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Reactions of methylenecyclopropanes and vinylidenecyclopropanes with *N*-fluorodibenzenesulfonimide

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ABSTRACT

Methylenecyclopropanes and vinylidenecyclopropanes undergo ring-opening reactions with *N*-fluorodibenzenesulfonimide (NFSI) upon heating at 60 °C in tetrahydrofuran to give the corresponding fluorinated derivatives **2** and **6** in good to excellent yields. A plausible reaction mechanism has been discussed on the basis of previous literature.

1. Introduction

Methylenecyclopropanes (MCPs) and vinylidenecyclopropanes (VDCPs) are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis.[1–4] Thus far, many novel transformations of these interesting small molecules have been disclosed by organic chemists. For example, we and others have recently been investigating the Lewis acid/transition metal-mediated/catalyzed ring-opening reactions of MCPs **1** and VDCPs **5** with a variety of nucleophiles such as alcohols and aromatic amines as well as other reactants under mild conditions to produce a variety of interesting compounds.[5] However, to the best of our knowledge, the investigation on the fluorine-containing transformation of MCPs **1** and VDCPs **5** is rare. For example, although thermal and photochemical skeletal conversions of VDCPs **5** as well as their Lewis acid-catalyzed transformations with electrophiles had been made great progress from mechanistic, theoretical, spectroscopic, and synthetic viewpoints in past decades,[3,4] no example on the reaction of VDCPs **5** with fluorinating agents has been disclosed thus far. The specific properties of fluorine as a substituent in organic compounds have resulted in a steadily growing interest in organofluorine chemistry, which has proved to be a research area with numerous applications in agrochemistry and pharmaceutical chemistry.[6] In addition, the commercialization of safe and efficient fluorinating agents has paved the way for the development of a wide scope of synthetic pathways to various fluorinated compounds.[7,8] Therefore, as the ongoing studies on the chemistry of highly strained small ring, we investigated the reactions of MCPs **1** and VDCPs **5** with fluorinating agent such as *N*-fluorodibenzenesulfonimide (NFSI) under various reaction conditions. In this paper, we wish to report the full details.

2. Results and discussion

Initial examinations using methylenecyclopropane **1a** as the substrate to react with NFSI under a variety of reaction conditions were aimed at determining the reaction outcome and the optimal reaction conditions. The results of these experiments are summarized in Table 1. Using **1a** (1.0 equiv) with NFSI (1.0 equiv) in DCE at 60 °C, the ring-opened products **2a** and **3a** were produced in 73% and 18% yields, respectively, after 12 h under ambient atmosphere (Table 1, entry 1). Changing the ratio of **1a**/NFSI to 1/2 or 1/1.5 also provided **2a** and **3a** in similar yields, respectively (Table 1, entries 2 and 3). Thus, we chose the ratio of **1a**/NFSI=1/1 as the best combination to further optimize the reaction conditions. When the reaction temperature was changed to room temperature (20 °C), **2a** and **3a** were obtained in 69% and 12% yields, respectively, after 38 h (Table 1, entry 4). Adding a variety of Lewis acids such as $Sc(OTf)_3$, $Sn(OTf)_2$, $Yb(OTf)_3$, $Nd(OTf)_3$, and $Sm(OTf)_2$ to the reaction system did not significantly improve the yields of **2a** and **3a**, although the reactions could complete within 3–10 h (Table 1, entries 5–9). Further examination of solvent effects revealed that in tetrahydrofuran (THF), the product **2a** was obtained in 83% yield as a sole product without compound **3a** within 15 h (Table 1, entry 10). In toluene, the yields of **2a** and **3a** were 52% and 26%, respectively,

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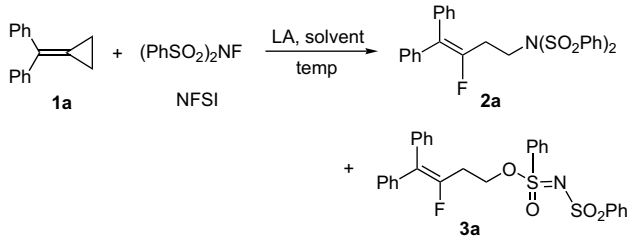
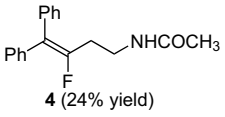
Table 1
Optimization of the reaction conditions between **1a** and NFSI



Entry[a]	**1a**/NFSI	LA	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	
						2a	**3a**
1	1/1	—	DCE	60	12	73	13
2	1/2	—	DCE	60	12	72	12
3	1/1.5	—	DCE	60	12	73	11
4	1/1	—	DCE	rt	38	69	12
5	1/1	$Sc(OTf)_3$	DCE	60	3	66	14
6	1/1	$Sn(OTf)_2$	DCE	60	7	65	19
7	1/1	$Yb(OTf)_3$	DCE	60	8	68	21
8	1/1	$Nd(OTf)_3$	DCE	60	10	66	17
9	1/1	$Sm(OTf)_2$	DCE	60	10	67	18
10	*1/1*	—	*THF*	*60*	*15*	*83*	*Trace*
11	1/1	—	Toluene	60	24	52	26
12	1/1	—	Et_2O	30	42	54	25
13	1/1	—	CH_2Cl_2	30	40	61	25
14	1/1	—	CH_3CN	60	18	52	9

[a] Reaction conditions: **1a** (0.2 mmol), NFSI (*x* mmol), solvent (2.0 mL) and the reactions were carried out at various temperatures.
[b] Isolated yields.

