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Access to Branched Allylarenes via Rhodium(III)-Catalyzed C−H Allylation of (Hetero)arenes with 2-Methylidenetrimethylene Carbonate

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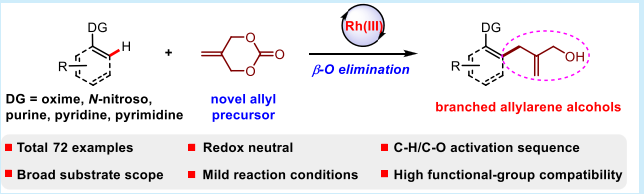
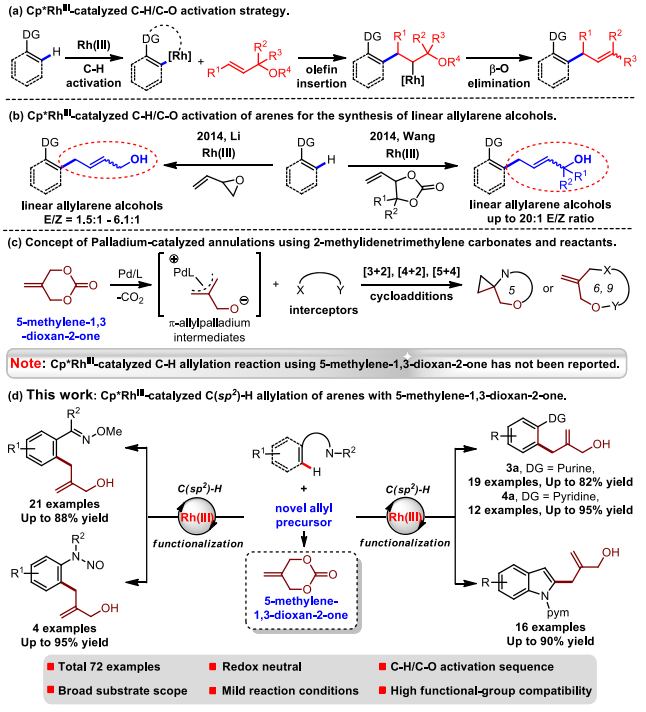
ABSTRACT: A rhodium(III)-catalyzed C−H allylation of (hetero)arenes by using 2-methylidenetrimethylene carbonate as an efficient allylic source has been developed for the first time. Five different directing groups including oxime, *N*-nitroso, purine, pyridine, and pyrimidine were compatible, delivering various branched allylarenes bearing an allylic hydroxyl group in moderate to excellent yields.



The allylic alcohol motif is one of the most widely used synthons, and its transformations into diverse functional groups are of fundamental importance in synthetic chemistry.[1] Besides, allylarenes bearing a hydroxyl group at the allylic position are considered as privileged scaffolds found in many biological compounds.[2] Consequently, various approaches have been developed to access this useful scaffold. The classic method for the synthesis of allylarenes bearing an allylic hydroxyl group was Friedel−Crafts-type allylation using vinyl epoxide as the coupling partner.[3] An alternative is via cross coupling of organometallic reagents with vinyl epoxide electrophiles.[4] However, harsh reaction conditions, poor regioselectivity, and substrate specificity limited their applications.

In recent years, transition-metal-catalyzed C−H functionalization provides a convenient pathway for allyl arene synthesis. Direct C−H allylation of arenes bearing a directing group could be achieved in the presence of various transition metals, such as Rh,[5] Ru,[6] Co,[7] Ni,[8] Mn,[9] and others.[10] Among them, the Rh(III)-catalyzed C−H/C−O activation strategy, which mainly includes the continuous reaction process of C−H activation, olefin insertion, and *β*-O elimination, has received increasing popularity owing to its distinct superiorities for assembly of allyl arenes with more convenience and efficiency (Scheme 1a).[11] Until now, various allylic reagents including allyl carbonates,[11b−d] allyl acetates,[11e,f] allylic alcohols,[11g] methyleneoxetanones,[11h−j] vinyl benzoxazinanones,[11k] and others[11l,m] have been proved to be effective coupling partners in Rh(III)-catalyzed allylation reactions. Despite these achievements, the methods for the synthesis of allylarenes bearing an allylic hydroxyl group are still rare. In 2014, Li and co-workers reported a Rh(III)-catalyzed allylation of arenes with 2-vinyloxiranes for the synthesis of allylic alcohols (Scheme 1b).[12] Subsequently, by using vinyl-1,3-dioxolan-2-ones as

