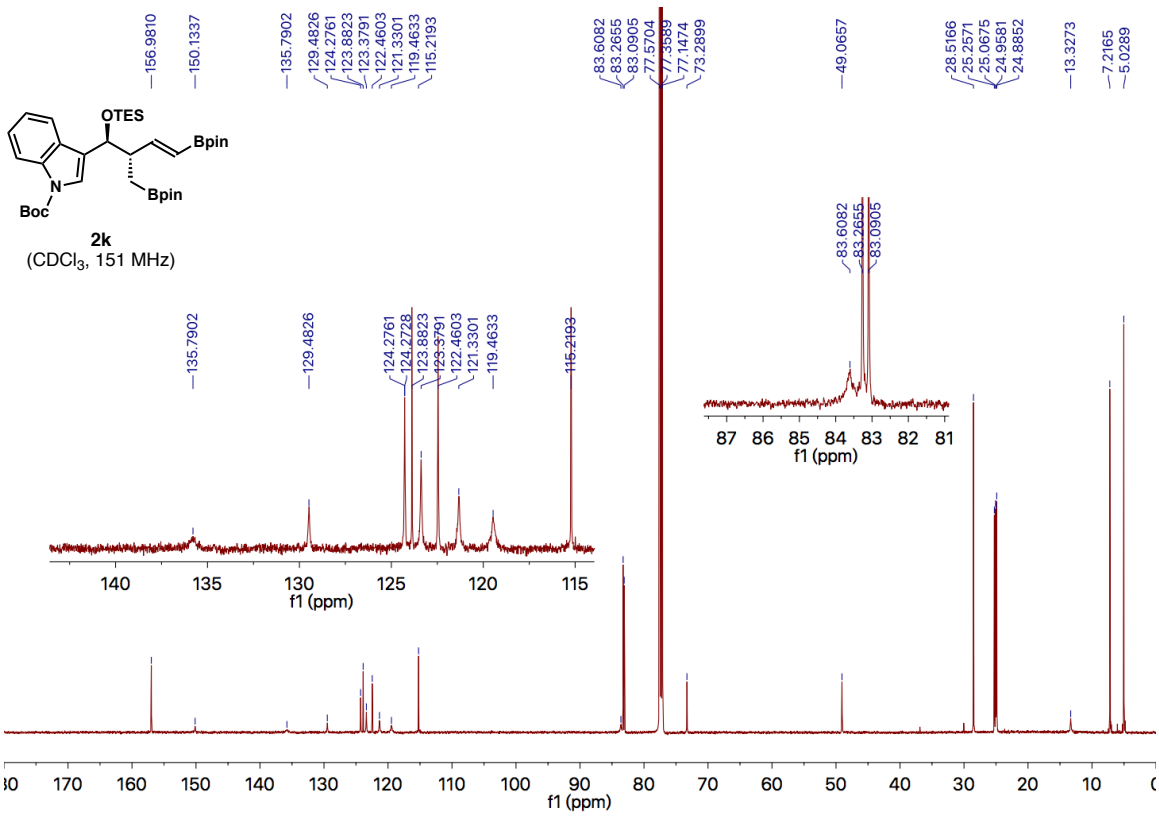
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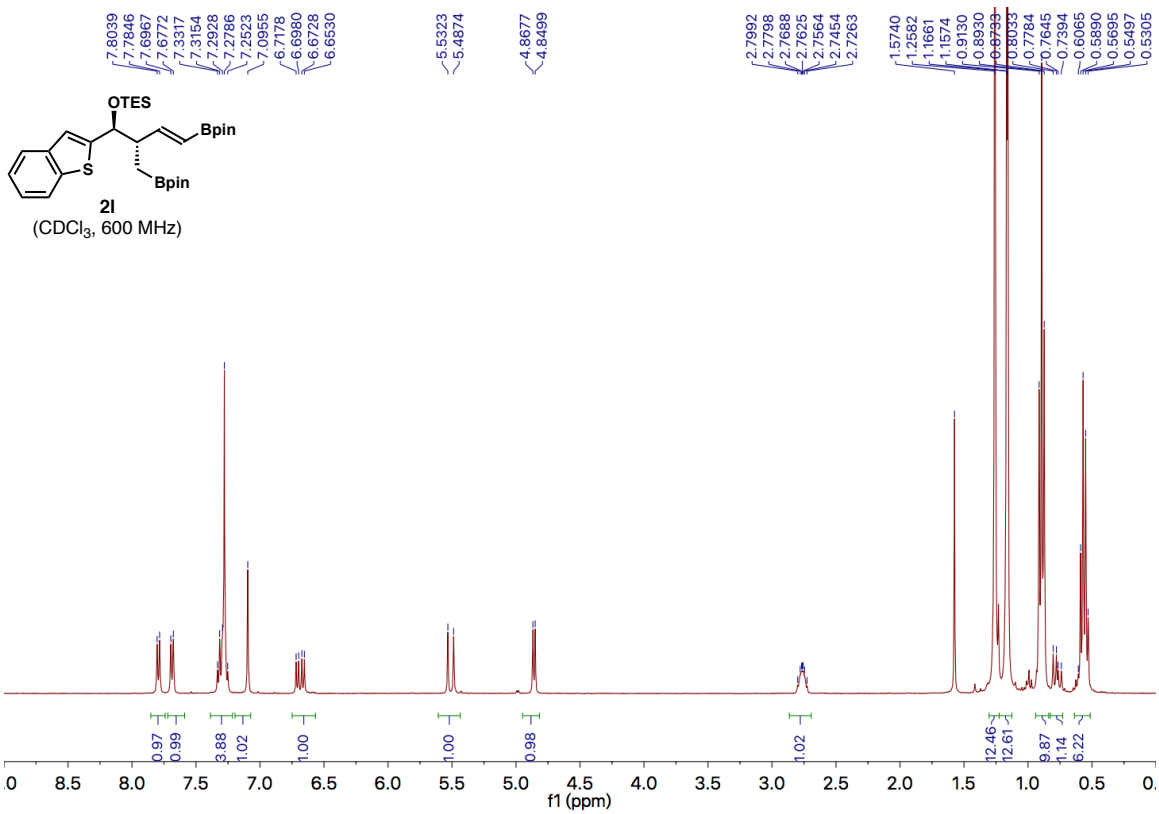
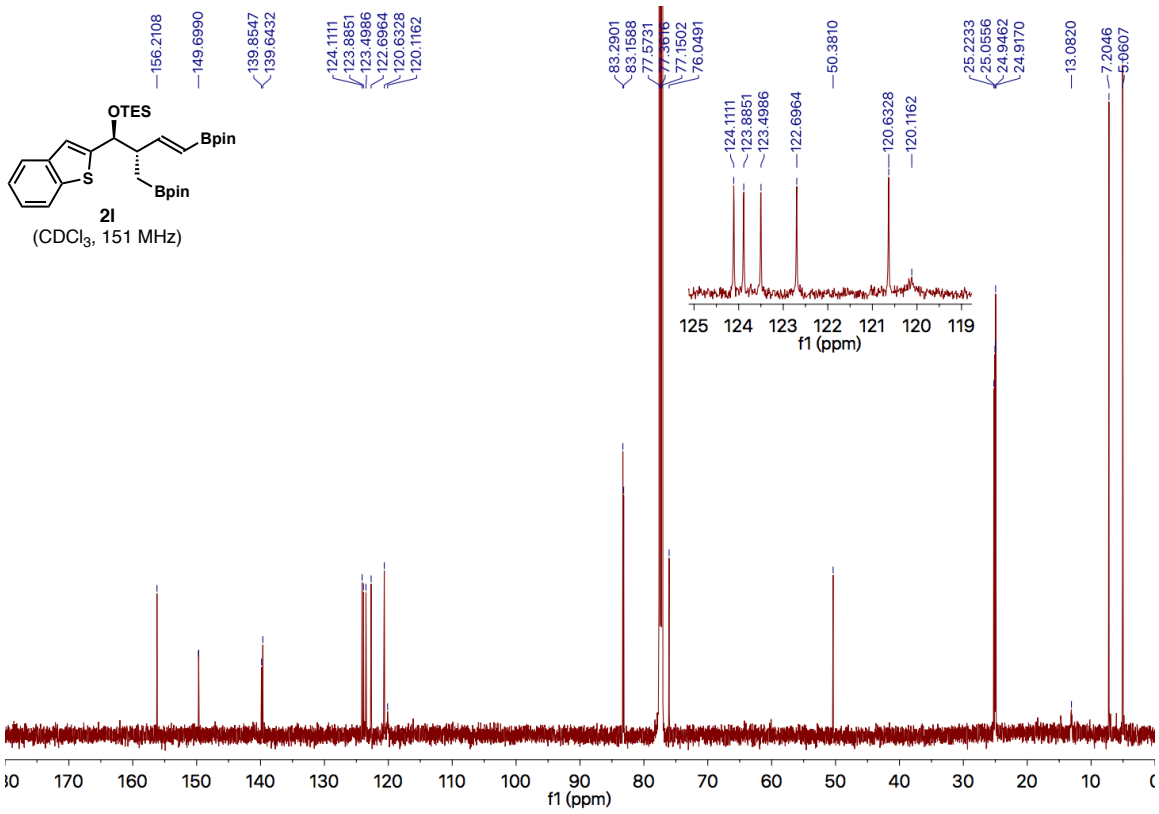
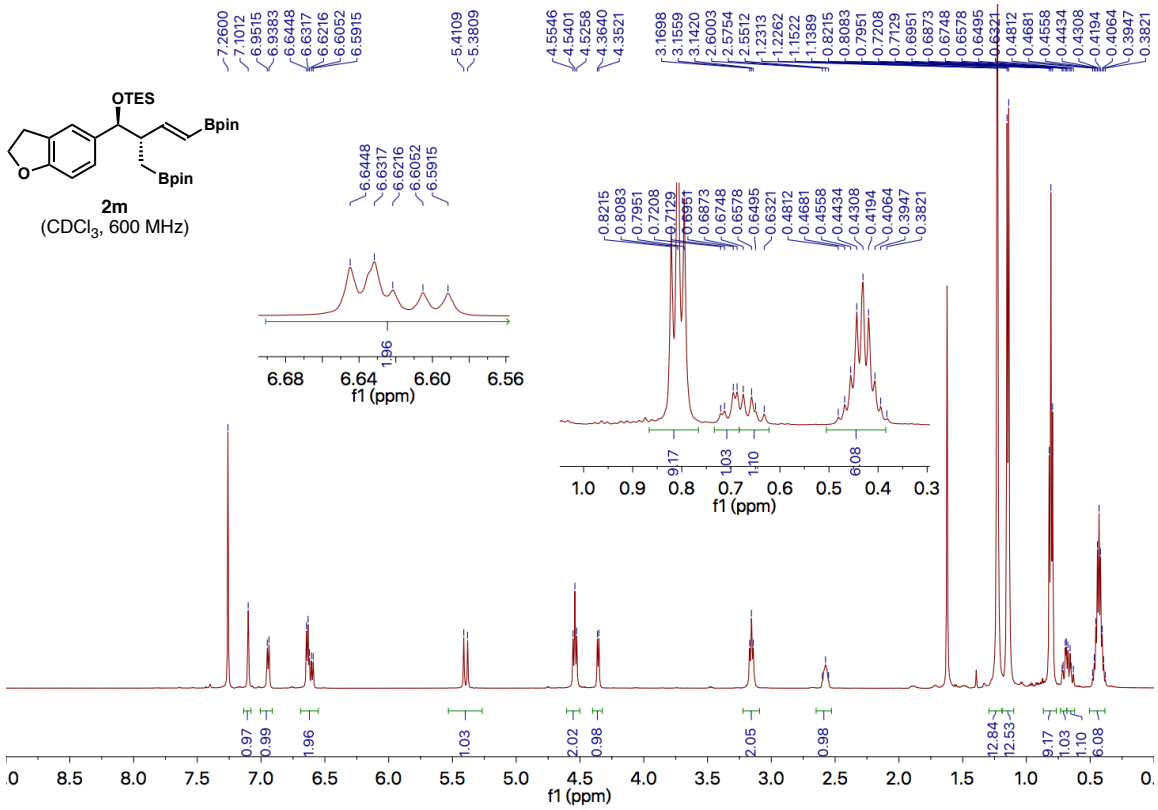
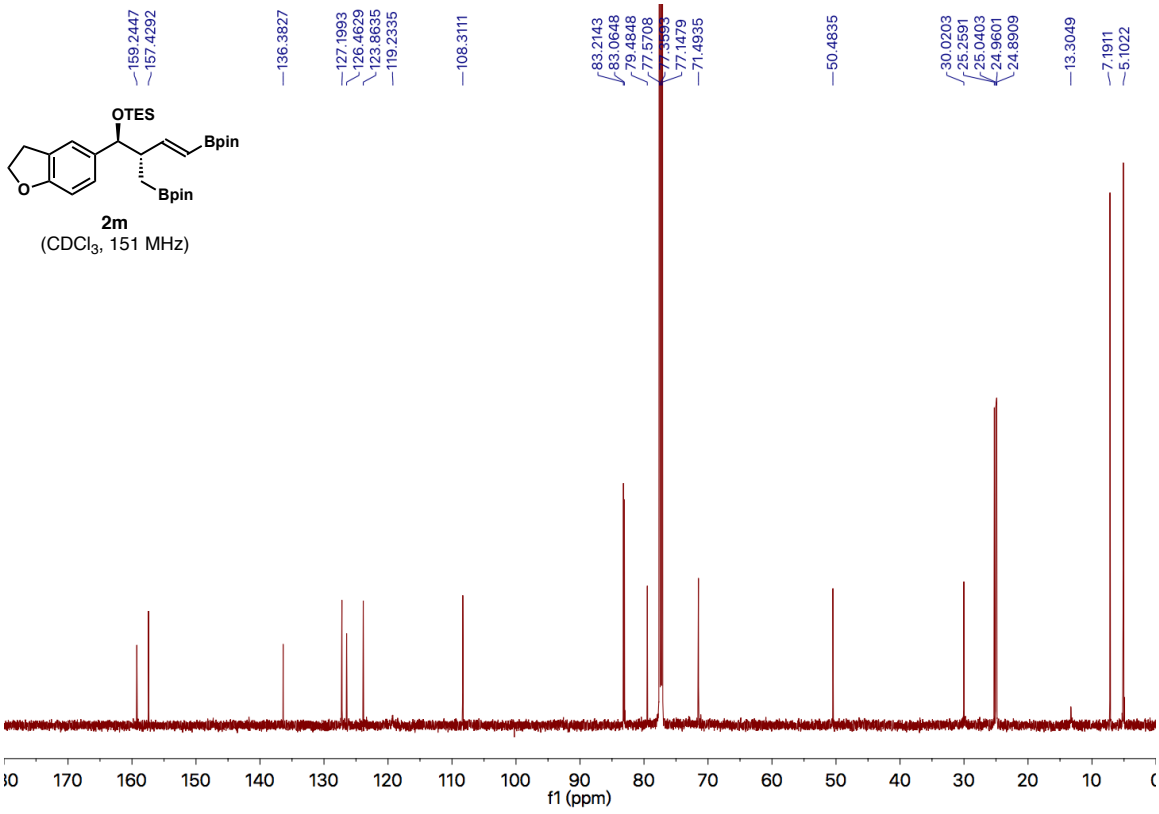
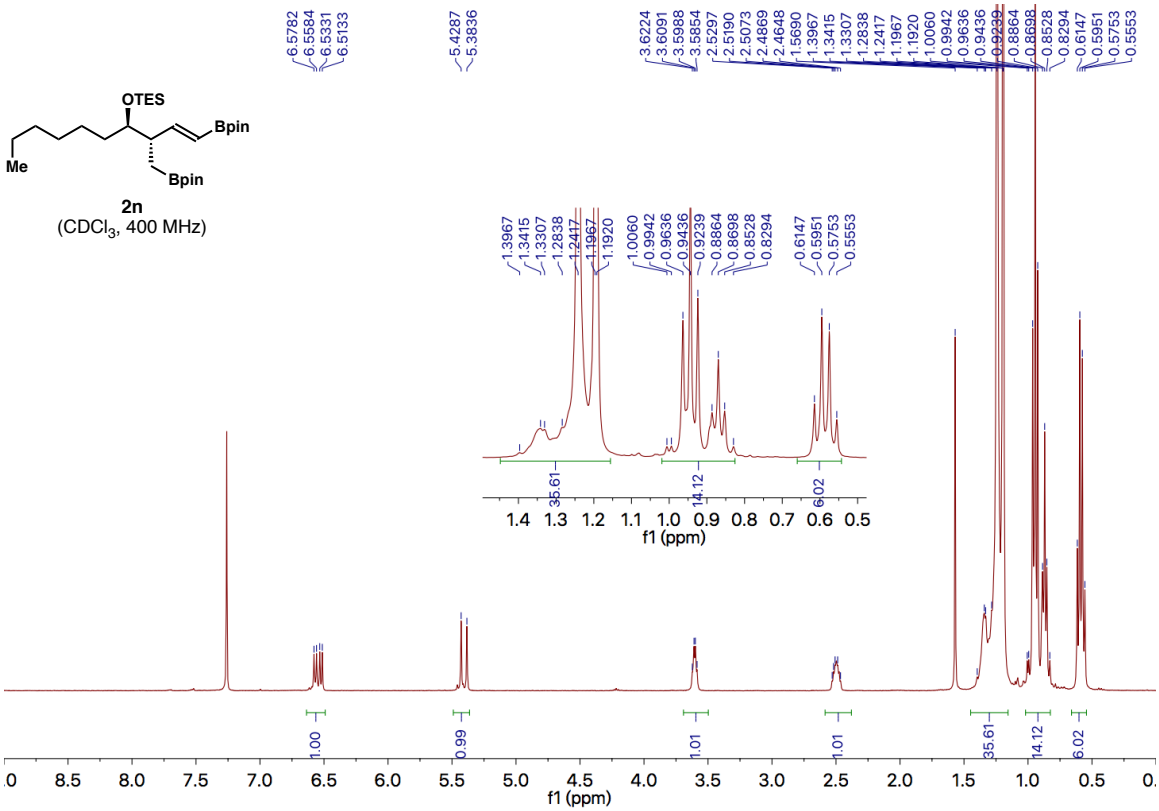
2k
(CDCl3, 151 MHz)
f1 (ppm)

