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Ruthenium-Catalyzed Regioselective Allylic Trifluoromethylthiolation Reaction

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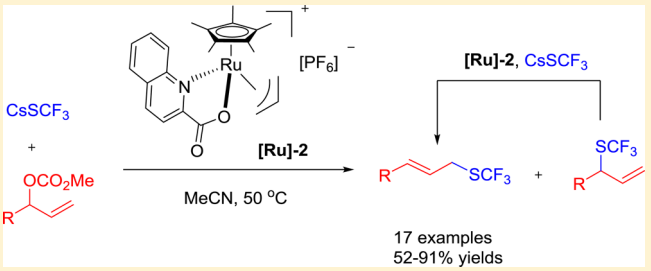
Supporting Information

ABSTRACT: An efficient Ru-catalyzed regioselective allylic trifluoromethylthiolation reaction of allylic carbonates was developed. The linear allylic trifluoromethyl thioethers were obtained in 52−91% yields. Mechanistic investigation revealed that this reaction proceeds via a double allylic trifluoromethylthiolation sequence.



INTRODUCTION

Compounds containing a trifluoromethylthio moiety (−SCF_3) are widely spread in many pharmaceuticals and agrochemicals and thus have fascinated synthetic chemists for a long time (Figure 1).[1,2] Therefore, a large number of procedures to

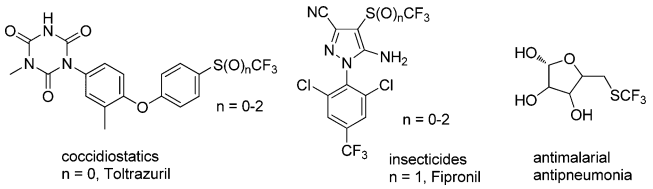


Figure 1. Examples of SCF_3-containing pharmacologically active compounds.

introduce the SCF_3 group into organic structures have been documented.[3] These methods generally involve halogen−fluorine exchange reactions[4] or the trifluoromethylation of sulfur-containing compounds.[5] Recently, various new methods for direct introduction of the SCF_3 group have been described.[6,7] However, most of these reported methods employ stoichiometric amounts of SCF_3 sources such as $AgSCF_3$ and $CuSCF_3$, which are rather expensive. Therefore, an efficient and direct introduction of a SCF_3 unit with a readily available trifluoromethylthiolation reagent under mild conditions with a simple operation is highly desirable.

As one of the most powerful tools for constructing carbon−carbon and carbon−heteroatom bonds, the transition-metal-catalyzed allylic substitution reaction[8] would be a very straightforward strategy to introduce the SCF_3 moiety into organic structures in a highly selective manner. However, there is no report on the transition-metal-catalyzed allylic trifluoromethylthiolation reaction to date. Notably, Weng and coworkers have reported nucleophilic trifluoromethylthiolation of allylic halides with stoichiometric amounts of Cu−SCF_3 complexes ligated by a bpy[9] or a phosphine[10] ligand. As part of our ongoing program toward transition-metal-catalyzed allylic substitution reactions,[11] we envisaged that an appropriate nucleophilic SCF_3 reagent could be utilized in the direct introduction of a SCF_3 unit in a catalytic manner. Herein, we report the first ruthenium-catalyzed highly regioselective allylic trifluoromethylthiolation reaction. The current method features high yields, excellent linear regioselectivity, broad substrate scope, and an extremely simple operation. Moreover, mechanistic investigations suggest that a double allylic trifluoromethylthiolation results in the linear selectivity.