Scheme 1. Cp*Rh(III)-Catalyzed C−H Allylation of Arenes with 5-Methylene-1,3-dioxan-2-one



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novel allylic precursors, Wang's group developed a Rh(III)-catalyzed C−H allylation of benzamides for highly chemo- and stereoselective synthesis of allylic alcohols (Scheme 1b).[13] However, the allylarenes obtained were featured with linear allylic alcohol, while the methods for the synthesis of branched allylarenes bearing an allylic hydroxyl group were not reported.

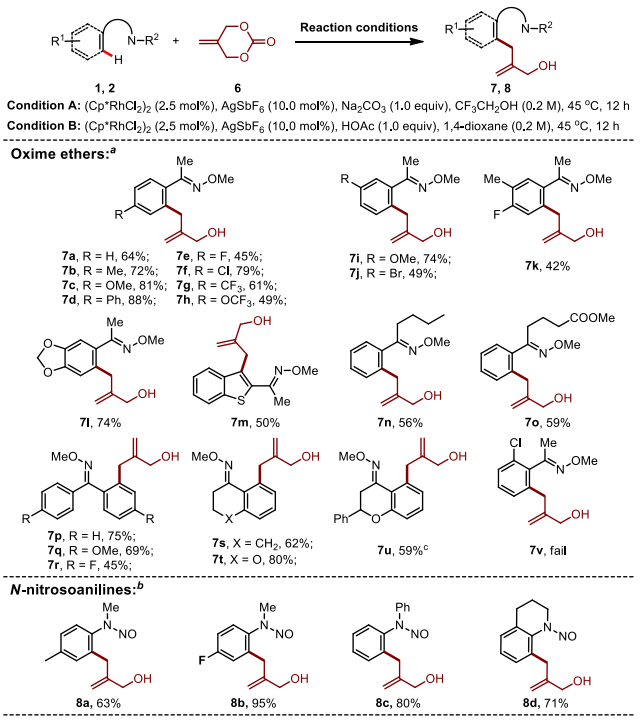
2-Methylidenetrimethylene carbonates were effective building blocks in cycloaddition reactions.[14] They underwent decarboxylation to afford zwitterionic π-allylpalladium species which could serve as three-atom or four-atom synthons to deliver the cycloaddition products (Scheme 1c). However, to the best of our knowledge, they have not been utilized as novel allylic reagents in transition-metal-catalyzed C−H allylation reactions. Based on our continuable research interest in Rh(III)-catalyzed C−H functionalization and previous work,[15] we herein disclose the first example of Rh(III)-catalyzed C−H allylation of (hetero)arenes by employing 2-methylidenetrimethylene carbonate as an efficient allyl precursor (Scheme 1d). This practical and scalable protocol proceeds under redox-neutral conditions and displays broad substrate scope (total of 72 examples, up to 95% yield, five different directing groups including oxime, *N*-nitroso, purine, pyridine, and pyrimidine were explored), mild reaction conditions, and high functional group compatibility.

Initially, by using 2-methylidenetrimethylene carbonate as an allylic reagent and $(Cp^*RhCl_2)_2$ as the catalyst, we screened several directing groups (see the Supporting Information for details). Delightfully, the allylic alcohol product was obtained in 64% yield when oxime ether was utilized as the directing group in CF_3CF_2OH at 45 °C (see SI, Table 1, entry 1), and arenes bearing the *N*-nitroso directing group could also be transformed into the allylation product when 1,4-dixoane was used as the solvent and HOAc as the additive at 45 °C (see SI, Table 1, entry 2). Notably, 6-phenylpurine was also compatible when the allylation reaction was conducted in MeOH with adamantoic acid as the additive at 80 °C (see SI, Table 1, entry 3). Besides, it was found that 2-phenypyridine and *N*-(2-pyrimidinyl)-indole could successfully couple with 2-methylidenetrimethylene carbonate under modified conditions, delivering the corresponding allylic alcohols with yields of 95% (see SI, Table 1, entry 4) and 81% (see SI, Table 1, entry 5), respectively.