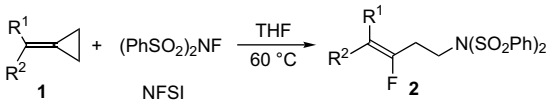


4 (24% yield)

within 24 h (Table 1, entry 11). When the reaction was carried out at 30 °C, **2a** and **3a** were formed in 54% and 25% yields in ether and 61% and 25% yields in dichloromethane, respectively (Table 1, entries 12 and 13). Using acetonitrile as the solvent, the unexpected product **4** was obtained in 24% yield along with the production of **2a** and **3a** in 52% and 9% yields (Table 1, entry 14). Therefore, the best conditions are to carry out the reaction in THF at 60 °C using 1.0 equiv of **1a** and 1.0 equiv NFSI as the starting materials.

Under these optimal reaction conditions, we next carried out this ring-opening reaction of a variety of methylenecyclopropanes **1** with NFSI. The results of these experiments are summarized in Table 2. We found that the electronic nature of the substituents on the benzene rings of **1** is very significant. As can be seen from Table 2, in the presence of an electron-donating substituent at the *para* or *meta* positions of the benzene rings led to **2a** in higher yields within less reaction time than those with electron-withdrawing substituents (Table 2, entries 1, 2, and 4). For unsymmetrical MCPs **1d**, **1f**, and **1g**, the corresponding products **2d**, **2f**, and **2g** were obtained as mixtures of *E*- and *Z*-isomers on the basis of ^1H or ^{19}F NMR spectroscopic data (Table 2, entries 3 and 5 and 6) (Supplementary data). As for unsymmetrical MCPs **1h** and **1i** with electron-donating substituent on the benzene rings, the corresponding products **2h** and **2i** were also obtained as isomeric mixtures in which the ratios were determined by ^1H NMR spectroscopic data and the products *E*-**2h** and *E*-**2i** were the major ones, perhaps due to that the aromatic group is more sterical than a hydrogen atom (Table 2, entries 7 and 8) (Supplementary data). As for aliphatic MCP **1j**, the complicated reaction products were formed without the isolation of the expected product **2j** (Table 2, entry 9). Using unsymmetrical aliphatic MCP **1k** as the substrate, no reaction occurred (Table 2, entry 10).

Table 2
Scope and limitations of the reaction of MCPs **1** with NFSI



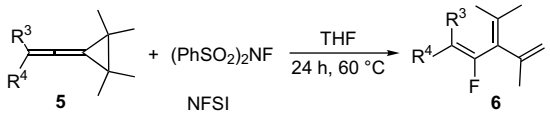
Entry[a]	**1** (R^1/R^2)	Time (h)	Yield[b] (%)
			2
1	**1b** (*p*-MeC_6H_4/*p*-MeC_6H_4)	12	**2b**, 86
2	**1c** (*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$)	10	**2c**, 91
3	**1d** (*m*,*p*-$Me_2C_6H_3$/C_6H_5)	12	**2d**,[c] 85 (1.1:1)
4	**1e** (*p*-ClC_6H_4/*p*-ClC_6H_4)	24	**2e**, 62
5	**1f** (*p*-ClC_6H_4/C_6H_5)	24	**2f**,[d] 78 (13:7)
6	**1g** (*p*-FC_6H_4/C_6H_5)	24	**2g**,[d] 71 (1:1)
7	**1h** (*m*,*p*-$(MeO)_2C_6H_3$/H)	3	**2h**,[c] 90 (>99:1)
8	**1i** (*p*-MeC_6H_4/H)	11	**2i**,[c] 84 (4:1)
9	**1j** (C_4H_9/C_4H_9)	8	complex
10	**1k** (C_4H_9/H)	30	NR

[a] Reaction conditions: **1** (0.2 mmol), NFSI (0.2 mmol), solvent (2.0 mL) and the reactions were carried out at various temperatures.
[b] Isolated yields.
[c] The ratios were determined by ^1H NMR spectroscopic data.
[d] The ratios were determined by ^{19}F NMR spectroscopic data.

If using vinylidenecyclopropanes **5** as substrates to react with NFSI under the standard reaction conditions, we found that the products are compounds **6**. The results are summarized in Table 3. We also found the electronic nature of the substituents on the benzene rings is significant on the reaction outcomes. Using vinylidenecyclopropane **5a** as the substrate, the corresponding product **6a** was obtained in 82% yield after 24 h (Table 3, entry 1). As for the substrates **5b**–**5d** having electron-donating substituents on the benzene rings, the yields of **6b**–**6d** could reach 91–95%, respectively (Table 3, entries 2–4). However, as for VDCPs **5e** and **5f** with electron-poor substituents on the benzene rings, the corresponding products **6e** and **6f** were obtained in lower yields (76–79%) after 24 h under the standard conditions (Table 3, entries 5 and 6). For unsymmetrical VDCPs **5d** and **5f**, the corresponding products **6d** and **6f** were obtained as isomeric mixtures in which the ratios were determined by ^1H NMR spectroscopic data (Table 3, entries 4 and 6) (Supplementary data).

