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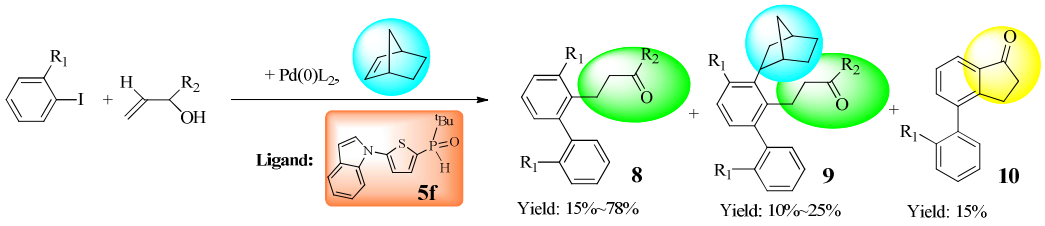
Ting-Wei Chang, Pei-Yun Ho, Kuo-Chung Mao, and Fung-E Hong*

Department of Chemistry, National Chung Hsing University,

250 Kuo-Kuang Road, Taichung 40227, Taiwan

E-mail: fehong@dragon.nchu.edu.tw

Several secondary phosphine oxides (SPOs) were prepared. Organic products with unexpected conformations (**9** and **10**) were obtained besides **8** from Heck-type Catellani reactions with the assistance of selected SPO ligand **5f**.



Developing Five-membered Heterocycle Substituted Phosphinous Acids as Ligands for Palladium-Catalyzed Suzuki-Miyaura and Catellani Reactions

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* Author to whom correspondence should be addressed.

Abstract

A new category of secondary phosphine oxides (SPOs) (**5a**-**5j**) with/without benzo-fused five-membered heterocyclic substituents were prepared. These new compounds are air- and moisture-stable ligands and have the advantage for long-term storage. Some of ligands as well as ligands coordinated palladium complexes (**6f'** and **6f"**) and platinum complexes (**7b**_***trans*** & **7i**_***trans***) were prepared and structures were determined by single crystal X-ray diffraction methods. Crystal structure of **6f'** revealed the formations of diamond shape di-palladium complexes with Pd_2Cl_2 core. As for the structures of **7b**_***trans*** & **7i**_***trans***, the processes for the generations of *trans*-form of *bis*-phosphine ligands coordinated platinum complexes are shown. These SPOs exhibit notable efficiencies in palladium-catalyzed Suzuki-Miyaura reactions. Moreover, organic compounds (**9k** and **10c**) with unexpected conformations were obtained from Heck-type Catellani reactions. Reaction pathways are proposed to accommodate the probable routes for the formations of all organic products.

Keywords: Catellani Reaction; Suzuki-Miyaura Reaction; Secondary Phosphine Oxide; Heterocyclic Ring; Palladium; Platinum.

1. Introduction

Catalytic reactions employing ligand-assisted transition metal complexes as catalysts (or catalyst precursors) are the most commonly used means in modern synthetic methods for achieving desirable efficiency and selectivity.[1] Since 1970s, various forms of Cross-coupling reactions with the assistance of phosphine-coordinated palladium complexes have been the target of fervent studies.[2] Suzuki-Miyaura and Heck reactions represent two distinct and probably the most investigated categories among all types of Cross-coupling reactions.[3]

The fame of cross-coupling reactions arise from their efficiencies in reactions and various accessible ways of joining two different components together, especially, the formation of C(Ar)-C(Ar) bonds. Nevertheless, it is limited in its scope for combining only two substances at a time. To expand the entity of molecule, further step(s) must be pursued to incorporate another substance to the final coupled compound. It shall be beneficial if three components can be linked together in one pot reaction. Among all the available methods, Catellani reaction is regarded as one of the most intriguing three components reactions.[4] In one sense, it can be looked as a shrewd extension of conventional cross-coupling reactions.[5]

In the Catellani's early work, no ligands were added to the reaction. In addition, the stoichiometric amount of palladium catalyst employed against the substance is high.[6, 5b] Later, Lautens applied ligands to burst the speed of the reaction rates and enhanced the yields.[7] Phosphine ligands in some occasions indeed exhibit positive effect on the Catellani type reactions. Nevertheless, the effect of ligand in Catellani type reactions is not always as affirmative as that in Cross-coupling reactions. These differences could be arose from the distinct reaction pathways for these two types of reactions, especially, the formation of Pd(IV) species in Catellani reaction. A generally accepted mechanism for the Catellani reaction is shown below (Diagram 1).

Here, norbornene plays a unique role. Without the presence of norbornene, the reaction is merely another version of Cross-coupling reactions. The most significant result of the Catellani reaction is the C-H activation of the initial arylhalide on its *ortho*-position.

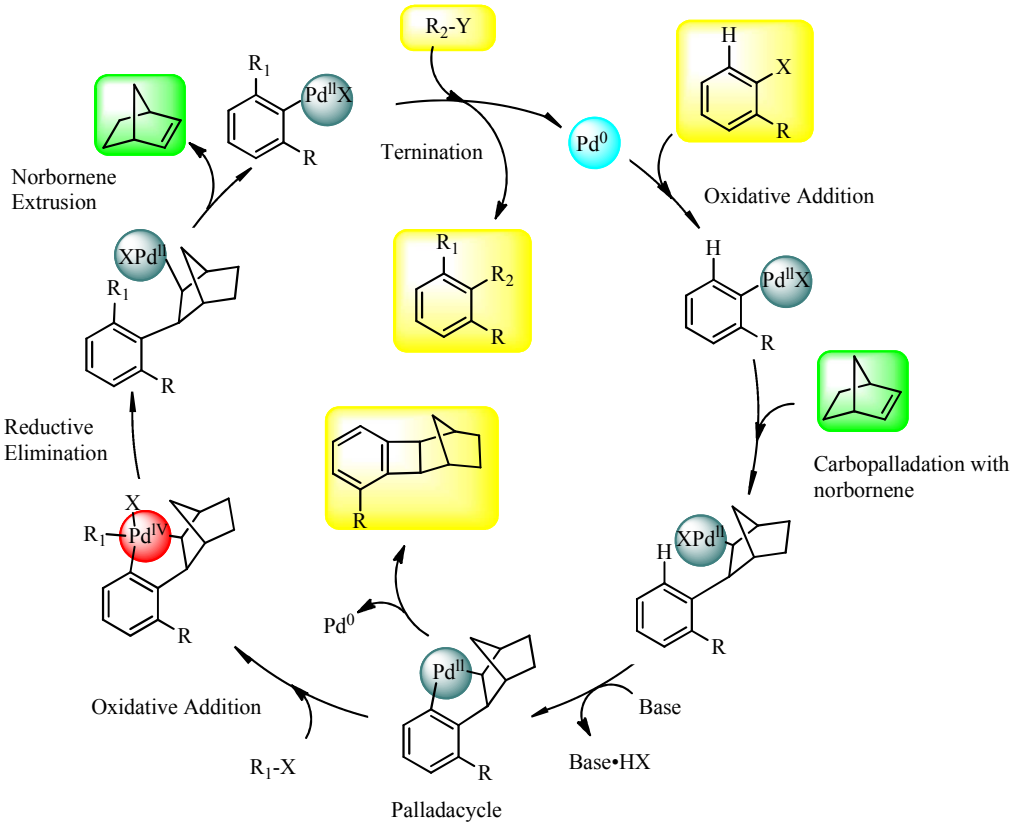
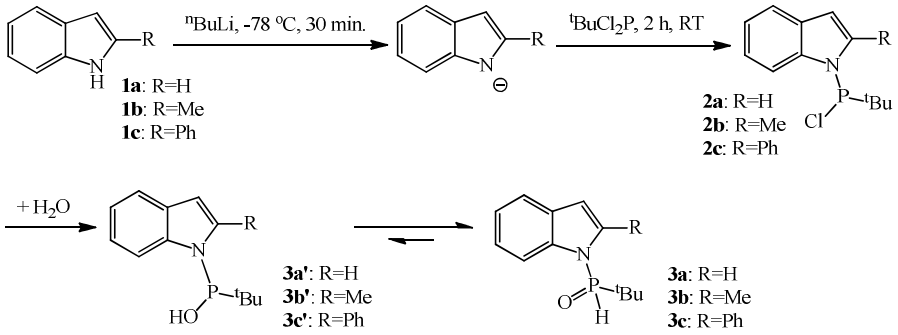


Diagram 1. A generally accepted mechanism for Catellani reaction

Although various kinds of ligands are available, phosphines having flexible shapes and functions remain one of the most important categories of ligands employed in transition metal complexes catalyzed reactions.[3] Nevertheless, most phosphines are sensitive to air/moisture and are malodorous, which makes these compounds unpleasant and difficult to handle.[8] To overcome these obstacles, a trend has been emerged in the last few years by using air/moisture stable secondary phosphine oxides (SPOs) as the acting ligands rather than the air/moisture-sensitive

tri-substituted phosphines.[9] Nevertheless, caution should be taken for using SPOs as ligands since they might undergo undesired reductive elimination with aryl (or alkyl) group in the transition metal complex intermediate(s) during catalytic cycle and forming undesirable tri-substituted phosphine oxide.[10]

Our previous work has demonstrated that a new type of indolyl scaffolding secondary phosphine oxides (SPOs, C_8H_5RN-P(=O)(H)(^{t}Bu) (**3a-3c**)) could be prepared from the reactions of corresponding 1*H*-indoles (**1a-1c**) with P^{t}BuCl$_2$ and hydrolysis followed (Scheme 1). These SPOs combined with palladium salts have been employed in the Suzuki-Miyaura cross-coupling reactions as catalytic precursors and exhibited reasonable efficiencies.[11] Recently, Ackermann also demonstrated the syntheses of several related SPOs and their applications in SPO assisted palladium-catalyzed coupling reactions as well as C-H functionalization. [12]



Scheme 1. Preparations of indolyl scaffolding secondary phosphine oxides (**3a-3c**)

Recently, the preparations of a series of dialkylbiarylphosphines were reported from the diligent design of Buchwald's group[13] by employing the concept of hemilabile ligand.[14] This types of ligands have been proven to be rather effective in various cross-coupling reactions. The backbone of these ligands are typically consisted of one strong bonding site like phosphorous and accompanied with a

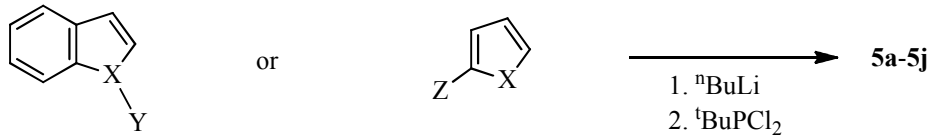
relatively weak one such as oxo- or azo-containing group.

