Supporting Information

An Efficient Method for Constructing C3-Stannyl-Tetrahydroquinoline: Cascade Hydroboration and Hydrostannation of Quinoline

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1. Materials, Reagents and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or an argon-filled glovebox. Hexane was refluxed over sodium/potassium alloy distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. Benzene-d_6 or benzene was dried over molecular sieves 4 Å. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C; 471 MHz, ^{19}F) instrument at room temperature (RT). Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and reported as parts per million relative to $SiMe_4$, whereas ^{19}F NMR spectra was referenced to external $CFCl_3$. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes. It should be noted that all new compounds reported in the manuscript were characterized by ^{1}H, ^{13}C spectroscopy without HRMS or elemental analyses, due to their extreme sensitivity to air and moisture.

Quinoline, 2-methylquinoline, 3-methylquinoline, 4-methylquinoline, 5-methylquinoline, 6-methylquinoline, 7-methylquinoline, 8-methylquinoline, 5-bromoquinoline, 6-bromoquinoline, 6-fluoroquinoline, 6-chloroquinoline, 6-methoxyquinoline, 6-iodoquinoline, 6-bromo-5,7-difluoroquinoline, 7-chloroquinoline, 8-fluoroquinoline, 8-chloroquinoline, 8-bromoquinoline, pinacolboane (HBpin) were purchased from Energy Chemical, Catecholborane (HBcat) was purchased from Adamas-beta®, and freshly distilled prior to use, tri-n-butyltin hydride ((^{n}Bu)$_3$SnH) was purchased from TCI and freshly distilled prior to use, All chemicals were used as received unless otherwise specified. $B(C_6F_5)_3$ was prepared according to literature procedures.[1] (^{n}Bu)$_3$SnD was prepared according to literature procedures.[2]

General procedures for the reaction

1. General procedures for the reaction

In a glove box, $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg) was added to a solution containing catecholborane or pinacolborane (HBcat or HBpin) (0.1 mmol, 12.0 or 12.8 mg), $(^nBu)_3SnH$ (0.1 mmol, 29.1 mg) and mesitylene (0.1 mmol, 12.0 mg) in 0.6 mL C_6D_6 in NMR tube, then quinoline (0.1 mmol) was added to the resulting mixture. It was measured by ^1H NMR spectroscopy after 2 h at RT. Using micro vacuum distillation device to remove by-products or substrates quickly (70°C, 500 mTorr, on the outside). Move the device into the glove box, the reaction mixture was added with 0.5 mL hexane and then put in a refrigerator at -35°C for 24 h. The up-layer of hexane was collected and dried in vacuo to afford the final product.

2. Procedures for the gram reaction

In a glove box, $B(C_6F_5)_3$ (0.1 mmol, 51.2 mg) was added to a solution containing HBpin (21 mmol, 2.7 g) and $(^nBu)_3SnH$ (21 mmol, 6.1 g) in 5 mL C_6H_6 in NMR tube, then quinoline **1a** (20 mmol, 2.6 g) was added to the resulting mixture. It was measured by ^1H NMR spectroscopy after 24 h or 72 h at RT. Using vacuum distillation device to remove by-products or substrates quickly (70°C, 500 mTorr, on the outside). Move the device into the glove box, the reaction mixture was added with 20 mL hexane and then put in a refrigerator at -35°C for 24 h. The up-layer of hexane was collected and dried in vacuo to afford the product (**11a**, isolated yield: 89%).

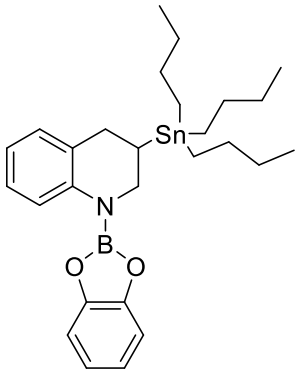
3. Procedures for the post-modification

1) Procedures for **12** (Known compound).[3] Methanol was added to **11a** (1 mmol, 550 mg), and the solvent was removed using a vacuum pump. The aluminum oxide was then loaded into a column, and the first eluted fraction using hexane was identified as the pure product, a pale yellow liquid labeled as 3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline, with a yield of 65%. Subsequently, 0.2 mmol of the 3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline was taken, and 0.2 mmol of $AlCl_3$ and 0.2 mmol of BrCN were added at 0°C. The reaction mixture was then allowed to react at room temperature for 12 h. Purification was carried out using silica gel column chromatography. It is worth noting that the byproduct $(^nBu)_3SnCl$ was difficult to separate from the product.

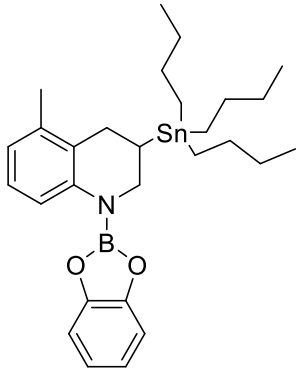
Ultimately, the yield of this step was determined through NMR analysis after separation, and the overall yield for the two steps is 33%.

2) Procedures for **13** (Known compound).[4,5] Dissolve 3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (1 mmol, 422 mg) in a Schlenk bottle containing 20 mL of DMF. Add anhydrous potassium carbonate (3 mmol, 414 mg) at 0°C, and slowly raise the temperature to room temperature. Adding benzyl bromide (1.5 mmol, 256.5 mg) and reaction for 12 h. Quench the reaction by adding water, extract with ether (using small volumes multiple times), dry the extract over anhydrous magnesium sulfate, and purify by column chromatography using hexane as the eluent, the yield of 1-benzyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline is 85%. Subsequently, 0.2 mmol of the 1-benzyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline was taken, and 0.2 mmol of $AlCl_3$ and 0.2 mmol of BrCN were added at 0°C. The reaction mixture was then allowed to react at room temperature for 12 h. Purification was carried out using silica gel column chromatography and obtained product **13**. The overall yield for the three steps is 28%.

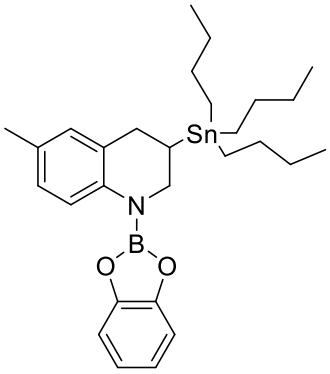
2. Characterization data



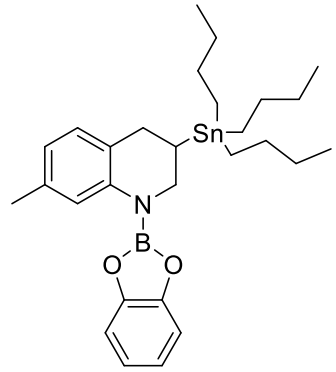
1-(benzo[d][1,3,2]dioxaborol-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10a**) colorless sticky oil (90%); ^{1}H NMR (500 MHz, C_6D_6) δ 8.02 (d, J = 5.0 Hz, 1H, HAr), 7.16 (t, J = 10.0 Hz, 1H, HAr), 6.96 – 7.03 (m, 3H, HAr), 6.88 (t, J = 10.0 Hz, 1H, HAr), 6.75 – 6.79 (m, 2H, HAr), 3.97 – 4.10 (m, 1H, CH_2), 3.62 – 3.70 (m, 1H, CH_2), 2.85 – 3.03 (m, 2H, CH_2), 1.64 – 1.68 (m, 1H, CH), 1.45 – 1.51 (m, 6H, CH_2), 1.27 – 1.35 (m, 6H, CH_2), 0.89 (t, J = 10.0 Hz, 9H, CH_3), 0.84 – 0.87 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 148.5, 141.2, 137.2, 129.2, 126.6, 122.0, 121.5, 120.5, 111.6, 48.7, 32.8, 29.3, 27.5, 21.0, 13.6, 8.1.



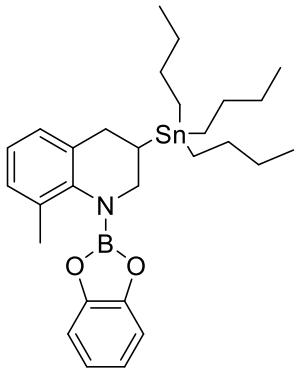
1-(benzo[d][1,3,2]dioxaborol-2-yl)-5-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10e**) brown sticky oil (86%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.90 (d, J = 5.0 Hz, 1H, HAr), 7.14 (t, J = 5.0 Hz, 1H, HAr), 6.99 – 7.02 (m, 2H, HAr), 6.80 (d, J = 10.0 Hz, 1H, HAr), 6.75 – 6.79 (m, 2H, HAr), 4.04 – 4.07 (m, 1H, CH_2), 3.62 – 3.66 (m, 1H, CH_2), 2.72 – 2.87 (m, 2H, CH_2), 2.09 (s, 3H, CH_3), 1.67 – 1.73 (m, 1H, CH), 1.47 – 1.53 (m, 6H, CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.86 – 0.94 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 141.3, 136.2, 126.1, 125.6, 123.5, 122.0, 118.8, 111.6, 48.1, 29.9, 29.3, 27.5, 21.5, 19.3, 13.6, 8.1.



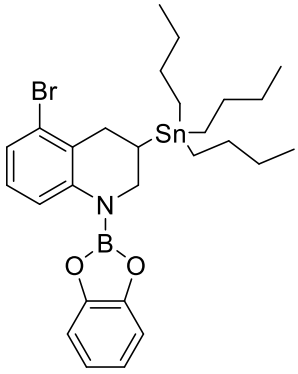
1-(benzo[d][1,3,2]dioxaborol-2-yl)-6-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10f**) colorless sticky oil (83%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.95 (d, J = 10.0 Hz, 1H, HAr), 6.95 – 7.04 (m, 3H, HAr), 6.72 – 6.78 (m, 3H, HAr), 3.97 – 4.10 (m, 1H, CH_2), 3.66 – 3.73 (m, 1H, CH_2), 2.85 – 3.13 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 1.66 – 1.72 (m, 1H, CH), 1.46 – 1.54 (m, 6H, CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.85 – 0.96 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 138.7, 130.4, 129.8, 127.3, 126.7, 121.9, 120.3, 111.6, 48.7, 32.7, 29.3, 27.6, 21.2, 20.3, 13.5, 8.1.



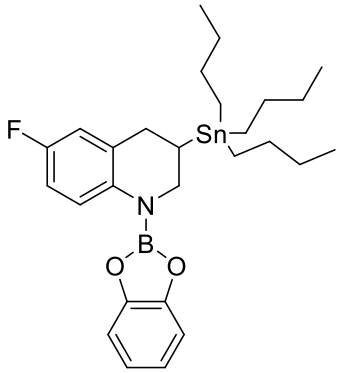
1-(benzo[d][1,3,2]dioxaborol-2-yl)-7-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10g**) colorless sticky oil (81%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (s, 1H, HAr), 6.99 – 7.01 (m, 2H, HAr), 6.91 – 6.93 (d, J = 10.0 Hz, 1H, HAr), 6.74 – 6.77 (m, 3H, HAr), 3.99 – 4.13 (m, 1H, CH_2), 3.63 – 3.76 (m, 1H, CH_2), 2.84 – 3.07 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.65 – 1.71 (m, 1H, CH), 1.44 – 1.53 (m, 6H, CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.80 – 0.99 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 148.5, 141.0, 135.9, 129.2, 124.1, 122.5, 122.0, 120.9, 111.6, 48.8, 32.4, 29.4, 29.3, 27.5, 21.3, 13.5, 8.1.



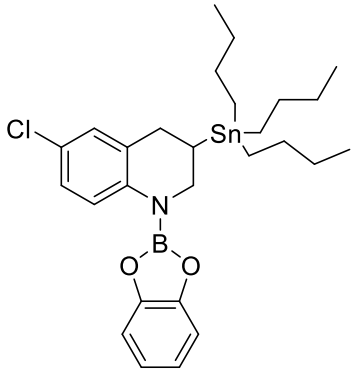
1-(benzo[d][1,3,2]dioxaborol-2-yl)-8-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10h**) colorless sticky oil (78%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.08 (d, J = 10.0 Hz, 1H, HAr), 6.95 – 7.00 (m, 3H, HAr), 6.89 (d, J = 10.0 Hz, 1H, HAr), 6.73 – 6.77 (m, 2H, HAr), 3.90 – 4.07 (br, 1H, CH_2), 3.51 – 3.68 (br, 1H, CH_2), 2.72 – 3.91 (m, 2H, CH_2), 2.38 (s, 3H, CH_3), 1.48 – 1.68 (m, 7H, CH, CH_2), 1.31 – 1.40 (m, 6H, CH_2), 0.86 – 0.96 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 149.0, 148.9, 140.7, 131.4, 128.9, 128.8, 125.3, 123.8, 123.7, 121.9, 111.5, 48.7, 31.7, 29.3, 27.5, 22.6, 18.2, 13.6, 8.7, 8.1.



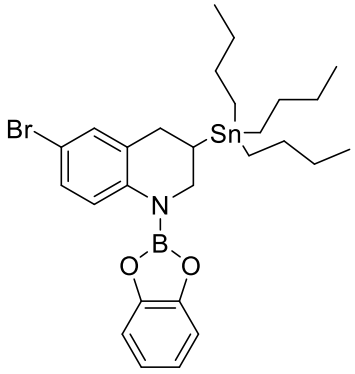
1-(benzo[d][1,3,2]dioxaborol-2-yl)-5-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10i**) yellow sticky soild (79%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.83 (d, J = 10.0 Hz, 1H, HAr), 7.19 (d, J = 10.0 Hz, 1H, HAr), 6.97 – 7.00 (m, 2H, HAr), 6.82 (t, J = 10.0 Hz, 1H, HAr), 6.75 – 6.79 (m, 2H, HAr), 3.96 – 3.99 (m, 1H, CH_2), 3.42– 3.47 (m, 1H, CH_2), 3.10– 3.14 (m, 1H, CH_2), 2.90 – 2.96 (m, 1H, CH_2), 1.40 – 1.60 (m, 7H, CH, CH_2), 1.28 – 1.34 (m, 6H, CH_2), 0.85 – 0.96 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 148.4, 143.2, 127.3, 126.9, 125.8, 125.7, 122.2, 119.8, 111.7, 48.2, 33.8, 29.3, 27.5, 20.9, 13.6, 8.1.



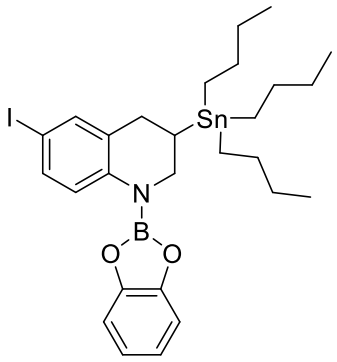
1-(benzo[d][1,3,2]dioxaborol-2-yl)-6-fluoro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10j**) colorless sticky oil (80%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.81 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 6.97 (m, *2*H, HAr), 6.84 (td, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1H, HA), 6.76 – 6.79 (m, 2H, HAr), 6.63 (td, J = 10.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 3.92 – 4.04(m, 1H, CH_2), 3.52– 3.56 (m, 1H, CH_2), 2.70 – 2.82 (m, 2H, CH_2), 1.42 – 1.56 (m, 7H, CH, CH_2), 1.27 – 1.35(m, 6H, CH_2), 0.90 (t, J = 5.0 Hz, 9H, CH_3), 0.82 – 0.86 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 158.9, 157.0, 148.4, 137.1, 128.8, 128.8, 122.1, 121.6, 121.6, 115.3, 113.1, 111.6, 48.5, 32.6, 29.3, 27.5, 20.5, 13.5, 8.1.



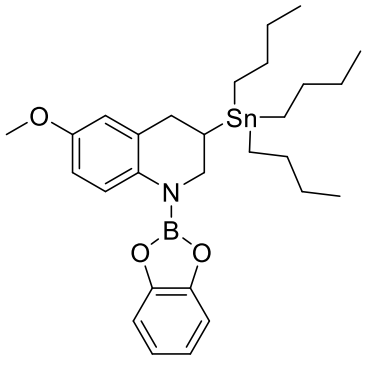
1-(benzo[d][1,3,2]dioxaborol-2-yl)-6-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10k**) colorless sticky oil (90%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.79 (d, J = 10.0 Hz, 1H, HAr), 7.14 – 7.16 (m, 1H, HAr), 6.93 – 7.00 (m, 3H, HAr), 6.75 – 6.79 (m, 2H, HAr), 3.88 – 4.09 (m, 1H, CH_2), 3.47– 3.55 (m, 1H, CH_2), 2.65 – 2.79 (m, 2H, CH_2), 1.44 – 1.59 (m, 7H, CH, CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.82 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 148.3, 139.7, 128.9, 128.8, 126.5, 126.2, 122.1, 121.6, 111.7, 48.5, 32.4, 29.3, 27.5, 20.2, 13.5, 8.1.



1-(benzo[d][1,3,2]dioxaborol-2-yl)-6-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10l**) yellow sticky soild (88%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.73 (d, J = 10.0 Hz, 1H, HAr), 7.27 (dd, J = 10.0 Hz, J_2 = 1.0 Hz, 1H, HAr), 7.07 (s, 1H, HAr), 6.96 – 6.99 (m, 2H, HAr), 6.75 – 6.79 (m, 2H, HAr), 3.90 – 4.02 (m, 1H, CH_2), 3.45 – 3.53 (m, 1H, CH_2), 2.64 – 2.74 (m, 2H, CH_2), 1.44 – 1.52 (m, 7H, CH, CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.82 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 148.3, 140.2, 131.9, 129.4, 129.3, 122.1, 122.0, 113.9, 111.7, 48.5, 32.4, 29.3, 27.5, 20.1, 13.6, 8.1.

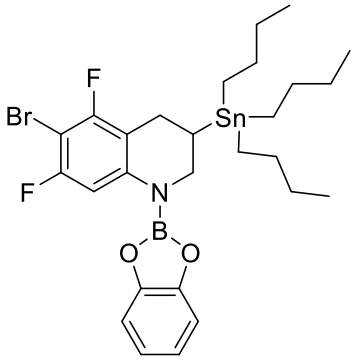


1-(benzo[d][1,3,2]dioxaborol-2-yl)-6-iodo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10m**) white sticky soild (89%)； ^{1}H NMR (500 MHz, C_6D_6) δ 7.61 (d, J = 10.0 Hz, 1H, HAr), 7.44 (dd, J = 10.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 7.27 (s, 1H, HAr), 6.95 – 6.99 (m, 2H, HAr), 6.75 – 6.79 (m, 2H, HAr), 3.87 – 4.01 (m, 1H, CH_2), 3.46 – 3.52 (m, 1H, CH_2), 2.61 – 2.71 (m, 2H, CH_2), 1.43 – 1.53 (m, 7H, CH CH_2), 1.27 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.82 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 148.3, 140.9, 137.8, 135.4, 129.8, 122.4, 122.1, 111.7, 84.2, 48.5, 32.3, 29.3, 27.5, 20.1, 13.6, 8.1.

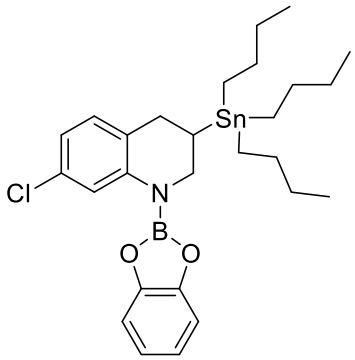


1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-methoxy-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10n**) colorless sticky oil (92%)； ^{1}H NMR (500 MHz, C_6D_6) δ 7.91 (d, J = 10.0 Hz, 1H, HAr), 6.99 – 7.03 (m, 2H, HAr), 6.80 (dd, J = 15.0 Hz, J_2 = 1.0 Hz, 1H, HAr), 6.76 – 6.79 (m, 2H, HAr), 6.66 (d, J = 3.0 Hz, 1H, HAr), 4.03 – 4.06 (m, 1H, CH_2), 3.64 – 3.69 (m, 1H, CH_2), 3.41 (s, 3H, OMeH), 2.86 – 3.01 (m, 2H, CH_2), 1.63 – 1.72 (m, 1H, CH), 1.46 – 1.55 (m, 6H, CH_2),

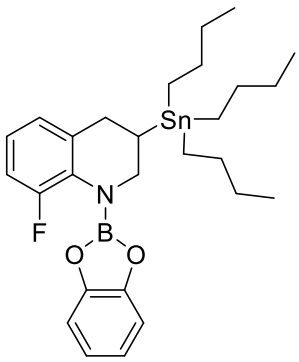
1.28 – 1.35 (m, 6H, CH_2), 0.85 – 0.93 (m, 15H, CH_2CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 154.7, 148.6, 134.5, 128.1, 121.9, 121.5, 114.2, 112.4, 111.6, 54.6, 48.6, 32.9, 29.3, 27.5, 21.3, 13.6, 8.1.



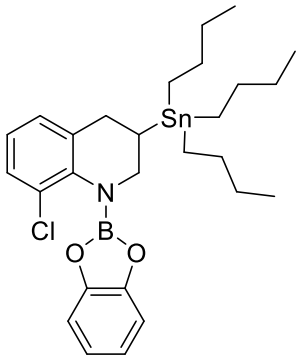
6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10o**) white sticky soild (88%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.66 (d, J = 15.0 Hz, 1H, HAr), 6.90 – 6.94 (m, 2H, HAr), 6.74 – 6.77 (m, 2H, HAr), 3.91 – 3.94 (m, 1H, CH_2), 3.33 – 3.37 (m, 1H, CH_2), 2.85 – 2.89 (m, 1H, CH_2), 2.63 – 2.68 (m, 1H, CH_2), 1.41 – 1.53 (m, 7H, CH CH_2), 1.26 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.81 – 0.84 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 158.5, 156.6, 147.9, 142.1, 127.8, 122.4, 111.8, 103.5, 103.3, 88.7, 48.2, 29.2, 27.5, 25.2, 18.3, 13.5, 8.0.



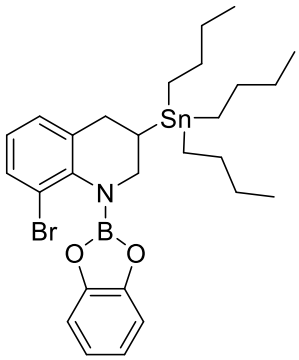
1-(benzo[d][1,3,2]dioxaborol-2-yl)-7-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline(**10p**) colorless sticky oil (90%); ^{1}H NMR (500 MHz, C_6D_6) δ 8.14 (s, 1H, HAr), 6.88 – 6.91 (m, 3H, HAr), 6.72 – 6.76 (m, 2H, HAr), 6.65 (d, J = 10.0 Hz, 1H, HAr), 3.88 – 4.01 (m, 1H, CH_2), 3.50 – 3.56 (m, 1H, CH_2), 2.66 – 2.86 (m, 2H, CH_2), 1.42 – 1.57 (m, 7H, CH CH_2), 1.27 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.82 – 0.87 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 148.2, 142.3, 132.1, 130.2, 125.3, 122.1, 121.3, 120.1, 111.8, 48.5, 32.2, 29.3, 27.5, 20.2, 13.5, 8.1.



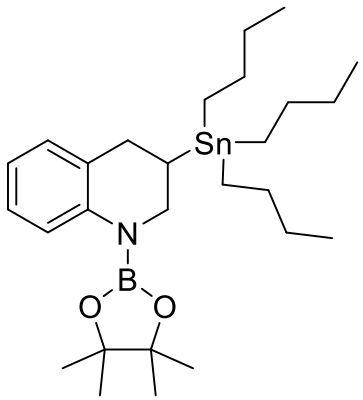
1-(benzo[d][1,3,2]dioxaborol-2-yl)-8-fluoro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline(**10q**) colorless sticky oil (79%); ^{1}H NMR (500 MHz, C_6D_6) δ 6.96 – 7.01 (m, 2H, HAr), 6.89 (t, J = 10.0 Hz, 1H, HAr), 6.70 – 6.75 (m, 3H, HAr), 6.65 (d, J = 5.0 Hz, 1H, HAr), 3.96 – 4.07 (m, 1H, CH_2), 3.37 – 3.46 (m, 1H, CH_2), 2.72 – 2.89 (m, 2H, CH_2), 1.42 – 1.54 (m, 7H, CH CH_2), 1.28 – 1.35 (m, 6H, CH_2), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.83 – 0.86 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 156.0, 154.1, 148.9, 133.3, 123.5, 122.8, 121.9, 113.5, 111.7, 48.5, 31.4, 29.3, 27.5, 21.9, 13.5, 7.9.



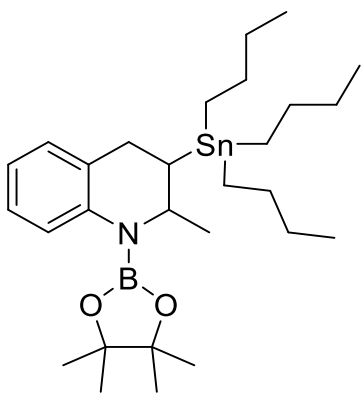
1-(benzo[d][1,3,2]dioxaborol-2-yl)-8-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10r**) colorless sticky oil (85%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.23 (dd, J_1 = 10.0 Hz, J_2 = 1.5 Hz, 1H, HAr), 6.98 – 7.02 (m, 2H, HAr), 6.68 – 6.76 (m, 4H, HAr), 3.90 – 4.02 (m, 1H, CH_2), 3.48 (t, J = 15.0 Hz, 1H, CH_2), 2.58 – 2.80 (m, 2H, CH_2), 1.44 – 1.60 (m, 7H, CH, CH_2), 1.27 – 1.34 (m, 6H, CH_2), 0.82 – 0.96 (m, 15H, CH_2, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 149.0, 139.4, 135.9, 128.2, 126.0, 124.1, 123.9, 122.0, 111.7, 48.7, 31.7, 29.3, 27.5, 22.2, 13.5, 8.0.



1-(benzo[d][1,3,2]dioxaborol-2-yl)-8-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline(**10s**) yellow sticky soild (77%); ^{1}H NMR (500 MHz, C_6D_6) δ 7.41 (d, J = 10.0 Hz, 1H, HAr), 6.99 – 7.03 (m, 2H, HAr), 6.73 – 6.77 (m, 3H, HAr), 6.61 (t, J = 10.0 Hz, 1H, CH_2), 3.92 – 3.99 (m, 1H, CH_2), 3.48 – 3.59 (m, 1H, CH_2), 2.58 – 2.76 (m, 2H, CH_2), 1.38 – 1.54 (m, 7H, CH, CH_2), 1.27 – 1.34 (m, 6H, CH_2), 0.89 (t, J = 10.0 Hz, 9H, CH_3), 0.81 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D6) δ 149.0, 140.8, 136.6, 131.1, 126.6, 124.6, 122.0, 118.8, 111.7, 48.7, 31.9, 29.3, 27.5, 22.2, 13.5, 8.0.

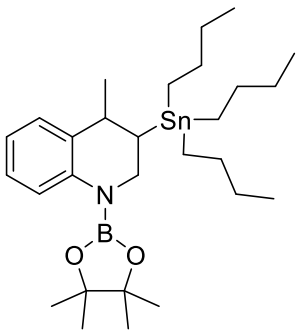


1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11a**) colorless sticky oil (90%); ^{1}H NMR (500 MHz, C_6D_6) δ 8.16 (d, J = 10.0 Hz, 1H, HAr), 7.14 (d, J = 10.0 Hz, 1H, HAr), 6.96 (d, J = 10.0 Hz, 1H, HAr), 6.83 (t, J = 5.0 Hz, 1H, HAr), 4.00 – 4.09 (m, 1H, CH_2), 3.70 – 3.74 (m, 1H, CH_2), 2.90 – 3.05 (m, 2H, CH_2), 1.72 – 1.77 (m, 1H, CH), 1.47 – 1.55 (m, 6H, CH_2), 1.28 – 1.39 (m, 6H, CH_2), 1.12 (d, J = 4.0 Hz, 12H, CH_3), 0.91 (t, J = 10.0 Hz, 9H, CH_3), 0.85 – 0.88 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 143.1, 129.1, 126.4, 126.0, 120.5, 120.2, 82.3, 48.6, 33.3 29.3, 27.6, 24.6, 24.3, 21.4, 13.6, 8.2.

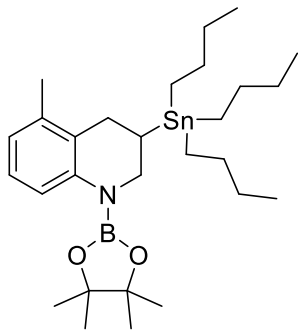


2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11b**) colorless sticky oil (87%); ^{1}H NMR (500 MHz, C_6D_6) δ 8.17 (d, J = 5.0 Hz, 1H, HAr), 7.18 (t, J = 5.0 Hz, 1H, HAr), 7.02 (d, J = 5.0 Hz, 1H, HAr), 6.86 (t, J = 10.0 Hz, 1H, HAr), 4.59 – 4.64 (m, 1H, CH_2), 3.10 – 3.25 (m, 1H, CH_2), 2.85 – 2.89 (m, 1H, CH_2), 1.89 – 2.02 (m, 1H, CH), 1.48 – 1.61 (m, 6H, CH_2), 1.32 – 1.39 (m, 6H, CH_2), 1.29 (d, J = 5.0 Hz, 3H, CH_3), 1.09 (d, J = 5.0 Hz, 12H, CH_3), 0.89 – 0.96 (m, 15H, CH_2 CH_3), ^{13}C NMR

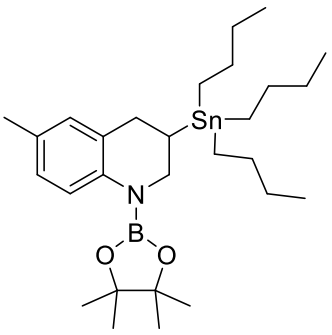
(126 MHz, C_6D_6) δ 141.3, 128.9, 126.5, 125.3, 121.6, 120.0, 82.1, 50.6, 29.3, 27.5, 26.0, 24.4, 24.3, 19.0, 13.6, 8.4.



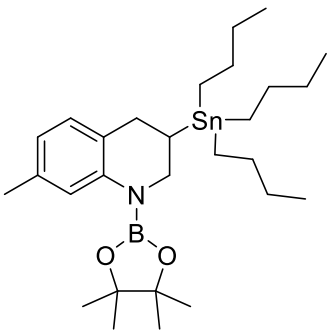
4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11d**) colorless sticky oil (90%); δ 8.21 (d, J = 15.0 Hz, 1H, HAr), 7.16 (t, J = 10.0 Hz, 1H, HAr), 7.06 (d, J = 10.0 Hz, 1H, HAr), 6.86 (t, J = 10.0 Hz, 1H, HAr), 3.79 – 4.06 (m, 2H, CH_2), 3.08 – 3.15 (m, 1H, CH_2), 1.80 – 1.85 (m, 1H, CH), 1.48 – 1.57 (m, 6H, CH_2), 1.26 (d, J = 10.0 Hz, 3H, CH_3), 1.31 – 1.14 (m, 6H, CH_2), 1.13 – 1.15 (m, 12H, CH_3), 0.87 – 1.01 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 142.5, 130.7, 129.4, 126.4, 120.3, 120.0, 82.3, 45.5, 43.9, 35.8, 29.4, 27.6, 24.7, 24.3, 13.6, 8.6.



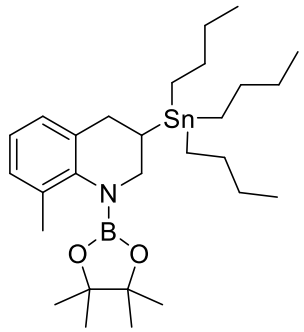
5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11e**) brown sticky oil (88%); δ 8.03 (d, J = 10.0 Hz, 1H, HAr), 7.10 (t, J = 10.0 Hz, 1H, HAr), 6.75 (d, J = 5.0 Hz, 1H, HAr), 3.97 – 4.13 (m, 1H, CH_2), 3.62 – 3.69 (m, 1H, CH_2), 2.72 – 2.94 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 1.76 – 1.82 (m, 1H, CH), 1.49 – 1.58 (m, 6H, CH_2), 1.31 – 1.38 (m, 6H, CH_2), 1.12 (d, J = 10.0 Hz, 12H, CH_3), 0.87 – 0.97 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 143.1, 135.8, 125.8, 124.8, 122.2, 119.0, 82.2, 48.0, 30.3, 29.4, 27.6, 24.6, 24.3, 21.9, 19.5, 13.6, 8.2.



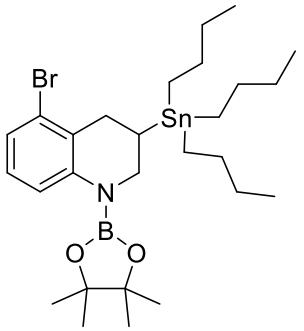
6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11f**) colorless sticky oil (86%); δ 8.08 (d, J = 5.0 Hz, 1H, HAr), 6.98 (d, J = 10.0 Hz, 1H, HAr), 6.78 (s, 1H, HAr), 3.94 – 4.09 (m, 1H, CH_2), 3.70 – 3.78 (m, 1H, CH_2), 2.85 – 3.12 (m, 2H, CH_2), 2.17 (s, 3H, CH_3), 1.75 – 1.80 (m, 1H, CH), 1.49 – 1.58 (m, 6H, CH_2), 1.29 – 1.39 (m, 6H, CH_2), 1.12 (d, J = 5.0 Hz, 12H, CH_3), 0.86 – 0.95 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 140.5, 129.7, 128.8, 127.1, 125.7, 120.4, 82.2, 48.7, 33.3, 29.4, 27.6, 24.6, 24.4, 21.6, 20.3, 13.6, 8.2.



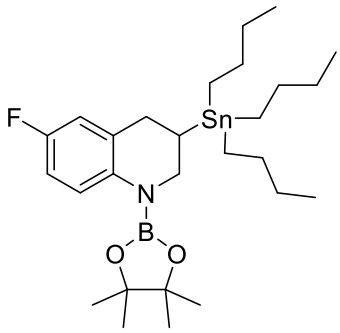
7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11g**) colorless sticky oil (90%); δ 7.97 (s, 1H, HAr), 6.91 (d, J = 5.0 Hz, 1H, HAr), 6.70 (d, J = 5.0 Hz, 1H, HAr), 3.95 – 4.10 (m, 1H, CH_2), 3.68 – 3.77 (m, 1H, CH_2), 2.87 – 3.12 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.74 – 1.84 (m, 1H, CH), 1.45 – 1.59 (m, 6H, CH_2), 1.30 – 1.39 (m, 6H, CH_2), 1.13 (d, J = 5.0 Hz, 12H, CH_3), 0.86 – 0.97 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 142.9, 135.5, 129.1, 123.2, 121.2, 121.0, 82.2, 48.7, 33.0, 29.3, 27.6, 24.6, 24.3, 21.7, 21.5, 13.6, 8.2.



