Supporting Information

Development of organosilica material containing ordered triene coordination sites and its application towards borylation of aryl iodides

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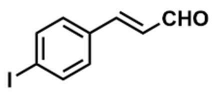
1. Materials and methods

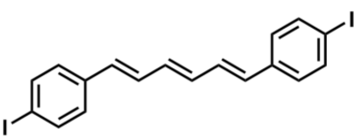
All reactions for organic synthesis were carried out under nitrogen using Schlenk-line techniques or a glovebox unless otherwise noted. Tetrahydrofuran was purified by using a solvent purification system (MBraun SPS-800). 1,4-Dioxane and ethanol were purchased from Wako Pure Chemical Industries, Ltd., as “superdehydrated”. Mesitylene was purchased from Wako Pure Chemical Industries, Ltd., and distilled over CaH_2 before use. Other reagents were purchased from commercial suppliers. ^1H and ^{13}C NMR spectra were recorded using a Bruker AVANCE III 400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) at room temperature. ^{13}C CP-MAS NMR and ^{29}Si CP-MAS NMR measurements were performed using a 4 mm diameter ZrO_2 rotor at a sample spinning frequency of 12.5 kHz using a Bruker AVANCE NEO NMR spectrometer (^{13}C CP-MAS NMR at 100.6 MHz; ^{29}Si CP-MAS NMR at 79.49 MHz) at room temperature. High-resolution electroionization spray mass spectra were recorded on a Bruker micrOTOF II instrument. Nitrogen adsorption/desorption isotherms were measured using a NOVA (Anton Paar QuantaTec) instrument. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear sections of the BET plots ($P/P_0 = 0.05–0.35$). Pore-size distributions were calculated from the adsorption branches using the density functional theory (DFT) method (DFT kernel: N_2 at 77 K on silica, cylindrical pores, and non-local DFT (NLDFT) adsorption model). Pore volumes were evaluated by t-plot method. Scanning electron microscope with EDX (SEM-EDX) measurements are performed by Hitachi FE-SEM S-4800 equipped with HORIBA EMAX X-act (Model: 51-ADD0014). Acceleration voltage in the SEM-EDX measurement was adjusted to be 15.0 kV. X-ray diffraction (XRD) patterns were recorded using an M18X diffractometer (MACScience, Japan). The incident X-ray radiation was produced by a Curotating anode operating at 40 kV and 200 mA, with a Cu Kαradiation of 1.54178 Å. Pd NPs immobilized on silica materials were analyzed by a transmission electron microscope (TEM) using JEM-2100F (JEOL). Acceleration voltage in the TEM measurement was adjusted to be 200 kV. Elemental analysis was performed by a MICRO CORDER JM-10 (J-science Co., Ltd.).

2. Synthetic procedure



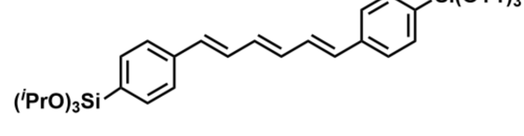
(*E*)-4-(2-Iodovinyl)benzaldehyde was synthesized according to the literature procedure.[S1] To a stirred solution of 4-iodobenzaldehyde (6.08 g, 26.2 mmol), 18-crown-6-ether (101.0 mg, 0.38 mmol) and (1,3-dioxolan-2-ylmethyl)-triphenylphosphoniumbromide (16.9 g, 39.4 mmol) in THF (200 mL) under N_2, NaH (60%, dispersion in mineral oil, 2.63 g, 65.8 mmol) was added in one portion. After 2 h stirring at room temperature, the reaction mixture was quenched with water and extracted with EtOAc. After evaporation of EtOAc, the residue was dissolved in the mixture of THF (200 mL) and conc. hydrochloric acid (22 mL), and stirred for 2 h at room temperature. After the mixture was turned basic with 2 N NaOHaq and extracted with EtOAc. The combined EtOAc extracts were washed with brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by silica gel chromatography (eluent: hexane: EtOAc = 8.5:1.5) to give the desired product as a pale yellow solid (5.19 g, 20.1 mmol, 77%). The obtained compound was identified by ^{1}H NMR spectroscopy, and the spectra were consistent with reported in the literature.[S1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 16.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 6.72 (dd, J_1 = 7.6 Hz, J_2 = 16.0 Hz, 1H).

(*E,E,E*)-1,6-Di(4-iodophenyl)hexa-1,3,5-triene[S2]



Mo(CO)$_6$ (582 mg, 2.2 mmol, 11 mol%), 3,5-di-tert-butyl-1,2-benzoquinone (473 mg, 2.2 mmol, 11 mol%), and mesitylene (10 mL) were placed in a Schlenk tube. The Schlenk tube was sealed with a screw cap and was stirred at 140 °C for 15 min. The color of the reaction mixture turned dark violet from green within a few minutes. After cooling to ambient temperature, Ph_3P (6.45 g, 24.6 mmol, 1.2 equiv) was added to the reaction mixture followed by the addition of (*E*)-4-(2-Iodovinyl)benzaldehyde (5.21 g, 20.2 mmol) and another portion of mesitylene (10 mL). After stirring for 16 h, the dark brown reaction mixture was cooled to ambient temperature, yielding yellow precipitate. The precipitate was filtered, and the residue was washed with chloroform and acetone to give the desired product as a yellow solid (3.17 g, 6.5 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 6.0 Hz, 4H), 7.14 (d, J = 6.0 Hz, 4H), 6.89-6.83 (m, 2H), 6.53-6.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 136.8, 133.9, 131.9, 129.8, 128.1, 92.8. Signal at 92.8 ppm was determined by HMBC.

(*E,E,E*)-1,6-Bis(4-(triisopropoxysilyl)phenyl)hexa-1,3,5-triene (1)[S3]



A dry Schlenk tube was charged with (*E,E,E*)-1,6-Di(4-iodophenyl)hexa-1,3,5-triene (3.13 g, 6.5 mmol), [Rh(cod)-(CH_3CN)$_2$]BF_4 (76 mg, 0.2 mmol, 3 mol%) and *n*-Bu_4NI (5.75 g, 15.6 mmol, 2.4 equiv) under N_2. Dry DMF (64 mL), dry Et_3N (10.2 mL) and (iPrO)$_3$SiH (4.14 mg, 20.0 mmol, 3.1 equiv) were added. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was evaporated, extracted with hexane (100 mL), and filtered. The filtrate was concentrated to the dryness under vacuum, and the residue was purified by silica gel column chromatography (eluent: hexane: EtOAc = 10:1) to give the desired product as a light yellow solid (2.49 g, 3.9 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.1 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H), 6.96-6.90 (m, 2H), 6.60 (d, J = 15.4 Hz, 2H), 6.55-6.52 (m, 2H), 4.27 (q, J = 6.1 Hz, 6H), 1.22 (d, J = 6.1 Hz, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 135.3, 133.9, 132.9, 132.3, 129.7, 125.6, 65.4, 25.5. HRMS (ESI-TOF) calculated for $C_{18}H_{14}I_2$ $[M + Na]^+$: 663.3508, found: 663.3504.

Triene-SiO_2

A 200 mL one-neck flask was charged with octadecyltrimethylammonium chloride (C_{18}TMACl: 3.28 g, 9.4 mmol), 6 N NaOH solution (0.26 mL), and distilled water (44.5 mL). The mixture was stirred at 50 °C. To the solution, was added a mesitylene solution (4.5 mL) of **1** (1.14 g, 1.77 mmol) at a constant speed of 1.98 mL/h using a syringe-pump with vigorous stirring at 50 °C. The mixture was stirred for another 24 h and continued heating at 90 °C for 24 h under static conditions. Then, the resulting precipitation was filtered and washed with distilled water, affording a pale yellow powder. The obtained solid was stirred in acidic ethanol solution (2 N HCl solution (2.0 mL) and ethanol (72 mL)) at room temperature for 12 h to give **triene-SiO_2** (575 mg) as a pale yellow powder.

Triene-SiO_2-TMS

To a 100 mL Schlenk tube equipped with a Teflon cock, were added **triene-SiO_2** (1.68 g) and toluene (42 mL) under N_2. *N*-trimethylsilyl imidazole (6.7 mL, 48 mmol) was furthermore added dropwise. The mixture was stirred at 60 °C overnight and then diluted with toluene (30 mL). The resulting precipitate was filtered and washed with toluene and methanol to give **triene-SiO_2-TMS** (1.74 g) as a pale yellow powder.

Pd-triene-SiO_2-TMS

A 500 mL Schlenk tube was charged with **triene-SiO_2-TMS** (304.0 mg), $Pd(dba)_2$ (211.0 mg, 0.67 mmol) and THF (300 mL) under N_2. The resulting suspension was vigorously stirred at room temperature overnight. The mixture was filtrated, and the obtained solid was washed with THF until the filtrate become clear. The solid material was dried under the reduced pressure to give **Pd-triene-SiO_2-TMS** as a black powder (279 mg). Pd amount was estimated to be 2.6 mmol g^{-1} by CH elemental analysis and EDX analysis.

Pd-AEROSIL

A 500 mL Schlenk tube equipped with a stirrer bar was charged with AEROSIL® 200 (69.0 mg), $Pd(dba)_2$ (37.9 mg, 0.066 mmol) and THF (54 mL). The suspension was vigorously stirred at room temperature overnight. The mixture was filtrated, and the obtained solid part was washed with THF until the filtrate become clear. The material was dried under the reduced pressure to give **Pd-AEROSIL** as a navy powder (72.3 mg). Pd amount was estimated to be 0.11 mmol g^{-1} by CH elemental analysis and EDX analysis.

Pd-Ph-SiO_2

Ph-SiO_2 was synthesized according to the literature procedure.[S4] 1,4-Bis(triethoxysilyl)benzene (2 g) was added to a mixture of ion-exchanged water (50 g) and 6 N NaOH aqueous solution (4 g) under vigorous stirring at room temperature. The heterogeneous mixture was ultrasonicated in a round-bottom flask for 20 min to obtain an emulsion-like solution. The solution was subsequently stirred at room temperature for 3 days using a magnetic stirrer. The flask, fitted with a condenser, was then immersed in an oil bath to heat the solution at 98 °C for 5 days under static conditions. The white precipitate obtained was recovered by filtration (925.2 mg). The nitrogen adsorption–desorption isotherm of the resulting white powder was consistent with that previously reported.[S4]

A 200 mL round-bottom flask equipped with a stirrer bar was charged with **Ph-SiO_2** (100.0 mg), $Pd(dba)_2$ (70.2 mg, 0.12 mmol) and THF (54 mL). The suspension was vigorously stirred at room temperature overnight. The mixture was filtrated, and the obtained solid part was washed with THF until the filtrate become clear. The material was dried under the reduced pressure to give **Pd- Ph-SiO_2** as a gray powder (104.2 mg). Pd amount was estimated to be 0.12 mmol g^{-1} by EDX analysis.

Typical procedure for catalytic borylation reactions (Table 1, Entry 9)[S5]

A 100 mL Schlenk tube equipped with a Teflon cock was charged with **Pd-triene-SiO_2-TMS** (5.0 mg, 0.013 mmol/Pd), 4-iodoanisole (117.0 mg, 0.50 mmol) 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, 74 μL, 0.50 mmol), NEt_3 (70 μL, 0.50 mmol) and 1,4-dioxane (1 mL). The reaction mixture was stirred at 110 °C for 24 h. To the resulting mixture, mesitylene (43.4 mg, 0.36 mmol) was added as an internal standard. Yields of the products were analyzed by ^1H NMR. The yields of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole and anisole were determined to be 80% and 14%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S5]

2-(2-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S5]

Following typical procedure, a mixture of 2-iodoanisole (117.1 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and anisole were determined to be 78% and 12%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S5]

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane[S6]

Following typical procedure, a mixture of iodobenzene (101.2 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane and benzene were determined to be 71% and 13%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S6]

4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane[S6]

Following typical procedure, a mixture of 4-iodotoluene (109.7 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-**

TMS (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane and toluene were determined to be 55% and 22%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S6]

_N,N_-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline[S5]

Following typical procedure, a mixture of 4-bromo-*N,N*-dimethylaniline (109.5 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of *N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and *N,N*-dimethylaniline were determined to be 75% and 12%, by comparing their ^{1}H NMR spectra with those reported in the literature. [S5]

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane[S7]

Following typical procedure, a mixture of 4-iodobenzotrifluoride (135.1 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane and benzotrifluoride were determined to be 79% and 16%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S7]

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate[S6]

Following typical procedure, a mixture of methyl 4-iodobenzoate (131.5 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate and methyl benzoate were determined to be 81% and 16%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S6]

4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane[S8]

Following typical procedure, a mixture of 1-iodo-4-nitrobenzene (131.1 mg, 0.53 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane, nitrobenzene and 4,4'-dinitro-1,1'-biphenyl were determined to be 78%, 12% and 7%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S8]

2-(4-Bromo-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S9]

Following typical procedure, a mixture of 1-bromo-4-iodobenzene (141.4 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 2-(4-bromo-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and nitrobenzene were determined to be 65% and 12%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S9]

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone[S7]

Following typical procedure, a mixture of 4'-iodoacetophenone (122.9 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone and acetophenone were determined to be 68% and 20%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S7]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol[S10]

Following typical procedure, a mixture of 4-iodophenol (110.5 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yield of phenol was determined to be 44% by comparing ^{1}H NMR spectrum with that of authentic sample. 45% of the starting material, 4-iodophenol, was recovered.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline[S7]

Following typical procedure, a mixture of 4-iodoaniline (109.5 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yield of aniline was determined to be 32% by comparing ^{1}H NMR spectrum with that of authentic sample. 63% of the starting material, 4-iodoaniline, was recovered.

2-Mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S5]

Following typical procedure, a mixture of mesityl iodide (123.4 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 2-mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and mesitylene were determined to be 8% and 2%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S5]

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane[S7]

Following typical procedure, a mixture of 2-iodonaphthelene (123.0 mg, 0.48 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane and naphthalene were determined to be 77% and 13%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S7]

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane[S8]

Following typical procedure, a mixture of 1-iodonaphthelene (121.5 mg, 0.48 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane and naphthalene were determined to be 45% and 26%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S8]

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane[S8]

Following typical procedure, a mixture of 2-iodothiophene (103.5 mg, 0.49 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane and thiophene were determined to be 80% and 14%, respectively, by comparing their ^{1}H NMR spectra with those reported in the literature.[S8]

4,4,5,5-Tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane[S8]

Following typical procedure, a mixture of 3-iodothiophene (107.3 mg, 0.51 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane and thiophene were determined to be 79% and 11%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S8]

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[S10, S11]

Following typical procedure, a mixture of 3-iodopyridine (102.5 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. The yields of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, pyridine and 3,3'-bipyridine were determined to be 3%, 48% and 16%, respectively, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S10, S11]

Borylation reaction of 4-bromoanisole

Following typical procedure, a mixture of 4-bromoanisole (94.0 mg, 0.50 mmol), HBpin, NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole and anisole were determined to be 3% and 25%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S5]

Borylation reaction of 4-iodoanisole with bis(pinacolato)diboron (B_2pin_2)

Following typical procedure, a mixture of 4-iodoanisole (120.1 mg, 0.51 mmol), B_2pin_2 (127.5 mg, 0.50 mmol), NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole and anisole were determined to be 7% and 2%, respectively, by comparing their ^1H NMR spectra with those reported in the literature.[S5]

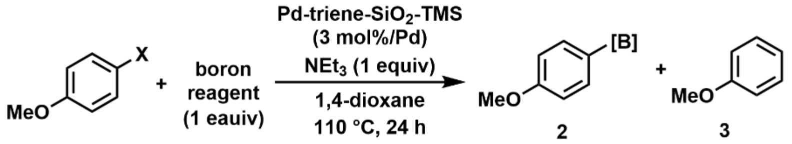
Borylation reaction of 4-iodoanisole with bis(neopentylglycolato)diboron (B_2nep_2)

Following typical procedure, a mixture of 4-iodoanisole (117.8 mg, 0.50 mmol), B_2nep_2 (117.7 mg, 0.52 mmol), NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane was determined to be 10%, by comparing their ^1H NMR spectra with those reported in the literature.[S12]

Borylation reaction of 4-iodoanisole with bis (hexylene glycolato) diboron (B_2hex_2)

Following typical procedure, a mixture of 4-iodoanisole (120.6 mg, 0.51 mmol), B_2hex_2 (117.7 mg, 0.51 mmol), NEt_3, **Pd-triene-SiO_2-TMS** (3 mol%/Pd) was heated in 1,4-dioxane for 24 h. 2-(4-methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane was determined to be 20%, by comparing their ^1H NMR spectra with those reported in the literature.[S13]

Table S1. Optimization of reaction conditions.[a]



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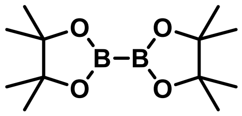
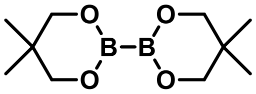
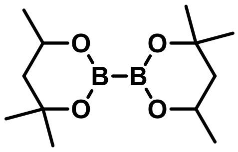
2	I	 B_2pin_2	7	2
3	I	 B_2nep_2	10	trace
4	I	 B_2hex_2	20	trace

[a] Reaction conditions: aryl halide (0.5 mmol), boron reagent (0.5 mmol), NEt_3 (0.5 mmol) and **Pd-triene-SiO_2-TMS** (3 mol% Pd) in 1,4-dioxane (1 mL) under a N_2 atmosphere. [b] Yield was determined by ^1H NMR using mesitylene as an internal standard.

3. Time-course reaction curve and hot filtration

A reaction mixture of 4-iodoanisole (233.8 mg, 1.0 mmol), pinacolborane (HBpin, 144 µL, 1.0 mmol), Pd–triene–SiO_2–TMS (11.2 mg, 3 mol% based on Pd), triethylamine (140 µL, 1.0 mmol), and mesitylene (85.5 µL, 0.62 mmol) as an internal standard in 1,4-dioxane (2 mL) was stirred at 110 °C.