It is of interest to us to incorporate the idea of hemilabile ligand to our previously investigated indolyl system and, thereby, to generate another new type of ligands. Herein, we report the preparation of various five-membered heterocycle substituted phosphinous acids, tautomeric forms of SPOs, coordinated palladium complexes and their applications in Suzuki-Miyaura and Catellani reactions.

2. Results and Discussion

*2.1 Preparation of heterocyclic ring substituted secondary phosphine oxide ligands (SPOs, **5a-5j**) and their coordinated palladium and platinum complexes (**6b**, **6f'**, **6f"**, **7b_trans** and **7i_trans**)*

Several secondary phosphine oxide ligands (SPOs, **5a-5j**, Diagram 2) were prepared as shown in Scheme 2. The general procedures for making these ligands are demonstrated by taking the preparation of **5a** as an example. Firstly, 1-methylindole was deprotonated by ^{n}BuLi and then was reacted with P(^{t}Bu)Cl$_2$. Subsequently, the resulted residue was processed with acidic work-up. The corresponding secondary phosphine oxide product, tert-butyl(1-methyl-1H-indol-2-yl) phosphine oxide (**5a**), was obtained. Similar procedures were pursued for making all the rest of SPOs, except **5f**, from each corresponding indoles, thiophenes and furans. The formation of **5f** is believed through the deprotonation on the thiophene rather than the indole moiety of 1-(thiophen-2-yl)-1*H*-indole **4f**.



4a: 1-methyl-1*H*-indole
4b: benzo[*b*]thiophene
4c: benzofuran
4d: 1-phenyl-1*H*-indole
4e: 1-(5-methylthiophen-2-yl)-1*H*-indole
4f: 1-(thiophen-2-yl)-1*H*-indole

4g: 2-methylfuran
4h: 2-methoxyfuran
4i: 2-methylthiophene
4j: 2-methoxythiophene

Scheme 2. Preparations of heterocyclic ring substituted secondary phosphine oxide ligands (SPOs, **5a**-**5j**).

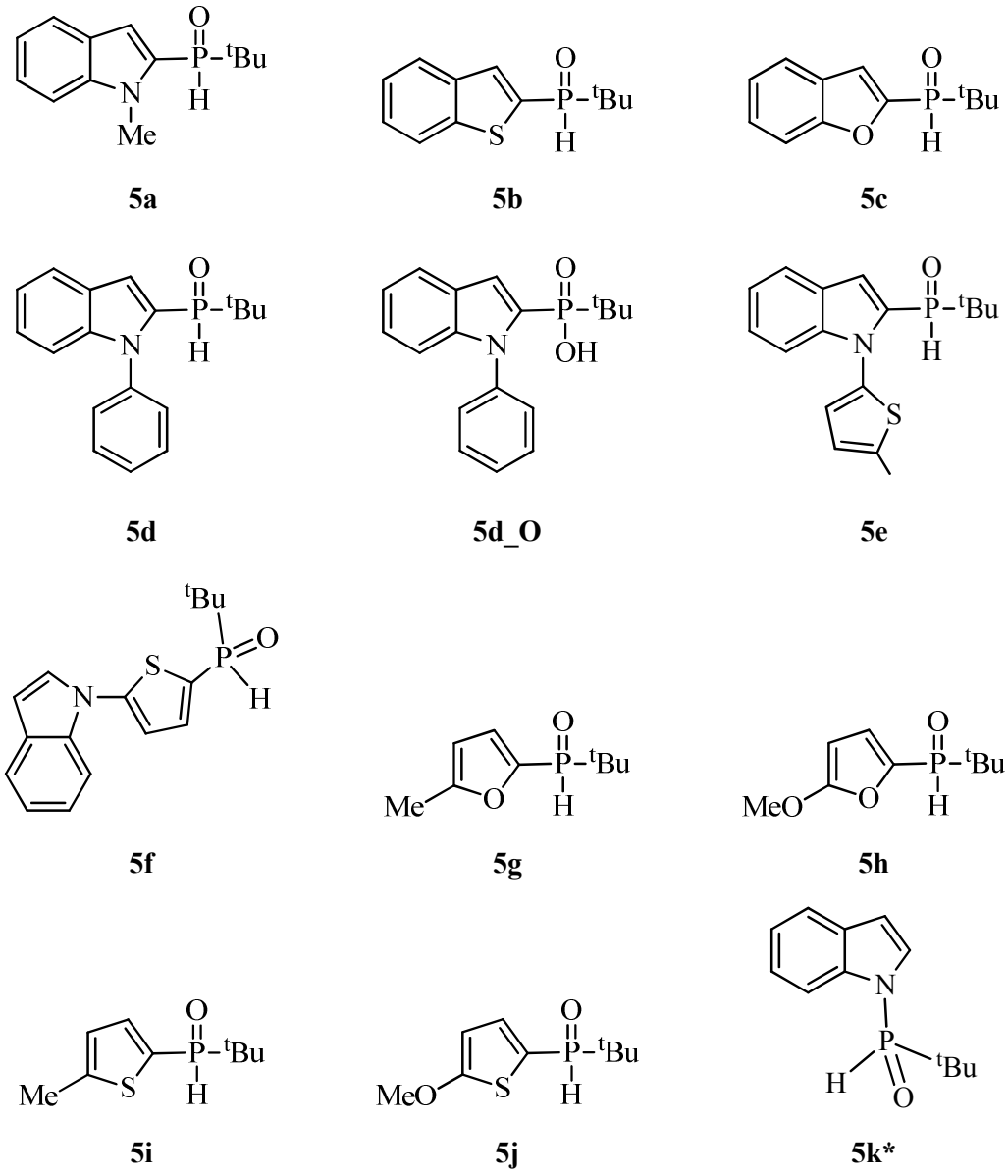


Diagram 2. Several heterocyclic ring substituted secondary phosphine oxide ligands (SPOs, **5a**-**5j** & **5d_O**) prepared from this work. The synthesis of **5k** has been reported in ref. 11.

To our delight, suitable crystals for **5a** and **5f** were obtained and their crystal structures were determined by X-ray diffraction methods. Besides, the structure of an oxide product **5d_O**, presumably an oxidized product from **5d**, was resolved as well. Moreover, as revealed from the crystal structure of **5f**, the location of the SPO functional group on the molecule is quite unusual. The ORTEP drawings of **5a**, **5d_O** and **5f** are depicted in Figure S1 (For detail see Supporting Information S1). As shown, the P-O bond lengths are 1.4789(12), 1.4952(15), and 1.481(2) Å for **5a**, **5d_O** and **5f**, respectively. Obviously, they are all typical P=O double bonds for each cases. All the phosphorus atoms are surrounded by distorted tetrahedral environments.

Further reactions of **5f** with either Pd[COD]Cl_2 or Pd[COD]Br_2 led to the formations of dipalladium complexes **6f'** and **6f"**, respectively. The disappearance of the distinctly large P-H coupling constant indicates the conversion of SPO to its tautomeric phosphinous acid form during the formation of palladium complex. There are two signals being observed in ^{31}P NMR for each **6** (**6f'** and **6f"**) which implies that the phosphine atoms are in different environments in solution. It is probably caused by the different geometric arrangements of substituents on the phosphine atoms that leads the products to corresponding R- and S-conformations. A 40~50 ppm downfielded shift in ^{31}P NMR, compared to its free state, was observed for the palladium-coordinated phosphine. Meanwhile the reactions of **5b** and **5i** with $PtCl_2$ also yielded *uni*-platinum complexes **7b_*trans*** and **7i_*trans*** with bright yellow color (Diagram 3).

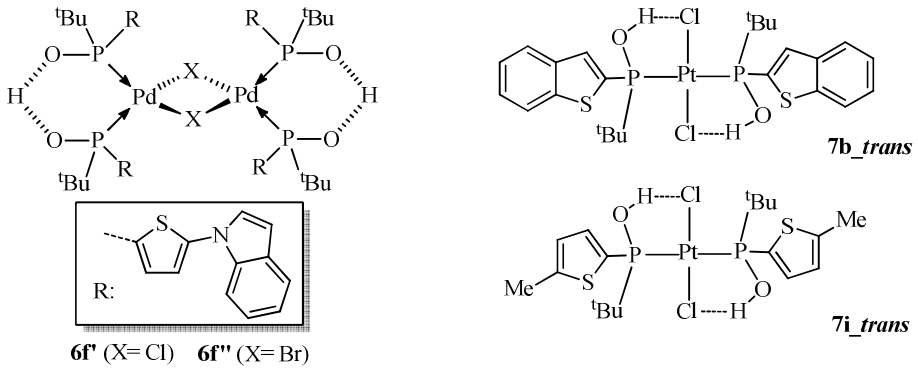


Diagram 3. SPO ligands coordinated palladium complexes (**6f'**, **6f"**) and platinum complexes (**7b_*trans***, **7i_*trans***)

The crystal structures of **6f'**, **7b_*trans*** and **7i_*trans*** were also determined by X-ray diffraction methods. As revealed from their ORTEP drawings in Figure 1, the core structure of **6f'** is a diamond shape with Pd_2Cl_2 unit. Two SPO ligands are joined through hydrogen bonding by deprotonation of one of the hydroxyl groups. The four ^{t}Bu groups are located on different sides of the plane alternatively.

