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Advanced Synthesis & Catalysis

Formal Olefinic C–H Phosphinylation *via* Alkenyl Sulfonium Salts

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Abstract: Formal olefinic C–P cross-coupling between alkenyl sulfonium salts and secondary phosphine oxides and H-phosphinates has been developed. A base enables construction of alkenyl C–P bonds as well as aliphatic C–P bonds at ambient temperature under an air atmosphere. This protocol provides an alternative access to multisubstituted alkenyl phosphine oxides and phosphinates in 40–99% yield from functionalized alkenes through an interrupted Pummerer activation/base-promoted olefinic C–S bond phosphinylation sequence. Gram-scale preparation and feasible derivatization demonstrated the applicability of the resultant alkenylphosphine oxides.

Keywords: C–H functionalization; Alkenyl sulfonium salts; C–S activation; Phosphinylation; Transition metal-free

Introduction

Site-selective functionalization of multiply reactive arenes and alkenes *via* sulfonium salts through interrupted Pummerer activation has attracted much attention in organic synthesis due to the high reactivity, ease of accessibility and bench stability of the resultant sulfonium salts.[1] Recently, transformations of sulfonium salts have been paid more and more attention[1b,2] since the breakthrough of Ritter thianthrenation enabling highly site-selective aromatic C–H functionalization.[3] However, exploration of alkenyl sulfonium salts is relatively insufficient,[4–9] which is attributed to the multiple reactivity of an alkenyl moiety compared to its aromatic analog. Liebeskind, *et al.* documented the pioneering palladium and nickel-catalyzed C–C bond construction of alkenyl sulfonium salts with organometallic reagents in 1997.[4] Until recent years, alkenyl sulfonium salts, that is, alkenyl thianthrenium salts, have begun to be applied for nickel-catalyzed arylation,[5a] photocatalytic alkylation,[5b] palladium and ruthenium-catalyzed cross-coupling for constructing olefinic C–C and C–halogen bonds,[5c] functionalization of ethylene,[5d] copper-catalyzed selective silylation and borylation,[5e] rhodium-catalyzed/ligand-controlled divergent *ipso*-arylation and *cine*-arylation,[5f] and base-promoted synthesis of allylic amines,[6] *N*-vinylazoles,[7] and alkenyl sulfoxides.[8] These transformations have expanded the applications of alkenyl sulfonium salts as valuable organic building blocks.

Vinyl organophosphorus compounds play an important role in bioactive chemicals,[9] functional materials,[10] and applied chemistry (Figure 1).[11] For example, 1-phenylpropadienyl phosphine oxide

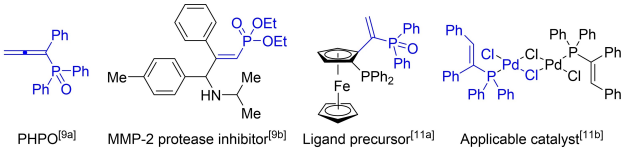


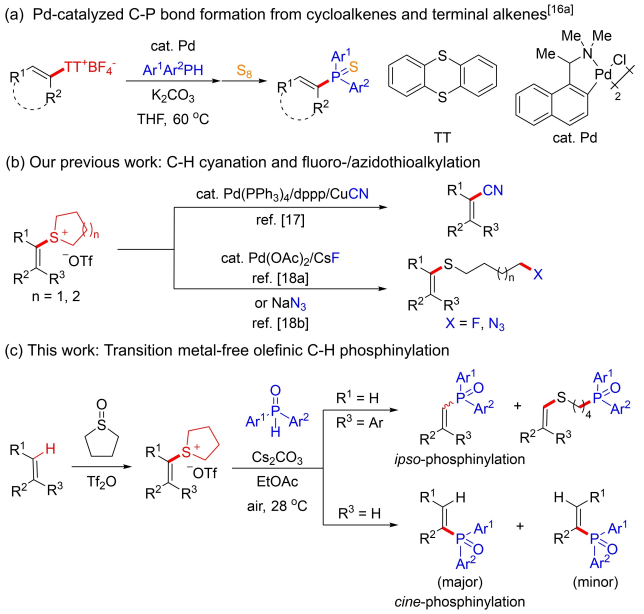
Figure 1. Examples of important organophosphorus molecules.