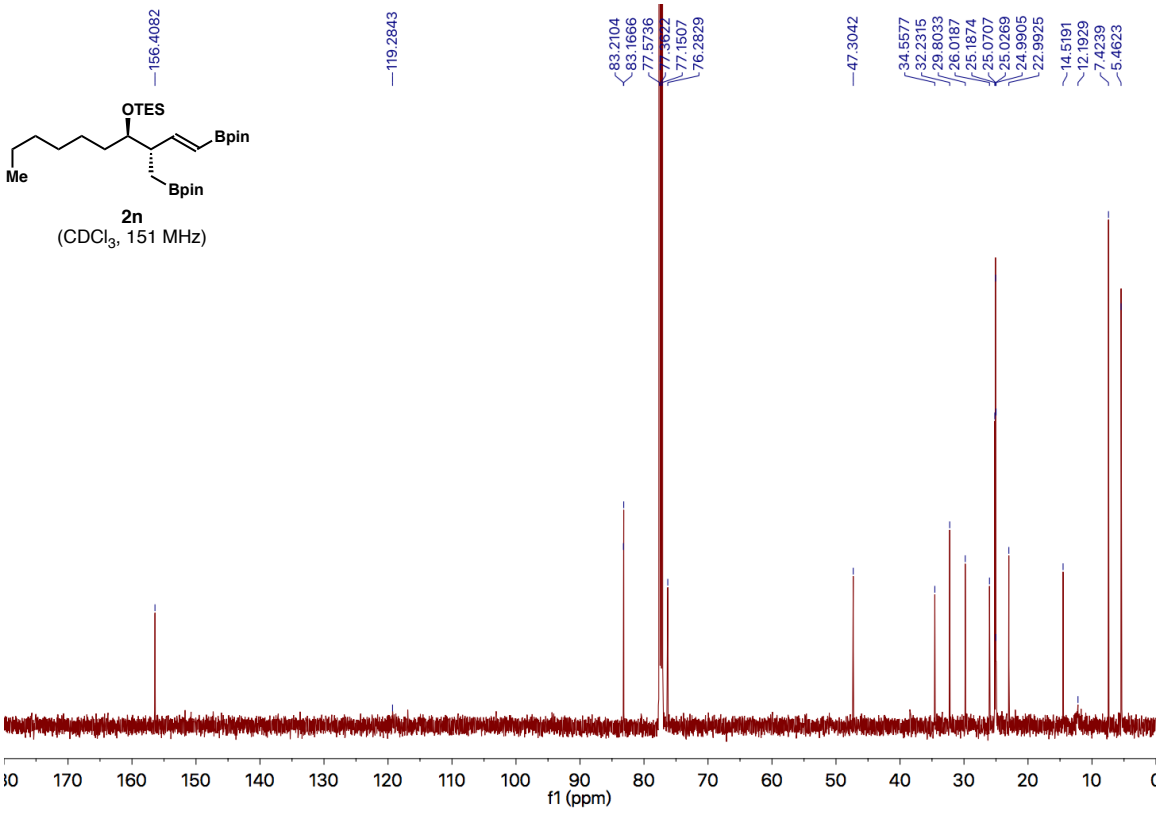

OTES
Bpin
Bpin
S
2l
(CDCl3, 600 MHz)
f1 (ppm)

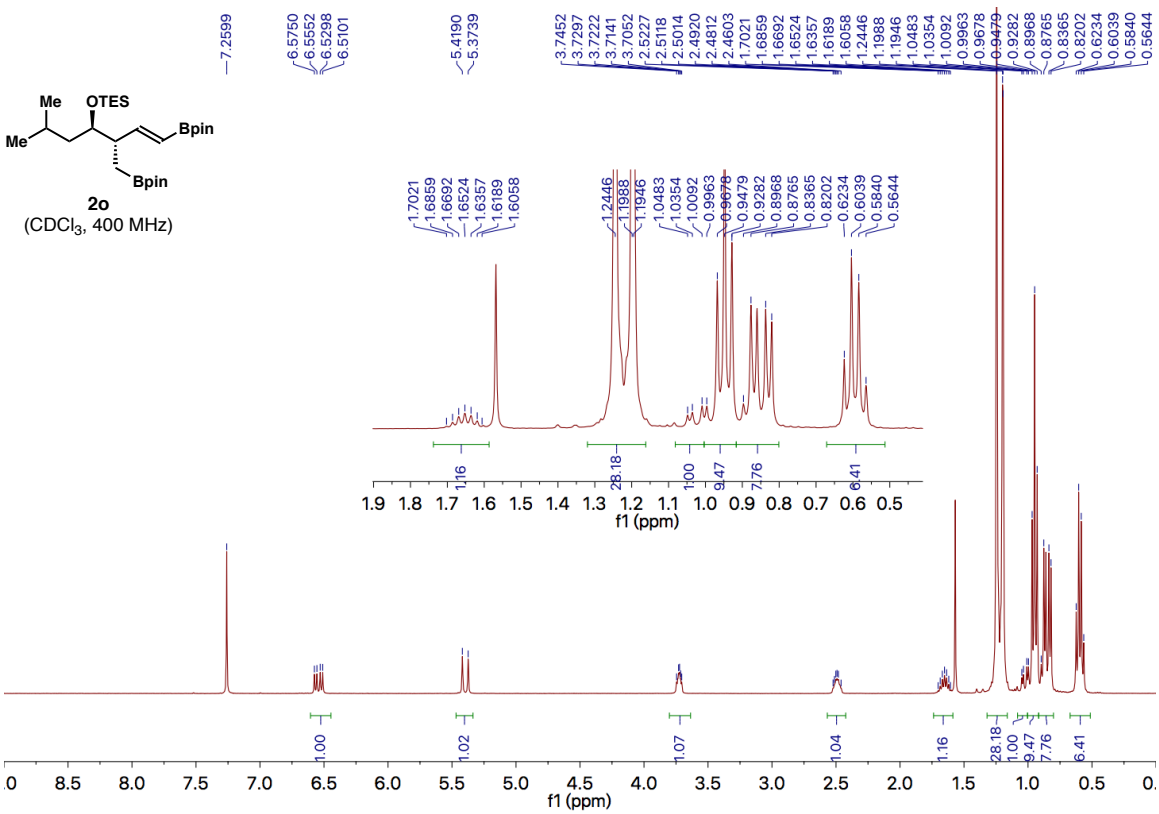

OTES
Bpin
Bpin
S
2l
(CDCl3, 151 MHz)
f1 (ppm)

