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α,α-Difluoro-α-phenylsulfanylmethyl carbanion equivalent: a novel *gem*-difluoromethylenation of carbonyl compounds

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Abstract—α,α-Difluoro-α-phenylsulfanyl-α-trimethylsilylmethane ($PhSCF_2SiMe_3$) has been demonstrated as an α,α-difluoro-α-phenylsulfanylmethyl carbanion equivalent. *gem*-Difluorophenylsulfanylmethylation of carbonyl compounds has been successfully achieved by using $PhSCF_2SiMe_3$ in the presence of TBAF in THF. The adducts have been converted to the corresponding *gem*-difluoroalkenes by a novel pyrolytic and/or FVP elimination of the β-hydroxy-α-phenylsufinyl derivatives under reduced pressure.

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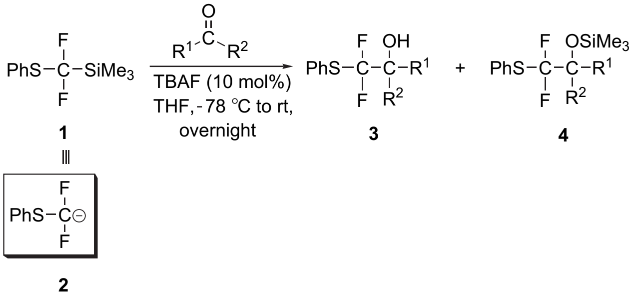
1. Introduction

Organofluorine chemistry is receiving remarkable interest due to the enormous utility of organofluorine compounds in several fields, such as medicine, biology, agriculture and analytical chemistry.[1] The development of synthetic routes of such compounds and investigations for the use of new fluorinated compounds as building blocks are of great importance. Of particular interest is the introduction of a *gem*-difluoromethylene group into organic molecules, which have been the subject of recent reports by several prominent research groups such as those of Prakash et al.,[2] Hu[3] and Qing.[4] In continuation with our research on utilizing bromodifluorophenylsulfanylmethane as the *gem*-difluoromethylene building block,[5] we have investigated the utilization of α,α-difluoro-α-phenylsulfanyl-α-trimethylsilylmethane (**1**)[2b] as the synthetic equivalent of difluorinated carbanion **2** (Scheme 1).[6] In this paper, we wish to report our findings on the chemistry of the carbanion **2** and also provide novel examples of pyrolytic elimination of β-hydroxy-α-phenylsulfinyl derivatives to *gem*-difluoroalkenes.



Scheme 1.

2. Results and discussion

We first examined the nucleophilic difluorophenylsulfanylmethylation of benzaldehyde using compound **1** under the catalysis of fluoride ion (Scheme 1). It was found that the reaction of **1** (1.1 equiv) with benzaldehyde (1 equiv) took place between −78 °C and room temperature over 15 h in the presence of 10 mol % of anhydrous tetra-*n*-butylammonium fluoride (TBAF) in dry THF,[7] giving the desired **3a** and **4a** in 52 and 31% yields, respectively, after chromatography on silica gel. The reactions employing 20 or 50 mol % of TBAF afforded lower yields of the expected adducts **3a** and **4a**.[8] Thus, the standard conditions using 10 mol % of TBAF at −78 °C to room temperature overnight were used for the reactions of **1** with other carbonyl compounds. It was found that fluoride-catalyzed condensation of **1** with aromatic aldehydes gave mixtures of **3** and **4** in good yields (Table 1, entries 1–4 and 7–9), whereas

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Keywords: Difluoro(phenylsulfanyl)trimethylsilane; *gem*-Difluoroalkene; *gem*-Difluoromethylenation; Fluoride-catalyzed reaction; Carbonyl compounds.

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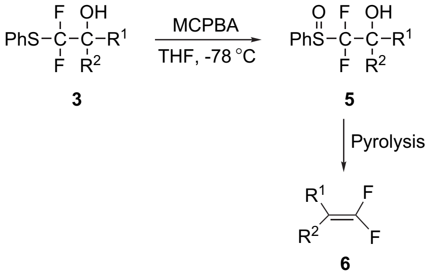
Table 1. Fluoride-catalyzed condensation of **1** with carbonyl compounds

Entry	Carbonyl compounds	**3** (%)[a]	**4** (%)[a]	**3**+**4** (%)[a]
1	Benzaldehyde	**3a** (52)	**4a** (31)	83
2	4-Methoxybenzaldehyde	**3b** (41)	**4b** (48)	89
3	2,4-Dimethoxybenzaldehyde	**3c** (28)	**4c** (60)	88
4	3,4-Dimethoxybenzaldehyde	**3d** (37)	**4d** (48)	85
5	Cinnamaldehyde	**3e** (50)	**4e** (18)	68
6	2-Methoxycinnamaldehyde	**3f** (53)	**4f** (37)	90
7	4-Methylbenzaldehyde	**3g** (35)	**4g** (51)	86
8	4-Bromobenzaldehyde	**3h** (61)	**4h** (31)	92
9	2-Furaldehyde	**3i** (73)	—	73
10	*n*-Butanal	**3j** (69)	—	69
11	Crotonaldehyde	**3k** (70)	—	70
12	1-Tetralone	**3l** (22)	**4l** (26)	48
13	6-Methoxy-1-tetralone	**3m** (21)	**4m** (29)	50
14	Acetophenone	**3n** (30)	**4n** (21)	51
15	Benzophenone	**3o** (33)	**4o** (6)	39
16	Cyclohexanone	**3p** (63)	—	63
17	Cyclopentanone	**3q** (45)	—	45
18	Acetone	**3r** (65)	—	65
19	2-Cyclohexenone	**3s** (60)	—	60

[a] Isolated yield.

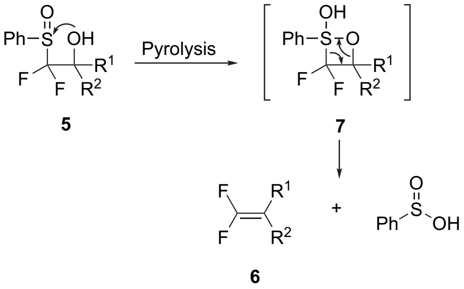
aromatic ketones afforded moderate yields of **3** and **4** (entries 12–15). The reactions proceeded well with aliphatic aldehydes and ketones (Table 1, entries 10 and 16–18) to give the adduct **3** as the sole products. Interestingly, 1,2-addition products were obtained, when **1** was combined with α,β-unsaturated carbonyl compounds, indicating the nature of non-stabilized carbanion **2** (Table 1, entries 5, 6, 11 and 19).[9] The silyl ether **4b** could be converted into the corresponding adduct **3b** in quantitative yield by employing KF in acetonitrile/THF at room temperature overnight.

The synthetic utility of this reaction for the synthesis of *gem*-difluoromethylene compounds as described in Scheme 1 was further demonstrated by transformation of selected adduct **3** to *gem*-difluoroalkene **6**. Logically, we expected that the pyrolysis of the sulfoxide **5**, obtained from the oxidation of the aromatic aldehyde adduct **3** with MCPBA would lead to the corresponding α,α-difluoromethylketones (Scheme 2).[10] Thus, the oxidation of **3b** proceeded smoothly by using 1.1 equiv MCPBA in THF at −78 °C to room temperature overnight (15 h) to give the corresponding sulfoxide **5b** in 74% yield. To our surprise, neat pyrolysis of **3b** at 200 °C under reduced pressure (0.05 mmHg) furnished *gem*-difluoroalkene **6b** in 79% yield instead of the expected α,α-difluoromethyl 4-methoxyphenyl ketone. Similar result was observed when flash vacuum pyrolysis (FVP) of **5b** was performed. A good yield of **6b** (82%) resulted (Table 2, entries 1). Moreover, this novel synthetic conversion was extended to compounds **3c–f**, **3l** and **3n** to give *gem*-difluoroalkenes **6c–f**, **6l** and **6n** in moderate to good yields. It should be mentioned here that the sulfoxide elimination of **5b–f** proceeded equally well under both neat pyrolysis and FVP, while **5l** and **5o** proceeded only under FVP conditions as summarized in Table 2 (entries 6 and 7). Our synthetic route thus provides a general entry to *gem*-difluoromethylenation of carbonyl compounds.[2d,2e,11]



Scheme 2.

