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Rhodium(II)-Catalyzed Reaction of 1-Tosyl-1,2,3-triazoles with Morita–Baylis–Hillman adducts: Synthesis of 3,4-Fused Pyrroles

Renmeng Jia, Jiang Meng, Jiaying Leng, Xingxin Yu* and Wei-Ping Deng*

Abstract: A cascade reaction of rhodium azavinylcarbenes with MBH adducts enables a novel synthetic approach to 3,4-fused pyrroles. The cascade reaction begins with the insertion of O-H bond into rhodium azavinylcarbenes, subsquent sigmatropic rearrangement provides substituted α,β-unsaturated cyclic ketone intermediates. Then the intramolecular aza Michael addition/oxidative aromatization sequence give rise to a wide range of 3,4-fused pyrroles in good yields, and with excellent functional group compatibility.

As one of the most valuable heterocycle skeletons, 3,4-fused pyrroles are widely found in natural products and bioactive compounds.[1] For instance, Bhimamycin D shows good antibacterial activities.[2] The cycloprodigiosin isolated from the marine bacteria, Beneckea gazogenes and Alteromonas rubra, has been used as an effective anti-cancer compound and immunosuppressant.[3] In addition, a series of compounds containing a fused pyrrole framework have been evaluated as BET inhibitors[4] and COX-2 inhibitors.[5] (Figure 1)

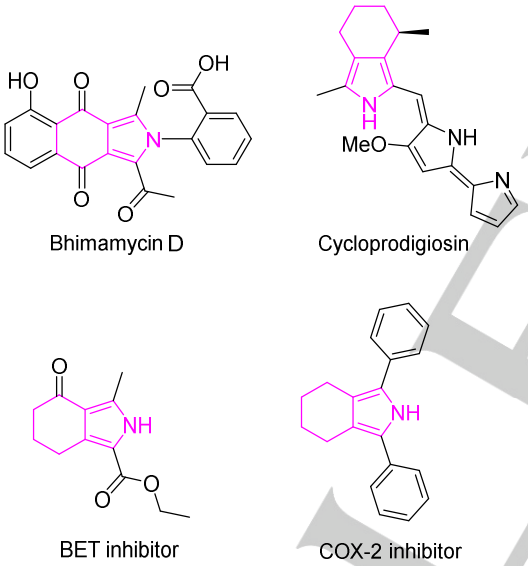
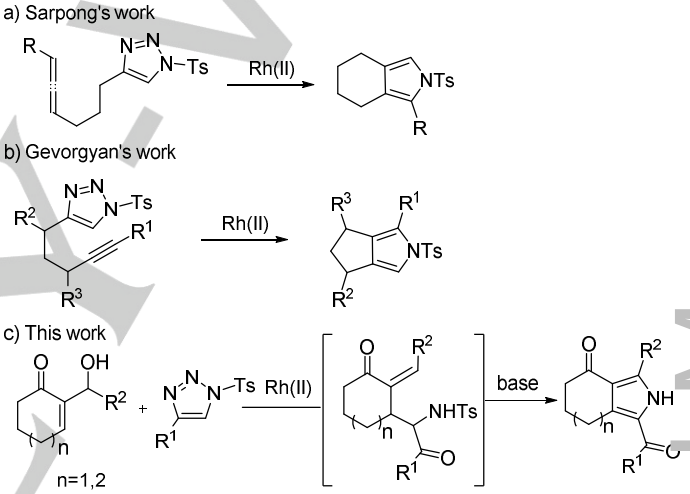


Figure 1 Selected natural products and pharmaceutical compounds.

In view of the impressive biological activities of 3,4-fused pyrroles, several strategies for the synthesis of this skeleton have been developed.[6] However, to the best of our knowledge, the efficient method for the construction of 3,4-fused cycloalkanopyrroles is rarely achieved up to now. Generally, the way to synthesize 3,4-fused cycloalkanopyrroles is the 1,3-dipolar cycloaddition of Michael acceptors and isonitrile anions.[6k] Recently, Sarpong and coworkers[6h] reported an elegant method for the synthesis of 3,4-fused pyrroles using in situ generated Rh-bound trimethylenemethane variants (Scheme 1a). At nearly the same time, the group of Gevorgyan[6i] developed an intramolecular Rh-catalyzed transannulation reaction of alkynyl-tethered triazoles to construct the 3,4-fused pyrroles (Scheme 1b). However, these reported methods have drawbacks such as limitations of substitution of products and ring members of pyrroles-fused cyclanes. Thus, the development of a streamlined method for the synthesis of 3,4-fused pyrroles containing a variety of substituents starting from easily available substrates is highly desired.