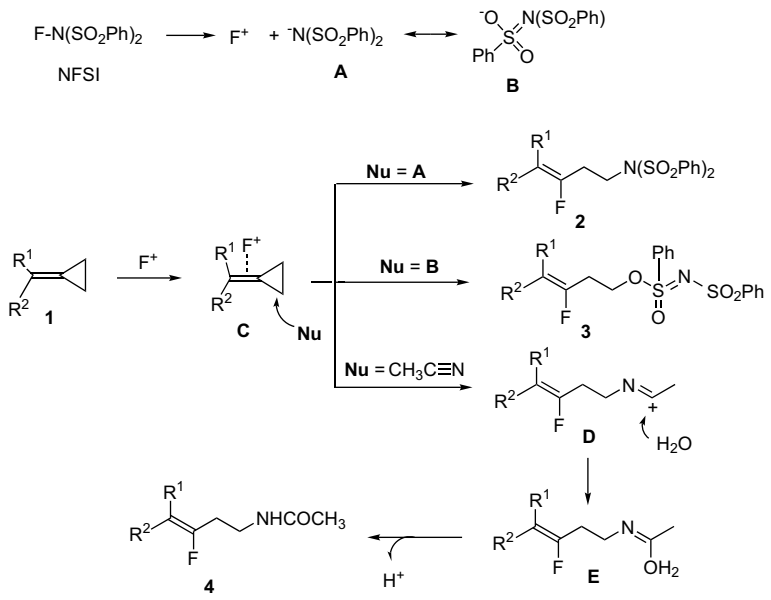
The reaction mechanism of MCPs with NFSI is outlined in Schemes 1 and 2, respectively. Initially, the fluoric cation F^+ and the anionic intermediate **A** ($^-N(SO_2Ph)_2$) are generated from NFSI under the standard reaction conditions,[9] in which the anionic intermediate **A** can be transformed to another anionic intermediate **B** ($^-OS(O)(Ph)SO_2Ph$). The MCP **1** is added by F^+ to form intermediate **C**.[10] Then, the anionic intermediates **A** and **B** attack intermediate **C**

Table 3
Scope and limitations of the reaction of VDCPs with NFSI

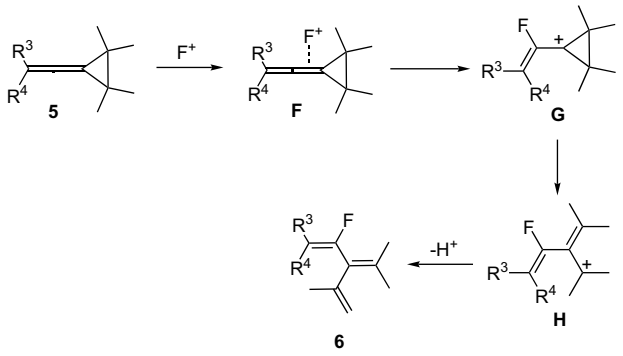


Entry[a]	**5** (R^3/R^4)	Yield[b] (%)
		6
1	**5a** (C_6H_5/C_6H_5)	**6a**, 82
2	**5b** (*p*-MeC_6H_4/*p*-MeC_6H_4)	**6b**, 91
3	**5c** (*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$)	**6c**, 95
4	**5d** (*p*-$MeOC_6H_4$/C_6H_5)	**6d**,[c] 94 (1:1)
5	**5e** (*p*-ClC_6H_4/*p*-ClC_6H_4)	**6e**, 76
6	**5f** (*p*-ClC_6H_4/C_6H_5)	**6f**,[c] 79 (17:3)

[a] Reaction conditions: **5** (0.2 mmol), NFSI (0.2 mmol), THF (2.0 mL) and the reactions were carried out at various temperatures.
[b] Isolated yields.
[c] The ratios were determined by ^1H NMR spectroscopic data.



Scheme 1. Proposed mechanism for the reaction of MCPs with NFSI.



Scheme 2. Proposed mechanism for the reaction of VDCPs with NFSI.

to produce the products **2** and **3**, respectively. When the reaction is carried out in acetonitrile, the solvent also can act as a nucleophile to attack intermediate **C**, affording intermediate **D**. Intermediate **D** undergoes hydrolysis with water to give intermediate **E**, which produces the product **4** via deprotonation (Scheme 1).

In the case of VDCPs **5**, fluoric cation F^+ adds to a double bond of **5** to give cationic intermediate **G** via intermediate **F**. Intermediate **G** can give the cyclopropane opened cationic intermediate **H** rapidly under the standard conditions, which produces the product **6** via depronotation.[11]

3. Conclusion

In summary, we have disclosed the reactions of methylenecyclopropanes (MCPs) and vinylidenecyclopropanes (VDCPs) with NFSI at 60 °C in tetrahydrofuran (THF) to give the corresponding fluorinated derivatives **2** and **6** in moderate to excellent yields. A plausible reaction mechanism has been discussed on the basis of previous literature. The particular highly strained three-membered cyclopropane plays a key role for this transformation. The corresponding fluorinated products **2** and **6** may be useful intermediates in organic synthesis. Efforts are in progress to further elucidate the mechanistic details of this reaction and to determine its scope and limitations.

