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A Diheteroatom Fluoroalkylation Reagent for Preparation of S- and N-Containing Fluoroalkyl Compounds and Sulfonic Acid Polymer

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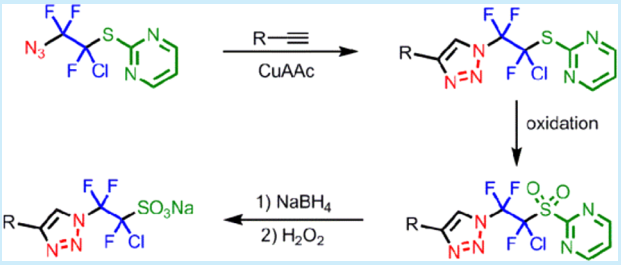
Supporting Information

ABSTRACT: The first stable diheteroatom fluoroalkylation reagent, 2-((2-azido-1-chloro-1,2,2-trifluoroethyl)thio)-pyrimidine (ACTP), has been prepared by a novel method. By using this reagent, various fluorinated thioethers and sulfones have been successfully prepared. The dearylation and dearylation−oxidation of fluoroalkyl 2-pyrimidyl sulfone in one-pot reaction were investigated systematically, and the results demonstrated that both fluoroalkyl sulfinates and sulfonates could be obtained in high yields. In addition, ACTP proved to be useful for the preparation of a fluorinated sulfonic acid proton-exchange membrane.



In recent years, methods for preparation of fluoroalkyl thio-compounds have been of growing interest because the simultaneous incorporation of both sulfur and fluorine into the target molecules can give rise to attractive new properties, leading to a wide range of applications in many areas.[1] An interesting example is from the area of medical chemistry: the CF_3S or HCF_2S moiety as an intriguing structural motif has been used to improve the membrane permeability of drug candidates owing to the high stability and lipophilicity.[2] Consequently, a number of methods have been developed for the preparation of the fluoroalkyl thio-compounds. Among these methods, thiofluoroalkylation reagents play a very important role. By employing these reagents, both S and F can be incorporated into molecules directly and efficiently.[3] Recently, several thiofluoroalkylation reagents have been reported, such as the trifluoromethanesulfenamide,[4] *N*-(trifluoromethylthio)phthalimide,[5] trifluoromethanesulfonyl hypervalent iodoniumylide,[6] *N*-difluoromethylthiophthalimide,[7] and phenylthiolfluoroalkyl bromides.[8]

On the other hand, fluorinated sulfonic acids as a class of strong Bronsted acids are very useful for preparation of high performance polymer materials, such as a proton-exchange membrane in fuel cells.[9] However, very few methods are available for the synthesis of fluorinated sulfonic acids and their derivatives. In 1981, Huang reported an approach for the preparation of fluorinated sulfinates and sulfonates by sulfinatodehalogenation via the reaction between fluoroalkyl iodides and sodium dithionite.[10] Then, Prakash et al. prepared fluorinated sodium sulfinates by the reaction of difluoroalkyl 2-pydidyl sulfone with EtSNa, which was further converted into difluoroalkyl sulfonates in excellent yield by an oxidation reaction.[11] Sanchez et al. synthesized perfluoroalkanesulfonyl fluorides from perfluoro-alkyl trimethyl silanes in several successive steps.[12] More recently, Hu reported a simple and efficient pathway for large-scale preparation of difluoromethanesulfinate salts via $NaBH_4$-mediated reduction of benzo[*d*]thiazol-2-yl sulfones.[13]

To date, investigation of fluoroalkyl thio-compounds including thioethers, sulfones, and sulfonates is still limited due to the lack of practical synthetic methods. Therefore, it is of high demand to develop facile, efficient methods for the synthesis of fluoroalkyl thio-compounds as the possibility to modulate the intrinsic properties of molecules, which can provide powerful tools for the discovery of new bioactive molecules. Recently, we have prepared a stable and versatile heterobifunctional fluoroalkylation reagent that was successfully used in the synthesis of the different fluorinated compounds with an asymmetric molecular structure.[14] Inspired by the achievement of the previous work, we tried to develop a versatile method for preparation of new fluoroalkyl thio-compounds. Meanwhile, we noticed that, to date, there is no report published on a fluoroalkylation reagent containing both S and N atoms, which can be used to simultaneously incorporate both sulfur and nitrogen atoms into one fluoroalkyl molecule.[15] Herein, we report a fluoroalkylation reagent bearing both azide and thiother groups, and its application in the synthesis of various fluorinated thioethers, sulfones, and sulfonates.

