Supporting Information

Efficient and Selective Hydroboration of Alkenes Catalyzed by an Air-Stable ($PP^{CF3}P$)CoI_2 Precatalyst

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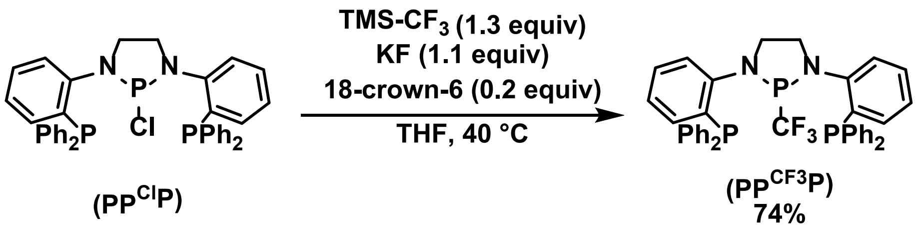
Experimental Details:

General Considerations

Unless otherwise noted, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. Glassware was oven-dried before use. All proteo solvents were degassed by sparging with ultra-high purity argon and dried via passage through columns of drying agents using a Glass Contours solvent purification system from Pure Process Technologies. Benzene-*d₆* was degassed via repeated freeze-pump-thaw cycles and dried over 3 Å molecular sieves before use. CD_2Cl_2 was dried over CaH_2, vacuum transferred, and degassed via repeated freeze-pump-thaw cycles. All alkenes not containing an enolizable functional group were stored over 3 Å molecular sieves before use. $KBEt_3H$ was purchased from Sigma-Aldrich as a 1 M solution in THF and used without further purification. ($PP^{Cl}P$) was synthesized according to literature procedures.[1] NMR spectra were recorded at ambient temperature unless otherwise stated on a Bruker NEO 400 MHz or Bruker AVIII 600 MHz instrument. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual solvent resonances and are reported in ppm. ^{31}P and ^{19}F NMR chemical shifts (in ppm) were referenced to 85% H_3PO_4 (0 ppm) and neat trifluoroacetic acid (-76.55 ppm) external standards, respectively. All other reagents and solvents were obtained from commercial sources and used without further purification. GC-MS analysis was performed using an Agilent 7890B GC system equipped with the HP-5 Ultra Inert column (30 m, 0.25 mm, 0.25 µm) and an FID detector. For MS detection, an electron ionization system was used with an ionization energy of 70 eV. Elemental microanalyses were performed by Midwest Microlab, Indianapolis, IN.

Synthesis of (PP^{CF3}P)



Under a nitrogen atmosphere, (PP^{Cl}P) (0.334 g, 0.520 mmol) was dissolved in a minimal amount of THF (5 mL) in a 20 mL scintillation vial equpped with a stir bar and stirred at room temperature. To this stirring solution, KF (33.1 mg, 0.570 mmol, 1.1 equiv), 18-crown-6 (27.4 mg, 0.104 mmol, 0.2 equiv), and TMSCF$_3$ (95.7 mg, 0.673 mmol, 1.3 equiv) were added and the reaction mixture warmed to 40 °C. Reaction progress was monitored by ^{31}P NMR spectroscopy for the disappearance of the (PP^{Cl}P) starting material and formation of TMSF. Once the starting material has been completely consumed (usually after 16-48 h), the excess KF was removed via filtration through Celite. The filtrate, upon partial drying, rapidly forms a sticky off-white solid that becomes brittle upon complete drying. Once dry, the crude solids were dissolved in Et$_2$O (3 mL), followed by the addition of *n*-pentane (15 mL) and stirring for for several hours. The supernatant (enriched in undesired side-products) was decanted Repeated washing (3x) in this manner, following by drying in vacuo affords nearly pure (PP^{CF3}P) as a white to off-white solid. Further purification by crystallization from a mixture of diethyl ether and pentane at -35 °C for several days yields pure (PP^{CF3}P) in amorphous and crystalline form in 74% yield. **^{1}H{^{31}P} NMR (400 MHz, C$_6$D$_6$)** δ 7.37 – 7.28 (m, 10H, overlapping Ar and PPh$_2$), 7.11 (dd, *J* = 7.6, 1.6, 2H, Ar), 7.09 – 6.98 (m, 14H, overlapping Ar and PPh$_2$), 6.80 (dt, *J* = 7.5, 1.2 Hz, 2H, Ar), 3.78 (m, 2H, NC*H*$_2$), 3.03 (m, 2H, NC*H*$_2$). **^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$)** δ 75.0 ppm (tq, $J_{P\text{-}P}$ = 69.2 Hz, $J_{P\text{-}F}$ = 44.0 Hz, 1P, P-CF$_3$), -16.8 (dq, $J_{P\text{-}P}$ = 69.2, $J_{P\text{-}F}$ = 11.9 Hz, 2P, PPh$_2$). **^{19}F NMR (376 MHz, C$_6$D$_6$)** δ -62.4 (dt, $J_{F\text{-}P}$ = 44.5, 12.1 Hz). **^{13}C{^{1}H} NMR (151 MHz, THF-*d*$_8$)** δ 149.9 (m), 138.3 (m), 135.8 (s), 134.8 (m), 134.4 (m, overlapping signals), 130.9 (s), 129.0 (m, overlapping signals), 126.2 (m), 125.8 (s), 54.3 (m). Note: The ^{13}C NMR resonance corresponding to the CF$_3$ carbon was not detected due to low signal intensity due to extensive coupling to ^{31}P and ^{19}F. **Elemental Analysis** $C_{39}H_{32}N_2P_3F_3$, **Calc:** C, 69.03; H, 4.53; N, 4.13); **Found:** C, 68.99; H, 4.73; N, 4.11.

Figure S1. ^{1}H{^{31}P} NMR (C$_6$D$_6$, 400 MHz) spectrum of (PP^{CF3}P). Residual solvent denoted with an asterisk (*).

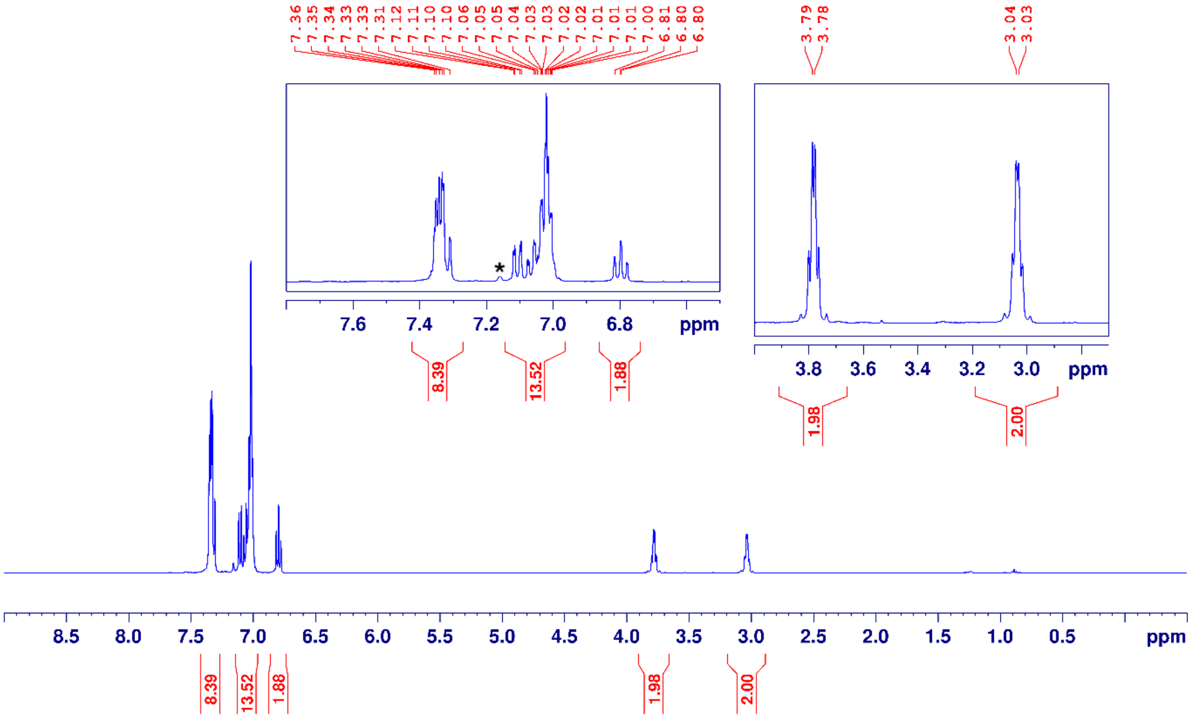


Figure S2. ^{1}H NMR (C_6D_6, 400 MHz) spectrum of ($PP^{CF3}P$).

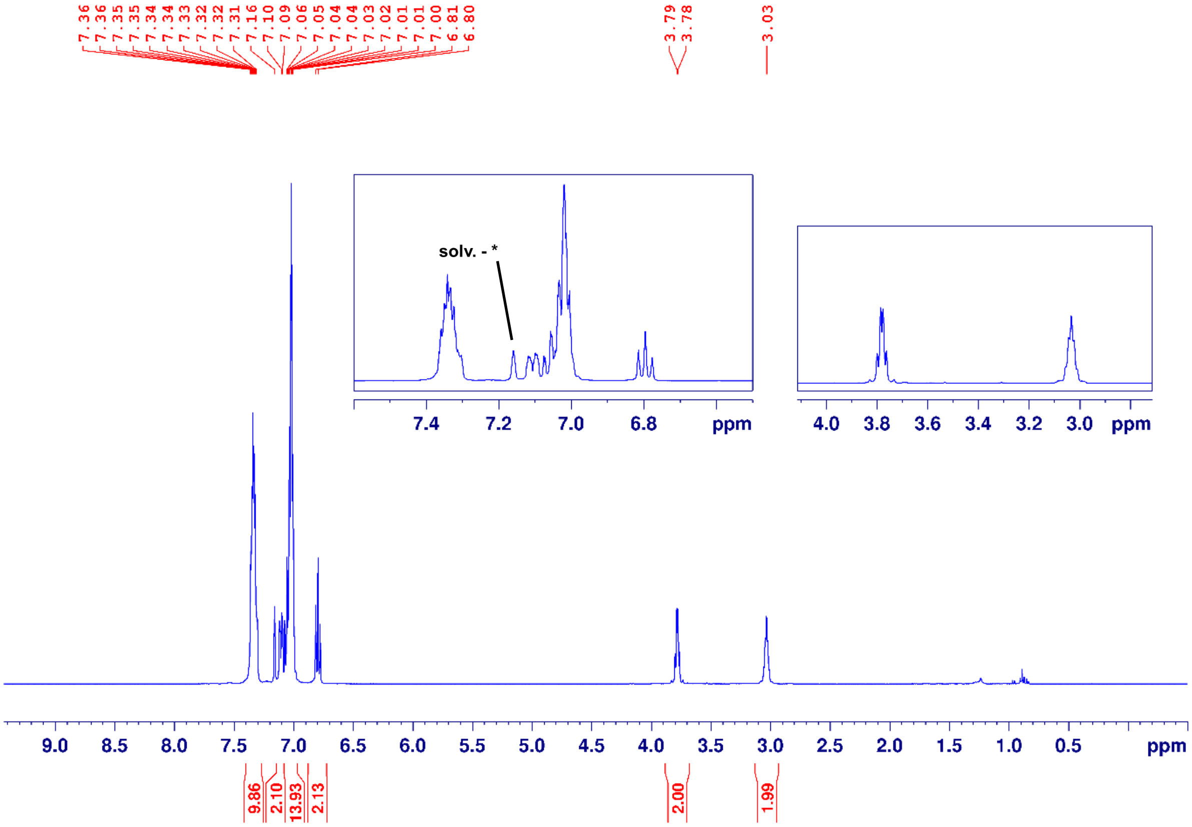


Figure S3. ^{19}F NMR (C_6D_6, 376 MHz) spectrum of ($PP^{CF3}P$).

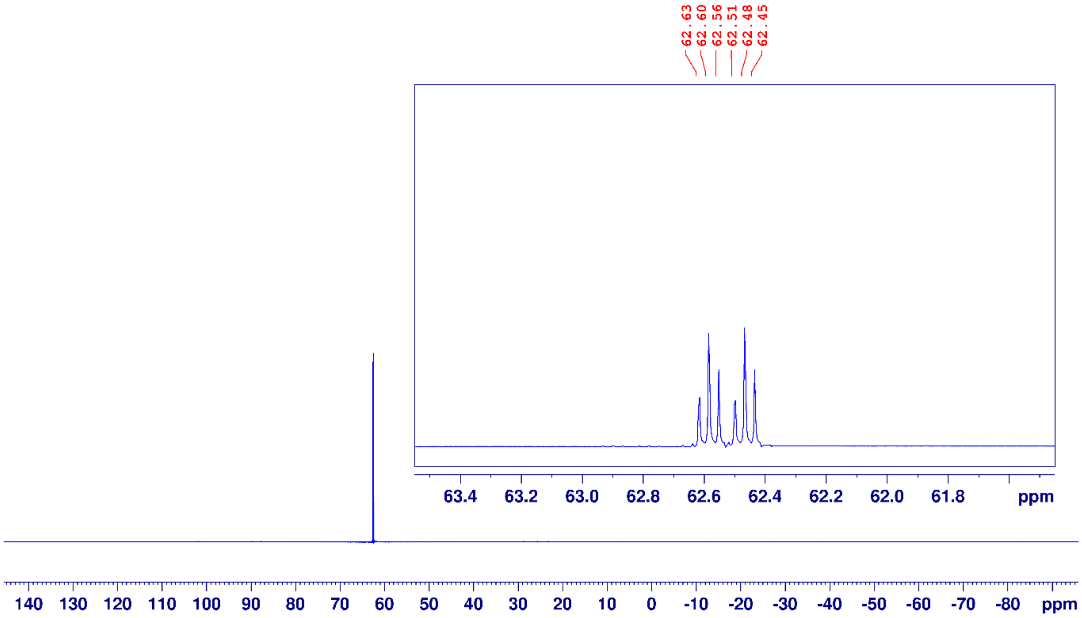


Figure S4. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz) spectrum of ($PP^{CF3}P$).

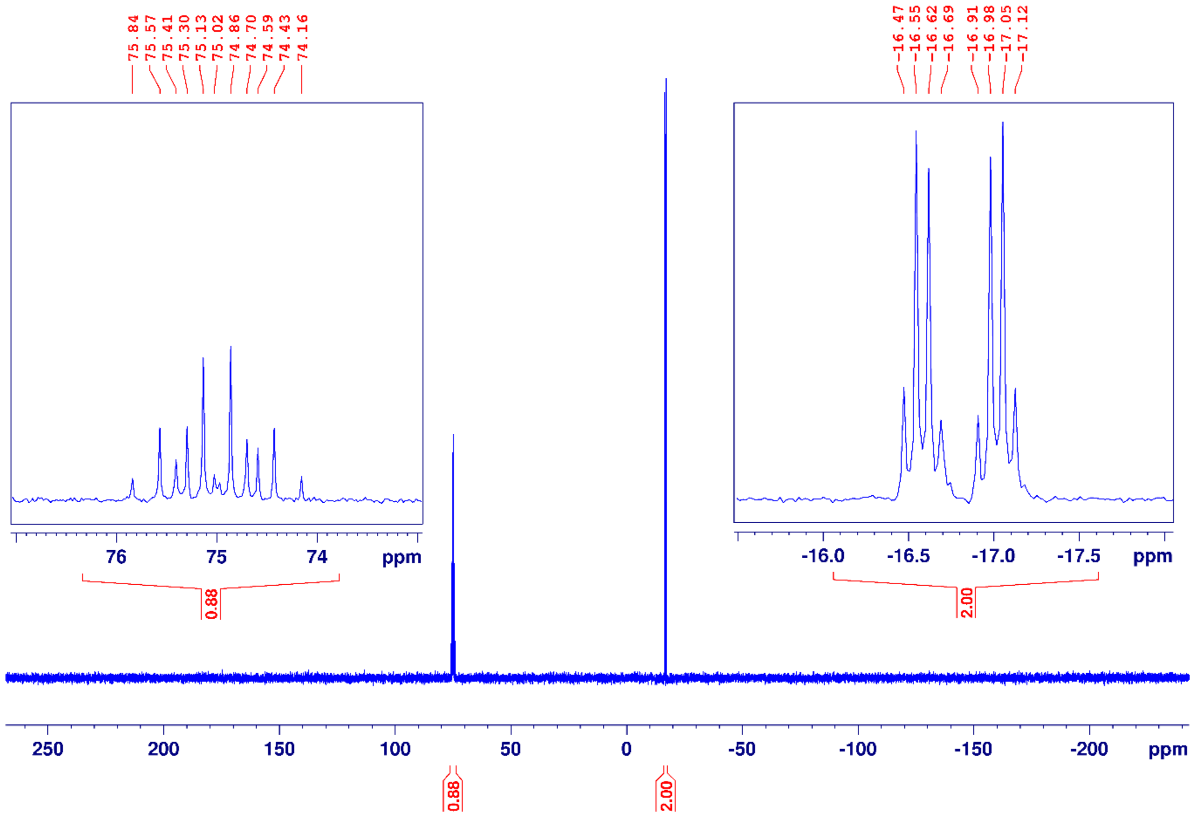
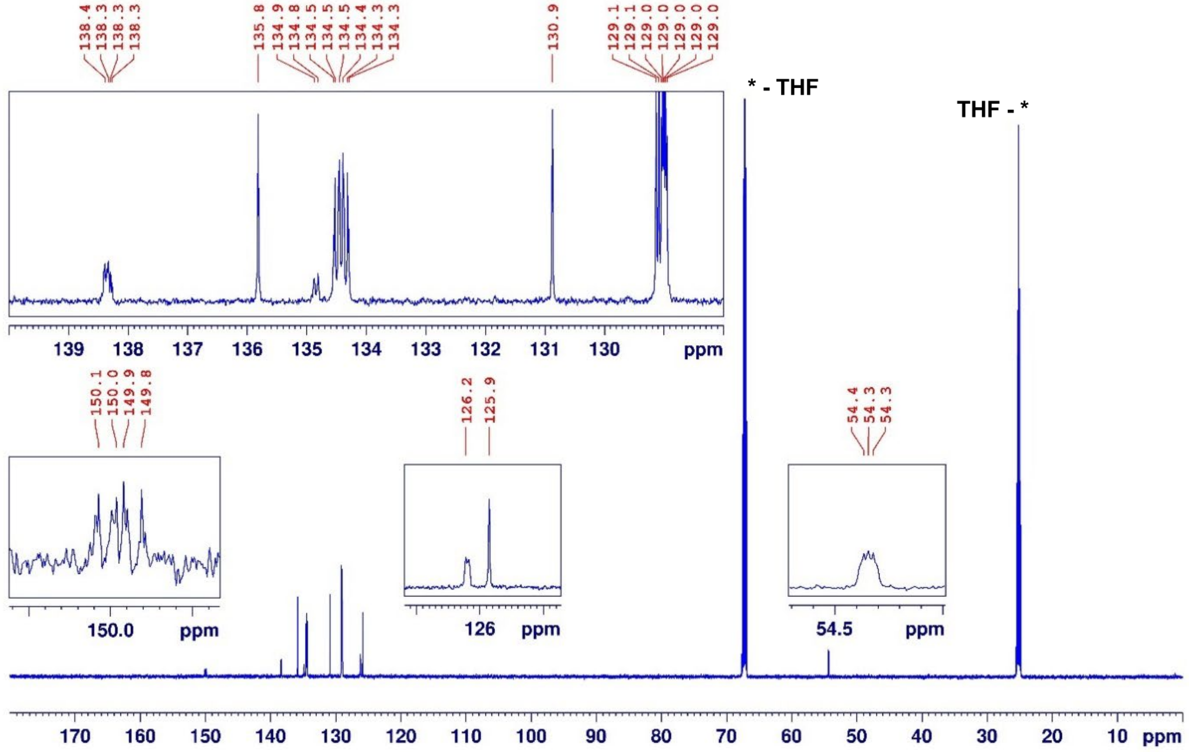
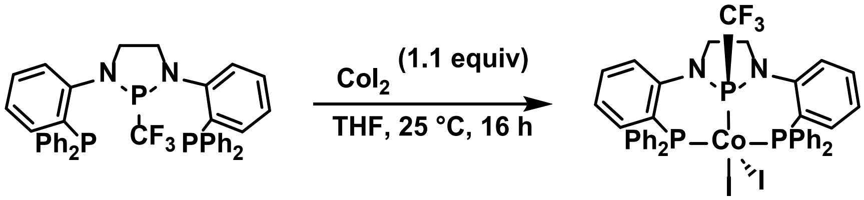


Figure S5. $^{13}C\{^1H\}$ NMR (THF-d_8, 151 MHz) spectrum of ($PP^{CF3}P$).

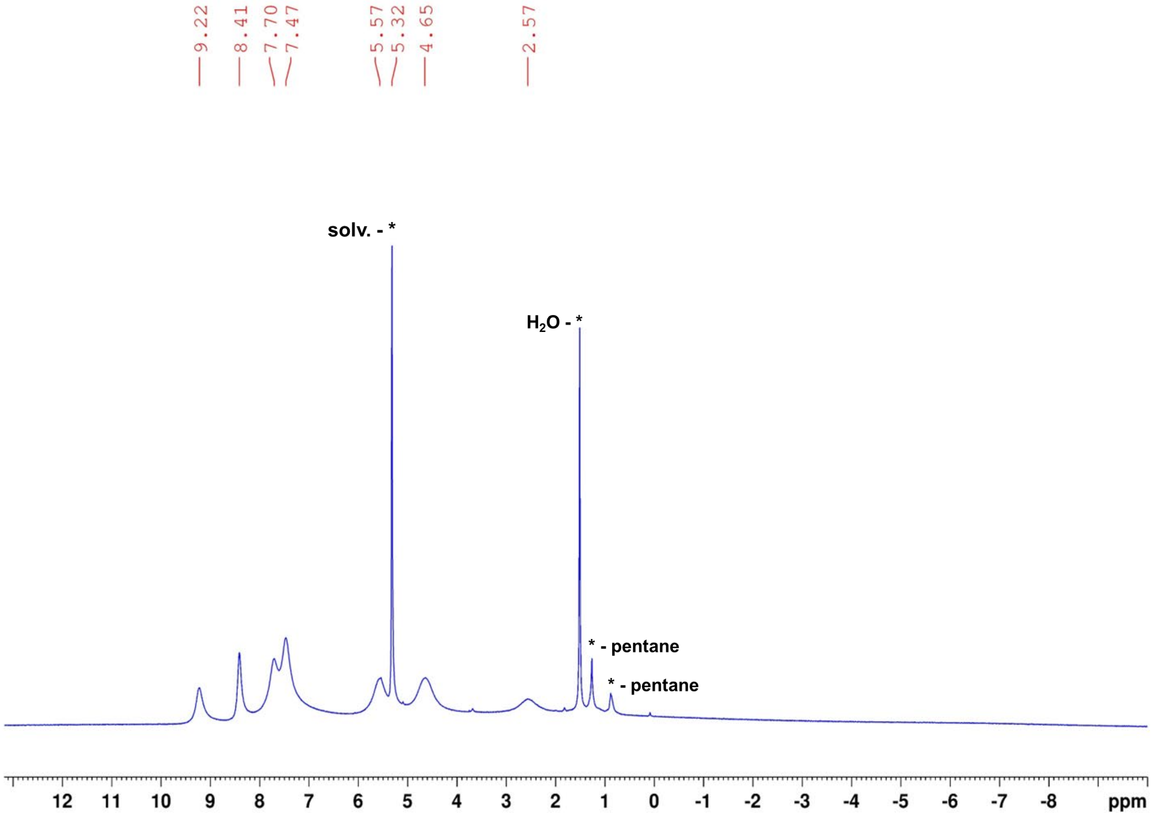


Synthesis of (PP^{CF3}P)CoI$_2$ (1)

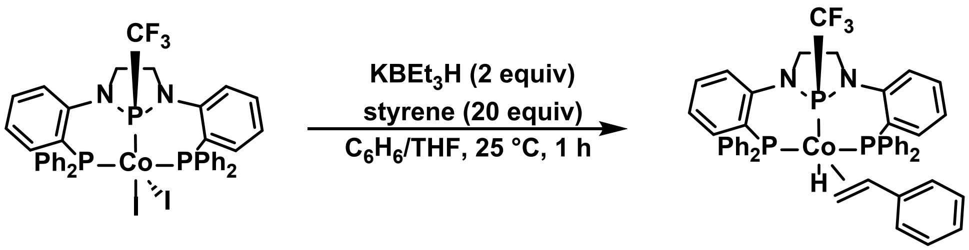


Under a nitrogen atmosphere, cobalt(II) iodide (0.154 g, 491 μmol, 1.1 equiv) was suspended in THF (5 mL) in a 20 mL scintillation vial equipped with stir bar and stirred at room temperature. (PP^{CF3}P) (0.303 g, 447 μmol) was dissolved in THF (5 mL) then added to the stirring solution of cobalt(II) iodide. The color of the solution immediately took on a green-brown coloration. The reaction mixture was allowed to stir for 16 hours. During this time, the product, **1**, precipitated from solution as a green powder. The green solid was then collected on a frit and washed with THF (2 x 10 mL), C_6H_6 (2 x 10 mL), and hexanes (20 mL). The solid was dried *in vacuo* to yield **1** as an analytically pure, golden-brown powder (0.397 g, 90%). Crystals of **1** suitable for X-ray diffraction were grown via slow evaporation of a concentrated CH_2Cl_2 solution of **1** at room temperature. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.22 (br s), 8.41 (s), 7.70 (br s), 7.47 (br s), 5.57 (br s), 4.65 (br s), 2.57 (br s). **Evans' Method:** μ_{eff} = 1.78 μ_B. **Elemental Analysis** $C_{39}H_{32}N_2P_3CoF_3I_2$, **Calc:** C, 47.25; H, 3.25; N, 2.83; **Found:** C, 47.33; H, 3.78; N, 2.89.

Figure S6. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **1**.



Synthesis of (PP^{CF3}P)CoH(η^2-styrene) (2)



Under an atmosphere of nitrogen, complex **1** (108.1 mg, 109 µmol) was loaded to a 20 mL scintillation vial equipped with a magnetic stir bar and C_6H_6 (2 mL) was added to afford a largely heterogeneous mixture that was gently stirred. To this mixture, styrene (250 µL, 2.18 mmol, 20 equiv) was added using a micropipette, followed by $KBEt_3H$ (218.1 µL, 1 M in THF, 218 µmol, 2.0 equiv), resulting in the formation of a yellow, turbid solution over the course of 60 minutes. The reaction mixture was then filtered through Celite and the filtrate was concentrated in vacuo. The resulting yellow and black residue was extracted into hexanes (18 mL) with vigorous stirring until no additional yellow color was taken up by the hexanes; these extracts were combined and filtered through glass microfiber filter paper using a pipette filter. The collected yellow filtrate was dried under vacuum to afford **2** as a yellow powder (64.4 mg, 70% yield). Crystals of **2** suitable for single-crystal XRD were obtained from a saturated *n*-pentane solution stored at -35 °C over several weeks, affording bright yellow needles.

^{1}H{^{31}P} NMR (400 MHz, C_6D_6) δ 7.82 (d, *J* = 7.4 Hz, 2H, Ar), 7.63 (d, *J* = 7.4 Hz, 2H, Ar), 7.57 (d, *J* = 7.7 Hz, 1H, Ar), 7.17 – 6.75 (overlapping m, 23H, Ar), 6.71 (t, *J* = 7.2 Hz, 1H, Ar), 6.63 (t, *J* = 7.3 Hz, 1H, Ar), 6.52 (t, *J* = 7.4 Hz, 3H, Ar), 3.92 (dd, *J* = 10.0 Hz, 1H, PhC*H*CH$_2$), 3.67 (m, 1H, NC*H*$_2$), 3.33 (m, 1H, NC*H*$_2$), 3.10 (d, *J* = 6.9 Hz, 1H, PhCHC*H*$_2$), 2.72 (d, *J* = 11.7 Hz, 1H, PhCHC*H*$_2$), 2.32 (m, 1H, NC*H*$_2$), 2.01 (m, 1H, NC*H*$_2$), -14.40 (d, *J* = 135.9 Hz, 1H, Co-*H*; in ^{1}H NMR spectrum: ddd, J_{H-P} = 148, 56, 40 Hz). **^{31}P{^{1}H} NMR (162 MHz, C_6D_6)** δ 124.2 (br s, 1P, *P*CF$_3$,), 47.1 (br s, 1P, *P*Ph$_2$), 44.8 (br s, 1P, *P*Ph$_2$). **^{19}F NMR (376 MHz, C_6D_6)** δ -61.9 (d, *J* = 44.4 Hz). **^{13}C (160 MHz, THF-D$_8$)** δ 150.6, 150.4, 140.3, 140.0, 138.3, 135.4, 135.0, 133.7, 132.2, 132.1, 132.0, 131.0, 130.6, 129.3, 129.1, 128.9, 128.1, 128.1, 128.0, 127.9, 127.8, 127.4, 127.3, 126.7, 126.0, 125.1, 123.4, 123.1, 120.1, 118.1, 57.1 (Ph*C*HCH$_2$), 48.6, 47.6, 42.6 (PhCH*C*H$_2$). **Elemental Analysis** $C_{47}H_{41}N_2P_3CoF_3$, **Calc:** C, 66.99; H, 4.90; N, 3.32; **Found:** C, 62.78; H, 5.11; N, 3.21 (**Note:** a satisfactory result was not obtained after three attempts using spectroscopically pure material. We attribute this to the transient stability of **2** under prolonged exposure to atmospheric conditions).

Figure S7. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **2**. Signals marked with a ‡ denote residual solvents, in this case hexanes and *n*-pentane.

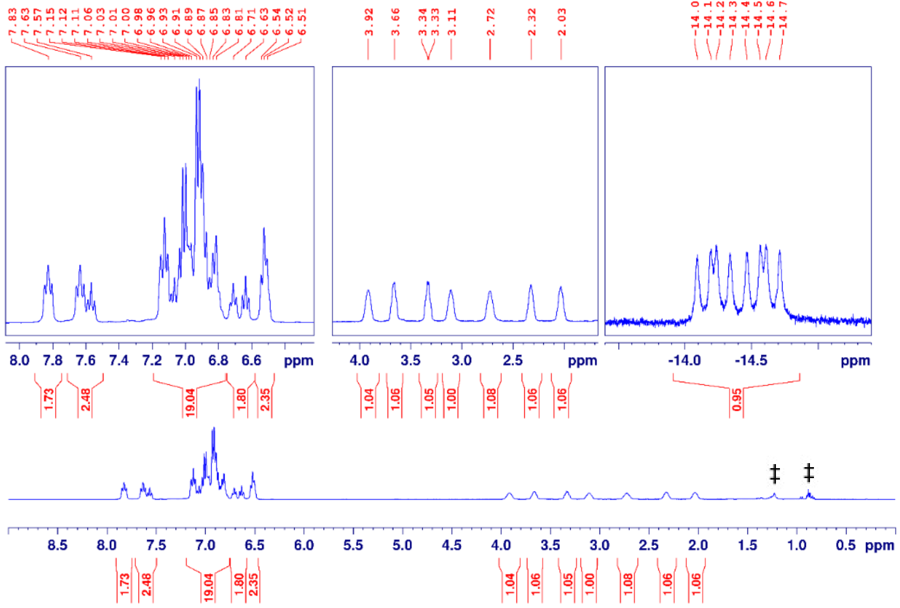


Figure S8. $^{1}H\{^{31}P\}$ NMR (400 MHz, C_6D_6) spectrum of **2**. Signals marked with a ‡ denote residual solvents, in this case hexanes and *n*-pentane. Note: Coupling between the central phosphorus atom and the cobalt-hydride is still observed owing to incomplete decoupling to the far downfield ^{31}P resonance.

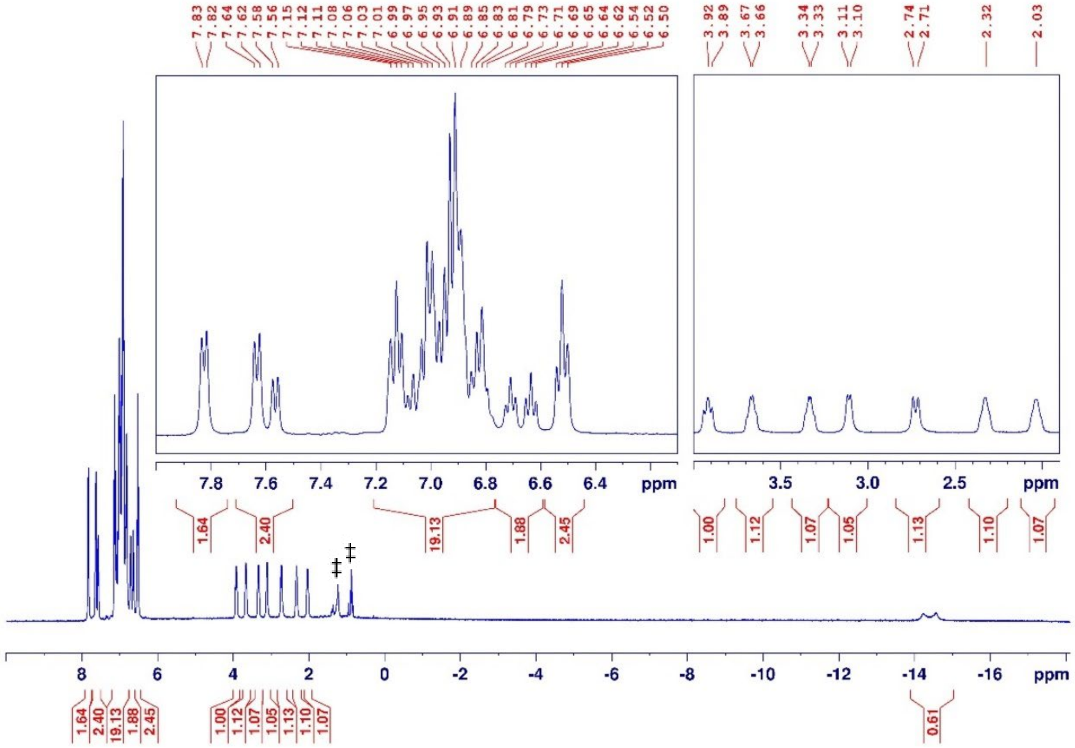


Figure S9. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) spectrum of **2**.

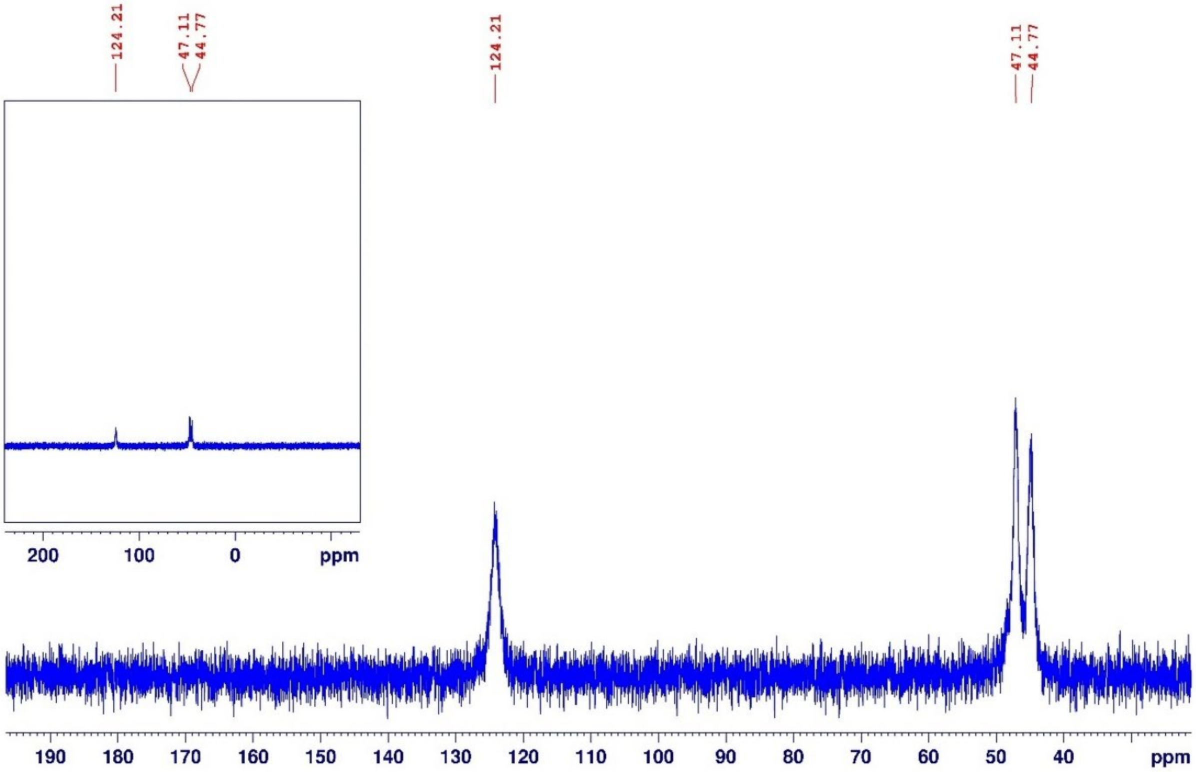


Figure S10. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **2**.

