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$Mn(OAc)_3$-Mediated Hydrotrifluoromethylation of Unactivated Alkenes Using CF_3SO_2Na as the Trifluoromethyl Source

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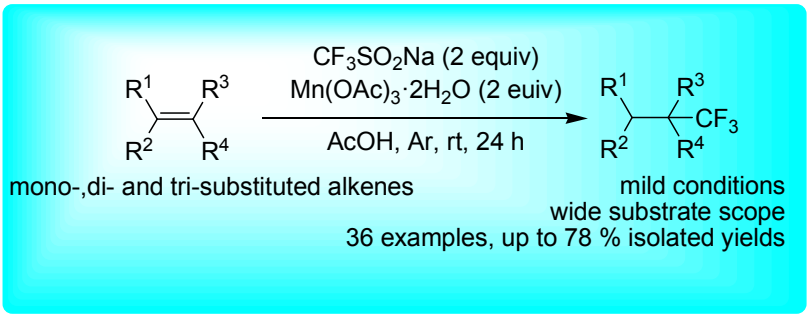
ABSTRACT



A simple and efficient method for hydrotrifluoromethylation of unactivated alkenes was reported. The reaction relied on the single electron oxidation of a commercially available sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois' reagent) using $Mn(OAc)_3·2H_2O$ as the oxidant, and the subsequent addition of trifluoromethyl radical to C=C double bonds. The reaction proceeded readily under mild conditions with good tolerance of a variety of functional groups in the substrates. Preliminary reaction mechanism was studied with deuteration, radical clock and TEMPO inhibition experiments.

INTRODUCTION

Trifluoromethyl group has been well recognized in medicinal chemistry due to its strong electron-withdrawing and lipophilic properties. The lipophilicity, bioavailability, binding

selectivity and metabolic stability of a compound can be significantly improved by the incorporation of trifluoromethyl group,[1] and significant efforts have been made to develop new and efficient methods for trifluoromethylation of different substrates. Among the variety of methods developed, direct trifluoromethylation of C=C double bonds has been proved to be one of the most straightforward methods for the incorporation of trifluoromethyl group.[2] In this connection, Togni's reagents,[3] Umemoto's reagents,[4] Langlois' reagents (trifluoromethanesulfinate, CF_3SO_2Na),[5] Ruppert's and related reagents,[6] fluoroalkyl halides[7] and fluoroform derived trifluoromethyl agents[8] have all been studied for their potential of trifluoromethylation of different unactivated alkenes. Among the trifluoromethylating agents studied, Langlois' reagent has attracted considerable attention as the trifluoromethyl radical precursor and found numerous applications in a variety of trifluoromethylation reactions such as photoredox system-promoted[9] or visible-light-induced photocatalytic reactions.[10]

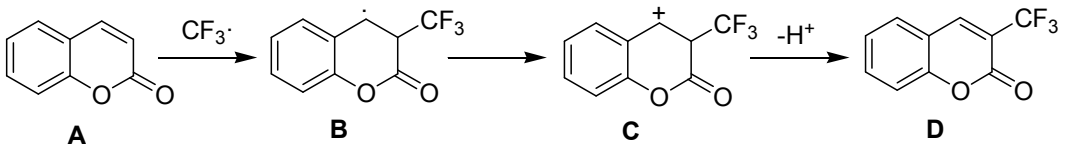
We have shown that trifluoromethylation of ketones and esters/lactones could be realized using Ruppert's reagent as the trifluoromethylating agent and 10 mol% of $MgCl_2$ as the catalyst.[11] Herein we wish to report our recent results on $Mn(OAc)_3 \cdot 2H_2O$-mediated free radical hydrotrifluoromethylation of unactivated alkenes as a continuation of our program on trifluoromethylation and manganese-catalyzed reactions.

RESULTS AND DISCUSSION

Manganese-mediated oxidative radical reactions have been proved to be simple and efficient methods for the functionalization of C-H and C-C bonds.[12] Vicic et al. reported the Mn(II)-catalyzed aerobic oxytrifluoromethylation of styrene derivatives using CF_3SO_2Na as the trifluoromethyl source.[13] Zou et al. reported an Mn(III)-mediated direct Csp^2-H radical

trifluoromethylation of coumarins using CF_3SO_2Na as the trifluoromethylation agent.[5a] The reaction involved the addition of trifluoromethyl radical to 3-position of coumarins **A** and subsequent oxidation of the intermediate radical **B** by $Mn(OAc)_3$. Deprotonation of the resulted carbenium cation intermediate **C** gave the desired 3-trifluoromethylcoumarins **D** as the final products (Scheme 1).[5a]

Scheme 1. Csp2-H radical trifluoromethylation of coumarins

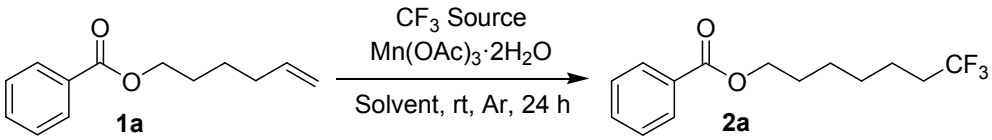


We anticipated that the formation of carbenium cation may be avoided if the reactions were carried out under inert atmosphere with reduced amount of $Mn(OAc)_3$, and a hydrotrifluoromethylation reaction should be possible under carefully controlled conditions.

To verify this assumption, hydrotrifluoromethylation of model substrate hex-5-en-1-yl benzoate (**1a**) was carried out using $Mn(OAc)_3{\cdot}2H_2O$ as the oxidant in the presence of a variety of trifluoromethylating agents. To our delight, 77% of the substrate was converted to the desired **2a** when a solution of **1a**, CF_3SO_2Na (2 equiv) and $Mn(OAc)_3{\cdot}2H_2O$ (3 equiv) in AcOH was stirred at room temperature for 24 h under argon atmosphere (entry 1, Table 1). Further studies indicated that AcOH was superior to other solvents such as MeOH, DMF, DCE or acetone (Table 1, entry 1 vs entries 2-5). Reaction with other trifluoromethylating agent such as Ruppert's reagent $TMSCF_3$ was not successful (Table 1, entry 6). Similar substrate conversion was observed when the amount of $Mn(OAc)_3{\cdot}2H_2O$ was reduced from 3 equiv to 2 equiv (Table 1, entry 7), and further reducing the amount of $Mn(OAc)_3{\cdot}2H_2O$ or CF_3SO_2Na led to drops of substrate conversions (Table 1, entries 8-10). Reactions without

argon protection were also tested.[13] However, complex mixtures were obtained under otherwise identical conditions. The desired hydrotrifluoromethylation product **2a** was obtained in 57% isolated yield after careful separation and purification (Table 1, entry 11). Therefore, the hydrotrifluoromethylation reaction was finally carried out for 24 h in AcOH in the present of 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 2 equiv of CF_3SO_2Na under argon atmosphere.

