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Electronic Supplementary Information

Catalytic Dehydrogenative Borylation of Terminal Alkynes by POCOP-Supported Palladium Complexes

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<u>Table of Contents</u>

I. General Considerations……………………………………………………….S3

II. Synthesis and Characterization…………………………………………………S4

III. Stoichiometric Reactions………………………………………………………….S21

IV. General Procedure for Catalytic Reactions…………………………………..S31

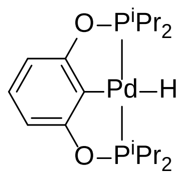
V. Characterization of Alkynylboronates………………………………………..S37

VI. References……………………………………………………………………….S38

General Considerations. Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glove box. C_6D_6 was dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. 1,4-Dioxane, CH_2Cl_2, and $CDCl_3$ were dried with CaH_2 and vacuum transferred to be stored over molecular sieves in an Ar-filled glove box. NMR spectra were recorded on a Varian NMRS 500 (^1H NMR, 499.686 MHz; ^{13}C NMR, 125.659 MHz; ^{31}P NMR, 202.298 MHz) and Varian Inova 400 (^{11}B NMR, 128.185 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 to $\delta = 0$ ppm. For ^{11}B NMR, spectra were referenced externally to $\delta = 0$ ppm by using $BF_3 \cdot Et_2O$. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ). **2**,[1] **2b**,[2] **3**,[3] **4a**,[4] (4,6-ditertbutylPOCOP)PdCl,[5] and **6b**[2] were synthesized according to literature procedures.

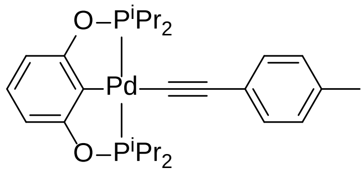
Synthesis and Characterization

Synthesis of (POCOP^{iPr})PdH (2a)



In a Schlenk flask, **2**[1] (362 mg, 0.750 mmol) was dissolved in pyridine and treated with $NaBEt_3H$ (750 μL, 1.0 M solution in toluene). The reaction was stirred for 1 h at room temperature. The volatiles were removed and the resulting solid was dissolved in toluene and passed through a pad of Celite. The volatiles were removed, and the resulting yellow solid was dissolved in minimum of Et_2O and places in a -35 °C freezer. The resulting light yellow crystals were dissolved in Et_2O and placed back into a -35 °C freezer to be recrystallized again. The resulting yellow crystals were washed with cold pentane and dried under vacuum (77 mg, 23%). The spectral data matched that reported in the literature.[4]

Synthesis of $(POCOP^{iPr})Pd(-C{\equiv}C\text{-}p\text{-}C_6H_4Me)$ (2c)



In a Schlenk flask, **2**[1] (227 mg, 0.47 mmol) was dissolved in toluene and treated with NaO^tBu (68 mg, 0.705 mmol) and 4-ethynyltoluene (60 μL, 0.47 mmol). The reaction was stirred overnight and the volatiles removed under vacuum in the morning. The product was extracted with pentane and filtered through a plug of silica and Celite to be recrystallized from pentane at -35 °C to yield beige crystals (180 mg, 68%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 193.0 (s); ^1H NMR (C_6D_6): δ 7.59 (d, 2H, J = 8.0 Hz, Ar-*H*), 6.97 (d, 2H, J = 8.0 Hz, Ar-*H*), 6.93 (t, 1H, J = 8.0 Hz, POCOP-*H*), 6.77 (d, 2H, J = 8.0 Hz, Ar-*H*), 2.18 (m, 4H, PC*H*Me$_2$), 2.07 (s, 3H, Ar-*Me*), 1.30 (m, 12H, PCH*Me*$_2$), 1.11 (apparent q (dvt), 12H, J = 7 Hz, PCH*Me*$_2$). $^{13}C\{^1H\}(C_6D_6)$: δ 167.0 (t, J = 6.7 Hz, *Ar*-OP), 138.4 (t, J = 4.7 Hz, *Ar*-Pd), 134.4 (s), 131.3 (s), 129.1 (s), 128.8 (s), 127.2 (s), 119.2 (s, C≡*C*-tolyl), 108.6 (t, $J_{C\text{-}P}$ = 17.9 Hz, Pd-*C*≡C-tolyl), 105.7 (t, $J_{C\text{-}P}$ = 7.2 Hz, (POCOP)*Ar*-H), 29.5 (t, $J_{C\text{-}P}$ = 12.1 Hz, P*C*HMe$_2$), 21.3 (s, Ar-*Me*), 17.8 (t, $J_{C\text{-}P}$ = 3.8 Hz, PCH*Me*$_2$), 17.0 (s, PCH*Me*$_2$). Elem. Anal. Found (Calculated) for $C_{27}H_{38}O_2P_2Pd$: C, 57.71 (57.61); H, 6.83 (6.80).

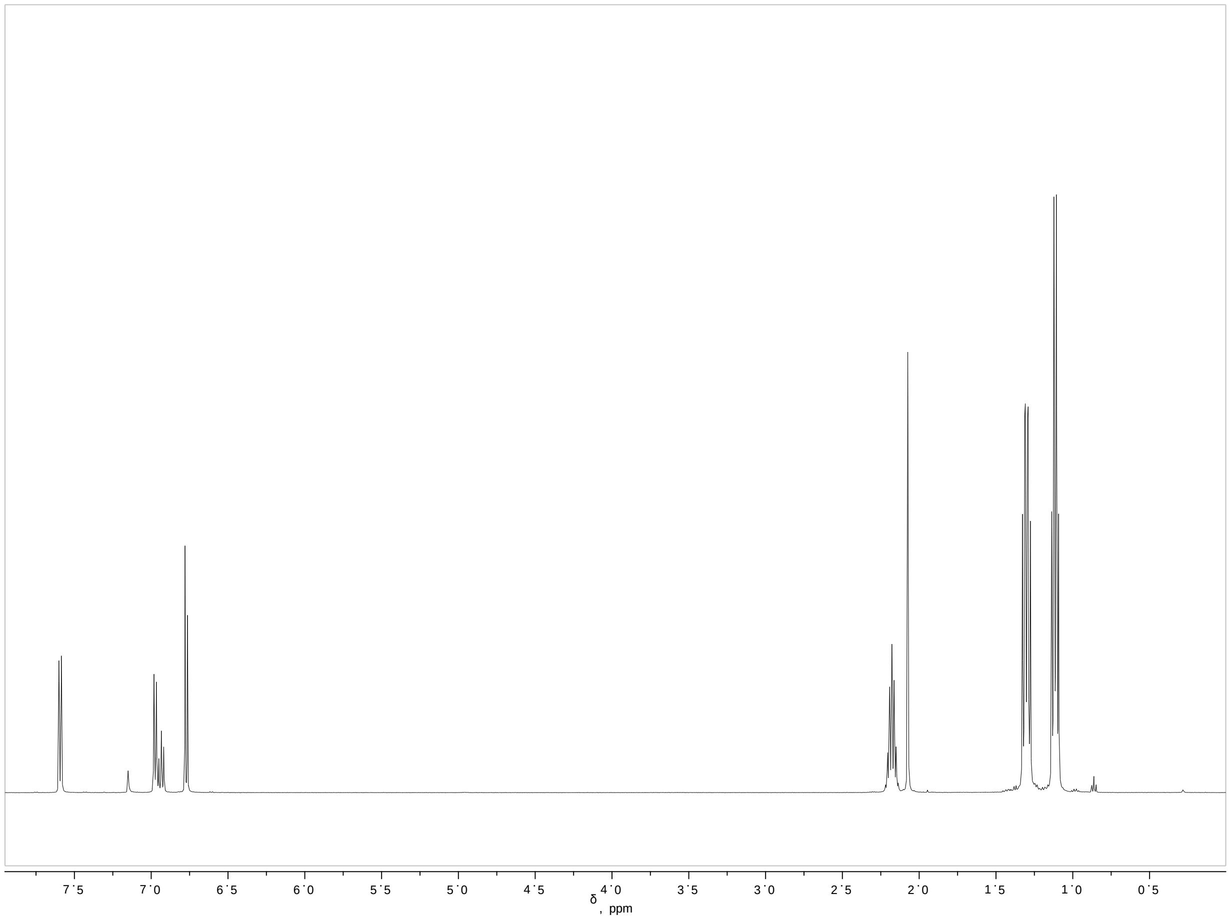
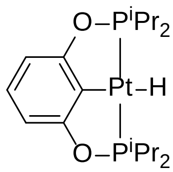


Figure 1: ^{1}H NMR spectrum of **2c** in C_6D_6. Pentane resonances visible at 0.86 and 1.22 ppm.

Synthesis of (POCOP^{iPr})PtH (3a)



3[3] (250 mg, 0.437 mmol) was dissolved in THF and treated with $NaHBEt_3$ (480 μL, 1.0 M toluene) and left to stir for 10 minutes. The volatiles were removed and the product was extracted with pentane and filtered through Celite. The volatiles were removed and the resulting solid was dissolved in a minimum amount of pentane and placed in a -35 °C freezer to recrystallize. **3a** was isolated as a white solid (102 mg, 43% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 190.5 (s, $J_{P\text{-}Pt}$ = 3002 Hz); ^1H NMR (C_6D_6): δ 7.04 (m, 1H, Ar-*H*), 6.49 (m, 2H, Ar-*H*), 2.13 (m, 4H, PC*H*Me$_2$), 1.12 (dvt, *J* = 9 Hz, *J* = 7 Hz, 12H, PCH*Me*$_2$), 1.07 (apparent q (dvt), *J* = 7 Hz, 12H, PCH*Me*$_2$), 1.01 (t, $J_{H\text{-}P}$ = 17 Hz, $J_{H\text{-}Pt}$ = 444 Hz, 1H, Pt-*H*); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 165.3 (t, $J_{C\text{-}P}$ = 6.4 Hz, $J_{C\text{-}Pt}$ = 33 Hz, *Ar*-OP), 144.3 (t, $J_{C\text{-}P}$ = 6.0 Hz, $J_{C\text{-}Pt}$ = 467 Hz, *Ar*-Pt), 127.6 (s, *Ar*-H), 105.0 (t, $J_{C\text{-}P}$ = 6.0 Hz, *Ar*-H), 30.3 (t, $J_{C\text{-}P}$ = 17 Hz, $J_{C\text{-}Pt}$ = 58.5 Hz, P-*C*HMe$_2$), 18.7 (vt, $J_{C\text{-}P}$ = 3.9 Hz, $J_{C\text{-}Pt}$ = 19.0 Hz, PCH*Me*), 17.2 (s, $J_{C\text{-}Pt}$ = 24.7 Hz, PCH*Me*$_2$).

