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Trifluoromethylthiolation

Ionic Liquids for Fast and Solvent-Free Nucleophilic Trifluoromethylthiolation of Alkyl Halides and Alcohols

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Abstract: The trifluoromethylthio group is of rising interest in medicinal, agrochemical, and materials chemistry. Although several strategies for the introduction of this functional group have been described, new synthetic methods are needed. A novel ionic liquid, 1-*n*-butyl-3-methylimidazolium trifluoromethylthiolate, has been developed and is herein reported as an efficient and recyclable in situ generated trifluoromethylthiolating reagent for alkyl halides, sulfonates, and even unactivated alcohols under solvent-free conditions.

Introduction

The late and selective incorporation of fluorine-containing groups into organic molecules has become a very important target in various fields of research (e.g., pharmaceuticals, agrochemicals, materials).[1] Among these substituents, the introduction of the trifluoromethylthio moiety (SCF_3) has attracted considerable attention in recent years because of its strong electron-withdrawing effect and extremely high lipophilicity (Hansch parameter $\pi_R = 1.44$).[2]

Indirect strategies for its incorporation into molecules involve the construction of SCF_3 by the trifluoromethylation of sulfur compounds,[3] or recently by an elegant alternative one-pot thiocyanation/trifluoromethylation reaction.[4] Numerous methods have also been developed for the direct introduction of the trifluoromethylthio group into organic compounds.[5] The recent developments of many efficient novel shelf-stable reagents based on N-SCF_3,[6] O-SCF_3,[7] or hypervalent iodide[8] structures, specially designed to substitute toxic CF_3SCl,[9] are very attractive. They are described as electrophilic trifluoromethylthiolating entities and they have indeed greatly contributed to establishing the electrophilic pathway as an essential methodology. However, although versatile, this pathway suffers from limitations and is less popular for the synthesis of alkyl trifluoromethyl thioethers because of the need for nucleophilic partners. Some answers to this issue have been provided with the help of transition-metal catalysis or radical pathways, including, very recently, photocatalysis.[10] The most convincing preparation of the C(sp_3)–SCF_3 group nevertheless remains nucleophilic substitution because of widely available leaving groups and inexpensive starting materials. This approach involves the use of various nucleophilic SCF_3 transfer reagents. Usually, the trifluoromethanethiolate anion is associated with either a transition metal (Hg, Ag, or Cu),[9d,11] to stabilize the CF_3S group, or tetramethylammonium or caesium (Me_4NSCF_3 or $CsSCF_3$),[12,13] as stable salts. Among these, the stable CF_3SAg salt and CF_3SCu–phenanthroline complex have been the most widely used until now.[14] Long reaction times and polar aprotic solvents (acetonitrile, toluene, and dimethylformamide) are frequently needed for such nucleophilic displacements. Despite already existing methods, the development of efficient methods with easy-to-use reagents for late-stage introduction of trifluoromethylthio groups, especially into aliphatic molecules, are still highly sought after. Recently, as part of our ongoing program of development of ecofriendly nucleophilic fluorination processes, we have shown the potential of the 1-*n*-butyl-3-methylimidazolium fluoride ([bmim][F]) ionic liquid (IL) as a fluorinating agent to provide soft nucleophilic substitution.[15] This result proved the great potential of ionic liquids,[16] not only as media for fluorination reactions,[17] but also as a reagent for the introduction of a perfluorinated group. It also prompted us to prepare an innovative ionic liquid with a cation designed to stabilize the trifluoromethylthiolate anion.

Herein we report the synthesis of a new ionic liquid, [bmim][SCF_3], and its application as a nucleophilic trifluoromethylthiolating reagent. The structure, reactivity, and stability of our reagent were carefully examined. All the reactions described in this paper were conducted under microwave irradiation, which is known to be very efficient for the organic synthesis of ionic liquids.[18] Finally, the recyclability of the ionic liquid was investigated.

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Results and Discussion

We first envisioned preparing our target compound [bmim][SCF_3] (**2**) in one step. We tried to adapt the methodology developed by Tyrra et al.[12] for the one-step synthesis of Me_4NSCF_3. Unfortunately, the mixture of elemental sulfur S_8, the Ruppert–Prakash reagent, and our IL [bmim][F] as fluorine source did not lead to the desired IL. This could probably be explained by the presence of water in our [bmim][F], which is probably deleterious for this reaction. We then turned our attention to the classic two-step methodology for the preparation of imidazolium salts. The ionic liquid [bmim][Cl] (**1**) was first prepared according to the literature.[19] The second step was carried out with silver(I) trifluoromethanethiolate in acetonitrile (Scheme 1).