The mechanism for the formation of *gem*-difluoroalkene **6** from the corresponding sulfoxide **5** is unclear but can be rationalized as proposed in Scheme 3. An intramolecular nucleophilic addition of the hydroxyl group to the electron deficient sulfur atom of **5** (due to the electronegativity of α,α-difluoro atoms) furnishes a cyclic intermediate **7**, which undergoes fragmentation to give *gem*-difluoroalkene **6**.



Scheme 3.

In conclusion, we have demonstrated that α,α-difluoro-α-phenylsulfanyl-α-trimethylsilylmethane (**1**) can serve as a practical and useful synthetic equivalent of α,α-difluoro-α-phenylsulfanylmethyl carbanion **2**, which is not easy to access. Both aldehydes and ketones undergo facile α,α-difluorophenylsulfanylmethylation with **1** in the presence of 10 mol % TBAF in THF, providing *gem*-difluoro substituted alcohols in moderate to good yields. We have also illustrated that these adducts can be used as useful precursors for preparing *gem*-difluoroalkenes through the β-hydroxy-α-phenylsulfinyl derivatives.

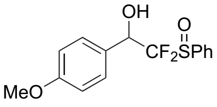
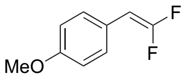
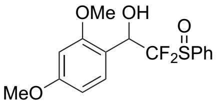
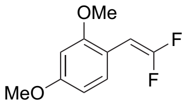
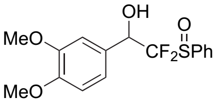
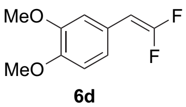
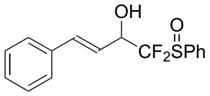
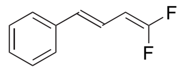
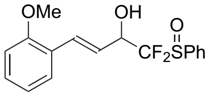
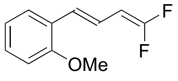
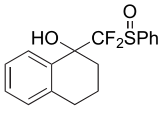
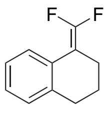
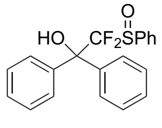
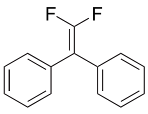
3. Experimental

3.1. General methods

The ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX-300 or a Bruker DPX-400 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. The ^{19}F NMR spectra were recorded on a Bruker DPX-400 (376 MHz) spectrometer and chemical shifts (δ) were measured with fluorotrichloromethane (δ=0) as an internal standard. The IR spectra were recorded on either a Jasco A-302 or a Perkin Elmer 683 infrared spectrometer. The electron impact mass spectra were recorded by using Thermo Finnigan Polaris Q mass spectrometer. The high resolution mass spectra were recorded on HR-TOF-MS Micromass model VQ-TOF2. Elemental analyses were performed on a Perkin Elmer Elemental Analyzer 2400 CHN. Melting points were recorded on a Buchi 501 melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Dry dichloromethane (CH_2Cl_2) and dry

Table 2. Preparation of *gem*-difluoroalkene **6**

Entry	**3**	**5**[a]	**6**	Conditions, % yield of **6**[b]	
				200 °C (0.05 mmHg)	FVP (temp, 0.05 mmHg)
1	**3b**	 **5b** (74%)	 **6b**	79%	82% (425 °C)
2	**3c**	 **5c** (69%)	 **6c**	74%	70% (425 °C)
3	**3d**	 **5d** (70%)	 **6d**	71%	68% (425 °C)
4	**3e**	 **5e** (50%)	 **6e**	70%	60% (425 °C)
5	**3f**	 **5f** (60%)	 **6f**	78%	70% (425 °C)
6	**3l**	 **5l** (68%)	 **6l**	—	41% (518 °C)
7	**3o**	 **5o** (71%)	 **6o**	—	80% (518 °C)

[a] Number in parenthesis is the isolated yield of **5** from **3** and obtained as a mixture of diastereomers.

[b] Isolated yield.

N,*N*-dimethylformamide (DMF) were obtained by distilling over phosphorus pentoxide and calcium hydride, respectively. Other common solvents (dichloromethane, hexane, ethyl acetate and acetone) were distilled before use.

The starting compound $PhSCF_2SiMe_3$ (**1**) was prepared according to the literature procedure.[2b]

The reactions of compound **1** with carbonyl compounds were run under an argon atmosphere. All glasswares and syringes were oven-dried and kept in a desiccator before use. Radial chromatography (chromatotron) and column chromatography were performed by using Merck silica gel 60 F_{254} (Art. 7749) and silica gel 60H (Art. 7736), respectively.

3.2. Preparation of compounds 3 and 4 by fluoride-catalyzed condensation of compound 1 with carbonyl compounds

3.2.1. 2,2-Difluoro-1-phenyl-2-phenylsulfanylethanol (3a) and 2,2-difluoro-1-phenyl-2-phenylsulfanyl-1-trimethylsiloxyethane (4a). *General procedure*: To a mixture of compound **1** (2.32 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) in THF (25 mL), was added TBAF (1.0 mL, 1.0 mmol, 1 M solution in THF). The reaction mixture was stirred at −78 °C, followed by slow warming up to room temperature overnight. The solution was quenched with a saturated aqueous NH_4Cl solution and extracted with EtOAc (3×70 mL). The organic phase was washed successively with brine, water and dried over anhydrous Na$_2$SO$_4$. After solvent removal, the crude product was purified by column chromatography (SiO$_2$, 5% EtOAc in hexanes) to give a pale yellow liquid of **3a** (1.373 g, 52% yield) and a white powder of **4a** (1.035 g, 31% yield, mp=45–46 °C). **3a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63–7.58 (m, 2H, Ar*H*), 7.54–7.48 (m, 2H, Ar*H*), 7.49–7.35 (m, 6H, Ar*H*), 5.02 (dd, *J*=11.3, 7.9 Hz, 1H, C*H*OH), 2.62 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.1 (2×CH), 135.9 (C), 130.6 (CH), 129.8 (CH), 129.7 (2×CH), 129.6 (t, *J*=283.1 Hz, CF$_2$), 129.0 (2×CH), 128.5 (2×CH), 126.5 (C), 76.8 (t, *J*=26.6 Hz, CH). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.18 (dd, *J*=209.3, 11.2 Hz, 1F), −81.60 (dd, *J*=209.3, 7.5 Hz, 1F). IR (neat): ν_{max} 3419br s, 3065m, 3036m, 2901w, 1958w, 1889w, 1811w, 1604w, 1581w, 1496m, 1475s, 1455s, 1441s, 1394m, 1309m, 1201m, 1158s, 1059s, 1028s, 984s, 966s, 919w, 848m, 802m, 750s, 699s, 637s cm^{-1}. EIMS: *m*/*z* (% relative intensity) 266 (M$^+$, 68), 249 (40), 247 (9), 227 (7), 171 (36), 160 (77), 109 (23), 107 (51), 80 (100), 78 (51), 65 (6), 51 (14). Anal. Calcd for C$_{14}$H$_{12}$F$_2$OS: C, 63.14; H, 4.54. Found: C, 63.28; H, 4.44. **4a**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.63–7.53 (m, 2H, Ar*H*), 7.53–7.43 (m, 2H, Ar*H*), 7.43–7.29 (m, 6H, Ar*H*), 5.10 (dd, *J*=10.9, 7.5 Hz, 1H, C*H*OSiMe$_3$), 0.15 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 136.9 (d, *J*=41.1 Hz, C), 136.3 (2×CH), 129.4 (CH), 128.9 (t, *J*=284.0 Hz, CF$_2$), 128.8 (2×CH), 128.7 (CH), 128.0 (3×CH), 126.9 (C), 77.6 (t, *J*=27.4 Hz, CH), −0.1 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.49 (dd, *J*=203.8, 11.1 Hz, 1F), −80.14 (dd, *J*=204.4, 7.0 Hz, 1F). IR (Nujol): ν_{max} 3062w, 3036w, 2924s, 2855s, 1952w, 1881w, 1658w, 1584w, 1455s, 1442s, 1417w, 1377m, 1358w, 1337w, 1309w, 1280w, 1250s, 1202m, 1173m, 1120s, 1108s, 1075s, 1060s, 1026m, 1003w, 983s, 925w, 878s, 847s, 803m, 748s, 728s, 699s, 690s, 662w, 634m, 612s, 505s, 439w, 419w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 338 (M$^+$, 0.18), 199 (16), 181 (5), 180 (16), 179 (100), 118 (5), 109 (10), 90 (5), 77 (4), 75 (5), 73 (63). HRMS Calcd for C$_{17}$H$_{20}$F$_2$OSSi (M$^+$): 338.0972; found: 338.0972.

