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A New and Direct Trifluoromethoxylation of Aliphatic Substrates with 2,4-Dinitro(trifluoromethoxy)benzene

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Dedicated to the memory of Prof. Lev M. Yagupolskii

Abstract: The reaction of tetrabutylammonium triphenyldifluorosilicate with 2,4-dinitro(trifluoromethoxy)benzene, in acetonitrile and under microwave irradiation, generates a trifluoromethoxide anion which is able to substitute activated bromides (benzyl bromide, cinnamyl bromide), as well as, to some extent, alkyl iodides. Aliphatic trifluoromethyl ethers are thus formed. This is the first example of the nucleophilic displacement of the trifluoromethoxy group from an activated aromatic ring.

Keywords: aromatic substitution; 2,4-dinitro(trifluoromethoxy)benzene; fluorine; trifluoromethoxide; trifluoromethoxylation

Introduction

Because of the intrinsic properties of the fluorine atom (small size, high electronegativity, formation of strong C–F bonds, etc.), the introduction of fluorinated moieties on organic skeletons induces dramatic changes in their electronic, steric and hydrophobic parameters. Consequently, their pharmacodynamic and pharmacokinetic properties are deeply modified.[1,2] This is the reason why fluorine chemistry is now so popular in the life sciences.

Among the fluorinated moieties currently used, the trifluoromethoxy group (OCF_3) is becoming more and more prominent.[3,4] For example, in addition to trifluoromethoxy-substituted liquid crystals[5] and dyes,[6] several trifluoromethoxylated pesticides and pharmaceuticals are now present on the market (Figure 1).[5,7,8]

This growing interest for trifluoromethyl ethers is related to the very peculiar characteristics of the CF_3O group. On one hand, this substituent looks like chlorine[9] in the sense that it is electron-withdrawing by induction ($\chi = 3.7$,[10] $\sigma_I = +0.51$ to $+0.60$[11]), but more than chlorine ($\sigma_I = +0.47$[11a]), and electron-donating by resonance ($\sigma_R = -0.13$ to -0.18[11]), but less than chlorine ($\sigma_R = -0.25$[11a]). For this reason, it has been named "super-halogen"[12] or "pseudo-halogen".[13] On the other hand, OCF_3 is one of the most hydrophobic substituents, just after SCF_3, as indicated by its Hansch–Leo parameter [Π_R (SCF_3) = +1.44, Π_R

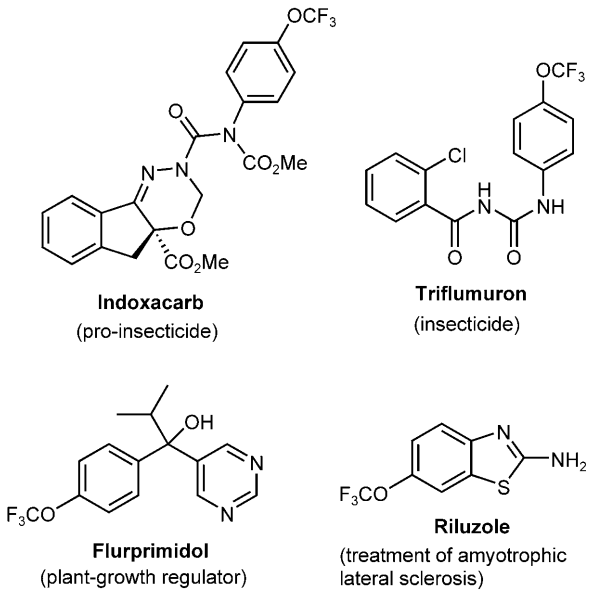
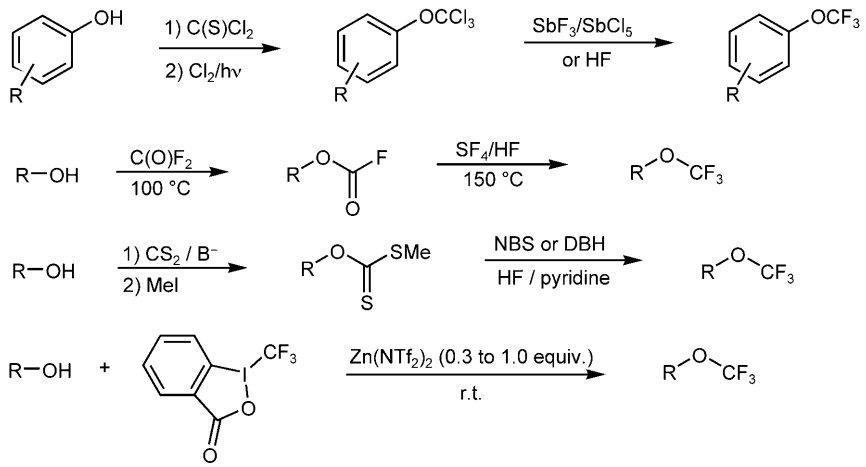