Scheme 1 Rh (II) catalyzed reaction for the construction of 3,4-fused pyrroles.

Triazole chemistry has been extensively studied over the last decade, in which the *N*-sulfuryl-1,2,3-triazoles have been used as versatile synthetic precursors for the synthesis of nitrogen-containing heterocycles.[7-11] We have a great interest in azaheterocycle synthesis and *N*-sulfonyl-1,2,3-triazoles chemistry. We have reported a practical and efficient method for divergent synthesis of 3,6-disubstituted- and 3,5,6-trisubstituted-1,2,4-triazines via unexpected rhodium-catalyzed O−H insertion/rearrangement/ conditions-controlled intramolecular cyclization and oxidation reaction under mild conditions.[12] Soon afterwards, a novel protocol for the synthesis of unsymmetrical indigo-like (E)-*α*-amino enaminones by rhodium catalyzed O−H insertion and subsequent rearrangement of isatins with 1-tosyl-1,2,3-triazoles has also been reported by us.[13] Up to now, the direct O-H insertions of *α*-imino rhodium carbenoids with proper substrates[14], taking benzylic alcohol[14e] for example, have been well studied. Moreover, some methods have been developed for the construction of nitrogen-containing heterocycles (such as pyrrole skeleton) based on O-H insertion and subsequent rearrangement.[14a] With our continuing studies on the Rh(II)-catalyzed transformation of triazoles, we supposed this rhodium-catalyzed O−H insertion/rearrangement strategy can be further applied to afford more attractive nitrogen-containing heterocycles such as 3,4-fused pyrroles by using Morita-Baylis-

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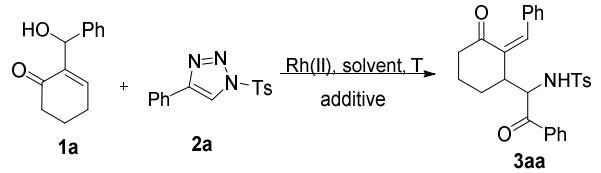
Hillman adducts as starting materials. Thus, we envisioned that triazoles could first react with Morita-Baylis-Hillman adducts of *α,β*-unsaturated cyclic ketones.[15] through O-H insertion and rearrangement to provide an intermediate, which can be further converted into 3,4-fused pyrroles (Scheme 1c). Herein, we disclose a novel method for the synthesis of 3,4-fused pyrroles via a tandem rhodium catalyzed O−H insertion, [3,3]-sigmatropic rearrangement, intramolecular *aza*-Michael addition and oxidation.

Table 1 Optimization of reaction conditions for the Rh-catalyzed reaction of MBH adduct **1a** and triazole **2a**[a]



1a **2a** **3aa**

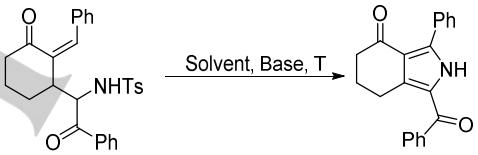
entry	catlyst	solvent	additive	temp (°C)	yield[b] (%)
1[c]	$Rh_2(OAc)_4$	$CHCl_3$	-	75	65
2[c]	$Rh_2(Oct)_4$	$CHCl_3$	-	75	82
3[c]	$Rh_2(Piv)_4$	$CHCl_3$	-	75	78
4[c]	$Rh_2(S\text{-nttl})_4$	$CHCl_3$	-	75	67
5[d]	$Rh_2(Oct)_4$	$CHCl_3$	-	75	86
6	$Rh_2(Oct)_4$	$CHCl_3$	-	75	90[g]
7	$Rh_2(Oct)_4$	$CHCl_3$	-	85	88
8	$Rh_2(Oct)_4$	CH_2Cl_2	-	75	77
9	$Rh_2(Oct)_4$	toluene	-	75	73
10[f]	$Rh_2(Oct)_4$	$CHCl_3$	$Cu(OTf)_2$	75	trace[e]
11[f]	$Rh_2(Oct)_4$	$CHCl_3$	$ZnCl_2$	75	trace[e]
12[f]	$Rh_2(Oct)_4$	$CHCl_3$	TsOH	75	66
13[f]	$Rh_2(Oct)_4$	$CHCl_3$	CF_3COOH	75	70
14[f]	$Rh_2(Oct)_4$	$CHCl_3$	$Ni(acac)_2$	75	73

