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Manganese-Catalyzed Aerobic Oxytrifluoromethylation of Styrene Derivatives Using CF_3SO_2Na as the Trifluoromethyl Source

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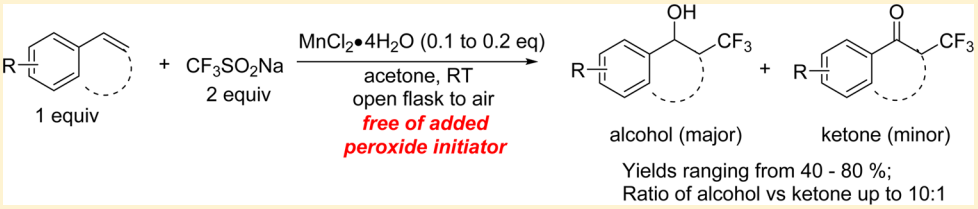
Supporting Information



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 CF_3 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 CF_3 radical species have drawn increasing attention because they can employ benchtop stable and cost-effective reagents, such as CF_3SO_2Na (the Langlois reagent), as CF_3 radical sources.[3] Recently, several strategies for selective vicinal trifluoromethylation-based difunctionalization[4−7] of olefins via three-component (alkene, CF_3SO_2Na, reactive trapping agents) intermolecular reactions[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 (^{t}BuOOH, $K_2S_2O_8$) 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 well-known that dioxygen is an ideal environment-friendly oxidant and offers fascinating academic and industrial prospects.[9] Therefore, developing a new mode to activate CF_3SO_2Na 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, acetoxyphosphorylation, and hydroxyazidation.[10] Moreover, manganese catalysts were proven to play an important role in accelerating the autoxidation of sulfur(IV) species (SO_2, 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 CF_3SO_2Na 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 $MnCl_2\cdot 4H_2O$ (entry 1, Table 1). In contrast with $MnCl_2\cdot 4H_2O$, $MnSO_4\cdot H_2O$ gave decreased selectivity (**3a**:**4a** = 1.5:1) and decreased catalytic efficiency with prolonged reaction time

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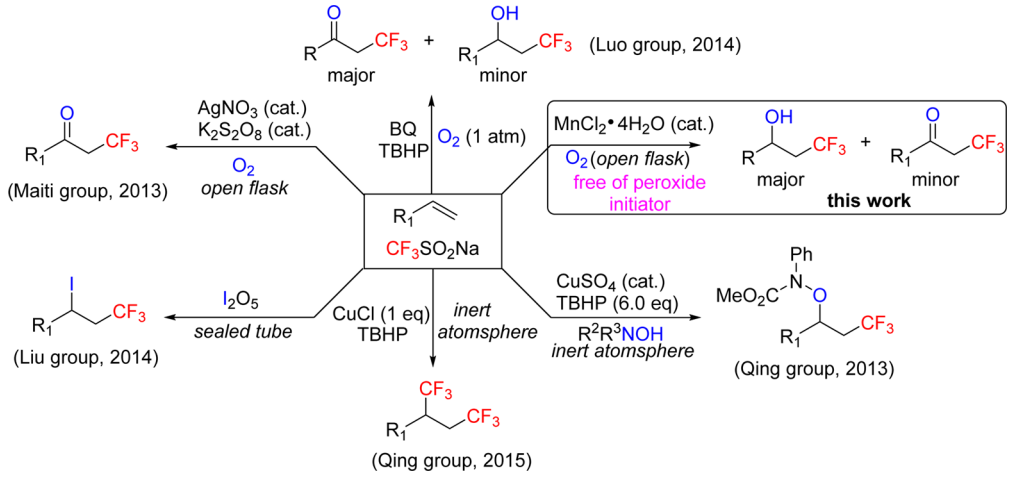
Scheme 1. Trifluoromethylation-Based Difunctionalization of Olefins by Using CF_3SO_2Na