Figure 1. Some bioactive trifluoromethoxylated products.



Scheme 1. Usual accesses to trifluoromethyl ethers.

$(OCF_3) = +1.04$, Π_R $(CF_3) = +0.88$, Π_R $(OCH_3) = -0.02$].[14] Thus, such a hydrophobic substituent dramatically increases the bioavailability of the products bearing it. It must be also noticed that the very peculiar conformation of (trifluoromethoxy)arenes (in which the OCF_3 moiety is orthogonal to the ring plane) could contribute to the original bioactivities of trifluoromethoxylated aromatic compounds (for a discussion, see[15]).

Until now, mainly aryl trifluoromethyl ethers have been described. Their different preparations have been recently reviewed.[6,15] The best-established ones can be divided into four methods that are, chlorine/fluorine exchange on trichlorinated precursors,[16] action of sulfur tetrafluoride on fluoroformates (Sheppard's method),[17] Hiyama's oxidative fluorodesulfurization[18] and electrophilic trifluoromethylation of hydroxy functions[19,20] (Scheme 1).

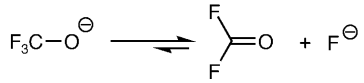
L. M. Yagupolskii et al. pioneered the chlorination/fluorination technique,[16] applied to $ArOCCl_3$ precursors,[16,21] in the late 1950s. It is now currently employed on an industrial scale but is only applicable to aromatic compounds. Deoxyfluorination of fluoroformates[17] is greatly limited by the high toxicity of SF_4. Oxidative fluorodesulfurization[18] can be applied to phenols, primary and even secondary alcohols, but this method is not compatible with numerous functional groups. Electrophilic trifluoromethylation of alcohols and phenols has been first reported by Umemoto et al.,[19] using poorly stable *O*-trifluoromethyldibenzofuranium salts, then by Togni et al. who developed easily accessible trifluoromethyl-containing iodine(III) reagents.[20] When these reagents are applied to phenols, *C*-trifluoromethylation competes with *O*-trifluoromethylation but, in the presence of substoichiometric amounts of zinc triflimide, they allow the *O*-trifluoromethylation of aliphatic alcohols to proceed.[20e]

Obviously, the best synthesis of trifluoromethyl ethers would be the direct introduction of the whole OCF_3 moiety. It was first done by radical condensation of olefins and trifluoromethyl hypofluorite,[22] which is highly hazardous and toxic. Then, numerous attempts to carry out nucleophilic trifluoromethoxylation with trifluoromethoxide salts failed since, generally, the CF_3O^- anion collapses into fluoride and fluorophosgene, even at low temperature (Scheme 2).