(PHPO) can be used as a prospective agent to effectively treat ovarian cancer.[9a] 3-Aminovinylphosphonate has been found to be a potent and effective MMP-2 protease inhibitor.[9b] Josiphos-type ligands synthesized by asymmetric hydrogenation of vinylphosphine oxides,[11a] have found industrial application in the production of pharmaceuticals and agrochemicals, and alkenylphosphine palladium catalyst[11b] can exhibit excellent catalytic activity in Suzuki-Miyaura cross-coupling. Several strategies have been developed to synthesize functionalized alkenylphosphine oxides.[12–14] Among them, the direct approaches through nucleophilic addition of alkynes[12] and oxidative cross-coupling of alkenes[13] with secondary phosphine oxides under copper, cobalt, and palladium catalysis are effective and practicable. The cross-coupling reactions of vinyl (pseudo)halides with secondary phosphine oxides are also known for constructing alkenyl C(sp^2)–P bonds.[14] Transition metal-free reaction of vinylbenzoiodoxolones with secondary phosphine oxides was applied to deliver terminal alkenylphosphines.[15] In spite of these significant advances, these known transformations have often encountered hazardous/harsh conditions such as transition metal residuals, stoichiometric oxidants, high temperature, and moisture- and/or air-sensitive conditions. In this regard, environmentally benign and efficient methods are highly desired to construct C–P bonds under mild conditions.

Very recently, Huang, *et al.* reported a one pot, two-step *C,N*-palladacycle-catalyzed cross-coupling between the thianthrenium salts of cyclic and terminal alkenes with diarylphosphines (Scheme 1a).[16] During our continuous exploration of alkene functionalization, site-selective palladium-catalyzed olefinic C–H cyanation[17] and fluorothioalkylation,[18a] and transition-metal-free azidothioalkylation[18b] by tetrahydrothiophenation have been achieved (Scheme 1b). Based on the controllable/enhanced reactivity of the resultant olefinic C(sp^2)–S bonds and the compatibility of the coupling partners, we envisioned that an interrupted Pummerer activation/base-promoted olefinic C–S phosphinylation sequence might be established for the construction of multisubstituted alkenylphosphine oxides and phosphinates under mild conditions (Scheme 1c).

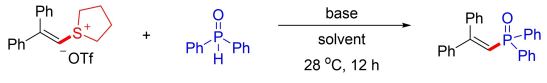
Results and Discussion

Initially, phosphinylation of 1-(2,2-diphenylvinyl)-tetrahydro-1*H*-thiophen-1-ium triflate (**1 a**) with diphenylphosphine oxide (**2 a**) was conducted to explore the optimal conditions (Table 1). The reaction proceeded in the presence of Na_2CO_3 base in THF, but the target *ipso*-phosphinylation product (2,2-diphenylvinyl)diphenylphosphine oxide (**3 a**) was only obtained in 6% yield at ambient temperature within



Scheme 1. C–H Phosphinylation strategies *via* alkenyl sulfonium salts.

Table 1. Optimization of reaction conditions.[a]