[a] Reaction conditions: under N_2, **1a** (0.2 mmol), **2a** (0.24 mmol), Rh cat. (2 mol %), and solvent (1.0 mL) were heated until **1a** was consumed; [b] Isolated overall yield in two isomers of **3aa**; [c] **1a** (0.2 mmol) and **2a** (0.22 mmol) were used; [d] **1a** (0.22 mmol) and **2a** (0.2 mmol) were used; [e] degradation of **1a**; [f] 20 mol% of additive was added after 1 h; [g] The diastereo ratio of two isomers is 1:1.16 and two diastereomers of **3aa** could be isolated, in 40% and in 46% yield, respectively.

We commenced the study by choosing MBH adduct **1a** and ready available triazole **2a** as model substrates. Gratifyingly, when 2 mol% $Rh_2(OAc)_4$ was used as catalyst in $CHCl_3$ at 75 °C for 15 h, two isomers of **3aa** were isolated in 65% overall yield (Table 1, entry 1). These two isomers were assigned as *syn*- and *anti*- diastereomers caused by two chiral centers according to mechanistic speculation (See SI for more details). Encouraged by this result, other catalysts, such as $Rh_2(Oct)_4$, $Rh_2(Piv)_4$, and $Rh_2(S\text{-nttl})_4$, were screened and found more effective, providing higher yields of **3aa** (Table 1, entry 2-4). Increasing the amount of **2a** to 1.2 equivalent (Table 1, entry 5-6), the overall yield of **3aa** was improved to 90%. However, raising the temperature to 85 °C resulted in a lower yield (Table 1, entry 7). Moreover, the use of 1,2-dichloroethane (DCE) or toluene as the solvent did not increase the yield of **3aa** (Table 1, entry 8-9). The addition of Lewis acid have no positive effects (Table 1, entry 10-14). Finally, the reaction of MBH adduct **1a** with 1.2 equiv of triazole **2a** catalyzed by $Rh_2(Oct)_4$ in $CHCl_3$ at 75 °C were set as the optimum reaction conditions.

As envisaged, key step for the formation of 3,4-fused pyrrole **4aa** is the intramolecular aza-Michael addition of **3aa**. Certainly, base would promote the intramolecular cyclization of **3aa** to afford **4aa**. So, 2 equiv CH_3ONa was added into the solution of **3aa** (two diastereomers) to promote the cyclization. As expected, 3,4-fused pyrrole **4aa** was obtained in 53% yield within 12 hours (Table 2, entry 1). The structure of **4aa** was unambiguously determined by spectroscopic analysis and X-ray crystallography (Figure 2). After the screening of different bases, we found that t-BuOK, NaH, TEA, Cs_2CO_3, DABCO did not give a better result (Table 2, entry 2-6). Gratifyingly, we found that DBU promoted the cyclization smoothly to afford **4aa** in 63% yield (Table 2, entry 7). Solvent effect was then tested with DBU as the base (Table 2, entry 8-11). The results show that the nonpolar solvent toluene is the best choice. Moreover, the yield did not increase either at a higher reaction temperature or a lower reaction temperature (Table 2, entry 12-14). We envisioned that the additional oxidants would promote the reaction. Therefore, oxidants like DDQ or PIDA were added, but the desired product could not be obtained (Table 2, entry 15-16). After optimization, the combination of **3aa** and DBU (2 equiv) in toluene at 75 °C was determined as the optimum reaction conditions.