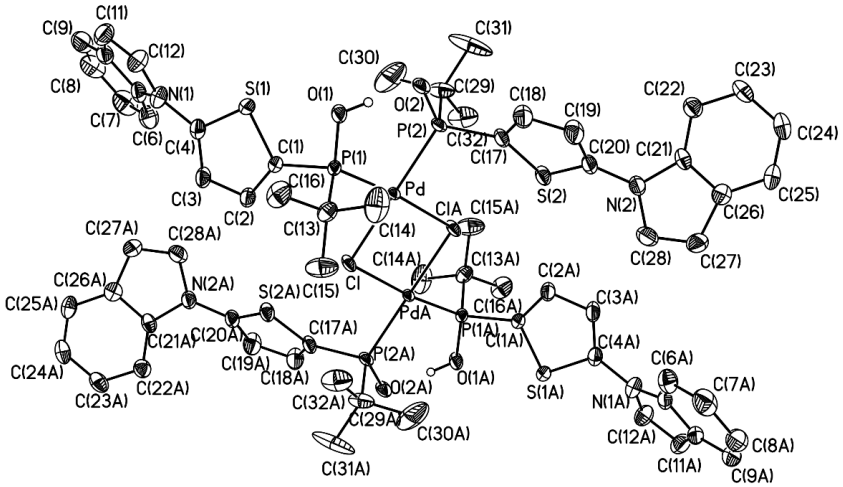


Figure 1. ORTEP drawing of **6f'**.

Crystal structures of **7b_*trans*** and **7i_*trans*** show that these two compounds are *bis*-phosphine ligands coordinated platinum complexes and two phosphine ligands are on the *trans*-positions of metal center (Figure 2). Interestingly, the arrangement of two phosphine ligands is different from the Roundhill's original report.[15] Yet, it is in accord with Buono's prediction which stated that a *trans*-form of *bis*-phosphine ligands coordinated platinum complex will be resulted while the SPO ligands furnishing with bulky substituents.[16] It is believed that the *cis*-form of another isomer, **7b_*cis*** (or **7i_*cis***), had been formed firstly, then it was converted to a more stable **7b_*trans*** (or **7i_*trans***) later. The revealed crystal structure of **7i_*trans*** substantiates the conformation of **5i** of which the crystals growing was not accessible due to its oily nature. The ^{31}P NMR shows distinct signal pattern for **7b_*trans*** due to the numerous isotopes of Pt.[17] There is one large singlet peak appears at 91.2 ppm and a small doublet at 99.1 and 83.4 ppm (d, $J^{195}_{\text{Pt-P}}$ = 2556.0 Hz). The bond lengths of Pt-P and Pt-Cl are 2.311(1) and 2.310(1) Å, respectively. There are intramolcular hydrogen bondings between O(1)-H$\cdots$Cl(1) as well as O(2)-H$\cdots$Cl(2). Thereby, an *anti*-form of this platinum complex is resulted. The ^{31}P NMR of **7i_*trans*** also shows similar pattern as that of **7b_*trans***. There is one large singlet peak appears at 89.6 ppm and a small doublet at 97.5 and 81.8 ppm (d, $J^{195}_{\text{Pt-P}}$ = 2537.7 Hz). The bond lengths of Pt-P and Pt-Cl are 2.3134(8) and 2.3028(8) Å, respectively. Similar to **7b_*trans***, there are intramolcular hydrogen bondings between O-H$\cdots$Cl(A) as well as O(0A)-H$\cdots$Cl in **7i_*trans***. Presumably, the *thio*-site of ligand **5b** (or **5i**) has the potential to be a coordinating site. Nevertheless, there is no *thio*-coordinated complex being observed here. One may notice that palladium complexes (**7b_*trans*** & **7i_*trans***) exhibit different coordination patterns from that of palladium complex **6f'**.

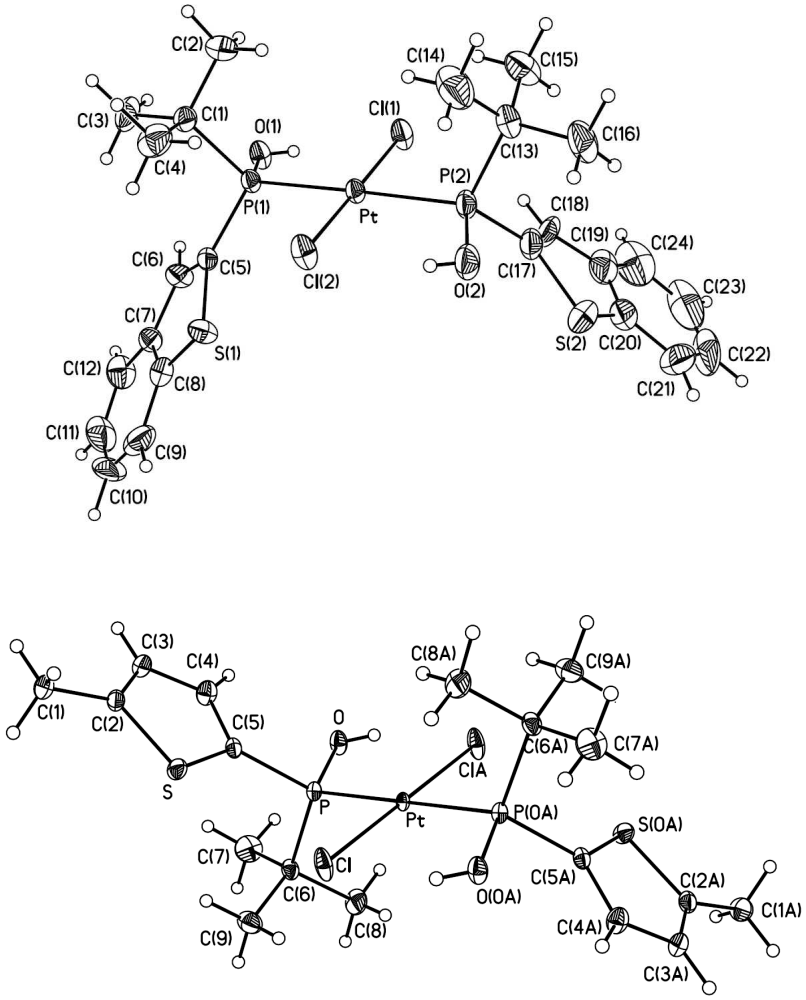


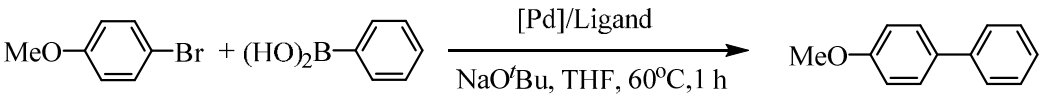
Figure 2. ORTEP drawings of **7b_*trans*** and **7i_*trans***.

2.2 Application of SPOs in Suzuki-Miyaura Reaction

Palladium complexes catalyzed Suzuki-Miyaura cross-coupling reactions of arylhalides and phenylboronic acid were carried out by employing some selected SPOs (**5a-5c** & **5g-5j**) as ligands. Several factors that potentially affect the efficiency of the reaction, including temperature, time, concentration, base, transition metal/ligand ratio and solvent etc., had been screened in order to achieve its optimized reaction condition.

The general procedure for the Suzuki-Miyaura cross-coupling reaction under investigation is presented as the follows (Scheme 3). Under N_2 atmosphere, a 20 mL

Schlenk tube was charged with 1.0 mmol of arylhalide, 1.5 mmol of phenylboronic acid, 1.0 mL of solvent, 3.0 mmol of base, 1.0 mol% of palladium salt and 2.0 mol% of ligand. The reaction was executed at preset temperature (60 °C) and time (1 h). It was then followed by work-up required. The conversion rates were determined from the measurements of products' distinct ^{1}H NMR signals against the standard one; while, the isolated yields were calculated from the products purified by column chromatography.



Scheme 3. Palladium catalyzed Suzuki-Miyaura reactions of 4-bromoanisole and phenylboronic acid employing ligands (**5a-5c** & **5g-5j**)

In the preliminary screening, the combinations of $Pd(OAc)_2$ with the newly-made SPOs (**5a-5c** & **5g-5j**) show certain catalytic efficiency towards Suzuki-Miyaura reactions (Table 1). Among all, ligand **5h** exhibits predominating effect than others. After carefully examine the most influential factors, it was found that the optimal reaction condition is as the follows: **5h**/$Pd(OAc)_2$ in the ratio of 2:1 as the catalyst precursor with the combination of KOH/THF and reacting under 60 °C for 1 h (For detail see Supporting Information S2). While 4-bromoacetophenone, with an electron-withdrawing group, was employed as the source of arylhalide, the conversion rate was almost quantitatively even within 30 minutes.

Table 1. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various ligands[a]

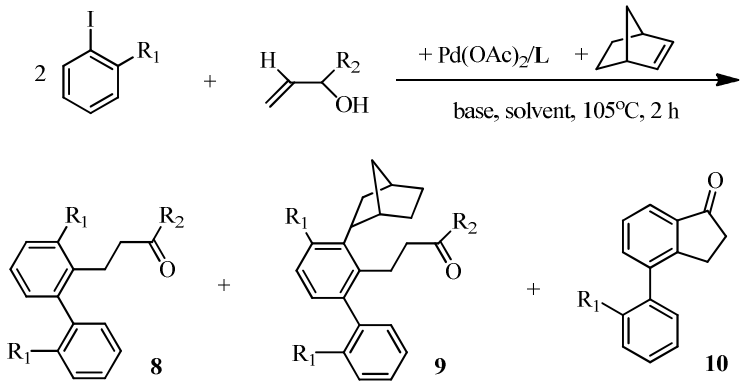
Entry	Ligand	Yield (%)[b]
1	**5a**	19
2	**5b**	37
3	**5c**	50
4	**5g**	64
5	**5h**	95
6	**5i**	74
7	**5j**	31

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, 1.0 mL THF, 1.0 mol% $Pd(OAc)_2$, 2.0 mol% ligand, 60 °C. Yield was determined by ^1H NMR and average of two runs; [b] 1 hour reaction.