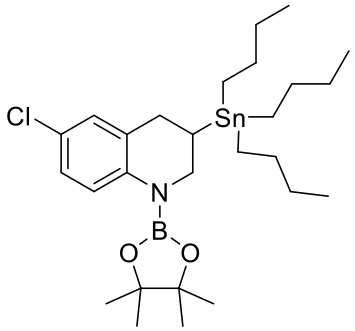
8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11h**) colorless sticky oil (80%); δ 7.07 (d, J = 10.0 Hz, 1H, HAr), 6.92 (t, J = 5.0 Hz, 1H, HAr), 6.87 (d, J = 10.0 Hz, 1H, HAr), 3.91 – 4.06 (br, 1H, CH_2), 3.38 – 3.55 (br, 1H, CH_2), 2.84 – 2.98 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 1.71 – 1.86 (m, 1H, CH), 1.47 – 1.59 (m, 6H, CH_2), 1.32 – 1.38 (m, 6H, CH_2), 1.09 (d, J = 10.0 Hz, 12H, CH_3), 0.82 – 0.94 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 142.6, 131.4, 128.6, 125.2, 122.6, 82.2, 48.5, 32.0, 29.4, 27.5, 24.6, 24.3, 23.6, 18.8, 13.6, 8.0.



5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11i**) yellow sticky soild (92%); δ 8.01 (d, J = 5.0 Hz, 1H, HAr), 7.13 (d, J = 10.0 Hz, 1H, HAr), 6.81 (t, J = 5.0 Hz, 1H, HAr), 3.88 – 4.02 (m, 1H, CH_2), 3.45 – 3.52 (m, 1H, CH_2), 2.93 – 3.20 (m, 2H, CH_2), 1.60 – 1.70 (m, 1H, CH), 1.48 – 1.55 (m, 6H, CH_2), 1.29 – 1.38 (m, 6H, CH_2), 1.09 (d, J = 5.0 Hz, 12H, CH_3), 0.92(t, J = 5.0 Hz, 9H, CH_3), 0.86– 0.89 (m, 6H, CH_2),^{13}C NMR (126 MHz, C_6D_6) δ 145.2, 127.1, 125.9, 125.7, 124.4, 119.9, 82.5, 48.1, 34.2, 29.3, 27.5, 24.5, 24.3, 21.3, 13.6, 8.2.

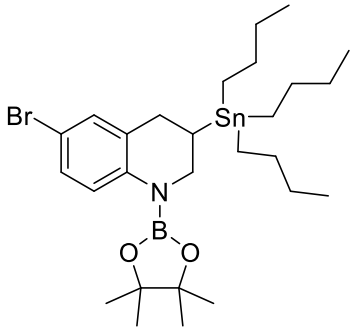


6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11j**) colorless sticky oil (81%); δ 7.98 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 6.82 (td, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H, HA), 6.64 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 3.88 – 4.02 (m, 1H, CH_2), 3.57 – 3.65 (m, 1H, CH_2), 2.70 – 2.94 (m, 2H, CH_2), 1.61 – 1.66 (m, 1H, CH), 1.46 – 1.55 (m, 6H, CH_2), 1.29 – 1.37 (m, 6H, CH_2), 1.10 (d, J = 5.0 Hz, 12H, CH_3), 0.92(t, J = 5.0 Hz, 9H, CH_3), 0.83 – 0.87 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) 158.2, 156.3, 139.0, 121.6, 114.9, 112.8, 82.3, 48.4, 33.1, 29.3, 27.5, 24.6, 24.3, 20.9, 13.6, 8.1.

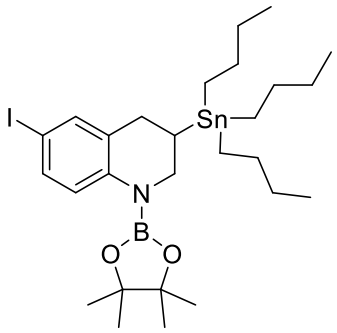


6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11k**) colorless sticky oil (90%); δ 7.98 (d, J = 10.0 Hz, 1H, HAr), 7.11 (dd, J_1 = 10.0 Hz, J_2 = 2.5 Hz, 1H, HAr), 6.93 (d, J = 2.0 Hz, 1H, HAr), 3.81 – 4.00 (m, 1H, CH_2), 3.55 – 3.63 (m, 1H, CH_2), 2.65 – 2.87 (m, 2H, CH_2), 1.57 – 1.63 (m, 1H, CH), 1.45 – 1.51 (m, 6H, CH_2), 1.28 – 1.36 (m, 6H, CH_2), 1.09 (d, J = 2.5 Hz, 12H, CH_3), 0.92 (t, J = 5.0 Hz, 9H, CH_3), 0.82 – 0.86 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 141.6, 128.8, 126.3, 124.9, 121.7, 82.4,

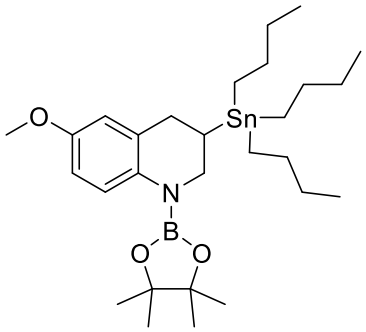
48.5, 33.0, 29.3, 27.5, 24.5, 24.3, 20.6, 13.6, 8.1.



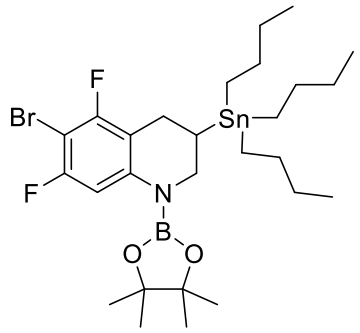
6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11l**) yellow sticky solid (87%); δ 7.92 (d, J = 5.0 Hz, 1H, HAr), 7.24 (dd, J_1 = 5.0 Hz, J_2 = 2.5 Hz, 1H, HAr), 7.07 (d, J = 2.5 Hz, 1H, HAr), 3.85 – 4.00 (m, 1H, CH_2), 3.54 – 3.61 (m, 1H, CH_2), 2.64 – 2.85 (m, 2H, CH_2), 1.56 – 1.61 (m, 1H, CH), 1.42 – 1.54 (m, 6H, CH_2), 1.29 – 1.37 (m, 6H, CH_2), 1.08 (d, J = 2.5 Hz, 12H, CH_3), 0.92 (t, J = 5.0 Hz, 9H, CH_3), 0.82 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 142.1, 131.7, 129.2, 128.4, 122.1, 112.4, 82.5, 48.4, 32.9, 29.3, 27.5, 24.5, 24.3, 20.5, 13.6, 8.1.



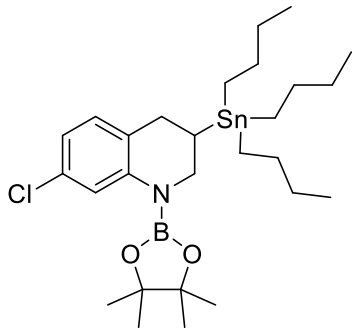
6-iodo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11m**) white sticky solid (91%); δ 7.79 (d, J = 10.0 Hz, 1H, HAr), 7.40 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H, HAr), 7.26 (s, 1H, HAr), 3.86 – 3.99 (m, 1H, CH_2), 3.54 – 3.60 (m, 1H, CH_2), 2.61 – 2.81 (m, 2H, CH_2), 1.44 – 1.60 (m, 7H, CH CH_2), 1.29 – 1.36 (m, 6H, CH_2), 1.08 (d, J = 2.0 Hz, 12H, CH_3), 0.92 (t, J = 5.0 Hz, 9H, CH_3), 0.82 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 142.8, 137.7, 135.2, 129.0, 122.6, 82.5, 48.4, 32.8, 29.3, 27.6, 24.5, 24.3, 20.5, 13.6, 8.1.



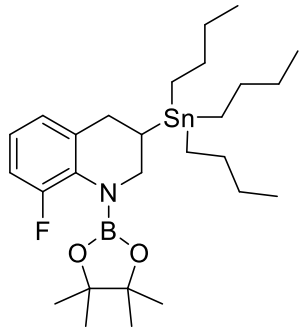
6-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11n**) colorless sticky oil (55%); δ 8.06 (d, J = 5.0 Hz, 1H, HAr), 6.78 (dd, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1H, HAr), 6.64 (d, J = 5.0 Hz, 1H, HAr), 3.94 – 4.10 (m, 1H, CH_2), 3.68 – 3.75 (m, 1H, CH_2), 3.40 (s, 3H, CH_3) 2.87 – 3.08 (m, 2H, CH_2), 1.73 – 1.80 (m, 1H, CH), 1.46 – 1.60 (m, 6H, CH_2), 1.30 – 1.38 (m, 6H, CH_2), 1.13 (d, J = 5.0 Hz, 12H, CH_3), 0.92 (t, J = 5.0 Hz, 9H, CH_3), 0.87 – 0.90 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 153.8, 136.5, 127.0, 121.5, 114.0, 112.4, 82.1, 54.6, 48.6, 33.5, 29.4, 27.6, 24.6, 24.4, 21.6, 13.6, 8.2.



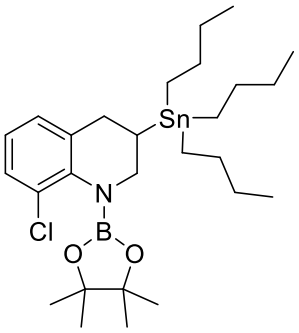
6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11o**) white sticky solid (92%); δ 7.86 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H, HAr), 3.76 – 3.92 (m, 1H, CH_2), 3.41 – 3.50 (m, 1H, CH_2), 2.70 – 2.88 (m, 2H, CH_2), 1.42 – 1.50 (m, 7H, CH CH_2), 1.26 – 1.34 (m, 6H, CH_2), 1.03 (s, 12H, CH_3), 0.90 (t, J = 10.0 Hz, 9H, CH_3), 0.80 – 0.85 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 158.4, 156.5, 144.2, 111.0, 103.3, 82.9, 48.0, 29.2, 27.5, 25.5, 24.4, 24.2, 18.7, 13.5, 8.1.



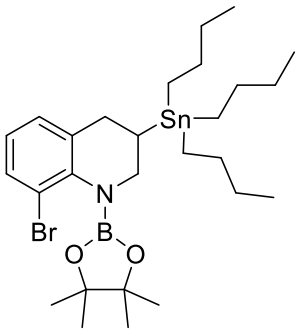
7-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11p**) colorless sticky oil (87%); 8.30 (d, J = 2.0 Hz, 1H, HAr), 6.83 (dd, J_1 = 5.0 Hz, J_2 = 2.5 Hz, 1H, HAr), 6.66 (d, J = 10.0 Hz, 1H, HAr), 3.58 – 3.65 (m, 1H, CH_2), 3.84 – 3.98 (m, 1H, CH_2), 2.69 – 2.92 (m, 2H, CH_2), 1.60 – 1.65 (m, 1H, CH), 1.42 – 1.52 (m, 6H, CH_2), 1.29 – 1.36 (m, 6H, CH_2), 1.05 (d, J = 5.0 Hz, 12H, CH_3), 0.92 (t, J = 5.0 Hz, 9H, CH_3), 0.82 – 0.86 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 144.2, 131.9, 130.1, 124.4, 120.1, 120.0, 82.6, 48.4, 32.7, 29.3, 27.5, 24.4, 24.2, 20.6, 13.6, 8.2.



8-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11q**) colorless sticky oil (38%); 6.85 – 6.89 (m, 1H, HAr), 6.62 – 6.67 (m, 2H, HAr), 4.02 – 4.11 (m, 1H, CH_2), 3.27 – 3.36 (m, 1H, CH_2), 2.80 – 2.90 (m, 2H, CH_2), 1.64 – 1.70 (m, 1H, CH), 1.46 – 1.54 (m, 6H, CH_2), 1.29 – 1.37 (m, 6H, CH_2), 1.20 (s, 6H, CH_3), 1.14 (s, 6H, CH_3), 0.84 – 0.94 (m, 15H, CH_2 CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 156.1, 154.1, 132.5, 123.3, 121.5, 113.3, 82.5, 48.2, 31.7, 29.3, 27.5, 24.7, 24.3, 24.0, 13.6, 7.9.

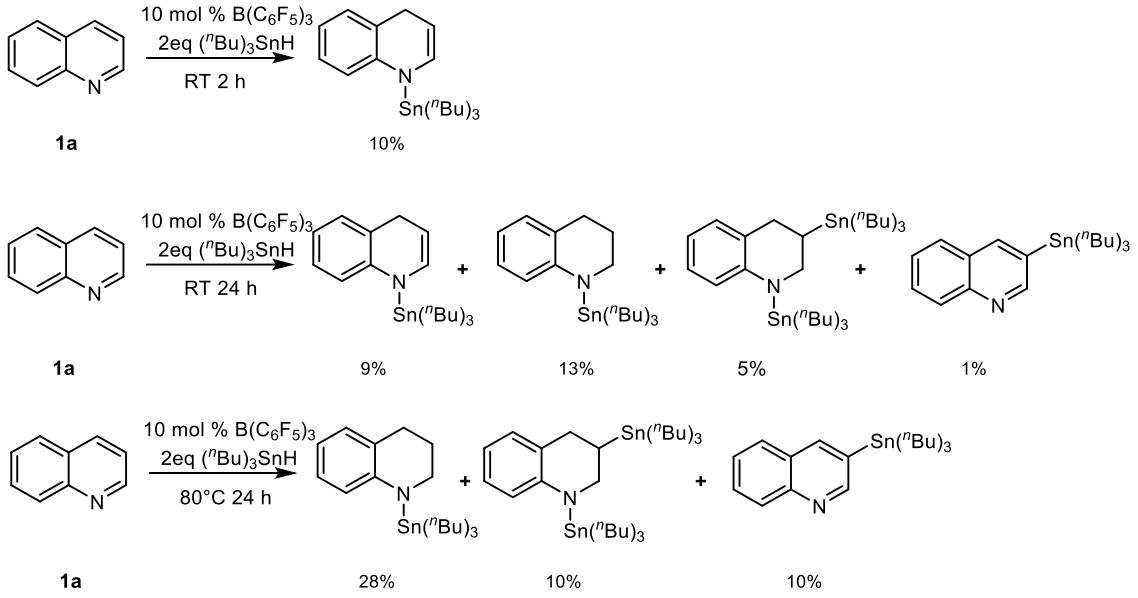


8-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11r**) colorless sticky oil (75%); δ 7.22 (d, J = 10.0 Hz, 1H, HAr), 6.70 (d, J = 5.0 Hz, 1H, HAr), 6.63 (t, J = 5.0 Hz, 1H, HAr), 3.93 – 4.00 (m, 1H, CH_2), 3.32 – 3.42 (m, 1H, CH_2), 2.67 – 2.86 (m, 2H, CH_2), 1.47 – 1.63 (m, 7H, CH CH_2), 1.29 – 1.36 (m, 6H, CH_2), 1.18 (s, 6H, CH_3), 1.14 (s, 6H, CH_3), 0.91 (t, J = 5.0 Hz, 9H, CH_3), 0.84 – 0.88 (m, 6H, CH_2), ^{13}C NMR (126 MHz, C_6D_6) δ 141.4, 135.1, 128.3, 125.9, 122.9, 82.6, 48.4, 32.0, 29.3, 27.5, 24.7, 24.3, 23.0, 13.6, 7.9.



8-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11s**) yellow sticky solid (45%); δ 7.41 (d, J = 5.0 Hz, 1H, HAr), 6.72 (d, J = 10.0 Hz, 1H, HAr), 6.56 (t, J = 5.0 Hz, 1H, HAr), 3.88 – 3.92 (m, 1H, CH_2), 3.37 – 3.42 (m, 1H, CH_2), 2.64 – 2.84 (m, 2H, CH_2), 1.47 – 1.60 (m, 7H, CH CH_2), 1.29 – 1.36 (m, 6H, CH_2), 1.18 (s, 6H, CH_3), 1.16 (s, 6H, CH_3), 0.91 (t, J = 5.0 Hz, 9H, CH_3), 0.84 – 0.87 (m, 6H, CH_2),^{13}C NMR (126 MHz, C_6D_6) δ 142.7, 136.1, 131.0, 126.4, 123.6, 119.2, 82.7, 48.4, 32.2, 29.3, 27.5, 24.7, 24.4, 23.1, 13.6, 8.0.

3. Reaction of quinoline 1a and (^{n}Bu)$_3$SnH catalyzed by B(C_6F_5)$_3$



In a glove box, 0.1 mmol (12.9 mg) quinoline **1a** was added to the 0.6 mL C_6D_6 solution containing 0.2 mmol (58.2 mg) (^{n}Bu)$_3$SnH and 0.01 mmol (5.1 mg) B(C_6F_5)$_3$, after 2 h or 24 h at RT, it was measured by ^{1}H NMR spectroscopy. After 2 h, 10% yield of 1,4-addition product was obtained. 9% yield of 1,4-addition product, 13% yield of *N*-stannyl-tetrahydroquinoline, 5% yield of double hydrostannation product and 1% yield of C3-stannyl-quinoline were gained after 24 h at RT. After elevating the temperature to 80°C, there were only 10% yield of double hydrostannation product attained after 24 h, while other by-product gained including 28% yield of *N*-stannyl-tetrahydroquinoline, 10% yield of C3-stannyl-quinoline (identify C3-stannyl-quinoline based on

literature).[6]

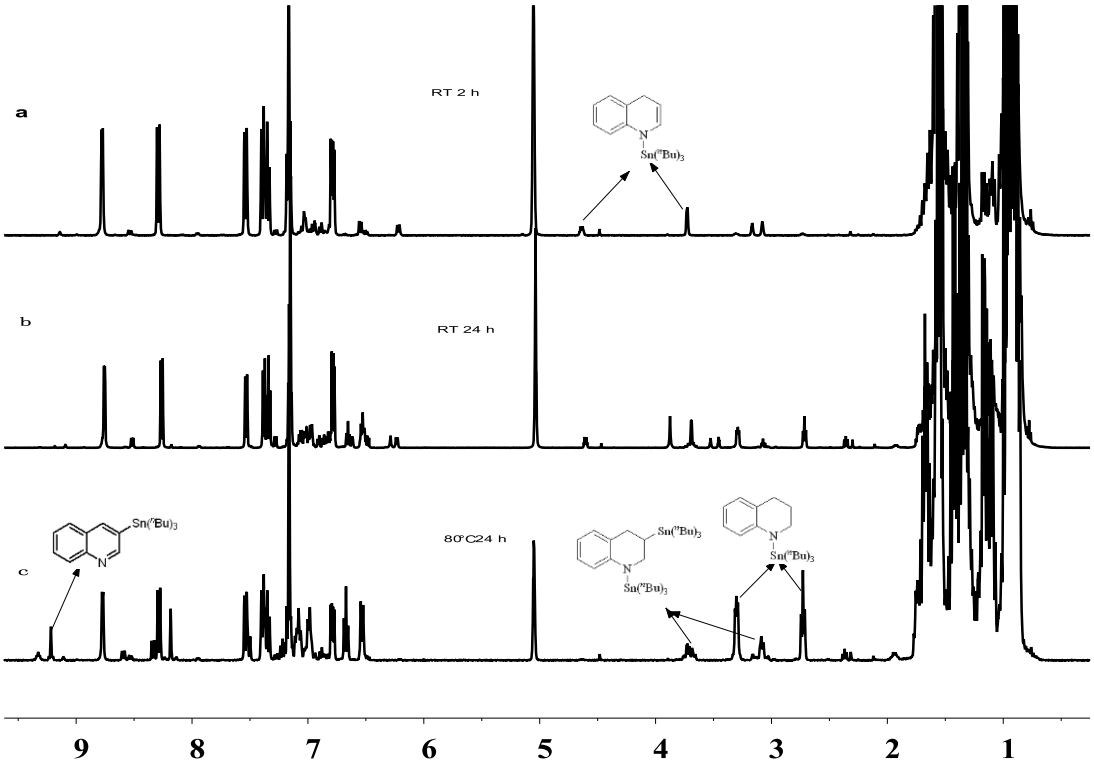
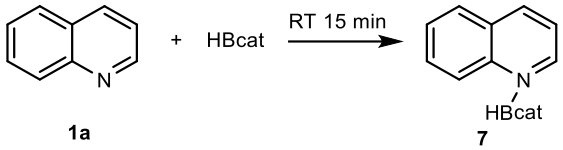


Figure S1 Overlay of ^{1}H NMR spectra for (a) reaction at RT for 2 h (b) reaction at RT for 24 h (c) reaction at 80°C for 24 h.

4. Reaction of quinoline 1a and HBcat

In a glove box, 0.1 mmol (12.9 mg) quinoline **1a** was added to the 0.6 mL C_6D_6 solution containing 0.1 mmol (12.0 mg) HBcat, after 15 min at RT, it was measured by NMR spectroscopy. There was fully convert from **1a** to **7**.



1a **7**

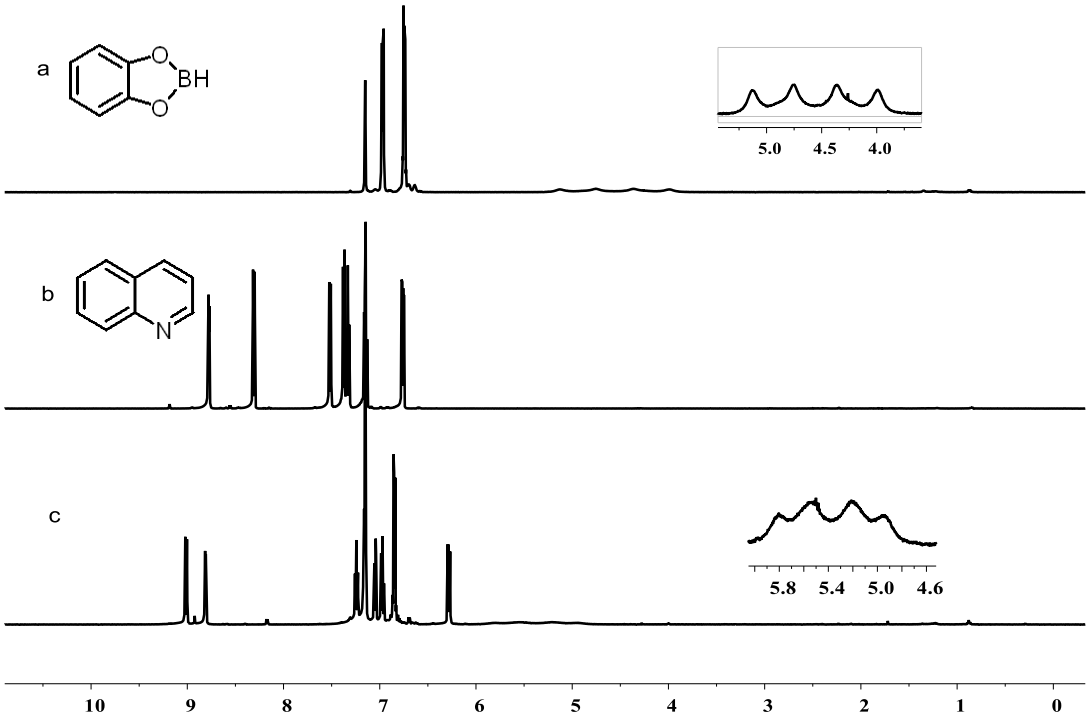


Figure S2 Overlay of ^{1}H NMR spectra for (a) HBcat (b) quinoline **1a** (c) in-situ NMR reaction.

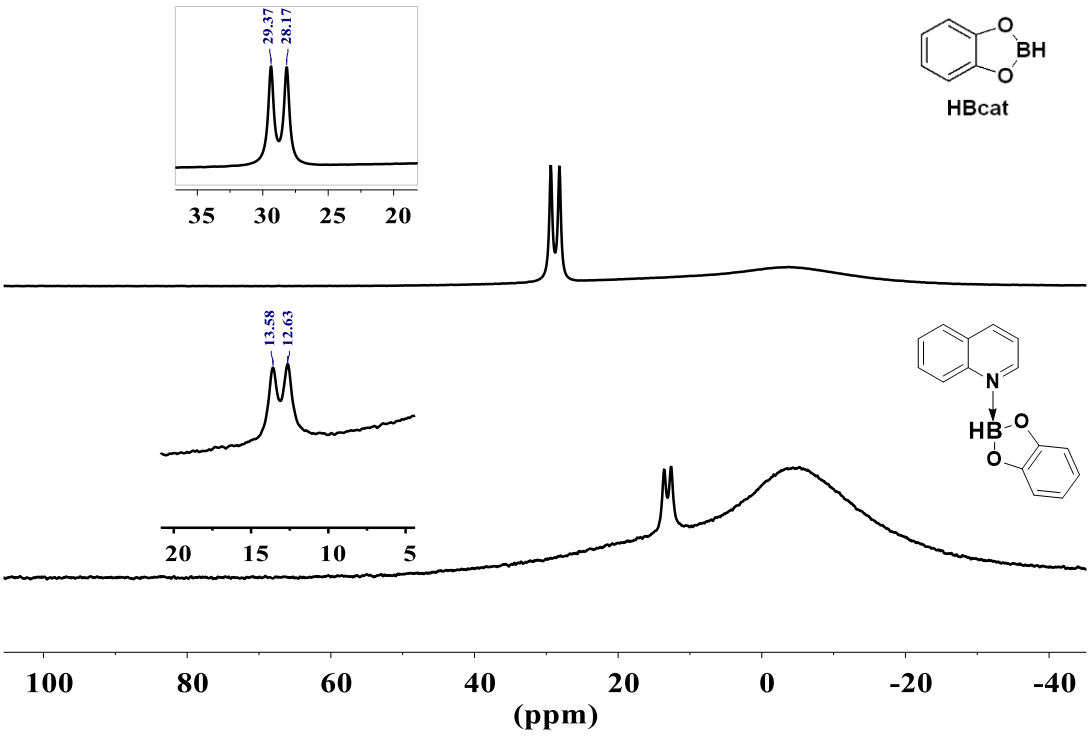


Figure S3 Overlay of ^{11}B NMR spectra for HBcat (top) and the adduct **7** (bottom).

5. Raction of quinoline 1a and (^{n}Bu)$_3$SnH

In a glove box, 0.1 mmol (12.9 mg) quinoline **1a** was added to the 0.6 mL C_6D_6 solution containing 0.1 mmol (29.1 mg) (nBu)$_3$SnH, after 15 min at RT, it was measured by NMR spectroscopy.

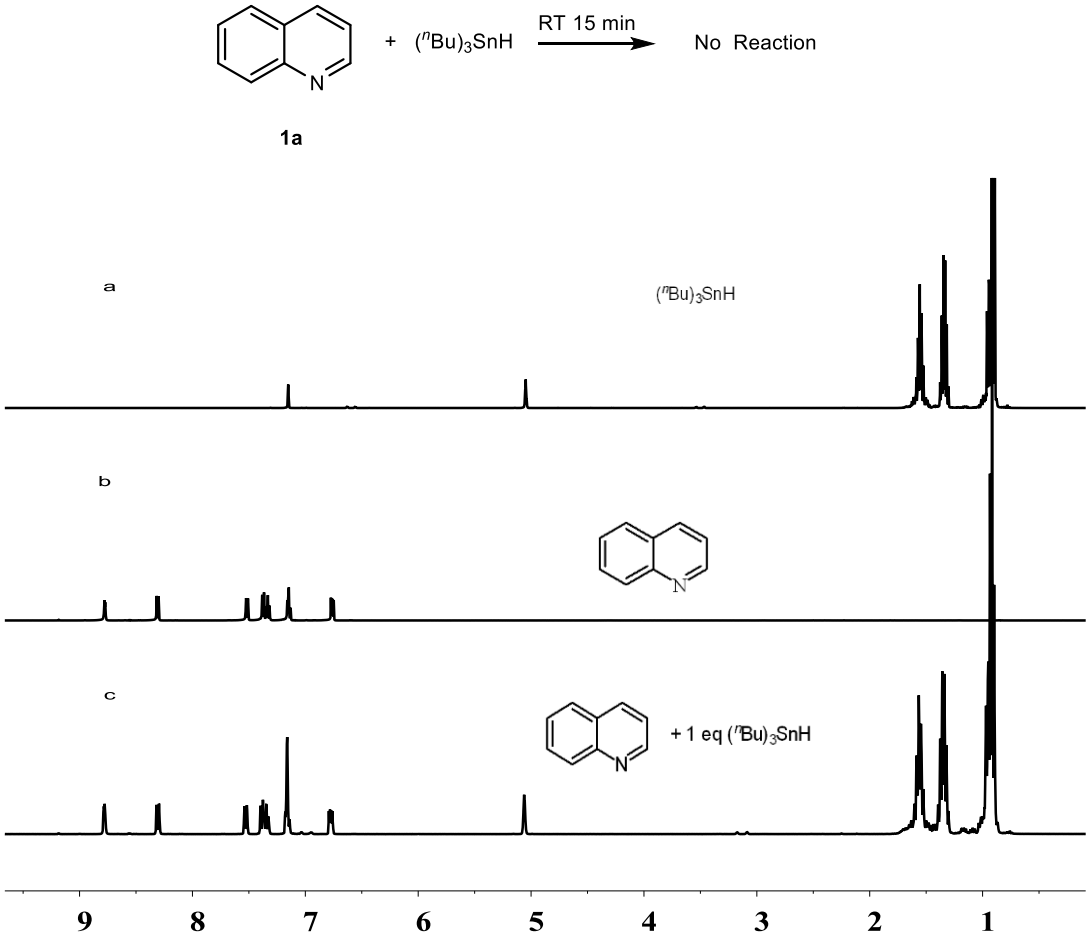


Figure S4 Overlay of ^{1}H NMR spectra for (a) (^{n}Bu)$_3$SnH (b) quinoline **1a** (c) in-situ NMR reaction.

6. Reaction of 7 and B(C_6F_5)$_3$ and then with (^{n}Bu)$_3$SnH

In a glove box, 0.1 mmol (24.9 mg) light yellow powder **7** was added to the 0.6 mL C_6D_6 solution containing 0.005 mmol (2.6 mg) B(C_6F_5)$_3$, after 15 min at RT, it was measured by ^{1}H NMR spectroscopy. There was fully convert of **7** to 28% yield of **8**, 63% yield of **9**, 5% yield of **6** and others,

0.1 mmol (^{n}Bu)$_3$SnH (29.1 mg) was added to the above mixture and measured by ^{1}H NMR measurement after 2 h, 95% yield of **10a** obtained.

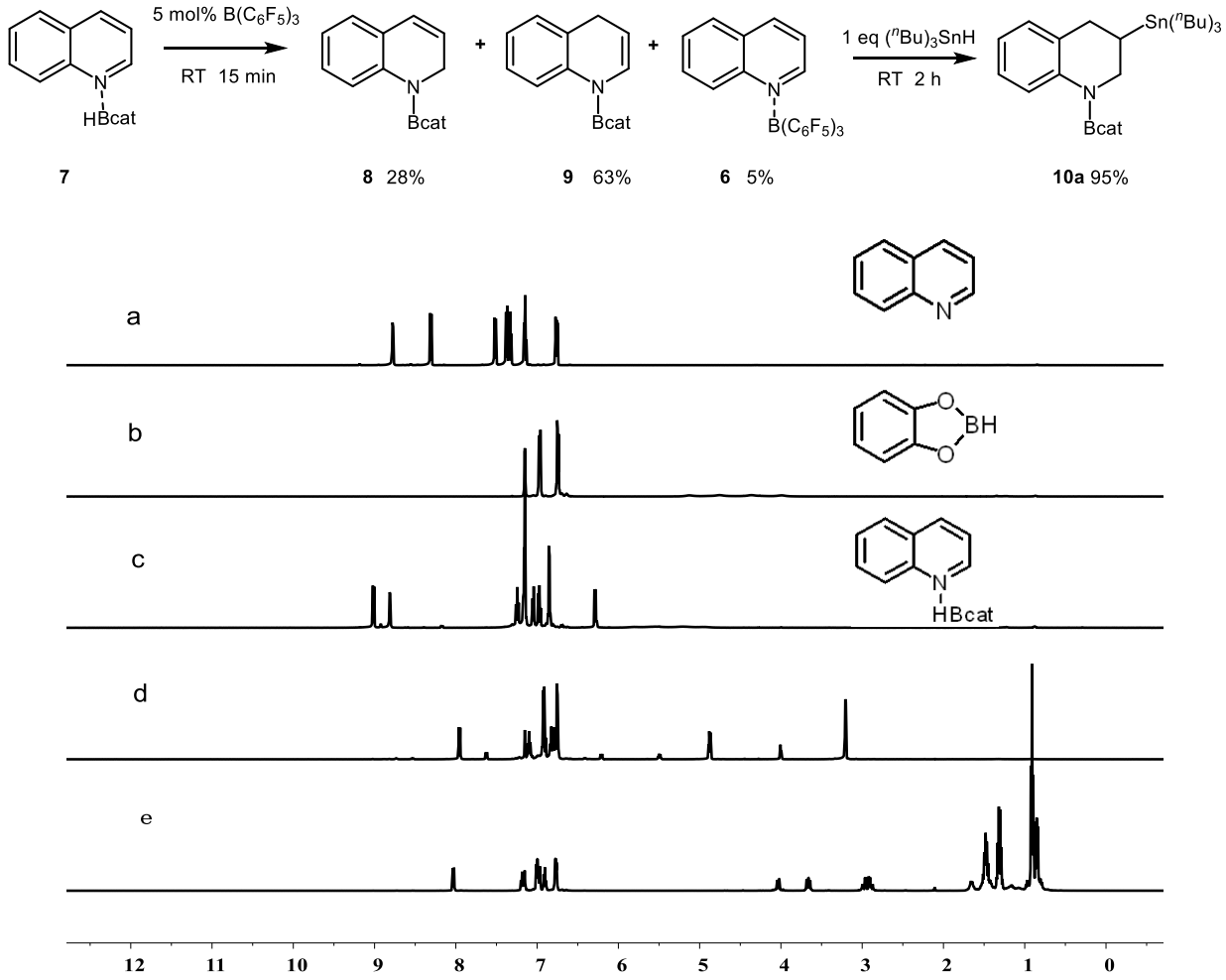


Figure S5 Overlay of ^{1}H NMR spectra for (a) quinoline **1a** (b) HBcat (c) **7** (d) reaction **7** and B(C_6F_5)$_3$ (e) 0.1 mmol (^{n}Bu)$_3$SnH adding to above mixture.

7. Reaction of (^{n}Bu)$_3$SnH and B(C_6F_5)$_3$

In a glove box, 0.1 mmol (29.1 mg) (^{n}Bu)$_3$SnH was added to the 0.6 mL C_6D_6 solution containing 0.1 mmol (51.2 mg) B(C_6F_5)$_3$, after 15 min or 2 h, it was measured by NMR spectroscopy.