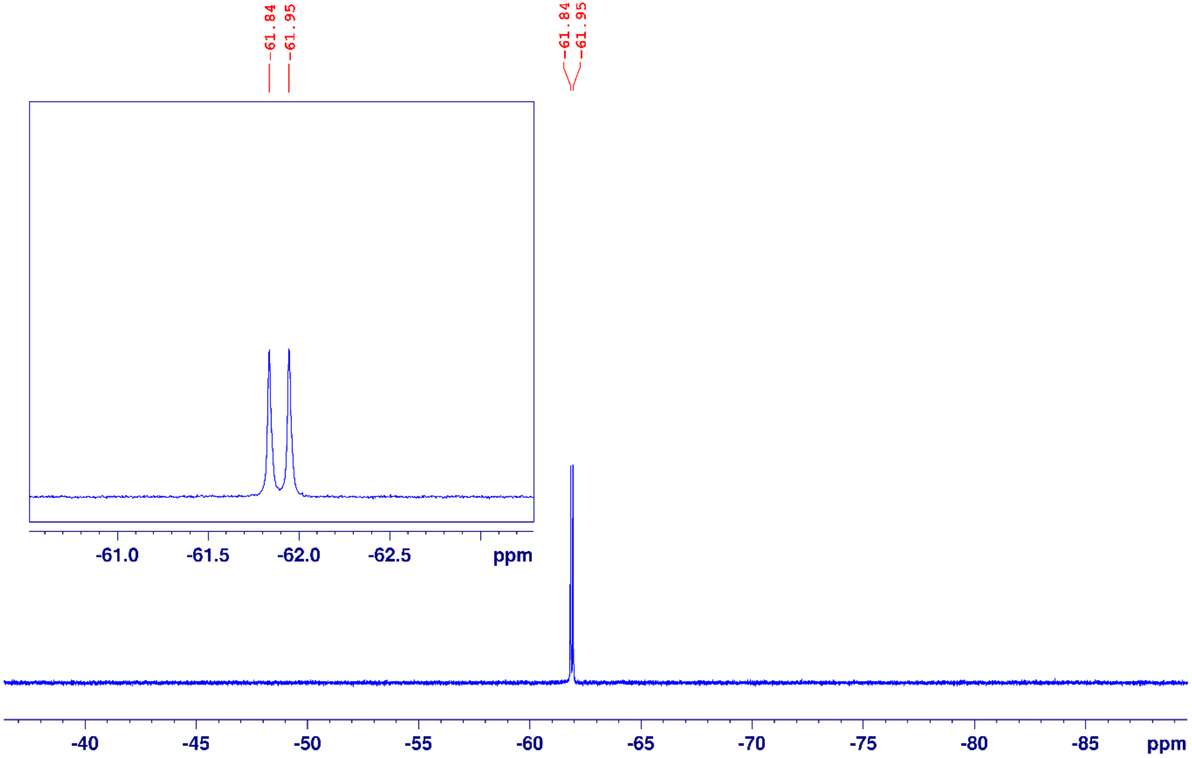


Figure S11. $^{13}C\{^{1}H\}$ NMR (151 MHz, THF-d_8) spectrum of **2**. **a)** Full-window view of ^{13}C NMR spectrum of **2**. **b)** Expanded view of aromatic C_{sp2} region.

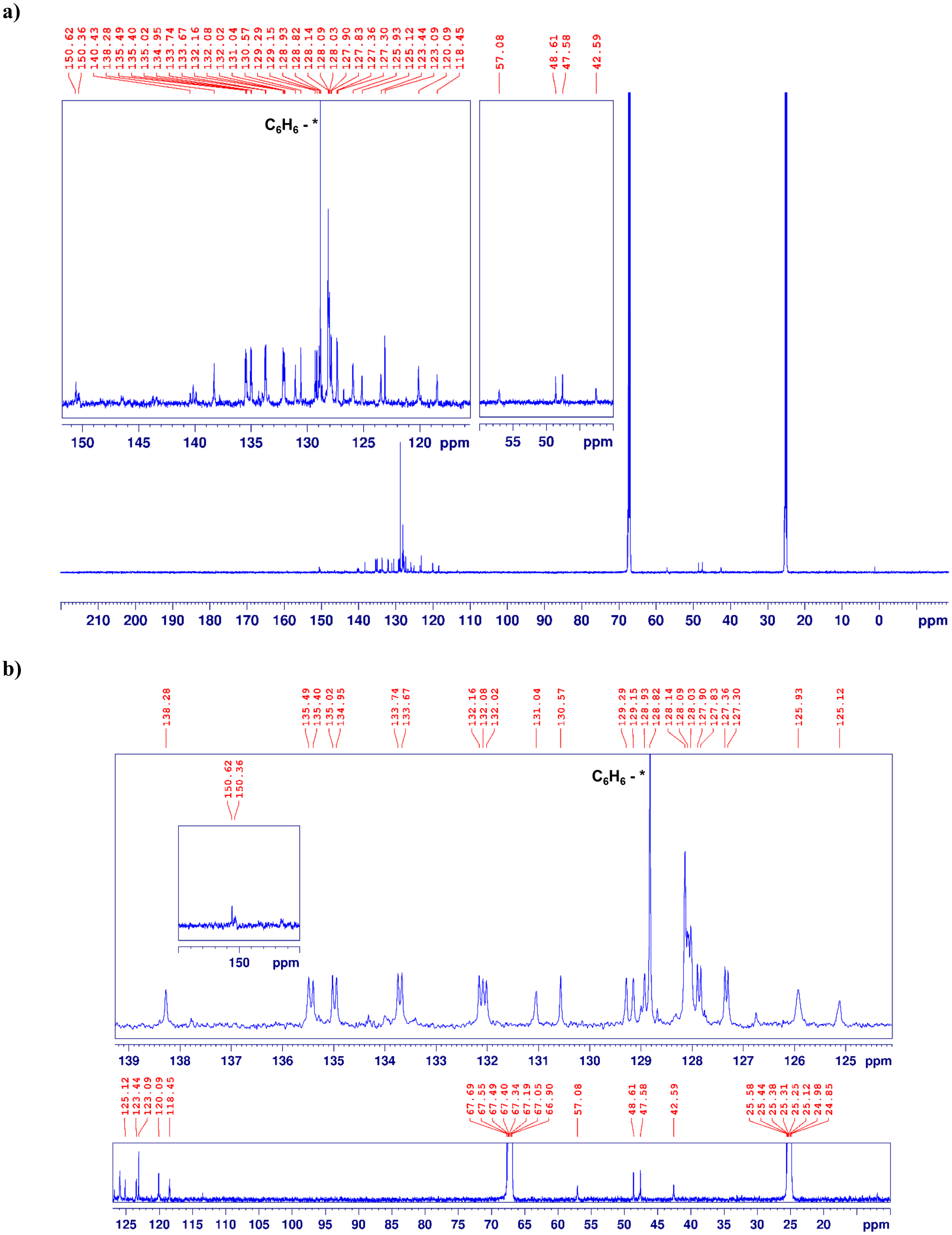


Figure S12. ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6) spectrum of **2**. No correlations to the hydride signal are observed.

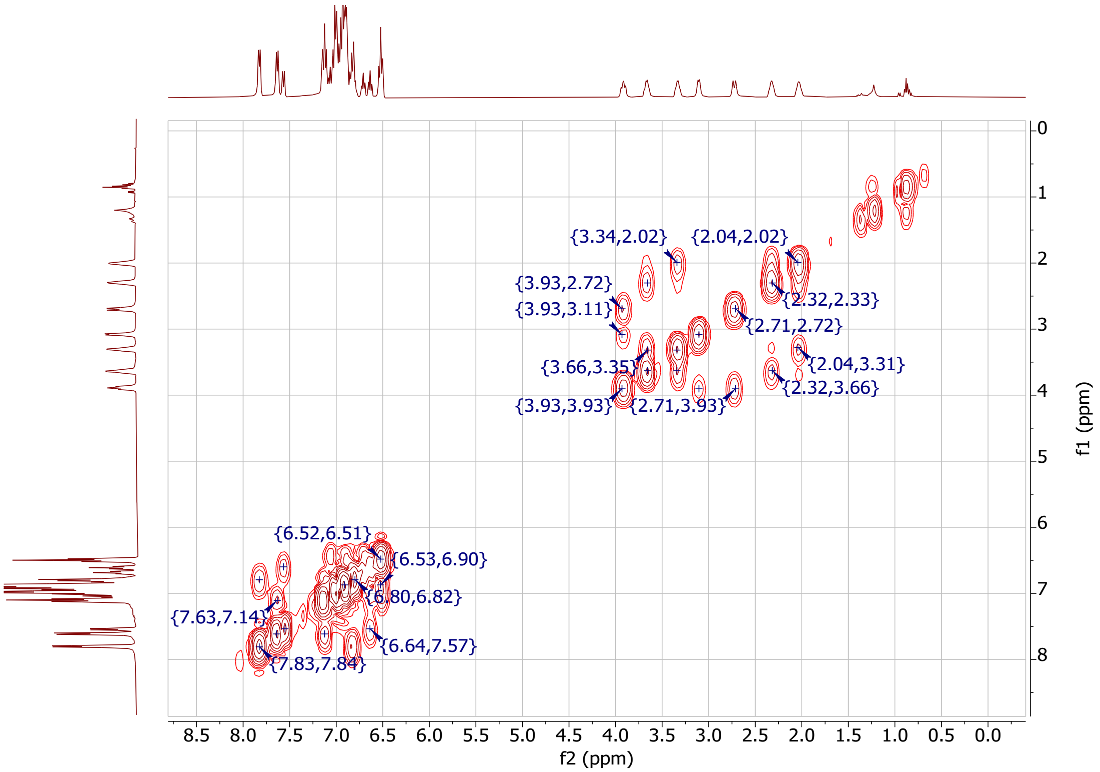
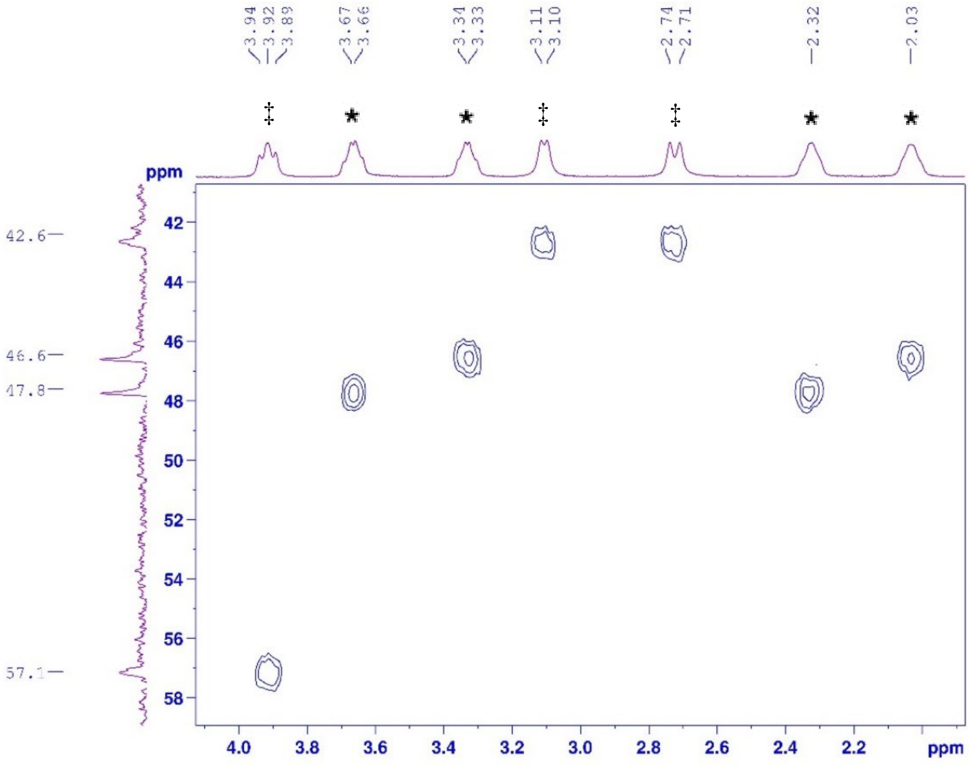
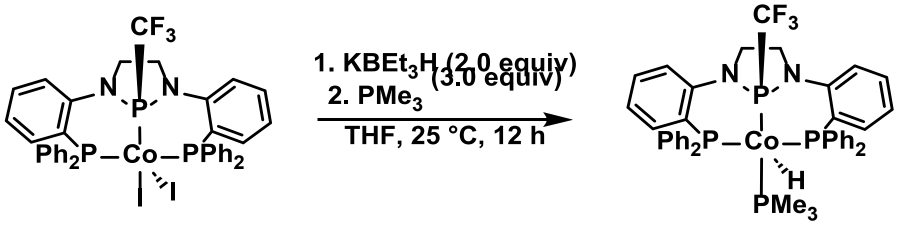


Figure S13. ^{13}C-^{1}H HSQC-ME NMR (101 MHz, C_6D_6) spectrum of **2**. Methylene protons of the backbone denoted with an asterisk. The vinylic protons of the bound styrene are denoted with a ‡.



Synthesis of (PP^{CF_3}P)Co(PMe$_3$)H (3)



Complex **1** (21.4 mg, 22 μmol) was loaded to a 20 mL scintillation vial equipped with a magnetic stir bar and THF (4 mL) was added to afford a heterogeneous mixture that was gently mixed. To this mixture, $KBEt_3H$ (43.2 μL, 1 M in THF, 43 μmol, 2.0 equiv) was added using a micropipette and the reaction mixture was allowed to stir for three minutes before addition of PMe_3 (6.6 μL, 65 μmol, 3.0 equiv) by micropette. The reaction mixture rapidly took on a vivid orange coloration and was allowed to stir for 12 hours. After this time, the solution was filtered through glass microfiber filter paper using a pipette filter and the filtrate was dried in vacuo to yield crude **3** as a dark-red residue. Crystallization of crude **3** from a sautrated solution of *n*-pentane at -35 °C affords the spectroscopically pure complex as an orange crystalline solid of single-crystal X-ray diffraction quality (17.0 mg, 96.7%). **^{1}H{^{31}P} NMR** (400 MHz, C_6D_6) δ 7.79 (d, *J* = 7.9 Hz, 4H, Ar), 7.63 (d, *J* = 7.3 Hz, 4H, Ar), 7.46 (d, *J* = 7.60 Hz, 2H, Ar), 7.17 – 7.01 (m, 8H, overlapping Ar), 6.88 – 6.68 (m, 10H, overlapping), 3.64 (m, 2H, NC*H*$_2$), 2.37 (m, 2H, NC*H*$_2$), 0.93, (s, 9H, PMe_3), -11.56 (d, *J* = 67.0 Hz, 1H, Co-*H*; in ^{1}H NMR spectrum: ddt, $J_{H\text{-}P}$ = 88, 44, 44 Hz). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ 132.1 (br s, 1P, *P*CF_3,), 41.1 (br m, 2P, *P*Ph_2), -2.5 (br m, 1P, *P*Me_3). **^{19}F NMR** (376 MHz, C_6D_6) δ -64.4 (d, *J* = 52.6 Hz). **^{13}C (100 MHz, THF-H_8)** δ 148.1, 142.6, 133.5, 132.6, 132.4, 129.4, 127.6, 127.4, 126.6, 120.6, 120.2, 47.0 (s, N*C*H_2), 23.3 (d, $J_{C\text{-}P}$ = 20 Hz, *P*$(CH_3)_3$). **Elemental Analysis** $C_{42}H_{42}N_2P_4CoF_3$, **Calc:** C, 61.92; H, 5.20; N, 3.44; **Found:** C, 61.92; H, 5.48; N, 3.51.

Figure S14. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **3**.

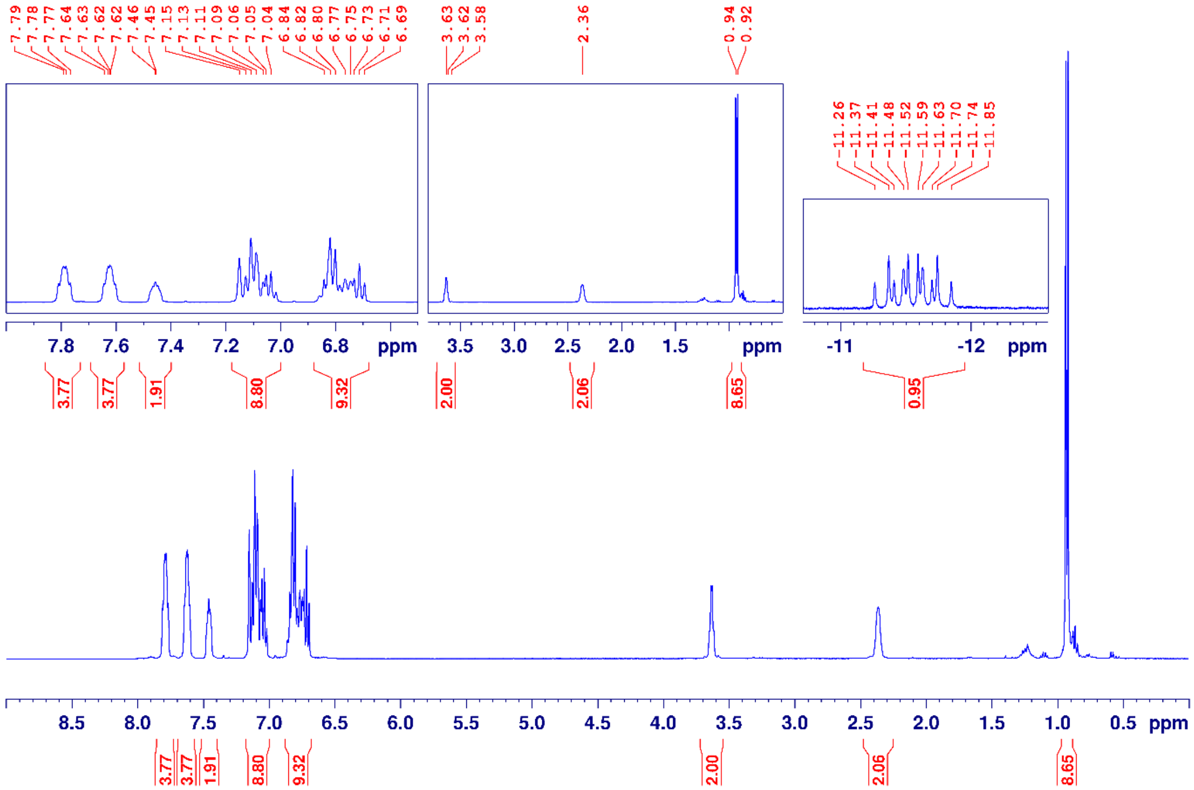


Figure S15. $^{1}H\{^{31}P\}$ NMR (400 MHz, C_6D_6) spectrum of **3**. Residual solvent denoted with an asterisk. Note: Coupling between the central phosphorus atom and the cobalt-hydride is still observed owing to incomplete decoupling to the far downfield ^{31}P resonance.

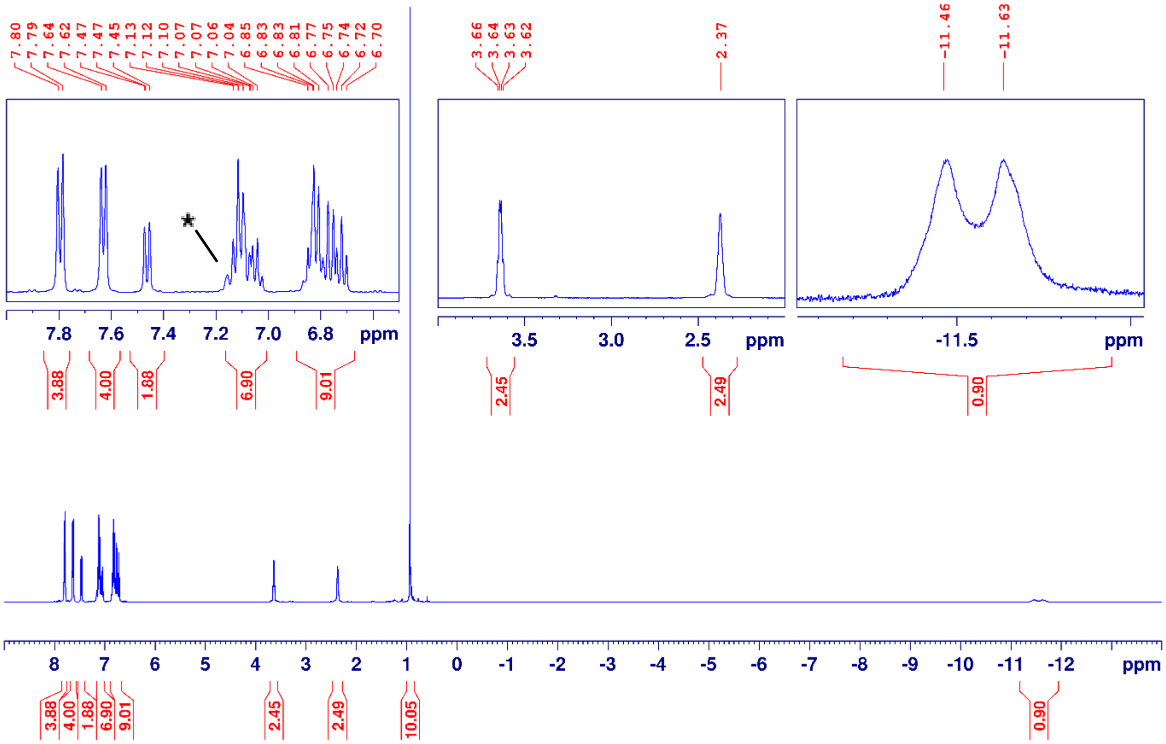


Figure S16. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) spectrum of **3**.

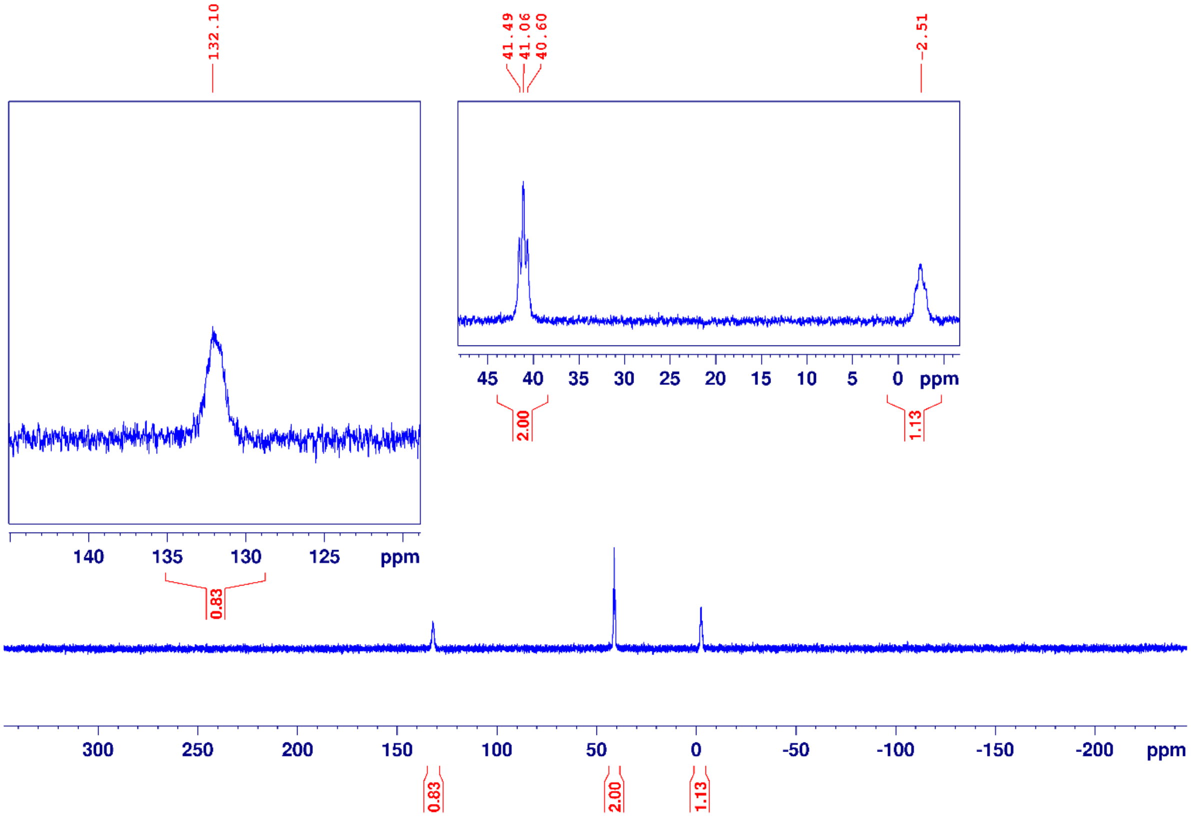


Figure S17. ^{19}F NMR (376 MHz, C_6D_6) spectrum of **3**.

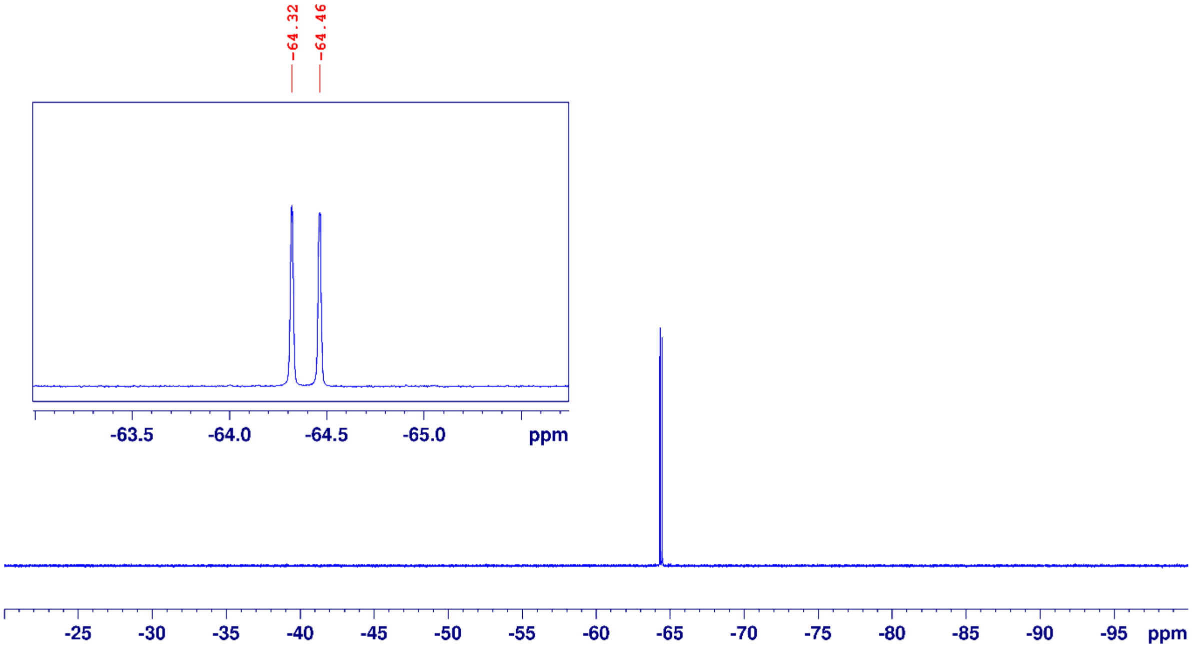
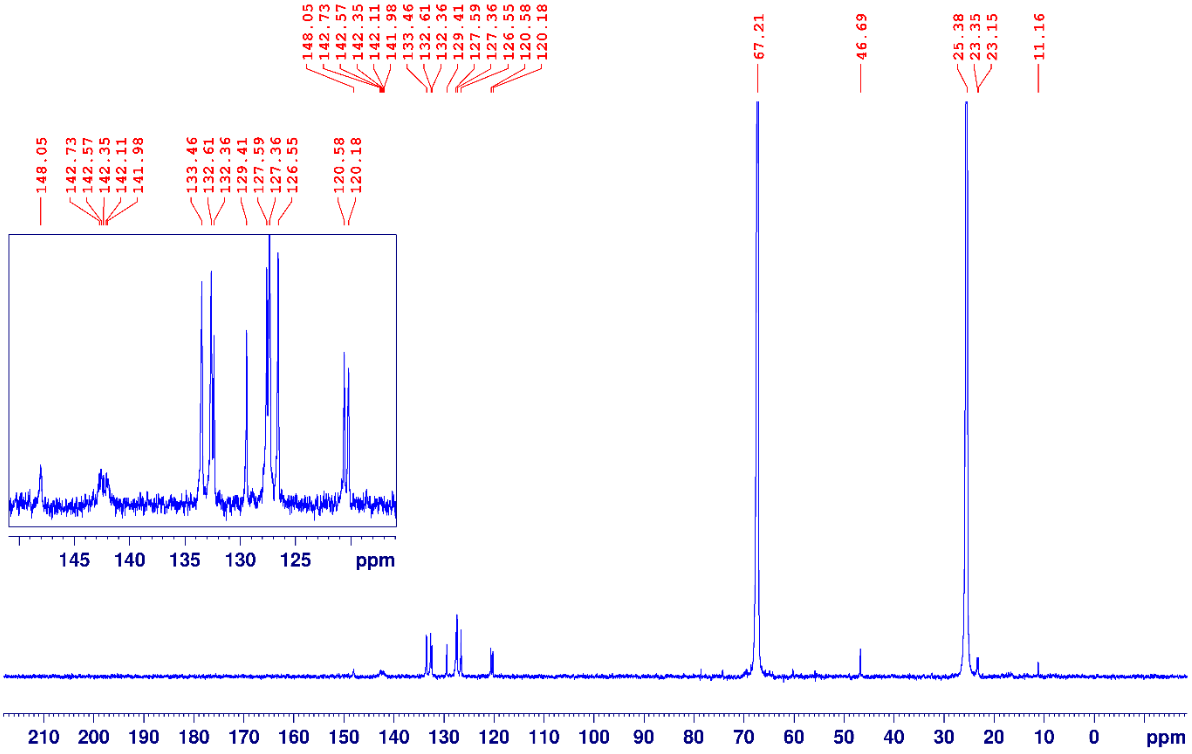
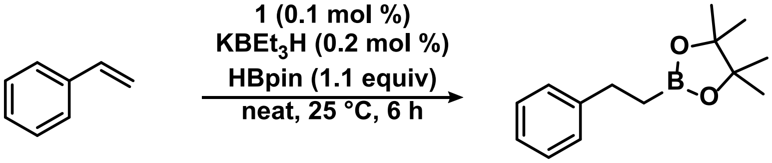


Figure S18. ${}^{13}C\{{}^{1}H\}$ NMR (101 MHz, THF-H_8) spectrum of **3**.



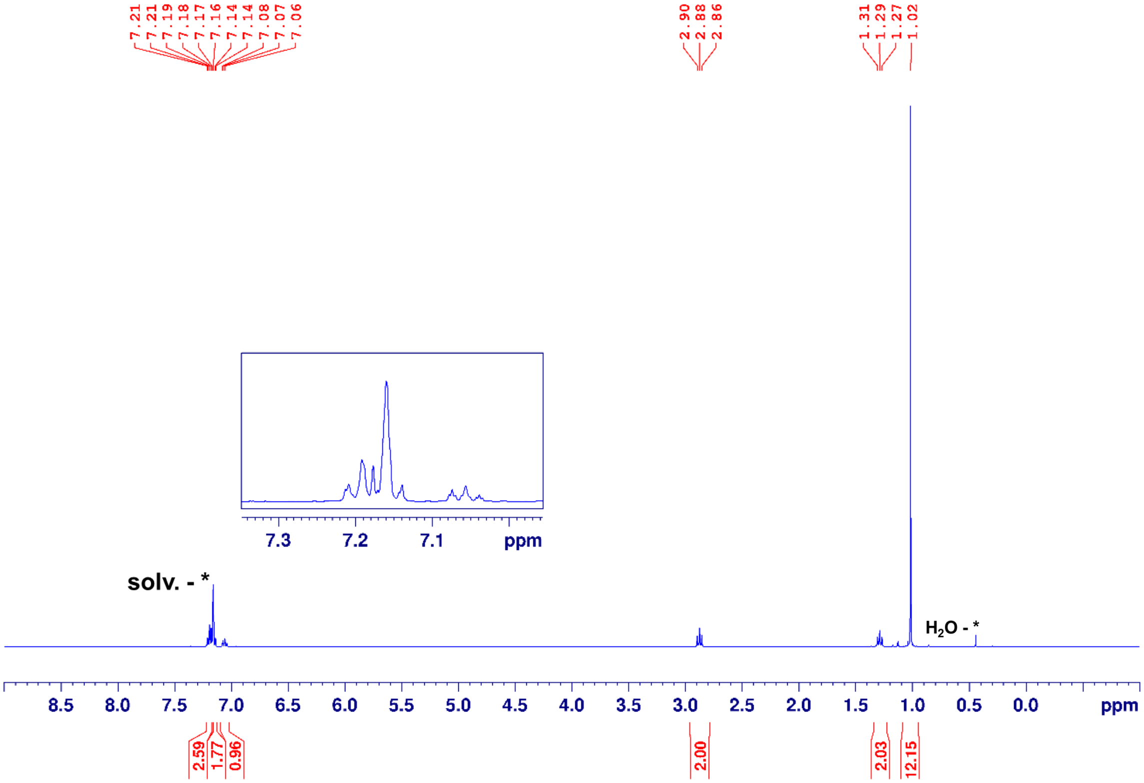
Hydroboration Conditions

Representative Procedure - 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane

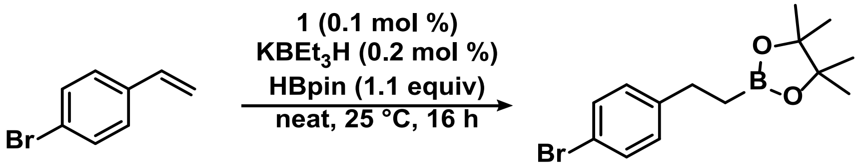


To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (8.2 mg, 8.3 µmol, 0.1 mol %), styrene (0.86 g, 8.3 mmol), and HBpin (1.16 g, 9.1 mmol, 1.1 equiv) and the resultant heterogenous mixture was stirred. The activator, KBEt$_3$H (16.5 µL, 1 M in THF, 16.5 µmol, 0.2 mol %), was added by micropipette, affording a yellow, homogenous solution that was stirred for 6 hours. It is noted that the solution gradually darkens and takes on an orange coloration as catalysis nears completion. The reaction vial was removed from the glovebox, exposed to air, and pentanes (3 mL) were added to encourage precipitation of deactivated cobalt species, with gentle stirring for approximately 15 minutes. The quenched mixture was then filtered through a pad of Celite, washing the filter several times with fresh solvent to extract the desired product. The filtrate was concentrated by rotary evaporation (water bath, c. 30 °C) to afford nearly pure 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane as a colorless, viscous oil. The product was further purified by column chromatography (silica, hexanes/EtOAc 9:1), affording the product as a white amorphous solid (1.81 g, 94.4% yield). **^{1}H NMR (400 MHz, C$_6$D$_6$):** δ 7.22 – 7.12 (m, 4H, overlapping), 7.05 (tt, *J* = 7.1, 1.7 Hz, 1H), 2.88 (t, *J* = 7.9 Hz, 2H), 1.29 (t, *J* = 7.9 Hz, 2H), 1.02 (s, 12H). **^{11}B NMR (128 MHz, C$_6$D$_6$): δ** 34.1 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane.[2]

Figure S19. ^{1}H NMR spectrum (C$_6$D$_6$, 400 MHz) of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane.



