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Oxidation of α-Trifluoromethyl Alcohols Using a Recyclable Oxoammonium Salt

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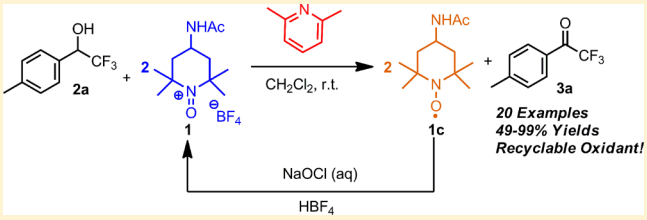
Supporting Information

ABSTRACT: A simple, mild method for the oxidation of α-trifluoromethyl alcohols to trifluoromethyl ketones (TFMKs) using the oxoammonium salt 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate (**1**) is described. Under basic conditions, oxidation proceeds rapidly and affords good to excellent yields of TFMKs, without concomitant formation of the hydrate. The byproduct of the oxidation, 4-acetylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (**1c**), is easily recovered and can be conveniently reoxidized to regenerate the oxoammonium salt.



INTRODUCTION

Incorporation of the trifluoromethyl (CF_3) group into organic molecules is known to have profound effects on their physical and chemical properties.[1] One of the most important effects, enhancement of lipophilicity, is of great utility to medicinal chemists.[1d−f] Many recent drugs and drug candidates for treating a variety of ailments from cancer to viral infections feature this moiety.[1e,2]

One class of compounds containing the CF_3 group that is of particular interest is the trifluoromethyl ketone (TFMK). TMFKs are themselves potent enzyme inhibitors[3] and also serve as critical intermediates in constructing trifluoromethylated heterocycles,[4] medicinal compounds,[5] and fluorinated analogues of natural products.[6] The importance of this motif is exemplified in the synthesis of one of the leading antiretroviral drugs in the treatment of HIV, Efavirenz (Sustiva).[7] TFMKs have also found application in probing enzymatic mechanisms by mimicking transition states because of their ability to readily form stable hydrates.[8]

Despite their importance, the incorporation of TFMKs into organic molecules is nontrivial. Current methods typically involve using one of two major routes: acetylation with trifluoroacetic acid derivatives (via organometallic intermediates) or oxidation of α-CF_3 alcohols.[9] Due to the inherent danger of working with main-group organometallics and their high degree of reactivity with a variety of functional groups, the latter route is often preferred.[10]

Perfluoroalcohols are notoriously difficult to oxidize, a property that can likely be attributed to their electron-deficient nature.[11] Unlike their hydrocarbon analogues, many traditional methods for oxidation (metal or DMSO-based) are ill-suited to oxidize a broad range of α-CF_3 alcohols and attempts using these methods result in poor yields or failure.[12] The overwhelming majority of oxidation methodologies employ the powerful Dess−Martin periodinane (DMP). However, there are significant drawbacks of using DMP, including its cost and the fact that spent oxidant cannot be easily recovered.[13] Moreover, in the case of α-CF_3 alcohols, a large excess of the oxidant is required to obtain acceptable yields of TFMKs.[10,11] Another problem with the use of most current oxidation methodologies is the concomitant formation of the hydrate of the TFMK rather than the desired ketone product. Subsequently, diminished yields of TFMKs are obtained because of the high degree of solubility of these hydrates in water and difficulties in dehydrating them back to the TFMK. To address this, one option is to use polymer-supported permanganate in conjunction with supported scavengers where the oxidation can be performed and the product obtained without the need for an aqueous workup or column chromatography.[14]

Seeking an alternative oxidant for α-CF_3 alcohols as well as avoiding formation of the hydrate, our attention turned to the possibility of using oxoammonium ions to perform this transformation. TEMPO and its other oxyl analogues (including AcNH-TEMPO, **1c**) are known to be effective catalysts for the oxidation of a variety of functional groups in the presence of a stoichiometric terminal oxidant (typically using commercial bleach containing NaOCl).[15] While examples of oxidation of α-CF_3 alcohols using TEMPO-based catalysts are known,[16,17] the reactions are biphasic (typically DCM/basic water) and hence diminished yields of the TFMK product are obtained due to hydrate formation. Therefore, TEMPO-based catalysts have been sparsely employed in the literature to

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oxidize these alcohols. Alternatively, we were interested in determining whether 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (**1**; "Bobbitt's salt"),[18] could be used as a stoichiometric oxidant of α-CF_3 alcohols. Such a methodology would have several advantages over current methods: (1) oxoammonium salts are extremely mild and *selective* oxidants, allowing for a broad functional group tolerance, (2) oxidations of alcohols using these salts can be conducted without water, (3) oxoammonium salts are metal-free, nontoxic, and, most importantly, *recyclable*, and (4) **1** can easily be prepared in house on a large scale at minimal expense ($0.50/g on a mole scale).[18a,b] We report our results here.

RESULTS AND DISCUSSION

We began our investigation by probing whether oxidation of α-CF_3 alcohols could be achieved using the standard conditions for stoichiometric oxoammonium-mediated oxidations.[18a] Using 2,2,2-trifluoro-1-(*p*-tolyl)ethanol (**2a**) as a representative substrate, prepared via trifluoromethylation of the corresponding aldehyde using the Ruppert–Prakash reagent (TMS-CF_3),[19] we attempted oxidation in both neutral and weakly acidic media.[18a] However, even after extended reaction times, the desired product, **3a**, was not detected in either case. On the basis of the posited mechanism of Bailey,[18c,g] oxidation under these conditions would result in a highly destabilized α-CF_3 carbocation following the required hydride transfer (Figure 1).

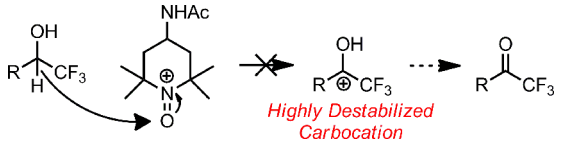


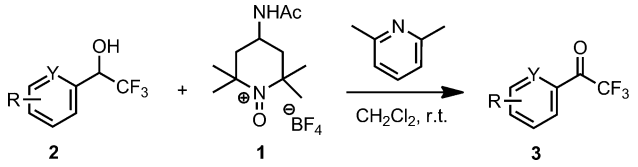
Figure 1. Postulation as to why oxidation in neutral and weakly acidic media was unsuccessful.

Our attempts to oxidize these α-CF_3 alcohols likely failed due to the high activation barrier of this process.[18c,g] It is known that β-oxygen compounds, which share electronics similar to those of α-CF_3 alcohols, fail to oxidize readily when treated with **1** under standard conditions, likely for the same reason.[18d,f]

We therefore attempted the base-mediated oxidation of **2a**. To our delight, upon treatment of **2a** with 2.5 equiv of **1** and 2.25 equiv of pyridine in dichloromethane, we observed slow but steady formation of **3a**. Seeking to accelerate the rate of oxidation, we switched to the more basic 2,6-lutidine.[20] While the reaction in the presence of pyridine typically took overnight to reach completion, in the case of 2,6-lutidine the reaction was complete within a few hours. Attempts using a stronger base, 2,4,6-collidine,[20] were successful, and the rate of the reaction was dramatically accelerated, but difficulties in purification of the TFMK product led us to choose 2,6-lutidine as the optimal base for our methodology.

With reaction conditions in hand, we sought to explore the substrate scope of the oxidation by first screening a variety of aryl systems (Table 1). Both electron-rich (entries 1–3, 7, and 9) and electron-poor (entries 4–6, 8, and 10) arenes are well-tolerated under our oxidation conditions. We attribute the slightly diminished yield of certain substrates (entries 1 and 8) to the volatility of their corresponding TFMK products. A representative pyridyl-functionalized substrate (**2k**, entry 11) is equally well-tolerated, affording **3k** in excellent yield.

Table 1. Oxidation of Aryl-Functionalized Substrates[a]



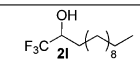
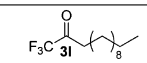
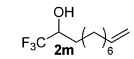
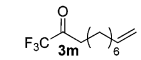
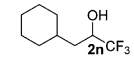
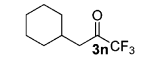
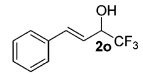
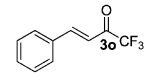
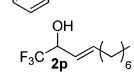
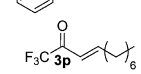
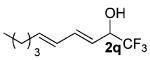
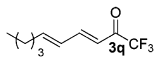
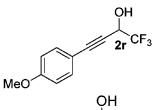
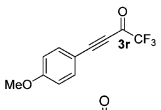
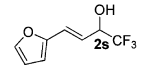
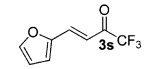
2 1 3

entry	substrate	R[b]	Y	product	yield, %[c]
1	**2a**	4-Me	C–H	**3a**	71
2	**2b**	4-OMe	C–H	**3b**	90
3	**2c**	3-OMe	C–H	**3c**	89
4	**2d**	4-NO_2	C–H	**3d**	99
5	**2e**	3-NO_2	C–H	**3e**	96
6	**2f**	2-Br, 4-F	C–H	**3f**	78
7	**2g**	3,4-OCH_2O-	C–H	**3g**	97
8	**2h**	2-F	C–H	**3h**	73
9	**2i**	2-OMe	C–H	**3i**	96
10	**2j**	2-NO_2	C–H	**3j**	89
11	**2k**	H	N	**3k**	96

[a]Conditions unless otherwise noted: α-CF_3 alcohol (1 equiv), **1** (2.5 equiv), 2,6-lutidine (2.25 equiv), CH_2Cl_2 (0.4 M in starting alcohol). [b]α-CF_3 alcohols were prepared via trifluormethylation of the corresponding aldehydes using TMS-CF_3. [c]Isolated yield after purification.

In addition to investigating aryl-functionalized substrates, we also investigated aliphatic, allylic, and propargylic α-CF_3 alcohols to see if they too would be compatible with our oxidation conditions (Table 2). Aliphatic substrates (entries 1–3) failed to oxidize appreciably under our standard conditions, affording primarily starting material, despite increased reaction times and additional oxidant loading. However, when a stronger base was utilized (1,5-diazabicyclo[4.3.0]non-5-ene, DBN),

Table 2. Oxidation of Alkyl- And Allyl-Functionalized Substrates[a]

entry	CF_3 alcohol	CF_3 ketone	yield[b]
1[c]			50%
2[c]			60%
3[c]			49%
4[d]			72%
5[d]			93%
6[d]			99%
7[d]			85%
8[d]			68%

[a]α-CF_3 alcohols were prepared via trifluormethylation of the corresponding aldehydes using TMS-CF_3. [b]Isolated yield after purification. [c]Conditions: α-CF_3 alcohol (1 equiv), **1** (3.0 equiv), DBN (2.5 equiv), CH_2Cl_2 (0.1 M in starting alcohol). [d]Conditions: α-CF_3 alcohol (1 equiv), **1** (2.5 equiv), 2,6-lutidine (2.25 equiv), CH_2Cl_2 (0.4 M in starting alcohol).