Table 1. Optimization of reaction conditions[a]



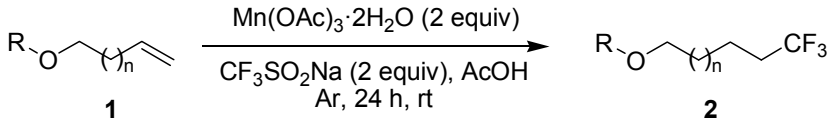
entry	$Mn(OAc)_3 \cdot 2H_2O$ (equiv)	CF_3SO_2Na (equiv)	solvent	yield (%)[b]
1	3	2	AcOH	77
2	3	2	MeOH	-
3	3	2	DMF	-
4	3	2	DCE	-
5	3	2	Actone	-
6[c]	3	-	AcOH	-
7	2	2	AcOH	75
8	1.5	1.5	AcOH	69
9	1.2	1.2	AcOH	61
10	1.1	1.1	AcOH	53
11[d]	2	2	AcOH	57

[a]All reactions were carried out with 0.25 mmol of **1a**, 0.50 mmol of $Mn(OAc)_3 \cdot 2H_2O$ and 0.50 mmol of CF_3 source in 10 mL of solvent, rt = room temperature. [b]Isolated yield.

[c]$TMSCF_3$ was used. [d]Reaction without argon protection.

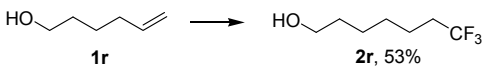
With the optimized reaction conditions in hand, the scope and limitations of this reaction were studied. Different esters and ethers were first tested. The results are summarized in Table 2. The use of chromophore-containing substrates is to increase the molecular weight of products, and to facilitate the work-up process. As these results showed, a variety of isolated unactivated C=C double bonds could be hydrotrifluoromethylated in good yields, and a wide array of functional groups such as halogen atoms and alkyl groups could be tolerated (Table 2, entries 1-10, entry 14). Electronic properties of the substituents on the arene rings generally showed less effect on the reactions (Table 2, entry 1 vs entries 3-10). The effect of carbon chain length in the substrates was investigated, and this also showed little impact on the course of the reactions (Table 2, entries 1 and 2, entries 7-9). Other substrates such as heteroaromatic carboxylates (Table 2, entries 11 and 12), naphthyl carboxylate (Table 2, entry 13), aliphatic carboxylate (Table 2, entry 14) and sulfonate (Table 2, entry 15) could also be converted to the hydrotrifluoromethylation products in acceptable isolated yields. In addition, ethers **1p**/**1q** and alcohol **1r** were also viable substrates for the hydrotrifluoromethylation reaction (Table 2, entries 16-18).

Table 2. Hydrotrifluoromethylation of ester and ether substrates[a]



1 **2**

entry	product	R	n	yield (%)[b]
1	**2a**	PhCO	3	77
2	**2b**	PhCO	2	69

3	**2c**	4-MePhCO	3	74
4	**2d**	4-FPhCO	3	65
5	**2e**	4-BrPhCO	3	78
6	**2f**	4-IPhCO	3	64
7	**2g**	2-MeOPhCO	3	73
8	**2h**	2-MeOPhCO	2	64
9	**2i**	2-MeOPhCO	0	61
10	**2j**	4-NCPhCO	0	44
11	**2k**	(3-pyridyl)CO	3	59
12	**2l**	(4-pyridyl)CO	3	64
13	**2m**	(2-naphthyl)CO	3	68
14	**2n**	(Cyclohexyl)CO	3	57
15	**2o**	4-MePhSO$_2$	3	67
16	**2p**	Bn	3	74
17	**2q**	Ph	3	64
18				

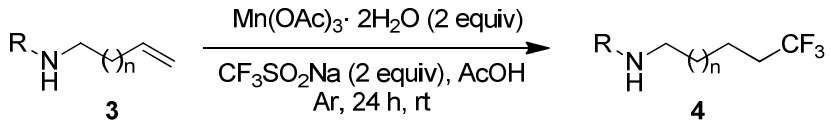
1r **2r**, 53%

[a]All reactions were carried out with 0.25 mmol of **1**, 0.50 mmol of $Mn(OAc)_3 \cdot 2H_2O$ and 0.50 mmol of CF_3SO_2Na in 10 mL of solvent, rt = room temperature. [b]Isolated yield.

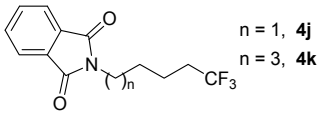
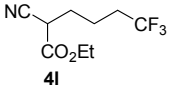
After trifluoromethylation of ester, ether and alcohol substrates, amide substrates were also subjected to the same reaction. The results are summarized in Table 3. As could be expected, a variety of substitutents such as alkoxyl groups, alkyl group and halogens were tolerated, and the desired products could be obtained in satisfactory isolated yields (Table 3, entries 2-4, entries 7-8). The presence of halogen atoms on arene rings would allow additional functional group transformation reactions (Table 2, entries 4-6. Table 3, entry 8). The effect of carbon

chain length in the substrates also showed little impact on the course of the reactions (Table 3, entries 1 and 5, entries 10 and 11). Substrates without aryl group such as **3i** and **3l** could also be transformed into the desired products (Table 3, entries 9 and 12).

Table 3. Hydrotrifluoromethylation of amide substrates[a]



3 **4**

entry	product	R	n	yield (%)[b]
1	**4a**	PhCO	0	72
2	**4b**	4-MeOPhCO	0	73
3	**4c**	3-MeOPhCO	0	62
4	**4d**	2-MeOPhCO	0	71
5	**4e**	PhCO	3	73
6	**4f**	$PhSO_2$	3	69
7	**4g**	4-$MePhSO_2$	3	71
8	**4h**	2-$ClPhSO_2$	3	63
9	**4i**	$MeSO_2$	3	52
10				68
11				76
12				77

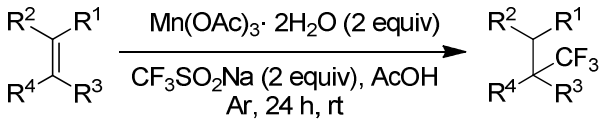
4l

[a]All reactions were carried out with 0.25 mmol of **3**, 0.50 mmol of $Mn(OAc)_3 \cdot 2H_2O$ and 0.50 mmol of CF_3SO_2Na in 10 mL of solvent, rt = room temperature. [b]Isolated yield.

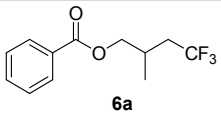
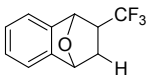
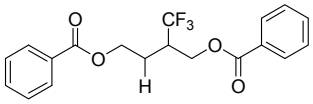
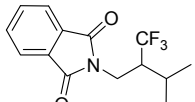
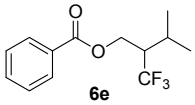
After the hydrotrifluoromethylation of terminal unactivated alkenes, the substrates were extended to internal olefins bearing different substituents and the results are summarized in

Table 4. Results showed that *gem*-disubstituted terminal alkenes were viable substrates for the current reaction system, and Markovnikov product **6a** was obtained in 71% yield (Table 4, entry 1). It is remarkable that 1,2-disubstituted cyclic and acyclic internal alkenes could be hydrotrifluoromethylated under optimized conditions, furnishing products **6b** and **6c** in moderate yields (Table 4, entries 2 and 3). Markovnikov products **6d** and **6e** were obtained in good yields when trisubstituted internal alkenes were subjected to the reaction (Table 4, entries 4 and 5).

