Bulky Di(1-adamantyl)phosphinous Acid-Ligated Pd(II) Pre-Catalysts for Suzuki Reactions of Unreactive Aryl Chlorides

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1. General experimental and computational methods

General experimental methods. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-flushed glovebox. Unless otherwise noted, all manipulations were performed in air. Freshly distilled solvents were used or were purified by a Vigor solvent purification system to remove water and oxygen from solvents. All and reagents were directly used as received. All processes of separations of the catalytic products were performed by column chromatography. Pre-catalysts, POPd1-toly1, POPd-tBu, POPd1-tBu, and POPd2-tBu, were synthesized based on the reported methods. The Suzuki cross-coupling reactions were monitored by a GC-MS on a Bruker SCION 436 SQ instrument equipped with a Bruker BR-5ms column. The MS detector was configured with an electronic impact ionization source. Or, the Suzuki reactions were monitored by a GC-BID on a Shimadzu Nexis GC-2030 instrument where the barrier discharge ionization detector (BID-2030) was installed.

Routine $^1$H NMR spectra were recorded on a Brucker-AV-400 (400 MHz) spectrometer. The chemical shifts were reported in ppm relative to the internal standards TMS (δ 0.00 ppm) and CHCl$_3$ (δ 7.26 ppm). $^{31}$P and $^{13}$C{H} NMR spectra were recorded at 162.0 and 100.6 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to external standards H$_3$PO$_4$ (δ 0.0 ppm) and CHCl$_3$ (δ 77.0 ppm), respectively. Elemental analyses were carried out on an Elementar Vario EL cube analyzer. A Thermo Scientific LTQ XL linear ion trap mass spectrometer performed the analysis in this study.
The crystals were immersed with FOMBLIN Y under N\textsubscript{2} and mounted on a diffractometer employing graphite-monochromated Mo-K\textalpha{} radiation ($\lambda = 0.71073$ Å). Intensity data were collected with $\omega$ scans. Data collection and reduction were performed with the CrysAlisPro software,\textsuperscript{4} and the absorptions were corrected by using the SCALE3 ABSPACK multiscan method.\textsuperscript{5} The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by structure solution, performed by direct methods with the SHELXTL package.\textsuperscript{6} All non-hydrogen atoms except for the P-OH functional groups were located from successive Fourier maps and hydrogen atoms were refined by using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms.\textsuperscript{7}

**Computational methods.** All geometry optimizations and vibrational frequency calculations were performed with the Gaussian 09 package.\textsuperscript{8} The $\omega$B97XD functional\textsuperscript{9} was used in conjunction with MWB28 ECP and valence basis set for Pd\textsuperscript{10} and 6-31G(d) basis set for the other atoms.\textsuperscript{11} The optimized structures were confirmed to be local minima by frequency calculations (no imaginary frequency). The most stable isomer for each species was selected for calculating relevant dissociation free energy. With the gas-phase optimized structures, polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) was employed to account for the solvation effect of 1,4-dioxane.\textsuperscript{12} Moreover, energy correction of 1.89 kcal/mol was added to deal with the change of standard state of a solute from gas phase to solution (1 atm to 1 M).\textsuperscript{13}
electron density of the optimized structures of POPd-Ad, POPd-tBu, POPd2-Ad, and POPd2-tBu, Multiwfn\textsuperscript{14} was employed to perform the interaction region indicator (IRI) analysis.\textsuperscript{15} IRI can illustrate chemical bonding and weak interaction regions in a molecule.

The extrapolated Tolman’s electronic parameters (TEP) for 6R\textsubscript{2}(K\textsuperscript{+}O\textsuperscript{-})P\rightarrow Ni(CO)\textsubscript{3} (R = tBu or Ad) were calculated based on the reported theoretical methods.\textsuperscript{16} Geometry optimizations and frequency calculations were performed using the MPW1PW91 functional\textsuperscript{17} and 6-311+G(2d) for Ni and 6-311+G(d,p) for the other atoms. Subsequently, the A\textsubscript{1} carbonyl stretching mode (\(\tilde{\nu}_{CO}\)) of R\textsubscript{2}(K\textsuperscript{+}O\textsuperscript{-})P\rightarrow Ni(CO)\textsubscript{3} were identified, and the empirical linear correlation TEPs were calculated by the equation of \(\tilde{\nu}_{CO} \times 0.9540 \text{ cm}^{-1} \textsuperscript{18}\).
2. Synthesis of Ad$_2$P(=O)H pre-ligand

2.1 The synthesis of Ad$_2$P(=O)Cl. The procedure was modified from the method used by Peter R. Schreiner et al.$^{19}$ The adamantane (3.5 g, 25 mmol) and aluminum chloride (10.2 g, 75 mmol) were put into a 100-mL round-bottom flask with a stir bar. After the injection of 25 mL of dichloromethane, the phosphorus trichloride (2.2 mL, 12.5 mmol) was added to the reaction mixture. The reaction was reflux at 70°C for 11 hours. Afterwards, the reaction mixture was cooled to room temperature and quenched by water (25 mL). After standing for a few minutes, the solution was separated into the aqueous and organic layers. The aqueous layer was extracted with dichloromethane (3*25 mL), while the organic layer was extracted with water (3*25 mL). The organic layers were collected and dried over MgSO$_4$(s) then filtered and washed by dichloromethane (50 mL). The resultant mixture was evaporated and purified by column chromatography on silica gel (95% DCM + 5% Et$_2$O). After evaporation, the white solids were obtained as pure di-1-adamantylphosphinic acid chloride (54%).

