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Rhodium(III)-Catalyzed [3+2]/[5+2] Annulation of 4-Aryl 1,2,3-Triazoles with Internal Alkynes through Dual C(sp^2)–H Functionalization**

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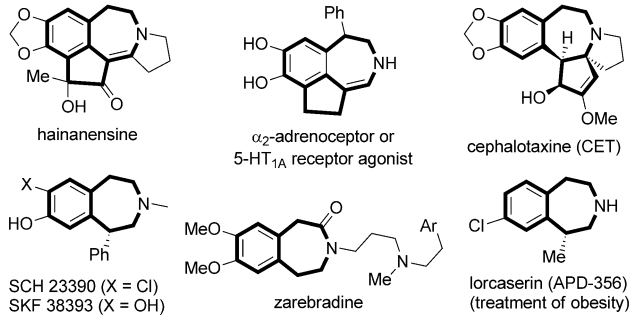
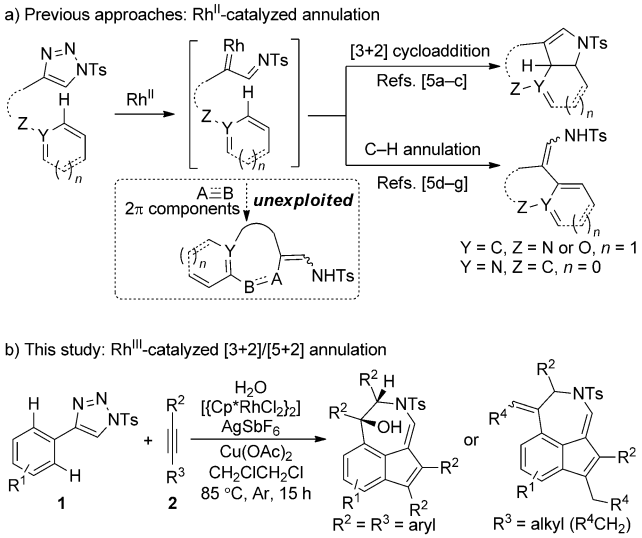
Abstract: *A rhodium(III)-catalyzed [3+2]/[5+2] annulation of 4-aryl 1-tosyl-1,2,3-triazoles with internal alkynes is presented. This transformation provides straightforward access to indeno[1,7-cd]azepine architectures through a sequence involving the formation of a rhodium(III) azavinyl carbene, dual C(sp^2)–H functionalization, and [3+2]/[5+2] annulation.*

Azepines and their derivatives,[1,2] including 1*H*-benzo[*d*]-azepines (Scheme 1),[2] are structural motifs in numerous natural products and pharmaceuticals with diverse biological and medicinal properties, such as antitumor, antibiotic, and anti-inflammatory activity. For example, hainanensine[2a–e] and cephalotaxine[2g–i] were isolated from the antileukemia plants, *Cephalotaxus hainanensis* and *C. fortunei*, and found to have marginal antitumor activity. Lorcaserin (APD-356)[2p] has high affinity for the serotonin 5-HT_{2C} receptor and gained FDA approval in 2012 for the treatment of obesity. Therefore, considerable effort has been devoted to the development of efficient methods for the synthesis of such 1*H*-benzo[*d*]azepines. Generally, these methods require several steps for the construction of the core 1*H*-benzo[*d*]azepine structure.[2,3] Thus, the development of new efficient methods, and especially straightforward strategies, for building these core structures is desirable.



Scheme 1. Important benzo[*d*]azepine compounds.

Recently, the use of 1-sulfonyl-1,2,3-triazoles as ideal precursors of Rh^{II} azavinyl carbenes has attracted more and more attention, as their conversion into valuable nitrogen-containing compounds, in particular N-heterocyclic compounds, is uniquely practical.[4–6] Attractive transformations include the rhodium(II)-catalyzed reaction of 1-sulfonyl-1,2,3-triazoles with various aromatic rings (Scheme 2a).[5]



Scheme 2. Annulation with 1-sulfonyl 1,2,3-triazoles. Cp* = pentamethylcyclopentadienyl, Ts = *p*-toluenesulfonyl.

