CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Asian J.* 10.1002/asia.201800889

Link to VoR: http://dx.doi.org/10.1002/asia.201800889

A Journal of
ACES Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

WILEY-VCH

10.1002/asia.201800889

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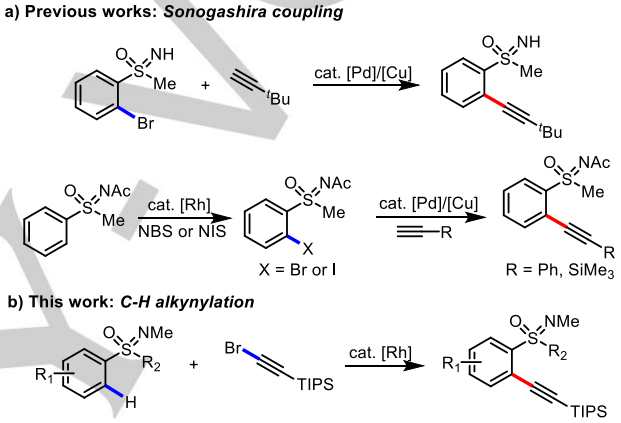
Rhodium(III)-Catalyzed C-H Alkynylation of *N*-Methylsulfoximines

Tao Wang, Yi-Ning Wang, Rui Wang, and Xi-Sheng Wang*[a]

Abstract: A Rhodium(III)-catalyzed direct C-H alkynylation of a wide range of *N*-methylsulfoximines with (bromoethynyl)triisopropylsilane has been developed. This protocol is compatible with both *S*,*S*-diaryl sulfoximines and *S*,*S*-alkyl aryl sulfoximines, and demonstrates mild conditions, good functional group tolerance. The synthetic utility of this method has been demonstrated by subsequent various transformations of the products.

As an interesting and important class of scaffolds in organic molecules, sulfoximines not only exist widely in diverse natural products, pharmaceuticals and agrochemicals,[1] but also are utilized as chiral auxiliaries and ligands in organic synthesis.[2] Therefore, the development of novel synthetic approaches to construct new sulfoximines has long received intensive attentions.[2c,2g,3] In the past several decades, transition-metal-catalyzed direct functionalization of C-H bonds has emerged as an strategy for total synthesis of complex molecules and intermediates,[4] which clearly demonstrates that the direct C-H functionalization stands out as the most straightforward strategy to synthesize functionalized sulfoximine. After the pioneering work on rhodium-catalyzed oxidative annulation of sulfoximines and alkynes from Bolm and coworkers,[5a] several groups have expanded the coupling partners of sulfoximines to diazo compounds,[5b] olefins,[5c-g] pyridotriazoles,[5h] 3-diazoindolin-2-imines,[5i] α-MsO/TsO ketones,[5j] sulfoxonium ylides,[5k] *etc*.[5l,5m] Furthermore, inspired by the well established Rh(III) catalytic system, several other transition-metals, including Ru(II),[5n] Cp*Co(III),[5o] and Cp*Ir(III),[5p] have been successfully applied to direct C-H functionalization of sulfoximines. However, to the best of our knowledge, direct alkynylation of C-H bonds of sulfoximines has never been reported and remains as a challenge.

Alkynes are versatile building blocks in synthetic chemistry and exist widely in natural products, drugs and organic materials,[6] thus the selective incorporation of alkyne groups into organic molecules is of great significance. For example, the palladium/copper co-catalyzed cross-coupling between aryl halides and terminal alkynes, known as Sonogashira coupling reaction, has long been realized as a common and valuable tool for the construction of $C(sp^2)$–$C(sp)$ bonds.[7] Along with the rapid expansion of transition-metal-catalyzed C-H activation in recent decades, direct C-H alkynylation reactions have recently been developed as a desirable method for facile synthesis of alkyne derivatives from $C(sp^2)$-H and $C(sp^3)$-H bonds.[8] But till now, the only known method to make *ortho*-alkynylated sulfoximines is still normal Sonogashira-type cross-coupling from *ortho*-bromo or -iodo sulfoximines (Scheme 1a),[5m,9] where the requirement of preinstalling halogen atoms onto the arenes definitely caused some problems on atom- and step-economy for the synthesis of target sulfoximines. Herein, we reported a rhodium(III)-catalyzed direct alkynylation of *ortho*-C-H bonds on aryl sulfoximines, in which both diaryl and *S*,*S*-alkyl aryl sulfoximines are well compatible with this transformation (Scheme 1b). This air- and moisture-tolerant reaction is easy-to-handle and proceeds under mild conditions.