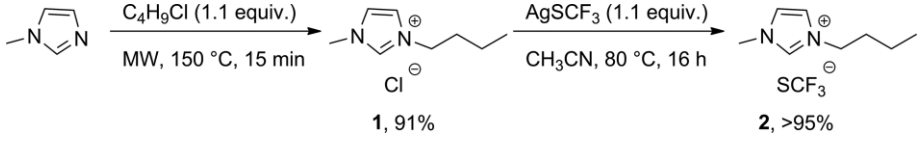
The fluorinated IL **2** was isolated and the anion exchange was carefully verified. Detailed examination of the ^1H NMR spectra revealed a slight shift of each signal, especially for the hydrogen located at the 2-position, that is, between the two nitrogen atoms, which shifted from 10 to 8.84 ppm. Similarly, the ^{19}F NMR spectra showed a shift of the SCF_3 signal from –21 to –17.5 ppm. Unfortunately, after a few minutes, the pure [bmim][SCF_3] started to decompose.

This phenomenon was clearly observed by the appearance of a fluoride signal in the ^{19}F NMR spectrum. This rather poor stability and the possible generation of a fluoride anion led us to an in situ preparation of this reagent to enable nucleophilic substitution.

The trifluoromethylthiolation of 3-phenylpropyl *p*-toluenesulfonate (**3a**) was investigated as a model reaction (Table 1). During this study, no particular handling precautions were required. With only 1 equiv. of [bmim][Cl] and a slight excess of $AgSCF_3$, the trifluoromethylthiolation of **3a** occurred with an encouraging yield of 25 % in 15 minutes at 120 °C under microwave (MW) irradiation (Table 1, entry 1). An increase in the amount of IL, silver trifluoromethylthiolate, or reaction time slightly improved the yield to a maximum of 48 % (entries 2–4). To our delight, by changing the IL from [bmim][Cl] to [bmim][I] a very good yield of 90 % was obtained (entry 5). Importantly, when the reaction was stopped before its completion, only the ^{19}F NMR signal of [bmim][SCF_3] at –17.5 ppm was detected, with no traces of $AgSCF_3$ being observed. We also noticed a change of color during the reaction, switching from orange-red, the color of [bmim][I], to light yellow, the color of **2**, and a return to orange-red at the end. This unambiguously indicated that the real active species was [bmim][SCF_3]. The IL [bmim][I] is not simply a solvent, but also an active player in this transformation. Other imidazolium halides, [bmim][Br] and [bmim][F], were also tested. Surprisingly, with these ILs, only the decomposition of the $AgSCF_3$ was observed (entries 9 and 10).

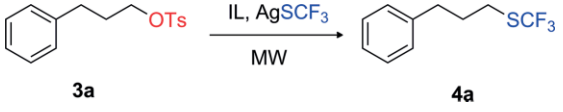
Finally, the best conditions for the trifluoromethylthiolation of 3-phenylpropyl *p*-toluenesulfonate (**3a**) were 2 equiv. of the IL [bmim][I] and 1.2 equiv. of $AgSCF_3$ at 110 °C in 15 minutes (88 % yield, entry 7). Because no additional solvent was added, even though the reaction was efficient with 1 equiv. of IL, the use of 2 equiv. was more convenient to avoid a heterogeneous or very viscous mixture. To demonstrate its practical utility, our methodology was carried out on a 0.5 g (2.5 mmol) scale without erosion of the yield (86 %, 0.47 g). For comparison, the reaction proceeded more slowly with conventional heating, but was still very efficient; 1 hour was necessary to obtain a comparable yield (entry 8).

The scope of this transformation was next assessed by using the best conditions in the reactions of various substrates to



Scheme 1. Synthesis of [bmim][SCF_3] (**2**).