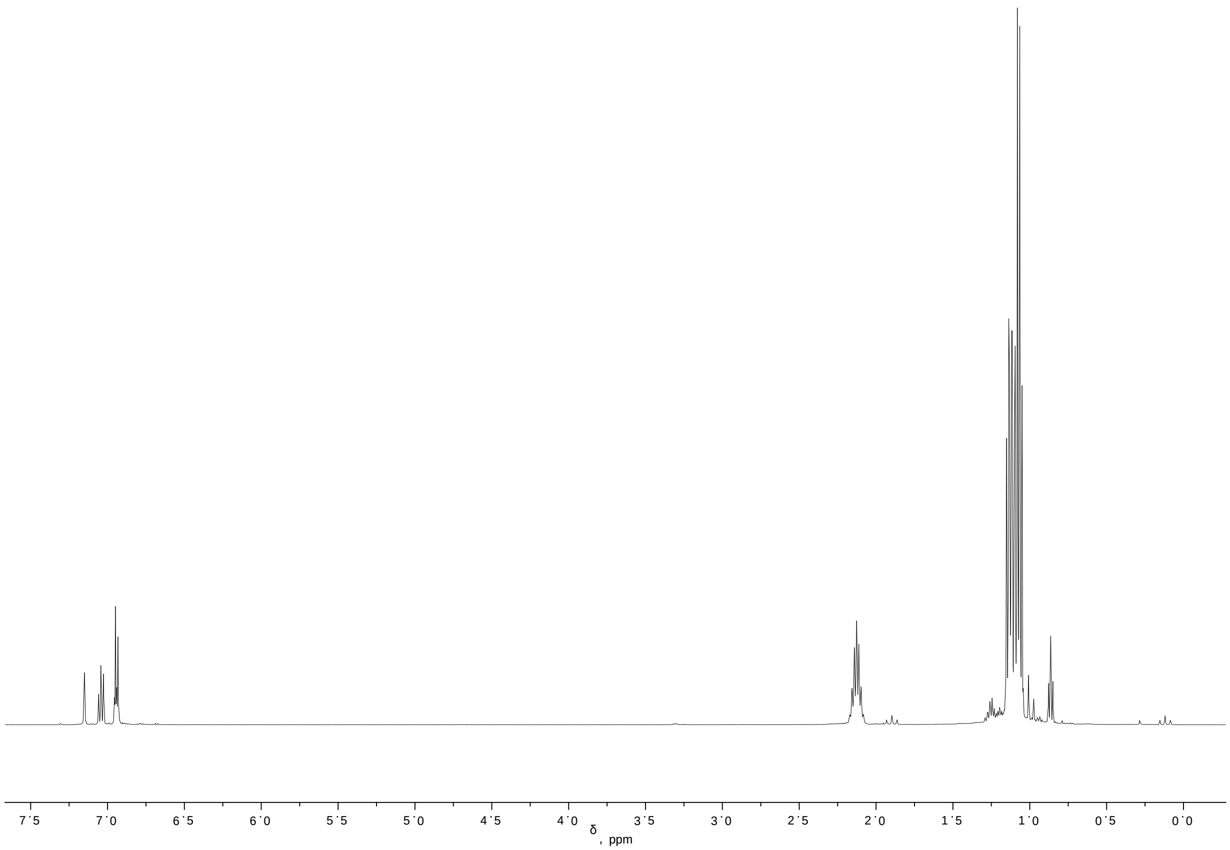
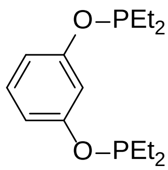


Figure 2: [1]H NMR spectrum of **3a** in C_6D_6. Pentane resonances visible at 0.86 and 1.22 ppm.

Synthesis of (POCOP^{Et})



In a Schlenk flask, resorcinol (443 mg, 4.015 mmol) was dissolved in THF and treated with triethylamine (1.22 grams, 12.1 mmol). Diethylchlorophosphine (1.00 gram, 8.03 mmol) was added dropwise and the solution was left to stir overnight at room temperature. The volatiles were removed under vacuum, and the product was extracted with pentane and filtered through Celite. The volatiles were removed under vacuum to leave a clear oil that was determined to be >95% pure by ^{1}H NMR spectroscopy and could be used in further reactions (1.04 g, 90% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 138.7 (s); ^{1}H NMR (C_6D_6): δ 7.26 (m, 1H, Ar-*H*), 7.01 (t, 1H, *J* = 8.0 Hz, Ar-*H*), 6.88 (m, 2H, Ar-*H*), 1.58 (m, 4H, PCH_2Me), 1.36 (m, 4H, PCH_2Me), 0.99 (dt, 12H, $J_{H\text{-}P}$ = 14.5 Hz, $J_{H\text{-}H}$ = 7.5 Hz, PCH_2*Me*); ^{13}C{^{1}H} (C_6D_6): δ 160.1 (d, $J_{C\text{-}P}$ = 8.2 Hz, *Ar*-OP), 130.2 (s, *Ar*-H), 112.5 (d, $J_{C\text{-}P}$ = 11.2 Hz, *Ar*-H), 109.7 (t, $J_{C\text{-}P}$ = 11.2 Hz, *Ar*-H), 25.4 (d, $J_{C\text{-}P}$ = 18.6 Hz, P*C*H_2), 8.0 (d, $J_{C\text{-}P}$ = 13.2, PCH_2*Me*).

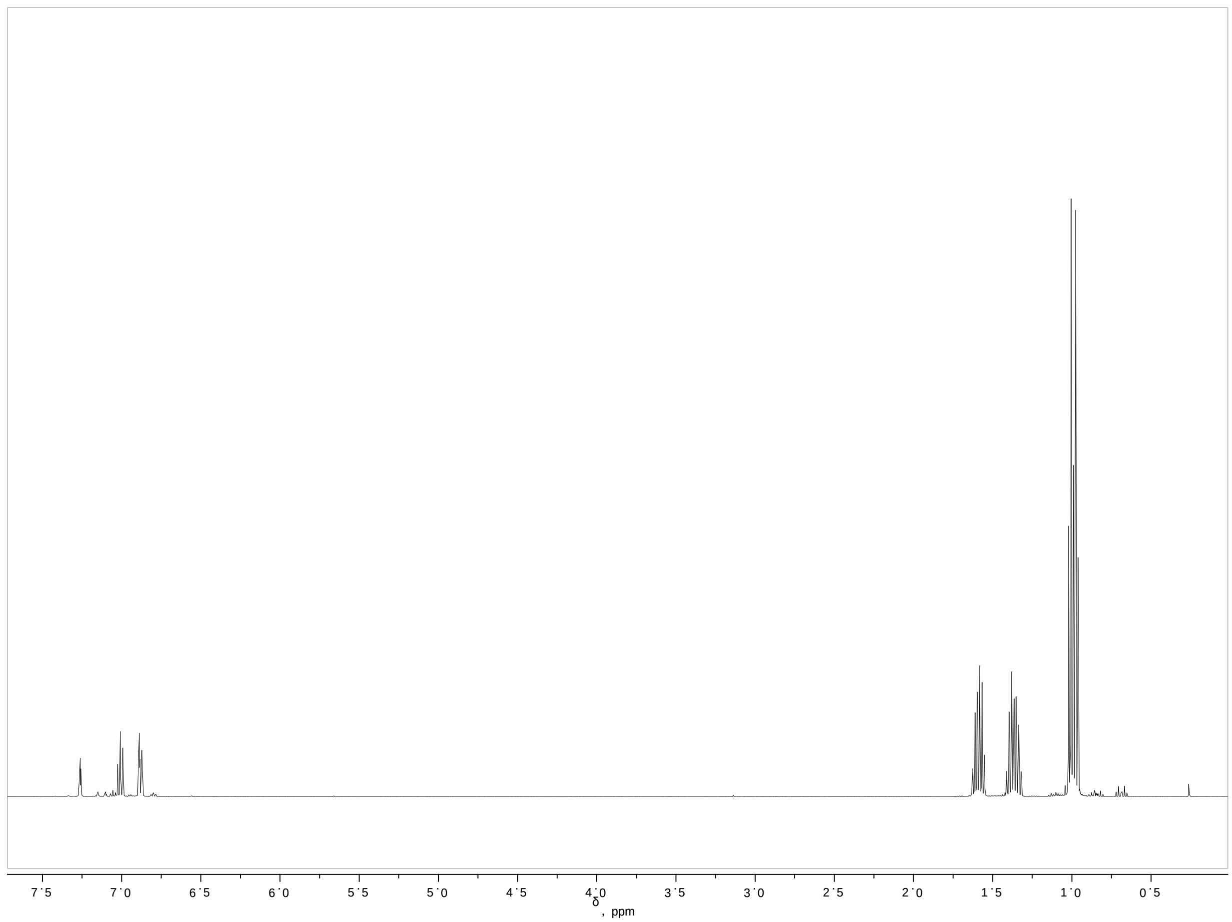
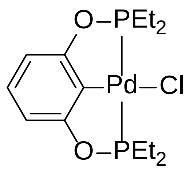


Figure 3: ^{1}H NMR spectrum of (POCOP^{Et}) in C_6D_6.

(POCOP^{Et})PdCl (5)



In a Schlenk flask, (POCOP^{Et}) (380 mg, 1.33 mmol) was refluxed in toluene with Pd(COD)Cl_2 (379 mg, 1.33 mmol) overnight. The volatiles were removed from the reaction mixture, which was then dissolved in dichloromethane and passed through a pad of silica and Celite. The volatiles were removed under vacuum and the resulting solid was washed with diethyl ether and pentane to yield a white solid (438 mg, 77% Yield). $^{31}P\{^1H\}$ NMR (C_6D_6): 177.8 (s); ^1H NMR (C_6D_6): δ 6.86 (t, 1H, J = 8.5 Hz, Ar-*H*), 6.67 (d, 2H, J = 8.0 Hz, Ar-*H*), 1.76 (m, 4H, PCH_2Me), 1.67 (m, 4H, PCH_2Me), 1.08 (m, 12H, PCH_2*Me*); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.5 (t, $J_{C\text{-}P}$ = 7.0 Hz, *Ar*-OP), 129.8 (t, $J_{C\text{-}P}$ = 3.0 Hz, *Ar*-Pd), 128.4 (s, *Ar*-H), 106.3 (t, $J_{C\text{-}P}$ = 8 Hz, *Ar*-H), 24.0 (t, $J_{C\text{-}P}$ = 13 Hz, P*C*H_2Me), 7.6 (s, PCH_2*Me*).

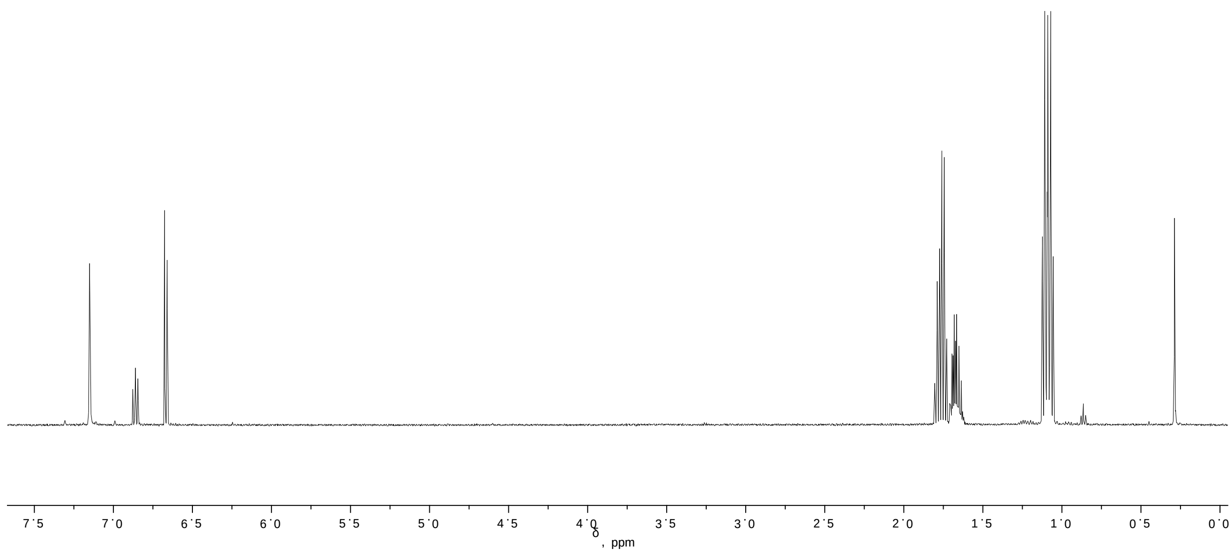
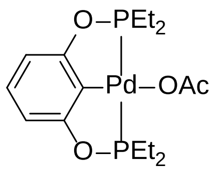


Figure 4: ^{1}H NMR spectrum of **5** in C_6D_6. Pentane resonances visible at 1.22 and 0.86 ppm. Silicone grease is visible at 0.28 ppm.

