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SPECIAL ISSUE

C–H Bond Activation

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COVER The oxidative C–H/C–H cross-coupling between two heteroarenes has attracted much attention in recent years. Various natural products, pharmaceuticals and organic functional materials can be rapidly synthesized by this powerful strategy. The C–H activation strategy has many advantages over traditional coupling reactions, such as atom economy, low cost and synthetic simplicity. However, there are still some problems with transition metal-catalyzed C–H/C–H cross-coupling. The major one is the use of stoichiometric amounts of metal oxidants, which limits its practicability. In this work, a palladium/copper-cocatalyzed oxidative C–H/C–H cross-coupling between two heteroarenes by using molecular oxygen as an oxidant has been developed to construct biheteroaryl motifs. As oxygen is a green and cheap oxidant, the current catalytic system would be emerged as a significant tool for constructing unsymmetrical biheteroaryls (see the article by Yang Shi, Zhen Wang, Yangyang Cheng, Jingbo Lan, Zhijie She & Jingsong You on page 1292–1296).

Special Issue: C–H bond activation

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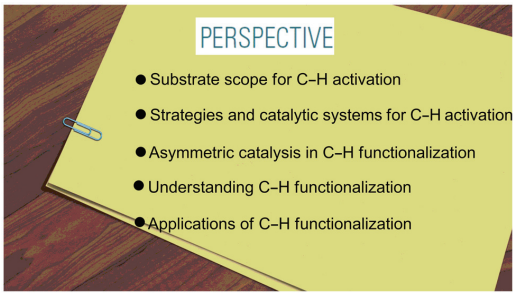

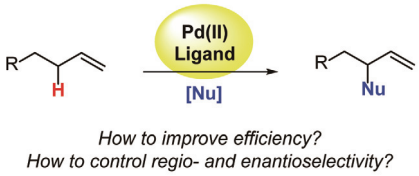

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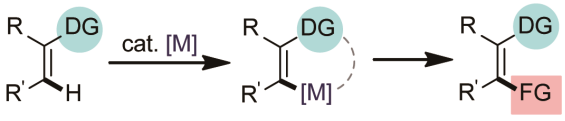

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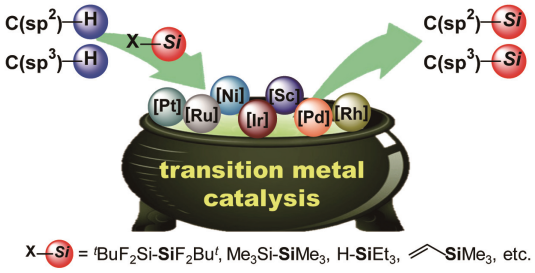

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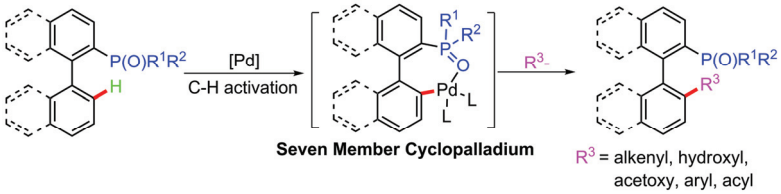

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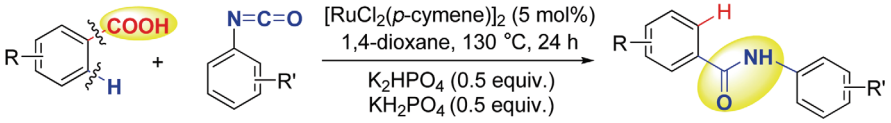

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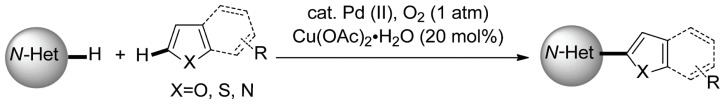

