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Regiodivergent Rhodium(I)-Catalyzed Azide−Alkyne Cycloaddition (RhAAC) To Access Either Fully Substituted Sulfonyl-1,2,3-triazoles under Mild Conditions

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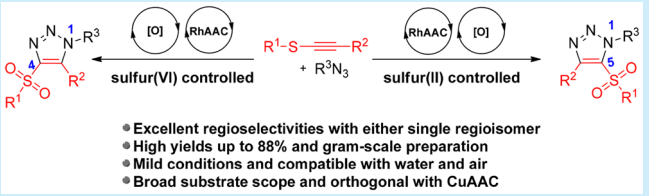
Supporting Information

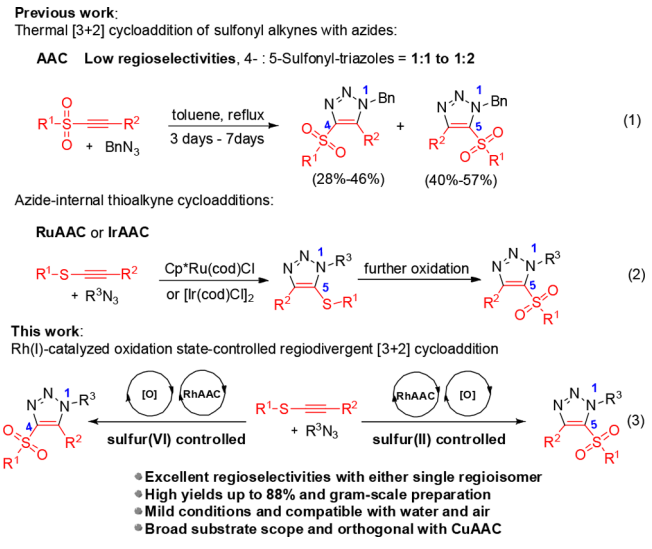
ABSTRACT: A regiodivergent Rh(I)-catalyzed azide−alkyne cycloaddition (RhAAC) was developed for the synthesis of both fully substituted 4-sulfonyl-1,2,3-triazoles and 5-sulfonyl-1,2,3-triazoles in high regioselectivities and yields under mild conditions in one step. Nonmetallic sulfur(II) or sulfur(VI) could efficiently control the regioselectivity of RhAAC reactions by chelation or nonchelation mechanisms to give excellent 1,4- or 1,5-regioselectivities. The utility of this method is further highlighted by its compatibility with water and air, broad substrate scope, good functional group tolerance, gram-scale preparation, applicability to carbohydrates, and the tandem CuAAC-RhAAC reaction.



The Azide−Alkyne Cycloaddition (AAC) reaction has a profound impact on not only every area of chemistry but also many other fields of science.[1] The original thermal AAC reaction discovered by Huisgen suffered from high temperature, long reaction time, and most importantly low regioselectivity for the formation of 1,2,3-trazoles.[2] In 2002, Sharpless and Meldal's groups independently developed the copper-catalyzed azide−alkyne cycloaddition (CuAAC) reaction.[3] The concept of "click chemistry" illustrates the ease of the CuAAC reaction under mild conditions.[1] However, it is limited to the preparation of 1,4-disubstituted 1,2,3-triazoles from terminal alkyne substrates. In 2005, Jia and Fokin's groups first developed the ruthenium-catalyzed AAC reaction (RuAAC) to access 1,5-disubstituted 1,2,3-triazoles in high 1,5-regioselectivity from azides and terminal alkynes.[4] The scope of alkynes in RuAAC can be expanded to symmetric internal alkynes and certain unsymmetrical alkynes with good regioselectivity. Regioselective preparation of fully substituted 1,2,3-triazoles has always been a challenge. Some of them could be obtained by postmodifications of 1,4-disubstituted 1,2,3-triazoles including Pd-catalyzed direct arylation, Cu-catalyzed C−H bond functionalization, and Cu-catalyzed interrupted click reaction.[5] Other methods mediated by organocatalyst[6] and MultiComponent Reactions (MCRs)[7] have been developed to prepare fully substituted 1,2,3-triazoles. However, only one major regioisomer could be obtained using all of these methods. Until now, there was still no general method for regiodivergent [3 + 2]-AAC reaction to give both fully substituted 1,2,3-triazoles with exclusive regioselectivity.