(POCOP^{Et})Pd(OAc) (5b)



5 (185 mg, 0.433 mmol) was dissolved in toluene in a culture tube and treated with AgOAc (80 mg, 0.476 mmol) and stirred overnight in the dark. The solution was filtered through a plug of silica and Celite and the volatiles were removed under vacuum. The product was recrystallized from pentane to yield a white crystalline solid (137 mg, 70%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 172.6 (s); ^1H NMR (C_6D_6): δ 6.90 (m, 1H, Ar-*H*), 6.68 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 2.26 (s, O*Ac*), 2.14 (m, 4H, PCH_2Me), 1.84 (m, 4H, PCH_2Me), 1.12 (m, 12H, PCH_2*Me*); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 175.0 (t, $J_{C\text{-}P}$ = 2.3 Hz, O*Ac*), 166.7 (t, $J_{C\text{-}P}$ = 7.1 Hz, *Ar*-OP), 129.0 (s), *Ar*-Pd signal not present (obscured by C_6D_6), 106.1 (s), 25.4 (t, $J_{C\text{-}P}$ = 14.5 Hz, P*C*H_2Me), 22.3 (s, O*Ac*), 8.4 (s, PCH_2*Me*). Elem. Anal. Found (Calculated) for $C_{16}H_{26}O_4P_2Pd$: C, 42.59 (42.63); H, 5.89 (5.81).

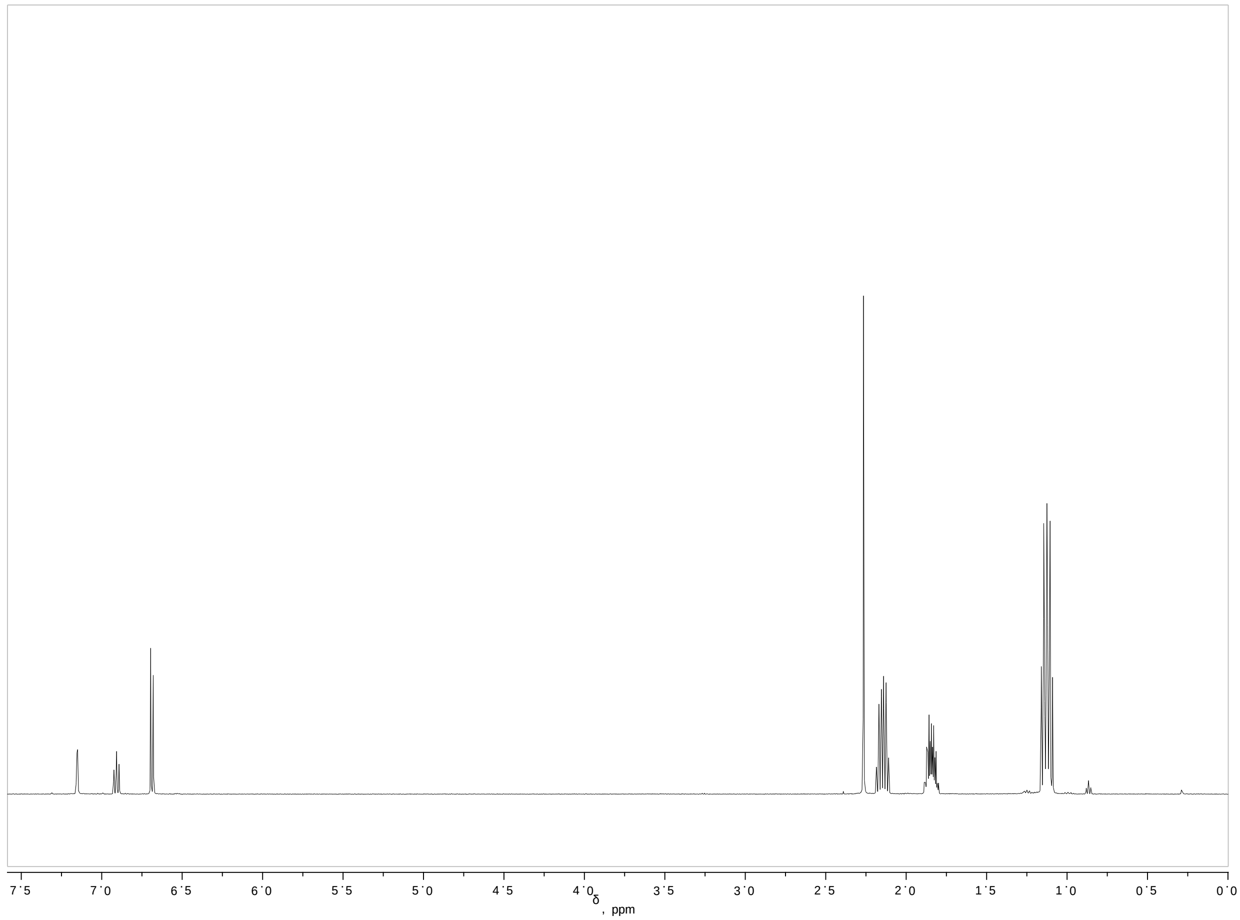
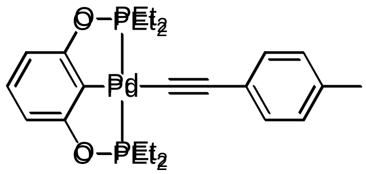


Figure 5: ^{1}H NMR spectrum of **5b** in C_6D_6. Resonances of pentane visible at 1.22 and 0.87 ppm. Silicone grease resonance visible at 0.28 ppm.

Synthesis of $(POCOP^{Et})Pd(C\equiv C\text{-}p\text{-}C_6H_4Me)$ (5c)



In a Schlenk flask, **5** (111 mg, 0.26 mmol) was dissolved in toluene and was treated with NaO^tBu (37 mg, 0.39 mmol), and 4-ethynyltoluene (33 ml, 0.26 mmol). The reaction was stirred overnight and the volatiles were removed under vacuum. The product was extracted in benzene and filtered through Celite. The volatiles were removed and the product was recrystallized from pentane in a -35 °C freezer (94 mg, 71%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 179.5 (s); ^1H (C_6D_6): δ 7.63 (d, J = 8.0 Hz, 2H, Ar-*H*), 6.96 (d, J = 8.0 Hz, 2H, Ar-*H*), 6.95 (t, J = 8.0 Hz, 1H, Ar-*H*), 6.78 (d, J = 8.0 Hz, 2H, Ar-*H*), 2.06 (s, 3H, Ar-*Me*), 1.81 (m, 8H, $P(CH_2Me)_2$, 1.12 (app. pent. (overlapping tvt), J = 7.5 Hz, 12H, $P(CH_2CH_3)_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 166.2 (t, $J_{C\text{-}P}$ = 7.3 Hz, *Ar*-OP), 139.1 (t, $J_{C\text{-}P}$ = 5.2, *Ar*), 134.5 (s), 131.4 (s), 129.1 (s), 128.4 (s), 127.0 (s), 117.0 (s, C≡*C*-tolyl), 109.2 (t, $J_{C\text{-}P}$ = 18.1 Hz, *C*≡C-tol), 106.1 (t, $J_{C\text{-}P}$ = 18.1 Hz, *Ar*), 24.7 (t, $J_{C\text{-}P}$ = 13.5 Hz, PCH_2Me), 21.3 (s, Ar-*Me*), 8.0 (s, PCH_2Me). Elem. Anal. Found (Calculated) for $C_{23}H_{30}O_2P_2Pd$: C, 54.29 (54.50); H, 5.79 (5.97).

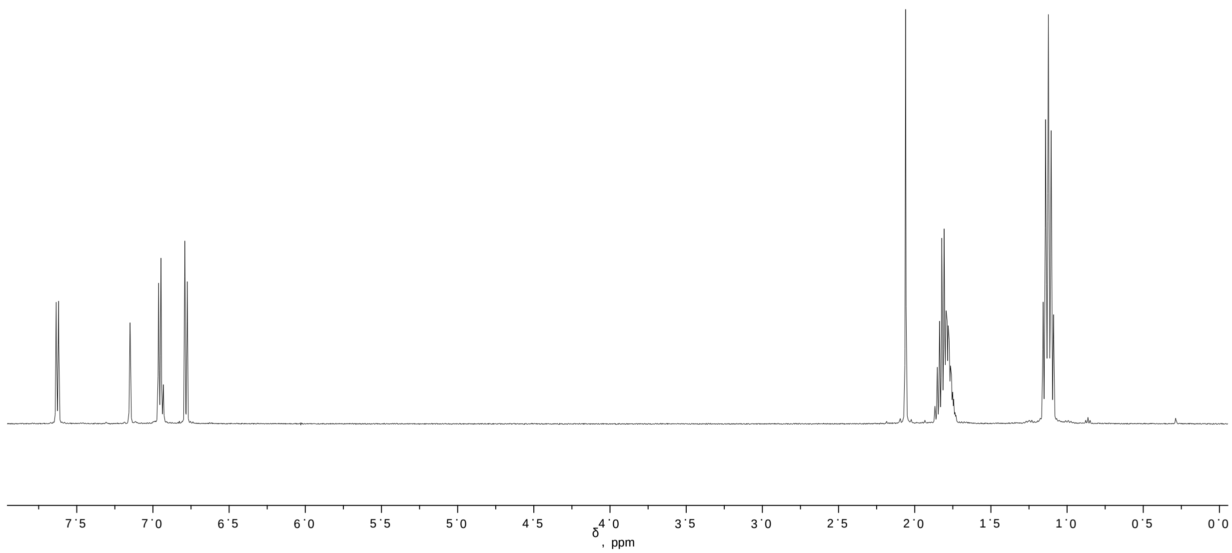
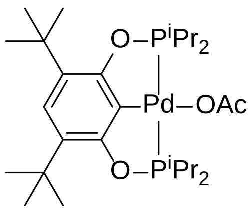


Figure 6: ^{1}H NMR spectrum of **5c** in C_6D_6. Resonances of pentane visible at 1.22 and 0.87 ppm. Silicone grease is also visible at 0.28 ppm.

Synthesis of (4,6-ditertbutylPOCOP)Pd(OAc) (7b)



In a culture tube, (4,6-ditertbutylPOCOP)PdCl[5] (155 mg, 0.26 mmol) was dissolved in toluene and treated with Ag(OAc) (48 mg, 0.29 mmol) and stirred overnight. The reaction mixture was passed through a pad of silica and Celite and stripped down. The product was recrystallized from isooctane as white crystals (72 mg, 44% yield). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 185.1 (s); ^{1}H NMR (C_6D_6): δ 7.26 (s, 1H, Ar-*H*), 2.40 (m, 4H, P(C*H*Me$_2$)$_2$), 2.28 (s, 3H, O*Ac*), 1.46 (s, 18H, ArC*Me*$_3$), 1.30 (apparent q (dvt), 12H, J = 9.0 Hz, PCH*Me*$_2$), 1.16 (apparent q (dvt), 12H, J = 7.0 Hz, PCH*Me*$_2$); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 174.8 (s, O*Ac*), 162.7 (t, $J_{C\text{-}P}$ = 6.2 Hz, *Ar*-OP), 130.9 (t, $J_{C\text{-}P}$ = 4.2 Hz, *Ar*-Pd), 127.4 (t, $J_{C\text{-}P}$ = 5.9 Hz, *Ar*-^{t}Bu), 123.3 (s, *Ar*-H), 34.8 (s, Ar-*C*Me$_3$), 30.4 (s, O*Ac*), 29.8 (t, $J_{C\text{-}P}$ = 12.0 Hz, P*C*HMe$_2$), 17.9 (t, $J_{C\text{-}P}$ = 3.8 Hz, PCH*Me*$_2$), 17.3 (s, ArC*Me*$_3$). Elem. Anal. Found (Calculated) for $C_{28}H_{50}O_4P_2Pd$: C, 54.24 (54.32); H, 8.06 (8.14).

