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AgSCF₃-mediated trifluoromethylthiolation of α,α-diaryl allylic alcohols *via* radical neophyl rearrangement†

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A novel example of AgSCF₃-mediated oxidative radical trifluoromethylthiolation of α,α-diaryl allylic alcohols is presented, producing various α-aryl-β-trifluoromethylthiolated carbonyl ketones *via* radical neophyl rearrangement under mild conditions. This protocol involves formation of C(Ar)–C(sp³) and C(sp³)–S bonds in one step and tolerates a wide range of symmetrical and nonsymmetrical α,α-diaryl allylic alcohols.

Introduction

Fluorine-containing functional groups have achieved great application in many pharmaceuticals and agrochemicals because of their remarkable potential for modulating molecular chemical, physical, and biochemical properties.[1] Among these intriguing fluorine-containing groups, the trifluoromethylthio (SCF₃) group has attracted increasing attention because of its special biological properties such as enhancement of membrane permeability and absorption rate and improvement of the stability of parent molecules, due to its high electronegativity and lipophilicity.[2] This has led to growing interest in developing new routes to incorporating the trifluoromethylthio group into organic molecules of interest.[3] To date, numerous nucleophilic and electrophilic SCF₃ reagents have been developed to construct C–SCF₃, and these reagents are widely used because they require mild conditions and show satisfied substrate scope.[4,5] Recently, the efficient radical-type protocols for constructing C–SCF₃ using a combination of AgSCF₃ and oxidant have drawn great attention, but only a few protocols focused on the difunctionalization of alkene have been reported.[6–8]

In 2014, the first radical silver-mediated oxidative aryltrifluoromethylthiolation of activated alkenes was reported by Wang group (Scheme 1a).[7a] Subsequently, an intramolecular oxytrifluoromethylthiolation of unactivated alkenes was reported (Scheme 1b).[7b] Soon afterward, the Qing group demonstrated direct trifluoromethylthiolation of an unactivated terminal alkene, affording various allyl trifluoromethyl sulfides

(Scheme 1c).[7c] In the following year, the same group reported another radical protocol for the trifluoromethylthiolation of quinones (Scheme 1d).[7d] Recently, the Nevado group has
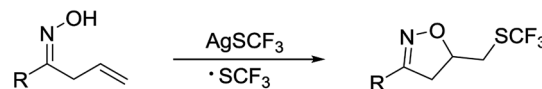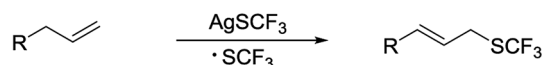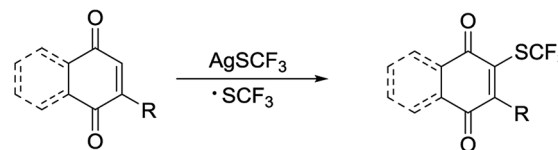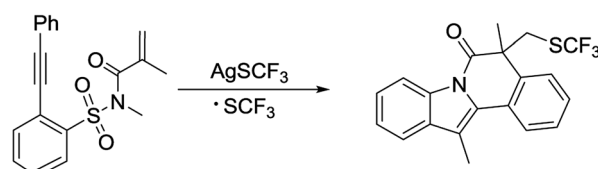

Scheme 1 Radical-initiated trifluoromethylthiolation of alkenes.

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reported a silver-catalyzed radical cascade trifluoromethylthiolation affording highly functionalized heterocyclic scaffolds (Scheme 1e).[7e] Despite these achievements, new methods involving difunctionalization-type trifluoromethylthiolation of alkenes remain highly desirable.

Recently, the neophyl rearrangement as an efficient and ingenious strategy to constructing multiple chemical structures and reorganizing molecular skeletons has attracted increasing attention.[9–14] Inspired by the Tu semipinacol rearrangement protocol[15] and recent literatures for forming β-trifluoromethyl ketones[9] and previous advances in silver-mediated radical additions,[16] we speculated that a neophyl-type rearrangement could be triggered after adding SCF₃ radical to α,α-diaryl allylic alcohols, generating α-aryl-β-trifluoromethylthiolated carbonyl ketones which suffered from poor yield in previous literature.[17] As part of our continuing efforts at introducing fluorine-containing groups into organic molecules,[18] we report here a novel SCF₃ radical-initiated radical neophyl rearrangement of α,α-diaryl allylic alcohols to afford trifluoromethylthiolated carbonyl ketones under mild conditions (Scheme 1f).