Scheme 1. Synthesis of *ortho*-alkynylated sulfoximines.

Our initial investigation commenced with *N*-methylsulfoximine **1c** as the pilot substrate and TIPS-protected bromoacetylene **2** as the coupling partner in the presence of catalytic amount of $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (7 mol%) at 90 °C for 12 h. To our delight, the desired alkynylated sulfoximines **3c** was obtained successfully in 86% yield when Ag_2CO_3 (0.8 equiv) was used as oxidant and MeOH as solvent (Table 1, entry 1). Interestingly, a careful screening of solvents indicated that 1,4-dioxane, toluene, THF and 1,2-DCE gave almost the same yields as MeOH, while only CH_3CN and DMF afforded **3c** in low yields (entries 2-7). To further improve the yield, we next examined silver salts (entries 8-12) and rhodium catalysts (See Table S3, SI) using 1,2-DCE as solvent, which revealed that Ag_2CO_3 and $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ were the best choices. Furthermore, the decrease of the amount of sulfoximine **1c** to 1.2 equiv could result in a somewhat lower yield (81%, entry 13). Notably, almost the same yield was afforded when the Rh(III) catalyst loading was decreased to 5 mol% (entry 14). Finally, control experiments indicated that only trace amount of **3c** was obtained without adding Ag_2CO_3 (entry 15), and no desired product was detected in the absence of the rhodium catalyst (entry 16).

With the optimal reaction conditions in hand, we next sought to evaluate the scope and generality of the *N*-methylsulfoximines in this protocol. As shown in Scheme 2, a variety of symmetrical and unsymmetrical diphenyl sulfoximines with different substituents, including both electron-donating groups, such as

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

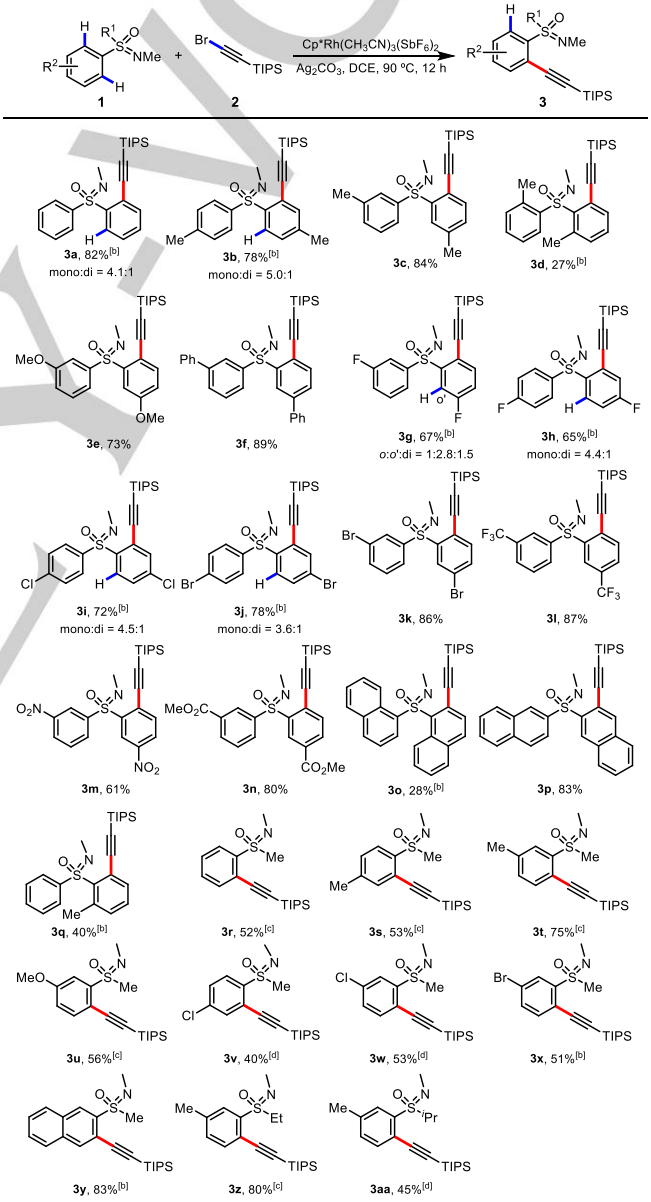
Entry	Solvent	AgX	Yield(%)[b]
1	MeOH	Ag_2CO_3	86
2	CH_3CN	Ag_2CO_3	12
3	dioxane	Ag_2CO_3	87
4	toluene	Ag_2CO_3	88
5	THF	Ag_2CO_3	88
6	DMF	Ag_2CO_3	27
7	DCE	Ag_2CO_3	88
8	DCE	$AgNO_3$	8
9	DCE	AgOTf	72
10	DCE	Ag_2O	85
11	DCE	AgOAc	67
12	DCE	AgOTFA	trace
13[c]	DCE	Ag_2CO_3	81
14[d]	DCE	Ag_2CO_3	87(84)
15	DCE	none	5
16[e]	DCE	Ag_2CO_3	0

