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Monofluoromethylation of Cyclic Sulfamidates and Sulfates with α -Fluorocarbanions of Fluorobis(phenylsulfonyl)methane and Ethyl 2-Fluoroacetoacetate

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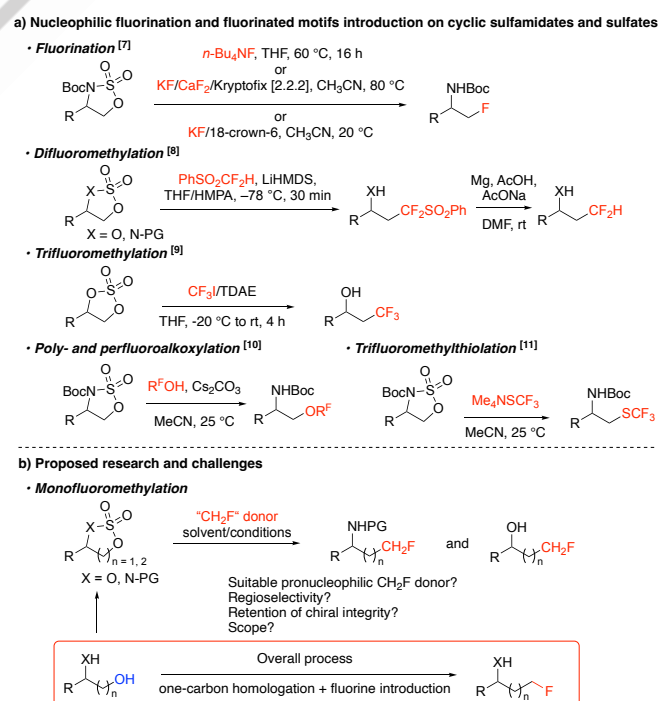
Abstract: A regioselective fluoromethylation by ring-opening of cyclic sulfamidates and sulfates with α -fluorocarbanions and subsequent reductive desulfonylation is developed. Fluorobis(phenylsulfonyl)methane (FBSM) was explored as fluoromethide equivalent and the reaction was extended to the α -fluorocarbanion of ethyl 2-fluoroacetoacetate. This approach allows access to γ - and δ -fluoroamines as well as γ - and δ -fluoroalcohols in high yields.

Introduction

Advances in the knowledge of organofluorine chemistry continue to grow at a steady pace. The small size of fluorine and its electronic properties account for its success as a bioisostere in drug design.^[1] Fluorine affects lipophilicity and solubility, modulates basicity of neighboring functional groups, influences conformation, addresses metabolism and toxicity issues, and thus impacts potency and selectivity of drugs.^[2] The current trend is to focus on the development of methods for the introduction of fluorinated motifs distinct from a single fluorine atom and the trifluoromethyl group. The fluorinated patterns that stand out are fluorine-containing alkyl groups (CH₂F, CH₂F, R^F) and those that combine a heteroatom (O, S, Se, N, P) with either fluorine atom(s) or a fluorine-containing group.^[3] The lightest fluoroalkyl group, namely monofluoromethyl group CH₂F, has demonstrated bioisosterism of methyl, hydroxymethyl and aminomethyl groups.^[4] Radical, electrophilic and nucleophilic monofluoromethylating agents have been designed and explored in numerous reactions.^[5] In the context of our study on the valorization of cyclic sulfamidates as electrophilic partners, we required nucleophilic CH₂F donors to investigate the reactivity of α -fluorocarbanions in a nucleophilic substitution process. Cyclic sulfamidate scaffolds have gained high interest in a wide range of nucleophilic ring-opening reactions with reliable regio- and stereoselectivity.^[6] Fluorinated nucleophiles contributed to produce a library of variously decorated amino derivatives featuring just one fluorine atom up to perfluorinated chains (Scheme 1a). The fluorination by means of *n*-Bu₄NF or KF with additives has been the subject of several works leading to α -

monofluoromethylamines.^[7] A single case of difluoromethylation was reported by Hu *et al* using the α -fluorocarbanion of PhSO₂CF₂H generated with the aid of a strong base (LiHMDS).^[8] The nucleophilic trifluoromethylation was demonstrated on simple 1,2 cyclic sulfates by reduction of trifluoromethyl iodide by tetrakis(dimethylamino)ethylene (TDAE).^[9] Chalcogen-containing fluorinated motifs that are the OR^F group^[10] and SCF₃^[11] also illustrated the versatility of the cyclic sulfamidate scaffold. In order to fill a gap in this nucleophilic reagent set, we tackled the challenge of monofluoromethylation (Scheme 1b).