$^1$H NMR (CDCl$_3$,δ/ppm): 1.75 (br, 12H, CH$_2$), 2.05 (br, 6H, CH), 2.14-2.16 (br, 12H, CH$_2$)

$^{31}$P{H} NMR (CDCl$_3$,δ/ppm): 85.9
2.2 The synthesis of SPO-Ad.\cite{20} Into a 100-mL round-bottom flask with a stir bar was put the di-1-adamantylphosphinic acid chloride (1.76 g, 5.0 mmol). The round-bottom flask was capped, vacuumed and back-filled with N$_2$ for three times. Afterwards, the dry toluene (40 mL) was injected to dissolve the solids. The tBuLi (18.8 mL of 1.6 M in hexane solution) was slowly added to the solution at -78°C in 15 minutes. After removing the cold bath, the reaction mixture was gradually warmed to room temperature. After reacted for 5 days, H$_2$O was slowly added to the round-bottom flask, and the reaction continued for another 1 hour. Afterwards, the reaction mixture was cooled to room temperature and quenched by water (25 mL). After standing for a few minutes, the solution was separated into the aqueous and organic layers. The aqueous layer was extracted with dichloromethane (3*25 mL), while the organic layer was extracted with water (3*25 mL). The organic layers were collected and dried over MgSO$_4$(s) then filtered and washed by dichloromethane (50 mL). After evaporation, the white solids were obtained as pure SPO-Ad was obtained white solid (92%).

$^1$H NMR (CDCl$_3$,δ/ppm): 1.76 (br, 12H, CH$_2$), 1.97-2.01 (br, 18H, CH, CH$_2$), 5.63 (d, $^1$J$_{P-H}$=424 Hz,1H, H-P).

$^{31}$P NMR (CDCl$_3$,δ/ppm): 59.4 (d, $^{1}$J$_{P-H}$=424 Hz, 1P, H-P).

$^{31}$P{H} NMR (CDCl$_3$,δ/ppm): 59.4 (s, 1P, P-H)
3. Synthesis of POPd-Ad

The SPO-Ad (0.318 g, 1.0 mmol) and palladium(II) chloride (0.085 g, 0.5 mmol) were put into a 100-mL round-bottom flask with a stir bar. The round-bottom flask was capped, vacuumed and back-filled with N₂ for three times. After the injection of 15 mL of THF, the reaction was performed at 60 °C for 18 hours. Then, the reaction mixture was cooled down to room temperature and filtered through a Celite bed and was washed by dichloromethane (30 mL). The solution was evaporated and recrystallized in dichloromethane/hexanes (1 mL/10 mL) for 10 minutes. The precipitate was obtained in 10 minutes and was isolated as yellow solids of POPd-Ad (66%).

\[ \text{1H NMR (CDCl}_3, \delta/\text{ppm): } 1.71-1.79 (m, 24H, CH}_2, 2.02 (s, 12H, CH), 2.26 (m, 24H, CH}_2, 6.40 (s, 2H, OH) \]

\[ \text{13C NMR (CDCl}_3, \delta/\text{ppm): } 28.3 (m, 12C, CH), 36.7 (s, 12C, CH}_2, 38.5 (d, J_{C-P} = 10.1 \text{ Hz}, 12C, CH}_2) 44.1 (m, 4C, P-C) \]

\[ \text{31P\{H\} NMR (CDCl}_3, \delta/\text{ppm): } 112.5 \]

**Anal. Calcd for C\(_{40}\)H\(_{62}\)Cl\(_2\)O\(_2\)P\(_2\)Pd:** C, 59.01; H, 7.68. Found: C, 56.67; H, 7.62.

**MS (ESI-)** calcd for C\(_{40}\)H\(_{62}\)Cl\(_2\)O\(_2\)P\(_2\)Pd (m/z [M-H]\(^-\)) 813.19, found 813.33.
4. The synthesis of POPd2-Ad

The SPO-Ad (0.318g, 1.0 mmol) and palladium(II) chloride (0.177 g, 1.0 mmol) were put into a 100-mL round-bottom flask with a stir bar. The round-bottom flask was capped, vacuumed and back-filled with N₂ for three times. After the injection of 4 mL of toluene, the reaction was performed at 110 °C for 15 hours. Then, the reaction mixture was cooled down to room temperature and filtered through a Celite bed and was washed by dichloromethane (30 mL). The solution was evaporated and recrystallized in toluene (10 mL) for 10 minutes. The precipitate was obtained in 10 minutes and was isolated as orange solids of POPd2-Ad (63%).

\[ ^{1}H \text{ NMR (CDCl}_{3}, \delta/\text{ppm):} \ 1.72-1.84 \ \text{(m, 24H, CH}_2) \ 2.06-2.07 \ \text{(m, 12H, CH)} \ 2.30-2.43 \ \text{(m, 24H, CH}_2) \ 6.60 \ \text{(s, 2H, OH)} \]

\[ ^{13}C \text{ NMR (CDCl}_{3}, \delta/\text{ppm):} \ 28.3 \ \text{(d, }^{1}J_{\text{C-P}} = 10.1 \text{ Hz, 12C, CH)} \ 36.3 \ \text{(s, 12C, CH}_2) \ 38.4 \ \text{(s, 12C, CH}_2) \ 47.3 \ \text{(d, }^{1}J_{\text{C-P}} = 10.1 \text{ Hz, 4C, C-P)} \]

\[ ^{31}P\{H\} \text{ NMR (CDCl}_{3}, \delta/\text{ppm):} \ 136.8 \]

Anal. Calcd for C\textsubscript{40}H\textsubscript{62}Cl\textsubscript{4}O\textsubscript{2}P\textsubscript{2}Pd\textsubscript{2}: C, 48.45; H, 6.30. Found: C, 47.59; H,6.33.