3.2.2. 2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylsulfanylethanol (3b) and 2,2-difluoro-1-(4-methoxyphenyl)-2-phenylsulfanyl-1-trimethylsiloxyethane (4b).

The reaction of **1** (1.86 g, 8 mmol) with 4-methoxybenzaldehyde (1.09 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3b** (0.970 g, 41% yield) and a white powder of **4b** (1.425 g, 48% yield, mp=39–40.5 °C). **3b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64–7.56 (m, 2H, Ar*H*), 7.47–7.33 (m, 5H, Ar*H*), 6.97–6.90 (m, 2H, Ar*H*), 4.97 (dd, *J*=10.9, 8.3 Hz, 1H, C*H*OH), 3.83 (s, 3H, OC*H*$_3$), 2.68 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.9 (C), 137.0 (2×CH), 130.4 (CH), 129.7 (2×CH), 129.68 (2×CH), 129.62 (t, *J*=283.6 Hz, CF$_2$), 128.0 (C), 126.6 (C), 114.4 (2×CH), 76.5 (t, *J*=26.6 Hz, CH), 55.9 (CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.11 (dd, *J*=208.5, 11.1 Hz, 1F), −82.26 (dd, *J*=208.3, 8.1 Hz, 1F). IR (neat): ν_{max} 3446br s, 3062w, 3006w, 2960w, 2936w, 2910w, 2839w, 2028w, 1892w, 1772w, 1613s, 1586m, 1515s, 1474m, 1441s, 1306m, 1252s, 1177s, 1159s, 1056s, 1029s, 983s, 966s, 858m, 835m, 792s, 750s, 704m, 691s cm^{-1}. EIMS: *m*/*z* (% relative intensity) 296 (M$^+$, 1), 279 (4), 167 (15), 139 (15), 137(100), 109 (45), 94 (24), 77 (16). Anal. Calcd for C$_{15}$H$_{14}$F$_2$O$_2$S: C, 60.80; H, 4.76. Found: C, 60.73; H, 4.94. **4b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60–7.56 (m, 2H, Ar*H*), 7.42–7.30 (m, 5H, Ar*H*), 6.91 (m, 2H, Ar*H*), 4.96 (dd, *J*=10.8, 7.7 Hz, 1H, C*H*OSiMe$_3$), 3.80 (s, 3H, OC*H*$_3$), 0.13 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.6 (C), 136.9 (2×CH), 130.0 (CH), 129.8 (2×CH), 129.6 (t, *J*=283.3 Hz, CF$_2$), 129.4 (2×CH), 127.4 (C), 126.8 (C), 114.1 (2×CH), 77.7 (t, *J*=27.0 Hz, CH), 55.8 (CH$_3$), 0.6 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.55 (dd, *J*=203.0, 11.2 Hz, 1F), −80.59 (dd, *J*=203.0, 7.4 Hz, 1F). IR (neat): ν_{max} 3063w, 2956s, 2924s, 2855s, 1644w, 1611s, 1586m, 1513s, 1463s, 1442s, 1421w, 1377m, 1330w, 1340m, 1288m, 1251s, 1205m, 1171s, 1121s, 1103s, 1065s, 1038s, 984s, 943w, 858s, 875s, 844s, 809m, 780m, 746s, 711w, 703w, 689m, 638w, 601m, 573m, 561m, 534m, 497m, 444m, 417m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 278 (3), 244 (5), 229 (4), 211 (5), 210 (17), 209 (100), 167 (12), 139 (5), 135 (10), 75 (5), 73 (43). HRMS Calcd for C$_{18}$H$_{22}$F$_2$O$_2$SSi (M$^+$): 368.1078; found: 368.1075.

3.2.3. 2,2-Difluoro-1-(2,4-dimethoxyphenyl)-2-phenylsulfanylethanol (3c) and 2,2-difluoro-1-(2,4-dimethoxyphenyl)-2-phenylsulfanyl-1-trimethylsiloxyethane (4c).

The reaction of **1** (1.86 g, 8 mmol) with 2,4-dimethoxybenzaldehyde (1.33 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3c** (0.742 g, 28% yield) and a colourless liquid of **4c** (1.911 g, 60% yield). **3c**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70–7.59 (m, 2H, Ar*H*), 7.45–7.3 (m, 4H, Ar*H*), 6.55 (dd, *J*=8.5, 2.4 Hz, 1H, Ar*H*), 6.52 (d, *J*=2.4 Hz, 1H, Ar*H*), 5.36 (dd, *J*=12.6, 8.6 Hz, 1H, C*H*OH), 3.88 (s, 3H, OC*H*$_3$), 3.85 (s, 3H, OC*H*$_3$), 1.7 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.0 (C), 159.4 (C), 137.0 (2×CH), 131.1 (CH), 130.2 (CH), 130.0 (t, *J*=284.0 Hz, CF$_2$), 129.5 (2×CH), 127.1 (C), 116.5 (C), 105.4 (CH), 99.6 (CH), 73.7 (t, *J*=26.6 Hz, CH), 56.3 (CH$_3$), 56.0 (CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −84.90 (dd, *J*=204.0, 13.4 Hz, 1F), −81.98 (dd, *J*=204.4, 7.8 Hz, 1F). IR (neat): ν_{max} 3460br s, 3062w, 3005w, 2940m, 2839m, 1614s, 1589s, 1464s, 1509s, 1440s, 1421s, 1296s, 1268s, 1210s, 1160s, 1126s, 1035s, 981s, 965s, 936m, 921m, 835s, 781m, 751s, 704s, 692m, 642m, 593w, 570m, 502m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 326 (M$^+$, 0.08), 242 (14), 167 (100), 139 (12), 137 (24), 109 (6), 91 (5), 77 (5). HRMS Calcd for C$_{16}$H$_{16}$F$_2$O$_3$ (M$^+$): 326.0788; found: 326.0788. **4c**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.52–7.42 (m, 3H, Ar*H*), 7.39–7.25 (m, 3H, Ar*H*), 6.52 (dd, *J*=8.6, 2.2 Hz, 1H, Ar*H*), 6.41 (d, *J*=2.1 Hz, 1H, Ar*H*), 5.51 (dd, *J*=10.6, 8.4 Hz, 1H, C*H*OSiMe$_3$), 3.8 (s, 6H, OC*H*$_3$), 0.10 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 161.0 (C), 157.9 (C), 136.1 (2×CH), 130.3 (CH), 129.2 (t, *J*=284.8 Hz, CF$_2$), 129.1 (CH), 128.6 (2×CH), 127.1 (C), 118.0 (C), 104.6 (CH), 97.9 (CH), 69.6 (dd, *J*=28.4, 25.7 Hz, CH), 55.5 (CH$_3$), 55.2 (CH$_3$), 0.2 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −84.12 (dd, *J*=201.0, 10.8 Hz, 1F), −81.98 (dd, *J*=201.0, 8.1 Hz, 1F). IR (neat): ν_{max} 3062w, 3004m, 2959s, 2838m, 1614s, 1589s, 1507s, 1465s, 1440s, 1420m, 1361m, 1329w, 1305s, 1293s, 1264s, 1253s, 1209s, 1159s, 1126s, 1097s, 1035s, 982s, 937m, 922m, 879s, 844s, 793w, 775w, 750s, 704m, 691s, 637w, 610w, 568m, 519w, 502m, 478w cm^{-1}. EIMS: *m*/*z*

(% relative intensity) 398 (M$^+$, 0.06), 240 (18), 239 (100), 209 (4), 166 (6), 165 (22), 77 (5), 73 (33). HRMS Calcd for $C_{19}H_{24}F_2O_3SSi$ (M$^+$): 398.1183; found: 398.1182.