2.3 Application of SPOs in Heck-type Catellani Reactions

As mentioned, there was no ligand being used in the early works of Catellani's related reactions. Although some types of ligands were employed later by others, there has no report on the usage of SPO type of phosphine ligands in Catellani reaction as yet.[7] Here, the roles of the newly-made SPOs played in Heck- and Suzuki-type Catellani reactions were examined.

Catellani reported a Heck-type reaction of *o*-substituted aryl iodides and allyl alcohols by using norbornene as co-catalyst, which led to the formation of the major product 3-(2',3-dimethyl-[1,1'-biphenyl]-2-yl)propanal (**8**) in 8 hours at 105 °C. (Scheme 4).[18] Here, similar reaction procedures were carried out except some selected SPOs (**5a**, **5d**, **5e**, **5f**, **5k**) and PPh_3 as ligands being used. Interestingly, there is one more side product probably obtained from further reaction of **8** with excess allyl alcohol while the reaction was carried out for 24 hours.



Scheme 4. Heck-type Calellani reactions of *o*-substituted aryl iodides and allyl alcohols by using SPOs as ligands

Several factors that potentially affect the efficiency of the reaction, including temperature, time, solvent, base, transition metal/ligand ratio etc., had been screened to access its optimized reaction condition (For detail see Supporting Information S3). For the preliminary screening of these ligands, **5f** exhibited the best performance. It is even better than the case of using a commonly employed PPh_3 as ligand. Therefore, the following reactions were carried out by using **5f** as ligand.

Table 2. Heck-type Catellani reactions employed various preligands[a]

Entry	Ligand	Yield (%)[b]
1	**5a**	53
2	**5d**	13
3	**5e**	13
4	**5f**	68
5	**5k**	66
6	PPh_3	51

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 2 mol% $Pd(OAc)_2$, 4 mol% preligand, 5 mL DMF, 105 ^oC, 8 h; [b] Determined by GC-MS using calibration curve.

The following reactions were carried out to monitor the formation of **8** in Heck-type Catellani reactions under three different conditions. The first run is employing the combination of 2.0 mol% $Pd(OAc)_2$ and 4.0 mol% **5f** as catalyst precursor. The second and third runs are under 2.0 mol% and 5.0 mol% $Pd(OAc)_2$, respectively. The results for the formation of **8** in the reactions under different conditions are shown in Diagram 4 (Also see the Supporting Information S4, Table S12). As shown, the rate for the formation of **8** is enhanced in a short period of time in the presence of ligand **5f**. The curve turns flat after one hour reaction and then gradually decayed. The large amount of $Pd(OAc)_2$ in fact is unfavorable for the formation of **8**. It is reasoning by the fact that further conversion of **8** to other side products was observed.

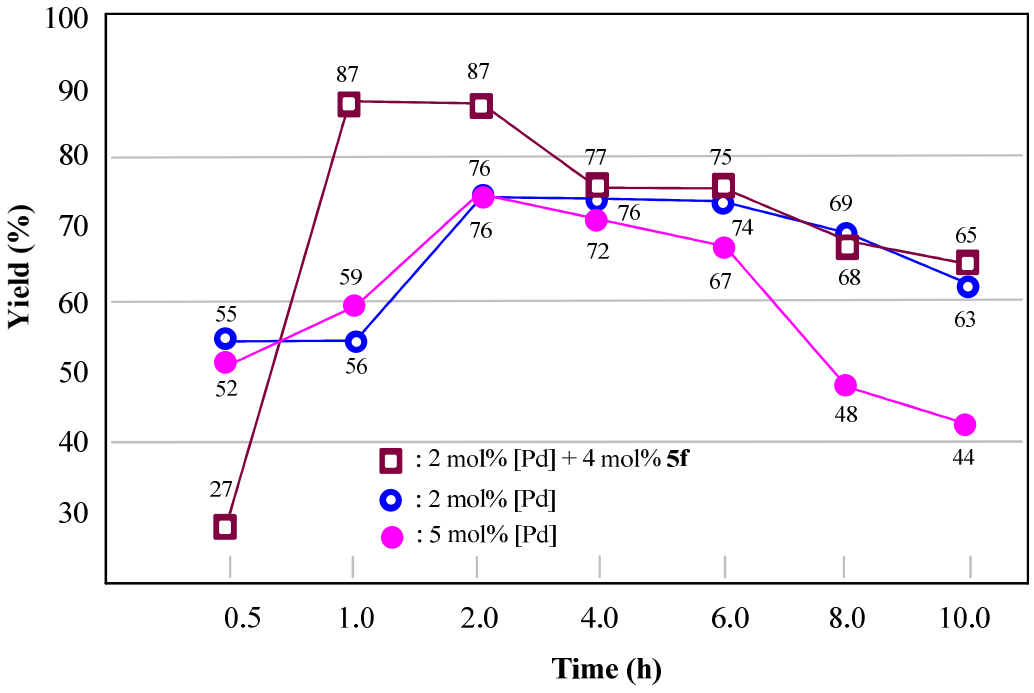
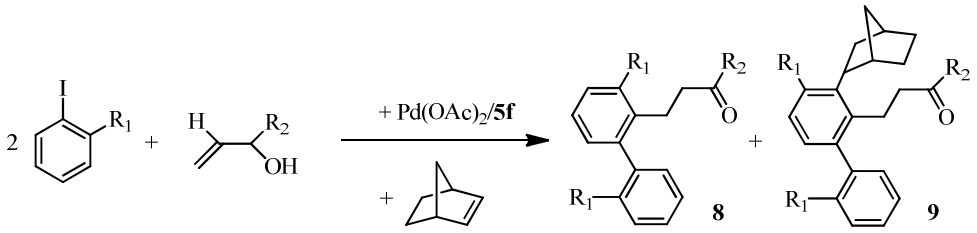


Diagram 4. The formation of **8** in Heck-type Catellani reactions under three different reaction conditions

Similar reactions were carried out with variations on the substituents of starting materials. The targeted products, **8**, were produced in wide range of yields depending on the nature of the attached substituents (Table 3). Besides, two kinds of side products, **9** & **10**, were observed accompanied with **8** (For detail see Supporting Information S5).

Table 3. Heck-type Catellani reactions with variations in substituents of reactants.[a]



Entry	R_1	R_2	Extension	Yield(%)[b]		
				8	**8**[d]	**9**
1	Me	H	**a**	78	56(8h)	-
2	OMe	H	**b**	51	-	17
3	CO_2Me	H	**c**	0[c]	-	10
4	Me	Me	**d**	49	60(24h)	-
5	^{i}Pr	Me	**e**	36	61(24h)	-
6	OMe	Me	**f**	45	62(24h)	25
7	CO_2Me	Me	**g**	75	93(6h)	20
8	CF_3	Me	**h**	15	-	-
9	Me	Ph	**i**	47	53(24h)	-
10	^{i}Pr	Ph	**j**	34	62(72h)	-
11	OMe	Ph	**k**	44	-	24
12	CO_2Me	Ph	**l**	46	-	-

[a] Conditions: 2.0 mmol *o*-substituted aryl iodides, 1.1 mmol allylic alcohols, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 2 mol% $Pd(OAc)_2$, 4 mol% **5f**, 5 mL DMF, 105 ^{o}C, 2 h; [b] Isolated yield on charged amount of the aryl iodide; [c] **10c** was isolated in 15% yield. [d] From Catellani's work, ref. 18.

Interestingly, two unexpected categories of organic products, **9** & **10**, were obtained while the starting materials (substituted iodotoluene and allyl alcohol) furnishing specific substituents (R_1 = OMe, CO_2Me; R_2 = H, Me, Ph). Compounds **9k** (3-(3-((1S,2R,4R)-bicyclo[2.2.1]heptan-2-yl)-2',4-dimethoxy -[1,1'-biphenyl]-2-yl)-1-phenylpropan-1-one) and **10c** (methyl-2-(1-oxo-2,3-dihydro-1H-inden-4-yl)benzoate) were obtained from the above reactions while R_1 = OMe and R_2 = Ph for the former and R_1 = CO_2Me and R_2 = H for the latter case. The structure of **10c** was determined by single crystal X-ray diffraction methods and ORTEP drawing is depicted in Figure 3.

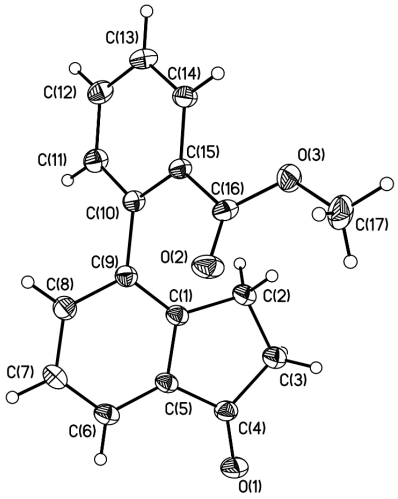


Figure 3. ORTEP drawing of **10c**.

Two reaction pathways are proposed to account for the formation of **9k** (Diagram 5). Cycle A represents a route in which the allylic alcohol attacks on palladium active species first and *o*-substituted aryl iodide oxidation addition followed; while, Cycle B describes the reverse course. In Cycle A, the initial allylic alcohol coordination (or regarded as insertion) process is favorable than the initial norbornene coordination in Cycle B due to less steric hindrance for the former process.