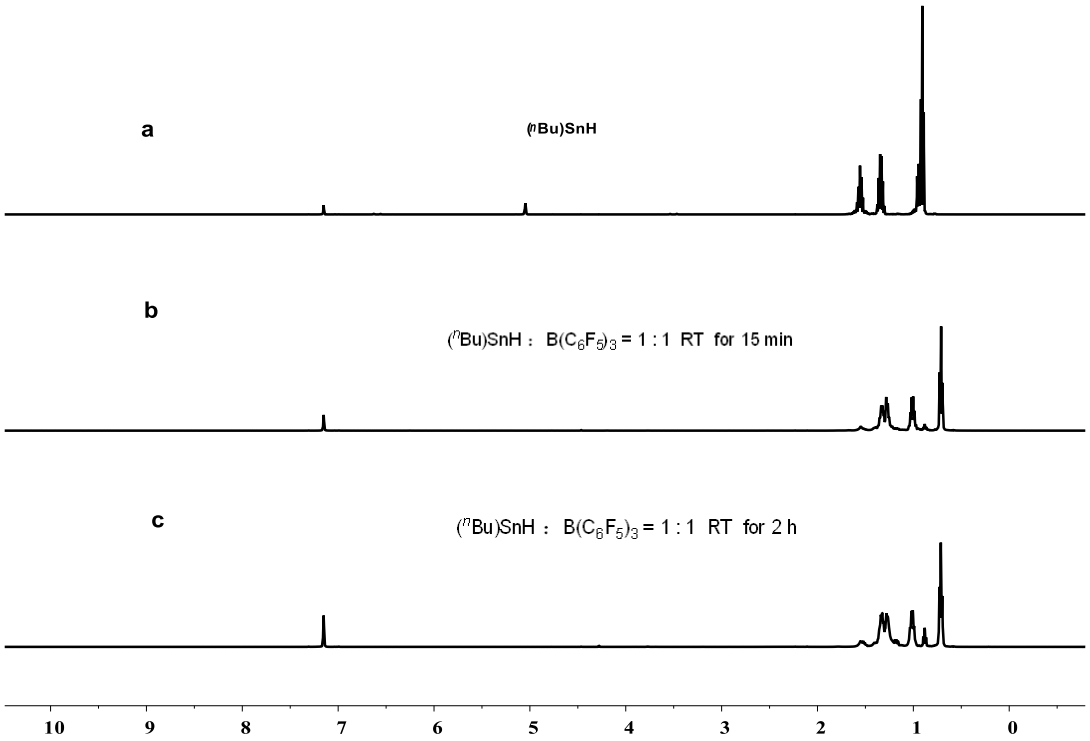


Figure S6 Overlay of ^{1}H NMR spectra for (a) $(^{n}Bu)_3SnH$ (b) $(^{n}Bu)_3SnH$ ： $B(C_6F_5)_3$= 1: 1 at RT for 15 min (c) $(^{n}Bu)_3SnH$ ： $B(C_6F_5)_3$= 1: 1 at RT for 2 h.

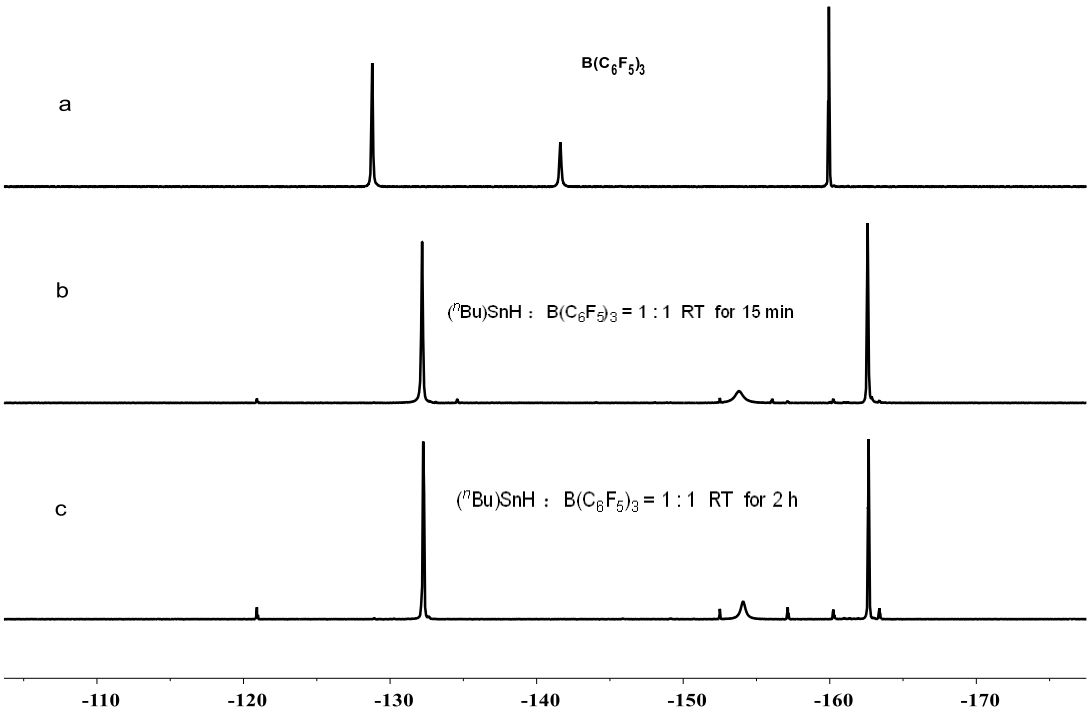


Figure S7 Overlay of ^{19}F NMR spectra for (a) $B(C_6F_5)_3$ (b) $(^{n}Bu)_3SnH$**:** $B(C_6F_5)_3$ = 1: 1 at RT for 15 min (c) $(^{n}Bu)_3SnH$**:** $B(C_6F_5)_3$ = 1: 1 at RT for 2 h.

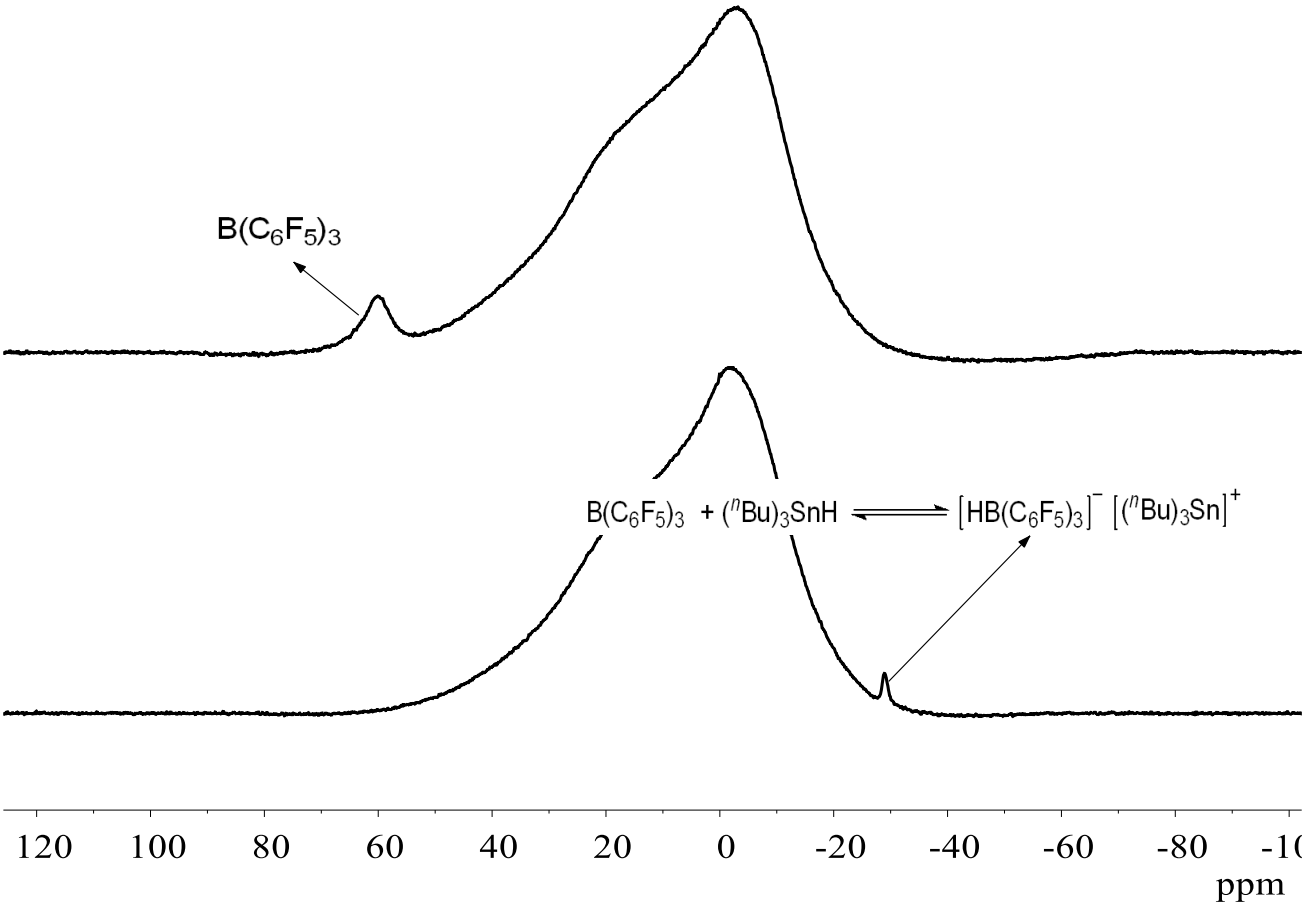
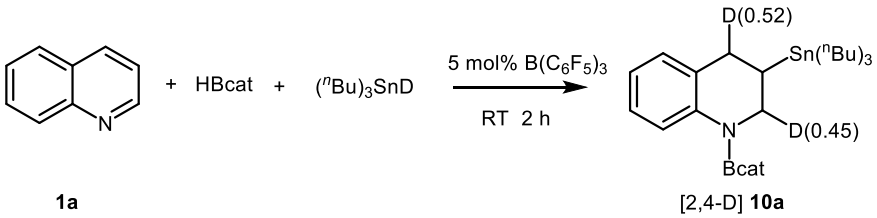


Figure S8 Overlay of ^{11}B NMR spectra for (top) $B(C_6F_5)_3$, (bottom) $(^nBu)_3SnH$: $B(C_6F_5)_3$ = 1: 1 at RT for 2 h (It is noteworthy that when tetrahydrofuran is added as a base in the reaction of $(^nBu)_3SnH$ and $B(C_6F_5)_3$ as reported in the literature, the ^{11}B NMR spectra exhibits a doublet peak.[7] In contrast, this reaction displays a broad singlet peak in the absence of a base. This phenomenon may be attributed to the reversibility of the reaction between $(^nBu)_3SnH$ and $B(C_6F_5)_3$ in the absence of a base to stabilize the intermediate, the interaction of free $B(C_6F_5)_3$ with hydridoborate $[HB(C_6F_5)_3]^-$ would result this phenomenon.[8, 9])

8. Deuterium experiment



1a [2,4-D] **10a**

In a glove box, $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg) was added to a solution containing catecholborane (HBcat) (0.1

mmol, 12.0 mg), $(nBu)_3SnD$ (0.1 mmol, 29.2 mg) in 0.6 mL C_6D_6 in NMR tube, then quinoline (0.1 mmol, 12.9 mg) was added to the resulting mixture. It was measured by ^1H NMR spectroscopy after 2 h at RT.

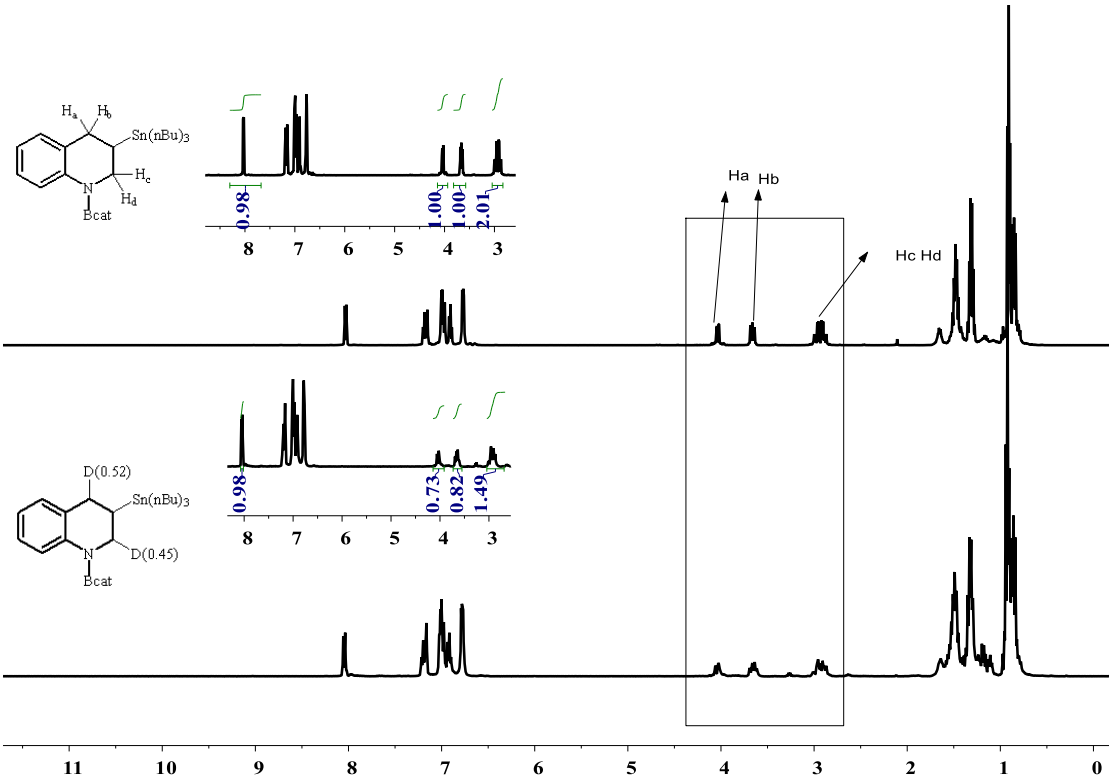
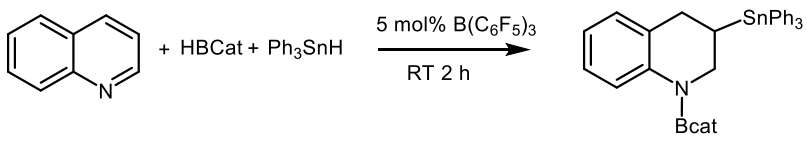


Figure S9 Overlay of ^1H NMR spectra for (a) product **10a** (b) product **2,4-D 10a** in situ NMR.

9. Changing reductant from $(^nBu)_3SnH$ to Ph_3SnH.



1a **10a-Ph** 87%

In a glove box, $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg) was added to a solution containing catecholborane (HBcat) (0.1 mmol, 12.0 mg), Ph_3SnH (0.10 mmol, 35.1 mg) in 0.6 mL C_6D_6 in NMR tube, then quinoline (0.1 mmol, 12.9 mg) was added to the resulting mixture. It was measured by ^1H NMR spectroscopy after 2 h at RT.

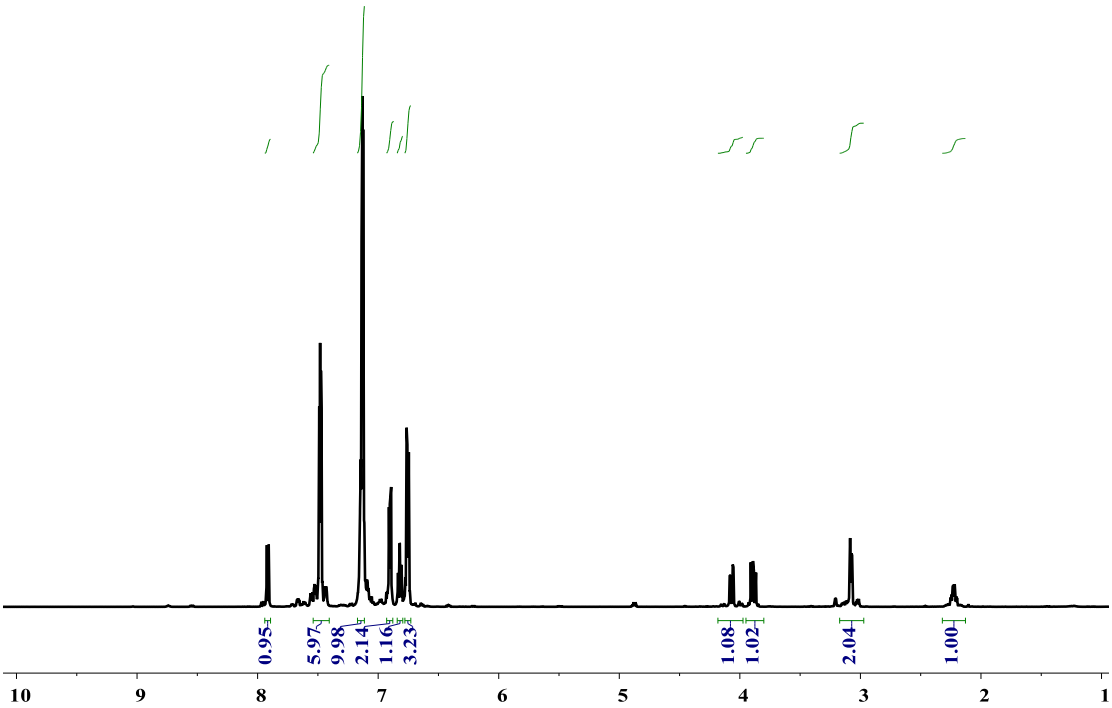
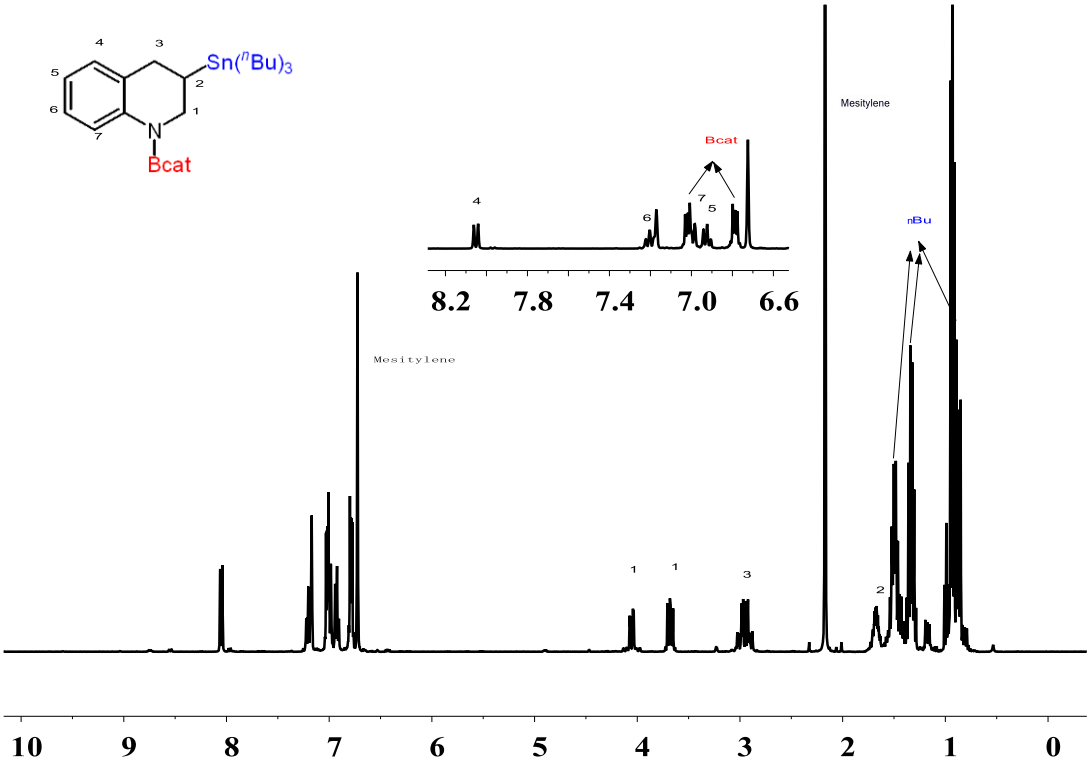
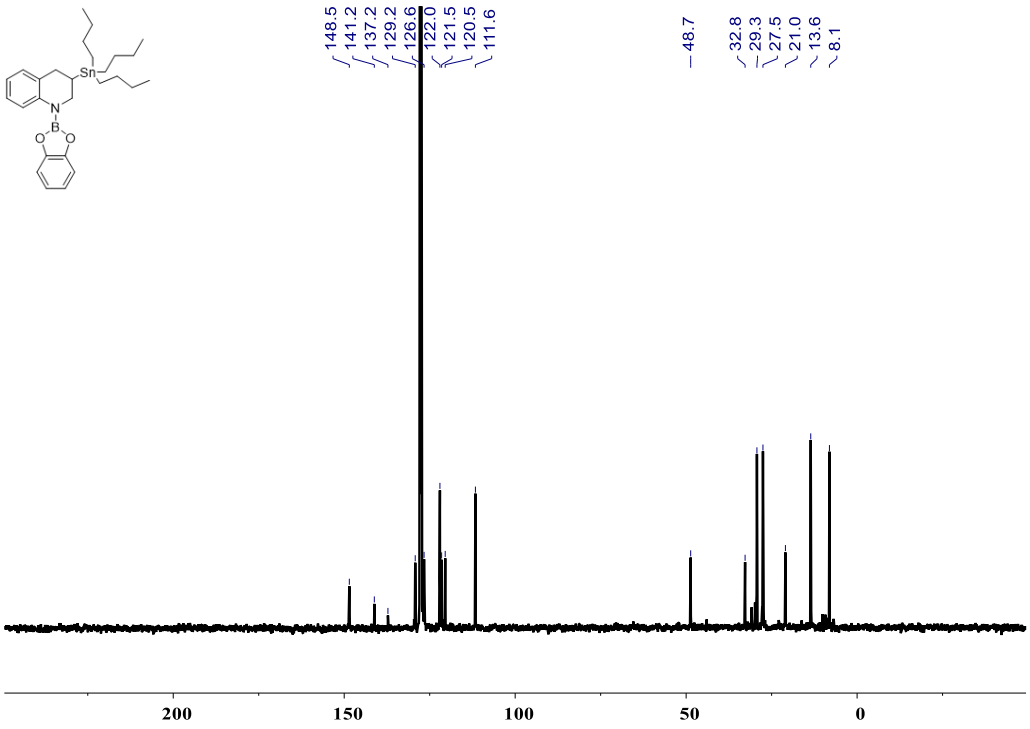


Figure S10 In-situ ^{1}H NMR spectra for changing (^{n}Bu)$_3$SnH to Ph$_3$SnH.

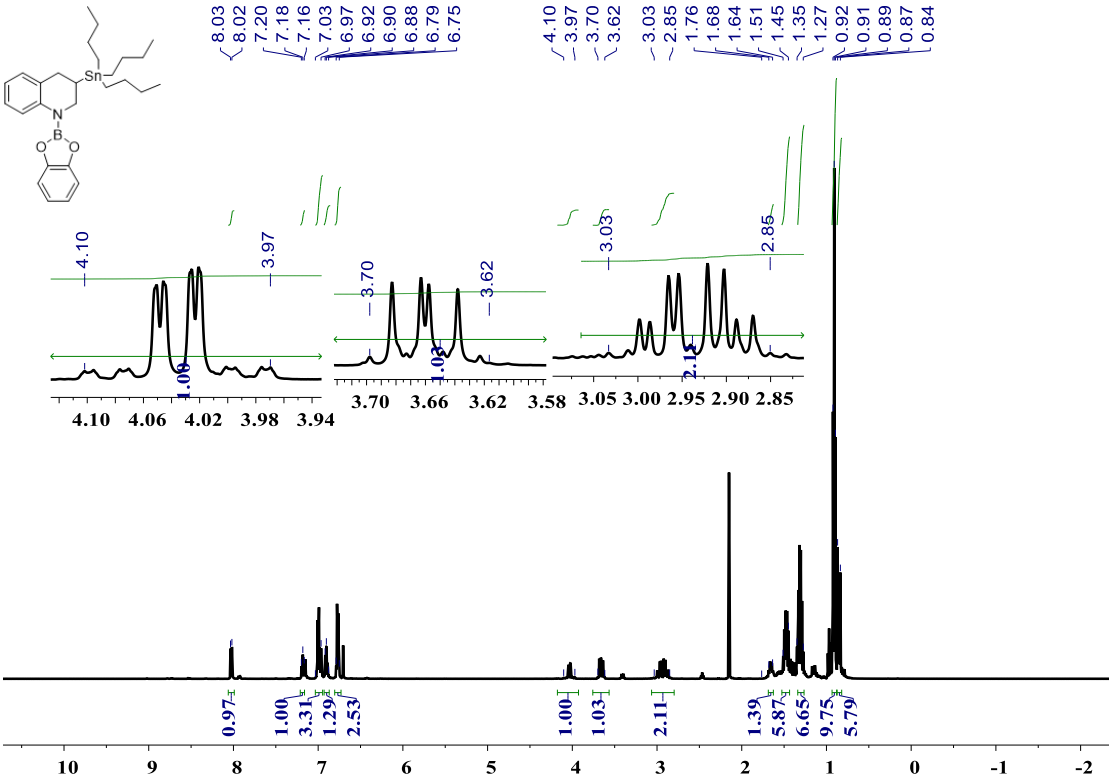
10. NMR spectra



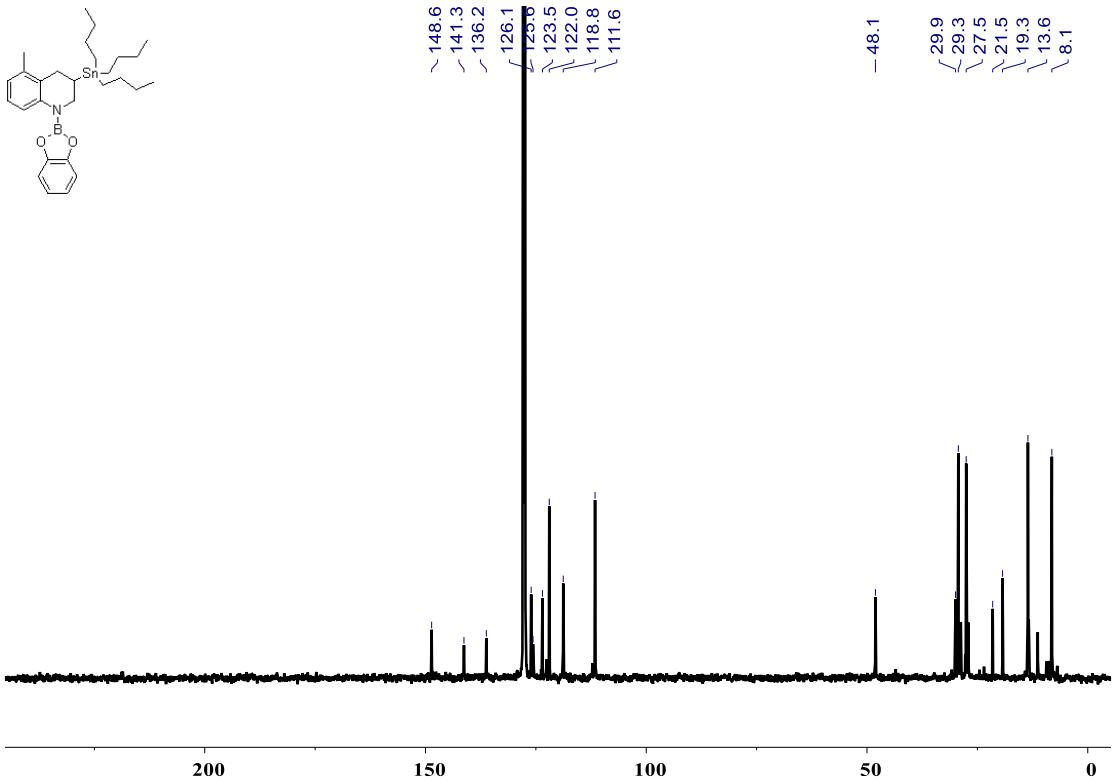
Assignment of peaks in the ^{1}H NMR spectrum of the reaction crude mixture for **1a**



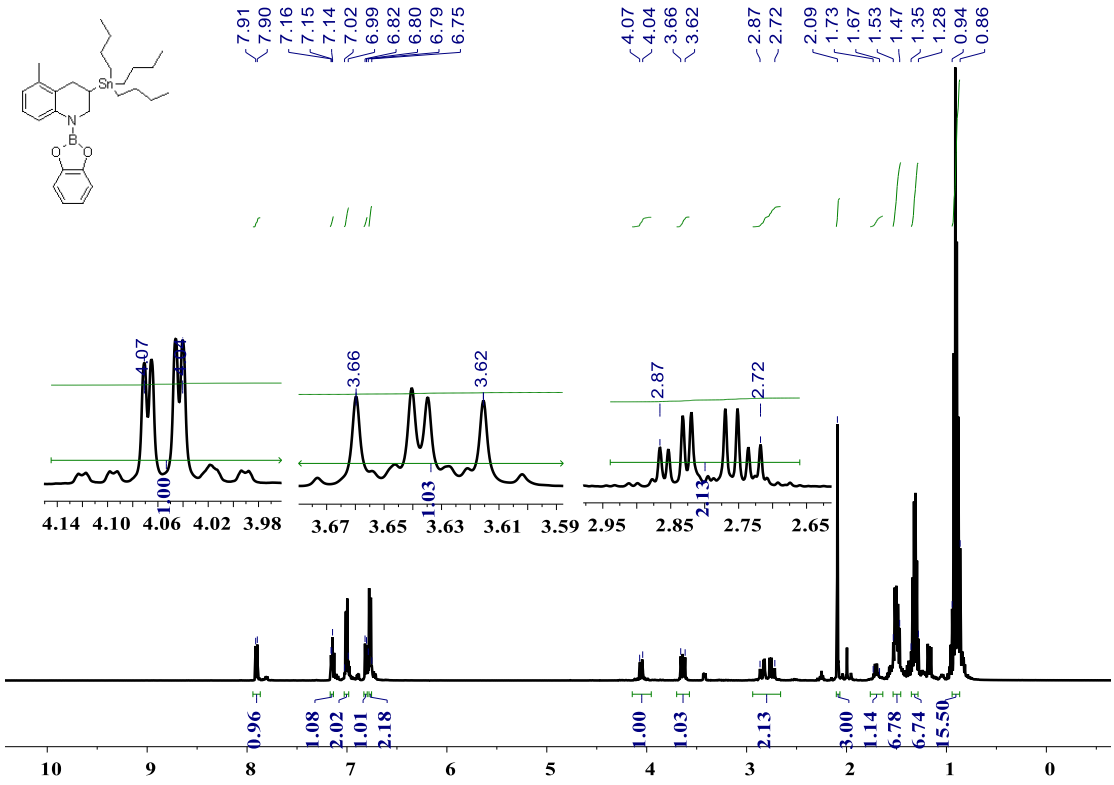
^{13}C NMR spectrum of 1-(benzo[d][1,3,2] dioxaborol-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10a**) (126 MHz, C_6D_6)



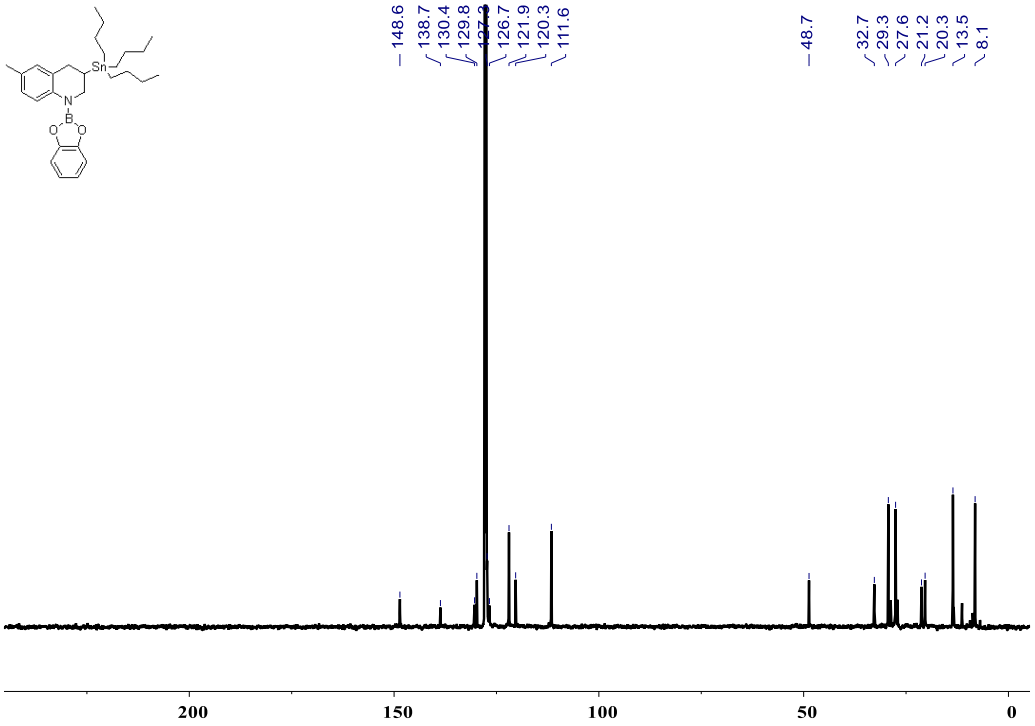
^{1}H NMR spectrum of 1-(benzo[d][1,3,2] dioxaborol-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10a**) (500 MHz, C_6D_6)



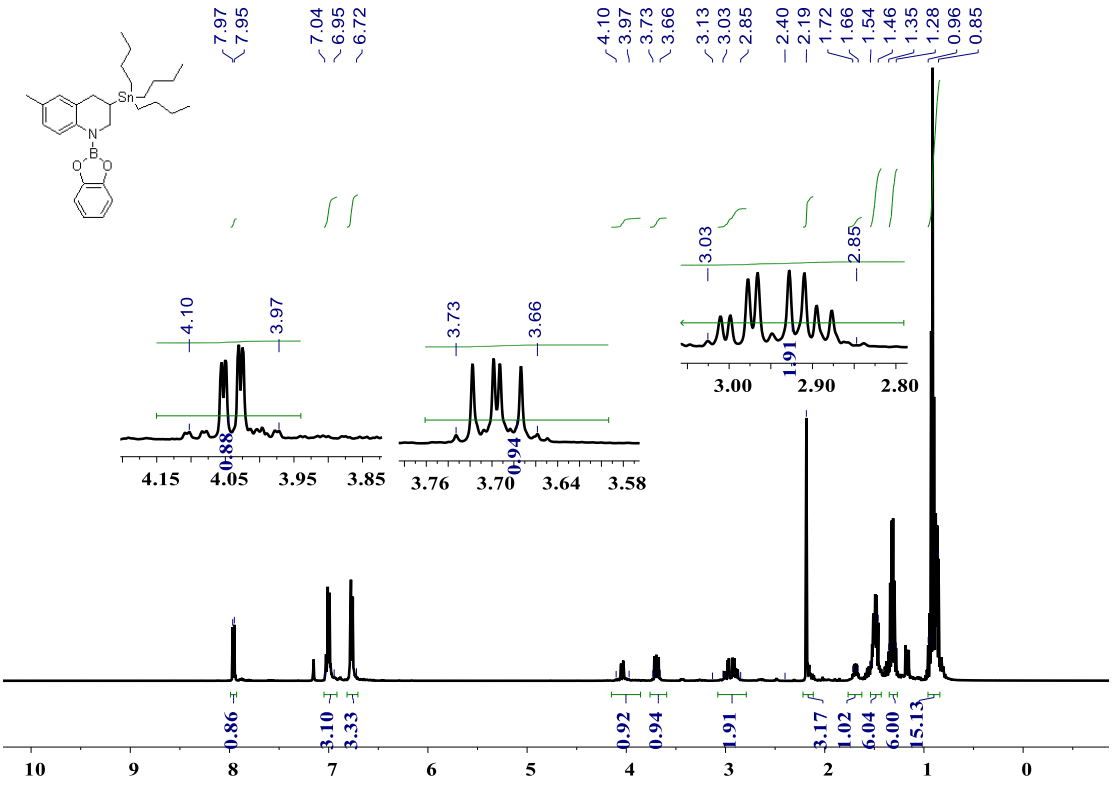
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-5-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10e**) (126 MHz, C_6D_6)



