Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4ob01451k

A concise synthesis of (alkynyl)(trifluoromethyl)-sulfanes *via* a bismuth(III)-promoted reaction of trimethyl(alkynyl)silane with trifluoromethanesulfanylamide†

Jie Sheng[a] and Jie Wu*[a,b]

Received 10th July 2014,
Accepted 6th August 2014

DOI: 10.1039/c4ob01451k

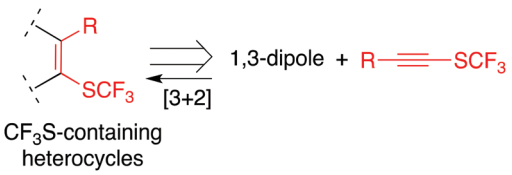
www.rsc.org/obc

A bismuth(III)-promoted reaction of trimethyl(alkynyl)silanes with trifluoromethanesulfanylamide is developed, giving rise to (alkynyl)(trifluoromethyl)sulfanes in good yields.

1. Introduction

In the last decade, we have focused on the synthesis of natural product-like compounds with privileged structures.[1] The subsequent construction and screening of related libraries result in the discovery of some hits for several biological assays. With an expectation to improve the corresponding biological activities and find more active compounds, we have been interested in the introduction of the fluoro atom into small molecules.[2] So far, some approaches have been appeared for the incorporation of fluoro-containing groups into organic compounds,[3,4] such as the (trifluoromethyl)thio moiety (SCF_3). Due to the high hydrophobicity of the (trifluoromethyl)thio moiety,[5] methods for nucleophilic trifluoromethylthiolation and electrophilic trifluoromethylthiolation have been developed.[6–8] Among the reagents reported for trifluoromethylthiolation, much attention has been paid to trifluoromethanesulfanylamide, which was recognized as an equivalent of the trifluoromethanesulfanyl cation (CF_3S^+). Its good reactivity for the formation of the C–SCF_3 bond has been demonstrated.[7a] Recently, we reported the formation of (trifluoromethyl)thio-substituted indoles, benzofurans, and benzothiophenes using trifluoromethanesulfanylamide as the source of the trifluoromethanesulfanyl cation.[2a–c] During the reaction process, the presence of bismuth(III) chloride was crucial for the successful transformation.

As mentioned above, we have generated some libraries with privileged scaffolds.[1] In order to get more active molecules in the subsequent biological evaluation, we conceived that trifluoromethylthiolation would be a good vehicle to generate the (trifluoromethyl)thio-containing heterocycles. Prompted by our interest in the [3 + 2] cycloaddition of isoquinoline-*N*-oxide[9] or isoquinolinium-2-ylamide,[10] we envisioned that (alkynyl)(trifluoromethyl)sulfanes would be a good choice as the reaction partner (Scheme 1). However, examples for access to (arylethynyl)(trifluoromethyl)sulfanes remain rare.[6a,b,8a,b] Therefore, we initiated a program to consider to produce (alkynyl)(trifluoromethyl)sulfanes.

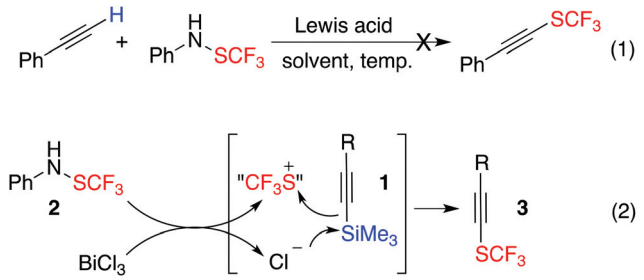


Scheme 1 Proposed route for the synthesis of CF_3S-containing heterocycles.

