New Catalysts for Suzuki-Miyaura Coupling

Processes: Scope and Studies of the Effect of

Ligand Structure

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Experimental Section

General. All reactions were carried out under an argon or nitrogen atmosphere, unless otherwise noted. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Unless otherwise noted, THF, Et₂O, CH₂Cl₂ and toluene were purchased from J.T. Baker in CYCLE-TAINER[®] solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF and Et₂O) or through neutral alumina and copper (II) oxide (for toluene and CH₂Cl₂).¹ Unless otherwise stated, commercially obtained materials were used without further purification. Aryl halides were purchased from Aldrich Chemical Co. Aryl halides were purified by filtration through a thin pad of basic alumina prior to use. Pd(OAc)₂ was purchased from Strem, Inc. or supplied by Englehard. Boronic acids were purchased from Aldrich Chemical Co., Alfa Aesar or Frontier Scientific, Inc. Best results were obtained with newly purchased or freshly recrystallized boronic acids. Alkyl boranes were prepared by the reaction of 9-BBN with the requisite alkene in THF at room temperature for 4 h and were used without isolation. Magnesium powder, -50 mesh, (99 %) and 1,2-dibromoethane (99+%) were purchased from Aldrich. 1-Bromo-2,4,6-triisopropylbenzene (95 %) and 2-bromochlorobenzene (99 %) were purchased from Alfa Aesar. Anhydrous CuCl (97 %) was purchased from Strem

and stored in a nitrogen-filled glove box. ClPCy_2 and ClPPh_2 was also purchased from Strem and stored under argon. *Anhydrous tribasic potassium phosphate was purchased from Fluka Chemical Co. and used as supplied. Tribasic potassium phosphate monohydrate was purchased from Fluka Chemical Co. and was finely ground (using a mortar and pestle) prior to use.* The source (and thus the particle size) of the base employed may be critical for achieving efficient reactions.

All new compounds were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy, in addition to elemental analysis (Atlantic Microlabs, Inc) and/or low resolution mass spectroscopy. For those new compounds for which a satisfactory elemental analysis was not obtained, copies of the ^1H and ^{13}C NMR are attached. Nuclear Magnetic Resonance spectra were recorded on a Varian Mercury 300, a Varian Unity 300 or 500, or a Bruker 400 instrument. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 (neat samples were placed directly on the DiComp probe). All ^1H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were measured relative to the signals for residual chloroform (7.26 ppm), methylene chloride (5.32 ppm) or benzene (7.16 ppm) in the deuterated solvents. All ^{13}C NMR spectra are reported in ppm relative to deuteriochloroform (77.23 ppm), deuteromethylene chloride (54.00 ppm) or deuterobenzene (128.39 ppm), and all were obtained with ^1H decoupling. All ^{31}P NMR spectra are reported in ppm relative to H_3PO_4 (0 ppm). All ^{19}F NMR spectra are reported in ppm relative to trichlorofluoromethane (0 ppm). Melting points (uncorrected) were obtained on a Mel-Temp capillary melting point apparatus. Gas Chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatography instrument with an FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

The yields in Tables 1-8 refer to isolated yields (average of two runs) of compounds estimated to be $\geq 95\%$ pure as determined by ^1H NMR and GC analysis and/or combustion analysis. The procedures described in this section are representative, and thus the yields may differ from those shown in Tables 1-8.

Preparation of 2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl [S-PHOS (1)].

To a cold (0 °C), stirred solution of 1,3-dimethoxybenzene (2.00 mL, 15.3 mmol, 1.1 equiv.) in dry THF (35 mL) was added *n*-BuLi (6.20 mL, 2.5 M solution in hexanes, 15.5 mmol, 1.1 equiv.) dropwise via syringe over 5 min. The reaction mixture was allowed to warm to room temperature and then stirred at room temperature for 3.5 h. The mixture was re-cooled to 0 °C and neat 2-bromochlorobenzene (1.60 mL, 13.7 mmol, 1.0 equiv) was added dropwise via syringe over 15 min with vigorous stirring. The resulting burgundy colored mixture was stirred at 0 °C for an additional 15 min. At this point, GC analysis of an aliquot of the reaction mixture,

quenched into ether/water, indicated that complete consumption of the bromochlorobenzene starting material and clean conversion to 2-bromo-2',6'-dimethoxybiphenyl had occurred. The reaction mixture was cooled to -78 °C and *n*-BuLi (6.20 mL, 2.5 M solution in hexanes, 15.5 mmol, 1.1 equiv.) was added dropwise via syringe over 5 min. The resulting mixture was stirred at -78 °C (periodic swirling of the reaction flask by hand was required as stirring with a magnetic stirrer became difficult) for 30 min. Neat chlorodicyclohexylphosphine (3.03 mL, 13.7 mmol, 1.0 equiv) was then added via syringe. The reaction mixture was stirred at -78 °C for 1 h and then allowed to slowly warm to room temperature. The resulting mixture was filtered through a pad of flash silica gel topped with a layer of celite, eluting with ethyl acetate (400 mL). The filtrate was concentrated under reduced pressure to provide a yellow solid. Recrystallization from acetone provided 2.90 g of **1** as a white solid. Concentration of the mother liquor followed by trituration of the residue thus obtained with methanol, provided additional solid material. This material was recrystallized from acetone to afford a further 0.42 g of the title compound. The overall yield of **1** was 3.32 g (59%), a white solid, mp 162-162.5 °C. ¹H NMR (300 MHz, C₆D₆) δ: 7.59 (dm, *J* for the doublet = 7.2 Hz, 1H), 7.39-7.42 (m, 1H), 7.15-7.25 (m, 3H), 6.43 (d, *J* = 8.5 Hz, 2H), 3.33 (s, 6H), 1.60-1.94 (m, 12H), 1.06-1.36 (m, 10 H). ¹³C NMR (75 MHz, C₆D₆) δ: 158.49, 158.48, 144.3, 143.9, 137.3, 137.0, 132.82, 132.77, 132.4, 132.3, 129.2, 128.82, 128.81, 128.2, 126.8, 121.2, 121.1, 104.0, 55.2, 35.0, 34.8, 31.0, 30.8, 30.3, 30.1, 28.22, 28.15, 28.07, 28.05, 27.40, 27.39 (observed complexity due to P-C splitting; definitive assignments have not yet been made). ³¹P NMR (121 MHz, C₆D₆) δ: -8.6. IR (neat, cm⁻¹): 2921, 2848, 1588, 1470, 1459, 1430, 1245, 1109, 909, 722. Anal. Calcd for C₂₆H₃₅O₂P: C, 76.07; H, 8.59. Found: C, 75.97; H, 8.61.

Preparation of 2-Bromo-2',6'-dimethoxybiphenyl.

To a cold (0 °C), stirred solution of 1,3-dimethoxybenzene (2.00 mL, 15.3 mmol, 1.2 equiv.) in dry THF (30 mL) was added *n*-BuLi (9.60 mL, 1.6 M solution in hexanes, 15.4 mmol, 1.2 equiv.) dropwise via syringe over 5 min. The reaction mixture was allowed to warm to room temperature and then stirred at room temperature for 5 h. The mixture was recooled to 0 °C and neat 2-bromochlorobenzene (1.50 mL, 12.8 mmol, 1.0 equiv) was added dropwise via syringe over 15 min with vigorous stirring. The resulting burgundy colored mixture was stirred at 0 °C for an additional 15 min. Methanol (0.25 mL) was added via syringe and the resulting mixture was concentrated under reduced pressure. To the residue so obtained was added diethyl ether (50 mL) and water (50 mL). The layers were separated and the aqueous phase was extracted with diethyl ether (2 x 25 mL). The combined organic extracts were washed with brine (1 x 20 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to provide a yellow solid. The crude product was recrystallized from methanol to afford the title compound (3.03 g, 81% yield) as a pale yellow solid, mp = 141-142 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.69 (dd, *J* = 6.9, 1.1 Hz, 1H), 7.34-7.40 (m, 2H), 7.20-7.28 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 3.76 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.8, 136.25, 132.52, 132.47, 129.6, 128.8, 127.1, 125.4, 119.0, 104.2, 56.2. IR (neat, cm⁻¹): 2946, 1584, 1472, 1432, 1248, 1108, 1025, 783. Anal. Calcd for C₁₅H₂₅NO: C, 57.36; H, 4.47. Found: C, 57.11; H, 4.47.

Preparation of 2,4,6-Triisopropyl-2'-diphenylphosphinobiphenyl (**2**)

A flame dried 100 mL, 3 neck, round bottom flask equipped with a Teflon coated magnetic stir bar, reflux condenser, glass stopper, gas inlet adapter and rubber septum was purged with argon and charged with Mg powder, -50 mesh (0.58 g, 24.0 mmol), THF (13 mL) and 2,4,6-triisopropylbromobenzene (2.51 mL, 10.0 mmol). While stirring vigorously under argon, the reaction mixture was then heated to 65 °C in an oil bath and 1,2-dibromoethane (40 μ L) was added dropwise via syringe to initiate the reaction. After 40 – 60 min, Grignard formation was complete as judged by G.C. analysis, and 2-bromochlorobenzene (1.3 mL, 11.0 mmol) was added at 65 °C over 1.1 h with the aid of a syringe pump. After an additional 1 h of stirring at 65 °C, the reaction mixture was cooled to room temperature. Then, anhydrous CuCl (0.05 g, 0.5 mmol) was weighed out in a nitrogen-filled glove box and removed from the glove box prior to its addition by removing the septum and adding the CuCl as rapidly as possible. To this, ClPPh₂ (1.85 mL, 10 mmol) was then added via syringe; the addition was preformed in a dropwise manner to control the exotherm (Caution!). The resulting mixture was stirred at room temperature for 25 h. The reaction mixture was then placed in an ice bath (as a precaution) prior to quenching with methanol (2 mL). The mixture was transferred to a 500 mL round bottom flask and diluted with ethyl acetate (200 mL), stirred for 15 min, concentrated to one third its original volume in *vacuo* and filtered by gravity through a pad of celite eluting with additional portions of ethyl acetate (400 mL). The solvent was removed from the combined organic layers and the crude product was dissolved in a minimal amount of diethyl ether via sonication. An equal volume of methanol was then added to the homogeneous solution, the flask was sealed and the solution was allowed to stand in a refrigerator (-40 °C) for 24 h. The resulting crystals (2.6 g, 56 %) were collected via vacuum filtration and washed with ice-cold diethyl ether. A second crop of crystals was harvested from the mother liquor using the same procedure that was used to obtain the first crop. The resulting crystals (0.72 g) were collected via vacuum filtration and washed with cold diethyl ether. The crops of crystals were then combined and dried under vacuum for 24 h, yielding 3.3 g of **2** (7.1 mmol, 71 %) as a white crystalline solid, m.p. = 136 - 138 °C. (This procedure has been scaled to 50 mmol providing 14.4 g, 31 mmol, 62 %). ¹H NMR (300 MHz, C₆D₆) δ : 7.39 (ddd, J = 7.4, 3.3, 1.1 Hz, 1H), 7.23 – 7.35 (m, 5H), 7.20 (s, 2H), 7.12 (td, J = 7.4, 1.4 Hz), 6.98 – 7.08 (m, 7H), 2.85 (septet, J = 6.9 Hz, 1H), 2.72 (septet, J = 6.6 Hz, 2H), 1.24 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.9 Hz, 6H), 1.07 (d, J = 6.9 Hz, 6H). ¹³C NMR (75 MHz, C₂D₂Cl₂) δ : 148.7, 148.2, 147.8, 147.2, 138.4, 138.2, 137.3, 137.1, 136.9, 136.8, 135.9, 134.1, 133.9, 131.6, 131.5, 129.3, 129.0, 128.9, 128.8, 127.6, 121.0, 34.7, 31.3, 25.7, 24.4, 22.7 (observed complexity due to P-C splitting; definitive assignments have not yet been made). ³¹P NMR (121 MHz, C₆D₆) δ : -17.5. IR (neat, cm⁻¹): 3059, 2958, 2873, 1607, 1460, 1430, 1383, 1313, 1074, 1004. Anal. Calcd for C₃₃H₃₇P: C, 85.31; H, 8.03. Found: C, 85.02; H, 8.03. (Pumping on high vacuum at 140 °C for 5 h was required to remove trace solvent trapped in the crystals)

General Procedure A: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Halides with Aryl Boronic Acids.

An oven-dried resealable Schlenk tube containing a magnetic stir bar was charged with Pd(OAc)₂ (2.2 mg, 1.0 mol%), **1** (8.2 mg, 2.0 mol%), the boronic acid (1.5 mmol, 1.5 equiv.) and powdered, anhydrous K₃PO₄ (424 mg, 2.0 mmol, 2.0 equiv.). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was repeated three times). Dry toluene (2.0 mL) was added through the septum via syringe and the resulting mixture

was stirred at room temperature for ~2 min. The aryl halide (1.0 mmol, 1.0 equiv.) was added dropwise via syringe (aryl halides which were solids at room temperature were added during the initial charge, prior to the evacuation/backfill cycles). The septum was replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was heated at 100 °C with vigorous stirring until the aryl halide had been completely consumed as judged by GC analysis. The reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (10 mL), filtered through a thin pad of silica gel (eluting with diethyl ether) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

For reactions conducted at low catalyst loadings (≤ 0.1 mol% Pd) the general procedure was followed with the following modification: A separate vial was charged with $\text{Pd}(\text{OAc})_2$ (1 mol%) and ligand **1** (2 mol%). The vial was sealed with a Teflon coated screwcap, a needle was inserted through the cap and the vial was then evacuated and backfilled with argon (this sequence was repeated three times). Dry THF (1 mL) was added and the mixture was sonicated for ~1 min to afford a homogeneous solution. 100 μL of this solution (0.1% Pd, 0.2% ligand **1**) was removed via syringe and then added to the Schlenk flask containing the base and boronic acid.

General Procedure B: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Halides with Alkylboranes or Alkylboronic acids.

Procedure A was used with the following modifications: an alkyl boronic acid or an alkyl borane was used in place of an aryl boronic acid and $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ was used in lieu of anhydrous K_3PO_4 .

General Procedure C: Pd-Catalyzed Suzuki-Miyaura Coupling of Hindered Aryl Halides with Aryl Boronic Acids.

Procedure A was used with $\text{Pd}_2(\text{dba})_3$ (18 mg, 4.0 mol% Pd) and **1** (33 mg, 8 mol%), and with 3 equiv. of anhydrous K_3PO_4 (636 mg, 3.0 mmol). The reaction temperature was 100-110 °C (as indicated).

General Procedure D: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Aryl Boronic Acids at Room Temperature.

