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Versatile application of trifluoromethyl triflate ☆

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Abstract

Hydrolytically stable and easy to handle trifluoromethyl triflate was found to be a liquid reservoir of 'masked' difluorophosgene. Anhydrous F^- sources cleave the S–O bond in trifluoromethyl triflate yielding quantitatively the trifluoromethanolate salts, being useful trifluoromethoxy group carriers. Reaction of trifluoromethanolates with in situ generated from *o*-trimethylsilylphenyl triflate benzyne leads to (trifluoromethoxy)benzene and fluorobenzene (ratio 85:15). Whereas an addition of trifluoromethanethiolate anion across a triple bond of benzyne leads to [(trifluoromethyl)sulfanyl]benzene solely.

Keywords: Trifluoromethyl triflate; Trifluoromethanolates; Trifluoromethyl ethers; Arynes; Delocalized lipophilic cations

Organic triflates are of great interest and wide utility in organic synthesis.[2] However, trifluoromethyl trifluoromethanesulfonate, $CF_3OSO_2CF_3$, (TFMT, **1**)[3] was the subject of just a few controversial reports.[4–6] Though **1** is a commercially available compound, it can be simply prepared from triflic acid or its anhydride.[3] Contrary to the relatively unstable alkyl triflates, **1** (bp 20 °C) is a thermally stable and a resistant to hydrolysis compound. Principally, **1** has a potential to be either CF_3 or CF_3SO_2 transfer reagent. Trifluoromethylation of pyridine was observed by Olah and Ohyama (path A, Fig. 1).[4] Whereas Martin and Taylor found out that reactions of **1** with diverse nucleophiles resulted in the quantitative fragmentation of **1** to CF_3SO_2F and COF_2 (path B).[6] This limits the synthetic utility of **1**. An attempt to obtain $CsOCF_3$ from **1** and CsF also failed.[6]

Alkyl, aryl, and heteroaryl trifluoromethyl ethers are important intermediates in the synthesis of liquid crystals, which are used in active matrix liquid crystal displays, as pesticides, and for drug design.[7] The oxidative desulfurization–fluorination of alkyl xanthates is the most widely used procedure for the synthesis of primary $AlkOCF_3$ derivatives on laboratory and semi-industrial scale.[7] It includes an operation with huge excesses of highly toxic and flammable carbon disulfide, methyl iodide and Py/HF (Olah's reagent). Unfortunately, in the case of the most synthetically useful secondary alcohols the yield of trifluoromethyl ethers is low. The method does not work at all in the case of benzyl alcohols.[7] It was also anticipated that the reactions of $(Me_2N)_3S^+\ ^-OCF_3$ ($TAS^+\ ^-OCF_3$), prepared from a toxic COF_2 and TASF, with alkyl triflates and some alkyl bromides would produce $AlkOCF_3$ compounds. However, an operation with carbonyldifluoride limits the laboratory application.[8]

In dramatic contrast to alkali metal methanolates, the respective trifluoromethanolates exist in equilibrium with

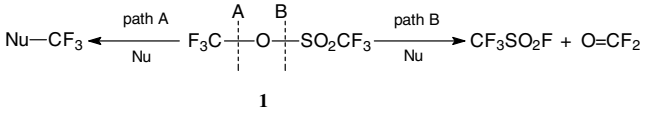

Fig. 1.

☆ See Ref. 1.

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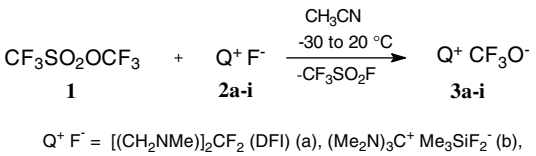
alkali metal fluoride and difluorophosgene. Therefore, in nucleophilic displacement reactions these species can either transfer CF_3O unit, or provide a fluoride ion. Due to electron-withdrawing effect of pseudo halogen CF_3O group, the trifluoromethanol[9a,b] itself, prepared at low temperature from dangerous to handle CF_3OCl and HF, is a strong O–H acid (gas-phase acidity $\Delta H^0 = 329.8$ kcal/mol).[10] Because of rapid elimination of HF, it decomposes readily above −20 °C.[9] Quite recently, the results on a mild generation of CF_3OH from CF_2O and HF (maximum equilibrium concentration of CF_3OH ca. 33 mol %) were reported.[9c] Insoluble in aprotic solvents cesium trifluoromethanolate was found to be the only reasonably stable perfluorinated alkali metal methanolate.[11]