Result and discussion

Previous study showed that the SCF₃ radical could be efficiently generated from AgSCF₃ using K₂S₂O₈ as an oxidant.[6–8] Therefore we began our studies using α,α-diphenylprop-2-en-1-ol (**1a**) as substrate in the presence of AgSCF₃ (1.5 equiv.) in CH₃CN at 65 °C. A wide range of oxidants, including PhI(OAc)₂, TBHP (*tert*-butyl hydroperoxide), NFSI (*N*-fluorobenzenesulfonimide), Mn(OAc)₃, (NH₄)₂S₂O₈, Na₂S₂O₈ and K₂S₂O₈ were investigated for their ability to promote the reaction by generating the SCF₃ radical. To our delight, the desired product **3a** was obtained using persulfate salts as the oxidants, and 2 equiv. K₂S₂O₈ gave the best yield of 26% (Table 1, entries 1–7). Decreasing the load of K₂S₂O₈ improved the yield of the reaction (Table 1, entry 8). A brief survey of various representative solvents showed that CH₃CN gave the best yield (Table 1, entries 9–13). A series of inorganic and organic bases were investigated to improve the yield further. While the inorganic or organic bases such as K₂CO₃, HMPA (hexamethylphosphoramide), DABCO (1,4-diazabicyclo[2.2.2]octane), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) did not appreciably affect the transformation (Table 1, entries 14–19), pyridine (1 equiv.) increased the yield to 82% (entry 19). Changing the amount of pyridine did not improve yield (Table 1, entries 20 and 21). In a control experiment, we confirmed that no desired product was obtained when K₂S₂O₈ was omitted from the reaction system (entry 22).

After determining the standard reaction conditions, we explored the scope of this difunctionalization protocol with various α,α-diaryl allylic alcohols (**1**), and the corresponding products **3a–3u** were obtained in moderate to good isolated yields (Table 2). Note that the minor regioisomers **3f′**, **3g′**, **3i′**, **3j′**, **3l′**, **3m′** and **3n′**, in which R¹ migrated instead of R², were observed as byproducts in the reactions of corresponding substrates and the yields are indicated in the parentheses. When the symmetric allylic alcohols containing *para*-substituted bromo-group or chloro-group underwent rearrangement, the corresponding

Table 1 Optimization of conditions for reaction of **1a** and **2a**[a]

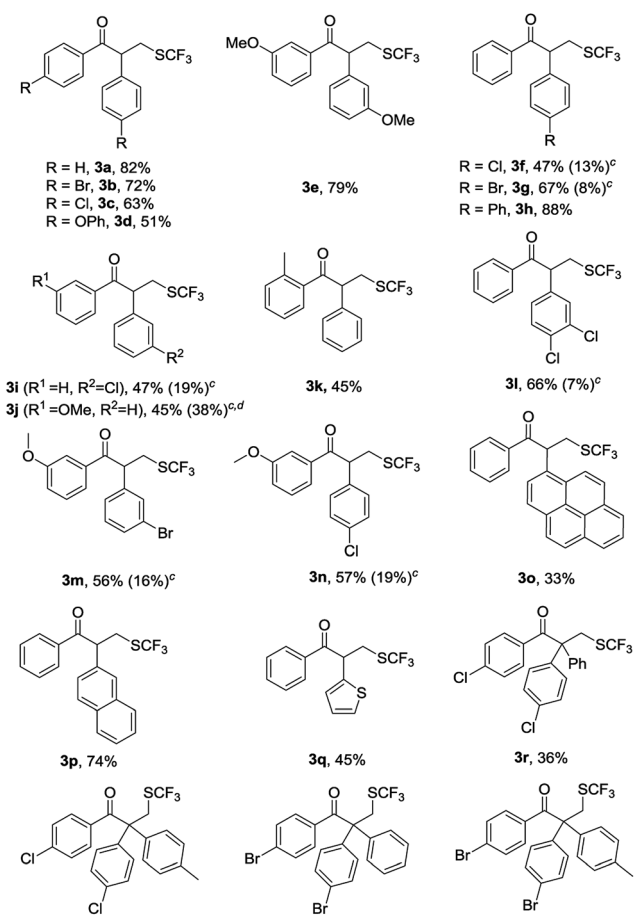| Entry	Oxidant	Base	Solvent	Yield[b] (%)
1	PhI(OAc)₂	None	CH₃CN	N. D.
2	TBHP	None	CH₃CN	N. D.
3	NFSI	None	CH₃CN	N. D.
4	Mn(OAc)₃	None	CH₃CN	N. D.
5	(NH₄)₂S₂O₈	None	CH₃CN	15
6	Na₂S₂O₈	None	CH₃CN	22
7	K₂S₂O₈	None	CH₃CN	26
8[c]	K₂S₂O₈	None	CH₃CN	30
9[c]	K₂S₂O₈	None	DCE	Trace
10[c]	K₂S₂O₈	None	EA	11
11[c]	K₂S₂O₈	None	NMP	20
12[c]	K₂S₂O₈	None	DMF	13
13[c]	K₂S₂O₈	None	DMSO	10
14[c]	K₂S₂O₈	K₂CO₃	CH₃CN	Trace
15[c]	K₂S₂O₈	HMPA	CH₃CN	Trace
16[c]	K₂S₂O₈	DABCO	CH₃CN	Trace
17[c]	K₂S₂O₈	DBU	CH₃CN	Trace
18[c]	K₂S₂O₈	(i-Pr)₂NEt	CH₃CN	45
19[c]	K₂S₂O₈	Pyridine	CH₃CN	82
20[c,d]	K₂S₂O₈	Pyridine	CH₃CN	74
21[c,e]	K₂S₂O₈	Pyridine	CH₃CN	76
22	None	Pyridine	CH₃CN	0