MS (ESI-) calcd for C\textsubscript{40}H\textsubscript{62}Cl\textsubscript{4}O\textsubscript{2}P\textsubscript{2}Pd (m/z [M-H]) 990.51, found 991.17.
### 5. Crystallographic data table for the POPd-Ad and POPd2-Ad

![POD-Ad](image1.png)  ![POD2-Ad](image2.png)

**Table S1.** Crystallographic data for POPd-Ad and POPd2-Ad, respectively.

|                | POPd-Ad     | POPd2-Ad    |
|----------------|-------------|-------------|
| **Formula**    | C_{40}H_{62}Cl_{2}O_{2}P_{2}Pd | C_{40}H_{62}Cl_{4}O_{2}P_{2}Pd_{2} |
| **Fw**         | 814.13      | 991.43      |
| **T, K**       | 150(2)      | 150(2)      |
| **Crystal system** | Triclinic  | Triclinic  |
| **Space group** | P -1        | P-1         |
| **a, Å**       | 7.1568(4)   | 11.369(2)   |
| **b, Å**       | 10.3786(5)  | 12.112(3)   |
| **c, Å**       | 13.3686(7)  | 19.253(4)   |
| **a°**         | 101.691(2)  | 79.912(8)   |
| **β°**         | 103.420(2)  | 87.787(9)   |
| **γ°**         | 97.061(2)   | 63.274(7)   |
| **V, Å³**      | 930.66(8)   | 2328.9(8)   |
| **Z**          | 1           | 2           |
| **ρ_{calc}, Mg/m³** | 1.453      | 1.414      |
| **μ(MoKα), mm⁻¹** | 0.763      | 1.101      |
| **Reflections collected** | 18758      | 41245      |
| **No. of parameters** | 218        | 451        |
| **Indep. reflns (R_{m})** | 4444 (0.0274) | 11078 (0.0884) |
| **Final R indices** | 0.0310, 0.0921 | 0.2081, 0.5440 |
| **GoF**        | 1.018       | 1.074       |

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\[^{a}\] R_{I} = [(|F_{0}| - |F_{c}|) / |F_{0}|], \[wR_{2} = \frac{\sum[w(F_{0}^{2} - F_{c}^{2})^{2}]{\sum w(F_{0}^{2})^{2}}}^{1/2}, w = 0.10.\]

\[^{b}\] GoF = \[\sqrt{\frac{\sum[w(F_{0}^{2} - F_{c}^{2})^{2}]{\sum w(F_{0}^{2})^{2}}}^{1/2}(N_{\text{refl}} - N_{\text{params}})}^{1/2}].

**Note:** Several attempts to grow suitable crystals of POPd2-Ad were failed at the present.
6. The transformation of POPd2-Ad to POPd-Ad

\[
\text{POPd2-Ad} \xrightarrow{\text{r.t., 5min}} \text{POPd-Ad}
\]

6.1 The orange **POPd2-Ad** (0.0099g, 0.01 mmol) was dissolved in 1 mL solvent and stirred at room temperature for 5 minutes in ambient. Afterwards, the solvent was evaporated. Then, the reaction mixture was filtered through a Celite bed and was washed by dichloromethane (30 mL). The resultant solids were dissolved in CDCl\textsubscript{3} and analyzed by the \textsuperscript{31}P NMR spectroscopy. No reaction was occurred when toluene, THF, or 1,4-dioxane was used as solvent. In acetonitrile, the yellow precipitate was isolated and characterized as the **POPd-Ad** (42%).

| Table S2. The formation of **POPd-Ad** in acetonitrile. |
|-----------------|-----------------|-------------|
| **Entry**       | **Solvent**     | **Yield(%)**|
| 1               | Toluene         | ND          |
| 2               | THF             | ND          |
| 3               | 1,4-dioxane     | ND          |
| 4               | CH\textsubscript{3}CN | 42          |
6.2 The orange POPd2-Ad (0.0099g, 0.01 mmol) and two equivalents of SPO-Ad (0.0064g, 0.02 mmol) were dissolved in 1 mL of acetonitrile and stirred at room temperature for 5 minutes in ambient. Precipitate was observed in the duration of reaction. The precipitate was washed by acetonitrile and analyzed by the $^1$H and $^{31}$P NMR spectroscopy (POPd-Ad: 90%).
7. General experimental method for searching the optimized Suzuki reaction condition

7.1 Method for searching the optimal set of solvent and base

The POPd-Ad (2 mol%), the designated base (3 eq.), 4-tolylboronic acid (1.1 eq.) and were put into a 4-mL vial. Subsequently, the vial was sealed with a screw cap. The designated solvent (2 mL) and chlorobenzene (0.5 mmol) were then injected into the vial. The reaction was carried out in 65 °C for 12 hours. The conversion yield was determined by GC-MS.

