Organic LETTERS

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Rh- and Cu-Cocatalyzed Aerobic Oxidative Approach to Quinazolines via [4 + 2] C−H Annulation with Alkyl Azides

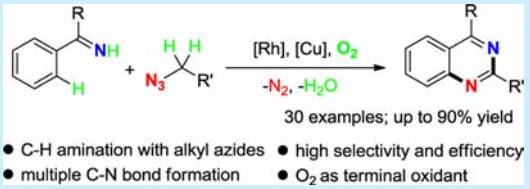
Xiaoyang Wang[†] and Ning Jiao*[,†,‡]

[†]State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Xue Yuan Road 38, Beijing 100191, China

[‡]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

ABSTRACT: A novel and efficient rhodium- and copper-co-catalyzed C−H bond activation and annulation for the construction of bioactively important quinazolines has been developed. This [4 + 2] annulation strategy utilizing alkyl azides as the carbon−heteroatom synthons shows high efficiency in the synthesis of six-membered benzoheterocycles containing two heteroatoms. This aerobic oxidative protocol provides a useful application of simple alkyl azides in N-heterocycle synthesis with N_2 and H_2O as byproducts.



Six-membered benzoheterocycles are important and common components of cyclic compounds. Among them, quinazolines are ubiquitous structural motifs found in many bioactive compounds, natural products and pharmaceuticals.[1] For example, erlotinib and gefitinib are well-known lung cancer drugs (Figure 1).[2] Prazosin is used for curing high blood

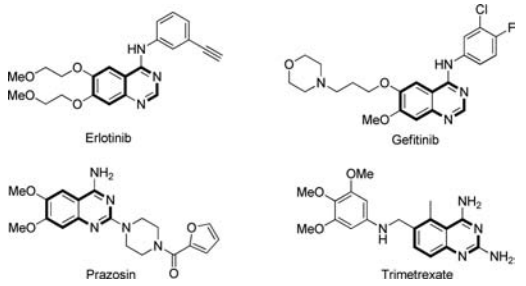
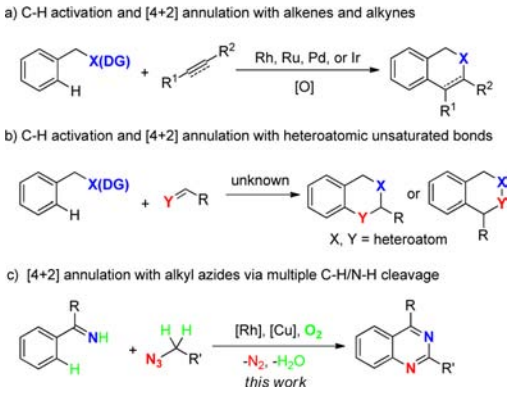


Figure 1. Quinazolines as core structures in pharmaceuticals.

pressure, anxiety, and panic disorder (Figure 1).[3] Trimetrexate has been used in the treatment of pneumocystis pneumonia (Figure 1).[4] Moreover, quinazolines are valuable precursors used in the synthesis of functionalized materials.[5] Therefore, the construction of quinazolines has attracted considerable attention during the past decades using preactivated substrates or multistep reactions.[6]

Recently, the annulation through C−H activation has been considered as an efficient and atom-economic strategy for the construction of aryl and heterocyclic compounds (Scheme 1),[7] which avoids the multistep preparation of preactivated starting materials and tolerates a wide variety of functional groups. Through this C−H annulation strategy, the [4 + 2] annulation with alkenes and alkynes for the construction of six-membered rings has been significantly developed (Scheme 1, path a),[8,9] which provides efficient approaches to benzoheterocyclic compounds containing one heteroatom originated from the

Scheme 1. C−H Annulation for Heterocycle Construction



directing group (Scheme 1, path a). In contrast, the construction of six-membered benzoheterocycles containing two heteroatoms with carbon−heteroatom synthons is rarely achieved (Scheme 1, path b).[10]

By using alkyl azides as substitutes for unsaturated reagents, we developed a novel aerobic oxidative [4 + 2] C−H annulation of imidate esters and alkyl azides (Scheme 1, path c). This chemistry provides a practical approach for the efficient synthesis of quinazoline derivatives. This C−H annulation strategy is undoubtedly atom-economic and efficient (Scheme 1, path c), but three challenging issues should be addressed to achieve this novel quinazoline synthesis: (1) Recently, azides[11] as prospective N-sources show great advantages and high reactivity in metal-catalyzed C−N bond formation through C−H activation even in the absence of external oxidants.[12,13] However, compared to the well-developed amidation reactions with sulfonyl and acyl azides,[13i−m] the C−H amination with alkyl azides is very

