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Authors: Wen-Jing Xiao, Hong-Mei Guo, Quan-Quan Zhou, Xuan Jiang, and De-Qing Shi

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Catalyst- and Oxidant-Free Desulfonative C-P Couplings for the Synthesis of Phosphine Oxides and Phosphonates

Hong-Mei Guo,[a,‡] Quan-Quan Zhou,[a,‡] Xuan Jiang,[a] De-Qing Shi[a,]* and Wen-Jing Xiao[a,]*

[a] Hubei International Scientific and Technological Cooperation Base of Pesticide and Green Synthesis, Key Laboratory of Pesticides & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China
Fax: (+86)-27-67862041; Tel: (+86)-27-67862041; E-mail: chshidq@mail.ccnu.edu.cn; wxiao@mail.ccnu.edu.cn

[‡] These two authors contribute to this work equally.

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Abstract: An efficient and practical approach towards phosphine oxides and phosphonates has been successfully developed through the desulfonative coupling of various sulfones with secondary phosphine oxides and phosphites. This protocol features simple experimental procedures under mild conditions (i.e., catalyst- and oxidant-free, room temperature and open to air). By doing so, a variety of alkynyl, alkenyl and allyl phosphine oxides or phosphonates can be produced in generally good reaction efficiency and selectivity (31 examples, up to 98% yield).

Keywords: phosphorus compounds; sulfones; desulfonative coupling; catalyst-free; oxidant-free

Organophosphorus compounds are of great importance in many functional materials and bioactive fine chemicals, such as agrochemicals, pharmaceuticals and natural products.[1,2] Moreover, they are widely employed as versatile synthetic reagents or precursors in organic synthesis,[3] i.e., phosphonates in Wadsworth- Horner-Emmons reaction, phosphonium salts in Wittig reaction, phosphine ligands in transition metal catalysis or nucleophilic catalysts.[4] In particular, alkynyl, alkenyl and allyl phosphorus compounds not only display significant pharmaceutical properties, for example, the progesterone receptor antagonist,[2c] the blood-pressure lowering fosinopril[2d] and the biologically active ethisterone (Figure 1),[2e] but also function as important building blocks in organic chemistry for the synthesis of bifunctional adducts, carbo- and hetero-cyclic compounds.[5] Therefore, it is not surprising that many synthetic endeavours have been made to access the P-containing compounds.[6] Among them, the transition-metal-catalyzed cross-coupling reaction of aryl halides or triflates (-OTf) with secondary phosphines has established as one of the most efficient and promising procedures for C-P bond formations.[7] The pioneering work was disclosed by Hirao and coworkers, who developed a palladium -catalyzed phosphination of aryl halides with P(O)H compounds.[8] Since then, a variety of C-P coupling reactions have been established, especially using palladium,[9] copper,[10] silver[11] or nickel[12] catalysis. Despite these remarkable advances, many transformations often suffered from harsh and hazardous

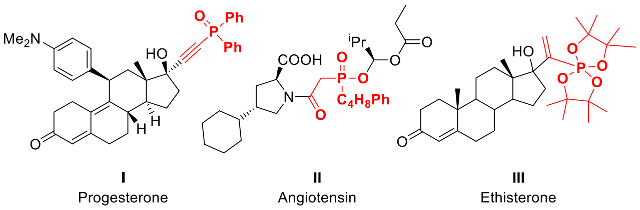
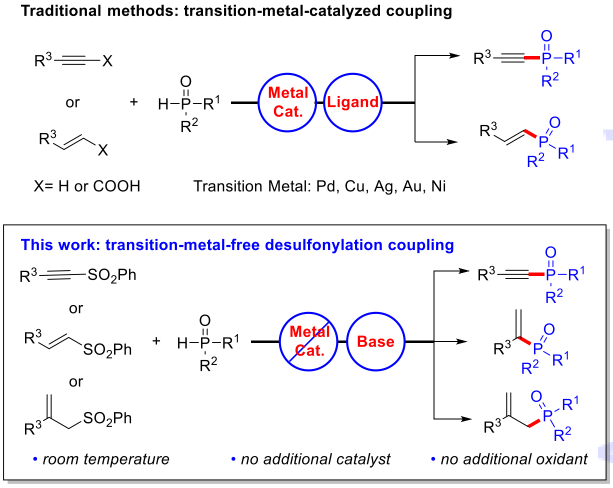


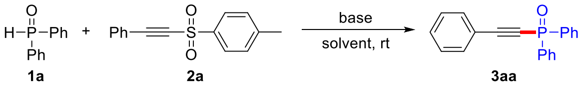
Figure 1. Some important biologically active P-containing molecules.