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rapid conversion to the desired TMFK was observed (entries 1−3). We attribute this change in reactivity to a more tightly bound ion pairing between the now formally deprotonated α-CF_3 alcohol and **1**, resulting in a facile hydride transfer. As a practical matter, additional base and salt were necessary for optimal conversion, since DBN is slowly oxidized by the oxoammonium salt. Additionally, because of this degradation of the base, further purification was necessary, resulting in diminished isolated yields. When a point of unsaturation was introduced at the carbon adjacent to the α-CF_3 alcohol moiety, oxidation proceeded smoothly with 2,6-lutidine as the base. Both conjugated (Table 2, entries 4, 6, and 8) and nonconjugated (entry 5) allylic alcohols afford excellent yields. A propargylic substrate (**2r**, entry 7) is equally well-tolerated and the reaction proceeds much faster than expected on the basis of previous propargylic oxidations using **1**.[18a]

To further demonstrate the power of our oxidation methodology over current methods and exploit the selectivity of **1**, a substrate (**2t**) containing both α-CF_3 alcohol (Figure 2, in blue) and benzyl alcohol (Figure 2, in red) functionalities was prepared. In the case of most other oxidants, selective oxidation would be unlikely and hence a protecting group strategy would need to be used. However, by simple adjustment of the reaction conditions, *chemoselective* oxidation was possible. The unsubstituted alcohol was readily oxidized to **2t′** in excellent yield under weakly acidic conditions, while the α-CF_3 alcohol group remained intact. The α-CF_3 alcohol **2t′** could then be oxidized using the standard basic conditions to afford **3t** in good yield.

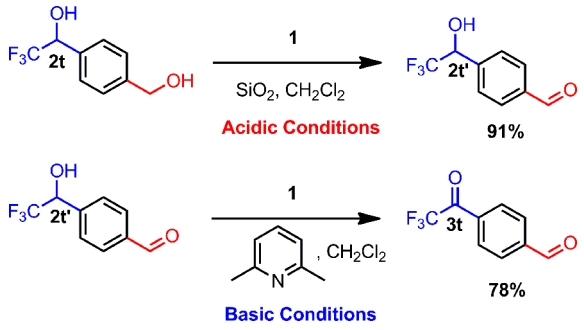
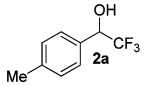
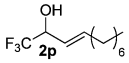
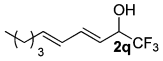
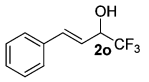
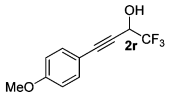


Figure 2. Chemoselective oxidations based on reaction media.

To gain further insight into the reaction, we obtained rate data for our oxidation using the method of Mullet and Nodding.[21] Unlike the competitive rate studies typically used,[18a] we believed that this alternative method would be more effective for our systems in obtaining this information because of complications that arose when analyzing ^1H and ^{19}F NMR spectra. We determined the relative rates of oxidation of five representative substrates (Table 3).

Aryl-substituted substrates all oxidized at about the same rate, and therefore, we utilized **2a** as our model substrate for comparison. From the data in Table 3, we theorize that there is a large steric component to the reaction. We suggest that the combined electronic repulsion by the highly electron-rich CF_3 group and the steric repulsion by any β-substituent contribute significantly to oxidant/alcohol complexation and hence successful oxidation. This likely explains the drastic increase in rate with increasing conjugation as well as the large rate acceleration observed for **2r** over **2a** and is in agreement with the current model for oxidation by oxoammonium cations under basic conditions.[18c]

Table 3. Relative Rates of Oxidation of α-CF_3 Alcohols to Their Corresponding TFMKs by Oxoammonium Salt Oxidation

entry	CF_3 alcohol	relative oxidation rate
1		1.00
2		0.24
3		0.50
4		0.61
5		120

Finally, to determine if the spent oxidant could be recycled, crude 4-acetylamino-2,2,6,6-tetramethyl-1-piperidinyloxy (**1c**) from several runs was dissolved in water and salted out with sodium chloride to afford an 87% recovery of **1c**. This recovered nitroxide was converted into **1** in the standard manner in comparable yield (70%) and used for later oxidations with no detrimental effect on oxidant reactivity and with a TFMK yield no more than 5% different than that using freshly made **1**.

CONCLUSION

We have reported here an effective, mild method for the oxidation of α-CF_3 alcohols to their corresponding TFMKs. The reaction is compatible with a wide array of substrates, proceeds rapidly, can be used to affect chemoselective oxidations, and affords TFMKs in excellent yield. Moreover, the spent oxidant is easily recovered and recycled.

EXPERIMENTAL SECTION

General Considerations. All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a three- or four-port dual-bank manifold. Nitrogen was used to provide such an atmosphere. ^1H NMR spectra obtained in $CDCl_3$ were referenced to residual nondeuterated chloroform (7.26 ppm) in the deuterated solvent or in deuterated methanol referenced to TMS (0.00 ppm). ^{13}C NMR spectra obtained in $CDCl_3$ were referenced to chloroform (77.3 ppm) or in deuterated methanol referenced to TMS (0.00 ppm). ^{19}F NMR spectra were referenced to fluorobenzene (−115.3 ppm) or hexafluorobenzene (−164.9 ppm).[22] Reactions were monitored by GCMS, ^1H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/ethyl acetate as the eluent and visualized using permanganate stain, *p*-anisaldehyde stain, Seebach's stain, and/or UV light. Flash chromatography and silica plugs utilized flash silica gel (60 Å porosity, 32−63 μm).

Chemicals. $CDCl_3$ was stored over 4 Å molecular sieves and anhydrous K_2CO_3. Unless otherwise specified, all aldehydes were purchased from commercial sources and used without further purification. (Trifluoromethyl)trimethylsilane and 2-bromo-4-fluorobenzaldehyde were purchased from Synquest Laboratories. 4-Amino-2,2,6,6-tetramethylpiperidine and sodium tungstate, used to prepare oxoammonium salt **1**, were supplied by Dr. James M. Bobbitt via the TCI America Corp.

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Oxidant Preparation.[18a] *4-Acetamido-2,2,6,6-tetramethylpiperidin-1-ium Acetate (**1b**).* To a 4 L Erlenmeyer flask was added 2,2,6,6-tetramethylpiperidin-4-amine (**1a**; 156.27 g, 1 mol, 1 equiv) and anhydrous Et_2O (564 mL, 1.774 M in **1a**) along with a large stir bar. The flask was cooled to 0 °C in a large ice bath. While the mixture was vigorously stirred, acetic anhydride (306.27 g, 3 mol, 3 equiv) in 138 mL of anhydrous Et_2O was added dropwise over 1 h via an addition funnel. Upon addition of the anhydride, the solution instantaneously turned white and a precipitate formed. The milk-white mixture was allowed to react overnight. The next day the white solid was filtered through a large medium-porosity fritted funnel and washed four times (150 mL each) with anhydrous Et_2O and placed on a large watch glass to dry overnight to give **1b** (242.22 g, 94%), which was carried on directly to the next step without further purification. (*Note*: normally **1b** was allowed to dry overnight. However, if it was gently warmed by placing the watch glass on top of an oven, the solid dried much faster and was usable the same day.)

*4-Acetamido-2,2,6,6-tetramethylpiperidin-1-yl)oxyl (**1c**).* In a 6 L beaker equipped with a large stir bar was added **1b** (242.22 g, 0.9375 mol, 1 equiv) and deionized water (1.736 L, 0.54 M in **1b**). The solution was stirred vigorously, and once all of the **1b** had dissolved, Na_2CO_3 (231.52 g, 2.18 mol, 2.33 equiv) was added in four portions over 10 min. After addition of Na_2CO_3 was complete, Na_2WO_4 (15.426 g, 0.052 mol, 0.056 equiv) and EDTA (12.33 g, 0.0422 mol, 0.045 equiv) were added all at once. After 5 min, 30 wt % H_2O_2 (300 mL, 99.80 g, 2.934 mol, 3.13 equiv) was added dropwise via an addition funnel over the course of 2 h. Once the addition was complete, the solution gradually began to foam and became yellow. The solution then became a vivid orange while continuing to produce a small foam layer. The solution was stirred for 72 h. The beaker was then cooled to 0 °C in a large ice bath for 30−45 min, causing an orange precipitate to form. The solid was filtered through a large medium-porosity fritted funnel and washed with ice-cold water. The orange solid was placed on a watch glass and allowed to dry in the same way as for **1b**. The volume of the filtrate was estimated, and enough NaCl was added to this aqueous orange liquid to bring it to 3 M in NaCl. This resulted in the immediate "salting out" of the remaining **1c** in this layer. The solid was filtered and washed with a minimum amount of ice-cold water. This orange solid was also placed on the watch glass and dried, giving **1c** (yield 164.676 g, 82.5%; mp 145−146 °C, lit. mp 145−147 °C).

*4-Acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium Tetrafluoroborate (**1**).* In a 2 L beaker, equipped with a large stir bar ,was added **1c** (164.676 g, 0.772 mol, 1 equiv) and deionized water (330 mL, 2.34 M in **1c**). While the mixture was stirred vigorously, 48 wt % HBF_4 (163.1 g, 0.891 mol, 1.154 equiv) was added dropwise to the beaker via an addition funnel over the course of 15 min. The solution turned a light yellow and was stirred for 30 min. Upon completion of this time, the beaker was cooled to 0 °C for 10 min. At this time, fresh commercial sodium hypochlorite (Chlorox 6.00 wt %, 28.735 g, 0.386 mol, 0.5 equiv) was added dropwise via an addition funnel over the course of 1 h. Once completely added, to the yellow-orange solution was added $NaBF_4$ (84.76 g, 0.772 mol, 1 equiv) and the reaction mixture was stirred for 3 h (addition of $NaBF_4$ improved the yield substantially, likely due to reduced solubility of **1** via the common ion effect). The reaction mixture was then filtered through a large medium-porosity filter funnel and washed with a minimum amount of cold CH_2Cl_2 and cold water. Upon drying, **1** (211.0 g, 91%) was obtained as a fine yellow powder.

For enhanced purity, **1** can be recrystallized from boiling deionized water followed by filtration through coarse filter paper and rapid cooling to 0 °C in an ice bath. However, this often leads to only 50−60% recovered of pure **1**. In the case of this study, recrystallized **1** did not have any beneficial effect. In fact, oxidation of α-CF_3 alcohols seemed to occur faster, likely due to the enhanced surface area to volume when in the powdered form.

Synthesis of α-Trifluoromethyl Alcohols and Aldehyde Precursors When Applicable: Representative Procedure for Preparation of α-CF_3 Alcohols. *Preparation of 2,2,2-Trifluoro-1-(p-tolyl)ethanol*[23] *(**2a**).* The following is a modification of the procedure outlined by Kelly et al.[24] To a 100 mL round-bottom flask equipped with a stir bar was added THF (24 mL), *p*-tolualdehyde (2.723 g, 0.020 mol, 0.83 M, 1 equiv), and (trifluoromethyl)-trimethylsilane (3.12 g, 0.022 mol, 1.3 equiv). The flask was sealed with a rubber septum and placed under a N_2 atmosphere via an inlet needle. The reaction mixture was cooled to 0 °C in an ice−water bath and stirred via a magnetic stir plate. After approximately 10 min, TBAF (1 M in THF, 0.2 mL, 0.0002 mol, 0.01 equiv) was added dropwise via a syringe. Note: on small scales, i.e. <20 mmol, the TBAF could be added relatively quickly. However, upon scale-up the addition of TBAF is quite exothermic. Hence, it is recommended that the TBAF be added as slowly as possible and/or the reaction mixture be cooled to a temperature lower than 0 °C.