Procedure A was used with the following changes: a 16 x 100 mm culture tube fitted with a rubber septum was used in place of a Schlenk tube, and the reaction were conducted in THF under nitrogen. Also, for the indicated cases, degassed water (10 μL /mmol halide) was added and the mixture was stirred for ~10 min prior to the addition of the aryl halide.

General Procedure E: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Aryl Boronate Esters.

A screw-cap test tube containing a magnetic stir bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 1.0 mol%), **1** (8.2 mg, 2.0 mol%), the aryl boronate ester (1.5 mmol, 1.5 equiv.) and K_3PO_4 (424

mg, 2.0 mmol, 2.0 equiv.). The tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was repeated three times). Deionized water (200 μ L, sparged with argon for 10 min prior to use) and dry toluene (2.0 mL) and were added sequentially via syringe through the septum and the resulting mixture was stirred at room temperature for ~2 min. The aryl halide (1.0 mmol, 1.0 equiv.) was added dropwise via syringe through the septum (solid aryl halides can be added to the test tube during the initial charge). The septum was replaced with a teflon-coated screwcap and the test tube was sealed. The reaction mixture was heated at 100 °C with vigorous magnetic stirring until the aryl halide had been completely consumed as judged by GC analysis (0.5-12 h). The reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (10 mL), filtered through a thin pad of silica gel (eluting with diethyl ether) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

General Procedure F: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Aryl Boronate Esters at Room Temperature.

Procedure E was used with the following modification: Dry THF (2.0 mL) was used instead of toluene.

General Procedure G: Pd-Catalyzed Suzuki-Miyaura Couplings of Vinyl Boronic Acids.

A screw-cap test tube containing a magnetic stir bar was charged with Pd(OAc)₂ (2.2 mg, 1.0 mol%), **1** (8.2 mg, 2 mol%), the boronic acid (1.5 mmol, 1.5 equiv.) and K₃PO₄ (424 mg, 2.0 mmol, 2.0 equiv.). The tube was sealed with a teflon-coated screw cap and then evacuated and backfilled with argon through an 18 gauge needle (this sequence was repeated three times). The aryl halide (1.0 mmol, 1.0 equiv.) and dry THF (2.0 mL) were added sequentially via syringe through the septum. The screwcap was quickly replaced with a non-punctured teflon-coated screwcap. The reaction mixture was vigorously stirred at 40 °C or room temperature until the aryl halide had been completely consumed as judged by GC analysis (12-24 h). The reaction mixture was then diluted with ethyl acetate (10 mL), filtered through a thin pad of silica gel (eluting with ethyl acetate) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

General Procedure H: Pd-Catalyzed Suzuki-Miyaura Coupling of 3-Pyridyl Boronic Acid.

Procedure G was used with the following modifications: Pd₂(dba)₃ was used instead of Pd(OAc)₂, *n*-BuOH (2.0 mL) was used instead of THF, and the reaction mixture was heated to either 90 or 100 °C.

General Procedure I: Pd-Catalyzed Suzuki-Miyaura Couplings of *n*-Fluorophenyl Boronic Acids.

Procedure G was used with the following modification: The reaction mixture was heated to either 80 or 90 °C.

General Procedure J: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Aryl Boronic Acids at Room Temperature using Ligand 2.

An oven dried 4 mL vial containing a magnetic stir bar was equipped with an open top phenolic screwcap preassembled with a securely seated septum, evacuated while hot, backfilled with nitrogen gas and cooled under nitrogen. The vial was then charged with Pd(OAc)₂ (13.5 mg, 0.06 mmol) and **2** (83.6 mg, 0.18 mmol). The vial was then evacuated and backfilled with nitrogen gas (this sequence was repeated three times). Then, dry THF (3 mL) was added via syringe and the catalyst stock solution was allowed to stir for ~30 min. An oven-dried resealable Schlenk tube containing a magnetic stir bar was equipped with a Teflon coated screwcap, evacuated while hot, backfilled with nitrogen gas and cooled under nitrogen. The tube was then charged with the boronic acid (1.5 mmol, 1.5 equiv.) and powdered K₃PO₄•H₂O (691 mg, 3.0 mmol, 3.0 equiv.). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with nitrogen gas (this sequence was repeated three times). All liquid reagents were added: the aryl chloride (1.0 mmol, 1.0 equiv.) was added dropwise via syringe (aryl halides which were solids at room temperature were added during the initial charge, prior to the evacuation/backfill cycles), catalyst stock solution (250 µL, 0.5 mol % Pd, 1.5 mol % **2**) was added via micro syringe and dry THF (2 mL) was added via syringe. The septum was replaced with a Teflon screwcap and the Schlenk tube was sealed. The reaction mixture was maintained at room temperature with vigorous stirring until the aryl halide had been completely consumed as judged by GC analysis. The reaction mixture was then diluted with ethyl acetate (10 mL), filtered through a pad of Celite (eluting with ethyl acetate) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

2,4,6-Triisopropyl-2'-methylbiphenyl (Table 1, entry 1) (0.1% Pd). Following general procedure C, a mixture of 2,4,6-triisopropylbromobenzene (251 µL, 1.0 mmol), 2-methyl phenyl boronic acid (272 mg, 2.0 mmol), K₃PO₄ (637 mg 3.0 mmol) and 200 µL of a catalyst solution composed of Pd₂(dba)₃ (4.6 mg, 0.005 mmol), **1** (8.2 mg, 0.02 mmol), and THF (2.0 mL) was heated at 100 °C in toluene (2.0 mL) for 24 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a white solid (279 mg, 95%), mp 95.5-96.5 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.13-7.27 (m, 4H), 7.05-7.08 (m, 2H), 2.94 (septet, *J* = 6.9 Hz, 1H), 2.44 (septet, *J* = 6.9 Hz, 2H), 1.99 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 6H), 1.03 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ: 147.9, 146.3, 140.6, 136.9, 136.0, 130.3, 129.8, 127.0, 125.6, 120.8, 34.4, 30.5, 25.1, 24.3, 23.7, 20.5. IR (neat, cm⁻¹): 2962, 2869, 1607, 1461, 1362, 1057, 1007. Anal. Calcd for C₂₂H₃₀: C, 89.73; H, 10.27. Found: C, 89.61; H, 10.42.

1-(2,4,6-Triisopropylphenyl)naphthalene (Table 1, entry 2) (0.1% Pd). Following general procedure C, a mixture of 2,4,6-triisopropylbromobenzene (251 μ L, 1.0 mmol), 1-naphthyl boronic acid (344 mg, 2.0 mmol), K_3PO_4 (637 mg 3.0 mmol) and 200 μ L of a catalyst solution composed of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), **1** (8.2 mg, 0.02 mmol), and THF (2.0 mL) was heated at 100 $^{\circ}C$ in toluene (2.0 mL) for 12 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a white solid (324 mg, 98%), mp 169-170 $^{\circ}C$. 1H NMR (300 MHz, $CDCl_3$) δ : 7.92 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.30-7.56 (m, 5H), 7.15 (s, 2H), 3.03 (septet, J = 6.9 Hz, 1H), 2.36 (septet, J = 6.9 Hz, 2H), 1.38 (d, J = 6.9 Hz, 6H), 1.06 (d, J = 6.9 Hz, 6H), 0.97 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 148.4, 147.5, 138.8, 134.6, 133.6, 133.5, 128.3, 127.5, 127.2, 126.7, 125.94, 125.85, 125.5, 120.9, 34.5, 30.8, 25.0, 24.4, 24.1. IR (neat, cm^{-1}): 3041, 2960, 2869, 1461, 1071, 907. Anal. Calcd for $C_{22}H_{30}$: C, 90.85; H, 9.15. Found: C, 90.96; H, 9.21.

2,4,6-Triisopropyl[1,1';2',1'']terphenyl (Table 1, entry 3). Following general procedure C, a mixture of 2,4,6-triisopropylbromobenzene (251 μ L, 1.0 mmol), $Pd_2(dba)_3$ (13.9 mg, 0.015 mmol), **1** (24.6 mg, 0.06 mmol), 2-biphenyl boronic acid (396 mg, 2.0 mmol) and K_3PO_4 (637 mg, 3.0 mmol) in toluene (2.0 mL) was heated at 100 $^{\circ}C$ with vigorous stirring for 20 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a white solid (333 mg, 93%), mp 140-141.5 $^{\circ}C$. 1H NMR (300 MHz, $CDCl_3$): δ 7.33-7.52 (m, 3H), 7.23 (dd, J = 7.5, 1.3 Hz, 1H), 7.06-7.14 (m, 5H), 6.91 (s, 2H), 2.88 (septet, J = 6.8 Hz, 1H), 2.55 (septet, J = 6.8 Hz, 2H), 1.26 (d, J = 6.8 Hz, 6H), 1.03 (d, J = 6.8 Hz, 6H), 0.86 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 146.4, 141.4, 139.0, 135.8, 131.5, 129.9, 129.6, 127.7, 127.5, 126.9, 126.6, 120.7, 34.4, 30.6, 25.7, 24.3, 23.0. IR (neat, cm^{-1}): 2958, 2869, 1463, 1382, 1007, 911. Anal. Calcd for $C_{27}H_{32}$: C, 90.95; H, 9.05. Found: C, 90.83; H, 9.17.

2,6-Dimethoxy-2',6'-dimethylbiphenyl (Table 1, entry 4). Following general procedure C, a mixture of 2-bromo-1,3-dimethoxybenzene (217 mg, 1.0 mmol), $Pd_2(dba)_3$ (13.9 mg, 0.015 mmol), **1** (24.6 mg, 0.06 mmol), 2,6-dimethylphenyl boronic acid (300 mg, 2.0 mmol) and K_3PO_4 (637 mg, 3.0 mmol) in toluene (2.0 mL) was heated at 100 $^{\circ}C$ with vigorous stirring for 10 h. The crude product was purified by flash chromatography on silica gel (95:5 hexane:diethyl ether) to provide the title compound as a white solid (213 mg, 88%), mp 107-109 $^{\circ}C$. 1H NMR (300 MHz, $CDCl_3$) δ : 7.26-7.36 (m, 1H), 7.09-7.18 (m, 3H), (dm, J for the d = 8.3 Hz, 2H), 3.77 (s, 6H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 157.6, 137.3, 134.3, 128.9, 127.3, 127.0, 117.7, 104.1, 55.9, 20.3. IR (neat, cm^{-1}): 3012, 2958, 2838, 1590, 1468, 1432, 1283, 1246, 1108, 1003. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.15; H, 7.45.

2,2',4,6,6'-Pentamethylbiphenyl¹ (Table 1, entry 5). Following general procedure C, a mixture of 2-bromomesitylene (199 mg, 1.0 mmol), Pd₂(dba)₃ (18 mg, 0.020 mmol), **1** (33 mg, 0.08 mmol), 2,6-dimethylphenyl boronic acid (300 mg, 2.0 mmol) and K₃PO₄ (849 mg 4.0 mmol) in toluene (2.0 mL) was heated at 110 °C with vigorous stirring for 10 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a colorless oil (184 mg, 82%). The spectra were in agreement with those described in the literature.

4,6-Di-tert-butyl-2-methylbiphenyl (Table 1, entry 6). Following general procedure C, a mixture of 2-Bromo-1,5-di-tert-butyl-3-methyl-benzene (59 mg, 0.21 mmol), Pd₂(dba)₃ (4.8 mg, 0.053 mmol), **1** (8.6 mg, 0.021 mmol), phenyl boronic acid (51 mg, 0.41 mmol) and K₃PO₄ (177 mg, 0.84 mmol) in toluene (1.0 mL) was heated at 110 °C with vigorous stirring for 18 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a colorless oil (50 mg, 85%). ¹H NMR (300 MHz, CDCl₃) δ: 7.03-7.52 (m, 7H), 1.85 (s, 3H), 1.37 (s, 9H), 1.17 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 149.3, 147.3, 143.5, 138.7, 137.3, 131.1, 127.8, 126.5, 124.6, 121.7, 37.1, 34.8, 33.1, 31.7, 22.4. IR (neat, cm⁻¹): 3061, 2967, 2866, 1604, 1478, 1362, 1236, 1009. Anal. Calcd for C₂₁H₂₈: C, 89.94; H, 10.06. Found: C, 89.78; H, 10.17.

4,6-Di-tert-butyl-2,2'-dimethyl-biphenyl (Table 1, entry 7). Following general procedure C, a mixture of 2-Bromo-1,5-di-tert-butyl-3-methyl-benzene (59 mg, 0.21 mmol), Pd₂(dba)₃ (4.8 mg, 0.053 mmol), **1** (8.6 mg, 0.021 mmol), 2-methylphenyl boronic acid (57 mg, 0.41 mmol) and K₃PO₄ (177 mg, 0.84 mmol) in toluene (1.0 mL) was heated at 110 °C with vigorous stirring for 18 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a colorless oil (55 mg, 89%). ¹H NMR (300 MHz, CDCl₃) δ: 7.44 (d, *J* = 1.9 Hz, 1H), 7.09-7.28 (m, 5 H), 1.98 (s, 3H), 1.78 (s, 3H), 1.37 (s, 9H), 1.15 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 149.1, 146.7, 143.0, 137.3, 137.1, 136.6, 131.0, 129.9, 126.9, 125.3, 124.7, 122.2, 37.1, 34.8, 32.5, 31.7, 21.7, 20.5. IR (neat, cm⁻¹): 3060, 2964, 2868, 1604, 1479, 1361, 1236, 1004. Anal. Calcd for C₂₂H₃₀: C, 89.73; H, 10.27. Found: C, 89.50; H, 10.37.

4-*t*-butyl-2'-methylbiphenyl² (Table 3, entry 1) (0.0005% Pd). Following general procedure A, a mixture of 4-*tert*-butylbromobenzene (173 μ L, 1.0 mmol), 2-methylphenyl boronic acid (204 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol) and 4 μ L of a catalyst solution composed of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), **1** (5.2 mg, 0.01 mmol) and THF (4.0 mL) in toluene (3.0 mL) was heated at 100 $^{\circ}C$ for 24 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a colorless oil (202 mg, 90%). The spectra were in agreement with those described in the literature.

2-(4-*t*-Butylphenyl)biphenyl (Table 3, entry 2) (0.001% Pd). Following general procedure A, a mixture of 4-*tert*-butylbromobenzene (173 μ L, 1.0 mmol), 2-biphenylboronic acid (297 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol) and 8 μ L of a catalyst solution composed of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), **1** (5.2 mg, 0.01 mmol) and THF (4.0 mL) in toluene (3.0 mL) was heated at 100 $^{\circ}C$ for 24 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a white solid (276 mg, 96%), mp 55-56 $^{\circ}C$. 1H NMR (300 MHz, $CDCl_3$) δ : 7.48-7.41 (m, 5H), 7.29-7.09 (m, 8H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 149.5, 141.9, 140.7, 140.6, 138.6, 130.9, 130.8, 130.1, 129.7, 128.0, 127.6, 127.4, 126.6, 125.0, 34.6, 31.6. IR (neat, cm^{-1}): 3066, 2988, 1476, 1422, 1266, 896.