Table 2 Optimization of reaction conditions for the intramolecular Michael cyclization of **3aa**[a]

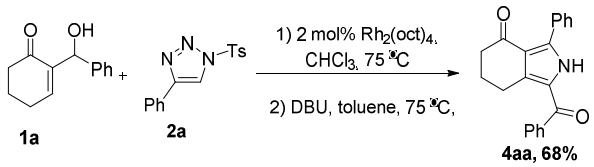


3aa **4aa**

entry	base	solvent	oxidation	temp (°C)	yield[b] (%)
1	CH_3ONa	CH_3OH	Air	rt	53
2	*t*-BuOK	*t*-BuOH	Air	rt	trace
3	NaH	THF	Air	75	trace
4	TEA	$CHCl_3$	Air	75	trace
5	Cs_2CO_3	$CHCl_3$	Air	75	40
6	DABCO	$CHCl_3$	Air	75	NR
7	DBU	$CHCl_3$	Air	75	63
8	DBU	THF	Air	75	66
9	DBU	DMF	Air	75	65
10	DBU	toluene	Air	75	78
11	DBU	CH_3CN	Air	75	56
12	DBU	toluene	Air	rt	NR
13	DBU	toluene	Air	85	78
14	DBU	toluene	Air	115	78
15	DBU	toluene	DDQ	75	trace
16	DBU	toluene	PIDA	75	trace

[a] Reaction conditions: **3a** (0.2 mmol), base (0.4 mmol) and solvent (1.0 mL) were heated until **3a** was consumed; [b] Isolated yield; PIDA = phenyliodine(III) diacetate

In order to improve the convenience and practicability of this transformation, DBU and toluene were added directly after the rhodium catalyzed reaction in the one-pot process. The desired product **4aa** could also been obtained in comparable yield (Scheme 2).



Scheme 2 One-pot process for the synthesis **4aa**

With the optimized reaction conditions in hand, the generality and substrate scope of this process was investigated, and the result was presented in Table 3 and Table 4. Firstly, a series of 4-substituted triazoles were tested (Table 3). The results showed that various substituted triazoles **2b-2p** reacted smoothly with MBH adduct **1a** to afford **4ab-4ap** in moderate to good yields.This proved that the reactions were not affected by the substituent position or the electronic properties of C4 aryl-substituted triazoles **4ab-4ai.** Moreover, the substrates can also be extended to heteroaromatic substituted triazoles, such as thienyl substituted **2j** and indolyl substituted triazoles **2k**, to yield product **4aj** in 62% and **4ak** in 46% yield, respectively. However, when using C4 alkyl-substituted triazoles such as cyclopropyl **2l** and tert-butyl substituted **2m** as substrates, only a trace amount of the desired products were observed. It is noteworthy that the MBH adducts of cyclohept-2-en-1-one can also be used to synthesize a variety of seven-membered ring fused pyrroles **4an-4ap** in good yields.

Next, various MBH adducts were investigated under the optimized conditions to test the scope of this reaction, and the results were summarized in Table 4. The MBH adducts **1b-1n** bearing ortho- para- or meta-substituents including OMe, F, Br, Cl, CN, CF_3 on the benzene ring reacted smoothly with triazole **2a** to afford the corresponding products **4ba-4na** in moderate to good yields and the reactions were less affected by electronic properties. Reactions with naphthyl substituted MBH adducts **1o-1p** and heteroaromatic substituted MBH adducts **1q-1r** also successfully provided the desired products **4oa-4ra**. However, when the alkyl-substituted MBH adducts **1s-1t** were used, a slightly reduced yields were obtained. Likewise, the MBH adducts of cyclohept-2-en-1-one can also be used to synthesize a variety of seven-membered ring 3,4-fused pyrroles **4ua-4wa** in good yields.

Based on the known N-sulfonyl-1,2,3-triazole chemistry and the above results, a plausible mechanism for the formation of the 3,4-fused pyrrole was provided in Figure 3. Initially, the reaction of N-sulfonyl-1,2,3-triazole **2a** with Rh(II) catalyst generates a rhodium-stablized carbene, along with release of molecular nitrogen. The azavinyl carbene reacts with the MBH adduct via an O-H 1,1-insertion followed by tautomerization, which could lead to an isomeric mixture of enamide intermediate **I**.Then intermediate **I** undergoes intramolecular [3,3]-sigmatropic rearrangement to afford **3aa** (two diastereomers). Under basic conditions, subsequent intramolecular cyclization and oxidative aromatization gives rise to the desired 3,4-fused pyrrole **4aa**.