Nevertheless, the in situ generation of potassium and cesium trifluoromethanolates in industrially important processes has been postulated[12] and easily soluble in aprotic solvents perfluoroalkanolates with lipophilic and delocalized lipophilic cations were utilized as facile R_FO^- transfer carriers.[8,13,14] Therefore, our first objective was to provide a new and convenient means of access to the stable CF_3O^- transfer reagents, which allows to exclude an operation with a toxic difluorophosgene.

This Letter reports: (1) a convenient access to the trifluoromethanolates from **1**; (2) their application as trifluoromethoxy carriers in nucleophilic displacement reactions; (3) the first results obtained with CF_3O^- anion (also with CF_3S^-) in addition reactions across a triple bond of in situ generated arynes. We have found that treatment of **1** with covalent **2a**,[15] and ionic anhydrous F^- sources **2b–i**[13,14,16–18] in CH_3CN (CH_2Cl_2 or diglyme) affords trifluoromethanolates **3a**,**f–i**, which are stable in solvent media, and trifluoromethanolates **3b–e**, which are stable in solid state and easily soluble in CH_3CN or CH_2Cl_2 (Scheme 1). After the separation of CF_3SO_2F[19] the solvent was removed in vacuum and the residues were washed with ether and dried in vacuum at −30 °C for 3 h, providing salts **3b–e** in 97–99% yield (Scheme 1).[20] Surprisingly, salt **3a** can be distilled in static vacuum along with the solvent used.

Salts **3a–c**,**e** were also synthesized alternatively via COF_2 (**Caution!** COF_2 is extremely corrosive to human tissue. All work with this gas should be conducted in an efficient hood) reaction with **2a–c**,**e**, respectively.[21]

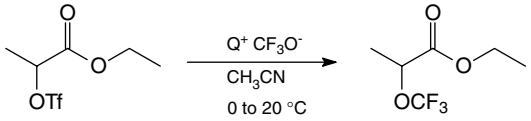
Under mild reaction conditions (CH_3CN, 0 °C for 1 h, then 20 °C for 2 h), salt **3b** readily reacted with the ethyl 2-{[(trifluoromethyl)sulfonyl]oxy}propanoate (**4**) yielding, after a simple work up, the ethyl 2-(trifluoromethoxy)propanoate (**4**-OCF_3) in 87% isolated yield (^{19}F NMR yield 96%, Table 1, entry 2). A similar result was obtained also via in situ generation of **3b** followed by the separation of CF_3SO_2F and the addition of **4** (Table 2, entry 2).[22]

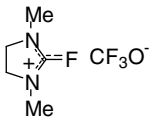


$Q^+ F^-$ = $[(CH_2NMe)]_2CF_2$ (DFI) (a), $(Me_2N)_3C^+ Me_3SiF_2^-$ (b), $[(CH_2NMe)]_2CNMe_2^+ Me_3SiF_2^-$ (c), $(Me_2N)_3S^+ Me_3SiF_2^-$ (d), Me_4NF (e), Et_3N /HF (f), CsF (g), KF (s.d.) (h), AgF (i)

Scheme 1.