Aliquots of approximately 0.1 mL were taken from the reaction mixture at 10 and 30 minutes, and at 1, 1.5, 2.5, 3.5, 7.5, 12, 18, 22, and 26 hours after the start of heating. The yield of the borylated product, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole, at each time point was determined by quantitative ^{1}H NMR analysis using mesitylene as an internal standard.

Additionally, a separate reaction was conducted under identical conditions, and aliquots (ca. 0.1 mL) were withdrawn at 1.5, 3.5, and 7.5 hours. The yield of the borylated product at each time point was similarly determined by quantitative ^{1}H NMR analysis. After the 7.5-hour time point, the reaction mixture was subjected to hot filtration under a nitrogen atmosphere using a membrane filter to remove the solid catalyst. The resulting transparent filtrate was stirred at 110 °C for an additional 16.5 hours, after which the ^{1}H NMR yield of the product was measured.

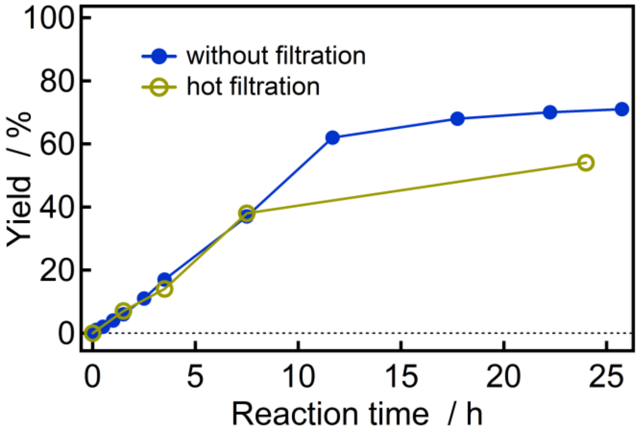


Figure S1. (Blue line) Time-course reaction curve and (yellow line) hot filtration test for the borylation reaction of 4-iodoanisole catalyzed by **Pd-triene-SiO_2-TMS**.

4. Recycling test

A 100 mL Schlenk tube equipped with a Teflon cock was charged with a stirrer bar under nitrogen atmosphere. To the Schlenk, **Pd-triene-SiO$_2$-TMS** (25.9 mg, 0.067 mmol/Pd), 4-iodoanisole (585.4 mg, 2.5 mmol) 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (360 μL, 2.5 mmol), NEt$_3$ (350 μL, 2.5 mmol) and 1,4-dioxane (5 mL) were added. The reaction mixture was stirred at 110 °C for 24 h. To the resulting mixture, mesitylene was added as an internal standard. Yields of the products were analyzed by ^{1}H NMR. After the reaction, the reaction mixture was filtered, and the residue was washed with 1,4-dioxane and ethanol, and dried in vacuo. The collected residue was submitted to the next reaction as the catalyst, i.e. 4-iodoanisole (488.1 mg, 2.09 mmol) was carried out in 1,4-dioxane (4.2 mL) at 110 °C for 24 h. After the reaction, the reaction mixture was again filtered to determine the product yield and to recover the catalyst. The reaction was repeated for four times using the recovered catalyst by following the same procedure.

The recycling test for **Pd-AEROSIL** (69.0 mg, 7.6 μmol) using 4-iodoanisole (59.1 mg, 0.25 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36 μL, 0.25 mmol), NEt$_3$ (35 μL, 0.25 mmol) and 1,4-dioxane (1 mL) was carried out by a similar procedure.

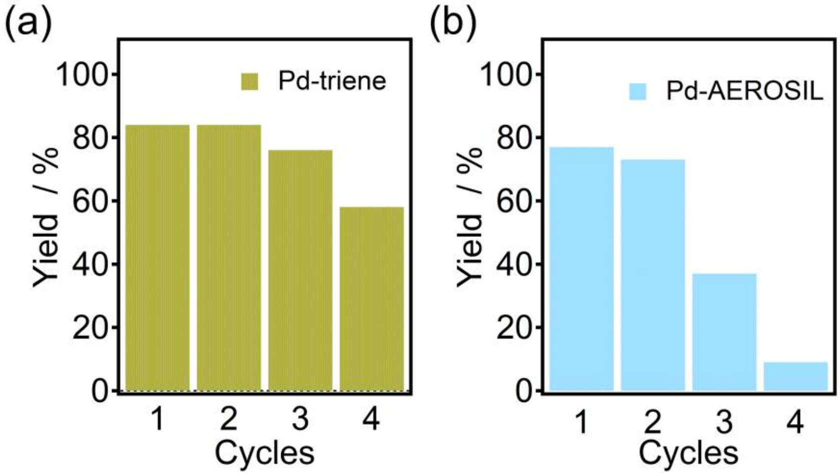


Figure S2. Catalyst recycling experiments for borylation reaction of 4-iodoanisole catalyzed by (a) **Pd-triene-SiO$_2$-TMS** and (b) **Pd-AEROSIL**.

5. NMR spectra for prepared materials

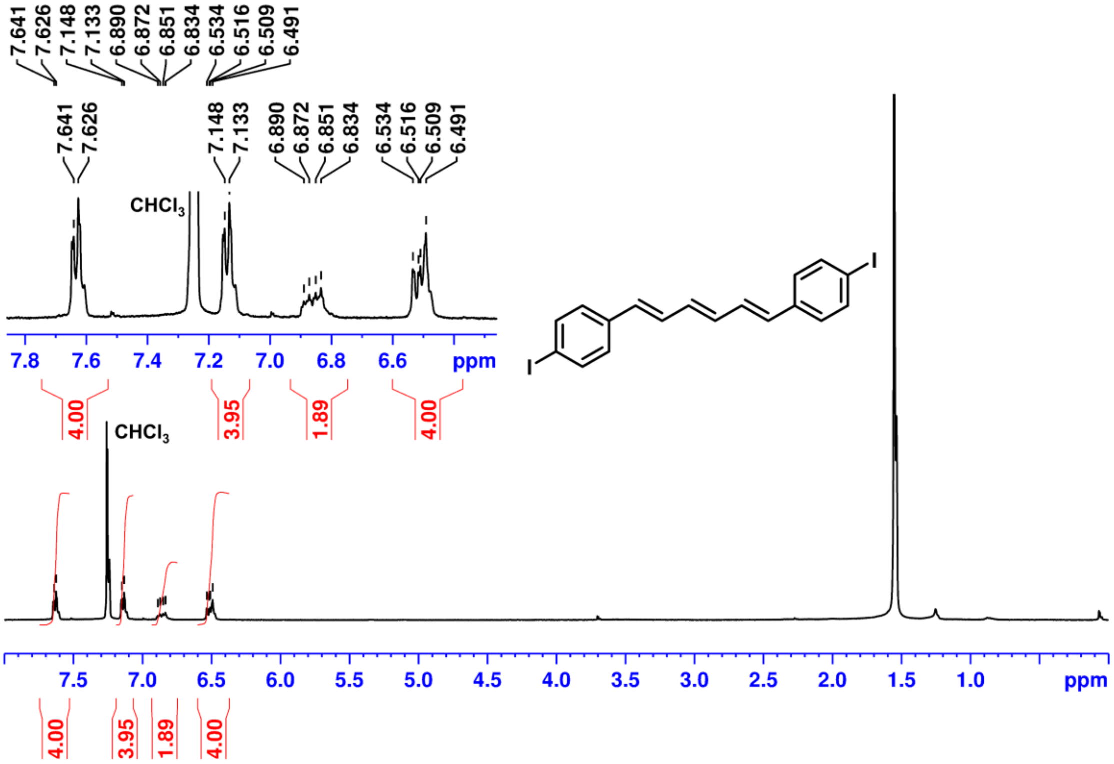


Figure S3. ^{1}H NMR spectrum of **(*E,E,E*)-1,6-Di(4-iodophenyl)hexa-1,3,5-triene**.

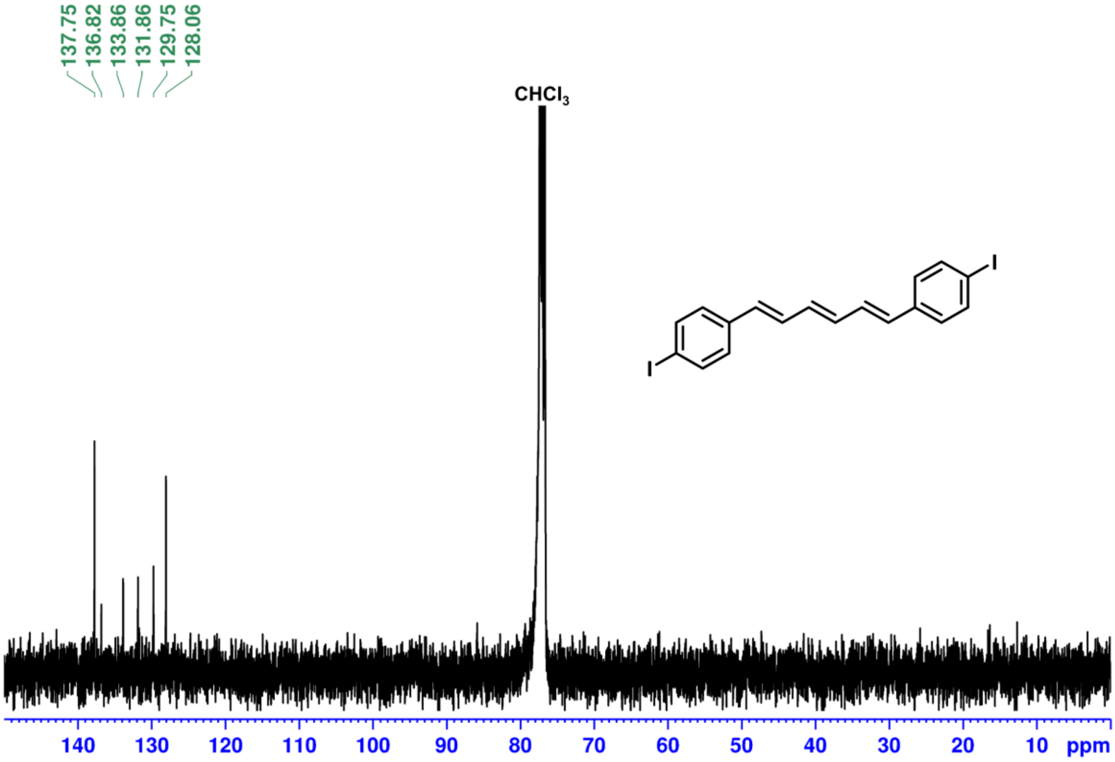


Figure S4. ^{13}C NMR spectrum of **(*E,E,E*)-1,6-Di(4-iodophenyl)hexa-1,3,5-triene**.

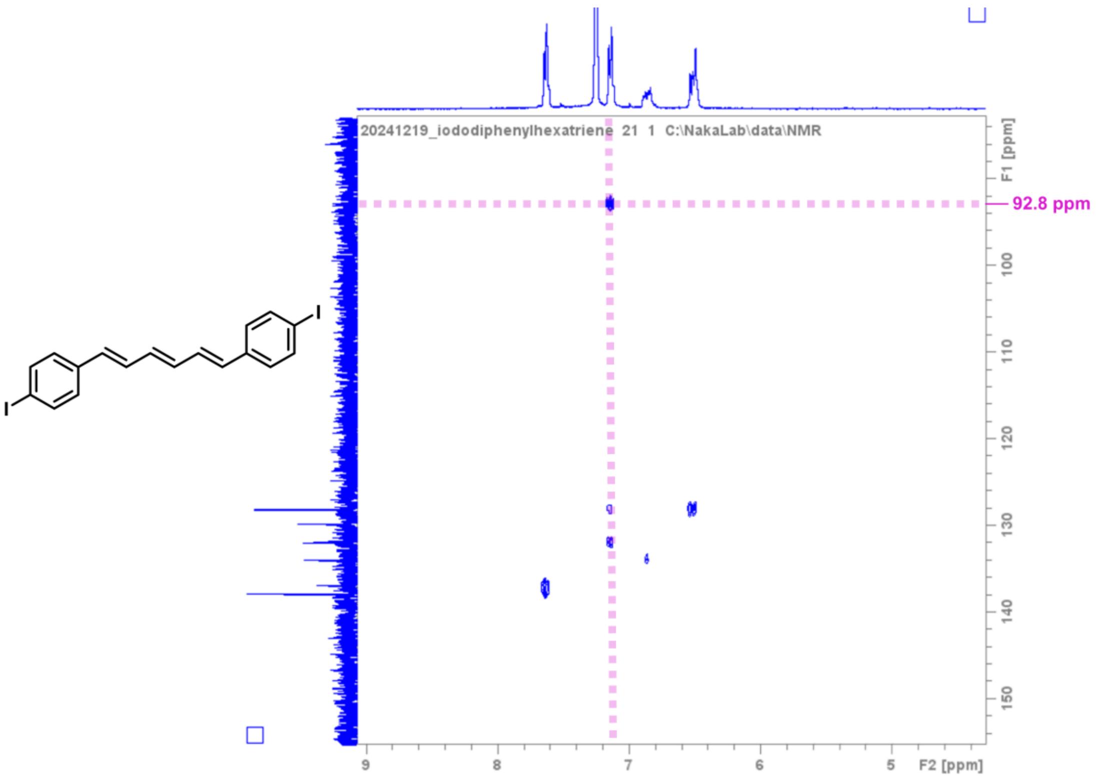


Figure S5. HMBC spectrum of ***(E,E,E)*-1,6-Di(4-iodophenyl)hexa-1,3,5-triene**.

Spectra for (*E*,*E*,*E*)-1,6-bis(4-(triisopropoxysilyl)phenyl)hexa-1,3,5-triene (1)

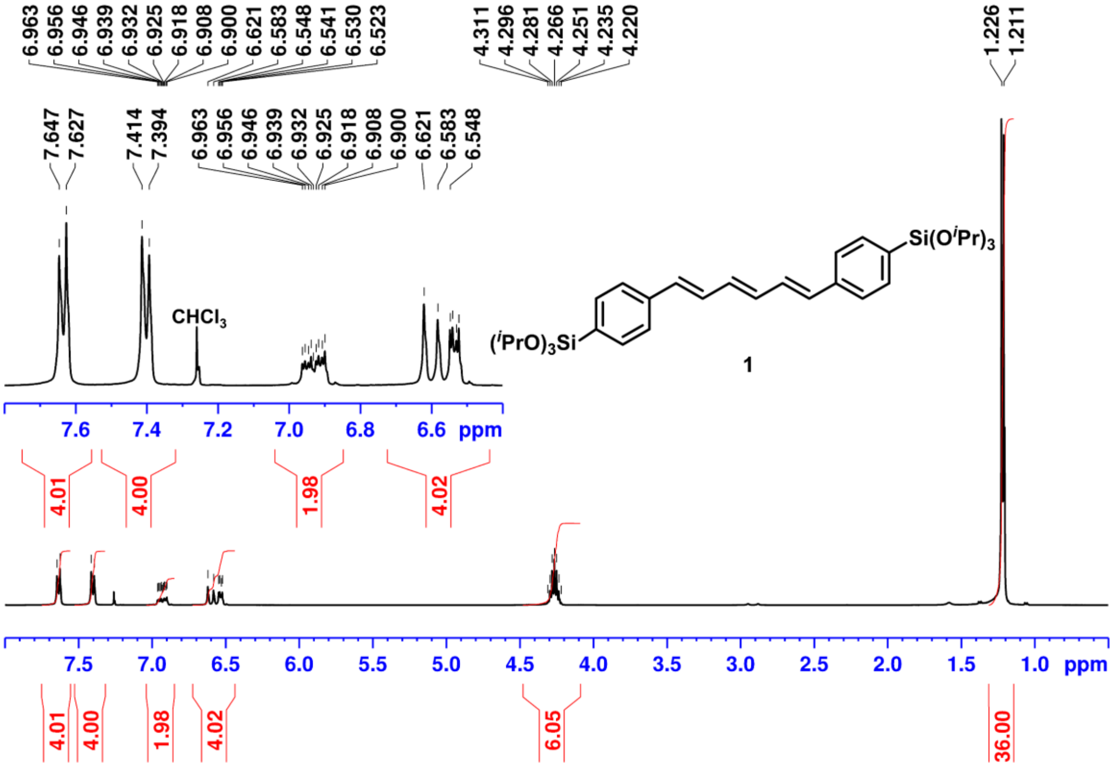


Figure S6. ^{1}H NMR spectrum of precursor **1**.

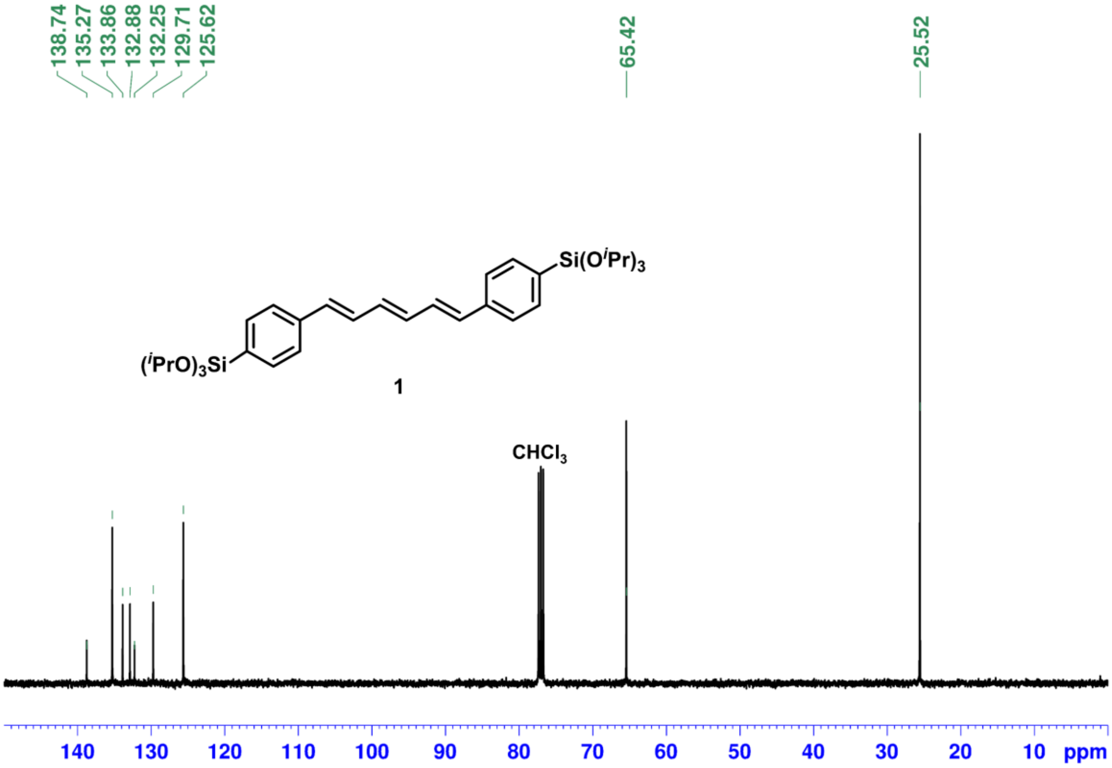


Figure S7. ^{13}C NMR spectrum of precursor **1**.

