

Trifluoromethylthiolation-Based Bifunctionalization of Diazocarbonyl Compounds by Rhodium Catalysis

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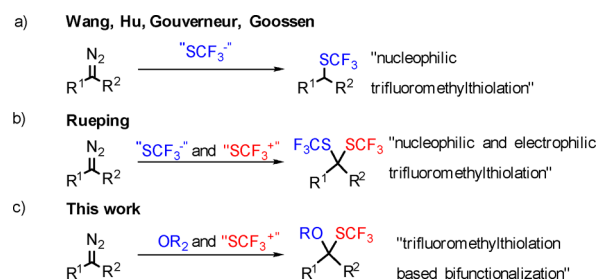
Supporting Information

ABSTRACT: A new Rh-catalyzed, three-component reaction for the oxytrifluoromethylthiolation of α -diazoketones was developed. The SCF₃ functionality was introduced using a stable dibenzenesulfonimide reagent under mild conditions. Alcohols, acetals, and ethers were used as the alkoxy sources. Cyclic ethers underwent a trifunctionalization reaction through the introduction of SCF₃, OR, and N(SO₂Ph)₂ substituents in a single step.



Organofluorine compounds have many important applications in the life sciences due to their favorable properties, such as high metabolic stability, lipophilicity, and easily tuned acid–base properties.¹ Over 20% of pharmaceuticals (30% of the blockbusters) and agrochemicals contain at least one carbon–fluorine bond.^{1a,b,2} In addition, due to the unique nuclear properties of both the ¹⁸F and ¹⁹F isotopes, organofluorine compounds are widely used in medical diagnostics, such as positron emission tomography (PET) and magnetic resonance imaging (MRI).³ The broad application of organofluorine compounds in the life sciences has generated a large demand for the development of new synthetic routes to these species.⁴ In the past decade, many excellent fluorination and trifluoromethylation/alkylation methods have been reported based on the application of new reagents and catalytic methods.⁴ Recently, method development for the efficient introduction of the trifluoromethylthio group (SCF₃) has received broad interest.⁵ The SCF₃ group is strongly electron-withdrawing,⁶ and it has an exceptional effect on improving the lipophilicity of organic molecules (Hansch parameter $\pi = 1.44$).^{5b,c,7} Traditionally, SCF₃ groups have been introduced by trifluoromethylation of thiols, halogen fluorine exchange reactions, nucleophilic trifluoromethylthiolation, or the usage of very reactive and toxic electrophilic reagents including ClSCF₃ and F₃CS–SCF₃.⁸ Recently, stable, easy to handle electrophilic reagents have been reported, which are suitable for the selective introduction of the SCF₃ group under mild conditions.^{5b,c} An important strategy for the introduction of SCF₃ groups into organic compounds is the application of diazo compounds as substrates.⁹ In particular, transition-metal-catalyzed coupling of trifluoromethylthiolation reagents has become an emerging technology for the efficient synthesis of aromatic¹⁰ and aliphatic^{9,11} SCF₃ derivatives (Scheme 1a). The latter reaction is particularly interesting as it is suitable for formation of C(sp³)–SCF₃ bonds. In these reactions, aliphatic diazo compounds are most often treated with nucleophilic SCF₃ sources (formally SCF₃[–]), such as AgSCF₃ or in situ generated CuSCF₃. The coupling reactions of aliphatic

Scheme 1. Nucleophilic and Electrophilic Trifluoromethylthiolation of Aliphatic Diazo Compounds



diazo compounds with electrophilic trifluoromethylthiolation reagents (formally SCF₃⁺) are much less explored. In fact, we have found only a single example for this reaction by Rueping and co-workers.¹² In their study, two SCF₃ groups were introduced to a diazoester, one from an electrophilic SCF₃ source and the other from a nucleophilic one (Scheme 1b).

