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Rhodium(III)-catalyzed heteroatom-directed C–H allylation with allylic phosphonates and allylic carbonates at room temperature

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ABSTRACT

The rhodium(III)-catalyzed mild and site-selective C–H allylation of 2-arylbenzo[*d*]thiazoles and 2-arylbenzo[*d*]oxazoles with allylic phosphonates and allylic carbonates is described. This transformation provides an efficient construction of C2-allylated, crotylated and prenylated 2-arylbenzo[*d*]thiazoles and 2-arylbenzo[*d*]oxazoles. In addition, this protocol can be applied to the formation of 2-arylbenzo[*d*]thiazole scaffolds containing an allylic alcohol group by using of 4-vinyl-1,3-dioxolan-2-one and vinyl oxirane as coupling partners.

1. Introduction

2-Arylbenzo[*d*]thiazoles are common structural motifs found in heterocyclic compounds with biological and medicinal applications including anticancer,[1] antibacterial,[2] potassium channels activation,[3] neurotransmission blockage,[4] and neuroprotection.[5] They also serve as versatile building blocks for organic light-emitting diodes (OLEDs),[6] chemosensors,[7] and photosensitizers.[8] Therefore, the development of efficient protocols for the functionalization of these heterocyclic architectures are of great interest in organic synthesis.[9] Recently, the transition-metal-catalyzed C–H functionalization of 2-arylbenzothiazoles and 2-arylbenzoxazoles with diverse coupling partners has been investigated. In this area, arylation,[10] acetoxylation,[11] acylation,[12] hydroxylation,[13] and halogenations[14] under palladium catalysis were explored. In addition, the ruthenium-catalyzed olefination[15] and amination[16] reactions of 2-arylbenzothiazoles were also examined. Moreover, the rhodium-catalyzed C–H alkylation reactions of 2-arylbenzothiazoles with α-diazo compounds were reported.[17] However, to the best of our knowledge, the direct and catalytic C–H allylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles with allylic compounds has been unexplored.

Catalytic C–H allylation reaction has recently emerged as a versatile tool to deliver structurally intricate organic molecules.[18] For example, Oi and Inoue first described the Ru(II)-catalyzed C–H allylation of 2-phenylpyridines with allylic acetates providing a regioisomeric mixture of olefin products.[18a] Later, Glorius reported beautiful works on the Rh(III)- or Co(III)-catalyzed regioselective terminal allylations of benzamides and indoles with allylic carbonates.[18c,d] Direct C–H allylations of electron-deficient polyfluoroarenes with allylic phosphonates and allylic carbonates under Cu(0),[18f] Cu(I)[18g] and Pd(II)[18h] catalysis were respectively reported. In addition, allenes were used in the Ir(I)-,[18i] Rh(I)-,[18j] and Rh(III)[18k]-catalyzed allylation reactions to give allylated benzamide adducts. More recently, Li[18l] and Wang[18m] independently applied vinyl oxiranes and 4-vinyl-1,3-dioxolan-2-ones into aryl C–H allylation reaction under rhodium catalysis affording aromatic products with allylic alcohol moieties.

Inspired by our recent studies on the rhodium-catalyzed C–H functionalization of (hetero)aromatic compounds[19] and in consideration of the biological application of functionalized 2-arylbenzothiazoles, we herein present the Rh(III)-catalyzed allylation, crotylation and prenylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles with allylic phosphonates or allylic carbonates to afford *ortho*-allylated 2-arylbenzothiazoles and 2-arylbenzoxazoles via C–H bond activation.

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2. Results and discussion

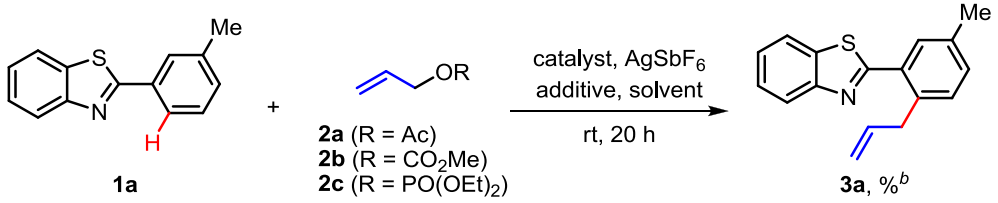
In a previous literature, we found that the combination of $[Cp^*RhCl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2$ in DCE solvent was most effective catalytic system to couple with indoline C–H bonds and allylic substrates.[20] Thus, we used above reaction conditions in our initial study to couple with **1a** and allyl acetate (**2a**) (Table 1), but our desired allylated product **3a** was formed in 13% yield (Table 1, entry 1). Additionally, allylic carbonate **2b** did not also provide a reasonable yield (Table 1, entry 2). Further investigation revealed that allylic phosphonate **2c** as a coupling partner is unique in its ability to facilitate high levels of conversion (Table 1, entry 3). However, cationic ruthenium and cobalt catalysts were found to be ineffective for this transformation (Table 1, entries 4 and 5). Also, exclusion of either $[Cp^*RhCl_2]_2$ and $AgSbF_6$ resulted in no observation of the desired product **3a** (data not shown). Screening of solvents under otherwise identical conditions revealed that THF is found to be an optimal solvent to furnish **3a** in 76% yield, but other solvents such as toluene, MeCN, and *t*-AmOH were less effective (Table 1, entries 6–9). Further screening of additives revealed that $Cu(OAc)_2$ was found to be the most effective in this coupling reaction (Table 1, entries 10 and 11). Furthermore, decreasing amount of $Cu(OAc)_2$ to 50 or 30 mol % provided comparable yields (Table 1, entries 12 and 13). Finally, the coupling reaction was performed under a nitrogen atmosphere leading to a comparable yield (83%) of **3a** (Table 1, entry 14). This result indicate that a role of $Cu(OAc)_2$ as an oxidant can be ruled out in the catalytic cycle.

