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Quinazoline Synthesis via Rh(III)-Catalyzed Intermolecular C−H Functionalization of Benzimidates with Dioxazolones

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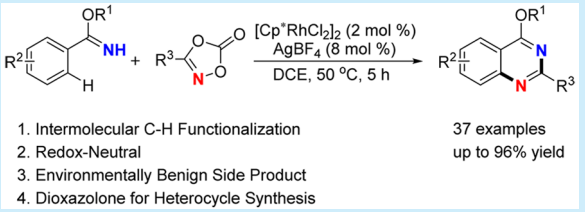
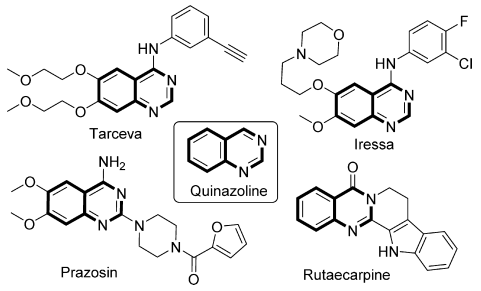
Supporting Information

ABSTRACT: An efficient double C−N bond formation sequence to prepare highly substituted quinazolines utilizing benzimidates and dioxazolones under the catalytic redox-neutral $[Cp^*RhCl_2]_2/AgBF_4$ system, where dioxazolones could work as an internal oxidant to maintain the catalytic cycle, is reported. *N*-Unsubstituted imine not only acts as a directing group but also functions as a nucleophile in postcoupling cyclization, and dioxazolone acts as a coupling partner for access to heterocycle.



The quinazoline moiety, an abundant core of nitrogen-containing heterocycles, is exemplified as a privileged structure that exhibits diverse biological and therapeutic activities such as antibacterial,[1] antiviral,[2] anticonvulsant,[3] and anticancer activities.[4] For example (Scheme 1), erlotinib (Tarceva)[5] and

Scheme 1. Quinazoline and Popular Drugs Containing the Quinazoline Unit



gefitinib (Iressa)[6] are well-known drugs used for the treatment of lung cancer. Prazosin[7] is utilized as α-adrenergic blockers for the treatment of high blood pressure, anxiety, and panic disorder, and Rutaecarpine[8] is one of the main active alkaloids which has long been used to treat gastrointestinal disorders, anti-inflammatory, headaches, and postpartum hemorrhage. Consequently, increasing efforts have been devoted to developing useful preparation methods for the generation of quinazolines, which mainly involve (1) oxidative coupling of anilines bearing an ortho-functional group with different carbon and nitrogen sources;[9] (2) 2-halobenzenes or 2-halobenzyl amination-involved cyclization.[10] Despite these contributions, many of them require the addition of excess oxidants and the use of special prefunctionalized reagents, which could result in preparation difficulties. Therefore, the development of effective new methods for the facile construction of quinazolines is highly desirable.

Transition-metal-catalyzed C−H functionalization promises a shortened synthetic sequence and has recently been explored for building desired valuable C−C/C−hetero bonds or heterocycle skeletons.[11] However, due to the ubiquity of C−H bonds in organic molecules, the presence of a nearby directing group (DG) is usually required in order to direct positioning of a metal catalyst so that specific C−H bond activation occurs. Based on this strategy, while access to heterocycles (such as isoquinolones,[12] isoquinoline,[13] indole,[14] and others[15]) has been extensively explored in Pd-, Rh-, Ir-, Co-, and Ru-catalyzed C−H activation, examples of quinazoline synthesis via a C−H activation pathway are rarely reported. To date, only a few examples[16] of Pd-catalysis, starting from benzamidine, were reported to synthesize quinazolines through intramolecular C−H activation/cyclization. Moreover, there are several limitations, including relatively harsh reaction conditions and/or the requirement of external oxidants for unactivated precursors to maintain the catalytic cycle, resulting in the generation of undesired waste byproduct and off-cycle side reaction. In addition, the substrates are limited to benzamidine derivatives that suffered from not only regioselectivity but also substitution pattern issues; thus, synthetic applications to complex molecules might not be feasible.

