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Palladium-catalyzed $R_2(O)P$-directed $C(sp^2)$–H activation

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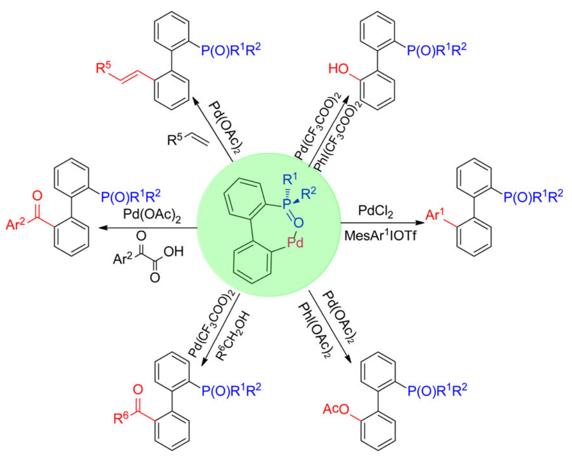
In recent years, transition-metal-catalyzed inert C–H bond activation has developed rapidly and is a powerful protocol for the construction of new C–C or C–X bonds and the introduction of new functional groups. Our group has also developed a series of $R_2(O)P$-directed Pd-catalyzed C–H functionalizations involving olefination, hydroxylation, acetoxylation, arylation, and acylation through an uncommon seven-membered cyclo-palladium pretransition state. Unlike previously used directing groups, the $R_2(O)P$ group acts as a directing group and is also involved in the construction of P,-hetero-ligands.

C–H bond activation, Pd-catalyzed, $R_2(O)P$-directed

1 Introduction

Transition-metal-catalyzed directed selective C–H activation and functionalization has become a powerful tool in organic synthesis because of its significance in basic studies of inert C–H bond chemistry, and its broad substrate range and high atom economy in potential synthetic applications. [1–5]. Over the past ten years, much effort has been devoted to this strategy and many directing groups such as heterocycles [6–9], amides [10–14], imines [15–17], ketones [18–23], esters [24–29], and carboxylic acid [30–33] have been identified. Here, we report the use of the relatively weak coordinating $R_2(O)P$ group as a new directing group with great promise for improving catalytic turnovers and broadening reaction scopes. Compared with previously reported directing groups, $R_2(O)P$ has some useful features: (1) organophosphorus molecules occur widely as structural motifs in the life sciences and pharmaceuticals [34–37]; (2) the $R_2(O)P$ group acts as a directing group, and is also involved in the construction of the desired products [38]; (3) unlike previously reported syntheses involving C–H functionalizations directed by phosphoric acid or phosphate esters [39–46], our reactions feature a seven-membered cyclopalladium intermediate. In the last year, we have focused on establishing efficient and widespread catalytic systems and have reported a series of $R_2(O)P$-directed Pd-catalyzed C–H functionalizations involving olefination [47], hydroxylation [48], acetoxylation [49], arylation [50] and acylation [51] (Scheme 1). These methods provide a concise and effective route for the preparation of substituted chiral 2′-phosphorylbiphenyl compounds [52]. We expect that our results will have a significant impact in this field.



Scheme 1 $P(O)R_2$-directed C–H functionalization via seven-membered cyclopalladium transition state.

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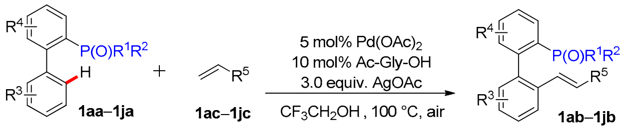
2 Results and discussion

2.1 $R_2(O)P$-directed Pd(II)-catalyzed C–H olefination

We first explored $R_2(O)P$-directed Pd(II)-catalyzed C–H olefination of structure C–C bonds via Heck reaction [53]. We chose this reaction for two reasons: (1) Heck coupling reactions have become an indispensable strategic tool for C–C bond formation and play a pivotal role in modern organic synthesis. The development of complementary methods for coupling inactivated C–H bonds with olefins is therefore attractive; (2) the expected products are precursors of olefin-phosphine hybrid ligands. 2-Diphenylphosphino-2′-methylbiphenyl (**1aa**) and ethyl acrylate (**1ac**) were used as the model substrates in the initial tests. The optimum reaction conditions were found to be $Pd(OAc)_2$ (5 mol%) as the catalyst, Ac–Gly–OH (10 mol%) as the ligand, and AgOAc (3.0 equiv.) as the oxidant, in CF_3CH_2OH (2.0 mL), with **1aa** (0.2 mmol) and ethyl acrylate (3.0 equiv.) at 100 °C in air (Table 1).