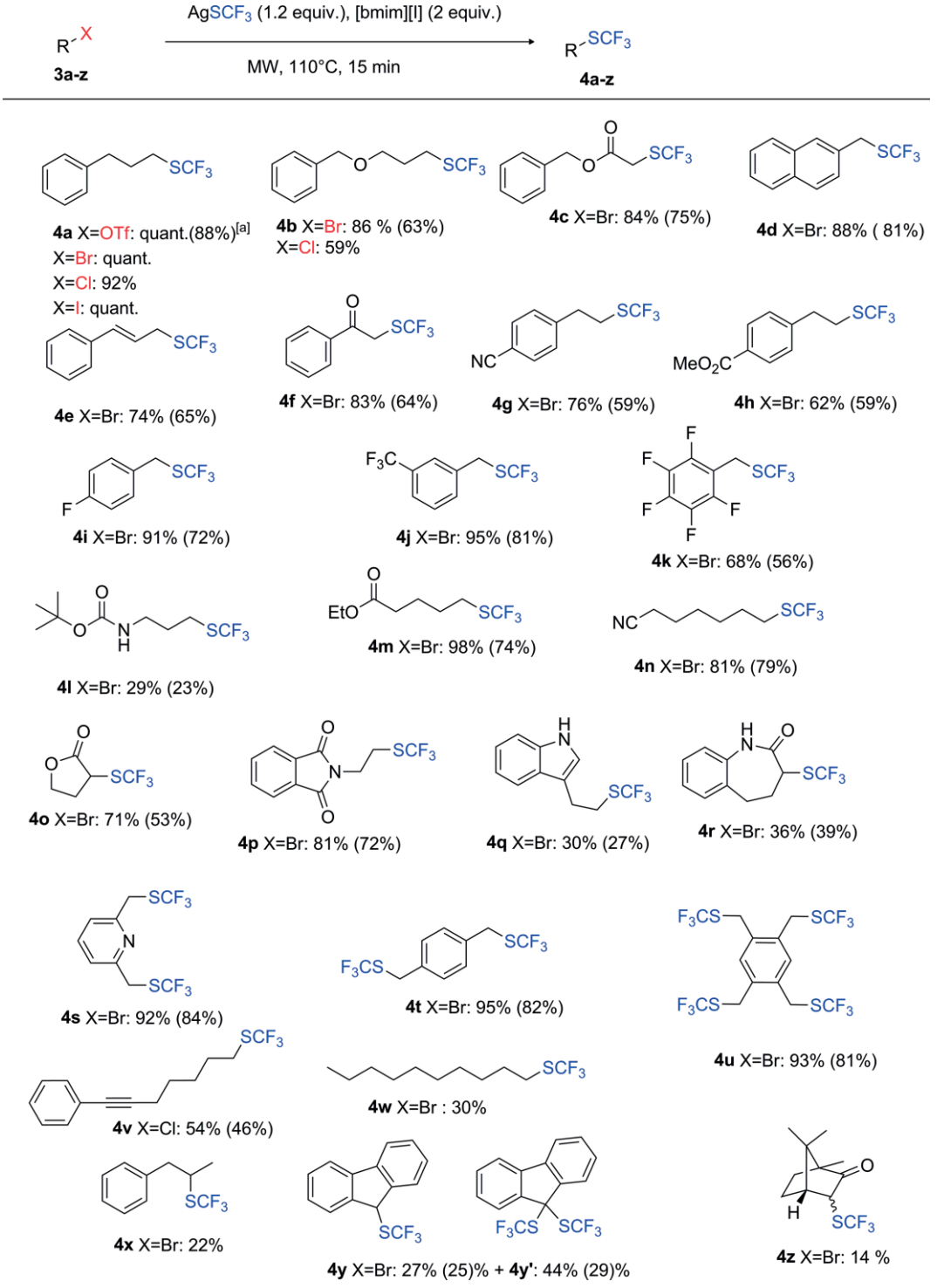
Table 1. Trifluoromethylthiolation of 3-phenylpropyl *p*-toluenesulfonate with ILs.



Entry	IL, Amount [equiv.]	$AgSCF_3$ [equiv.]	Time [min]	Temperature [°C]	Yield [%][a]
1	[bmim][Cl], 1	1.2	15	120	25
2	2	1.2	15	120	35
3	2	2	15	120	38
4	2	1.2	45	120	48
5	[bmim][I], 1	1.2	15	120	90
6	2	1.2	15	120	93
7	2	1.2	15	110	Quant. (88)[b]
8[c]	2	1.2	60	120	Quant.
9	[bmim][Br], 2	1.2	15	110	0
10	[bmim][F], 2	1.2	15	110	0

[a] Yield determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference. [b] Isolated yield. [c] Reaction conducted under conventional heating.

synthesize previously unreported compounds (Scheme 2). A wide range of electrophiles were converted into the corresponding trifluoromethyl sulfides in moderate-to-excellent yields. With iodine and bromine as the leaving group, the yields were excellent, whereas with chlorine lower but still reasonable yields were obtained (**4a**, **4b**). Concerning the benzylic series, good yields were obtained irrespective of the nature of the aromatic ring (**4d**, **4i**, **4j**, **4k**), and by adjusting the amount of reagent, bis- or tetrakis-substituted compounds were easily obtained (**4t**, **4u**). This transformation was also compatible with various other functionalities, such as esters (**4c**, **4h**, **4m**), cyano (**4g**, **4n**), imide (**4p**), and lactone (**4o**) groups. The original pyridine derivative **4s** could also be isolated in good yield without any protection.



Scheme 2. Scope of trifluoromethylthiolation of alkyl halides. [a] Yield determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference. Isolated yields are given in parentheses.

However, with substrates bearing the N–H moiety (**4l**, **4q**, **4r**), only medium yields were observed. Nevertheless, none of them has previously been described in the literature. The reaction seems to be sensitive to steric hindrance, because only modest yields were observed with secondary bromine derivatives (**4x**, **4z**). With 9-bromofluorene (**3y**), two compounds were isolated; in addition to the expected compound **4y**, the bis-trifluoromethylthiolated skeleton **4y′** was obtained in a yield of 29 %. The structure of **4y′** was confirmed by X-ray diffraction analysis (Figure 1) and the nature of the transformation is currently under investigation.