Spectra for triene-SiO_2

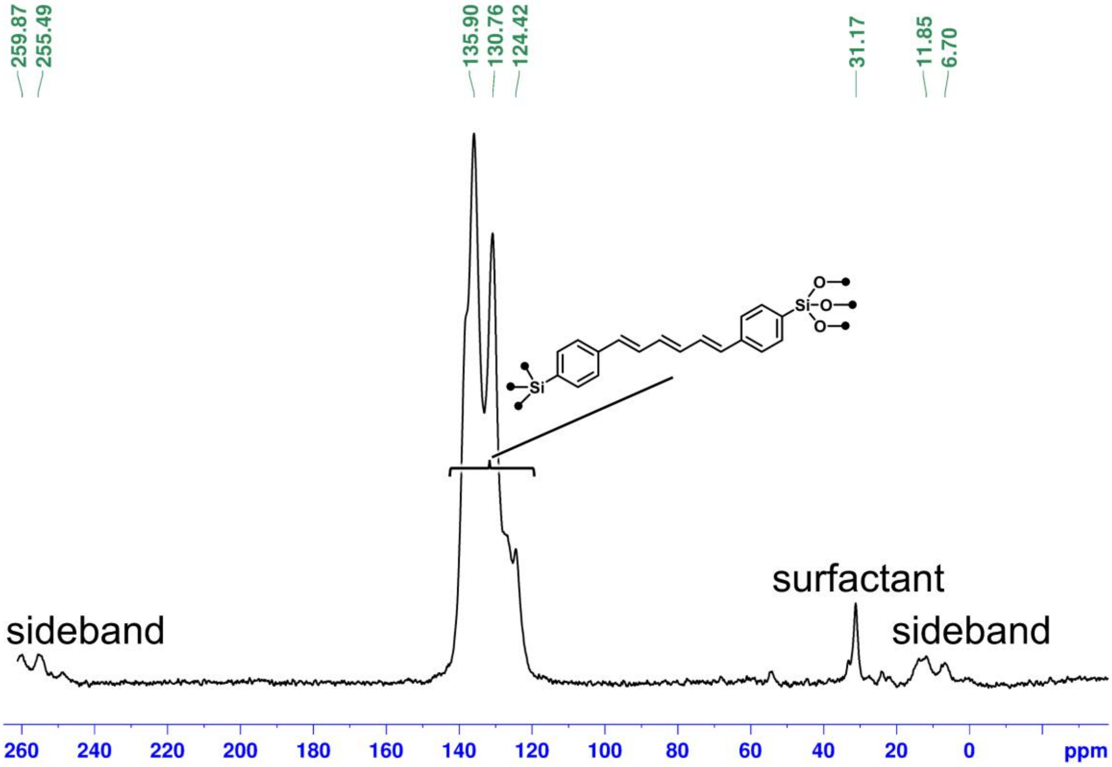


Figure S8. ^{13}C CP-MAS NMR spectrum of **triene-SiO_2**.

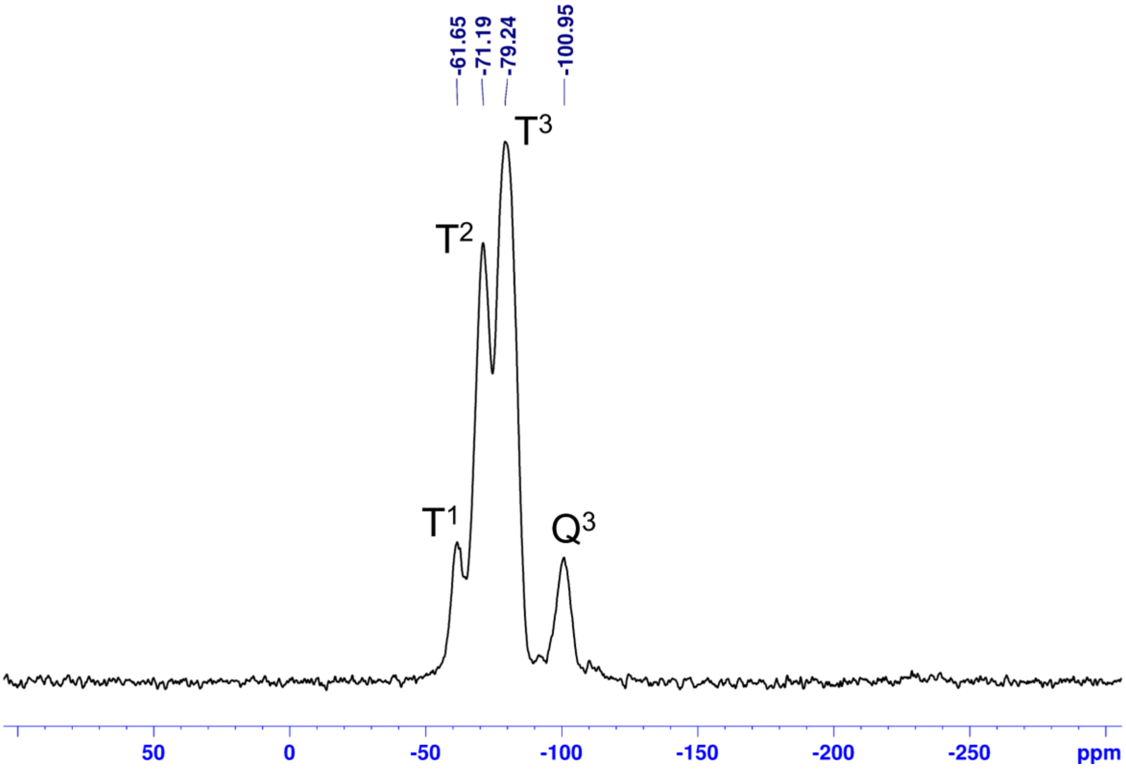


Figure S9. ^{29}Si CP-MAS NMR spectrum of **triene-SiO_2**.

Spectra for triene-SiO_2-TMS

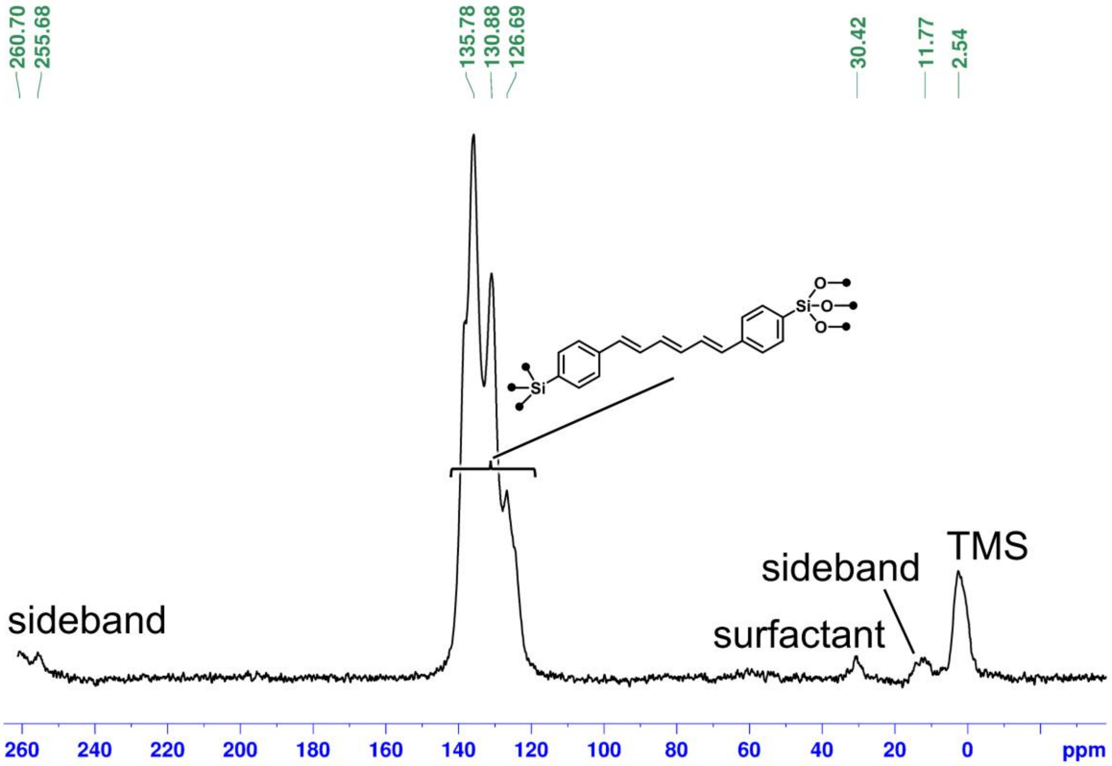


Figure S10. ^{13}C CP-MAS NMR spectrum of **triene-SiO_2-TMS**.

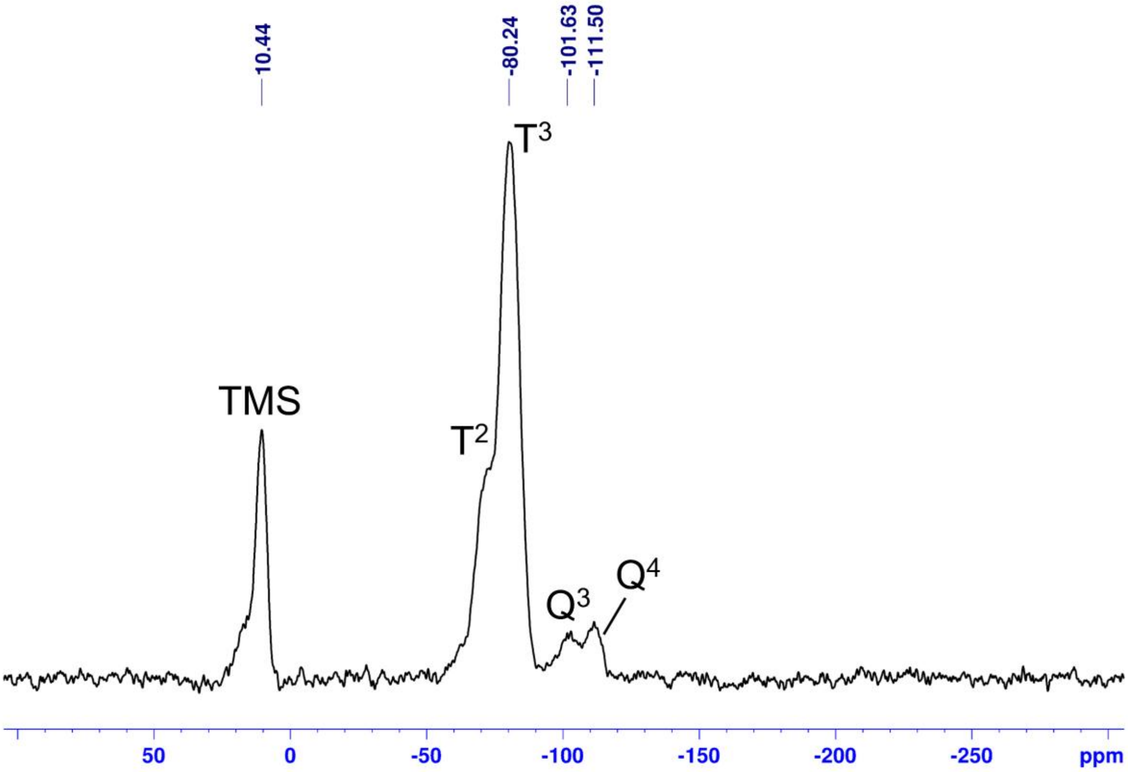


Figure S11. ^{29}Si CP-MAS NMR spectrum of **triene-SiO_2-TMS**.

Spectra for Pd-triene-SiO_2-TMS

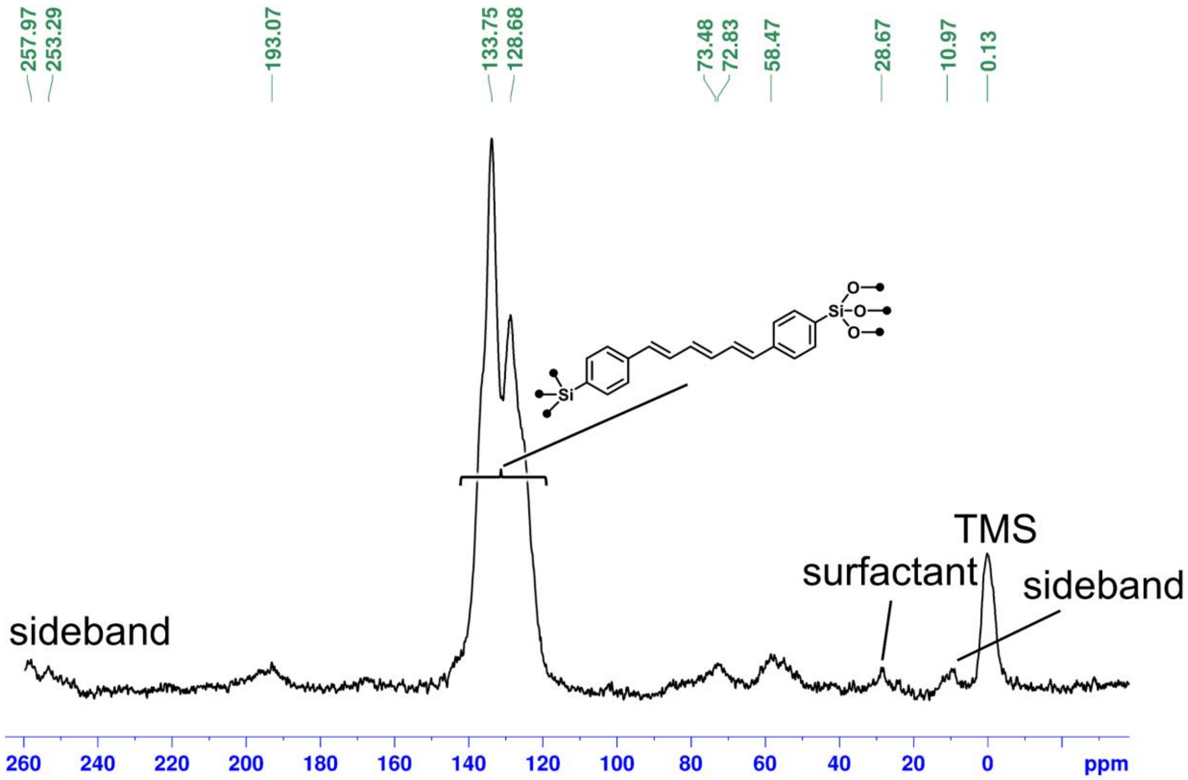


Figure S12. ^{13}C CP-MAS NMR spectrum of **Pd-triene-SiO_2-TMS**. The Pd-coordinated carbons were obscured due to the low signal intensity.

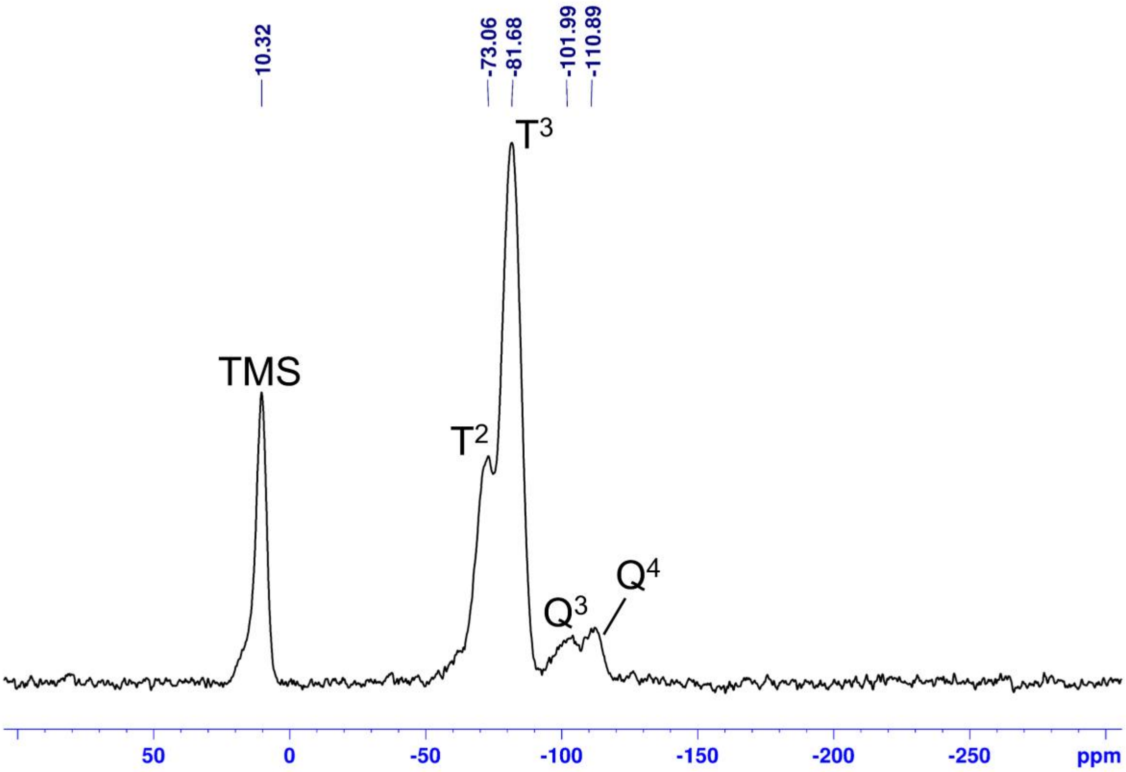


Figure S13. ^{29}Si CP-MAS NMR spectrum of **Pd-triene-SiO_2-TMS**.