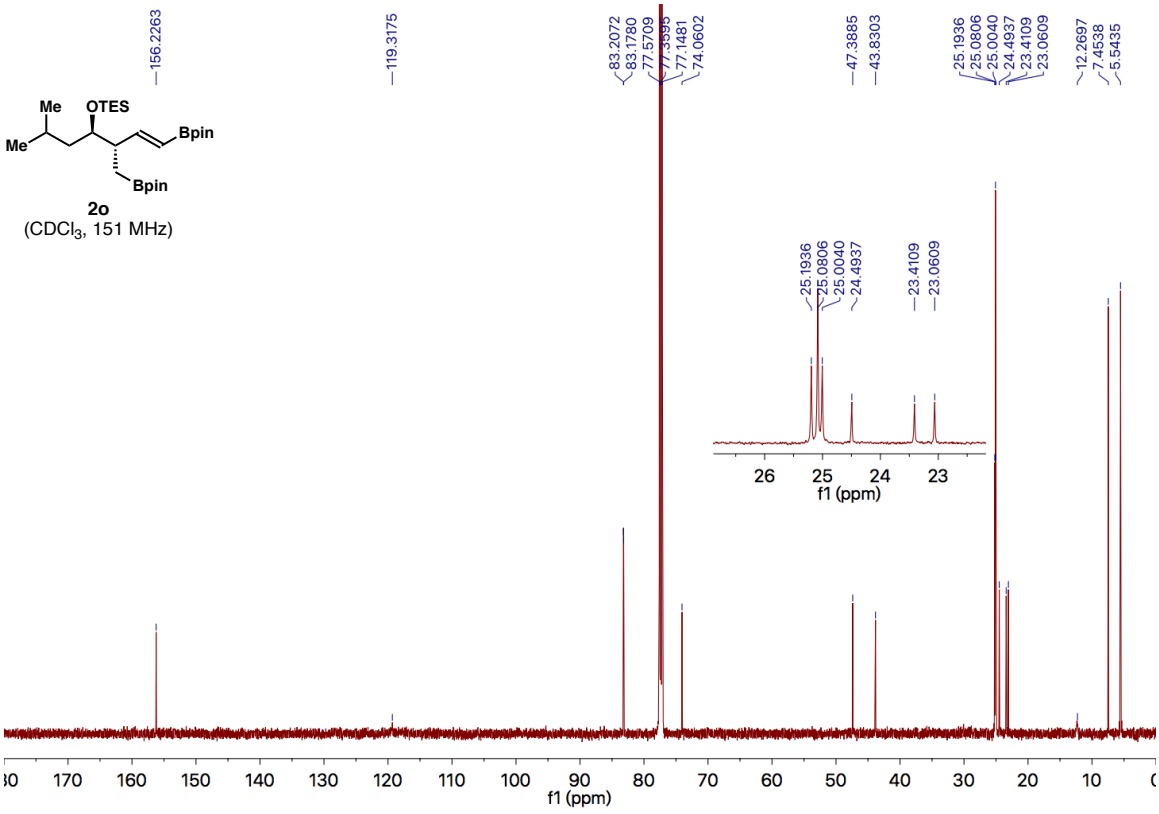

OTES
Bpin
Bpin
O
2m
(CDCl3, 600 MHz)
f1 (ppm)

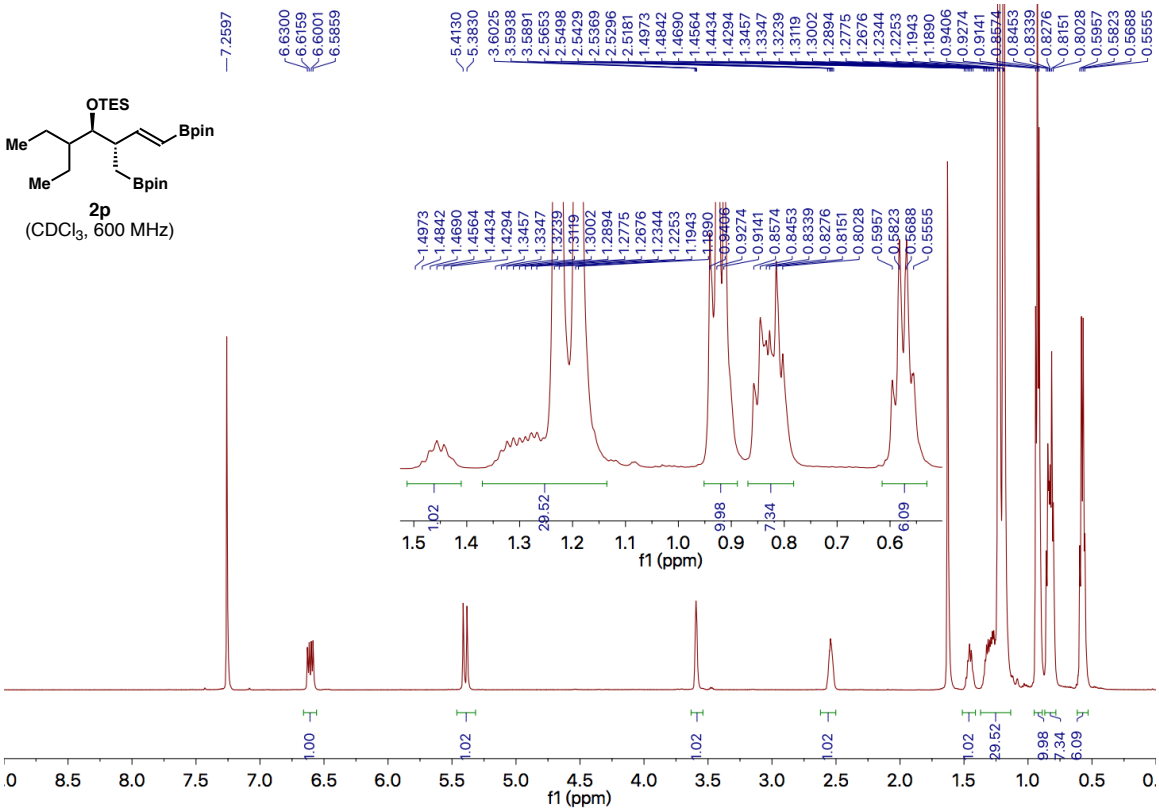

OTES
Bpin
Bpin
O
2m
(CDCl3, 151 MHz)
f1 (ppm)

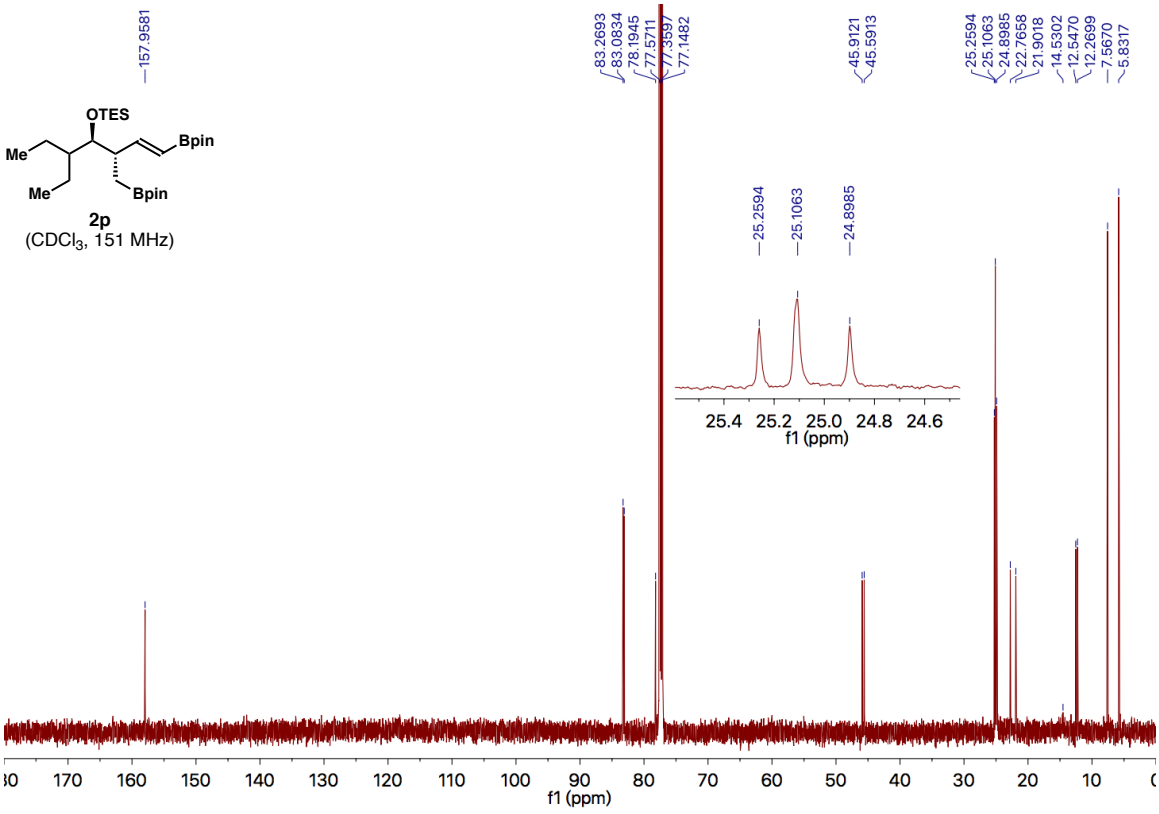

OTES
Bpin
Me
Bpin
2n
(CDCl3, 400 MHz)
f1 (ppm)