RESULTS AND DISCUSSION

Ru-Catalyzed Allylic Trifluoromethylthiolation Reaction. We began our studies on the direct allylic trifluoromethylthiolation reaction by utilizing $CsSCF_3$ (**1a**)[12] as the nucleophilic trifluoromethylthiolation reagent. The results are summarized in Table 1. No detectable amount of the desired trifluoromethyl thioether can be observed with 5 mol % of $Pd(PPh_3)_4$ as the catalyst (entry 1, Table 1). We then turned our attention to the ruthenium catalysts.[13,14] In the presence of 1 mol % of catalyst [**Ru**]-**1**,[15] the reaction of cinnamyl methyl carbonate (**2a**) in MeCN at 50 °C in 12 h afforded (*E*)-cinnamyl(trifluoromethyl)sulfane (**4a**) in 17% yield (entry 2, Table 1). This reaction is highly regioselective as only a thermodynamically more stable *E*-isomer **4a** was formed exclusively. Examination of various linear allyl precursors revealed that allylic phosphate was the most reactive one, resulting in the isolation of **4a** in 68% yield (entries 2−4, Table

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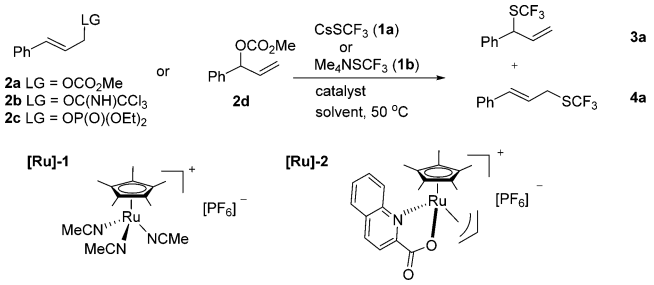
Table 1. Optimization of the Reaction Conditions[a]



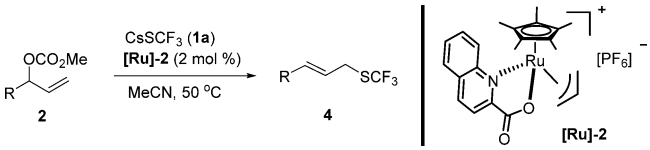
entry	1	2	catalyst	solvent	time (h)	yield (%)[b]
1	**1a**	**2a**	$Pd(PPh_3)_4$ (5 mol %)	MeCN	12	n.d.
2	**1a**	**2a**	[**Ru**]-**1** (1 mol %)	MeCN	12	**4a**, 17
3	**1a**	**2b**	[**Ru**]-**1** (1 mol %)	MeCN	12	**4a**, 14
4	**1a**	**2c**	[**Ru**]-**1** (1 mol %)	MeCN	12	**4a**, 68
5	**1a**	**2c**	[**Ru**]-**2** (1 mol %)	MeCN	12	**4a**, 65
6	**1a**	**2c**	[**Ru**]-**2** (2 mol %)	MeCN	12	**4a**, 80
7	**1b**	**2c**	[**Ru**]-**2** (2 mol %)	MeCN	12	**4a**, 31
8	**1a**	**2c**	[**Ru**]-**2** (2 mol %)	THF	12	**4a**, 8
9	**1a**	**2c**	[**Ru**]-**2** (2 mol %)	CH_2Cl_2	12	**4a**, 44
10	**1a**	**2c**	[**Ru**]-**2** (2 mol %)	*c*-hexane	12	**4a**, 26
11	**1a**	**2c**	[**Ru**]-**2** (2 mol %)	toluene	12	**4a**, 20
12	**1a**	**2d**	[**Ru**]-**2** (2 mol %)	MeCN	4	**4a**, 89
13	**1a**	**2d**		MeCN	24	n.d.

[a]Reaction conditions: **1**/**2** = 2.0/1.0, 0.1 M of **2**, 50 °C. [b]Yield determined by ^{19}F NMR of the crude reaction mixture with $PhCF_3$ as an internal standard.