Received: March 16, 2016
Published: April 15, 2016

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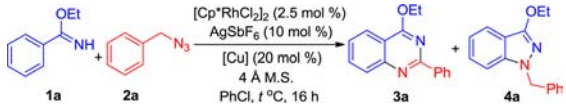
DOI: 10.1021/acs.orglett.6b00774
Org. Lett. 2016, 18, 2150−2153

challenging and limited.[14] (2) More recently, the C−N bond formation through C−H activation with azides and the subsequent N−N bond formation coupling with the directing group for the construction of 5-membered rings ([4 + 1]) have been elegantly achieved by the groups of Glorius,[15a] Jiao,[15b] and Zhu.[15c] Therefore, in the present design, the selectivity between [4 + 1] for the formation of 5-membered rings and [4 + 2] for the construction of 6-membered rings should be efficiently controlled. To the best of our knowledge, the [4 + 2] C−H annulation with carbon−heteroatom synthons has been unknown until this work. (3) Four hydrogens are removed by this synthetic design; therefore, a suitable oxidant, ideally green and sustainable molecular oxygen,[16] is desired for this oxidative process with the generation of H_2O as byproduct.

This project commenced with the reaction of imidate ester **1a** with benzyl azide **2a** catalyzed by $[Cp^*RhCl_2]_2$. Interestingly, quinazoline product **3a** was obtained in 18% yield with the formation of a trace amount of 5-membered ring **4a** when the reaction was investigated in the presence of silver and copper salts under air (entry 1, Table 1). The oxygen atmosphere slightly

Table 1. Optimization of the Reaction Conditions[a]



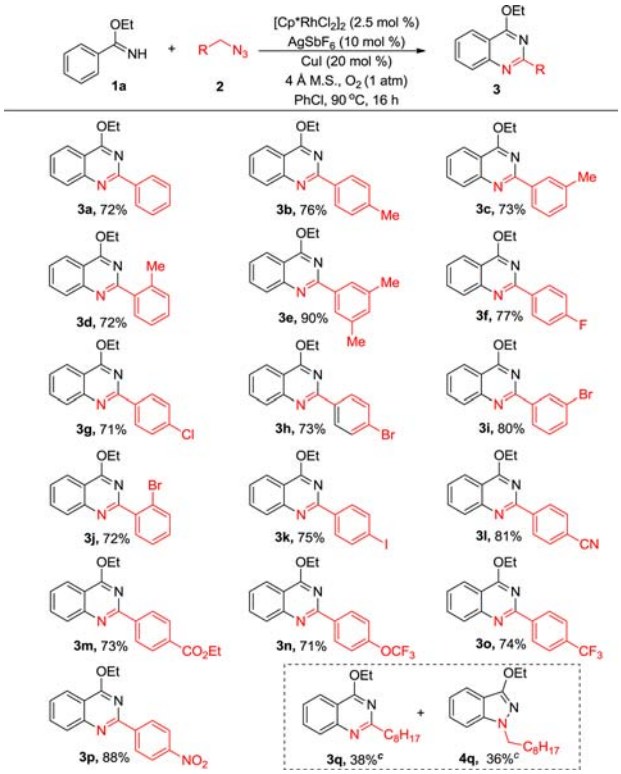
entry	[Rh]	[Ag]	[Cu]	atmosphere	t (°C)	3a[b] (%)	4a[b] (%)
1	+	+	$Cu(OAc)_2$	air	120	18	trace
2	+	+	$Cu(OAc)_2$	air	100	54	19
3	+	+	$Cu(OAc)_2$	O_2	100	65	16
4	+	+	Cu(Tc)	O_2	100	41	34
5	+	+	$Cu(OPiv)_2$	O_2	100	52	16
6	+	+	CuI	O_2	100	67	6
7	+	+	CuI	O_2	90	74	4
8	+	+	CuI	Ar	90	trace	–
9	–	+	CuI	O_2	90	–	–
10	+	–	CuI	O_2	90	–	–
11	+	+	–	O_2	90	–	–

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), 4 Å MS (50 mg), PhCl (2.0 mL), 16 h. [b]Determined by NMR using 1,1,2,2-tetrachloroethane as internal standard on 0.2 mmol scale.