After 10 min, the ice bath was removed and the solution was stirred for approximately 6 h at room temperature. To cleave the silyl ether intermediate, the reaction mixture was cooled to 0 °C in an ice bath. After 10 min, water (2 mL, 0.110 mol, 5.5 equiv) was added via a syringe. TBAF (1 M in THF, 2 mL, 0.002 mol, 0.1 equiv) was then added. After 10 min the ice bath was removed and the reaction mixture was stirred at room temperature. When the cleavage was judged to be complete (determined by GC-MS or NMR), the contents of the flask were transferred to a separatory funnel. *Note*: some of the silyl ethers were very slow to cleave and required another addition of TBAF and water. Brine (∼100 mL) and Et_2O (∼150 mL) were added, and the layers were partitioned. The aqueous layer was back-extracted (3 × ∼50 mL) with Et_2O. The combined ether layers were dried with Na_2SO_4, and the solvent was removed in vacuo via rotary evaporation to afford crude **2**, which was further purified by vacuum distillation (bp 85−87 °C @ 11.5 mmHg) to give the pure α-CF_3 alcohol **2** (2.75 g, 78%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.79 (br s, 1 H), 4.95 (q, J = 6.68 Hz, 1 H), 7.40−7.51 (m, 5 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 73.0 (q, J_{C-C-F} = 32.0 Hz, CH), 120.3−128.8 (q, J_{C-F} = 281.7 Hz, CF_3), 127.7 (CH), 127.7 (CH), 128.9 (CH), 129.8 (CH), 134.2 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.13 (d, J = 6.81 Hz); GC-MS (EI) 190 ($[M]^+$, 45%), 122 (10%), 121 (100%), 93 (54%), 91 (60%), 77 (35%), 69 (6%), 65 (12%).

2,2,2-Trifluoro-1-(p-tolyl)ethanol[25] *(**2a**).* The title compound (3.02 g, 79%) was prepared according to the representative procedure from *p*-tolualdehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp 59−62 °C @ 0.4 mmHg) to give the pure α-CF_3 alcohol **2a** as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm) 2.39 (s, 3 H), 2.84−2.97 (m, 1 H), 4.95 (q, J = 6.52 Hz, 1 H), 7.23 (d, J = 7.57 Hz, 2 H), 7.36 (d, J = 7.57 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 126 MHz; δ, ppm) 21.4 (CH_3), 73.0 (q, J_{C-C-F} = 32.1 Hz, CH), 121.4−128.0 (q, J_{C-F} = 283.2 Hz, CF_3), 127.6 (CH), 129.6 (CH), 131.4 (C), 139.8 (C); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −78.25 (d, J = 6.81 Hz); GC-MS (EI) 190 ($[M]^+$, 45%), 122 (10%), 121 (100%), 93 (54%), 91 (60%), 77 (35%), 69 (6%), 65 (12%).

2,2,2-Trifluoro-1-(4-methoxyphenyl)ethanol[28] *(**2b**).* The title compound (3.284 g, 80%) was prepared according to the representative procedure from *p*-anisaldehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp 87−90 °C @ 1 mmHg) to give the pure α-CF_3 alcohol **2b** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.24−3.37 (m, 1 H), 3.80 (s, 3 H), 4.91 (q, J = 6.85 Hz, 1 H), 6.92 (d, J = 8.80 Hz, 2 H), 7.37 (d, J = 8.80 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.5 (CH_3), 72.6 (q, J_{C-C-F} = 31.5 Hz, CH), 114.3 (CH), 120.4−128.8 (q, J_{C-F} = 281.7 Hz, CF_3), 126.5 (d, $J_{C-C-C-F}$ = 1.5 Hz, CH), 129.1 (C), 160.6 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.61 (d, J = 6.81 Hz); GC-MS (EI) 206 ($[M]^+$, 37%), 137 (100%), 109 (27%), 94 (28%), 77 (25%), 69 (4%).

*2,2,2-Trifluoro-1-(3-methoxyphenyl)ethanol (**2c**).* The title compound (3.405 g, 83%) was prepared according to the representative procedure from *m*-anisaldehyde (2.723 g, 0.020 mol) followed by vacuum distillation (bp 78−80 °C @ 0.5 mmHg) to give the pure α-CF_3 alcohol **2c** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.81 (s, 3 H), 4.95 (q, J = 6.85 Hz, 1 H), 6.95 (ddd, J = 8.25, 2.51, 0.98 Hz, 1 H), 7.01−7.06 (m, 2 H), 7.32 (t, J = 7.80 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.6 (CH_3), 73.0 (q, J_{C-C-F} = 32.3 Hz, CH), 113.3 (d, $J_{C-C-C-F}$ = 1.5 Hz, CH), 115.4 (CH), 120.5−128.7 (q, J_{C-F} = 281.7 Hz, CF_3), 120.1 (CH), 130.0 (CH), 135.8 (C),

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159.9 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.26 (d, J = 6.81 Hz); GC-MS (EI) 206 ([M]$^+$, 80%), 137 (65%), 135 (11%), 109 (100%), 107 (10%), 94 (43%), 77 (39%), 69 (6%), 66 (12%), 64 (11%); HRMS (ESI+) calcd for $C_9H_9F_3O_2$ [M + H]$^+$ 207.0633, found 207.0641.

2,2,2-Trifluoro-1-(4-nitrophenyl)ethanol[28] ***(2d)***. The title compound (2.690 g, 61%) was prepared according to the representative procedure from *p*-nitrobenzaldehyde (3.022 g, 0.020 mol) followed by recrystallization from boiling water to give the pure α-CF_3 alcohol **2d** as a light yellow crystalline solid (mp 132−133 °C, lit.[28] mp 129−131 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 5.40 (q, J = 7.09 Hz, 1 H), 7.94 (apparent doublet, J = 8.80 Hz, 2 H), 8.44 (dt, J = 8.80, 2.00 Hz, 2 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 73.5 (q, J_{C-C-F} = 31.5 Hz, CH), 123.1−131.5 (q, J_{C-F} = 281.7 Hz, CF_3), 125.7 (CH), 131.3 (CH), 145.5 (C), 151.2 (C); ^{19}F NMR (MeOD, 376 MHz; δ, ppm) −77.26 (d, J = 6.81 Hz); GC-MS (EI) 221 ([M]$^+$, 7%), 152 (97%), 150 (58%), 127 (16%), 106 (11%), 105 (16%), 104 (26%), 94 (12%), 92 (10%), 78 (11%), 77 (19%), 76 (20%), 75 (11%), 69 (9%), 51 (11%), 50 (15%), 44 (17%), 40 (100%).

2,2,2-Trifluoro-1-(3-nitrophenyl)ethanol[28] ***(2e)***. The title compound (4.010 g, 91%) was prepared according to the representative procedure from *m*-nitrobenzaldehyde (3.022, 0.020 mol) followed by filtration through a silica gel plug using anhydrous Et_2O as an eluant to give the pure α-CF_3 alcohol **2e** as a yellow solid (mp 49−50 °C, lit.[28] 50.6−52.2 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 5.42 (q, J = 7.01 Hz, 1 H), 7.83 (t, J = 8.07 Hz, 1 H), 8.08 (dd, J = 7.70, 0.61 Hz, 1 H), 8.43 (ddd, J = 8.31, 2.45, 0.98 Hz, 1 H), 8.58 (s, 1 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 72.0 (q, J_{C-C-F} = 31.6 Hz, CH), 121.8−130.2 (q, J_{C-F} = 281.9 Hz, CF_3), 123.6 (CH), 124.9 (CH), 135.0 (CH), 139.4 (C), 149.7 (C); ^{19}F NMR (MeOD, 377 MHz; δ, ppm) −77.78 (d, J = 6.81 Hz); GC-MS (EI) 221 ([M]$^+$, 5%), 152 (100%), 150 (16%), 127 (18%), 106 (11%), 105 (24%), 78 (12%), 77 (20%), 69 (5%).

1-(2-Bromo-4-fluorophenyl)-2,2,2-trifluoroethanol[26] ***(2f)***. The title compound (3.960 g, 72%) was prepared according to the representative procedure from 2-bromo-4-fluorobenzaldehyde (4.06 g, 0.020 mol) followed by vacuum distillation (bp 68−70 °C @ 0.25 mmHg) to give the pure α-CF_3 alcohol **2f** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.52 (br s, 1 H), 5.56 (q, J = 6.28 Hz, 1 H), 7.10 (td, J = 8.10, 2.20 Hz, 1 H), 7.33 (dd, J = 8.07, 2.69 Hz, 1 H), 7.64 (dd, J = 8.68, 5.99 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 70.8 (q, J_{C-C-F} = 33.0 Hz, CH), 115.5 (d, J_{C-C-F} = 22.0 Hz, CH), 120.2−128.6 (qd, J_{C-F} = 282.4, 1.5 Hz, CF_3), 120.4 (d, J_{C-C-F} = 24.9 Hz, CH), 124.3 (d, $J_{C-C-C-F}$ = 9.5 Hz, CH), 130.1 (dd, $J_{C-C-C-F}$ = 3.7, 1.5 Hz, C), 130.8 (d, $J_{C-C-C-F}$ = 9.0 Hz, C), 163.0 (d, J_{C-F} = 253.8 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −109.34 (q, J = 6.81 Hz, 1 F), −77.79 (d, J = 5.45 Hz, 3 F); GC-MS (EI) 274 ([M]$^+$, 20%), 272 ([M]$^+$, 21%), 205 (95%), 203 (100%), 175 (10%), 172 (6%), 123 (21%), 96 (68%), 95 (40%), 94 (14%), 75 (18%), 69 (10%).

1-(Benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol[27] ***(2g)***. The title compound (3.560 g, 81%) was prepared according to the representative procedure from piperonal (3.003 g, 0.020 mol) followed by vacuum distillation (bp 102−105 °C @ 0.6 mmHg) to give the pure α-CF_3 alcohol **2g** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 2.95 (s, 1 H), 4.90 (q, J = 6.60 Hz, 1 H), 5.98 (s, 2 H), 6.82 (d, J = 7.83 Hz, 1 H), 6.91 (apparent doublet, J = 7.83 Hz, 1 H), 6.96 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 72.8 (q, J_{C-C-F} = 32.3 Hz, CH), 101.6 (CH_2), 107.9 (d, J = 1.5 Hz, CH), 108.5 (CH), 120.3−128.7 (q, J_{C-F} = 281.7 Hz, CF_3), 121.8 (CH), 128.0 (d, $J_{C-C-C-F}$ = 1.5 Hz, C), 148.2 (C), 148.8 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.53 (d, J = 6.81 Hz); GC-MS (EI) 220 ([M]$^+$, 80%), 152 (10%), 151 (100%), 149 (24%), 123 (16%), 121 (18%), 93 (100%), 75 (13%), 69 (8%), 65 (58%), 63 (18%), 40 (11%), 39 (11%).

2,2,2-Trifluoro-1-(2-fluorophenyl)ethanol[7] ***(2h)***. The title compound (3.000 g, 77%) was prepared according to the representative procedure from *o*-fluorobenzaldehyde (2.480 g, 0.020 mol) followed by vacuum distillation (bp 49−51 °C @ 1.0 mmHg) to give the pure α-CF_3 alcohol **2h** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.87 (br s, 1 H), 5.41 (q, J = 6.60 Hz, 1 H), 7.10 (ddd, J = 10.03, 8.56, 0.98 Hz, 1 H), 7.21 (td, J = 7.58, 0.98 Hz, 1 H), 7.34−7.43 (m, 1 H), 7.61 (t, J = 7.34 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 66.5 (qd, J_{C-C-F} = 33.7, 3.7 Hz, CH), 115.8 (d, J_{C-C-F} = 21.3 Hz, CH), 120.2−128.7 (qd, J_{C-F} = 282.4, 2.2 Hz, CF_3), 121.7 (d, J_{C-C-F} = 11.7 Hz, C), 124.8 (d, J_{C-C-F} = 3.7 Hz, CH), 128.9 (d, $J_{C-C-C-F}$ = 2.9 Hz, CH), 131.5 (d, $J_{C-C-C-F}$ = 8.8 Hz, CH), 160.7 (d, J_{C-F} = 248.0 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −118.06 to −117.93 (m, 1 F), −78.45 (t, J = 6.13 Hz, 3 F); GC-MS (EI) 194 ([M]$^+$, 27%), 127 (19%), 125 (100%), 123 (13%), 97 (56%), 95 (16%), 77 (36%), 75 (11%), 69 (9%), 51 (10%).