To achieve the catalytic process for the synthesis of quinazolines that is tolerant of a diversity of functional groups and proceeds under milder reaction conditions, our attention has been drawn to the potential chemical reactivity of readily available benzimidate derivatives,[17] which not only act as a directing group but also work as a nucleophile in postcoupling cyclization. Recently, dioxazolones as an amidation reagent have played an important role in C−H activation for the synthesis of amide derivatives.[18] However, the generated amide further undergoes intramolecular cyclization nucleophilic addition to

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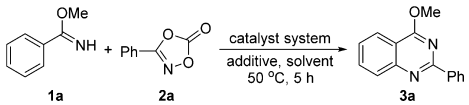
C═O and then dehydration to furnish a heterocycle, which has never been reported. Herein, we report the preliminary result of an efficient double C−N bond formation sequence to prepare highly substituted quinazolines utilizing benzimidates and dioxazolones under the catalytic redox-neutral $[Cp^*RhCl_2]_2$/$AgBF_4$ system, where dioxazolone could work as an internal oxidant to maintain the catalytic cycle meanwhile as a coupling partner for access to the heterocycle.

We initiated our studies with the screening of reaction conditions in the coupling of methyl phenylimidate (**1a**) with 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (Table 1). Using the rhodium

Table 1. Optimization of Reaction Conditions[a,b]



1a 2a 3a

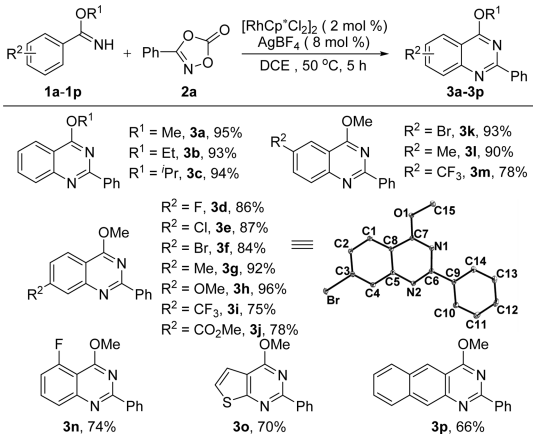
entry	catalyst system	solvent	additive	yield (%)[b]
1	$[RhCp^*Cl_2]_2$/$AgSbF_6$	DCE		82
2	$[RhCp^*Cl_2]_2$/$AgSbF_6$	CH_3CN		54
3	$[RhCp^*Cl_2]_2$/$AgSbF_6$	THF		46
4	$[RhCp^*Cl_2]_2$/$AgSbF_6$	1,4-dioxane		35
5	$[RhCp^*Cl_2]_2$/$AgSbF_6$	MeOH		61
6	$[RhCp^*Cl_2]_2$/AgOAc	DCE		66
7	$[RhCp^*Cl_2]_2$/$AgCO_2CF_3$	DCE		72
8	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE		95
9	$[RhCp^*Cl_2]_2$/$AgNTf_2$	DCE		80
10	$[RhCp^*Cl_2]_2$/$AgPF_6$	DCE		83
11	$AgBF_4$	DCE		0
12	$[RhCp^*Cl_2]_2$	DCE		0
13	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE	NaOAc	90
14	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE	CsOAc	92
15	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE	HOAc	80
16	$[(p\text{-Cymene})RuCl_2]_2$/$AgBF_4$	DCE		0
17	$[Cp^*IrCl_2]_2$/$AgBF_4$	DCE		42
18[c]	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE		75
19[d]	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE		6
20[e]	$[RhCp^*Cl_2]_2$/$AgBF_4$	DCE		0

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), silver salt (8 mol %), solvent (2 mL). [b]Isolated yields. [c]$[RhCp^*Cl_2]_2$ (1 mol %), $AgBF_4$ (4 mol %). [d]$[RhCp^*Cl_2]_2$ (0.5 mol %), $AgBF_4$ (2 mol %). [e]$[RhCp^*Cl_2]_2$ (0.1 mol %), $AgBF_4$ (0.4 mol %).