With the optimized conditions in hand, we then explored the substrate scope of oxime ethers in this allylation reaction, and the results were displayed in Scheme 2. Gratifyingly, both electron-donating functional groups such as methyl (**7b**, **7k**), methoxyl (**7c**, **7i**), and phenyl (**7d**) and electron-withdrawing groups such as halogen (**7e**, **7f**, **7j**, **7k**), trifluoromethyl (**7g**), and trifluoromethoxy (**7h**) in arenes could be well tolerated, affording the allylic alcohols with yields ranging from 45% to 88%. The allylation occurred at the less hindered site for the *meta*-substituted oxime ethers (**7k**, **7l**). Besides, various carbonyl *O*-methyl oximes were also compatible (**7n**−**7u**). The reaction was also applied to the benzothiophene heterocycle substrate, furnishing the target product **7m** in 50% yield. Unfortunately, the *ortho*-substituted oximes showed no reactivities due to the steric hindrance between the directing group and substitute (**7v**). Delightfully, *N*-nitroanilines have also been proved to be effective substrates, and the desired products were obtained in 63%−95% yields (**8a**−**8d**).

6-Arylpurines served as privileged scaffolds that possess a wide spectrum of pharmacological activities. Therefore, developing novel methods to modify 6-arylpurines is of vital

Scheme 2. Synthesis of Products 7 and 8[a,b]



[a]Reaction Conditions: **1** (0.2 mmol), **6** (1.5 equiv), $(Cp^*RhCl_2)_2$ (2.5 mol %), $AgSbF_6$ (10.0 mol %), Na_2CO_3 (1.0 equiv), CF_3CH_2OH (0.2 M), 45 °C, 12 h. [b]Reaction Conditions: **2** (0.2 mmol), **6** (1.5 equiv), $(Cp^*RhCl_2)_2$ (2.5 mol %), $AgSbF_6$ (10.0 mol %), HOAc (1.0 equiv), 1,4-dioxane (0.2 M), 45 °C, 12 h. [c]48 h.

importance. In this regard, various 6-arylpurines were subjected to allylation reaction, and the results were summarized in Scheme 3.

In general, commonly encountered functional groups such as methoxyl (**9b**, **9g**), methyl (**9h**, **9i**), phenyl (**9c**), phenoxyl (**9d**), and halogen (**9e**−**9i**) were all compatible. Besides, several heterocyclic compounds including benzothiophene (**9j**), benzofuran (**9k**), dibenzofuran (**9m**), and benzo[*d*]-[1,3]dioxole (**9n**) could be smoothly allylated, albeit with a decreased yield. The substituent at the *N*-9 position did not affect the reaction efficiency (**9o**−**9r**), especially for the substrate **9s** bearing a glycosidic substitutional group.

Subsequently, the scope of 2-phenylpyridines was also examined under the same conditions. It was observed that the electronic properties of the substituents have no obvious effect on the products' formation (**10a**−**10g**). Notably, 2-phenylpyridine bearing a substituent at the *ortho* position was amenable to the reaction system, affording the allylic alcohol product in 62% yield (**10h**). Meanwhile, heteroarenes such as benzo[*d*][1,3]dioxole (**10j**), dibenzofuran (**10k**), and benzofuran (**10l**) were also compatible in standard conditions.

To further expand the scope of this rhodium-catalyzed allylation reaction, we turned our attention to the indole substrates. As shown in Scheme 4, *N*-pyrimidylindole derivatives bearing various substituents such as formyl (**11b**), methyl (**11g**), halogen (**11c**−**11e**, **11h**, **11i**), trifluoromethyl (**11j**), ester (**11k**), nitryl (**11f**), and 4-methoxy phenyl (**11l**) at C4, C5, and C6 positions could be smoothly transformed into allylic alcohol products in 25%−90% yields. Besides, C5- and C6-disubstituted indole substrates could be well tolerated and