2,2,2-Trifluoro-1-(2-methoxyphenyl)ethanol ***(2i)***. The title compound (3.520 g, 85%) was prepared according to the representative procedure from *o*-methoxybenzaldehyde (2.720 g, 0.020 mol) followed by vacuum distillation (bp 68−70 °C @ 0.4 mmHg) to give the pure α-CF_3 alcohol **2i** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm) 3.86 (s, 3 H), 3.96 (br s, 1 H), 5.31 (q, J = 7.30 Hz, 1 H), 6.96 (d, J = 8.20 Hz, 1 H), 7.03 (td, J = 7.57, 1.26 Hz, 1 H), 7.36−7.40 (m, 1 H), 7.42 (d, J = 7.57 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz; δ, ppm) 55.9 (CH_3), 69.7 (q, J_{C-C-F} = 32.1 Hz, CH), 111.5 (CH), 121.3 (CH), 121.6−128.3 (q, J_{C-F} = 283.2 Hz, CF_3), 122.4 (CH), 129.4 (C), 130.8 (CH), 157.8 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.10 (d, J = 6.81 Hz); GC-MS (EI) 206 ([M]$^+$, 46%), 137 (100%), 122 (10%), 121 (25%), 109 (15%), 107 (68%), 94 (14%), 77 (26%), 69 (5%); HRMS (ESI+) calcd for $C_9H_9F_3O_2$ [M + H − H_2O]$^+$ 189.0527, found 189.0519.

2,2,2-Trifluoro-1-(2-nitrophenyl)ethanol[28] ***(2j)***. The title compound (3.340 g, 76%) was prepared according to the representative procedure from *o*-nitrobenzaldehyde (3.020 g, 0.020 mol) followed by vacuum distillation (bp 94−96 °C @ 0.4 mmHg) to give the pure α-CF_3 alcohol **2j** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm) 3.59 (br s, 1 H), 6.16 (q, J = 6.10 Hz, 1 H), 7.55 (td, J = 7.80, 1.50 Hz, 1 H), 7.71 (td, J = 7.57, 1.26 Hz, 1 H), 7.95 (d, J = 8.20 Hz, 1 H), 7.99 (dd, J = 8.20, 1.26 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz; δ, ppm) 67.0 (q, J_{C-C-F} = 31.2 Hz, CH), 120.7−127.5 (q, J_{C-F} = 282.3 Hz, CF_3), 125.2 (CH), 129.2 (C), 129.7 (CH), 130.5 (CH), 134.0 (CH), 148.6 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −77.50 (d, J = 5.45 Hz); GC-MS (EI) 221 ([M]$^+$, 1%), 203 (10%), 152 (45%), 141 (15%), 135 (10%), 134 (87%), 127 (62%), 123 (100%), 121 (70%), 105 (41%), 104 (77%), 97 (14%), 95 (23%), 78 (14%), 77 (75%), 76 (19%), 75 (12%), 74 (10%), 69 (14%), 65 (12%), 51 (31%), 50 (17%).

2,2,2-Trifluoro-1-(pyridin-2-yl)ethanol[29] ***(2k)***. The title compound (2.920 g, 82%) was prepared according to the representative procedure from picolinaldehyde (2.142 g, 0.020 mol) followed by vacuum distillation (bp 75−77 °C @ 2.5 mmHg) to give the pure α-CF_3 alcohol **2k** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 5.03 (q, J = 6.60 Hz, 1 H), 5.55 (br s, 1 H), 7.37 (apparent triplet, J = 5.80 Hz, 1 H), 7.43 (apparent doublet, J = 8.07 Hz, 1 H), 7.78 (tt, J = 7.70, 1.71 Hz, 1 H), 8.61 (dd, J = 4.65, 1.22 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 71.0 (q, J_{C-C-F} = 32.3 Hz, CH), 120.1−128.6 (q, J_{C-F} = 283.9 Hz, CF_3), 122.9 (CH), 124.7 (CH), 137.5 (CH), 148.6 (CH), 151.4 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.08 (d, J = 6.81 Hz); GC-MS (EI) 177 ([M]$^+$, 1%, 110 (10%), 108 (100%), 106 (40%), 80 (16%), 79 (16%), 78 (87%), 69 (9%), 52 (13%), 51 (21%), 50 (10%).

1,1,1-Trifluorotridecan-2-ol ***(2l)***. The title compound (6.470 g, 67%) was prepared according to the representative procedure from dodecanal (6.920 g, 0.038 mol) followed by vacuum distillation (bp 90−92 °C @ 0.6 mmHg) to give the pure α-CF_3 alcohol **2l** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.88 (t, J = 7.10 Hz, 3 H), 1.21−1.36 (m, 16 H), 1.57 (qd, J = 9.50, 4.77 Hz, 2 H), 1.65−1.75 (m, 1 H), 2.48 (br s, 1 H), 3.89 (ddd, J = 9.78, 6.60, 3.18 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 14.3 (CH_3), 22.9 (CH_2), 25.1 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.8−29.9 (CH_2 × 4), 32.2 (CH_2), 70.8 (q, J_{C-C-F} = 30.8 Hz, CH), 121.3−129.7 (q, J_{C-F} = 283.2 Hz, CF_3); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −80.12 (d, J = 6.81 Hz); GC-MS (EI) 254 ([M]$^+$, 1%), 208 (6%), 193 (8%), 165 (8%), 155 (13%), 151 (17%), 141 (26%), 137 (21%), 131 (10%), 123 (18%), 117 (10%), 112 (11%), 111 (27%), 98 (18%), 97

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(42%), 85 (29%), 84 (34%), 83 (35%), 82 (10%), 81 (10%), 73 (11%), 71. (43%), 70 (49%), 69 (50%), 97 (15%), 57 (100%), 56 (48%), 55 (59%), 43 (91%), 42 (17%), 41 (65%), 40 (10%), 39 (13%); HRMS (ESI+) calcd for $C_{13}H_{25}F_3O$ $[M - H]^+$ 253.1779, found 253.1793.

*1,1,1-Trifluoroundec-10-en-2-ol (**2m**).* The title compound (8.020 g, 92%) was prepared according to the representative procedure from dec-9-enal (6.000 g, 0.0388 mol) followed by vacuum distillation (bp 63−65 °C @ 0.1 mmHg) to give the pure α-CF_3 alcohol **2m** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 1.21−1.47 (m, 9 H), 1.49−1.75 (m, 3 H), 2.04 (q, J = 7.01 Hz, 2 H), 2.62 (br s, 1 H), 3.88 (br s, 1 H), 4.89−5.05 (m, 2 H), 5.81 (ddt, J = 16.99, 10.21, 6.69, 6.69 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 101 MHz): δ ppm 25.2 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.8 (q, $J_{C-C-C-F}$ = 1.0 Hz, CH_2) 34.0 (CH_2), 70.8 (q, J_{C-C-F} = 31.0 Hz, 7 C), 114.5 (CH_2), 125.5 (q, J_{C-F} = 282.0 Hz, 2 C), 139.4 (CH); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −83.05 (d, J = 6.81 Hz); GC-MS (EI) 224 ($[M]^+$, 1%), 153, (14%), 150 (14%), 149 (11%), 139 (30%), 136 (25%), 135 (14%), 123 (15%), 113 (12%), 103 (14%), 99 (11%), 97 (22%), 95 (26%), 84 (14%), 83 (32%), 82 (10%), 81 (30%), 79 (18%), 77 (13%), 73 (12%), 71 (10%), 70 (37%), 69 (55%), 68 (24%), 67 (35%), 59 (14%), 57 (25%), 56 (37%), 55 (100%), 54 (20%), 53 (16%), 43 (27%), 42 (21%), 41 (82%), 39 (37%); HRMS (ESI+), calcd for $C_{11}H_{20}F_3O$ $[M + H]^+$ 225.1466, found 225.1451.

*3-Cyclohexyl-1,1,1-trifluoropropan-2-ol (**2n**).* The title compound (5.470 g, 71%) was prepared according to the representative procedure from 2-cyclohexylacetaldehyde (5.000 g, 0.0396 mol) followed by vacuum distillation (bp 51−53 °C @ 0.25 mmHg) to give the pure α-CF_3 alcohol **2n** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.81−0.93 (m, 1 H), 0.94−1.06 (m, 1 H), 1.09−1.34 (m, 3 H), 1.40−1.59 (m, 3 H), 1.61−1.83 (m, 5 H), 3.04 (br s, 1 H), 3.99 (dqd, J = 9.89, 6.65, 6.65, 6.65, 3.42 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 101 MHz; δ, ppm) 26.1 (CH), 26.4 (CH), 26.6 (CH), 32.2 (CH), 33.3 (CH), 34.3 (CH), 37.1 (CH), 68.4 (q, J_{C-C-F} = 30.8 Hz, CH), 121.5−129.9 (q, J_{C-F} = 283.2 Hz, CF_3); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −80.21 (d, J = 6.81 Hz, 213 F); GC-MS (EI) 196 ($[M]^+$, 1%), 178 (8%), 109 (8%), 83 (96%), 82 (100%), 81 (24%), 69 (13%), 67 (33%), 55 (60%), 41 (25%), 39 (12%); HRMS (ESI+) calcd for $C_9H_{15}F_3O$ $[M - H]^+$ 195.0997, found 195.1019.

(E)-1,1,1-Trifluoro-4-phenylbut-3-en-2-ol[30] *(**2o**).* The title compound (3.360 g, 76%) was prepared according to the representative procedure from *trans*-cinnamaldehyde (3.045 g, 0.020 mol) followed by vacuum distillation (bp 65−67 °C @ 1 mmHg) to give the pure α-CF_3 alcohol **2o** as a clear oil, which solidified upon standing to give a white solid (mp 44−45 °C, lit.[33] mp 42−43 °C): ^{1}H NMR ($CDCl_3$, 300 MHz; δ, ppm) 2.27 (br s, 1 H), 4.64 (quin, J = 6.50 Hz, 1 H), 6.21 (dd, J = 16.10, 6.59 Hz, 1 H), 6.87 (d, J = 16.10 Hz, 1 H), 7.28−7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 71.9 (q, J_{C-C-F} = 32.3 Hz, CH), 120.4−128.8 (q, J_{C-F} = 283.2 Hz, CF_3), 120.8 (CH), 127.2 (CH), 128.9 (CH), 129.2 (CH), 135.6 (CH), 136.7 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −78.94 (d, J = 6.81 Hz); GC-MS (EI) 202 ($[M]^+$, 48%), 134 (12%), 133 (100%), 131 (16%), 115 (43%), 105 (21%), 103 (27%), 91 (19%), 78 (11%), 77 (33%), 69 (6%), 55 (27%), 51 (16%); HRMS (ESI+) calcd for $C_{10}H_9F_3O$ $[M + H - H_2O]^+$ 185.0578, found 185.0571.