Scheme 1. State of the art and research proposal.



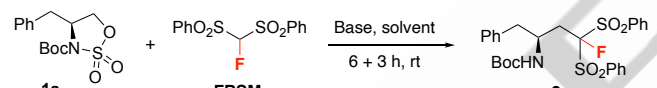
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We herein report our investigation that had successfully provided a novel route to γ - and δ -fluoroamines and γ - and δ -alcohols. Since cyclic sulfamidates and sulfates are synthesized from amino-alcohols and diols, respectively, the overall process is tantamount to one-carbon homologation and concomitant fluorine introduction.

Results and Discussion

At the outset, we investigated suitable pronucleophilic CH_2F donor reagents considering that carbanion formation, stability and reactivity issues will be encountered. Initially, we used fluoromethyl phenyl sulfone ($\text{PhSO}_2\text{CH}_2\text{F}$)^[12] as precursor of fluorocarbanion to react with cyclic sulfamidate **1a** (chiral non-racemic prepared from L-phenylalanine). However, all our attempts failed to afford significant amount of the desired product. Next, fluorobis(phenylsulfonyl)methane (FBSM) was evaluated as precursor of α -fluoromethyl carbanion. FBSM was introduced in 2006 in the ring-opening of epoxides and in allylic monofluoromethylations.^[12b, 13] This reagent became versatile, for example in the $\text{S}_{\text{N}}2$ -type Mitsunobu reaction.^[14] Compared to $\text{PhSO}_2\text{CH}_2\text{F}$, FBSM requires less strong bases for its deprotonation and the negative charge of the resulting anion is delocalized to the two phenylsulfonyl moieties thereby mitigating the repulsion of anionic carbon center lone pairs and those of the α -fluorine atom.^[15] Such persistent anion was easily generated to react with **1a**; Table 1 gathers selected optimization reactions yielding product **2a** as a single enantiomer.

Table 1. Optimization of the reaction parameters.^[a]



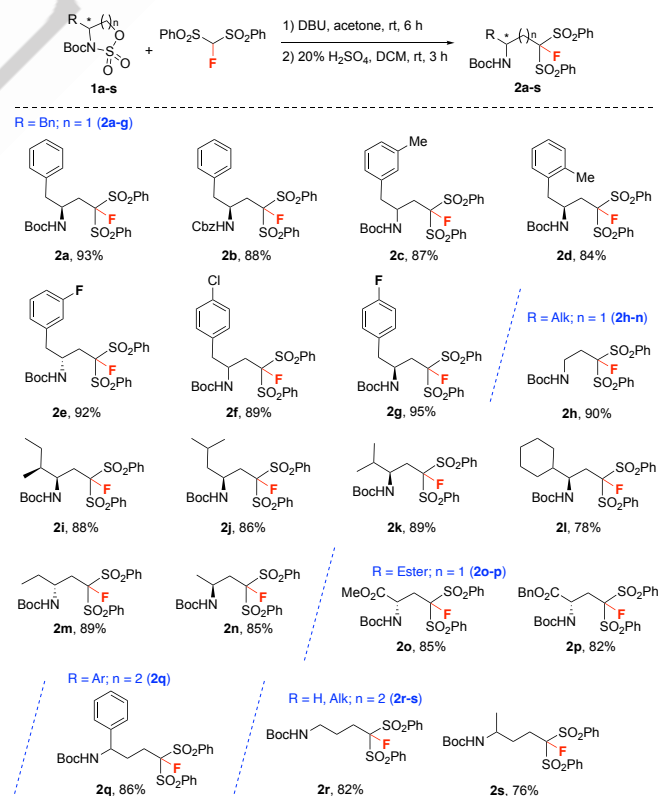
entry	FBSM [equiv.]	solvent	base	Yield [%] ^[b]
1	2.0	CH_3CN	NaH	75
2	2.0	CH_3CN	<i>t</i> -BuOK	83
3	2.0	CH_3CN	K_2CO_3	73
4	2.0	CH_3CN	Cs_2CO_3	80
5	2.0	CH_3CN	EtONa	68
6	2.0	CH_3CN	DBU	85
7	2.0	CH_3CN	Et_3N	21
8	2.0	CH_3CN	DIPEA	17
9	2.0	CH_3CN	DMAP	24
10	2.0	DCM	DBU	83
11	2.0	THF	DBU	86
12	2.0	acetone	DBU	93
13	2.0	1,4-dioxane	DBU	83
14	1.5	acetone	DBU (1.5 equiv.)	94
15	1.3	acetone	DBU (1.3 equiv.)	90
16	1.3	acetone	DBU (1.5 equiv.)	93