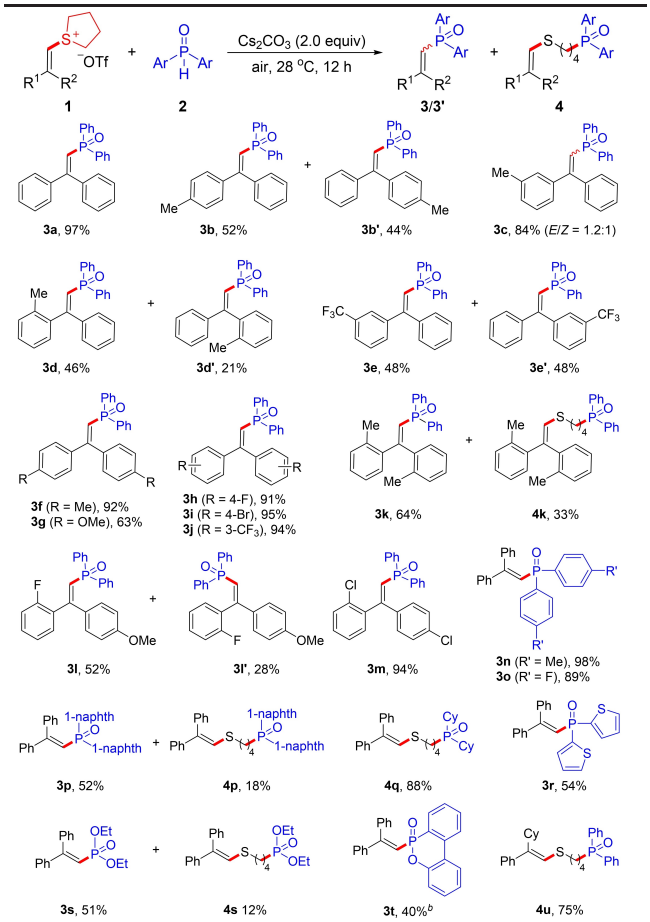
Entry	Base (equiv.)	Solvent	$Ph_2P(O)H$ (equiv.)	Yield[b] [%]
1	Na_2CO_3 (2.0)	THF	2	6
2	K_2CO_3 (2.0)	THF	2	43
3	Cs_2CO_3 (2.0)	THF	2	91
4	DBU (2.0)	THF	2	47
5	Et_3N (2.0)	THF	2	N.D.
6	Cs_2CO_3 (2.0)	CH_2Cl_2	2	81
7	Cs_2CO_3 (2.0)	EtOAc	2	99
8	Cs_2CO_3 (2.0)	DMSO	2	97
9	Cs_2CO_3 (2.0)	DMF	2	71
10	Cs_2CO_3 (2.0)	EtOAc	1.1	99
11	Cs_2CO_3 (2.0)	EtOAc	1.0	90
12	Cs_2CO_3 (1.5)	EtOAc	1.1	93
13	Cs_2CO_3 (1.0)	EtOAc	1.1	58
14		EtOAc	1.1	N.D.
15[c]	Cs_2CO_3 (2.0)	EtOAc	1.1	99
16[c,d]	Cs_2CO_3 (2.0)	EtOAc	1.1	84
17[c,e]	Cs_2CO_3 (2.0)	EtOAc	1.1	98 (97)[f]

[a] Conditions: **1 a** (0.2 mmol), **2 a** (0.4 mmol), Cs_2CO_3 (0.4 mmol), solvent (2.0 mL), 28 °C, 0.1 MPa N_2, 12 h.
[b] Determined by ^1H NMR analysis with $MeNO_2$ as an internal standard.
[c] Under air.
[d] 6 h.
[e] **1 a** (0.3 mmol).
[f] Isolated yield given in parentheses.

12 h (Table 1, entry 1). To our delight, K_2CO_3, Cs_2CO_3 and DBU promoted the formation of **3a** in 43%, 91%, and 47% yields, respectively, while Et_3N completely suppressed the reaction (Table 1, entries 2–5). EtOAc was found to be the best reaction medium to quantitatively give the target product and DMSO was also a suitable reaction medium (Table 1, entries 3 and 6–10). Lowering the amount of **2a** to 1.1 equiv. could also efficiently lead to **3a** (99%) (Table 1, entries 7 and 10–11). Two equivalents of Cs_2CO_3 base are crucial for the efficient *ipso*-phosphinylation and the reaction did not occur in the absence of a base (Table 1, entries 7 and 12–14). Under an air atmosphere, the reaction also efficiently occurred (Table 1, entry 15). Shortening the reaction time to 6 hours, the reaction efficiency was significantly reduced to form **3a** in 84% yield (Table 1, entry 16). A 97% isolated yield of **3a** was obtained on a 0.3 mmol scale of **1a** (Table 1, entry 17). It is noteworthy that addition of water (5 equiv.) lessened the yield to 75%.

Next, the scope of terminal alkenyl sulfonium salts (**1**) was investigated under the optimal reaction conditions (Table 2). Alkenyl sulfonium salt **1a** bearing two unsubstituted phenyl groups reacted with **2a** to nearly quantitatively form the target *ipso*-phosphoinlation product **3a** (97%). When one of the aryl groups in the 1,1-diaryl moiety of sulfonium salts **1** was monosubstituted at the *para*-, *meta*-, or *ortho*-position, the target products, that is, **3b**/**3b**′–**3e**/**3e**′, were produced in good to excellent yields (67–96%). It is noteworthy that (*E*)-**3b**/(*Z*)-**3b**′, (*E*)-**3d**/(*Z*)-**3d**′ and (*E*)-**3e**/(*Z*)-**3e**′ were isolated as separable isomers and the (*E*)-isomers were predominantly formed. 2-Methyl exhibited an obvious steric impact on forming **3d** (46%) and **3d**′ (21%), and 3-CF_3 did not exhibit a steric effect on the formation of **3e** (48%) and **3e**′ (48%). When both the aryl groups of **1** were substituted by electron-donating or withdrawing groups such as methyl, methoxy, fluoro, bromo, and 3-trifluoromethyl, the target products **3f** and **3h**–**3j** were obtained in excellent yields (91–95%), while 4-methoxy exhibited an obvious steric effect to result in **3g** in only 63% yield. Unexpectedly, 2,2′-dimethyl-substituted diaryl sulfonium salt **1k** reacted with **2a**, forming the target alkenyl C–P product **3k** (64%) through the desired alkenyl C–S bond cleavage as well as an aliphatic C–P product **4k** (33%) through ring-opening aliphatic C–S bond cleavage. 2-Fluoro and 2-chloro groups compromised both the steric effects on generating **3l** (52%)/**3l**′ (28%) and **3m** (94%), respectively. Diphenyl sulfonium salt **1a** could also efficiently undergo the phosphinylation reaction with different secondary phosphine oxides. 4-Methyl/fluoro-substituted diarylphosphine oxides exhibited an obvious electronic effect on generation of **3n** (98%) and **3o** (89%), respectively. Bulky di(1-napthyl)phosphine oxide (**2p**) showed a reactivity much lower than its