3.2.4. 2,2-Difluoro-1-(3,4-dimethoxyphenyl)-2-phenylsulfanylethanol (3d) and 2,2-difluoro-1-(3,4-dimethoxyphenyl)-2-phenylsulfanyl-1-trimethylsiloxyethane (4d). The reaction of **1** (1.86 g, 8 mmol) with 3,4-dimethoxybenzaldehyde (1.329 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a white powder of **3d** (0.967 g, 37% yield, mp=92–93 °C) and a white powder of **4d** (1.542 g, 48% yield, mp=61–62 °C). **3d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.55 (m, 2H, Ar*H*), 7.45–7.33 (m, 3H, Ar*H*), 7.06–6.99 (m, 2H, Ar*H*), 6.87 (d, J=8.1 Hz, 1H, Ar*H*), 4.96 (dd, J=10.9, 8.2 Hz, 1H, C*H*OH), 3.90 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 2.35 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (C), 149.5 (C), 137.1 (2×CH), 130.5 (CH), 129.7 (2×CH), 129.6 (t, J=283.1 Hz, CF_2), 128.3 (C), 126.5 (C), 121.2 (CH), 111.3 (CH), 111.2 (d, J=1.2 Hz, CH), 76.6 (t, J=26.4 Hz, CH), 56.6 (CH_3), 56.5 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −84.72 (dd, J=208.4, 10.9 Hz, 1F), −82.17 (dd, J=208.4, 8.2 Hz, 1F). IR (neat): ν_{max} 3480s, 3082m, 3060m, 3011m, 2969m, 2943m, 2913m, 2842m, 2597w, 2031w, 1961w, 1733w, 1608s, 1594s, 1515s, 1471s, 1456s, 1442s, 1387m, 1346m, 1309m, 1256s, 1141s, 1096s, 1056s, 1019s, 990s, 930m, 869m, 821w, 785s, 764s, 745s, 690s, 663m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 326 (M$^+$, 1), 167 (100), 139 (57), 124 (15), 109 (8), 108 (6), 95 (4), 79 (5), 77 (8), 65 (3). HRMS Calcd for $C_{16}H_{16}F_2O_3S$ (M$^+$): 326.0788; found: 326.0788. **4d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, J=7.6 Hz, 2H, Ar*H*), 7.39–7.22 (m, 3H, Ar*H*), 7.02–6.90 (m, 2H, Ar*H*), 6.78 (d, J=8.2 Hz, 1H, Ar*H*), 4.91 (dd, J=11.0, 7.5 Hz, 1H, C*H*OSiMe$_3$), 3.85 (s, 6H, 2×OCH_3), 0.10 (s, 9H, OSi(CH_3)$_3$). ^{13}C NMR (75 MHz $CDCl_3$): δ 149.3 (C), 148.6 (C), 136.3 (2×CH), 129.4 (CH), 129.2 (C), 128.9 (t, J=283.0 Hz, CF_2), 128.8 (2×CH), 126.7 (C), 120.5 (CH), 110.8 (CH), 110.3 (CH), 77.2 (t, J=27.2 Hz, CH), 55.9 (CH_3), 55.8 (CH_3), −0.1 (3×CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$) δ −83.44 (dd, J=203.0, 11.0 Hz, 1F), −80.69 (dd, J=203.0, 7.3 Hz, 1F). IR (neat): ν_{max} 3056w, 3015m, 2956s, 2925s, 2855s, 1605m, 1591m, 1519s, 1466s, 1442s, 1420m, 1377m, 1360m, 1337w, 1308w, 1264s, 1256s, 1233s, 1168m, 1152s, 1141s, 1102s, 1066s, 1037m, 1023s, 992s, 938s, 874s, 853s, 803m, 775m, 767m, 749s, 728m, 703w, 691m, 625m, 604w, 586m, 571w, 498m, 456w, 417w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 398 (M$^+$, 2), 274 (5), 240 (17), 239 (100), 165 (14), 109 (5), 77 (4), 73 (51). HRMS Calcd for $C_{19}H_{24}F_2O_3SSi$ (M$^+$): 398.1183; found: 398.1185.

3.2.5. 1,1-Difluoro-4-phenyl-1-phenylsulfanyl-3-buten-2-ol (3e) and 1,1-difluoro-4-phenyl-1-phenylsulfanyl-2-trimethylsiloxy-3-butene (4e). The reaction of **1** (2.32 g, 10 mmol) with cinnamaldehyde (1.29 g, 9.8 mmol) and TBAF (1.0 mL, 1.0 mmol, 1 M solution in THF) gave a pale yellow liquid of **3e** (1.420 g, 50% yield) and a white powder of **4e** (0.661 g, 18% yield, mp=39–40 °C). **3e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.62 (m, 2H, Ar*H*), 7.48–7.26 (m, 8H, Ar*H*), 6.83 (d, J=15.9 Hz, 1H, PhC*H*═CH), 6.28 (dd, J=15.9, 6.3 Hz, 1H, PhCH═C*H*), 4.68–4.58 (m, 1H, C*H*OH), 2.12 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2 (2×CH), 136.5 (C), 135.9 (CH), 130.6 (CH), 129.8 (2×CH), 129.6 (t, J=286.0 Hz, CF_2), 129.3 (2×CH), 129.1 (CH), 127.5 (2×CH), 126.4 (C), 123.1 (CH), 75.7 (t, J=27.0 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −85.12 (dd, J=209.0, 9.1 Hz, 1F), −83.13 (dd, J=209.0, 8.4 Hz, 1F). IR (neat): ν_{max} 3392br m, 3061m, 3028w, 2911w, 1955w, 1885w, 1803w, 1654m, 1599w, 1579m, 1497m, 1475s, 1449m, 1441s, 1388m, 1309m, 1164s, 1058s, 966s, 861m, 748s, 704s, 691s cm^{-1}. EIMS: *m*/*z* (% relative intensity) 292 (M$^+$, 4), 275 (26), 235 (3), 165 (5), 162 (9), 160 (20), 133 (100), 116 (44), 103 (9), 92 (7), 77 (13), 65 (4), 55 (32). Anal. Calcd for $C_{16}H_{14}F_2OS$: C, 65.73; H, 4.83. Found: C, 65.97; H, 4.91. **4e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J=6.5 Hz, 2H, Ar*H*), 7.51–7.24 (m, 8H, Ar*H*), 6.75 (d, J=15.8 Hz, 1H, PhC*H*═CH), 6.30 (dd, J=15.8, 6.2 Hz, 1H, PhCH═C*H*), 4.64 (app. dd, J=15.4, 8.1 Hz, 1H, C*H*OSiMe$_3$), 0.22 (s, 9H, OSi(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.4 (2×CH), 136.1 (C), 134.0 (CH), 129.4 (CH), 128.9 (t, J=283.0 Hz, CF_2), 128.8 (2×CH), 128.5 (2×CH), 128.1 (CH), 126.8 (2×CH), 126.4 (t, J=2.0 Hz, C), 124.3 (CH), 76.3 (t, J=27.5 Hz, CH), 0.1 (3×CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −83.07 (dd, J=204.0, 7.9 Hz, 1F), −81.24 (dd, J=204.0, 8.5 Hz, 1F). IR (neat): ν_{max} 3066w, 3029w, 2958s, 2925s, 2863s, 1959w, 1890w, 1815w, 1474s, 1450s, 1441s, 1377m, 1357w, 1332s, 1305w, 1251s, 1205w, 1164m, 1117s, 1085s, 1067s, 1042s, 1022s, 974s, 917w, 878s, 844s, 779m, 750s, 705m, 692s, 672m, 638w, 611w, 600w, 543m, 499m, 459m, 419m cm^{-1}. EIMS: *m*/*z* (% relative intensity): 207 (5), 206 (18), 205 (100), 146 (5), 116 (9), 115 (23), 77 (4), 73 (45). HRMS Calcd for $C_{19}H_{22}F_2OSSi$ (M$^+$): 364.1128; found: 364.0031.