Table 4. Hydrotrifluoromethylation of ester and ether substrates[a]



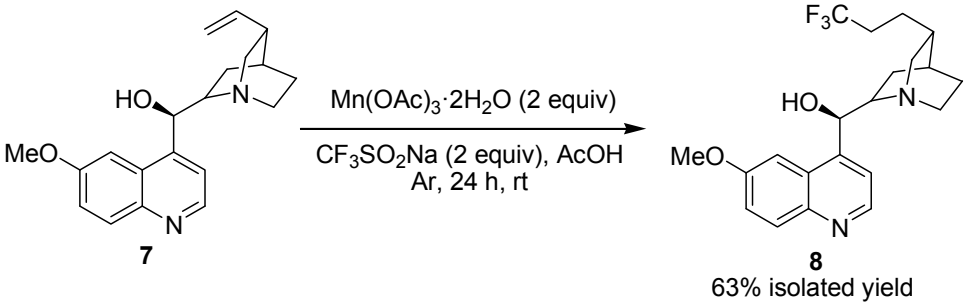
5 **6**

entry	product	yield (%)[b]
1	 **6a**	76
2	 **6b**	56
3	 **6c**	47
4	 **6d**	76
5	 **6e**	69

[a]All reactions were carried out with 0.25 mmol of **5**, 0.50 mmol of $Mn(OAc)_3 \cdot 2H_2O$ and 0.50 mmol of CF_3SO_2Na in 10 mL of solvent, rt = room temperature. [b]Isolated yield.

After hydrotrifluoromethylation of different unactivated alkene substrates, reaction of quinine was carried out under optimized conditions. Again, quinine could be hydrotrifluoromethylated with 69% isolated yield with intact of both the functional groups and the quinoline ring (Scheme 2).

Scheme 2. Hydrotrifluoromethylation of quinine



Compound **4b** was subjected to X-ray diffraction experiment to further determine the skeleton of the product. The ORTEP drawing clearly confirmed the hydrotrifluoromethylation structure (Figure 1).[14]

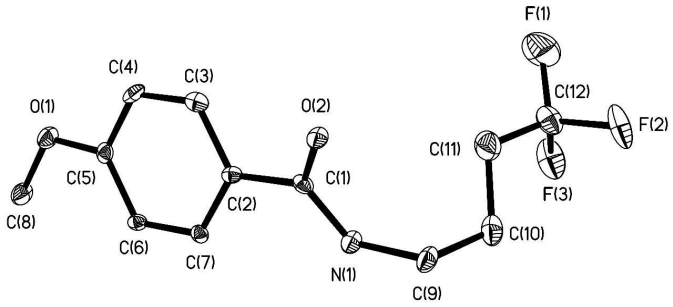
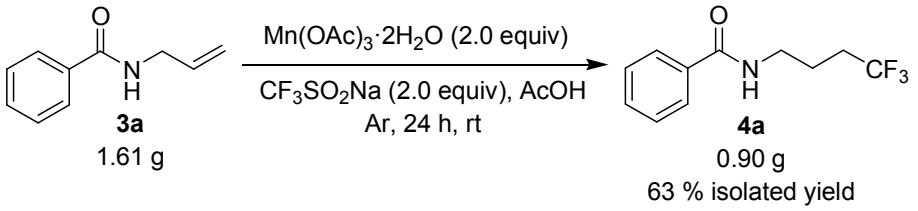


Figure 1. ORTEP drawing of 4b at 30% probability displacement ellipsoid (the hydrogen atoms are omitted for clarity)

Hydrotrifluoromethylation of substrate **3a** was also carried out on gram scale under the optimized conditions, and the desired product **4a** was obtained in 63% isolated yield (Scheme 3).

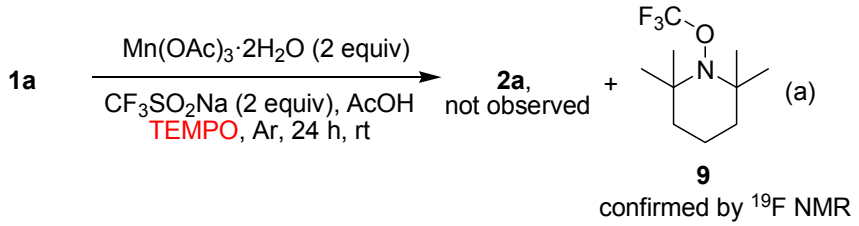
Scheme 3. Gram-scale hydrotrifluoromethylation of substrate 3a

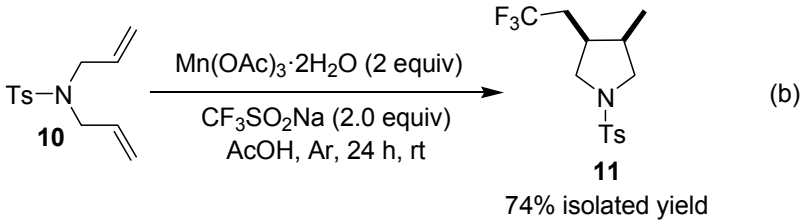


Mn(III) was known to promote oxidative radical reactions. In the current study, clean reactions were observed in argon atmosphere, and reactions carried out in open air gave complex mixtures. These results indicated that the current reaction may also proceed via a free radical pathway. Trifluoromethyl free radical may be generated *in situ* via reaction between $Mn(OAc)_3 \cdot 2H_2O$ and CF_3SO_2Na, Markovnikov addition of trifluoromethyl radical to C=C double bond and subsequent hydrogen abstraction afforded the desired hydrotrifluoromethylation product.

To prove the free radical pathway of the reaction, control experiments in the presence of 3 equiv of free radical capturer TEMPO was carried out under otherwise identical conditions. Complete suppression of the reaction was observed and free radical capture product **9** was detected by ^{19}F NMR (Scheme 4a). Further, a radical clock reaction of **10** under the standard reaction conditions gave the trifluoromethylated pyrrolidine **11** in 74% yield (Scheme 4b).[15] These results supported a CF_3 free radical pathway under the optimized reaction conditions.

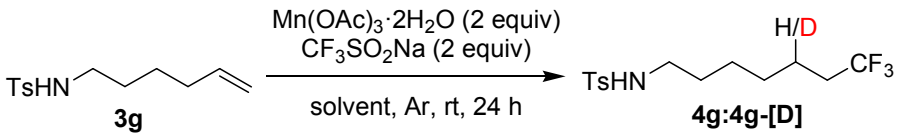
Scheme 4. Mechanistic studies involving (a) the use of TEMPO and (b) a radical clock reaction.





To get detailed insights into the proton abstraction process, control experiments were carried out by replacing the reaction medium CH_3COOH with CH_3COOD and CD_3COOD (Table 5). Hydrotrifluoromethylation of alkene **3g** in CH_3COOH proceeded smoothly under standard condition. When the reaction was carried out in CH_3COOD, no deuterated product **4g**-[D] was observed (Table 5, entry 2). This result suggested that the proton was not from the carboxyl group of the solvent. When the reaction was carried out in CD_3COOD (Table 5, entry 3), 71% of the product was deuterated. When the reaction was run in a 1:1 mixture of CD_3COOD and CH_3COOH (Table 5, entry 4), the product distribution revealed a normal kinetic isotope effect (k_H/k_D = 2.4). These results implied that the α-H of CH_3COO^- served as the hydrogen source during the reaction.[16]

Table 5. Trifluoromethylation of 3g in different deuterated acetic acids[a]