Scheme 2. Reaction Development Considerations

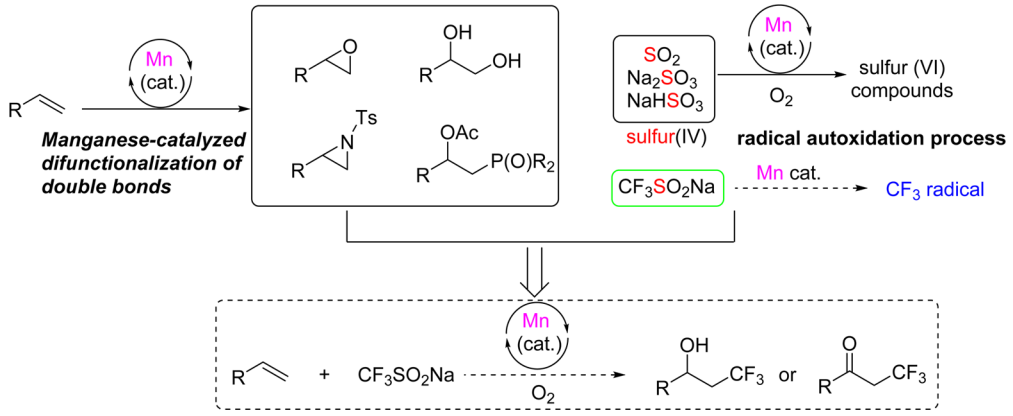
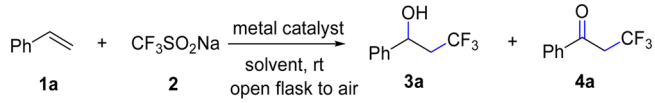


Table 1. Optimization of the Oxytrifluoromethylation of Styrene[a]



entry	metal catalyst (loading, equiv)	solvent	time (h)	ratio (**3a**:**4a**)[b,c]	yield (**3a**+**4a**)[d] (%)
1	$MnCl_2·4H_2O$ (0.1)	acetone	12	3.2:1	52 + 16
2	$MnSO_4·H_2O$ (0.1)	acetone	48	1.5:1	37 + 25
3	$Mn(OAc)_2·4H_2O$ (0.1)	acetone	48	NR[e]	NR[e]
4	$Mn(OAc)_3·2H_2O$ (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	$MnCl_2·4H_2O$ (0.2)	DMF	48	1:6	5 + 30
10	$MnCl_2·4H_2O$ (0.2)	DMSO	48	1:12.3	2 + 25
11[f]	$MnCl_2·4H_2O$ (0.2)	acetone	12	6:1	66 + 11
12	no catalyst addition	acetone	48	NR	NR
13[g]	$MnCl_2·4H_2O$ (0.2)	acetone	48	NR	NR

[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 ^{19}F NMR spectroscopy of the crude product (after workup and extraction). [c]A trace amount of vinyl triflone **5a** ($PhCH{=}CHSO_2CF_3$) was also observed by ^{19}F 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 ^{19}F NMR using $PhCF_3$ as an internal standard. [e]TLC analysis indicated no conversion of styrene and no formation of oxytrifluoromethylation products; only CF_3SO_2Na was transformed partially or completely into CF_3SO_3Na. [f]CF_3SO_2Na (0.4 mmol, 2.0 equiv) was utilized. [g]The reaction was conducted under a N_2 atmosphere.

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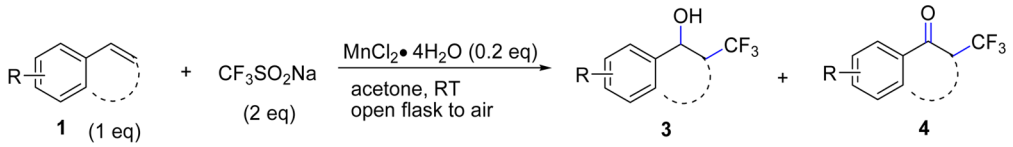
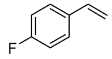
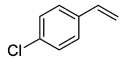
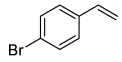
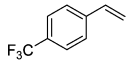
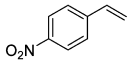
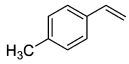
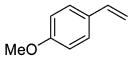
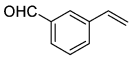
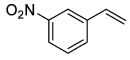
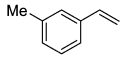
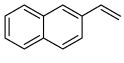
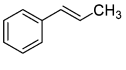
Table 2. Substrate Scope of Mangenese-Catalyzed Oxytrifluoromethylation of Styrene Derivatives[a]