3.2.6. 1,1-Difluoro-4-(2-methoxyphenyl)-1-phenylsulfanyl-3-buten-2-ol (3f) and 1,1-difluoro-4-(2-methoxyphenyl)-1-phenylsulfanyl-2-trimethylsiloxy-3-butene (4f). The reaction of **1** (1.86 g, 8 mmol) with 2-methoxycinnamaldehyde (1.298 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3f** (1.367 g, 53% yield) and a white powder of **4f** (1.138 g, 37% yield, mp=43.5–45 °C). **3f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J=6.7 Hz, 2H, Ar*H*), 7.53–7.36 (m, 4H, Ar*H*), 7.35–7.25 (m, 1H, Ar*H*), 7.17 (d, J=16.1 Hz, 1H, PhC*H*═CH), 7.02–6.85 (m, 2H, Ar*H*), 6.33 (dd, J=16.1, 6.6 Hz, 1H, PhCH═C*H*), 4.63 (dd, J=15.7, 8.1 Hz, 1H, C*H*OH), 3.89 (s, 3H), 2.51 (br s, 1H, CHO*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1 (C), 136.5 (2×CH), 130.5 (CH), 129.8 (CH), 129.5 (CH), 129.1 (2×CH), 129.0 (t, J=283.5 Hz, CF_2), 127.4 (CH), 126.0 (C), 124.9 (C), 123.0 (t, J=2.3 Hz, CH), 120.7 (CH), 111.0 (CH), 75.60 (t, J=26.8 Hz, CH), 55.5 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −85.15 (dd, J=208.9, 9.2 Hz, 1F), −83.33 (dd, J=208.0, 8.4 Hz, 1F). IR (Nujol): ν_{max} 3264br s, 2924s, 2855s, 2722w, 1651w, 1597m, 1580w, 1489s, 1463s, 1439s, 1377m, 1349m, 1294m, 1247s, 1175w, 1154m, 1118w, 1100w, 1087w, 1053s, 1028s, 981m, 959s, 866m, 852w, 779m, 758s, 747s, 725w, 703w, 690m, 630w, 582w, 554w, 530w, 498w, 448w cm^{-1}. EIMS: *m*/*z* (% relative intensity): 322 (M$^+$, 5), 164 (11), 163 (100), 145 (10), 135 (21), 107 (11), 91 (7), 77 (6), 55 (16). HRMS Calcd for $C_{17}H_{16}F_2O_2S$ (M$^+$): 322.0839; found: 322.0844. **4f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d,

J=7.8 Hz, 2H, ArH), 7.51–7.18 (m, 5H, ArH), 7.05 (d, J=16.0 Hz, 1H, PhCH=CH), 6.98–6.82 (m, 2H of ArH), 6.28 (dd, J=16.1, 6.7 Hz, 1H, PhCH=CH), 4.61 (app. dd, J=16.1, 7.9 Hz, 1H, CHOSiMe$_3$), 3.86 (s, 3H, OCH_3), 0.2 (s, 9H, OSi(CH_3)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 157.0 (C), 136.4 (2×CH), 129.4 (2×CH), 129.2 (CH), 129.0 (t, J=283.5 Hz, CF$_2$), 128.8 (2×CH), 127.3 (CH), 126.7 (C, t, J=2.0 Hz), 125.2 (C), 124.6 (t, J=2.4 Hz, CH), 120.6 (CH), 111.0 (CH), 77.0 (t, J=27.2 Hz, CH), 55.0 (CH$_3$), 0.2 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.35 (dd, J=203.5, 9.0 Hz, 1F), −81.59 (dd, J=202.8, 8.8 Hz, 1F). IR (Nujol): $\nu_{\max}$ 3057w, 2998m, 2958s, 2926s, 2855s, 1650w, 1599m, 1580m, 1492s, 1466s, 1439s, 1377w, 1356m, 1338m, 1298m, 1265m, 1251s, 1179s, 1158m, 1128s, 1105s, 1079s, 1047s, 1030s, 973s, 883s, 842s, 814w, 758s, 750s, 703m, 688s, 671w, 639w, 610w, 583w, 524m, 502m, 439w cm^{-1}. EIMS: m/z (% relative intensity): 394 (M$^+$, 0.63), 237 (6), 236 (19), 235 (100), 177 (5), 147 (4), 146 (11), 145 (27), 117 (4), 77 (2), 73 (37). HRMS Calcd for $C_{20}H_{24}F_2O_2SSi$ (M$^+$): 394.1234; found: 394.1234.

3.2.7. 2,2-Difluoro-1-(4-methylphenyl)-2-phenylsulfanylethanol (3g) and 2,2-difluoro-1-(4-methylphenyl)-2-phenylsulfanyl-1-trimethylsiloxyethane (4g). The reaction of **1** (1.86 g, 8 mmol) with 4-methylbenzaldehyde (0.96 g, 8 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a white powder of **3g** (0.786 g, 35% yield, mp=49–50 °C) and a white powder of **4g** (1.437 g, 51% yield, mp=55–57 °C). **3g**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63–7.54 (m, 2H, ArH), 7.47–7.31 (m, 5H, ArH), 7.21 (d, J=7.9 Hz, 2H, ArH), 4.98 (t, J=9.6 Hz, 1H, CHOH), 2.68 (br s, 1H, CHOH), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.7 (C), 137.0 (2×CH), 132.9 (C), 130.4 (CH), 129.7 (2×CH), 129.6 (2×CH), 129.6 (t, J=283.0 Hz, CF$_2$), 128.3 (2×CH), 126.6 (C), 76.7 (t, J=26.7 Hz, CH), 21.9 (CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.14 (dd, J=209.0, 11.3 Hz, 1F), −82.03 (dd, J=208.9, 7.4 Hz, 1F). IR (Nujol): $\nu_{\max}$ 3331br m, 2955s, 2925s, 2855s, 1516w, 1459m, 1441m, 1377m, 1310w, 1279w, 1241w, 1201w, 1182w, 1158m, 1149m, 1116w, 1061m, 1021m, 1002w, 970m, 860w, 824w, 779m, 749m, 719w, 691m, 621w, 568w, 519w, 498w cm^{-1}. EIMS: m/z (% relative intensity): 280 (M$^+$, 0.7), 171 (5), 162 (4), 161 (7), 160 (91), 123 (12), 122 (10), 121 (97), 110 (7), 109 (7), 103 (5), 93 (100), 91 (77), 77 (30), 65 (10), 51 (8). HRMS Calcd for $C_{15}H_{14}F_2OS$ (M$^+$): 280.0733; found: 280.0731. **4g**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63–7.51 (2H, m, ArH), 7.44–7.29 (5H, m, ArH), 7.18 (d, J=7.9 Hz, 2H, ArH), 4.97 (dd, J=10.8, 7.8 Hz, 1H, CHOSiMe$_3$), 2.37 (s, 3H, CH_3), 0.14 (s, 9H, OSi(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.1 (C), 136.9 (2×CH), 134.4 (C), 130.0 (CH), 129.6 (t, J=283.5 Hz, CF$_2$), 129.4 (4×CH), 128.5 (2×CH), 127.4 (C), 77.9 (t, J=27.2 Hz, CH), 21.9 (CH$_3$), 0.6 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.35 (dd, J=203.9, 11.0 Hz, 1F), −80.40 (dd, J=203.2, 7.6 Hz, 1F). IR (Nujol): $\nu_{\max}$ 3407br w, 2926s, 2730w, 2305w, 1948w, 1923w, 1878w, 1711w, 1614w, 1583w, 1513m, 1461s, 1442s, 1414w, 1377s, 1303w, 1253s, 1202m, 1173m, 1126s, 1103s, 1065s, 1028m, 984s, 954w, 878s, 844s, 805m, 775m, 746s, 706w, 689s, 632w, 640w, 601w, 554m, 513s, 496w, 443w, 419w cm^{-1}. EIMS: m/z (% relative intensity): 333 (2), 263 (4), 213 (24), 193 (100), 171 (3), 151 (3), 133 (3), 119 (4), 104 (2), 77 (2), 73 (30). HRMS Calcd for $C_{18}H_{22}F_2OSSi$ (M$^+$): 352.1128; found: 352.1128.