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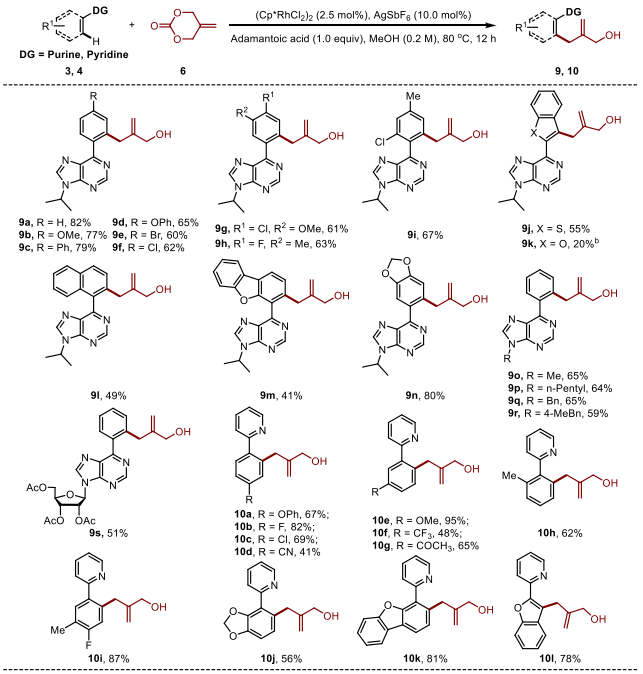
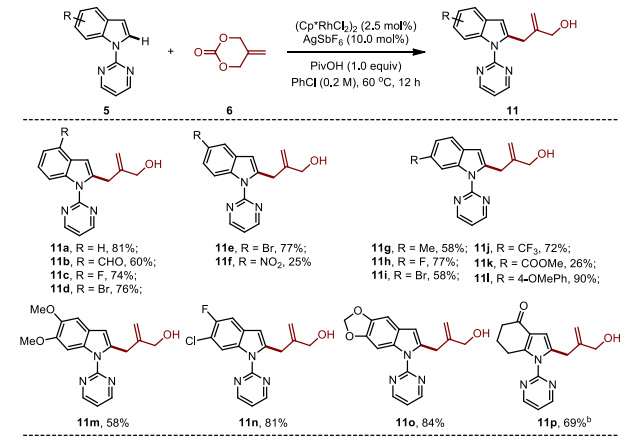
Scheme 3. Synthesis of Products 9 and 10[a]



[a]Reaction conditions: **3** (0.2 mmol), **6** (1.1 equiv), $(Cp^*RhCl_2)_2$ (2.5 mol %), $AgSbF_6$ (10.0 mol %), adamantoic acid (1.0 equiv), MeOH (0.2 M), 80 °C, 12 h. [b]110 °C.

Scheme 4. Synthesis of Product 11[a]

