Manganese-Catalyzed Aerobic Oxytrifluoromethylation of Styrene Derivatives Using CF₃SO₂Na as the Trifluoromethyl Source

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Supporting Information



ABSTRACT: A mild and practical protocol for manganese-catalyzed aerobic oxytrifluoromethylation of olefinic bonds of styrene derivatives using CF_3SO_2Na (Langlois' reagent) as the CF_3 source is described. A distinguishing feature of this method is the generation of trifluoromethyl radicals from CF_3SO_2Na using the simple manganese salt/ O_2 system. The reaction proceeds under ambient conditions, free of added peroxide initiators, and provides moderate to good selectivities for alcohol versus ketone product.

INTRODUCTION

The trifluoromethyl group is a privileged structural motif of great interest in the pharmaceutical and agrochemical fields due to its excellent performance in regulating the physical, chemical, and biological properties of potential drug candidates.¹ It is therefore greatly desirable to develop new practical and efficient methods for incorporating the CF₃ substituent into organic substrates. During the past few years, a wide range of trifluoromethylation methods have been disclosed based on transition-metal-mediated/catalyzed strategies, photoredox catalysis, and radical pathways.² Among these various trifluomethylation methods, the approaches involving CF₃ radical species have drawn increasing attention because they can employ benchtop stable and cost-effective reagents, such as CF₃SO₂Na (the Langlois reagent), as CF₃ radical sources.³ Recently, several strategies for selective vicinal trifluoromethylation-based difunctionalization⁴⁻⁷ of olefins via three-component (alkene, CF₃SO₂Na, reactive trapping agents) intermolecular reaction $s^{4h,7a-d}$ have been established for the synthesis of α trifluoromethylated ketones, β -trifluoromethylated alkyl iodides, and 1,2- bis(trifluoromethylated) alkanes (Scheme 1). In previous representative oxytrifluoromethylations of double bonds of olefins, substoichiometric or stoichiometric peroxide oxidants/initiators (^tBuOOH, K₂S₂O₈) were required to activate CF_3SO_2Na to liberate CF_3 radicals through single-electron oxidations (Scheme 1),^{4h,7a-d,8} thus possibly limiting the compatibility of sensitive functional groups of substrates and being detrimental to environmental benefits. It is wellknown that dioxygen is an ideal environment-friendly oxidant and offers fascinating academic and industrial prospects.⁹ Therefore, developing a new mode to activate CF₃SO₂Na

under an aerobic atmosphere rather than in an environment of additional peroxide initiators and achieving subsequent oxytrifluoromethylation of the olefinic double bond with high efficiency are particularly intriguing and desirable (Scheme 1).

With regard to the difunctionalizations of alkenes, manganese catalysts have been broadly applied for the construction of two chemical bonds on the unsaturated double bond in reactions such as epoxidation, aziridination, *syn*-dihydroxylation, acetox-yphosphorylation, and hydroxyazidation.¹⁰ Moreover, manganese catalysts were proven to play an important role in accelerating the autoxidation of sulfur(IV) species (SO₂, sulfite, or bisulfite) to sulfur(VI) through a radical process (Scheme 2).¹¹ In this context, we envisioned that manganese catalysts were good candidates for activating CF₃SO₂Na under aerobic conditions, leading to oxytrifluoromethylations of double bonds.

RESULTS AND DISCUSSION

To test our hypothesis, initial studies were focused on the reaction of 1a with CF_3SO_2Na (2) in the presence of a manganese catalyst under aerobic conditions (Table 1). Gratifyingly, the desired oxytrifluoromethylation products 3a and 4a were indeed observed in a ratio of 3.2:1 when the reaction was conducted in acetone with 0.1 equiv of $MnCl_2$ · $4H_2O$ (entry 1, Table 1). In contrast with $MnCl_2·4H_2O$, $MnSO_4·H_2O$ gave decreased selectivity (3a:4a = 1.5:1) and decreased catalytic efficiency with prolonged reaction time

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Scheme 1. Trifluoromethylation-Based Difunctionalization of Olefins by Using CF₃SO₂Na



Scheme 2. Reaction Development Considerations



Tabla	1	Ontimization	of the	Overt	rifluoromot	hylation	of	turonoa
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	Ph + 1a	CF ₃ SO ₂ Na 2 metal catalyst solvent, rt open flask to a	Ph CF ₃	+ Ph CF ₃	
entry	metal catalyst (loading, equiv)	solvent	time (h)	ratio (3a:4a) ^{<i>b,c</i>}	yield (3a+4a) ^d (%)
1	$MnCl_{2} \cdot 4H_{2}O(0.1)$	acetone	12	3.2:1	52 + 16
2	$MnSO_4 \cdot H_2O(0.1)$	acetone	48	1.5:1	37 + 25
3	$Mn(OAc)_2 \cdot 4H_2O(0.1)$	acetone	48	NR^{e}	NR^{e}
4	$Mn(OAc)_{3} \cdot 2H_{2}O(0.1)$	acetone	48	NR^{e}	NR^{e}
5	(R,R)-Jacobsen catalyst (0.1)	acetone	24	3:1	49 + 18
6	MnO (0.1)	acetone	48	1.6:1	34 + 21
7	Mn_2O_3 (0.1)	acetone	48	NR^{e}	NR^{e}
8	$MnO_{2}(0.1)$	acetone	48	NR^{e}	NR^{e}
9	$MnCl_{2} \cdot 4H_{2}O(0.2)$	DMF	48	1:6	5 + 30
10	$MnCl_2 \cdot 4H_2O(0.2)$	DMSO	48	1:12.3	2 + 25
11^{f}	$MnCl_2 \cdot 4H_2O(0.2)$	acetone	12	6:1	66 + 11
12	no catalyst addition	acetone	48	NR	NR
13 ^g	$MnCl_{2}\cdot 4H_{2}O(0.2)$	acetone	48	NR	NR

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^{*a*}General conditions: the reactions were run on a 0.2 mmol scale in solvent (2.0 mL), CF_3SO_2Na (0.3 mmol, 1.5 equiv), open flask to air. ^{*b*}The ratio of **3a** to **4a** was determined by ¹⁹F NMR spectroscopy of the crude product (after workup and extraction). ^{*c*}A trace amount of vinyl triflone **5a** (PhCH=CHSO₂CF₃) was also observed by ¹⁹F NMR at -77.45 ppm, and its structure was determined by preparative TLC isolation and GC-MS/¹H NMR characterization. ^{*d*}The yield was determined by ¹⁹F NMR using PhCF₃ as an internal standard. ^{*e*}TLC analysis indicated no conversion of styrene and no formation of oxytrifluoromethylation products; only CF₃SO₂Na was transformed partially or completely into CF₃SO₃Na. ^{*f*}CF₃SO₂Na (0.4 mmol, 2.0 equiv) was utilized. ^{*g*}The reaction was conducted under a N₂ atmosphere.

