Electronic Supplementary Material (ESI) for ChemComm.

Hydroboration of Alkynes and Nitriles Using an α-Diimine Cobalt Hydride Catalyst

Electronic Supplementary Information

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General Considerations: All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen. Toluene, tetrahydrofuran, diethyl ether, and pentane were purchased from Sigma-Aldrich, purified using a Pure Process Technology solvent system, and stored in the glovebox over activated 4Å molecular sieves and sodium before use. Benzene-d_6 was purchased from Cambridge Isotope Laboratories or Oakwood Chemicals and dried over 4Å molecular sieves and potassium. Acetonitrile-d_3 was obtained from Oakwood Chemicals and dried over 3Å molecular sieves prior to use. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves. Celite was purchased from Acros Organics. Cobalt dichloride was purchased from Strem. 1-Octyne and phenyl propargyl ether were purchased from Fisher Scientific. 4-Ethynyltoluene was purchased from Santa Cruz Biotechnology. 5-Methyl-1-hexyne and cyclohexylacetylene were purchased from Alfa Aesar. 2-Phenoxyacetonitrile, 3-fluorophenylacetylene, and 4-phenyl-1-butyne were obtained from Oakwood Chemicals. Cyclopropylacetylene, *N*-propargyl phthalimide, and 4-ethynylanisole were purchased from Combi-Blocks. Benzonitrile was purchased from TCI. 1-Hexyne, phenylacetylene, anisole, 1,4-dioxane, pinacolborane, catecholborane, 4-phenylbutyronitrile, 4-acetylbenzonitrile, and sodium triethyl borohydride were purchased from Sigma Aldrich. Acetonitrile was purchased from Sigma Aldrich and dried over 3Å molecular sieves prior to use. All substrates were dried over 4Å molecular sieves prior to catalyst screening. 3-(diphenylphosphino)propanenitrile[1] and ^{Ph2PPr}DI[2] were synthesized according to literature procedures.

Solution nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 400 MHz, a Bruker 400 MHz, or a Varian 500 MHz NMR spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) are reported relative to $Si(Me)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR chemical shifts (ppm) are reported relative to phosphoric acid. Elemental analyses were performed at the Goldwater Environmental Laboratory at Arizona State University and Robertson Microlit Laboratories Inc. (Ledgewood, NJ). Solution phase magnetic susceptibility was determined using Evans method.[3] Solid state magnetic susceptibility was determined at 25 °C using a Johnson Matthey magnetic susceptibility balance calibrated with $HgCo(SCN)_4$.

X-ray Crystallography: Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to a glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer equipped with Mo Kα radiation (Arizona State University). A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct method (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least square procedures on [F^2] (SHELXL). The solid state structure of **(^{Ph2PPr}DI)$CoCl_2$** was found to feature two molecules in the asymmetric unit with two co-crystallized acetonitrile molecules; however, the data is not of sufficient quality to report in CIF format (R = 0.0984).

DFT Calculations: All DFT calculations were carried out using the ORCA program,[4] and all compounds were optimized with the B3LYP functional.[5] Empirical van der Waals corrections were included in the geometry optimization of all molecules.[6] The self-consistent field (SCF) calculations were tightly converged (1×10^{-8} E_h in energy, 1×10^{-7} E_h in density charge). Ahlrichs triple-ξ valence basis sets with one set of first polarization functions (def2-TZVP) were used for the cobalt, phosphorus, and nitrogen atoms.[7] Ahlrichs split valence basis sets with one set of first polarization functions (def2-SVP) were used for the carbon and hydrogen atoms.[7] Auxiliary basis sets were chosen to match the orbital basis sets used. Molecular orbitals were visualized using the Molekel program.[8]

Electron Paramagnetic Resonance Spectroscopy:

Instrumentation. Studies were performed at the EPR Facility of Arizona State University. Continuous wave (CW) EPR spectra were recorded at 113 K using a Bruker ELEXSYS E580 CW X-band spectrometer (Bruker, Rheinstetten, Germany) equipped with a liquid nitrogen temperature control system (ER 4131VT). The magnetic field modulation frequency was 100 kHz with a field modulation of 1 mT peak-to-peak. The microwave power was 4 mW, the microwave frequency was 9.40 GHz and the sweep time was 168 seconds.

Spin Hamiltonian. The EPR spectrum of **(^{Ph2PPr}DI)$CoCl_2$** was interpreted using a spin Hamiltonian, $\mathcal{H}$, containing the electron Zeeman interaction with the applied magnetic field B_o and the hyperfine coupling (hfc) term:[9]

$$\mathcal{H} = \beta_e \, \mathbf{S}.\boldsymbol{g}.\mathbf{Bo} + h \, \mathbf{S}.\boldsymbol{A}.\mathbf{I} \qquad (1)$$

where **S** is the electron spin operator, **I** is the nuclear spin operator of ^{59}Co, $\boldsymbol{A}$ is the hfc tensor in frequency units, $\boldsymbol{g}$ is the electronic *g*-tensor, β_e is the electron magneton, and *h* is Planck's constant. The best fit of the spectrum was obtained considering a single Co(0) ion (S = ½, I = 7/2).

Fitting of EPR spectra. To quantitatively compare experimental and simulated spectra, we divided the spectra into N intervals, i.e. we treated the spectrum as an N-dimensional vector **R**. Each component R_j has the amplitude of the EPR signal at a magnetic field B_j, with j varying from 1 to N. The amplitudes of the experimental and simulated spectra were normalized so that the span between the maximum and minimum values of R_j is 1. We compared the calculated amplitudes R_j^{calc} of the signal with the observed values R_j defining a root-mean-square deviation σ by:

$$\sigma(p_1, p_2, \ldots, p_n) = [\sum_j (R_j^{calc}(p_1, p_2, \ldots, p_n) - R_j^{exp})^2/N]^{½} \qquad (2)$$

where the sums are over the N values of j, and p's are the fitting parameters that produced the calculated spectrum. For our simulations, N was set equal to 2048. The EPR spectra were simulated using EasySpin (v 5.0.20), a computational package developed by Stoll and Schweiger[10] and based on Matlab (The MathWorks, Natick, MA, USA). EasySpin calculates EPR resonance fields using the energies of the states of the spin system obtained by direct diagonalization of the spin Hamiltonian (see Eq. 1). The EPR fitting procedure used a Monte Carlo type iteration to minimize the root-mean-square deviation, σ (see Eq. 2) between measured and simulated spectra. We searched for the optimum values of the following parameters: the principal components of $\boldsymbol{g}$ (i.e. g_x, g_y, g_z), the principal components of the hfc tensor $\boldsymbol{A}$ (i.e. A_x, A_y, A_z) and the peak-to-peak line-widths (ΔB_x, ΔB_y, and ΔB_z).

Table S1. Crystallographic Data for **(^{Ph2PPr}DI)CoH**.

	(^{Ph2PPr}DI)CoH
chemical formula	$C_{34}H_{39}CoN_2P_2$
formula weight	596.54
crystal dimensions	0.174 x 0.146 x 0.138
crystal system	monoclinic
space group	P 1 21/c 1
a (Å)	17.6171(9)
b (Å)	9.4154(5)
c (Å)	18.1381(9)
α (deg)	90
β (deg)	101.3560(10)
γ (deg)	90
V (Å^3)	2949.7(3)
Z	4
T (°C)	123.(2)
ρcalcd (g cm^{-3})	1.343
μ (mm^{-1})	0.717
reflections collected	22879
data/restraints/parameters	5187/0/358
R_1 [I > 2σ(I)]	0.0275
wR_2 (all data)	0.0715
Goodness-of-fit	1.038
Largest peak, hole (eÅ^{-3})	0.325, -0.362

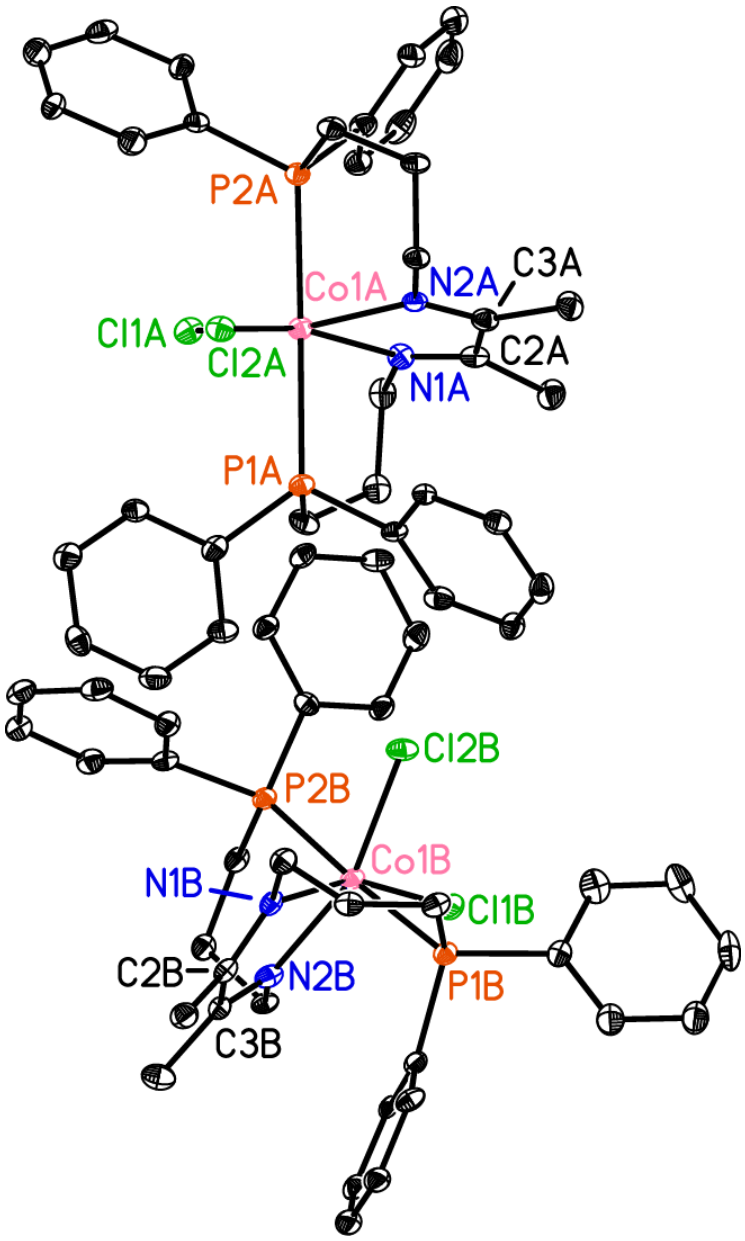


Figure S1. The molecular structure of **(^{Ph2PPr}DI)CoCl$_2$** shown at 30% probability ellipsoids. Hydrogen atoms and two co-crystallized acetonitrile molecules are omitted for clarity. Important bond distances: Co1A-N1A, 2.190(6); Co1A-N2A, 2.132(6); Co1A-P1A, 2.510(2); Co1A-P2A, 2.472(2); Co1A-Cl1A, 2.390(2); Co1A-Cl2A, 2.415(2); N1A-C2A, 1.273(10); N2A-C3A, 1.303(10); C2A-C3A, 1.492(10) Å. Important angles: N2A-Co1A-N1A, 73.7(2); P2A-Co1A-P1A, 177.20(7); N1A-Co1A-P1A, 76.60(17); N1A-Co1A-P2A, 102.15(17); N1A-Co1A-Cl1A, 96.55(17); N1A-Co1A-Cl2A, 159.67(17); Cl1A-Co1A-Cl2A, 99.62(7) °.

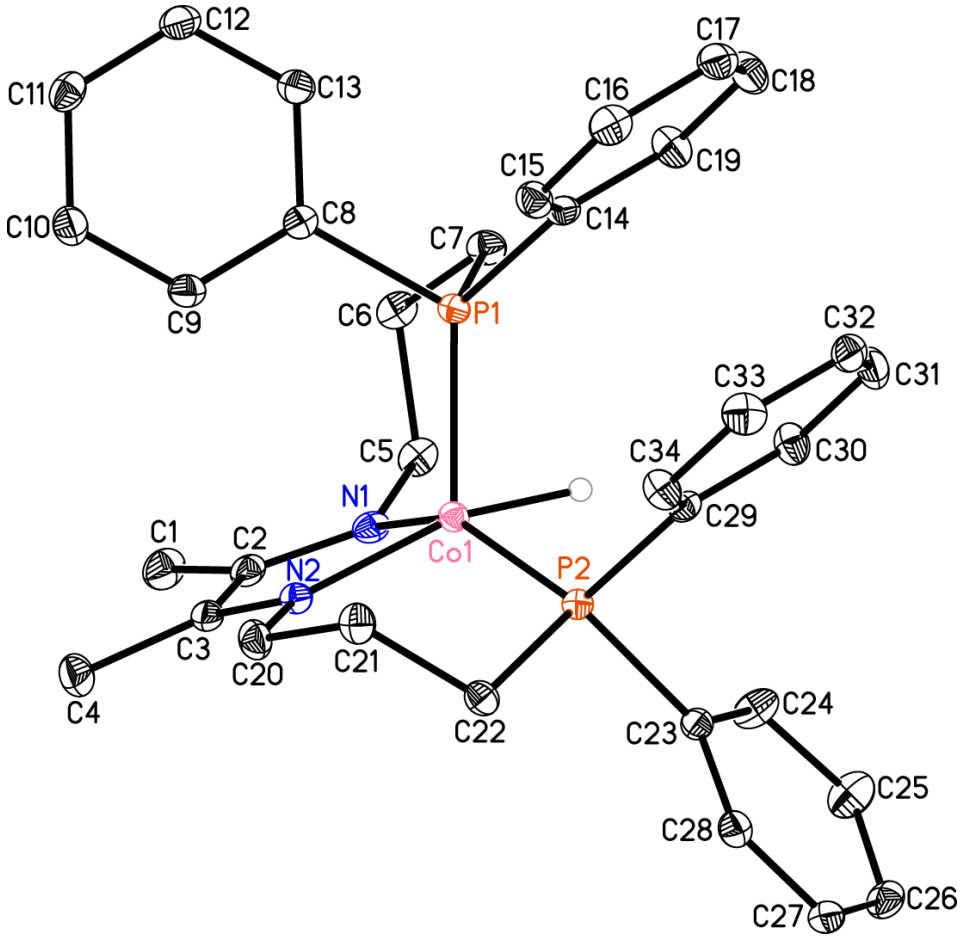


Figure S2. The molecular structure of **(^{Ph2PPr}DI)CoH** shown at 30% probability ellipsoids. Hydrogen atoms except for H1 omitted for clarity.

Table S2. Metrical parameters for **(^{Ph2PPr}DI)CoH**.

Co1-N1	1.8869(14)	C2-C3	1.401(3)	C20-C21	1.516(3)
Co1-N2	1.9164(15)	C3-C4	1.505(3)	C21-C22	1.530(3)
Co1-P2	2.1367(5)	C5-C6	1.537(3)	C23-C24	1.393(3)
Co1-P1	2.1464(5)	C6-C7	1.535(3)	C23-C28	1.396(2)
Co1-H1	1.439(19)	C8-C9	1.384(3)	C24-C25	1.395(3)
P1-C14	1.8362(18)	C8-C13	1.395(3)	C25-C26	1.376(3)
P1-C8	1.8474(18)	C9-C10	1.392(3)	C26-C27	1.383(3)
P1-C7	1.8475(18)	C10-C11	1.382(3)	C27-C28	1.386(3)
P2-C22	1.8361(18)	C11-C12	1.378(3)	C29-C30	1.393(3)
P2-C29	1.8392(17)	C12-C13	1.387(3)	C29-C34	1.393(2)
P2-C23	1.8432(18)	C14-C19	1.386(3)	C30-C31	1.385(3)
N1-C2	1.347(2)	C14-C15	1.389(3)	C31-C32	1.383(3)
N1-C5	1.468(2)	C15-C16	1.389(3)	C32-C33	1.369(3)
N2-C3	1.357(2)	C16-C17	1.376(3)	C33-C34	1.391(3)
N2-C20	1.466(2)	C17-C18	1.375(3)		
C1-C2	1.511(2)	C18-C19	1.393(3)		

N1-Co1-N2	81.83(6)	C5-N1-Co1	122.78(12)	C16-C15-C14	121.25(18)
N1-Co1-P2	148.54(5)	C3-N2-C20	115.47(15)	C17-C16-C15	119.78(19)
N2-Co1-P2	96.85(5)	C3-N2-Co1	114.42(12)	C18-C17-C16	119.83(18)
N1-Co1-P1	93.82(5)	C20-N2-Co1	130.06(12)	C17-C18-C19	120.41(19)
N2-Co1-P1	115.86(5)	N1-C2-C3	113.56(15)	C14-C19-C18	120.56(18)
P2-Co1-P1	114.437(19)	N1-C2-C1	122.00(17)	N2-C20-C21	114.65(15)
N1-Co1-H1	95.0(7)	C3-C2-C1	124.44(17)	C20-C21-C22	112.12(15)
N2-Co1-H1	165.0(7)	N2-C3-C2	113.86(16)	C21-C22-P2	109.03(12)
P2-Co1-H1	78.2(7)	N2-C3-C4	121.70(17)	C24-C23-C28	117.94(16)
P1-Co1-H1	78.9(7)	C2-C3-C4	124.42(17)	C24-C23-P2	120.31(13)
C14-P1-C8	98.83(8)	N1-C5-C6	111.46(14)	C28-C23-P2	121.70(14)
C14-P1-C7	102.89(8)	C7-C6-C5	113.02(15)	C23-C24-C25	120.79(18)
C8-P1-C7	99.06(8)	C6-C7-P1	112.00(13)	C26-C25-C24	120.49(18)
C14-P1-Co1	123.98(6)	C9-C8-C13	118.92(17)	C25-C26-C27	119.25(18)
C8-P1-Co1	119.01(6)	C9-C8-P1	120.18(13)	C26-C27-C28	120.60(17)
C7-P1-Co1	109.36(6)	C13-C8-P1	120.82(14)	C27-C28-C23	120.86(17)
C22-P2-C29	103.43(8)	C8-C9-C10	120.32(17)	C30-C29-C34	117.87(16)
C22-P2-C23	102.73(8)	C11-C10-C9	120.27(18)	C30-C29-P2	119.88(13)
C29-P2-C23	98.83(8)	C12-C11-C10	119.81(18)	C34-C29-P2	122.23(14)
C22-P2-Co1	110.37(6)	C11-C12-C13	120.13(18)	C31-C30-C29	120.62(17)
C29-P2-Co1	121.64(6)	C12-C13-C8	120.51(18)	C32-C31-C30	120.85(18)
C23-P2-Co1	117.40(6)	C19-C14-C15	118.16(17)	C33-C32-C31	119.13(17)
C2-N1-C5	118.73(15)	C19-C14-P1	124.04(14)	C32-C33-C34	120.55(18)
C2-N1-Co1	115.90(12)	C15-C14-P1	117.81(14)	C33-C34-C29	120.98(18)

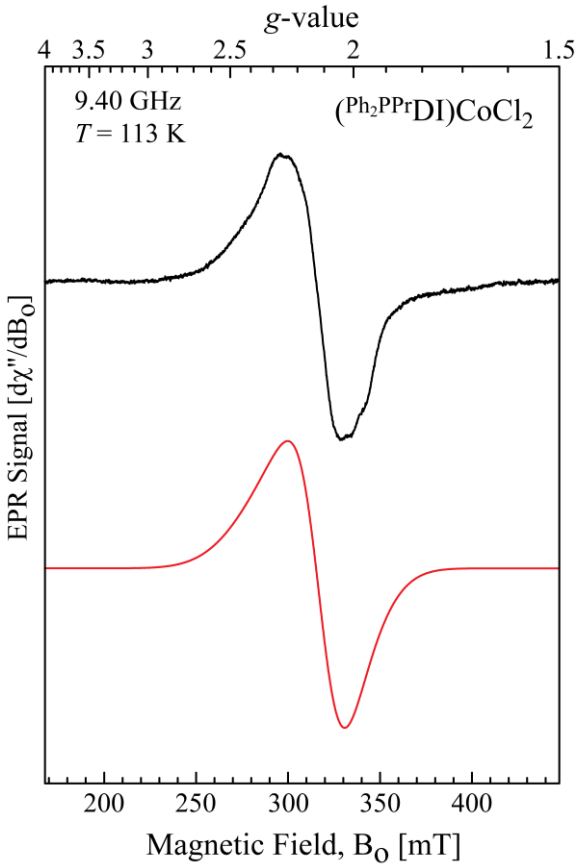


Figure S3. EPR Spectrum of **(^{Ph2PPr}DI)CoCl$_2$** in acetonitrile at 113 K.