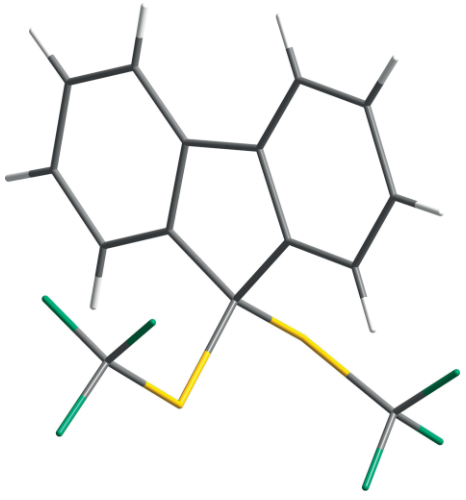


Figure 1. Crystallographic structure of **4y′**.

In previous studies, and despite the use of excess reagents, additives, activators, and ligands, recycling of the ionic liquid has never been mentioned. We therefore turned our attention to the recovery of the IL. 1-Bromo-3-phenylpropane (**3a**) was chosen for this study (Table 2).

After completion of the trifluoromethylthiolation process, simple extraction of the crude mixture with diethyl ether afforded product **4a** along with traces of unreacted starting material. After extraction of the product **4a** from the first run, 1-bromo-3-phenylpropane (**3a**) and 1.2 equiv. of $AgSCF_3$ were added directly to the crude IL, which afforded the product **4a** in 95 % yield. Further direct reloading of the starting substrates was not convenient due to the accumulation of salts, which led to problems with stirring. The IL phase was then dissolved in CH_2Cl_2 and the salts were filtered and then recovered as a pure material after the evaporation of CH_2Cl_2. The [bmim][I] IL could then be re-engaged in a new transformation. We were able to perform five reactions with the same batch without significant loss of efficiency.

Table 2. Recycling of [bmim][I] for the nucleophilic trifluoromethylthiolation of 1-bromo-3-phenylpropane (**3a**).[a]

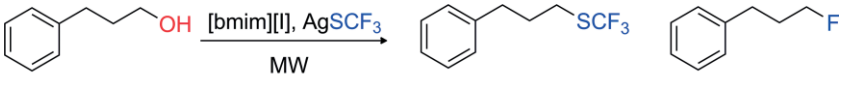
Cycle	1	2	3	4	5
Yield [%][a]	99	95	92	97	96

[a] Reagents and conditions: $AgSCF_3$ (1.2 equiv.), [bmim][I] (2 equiv.), 110 °C, 15 min. Yields determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference.

Among the various reagents to have been used for trifluoromethylthiolation reactions, trifluoromethanesulfenamides are perhaps the most versatile. As a result of umpolung activation, they have shown great efficiency with a large range of alkyl substrates including alcohols.[20] Despite the wide availability of alcohols, very few examples of direct dehydroxytrifluoromethylthiolation reactions have been described in the literature.[21] To extend our methodology even further, the direct dehydroxytrifluoromethylthiolation of alcohols without prefunctionalization could be a pertinent target. Inspired by our previous results, the reaction conditions were optimized with 3-phenylpropan-1-ol (**5a**) with [bmim][I] as the IL (Table 3).

Based on the mechanism proposed in the literature,[19,20] we initially employed 2 equiv. of $AgSCF_3$. One equiv. collapses into difluorothiophosgene to form carbonofluoridothiolate as leaving group and the second equiv. enables the nucleophilic substitution to provide the expected trifluoromethylthiolated product. Under these conditions, the trifluoromethylthiolated product was produced in moderate yield and was accompanied by the formation of alkyl fluoride **6a** in a ratio of 1:1 (Table 3, entry 1). This was in accord with our previous work, which demonstrated that nucleophilic fluorination proceeded extremely well under these conditions.[15] Decreasing the temperature re-