[a] Unless otherwise noted, reactions were carried out with **1c** (0.225 mmol, 1.5 equiv), **2** (0.15 mmol, 1.0 equiv), $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (7 mol%), AgX (1.6 equiv) in 1.0 mL solvent at 90 ˚C for 12 h. [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as the internal standard. Isolated yield is shown in parentheses. [c] **1c** (0.18 mmol). [d] $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (5 mol%). [e] No $Cp^*Rh(CH_3CN)_3(SbF_6)_2$.

methyl (**1c**), methoxy (**1e**), phenyl (**1f**), and electron-withdrawing groups, such as bromo (**1k**), trifluoromethyl (**1l**), nitro (**1m**) and ester (**1n**), were smoothly alkynylated with (bromoethynyl)triisopropylsilane. Moreover, the tolerance of halogens in this new method enabled the facile synthesis of multi-substituted sulfoximines by transition-metal-catalyzed cross-coupling reactions. Not surprisingly, diphenyl sulfoximine (**1a**) and *para*-substituted sulfoximines bearing methyl (**1b**), fluoro (**1h**), chloro (**1i**), bromo (**1j**) could afford the desired products in good total yields (65% to 82%), albeit as mixtures of mono- and dialkynylated sulfoximines with ratios ranging from 3.6:1 to 5.0:1. Notably, the alkynylation occurred at the less hindered C-H bonds on the phenyl rings for almost all *meta*-substituted sulfoximines with excellent regioselectivity, and the coupling products could be obtained with even better yields (61% to 89%). It should be noted that *meta*-fluoro substituted substrate furnished three separable alkynylated products (**3g**, *o*:*o*‘:di = 1:2.8:1.5), because of the little steric hindrance of fluorine atom for C-H activation. β-Naphthyl-substituted sulfoximine (**1p**) was also compatible with this reaction, providing **3p** in good yield with excellent selectivity. As we expected, direct alkynylation of *ortho*-substituted sulfoximines exhibited lower reactivity, probably due to the steric hindrance of *ortho*-substituents (**1d, 1o, 1q**). It is noteworthy that C-H alkynylation occurred mainly at *ortho*-Me-substituted aromatic ring instead of phenyl group in the case of unsymmetrical diaryl sulfoximine **1q**. Presumably, the unexpected consequence could be explained by an unfavorable steric interaction between the Me-containing aryl ring and the bulky pentamethylcyclopentadienyl (Cp*) ligand on rhodium during the process of C-H cleavage.[10]