Table S3. Parameters used to fit the EPR spectrum of **(^{Ph2PPr}DI)CoCl$_2$** at 9.40 GHz and T = 113 K.

Parameter	**(^{Ph2PPr}DI)CoCl$_2$**
g_x	2.310
g_y	2.110
g_z	2.048
$\|A_x\|$ (MHz)	< 150
$\|A_y\|$ (MHz)	< 50
$\|A_z\|$ (MHz)	< 75
ΔB_x (MHz)	1653
ΔB_y (MHz)	646
ΔB_z (MHz)	1304

Table S4. Relative energies calculated for **(^{Ph2PPr}DI)CoH**.

	Energy (Hartree)	**ΔE (kJ/mol)**	**ΔE (kcal/mol)**
rks	-3492.163067931415	4.915345	1.174783
uks (*S* = 0)	-3492.163068074221	4.914970	1.174694
BS(1,1)	-3492.164940087330	0.000000	0.000000
uks (*S* = 0) xtal (no opt)	-3491.617720739870	2.648872	0.633089
BS(1,1) xtal (no opt)	-3491.618729641740	0.000000	0.000000

Table S5. A comparison of metrical parameters calculated for **(^{Ph2PPr}DI)CoH**.

	Expt.	**rks**	**uks (*S* = 0) xtal (no opt)**	**uks (*S* = 0)**	**BS(1,1)**	**BS(1,1) xtal (no opt)**
C-N	1.347 1.357	1.349 1.355	1.347 1.357	1.349 1.355	1.347 1.352	1.347 1.357
C-C	1.401	1.414	1.401	1.414	1.420	1.401
Co-N_{DI}	1.887 1.916	1.894 1.922	1.887 1.916	1.894 1.922	1.924 1.961	1.887 1.916
Co-H	1.439	1.498	1.439	1.498	1.502	1.439
Co-P	2.146 2.137	2.173 2.165	2.146 2.137	2.173 2.165	2.238 2.183	2.146 2.137
P-Co-P	114.4	115.6	114.4	115.6	111.7	114.4
N-Co-N	81.9	82.1	81.9	82.1	81.7	81.9
$N_{DI,1}$-Co-H	95.0	91.6	95.0	91.6	91.4	95.0
$N_{DI,2}$-Co-H	165.0	159.8	165.0	159.8	159.7	165.0
$N_{DI,1}$-Co-P_1	93.8	94.6	93.8	94.6	94.2	93.8
$N_{DI,1}$-Co-P_2	148.5	146.7	148.5	146.7	153.0	148.5
$N_{DI,2}$-Co-P_1	115.9	117.0	115.9	117.0	115.3	115.9
$N_{DI,2}$-Co-P_2	96.9	95.0	96.9	95.0	93.5	96.9

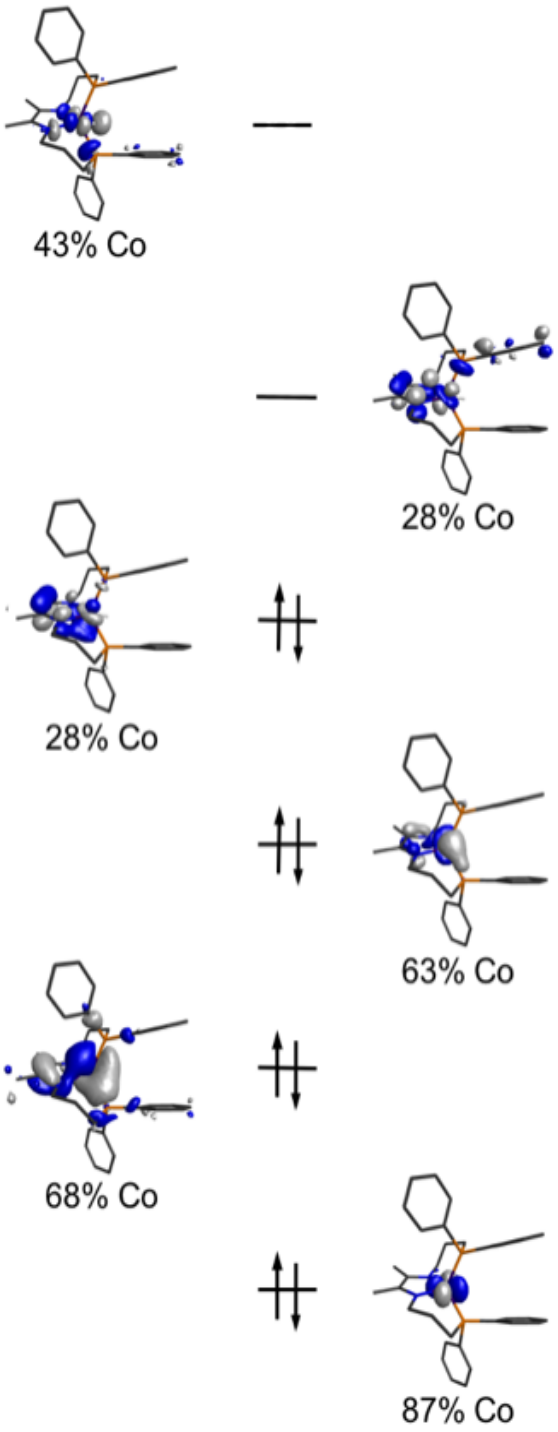


Figure S4. Qualitative molecular orbital diagram and representations for the **(^{Ph2PPr}DI)CoH** rks (S = 0) solution.

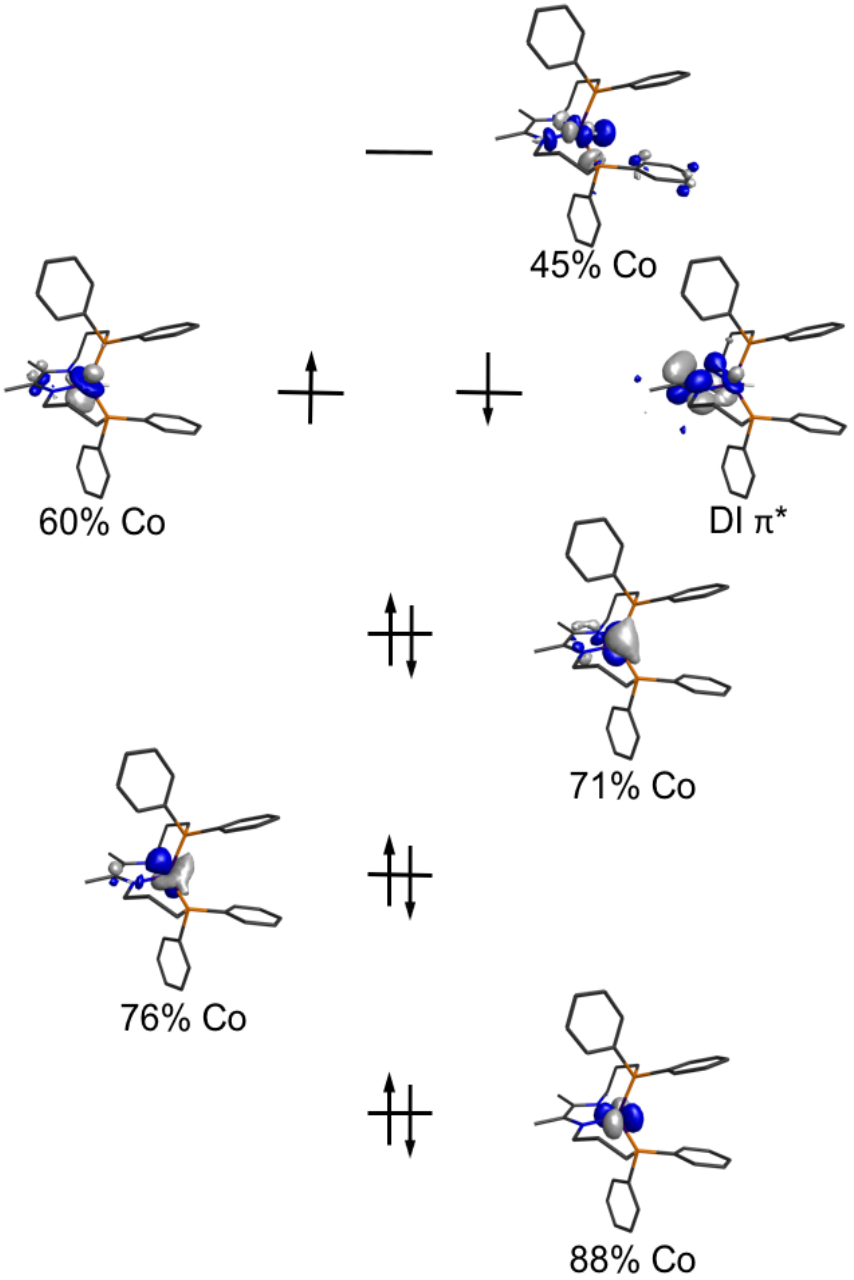


Figure S5. Qualitative molecular orbital diagram and representations for the **(^{Ph2PPr}DI)CoH** BS(1,1) solution.

Preparation and Characterization of Newly Prepared Complexes:

Preparation of (^{Ph2PPr}DI)$CoCl_2$: Under inert atmosphere, acetonitrile solutions (approx. 8 mL) of $CoCl_2$ (0.060 g, 0.458 mmol) and ^{Ph2PPr}DI (0.247 g, 0.461 mmol) were prepared in 20 mL scintillation vials and stirred for 15 min. The ligand solution was then pipetted into the $CoCl_2$ solution and the reaction was stirred for 24 h. The solution was filtered through Celite, the solvent was removed under reduced pressure, and the product was washed with pentane (10 mL). A dark red microcrystalline solid was isolated, yielding 0.213 g (0.151 mmol, 80%) of **(^{Ph2PPr}DI)$CoCl_2$**. Magnetic Susceptibility (Evans method and magnetic susceptibility balance, 25 °C): μ_{eff} = 2.8 μ_B. Analysis for $C_{34}H_{38}N_2P_2CoCl_2$ (666.44): Calcd. C, 61.27%; H, 5.75%; N, 4.20%. Found: C, 61.48%; H, 5.82%; N, 4.01%. ^{1}H NMR (acetonitrile-d_3, 25 °C, 500 MHz, peak width at half height in parenthesis): δ 21.84 (69.24), 11.60 (30.70), 10.12 (73.97), 0.22 (163.75), -2.80 (193.01), -3.96 (39.01), -6.00 (705.03), -10.63 (134.17), -11.93 (160.24), -13.81 (144.94). ^{1}H NMR (acetonitrile-d_3, -20 °C): δ 10.67 (244.02), -1.36 (265.41).

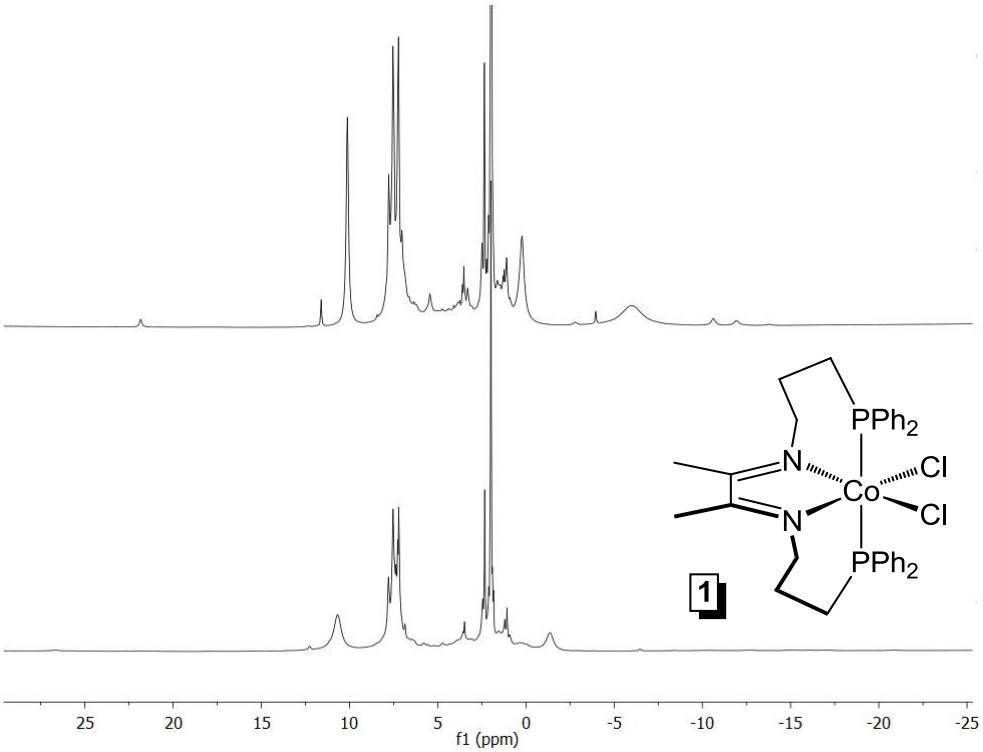


Figure S6. ^{1}H NMR spectrum of **(^{Ph2PPr}DI)$CoCl_2$** in acetonitrile-d_3 at 23 °C (top) and -20 °C (bottom).

Preparation of (^{Ph2PPr}DI)CoH: Under inert atmosphere, a scintillation vial was charged with diethyl ether (12 mL) and **(^{Ph2PPr}DI)CoCl$_2$** (0.138 g, 0.207 mmol). A 1.0 M solution of $NaEt_3BH$ in toluene (0.45 mL, 0.45 mmol) was then added and the reaction rapidly turned dark green as a soluble product formed. The solution was stirred for 24 h, filtered through Celite, and dried under reduced pressure. A dark green microcrystalline solid was isolated, yielding 0.082 g (0.137 mmol, 66%) of **(^{Ph2PPr}DI)CoH**. Analysis for $C_{34}H_{39}N_2P_2Co$ (596.57): Calcd. C, 68.45%; H, 6.59%; N, 4.70%. Found: C, 68.86%; H, 7.51%; N, 4.86%. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 7.63 (t, 8.4 Hz, 2H, *phenyl*), 7.12 (t, 8.4 Hz, 2H, *phenyl*), 7.00 (m, 5H, *phenyl*), 6.88 (m, 6H, *phenyl*), 6.72 (t, 7.4 Hz, 3H, *phenyl*), 6.65 (t, 7.4 Hz, 2H, *phenyl*), 4.81 (t, 12.1 Hz, 1H, C*H*$_2$), 4.51 (m, 1H, C*H*$_2$), 3.26 (m, 1H, C*H*$_2$), 3.09 (m, 1H, C*H*$_2$), 2.52 (m, 2H, C*H*$_2$), 2.11 (m, 4H, C*H*$_2$), 2.00 (pseudo q, 2H, C*H*$_2$), 1.51 (dd, 22.3 Hz, 7.8 Hz, 6H, C*H*$_3$), -19.80 (dd, 90.2 Hz, 39.3 Hz, 1H, Co*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz, 25 °C): δ 142.66 (*phenyl*), 140.09 (*phenyl*), 139.72 (*phenyl*), 139.52 (*phenyl*), 135.72 (d, J_{CP} = 13.0 Hz, *phenyl*), 133.42 (d, J_{CP} = 11.4 Hz, phenyl), 131.05 (dd, J_{CP} = 10.3, 3.2 Hz, *phenyl*), 128.83 (*phenyl*), 128.74 (*phenyl*), 128.65 (*phenyl*), 128.46 (*phenyl*), 128.27 (*phenyl*), 128.09 (*phenyl*), 128.05 (*phenyl*), 128.02 (*phenyl*), 127.99 (*phenyl*), 127.94 (*phenyl*), 127.87 (*phenyl*), 127.64 (*C*CH$_3$), 127.43 (*C*CH$_3$), 61.79 (*C*H$_2$), 55.19 (*C*H$_2$), 31.12 (d, J_{CP} = 25.2 Hz, *C*H$_2$), 30.54 (*C*H$_2$), 28.95 (d, J_{CP} = 15.7 Hz, *C*H$_2$), 26.86 (d, J_{CP} = 12.6 Hz, *C*H$_2$), 17.25 (d, J_{CP} = 4.0 Hz, *C*H$_3$), 15.19 (d, J_{CP} = 4.0 Hz, *C*H$_3$). ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz, 25 °C): δ 75.33 (br), 50.59 (br).

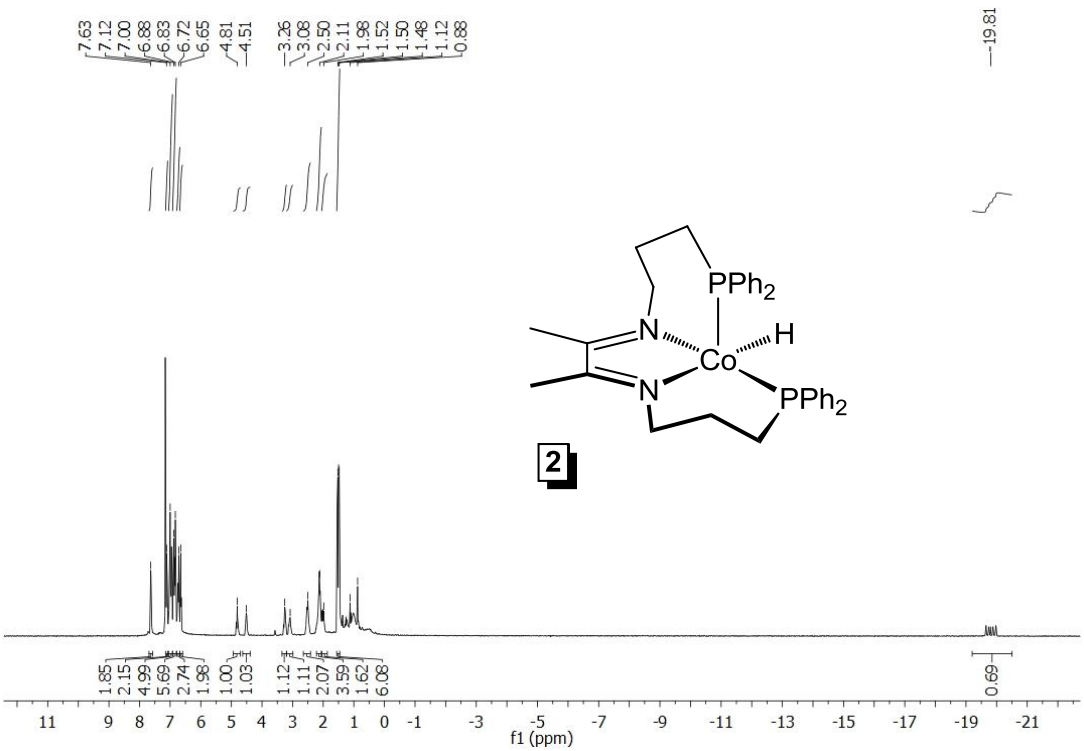


Figure S7. ^{1}H NMR spectrum of **(**$^{\mathbf{Ph2PPr}}$**DI)CoH** in benzene-d_6.