Nevertheless, in the process of Cycle A the release of PdL_2 active species from the complex to the solution and later the release PdL_2 attaches back to it was proposed, which is not a favorable step. Presumably, a C(Ar)-H bond activation process takes place after that.[19] Besides, in Cycle B a step involved the norbornene extrusion from the reaction intermediate before Heck reaction was proposed, which is a favorable step. Judging from all the experimental observations, Cycle B is regarded as a more favorable reaction pathway.

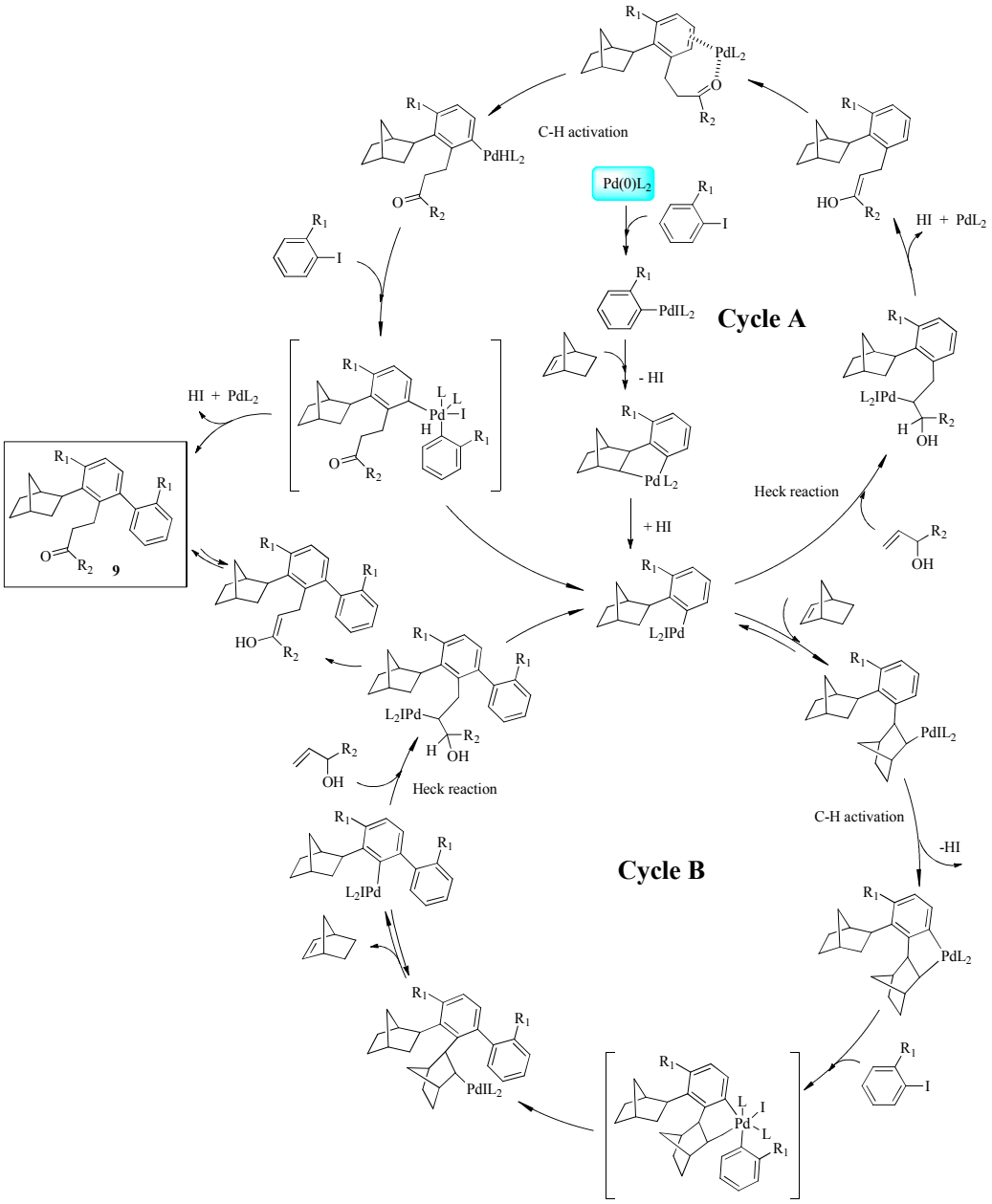


Diagram 5. Proposed mechanism for the formation of **9** *via* two possible routes.

Since the framework of **9k** containing a norbornene moiety, it is worthy of examining the effect caused by the amount of norbornene usage in reaction. The following reactions were carried out by using starting materials where R_1 = OMe and

R_2 = H. The results are shown in Diagram 6 (Also see the Supporting Information S6, Table S13). As shown in Table S13, large amount of product 3-(2-methoxyphenyl)propanal, **11a**, from direct Heck reaction was obtained while the ratio of norbornene is small (Entry 1). It decreases to minimum while the ratio of norbornene to 2-iodoanisole increases (Entry 3). The formation of **9b** reaches its maximum while the ratio is close to 4:1 and only small variations were observed after that (Entries 4-7). The final ratio of **8** to **9k** is about 6 to 4. Note here, the yields of products are presented in relative manner and summed up to 100% in total.

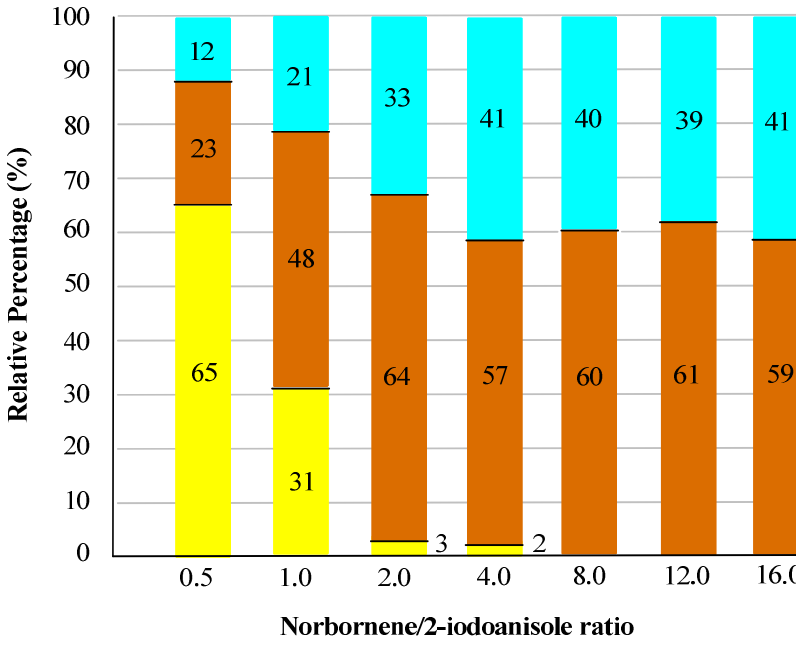


Diagram 6. The distribution of products is presented (from top down: **9b**, **8b**, **11a**). Reactions were carried out employing different ratios of norbornene to 2-iodoanisole.

The observation of **10c** is also unexpected and appealing. The route for the formation of it is proposed as shown (Diagram 7). It is presumably through a sequential steps started from **8c** in the presence of base coupled with oxidant. As for the reactions carried out, it only takes place for the case of R_1 = COOMe and R_2 = H.

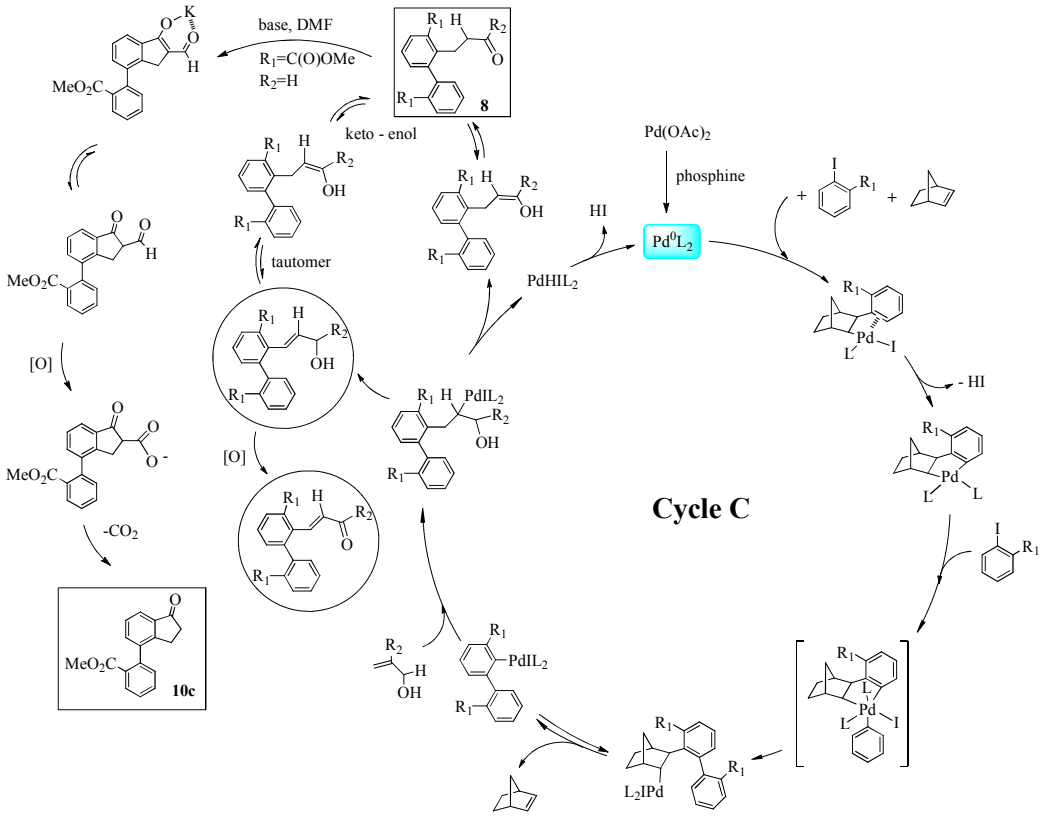


Diagram 7. Proposed mechanism for the formation of **10c**.