Sulfonyl-containing 1,2,3-triazoles display promising antibacterial, antifungal, anti-inflammatory, and antioxidant activities.[8] However, the methods to access fully substituted sulfonyl-1,2,3-triazoles are still very limited. Low regioselectivities and yields are achieved in AAC reactions at high temperatures over several days (Scheme 1, eq 1).[9] Unfortunately, CuAAC reactions also failed to control the regioselectivities in this transformation due to decomposition

Scheme 1. Controllable Regiodivergent Synthesis of Either Fully Substituted Sulfonyl-1,2,3-Triazoles



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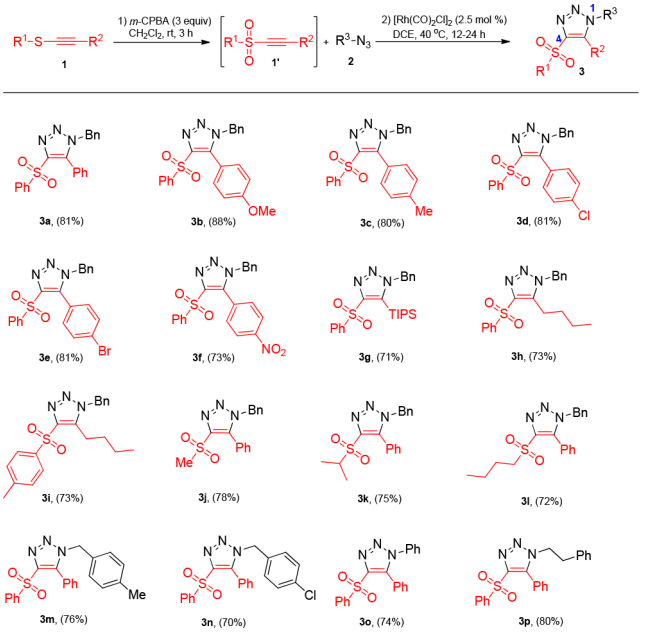
of the internal sulfonyl alkynes competing with the cycloaddition in the presence of Cu(I).[9] The recently developed transition Metal-Catalyzed AAC reactions (MAAC) may give the opportunity to address this long-standing issue.[10] The azide-internal thioalkyne cycloadditions independently developed by López, Mascareñas, Jia and Sun's groups could provide fully substituted 5-thio-1,2,3-triazoles with high 1,5-regioselectivities by RuAAC[11] or IrAAC[12] reactions, which partially resolve the problem in the synthesis of the fully substituted 5-sulfonyl-1,2,3-triazoles by the further oxidation of the relative 5-thio-products step by step (Scheme 1, eq 2). Jia and Sun's group also proposed the internal thioalkyne chelating mechanism to rationalize the excellent 1,5-regioselectivities.[12] If the internal thioalkynes are oxidized to internal sulfoxyl alkynes and internal sulfonyl alkynes, during the oxidation from sulfide to sulfone, the electron density on the internal alkynes changes due to electronic effects, which is very important for reversing the initial regioselectivities of 1,3-dipolar cycloadditions. Recently, we developed a rhodium(I)-catalyzed AAC reaction (RhAAC) to access fully substituted 1,2,3-triazolyl-4-phosphonates in high 1,4-regioselectivity.[13a] We also reported the iridium(I)-catalyzed AAC reaction (IrAAC) to access fully substituted 5-amido-1,2,3-triazoles in high 1,5-regioselectivity by a strong chelation mechanism between the metals and ynamides.[13b] As a continuation of our studies on regioselective AAC reactions, herein, we disclose the regiodivergent synthesis of both fully substituted 4-sulfonyl-1,2,3-triazoles and 5-sulfonyl-1,2,3-triazoles in high regioselectivities and yields under mild conditions in one step and in one pot respectively by nonmetallic sulfur(II) or sulfur(VI) control (Scheme 1, eq 3).