2,4,6-Triisopropylbiphenyl (Table 3, entry 3). Following general procedure A, a mixture of 2,4,6-triisopropylbromobenzene (251 μ L, 1.0 mmol), phenyl boronic acid (183 mg, 1.5 mmol) and K_3PO_4 (424 mg, 2.0 mmol) and 20 μ L of a catalyst solution composed of Pd_2dba_3 (4.6 mg, 0.005 mmol), **1** (8.2 mg, 0.02 mmol) and THF (2.0 mL) in toluene (2.0 mL) was heated at 100 $^{\circ}C$ with vigorous stirring for 16 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a white solid (278 mg, 99%), mp 120-121 $^{\circ}C$. 1H NMR (300 MHz, $CDCl_3$) δ : 7.32-7.44 (m, 3H), 7.19-7.23 (m, 2H), 7.08 (s, 2H), 2.97 (septet, J = 6.9 Hz, 1H), 2.62 (septet, J = 6.9 Hz, 2H), 1.33 (d, J = 6.9 Hz, 6H), 1.10 (d, J = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 148.0, 146.7, 141.1, 137.3, 130.0, 128.1, 126.6, 120.7, 34.5, 30.5, 24.4, 24.3. IR (neat, cm^{-1}): 2960, 2929, 2867, 1609, 1459, 1362, 1069. Anal. Calcd for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 89.66; H, 10.01.

4-*n*-Butylbiphenyl³ (Table 3, entry 4) (0.003% Pd). Following general procedure A, a mixture of 4-*n*-butylchlorobenzene (165 μ L, 1.0 mmol), phenyl boronic acid (183 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (460 mg, 2.0 mmol) and 24 μ L of a catalyst solution composed of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), **1** (10.3 mg, 0.025 mmol) and THF (4.0 mL) in toluene (2.0 mL) was heated at 100 $^{\circ}C$ for 24 h. The crude product was purified by flash chromatography on silica gel (hexane) to provide the title compound as a colorless oil (195 mg, 93%). The spectra were in agreement with those described in the literature.

4-phenylquinoline⁴ (Table 4, entry 1). Following general procedure E, a mixture of 4-chloroquinoline (82 mg, 0.50 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), **1** (4.1 mg, 0.01 mmol), 4,4,5,5-Tetramethyl-2-phenyl-[1,3,2]dioxaborolane (153 mg, 0.75 mmol) and K_3PO_4 (212 mg, 1.0 mmol) in toluene (1.0 mL) and water (100 μ L) was heated at 100 $^{\circ}C$ with vigorous stirring for 30 min. The crude product was purified by flash chromatography on silica gel (4:1 hexane:ethyl acetate) to provide the title compound as a colorless oil (91 mg, 89 %). The spectra were in agreement with those described in the literature.

3-(2',6'-Dimethylphenyl)phenol (Table 4, entry 2). Following general procedure E, a mixture of 2-chloro-*m*-xylene (133 μ L, 1.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1** (8.2 mg, 0.02 mmol), 3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenol (330 mg, 1.50 mmol) and K_3PO_4 (424 mg, 2.0 mmol) in toluene (2.0 mL) and water (200 μ L) was heated at 100 $^{\circ}C$ with vigorous stirring for 30 min. The crude product was purified by flash chromatography on silica gel (9:1 hexane:diethyl ether) to provide the title compound as a colorless oil (189 mg, 95%). 1H NMR (300 MHz, $CDCl_3$) δ : 7.33 (t, J = 7.7 Hz, 1H), 7.12-7.23 (m, 3H), 6.85 (ddd, J = 8.3, 2.8, 1.1 Hz), 6.76 (ddd, J = 7.4, 1.2, 1.2 Hz), 6.65-6.67 (m, 1H), 5.09 (br s, 1H), 2.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 155.6, 143.0, 141.6, 136.2, 129.9, 127.4, 127.3, 121.9, 116.1, 113.8, 20.9. IR (neat, cm^{-1}): 3320, 3060, 2920, 1581, 1446, 1289, 1187, 999. A satisfactory elemental analysis was not obtained for this compound. The 1H and ^{13}C NMR spectra follow.

5,6-Dimethoxy-3'-trifluoromethyl-2-cyano-biphenyl (Table 4, entry 3). Following general procedure E, a mixture of 2-chloro-3,4-dimethoxybenzonitrile (99 mg, 0.50 mmol), Pd(OAc)₂ (1.1 mg, 0.005 mmol), **1** (4.1 mg, 0.01 mmol), 4,4,5,5-Tetramethyl-2-(3-trifluoromethyl-phenyl)-[1,3,2]dioxaborolane (204 mg, 0.75 mmol) and K₃PO₄ (212 mg, 1.0 mmol) in toluene (1.0 mL) and water (100 μ L) was heated at 100 °C with vigorous stirring for 30 min. The crude product was purified by flash chromatography on silica gel (4:1 hexane:diethyl ether) to provide the title compound as a white solid (151 mg, 98%), mp 87-88 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.59-7.75 (m, 3H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 3.99 (s, 3H), 3.58 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ : 157.2, 147.1, 138.3, 135.0, 133.3, 131.0, 130.6, 130.4, 129.0, 127.0, 126.9, 126.0, 125.53, 125.48, 122.4, 118.26, 112.32, 105.0, 61.1, 56.3 (observed complexity due to F-C splitting). IR (neat, cm⁻¹): 3061, 2948, 2846, 2228, 1590, 1484, 1332, 1126, 1031. Anal. Calcd for C₁₆H₁₂F₃NO₂: C, 62.54; H, 3.94. Found: C, 62.55; H, 3.87.

5-(2-Methoxyphenyl)-2-methyl-benzothiazole (Table 4, entry 4). Following general procedure F, a mixture of 5-chloro-2-methyl-benzothiazole (184 mg, 1.0 mmol), Pd(OAc)₂ (2.2 mg, 0.01 mmol), **1** (4.1 mg, 0.01 mmol), 2-(2-methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (351 mg, 1.5 mmol) and K₃PO₄ (424 mg, 2.0 mmol) in THF (2.0 mL) and water (200 μ L) was vigorously stirred at room temperature for 30 min. The crude product was purified by flash chromatography on silica gel (9:1 to 9:2 hexane:diethyl ether) to provide the title compound as a thick colorless oil (244 mg, 96%). ¹H NMR (300 MHz, CDCl₃) δ : 8.19 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.86 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.57 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.34-7.44 (m, 2H), 7.02-7.12 (m, 2H), 3.84 (s, 3H), 2.87 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ : 167.3, 156.6, 153.6, 136.7, 134.4, 131.2, 130.2, 128.9, 126.7, 123.4, 121.1, 120.8, 111.3, 55.6, 20.3. IR (neat, cm⁻¹): 3072, 2957, 2834, 1598, 1496, 1241, 1026. A satisfactory elemental analysis was not obtained for this compound. The ¹H and ¹³C NMR spectra follow.

3-Cyano-2'-methylbiphenyl⁵ (Table 5, entry 1). Following general procedure J, a mixture of 3-chlorobenzonitrile (137 mg, 1.0 mmol), 2-methylphenyl boronic acid (204 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.11 mg, 0.0005 mmol) and **2** (0.7 mg, 0.0015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes: ethyl acetate) to provide the title compound as a colorless oil (182 mg, 94%). 1H NMR (300 MHz, CD_2Cl_2) δ : 7.51-7.70 (m, 4H), 7.17-7.38 (m, 4H), 2.26 (s, 3H). The spectra were in agreement with those described in the literature.

3-Cyano-2'-phenylbiphenyl (Table 5, entry 2). Following general procedure J, a mixture of 3-chlorobenzonitrile (137 mg, 1.0 mmol), 2-biphenyl boronic acid (297 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.11 mg, 0.0005 mmol) and **2** (0.7 mg, 0.0015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a white solid (237 mg, 93%), mp 108-110 °C. 1H NMR (300 MHz, CD_2Cl_2) δ : 7.30-7.55 (m, 8H), 7.22-7.29 (m, 3H), 7.09-7.17 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 143.3, 141.2, 138.8, 134.9, 133.7, 131.3, 130.8, 130.6, 130.4, 129.2, 128.9, 128.6, 128.3, 127.4, 119.2, 112.6. IR (neat, cm^{-1}): 3063, 3053, 2985, 1601, 1577, 1487, 1476, 1471, 1450, 1435, 1411, 1266, 1173, 1075, 1009 (-CN obscured by diamond probe). Anal. Calcd for $C_{19}H_{13}N$: C, 89.38; H, 5.13. Found: C, 89.40; H, 5.16.

3,5-Dimethoxy-2'-methylbiphenyl (Table 5, entry 3). Following general procedure J, a mixture of 3,5-dimethoxychlorobenzene (173 mg, 1.0 mmol), 2-methylphenyl boronic acid (204 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) and **2** (1.4 mg, 0.003 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 95:5 hexanes: ethyl acetate) to provide the title compound as a colorless oil (221 mg, 97%). 1H NMR (300 MHz, CD_2Cl_2) δ : 7.22-7.30 (m, 4H), 6.47-6.50 (m, 3H), 3.82 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 161.1, 144.5, 142.5, 135.9, 130.8, 129.9, 127.9, 126.2, 107.8, 99.3, 55.9, 20.7. IR (neat, cm^{-1}): 2927, 2858, 1599, 1460, 1421, 1344, 1267, 1205, 1159, 1066, 1035. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.88; H, 7.06.

Methyl-3-(4'-N,N-dimethylphenyl)benzoate⁶ (Table 5, entry 4). Following general procedure J, a mixture of 3-chloromethylbenzoate (171 mg, 1.0 mmol), 4-N,N-dimethylphenyl boronic acid (248 mg, 1.5 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 95:5 hexanes:ethyl acetate) to provide the title compound as an off-white solid (247 mg, 97%), mp 140-142 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ : 8.20-8.26 (m, 1H), 7.85-7.92 (m, 1H), 7.73-7.81 (m, 1H), 7.38-7.60 (m, 3H), 6.74-6.86 (m, 2H), 3.91 (s, 3H), 2.99 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 167.6, 150.9, 141.9, 131.2, 130.8, 129.3, 128.0, 127.9, 127.4, 127.3, 113.1, 52.5, 40.8. The spectra were in agreement with those described in the literature.

Methyl-3-(2',6'-dimethoxyphenyl)benzoate (Table 5, entry 5). Following general procedure J, a mixture of 3-chloromethylbenzoate (171 mg, 1.0 mmol), 2,6-dimethoxyphenyl boronic acid (364 mg, 3.0 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes:ethyl acetate) to provide the title compound as an off-white solid (267 mg, 98%), mp 91-93 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ : 7.95-8.30 (m, 2H), 7.45-7.57 (m, 2H), 7.33 (t, J = 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ : 167.5, 158.1, 136.2, 135.5, 132.7, 130.4, 129.8, 128.3, 118.7, 104.6, 56.2, 52.4. IR (neat, cm^{-1}): 3066, 3012, 2958, 2920, 2850, 1716, 1591, 1476, 1437, 1298, 1244, 1112, 1035. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C, 70.57; H, 5.92. Found: C, 70.65; H, 6.02.

Methyl-2-(2'-methoxyphenyl)benzoate⁷ (Table 5, entry 6). Following general procedure J, a mixture of 2-chloromethylbenzoate (171 mg, 1.0 mmol), 2-methoxyphenyl boronic acid (228 mg, 1.5 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes:ethyl acetate) to provide the title compound as a colorless oil (237 mg, 98%). ^1H NMR (300 MHz, CD_2Cl_2) δ : 7.83 (dd, J = 7.7, 1.4 Hz, 1H), 7.56 (td, J = 7.7, 1.7, 1H), 7.43 (dd, J = 7.7, 1.4 Hz, 1H), 7.31-7.40 (m, 2H), 7.25 (dd, J = 7.4, 1.9 Hz, 1H), 7.05 (td, J = 7.4, 1.1 Hz, 1H),

6.93 (d, $J = 8.3$ Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H). The spectra were in agreement with those described in the literature.

2-Formyl-2'-methoxybiphenyl⁸ (Table 5, entry 7). Following general procedure J, a mixture of 2-chlorobenzaldehyde (141 mg, 1.0 mmol), 2-methoxyphenyl boronic acid (228 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) and **2** (1.4 mg, 0.003 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes:ethyl acetate) to provide the title compound as a colorless oil (208 mg, 98%). 1H NMR (300 MHz, CD_2Cl_2) δ : 9.76 (d, $J = 0.8$ Hz, 1H), 7.95 (dd, $J = 1.4, 0.5$ Hz, 1H), 7.66 (td, $J = 7.4, 1.4$ Hz, 1H), 7.51 (dt, $J = 7.7, 0.8$ Hz, 1H), 7.44 (ddd, $J = 8.3, 7.4, 1.7$ Hz, 1H), 7.29 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.09 (td, $J = 7.4, 1.1$ Hz, 1H), 7.01 (dd, $J = 8.3, 0.8$ Hz, 1H), 3.74 (s, 3H). The spectra were in agreement with those described in the literature.

2,2',6-trimethylbiphenyl⁹ (Table 5, entry 8). Following general procedure J, a mixture of 2-chloro-*m*-xylene (141 mg, 1.0 mmol), 2-methylphenyl boronic acid (204 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) and **2** (1.4 mg, 0.003 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (185 mg, 94%). 1H NMR (300 MHz, CD_2Cl_2) δ : 7.12-7.42 (m, 6H), 7.01-7.11 (m, 1H), 2.02 (s, 3H), 1.99 (s, 6H). The spectra were in agreement with those described in the literature.

2,2',6-trimethylbiphenyl⁹ (Table 5, entry 9). Following general procedure J, a mixture of 2-chlorotoluene (127 mg, 1.0 mmol), 2,6-dimethylphenyl boronic acid (450 mg, 3.0 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) and **2** (1.4 mg, 0.003 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (182 mg, 93%). 1H NMR (300 MHz, CD_2Cl_2) δ : 7.12-7.42 (m, 6H), 7.01-7.11 (m, 1H), 2.02 (s, 3H), 1.99 (s, 6H). The spectra were in agreement with those described in the literature.