[a] Reaction conditions: **1a** (0.5 mmol), FBSM (1.3–2 equiv.), base (2 equiv. unless otherwise noted), solvent (8 mL); then, 20% aq $\text{H}_2\text{SO}_4/\text{DCM}$ (3:8) (11 mL), 3 h. [b] Yields were determined by ^{19}F NMR using fluorobenzene as an internal standard.

Inorganic (NaH), organic alkoxides, carbonates and nitrogen-containing bases are appropriate. Of the amines and amidines, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave the highest yield in acetonitrile at room temperature (Table 1, entry 6). Further screening of solvents pointed out acetone as optimal media. Finally, reagents/base ratio was optimized in order to minimize consumption of chemicals and we validated the conditions of Table 1, entry 16 for the next stage of scope assessment.

A variety of enantiopure or racemic cyclic sulfamidates **1a-s** were engaged in the ring-opening monofluoromethylation with the anion of FBSM to end up with novel compounds **2a-s** (Scheme 2). Five-membered ring sulfamidates featuring benzylic R group (**1a-g**), alkyl R group (**1h-n**) and ester group (**1o-p**) readily reacted to afford product in high isolated yields (78–95%) and complete regioselectivity. Less ring-strained six-membered ring 1,3-sulfamidates **1q-s** also well performed albeit in slightly lower yields (76–86%). The nitrogen protecting groups (N-PG), *tert*-butoxycarbonyl (Boc) and carboxybenzyl (Cbz), are compatible with the nucleophilic substitution reaction; N-Boc was preferred as it gave better yields (product **2a** versus **2b**). Most of the cyclic sulfamidates were prepared from chiral amino acid derivatives, offering chiral γ - and δ -fluoroamines. It was thus necessary to control the retention of chiral integrity at the stereogenic centers. Product **2i** (from L-isoleucine), which has two stereogenic centers, was obtained as a single diastereomer (NMR determined) while product **2o** (from L-serine) was obtained as a single enantiomer (HPLC determined). Note that these N-Boc products are in the form of rotamers as evidenced by ^{19}F NMR (see spectra in SI).^[16]

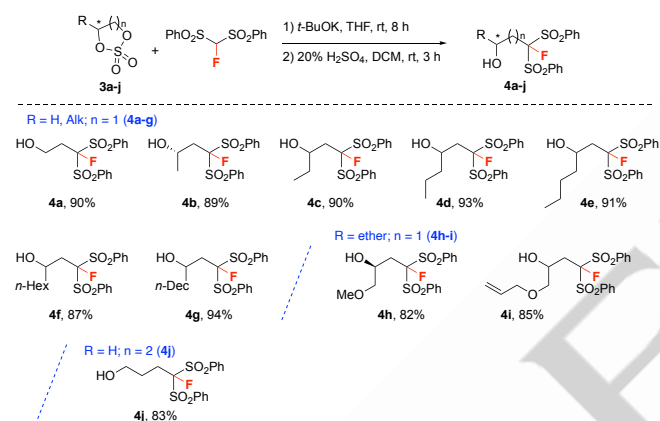
Scheme 2. Monofluoromethylation of cyclic sulfamidates.