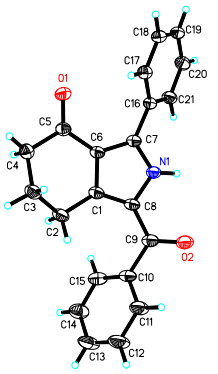
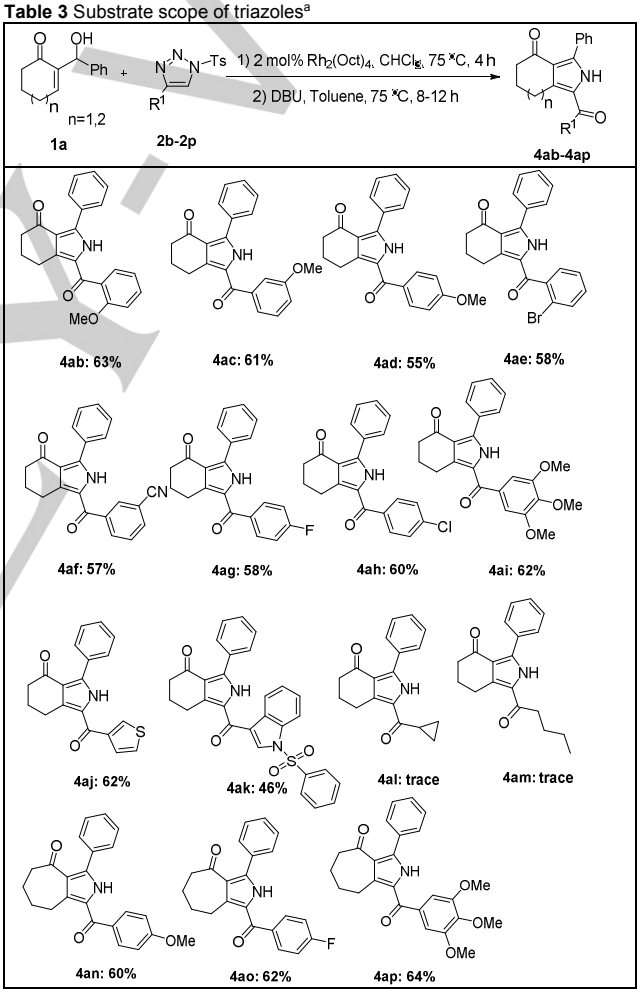


Figure 2 X-ray structure for **4aa**

Table 3 Substrate scope of triazoles[a]



[a] All reactions were carried out with 0.2 mmol of **1** and 0.24 mmol of **2** in 1 mL of $CHCl_3$ at 75°C for 2-4 h until consumption of **2** was apparent by TLC analysis. Then, toluene and DBU (2.0 equiv) were added, and the mixture was heated at 75°C for 8-12 h. Isolated yields of purified products are shown