6. NMR spectra for crude mixture of catalytic reaction

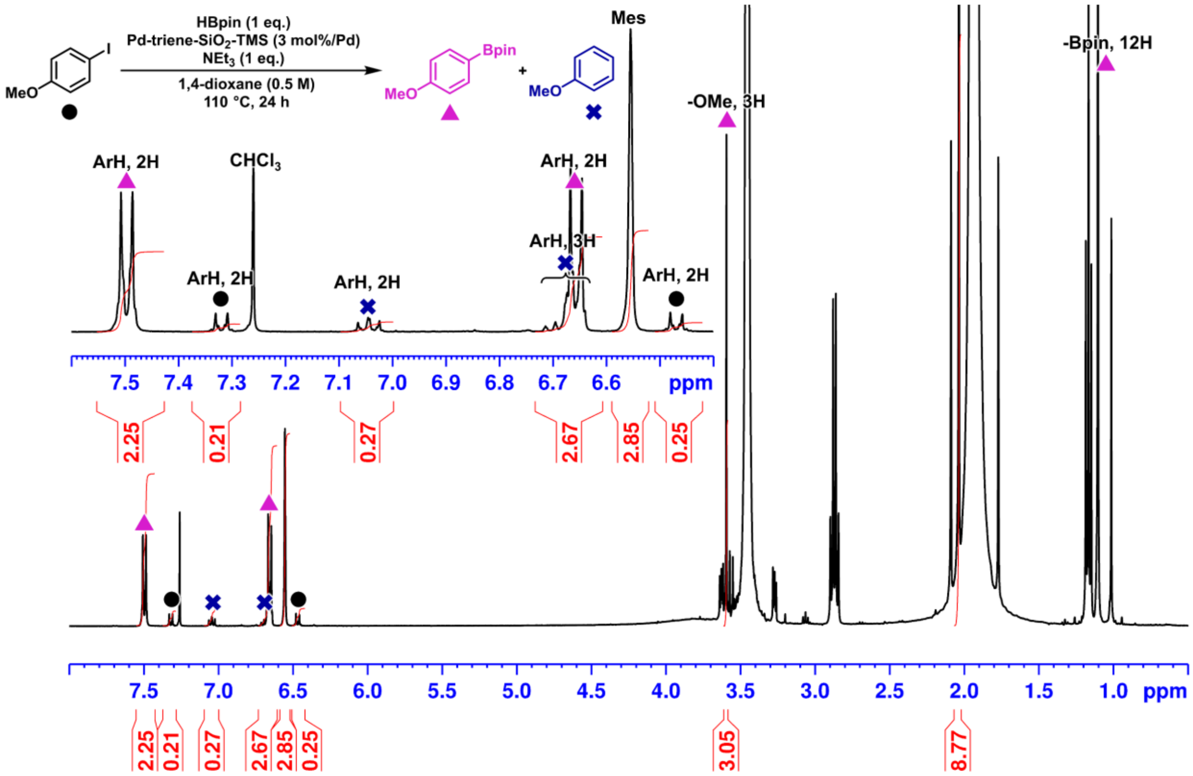


Figure S14. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoanisole.

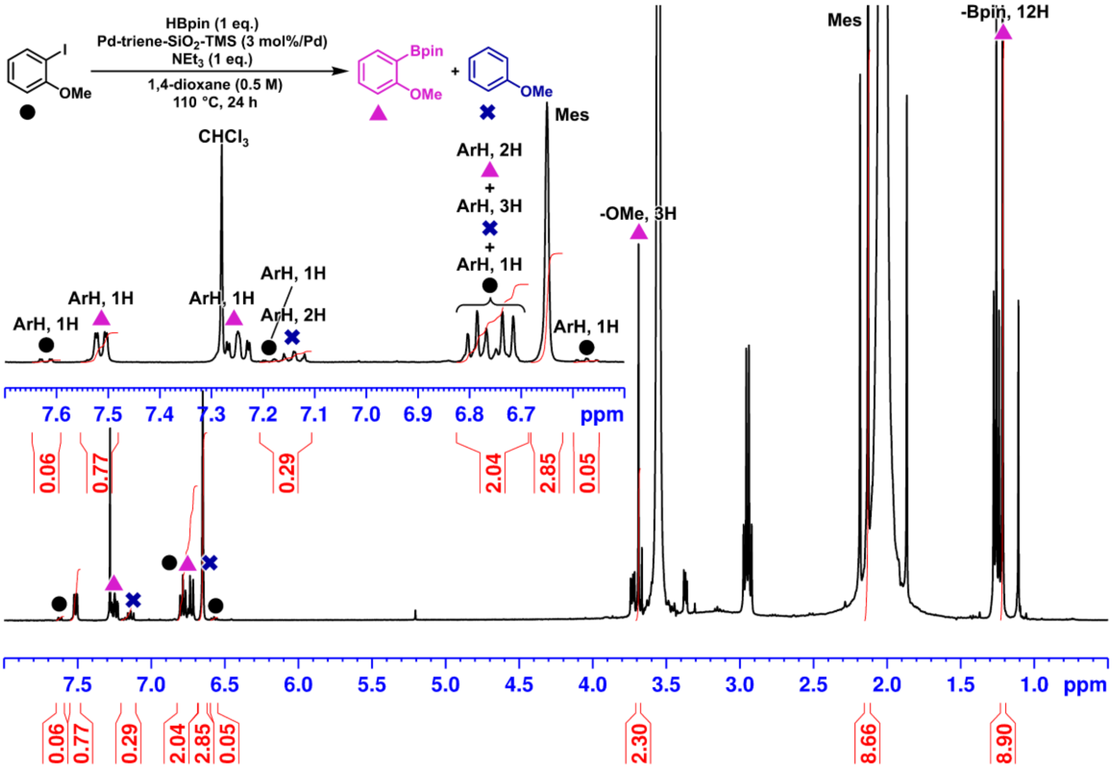


Figure S15. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 2-iodoanisole.

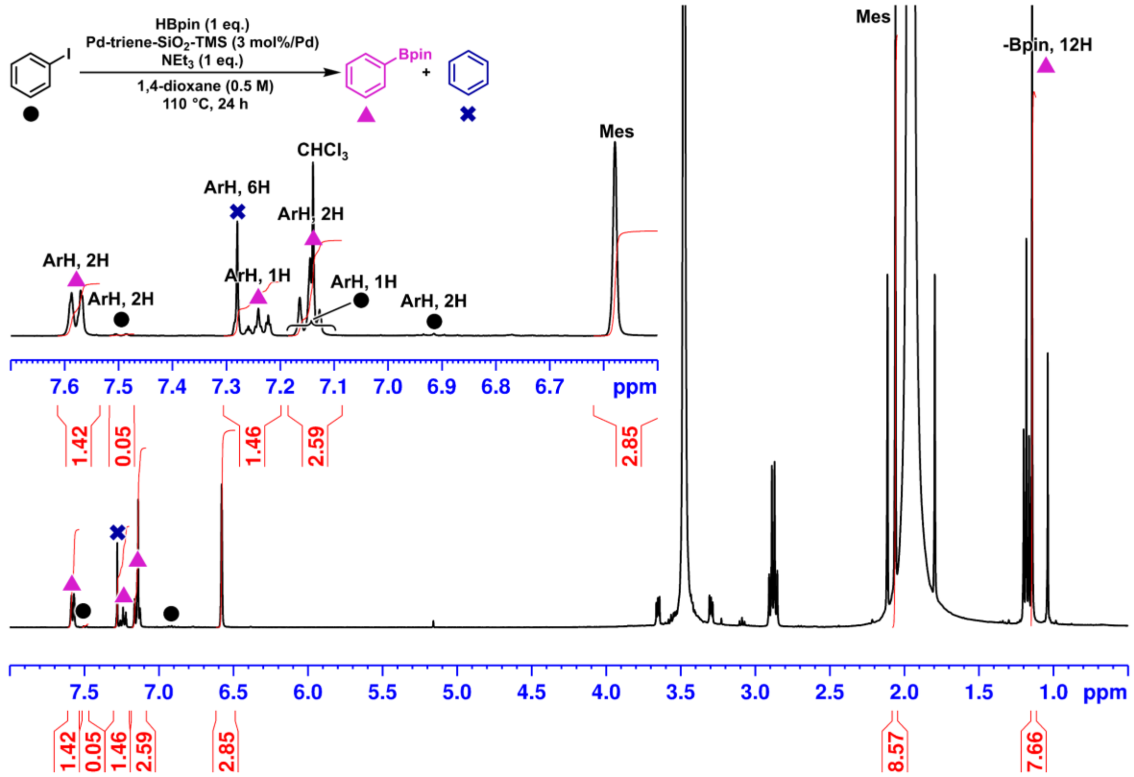


Figure S16. ^{1}H NMR spectrum of crude mixture in the borylation reaction of iodobenzene.

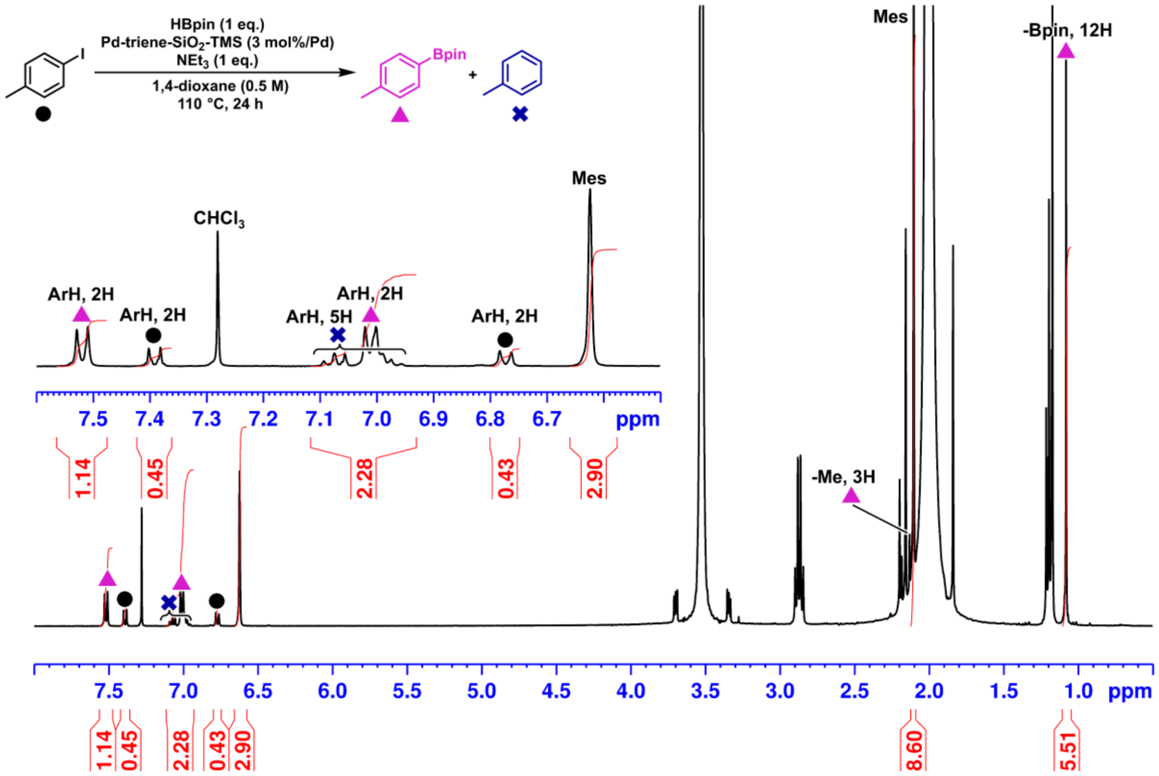


Figure S17. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodotoluene.

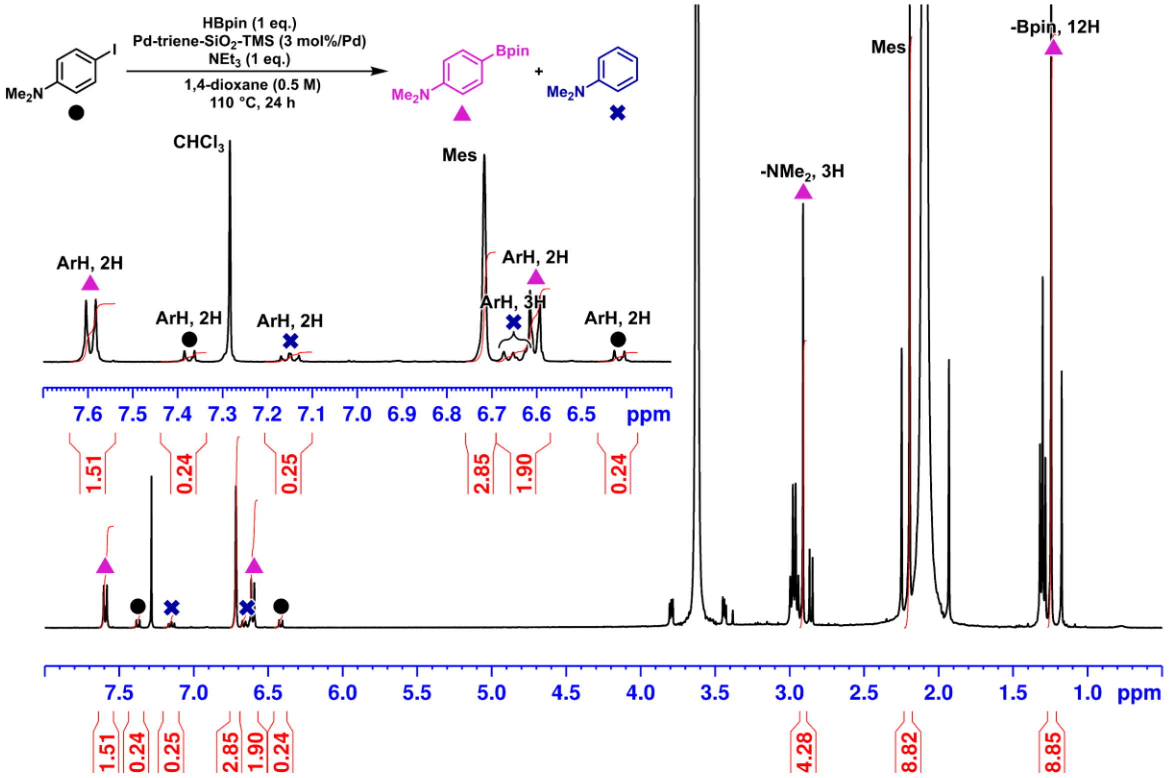


Figure S18. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-bromo-*N,N*-dimethylaniline.

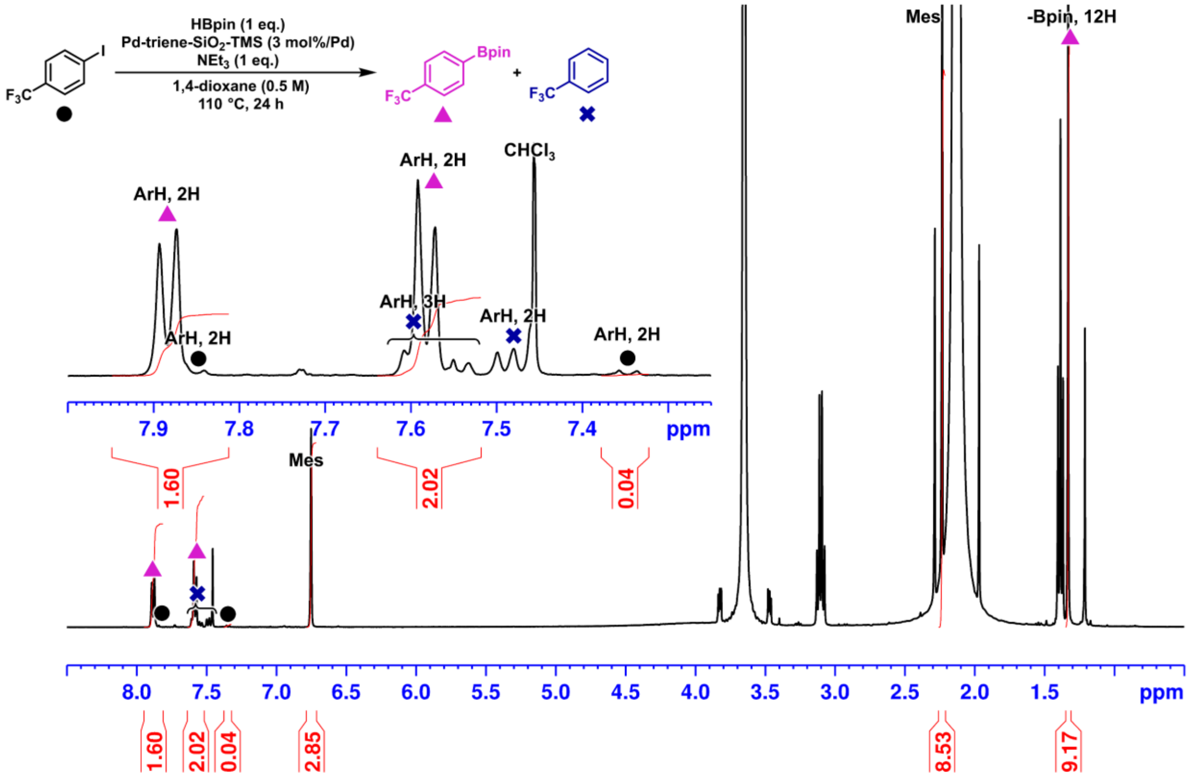


Figure S19. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodobenzotrifluoride.