improved the efficiency, but the selectivity was still unsatisfactory (entry 3, Table 1). After a great deal of screening of different catalysts, solvents, and additives, it is noteworthy that the yield of the desired quinazoline **3a** was improved to 74% when the reaction was co-catalyzed by $[Cp^*RhCl_2]_2$ and CuI in the presence of $AgSbF_6$ under oxygen atmosphere at 90 °C (entry 7, Table 1), in which the chemoselectivity was highly selectively controlled with only 4% 5-membered ring formation. Only trace amount of desired product was detected when the reaction was taken under Ar atmosphere (entry 8, Table 1), which demonstrates the importance of O_2 as an oxidant. The metal catalysts are essential to this novel transformation (entries 9−11, Table 1).

With the optimized conditions in hand, different kinds of substituted benzyl azides were then tested with model imidate ester **1a** (Scheme 2). All of the reactions worked well to produce the corresponding quinazolines in moderate to excellent yields. The chemoselectivities were also very high, and the 5-membered byproduct **4a** was not obtained in most cases. The efficiency was

Scheme 2. [4 + 2] C−H Annulation with Different Alkyl Azides[a,b]



[a]Reaction conditions: see entry 7, Table 1. Isolated yields. [b]Unless specially noted the five-membered ring product was not obtained or less than 5%. [c]The reaction time is 40 h.

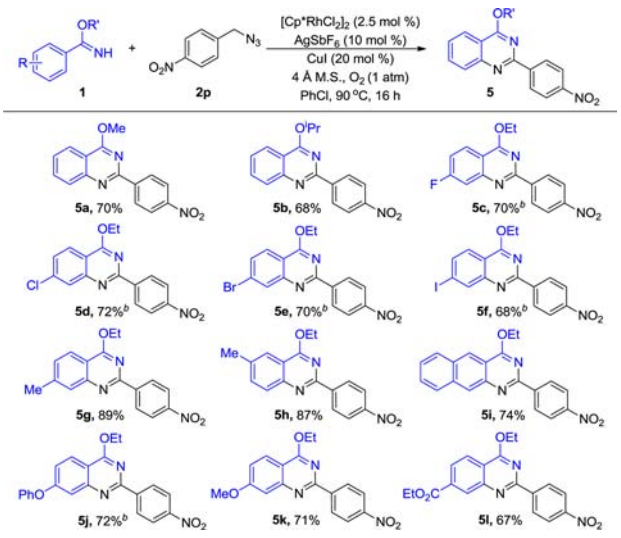
not affected by the steric bulk of the azides. The *o*-, *m*-, and *p*-methyl-substituted benzyl azides showed similar yields (**3b−d**, Scheme 2). The halogenated substrates were also tolerated in this transformation, producing the halo-substituted quinazolines which could be used for further coupling transformations (**3g−k**). Some functional groups such as cyano, ester, and nitro groups were compatible in the benzyl azide substrates (**3l**, **3m**, **3p**). Notably, the simple nonyl azide containing long carbon chain also performed well, providing the desired quinazoline **3q** in 38% yield despite the low selectivity with generation of 5-membered ring product **4q** in 36% yield.

The substrate scope of aryl imidate was further investigated (Scheme 3). Replacing ethoxy by methoxy and isopropoxy did not decrease the reactivity, giving **5a** and **5b** in 70% and 68% yield, respectively. Various aryl imidate esters containing electron-donating groups, electron-withdrawing groups, or halo substituents worked well under these conditions, leading to the functionalized quinazolines with high efficiency. Naphthylimide afforded **5i** in 74% yield. It is noteworthy that the chemoselectivities were also very high, with no 5-membered ring obtained in most cases (Scheme 3).