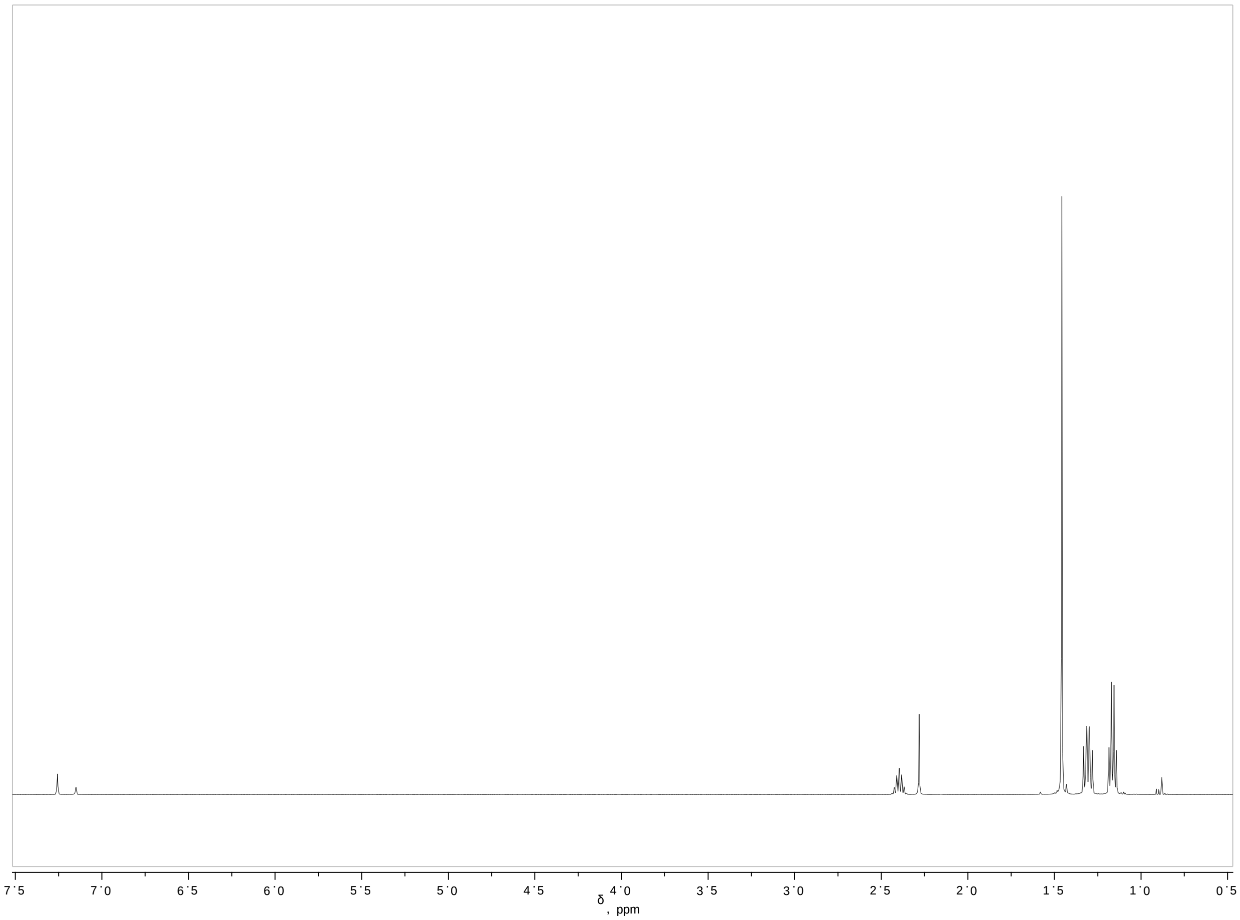
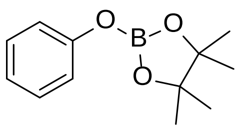


Figure 7: ^{1}H NMR spectrum of **7b** in C_6D_6. Residual isooctane resonances are visible at 1.60, 1.10, 0.91, and 0.88 ppm.

Synthesis of PhOBpin[6]



In a J. Young tube, phenol (32 mg, 0.34 mmol) was dissolved in C_6D_6 and treated with pinacolborane (49 μL, 0.34 mmol). Hydrogen gas was produced immediately upon mixing. Analysis by ^{1}H NMR spectroscopy showed that the reaction was completed within minutes. The reaction mixture was transferred to a flask, and the volatiles were removed under vacuum to yield a fine white powder (54 mg, 72%). ^{1}H NMR (C_6D_6): 7.22 (d, J = 8 Hz, 2H), 7.06 (m, 2H), 6.83 (t, J = 7.5 Hz, 1H), 1.01 (s, 12H); ^{13}C{^{1}H} NMR (C_6D_6): 154.4, 129.6, 123.3, 120.1, 83.3, 24.6; ^{11}B{^{1}H} NMR (C_6D_6): 21.9 (s).

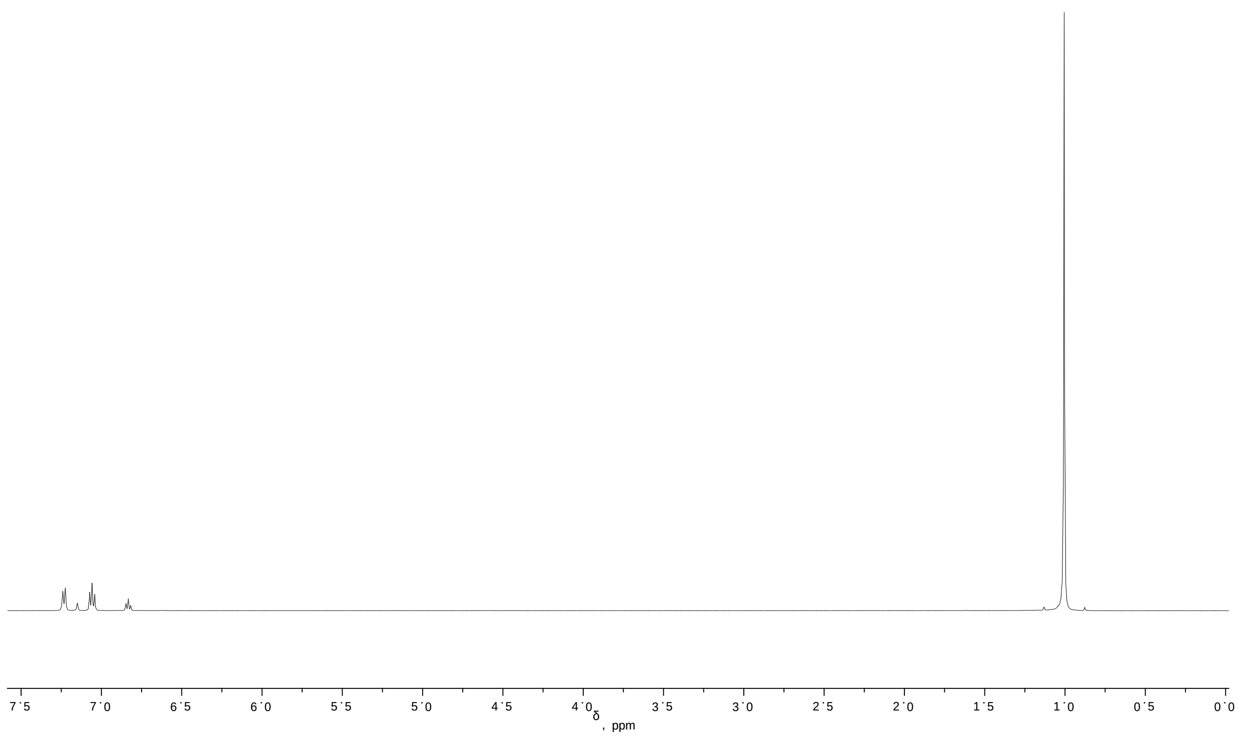


Figure 8: ^{1}H NMR spectrum of PhOBpin in C_6D_6.

Stoichiometric Reactions

Treatment of 2a with 4-ethynyltoluene

2a (15 mg, 0.033 mmol) was dissolved and treated with 4-ethynyltoluene (4 μL, 0.033 mmol). Analysis by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy <15 minutes after the addition of 4-ethynyltoluene showed complete conversion to **2c** by ^{31}P{^{1}H} NMR spectroscopy and ^{1}H NMR spectroscopy showed the evolution of H_2.

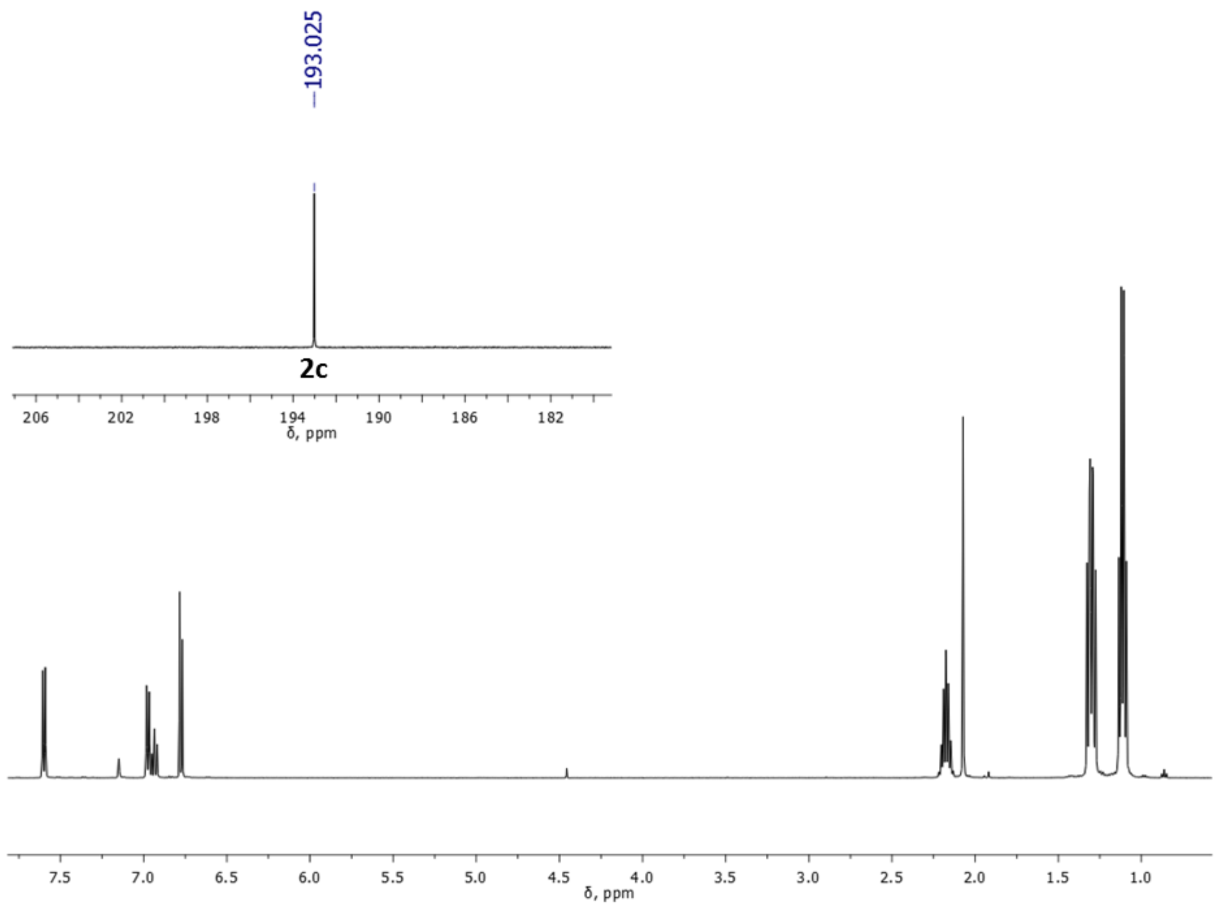


Figure 9: ^{1}H NMR spectrum of the treatment of **2a** with 1 eq. of 4-ethynyltoluene. Inset is the ^{31}P{^{1}H} NMR spectrum of the same reaction.