Table 1
Salts **3a**,**b**,**d**,**e–g** in reaction with **4** (^{19}F NMR study, yield of **4**-OCF_3 versus internal $PhCF_3$)



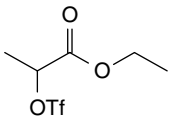
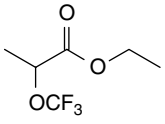
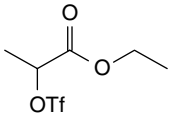
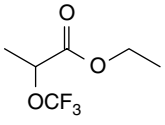
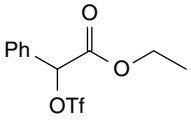
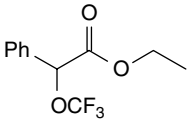
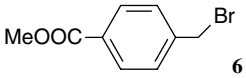
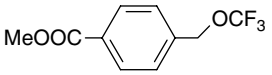
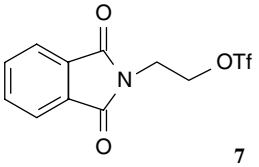
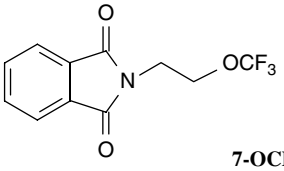
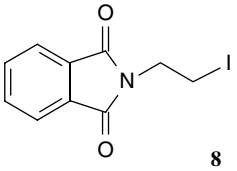
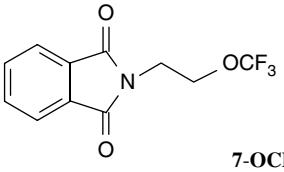
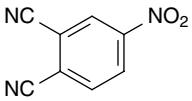
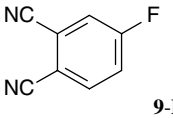
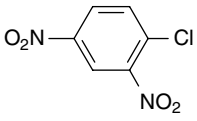
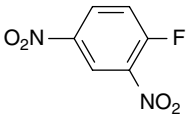
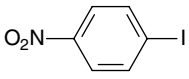
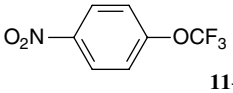
Entry	$Q^+ CF_3O^-$	**4**-OCF_3 (%)	**4**-F (%)
1	 **3a**	99	0
2	$(Me_2N)_3C^+ CF_3O^-$ **3b**	96	2
3	$(Me_2N)_3S^+ CF_3O^-$ **3d**	87	9
4	$Me_4N^+ CF_3O^-$ **3e**	95	<2
5	$Et_3NH^+ CF_3O^-$ **3f**	43	30
6	$Cs^+ CF_3O^-$ **3g**	74	15

Properties of the salts **3a**,**b**,**d**,**e–g** in reaction with **4** were compared. The reagents **3a–c**,**e** were selected as the CF_3O-carriers of choice (high ^{19}F NMR yield of **4**-OCF_3 and chemoselectivity). Reactions (Table 1) were conducted on 1 mmol scale with 1.1 mmol of **3a**,**b**,**d**,**e–g** in 1.5 mL CH_3CN at 0 °C (for 0.5 h), then at 20 °C for 12 h. Reagents **3a–c**,**i** were applied to the synthesis of trifluoromethyl ethers from the functionalized secondary triflates **4**, **5**, benzyl bromide **6**, primary triflate **7**. and iodide **8** (Table 2).[23,25,26]