For the formation of fully substituted 5-sulfonyl-1,2,3-triazole **4a**, an internal thioalkyne, phenyl(phenylethynyl)-sulfane **1a**, and benzyl azide **2a** were chosen as the model substrates to optimize the cycloaddition conditions followed by *m*-CPBA oxidation without inert gas protection (see Table S1 in the Supporting Information (SI)). After screening different transition metal catalysts, $[Rh(CO)_2Cl]_2$ was demonstrated to efficiently catalyze this [3 + 2] reaction and be compatible with the *m*-CPBA in the subsequent oxidation process. The yield could be further improved to 77%, and the absolute regioselectivity could be maintained when using chloroform as the solvent and increasing the reaction temperature from room temperature to 40 °C. For the preparation of fully substituted 4-sulfonyl-1,2,3-triazole **3a**, an internal sulfonylalkyne, ((phenylethynyl)sulfonyl)benzene **1a′**, and benzyl azide **2a** were chosen as the model substrates to optimize the cycloaddition conditions without inert gas protection (see Table S2 in the Supporting Information). $[Rh(CO)_2Cl]_2$ was also revealed to be the best catalyst using dichloroethane (DCE) as the solvent at 40 °C in this transformation. Impressively, if crude **1a′** from pretreating phenyl(phenylethynyl)sulfane **1a** with *m*-CPBA was used as the starting material without further purification, the reaction still occurred in 83% yield and excellent regioselectivity.

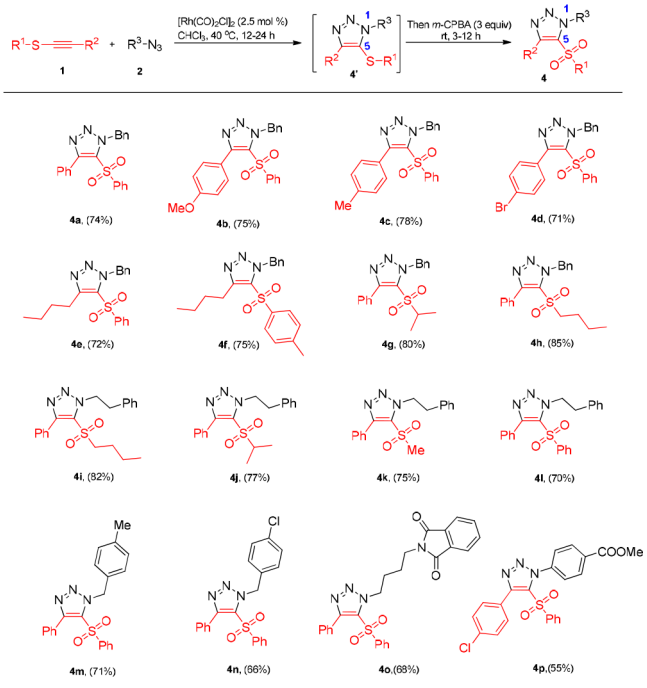
With the two sets of optimized conditions in hand, we explored the scope of the regiodivergent RhAAC reactions. Various internal thioalkynes were used as substrates at 40 °C without inert gas protection to afford both fully substituted 4-sulfonyl-1,2,3-triazoles and fully substituted 5-sulfonyl-1,2,3-triazoles in good yields (up to 88%) and excellent regioselectivities (Schemes 2 and 3). As shown in Scheme 2, fully substituted 4-sulfonyl-1,2,3-triazoles could be obtained by

Scheme 2. Reaction Scope of the Fully Substituted 4-Sulfonyl-1,2,3-triazoles[a,b]



[a]Reaction conditions: **1** (1.0 equiv), *m*-CPBA (3 equiv), CH_2Cl_2 (0.1 M), rt for 3 h, then worked up to give the crude product which was directly added to a vial containing $[Rh(CO)_2Cl]_2$ (2.5 mol %) and **2** (1.5 equiv) in DCE (0.1 M) under air. The vial was closed, and the mixture was stirred at 40 °C for 12−24 h. [b]Yield of isolated product.