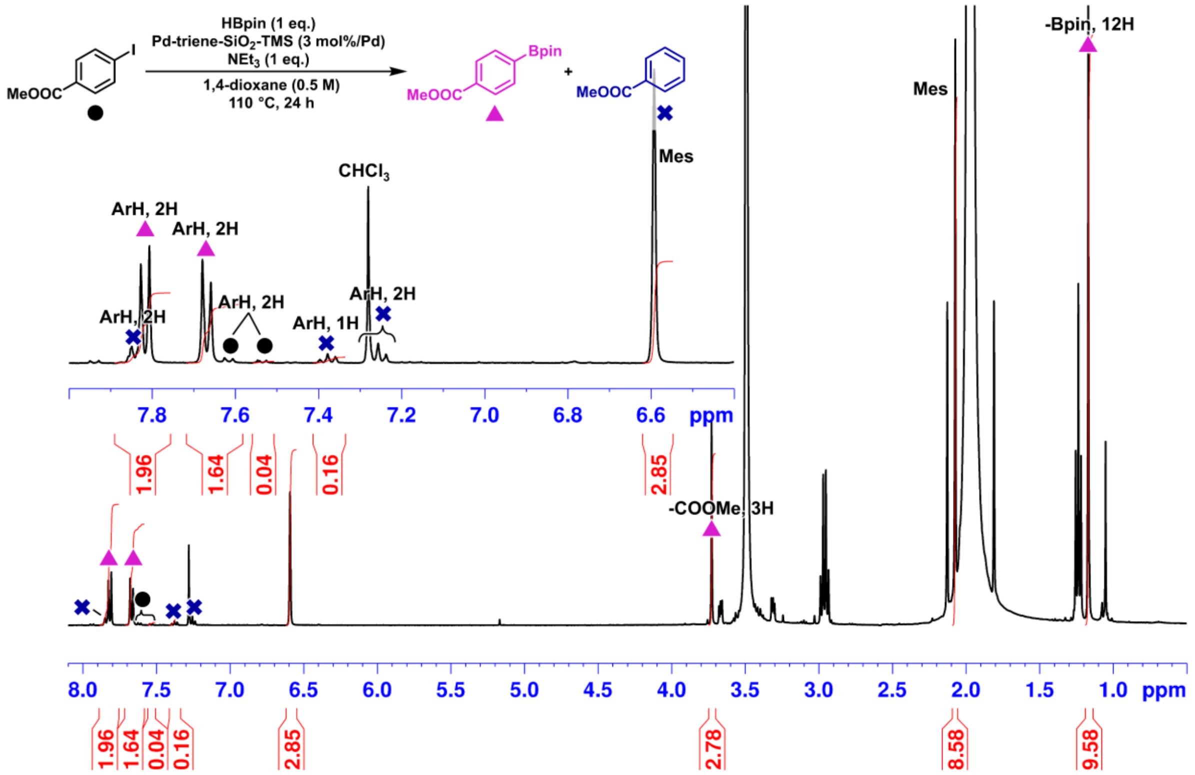


Figure S20. ^{1}H NMR spectrum of crude mixture in the borylation reaction of methyl 4-iodobenzoate.

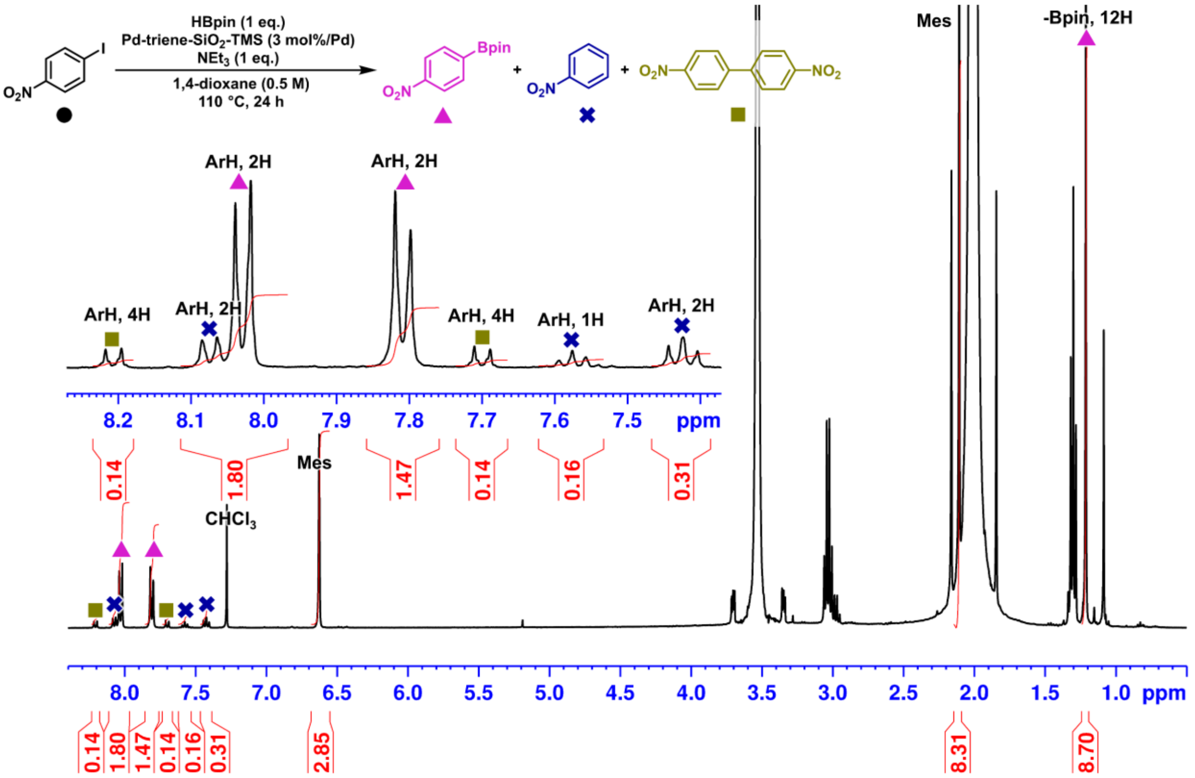


Figure S21. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 1-iodo-4-nitrobenzene.

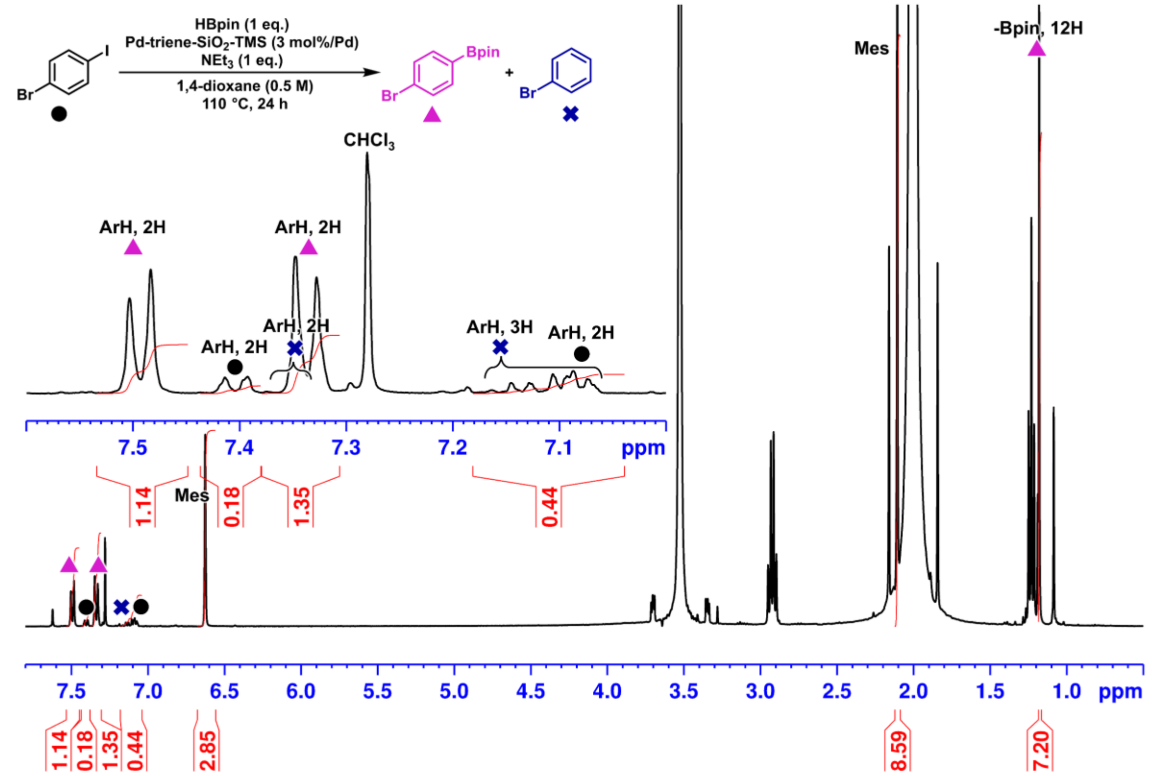


Figure S22. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 1-bromo-4-iodobenzene.

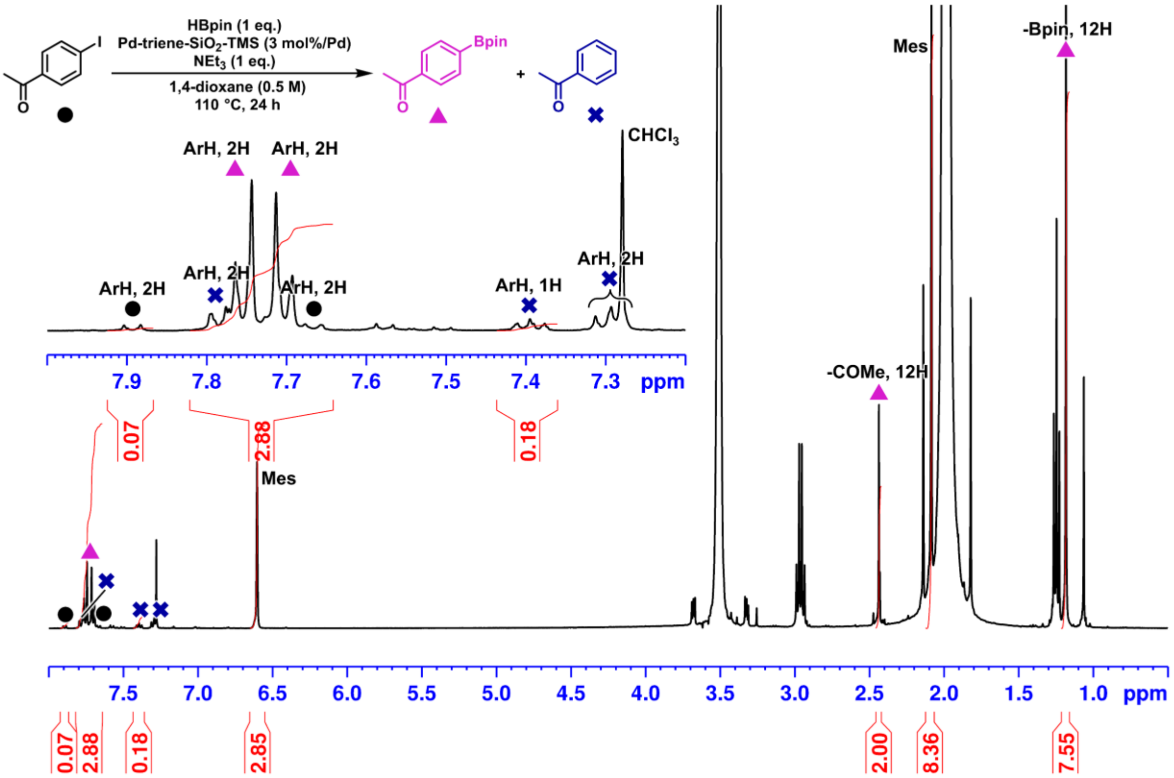


Figure S23. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4'-iodoacetophenone.

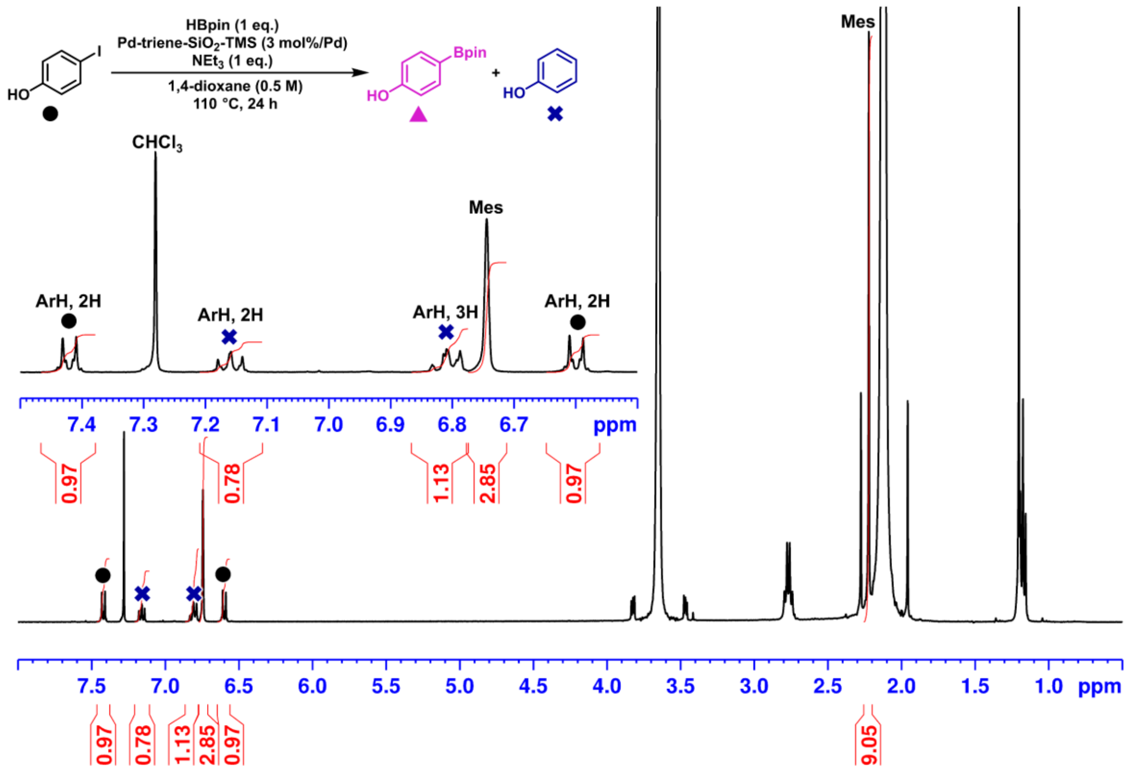


Figure S24. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodophenol.

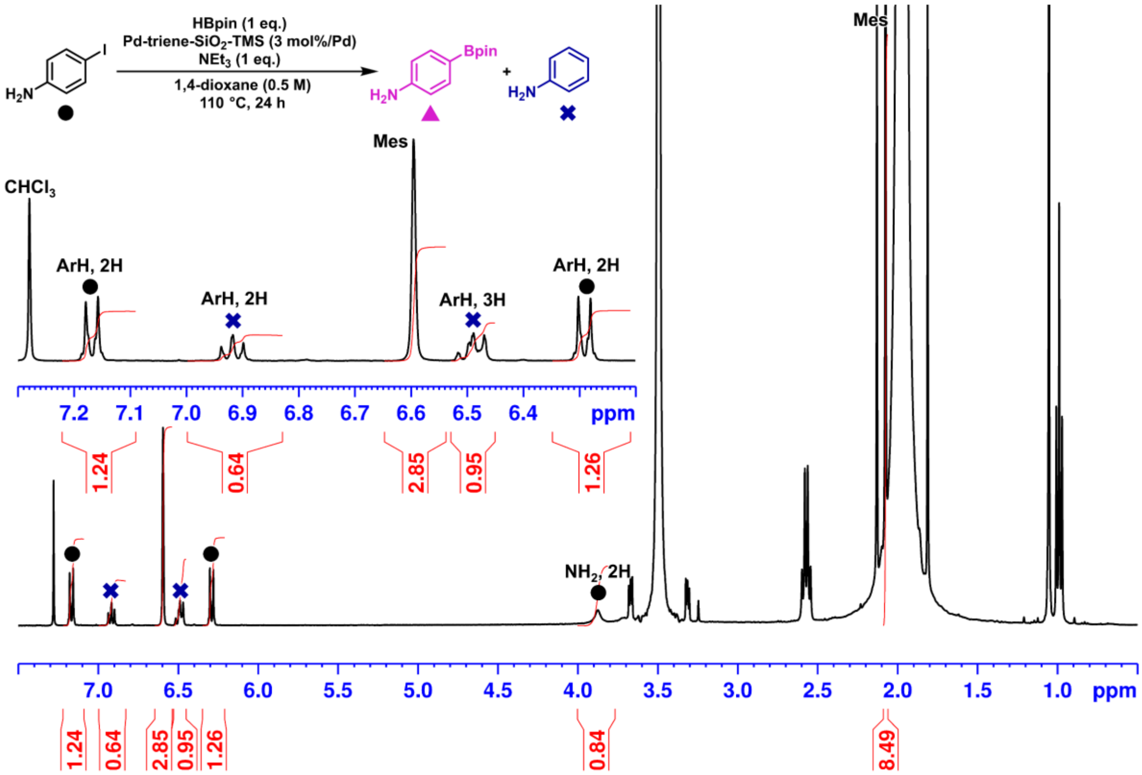


Figure S25. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoaniline.