*1,1,1-Trifluoroundec-3-en-2-ol (**2p**).* The title compound (3.880 g, 86%) was prepared according to the representative procedure from *trans*-dec-2-en-1-al (3.045 g, 0.020 mol) followed by vacuum distillation (bp 69−71 °C @ 0.35 mmHg) to give the pure α-CF_3 alcohol **2p** as a clear pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.88 (t, J = 6.80 Hz, 3 H), 1.19−1.34 (m, 8 H), 1.35−1.45 (m, 2 H), 2.10 (q, J = 6.80 Hz, 2 H), 2.70 (br s, 1 H), 4.37 (quin, J = 6.72 Hz, 1 H), 5.50 (dd, J = 15.65, 6.85 Hz, 1 H), 5.97 (dt, J = 15.40, 6.80 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 14.2 (CH_3), 22.8 (CH), 28.8 (CH), 29.0 (CH), 29.5 (CH), 32.0 (CH), 32.5 (CH), 71.9 (q, J_{C-C-F} = 32.1 Hz, CH), 124.4−128.8 (q, J_{C-F} = 281.7 Hz, CF_3), 121.9−122.4 (CH), 139.4 (CH); ^{19}F NMR (376 MHz; δ, ppm) −79.48 (d, J = 6.81 Hz); GC-MS (EI) 224 ($[M]^+$, 1%), 163 (13%), 155 (12%), 153 (16%), 150 (16%), 149 (12%), 139 (22%), 136 (11%), 98 (11%), 97 (26%), 95 (33%), 91 (12%), 85 (13%), 84 (43%), 83 (47%), 81 (34%), 77 (11%), 71 (16%), 70 (67%), 69 (100%), 68 (13%), 67 (24%), 57 (72%), 56 (84%), 55 (86%), 54 (10%), 53 (13%), 43 (92%), 42 (24%), 41 (79%), 39 (27%); HRMS (ESI+) calcd for $C_{11}H_{19}F_3O$ $[M - H]^+$ 223.1310, found 223.1312.

*1,1,1-Trifluorodeca-3,5-dien-2-ol (**2q**).* The title compound (3.420 g, 82%) was prepared according to the representative procedure from *trans,trans*-2,4-nonadienal (2.764 g, 0.020 mol) followed by vacuum distillation (bp 63−65 °C @ 0.15 mmHg) to give the pure α-CF_3 alcohol **2q** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.90 (t, J = 7.10 Hz, 3 H), 1.26−1.46 (m, 4 H), 2.11 (q, J = 6.85 Hz, 2 H), 2.89 (br s, 1 H), 4.43 (quin, J = 6.54 Hz, 1 H), 5.54 (dd, J = 15.41, 6.85 Hz, 1 H), 5.84 (dt, J = 15.16, 6.80 Hz, 1 H), 6.07 (dd, J = 14.92, 10.27 Hz, 1 H), 6.42 (dd, J = 15.28, 10.39 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 14.1 (CH_3), 22.5 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 71.7 (q, J_{C-C-F} = 32.3 Hz, CH), 120.4−128.8 (q, J_{C-F} = 281.7 Hz, CF_3), 121.5 (CH), 128.8 (CH), 137.3 (CH), 139.2 (CH); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −79.24 (d, J = 6.81 Hz); GC-MS (EI) 208 ($[M]^+$, 53%), 152 (38%), 148 (14%), 147 (14%), 141 (12%), 139 (22%), 127 (38%), 109 (16%), 103 (11%), 97 (17%), 95 (17%), 91 (13%), 83 (100%), 82 (11%), 81 (20%), 79 (41%), 77 (22%), 69 (22%), 67 (41%), 65 (11%), 55 (38%), 53 (12%), 43 (13%), 41 (29%), 39 (17%); HRMS (ESI+) calcd for $C_{10}H_{15}F_3O$ $[M - H]^+$ 207.0997, found 207.0991.

Synthesis of 1,1,1-Trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (2r). *3-(4-Methoxyphenyl)prop-2-yn-1-ol.* This procedure is a modification of the procedure outlined by Krause and Alexakis et al.[31] In a 250 mL round-bottom flask equipped with a stir bar was added Et_3N (150 mL) and 1-iodo-4-methoxybenzene (4.680 g, 0.020 mol, 0.134 M, 1 equiv). The solution was placed under a nitrogen atmosphere via a gas inlet adapter. To this solution was added $PdCl_2(PPh_3)_2$ (0.702 g, 0.001 mol, 0.05 equiv) and CuI (0.191 g, 0.001 mol, 0.05 equiv) all at once, turning the solution yellow. Propargyl alcohol (1.46 g, 0.026 mol, 1.3 equiv) was added at this time, turning the solution cloudy green. The reaction mixture was stirred for 18 h at room temperature. Upon completion of this time, the solution was filtered through Celite, with EtOAc as eluent. The filtrate was then further diluted with EtOAc (∼50 mL) and deionized water (∼100 mL), and the layers were separated. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried with Na_2SO_4, and the solvent was removed in vacuo, yielding a thick dark liquid. Purification was accomplished by flash column chromatography (gradient 9/1 to 8/2 Hex/EtOAc), affording the pure propargyl alcohol as a tan powdery solid (2.750 g, 85% yield, mp 62−64 °C, lit.[32] mp 65−68 °C): ^{1}H NMR ($CDCl_3$, 300 MHz; δ, ppm) 1.65 (t, J = 6.14 Hz, 1 H), 3.81 (s, 3 H), 4.48 (d, J = 6.14 Hz, 2 H), 6.84 (d, J = 9.10 Hz, 2 H), 7.38 (d, J = 8.77 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 51.9 (CH_2), 55.5 (CH_3), 85.8 (C), 86.2 (C), 114.2 (CH), 114.9 (C), 133.4 (CH), 156.0 (C); GC-MS (EI) 162 ($[M]^+$, 22%), 161 (11%), 135 (17%), 131 (7%), 89 (8%), 77 (7%), 44 (17%), 40 (100%).

3-(4-Methoxyphenyl)propiolaldehyde. This procedure is a modification of the procedure outlined by Bobbitt.[18a] In a 250 mL flask equipped with a stir bar were added DCM (170 mL), the previously prepared propargyl alcohol, 3-(4-methoxyphenyl)prop-2-yn-1-ol (2.750 g, 0.01696 mol, 0.1 M, 1 equiv), and **1** (5.340 g, 0.01780 mol, 1.05 equiv) followed by 2.750 g of SiO_2 (1 mass equiv to substrate), and the mixture was stirred for 24 h at room temperature. Upon reaction completion (confirmed by TLC, 8/2 Hex/EtOAc), the solvent was carefully removed in vacuo and the crude residue was filtered though a medium-porosity fritted funnel filled halfway with silica gel. The plug was washed several times with diethyl ether. The solvent was removed in vacuo by rotary evaporation to afford the pure aldehyde (1.720 g, 63%, mp 42−43 °C, lit.[25] mp 48−50 °C) as a tan solid: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.83 (s, 3 H), 6.89 (d, J = 8.80 Hz, 2 H), 7.54 (d, J = 8.80 Hz, 2 H), 9.37 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.7 (CH_3), 89.0 (C), 96.8 (C), 111.3 (C), 114.7 (CH), 135.6 (CH), 162.4 (C), 176.9 (CH); GC-MS (EI) 161 ($[M]^{2+}$, 11%), 160 ($[M]^+$, 100%), 159 (59%), 144 (13%), 132 (46%), 117 (34%), 116 (11%), 89 (44%), 88 (11%), 63 (20%), 62

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(16%), 44 (10%), 40 (36%); HRMS (ESI+) calcd for $C_{10}H_9F_3O_2$ [M + H]$^+$ 161.0603, found 161.0604.

*1,1,1-Trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (**2r**).* The title compound (1.480 g, 55%) was prepared according to the representative procedure from the previously prepared aldehyde, 3-(4-methoxyphenyl)propiolaldehyde, (1.860 g, 0.0116 mol) followed by vacuum distillation (bp 109−111 °C @ 0.1 mmHg) to give the pure α-CF_3 alcohol **2r** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.27 (br s, 1 H), 3.81 (s, 3 H), 4.91 (q, J = 5.71 Hz, 1 H), 6.85 (d, J = 8.80 Hz, 2 H), 7.39 (d, J = 8.80 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.6 (CH_3), 63.2 (q, J_{C-C-F} = 36.7 Hz, CH), 79.6 (q, $J_{C-C-C-F}$ = 2.2 Hz, C), 88.2 (C), 113.3 (CH), 114.3 (C), 119.0−127.4 (q, J_{C-F} = 281.0 Hz, CF_3), 133.9 (CH), 160.6 (C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −79.38 (dd, J = 5.45, 2.72 Hz); GC-MS (EI) 230 ([M]$^+$, 74%), 162 (12%), 161 (100%), 133 (15%), 118 (19%), 90 (12%), 89 (16%), 69 (4%); HRMS (ESI+) calcd for $C_{11}H_9F_3O_2$ [M + H]$^+$ 231.0633, found 231.0644.

*1,1,1-Trifluoro-4-(furan-2-yl)but-3-en-2-ol (**2s**).* The title compound (3.420 g, 89%) was prepared according to the representative procedure from 3-(furan-2-yl)acrylaldehyde (2.442 g, 0.020 mol) followed by vacuum distillation (bp 64−67 @ 0.3 mmHg) to give the pure α-CF_3 alcohol **2s** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.53 (s, 1 H), 4.59 (quind, J = 6.54, 6.54, 6.54, 6.54, 1.22 Hz, 1 H), 6.15 (dd, J = 15.77, 6.48 Hz, 1 H), 6.35 (d, J = 3.42 Hz, 1 H), 6.40 (dd, J = 3.30, 1.83 Hz, 1 H), 6.65 (dd, J = 15.89, 0.98 Hz, 1 H), 7.39 (d, J = 1.47 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 71.4 (q, J_{C-C-F} = 32.3 Hz, CH), 110.6 (CH), 111.8 (CH), 119.0 (q, $J_{C-C-C-F}$ = 2.2 Hz, CH), 120.3−128.7 (q, J_{C-F} = 281.7 Hz, CF_3), 124.2 (CH), 143.2 (CH), 151.4 (C); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −78.92 (d, J = 6.81 Hz); GC-MS (EI) 192 ([M]$^+$, 74%), 127 (11%), 123 (100%), 95 (21%), 81 (26%), 77 (17%), 69 (8%), 67 (21%), 65 (17%), 55 (22%), 39 (13%); HRMS (ESI+) calcd for $C_8H_7F_3O_2$ [M−H_2O]$^+$ 175.0371.0633, found 175.0377

Synthesis of 2,2,2-Trifluoro-1-(4-(hydroxymethyl)phenyl)-ethanol (2t). *4-(Hydroxymethyl)benzaldehyde.*[33] The title compound was prepared via a modification of the procedure of Tanner.[34] To a 500 mL round-bottom flask, equipped with stir bar was added methanol (250 mL) and terephthalaldehyde (10.000 g, 0.07455 mol, 0.29 M, 1 equiv). After complete dissolution of the dialdehyde, $NaBH_4$ (0.700 g, 0.01850 mol, 0.248 equiv) was added all at once to the yellow-tinged reaction mixture. Within 15 min, the solution went clear deep-yellow/orange solution. The solution was stirred at room temperature for 1 h. After this time the solvent was removed *in vacuo* by rotary evaporation in a 40 °C water bath to afford a thick orange residue. The residue was taken up in boiling water (≈200 mL) causing the water to become cloudy then clear. Upon cooling to room temperature in a water bath, a crystalline precipitate (starting material) formed. The precipitate was removed from the aqueous layer by filtration via a funnel and Kim Wipe. The filtrate was transferred to a 500 mL separatory funnel. The aqueous layer was extracted Et_2O (4 × 100 mL) and the combined organic layers were dried with Na_2SO_4. The solvent was removed *in vacuo* via rotary evaporation and the crude clear yellow oil was further purified by column chromatography (gradient 8:2 Hex:EtOAc to 7:3 Hex:EtOAc to 6:4 Hex:EtOAc). After removal of the solvent, the oil obtained from chromatography solidified upon standing, giving 4-(hydroxymethyl)benzaldehyde as a powdery while solid (4.650 g, 46%, mp 43−44 °C, lit. 42 °C).[35] ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.17 (br s, 1 H), 4.73 (s, 2 H), 7.46 (d, J = 8.07 Hz, 2 H), 7.79 (d, J = 8.31 Hz, 2 H), 9.90 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 64.5 (CH_2), 127.1 (CH), 130.2 (CH), 135.6 (C), 148.3 (C), 192.6 (CH); GC-MS (EI) 136 ([M]$^+$, 49%), 135 (32%), 134 (67%), 133 (60%), 108 (13%), 107 (92%), 105 (40%), 91 (11%), 90 (13%), 89 (29%), 79 (87%), 78 (14%), 77 (100%), 76 (10%), 74 (14%), 63 (10%), 51 (38%), 50 (22%), 40 (27%).