To obtain the new diheteroatom bifunctional fluoroalkylation reagents, we carefully investigated the three-component reaction of NaN_3, chlorotrifluoroethylene (CTFE), and 2-thiocyanatopyrimidine in DMF at rt (Table 1, entries 1−2). Initially, the desired product, 2-((2-azido-1-chloro-1,2,2-trifluoroethyl)thio)-pyrimidine (ACTP), was obtained in a yield of 21% when 2 equiv of NaN_3 were used without any catalyst or promoter (entry 2).

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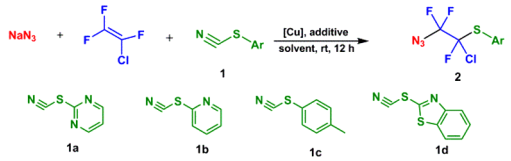
Table 1. Optimization of Reaction Conditions[a]



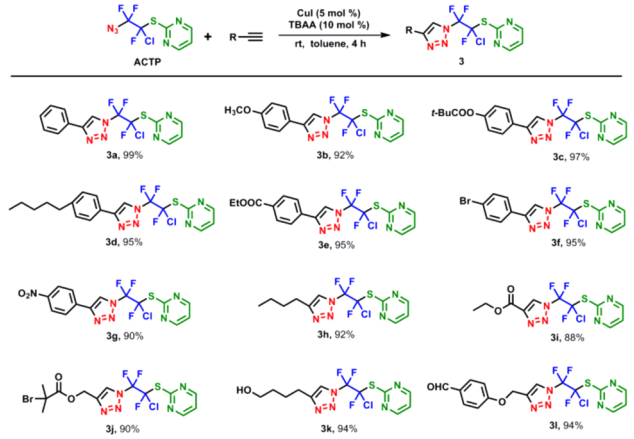
entry	NaN_3 (equiv)	[Cu] (equiv)	ligands (equiv)	solvent	yield[b] (%)
1	1.0	–	–	DMF	trace
2	2.0	–	–	DMF	21
3	2.0	CuSCN (1)	Phen (1)	DMF	54
4	2.0	$Cu(BF_4)\cdot$ 4MeCN (1)	Phen (1)	DMF	46
5	2.0	CuBr (1)	Phen (1)	DMF	52
6	2.0	CuI (1)	Phen (1)	DMF	58
7	2.0	$Br(PPh_3)_3Cu$ (1)	–	DMF	18
8	2.0	$CuBr_2$ (1)	Phen (1)	DMF	22
9	2.0	Cu (1)	Phen (1)	DMF	17
10	2.0	CuI (1)	Phen (1)	CH_3CN	0
11	2.0	CuI (1)	Phen (1)	dioxane	0
12	2.0	CuI (1)	Phen (1)	THF	0
13	2.0	CuI (1)	Phen (1)	DMSO	47
14	2.0	CuI (1)	Phen (1)	DMSO/ DMF	67
15	2.0	CuI (0.1)	Phen (0.1)	DMSO/ DMF	19
16	2.0	CuI (0.3)	Phen (0.3)	DMSO/ DMF	36
17	2.0	CuI (0.5)	Phen (0.5)	DMSO/ DMF	74
18	**2.5**	**CuI (0.5)**	**Phen (0.5)**	**DMSO/ DMF**	**78**
19	3.0	CuI (0.5)	Phen (0.5)	DMSO/ DMF	75
20[c]	2.5	CuI (0.5)	Phen (0.5)	DMSO/ DMF	32
21[d]	2.5	CuI (0.5)	Phen (0.5)	DMSO/ DMF	38
22	2.5	CuI (0.5)	PMDETA (0.5)	DMSO/ DMF	67
23	2.5	CuI (0.5)	Bpy (0.5)	DMSO/ DMF	74
24[e]	2.5	CuI (0.5)	Phen (0.5)	DMSO/ DMF	60
25[f]	2.5	CuI (0.5)	Phen (0.5)	DMSO/ DMF	63
26[g]	2.5	CuI (0.5)	Phen (0.5)	DMSO/ DMF	51

[a]Reaction conditions: 2-thiocyanatopyrimidine **1a** (2 mmol), NaN_3 (4 mmol), CTFE (1.5 g, 0.2 MPa), CuI (1 mmol) and phen (1 mmol) in 2 mL of solvents (DMSO/DMF = 1/1) at rt for 12 h. [b]Yields refer to isolation after chromatography. [c]This reaction was performed at 50 °C. [d]This reaction was performed at −30 °C. [e]**1b** was used instead of **1a**. [f]**1c** was used instead of **1a**. [g]**1d** was used instead of **1a**.