As a part of our organofluorine chemistry program, we studied the possibility of developing catalytic oxyfluorination and oxytrifluoromethylation reactions of diazocarbonyl compounds.¹³ In these studies, the fluoro- and trifluoromethyl groups were introduced by NFSI or by hypervalent iodine reagents, such as fluoriodoxoles¹⁴ and the Togni reagent.^{4a} A conceptual extension of this cross-coupling strategy would be the application of an analogous trifluoromethylthiolation reagent for geminal bifunctionalization of diazocarbonyl compounds (Scheme 1c). We hypothesized that NFSI analogue SCF₃-dibenzenesulfonimide **1**, recently reported by Shen and co-workers,¹⁵ could be a suitable electrophilic SCF₃ source for a geminal oxytrifluoromethylthiolation reaction. After careful optimization, we have found that a three-component cross-coupling reaction of α -diazoketone **2a**, **1**, and 4 equiv of benzyl

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alcohol **3a** can be carried out in the presence of catalytic amounts of Rh catalyst **4** and NaOAc (Table 1). In this process, the benzyl ether and SCF₃ functionalities were introduced in a single step to the same carbon atom of **2a** to provide **5a** in 71% yield (entry 1).

Table 1. Deviation of Reaction Conditions for 1,1-Trifluoromethylthiolation/Benzyloxylation of Diazoketone **2a^a**

entry	deviation from the standard conditions	yield (%) ^b
1	none	71
2	0.12 mmol of 3a	34
3	1.0 mmol of 3a	61
4	without NaOAc	21
5	Na ₂ CO ₃ instead of NaOAc	22
6	CsF instead of NaOAc	55
7	2,6-di- <i>tert</i> -butylpyridine instead of NaOAc	48
8	without Rh ₂ (OAc) ₄	0
9	(PPh ₃)AuCl (2 mol %) instead of Rh ₂ (OAc) ₄	<5
10	(PPh ₃)AuCl (2 mol %), without NaOAc	10
11	(PPh ₃)AuCl (2 mol %), without NaOAc, 24 h	35
12	CuTc (4 mol %) instead of Rh ₂ (OAc) ₄	7
13	Cu(OTf) ₂ (4 mol %) instead of Rh ₂ (OAc) ₄	17

^aTo reagent **1** (0.1 mmol), NaOAc (0.2 mmol), and Rh₂(OAc)₄ (**4**) (0.001 mmol) was added a solution of alcohol **3a** (0.4 mmol) and diazoketone **2a** (0.12 mmol) in CDCl₃ (1.5 mL). This mixture was stirred at 25 °C for 30 min. ^bIsolated yield.

Decreasing the amount of benzyl alcohol **3a** to 1.2 equiv led to a decrease in yield to 34% (entry 2), whereas increasing the excess to 10-fold led to 61% yield (entry 3). Application of NaOAc was essential to get acceptable yields, as in its absence the yield decreased to 21% (entry 4). In the absence of any base, a considerable amount of side product was formed by protonation instead of introduction of the SCF₃ group. An obvious proton source was the applied benzyl alcohol **3a**. When NaOAc was replaced by other bases, the yield was decreased (cf. entries 5–7 with 1). In the absence of Rh catalyst **4**, product **5a** did not form at all (entry 8). When we replaced **4** with the gold catalyst (PPh₃)AuCl, formation of a trace amount of **5a** was detected (entry 9). When the same reaction was performed without addition of NaOAc, the yield increased to 10% (entry 10). (PPh₃)AuCl (in the absence of NaOAc) is apparently also a competent catalyst but much slower than Rh₂(OAc)₄ **4**. When the reaction time with (PPh₃)AuCl was extended to 24 h (which was 48 times longer than with Rh catalyst **4**), the yield increased to 35% (entry 11). Copper catalysts, such as CuTc (Tc = thiophene carboxylate) and Cu(OTf)₂, were much less efficient than Rh catalyst **4** (entries 12 and 13).

With the optimized reaction conditions in hand, we studied the substrate scope of the reaction by varying the diazocarbonyl **2a–g** and alcohol **3a–j** components (Table 2). Naphthalene-methanol **3b** reacted with **2a** in a similar yield (67%) to the corresponding reaction with benzyl alcohol **3a** (cf. entries 1 and 2). Benzylic alcohols with electron-withdrawing bromo (**3c**) and nitro (**3d**) groups in the aromatic ring reacted with lower yields (50 and 33%) than **3a** (entries 3 and 4). The reaction with benzyl alcohol **3e** bearing an electron-donating substituent on the aromatic ring afforded **5e** with 58% yield (entry 5). The reaction proceeds smoothly with aliphatic alcohols, such as **3f**, as well,