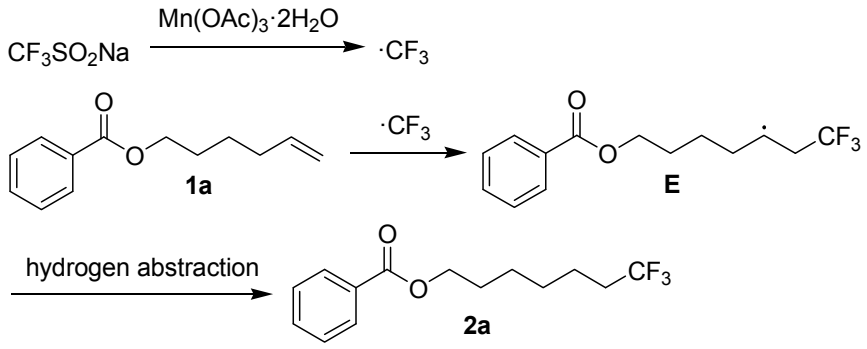
entry	solvent	**4g**:**4g**-[D][b]
1	CH_3COOH	100:0

2	CH_3COOD	100:0
3	CD_3COOD	29:71
4	CD_3COOD:CH_3COOH=1:1	71:29

[a]Reaction conditions: **3g** (0.25 mmol), solvent (5 mL). [b]determined by ^1H NMR analysis. The deuterated product was verified by HRMS.[14]

On the basis of these results, a preliminary reaction mechanism was proposed in Scheme 5. At first, CF_3 radical was generated from CF_3SO_2Na in the presence of $Mn(OAc)_3{\cdot}2H_2O$. Markovnikov addition of trifluoromethyl radical to C=C double bond of the substrate led to formation of the radical species **E**. Finally, species **E** underwent hydrogen abstraction from CH_3COO^- to afford the desired hydrotrifluoromethylation product. [4a,6a,9a]

Scheme 5. Proposed mechanism for hydrotrifluoromethylation of alkenes



CONCLUSION

In summary, a simple and efficient method for hydrotrifluoromethylation of unactivated alkenes was explored using CF_3SO_2Na as the trifluoromethyl source in the presence of $Mn(OAc)_3{\cdot}2H_2O$. The mild reaction conditions allowed efficient access to a variety of trifluoromethyl-containing products bearing a wide range of functional groups. Deuteration,

radical clock and TEMPO trapping experiments revealed the mechanism of this reaction. Further studies on synthetic application of hydrotrifluoromethylation of unactivated alkenes and the understanding of $Mn(OAc)_3$-mediated oxidative radical reactions are underway.

EXPERIMENTAL SECTION

General experimental information. All reactions were carried out at room temperature and using dry solvents under anhydrous conditions unless otherwise stated. $Mn(OAc)_3 \cdot 2H_2O$, CF_3SO_2Na were purchased at the highest commercial quality and were used without further purification. Thin layer chromatography (TLC) was performed on silica gel plates (silica gel GF_{254}) and visualized with iodine or UV light. Column chromatography was performed on silica gel (200–300 mesh). ^1H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) were recorded at 298 K using deuterated chloroform as solvent. Infrared (IR) spectra were reported as wavenumber (cm^{-1}). HRMS analyses were carried out with Varian FTICR-MS 7.0T.

General procedure for the hydrotrifluoromethylation of unactivated alkenes. Alkenes (0.25 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol), and CF_3SO_2Na (0.5 mmol) were placed in a 25 mL round-bottom flask. The flask was evacuated and backfilled with argon for 3 times. CH_3COOH (10 mL) was added with syringe under argon protection and the mixture was stirred vigorously at room temperature for 24 h. After the reaction was complete (TLC analysis), the reaction mixture was poured into a beaker (500 mL) containing H_2O (200 mL) and $Na_2S_2O_4$ (3 g). Then the beaker was added slowly with Na_2CO_3 until no bubbles of CO_2 were formed. The mixture in the beaker was poured into a separating funnel (1 L) and was extracted with CH_2Cl_2 (3 × 400 mL). The combined organic layers were dried over

anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (using 100:1 hexane/ethyl acetate solvent system) to afford the desired product.

Gram-scale procedure for the hydrotrifluoromethylation of 3a. Substrate **3a** (1.61 g), $Mn(OAc)_3 \cdot 2H_2O$ (5.36 g), and CF_3SO_2Na (3.12 g) were placed in a 25 mL round-bottom flask. The flask was evacuated and backfilled with argon for 3 times. CH_3COOH (50 mL) was added with syringe under argon gas protection and the mixture was stirred vigorously at room temperature for 24 h. After the reaction was complete (TLC analysis), the reaction mixture was poured into a beaker (500 mL) containing H_2O (300 mL) and $Na_2S_2O_4$ (15 g). Then the beaker was added slowly with Na_2CO_3 until no bubbles of CO_2 were formed. The mixture in the beaker was poured into a separating funnel (1 L) and was extracted with CH_2Cl_2 (3 × 600 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (using 100:1 hexane/ethyl acetate solvent system) to afford the desired product **4a** (0.90 g, 63 %).

7,7,7-trifluoroheptylbenzoate (2a)

According to the general procedure, **1a** (0.25 mmol, 51.1 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2a** (53.0 mg, 77% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 4.25 (t, J = 6.5 Hz, 2H), 2.11 – 1.91 (m, 2H), 1.77 – 1.62 (m, 2H), 1.62 – 1.45 (m, 2H), 1.46 – 1.27 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 131.9, 129.3, 128.5, 127.3, 126.2 (q, ^1J(C, F)= 276.0 Hz), 63.8,

32.6 (q, ^{2}J(C, F) = 28.4 Hz), 27.5, 27.3, 24.7, 20.8 (q, ^{3}J(C, F) = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(F, H) = 10.2 Hz). The NMR data were in agreement with reported results.[17]

6,6,6-trifluorohexyl benzoate (2b)

According to the general procedure, **1b** (0.25 mmol, 47.6 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2b** (44.8 mg, 69% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 4.27 (t, *J* = 6.5 Hz, 2H), 2.16 – 1.93 (m, 2H), 1.80 – 1.68 (m, 2H), 1.65 – 1.53 (m, 2H), 1.53 – 1.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 131.9, 129.3, 128.5, 127.3, 126.2 (q, ^{1}J(C, F)= 276.1 Hz), 63.8, 32.6 (q, ^{2}J(C, F) = 28.4 Hz), 27.5, 24.7, 20.8 (q, ^{3}J(C, F) = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ-66.4 (t, ^{3}J(F, H) = 10.2 Hz). The NMR data were in agreement with reported results.[18]

7,7,7-trifluoroheptyl 4-methylbenzoate (2c)

According to the general procedure, **1c** (0.25 mmol, 54.6 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2c** (53.5 mg, 74% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 2.10 – 1.90 (m, 2H), 1.78 – 1.60 (m, 2H), 1.59 – 1.45 (m, 2H), 1.45 – 1.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 142.5, 128.5, 128.0, 126.6, 126.2 (q, ^{1}J(C, F)= 276.3 Hz), 63.6, 32.6

(q, ^{2}J(C, F) = 28.4 Hz), 27.5, 27.3, 24.7, 20.8 (q, ^{3}J(C, F) = 2.7 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(F, H) = 10.6 Hz). IR (KBr): 2946, 1718, 1613, 1275, 1109, 1021, 842, 755 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}F_3O_2$: 289.1415; Found: 289.1416.