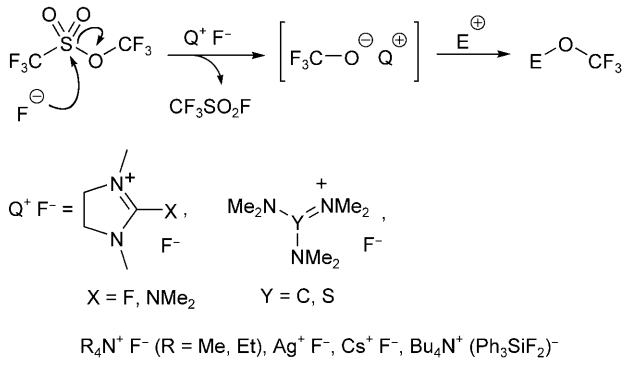
Several teams tried to draw this equilibrium towards CF_3O^- and demonstrated that if fluorides are associated with rather bulky cations [CsF,[23,24] $(Me_2N)_3S^+$ $Me_3SiF_2^-$[25]], the resulting trifluoromethoxide could be stable enough, in solution, to react with reactive electrophiles such as benzyl bromide[24] or primary triflates and bromides.[26] Nevertheless, the development of this reaction was limited by the high toxicity of gaseous fluorophosgene.

Recently, Kolomeitsev et al. have described a more convenient generation of trifluoromethoxide salts, from trifluoromethyl triflate (TFMT) and bulky fluorides, and its application to the trifluoromethoxylation of aliphatic triflates.[27] We also studied this trifluoromethoxylating system and extended its synthetic scope to the substitutive trifluoromethoxylation of numerous aliphatic bromides and iodides[15] (Scheme 3).

TFMT is a volatile liquid (bp = 19 °C), far less toxic than fluorophosgene but expensive, since it is prepared from triflic anhydride,[28,29] and is only available on the bench scale. Thus, we turned our interest to possibly more convenient precursors, especially (trifluoromethoxy)benzenes bearing mesomeric electron-withdrawing substituents, which are, for most of them,



Scheme 2. Decomposition of the trifluoromethoxide anion.



Scheme 3. Generation and use of trifluoromethoxide from TFMT.

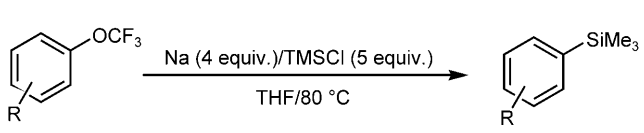
available on the industrial scale. We anticipated that, when attacked by an auxiliary nucleophile associated to a bulky counterion, these electron-poor compounds could expel, through an aromatic nucleophilic substitution, a trifluoromethoxide anion.

Results and Discussion

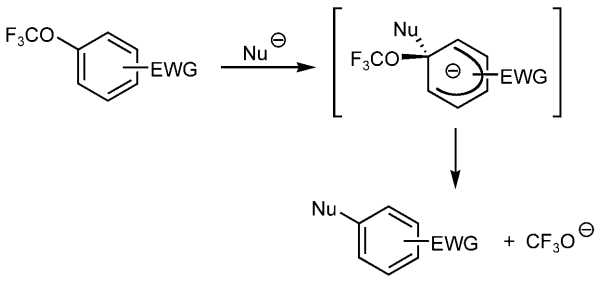
Aryl trifluoromethyl ethers are usually thermally and chemically stable, except under harsh acidic conditions, which cause the hydrolysis of the trifluoromethyl group and the formation of the corresponding phenols, or in the presence of aluminium trichloride which leads to their rapid transformation into aryl trichloromethyl ethers.[21] Except for that, no cleavage of the C_{Ar}–OCF_3 bond had been reported until Iijima and Amii described the reduction of Ar–OCF_3 by sodium[30] (Scheme 4).

Thus, it appeared that the cleavage of a C_{Ar}–OCF_3 bond is thermodynamically possible. Moreover, owing to the inductive electron-withdrawing power of the OCF_3 substituent ($\sigma_I = +0.51$ to $+0.60$),[11] we thought that this moiety could be a good leaving-group and could be displaced from an electron-poor (trifluoromethoxy)benzene (Scheme 5).

In order to verify this assumption, 2,4-dinitro(trifluoromethoxy)benzene **1** appeared to be the best candidate among the commercially available reagents. Thus, by analogy with our previous work on TFMT,[15] **1** was exposed to silver fluoride (1 equiv.) in acetonitrile. ^{19}F NMR indicated that, after three hours at room temperature, up to 22% of 2,4-dinitrofluorobenzene **2** was formed and that after two more hours at reflux, **1** was completely converted into **2**. Consequently, the hypothesis summarized in Scheme 5 was proven to be true. This was the first example of a nucleophilic displacement of the OCF_3 group from an aromatic ring.