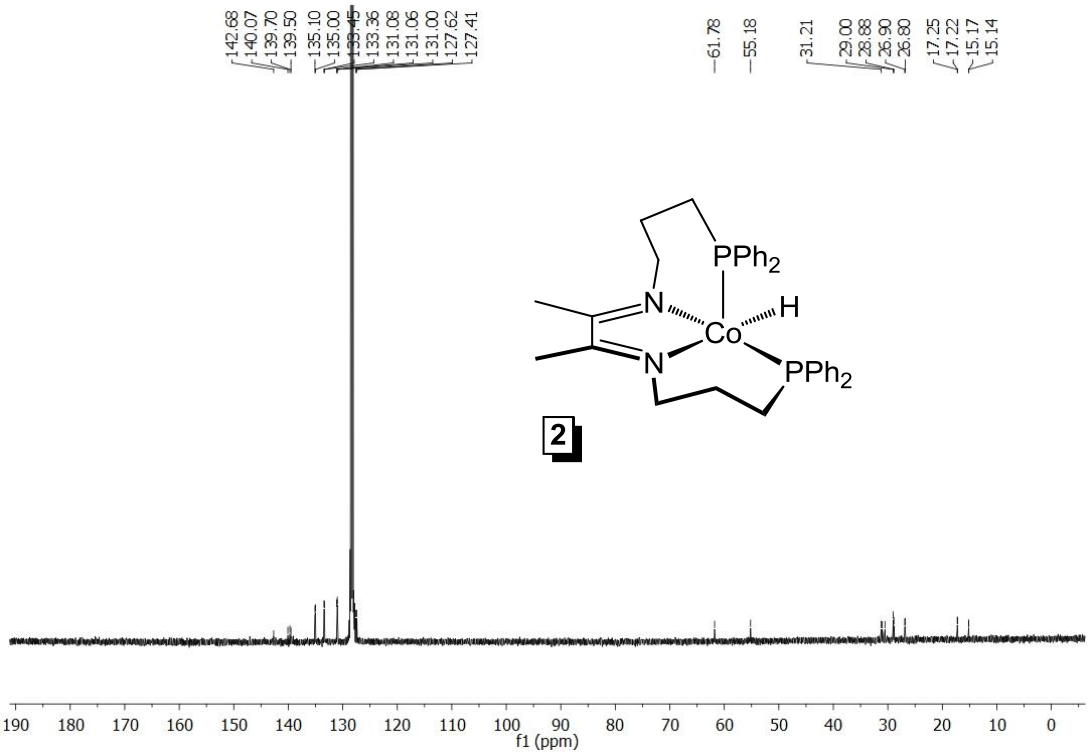


Figure S8. ^{13}C NMR spectrum of **(**$^{\mathbf{Ph2PPr}}$**DI)CoH** in benzene-d_6.

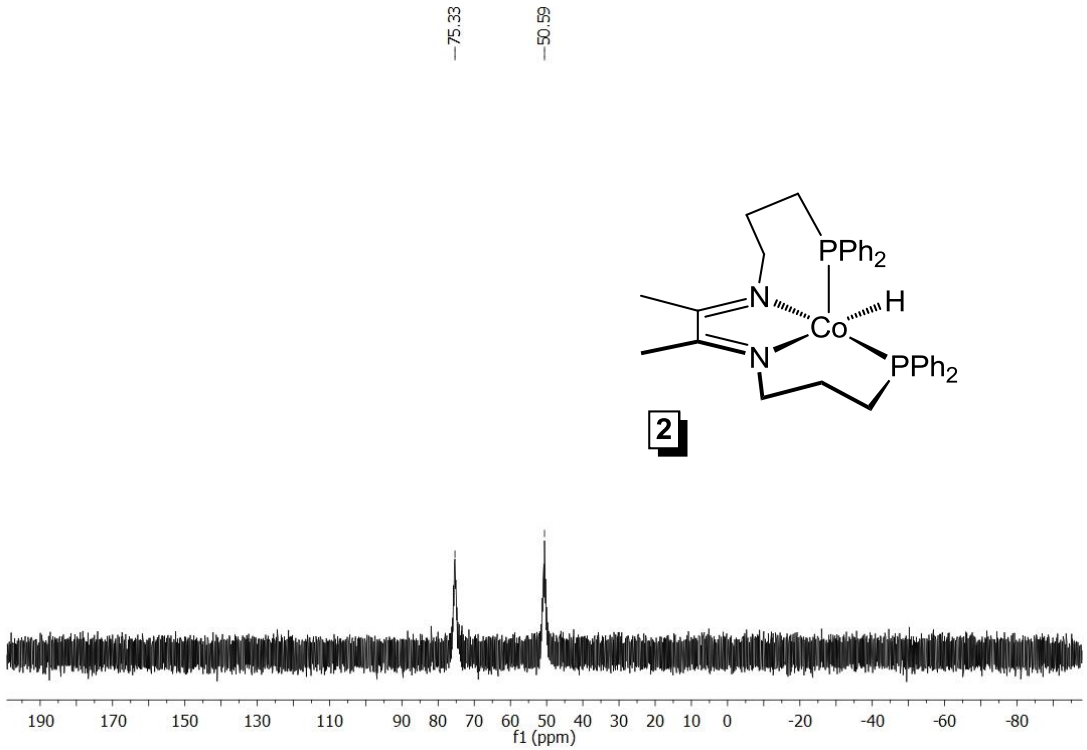
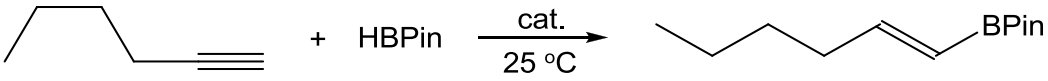


Figure S9. ^{31}P NMR spectrum of **(^{Ph2PPr}DI)CoH** in benzene-d_6.

Hydroboration Reactions:

Table S6. Optimization of 1-Hexyne Hydroboration Conditions.



Entry	Catalyst	Mol%	Solvent	Time	1-Hexyne:HBPin	% Conv.[a]
1	$CoCl_2$	5.0	benzene-d_6	2 h	1:1	0
2	$CoCl_2$	5.0	benzene-d_6	24 h	1:1	0
3	**(^{Ph2PPr}DI)CoH**	5.0	benzene-d_6	2 h	1:1	81[b]
4	**(^{Ph2PPr}DI)CoH**	5.0	diethyl ether	2 h	1:1	>99
5	**(^{Ph2PPr}DI)CoH**	5.0	benzene-d_6	2 h	1:1.25	>99
6	**(^{Ph2PPr}DI)CoH**	1.0	benzene-d_6	2 h	1:1.25	>99
7	**(^{Ph2PPr}DI)CoH**	1.0	THF	2 h	1:1.25	>99
8	**(^{Ph2PPr}DI)CoH**	0.1	neat	2 h	1:1.25	>99
9	**(^{Ph2PPr}DI)CoH**	0.1	neat	1 h	1:1.25	90
10	none	-	neat	2 h	1:1.25	0

[a]Percent conversion determined by integrating product and residual substrate ^{1}H NMR resonances. [b]Average of 5 trials.

General Procedure for Alkyne Hydroboration Using 1.0 mol% 2: Under an inert atmosphere, alkyne (approx. 0.5 mmol), pinacolborane (approx. 0.8 mmol), and 0.5 mL of benzene-d_6 were combined in a 20 mL scintillation vial. This solution was then transferred into a vial charged with **2** (approx. 0.005 mmol) and stirred at 25 °C for 2 h. The solution was then exposed to air to deactivate the catalyst and percent conversion was determined by integrating the product and residual substrate ^{1}H NMR resonances. Remaining solvent was removed under reduced pressure and the product was purified by silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. Solvent was removed under reduced pressure and the resulting alkenyl boronate esters were isolated as oils.

General Procedure for Alkyne Hydroboration Using 0.1 mol% 2: Under an inert atmosphere, alkyne (approx. 5.0 mmol) and pinacolborane (approx. 8.0 mmol) were combined in a 20 mL scintillation vial. This solution was then transferred into a vial charged with **2** (approx. 0.005 mmol) and stirred at 25 °C for 2 h. The solution was then exposed to air to deactivate the catalyst and percent conversion was determined by integrating the product and residual substrate ^{1}H NMR resonances. The product was purified by silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. The solvent was removed under reduced pressure and the resulting alkenyl boronate esters were isolated as oils.

General Procedure for Nitrile Hydroboration Using 1.0 mol% 2: Under an inert atmosphere, nitrile (approx. 0.8 mmol), HBPin (approx. 2.0 mmol), and 0.5 mL of benzene-d_6 were combined. The solution was then transferred into a 20 mL scintillation vial charged with **2** (0.0050 g) and stirred at 60 °C for 24 h. The vial was then opened to air to deactivate the catalyst and percent conversion determined by integrating the product and residual substrate ^{1}H NMR resonances. Remaining solvent was removed under reduced pressure and diboryl amines were isolated as white crystals following recrystallization from pentane.

Hydroboration of 1-hexyne using 0.1 mol% 2: Under an inert atmosphere, 1-hexyne (0.58 mL, 5.03 mmol) and pinacol borane (0.91 mL, 6.29 mmol) were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0030 g **2** (0.00503 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified by silica gel column chromatography following deactivation with NEt_3 with 20:1 hexane:diethyl ether as the eluent. Upon removing the solvent, a clear oil was identified as (*E*)-2-(hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.985 g, 93%) was isolated.[11] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.62 (dt, J = 18.4 Hz, 6.7 Hz, 1H, C*H*), 5.42 (dd, J = 18.0 Hz, 1.5 Hz, 1H, C*H*), 2.17 (q, J = 7.0, 2H, CH_2), 1.36 (m, 4H, CH_2), 1.26 (s, 12H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 154.98 (*C*H), 83.16 (*C*CH_3), 35.70 (*C*H_2), 30.56 (*C*H_2), 24.97 (*C*H_3), 22.45 (*C*H_2), 14.11 (*C*H_3), one resonance not located (*C*-B).

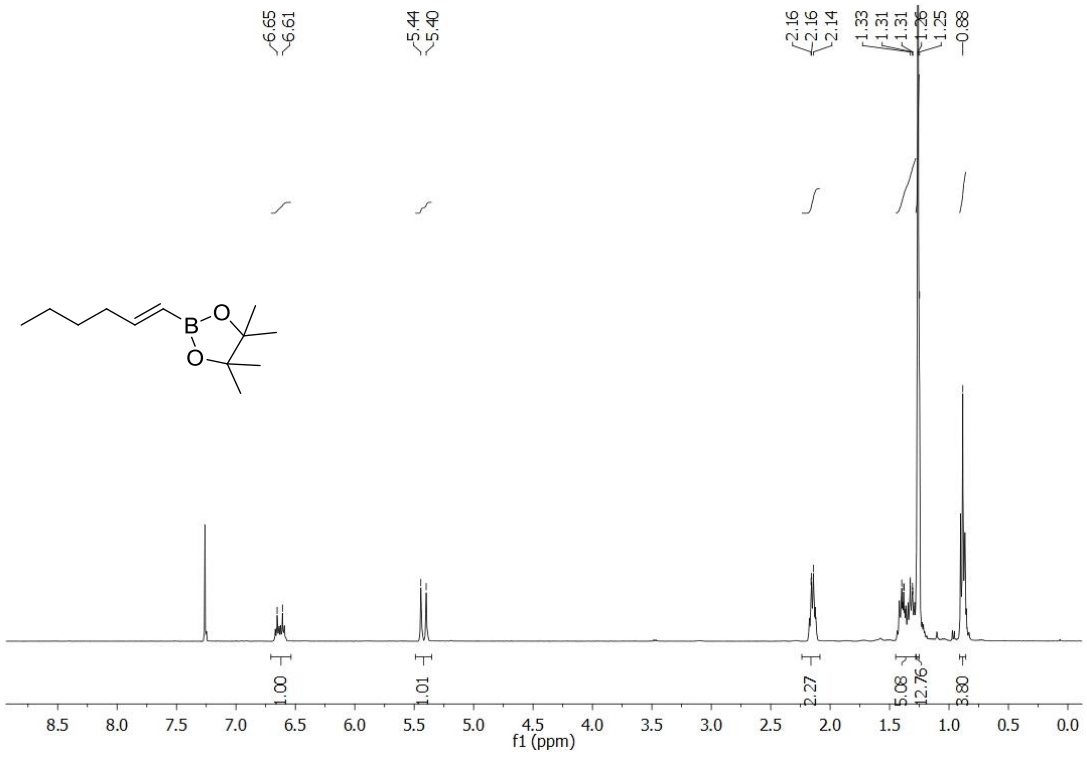


Figure S10. ^{1}H NMR spectrum of (*E*)-2-(hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

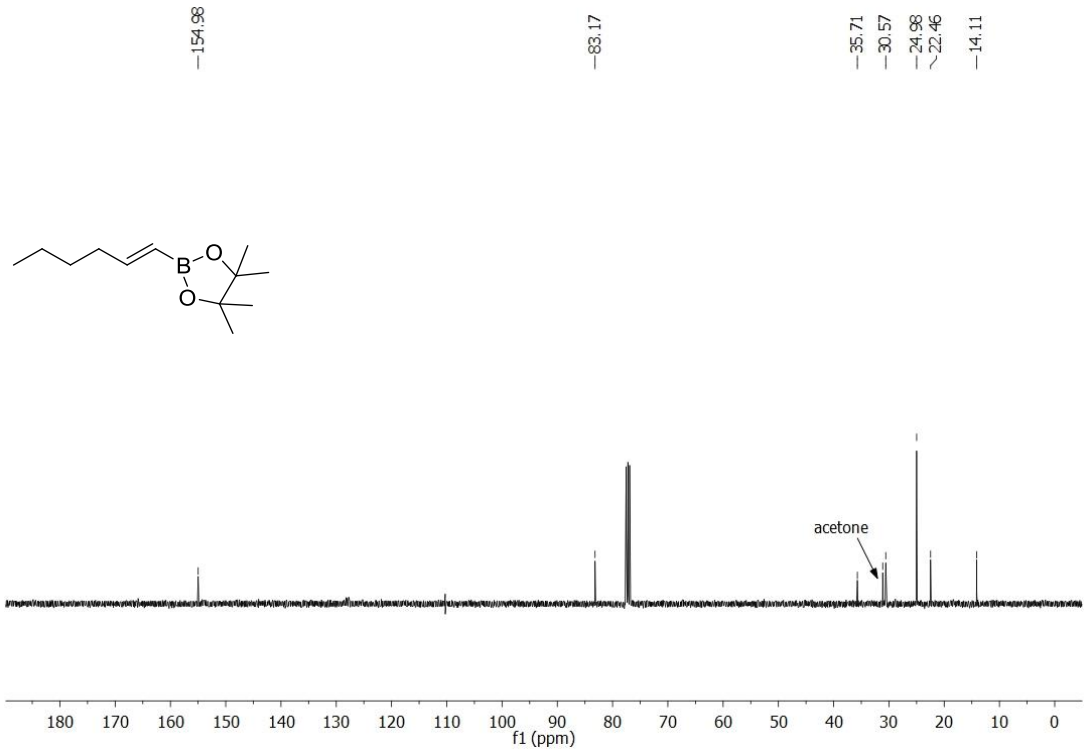


Figure S11. ^{13}C NMR spectrum of (*E*)-2-(hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of cyclopropylacetylene using 1.0 mol% 2: Under an inert atmosphere, cyclopropylacetylene (58 µL, 0.687 mmol), pinacol borane (110 µL, 0.859 mmol), and 0.50 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0041 g **2** (0.00687 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified by silica gel column chromatography following deactivation with NEt_3 with 20:1 hexane:ethyl acetate as the eluent. Upon removing the solvent, a clear oil identified as (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.0811 g, 61%) was isolated.[12] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.03 (dd, J = 17.8, 9.3 Hz, 1H, =C*H*), 5.45 (d, J = 17.8 Hz, 1H, =C*H*), 1.54 – 1.42 (m, 1H, C*H*), 1.21 (s, 12H, CH_3), 0.80 – 0.72 (m, 2H, CH_2), 0.52 – 0.45 (m, 2H, CH_2). ^{13}C NMR (chloroform-*d*, 101 MHz): δ 158.61 (*C*H), 83.00 (*C*CH_3), 24.88 (*C*H_3), 17.11 (*C*H), 7.99 (*C*H_2), one resonance not located (*C*-B).

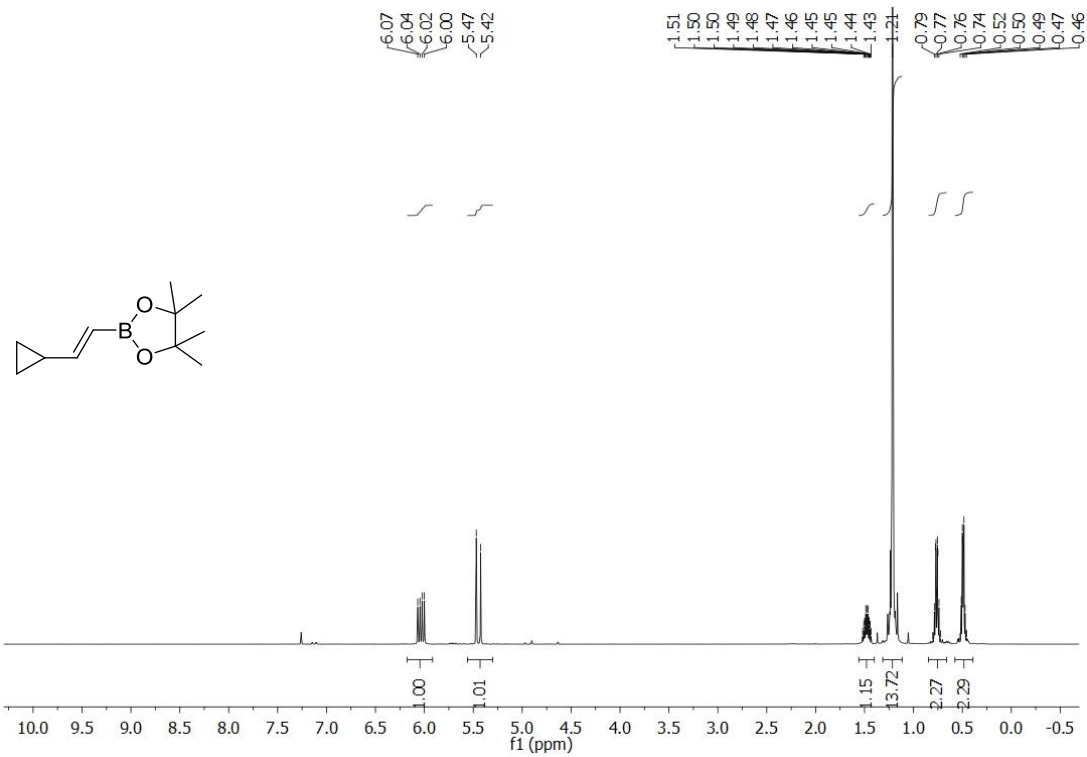


Figure S12. ^{1}H NMR spectrum of (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

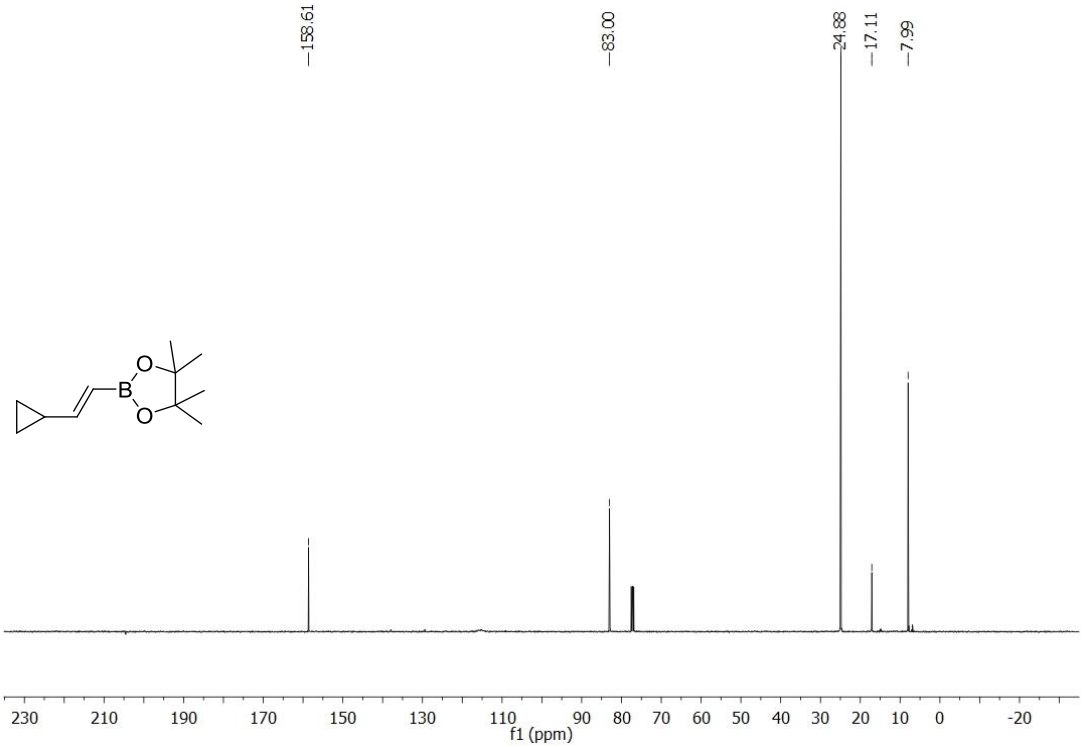


Figure S13. ^{13}C NMR spectrum of (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of cyclohexylacetylene using 1.0 mol% 2: Under an inert atmosphere, cyclohexylacetylene (63 µL, 0.486 mmol), pinacol borane (94 µL, 0.608 mmol), and 0.50 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0029 g **2** (0.00486 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified using silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. Upon removing the solvent, a clear oil (0.102 g, 89%) identified as (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was isolated.[13] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.55 (dd, J = 18.2, 6.2 Hz, 1H, =C*H*), 5.35 (dd, J = 18.2, 1.5 Hz, 1H, =C*H*), 2.04 – 1.92 (m, 1H, C*H*), 1.75 – 1.65 (m, 4H, CH_2), 1.65 – 1.57 (m, 2H, CH_2), 1.24 (s, 12H, CH_3), 1.16 – 1.00 (m, 4H, CH_2). ^{13}C NMR (chloroform-*d*, 101 MHz): δ 159.96 (*C*H), 115.98 (*C*-B), 83.13 (*C*CH_3), 43.41 (CH_2*C*HCH_2), 32.10 (*C*H_2), 26.35 (*C*H_2), 26.13 (*C*H_2), 24.94 (*C*H_2), 24.71 (*C*H_3).