Table S3. Optimization of base-solvent pair for POPd-Ad catalyzed Suzuki reaction.

| Entry | Base  | Solvent | Yield | Entry | Base  | Solvent        | Yield |
|-------|-------|---------|-------|-------|-------|----------------|-------|
| 1     | KF    |         | 1     | 13    | KF    |                | 17    |
| 2     | K$_2$CO$_3$ |         | 2     | 14    | K$_2$CO$_3$ | 32    |
| 3     | K$_3$PO$_4$ | Toluene | 9     | 15    | K$_3$PO$_4$ | 1,4-dioxane | 66    |
| 4     | KO'Bu |         | 44    | 16    | KO'Bu |                | 91    |
| 5     | CsF   |         | 17    | 17    | CsF   |                | 50    |
| 6     | Cs$_2$CO$_3$ |       | 14    | 18    | Cs$_2$CO$_3$ |        | 47    |
| 7     | KF    |         | 49    | 19    | KF    |                | < 1   |
| 8     | K$_2$CO$_3$ |         | 11    | 20    | K$_2$CO$_3$ | < 1   |
| 9     | K$_3$PO$_4$ | THF     | 62    | 21    | K$_3$PO$_4$ | CH$_3$CN | < 1   |
| 10    | KO'Bu |         | 91    | 22    | KO'Bu |                | ND    |
| 11    | CsF   |         | 30    | 23    | CsF   |                | 7     |
| 12    | Cs$_2$CO$_3$ |       | 54    | 24    | Cs$_2$CO$_3$ |        | < 1   |

Reaction condition: 0.5 mmol PhCl, 1.1 eq. of 4-tolylboronic acid, 2 mol% of POPd-Ad, 3 eq. of base, 2 mL of solvent, 65 °C, 12 hours.
7.2 Further optimization for the solvent/base set of THF/KO\textsubscript{t}Bu and 1,4-dioxane/KO\textsubscript{t}Bu

Because the GC-conversion yields by using the THF/KO\textsubscript{t}Bu and 1,4-dioxane/KO\textsubscript{t}Bu pairs are all 91% (Table S2), we next pursued the rate of the Suzuki reactions for these two solvent/base sets. The POPd-Ad (2 mol%), the KO\textsubscript{t}Bu (3 equiv.), 4-tolylboronic acid (1.1 equiv.) and were put into a 4-mL vial. Subsequently, the vial was sealed with a screw cap. The designated solvent (2 mL) and chlorobenzene (0.5 mmol) were then injected into the vial. The reaction was carried out at 65 °C. The conversion yields were determined by gas chromatography. We found that using the set of 1,4-dioxane/KO\textsubscript{t}Bu showed the faster rate than the set of THF/KO\textsubscript{t}Bu.

**Table S4.** Optimization of reaction time for POPd-Ad catalyzed Suzuki reactions at 65 °C in THF and 1,4-dioxane, respectively.

| Entry | Solvent         | 0.5 h | 1 h  | 2 h  | 3 h  | 6 h  | 12 h |
|-------|-----------------|-------|------|------|------|------|------|
| 1     | THF             | 38    | 48   | 68   | 72   | 74   | 91   |
| 2     | 1,4-dioxane     | 49    | 64   | 76   | 76   | 79   | 91   |

**Reaction condition:** 0.5 mmol of PhCl, 1.1 eq. of 4-tolylboronic acid, 2 mol% POPd-Ad, 3 eq. of KO\textsubscript{t}Bu, 2 mL of solvent, 65 °C. Conversion yields were determined by GC-BID.
7.3 The search of optimized reaction time and temperature for the solvent/base set of 1,4-dioxane/KO'Bu

Aiming at finding the optimized reaction temperature and time, we then conducted the Suzuki reactions with the solvent/base set of 1,4-dioxane/KO'Bu. The POPd-Ad (2 mol%), the KO'Bu (3 equiv.), 4-tolylboronic acid (1.1 equiv.) and were put into a 4-mL vial. Subsequently, the vial was sealed with a screw cap. The 1,4-dioxane (2 mL) and chlorobenzene (0.5 mmol) were then injected into the vial. The reactions were carried out at 95 °C and 85 °C, respectively. The conversion yields were determined by gas chromatography. We found that the Suzuki reaction could be completed in 0.5 hour at both temperatures.

Table S5. Optimization of reaction time for POPd-Ad catalyzed Suzuki reactions at higher temperature in 1,4-dioxane.

| Entry | T(°C) | 0.5 h | 1 h | 2 h |
|-------|-------|-------|-----|-----|
| 1     | 85    | 68    | 68  | 68  |
| 2     | 95    | 75    | 75  | 75  |

**Reaction condition:** 0.5 mmol of PhCl, 1.1 eq. of 4-tolylboronic acid, 2 mol% of POPd-Ad, 3 eq. of KO'Bu, 2 mL of 1,4-dioxane. Conversion yields were determined by GC-BID.
7.4 The optimized amount of 4-tolylboronic acid employed in the Suzuki reaction

After locating the optimized reaction condition (1,4-dioxane/KO\textsubscript{t}Bu/95 °C/0.5 hour), we continued to tune the amount of phenylboronic acid. The POPd-Ad (2 mol%), the KO\textsubscript{t}Bu (3 equiv.), 4-tolylboronic acid (1.1 or 1.5 equiv.) and were put into a 4-mL vial. Subsequently, the vial was sealed with a screw cap. The 1,4-dioxane (2 mL) and chlorobenzene (0.5 mmol) were then injected into the vial. The conversion yields were determined by gas chromatography. We found that the quantitative conversion of product could be obtained if 1.5 equiv. of phenylboronic acid was employed.