Scheme 4. Reduction of aryl trifluoromethyl ethers with sodium.

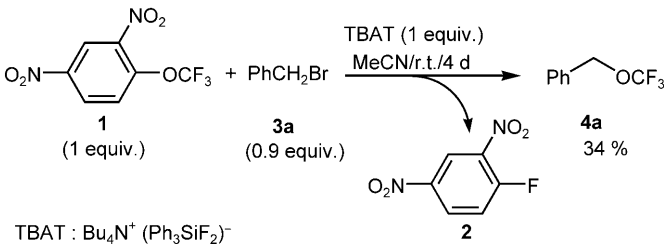


Scheme 5. Putative displacement of CF_3O^- from an electron-poor aryl trifluoromethyl ether.

This experiment was repeated, except that benzyl bromide **3a**, chosen as an electrophilic model, was added at the beginning: ^{19}F NMR indicated that, after four days at room temperature, only benzyl fluoride was formed (20%) and no trace of benzyl trifluoromethyl ether **4a** was detected. It was suspected that this surprising result could be due to the strong interaction between silver and bromine. Consequently, silver fluoride was successfully replaced by tetrabutylammonium triphenyldifluorosilicate (TBAT): under the previous conditions, benzyl trifluoromethyl ether **4a** was obtained in a 34% yield (by ^{19}F NMR) after four days at room temperature (Scheme 6).

This interesting result was optimized through a parametric study. The influences of the reactant ratio and of temperature were firstly examined, as shown in Table 1.

It appeared, from Table 1, firstly that the fluoride source could not be used in a catalytic amount (that means that Br^- was not able to displace CF_3O^- from **1**) (entry 2) and, secondly, that one of the components must be used in excess, the excess of **1** being the most crucial parameter (entries 5 to 8). The reaction was rather sluggish at room temperature but its kinetics



Scheme 6. First trifluoromethoxylation of benzyl bromide from **1** and TBAT.

Table 1. Influence of the reactant ratio and of temperature.

Entry	**1** [equiv.]	TBAT [equiv.]	**3a** [equiv.]	*T* [°C]	Yield of **4a** (time)[a]
1	1.0	1.0	0.9	r.t.	34% (4 d)
2	1.0	0.1	0.9	r.t.	1.3% (4 d)
3	1.0	1.0	1.8	r.t.	41% (4 d)
4	1.0	2.0	0.9	r.t.	40% (4 d)
5	2.0	2.0	0.9	r.t.	55% (4 d)
6	2.0	1.0	0.9	r.t.	60% (4 d)
7	2.0	1.0	0.9	50	60% (20 h)
8	2.0	1.0	0.9	100	0% (16 h)[b]

[a] Crude Yield from ^{19}F NMR with $PhCF_3$ as internal standard.
[b] Formation of **2** (100%) and benzyl fluoride (48%).

Table 2. Influence of the solvent.

Entry	Solvent	Yield of **4a**[a]
1	acetonitrile	60%
2	benzonitrile	50%
3	THF	49%
4	DMF	42%
5	BMIM PF_6[b,c]	6%
6	DMSO[c]	0.5%
7	nitromethane	no reaction
8	HFIP[d]	no reaction

[a] Crude yield, after 4 days at room temperature, from ^{19}F NMR with $PhCF_3$ as internal standard.
[b] BMIM PF_6 = 1-butyl-3-methylimidazolium hexafluorophosphate.
[c] **1** was significantly converted into **2**.
[d] HFIP = hexafluoroisopropyl alcohol.

were dramatically enhanced by heating at 50 °C (entry 7). Higher temperatures were deleterious to the yield of the desired product: no benzyl trifluoromethyl ether **4a** was detected at 100 °C, although **1** was totally transformed into **2**, and benzyl fluoride was significantly formed (entry 8). That means that, at 100 °C, the trifluoromethoxy group of **1** was completely displaced by the fluoride anion but that the generated trifluoromethoxide anion was not stable enough to react with benzyl bromide. Indeed, it probably collapsed into fluorophosgene and F^- and the latter substituted benzyl bromide **3a** to deliver benzyl fluoride. In conclusion from Table 1, the best result was obtained at 50 °C, within 20 h, with the reactant ratio **1**:TBAT:**3** = 2.0:1.0:0.9.