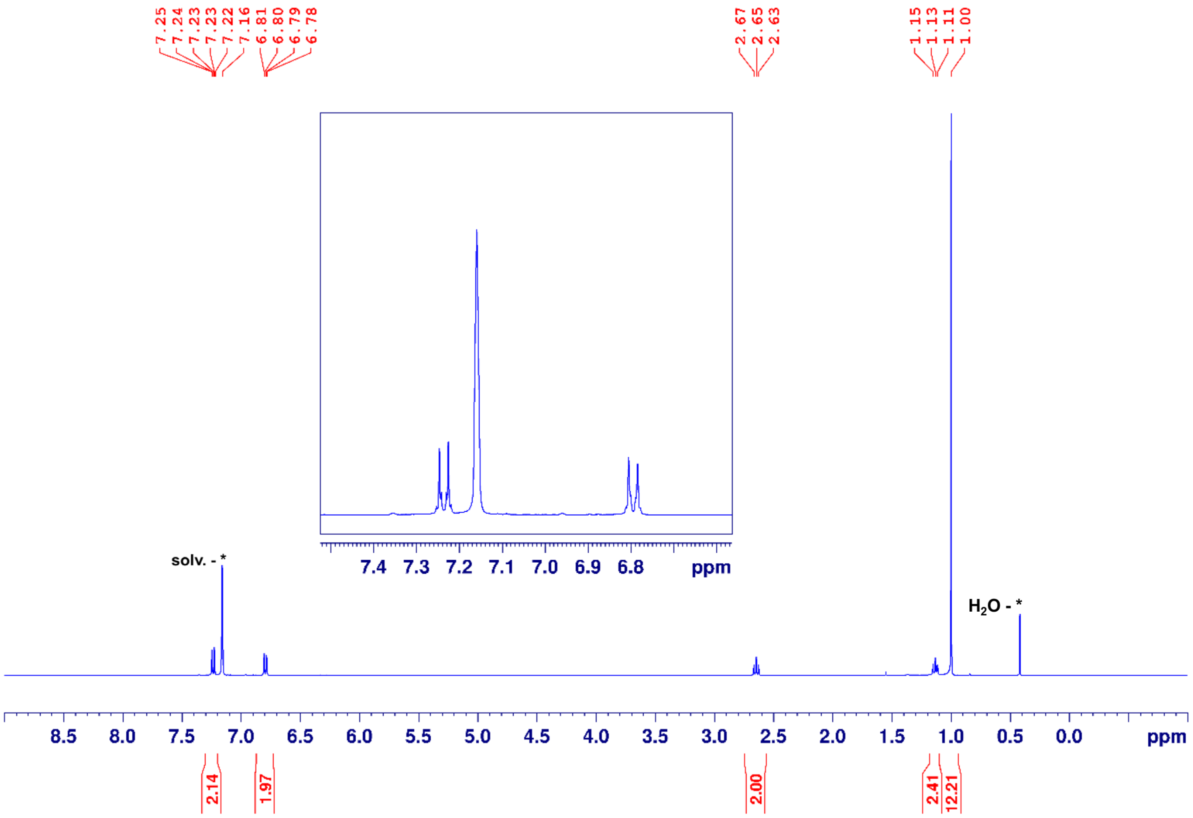
2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



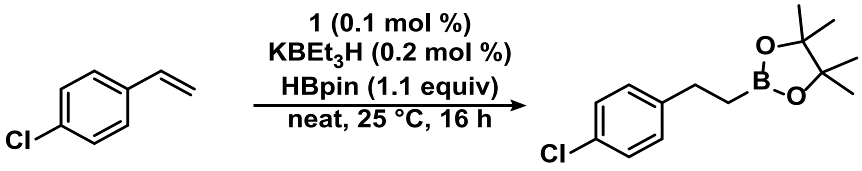
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (2.7 mg, 2.7 µmol, 0.1 mol %), 4-bromostyrene (0.500 g, 2.73 mmol), and HBpin (0.388 g, 3.03 mmol, 1.1 equiv), and the resultant heterogenous mixture was stirred. Then, $KBEt_3H$ (54.6 µL, 100 mM in THF, 5.5 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution which was stirred for 16 hours.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded the product as a white, amorphous solid (0.753 g, 87.7% yield). **^{1}H NMR (400 MHz, C_6D_6): δ** 7.24 (d, *J* = 8.0, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 7.9 Hz, 2H), 1.13 (t, *J* = 7.9 Hz, 2H), 1.00 (s, 12H). **^{11}B NMR (128 MHz, C_6D_6): δ** 34.0 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[2]

Figure S20. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of 2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



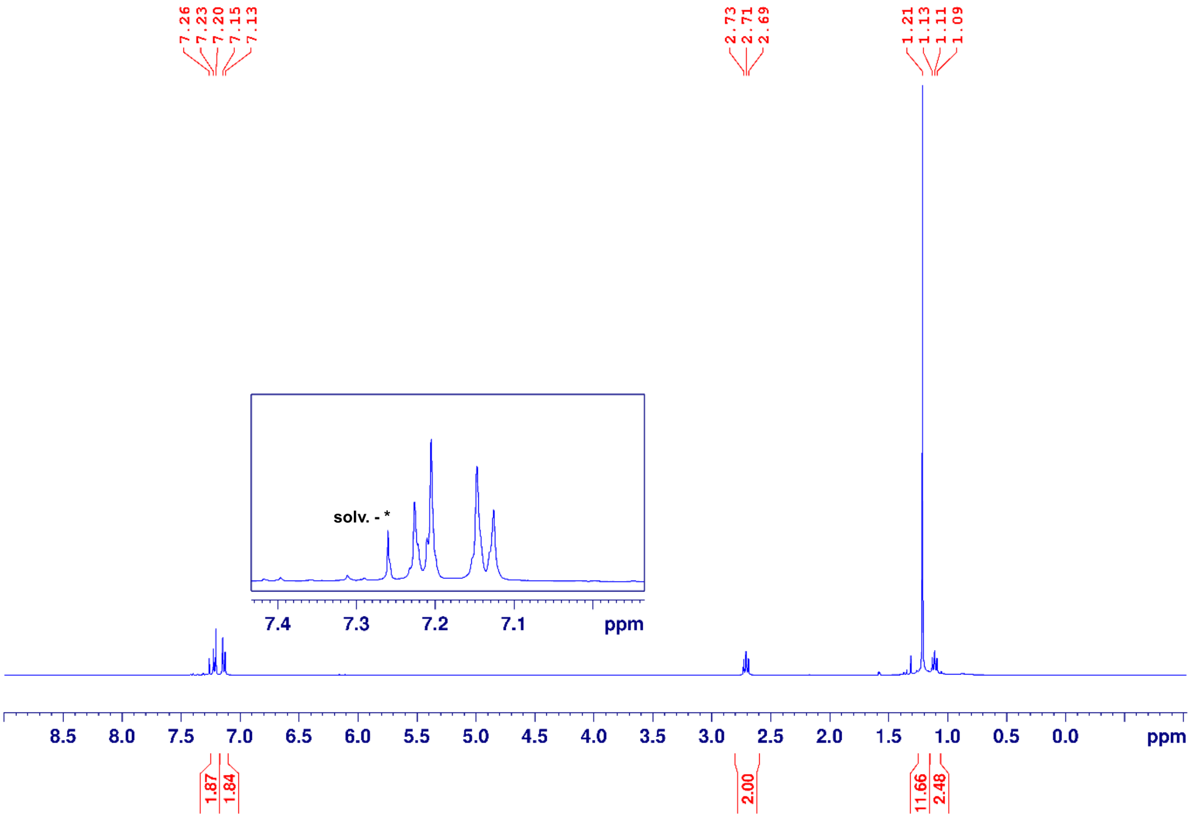
2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



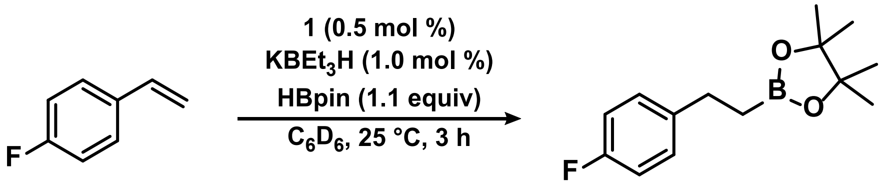
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (1.5 mg, 1.5 µmol, 0.1 mol %), 4-chlorostyrene (0.205 g, 1.48 mmol), and HBpin (0.209 g, 1.63 mmol, 1.1 equiv), and the resultant heterogenous mixture was stirred. Then, $KBEt_3H$ (29.6 µL, 100 mM in THF, 3.0 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution which was stirred for 16 hours.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded the product as a white amorphous solid (0.337 g, 85.3% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.1 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.60 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[2]

Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



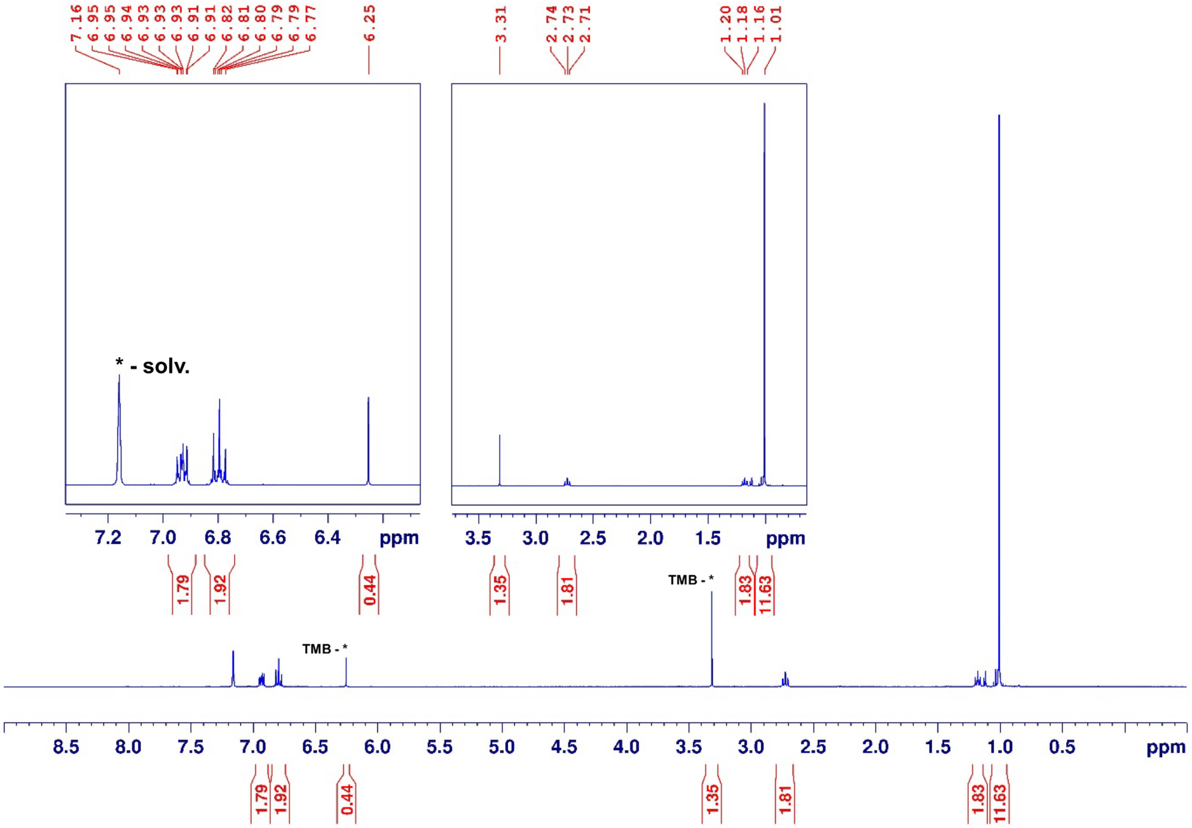
2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



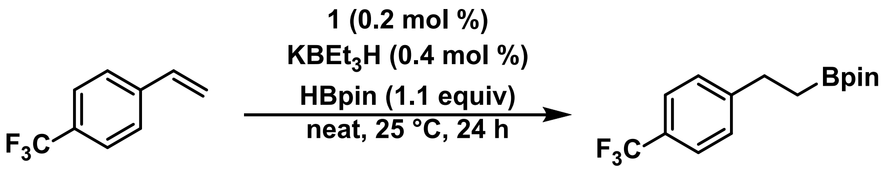
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (2.6 mg, 2.6 µmol, 0.5 mol %), C_6D_6 (0.4 mL), 4-fluorostyrene (67.8 mg, 0.56 mmol), and HBpin (78.1 mg, 0.61 mmol, 1.1 equiv), and the resultant heterogenous mixture was stirred. Then, $KBEt_3H$ (53.2 µL, 100 mM in THF, 5.3 µmol, 1.0 mol %) was added by micropipette, affording a yellow homogenous solution that was stirred for 3 hours. Trimethoxybenzene (0.15 equiv, 14.0 mg) was added as an internal standard and the yield determined by comparison of the integration of the normalized methyl resonance of trimethoxybenzene to the benzylic methylene resonance of the product. The reaction mixture was filtered through glass microfiber filter paper and gently concentrated in-vacuo.

Characterization: Yield: 90.5% (NMR). **^{1}H NMR (400 MHz, C_6D_6): δ** 7.24 – 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 2.73 (t, J = 8.0 Hz, 2H), 1.18 (t, J = 8.1 Hz, 2H), 1.01 (s, 12H). **^{11}B NMR (128 MHz, C_6D_6): δ** 33.34 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[3]

Figure S22. ^{1}H (C_6D_6, 400 MHz) spectrum of 2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



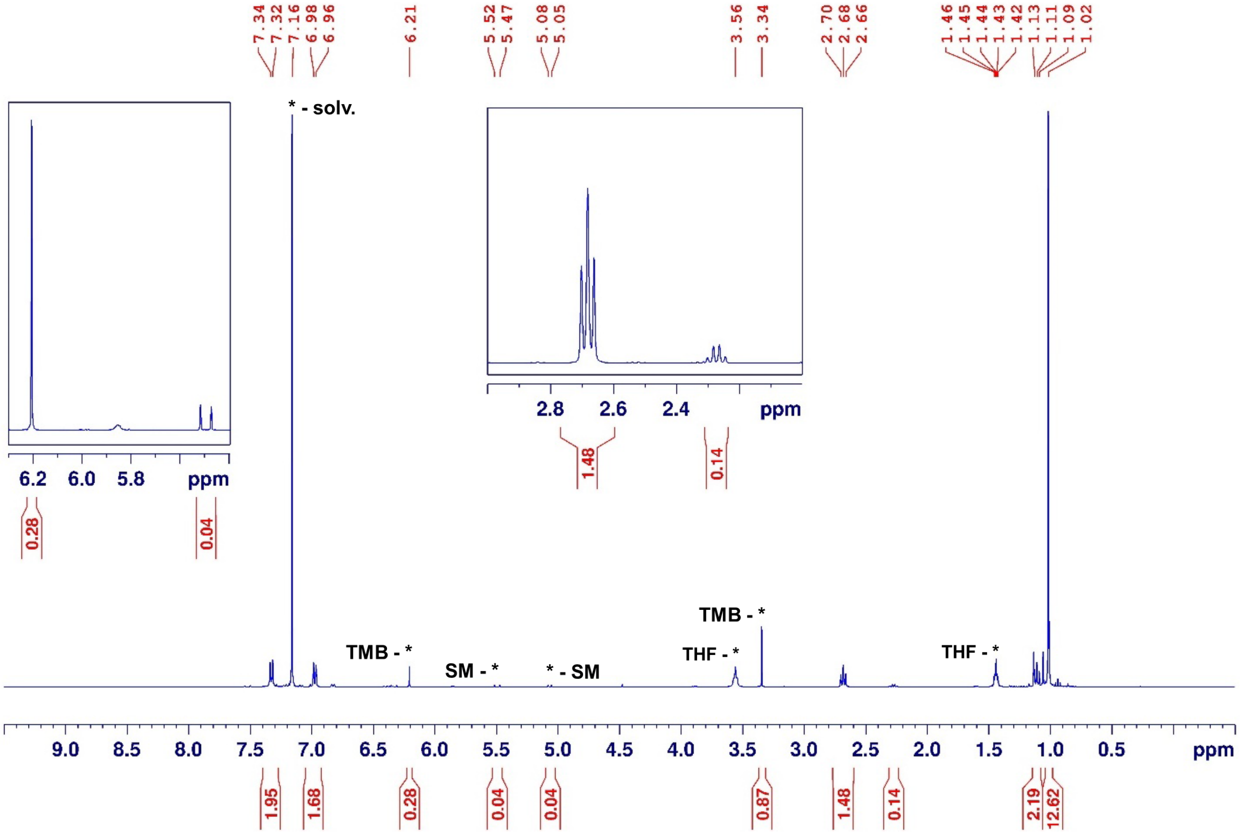
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane



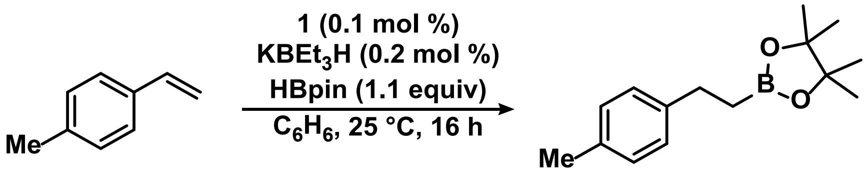
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (2.1 mg, 2.1 µmol, 0.2 mol %), C_6D_6 (0.50 mL), 4-trifluoromethylstyrene (183.0 mg, 1.06 mmol), and HBpin (147.2 mg, 1.17 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (41.8 µL, 100 mM in THF, 4.2 µmol, 0.4 mol %) was added by micropipette, affording a yellow homogenous solution that was stirred for 24 hours. Trimethoxybenzene (16.3 mg, 97 µmol, 0.091 equiv) was added as an internal standard and the yield determined by comparison of the integration of the normalized methyl resonance of trimethoxybenzene to the benzylic methylene resonance of the product.

Characterization: Yield: 74.0% (NMR). **^{1}H NMR (400 MHz, C_6D_6): δ** 7.32 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.10 (t, *J* = 7.9 Hz, 2H), 1.01 (s, 12H). **^{11}B NMR (128 MHz, C_6D_6): δ** 33.48 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane.[3]

Figure S23. ^{1}H (C_6D_6, 400 MHz) NMR spectrum of 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane.



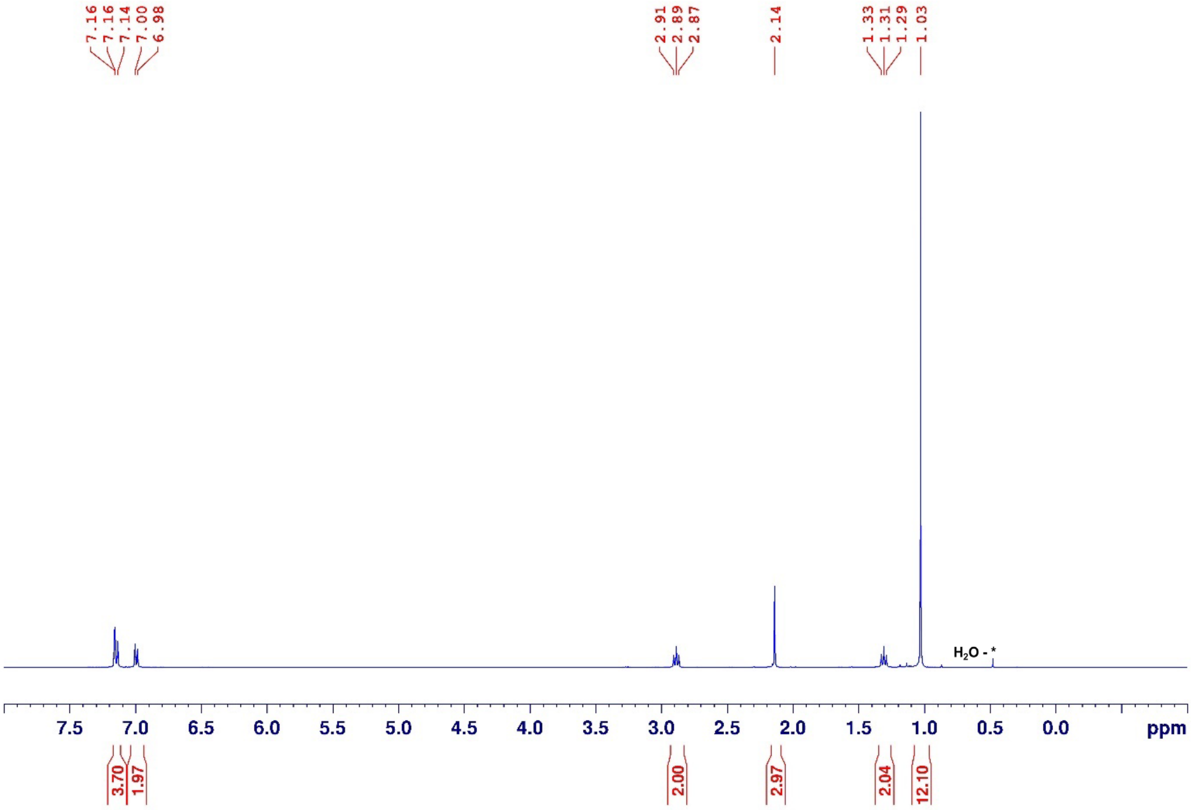
4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane



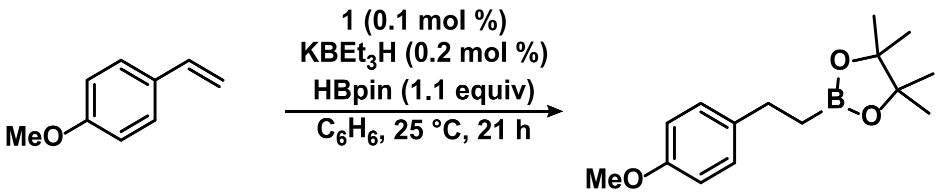
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (6.5 mg, 6.5 µmol, 0.1 mol %), C_6H_6 (0.5 mL), 4-methylstyrene (0.788 g, 6.67 mmol), and HBpin (1.07 mL, 7.33 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (132.0 µL, 100 mM in THF, 13.4 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution, which was stirred for 16 hours.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded the product as a clear, colorless oil (1.58 g, 96.3% yield). **^{1}H NMR (400 MHz, C_6D_6): δ** 7.15 (d, 8.0 Hz, 2H), 6.99 (d, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.14 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 2H), 1.03 (s, 12H). **^{11}B NMR (128 MHz, C_6D_6): δ** 33.57 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane.[2]

Figure S24. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane.



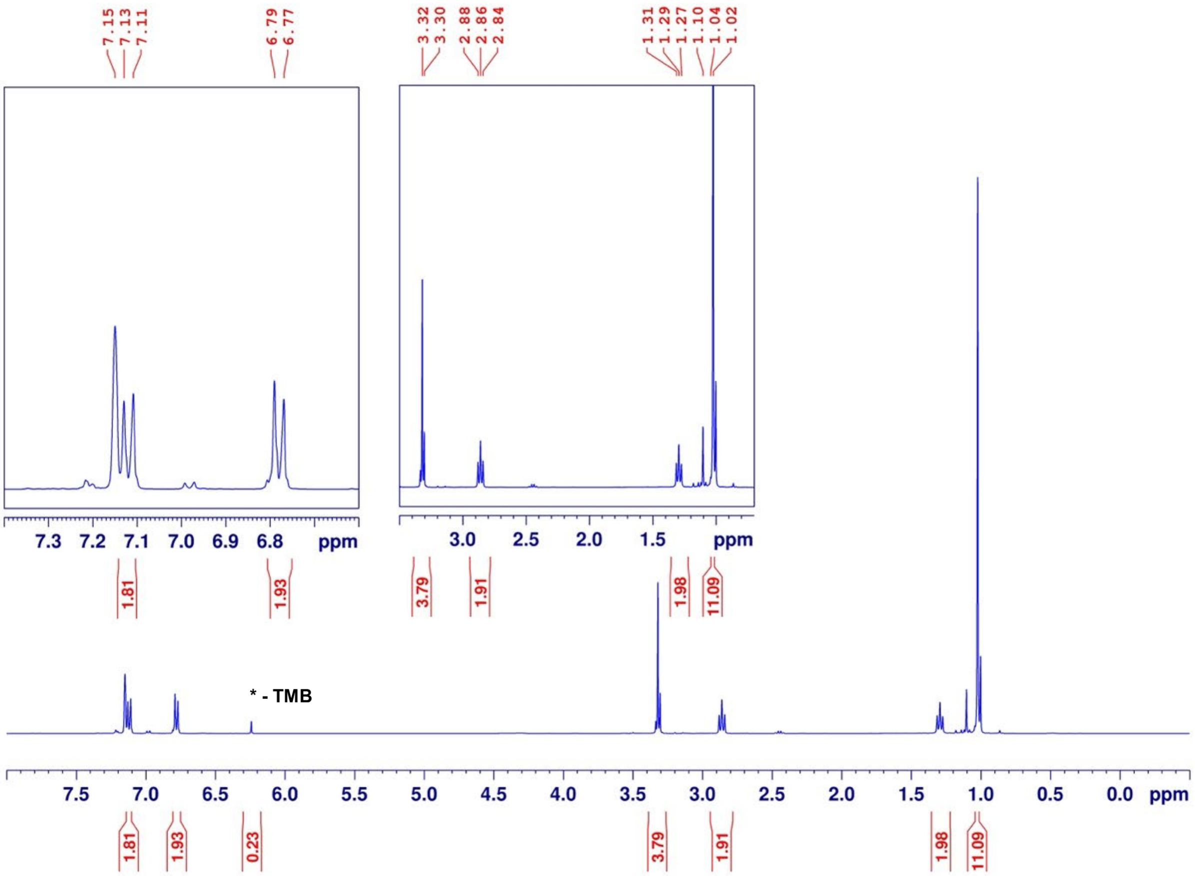
2-[2-(4-methoxy-phenyl)-ethyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane



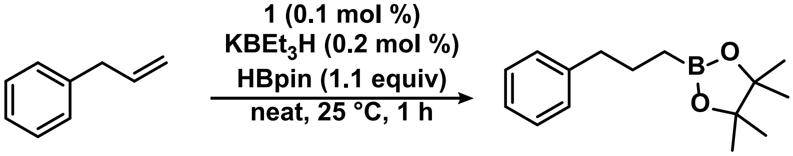
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (3.7 mg, 3.7 µmol, 0.1 mol %), C_6H_6 (0.5 mL), 4-vinylanisole (0.500 g, 3.73 mmol), and HBpin (1.1 equiv, 0.525 g, 4.1 mmol) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (74.6 µL, 100 mM in THF, 7.5 µmol, 0.2 mol%) was added by micropipette, affording a yellow homogenous solution which was stirred for 24 hours. After filtration, trimethoxybenzene (47.2 mg, 0.28 mmol, 0.075 equiv) was added as an internal standard and the normalized integration of the ArH resonance of trimethoxybenzene was compared to the benzylic methylene resonance of the product.

Characterization: Yield: 95.5% yield (NMR). **^{1}H NMR (400 MHz, C_6D_6): δ** 7.12 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 8.0 Hz, 2H), 1.03 (s, 12H). **^{11}B NMR (128 MHz, C_6D_6): δ** 33.57 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for 2-[2-(4-methoxy-phenyl)-ethyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane.[6]

Figure S25. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of 2-[2-(4-methoxy-phenyl)-ethyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane.



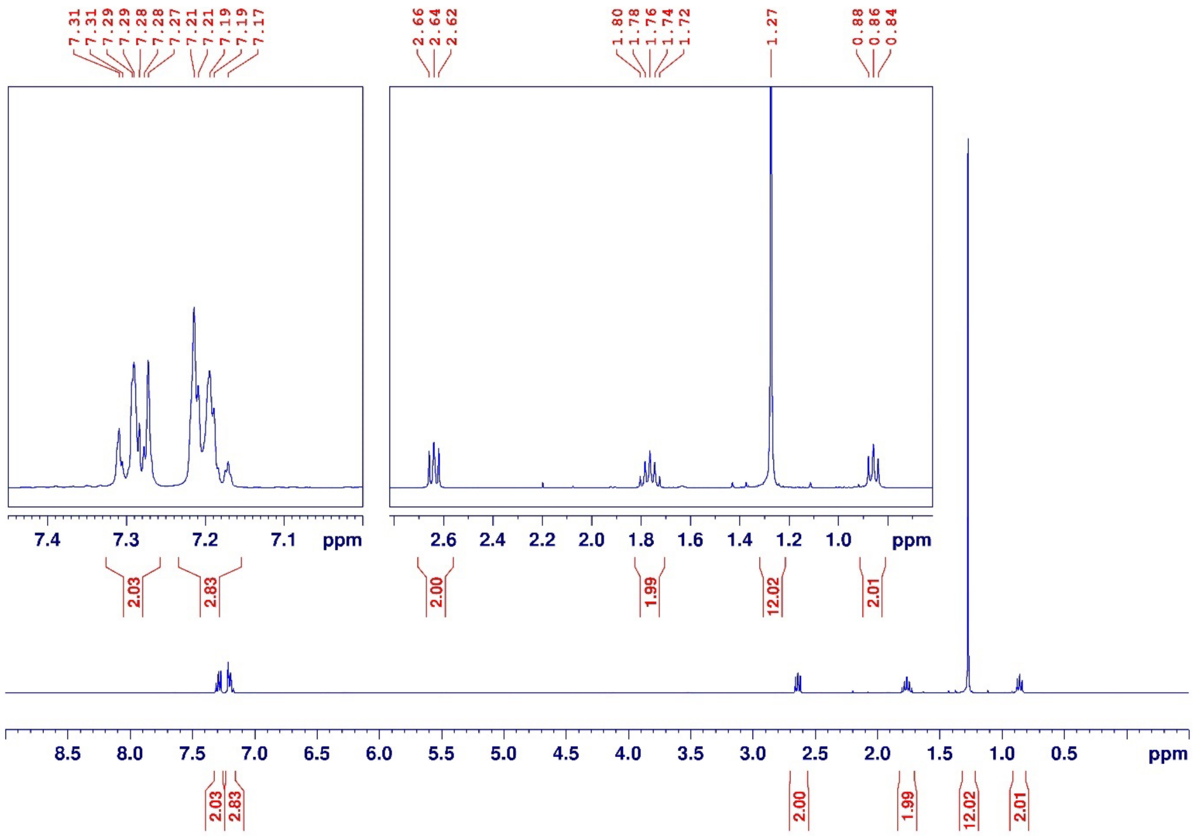
4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**A**)



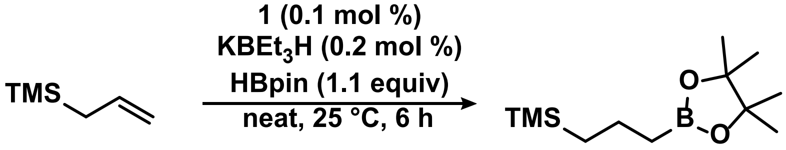
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (7.4 mg, 7.4 µmol, 0.1 mol %), 3-phenylpropene (0.881 g, 7.46 mmol), and HBpin (1.05 g, 8.20 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (14.9 µL, 1 M in THF, 14.9 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution that was stirred for 1 hour.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded product **A** as a clear, colorless oil (1.71 g, 93.2% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H, overlapping), 2.64 (t, *J* = 7.8 Hz, 2H), 1.76 (m, 2H), 1.27 (s, 12H), 0.86 (t, *J* = 7.7, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 34.34 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **A**.[3]

Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**A**).



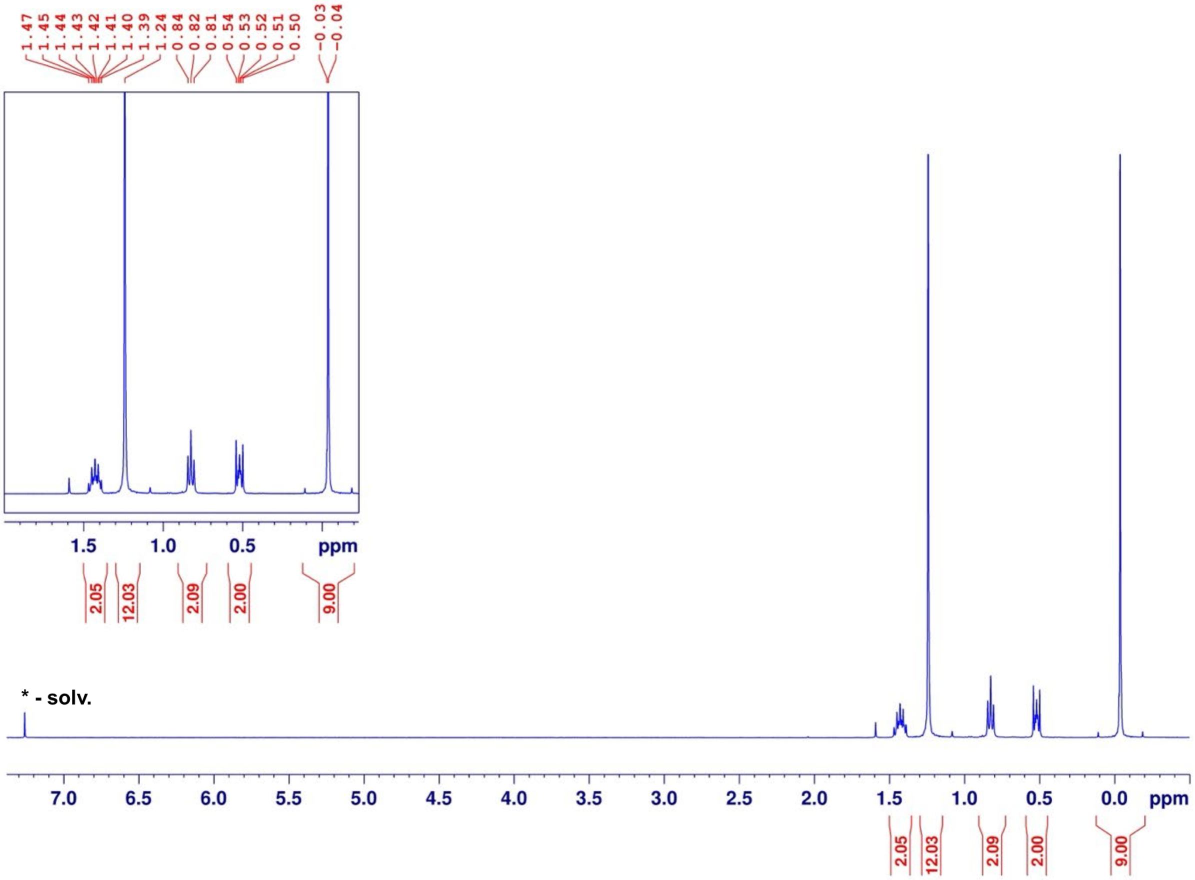
Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (**B**)



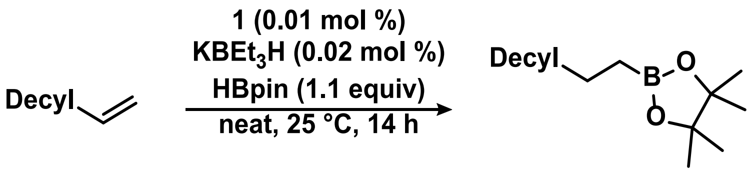
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (4.5 mg, 4.6 µmol, 0.1 mol %), allyltrimethylsilane (0.526 g, 4.60 mmol), and HBpin (0.616 g, 4.8 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (87.5 µL, 100 mM in THF, 9.2 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution which was stirred for 6 hours.

Characterization: After workup (as described in representative procedure with styrene), a silica plug afforded product **B** as a clear, colorless oil (1.12 g, >99% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.47 – 1.40 (m, 2H), 1.24 (s, 12H), 0.83 (t, J = 8.1 Hz, 2H), 0.54 – 0.50 (m, 2H), -0.04 (s, 9H). **^{11}B NMR (128 MHz, CDCl$_3$):** δ 34.08 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **B**.[8]

Figure S27. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (**B**).



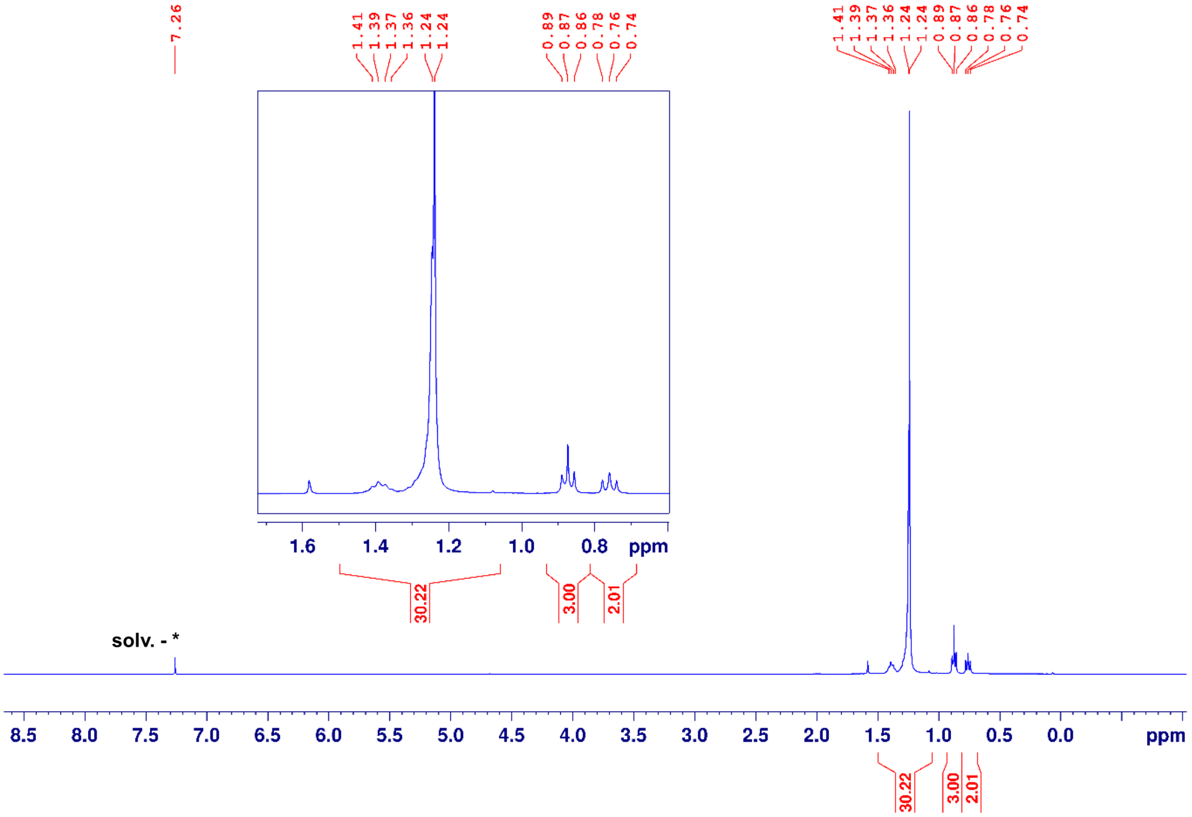
2-dodecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**C**)



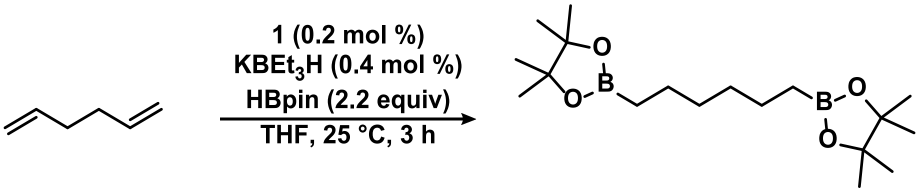
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (155.6 µL, 2.1 mM in THF, 0.3 µmol, 0.01 mol %) and the solvent removed under reduced pressure. Dodecene (0.550 g, 3.27 mmol) and HBpin (0.52 mL, 3.59 mmol 1.1 equiv) were added and the resultant mixture stirred. Then, $KBEt_3H$ (6.5 µL, 100 mM in THF, 0.7 µmol, 0.02 mol %) was added by micropipette, affording a yellow homogenous solution, which was stirred for 14 hours.

Characterization: After workup (as described in representative procedure with styrene), a short silica plug (4 cm, pipette) and removal of solvent afforded product **C** as a clear, colorless oil (0.932 g, 96.6% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 1.39 (m, 2H), 1.24 (overlapping signals, 30H), 0.87 (t, *J* = 6.5 Hz, 3H), 0.76 (t, *J* = 7.6 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 34.4 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **C**.[7]

Figure S28. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 2-dodecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**C**).