[a] Reactions were performed in sealed tubes containing **1a** (0.20 mmol), **2a** (0.30 mmol), oxidant (2 equiv.), base (1.0 equiv.), solvent (2 mL) under N₂ at 65 °C for 5 h. N. D. = not detected. [b] Isolated yield. [c] K₂S₂O₈ (1.5 equiv.) was used. [d] Pyridine (2 equiv.) was used. [e] Pyridine (0.5 equiv.) was used.

α-aryl-β-trifluoromethylthiolated carbonyl ketones **3b** and **3c** were obtained in respective yields of 72% and 63%. Similarly, the symmetric allylic alcohol substituted by *para*-OPh gave moderate 51% yield. When allylic alcohol substituted by *meta*-OMe was used as the substrate, no obvious substitution effect was observed and **3e** was obtained in 79% yield.

The allylic alcohols with a Ph group and a *p*-substituted-Ph group underwent *p*-substituted-Ph group migration as the major process, giving the corresponding products **3f–3h** in 47–88% yield. Interestingly, allylic alcohols with a Ph group and a *m*-Cl–Ph group or a *m*-OMe–Ph group proceeded *via* the migration of the more electron-deficient aryl group, delivered the products **3i** and **3j** in respective yields of 47% and 45%. Allylic alcohols with a Ph group and an *o*-methylphenyl group delivered the Ph group-migration product **3k** in 45% yield. Interestingly, allylic alcohols containing two different substituted aryl groups, also worked as substrates in the reaction, which selectively generated products **3l** *via* migration of the 3,4-disubstituted-Ph group. For substrates with *meta* or *para* and *meta* substituents, the more electron-deficient aryl group migrated preferentially to afford the desired products **3m** and **3n** in respective yields of 56% and 57%. This unique selectivity

**Table 2** Synthesis of products **3** from allylic alcohol **1**[a,b]

R = H, **3a**, 82%
R = Br, **3b**, 72%
R = Cl, **3c**, 63%
R = OPh, **3d**, 51%

3e, 79%

R = Cl, **3f**, 47% (13%)[c]
R = Br, **3g**, 67% (8%)[c]
R = Ph, **3h**, 88%

3i (R¹=H, R²=Cl), 47% (19%)[c]
3j (R¹=OMe, R²=H), 45% (38%)[c,d]

3k, 45%

3l, 66% (7%)[c]

3m, 56% (16%)[c]

3n, 57% (19%)[c]

3o, 33%

3p, 74%

3q, 45%

3r, 36%

3s, 31%

3t, 39%

3u, 32%

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), K₂S₂O₈ (0.30 mmol), pyridine (0.20 mmol), CH₃CN (2 mL), 5 h, 65 °C under N₂. [b] Isolated yields of products **3**. [c] The yields of minor regioisomer **3′**, in which R¹ migrated instead of R², were shown in the parentheses (determined by ¹H NMR). [d] **3j** and its isomer **3j′** were not separable.

suggested that the reaction might involve a radical neophyl rearrangement process rather than a simple semipinacol rearrangement.[9] In the reactions generating **3o** and **3p**, migration of the Ph group took precedence over the pyren-2-yl and the naphthalene-2-yl, giving the respective yields of 33% and 74%. Gratifyingly, the Ph- and thiophen-2-yl-substituted allylic alcohol also worked well and afforded mainly the thiophen-2-yl-migration product **3q** in good yield. Notably, the allylic alcohols with a tolyl or Ph attached to the vinyl group were also tolerated, affording the target products **3r–3u** in 31–36% yield.