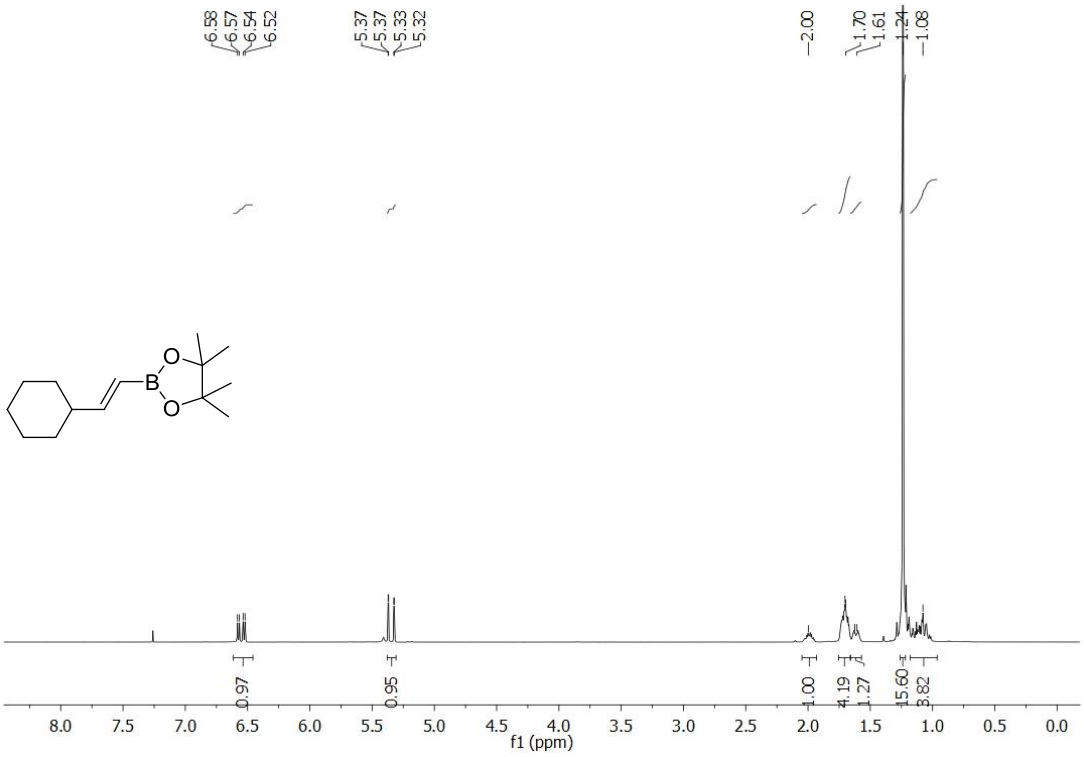


Figure S14. ^{1}H NMR spectrum of (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

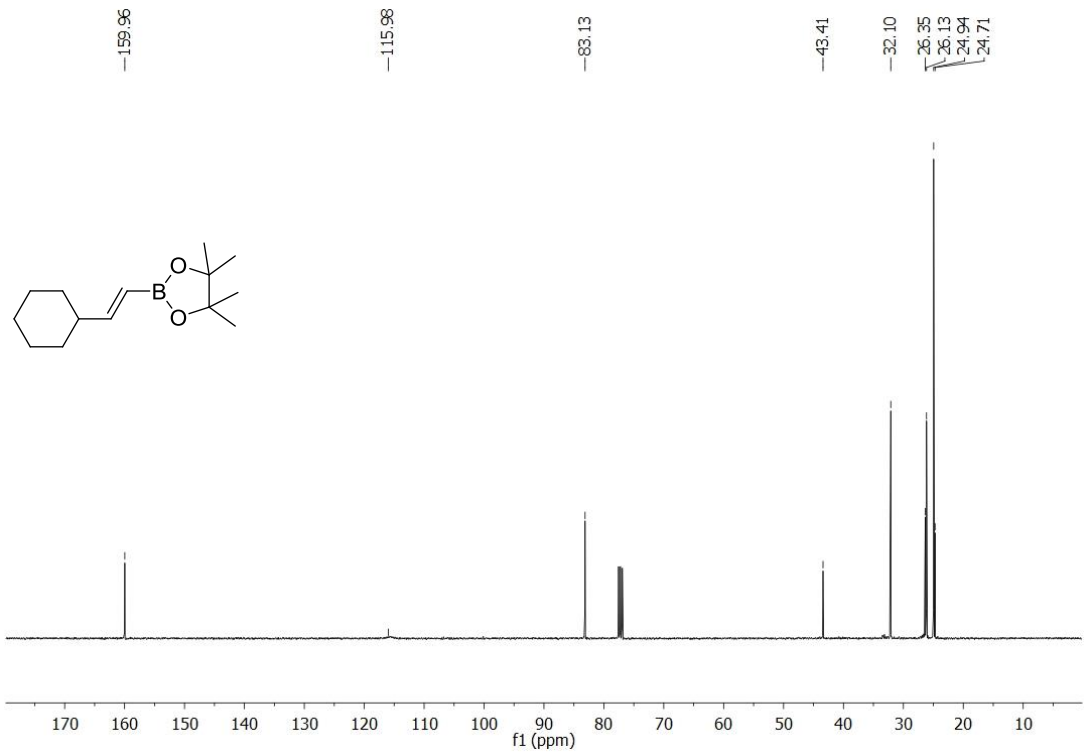


Figure S15. ^{13}C NMR spectrum of (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of phenylacetylene using 1.0 mol% 2: Under an inert atmosphere, phenyl acetylene (74 µL, 0.671 mmol), pinacol borane (121 µL, 0.839 mmol), and 0.50 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0040 g **2** (0.00671 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified using silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. Upon removing the solvent, a yellow oil identified as (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (0.148 g, 96%) was isolated.[12] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.52 – 7.46 (m, 2H, *phenyl*), 7.42 (d, J = 18.4 Hz, 1H, C*H*), 7.37 – 7.24 (m, 3H, *phenyl*), 6.19 (d, J = 18.4 Hz, 1H, C*H*), 1.31 (s, 12H, CH_3). ^{13}C NMR (chloroform-*d*, 101 MHz): δ 149.67 (*C*H), 137.60 (*phenyl*), 129.00 (*phenyl*), 128.67 (*phenyl*), 127.16 (*phenyl*), 83.46 (*C*CH$_3$), 24.90 (*C*H$_3$), one resonance not located (*C*-B).

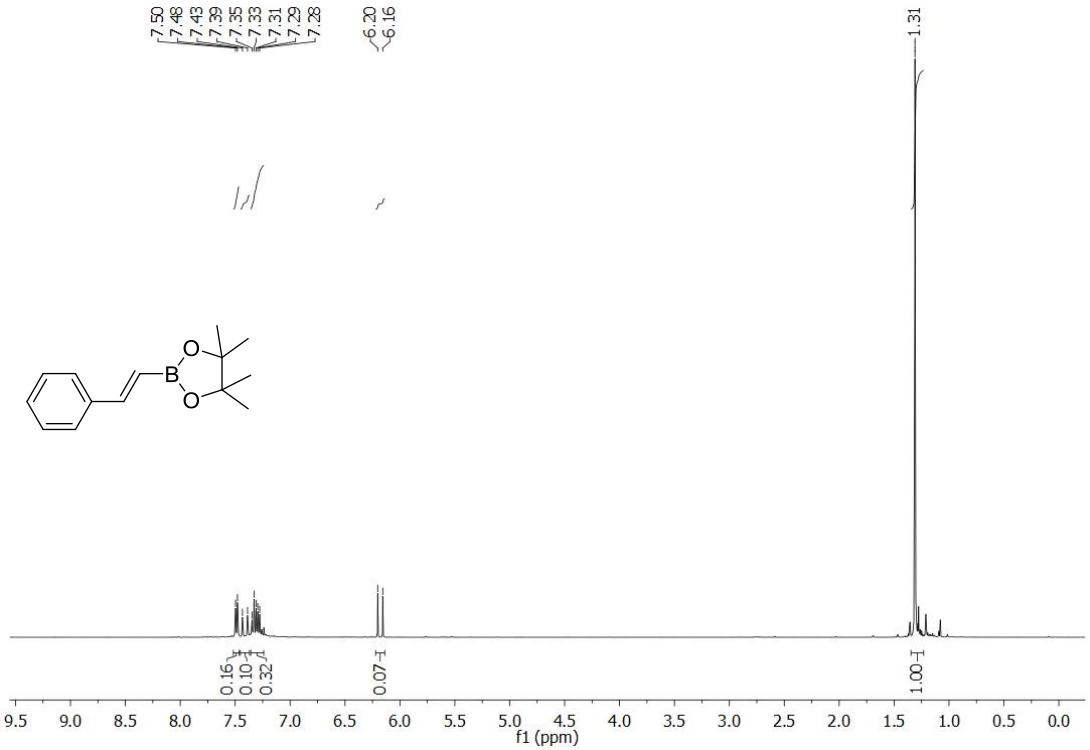


Figure S16. [1]H NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane in chloroform-*d*.

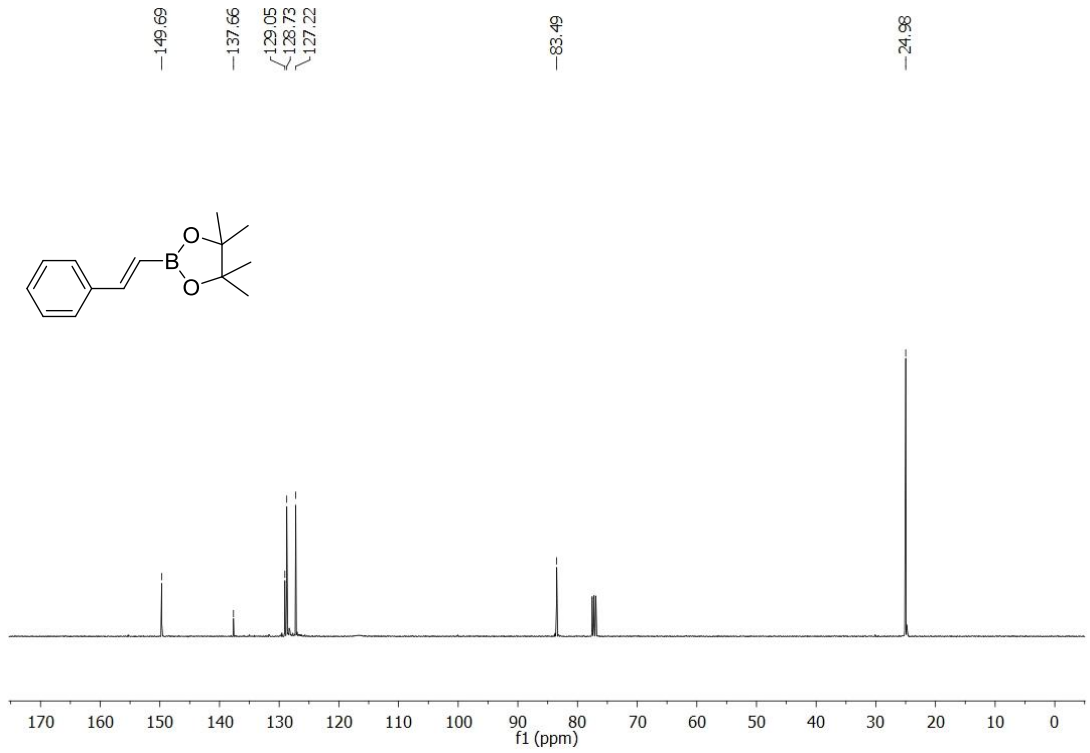


Figure S17. [13]C NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of 3-fluorophenylacetylene using 1.0 mol% 2: Under an inert atmosphere, 3-fluorophenylacetylene (56 µL, 0.486 mmol), pinacol borane (94 µL, 0.608 mmol), and 0.50 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0029 g **2** (0.00486 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified using silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. Upon removing the solvent, a yellow liquid and identified as (*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.0981 g, 81%) was isolated.[14] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.34 (d, *J* = 18.4 Hz, 1H, C*H*), 7.30 – 7.21 (m, 2H, *phenyl*), 7.20 – 7.13 (m, 1H, *phenyl*), 7.01 – 6.93 (m, 1H, *phenyl*), 6.16 (d, *J* = 18.4 Hz, 1H, C*H*), 1.31 (s, 12H). ^{13}C NMR (chloroform-*d*, 101 MHz): δ 163.27 (d, *J* = 245.6 Hz, *phenyl*), 148.26 (d, *J* = 2.5 Hz, *phenyl*), 140.11 (*C*H), 130.20 (d, *J* = 8.3 Hz, *phenyl*), 123.17 (d, *J* = 2.7 Hz, *phenyl*), 115.84 (d, *J* = 21.5 Hz, *phenyl*), 113.46 (d, *J* = 21.6 Hz, *phenyl*), 83.70 (*C*CH$_3$), 24.96 (*C*H$_3$), one resonance not located (*C*-B).

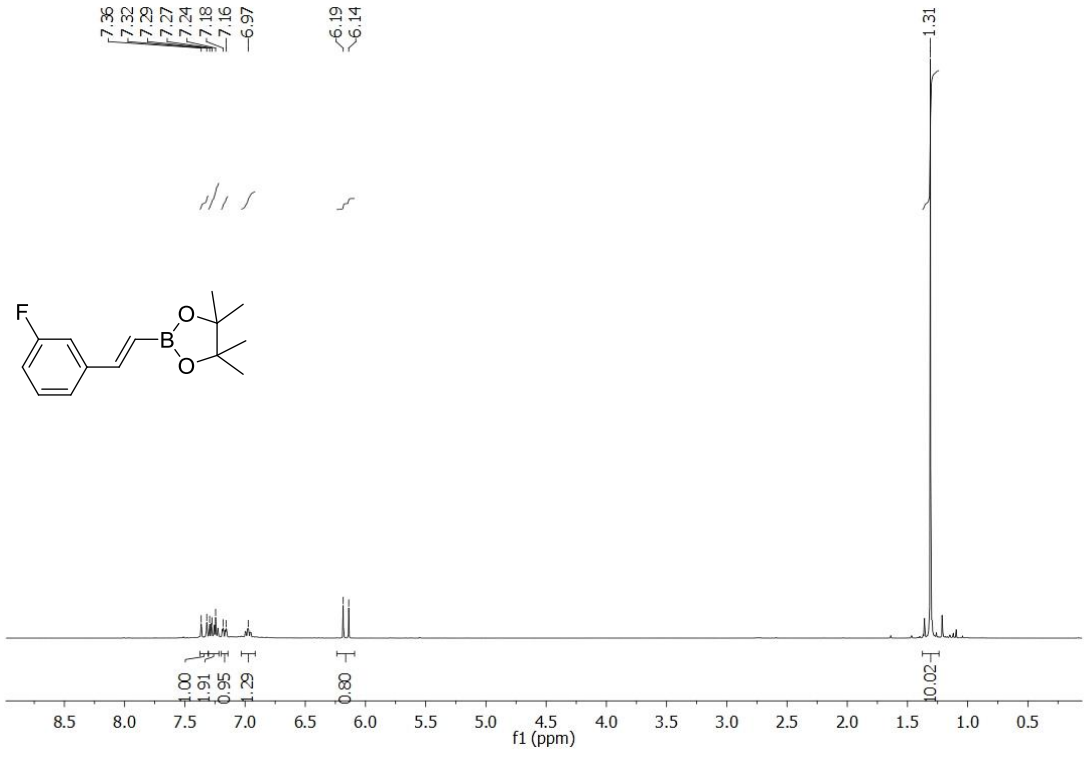


Figure S18. ^{1}H NMR spectrum of (*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

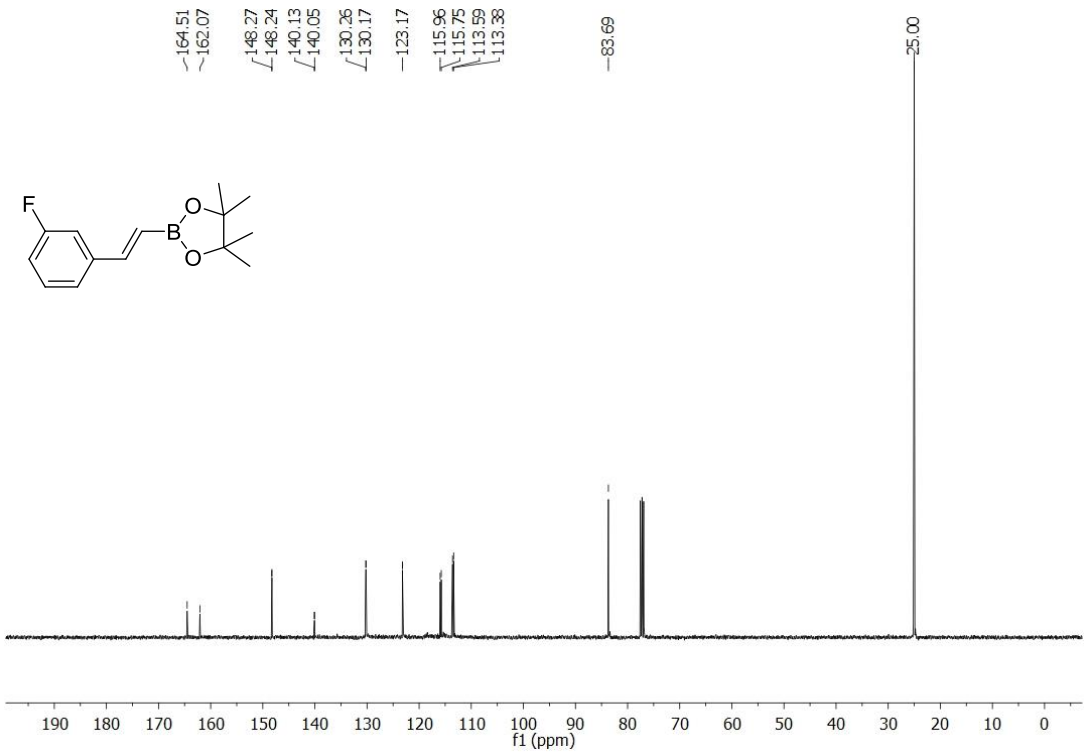


Figure S19. ^{13}C NMR spectrum of (*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of *p*-tolylacetylene using 1.0 mol% 2: Under an inert atmosphere, *p*-tolylacetylene (61 µL, 0.486 mmol), pinacol borane (94 µL, 0.608 mmol), and 0.50 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0029 g **2** (0.00486 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified using silica gel column chromatography with 20:1 hexane:ethyl acetate as the eluent. Upon removing the solvent, a yellow oil identified as (*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (0.0823 g, 69%) was isolated.[11] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.44-7.38 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H, *phenyl*), 6.14 (d, J = 18.5 Hz, 1H, C*H*), 2.36 (s, 3H, CH_3), 1.33 (s, 12H, CH_3). ^{13}C NMR (chloroform-*d*, 101 MHz): δ 149.65 (*C*H), 139.08 (*phenyl*), 134.99 (*phenyl*), 129.45 (*phenyl*), 127.18 (*phenyl*), 83.40 (*C*CH$_3$), 24.97 (*C*H$_3$), 21.47 (*C*H$_3$), one resonance not located (*C*-B).