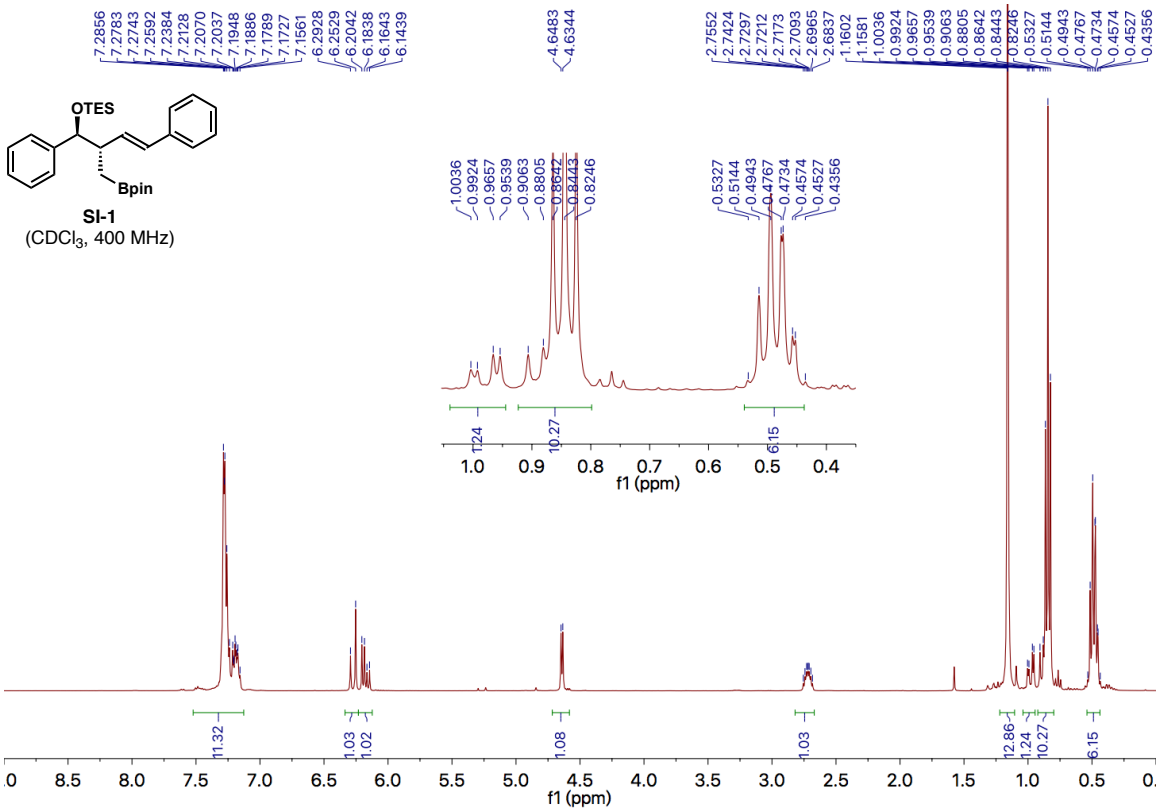

OTES
Bpin
Me
Bpin
2n
(CDCl3, 151 MHz)
f1 (ppm)

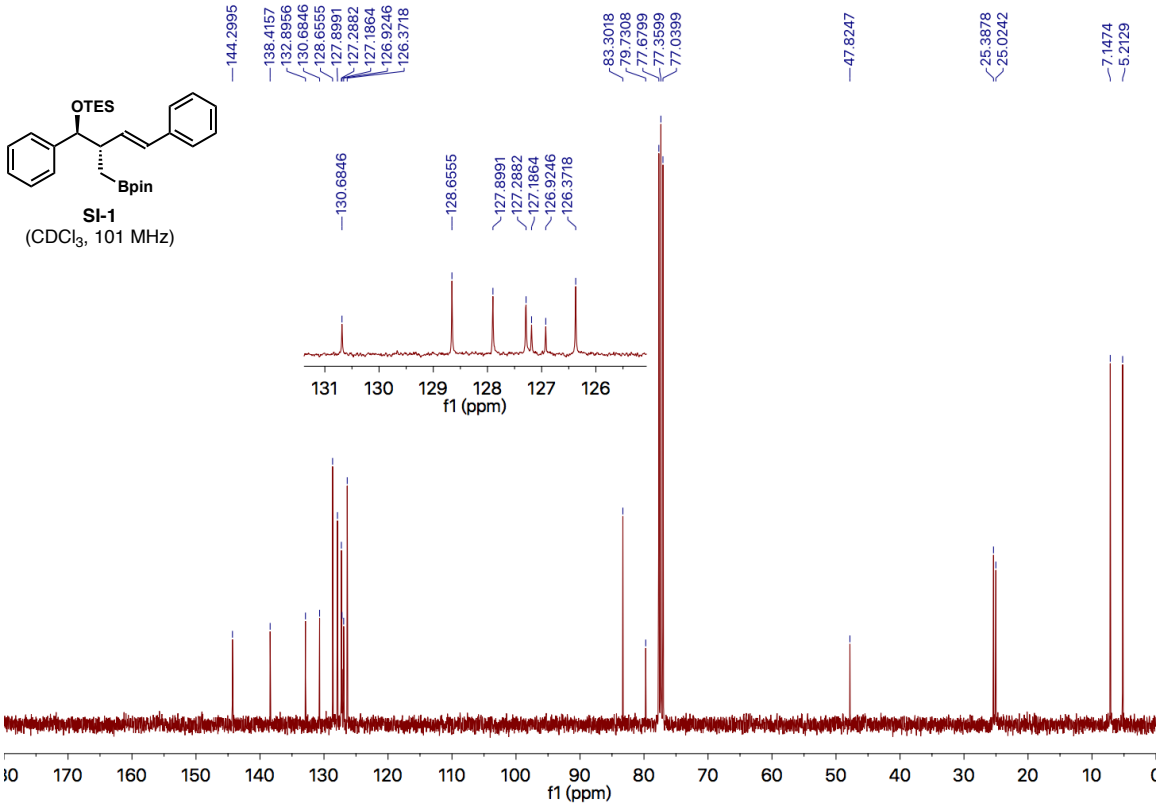

Me
OTES
Me
Bpin
Bpin
2o
(CDCl3, 400 MHz)
f1 (ppm)

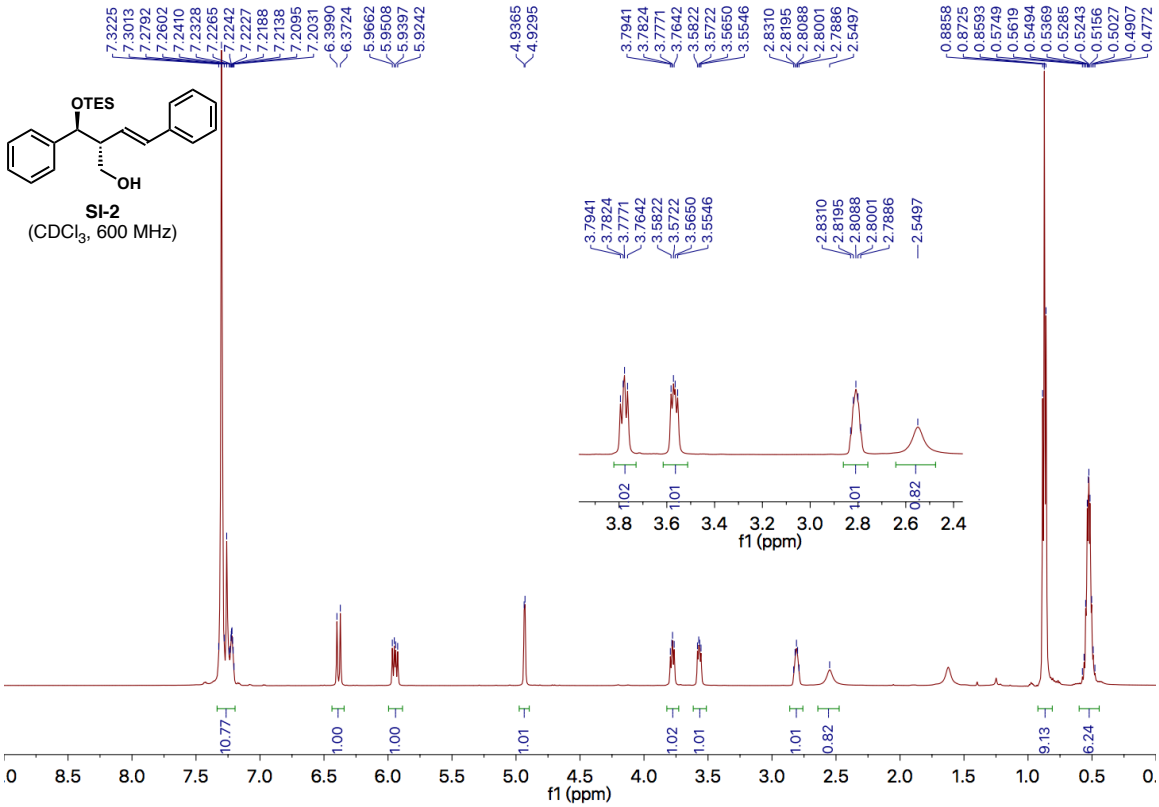

Me
OTES
Me
Bpin
Bpin
2o
(CDCl3, 151 MHz)
f1 (ppm)

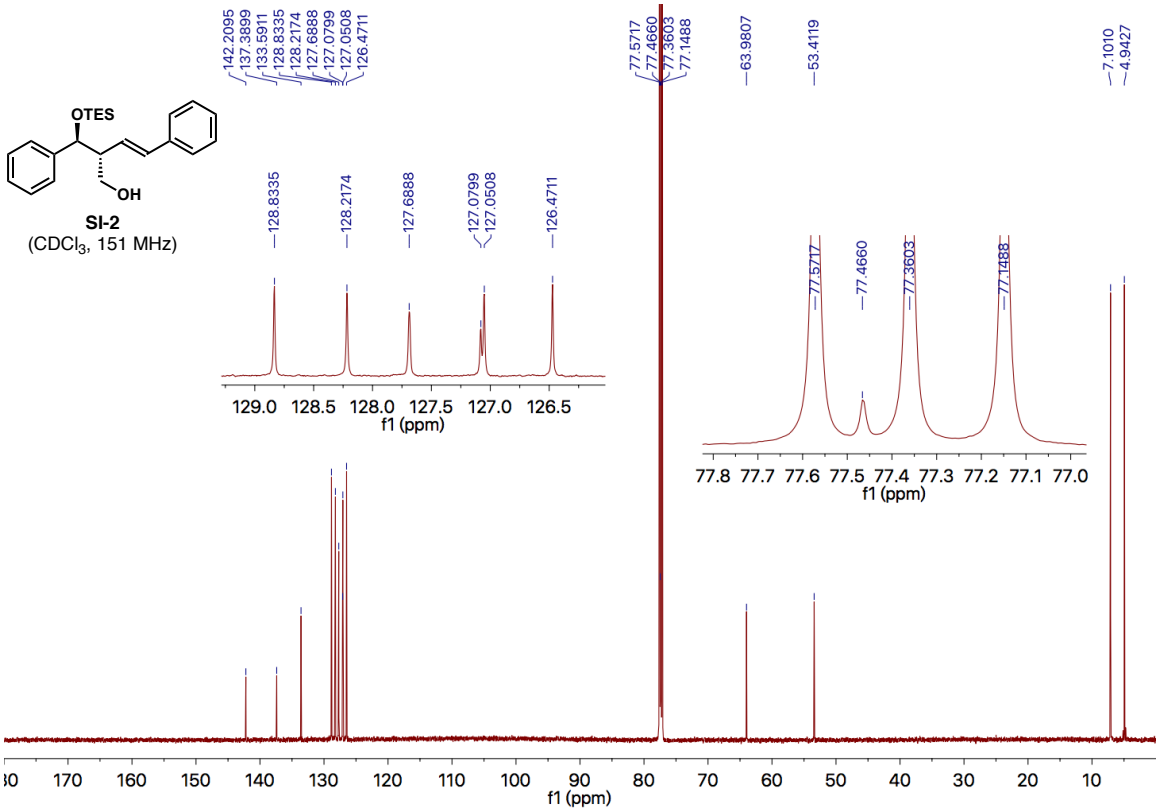

OTES
Me
Me
Bpin
Bpin
2p
(CDCl3, 600 MHz)
f1 (ppm)