Scheme 1. Synthetic methods for C-P bond formation.

conditions, for example, transition metal residual, moisture or air sensitivity, multi-step-manufactured ligands, stoichiometric oxidants, and/or elevated temperature. In this regard, the development of an efficient and environmentally benign method for the direct construction of C(sp, sp^2, sp^3)-P bonds under transition metal- and oxidant-free conditions is still highly desirable.[13] Based on our continued interest in the C-P bond formation reactions,[14] we herein present a novel and practical method for the formation of a variety of C-P bonds through the desulfonative coupling[15] of alkynyl, alkenyl and allyl sulfones with secondary phosphine oxides and phosphites in a single-flask operation under mild conditions. This strategy provides the highly regioselective synthesis of structural diversely functionalized organophosphorus compounds in good to excellent reaction efficiency.

Table 1. Optimization of the reaction conditions.[a]

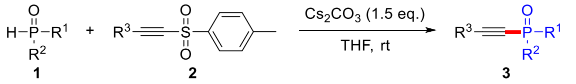


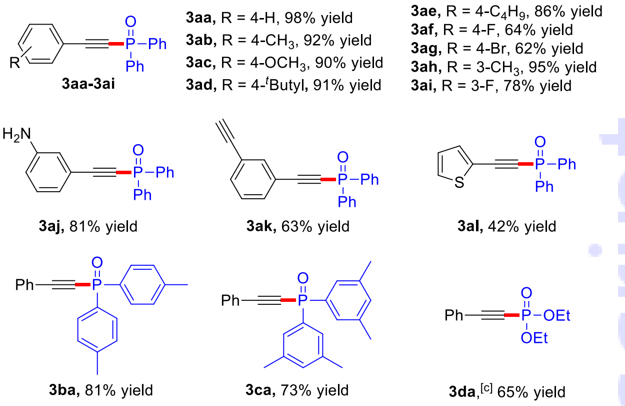
Entry	Base	Solvent	Time (h)	**3aa** Yield[b] (%)
1	Na_2CO_3	THF	1	8
2	K_3PO_4	THF	1	27
3	KOH	THF	1	56
4	Cs_2CO_3	THF	1	98
5[c]	Cs_2CO_3	THF	1	95
6		THF	1	5
7	Cs_2CO_3	$CHCl_3$	1	29
8	Cs_2CO_3	CH_3OH	1	37
9	Cs_2CO_3	$PhCF_3$	1	72
10	Cs_2CO_3	CH_3CN	3	80
11	Cs_2CO_3	DMSO	3	63

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), base (0.3 mmol), solvent (2.0 mL) at room temperature under air atmosphere. [b] Isolated yield. [c] In an open flask.

We initiated this study using 1-methyl-4-((phenylethynyl)sulfonyl)benzene (**2a**) and diphenylphosphine oxide (**1a**) as model substrates for the desulfonative coupling reaction. To our delight, this reaction did indeed work in THF with the use of Na_2CO_3 as the base and the desired product diphenyl(phenylethynyl)phosphine oxide (**3aa**) was isolated in 8% yield (Table 1, entry 1). Subsequently, some inorganic bases, such as K_3PO_4, KOH and Cs_2CO_3, were evaluated (Table 1, entries 2-4), and product **3aa** was delivered in 98% yield when Cs_2CO_3 was used (Table 1, entry 4). It is worth noting that, the reaction could be conducted in an open flask condition at room temperature without affecting the reaction efficiency (Table 1, entry 5: 95% yield). Control experiment showed that the base is crucial in the desulfonative alkynylation (Table 1, entry 6: 5% yield). Solvent screening indicated that THF is the optimal reaction media (Table 1, entry 5). Other solvents, such as protic solvent CH_3OH, medium polar solvent $CHCl_3$, or more high dielectric aprotic solvents ($PhCF_3$, CH_3CN, DMSO) proved detrimental for the reaction (Table 1, entries 7-11).