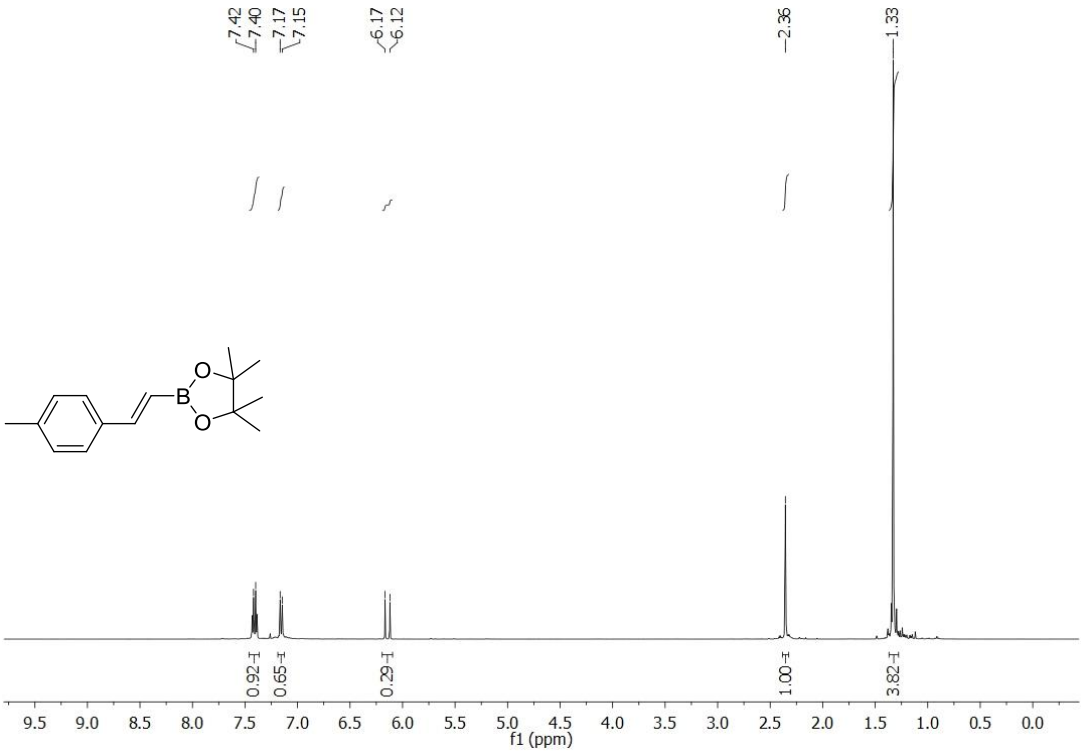


Figure S20. ^{1}H NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane in chloroform-*d*.

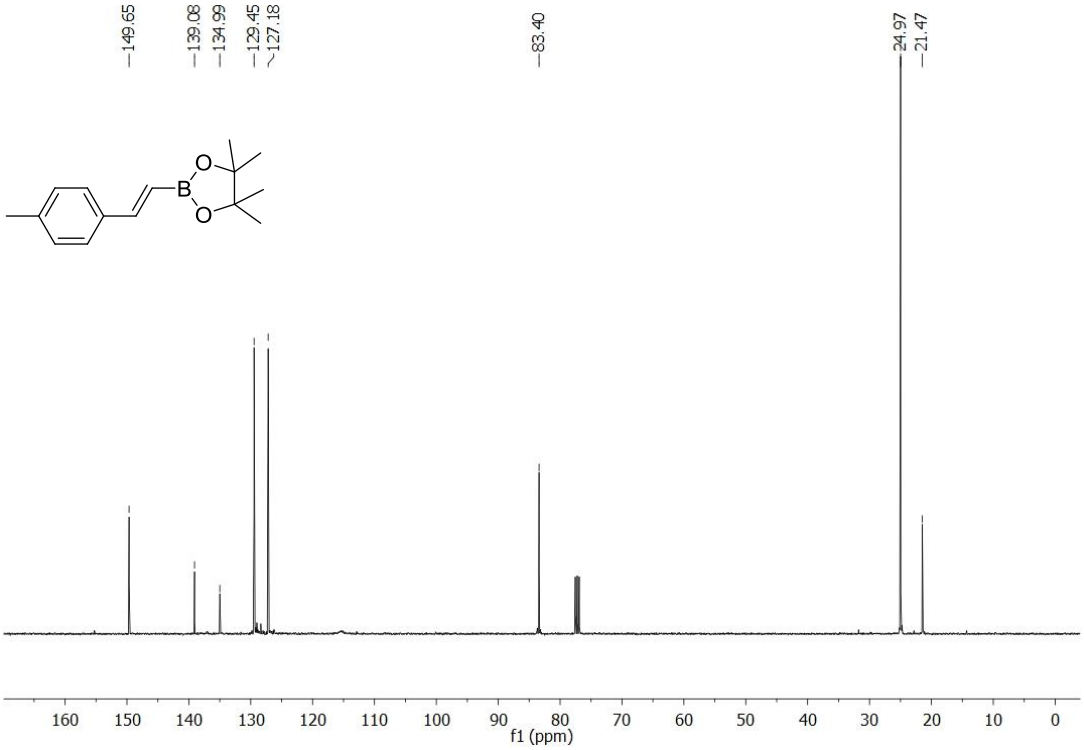


Figure S21. ^{13}C NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of phenyl propargyl ether using 1.0 mol% 2: Under an inert atmosphere, phenyl propargyl ether (0.536 mmol), pinacol borane (104 µL, 0.671 mmol), and 0.5 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0032 g **2** (0.00536 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. ^{1}H NMR spectroscopy revealed 58% conversion.[11]

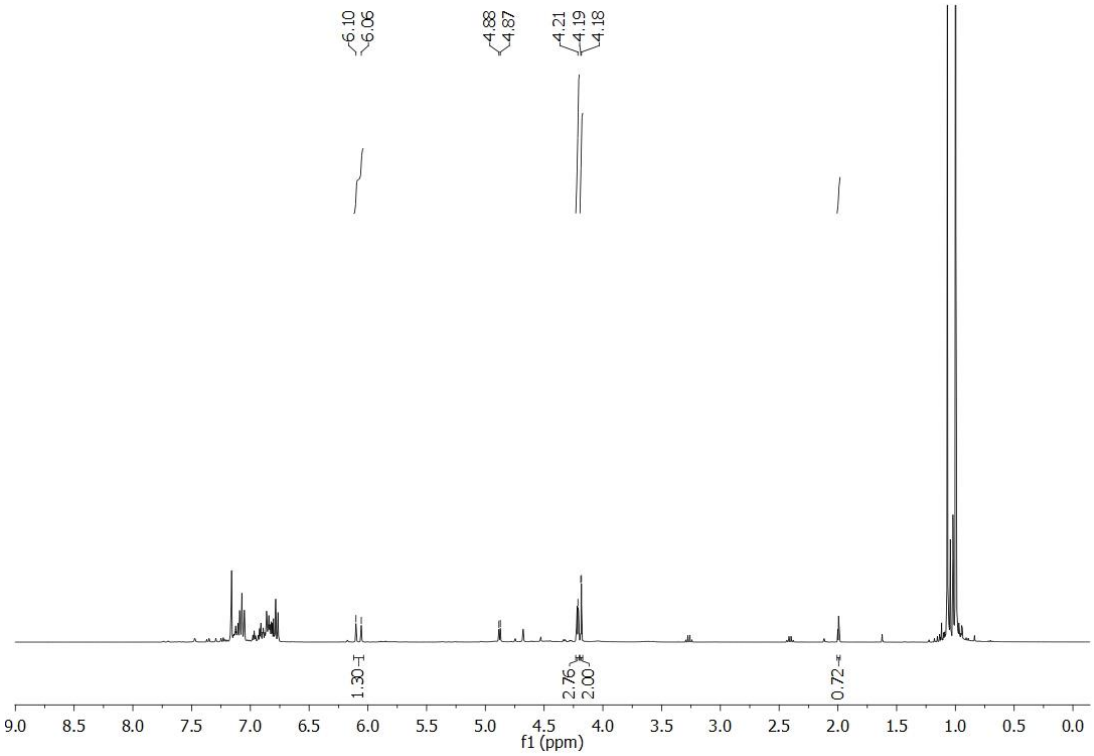


Figure S22. ^{1}H NMR spectrum showing 58% conversion to (*E*)-4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-enyl)-1,3,2-dioxaborolane in benzene-d_6.

Hydroboration of propargyl phthalimide using 1.0 mol% 2: Under an inert atmosphere, propargyl phthalimide (0.536 mmol), pinacol borane (104 µL, 0.671 mmol), and 1.0 mL benzene-d_6 were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0032 g **2** (0.00536 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. ^{1}H NMR spectroscopy revealed 70% conversion.[15]

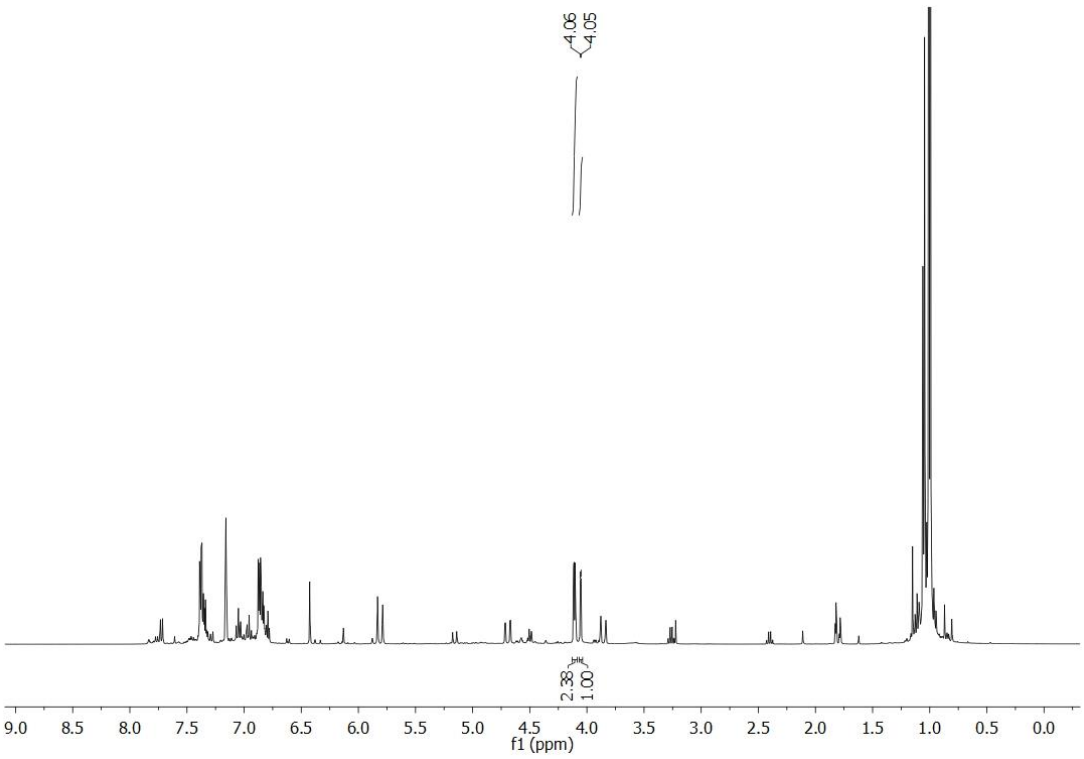


Figure S23. ^{1}H NMR spectrum showing 70% conversion to (*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione in benzene-d_6.

Hydroboration of 1-octyne using 0.1 mol% 2: Under an inert atmosphere, 1-octyne (0.74 mL, 5.03 mmol) and pinacol borane (0.91 mL, 6.29 mmol) were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0030 g **2** (0.00503 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified by silica gel column chromatography following deactivation with NEt_3 with 20:1 hexane:diethyl ether as the eluent. Upon removing the solvent, a clear oil identified as (*E*)-4,4,5,5-tetramethyl-2-(oct-1-enyl)-1,3,2-dioxaborolane (0.502 g, 44%) was obtained.[14] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.63 (dt, J = 17.9 Hz, 6.3 Hz, 1H, C*H*), 5.42 (dt, J = 17.9 Hz, 1.3 Hz, 1H, C*H*), 2.14 (q, J = 7.0 Hz, 2H, CH_2), 1.42 (p , J = 7.3 Hz, 2H, CH_2), 1.28 (m, 18H, CH_2, CH_3), 0.88 (m, 3H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 155.06 (*C*H), 83.18 (*C*H), 36.05 (*C*H_2), 31.93 (*C*CH_3), 29.13 (*C*H_2), 28.41 (*C*H_2), 24.98 (*C*H_3), 22.80 (*C*H_2), 14.30 (*C*H_3), one resonance not located (*C*-B).

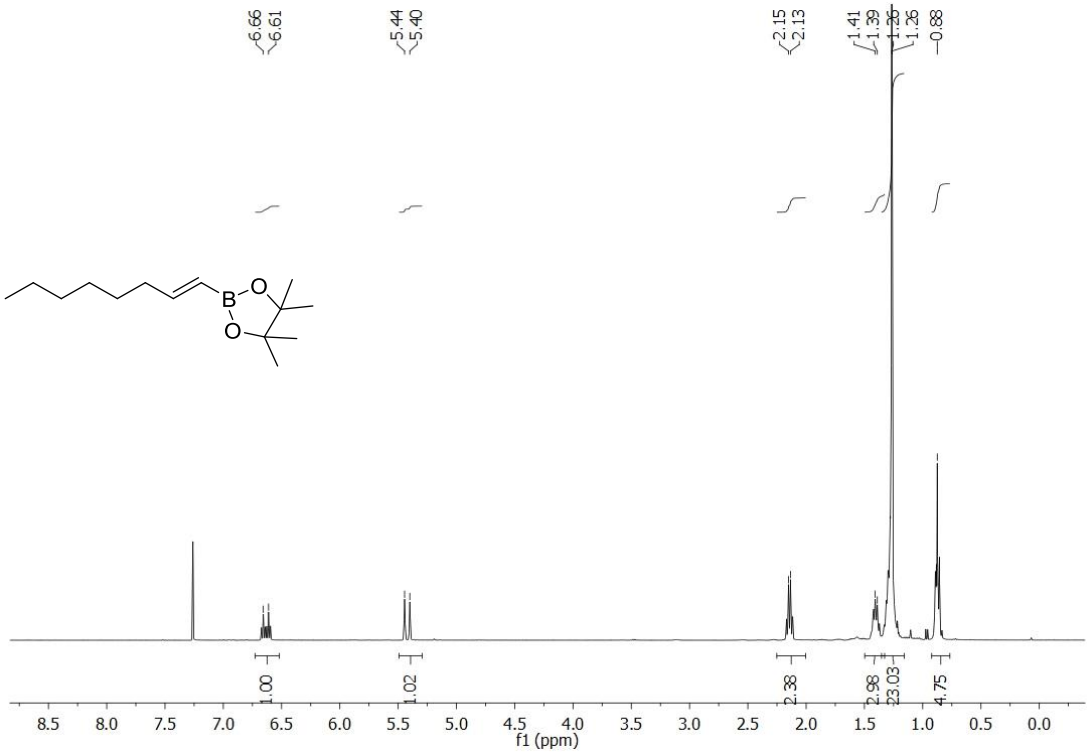


Figure S24. ^{1}H NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(oct-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

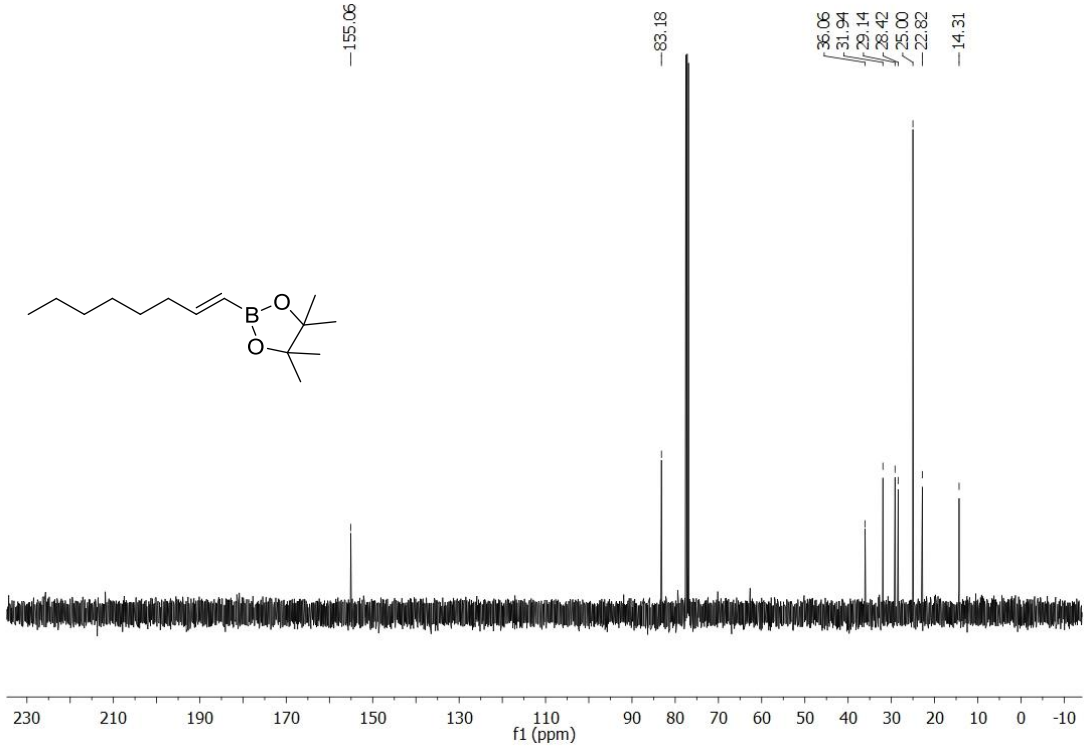


Figure S25. ^{13}C NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(oct-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of 5-methyl-1-hexyne using 0.1 mol% 2: Under an inert atmosphere, 5-methyl-1-hexyne (0.71 mL, 5.37 mmol) and pinacol borane (0.97 mL, 6.68 mmol) were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0032 g **2** (0.00537 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified by silica gel column chromatography following deactivation with NEt_3 with 20:1 hexane:diethyl ether as the eluent. Upon removing the solvent, a clear oil identified as (*E*)-4,4,5,5-tetramethyl-2-(5-methylhex-1-enyl)-1,3,2-dioxaborolane (1.028 g, 85%) was obtained.[11] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.63 (dt, J = 18.0 Hz, 6.5 Hz, 1H, C*H*), 5.42 (dt, J = 18.0 Hz, 1.5 Hz, 1H, C*H*), 2.15 (q, J = 7.8 Hz, 2H, CH_2), 1.56 (p, J = 6.4 Hz, 1H, C*H*), 1.30 (m, 2H, CH_2), 1.26 (s, 12H CH_3), 0.87 (d, J = 6.9 Hz, 6H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 155.17 (*C*H), 83.19 (*C*CH_3), 37.58 (*C*H_2), 33.88 (*C*H_2), 31.81 (*C*H_2), 27.67 (*C*H_2), 24.99 (*C*H_3), 22.67 (*C*H_3), one resonance not located (*C*-B).