	R	SO ₂ Na eq) MnCl ₂ • 4 acetone open fla	$\begin{array}{c} H_2O(0.2 \text{ eq}) \\ RT \\ \text{sk to air} \\ \end{array} R \xrightarrow{II} \\ 3 \end{array}$	OH CF ₃ + R 	CF ₃
Entry	Styrene Derivatives	Time	Product 3+4	Ratio of 3 / 4 ^b	Yield ^c
1		12 h	3a+4a	6:1	65+10 %
2	F	24 h	3b+4b	3:1	52+16 %
3	CI	24 h	3 c +4 c	2.4 : 1	53+22 %
4	Br	24 h	3d+4d	2.1 : 1	50+24 %
5	F ₃ C	24 h	3e+4e	2:1	48+22 %
6	O ₂ N	12 h	3f+4f	3:1	59+20 %
7	H ₃ C	24 h	3g+4g	2.2 : 1	36+17 %
8^d	MeO	12 h	3h+4h	3:1	32+10 %
9	CL	24 h	3i+4i	>10:1	60 %+~ ^e
10	CH3	24 h	3j+4j	>10:1	44 %+~ ^e
11	OHC	48 h	3k+4k	2.5 : 1	41+16 %
12	O ₂ N	12 h	31+41	>10:1	63 %+~ ^e
13	Me	24 h	3m+4m	3:1	44+14 %
14		12 h	3n+4n	4.2 : 1	50+12 %
15		12 h	30+40	2:1	35 ^f +18 %
16		12 h	3p+4p	1.5 : 1	36 ^g +23 %
17	CH ₃	12 h	3q+4q	1.2 : 1	31 ^h +25 %

Table 2. Substrate Scope of Mangenese-Catalyzed Oxytrifluoromethylation of Styrene Derivatives^a

^{*a*}All the reactions were run on a 0.4 mmol scale in acetone (4 mL) under ambient conditions, CF_3SO_2Na (0.8 mmol, 2 equiv), $MnCl_2\cdot 4H_2O$ (0.08 mmol, 0.2 equiv). ^{*b*}The ratio of **3** to **4** was determined by ¹⁹F NMR spectroscopy of the crude product (after workup and extraction). ^cIsolated yield. Alcohol **3** and ketone **4** were separated by flash chromatography. ^{*d*}The reaction was run at reflux temperature (60 °C). ^{*e*}A trace amount of ketone **4** was not able to be isolated. ^{*f*}The alcohol product **30** was obtained in a mixture of *syn* and *anti* isomers (1:4.5). ^{*g*}The alcohol product **3p** was obtained in a mixture of *syn* and *anti* isomers (1:2.6). ^{*h*}The *syn* and *anti* isomers of alcohol product **3q** were separated by flash chromatography (1:1).

(entry 2). For the catalysts $Mn(OAc)_2 \cdot 4H_2O$ and $Mn(OAc)_3 \cdot 2H_2O$ (single-electron oxidant), no conversion of styrene 1a

was detected, and CF_3SO_2Na was converted into the corresponding CF_3SO_3Na (entries 3 and 4). In contrast,

	R ¹ 1 (1	R ² + CF ₃ SO ₂ Na eq) (2 eq)	MnCl ₂ • 4H ₂ O (0.2 eq) acetone, RT open flask to air 3	$rac{c}{c}{c}{F_3}$ $rac{c}{c}{F_3}$ $rac{c}{c}{F_3}$ R^2 R^2 Q	
Entry	Alkenes	Time	Product 3+4	Ratio of 3 / 4 ^b	Yield ^c
1	n-C ₆ H ₁₃	12 h	3r+4r	3.6 : 1	45 % +13 % ^d
2		12 h	3s+4s	1.2 : 1	$35\%^{e}+30\%^{d}$
3	Ph CO ₂ CH ₃	48 h	3t + 4t ^f	2.7 : 1	42% $^{g}+\sim$ f
4		48 h	N. R. ^h	N. R. ^h	N. R. ^h

^{*a*}All the reactions were run on a 0.4 mmol scale in acetone (4 mL) under ambient conditions, CF_3SO_2Na (0.8 mmol, 2 equiv), $MnCl_2\cdot 4H_2O$ (0.08 mmol, 0.2 equiv). ^{*b*}The ratio of **3** to **4** was determined by ¹⁹F NMR spectroscopy of the crude product (after workup and extraction). ^{*c*}Isolated yield. ^{*d*}The ketone products **4r** and **4s** were volatile, and the yields were calculated by ¹⁹F NMR using PhCF₃ as a reference. ^{*c*}The alcohol product **3s** was obtained in a mixture of *syn* and *anti* isomers (3:7). ^{*f*}Ketone **4t** was not stable on silica gel and was not isolated by flash chromatography. ^{*g*}Single *syn* and *anti* isomers of **3t** were obtained by flash chromatography in a ratio of 1:1.5. ^{*h*}TLC analysis indicated no conversion of substrate and no formation of oxytrifluoromethylation products; only CF_3SO_2Na was oxidized into CF_3SO_3Na .

Scheme 3. Scale-Up Oxytrifluoromethylation of 2-Vinylnaphthalene 1n



when (1R, 2R)-(-)-[1,2-cyclohexanediamino-N,N'-bis(3,5-di*tert*-butylsalicylidene) manganese(III) chloride ((R,R)-Jacobsen catalyst) was employed in this reaction, the reaction proceeded, albeit with slightly decreased yield and selectivity (entry 5). These results indicated that the counterion of the manganese catalysts played an important role in the activation process of CF₃SO₂Na as well as in regulating catalytic activity and selectivity. Employment of heterogeneous manganese catalysts such as MnO, Mn₂O₃, and MnO₂ led to sluggish reactions, and only MnO delivered the oxytrifluoromethylation product in moderate yield (entries 6-8). Screening of other metal catalysts including AgNO₃, FeCl₂·4H₂O, Fe(acac)₃, CuCl, NiCl₂, and CoCl₂·6H₂O did not give better results than MnCl₂·4H₂O (see the Supporting Information). Interestingly, when the reaction was run in the solvent DMF or DMSO, the oxytrifluoromethylation reaction proceeded with inverse selectivity, albeit in lower yield (entries 9 and 10). Further optimization of the catalyst loading and reactant ratio revealed that a good yield (77%) and high selectivity of alcohol 3a vs ketone 4a (6:1) were obtained when using 20 mol % $MnCl_2 \cdot 4H_2O$ catalyst and 2.0 equiv of CF_3SO_2Na (entry 11). The observed selectivity for the alcohol product is notable, as Matti and Lei's groups showed that persulfate-mediated

oxytrifluoromethylations proceed exclusively to the ketone product. Finally, the control experiments proved that $MnCl_2$ and O_2 are essential factors for the activation of CF_3SO_2Na and the subsequent oxytrifluoromethylation process (entries 12 and 13).