These aromatic rings have served as dipolarophiles for [3+2] cycloaddition with the Rh^{II} azavinyl carbenes[5a–c] or provided aryl C(sp^2)–H bonds for intramolecular annulation with the carbenes.[5d–g] However, such successful approaches are quite rare,[4] and most are restricted to aromatic rings that contain or are directly linked to an electron-rich heteroatom (a nitrogen or oxygen atom) for the formation the key zwitterion intermediates. In light of these challenges and recent progress in rhodium(III)-catalyzed C–H oxidative annulation reactions with π components,[7] we envisioned that by adding a viable 2π component, both the carbene and the aryl C(sp^2)–H bond could be trapped in novel annulation reactions to build new cyclic compounds (Scheme 2a).

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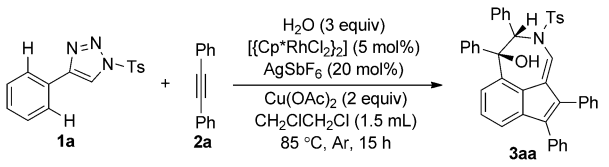
Herein, we report a new rhodium(III)-catalyzed [3+2]/[5+2] annulation of 4-aryl 1-tosyl-1,2,3-triazoles with internal alkynes (Scheme 2b). This method enables the functionalization of two aryl C(sp^2)–H bonds in 4-aryl 1,2,3-triazoles with two alkyne molecules, and provides a new straightforward route to the indeno[1,7-*cd*]azepine architecture.[3] To the best of our knowledge, no metal-catalyzed [3+2]/[5+2] annulation of 4-aryl 1,2,3-triazoles through dual C(sp^2)–H functionalization has been reported previously.

An initial investigation was carried out with 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**) and 1,2-diphenylethyne (**2a**) as reaction partners (Table 1). Extensive screening of various

Table 1: Screening of reaction conditions.[a]

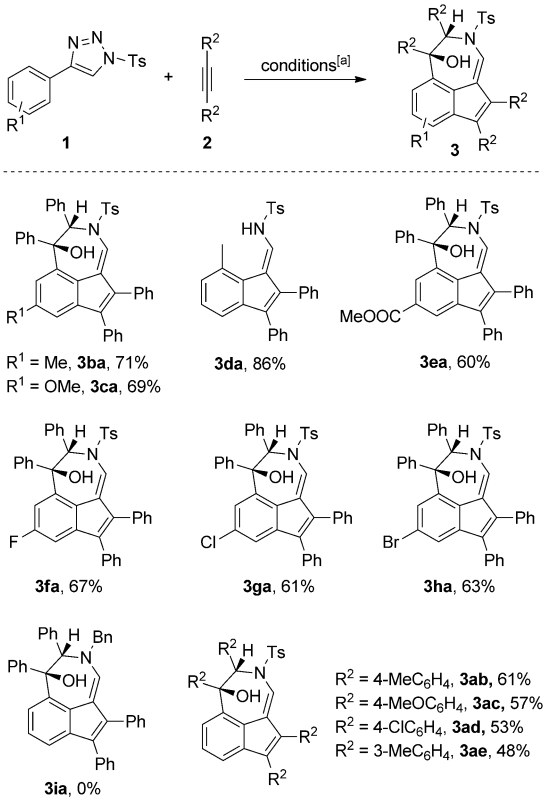


Entry	Variation from the standard conditions	Yield [%][b]
1	none	70
2	at 60 °C	23
3	at 100 °C	64
4	without [{Cp*RhCl$_2$}$_2$]	0
5	[{Cp*RhCl$_2$}$_2$] (2 mol%)	40
6	[{Cp*RhCl$_2$}$_2$] (10 mol%)	71
7	without $AgSbF_6$	0
8	AgOAc, Ag_2CO_3, or AgOTf instead of $AgSbF_6$	trace
9	without $Cu(OAc)_2{\cdot}H_2O$	0
10	*t*AmOH or toluene instead of CH_2ClCH_2Cl	< 10
11	H_2O (6 equiv)	63

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (2.5 equiv), H_2O (3 equiv), [{Cp*RhCl$_2$}$_2$] (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv), CH_2ClCH_2Cl (anhydrous, 1.5 mL), 85 °C, argon atmosphere, 15 h. The d.r. value of the product was > 20:1, as determined by ^{1}H NMR spectroscopic analysis of the crude product. [b] Yield of the isolated product.