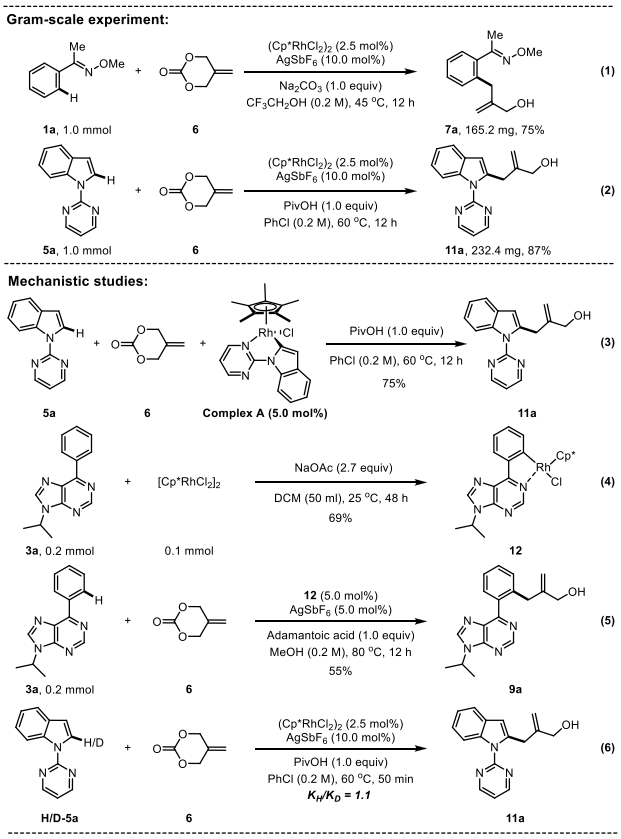


[a]Reaction conditions: **5** (0.2 mmol), **6** (1.5 equiv), $(Cp^*RhCl_2)_2$ (2.5 mol %), $AgSbF_6$ (10.0 mol %), PivOH (1.0 equiv), PhCl (0.2 M), 60 °C, 12 h. [b]80 °C.

generated the allylated products with satisfactory yields (**11n**, **11o**). Of note, the pyrrole derivative could also couple with **6** at elevated temperature and give the product in 69% yield (**11p**).

To demonstrate the synthetic applications, the scales for the synthesis of products **7a** (Scheme 5, eq 1) and **11a** (Scheme 5, eq 2) were extended to 1.0 mmol, and the products **7a** and **11a** were isolated in 75% and 87% yield, respectively. Next, some control experiments were carried out to probe the reaction mechanism. Coupling of *N*-pyrimidylindole **5a** with **6** using cyclometalated rhodium complex **A** as the catalyst afforded the allylic alcohol **11a** in 75% yield (Scheme 5, eq 3). Besides, cyclometalated rhodium complex **12** was synthesized accord-

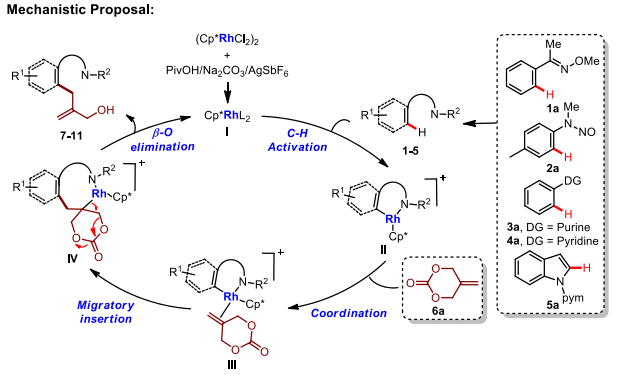
Scheme 5. Control Experiments



ing to the previous literature procedure[16] (Scheme 5, eq 4) and subjected to the same conditions for the coupling of **3a** and **6**, and the desired product **9a** was isolated in 55% yield (Scheme 5, eq 5). These above two experiments indicated that the allylation reaction likely took place via a C−H activation mechanism. Furthermore, a kinetic isotope effect value of 1.1 was obtained, suggesting that the C−H bond activation is not involved in the turnover-limiting step (Scheme 5, eq 6).

Based on the mechanistic investigations and literature precedents,[11] a plausible mechanism was proposed for the allylation reaction (Scheme 6). First, cyclometalated rhodium complex **II** was formed via C−H activation between active catalyst **I** and substrates **1**. Subsequently, coordination of **II** with alkene **6** followed by a migratory insertion generated intermediate **IV**, which underwent β-oxygen elimination and

Scheme 6. Mechanistic Proposal



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then released one molecule of CO_2. The allylic alcohol products **7**−**11** were formed via protodemetalation accompanied by regenerating the active rhodium catalyst.

In conclusion, we have developed the rhodium(III)-catalyzed C−H allylation reaction of (hetero)arenes by using 2-methylidenetrimethylene carbonate as an efficient allylic source. Five different directing groups including oxime, *N*-nitroso, purine, pyridine, and pyrimidine were applicable to the reaction catalytic system. Various branched allylarenes bearing an allylic hydroxyl group were obtained in moderate to excellent yields, and gram-scale synthesis and mechanistic studies were also accomplished. To the best of our knowledge, 2-methylidenetrimethylene carbonate was employed as an efficient allyl precursor for the first time in transition-metal-catalyzed direct C−H allylation reactions. Further efforts for strengthening the application of this transformation and developing other transition-metal-catalyzed cross-coupling reactions are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01832.

Reaction condition screening tables, detailed experimental procedures, and characterization data for all products including ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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