7,7,7-trifluoroheptyl 4-fluorobenzoate (2d)

According to the general procedure, **1d** (0.25 mmol, 55.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2d** (47.7 mg, 65% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.86 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.08 – 1.89 (m, 2H), 1.77 – 1.62 (m, 2H), 1.51 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.47 – 1.22 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 165.7 (d, ^{1}J(C, F) = 253.7 Hz), 132.1 (d, ^{3}J(C, F) = 9.3 Hz), 127.2 (q, ^{1}J(C, F) = 276.3 Hz), 126.6 (d, ^{4}J(C, F) = 2.8 Hz), 115.5(d, ^{2}J(C, F) = 21.9 Hz), 64.9, 33.6 (q, ^{2}J(C, F) = 28.4 Hz), 28.5, 28.4, 25.7, 21.8 (d, ^{3}J(C, F) = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(F, H) = 11.0 Hz), -105.9. IR (KBr): 2946, 1730, 1283, 1129, 1064, 852, 759 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}F_4O_2$: 293.1165; Found: 293.1163.

7,7,7-trifluoroheptyl 4-bromobenzoate (2e)

According to the general procedure, **1e** (0.25 mmol, 70.8 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2e** (68.6 mg, 78% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.10 – 1.92 (m, 2H),

1.76 – 1.64 (m, 2H), 1.64 – 1.45 (m, 2H), 1.48 – 1.26 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 130.7, 130.0, 128.2, 127.0, 126.1 (q, ^1J(C, F)= 276.5 Hz), 64.0, 32.6 (q, ^2J(C, F) = 28.4 Hz), 27.4, 27.3, 24.7, 20.8 (d, ^3J(C, F) = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ-66.4 (t, ^3J(F, H) = 10.9 Hz). The NMR data were in agreement with reported results.[9b]

7,7,7-trifluoroheptyl 4-iodobenzoate (2f)

According to the general procedure, **1f** (0.25 mmol, 82.5 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2f** (64.0 mg, 64% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR 400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 2.10 – 1.90 (m, 2H), 1.79 – 1.63 (m, 2H), 1.57 – 1.44 (m, 2H), 1.44 – 1.29 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 136.7, 130.0, 128.9, 126.17 (q, ^1J(C, F)= 276.4 Hz), 99.6, 64.0, 32.6 (q, ^2J(C, F) = 28.4 Hz) 27.4, 27.3, 24.7, 20.8 (q, ^3J(C, F) = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ-66.4 (t, ^3J(F, H) = 10.2 Hz). IR (KBr): 2947, 1721, 1605, 1270, 1118, 1015, 856, 769 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}F_3IO_2$: 401.0225; Found: 401.0221.

7,7,7-trifluoroheptyl 2-methoxybenzoate (2g)

According to the general procedure, **1g** (0.25 mmol, 58.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2g** (55.7 mg, 73% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.62 (m, 1H), 7.51 – 7.32 (m, 1H), 7.10 – 6.72 (m, 2H), 4.23 (t, J = 6.5 Hz, 2H), 3.83 (s, 3H), 2.11 – 1.92 (m, 2H), 1.75 – 1.63 (m, 2H), 1.52 (s, 2H), 1.47 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 159.1, 133.5, 131.6, 131.5, 127.2 (q, ^1J (C, F)= 276.3 Hz), 120.1, 112.0, 64.6, 55.9, 33.65 (q, ^2J (C, F)= 28.3 Hz), 28.5, 28.3, 25.7, 21.8 (q, ^3J (C, F)= 2.8 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, ^3J (H, F)= 10.2 Hz). IR (KBr): 3546, 2946, 1727, 1602, 1254, 1135, 1083, 757 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}F_3O_3$: 305.1365; Found: 305.1356.

6,6,6-trifluorohexyl 2-methoxybenzoate (2h)

According to the general procedure, **1h** (0.25 mmol, 55.1 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2h** (46.6 mg, 64% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.43 – 7.36 (m, 1H), 6.96 – 6.84 (m, 2H), 4.23 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 2.13 – 1.89 (m, 2H), 1.80 – 1.64 (m, 2H), 1.63 – 1.52 (m, 2H), 1.53 – 1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 159.1, 133.5, 131.5, 127.2 (q, ^1J(C, F)= 276.2 Hz), 120.2, 120.1, 112.0, 64.4, 55.9, 33.7 (q, ^2J (C, F)= 28.5 Hz), 28.4, 25.3, 21.7 (q, ^3J (C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (t, ^3J(H, F)= 10.9 Hz) . IR (KBr): 3546, 2951, 1727, 1602, 1255, 1134, 1084, 757 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}F_3O_3$: 291.1208; Found: 291.1208.

4,4,4-trifluorobutyl 2-methoxybenzoate (2i)

According to the general procedure, **1i** (0.25 mmol, 48.1 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2i** (40.0 mg, 61% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.39 (m, 1H), 7.13 – 6.91 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 3.90 (s, 3H), 2.22 – 2.01 (m, 2H), 1.87 – 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 156.4, 131.9, 131.3, 126.1 (q, ^1J(C, F)= 276.2 Hz) , 120.4, 120.2, 110.3, 62.3, 54.9, 30.3 (q, ^2J(C, F)= 28.9 Hz) , 21.4 (q, ^3J(C, F)= 2.6 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, ^3J(H, F)= 10.9 Hz). IR (KBr): 3402, 2948, 1650, 1537, 1253, 1150, 1023, 757 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}F_3O_3$: 263.0895; Found: 263.0892.

4,4,4-trifluorobutyl 4-cyanobenzoate (2j)

According to the general procedure, **1j** (0.25 mmol, 46.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2j** (28.5 mg, 44% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 4.36 (t, *J* = 6.3 Hz, 2H), 2.36 – 2.10 (m, 2H), 2.14 – 1.88 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 132.7, 131.3, 128.2 (q, ^1J(C, F)= 210.0 Hz), 129.1, 116.9, 115.7, 63.0, 29.8 (q, ^2J(C, F)= 29.4 Hz) , 20.6 (q, ^3J(C, F)= 2.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, ^3J(H, F)= 10.9 Hz). IR (KBr): 3552, 2964, 2233, 1728, 1280, 1108, 1008, 862, 768 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}F_3NO_2$: 258.0742; Found: 258.0738.

7,7,7-trifluoroheptyl nicotinate (2k)

According to the general procedure, **1k** (0.25 mmol, 51.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2k** (40.8 mg, 59% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.71 (s, 1H), 8.23 (d, *J* = 5.8 Hz, 1H), 7.33 (d, *J* = 2.8 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.14 – 1.90 (m, 2H), 1.83 – 1.65 (m, 2H), 1.64 – 1.47 (m, 2H), 1.48 – 1.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.4, 150.9, 137.0, 127.2 (q, ^1J(C, F)= 276.4 Hz), 126.2, 123.3, 65.3, 33.6 (q, ^2J(C, F)= 28.5 Hz), 28.4, 28.4, 25.7, 21.8 (q, ^3J(C, F)= 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.8 Hz). IR (KBr): 2946, 1730, 1284, 1129, 1064, 852, 759, 708 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}F_3NO_2$, 276,1211; Found: 276.1205.