reaction parameters revealed that the optimal conditions for the [3+2]/[5+2] annulation reaction were the use of H_2O (3 equiv), [{Cp*RhCl$_2$}$_2$] (5 mol%), $AgSbF_6$ (20 mol%), and $Cu(OAc)_2$ (2 equiv) in the medium CH_2ClCH_2Cl at 85 °C under an argon atmosphere. Under these conditions the desired indeno[1,7-*cd*]azepin-1-ol **3aa** was obtained in 70% yield (Table 1, entry 1).[8] A higher or lower reaction temperature had a negative effect on the reaction (Table 1, entries 1–3). Notably, control experiments confirmed that the Rh^{III} catalyst, $AgSbF_6$, and the Cu oxidant played an important role in the reaction: When any one of these species was omitted, no detectable product **3aa** was formed (Table 1, entries 4, 7, and 9). Furthermore, other Ag salts, including AgOAc, Ag_2CO_3, and AgOTf, did not promote the reaction (Table 1, entry 8). These results support the hypothesis that the only role of $AgSbF_6$ is to activate the Rh^{III} species.[7] Two other solvents, 2-methylbutan-2-ol (*tert*-amyl alcohol, *t*AmOH) and toluene, were found to be less effective than CH_2ClCH_2Cl (Table 1, entry 1 versus entry 10). The yield of **3aa** decreased when the amount of H_2O was increased to 6 equivalents (63%; Table 1, entry 11).

We next explored the scope of this rhodium-catalyzed [3+2]/[5+2] annulation reaction with regard to 4-aryl 1-tosyl-1,2,3-triazoles **1** and internal alkynes **2** [Schemes 2 and 3 and Eq. (1)]. The optimal conditions were compatible with a variety of substituents, namely, Me, MeO, CO_2Me, F, Cl, and Br, on the aromatic ring of the 4-aryl moiety (Scheme 3).

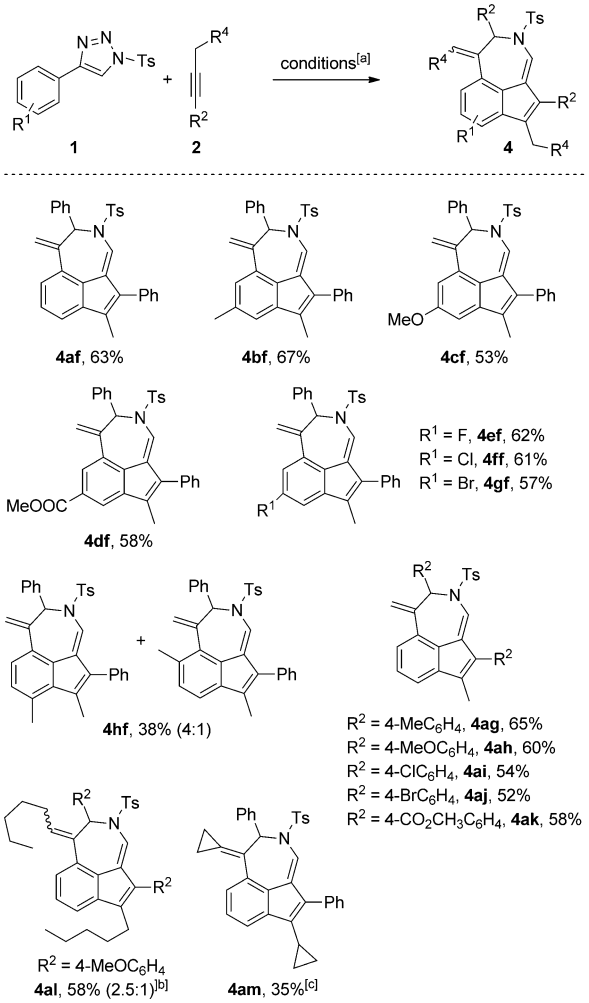


Scheme 3. Annulation of 4-aryl 1,2,3-triazoles **1** with 1,2-diaryl alkynes **2**. [a] Reaction conditions: **1** (0.15 mmol), **2** (2.5 equiv), [{Cp*RhCl$_2$}$_2$] (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv), H_2O (3 equiv), CH_2ClCH_2Cl (anhydrous, 1.5 mL), 85 °C, argon atmosphere, 15 h. The products were formed with d.r. > 20:1, as determined by ^{1}H NMR spectroscopic analysis of the crude product. Bn = benzyl.

