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Copper-Catalyzed P–H Insertions of α-Imino Carbenes for the Preparation of 3-Phosphinoylindoles

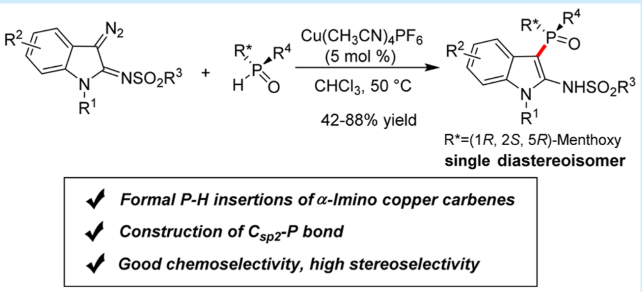
Lisheng Wang,[†] Yi Wu,[†] Yang Liu,[†] Hua Yang,[†] Xu Liu,[†] Jianyi Wang,[†] Xiaoxun Li,[‡] and Jun Jiang*[,†]

[†]School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, P. R. China

[‡]Department of Chemistry, Stanford University, Stanford, California 94305-5580, United States

S *Supporting Information*

ABSTRACT: A highly efficient P–H insertion of α-imino copper carbene into H-phosphine oxides, leading to 3-phosphinoylindoles with a broad substrate diversity and good chemoselectivity, is established. This methodology provides a rapid and efficient approach for the C (sp^2)–P bond formation via the P–H insertion strategy. The stereoselective P–H insertion of α-imino copper carbene represents a unique example of asymmetric P–H insertion, affording P-stereogenic 3-phosphinoylindoles with high stereoselectivities.

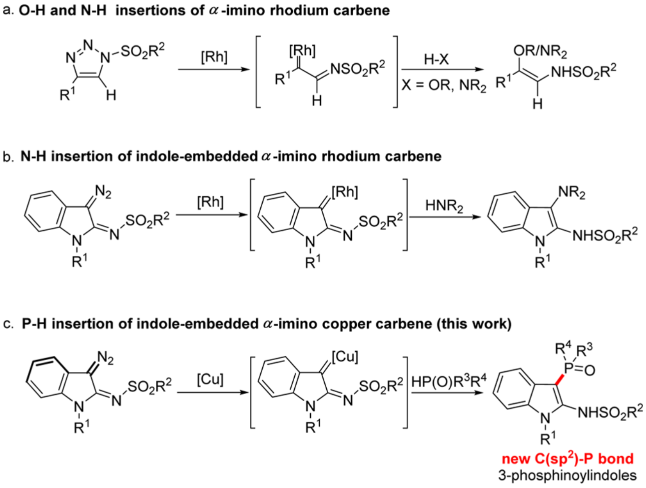


The highly efficient construction of carbon–heteroatom bonds is one of the most pursued goals in modern organic synthesis. Transition-metal-catalyzed insertion of carbenes and carbenoids generated in situ from α-diazo carbonyl compounds into heteroatom–hydrogen bonds (X–H, where X = O, N, S, P, etc.) is an efficient strategy for the construction of $C(sp^3)$–X bonds.[1] Recently, α-imino rhodium carbene, generated in situ from *N*-sulfonyl 1,2,3-triazoles, has emerged as an increasingly valuable intermediate possessing novel reactivity and synthetic potential.[2] Significant progress has been made by the research groups of Fokin,[3] Gevorgyan,[4] Davies,[5] Sarpong,[6] Shi,[7] and others. In particular, α-imino rhodium carbenes insertions have led to a novel synthetic method toward the formation of C–X bonds, including $C(sp^2)$–X bonds. For example, high regio- and stereoselectivities have been achieved with the insertion of α-imino rhodium carbene into O–H and N–H bonds, affording enamide products (Scheme 1a).[3a]

Indole and its derivatives are important bioactive heterocycles in natural products and pharmaceuticals.[8] More recently, indole-embedded α-imino metal carbene in situ generated from 3-diazoindolin-2-imine has been identified as a reactive intermediate in carbene insertions to furnish a variety of indole derivatives.[9] The transformation of rhodium-catalyzed N–H insertion was reported to build 3-substituted indole derivatives with the $C(sp^2)$–N bond formation (Scheme 1b).[9e] Despite progress in α-imino carbene insertion transformations, the insertion reactions of indole-embedded α-imino metal carbenes for the generation of $C(sp^2)$–X bonds is much less developed.