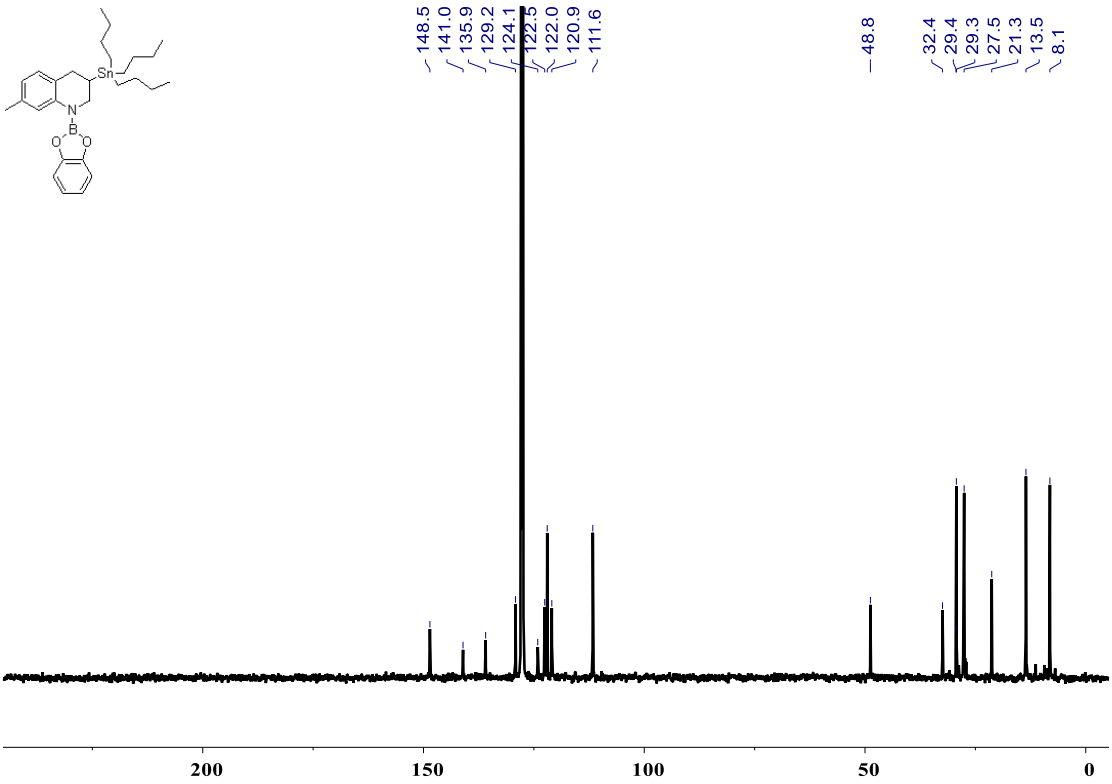
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-5-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10e**) (500 MHz, C_6D_6)



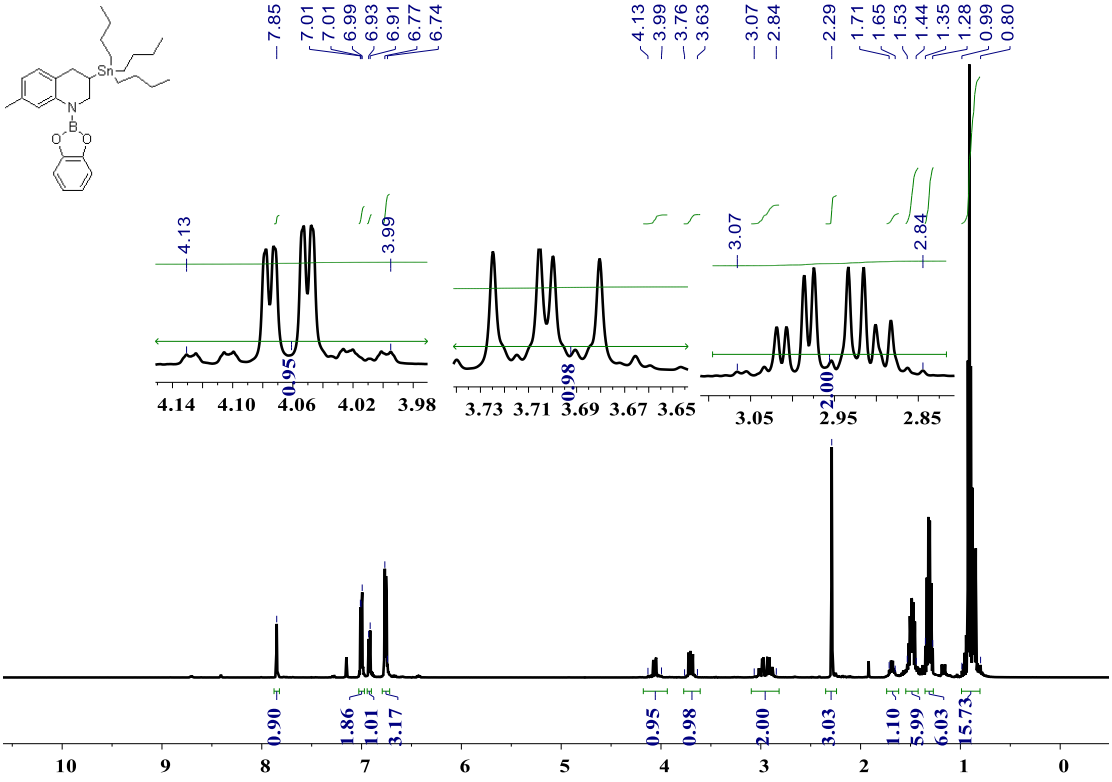
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10f**) (126 MHz, C_6D_6)



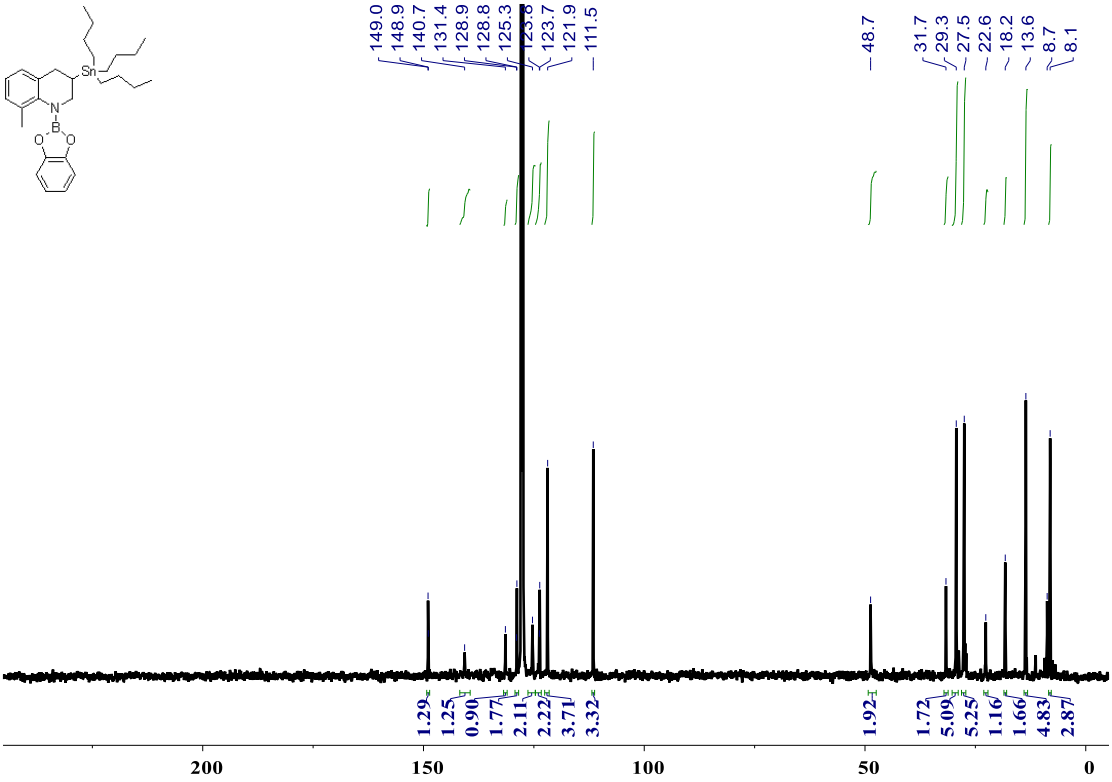
^{1}H NMR spectrum of 1-(benzo[d][1,3,2] dioxaborol-2-yl)-6-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10f**) (500 MHz, C_6D_6)



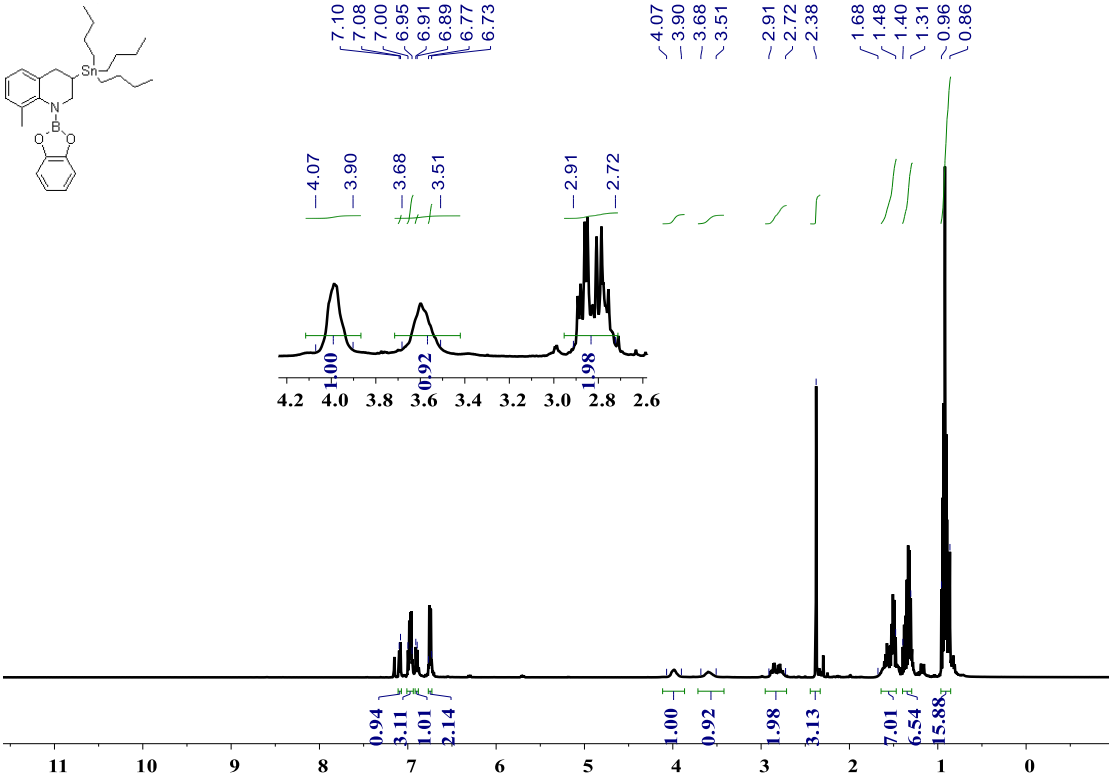
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-7-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10g**) (126 MHz, C_6D_6)



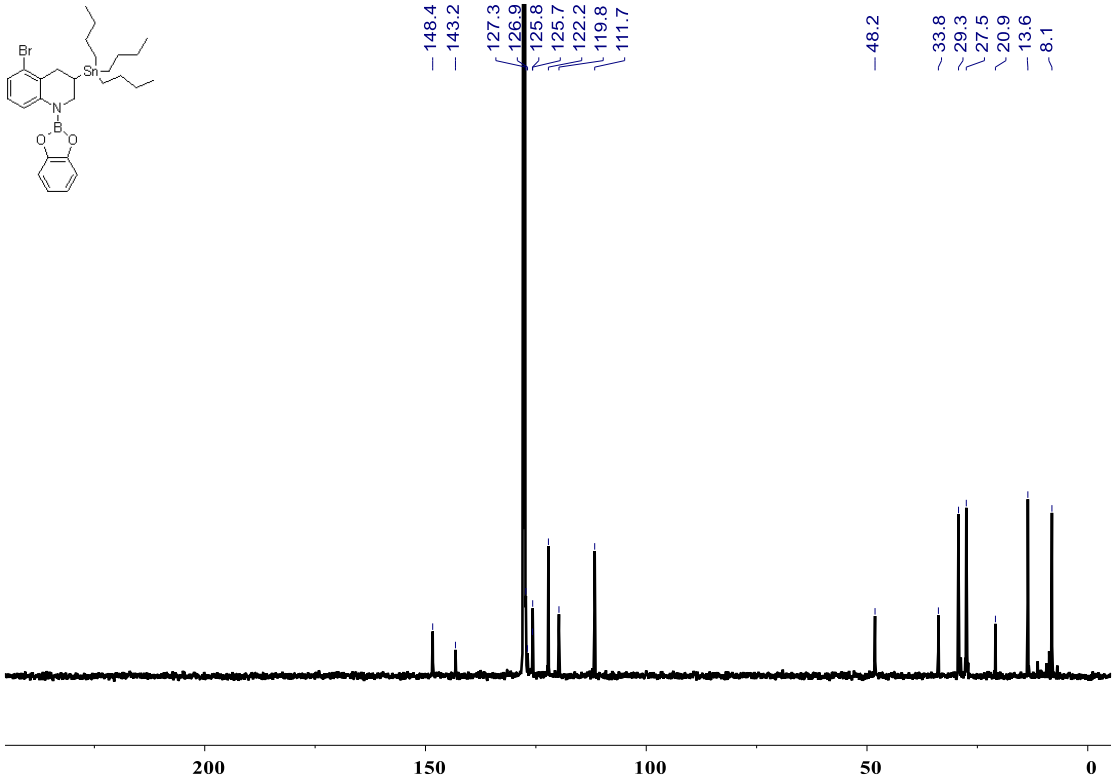
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-7-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10g**) (500 MHz, C_6D_6)



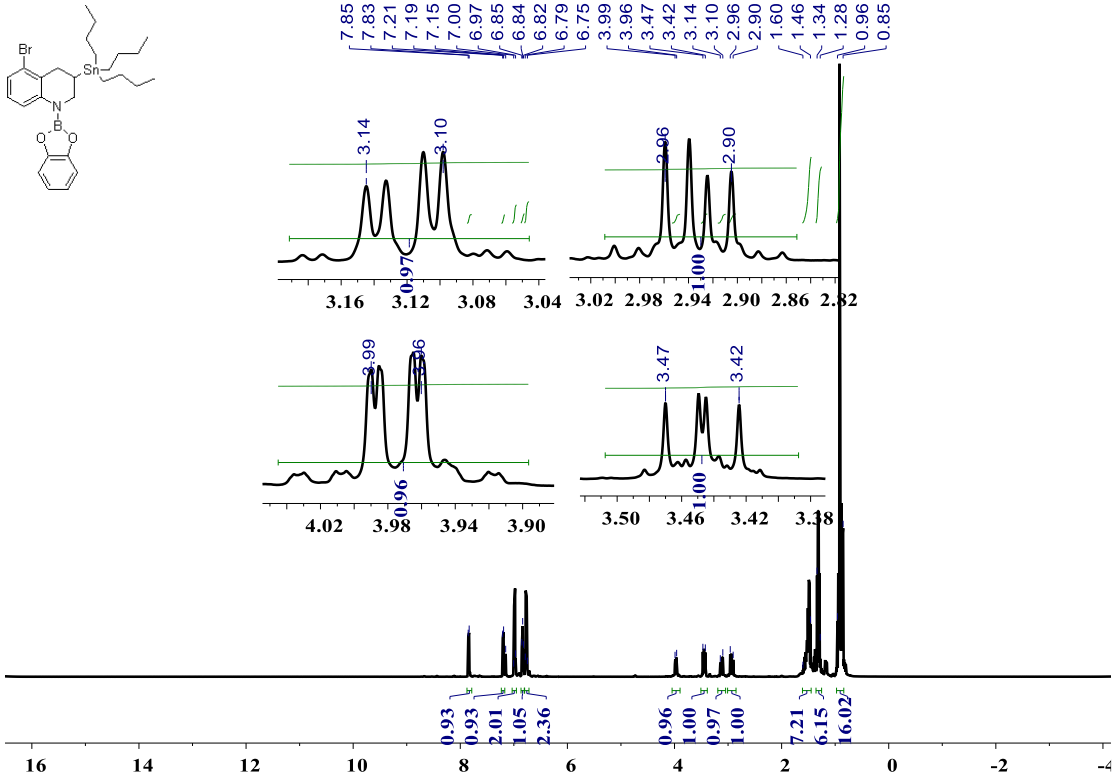
^{13}C NMR spectrum of 1-(benzo[d][1,3,2] dioxaborol-2-yl)-8-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10h**) (126 MHz, C_6D_6)



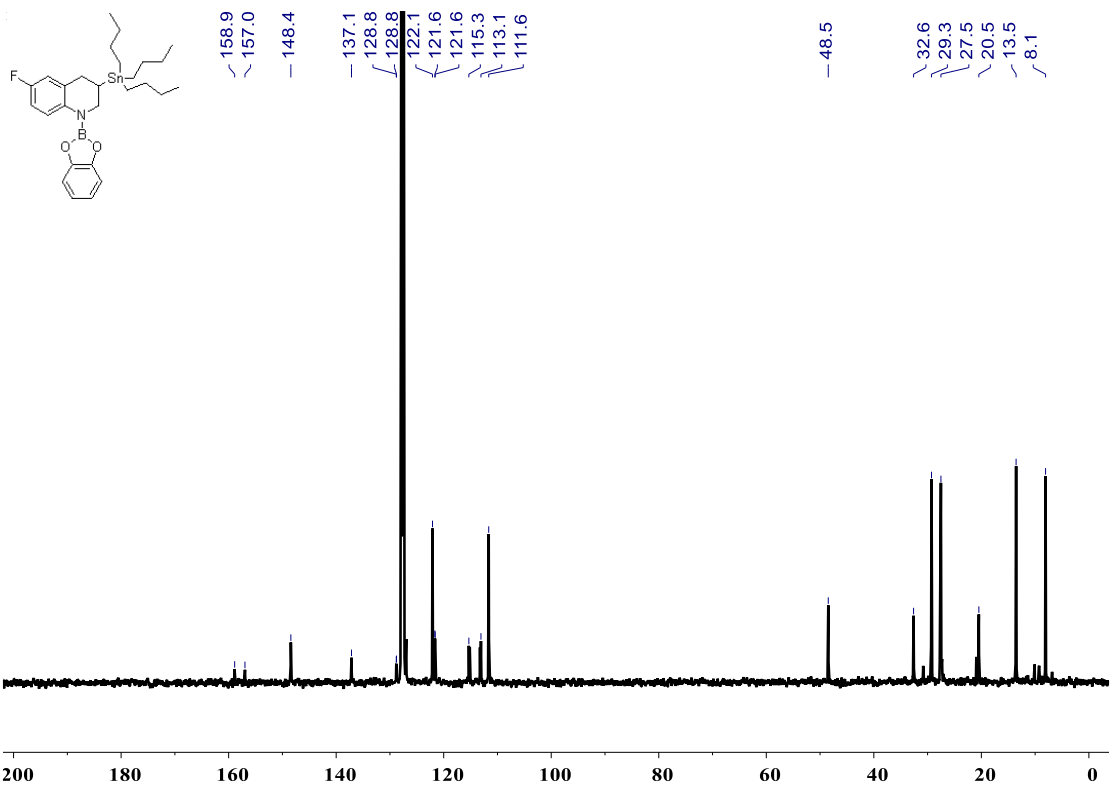
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8-methyl-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10h**) (500 MHz, C_6D_6)



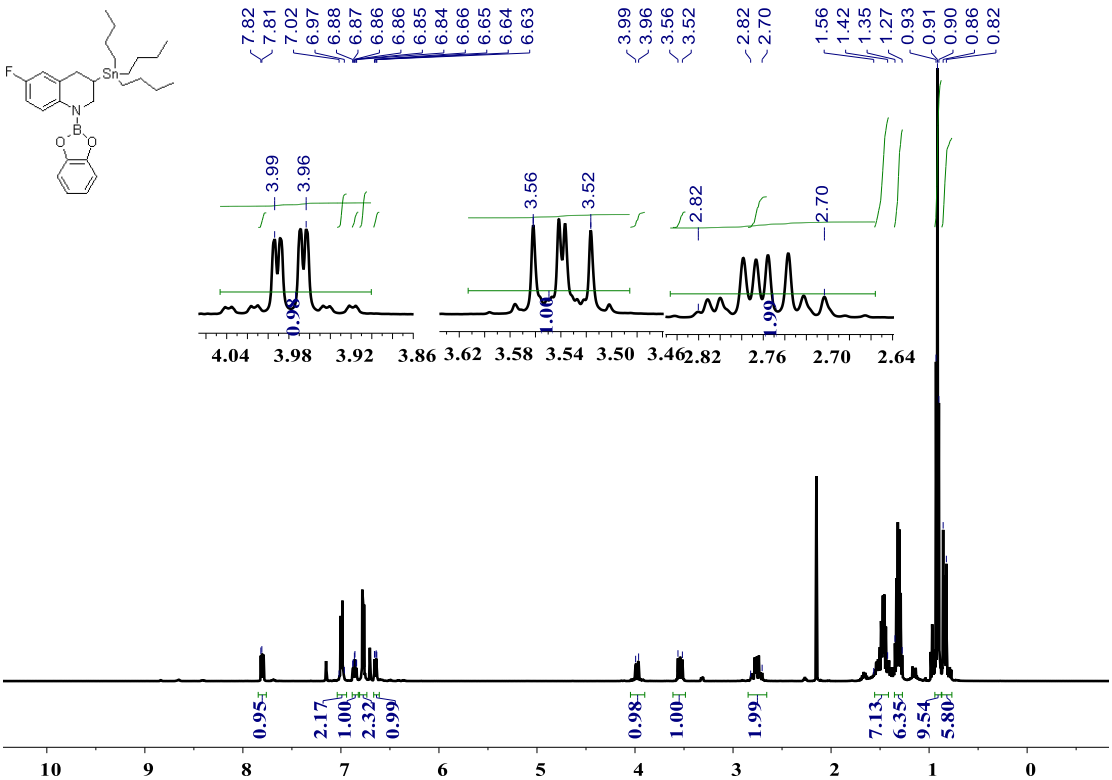
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-5-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10i**) (126 MHz, C_6D_6)



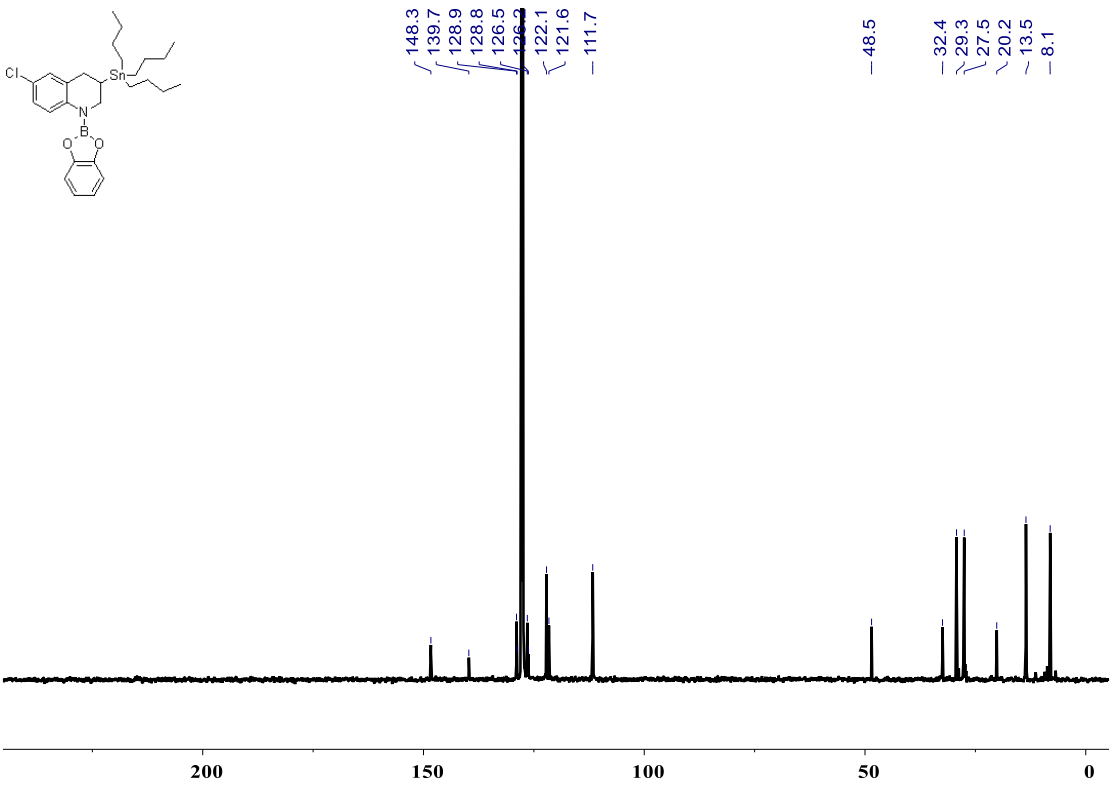
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-5-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10i**) (500 MHz, C_6D_6)



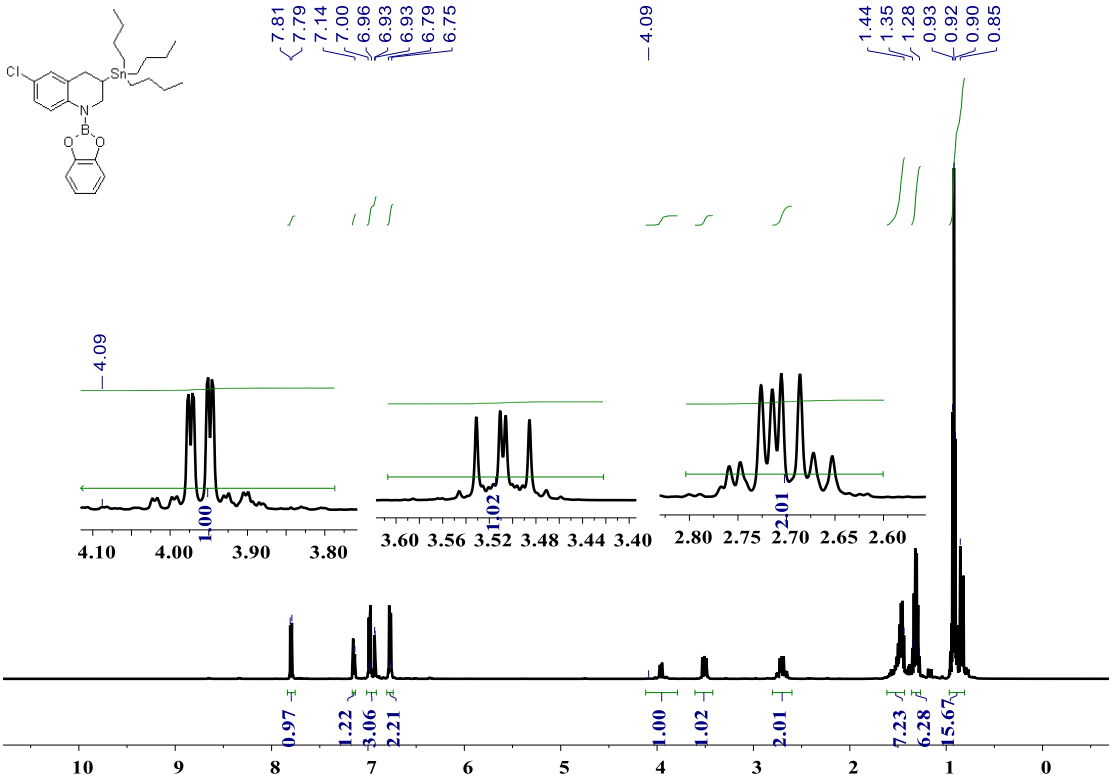
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-fluoro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10j**) (126 MHz, C_6D_6)



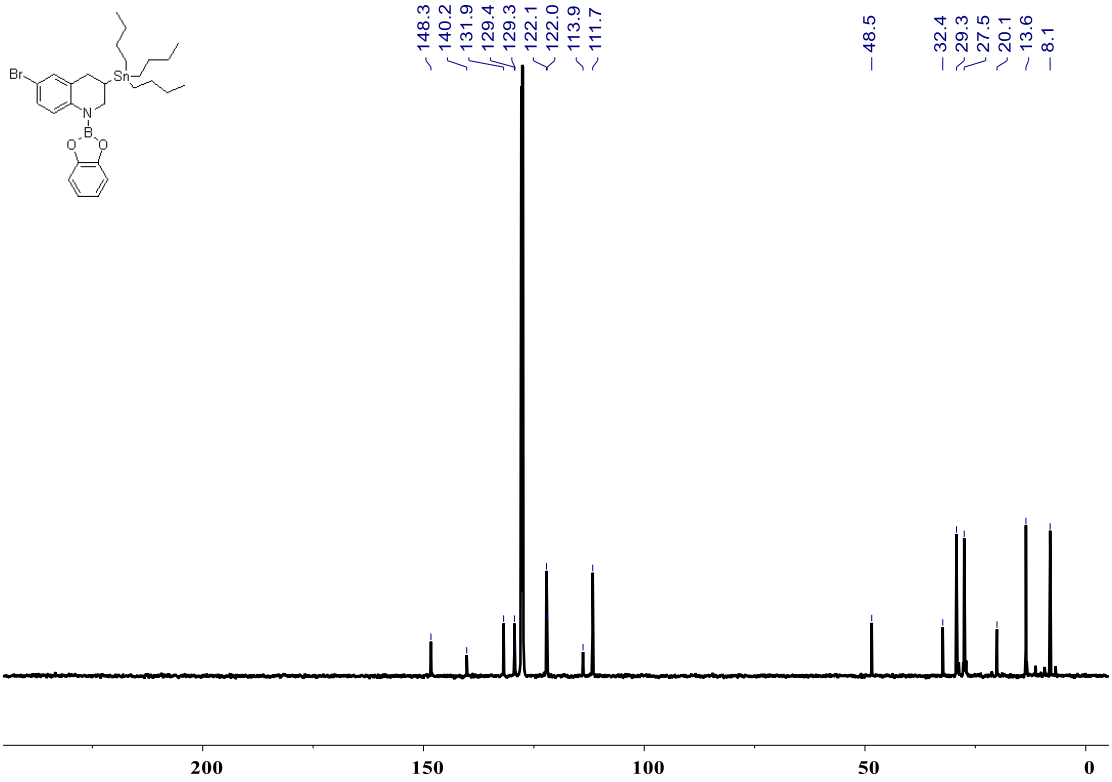
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-fluoro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10j**) (500 MHz, C_6D_6)



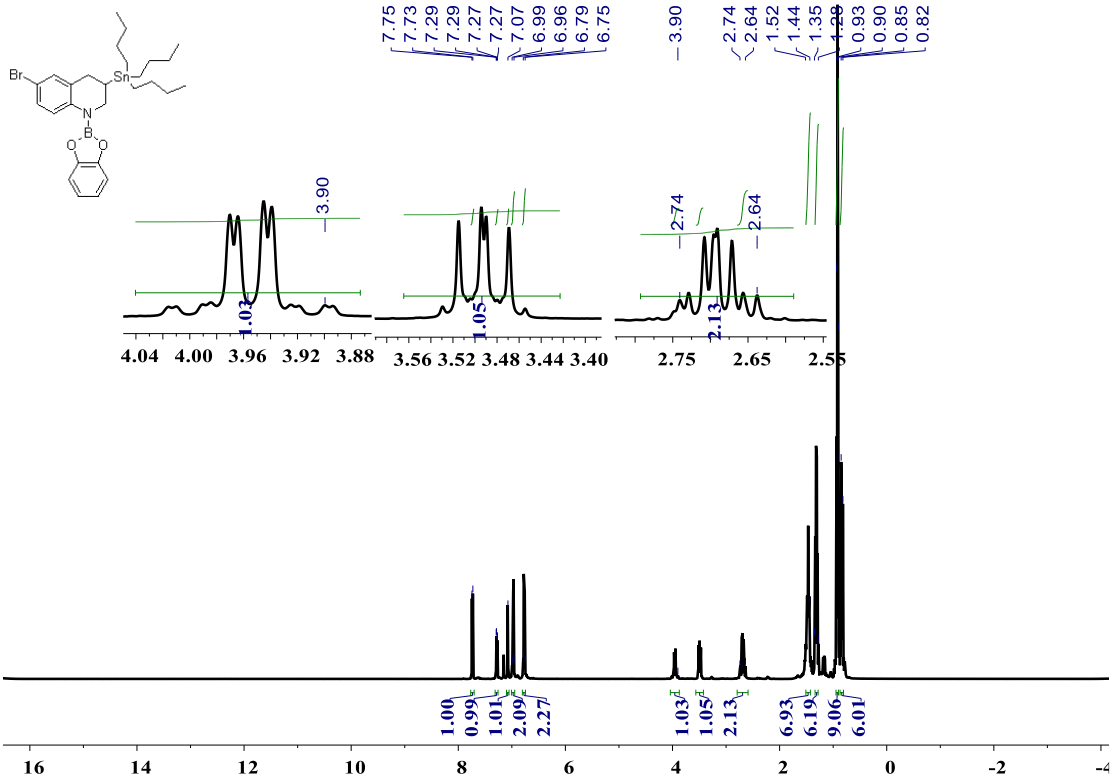
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10k**) (126 MHz, C_6D_6)



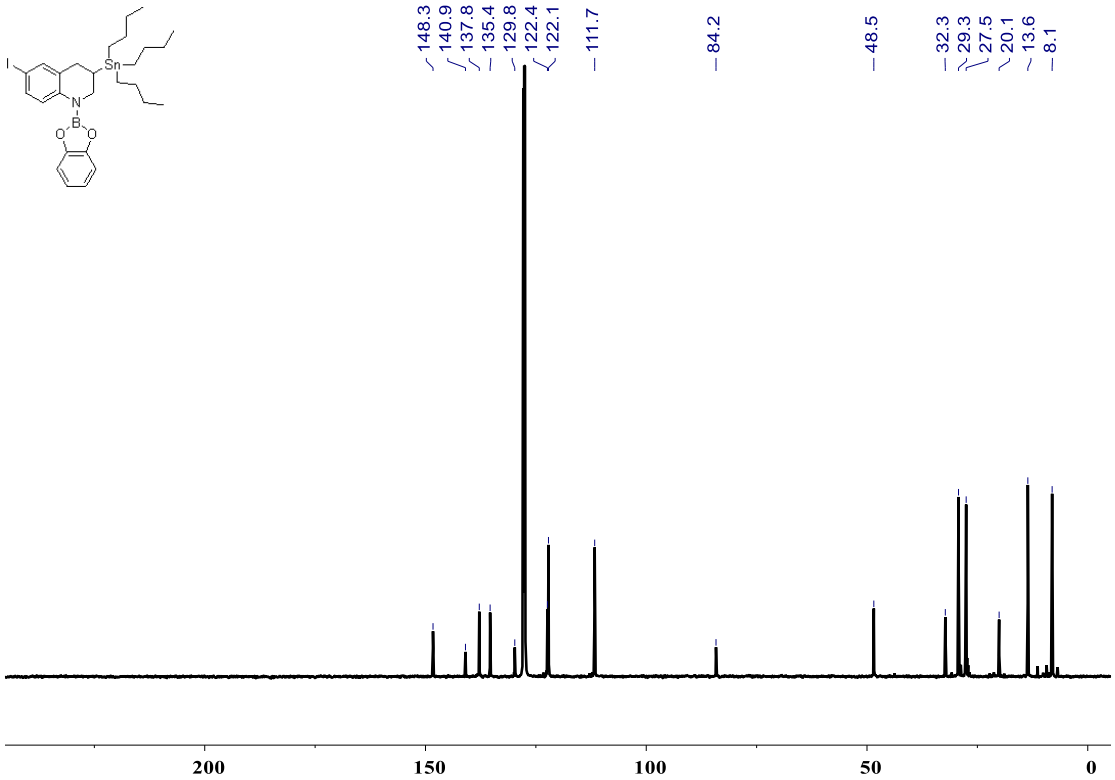
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10k**) (500 MHz, C_6D_6)