To gain further understanding of the reaction mechanism, the control experiments were performed (Scheme 2). When 2 equiv. of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or 2,6-
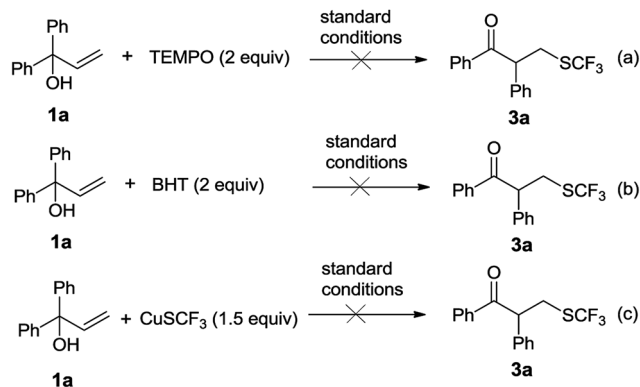
Scheme 2 Mechanistic studies of radical addition and radical neophyl rearrangement cascade reaction.
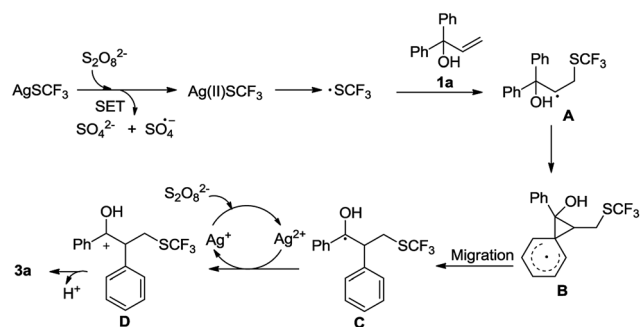
Scheme 3 Plausible reaction mechanism.

di-*tert*-butyl-4-methylphenol (BHT) were added to the reaction, the desired transformation was completely inhibited (Scheme 2a and b). This observation is consistent with the hypothesis that the reaction proceeds *via* a radical pathway through single-electron transfer. When CuSCF₃ was used as the SCF₃ source, the reaction led to no product, indicating that silver plays a vital role in this transformation (Scheme 2c).

On the basis of the experimental results and previous reports,[6,10–14] a plausible mechanism is proposed as depicted in Scheme 3. AgSCF₃ is oxidized by K₂S₂O₈ firstly to generate the SCF₃ radical.[6] Subsequent intermolecular addition of the SCF₃ radical to the double bond of allylic alcohol **1a** affords radical intermediate **A**. Within radical intermediate **A**, neophyl rearrangement of the aryl group occurs *via* spiro[2,5]octadienyl radical **B** to produce intermediate **C**.[10–14] Another single-electron transfer from intermediate **C** to Ag(ɪɪ) oxidant generates intermediate **D**, which affords product **3a** by release of a proton.

Conclusions

In summary, we have developed a AgSCF₃-mediated trifluoromethylthiolation of α,α-diaryl allylic alcohols for the synthesis of various α-aryl-β-trifluoromethylthiolated carbonyl ketones. The procedure involves the formations of C(Ar)–C(sp³) and C(sp³)–S bonds in one step *via* SCF₃ radical addition and a radical neophyl rearrangement cascade process under mild

conditions. The procedure tolerates a wide range of symmetrical and nonsymmetrical α,α-diaryl allylic alcohols. Given the frequent use of fluorine-containing compounds as bioactive agents, the convenience of this method affords an efficient approach in the future drug development and synthesis of fine chemicals.

Experimental

General

All manipulations were carried out in a sealed tube under a nitrogen atmosphere using standard Schlenk techniques. The solvents were distilled under nitrogen from sodium–benzophenone (THF, toluene, dioxane) or calcium hydride (DMF, MeCN, 1,2-DCE) before used. The α,α-diaryl allylic alcohols[19] and AgSCF₃[20] were prepared according to the literature methods. Other chemicals were obtained from commercial sources, and were used without further purification. Chemical shifts (δ, ppm) in the ¹H NMR spectra were recorded using TMS as internal standard. Chemical shifts in ¹³C{¹H} NMR spectra were internally referenced to CHCl₃ ($\delta = 77.16$ ppm).

General procedure for the synthesis of α-aryl-β-trifluoromethyl-thiolated carbonyl ketones

1a–u (0.2 mmol), **2a** (62.7 mg, 0.3 mmol), $K_2S_2O_8$ (81.1 mg, 0.3 mmol), pyridine (15.8 mg, 0.2 mmol), and CH_3CN (2 mL) were mixed in an oven-dried sealed tube under N_2. The tube was sealed and heated at 65 °C for 5 h. The resulting mixture was cooled to room temperature and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the product **3a–u**.

1,2-Diphenyl-3-((trifluoromethyl)thio)propan-1-one (3a). The compound **3a** was obtained in 82% yield (50.8 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.22 (1H, dd, J = 5.6, 14.0 Hz), 3.64 (1H, dd, J = 9.2, 14.0 Hz), 4.92 (1H, dd, J = 5.6, 9.2 Hz), 7.24–7.40 (5H, m), 7.36–7.40 (2H, m), 7.47–7.51 (2H, m), 7.92–7.95 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 32.8, 54.6, 128.2, 128.3, 128.8, 129.0, 129.6, 131.4 (q, J = 304 Hz) 133.6, 135.9, 137.2, 197.5; ¹⁹F NMR (CDCl₃, 376 MHz) δ −41.3; HRMS (EI, TOF) calcd for $C_{16}H_{13}F_3OS^+$ [M]⁺: 310.0639, found: 310.0638.