With the optimized reaction conditions in hand, the substrate scope of this manganese-catalyzed oxytrifluomethylation reaction was investigated. As shown in Table 2, a wide variety of styrenes bearing either electron-withdrawing or electrondonating substituents on the aryl ring could be transformed into the corresponding oxytrifluomethylation compounds 3 and 4 in moderate to good yields and selectivities. The halogens ranging from fluorine to bromine, trifluoromethyl, nitro, methyl, methoxy, and sensitive aldehyde groups were tolerated in this system owing to the mildness of the reaction conditions (entries 1-13). Interestingly, for the ortho-substituted (2-Cl, 2-Me) as well as 3-NO₂-substituted substrates, good selectivities of alcohol 3 vs 4 were observed (entries 9, 10, and 12). The α,β -disubstituted olefins including 1,2-dihydronaphthalene, indene, and *trans-\beta*-methylstyrene also underwent smooth reaction under standard conditions (entries 15-17), providing the preferential alcohol product in a mixture of syn and anti isomers.

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Scheme 4. Possible Mechanism of Mn-Catalyzed Oxytrifluoromethylation



Scheme 5. Mechanistic Investigations of Mn-Catalyzed Oxytrifluoromethylation

(a) Suppression effect of addition of radical scavenger CF_3 MnCl₂• 4H₂O (0.2 ea) CF₃SO₂Na TEMPO (2 ea) 2 ea acetone, RT 1 eq 4a 3a open flask to air reaction was completely suppressed no formation (b) Role of accelerating the autoxidation of CF₃SO₂Na exerted by MnCl₂•4H₂O MnCl₂• 4H₂O (0.2 eq) 2) extraction CF₃SO₃H -79.5 ppm white precipitate CF₃SO₂Na acetone, RT by ether detected by ¹⁹F NMR open flask to air (c) Interrogation of the generation of ketone product

$$\begin{array}{c} \mathsf{OH} \\ \mathsf{Ph} \\ \mathsf{Ph} \\ \mathsf{roc} \text{ conversion} \end{array} \xrightarrow{\mathsf{CF}_3} \begin{array}{c} \mathsf{MnCl}_2 \bullet 4\mathsf{H}_2\mathsf{O} \ (0.2 \ \mathsf{eq}) \\ \text{acetone, RT, 48 h} \\ \text{open flask to air} \end{array} \xrightarrow{\mathsf{Ph}} \begin{array}{c} \mathsf{CF}_3 \\ \mathsf{Ph} \\ \mathsf{no \ formation} \end{array}$$

This oxytrifluoromethylation reaction was also examined by using other types of alkenes such as 1-octene, *cis*-cyclooctene, methyl cinnamate, and 2-vinylpyridine (Table 3). The simple olefin 1-octene, cycloolefin *cis*-cyclooctene, and $\alpha_{,\beta}$ -unsaturated ester methyl cinnamate worked well under standard conditions, and delivered smoothly the corresponding alcohol and ketone products (entries 1–3). However, 2-vinylpyridine was not a suitable substrate in this reaction (entry 4). The failure of 2vinylpyridine could be attributed to the deactivation of manganese catalyst by the strong coordination of the heteroatom N. To test the synthetic utility of this method, oxytrifluoromethylation of 2-vinylnaphthalene was conducted on a gram scale under standard conditions (Scheme 3). A yield and a selectivity comparable to those of the small-scale experiment were furnished (Table 2, entry 14). In addition, single alcohol product **3n** can be obtained in 57% yield by reduction of the crude product (mixture of **3n** and **4n**, ratio 3.5:1) via a two-step successive manipulation.^{7c}

On the basis of previous studies, 3,7,11-14 a plausible mechanism involving the CF₃ radical is proposed as shown in Scheme 4. The radical pathway of this manganese-catalyzed oxytrifluoromethylation was supported by the following

experimental observations: (1) TLC monitoring revealed the existence of an induction period which could last for hours or even 1-2 days. After the first several hours of the induction period, the reaction was accelerated and styrene substrate was consumed at a much faster rate. (2) The formation of vinyl triflone PhCH=CHSO₂CF₃ (5a) in trace amounts was detected by ¹⁹F and ¹H NMR spectroscopies and was further confirmed by GC-MS, providing evidence for the formation of CF_3SO_2 radicals in the reaction system.³ (3) The addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the reaction system, a well-known radical scavenger, led to the complete suppression of this oxytrifluoromethylation process (Scheme 5a), and therein another type of radical oxidation species, $CF_3SO_3^-$, was detected by ¹⁹F NMR (-79.5 ppm) instead of the commonly conceivable adduct TEMPO-CF₃ (7). Moreover, the exploration of the catalytic roles of $MnCl_2$. 4H₂O was conducted on the basis of the following experiment: Stirring CF₃SO₂Na with MnCl₂·4H₂O in acetone under aerobic conditions, in the absence of olefins, led to the precipitation of a white salt which was identified as CF₃SO₃Na via¹⁹F NMR analysis (Scheme 5b). This result is consistent with our hypothesis that MnCl₂·4H₂O plays an important role in accelerating the autoxidation of bench-stable CF₃SO₂Na, although the thermodynamic impetus of the autoxidation of the Langlois reagent is remarkable from the analysis of redox potentials¹⁴ of $CF_3SO_2^-/CF_3SO_2^{\bullet}$ (0.6 V) and O_2 , $H^+/H_2O_2^{\bullet}$ (1.23 V). The CF_3SO_2 radical might be generated in the system of MnCl₂·4H₂O and O₂, which combined with an oxy species (O₂, HO[•], Mn(III)-OH) provides CF₃SO₃⁻. Finally, it was proven that ketone 4a was not formed by the in situ oxidation of benzylic alcohol 3a under the catalytic condition of MnCl₂. 4H₂O (Scheme 5c).

CONCLUSION

In summary, we have demonstrated a novel and convenient manganese-catalyzed aerobic oxytrifluoromethylation of styrene derivatives for selective synthesis of the corresponding β trifluoromethylated alcohol versus α -trifluoromethylated ketones. This methodology showcases the use of $MnCl_2{\cdot}4H_2O$ under aerobic conditions to liberate the CF₃ radical from CF₃SO₂Na without the assistance of additional peroxide oxidants. Such a method is operationally simple and greener than previously reported methods that require additional oxidants. The preliminary mechanistic studies suggest that a CF₃ radical involving process is highly likely. Additionally, the detection of vinyl triflone PhCH=CHSO₂CF₃ (5a) shed some light on the intermediacy of the CF₃SO₂ radical, an important species in the single-electron-oxdiation process of CF₃SO₂Na. Further applications of this new activation mode of CF₃SO₂Na for other radical trifluoromethylations and more systematic mechanistic investigations are under way, and the results will be reported in due course.