Treatment of 2b with pinacolborane

2b (35 mg, 0.069 mmol) was dissolved in C_6D_6 and treated with pinacolborane (10 µL, 0.069 mmol), which immediately made the solution turn from clear to a light yellow. Analysis by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy <15 minutes after the addition of pinacolborane showed 100% conversion to **2a** and the appearance of two new singlets at 1.597 ppm (3H) and 1.025 ppm (12H) showing the formation of pinBOAc.

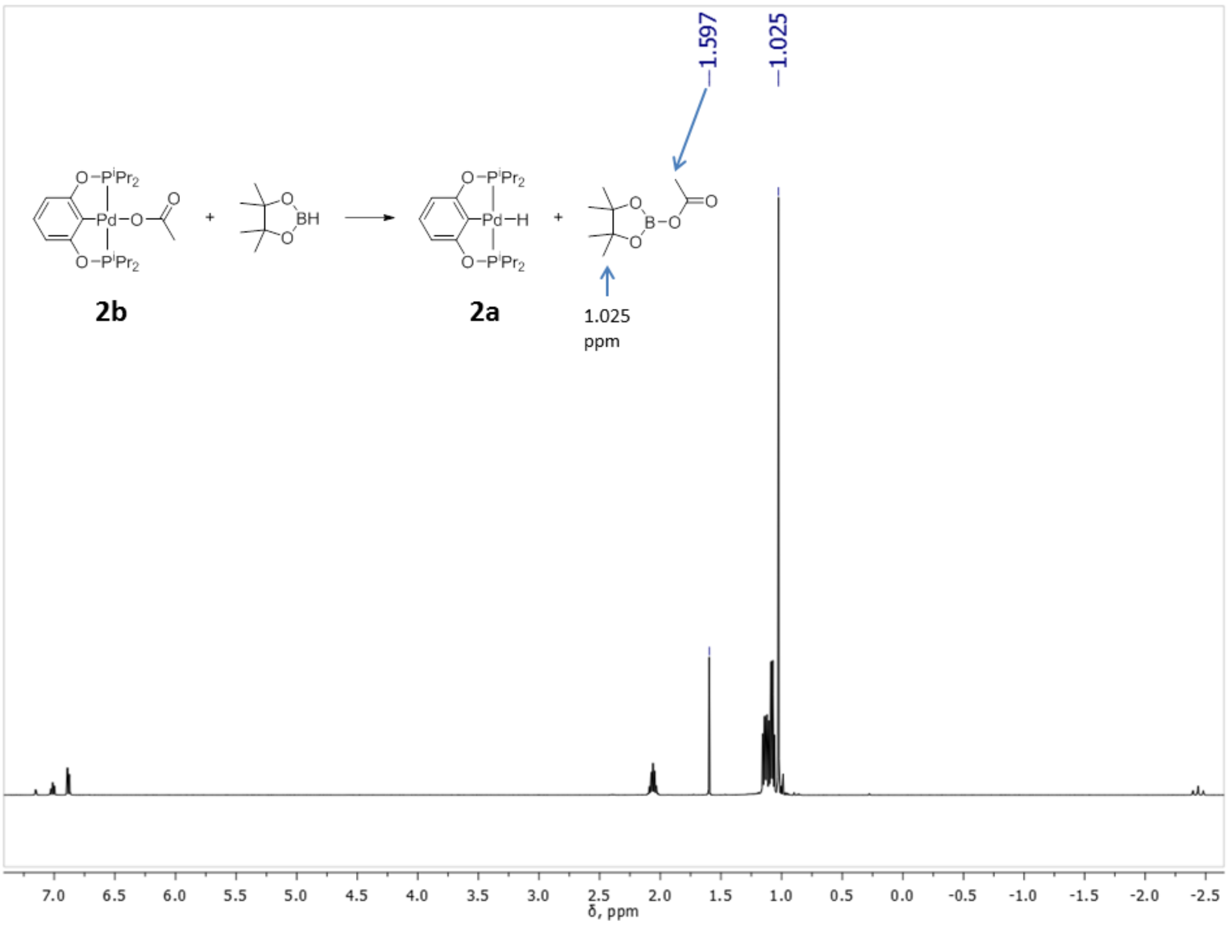


Figure 10: ^{1}H NMR spectrum resulting from the treatment of **2b** with pinacolborane in C_6D_6.

Treatment of 2b with 4-ethynyltoluene

2b (40 mg, 0.079 mmol) was treated with 4-ethynyltoluene (10 μL, 0.079 mmol). Within 23 h at room temperature, a 3:2 **2b**:**2c** equilibrium was established as seen by $^{31}P\{^{1}H\}$ NMR spectroscopy. ^{1}H NMR spectroscopy shows the formation of acetic acid from the characteristic broad singlet at 13.25 ppm. Addition of 1 equivalent of pinacolborane (11.5 μL, 0.079 mmol) consumed the acetic acid and gave immediate production of PinBOAc and **2a**, which subsequently reacted with free alkyne resulting in >98% conversion to **2c** by $^{31}P\{^{1}H\}$ NMR spectroscopy.

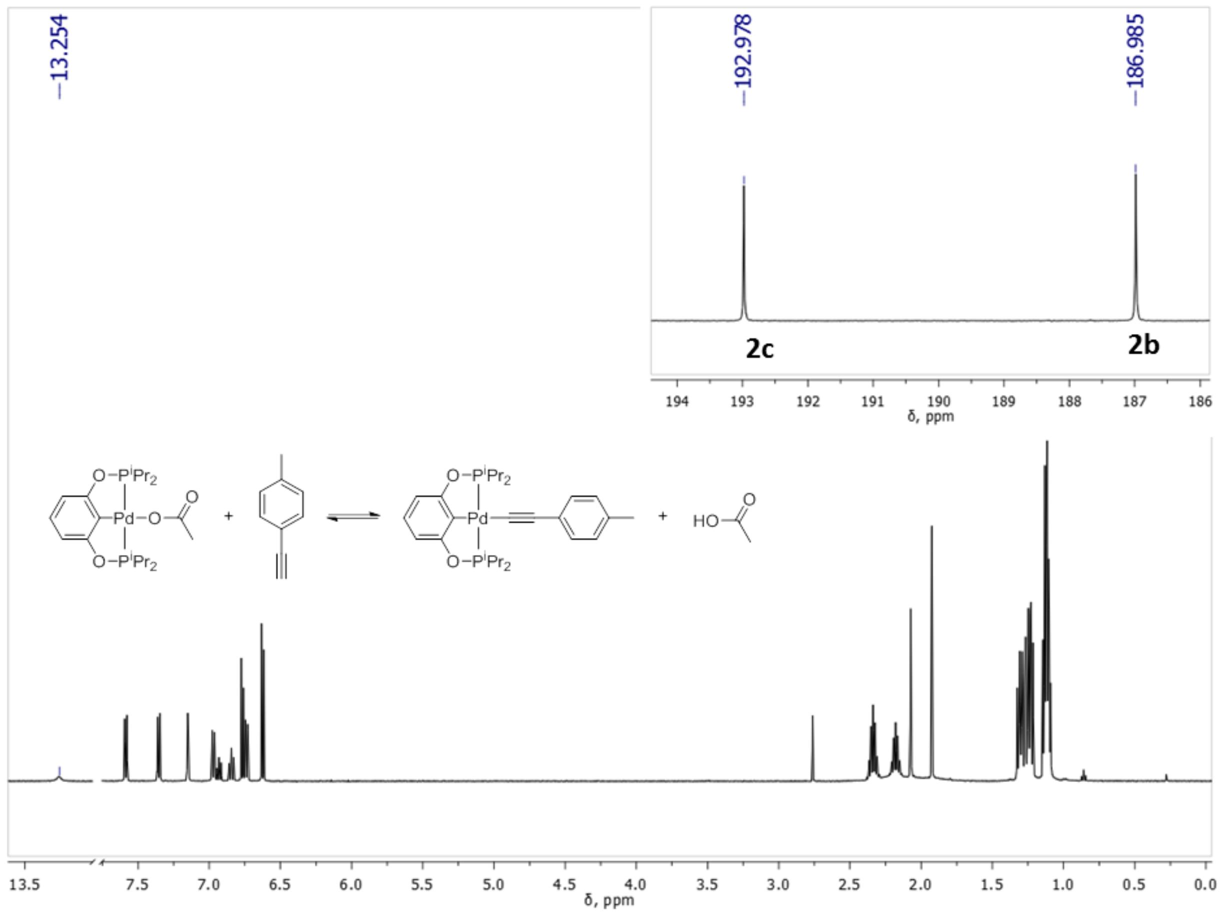


Figure 11: ^{1}H NMR spectrum resulting from the treatment of **2b** with 4-ethynyltoluene after 23 h at room temperature in C_6D_6. Inset is the $^{31}P\{^{1}H\}$ NMR spectrum of the same mixture.