7,7,7-trifluoroheptyl isonicotinate (2l)

According to the general procedure, **1l** (0.25 mmol, 51.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2l** (44.1 mg, 64% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). M.P. 35 - 36 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.68 (m, 2H), 7.83 – 7.70 (m, 2H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.12 – 1.92 (m, 2H), 1.81 – 1.66 (m, 2H), 1.60 – 1.47 (m, 2H), 1.46 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.6, 137.5, 127.2 (q, ^1J(C, F)= 276.4 Hz), 122.8, 65.6, 33.6 (q, ^2J(C, F)= 28.4 Hz), 28.4, 28.3, 25.7, 21.8 (q, ^3J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.0 Hz). IR (KBr): 3566, 2947, 1726, 1286, 1136, 1025, 803, 743 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}F_3NO_2$: 276,1211; Found: 276.1202.

7,7,7-trifluoroheptyl 2-naphthoate (2m)

According to the general procedure, **1m** (0.25 mmol, 63.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2m** (54.9 mg, 68% yield) which was isolated as a white solid after purification on silica gel

chromatography (petroleum ether:ethyl acetate = 100:1). M.P. 47 - 48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.04 – 7.95 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.42 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.13 – 1.90 (m, 2H), 1.81 – 1.69 (m, 2H), 1.61 – 1.48 (m, 2H), 1.47 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 135.5, 132.5, 131.0, 129.4, 128.3, 128.2, 127.8, 127.6, 127.2 (q, ^{1}J(C, F)= 282.8 Hz), 126.7, 125.2, 65.0, 33.7(q, ^{2}J(C, F)= 28.3 Hz), 28.6, 28.4, 25.8, 21.9 (q, ^{3}J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.1 Hz). IR (KBr): 3611, 2959, 1712, 1279, 1137, 1047, 779, 762 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}F_3O_2$: 325.1415; Found: 325.1413.

7,7,7-trifluoroheptyl cyclohexanecarboxylate (2n)

According to the general procedure, **1n** (0.25 mmol, 52.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2n** (40.0 mg, 57% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (t, *J* = 6.2 Hz, 2H), 2.73 – 2.57 (m, 1H), 2.10 – 1.91 (m, 2H), 1.92 – 1.76 (m, 2H), 1.79 – 1.68 (m, 2H), 1.68 – 1.60 (m, 2H), 1.61 – 1.54 (m, 2H), 1.54 – 1.42 (m, 4H), 1.40 – 1.24 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 126.2 (q, ^{1}J(C, F)= 276.3 Hz), 63.0, 42.9, 32.6 (q, ^{2}J(C, F)= 28.4 Hz), 29.0, 27.4, 27.3, 24.8, 24.6, 20.8 (q, ^{3}J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.9 Hz). IR (KBr): 3685, 2954, 1733, 1256, 1146, 1051 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{22}F_3O_2$: 267.1572; Found: 267.1568.

7,7,7-trifluoroheptyl 4-methylbenzenesulfonate (2o)

According to the general procedure, **1o** (0.25 mmol, 63.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2o** (54.1 mg, 67% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 3.95 (t, *J* = 6.2 Hz, 2H), 2.38 (s, 3H), 2.03 – 1.84 (m, 2H), 1.63 – 1.52 (m, 2H), 1.47 – 1.36 (m, 2H), 1.30 – 1.19 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 133.1, 129.8, 127.9, 127.1 (q, ^{1}J(C, F)= 276.4 Hz), 70.3, 33.5 (q, ^{2}J(C, F)= 28.4 Hz), 28.5, 28.0, 25.0, 21.7 (q, ^{3}J(C, F)= 2.9 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$)

δ -66.4 (t, ^{3}J(H, F)= 10.9 Hz). IR (KBr): 3406, 2947, 2362, 1600, 1361, 1141, 959, 818 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^{+}$ Calcd for $C_{14}H_{20}F_3O_3S$: 325.1085; Found: 325.1079.

(((7,7,7-trifluoroheptyl)oxy)methyl)benzene (2p)

According to the general procedure, **1p** (0.25 mmol, 47.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2p** (48.0 mg, 74% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.18 (m, 5H), 4.56 (s, 2H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.32 – 2.03 (m, 2H), 1.78 – 1.60 (m, 4H), 1.60 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 128.4, 127.8, 127.7, 127.4 (q, ^{1}J(C, F)= 276.4 Hz), 72.9, 70.1, 32.6 (q, ^{2}J(C, F)= 28.4 Hz), 27.5, 27.4, 24.7, 20.8 (q, ^{3}J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.0 Hz). The NMR data were in agreement with reported results.[9b]

((7,7,7-trifluoroheptyl)oxy)benzene (2q)

According to the general procedure, **1q** (0.25 mmol, 44.1 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2q** (39.5 mg, 64% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 2H), 6.93 – 6.73 (m, 3H), 3.88 (t, *J* = 6.2 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.85 – 1.71 (m, 2H), 1.69 – 1.55 (m, 2H), 1.53 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 129.41, 127.2 (q, ^{1}J(C, F)= 274.6 Hz), 120.5, 114.4, 67.5, 33.6 (q, ^{2}J(C, F)= 28.2 Hz), 29.0, 28.4, 25.7, 21.8 (q, ^{3}J(C, F)= 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.9 Hz). The NMR data were in agreement with reported results.[9b]

7,7,7-trifluoroheptan-1-ol (2r)

According to the general procedure, **1r** (0.25 mmol, 28.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **2r** (24.5 mg, 53% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.6 Hz, 2H), 2.79 (s, 1H), 2.23 – 1.97 (m, 2H), 1.68 – 1.52 (m, 4H), 1.49 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.2 (q, ^{1}J(C, F)= 273.6 Hz), 62.0, 36.5 (q, ^{2}J(C, F)=

28.4 Hz), 35.4, 31.6, 29.9, 23.8 (q, ^3J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.8 Hz). The NMR data were in agreement with reported results.[6a]

N-(4,4,4-trifluorobutyl)benzamide (4a)

According to the general procedure, **3a** (0.25 mmol, 40.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4a** (41.7 mg, 72% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 47 - 48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 6.40 (s, 1H), 3.44 (t, J = 10.0 Hz, 2H), 2.19 – 2.03 (m, 2H), 1.87 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 134.3, 131.7, 128.6, 126.9, 126.7 (q, ^1J(C, F)= 276.1 Hz), 38.8, 31.3 (q, ^2J(C, F)= 29.1 Hz), 22.5 (q, ^3J(C, F)= 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, ^3J(H, F)= 10.8 Hz, 3F). IR (KBr): 3334, 3065, 2954, 1636, 1541, 1309, 1152, 692, 667 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}F_3NO$: 232.0949; Found: 232.0943.

4-methoxy-N-(4,4,4-trifluorobutyl)benzamide (4b)

According to the general procedure, **3b** (0.25 mmol, 47.8 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4b** (47.5 mg, 73% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 82 - 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.19 (s, 1H), 3.78 (s, 3H), 3.45 (q, J = 6.7 Hz, 2H), 2.22 – 2.01 (m, 2H), 1.92 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 162.3, 128.7, 127.0 (q, ^1J(C, F)= 276.1 Hz), 126.5, 113.9, 54.4, 37.6, 30.3 (q, ^2J(C, F)= 29.0 Hz), 21.6 (q, ^3J(C, F)= 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, ^3J(H, F)= 10.8 Hz). IR (KBr): 3327, 2944, 1635, 1540, 1254, 1145, 848 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}F_3NO_2$: 262.1055; Found: 262.1055.