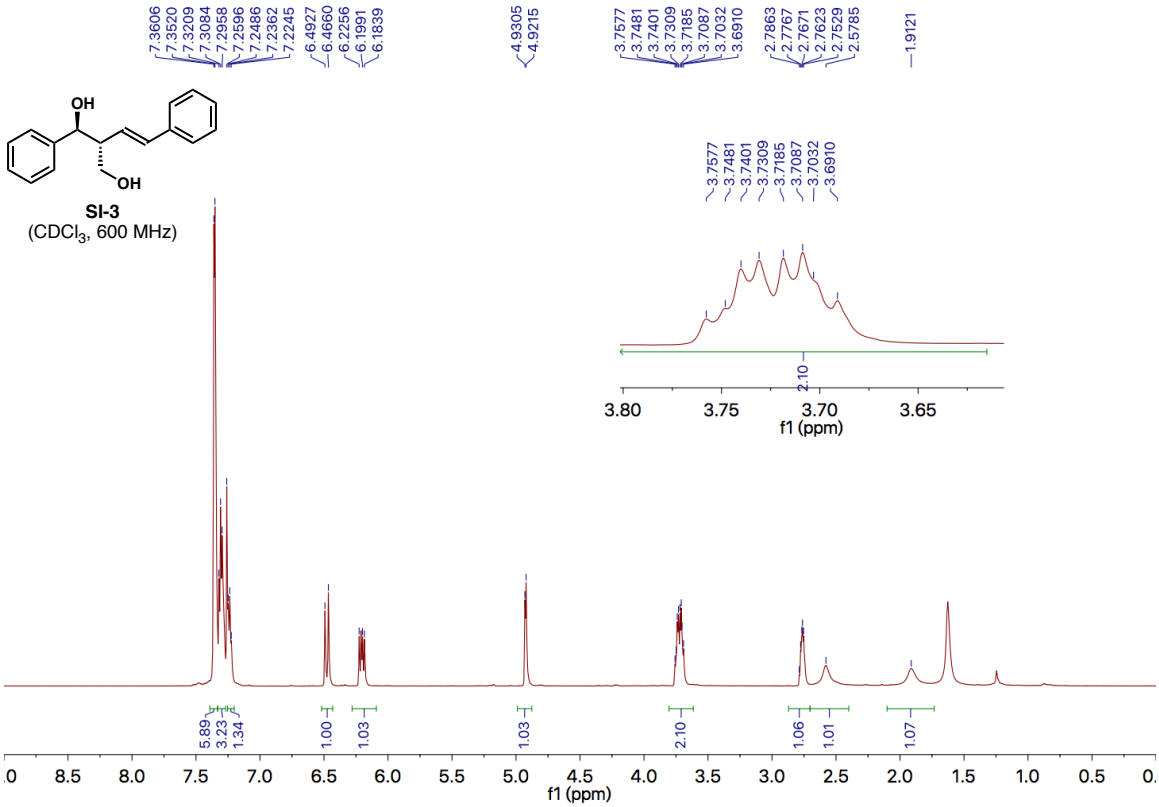

OTES
Me
Me
Bpin
Bpin
2p
(CDCl3, 151 MHz)
f1 (ppm)

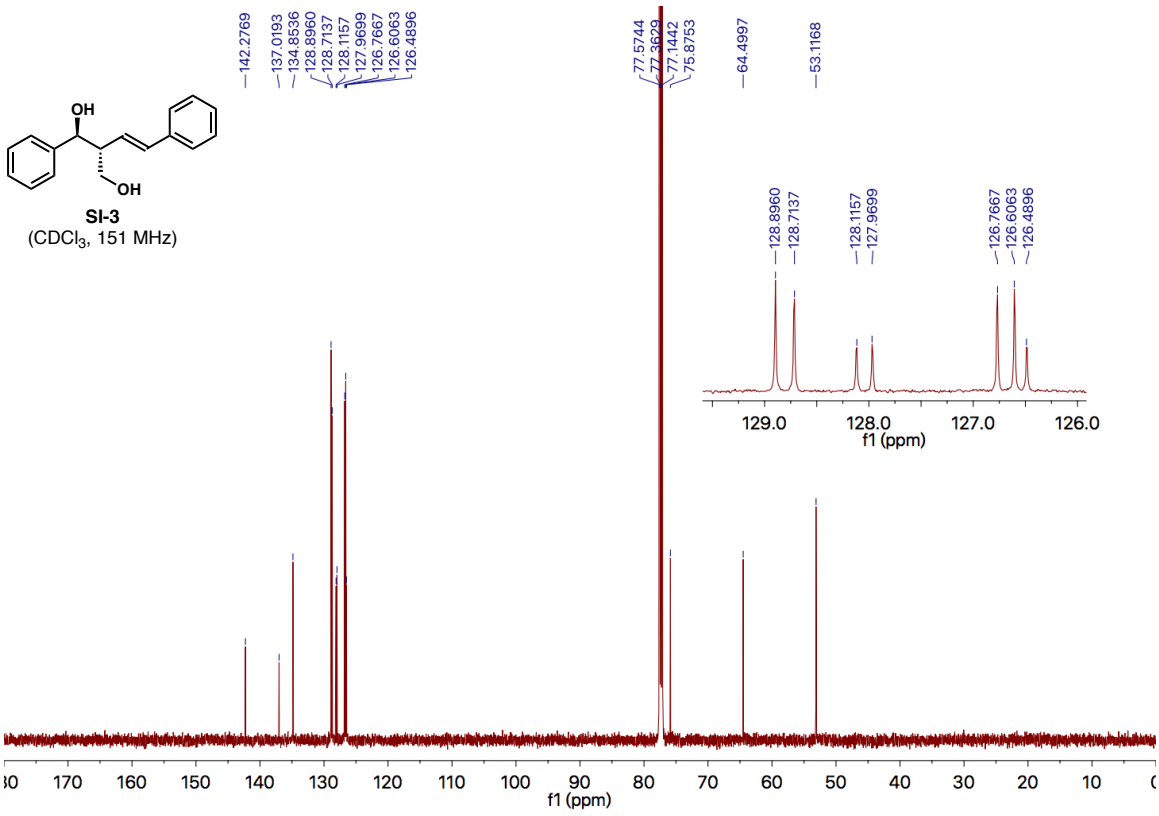

OTES
Bpin
SI-1
(CDCl3, 400 MHz)
f1 (ppm)

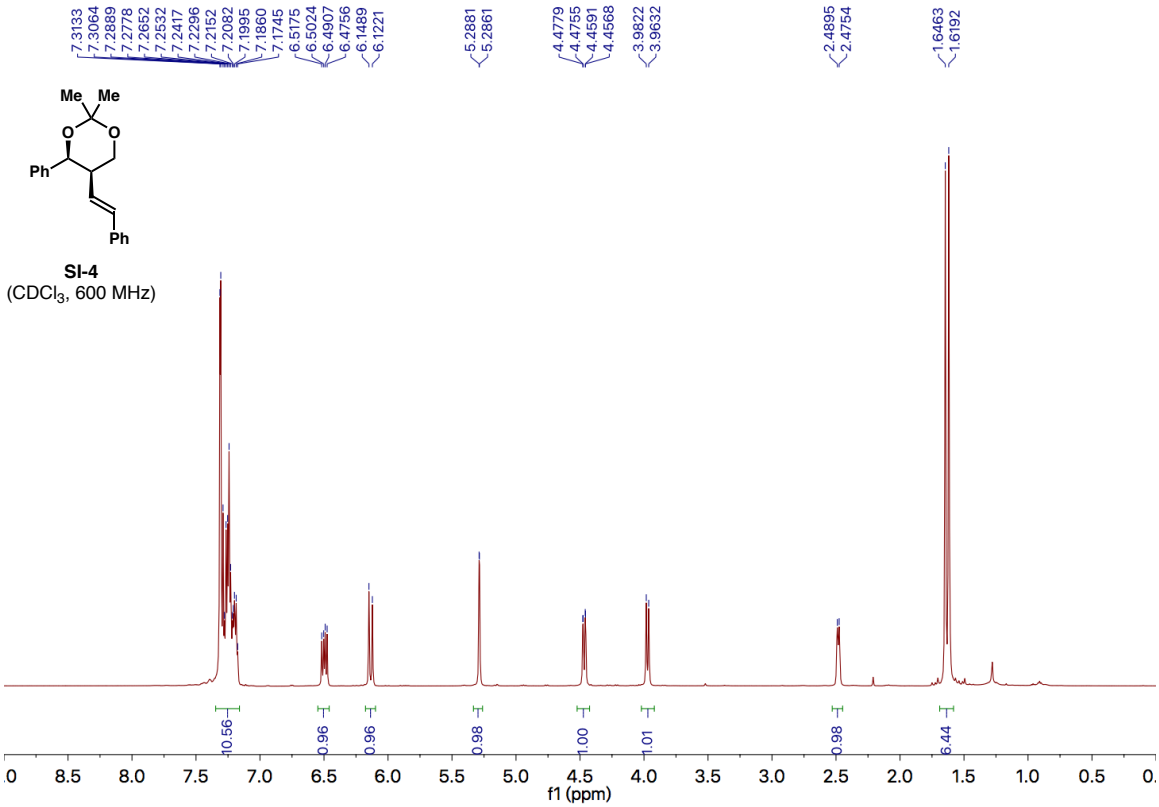

OTES
Bpin
SI-1
(CDCl3, 101 MHz)
f1 (ppm)


OTES
OH
SI-2
(CDCl3, 600 MHz)
f1 (ppm)

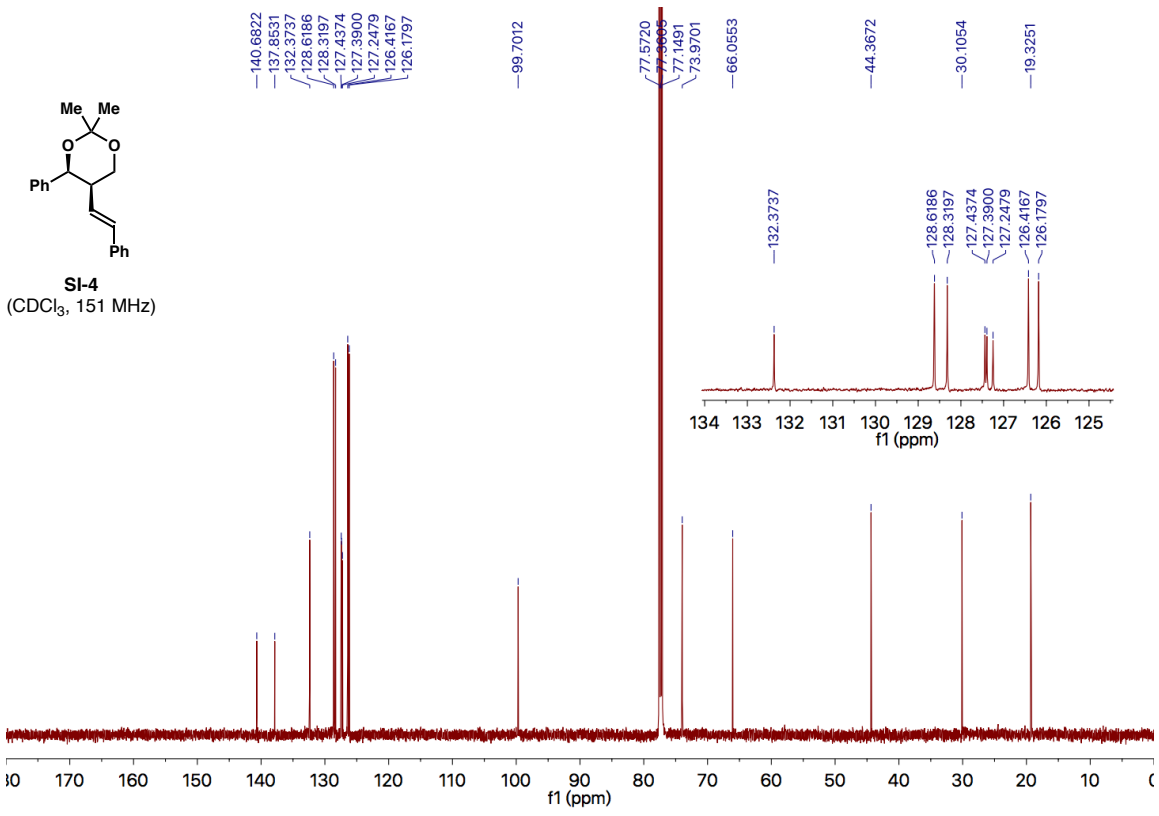

OTES
OH
SI-2
(CDCl3, 151 MHz)
f1 (ppm)


SI-3
(CDCl3, 600 MHz)
f1 (ppm)