3.2.8. 2,2-Difluoro-1-(4-bromophenyl)-2-phenylsulfanylethanol (3h) and 2,2-difluoro-1-(4-bromophenyl)-2-phenylsulfanyl-1-trimethylsiloxyethane (4h). The reaction of **1** (1.86 g, 8 mmol) with 4-bromobenzaldehyde (1.48 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a white powder of **3h** (1.679 g, 61% yield, mp=69–69.5 °C) and a white powder of **4h** (1.039 g, 31% yield, mp=94–96 °C). **3h**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.50 (m, 4H, ArH), 7.47–7.41 (m, 1H, ArH), 7.41–7.33 (m, 4H, ArH), 4.96 (dd, J=11.1, 7.6 Hz, 1H, CHOH), 2.86 (br s, 1H, CHOH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.1 (2×CH), 134.7 (C), 132.1 (2×CH), 130.7 (CH), 130.1 (2×CH), 129.8 (2×CH), 129.3 (t, J=283.0 Hz, CF$_2$), 126.1 (C), 124.0 (C), 76.2 (t, J=26.9 Hz, CH). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.65 (dd, J=210.4, 10.9 Hz, 1F), −81.55 (dd, J=210.6, 7.8 Hz, 1F). IR (Nujol): $\nu_{\max}$ 3585s, 2955s, 2926s, 2855s, 1592m, 1472m, 1441m, 1404w, 1377m, 1306w, 1226w, 1194w, 1169w, 1150w, 1117w, 1102w, 1080s, 1047s, 1011m, 985s, 955w, 845w, 819m, 772s, 752s, 692m, 659w, 631w, 618w, 534w, 502m, 419w cm^{-1}. EIMS: m/z (% relative intensity): 345 (M$^+$, 6), 343 (6), 328 (6), 187 (58), 185 (56), 161 (13), 160 (100), 159 (21), 157 (20), 110 (8), 109 (9), 108 (5), 78 (26), 77 (37), 51 (10). HRMS Calcd for $C_{14}H_{11}F_2OS$ (M$^+$): 343.9682; found: 343.9677. **4h**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60–7.47 (m, 4H, ArH), 7.40–7.30 (m, 5H, ArH), 4.96 (dd, J=10.6, 7.3 Hz, 1H, CHOSiMe$_3$), 0.13 (s, 9H, OSi(CH_3)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.0 (2×CH), 136.6 (C), 131.9 (2×CH), 130.2 (3×CH), 129.5 (2×CH), 129.2 (t, J=284.1, 283.4 Hz, CF$_2$), 127.0 (C), 123.5 (C), 77.5 (t, J=27.4 Hz, CH), 0.5 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.64 (dd, J=204.8, 11.0 Hz, 1F), −80.04 (dd, J=204.8, 7.0 Hz, 1F). IR (Nujol): $\nu_{\max}$ 3065w, 2956s, 2924s, 2855s, 1658w, 1591m, 1486m, 1463m, 1441m, 1404m, 1377m, 1346w, 1306w, 1292w, 1255s, 1200m, 1173m, 1124s, 1110s, 1096s, 1066s, 1025w, 1011m, 985s, 953m, 860s, 845s, 797s, 773s, 751s, 703s, 690m, 657m, 634w, 600w, 512m, 498m, 454m, 416w cm^{-1}. EIMS: m/z (% relative intensity): 417 (M$^+$, 0.8), 322 (4), 309 (5), 307 (6), 280 (10), 279 (64), 278 (12), 277 (64), 261 (8), 260 (25), 259 (93), 258 (29), 257 (68), 198 (5), 197 (5), 196 (9), 170 (5), 109 (5), 91 (4), 77 (5), 74 (82), 73 (100). Anal. Calcd for $C_{17}H_{19}BrF_2OSSi$: C, 48.92; H, 4.59. Found: C, 49.32; H, 4.47.

3.2.9. 2,2-Difluoro-1-(furan-2-yl)-2-phenylsulfanylethanol (3i). The reaction of **1** (0.464 g, 2 mmol) with 2-furaldehyde (0.185 g, 1.9 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a pale yellow liquid of **3i** (0.363 g, 73% yield). **3i**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.6 (d, J=6.9 Hz, 2H, ArH), 7.49–7.31 (m, 4H, ArH), 6.53 (d, J=3.2 Hz, 1H, ArH), 6.43 (dd, J=3.0, 1.8 Hz, 1H, ArH), 5.01 (dd, J=15.4, 9.3 Hz, 1H, CHOH), 2.77 (d, J=6.6 Hz, 1H, CHOH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.4 (t, J=1.95 Hz, C), 143.2 (CH), 136.5 (2×CH), 130.0 (CH), 129.1 (2×CH), 127.8 (t, J=283.6 Hz, CF$_2$), 125.5 (t, J=2.25 Hz, C), 110.6 (CH), 110.0 (CH), 70.5 (t, J=28.2 Hz, CH). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.03 (dd, J=210.9, 10.6 Hz, 1F), −83.46 (dd, J=210.9, 9.0 Hz, 1F). IR (neat): $\nu_{\max}$ 3418s, 3064m, 2913w, 1960w, 1888w, 1808w, 1738w, 1621w, 1584w, 1504m, 1475s, 1442s, 1384m, 1310m, 1266m, 1232m, 1212m, 1150s, 1063s, 1015s, 972s, 927s, 886s, 798s, 747s, 705s, 691s cm^{-1}. EIMS: *m/z* (% relative intensity) 256 (M$^+$, 56), 239 (46), 219 (14), 171 (11), 160 (60), 127 (5), 110 (9), 109 (7), 99 (10), 98 (5), 97 (100), 77 (5), 69 (30), 65 (6), 51 (8). Anal. Calcd for $C_{12}H_{10}F_2O_2S$: C, 56.24; H, 3.93. Found: C, 56.32; H, 3.65.

3.2.10. 1,1-Difluoro-1-phenylsulfanylpentan-2-ol (3j). The reaction of **1** (0.464 g, 2 mmol) with *n*-butanal (0.144 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a pale yellow liquid of **3j** (0.319 g, 69% yield). **3j**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.62 (d, J=6.6 Hz, 2H, Ar*H*), 7.47–7.33 (m, 3H, Ar*H*), 3.89 (dq, J=8.9, 2.7 Hz, 1H, C*H*OH), 1.96 (br s, 1H, CHO*H*), 1.83–1.52 (m, 3H, 2H of C*H*$_2$CH$_2$ and 1H and C*H*HCH$_3$), 1.50–1.32 (m, 1H, CH*H*CH$_3$), 0.97 (t, J=7.1 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 136.4 (2×CH), 129.9 (t, J=281.9 Hz, CF$_2$), 129.8 (CH), 129.0 (2×CH), 125.8 (t, J=2.2 Hz, C), 73.9 (t, J=26.0 Hz, CH), 32.4 (t, J=1.6 Hz, CH$_2$), 18.7 (CH$_2$), 13.7 (CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −86.43 (dd, J=209.5, 9.8 Hz, 1F), −83.13 (dd, J=209.5, 9.1 Hz, 1F). IR (neat): ν_{max} 3404br s, 3064w, 2963s, 2935s, 2876s, 1956w, 1885w, 1806w, 1711w, 1584w, 1475s, 1442s, 1383m, 1309m, 1269m, 1222w, 1182s, 1121s, 1057s, 1028s, 991s, 897m, 857m, 749s, 705s, 691s, 668m cm^{-1}. EIMS: *m/z* (% relative intensity) 232 (M$^+$, 30), 215 (2), 178 (6), 160 (100), 159 (9), 137 (5), 126 (15), 123 (7), 110 (71), 109 (21), 97 (5), 84 (8), 78 (18), 77 (16), 66 (14), 65 (3), 55 (33). Anal. Calcd for $C_{11}H_{14}F_2OS$: C, 56.88; H, 6.07. Found: C, 56.84; H, 6.21.