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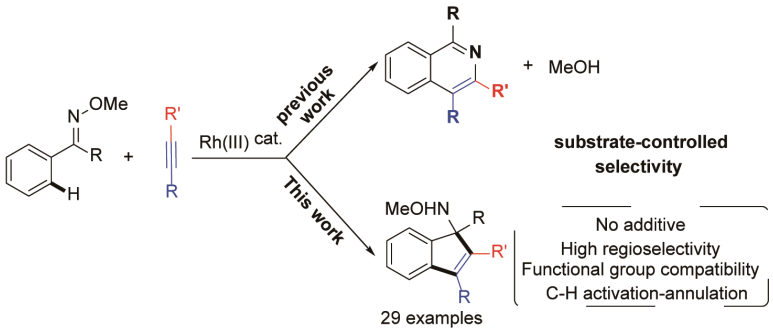

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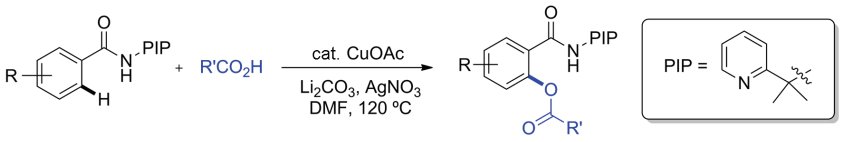

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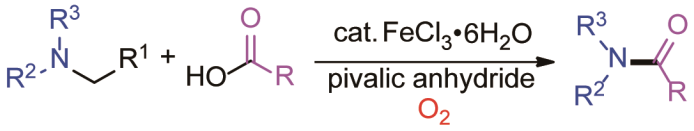

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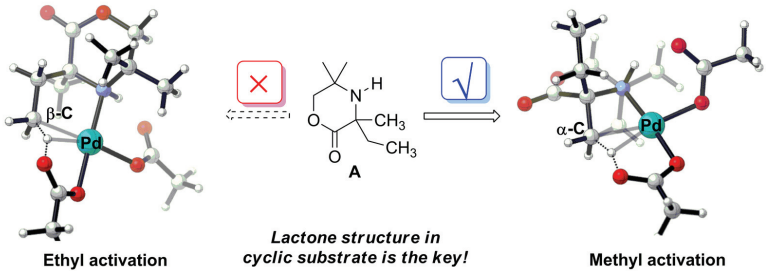

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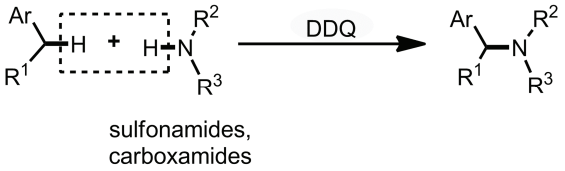

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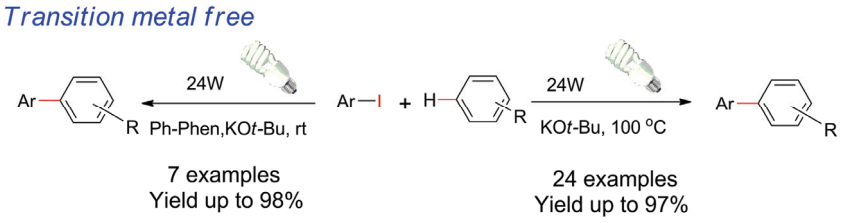

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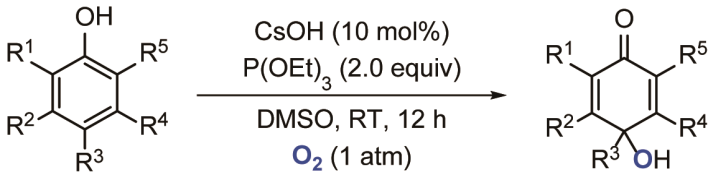

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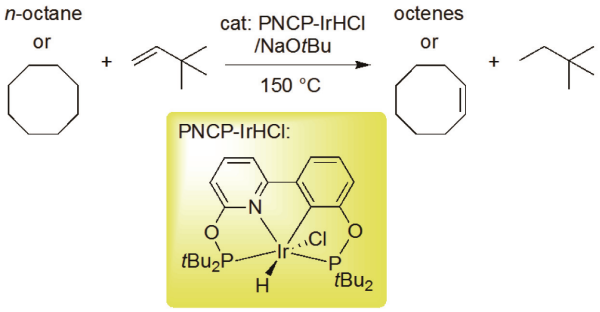