Crystal data for **4b**: $C_{24}H_{28}F_6N_2O_4$, M = 522.48, orthorhombic, a = 5.1273(14) Å, b = 7.9444(19) Å, c = 30.291(7) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1233.9(5) Å^3, T = 113(2) K, space group $P2(1)2(1)2(1)$, Z = 2, 13501 reflections measured, 2179 independent reflections ($Rint$ = 0.0486). The final R_1 values were 0.0778 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2407 ($I > 2\sigma(I)$). The final R_1 values were 0.0823 (all data). The final $wR(F^2)$ values were 0.2446 (all data). The goodness of fit on F^2 was 1.028. Flack parameter = 1(2).

3-methoxy-N-(4,4,4-trifluorobutyl)benzamide (4c)

According to the general procedure, **3c** (0.25 mmol, 47.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4c** (40.6 mg, 62% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.28 (s, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 1H), 3.77 (s, 3H), 3.56 – 3.35 (m, 2H), 2.26 – 2.00 (m, 2H), 1.96 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 159.9, 135.7, 129.6, 118.5, 117.8, 114.7 (q, ^1J(C, F)= 276.2 Hz), 112.3, 55.5, 38.8, 31.3 (q, ^2J(C, F)= 29.1 Hz) , 22.6 (q, ^3J(C, F)= 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, ^3J(H, F)= 10.9 Hz). IR (KBr): 3303, 2945, 1641, 1544, 1308, 1150, 788, 690 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}F_3NO_2$: 262.1055; Found: 262.1055.

2-methoxy-N-(4,4,4-trifluorobutyl)benzamide (4d)

According to the general procedure, **3d** (0.25 mmol, 47.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4d** (46.5 mg, 71% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.04 (m, 1H), 7.88 (s, 1H), 7.43 – 7.35 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.47 (q, *J* = 6.7 Hz, 2H), 2.21 – 2.04 (m, 2H), 1.89 – 1.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 157.4, 132.9, 132.3, 127.1 (q, ^1J(C, F)= 276.3 Hz), 121.4, 121.2, 111.3, 55.9, 38.3, 31.4 (q, ^2J(C, F)= 29.0 Hz), 22.5 (q, ^3J(C, F)= 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1(t, ^3J(H, F)= 10.9 Hz). IR (KBr): 3401, 2948, 1649, 1537, 1254, 1150, 758 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}F_3NO_2$: 262.1055; Found: 262.1055.

N-(7,7,7-trifluoroheptyl)benzamide (4e)

According to the general procedure, **3e** (0.25 mmol, 50.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4e** (50.1 mg, 73% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 43 - 44 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 6.07 (s,

1H), 3.39 (q, *J* = 6.9 Hz, 2H), 2.13 – 1.89 (m, 2H), 1.64 – 1.43 (m, 6H), 1.41 – 1.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.8, 131.4, 128.6, 126.8, 126.6 (q, ^{1}J(C, F)= 152.4 Hz), 39.9, 33.6 (q, ^{2}J(C, F)= 28.4 Hz), 29.5, 28.4, 26.6, 21.8 (q, ^{3}J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.9 Hz). IR (KBr): 3326, 2943, 2362, 1637, 1535, 1255, 1138, 803, 714 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}F_3NO$: 274.1419; Found: 274.1410.

N-(7,7,7-trifluoroheptyl)benzenesulfonamide (4f)

According to the general procedure, **3f** (0.25 mmol, 59.8 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4f** (53.5 mg, 69% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 4.64 (s, 1H), 2.88 (q, *J* = 6.7 Hz, 2H), 2.04 – 1.85 (m, 2H), 1.51 – 1.32 (m, 4H), 1.29 – 1.12 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 131.6, 128.1, 126.1 (q, ^{1}J(C, F)= 276.4 Hz), 126.0, 42.0, 32.51 (q, ^{2}J(C, F)= 28.3 Hz), 28.3, 27.1, 25.0, 20.7 (q, ^{3}J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 11.0 Hz). IR (KBr): 3286, 2943, 2867, 1596, 1325, 1158, 755, 724 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{19}F_3NO_2S$: 310.1089; Found: 310.1081.

4-methyl-N-(7,7,7-trifluoroheptyl)benzenesulfonamide (4g)

According to the general procedure, **3g** (0.25 mmol, 63.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4g** (57.2 mg, 71% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 3.95 (t, *J* = 6.2 Hz, 2H), 2.38 (s, 3H), 2.03 – 1.84 (m, 2H), 1.63 – 1.36 (m, 4H), 1.30 – 1.19 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 135.8, 128.7, 127.9, 126.1, 126.1 (q, ^{1}J(C, F)= 282.8 Hz), 42.0, 32.5 (q, ^{2}J(C, F)= 28.4 Hz), 28.2, 27.1, 25.0, 20.7 (q, ^{3}J(C, F)= 2.8 Hz), 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^{3}J(H, F)= 10.9 Hz). The NMR data were in agreement with reported results.[9b]

2-chloro-N-(7,7,7-trifluoroheptyl)benzenesulfonamide (4h)

According to the general procedure, **3h** (0.25 mmol, 68.4 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4h** (54.2 mg,

63% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.47 – 7.38 (m, 1H), 4.96 (t, *J* = 6.0 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.09 – 1.94 (m, 2H), 1.53 – 1.40 (m, 4H), 1.36 – 1.23 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 133.7, 131.5, 131.3, 131.2, 127.3, 127.1 (d, ^1J(C, F)= 276.3 Hz), 43.1, 33.5 (q, ^2J(C, F)= 28.5 Hz), 29.2, 28.0, 26.0, 21.6 (q, ^3J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.9 Hz). IR (KBr): 3314, 2944, 1577, 1334, 1165, 759 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}ClF_3NO_2S$: 344.0699; Found: 344.0693.

N-(7,7,7-trifluoroheptyl)methanesulfonamide (4i)

According to the general procedure, **3i** (0.25 mmol, 44.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4i** (32.3 mg, 52% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 35 - 36 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (s, 1H), 3.12 – 3.00 (m, 2H), 2.89 (s, 3H), 2.07 – 1.93 (m, 2H), 1.56 – 1.45 (m, 4H), 1.37 – 1.29 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ127.2 (q, ^1J(C, F)= 276.3 Hz), 43.1, 40.2, 33.6 (q, ^2J(C, F)= 28.3 Hz), 29.9, 28.2, 26.1, 21.8 (q, ^3J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.6 Hz). IR (KBr): 3268, 2940, 2362, 1439, 1309, 1143 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{17}F_3NO_2S$: 248.0932; Found: 248.0927.