2. Results and discussion

Initially, the reaction of ethynylbenzene with trifluoromethanesulfanylamide was investigated. Although bismuth(III) chloride was demonstrated as the most efficient one in several transformations,[2a–c] different Lewis acids including bismuth(III) chloride were examined. However, all reactions failed to give rise to the expected product (Scheme 2, eqn (1)). We reasoned that the addition of a base would be beneficial for the generation of the alkyne anion, which would facilitate the subsequent nucleophilic attack of the trifluoromethanesulfanyl cation. However, it would deactivate the role of the Lewis acid if a base was added in the reaction system. Therefore, we shifted our focus to trimethyl(alkynyl)silanes. We hypothesized that

[a]*Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China. E-mail: jie_wu@fudan.edu.cn; Fax: +8621 6564 1740; Tel: +86 21 6510 2412*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China*
† Electronic supplementary information (ESI) available: Experimental procedure, characterization data, and ^1H and ^{13}C NMR spectra of compounds **3**. See DOI: 10.1039/c4ob01451k

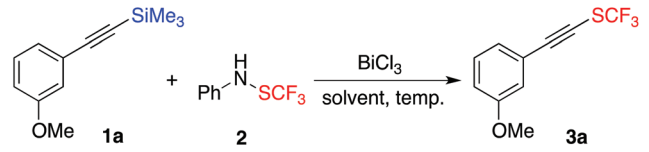


Scheme 2 Generation of (alkynyl)(trifluoromethyl)sulfanes.

the presence of bismuth(III) chloride would activate trifluoromethanesulfanylamide **2** to afford trifluoromethanesulfanyl cations and chloride, which would react with trimethyl(alkynyl)silane **1** leading to the desired (alkynyl)(trifluoromethyl)sulfane **3** (Scheme 2, eqn (2)). With this consideration in hand, we started to explore the possibility of this transformation.

At the beginning, the reaction of ((3-methoxyphenyl)ethynyl)trimethylsilane **1a** with trifluoromethanesulfanylamide **2** promoted by bismuth(III) chloride was selected as the model. The reaction was initially performed in dichloroethane (DCE) at 80 °C in the presence of bismuth(III) chloride (1.5 equiv.). To our delight, the corresponding product **3a** was obtained and isolated in 36% yield (Table 1, entry 1). The yield was lower when the amount of bismuth(III) chloride was decreased to 1.0 equiv. (Table 1, entry 2). Interestingly, ((3-methoxyphenyl)ethynyl)(trifluoromethyl)sulfane **3a** was produced in 88% yield when 2.0 equiv. of bismuth(III) chloride were added in the reaction (Table 1, entry 3). No reaction occurred in a control experiment without the addition of bismuth(III) chloride (Table 1, entry 4). The reaction was further screened at different temperatures (Table 1, entries 5–8). A similar yield was observed when the reaction took place at 100 °C, while inferior results were obtained when the reaction temperature was lowered. We next examined the transformation in various solvents (Table 1, entries 9–14). Only a trace amount of the product was detected when toluene was used as the solvent. Compound **3a** could be afforded in 73% yield when the reaction occurred in MeCN. The results were poor when other solvents were utilized. The efficiency was affected when the reaction was performed under an air atmosphere (Table 1, entry 15). Compared to the result obtained in DCE, the yield from a mixed solvent (DCE–MeCN = 1 : 1) was inferior, leading to compound **3a** in 75% yield (Table 1, entry 16). Only a trace amount of the product was detected when $BiCl_3$ was changed to $FeCl_3$, $CuCl_2$, or TsOH (Table 1, entries 17, 18 and 20). No desired product was detected when ZnF_2 was employed as the Lewis acid (Table 1, entry 19). A trace amount of the product was observed when TMS in the substrates was replaced by other leaving groups, such as TES, TBS, and TIPS (data not shown in Table 1).