Aryl and heteroaryl phosphorus compounds have been of particular interest due to their biological significance and synthetic value.[10] 3-Phosphoindoles represent novel second-generation NNRTIs (non-nucleoside reverse transcriptase inhibitors) which show remarkable effect on inhibiting the replication of HIV-1 virus (IDX899).[11] In consideration of the importance of 3-phosphoindoles in pharmaceuticals and inspired by these previous findings shown in Scheme 1, herein we describe our efforts toward the development of the copper-catalyzed P–H insertion of novel α-imino copper carbene to access a variety of 3-phosphoindole derivatives (Scheme 1c). This method will not only expand the repertoire of transformations of α-imino metal carbenes but also provide a straightforward route to $C(sp^2)$–P bond formation and creation of new phosphoindoles. To the best of our knowledge, the P–H insertion reactions of α-imino metal carbene for the construction of C–P bond has never been reported.

Scheme 1. Insertion Reactions of α-Imino Metal Carbenes for the Construction of $C(sp^2)$–Heteroatom Bonds



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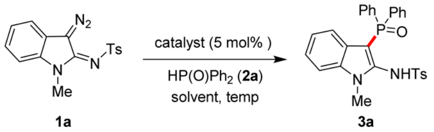
We began to explore the P−H insertion of 3-diazoindolin-2-imine (**1a**) and diphenylphosphine oxide (**2a**) with the common catalysts used for the decomposition of triazoles and diazo compounds, including $Rh_2(oct)_4$, $[Ru(p\text{-cymene})Cl_2]_2$, $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$, and $Ni(cod)_2$ (Table 1, entries 1−4).

Table 1. Optimization of the Reaction Conditions[a]