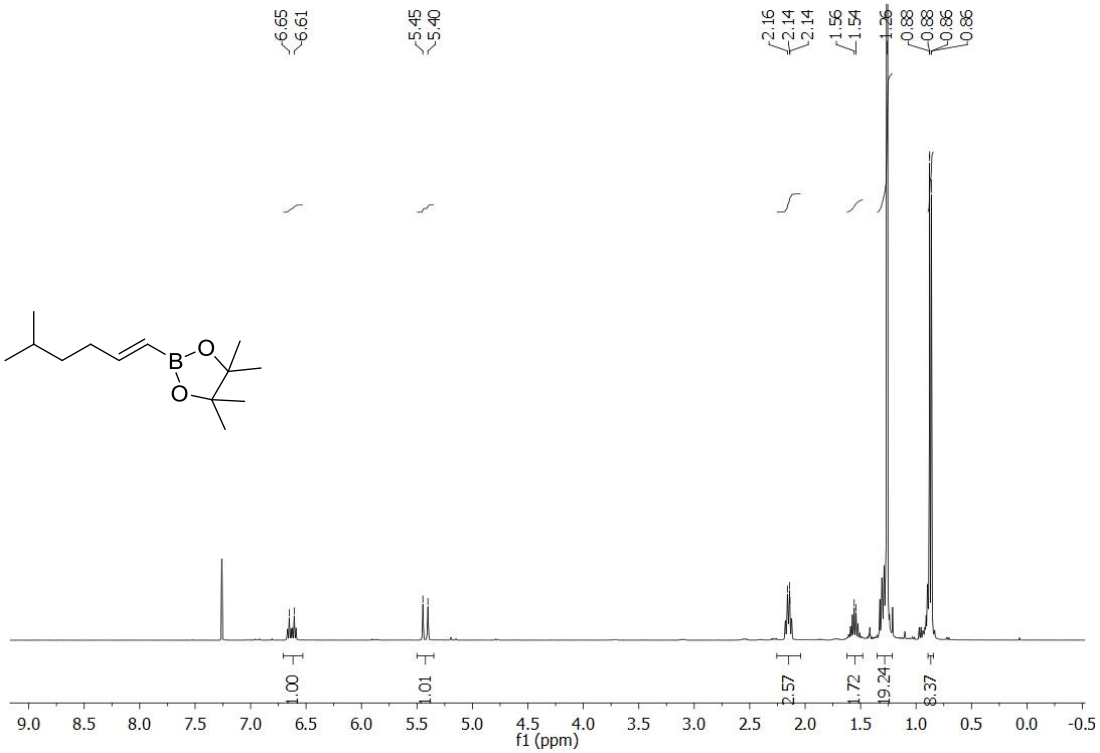


Figure S26. ^{1}H NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(5-methylhex-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

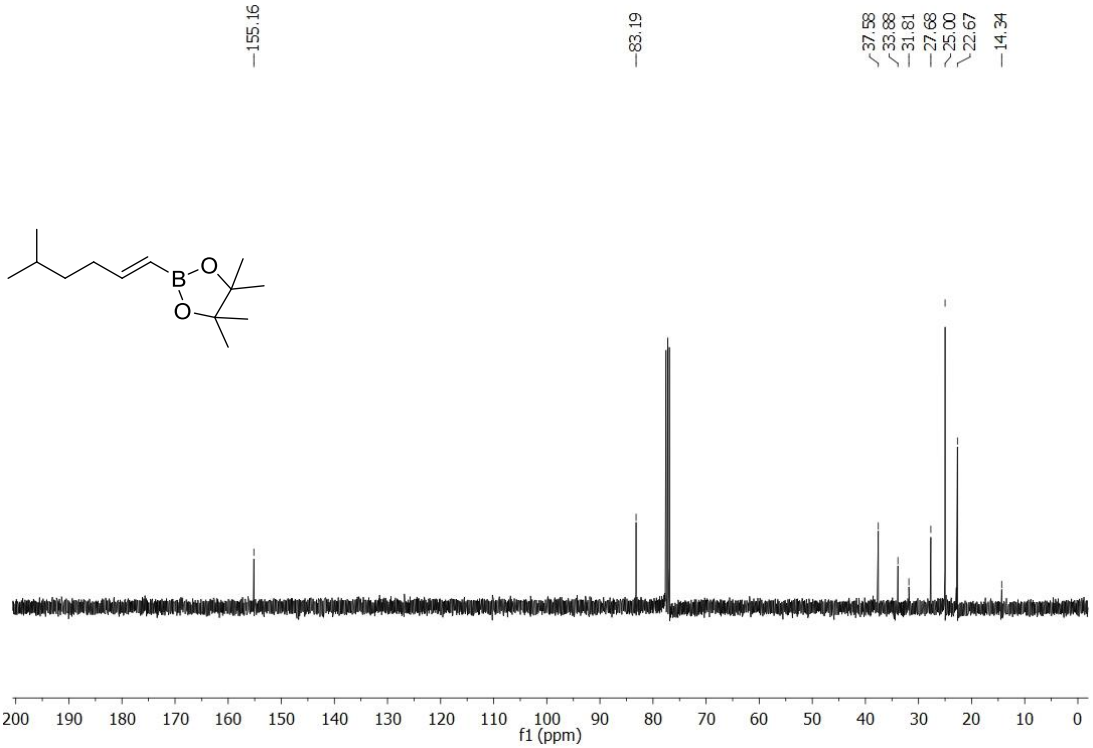


Figure S27. ^{13}C NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(5-methylhex-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

Hydroboration of 4-phenyl-1-butyne using 0.1 mol% 2: Under an inert atmosphere, 4-phenyl-1-butyne (0.80 mL, 5.69 mmol) and pinacol borane (1.03 mL, 7.10 mmol) were combined in a 20 mL scintillation vial. The solution was then transferred into a vial charged with 0.0034 g **2** (0.00569 mmol), stirred for 2 h, and exposed to air to deactivate the catalyst. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The crude material was purified by silica gel column chromatography following deactivation with NEt_3 with 20:1 hexane:diethyl ether as the eluent. Upon removing the solvent, a clear oil identified as (*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-enyl)-1,3,2-dioxaborolane (1.239 g, 84%) was isolated.[13] ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.28 (m, 2H, *phenyl*), 7.19 (m, 3H, *phenyl*), 6.71 (dt, J = 18.0 Hz, 6.2 Hz, 1H, C*H*), 5.51 (dt, J = 18.1 Hz, 1.5 Hz, 1H, C*H*), 2.75 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 1.27 (s, 12H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 153.62 (*C*H), 141.99 (*phenyl*), 128.54 (*phenyl*), 126.06 (*phenyl*), 83.26 (*C*CH_3), 37.69 (*C*H_2), 34.80 (*C*H_2), 24.99 (*C*H_3), two resonances not located (*C*-B, *i*-C).

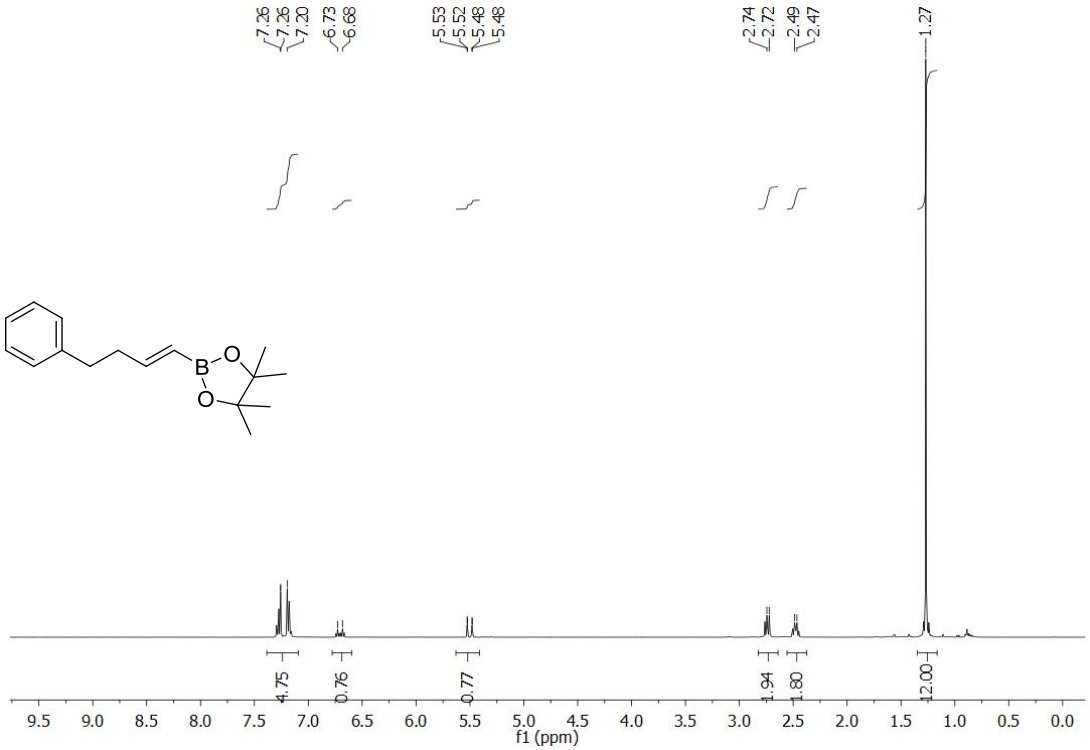


Figure S28. ^{1}H NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

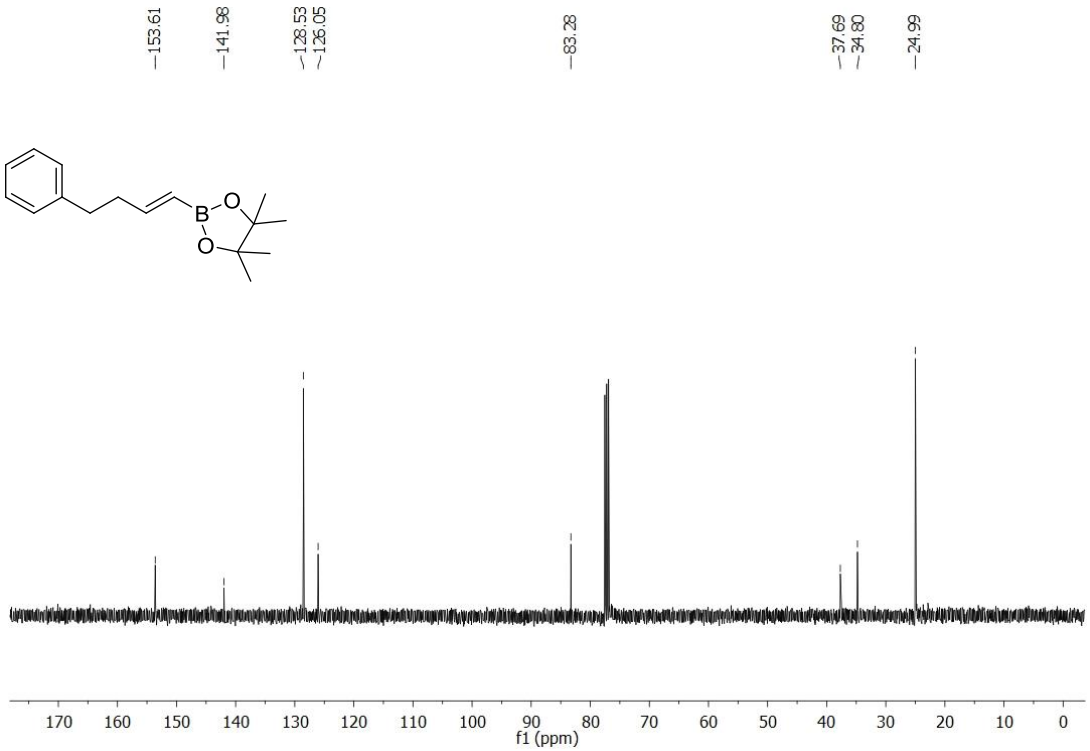


Figure S29. ^{13}C NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-enyl)-1,3,2-dioxaborolane in chloroform-*d*.

Dihydroboration of benzonitrile using 1.0 mol% 2: Under an inert atmosphere, benzonitrile (97 µL, 0.939 mmol) and pinacolborane (300 µL, 2.07 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0056 g of **2** (0.00939 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed by ^{1}H NMR spectroscopy. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from pentane at -35 °C yielded 0.153 g (45 %) of *N*-benzyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (benzene-d_6, 400 MHz) δ 7.58 (d, J = 7.6 Hz, 2H, *phenyl*), 7.27-7.22 (m, 2H, *phenyl*), 7.14-7.08 (m, 1H, *phenyl*), 4.60 (s, 2H, CH_2), 1.03 (s, 24H, CH_3). ^{13}C NMR (benzene-d_6, 101 MHz) δ 144.11 (*phenyl*), 128.68 (*phenyl*), 126.98 (*phenyl*), 82.91 (*C*CH$_3$), 48.25 (*C*H$_3$), 25.06 (*C*H$_3$), one phenyl resonance not located.

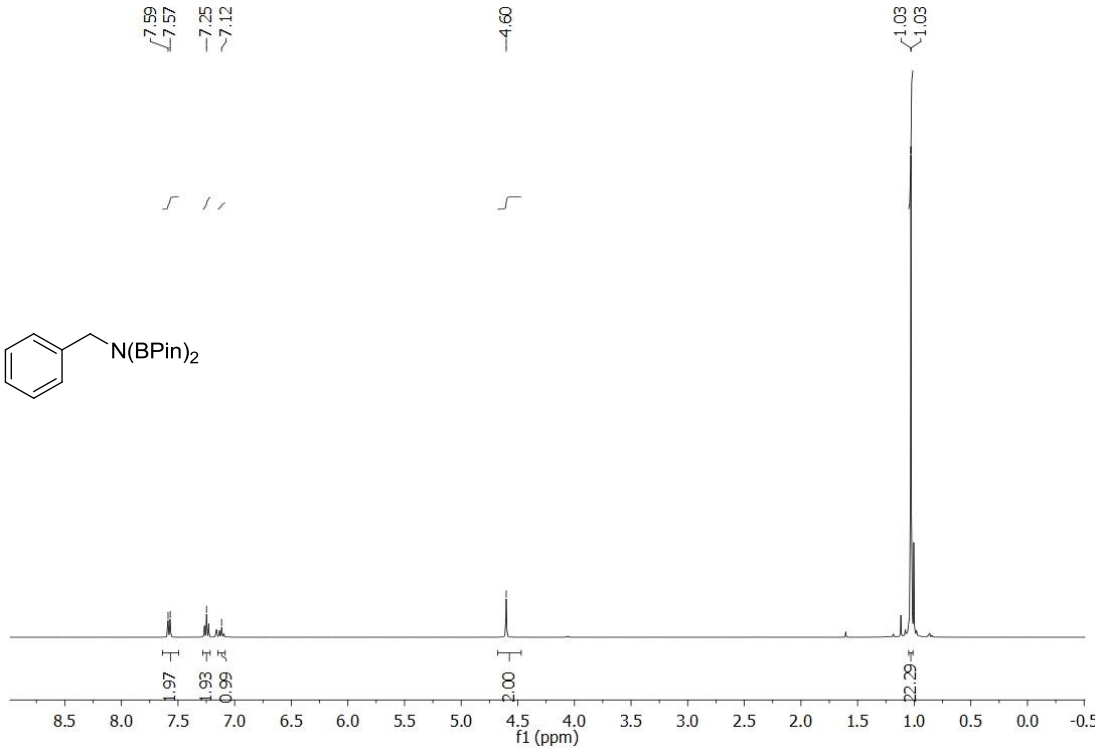


Figure S30. ^{1}H NMR spectrum of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

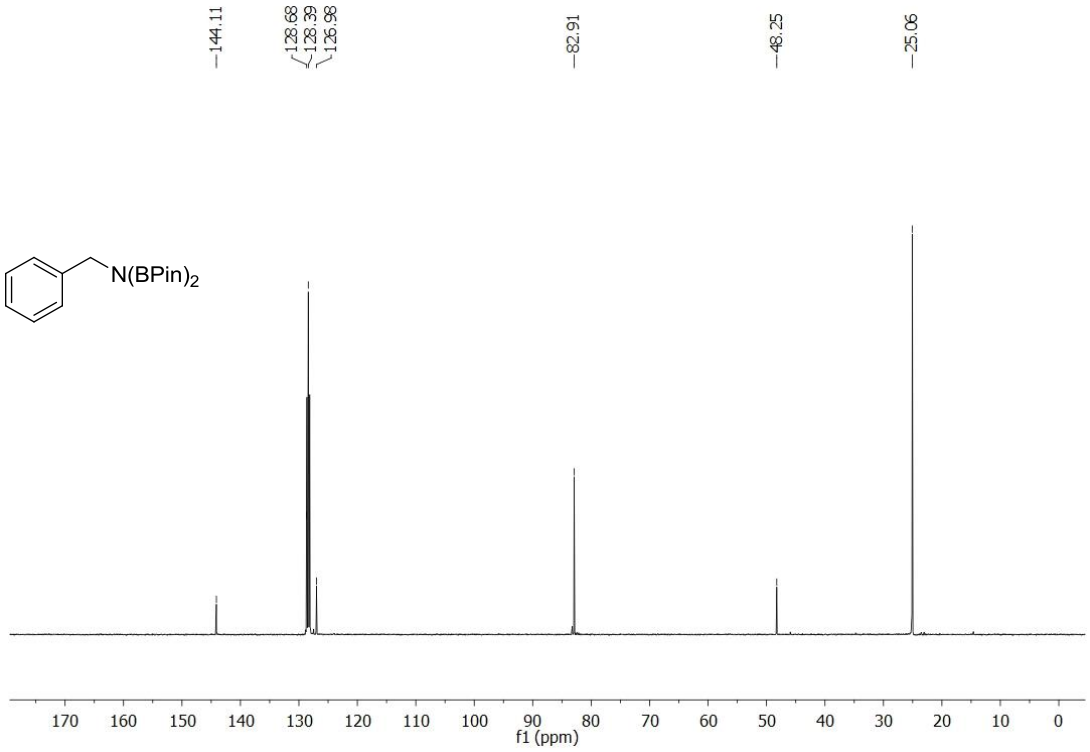


Figure S31. ^{13}C NMR spectrum of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

Dihydroboration of acetonitrile using 1.0 mol% 2: Under an inert atmosphere, acetonitrile (55 µL, 1.06 mmol) and pinacolborane (338 µL, 2.33 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0063 g of **2** (0.0106 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed using ^{1}H NMR spectroscopy. Solvent and residual borane were removed under reduced pressure, resulting in a white solid. Recrystallization from pentane at -35 °C yielded 0.134 g (43%) of *N*-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (benzene-d_6, 400 MHz) δ 3.49 (q, J = 7.0 Hz, 2H, CH_2), 1.34 (t, J = 7.0 Hz, 3H, CH_3), 1.07 (s, 24H, CH_3). ^{13}C NMR (benzene-d_6, 101 MHz) δ 82.58 (CCH$_3$), 39.51 (CH$_2$), 25.11 (CH$_3$), 19.58 (CH$_3$).