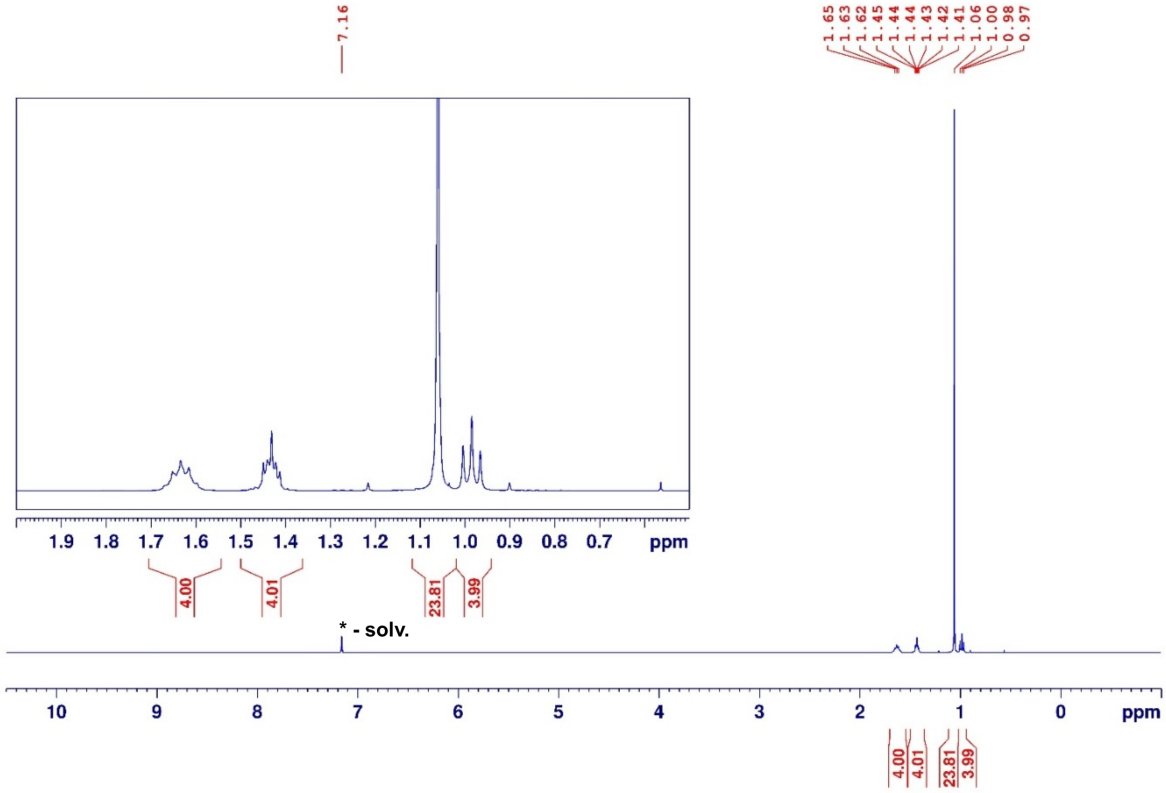
1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane (**D**)



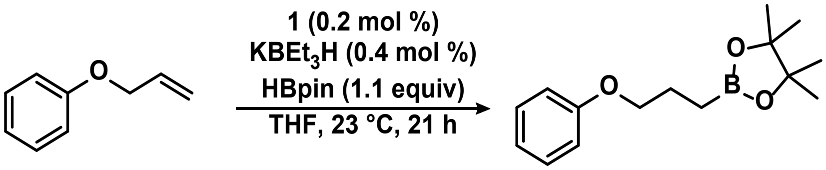
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (6.0 mg, 6.0 µmol, 0.2 mol %), THF (1 mL), 1,5-hexadiene (0.253 g, 3.08 mmol), and HBpin (0.850 g, 6.2 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (120.4 µL, 100 mM in THF, 12.0 µmol, 0.4 mol %) was added by micropipette, affording a yellow homogenous solution, which was stirred for 3 hours.

Characterization: After workup (as described in representative procedure with styrene), a short silica plug (4 cm, pipette) and removal of solvent afforded product **D** as an amorphous white solid (0.982 g, 94.5% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 1.63 (m, 4H), 1.44 (m, 4H), 1.06 (12H), 0.98 (t, *J* = 7.8, 4H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 34.19 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **D**.[10]

Figure S29. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of 1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane (**D**).



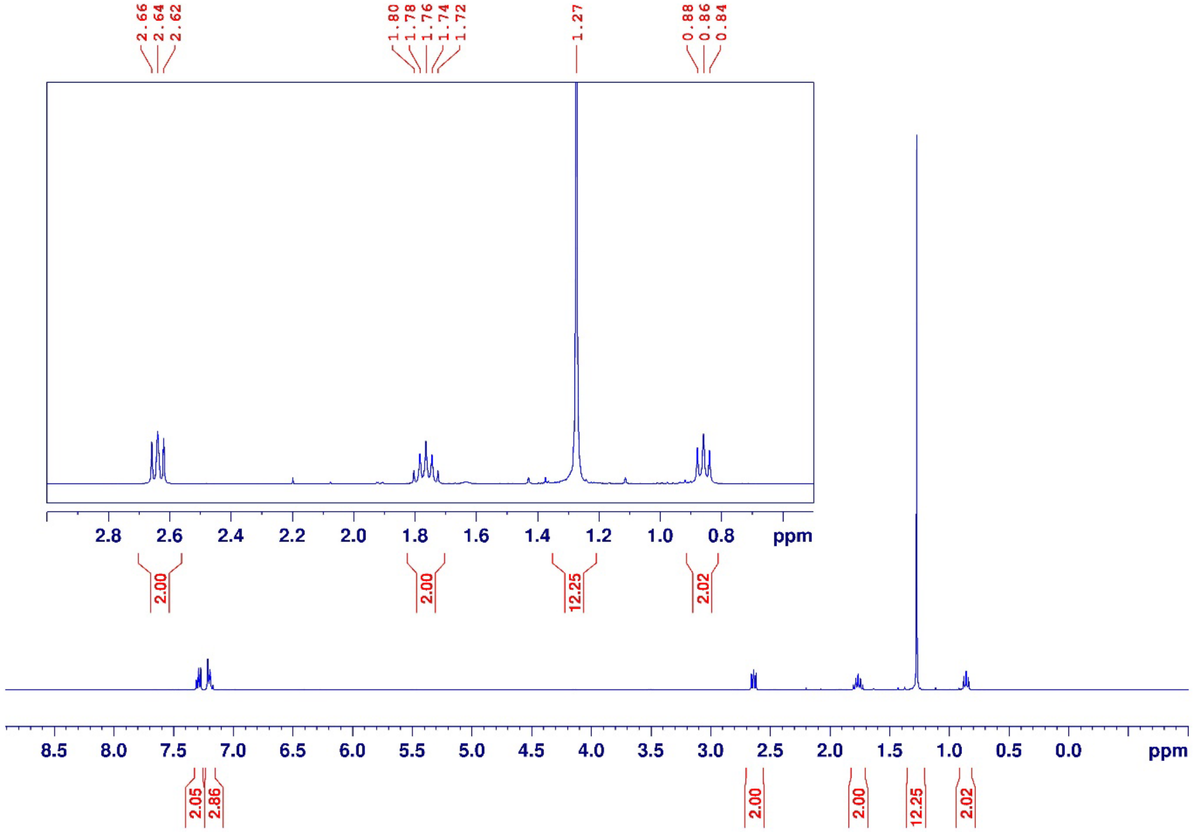
4,4,5,5-tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (**E**)



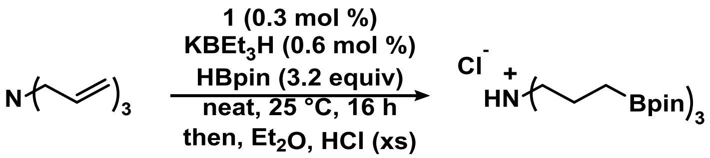
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (1.09 mL, 2.73 mM in THF, 3.0 µmol, 0.2 mol %) and the solvent was removed under vacuum. Allyl phenyl ether (0.205 g, 1.52 mmol), HBpin (0.236 mL, 1.6 mmol, 1.1 equiv), and THF (0.5 mL) were added and the resultant solution stirred. Then, $KBEt_3H$ (69.6 µL, 100 mM in THF, 7.0 µmol, 0.4 mol %) was added by micropipette, affording a yellow homogenous solution which was stirred for 21 h.

Characterization: After workup (as described in representative procedure with styrene), a short silica plug afforded product **E** as a clear, colorless oil (0.268 g, 67.0% yield). **^{1}H NMR (400 MHz, C_6D_6):** δ 7.29 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 2.64 (t, *J* = 6.7 Hz, 2H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.27 (s, 12H), 0.86 (t, *J* = 8.0 Hz, 2H). **^{11}B NMR (128 MHz, C_6D_6):** δ 33.75 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **E**.[13]

Figure S30. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of 4,4,5,5-tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (**E**).



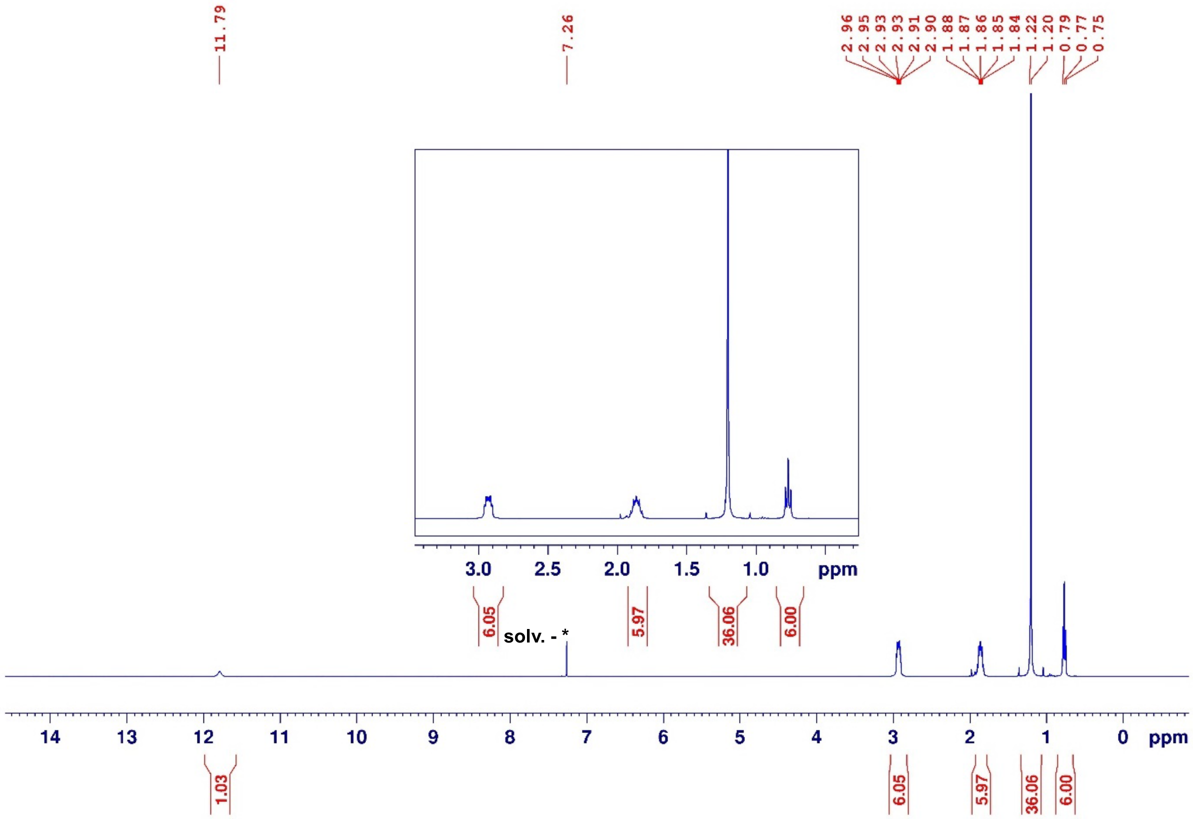
*Tris(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)ammonium chloride (**F**•HCl)*



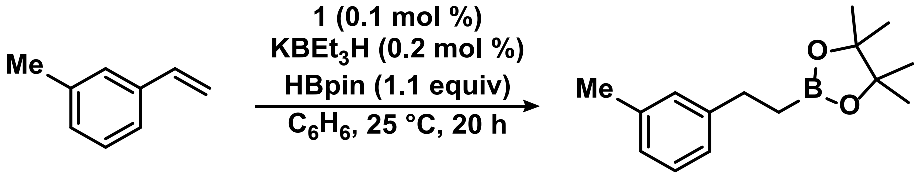
To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (2.1 mg, 2.1 µmol, 0.3 mol %), triallylamine (102.3 mg, 745 µmol), and HBpin (338.4 µL, 2.34 mmol, 3.2 equiv), and the resultant mixture stirred. Then, $KBEt_3H$ (44 µL, 100 M in THF, 44.0 µL, 0.6 mol %) was added by micropipette to afford an orange solution that was stirred for 16 hours at room temperature. The reaction was quenched by exposure to air and filtered through glass microfiber filter paper using Et_2O (3 mL) to remove metal salts. Volatile reaction components were removed from the filtrate in vacuo and Et_2O (10 mL) was added to the resulting oil. Stirring was applied and excess HCl (1.0 M in Et_2O) was added dropwise resulting in the immediate precipitation of the HCl salt of product **F** as a white, amorphous powder. The product was then collected onto a sintered glass frit, washed with Et_2O (2 x 10 mL), and dried under high-vacuum.

Characterization: Yield: 0.353 g, 84.5%. **^{1}H NMR (400 MHz, $CDCl_3$): δ** 11.79 (br s, 1H), 2.93 (m, 6H), 1.86 (m, 6H), 1.22 (s, 36H), 0.77 (t, *J* = 7.7, 6H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.36 (br s). **HRMS (HPLC-MS/MS) m/z:** $[M + H]^+$ Calcd for $C_{27}H_{55}B_3O_6N$ 522.4308; Found 522.4308.

Figure 31. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of tris(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)ammonium chloride (HCl salt of **F**).



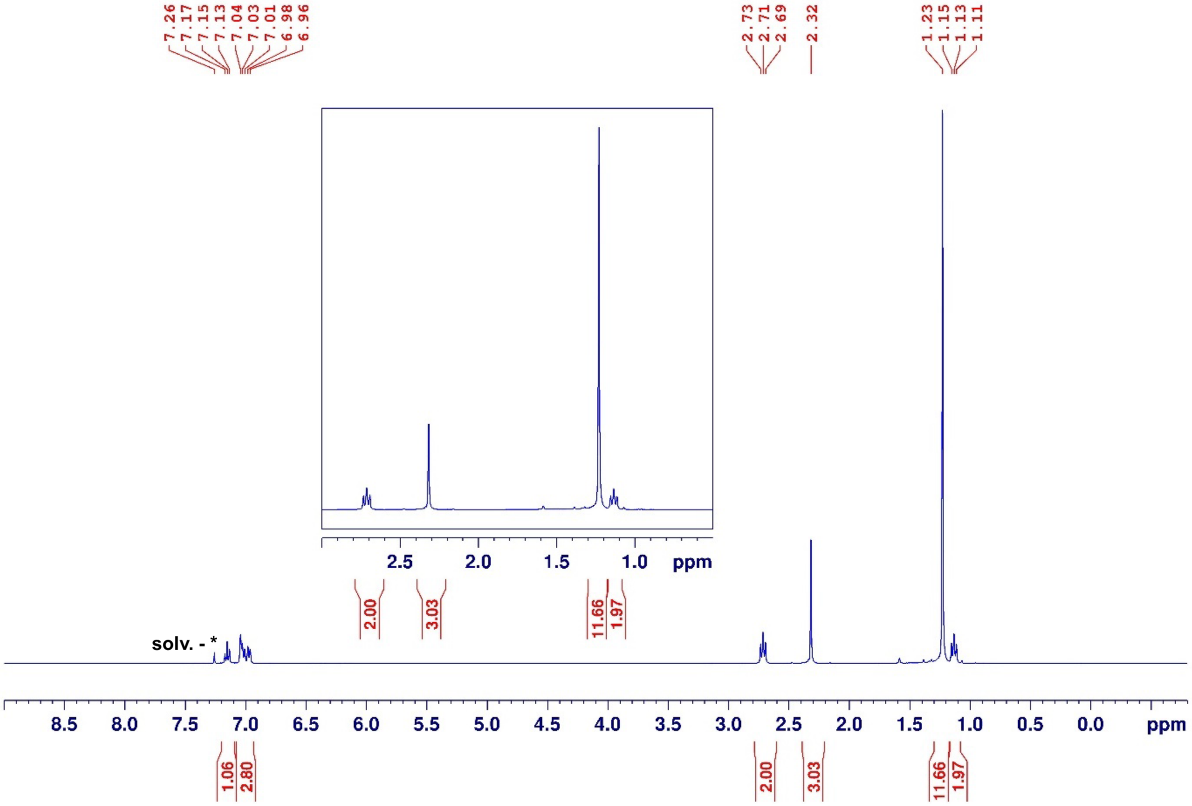
4,4,5,5-tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane (***G***)



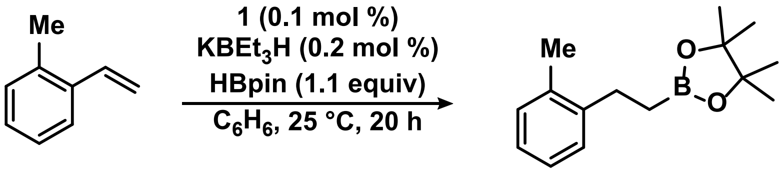
To an oven-dried 20 mL scintillation vial equipped with stir bar was added a solution of **1** (0.80 mL, 2.10 mM in THF, 1.7 µmol, 0.1 mol %) and the THF was subsequently removed under reduced pressure. C_6H_6 (0.3 mL), 3-methylstyrene (0.200 g, 1.69 mmol), and HBpin (270.0 µL, 1.86 mmol, 1.1 equiv) were added and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (33.9 µL, 100 mM in THF, 3.4 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution, which was stirred for 20 hours.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded product **G** as a clear, colorless oil (0.291 g, 68.5% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.15 (m, 1H), 7.06 - 6.92 (overlapping, 3H), 2.71 (t, *J* = 8.3 Hz, 2H), 2.32 (s, 3H), 1.23 (s, 12H), 1.13 (t, *J* = 8.1 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.75 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported for **G**.[4]

Figure S32. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane (**G**).



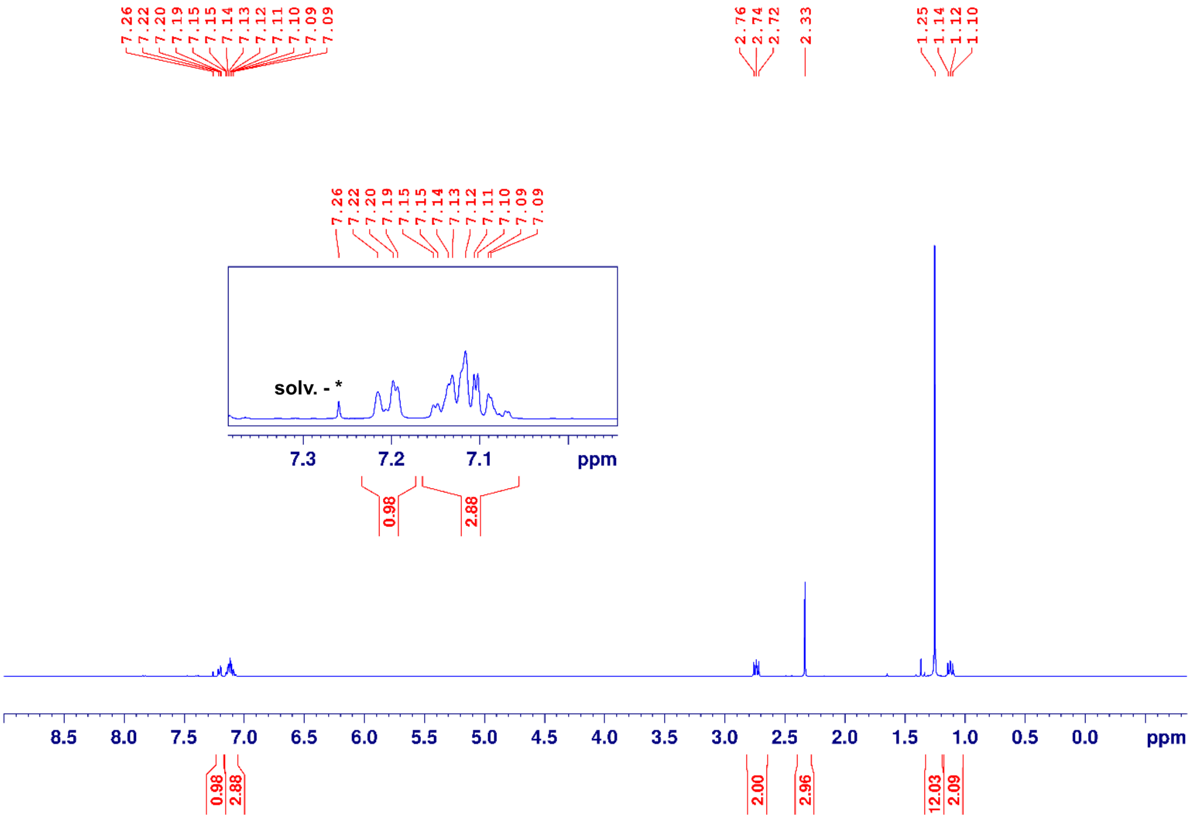
4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**H**)



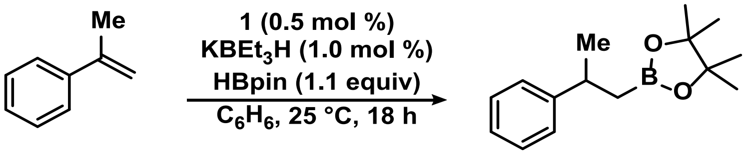
To an oven-dried 20 mL scintillation vial equipped with stir bar was added a solution of **1** (492 µL, 2.10 mM in THF, 1.0 µmol, 0.1 mol %) and the THF was subsequently removed under reduced pressure. C_6H_6 (0.5 mL), 2-methylstyrene (0.122 g, 1.03 mmol), and HBpin (165 µL, 1.14 mmol, 1.1 equiv) were added and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (20.7 µL, 100 mM in THF, 2.1 µmol, 0.2 mol %) was added by micropipette, affording a yellow homogenous solution, which was stirred for 20 hours.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 19:1) afforded product **H** as a clear, colorless oil (0.200 g, 78.7% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.23 – 7.19 (m, 1H), 7.16 – 7.05 (overlapping, 3H), 2.74 (t, J = 8.2 Hz, 2H), 2.33 (s, 3H), 1.25 (s, 12H), 1.12 (t, J = 8.3 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.6 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported **H**.[5]

Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**H**).



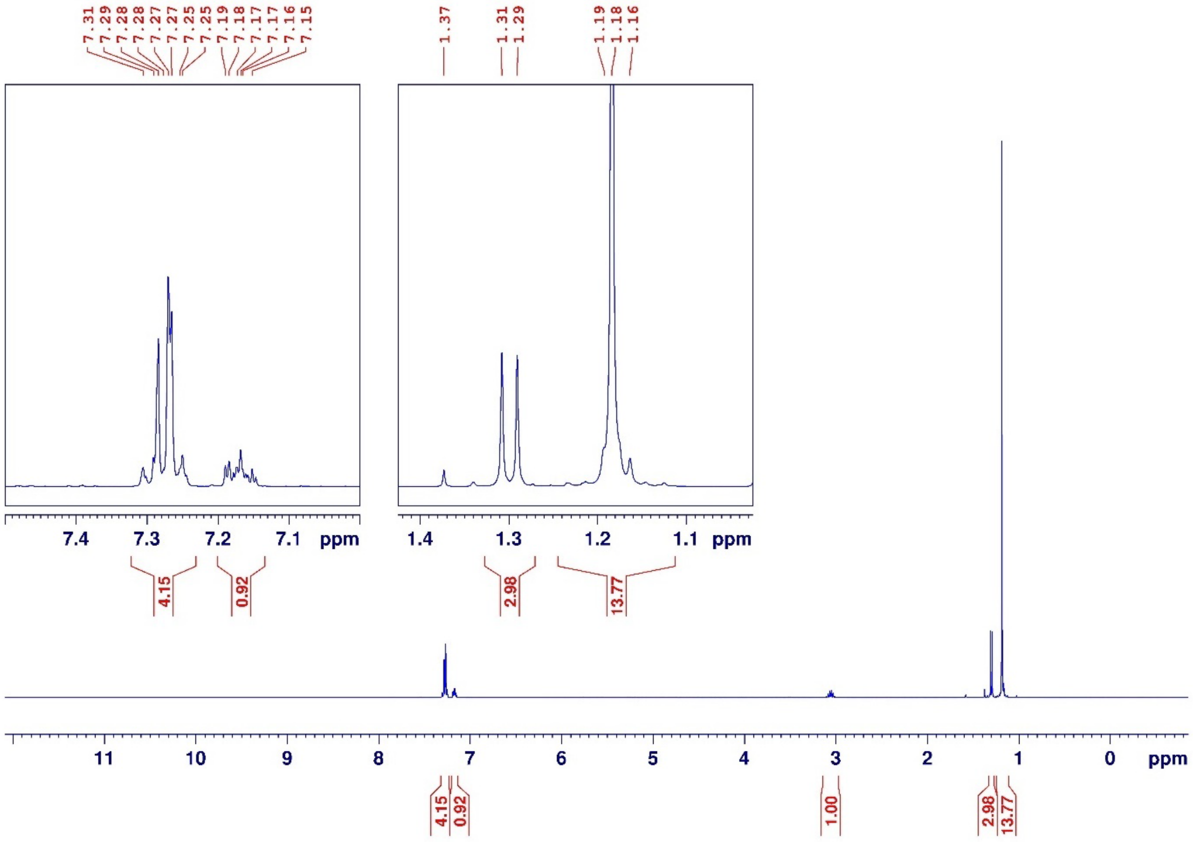
4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**I**)



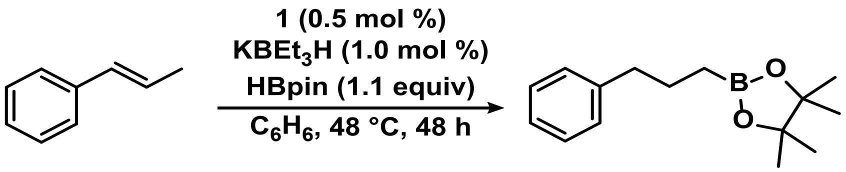
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (8.4 mg, 8.5 µmol, 0.5 mol %), C_6H_6 (0.4 mL), α-methylstyrene (0.204 g, 1.73 mmol), and HBpin (0.243 g, 1.9 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (169.3 µL, 100 mM in THF, 17 µmol, 1.0 mol %) was added by micropipette and the reaction stirred 18 h.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded product (**I**) as a highly viscous, colorless oil (0.399 g, 93.9% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.32 – 7.23 (m, overlapping, 4H), 7.20 -7.13 (m, 1H), 3.05 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H), 1.24 – 1.11 (overlapping signals, 14H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.7 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported **I**.[11]

Figure S34. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (**I**).



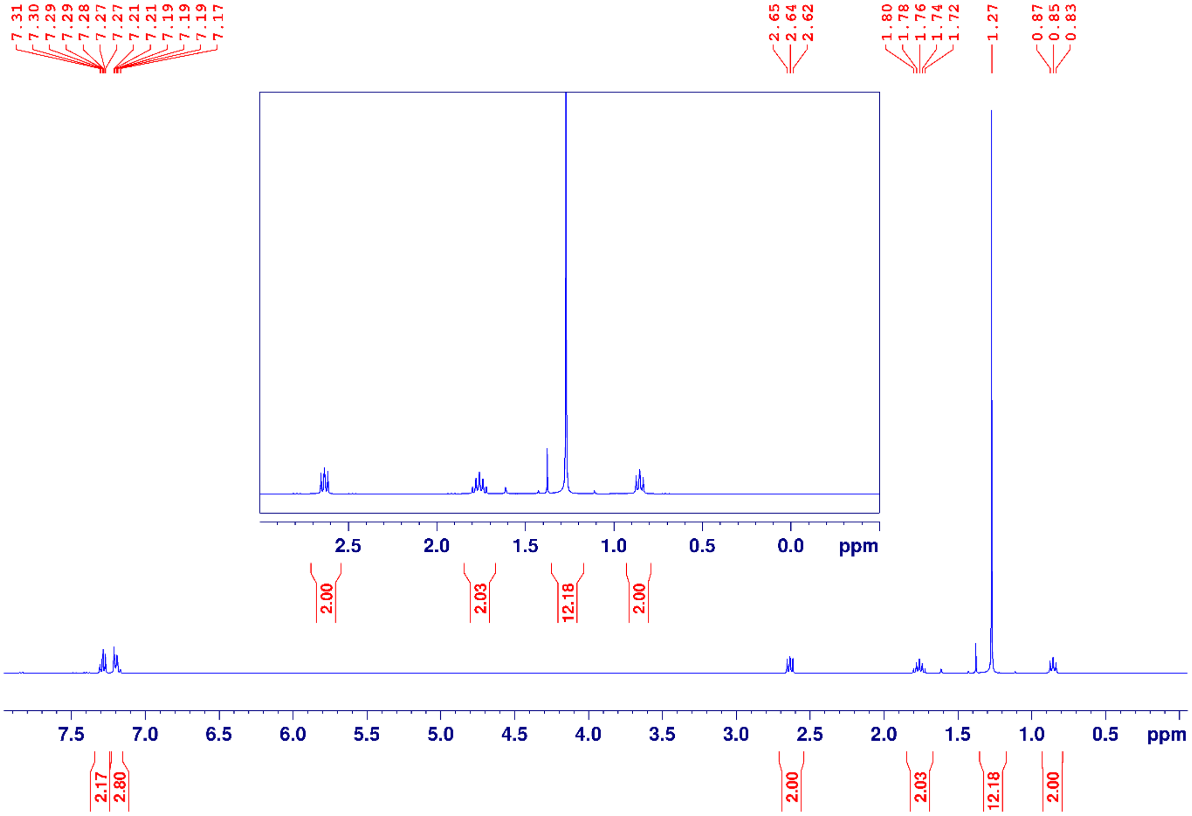
4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**J**)



To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (5.1 mg, 5.2 µmol, 0.5 mol %), C_6H_6 (0.4 mL), *trans*-β-methylstyrene (0.120 g, 1.03 mmol), and HBpin (143.0 µL, 1.12 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (101.5 µL, 100 mM in THF, 10.2 µmol, 1.0 mol %) was added by micropipette and the reaction stirred at 48 °C for 48 h.

Characterization: After workup (as described in representative procedure with styrene), column chromatography (silica, hexanes/EtOAc 9:1) afforded product **J** as a highly viscous, clear colorless oil (0.165 g, 66.0% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, overlapping, 3H), 2.64 (t, $J = 7.6$ Hz, 2H), 1.76 (quintet, $J = 7.9$ Hz, 3H), 1.27 (s, 12H), 0.85 (t, $J = 8.0$ Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.7 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported **J**.[2]

Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**J**).



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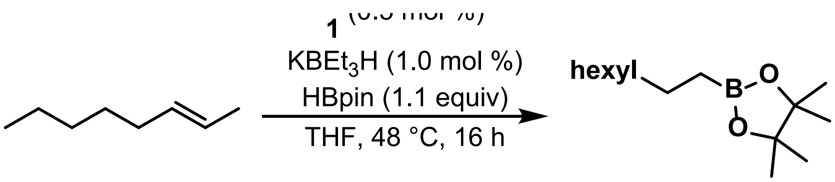
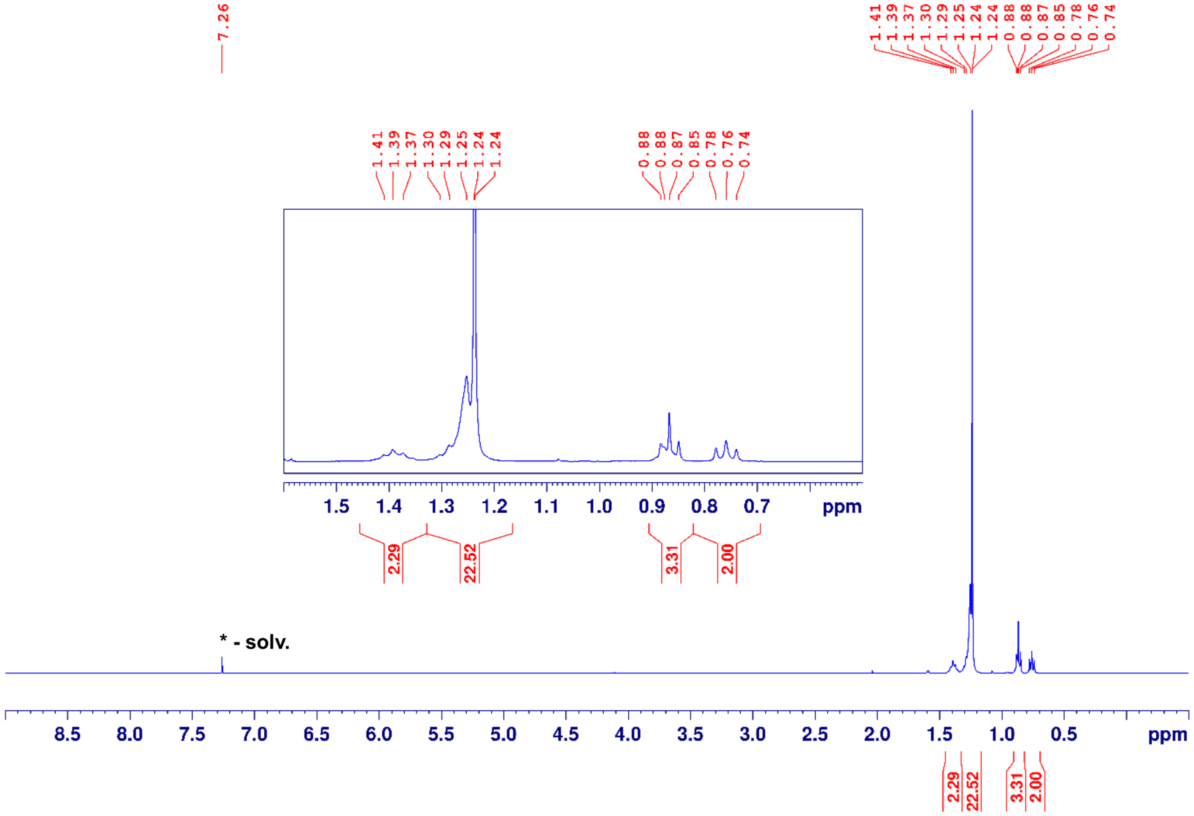
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**K**)



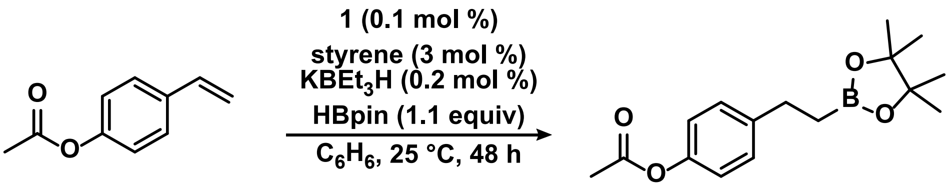
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (8.8 mg, 8.8 µmol, 0.5 mol %), THF (1 mL), *trans*-2-octene (0.200 g, 1.78 mmol), and HBpin (285 µL, 1.96 mmol, 1.1 equiv) and the resultant heterogenous mixture stirred. Then, $KBEt_3H$ (178.2 µL, 100 mM in THF, 17.8 µmol, 1.0 mol %) was added by micropipette, affording an orange homogenous solution, which was stirred for 16 hours at 48 °C.

Characterization: After workup (as described in representative procedure with styrene), a short silica plug (4 cm, pipette) and removal of solvent afforded product **K** as a clear, colorless oil (0.419 g, 97.9% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 1.39 (m, 2H), 1.33 – 1.22 (m, overlapping signals, 22H), 0.88 (t, J = 7.1 3H), 0.76 (t, J = 7.8 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 34.20 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported **K**.[9]

Figure S36. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**K**).



*4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (**L**)*



To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (300 µL, 2.1 mM in THF, 0.6 µmol, 0.1 mol %), C_6H_6 (300 µL), and styrene (3 µL, 26 µmol, 4 mol %) with stirring. Then, $KBEt_3H$ (12.3 µL, 100 mM in THF, 1.2 µmol, 0.2 mol %) was added to afford a nearly homogenous, yellow solution. After 10 minutes, 4-acetoxystyrene (93.4 µL, 0.62 mmol), followed by HBpin (98.5 µL, 0.68 mmol, 1.1 equiv) were added to the reaction mixture and allowed to stir at room temperature for 48 hours.

Characterization: After workup (as described in representative procedure with styrene) and purification using column chromatography (silica, hexanes/EtOAc, 0-30% gradient) the product was obtained as an amorphous white solid (80.0 mg, 45% yield). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.21 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.73 (t, *J* = 8.2 Hz, 2H), 2.27 (s, 3H), 1.21 (s, 12H), 1.13 (t, *J* = 8.4 Hz, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 34.48 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate.[12]

Figure S37. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate.