complex, derived from $[Cp^*RhCl_2]_2$ and $AgSbF_6$ as a catalyst, coupling occurred in DCE (entry 1) at 50 °C for 5 h to afford the product 4-methoxy-2-phenylquinazoline **3a** in 82% yield. Screening of other solvents showed that DCE was the best solvent in this transformation (compare entries 2−5). Afterward, the effect of silver salt was investigated (compare entries 6−10), and $AgBF_4$ gave the best result, as the yield of **3a** increased to 95% (entry 8). The control experiment uncovered that no target product was obtained in the absence of $[Cp^*RhCl_2]_2$ or $AgBF_4$ (entries 11 and 12). Several additives were screened (entries 13−15), but yields were slightly reduced compared to the yield in the absence of an additive. Poor or no conversion was observed when $[Cp^*RhCl_2]_2$ was replaced by $[(p\text{-cymene})RuCl_2]_2$ or $[Cp^*IrCl_2]_2$ catalysts (entries 16 and 17). Lower catalyst loadings (entries 18−20) gave lower yields.

Under the obtained optimal reaction conditions mentioned above, we explored the applicability of the scope of diversely substituted arylimidates **1a**−**1p**. 3-Phenyl-1,4,2-dioxazol-5-one (**2a**) was kept as a representative reaction partner (Scheme 2).

Scheme 2. Reaction Scope for Benzimidates[a,b]



[a]Reaction conditions: **1a**−**1p** (0.4 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgBF_4$ (8 mol %), DCE (2 mL). [b]Isolated yields.

First, the impact of an alkyl in the alkoxy group was investigated. We found that alkoxy groups with different sizes reacted to form the desired products **3a**−**3c** in 93−95% yields. Furthermore, various methyl arylimidates were applied in this reaction. A range of quinazolines were formed in good to excellent yields. It was found that the reaction was sensitive to the steric demand of the arenes. All *m*-substituted imidate (**1k**−**1m**) derivatives showed excellent selectivity to the C−H bond with less steric hindrance. The imidate with *o*-F (**1n**) also afforded the desired product in 74% yield. Various imidates having substituents at the *para*-position with electron-donating substituents (e.g., Me, OMe) reacted to form the desired products **3g**−**3h** in 92%−96% yields. Probably because of the electrophilic C−H activation process, substrates with strong electron-withdrawing groups (e.g., CF_3 and CO_2Me) at the same position inhibited the reaction, affording products **3i**−**3j** in slightly lower respective yields of 75%−78%. It is noteworthy that the halo-substituted (e.g., F, Cl, and Br) substrates performed well to afford the corresponding products (**3d**−**3f**) in good yields. Besides, the methyl thiophene-2-carbimidate (**1o**) and methyl 2-naphthimidate (**1p**) also showed good reactivity in this reaction to give the excellent regioselectivity products **3o** and **3p** in good yields (70% and 66%).

Furthermore, we investigated the scope of dioxazolone derivatives (**2b**−**2v**) with methyl arylimidates (**1a**) as the reaction partner (Scheme 3). 3-Phenyl-1,4,2-dioxazol-5-one reagents bearing different electron-donating and -withdrawing groups at different positions of the phenyl ring all coupled smoothly with **1a**. Furthermore, the 3-substituent in the 1,4,2-dioxazol-5-one reagent is not limited to a phenyl ring, as 3-(furan or thiophen-2-yl)-1,4,2-dioxazol-5-one also coupled to afford the products **4r** and **4s** in 84% and 87% yields. Meanwhile, 3-alkyl substituted reagents were also investigated and we were pleased to observe that a number of 1,4,2-dioxazol-5-ones having alkyl substituents at the 3-position were highly facile to afford 2-alkyquinazoline products (**4t**−**4v**) in good yields.

To demonstrate the utility of the product molecule, we investigated the catalytic functionalization of **3a**−**3c**, generated from a quinazoline formation protocol. We were delighted to find that the amidation reaction using 3-phenyl-1,4,2-dioxazol−5-one (**2a**) can be performed under slightly modified reaction conditions to provide the product **5a**−**5c** and **5d** in good yields