1). No detrimental effect on the yield was observed with [**Ru**]-**2**[16] as the catalyst (entry 5, Table 1). We chose [**Ru**]-**2** as the catalyst for further reaction condition optimization for its bench-stable and easy-to-handle characteristics. Increasing the catalyst loading to 2 mol % dramatically accelerated the reaction rate, thus affording a much higher yield (entry 6, Table 1). Me_4NSCF_3 (**1b**) was also tested and turned out to be a less efficient nucleophilic reagent in this Ru-catalyzed allylic trifluoromethylthiolation reaction (31% yield, entry 7, Table 1). Various solvents (MeCN, THF, CH_2Cl_2, *c*-hexane, and toluene) were examined, and MeCN was found to be the best one (entries 6, 8−11, Table 1). The reaction proceeded much faster when the branched allylic carbonate **2d** was used, providing the trifluoromethylthiolation product **4a** up to 89% yield (entry 12, Table 1). The control experiment in the absence of Ru catalyst could not afford any of the trifluoromethylthiolation product (entry 13, Table 1).

Under the optimal conditions (entry 12, Table 1), the substrate scope of the Ru-catalyzed regioselective allylic trifluoromethylthiolation reaction was explored, as summarized in Table 2. The reaction conditions tolerated a wide range of allylic substrates, affording the (*E*)-allylic trifluoromethyl thioethers exclusively in good to excellent yields. Aryl allylic carbonates with either electron-donating (4-Me, 4-^{t}Bu, 3-Me, 2-MeO) or electron-withdrawing (4-Br, 4-F, 4-CF_3, 3-Br, 3-Cl, 2-Cl, 2-F, 2,4-Cl_2) substituents at the *para*, *meta*, or *ortho* positions of the aryl ring all afforded their corresponding allylic trifluoromethyl thioethers in 75−91% yields (**4b**−**4m**, entries 2−13, Table 2). 1-Naphthyl substituted allylic trifluoromethyl thioether **4n** could be obtained in 79% yield (entry 14, Table 2). Alkyl substituted allylic carbonates also worked well (entry 15, Table 2). However, the reactions with alkyl substituted allylic carbonates were much slower. Only 52% yield of **4p** and 55% yield of **4q** could be obtained, even by increasing the catalyst loading to 5 mol % (entries 16 and 17, Table 2).

Table 2. Substrate Scope of Ru-Catalyzed Regioselective Allylic Trifluoromethylthiolation Reaction[a]



entry	product (**4**)	time (h)	yield (%)
1	**4a**, R = C_6H_5	4	89
2	**4b**, R = 4-MeC_6H_4	4	91
3	**4c**, R = 4-^{t}BuC_6H_4	4	80
4	**4d**, R = 4-BrC_6H_4	4	80
5	**4e**, R = 4-FC_6H_4	4	82
6	**4f**, R = 4-$CF_3C_6H_4$	4	88
7	**4g**, R = 3-MeC_6H_4	4	81
8	**4h**, R = 3-BrC_6H_4	4	79
9	**4i**, R = 3-ClC_6H_4	4	81
10	**4j**, R = 2-$MeOC_6H_4$	4	84
11	**4k**, R = 2-ClC_6H_4	4	75
12	**4l**, R = 2-FC_6H_4	4	75
13	**4m**, R = 2,4-$Cl_2C_6H_3$	4	83
14	**4n**, R = 1-naphthyl	4	79
15	**4o**, R = CH_2OBn	4	87
16[b]	**4p**, R = Bn	24	52
17[b]	**4q**, R = $BnCH_2$	24	55

[a]Reaction conditions: **1a**/**2**/[**Ru**]-**2** = 2.0/1.0/0.02, 0.5 mmol scale. [b]5 mol % of [**Ru**]-**2** was used.