*2,2,2-Trifluoro-1-(4-(hydroxymethyl)phenyl)ethanol (**2t**).* The title compound (3.790 g, 92%) was prepared according to the representative procedure for trifluoromethylation from 4-(hydroxymethyl)benzaldehyde (2.720 g, 0.020 mol, 1 equiv) and an excess of TMS-CF_3 (6.25 g, 0.044 mol, 2.2 equiv) and obtained as an light yellow solid (mp 86−88 °C, lit.[36] mp 92−94 °C); no further purification was necessary: ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 4.80 (s, 2 H), 5.13 (br s, 1 H), 5.23 (q, J = 7.09 Hz, 1 H), 7.57 (d, J = 8.31 Hz, 2 H), 7.69 (d, J = 8.07 Hz, 2 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 66.1 (CH_2), 74.3 (q, J_{C-C-F} = 32.3 Hz, CH), 123.3−131.7 (q, J_{C-F} = 281.7 Hz, CF_3), 129.2 (CH), 130.1 (CH), 137.0 (d, $J_{C-C-C-C-F}$ = 1.5 Hz, C), 144.8 (C); ^{19}F NMR (MeOD, 400 MHz; δ, ppm) −79.11 (d, J = 6.81 Hz); GC-MS (EI) 206 ([M]$^+$, 31%), 138 (10%), 137 (100%), 135 (34%), 133 (10%), 109 (15%), 107 (34%), 105 (13%), 91 (31%), 79 (87%), 77 (44%), 69 (7%), 51 (13%), 40 (14%); HRMS (ESI+) calcd for $C_9H_9F_3O_2$ [M + H − H_2O]$^+$ 189.0527, found 189.0521.

Representative Procedure for the Preparation of α-CF_3 Ketones: Preparation of 2,2,2-Trifluoro-1-(4-methylphenyl)-ethanone (3a). In a one-neck 50 mL round-bottom flask equipped with stir bar was added DCM (10 mL), the α-CF_3 alcohol **2a** (0.704 g, 0.004 mol, 0.4 M, 1 equiv), the oxoammonium salt **1** (3.010 g, 0.010 mol, 2.5 equiv), and 2,6-lutidine (0.964 g, 0.009 mol, 2.25 equiv). The flask was sealed with a rubber septum and stirred overnight at room temperature. The solvent was removed in vacuo to afford a thick red residue. Anhydrous diethyl ether (∼30 mL) was added to the flask and the mixture was stirred for 10 min. This caused immediate precipitation of the nitroxide **1c** (*note*: it is imperative that the sides of the flask be scraped to ensure all the **1c** precipitates out, releasing the product into solution). After stirring, the solution was filtered through a plug of silica (topped with a piece of filter paper to assist in recovery) and rinsed thoroughly (three to four times) with anhydrous diethyl ether. The solvent was removed in vacuo by rotary evaporation in a room-temperature water bath to give the pure α-CF_3 ketone **3a** (0.565 g, 75%) as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 2.46 (s, 3 H), 7.35 (d, J = 8.07 Hz, 2 H), 7.98 (d, J = 7.83 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 22.0 (CH_3), 112.6−121.3 (q, J_{C-F} = 292.0 Hz, CF_3), 127.6 (C), 130.0 (CH_2), 130.4 (CH_2), 147.2 (C), 180.3 (q, J_{C-C-F} = 35.9 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −71.38; GC-MS (EI) 188 ([M]$^+$, 15%), 119 (100%), 91 (67%), 89 (10%), 69 (5%), 65 (18%); HRMS (ESI+) calcd for $C_9H_7F_3O$ [M + H]$^+$ 189.0527, found 189.0518.

*2,2,2-Trifluoro-1-(4-methoxyphenyl)ethanone (**3b**).* The title compound (0.737 g, 90%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(4-methoxyphenyl)-ethanol (**2b**; 0.825 g, 0.004 mol) to give the pure α-CF_3 ketone **3b** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.90 (s, 3 H), 6.99 (apparent doublet, J = 9.05 Hz, 2 H), 8.04 (apparent doublet, J = 8.07 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.9 (CH_3), 112.9−121.6 (q, J_{C-F} = 294.2 Hz, CF_3), 114.7 (CH), 123.1 (C), 133.0 (q, $J_{C-C-C-C-F}$ =2.2 Hz, CH), 165.7 (C), 179.2 (q, J_{C-C-F} = 34.5 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −71.06; GC-MS (EI) 204 (21%), 135 (100%), 107 (12%), 92 (24%), 77 (26%), 69 (4%), 64 (10%), 63 (10%); HRMS (ESI+) calcd for $C_9H_7F_3O_2$ [M + H]$^+$ 205.0476, found 205.0475.

*2,2,2-Trifluoro-1-(3-methoxyphenyl)ethanone (**3c**).* The title compound (0.779 g, 89%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(3-methoxyphenyl)-ethane (**2c**; 0.825 g, 0.004 mol) to give the pure α-CF_3 ketone **3c** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.87 (s, 3 H), 7.25 (ddd, J = 8.31, 2.69, 1.00 Hz, 1 H), 7.45 (t, J = 8.07 Hz, 1 H), 7.56 (s, 1 H), 7.65 (dq, J = 7.80, 1.00 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.7 (CH_3), 112.5−121.2 (q, J_{C-F} = 289.8 Hz, CF_3), 114.2 (q, $J_{C-C-C-C-F}$ = 2.2 Hz, CH), 122.5 (CH), 123.0 (q, J = 2.9 Hz, CH), 130.3 (CH), 131.3 (C), 160.2 (C), 180.6 (q, J_{C-C-F} = 34.5 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −71.26; GC-MS (EI) 204 ([M]$^+$, 37%), 135 (87%), 107 (36%), 92 (30%), 77 (35%), 69 (6%), 64 (14%), 63 (14%), 44 (11%), 40 (100%); HRMS (ESI+) calcd for $C_9H_7F_3O_2$ [M + H]$^+$ 205.0476, found 205.0478.

2,2,2-Trifluoro-1-(4-nitrophenyl)ethanone[37] *(**3d**).* The title compound (0.870 g, 99%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(4-nitrophenyl)ethanol (**2d**; 0.885 g, 0.004 mol) to give the pure α-CF_3 ketone **3d** as a powdery white solid (mp 42−44 °C, lit.[38] mp 44−46 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 8.04 (apparent doublet, J = 9.05 Hz, 2 H), 8.45 (apparent

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doublet, J = 9.05 Hz, 2 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 98.8 (q, J = 31.5 Hz, 2 C), 121.2−129.7 (q, J_{C-F} = 287.6 Hz, CF_3), 125.6 (CH), 132.1 (d, $J_{C-C-C-C-F}$ = 1.5 Hz, CH), 144.6 (C), 151.6 (C); ^{19}F NMR (MeOD, 377 MHz; δ, ppm) −71.06; GC-MS (EI) 219 ([M]$^+$, 1%), 150 (100%), 104 (40%), 92 (18%), 76 (27%), 75 (13%), 69 (7%), 50 (14%); HRMS (ESI+) calcd for $C_8H_4F_3NO_3$ [M + H + H_2O]$^+$ 238.0327, found 238.0346.

2,2,2-Trifluoro-1-(3-nitrophenyl)ethanone[38] ***(3e)***. The title compound (0.830 g, 96%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(3-nitrophenyl)ethanol (**2e**; 0.885 g, 0.004 mol) to give the pure α-CF_3 ketone **3e** as an off-yellow solid (mp 50−52 °C, lit.[39] mp 54−56 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 7.86 (t, J = 7.80 Hz, 1 H), 8.17 (dd, J = 7.83, 0.73 Hz, 1 H), 8.47 (ddd, J = 8.25, 2.26, 0.98 Hz, 1 H), 8.62 (d, J = 1.71 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 110.9−119.6 (q, J_{C-F} = 291.2 Hz, CF_3), 123.9 (q, $J_{C-C-C-C-F}$ = 2.2 Hz, CH), 128.8 (CH), 129.9 (CH), 130.2 (C), 134.4 (q, $J_{C-C-C-C-F}$ = 2.2 Hz, CH), 147.7 (C), 177.9 (q, J_{C-C-F} = 36.7 Hz, C); ^{19}F NMR (MeOD, 377 MHz; δ, ppm) −71.90; GC-MS (EI) 219 ([M]$^+$, 1%), 204 (40%), 135 (95%), 107 (39%), 92 (33%), 77 (39%), 69 (7%), 64 (15%), 63 (15%), 22 (11%), 40 (100%); HRMS (ESI+) calcd for $C_8H_4F_3NO_3$ [M + H + H_2O]$^+$ 238.0327, found 238.0344.

1-(2-Bromo-4-fluorophenyl)-2,2,2-trifluoroethanone ***(3f)***. The title compound (0.847 g, 78%) was prepared according to the representative procedure from 1-(2-bromo-4-fluorophenyl)-2,2,2-trifluoroethanol (**2f**; 1.092 g, 0.004 mol) to give the pure α-CF_3 ketone **3f** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 7.19 (ddd, J = 8.80, 7.46, 2.57 Hz, 1 H), 7.50 (dd, J = 8.19, 2.57 Hz, 1 H), 7.78 (ddq, J = 8.76, 5.67, 1.30, 1.30, 1.30 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 111.6−120.3 (q, J_{C-F} = 292.0 Hz, CF_3), 115.2 (d, J_{C-C-F} = 21.3 Hz, CH), 123.4 (d, J_{C-C-F} = 24.2 Hz, CH), 124.3 (d, $J_{C-C-C-F}$ = 9.5 Hz, C), 128.3 (d, $J_{C-C-C-C-F}$ = 3.7 Hz, C), 132.7 (dq, $J_{C-C-C-F}$ = 9.8, $J_{C-C-C-C-F}$ = 3.2 Hz, CH), 164.9 (d, J_{C-F} = 263.4 Hz, C), 180.8 (q, J_{C-C-F} = 37.4 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −105.06 (q, J = 7.00 Hz, 1 F), −76.13 (s, 3 F); GC-MS (EI) 272 ([M]$^+$, 8%), 270 ([M]$^+$, 8%), 203 (97%), 201 (100%), 175 (46%), 173 (46%), 94 (57%), 93 (11%), 74 (11%), 69 (9%); HRMS (ESI+) calcd for $C_8H_3BrF_4O$ [M + H]$^+$ 270.9382, found 270.9379.