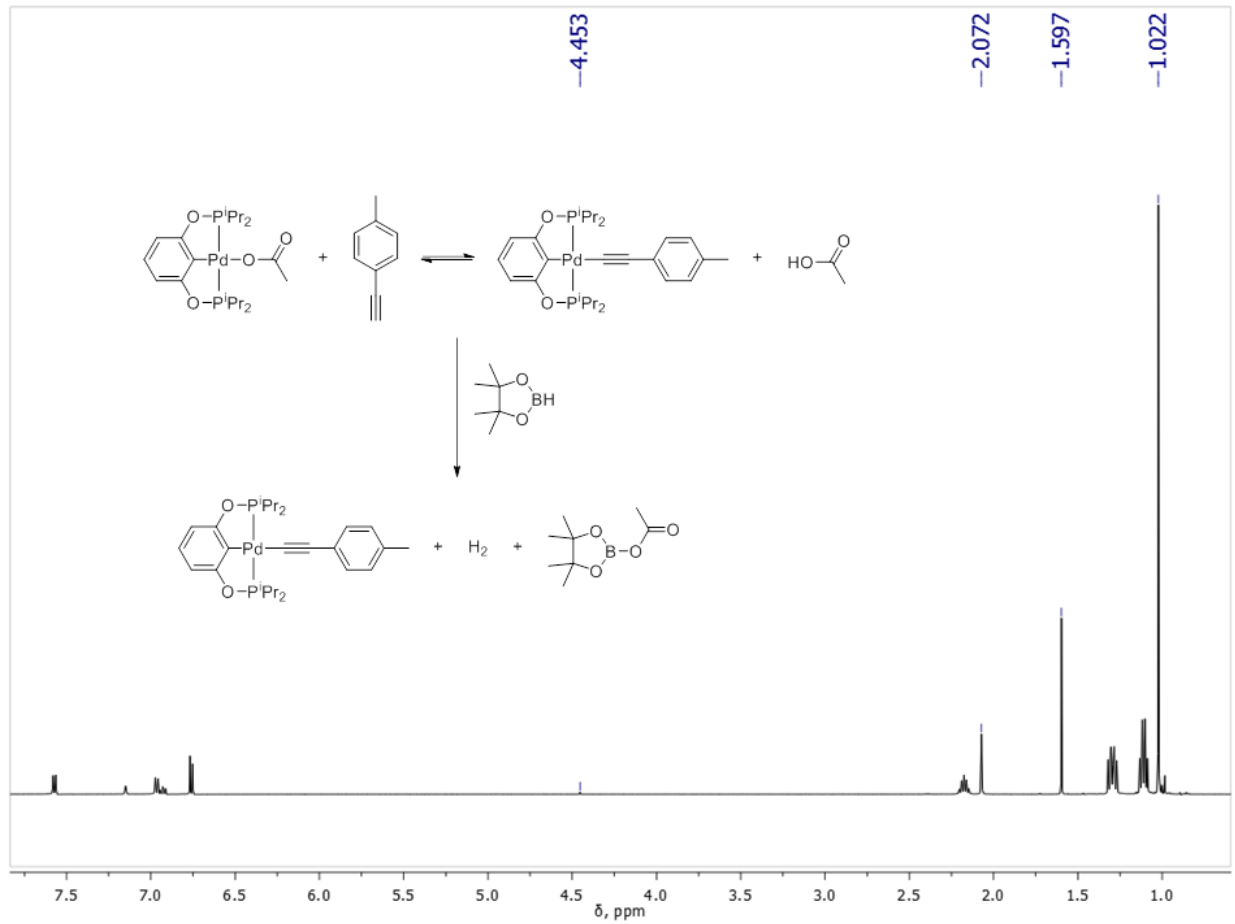


Figure 12: ^{1}H NMR spectrum resulting from the treatment of the equilibrium mixture of **2b** and **2c** with 1 eq. of pinacolborane.

Treatment of 2c with pinacolborane

2c (15 mg, 0.027 mmol) was dissolved in C_6D_6 and treated with pinacolborane (20 μL, 0.14 mmol) and heated at 80 °C. After 5 h, the reaction showed ~50% conversion to **2a** by $^{31}P\{^1H\}$ NMR spectroscopy, and ^1H NMR spectroscopy showed formation of **A**. However, further heating of the reaction mixture led to the formation of other products visible by $^{31}P\{^1H\}$ NMR spectroscopy at 198.5 (s), 185.1 (s), 183.6 (s) ppm.

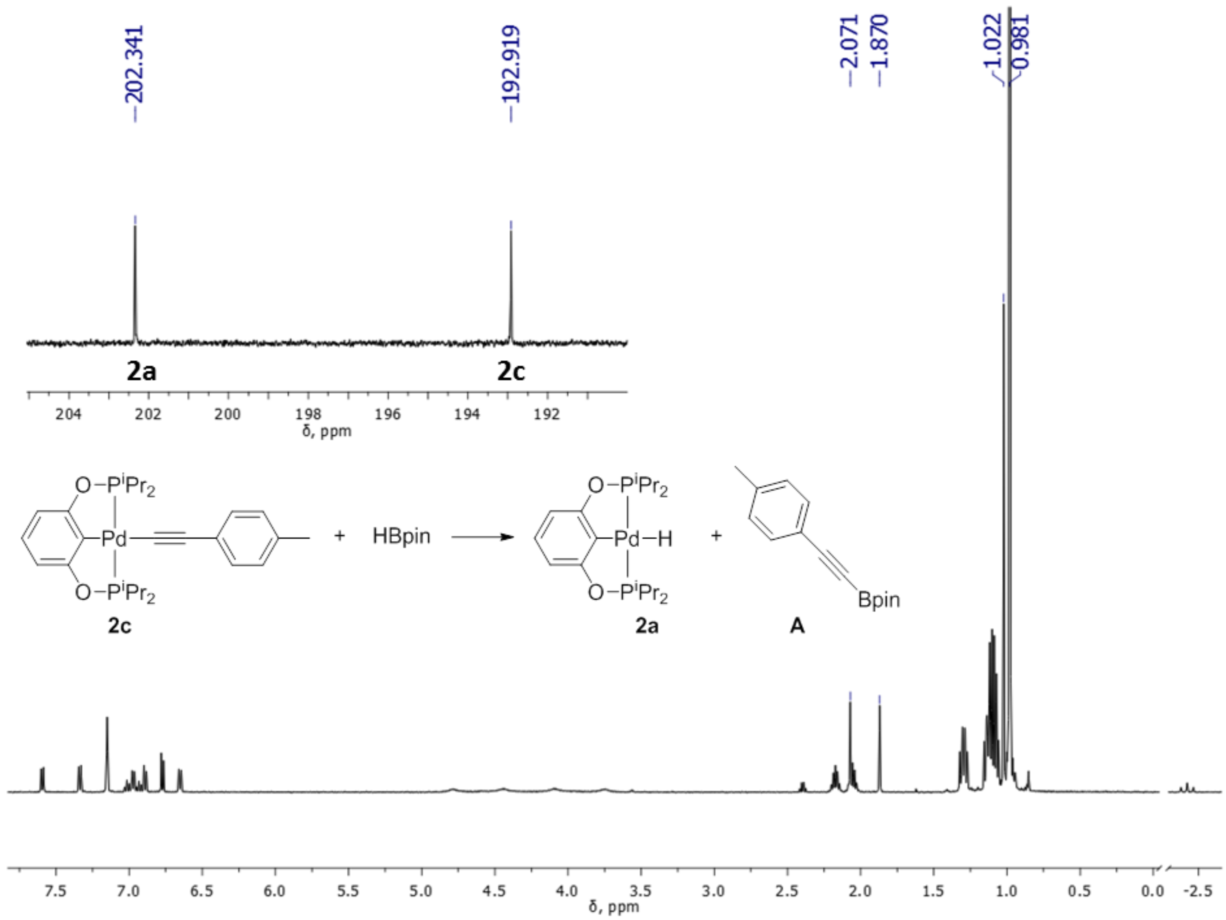


Figure 13: ^1H NMR spectrum resulting from 5 h of heating **2c** and 5 eq. of HBpin in C_6D_6 for 5 h. Inset is the $^{31}P\{^1H\}$ NMR of the same mixture.

Treatment of 2a with 4-Me-C_6H_4-C≡C-Bpin (A)

2a (14 mg, 0.031 mmol) was dissolved in C_6D_6 and treated with **A** (8 mg, 0.03 mmol) and heated at 80 °C. After 3 h, the sample was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed 16% conversion to **5c**, pinacolborane was also visible by ^1H NMR spectroscopy. After 6 h at 80 °C, $^{31}P\{^1H\}$ NMR analysis showed 23% conversion to **2c** and 8% formation of a product at 185.1 ppm. Heating the sample for 4 days at 80 °C showed a distribution of 8% **2a**, 21% **2c**, and 71% accounting for compounds **2d** and **2e** (62% 185.1 ppm, and 9% 183.6 ppm) by $^{31}P\{^1H\}$ NMR integration. Analysis of the mixtures by ^1H NMR spectroscopy showed two new singlets presumed to be olefinic protons at 7.39 ppm and 6.42 ppm. After HCl (50 μL, 37%) was added to the J. Young tube, analysis by $^{31}P\{^1H\}$ NMR spectroscopy showed complete conversion of phosphorus-containing compounds to **2**. The volatiles were removed under vacuum and the products extracted with diethyl ether. The ether solution was dried over magnesium sulfate, decanted, and the volatiles were removed under vacuum. The resulting solid was dissolved in $CDCl_3$, and ^1H NMR spectroscopy showed the presence of (Z)-(4-methylstyryl)Bpin.[7]

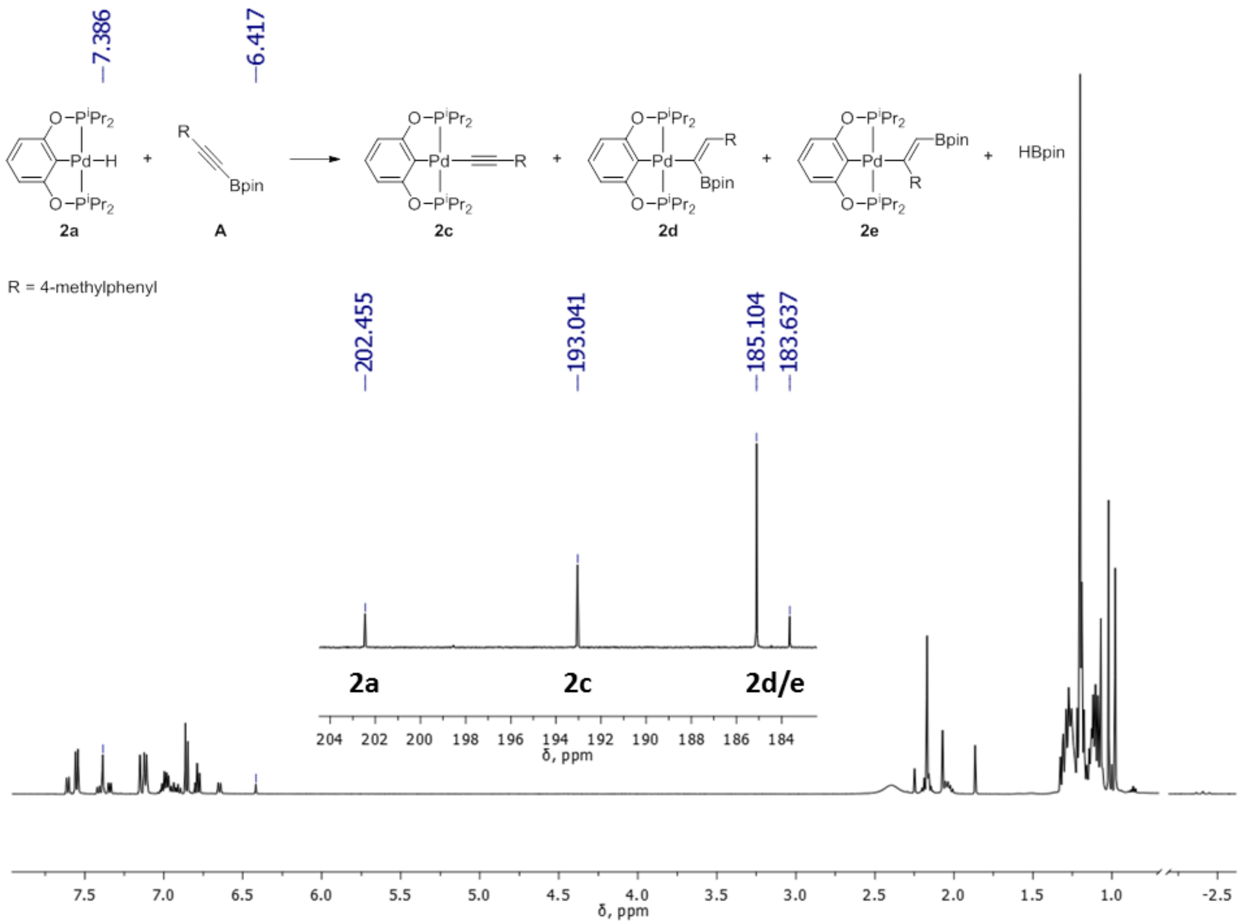


Figure 14: ^{1}H NMR spectrum of the treatment of **2a** with **A** after 4 days at 80 °C. Inset is the ^{31}P{^{1}H} NMR spectrum of the same mixture. Resonances at 185.1 and 183.6 ppm in the ^{31}P{^{1}H} NMR spectrum are expected to be products **2d** and **2e**, but which signal corresponds to which compound has not been determined.