2.4 Summary

Several new secondary phosphine oxides (SPOs) (**5a-5j**) with/without benzo-fused five-membered heterocyclic substituents were prepared. Metal complexes form the reactions of some selected SPOs with palladium and platinum salts exhibit different structural patterns. The former show diamond shape bi-palladium structures; while, the latter display *trans*-form of mono-platinum features. Some of the SPOs exhibit satisfactory efficiencies in palladium-catalyzed Suzuki-Miyaura reactions. Interestingly, two unusual organic compounds were obtained from Heck-type Catellani reactions through unique reaction pathways.

3. Experimental Section

3.1. General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-flushed glove box. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924) or column chromatography. GC-MS analysis was performed on an Agilent 5890 gas chromatograph (Restek Rtx-5MS fused silica capillary column: 30m, 0.25mm, 0.5μm) with an Agilent® 5972 mass selective detector. Routine ^{1}H NMR spectra were recorded on a Varian-400 spectrometer at 399.756 MHz. The chemical shifts are reported in ppm relative to internal standards TMS (δ = 0.0 ppm). ^{31}P and ^{13}C NMR spectra were recorded at 161.835 and 100.529 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to internal standards H_3PO_4 (δ = 0.0 ppm) and $CHCl_3$ (δ = 77 ppm), respectively. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Electrospray ionization-high resolution mass spectra (ESI-HRMS) were recorded on a Finnigan/Thermo Quest Mat 95 XL mass spectrometer.

*3.2. Synthesis and characterization of **5a-5j***

The following procedures are presented by taking the preparation of **5a** as an example. Into a 100 mL round-bottomed flask charged with magnetic stirrer was placed **4a** (1-methyl-1H-indole, 0.656 g, 5.0 mmol). Then, air in the flask was removed and refilled with nitrogen. Subsequently, 20 mL THF was added and the solution was cooled to -78 °C. Then, 2.0 mL ^{n}BuLi (2.5 M mmol in hexane) was added slowly to the solution alongside the flask wall. The mixed solution was stirred

for 0.5 hour before it was warmed up to 25 °C. Meanwhile, in dry box another 100 mL round-bottomed flask was placed with 5.0 mmol ^{t}BuPCl$_2$ and later with 5 mL THF. Both flasks were cooled to -78 °C before the solution in the first one was slowly added to the second flask via transfer needle. The mixed solution was stirred at 25 °C for 1 hour. Without further purification, water was added to the solution at 0 °C and it was stirred for another hour. Then, the organic layer was extracted twice with ethylacetate and the extract was dried with anhydrous $MgSO_4$. A dark yellow solid **5a** was purified by column chromatography and isolated in 60% yield (0.700 g, 3.0 mmol). Similar procedures were carried out for the preparations of **5b-5j** except the starting materials.

‡ *Spectroscopic data for **5a**:*

^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 7.27(d, 1H, J_{P-H} = 467.7 Hz, P-H), 7.66(d, 1H, J = 8.0 Hz, Ar), 7.37(m, 2H, Ar), 7.17(m, 1H, Ar), 6.78(d, 1H, J = 8.0 Hz, Ar), 4.07(s, 3H, N-Me), 1.22 (d, 9H, J = 17.6 Hz, ^{t}Bu); ^{13}C NMR(100 MHz, $CDCl_3$, δ/ppm): 140.06(s, Ar), 126.23(m, P-Ar), 125.14(s), 123.96(s), 121.41(s, Ar), 120.07(s, Ar), 111.68(d, J = 16.8 Hz, Ar), 109.43(s, Ar), 32.26(N-Me), 32.48(d, J = 72.9 Hz, P-^{t}Bu), 23.30 (d, J = 2.7 Hz, ^{t}Bu); ^{31}P NMR(162 MHz, $CDCl_3$, δ/ppm): 39.15(d, J_{P-H} = 471.4 Hz); HRMS(EI, M^+, *m/z*): Calcd. for $C_{13}H_{18}NOP$: 235.1126; Found: 235.1115; EA(%): Anal. calcd. for $C_{13}H_{18}NOP$: N, 5.95 %, C, 66.37 %, H, 7.71 %; Found: N, 5.55 %, C, 66.32 %, H, 7.60 %.

‡ *Spectroscopic data for **5b**:*

The general procedure for the preparation of **5b** was employed except using **4b** (benzo[b]thiophene, 0.67 g, 5.0 mmol) as the reactant. It yielded 60 % (3.0 mmol, 0.71 g) of the title compound. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 7.24(d, 1H, J_{P-H} = 468.5 Hz, P-H), 7.85(m, 3H, Ar), 7.39(m, 2H, Ar), 1.21(d, 9H, J = 16.0 Hz, ^{t}Bu); ^{13}C NMR(100 MHz, $CDCl_3$, δ/ppm):143.24(d, J = 4.5 Hz,), 139.15(d, J = 12.8 Hz),

133.50(d, J = 8.3 Hz,), 130.38(s), 129.50(s), 126.64(s), 125.18(d, J = 12.9 Hz,), 122.63(s), 32.51(d, J = 73.4 Hz, P-^{t}Bu), 23.60(d, J = 1.81 Hz, ^{t}Bu); ^{31}P NMR(162 MHz, $CDCl_3$, δ/ppm): 38.46 (d, $J_{P\text{-}H}$ = 466.6 Hz); HRMS(EI, M^+, *m/z*): Calcd. for $C_{12}H_{15}OPS$: 238.0581; Found: 238.0575; EA(%): Anal. calcd. for $C_{12}H_{15}OPS$: C, 60.49 %, H, 6.34 %; Found: C, 61.45 %, H, 6.92 %.

‡ *Spectroscopic data for* ***5c****:*

The general procedure for the preparation of **5c** was employed except using **4c** (benzofuran, 0.59 g, 5.0 mmol) as the reactant. It yielded 60 % (3.0 mmol, 0.67 g) of the title compound. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 7.14(d, 1H, $J_{P\text{-}H}$ = 472.9 Hz, PH), 7.49(m, 2H, Ar), 7.28(m, 2H, Ar), 1.20(d, 9H, J = 18.0 Hz, ^{t}Bu); ^{13}C NMR(100 MHz, $CDCl_3$, δ/ppm): 157.14(d, J = 7.2 Hz), 147.50(d, J = 111.0 Hz, P-Ar), 126.58(s), 126.05(d, J = 8.3 Hz), 123.39(s), 122.04(s), 118.94(d, J = 16.1 Hz,), 111.66(s), 31.86(d, J = 73.6 Hz, P-C-Me_3), 22.88(s, ^{t}Bu); ^{31}P NMR(162 MHz, $CDCl_3$, δ/ppm): 31.57 (d, $J_{P\text{-}H}$ = 472.2 Hz); HRMS(EI, M^+, *m/z*): Calcd. for $C_{12}H_{15}O_2P$: 222.0810; Found: 222.0803; EA(%): Anal. calcd. for $C_{12}H_{15}OPS$: C, 64.86 %, H, 6.80 %; Found: C, 64.88 %, H, 6.94 %.

‡ *Spectroscopic data for* ***5d****:*

The general procedure for the preparation of **5d** was employed except using **4d** (1-phenyl-1H-indole, 0.97 g, 5.0 mmol) as the reactant. It yielded 48 % (2.4 mmol, 0.71 g) of the title compound. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.98(d, 9H, J = 17.6 Hz, ^{t}Bu), 7.00(d, 1H, J = 467.2 Hz, P-H), 7.20~7.27(m, 4H, Ar), 7.31(d, 1H, J = 4.8Hz, Ar), 7.46~7.53(m, 4H, Ar), 7.73(d, 1H, J = 7.6Hz, Ar); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.65(d, J = 2.7 Hz, ^{t}Bu), 32.62(d, J = 73.6 Hz, P-C-Me_3), 111.11(s, Ar), 115.18(d, J = 13.6Hz, Ar), 121.23(s, Ar), 121.91(s, Ar), 125.00(s, Ar), 126.80(s, Ar), 126.92(s, Ar), 128.22(s, Ar), 128.37(s, Ar), 128.58(s, Ar), 129.22(s, Ar), 129.55(s, Ar), 137.62(s, Ar), 140.78(d, J = 6.1Hz, Ar); ^{31}P NMR ($CDCl_3$, δ/ppm): 33.11 (d, $J_{P\text{-}H}$ = 468.3 Hz); HRMS (EI, M^+,

m/z): Anal. calcd. for $C_{18}H_{20}NOP$: 297.1283 *m/z*. Found: 297.1286 *m/z*; EA (%): Anal. Calcd. for $C_{18}H_{20}NOP$: C, 72.71%; H, 6.78%; N, 4.71 %. Found: C, 70.09%; H, 6.98%; N, 4.33%.

‡ *Spectroscopic data for* ***5d_O****:*

Compound **5d_O** was converted from **5d**. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.93(d, 9H, *J* = 16.8 Hz, ^{t}Bu), 2.96(br s, 1H, P-OH), 7.02(d, 1H, *J* = 8.4 Hz), 7.11~7.24(m, 3H), 7.33~7.36(m, 2H), 7.39~7.41(m, 3H), 7.63(d, 1H, *J* = 8 Hz); ^{31}P NMR ($CDCl_3$, δ/ppm): 47.68; HRMS (EI, M^+, *m/z*): Calcd. for $C_{18}H_{20}NO_2P$: 313.1232; Found: 313.1236; EA (%): Anal. calcd. for $C_{18}H_{20}NO_2P$: C, 69.00%; H, 6.43%; N, 4.47%. Found: C, 66.86%; H, 7.72%; N, 3.38%.