4. Experimental procedures

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are in hertz. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. Solvents were used without further drying up. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.2. General procedure

General procedure for the reactions of MCPs **1** or VDCPs **5** with NFSI. Under ambient atmosphere, methylenecyclopropanes (MCPs) **1** or vinylidenecyclopropanes (VDCPs) **2** (0.2 mmol), NFSI (0.2 mmol) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **2** or **6** in moderate to good yields.

4.2.1. Compound ***2a***

A white solid, mp 98–100 °C; IR (CH_2Cl_2): ν 3061, 3024, 2925, 1664, 1494, 1447, 1379, 1168, 1085, 1071, 910, 850, 807, 720, 686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.65–2.74 (2H, m, CH_2), 3.95–3.99 (2H, m, CH_2), 7.20–7.28 (7H, m, ArH), 7.35–7.47 (7H, m, ArH), 7.59 (2H, t, J=7.6 Hz, ArH), 7.95 (4H, d, J=7.6 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.8 (d, J_{C-F}=26.7 Hz), 46.3, 122.8 (d, J_{C-F}=13.4 Hz), 127.2, 127.6, 128.0, 128.1, 128.6, 129.1, 129.4, 129.5, 130.0, 130.1, 133.9, 136.7, 138.0, 138.1, 139.6, 153.7 (d, J_{C-F}=259.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −107.6 (t, J_{H-F}=13.4 Hz); MS (ESI) m/z (%): 544 (100.00) [M^++23]. Anal. Calcd for $C_{28}H_{24}NO_4FS_2$ requires C, 64.47; H, 4.64; N, 2.69%. Found: C, 64.43; H, 4.77; N, 2.64%.

4.2.2. Compound ***2b***

A yellow oil; IR (CH_2Cl_2): ν 3064, 3025, 2921, 2867, 1910, 1660, 1479, 1448, 1378, 1179, 1068, 929, 702, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.31 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.63–2.76 (2H, m, CH_2), 3.95–4.00 (2H, m, CH_2), 7.05–7.16 (6H, m, ArH), 7.20 (2H, d, J=8.7 Hz, ArH), 7.45 (4H, t, J=7.8 Hz, ArH), 7.60 (2H, t, J=7.8 Hz, ArH), 7.91 (4H, d, J=8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.1, 21.2, 31.7 (d, J_{C-F}=27.3 Hz), 46.4, 122.5 (d, J_{C-F}=13.3 Hz), 128.1, 128.6, 129.0, 129.2, 129.3, 129.4, 129.9, 133.8, 134.0, 135.1, 135.3, 136.9, 137.2, 139.6, 153.1 (d, J_{C-F}=258.4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −108.4 (t, J_{H-F}=13.8 Hz); MS (ESI) m/z (%): 572 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{30}H_{28}NO_4FS_2Na^+$ (M^++23) requires 572.1336, found: 572.1330.

4.2.3. Compound ***2c***

A yellow oil; IR (CH_2Cl_2): ν 3065, 2956, 2935, 2837, 1660, 1573, 1463, 1381, 1169, 1032, 999, 927, 852, 720, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.67–2.79 (2H, m, CH_2), 3.78 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.98–4.03 (2H, m, CH_2), 6.84 (2H, d, J=8.4 Hz, ArH), 6.96 (2H, d, J=9.0 Hz, ArH), 7.12 (2H, d, J=8.1 Hz, ArH), 7.22 (2H, d, J=8.1 Hz, ArH), 7.48 (4H, t, J=7.2 Hz, ArH), 7.61 (2H, t, J=7.5 Hz, ArH), 7.94 (4H, d, J=7.8 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.7 (d, J_{C-F}=27.7 Hz), 46.3, 55.1, 55.2, 113.2, 113.6, 113.9, 121.8, 128.0, 128.4, 129.0, 129.4, 130.3, 130.4, 130.6, 130.7, 131.1, 133.7, 133.8, 139.5, 152.7 (d, J_{C-F}=257.3 Hz), 158.5, 158.9; ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −109.4 (t, J_{H-F}=14.1 Hz); MS (ESI) m/z (%): 604 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{30}H_{28}NO_6FS_2Na^+$ (M^++23) requires 604.1234, found: 604.1218.

4.2.4. Compound ***2d***

A yellow oil; IR (CH_2Cl_2): ν 3064, 2924, 1664, 1585, 1492, 1448, 1378, 1169, 1090, 1070, 1016, 930, 850, 752, 721, 686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.19 (1.65H, s, CH_3), 2.22 (1.65H, s, CH_3), 2.27 (1.35H, s, CH_3), 2.31 (1.35H, s, CH_3), 2.61–2.74 (2H, m, CH_2), 3.93–4.01 (2H, m, CH_2), 6.89–6.97 (2H, m, ArH), 7.03–7.06 (1H, m, ArH), 7.15–7.28 (4H, m, ArH), 7.36–7.49 (5H, m, ArH), 7.61 (2H, t, J=10.0 Hz, ArH), 7.88–7.92 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.4, 19.5, 19.7, 19.8, 31.7 (d, J_{C-F}=26.8 Hz), 31.8 (d, J_{C-F}=26.4 Hz), 46.3, 46.4, 122.7 (d, J_{C-F}=12.5 Hz), 122.8 (d, J_{C-F}=13.7 Hz), 126.9, 127.0, 127.1, 127.4, 127.5, 127.9, 128.1, 128.3, 128.6, 128.9, 129.0, 129.1, 129.2, 129.4, 129.5, 129.8, 130.0, 130.5, 130.6, 131.1, 133.8, 134.2, 135.4, 135.5, 135.7, 135.9, 136.1, 136.9, 137.0, 138.2, 138.3, 139.6, 139.7, 153.1 (d, J_{C-F}=257.7 Hz), 153.4 (d, J_{C-F}=258.4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −109.3 (t, J_{H-F}=16.6 Hz); MS (ESI) m/z (%): 572 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{30}H_{28}NO_4FS_2Na^+$ (M^++23) requires 572.1336, found: 572.1337.

