C–H Activation

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Mild Rhodium(III)-Catalyzed Direct C–H Allylation of Arenes with Allyl Carbonates**

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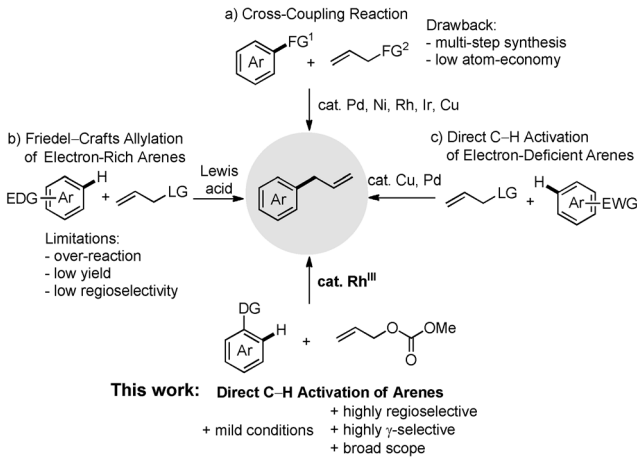
Owing to the versatility of the allyl group as a handle to access various functional groups, the introduction of an allyl moiety to an aromatic ring allows for rapid buildup of molecular complexity. Besides, allylarene fragment itself is found in a range of natural products and biologically active compounds.[1] Therefore, the synthesis of allylarenes has attracted the attention of synthetic chemists for many years. Cross-coupling reactions based on a prefunctionalized arene have proven to be a powerful method to this purpose (Scheme 1 a).[2] Nevertheless, from a step- and atom-economic point of view, the synthesis starting from a simple C–H bond would be a more straightforward and attractive alternative.[3] In this regard, Lewis acid-mediated Friedel–Crafts-type allylation of electron-rich arene has been known for years. However, the application of this strategy suffers from limited substrate scope, poor regioselectivity, and overreaction (Scheme 1 b).[4]



Scheme 1. Different approaches toward allyl arenes. DG = directing group, EDG = electron-donating group, EWG = electron-withdrawing group, FG = functional group, LG = leaving group.

Over the past few years, metal-catalyzed direct C–H functionalization has been demonstrated to be effective for various C–C and C–X bond formation reactions.[5] However, the direct C–H allylation of arenes, despite its critical importance, has been rarely realized. For example, independent work by Miura, Zhang, and Sawamura revealed that electron-deficient arenes, such as polyfluoroarenes and azoles, could be allylated in the presence of copper[6] or palladium[7] catalysts (Scheme 1 c). It is also known that ruthenium[8] and rhenium[9] could catalyze the *ortho*-allylation of 2-phenylpyridines and benzoates, respectively, at high temperatures. However, significant migration of the double bond, poor regioselectivity, and/or limited substrate scope were observed. Very recently, elegant direct C–H allylations by using allene as allyl source were reported.[10] The essential use of polysubstituted allenes limits the diversity of products owing to their specific substitution patterns. Herein, we report a rhodium(III)-catalyzed[11] direct C–H allylation reaction by using more readily available allyl carbonates as the allyl electrophile.[12] The reaction proceeds under mild conditions[5s] with excellent γ-selectivity and broad substrate scope.

We initiated our study by examining the allylation of *N*,*N*-diisopropylbenzamide **1a**.[13] The influence of different allyl electrophiles was first evaluated in the presence of preformed cationic $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ catalyst and PivOH (1.0 equiv) in toluene at 120 °C (Table 1). To our delight, although allyl bromide **2a** showed no reactivity at all, other allyl sources, such as allyl acetate **2b**, allyl phosphate **2c** and allyl carbonate **2d** provided some of the desired product (entries 1–4). It should be mentioned that a significant amount of thermodynamically more stable product **4a** was also formed, in agreement with previous observations.[8] No diallylation product was ever detected. Interestingly, the reaction temperature could be lowered to 65 °C when a $[\{Cp^*RhCl_2\}_2]/AgSbF_6$ (1:4) catalyst system was applied in chlorobenzene. In this case, allyl carbonate **2d** gave better reactivity but a worse isomeric **3a**/**4a** ratio was observed (entries 5 and 6). We suspected that in the reaction of allyl phosphate **2c** the generated phosphoric acid might account for the higher **3a**/**4a** ratio. Surprisingly, the reactivity was maintained when the reaction temperature was lowered to 35 °C, while the **3a**/**4a** ratio was greatly increased to 12:1 (entry 7). The isomeric ratio was indeed sensitive to acid loading. A decrease of PivOH loading (0.5 equiv) gave inferior isomeric ratio, whereas an excess loading (2.0 equiv) gave a better ratio of 32:1 (entries 8 and 9). However, the use of excess PivOH showed an inhibitive