To our satisfaction, this protocol displayed good tolerance toward *S*-alkyl *S*-aryl sulfoximine as well, albeit in a slightly lower

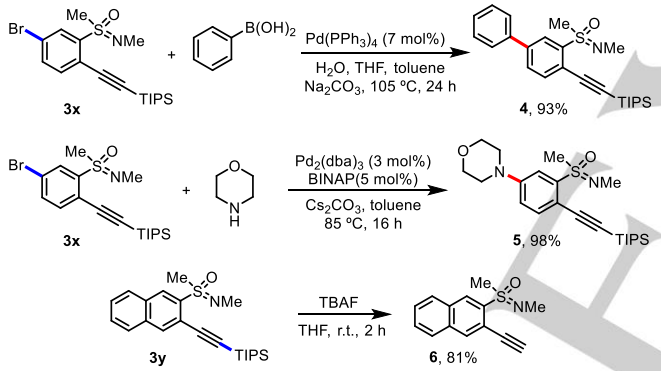
Scheme 2. Scope of sulfoximines.[a]



[a] Unless otherwise noted, the reaction conditions were as follow: **1** (0.225 mmol, 1.5 equiv), **2** (0.15 mmol, 1.0 equiv), $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (5 mol%) and Ag_2CO_3 (0.8 equiv) in 1,2-DCE (1.0 mL) at 90 ˚C for 12 h; isolated yields were reported. [b] $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (7 mol%), **1** (0.3 mmol, 2.0 equiv). [c] $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (7 mol%), **1** (0.45 mmol, 3.0 equiv). [d] $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (10 mol%), **1** (0.45 mmol, 3.0 equiv).

but still acceptable yield. Similarly, C-H bonds located in the less hindered position of *meta*-substituted sulfoximines could be selectively alkynylated with comparatively higher yields. A variety of functional groups, such as methyl (**1t**), methoxy (**1u**), chloro (**1w**) and bromo (**1x**), were also compatible with this transformation. Particularly, *S*-2-naphthyl *S*-methyl sulfoximine **1y** showed excellent site-selectivity in this reaction, furnishing **3y** in 83% yield. Meanwhile, *para*-substituted sulfoximines (**1s**, **1v**) and **1r** gave only moderate yields in this catalytic system. Additionally, *S*-ethyl- and isopropyl-substituted *S*-aryl sulfoximines (**1z** and **1aa**) were also proved to be suitable substrates, which could be alkynylated in 80% and 45% yield, respectively.

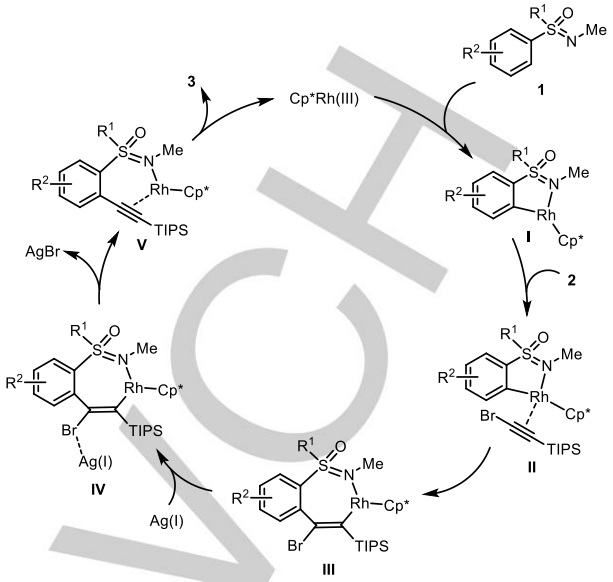
To demonstrate the synthetic utility of this new methodology, further derivatizations of the *ortho*-alkynylated sulfoximines were next carried out. As shown in Scheme 3, palladium-catalyzed Suzuki coupling reaction and Buchwald-Hartwig reaction were applied with *meta*-Bromo-substituted product **3x** to get multi-functionalized sulfoximines. Both phenyl and morpholine group were incorporated into *ortho*-alkynylated sulfoximines with excellent yields (**4**, **5**). More interestingly, TBAF-mediated cleavage of the TIPS group of **3y** proceeded smoothly to give terminal alkyne **6**, which could definitely be used for further elaboration in organic synthesis.