Entry	Styrene Derivatives	Time	Product **3**+**4**	Ratio of **3**/**4**[b]	Yield[c]
1		12 h	**3a**+**4a**	6 : 1	65+10 %
2		24 h	**3b**+**4b**	3 : 1	52+16 %
3		24 h	**3c**+**4c**	2.4 : 1	53+22 %
4		24 h	**3d**+**4d**	2.1 : 1	50+24 %
5		24 h	**3e**+**4e**	2 : 1	48+22 %
6		12 h	**3f**+**4f**	3 : 1	59+20 %
7		24 h	**3g**+**4g**	2.2 : 1	36+17 %
8[d]		12 h	**3h**+**4h**	3 : 1	32+10 %
9		24 h	**3i**+**4i**	>10 : 1	60 %+~[e]
10		24 h	**3j**+**4j**	>10 : 1	44 %+~[e]
11		48 h	**3k**+**4k**	2.5 : 1	41+16 %
12		12 h	**3l**+**4l**	>10 : 1	63 %+~[e]
13		24 h	**3m**+**4m**	3 : 1	44+14 %
14		12 h	**3n**+**4n**	4.2 : 1	50+12 %
15		12 h	**3o**+**4o**	2 : 1	35[f]+18 %
16		12 h	**3p**+**4p**	1.5 : 1	36[g]+23 %
17		12 h	**3q**+**4q**	1.2 : 1	31[h]+25 %

[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 ^{19}F NMR spectroscopy of the crude product (after workup and extraction). [c]Isolated 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 **3o** 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,

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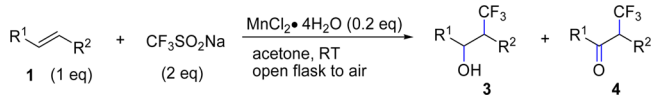
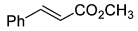
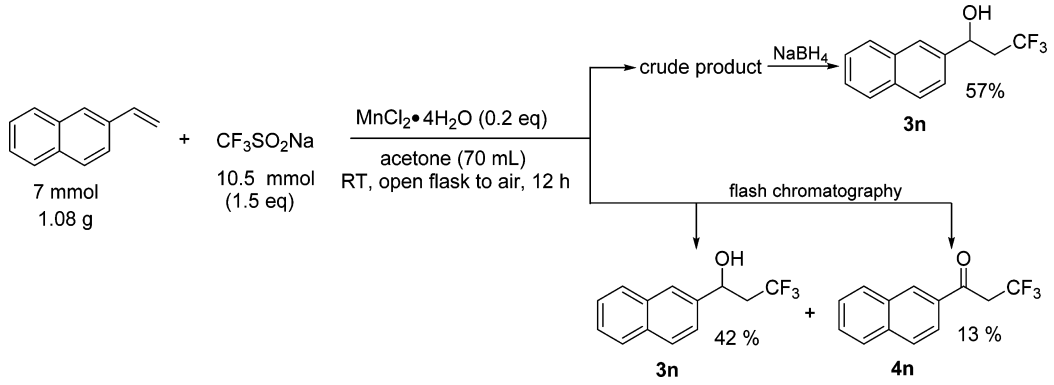
Table 3. Mangenese-Catalyzed Oxytrifluoromethylation of Other Types of Alkenes[a]