Table 2. Scope of the alkynylation of phosphine oxides and phosphites.[a,b]



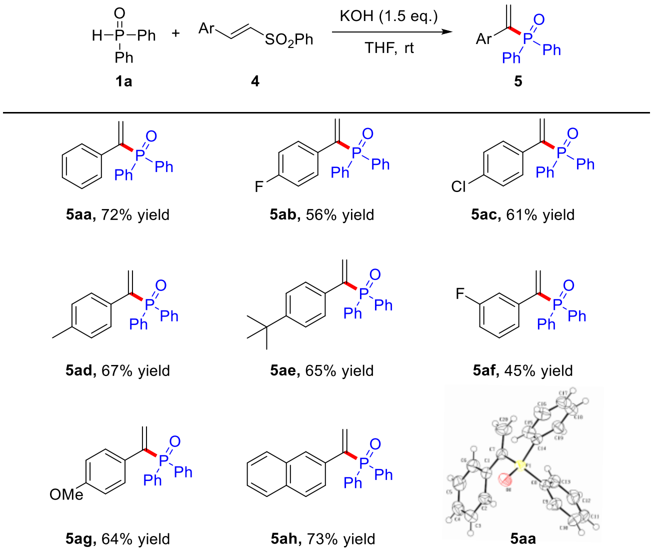

3aa-3ai
3aa, R = 4-H, 98% yield
3ab, R = 4-CH$_3$, 92% yield
3ac, R = 4-OCH$_3$, 90% yield
3ad, R = 4-^{t}Butyl, 91% yield
3ae, R = 4-C$_4$H$_9$, 86% yield
3af, R = 4-F, 64% yield
3ag, R = 4-Br, 62% yield
3ah, R = 3-CH$_3$, 95% yield
3ai, R = 3-F, 78% yield
3aj, 81% yield
3ak, 63% yield
3al, 42% yield
3ba, 81% yield
3ca, 73% yield
3da,[c] 65% yield

[a] Standard condtions as indicated in entry 4 of Table 1. [b] Isolated yield. [c] At 60 ºC.

Under optimized reaction conditions, we probed the substrates scope of the C-P coupling reaction of diphenylphosphine oxide (**1a**) with various alkynyl sulfones. As highlighted in Table 2, the coupling reaction underwent well and gave the desired products in good to excellent yields. Substrates bearing either electron-donating groups (e.g., CH_3, OCH_3, ^{t}Bu, and ^{n}Bu) or electron- withdrawing groups (e.g., F and Br), either para- or meta-substituted on the benzene ring, were found to be suitable for the reaction, and corresponding products **3aa-3ai** were obtained in moderate to high yields (Table 2, 62-98% yields). Notably, the bromo-substituted substrate tolerated well in this reaction and gave the bromo-containing product **3ag** (Table 2, 62% yield), which is usually difficult for transition-metal-catalyzed C-P coupling reactions. Moreover, functional groups typically sensitive to transition metal catalysis were tolerated, which included unactivated alkynyl and unprotected amino groups (Table 2, **3aj-3ak**: 63-81% yields). Furthermore, heteroaryl-substituted alkynyl sulfone reagent **2l** was applicable as well, affording the desired product **3al** in a moderate yield (Table 2, 42% yield). In addition, the effect of the different leaving groups of alkynes on the alkynylation were also explored. When [(methylsulfonyl)ethynyl]benzene (**2m**) or [(trifluoromethylsulfonyl)ethynyl]benzene (**2n**) was used as the substrate under the standard condition, to our delight, the P-alkynylation reaction underwent smoothly and the desired product **3aa** was afforded in 81% and 43% isolated yields, respectively. When (bromoethynyl)benzene (**2o**) was employed, unfortunately, the reaction did not occurred and no desired product was obtained. These results might imply that substituted sulfonyl groups played a vital role on the P-alkynylation (see the supporting information). With regard to secondary phosphine oxides, bis-(4-tolyl)- and bis-(3,5-dimethylphenyl) substituted phosphine oxides could undergo this coupling reaction and structurally diverse products **3ba-3ca** were delivered in good to excellent yields (Table 2, 73-81% yields). In addition, diethyl phosphite was amenable to the coupling reaction and gave the desired phosphonate product **3da** in moderate yield (Table 2, 65% yield).