Copper salts as promoters are usually used in nucleophilic fluoroalkylation reactions, due to their ability to stabilize the fluorocarbon anion.[16] When the reaction was performed with a mixture of CuSCN (1 equiv) and ligand Phen, the yield of the product was increased to 54% (entry 3). The results of the screening of promoters revealed that CuI/Phen was the most efficient promoter for the reaction (entries 4−9). Moreover, polar solvents were favorable for this reaction (entries 10−13). ACTP was obtained in 67% yield in a mixed solvent of DMSO/DMF (1/1, v/v) (entry 14). The product yield was related to the ratio of the reactants, and the highest yield (78%) was obtained when the molar ratio of NaN_3 to **1a** was 2.5 using 0.5 equiv of CuI/Phen as the promotor (entries 15−19). Notably, compared to the reaction at rt, the yield of the product was decreased significantly when the reaction was conducted at either −30 or 50 °C (entries 20−21). Other ligands such as PMDETA and Bpy gave a slightly lower yield (entries 22−23). With the optimized reaction conditions in hand, we further investigated the behaviors of other thiocynates **1b−1d** and found that all the corresponding products could be obtained in modest yields (entries 24−26). Consequently, a new diheteroatom bifunctional S- and N-containing fluoroalkylation reagent ACTP was synthesized successfully. Moreover, the stability of ACTP was examined by ^{19}F NMR spectroscopy, and the result indicates that ACTP is a fairly stable colorless liquid at rt in the dark. No detectable decomposition was observed after storage in a glass vial for 6 months in the dark at rt. To the best of our knowledge, it is the first diheteroatom bifunctional fluoralkylation reagent containing both S and N atoms.

It is well-known that the Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) reaction is commonly described as a "click reaction" and widely used in the synthesis of organic compounds, polymers and biomaterials.[17] In our previous work, we have demonstrated that CuI and TBAA as a combined catalyst was highly effective for the CuAAC reaction of fluoroalkyl azides.[14] To explore the reactivity of azide group in the new diheteroatom fluoroalkylation reagent, we conducted the CuAAC reactions of azide with different alkynes using CuI/TBAA as the catalyst in toluene (Scheme 1). The target products can be

Scheme 1. Substrate Scope of Alkynes[a,b]



[a]Reaction used ACTP (1 mmol) and alkynes (1.1 mmol) with CuI (0.05 mmol) and TBAA (0.1 mmol) in 1 mL of toluene at rt under N_2 for 4 h. [b]Yields refer to isolation after chromatography.

obtained in excellent yields for both the aromatic alkynes with electron-withdrawing or -donating groups and aliphatic alkynes, tolerating various functional groups. Obviously, this approach is more feasible and efficient to synthesize fluoroalkyl thioethers than a previously published method,[14] the latter requiring two-step chemical reactions.

In the past decade, increasing attention has been focused toward the synthesis of fluorinated sulfones because they have shown wide applications for the incorporation of diverse fluoroalkyl groups into organic molecules.[18] We tried to convert the substituted fluoroalkyl 2-pyrimidyl thioethers to corresponding sulfones by an oxidation reaction. The reactions were performed by using $RuCl_3/NaIO_4$ as the oxidation reagents in the combined solvents of CH_3CN, CCl_4, and H_2O at rt, and the

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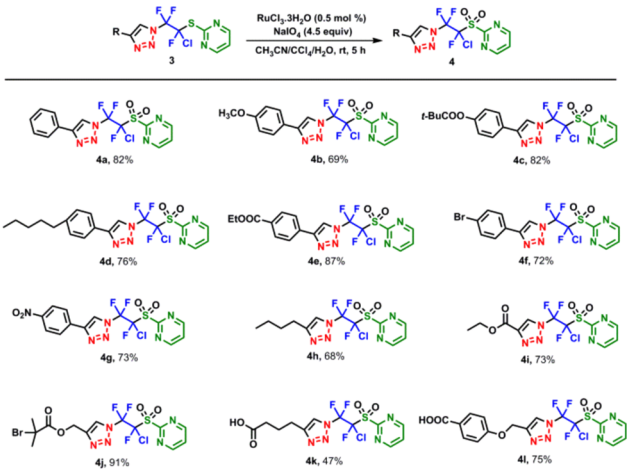
results of the oxidation reactions are summarized in Scheme 2. All the expected products were obtained in moderate yields (**4a**–**4j**),