1,2-Bis(4-bromophenyl)-3-((trifluoromethyl)thio)propan-1-one (3b). The compound **3b** was obtained in 72% yield (66.9 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.18 (1H, q, J = 5.7, 14.2 Hz), 3.59 (1H, q, J = 8.9, 14.2 Hz), 4.80 (1H, J = 6.8 Hz), 7.46 (2H, d, J = 7.8 Hz), 7.46 (2H, d, J = 7.7 Hz), 7.54 (2H, d, J = 7.9 Hz), 7.76 (2H, d, J = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 32.5, 53.9, 122.7, 129.2, 129.8, 130.4, 130.7 (q, J = 304 Hz), 132.3, 132.9, 134.3, 135.8, 196.2; ¹⁹F NMR (376 MHz, CDCl₃) δ −41.3; HRMS (EI, TOF) calcd for $C_{15}H_{10}Br_2O^+$ [M − H − SCF₃]⁺: 363.9087, found: 363.9105.

1,2-Bis(4-chlorophenyl)-3-((trifluoromethyl)thio)propan-1-one (3c). The compound **3c** was obtained in 63% yield (47.5 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.18 (1H, dd, J = 5.8, 14.2 Hz), 3.60

(1H, dd, J = 8.9, 14.2 Hz), 4.82 (1H, t, J = 7.2 Hz), 7.20 (2H, d, J = 8.1 Hz), 7.31 (2H, d, J = 7.9 Hz), 7.38 (2H, d, J = 8.1 Hz), 7.85 (2H, d, J = 8.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 32.6, 53.8, 129.3, 129.5, 129.9, 130.3, 131.3 (q, J = 304 Hz), 133.9, 134.5, 135.3, 140.4, 196.1; ¹⁹F NMR (376 MHz, CDCl₃) δ −41.3; HRMS (EI, TOF) calcd for $C_{15}H_{11}Cl_2O^+$ [M − SCF₃]⁺: 277.0181, found: 277.0168.

1,2-Bis(4-phenoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3d). The compound **3d** was obtained in 51% yield (50.3 mg) as colorless liquid after column chromatography (PE/EA = 50 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.20 (1H, dd, J = 5.7, 14.0 Hz), 3.62 (1H, dd, J = 9.0, 14.0 Hz), 4.80 (1H, dd, J = 5.7, 9.0 Hz), 7.13 (2H, d, J = 8.2 Hz), 7.47 (2H, d, J = 8.2 Hz), 7.55 (1H, d, J = 8.4 Hz), 7.76 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 32.9, 53.5, 117.2, 119.3, 119.5, 120.5, 123.9, 124.9, 129.5, 129.9, 130.2, 130.3, 131.4 (q, J = 304 Hz), 131.8, 155.2, 156.5, 157.5, 162.5; ¹⁹F NMR (CDCl₃, 376 MHz) δ −41.2; HRMS (EI, TOF) calcd for $C_{28}H_{21}F_3O_3S^+$ [M]⁺: 494.1163, found: 494.1165.

1,2-Bis(3-methoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3e). The compound **3e** was obtained in 79% yield (58.5 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.22 (1H, dd, J = 5.6, 14.0 Hz), 3.63 (1H, dd, J = 9.2, 14.0 Hz), 3.76 (3H, s), 3.8 (3H, s), 4.85 (1H, dd, J = 5.6, 9.2 Hz), 6.78–6.88 (3H, m), 7.03–7.06 (1H, m), 7.22–7.30 (2H, m), 7.47–7.52 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 32.7, 54.7, 55.4, 55.5, 113.2, 113.3, 113.9, 120.1, 120.5, 121.6, 129.8, 130.6, 131.4 (q, J = 304 Hz), 137.2, 138.7, 159.9, 160.3, 197.2; ¹⁹F NMR (376 MHz, CDCl₃) δ −41.3; HRMS (EI, TOF) calcd for $C_{18}H_{17}F_3O_3S^+$ [M]⁺: 370.0850, found: 370.0853.

2-(4-Chlorophenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3f). The compound **3f** was obtained in 47% yield (32.3 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.19 (1H, dd, J = 5.9, 14.2 Hz), 3.61 (1H, dd, J = 8.8, 14.2 Hz), 4.89 (1H, dd, J = 5.9, 8.8 Hz), 7.21–7.23 (2H, d, J = 8.5 Hz), 7.29–7.31 (2H, m), 7.39–7.43 (2H, m), 7.51–7.55 (1H, m), 7.89–7.91 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 32.8, 53.7, 128.9, 129.0, 129.6, 129.8, 131.3 (q, J = 304 Hz), 133.8, 134.3, 135.6, 135.7, 197.3; ¹⁹F NMR (376 MHz, CDCl₃) δ −41.3; HRMS (EI, TOF) calcd for $C_{16}H_{12}ClF_3OS^+$ [M]⁺: 344.0249, found: 344.0255.