Entry	Alkenes	Time	Product **3**+**4**	Ratio of **3**/**4**[b]	Yield[c]
1		12 h	**3r**+**4r**	3.6 : 1	45 % +13 %[d]
2		12 h	**3s**+**4s**	1.2 : 1	35 %[e] +30 %[d]
3		48 h	**3t** +**4t**[f]	2.7 : 1	42%[g] +~[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 ^{19}F 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 ^{19}F NMR using $PhCF_3$ as a reference. [e]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 (1*R*, 2*R*)-(−)-[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 CF_3SO_2Na as well as in regulating catalytic activity and selectivity. Employment of heterogeneous manganese catalysts such as MnO, Mn_2O_3, and MnO_2 led to sluggish reactions, and only MnO delivered the oxytrifluoromethylation product in moderate yield (entries 6−8). Screening of other metal catalysts including $AgNO_3$, $FeCl_2{\cdot}4H_2O$, $Fe(acac)_3$, CuCl, $NiCl_2$, and $CoCl_2{\cdot}6H_2O$ did not give better results than $MnCl_2{\cdot}4H_2O$ (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 electron-donating 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-NO_2-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*-*β*-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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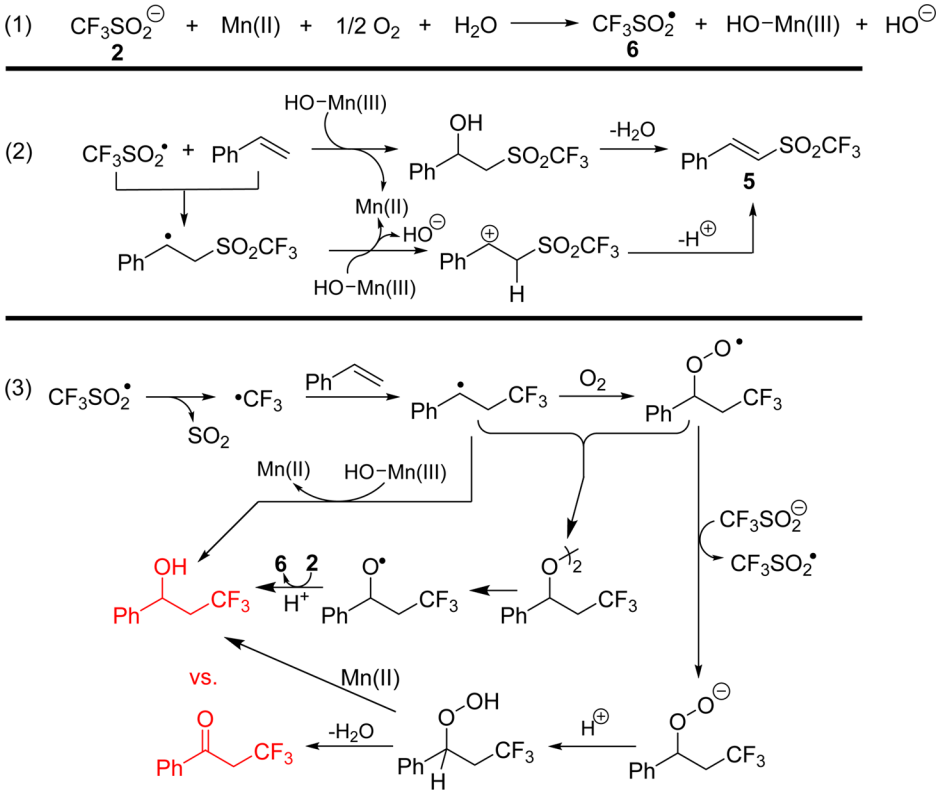
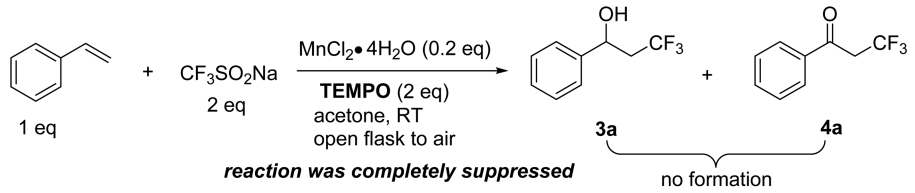
Scheme 4. Possible Mechanism of Mn-Catalyzed Oxytrifluoromethylation