2'-Methyl-[1,1';3',1'';2'',1''']quaterphenyl (Table 5, entry 10). Following general procedure J, a mixture of 3-chloro-2-methylbiphenyl (203 mg, 1.0 mmol), 2-biphenyl boronic acid (298 mg, 1.5 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (0.56 mg, 0.0025 mmol) and **2** (3.5 mg, 0.0075 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a white solid (318 mg, 99%), mp 105-108 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ : 7.26-7.52 (m, 7H), 7.10-7.25 (m, 10H), 1.74 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ : 143.1, 142.9, 142.7, 142.1, 141.7, 141.4, 133.9, 131.7, 130.5, 130.3, 130.1, 129.8, 129.2, 128.6, 128.3, 128.2, 127.8, 127.3, 127.1, 125.6, 18.8. IR (neat, cm^{-1}): 3059, 3028, 2927, 1576, 1460, 1429, 1074, 1004. Anal. Calcd for $\text{C}_{25}\text{H}_{20}$: C, 93.71; H, 6.29. Found: C, 93.89; H, 6.31.

3-Acetyl-2'-methoxybiphenyl¹⁰ (Table 5, entry 11). Following general procedure J, a mixture of 2-chloroanisole (143 mg, 1.0 mmol), 3-acetylphenyl boronic acid (246 mg, 1.5 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes:ethyl acetate) to provide the title compound as a light yellow oil (201 mg, 89%). ^1H NMR (300 MHz, CD_2Cl_2) δ : 8.07-8.15 (m, 1H), 7.92 (dq, $J = 7.7, 1.1$ Hz, 1H), 7.74 (dq, $J = 7.7, 1.1$ Hz, 1H), 7.52 (td, $J = 7.7, 0.6$ Hz, 1H), 7.31-7.43 (m, 2H), 7.0-7.12 (m, 2H). The spectra were in agreement with those described in the literature.

2-methoxy-2'-methylbiphenyl¹¹ (Table 5, entry 12). Following general procedure J, a mixture of 2-chloroanisole (143 mg, 1.0 mmol), 2-methylphenyl boronic acid (204 mg, 1.5 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (0.56 mg, 0.0025 mmol) and **2** (3.6 mg, 0.0075 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 9:1 hexanes:ethyl acetate) to provide the title compound as a white crystalline solid (192 mg, 97%), mp 42-44 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ : 7.37-7.46 (m, 1H), 7.17-7.35 (m, 5H), 7.01-7.12 (m, 2H), 3.81 (s, 3H), 2.18 (s, 3H). The spectra were in agreement with those described in the literature.

2-methoxy-2'-phenylbiphenyl¹² (Table 5, entry 13). Following general procedure J, a mixture of 2-chloroanisole (143 mg, 1.0 mmol), 2-biphenyl boronic acid (298 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) and **2** (3.6 mg, 0.0075 mmol) was maintained at room temperature with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a thick oil (252 mg, 97%). 1H NMR (300 MHz, CD_2Cl_2) δ 7.36-7.51 (m, 4H), 7.14-7.32 (m, 7H), 6.96 (t, $J = 7.4$, 1H), 6.77 (d, $J = 8.3$ Hz, 1H), 3.42 (s, 3H). The spectra were in agreement with those described in the literature.

4-methoxy-2'-phenylbiphenyl¹³ (Table 5, entry 14). Following general procedure J, a mixture of 4-chloroanisole (143 mg, 1.0 mmol), 2-biphenyl boronic acid (298 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) and **2** (3.6 mg, 0.0075 mmol) was heated to 40 °C with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a viscous oil (241 mg, 93%). 1H NMR (300 MHz, CD_2Cl_2) δ 7.39-7.47 (m, 4H), 7.16-7.32 (m, 5H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H). The spectra were in agreement with those described in the literature.

2,6-dimethoxy-2'-phenylbiphenyl¹⁴ (Table 5, entry 15). Following general procedure J, a mixture of 2,6-dimethoxychlorobenzene (173 mg, 1.0 mmol), 2-biphenyl boronic acid (298 mg, 1.5 mmol), $K_3PO_4 \cdot H_2O$ (691 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was heated to 40 °C with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a white solid (287 mg, 99%), mp 102-103 °C. 1H NMR (300 MHz, CD_2Cl_2) δ 7.34-7.48 (m, 3H), 7.23-7.29 (m, 1H), 7.08-7.22 (m, 6H), 6.48 (d, $J = 8.5$ Hz, 2H), 3.54 (s, 3H). The spectra were in agreement with those described in the literature.

2,6-dimethyl-2'-methoxybiphenyl¹⁵ (Table 5, entry 16). Following general procedure J, a mixture of 2-chloroanisole (143 mg, 1.0 mmol), 2,6-dimethylphenyl boronic acid (450 mg, 3.0

mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (691 mg, 3.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and **2** (6.9 mg, 0.015 mmol) was heated to 40 °C with vigorous stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (207 mg, 98%). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.34-7.44 (m, 1H), 7.08-7.22 (m, 3H), 7.01-7.08 (m, 3H), 3.77 (s, 3H), 2.02 (s, 6H). The spectra were in agreement with those described in the literature.

2-Fluoro-2',4'-dimethylbiphenyl (Table 6, entry 1). Following general procedure I, a mixture of 2-chloro-*m*-xylene (141 mg, 1.0 mmol), 2-fluorophenyl boronic acid (210 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 90 °C with stirring for 90 min. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (184 mg, 92%). ^1H NMR (500 MHz, CDCl_3) δ : 7.31-7.36 (m, 2H), 7.11-7.21 (m, 5H), 2.05 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ : 160.4, 158.5, 136.7, 135.2, 131.3, 131.3, 129.0, 128.9, 128.0, 127.9, 127.7, 127.2, 124.1, 124.1, 115.8, 115.6, 20.5. ^{19}F NMR (282 MHz, CDCl_3) δ : -115.4. IR (neat, cm^{-1}): 3064, 2923, 2863, 1577, 1447, 1208, 1110, 1006. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{F}$: C, 83.97; H, 6.54. Found: C, 83.74; H, 6.52.

2,4-Difluoro-4'-methoxybiphenyl (Table 6, entry 2). Following general procedure I, a mixture of 4-chloroanisole (143 mg, 1.0 mmol), 2,4-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 80 °C with stirring for 16 h. The crude product was purified via flash column chromatography on silica gel (2% ethyl acetate in hexanes) to provide the title compound as a white solid (219 mg, 99%), mp 78-79 °C. ^1H NMR (500 MHz, CDCl_3) δ : 7.47 (d, J = 7 Hz, 2H), 7.37-7.41 (m, 1H), 7.01 (d, J = 9 Hz, 2H), 6.91-6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ : 162.9, 162.8, 160.9, 160.8, 160.6, 160.5, 159.2, 158.6, 158.5, 131.1, 131.0, 131.0, 130.9, 130.0, 129.9, 127.3, 127.2, 125.0, 124.9, 124.9, 124.8, 113.9, 111.5, 111.4, 111.3, 111.2, 104.4, 104.2, 104.2, 104.0, 55.2. ^{19}F NMR (282 MHz, CDCl_3) δ : -112.7 (t, J = 6 Hz, 1F), -114.1 (d, J = 6 Hz, 1F). IR (neat, cm^{-1}): 3056, 2840, 1611, 1496, 1266, 1140, 965. A satisfactory elemental analysis was not obtained for this compound. The ^1H and ^{13}C NMR spectra follow.

3-(2,3-Difluorophenyl)-2-fluoro-5-(trifluoromethyl)pyridine (Table 6, entry 3). Following general procedure I, a mixture of 2-fluoro-3-chloro-5-(trifluoromethyl)pyridine (199 mg, 1.0 mmol), 2,3-difluorophenyl boronic acid (316 mg, 2.0 mmol), K_3PO_4 (637 mg, 3.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in toluene (2 mL) was heated to 90 °C with stirring for 16 h. The crude product was purified via flash column chromatography on silica gel (3% ethyl acetate in hexanes) to provide the title compound as a pale yellow oil (265 mg, 96%). 1H NMR (500 MHz, $CDCl_3$) δ : 8.59 (s, 1H), 8.11 (d, J = 8 Hz, 1H), 7.17-7.34 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 163.5, 160.2, 152.6, 152.4, 149.8, 149.6, 149.2, 149.1, 146.5, 146.3, 145.6, 145.5, 145.4, 145.4, 145.3, 145.3, 145.2, 145.1, 139.4, 139.3, 139.3, 139.3, 139.2, 125.8, 125.6, 125.5, 125.1, 125.1, 124.7, 124.7, 124.6, 124.6, 122.4, 122.3, 122.2, 122.2, 121.1, 118.6, 118.4, 118.2, 118.1, 117.8, 117.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ : -62.1 (s, 3F), -63.8 (q, J = 6 Hz, 1F), -136.8 (q, J = 6 Hz, 1F), -139.8 (m, 1F). IR (neat, cm^{-1}): 3086, 1598, 1496, 1483, 1454, 1418, 1343, 1293, 1260, 1160, 1132, 1092. Anal. Calcd for $C_{12}H_5F_6N$: C, 52.00; H, 1.82. Found: C, 52.03; H, 1.83.

2,4-Difluoro-4'-aminobiphenyl (Table 6, entry 4). Following general procedure I, a mixture of 4-chloroaniline (128 mg, 1.0 mmol), 2,4-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in toluene (2.0 mL) was heated to 80 °C with stirring for 10 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a pale brown solid (197 mg, 96%), mp 110-111 °C. 1H NMR (500 MHz, $CDCl_3$) δ : 7.34-7.40 (m, 3H), 6.89-6.96 (m, 2H), 6.77 (d, J = 8 Hz, 2H), 3.78 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 162.5, 162.4, 160.6, 160.5, 160.5, 160.4, 158.5, 158.4, 146.1, 130.9, 130.8, 130.7, 130.7, 129.8, 129.7, 125.3, 125.3, 125.2, 125.1, 124.8, 124.8, 114.9, 111.3, 111.3, 111.2, 111.1, 104.3, 104.1, 104.0, 103.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ : -113.3 (quintet, J = 6 Hz, 1F), -114.2 (t, J = 6 Hz, 1F). IR (neat, cm^{-1}): 3487, 3397, 3039, 1626, 1606, 1490, 1412, 1263, 1138, 1103. Anal. Calcd for $C_{12}H_9F_2N$: C, 70.24; H, 4.42. Found: C, 70.04; H, 4.34.

3-(2,3-Difluorophenyl)-benzaldehyde (Table 6, entry 5). Following general procedure I, a mixture of 3-chlorobenzaldehyde (141 mg, 1.0 mmol), 2,3-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 90 °C with stirring for 3 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate in hexanes) to provide the title compound as a white solid (175 mg, 80%), mp 42-43 °C. 1H NMR (300 MHz, $CDCl_3$) δ :

10.0 (s, 1H), 8.01 (s, 1H), 7.89 (d, $J = 8$ Hz, 1H), 7.78 (d, $J = 7$ Hz, 1H), 7.60 (t, $J = 8$ Hz, 1H), 7.13-7.22 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ : 191.8, 152.7, 125.5, 149.6, 149.4, 149.3, 149.2, 146.2, 146.1, 136.6, 135.5, 135.4, 134.7, 134.6, 130.0, 129.9, 129.7, 129.6, 129.2, 125.1, 125.1, 125.0, 125.0, 124.4, 124.3, 124.3, 124.2, 116.8, 116.6. ^{19}F NMR (282 MHz, CDCl_3) δ : -137.7 (quintet, $J = 6$ Hz, 1F), -143.9 (t, $J = 6$ Hz, 1F). IR (neat, cm^{-1}): 3067, 2830, 1699, 1593, 1579, 1482, 1468, 1266, 1189, 1100, 986. Anal. Calcd for $\text{C}_{13}\text{H}_8\text{F}_2\text{O}$: C, 71.56; H, 3.70. Found: C, 71.35; H, 3.61.

3-(4-*n*-Butylphenyl)-pyridine¹⁶ (Table 7, entry 1). Following general procedure H, a mixture of 4-*n*-butylchlorobenzene (169 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 100 °C with stirring for 15 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to provide the title compound as a pale yellow oil (209 mg, 99%). The spectra were in agreement with those described in the literature.

3-(2-Methylphenyl)-pyridine⁹ (Table 7, entry 2). Following general procedure H, a mixture of 2-chlorotoluene (127 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 100 °C with stirring for 20 h. The crude product was purified via flash column chromatography on silica gel (10% ethyl acetate in hexanes to 1:3 ethyl acetate:hexanes) to provide the title compound as a pale yellow oil (149 mg, 88%). The spectra were in agreement with those described in the literature.

3-(2,6-Dimethoxyphenyl)-pyridine (Table 7, entry 3). Following general procedure H, a mixture of 2,6-dimethoxychlorobenzene (173 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (13.7 mg, 0.015 mmol), and **1** (24.6 mg, 0.06 mmol) in *n*-butanol (2.0 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:3 ethyl acetate:hexanes) to provide the title compound as a off-white solid (177 mg, 82%), mp 87-88 °C. ^1H NMR (500 MHz, CDCl_3) δ : 8.60 (d, $J = 2$ Hz, 1H), 8.52 (d, $J = 5$ Hz, 1H), 7.69 (d, $J = 8$ Hz, 1H), 7.30-7.33 (m, 2H), 6.67 (d, $J = 8$ Hz, 2H), 3.74 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ : 157.6, 151.8, 147.6, 138.4, 129.9, 129.5, 122.6, 120.2, 115.6, 55.8. IR (neat, cm^{-1}): 3004, 2939, 2837, 1588, 1473, 1407, 1260, 1102, 998. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_2$: C, 72.54; H, 6.09. Found: C, 72.23; H, 6.08.

3-(3-Trifluoromethylphenyl)-pyridine¹⁷ (Table 7, entry 4). Following general procedure H, a mixture of 3-(trifluoromethyl)chlorobenzene (181 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K₃PO₄ (425 mg, 2.0 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 90 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a pale yellow oil (200 mg, 90%). ¹H NMR (300 MHz, CDCl₃) δ: 8.85 (d, *J* = 5 Hz, 1H), 8.64 (dd, *J* = 2, 5 Hz, 1H), 7.88 (ddd, *J* = 2, 5, 8 Hz, 1H), 7.81 (s, 1H), 7.75 (d, *J* = 8 Hz, 1H), 7.57-7.67 (m, 2H), 7.39 (dd, *J* = 5, 8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 149.5, 148.5, 138.9, 135.5, 134.7, 132.0, 131.5, 130.7, 130.6, 129.9, 126.0, 125.1, 125.0, 125.0, 124.2, 124.1, 123.9, 122.4. ¹⁹F NMR (282 MHz, CDCl₃) δ: -63.0. IR (neat, cm⁻¹): 3039, 1571, 1437, 1402, 1333, 1266, 1166, 1121, 1028, 1017.