Table 2. Bifunctionalization of Diazo Compounds **2 with SCF₃ Source **1** and Alcohols **3**^a**

entry	diazo ketone 2	alcohol 3	product 5	yield (%) ^b
1				71 (67) ^c
2				67
3				50
4				33
5				58
6				68
7				54
8				46 dr 1:1.4
9				66
10				49
11				63
12				51
13				62
14				75
15				27
16				20

^aUnless otherwise stated, to a mixture of **1** (0.1 mmol), NaOAc (0.2 mmol), and Rh₂(OAc)₄ (**4**) (0.001 mmol) was added a solution of alcohol **3** (0.4 mmol) and diazoketone **2** (0.12 mmol) in CDCl₃ (1.5 mL). This mixture was stirred at 25 °C for 30 min. ^bIsolated yield. ^cThe reaction was performed in 1.0 mmol scale.

giving **5f** with 68% yield (entry 6). The yields were slightly decreased when using secondary alcohols **3g,h**, indicating the adverse effects of steric hindrance (entries 7 and 8). Using menthol **3h** as the alcohol component provided the product with low diastereoselectivity (entry 8). Prenol **3i** reacted with a relatively good yield (66%), indicating that under the applied mild conditions (25 °C, 30 min) the double bond¹⁵ remained intact. Substituted aromatic diazoketones such as **2b** reacted in a

similar fashion to **2a** (cf. entries 3 and 10). We could also employ aliphatic diazoketones **2c–e** (entries 11–14). The reactions can be performed with both benzylic **3a** and aliphatic **3f** alcohols, with yields ranging from 51 to 62% (entries 11–13). Disubstituted cyclic diazoketone **2e** reacted with high yield, resulting in **5n** bearing a quaternary carbon bonded directly to the SCF₃ moiety (entry 14). Diazoesters **2f,g** gave **5o,p** with poor yields of 20 and 27%, respectively (entries 15 and 16). We observed similarly poor yields for the analogous oxyfluorination reactions.^{13a} In these reactions, the starting materials were consumed, but we did not observe dimerization of **2f,g**. Probably some of the intermediates (such as onium ylides) are less reactive in the case of using diazoester than for diazoketone types of substrates. The reaction could be easily scaled up to 10 times scale (1.0 mmol) without altering the yield (entry 1).

Ethers have also been used in three-component Rh-catalyzed coupling reactions with diazoketones.^{13b,16} Therefore, it was appealing to attempt the reactions using ethers or acetals instead of alcohols in the trifluoromethylthiolation processes. As in the presence of ether substrates undesired protonation (which occurred with alcohols) was not expected, NaOAc was not used as additive. Acyclic ethers **6a–e** were much less reactive substrates than the corresponding alcohols. When we employed **4** equiv excess of **6**, similarly to the reaction with alcohol substrates (see Table 1), only traces of coupling product were formed. However, when acyclic ethers **6a–e** were used as solvents, they reacted with diazoketones **2a** and **2h** (Table 3),

Table 3. Rh-Catalyzed Cleavage of Acetals and Ethers **6^a**

entry	diazo ketone 2	ether 6	product 5	yield (%) ^b
1	2a	6a	5q	41
2	2a	6b	5q	55
3	2h	6c	5r	34
4	2a	6d	5s	72
5	2a	6e^c	5a	32

^aUnless otherwise stated, to reagent **1** (0.1 mmol) and Rh₂(OAc)₄ (**4**) (0.001 mmol) was added a solution of diazoketone **2** (0.12 mmol) in solvent **6** (1.0 mL). This mixture was stirred at 25 °C for 2 h. ^bIsolated yield. ^c0.4 mmol of **6e** in 1 mL of dry CDCl₃.

affording oxytrifluoromethylthiolation products **5a** and **5q–s**. Acetal **6a** and orthoester **6b** gave **5q**, indicating that the methoxy group was transferred from **6a,b** to the diazo compound (entries 1 and 2). In the case of using methylbenzylether **6c**, either the benzyloxy or the methoxy group could be transferred, and therefore, two different products were expected. However, we obtained exclusively **5r** in 34% yield (entry 3), indicating that the smaller group of the ether is preferentially transferred from **6c**. On the other hand, when using aliphatic ether dimethoxyethane **6d**, we could isolate **5s** with high yield (72%) without formation of the methoxy product **5q**. Not only methyl ethers but silyl ether

6e also reacted, albeit with poor yield (32%). In this reaction, **6e** served as a benzylether source (entry 5), whereas formation of the silylether analogue of **5a** was not observed.