For example, triazole **1b** with a *p*-methyl-substituted aryl ring was smoothly converted into the desired indeno[1,7-*cd*]azepin-1-ol **3ba** in the presence of 1,2-diphenylethyne (**2a**), H_2O, [{Cp*RhCl$_2$}$_2$], $AgSbF_6$, and $Cu(OAc)_2$. However, the *o*-methyl-substituted substrate **1d** formed only the [3+2] annulation product **3da** in 86% yield. Triazole **1e** with an electron-withdrawing CO_2Me substituent was also suitable for the construction of **3ea**, albeit in lower yield. Interestingly, halogen groups, F, Cl, and Br, were well-tolerated under the optimal conditions (products **3fa–ha**), thus providing opportunities for additional modification of the product. However, triazole **1i**, with a benzyl group instead of the Ts group, was inert (no formation of **3ia**). Four other symmetrical 1,2-diaryl-substituted alkynes **2b–e** were subsequently subjected to

reaction with triazole **1a** and gave the corresponding products **3ab**–**ae** in moderate yields.

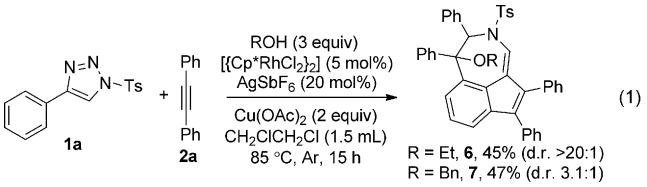
Gratifyingly, this [3+2]/[5+2] annulation reaction was applicable to internal alkyl alkynes; however, the chemoselectivity was shifted toward the formation of 1-methyleneindeno[1,7-*cd*]azepines **4** rather than indeno[1,7-*cd*]azepin-1-ols **3** (Scheme 4). When phenylpropyne (**2f**) was



Scheme 4. Annulation of 4-aryl 1,2,3-triazoles **1** with alkyl alkynes **2**. [a] For reaction conditions, see Table 1. [b] The *Z*/*E* isomer ratio is given in parenthesis. [c] A side product **5am** was obtained in 14% yield (see Scheme S1 in the Supporting Information).

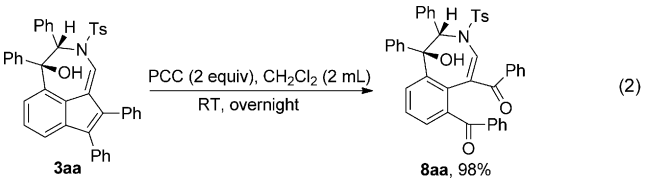
used as the alkyne substrate with various 4-aryl 1-tosyl-1,2,3-triazoles **1a**–**g**, 1-methyleneindeno[1,7-*cd*]azepines **4af**–**gf** were furnished selectively in moderate to good yields.[8] In contrast, the reaction of 4-(*m*-tolyl)-1-tosyl-1*H*-1,2,3-triazole (**1h**) with phenylpropyne (**2f**) delivered a mixture of regioisomers **4hf**. We were pleased to find that an array of propynes **2g**–**k** with various aryl substituents (4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, and 4-$CO_2MeC_6H_4$) at the terminal alkyne position were suitable substrates for this reaction. Thus, products **4ag**–**ak** were obtained in 52–65% yield. In the case of 1-(4-methoxyphenyl)hept-1-yne (**2l**), a mixture of *Z* and *E* isomers **4al** was obtained in 58% yield. Interestingly, cyclopropyl groups could be readily introduced into the azepine structure (product **4am**) by using a cyclopropyl-substituted alkyne.

The [3+2]/[5+2] annulation was examined with nucleophiles other than H_2O [Eq. (1)]. The alcohols EtOH and



(1)

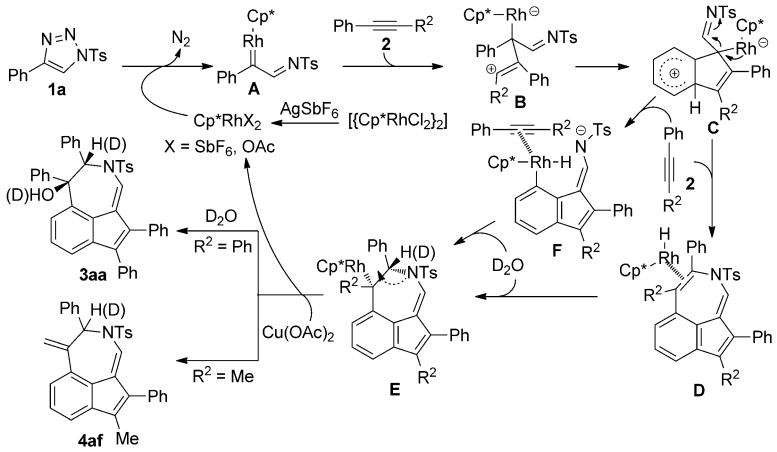
$PhCH_2OH$ were found to successfully participate in the [3+2]/[5+2] annulation reaction, but they were less reactive than H_2O, and the products were formed in moderate yield. Gratifyingly, oxidation of the indeno[1,7-*cd*]azepin-1-ol **3aa** by pyridinium chlorochromate (PCC) readily occurred to afford a new azepine, (benzo[*d*]azepine-5,6-diyl)bis(phenylmethanone) (**8aa**),[8] in quantitative yield [Eq. (2)].[9]