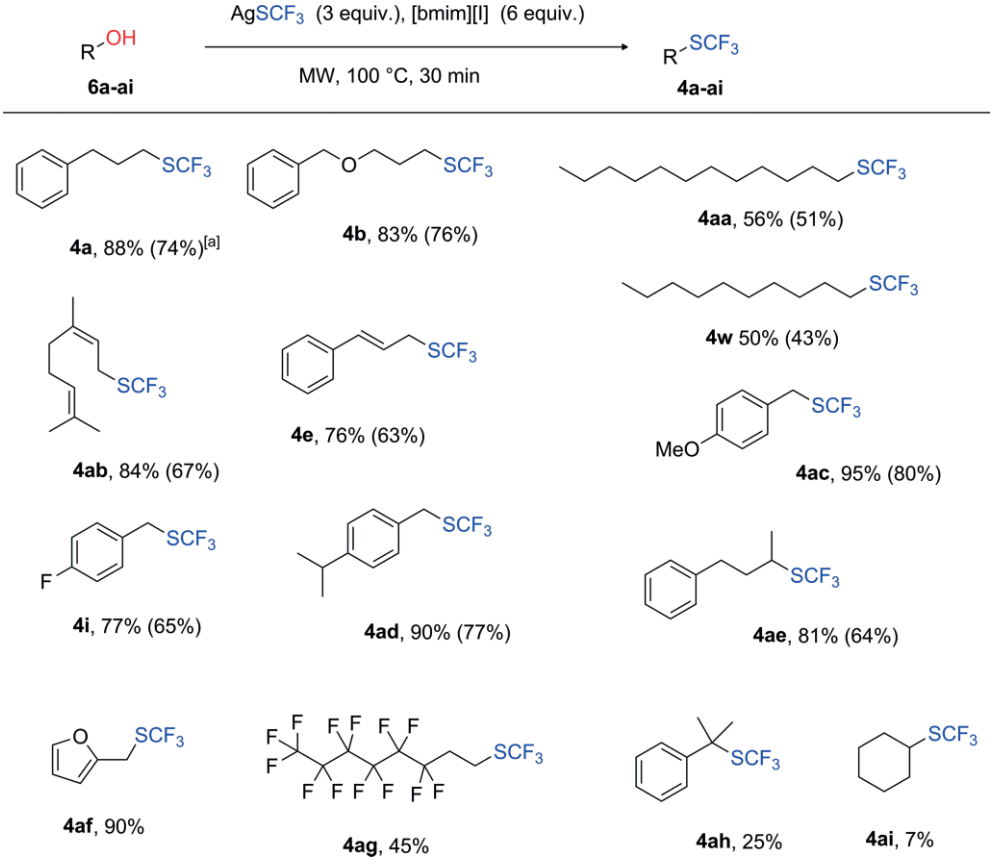
Table 3. Trifluoromethylthiolation of 3-phenylpropan-1-ol with [bmim][I].



5a **4a** **6a**

Entry	IL [equiv.]	$AgSCF_3$ [equiv.]	Time [min]	*T* [°C]	Yield [%][a]	
					4a	**6a**
1	2	2.2	30	110	44	45
2	2	2.2	15	100	39	30
3	2	2.2	60	90	30	15
4	4	2.2	30	110	52	18
5	4	2.2	30	100	70	9
6	6	3	30	100	88 (74 %)[b]	2
7[c]	6	3	120	100	68	–

[a] Yields determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference. [b] Isolated yield. [c] Reaction conducted under conventional heating.



Scheme 3. Scope of the dehydroxytrifluoromethylthioation of alcohols. [a] Yields determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference. Isolated yields are given in parentheses.

duced the monofluorination, but also the yield of compound **4a**, even with a longer reaction time (entries 1–3). We then changed the [bmim][I]/$AgSCF_3$ ratio to 2:1, as used in the reactions of the alkyl halides. The positive consequences were an increase in the yield of **4a** to 70 % and a decrease in the yield of the monofluorinated compound **6a** to below 10 % (entry 5). Finally, with 6 equiv. of IL and 3 equiv. of $AgSCF_3$ at 100 °C, the desired compound was obtained in a good yield of 88 % in only 30 minutes (entry 6). Under conventional heating, the reaction was less effective; after 2 hours, only 68 % yield of trifluoromethylthiolated compound **4a** was obtained (entry 7).

The scope of this reaction was successfully explored with various alcohols (Scheme 3). Primary benzyl, alkyl, and allylic alcohols gave rise to the corresponding trifluoromethylthiolated molecules in good yields. Long-chain aliphatic alcohols delivered moderate yields (**4aa**, **4w**) because of the poor solubility of the starting materials in the reaction media. A furan derivative was also compatible with this methodology, but the resulting compound **4af** was too volatile to be isolated in pure form. A secondary alcohol reacted smoothly to form the product **4ae** in 64 % yield, and tertiary and secondary cyclic alcohols were also suitable substrates, albeit the corresponding products (**4ah** and **4ai**) were isolated in poor yields.

Finally, the recyclability of the ionic liquid in this reaction was investigated by using 3-phenylpropan-1-ol (**5a**; Table 4). Despite a slight decrease in the yield in the second run, we showed that the reaction could be carried out with the same IL batch for at least three turns.

Table 4. Recycling of [bmim][I] for the nucleophilic trifluoromethylthiolation of 3-phenylpropan-1-ol (**5a**).

Cycle	1	2	3
Yield [%][a]	82	69	72

[a] Reagents and conditions: $AgSCF_3$ (3 equiv.), [bmim][I] (6 equiv.), 100 °C, 30 min. Yields determined by ^{19}F NMR analysis using $PhOCF_3$ as internal reference.