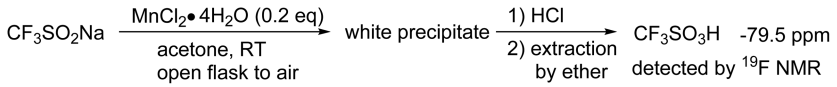


Scheme 5. Mechanistic Investigations of Mn-Catalyzed Oxytrifluoromethylation

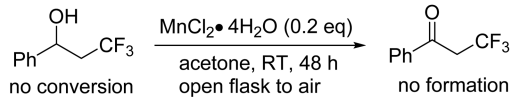
(a) Suppression effect of addition of radical scavenger



(b) Role of accelerating the autoxidation of CF_3SO_2Na exerted by $MnCl_2 \bullet 4H_2O$



(c) Interrogation of the generation of ketone product



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 α,β-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 2-vinylpyridine 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 CF_3 radical is proposed as shown in Scheme 4. The radical pathway of this manganese-catalyzed oxytrifluoromethylation was supported by the following

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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=CHSO$_2$CF$_3$ (**5a**) in trace amounts was detected by ^{19}F and ^{1}H 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 ^{19}F NMR (−79.5 ppm) instead of the commonly conceivable adduct TEMPO−CF_3 (**7**). Moreover, the exploration of the catalytic roles of $MnCl_2\cdot 4H_2O$ was conducted on the basis of the following experiment: Stirring CF_3SO_2Na with $MnCl_2\cdot 4H_2O$ in acetone under aerobic conditions, in the absence of olefins, led to the precipitation of a white salt which was identified as CF_3SO_3Na via ^{19}F NMR analysis (Scheme 5b). This result is consistent with our hypothesis that $MnCl_2\cdot 4H_2O$ plays an important role in accelerating the autoxidation of bench-stable CF_3SO_2Na, although the thermodynamic impetus of the autoxidation of the Langlois reagent is remarkable from the analysis of redox potentials[14] of $CF_3SO_2^-/CF_3SO_2^\bullet$ (0.6 V) and O_2, H^+/H_2O (1.23 V). The CF_3SO_2 radical might be generated in the system of $MnCl_2\cdot 4H_2O$ and O_2, which combined with an oxy species (O_2, HO$^\bullet$, Mn(III)−OH) provides $CF_3SO_3^-$. Finally, it was proven that ketone **4a** was not formed by the in situ oxidation of benzylic alcohol **3a** under the catalytic condition of $MnCl_2\cdot 4H_2O$ (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 CF_3 radical from CF_3SO_2Na 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 CF_3 radical involving process is highly likely. Additionally, the detection of vinyl triflone PhCH=CHSO$_2$CF$_3$ (**5a**) shed some light on the intermediacy of the CF_3SO_2 radical, an important species in the single-electron-oxdiation process of CF_3SO_2Na. Further applications of this new activation mode of CF_3SO_2Na 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 $NaHCO_3$ 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. R_f(10% ethyl acetate/hexane) = 0.35, 65% yield (49 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.70 (t, J = 10.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_9F_3O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.12 (t, J = 9.9 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_7F_3O$ 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 15.5 Hz, 1H), 7.53−7.41 (m, 5H), 6.76 (d, J = 15.5 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −77.74 (s, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_7F_3O_2SNa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.75 (t, J = 10.4 Hz, 3F), −113.58 to −113.64 (m, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_8F_4O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00−7.96 (m, 2H), 7.22−7.17 (m, 2H), 3.78 (q, J = 9.9 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.00 (t, J = 9.9 Hz, 3F), −102.81—-102.87 (m, 1F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_6F_4O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.75 (t, J = 10.5 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_8ClF_3O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90−7.87 (m, 2H), 7.51−7.48 (m, 2H), 3.78 (q, J = 9.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.03 (t, J = 9.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_6F_3O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.65 (t, J = 10.4 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.4, 132.2,

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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 $C_9H_8BrF_3O$ 267.9711, found 267.9731.