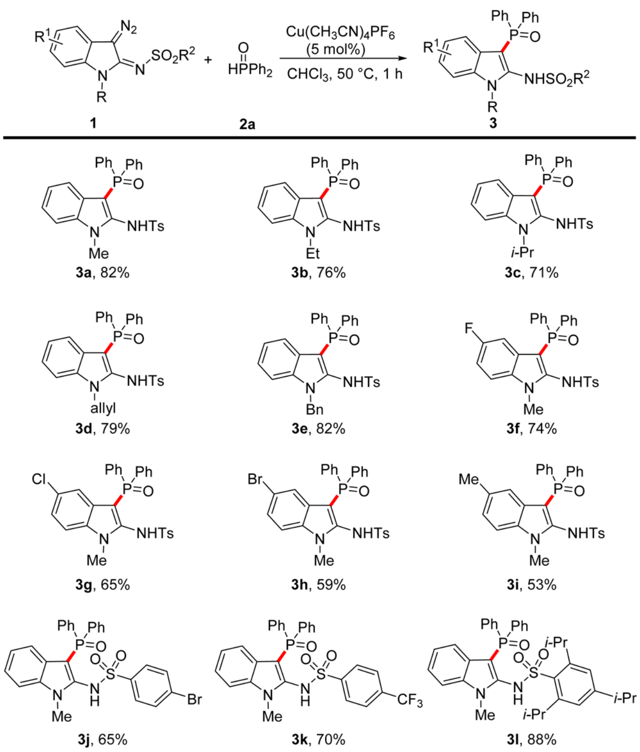


entry	catalyst	solvent	temp (°C)	time (h)	yield[b] (%)
1	$Rh_2(oct)_4$	DCE	35	24	0
2	$[Ru(p\text{-cymene})Cl_2]_2$	DCE	35	24	0
3	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	DCE	35	24	0
4	$Ni(cod)_2$	DCE	35	24	0
5	$Cu(OTf)_2$	DCE	35	24	20
6	$Cu(OAc)_2$	DCE	35	24	15
7	$Cu(acac)_2$	DCE	35	24	15
8	Cu_2O	DCE	35	24	23
9	$Cu(CH_3CN)_4PF_6$	DCE	35	24	42
10	$Cu(CH_3CN)_4PF_6$	DCE	35	1	42
11	$Cu(CH_3CN)_4PF_6$	DCE	50	1	56
12	$Cu(CH_3CN)_4PF_6$	DCE	15	1	trace
13		DCE	50	1	0
14	$Cu(CH_3CN)_4PF_6$	DCM	50	1	26
15	$Cu(CH_3CN)_4PF_6$	$CHCl_3$	50	1	82
16	$Cu(CH_3CN)_4PF_6$	1, 4-dioxane	50	1	64
17	$Cu(CH_3CN)_4PF_6$	toluene	50	1	52

[a] Reaction conduction: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.01 mmol), solvent (0.8 mL). [b] Isolated yield.

Unfortunately, no desired product but a significant amount of starting material was observed. To our delight, the reaction gave **3a** in 20% yield in the presence of 5 mol % of $Cu(OTf)_2$ in DCE at 35 °C (Table 1, entry 5). Encouraged by this initial result, we then screened other copper catalysts, of which $Cu(CH_3CN)_4PF_6$ proved superior (Table 1, entries 5−9). By screening the reaction temperature and reaction time, the optimal reaction temperature and reaction time were found to be 50 °C and 1 h, respectively. A trace amount of the desired **3a** was exactingly detected when the reaction was carried out at 15 °C (entry 12). A control reaction in the absence of metal catalyst afforded no desired product, indicating the critical role of the copper catalyst in generating the *α*-imino metal carbene intermediate (entry 11 vs 13). The reaction was subjected to notable solvent effects. Chloroform ($CHCl_3$) was a better solvent over $ClCH_2CH_2Cl$ (DCE), CH_2Cl_2 (DCM), 1, 4-dioxane, and toluene, providing **3a** in 82% yield (entries 15−17).

Scheme 2. Scope of 3-Diazoindolin-2-imines[a,b]



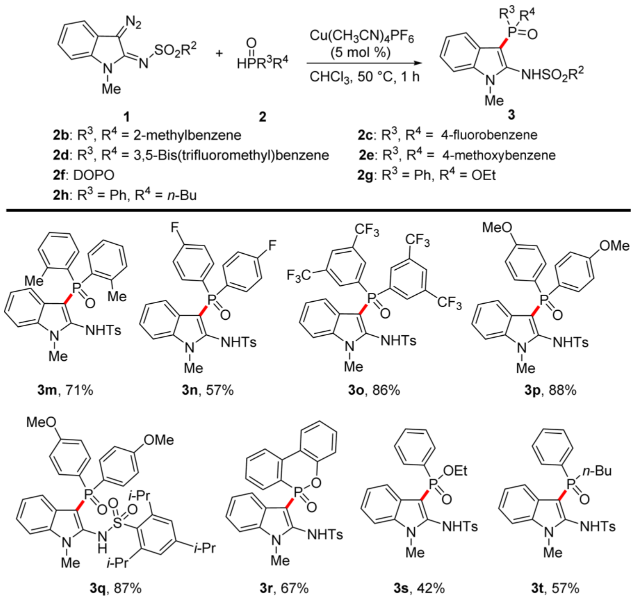
[a] Reaction conditions: $Cu(CH_3CN)_4PF_6$ (0.01 mmol), **1** (0.20 mmol) and $HP(O)Ph_2$ (0.20 mmol) in $CHCl_3$ (0.8 mL) at 50 °C for 1 h. [b] Isolated yield.