Mechanistic Study. The Ru-catalyzed allylic substitution reactions generally afford branched products with high regioselectivity[13] with few exceptions.[17] Therefore, the

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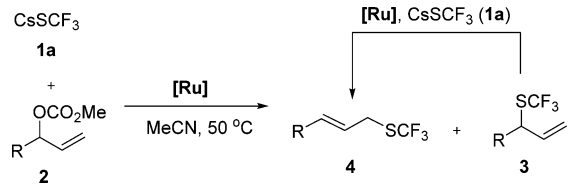
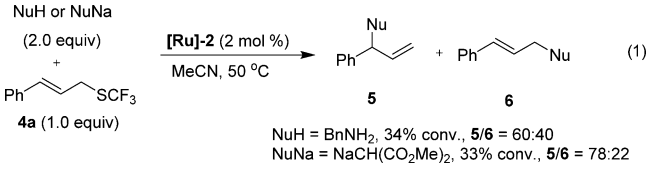
complete formation of the linear (*E*)-allylic trifluoromethyl thioethers suggests a second allylic trifluoromethylthiolation might occur, after the initial substitution step.[18] The branched allylic trifluoromethyl thioether **3** would act as a potential electrophile, leading to the thermodynamically more stable linear allylic counterpart **4** (Scheme 1).

Scheme 1. Proposed Mechanism of the Ru-Catalyzed Allylic Trifluoromethylthiolation Reaction



In order to test this hypothesis, we employed the allylic trifluoromethyl thioether **4a** as the electrophile in the Ru-catalyzed allylic substitution reaction. The linear allylic trifluoromethyl thioether **4a** turned out to be a suitable electrophile as the reaction proceeded with benzyl amine or $NaCH(CO_2Me)_2$ as the nucleophile, though only in moderate conversions (eq 1). It is well-known that the branched allylic

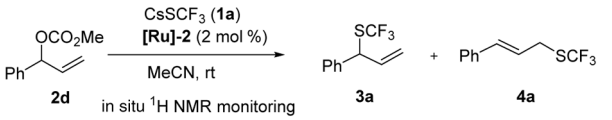


precursors with a terminal double bond are more reactive in the transition-metal-catalyzed allylic substitution reaction than linear ones. Therefore, it is reasonable that the initial formed branched allylic trifluoromethyl thioether **3** would further react with **1a** in the presence of the Ru-catalyst, giving the thermodynamically more stable linear allylic trifluoromethyl thioether **4** (Scheme 1).

The in situ ^{1}H NMR monitoring of the reaction process (molar ratio of **1a**:**2d** = 1:1) at room temperature provided further evidence supporting the mechanistic hypothesis. The plots of product distribution during the conversion of **2d** to **4a** at room temperature are depicted in Figure 2. This process follows the proposed reaction pathway that the initially formed branched allylic trifluoromethyl thioether **3a** would further react with $CsSCF_3$, leading to the linear product **4a**. The plot (blue one) clearly shows that the relative concentration of **B**/**L** goes down along with reaction time. From these results, we anticipate that a proper transition metal that could catalyze the first allylic trifluoromethylthiolation while not the second substitution reaction might provide the allylic trifluoromethyl thioether with highly branched regioselectivity.

CONCLUSION

In summary, we have developed a highly efficient Ru-catalyzed regioselective allylic trifluoromethylthiolation reaction. This reaction merits a broad substrate scope and good to excellent yields, providing linear (*E*)-allylic trifluoromethyl thioethers exclusively. Mechanistic investigation revealed that this reaction proceeds via a double allylic trifluoromethylthiolation sequence. Further expanding the substrate scope and tuning the reaction into a branch selective manner are in progress in our lab.



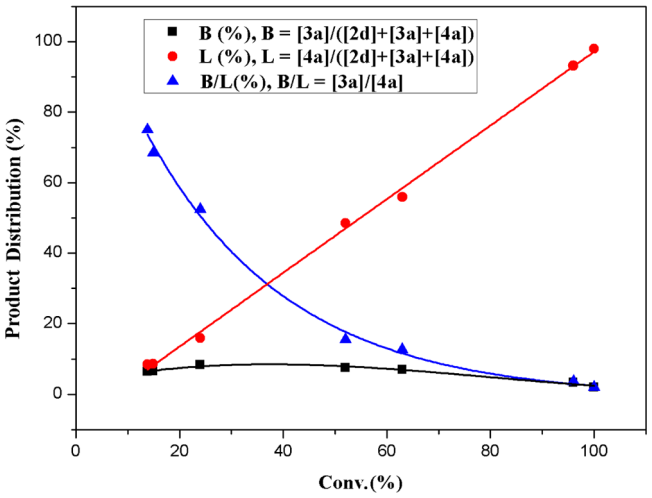


Figure 2. Plot of product distribution vs reaction conversion.