*Data for 1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-one (**4d**).*[7c] Light yellow solid. R_f(10% ethyl acetate/hexane) = 0.41, 24% yield (25 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.01 (t, J = 9.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_6BrF_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.56 (s, 3F), −63.59 (t, J = 10.4 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_8F_6O$ 258.0479, found 258.0459.

*Data for 3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-one (**4e**).*[7c] White solid. R_f(10% ethyl acetate/hexane) = 0.44, 22% yield (22 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.06 (t, J = 9.7 Hz, 3F), −63.38 (s, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_6F_6O$ 256.0323, found 256.0364.

*Data for 3,3,3-Trifluoro-1-(4-nitrophenyl)propan-1-ol (**3f**).*[7c] Light yellow solid. R_f(20% ethyl acetate/hexane) = 0.35, 59% yield (55 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.59 (t, J = 10.5 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_8F_3NO_3$ 235.0456, found 235.0420.

*Data for 3,3,3-Trifluoro-1-(4-nitrophenyl)propan-1-one (**4f**).*[7c] Light yellow solid. R_f(10% ethyl acetate/hexane) = 0.40, 20% yield (18 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38−8.36 (m, 2H), 8.13−8.11 (m, 2H), 3.87 (q, J = 9.7 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.97 (t, J = 9.8 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_6F_3NO_3$ 233.0300, found 233.0287.

*Data for 3,3,3-trifluoro-1-p-tolylpropan-1-ol (**3g**).*[7c] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.36, 36% yield (29 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.77 (t, J = 9.9 Hz, 3F). ^{13}C 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 $C_{10}H_{11}F_3O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.03 (t, J = 10.0 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_9F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.75 (t, J = 10.4 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_{12}F_3O_2$ 221.0789, found 221.0794.

*Data for 3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one (**4h**).*[7c] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.32, 10% yield (9 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.98 (t, J = 10.0 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_9F_3O_2Na$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.88 (t, J = 10.6 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_9ClF_3O$ 225.0294, found 225.0288.

*Data for 3,3,3-Trifluoro-1-o-tolylpropan-1-ol (**3j**).* Colorless oil. R_f(10% ethyl acetate/hexane) = 0.34, 44% yield (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −64.15 (t, J = 10.6 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_{11}F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.65 (t, J = 10.3 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_{10}F_3O_2$ 219.0627, found 219.0608.

*Data for 3-(3,3,3-Trifluoropropanoyl)benzaldehyde (**4k**).*[7c] Colorless oil. R_f(25% ethyl acetate/hexane) = 0.33, 16% yield (14 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.99 (t, J = 9.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_7F_3O_2Na$ 239.0290, found 239.0275.

*Data for 3,3,3-Trifluoro-1-(3-nitrophenyl)propan-1-ol (**3l**).* Yellow oil. R_f(25% ethyl acetate/hexane) = 0.38, 63% yield (59 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.58 (t, J = 10.5 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_9F_3NO_3$ 236.0529, found 236.0517.

*Data for 3,3,3-Trifluoro-1-m-tolylpropan-1-ol (**3m**).* Colorless oil. R_f(10% ethyl acetate/hexane) = 0.35, 44% yield (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (t, 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.80 (t, J = 10.6 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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

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(q, J = 26.9 Hz), 21.6. MS (ESI): m/z 227 (M + Na)$^+$. HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{10}H_{11}F_3ONa$ 227.0654, found 227.0636.

*Data for 3,3,3-Trifluoro-1-m-tolylpropan-1-one (**4m**).*[7c] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.45, 14% yield (11 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.06 (t, J = 10.0 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_9F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.66 (t, J = 10.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{13}H_{11}F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43, 8.04−7.90 (m, 4H), 7.68−7.59 (m, 2H), 3.95 (q, J = 10.0 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.92 (t, J = 9.9 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{13}H_9F_3ONa$ 261.0498, found 261.0477.