EXPERIMENTAL SECTION

Typical Procedure for the Manganese-Catalyzed Aerobic Oxytrifluoromethylation of Styrene Derivatives. To a solution of CF_3SO_2Na (128 mg, 0.8 mmol) in acetone (4 mL) were added styrenes (0.4 mmol) and then $MnCl_2 \cdot 4H_2O$ (16 mg, 0.08 mmol). The reaction mixture was stirred vigorously under an open atmosphere at room temperature for 12–48 h until the styrene substrate disappeared by TLC monitoring. After completion of the reaction, the reaction mixture was poured into 5% aqueous NaHCO₃ solution (20 mL) and then was diluted with ether (20 mL) and filtered through Celite. The filtrate was separated, and the aqueous layer was extracted by ether (20

mL). The organic phase was washed with saturated NaCl aqueous solution and then dried over sodium sulfate. After removal of the solvent in vacuo, the residue was purified by flash chromatography (hexane:ethyl acetate = 20:1 to 8:1, volume ratio) on silica gel to afford the corresponding ketone and alcohol products, respectively.

Data for 3,3,3-Trifluoro-1-phenylpropan-1-ol (**3a**).^{7c} Colorless oil. R₁(10% ethyl acetate/hexane) = 0.35, 65% yield (49 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.42–7.34 (m, 5H), 5.08–5.04 (m, 1H), 2.68–2.57 (m, 1H), 2.50–2.39 (m, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -63.70 (t, *J* = 10.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 142.5, 129.0, 128.6, 126.1 (q, *J* = 277.4 Hz), 125.9, 68.9 (q, *J* = 2.9 Hz), 42.9 (q, *J* = 26.9 Hz). MS (EI): *m*/*z* 190 (M⁺). HRMS (EI-TOF): *m*/*z* [M]⁺ calcd for C₉H₃F₃O 190.0605, found 190.0600.

Data for 3,3,3-Trifluoro-1-phenylpropan-1-one (4a).^{7c} White solid. $R_{f}(10\%$ ethyl acetate/hexane) = 0.40, 10% yield (7 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 3.81 (q, J = 7.5 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.12 (t, J = 9.9 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 189.9, 136.0, 134.4, 129.2, 128.6, 124.2 (q, J = 276.9 Hz), 42.3 (q, J = 28.1 Hz). MS (EI): m/z 188 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₇F₃O 188.0449, found 188.0451.

Data for 1-((E)-2-((Trifluoromethyl)sulfonyl)vinyl)benzene (5a)..^{15a,b} White solid. $R_f(10\%$ ethyl acetate/hexane) = 0.41. ¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, J = 15.5 Hz, 1H), 7.53–7.41 (m, SH), 6.76 (d, J = 15.5 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -77.74 (s, 3F). ¹³C NMR (125 MHz, CDCl₃): 154.0, 133.4, 131.4, 129.8, 129.7, 119.9 (q, J = 324.9 Hz), 116.8. MS (ESI): m/z 259 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₉H₇F₃O₂SNa 259.0011, found 259.0014.

Data for 3,3,3-Trifluoro-1-(4-fluorophenyl)propan-1-ol (**3b**).^{7c} Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.36, 52% yield (43 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.38–7.30 (m, 2H), 7.09–7.05 (m, 2H), 5.10–5.06 (m, 1H), 2.68–2.57 (m, 1H), 2.48–2.38 (m, 1H), 2.15 (d, *J* = 3.1 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.75 (t, *J* = 10.4 Hz, 3F), -113.58 to -113.64 (m, 1F). ¹³C NMR (125 MHz, CDCl₃): δ 162.8 (d, *J* = 246.8 Hz), 138.3, 127.7 (d, *J* = 8.4 Hz), 126.0 (q, *J* = 277.5 Hz), 116.0 (d, *J* = 21.6 Hz), 68.4 (q, *J* = 3.0 Hz), 43.2 (q, *J* = 27.1 Hz). MS (EI): *m*/*z* 208 (M⁺). HRMS (EI-TOF): *m*/*z* [M]⁺ calcd for C₉H₈F₄O 208.0511, found 208.0506.

Data for 3,3,3-Trifluoro-1-(4-fluorophenyl)propan-1-one (**4b**).^{7c} White solid. $R_f(10\%$ ethyl acetate/hexane) = 0.42, 16% yield (13 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.00–7.96 (m, 2H), 7.22–7.17 (m, 2H), 3.78 (q, *J* = 9.9 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.00 (t, *J* = 9.9 Hz, 3F), -102.81—-102.87 (m, 1F). ¹³C NMR (125 MHz, CDCl₃): δ 188.3, 166.6 (d, *J* = 257.2 Hz), 132.5, 131.4 (d, *J* = 9.6 Hz), 124.1 (q, *J* = 277.0 Hz), 116.4 (d, *J* = 22.1 Hz), 42.3 (q, *J* = 28.2 Hz). MS (EI): m/z 206 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₆F₄O 206.0355, found 206.0372.

Data for 1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-ol (3c).^{7c} Light yellow oil. $R_{f}(10\%$ ethyl acetate/hexane) = 0.36, 53% yield (48 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.37–7.31 (m, 4H), 5.09– 5.06 (m, 1H), 2.66–2.55 (m, 1H), 2.47–2.40 (m, 1H), 2.24 (d, *J* = 3.0 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.75 (t, *J* = 10.5 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 140.9, 134.3, 129.2, 127.3, 125.9 (q, *J* = 277.3 Hz), 68.3, 43.0 (*J* = 27.0 Hz). MS (EI): m/z 224 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₈ClF₃O 224.0216, found 224.0256.

Data for 1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-one (4c).^{7c} White solid. $R_f(10\%$ ethyl acetate/hexane) = 0.42, 22% yield (19 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.90–7.87 (m, 2H), 7.51–7.48 (m, 2H), 3.78 (q, J = 9.9 Hz). ¹⁹F NMR (470 MHz, CDCl₃): δ –62.03 (t, J= 9.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 188.7, 141.1, 134.3, 130.0, 129.5, 124.0 (q, J = 277.1 Hz), 42.4 (q, J = 28.5 Hz). MS (EI): m/z 222 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₆F₃O 222.0059, found 222.0058.

Data for 1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-ol (**3d**).^{7c} Light yellow oil. $R_{f}(10\%$ ethyl acetate/hexane) = 0.36, 50\% yield (54 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.45–7.43 (m, 2H), 7.19–7.18 (m, 2H), 4.99–4.96 (m, 1H), 2.58–2.47 (m, 1H), 2.40–2.29 (m, 1H), 2.14 (d, *J* = 3.2 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.65 (t, *J* = 10.4 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 141.4, 132.2,

127.6, 125.9 (q, J = 277.7 Hz), 122.5, 68.4, 43.0 (q, J = 27.0 Hz). MS (EI): m/z 268 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₈BrF₃O 267.9711, found 267.9731.

Data for 1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-one (**4d**).^{7c} Light yellow solid. R_j(10% ethyl acetate/hexane) = 0.41, 24% yield (25 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 3.77 (q, J = 9.9 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.01 (t, J = 9.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 189.0, 134.7, 132.6, 130.0, 129.9, 124.0 (q, J = 278.0 Hz), 42.3 (q, J = 28.4 Hz). MS (ESI): m/z 289 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₉H₆BrF₃ONa 288.9446, found 288.9439.