To evaluate the scope and limitation of this process, the optimal reaction conditions were applied to a range of 2-aryl substituted heteroarenes **1b**–**1o** (Table 2). The reactions of *meta*-substituted 2-arylbenzothiazoles **1b**–**1d** were found to be favored for this transformation to afford the desired products **3b**–**3d** in moderate to good yields. Particularly noteworthy were the mono-selectivity and site-selectivity found at the less hindered position, as well as the tolerance of the reaction conditions to the bromo moiety, providing a versatile synthetic handle for further cross-coupling reactions. However, highly electron-rich 2-arylbenzothiazole **1e** at the *meta*-position was found to be relatively less reactive under the present reaction conditions. This reaction was also compatible with *ortho*-substituted 2-arylbenzothiazole **1f** to furnish **3f** in 74% yield. In addition, symmetric 2-phenylbenzothiazole (**1g**) was coupled with **2c** under the optimal reaction conditions, resulting in a mixture of bis-allylated product **3g** and mono-allylated product **3ga** with 1:1 ratio in 51% combined yield. Logically, it was thought that the ratio of **3g** and **3ga** can be controlled by the amount of allylic phosphonate. Indeed, upon use of 3 equiv of **2c**, the bis-allylated compound **3g** was obtained as a major compound in 63% combined yield, albeit resulting in a low level of bis-selectivity (2:1). Moreover, 2-(*p*-methoxyphenyl)benzothiazole (**1h**) underwent smooth the bis-allylation reaction to afford the corresponding product **3h** in 61% yield.

However, 2-(4-fluorophenyl)benzothiazole (**1i**) gave the bis-allylated compound **3i** in 37% yield in conjunction with mono-allylated compound **3ia** in 36% yield. In sharp contrast, 2-phenylbenzoxazole (**1j**) displayed a significant bis-selectivity under the identical reaction conditions to furnish the corresponding bis-allylated product **3j** in 61% yield, and a trace amount of mono-allylated product was observed by ^1H NMR or GC–MS analysis. In addition, *meta*-substituted 2-arylbenzoxazole **1k** was found to be a good substrate in this transformation. Furthermore, we were pleased to observe the allylation reaction at a vinyl C–H bond, which provided the corresponding product **3l** in 83% yield. Finally, this reaction was found to be comparable with 2-arylthiazoles **1m** and **1n**, but in the case of 2-arylbenzimidazole **1o**, a relatively low amount of product **3o** was formed.

To further explore the scope and limitation of this transformation, substituted allylic phosphonates and allylic carbonates **2d**–**2g** were screened to couple with 2-arylbenzothiazole **1a** and 2-arylbenzoxazoles **1j** and **1k**, as shown in Table 3. In sharp contrast to results of allylation reaction with allyl methyl carbonate (**2b**), both α-methyl-substituted allylic phosphonate **2d** and α-methyl-substituted allylic carbonate **2e** provided a crotylation product **4a** in high yield. In addition, allyl octyl carbonate **2f** was smoothly coupled with **1a** to give a diastereomeric mixture of crotylation product **4b** in 42% yield. Notably, these crotylation reactions proceeded readily with complete γ-selectivity in case of branched allylic

Table 1
Selected optimization of reaction conditions[a]



Entry	Allyl source	Catalyst (mol %)	Additive (mol %)	Solvent	Yield (%)[b]
1	**2a**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	DCE	13
2	**2b**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	DCE	24
3	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	DCE	52
4	**2c**	$[Ru(p\text{-cymene})Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	DCE	35
5	**2c**	$[CoCp^*(CO)I_2]$ (5)	$Cu(OAc)_2$ (100)	DCE	N.R.
6	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	Toluene	Trace
7	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	MeCN	31
8	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	*t*-AmOH	52
9	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	THF	76
10	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (100)	THF	Trace
11	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	PivOH (100)	THF	38
12	**2c**	**$[RhCp^*Cl_2]_2$ (2.5)**	**$Cu(OAc)_2$ (50)**	**THF**	**92**
13	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (30)	THF	78
14[c]	**2c**	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (50)	THF	83

[a] *Reaction conditions*: **1a** (0.3 mmol), **2a**–**2c** (0.6 mmol), catalyst (quantity noted), $AgSbF_6$ (10 mol %), additive (quantity noted), solvent (1 mL) under air at room temperature for 20 h in reaction tubes.
[b] Isolated yield by flash column chromatography.
[c] Under N_2 atmosphere.