After our success on the C(sp)-P coupling, we wonder whether this procedure is suitable for C(sp^2)-P bond formations. After briefly screening the reaction conditions,[16] we successfully carried out the desulfonative alkenylation of $Ph_2P(O)H$ with a variety of vinyl sulfones under mild conditions. Note that the reaction displayed high regioselectivity and afforded the α-aryl vinyl phosphine oxides in moderate yields. The structure **5aa** was confirmed by X-ray single-crystal diffraction.[17] Based on the importance of α-aryl vinyl phosphine oxides,[2e,18] we explored the functional group tolerance of various vinyl sulfones in the direct P-alkenylation. As summarized in Table 3, a range of vinyl sulfones could be employed successfully in this desulfonative alkenylation. The electronic and steric properties of substituents on the benzene ring (e.g., F, Cl, Me, OMe and ^{t}Bu) had no obvious influence on the reaction efficiency, and the corresponding coupling products **5aa-5ag** were provided in moderate isolated yields (Table 3, 45-72% yields). It was found that naphthalene-containing substrate could also be transformed successfully into the corresponding product **5ah** (Table 3, 73% yield).

Table 3. Scope of the alkenylation of phosphine oxides.[a,b]



5aa, 72% yield **5ab**, 56% yield **5ac**, 61% yield

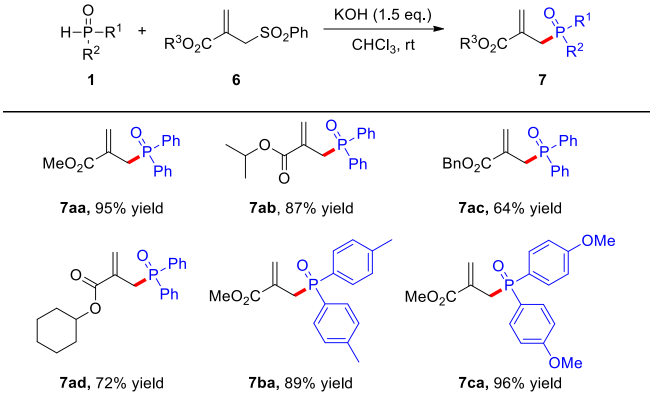
5ad, 67% yield **5ae**, 65% yield **5af**, 45% yield

5ag, 64% yield **5ah**, 73% yield **5aa**

[a] Reaction conditions: **1a** (0.3 mmol), **4** (0.2 mmol), KOH (0.3 mmol) and THF (5.0 mL) at room temperature in air atmosphere . [b] Isolated yield.

In addition, allylphosphine oxides are also very useful building blocks for the synthesis of natural products and pharmaceutical molecules.[19] However, to the best of our knowledge, there is no report on the direct P-allylation of phosphine oxides with allyl sulfones under transition metal- and oxidant-free conditions. Encouraged by above results, we tried to extend our strategy to the direct P-allylation under mild conditions. To our delight, P-allylation product **7aa** was obtained in an excellent yield after a simple optimization study.[20] As presented in Table 4, a variety of allyl sulfone substrates exhibited good reactivity (Table 4, **7aa-7ad**: 64-95% yields). Furthermore, a variety of secondary phosphine oxides were compatible in the P-allylation, affording the corresponding products **7ba-7ca** in excellent yields (Table 4, 89-96% yields).

Table 4. Scope of the allylation of phosphine oxides.[a,b]



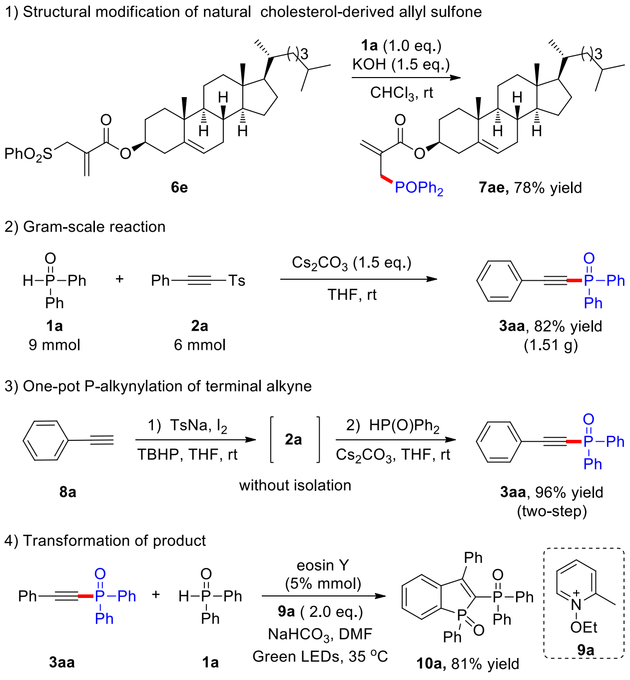
7aa, 95% yield **7ab**, 87% yield **7ac**, 64% yield