Table S6. Optimization of the amounts of KO\textsubscript{t}Bu in POPd-Ad catalyzed Suzuki reactions at 95 °C in 1,4-dioxane.

| Entry | 4-tolylboronic acid | Yield |
|-------|---------------------|-------|
| 1     | 1.1 equivalents     | 75    |
| 2     | 1.5 equivalents     | 99    |

**Reaction condition:** 0.5 mmol of PhCl, 1.1 or 1.5 eq. of 4-tolylboronic acid, 2 mol% of POPd-Ad, 3 eq. of KO\textsubscript{t}Bu, 2 mL of 1,4-dioxane. Conversion yields were determined by GC-BID.
8. Experimental method for determining the ligation state of Pd catalyst

The POPd2-Ad (1 mol%), KOtBu (3 equiv), 4-tolylboronic acid (1.1 equiv), and SPO-Ad were put into a 15-mL Schlenk tube with a stir bar. The Schlenk tube was capped, vacuumed and back-filled with N$_2$ for three times. Subsequently, 1,4-dioxane (2 mL) and chlorobenzene (0.5 mmol) were injected into the Schlenk tube. The reaction was performed at 65°C for 12 hours. The conversion yields were determined by gas chromatography.
9. Suzuki reactions catalyzed by PA-Ad coordinated Pd(II) complexes at the lower temperature

Table S7. The effect of ligation state of POPd-Ad and POPd2-Ad catalyzed Suzuki reactions, respectively.\textsuperscript{a,b}

| Entry | Pre-catalyst | 45 °C | 55 °C |
|-------|--------------|-------|-------|
| 1     | POPd-Ad      | 3     | 54    |
| 2     | POPd2-Ad     | 10    | 83    |

\textsuperscript{a}Phenyl chloride (0.5 mmol) and 4-tolylboronic acid (0.75 mmol) were employed as the substrates. POPd-Ad (2 mol\%) or POPd2-Ad (1 mol\%) was used as the pre-catalyst. Three equivalents of KO\textsubscript{Bu} were employed. The catalytic reactions were conducted for 4 hours. \textsuperscript{b}Conversion yields (%) were determined by GC-BID.
10. Experimental method for probing the plausible reduction pathways of Pd(II) of POPd-Ad or POPd2-Ad

The pre-catalyst (0.1 mol), KOtBu (30 equiv.), 4-tolyboronic acid (4 equiv) were put into a 15-mL Schlenk tube with a stir bar. The Schlenk tube was sealed, vacuumed and back-filled with N\textsubscript{2} for three times. Subsequently, 1,4-dioxane (2 mL) was injected into the Schlenk tube, and the reaction was carried out at 95 °C for 0.5 hours. Then, the reaction mixture was cooled down to room temperature and filtered through a Celite bed and was washed by dichloromethane. The crude mixture was purified by column chromatography on silica gel to isolate the biphenyl (hexanes) and SPO-Ad (EtOAc/MeOH = 95/5).

**Table S8.** Reaction of POPd-Ad or POPd2-Ad with 4-tolyboronic acid and KOtBu in 1,4-dioxane.

| Entry | Pre-catalyst | Biphenyl(%) | SPO-Ad(%) | Phosphine oxide(%) |
|-------|--------------|-------------|-----------|-------------------|
| 1     | POPd-Ad      | 14          | 30        | ND                |
| 2     | POPd2-Ad     | 73          | 5         | ND                |

Reaction condition: 0.1mol POPd2-Ad, 4eq 4-tolyboronic acid, 30eq KOtBu, 2mL 1,4-dioxane, 95°C, 0.5 hr.
11. General methods for conducting the Suzuki reactions

**Method A.** The **POPD2-Ad** (4.95 mg, 1.0 mol%), arylboronic acid (1.5 equiv.) and KO'Bu (168.0 mg, 3.0 equiv.) were put into a 15-mL Schlenk tube with a stir bar. The Schlenk tube was capped, vacuumed and back-filled with N₂ for three times. The 1,4-dioxane (2 mL) and aryl chlorides (0.5 mmol) were then injected into the Schlenk tube. The reaction was carried out at 95 °C for 0.5 hours. Subsequently, the reaction mixture was cooled down to room temperature and filtered through a Celite bed and was washed by ethyl acetate (30 mL). The crude product was purified by column chromatography on silica gel. After evaporation, the pure product was obtained.

**Method B.** The **POPD2-Ad** (4.95 mg, 1.0 mol%), difference of boronic acid (1.5 equiv.) and CsF (226.5 mg, 3.0 equiv.) were put into a 15-mL Schlenk tube with a stir bar. The Schlenk tube was capped, vacuumed and back-filled with N₂ for three times. The 1,4-dioxane (2 mL) and aryl chloride (0.5 mmol) were then injected into the Schlenk tube. The reaction was carried out at 95 °C for 1 hours. Subsequently, the reaction mixture was cooled down to room temperature and filtered through a Celite bed and was washed by ethyl acetate (30 mL). The crude product was purified by column chromatography on silica gel. After evaporation, the pure product was obtained.
12. The DEPT-90, DEPT-135 and the full 1-D $^{13}$C NMR spectra for POPd-Ad and POPd2-Ad

The DEPT-90, DEPT-135 and the full 1-D $^{13}$C NMR spectra for POPd-Ad are listed in Figure 4. Four distinct resonances were found in the $^{13}$C NMR spectrum. In the DEPT-90 NMR spectrum, the carbon signal at 28.3 ppm was assigned to the twelve C-H carbons (Figure S1a). The two negative-phase signals at 38.5 (C1) and 36.7 (C2) ppm shown in the DEPT-135 NMR spectrum were the two sets of twelve -CH$_2$ carbons. Finally, the only quaternary carbon atom was detected at 44.1 ppm. Therefore, the $^{13}$C NMR spectra for the POPd-Ad were unambiguously analysed. Very similar $^{13}$C NMR patterns can be found for the POPd2-Ad (Figure S1b).