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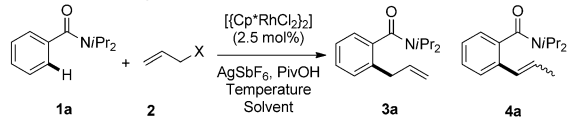
Table 1: Reaction Optimization.[a]

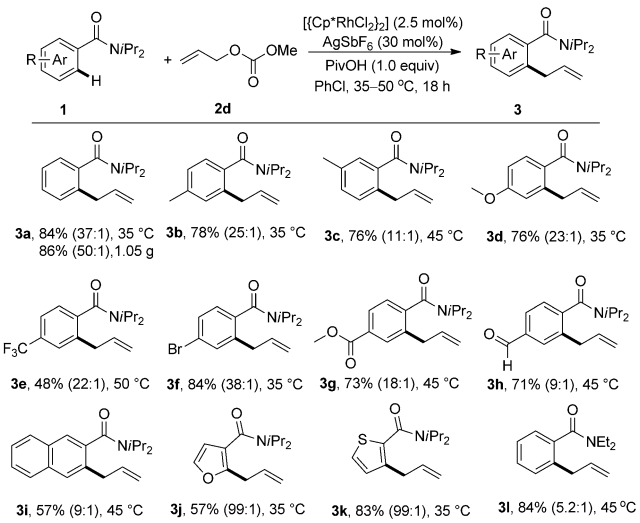


Entry	X	Solvent	*T* [°C]	$AgSbF_6$ [mol%]	**3a**/**4a**[b]	Yield [%][c]
1[d]	Br (**2a**)	$PhCH_3$	120	–	–	0
2[d]	OAc (**2b**)	$PhCH_3$	120	–	5.2:1	8
3[d]	$OPO(OEt)_2$ (**2c**)	$PhCH_3$	120	–	10:1	61
4[d]	OCOOMe (**2d**)	$PhCH_3$	120	–	1.6:1	30
5	**2c**	PhCl	65	10	7:1	62
6	**2d**	PhCl	65	10	1:1	86
7	**2d**	PhCl	35	10	12:1	85
8[e]	**2d**	PhCl	35	10	4.4:1	83
9[f]	**2d**	PhCl	35	10	32:1	66
10	**2d**	DCE	35	10	8:1	70
11	**2d**	$PhCF_3$	35	10	10:1	69
12	**2d**	*t*AmylOH	35	10	24:1	49
13	**2d**	PhCl	35	15	15:1	80
14	**2d**	PhCl	35	20	25:1	79
15	***2d***	*PhCl*	*35*	*30*	*37:1*	*84*
16	**2d**	PhCl	35	30	50:1	86[g]

[a] **1a** (0.2 mmol), **2** (0.4 mmol), $[\{Cp^*RhCl_2\}_2]$ (2.5 mol%), $AgSbF_6$ (0–30 mol%), PivOH (1.0 equiv), solvent (1 mL), 18 h. [b] Determined by GC-MS. [c] Yields of isolated products. [d] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5 mol%). [e] PivOH (0.5 equiv). [f] PivOH (2.0 equiv). [g] 5 mmol scale.

effect, which is probably because of the competitive coordination to the metal with the substrate.[14] Screening of a range of solvents revealed chlorobenzene is the solvent of choice (entries 10–12). The critical improvement of both reactivity and selectivity was achieved by the use of a slight excess of $AgSbF_6$ (entries 13–15). Thus, in the presence of $[\{Cp^*RhCl_2\}_2]$ (2.5 mol%)/$AgSbF_6$ (30 mol%), a yield of 84% was obtained with the **3a**/**4a** ratio being as high as 37:1. To demonstrate the robustness of this catalyst system, a gram-scale reaction was conducted and a yield of 86% was obtained with an excellent isomeric ratio of 50:1 (entry 16).