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In the same vein, we questioned if this synthetic approach could be applied to 1,2- and 1,3-cyclic sulfates **3a-j**. The reactivity of cyclic sulfates is different than that of cyclic sulfamidates because of the two C–O bonds instead of C–N and C–O bonds in sulfamidates leading to acyclic sulfate intermediates instead of sulfamic acid intermediates; it was therefore necessary to adapt the reaction conditions, in particular we switched the combination base/solvent from DBU/acetone to *t*-BuOK/THF. Under simple conditions at room temperature the potassium α -fluorocarbanion of FBSM smoothly displaced the sulfate leaving group regioselectively at the primary alcohol moiety (Scheme 3). Simple γ - and δ -fluoroalcohols (R = H, Alk) **4a-g** and **4j** were prepared as well as functionalized ether derivatives (R = MeOCH₂, AllylOCH₂) **4h,i** in high yields ranging from 82 to 94 %. Here again, retention of chirality was confirmed when chiral substrates were used. We scaled-up the reaction to 2 grams for product **4g**, which was obtained in 94% yield.

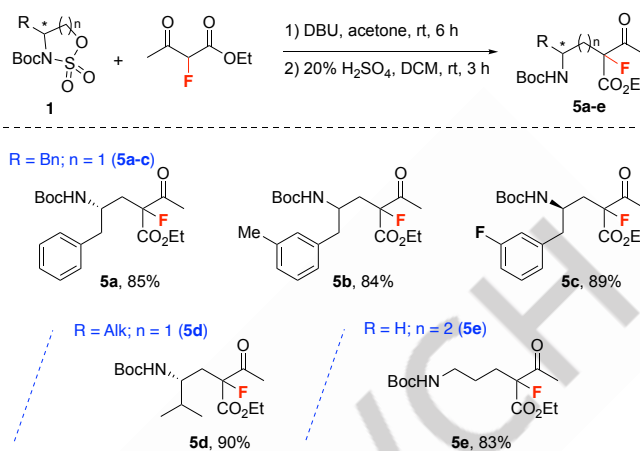
Scheme 3. Monofluoromethylation of cyclic sulfates.



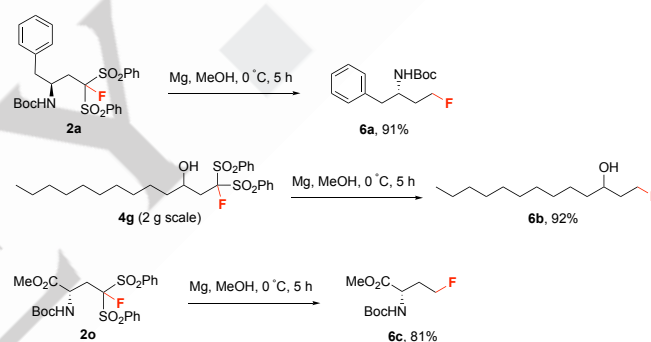
The nucleophilic ring-opening of cyclic sulfamidates **1** was successfully extended to a β -ketoester-derived α -fluorocarbanion. Ethyl 2-fluoroacetoacetate as carbanion precursor was easily treated with DBU in acetone to afford γ - and δ -fluoroamines **5a-e** in 83-90% yields and diastereoselectivities >95:5 for **5a-d** (Scheme 4). Other monofluoro active methylene reagents were tested: (EtO)₂P(O)CHFCO₂Et, CHF(CO₂Me)₂, CHF(CO₂Et)₂ and PhSO₂CHFCN; however, under the standard conditions of DBU/acetone or *t*-BuOK/THF only small amounts of desired products were identified in yields lower than 40%. Further optimization of experimental conditions has not been carried out. With equal disappointment, cyclic sulfates **3** could not react with the carbanion of ethyl 2-fluoro-3-oxobutanoate using *t*-BuOK or DBU as base.

Having prepared a wide range of bis(phenylsulfonyl)-containing γ - and δ -fluoroamines **2a-s** and γ - and δ -alcohols **4a-j**, we examined the reductive desulfonation to terminate the overall sequence of monofluoromethylation. The system Mg/AcOH/AcONa in DMF/H₂O (5:1) gave low conversions.^[17] More successfully, using magnesium in methanol at 0 °C resulted in a clean and complete desulfonation.^[14] This protocol afforded γ -fluoroamine **6a**, γ -fluoroalcohol **6b** and fluoromethyl alanine ester **6c** in high yields (Scheme 5).

Scheme 4. Extension to monofluoromethylation of cyclic sulfamidates with α -fluorocarbanion of ethyl 2-fluoroacetoacetate.



Scheme 5. Reductive desulfonation.