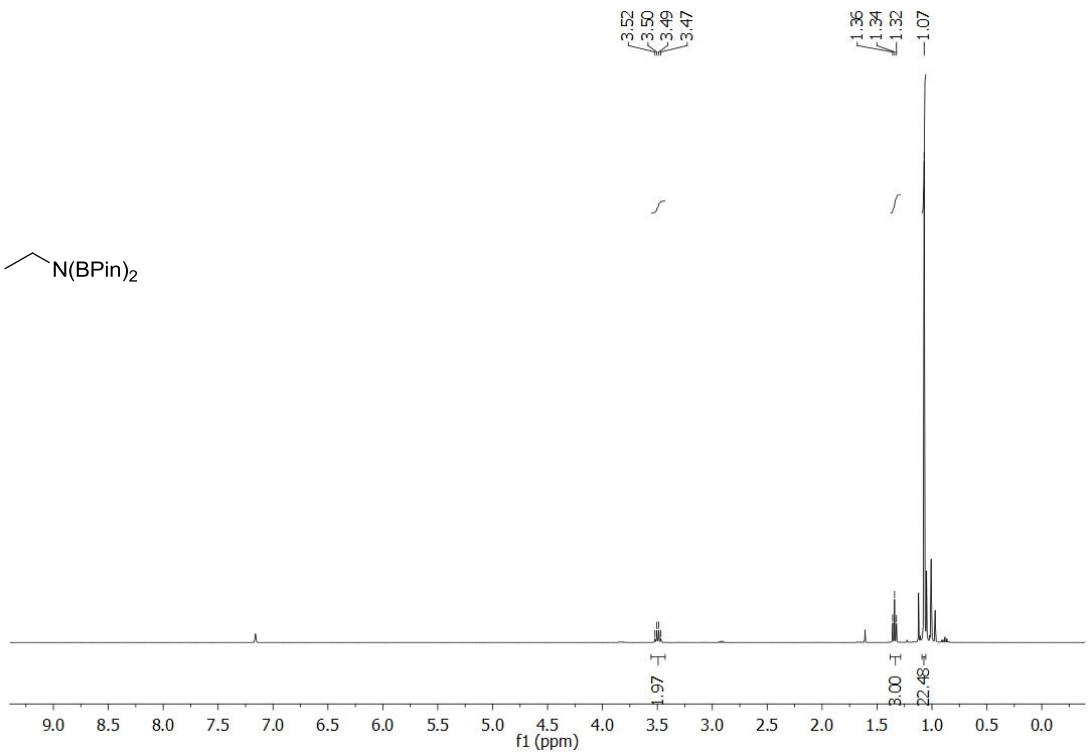


Figure S32. [1]H NMR spectrum of *N*-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

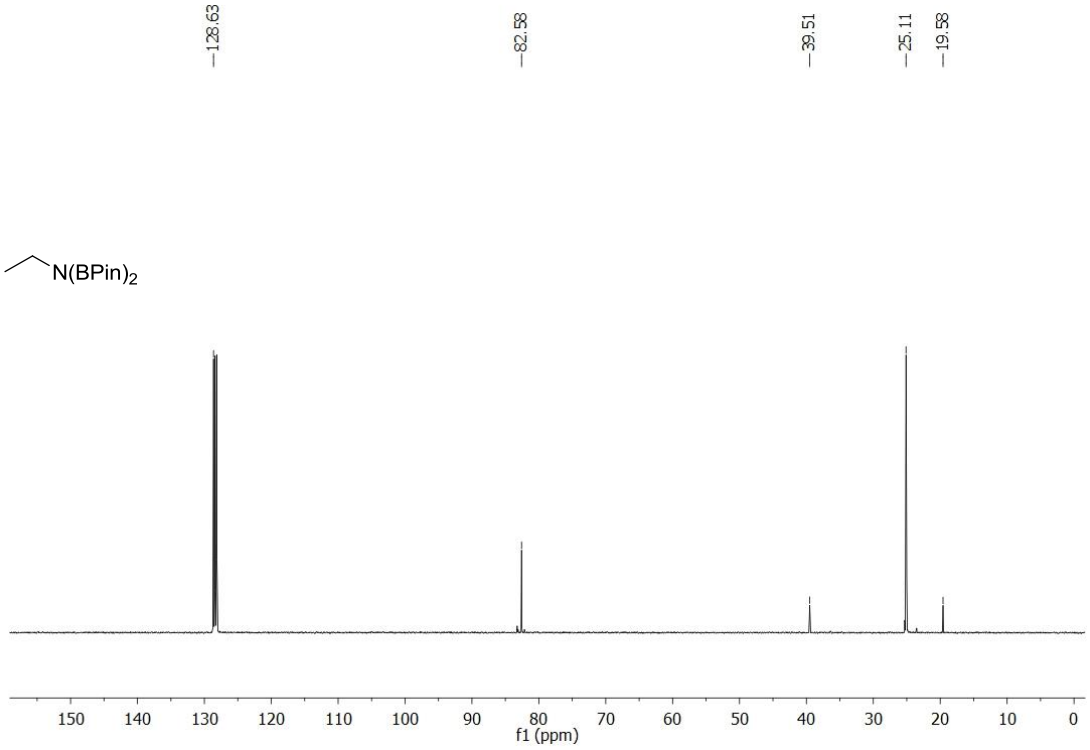


Figure S33. [13]C NMR spectrum of *N*-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

Dihydroboration of 4-phenylbutyronitrile using 1.0 mol% 2: Under an inert atmosphere, 4-phenylbutyronitrile (130 µL, 0.872 mmol) and pinacolborane (278 µL, 1.91 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0052 g of **2** (0.00872 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. By ^{1}H NMR spectroscopy, it was determined that 85% conversion was reached. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from pentane at -35 °C, yielded 0.250 g (72%) of 4,4,5,5-tetramethyl-*N*-(4-phenylbutyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.22 – 7.14 (m, 2H, *phenyl*), 7.11 – 7.05 (m, 3H, *phenyl*), 3.45 (t, J = 6.9 Hz, 2H, CH_2), 2.58 (t, J = 7.3 Hz, 2H, CH_2), 1.81 – 1.61 (m, 4H, CH_2), 1.08 (s, 24H, CH_3). ^{13}C NMR (benzene-d_6, 100 MHz): δ 143.32 (*phenyl*), 129.15 (*phenyl*), 128.78 (*phenyl*), 126.16 (*phenyl*), 82.57 (*C*CH$_3$), 44.45 (*C*H$_2$), 36.37 (*C*H$_2$), 33.56 (*C*H$_2$), 29.24 (*C*H$_2$), 25.09 (*C*H$_3$).

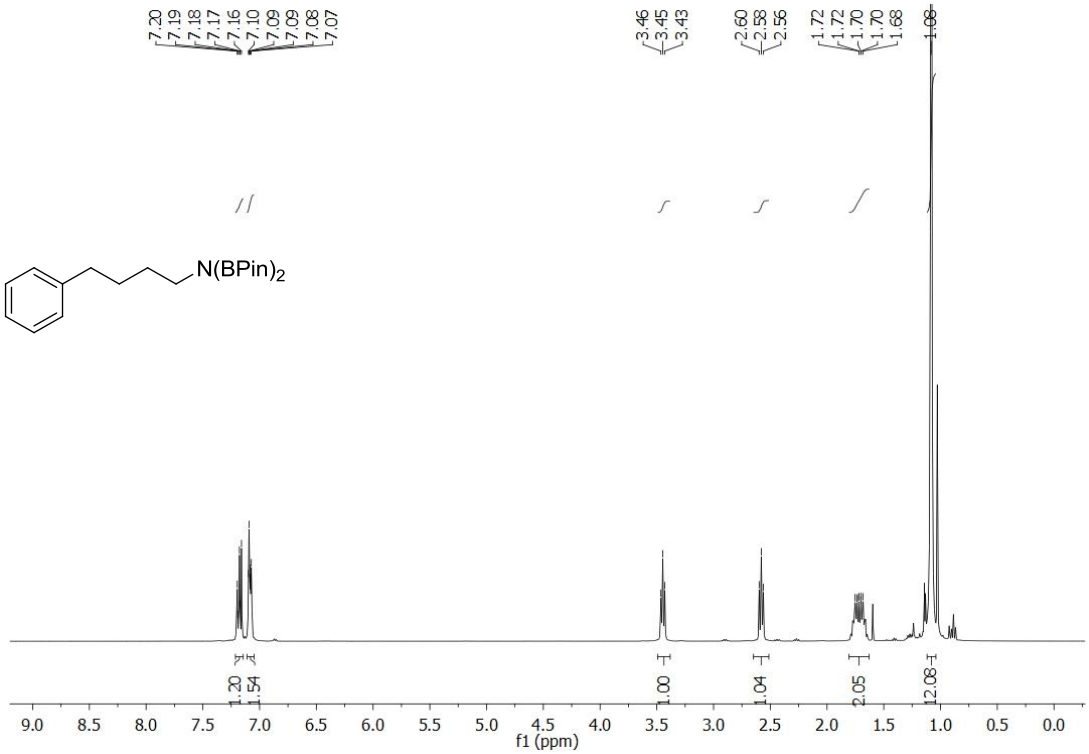


Figure S34. ^{1}H NMR spectrum of 4,4,5,5-tetramethyl-*N*-(4-phenylbutyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

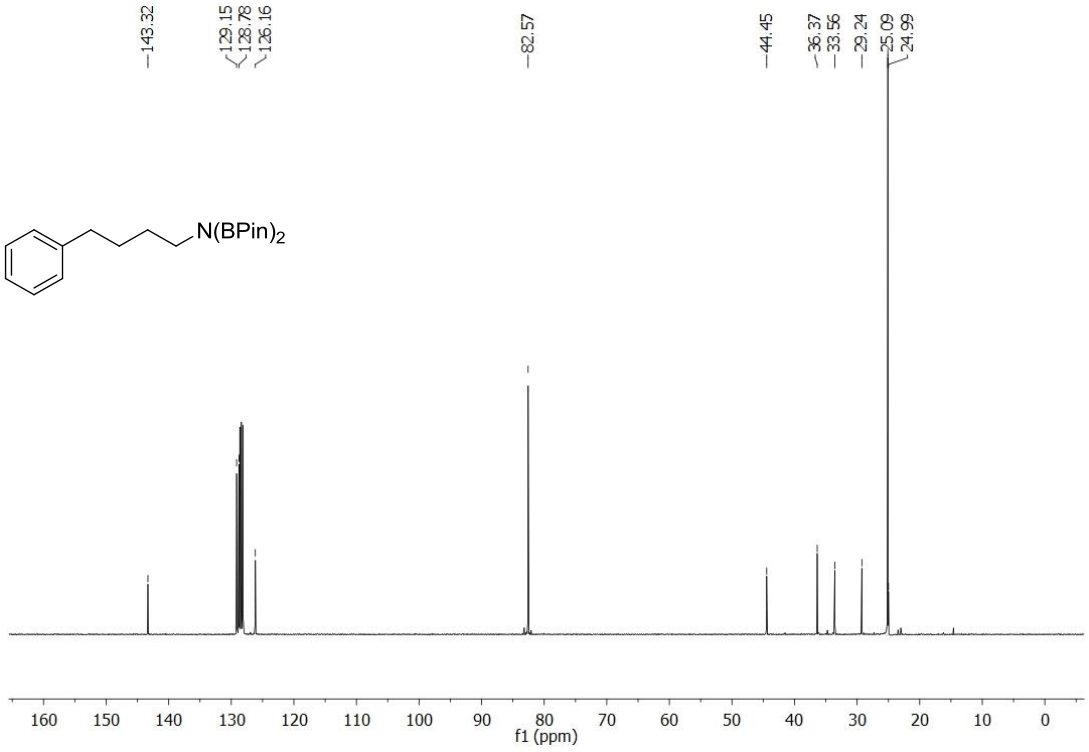


Figure S35. ^{13}C NMR spectrum of 4,4,5,5-tetramethyl-*N*-(4-phenylbutyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

Dihydroboration of 2-phenoxyacetonitrile using 1.0 mol% 2: Under an inert atmosphere, 2-phenoxyacetonitrile (117.0 µL, 0.955 mmol) and pinacolborane (305 µL, 2.10 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0057 g of **2** (0.00955 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed by ^{1}H NMR spectroscopy. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from diethyl ether/pentane at -35 °C yielded 0.325 g (88%) of 4,4,5,5-tetramethyl-*N*-(2-phenoxyethyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.16 (m, 2H, *phenyl*), 7.03 (m, 2H, *phenyl*), 6.85 (m, 1H, *phenyl*), 4.13 (t, J = 6.5 Hz, 2H, CH_2), 3.82 (t, J = 6.5 Hz, 2H, CH_2), 1.06 (s, 24H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 160.27 (*phenyl*), 130.03 (*phenyl*), 121.00 (*phenyl*), 115.33 (*phenyl*), 82.93 (*C*CH$_3$), 69.59 (*C*H$_2$), 43.71 (*C*H$_2$), 25.07 (*C*H$_3$).

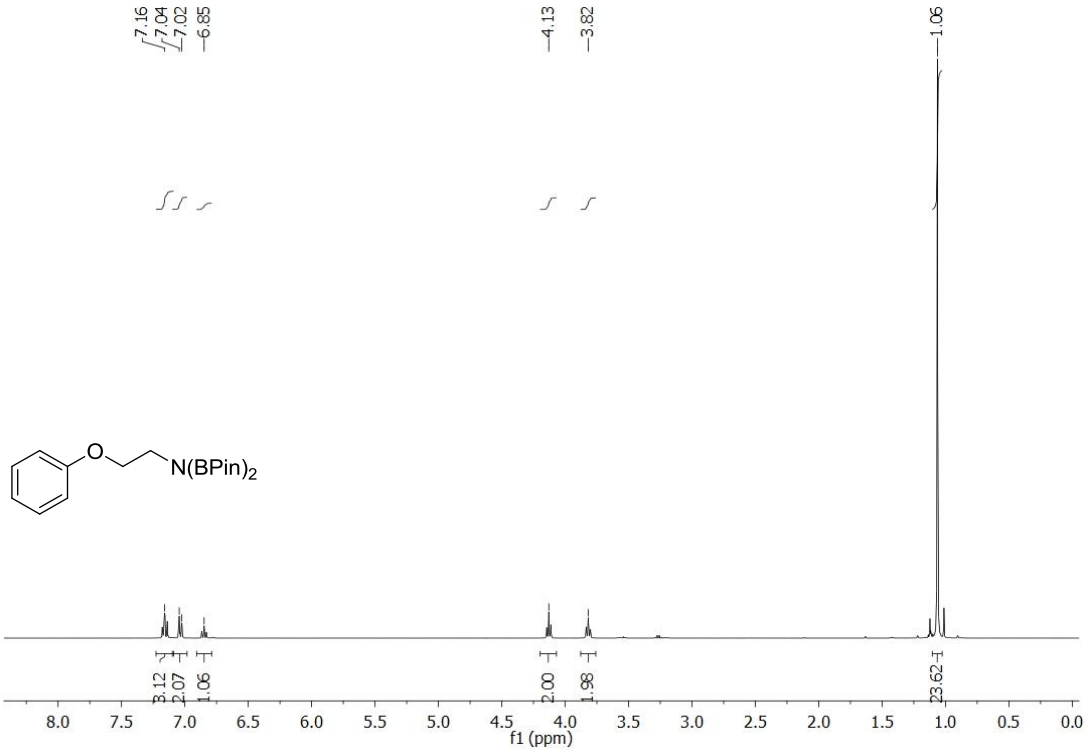


Figure S36. [1]H NMR spectrum of 4,4,5,5-tetramethyl-*N*-(2-phenoxyethyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

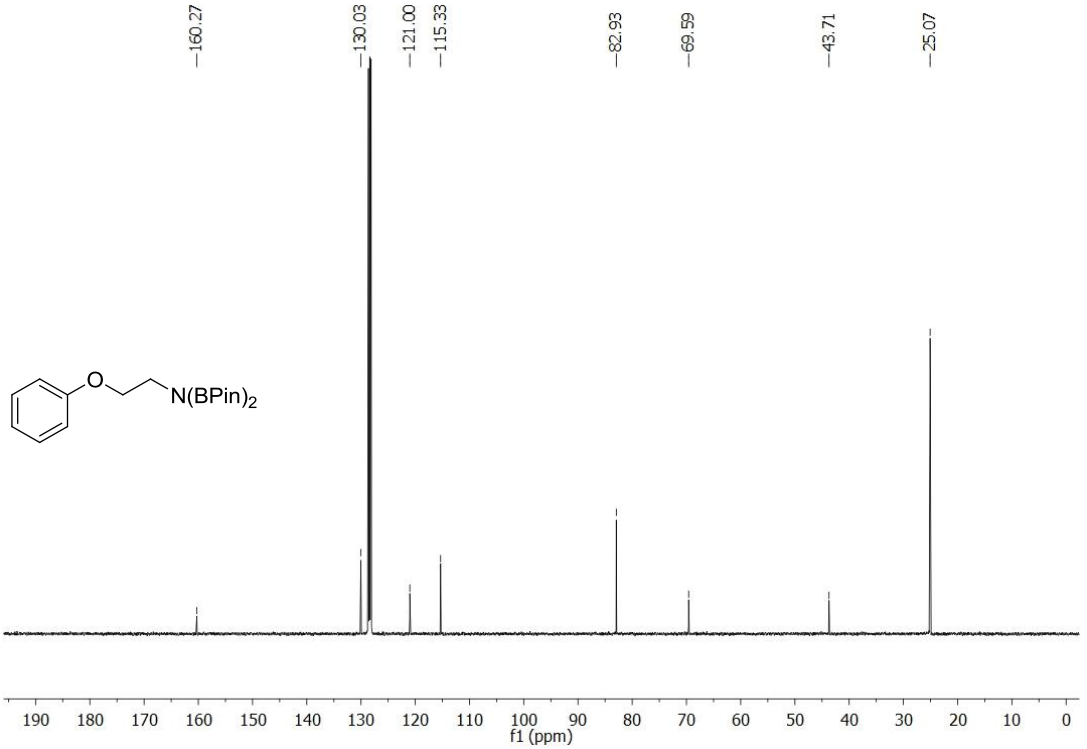


Figure S37. [13]C NMR spectrum of 4,4,5,5-tetramethyl-*N*-(2-phenoxyethyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

Dihydroboration of 3-(dimethylamino)propanenitrile using 1.0 mol% 2: Under an inert atmosphere, 3-(dimethylamino)propanenitrile (106.0 µL, 0.939 mmol) and pinacolborane (300 µL, 2.07 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0056 g of **2** (0.00939 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed by ^{1}H NMR spectroscopy. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from pentane at -35 °C yielded 0.0996 g (30%) of N^1,N^1-dimethyl-N^3,N^3-*bis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane-1,3-diamine. ^{1}H NMR (chloroform-*d*, 400 MHz): δ 3.56 (t, J = 7.5 Hz, 2H, CH_2), 2.35 (t, J = 7.0 Hz, 2H, CH_2), 2.17 (s, 6H, NCH_3), 1.98 (t, J = 7.3 Hz, 2H, CH_2), 1.08 (s, 24H, CH_3). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 82.63 (CCH$_3$), 58.21 (CH$_2$), 45.97 (NCH$_3$), 43.16 (CH$_2$), 32.65 (CH$_2$), 25.12 (CH$_3$).