The obtained quinazoline products could be used for further transformation or synthesis. The initial directing group contains an alkoxy group whose conversion might further enrich the application of the products. After being heated with hydrochloric acid in ethanol for 1 h, the hydrolyzed product **6** was obtained quantitatively (eq 1, Scheme 4). Further treatment with thionyl chloride enabled the conversion of the carbonyl group to the C−Cl bond, forming **7** in 88% yield (eq 2, Scheme 4). The chlorinated quinazoline **7** could undergo coupling reactions for

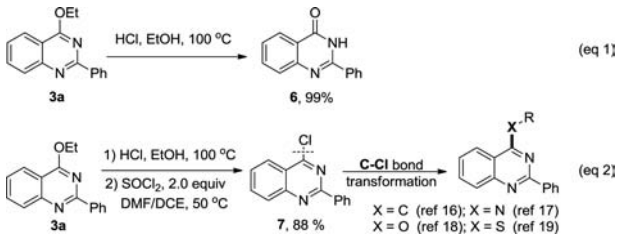
DOI: 10.1021/acs.orglett.6b00774
Org. Lett. 2016, 18, 2150−2153

Scheme 3. [4 + 2] C−H Annulation with Different Aryl Imidates[a]



[a]Reaction conditions: see entry 7, Table 1. Isolated yields. [b]The yields of five-membered ring products were 5−8% in these cases.

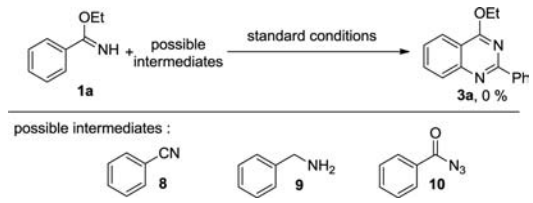
Scheme 4. Further Transformation of the Quinazoline Products



further synthesis via the formation of C−C,[17] C−N,[18] C−O,[19] and C−S[20] bonds.

To probe the mechanism, many controlled experiments were conducted (Scheme 5). When benzonitrile **8**, benzylamine **9**, and

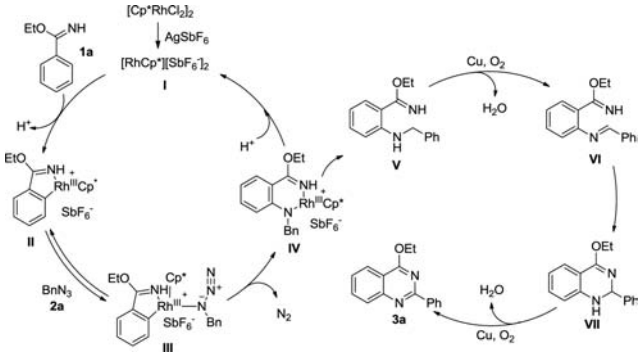
Scheme 5. Controlled Experiments



benzoyl azide **10** were applied, respectively, in the system instead of benzyl azide **2a**, no desired quinazoline product was detected. These results demonstrate that the corresponding benzonitrile, benzylamine, or benzoyl azide intermediates were not involved in this transformation.

According to the above results and previously reported studies,[21] the mechanism as shown in Scheme 6 was proposed. Initially, the cationic Cp*Rh(III) catalyst **I** is generated with the assistance of $AgSbF_6$. Then the imidate group directed C−H bond activation forms the rhodacyclic intermediate **II**, which could coordinate with benzyl azide to generate species **III**. Subsequently, the intermediate **III** undergoes migratory insertion to afford Rh species **IV**. Protonation of the complex

Scheme 6. Proposed Reaction Mechanism



IV regenerates the cationic Cp*Rh(III) and furnishes the amination process with **V** as product. The amine **V** executes the Cu-catalyzed aerobic oxidation[22] to produce the corresponding imine **VI** with the release of H_2O as byproduct. Finally, the cascade intramolecular addition and aerobic oxidative aromatization occur, leading to the final quinazoline product.

In summary, we have developed a novel Rh- and Cu-co-catalyzed [4 + 2] C−H annulation of imidates and alkyl azides for the efficient synthesis of quinazolines. This chemistry provides not only a novel approach to six-membered benzoheterocycles containing two heteroatoms with carbon−heteroatom synthons but also a useful application of simple alkyl azides in N-containing compounds synthesis. With azides as N source and O_2 as the terminal oxidant, this protocol gives N_2 and H_2O as environmentally benign byproducts. Meanwhile, good functional group tolerance and high atom efficiency make this protocol useful in preparing various substituted quinazoline derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00774.

Experimental procedures, full characterization of products, and copies of NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jiaoning@pku.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (973 Program) (Grant No. 2015CB856600), the National Natural Science Foundation of China (No. 21325206), and the National Young Top-notch Talent Support Program is greatly appreciated. We thank Kai Wu in this group for reproducing the results for **3f** and **5e**.

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DOI: 10.1021/acs.orglett.6b00774
Org. Lett. 2016, 18, 2150−2153