Data for 3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-ol (3e). ^{7c} Colorless oil. $R_{f}(10\%$ ethyl acetate/hexane) = 0.37, 48% yield (49 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 5.17 (m, 1H), 2.69–2.58 (m, 1H), 2.52–2.42 (m, 1H), 2.31 (d, J = 3.3 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.56 (s, 3F), -63.59 (t, J = 10.4 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 146.3, 130.8 (q, J = 32.6 Hz), 126.3, 126.0 (q, J = 3.7 Hz), 125.9 (q, J = 276.3 Hz), 124.2 (q, J = 271.3 Hz), 68.5, 43.1 (q, J = 27.1 Hz). MS (EI): m/z 258 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₁₀H₈F₆O 258.0479, found 258.0459.

Data for 3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1one (**4e**).^{7c} White solid. R_i(10% ethyl acetate/hexane) = 0.44, 22% yield (22 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 3.84 (q, J = 9.9 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.06 (t, J = 9.7 Hz, 3F), -63.38 (s, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 189.1, 138.5, 135.7 (d, J = 32.7 Hz), 129.0, 126.3 (q, J = 3.7 Hz), 123.9 (q, J = 276.3 Hz), 123.6 (q, J = 271.3 Hz), 42.7 (q, J = 28.7 Hz). MS (EI): m/z 256 (M⁺). HRMS (EI-TOF): m/z[M]⁺ calcd for C₁₀H₆F₆O 256.0323, found 256.0364.

Data for 3,3,3-Trifluoro-1-(4-nitrophenyl)propan-1-ol (3f).^{7c} Light yellow solid. *R*₁(20% ethyl acetate/hexane) = 0.35, 59% yield (55 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 0.5.24–5.20 (m, 1H), 2.68–2.57 (m, 1H), 2.51 (s, 1H), 2.50–2.42 (m, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.59 (t, *J* = 10.5 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 149.4, 147.9, 126.8, 125.7 (q, *J* = 275.0 Hz), 124.2, 68.1, 43.0 (q, *J* = 27.2 Hz). MS (EI): *m/z* 235 (M⁺). HRMS (EI-TOF): *m/z* [M]⁺ calcd for C₉H₈F₃NO₃ 235.0456, found 235.0420.

Data for 3,3,3-Trifluoro-1-(4-nitrophenyl)propan-1-one (4f).^{7c} Light yellow solid. R_j(10% ethyl acetate/hexane) = 0.40, 20% yield (18 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.38–8.36 (m, 2H), 8.13– 8.11 (m, 2H), 3.87 (q, J = 9.7 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ –61.97 (t, J = 9.8 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 188.6, 151.1, 140.1, 129.7, 124.4, 123.8 (q, J = 274.3 Hz), 42.9 (q, J = 29.0 Hz). MS (EI): m/z 233 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₆F₃NO₃ 233.0300, found 233.0287.

Data for 3,3,3-trifluoro-1-p-tolylpropan-1-ol (**3g**).^{7c} Colorless oil. $R_f(10\% \text{ ethyl acetate/hexane}) = 0.36, 36\% \text{ yield (29 mg).} ¹H NMR (500 MHz, CDCl_3): <math>\delta$ 7.27–7.25 (m, 2H), 7.20–7.18 (m, 2H), 5.07–5.04 (m, 1H), 2.69–2.57 (m, 1H), 2.45–2.39 (m, 1H), 2.36 (s, 3H), 2.05 (s, 1H). ¹⁹F NMR (470 MHz, CDCl_3): δ –63.77 (t, J = 9.9 Hz, 3F). ¹³C NMR (125 MHz, CDCl_3): δ 139.6, 138.5, 129.7, 126.1 (q, J = 277.0 Hz), 125.8, 68.9 (q, J = 3.0 Hz), 43.0 (q, J = 26.8 Hz), 21.3. MS (EI): m/z 204 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₁₀H₁₁F₃O 204.0762, found 204.0750.

Data for 3,3,3-Trifluoro-1-p-tolylpropan-1-one (**4g**).^{7c} White solid. R_f(10% ethyl acetate/hexane) = 0.45, 17% yield (14 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.84 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.77 (q, J = 10.1 Hz, 2H), 2.44 (s, 3H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.03 (t, J = 10.0 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 189.5, 145.5, 133.7, 129.8, 128.7, 124.3 (q, J = 277.0 Hz), 42.2 (q, J = 28.2 Hz), 21.9. MS (ESI): m/z 225 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₉F₃ONa 225.0498, found 225.0470.

Data for 3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-ol (3h).^{7c} Colorless oil. $R_{f}(15\%$ ethyl acetate/hexane) = 0.30, 32% yield (28 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.32–7.29 (m, 2H), 6.93–6.90 (m, 2H), 5.05 (dt, J = 7.4 Hz, 3.4 Hz, 1H), 3.82 (s, 3H), 2.70–2.59 (m, 1H), 2.49–2.39 (m, 1H), 2.06 (d, J = 3.1 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.75 (t, J = 10.4 Hz, 3F). ¹³C NMR (125 MHz,

CDCl₃): δ 159.9, 134.7, 127.2, 126.1 (q, J = 275.0 Hz), 114.4, 68.6, 55.6, 43.0 (q, J = 26.7 Hz). MS (ESI): m/z 221 (M + H)⁺. HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₁₀H₁₂F₃O₂ 221.0789, found 221.0794.

Data for 3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one (**4**h).^{7c} Colorless oil. $R_{f}(10\%$ ethyl acetate/hexane) = 0.32, 10% yield (9 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.94–7.91 (m, 2H), 6.99–6.96 (m, 2H), 3.89 (s, 3H), 3.74 (q, *J* = 10.1 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ –61.98 (t, *J* = 10.0 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 188.3, 164.6, 132.2, 131.0, 124.3 (q, *J* = 277.1 Hz), 114.3, 55.8, 42.0 (q, *J* = 28.0 Hz). MS (ESI): m/z 241 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₉F₃O₂Na 241.0447, found 241.0438.

Data for 1-(2-Chlorophenyl)-3,3,3-trifluoropropan-1-ol (3i).^{7c} Light yellow oil. $R_f(10\%$ ethyl acetate/hexane) = 0.35, 60% yield (54 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.56–7.54 (m, 1H), 7.29–7.24 (m, 2H), 7.20–7.17 (m, 1H), 5.43 (dt, J = 9.3 Hz, 3.0 Hz, 1H), 2.54–2.34 (m, 2H), 2.27 (d, J = 3.8 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.88 (t, J = 10.6 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 139.8, 131.5, 129.9, 129.5, 127.6, 127.2, 126.1 (q, J = 277.8 Hz), 65.7, 41.5 (q, J = 27.3 Hz). MS (ESI): m/z 225 (M + H)⁺. HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₉H₉ClF₃O 225.0294, found 225.0288.