With the optimal reaction conditions, we then explored the substrate scope with respect to the 3-diazoindolin-2-imines. As illustrated in Scheme 2, the alkyl group on the 1-position of indole could be varied from methyl, ethyl, isopropyl, allyl, and benzyl to produce **3a**, **3b**, **3c**, **3d**, and **3e** in 82%, 76%, 71%, 79%, and 58% yields, respectively. The structure of **3e** was unambiguously determined by single-crystal X-ray analysis (as shown in the Supporting Information). No insertion product was observed by using *N*-unprotected 3-diazoindolin-2 mines. Various 3-diazoindolin-2-imines with substituents on the 5-position of indole were feasible substrates in this reaction and delivered **3f−i** in 53−74% yields. The process was tolerant to 3-diazoindolin-2-imines bearing different sulfonyl groups (R^3 = 4-BrC_6H_4, 4-$CF_3C_6H_4$, 2,4,6-i-$Pr_3C_6H_2$), thus giving the corresponding products **3j−l** with high chemoselectivities (65−88% yield).

We next investigated the scope with respect to the H-phosphine oxides (Scheme 3). H-Phosphine oxides **2** under the optimal reaction conditions and reacted with **1** generally proceeded in good yields. Both electron-poor and electron-rich substituted groups in H-phosphine oxides (**2d**,**e**) could be tolerated and afforded **3o** and **3p** in 86% and 88% yield, respectively. Notably, heterocyclic H-phosphine oxides such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO, **2f**) could be introduced to the insertion product. Moreover, ethyl phenylphosphinate (**2g**) was also viable for this transformation, giving the expected product **3s** in 42% yield. In the case where butyl(phenyl)phosphine oxide (**2h**) was used as a substrate, the desired product was isolated in 57% yield. The tosyl group can be removed with concentrated sulfuric acid to afford stable 2-free amino indole **6** in 91% yield (Supporting Information).

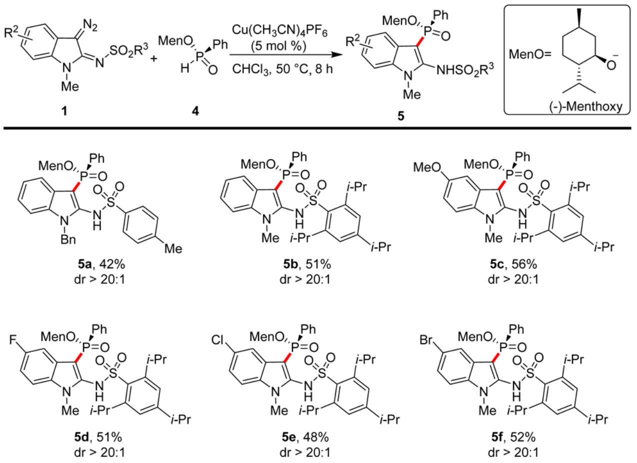
Inspired by the success in the P−H insertions of *α*-imino copper carbene, we then turned our attention to the asymmetric synthesis in an attempt to obtain a chiral 3-phosphoindoles. (1*R*,2*S*,5*R*)-(−)-Menthoxyphenylphosphinate (**4**) was employed as the chiral reagent for the chirality induction (Scheme 4). The P−H insertion of *α*-imino copper carbene proceeded smoothly to give the chiral 3-phosphindoles (**5a−f**) in moderate yield with very high diastereoselectivity. The absolute configuration of **5f** was established by X-ray single-crystal analysis (Figure 1).

Scheme 3. Scope of H-Phosphine Oxides[a,b]



[a]Reaction conditions: $Cu(CH_3CN)_4PF_6$ (0.01 mmol), **1a** (0.20 mmol) and **2** (0.20 mmol) in $CHCl_3$ (0.8 mL) at 50 °C for 1 h. [b]Isolated yield.