The influence of the solvent (aprotic, protic or ionic) was also studied (Table 2). It appeared that acetonitrile (yield: 60%, entry 1) was the most efficient, followed by benzonitrile (yield: 50%, entry 2), THF (yield: 49%, entry 3) and DMF (yield: 42%, entry 4). Surprisingly, DMSO delivered a very poor yield (yield: 0.5%, entry 6) and no reaction occurred in nitromethane (entry 7) or hexafluoroisopropyl alcohol (entry 8). Maybe these three solvents are too acidic and protonate the generated CF_3O^- anion to give trifluoromethanol which is known to decompose into HF and fluorophosgene above −27 °C. The yield was also poor in an ionic liquid such as 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6) (yield: 6%, entry 5), though **2** was significantly formed. Maybe BMIM PF_6 is a too dissociating solvent and favors the decomposition of the CF_3O^- anion.

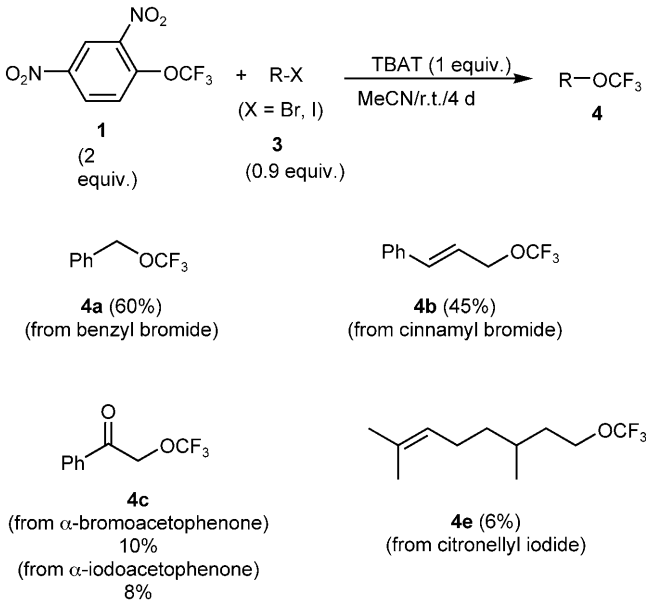
Then, the nature of the fluoride source was examined under the conditions depicted in Table 1 and Table 2. Except TBAT, which delivered **4a** in a 60% yield, only tris(dimethylamino)sulfonium trimethyldifluorosilicate (TASF) provided a significant amount of benzyl trifluoromethyl ether **4a** (yield: 29%). As already mentioned, silver fluoride partly converted **1** into **2** but essentially reacted with **3a** to give benzyl fluoride. Tetramethylammonium fluoride completely converted **1** into **2**, but without formation of **4a**, whereas triphenylphosphine and hexamethylphosphoric triamide (HMPT) induced the degradation of the starting material. Finally, no reaction occurred with tetra-*n*-butylammonium chloride or diethylaminosulfur trifluoride (DAST).

It must be noted that, when 2,4-dinitro(trifluoromethoxy)benzene **1** was replaced by 4-nitro(trifluoromethoxy)benzene **5** (2.0 equiv.), no benzyl trifluoromethyl ether was formed from benzyl bromide **3a** (0.9 equiv.) and TBAT (1 equiv.), even after 4 days at 50 °C or at reflux. Benzyl fluoride was only obtained and **5**, which is probably not activated enough, was recovered unchanged.

Finally, other halogenated substrates **3b–e** were reacted with **1** and TBAT (Scheme 7). The results were rather disappointing since, except for the reactive cinnamyl bromide **3b** which provided **4b** in a medium yield (45%). α-Bromoacetophenone **3c**, α-iodoacetophenone **3d** and citronellyl iodide **3e** (chosen as a model alkyl iodide) delivered poor yields (respectively 10%, 8% and 6%).