Table 1 $R_2(O)P$-directed Pd(II)-catalyzed C–H olefination [a)]



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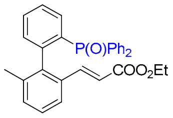
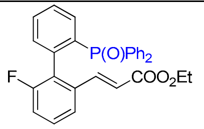
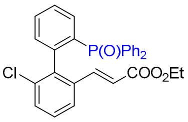
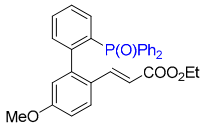
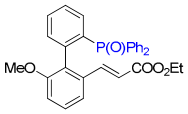
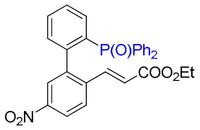
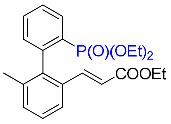
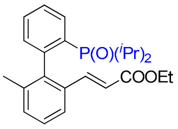
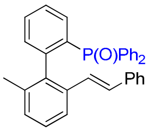
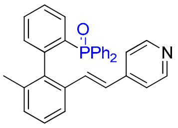
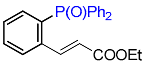
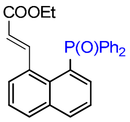
1ab		87	**1bb**		67
1cb		62	**1db**		31
1eb		54	**1fb**		60
1gb		68 [c)]	**1hb**		67 [c)]
1ib		58	**1jb**		87
1kb		0	**1lb**		0

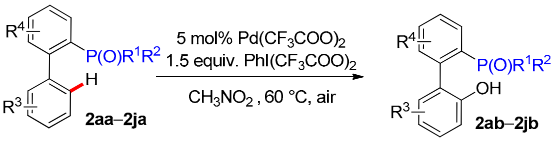
a) All reactions were carried out in the presence of 0.2 mmol of **1aa–1ja** in 2.0 mL CF_3CH_2OH; b) isolated yield; c) 10 mol% $Pd(OAc)_2$ was used.

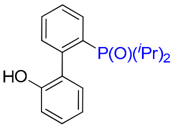
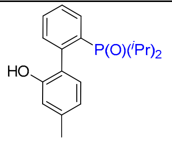
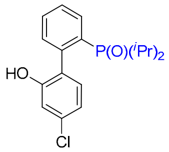
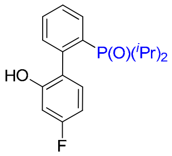
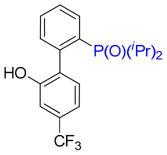
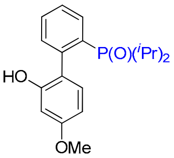
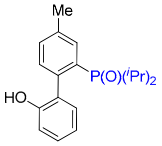
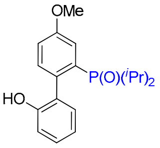
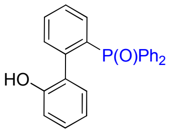
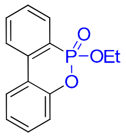
We evaluated various diphenylphosphine oxide derivatives and phosphate directing groups under the optimum conditions. These compounds were also effective in this transformation and corresponding products were obtained in good yields. We discovered that styrenes were also compatible with the C–H olefination reaction. Triphenylphosphine oxide and (naphthalen-1-yl)diphenylphosphine oxide failed to induce C–H olefination. These results imply that a seven-membered cyclopalladium pre-transition state may play a critical role in this transformation.

2.2 $R_2(O)P$-directed Pd(II)-catalyzed C–H hydroxylation

Inspired by these results, we extended this method to $R_2(O)P$-directed Pd(II)-catalyzed C–H hydroxylation, these products are important precursors in syntheses of various P,-O-ligands. Also, phenols function as important building blocks for common subunits in biomolecules and drug molecules [54]. We found that the best conditions were $Pd(CF_3COO)_2/PhI(CF_3COO)_2$ as the catalytic system, CH_3NO_2 as the solvent, 60 °C, and an air atmosphere (Table 2).