7ad, 72% yield **7ba**, 89% yield **7ca**, 96% yield

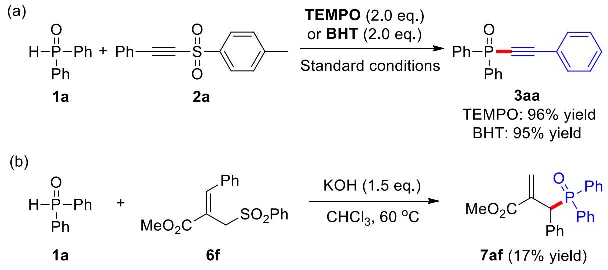
[a] Reaction conditions: **1** (0.2 mmol), **6** (0.3 mmol), KOH (0.3 mmol), and $CHCl_3$ (2.0 mL) at room temperature under air atmosphere. [b] Isolated yield.

The synthetic application of this direct C-P bond formation was performed. Firstly, the reaction of diphenylphosphine oxide (**1a)** and cholesterol-derived allyl sulfone (**6e**) was carried out, producing allylphosphine oxide **7ae** in 78% yield (Scheme 2, eq. 1). Then, a gram-scale alkynylation reaction of substrates **1a** and **2a** was implemented and this reaction proceeded smoothly to afford the desired coupling product **3aa** in 82% yield (Scheme 2, eq. 2). Additionally, a “one-pot” alkynylation of diphenylphosphine oxide (**1a)** with ethynylbenzene (**8a)** was also executed, P-alkynylation product **3aa** could be obtained in 96% yield under the optimal condition (Scheme 2, eq. 3). Furthermore, diphenyl(phenylethynyl)phosphine oxide **3aa** can be easily transformed to benzo[b]phosphole oxide **10a** through a photoredox catalyzed oxidative C−H/P−H functionalization. As a result, a promising scaffold of organic electronics and bioimaging probes was constructed in 81% yield (Scheme 2, eq. 4).[21]

Some control experiments were performed in order to probe a possible mechanism for this transformation. As shown in Scheme 3, when radical scavengers, such as TEMPO or BHT, were introduced to the model reaction of substrates **1a** and **2a**, reaction efficiencies were not affected. These results can rule out the radical pathway (Scheme 3a). In addition, the desulfonative coupling reaction of diphenylphosphine oxide (**1a**) and (Z)-methyl-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**6f**) was performed under the standard condition, the single product **7af** was obtained in 17% yield (Scheme 3b), which suggested a S_N2' substitution mechanism.

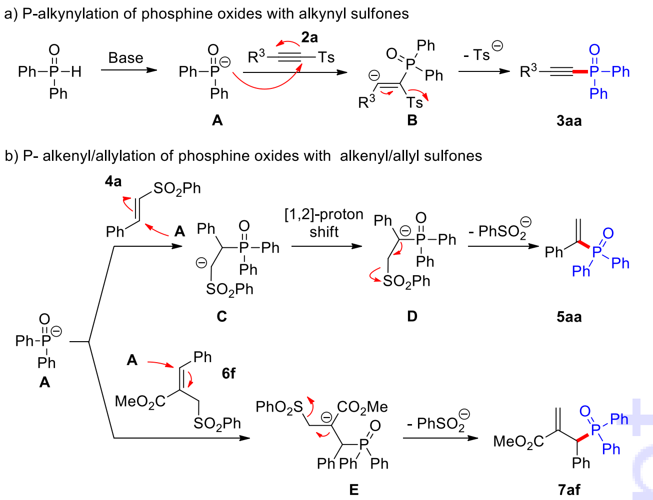


Scheme 2. Synthetic applications of the methodology.