Data for 3,3,3-Trifluoro-1-o-tolylpropan-1-ol (**3***j*). Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.34, 44% yield (36 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.51 (d, J = 7.6 Hz, 1H), 7.29–7.22 (m, 2H), 7.18 (d, J = 7.4 Hz, 1H), 5.35–5.33 (m, 1H), 2.65–2.54 (m, 1H), 2.49–2.38 (m, 1H), 2.36 (s, 3H), 2.12 (s, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –64.15 (t, J = 10.6 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 140.7, 134.3, 131.0, 128.3, 126.9, 126.3 (q, J = 276.3 Hz), 125.3, 65.4, 42.1 (q, J = 26.9 Hz), 19.0. MS (ESI): m/z 227 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₁₁F₃ONa 227.0654, found 227.0641.

Data for 3-(3,3,3-Trifluoro-1-hydroxypropyl)benzaldehyde (**3k**). Colorless oil. $R_f(25\%$ ethyl acetate/hexane) = 0.30, 41% yield (36 mg). ¹H NMR (500 MHz, CDCl₃): δ 10.05 (s, 1H), 7.93 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 5.21 (d, *J* = 8.9 Hz, 1H), 2.72–2.61 (m, 1H), 2.56–2.45 (m, 1H), 2.32 (d, *J* = 2.8 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -63.65 (t, *J* = 10.3 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 192.3, 143.7, 137.0, 132.0, 130.1, 129.8, 126.8, 125.9 (q, *J* = 275.0 Hz), 68.4 (q, *J* = 3.0 Hz), 43.1 (q, *J* = 27.2 Hz). MS (ESI): m/z 219 (M + H)⁺. HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₁₀H₁₀F₃O₂ 219.0627, found 219.0608.

Data for 3-(3,3,3-Trifluoropropanoyl)benzaldehyde (4k).^{7c} Colorless oil. R₁(25% ethyl acetate/hexane) = 0.33, 16% yield (14 mg). ¹H NMR (500 MHz, CDCl₃): δ 10.12 (s, 1H), 8.42 (t, J = 1.7 Hz, 1H), 8.23 (dt, J = 7.8 Hz, 1.3 Hz, 1H), 8.16 (dt, J = 7.6 Hz, 1.3 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 3.87 (q, J = 9.8 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -61.99 (t, J = 9.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 191.2, 189.0, 137.1, 136.7, 135.0, 133.9, 130.2, 129.4, 124.0 (q, J = 277.1 Hz), 42.5 (q, J = 28.6 Hz). MS (ESI): m/z 239 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₇F₃O₂Na 239.0290, found 239.0275.

Data for 3,3,3-Trifluoro-1-(3-nitrophenyl)propan-1-ol (**3**). Yellow oil. R_j (25% ethyl acetate/hexane) = 0.38, 63% yield (59 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.28 (t, *J* = 1.8 Hz, 1H), 8.19 (ddd, *J* = 8.2 Hz, 2.2 Hz, 1.0 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 5.25–5.22 (m, 1H), 2.72–2.61 (m, 1H), 2.56–2.46 (m, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.58 (t, *J* = 10.5 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 148.7, 144.5, 132.0, 130.1, 125.8 (q, *J* = 277.3 Hz), 123.5, 121.0, 68.1, 43.1 (q, *J* = 27.2 Hz). MS (ESI): *m*/*z* 236 (M + H)⁺. HRMS (ESI-TOF): *m*/*z* [M + H]⁺ calcd for C₉H₉F₃NO₃ 236.0529, found 236.0517.

Data for 3,3,3-Trifluoro-1-m-tolylpropan-1-ol (**3m**). Colorless oil. $R_{f}(10\% \text{ ethyl acetate/hexane}) = 0.35, 44\% \text{ yield (36 mg).} ¹H NMR$ (500 MHz, CDCl₃): δ 7.19 (t, <math>J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.07 (t, J = 7.6 Hz, 1H), 4.96–4.93 (m, 1H), 2.59–2.48 (m, 1H), 2.41–2.30 (m, 1H), 2.29 (s, 3H), 2.10 (s, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -63.80 (t, J = 10.6 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 142.5, 138.8, 129.3, 128.9, 126.5, 126.1 (q, J = 276.3 Hz), 122.9, 0.69.1, 43.0 (q, J = 26.9 Hz), 21.6. MS (ESI): m/z 227 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₁₁F₃ONa 227.0654, found 227.0636.

Data for 3,3,3-Trifluoro-1-*m*-tolylpropan-1-one (4*m*).^{7c} Colorless oil. R₍(10% ethyl acetate/hexane) = 0.45, 14% yield (11 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.76 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.79 (q, *J* = 10.0 Hz, 2H), 2.44 (s, 3H). ¹⁹F NMR (470 MHz, CDCl₃): δ -62.06 (t, *J* = 10.0 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 190.1, 139.1, 136.1, 135.2, 129.0, 129.0, 125.8, 124.3 (q, *J* = 276.8 Hz), 42.3 (q, *J* = 28.1 Hz), 21.5. MS (ESI): *m*/*z* 225 (M + Na)⁺. HRMS (ESI-TOF): *m*/*z* [M + Na]⁺ calcd for C₁₀H₉F₃ONa 225.0498, found 225.0483.

Data for 3,3,3-Trifluoro-1-(naphthalen-6-yl)propan-1-ol (**3n**).^{7c} Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.34, 50\% yield (48 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.89–7.84 (m, 4H), 7.55–7.47 (m, 3H), 5.25 (dd, J = 9.0 Hz, 3.5 Hz, 1H), 2.78–2.67 (m, 1H), 2.61–2.51 (m, 1H), 2.30 (s, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –63.66 (t, J = 10.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 139.8, 133.4, 133.4, 129.1, 128.2, 128.0, 126.7, 126.6, 126.1 (q, J = 276.3 Hz), 124.9, 123.5, 69.1 (q, J = 2.8 Hz), 43.0 (q, J = 26.9 Hz). MS (ESI): m/z 263 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₃H₁₁F₃ONa 263.0654, found 263.0636.

Data for 3,3,3-trifluoro-1-(naphthalen-6-yl)propan-1-one (4n).^{7c} White solid. $R_{f}(10\%$ ethyl acetate/hexane) = 0.45, 12% yield (11 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.43, 8.04–7.90 (m, 4H), 7.68–7.59 (m, 2H), 3.95 (q, *J* = 10.0 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ -61.92 (t, *J* = 9.9 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 189.8, 136.2, 133.4, 132.6, 130.8, 129.9, 129.4, 129.2, 128.1, 127.4, 123.3 (q, *J* = 275.0 Hz), 42.4 (q, *J* = 28.3 Hz). MS (ESI): *m*/*z* 261 (M + Na)⁺. HRMS (ESI-TOF): *m*/*z* [M + Na]⁺ calcd for C₁₃H₉F₃ONa 261.0498, found 261.0477.