EXPERIMENTAL SECTION

General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under an argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H NMR spectra were obtained at 300 or 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 75 or 100 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.0 ppm). ^{19}F NMR spectra were obtained at 282 or 376 MHz and recorded relative to $CFCl_3$ (0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The ruthenium complex [**Ru**]-**2**,[16] trifluoromethylthiolation reagents ($CsSCF_3$, Me_4NSCF_3),[12] and substituted allylic carbonates[19] were prepared according to the known procedures.

General Procedure for Ru-Catalyzed Allylic Trifluoromethylthiolation. $CsSCF_3$ (234 mg, 1.0 mmol), [**Ru**]-**2** (5.95 mg, 0.01 mmol), allylic carbonate **2** (0.50 mmol), and CH_3CN (5.0 mL) were added to a reaction tube equipped with a magnetic stir bar under argon. The tube was then placed into a preheated 50 °C oil bath. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through Celite and washed with *n*-pentane. The solvents were removed under reduced pressure (>200 Pa). Then, the residue was purified by silica gel column chromatography to afford product **4** with *n*-pentane.

4a.[9] Colorless oil, 110.3 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J = 7.6 Hz, 2H), 6.20 (dt, J = 15.6, 7.2 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 7.21–7.27 (m, 1H), 7.28–7.33 (m, 2H), 7.33–7.38 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.8 (s).

4b.[9] Colorless oil, 129.0 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.70 (d, J = 7.2 Hz, 2H), 6.16 (dt, J = 15.6, 7.6 Hz, 1H), 6.55 (d, J = 15.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.4 (s).

4c.[9] Colorless oil, 116.3 mg, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 3.70 (d, J = 7.2 Hz, 2H), 6.17 (dt, J = 15.3, 7.5 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 7.26–7.41 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −39.6 (s).

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4d.[9] Colorless oil, 116.3 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J = 7.2 Hz, 2H), 6.20 (dt, J = 15.6, 8.4 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.8 (s).

4e. Colorless oil, 101.3 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J = 7.6 Hz, 2H), 6.12 (dt, J = 15.2, 7.6 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 7.00 (t, J = 8.8 Hz, 2H), 7.32 (dd, J = 8.8, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6 (CH_2), 115.6 (CH, d, J = 21.6 Hz, 2C), 122.8 (CH, d, J = 1.9 Hz, 1C), 128.1 (CH, d, J = 8.2 Hz, 2C), 130.8 (q, J = 304.9 Hz, 1C), 132.2 (CH, d, J = 3.4 Hz, 1C), 133.1, 162.6 (d, J = 246.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.9 (s), −113.5 (m); IR (thin film): ν_{max} (cm^{-1}) = 3042, 1602, 1508, 1231, 1147, 1100, 963, 768, 679; MS (EI, m/z): 236 (M^+); HRMS (EI-TOF) calcd for $C_{10}H_8F_4S$ (M^+): 236.0283. Found: 236.0282.

4f.[9] Colorless oil, 127.5 mg, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (d, J = 7.5 Hz, 2H), 6.32 (dt, J = 15.3, 7.8 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −39.6 (s), −61.4 (s).

4g.[9] Colorless oil, 92.1 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.67 (d, J = 7.2 Hz, 2H), 6.18 (dt, J = 15.6, 8.0 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.12−7.25 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.9 (s).