Scheme 2. Oxidation Reaction of Fluoroethyl 2-Pyrimidyl Thioether Derivatives[a,b]

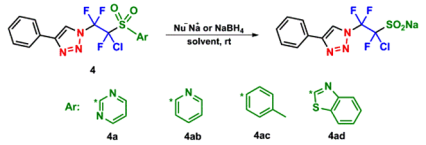


[a]Reaction used **3** (1 mmol), $NaIO_4$ (4.5 mmol), and 3 mg of $RuCl_3 \cdot 3H_2O$ in a solution of 1.5 mL of CH_3CN, 1.5 mL of CCl_4, and 3.2 mL of H_2O at rt for 8 h. [b]Yields refer to isolation after chromatography.

except **4k** and **4j**, in which the hydroxyl and aldehyde groups on the substrates were oxidized into carboxyl groups.

Subsenquently, the transformation of fluorinated sulfones to corresponding fluorinated sulfinates was investigated. The compound **4a** was selected as the model substrate. A series of nucleophiles were examined, and the results showed that CH_3ONa was more effective than others. However, the yield of sulfinate was not satisfactory (Table 2, entries 1–4). Fortunately, we found that $NaBH_4$ was an excellent reagent to transform the

Table 2. Screening of Conditions for Dearylation[a]



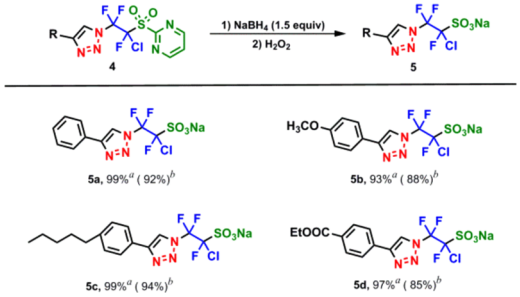
entry	sulfone	reagent (equiv)	solvent	t (h)	yield[b] (%)
1	**4a**	C_2H_5SNa (2.0)	C_2H_5SH/THF (1/2)	12	0
2	**4a**	C_2H_5SNa (2.0)	THF	12	0
3	**4a**	CH_3ONa (1.5)	THF	0.5	79
4	**4a**	CH_3ONa (1.5)	CH_3OH	0.5	85
5	**4a**	$NaBH_4$ (1.5)	CH_3OH	1	88
6	**4a**	$NaBH_4$ (1.5)	CH_3OH/THF (1/1)	1	99
7	**4a**	$NaBH_3CN$ (1.5)	THF	12	0
8	**4a**	$(CH_3COO)_3BHNa$ (1.5)	THF	12	0
9	**4ab**	$NaBH_4$ (1.5)	CH_3OH/THF (1/1)	12	0
10	**4ac**	$NaBH_4$ (1.5)	CH_3OH/THF (1/1)	12	0
11	**4ad**	$NaBH_4$ (1.5)	CH_3OH/THF (1/1)	12	0

[a]Reaction used **4a** (0.2 mmol) and $NaBH_4$ (0.3 mmol) in a 0.5 mL solution of CH_3OH and THF at rt. [b]Determined by ^{19}F NMR.

fluorinated sulfones into a fluorinated sulfinate via reductive dearylation, and the desired sulfinate could be obtained in 88% yield (entry 5). We also noticed that solvent had a significant effect on the reaction. For example, the fluorinated sulfinate could be obtained in 99% yield in a mixture of CH_3OH/THF(1/1, v/v) with $NaBH_4$ as the reductant (entry 6). In contrast, when other reductants, such as $NaBH_3CN$ and $(CH_3COO)_3BHNa$ were used, no products could be detected in the reactions (entries 7–8). Moreover, the behavior of the reductive dearylation reaction is also highly related to the structure of the fluorinated sulfones. When the sulfonyl group was linked to 2-pyridyl, phenyl, and benzothiazol-2-yl, respectively, instead of pyrimidyl, the reactions of dearylation were failed (entries 9–11). This result indicates that the rational design of the molecular structures is a crucial issue for preparation of fluorinated sulfinate from fluorinated sulfones. Encouraged by the initial success, we further investigated the dearylation reactions of common perfluoroalkyl sulfones with different Ar groups (Table S1, Figure S1 in Supporting Information (SI)). Perfluorohexylsulfones were chosen as the model substrates to test the reactivity under the dearylation reaction conditions optimized for **4a**. The comparisons of the different perfluorohexylsulfones proved that only 2-pyrimidyl sulfones could be transformed into the corresponding sulfinate effectively. These results demonstrate that the $NaBH_4$-mediated dearylation reaction of fluoroalkyl 2-pyrimidyl sulfones provides a general and efficient synthetic method for the preparation of fluoroalkyl sulfinates.