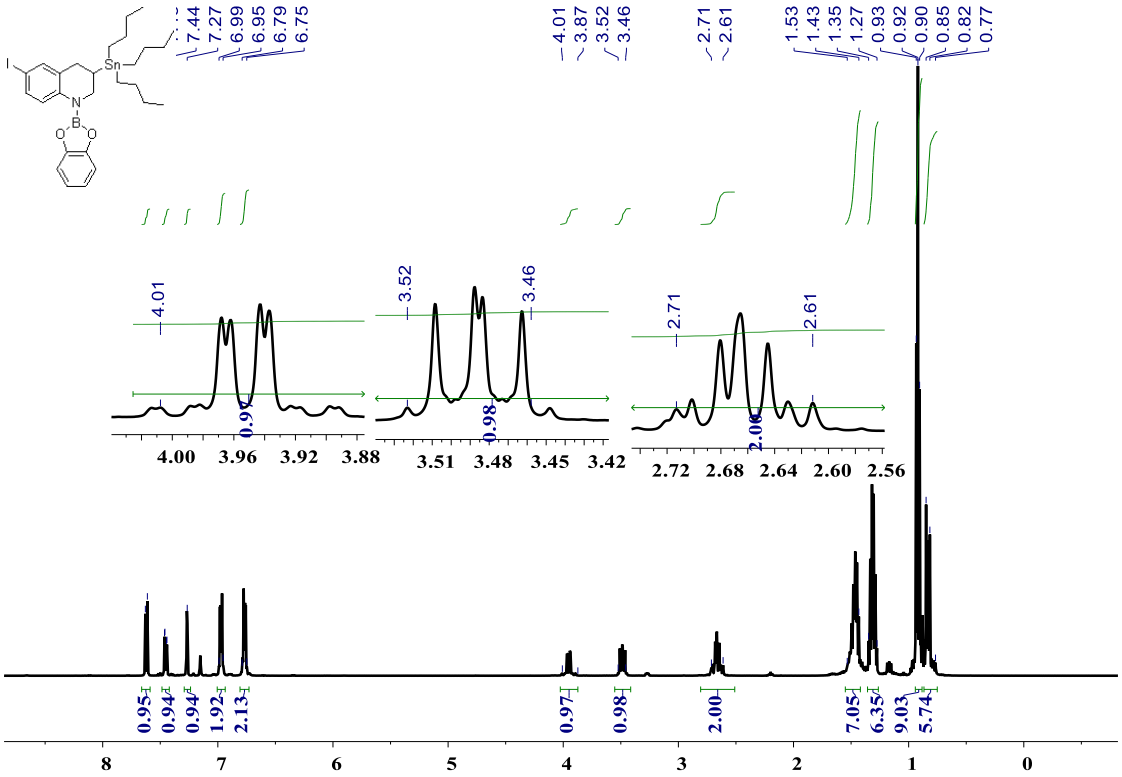
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10l**) (126 MHz, C_6D_6)



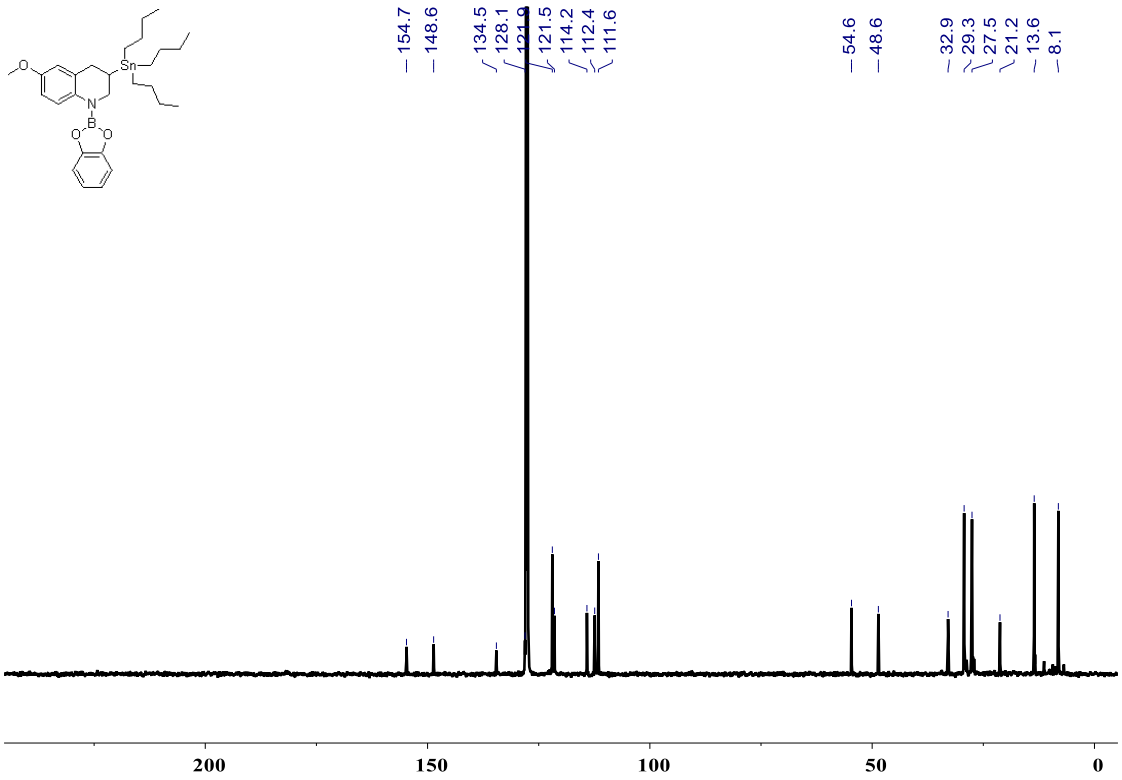
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10l**) (500 MHz, C_6D_6)



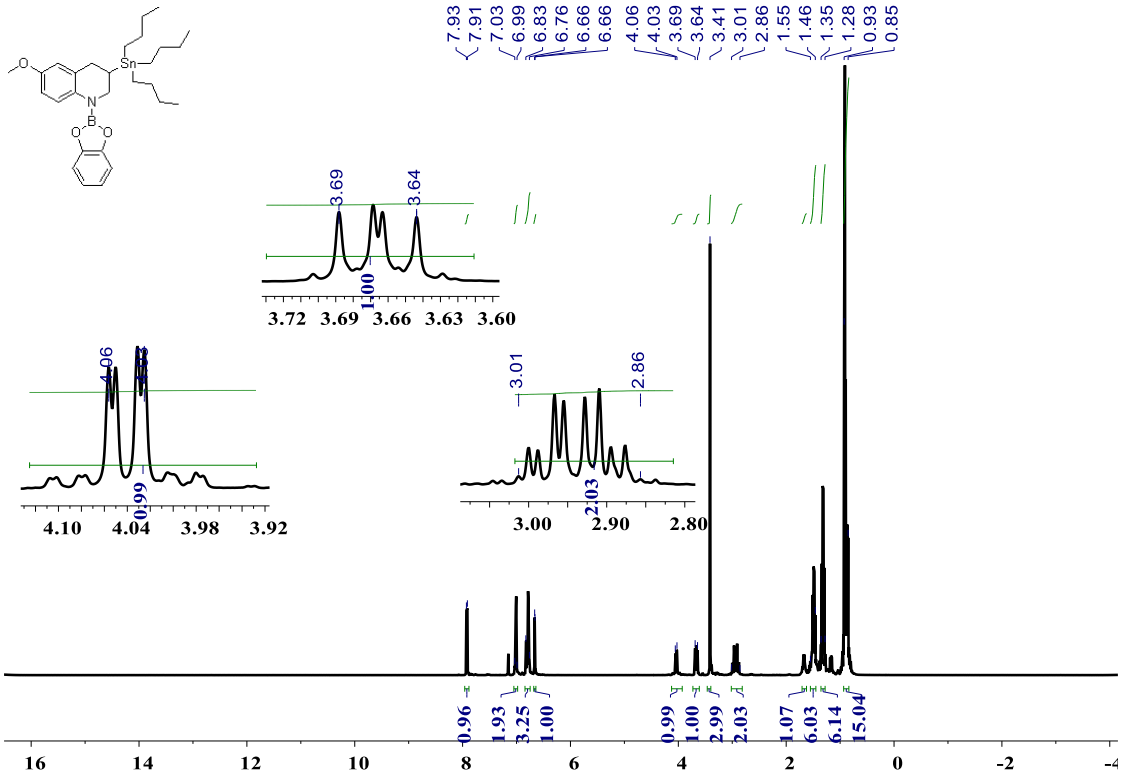
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-iodo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10m**) (126 MHz, C_6D_6)



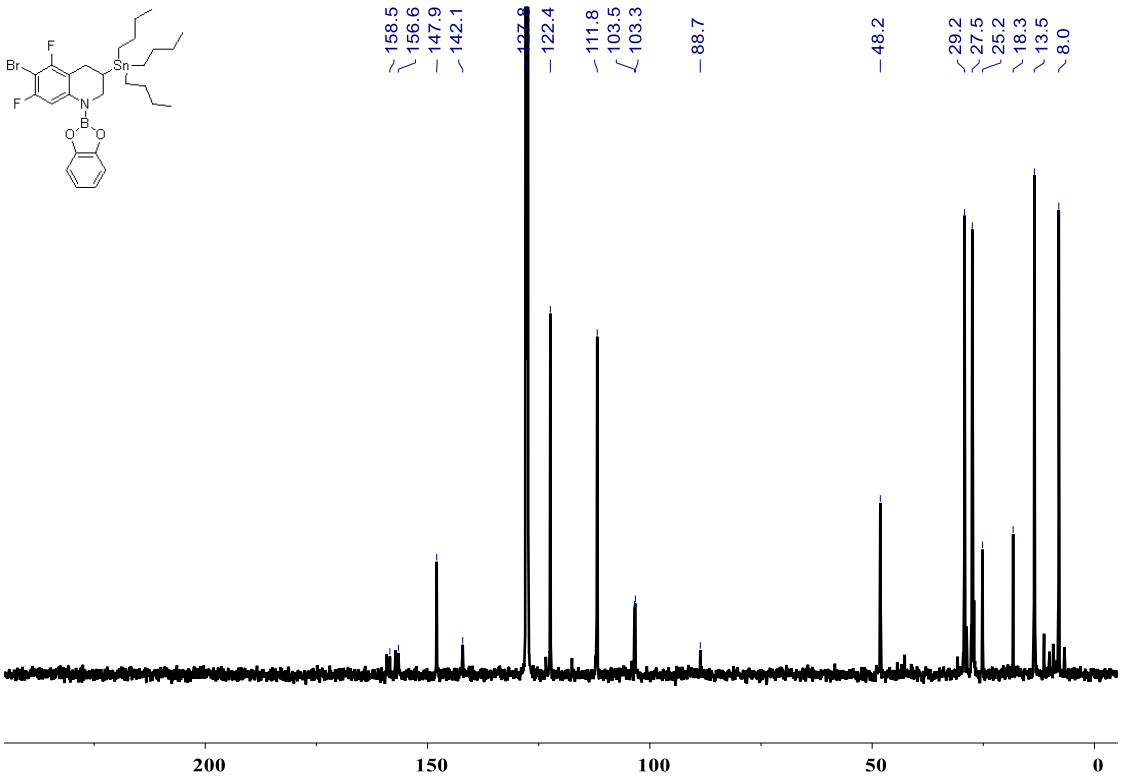
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-iodo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10m**) (500 MHz, C_6D_6)



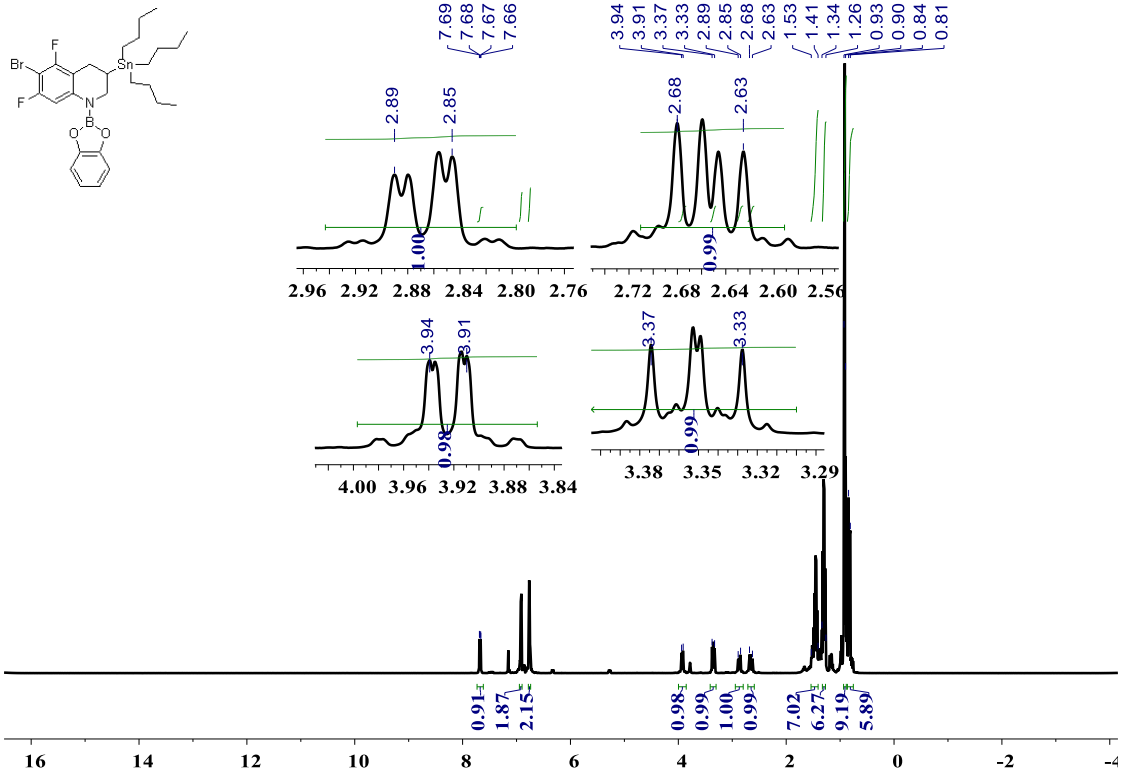
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-methoxy-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10n**) (126 MHz, C_6D_6)



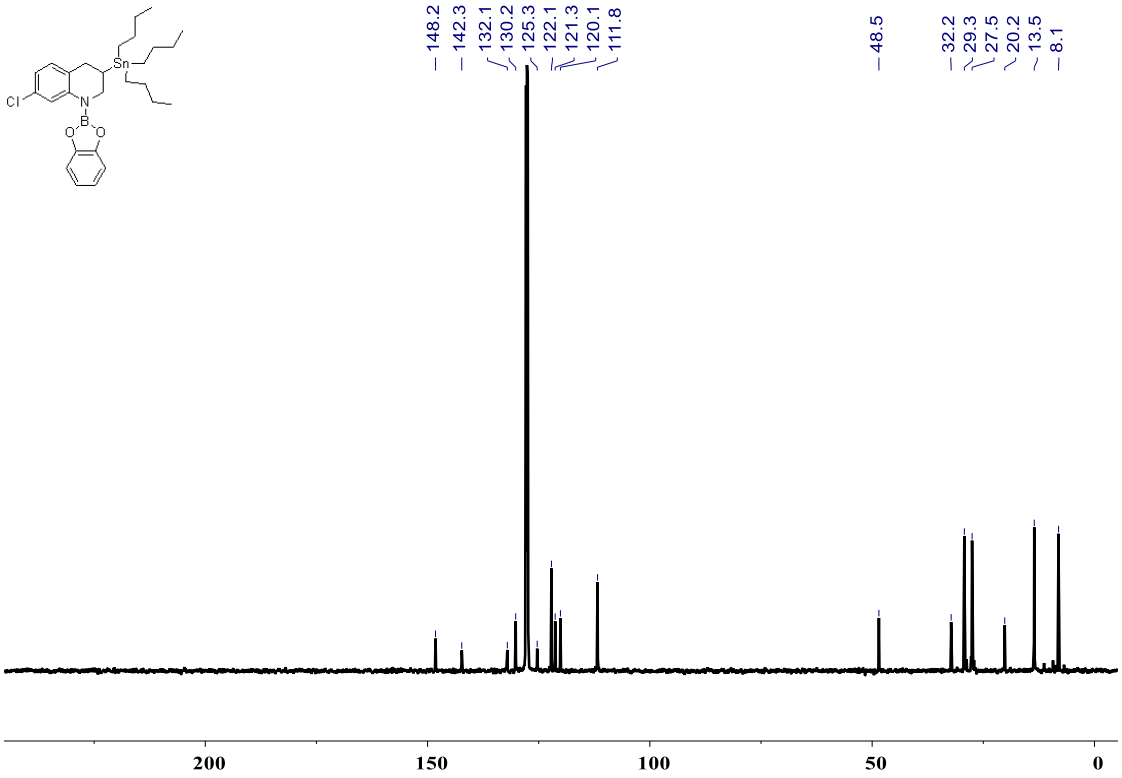
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-6-methoxy-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10n**) (500 MHz, C_6D_6)



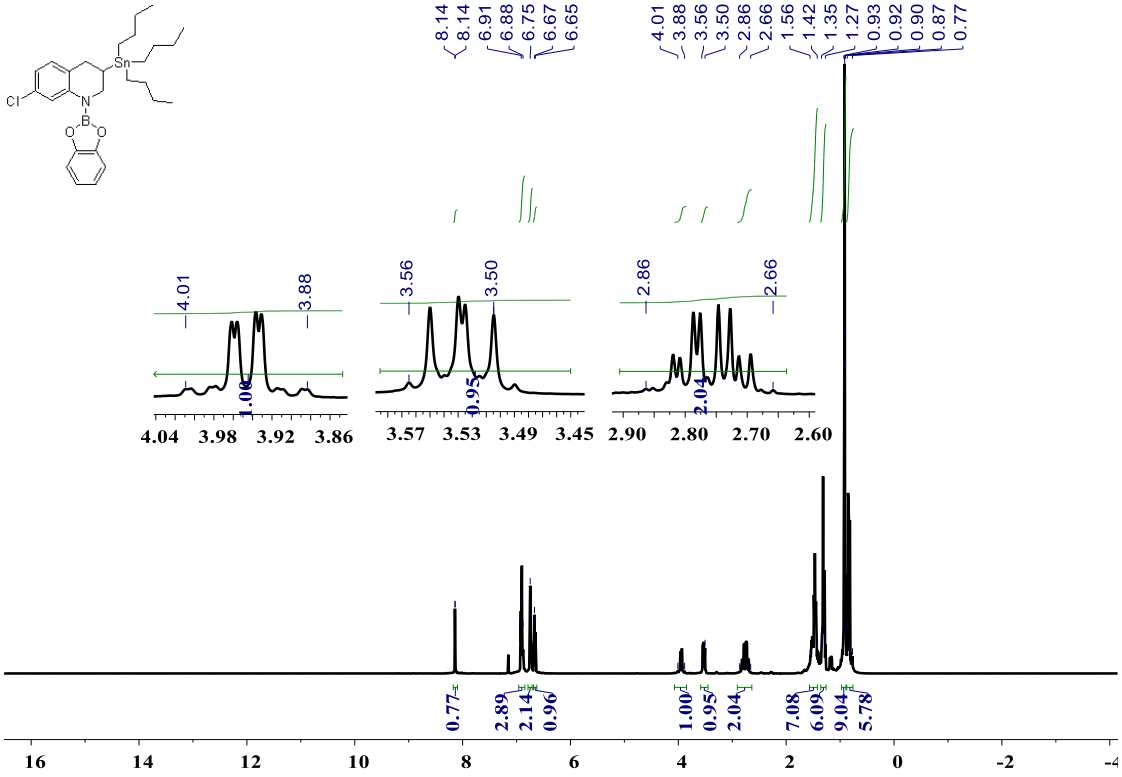
^{13}C NMR spectrum of 6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10o**) (126 MHz, C_6D_6)



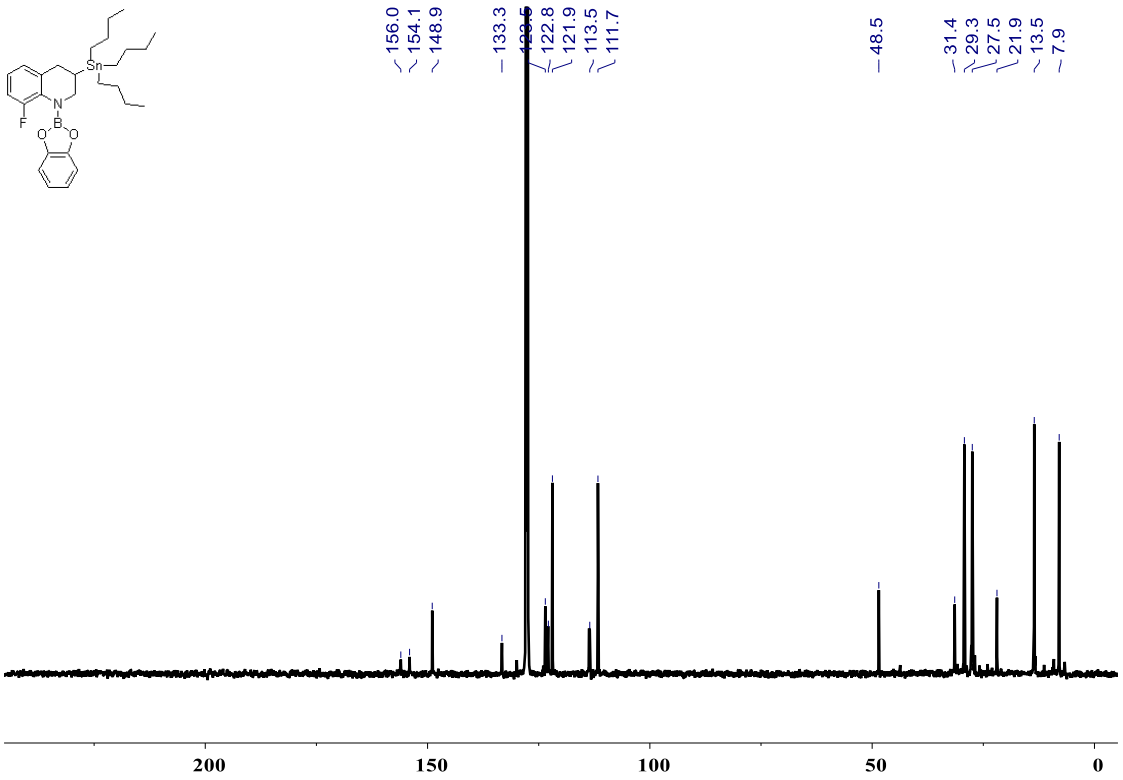
^{1}H NMR spectrum of 6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10o**) (500 MHz, C_6D_6)



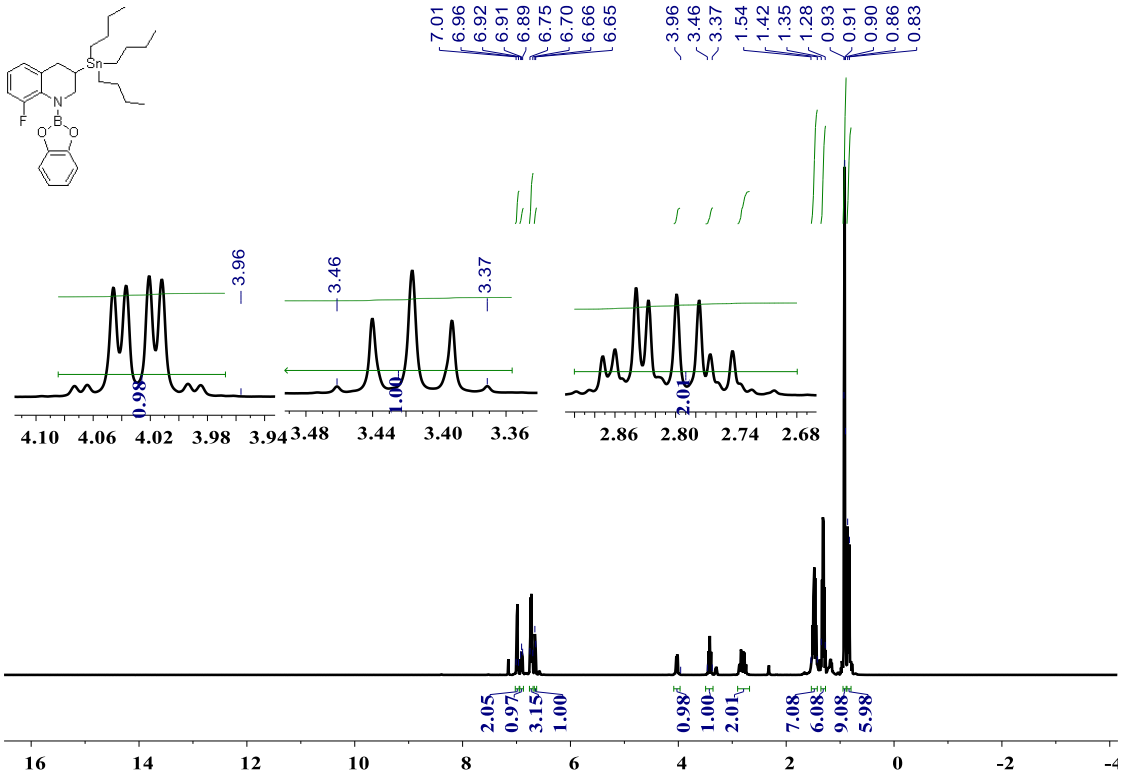
^{13}C NMR spectrum of 1-(benzo[d][1,3,2] dioxaborol-2-yl)-7-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10p**) (126 MHz, C_6D_6)



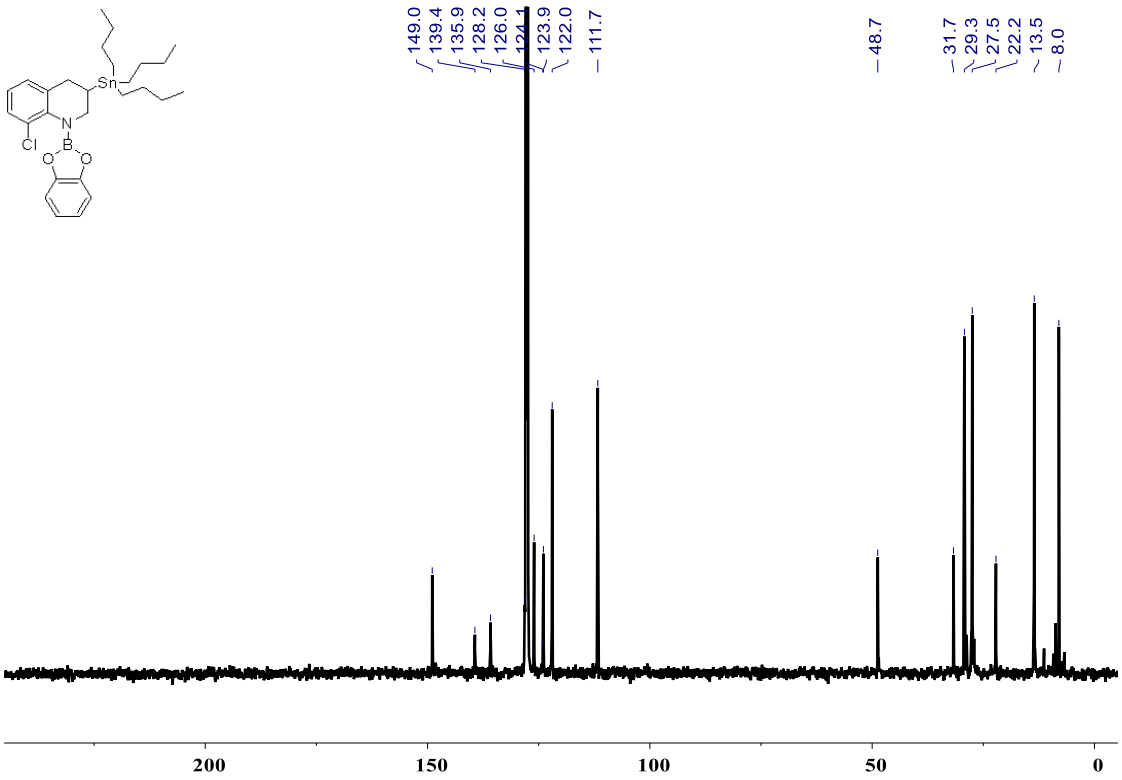
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-7-chloro-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**10p**) (500 MHz, C_6D_6)



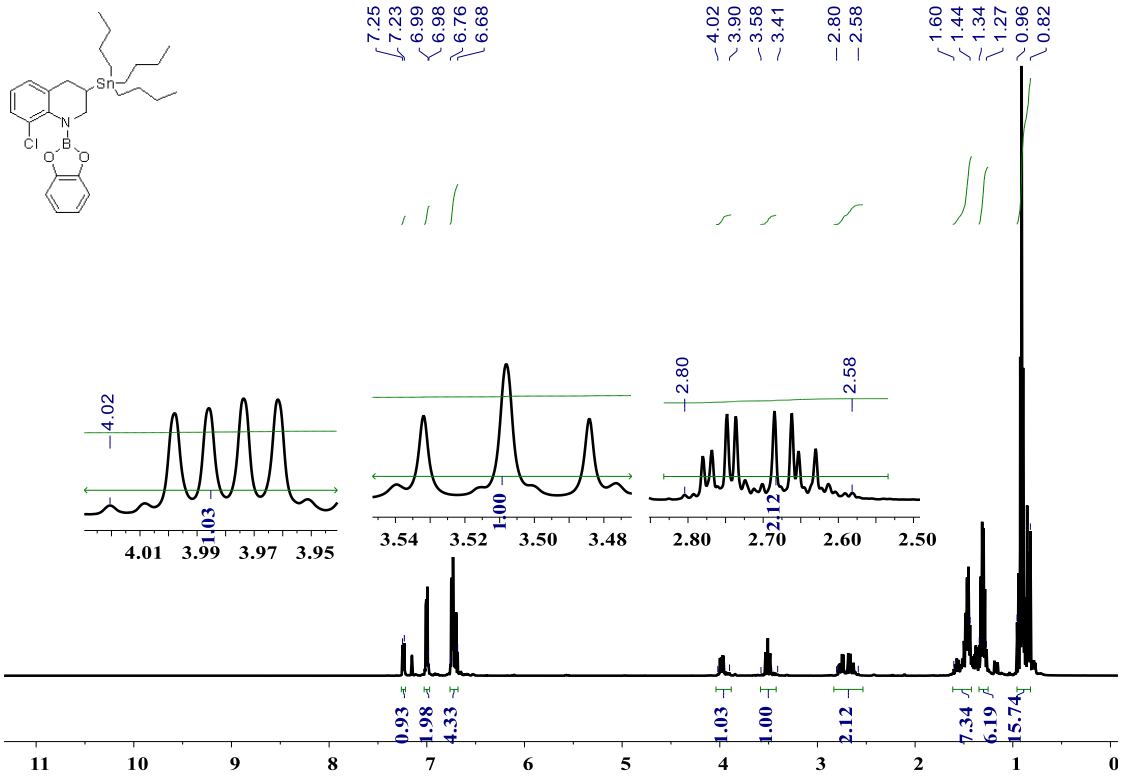
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8-fluoro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10q**) (126 MHz, C_6D_6)



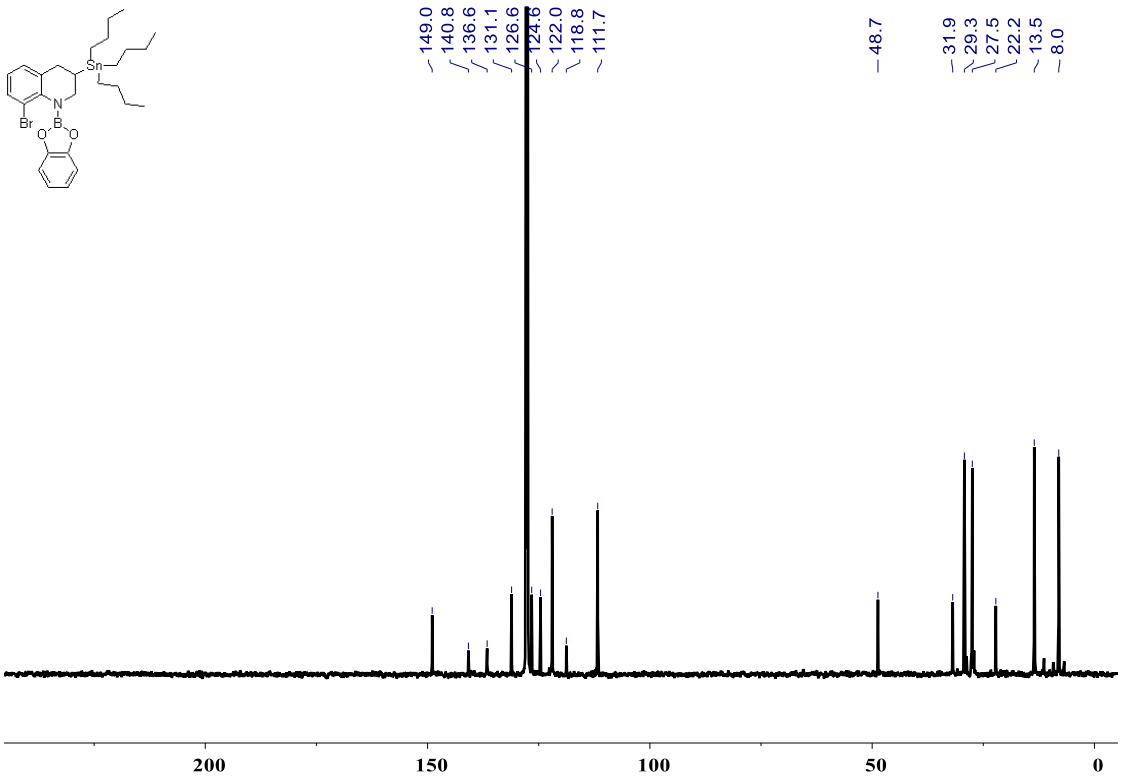
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8-fluoro -3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline(**10q**) (500 MHz, C_6D_6)