3.2.11. (*E*)-1,1-Difluoro-1-phenylsulfanylpent-3-en-2-ol (3k). The reaction of **1** (0.464 g, 2 mmol) with crotonaldehyde (0.140 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a pale yellow liquid of **3k** (0.321 g, 70% yield). **3k**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.63 (d, J=6.6 Hz, 2H, Ar*H*), 7.47–7.37 (m, 3H, Ar*H*), 6.02–5.88 (m, 1H, CH$_3$C*H*=CH), 5.65–5.53 (m, 1H, CH$_3$CH=C*H*), 4.37 (app. dd, J=16.2, 8.9 Hz, 1H, C*H*OH), 1.95 (br s, 1H, CHO*H*), 1.78 (dd, J=6.6, 0.7 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 136.9 (2×CH), 133.4 (CH), 130.3 (CH), 129.5 (2×CH), 129.4 (t, J=282.5 Hz, CF$_2$), 126.3 (t, J=2.0 Hz, C), 125.2 (t, J=2.4 Hz, CH), 75.5 (t, J=26.7 Hz, CH), 18.4 (CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −85.82 (dd, J=207.8, 9.5 Hz, 1F), −83.78 (dd, J=207.8, 9.0 Hz, 1F). IR (neat): ν_{max} 3404br s, 3063m, 2970m, 2943m, 2918m, 2857m, 1957w, 1887w, 1807w, 1674m, 1584m, 1475s, 1442s, 1379m, 1309m, 1286m, 1170s, 1134m, 1058s, 964s, 924m, 823m, 750s, 704s, 691s, 663m cm^{-1}. EIMS: *m/z* (% relative intensity) 230 (M$^+$, 100), 213 (42), 193 (4), 160 (87), 159 (11), 139 (3), 110 (33), 109 (16), 84 (4), 77 (13), 71 (35), 65 (13), 53 (12). Anal. Calcd for $C_{11}H_{12}F_2OS$: C, 57.37; H, 5.25. Found: C, 57.41; H, 5.22.

3.2.12. 1-(Difluoro(phenylsulfanyl)methyl)-1,2,3,4-tetrahydronapthalen-1-ol (3l) and (1-(difluoro(phenylthio)methyl)-1,2,3,4-tetrahydronaphthalen-1-yloxy)trimethylsilane (4l). The reaction of **1** (1.86 g, 8 mmol) with α-tetralone (1.17 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3l** (0.529 g, 22% yield) and a white powder of **4l** (0.78 g, 26% yield, mp=34–35.5 °C). **3l**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.74 (m, 1H, Ar*H*), 7.62–7.56 (m, 2H, Ar*H*), 7.45–7.33 (m, 3H, Ar*H*), 7.32–7.23 (m, 2H, Ar*H*), 7.20–7.14 (m, 1H, Ar*H*), 2.86 (t, J=6.3 Hz, 2H, PhC*H*$_2$CH$_2$), 2.47 (ddd, J=13.8, 10.2, 3.5 Hz, 1H, C*H*HCOH), 2.28 (br s, 1H, CO*H*), 2.21–2.11 (m, 1H, CH*H*COH), 2.11–2.00 (m, 1H, CH$_2$C*H*HCH$_2$), 1.95–1.83 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.6 (C), 137.2 (2×CH), 135.2 (C), 132.5 (t, J=287.9 Hz, CF$_2$), 130.3 (CH), 129.8 (CH), 129.6 (2×CH), 129.3 (CH), 128.7 (t, J=3.4 Hz, CH), 127.0 (C), 126.9 (CH), 76.63 (t, J=21.7 Hz, C), 34.9 (CH$_2$), 31.4 (CH$_2$), 19.5 (CH$_2$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −83.0 (d, J=203.7 Hz, 1F), −79.0 (d, J=203.7 Hz, 1F). IR (neat): ν_{max} 3446br s, 3061m, 3025m, 2943s, 2880m, 2839m, 1957w, 1826w, 1671w, 1583w, 1492s, 1475s, 1452s, 1441s, 1369m, 1331m, 1248m, 1191m, 1140m, 1121s, 1060s, 1024s, 984s, 906s, 876m, 842m, 749s, 704m, 691s cm^{-1}. EIMS: *m/z* (% relative intensity) 306 (M$^+$, 0.4), 289 (52), 269 (73), 160 (12), 147 (100), 130 (46), 128 (10), 117 (6), 109 (3), 91 (30), 77 (3), 65 (3). Anal. Calcd for $C_{17}H_{16}F_2OS$: C, 66.65; H, 5.26. Found: C, 66.86; H, 5.30. **4l**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88–7.78 (m, 1H, Ar*H*), 7.64–7.52 (m, 2H, Ar*H*), 7.43–7.29 (m, 3H, Ar*H*), 7.28–7.18 (m, 2H, Ar*H*), 7.15–7.07 (m, 1H, Ar*H*), 2.84 (t, J=6.4 Hz, 2H, PhC*H*$_2$CH$_2$), 2.7–2.5 (m, 1H, C*H*HCOH), 2.18–1.99 (m, 2H, 1H of CH*H*COSiMe$_3$ and 1H of CH$_2$C*H*HCH$_2$), 1.98–1.76 (m, 1H, CH$_2$CH*H*CH$_2$), 0.07 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.1 (C), 137.2 (2×CH), 136.3 (C), 132.8 (t, J=289.6 Hz, CF$_2$), 130.1 (CH), 129.9 (CH), 129.3 (2×CH), 129.2 (CH), 128.8 (CH), 128.1 (C), 126.0 (CH), 79.3 (t, J=23.0 Hz, C), 35.0 (CH$_2$), 29.7 (CH$_2$), 19.6 (CH$_2$), 2.6 (3×CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$/CFCl$_3$): δ −78.90 (d, J=200.1 Hz, 1F), −78.13 (d, J=200.1 Hz, 1F). IR (CHCl$_3$): ν_{max} 3065w, 3009m, 2957s, 2899m, 2841w, 1954w, 1884w, 1604w, 1583w, 1489m, 1474m, 1450m, 1441m, 1407w, 1342w, 1284m, 1253s, 1146s, 1095s, 1084s, 1056s, 1013m, 948m, 992s, 924s, 901s, 886s, 845s, 629m, 586w, 556m cm^{-1}. EIMS: *m/z* (% relative intensity) 269 (4), 221 (6), 220 (20), 219 (100), 177 (4), 159 (5), 130 (4), 129 (10), 77 (2), 73 (39). HRMS Calcd for $C_{20}H_{24}F_2OSSi$ (M$^+$): 378.1285; found: 378.1291.

3.2.13. 1-(Difluoro(phenylsulfanyl)methyl)-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (3m) and (1-(difluoro(phenylsulfanyl)methyl)-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yloxy)trimethylsilane (4m). The reaction of **1** (1.86 g, 8 mmol) with 6-methoxy-1-tetralone (1.41 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3m** (0.587 g, 21% yield) and a colourless liquid of **4m** (0.976 g, 29% yield). **3m**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.71 (d, J=8.8 Hz, 1H, Ar*H*), 7.65–7.55 (m, 2H, Ar*H*), 7.49–7.31 (m, 3H, Ar*H*), 6.82 (dd, J=8.8, 2.7 Hz, 1H, Ar*H*), 6.70 (d, J=2.7 Hz, 1H, Ar*H*), 3.82 (s, 3H, OC*H*$_3$), 2.84 (t, J=6.2 Hz, 2H, PhC*H*$_2$CH$_2$), 2.53–2.25 (m, 2H, C*H*$_2$COH), 2.25–1.76 (m, 3H, 2H of CH$_2$C*H*$_2$CH$_2$ and CO*H*). ^{13}C NMR (75 MHz, CDCl$_3$): δ 159.4 (C), 140.7 (C), 136.4 (2×CH), 131.9 (CF$_2$, t, J=288.0 Hz), 129.6 (CH), 128.8 (3×CH), 126.8 (d, J=1.6 Hz, C), 126.5 (d, J=2.8 Hz, C), 113.4 (CH), 112.5 (CH), 75.73 (t, J=21.6 Hz, C), 55.1 (OCH$_3$), 34.2