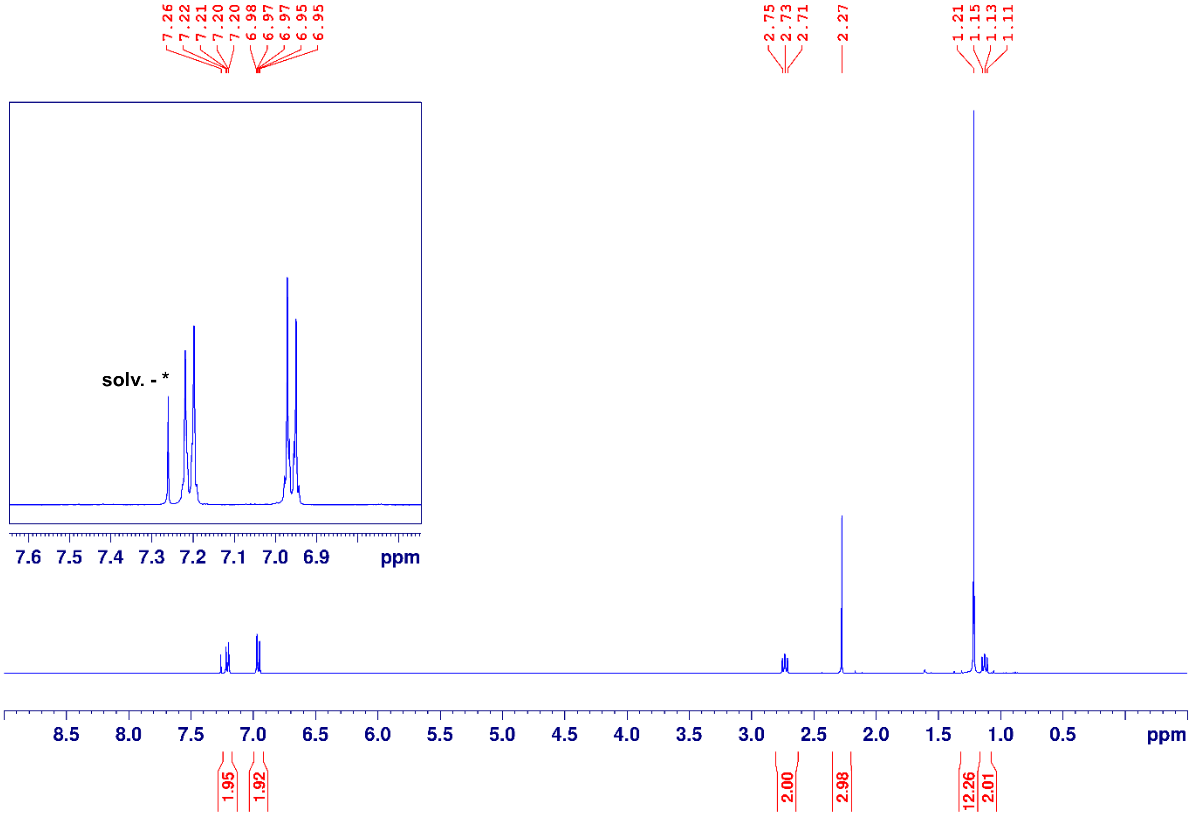
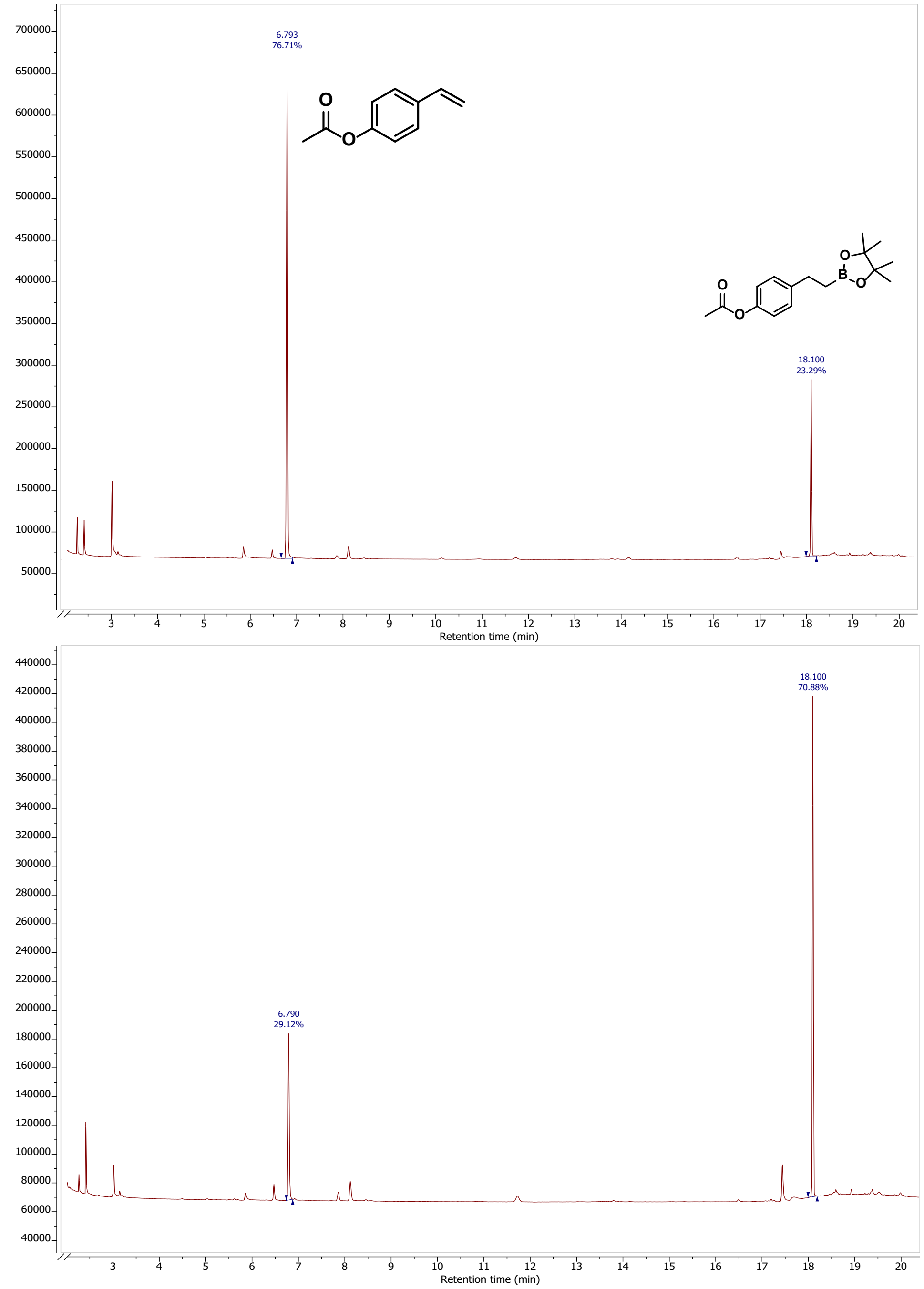
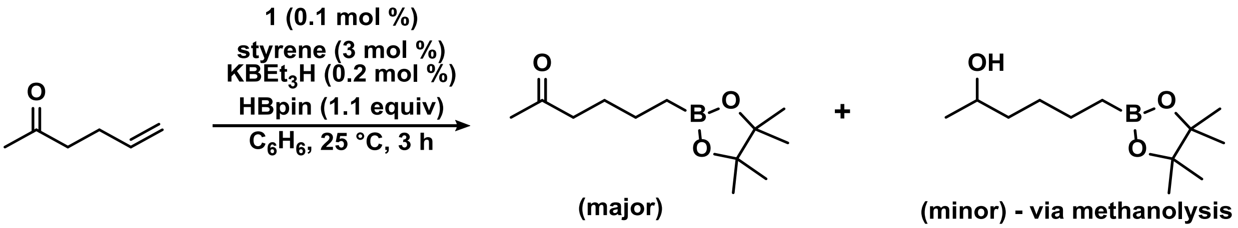


Figure S38. Reaction progress tracked by GC-FID after 24 (top) and 48 (bottom) hours. Note that minor products are detected growing in over 48 hours, while the major product observed is the linear hydroboration product of 4-acetoxystyrene (retention ~18.1 min). The starting material 4-acetoxystyrene is observed at retention time ~6.85 min.



6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one



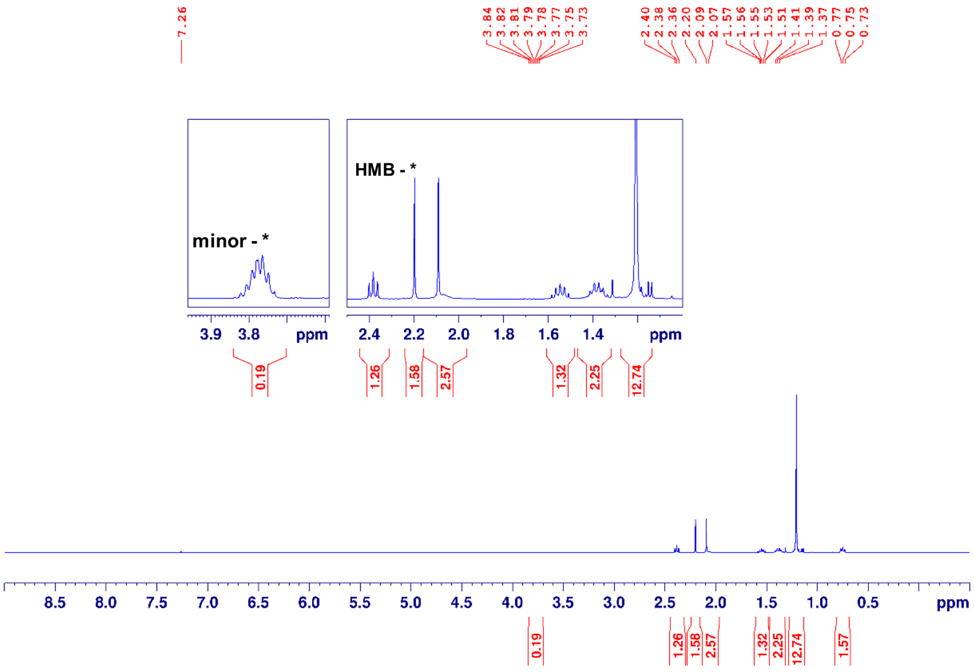
To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (2.0 mg, 2.1 µmol, 0.1 mol %), C_6H_6 (0.3 mL), styrene (7 µL, 61.1 µmol, 3 mol %) with stirring. Then, $KBEt_3H$ (41.0 µL, 100 mM in THF, 4.1 µmol, 0.2 mol %) was added to afford a nearly homogenous, yellow solution. After stirring for 15 minutes, 5-hexen-2-one (242.0 µL, 2.1 mmol), followed by HBpin (325.3 µL, 2.24 mmol, 1.1 equiv) were added to the reaction mixture using a micropipette and allowed to stir at room temperature for 3 hours. Afterwards, silica gel (0.6 g) and methanol (10 mL) were added with vigorous stirring for an additional 3 hours. Hexamethylbenzene (29.8 mg, 184 µmol, 0.1 equiv) was added as an NMR standard prior to filtration of the crude mixture through a pad of Celite and concentration of the filtrate to afford a clear, colorless oil with two primary components. An NMR yield was obtained by comparison of the methyl resonance of hexamethylbenzene to the protons of the α-methylene carbon of the major product and the methine resonance of the minor product.

Characterization:

Major Product – Yield: 62.9% (NMR). **^{1}H NMR (400 MHz, $CDCl_3$): δ** 2.38 (t, J = 7.3 Hz, 2H), 2.09 (s, 3H), 1.55 (quintet, J = 7.6 Hz, 2H), 1.46 – 1.32 (m, 2H), 1.28 (s, 12H), 0.75 (t, J = 7.8, 2H). **^{11}B NMR (128 MHz, $CDCl_3$): δ** 33.8 (br s). ^{1}H and ^{11}B NMR data compares well to spectral data previously reported 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one.[13]

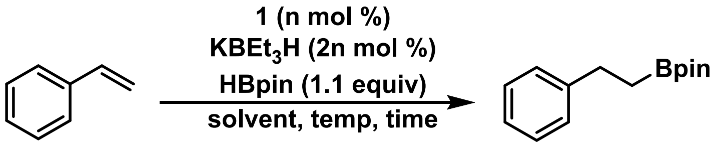
Minor Product – Yield: 19.1% (NMR). **^{1}H NMR: δ** 3.84 – 3.70 (m, 1H). This signal is consistent with a signal for the alcohol product previously reported in the literature.[14] Remaining resonances not assigned due to signal overlap with major product.

Figure S39. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of reaction mixture after catalytic hydroboration of 5-hexen-2-one with 1.1 equiv pinacolborane followed by methanolysis over silica.



Catalytic Condition Optimizations with Styrene

GCMS-FID was used to determine reaction progress by the disappearance of the starting material and appearance of the indicated linear hydroboration product. Reactions were sampled shortly after activation and at least once more to allow for an estimate of reaction window and sampling of the reaction prior to complete disappearance of the starting material (~1:19 SM:TM, GC-FID).



Example procedure for Table 1, entry 1: To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (3.63 mL, 2.78 mM in THF, 10.1 µmol, 1.0 mol %), styrene (105 mg, 1.01 mmol), HBpin (161 µL, 1.11 mmol, 1.1 equiv), and C_6H_6 (0.5 mL) and the resultant mixture was stirred. The activator, KBEt$_3$H (211.2 µL, 100 M in THF, 21.2 µmol, 2.1 mol %), was added by micropipette and the reaction stirred for one hour. The reaction progress was sampled by aliquots which were analyzed using GC-FID.

Figure S40. GC-FID of reaction mixture of catalysis carried out with 1.0 mol % **1** and using benzene as solvent after 45 minutes (Table 1, entry 1).

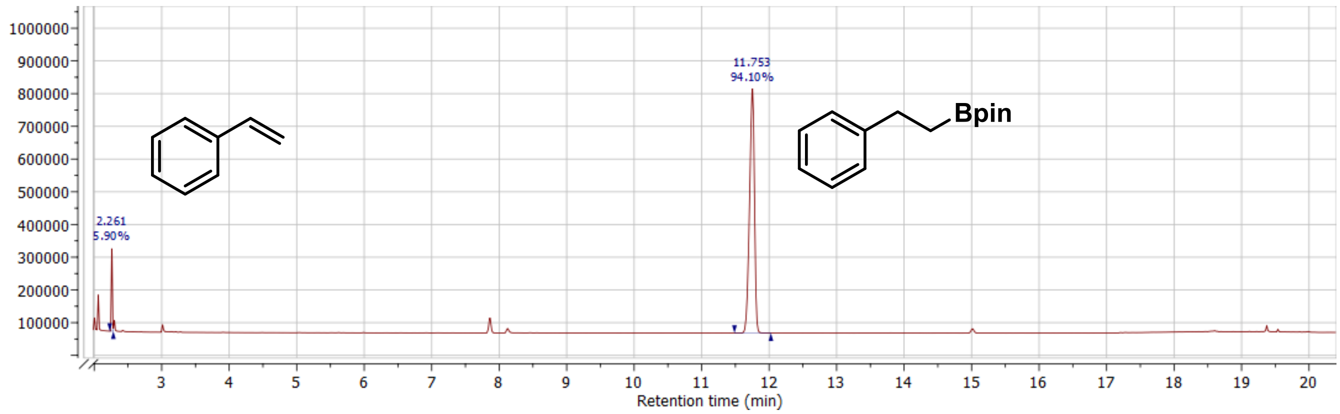


Figure S41. GC-FID of reaction mixture of catalysis carried out with 1.0 mol % **1** and using toluene as solvent after 60 minutes (Table 1, entry 2).

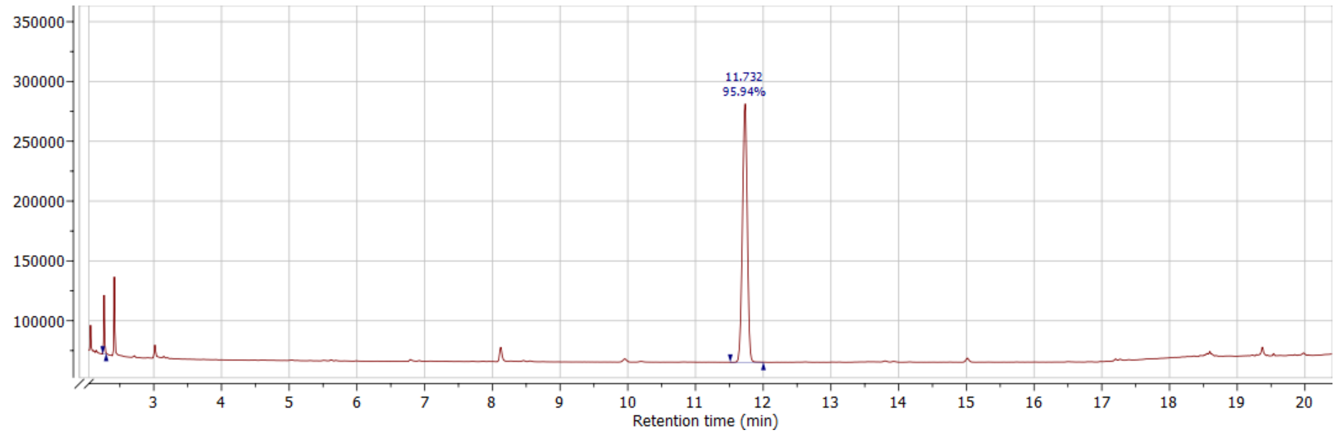


Figure S42. GC-FID of reaction mixture of catalysis carried out with 1.0 mol % **1** and using THF as solvent after 85 minutes (Table 1, entry 3).

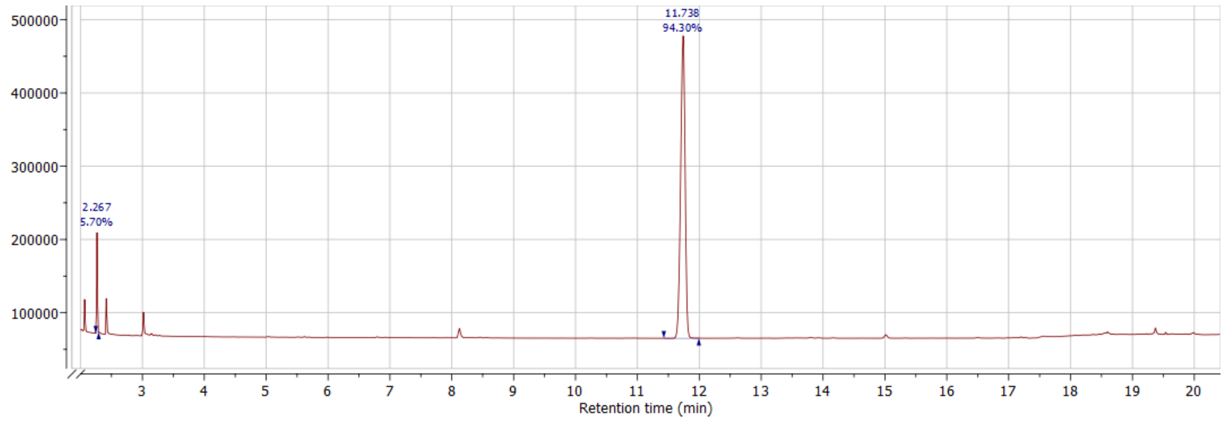


Figure S43. GC-FID of reaction mixture of catalysis carried out with 0.5 mol % **1** @ 25 °C using as benzene as solvent after 80 minutes (Table 1, entry 4).

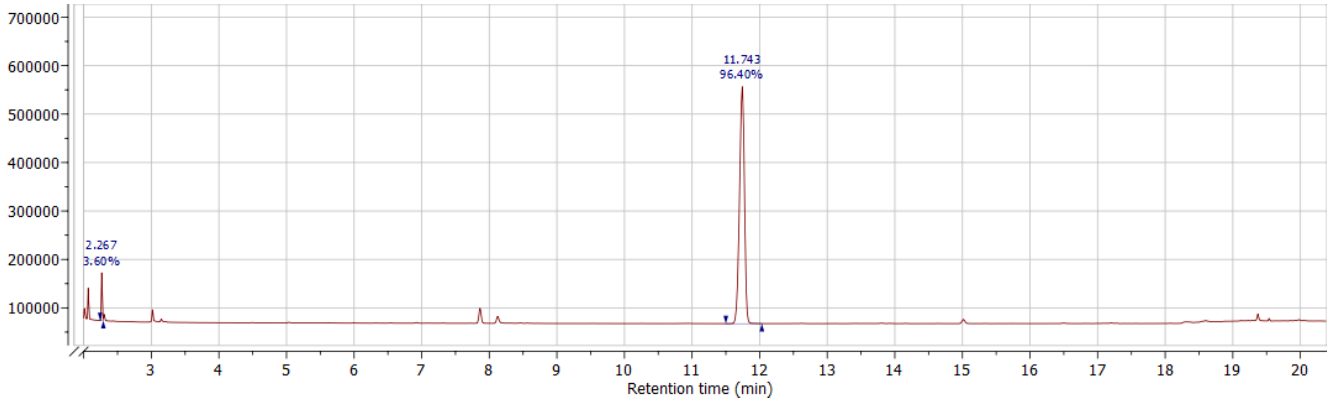


Figure S44. GC-FID of reaction mixture of catalysis carried out with 0.5 mol % **1** @ 37 °C using as benzene as solvent after 40 minutes (Table 1, entry 5).

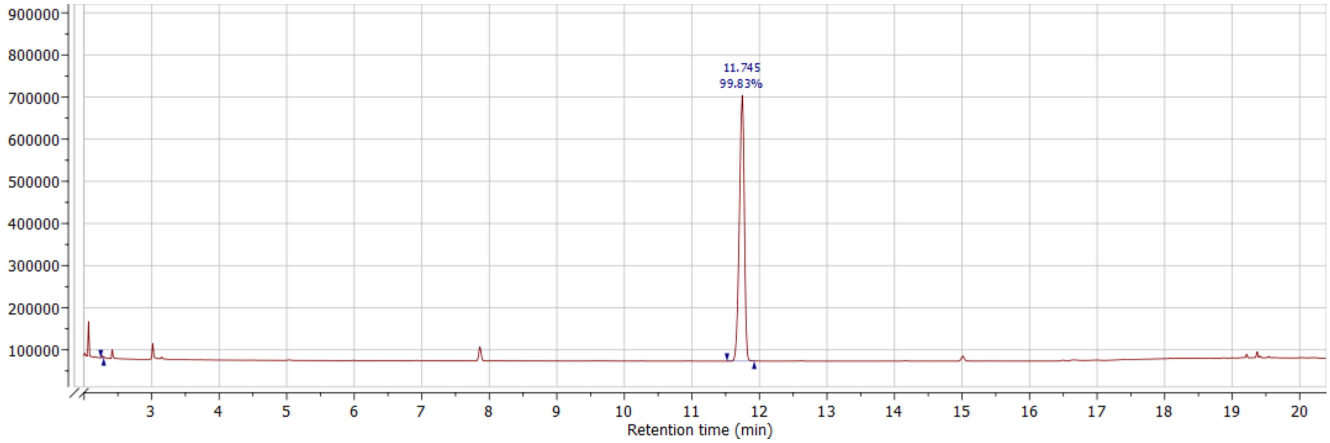


Figure S45. GC-FID of reaction mixture of catalysis carried out with 0.5 mol % **1** @ 50 °C using as benzene as solvent after 12 minutes (Table 1, entry 6).

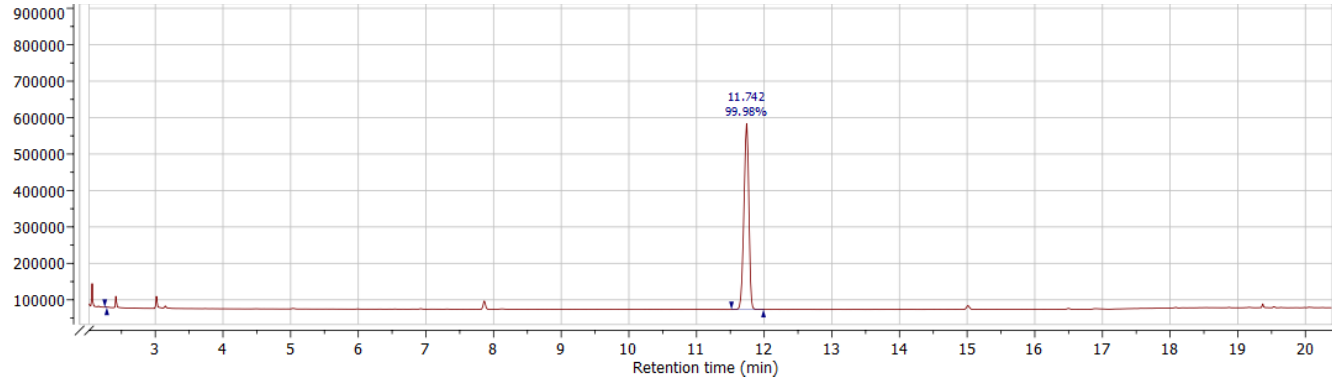


Figure S46. GC-FID of reaction mixture of catalysis carried out with 0.3 mol % **1** @ 25 °C using as benzene as solvent after 195 minutes (Table 1, entry 7).

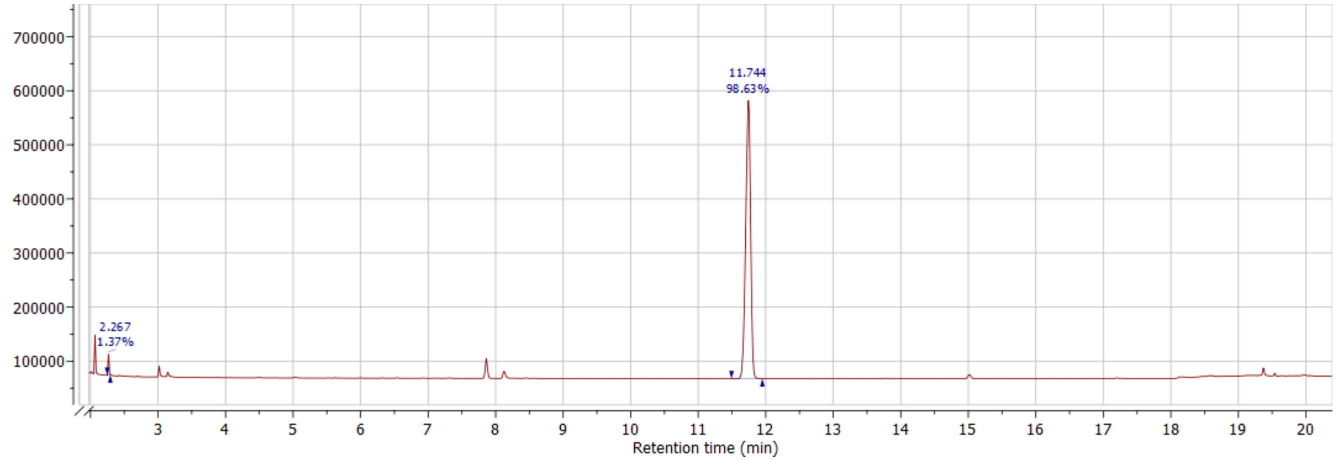


Figure S47. GC-FID of reaction mixture of catalysis carried out with 0.1 mol % **1** @ 50 °C after 90 minutes (Table 1, entry 9).

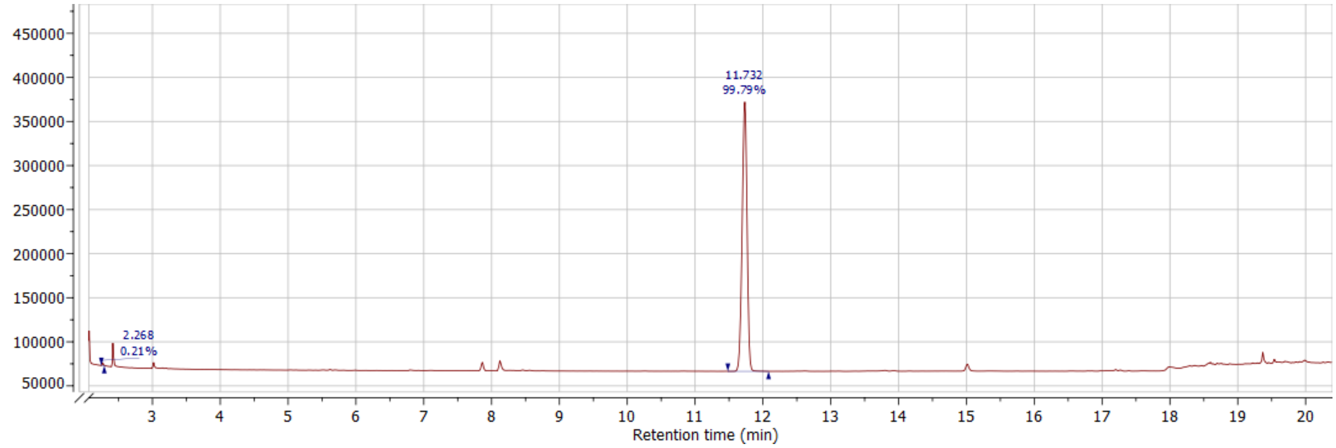


Figure S48. GC-FID of reaction mixture of catalysis carried out neat with 0.03 mol % **1** @ 50 °C after 5 hours (Table 1, entry 10).

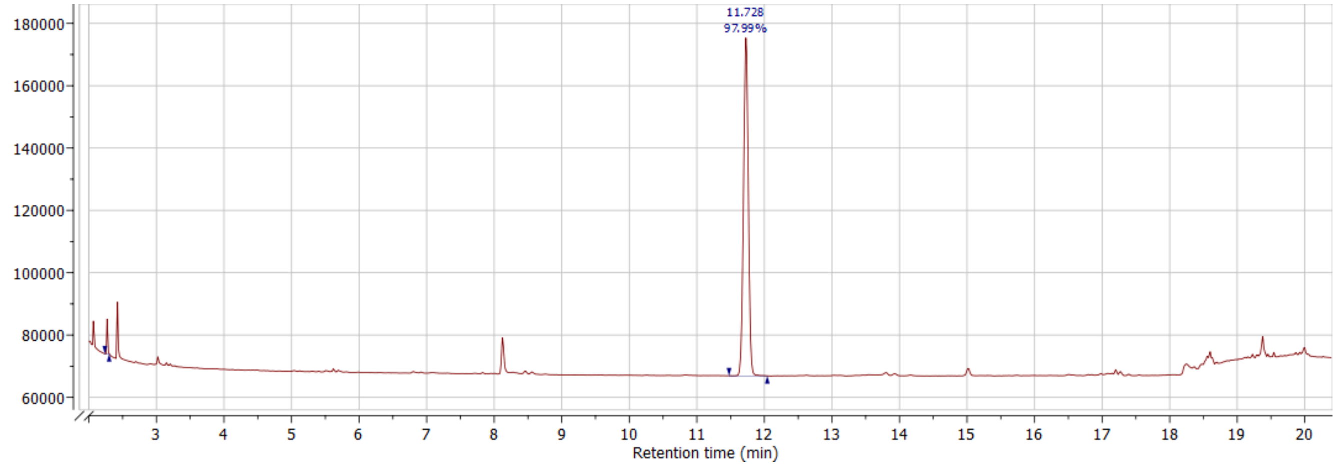


Figure S49. Quantitative ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of catalysis carried out neat with 0.01 mol % **1** @ 25 °C after 48 hours (Table 1, entry 11) after reaction mixture was quenched and gently concentrated under reduced pressure.

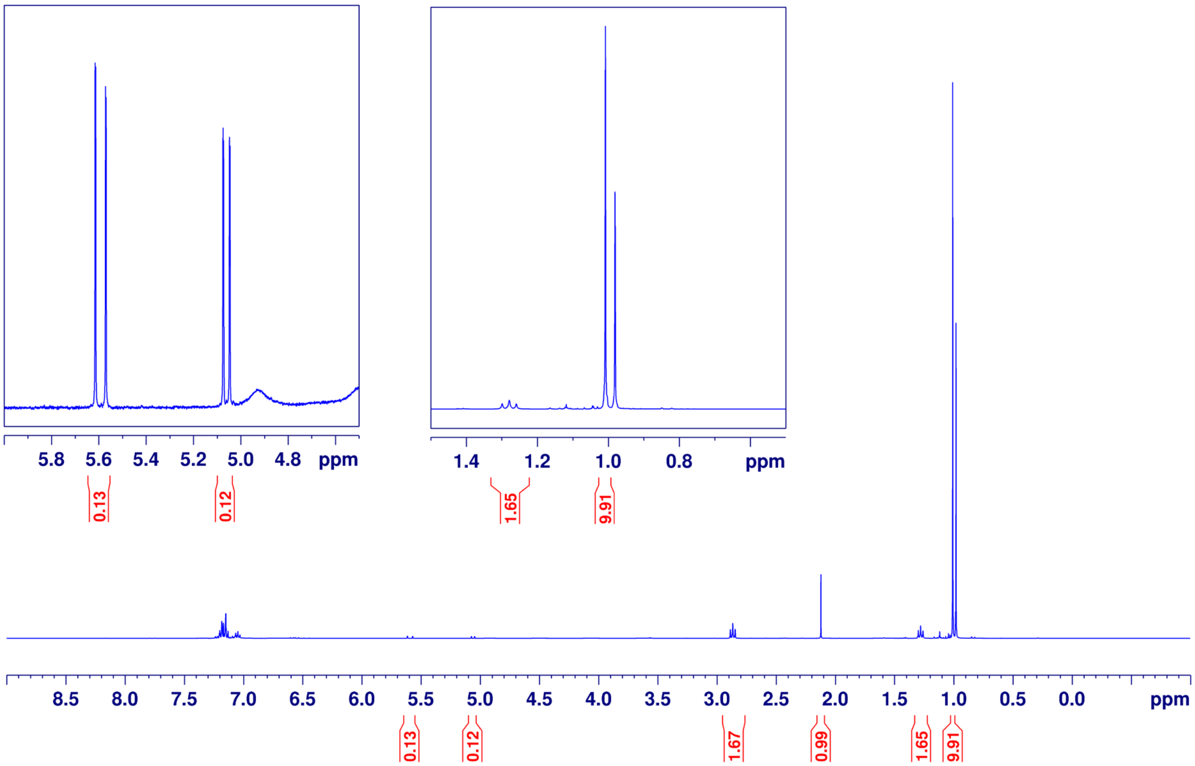
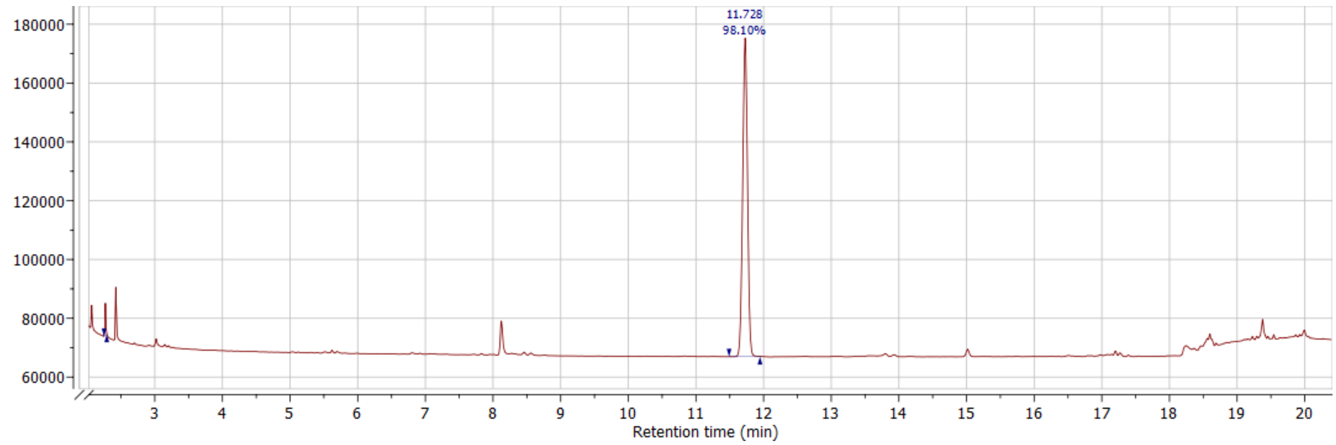
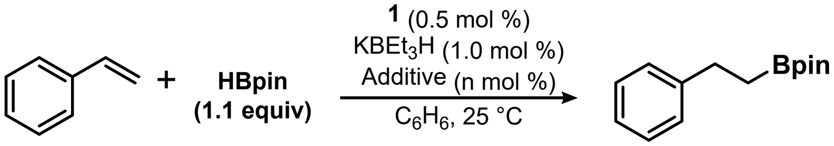


Figure S50. GC-FID of reaction mixture of catalysis carried out with 0.01 mol % **1** @ 50 °C after 12 hours (Table 1, entry 12).



Rapid tolerance screening of the catalytic system to the presence of significant amounts (20 mol %) of common reagents and solvents

Where applicable, additives were not further purified and were used as received. Reactions were run under inert atmosphere and upon completion, were quenched by exposure to air, and the reaction mixture was subsequently passed through a short silica pipette using pentanes as an eluent. Additives were present prior to activation of the precatalyst unless otherwise specified.



Representative procedure for additive screening

To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (6.9 mg, 7.0 µmol, 0.5 mol %), styrene (0.145 g, 1.39 mmol), HBpin (223 µL, 1.53 mmol, 1.1 equiv), and MeCN (15 µL, 278 µmol, 20 mol %) and the resultant mixture was stirred. The activator, $KBEt_3H$ (140.0 µL, 100 M in THF, 14.0 µmol, 1.0 mol %), was added by micropipette and the reaction stirred for 12 hours. Then, the reaction mixture was quenched by exposure to air and dilution with pentanes (3 mL). This solution was passed through a short silica pipette filter, and the filtrate concentrated under reduced pressure to obtain the nearly pure target material. The same procedure was carried out for additive tolerance tests with DMA, EtOAc, *ᵗ*BuOH, *ⁱ*$PrNH_2$, and $HNEt_2$.

The procedure above was also followed for screening of H_2O and air tolerance, with the following modification: The additive was not introduced to the reaction mixture until 10 minutes after the $KBEt_3H$ activator had been added. An additional experiment using this modified procedure was performed with *ᵗ*BuOH to assess the impacts of the additive when added pre- and post-activation with $KBEt_3H$.

Table S1. Additive tolerance studies using styrene as a model substrate using **1** as a precatalyst.

entry	additive	n (mol %)	isol. yield (%)[a]
1	MeCN	20	98
2	DMA	20	92
3	EtOAc	20	82
4[b]	Air	1 mL	90
5[b]	H_2O	1.5	86
6	ᵗBuOH	20	41
7[b]	ᵗBuOH	20	70 (>99)[d]
8	ⁱ$PrNH_2$	20	69
9	$HNEt_2$	20	70
10[c]	$HNEt_2$	20	79

[a] Crude reaction mixtures were quenched by exposure to air and filtration through a short silica plug to afford nearly pure organic product. [b] Additive was added 10 minutes after activation of the precatalyst. [c] HBpin loading was increased to 1.4 equiv. [d] Value in parentheses represents conversion observed by GC-FID.

Figure S51. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence of MeCN (20 mol %).

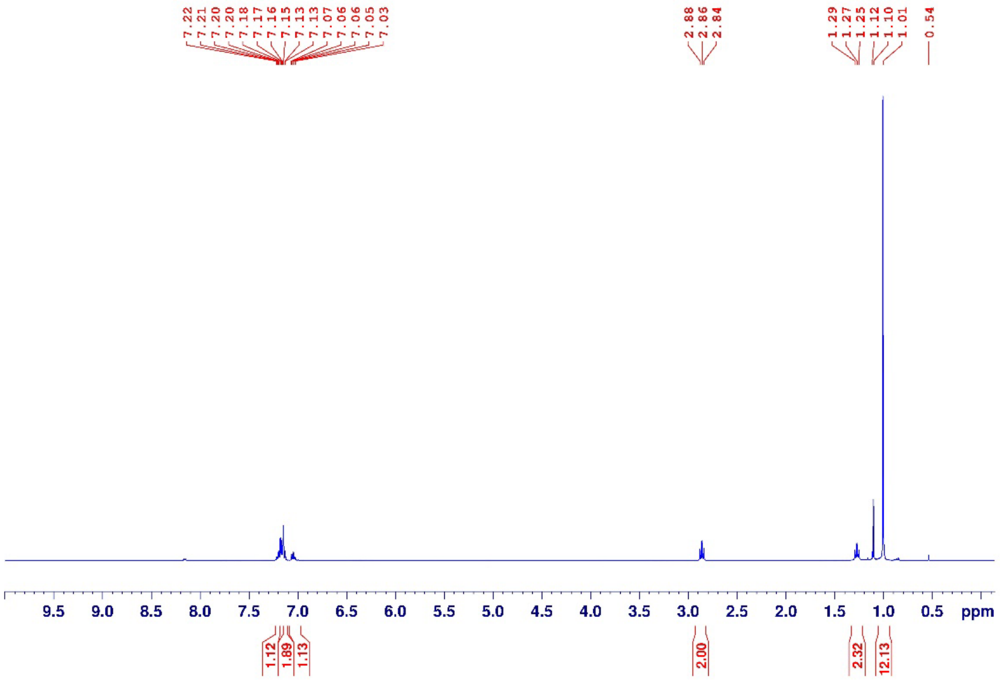


Figure S52. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence of ^{t}BuOH (20 mol %).