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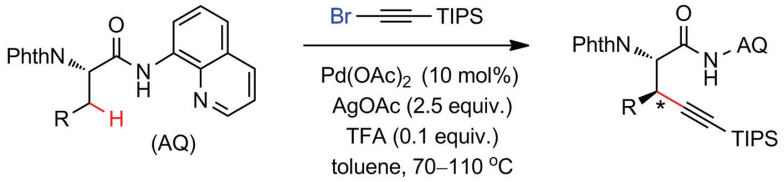

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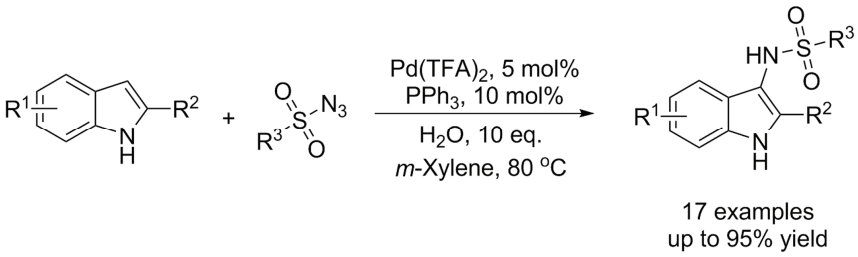

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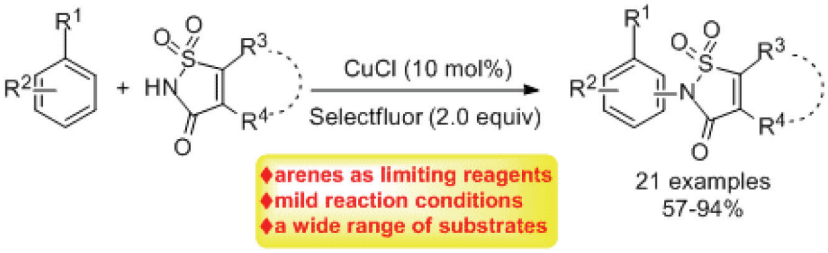

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• ARTICLES •

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• SPECIAL ISSUE • C–H bond activation

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Rhodium(III)-catalyzed [3+2] annulative coupling between oximes and electron-deficient alkynes

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Rhodium(III)-catalyzed coupling between ketoximes and alkynes via C–H activation and annulation typically followed the [4+2] selectivity to afford isoquinolines. By designing alkynes bearing a highly electron-withdrawing group and under substrate control, we have successfully switched the selectivity of the coupling between oximes and alkynes to the alternative [3+2] annulation, leading to the efficient synthesis of indenamines. This process features good regioselectivity for both substrates, high efficiency, broad substrate scope, and excellent functional group tolerance.

rhodium(III), C–H activation, annulation, oxime, alkyne

1 Introduction

Substituted indenes are a valuable structural motif in many biologically active molecules [1], functional materials [2], and natural products [3]. Thus, the synthesis of compounds with an indene scaffold has attracted increasing attention over the past decades. In particular, transition-metal-catalyzed direct functionalization of C–H bonds of arenes has emerged as a powerful tool for the construction of a broad variety of such building blocks [4]. From a step- and atom-economic point of view, the synthesis via a C–H activation pathway would be a more straightforward and attractive alternative to the traditional functional group transformation chemistry that heavily relied on pre-functionalized arenes.

In 2005 and 2006, Takai *et al*. [5] reported the synthesis of indenamines and derivatives via C–H activation of imines followed by functionalization with alkynes when catalyzed by $[ReBr(CO)_3(thf)]_2$. In this system, the polar Re–C bond generated via C–H activation acts as an intramolecular nucleophile. Later in 2010, Zhao *et al*. [6] reported the coupling of protic benzophenone imines with alkynes to give primary indenamines, and an asymmetric variant was subsequently developed by Cramer *et al*. [7]. In 2012, our group [8] reported Ru(II)- and sulfonamide-catalyzed coupling of *N*-sulfonyl imines with alkynes to furnish the same type of product via C–H activation. This strategy of C–H activation and [3+2] annulations has been further developed by others for the synthesis of other indenamides using Rh(III), Ru(II) and Mn catalysts [9]. In fact, this annulative strategy is not limited to indenamines, and the related syntheses of indenols and indenones have been achieved by Glorius *et al*. [10], Cheng *et al*. [11], Shi *et al*. [12], our group [13], and others [14]. In all these systems, the imine, ketone, and amide functionality play a bifunctional role: the nucleophilic heteroatom offers chelation assistance, while the electrophilic C=E bond is then attacked by the resultant M–C bond (M=Ru, Ir, Rh, and Co) [15].