In order to improve the scope and the kinetics of this reaction, the reaction was carried out under microwave irradiation. The influence of such an irradiation was first examined with benzyl bromide **3a** as substrate and the influence of the reactant ratio was also revisited under these conditions (Table 3).

It appeared that this activation was extremely efficient since, after 2 h only at 50 °C, **4a** was already obtained in a 24% yield (Table 3 - entry 2, to be compared to Table 1, entry 7). As the kinetics were dramatically accelerated, it was possible to carry out the reaction at 100 °C without extensive decomposition of the CF_3O^- intermediate. At this temperature, **4a** was produced in a 50% after 30 min (Table 3, entry 4) but, as observed in the absence of microwave irradiation



Scheme 7. Trifluoromethoxylation of halogenated substrates (crude yields from ^{19}F NMR with $PhCF_3$ as internal standard).

Table 3. Influence of the microwave irradiation.

Entry	**1**:TBAT:**3a** [equiv.]	*T* [°C]	Time	Yield of **4a**[a]
1	2:1:0.9	50	30 min	10%
2	2:1:0.9	50	2 h	24%
3	2:1:0.9	100	10 min	39%
4	2:1:0.9	100	30 min	50%
5	2:1:0.9	100	1 h	32%
6	2:2:0.9	100	20 min	46%
7	4:1:0.9	100	20 min	48%
8	4:2:0.9	100	20 min	70%
9	6:2:0.9	100	25 min	65%

[a] Crude yield from ^{19}F NMR with $PhCF_3$ as internal standard.

(Table 1, entry 8), prolonged heating was deleterious to the yield: after 1 h at 100 °C, the yield of **4a** dropped down to 32% (Table 3, entry 5). However, an increase of the reagent ratios successfully counterbalanced the decrease of yield due to the high temperature: with **1**:TBAT:**3a** = 4:2:0.9, **4a** was obtained in a 70% yield within 20 min.

Similar conditions (microwave irradiation, 100 °C, 20 min, **1**:TBAT:**3a** = 4:2:1) were successfully applied to the substitutive trifluoromethoxylation of cinnamyl bromide **3b** and citronellyl iodide **3e**: **4b** and **4e** were obtained in 60% and 48% yields, respectively (*vs.* 45% and 6% without MW irradiation, *cf.* Scheme 7). It must be emphasized that this procedure significantly broadened the scope of the reaction since it allowed the trifluoromethoxylation of a non-activated alkyl iodide such as citronellyl iodide. However, α-bromoacetophenone **3c** was not stable enough to resist to such harsh conditions and did not delivered any **4c**.

Conclusions

We have demonstrated for the first time that the trifluoromethoxy moiety of 2,4-dinitro(trifluoromethoxy)benzene **1** can be displaced by TBAT, through an S_NAr mechanism. In our preliminary study, we showed that the trifluoromethoxide anion, generated in such a way, can substitute reactive bromides, such as benzyl and allylic bromides. The kinetics of the reaction and the yields of the expected products are dramatically increased by microwave irradiation, so that the reaction time can be sufficiently reduced to carry out the reaction at 100 °C. Moreover, microwave irradiation broadened the scope of the reaction since it allowed the trifluoromethoxylation of non-activated alkyl iodides. In order to extend the scope of this method, we are currently examining its application to the substitutive trifluoromethoxylation of aryl iodides in the presence of Cu(I) salts.

Experimental Section

THF was distilled over sodium/benzophenone prior to use. Dichloromethane was dried over molecular sieves. Other reagents were used as purchased. 2,6-Dimethyl-8-iodo-oct-2-ene (citronellyl iodide) was prepared according to ref.[31]

Typical Procedure at Room Temperature

To TBAT (540 mg, 1 mmol) were added, under nitrogen, anhydrous acetonitrile (2 mL) followed, successively, by 2,4-dinitro(trifluoromethoxy)benzene (155 mL, 2 mmol) and the electrophile (0.9 mmol). Then, the reaction vessel was closed and the mixture was stirred at room temperature for 4 days. Crude yields were determined by ^{19}F NMR after addition of benzotrifluoride (30 mL, 0.23 mmol) as internal standard.