Table 2 $R_2(O)P$-directed Pd(II)-catalyzed C–H hydroxylation [a)]



Entry	Product	Yield (%) [b)]	Entry	Product	Yield (%) [b)]
2ab		85	**2bb**		76
2cb		87 [c)]	**2db**		93 [c)]
2eb		90 [c)]	**2fb**		73 [d)]
2gb		83	**2hb**		81
2ib		66	**2jb**		37

a) All reactions were carried out in the presence of 0.3 mmol of **2aa–2ja** in 2.0 mL CH_3NO_2; b) isolated yield; c) 10 mol% $Pd(CF_3COO)_2$ was used at 80 °C; d) 1.4 equiv. of $PhI(CF_3COO)_2$ was used.

The reaction had good functional-group tolerance and substrates scope. Electron-withdrawing substituents such as F, Cl, and CF_3 at the 4′-position gave the corresponding products in excellent yields in the presence of 10 mol% $Pd(CF_3COO)_2$ at 80 °C (**2cb**–**2eb**). However, for a methoxy substituent at this position, the oxidant loading had to be decreased to 1.4 equiv. (**2fb**). When diethylbiphenyl-2-ylphosphonate was used, only phosphoryl lactone **2jb** was obtained, in 37% yield.

2.3 R_2(O)P-directed Pd(II)-catalyzed C–H acetoxylation

The above results suggest that using more moderately active $PhI(OAc)_2$ as the oxidant might lead to acetoxylation under a similar catalytic system, because the phenol products of hydroxylation might derive from the labile corresponding trifluoroacetation. We obtained the desired acetoxylation products using $Pd(OAc)_2$ as the catalyst and $PhI(OAc)_2$ as the oxidant in CF_3CH_2OH. The moderate oxidant enabled the reactions of compounds with some useful and sensitive functional groups to proceed smoothly, and the corresponding products were obtained in good yields (Table 3).

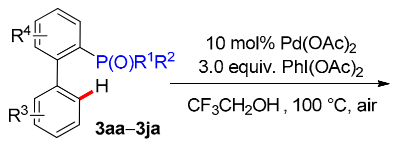
2.4 R_2(O)P-directed Pd(II)-catalyzed C–H arylation

In the meantime, similar hypervalent iodine reagents were used to synthesize a series of polyaromatic monophosphorus compounds via R_2(O)P-directed Pd(II)-catalyzed C–H arylation. These compounds can be easily reduced to trivalent phosphorus by trichlorosilane, which are useful ligands for transition-metal-catalyzed cross-coupling reactions [55]. After systematic studies, we concluded that the cheap $PdCl_2$ catalyst with pivalic acid/Ag_2CO_3 as an additive was the best choice. Under the optimized conditions, various polyaromatic monophosphorus compounds were obtained in moderate to good yields. Hypervalent iodine arylation reagents also reacted smoothly to give various substituted products (Table 4).

2.5 R_2(O)P-directed Pd(II)-catalyzed C–H acylation

Based on these results, we have developed an efficient

Table 3 R_2(O)P-directed Pd(II)-catalyzed C–H acetoxylation a)



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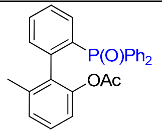
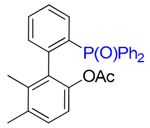
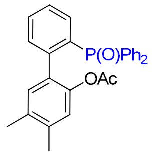
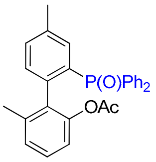
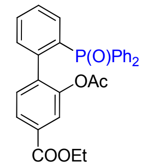
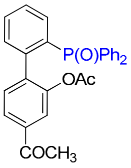
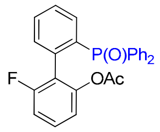
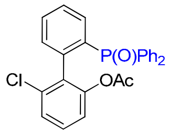
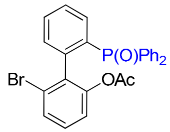
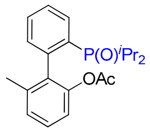
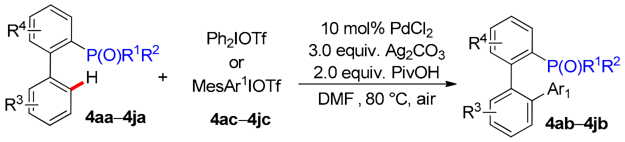
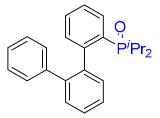
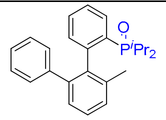
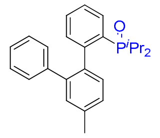
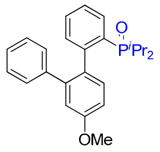
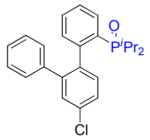
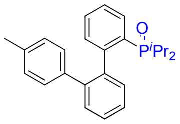
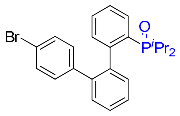
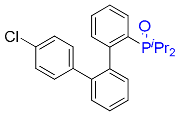
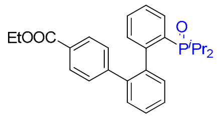
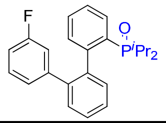
3ab		87	**3bb**		82
3cb		77	**3db**		79
3eb		45	**3fb**		43
3gb		55	**3hb**		64
3ib		58	**3jb**		80