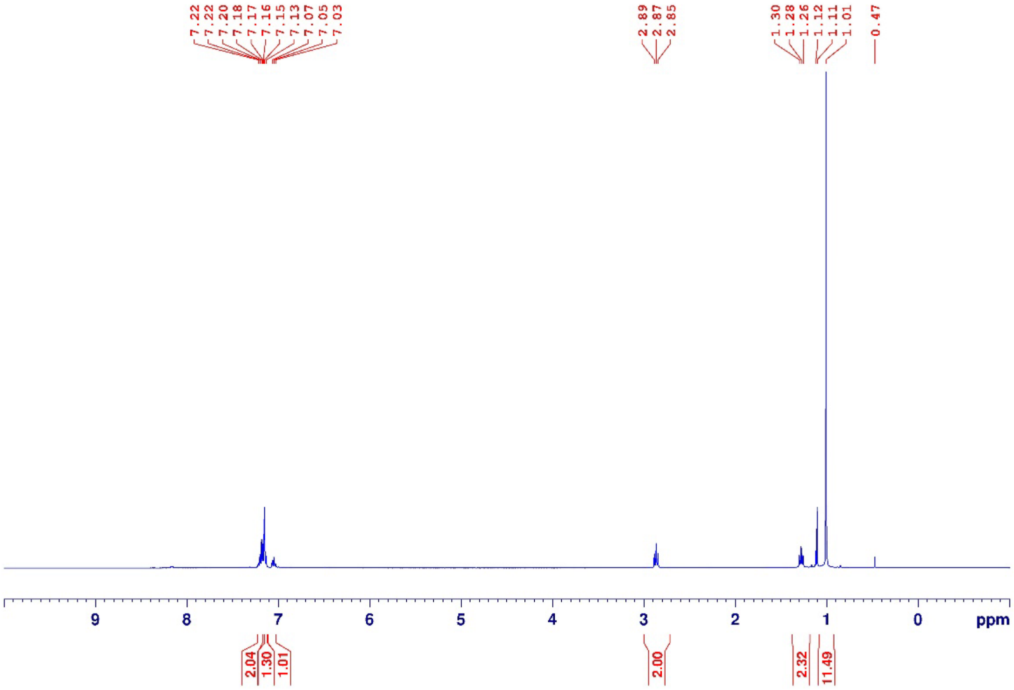


Figure S53. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence of ^{t}BuOH (20 mol %) added post-activation of the precatalyst.

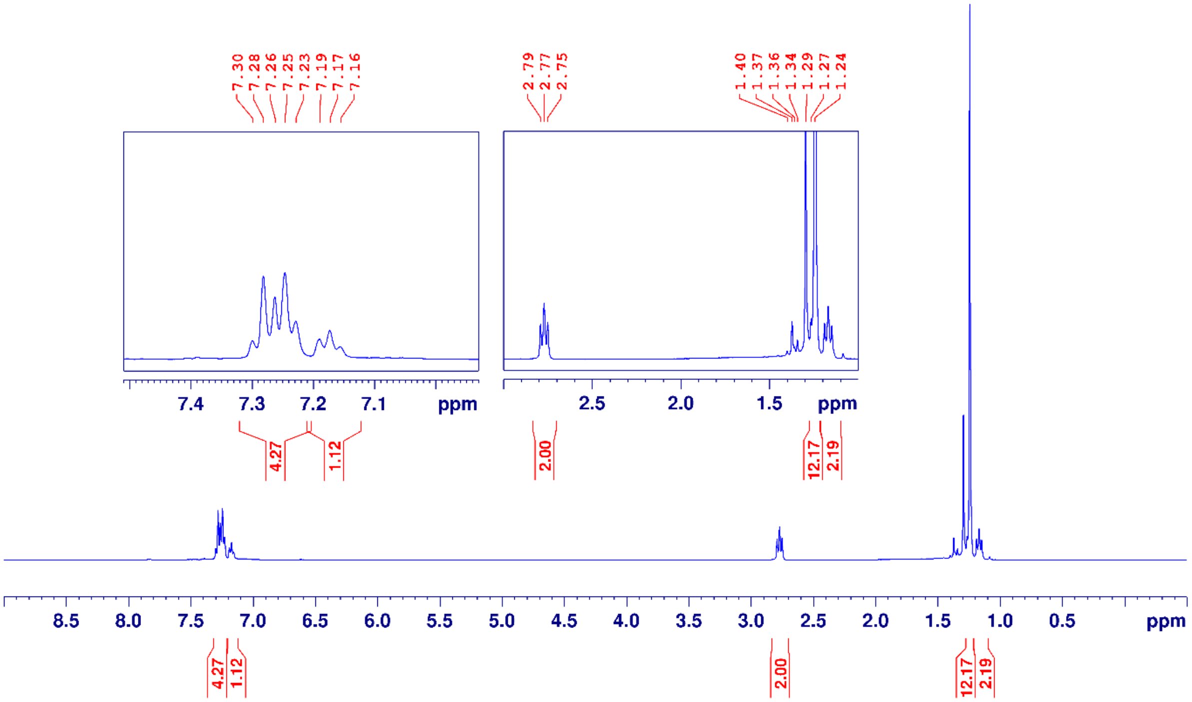


Figure S54. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence of air (1 mL by syringe) added post-activation of the precatalyst.

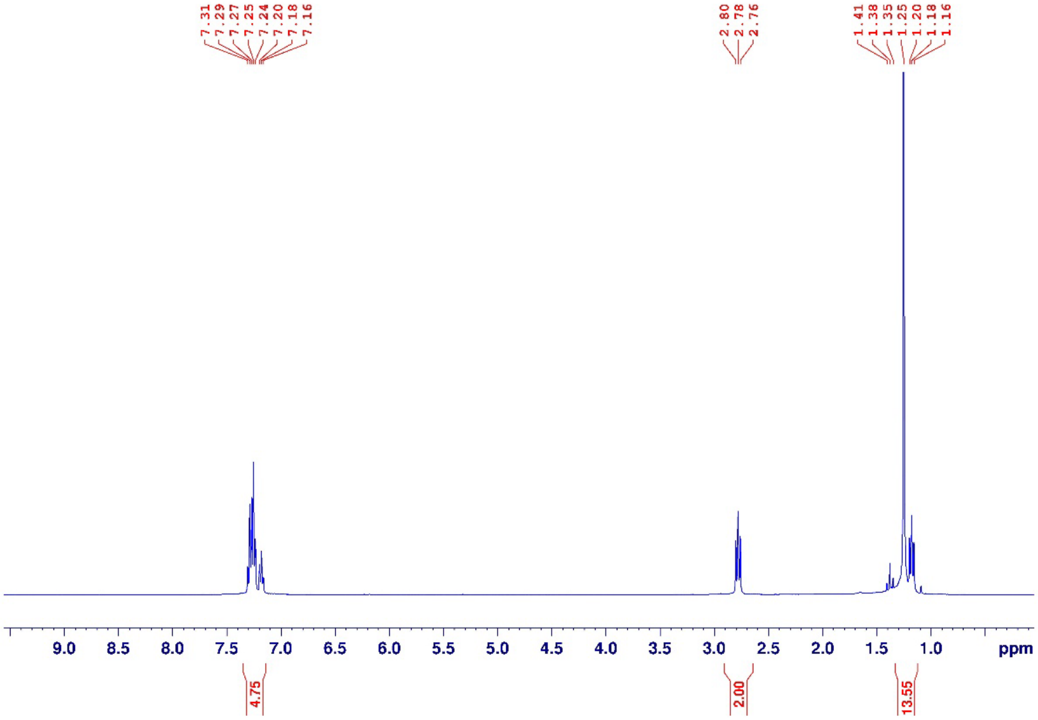


Figure S55. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence H_2O (1.5 mol %, 3 equiv with respect to **1**) added post-activation of the precatalyst.

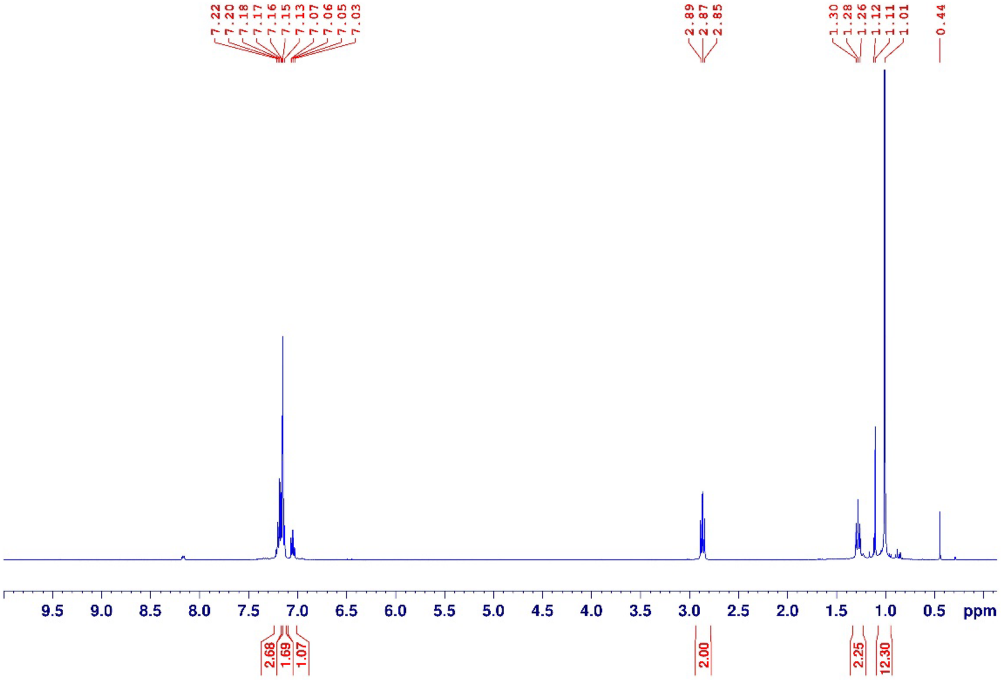


Figure S56. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence EtOAc (20 mol %).

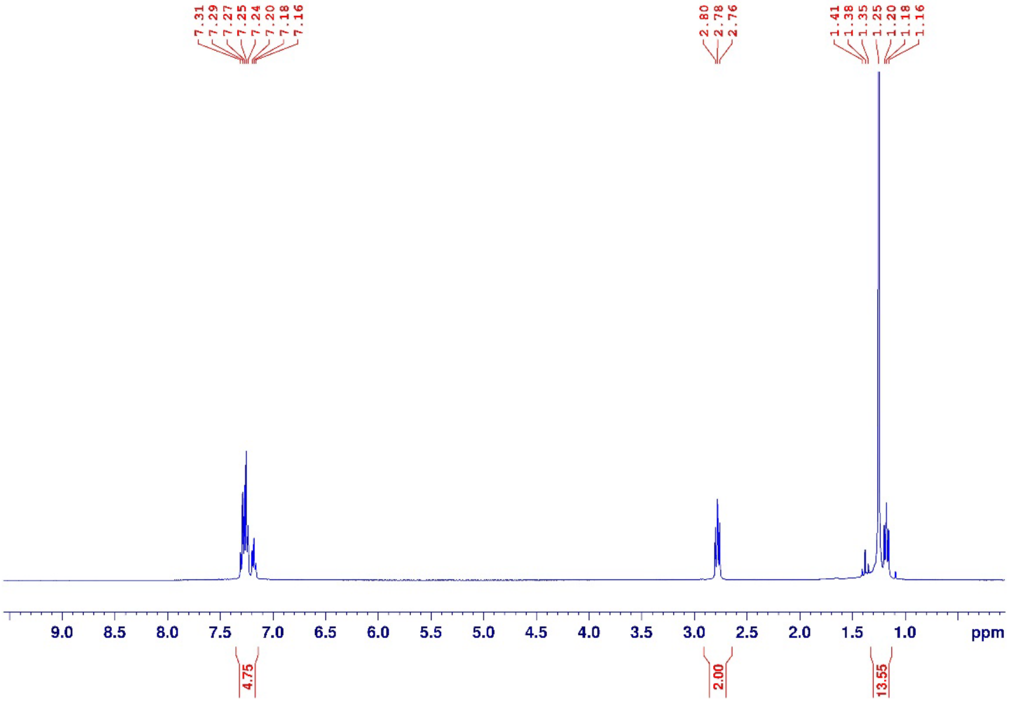


Figure S57. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence DMA (20 mol %).

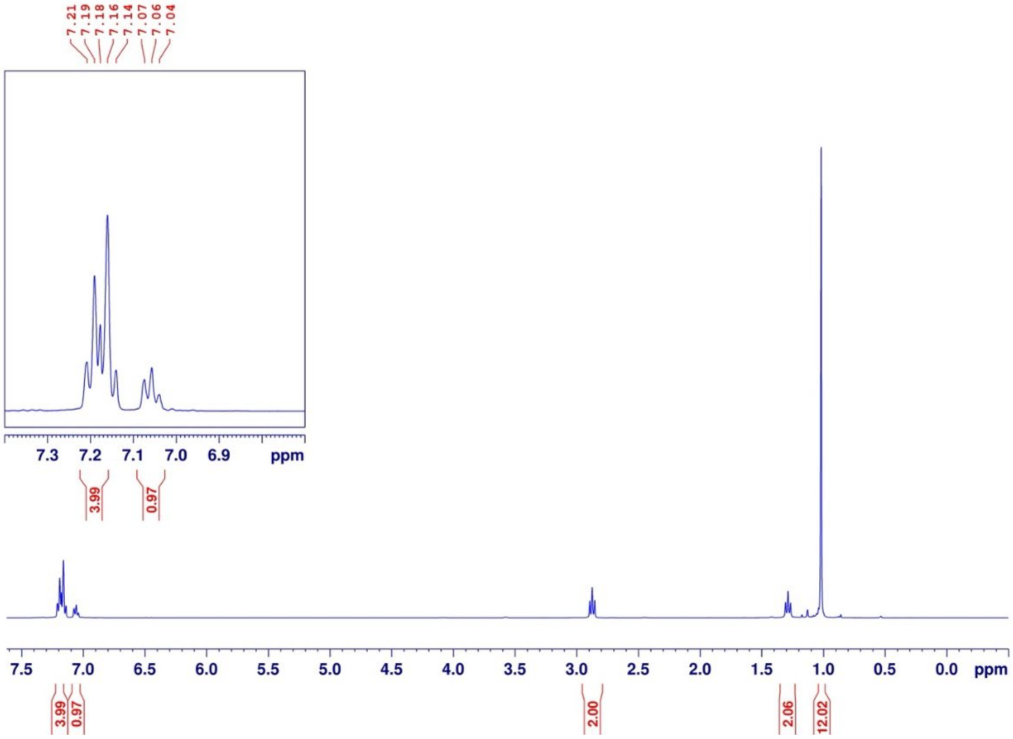


Figure S58. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence ^{i}PrNH$_2$ (20 mol %).

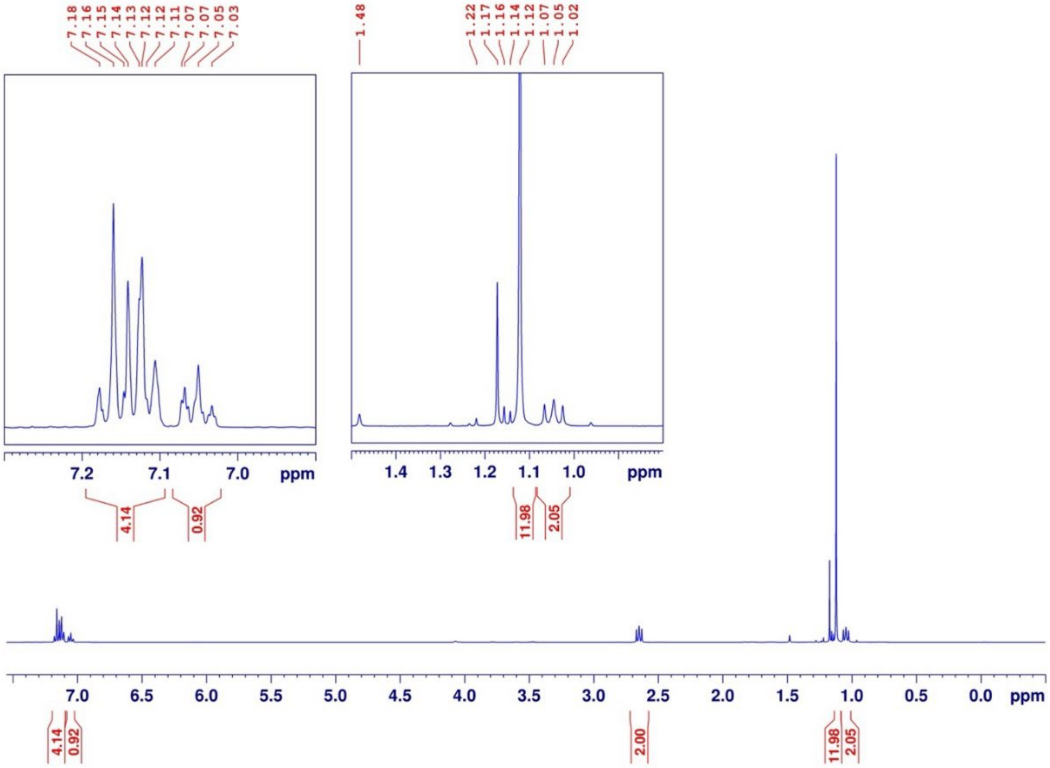
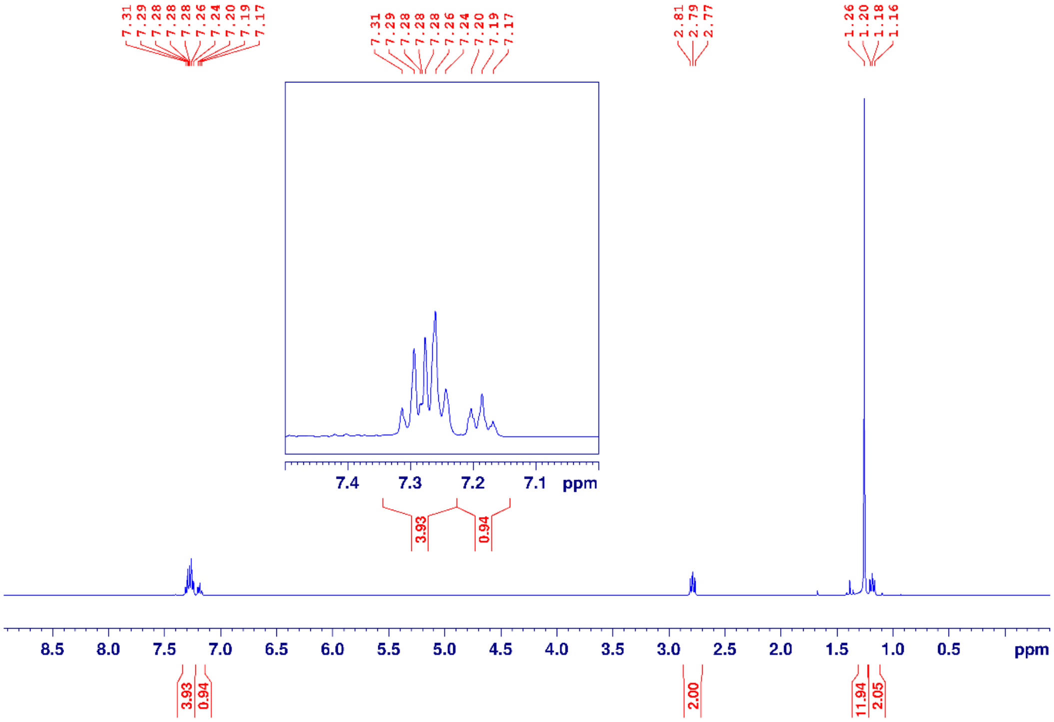


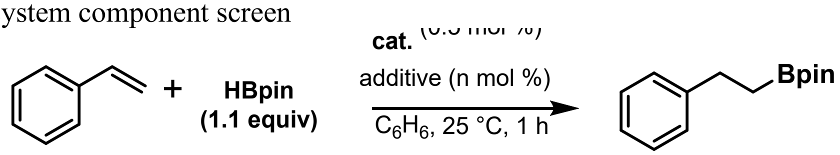
Figure S59. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of the reaction mixture obtained after a short silica plug when the hydroboration of styrene is carried out in the presence $HNEt_2$ (20 mol %) using 1.4 equiv HBpin.



Control experiments

Individual reaction components were screened for the effect on catalysis through the addition, or removal of reactants.

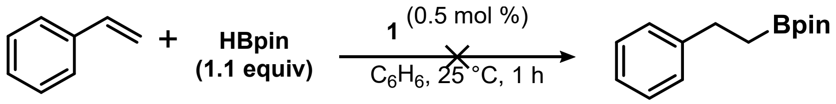
Table S2. Catalytic system component screen



entry	complex	additive	n (mol %)	conv. (%)[a]
1	**1**	-	-	0
2	**-**	$KBEt_3H$	1	0
3	**-**	-	-	0
4	**3**	-	-	0
5	**1**	$KBEt_3H$, TMEDA[b]	1, 10	89
6[*c*]	**1**	Cs_2CO_3	0.2	>99
7	**1**	$KBEt_3H$	1	95

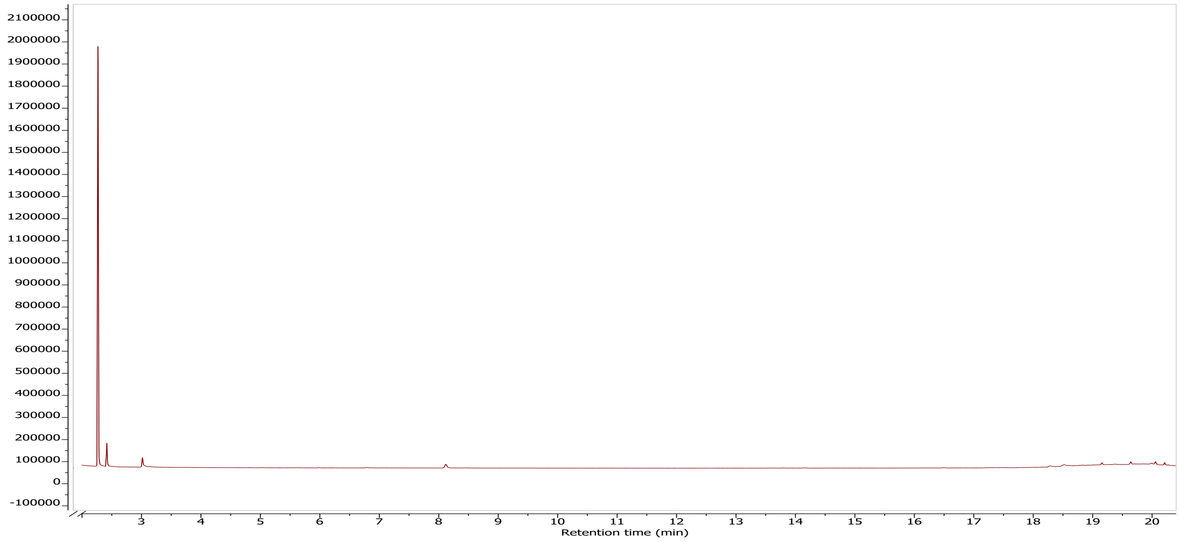
[a] Represents conversion observed by GC-FID. [b] Additive was added 3 minutes after activation of the precatalyst with $KBEt_3H$ (1 mol %). [c] Reaction was carried out with 0.1 mol% loading of catalyst **1** and stirred for 24 hours before analysis.

Attempted hydroboration of styrene in the absence of $KBEt_3H$

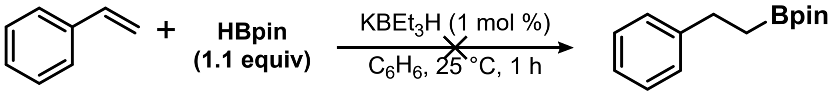


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (5.3 mg, 5.3 µmol, 0.5 mol %), C_6H_6 (0.48 mL), styrene (121.0 µL, 1.06 mmol), and HBpin (168.6 µL, 1.16 mmol, 1.1 equiv) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 hour, then an aliquot was analyzed to determine the distribution of starting material and linear hydroboration product (no product detected).

Figure S60. GC-FID of reaction mixture aliquot (60 min) from attempted hydroboration of styrene without $KBEt_3H$. No hydroboration products were observed (expected retention time = 11.75 min).

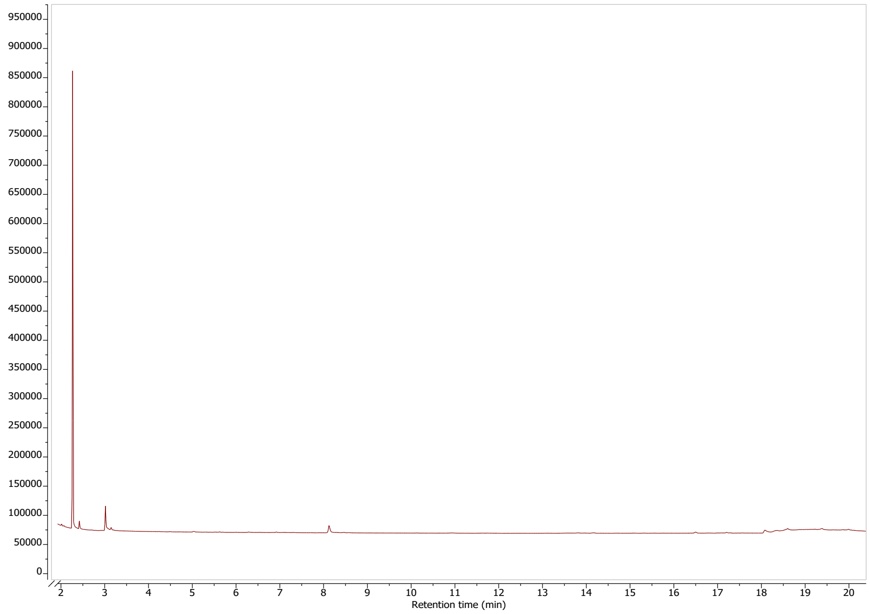


Attempted hydroboration of styrene in the absence of precatalyst

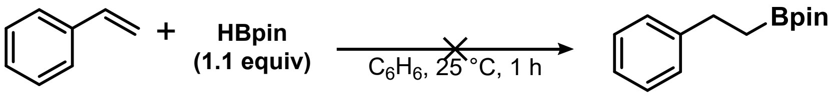


To an oven-dried 20 mL scintillation vial equipped with stir bar was added C_6H_6 (0.48 mL), styrene (110.0 µL, 0.96 mmol), HBpin (153.3 µL, 1.06 mmol, 1.1 equiv), and $KBEt_3H$ (96 µL, 100 mM in THF, 1 mol %) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 hour, then an aliquot was analyzed to determine the distribution of starting material and linear hydroboration product (no product detected).

Figure S61. GC-FID of reaction mixture aliquot (60 min) from attempted hydroboration of styrene in the absence of **1**. No hydroboration products were observed (expected retention time = 11.75 min).

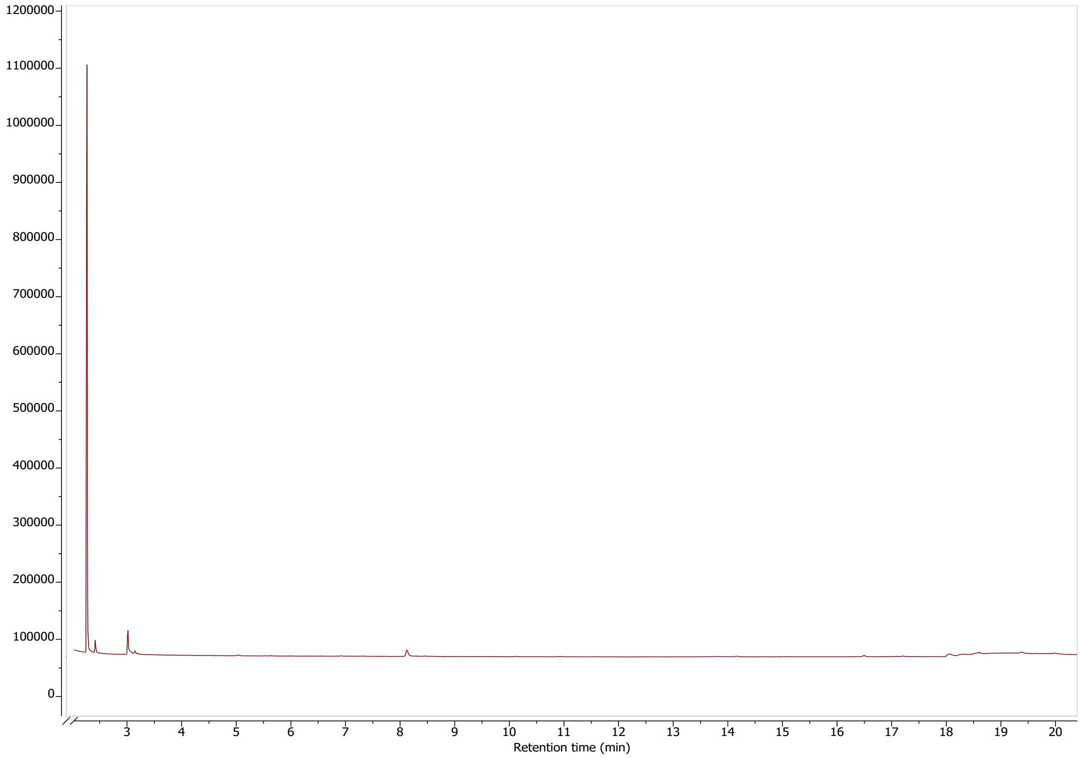


Attempted hydroboration of styrene in the absence of precatalyst 1 and $KBEt_3H$

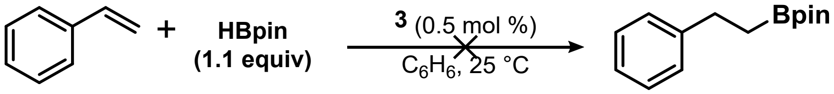


To an oven-dried 20 mL scintillation vial equipped with stir bar was added C_6H_6 (0.58 mL), styrene (110.0 µL, 0.96 mmol), and HBpin (153.3 µL, 1.06 mmol, 1.1 equiv) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 hour, then an aliquot was analyzed to determine the distribution of starting material and linear hydroboration product (no product detected).

Figure S62. GC-FID of reaction mixture aliquot (60 min) from attempted hydroboration of styrene in the absence of both precatalyst **1** and $KBEt_3H$. No hydroboration products were observed (expected retention time = 11.75 min).

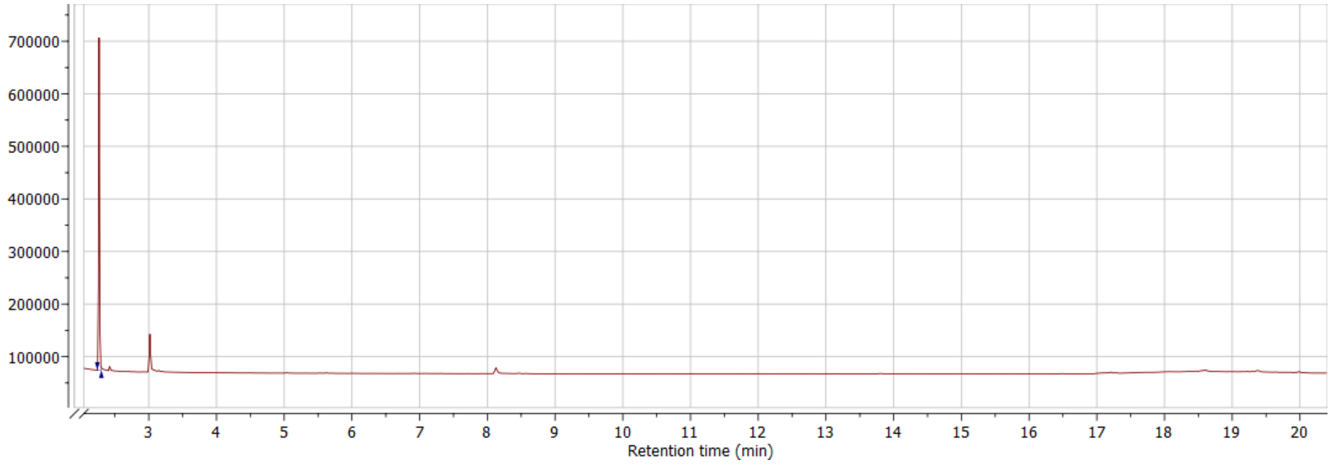


Attempted Alkene Hydroboration using $(PP^{CF3}P)Co(PMe_3)H$ (3)

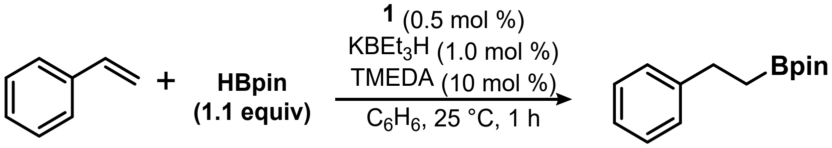


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **3** (2.0 mg, 2.4 µmol, 0.5 mol%), C_6D_6 (0.35 mL), styrene (55.0 µL, 0.48 mmol), and HBpin (76.6 µL, 0.53 mmol, 1.1 equiv) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 1 hour, during which time, aliquots were taken to determine the distribution of starting material to linear hydroboration product (no product detected).

Figure S63. GC-FID of reaction mixture aliquot (60 min) from attempted hydroboration of styrene using **3** as a catalyst. No hydroboration products were observed (expected retention time = 11.75 min).

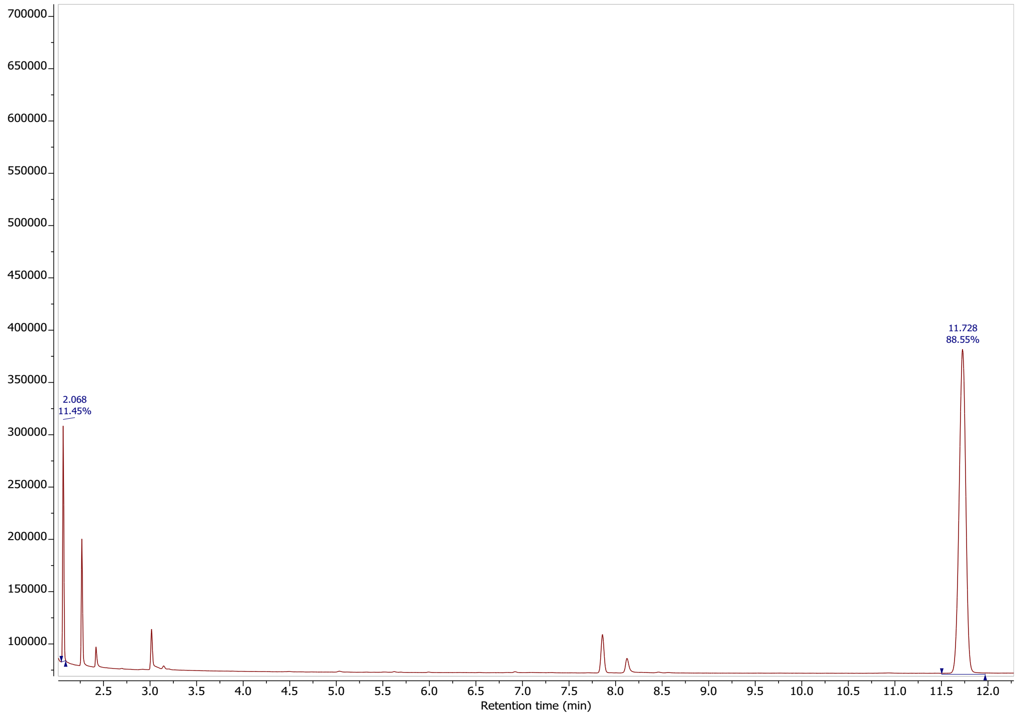


Catalytic Hydroboration of Styrene with 1 in the presence of TMEDA



To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (3.8 mg, 3.8 µmol, 0.5 mol %), styrene (88.0 µL, 0.77 mmol), HBpin (122.6 µL, 0.85 mmol, 1.1 equiv), and C_6H_6 (0.5 mL) and the resultant mixture was stirred. The activator, $KBEt_3H$ (76.8 µL, 100 M in THF, 7.6 µmol, 1.0 mol %), was added by micropipette and the reaction stirred for three minutes prior to the addition of TMEDA (11.5 µL, 0.07 mmol, 10 mol %). The reaction progress was sampled after 60 minutes and analyzed by GC-FID to determine conversion of starting material to the linear anti-Markovnikov product (89%)

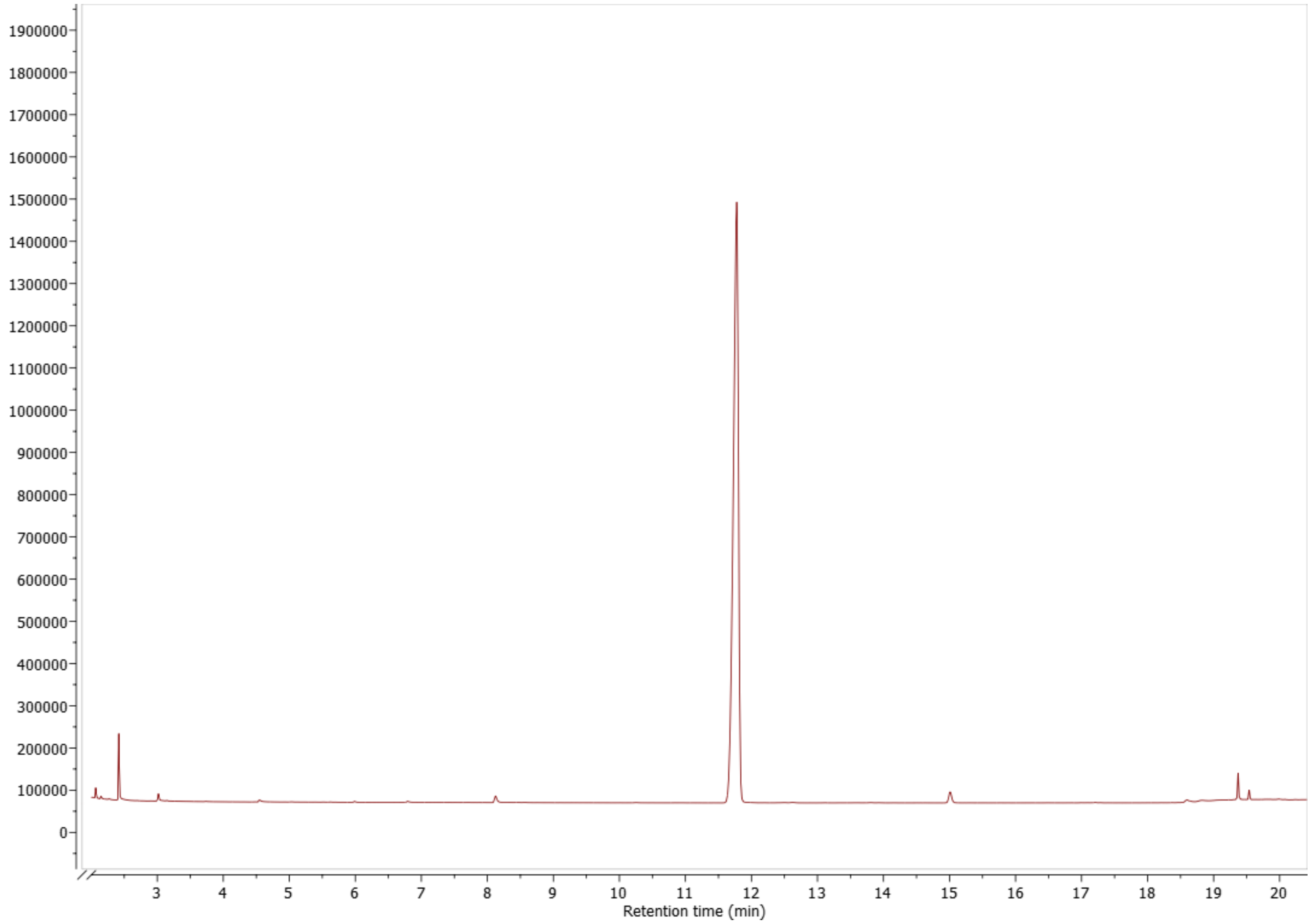
Figure S64. GC-FID of reaction mixture aliquot (60 min) from attempted hydroboration of styrene in the presence of TMEDA (10 mol %).