Scheme 3. Reaction Scope of the Fully Substituted 5-Sulfonyl-1,2,3-triazoles[a,b]



[a]Reaction conditions: **1** (1.0 equiv) and **2** (1.5 equiv) were sequentially added to a vial containing $[Rh(CO)_2Cl]_2$ (2.5 mol %) in $CHCl_3$ (0.1 M) under air. The vial was closed, the mixture was stirred at 40 °C for 12−24 h, and then *m*-CPBA (3 equiv) was added to the vial, rt for 3−12 h. [b]Yield of isolated product.

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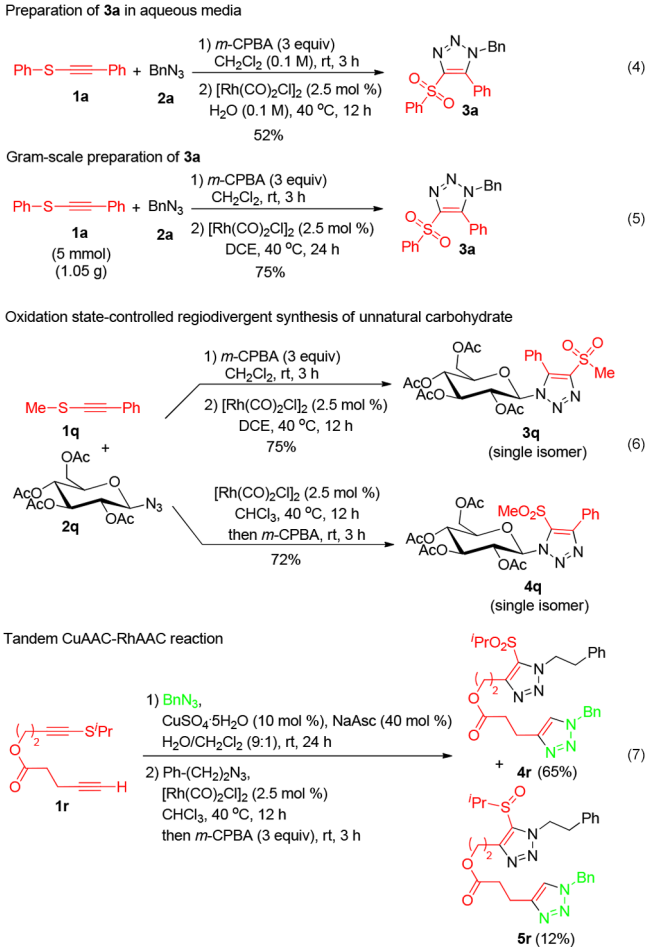
the oxidation followed by the cycloaddition. Internal thioalkynes **1** were oxidized to internal sulfonyl alkynes **1′**, which further reacted with azides **2** by the RhAAC process. Both electron-rich and -deficient aryl groups gave 5-aryl-4-sulfonyl-1,2,3-triazoles (**3a**−**3e**) in similar yields (80%−88%) despite a decreased yield (73%) for the *p*-nitrophenyl substituted derivative (**3f**). In addition to aryl groups, other alkyl groups, such as triisopropylsilyl (TIPS) and *n*-butyl groups, were also well tolerated and gave the corresponding products with excellent regioselectivities and relatively lower yields (71%−73%) in this RhAAC reaction (**3g**−**3i**). If alkyl sulfanes were used instead of aryl ones, the reactions could also proceed smoothly (**3j**−**3l**) but with slightly lower yields than aryl sulfanes. Other azides substituted with *p*-methylbenzyl, *p*-chlorobenzyl, phenyl, and phenylethyl groups also efficiently delivered the corresponding products (**3m**−**3p**).