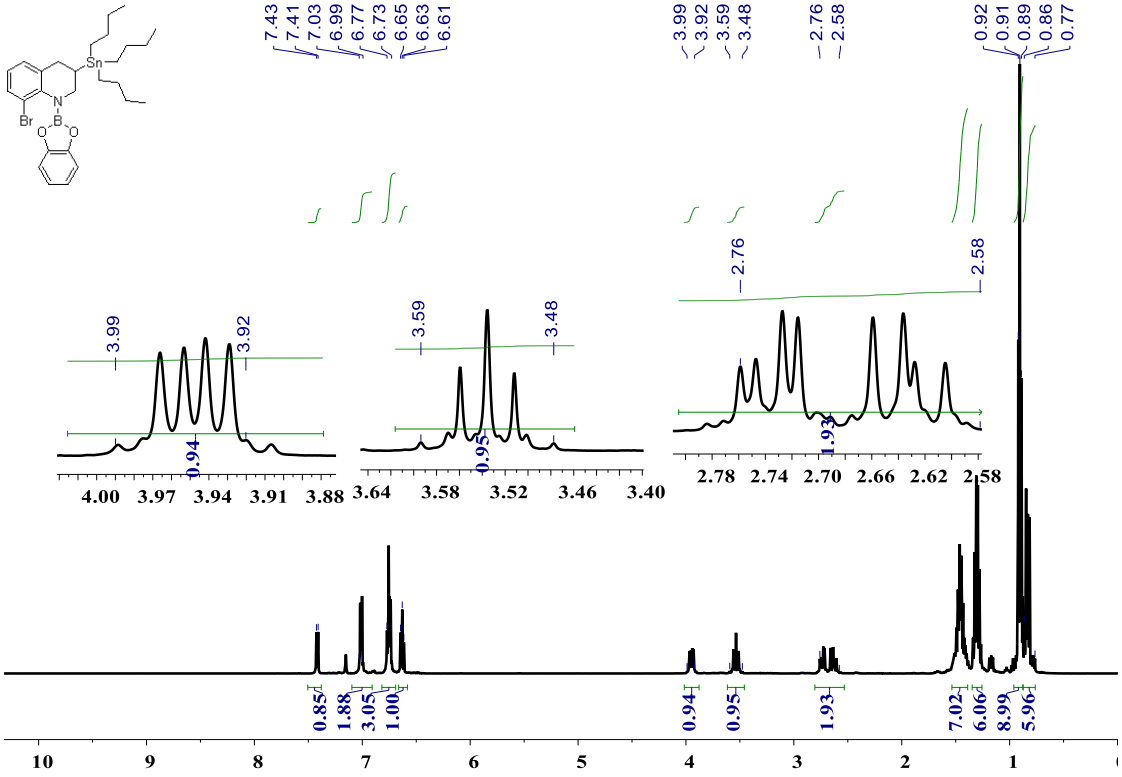
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8-chloro-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10r**) (126 MHz, C_6D_6)



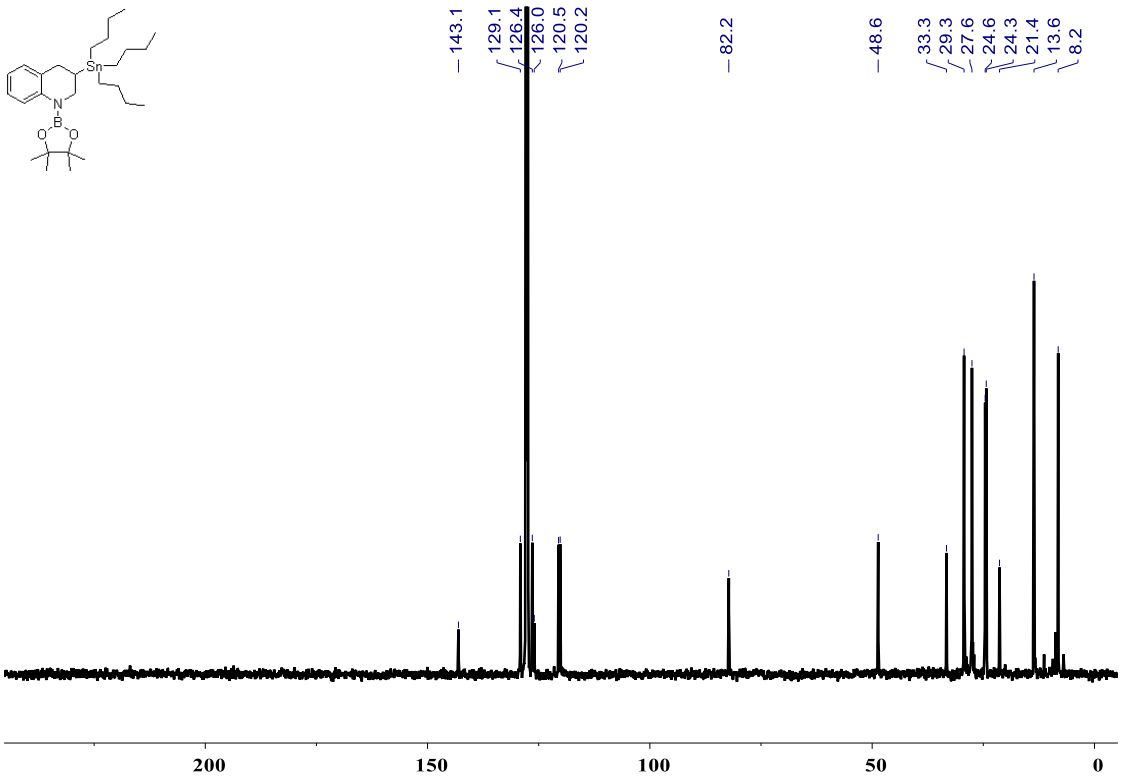
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8- chloro -3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline(**10r**) (500 MHz, C_6D_6)



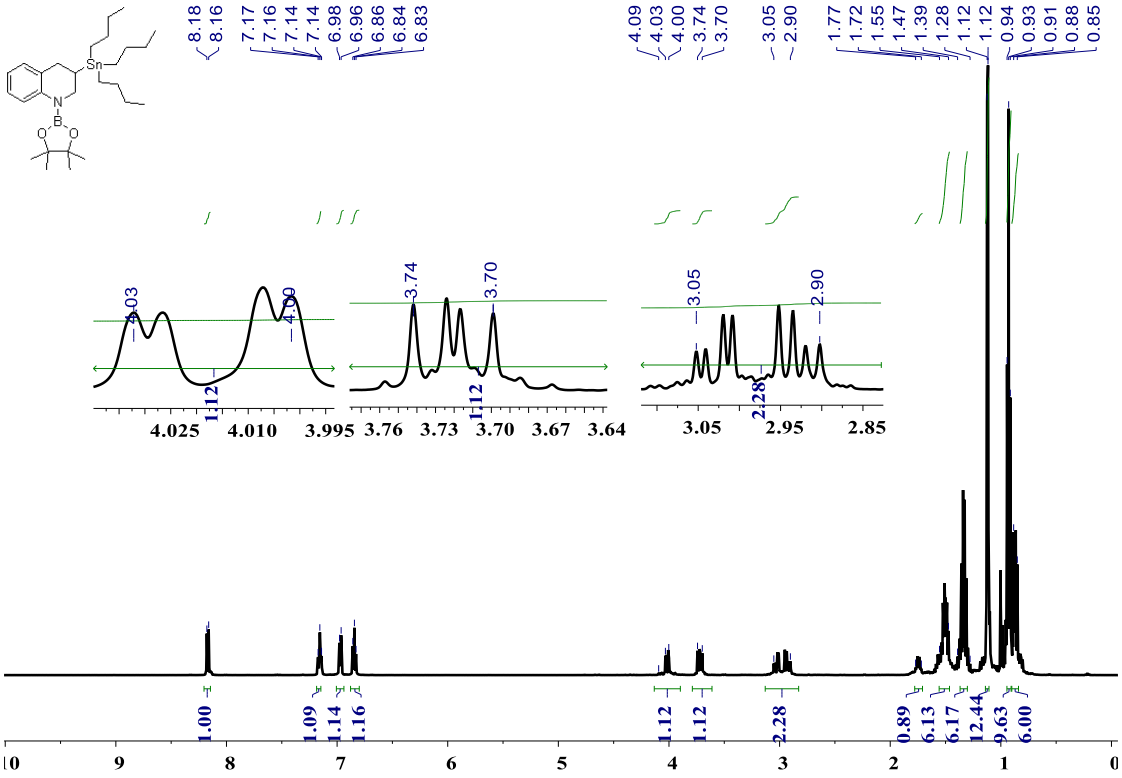
^{13}C NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8-bromo-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**10s**) (126 MHz, C_6D_6)



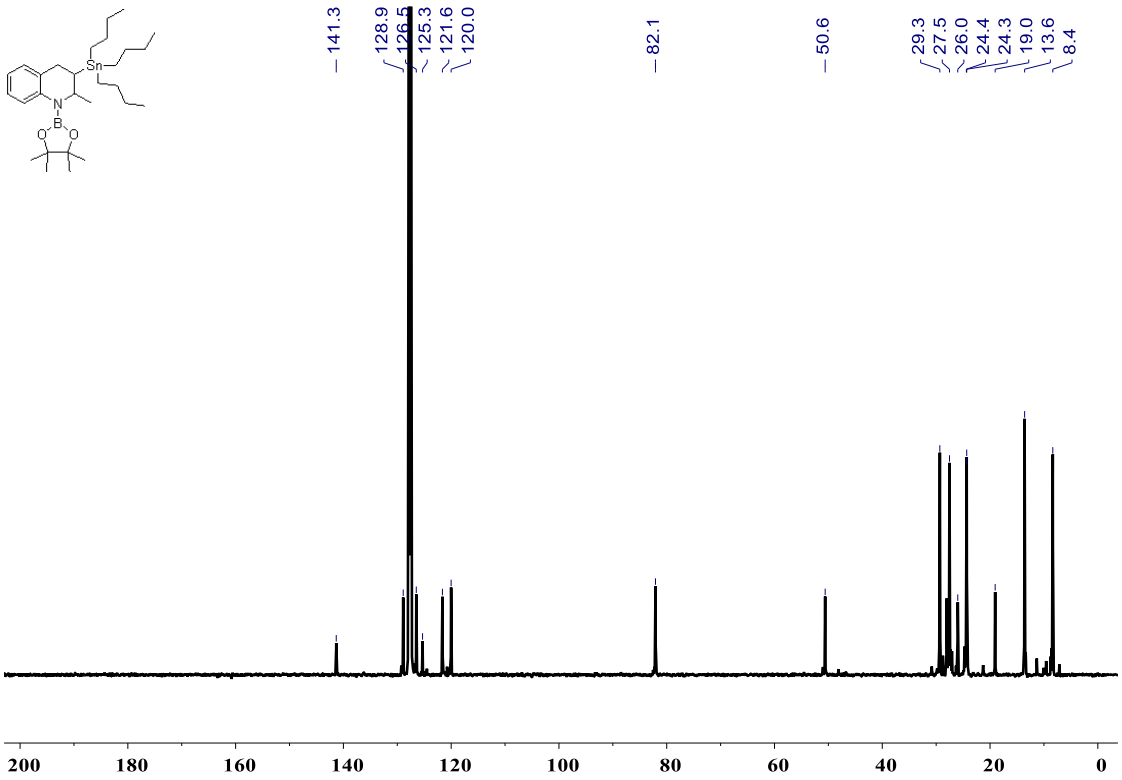
^{1}H NMR spectrum of 1-(benzo[d] [1,3,2] dioxaborol-2-yl)-8- bromo -3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline(**10s**) (500 MHz, C_6D_6)



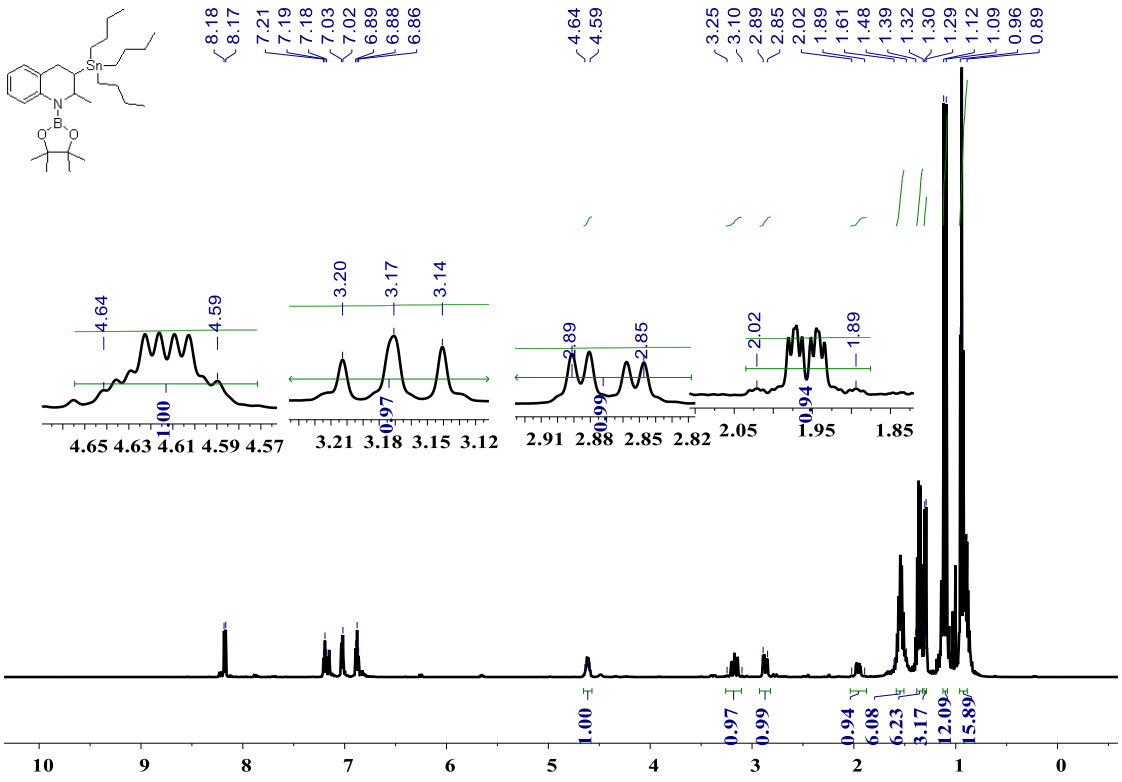
^{13}C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11a**) (126 MHz, C_6D_6)



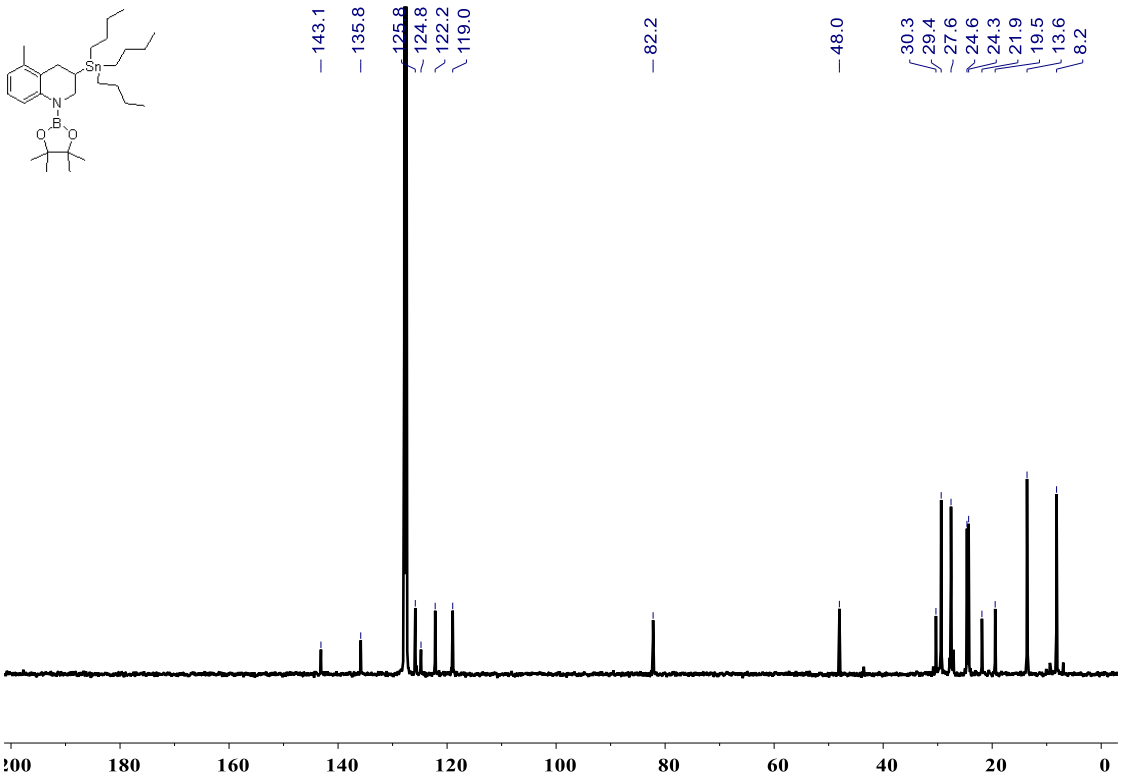
^{1}H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11a**) (500 MHz, C_6D_6)



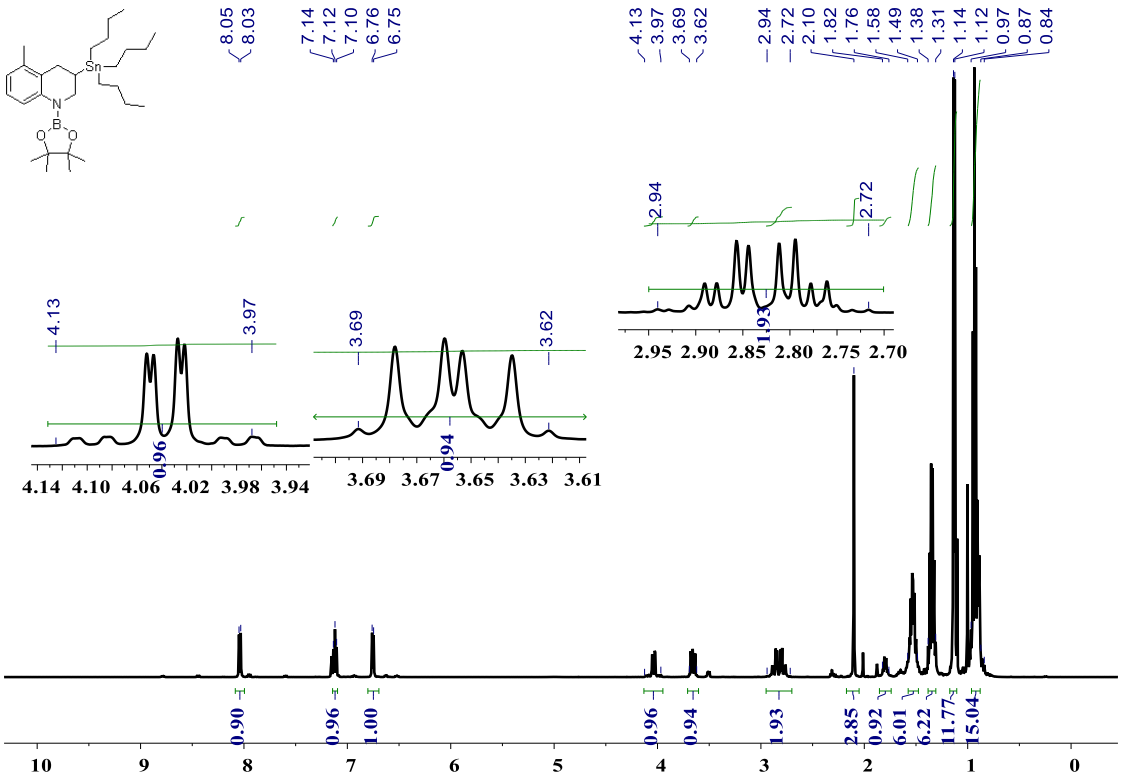
^{13}C NMR spectrum of 2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11b**) (126 MHz, C_6D_6)



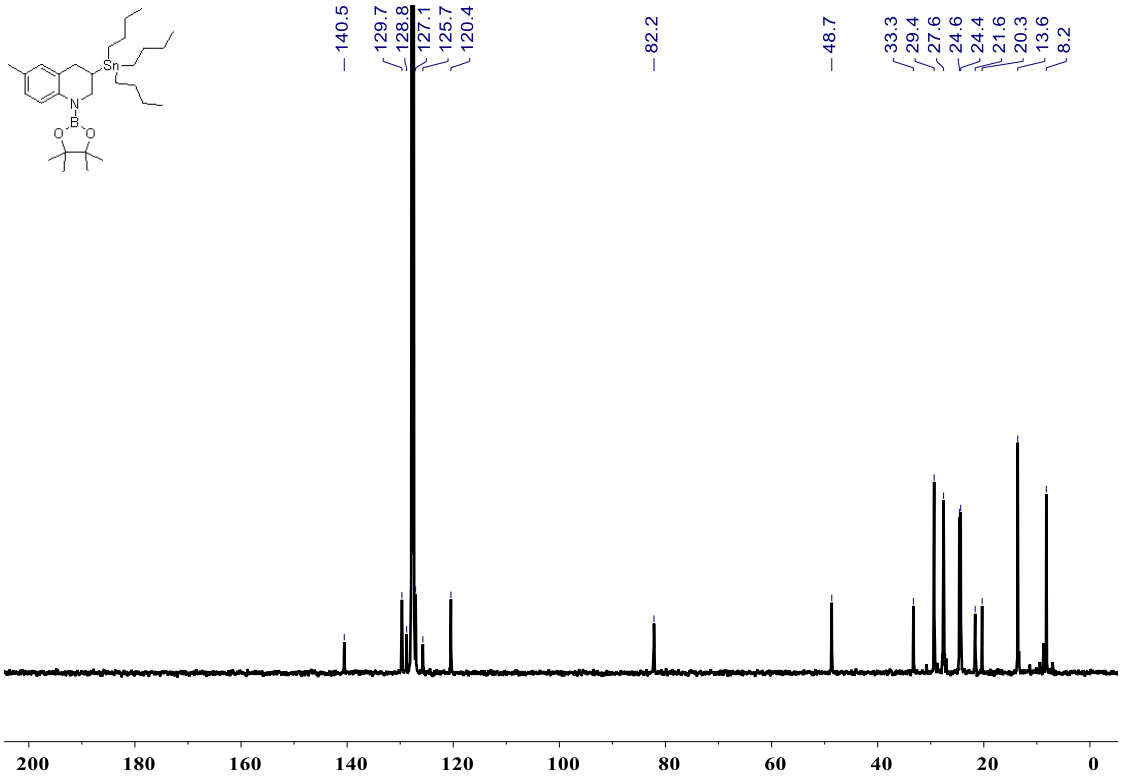
^{1}H NMR spectrum of 2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11b**) (500 MHz, C_6D_6)



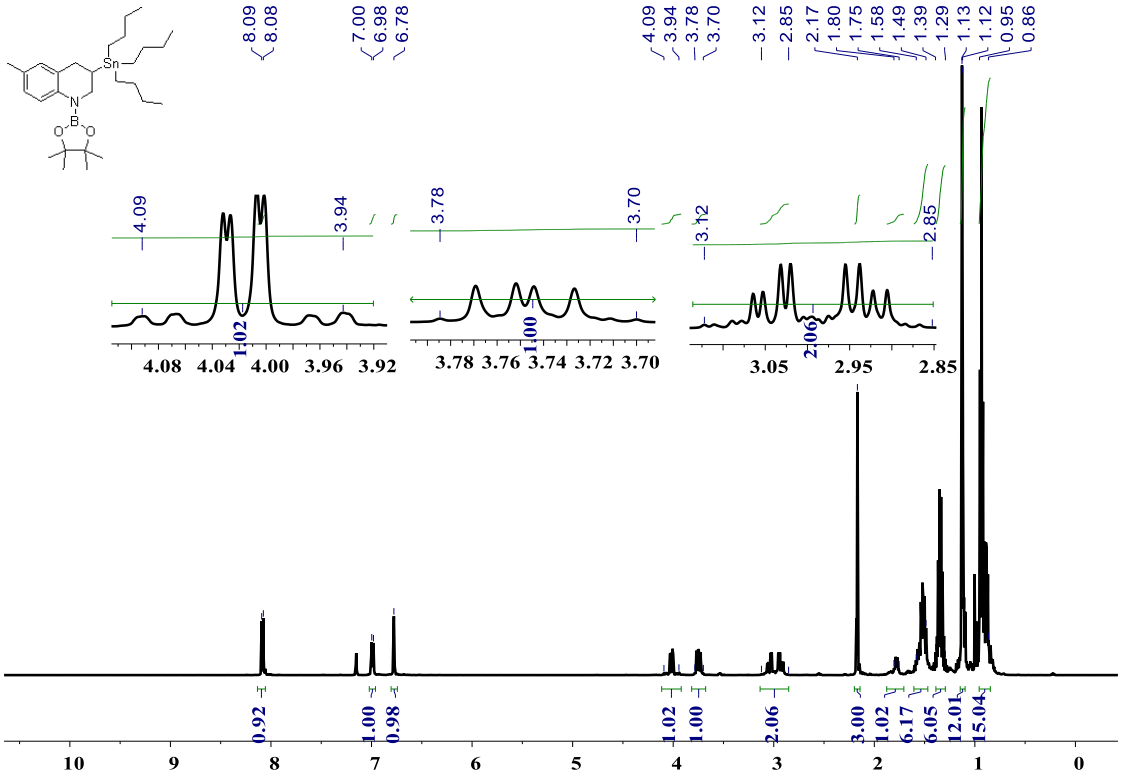
^{13}C NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11e**) (126 MHz, C_6D_6)



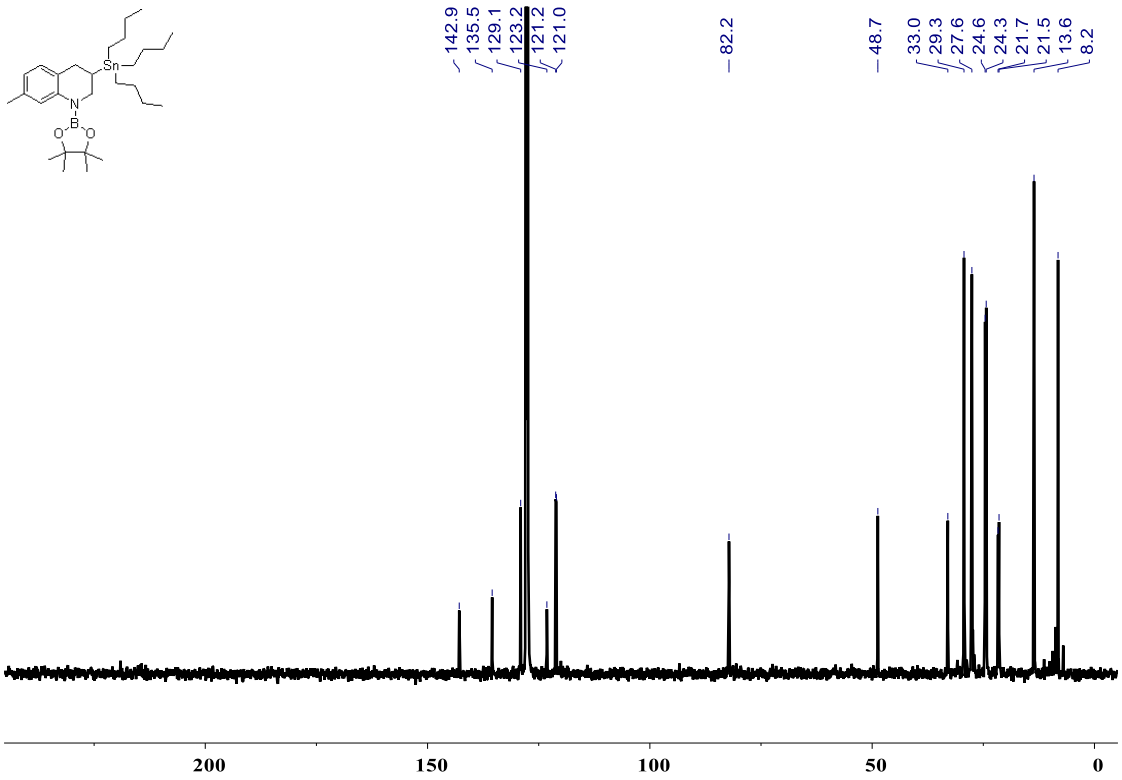
^{1}H NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11e**) (500 MHz, C_6D_6)



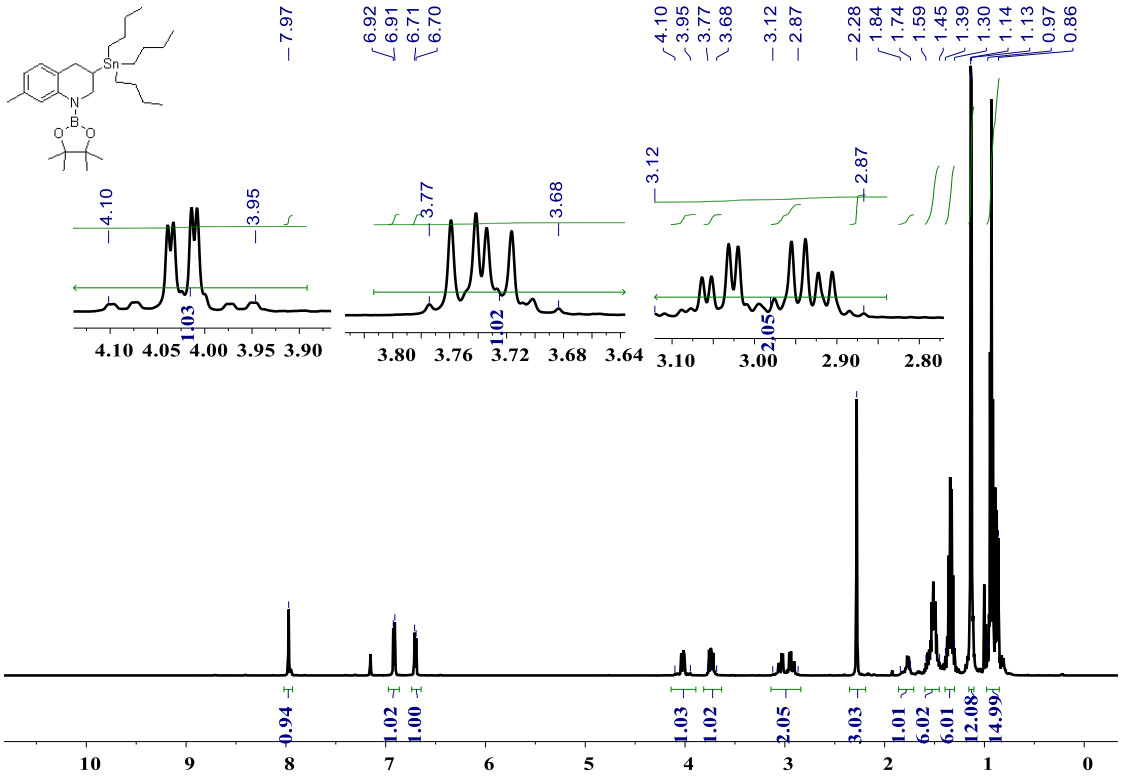
^{13}C NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11f**) (126 MHz, C_6D_6)



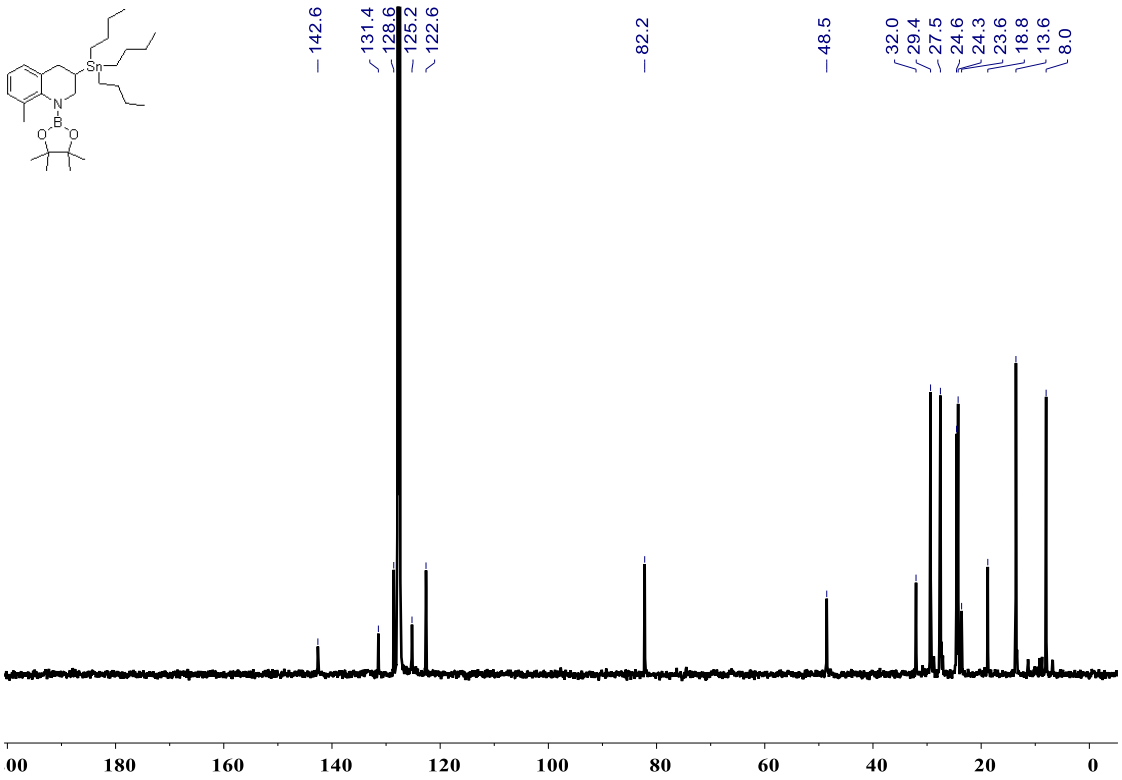
^{1}H NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11f**) (500 MHz, C_6D_6)