3-(2,4,6-Trimethylphenyl)-pyridine (Table 7, entry 5). Following general procedure H, a mixture of 2-bromomesitylene (199 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K₃PO₄ (425 mg, 2.0 mmol), Pd₂(dba)₃ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 90 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a white solid (168 mg, 85%), mp 46-47 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.60 (dd, *J* = 2, 5 Hz, 1H), 8.44 (d, *J* = 2 Hz, 1H), 7.50 (dt, *J* = 2, 8 Hz, 1H), 7.36 (dd, *J* = 5, 8 Hz, 1H), 6.98 (s, 2H), 2.35 (s, 3H), 2.01 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ: 150.3, 148.0, 137.4, 136.9, 136.6, 136.1, 134.9, 128.2, 123.3, 21.0, 20.7. IR (neat, cm⁻¹): 3024, 2920, 2860, 1614, 1563, 1470, 1406, 999. Anal. Calcd for C₁₄H₁₅N: C, 85.24; H, 7.66. Found: C, 84.90; H, 7.67.

(E)-1-(2,4-Dimethoxyphenyl)-octene (Table 8, entry 1). Following general procedure G, a mixture of 2,5-dimethoxybromobenzene (217 mg, 1.0 mmol), (*E*)-1-octenyl boronic acid (234 mg, 1.5 mmol), K₃PO₄ (425 mg, 2.0 mmol), Pd(OAc)₂ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (4% ethyl acetate in hexanes) to provide the title compound as pale yellow oil (241 mg, 97%). ¹H NMR (500 MHz, CDCl₃) δ: 7.00 (d, *J* = 3 Hz, 1H), 6.79 (d, *J* = 9 Hz, 1H), 6.73 (dd, *J* = 3, 9 Hz, 1H), 6.69 (d, *J* = 16 Hz, 1H), 6.22 (dt, *J* = 7, 16 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.23 (q, *J* = 4 Hz, 2H), 1.48 (quintet, *J* = 7 Hz, 2H), 1.29-1.38 (m, 4H), 0.90 (t, *J* = 7 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ: 153.7, 150.7, 132.3,

127.9, 124.0, 112.5, 112.1, 111.8, 56.2, 55.7, 33.4, 31.7, 29.4, 28.9, 22.6, 14.1. IR (neat, cm^{-1}): 2996, 2926, 2864, 1583, 1496, 1282, 1218, 1060. A satisfactory elemental analysis was not obtained for this compound. The ^1H and ^{13}C NMR spectra follow.

(*E*)-1-(2-Fluoro-5-cyanophenyl)-octene (Table 8, entry 2). Following general procedure G, a mixture of 3-bromo-4-fluorobenzonitrile (200 mg, 1.0 mmol), (*E*)-1-octenyl boronic acid (234 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was stirred at RT for 24 h. The crude product was purified via flash column chromatography on silica gel (4% ethyl acetate in hexanes) to provide the title compound as a yellow oil (224 mg, 97%). 1H NMR (500 MHz, $CDCl_3$) δ : 7.74 (dd, $J = 3, 7$ Hz, 1H), 7.46 (m, 1H), 7.11 (dd, $J = 9, 10$ Hz, 1H), 6.47 (d, $J = 16$ Hz, 1H), 6.37 (dt, $J = 7, 16$ Hz, 1H), 2.25 (q, $J = 7$ Hz, 2H), 1.47 (quintet, $J = 7$ Hz, 2H), 1.26-1.37 (m, 4H), 0.89 (t, $J = 7$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 162.8, 160.8, 136.9, 136.8, 131.7, 131.6, 131.3, 131.2, 127.4, 127.3, 120.0, 119.9, 118.2, 117.0, 116.8, 108.5, 108.4, 33.3, 31.6, 28.9, 28.8, 22.5, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ : -109.4. IR (neat, cm^{-1}): 2967, 2927, 2868, 2234, 1606, 1488, 1246, 1104, 969. A satisfactory elemental analysis was not obtained for this compound. The 1H and ^{13}C NMR spectra follow.

***trans*-2,5-Dimethylstilbene (Table 8, entry 3).** Following general procedure G, a mixture of 2-bromo-*p*-xylene (185 mg, 1.0 mmol), (*E*)- β -styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 5% ethyl acetate in hexanes) to provide the title compound as a white solid (211 mg, 97%), mp 42-43 °C. 1H NMR (300 MHz, $CDCl_3$) δ : 7.50(d, J = 8 Hz, 2H), 7.28-7.40(m, 3H), 7.23 (d, J = 8 Hz, 2H), 6.96-7.06 (m, 3H), 2.36 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 137.7, 136.0, 135.4, 132.7, 130.3, 130.0, 128.6, 128.3, 127.4, 126.5, 126.4, 125.9, 21.0, 19.4. IR (neat, cm^{-1}): 3026, 2922, 1599, 1499, 1448, 1266, 961. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.70.

***trans*-2,4,6-Trimethylstilbene (Table 8, entry 4).** Following general procedure G, a mixture of 2-bromomesitylene (199 mg, 1.0 mmol), (*E*)- β -styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 1% ethyl acetate in hexanes) to provide the title compound as a white solid (219 mg, 99%), mp 49-50 °C. 1H NMR (300 MHz, $CDCl_3$) δ : 7.47 (d, J = 7 Hz, 2H), 7.34 (t, J = 7 Hz, 2H), 7.25 (d, J = 7 Hz, 1H), 7.08 (d, J = 16 Hz, 1H), 6.88 (s, 2H), 6.58 (d, J = 16 Hz, 1H), 2.33 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 137.7, 136.2, 136.1, 133.9, 133.6, 128.7, 128.6, 127.4, 126.9, 126.2, 21.0, 20.9. IR (neat, cm^{-1}): 3024, 2917, 1598, 1496, 1449, 1377, 1266, 970. A satisfactory elemental analysis was not obtained for this compound. The 1H and ^{13}C NMR spectra follow.

***trans*-4-Aminostilbene (Table 8, entry 5).** Following general procedure G, a mixture of 4-bromoaniline (172 mg, 1.0 mmol), (*E*)- β -styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 °C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a orange solid (171 mg, 88%), mp 147-148 °C. 1H NMR (300 MHz, $CDCl_3$) δ : 7.47 (d, J = 7 Hz, 2H), 7.32 (t, J = 7 Hz, 4H), 7.20 (t, J = 7 Hz, 1H), 6.97 (q, J = 16 Hz, 2H), 6.66 (d, J = 8 Hz, 2H), 3.71 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 146.1, 137.9, 128.6, 128.5, 127.9, 127.7, 126.8, 126.1, 125.0, 115.1. IR (neat, cm^{-1}): 3453, 3362, 3029, 1616, 1591, 1517, 1286, 1180, 969. A satisfactory elemental analysis was not obtained for this compound. The 1H and ^{13}C NMR spectra follow.

X-Ray Crystal Data for **1**•Pd(dba)Table 1. Crystal data and structure refinement for **1**•Pd(dba).

Identification code	1•Pd(dba).		
Empirical formula	C ₄₃ H ₄₉ O ₃ PPd		
Formula weight	727.17		
Temperature	193(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 11.4552(15) Å	a = 94.058(2)°.	
	b = 11.6697(15) Å	b = 96.084(2)°.	
	c = 15.5298(19) Å	g = 114.705(2)°.	
Volume	1860.1(4) Å ³		
Z	2		
Density (calculated)	1.298 Mg/m ³		
Absorption coefficient	0.577 mm ⁻¹		
F(000)	760		
Crystal size	0.20 x 0.18 x 0.14 mm ³		
Theta range for data collection	2.09 to 23.29°.		
Index ranges	-12<=h<=12, -12<=k<=11, -15<=l<=17		
Reflections collected	7703		
Independent reflections	5293 [R(int) = 0.0200]		
Completeness to theta = 23.29°	98.5 %		
Absorption correction	SADABS		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	5293 / 0 / 435		
Goodness-of-fit on F ²	1.052		
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0676		
R indices (all data)	R1 = 0.0330, wR2 = 0.0695		
Largest diff. peak and hole	0.509 and -0.338 e. Å ⁻³		

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **1**•Pd(dba). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1335(1)	3807(1)	2877(1)	24(1)
P(2)	3200(1)	4741(1)	2281(1)	26(1)
O(1)	-2088(2)	1661(2)	3238(1)	34(1)
O(3)	3192(2)	3782(2)	4661(1)	35(1)
O(2)	1497(2)	1074(2)	2030(1)	41(1)

C(32)	-472(2)	3717(3)	3218(2)	27(1)
C(6)	3643(2)	2904(3)	3093(2)	25(1)
C(33)	-1432(3)	2479(3)	2797(2)	28(1)
C(1)	4176(3)	3898(3)	2596(2)	27(1)
C(31)	151(3)	4790(3)	2778(2)	27(1)
C(34)	-1627(3)	2187(3)	1833(2)	30(1)
C(2)	5413(3)	4176(3)	2364(2)	33(1)
C(4)	5589(3)	2554(3)	3157(2)	38(1)
C(7)	2295(3)	2459(3)	3339(2)	27(1)
C(5)	4356(3)	2245(3)	3373(2)	31(1)
C(26)	1605(3)	7654(3)	4531(2)	38(1)
C(14)	4262(3)	6574(3)	3724(2)	40(1)
C(12)	1251(3)	1381(3)	2838(2)	32(1)
C(25)	1073(3)	6409(3)	4135(2)	33(1)
C(30)	747(3)	6110(3)	3231(2)	27(1)
C(8)	2129(3)	2794(3)	4196(2)	30(1)
C(9)	1005(3)	2079(3)	4533(2)	38(1)
C(13)	4174(3)	6430(3)	2727(2)	31(1)
C(36)	-2900(3)	674(3)	485(2)	36(1)
C(29)	987(3)	7122(3)	2740(2)	37(1)
C(81)	3008(3)	4409(3)	5423(2)	48(1)
C(27)	1816(3)	8637(3)	4032(2)	41(1)
C(41)	-3809(3)	-573(3)	189(2)	51(1)
C(19)	3175(3)	4670(3)	1081(2)	36(1)
C(3)	6103(3)	3516(3)	2644(2)	38(1)
C(28)	1519(3)	8368(3)	3137(2)	45(1)
C(35)	-2550(3)	1105(3)	1425(2)	35(1)
C(10)	38(3)	1024(3)	4031(2)	42(1)
C(37)	-2408(4)	1467(3)	-139(2)	54(1)
C(18)	5503(3)	7118(3)	2461(2)	49(1)
C(11)	139(3)	681(3)	3182(2)	40(1)
C(20)	2525(4)	3291(3)	650(2)	51(1)
C(40)	-4197(4)	-996(4)	-692(3)	61(1)
C(121)	434(3)	164(3)	1415(2)	59(1)
C(38)	-2820(4)	1041(4)	-1015(2)	72(1)
C(16)	6188(4)	8679(3)	3838(2)	61(1)
C(17)	6104(3)	8529(3)	2847(2)	57(1)
C(24)	2525(5)	5431(4)	667(2)	69(1)
C(15)	4876(4)	7979(3)	4099(2)	56(1)
C(21)	2522(4)	3211(4)	-336(2)	63(1)
C(22)	1866(4)	3967(4)	-746(2)	72(1)
C(39)	-3704(4)	-189(4)	-1292(3)	69(1)
C(23)	2511(6)	5327(5)	-325(2)	92(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **1**•Pd(dba).

Pd(1)-C(31)	2.113(3)
Pd(1)-C(32)	2.153(3)
Pd(1)-P(2)	2.2850(8)
Pd(1)-C(7)	2.374(3)
P(2)-C(1)	1.825(3)
P(2)-C(13)	1.847(3)
P(2)-C(19)	1.856(3)
O(1)-C(33)	1.243(3)
O(3)-C(8)	1.362(3)
O(3)-C(81)	1.429(3)
O(2)-C(12)	1.370(4)
O(2)-C(121)	1.432(4)
C(32)-C(31)	1.422(4)
C(32)-C(33)	1.452(4)
C(6)-C(5)	1.394(4)
C(6)-C(1)	1.395(4)
C(6)-C(7)	1.511(4)
C(33)-C(34)	1.483(4)
C(1)-C(2)	1.408(4)
C(31)-C(30)	1.483(4)
C(34)-C(35)	1.321(4)
C(2)-C(3)	1.375(4)
C(4)-C(3)	1.384(4)
C(4)-C(5)	1.390(4)
C(7)-C(8)	1.415(4)
C(7)-C(12)	1.423(4)
C(26)-C(27)	1.382(4)
C(26)-C(25)	1.384(4)
C(14)-C(15)	1.528(4)
C(14)-C(13)	1.533(4)
C(12)-C(11)	1.383(4)
C(25)-C(30)	1.394(4)
C(30)-C(29)	1.397(4)
C(8)-C(9)	1.391(4)
C(9)-C(10)	1.375(4)
C(13)-C(18)	1.513(4)
C(36)-C(37)	1.386(5)
C(36)-C(41)	1.396(4)
C(36)-C(35)	1.465(4)
C(29)-C(28)	1.384(4)
C(27)-C(28)	1.377(4)
C(41)-C(40)	1.380(5)
C(19)-C(24)	1.512(5)
C(19)-C(20)	1.528(4)

C(10)-C(11)	1.381(5)
C(37)-C(38)	1.375(5)
C(18)-C(17)	1.539(5)
C(20)-C(21)	1.527(5)
C(40)-C(39)	1.366(6)
C(38)-C(39)	1.370(5)
C(16)-C(15)	1.497(5)
C(16)-C(17)	1.523(5)
C(24)-C(23)	1.536(5)
C(21)-C(22)	1.509(5)
C(22)-C(23)	1.505(6)