![Figure S1](image_url)

**Figure S1.** The DEPT-90, DEPT-135, and 1-D $^{13}$C NMR spectra for the (a) POPd-Ad and (b) POPd2-Ad.
13. ESI-mass spectrum (negative ion mode) of POPd2-Ad and the related metal species

**Explanation of calculated isotopic patterns**

The observed species provide the information of m/z but not chemical compositions in mass spectrometry. The analysis of isotopic distribution completes the leak of information because all the species at a given range overlay represent their distinct pattern. The simulated isotopic patterns were all calculated by a home-written process using Python in this work. The similarity between theoretical and observed isotope patterns were examined to confirm the species in the mass spectra.
Figure S2. (a) ESI- mass spectra of POPd2-Ad, and (b) the related metal species. A comparison between the theoretical and observed isotope patterns for the detected metal ion species shown in Figure 3 was made.
14. The relative energies for POPd-R and POPd2-R and their related complexes

(a)

(b) 0.0 kcal/mol 10.4 (8.7) kcal/mol 21.5 (18.2) kcal/mol

(c) 0.0 kcal/mol 12.8 (11.1) kcal/mol 22.8 (19.4) kcal/mol

(d) 0.0 kcal/mol 12.2 (10.3) kcal/mol 23.0 (19.2) kcal/mol

Figure S3. The relative stability of isomers in gas-phase (1,4-dioxane) for (a) POPd-Ad, (b) POPd-tBu, (c) POPd2-Ad and (d) POPd2- tBu.
Figure S4. The relative stability of isomers in gas-phase (1,4-dioxane) for monomers dissociated from (a) POPd-Ad, and (b) POPd-tBu.

Figure S5. The relative stability of isomers in gas-phase (1,4-dioxane) for (a) PA-Ad and (b) PA-tBu.
15. Isosurface maps of the interaction region indicator for POPd-R and POPd2-R complexes

Figure S6. Isosurface maps of the interaction region indicator (IRI = 1.0) were generated by Multiwfn program. $\text{sign}(\lambda^2) \rho$ is mapped on the isosurfaces according to coloring method shown in Figure S5a. (a) POPd-tBu, (b) POPd-Ad, (c) POPd2-tBu, and (d) POPd2-Ad.
16. PA-R dissociation free energies for the singly deprotonated POPd-Ad, POPd-tBu, POPd2-Ad, and POPd2-tBu

(a) 12.5 (9.5) kcal/mol

(b) 14.0 (11.7) kcal/mol

Figure S7. Gas-phase (in 1,4-dioxane) ligand dissociation free energies for the (a) singly deprotonated POPd-Ad, and (b) singly deprotonated POPd-tBu.

(a) 20.4 (15.3) kcal/mol

(b) 16.9 (12.1) kcal/mol

Figure S8. Gas-phase (in 1,4-dioxane) dissociation free energies for the (a) singly deprotonated POPd2-Ad, and (b) singly deprotonated POPd2-tBu.
17. The relative energies for the singly deprotonated POPd-R and POPd2-R and their related complexes

**Figure S9.** The relative stability of isomers in gas-phase (1,4-dioxane) for (a) singly deprotonated POPd-Ad, and (b) singly deprotonated POPd-tBu.

**Figure S10.** The relative stability of isomers in gas-phase (1,4-dioxane) for (a) singly deprotonated POPd-Ad, and (b) singly deprotonated POPd-tBu.
Figure S11. Gas-phase (in 1,4-dioxane) ligand dissociation free energies for the (a) fully deprotonated POPd-Ad, and (b) fully deprotonated POPd-tBu.

Figure S12. Gas-phase (in 1,4-dioxane) dissociation free energies for the (a) fully deprotonated POPd2-Ad, and (b) fully deprotonated POPd2-tBu.
18. Characterizations and NMR spectra

Biphenyl (a)

**Reagents:** phenylboronic acid (91.4 mg, 1.5 equiv.) and chlorobenzene (51.0 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 61.2 mg (80 %). (white solid).

$^1$H NMR (CDCl$_3$, δ/ppm): 7.35 (t, $^3$J$_{H-H}$ = 16.0 Hz, 2H, ArH), 7.44 (d, $^3$J$_{H-H}$ = 8.0 Hz, 4H, ArH), 7.60 (t, $^3$J$_{H-H}$ = 8.0 Hz, 4H, ArH).

4-methyl-biphenyl (b)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and chlorobenzene (51.0 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 83.6 mg (99 %). (white solid).

$^1$H NMR (CDCl$_3$, δ/ppm): 2.36 (s, 3H, CH$_3$), 7.22 (d, $^3$J$_{H-H}$ = 4.0 Hz, 2H, ArH), 7.30 (t, $^3$J$_{H-H}$ = 4.0 Hz, 1H, ArH), 7.39 (t, $^3$J$_{H-H}$ = 12.0 Hz, 2H, ArH), 7.47 (d, $^3$J$_{H-H}$ = 4.0 Hz, 2H, ArH), 7.55 (d, $^3$J$_{H-H}$ = 4.0 Hz, 2H, ArH).

4-(trifluoromethyl)-1,1'-biphenyl (c)
**Reagents:** 4-(trifluoromethyl)phenylboronic acid (142.4 mg, 1.5 equiv.) and chlorobenzene (51.0 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 68.8 mg (31 %). (white solid).

**^1H NMR (CDCl₃, δ/ppm):** 7.42 (d, 3 Jₕ-H = 8.0 Hz, 1H, ArH), 7.46-7.50 (m, 2H, ArH), 7.60 (d, 3 Jₕ-H = 8.0 Hz, 2H, ArH), 7.70 (br, 4H, ArH).

![2-methyl-1,1'-biphenyl](image)

**2-methyl-1,1'-biphenyl (d)**

**Reagents:** phenylboronic acid (91.4 mg, 1.5 equiv.) and 2-Chlorotoluene (58.0 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 83.6 mg (90 %). (colorless liquid).