Table 2. *ipso*-Phosphinylation of terminal alkenyl sulfonium salts.[a]



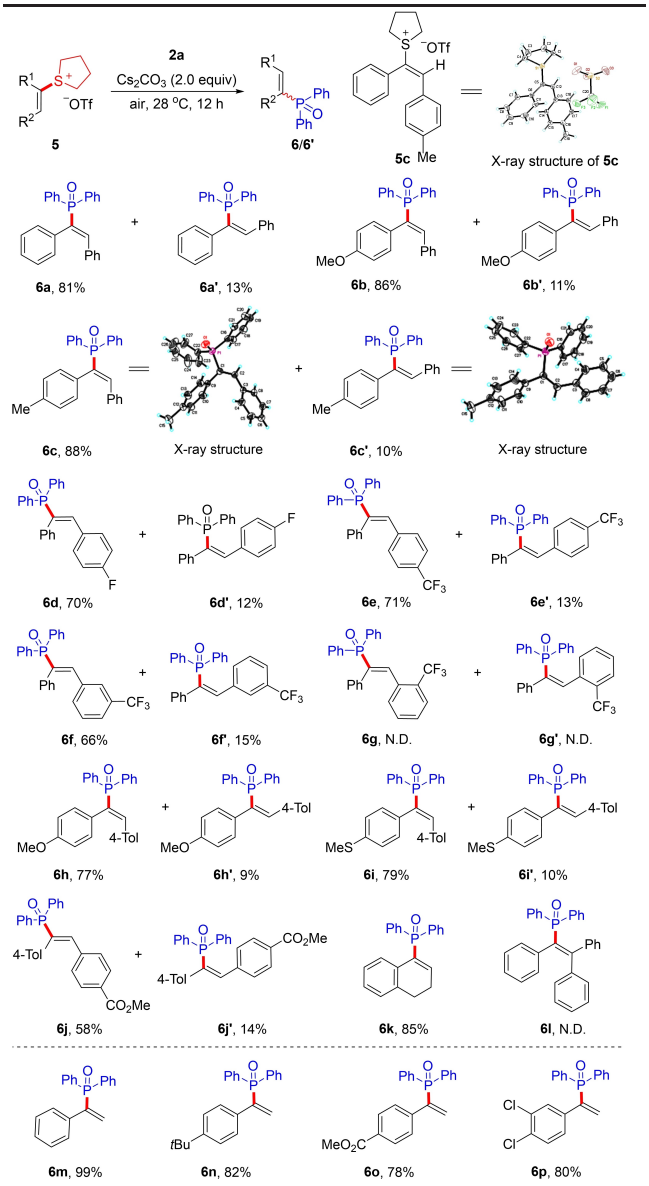
[a] Conditions: **1** (0.3 mmol), **2** (0.33 mmol), Cs_2CO_3 (0.6 mmol), EtOAc (2 mL), 28 °C, air, 12 h. Isolated yields. Ratio of (*E*)/(*Z*)-isomers determined through ^{1}H NMR analysis.
[b] 48 h.