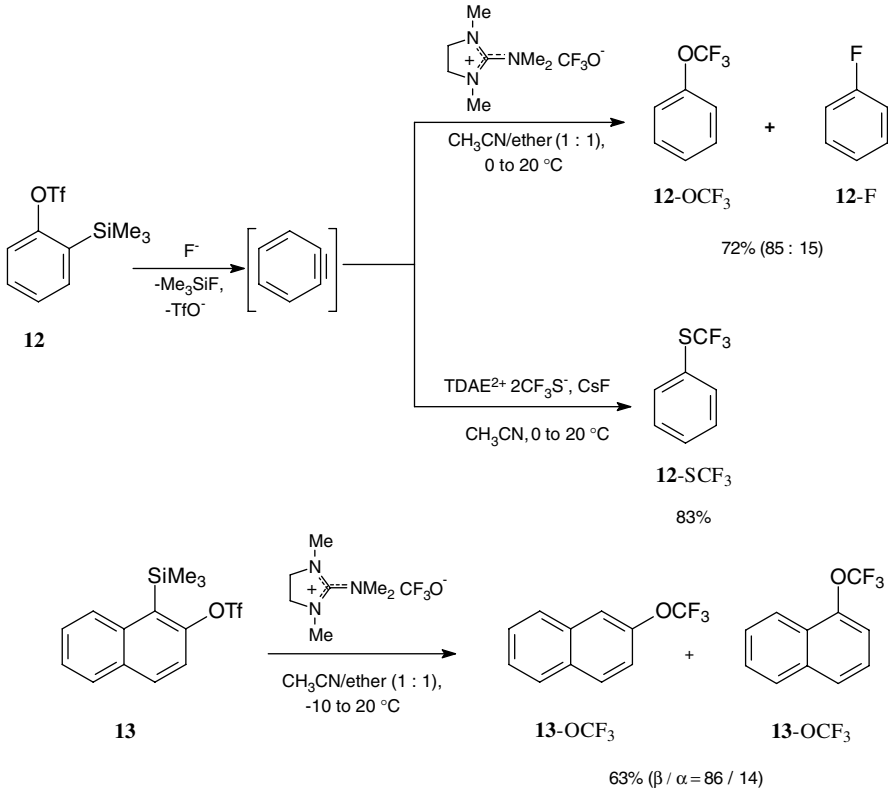
Unfortunately, no S_N2Ar trifluoromethoxylation occurred with **3b**, **e**. 4-Nitrobenzene-1,2-dicarbonitrile **9** readily undergoes fluorodenitration with **3b** to give **9**-F. Selective nucleophilic substitution of chlorine by fluoride (halex) occurs in the reaction of 2,4-dinitrochlorobenzene **10** with **3e**. Due to activation by two nitro groups the chloride is the most mobile leaving group in the multiply substituted substrate **10** (Table 2, entries 7 and 8). In this respect the behavior of **3b**,**e** differs from the reactivity of the related ionic trifluoromethanethiolates $Q^+CF_3S^-$ being highly efficient CF_3S-transfer reagents in the case of both aliphatic and aromatic nucleophilic substitution reactions.[27] No reaction occurs at all upon heating of 1-iodo-4-nitrobenzene **11** with CH_3CN solution of the copper trifluoromethanolate, CF_3OCu, **3j** (Table 2, entry 9). A solution of **3j** (δ_F −24.3 ppm, br s, $\Delta_{1/2} = 374$ Hz) was obtained similarly to synthesis of CF_3SCu by treating of salt **3i** (δ_F −22.1 ppm, br s, $\Delta_{1/2} = 277$ Hz) with CuBr in CH_3CN followed by the filtration of the quantitatively precipitated AgBr.[28]

In contrast, the addition of the trifluoromethanolate anion across a triple bond of arynes[29] does lead to aryl trifluoromethyl ethers. In the reaction between *o*-trimethylsilylphenyl triflate (**12**) and **3c** (3 equiv) in CH_3CN/ether

Table 2
Reactions of reagents **3a**–**c**,**e**,**i**,**j** with electrophiles **4**–**11**

Entry	Reagent	Substrate	Products	Isolated (^{19}F NMR) yield[a]
1	**3a**	 **4**	 **4-OCF$_3$**	81(99)
2	**3b**	 **4**	 **4-OCF$_3$**[22]	87(96)
3	**3c**	 **5**[23,24]	 **5-OCF$_3$**[23]	57(71)
4	**3i**	 **6**	 **6-OCF$_3$**[25]	87(99)
5	**3c**	 **7**	 **7-OCF$_3$**[26]	91(99)
6	**3i**	 **8**	 **7-OCF$_3$**	85(97)
7	**3b**	 **9**	 **9-F**[b]	87(96)
8	**3e**	 **10**	 **10-F**[b]	81(95)
9	**3j**[c]	 **11**	 **11-OCF$_3$**[d]	0