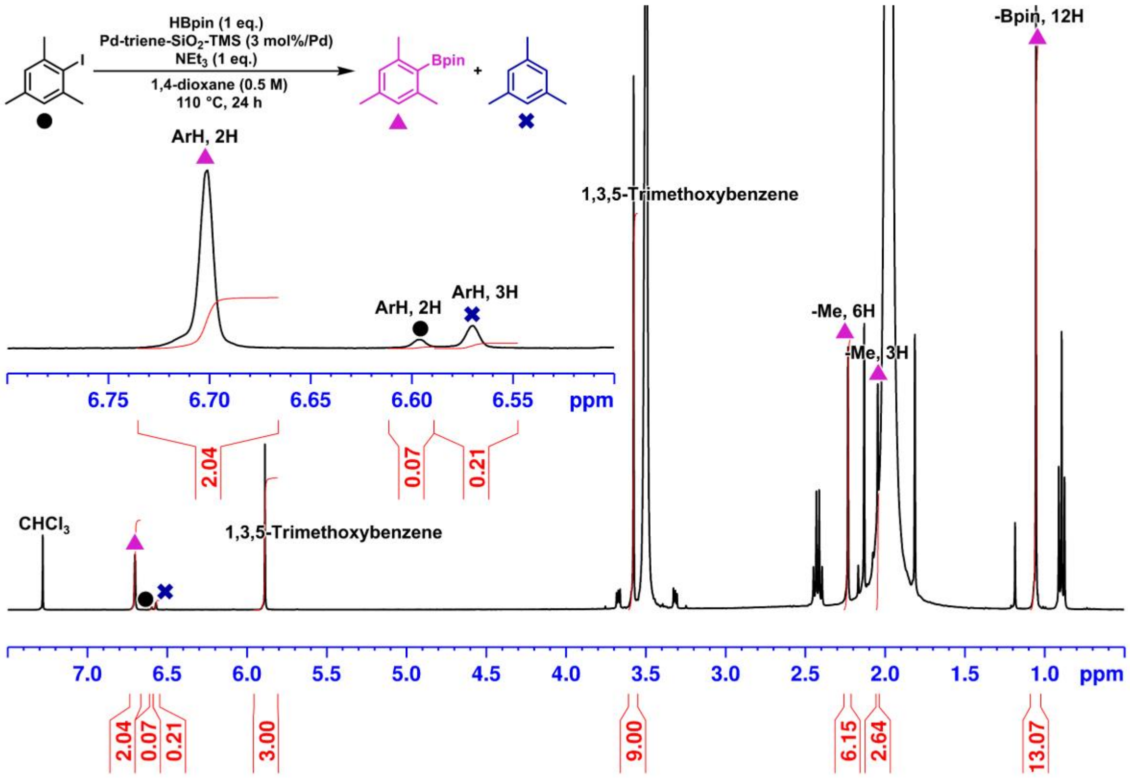


Figure S26. ^{1}H NMR spectrum of crude mixture in the borylation reaction of mesityl iodide.

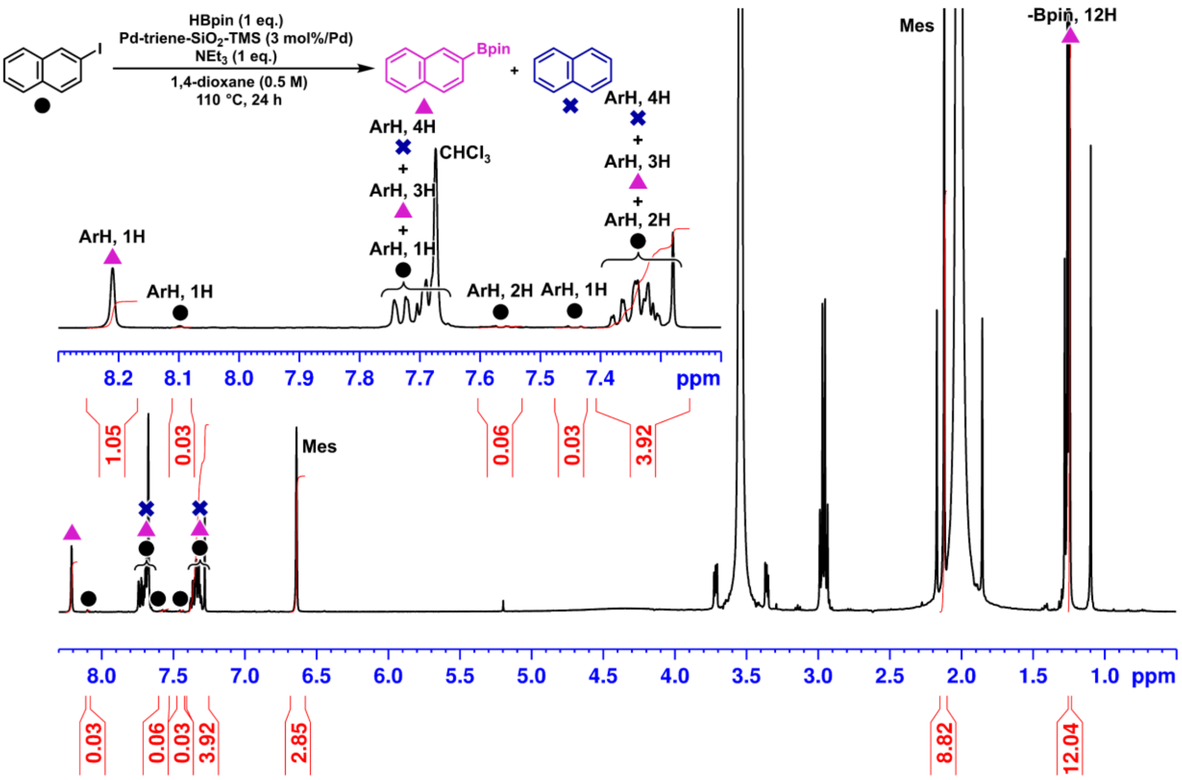


Figure S27. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 2-iodonaphthelene.

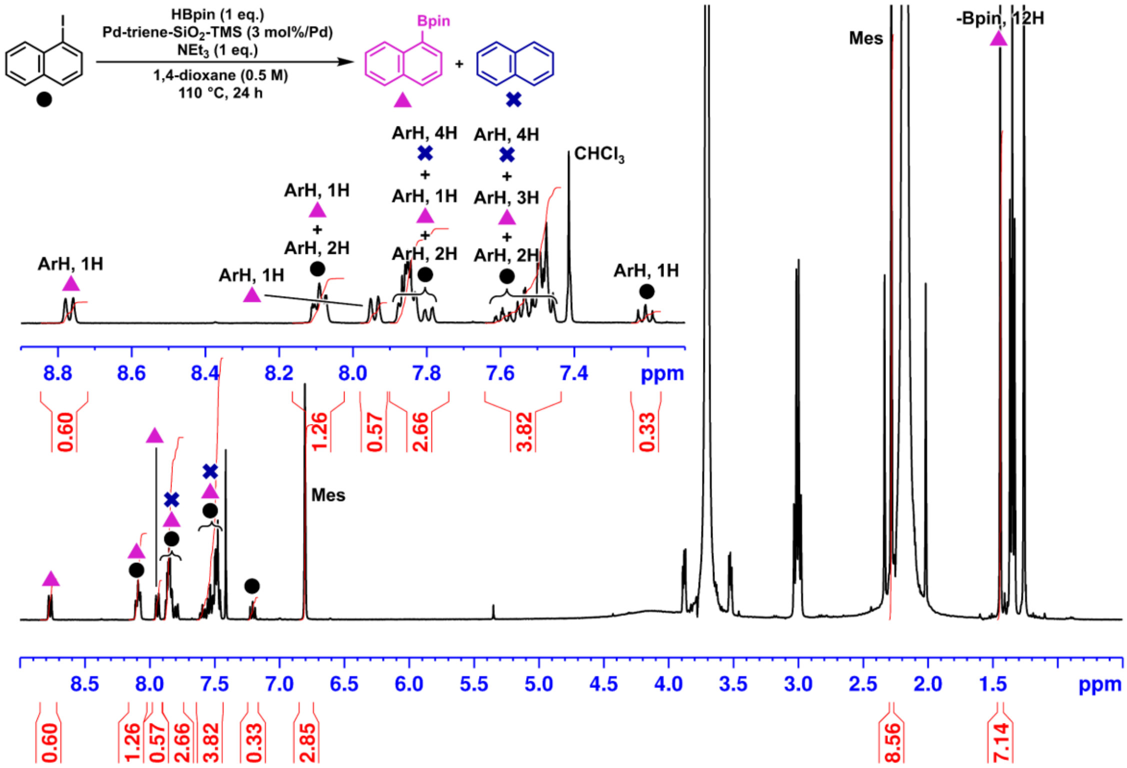


Figure S28. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 1-iodonaphthelene.

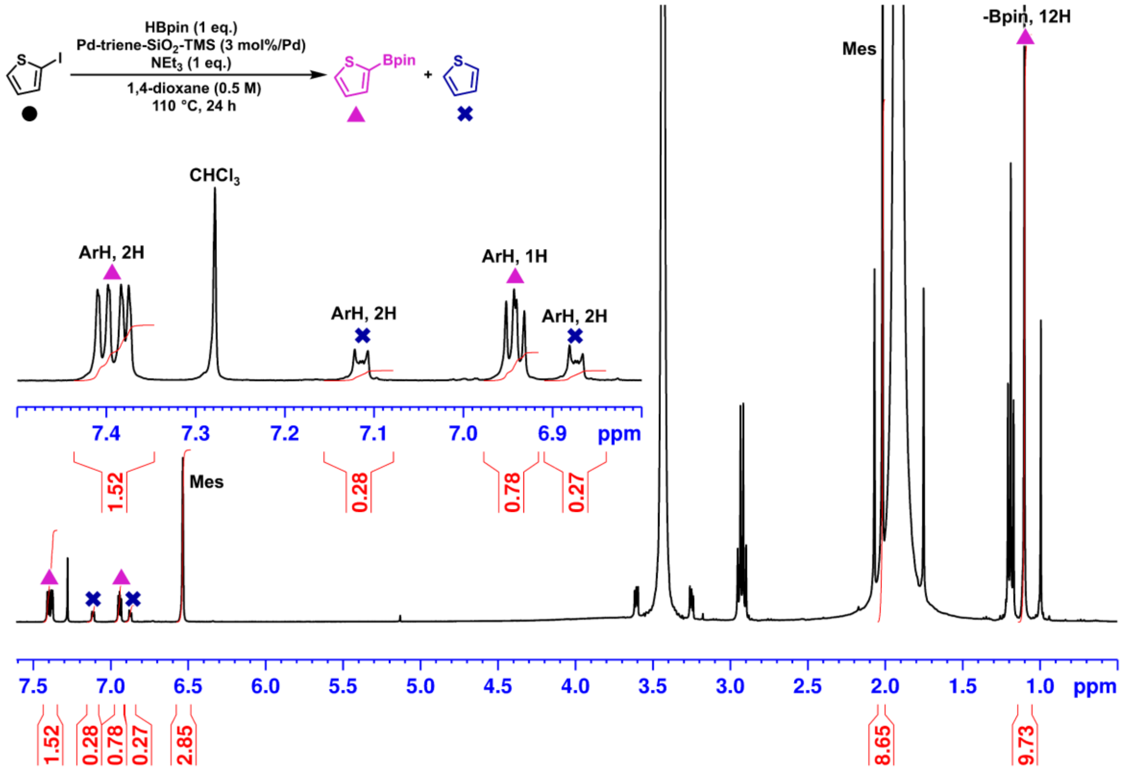


Figure S29. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 2-iodothiophene.

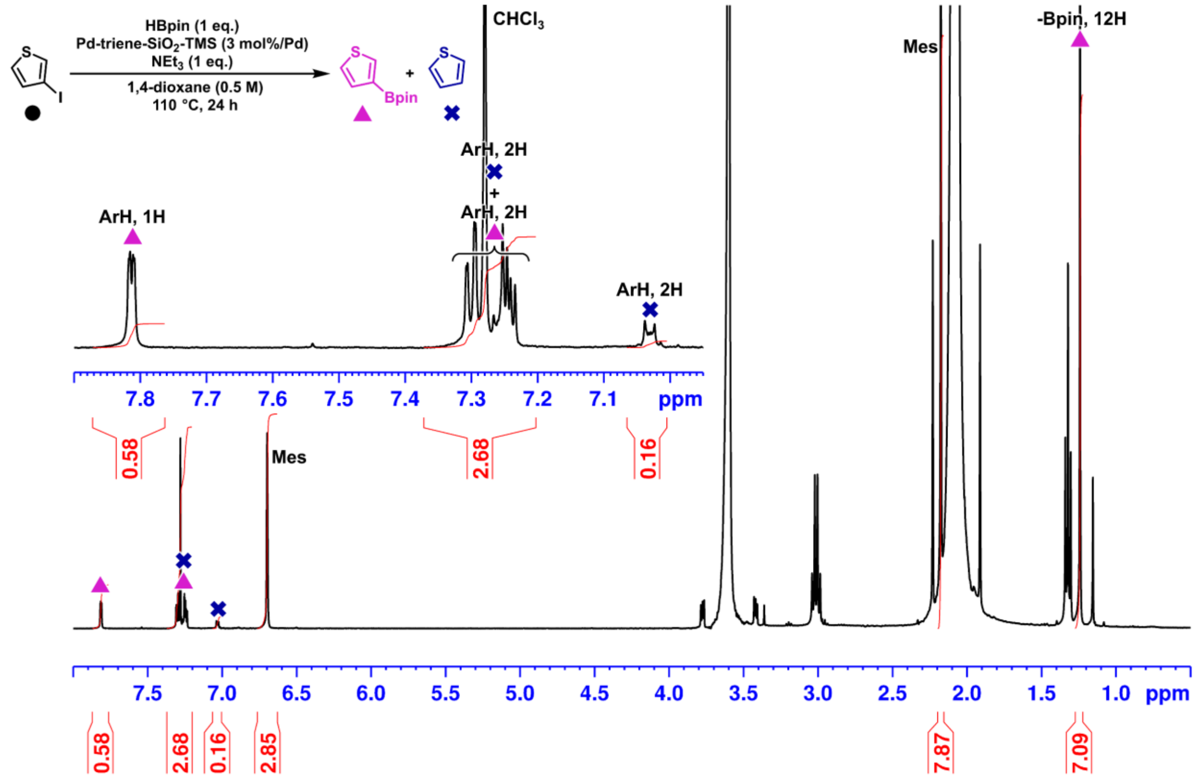


Figure S30. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 3-iodothiophene.

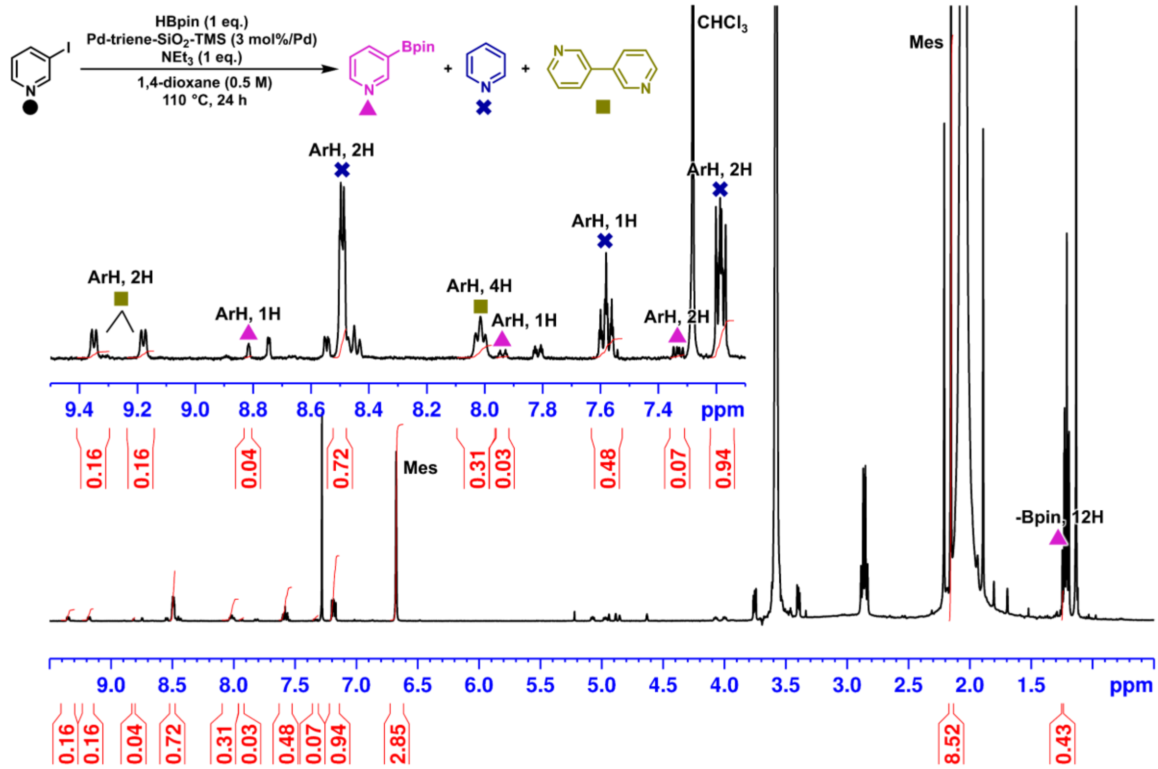


Figure S31. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 3-iodopyridine.