diphenyl analog (**2a**), giving the target product **3p** in 52% yield with formation of the ring-opening aliphatic C–P product **4p** (18%) as the side product. Notably, the dialkyl phosphine oxide, that is, dicyclohexylphosphine oxide (**2q**), could also efficiently react with **1a**, forming the corresponding aliphatic C–P product **4q** (88%) as the only product. Di(2-thienyl)phosphine oxide (**2r**) reacted less efficiently with **1a** to offer **3r** (54%). H-phosphinate $HP(O)(OEt)_2$ reacted with **1a** to give the corresponding alkenyl phosphinate **3s** (51%) and the aliphatic C–P product **4s** (12%). However, cyclic H-phosphinate **2t** only demonstrated a low reactivity to form **3t** (40%) by extending the reaction time to 48 h. Terminal 2-phenyl-2-cyclohexylvinyl sulfonium salt (**1u**) also exhibited a good reactivity to **2a**, leading to aliphatic C–P product **4u** in 75% yield.

Then, internal alkenyl sulfonium salts (**5**) were used as the substrates to extend the protocol generality

(Table 3). Different from the *ipso*-phosphinylation of terminal alkenyl sulfonium salts **1**, internal alkenyl sulfonium salts **5** only underwent *cine*-phosphinylation under the standard conditions. Unsubstituted stilbenyl sulfonium salt **5a** reacted with **2a** to efficiently generate the *cine*-phosphinylation product **6a** (81%)/**6a′** (13%) which are two separable isomers with a (*E*)/(*Z*) ratio of 6.2:1.0. When an internal alkene was transformed to a sulfonium salt by interrupted Pummerer activation of its olefinic C–H bonds, the reaction usually occurs at the relatively electron-poor olefinic carbon atom, forming a new alkenyl C–S bond.

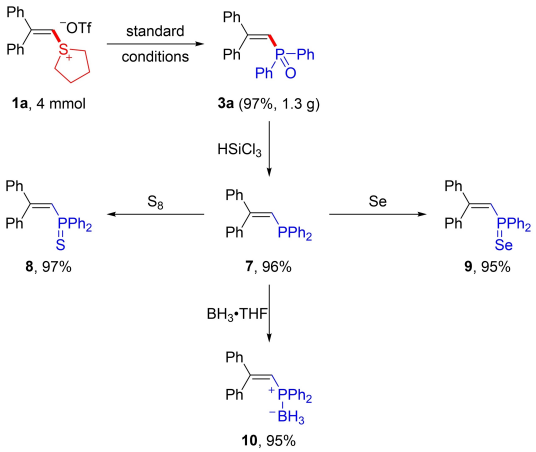
Table 3. *cine*-Phosphinylation of internal alkenyl and styryl sulfonium salts.[a]



[a] Conditions: **5** (0.3 mmol), **2a** (0.33 mmol), Cs_2CO_3 (0.6 mmol), EtOAc (2 mL), 28 °C, air, 12 h. Isolated yields.

However, during the studied phosphinylation process, the reaction occured at the relatively electron-rich olefinic carbon atom, presenting a *cine* reaction model. The *cine*-phosphinylation products from the unsymmetrical internal alkenes, that is, **6b** (86%)/**6b′** (11%), and **6c** (88%)/**6c′** (10%), were efficiently formed in the same fashion. Such a *cine* reaction model was identified by the X-ray crystallographic structural characterization of alkenyl sulfonium salt **5c** and its corresponding alkenyl C–P products **6c** and **6c′** (see the SI). Electron-withdrawing groups fluoro and trifluoromethyl at the 4- or 3-position of one phenyl group in the stilbenyl moiety of **5** deteriorated the reaction efficiency to some extent, resulting in **6d** (70%)/**6d′** (12%), **6e** (71%)/**6e′** (13%), and **6f** (66%)/**6f′** (15%), respectively. It should be noted that 2-CF_3 completely inhibited the reaction to give no detectable amount of the target products **6g**/**6g′**. When both the two aryl moieties were substituted by electron-donating groups such as methyl, methoxy, or methylthio, the target products **6h** (77%)/**6h′** (9%) and **6i** (79%)/**6i′** (10%) could also be efficiently accessed, whereas electron-withdraw CO_2Me group obviously lessened the product yields for **6j** (58%)/**6j′** (14%). Interestingly, cyclic alkenyl sulfonium salt, that is, (3,4-dihydronaphthyl)-sulfonium salt (**5k**) reacted with **2a** to afford **6k** in 85% yield. Increasing the steric bulkiness by using triphenylvinyl sulfonium salt (**5l**), no target product **6l** was detected. Unexpectedly, terminal styryl sulfonium salts (**5m**–**5p**) underwent the *cine*-type phosphinylation with **2a**, affording the *cine*-phosphinylation products **6m**–**6p** (78–99%).