(2)

We propose the mechanism outlined in Scheme 5 for the [3+2]/[5+2] annulation reaction on the basis of the present results (see Scheme S1 in the Supporting Information) and previous reports.[4–6] Initially, the reaction of triazole **1a** with the active Cp^*RhX_2 species (generated in situ from [{Cp^*RhCl_2}$_2$] and $AgSbF_6$)[7] readily produces the rhodium(III) carbenoid intermediate **A**.[10] The addition of intermediate **A** to an alkyne **2** affords intermediate **B**, which undergoes electrophilic cyclization involving one of the phenyl groups to give intermediate **C**.[4–6] A second annulation of intermediate **C** with alkyne **2** leads to the formation of the Cp*(H)Rh-coordinated intermediate **D**.[4] Intermediate **D** undergoes *trans* addition to give intermediate **E** as a result of the coordination of Rh with the nitrogen atom;[8] at this stage a hydrogen atom from H_2O is introduced (see Scheme S1 and Figure S1 in the Supporting Information). When 1,2-diphenylacetylene (**2a**) is used, cleavage of the C–Rh bond with the aid of $Cu(OAc)_2$ through hydration with H_2O by backside attack of the C–Rh bond take place to furnish product **3aa** and regenerate the active Cp^*RhX_2 species. On the other hand, when phenylpropyne (**2f**) is used, the C–Rh bond is cleaved by $Cu(OAc)_2$, and selective β-H elimination then provides product **4af**. It is also possible that the second annulation proceeds by a C–H activation process (from intermediate **C** to intermediate **F**).

In summary, we have developed a novel rhodium-catalyzed [3+2]/[5+2] annulation of 4-aryl 1,2,3-triazoles with internal alkynes for the selective synthesis of indeno[1,7-*cd*]azepin-1-ols and 1-methyleneindeno[1,7-*cd*]azepines.



Scheme 5. Possible reaction mechanism.

This method features a [3+2]/[5+2] annulation through dual C–H functionalization and represents the first straightforward procedure for the construction of the indeno[1,7-*cd*]azepine architecture with excellent functional-group tolerance and good levels of selectivity. Further mechanistic studies and applications of this rhodium(III)-catalyzed triazole-annulation strategy are currently under way in our laboratory.

Keywords: alkynes · annulation · indeno[1,7-*cd*]azepines · rhodium · triazoles

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[8] CCDC 1048349 (**4gf**) and CCDC 1048350 (**8aa**) contain 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. The structure of diastereoisomers **3** was determined by 2D NMR spectroscopic analysis of **3aa** and from the single-crystal structure of **8aa** (see Supporting Information).

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Communications

Synthetic Methods

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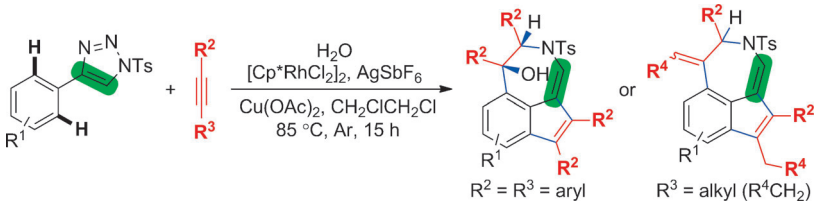
Rhodium(III)-Catalyzed [3+2]/[5+2] Annulation of 4-Aryl 1,2,3-Triazoles with Internal Alkynes through Dual C(sp^2)–H Functionalization



A quantum leap in complexity: A general strategy based on rhodium(III) azavinyl carbene intermediates was established for the oxidative [3+2]/[5+2] annulation of 4-aryl 1-tosyl-1,2,3-triazoles with alkynes. This general method provided densely functionalized indeno[1,7-*cd*]azepine architectures with excellent selectivity through the functionalization of two C(sp^2)–H bonds (see scheme; Cp* = pentamethylcyclopentadienyl, Ts = *p*-toluenesulfonyl).