Data for 2-(Trifluoromethyl)-2,3-dihydro-1H-inden-1-ol (30).7h Colorless oil. $R_{f}(10\% \text{ ethyl acetate/hexane}) = 0.37, 35\% \text{ yield } (28 \text{ mg}).$ ¹H NMR (500 MHz, CDCl₃) (ca. 1:4 mixture of syn and anti isomers, both reported): δ 7.47-7.41 (m, 1H), 7.37-7.29 (m, 2H), 7.27-7.25 (m, 1H), 5.47 (d, J = 6.3 Hz, 0.80H), 5.37 (d, J = 5.7 Hz, 0.20H), 3.40-3.33 (m, 0.20H), 3.29-3.23 (m, 0.80H), 3.14-3.09 (m, 0.40 H), 3.07-2.96 (m, 1.60H), 2.34 (s, 0.80H), 1.81 (s, 0.20H). ¹⁹F NMR (470 MHz, CDCl₃) (ca. 1:4.6 mixture of syn and anti isomers, both reported): δ -65.44 (d, J = 8.6 Hz) (syn), -69.96 (d, J = 8.5 Hz) (anti). ¹³C NMR (125 MHz, CDCl₃) (ca. 1:4.6 mixture of syn and anti isomers, both reported): $\delta(anti \text{ isomer})$ 142.4, 139.3, 129.8, 127.8, 127.8 (q, J = 276.3 Hz), 125.0, 124.6, 76.2 (q, J = 2.8 Hz), 53.2 (q, J = 26.1 Hz), 30.5; δ(syn isomer) 141.0, 138.9, 129.8, 127.9, 125.3, 125.3, 74.7 (q, J = 2.0 Hz), 47.6 (q, J = 26.0 Hz), 30.5. MS (ESI): m/z 225 $(M + Na)^+$. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for C₁₀H₉F₃ONa 225.0498, found 225.0492.

Data for 2-(Trifluoromethyl)-2,3-dihydroinden-1-one (40).^{7a} Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.45, 18% yield (14 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 3.49–3.41 (m, 2H), 3.35–3.27 (m, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -67.77 (d, J = 9.5 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 197.1, 152.3, 136.0, 128.4, 126.9, 126.7, 125.4 (q, J = 277.5 Hz), 124.9, 50.0 (q, J = 27.5 Hz), 27.8. MS (ESI): m/z 223 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₇F₃ONa 223.0341, found 223.0319.

Data for 2-(Trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**3p**). Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.37, 36% yield (31 mg). ¹H NMR (500 MHz, CDCl₃) (ca. 24:76 mixture of *syn* and *anti* isomers, both reported): δ 7.57 (d, *J* = 7.5 Hz, 0.76H), 7.36 (d, *J* = 7.5 Hz, 0.24H), 7.27–7.22 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 0.24H), 7.13 (d, *J* = 7.4 Hz, 0.76H), 5.04–5.02 (m, 1H), 3.05–3.01 (m, 0.48H), 2.94–2.82 (m, 1.52H), 2.60–2.43 (m, 1H), 2.27–2.22 (m, 0.76H), 2.22–2.15 (m, 1H), 2.07–2.03 (m, 0.24H), 1.87–1.79 (m, 1H). ¹⁹F NMR (470 MHz, CDCl₃) (ca. 1:2.6 mixture of *syn* and *anti* isomers, both reported): δ –68.70 (d, *J* = 8.6 Hz) (*syn*), –69.79 (d, *J* = 8.1 Hz) (*anti*). ¹³C NMR (125 MHz, CDCl₃) (ca. 1:2.6 mixture of *syn* and *anti* isomers, both reported): δ (*anti* isomer) 136.9, 136.2, 129.0, 128.2, 128.1, 127.9 (q, *J* = 277.5 Hz), 127.0, 67.7, 47.3 (q, *J* = 24.4 Hz), 27.8,

21.2; $\delta(syn \text{ isomer})$ 136.5, 135.8, 130.3, 129.4, 129.0, 126.7, 66.0, 44.7 (q, *J* = 25.6 Hz), 28.4, 16.5. MS (ESI): *m*/*z* 239 (M + Na)⁺. HRMS (ESI-TOF): *m*/*z* [M + Na]⁺ calcd for C₁₁H₁₁F₃ONa 239.0654, found 239.0639.

Data for 2-(*Trifluoromethyl*)-3,4-*dihydronaphthalen*-1(2*H*)-one (**4p**).^{7a} Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.47, 23% yield (20 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.07 (dd, J = 7.9 Hz, 1.1 Hz, 1H), 7.53 (td, J = 7.5, 1.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.29–7.27 (m, 1H), 3.33–3.24 (m, 1H), 3.17–3.05 (m, 2H), 2.54–2.48 (m, 1H), 2.33–2.25 (m, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –67.55 (d, J = 8.7 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 190.4, 143.3, 134.4, 132.2, 129.0, 128.6, 128.1, 125.3 (q, J = 280.2 Hz), 51.1 (q, J = 25.7 Hz), 27.8, 23.7. MS (ESI): m/z 237 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₁H₃F₃ONa 237.0498, found 237_0474.

Data for 2-(Trifluoromethyl)-1-phenylpropan-1-ol (3a).^{7h} Colorless oil. R_f(10% ethyl acetate/hexane) = 0.35, 16% yield (13 mg) (anti isomer). $R_{f}(10\% \text{ ethyl acetate/hexane}) = 0.33, 15\% \text{ yield } (12 \text{ mg}) (syn)$ isomer). The following are the spectral data for the anti isomer (anti-**3q**). ¹H NMR (500 MHz, CDCl₃): δ 7.43–7.30 (m, 5H), 5.24 (d, J = 3.0 Hz, 1H), 2.51–2.45 (m, 1H), 1.98 (s, 1H), 1.10 (d, J = 7.1 Hz, 3H). ¹⁹F NMR (470 MHz, CDCl₂): δ -70.15 (d, J = 9.5 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 141.7, 128.7, 128.0, 127.9 (q, J = 278.8 Hz), 125.4, 70.7, 45.4 (q, J = 24.4 Hz), 8.1. MS (ESI): m/z 227 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₁₁F₃ONa 227.0654, found 227.0641. The following are the spectral data for the syn isomer (syn-3q). ¹H NMR (500 MHz, CDCl₃): δ 7.42-7.31 (m, 5H), 4.82 (d, J = 8.2 Hz, 1H), 2.70–2.61 (m, 1H), 2.19 (s, 1H), 0.88 (d, J = 7.2 Hz, 3H). ¹⁹F NMR (470 MHz, CDCl₃): δ -69.62 (d, J = 8.6 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 141.1, 128.9, 128.7, 127.3 (q, J = 278.5 Hz), 74.2, 44.9 (q, J = 24.4 Hz), 10.8. MS (ESI): m/z 227 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₁₁F₃ONa 227.0654, found 227.0641.