Scheme 4. Stereoselective Synthesis of Chiral 3-Methoxyarylphosphoindoles[a,b]



[a]Reaction conditions: $Cu(CH_3CN)_4PF_6$ (0.01 mmol), **1a** (0.20 mmol), and HP(O) (OMen)Ph (0.20 mmol) in $CHCl_3$ (0.8 mL) at 50 °C for 8 h. [b]Isolated yield and the diastereomeric ratio were detected by ^1H NMR (600 MHz) spectroscopy.

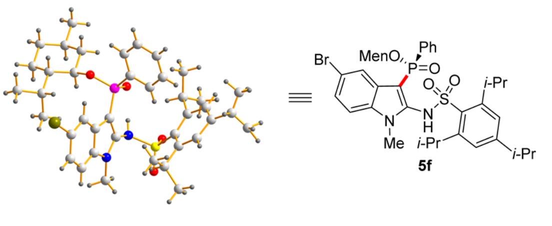
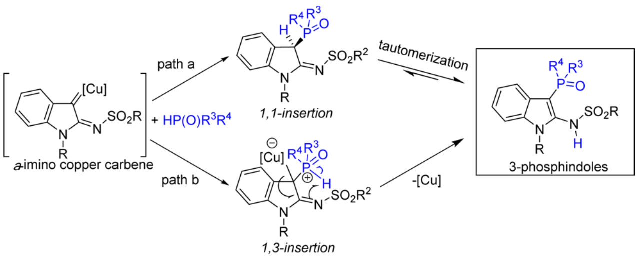


Figure 1. X-ray structure of **5f**.

P-Stereogenic phosphorus compounds have attracted considerable attention due to their wide applications as chiral ligands for asymmetric synthesis.[12] The stereoselective synthesis of *P*-stereogenic compounds is one of the most important and challenging subjects in synthetic organic chemistry.[13,14] In this asymmetric P−H insertion, the H−P bond in (1*R*,2*S*,5*R*)-(−)-menthoxylphenylphosphinate (**4**) was converted into a C(sp^2)−P bond to give chiral 3-phosphoindoles with high seteroselectivities. Although there are several examples of P−H insertions reported in the formation of the C(sp^3)−P bond,[15] no asymmetric P−H insertion reaction has been achieved to date. The stereoselective P−H insertion of α-imino copper carbene represents a unique example of asymmetric P−H insertion, affording chiral 3-phosphinoylindoles with a *P*-stereogenic center.

On the basis of the preliminary results of control reactions (as shown in Table 1, entry 11 vs 13) and previous work,[3a,16] we envisioned that the insertion of α-imino copper carbene into P−H bonds may proceed in two plausible pathways (Scheme 5). The α-imino copper carbene intermediate derived from 3-diazoindolin-2-imines may undergo direct 1,1-insertion into the P−H bond, followed by tautomerization leading to product of 3-phosphindoles (path a). Alternatively, the insertion may proceed by the formation of zwitterionic P-ylide intermediate. Subsequent dissociation of copper results in a proton transfer from the phosphorus to imine moiety, finally furnishing the 1,3-insertion product of 3-phosphindoles (path b).

Scheme 5. Proposed Mechanism



In summary, we have developed P−H insertions of α-imino copper carbenes for the construction of C(sp^2)−P bonds. The protocol provides an efficient approach to 3-phosphinoylindoles from 3-diazoindolin-2-imines and H-phosphine oxides with good chemoselectivity. In addition, the stereoselective P−H insertion was also successfully developed with high diastereoselectivity. The investigations on the biological activities of the new 3-phosphinoylindoles are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03752.

Experimental procedures, characterization data, and NMR spectra of all new compounds (PDF)
X-ray crystallography of **3e** (CIF)
X-ray crystallography of **5f** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jiangjun@gxu.edu.cn.

ORCID

Jun Jiang: 0000-0002-5542-7592

Notes

The authors declare no competing financial interest.

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