2-(4-Bromophenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3g). The compound **3g** was obtained in 67% yield (51.8 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.19 (1H, dd, J = 5.9, 14.2 Hz), 3.61 (1H, dd, J = 8.8, 14.2 Hz), 4.87 (1H, dd, J = 5.9, 8.8 Hz), 7.14–7.18 (2H, m), 7.39–7.47 (4H, m), 7.50–7.55 (1H, m), 7.89–7.91 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 32.8, 53.8, 122.5, 128.9, 129.0, 129.9, 131.2 (q, J = 304 Hz), 132.8, 133.8, 135.6, 136.2, 197.2; ¹⁹F NMR (376 MHz, CDCl₃) δ −41.3; HRMS (EI, TOF) calcd for $C_{15}H_{12}BrO^+$ [M − SCF₃]⁺: 287.0072, found: 287.0039.

2-([1,1′-Biphenyl]-4-yl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3h). The compound **3h** was obtained in 88% yield (67.9 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ¹H NMR (400 MHz, CDCl₃) δ 3.25 (1H, dd, J = 5.6, 14.2 Hz), 3.68 (1H, dd, J = 9.1, 14.2 Hz), 4.96 (1H, t, J = 6.9 Hz), 7.32–7.36 (3H, m), 7.39–7.42 (4H, m), 7.49–7.55 (5H, m), 7.97

(2H, d, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.8, 54.1, 127.1, 127.7, 128.2, 128.6, 128.8, 128.9, 129.0, 131.4 (q, $J = 304$ Hz), 133.6, 135.9, 136.1, 140.3, 141.2, 197.5; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{22}$H$_{17}$F$_3$OS$^+$ [M]$^+$: 386.0952, found: 386.0951.

2-(3-Chlorophenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3i). The compound 3i was obtained in 47% yield (32.3 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.20 (1H, dd, $J = 4.0$, 16.0 Hz), 3.63 (1H, dd, $J = 8.0$, 16.0 Hz), 4.90 (1H, dd, $J = 4.0$, 8.0 Hz), 7.16–7.18 (1H, m), 7.23–7.29 (3H, m), 7.42 (2H, d, $J = 8.0$ Hz), 7.54 (1H, d, $J = 8.0$ Hz), 7.91–7.94 (1H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.7, 53.9, 126.5, 128.3, 128.6, 128.9, 129.0, 130.8, 131.3 (q, $J = 305$ Hz), 133.9, 135.4, 135.6, 139.1, 197.0; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{16}$H$_{12}$ClF$_3$OS$^+$ [M]$^+$: 344.0249, found: 344.0251.

1-(3-Methoxyphenyl)-2-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j) and 2-(3-methoxyphenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3j′). The compounds 3j and 3j′ were obtained in total 83% yield (56.4 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.21 (2H, dd, $J = 5.6$, 14.0 Hz), 3.64 (2H, dd, $J = 9.1$, 14.0 Hz), 3.77 (2.68H, s), 3.80 (3.20H, s), 4.87 (2H, m), 6.78–6.80 (2H, m), 6.87 (1H, d, $J = 7.6$ Hz), 7.03–7.06 (1H, m), 7.22–7.41 (9H, m), 7.46–7.52 (3H, m), 7.93–7.95 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.75, 32.84, 54.6, 54.7, 55.4, 55.5, 113.2, 113.4, 113.9, 120.1, 120.6, 121.6, 128.2, 128.3, 128.8, 129.0, 129.6, 129.8, 130.6, 131.4 (q, $J = 304$ Hz), 133.6, 135.9, 137.2, 137.3, 138.7, 159.9, 160.4, 197.4; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{17}$H$_{15}$F$_3$O$_2$S$^+$ [M]$^+$: 340.0745, found: 340.0749.

2-Phenyl-1-(o-tolyl)-3-((trifluoromethyl)thio)propan-1-one (3k). The compound 3k was obtained in 45% yield (29.2 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.37 (3H, s), 3.21 (1H, dd, $J = 5.4$, 14.0 Hz), 3.67 (1H, dd, $J = 9.5$, 14.0 Hz), 4.80 (1H, dd, $J = 5.4$, 9.5 Hz); 7.15–7.27 (4H, m), 7.28–7.32 (4H, m), 7.57 (1H, d, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.4, 32.4, 57.0, 125.7, 128.2, 128.3, 128.5, 129.4, 131.4 (q, $J = 304$ Hz), 131.7, 132.0, 136.6, 137.3, 138.9, 201.2; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (ESI, TOF) calcd for C$_{17}$H$_{15}$F$_3$OS$^+$ [M]$^+$: 324.0796, found: 324.0798.