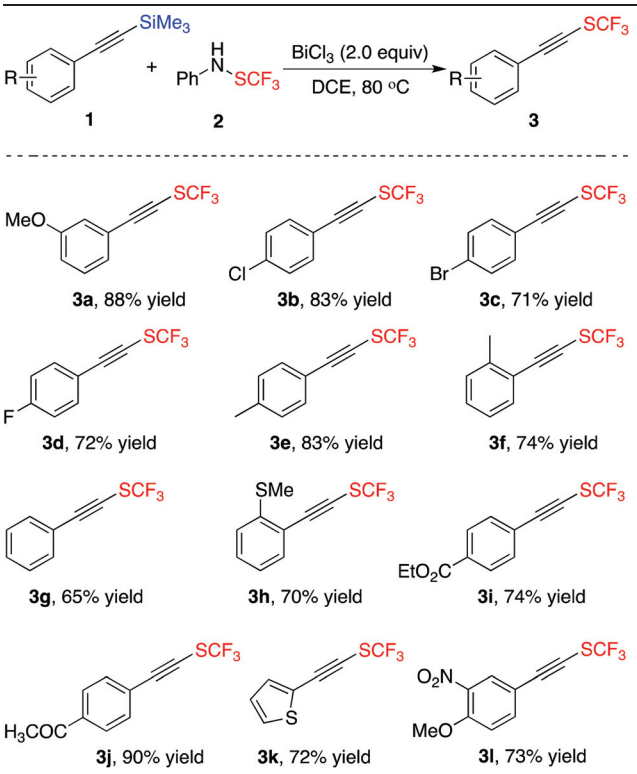
Table 1 Initial studies for the bismuth(III)-promoted reaction of ((3-methoxyphenyl)ethynyl)trimethylsilane **1a** with trifluoromethanesulfanylamide **2**



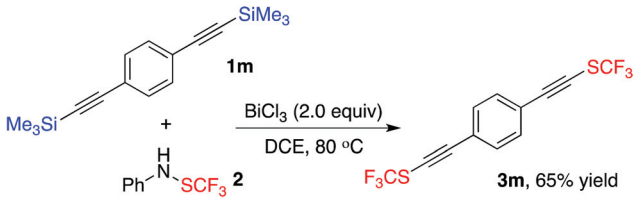
Entry	[Bi]	Solvent	T (°C)	Yield[a] (%)
1	$BiCl_3$ (1.5 equiv.)	DCE	80	36
2	$BiCl_3$ (1.0 equiv.)	DCE	80	29
3	$BiCl_3$ (2.0 equiv.)	DCE	80	88
4	—	DCE	80	NR
5	$BiCl_3$ (2.0 equiv.)	DCE	rt	Trace
6	$BiCl_3$ (2.0 equiv.)	DCE	40	62
7	$BiCl_3$ (2.0 equiv.)	DCE	60	66
8	$BiCl_3$ (2.0 equiv.)	DCE	100	87
9	$BiCl_3$ (2.0 equiv.)	DMA	80	ND
10	$BiCl_3$ (2.0 equiv.)	DMSO	80	ND
11	$BiCl_3$ (2.0 equiv.)	Toluene	80	Trace
12	$BiCl_3$ (2.0 equiv.)	CH_3CN	80	73
13	$BiCl_3$ (2.0 equiv.)	THF	80	ND
14	$BiCl_3$ (2.0 equiv.)	DMF	80	ND
15[b]	$BiCl_3$ (2.0 equiv.)	DCE	80	62
16	$BiCl_3$ (2.0 equiv.)	DCE–CH_3CN (1 : 1)	80	75
17	$FeCl_3$ (2.0 equiv.)	DCE	80	Trace
18	$CuCl_2$ (2.0 equiv.)	DCE	80	Trace
19	ZnF_2 (2.0 equiv.)	DCE	80	ND
20	TsOH (2.0 equiv.)	DCE	80	Trace

[a] Isolated yield based on ((3-methoxyphenyl)ethynyl)trimethylsilane **1a**. [b] Under an air atmosphere.

Table 2 Synthesis of (alkynyl)(trifluoromethyl)sulfanes *via* a bismuth(III)-promoted reaction of trimethyl(alkynyl)silane with trifluoromethanesulfanylamide[a]



[a] Isolated yield based on trimethyl(arylethynyl)silane **1**.



Scheme 3 Reaction of 1,4-bis((trimethylsilyl)ethynyl)benzene **1m** with trifluoromethanesulfanylamide **2**.