In contrast, the synthesis of fully substituted 5-sulfonyl-1,2,3-triazoles is shown in the Scheme 3. The RhAAC reaction occurred first accompanied by the *in situ* oxidation. The desired fully substituted 5-sulfonyl-1,2,3-triazoles **4** were acquired from 5-sulfur-1,2,3-triazoles **4′** by the *in situ* oxidation in a one-pot manner with excellent 1,5-regioselectivities. The yields were generally lower than those of the fully substituted 4-sulfonyl-1,2,3-triazoles, which may be due to the more difficult oxidation for the 5-sulfur-1,2,3-triazoles.[14] The electronic effect was not obvious for the electron-rich and -deficient aryl-substituted substrates, as they showed similar yields (**4a**−**4d**). Alkyl-substituted internal thioalkynes could also undergo the RhAAC reaction (**4e** and **4f**). We were pleased to find alkyl sulfanes could provide higher yields than aryl sulfanes **4g** and **4h**. Phenylethyl azide was examined carefully, which could react with alkyl and aryl sulfanes efficiently (**4i**−**4l**). This substrate could be utilized later to study the mutual orthogonality of the CuAAC and RhAAC reactions. The yield (**4m**) for the electron-rich alkyl azide was slightly higher (71%) than that of the electron-poor substrate (**4n**). To our delight, the complicated butyl azide could offer **4o** in moderate yield and excellent regioselectivity. Unfortunately, when the aryl azide was used as substrate, **4p** was afforded in moderate yield (55%).

Subsequently, the applicability of the regiodivergent RhAAC reactions was investigated. Inspired by Mascareñas and Zimmerman's pioneering work, the ability to carry out the AAC reaction in aqueous media can be important for potential biological applications.[15] Encouragingly, the RhAAC reaction could be conducted in aqueous media to access fully substituted 4-sulfonyl-1,2,3-triazole albeit in moderate yield (Scheme 4, eq 4). The reaction could also be performed on gram scale. By treatment with **1a** (5.0 mmol, 1.05 g) under conditions A, **3a** was afforded in 75% yield (3.75 mmol, 1.41 g) after column purification (Scheme 4, eq 5). Some unnatural carbohydrates could be successfully prepared by the regiodivergent RhAAC reactions. Internal thioalkyne **1q** and glycosyl azide **2q** were used as substrates, which offered the unique glycosyl sulfones **3q** and **4q** efficiently (Scheme 4, eq 6). Glycosyl sulfones **3q** and **4q** are different regioisomers but share the same stereochemistry, which could be potentially useful in glycomics studies as a structure-confirmed bioconjugation strategy. The CuAAC reactions were not amenable to internal thioalkynes in the presence of CuI or $CuSO_4$ (see Tables S1 and S2 in the Supporting Information), which indicates that the CuAAC and RhAAC reactions may be mutually orthogonal. Diyne **1r**, containing both internal and

Scheme 4. Application of the Regiodivergent RhAAC Reactions



terminal alkyne moieties, was prepared according to López and Mascareñas' method to achieve the tandem CuAAC-RhAAC reaction[11] (Scheme 4, eq 7). First, the CuAAC reaction between benzyl azide and terminal alkyne proceeded smoothly in a nearly quantitative yield. Then, the crude disubstituted triazole was directly used without purification in the reaction with phenylethyl azide *via* the oxidation-state-controlled regiodivergent RhAAC reaction. Fully substituted 5-sulfonyl-1,2,3-triazole **4r** was obtained as the major product. Surprisingly, fully substituted 5-sulfoxyl-1,2,3-triazole **5r** was isolated as a minor product. **5r** could be quantitatively transformed to **4r** by oxidation with another 1.5 equiv of *m*-CPBA. This also explains why the yields of 5-sulfonyl-1,2,3-triazoles were generally lower than those of 4-sulfonyl-1,2,3-triazoles.