‡ *Spectroscopic data for* ***5e****:*

The general procedure for the preparation of **5e** was employed except using **4e** (1-(5-methylthiophen-2-yl)-1H-indole, 1.1 g, 5.0 mmol) as the reactant. It yielded 31% (1.55 mmol, 0.49 g) of the title compound. ^{1}H NMR ($CDCl_3$, δ/ppm): 1.14(d, 9H, *J* = 17.6 Hz, ^{t}Bu), 2.54(d, 3H, *J* = 0.8 Hz, Thiophene-Me), 7.08(d, 1H, *J* = 468 Hz, P-H), 6.73(d, 1H, *J* = 2.4 Hz, Ar), 7.01(t, 1H , *J* = 3.2Hz, Ar), 7.21~7.25(m, 1H, Ar), 7.28~7.33(m, 3H, Ar), 7.70(d, 1H, *J* = 7.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, δ/ppm):15.63(s, Thiophene-Me), 23.51(d, *J* = 2.6 Hz, ^{t}Bu), 32.26(d, *J* = 74.0 Hz, P-C-Me_3), 111.24(s, Ar), 115.09(d, *J* = 6.5 Hz), 121.55(d, *J* = 9.4Hz), 123.64(s, Ar), 125.10(s, Ar), 126.68(d, *J* = 11.4 Hz), 127.13(s, Ar), 129.61(s, Ar), 130.62(s, Ar), 135.21(s, Ar), 139.83(s, Ar), 141.78(d, *J* = 5.7Hz); ^{31}P NMR ($CDCl_3$, δ/ppm): 31.05 (d, $J_{P\text{-}H}$ = 469.6 Hz); HRMS (EI, M^+, *m/z*): Calcd. for $C_{17}H_{20}NOPS$: 317.1003 *m/z*. Found: 317.1001 *m/z*; EA (%): Anal. calcd. for $C_{17}H_{20}NOPS$: C, 64.33%; H, 6.35%; N, 4.41%. Found: C, 61.89%; H, 6.06%; N, 3.86%.

‡ *Spectroscopic data for* ***5f****:*

The general procedure for the preparation of **5f** was employed except using **4f**

(1-(thiophen-2-yl)-1H-indole, 1.0 g, 5.0 mmol) as the reactant. It yielded 35 % (1.75 mmol, 0.53 g) of the title compound. ^{1}H NMR ($CDCl_3$, δ/ppm):1.27(d, 9H, *J* = 18 Hz, ^{t}Bu), 7.21(d, 1H, *J* = 466.4 Hz, P-H), 6.72(d, 1H, *J* = 3.6Hz, Ar), 7.19~7.24(m, 2H, Ar), 7.319(t, 2H, *J* = 3.6Hz, Ar), 7.56~7.58(m, 1H, Ar), 7.68(t, 2H, *J* = 7.6Hz, Ar); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.33(d, *J* = 2.7Hz, ^{t}Bu), 32.80(d, *J* = 78.2Hz, P-C-Me_3), 105.76(s, Ar), 110.62(s, Ar), 119.20(d, *J* = 10.7Hz, Ar), 121.39(s, Ar), 121.54(s, Ar), 123.35(s, Ar), 123.46(s ,Ar), 128.43(s, Ar), 129.47(s, Ar), 135.15(d, *J* = 7.5Hz, Ar), 136.13(s, Ar), 149.39(s, Ar); ^{31}P NMR ($CDCl_3$, δ/ppm): 37.41 (d, $J_{P\text{-}H}$ = 467.5 Hz); HRMS (EI, M^+, *m/z*): Anal. Calcd. for $C_{16}H_{18}NOPS$: 303.0847 *m/z*. Found: 303.0843 *m/z*; EA (%): Anal. calcd. for $C_{16}H_{18}NOPS$: C, 63.35%; H, 5.98%; N, 4.62%. Found: C, 63.25%; H, 6.31%; N, 4.69%.

‡ *Spectroscopic data for* ***5g****:*

The general procedure for the preparation of **5g** was employed except using **4g** (2-methylfuran, 0.443 mL, 5.0 mmol) as the reactant. It yielded 65 % (3.3 mmol, 0.61 g) of the title compound. ^{1}H NMR($CDCl_3$, δ/ppm): 1.16(d, 9H, *J* = 17.6 Hz, ^{t}Bu), 2.32(s, 3H, Me), 6.08(m, 1H, Furan), 7.00(m, 1H, Furan), 6.95(d, 1H, *J* = 467.3 Hz, P-H); ^{13}C NMR($CDCl_3$, δ/ppm): 13.67(s, Me), 23.11(d, *J* = 2.7 Hz, ^{t}Bu), 31.86(d, *J* = 74.8 Hz, P-C-Me_3), 107.08(d, *J* = 7.6 Hz, P-Furan), 123.76(S, Furan), 123.93(S, Furan), 158.57(d, *J* = 6.5 Hz, Furan); ^{31}P NMR ($CDCl_3$, δ/ppm): 30.28(d, *J* = 466.1 Hz); HRMS(EI, M^+, *m/z*): Anal. Calcd. for $C_9H_{15}O_2P$: 186.0810; Found: 186.0800; EA(%): Anal. calcd.: C, 58.06; H, 8.12 %; Found: C, 51.12 %; H, 7.52 %.

‡ *Spectroscopic data for* ***5h****:*

The general procedure for the preparation of **5h** was employed except using **4h** (2-methylthiophene, 0.461 mL, 5.0 mmol) as the reactant. It yielded 34 % (1.7 mmol, 0.34 g) of the title compound. ^{1}H NMR ($CDCl_3$, δ/ppm): 1.13(d, 9H, *J* = 18.6 Hz, ^{t}Bu), 3.84(s, 3H, O-Me), 5.26(m, 1H, Furan), 7.01(m, 1H, Furan), 6.87(d, 1H, *J* = 468.0 Hz,

P-H); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.39(d, J = 2.7 Hz, ^{t}Bu), 32.40(d, J = 75.6 Hz, P-C-Me_3), 57.85(s, O-Me), 125.62(d, J = 13.5 Hz, P-Furan), 133.78(S, Furan), 135.00(S, Furan), 165.48(d, J = 8.0 Hz, Furan); ^{31}P NMR ($CDCl_3$, δ/ppm): 29.62(d, J = 467.1 Hz); HRMS(EI, M^+, *m/z*): Calcd. for $C_9H_{15}O_3P$: 202.0759; Found: 202.0754; EA (%): Anal. calcd. for $C_9H_{15}O_3P$: C, 53.46 %; H, 7.48 %; Found: C, 55.57 %; H, 8.15 %.

‡ *Spectroscopic data for* ***5i****:*

The general procedure for the preparation of **5i** was employed except using **4i** (2-methoxyfuran, 0.484 mL, 5.0 mmol) as the reactant. It yielded 72 % (3.6 mmol, 0.73 g) of the title compound. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 1.16(d, 9H, J = 17.6 Hz, ^{t}Bu), 2.53(s, 3H, Me), 6.86(m, 1H, Thiophene), 7.38(m, 1H, Thiophene), 7.09(d, 1H, J = 462.1 Hz, P-H): ^{13}C NMR(100 MHz, $CDCl_3$, δ/ppm): 15.26(s, Me), 23.27(d, J = 2.7 Hz, ^{t}Bu), 32.06(d, J = 74.4 Hz, P-C-Me_3), 126.61(d, J = 12.2 Hz, P-Thiophene), 136.00(S, Thiophene), 136.08(S, Thiophene), 148.62(d, J = 3.8 Hz, Thiophene); ^{31}P NMR(162 MHz, $CDCl_3$, δ/ppm): 37.27(d, J = 462.4 Hz); HRMS(EI, M^+, *m/z*): calcd.: 202.0581; Found: 202.0578; EA (%): Anal. Calcd. for $C_9H_{15}OPS$: C, 53.45 %; H, 7.48 %; Found: C, 53.80 %; H, 7.83 %.

‡ *Spectroscopic data for* ***5j****:*

The general procedure for the preparation of **5j** was employed except using **4j** (2-methoxythiophene, 0.504 mL, 5.0 mmol) as the reactant. It yielded 56 % (2.8 mmle, 0.61 g) of the title compound. ^{1}H NMR ($CDCl_3$, δ/ppm): 1.08(d, 9H, J = 16.0 Hz, ^{t}Bu), 3.85(s, 3H, O-Me), 6.24(m, 1H, Thiophene), 7.72(m, 1H, Thiophene), 6.95(d, 1H, J = 461.7 Hz, P-H); ^{13}C NMR($CDCl_3$, δ/ppm): 22.51(d, J = 2.2 Hz, ^{t}Bu), 31.44(d, J = 75.2 Hz, P-C-Me_3), 59.81(s, O-Me), 104.60(d, J = 10.7 Hz, Thiophene), 112.12(d, J = 100.0 Hz, P-Thiophene), 134.18(d, J = 7.9 Hz, Thiophene), 172.64(d, J = 5.7 Hz, Thiophene); ^{31}P NMR($CDCl_3$, δ/ppm): 38.13(d, J = 462.4 Hz); HRMS(EI, M^+, *m/z*):

Calcd. for $C_9H_{15}O_2PS$: 218.0530; Found: 218.0528; EA (%): Anal. calcd. for $C_9H_{15}O_2PS$: C, 49.53 %; H, 6.93 %; Found: C, 47.79 %; H, 7.47 %.