a) All reactions were carried out in the presence of **3aa–3ja** (0.2 mmol), $PhI(OAc)_2$ (3.0 equiv.), $Pd(OAc)_2$ (10 mol%), CF_3CH_2OH (2.0 mL), air atmosphere, 100 °C; b) isolated yields of products.

Table 4 R_2(O)P-directed Pd(II)-catalyzed C–H arylation a)



Entry	Product	Yield (%) b)	Entry	Product	Yield (%) b)
4ab		83	**4bb**		67
4cb		72	**4db**		66
4eb		63 c)	**4fb**		70 c)
4gb		56 c)	**4hb**		60 c)
4ib		67 c)	**4jb**		62 c)

a) All reactions were carried out in the presence of 0.2 mmol of **4aa–4ja**, **4ac–4jc** (2.5 equiv.), $PdCl_2$ (10 mol%), Ag_2CO_3 (0.2 equiv.), PivOH (2.0 equiv.), DMF (4.0 mL); b) isolated yield; c) $PdCl_2$ (20 mol%), Ag_2CO_3 (0.4 equiv.) was used.

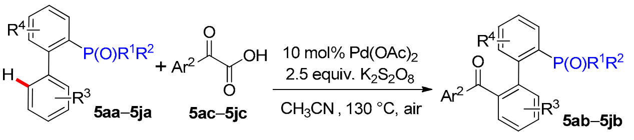
method for the synthesis of 2-phosphorylbiphenyl ketones by Pd-catalyzed C–H acylation with α-oxocarboxylic acids. After systematic screening, the desired product was obtained in 72% yield in the presence of $Pd(OAc)_2$ (10 mol%) and phenylglyoxylic acid (2.0 equiv.) at 130 °C in CH_3CN using $K_2S_2O_8$ (2.5 equiv.) as the oxidant. We then investigated the reactions of various substituted 2-phosphorylbiphenyl derivatives and α-oxocarboxylic acids; the reactions gave the mono-acylation products in all cases (Table 5).

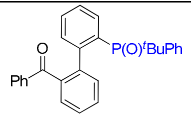
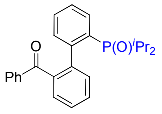
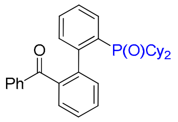
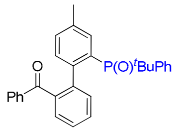
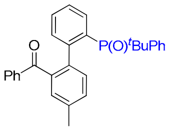
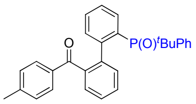
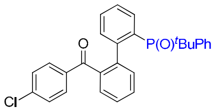
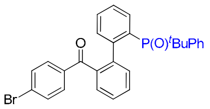
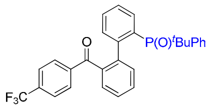
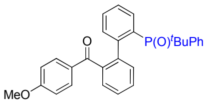
We then performed these reactions using cheaper and readily available benzyl alcohols. After screening various oxidants and solvents, the desired acylated product was obtained in 80% yield with a good ratio (10:1) of mono-acylation to diacylation. The aliphatic alcohol ethanol was also compatible with this reaction, but the yield was low (**6jb**, Table 6).