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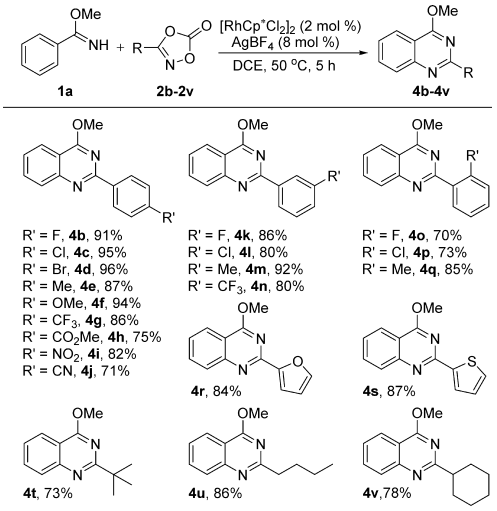
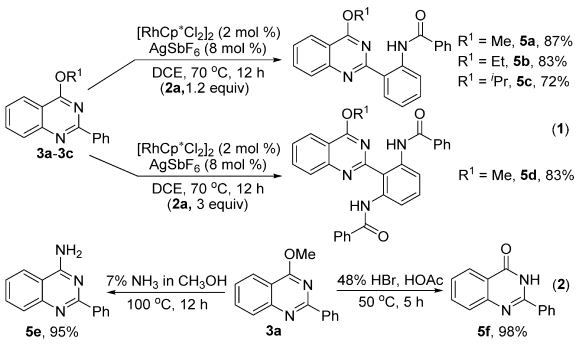
Scheme 3. Reaction Scope for Dioxazolones[a,b]



[a]Reaction conditions: **1a** (0.4 mmol), **2b−2v** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgBF_4$(8 mol %), DCE (2 mL). [b]Isolated yields.

(Scheme 4, eq 1). Owing to the fact that quinazolin-4-amine and quinazolin-4-one derivatives widely occur in natural products,

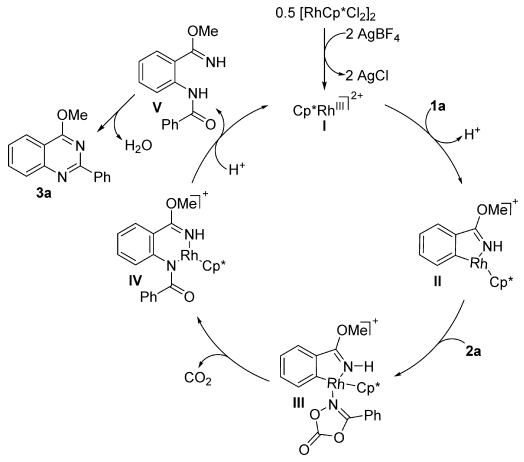
Scheme 4. Functionalization and Transformation of Product Molecule



and they show a wide range of useful biological and pharmacological activities, we further investigated transformations of **3a**. Selective transformation of the methoxy group was realized in different reaction conditions in the absence of transition metals. For example, ammoniation gave 2-phenylquinazolin-4-amine (**5e**) in high yield under basic acidic reaction conditions, while hydrolysis of the methoxy group generated 2-phenylquinazolin-4(3*H*)-one (**5f**) in excellent yields under acidic reaction conditions (Scheme 4, eq 2).

Based on the previous mechanistic studies,[19] a plausible mechanism was proposed (Scheme 5). In the presence of $AgBF_4$, cationic $[Cp^*Rh^{III}]$ (**I**) is generated in situ as the active catalyst, which coordinates to imine and further undergoes C−H activation to afford rhodacyclic complex (**II**). Coordination of 3-phenyl-1,4,2-dioxazol-5-one (**2a**) to rhodium (**III**) with further intramolecular migratory insertion generates the Rh^{III} amido species (**IV**) with release of CO_2. The complex may undergo protonation to regenerate the active $[Cp^*Rh^{III}]$ catalyst (**I**) for a new catalytic cycle and simultaneously give the intermediate (**V**), which undergoes cyclization/denitrosation to afford the quinazoline product **3a**.

Scheme 5. Proposed Reaction Pathway



In summary, we have developed a novel method for the convenient synthesis of quinazolines. By employing a commercially available catalyst system, a series of benzimidates were efficiently converted in combination with a different type of dioxazolones into various desired products in good to excellent yields upon isolation. The synthetic protocol proceeds with the advantages of operational simplicity, high atom efficiency, and broad substrate scope and offers an important basis for access to quinazolines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00691.

Experimental procedure, characterization of the products (PDF)

Copies of the ^1H and ^{13}C NMR spectra of selected products (PDF)

Crystallographic data of complexes **3f** (CIF)

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Notes

The authors declare no competing financial interest.

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