After establishing the optimized conditions (2.0 equiv. of bismuth(III) chloride, DCE, 80 °C), we next explored the scope generality of this bismuth(III)-promoted reaction of trimethyl(alkynyl)silanes with trifluoromethanesulfanylamide. The results are presented in Table 2. It was found that all reactions worked well to furnish the desired products in good yields. Trimethyl(alkynyl)silanes with different substitutions on the aromatic ring were all good partners. Different functional groups including halo, methoxy, methyl, methylthio, carbonyl (ester or ketone), and nitro were compatible under the standard conditions. For instance, 1-(4-(((trifluoromethyl)thio)ethynyl)phenyl)-ethanone **3j** was formed in 90% yield. Additionally, trimethyl(thiophen-2-ylethynyl)silane reacted with trifluoromethanesulfanylamide well, providing the desired product **3k** in 72% yield.

The reaction of 1,4-bis((trimethylsilyl)ethynyl)benzene **1m** with trifluoromethanesulfanylamide **2** was examined as well (Scheme 3). As expected, the corresponding 1,4-bis(((trifluoromethyl)thio)ethynyl)benzene **3m** was formed in 65% yield. Reactions of alkyl-substituted silanes were explored under the standard conditions subsequently. However, no desired product was formed.

3. Conclusion

In conclusion, we have described a concise synthesis of (alkynyl)(trifluoromethyl)sulfanes through a bismuth(III)-promoted reaction of trimethyl(alkynyl)silanes with trifluoromethanesulfanylamide. The transformation proceeds smoothly under mild conditions affording the corresponding products in good yields. The presence of bismuth(III) chloride shows its efficiency once again for the introduction of the (trifluoromethyl)thio moiety into small molecules. Currently, synthesis of CF_3S-containing heterocycles using (alkynyl)-(trifluoromethyl)sulfanes as the starting materials is ongoing in our laboratory.

4. Experimental section

General procedure for the synthesis of (alkynyl)-(trifluoromethyl)sulfanes *via* a bismuth(III)-promoted reaction of trimethyl(alkynyl)silane with trifluoromethanesulfanylamide

Trifluoromethanesulfanylamide **2** (0.3 mmol, 58.0 mg) was added to a solution of trimethyl(alkynyl)silane **1** (0.2 mmol) and bismuth(III) chloride (0.4 mmol, 126.2 mg) in DCE (2.0 mL). The mixture was stirred at 80 °C for 8–12 hours. After completion of the reaction as indicated by TLC, the reaction mixture was filtered with silica gel and washed with CH_2Cl_2 (3 × 5.0 mL). The mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to provide the product **3**.

(2-(3-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane (3a). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.93–7.00 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 66.5, 101.2, 116.4, 116.8, 122.4, 124.7, 128.1 (q, J = 310.3 Hz), 129.6, 159.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.00 (s); HRMS (ESI) calcd for $C_{10}H_8F_3OS$: 233.0242 ($M + H^+$), found: 233.0248.

(2-(4-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane (3b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J_1 = 6.8 Hz, J_2 = 1.8 Hz, 2H), 7.43 (dd, J_1 = 6.8 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.9, 100.1, 120.0, 128.0 (q, J = 311.0 Hz), 128.9, 133.4, 136.0; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.86 (s); HRMS (ESI) calcd for $C_9H_5ClF_3S$: 236.9747 ($M + H^+$), found: 236.9758.

(2-(4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane (3c). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.49 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.1, 100.2, 120.4, 124.3, 127.9 (q, J = 311.0 Hz), 131.8, 133.5; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.83 (s); HRMS (ESI) calcd for $C_9H_5BrF_3S$: 280.9242 ($M + H^+$), found: 280.9240.

(2-(4-Fluorophenyl)ethynyl)(trifluoromethyl)sulfane (3d). Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03–7.07 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.7, 100.2, 111.8, 115.9 (d, $^2J_{CF}$ = 22.6 Hz), 128.1 (q, J = 310.8 Hz), 134.52 (d, $^3J_{CF}$ = 8.6 Hz), 163.4 (d, $^1J_{CF}$ = 251.6 Hz); ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.03 (s), −108.37 (s); HRMS (ESI) calcd for $C_9H_5F_4S$: 221.0043 ($M + H^+$), found: 221.0057.