Conclusions

We have shown that the IL 1-*n*-butyl-3-methylimidazolium trifluoromethylthiolate (**2**) could be prepared from 1-*n*-butyl-3-methylimidazolium chloride (**1**) by anion exchange with $AgSCF_3$. Prepared in situ, this compound demonstrated its potential as a trifluoromethylthiolating reagent to enable the soft nucleophilic substitution of various alkyl halides and even alcohols. Except for the work-up procedures and recycling processes, no solvent, special precautions, or complex or hazardous additives were necessary for this transformation. The use of microwave irradiation allowed a short reaction time. The IL could be reused for several cycles with high efficiency, thereby contributing to a decrease in reaction waste. Further develop-

ments of this new reagent and other applications are under study in our laboratory.

Experimental Section

General: Chemicals were purchased from commercial sources unless otherwise stated in the Supporting Information. Reactions were monitored by ^{19}F NMR spectroscopy. Yields refer to materials purified by preparative TLC chromatography. NMR spectra were collected with a Bruker AC-200 or AC-300 spectrometer. The reported coupling constants and chemicals shifts are based on first-order analysis. The residual peak of $CHCl_3$ (δ = 7.26 ppm) for ^1H NMR (200 or 300 MHz), the central peak of $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR (75 or 50 MHz), and $CFCl_3$ (δ =0.00 ppm) for ^{19}F NMR (188 MHz) were used as internal references. HRMS was performed with a XEVO-QTOF Mass Spectrometer at the Institute Lavoisier of Versailles – University of Versailles Saint Quentin. The compounds described in this section are limited to new products. The analytical data for molecules that have previously been reported can be found in the Supporting Information. X-ray Diffraction: Data collection: Bruker APEX2; cell refinement: Bruker SAINT; data reduction: Bruker SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Bruker SHELXTL; software used to prepare material for publication: Bruker SHELXTL.

General Procedure for the Trifluoromethylthiolation of Halide and Tosylate Substrates: A microwave tube with a magnetic stirring bar was charged with a halide or tosylate (1.0 equiv., 0.3 mmol) and [bmim][I] (2.0 equiv., 0.6 mmol, 0.16 g). After stirring the mixture, $AgSCF_3$ (1.2 equiv., 0.36 mmol, 75 mg) was added in one portion and the mixture was subjected to microwave irradiation at 110 °C during 15 min. The mixture was then cooled to room temperature, diluted with acetonitrile, and the conversion was verified by ^{19}F NMR analysis with $PhOCF_3$ as internal reference. The crude was directly purified by preparative TLC chromatography on silica gel to give the desired product.

Methyl 4-{2-[(Trifluoromethyl)thio]ethyl}benzoate (4h): Yield: 47 mg, 59 %; colorless liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (2:8). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.7 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 3.91 (s, 3 H), 3.11 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 144.1, 131.1 (q, J = 306.6 Hz), 130.1, 129.0, 128.7, 52.2, 36.1, 30.8 (q, J = 2.1 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.49 (s) ppm. HRMS: calcd. for $C_{11}H_{12}F_3O_2S$ 265.0516; found 265.0516 [M + H]$^+$ (δ = 2.3 ppm).

(4-Fluorobenzyl)(trifluoromethyl)sulfane (4i): Yield: 45 mg, 72 %; yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 2 H), 7.05 (t, J = 8.5 Hz, 2 H), 4.11 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5 (d, J = 247.0 Hz), 131.0 (d, J = 3.3 Hz), 130.7 (d, J = 8.1 Hz), 130.6 (q, J = 306.1 Hz), 115.9 (d, J = 22.0 Hz), 33.7 (q, J = 2.2 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.08 (s, 3 F), –114.40 (m, 1 F) ppm.

[(Perfluorophenyl)methyl](trifluoromethyl)sulfane (4k): Yield: 47 mg, 56 %; pale-yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.15 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2 (dm, J = 250.1 Hz), 141.5 (dm, J = 255.0 Hz), 137.8 (dm, J = 251.7 Hz), 130.3 (q, J = 307.6 Hz), 110.8 (td, J = 17.0, 4.2 Hz), 20.9 (m) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.59 (t, J = 3.5 Hz, 3 F), –142.56 (m, 2 F), –154.02 (t, J = 2.0 Hz, 1 F), –161.90 (m, 2 F) ppm. HRMS: calcd. for C_8HF_8S 280.9671; found 280.9678 [M – H]$^-$ (δ = –0.7).

***tert*-Butyl {3-[(Trifluoromethyl)thio]propyl}carbamate (4l):** Yield: 18 mg, 23 % %; colorless liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.58 (br. s, NH), 3.27–3.20 (m, 2 H), 2.91 (t, J = 6.9 Hz, 2 H), 1.89 (quint., J = 6.9 Hz, 2 H), 1.44 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 131.1 (q, J = 305.6 Hz), 28.4, 27.2 (d, J = 2.2 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.72 (s) ppm. HRMS: calcd. for $C_9H_{16}F_3NO_2SNa$ 282.0752; found 282.0748 [M + Na]$^+$ (δ = –1.4).