2-(5,5,5-trifluoropentyl)isoindoline-1,3-dione (4j)

According to the general procedure, **3j** (0.25 mmol, 50.3 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4j** (46.1 mg, 68% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 74 - 75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.71 – 7.61 (m, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.76 – 1.64 (m, 2H), 1.59 – 1.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.0, 132.0, 127.0 (q, ^1J(C, F)= 276.4 Hz), 123.3, 37.3, 33.2 (q, ^2J(C, F)= 28.7 Hz), 27.7, 19.3 (q, ^3J(C, F)= 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, ^3J(H, F)= 10.8 Hz). The NMR data were in agreement with reported results.[19]

2-(7,7,7-trifluoroheptyl)isoindoline-1,3-dione (4k)

According to the general procedure, **3k** (0.25 mmol, 57.3 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4k** (57.1 mg, 76% yield) which was isolated as a white solid after purification on silica gel chromatography (petroleum ether:ethyl acetate = 10:1). M.P. 54 - 55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.68 – 7.62 (m, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 2.07 – 1.90 (m, 2H), 1.68 – 1.57 (m, 2H), 1.53 – 1.41 (m, 2H), 1.40 – 1.24 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 132.9, 131.1, 126.1 (q, ^1J(C, F)= 276.3 Hz), 122.2, 36.8, 32.6 (q, ^2J(C, F)= 28.3 Hz), 27.3, 27.2, 25.4, 20.7 (q, ^3J(C, F)= 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.9 Hz). The NMR data were in agreement with reported results.[6a]

ethyl 2-cyano-6,6,6-trifluorohexanoate (4l)

According to the general procedure, **3l** (0.25 mmol, 38.3 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **4l** (42.8 mg, 77% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (q, *J* = 7.1 Hz, 2H), 3.54 (t, *J* = 6.8 Hz, 1H), 2.28 – 2.10 (m, 2H), 2.10 – 1.99 (m, 2H), 1.88 – 1.72 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 126.6 (q, ^1J(C, F)= 276.5 Hz), 116.0, 63.1, 37.2, 33.0 (q, ^2J(C, F)= 29.2 Hz), 28.6, 19.5 (q, ^3J(C, F)= 3.0 Hz), 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, ^3J(H, F)= 10.6 Hz). IR (KBr): 3567, 2962, 1747, 1260, 1140, 1022 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{13}F_3NO_2$: 224.0898; Found: 224.0891.

4,4,4-trifluoro-2-methylbutyl benzoate (6a)

According to the general procedure, **5a** (0.25 mmol, 44.1 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **6a** (47.0 mg, 76% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.55 – 7.47 (m, 1H), 7.41 – 7.35 (m, 2H), 4.24 – 4.08 (m, 2H), 2.40 – 2.21 (m, 2H), 2.10 – 1.88 (m, 1H), 1.10 (d, *J* = 6.5 Hz, 3H).. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 132.1, 128.6, 128.5, 127.4, 126.1 (q, ^1J(C, F)= 275.3 Hz), 67.3, 36.1 (q, ^2J(C, F) = 28.2 Hz), 26.9 (q, ^3J(C, F) = 2.4 Hz), 16.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ-63.6 (t, ^3J(F, H) = 11.4 Hz). The NMR data were in agreement with reported results.[9a]

2-(trifluoromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (6b)

According to the general procedure, **5b** (0.25 mmol, 36.0 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **6b** (30.1 mg, 56% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.19 (m, 2H), 5.53 – 5.48 (m, 2H), 2.46 – 2.34 (m, 1H), 2.19 (dt, *J* = 12.1, 4.8 Hz, 1H), 1.77 (dd, *J* = 12.1, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.5, 128.9, 128.8 (q, ^1J(C, F)= 272.7 Hz), 128.6, 120.3, 119.9, 78.7, 78.6, 44.8 (q, ^2J(C, F) = 28.1 Hz), 29.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ-68.7 (t, ^3J(F, H) = 10.0 Hz). The NMR data were in agreement with reported results.[6a]

2-(trifluoromethyl)butane-1,4-diyl dibenzoate (6c)

According to the general procedure, **5c** (0.25 mmol, 74.1 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **6c** (43.3 mg, 47% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.94 (m, 4H), 7.59 – 7.48 (m, 2H), 7.45 – 7.33 (m, 4H), 4.82 – 4.62 (m, 2H), 4.60 – 4.40 (m, 2H), 3.36 – 3.24 (m, 1H), 2.09 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 162.1, 132.9, 132.4, 129.1, 128.7, 128.6, 127.6, 127.5, 127.5, 127.1 (q, ^1J(C, F)= 242.4 Hz), 64.6, 60.7 (q, ^3J(C, F) = 2.4 Hz), 44.8 (q, ^2J(C, F) = 31.2 Hz), 28.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ-69.4 (t, ^3J(F, H) = 8.2 Hz). IR (KBr): 2962, 1729, 1262, 1107, 1025, 801, 709 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}F_3O_4$: 367.1157; Found: 367.1159.

2-(3-methyl-2-(trifluoromethyl)butyl)isoindoline-1,3-dione (6d)

According to the general procedure, **5d** (0.25 mmol, 53.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **6d** (54.1 mg, 76% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.68 – 7.65 (m, 2H), 4.01 – 3.92 (m, 1H), 3.72 – 3.61 (m, 1H), 2.74 – 2.57 (m, 1H), 2.13 – 1.98 (m, 1H), 1.09 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 133.1, 130.8, 126.4 (q, ^1J(C, F)= 281.9 Hz), 122.4, 45.0 (q, ^2J(C, F)= 23.8 Hz), 32.9 (q, ^3J(C, F)= 2.8 Hz), 25.1(d, ^3J(C, F)= 1.1 Hz), 18.7, 17.7. ^{19}F NMR (376

MHz, $CDCl_3$) δ -66.4 (d, ^3J(H, F)= 6.6 Hz). The NMR data were in agreement with reported results.[9a]

3-methyl-2-(trifluoromethyl)butyl benzoate (6e)

According to the general procedure, **5e** (0.25 mmol, 47.6 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **6e** (45.0 mg, 69% yield) which was isolated as a colorless oil after purification on silica gel chromatography (petroleum ether:ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz,) δ 8.22 – 8.04 (m, 2H), 7.74 – 7.59 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 4.81 – 4.57 (m, 2H), 2.63-2.47 (m, 1H), 2.43-2.26 (m, 1H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 132.4, 129.9, 129.1, 127.9, 126.7 (q, ^1J(C, F)= 282.1 Hz), 59.9 (q, ^3J(C, F)= 3.0 Hz), 48.1 (q, ^2J(C, F)= 24.5 Hz), 25.6, 20.9, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.0 (d, ^3J(H, F)= 9.6 Hz). The NMR data were in agreement with reported results.[9a]

(1*R*)-(6-methoxyquinolin-4-yl)((1*S*,4*S*,5*R*)-5-(3,3,3-trifluoropropyl)quinuclidin-2-yl)methanol (8)

According to the general procedure, **7** (0.25 mmol, 81.1 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.5 mmol, 134.1 mg) and CF_3SO_2Na (0.5 mmol, 78.0 mg) in CH_3COOH (10 mL) afforded **8** (62.0 mg, 63% yield) which was isolated as a yellow solid after purification on silica gel chromatography (ethyl acetate:methanol = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.5 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 4.5 Hz, 1H), 7.12 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.12 (s, 1H), 3.87 – 3.71 (m, 4H), 3.22 – 3.11 (m, 2H), 2.81 – 2.70 (m, 1H), 2.41 (d, *J* = 13.6 Hz, 1H), 2.04 – 1.75 (m, 6H), 1.64 (s, 1H), 1.45 – 1.23 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 147.3, 146.7, 143.9, 131.2, 126.8 (q, ^1J(C, F)= 274.8 Hz), 126.6, 121.4, 118.5, 101.4, 71.9, 60.0, 57.1, 55.7, 43.2, 34.1, 31.7(q, ^2J(C, F)= 28.6 Hz), 27.0, 26.3 (q, ^3J(C, F)= 2.0 Hz), 25.3, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, ^3J(H, F)= 10.8 Hz). The NMR data were in agreement with reported results.[20]

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/XXXXXXXX.

Optimization of reaction conditions, copies of NMR spectra, and X-ray diffraction data for compound **4b** (pdf)

Crystallographic data for compound **4b** (CIF).

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Notes

The authors declare no competing financial interest.

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