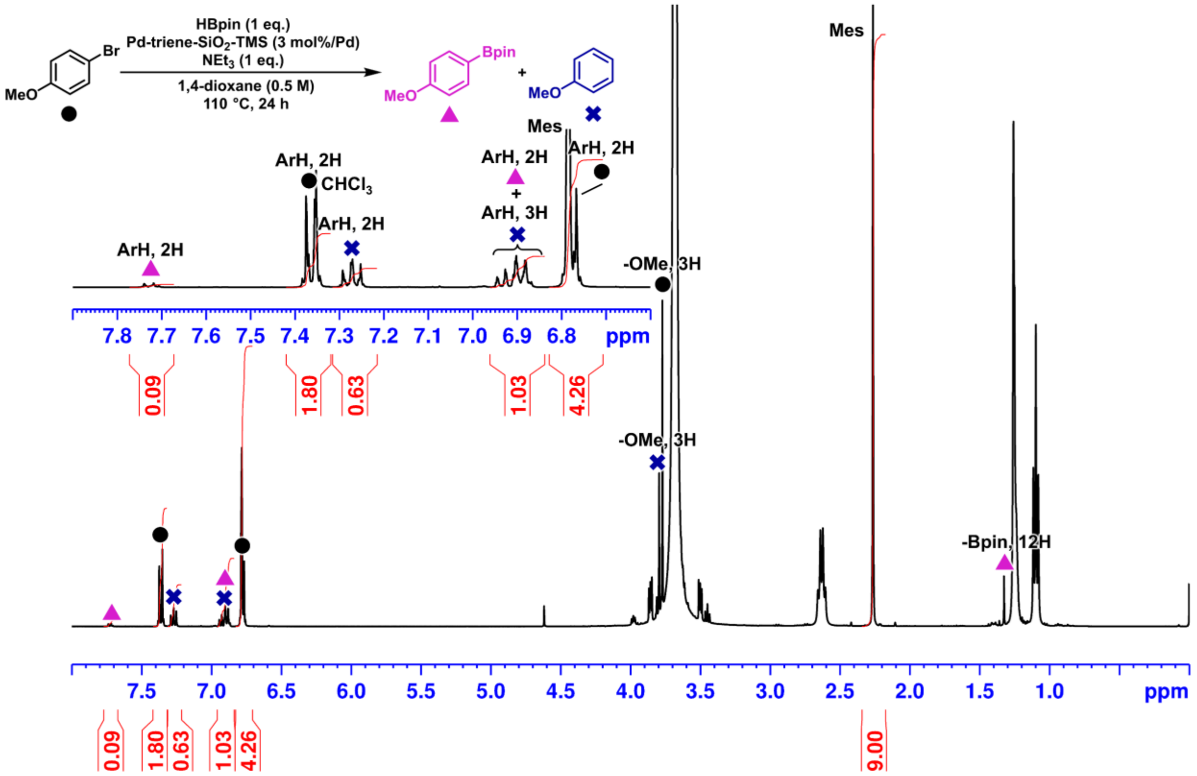


Figure S32. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-bromoanisole.

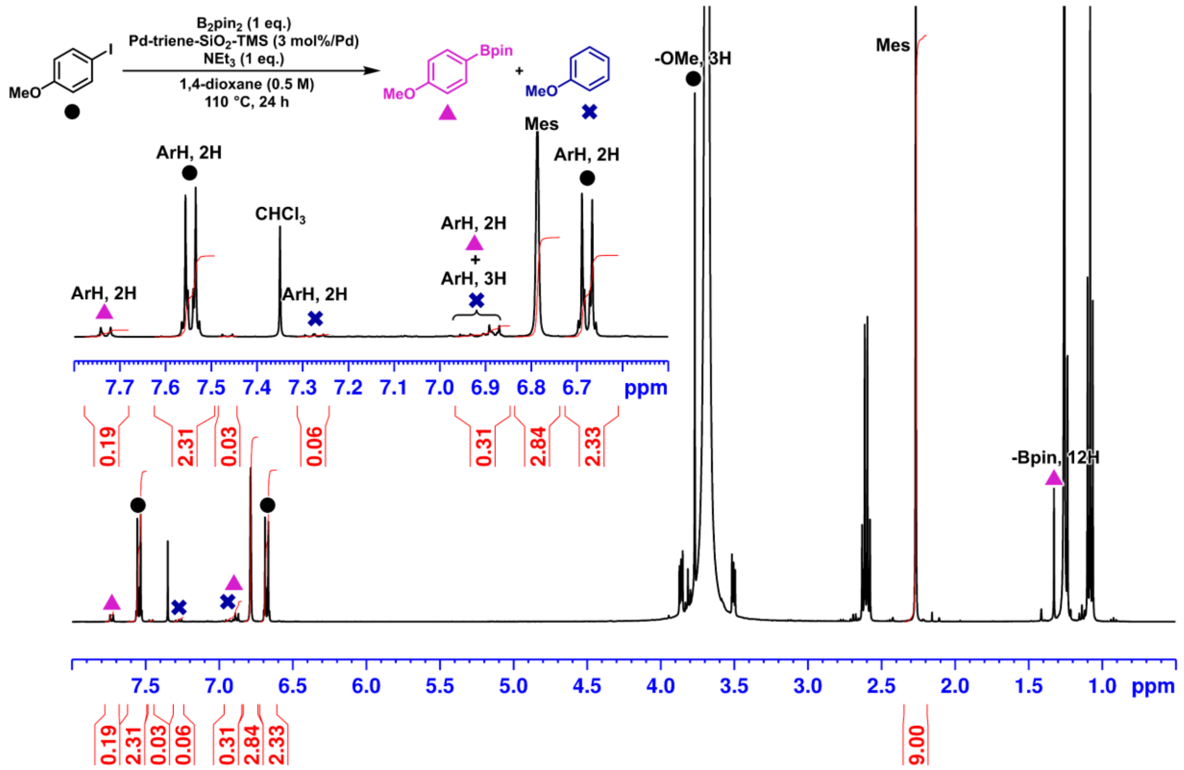


Figure S33. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoanisole with bis(pinacolato)diboron (B_2pin_2).

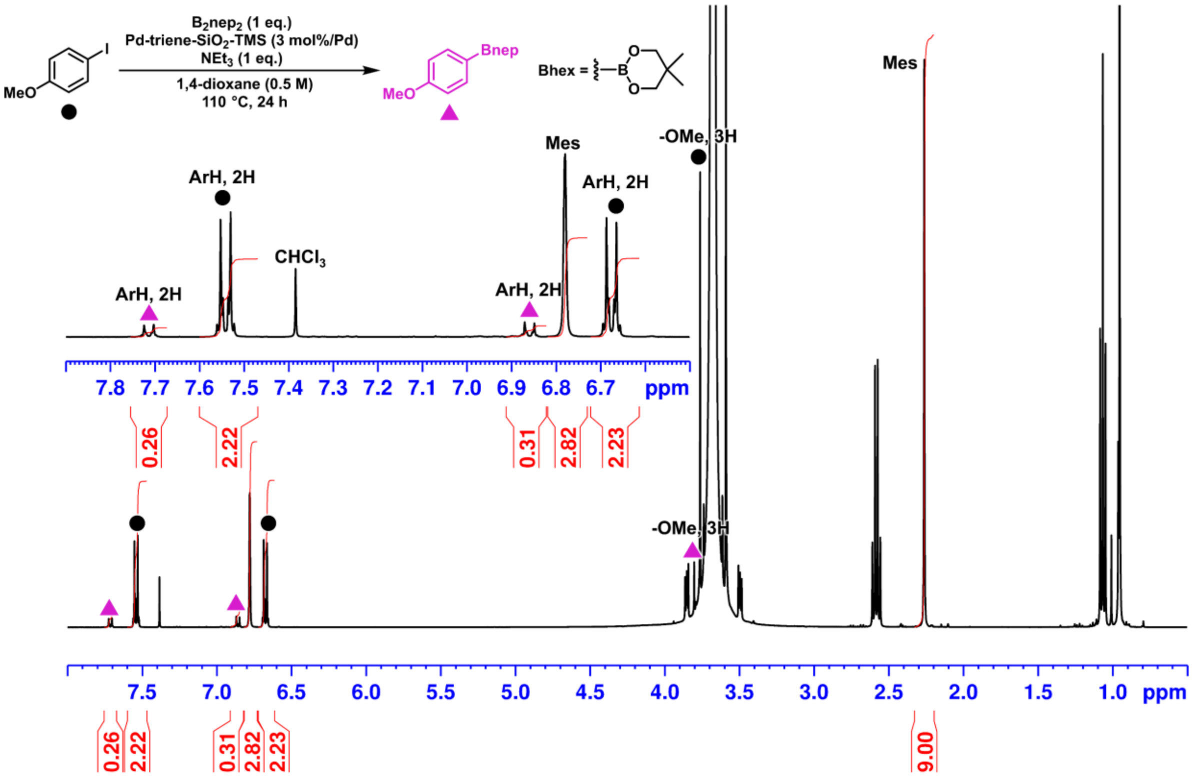


Figure S34. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoanisole with bis(neopentylglycolato)diboron (B_2nep_2).

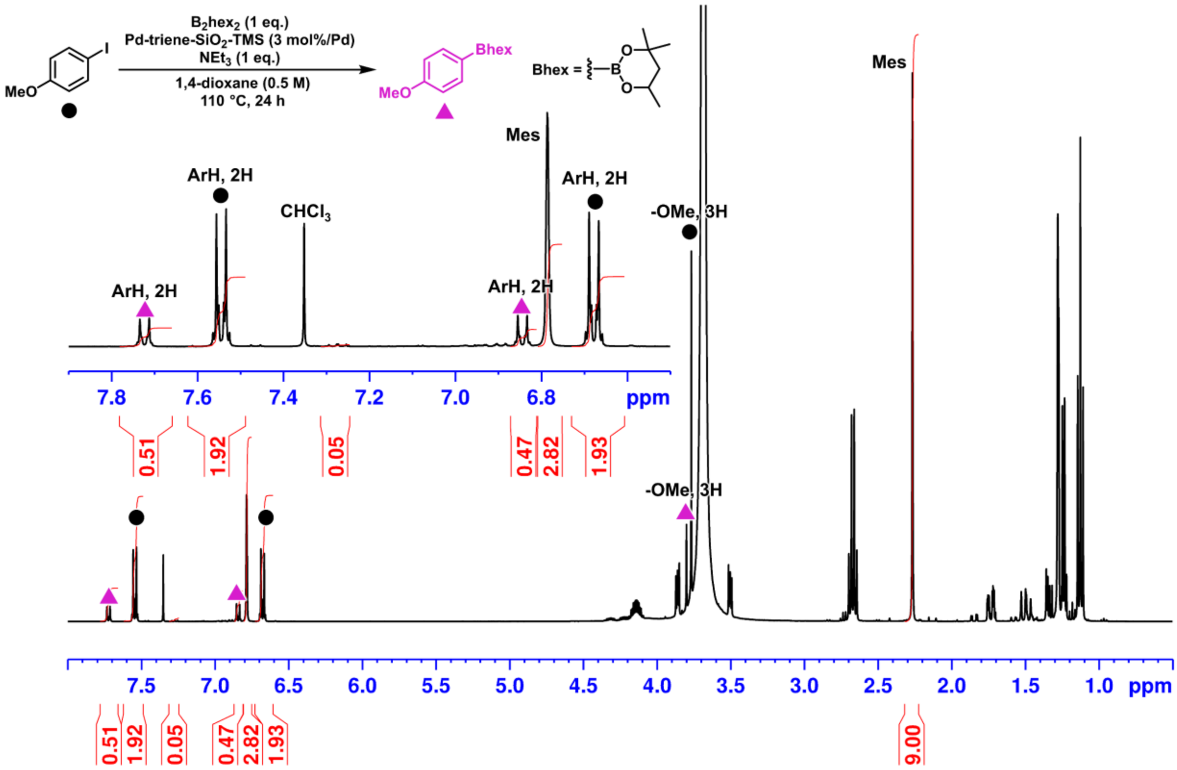


Figure S35. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoanisole with bis (hexylene glycolato) diboron (B_2hex_2).

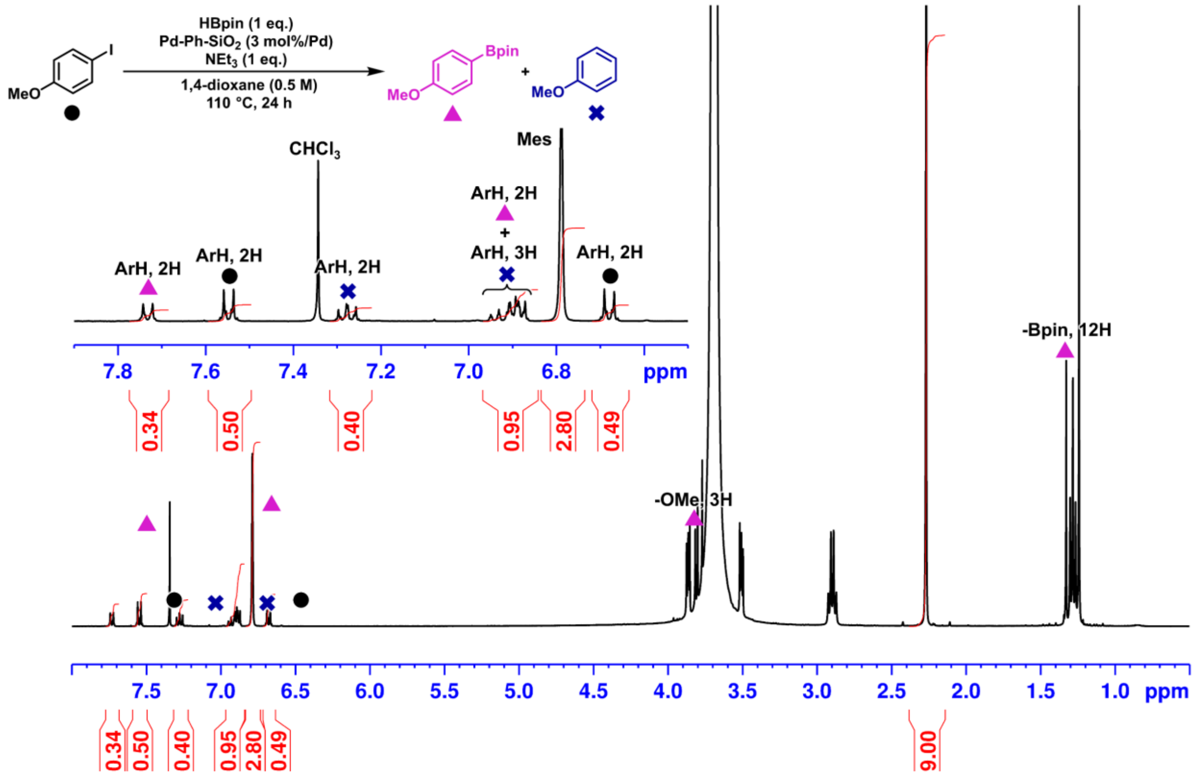


Figure S36. ^{1}H NMR spectrum of crude mixture in the borylation reaction of 4-iodoanisole catalyzed by **Pd-Ph-SiO$_2$**.

7. XRD data for the prepared materials

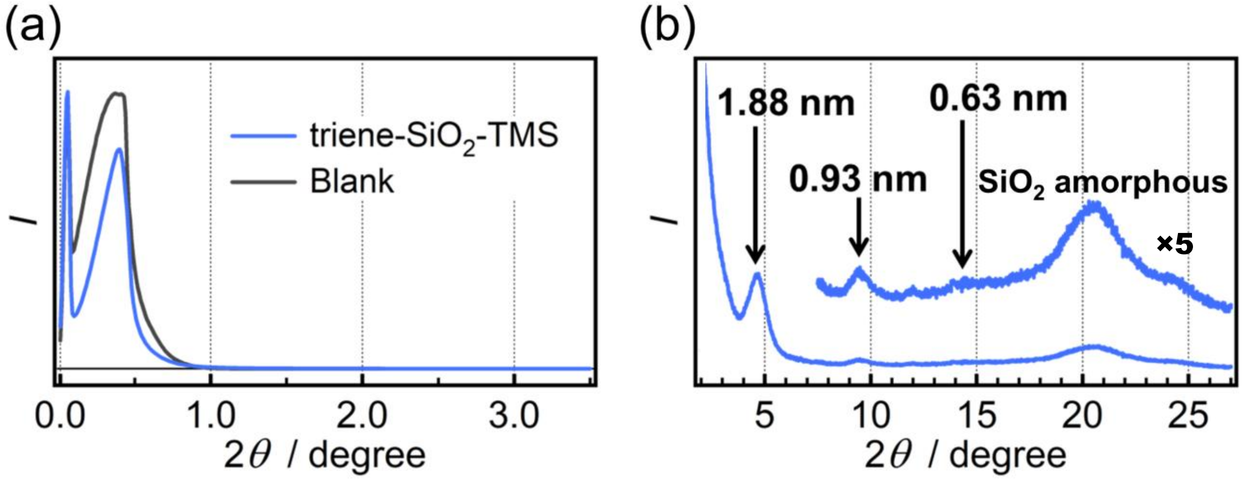


Figure S37. XRD profile at (a) a low angle and (b) a medium angle for **triene-SiO$_2$-TMS**.

8. Nitrogen adsorption/desorption isotherms and NLDFT pore size distribution

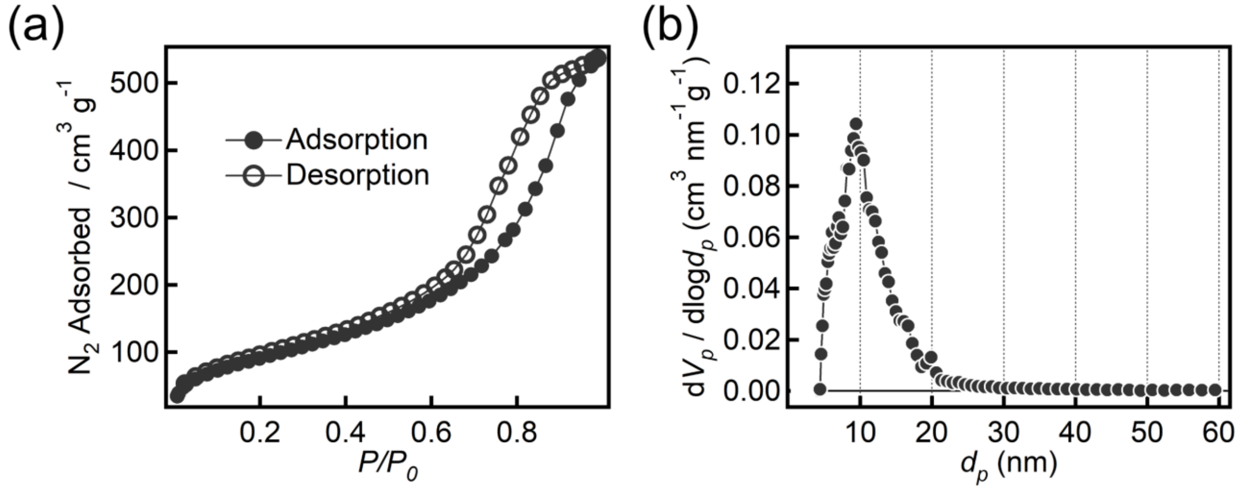


Figure S38. Nitrogen adsorption/desorption isotherms (a) and NLDFT pore size distribution (b) of **triene-SiO_2**.