*Data for 2-(Trifluoromethyl)-2,3-dihydro-1H-inden-1-ol (**3o**).*[7h] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.37, 35% yield (28 mg). ^{1}H NMR (500 MHz, $CDCl_3$) (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). ^{19}F NMR (470 MHz, $CDCl_3$) (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*). ^{13}C NMR (125 MHz, $CDCl_3$) (ca. 1:4.6 mixture of *syn* and *anti* isomers, both reported): δ(*anti* 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 $C_{10}H_9F_3ONa$ 225.0498, found 225.0492.

*Data for 2-(Trifluoromethyl)-2,3-dihydroinden-1-one (**4o**).*[7a] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.45, 18% yield (14 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −67.77 (d, J = 9.5 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_7F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$) (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). ^{19}F NMR (470 MHz, $CDCl_3$) (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*). ^{13}C NMR (125 MHz, $CDCl_3$) (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; δ(*syn* 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 $C_{11}H_{11}F_3ONa$ 239.0654, found 239.0639.

*Data for 2-(Trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (**4p**).*[7a] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.47, 23% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −67.55 (d, J = 8.7 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{11}H_9F_3ONa$ 237.0498, found 237.0474.

*Data for 2-(Trifluoromethyl)-1-phenylpropan-1-ol (**3q**).*[7h] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.35, 16% yield (13 mg) (*anti* isomer). R_f(10% ethyl acetate/hexane) = 0.33, 15% yield (12 mg) (*syn* isomer). The following are the spectral data for the *anti* isomer (*anti*-**3q**). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −70.15 (d, J = 9.5 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_{11}F_3ONa$ 227.0654, found 227.0641. The following are the spectral data for the *syn* isomer (*syn*-**3q**). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −69.62 (d, J = 8.6 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_{11}F_3ONa$ 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{19}F NMR (470 MHz, $CDCl_3$) δ −68.28 (d, J = 8.0 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{10}H_9F_3ONa$ 225.0498, found 225.0482.

*Data for 1,1,1-Trifluorononan-3-ol (**3r**).*[15c] Colorless oil. R_f(10% ethyl acetate/hexane) = 0.39, 45% yield (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{19}F NMR (470 MHz, $CDCl_3$) δ −63.55 (t, J = 10.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_9H_{17}F_3O$ 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). ^{1}H NMR (500 MHz, $CDCl_3$) (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). ^{19}F NMR (470 MHz, $CDCl_3$) (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*). ^{13}C NMR (125 MHz, $CDCl_3$) (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 $C_9H_{15}F_3O$ 196.1075, found 196.1065.

*Data for anti-Methyl 2-(Trifluoromethyl)-3-hydroxy-3-phenylpropanoate (anti-**3t**).* Colorless oil. R_f(25% ethyl acetate/hexane) = 0.30, 25% yield (25 mg). ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −64.55 (d, J = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 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

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(EI): m/z 248 (M^+). HRMS (EI-TOF): m/z [M^+] calcd for $C_{11}H_{11}F_3O_3$ 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). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.34 (m, 5H), 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). ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.95 (d, J = 7.4 Hz, 3F). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 139.5, 129.3, 129.0, 126.8, 124.1 (q, J = 280.0 Hz), 72.0, 58.1 (q, J = 26.3 Hz), 52.8. MS (EI): m/z 248 (M^+). HRMS (EI-TOF): m/z [M^+] calcd for $C_{11}H_{11}F_3O_3$ 248.0660, found 248.0669.

Procedure for Scale-Up Oxytrifluoromethylation of 2-Vinylnaphthalene and Successive Reduction Manipulation. To a solution of CF_3SO_2Na (1.64 g, 10.5 mmol) in acetone (70 mL) were added 2-vinylnaphthalene (1.08 g, 7.0 mmol) and then $MnCl_2·4H_2O$ (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 $NaHCO_3$ 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 $NaBH_4$ (3.5 mmol, 132 mg) was added in portions. After being stirred for 1 h, the reaction mixture was poured into saturated NH_4Cl 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

Supporting Information

Description of the general methods used in this study and ^{1}H NMR, ^{19}F NMR, and ^{13}C 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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