As special imines, oximes and derivatives are well-known arenes that can undergo Ru(II)- and Rh(III)-catalyzed redox-neutral [4+2] coupling with alkynes (Scheme 1), leading to the synthesis of isoquinolines or pyridines [16]. In these systems, the oxime group functions as an oxidizing directing group that effects C–H activation under mild conditions with high efficiency and regioselectivity. In previous

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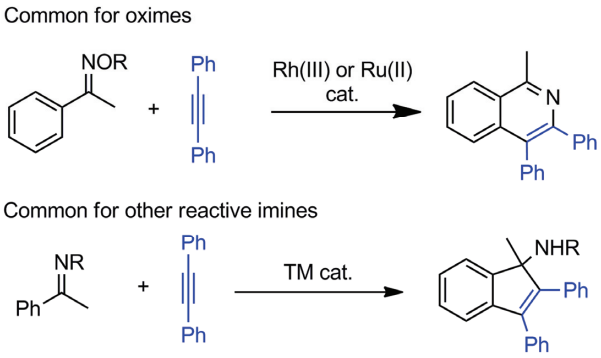


Scheme 1 [4+2] versus [3+2] coupling between imines and alkynes.

studies, the coupling of oxime derivatives with alkynes almost invariably afforded the [4+2] coupling product, as a result of the oxidizing potential of the N–O bond herein. However, it still remains a question whether the alternative [3+2] coupling selectivity can be reached for such specific imines. We reasoned that a highly polar M–C bond should favor the [3+2] coupling. To increase the polarity of the $M^{\delta+}$–$C^{\delta-}$ bond, the installation of a highly electron-withdrawing group to the metal-bond carbon (M–C(EWG)) should fulfill this task because the M–C bond is more ionic and more polarized. Therefore, acetylenic triflones could be an appropriate choice of such alkyne substrates.

2 Experimental

All chemicals which were obtained from commercial suppliers were used as received. All reactions were carried out using Schlenk techniques or in a nitrogen-filled dry box. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent on a Bruker 400 MHz or 500 MHz NMR spectrometer (Switzerland). The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 (USA). Column chromatography was performed on silica gel (200–300 mesh) with freshly distilled ethyl acetate and petroleum ether (bp 60–90 °C).

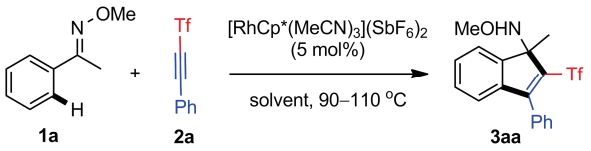
O-methyl oximes (0.20 mmol), trifluoromethanesulfonyl-phenylacetylene (0.22 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (5 mol %, 8.3 mg) and 1,2-dichloroethane (DCE, 2.5 mL) were charged into a schlenk tube under nitrogen. The mixture was heated in an oil bath at 110 °C for 6 h. Afterwards, the solvent was removed under a reduced pressure to afford a crude product, which was further purified by silica gel column chromatography with petroleum ether/ethyl acetate eluents.

3 Results and discussion

We initiated our studies with the coupling of *O*-methyl oxime (**1a**) with trifluoromethanesulfonyl phenylacetylene (**2a**) catalyzed by [RhCp*Cl$_2$]$_2$ (4 mol %) in the presence of AgSbF$_6$ (16 mol%) in DCE, from which the desired product **3aa** was isolated in 52% yield (Table 1, Entry **1**). Product (**3aa**) was fully characterized as an indenamine, including by X-ray crystallography for one of its analogues (**3ea**). To our delight, the yield of (**3aa**) was augmented to 71% when the catalyst was switched to [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (Entry 2). Further screening of solvents gave DCE as the best choice, while trace or no product was detected in other solvents such as toluene, *n*-pentane, DCM, THF, MeCN, acetone, or NMP (Entries 4–11). Increasing the reaction temperature to 110 °C gave rise to a higher yield (Entry 12). The metal catalyst proved necessary because no desired product was observed when it was omitted (Entry 13).