C(31)-Pd(1)-C(32)	38.93(10)
C(31)-Pd(1)-P(2)	113.46(8)
C(32)-Pd(1)-P(2)	152.39(8)
C(31)-Pd(1)-C(7)	162.39(10)
C(32)-Pd(1)-C(7)	124.34(10)
P(2)-Pd(1)-C(7)	83.01(7)
C(1)-P(2)-C(13)	106.83(13)
C(1)-P(2)-C(19)	102.59(13)
C(13)-P(2)-C(19)	105.85(13)
C(1)-P(2)-Pd(1)	105.73(9)
C(13)-P(2)-Pd(1)	113.04(9)
C(19)-P(2)-Pd(1)	121.50(10)
C(8)-O(3)-C(81)	117.6(2)
C(12)-O(2)-C(121)	118.2(3)
C(31)-C(32)-C(33)	125.0(3)
C(31)-C(32)-Pd(1)	69.02(15)
C(33)-C(32)-Pd(1)	103.94(18)
C(5)-C(6)-C(1)	119.8(3)
C(5)-C(6)-C(7)	116.5(2)
C(1)-C(6)-C(7)	123.7(2)
O(1)-C(33)-C(32)	120.6(3)
O(1)-C(33)-C(34)	119.7(3)
C(32)-C(33)-C(34)	119.6(3)
C(6)-C(1)-C(2)	118.5(3)
C(6)-C(1)-P(2)	117.1(2)
C(2)-C(1)-P(2)	124.4(2)
C(32)-C(31)-C(30)	122.3(2)
C(32)-C(31)-Pd(1)	72.05(15)
C(30)-C(31)-Pd(1)	115.57(18)
C(35)-C(34)-C(33)	121.2(3)
C(3)-C(2)-C(1)	121.0(3)
C(3)-C(4)-C(5)	119.2(3)
C(8)-C(7)-C(12)	116.9(3)
C(8)-C(7)-C(6)	120.1(2)

C(12)-C(7)-C(6)	119.5(2)
C(8)-C(7)-Pd(1)	86.84(16)
C(12)-C(7)-Pd(1)	90.96(17)
C(6)-C(7)-Pd(1)	110.26(17)
C(4)-C(5)-C(6)	120.9(3)
C(27)-C(26)-C(25)	120.2(3)
C(15)-C(14)-C(13)	110.6(3)
O(2)-C(12)-C(11)	124.6(3)
O(2)-C(12)-C(7)	114.0(3)
C(11)-C(12)-C(7)	121.3(3)
C(26)-C(25)-C(30)	121.5(3)
C(25)-C(30)-C(29)	117.2(3)
C(25)-C(30)-C(31)	123.4(3)
C(29)-C(30)-C(31)	119.4(2)
O(3)-C(8)-C(9)	124.6(3)
O(3)-C(8)-C(7)	114.1(2)
C(9)-C(8)-C(7)	121.1(3)
C(10)-C(9)-C(8)	119.8(3)
C(18)-C(13)-C(14)	110.6(3)
C(18)-C(13)-P(2)	118.3(2)
C(14)-C(13)-P(2)	109.40(19)
C(37)-C(36)-C(41)	117.4(3)
C(37)-C(36)-C(35)	123.0(3)
C(41)-C(36)-C(35)	119.6(3)
C(28)-C(29)-C(30)	121.4(3)
C(28)-C(27)-C(26)	119.4(3)
C(40)-C(41)-C(36)	121.1(4)
C(24)-C(19)-C(20)	110.3(3)
C(24)-C(19)-P(2)	113.0(2)
C(20)-C(19)-P(2)	110.5(2)
C(2)-C(3)-C(4)	120.5(3)
C(27)-C(28)-C(29)	120.4(3)
C(34)-C(35)-C(36)	128.6(3)
C(9)-C(10)-C(11)	121.2(3)
C(38)-C(37)-C(36)	121.0(3)
C(13)-C(18)-C(17)	109.9(3)
C(10)-C(11)-C(12)	119.6(3)
C(21)-C(20)-C(19)	111.3(3)
C(39)-C(40)-C(41)	120.1(4)
C(39)-C(38)-C(37)	120.7(4)
C(15)-C(16)-C(17)	110.7(3)
C(16)-C(17)-C(18)	111.4(3)
C(19)-C(24)-C(23)	111.0(3)
C(16)-C(15)-C(14)	111.5(3)
C(22)-C(21)-C(20)	111.3(3)
C(23)-C(22)-C(21)	110.3(3)

C(40)-C(39)-C(38)	119.6(4)
C(22)-C(23)-C(24)	111.9(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**•Pd(dba). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + \dots + 2hk a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	20(1)	26(1)	27(1)	4(1)	3(1)	11(1)
P(2)	22(1)	32(1)	25(1)	5(1)	3(1)	12(1)
O(1)	29(1)	36(1)	37(1)	10(1)	8(1)	13(1)
O(3)	36(1)	41(1)	27(1)	-4(1)	1(1)	17(1)
O(2)	35(1)	38(1)	42(1)	-14(1)	-8(1)	14(1)
C(32)	22(1)	32(2)	29(2)	6(1)	6(1)	14(1)
C(6)	23(1)	27(2)	23(1)	-7(1)	-3(1)	11(1)
C(33)	22(1)	33(2)	37(2)	6(1)	6(1)	18(1)
C(1)	24(1)	34(2)	22(1)	-4(1)	-1(1)	14(1)
C(31)	22(1)	33(2)	27(2)	2(1)	1(1)	14(1)
C(34)	28(2)	29(2)	36(2)	7(1)	7(1)	14(1)
C(2)	27(2)	43(2)	29(2)	-1(1)	5(1)	14(1)
C(4)	35(2)	43(2)	40(2)	-7(2)	-4(1)	26(2)
C(7)	25(2)	24(2)	32(2)	4(1)	0(1)	12(1)
C(5)	32(2)	33(2)	30(2)	-2(1)	-1(1)	18(1)
C(26)	45(2)	40(2)	28(2)	-1(1)	8(1)	18(2)
C(14)	43(2)	36(2)	32(2)	5(1)	4(1)	11(2)
C(12)	30(2)	28(2)	41(2)	0(1)	-2(1)	17(1)
C(25)	36(2)	36(2)	30(2)	8(1)	9(1)	17(1)
C(30)	24(1)	32(2)	28(2)	4(1)	4(1)	15(1)
C(8)	31(2)	32(2)	33(2)	5(1)	3(1)	19(1)
C(9)	40(2)	46(2)	40(2)	18(2)	13(2)	25(2)
C(13)	34(2)	31(2)	30(2)	8(1)	6(1)	13(1)
C(36)	35(2)	31(2)	41(2)	-2(1)	2(1)	14(1)
C(29)	46(2)	35(2)	29(2)	6(1)	1(1)	19(2)
C(81)	58(2)	58(2)	32(2)	-5(2)	1(2)	33(2)
C(27)	51(2)	28(2)	43(2)	-5(1)	7(2)	15(2)
C(41)	49(2)	41(2)	53(2)	-2(2)	-6(2)	13(2)
C(19)	30(2)	48(2)	27(2)	6(1)	4(1)	14(2)
C(3)	24(2)	52(2)	37(2)	-10(2)	0(1)	19(2)
C(28)	60(2)	34(2)	44(2)	10(2)	8(2)	22(2)
C(35)	35(2)	32(2)	37(2)	7(1)	5(1)	13(2)
C(10)	31(2)	40(2)	62(2)	28(2)	14(2)	17(2)
C(37)	60(2)	45(2)	41(2)	-7(2)	13(2)	7(2)
C(18)	40(2)	45(2)	54(2)	10(2)	11(2)	9(2)
C(11)	26(2)	27(2)	61(2)	7(2)	-3(2)	9(1)

C(20)	61(2)	57(2)	33(2)	-4(2)	-2(2)	26(2)
C(40)	57(2)	46(2)	68(3)	-21(2)	-9(2)	21(2)
C(121)	51(2)	49(2)	60(2)	-18(2)	-22(2)	17(2)
C(38)	88(3)	68(3)	40(2)	-8(2)	19(2)	16(2)
C(16)	54(2)	41(2)	65(3)	-5(2)	-11(2)	5(2)
C(17)	44(2)	43(2)	67(3)	14(2)	8(2)	1(2)
C(24)	117(4)	85(3)	32(2)	8(2)	-1(2)	70(3)
C(15)	64(2)	44(2)	44(2)	-4(2)	0(2)	10(2)
C(21)	68(3)	76(3)	36(2)	-10(2)	-1(2)	27(2)
C(22)	76(3)	110(4)	29(2)	1(2)	-5(2)	45(3)
C(39)	73(3)	82(3)	43(2)	-28(2)	2(2)	32(3)
C(23)	166(5)	98(4)	33(2)	13(2)	-3(3)	81(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**•Pd(dba).

	x	y	z	U(eq)
H(32)	-484	3907	3854	32
H(31)	-293	4707	2171	32
H(34)	-1077	2790	1503	36
H(2)	5777	4830	2008	40
H(4)	6074	2109	3359	45
H(5)	3993	1576	3717	37
H(26)	1827	7833	5148	45
H(14A)	3381	6149	3885	48
H(14B)	4792	6159	3976	48
H(25)	927	5742	4487	40
H(9)	905	2318	5108	46
H(13)	3656	6889	2512	38
H(29)	781	6952	2122	44
H(81A)	2284	4635	5278	71
H(81B)	3802	5181	5639	71
H(81C)	2811	3839	5875	71
H(27)	2163	9490	4304	50
H(41)	-4165	-1139	601	61
H(19)	4097	5043	970	43
H(3)	6939	3722	2484	45
H(28)	1680	9041	2789	54
H(35)	-3054	529	1789	42
H(10)	-714	523	4272	51
H(37)	-1777	2316	40	65
H(18A)	5424	7048	1817	59

H(18B)	6074	6722	2675	59
H(11)	-552	-32	2836	48
H(20A)	2995	2819	903	61
H(20B)	1620	2886	772	61
H(40)	-4809	-1851	-881	73
H(12A)	96	-661	1639	88
H(12B)	735	78	857	88
H(12C)	-255	451	1329	88
H(38)	-2489	1607	-1432	86
H(16A)	6790	8344	4097	73
H(16B)	6538	9592	4064	73
H(17A)	6986	8965	2690	68
H(17B)	5569	8938	2593	68
H(24A)	2995	6334	923	83
H(24B)	1621	5113	795	83
H(15A)	4301	8373	3889	67
H(15B)	4960	8053	4744	67
H(21A)	3428	3542	-459	75
H(21B)	2061	2311	-600	75
H(22A)	1918	3935	-1379	86
H(22B)	937	3587	-674	86
H(39)	-3973	-479	-1899	83
H(23A)	2043	5798	-582	110
H(23B)	3415	5727	-451	110

X-Ray Crystal Data for **10**:

Table 1. Crystal data and structure refinement for **10**

Identification code	10	
Empirical formula	C ₅₂ H ₇₀ Cl ₂ O ₄ P ₂ Pd	
Formula weight	1237.06	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9866(16) Å b = 12.598(2) Å c = 23.797(4) Å	a = 90°. b = 99.089(3)°. g = 90°.
Volume	2956.3(8) Å ³	
Z	2	
Density (calculated)	1.390 Mg/m ³	
Absorption coefficient	0.771 mm ⁻¹	

F(000)	1280
Crystal size	0.31 x 0.30 x 0.19 mm ³
Theta range for data collection	2.37 to 23.31°.
Index ranges	-8<=h<=11, -14<=k<=11, -26<=l<=25
Reflections collected	11760
Independent reflections	4239 [R(int) = 0.0221]
Completeness to theta = 23.31°	99.5 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4239 / 0 / 344
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0588
R indices (all data)	R1 = 0.0274, wR2 = 0.0601
Extinction coefficient	0.00100(18)
Largest diff. peak and hole	0.308 and -0.242 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	10000	10000	5000	25(1)
Cl	9524(1)	11073(1)	4212(1)	37(1)
P	8809(1)	8624(1)	4474(1)	24(1)
O(1)	7990(2)	9713(1)	2769(1)	48(1)
O(2)	5910(2)	6711(1)	3369(1)	41(1)
C(1)	7208(2)	9118(2)	4066(1)	26(1)
C(2)	6542(2)	8852(2)	3520(1)	27(1)
C(3)	7108(2)	8166(2)	3101(1)	30(1)
C(4)	7851(2)	8633(2)	2716(1)	38(1)
C(5)	8371(2)	8027(3)	2314(1)	52(1)
C(6)	8127(3)	6953(3)	2291(1)	55(1)
C(7)	7344(2)	6466(2)	2644(1)	47(1)
C(8)	6799(2)	7085(2)	3037(1)	35(1)
C(9)	5271(2)	9308(2)	3331(1)	37(1)
C(10)	4666(2)	10002(2)	3658(1)	41(1)
C(11)	5322(2)	10277(2)	4192(1)	37(1)
C(12)	6580(2)	9841(2)	4386(1)	32(1)
C(13)	5518(3)	5624(2)	3314(1)	62(1)
C(14)	8710(4)	10248(3)	2382(1)	81(1)
C(21)	9949(2)	7968(2)	4039(1)	28(1)
C(22)	11024(2)	7317(2)	4429(1)	35(1)
C(23)	11998(3)	6778(2)	4083(1)	47(1)

C(24)	12656(2)	7563(2)	3727(1)	51(1)
C(25)	11594(2)	8217(2)	3353(1)	42(1)
C(26)	10666(2)	8777(2)	3708(1)	32(1)
C(31)	8271(2)	7552(2)	4921(1)	29(1)
C(32)	7279(2)	7933(2)	5308(1)	34(1)
C(33)	7055(3)	7062(2)	5726(1)	46(1)
C(34)	6508(3)	6062(2)	5415(1)	57(1)
C(35)	7446(3)	5687(2)	5008(1)	55(1)
C(36)	7685(3)	6564(2)	4594(1)	40(1)
Cl(2)	6810(4)	3119(3)	4164(1)	69(1)
Cl(3)	8369(4)	3177(3)	3241(1)	81(1)
Cl(4)	5548(2)	2534(2)	3052(1)	67(1)
Cl(5)	6039(19)	2533(6)	2900(5)	149(4)
Cl(6)	6530(10)	3047(6)	4083(4)	81(2)
Cl(7)	8409(10)	3534(12)	3403(7)	172(5)
C(1S)	7111(3)	2550(2)	3525(1)	51(1)

Table 3. Bond lengths [Å] and angles [°] for **10**.