The two MAACs could be potentially utilized in a tandem manner without cross-reactivity in bioconjugation, medicinal chemistry, materials science, and other areas. To further understand the regiodivergent RhAAC process, control experiments and NMR analysis were conducted (for details, see the SI). The chelation between Rh(I) and the internal thioalkyne was apparent in the ^{1}H NMR study. However, no chelation between the Rh(I) and internal sulfonyl alkyne was detected. The proposed mechanism of the regiodivergent RhAAC reaction is shown in Scheme 5. For the sulfone-controlled RhAAC to access fully substituted 4-sulfonyl-1,2,3-triazoles, the oxidation occurs first followed by the cyclo-

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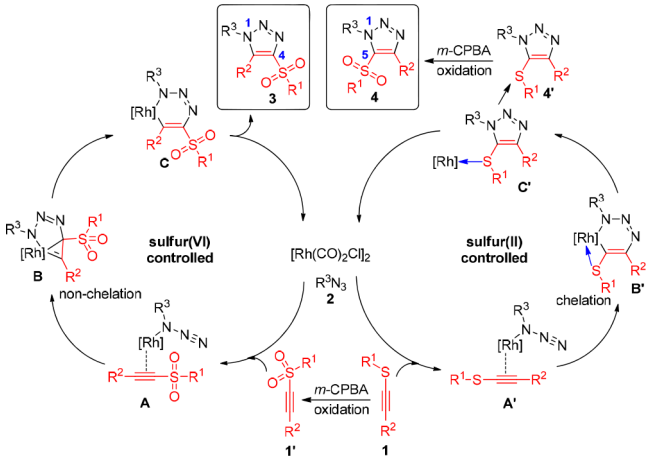
Scheme 5. Proposed Mechanism for the Regiodivergent RhAAC



addition. Internal thioalkyne **1** is oxidized to internal sulfonyl alkyne **1′**. Intermediate **A** could be generated by the initial combination of π-acidic Rh(I) with **1′** and azide **2**. The high 1,4-regioselectivity is derived from intermediate **A**. The electron-withdrawing sulfonyl group reverses the initial reactivity of the thioalkyne and could not coordinate with Rh(I). Then, Rh-carbene intermediate **B** is formed through the oxidative addition of the β-carbon of the alkyne and azide. After the subsequent Rh-assisted isomerization of intermediate **B** to intermediate **C** followed by the reductive elimination of intermediate **C**, desired fully substituted 4-sulfonyl-1,2,3-triazole **3** is formed with high 1,4-regioselectivity. For the sulfide-controlled RhAAC reaction to access fully substituted 5-sulfonyl-1,2,3-triazoles, the cycloaddition occurs first accompanied by the *in situ* oxidation. According to Sun and Jia's study in the IrAAC reaction,[12] we propose that the intermediate **A′** could be formed through internal thioalkyne **1** and azide **2** coordinating to the π-acidic Rh(I). Oxidative cyclization yields metallacycle **B′**, in which the sulfide strongly coordinates to the Rh, stabilizing the system and providing the high 1,5-regioselectivity. None of the other groups on the internal thioalkyne can coordinate to the rhodium. Then, **4′** is generated from intermediate **C′** by the reductive elimination of **B′**. Desired fully substituted 5-sulfonyl-1,2,3-triazole **4** could be acquired from **4′** by the *in situ* oxidation in one pot way with excellent 1,5-regioselectivity.

In summary, we have developed the regiodivergent synthesis of both fully substituted 4-sulfonyl-1,2,3-triazoles and 5-sulfonyl-1,2,3-triazoles in high regioselectivities and yields under mild conditions in one step and in one pot, respectively. The rhodium(I)-catalyzed azide−alkyne cycloaddition (RhAAC) reactions could be well controlled by sulfur(II) or sulfur(VI) to respectively give excellent 1,4- or 1,5-regioselectivities. The potential utility of this approach was validated by the gram-scale reactions, the application to carbohydrates, and the tandem CuAAC-RhAAC reaction. Further mechanistic studies and advanced theoretical calculations for the transition states and intermediates are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02794.

Detailed experimental procedures and characterization of new compounds (^{1}H NMR, ^{13}C NMR, HRMS) (PDF)

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Notes

The authors declare no competing financial interest.

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