Scheme 3. Derivatizations of *ortho*-alkynylated sulfoximines.

On the basis of previous reports,[11] a plausible mechanism was proposed as below (Scheme 4). The catalytic cycle is initiated by coordination of Rh(III) species to sulfoximines and subsequent C-H activation with assistance of ligated base generates a five-membered rhodacycle intermediate **I**. The intermediate undergoes ligand exchange to coordinate with bromoacetylene **2**, followed by alkyne insertion and Ag_2CO_3-assisted bromide elimination delivers the final products **3** and regenerates rhodium(III) catalyst.

In conclusion, we have developed a Cp*Rh(III)-catalyzed direct C-H alkynylation of *N*-methylsulfoximines. Both *S*,*S*-diaryl and *S*,*S*-alkyl aryl sulfoximines are compatible with the transformation, and a broad range of functional groups are well tolerated in this method under mild conditions. The synthetic utility of this protocol has been demonstrated by subsequent various derivatizations of the alkynylated products.



Scheme 4. Proposed reaction mechanism.

Experimental Section

General Procedure for Rhodium-Catalyzed C-H Alkynylation of *N*-Methylsulfoximines:

To an oven-dried 35 mL screw-cap sealed tube equipped with a magnetic stir bar was added $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (5-10 mol%, 0.0075-0.015 mmol, 6.2-12.4 mg), Ag_2CO_3 (0.8 equiv, 0.12 mmol, 33.1 mg), substrate **1** (1.5-3.0 equiv, 0.225-0.45 mmol), TIPS-protected bromoacetylene **2** (1.0 equiv, 0.15 mmol, 39.2 mg) and 1,2-dichloroethane (1.0 mL) under air atmosphere. The vessel was then sealed with a Teflon screw-cap and placed into a preheated oil bath at 90 °C for 12 h. After completion, the reaction mixture was cooled to room temperature and was directly filtered through a short pad of silica gel, washed with EtOAc. The filtrate was concentrated under vacuum and purified by chromatography on silica gel to obtain the corresponding product **3**.

Acknowledgements

We gratefully acknowledge the National Basic Research Program of China (973 Program 2015CB856600), the National Science Foundation of China (21522208, 21772187, 21602213) for financial support.

Keywords: Rhodium(III) • C-H activation • Alkynylation • Sulfoximine • Bromoacetylene

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10.1002/asia.201800889

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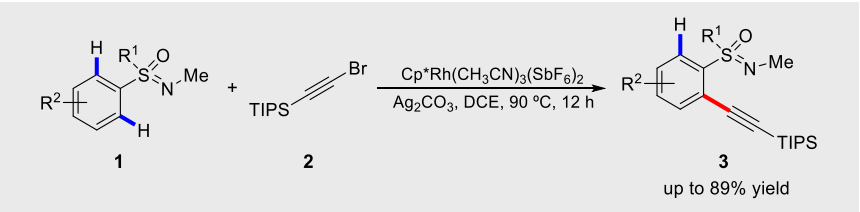

A Rhodium(III)-catalyzed direct C-H alkynylation of a wide range of *N*-methylsulfoximines with (bromoethynyl)triisopropylsilane has been developed. This protocol is compatible with both *S*,*S*-diaryl sulfoximines and *S*,*S*-alkyl aryl sulfoximines, and demonstrates mild conditions, good functional group tolerance. The synthetic utility of this method has been demonstrated by subsequent various transformations of the products.

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Rhodium(III)-Catalyzed C-H Alkynylation of *N*-Methylsulfoximines