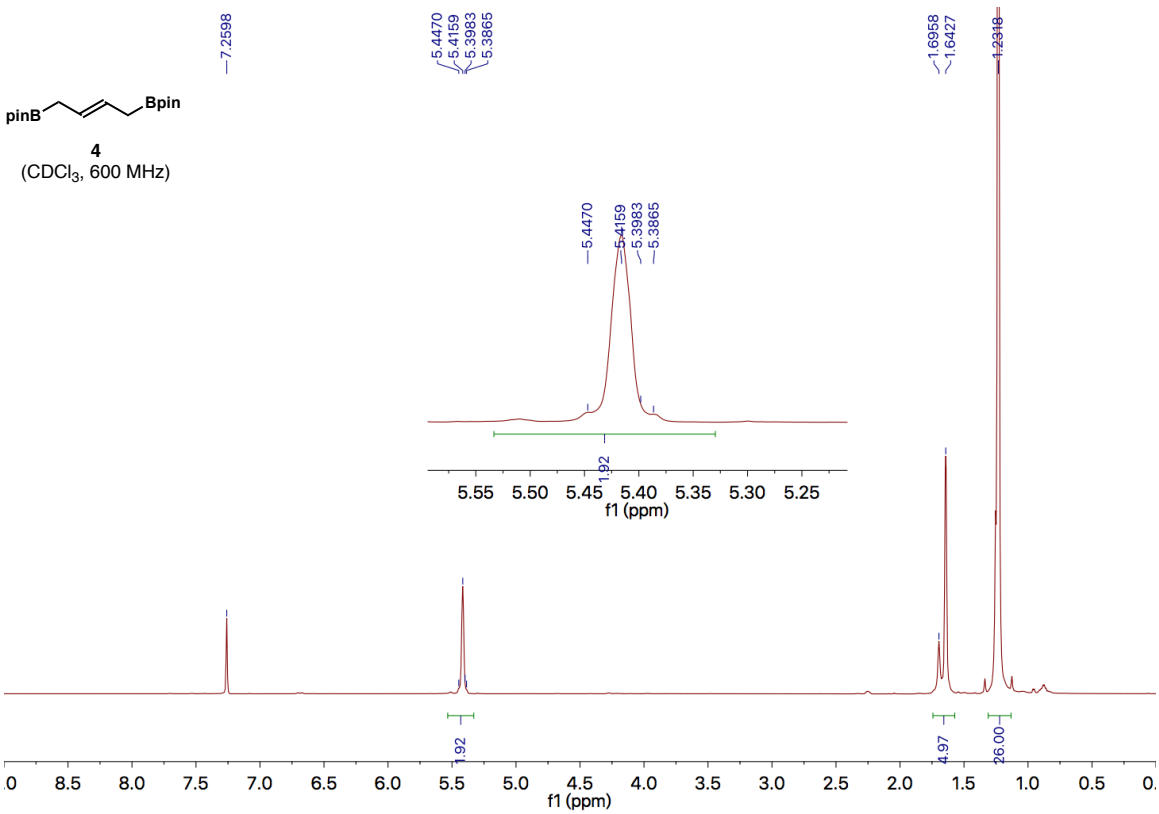

SI-3
(CDCl3, 151 MHz)
f1 (ppm)

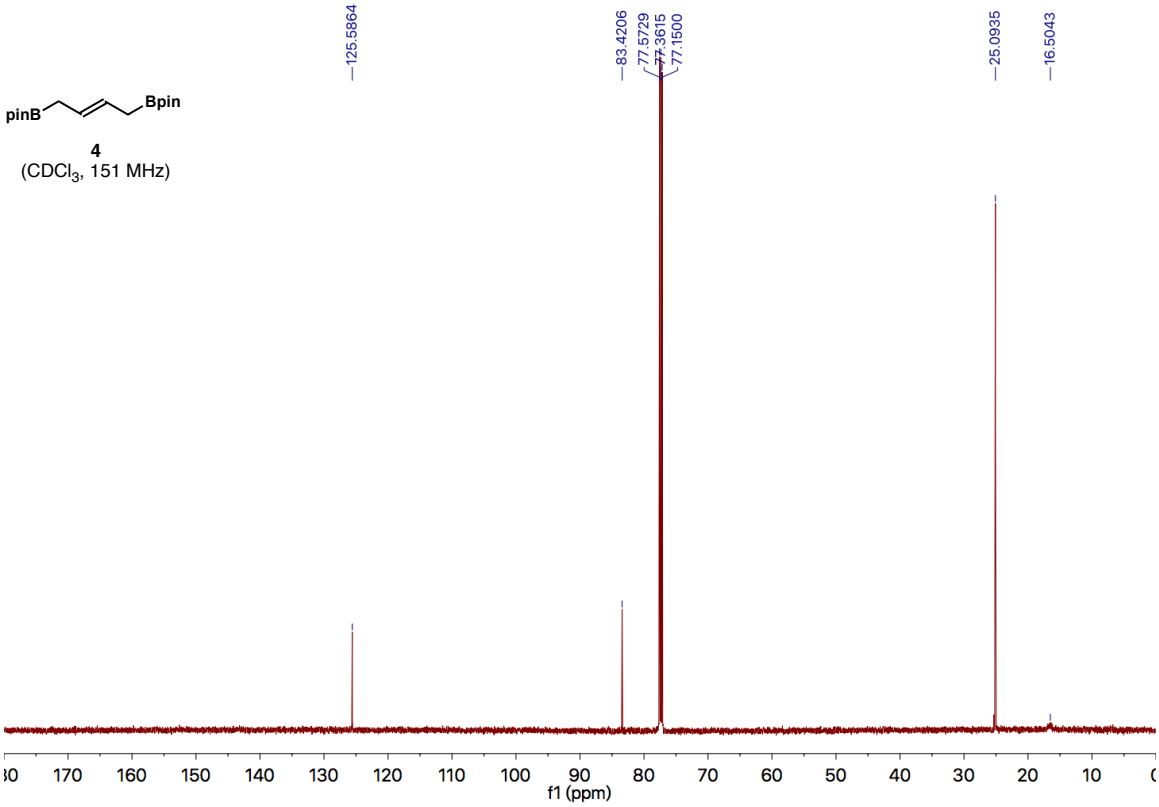


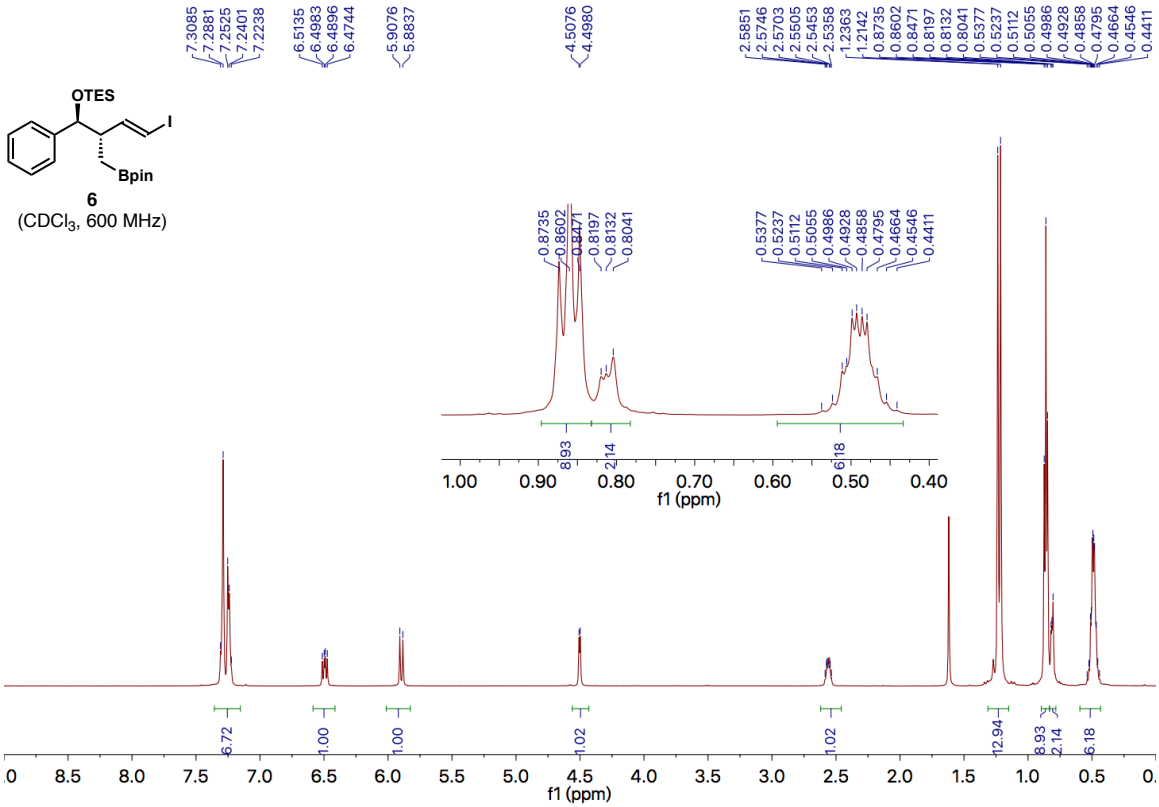
SI-4
($CDCl_3$, 600 MHz)