2.6 Preparation of substituted chiral 2′-phosphorylbiphenyl compounds

Phosphorus ligands play important roles in many metal-catalyzed organic transformations, including many asymmetric reactions [56,57]. The specific characteristics of these ligands are particularly in enhancing the metal catalyst efficiency and controlling chiral induction. The development of concise and efficient ways to construct various ligands is desirable. We easily synthesized various substituted chiral 2′-phosphorylbiphenyl compounds using the commercially available chiral binaphthyl-based diphenylphosphine oxide (*R*)-**1** as the substrate. The ease of this reaction is largely thanks to our $R_2(O)P$-directed Pa-catalyzed C–H functionalization (Table 7).

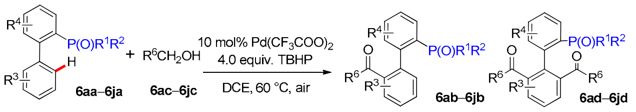
Table 5 $R_2(O)P$-directed Pd(II)-catalyzed C–H acylation $^{a)}$

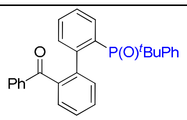
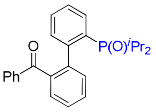
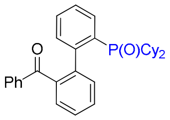
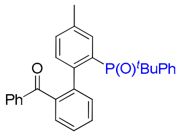
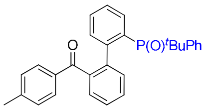
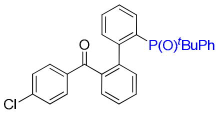
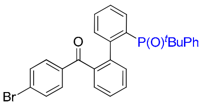
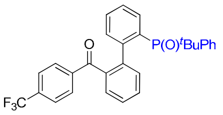
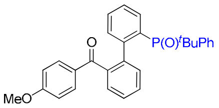
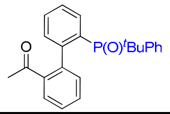


Entry	Product	Yield (%) $^{b)}$	Entry	Product	Yield (%) $^{b)}$
5ab		72	**5bb**		54
5cb		50	**5db**		68
5eb		77	**5fb**		62
5gb		68	**5hb**		58
5ib		52	**5jb**		64

a) All reactions were carried out in the presence of 0.3 mmol of **5aa–5ja** and **5ac–5jc** (2.0 equiv.) in 3 mL CH_3CN at 130 ºC; b) isolated yield.

Table 6 $R_2(O)P$-directed Pd(II)-catalyzed C–H acylation of alcohols $^{a)}$



Entry	Product	Yield (%) $^{b)}$	Entry	Product	Yield (%) $^{b)}$
6ab & **6ad**		80 (10:1)	**6bb**		50
6cb		50	**6db** & **6dd**		74 (8:1)
6eb & **6ed**		68 (8:1)	**6fb** & **6fd**		67 (8:1)
6gb & **6gd**		75 (7:1)	**6hb** & **6hd**		76 (7:1)
6ib & **6id**		76 (12:1)	**6jb**		27

a) All reactions were carried out in the presence of 0.3 mmol of **6aa–6ja** and **6ac–6jc** (4.0 equiv.) in 1.5 mL DCE at 60 ºC; b) isolated yield.