1-(Benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol ***(3g)***. The title compound (0.833 g, 97%) was prepared according to the representative procedure from 1-(benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol (**2g**; 0.881 g, 0.004 mol) to give the pure α-CF_3 ketone **3g** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 6.08 (d, J = 1.00 Hz, 2 H), 6.89 (d, J = 8.31 Hz, 1 H), 7.44 (d, J = 0.98 Hz, 1 H), 7.67 (d, J = 8.31 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 102.7 (CH_2), 108.7 (CH), 109.4 (q, $J_{C-C-C-C-F}$ = 2.2 Hz, CH), 112.7−121.4 (q, J_{C-F} = 291.2 Hz, CF_3), 124.6 (C), 127.8 (q, $J_{C-C-C-C-F}$ = 2.9 Hz, CH), 148.9 (C), 154.3 (C), 178.8 (q, J_{C-C-F} = 34.5 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −70.76; GC-MS (EI) 218 ([M]$^+$, 41%), 149 (100%), 121 (34%), 91 (10%), 69 (5%), 65 (24%), 63 (20%), 62 (10%); HRMS (ESI+) calcd for $C_9H_5F_3O_3$ [M + H]$^+$ 219.0269, found 219.0257.

2,2,2-Trifluoro-1-(2-fluorophenyl)ethanone ***(3h)***. The title compound (0.563 g, 73%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(2-fluorophenyl)ethanol (**2h**; 0.777 g, 0.004 mol) to give the pure α-CF_3 ketone **3h** as a clear orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 7.32 (t, J = 9.00 Hz, 1 H), 7.41 (t, J = 7.46 Hz, 1 H), 7.78 (d, J = 4.89 Hz, 1 H), 7.99 (t, J = 7.21 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 105.7−114.3 (q, J_{C-F} = 289.8 Hz, CF_3), 111.9 (d, J_{C-C-F} = 20.5 Hz, C), 113.6 (d, $J_{C-C-C-F}$ = 10.3 Hz, CH), 119.2 (CH), 125.8 (CH), 131.7 (d, $J_{C-C-C-F}$ = 8.8 Hz, CH), 156.1 (d, J_{C-F} = 262.6 Hz, C), 173.2 (q, J_{C-C-F} = 38.1 Hz, C); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −107.72 to −107.48 (m, 1 F), −74.79 (d, J = 16.35 Hz, 3 F); GC-MS (EI) 192 ([M]$^+$, 7%), 123 (100%), 95 (54%), 75 (22%), 69 (9%); HRMS (ESI+) calcd for $C_8H_4F_4O$ [M + H]$^+$ 193.0277, found 193.0310.

2,2,2-Trifluoro-1-(2-methoxyphenyl)ethanone ***(3i)***. The title compound (0.814 g, 96%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(2-methoxyphenyl)ethanol (**2i**; 0.825 g, 0.004 mol) to give the pure α-CF_3 ketone **3i** as a clear orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.92 (s, 3 H), 7.01−7.10 (m, 2 H), 7.60 (ddd, J = 8.56, 7.34, 1.71 Hz, 1 H), 7.68 (d, J = 7.82 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.5 (CH_3), 111.5−120.2 (q, J_{C-F} = 290.5 Hz, CF_3), 111.8 (CH), 120.3 (CH), 121.3 (C), 130.9 (d, $J_{C-C-C-C-F}$ = 1.5 Hz, CH), 135.5 (CH), 159.5 (C), 182.6 (q, J_{C-C-F} = 36.7 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −74.17; GC-MS (EI) 204 ([M]$^+$, 21%), 136 (20%), 135 (100%), 92 (25%), 77 (35%), 69 (4%); HRMS (ESI+) calcd for $C_9H_7F_3O_2$ [M + H]$^+$ 205.0476, found 205.0507.

2,2,2-Trifluoro-1-(2-nitrophenyl)ethanone ***(3j)***. The title compound (0.782 g, 89%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(2-nitrophenyl)ethanol (**2j**; 0.885 g, 0.004 mol) to give the pure α-CF_3 ketone **3j** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 7.55 (dd, J = 7.34, 1.22 Hz, 1 H), 7.82 (td, J = 8.10, 1.00 Hz, 1 H), 7.89 (td, J = 7.60, 1.22 Hz, 1 H), 8.31 (dd, J = 8.19, 0.86 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 110.4−119.0 (q, J_{C-F} = 290.5 Hz, CF_3), 123.8 (CH), 127.9 (CH), 129.2 (C), 132.3 (CH), 134.8 (CH), 145.3 (C), 183.4 (q, J_{C-C-F} = 38.9 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −75.86; GC-MS (EI) 218 ([M]$^+$, 1%), 150 (100%), 123 (12%), 95 (15%), 76 (32%), 75 (12%), 74 (10%), 69 (9%), 51 (23%), 50 (18%); HRMS (ESI+) calcd for $C_8H_4F_3NO_3$ [M + H]$^+$ 220.0222, found 220.0228.

2,2,2-Trifluoro-1-(pyridin-2-yl)ethanone[39] ***(3k)***. The title compound (0.759 g, 96%) was prepared according to the representative procedure from 2,2,2-trifluoro-1-(pyridin-2-yl)ethanol (**2k**; 0.769 g, 0.00433 mol) to give the pure α-CF_3 ketone **3k** as a powdery yellow solid (mp 81−83 °C, lit.[39] mp 84−85 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 7.61−7.71 (m, 1 H), 7.94−8.03 (m, 1 H), 8.06−8.16 (m, 1 H), 8.74−8.84 (m, 1 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 97.9 (q, J_{C-C-F} = 31.5 Hz, C), 120.7−129.2 (q, J_{C-F} = 286.8 Hz, CF_3), 125.4 (CH), 127.1 (CH), 139.9 (CH), 150.3 (CH), 154.7 (C); ^{19}F NMR (MeOD, 377 MHz; δ, ppm) −81.66; GC-MS (EI) 175 ([M]$^+$, 7%), 106 (70%), 78 (100%), 69 (12%), 51 (24%), 50 (11%); HRMS (ESI+) calcd for $C_7H_4F_3NO$ [M + H]$^+$ 176.0323, found 176.0300.

(E)-1,1,1-Trifluoro-4-phenylbut-3-en-2-one ***(3o)***. The title compound (0.571 g, 72%) was prepared according to the representative procedure from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-ol (**2o**; 0.809 g, 0.004 mol) to give the pure α-CF_3 ketone **3o** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 7.02 (dd, J = 16.14, 0.98 Hz, 1 H), 7.40−7.54 (m, 3 H), 7.62−7.67 (m, 2 H), 7.97 (d, J = 16.14 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 112.3−121.0 (q, J_{C-F} = 291.2 Hz, CF_3), 116.9 (CH), 127.2 (CH), 127.4 (CH), 129.0 (CH), 129.5 (CH), 132.6 (CH), 133.6 (C), 150.4 (d, $J_{C-C-C-F}$ = 1.5 Hz, CH), 180.3 (q, J_{C-C-F} = 35.2 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −77.70; GC-MS (EI) 200 ([M]$^+$, 56%), 199 (12%), 132 (10%), 131 (100%), 103 (81%), 102 (13%), 77 (42%), 69 (6%), 51 (16%); HRMS (ESI+) calcd for $C_{10}H_7F_3O$ [M + H]$^+$ 201.0527, found 201.0548.

(E)-1,1,1-Trifluoroundec-3-en-2-one ***(3p)***. The title compound (0.828 g, 93%) was prepared according to the representative procedure from 1,1,1-trifluoroundec-3-en-2-ol (**2p**; 0.897 g, 0.004 mol) to give the pure α-CF_3 ketone **3p** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.89 (t, J = 6.80 Hz, 3 H), 1.23−1.37 (m, 8 H), 1.51−1.56 (m, 2 H), 2.34 (qd, J = 7.60, 1.50 Hz, 2 H), 6.41 (dd, J = 15.65, 0.98 Hz, 1 H), 7.34 (dt, J = 15.89, 7.10 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 13.9 (CH_3), 22.5 (CH_2), 27.6 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 31.6 (CH_2), 33.2 (CH_2), 111.9−120.6 (q, J_{C-F} = 290.5 Hz, CF_3), 121.3 (CH), 156.9 (CH), 179.7 (q, J_{C-C-F} = 35.2 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −77.66; GC-MS (EI) 222 ([M]$^+$, 1%), 165 (13%), 153 (81%), 138 (37%), 110 (11%), 97 (23%), 95 (13%), 83 (19%), 81 (29%), 69 (63%), 68 (25%), 67 (18%), 57 (13%), 56 (15%), 55 (100%), 43 (53%), 41 (51%), 40 (22%), 39 (25%); HRMS (ESI+) calcd for $C_{11}H_{17}F_3O$ [M + H]$^+$ 223.1310, found 223.1316.

1,1,1-Trifluorodeca-3,5-dien-2-one ***(3q)***. The title compound (0.879 g, 99%) was prepared according to the representative procedure from 1,1,1-trifluorodeca-3,5-dien-2-ol (**2q**; 0.895 g, 0.0043 mol) to give the pure α-CF_3 ketone **3q** as a clear orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.92 (t, J = 7.21 Hz, 3 H), 1.30−1.53 (m, 4 H), 2.26 (q, J = 7.17 Hz, 2 H), 6.24−6.50 (m, 3 H), 7.55 (dd, J =

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15.28, 10.88 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 13.5 (CH_3), 22.0 (CH_2), 30.3 (CH_2), 32.9 (CH_2), 111.9−120.5 (q, J_{C-F} = 290.5 Hz, CF_3), 118.1 (CH), 128.5 (CH), 150.4 (CH), 151.6 (CH), 180.0 (q, J_{C-C-F} = 37.4 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −77.54; GC-MS (EI) 206 ([M]$^+$, 8%), 149 (100%), 137 (16%), 95 (13%), 81 (32%), 79 (12%), 77 (10%), 69 (9%), 67 (14%), 66 (12%), 56 (11%), 53 (11%), 41 (17%), 39 (11%); HRMS (ESI+) calcd for $C_{10}H_{13}F_3O$ [M + H]$^+$ 207.0997, found 207.0993.

1,1,1-Trifluoro-4-(4-methoxyphenyl)but-3-yn-2-one (**3r**). The title compound (0.773 g, 85%) was prepared according to the representative procedure from 1,1,1-trifluoro-4-(4-methoxyphenyl)-but-3-yn-2-ol (**2r**; 0.921 g, 0.004 mol) to give the pure α-CF_3 ketone **3r** as a clear orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.92 (s, 3 H), 6.99 (d, J = 8.56 Hz, 2 H), 7.68 (d, J = 8.31 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 55.0 (CH_3), 83.5 (C), 101.8 (C), 109.1 (C), 110.0−118.6 (q, J_{C-F} = 289.0 Hz, CF_3), 114.2 (CH), 135.7 (CH), 162.6 (C), 166.4 (q, J_{C-C-F} = 42.5 Hz, C); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −77.65; GC-MS (EI) 228 ([M]$^+$, 23%), 1620 (12%), 159 (100%), 144 (18%), 116 (15%), 88 (12%), 69 (3%); HRMS (ESI+) calcd for $C_{11}H_7F_3O_2$ [M + H]$^+$ 229.0476, found 229.0474.