[a] Characterized by ^{1}H, ^{13}C, and ^{19}F NMR methods and the molecular formulas for the novel compounds **4**–**6**-OCF$_3$[22,23,25] were confirmed by HRMS method.
[b] Reactions were performed in CH_3CN (20 °C for 12 h) with 2 equiv of **3b** (entry 7) and **3e** (entry 8), respectively.
[c] **3j** was generated from **3i** and CuBr in CH_3CN at 20 °C.
[d] Reaction was conducted in CH_3CN with 2 equiv of **3j** (80 °C for 12 h).



Scheme 2.

(1:1) we obtained the mixture (85:15) of (trifluoromethoxy) benzene **12**-OCF_3 and fluorobenzene **12**-F in overall 72% yield (GC–MS, ^{19}F NMR yield 90%) (Scheme 2). Comparable results were obtained in the presence and absence of CsF (2 equiv) as fluorodesilylating agent. On the contrary, the reaction of **12** with trifluoromethanethiolate salt[27] $TDAE^{2+}$ $2SCF_3^-$ (or $Me_4N^+CF_3S^-$)/CsF system in CH_3CN led to [(trifluoromethyl)sulfanyl]benzene **12**-SCF_3 solely (83%, ^{19}F NMR 99%, no PhF was found).[30]

Mechanistically, the process comprises the generation of benzyne from **12** and F-anion source (CsF or **3c**), followed by an addition of CF_3O^- (or CF_3S^-) anion across a triple bond of benzyne to form (trifluoromethoxy)benzenide or [(trifluoromethyl)sulfanyl]benzenide anions, and then an abstraction of proton by these anions from the surrounding to afford the target products **12**-OCF_3 and **12**-SCF_3, respectively (Scheme 2).

A reaction of CF_3O^- (**3c**, 3 equiv) with 1-trimethylsilylnaphthyl 2-trifluoromethanesulfonate[29b] **13** (Scheme 2) in CH_3CN/ether (1:1) afforded in 63% yield the mixture (86:14) of 2- and 1-(trifluoromethoxy)-naphthalenes, **13**-β and **13**-α, respectively.[31,32]

In summary, the proposed difluorophosgene free trifluoromethoxylation protocol can be easily adopted for laboratory synthesis of diverse functionalized trifluoromethyl ethers. Reactions of in situ generated arynes with trifluoromethanolate and trifluoromethanethiolate anions represent a promising laboratory route to R_FO- and R_FS-arenes. The results on a gentle straightforward transformation of alcohols into alkyl trifluoromethyl ethers by the usage of $CF_3OSO_2CF_3$ or COF_2 will be published in due course.