4h. Colorless oil, 117.4 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J = 7.6 Hz, 2H), 6.21 (dt, J = 15.2, 7.6 Hz, 1H), 6.50 (d, J = 15.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 6.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.4 (CH_2), 122.8, 124.8 (CH), 125.1 (CH), 129.3 (CH), 130.1 (CH), 130.7 (q, J = 305.3 Hz, 1C), 130.9 (CH), 132.7 (CH), 138.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.8 (s); IR (thin film): ν_{max} (cm^{-1}) = 3063, 1591, 1560, 1473, 1207, 1146, 1099, 960, 853, 774, 677; MS (EI, m/z): 296 (M^+); HRMS (EI-TOF) calcd for $C_{10}H_8F_3SBr$ (M^+): 295.9482. Found: 295.9481.

4i.[9] Colorless oil, 99.7 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, J = 7.6 Hz, 2H), 6.24 (dt, J = 15.6, 7.2 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 7.18−7.31 (m, 3H), 7.36 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.9 (s).

4j.[9] Colorless oil, 108.1 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, J = 7.2 Hz, 2H), 3.84 (s, 3H), 6.24 (dt, J = 15.2, 7.6 Hz, 1H), 6.82−6.97 (m, 3H), 7.24 (t, J = 8.4 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.4 (s).

4k. Colorless oil, 109.2 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (d, J = 7.5 Hz, 2H), 6.18 (dt, J = 15.3, 7.5 Hz, 1H), 6.97 (d, J = 15.6 Hz, 1H), 7.13−7.25 (m, 2H), 7.28−7.37 (m, 1H), 7.43−7.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.6 (CH_2, q, J = 3.8 Hz, 1C), 126.0 (CH), 126.9 (CH), 127.0 (CH), 129.1 (CH), 129.7 (CH), 130.4 (CH), 130.8 (q, J = 305.6 Hz, 1C), 133.1, 134.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −39.5 (s); IR (thin film): ν_{max} (cm^{-1}) = 3048, 1592, 1470, 1419, 1239, 1147, 1099, 962, 748, 694; MS (EI, m/z): 252 (M^+); HRMS (EI-TOF) calcd for $C_{10}H_8F_3SCl$ (M^+): 251.9987. Found: 251.9991.

4l. Colorless oil, 88.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (d, J = 7.2 Hz, 2H), 6.31 (dt, J = 15.6, 8.4 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 7.03 (t, J = 8.4 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.18−7.28 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9 (CH_2), 115.8 (d, J = 21.9 Hz, 1C), 123.9 (CH, d, J = 11.9 Hz, 1C), 124.2 (CH, d, J = 3.7 Hz, 1C), 125.7 (CH, d, J = 4.8 Hz, 1C), 126.8 (CH, d, J = 3.0 Hz, 1C), 127.5 (CH, d, J = 3.3 Hz, 1C), 129.4 (CH, d, J = 8.2 Hz, 1C), 130.8 (q, J = 304.9 Hz, 1C), 160.2 (d, J = 248.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.9 (s), −117.8 (m); IR (thin film): ν_{max} (cm^{-1}) = 3048, 1612, 1487, 1232, 1147, 1096, 965, 751, 683; MS (EI, m/z): 236 (M^+); HRMS (EI-TOF) calcd for $C_{10}H_8F_4S$ (M^+): 236.0283. Found: 236.0280.

4m. Colorless oil, 134.9 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, J = 7.2 Hz, 2H), 6.19 (dt, J = 15.2, 7.2 Hz, 1H), 6.91 (d, J = 15.6 Hz, 1H), 7.20 (dd, J = 8.4, 2.4 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5 (CH_2), 126.6 (CH), 127.3 (CH), 127.7 (CH), 129.3 (CH), 129.4 (CH), 130.7 (q, J = 305.7 Hz, 1C), 132.8, 133.6, 134.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.8 (s); IR (thin film): ν_{max} (cm^{-1}) = 2963, 1587, 1471, 1258, 1097, 1048, 1013, 868, 803, 756; MS (EI, m/z): 286 (M^+); HRMS (EI-TOF) calcd for $C_{10}H_7F_3SCl_2$ (M^+): 285.9598. Found: 285.9600.