Scheme 3. Experiments for the mechanistic study.

On the basis of our observations and some related literatures,[22] a plausible mechanism for direct desulfonative coupling reactions was proposed in scheme 4. Initially, phosphine oxide anion **A** was formed from H-phosphine oxides in the presence of base, then **A** processed a nucleophilic addition with **2a** to generated intermediate **B**, which subsequently underwent desulfonylation to provide alkynyl phosphine oxide **3aa** for P-alkynylation. The good regioselectivity of the reaction might be due to the elimination of benzenesulfinate anion and gave a stable alkynyl phosphine oxide. (Scheme 4a). On the other hand, **A** was acted with **4a** and **6f** respectively to give the intermediates **C** and **E** through a nucleophilic addition, which underwent the elimination of benzenesulfinate (a 1,2-proton transfer for P-alkenylation) to give the alkenyl/allyl phosphine oxide **5aa** and **7af**, respectively. (Scheme 4b).



Scheme 4. Proposed mechanisms.

In conclusion, we have developed a novel and convenient protocol for the desulfonative alkynylation, alkenylation and allylation of secondary phosphine oxides or phosphites. These desulfonative C-P coupling reactions proceeded well in the absence of any catalyst and oxidant. This process features a broad substrate scope and functional group tolerance, thus providing an attractive access to construct C(sp)-P, C(sp^2)-P and C(sp^3)-P bonds in moderate to good yields under very mild conditions.

Experimental Section

Typical Procedure for the Synthesis of Alkynylphosphine Oxides: To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.30 mmol, 60.66 mg), **2a** (0.20 mmol, 51.26 mg) and Cs_2CO_3 (0.30 mmol, 97.75 mg) in 2 mL of THF. The solution was stirred at room temperature and monitored to completion by TLC analysis. After that the reaction solution was concentrated under vacuum and the crude was purified by flash chromatography, eluting with petroleum ether and ethyl acetate to afford the product **3aa** as a white solid in 98% yield.

Typical Procedure for the Synthesis of alkenylphosphine Oxides: To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.30 mmol, 60.66 mg), **4a** (0.20 mmol, 48.82 mg) and KOH (0.30 mmol, 16.83 mg) in 5 mL of THF. The solution was stirred at room temperature and monitored to completion by TLC analysis. After that the reaction solution was concentrated under vacuum and the crude was purified by flash chromatography, eluting with petroleum ether and ethyl acetate to afford the product **5aa** as a white solid in 72% yield.

Typical Procedure for the Synthesis of allylphosphine Oxides: To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.20 mmol, 40.44 mg), **6a** (0.30 mmol, 72.09 mg) and KOH (0.30 mmol, 16.83 mg) in 2 mL of $CHCl_3$. The solution was stirred at room temperature and monitored to completion by TLC analysis. After that the reaction solution was concentrated under vacuum and the crude was purified by flash chromatography, eluting with petroleum ether and ethyl acetate to afford the product **7aa** as a white solid in 95% yield.

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[16] For the detailed condition optimization of desulfonyl alkenylation, please see Supporting Information.

[17] The structure based on the X-ray-diffraction analysis can be found in the Supporting Information. CCDC-1546010 contains 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/data_request/cif.

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COMMUNICATION

Catalyst- and Oxidant-Free Desulfonative C-P Couplings for the Synthesis of Phosphine Oxides and Phosphonates

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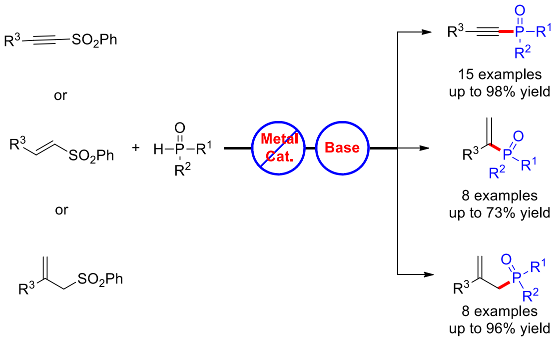
Hong-Mei Guo,[a,‡] Quan-Quan Zhou,[a,‡] Xuan Jiang,[a]
De-Qing Shi[a,]* and Wen-Jing Xiao[a]*



• *room temperature* • *no additional catalyst* • *no additional oxidant*