*3.3. Synthesis and characterization of **6f'** and **6f"***

Under nitrogen, a 20 mL Schlenk tube charged with magnetic stirrer was placed 2 mL THF, $PdCl_2$ (0.0177 g, 0.1 mmol), and two molar equivalent of **5f** (0.0606 g, 0.2 mmol). The solution was stirred at 60°C for 1 h before it was cooled down to room temperature. Then, the solvent was completely removed under reduced pressure. The residue was dissolved in 1 mL CH_2Cl_2 again and purified through column chromatography and the target compound **6f'** was obtained.

‡ *Spectroscopic data for **6f'**:*

^{1}H NMR ($CDCl_3$, δ/ppm): 1.23(d, 18H, *J* = 18.4 Hz, ^{t}Bu), 1.33(d, 18H, *J* = 18 Hz, ^{t}Bu), 6.64~6.72(m, Ar), 7.05~7.37(m, Ar), 7.58~7.76(m, Ar); ^{13}C NMR ($CDCl_3$, δ/ppm): 26.88(d, *J* = 11 Hz, ^{t}Bu), 41.97(t, *J* = 19.7 Hz, P-C-Me_3), 105.40(s, Ar), 110.77(d, *J* = 4.2 Hz, Ar), 118.65(s, Ar), 118.93(s, Ar), 121.33(s, Ar), 121.35(d, *J* = 3.4 Hz, Ar), 128.35(d, *J* = 9.1 Hz, Ar), 129.42(s, Ar), 134.55(s, Ar), 135.93(s, Ar), 136.10(s, Ar), 148.20(s, Ar); ^{31}P NMR ($CDCl_3$, δ/ppm): 95.75, 95.39; LC/MS/MS (ESI-, M^+, *m/z*): Calcd. For $C_{64}H_{70}Cl_2N_4O_4P_4Pd_2S_4$: 1492.0766 *m/z*. Found: 1492.0760 *m/z;* EA (%): Anal. Calcd. for $C_{64}H_{70}Cl_2N_4O_4P_4Pd_2S_4$: C, 51.41%; H, 4.72%; N, 3.75%. Found: C, 53.42%; H, 5.18%; N, 3.48%.

‡ *Spectroscopic data for **6f"**:*

The general procedure for the preparation of **6f"** was employed except using **5f** (0.0606 g, 0.1 mmol) as the reactant and $PdBr_2$ (0.0266 g) as palladium source. ^{1}H NMR ($CDCl_3$, δ/ppm): 1.29(d, *J* = 18 Hz, ^{t}Bu), 1.34(d, *J* = 7.6 Hz, ^{t}Bu), 6.61~6.67(m, Ar), 7.08~7.29(m, Ar), 7.62~7.72(m, Ar); ^{13}C NMR ($CDCl_3$, δ/ppm): 26.88(d, *J* = 11.4 Hz, ^{t}Bu), 41.96(t, *J* = 20.5 Hz, P-C-Me_3), 105.40(s, Ar), 110.77(d, *J* = 4.2 Hz, Ar),

118.69(s, Ar), 118.94(s, Ar), 121.35(d, J = 3.8 Hz, Ar), 123.23(s, Ar), 128.35(d, J = 9.1 Hz, Ar), 129.42(s, Ar), 134.59(s, Ar), 135.93(s, Ar), 136.1(s, Ar), 148.21(s, Ar); ^{31}P NMR ($CDCl_3$, δ/ppm): 97.66, 96.95; LC/MS/MS (APCI-, M^+, *m/z*): Calcd. for $C_{64}H_{70}Br_2N_4O_4P_4Pd_2S_4$: 1580.9657 *m/z*. Found: 1580.5850 *m/z*. EA (%): Anal. Calcd. For $C_{64}H_{70}Br_2N_4O_4P_4Pd_2S_4$: C, 48.53%; H, 4.45%; N, 3.54%. Found: C, 47.64%; H, 4.94%; N, 2.99%.

*3.5. Syntheses and characterization of **7b_trans** and **7i_trans***

Into a 20 mL Schlenk tube charged with magnetic stirrer was placed **5b** (0.0477 g, 0.2 mmol) with $PtCl_2$ (0.0266 g, 0.1 mmol). Then, the flask was refilled with nitrogen after the air was removed. Afterwards, 20 mL THF was added and the mixture was stirred at 60 °C for 1 hour. A pale yellow solid **7b_*trans*** yielded in 67% (0.044 g, 0.067 mmol) was purified by column chromatography using dichloromethane as eluent.

‡ *Spectroscopic data for **7b_trans**:*

^{1}H NMR ($CDCl_3$, δ/ppm): 8.13(m, 1H, Ar), 7.87(m, 2H, Ar), 7.40(m, 2H, Ar), 1.40-1.32(m, 9H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, δ/ppm): 143.31(s), 139.31(d, $J_{P\text{-}C}$ = 6.1 Hz), 133.67 (d, $J_{P\text{-}C}$ = 25 Hz), 133.49(s), 132.66(s), 125.72(s), 124.62(t, $J_{P\text{-}C}$ = 16 Hz, Ar), 122.03(d, $J_{P\text{-}C}$ = 8.0 Hz), 37.95(t, $J_{P\text{-}C}$ = 21.6 Hz, P-C-Me_3), 25.43(t, $J_{P\text{-}C}$ = 3.1 Hz, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 91.24 (s + d, $J_{P\text{-}Pt}$ = 2556.0 Hz); LC/MS/MS(ESI, M^+, *m/z*): 739.0052; Anal. calcd. for $C_{24}H_{30}Cl_2O_2P_2PtS_2$: 739.0025; Found: 739.0052.

‡ *Spectroscopic data for **7i_trans**:*

The general procedure for the preparation of **7i_trans** was employed except using **5i** (0.0404 g, 0.2 mmol) as the reactant and $PtCl_2$ (0.0266 g, 0.1 mmol) as platinum source. It yielded 67 % (0.067 mmol, 0.044 g) of the title compound.

^{1}H NMR($CDCl_3$, δ/ppm): 1.30-1.26(m, 18H, ^{t}Bu), 2.55(s, 6H, Me), 6.85(m, 2H,

Thiophene), 7.66(m, 2H, Thiophene); ^{13}C NMR($CDCl_3$, δ/ppm): 148.26(s), 137.14(t, J_{P-C} = 12.6 Hz), 128.28(s), 126.52(t, J_{P-C} = 11.1 Hz), 37.60(t, J_{P-C} = 45.3 Hz, P-C-Me_3), 25.36(t, J_{P-C} = 6.0 Hz, ^{t}Bu), 15.29(s); ^{31}P NMR ($CDCl_3$, δ/ppm): 89.63(s + d, J_{P-Pt} = 2537.7 Hz); LC/MS/MS(ESI-, M^+, *m/z*): Anal. Calcd. For $C_{18}H_{30}Cl_2O_2P_2PtS_2$: 660.0104; Found: 660.0111.

3.6. General procedure for the Suzuki-Miyaura cross-coupling reactions

Suzuki-Miyaura cross-coupling reactions were performed according to the following procedures. Four reactants, including $Pd(OAc)_2$, ligand, boronic acid and base, were placed in a suitable oven-dried Schlenk flask. It was evacuated for 0.5 hour and backfilled with nitrogen gas before adding solvent and aryl halide through a rubber septum. The aryl halides being solids at room temperature were added prior to the evacuation/backfill cycle. The flask was sealed with a rubber septum and the solution was stirred at the required temperature for designated hours. Then, the reaction mixture was diluted with ethyl acetate (3 mL) and the cooled solution poured into a separatory funnel. The mixture was washed with aqueous NaOH (1.0 M, 5 mL) and the aqueous layer was extracted with ethyl acetate (2 x 5 mL). The combined organic layer were washed with brine and dried with anhydrous magnesium sulfate. The dried organic layer was concentrated *in vacuo*. The residue was purified by column chromatography to give the desired product.

3.7. General procedure for Heck-type Catellani reactions

A nitrogen filled 20 mL Schlenk tube charged with a magnetic stirrer was placed with $Pd(OAc)_2$ (0.01 mmol, 2.24 mg), **5b** (0.02 mmol, 4.49 mg) (or other ligands) and K_2CO_3 (2.0 mmol, 0.28 g). Then, norbornene (0.5 mmol, 47.08 mg) was added to the tube in fume hood and was sealed with septum. The mixture was frozen by liq. N_2 and

air was pumped out then backup with nitrogen. Repeat the process for three times. Subsequently, under nitrogen 5.0 mL DMF, 2-iodotoluene (2.0 mmol, 0.254 mL) and allyl alcohol (1.1 mmol, 0.075 mL) were added. The solution was then heated in oil bath for 72 hours at 105 °C. Afterwards, it was cooled down to room temperature and the resulted products were extracted with dichloromethane. The extracted solution was dried over pre-dried $MgSO_4$. The solution was filtrated and concentrated before carrying out column chromatograph. Finally, the compositions of the isolated products were analyzed by GC-MS.

3.8. X-ray crystallographic studies

Crystals of **5a**, **5b**, **5d_O**, **5f**, **6f'**, **6f"**, **7b_*trans***, **7i_*trans***, **9b**, and **10b**, were obtained by placing crystal growing glassware, which contains two layers solution (ether/CH_2Cl_2), at 4 ^oC environment for a few days. Suitable crystals of **5a**, **5b**, **5d_O**, **5f**, **6f'**, **6f"**, **7b_*trans***, **7i_*trans***, **9b**, and **10b**, were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

4. Supplementary Material Available

Crystallographic data for the structural analysis have been deposited with the

Cambridge Crystallographic Data Center. The CCDC numbers for each crystal are in parentheses: **5a**(1402341), **5b**(1402342), **5d_O**(1403220), **5f**(1403221), **6f'**(1403222), **6f"**(1403223), **7b_*trans***(1402345), **7i_*trans***(1402346), **9b**(1403224), and **10b**(1403225).

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