4n. Colorless oil, 105.1 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (d, J = 7.2 Hz, 2H), 6.18 (dt, J = 15.2, 8.0 Hz, 1H), 7.29 (d, J = 15.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.43−7.55 (m, 3H), 7.75 (d, J = 8.0 Hz, 1H), 7.81 (dd, J = 7.6, 2.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8 (CH_2), 123.5 (CH), 124.2 (CH), 125.6 (CH), 125.9 (CH), 126.2 (CH), 126.4 (CH), 128.4 (CH), 128.5 (CH), 131.0, 131.6 (CH), 131.7 (q, J = 305.2 Hz, 1C), 133.5, 133.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.6 (s); IR (thin film): ν_{max} (cm^{-1}) = 3047, 2930, 1591, 1509, 1238, 1107, 961, 795, 775, 755; MS (EI, m/z): 268 (M^+); HRMS (EI-TOF) calcd for $C_{14}H_{11}F_3S$ (M^+): 268.0534. Found: 268.0537.

4o. Colorless oil, 102.2 mg, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (d, J = 5.1 Hz, 2H), 4.00 (d, J = 3.6 Hz, 2H), 4.50 (s, 2H), 5.71−5.92 (m, 2H), 7.23−7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.6 (CH_2, d, J = 2.3 Hz, 1C), 69.5 (CH), 72.2 (CH), 126.5 (CH), 127.6 (CH), 127.7 (CH), 128.4 (CH), 130.7 (q, J = 305.1 Hz, 1C), 131.5 (CH), 137.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −39.7 (s); IR (thin film): ν_{max} (cm^{-1}) = 3032, 2854, 1496, 1361, 1243, 1102, 1028, 966, 735, 665; MS (ESI): 280 $(M + NH_4)^+$; HRMS (ESI-TOF) calcd for $C_{12}H_{17}F_3NOS$ $(M + NH_4)^+$: 280.0977. Found: 280.0983.

4p. Colorless oil, 66.9 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (d, J = 6.8 Hz, 2H), 3.53 (d, J = 7.6 Hz, 2H), 5.58 (dt, J = 14.4, 6.8 Hz, 1H), 5.86 (dt, J = 14.4, 6.0 Hz, 1H), 7.14−7.19 (d, J = 7.6 Hz, 2H), 7.19−7.24 (m, 1H), 7.24−7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1 (CH_2, d, J = 2.3 Hz, 1C), 38.6 (CH), 124.9 (CH), 126.3 (CH), 128.4 (CH), 128.5 (CH), 130.8 (q, J = 308.2 Hz, 1C), 134.4 (CH), 139.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.9 (s); IR (thin film): ν_{max} (cm^{-1}) = 3064, 1665, 1494, 1241, 1101, 1030, 967, 745, 697; MS (EI, m/z): 232 (M^+); HRMS (EI-TOF) calcd for $C_{11}H_{11}F_3S$ (M^+): 232.0534. Found: 232.0532.

4q. Colorless oil, 69.7 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30−2.45 (m, 2H), 2.69 (t, J = 7.2 Hz, 2H), 3.49 (d, J = 7.2 Hz, 2H), 5.52 (dt, J = 14.4, 7.2 Hz, 1H), 5.74 (dt, J = 14.0, 6.8 Hz, 1H), 7.10−7.23 (m, 3H), 7.23−7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2 (CH_2), 34.0 (CH_2), 35.3 (CH_2), 124.1 (CH), 125.9 (CH), 128.3 (CH), 128.4 (CH), 130.8 (q, J = 304.6 Hz, 1C), 135.1 (CH), 141.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.0 (s); IR (thin film): ν_{max} (cm^{-1}) = 3029, 2928, 2858, 1605, 1496, 1454, 1242, 1106, 967, 928, 747, 698; MS (EI, m/z): 246 (M^+); HRMS (EI-TOF) calcd for $C_{12}H_{13}F_3S$ (M^+): 246.0690. Found: 246.0686.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectral data for all the new and known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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