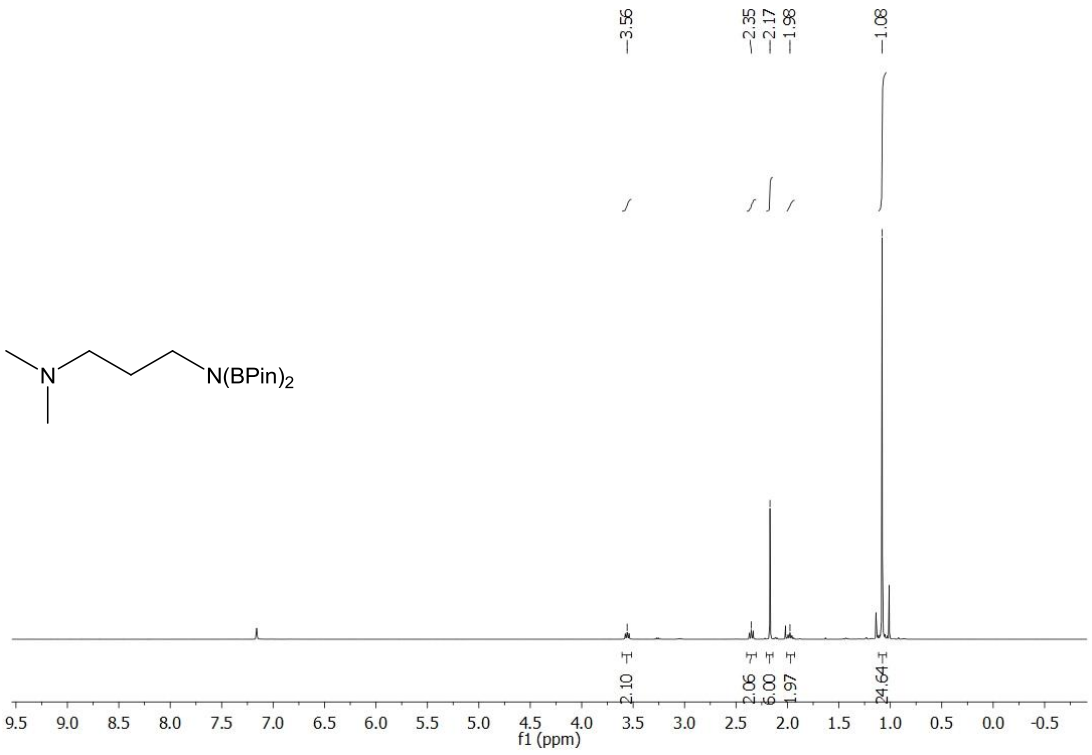


Figure S38. ^{1}H NMR spectrum of N^1,N^1-dimethyl-N^3,N^3-*bis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane-1,3-diamine in benzene-d_6.

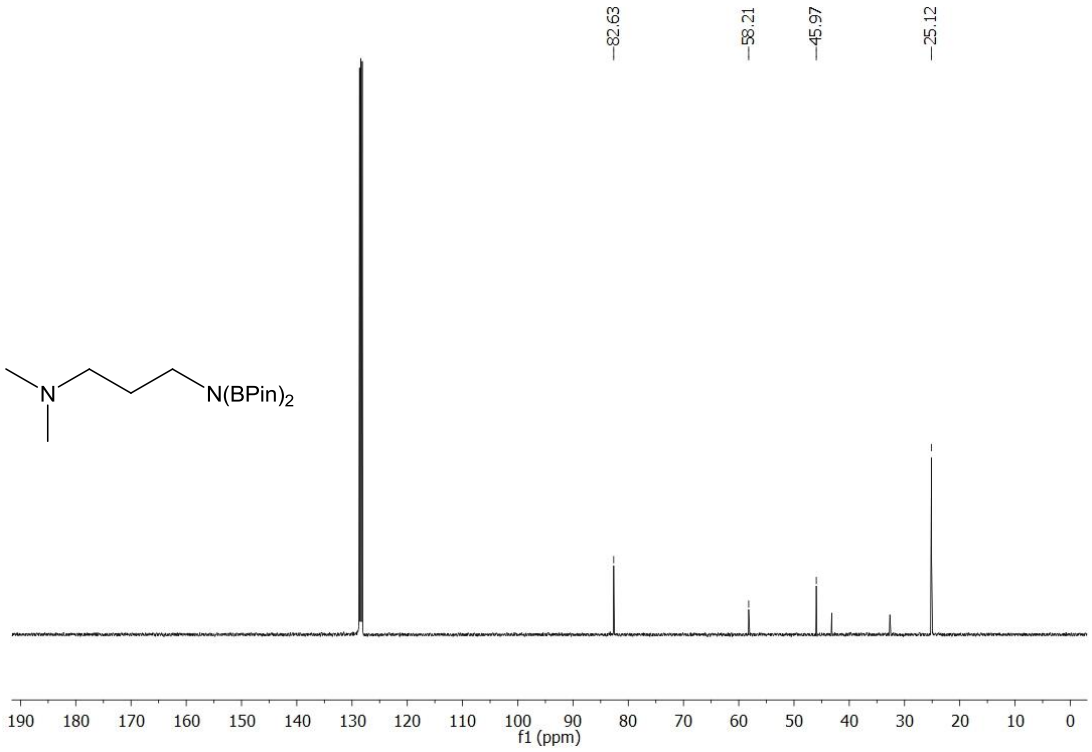


Figure S39. ^{13}C NMR spectrum of N^1,N^1-dimethyl-N^3,N^3-*bis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane-1,3-diamine in benzene-d_6.

Dihydroboration of 3-(diphenylphosphino)propanenitrile using 1.0 mol% 2: Under an inert atmosphere, 3-(diphenylphosphino)propanenitrile (225.7 mg, 0.955 mmol) and pinacolborane (305 µL, 2.10 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0057 g of **2** (0.00955 mmol). The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed by ^{1}H NMR spectroscopy. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from diethyl ether at -35 °C yielded 0.211 g (45%) of *N*-(3-(diphenylphosphino)propyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.45 (t, J = 6.7 Hz, 4H, *phenyl*), 7.12 – 7.02 (m, 6H, *phenyl*), 3.48 (t, J = 6.9 Hz, 2H, CH_2), 2.12 – 2.03 (m, 2H, CH_2), 1.96 – 1.80 (m, 2H, CH_2), 1.03 (s, 24H, CH_3). ^{13}C NMR (benzene-d_6, 100 MHz): δ 139.76 (d, J = 15.1 Hz, *phenyl*), 132.81 (d, J = 18.5 Hz, *phenyl*), 130.79 (d, J = 9.0 Hz, *phenyl*), 128.21 (d, J = 6.2 Hz, *phenyl*), 81.95 (CCH$_3$), 45.15 (d, J = 14.8 Hz, CH$_2$), 29.70 (d, J = 15.7 Hz, CH$_2$), 25.52 (d, J = 12.3 Hz, CH$_2$), 24.38 (CH$_3$). ^{31}P NMR (benzene-d_6, 162 MHz): δ -16.20.

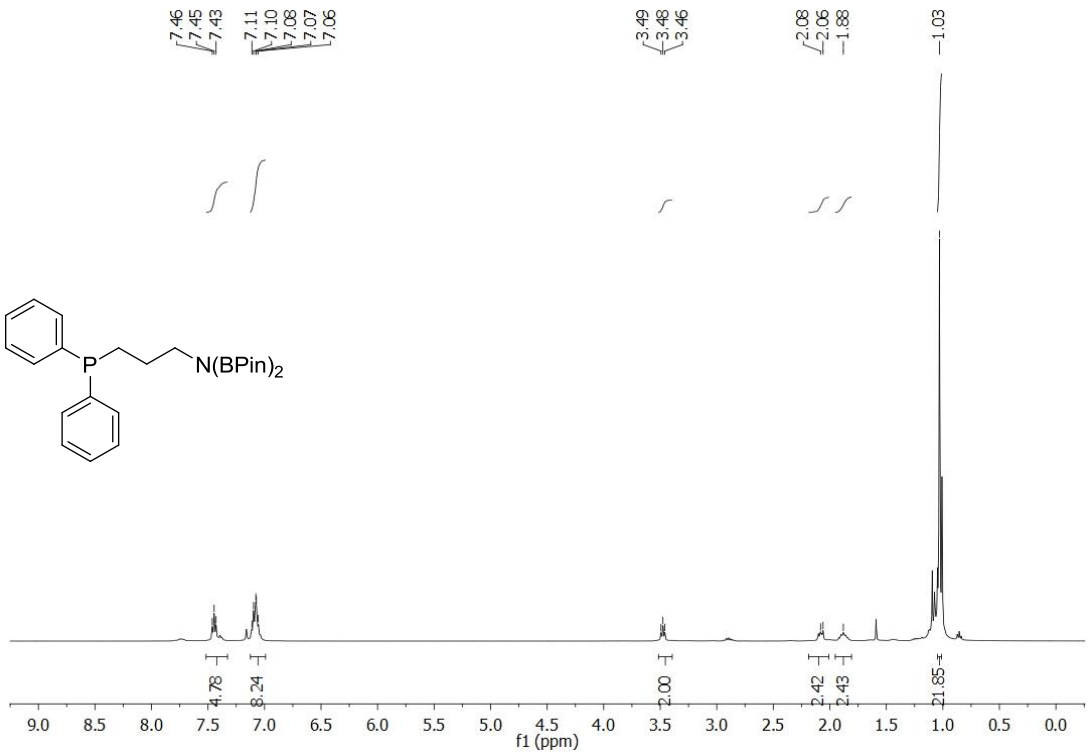


Figure S40. ^{1}H NMR spectrum of *N*-(3-(diphenylphosphino)propyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

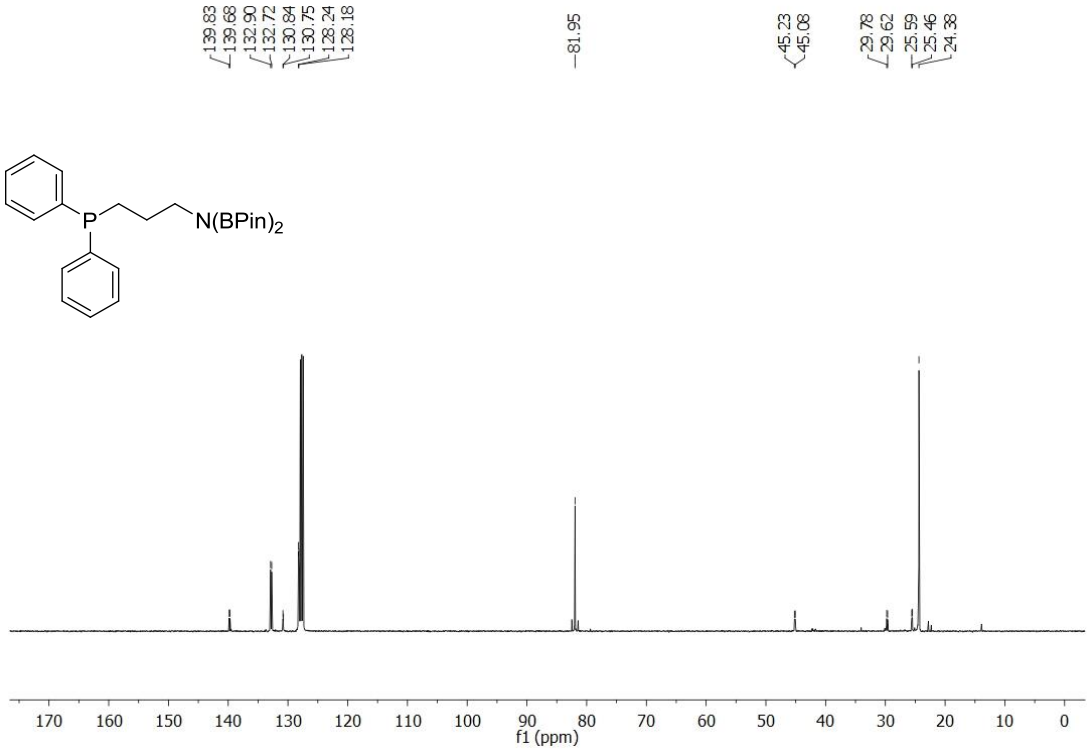


Figure S41. ^{13}C NMR spectrum of *N*-(3-(diphenylphosphino)propyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine in benzene-d_6.

Trihydroboration of 4-acetylbenzonitrile using 1.0 mol% 2: Under an inert atmosphere, 4-acetylbenzonitrile (124.0 mg, 0.855 mmol) and pinacolborane (409 µL, 2.82 mmol) were combined in a 20 mL scintillation vial with 0.5 mL benzene-d_6. This solution was transferred to a vial containing 0.0051 g of **2** (0.00855 mmol). Bubbling and heat generation was observed. The solution was stirred at 25 °C for 30 min, after which >99% carbonyl reduction was observed by ^{1}H NMR spectroscopy. The vial was sealed and stirred at 60 °C for 24 h. The solution was then exposed to air to deactivate the catalyst. Greater than 99% conversion was observed by ^{1}H NMR spectroscopy. Solvent and remaining borane were removed under reduced pressure, resulting in a white solid. Recrystallization from diethyl ether/pentane at -35 °C yielded 0.150 g (33%) of 4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)ethyl)benzyl)-1,3,2-dioxaborolan-2-amine. ^{1}H NMR (benzene-d_6, 400 MHz): δ ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.54 (d, J = 8.1 Hz, 2H, *phenyl*), 7.42 (d, J = 8.2, 2H, *phenyl*), 5.44 (q, J = 6.2, 1H, C*H*), 4.58 (s, 2H, CH_2), 1.48 (d, J = 6.4 Hz, 3H, CH_3), 1.03 (s, 24H, CH_3), 1.01 (s, 12H, CH_3). ^{13}C NMR (benzene-d_6, 101 MHz): δ 143.72 (*phenyl*), 142.96 (*phenyl*), 125.86 (*phenyl*), 82.90 (*C*CH$_3$), 82.78 (*C*CH$_3$), 73.28 (*C*H), 47.98 (*C*H$_2$), 26.02 (*C*H$_3$), 25.07 (*C*H$_3$), 24.93 (*C*H$_3$).

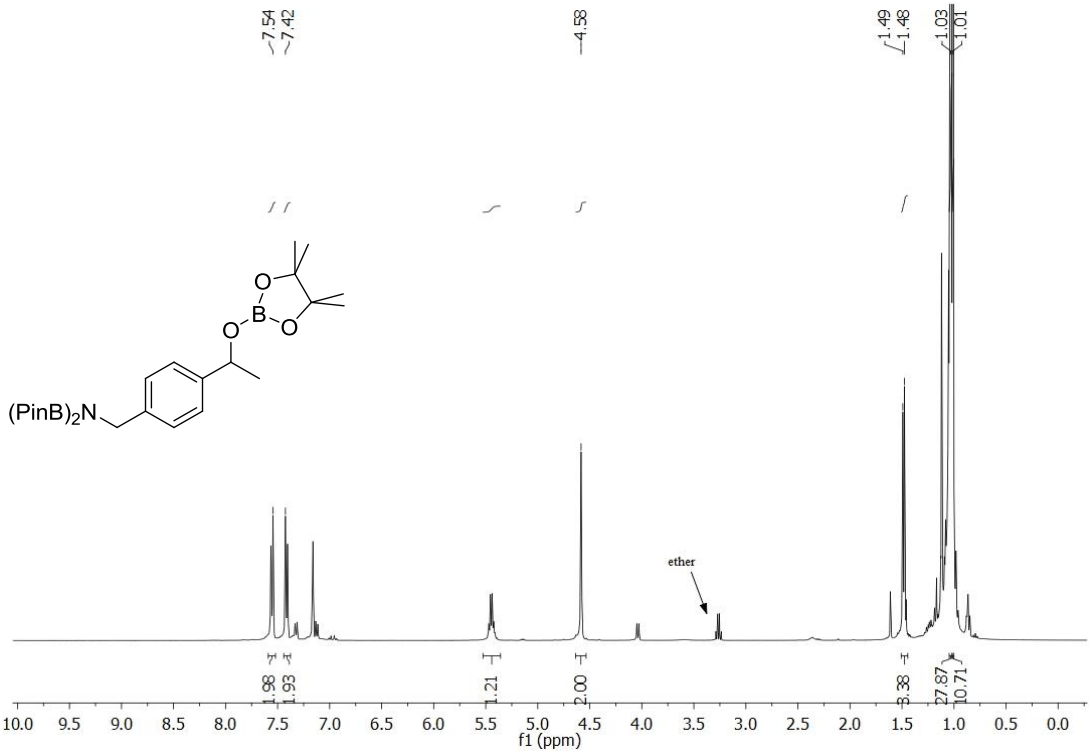


Figure S42. ^{1}H NMR spectrum of 4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)ethyl)benzyl)-1,3,2-dioxaborolan-2-amine in chloroform-*d*.

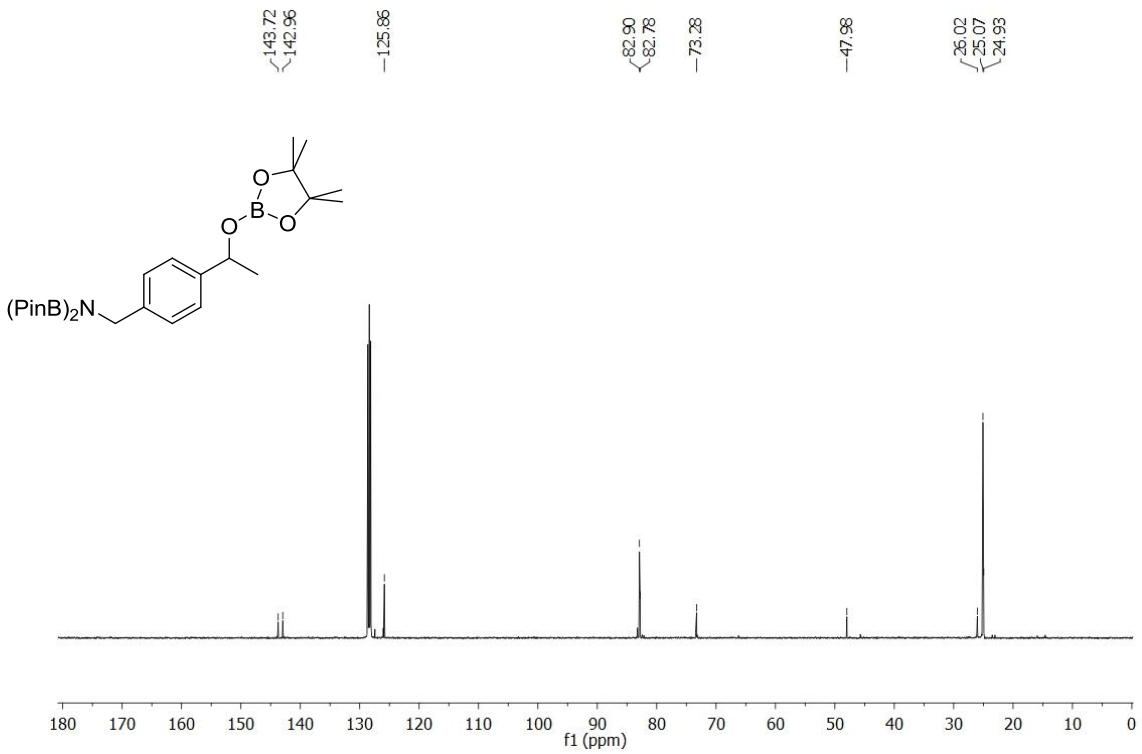


Figure S43. ^{13}C NMR spectrum of 4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)ethyl)benzyl)-1,3,2-dioxaborolan-2-amine in chloroform-*d*.

References:

1. Y. Li, Z. Li, F. Li, Q. Wang and F. Tao *Tetrahedron Lett.*, 2005, **46**, 6159.

2. T. M. Porter, G. B. Hall, T. L. Groy and R. J. Trovitch, *Dalton Trans*., 2013, **42**, 14689.

3. (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003. (b) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.

4. Neese, F. Orca, an Ab Initio, Density Functional and Semiempirical Electronic Structure Program Package, version 2.9.1; Max Planck Institute for Bioinorganic Chemistry: Mülheim an der Ruhr, Germany, 2012.

5. (a) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648. (b) C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev.*, 1988, **37**, 785.

6. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.

7. D. A. Pantazis, X. Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theory Comput*., 2008, **4**, 908.

8. Molekel, Advanced Interactive 3D-Graphics for Molecular Sciences; Swiss National Supercomputing Center; http:// www.cscs.ch/molekel.

9. J. A. Weil and J. R. Bolton, *Electron paramagnetic resonance: Elementary theory and practical applications.* Wiley, Hoboken, NJ, 2007.

10. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42.

11. Z.-J. Yao, S. Hong, W. Zheng, M. Liu and W. Deng, *Tetrahedron Lett.*, 2016, **57**, 910-913.

12. Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran and H. W. Roesky, *J. Am. Chem. Soc*., 2016, **138**, 2548.

13. M. Morimoto, T. Miura and M. Murakami, *Angew. Chem. Int. Ed.*, 2015, **54**, 12659-12663.

14. J. Zhao, Z. Niu, H. Fu and Y. Li, *Chem. Commun.*, 2014, **50**, 2058-2060.

15. C. Feng, H. Wang, L. Xu and P. Li, *Org. Biomol. Chem.*, 2015, **13**, 7136.