Typical Procedure under Microwave Irradiation

To TBAT (540 mg, 1 mmol) were added, under nitrogen, anhydrous acetonitrile (2 mL) followed, successively, by 2,4-dinitro(trifluoromethoxy)benzene (310 mL, 4 mmol) and the electrophile (0.9 mmol). Then, the reaction vial was sealed and introduced in a Biotage Initiator™ Eight apparatus where the reaction mixture was heated at 100 °C under microwave irradiation (initial power P = 30 W, this power being monitored by temperature). After depressurization, crude yields were determined by ^{19}F NMR after addition of benzotrifluoride (30 mL, 0.23 mmol) as internal standard.

Benzyl trifluoromethyl ether **(4a):** Colorless oil; yield: 76%. ^{1}H NMR: δ = 7.40–7.35 (m, 5H), 4.99 (s, 2H); ^{13}C NMR: δ = 134.0, 129.1, 128.7, 127.5, 121.8 (q, $^1J_{C,F}$ = 255.4 Hz), 69.2 (q, $^3J_{C,F}$ = 3.5 Hz); ^{19}F NMR: δ = −60.78 (s);

anal. calcd. for $C_8H_7F_3O$: C 54.55, H 4.01; found: C 54.34, H 3.90.

1-Phenyl-2-(trifluoromethoxy)ethanone [α-(trifluoromethoxy)acetophenone] **(4c):** Yellow oil; yield: 69%. ^{1}H NMR: δ = 7.91 (m, 2H), 7.65 (m, 1H), 7.52 (m, 2H), 5.18 (s, 2H); ^{13}C NMR: δ = 190.2, 134.4, 133.8, 129.1, 127.9, 121.8 (q, $^1J_{C,F}$ = 256.3 Hz), 68.4 (q, $^3J_{C,F}$ = 2.9 Hz); ^{19}F NMR: δ = −61.44 (s); anal. calcd. for $C_9H_7F_3O_2$: C 52.95, H 3.46; found: C 53.12, H 3.15.

(2E)-3-Phenylprop-2-en-1-yl trifluoromethyl ether (cinnamyl trifluoromethyl ether) **(4b):** Colorless oil; yield: 47%. ^{1}H NMR: δ = 7.45–7.29 (m, 5H), 6.72 (bd, 1H, $^3J_{H,H}$ = 15.8 Hz), 6.29 (dt, 1H, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 6.4 Hz), 4.65 (dd, 2H, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 1.3 Hz); ^{13}C NMR: δ = 135.8, 135.3, 128.8, 128.6, 126.9, 121.9 (q, $^1J_{C,F}$ = 255.2 Hz), 121.5, 68.1 (q, $^3J_{C,F}$ = 3.5 Hz); ^{19}F NMR: δ = −60.54 (s); anal. calcd. for $C_{10}H_9F_3O$: C 59.41, H 4.49; found: C 59.53, H 4.40.

2,6-Dimethyl-8-(trifluoromethoxy)oct-2-ene (citronellyl trifluoromethyl ether) **(4e):** Colorless oil; yield: 58%. ^{1}H NMR: δ = 5.09 (m, 1H), 4.00 (m, 2H), 1.98 (m, 2H), 1.63–1.12 (massif, 11H) ; 0.91 (d, 3H, $^3J_{H,H}$ = 6.4 Hz); ^{13}C NMR: δ = 131.7, 124.5, 121.9 (q, $^1J_{C,F}$ = 253.6 Hz), 66.0 (q, $^3J_{C,F}$ = 3.1 Hz), 37.0, 35.7, 29.1, 25.8, 25.5, 19.3, 17.7; ^{19}F NMR: δ = −61.13 (s); anal. calcd. for $C_{11}H_{19}F_3O$: C 58.91, H 8.54; found: C 59.12, H 8.45.

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