Pd-Cl	2.3005(6)
Pd-Cl#1	2.3005(6)
Pd-P	2.3486(6)
Pd-P#1	2.3486(6)
P-C(1)	1.843(2)
P-C(31)	1.849(2)
P-C(21)	1.850(2)
O(1)-C(4)	1.372(3)
O(1)-C(14)	1.424(3)
O(2)-C(8)	1.363(3)
O(2)-C(13)	1.424(3)
C(1)-C(12)	1.398(3)
C(1)-C(2)	1.403(3)
C(2)-C(9)	1.401(3)
C(2)-C(3)	1.496(3)
C(3)-C(4)	1.397(3)
C(3)-C(8)	1.399(3)
C(4)-C(5)	1.387(3)
C(5)-C(6)	1.374(4)
C(6)-C(7)	1.377(4)
C(7)-C(8)	1.393(3)
C(9)-C(10)	1.372(3)
C(10)-C(11)	1.378(3)
C(11)-C(12)	1.382(3)
C(21)-C(26)	1.534(3)

C(21)-C(22)	1.540(3)
C(22)-C(23)	1.529(3)
C(23)-C(24)	1.519(3)
C(24)-C(25)	1.516(3)
C(25)-C(26)	1.521(3)
C(31)-C(32)	1.533(3)
C(31)-C(36)	1.534(3)
C(32)-C(33)	1.521(3)
C(33)-C(34)	1.518(4)
C(34)-C(35)	1.525(4)
C(35)-C(36)	1.524(3)
Cl(2)-C(1S)	1.750(5)
Cl(3)-C(1S)	1.710(4)
Cl(4)-C(1S)	1.774(3)
Cl-Pd-Cl#1	180.000(16)
Cl-Pd-P	88.71(2)
Cl#1-Pd-P	91.29(2)
Cl-Pd-P#1	91.29(2)
Cl#1-Pd-P#1	88.71(2)
P-Pd-P#1	180.0
C(1)-P-C(31)	104.09(9)
C(1)-P-C(21)	114.49(9)
C(31)-P-C(21)	104.81(9)
C(1)-P-Pd	110.84(7)
C(31)-P-Pd	113.69(7)
C(21)-P-Pd	108.85(7)
C(4)-O(1)-C(14)	117.6(2)
C(8)-O(2)-C(13)	118.23(19)
C(12)-C(1)-C(2)	118.14(18)
C(12)-C(1)-P	111.05(15)
C(2)-C(1)-P	130.75(15)
C(9)-C(2)-C(1)	118.21(19)
C(9)-C(2)-C(3)	116.21(18)
C(1)-C(2)-C(3)	125.47(18)
C(4)-C(3)-C(8)	117.9(2)
C(4)-C(3)-C(2)	119.4(2)
C(8)-C(3)-C(2)	122.35(19)
O(1)-C(4)-C(5)	124.5(2)
O(1)-C(4)-C(3)	114.4(2)
C(5)-C(4)-C(3)	121.1(2)
C(6)-C(5)-C(4)	119.0(2)
C(5)-C(6)-C(7)	121.9(2)
C(6)-C(7)-C(8)	118.7(2)
O(2)-C(8)-C(7)	123.8(2)
O(2)-C(8)-C(3)	115.15(19)

C(7)-C(8)-C(3)	121.0(2)
C(10)-C(9)-C(2)	122.4(2)
C(9)-C(10)-C(11)	119.7(2)
C(10)-C(11)-C(12)	118.9(2)
C(11)-C(12)-C(1)	122.7(2)
C(26)-C(21)-C(22)	108.98(17)
C(26)-C(21)-P	111.72(14)
C(22)-C(21)-P	109.45(14)
C(23)-C(22)-C(21)	110.81(18)
C(24)-C(23)-C(22)	112.3(2)
C(25)-C(24)-C(23)	110.9(2)
C(24)-C(25)-C(26)	111.00(19)
C(25)-C(26)-C(21)	110.61(18)
C(32)-C(31)-C(36)	109.13(18)
C(32)-C(31)-P	112.96(14)
C(36)-C(31)-P	115.08(14)
C(33)-C(32)-C(31)	110.05(18)
C(34)-C(33)-C(32)	111.03(19)
C(33)-C(34)-C(35)	110.9(2)
C(36)-C(35)-C(34)	111.1(2)
C(35)-C(36)-C(31)	110.29(19)
Cl(3)-C(1S)-Cl(2)	113.0(2)
Cl(3)-C(1S)-Cl(4)	112.49(19)
Cl(2)-C(1S)-Cl(4)	107.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd	27(1)	22(1)	23(1)	-2(1)	-1(1)	4(1)
Cl	44(1)	30(1)	32(1)	4(1)	-7(1)	2(1)
P	26(1)	23(1)	23(1)	-2(1)	3(1)	3(1)
O(1)	50(1)	56(1)	39(1)	14(1)	9(1)	-13(1)
O(2)	50(1)	32(1)	41(1)	-2(1)	10(1)	-7(1)
C(1)	25(1)	24(1)	28(1)	2(1)	4(1)	0(1)
C(2)	27(1)	26(1)	29(1)	4(1)	5(1)	-5(1)
C(3)	25(1)	40(1)	23(1)	-1(1)	-2(1)	0(1)
C(4)	31(1)	55(2)	26(1)	3(1)	-1(1)	-7(1)
C(5)	37(1)	92(2)	28(1)	-6(1)	9(1)	-9(1)
C(6)	41(2)	86(2)	39(1)	-25(2)	5(1)	5(1)
C(7)	45(2)	50(2)	42(1)	-16(1)	-2(1)	4(1)

C(8)	32(1)	41(1)	29(1)	-4(1)	-1(1)	1(1)
C(9)	33(1)	43(1)	33(1)	3(1)	-5(1)	1(1)
C(10)	29(1)	41(1)	52(2)	6(1)	0(1)	7(1)
C(11)	34(1)	34(1)	46(1)	0(1)	11(1)	8(1)
C(12)	34(1)	30(1)	32(1)	-2(1)	4(1)	4(1)
C(13)	77(2)	35(2)	76(2)	-4(1)	17(2)	-10(1)
C(14)	88(2)	88(2)	73(2)	28(2)	30(2)	-24(2)
C(21)	30(1)	27(1)	26(1)	-4(1)	4(1)	3(1)
C(22)	35(1)	34(1)	37(1)	1(1)	8(1)	10(1)
C(23)	46(2)	45(2)	54(2)	5(1)	20(1)	19(1)
C(24)	41(1)	56(2)	59(2)	3(1)	23(1)	14(1)
C(25)	41(1)	47(1)	41(1)	0(1)	17(1)	-1(1)
C(26)	32(1)	33(1)	31(1)	1(1)	4(1)	2(1)
C(31)	35(1)	27(1)	25(1)	0(1)	5(1)	3(1)
C(32)	35(1)	35(1)	34(1)	-3(1)	9(1)	4(1)
C(33)	54(2)	50(2)	38(1)	4(1)	22(1)	5(1)
C(34)	75(2)	44(2)	61(2)	8(1)	33(2)	-8(1)
C(35)	84(2)	32(1)	55(2)	-2(1)	29(2)	-10(1)
C(36)	55(2)	30(1)	37(1)	-5(1)	15(1)	-7(1)
Cl(2)	91(2)	72(2)	38(1)	-9(1)	-3(1)	32(1)
Cl(3)	60(1)	103(2)	87(2)	45(1)	36(1)	10(1)
Cl(4)	58(1)	74(1)	57(1)	13(1)	-25(1)	-6(1)
Cl(5)	228(9)	117(4)	78(4)	13(3)	-51(5)	44(5)
Cl(6)	98(4)	53(2)	109(5)	-3(3)	68(3)	-18(3)
Cl(7)	98(5)	155(8)	288(10)	112(7)	111(6)	65(5)
C(1S)	54(2)	56(2)	42(1)	10(1)	2(1)	16(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**.

	x	y	z	U(eq)
H(5)	8888	8349	2058	62
H(6)	8508	6534	2025	66
H(7)	7180	5724	2619	56
H(9)	4810	9130	2963	45
H(10)	3800	10291	3518	49
H(11)	4917	10758	4422	45
H(12)	7036	10041	4751	39
H(13A)	5060	5490	2925	94
H(13B)	4900	5461	3584	94
H(13C)	6326	5174	3395	94
H(14A)	9641	9978	2426	121

H(14B)	8727	11012	2462	121
H(14C)	8258	10123	1991	121
H(21)	9402	7477	3763	33
H(22A)	11541	7791	4716	42
H(22B)	10570	6772	4632	42
H(23A)	12714	6405	4346	56
H(23B)	11496	6240	3829	56
H(24A)	13265	8040	3981	61
H(24B)	13212	7173	3485	61
H(25A)	11048	7749	3072	50
H(25B)	12047	8751	3143	50
H(26A)	9982	9198	3455	38
H(26B)	11206	9271	3977	38
H(31)	9107	7314	5178	35
H(32A)	7648	8573	5519	41
H(32B)	6403	8126	5074	41
H(33A)	7924	6900	5974	55
H(33B)	6405	7313	5971	55
H(34A)	5596	6205	5199	69
H(34B)	6421	5496	5696	69
H(35A)	8325	5464	5229	66
H(35B)	7038	5064	4792	66
H(36A)	6818	6747	4351	48
H(36B)	8323	6310	4345	48
H(1S)	7398	1797	3604	61

X-Ray Crystal Data for **11**:

Table 1. Crystal data and structure refinement for **11**.

Identification code	11	
Empirical formula	C ₅₂ H ₇₀ O ₄ P ₂ Pd	
Formula weight	927.42	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2288(11) Å b = 13.9949(13) Å c = 15.4425(14) Å	a = 96.770(2)°. b = 94.380(2)°. g = 113.116(2)°.
Volume	2391.8(4) Å ³	
Z	2	

Density (calculated)	1.288 Mg/m ³
Absorption coefficient	0.498 mm ⁻¹
F(000)	980
Crystal size	0.37 x 0.23 x 0.08 mm ³
Theta range for data collection	1.60 to 23.31°
Index ranges	-13<=h<=9, -15<=k<=15, -15<=l<=17
Reflections collected	11251
Independent reflections	6907 [R(int) = 0.0290]
Completeness to theta = 23.31°	99.7 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6907 / 0 / 536
Goodness-of-fit on F ²	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0763
R indices (all data)	R1 = 0.0501, wR2 = 0.0817
Largest diff. peak and hole	0.564 and -0.457 e. Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	1916(1)	3077(1)	2117(1)	33(1)
P(1)	1729(1)	1598(1)	2688(1)	27(1)
P(2)	1585(1)	4265(1)	1390(1)	29(1)
O(3)	5052(2)	4820(2)	1105(1)	37(1)
O(2)	5051(2)	1432(2)	4161(2)	47(1)
O(1)	981(2)	-532(2)	4148(1)	42(1)
C(32)	4138(3)	456(3)	3975(2)	40(1)
O(4)	3579(2)	6009(2)	3502(1)	45(1)
C(7)	4326(3)	5387(2)	2330(2)	28(1)
C(6)	3873(3)	6006(2)	1784(2)	27(1)
C(1)	2701(3)	5617(2)	1357(2)	26(1)
C(30)	2850(3)	1407(2)	4407(2)	29(1)
C(3)	3187(3)	7269(2)	799(2)	38(1)
C(31)	3006(3)	425(2)	4087(2)	31(1)
C(4)	4345(3)	7650(2)	1227(2)	39(1)
C(5)	4684(3)	7021(2)	1716(2)	34(1)
C(44)	-417(3)	894(3)	3440(2)	37(1)
C(37)	2503(3)	839(2)	2139(2)	33(1)
C(27)	2592(3)	3198(2)	5176(2)	38(1)
C(8)	4163(3)	5403(2)	3217(2)	35(1)
C(36)	2044(3)	-556(2)	3963(2)	36(1)
C(29)	3259(3)	1836(2)	5290(2)	36(1)

C(42)	1928(3)	367(3)	1185(2)	40(1)
C(12)	4944(3)	4813(2)	1982(2)	33(1)
C(9)	4587(3)	4846(3)	3733(2)	41(1)
C(48)	-623(3)	601(3)	1795(2)	39(1)
C(25)	2324(3)	1912(2)	3885(2)	28(1)
C(28)	3126(3)	2716(3)	5683(2)	38(1)
C(20)	36(3)	2861(3)	-139(2)	41(1)
C(10)	5201(3)	4293(3)	3373(2)	43(1)
C(38)	3811(3)	1592(3)	2159(2)	41(1)
C(11)	5401(3)	4278(3)	2501(2)	38(1)
C(43)	144(3)	628(2)	2645(2)	29(1)
C(14)	725(3)	5317(3)	2627(2)	42(1)
C(21)	-138(3)	2581(3)	-1140(2)	48(1)
C(26)	2218(3)	2810(2)	4295(2)	33(1)
C(13)	297(3)	4538(2)	1755(2)	33(1)
C(50)	6234(3)	1522(4)	4041(3)	68(1)
C(35)	2173(4)	-1477(3)	3657(2)	48(1)
C(51)	5377(3)	4036(3)	657(2)	47(1)
C(2)	2383(3)	6269(2)	872(2)	35(1)
C(49)	0(3)	-1503(3)	4171(2)	51(1)
C(45)	-1737(3)	165(3)	3392(2)	44(1)
C(19)	1212(3)	3815(2)	173(2)	35(1)
C(46)	-2461(3)	176(3)	2554(2)	48(1)
C(17)	-1739(3)	3725(3)	2279(3)	56(1)
C(18)	-714(3)	3516(3)	1902(2)	45(1)
C(15)	-302(3)	5494(3)	3017(3)	54(1)
C(47)	-1943(3)	-132(3)	1764(2)	47(1)
C(22)	899(4)	2362(3)	-1451(2)	59(1)
C(33)	4286(4)	-461(3)	3680(2)	52(1)
C(23)	2080(3)	3278(3)	-1143(2)	56(1)
C(24)	2259(3)	3590(3)	-136(2)	45(1)
C(39)	4536(3)	1077(3)	1676(3)	61(1)
C(52)	3385(4)	6065(3)	4397(2)	59(1)
C(34)	3298(4)	-1409(3)	3517(2)	57(1)
C(41)	2665(4)	-157(3)	728(2)	56(1)
C(16)	-1300(3)	4476(3)	3140(3)	59(1)
C(40)	3947(4)	603(3)	736(3)	67(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **11**.