Treatment of 5b with 4-ethynyltoluene

5b (36 mg, 0.079 mmol) was dissolved in C_6D_6 and treated with 4-ethynyltoluene (10 µL, 0.079 mmol). Within 30 minutes at room temperature, the reaction mixture reached an equilibrium mixture of 15:85 **5c**:**5b**, observed by ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR spectroscopy showed that free acetic acid was present in the reaction mixture. **5b** has been shifted in the $^{31}P\{^1H\}$ NMR spectrum to 173.3 ppm due to an interaction with free acetic acid in solution. Further treatment with pinacolborane forms a black solution and decomposition of the palladium complex.

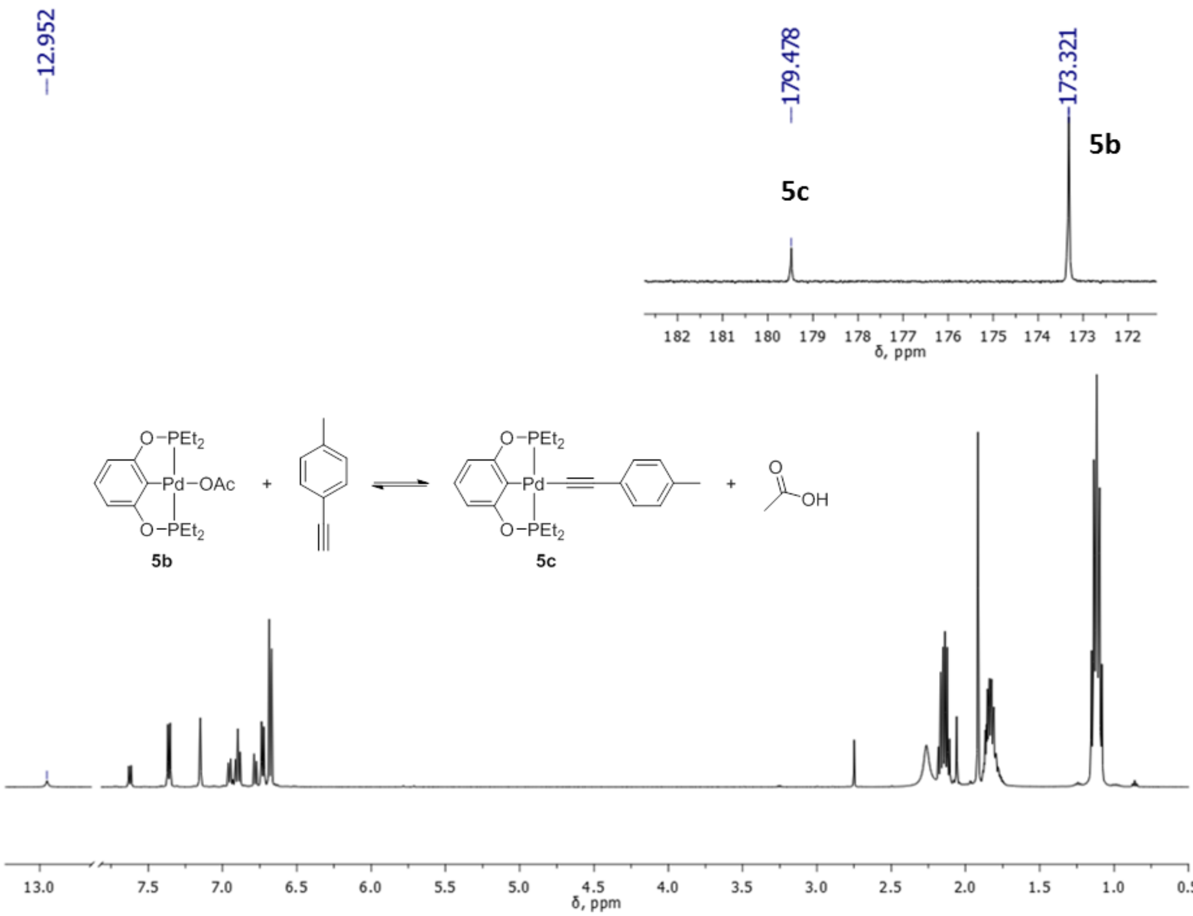


Figure 15: ^{1}H NMR spectrum resulting from the treatment of **5b** with 4-ethynyltoluene after 30 min at room temperature in C_6D_6. Inset is the $^{31}P\{^1H\}$ NMR spectrum of the same mixture.

Treatment of 5b with acetic acid

5b (9 mg, 0.02 mmol) was dissolved in C_6D_6 and treated with acetic acid (1 μL, 0.02 mmol). Analysis of mixture by $^{31}P\{^1H\}$ NMR spectroscopy showed a downfield shift of the signal for **5b** to 174.2 ppm.

Treatment of 5b with pinacolborane

5b (25 mg, 0.055 mmol) was dissolved in C_6D_6 and treated with pincacolborane (8 μL, 0.552 mmol). Upon mixing, the solution formed bubbles and quickly turned from clear to orange, red, and finally a dark brown. ^{1}H NMR spectroscopy showed the formation of dihydrogen, and **5b** was observed to the major identifiable complex by $^{31}P\{^{1}H\}$ NMR spectroscopy. The reaction mixture was filtered through silica and Celite and the volatiles were removed under vacuum to produce a brown solid, which contained **5b** and other unidentifiable decomposition products.

Treatment of 5 with $NaHBEt_3$

5 (30 mg, 0.070 mmol) was dissolved in C_6D_6 and treated with $NaBHEt_3$ (77 μL, 1.0 M solution in toluene). The reaction mixture turned bright orange and quickly turned to red and finally brown with black precipitate. Analysis by $^{31}P\{^{1}H\}$ NMR spectroscopy showed several products.

Treatment of 5c with pinacolborane

5c (27 mg, 0.053 mmol) was dissolved in C_6D_6 and treated with pinacolborane (8 μL, 0.055 mmol). After 1 day at room temperature, there was a 20% conversion of the pinacolborane to **A**, and the solution turned from a clear yellow to brown. Dihydrogen was also detected by ^{1}H NMR spectroscopy. $^{31}P\{^{1}H\}$ NMR spectroscopy showed only the presence of **5c**.

General Procedure for Catalytic Reactions

A stock solution of the desired catalyst was used to deliver 0.017 mmol of catalyst in C_6D_6. 1,4-dioxane (100 µL of 0.035 mmol stock solution in C_6D_6), pinacolborane (49 µL, 0.34 mmol), and 4-ethynyltoluene (43 µL, 0.34 mmol) were added to the J. Young tube. The reaction was then heated at 80 °C until completion. In addition to the hydrogenation of 4-ethynyltoluene to 4-methylstyrene, there was trace production of 4-ethyltoluene in reactions where hydrogenation was significant.

Catalysis with (POCOP^{iPr})NiH (1a)

1a (0.017 mmol) was dissolved in C_6D_6 in a J. Young tube and 1,4-dioxane (100 µL of 0.035 mmol stock solution in C_6D_6), pinacolborane (49 µL, 0.34 mmol), and 4-ethynyltoluene (43 µL, 0.34 mmol) were added. The reaction was heated at 80 °C for 1 day. Analysis by ^{1}H NMR spectroscopy showed complete consumption of 4-ethynyltoluene and a complex mixture of compounds with olefinic signals. However, 83% of the pinacolborane was still present at the end of the reaction time.

Catalysis with (POCOP^{iPr})PtH (3a)

3a (0.017 mmol) was dissolved in C_6D_6 in a J. Young tube and 1,4-dioxane (100 µL of 0.035 mmol stock solution in C_6D_6), pinacolborane (49 µL, 0.34 mmol), and 4-ethynyltoluene (43 µL, 0.34 mmol) were added. The reaction was heated at 80 °C for 1 day. Analysis by ^{31}P{^{1}H} NMR spectroscopy showed that 5% of 4-ethynyltoluene was converted to (E)-(4-methylstyryl)Bpin, which was identified by ^{1}H NMR spectroscopy and comparison to the reported ^{1}H NMR spectral data.[8]

NMR analysis of catalytic mixtures with 5b

Approximately 10 min. after mixing **5b** (5%, 0.017 mmol) with 4-ethynyltoluene, pinacolborane, and a dioxane standard, the sample was monitored by ^{1}H and $^{31}P\{^{1}H\}$NMR spectroscopy. PinBOAc and dihydrogen were visible by ^{1}H NMR spectroscopy, and **5c** was observed by $^{31}P\{^{1}H\}$ NMR spectroscopy.