Based on the achievement of the fluorinated sulfinate, we further tried to prepare the fluorinated sulfonates in a one-pot reaction by a combined dearylation–oxidation procedure. The results showed the fluoroalkyl sulfones with 2-pyridyl groups could be transformed into sulfonates in excellent yield by the one-pot approach (Scheme 3, **5a**–**5d**). Thus, this is a new facile and efficient method for the preparation of fluoroalkyl sulfonic acids.

Scheme 3. One-Pot Synthesis of Fluorinated Sulfonates[a,b]



[a]Determined by ^{19}F NMR. [b]Yields refer to isolation after chromatography.

To understand the relationship between the structure and reactivity of the fluoroalkyl sulfones, theoretical calculations based on the density functional theory (DFT) were performed at the B3LYP/6-31G+(d) levels (Tables 3 and S2 in SI). The results reveal that, compared to other fluoroalkyl analogues, fluoroalkyl 2-pyrimidyl sulfones possess a longer bond length and a lower bond order, implying the weaker C–S bond in the S-CFCl and S-CF_2 moieties; thus, 2-pyrimidyl is easily removed by the dearylation reaction. Moreover, the Mulliken charges of the aryl carbon associated with the sulfur were higher than that of others, thus showing a higher electrophilicity.[19]

Synthesis of new fluorinated sulfonic acid polymers has received considerable attention since the use of a Nafion

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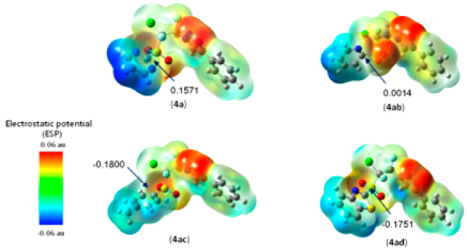
Table 3. Structural Parameters Associated with Fluorinated Sulfone[a]



substrates	bond length S-Ar	mayer bond order S-Ar	LBO bond order S-Ar	mulliken charge ClFC-S-C*
4a	1.848	0.698	0.738	0.1571
4ab	1.821	0.743	0.774	0.0014
4ac	1.784	0.792	0.843	-0.1800
4ad	1.803	0.741	0.835	-0.1751

[a]Electrostatic potential maps, bond length, and bond order calculated by DFT method with B3LYP functional and 6-31G+(d) basis set. The color scale represents the electrostatic potential, and the values specified with arrows refer to the Mulliken charge.

proton-exchange membrane as a proton conductor in fuel cells. Based on our success in the preparation of fluoroalkyl sulfonates, we further used ACTP to prepare new fluorinated sulfonic acid polymers. A linear polymer with pendant fluoroalkyl 2-pyrimidyl sulfone groups was obtained by radical copolymerization (Scheme S1, Table S3 in SI). Subsequently, the fluoroalkyl 2-pyrimidyl sulfone groups were converted into fluoroalkyl sulfonate group by the one-pot dearylation−oxidation reaction with 78% conversion, which was determined by ^{19}F NMR. Finally, the fluorinated sulfonic acid polymer membrane was fabricated by using a solution casting method and acidified with 1 M H_2SO_4. The proton conductivity of the membrane was measured at different temperatures. The data showed that the proton conductivity increased with temperature, from 6.3 mS/cm at 20 °C to 21.3 mS/cm at 80 °C. These results prove that ACTP can be used for the preparation of a fluorinated sulfonic acid proton-exhange membrane.

In summary, we have developed a diheteroatom fluoroalkylation reagent ACTP by a facile and highly efficient approach. As the first diheteroatom bifunctional fluoroalkylation agent, ACTP can be used to simultaneously incorporate both S and N atoms into fluorinated compounds. Therefore, a variety of organic fluorinated thio-compounds with N-containing functional groups, such as fluorinated ethers and sulfones with a trizole group, were successfully prepared. These fluorinated compounds may be very useful in many applications, such as promising candidates for pharmaceuticals and agrochemicals. On the other hand, the fluorinated sulfones were successfully converted to the fluoroalkyl sulfinates and sulfonates in high yields by dearylation and oxidation reactions. Based on this approach, a fluorinated sulfonic acid proton-exchange membrane was prepared using ACTP. Therefore, ACTP is a very useful reagent not only for the synthesis of various organic fluorinated compounds but also for the preparation of new fluorinated sulfonic acid polymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00347.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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