4.2.5. Compound ***2e***

A white solid, mp 105–107 °C; IR (CH_2Cl_2): ν 3066, 3049, 2921, 2854, 1967, 1666, 1603, 1507, 1448, 1373, 1168, 1085, 1064, 929, 853, 811, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.62–2.72 (2H, m, CH_2), 3.92–3.99 (2H, m, CH_2), 7.08 (2H, d, J=7.5 Hz, ArH), 7.14 (2H, d, J=8.4 Hz, ArH), 7.24–7.30 (3H, m, ArH), 7.37 (2H, d, J=8.4 Hz, ArH), 7.42–7.52 (4H, m, ArH), 7.64 (2H, t, J=7.5 Hz, ArH), 7.91 (3H, d, J=8.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.8 (d, J_{C-F}=26.0 Hz), 46.3, 122.8 (d, J_{C-F}=13.4 Hz), 127.2, 127.6, 128.0, 128.1, 128.6, 129.1, 129.4, 129.5, 130.0, 130.1, 133.9, 136.7, 138.0, 138.1, 139.6, 153.7 (d, J_{C-F}=259.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −105.6 (t, J_{H-F}=15.5 Hz); MS (ESI) m/z (%): 612 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{28}H_{22}NO_4FCl_2S_2Na^+$ (M^++23) requires 612.0243, found: 612.0241.

4.2.6. Compound ***2f***

A yellow oil; IR (CH_2Cl_2): ν 3064, 2924, 2854, 1664, 1585, 1492, 1448, 1378, 1169, 1090, 1016, 930, 850, 752, 686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.64–2.72 (2H, m, CH_2), 3.96–3.99 (2H, m, CH_2), 7.10 (1H, d, J=8.8 Hz, ArH), 7.15–7.31 (6H, m, ArH), 7.35–7.42 (2H, m, ArH), 7.44–7.51 (4H, m, ArH), 7.58–7.64 (2H, m, ArH), 7.88–7.93 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.9 (d, J_{C-F}=25.8 Hz), 46.3, 121.7 (d, J_{C-F}=14.4 Hz), 127.2, 127.7, 127.8, 127.9, 128.6, 128.7, 128.9, 129.2, 129.3, 129.8, 130.5, 130.6, 131.2, 131.3, 132.8, 133.5, 133.7, 134.9, 136.1, 136.2, 136.3, 137.4, 139.3, 153.0 (d, J_{C-F}=258.7 Hz), 153.8 (d, J_{C-F}=249.4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −107.4 (0.35F, t, J_{H-F}=18.9 Hz), −107.5 (0.65F, t, J_{H-F}=21.4 Hz); MS (ESI) m/z (%): 578 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{28}H_{23}NO_4FS_2ClNa^+$ (M^++23) requires 578.0633, found: 578.0638.

4.2.7. Compound ***2g***

A colorless oil; IR (CH_2Cl_2): ν 3066, 3921, 1907, 1666, 1603, 1506, 1448, 1373, 1168, 1085, 1064, 999, 929, 848, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.64–2.73 (2H, m, CH_2), 3.95–3.99 (2H, m, CH_2), 6.96 (1H, t, J=8.8 Hz, ArH), 7.06–7.28 (6H, m, ArH), 7.38–7.49 (6H, m, ArH), 7.58–7.63 (2H, m, ArH), 7.90 (4H, t, J=9.6 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.5, 31.7 (d, J_{C-F}=26.8 Hz), 46.1, 46.2, 114.8 (d, J_{C-F}=20.8 Hz), 115.6 (d, J_{C-F}=20.8 Hz), 121.80, 121.83, 121.93, 121.98, 127.0, 127.3, 127.8, 128.01, 128.06, 128.7, 129.1, 129.3, 129.4, 129.9, 130.0, 131.13, 131.18, 131.20, 131.26, 131.6, 131.72, 131.77, 132.7, 133.90, 133.93, 136.5, 137.7, 137.8, 139.50, 139.51, 153.6 (d, J_{C-F}=268.0 Hz), 153.7 (d, J_{C-F}=259.6 Hz), 161.7 (d, J_{C-F}=246.9 Hz), 162.2 (d, J_{C-F}=246.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −116.8 (0.5F, s), −116.4 (0.5F, s), −110.1 (0.5F, t, J_{H-F}=17.2 Hz), −109.4 (0.5F, t, J_{H-F}=16.1 Hz); MS (EI) m/z (%): 539 (6.32) [M^+], 310 (29.43), 242 (98.64), 209 (24.23), 183 (6.49), 141 (100.00), 77 (83.56), 51 (13.74); HRMS (EI) calcd for $C_{28}H_{23}NO_4F_2S_2$ (M^+) requires 539.1037, found: 539.1038.