To verify the practicality of the present phosphinylation protocol, gram-scale synthesis of alkenylphosphine oxide **3a** was performed, giving a 97% isolated yield (Scheme 2). Reduction of **3a** with excessive $HSiCl_3$ conveniently offered (2,2-diphenylvinyl)phosphine **7** in 96% isolated yield.



Scheme 2. Gram-scale preparation and derivatization of alkenylphosphine oxide **3a**.

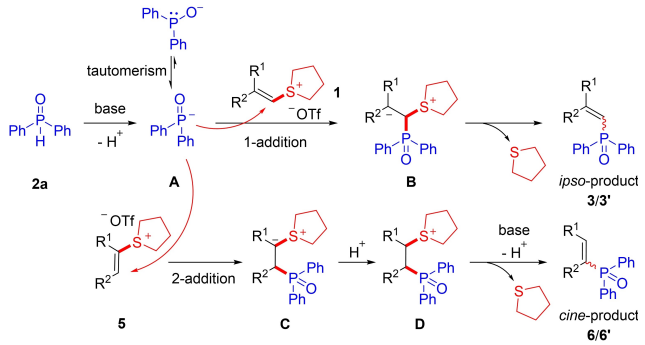
Various modifications of the hydrophosphination product **7** were also readily carried out. Treated it with S_8, Se, and BH_3·THF, alkenyl phosphine sulfide **8**, phosphine selenide **9**, and phosphine-borane adduct **10** were obtained with high efficiency and improved stability, respectively. All these derivatives are potentially valuable compounds in synthetic chemistry, material science, and other areas.

Radical trapping experiments were carried out to investigate the reaction mechanism. Under the standard conditions addition of radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the reaction system of sulfonium salt **1a** and **2a** led to **3a** in 94–99% yields, excluding a radical reaction pathway (see the SI).

Based on the literature work on functionalization of alkenyl sulfonium salts and synthesis of alkenylphosphine oxide,[7b,8,14b] a plausible phosphinylation mechanism is proposed (Scheme 3). Initially, the H-phosphine oxide (**2a**) undergoes deprotonation in the presence of Cs_2CO_3 base to form phosphine oxide anion **A** which then nucleophilically attacks the terminal alkenyl C–S bond of **1** to generate intermediate **B** through 1-addition. Species **B** subsequently releases tetrahydrothiophene to provide the *ipso*-phosphinylation product **3**/**3′**. A minority of sulfonium salt **1** proceeds nucleophilic substitution by anion **A** *via* C(sp^3) –S bond cleavage to form an aliphatic C–P bond and generate phosphoalkylation product **4**.[18b] On the other hand, anion **A** undergoes nucleophilic addition to the internal alkenyl sulfonium salt of type **5** *via* 2-addition to form intermediate **C**,[8,19] followed by protonation to give intermediate **D**. Eventually, species **D** occurs base-promoted elimination to produce the *cine*-phosphinylation product **6**/**6′** with loss of tetrahydrothiophene.

Conclusions

In conclusion, an interrupted Pummerer/base-promoted cross-coupling strategy has been successfully developed to access multisubstituted alkenylphosphine oxides as well as phosphothioalkylation products. The formal transition metal-free olefinic C–H phosphinylation with secondary phosphine oxides and H-phosphinates *via* alkenyl sulfonium salts features broad substrate scopes, excellent functional group compatibility, mild conditions, and simple operation. Scale-up preparation and product derivatization have demonstrated the prospective practicality of the resultant alkenylphosphine oxides.



Scheme 3. Proposed mechanism.

Experimental Section

Typical Procedure for the Synthesis of 3a

A mixture of **1a** (124.9 mg, 0.3 mmol), $Ph_2P(O)H$ (**2a**) (66.7 mg, 0.33 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol) in EtOAc (2 mL) was stirred at 28 °C for 12 h under air atmosphere. After **1a** was completely consumed by TLC monitoring on silica gel, the reaction mixture was filtered through a short pad of celite, and rinsed with CH_2Cl_2/EtOAc (10 mL, v/v = 1:1). The combined filtrate was concentrated under reduced pressure, and the resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/EtOAc = 2:1, v/v), affording **3a** (110.8 mg, 97%) as white solid.

CCDC-2308673 (**5c**), 2308671 (**6c**), and 2308670 (**6c′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Acknowledgements

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