With the optimal conditions in hand, we next examined the scope and generality of this coupling reaction (Scheme 2). Various *para* substituted *O*-methyl oximes readily coupled with **2a** under the standard conditions to afford the annulations products in 42%–85% yields (Scheme 2, **3ba**–**3la**). Electron-withdrawing groups and halogen groups at the *para* position of the benzene ring are also tolerated (70%–85%, **3ba**–**3ia**), although a nitro group and trifluromethanesulfonyl group afforded lower coupling efficiency (57% for **3da** and 55% for **3ea**). In contrast, donating groups such as 4-methoxy-substituted oxime gave a diminished yield (42% for **3la**), so did a *para tert*-butyl substituted oxime (46% for **3ka**). Gratifyingly, 4-methyl oxime coupled to give **3ja** in 70% isolated yield. Interestingly, the regioselectivity of *meta*-substituted *O*-methyl oximes varies

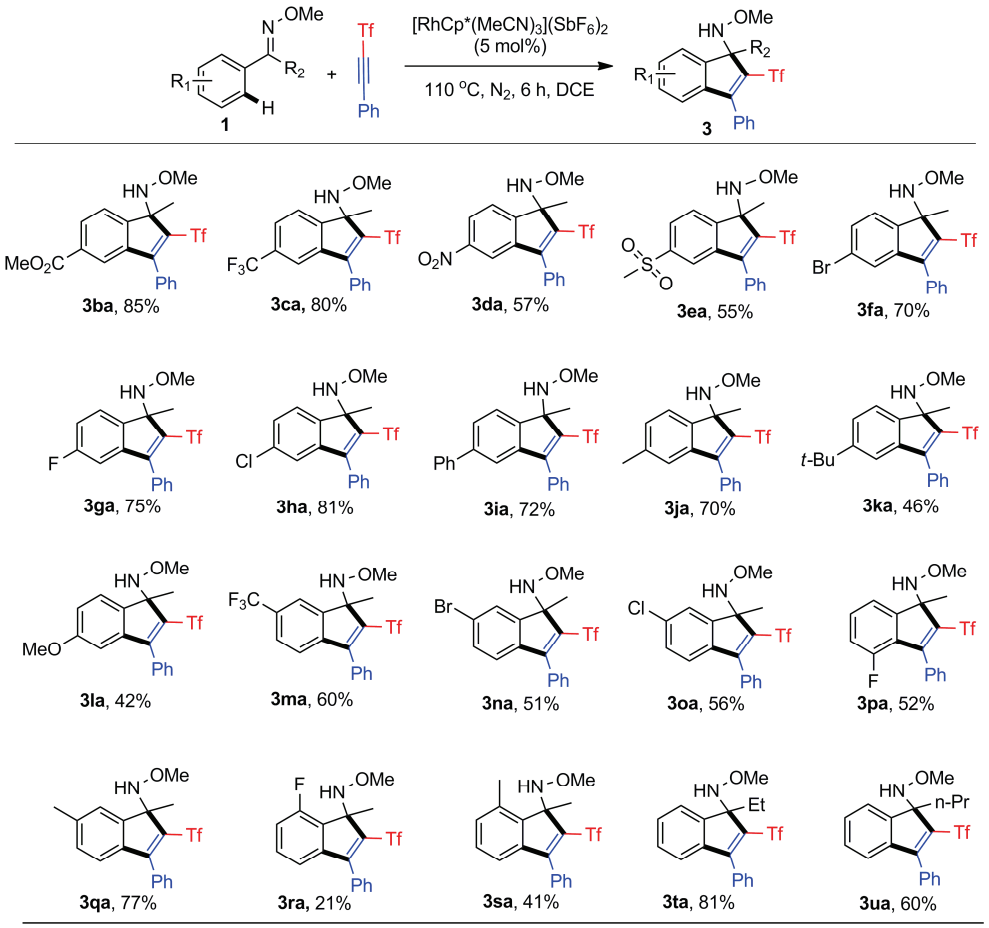
Table 1 Optimization studies [a]