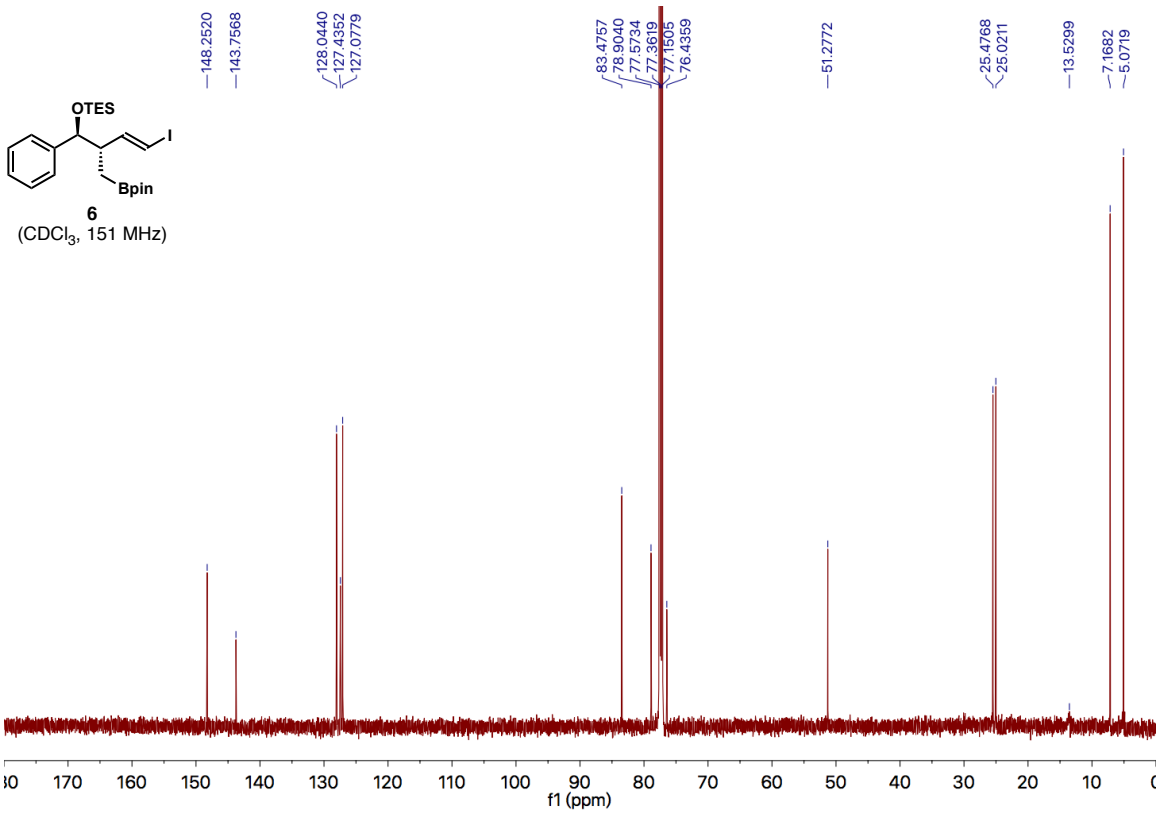


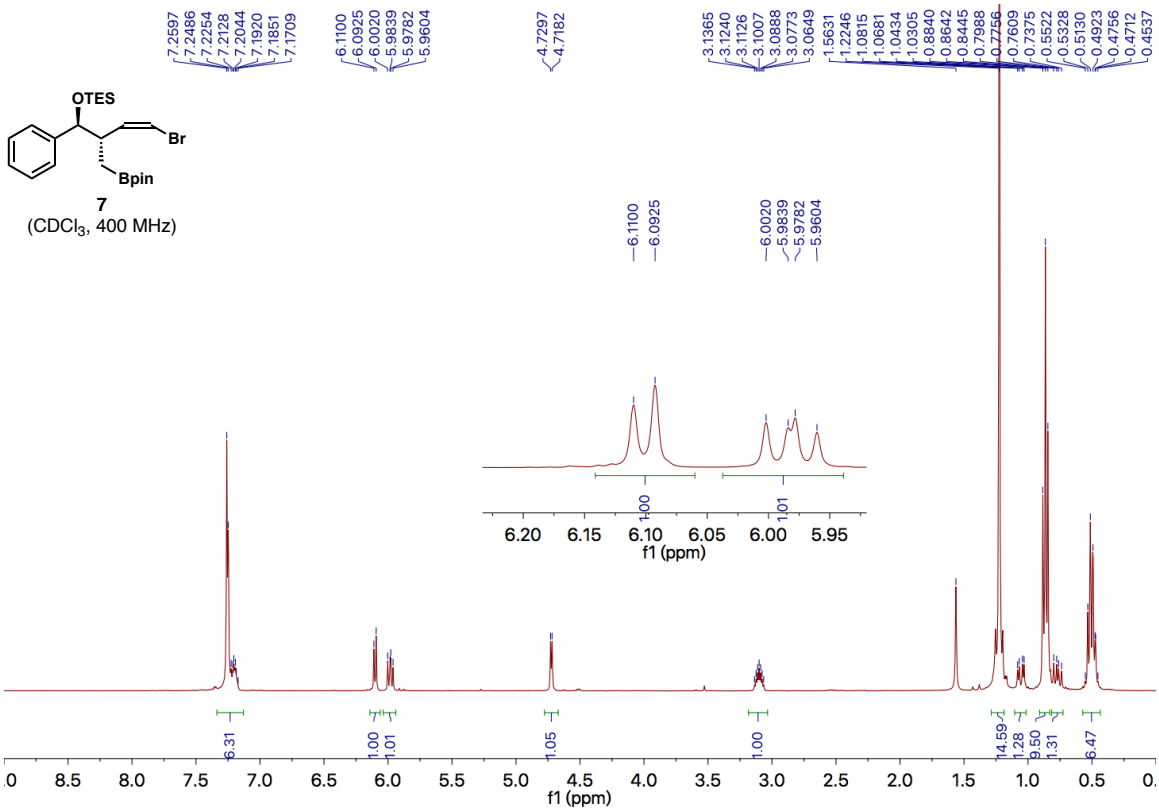
SI-4
($CDCl_3$, 151 MHz)

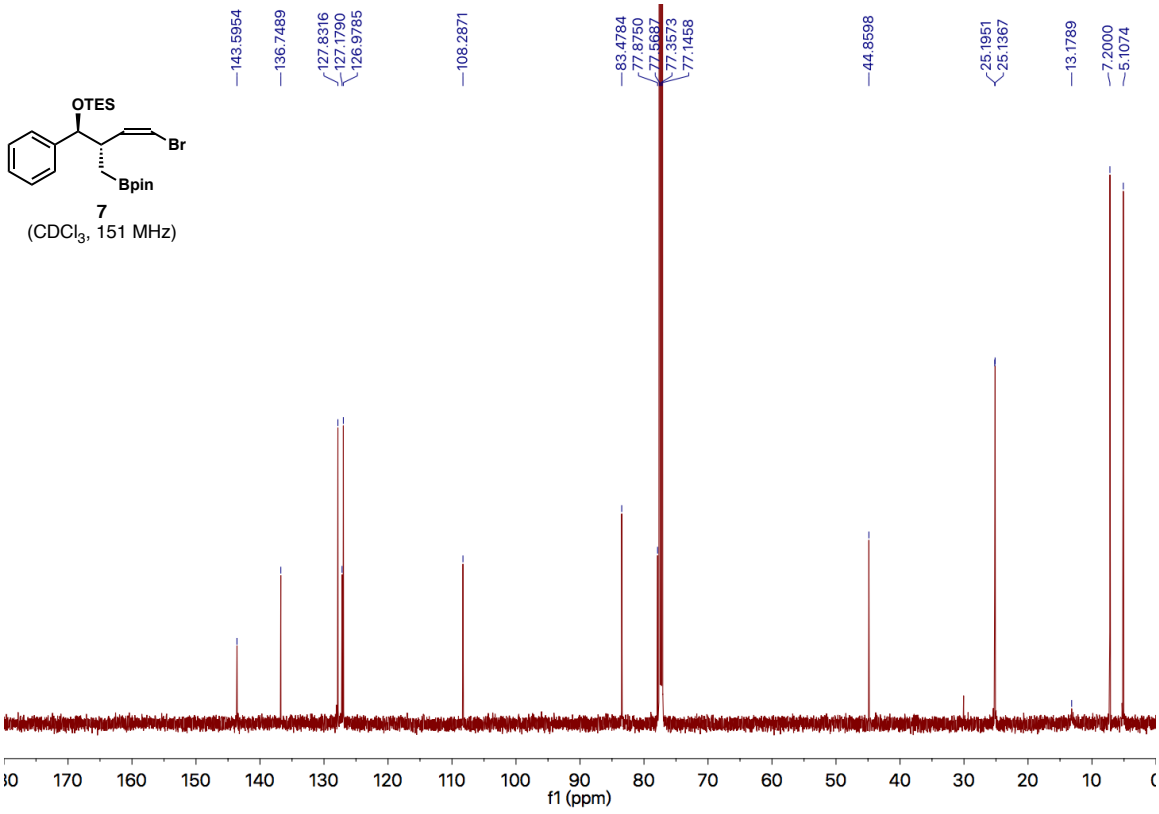

pinB
Bpin
4
(CDCl3, 600 MHz)
7.2598
5.4470
5.4159
5.3983
5.3865
1.6958
1.6427
1.2310
1.92
4.97
26.00
f1 (ppm)

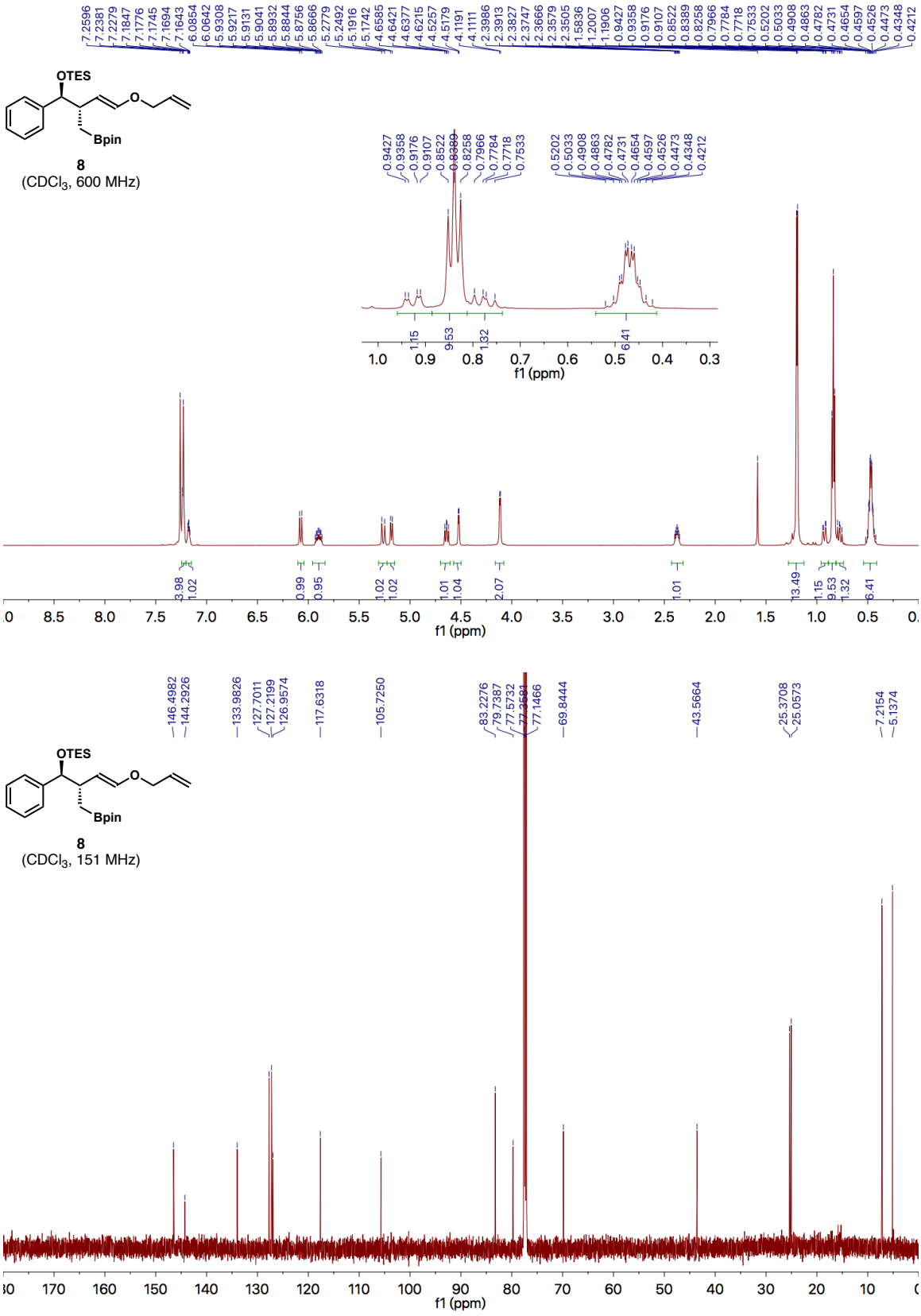

pinB
Bpin
4
(CDCl3, 151 MHz)
125.5864
83.4206
77.5729
77.3615
77.1500
25.0935
16.5043
f1 (ppm)