Acknowledgments

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18. Synthesis of $(CF_3)_2N^-$ salts from bis(trifluoromethyl)perfluoroalkanesulfonamides was claimed: Hilarius, V.; Buchholz, H.; Sartori, P; Ignatiev, N.; Kucherina, A.; Datsenko, S. WO 2000046180 (to Merck patent G.m.b.H., Germany), August, 10, 2000.
19. (a) The all operations with the reagents **2a**–**i** and **3a**–**i** were performed in oven-dried glassware under an atmosphere of dry nitrogen. CF_3SO_2F was quantitatively collected in a cooled with liquid nitrogen trap at the reduced temperature (−30 °C) and pressure (3 Torr). For application of CF_3SO_2F in organic synthesis as fluorinating or CF_3SO_2 transfer reagent see: Nagamori, M.; Narizuka, S. JP 2007119355 (to Central Glass Co., Ltd), May, 17, 2007; Desmarteau, D. D.; Witz, M. *J. Fluorine Chem.* **1991**, *52*, 7–12.
20. *Tris(dimethylamino)methylium trifluoromethanolate* (**3b**). Into a Schlenk vessel (500 mL) containing a magnetically stirred solution of 10.1 g (39.6 mmol) of $(Me_2N)_3C^+Me_3SiF_2^-$ (**2b**)[13] in 75 mL of CH_3CN cooled till −30 °C was condensed 8.6 g (39.6 mmol) of **1**. The vessel was closed and during a period of 2 h the reaction temperature was raised from −30 °C to ambient temperature. The vessel was cooled again till −35 °C and CF_3SO_2F was pumped off in vacuum (3 Torr, for ca. 5 min) into a trap cooled with liquid nitrogen to afford a solution of **3b** in CH_3CN. Then the mixture was warmed to 0 °C and the solvent was removed in vacuo and the residue was washed with diethyl ether (1 × 70 mL) to leave a colorless solid, which was dried in vacuo 0.05 Torr at −30 °C for 3 h to furnish 8.9 g (98%) of **3b**, purity 99.5%, mp 197–199 °C (from CH_3CN/ether at −30 °C). ^1H NMR (200.13 MHz, CD_3CN, 20 °C): δ 2.93 (s, 18H, CH_3); ^{13}C NMR (50.32 MHz, CD_3CN, 20 °C): δ 39.7 $(CH_3)_2N$]; 163.3 (C^+); the carbon atom from CF_3O^- is not observed at 20 °C; ^{19}F NMR (188.31 MHz, CD_3CN, 20 °C): δ −21.2 (br s, $\Delta_{1/2} = 370$ Hz, 3F, CF_3). Anal. Calcd for $C_8H_{18}F_3N_3O$: C, 41.91; H, 7.91; N, 18.33. Found: C, 41.73; H, 8.06; N, 18.43.
21. *2-(Dimethylamino)-1,3-dimethylimidazolidin-2-ylium trifluoromethanolate* (**3c**). The compound was alternatively prepared from carbonyl difluoride and 2-dimethylamino-1,3-dimethylimidazolinium difluorosilicate (**2c**)[13] in CH_2Cl_2 following the published method for **3d**.[8] Colorless powder, yield 98%, mp 122–124 °C (from CH_3CN/ether at −30 °C). ^1H NMR (200.13 MHz, CD_3CN, 20 °C): δ 2.92 (s, 6H, CH_3); 3.03 (s, 6H, CH_3); 3.59 (s, 4H, CH_2); ^{13}C NMR (50.32 MHz, CD_3CN, 20 °C): δ 36.6 (CH_3); 40.3 [$(CH_3)_2N$]; 50.1 (CH_2); 164.3 (C^+); the carbon atom from CF_3O^- is not observed at 20 °C; ^{19}F NMR (188.31 MHz, CD_3CN, 20 °C): δ −23.7 (br s, $\Delta_{1/2} = 540$ Hz, CF_3, 3F). Anal. Calcd for $C_8H_{16}F_3N_3O$: C, 42.29; H, 7.10; N, 18.49. Found: C, 42.41; H, 7.37; N, 18.71.
22. *Ethyl-2-(trifluoromethoxy)propanoate* (**4**-OCF_3). To a cooled with ice and magnetically stirred solution of **3b** in 37 mL CH_3CN, prepared from **1** (17.6 mmol) and **2b** (17.6 mmol) in situ as is described in Ref. 20, was added in one portion 4.0 g (16.0 mmol) of triflate **4**. The temperature was raised to 20 °C within 1 h and the mixture stirred for 2 h. The mixture was poured into sodium hydrocarbonate solution (3%, 50 mL) and extracted with pentane (3 × 50 mL). The combined organic extracts were washed with water and dried over $MgSO_4$. The final purification by distillation under reduced pressure gave the indicated compound (3.3 g, 87.4%) as a colorless liquid with bp 61–62 °C/ 55 Torr. ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.29 (t, $^3J_{HH} = 7.3$ Hz, 3H, CH_3); 1.51 (d, $^3J_{HH} = 7.2$ Hz, 3H, CH_3); 4.24 (q, $^3J_{HH} = 7.3$ Hz, 2H, CH_2), 4.82 (q, $^3J_{HH} = 7.2$ Hz, 1H, CH); ^{13}C NMR (50.32 MHz, C_6D_6): δ 14.0 (CH_3), 18.5 (CH_3), 61.4 (CH_2), 72.6 (q, $^3J_{CF} = 2$, 8 Hz, *C*H), 122.5 (q, $^1J_{CF} = 257.4$ Hz, CF_3); 169.7 (C=O); ^{19}F NMR (188.31 MHz, $CDCl_3$): δ −61.1 (s, CF_3). HRMS (EI) calcd for $C_6H_9F_3O_3$ (M^+): 186.05007. Found: 186.05038.
23. *Ethyl phenyl(trifluoromethoxy)acetate* (**5**-OCF_3). Triflate **8** was generated following Effenberger's method.[24] Triflic anhydride (1.6 g, 5.6 mmol) was added to a stirred solution of (*R*/*S*) ethyl hydroxy(phenyl)acetate (0.9 g, 5 mmol) in CH_2Cl_2 (55 mL) at −78 °C. At the mentioned temperature the mixture was consequently treated with 0.71 g (5.9 mmol) of 2,4,6-trimethylpyridine (collidine) and solution of the in situ generated (similarly to Ref. 20) from **1** and **2c** trifluoromethanolate **3c** (2.84 g, 12.5 mmol) in CH_3CN (20 mL) and was slowly (within 6 h) warmed up till 20 °C. After aqueous (basic) work up the crude product, contaminated with **5**-F impurity, was purified by column chromatography (hexane/ethyl acetate 10: 1) to give the title product **5**-OCF_3 (0.71 g, 57%) as a colorless oil. ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.26 (t, $^3J_{HH} = 7.3$ Hz, 3H, CH_3); 4.25 (m, 2H, CH_2); 5.54 (s, 1H, CH), 7.37–7.52 (m, 5H, Ar-H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 14.3(CH_3), 62.6 (CH_2), 77.4 (q, $^3J_{CF} = 2$, 8 Hz, *C*H), 121.9 (q, $^1J_{CF} = 257.3$ Hz, CF_3); 127.5, 129.3, 130.1, 133.7 ($C_{Ar}H$), 167.9 (C=O); ^{19}F NMR (188.31 MHz, $CDCl_3$): δ −60.5 (s, CF_3). HRMS (EI) calcd for $C_{11}H_{11}F_3O_3$ (M^+): 248.06603. Found: 248.06523.
24. Effenberger, F.; Burkard, U.; Willfahrt, J. *Angew. Chem., Int. Ed.* **1983**, *22*, 65–66.
25. *Methyl 4-[(trifluoromethoxy)methyl]benzoate* (**6**-OCF_3). Yield 87%. Colorless liquid with bp 79–81 °C/ 0.1 Torr. ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.58 (s, 3H, CH_3); 4.44 (s, 2H, CH_2); 6.84–6.93 (m, 2H, Ar-H); 8.02–8.10 (m, 2H, Ar-H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 52.6 (ester CH_3), 68.6 (q, $^3J_{CF} = 3.4$ Hz, CH_2), 122.1 (q, $^1J_{CF} = 255.9$ Hz, CF_3), 127.8, 130.5, 131.0, 139.1 ($C_{Ar}H$), 166.9 (C=O); ^{19}F NMR (188.31 MHz, $CDCl_3$): δ −60.5 (s, CF_3). HRMS (EI) calcd for $C_{10}H_9F_3O_3$ (M^+): 234.05038. Found: 234.05077.
26. *N-[2-(Trifluoromethoxy)ethyl]phthalimide* (**7**-OCF_3). Yield 91% (from the triflate **7**). Colorless solid with mp 77–78 °C (lit. mp 77–77.4 °C).[26] The ^1H, ^{19}F and ^{13}C NMR data for **7**-OCF_3 were identical to those found for the prepared by desulfurization–fluorination method[7] compound: Blazejewski, J.-C.; Anselmi, E.; Wakselman, C. *J. Org. Chem.* **2001**, *66*, 1061–1063.
27. (a) Kolomeitsev, A. A.; Médebielle, M.; Kirsch, P.; Lork, E.; Röschenthaler, G.-V. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2183–2185; (b) Kirsch, P.; Röschenthaler G.-V.; Bissky, G.; Kolomeitsev, A. A. *DE* 10254597 (to Merck patent G.m.b.H., Germany), July, 3, 2003; (c) Kolomeitsev, A. A.; Röschenthaler, G.-V.; Chabanenko, K. Yu.; Yagupolskii, Yu. L. *Synthesis* **1994**, 145–146.