1a 2a 3aa

Entry	Solvent	*T* (°C)	Time (h)	Yield (%) [b]
1 [c]	DCE	90	6	52
2	DCE	90	6	71
3	DCE	90	12	68
4	DCM	90	6	18
5	toluene	90	6	NR
6	*n*-pentane	90	6	NR
7	THF	90	6	trace
8	*t*-AmOH	90	6	trace
9	NMP	90	6	NR
10	CH_3CN	90	6	NR
11	acetone	90	6	trace
12	DCE	110	6	84
13 [d]	DCE	110	6	NR

a) Reactions were carried out by using [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%), **1a** (0.2 mmol), and **2a** (0.22 mmol) in a solvent (2 mL) at 110 °C for 6 h; b) isolated yield after column chromatography; c) reactions were carried out by using [RhCp*Cl$_2$]$_2$ (4 mol %), AgSbF$_6$ (16 mol %), **1a** (0.2 mmol), and **2a** (0.22 mmol) in DCE at 110 °C for 6 h; d) no catalyst was used.

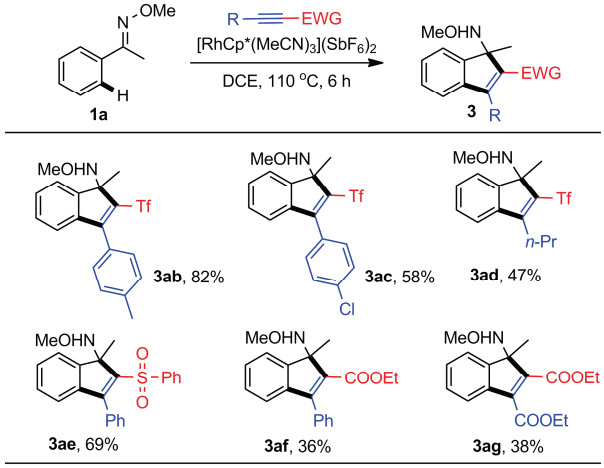


Scheme 2 Scope of the oxime substrates. Reaction conditions: $[RhCp^*(MeCN)_3](SbF_6)_2$ (5 mol %), **1a** (0.2 mmol), and **2a** (0.22 mmol) in DCE (2 mL) at 110 °C for 6 h. Isolated yield after column chromatography.

with the steric bulkiness of the substituent. For a relatively bulky group, the C–H functionalization occurs at the less hindered *ortho* position (**3ma**, **3na**, **3oa**, and **3qa**). In contrast, the coupling of *meta*-F substituted *O*-methyl oximes occurred exclusively at the more hindered *ortho* position (**3pa**) because the coordination effect of the fluoro group may dominate its minimal steric hindrance [17]. The steric hindrance of the *ortho* substituent was also examined (**3ra** and **3sa**), and the coupling turned out to be sensitive to steric hindrance. And the reaction yields were comparably high when the carbon chain in the imine moiety was extended (**3ta** and **3ua**).

The scope of alkynes bearing other electron-withdrawing groups (EWGs) was then explored. As given in Scheme 3, variation of the alkyne terminus in the triflone afforded the annulation product in 47%–82% yield, and the alkyne was not limited to a phenylacetylene (**3ad**). In addition, when the EWG in the alkyne was switched to a weaker one such as an ester, the yields of products (**3af** and **3ag)** decreased significantly (36% and 38%, respectively). Thus, our results clearly show that a more polar Rh–C bond correlates with a higher yield.