2-(3,4-Dichlorophenyl)-1-phenyl-3-((trifluoromethyl)thio)propan-1-one (3l). The compound 3l was obtained in 66% yield (49.9 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.20 (1H, dd, $J = 6.0$, 14.2 Hz), 3.61 (1H, dd, $J = 8.8$, 14.2 Hz), 4.87 (1H, dd, $J = 6.0$, 8.8 Hz), 7.14 (1H, dd, $J = 2.1$, 8.3 Hz), 7.39–7.45 (4H, m), 7.53–7.57 (1H, m), 7.90–7.92 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.7, 53.2, 127.6, 128.9, 129.0, 130.1, 130.5, 131.3 (q, $J = 303$ Hz), 131.5, 132.7, 133.7, 134.1, 135.5, 137.2, 196.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.2; HRMS (EI, TOF) calcd for C$_{16}$H$_{11}$Cl$_2$F$_3$OS$^+$ [M]$^+$: 377.9860, found: 377.9865.

2-(3-Bromophenyl)-1-(3-methoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3m). The compound 3m was obtained in 56% yield (46.7 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.20 (1H, dd, $J = 5.7$, 14.2 Hz), 3.62 (1H, dd, $J = 9.0$, 14.2 Hz), 3.82 (3H, s), 4.86 (1H, dd, $J = 5.7$, 9.0 Hz), 7.06–7.09 (1H, m), 7.20–7.22 (2H, m), 7.31 (1H, t, $J = 8.0$ Hz), 7.39–7.42 (1H, m), 7.43–7.49 (3H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.8, 54.0, 55.6, 113.2, 120.4, 121.6, 123.5, 126.9, 129.8, 129.9, 131.0, 131.1, 131.3 (q, $J = 304$ Hz), 131.5, 137.0, 139.4, 160.0, 196.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.2; HRMS (EI, TOF) calcd for C$_{17}$H$_{14}$BrF$_3$O$_2$S$^+$ [M]$^+$: 417.9850, found: 417.9854.

2-(4-Chlorophenyl)-1-(3-methoxyphenyl)-3-((trifluoromethyl)thio)propan-1-one (3n). The compound 3m was obtained in 57% yield (42.6 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.19 (1H, dd, $J = 5.9$, 14.2 Hz), 3.60 (1H, dd, $J = 8.8$, 14.2 Hz), 3.81 (3H, s), 3.87 (1H, dd, $J = 5.9$, 8.8 Hz), 7.07 (1H, dd, $J = 2.2$, 7.9 Hz), 7.20–7.23 (2H, m), 7.28–7.32 (3H, m), 7.44–7.48 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.7, 53.8, 55.6, 113.3, 120.2, 121.5, 129.6, 129.8, 129.9, 131.4 (q, $J = 304$ Hz), 134.3, 135.7, 137.0, 160.0, 197.1; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{17}$H$_{14}$ClF$_3$O$_2$S$^+$ [M]$^+$: 374.0355, found: 374.0358.

1-Phenyl-2-(pyren-2-yl)-3-((trifluoromethyl)thio)propan-1-one (3o). The compound 3o was obtained in 33% yield (28.6 mg) as yellow liquid after column chromatography (PE/EA = 50 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.37 (1H, dd, $J = 4.4$, 14.4 Hz), 3.84 (1H, dd, $J = 10.5$, 14.4 Hz), 5.97 (1H, dd, $J = 4.4$, 10.5 Hz), 7.21–7.26 (2H, m), 7.37 (1H, t, $J = 7.4$ Hz), 7.7 (1H, d, $J = 8.0$ Hz), 7.78–7.89 (2H, m), 7.98 (1H, d, $J = 8.9$ Hz), 8.03–8.09 (3H, m), 8.23 (1H, d, $J = 7.4$ Hz), 8.28 (1H, d, $J = 7.6$ Hz), 8.35 (1H, d, $J = 9.3$ Hz), 8.55 (1H, d, $J = 9.3$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.4, 51.0, 121.3, 124.9, 125.1, 125.6, 125.7, 125.8, 126.1, 126.5, 127.5, 128.1, 128.2, 128.8, 128.9, 129.6, 130.8, 131.0, 131.3, 131.4, 131.7 (q, $J = 303$ Hz), 133.5, 135.9, 198.0; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{26}$H$_{17}$F$_3$OS$^+$ [M]$^+$: 434.0952, found: 434.0954.

2-(Naphthalen-2-yl)-1-phenyl-3-((trifluoromethyl)thio)-propan-1-one (3p). The compound 3p was obtained in 74% yield (53.3 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.30 (1H, dd, $J = 5.7$, 14.1 Hz), 3.73 (1H, dd, $J = 9.1$, 141 Hz), 5.07 (1H, dd, $J = 5.7$, 9.1 Hz), 7.34–7.46 (3H, m), 7.46–7.49 (3H, m), 7.73 (1H, s), 7.77–7.84 (3H, m), 7.96–7.98 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.9, 54.7, 125.7, 126.6, 126.8, 127.5, 127.9, 128.0, 128.8, 129.0, 129.6, 131.5 (q, $J = 304$ Hz), 132.9, 133.6, 133.7, 134.7, 135.9, 197.5; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.3; HRMS (EI, TOF) calcd for C$_{20}$H$_{15}$F$_3$OS$^+$ [M]$^+$: 360.0796, found: 360.0797.