To our delight, cyclic ethers **7a–c** reacted readily with **1** and diazoketones **2a**, **2d**, and **2f**. In this process, a trifunctionalization reaction took place introducing the SCF₃ group, the ether moiety, and the N(SO₂Ph)₂ functionality in a single reaction step (Table 4), similarly to the analogous fluorination reaction.^{13b} In

Table 4. Rh-Catalyzed Cleavage of Cyclic Ethers **7^a**

entry	diazo ketone 2	ether 7	product 8	yield (%) ^b
1	2a	7a	8a	66
2	2a	7a^c	8b + 8a	42 45
3	2d	7a	8c	50
4	2f	7a	8d	38
5	2a	7b^c	8e	58
6	2a	7c^d	8f	52

^aUnless otherwise stated, to reagent **1** (0.1 mmol) and Rh₂(OAc)₄ (**4**) (0.001 mmol) was added a solution of diazoketone **2** (0.12 mmol) in dry CH₂Cl₂ (1.0 mL) followed by ether **7** (0.6 mmol). This mixture was stirred at 25 °C for 2 h. ^bIsolated yield. ^c6 mmol of **7** was used in dry CH₂Cl₂ (0.5 mL). ^dDioxane (**7c**) (1 mL) was used as solvent.

these reactions, the best yields were obtained when THF **7a** was used in a 6-fold excess (entries 1, 3, and 4); **7b** was used in a 60-fold excess (entry 5), and dioxane **7c** was used as the solvent (entry 6). When we employed **2a** and **1** with a 60-fold excess of THF, a large amount of diether product **8b** was also formed together with **8a** (entry 2). Apparently, THF **7a** reacts much faster than dioxane **7c**. Although we employed dioxane **7c** as solvent (entry 6), we obtained only **8f** without formation of a diether type of product, such as **8b** (cf. entries 2 and 6). Aliphatic diazoketone **2d** reacted with THF **7a**, affording trifunctionalized SCF₃-ether product **8c** with a 50% yield. α -Diazoester **2f** reacted with THF **7a** (entry 4) with a poor yield (38%), similar to the analogous reaction with benzylic alcohol **3a** (Table 2, entry 15). This indicates that the Rh-catalyzed oxytrifluoromethylthiolation reaction proceeds more efficiently with diazoketones than with diazoesters. Phthalan **7b** proved to be an efficient reaction partner in the tricomponent trifunctionalization reaction, affording **8e** with 58% yield. As both six- (entry 6) and five-membered ring ethers (entries 1–5) reacted with α -diazoketones and **1**, we attempted the analogous reaction with epoxides as well, but instead of epoxide opening, epoxide reduction to the corresponding alkene was observed (see Supporting Information for details).

Based on the above and previously reported studies, we conclude that the Rh-catalyzed oxyfluorination,¹³ oxytrifluoro-

methylation,^{13a} and the above presented oxytrifluoromethylthiolation reactions follow a very similar mechanism. The catalytic cycle most probably proceeds via formation of Rh-carbene and onium ylide type of intermediates¹⁷ followed by trapping the onium ylide by the SCF₃ electrophile (see Supporting Information). Although the trapping of onium ylides with electrophiles is a well-studied and documented process,^{17f,18} using F,^{13a} CF₃,^{13a} and SCF₃ (the above study) as electrophiles is a very new direction for this process.

In conclusion, we have presented a new three-component trifluoromethylthiolation reaction of α -diazocarbonyl compounds and SCF₃-dibenzenesulfonimide **1** with alcohols and ethers as oxygen nucleophiles. Alcohols and acyclic ethers reacted to provide geminal oxytrifluoromethylthiolated products. Cyclic ethers performed a trifunctionalization reaction by introduction of alkoxy, SCF₃ and N(SO₂Ph)₂ groups in a single step. The processes proceed with high regioselectivity and have a broad synthetic scope. This new Rh-catalyzed oxytrifluoromethylthiolation reaction can be a simple and efficient method for introduction of SCF₃ into organic molecules, broadening the methodology scope of organofluorine chemistry in the life sciences.¹

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02139.

Experimental procedures, suggested mechanism, and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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