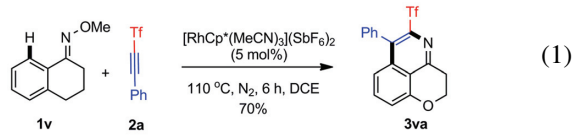
During our extension of the scope of the oxime substrate,



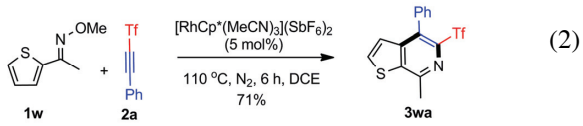
Scheme 3 Scope of the alkyne substrates. Reaction conditions: $[RhCp^*(MeCN)_3](SbF_6)_2$ (5 mol %), **1a** (0.2 mmol), and alkyne (0.22 mmol) in DCE (2 mL) at 110 °C for 6 h. Isolated yield after column chromatography.

we found that the coupling of oximes **1v** and **1w** did not lead to the expected [3+2] product under the standard conditions. Instead, the corresponding [4+2] product, isoquino-

line **3va** and **3wa**, were isolated in good yields (Eqs. (1, 2)), where stereo-electronic effects of substrates may play an important role in this coupling reaction.

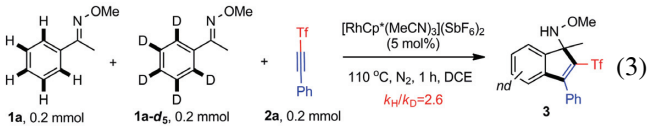


(1)



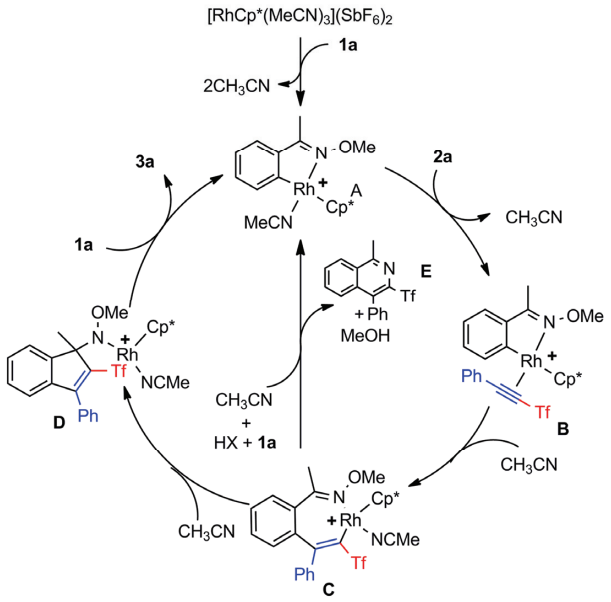
(2)

To briefly probe the mechanism of this reaction, kinetic isotope effect has been measured in the competition between **1a** and **1a-d_5** in their coupling with **2a** in equimolar ratio under a low conversion (Eq. (3)). A value of k_H/k_D=2.6 was obtained on the basis of ^{1}H NMR analysis. This moderate value suggests that the C–H activation process is probably involved in the rate-determining step.



(3)

A plausible mechanism is given in Scheme **4** on the basis of literature precedents [6,9a,9f,9h]. Cyclorhodation of oxime **1a** affords intermediate **A** which subsequently coordinates with alkyne **2a** and is followed by regio-selective migratory insertion to rhodacycle **C**. Nucleophilic attack of the Rh–C bond at the imine group gives intermediate **D**. The final product was released and the catalytic cycle was completed when an incoming oxime undergoes coordination and cyclometalation likely via σ-complex-assisted metathesis mechanism [17]. Alternatively, intermediate **C** could also lead to an isoquinoline product under a mechanism reported in previous literature [16f,18].



Scheme 4 Proposed catalytic cycle.

4 Conclusions

Rh(III)-catalyzed C–H activation of *O*-methyl oximes has been developed, and subsequent functionalization with trifluoromethanesulfonyl-phenylacetylenes leads to efficient synthesis of functionalized indenamines via a formal [3+2] cyclization process. This process features high efficiency, broad substrate scope, and excellent functional group tolerance. The selectivity stays in contrast to the commonly observed [4+2] coupling for oximes under rhodium and ruthenium catalysis. This coupling reaction, which extended the scope and applicability of Rh(III)-catalyzed C–H activation/coupling reactions of arenes, may be applied to the synthesis of complex structures.

Supporting information

The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entire with the authors.