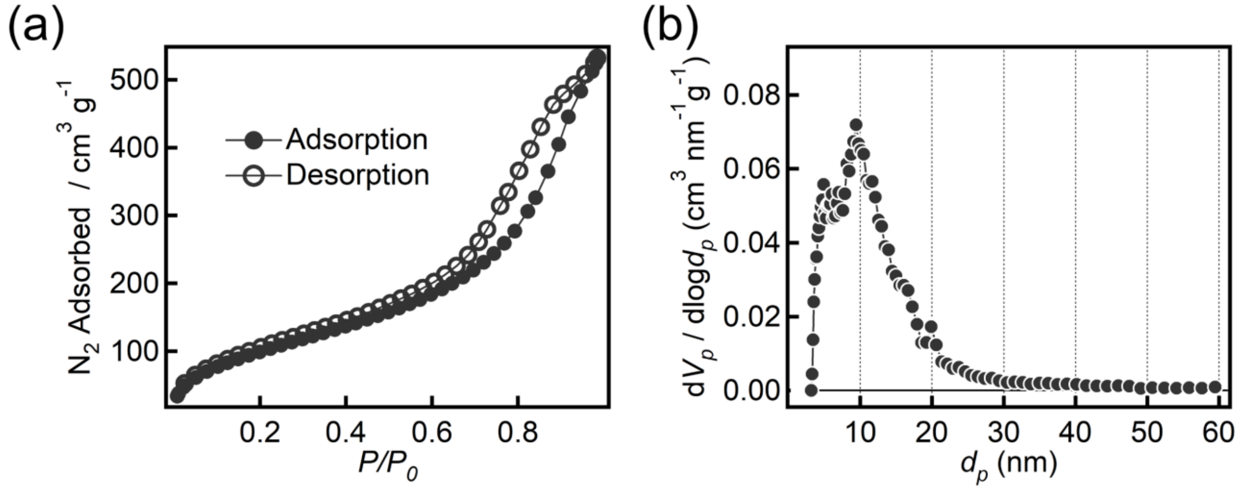


Figure S39. Nitrogen adsorption/desorption isotherms (a) and NLDFT pore size distribution (b) of **triene-SiO_2-TMS**.

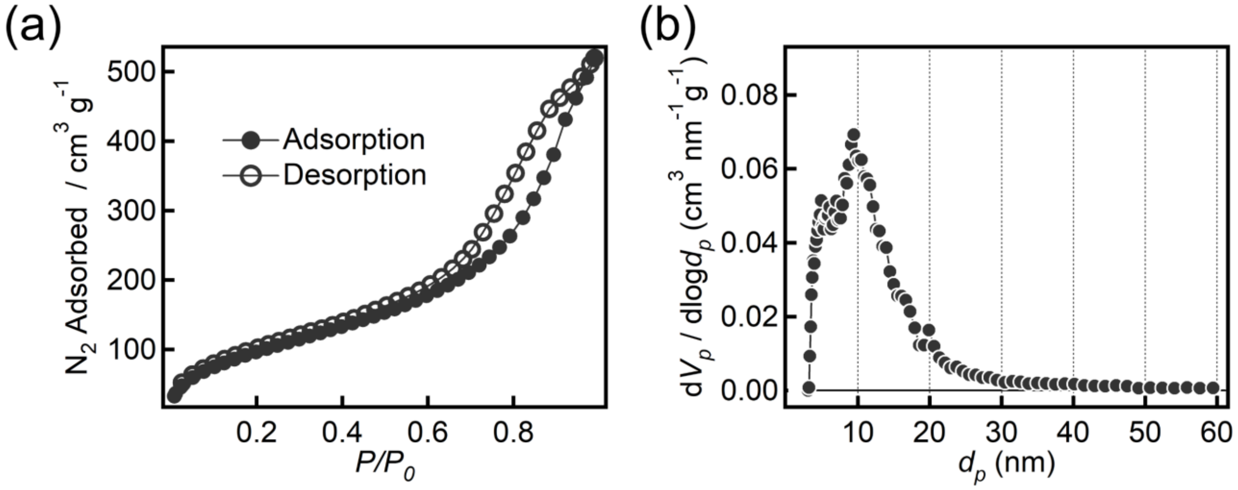


Figure S40. Nitrogen adsorption/desorption isotherms (a) and NLDFT pore size distribution (b) of **Pd-triene-SiO$_2$-TMS**.

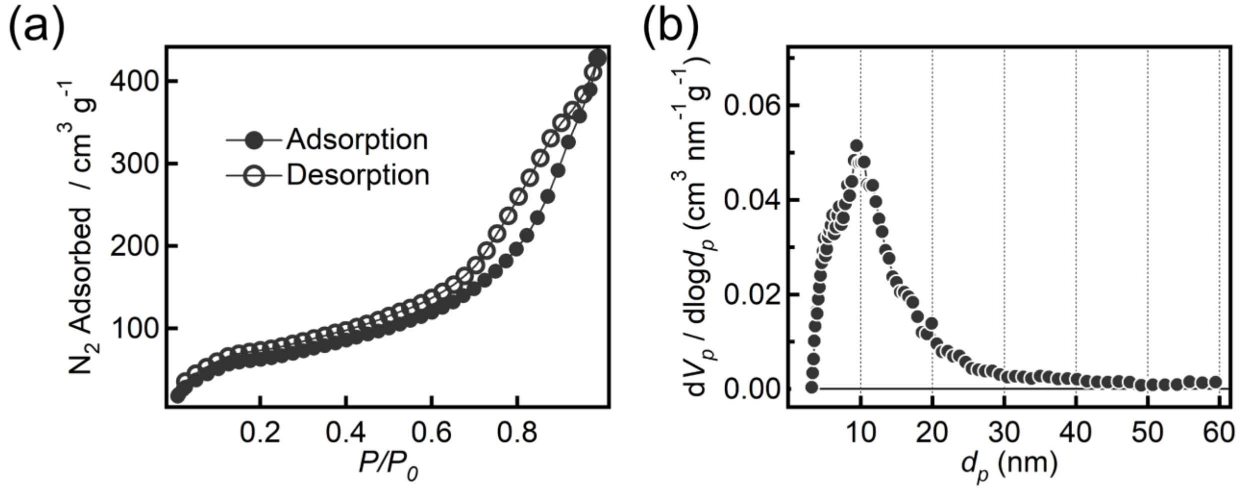


Figure S41. Nitrogen adsorption/desorption isotherms (a) and NLDFT pore size distribution (b) of **triene-SiO$_2$-TMS** after four cycles reaction.

Table S2. Structural parameters of various catalytic materials.

	BET surface area [m^2 g^{-1}]	DFT pore diameter [nm]	Pore volume [cm^3 g^{-1}]
triene-SiO$_2$	347.45	9.42	0.805
triene-SiO$_2$-TMS	383.05	9.42	0.785
Pd-triene-SiO$_2$-TMS	373.12	9.42	0.759
Pd-triene-SiO$_2$-TMS after four cycles reaction	231.19	9.42	0.609

9. TEM images and EDX spectra

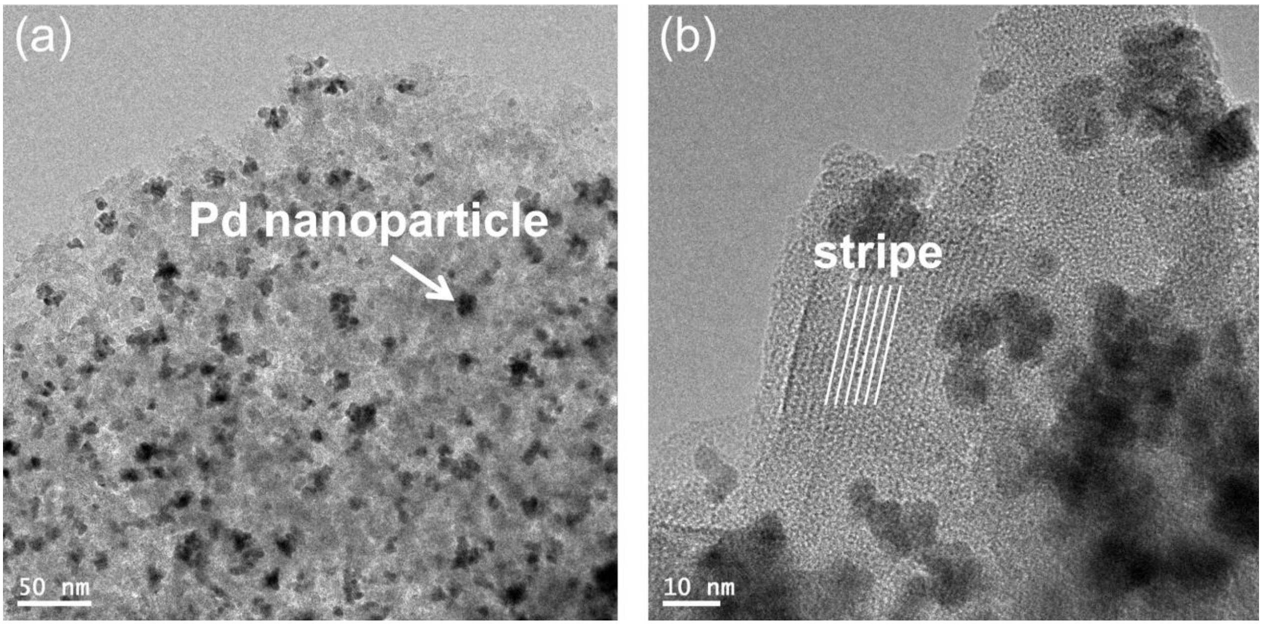


Figure S42. (a, b) TEM images of **Pd-triene-SiO$_2$-TMS**.

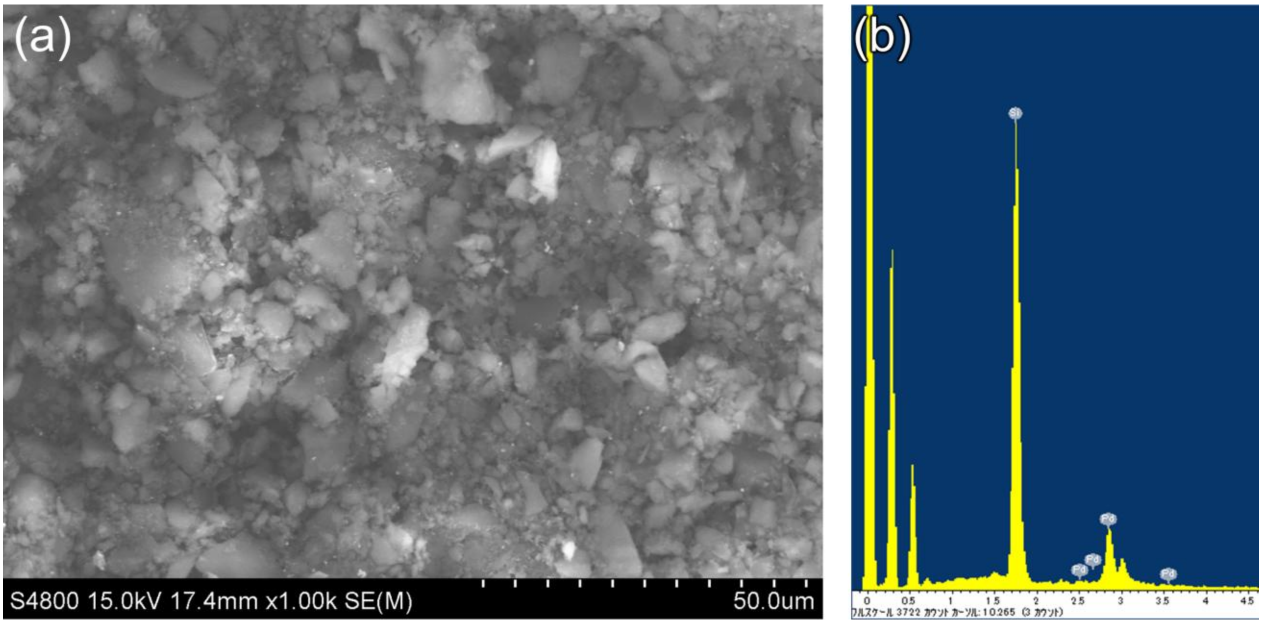


Figure S43. SEM-EDX (a) image and (b) spectrum of **Pd-triene-SiO$_2$-TMS**.

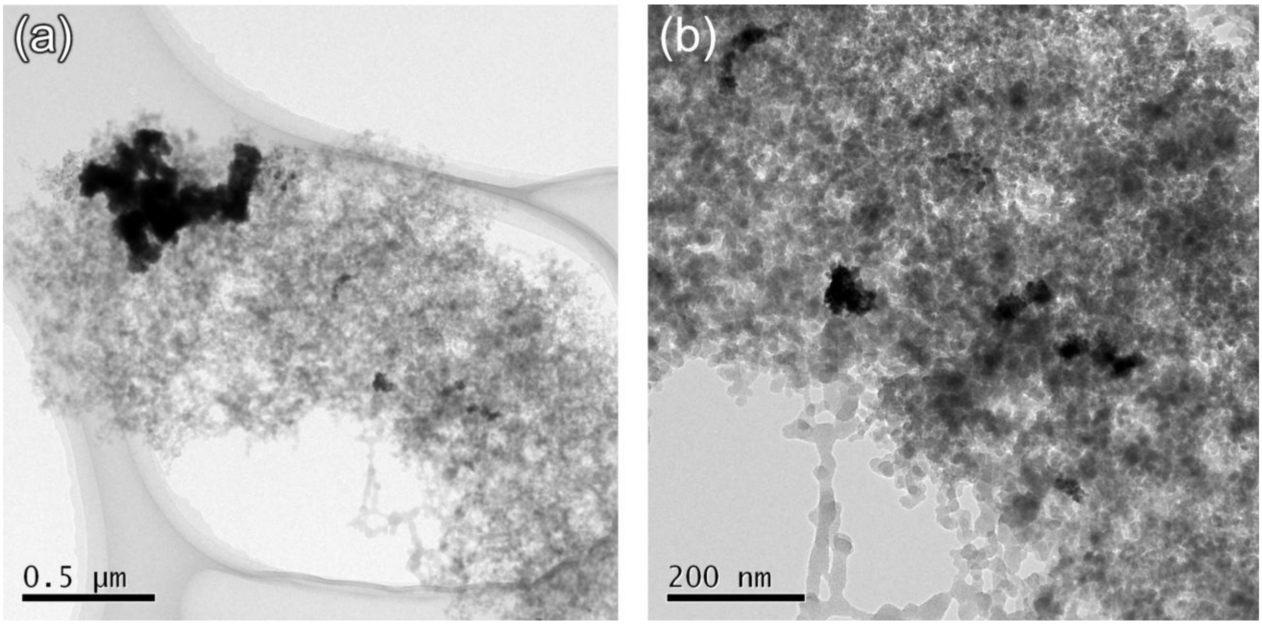


Figure S44. SEM-EDX (a) image and (b) spectrum of **Pd-AEROSIL**.

10. Refference

[S1] H. Watanabe, T. Ariyoshi, A. Ozaki, M. Ihara, M. Ono, H. Saji *Bioorg. Med. Chem.*, **2017**, *25*, 6398.

[S2] S. Banerjee, T. Kobayashi, K. Takai, S. Asako, L. Ilies *Org. Lett.*, **2022**, *24*, 7242.

[S3] M. Murata, M. Ishikura, M. Nagata, S. Watanabe, Y. Masuda *Org. Lett.*, **2002**, *4*, 1843.

[S4] K. Okamoto, Y. Goto and S. Inagaki *J. Mater. Chem.*, **2005**, *15*, 4136–4140.

[S5] K. L. Billingsley, S. L. Buchwald *J. Org. Chem.*, **2008**, *73*, 5589.

[S6] C.-F. Meng, B.-B. Zhang, Q. Liu, K.-Q. Chen, Z.-X. Wang, X.-Y. Chen *J. Am. Chem. Soc.*, **2024**, *146*, 7210.

[S7] A. Prakash, S. Basappa, B. Jeebula, D. H. Nagaraju, R. S. Dhayal, S. K. Bose *Org. Lett.*, **2024**, *26*, 2569.

[S8] P. B. Dzhevakov, M. A. Topchiy, D. A. Zharkova, O. S. Morozov, A. F. Asachenko, M. S. Nechaev *Adv. Synth. Catal.*, **2016**, *358*, 977.

[S9] C. Kleeberg, L. Dang, Z. Lin, T. B. Marder *Angew. Chem. Int. Ed.*, **2009**, *48*, 5350.

[S10] K. L. Billingsley, T. E. Barder, S. L. Buchwald *Angew. Chem. Int. Ed.*, **2007**, *46*, 5359.

[S11] M. Uzelac, P. Mastropierro, M. de Tullio, I. Borilovic, M. Tarrés, A. R. Kennedy, G. Aromí, E. Hevia *Angew. Chem. Int. Ed.*, **2021**, *60*, 3247.

[S12] P. Leowanawat, A.-M. Resmerita, C. Moldoveanu, C. Liu, N. Zhang, D. A. Wilson, L. M. Hoang, B. M. Rosen, V. Percec *J. Org. Chem.*, **2010**, *75*, 7822.

[S13] K. Matsuo, E. Yamaguchi, A. Itoh *J. Org. Chem.*, **2023**, *88*, 6176.