**^1H NMR (CDCl₃, δ/ppm):** 2.27 (s, 3H, ArCH₃), 7.22-7.27 (m, 4H, ArH), 7.31-7.35 (m, 3H, ArH), 7.41 (t, 3 Jₕ-H = 16.0 Hz, 2H, ArH)

![2,6-dimethyl-1,1'-biphenyl](image)

**2,6-dimethyl-1,1'-biphenyl (e)**

**Reagents:** phenylboronic acid (91.4 mg, 1.5 equiv.) and 2-Chloro-m-xylene (66.2 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on
silica gel (hexanes) The isolated yield was 90.6 mg (99 %). (colorless liquid).

$^1$H NMR (CDCl$_3$, $\delta$/ppm): 2.04 ($s$, 6H, ArCH$_3$), 7.10-7.17 ($m$, 5H, ArH), 7.35 ($d$, $^3J_{H-H} = 8.0$ Hz, 1H, ArH), 7.42 ($t$, $^3J_{H-H} = 12.0$ Hz, 2H, ArH).

$2,6$-dimethyl-$1,1'$-biphenyl (f)

Reagents: (2,6-dimethyl)phenylboronic acid (112.5 mg, 1.5 equiv.) and chlorobenzene (51.0 $\mu$L, 0.5 mmol)

Isolation: The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 24.7 mg (27 %). (colorless liquid).

$^1$H NMR (CDCl$_3$, $\delta$/ppm): 2.04 ($s$, 6H, ArCH$_3$), 7.10-7.17 ($m$, 5H, ArH), 7.35 ($d$, $^3J_{H-H} = 8.0$ Hz, 1H, ArH), 7.42 ($t$, $^3J_{H-H} = 12.0$ Hz, 2H, ArH).

$2$-methyl-$1,1'$-biphenyl (g)

Reagents: 2-tolyllboronic acid (102.0 mg, 1.5 equiv.) and chlorobenzene (51.0 $\mu$L, 0.5 mmol)

Isolation: The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 68.0 mg (81 %). (colorless liquid).
1H NMR (CDCl3, δ/ppm): 2.27 (s, 3H, ArCH3), 7.22-7.27 (m, 4H, ArH), 7.31-7.35 (m, 3H, ArH), 7.39-7.43 (t, 3JH-H = 16.0 Hz, 2H, ArH)

2,2'-dimethyl-1,1'-biphenyl (h)

**Reagents:** 2-tolyllboronic acid (102.0 mg, 1.5 equiv.) and 2-Chlorotoluene (58.0 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 64.9 mg (71 %). (colorless liquid).

1H NMR (CDCl3, δ/ppm): 2.05 (s, 6H, ArCH3), 7.09-7.11 (d, 3JH-H = 8.0 Hz, 2H, ArH), 7.22 (t, 3JH-H = 8.0 Hz, 2H, ArH), 7.25 (t, 3JH-H = 8.0 Hz, 4H, ArH).

2,2',6-trimethyl-1,1'-biphenyl (i)

**Reagents:** 2-tolylboronic acid (102 mg, 1.5 equiv.) and 2-Chloro-m-xylene (66.2 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 90.6 mg (74 %). (colorless liquid).
$^1$H NMR (CDCl$_3$, $\delta$/ppm): 1.99 (s, 6H, ArCH$_3$), 2.01 (s, 3H, ArCH$_3$), 7.05-7.07 (m, 1H, ArH), 7.15 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, ArH), 7.28-7.31 (m, 4H, ArH).

Phenylnaphthalene (j)

Reagents: 1-Naphthaleneboronic acid (129.0 mg, 1.5 equiv.) and chlorobenzene (51.0 $\mu$L, 0.5 mmol)

Isolation: The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 79.6 mg (78 %). (colorless liquid).

$^1$H NMR (CDCl$_3$, $\delta$/ppm): 7.40-7.44 (m, 3H, ArH), 7.46-7.54 (m, 6H, ArH), 7.91 (q, $^3J_{H-H}$ = 48.0 Hz, 3H, ArH).

1-(o-tolyl)naphthalene (k)

Reagents: 1-Naphthaleneboronic acid (129.0 mg, 1.5 equiv.) and 2-Chlorotoluene (58.0 $\mu$L, 0.5 mmol)

Isolation: The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 77.3 mg (71 %). (white solid).
$^1$H NMR (CDCl$_3$, $\delta$/ppm): 2.02 (s, 3H, ArCH$_3$), 7.23-7.39 (m, 5H, ArH), 7.44-7.54 (m, 3H, ArH), 7.88 ($q$, $^3J_{H-H} = 24.0$ Hz, 3H, ArH).

![Chemical Structure of 1-(2,6-dimethylphenyl)naphthalene](image)

1-(2,6-dimethylphenyl)naphthalene (l)

**Reagents:** 1-naphthaleneboronic acid (129.0 mg, 1.5 equiv.) and 2-chloro-$m$-xylene (66.2 $\mu$L, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 27.8 mg (24 %). (white solid).

$^1$H NMR (CDCl$_3$, $\delta$/ppm): 1.93 (s, 6H, ArCH$_3$), 7.20 ($d$, $^3J_{H-H} = 4.0$ Hz, 2H, ArH), 7.29 ($d$, $^3J_{H-H} = 8.0$ Hz, 2H, ArH), 7.37 ($d$, $^3J_{H-H} = 4.0$ Hz, 2H, ArH), 7.47-7.51 ($m$, 1H, ArH), 7.56 ($t$, $^3J_{H-H} = 16.0$ Hz, 1H, ArH).