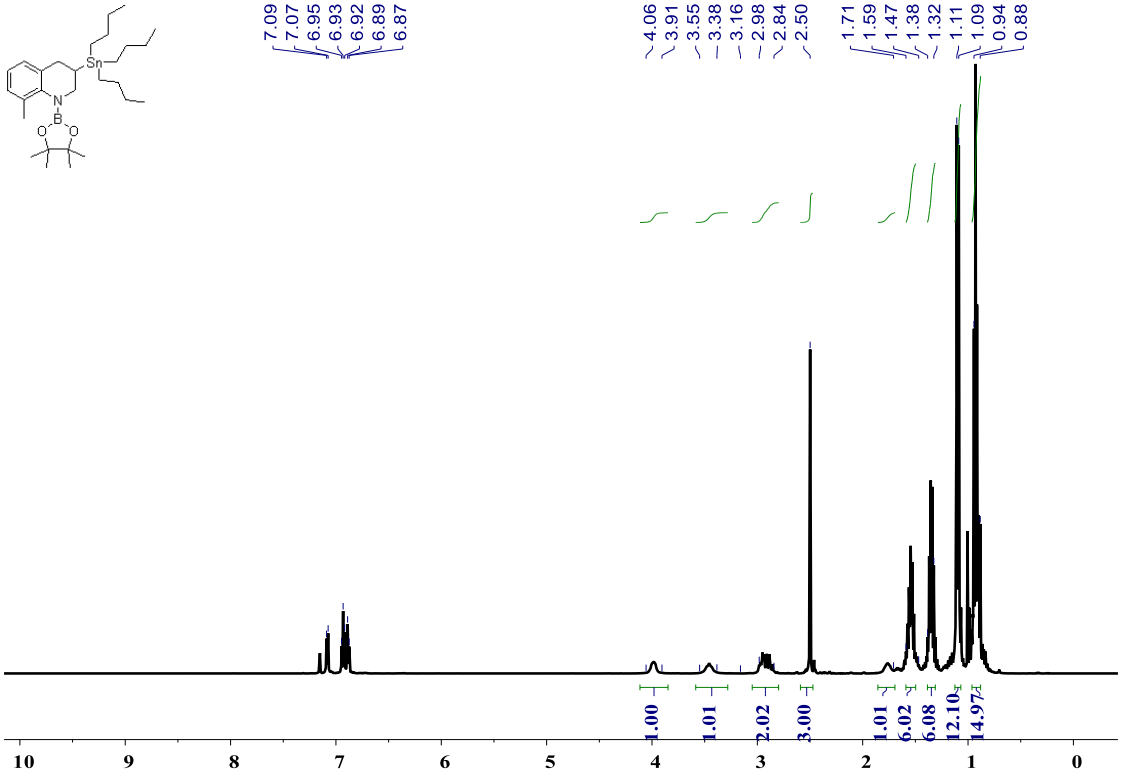
^{13}C NMR of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11g**) (126 MHz, C_6D_6)



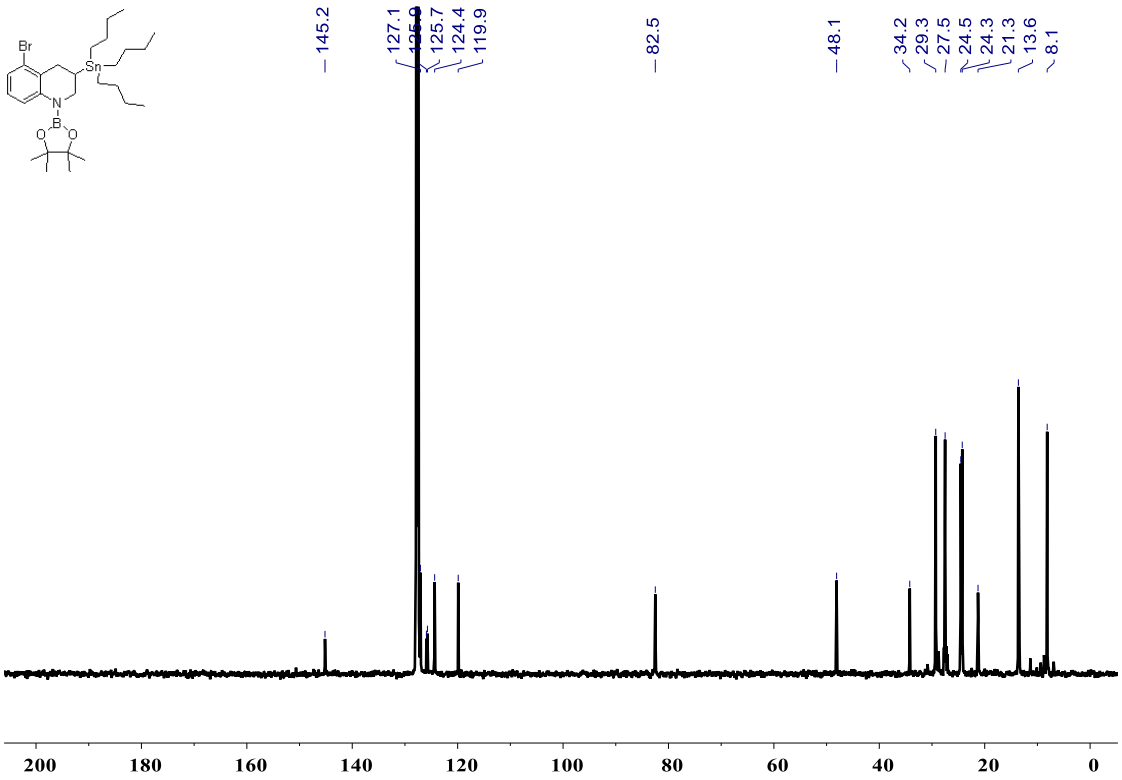
^{1}H NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11g**) (500 MHz, C_6D_6)



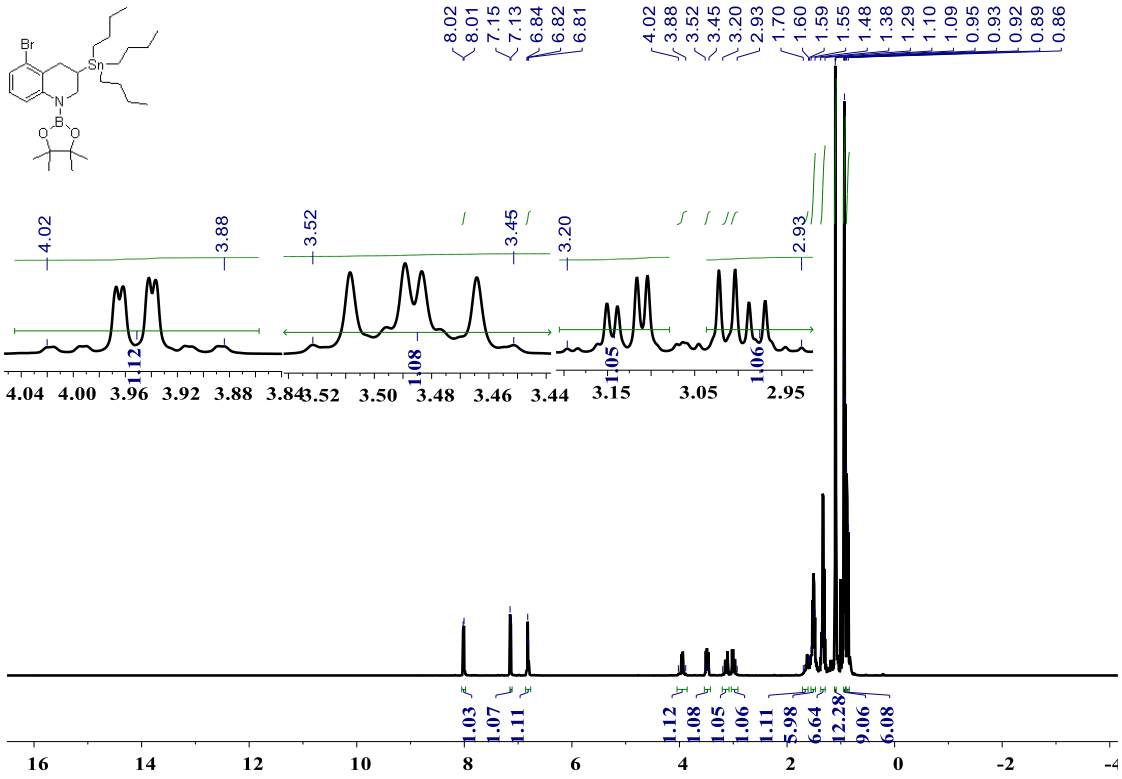
^{13}C NMR of 8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11h**) (126 MHz, C_6D_6)



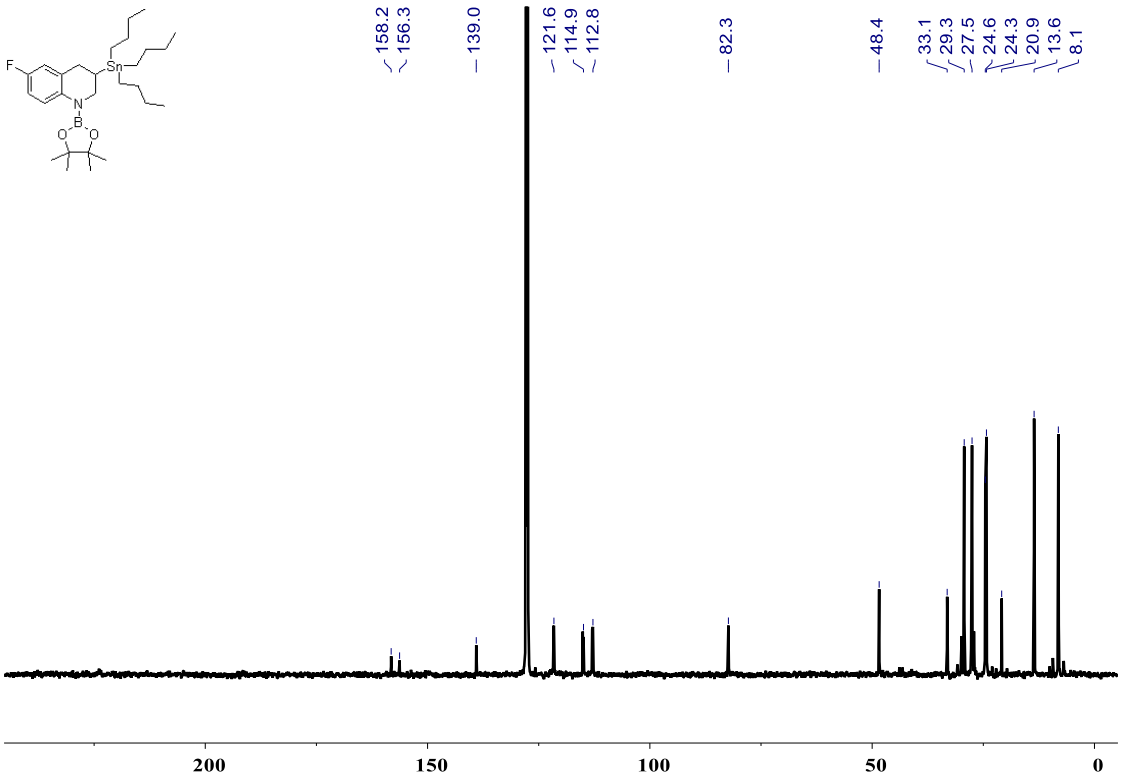
^{1}H NMR spectrum of 8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11h**) (500 MHz, C_6D_6)



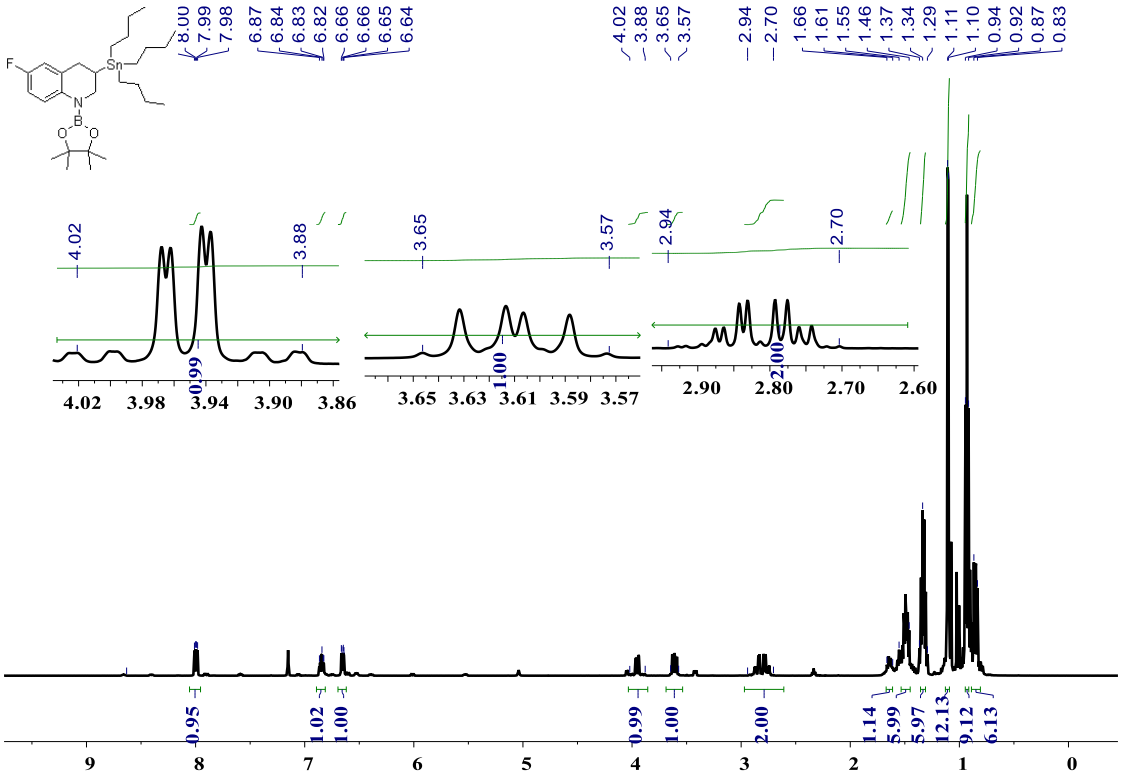
^{13}C NMR of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11i**) (126 MHz, C_6D_6)



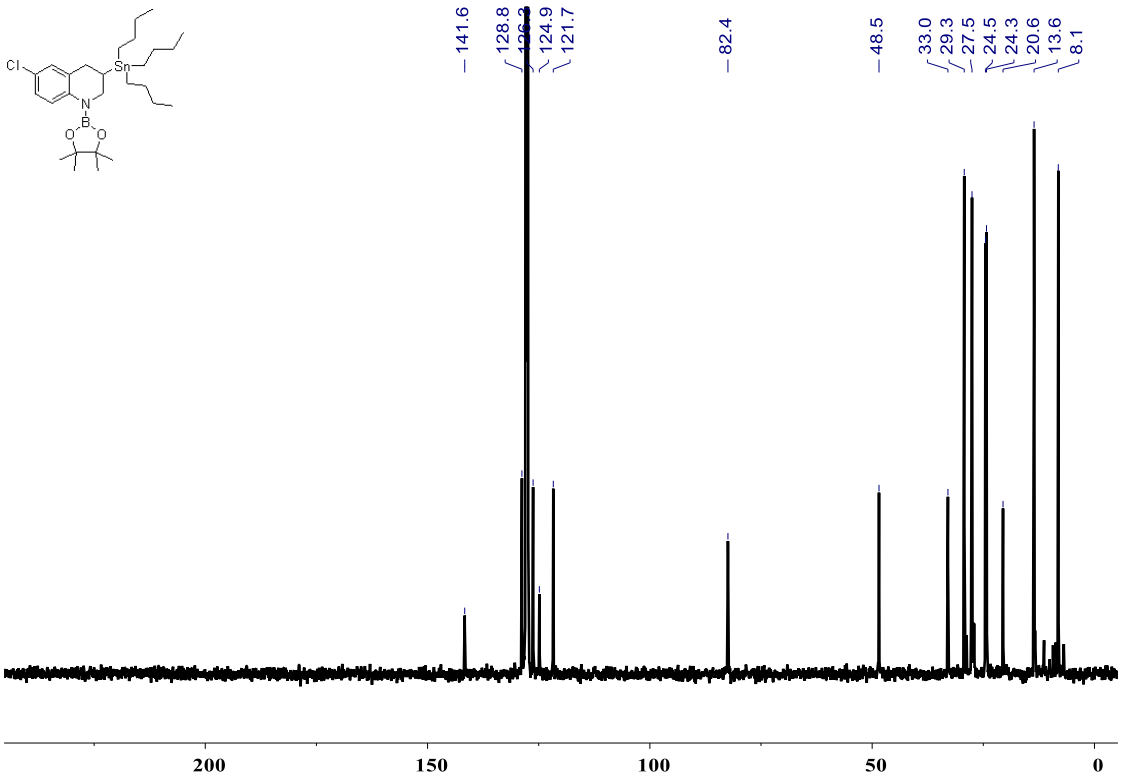
^{1}H NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11i**) (500 MHz, C_6D_6)



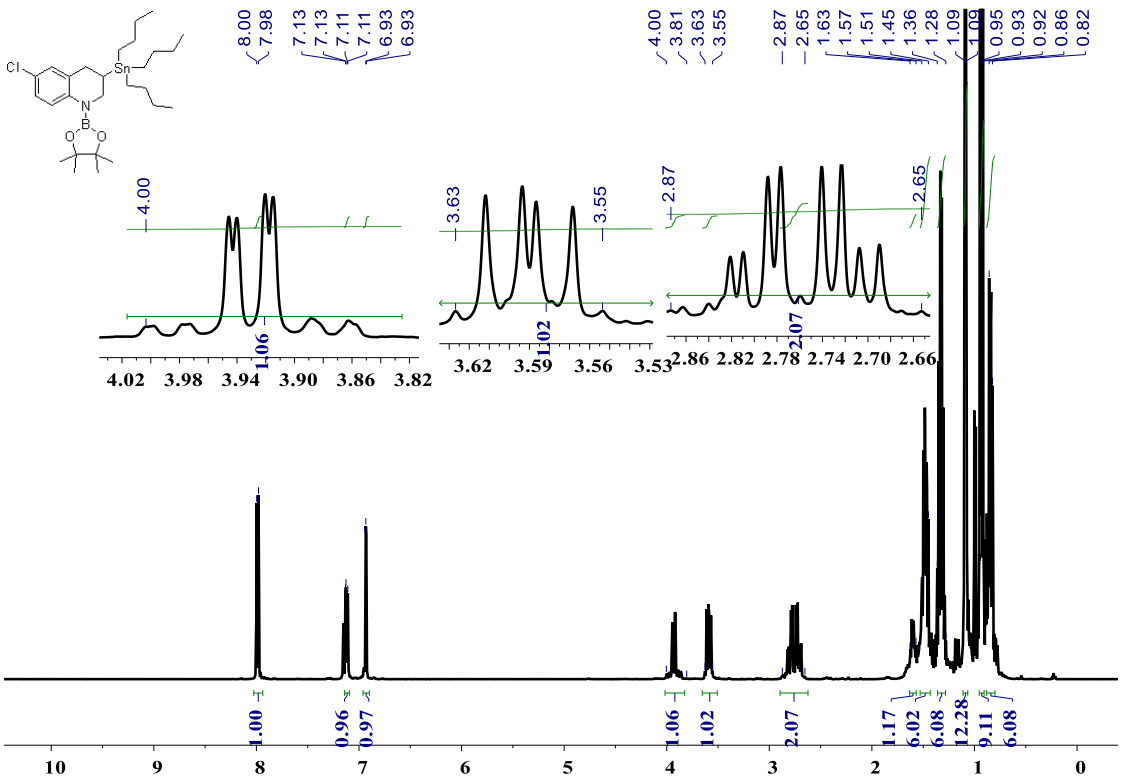
^{13}C NMR of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11j**) (126 MHz, C_6D_6)



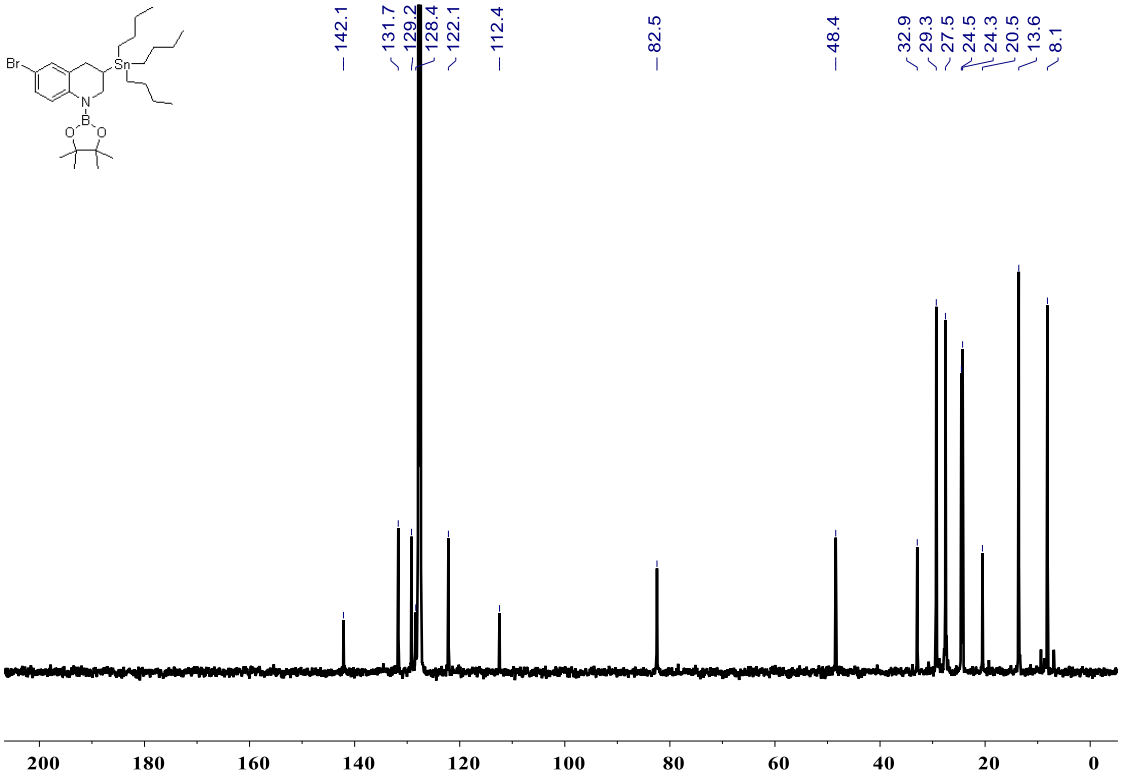
^{1}H NMR spectrum of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11j**) (500 MHz, C_6D_6)



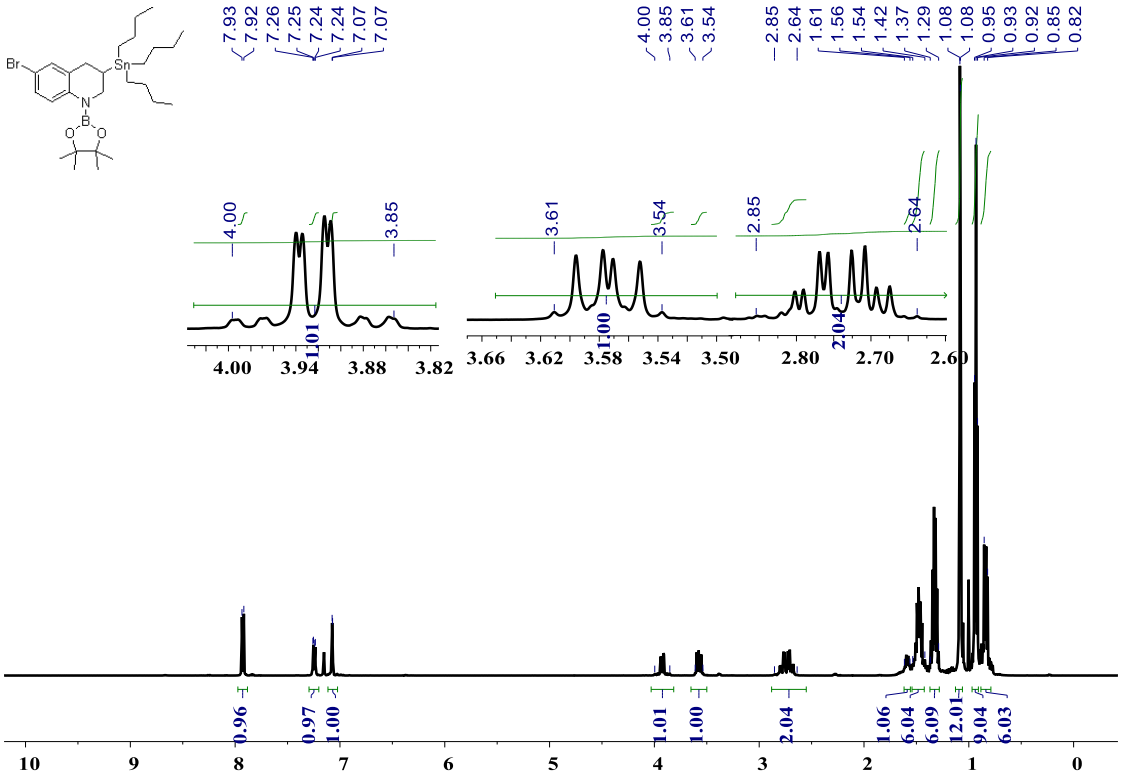
^{13}C NMR of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11k**) (126 MHz, C_6D_6)



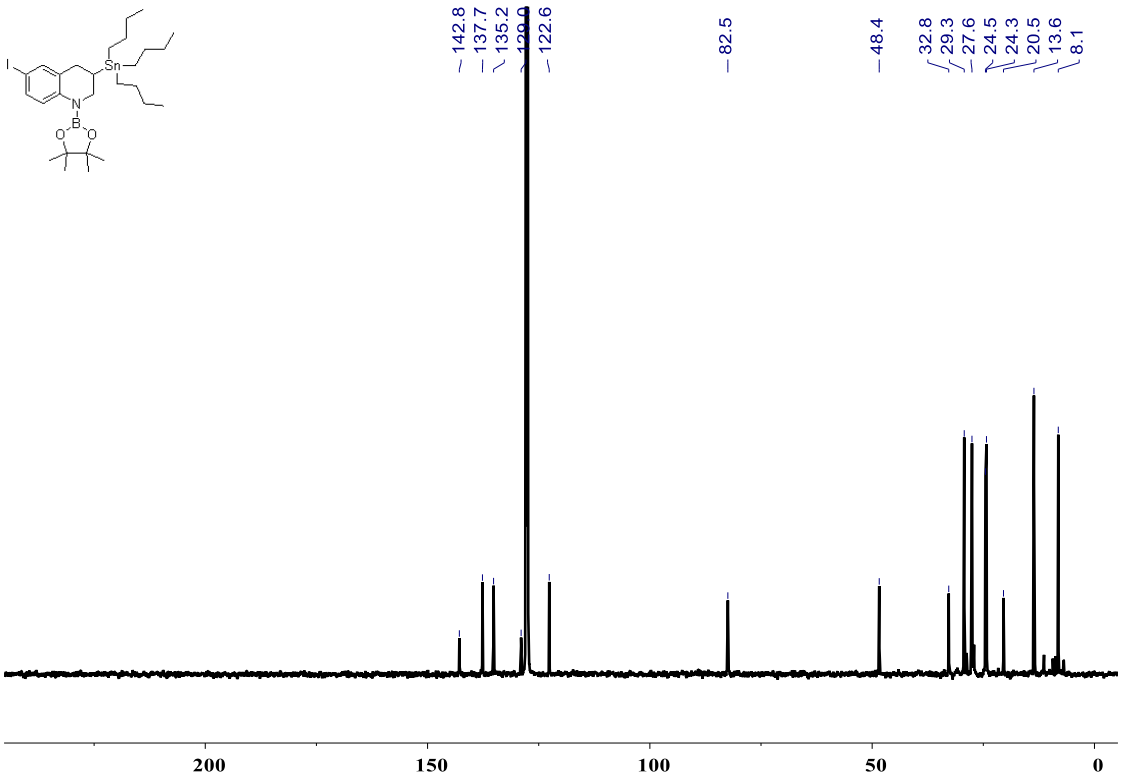
^{1}H NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11k**) (500 MHz, C_6D_6)



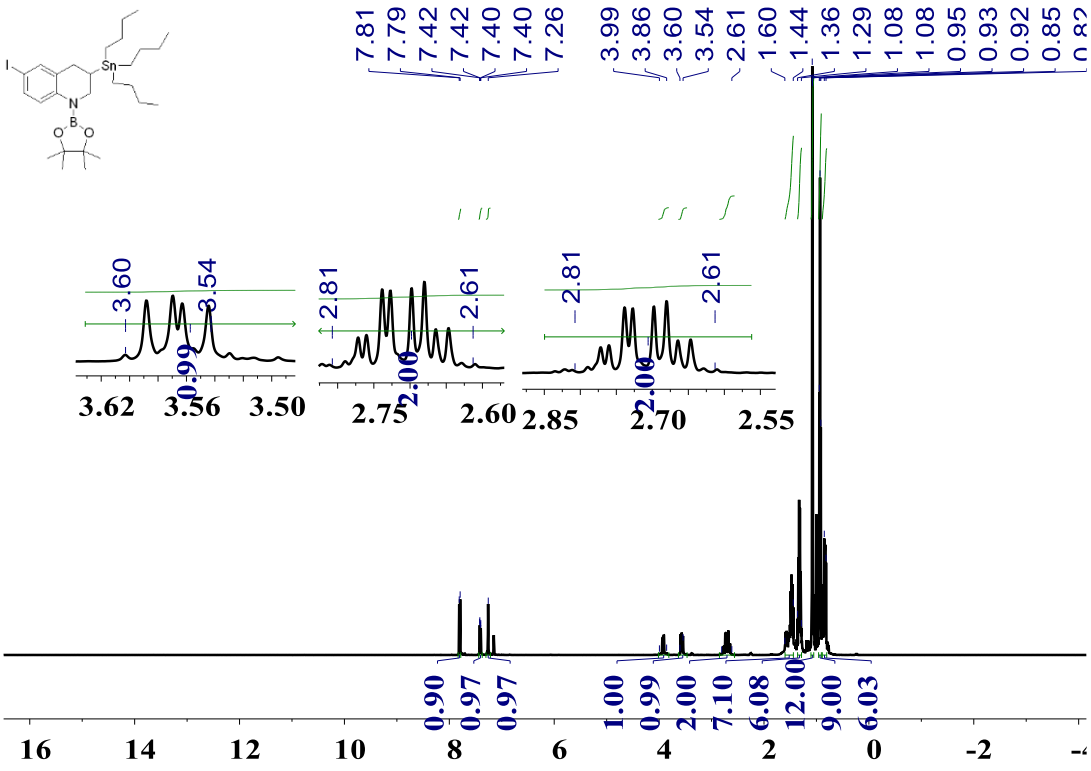
^{13}C NMR of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11l**) (126 MHz, C_6D_6)



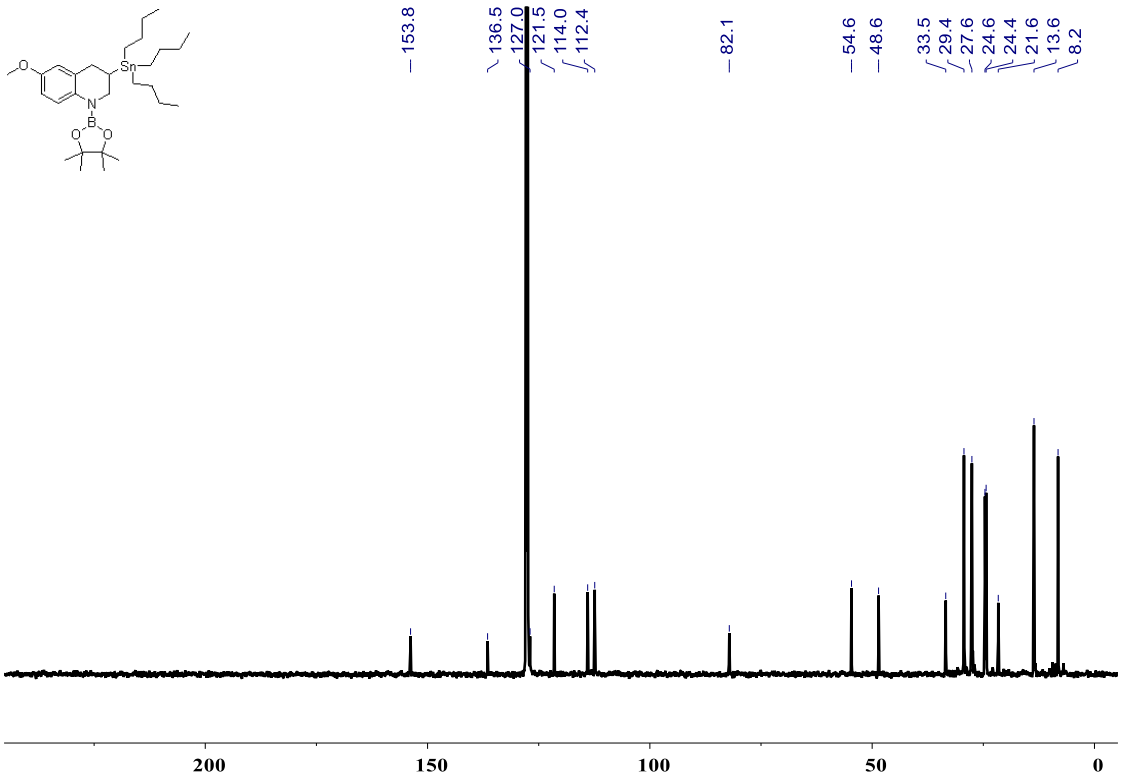
^{1}H NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11l**) (500 MHz, C_6D_6)



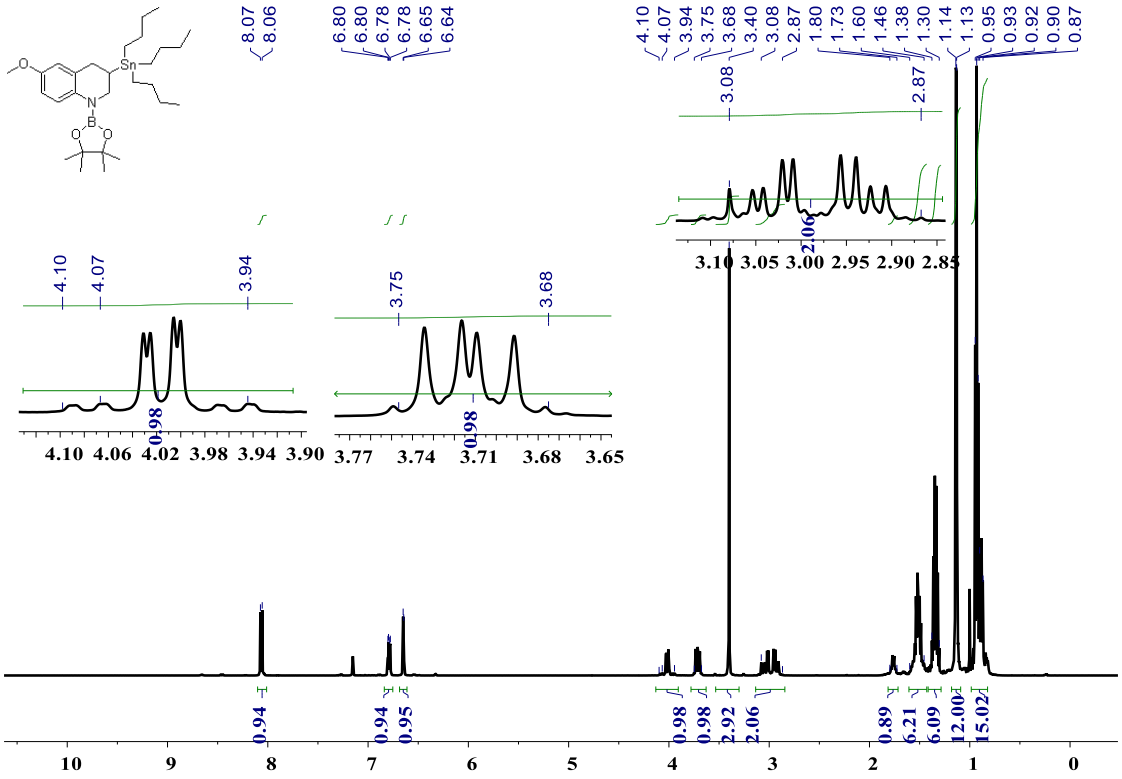
^{13}C NMR of 6-iodo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11m**) (126 MHz, C_6D_6)