Ethyl 5-[(Trifluoromethyl)thio]pentanoate (4m): Yield: 51 mg, 74 %; pale-yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.12 (q, J = 7.1 Hz, 2 H), 2.91–2.83 (m, 2 H), 2.36–2.28 (m, 2 H), 1.76–1.68 (m, 4 H), 1.25 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.1, 131.2 (q, J = 305.8 Hz), 60.5, 33.6, 29.6 (q, J = 2.0 Hz), 29.0, 23.8, 14.3 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.69 (s) ppm. HRMS: calcd. for $C_8H_{13}F_3O_2S$ 231.06611; found 231.06592 [M + H]$^+$ (δ = –0.8).

3-[(Trifluoromethyl)thio]dihydrofuran-2(3*H*)-one (4o): Yield: 30 mg, 53 %; pale-yellow liquid. Eluent for the preparative TLC chromatography: Et_2O. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.48 (td, J = 8.6, 3.1 Hz, 1 H), 4.34 (td, J = 9.1, 6.7 Hz, 1 H), 4.18 (t, J = 9.1 Hz, 1 H), 2.91–2.79 (m, 1 H), 2.50 (dq, J = 13.1, 9.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 130.0 (q, J = 306.7 Hz), 66.9, 41.2 (d, J = 2.2 Hz), 31.9 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –40.64 (s) ppm. HRMS: calcd. for $C_5H_5F_3O_2S$ 187.00351; found 187.00346 [M + H]$^+$ (δ = –0.2).

3-{2-[(Trifluoromethyl)thio]ethyl}-1*H*-indole (4q): Yield: 20 mg, 27 %; brown paste. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (2:8). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (br. s, NH), 7.59 (d, J = 7.8 Hz, 1 H), 7.39 (d, J = 7.8 Hz, 1 H), 7.24–7.07 (m, 2 H), 3.20 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 131.4 (q, J = 307.1 Hz), 127.0, 122.4, 122.2, 119.8, 118.5, 113.6, 111.4, 30.7 (d, J = 2.2 Hz), 26.0 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.40 (s) ppm. HRMS: calcd. for $C_{11}H_{11}F_3NS$ 246.0564; found 246.0571 [M + H]$^+$ (δ = 2.8 ppm).

3-[(Trifluoromethyl)thio]-1,3,4,5-tetrahydro-2*H*-benzo[*b*]azepin-2-one (4r): Yield: 31 mg, 39 %; brown solid. M.p. 138 °C. Eluent for the preparative TLC chromatography: Et_2O. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.16 (br. s, NH), 7.34–7.19 (m, 4 H), 7.07 (d, J = 7.8 Hz, 1 H), 4.07 (dd, J = 11.3, 7.5 Hz, 1 H), 3.07–2.95 (m, 1 H), 2.80–2.65 (m, 2 H), 2.54–2.42 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 136.4, 133.4, 130.6 (q, J = 306.6 Hz), 130.1, 128.3, 127.0, 122.6, 46.4, 38.3, 29.9 (d, J = 2.2 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –40.56 (s) ppm. HRMS: calcd. for $C_{11}H_{11}F_3NOS$ 262.0513; found 262.0517 [M + H]$^+$ (δ = 1.5 ppm).

2,6-Bis{[(trifluoromethyl)thio]methyl}pyridine (4s): Yield: 77 mg, 84 %; pale-yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 (t, J = 7.7 Hz, 1 H), 7.29 (d, J = 7.7 Hz, 2 H), 4.23 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.2, 130.7 (q, J = 306.7 Hz), 129.5, 35.8 (q, J = 2.0 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.99 (s) ppm. HRMS: calcd. for $C_9H_7F_6NS_2$ 308.0002; found 307.9999 [M + H]$^+$ (δ = –1.0).

1,2,4,5-Tetrakis{[(trifluoromethyl)thio]methyl}benzene (4u): Yield: 130 mg, 81 %; pale-orange solid. M.p. 39 °C. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37 (s, 2 H), 4.23 (s, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.4, 133.9, 130.3 (q, J = 307.4 Hz), 30.9 (q, J = 2.0 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –42.13 (s) ppm. HRMS: calcd. for $C_{14}H_{10}F_{12}S_4$ 532.9396; found 532.9388 [M – H]$^+$ (δ = –1.5).