Data for 2-(Trifluoromethyl)-1-phenylpropan-1-one (**4q**).^{7a} Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.45, 25% yield (20 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.1 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 4.35–4.14 (m, 1H), 1.49 (d, J = 7.1 Hz, 3H). ¹⁹F NMR (470 MHz, CDCl₃) δ –68.28 (d, J = 8.0 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 194.6, 135.9, 134.2, 129.1, 128.8, 125.5 (q, J = 278.8 Hz), 44.5 (q, J = 26.3 Hz), 11.9. MS (ESI): m/z 225 (M + Na)⁺. HRMS (ESI-TOF): m/z [M + Na]⁺ calcd for C₁₀H₃F₃ONa 225.0498, found 225.0482.

Data for 1,1,1-Trifluorononan-3-ol (**3***t*).^{15c} Colorless oil. $R_f(10\%)$ ethyl acetate/hexane) = 0.39, 45% yield (36 mg). ¹H NMR (500 MHz, CDCl₃) δ 4.04–3.99 (m, 1H), 2.32–2.22 (m, 2H), 1.80 (s, 1H), 1.58–1.48 (m, 2H), 1.39–1.27 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H). ¹⁹F NMR (470 MHz, CDCl₃) δ –63.55 (t, J = 10.9 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 126.7 (q, J = 275.0 Hz), 66.4 (q, J = 2.5 Hz), 41.3 (q, J = 26.3 Hz), 37.4, 31.9, 29.2, 25.4, 22.8, 14.3. MS (EI): m/z 198 (M⁺). HRMS (EI-TOF): m/z [M]⁺ calcd for C₉H₁₇F₃O 198.1231, found 198.1220.

Data for 2-(*Trifluoromethyl*)cyclooctanol (**3s**). Colorless oil. $R_f(10\%$ ethyl acetate/hexane) = 0.38, 35% yield (27 mg). ¹H NMR (500 MHz, CDCl₃) (ca. 30:70 mixture of *syn* and *anti* isomers, both reported): δ 4.25 (t, J = 6.2 Hz, 0.30H), 4.09–4.05 (m, 0.70H), 2.40–2.29 (m, 1H), 1.99–1.70 (m, 7H), 1.66–1.54 (m, 2H), 1.49–1.42 (m, 4H). ¹⁹F NMR (470 MHz, CDCl₃) (ca. 30:70 mixture of *syn* and *anti* isomers, both reported): δ -69.46 (d, J = 9.4 Hz) (*syn*), -69.48 (d, J = 9.4 Hz) (*anti*). ¹³C NMR (125 MHz, CDCl₃) (ca. 30:70 mixture of *syn* and *anti* isomers, both reported): δ (*anti* isomer) 129.2 (q, J = 278.8 Hz), 69.5, 49.0 (q, J = 21.3 Hz), 31.3, 28.5, 26.2, 25.6, 22.8, 20.9; δ (*syn* isomer) 128.8 (q, J = 278.8 Hz), 67.5 (q, J = 2.5 Hz), 45.2 (q, J = 27.5 Hz), 32.7, 27.6, 27.0, 24.6, 23.5, 19.7. MS (EI): m/z 196 (M⁺). HRMS (EI-TOF): m/z [M⁺] calcd for C₉H₁₅F₃O 196.1075, found 196.1065.

Data for anti-Methyl 2-(Trifluoromethyl)-3-hydroxy-3-phenylpropanoate (anti-**3**t). Colorless oil. $R_f(25\%$ ethyl acetate/hexane) = 0.30, 25\% yield (25 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.41–7.34 (m, 5H), 5.24 (d, *J* = 6.8 Hz, 1H), 3.77 (s, 3H), 3.62–3.56 (m, 1H), 3.15 (s, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ –64.55 (d, *J* = 7.4 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 167.1, 140.1, 129.8, 128.9, 126.8, 126.3, 123.5 (q, *J* = 278.8 Hz), 71.1, 57.2 (q, *J* = 26.2 Hz), 52.9. MS

(EI): m/z 248 (M⁺). HRMS (EI-TOF): m/z [M⁺] calcd for C₁₁H₁₁F₃O₃ 248.0660, found 248.0669.

Data for syn-Methyl 2-(Trifluoromethyl)-3-hydroxy-3-phenylpropanoate (syn-3t).^{15d} Colorless oil. $R_f(25\%$ ethyl acetate/hexane) = 0.32, 17% yield (17 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.38–7.34 (m, SH), 5.26 (d, J = 9.0 Hz, 1H), 3.63–3.55 (m, 1H), 3.49 (s, 3H), 2.43 (d, J = 2.8 Hz, 1H). ¹⁹F NMR (470 MHz, CDCl₃): δ -63.95 (d, J = 7.4 Hz, 3F). ¹³C NMR (125 MHz, CDCl₃): δ 166.0, 139.5, 129.3, 129.0, 126.8, 124.1 (q, J = 280.0 Hz), 72.0, S8.1 (q, J = 26.3 Hz), 52.8 MS (EI): m/z 248 (M⁺). HRMS (EI-TOF): m/z [M⁺] calcd for C₁₁H₁₁F₃O₃ 248.0660, found 248.0669.

Procedure for Scale-Up Oxytrifluoromethylation of 2-Vinylnaphthalene and Successive Reduction Manipulation. To a solution of CF₃SO₂Na (1.64 g, 10.5 mmol) in acetone (70 mL) were added 2-vinylnaphthalene (1.08 g, 7.0 mmol) and then MnCl₂·4H₂O (277 mg, 1.4 mmol). The reaction mixture was stirred vigorously under an open atmosphere at room temperature for 12 h until the substrate disappeared by TLC monitoring. After completion of the reaction, the reaction mixture was poured into 5% aqueous NaHCO₃ solution (100 mL) and then was diluted with ether (50 mL) and filtered through Celite. The filtrate was separated, and the aqueous layer was extracted by ether (50 mL). The organic phase was washed with saturated NaCl aqueous solution and then dried over sodium sulfate. After removal of the solvent in vacuo, residue A was purified by flash chromatography (hexane:ethyl acetate = 20:1 to 10:1, volume ratio) on silica gel to afford the corresponding ketone 4n (0.22 g, 13% yield) and alcohol 3n (0.71 g, 42% yield), respectively.

To obtain the single alcohol product 3n, a two-step successive manipulation was carried out. Residue A was dissolved in MeOH (25 mL) and cooled to 0 °C. Then NaBH₄ (3.5 mmol, 132 mg) was added in portions. After being stirred for 1 h, the reaction mixture was poured into saturated NH₄Cl aqueous solution (50 mL) and then extracted by ethyl acetate (30 mL × 3). The organic phase was washed with saturated NaCl aqueous solution and then dried over sodium sulfate. After removal of the solvent in vacuo, the residue was purified by flash chromatography (hexane:ethyl acetate = 10:1, volume ratio) on silica gel to afford single alcohol product 3n (0.96 g, 57% yield).

ASSOCIATED CONTENT

S Supporting Information

Description of the general methods used in this study and ¹H NMR, ¹⁹F NMR, and ¹³C NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00781.

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Notes

The authors declare no competing financial interest.

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