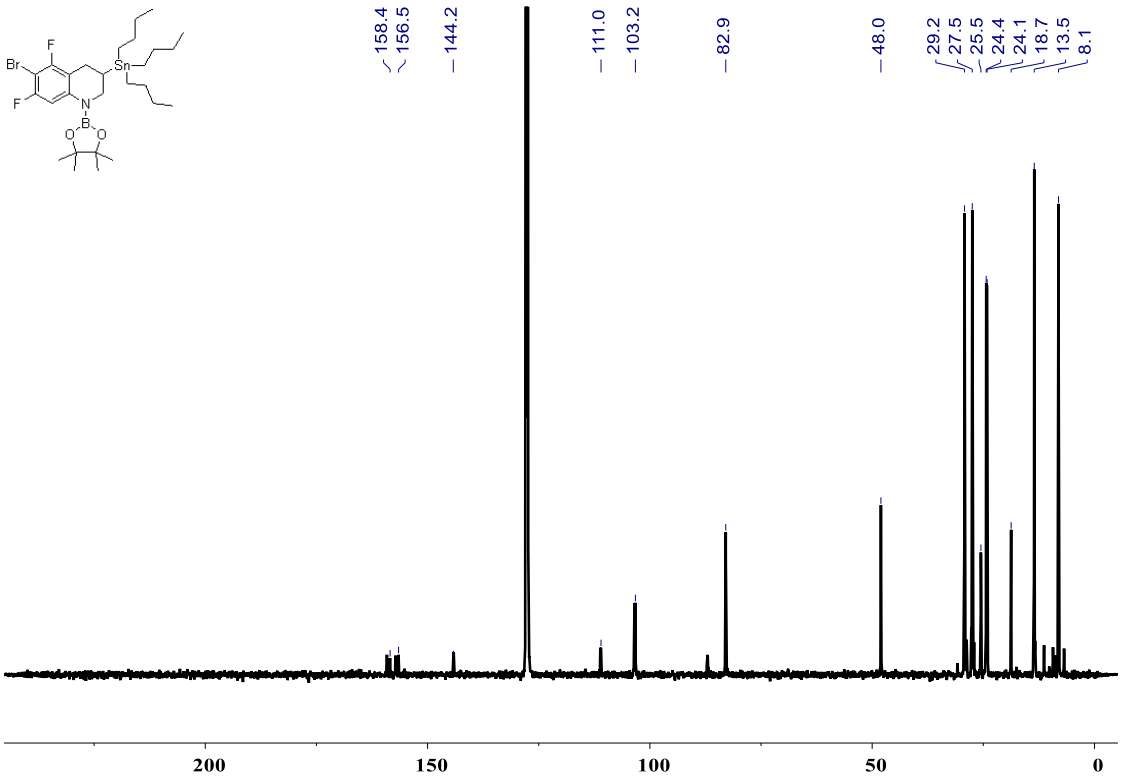
^{1}H NMR spectrum of 6-iodo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11m**) (500 MHz, C_6D_6)



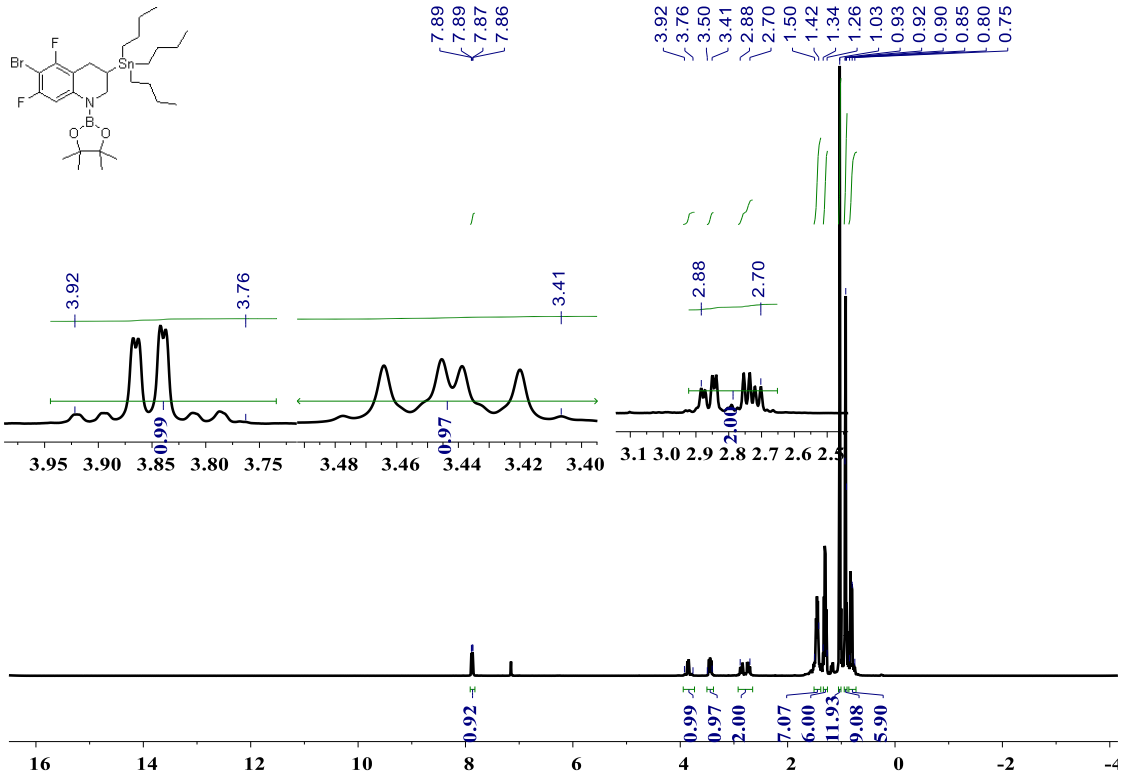
^{13}C NMR of 6-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11n**) (126 MHz, C_6D_6)



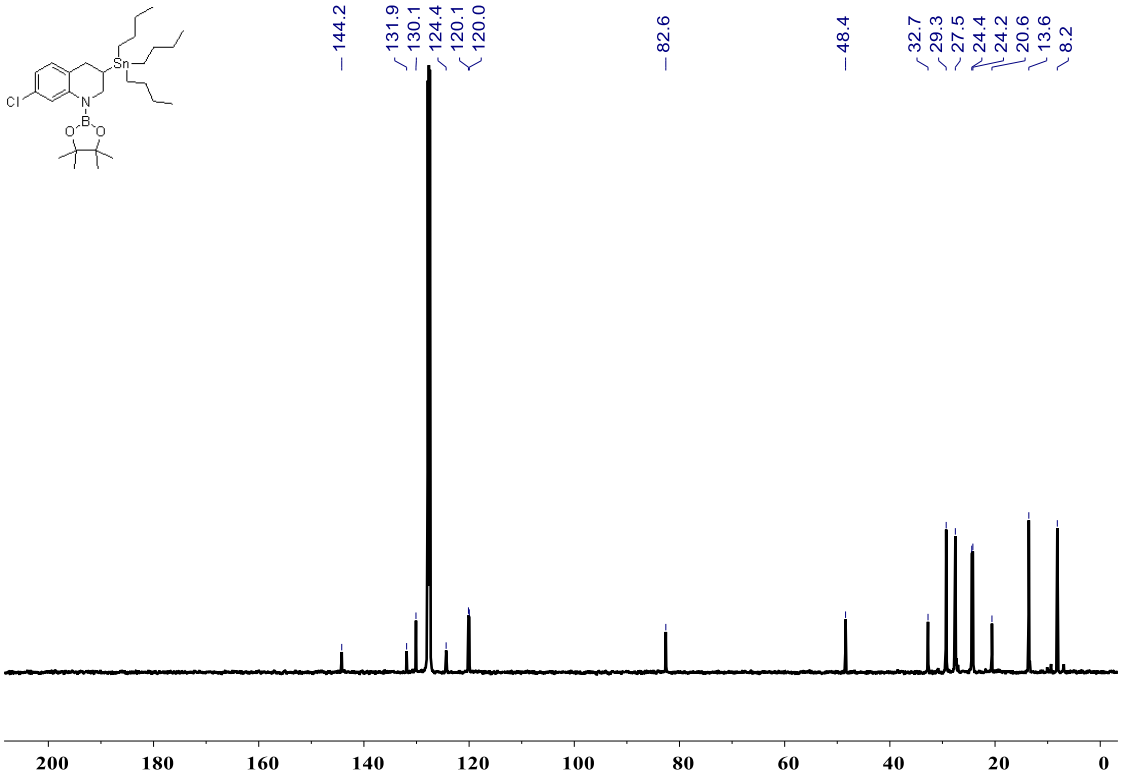
^{1}H NMR spectrum of 6-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11n**) (500 MHz, C_6D_6)



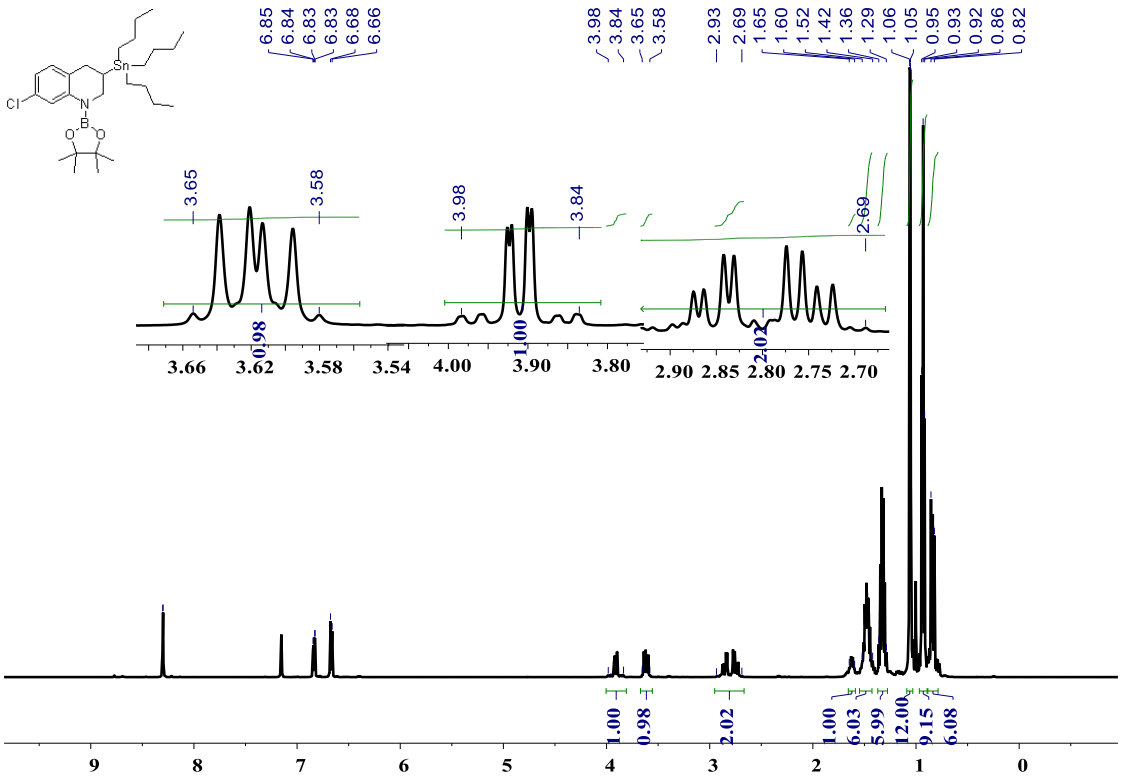
^{13}C NMR of 6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11o**) (126 MHz, C_6D_6)



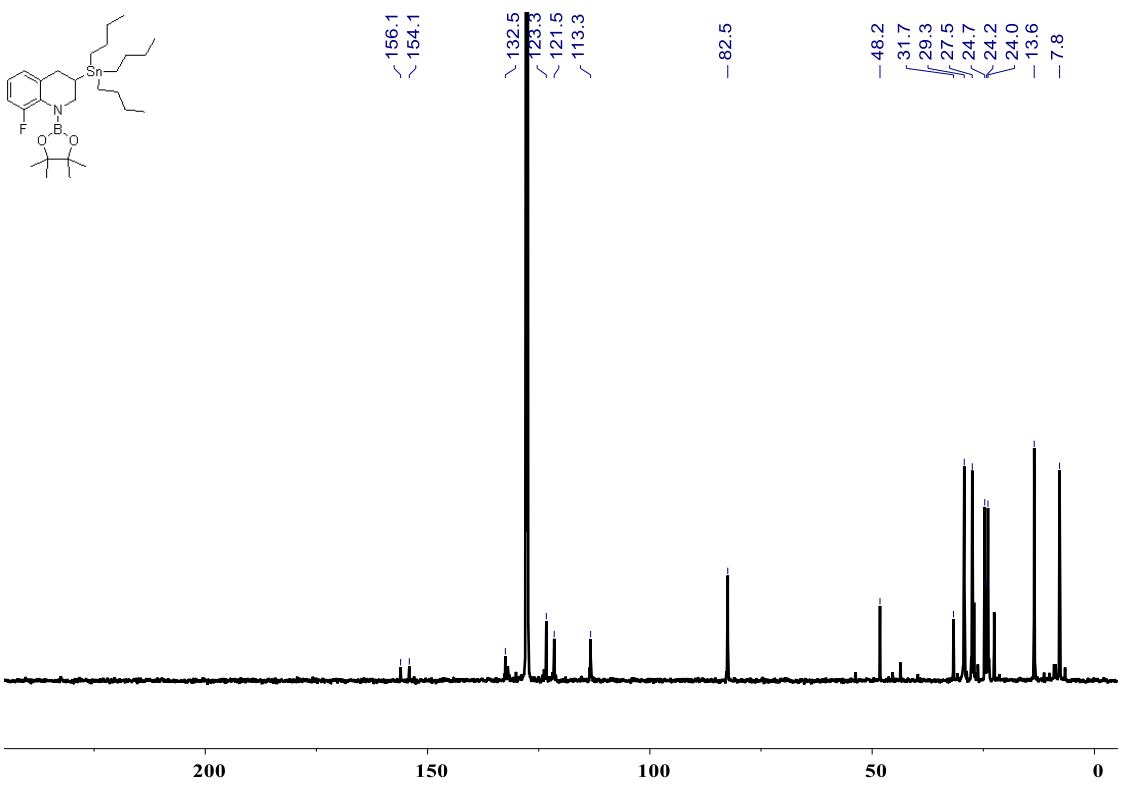
^{1}H NMR spectrum of 6-bromo-5,7-difluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11o**) (500 MHz, C_6D_6)



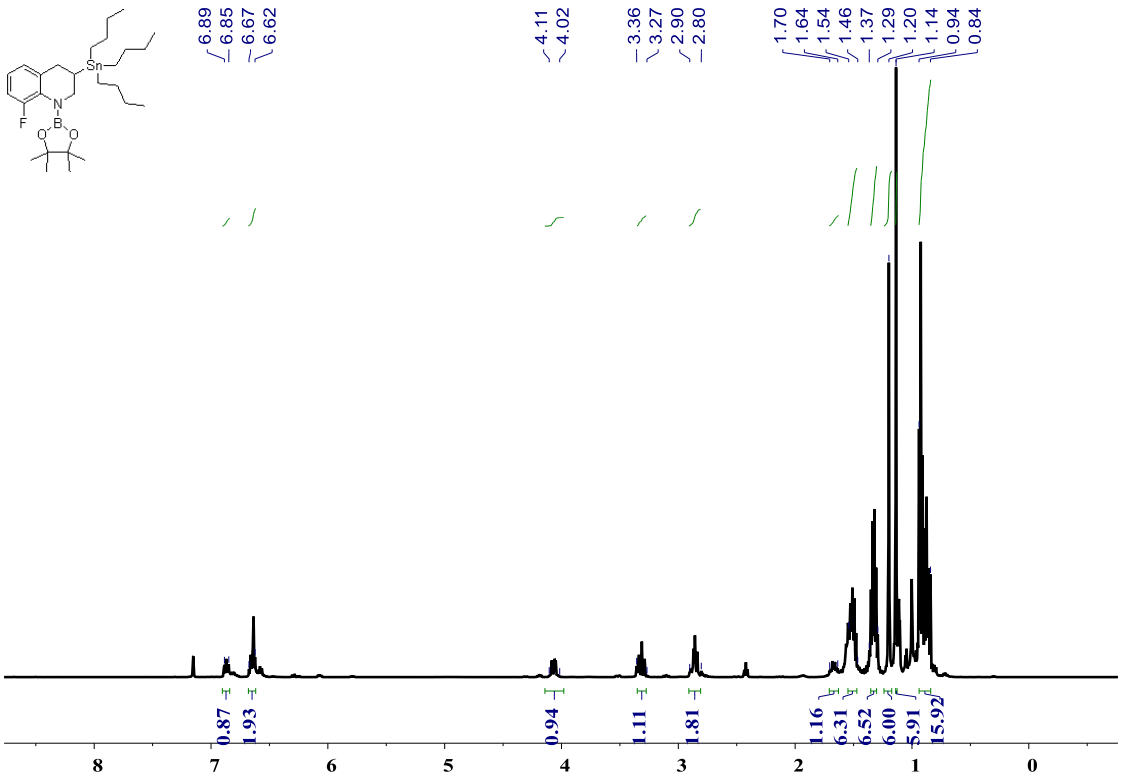
^{13}C NMR of 7-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11p**) (126 MHz, C_6D_6)



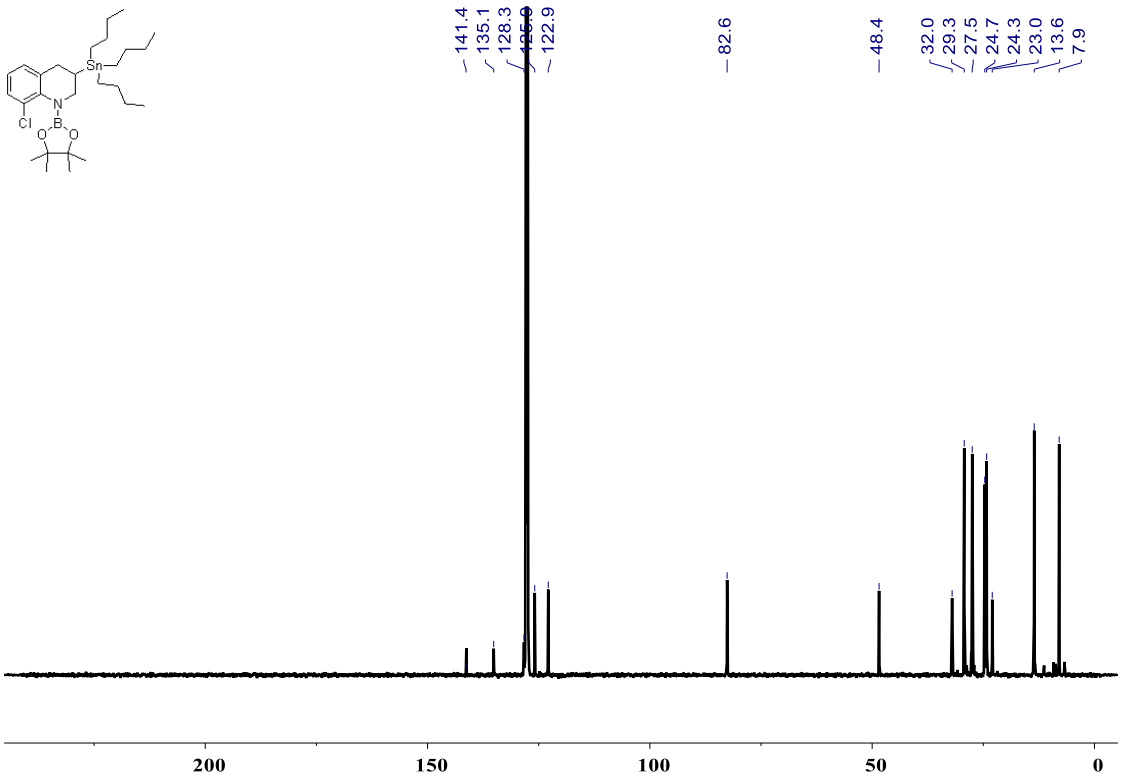
^{1}H NMR spectrum of 7-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11p**) (500 MHz, C_6D_6)



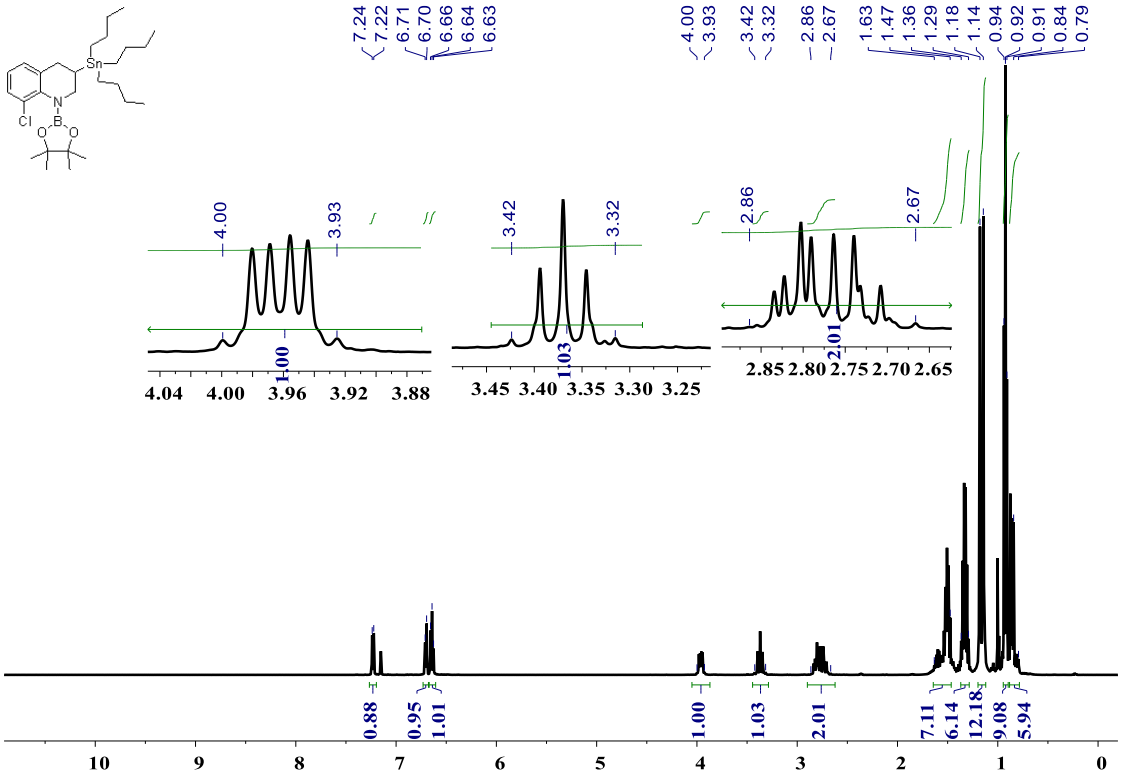
^{13}C NMR of 8-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11q**) (126 MHz, C_6D_6)



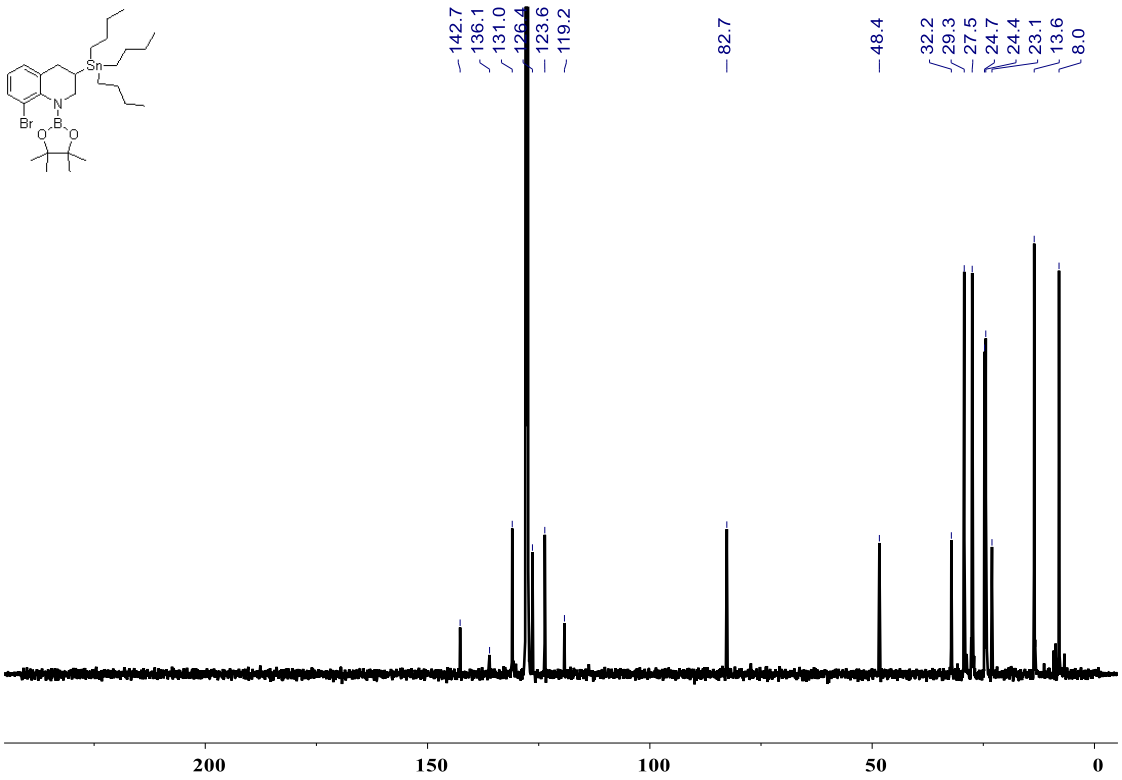
^{1}H NMR spectrum of 8-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11q**) (500 MHz, C_6D_6)



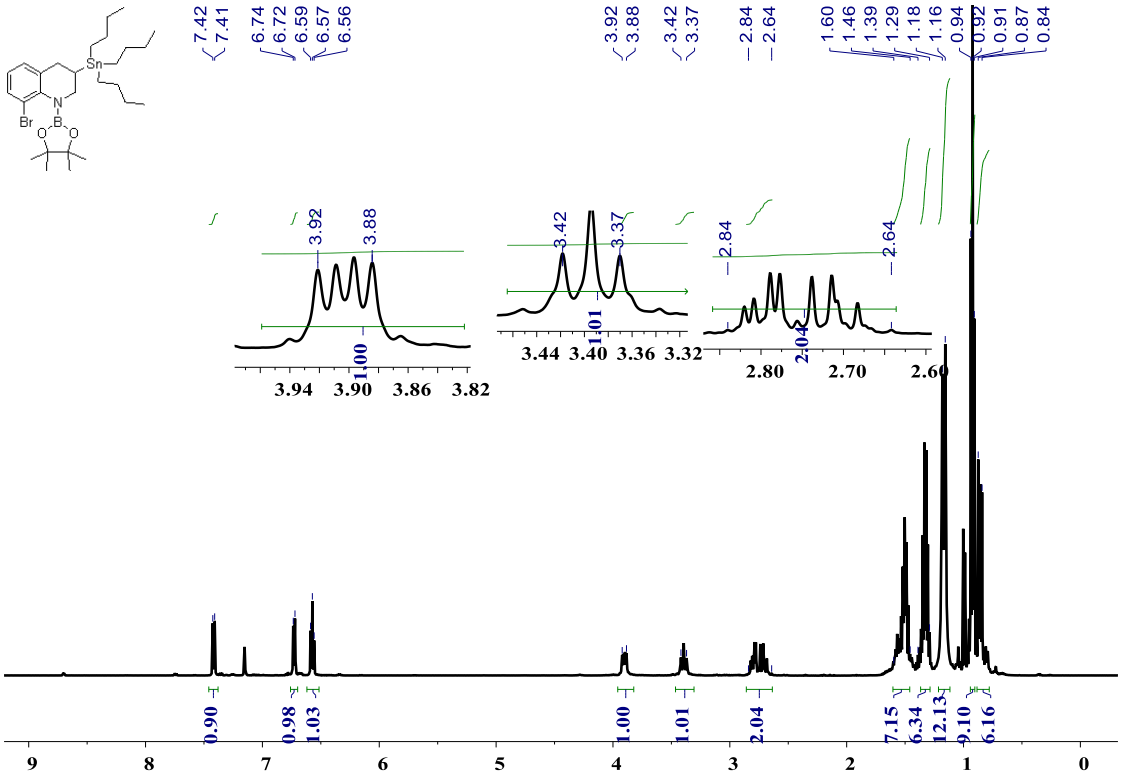
^{13}C NMR of 8-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11r**) (126 MHz, C_6D_6)



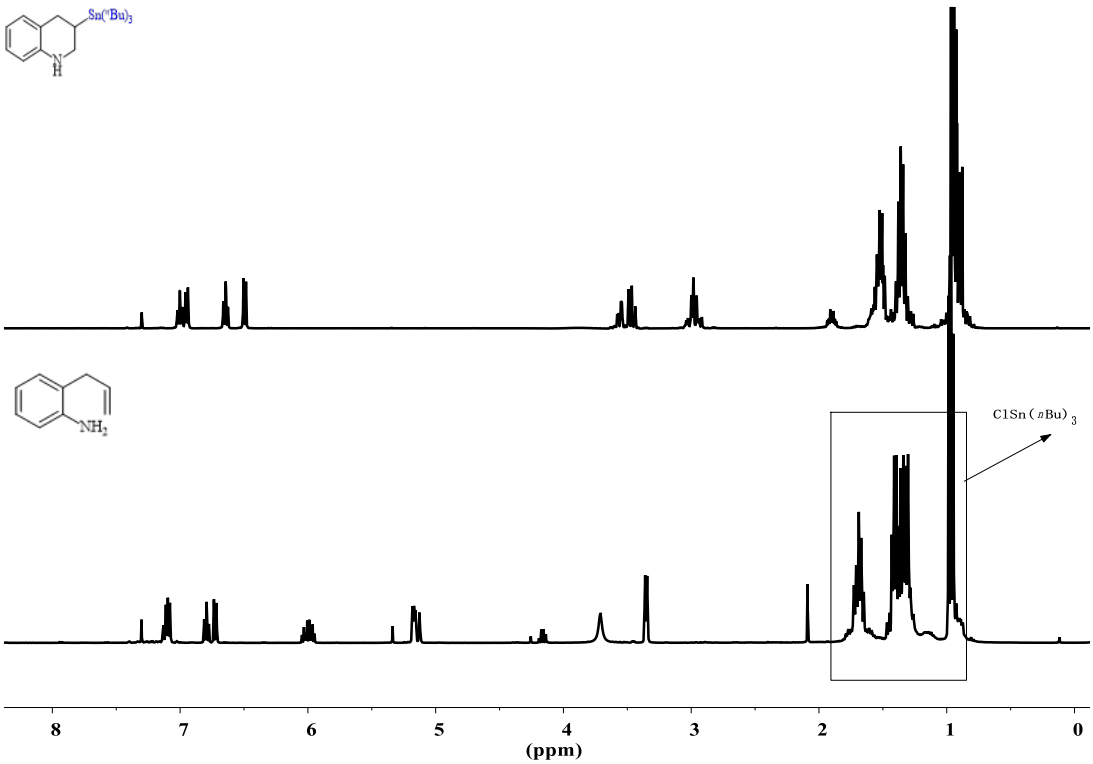
^{1}H NMR spectrum of 8-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11r**) (500 MHz, C_6D_6)



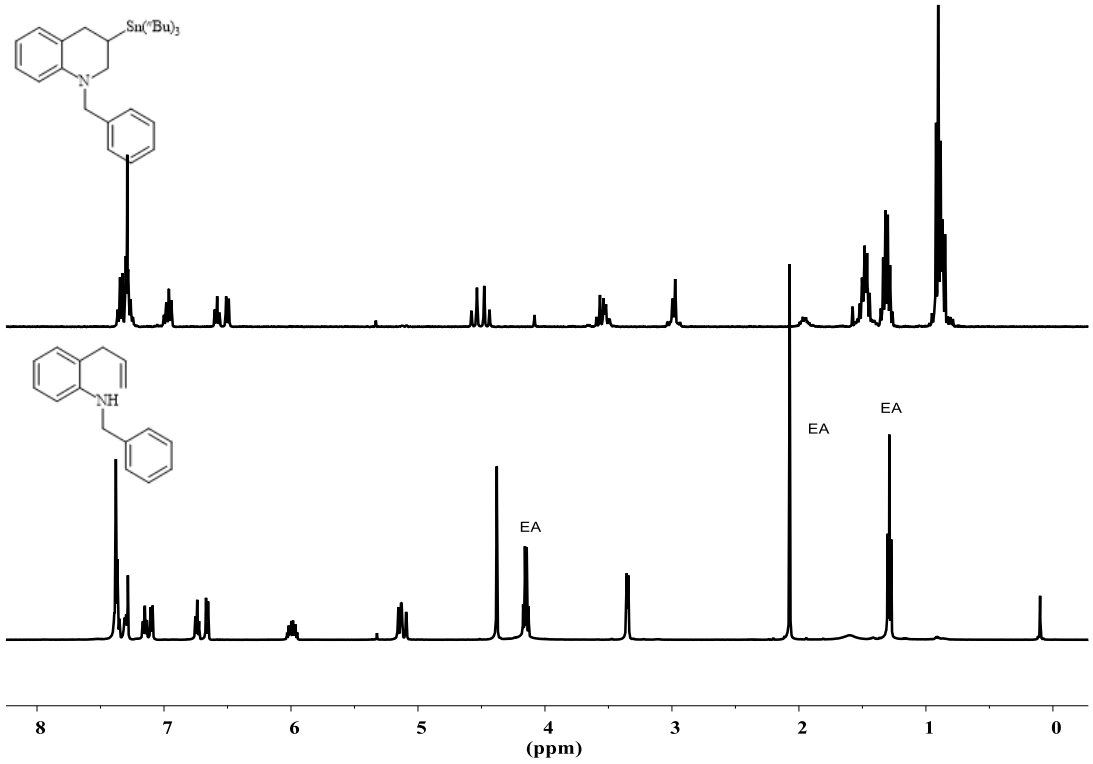
^{13}C NMR of 8-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(tributylstannyl) -1,2,3,4-tetrahydroquinoline (**11s**) (126 MHz, C_6D_6)



^{1}H NMR spectrum of 8-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -3-(tributylstannyl)-1,2,3,4-tetrahydroquinoline (**11s**) (500 MHz, C_6D_6)



Overlay of ^{1}H NMR spectra for *N*-H-C3-stannylated tetrahydroquinoline and its modified product **12** (400 MHz, $CDCl_3$)



Overlay of ^{1}H NMR spectra for *N*-benzyl-C3-stannylated tetrahydroquinoline and its modified product **13** (400 MHz, $CDCl_3$)

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