![Chemical Structure of 4-methoxy-4'-methyl-1,1'-biphenyl](image)

4-methoxy-4'-methyl-1,1'-biphenyl (m)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and 4-Chloroanisole (61.2 $\mu$L, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (90% hexanes + 10% EtOAc) The isolated yield was 82.2 mg (83 %). (white solid).

$^1$H NMR (CDCl$_3$, $\delta$/ppm): 2.38 (s, 3H, ArCH$_3$), 3.84 (s, 3H, OCH$_3$), 6.96 ($d$, $^3J_{H-H} = 8.0$ Hz, 2H, ArH), 7.22 ($d$, $^3J_{H-H} = 8.0$ Hz, 2H, ArH), 7.44 ($d$, 2H, ArH).
$^3J_{H-H} = 8.0 \text{ Hz, } 2\text{H, ArH}$), 7.51 ($d, ^3J_{H-H} = 12.0 \text{ Hz, } 2\text{H, ArH}$).

4,4'-dimethyl-1,1'-biphenyl (n)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and 4-Chlorotoluene (59.1 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (hexanes) The isolated yield was 81.9 mg (78 %). (white solid).

$^1H$ NMR (CDCl$_3$, δ/ppm): 2.42 ($s, 6\text{H, CH}_3$), 7.27 ($d, ^3J_{H-H} = 4.0 \text{ Hz, } 2\text{H, ArH}$), 7.51 ($d, ^3J_{H-H} = 8.0 \text{ Hz, } 2\text{H, ArH}$).

2-(p-tolyl)pyridine (o)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and 2-chloropyridine (47.3 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (90% hexanes + 10% EtOAc) The isolated yield was 82.2 mg (99 %). (colorless liquid).

$^1H$ NMR (CDCl$_3$, δ/ppm): 2.41 ($s, 3\text{H, ArCH}_3$), 7.18-7.21 ($m, 1\text{H, ArH}$), 7.28 ($d, ^3J_{H-H} = 8.0 \text{ Hz, } 2\text{H, ArH}$), 7.69-7.75 ($m, 2\text{H, ArH}$), 7.89 ($d, ^3J_{H-H} = 4.0 \text{ Hz, } 2\text{H, ArH}$), 8.68 ($d, ^3J_{H-H} = 4.0 \text{ Hz, } 1\text{H, ArH}$).
4'-methyl-[1,1'-biphenyl]-4-carbonitrile (p)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and chlorobenzonitrile (68.7 mg, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (90% hexanes + 10% EtOAc).

**Method A:** The isolated yield was 54.0 mg (56 %). (white solid).

**Method B:** The isolated yield was 72.4 mg (75 %). (white solid).

1H NMR (CDCl₃, δ/ppm): 2.41 (s, 3H, CH₃), 7.29 (d, J_H-H = 8.0 Hz, 2H, ArH), 7.49 (d, J_H-H = 8.0 Hz, 2H, ArH), 7.68 (d, J_H-H = 4.0 Hz, 2H, ArH), 7.70-7.72 (m, 2H, ArH).

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1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (q)

**Reagents:** 4-tolylboronic acid (102.0 mg, 1.5 equiv.) and 4-Chloroacetophenone (64.8 µL, 0.5 mmol)

**Isolation:** The crude product was purified by column chromatography on silica gel (90% hexanes + 10% EtOAc).

**Method A:** Non-reacted.

**Method B:** The isolated yield was 81.9 mg (78 %). (white solid).

1H NMR (CDCl₃, δ/ppm): 2.43 (s, 3H, ArCH₃), 2.65 (s, 3H, CH₃), 7.30 (d, J_H-H = 8.0 Hz, 2H, ArH), 7.55 (d, J_H-H = 8.0 Hz, 2H, ArH), 7.69 (d, J_H-H = 8.0 Hz, 2H, ArH), 8.04 (d, J_H-H = 8.0 Hz, 2H, ArH).
17. NMR spectra

$\text{Ad}_2\text{P(=O)}\text{Cl}^{31}\text{P}\{\text{H}\} \text{ NMR}$

$\text{Ad}_2\text{P(=O)}\text{Cl}^{1}\text{H} \text{ NMR}$
SPO-Ad\textsubscript{31}P NMR

SPO-Ad\textsubscript{31}P\{H\} NMR
SPO-Ad $^1$H NMR

POPD-Ad $^{31}$P{H} NMR
POPd-Ad\textsubscript{1}H NMR

POPd-Ad\textsubscript{13}C NMR
POPd2-Ad$_{31}^3$P{H} NMR

POPd2-Ad$_{1}^1$H NMR
POPd2-Ad$_{13}$C NMR

Biphenyl (Figure 5, a)
4-methyl-biphenyl (Figure 5, b)

4-(trifluoromethyl)-1,1'-biphenyl (Figure 5, c)
2-methyl-1,1'-biphenyl (Figure 5, d · g)

2,6-dimethyl-1,1'-biphenyl (Figure 5, e · f)
2,2'-dimethyl-1,1'-biphenyl (Figure 5, h)

2,2',6-trimethyl-1,1'-biphenyl (Figure 5, i)
Phenylnaphthalene (Figure 5, j)

1-(o-tolyl)naphthalene (Figure 5, k)
1-(2,6-dimethylphenyl)naphthalene (Figure 5, l)

4-methoxy-4'-methyl-1,1'-biphenyl (Figure 5, m)
4,4'-dimethyl-1,1'-biphenyl (Figure 5, n)

2-(p-tolyl)pyridine (Figure 5, o)
4'-methyl-[1,1'-biphenyl]-4-carbonitrile (Figure 5, p)

1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (Figure 5, q)
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