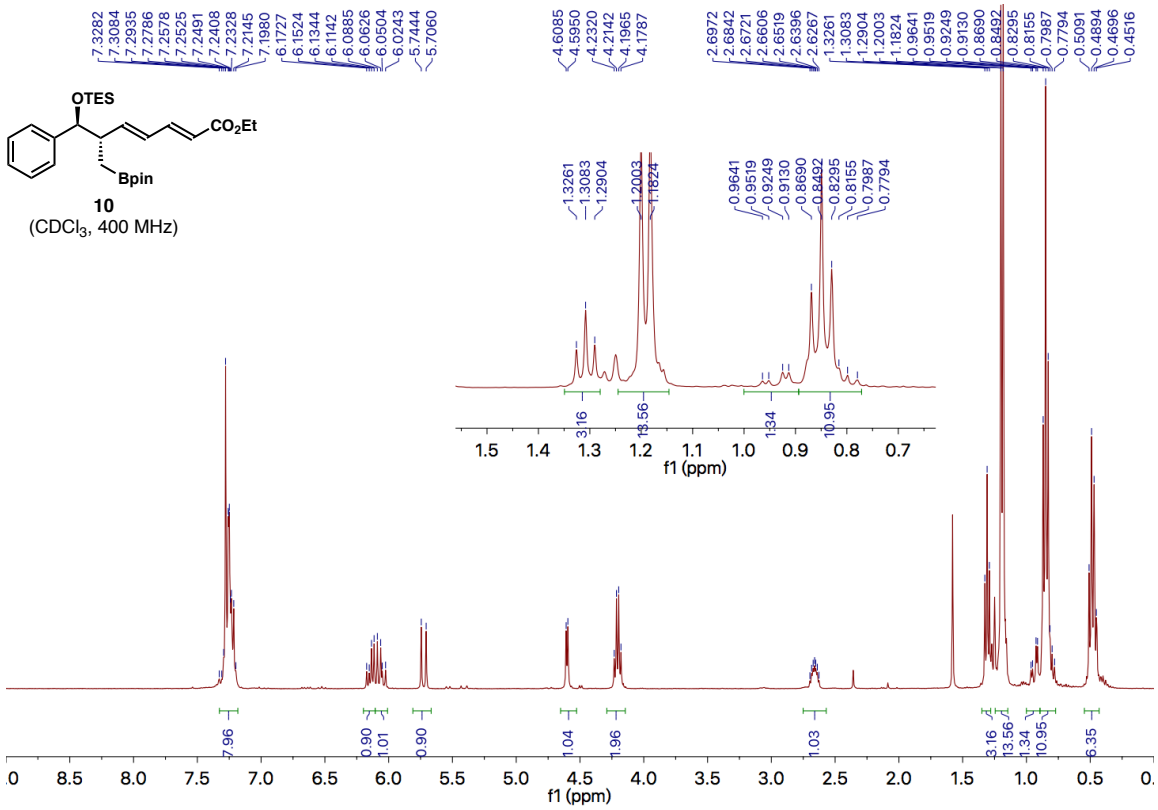

OTES
I
Bpin
6
(CDCl3, 600 MHz)
f1 (ppm)

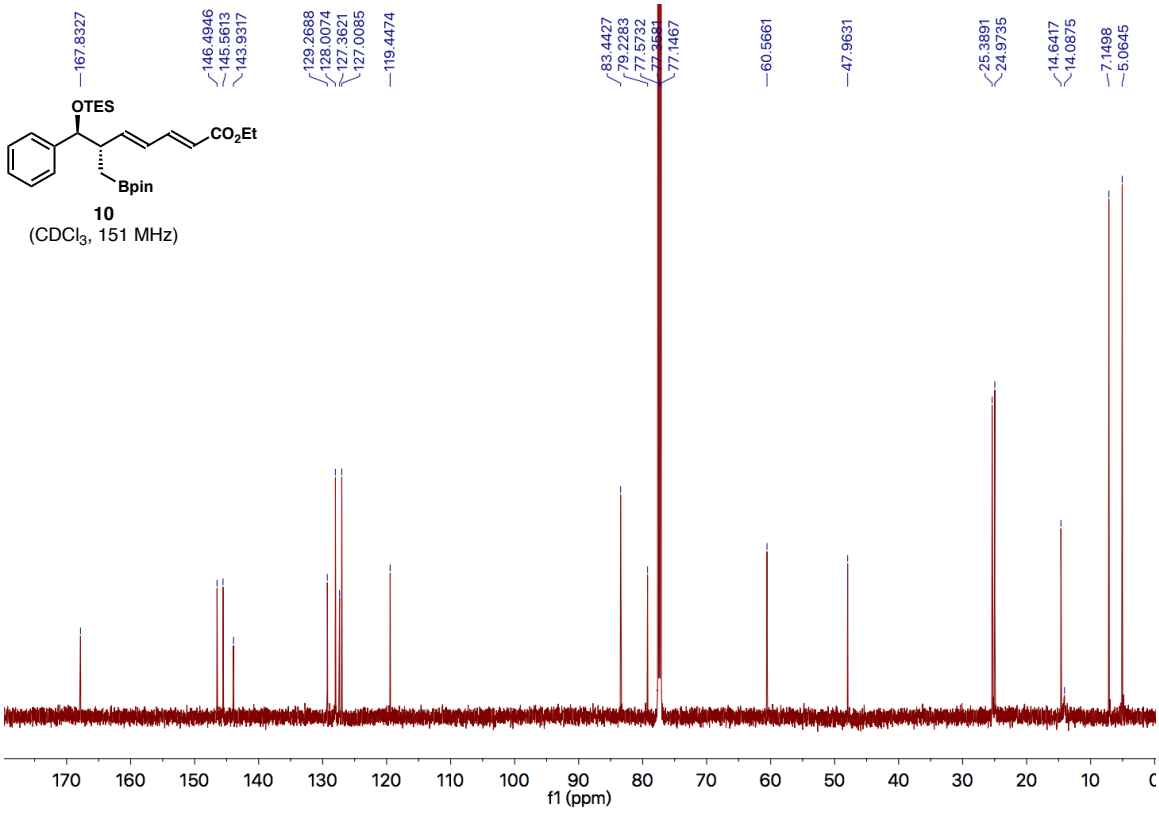

OTES
I
Bpin
6
(CDCl3, 151 MHz)
f1 (ppm)

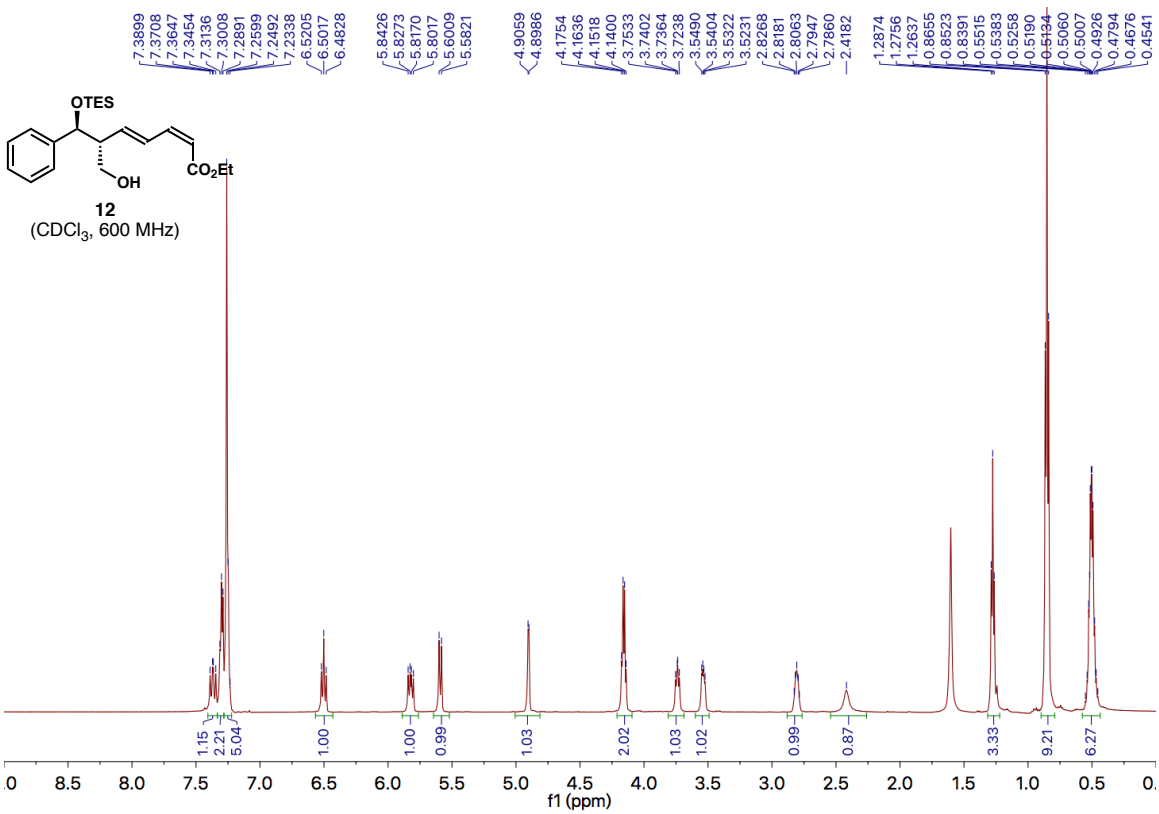

OTES
Br
Bpin
7
(CDCl3, 400 MHz)
f1 (ppm)

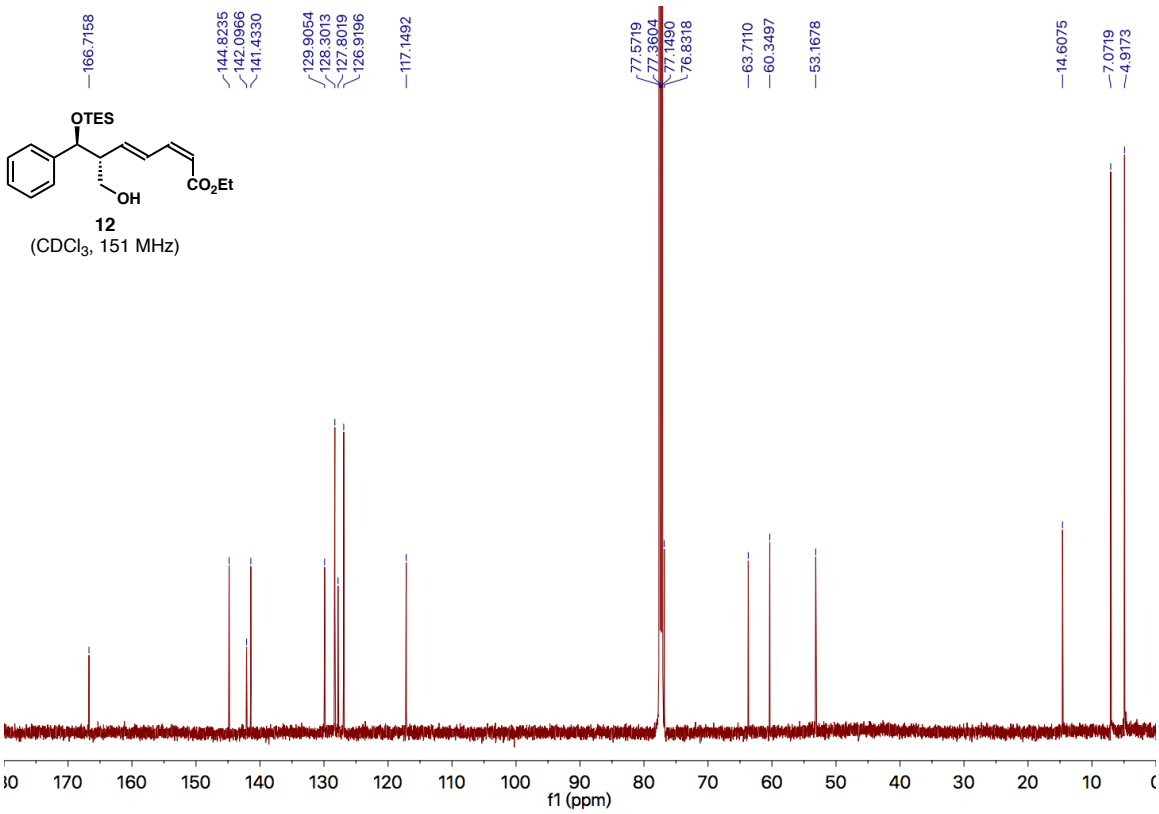

OTES
Br
Bpin
7
(CDCl3, 151 MHz)
f1 (ppm)


OTES
O
Bpin
8
(CDCl3, 600 MHz)
f1 (ppm)
OTES
O
Bpin
8
(CDCl3, 151 MHz)
f1 (ppm)


OTES
CO2Et
Bpin
10
(CDCl3, 400 MHz)
f1 (ppm)


OTES
CO2Et
Bpin
10
(CDCl3, 151 MHz)
f1 (ppm)


OTES
OH
CO2Et
12
(CDCl3, 600 MHz)
f1 (ppm)


OTES
OH
CO2Et
12
(CDCl3, 151 MHz)
f1 (ppm)