Conclusion

We leveraged the unique properties of the phenylsulfonyl activating group to generate persistent α -fluorocarbanion from FBSM for application in the unprecedented ring-opening monofluoromethylation of cyclic sulfamidates and sulfates. The reaction is regioselective and respects the stereochemical integrity of chiral substrates. We have filled the gap in the nucleophilic fluorine-containing reagent set with this monofluoromethylation reaction. Through this work, we are helping to make monofluorinated molecules of interest more accessible.

Experimental Section

General information

¹H, ¹³C and ¹⁹F were recorded on a Bruker AV 400 MHz instrument at 400 MHz (¹H NMR), 100MHz (¹³C NMR), and 376 MHz (¹⁹F NMR). Chemical shifts were reported in ppm downfield from Me₄Si and CCl₃F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Mass spectrometry (MS) spectra were recorded on a VG ZABHS spectrometer with the ESI resource.

High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker microTOF-QII instrument. Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone prior to use. Acetonitrile was distilled from phosphorus pentoxide. Fluorobis(phenylsulfonyl)methane (FBSM) was purchased from different suppliers in China. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

General procedure for the synthesis of cyclic sulfamidates

A procedure by Nelson and co-workers was followed.^[18] A solution of *N*-protected amino alcohol or hydroxy amino ester (50 mmol, 1.0 equiv) in dry CH₂Cl₂ (0.4 M) was added dropwise to a stirred solution of thionyl chloride (60 mmol, 1.2 equiv), trimethylamine (110 mmol, 2.2 equiv) and imidazole (200 mmol, 4.0 equiv) in dry CH₂Cl₂ (0.1 M) at -20 °C. The resulting solution was stirred until full consumption of the starting material was observed by TLC. The reaction mixture was warmed up to room temperature and quenched by addition of water. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The obtained crude cyclic sulfamidite was dissolved in CH₃CN (0.13 M), cooled to 0 °C, then NaIO₄ (55 mmol, 1.1 equiv), RuCl₃·3H₂O (5 mmol, 0.1 mol%) and water (0.16 M) were added to it sequentially. The reaction mixture was stirred at 0 °C until completion was indicated by TLC, then was diluted with water (equal volume to that used in reaction). After being warmed up to room temperature, the obtained solution was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated under vacuum to yield the crude expected product, which was purified by column chromatography (eluent: cyclohexane/EtOAc). Characterization data of sulfamidates **1a-s** are in agreement with literature data.^[7c, 10-11]

General procedure for the synthesis of cyclic sulfates

A procedure by E.M. Carreira and co-workers was followed.^[19] 1,2-Diol or 1,3-diol (50 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (30 mL) and the solution was cooled to 0 °C. A solution of SOCl₂ (65 mmol, 1.3 equiv) in CH₂Cl₂ (20 mL) was added via addition funnel over 1 h. The reaction mixture was then heated to reflux for 1 h and allowed to cool to room temperature. H₂O (50 mL) was added to the reaction mixture, the layers were separated and the organic layer was washed with H₂O (50 mL x 2) and brine (30 mL), dried (Na₂SO₄), filtered, then the solvent was evaporated in vacuo. The unpurified sulfite was used for the next step. The unpurified sulfite was dissolved in CH₃CN/CCl₄ (1:1) (100 mL). The solution was cooled to 0 °C. Precooled H₂O (100 mL) was added to the mixture. Solid NaIO₄ (100 mmol, 2.0 equiv) and RuCl₃·3H₂O (500 μmol, 0.5 mol%) were added in one portion. The reaction mixture was vigorously stirred for 1 h. The phases were separated and the aqueous layer was extracted with ethyl acetate (300 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under vacuum to yield the crude expected product, which was purified by column chromatography (eluent: cyclohexane/EtOAc). Characterization data of sulfates **3a-j** are in agreement with literature data.^[8]

General procedure for monofluoromethylation of cyclic sulfamidates

Fluorobis(phenylsulfonyl)methane (FBSM) (205 mg, 0.65 mmol, 1.3 equiv) and cyclic sulfamidate **1** (0.5 mmol, 1 equiv) were dissolved in 8 mL acetone at room temperature. Then, DBU (114 mg, 0.75 mmol, 1.5 equiv) was added to the solution. The reaction mixture was stirred for 6 h at rt. Subsequently, the solvent was evaporated and the residue was dissolved back in dichloromethane (8 mL) and 20% aqueous H₂SO₄ (3 mL). The resulting mixture was stirred vigorously at room temperature for 3 h. NaHCO₃ was then slowly added to the mixture until effervescence ceased. The aqueous layer was extracted with ethyl acetate (15 mL x 3). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by column chromatography (eluent: petroleum ether (60-90)/DCM) to afford the desired monofluorinated product.