Catalytic Hydroboration of Styrene with 1 using Cs_2CO_3 as an activator

To an oven-dried 20 mL scintillation vial equipped with a stir bar was added **1** (9.0 mg, 9.1 µmol, 0.1 mol %), styrene (1.05 mL, 9.12 mmol), HBpin (1.46 mL, 10.03 mmol, 1.1 equiv), and the resultant mixture was stirred. The activator, Cs_2CO_3 (6 mg, 18.2 µmol, 0.2 mol %), was added and the reaction stirred for 24 hours. The reaction progress was sampled after 24 hours and analyzed by GC-FID to determine conversion of starting material.

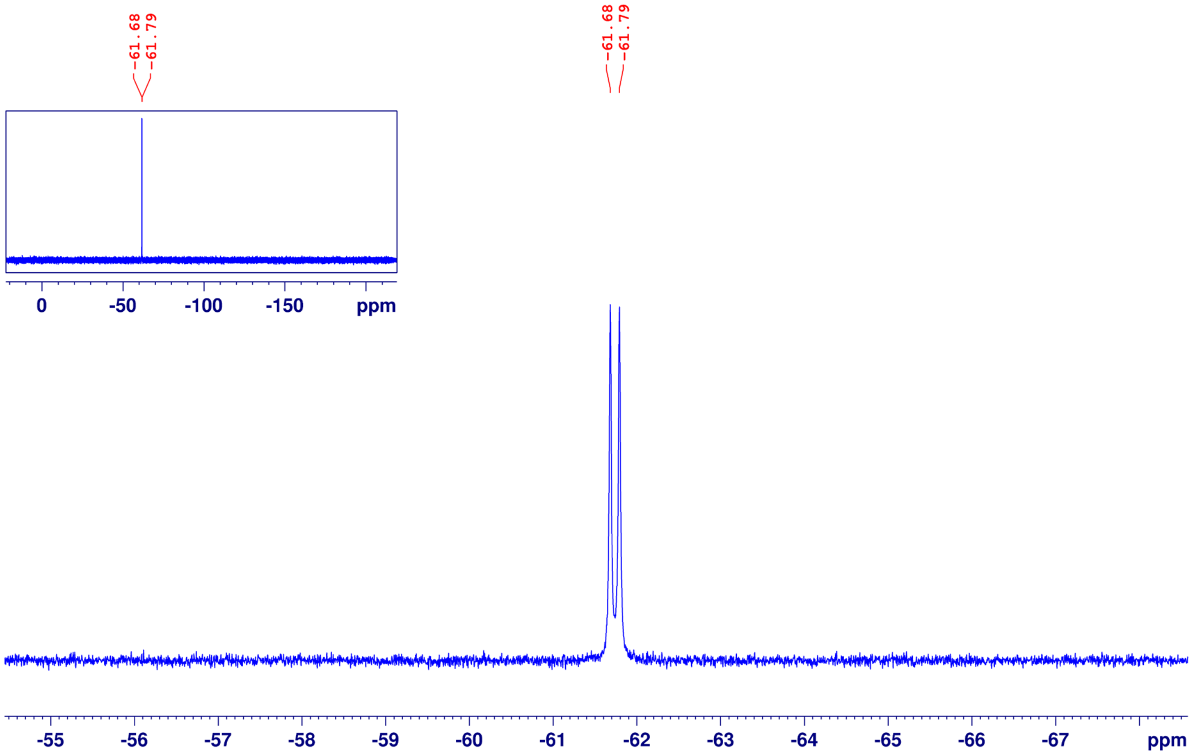
Figure S65. GC-FID of reaction mixture aliquot (24 h) for the catalytic hydroboration of styrene with **1** using Cs_2CO_3 as an activator



Experiment to Monitor the Speciation of (PP^{CF3}P)Co-Containing Species Under Catalytic Conditions

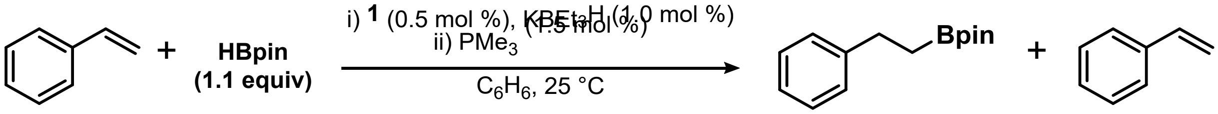
^{19}F NMR spectroscopy (Figure S66) was used to determine the number/identities of species in solution at different points in the catalytic regime. To a 20 mL vial was added **1** (9.0 mg, 9.1 µmol, 1.0 mol %), C_6D_6 (2 mL), styrene (104.0 µL, 0.912 mmol), and HBpin (119.1 µL, 0.821 µmol, 18.2 µmol, 0.9 equiv) with stirring to afford a brown, heterogeneous suspension. Then, $KBEt_3H$ (182.5 µL, 100 mM in THF, 2.0 mol %) was added by micropipette and the solution took on a bright yellow coloration over the next five minutes. After 60 minutes, an aliquot of the reaction mixture (0.5 mL) was removed, dried in vacuo, and analyzed by ^{19}F NMR spectroscopy.

Figure S66. ^{19}F NMR spectrum (C_6D_6, 376 MHz) of the diamagnetic species observed during the catalytic hydroboration of styrene. The ^{19}F NMR signal observed at -62 ppm was later determined to correspond to (PP^{CF3}P)Co(η^2-styrene)(H) (**2**).



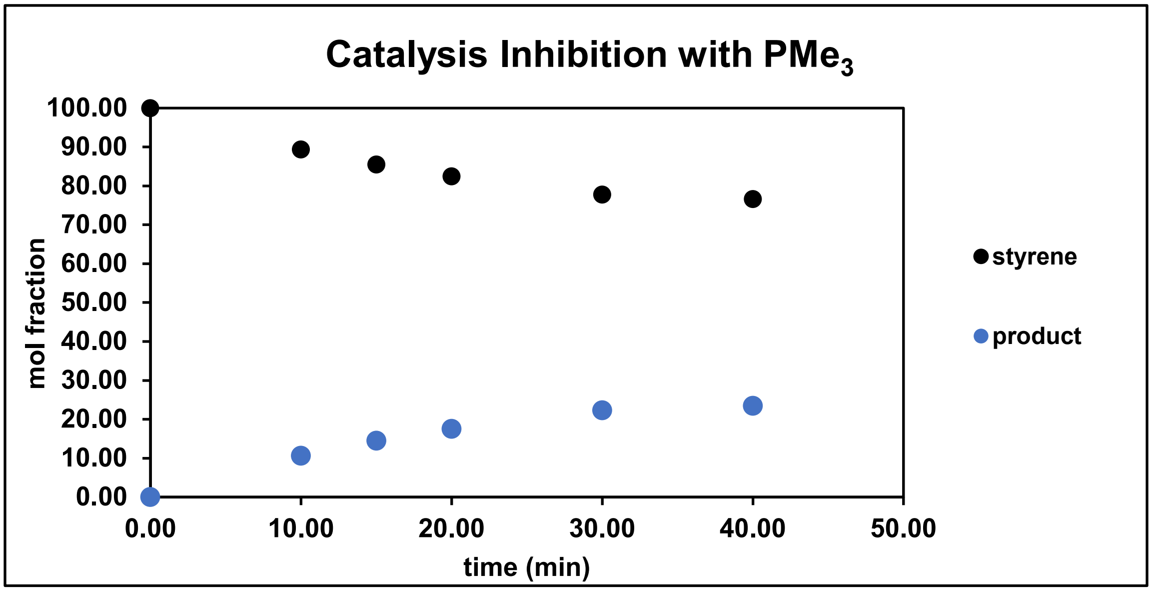
Supplementary Experiments

Alkene Hydroboration in the Presence of PMe$_3$

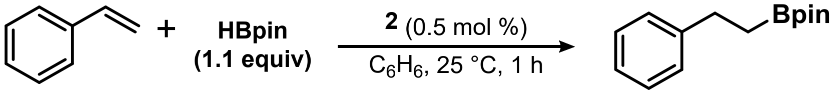


To a 20 mL vial was added **1** (5.7 mg, 5.8 µmol, 0.5 mol %), C_6H_6 (1 mL), styrene (120 mg, 1.15 mmol), and HBpin (162.2 mg, 1.27 mmol, 1.1 equiv) with stirring. An aliquot of this mixture was taken and analyzed by GC-MS/FID to confirm that no hydroboration products were observed prior to activation. Then, KBEt$_3$H (1.0 mol %, 100 mM in THF, 115.2 µL) was added by micropipette, resulting in a yellow, homogeneous solution over five minutes. A second time-point (t = 10 min) was taken followed by immediate addition of PMe$_3$ (17 µL, 1 M in THF, 17 µmol, 1.5 mol %) and the reaction mixture rapidly took on a light-orange coloration. Additional aliquots were analyzed after the addition of PMe$_3$ to determine the impact on catalytic activity .

Figure S67. Tracking the reaction progress of catalytic hydroboration of styrene using **1** (0.5 mol %) by GC-FID. The rate of reaction is observed to drop rapidly upon the addition of PMe$_3$ (0.015 equiv) after 10 minutes.

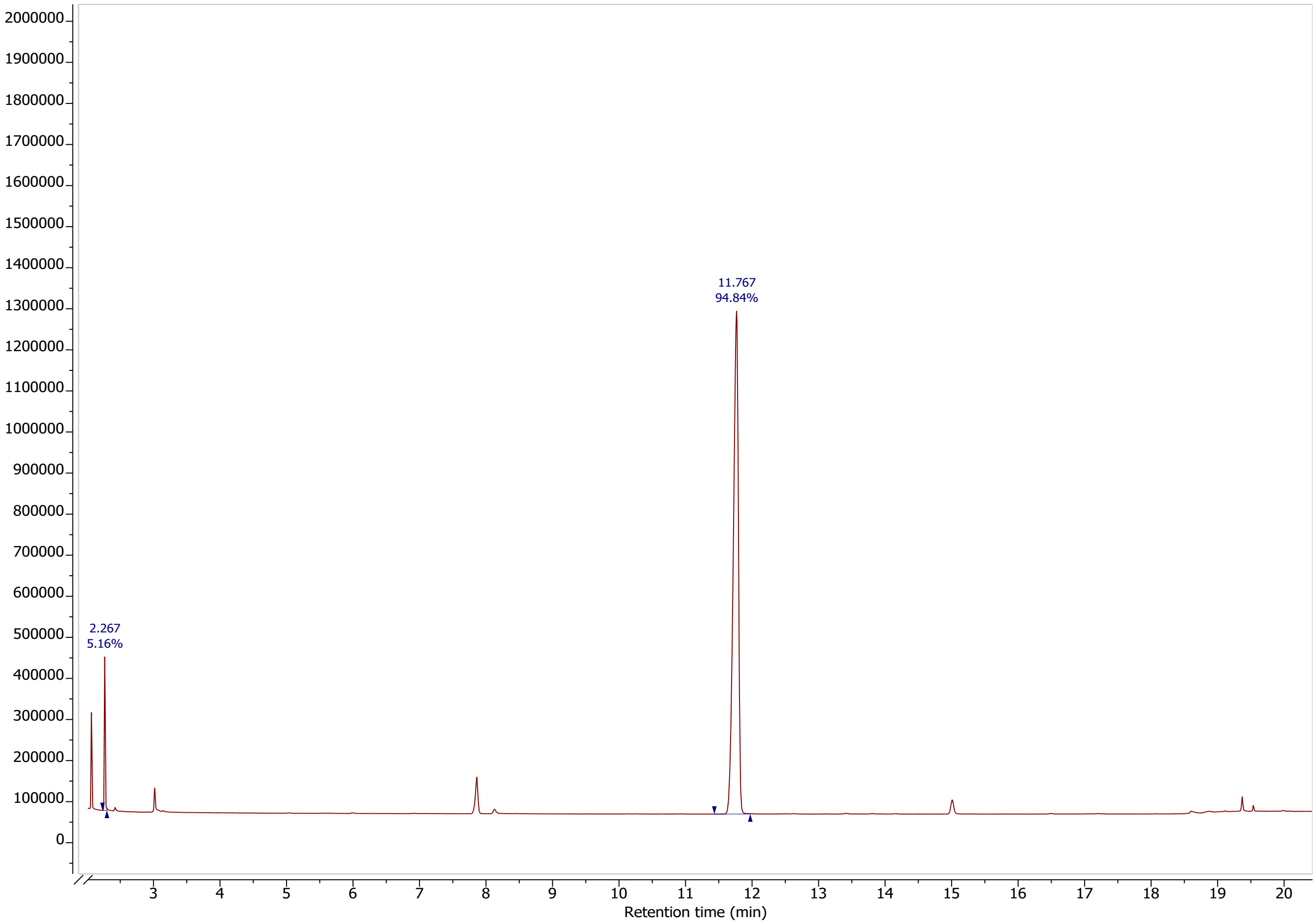


Catalytic Hydroboration of Styrene with (PP^{CF3}P)Co(η^2-styrene)H (2)

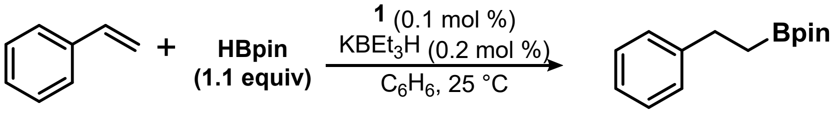


To an oven-dried 20 mL scintillation vial equipped with stir bar was added 2 (5.0 mg, 5.9 μmol, 0.5 mol %), C_6H_6 (0.50 mL), styrene (136.0 μL, 1.19 mmol), and HBpin (188.0 μL, 1.30 mmol, 1.1 equiv). The reaction mixture was allowed to stir for 1 hour, then an aliquot was analyzed to determine the distribution of starting material and linear hydroboration product (95% conversion).

Figure S68. GC-FID of reaction mixture aliquot (60 min) from hydroboration of styrene using **2** as a catalyst.



Substrate recharge experiment



To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (1.0 mg, 1.1 mL, 0.88 mM in THF, 1 µmol, 0.1 mol %) and the solvent subsequently removed under vacuum. Styrene (110.0 µL, 0.96 mmol), C_6H_6 (0.15 mL), and HBpin (153.3 µL, 1.06 mmol, 1.1 equiv) were added and the reaction mixture stirred. Then, $KBEt_3H$ (19.2 µL, 100 mM in THF, 1.9 µmol, 0.2 mol %) was added by micropipette, affording a faintly yellow homogenous solution, which was stirred for 24 hours. An aliquot was collected from the reaction mixture for analysis by GC-FID and an additional portion of styrene (110.0 µL, 0.96 mmol) and HBpin (153.3 µL, 1.06 mmol, 1.1 equiv) were added. After stirring for an additional 24-hour period, another aliquot was collected and analyzed by GC-FID. This process was repeated a third time. The conversion of styrene remained high with each subsequent recharge with substrates, as shown in Figure S69, indicating that the catalyst remains in an active form upon substrate depletion.

Figure S69. Relative conversion using GC-FID determined after recharging the catalyst with additional substrate for 3 consecutive 24-hour periods.

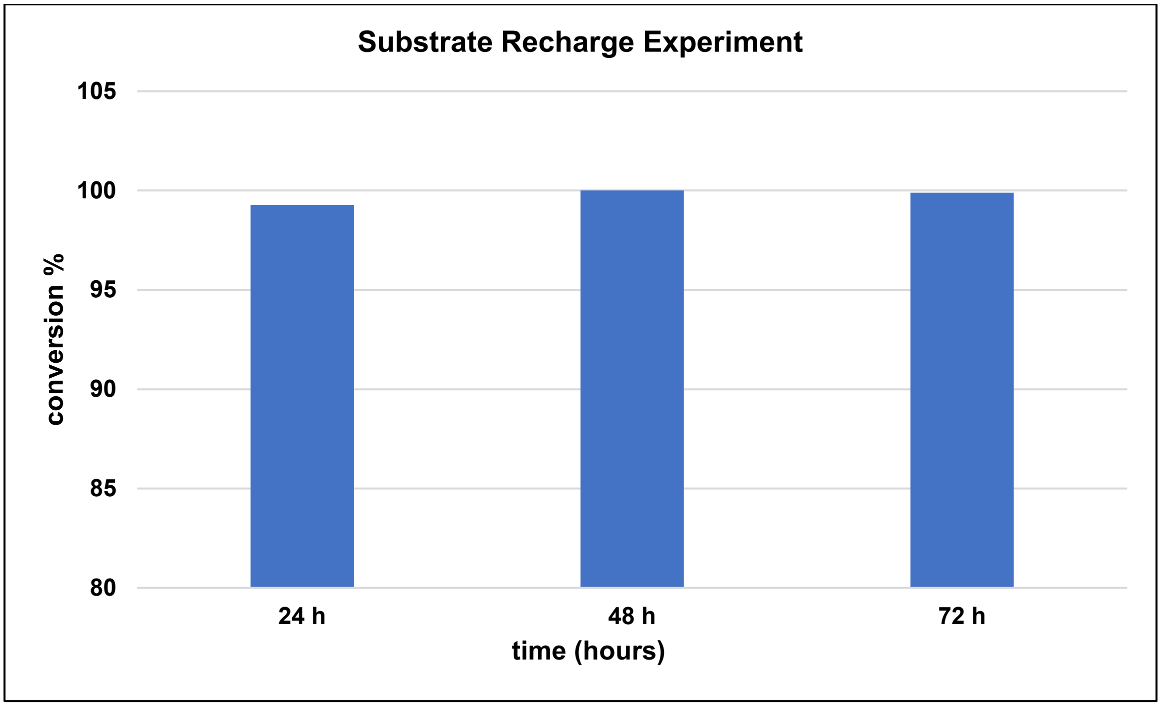
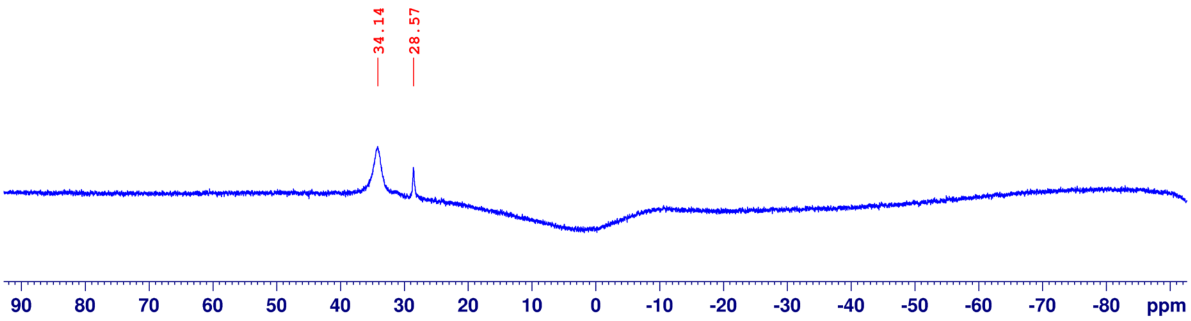
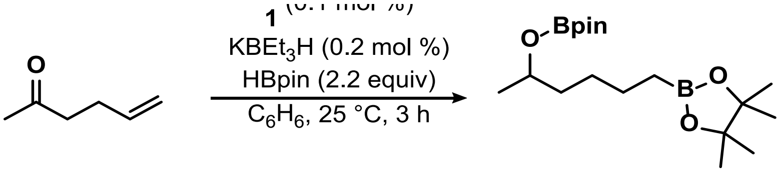


Figure S70. ^{11}B NMR spectrum (C_6D_6, 128 MHz) of reaction mixture for the catalytic hydroboration of styrene, prior to substrate recharge. The only signals observed are 34.1 ppm, consistent with literature reports of the terminal hydroboration product, and remaining pinacolborane (ca. 28 ppm).

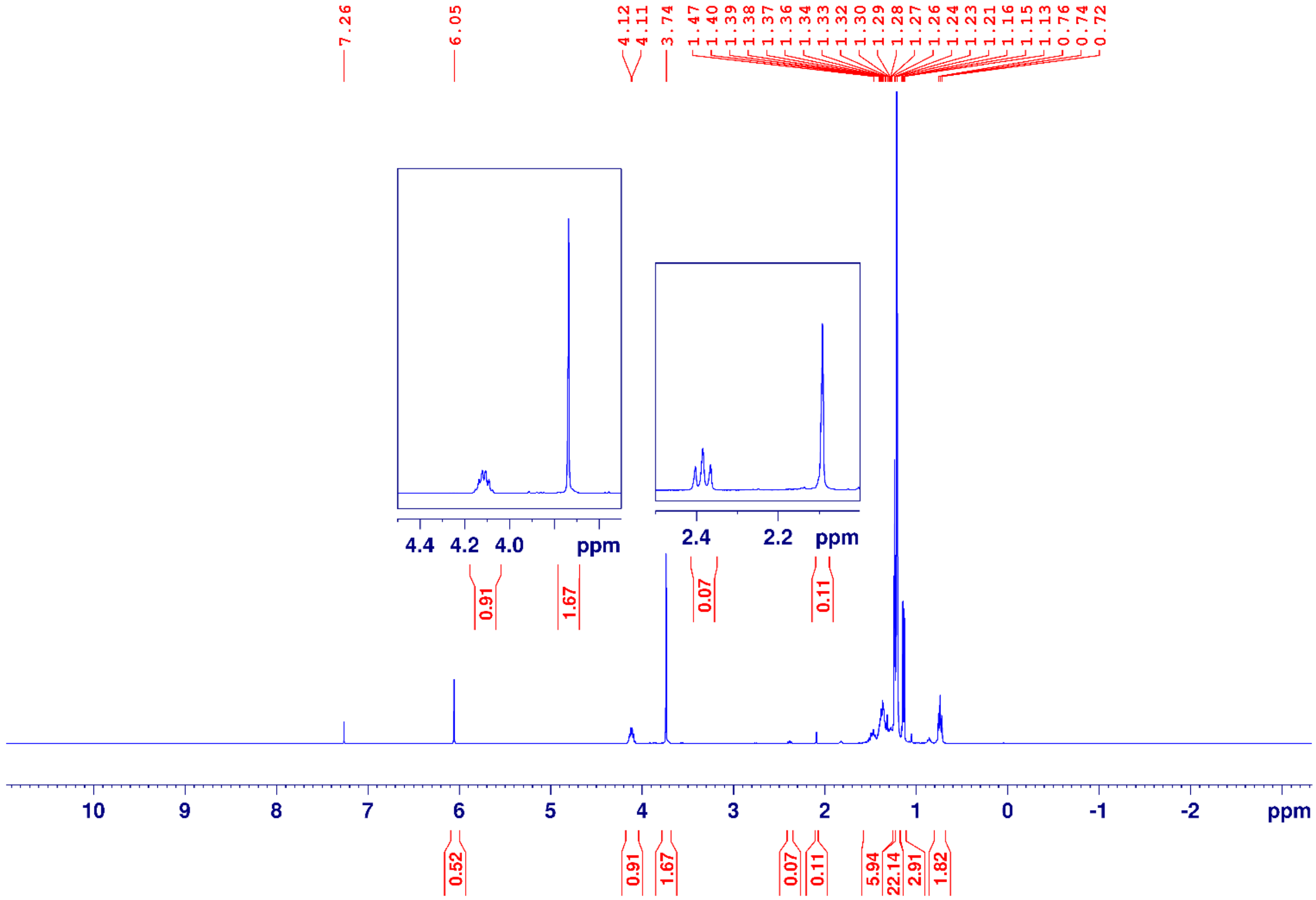


Catalytic Hydroboration of 5-Hexen-2-one with HBpin (2.2 equiv) (One-pot Methodology)

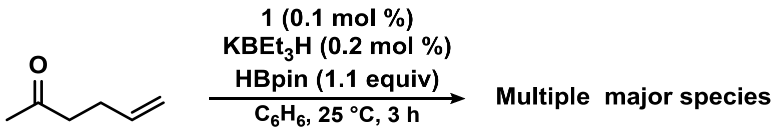


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (4.1 mg, 4.1 µmol, 0.2 mol %), C_6H_6 (0.5 mL), 5-hexen-2-one (202.3 mg, 2.06 mmol), and HBpin (0.66 mL, 4.55 mmol, 2.2 equiv) with stirring. Then, $KBEt_3H$ (82.5 µL, 100 mM in THF, 0.4 mol %) was added and the reaction mixture rapidly took on a yellow coloration and mild frothing was observed. After three hours, trimethoxybenzene (64.1 mg, 0.381 mmol, ~0.185 equiv) was added and pentanes (3 mL) were added to the reaction mixture prior to filtration through glass microfiber filter-paper. The filtrate was concentrated under reduced pressure to afford a clear, colorless oil with one major species resulting from the doubly hydroborated substrate in 91% yield (NMR, Figure S71). A small amount of the indicated minor product resulting from reactivity with the alkene is observed (4% NMR, Figure S71).

Figure S71. ^1H NMR spectrum (C_6D_6, 400 MHz) of reaction mixture using **1** and the one-pot activation before solvolysis.

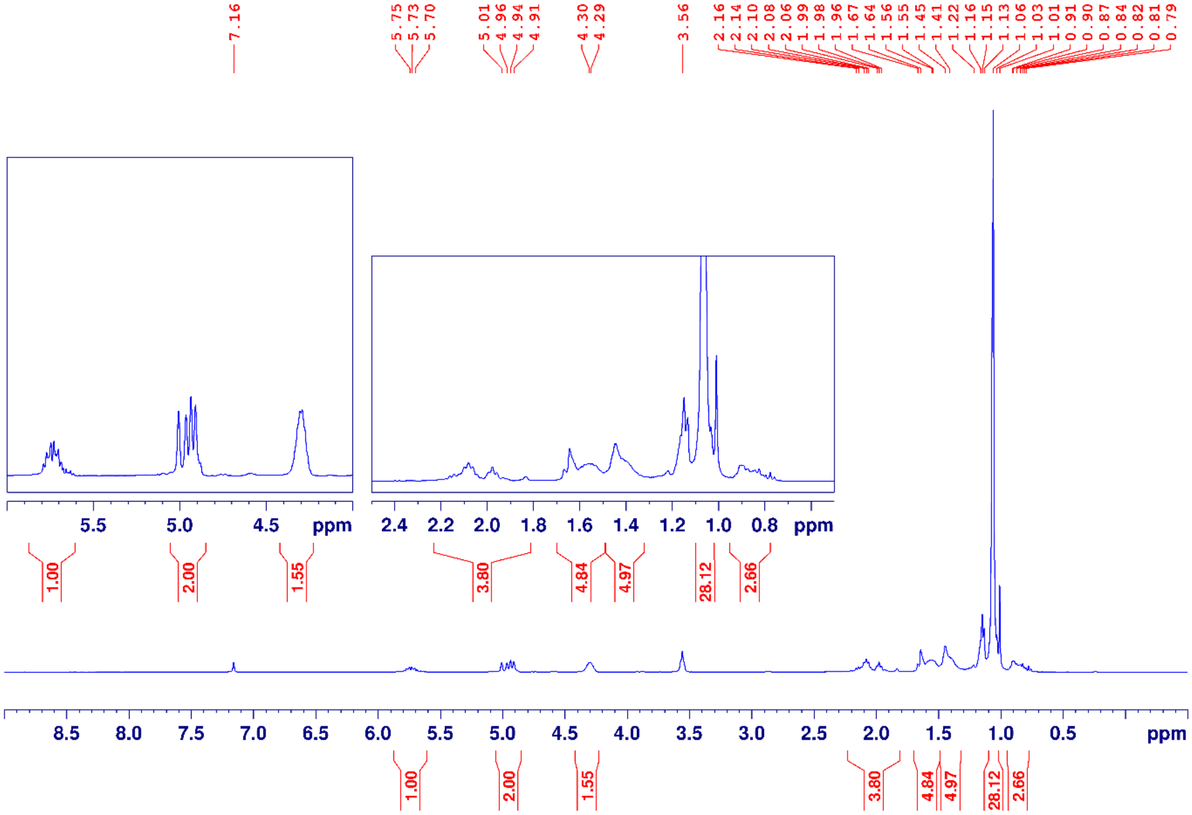


Catalytic Hydroboration of 5-Hexen-2-one with HBpin (1.1 equiv) (One-pot Methodology)

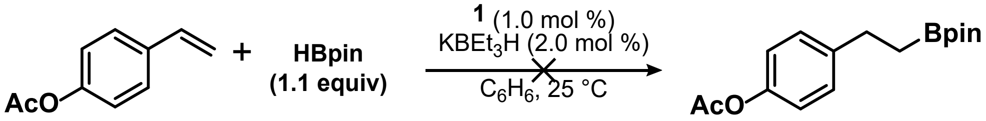


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (2.0 mg, 2.0 µmol, 0.1 mol %), C_6D_6 (0.50 mL), 5-hexen-2-one (197.8 mg, 2.02 mmol), and HBpin (0.65 mL, 4.48 mmol, 1.1 equiv) with stirring. Then, $KBEt_3H$ (41.4 µL, 100 mM in THF, 0.2 mol %) was added and the reaction mixture rapidly took on a yellow coloration and bubbling was observed. After 3 hours, an aliquot of the reaction mixture was taken for NMR analysis.

Figure S72. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of crude reaction mixture using **1** and the one-pot activation method. A number of products are present, mostly resulting from single and double functionalization of the substrate through the alkene/ketone functional groups.

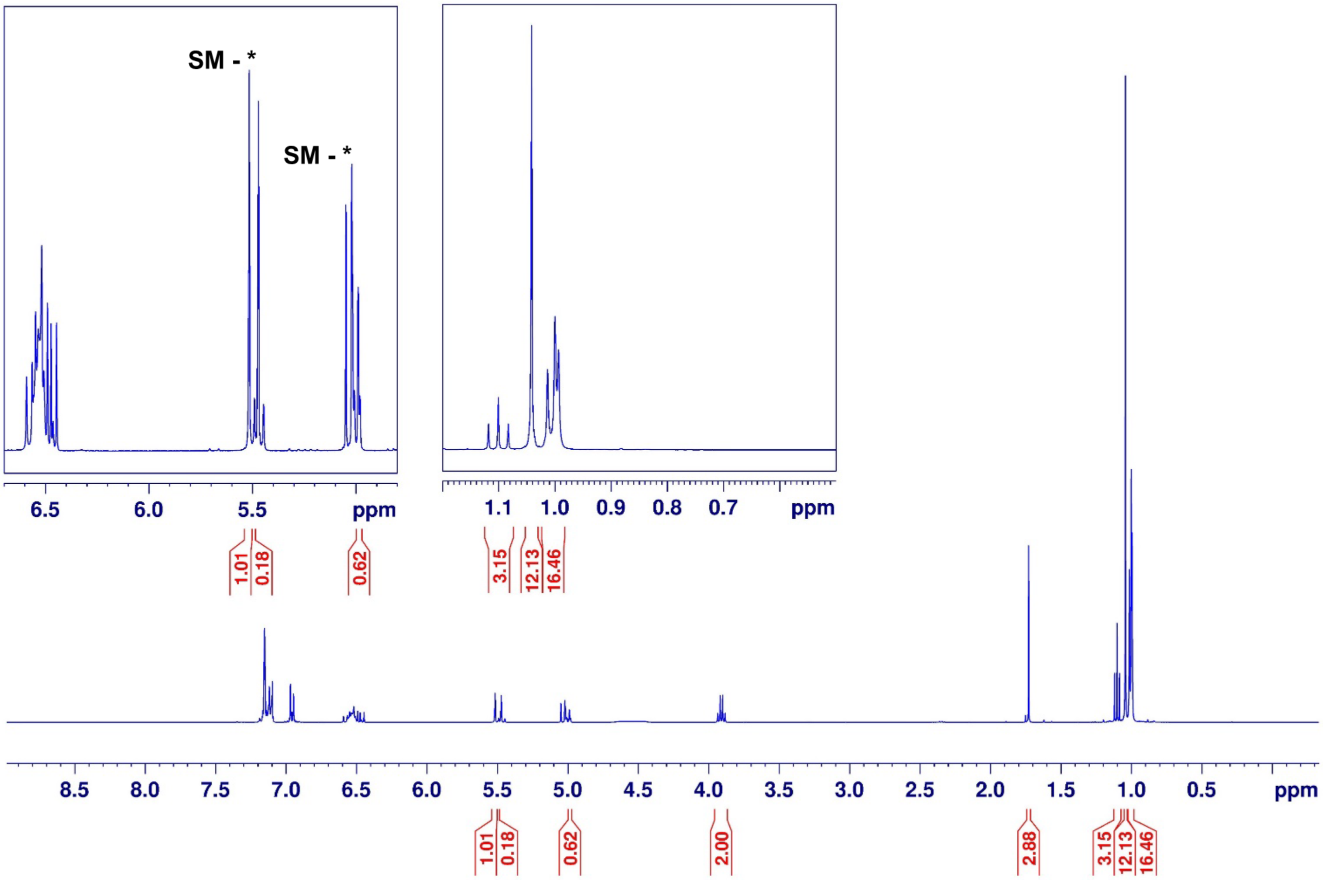


Attempted Catalytic Hydroboration of 4-acetoxystyrene (One-pot Methodology)

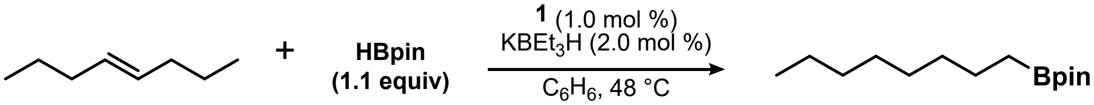


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (11.0 mg, 11.1 µmol, 1.0 mol %), C_6H_6 (0.50 mL), 4-acetoxystyrene (169.3 µL, 1.11 mmol), and HBpin (176.6 µL, 1.22 mmol, 1.1 equiv). Then, $KBEt_3H$ (22.1 µL, 1 M in THF, 2.0 mol %) was added and the resultant yellow-orange mixture was allowed to stir for 18 hours. The reaction mixture was exposed to air and EtOAc (3 mL) was added followed by stirring for 10 minutes prior to filtration through a short silica plug (ca. 4 cm). The filtrate was concentrated under reduced pressure to afford a slightly turbid, yellow oil. Analysis of this oil by NMR supports a mixture containing primarily starting material (4-acetoxystyrene) and new, minor alkene species most likely corresponding to 4-vinylphenol resulting from cleavage of the acyl group under these conditions. No ^{11}B signals corresponding to alkylboronate esters were detected.

Figure S73. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of attempted hydroboration of 4-acetoxystyrene using one-pot activation with **1**/$KBEt_3H$.