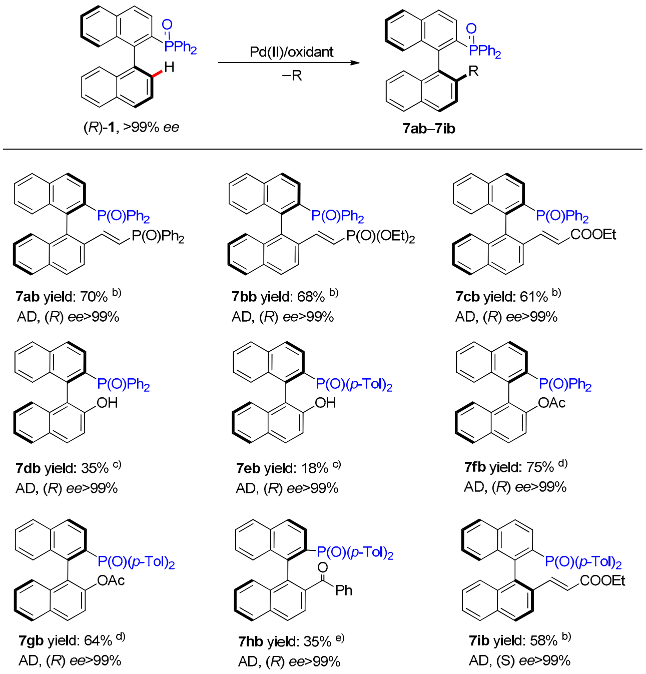
2.7 Proposed mechanisms

Finally, we discuss the reaction mechanism, using $R_2(O)P$-directed Pd(II)-catalyzed C–H olefination as an example. A plausible mechanistic pathway based on our experimental results and previous reports [58,59] is shown in Scheme 2. $Pd(OAc)_2$ first coordinates with the Ac–Gly–OH ligand to form the activate Pd catalyst, which reacts with substrate **1a** by electronic substitution to produce the cyclopalladium intermediate **1A**. This active pretransition intermediate then undergoes olefin insertion with ethyl acrylate to form complex **1B**, which then undergoes Heck-type olefination to give the intermediate **1C**. Finally, the product **2a** is produced by reductive elimination, and the catalyst reinitiates the catalytic cycle.

3 Conclusions and outlook

We developed original and efficient $R_2(O)P$-directed Pd-

Table 7 Preparation of substituted chiral 2′-phosphorylbiphenyl compounds [a)]



7ab yield: 70% [b)]
AD, (R) ee>99%

7bb yield: 68% [b)]
AD, (R) ee>99%

7cb yield: 61% [b)]
AD, (R) ee>99%

7db yield: 35% [c)]
AD, (R) ee>99%

7eb yield: 18% [c)]
AD, (R) ee>99%

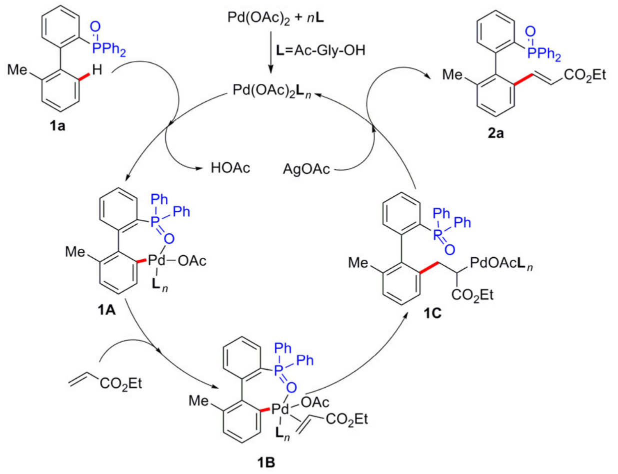
7fb yield: 75% [d)]
AD, (R) ee>99%

7gb yield: 64% [d)]
AD, (R) ee>99%

7hb yield: 35% [e)]
AD, (R) ee>99%

7ib yield: 58% [b)]
AD, (S) ee>99%

a) The yield was isolated and the *ee* value was determined by HPLC; b) **7aa–7ca**, **7ia** (0.3 mmol), **7ac–7cc**, **7ic** (0.9 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Gly–OH (20 mol%), AgOAc (0.9 mmol), CF_3CH_2OH (3.0 mL), 100 °C, 24 h, air atmosphere; c) **7da–7ea** (0.3 mmol), $Pd(CF_3COO)_2$ (10 mol%), $PhI(CF_3COO)_2$ (0.45 mmol), CH_3NO_2 (3.0 mL), 60 °C, 24 h, air atmosphere; d) **7fa–7ga** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (0.9 mmol), CF_3CH_2OH (3.0 mL), 100 °C, 24 h, air atmosphere (0.2 mmol); e) **7ha** (0.3 mmol), benzyl alcohol (0.75 mmol), $Pd(CF_3COO)_2$ (10 mol%), TBHP (1.2 mmol), DCE (3.0 mL), at 60 °C, air atmosphere.



Scheme 2 Proposed Mechanisms of $R_2(O)P$-directed Pd(II)-catalyzed C–H olefination.

catalyzed C–H functionalizations to synthesize various substituted 2′-phosphorylbiphenyl compounds. We expect the methods described in this paper to have significant practical applications, especially in the synthesis of substituted axially chiral oxygen-phosphine or olefin-phosphine ligands. Further studies on axially asymmetric induction are ongoing in our laboratory.

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