4.2.8. Compound ***2h***

A colorless oil; IR (CH_2Cl_2): ν 3068, 3003, 2938, 2838, 1689, 1610, 1581, 1449, 1208, 1035, 835, 752, 686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.67–2.75 (2H, m, CH_2), 3.79 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 3.94–3.99 (2H, m, CH_2), 5.81 (1H, d, J=40.8 Hz, CH), 7.53 (5H, t, J=8.0 Hz, ArH), 7.63–7.67 (4H, m, ArH), 8.05 (4H, d, J=7.8 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 34.5 (d, J_{C-F}=27.1 Hz), 46.4, 55.3, 55.4, 98.1, 101.5, 104.5, 114.6, 127.7, 128.2, 129.1, 130.3, 130.4, 133.9, 139.6, 155.6 (d, J_{C-F}=257.8 Hz), 157.1, 159.9; MS (EI) m/z (%): 505 (30.39) [M^+], 208 (27.06), 195 (100.00), 177 (11.56), 164 (9.71), 141 (24.48), 77 (35.70), 51 (9.34); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −108.5 (dt, J=30.2, 13.2 Hz); HRMS (EI) calcd for $C_{24}H_{24}NO_6FS_2$ (M^+) requires 505.1029, found: 505.1039.

4.2.9. Compound ***2i***

A colorless oil; IR (CH_2Cl_2): ν 3065, 3005, 2923, 1727, 1690, 1610, 1513, 1448, 1377, 1169, 1085, 926, 854, 752, 686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.31 (0.6H, s, CH_3), 2.33 (2.4H, s, CH_3), 2.66–2.75 (2H, m, CH_2), 3.95–3.99 (2H, m, CH_2), 5.41 (0.8H, d, J=39.2 Hz, CH), 6.23 (0.2H, d, J=22.0 Hz, CH), 6.80 (0.5H, d, J=8.0 Hz, ArH), 6.95 (1H, s, ArH), 7.11–7.18 (2H, m, ArH), 7.31 (2H, d,

J=8.0 Hz, ArH), 7.49–7.56 (5H, m, ArH), 7.61–7.68 (3H, m, ArH), 7.98–8.05 (5.5H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.2, 21.4, 34.3 (d, J_{C-F}=26.4 Hz), 46.3, 108.4, 108.5, 127.2, 127.4, 128.1, 128.2, 128.32, 128.34, 128.4, 128.5, 128.9, 129.1, 129.2, 129.3, 129.7, 130.0, 130.10, 130.14, 131.9, 133.9, 134.0, 134.1, 134.8, 137.0, 139.0, 139.5, 139.7, 155.6 (d, J_{C-F}=264.0 Hz); MS (EI) m/z (%): 459 (8.59) [M^+], 310 (26.36), 298 (30.47), 234 (22.04), 162 (56.71), 141 (96.15), 77 (100.00), 51 (14.49); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −108.3 to −108.1 (m); HRMS (EI) calcd for $C_{23}H_{22}NO_4S_2F$ (M^+) requires 459.0974, found: 459.0970.

4.2.10. Compound **3a**

A white solid, mp 102–104 °C; IR (CH_2Cl_2): ν 3169, 3059, 3029, 2920, 1663, 1494, 1448, 1375, 1169, 1085, 1072, 852, 1000, 934, 852, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.70 (2H, dt, J=15.3, 4.5 Hz, CH_2), 4.39–4.49 (2H, m, CH_2), 7.07–7.11 (2H, m, ArH), 7.20–7.32 (8H, m, ArH), 7.41–7.53 (5H, m, ArH), 7.61–7.65 (1H, m, ArH), 7.89–7.91 (2H, m, ArH), 7.95–7.97 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 30.3 (d, J_{C-F}=27.4 Hz), 67.7, 126.7, 127.3, 127.7, 127.9, 128.6, 128.7, 129.3, 1294, 130.0, 130.1, 132.4, 134.6, 135.4, 136.6, 142.6, 153.5 (d, J_{C-F}=258.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −107.7 to −107.5; MS (ESI) m/z (%): 544 (100.00) [M^++23]; HRMS (MALDI) calcd for $C_{28}H_{24}NO_4FS_2Na^+$ (M^++23) requires 544.1023, found: 544.1006.

4.2.11. Compound **4**

A white solid, mp 95–97 °C; IR (CH_2Cl_2): ν 3422, 3292, 3027, 2932, 2856, 1954, 1666, 1495, 1444, 1230, 1171, 1034, 935, 764 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.95 (3H, s, CH_3), 2.56 (2H, dt, J=30.0, 8.8 Hz, CH_2), 3.59 (2H, dt, J=8.8, 8.8 Hz, CH_2), 5.60 (1H, br s, NH), 7.17–7.20 (2H, m, ArH), 7.23–7.39 (8H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 23.3, 30.6 (d, J_{C-F}=26.0 Hz), 37.0, 122.5 (d, J_{C-F}=12.0 Hz), 127.1, 127.6, 128.0, 128.6, 129.4, 129.5, 130.0, 130.1, 137.0, 138.2, 138.3, 155.4 (d, J_{C-F}=258.0 Hz), 169.9; MS (EI) m/z (%): 283 (6.10) [M^+], 260 (10.48), 224 (100.00), 209 (21.98), 196 (32.52), 167 (16.37), 133 (15.84), 91 (10.54); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −106.9 (t, J_{H-F}=11.8 Hz); HRMS (EI) calcd for $C_{18}H_{18}NOF$ (M^+) requires 283.1372, found: 283.1371.