(7-Phenylhept-6-yn-1-yl)(trifluoromethyl)sulfane (4v): Yield: 38 mg, 46 %; colorless liquid. Eluent for the preparative TLC chromatography: petroleum ether. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2 H), 7.35–7.30 (m, 3 H), 2.96 (t, J = 7.0 Hz, 2 H), 2.48 (t, J = 6.5 Hz, 2 H), 1.83–1.61 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.6, 131.3 (q, J = 305.6 Hz), 128.3, 127.7, 124.0, 89.7, 81.1, 29.9 (d, J = 2.2 Hz), 29.1, 28.1, 27.8, 19.3 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.68 (s) ppm. HRMS: calcd. for $C_{11}H_{16}F_3S$ 237.09303; found 237.09123 $[M - H]^+$ (δ = –2.9).

Decyl(trifluoromethyl)sulfane (4w): Yield: 22 mg, 30 %; colorless liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.87 (t, J = 7.5 Hz, 2 H), 1.67 (q, J = 7.6 Hz, 2 H), 1.43–1.27 (m, 14 H), 0.88 (t, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.4 (q, J = 306.4 Hz), 32.0, 30.0 (q, J = 1.5 Hz), 29.6, 29.5 (2 C), 29.4, 29.1, 28.6, 22.8, 14.2 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –41.77 (s) ppm.

(9*H*-Fluoren-9-yl)(trifluoromethyl)sulfane (4y): Yield: 20 mg, 25 %; waxy solid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (2:8). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.71 (m, 4 H), 7.47–7.35 (m, 4 H), 5.32 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6, 140.6, 131.2 (q, J = 307.6 Hz), 129.0, 128.0, 125.9, 120.3, 47.8 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –39.51 (s) ppm. HRMS: calcd. for $C_{14}H_9F_3S$ 265.0299; found 265.0298 $[M - H]^+$ (δ = –0.4).

(9*H*-Fluorene-9,9-diyl)bis[(trifluoromethyl)sulfane] (4y′): Yield: 32 mg, 29 %; pale-yellow solid. M.p. 73 °C. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (2:8). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.74 (m, 4 H), 7.54–7.38 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 138.7, 130.6, 128.4, 128.3 (q, J = 310.8 Hz), 125.8, 120.9, 63.3 ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –38.68 (s) ppm. HRMS: calcd. for $C_{15}H_7F_6S_2$ 364.9893; found 364.9885 $[M - H]^+$ (δ = –2.2).

General Procedure for the Trifluoromethylthiolation of Alcohol Substrates: A microwave tube with a magnetic stirring bar was charged with the alcohol compound (1.0 equiv., 0.3 mmol) and [bmim][I] (6.0 equiv., 1.8 mmol, 0.47 g). After stirring the mixture, $AgSCF_3$ (3 equiv., 0.9 mmol, 188 mg) was added in one portion and the mixture subjected to microwave irradiation at 100 °C during 30 min. The mixture was then cooled to room temperature, diluted with acetonitrile, and the conversion was determined by ^{19}F NMR with $PhOCF_3$ as internal standard. The crude was directly purified by preparative TLC chromatography on silica gel to give the desired product.

(*Z*)-(3,7-Dimethylocta-2,6-dien-1-yl)(trifluoromethyl)sulfane (4ab): Yield: 48 mg, 67 %; pale-yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^{1}H NMR (300 MHz, CD_3CN): δ = 5.31 (t, J = 7.7 Hz, 1 H), 5.13 (m, 1 H), 3.64 (d, J = 7.8 Hz, 2 H), 2.05–2.19 (m, 4 H), 1.76 (s, 3 H), 1.69 (s, 3 H), 1.62 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 143.2, 133.0, 132.3 (q, J = 305.7 Hz), 124.6, 118.8, 32.3, 28.6 (q, J = 2.2 Hz), 27.1, 25.8, 23.5, 17.7 ppm. ^{19}F NMR (188 MHz, CD_3CN): δ = –42.09 (s) ppm. HRMS: calcd. for $C_{14}H_{14}F_3S$ 271.07738; found 271.07561 $[M + H]^+$ (δ = 2.4 ppm).

(4-Isopropylbenzyl)(trifluoromethyl)sulfane (4ad): Yield: 54 mg, 77 %; yellow liquid. Eluent for the preparative TLC chromatography: Et_2O/petroleum ether (1:9). ^{1}H NMR (300 MHz, CD_3CN): δ = 7.31–7.20 (m, 4 H), 4.13 (s, 2 H), 2.93 (sept., J = 6.7 Hz, 1 H), 1.26 (d, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 149.8, 132.0 (q, J = 306.8 Hz), 129.9, 129.4, 127.8, 118.2, 70.1, 34.5 (q, J = 2.2 Hz), 24.2 ppm. ^{19}F NMR (188 MHz, CD_3CN): δ = –42.24 (s) ppm.

CCDC 1571218 (for **4y′**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

Supporting Information (see footnote on the first page of this article): Materials and apparatus, general experimental procedures, and ^{1}H and ^{13}C NMR spectra of all the synthesized compounds.

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Keywords: Fluorinated compounds · Ionic liquids · Fluorine · Sulfur · Trifluoromethylthiolation · Nucleophilic substitution

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