(E)-1,1,1-Trifluoro-4-(furan-2-yl)but-3-en-2-one (**3s**). The title compound (0.518 g, 68%) was prepared according to the representative procedure from 1,1,1-trifluoro-4-(furan-2-yl)but-3-en-2-ol (**2s**; 0.761 g, 0.004 mol) to give the pure α-CF_3 ketone **3s** as a clear yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 6.55−6.63 (m, 1 H), 6.87−6.92 (m, 2 H), 7.62 (s, 1 H), 7.69 (d, J = 15.41 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 108.8−117.4 (q, J_{C-F} = 296.4 Hz, CF_3), 110.5 (2x CH), 117.1 (CH), 131.6 (CH), 144.4 (CH), 147.2 (C), 176.4 (q, J_{C-C-F} = 35.2 Hz, C); ^{19}F NMR ($CDCl_3$, 376 MHz; δ, ppm) −77.74; GC-MS (EI) 190 ([M]$^+$, 35%), 121 (100%), 69 (9%), 65 (49%), 63 (12%), 39 (15%); HRMS (ESI+) calcd for $C_8H_5F_3O_2$ [M + H]$^+$ 191.0320, found 191.0328.

Representative Procedure for the Preparation of Aliphatic α-CF_3 Ketones: Preparation of 1,1,1-Trifluorododecanone (3l). In a one-neck 250 mL round-bottom flask equipped with a stir bar was added DCM (160 mL), the α-CF_3 alcohol **2l** (4.07 g, 0.016 mol, 1 M, 1 equiv), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN; 5.48 g, 0.044 mol, 2.75 equiv). After the mixture was stirred at room temperature for about 10 min, the oxoammonium salt **1** (14.41 g, 0.048 mol, 3 equiv) was added to the flask (*Caution*! mildly exothermic) and the reaction mixture immediately began to turn red. The flask was sealed with a rubber septum with a vent needle and stirred for 4 h at room temperature. The solvent was removed in vacuo to afford an orange solid. Anhydrous diethyl ether (∼30 mL) was added to the flask, and the mixture was stirred for 10 min. *Note*: it is imperative that the sides of the flask be scraped to ensure all the nitroxide (**1c**) precipitates out, releasing the product into solution. After stirring, the solution was filtered through a plug of silica (topped with a piece of filter paper to assist in recovery of **1c**) and rinsed thoroughly (three to four times) with anhydrous diethyl ether. The solvent was removed in vacuo by rotary evaporation in a room temperature water bath to give the crude α-CF_3 ketone. Further purification was accomplished by vacuum distillation through a 130 mm Vigreux column (bp 71−74 °C @ 0.10 mmHg) to give the pure α-CF_3 ketone **3l** (2.010 g, 50%) as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 0.88 (t, J = 7.00 Hz, 3 H), 1.17−1.39 (m, 16 H), 1.67 (quin, J = 7.30 Hz, 2 H), 2.70 (td, J = 7.21, 0.73 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 14.4 (CH_3), 22.7 (CH_2), 23.0 (CH_2), 29.0 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 32.2 (CH_2), 36.7 (CH_2), 111.5−120.2 (q, J_{C-F} = 292.7 Hz, CF_3), 191.9 (q, J_{C-C-F} = 34.5 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −82.66; GC-MS (EI) 252 (M^+, 0.1%), 223 (3%), 209 (5%), 191.05 (5%), 183 (85%), 163 (10%), 153 (21%), 150 (10%), 139 (28%) 135 (11%), 125 (12%) 111 (31%) 109 (13%), 97 (55%), 83 (52%), 69 (84%), 43 (100%), 41 (95%); HRMS (ESI+) calcd for $C_{13}H_{23}F_3O$ [M + H]$^+$ 253.1779, found 253.1731.

3-Cyclohexyl-1,1,1-trifluoropropan-2-one (**3n**). The title compound (1.980 g, 49%) was prepared according to the representative procedure from 3-cyclohexyl-1,1,1-trifluoropropan-2-ol (**2n**; 4.120 g, 0.021 mol) *with the following modifications*. Addition of 0.5 equiv of **1** (3.15 g, 0.0105 mol) and DBN (1.31 g 0.0105 mol) was carried out after 4 h to achieve >90% conversion. Further purification was accomplished by vacuum distillation (bp 71−74 °C @ 10 mmHg) to give the pure α-CF_3 ketone as a clear pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm) 0.93−1.04 (m, 2 H), 1.09−1.22 (m, 1 H), 1.22−1.36 (m, 2 H), 1.66−1.75 (m, 5 H), 1.93 (apparent dddt, J = 14.58, 10.96, 7.25, 3.47, 3.47 Hz, 1 H), 2.57 (d, J = 6.94 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz; δ, ppm) 26.2 (CH_2), 26.3 (CH_2), 33.2 (CH_2), 33.2 (CH), 44.1 (CH_2), 115.8 (q, J_{C-F} = 292.3 Hz, CF_3), 191.3 (q, J_{C-C-F} = 33.9 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −82.75; GC-MS (EI) 194 ([M]$^+$, 0.01%), 125 (100%), 97 (96%), 82 (72%), 69 (31%), 67 (48%), 55 (87%), 41 (33%), 39 (22%); HRMS (ESI+) calcd for $C_9H_{13}F_3O$ [M + H]$^+$ 195.0997, found 195.1044.

1,1,1-Trifluoroundec-10-en-2-one (**3m**). The title compound (2.937 g, 60%) was prepared according to the representative procedure from 1,1,1-trifluoroundec-10-en-2-ol (**2m**; 4.930 g, 0.022 mol) *with the following modifications*. Addition of 0.5 equiv of **1** (3.15 g, 0.0105 mol) and DBN (1.31 g 0.0105 mol) was carried out after 4 h to achieve >90% conversion. Further purification was accomplished by vacuum distillation (bp 60−62 °C @ 1.5 mmHg) to give the pure α-CF_3 ketone as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm) 1.23−1.47 (m, 8 H), 1.61−1.74 (qint, J = 7.00 Hz, 2 H), 2.04 (q, J = 6.85 Hz, 2 H), 2.70 (t, J = 7.21 Hz, 2 H), 4.88−5.04 (m, 2 H), 5.80 (ddt, J = 16.96, 10.12, 6.76, 6.76 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz; δ, ppm) 22.6 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 34.0 (CH_2), 36.6 (CH_2), 115.9 (q, J_{C-F} = 290.0 Hz, CF_3), 114.5 (CH_2), 139.3 (CH), 191.9 (d, J_{C-C-F} = 35.0 Hz, C); ^{19}F NMR ($CDCl_3$, 377 MHz; δ, ppm) −82.44; GC-MS (EI) 222 ([M]$^+$, 2%), 153 (14%), 138 (15%), 135 (29%), 110 (30%), 97 (11%), 95 (22%), 93 (11%), 83 (19%), 82 (24%), 81 (34%), 79 (11%), 70 (10%), 69 (87%), 68 (55%), 67 (38%), 56 (19%), 55 (100%), 54 (25%), 53 (15%), 43 (14%), 42 (25%), 41 (88%), 40 (14%), 39 (41%); HRMS (ESI+) calcd for $C_{11}H_{17}F_3O$ [M + H]$^+$ 223.1309, found 223.1299.

Selective Oxidation of 2,2,2-Trifluoro-1-(4-(hydroxymethyl)-phenyl)ethanol (2t). *4-(2,2,2-Trifluoro-1-hydroxyethyl)-benzaldehyde* (**2t′**). This procedure is a modification of the procedure outlined by Bobbitt.[18a] In a 100 mL flask equipped with a stir bar was added DCM (20 mL) and **2t** (2.060 g, 0.010 mol, 0.5 M, 1 equiv). **1** (3.150 g, 0.0105 mol, 1.05 equiv) was added followed by 2.060 g of SiO_2 (1 mass equiv to substrate), and the mixture was stirred for 24 h at room temperature. Upon reaction completion (confirmed by TLC, 8/2 Hex/EtOAc), the solvent was carefully removed in vacuo and the crude residue was filtered though a medium-porosity fritted funnel filled halfway with silica gel. The plug was washed several times with diethyl ether. The solvent was removed in vacuo by rotary evaporation to afford the pure aldehyde **2t′** (1.865 g, 91%) as a powdery off-white solid (mp 67−69 °C): ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm) 3.60 (br s, 1 H), 5.15 (q, J = 6.36 Hz, 1 H), 7.67 (d, J = 8.07 Hz, 2 H), 7.90 (d, J = 8.31 Hz, 2 H), 9.99 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz; δ, ppm) 72.5 (q, J_{C-C-F} = 30.8 Hz, CH), 120.0−127.7 (q, J_{C-F} = 281.7 Hz, CF_3), 128.5 (d, $J_{C-C-C-C-F}$ = 1.5 Hz, CH), 130.1 (CH), 137.1 (C), 140.8 (C), 192.6 (CH); ^{19}F NMR (400 MHz, $CDCl_3$; δ, ppm) −79.11 (d, J = 6.81 Hz); GC-MS (EI) 204 ([M]$^+$, 29%), 135 (100%), 133 (16%), 127 (11%), 105 (16%), 79 (56%), 77 (41%), 69 (6%), 51 (13%); HRMS (ESI+) calcd for $C_9H_7F_3O_2$ [M + H]$^+$ 205.0476, found 205.0484.

4-(2,2,2-Trifluoroacetyl)benzaldehyde (**3t**). The title compound (0.626 g, 78%) was prepared according to the general oxidation procedure from 4-(2,2,2-trifluoro-1-hydroxyethyl)benzaldehyde (**2t′**) to give a yellow solid (mp 86−88 °C): ^{1}H NMR (MeOD, 400 MHz; δ, ppm) 7.66 (d, J = 7.83 Hz, 2 H), 7.80 (d, J = 7.34 Hz, 2 H), 10.19 (br s, 1 H); ^{13}C NMR (MeOD, 101 MHz; δ, ppm) 98.5 (q, J_{C-C-F} = 32.3 Hz, C), 120.8−129.4 (q, J_{C-F} = 286.1 Hz, CF_3), 128.3 (CH), 129.9 (CH), 137.0 (C), 141.6 (C); ^{19}F NMR (MeOD, 377 MHz; δ, ppm) −82.40; GC-MS (EI) 202 ([M]$^+$, 5%), 133 (100%), 105 (34%), 77 (26%), 76 (10%), 69 (5%), 51 (12%), 50 (10%); HRMS (ESI+) calcd for $C_9H_5F_3O_2$ [M + H]$^+$ 203.0320, found 203.0341.

Recovery and Regeneration of Spent Oxidant. The solid material from each oxidation was saved, and after seven oxidations the

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solid was dissolved in a minimum amount of deionized water (~300 mL) in a large Erlenmeyer flask. Once completely dissolved, NaCl was added to bring the solution to ~3 M in NaCl (approximately 53 g). The flask was cooled to 0 °C and allowed to stand for 2 h. Over time, a solid precipitate (**1c**) appeared and created a top layer. The top layer was decanted carefully and filtered through a medium-porosity fritted filter funnel. The orange solid was washed with cold brine and dried overnight to afford 12.97 g (87% recovery based on seven reactions at 0.010 mol of **1**) of **1c** (mp 146−148 °C). This nitroxide was then converted back to the oxoammonium salt **1** via the procedure outlined in the salt preparation section (12.85 g, 70%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and figures giving spectroscopic data for the compounds and details of the relative rate studies of the oxidation of α-CF_3 alcohols. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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