4.2.12. Compound **6a**

A colorless oil; IR (CH_2Cl_2): ν 3082, 3028, 2856, 1982, 1632, 1599, 1444, 1372, 1173, 1089, 1075, 1012, 900, 767, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.68 (3H, d, J=4.0 Hz, CH_3), 1.71 (3H, d, J=4.0 Hz, CH_3), 1.82 (3H, d, J=0.8 Hz, CH_3), 4.50–4.51 (1H, m, CH_2), 4.91–4.92 (1H, m, CH_2), 7.13–7.16 (2H, m, ArH), 7.18–7.24 (4H, m, ArH), 7.29–7.31 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.0, 21.6, 22.7, 116.4, 123.4 (d, J_{C-F}=19.3 Hz), 126.9, 127.0, 127.8, 127.9, 128.1, 128.2, 129.92, 129.97, 130.0, 130.1, 130.7, 138.1, 138.2, 138.3, 138.9, 139.0, 141.8, 154.7 (d, J_{C-F}=257.3 Hz); MS (EI) m/z (%): 292 (100.00) [M^+], 277 (99.72), 257 (25.19), 215 (58.49), 183 (23.83), 165 (24.47), 91 (33.53), 77 (18.21); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −92.1; HRMS (EI) calcd for $C_{21}H_{21}F$ (M^+) requires 292.1627, found: 292.1630.

4.2.13. Compound **6b**

A colorless oil; IR (CH_2Cl_2): ν 3028, 3024, 2920, 2858, 1906, 1631, 1512, 1371, 1168, 1088, 1025, 932, 898, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.65 (3H, d, J=3.6 Hz, CH_3), 1.71 (3H, d, J=3.6 Hz, CH_3), 1.82 (3H, d, J=0.8 Hz, CH_3), 2.30 (3H, s, CH_3), 2.32 (3H, s, CH_3), 4.53 (1H, s, CH_2), 4.92–4.93 (1H, m, CH_2), 7.02 (4H, s, ArH), 7.10 (2H, d, J=8.4 Hz, ArH), 7.20 (2H, d, J=8.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.2, 21.6, 22.7, 22.8, 116.3, 123.1 (d, J_{C-F}=20.0 Hz), 128.4, 128.6, 129.8, 129.9, 130.8, 131.1, 135.4, 136.0, 136.1, 136.4, 136.7, 137.7, 137.8, 142.0, 153.6 (d, J_{C-F}=257.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −93.2 (t, J_{H-F}=3.1 Hz); MS (EI) m/z (%): 320 (78.48) [M^+], 305 (100.00), 285 (17.66), 213 (30.49), 197 (16.51), 123 (20.26), 91 (10.19), 77 (7.93); HRMS (EI) calcd for $C_{23}H_{25}F$ (M^+) requires 320.1940, found: 320.1940.

4.2.14. Compound **6c**

A colorless oil; IR (CH_2Cl_2): ν 3301, 2926, 1652, 1494, 1446, 1376, 1275, 1262, 1092, 1027, 764, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.67 (3H, d, J=3.6 Hz, CH_3), 1.72 (3H, d, J=3.6 Hz, CH_3), 1.82 (3H, s, CH_3), 3.77 (3H, s, CH_3), 3.78 (3H, s, CH_3), 4.52–4.53 (1H, m, CH_2), 4.92–4.93 (1H, m, CH_2), 6.76 (2H, d, J=8.8 Hz, ArH), 6.84 (2H, d, J=8.8 Hz, ArH), 7.06 (2H, d, J=8.8 Hz, ArH), 7.24 (2H, d, J=8.8 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.6, 22.7, 22.8, 55.0, 55.1, 113.1, 113.2, 113.3, 113.6, 116.3, 122.4 (d, J_{C-F}=19.3 Hz), 130.1, 130.7, 130.8, 130.9, 131.0, 131.1, 131.2, 131.4, 131.5, 137.5, 137.6, 142.0, 153.2 (d, J_{C-F}=255.1 Hz), 158.4, 158.5; ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −90.1; MS (EI) m/z (%): 352 (45.22) [M^+], 337 (52.39), 291 (8.41), 267 (100.00), 135 (56.65), 121 (16.89), 91 (4.58), 77 (7.66); HRMS (EI) calcd for $C_{23}H_{25}O_2F$ (M^+) requires 352.1839, found: 352.1835.