General procedure for monofluoromethylation of cyclic sulfates

Fluorobis(phenylsulfonyl)methane (FBSM) (235 mg, 0.75 mmol, 1.5 equiv) and *t*-BuOK (84.2 mg, 0.75 mmol, 1.5 equiv) were dissolved in 10 mL THF at room temperature. The solution was stirred vigorously for 2 min. Then, the cyclic sulfates (0.5 mmol, 1 equiv) was added to the solution. The reaction mixture was stirred for 8 h at rt. Subsequently, the solvent was evaporated and the residue was dissolved back in dichloromethane (10 mL) and 20% aqueous H₂SO₄ (3 mL). The resulting mixture was stirred vigorously at room temperature for 3 h. NaHCO₃ was then slowly added to the mixture until effervescence ceased. The aqueous layer was extracted with ethyl acetate (15 mL x 3). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: petroleum ether (60-90)/DCM) to afford the desired monofluorinated product.

General procedure for monofluoromethylation of cyclic sulfamidates with ethyl 2-fluoroacetoacetate

Ethyl 2-fluoroacetoacetate (222 mg, 1.5 mmol, 1.5 equiv) and cyclic sulfamidate **1** (1 mmol, 1 equiv) were dissolved in 10 mL acetone at room temperature. Then, DBU (228 mg, 1.5 mmol, 1.5 equiv) was added to the solution. The reaction mixture was stirred for 6 h at rt. Subsequently, the solvent was evaporated and the residue was dissolved back in dichloromethane (10 mL) and 20% aqueous H₂SO₄ (3 mL). The resulting mixture was stirred vigorously at room temperature for 3 h. NaHCO₃ was then slowly added to the mixture until effervescence ceased. The aqueous layer was extracted with ethyl acetate (15 mL x 3). The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by column chromatography (eluent: petroleum ether (60-90)/DCM) to afford the desired monofluorinated product.

Typical Reductive desulfonylation. *tert*-Butyl (*S*)-(4-fluoro-1-phenylbutan-2-yl) carbamate (**6a**). Compound **2a** (1 mmol, 1.0 equiv) was dissolved in MeOH (20 mL) and the solution was cooled to 0 °C. Then, activated Mg turnings (240 mg, 10 mmol, 10 equiv) were added and the reaction mixture was stirred for 3 h at 0 °C. The completion of the reaction was monitored by TLC. Mg turnings (48 mg, 2 mmol, 2 equiv) were added after 2 h to ensure the complete conversion. The solvent was evaporated and the residue was dissolved in EtOAc (50 mL). The organic phase

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was washed with 5% acetic acid (20 mL x 2) and saturated NaHCO₃ (20 mL x 2) and then dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography to afford product **6a**.

Supporting Information

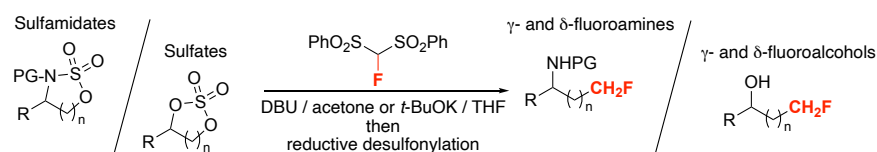
The data that support the findings of this study are available in the supplementary material of this article

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Keywords: fluorine • sulfamidate • sulfate • fluorocarbanion • ring-opening

Entry for the Table of Contents



The ring-opening of cyclic sulfamidates and sulfates with α -fluorocarbanion generated from fluorobis(phenylsulfonyl)methane (FBSM) and subsequent reductive desulfonylation have been developed. This fluoromethylation approach allows access to γ - and δ -fluoroamines as well as γ - and δ -fluoroalcohols in high yields. The monofluoromethylation of cyclic sulfamidates with α -fluorocarbanion of ethyl 2-fluoroacetoacetate was also described.

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