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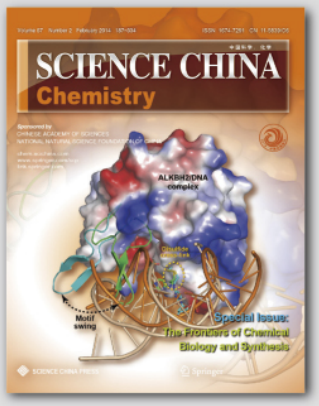

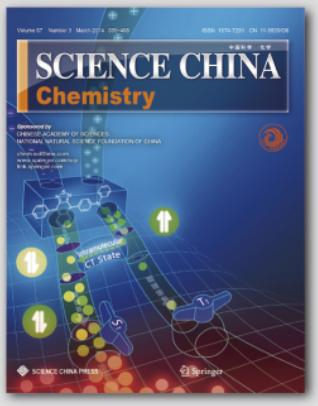

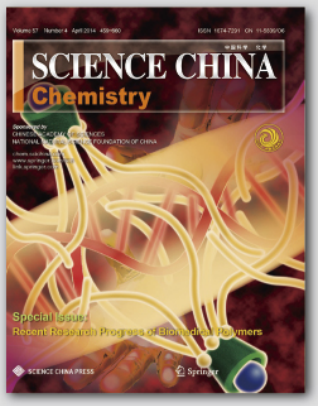

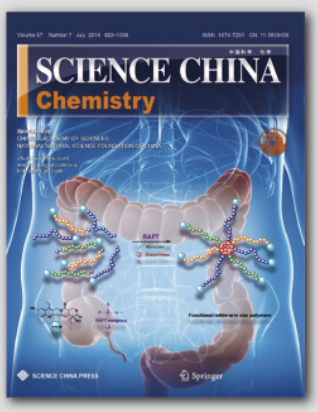

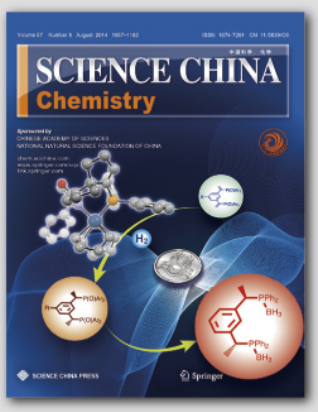

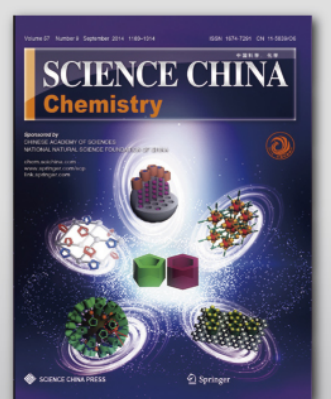

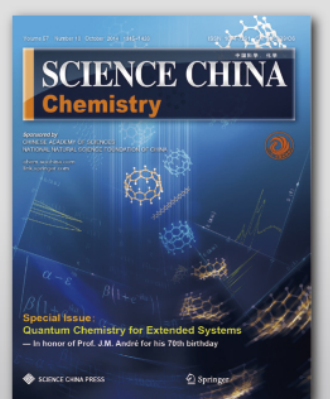

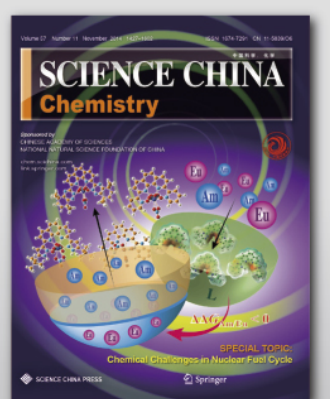

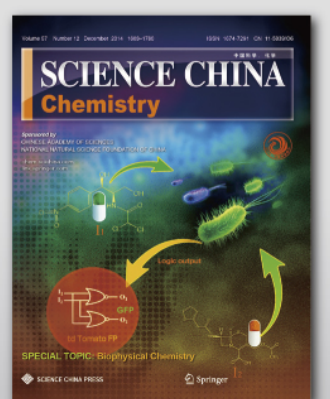

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