With the optimized procedure at hand, our attention turned to an evaluation of the scope and limitations of this reaction (Scheme 2). Given the great value of terminal alkenes, we used the simple allyl carbonate **2d** to examine the scope. To our delight, the mild reaction conditions allowed the *ortho*-allylation of benzamides containing a variety of functional groups, regardless of electron-donating or electron-withdrawing properties, delivering the corresponding products in moderate to good yields (48–86%). Notably, methoxy (**3d**), trifluoromethyl (**3e**), bromo (**3f**), ester (**3g**), and formyl (**3h**) were valuable functional groups amenable for further decoration of the products. Excellent regioselectivity was observed when 3-methyl-substituted substrate **1c** was used, favoring activation of the less-hindered C–H bond (**3c**). Electron-withdrawing substituents were found to retard the reaction (**3e**, **3g**, **3h**). However, by simply increasing the reaction temperature, good yields could be maintained. 2-Naphthamide **1i** was also a suitable substrate, giving the β-allylated product exclusively in 57% yield. It is noteworthy that heterocycles such as furan and thiophene were very well

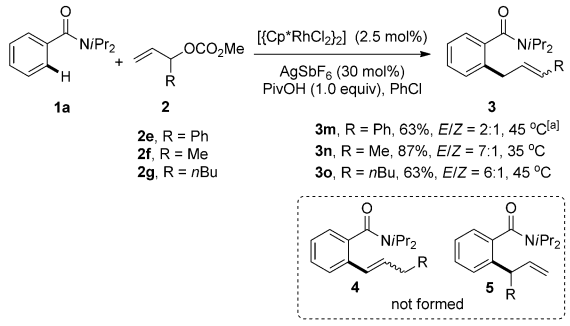


Scheme 2. Rh^{III}-catalyzed allylation of tertiary benzamides **1** with **2d**. General reaction conditions: **1** (0.4 mmol), **2d** (0.8 mmol), $[\{Cp^*RhCl_2\}_2]$ (2.5 mol%), $AgSbF_6$ (30 mol%), PivOH (1.0 equiv), PhCl (2 mL). Ratios for **3**:**4** given in brackets were determined by GC-MS.

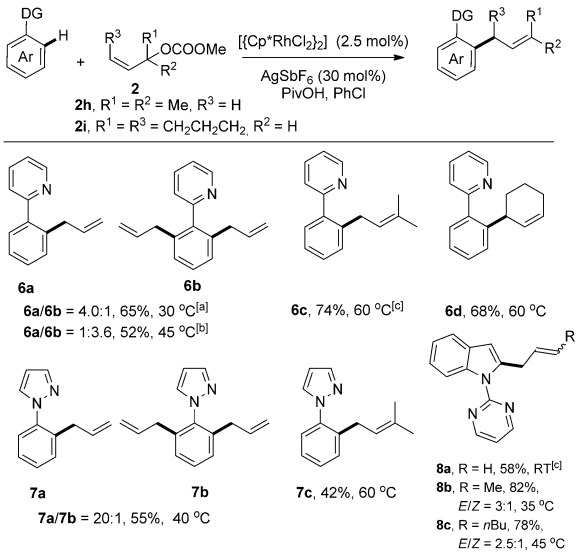
tolerated, leading to valuable allylated heterocycles. The reaction of furan derivative **1j** preferentially occurred at the α position. In all cases, good to excellent isomeric ratios (up to 99:1) were obtained, demonstrating the great value of this procedure. Again, no diallylation products were observed. The reaction is not restricted to bulky *N*,*N*-diisopropylbenzamide derivatives, and the use of less-hindered *N*,*N*-diethylbenzamide **1l** also assured a high yield, albeit with lower isomeric ratio.

Encouraged by these results, we next explored the scope of allyl electrophilic partners (Scheme 3). Whilst linear allyl carbonates, such as cinnamyl carbonate, were completely inert, the branched isomer 1-phenylallyl carbonate **2e** did show good reactivity. The reaction proceeded readily with complete γ-selectivity (no **5** was formed), affording **3m** as an *E*/*Z* diastereoisomer of 2:1. The subjection of alkyl-substituted **2** gave comparable or higher yields and significantly superior diastereoisomeric ratios of up to 7:1. Notably, in no cases were double-bond migration products **4** detected.

To further highlight the power of this procedure, the Rh^{III}-catalyzed direct C–H allylation reaction was applied to other



Scheme 3. Rh^{III}-catalyzed allylation of benzamide **1a** with substituted allyl carbonate **2**. For reaction conditions, see Scheme 2. [a] $AgSbF_6$ (10 mol%).