Pd-P(2)	2.2556(8)
Pd-P(1)	2.2814(8)
P(1)-C(37)	1.855(3)
P(1)-C(25)	1.868(3)

P(1)-C(43)	1.871(3)
P(2)-C(1)	1.858(3)
P(2)-C(13)	1.870(3)
P(2)-C(19)	1.872(3)
O(3)-C(12)	1.373(4)
O(3)-C(51)	1.430(4)
O(2)-C(32)	1.363(4)
O(2)-C(50)	1.430(4)
O(1)-C(36)	1.364(4)
O(1)-C(49)	1.423(4)
C(32)-C(31)	1.393(4)
C(32)-C(33)	1.394(5)
O(4)-C(8)	1.363(4)
O(4)-C(52)	1.418(4)
C(7)-C(12)	1.393(4)
C(7)-C(8)	1.398(4)
C(7)-C(6)	1.499(4)
C(6)-C(1)	1.394(4)
C(6)-C(5)	1.399(4)
C(1)-C(2)	1.392(4)
C(30)-C(29)	1.392(4)
C(30)-C(25)	1.406(4)
C(30)-C(31)	1.493(4)
C(3)-C(4)	1.380(5)
C(3)-C(2)	1.383(4)
C(31)-C(36)	1.393(4)
C(4)-C(5)	1.384(4)
C(44)-C(45)	1.525(4)
C(44)-C(43)	1.529(4)
C(37)-C(38)	1.528(4)
C(37)-C(42)	1.533(4)
C(27)-C(28)	1.374(4)
C(27)-C(26)	1.375(4)
C(8)-C(9)	1.384(4)
C(36)-C(35)	1.392(4)
C(29)-C(28)	1.381(4)
C(42)-C(41)	1.530(4)
C(12)-C(11)	1.385(4)
C(9)-C(10)	1.376(5)
C(48)-C(47)	1.529(4)
C(48)-C(43)	1.542(4)
C(25)-C(26)	1.396(4)
C(20)-C(19)	1.523(4)
C(20)-C(21)	1.527(4)
C(10)-C(11)	1.385(4)
C(38)-C(39)	1.528(5)

C(14)-C(15)	1.524(5)
C(14)-C(13)	1.540(4)
C(21)-C(22)	1.515(5)
C(13)-C(18)	1.535(4)
C(35)-C(34)	1.377(5)
C(45)-C(46)	1.516(5)
C(19)-C(24)	1.529(4)
C(46)-C(47)	1.510(4)
C(17)-C(16)	1.509(5)
C(17)-C(18)	1.534(5)
C(15)-C(16)	1.513(5)
C(22)-C(23)	1.500(5)
C(33)-C(34)	1.378(5)
C(23)-C(24)	1.539(5)
C(39)-C(40)	1.519(5)
C(41)-C(40)	1.508(5)

P(2)-Pd-P(1)	164.48(3)
C(37)-P(1)-C(25)	107.04(13)
C(37)-P(1)-C(43)	105.07(14)
C(25)-P(1)-C(43)	103.76(13)
C(37)-P(1)-Pd	114.18(10)
C(25)-P(1)-Pd	111.68(9)
C(43)-P(1)-Pd	114.26(10)
C(1)-P(2)-C(13)	101.32(13)
C(1)-P(2)-C(19)	97.09(13)
C(13)-P(2)-C(19)	106.34(14)
C(1)-P(2)-Pd	125.54(10)
C(13)-P(2)-Pd	111.58(10)
C(19)-P(2)-Pd	112.71(10)
C(12)-O(3)-C(51)	117.5(2)
C(32)-O(2)-C(50)	117.9(3)
C(36)-O(1)-C(49)	118.3(3)
O(2)-C(32)-C(31)	115.1(3)
O(2)-C(32)-C(33)	124.1(3)
C(31)-C(32)-C(33)	120.8(3)
C(8)-O(4)-C(52)	117.3(3)
C(12)-C(7)-C(8)	118.5(3)
C(12)-C(7)-C(6)	121.6(3)
C(8)-C(7)-C(6)	119.9(3)
C(1)-C(6)-C(5)	119.9(3)
C(1)-C(6)-C(7)	123.1(3)
C(5)-C(6)-C(7)	117.1(3)
C(2)-C(1)-C(6)	117.8(3)
C(2)-C(1)-P(2)	119.7(2)
C(6)-C(1)-P(2)	122.4(2)

C(29)-C(30)-C(25)	118.7(3)
C(29)-C(30)-C(31)	116.4(3)
C(25)-C(30)-C(31)	124.9(3)
C(4)-C(3)-C(2)	119.6(3)
C(32)-C(31)-C(36)	118.0(3)
C(32)-C(31)-C(30)	120.7(3)
C(36)-C(31)-C(30)	121.0(3)
C(3)-C(4)-C(5)	119.4(3)
C(4)-C(5)-C(6)	121.1(3)
C(45)-C(44)-C(43)	112.6(3)
C(38)-C(37)-C(42)	109.8(3)
C(38)-C(37)-P(1)	107.5(2)
C(42)-C(37)-P(1)	111.6(2)
C(28)-C(27)-C(26)	119.9(3)
O(4)-C(8)-C(9)	125.1(3)
O(4)-C(8)-C(7)	114.2(3)
C(9)-C(8)-C(7)	120.7(3)
O(1)-C(36)-C(35)	123.6(3)
O(1)-C(36)-C(31)	114.8(3)
C(35)-C(36)-C(31)	121.7(3)
C(28)-C(29)-C(30)	122.6(3)
C(41)-C(42)-C(37)	110.0(3)
O(3)-C(12)-C(11)	123.7(3)
O(3)-C(12)-C(7)	115.2(3)
C(11)-C(12)-C(7)	121.2(3)
C(10)-C(9)-C(8)	119.4(3)
C(47)-C(48)-C(43)	112.2(3)
C(26)-C(25)-C(30)	117.5(3)
C(26)-C(25)-P(1)	111.7(2)
C(30)-C(25)-P(1)	130.8(2)
C(27)-C(28)-C(29)	118.5(3)
C(19)-C(20)-C(21)	110.0(3)
C(9)-C(10)-C(11)	121.4(3)
C(37)-C(38)-C(39)	112.8(3)
C(12)-C(11)-C(10)	118.8(3)
C(44)-C(43)-C(48)	109.1(3)
C(44)-C(43)-P(1)	111.2(2)
C(48)-C(43)-P(1)	110.7(2)
C(15)-C(14)-C(13)	112.5(3)
C(22)-C(21)-C(20)	111.0(3)
C(27)-C(26)-C(25)	122.6(3)
C(18)-C(13)-C(14)	108.8(3)
C(18)-C(13)-P(2)	110.3(2)
C(14)-C(13)-P(2)	109.3(2)
C(34)-C(35)-C(36)	118.4(4)
C(3)-C(2)-C(1)	122.3(3)

C(46)-C(45)-C(44)	111.4(3)
C(20)-C(19)-C(24)	110.0(3)
C(20)-C(19)-P(2)	116.0(2)
C(24)-C(19)-P(2)	107.0(2)
C(47)-C(46)-C(45)	109.8(3)
C(16)-C(17)-C(18)	111.5(3)
C(17)-C(18)-C(13)	111.6(3)
C(16)-C(15)-C(14)	112.4(3)
C(46)-C(47)-C(48)	111.3(3)
C(23)-C(22)-C(21)	111.7(3)
C(34)-C(33)-C(32)	119.2(4)
C(22)-C(23)-C(24)	110.8(3)
C(19)-C(24)-C(23)	111.3(3)
C(40)-C(39)-C(38)	110.8(3)
C(35)-C(34)-C(33)	121.7(3)
C(40)-C(41)-C(42)	112.2(3)
C(17)-C(16)-C(15)	110.0(3)
C(41)-C(40)-C(39)	110.0(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd	35(1)	27(1)	43(1)	15(1)	7(1)	16(1)
P(1)	33(1)	24(1)	30(1)	9(1)	8(1)	15(1)
P(2)	28(1)	23(1)	38(1)	10(1)	4(1)	11(1)
O(3)	46(1)	45(1)	31(1)	14(1)	9(1)	28(1)
O(2)	34(1)	58(2)	55(2)	9(1)	13(1)	25(1)
O(1)	38(1)	34(1)	52(2)	16(1)	8(1)	10(1)
C(32)	45(2)	46(2)	38(2)	12(2)	10(2)	26(2)
O(4)	56(2)	57(2)	25(1)	5(1)	5(1)	28(1)
C(7)	23(2)	31(2)	27(2)	8(1)	-1(1)	7(1)
C(6)	31(2)	30(2)	25(2)	5(1)	7(1)	15(2)
C(1)	30(2)	23(2)	30(2)	7(1)	8(2)	13(1)
C(30)	22(2)	31(2)	33(2)	10(1)	8(2)	8(1)
C(3)	44(2)	31(2)	46(2)	16(2)	9(2)	21(2)
C(31)	38(2)	36(2)	28(2)	14(1)	8(2)	22(2)
C(4)	45(2)	20(2)	48(2)	11(2)	12(2)	6(2)
C(5)	31(2)	29(2)	37(2)	4(2)	3(2)	6(2)
C(44)	38(2)	41(2)	36(2)	6(2)	7(2)	19(2)
C(37)	43(2)	31(2)	33(2)	13(1)	15(2)	20(2)
C(27)	36(2)	29(2)	44(2)	1(2)	13(2)	8(2)
C(8)	31(2)	36(2)	32(2)	6(2)	-1(2)	7(2)

C(36)	47(2)	36(2)	31(2)	16(2)	5(2)	20(2)
C(29)	26(2)	40(2)	41(2)	13(2)	8(2)	12(2)
C(42)	49(2)	37(2)	37(2)	8(2)	14(2)	19(2)
C(12)	28(2)	32(2)	36(2)	10(2)	0(2)	10(2)
C(9)	41(2)	43(2)	29(2)	11(2)	-4(2)	7(2)
C(48)	41(2)	39(2)	38(2)	7(2)	5(2)	19(2)
C(25)	26(2)	25(2)	33(2)	10(1)	10(1)	9(1)
C(28)	32(2)	41(2)	30(2)	3(2)	6(2)	3(2)
C(20)	37(2)	36(2)	47(2)	9(2)	0(2)	14(2)
C(10)	40(2)	40(2)	42(2)	17(2)	-10(2)	9(2)
C(38)	38(2)	44(2)	47(2)	14(2)	18(2)	19(2)
C(11)	33(2)	42(2)	44(2)	15(2)	-1(2)	17(2)
C(43)	33(2)	26(2)	30(2)	5(1)	10(2)	15(2)
C(14)	43(2)	38(2)	46(2)	7(2)	12(2)	17(2)
C(21)	51(2)	39(2)	47(2)	1(2)	-9(2)	16(2)
C(26)	34(2)	27(2)	38(2)	5(2)	7(2)	12(2)
C(13)	32(2)	32(2)	42(2)	10(2)	5(2)	19(2)
C(50)	38(2)	93(3)	73(3)	-8(2)	13(2)	31(2)
C(35)	67(3)	33(2)	46(2)	14(2)	11(2)	20(2)
C(51)	64(3)	49(2)	46(2)	17(2)	20(2)	36(2)
C(2)	33(2)	32(2)	44(2)	10(2)	2(2)	18(2)
C(49)	51(2)	41(2)	42(2)	9(2)	3(2)	-1(2)
C(45)	37(2)	53(2)	47(2)	11(2)	15(2)	20(2)
C(19)	35(2)	29(2)	41(2)	5(2)	3(2)	12(2)
C(46)	33(2)	54(2)	57(2)	5(2)	6(2)	19(2)
C(17)	35(2)	55(2)	81(3)	17(2)	19(2)	17(2)
C(18)	36(2)	39(2)	60(2)	10(2)	8(2)	14(2)
C(15)	61(3)	53(2)	56(2)	7(2)	22(2)	28(2)
C(47)	37(2)	60(2)	43(2)	2(2)	1(2)	19(2)
C(22)	71(3)	53(2)	47(2)	-6(2)	1(2)	25(2)
C(33)	66(3)	65(3)	51(2)	19(2)	19(2)	50(2)
C(23)	53(3)	60(3)	50(2)	-4(2)	10(2)	22(2)
C(24)	36(2)	45(2)	51(2)	1(2)	6(2)	15(2)
C(39)	48(2)	74(3)	71(3)	18(2)	30(2)	29(2)
C(52)	83(3)	65(3)	33(2)	6(2)	15(2)	34(2)
C(34)	91(3)	43(2)	56(3)	17(2)	22(2)	44(3)
C(41)	78(3)	56(2)	43(2)	7(2)	27(2)	35(2)
C(16)	52(3)	66(3)	68(3)	17(2)	24(2)	31(2)
C(40)	81(3)	73(3)	65(3)	17(2)	48(3)	42(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11**.

	x	y	z	U(eq)
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H(3)	2945	7691	457	45
H(4)	4903	8339	1185	47
H(5)	5480	7283	2011	41
H(44A)	31	845	3983	45
H(44B)	-340	1630	3477	45
H(37)	2467	259	2473	39
H(27)	2480	3799	5433	45
H(29)	3644	1511	5636	43
H(42A)	1099	-159	1175	48
H(42B)	1891	930	866	48
H(9)	4455	4845	4332	49
H(48A)	-558	1322	1755	46
H(48B)	-305	363	1280	46
H(28)	3398	2983	6291	46
H(20A)	-640	3017	50	49
H(20B)	45	2255	131	49
H(10)	5494	3912	3729	51
H(38A)	4188	1853	2779	50
H(38B)	3839	2205	1887	50
H(11)	5845	3908	2264	46
H(43)	141	-87	2649	34
H(14A)	1124	5045	3056	51
H(14B)	1324	6000	2522	51
H(21A)	-896	1951	-1335	57
H(21B)	-199	3170	-1407	57
H(26)	1875	3168	3951	40
H(13)	-12	4851	1296	40
H(50A)	6489	1143	4452	102
H(50B)	6789	2267	4154	102
H(50C)	6233	1219	3436	102
H(35)	1502	-2137	3548	58
H(51A)	6209	4177	875	71
H(51B)	5303	4056	24	71
H(51C)	4844	3340	766	71
H(2)	1586	6018	581	41
H(49A)	-244	-1925	3582	76
H(49B)	-675	-1363	4365	76
H(49C)	243	-1888	4583	76
H(45A)	-1811	-562	3416	53
H(45B)	-2065	389	3907	53
H(19)	1176	4413	-106	42
H(46A)	-3306	-324	2529	58
H(46B)	-2442	889	2548	58
H(17A)	-2102	4026	1850	67

H(17B)	-2368	3051	2371	67
H(18A)	-1032	3029	1335	54
H(18B)	-388	3171	2313	54
H(15A)	13	5960	3593	65
H(15B)	-631	5854	2623	65
H(47A)	-2405	-103	1220	57
H(47B)	-2018	-864	1748	57
H(22A)	913	1732	-1227	71
H(22B)	779	2209	-2102	71
H(33)	5058	-432	3591	62
H(23A)	2107	3884	-1426	67
H(23B)	2739	3088	-1320	67
H(24A)	2328	3013	146	54
H(24B)	3015	4225	48	54
H(39A)	5358	1609	1674	73
H(39B)	4596	518	1990	73
H(52A)	2948	5353	4524	88
H(52B)	2914	6482	4510	88
H(52C)	4160	6398	4775	88
H(34)	3396	-2031	3303	68
H(41A)	2655	-747	1028	67
H(41B)	2288	-452	112	67
H(16A)	-1002	4152	3587	70
H(16B)	-1971	4622	3352	70
H(40A)	3966	1171	402	81
H(40B)	4396	231	447	81

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