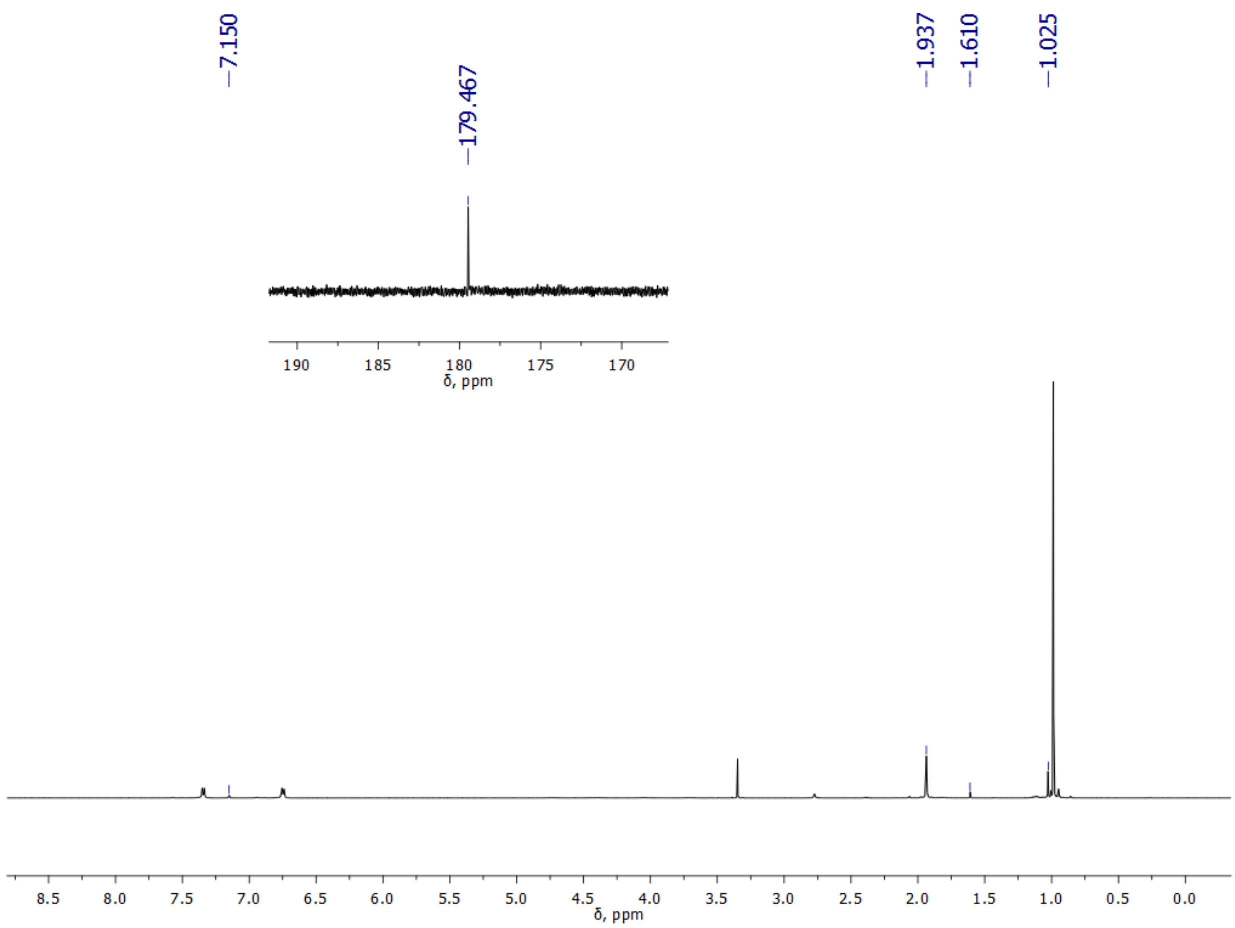


Figure 16: Initial ^{1}H NMR spectrum of catalytic mixture showing the presence of pinBOAc. Inset is $^{31}P\{^{1}H\}$ NMR spectrum showing **5c**.

Elemental Mercury as an Additive

Mercury was capable of drastically inhibiting the hydrogenation reaction, and allowed for nearly complete conversion of the terminal alkyne to the alkynylboronate and hydrogen. Monitoring the reaction with mercury (Entry 6) showed that after 1 day at 80 °C the reaction with mercury as an additive had undergone 37% conversion to the alkynylboronate. The control reaction (Entry 3) showed complete consumption of the terminal alkyne at this time with a 40% conversion to the alkynylboronate.

Turnover tests for 5b

A stock solution of the desired catalyst was used to deliver 0.0017 mmol of **5b** in C_6D_6. 1,4-dioxane (100 μL of 0.035 mmol stock solution in C_6D_6), pinacolborane (49 μL, 0.34 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added to the J. Young tube along with the desired amount of mercury or triphenylphosphine.. The reaction was then heated at 80 °C until completion.

Table SI-1: Turn over test with 5b

Entry	A	4-Methylstyrene	Time	Additives
1	39%	41%	2 d	x
2	45%	43%	4 d	0.0017 mmol PPh_3
3	37%	38%	5 d	0.0034 mmol PPh_3
4	25%	24%	2 d	0.017 mmol PPh_3
5	38%	2%	1 d	0.45 mmol Hg

When 0.0034 mmol of triphenylphosphine was used in entry 3, there was a significant inhibition of 4-methylstyrene production for the first 24 h, but hydrogenation did occur beyond the first day.

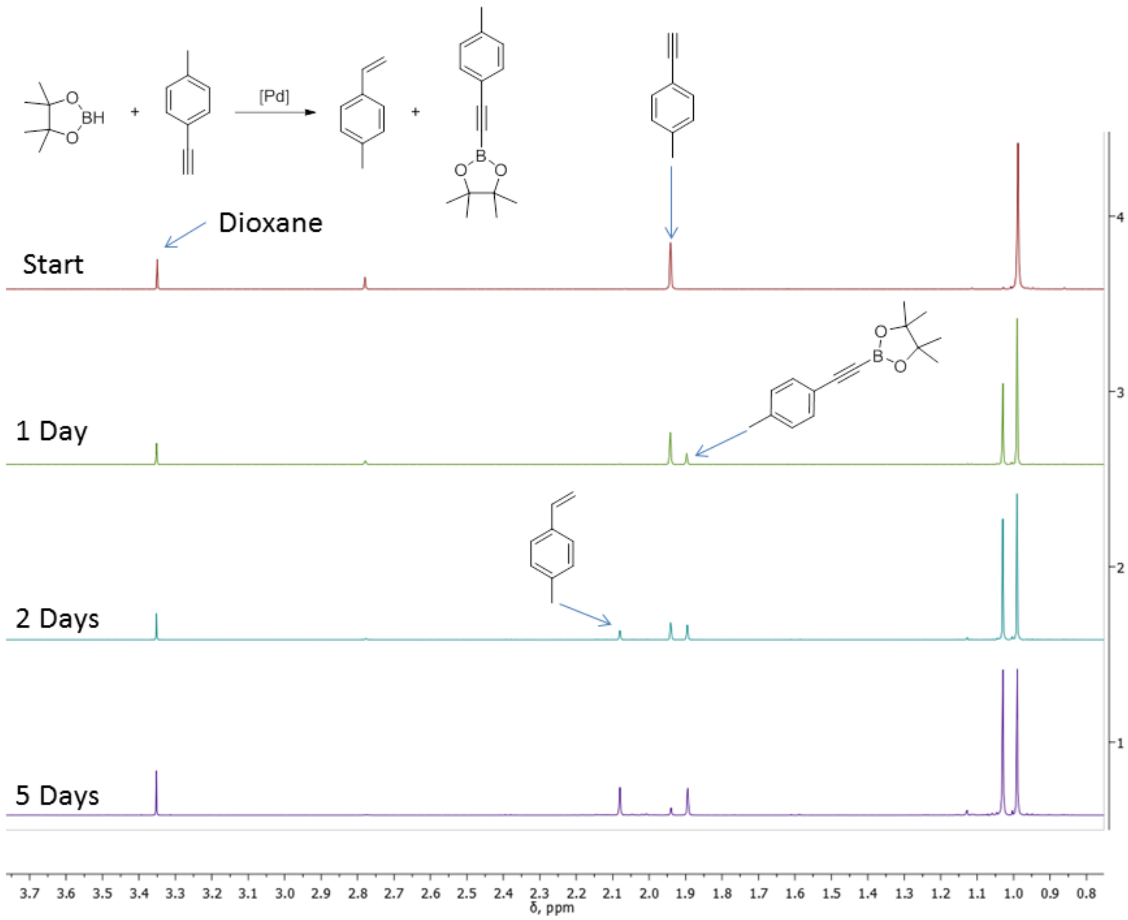


Figure 17: Stacked ^{1}H NMR spectra from (table SI-1, entry 3). 4-methylstyrene is not produced until after day 1.

5b Turnover test with mercury (Table SI-1, Entry 5)

When mercury was used as an additive the reaction was heated for 1 day at 80 °C. Palladium black had precipitated out on the sides of the J. Young tube, the solution was a pale clear yellow color, and no reactivity was seen after this point. 38% of the starting alkyne had been converted to **A** and there were trace amounts of 4-methylstyrene and trace amounts of 4-ethyltoluene. The catalyst was seen to perform about 76 turn overs.

Higher HBpin : Alkyne ratios

A stock solution of the desired catalyst was used to deliver 0.017 mmol of **5b** in C_6D_6. 1,4-dioxane (100 μL of 0.035 mmol stock solution in C_6D_6), pinacolborane (49 μL, 0.34 mmol), (54 μL, 0.37 mmol), (74 μL, 0.51 mmol), triphenylphosphine (0.034 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added to the J. Young tube. The reaction was then heated at 80 °C until completion.

Table SI-2: Higher HBpin:Alkyne Ratios

HBpin: alkyne	**4 Hours @ 80 °C**			**1 Day @ 80°C**		
	SM	**A**	**B**	**SM**	**A**	**B**
1:1	7%	6%	84%	<2%	7%	88%
1.1 : 1	13%	6%	81%	3%	7%	92%
1.5 : 1	14%	5%	81%	5%	7%	87%

Control reaction with $Pd(COD)Cl_2$

In a J. Young tube, $Pd(COD)Cl_2$ (5 mg, 0.0175 mmol) was dissolved in C_6D_6 with 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol). The reaction mixture was heated for 24 h at 80 °C. Analysis by ^1H NMR spectroscopy showed no visible production of **A** or 4-methylstyrene.

Control reactions with $Pd_2(DBA)_3$ and triphenylphosphine

In a J. Young tube, $Pd_2(DBA)_3$ (8 mg, 0.0087 mmol) was treated with PPh_3 (9 mg, 0.034 mmol), 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol) in C_6D_6. The reaction mixture was heated for 24 h at 80 °C. Analysis of the reaction mixture by ^1H NMR spectroscopy shows >90% of the starting alkyne remains, and there was no visible production of **A**.

Control reaction with $Pd_2(DBA)_3$

In a J. Young tube, $Pd_2(DBA)_3$ (8 mg, 0.0087 mmol) was dissolved in C_6D_6 and treated with 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol). The reaction mixture was heated for 24 h at 80 °C. Analysis of the reaction mixture by ^{1}H NMR spectroscopy shows that >90% of the pinacolborane remains. Broad signals at around 7.00 ppm and 2.00 ppm suggest that the alkyne has been converted to polymeric and oligomeric products.

<u>**Characterization of Alkynylboronates**</u>

Alkynylboronates were characterized *in situ* by ^{1}H NMR spectroscopy and compared to literature data.[9]

4-Me-C_6H_4-C≡C-Bpin (A): ^{1}H NMR (500 MHz, C_6D_6): δ 7.34 (d, *J* = 7.5 Hz, 2H), 6.65 (d, *J* = 7.5 Hz, 2H), 1.87 (s, 3H, Ar-CH_3), 1.02 (s, 12H, -CH_3 on Bpin).

n-Bu-C≡C-Bpin: ^{1}H NMR (500 MHz, C_6D_6): δ 1.95 (t, *J* = 7 Hz, 2H), 1.21 (m, 4H), 0.99 (s, 12H, -CH_3 on Bpin), 0.66 (t, *J* = 7 Hz, 3H).

Me_3Si-C≡C-Bpin: ^{1}H NMR (500 MHz, C_6D_6): δ 0.94 (s, 12H, -CH_3 on Bpin), 0.06 (s, 9H, -CH_3 on Me_3Si).

Me_3SiO-CH_2-C≡C-Bpin: ^{1}H NMR (500 MHz, C_6D_6): δ 4.07 (s, 2H, O-CH_2-C≡C), 0.97 (s, 12H, -CH_3), 0.07 (s, 9H, -CH_3 on Me_3Si). ^{11}B NMR (128 MHz, C_6D_6): δ 24.0.

PhO-CH_2-C≡C-Bpin: Selected data for PhO-CH_2-C≡C-Bpin: ^{1}H NMR (500 MHz, C_6D_6): δ 4.22 (s, 2H, O-CH_2-C≡C), 0.93 (s, 12H, -CH_3 on Bpin); ^{11}B NMR (128 MHz, C_6D_6): δ 23.7. Selected NMR data for PhO-CH_2-C≡CH: ^{1}H NMR (500 MHz, C_6D_6): δ 4.19 (d, *J* = 2Hz, 2H, O-CH_2-C≡C).

Me_3Si-O-Bpin: ^{1}H NMR (500 MHz, C_6D_6): δ 1.04 (s, 12H, -CH_3 on Bpin), 0.19 (s, 9H, -CH_3 on Me_3Si); ^{11}B NMR (128 MHz, C_6D_6): δ 20.8.[10]

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