28. Yagupolskii, L. M.; Kondratenko, N. V.; Sambur, V. P. *Synthesis* **1975**, 721–723.
29. For a mild generation of arynes from *o*-silylaryltriflates see: (a) Yoshida, H.; Morishita, T.; Fukushima, H.; Ohshita, J.; Kunai, A. *Org. Lett.* **2007**, *9*, 3367–3370; and references cited therein; (b) Peña, D.; Pérez, D.; Guitián, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 3579–3581; and references cited therein; (c) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 583–588; and references cited therein.
30. *[(Trifluoromethyl)sulfanyl]benzene* **12**-SCF_3. To a magnetically stirred mixture of tetrakis(dimethylamino)ethanebis(ylium) bis(trifluoro-methanethiolate),[27a] $TDAE^{2+}$ $2CF_3S^-$ (4.02 g, 10 mmol) and CsF (3.04 g, 20 mmol) in CH_3CN (35 mL) at 0 °C in one portion was added triflate **12** (2.98 g, 10 mmol). The resulting suspension was stirred at 0 °C for 3 h and at room temperature overnight. The dark brown mixture was treated with sodium hydrocarbonate solution (3%, 25 mL) and extracted with pentane (3 × 30 mL). The organic phase was washed with brine (2 × 15 mL) and dried. Evaporation of the solvent afforded **12**-SCF_3 as a light yellow liquid (1.85 g, purity 95%). Distillation under reduced pressure (bp 69–70 °C/100 Torr) provided the title product **12**-SCF_3 (1.47 g, 83%). The ^1H, ^{19}F, and ^{13}C NMR data were identical to those found for the commercial compound (ABCR).
31. *1-(Trifluoromethoxy)naphthalene* (**13**-α) and *2-(trifluoromethoxy)-naphthalene* (**13**-β). The mixture of regioisomers[32] was obtained by the reaction of 1-trimethylsilylnaphthyl 2-trifluoromethanesulfonate **13** (0.26 g, 0.75 mmol) with **3c** (0.51 g, 2.25 mmol) in 2.5 mL of CH_3CN/ether (1:1) at −10 °C for 24 h followed by a stirring at 20 °C for 4 h. After basic work up the dark orange oily product (140 mg) was purified by preparative HPLC (RP-18, Kromasil, 16μm, 100 Å, 250 × 50 mm, 83% MeOH–H_2O). Colorless oil, yield 99 mg (63%), purity 99%, contains 1 mol % of 1-fluoronaphthalene, ratio α/β 14:86. ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 118.6, 120.6, 121.1 (q, $^1J_{CF} = 257.2$ Hz, CF_3), 126.8, 127.5, 128.2, 130.5, 132.2, 134.0, 147.3 (**13**-β); δ 116.9, 121.4 (q, $^1J_{CF} = 257.5$ Hz, CF_3), 121.9, 123.7, 125.6, 127.3, 127.4, 128.3, 135.2, 145.7 (**13**-α). ^{19}F NMR (188.31 MHz, $CDCl_3$): δ −58.6 (s, CF_3, minor isomer, -α); −58.9 (s, CF_3, major isomer, -β).
32. The 1- and 2-(trifluoromethoxy)naphthalenes were prepared recently: Schlosser, M.; Castagnetti, E. *Eur. J. Org. Chem.* **2001**, 3291–3997.