(2-*p*-Tolylethynyl)(trifluoromethyl)sulfane (3e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 65.8, 101.6, 118.5, 128.2 (q, J = 310.8 Hz), 129.3, 132.3, 140.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.26 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S$: 217.0293 ($M + H^+$), found: 217.0281.

(2-*o*-Tolylethynyl)(trifluoromethyl)sulfane (3f). Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.17 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.29 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 70.1, 100.4, 121.4, 125.7, 128.2 (q, J = 303.9 Hz), 129.7, 132.3, 141.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.32 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S$: 217.0293, found: 217.0295.

(2-Phenylethynyl)(trifluoromethyl)sulfane (3g). Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.39 (m, 2H), 7.42–7.43 (m, 1H), 7.50–7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.7, 101.3, 121.5, 128.0 (q, J = 294.8 Hz), 128.5, 129.7, 132.2; ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.08 (s); HRMS (ESI) calcd for $C_9H_6F_3S$: 203.0137 ($M + H^+$), found: 203.0131.

1-(Methylthio)-2-(2-(trifluoromethylthio)ethynyl)benzene (3h). Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.11

(td, J_1 = 7.6 Hz, J_2 = 0.7 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.33–7.37 (m, 1H), 7.45 (dd, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 73.0, 98.7, 119.7, 124.3, 124.4, 128.0 (q, J = 311.0 Hz), 130.1, 133.1, 143.1; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.86 (s); HRMS (ESI) calcd for $C_{10}H_8F_3S_2$: 249.0014 ($M + H^+$), found: 249.0028.

Ethyl 4-(2-(trifluoromethylthio)ethynyl)benzoate (3i). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, J = 7.1 Hz, 3H), 4.39 (q, J = 7.1 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 61.3, 69.9, 100.5, 125.9, 127.9 (q, J = 293.9 Hz), 129.5, 131.1, 131.6, 165.7; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.62 (s); HRMS (ESI) calcd for $C_{12}H_{10}F_3O_2S$: 275.0348 ($M + H^+$), found: 275.0342.

1-(4-(2-(Trifluoromethylthio)ethynyl)phenyl)ethanone (3j). Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.55 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 70.4, 100.4, 127.9 (q, J = 311.2 Hz), 128.2, 128.3, 131.8, 137.2, 197.1; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.59 (s); HRMS (ESI) calcd for $C_{11}H_8F_3OS$: 245.0242 ($M + H^+$), found: 245.0236.

2-(2-(Trifluoromethylthio)ethynyl)thiophene (3k). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–7.04 (m, 1H), 7.27–7.30 (m, 1H), 7.38–7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.4, 99.5, 123.4, 126.7, 127.9 (q, J = 314.9 Hz), 127.7, 130.3; ^{19}F NMR (378 MHz, $CDCl_3$) δ −44.18 (s); HRMS (ESI) calcd for $C_7H_4F_3S_2$: 208.9701 ($M + H^+$), found: 208.9707.

(2-(4-Methoxy-3-nitrophenyl)ethynyl)(trifluoromethyl)sulfane (3l). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.04 (d, J = 8.7 Hz, 1H), 7.64 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 1H), 7.97 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 78.0, 81.0, 113.5, 114.6, 128.8 (q, J = 313.3 Hz), 129.3, 131.7, 137.6, 153.0; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.69 (s); HRMS (ESI) calcd for $C_{10}H_7F_3NO_3S$: 278.0093 ($M + H^+$), found: 278.0085.

1,4-Bis(2-(trifluoromethylthio)ethynyl)benzene (3m). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.6, 100.4, 122.6, 127.9 (q, J = 312.5 Hz), 131.9; ^{19}F NMR (378 MHz, $CDCl_3$) δ −43.71 (s); HRMS (ESI) calcd for $C_{12}H_5F_6S_2$: 326.9731 ($M + H^+$), found: 326.9745.

Acknowledgements

Financial support from the National Natural Science Foundation of China (no. 21032007, 21172038) is gratefully acknowledged.

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