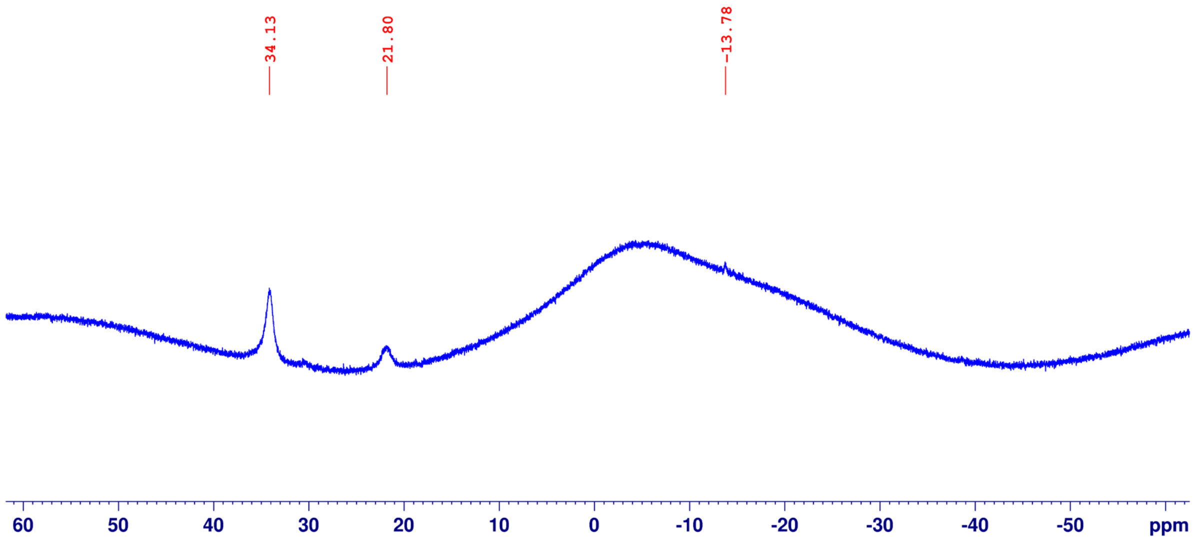


Attempted Catalytic Hydroboration of trans-4-octene

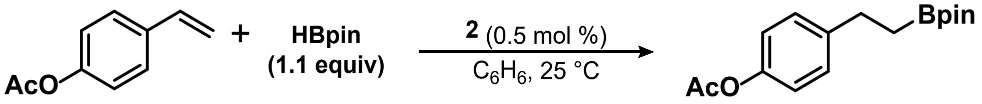


To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (4.7 mg, 4.7 µmol, 1.0 mol %), C_6H_6 (0.30 mL), trans-4-octene (74.1 µL, 0.47 mmol), and HBpin (75.4 µL, 0.52 mmol, 1.1 equiv). Then, $KBEt_3H$ (94.5 µL, 100 mM in THF, 2.0 mol %) was added and the resultant yellow-orange mixture was allowed to stir for 72 hours. The reaction mixture was exposed to air followed by stirring for 10 minutes prior to filtration through a short silica plug (ca. 4 cm). The filtrate was gently concentrated under reduced pressure to afford a slightly yellow oil. Analysis of this oil by ^{11}B NMR with extended scan count supports a small degree of hydroboration product (-34.1 ppm).

Figure S74. ^{11}B NMR spectrum ($CDCl_3$, 128 MHz) of attempted hydroboration of trans-4-octene after 72 hours at 48 °C followed by filtration through a short silica plug. Signal at 34.1 ppm is consistent with literature reports of the terminal hydroboration product. Additional signals are attributed to HBpin degradation products (*H*O-Bpin and BH_x) generated by the work-up procedure.

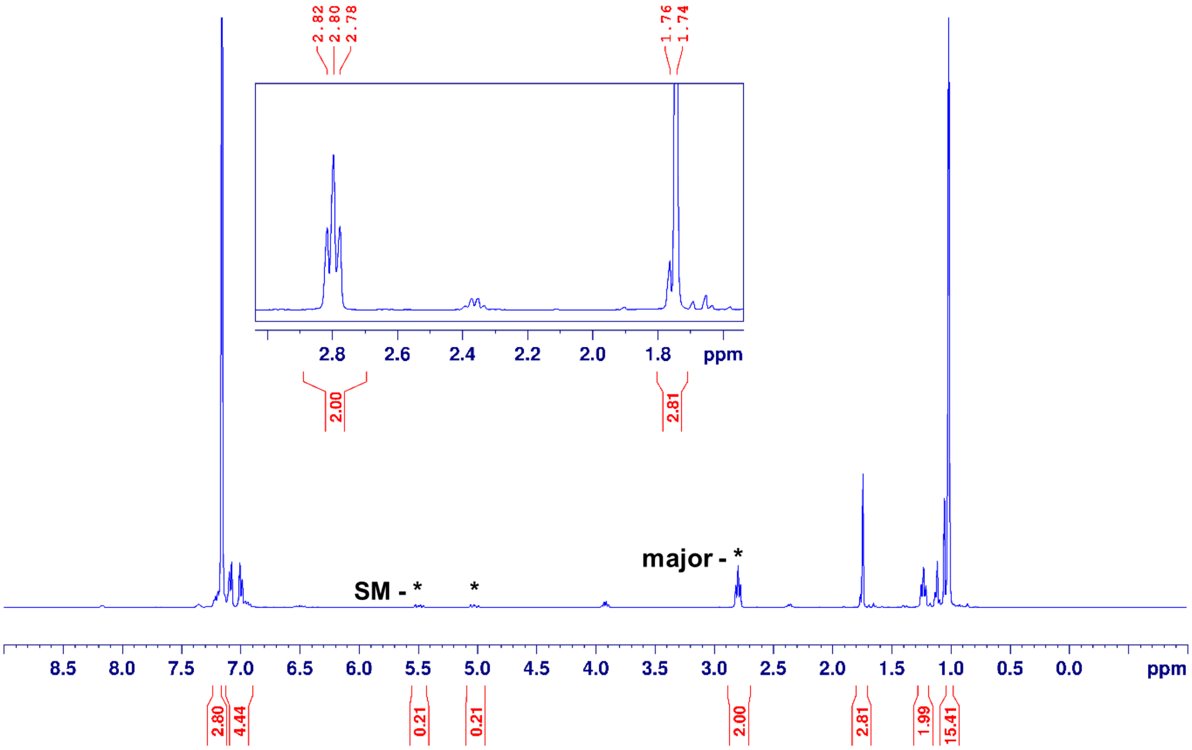


Catalytic Hydroboration of 4-acetoxystyrene with (PP^{CF3}P)Co(η^2-styrene)H



To an oven-dried 20 mL scintillation vial equipped with stir bar was added **2** (5.0 mg, 5.9 µmol, 0.5 mol%), C_6H_6 (0.50 mL), 4-acetoxystyrene (181.1 µL, 1.18 mmol), and HBpin (189.0 µL, 1.30 mmol, 1.1 equiv). The reaction mixture was allowed to stir for 18 hours before an aliquot was taken for crude analysis using ^{1}H NMR spectroscopy. The remainder of the mixture was passed through a short silica column to obtain a mixture with two primary organic components: the anti-Markovnikov alkene hydroboration product (~83%) and unreacted alkene (~17%).

Figure S75. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of reaction mixture (after short silica plug) using **2** as a catalyst for the hydroboration of 4-acetoxystyrene.



Hydroboration of Allyl Phenyl Ether using 1 with Benzene as Solvent

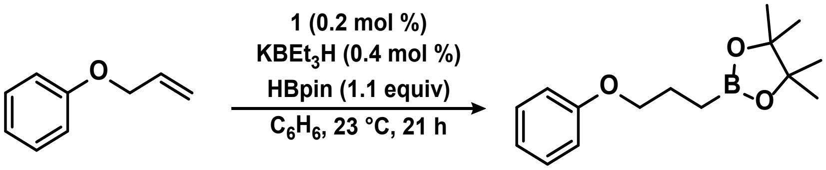
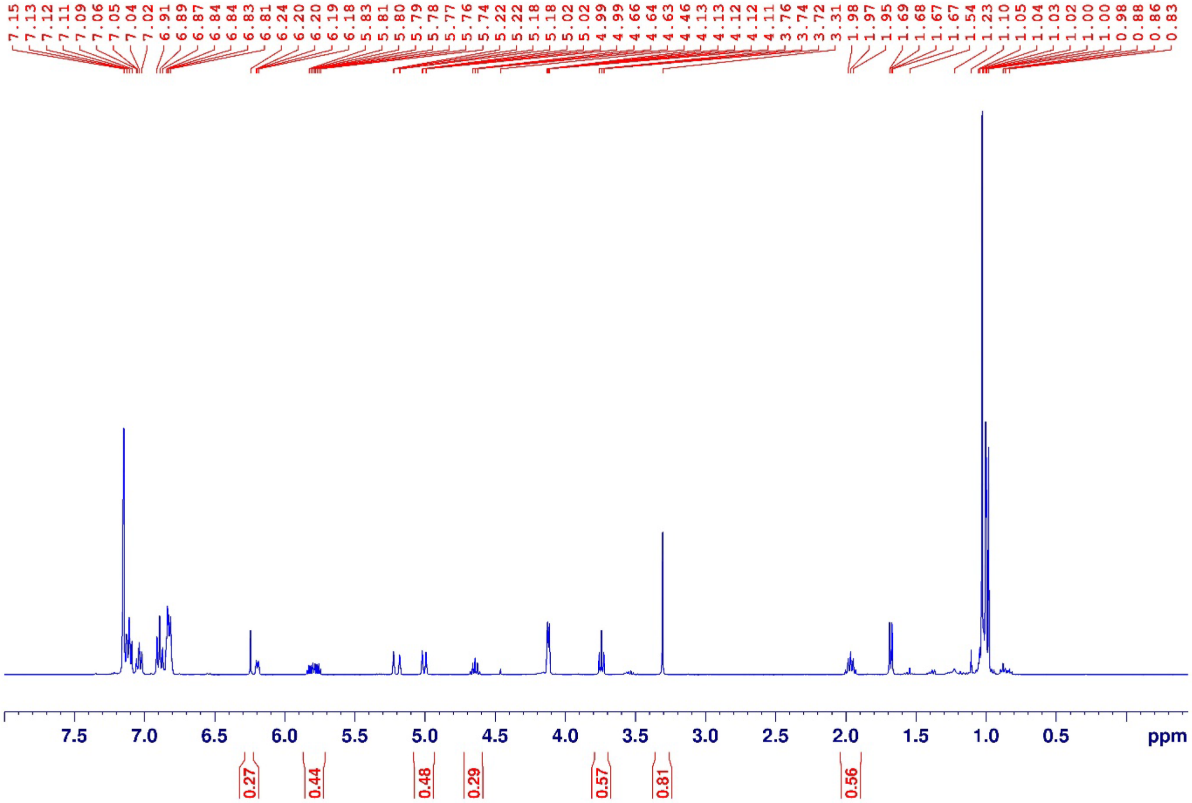
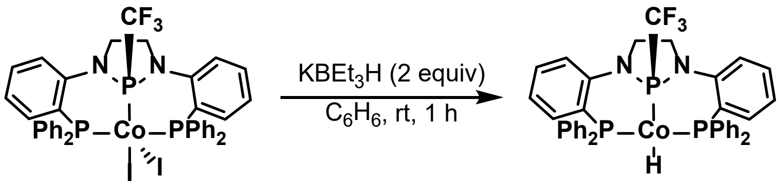


Figure S76. ^{1}H NMR spectrum (C$_6$D$_6$, 400 MHz) of catalytic mixture where benzene has been used as a reaction solvent showing significant starting material remaining.



Attempted Synthesis of a (PP^{CF3}P)CoH Species in the Absence of Additional Ligands/Substrates



To an oven-dried 20 mL scintillation vial equipped with stir bar was added **1** (14.0 mg, 14.1 µmol) and THF (3 mL) with stirring to afford a brown, heterogeneous suspension. Then, $KBEt_3H$ (28.2 µL, 1 M in THF, 2 equiv) was added by micropipette and the solution took on an orange-brown coloration with a significant decrease in the apparant turbidity. After 1 hour, the reaction mixture was filtered through glass microfiber filter-paper and the filtrate concentrated to afford a darkly colored residue. The obtained residue was analyzed by ^1H and ^{19}F NMR (Figure S77-S78).

Figure S77. $^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 400 MHz) of semi-purified mixture resulting from the reaction of **1** with $KBEt_3H$ (2 equiv).

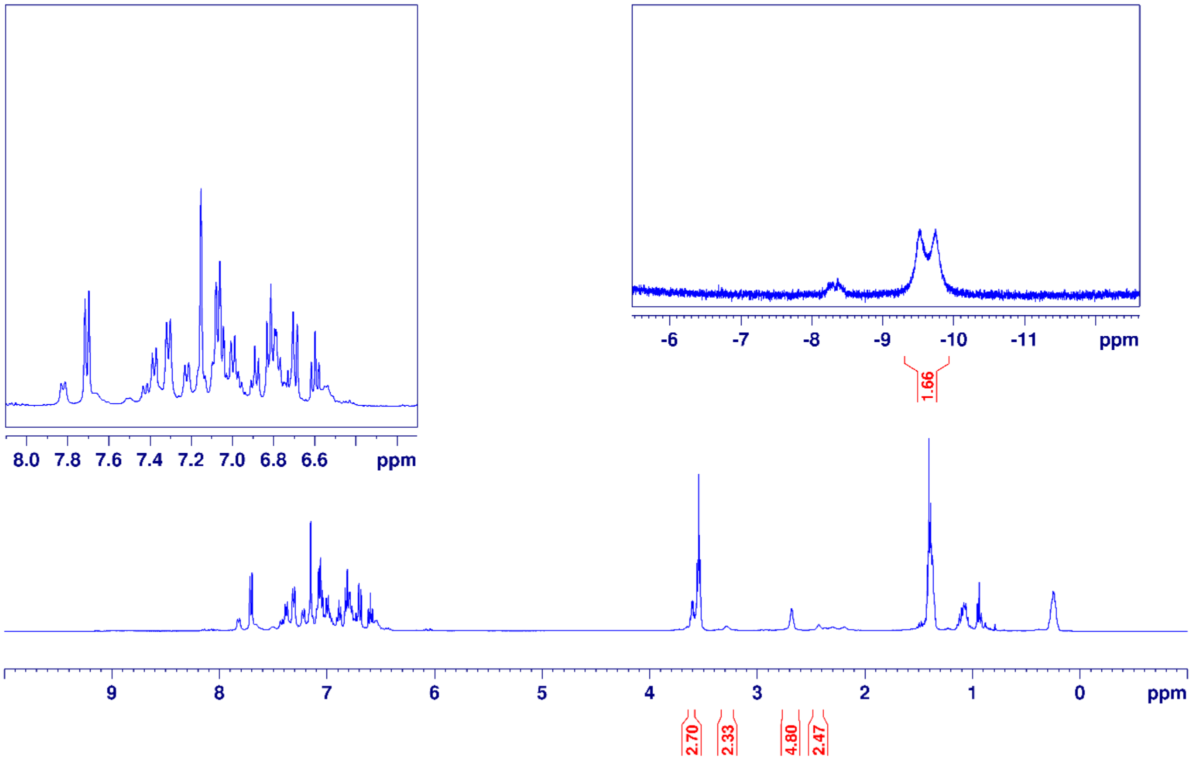
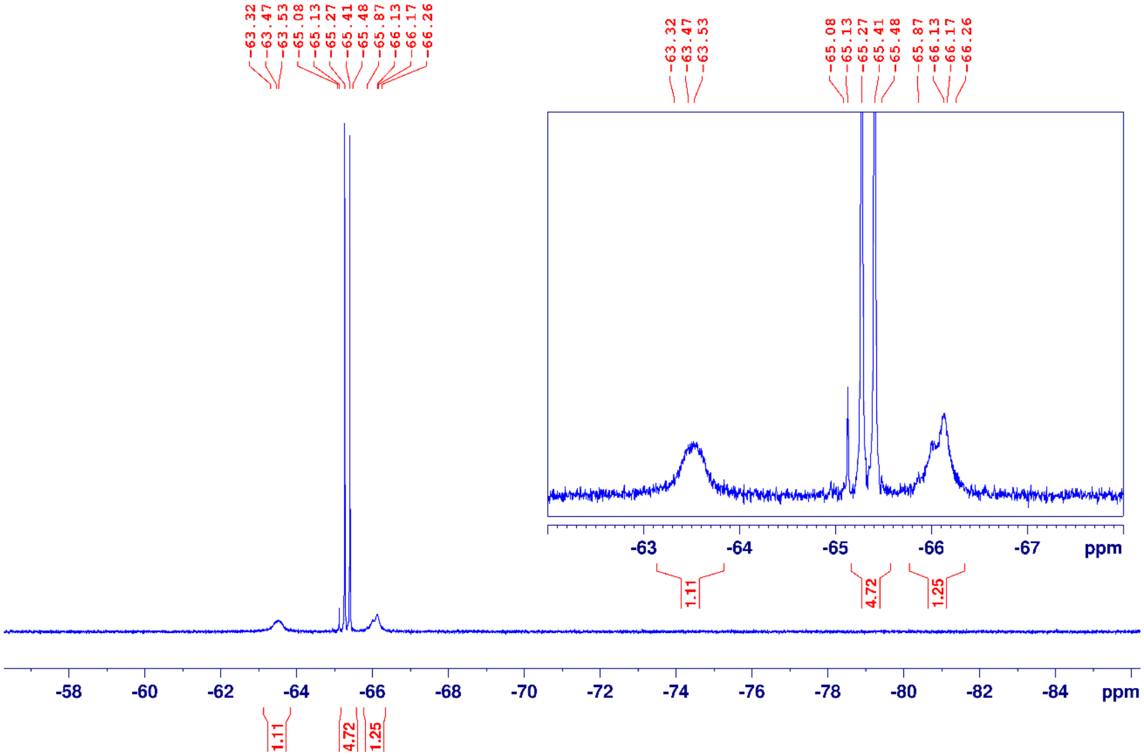


Figure S78. ^{19}F NMR spectrum (C_6D_6, 376 MHz) of semi-purified mixture resulting from the reaction of **1** with $KBEt_3H$ (2 equiv).



CRYSTALLOGRAPHIC DATA

*Experimental Summary - ($PP^{CF3}P$)CoI_2 (**1**)*

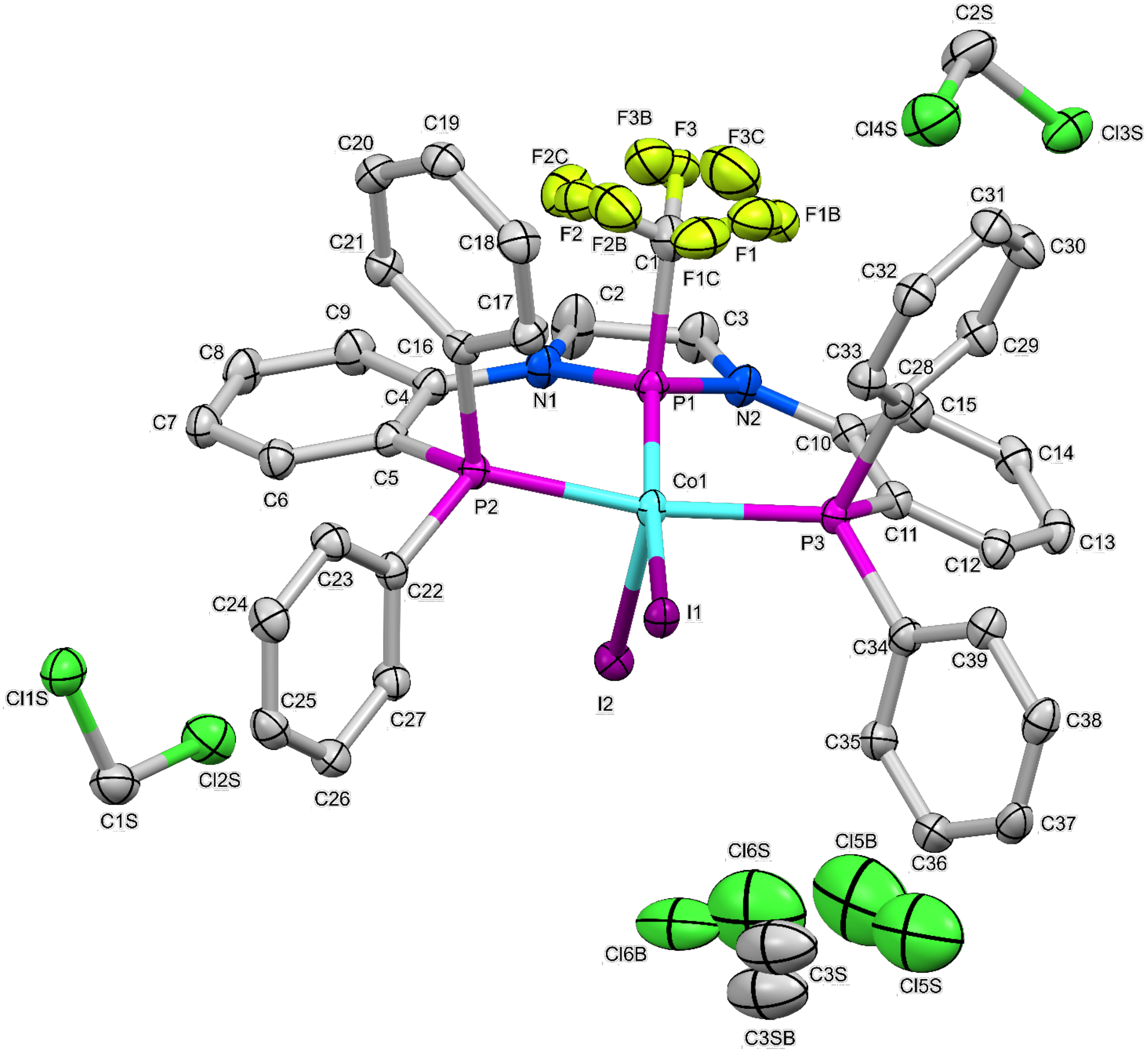
The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å). A 0.158 x 0.026 x 0.026 mm piece of an orange needle was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 60 mm using variable exposure time (1s-5s) depending on θ with a scan width of 1.0°. Data collection was 99.9% complete to 25.00° in θ (0.83 Å). A total of 106560 reflections were collected covering the indices, $-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$. 10975 reflections were found to be symmetry independent, with a R_{int} of 0.0403. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be *P*-1. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by dual-space method (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S3.

Table S3. Crystal data and structure refinement for **1●2.5CH$_2$Cl$_2$**.

CCDC Number	2382422
Empirical Formula	$C_{41.50}H_{37}Cl_5CoF_3I_2N_2P_3$
Molecular formula	$C_{39}H_{32}CoF_3I_2N_2P_3$, 2.5($CH_2Cl_2$)
Formula weight	1203.62
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit Cell Dimensions	
a (Å)	12.5715(6)
b (Å)	13.3397(6)
c (Å)	15.6881(8)
α (°)	87.496(2)
ß (°)	73.663(2)
γ (°)	62.0810(10)
Volume (Å^3)	2218.77(19)
Z	2
Density (calculated) (g/cm^3)	1.802
Absorption coefficient (mm^{-1})	2.234
F(000)	1180
Crystal size (mm^3)	0.158 x 0.026 x 0.026
Crystal color, habit	orange needle
Final R indices [I > 2σ(I)]	$R_1 = 0.0241$, $wR_2 = 0.0518$
R indices (all data)	$R_1 = 0.0321$, $wR_2 = 0.0553$

Figure S79. Fully labeled ellipsoid representation (50%) of **1•2.5CH$_2$Cl$_2$**.



*Experimental Summary - ($PP^{CF3}P$)Co(η^2-styrene)H (**2**)*

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å). A 0.105 x 0.099 x 0.039 mm piece of an orange plate was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 60 mm using variable exposure time (5s-30s) depending on θ with a scan width of 0.75°. Data collection was 99.9% complete to 25.00° in θ (0.83 Å). A total of 148292 reflections were collected covering the indices, $-29 \leq h \leq 29$, $-14 \leq k \leq 14$, $-40 \leq l \leq 40$. 18568 reflections were found to be symmetry independent, with a R_{int} of 0.0943. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be $Pca2_1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by dual-space method (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon-bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. All other hydrogen atoms (Co-bonded) were located in the difference map. Their relative positions were restrained using DFIX commands and their thermals freely refined. Due to unmodelable solvent disorder, Olex2 solvent mask was used to remove the electron density from the lattice due to the disordered solvent contribution. Solvent appeared to be THF. One void was found to contain approximately 700 electrons, which is consistent with the presence of 16 molecules of THF, two per formula unit. Crystal collected was refined as a racemic twin with an absolute structure parameter of 0.420(15). Crystallographic data are summarized in Table S4.

Table S4. Crystal data and structure refinement for **2●2THF.**

CCDC Number	2382423
Empirical Formula	$C_{55}H_{57}CoF_3N_2O_2P_3$
Molecular formula	$C_{47}H_{41}CoF_3N_2P_3$, 2[C_4H_8O]
Formula weight	986.86
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit Cell Dimensions	
a (Å)	24.0754(15)
b (Å)	12.3634(8)
c (Å)	34.026(2)
α (°)	90
ß (°)	90
γ (°)	90
Volume (Å^3)	10127.9(12)
Z	8
Density (calculated) (g/cm^3)	1.294
Absorption coefficient (mm^{-1})	0.487
F(000)	4128
Crystal size (mm^3)	0.105 x 0.099 x 0.039
Crystal color, habit	orange plate
Final R indices [I > 2σ(I)]	$R_1 = 0.0451$, $wR_2 = 0.0911$
R indices (all data)	$R_1 = 0.0719$, $wR_2 = 0.0986$

Figure S80. Fully labeled ellipsoid representation (50%) of **2**.

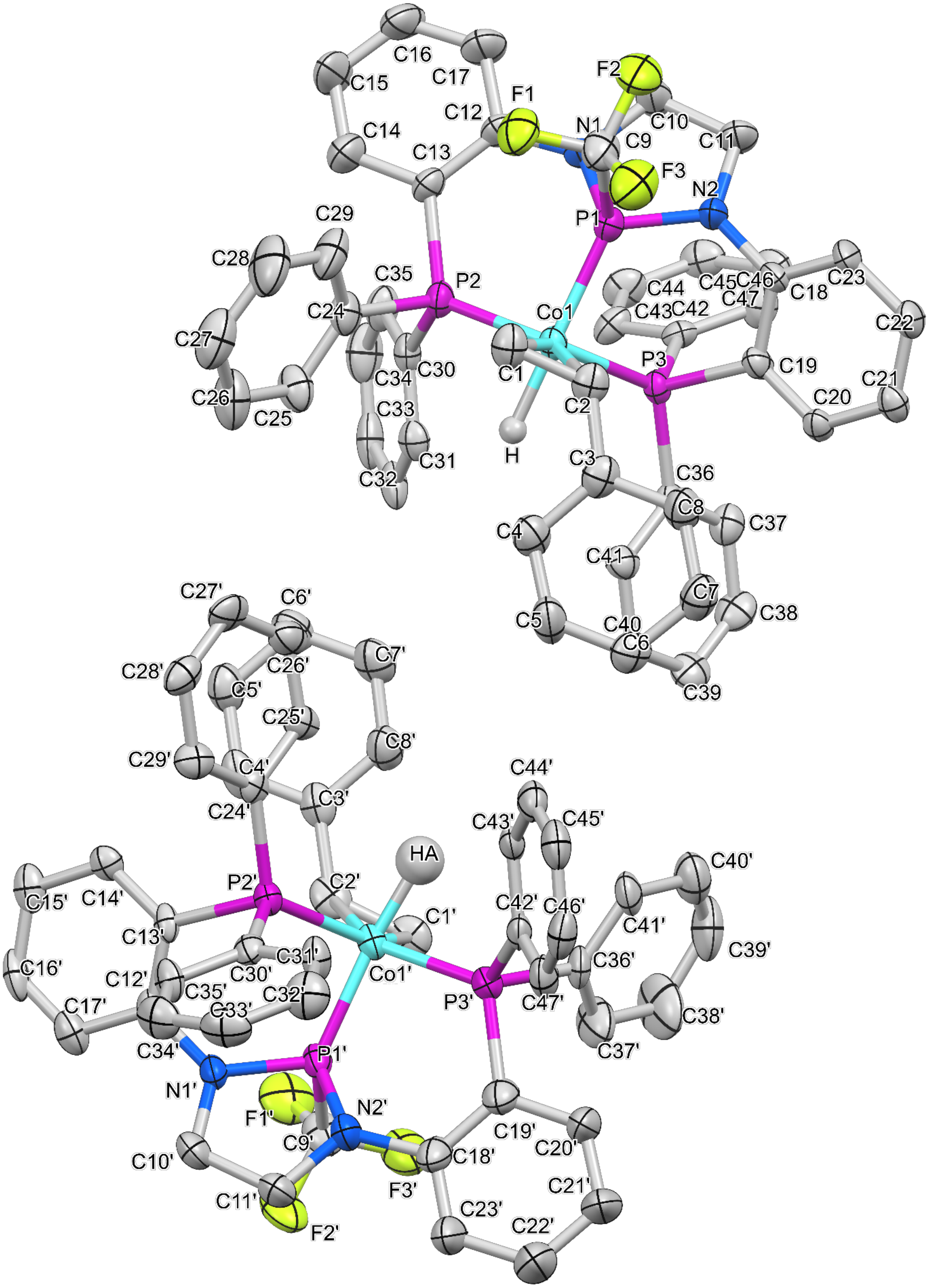
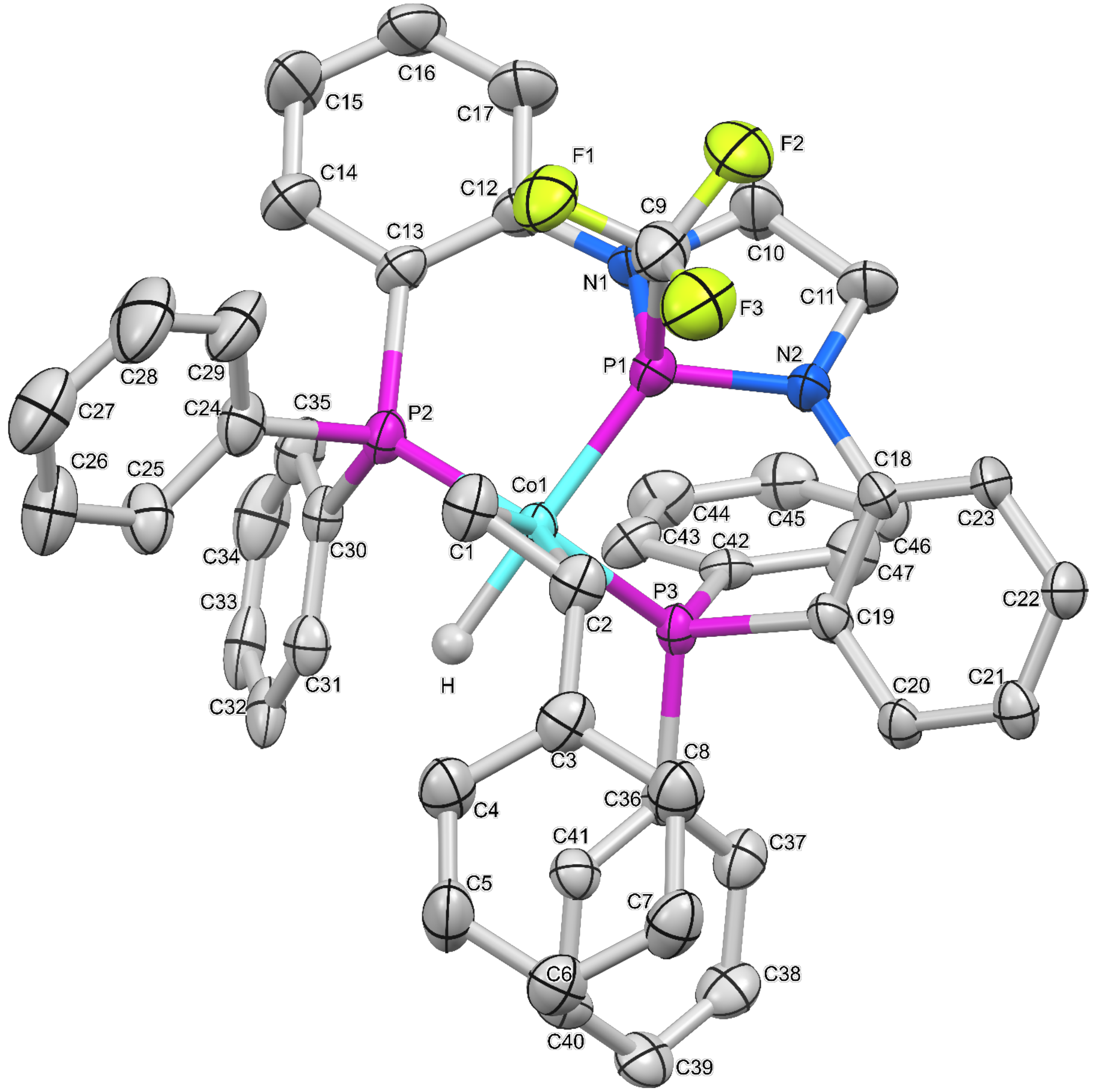


Figure S81. Fully labeled ellipsoid representation (50%) of **2** showing only one of the two molecules in the unit cell.



*Experimental Summary - (PP^{CF3}P)Co(PMe$_3$)H (**3**)*

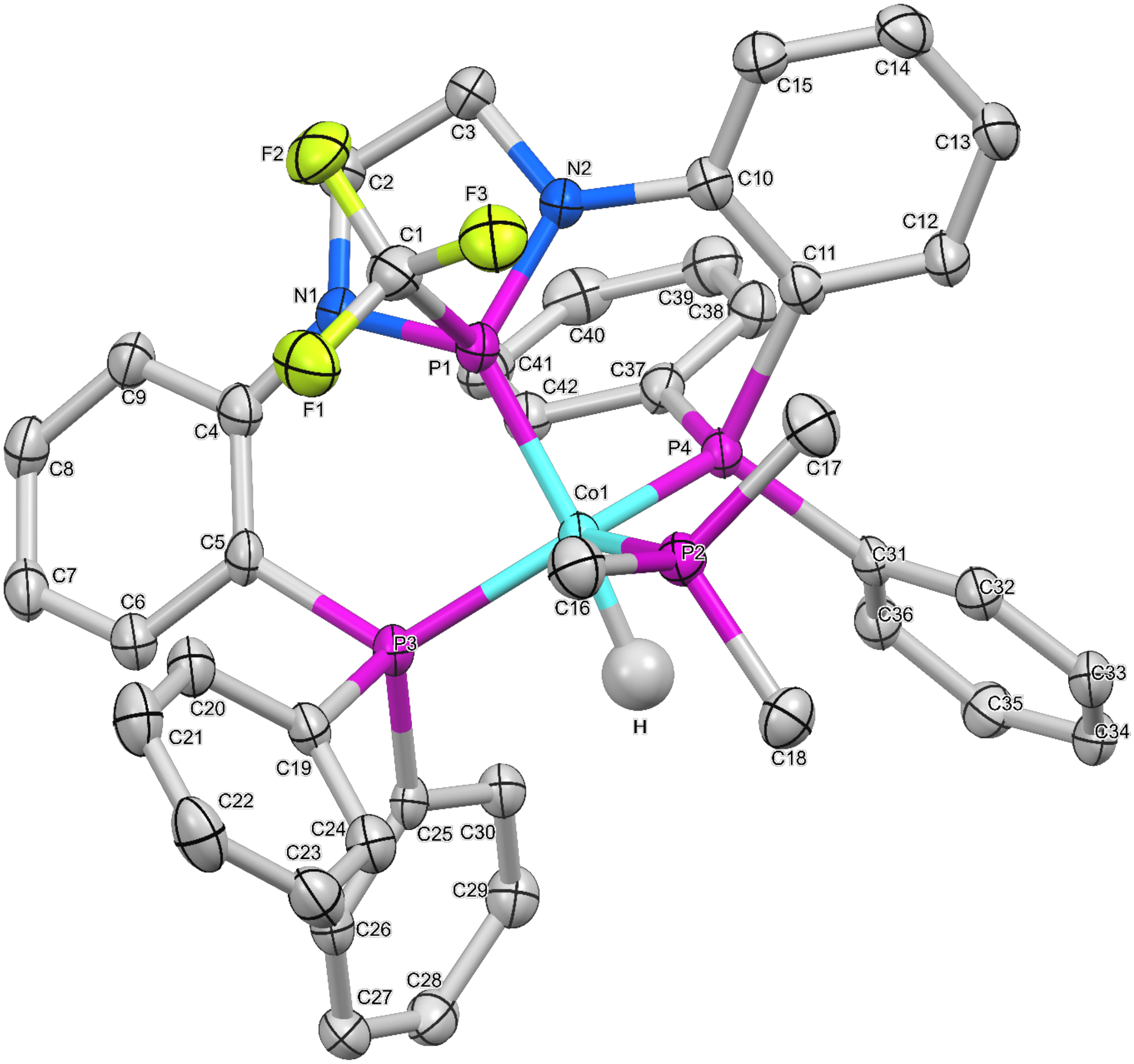
The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K$_\alpha$ radiation (λ = 0.71073 Å). A 0.117 x 0.051 x 0.032 mm piece of an orange needle was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 80 mm using variable exposure time (5s-20s) depending on θ with a scan width of 0.75°. Data collection was 99.9% complete to 25.00° in θ (0.83Å). A total of 244256 reflections were collected covering the indices, $-13 \leq h \leq 13$, $-27 \leq k \leq 27$, $-18 \leq l \leq 18$. 7059 reflections were found to be symmetry independent, with a R_{int} of 0.0943. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the TWINABS software program. Solution by dual-space method (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon-bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. All other hydrogen atoms (Co-bonded) were located in the difference map. Their relative positions were restrained using DFIX commands and their thermals freely refined. Crystallographic data are summarized in Table S5.

Table S5. Crystal data and structure refinement for **3**.

CCDC Number	**2382421**
Empirical Formula	$C_{42}H_{42}CoF_3N_2P_4$
Molecular formula	$C_{42}H_{42}CoF_3N_2P_4$
Formula weight	814.58
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit Cell Dimensions	
a (Å)	11.0941(4)
b (Å)	22.8380(9)
c (Å)	15.1920(6)
α (°)	90
ß (°)	93.182(2)
γ (°)	90
Volume (Å^3)	3843.2(3)
Z	4
Density (calculated) (g/cm^3)	1.408
Absorption coefficient (mm^{-1})	0.661
F(000)	1688
Crystal size (mm^3)	0.117 x 0.051 x 0.032
Crystal color, habit	orange needle
Final R indices [I>2σ(I)]	R1 = 0.0450, wR2 = 0.1092
R indices (all data)	R1 = 0.0519, wR2 = 0.1134

Figure S82. Fully labeled ellipsoid representation (50%) of **3**.



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