4.2.15. Compound **6d**

A colorless oil; IR (CH_2Cl_2): ν 3080, 2933, 2836, 2854, 1630, 1511, 1443, 1289, 1284, 1170, 1036, 900, 834, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.67 (1.5H, d, J=4.4 Hz, CH_3), 1.69 (1.5H, d, J=4.4 Hz, CH_3), 1.71 (1.5H, d, J=5.2 Hz, CH_3), 1.73 (1.5H, d, J=5.2 Hz, CH_3), 1.81 (1.5H, s, CH_3), 1.83 (1.5H, s, CH_3), 3.76 (1.5H, s, OCH_3), 3.78 (1.5H, s, OCH_3), 4.48 (0.5H, d, J=1.2 Hz, CH_2), 4.55 (0.5H, d, J=1.6 Hz, CH_2), 4.90–4.91 (0.5H, m, =CH_2), 4.94–4.95 (0.5H, m, =CH_2), 6.76 (1H, d, J=8.8 Hz, ArH), 6.84 (1H, d, J=8.8 Hz, ArH), 7.06 (1H, d, J=8.8 Hz, ArH), 7.13–7.15 (1H, m, ArH), 7.18–7.21 (2H, m, ArH), 7.23–7.26 (1H, m, ArH), 7.29–7.31 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.5, 21.6, 22.7, 22.8, 55.1, 55.2, 113.2, 113.3, 116.3, 116.4, 122.7, 122.8, 123.0, 126.8, 127.0, 127.7, 127.9, 129.8, 129.9, 130.0, 130.1, 130.5, 130.8, 131.0, 131.1, 131.2, 131.3, 137.8, 137.9, 138.4, 139.1, 139.2, 141.9, 153.6 (d, J_{C-F}=256.6 Hz), 153.7 (d, J_{C-F}=263.3 Hz), 158.4, 158.5; ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −93.5 (0.5F, s), −93.1 (0.5F, s); MS (EI) m/z (%): 322 (89.12) [M^+], 307 (100.00), 261 (15.71), 221 (15.94), 165 (14.96), 133 (21.35), 91 (16.85), 77 (13.75); HRMS (EI) calcd for $C_{22}H_{23}OF$ (M^+) requires 322.1733, found: 322.1736.

4.2.16. Compound **6e**

A colorless oil; IR (CH_2Cl_2): ν 3082, 2980, 2914, 2856, 1981, 1630, 1593, 1441, 1372, 1173, 1016, 933, 924, 830, 732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.68 (3H, d, J=4.0 Hz, CH_3), 1.73 (3H, d, J=4.0 Hz, CH_3), 1.81 (3H, s, CH_3), 4.51 (1H, d, J=0.4 Hz, CH_2), 4.95 (1H, d, J=0.4 Hz, CH_2), 7.06 (2H, d, J=8.4 Hz, ArH), 7.21 (4H, d, J=8.4 Hz, ArH), 7.25–7.29 (2H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.5, 21.6, 22.7, 116.9, 121.4 (d, J_{C-F}=20.1 Hz), 128.2, 128.3, 128.5, 129.2, 130.4, 130.6, 131.1, 131.2, 131.3, 131.4, 133.0, 136.1, 136.9, 137.0, 139.0, 139.1, 141.4, 154.8 (d, J_{C-F}=260.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −90.1; MS (EI) m/z (%): 360 (81.61) [M^+], 345 (100.00), 310 (19.60), 233 (65.83), 125 (38.12), 113 (16.99), 81 (67.39), 41 (41.79); HRMS (EI) calcd for $C_{21}H_{19}Cl_2F$ (M^+) requires 360.0848, found: 360.0845.

4.2.17. Compound **6f**

A colorless oil; IR (CH_2Cl_2): ν 3081, 2982, 2915, 2862, 1981, 1630, 1491, 1443, 1372, 1172, 1016, 833, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.66 (2.5H, d, J=4.4 Hz, CH_3), 1.69 (0.5H, d, J=4.4 Hz, CH_3), 1.71 (2.5H, d, J=5.2 Hz, CH_3), 1.74 (0.5H, d, J=5.2 Hz, CH_3), 1.81 (2.5H, s, CH_3), 1.82 (0.5H, s, CH_3), 4.49 (0.85H, d, J=1.2 Hz, CH_2), 4.51 (0.15H, d, J=0.8 Hz, CH_2), 4.92–4.93 (0.85H, d, J=1.2 Hz, CH_2), 4.94 (0.15H, d, J=0.8 Hz, CH_2), 7.11–7.13 (2H, m, ArH), 7.18–7.32 (7H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 20.9, 21.0, 21.6, 22.7, 32.0, 116.6, 116.7, 122.2, 122.4, 126.5, 127.1, 127.9, 128.0, 128.04, 128.1, 128.3, 128.4, 129.3, 129.5, 129.8, 129.9, 129.98, 130.0, 130.5, 130.7, 131.2, 131.3, 132.8, 136.6, 138.4, 138.51, 138.54, 138.6, 141.6, 154.6 (d, J_{C-F}=259.8 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ −91.4 (0.85F, s), −90.8 (0.15F, s); MS (EI) m/z (%): 326 (91.19) [M^+], 311 (100.00), 293 (48.58), 265 (51.07), 215 (89.61), 165 (35.43), 81 (40.53), 41 (66.39);

HRMS (EI) calcd for $C_{21}H_{20}ClF$ (M^+) requires 326.1238, found: 326.1235.

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Supplementary data

Spectroscopic data of the compounds shown in Tables 1–3 and the detailed descriptions of experimental procedures. This material is available free of charge via the Internet at the website. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.075.

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