1-Phenyl-2-(thiophen-2-yl)-3-((trifluoromethyl)thio)-propan-1-one (3q). The compound 3q was obtained in 45% yield (28.5 mg) as light yellow liquid after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.32 (1H, dd, $J = 5.7$, 14.2 Hz), 3.66 (1H, dd, $J = 9.1$, 14.0 Hz), 5.20 (1H, dd, $J = 5.7$, 9.1 Hz), 6.93–6.94 (2H, m), 7.23 (1H, t, $J = 3.2$ Hz), 7.42–7.46 (2H, m), 7.56 (1H, t, $J = 7.2$ Hz), 7.98 (1H, s), 7.99 (1H, s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 33.2, 48.6, 126.1, 126.8, 127.6, 128.9, 129.0, 131.3 (q, $J = 304$ Hz), 133.9, 135.5, 138.9, 196.4; ^{19}F NMR (376 MHz, CDCl$_3$) δ −41.2; HRMS (EI, TOF) calcd for C$_{14}$H$_{11}$F$_3$OS$_2$$^+$ [M]$^+$: 316.0203, found: 316.0197.

1,2-Bis(4-chlorophenyl)-2-phenyl-3-((trifluoromethyl)thio)-propan-1-one (3r). The compound 3r was obtained in 36% yield

(32.8 mg) as colorless liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.68 (2H, d, J = 12.8 Hz), 3.77 (1H, d, J = 12.8 Hz), 7.16 (2H, d, J = 8.9 Hz), 7.30–7.38 (9H, m), 7.56 (2H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 42.0, 64.8, 128.4, 128.9, 129.0, 129.1, 129.2, 130.8 (q, J = 304 Hz), 131.0, 132.0, 133.5, 134.3, 136.9, 138.2, 139.3, 198.1; ^{19}F NMR (376 MHz, CDCl$_3$) δ −42.8; HRMS (ESI, TOF) calcd for C$_{22}$H$_{15}$Cl$_2$F$_3$NaOS$^+$ [M + Na]$^+$: 477.0070, found: 477.0067.

1,2-Bis(4-chlorophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)-propan-1-one (3s). The compound **3s** was obtained in 31% yield (29.1 mg) as yellow liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.34 (3H, s), 3.65 (1H, d, J = 12.8 Hz), 3.77 (2H, d, J = 12.8 Hz), 7.14–7.18 (4H, m), 7.21 (2H, d, J = 8.4 Hz), 7.29–7.35 (4H, m), 7.55 (2H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.2, 42.0, 64.5, 128.5, 128.9, 129.1, 129.8, 131.0, 132.0, 133.7, 134.2, 135.1, 137.2, 138.4, 139.2, 199.2; ^{19}F NMR (CDCl$_3$, 376 MHz) δ −42.7; HRMS (EI, TOF) calcd for C$_{22}$H$_{17}$Cl$_2$O$^+$ [M]$^+$: 367.0656, found: 367.0653.

1,2-Bis(4-bromophenyl)-2-phenyl-3-((trifluoromethyl)thio)-propan-1-one (3t). The compound **3t** was obtained in 39% yield (42.4 mg) as yellow liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.34 (3H, s), 3.67 (1H, d, J = 12.8 Hz), 3.77 (2H, d, J = 12.8 Hz), 7.24–7.27 (2H, m), 7.34–7.37 (7H, m), 7.46–7.51 (4H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.9, 64.9, 122.5, 128.2, 128.5, 129.1, 129.2, 131.3, 131.5, 132.0, 132.1, 134.0, 137.5, 138.1, 198.2; ^{19}F NMR (CDCl$_3$, 376 MHz) δ −42.7; HRMS (EI, TOF) calcd for C$_{21}$H$_{15}$Br$_2$O$^+$ [M]$^+$: 440.9490, found: 440.9491.

1,2-Bis(4-bromophenyl)-2-(p-tolyl)-3-((trifluoromethyl)thio)-propan-1-one (3u). The compound **3u** was obtained in 33% yield (36.8 mg) as yellow liquid after column chromatography (PE/EA = 100 : 1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.34 (3H, s), 3.67 (1H, d, J = 12.8 Hz), 3.77 (2H, d, J = 12.8 Hz), 7.15–7.18 (2H, m), 7.23–7.26 (4H, m), 7.32–7.34 (2H, m), 7.46–7.49 (4H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 41.9, 64.9, 122.5, 128.2, 128.5, 129.1, 129.2, 131.3, 131.5, 132.0, 132.1, 134.0, 137.5, 138.1, 198.2; ^{19}F NMR (CDCl$_3$, 376 MHz) δ −42.7; HRMS (EI, TOF) calcd for C$_{22}$H$_{17}$Br$_2$O$^+$ [M]$^+$: 454.9646, found: 454.9644.

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