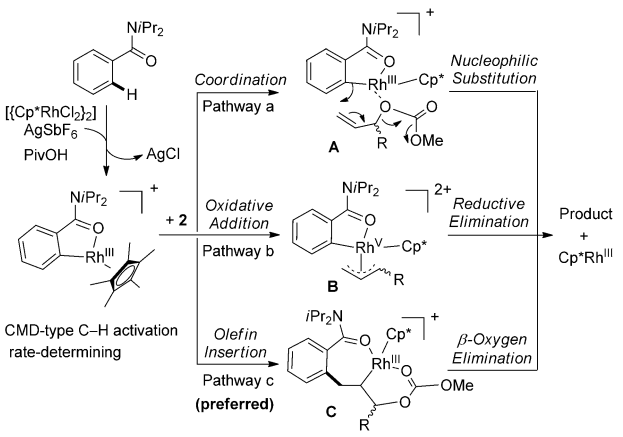


Scheme 4. Rh^{III}-catalyzed allylation of different substrates. For reaction conditions, see Scheme 2. [a] **2d** (2.0 equiv). [b] **2d** (4.0 equiv). [c] $AgSbF_6$ (10 mol%).

types of substrates (Scheme 4). 2-Phenylpyridine showed excellent reactivity. Thus, selective mono- and diallylation could be achieved by applying different temperatures and different loadings of **2d**. Gratifyingly, the prenyl group, which appears in numerous natural products and biologically active compounds,[1] could be installed efficiently in this case as a single isomer (**6c**).[15] The use of cyclohex-2-en-1-yl methyl carbonate also delivered the corresponding product in good efficiency (**6d**). Similarly, the allylation and prenylation of 1-phenyl-1*H*-pyrazole was also accessible, albeit in lower yields. The C2-selective allylation of indoles is highly interesting but also challenging.[16] We were pleased to find that by using a removable pyrimidyl directing group, the C2-allylation was successfully accomplished with complete selectivity. However, the use of phenyl-substituted allyl carbonate **2e** gave an inseparable mixture of C2- and C3-allylated product.

To gain insight into the mechanism, the kinetic isotope effect was measured by using **1a** and [D_5]-**1a** as substrates. A KIE value of 5.4 was obtained,[17] suggesting that the C–H bond cleavage are involved in the rate-limiting step[18] and might follow a concerted metalation–deprotonation (CMD)-type mechanism.[19]

Three possible mechanistic scenarios can be proposed for the subsequent C–C bond formation (Scheme 5). The coordination of the carbonate oxygen to Rh^{III} may facilitate an intramolecular nucleophilic substitution (pathway a).[20] Alternatively, oxidative addition of the allyl electrophile to a Rh^{III} species would generate a π-allyl rhodium(V) complex, which upon reductive elimination delivers the corresponding product and regenerates the rhodium catalyst (pathway b). Owing to the complete γ-selectivity for all cases and only a few examples of direct observations of rhodium(V) species,[21] this pathway seems less favorable. In pathway c, migratory insertion of the allyl double bond into Rh–C bond affords a seven-membered rhodium(III) species **C** with the carbonate oxygen chelating to the metal. β-oxygen elimination gives the product and Rh^{III} catalyst. The coordination of the directing group may prevent the syn β-hydride elimination with the benzylic hydrogen atom because of the conformational restriction.[22] Moreover, we speculated that β-oxygen elimination should be facile because the analogue β-oxygen elimination of an organorhodium(I) complex is very well-known.[23] Furthermore, numerous examples of Rh^{III}-catalyzed oxidative Mizoroki–Heck reactions wherein C–H activation is followed by a migratory insertion has been developed.[24,25] We thus believe pathway c to be the most likely path operating in this system. The $AgSbF_6$ may activate the allyl carbonate, change the polarity of the reaction medium or oxidize the Rh–H species, which may account for the migration of double bond.[26]



Scheme 5. Hypotheses for the reaction mechanism.

In conclusion, we have demonstrated a Rh^{III}-catalyzed intermolecular direct C–H allylation reaction with easily accessible allyl carbonates. This procedure provides an unprecedented opportunity for the allylation of electron-neutral arenes. The reaction features complete γ-selectivity, a high isomeric ratio, good substrate scope, and functional group compatibility. The key for success is the use of a slight excess of $AgSbF_6$ salt under mild reaction conditions. We expect this new method to complement existing methods to access allylated aromatics, which are of great interest in different disciplines.

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