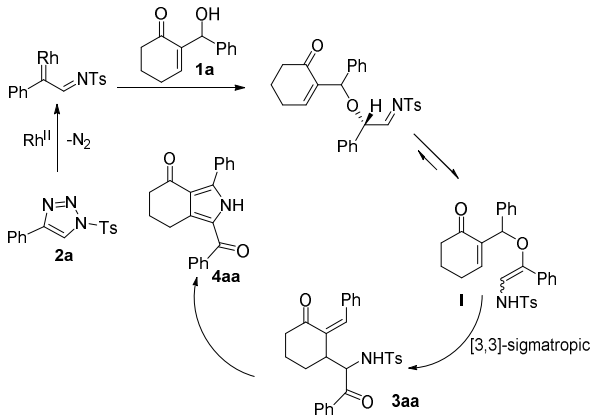
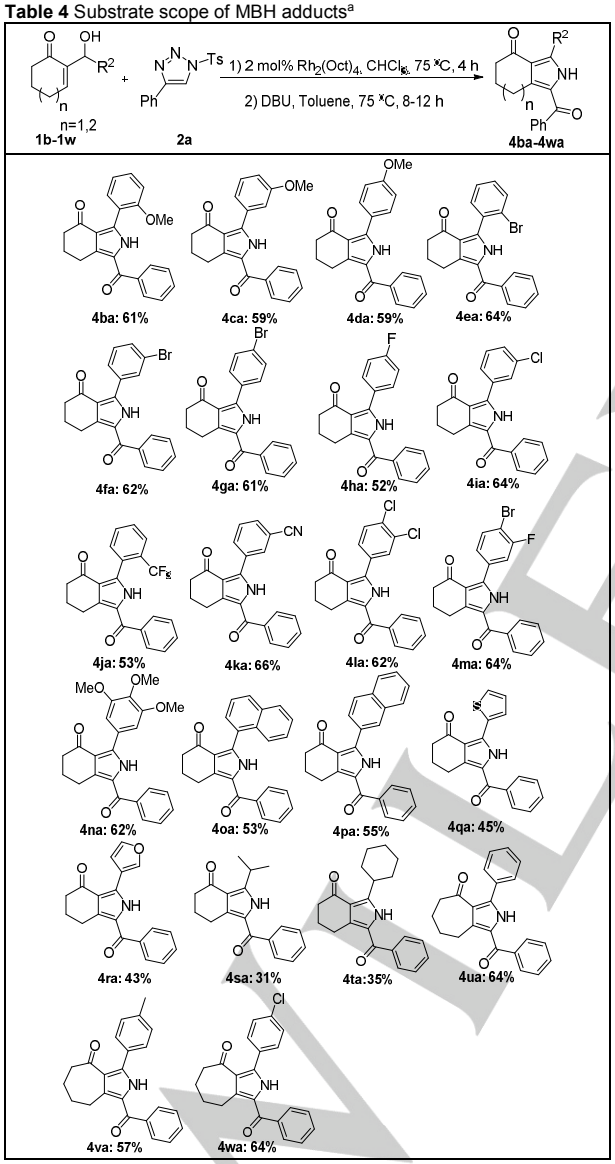


Figure 3 The proposed reaction pathway.

Table 4 Substrate scope of MBH adducts[a]



[a] All reactions were carried out with 0.2 mmol of **1** and 0.24 mmol of **2** in 1 mL of $CHCl_3$ at 75°C for 2-4 h until consumption of **2** was apparent by TLC analysis. Then, Toluene and DBU (2.0 equiv) were added, and the mixture was heated at 75°C for 8-12 h. Isolated yields of purified products are shown.

In summary, we have developed a novel and efficient way for the synthesis of potentially biological active 3,4-fused pyrroles in good yields via Rh(II)-catalyzed reaction of triazoles with MBH adducts derived from *α*, *β*-unsaturated cyclic ketones and subsequent rearrangement/aza-Michael addition/ oxidative aromatization tandem reactions. This new synthetic method enables the rapid availability of various 3,4-fused pyrroles from readily available starting materials under mild reaction conditions, which can be extended to more complex frameworks. Further exploration to construct important nitrogen-containing heterocycles are currently underway in our laboratory.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: triazoles • MBH adducts • 3,4-fused pyrroles • rhodium catalyzed

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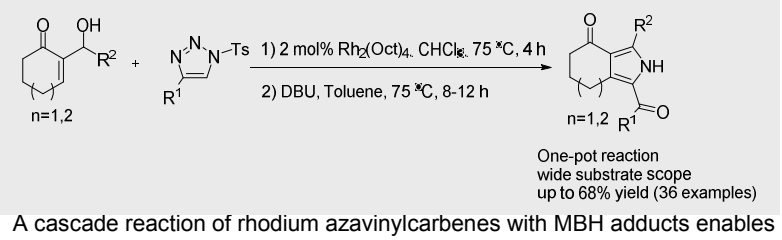

A cascade reaction of rhodium azavinylcarbenes with MBH adducts enables a novel synthetic approach to 3,4-fused pyrroles. The reaction is applicable to a broad scope of substrates and shows good compatibility of functional groups.

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Rhodium(II)-Catalyzed Reaction of 1-Tosyl-1,2,3-triazoles with Morita–Baylis–Hillman adducts: Synthesis of 3,4-Fused Pyrroles