(d, *J*=2.2 Hz, CH_2), 30.2 (CH_2), 18.9 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −83.37 (d, *J*=203.0 Hz, 1F), −79.24 (d, *J*=203.0 Hz, 1F). IR (neat): ν_{max} 3463s, 3061w, 3002w, 2942m, 2838w, 1957w, 1890w, 1609s, 1576m, 1505s, 1474s, 1465m, 1441s, 1322m, 1286m, 1244s, 1190m, 1120s, 1047s, 1023s, 985s, 909s, 892m, 870m, 839m, 817m, 790w, 751s, 704m, 691s, 660w, 632w, 587w, 557w, 503m, 420w cm^{-1}. EIMS: *m/z* (% relative intensity) 336 (M^+, 1), 321 (5), 320 (19), 319 (76), 318 (100), 300 (19), 299 (43), 298 (34), 297 (11), 279 (7), 209 (35), 207 (23), 206 (20), 178 (17), 177 (45), 159 (11). HRMS Calcd for $C_{18}H_{18}F_2O_2S$ (M^+): 336.0995; found: 336.1003. **4m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.8 Hz, 1H, Ar*H*), 7.65–7.52 (m, 2H, Ar*H*), 7.46–7.28 (m, 3H, Ar*H*), 6.81 (dd, *J*=8.8, 2.8 Hz, 1H, Ar*H*), 6.64 (d, *J*=2.7 Hz, 1H, Ar*H*), 3.84 (s, 3H, OC*H*$_3$), 2.82 (t, *J*=6.4 Hz, 2H, PhC*H*$_2$CH$_2$), 2.49–2.63 (m, 1H, C*H*HCOSiMe$_3$), 2.17–1.98 (m, 1H of CH*H*COSiMe$_3$ and 1H of CH$_2$C*H*HCH$_2$), 1.96–1.77 (m, 1H, CH$_2$CH*H*CH$_2$), 0.07 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (C), 140.8 (C), 137.1 (2×CH), 132.9 (t, *J*=289.5 Hz, CF_2), 131.6 (t, *J*=2.6 Hz, CH), 129.9 (CH), 129.3 (2×CH), 128.5 (C), 128.3 (C), 113.4 (CH), 112.4 (CH), 79.1 (t, *J*=23.4 Hz, C), 55.7 (CH_3), 35.2 (CH_2), 30.3 (CH_2), 19.8 (CH_2), 2.6 (3×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −79.47 (d, *J*=199.4 Hz, 1F), −78.31 (d, *J*=199.4 Hz, 1F). IR (neat): ν_{max} 3440br w, 3062w, 2956s, 2837m, 1884w, 1609s, 1576m, 1500s, 1475m, 1465m, 1441m, 1341m, 1324m, 1283m, 1251s, 1196m, 1135s, 1086s, 1052s, 1011m, 992s, 952m, 906m, 894m, 881s, 842s, 774m, 793m, 750s, 705m, 691s, 633w, 597w, 573w, 530w, 503m cm^{-1}. EIMS: *m/z* (% relative intensity) 408 (M^+, 0.1), 284 (2), 249 (100), 159 (7), 91 (1), 77 (3), 73 (36). HRMS Calcd for $C_{21}H_{26}F_2O_2SSi$ (M^+): 408.1391; found: 408.1391.

3.2.14. 1,1-Difluoro-2-phenyl-1-phenylsulfanylpropan-2-ol (3n) and (1,1-difluoro-2-phenyl-1-phenylsulfanylpropan-2-yloxy)trimethylsilane (4n).

The reaction of **1** (1.86 g, 8 mmol) with acetophenone (0.96 g, 8 mmol) and TBAF (0.8 mL, 0.8 mmol, 1 M solution in THF) gave a pale yellow liquid of **3n** (0.669 g, 30% yield) and a colourless liquid of **4n** (0.740 g, 21% yield). **3n**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*=7.8 Hz, 2H, Ar*H*), 7.58–7.52 (m, 2H, Ar*H*), 7.46–7.31 (m, 6H, Ar*H*), 2.62 (br s, 1H, CO*H*), 1.85 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7 (C), 137.2 (2×CH), 131.6 (t, *J*=287.5 Hz, CF_2), 130.3 (CH), 129.7 (3×CH), 128.9 (CH), 128.7 (2×CH), 127.0 (t, *J*=1.7 Hz, CH), 126.8 (C), 78.6 (t, *J*=24.4 Hz, C), 25.1 (t, *J*=1.9 Hz, CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −84.70 (d, *J*=204.5 Hz, 1F), −82.00 (d, *J*=204.5 Hz, 1F). IR (neat): ν_{max} 3474br s, 3062m, 2995m, 2943w, 1957w, 1889w, 1811w, 1762w, 1671w, 1603w, 1584w, 1497m, 1475s, 1449s, 1442s, 1380m, 1374m, 1179m, 1149m, 1055s, 1028s, 984s, 914s, 801m, 749s, 701s, 676m cm^{-1}. EIMS: *m/z* (% relative intensity) 280 (M^+, 8), 263 (19), 243 (1), 241 (2), 213 (11), 185 (13), 160 (64), 123 (10), 121 (100), 110 (10), 109 (8), 103 (7), 77 (15), 65 (6), 51 (9). HRMS Calcd for $C_{15}H_{14}F_2OS$ (M^+): 280.0733; found: 280.0733. **4n**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J*=7.4 Hz, 2H, Ar*H*), 7.39 (d, *J*=6.6 Hz, 2H, Ar*H*), 7.3–7.1 (m, 6H, Ar*H*), 1.78 (s, 3H, C*H*$_3$), 0.10 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6 (d, *J*=1.4 Hz, C), 136.4 (2×CH), 130.8 (t, *J*=289.0 Hz, CF_2), 129.2 (CH), 128.6 (3×CH), 127.9 (CH), 127.7 (2×CH), 127.2 (t, *J*=1.8 Hz, C), 127.1 (CH), 80.6 (t, *J*=25.0 Hz, C), 23.7 (t, *J*=2.1 Hz, CH_3), 2.22 (3×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −84.08 (d, *J*=199.8 Hz, 1F), −82.49 (d, *J*=199.8 Hz, 1F). IR (neat): ν_{max} 3418w, 3062w, 3027w, 3002w, 2959m, 2899w, 1953w, 1885w, 1584w, 1496w, 1475m, 1441m, 1376m, 1253s, 1237s, 1202m, 1099s, 1081s, 1064s, 1028s, 988m, 963s, 948s, 863s, 844s, 804w, 750s, 699s, 691s, 661w, 627w, 596m, 504m cm^{-1}. EIMS: *m/z* (% relative intensity) 352 (M^+, 0.08), 241 (5), 195 (4), 194 (17), 193 (100), 163 (5), 123 (4), 104 (6), 103 (5), 75 (5), 73 (50). HRMS Calcd for $C_{18}H_{22}F_2OSSi$ (M^+): 352.1128; found: 352.1129.

3.2.15. 2,2-Difluoro-1,1-diphenyl-2-phenylsulfanylethanol (3o) and (2,2-difluoro-1,1-diphenyl-2-phenylsulfanylethoxy)trimethylsilane (4o).

The reaction of **1** (0.698 g, 3 mmol) with benzophenone (0.546 g, 3 mmol) and TBAF (0.3 mL, 0.3 mmol, 1 M solution in THF) gave a white powder of **3o** (0.348 g, 33% yield, mp=45–46 °C) and a white powder of **4o** (86.1 mg, 6% yield, mp=92–94 °C). **3o**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.61 (m, 4H, Ar*H*), 7.61–7.56 (m, 2H, Ar*H*), 7.46–7.31 (m, 9H, Ar*H*), 3.1 (br s, 1H, CO*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3 (2×C), 136.6 (2×CH), 131.2 (t, *J*=290.9 Hz, CF_2), 129.7 (CH), 128.9 (2×CH), 128.2 (2×CH), 127.9 (4×CH), 127.8 (t, *J*=1.9 Hz, CH), 127.8 (3×CH), 126.4 (C), 81.6 (t, *J*=23.9 Hz, C). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −77.88 (2F, s). IR (Nujol): ν_{max} 3473m, 3059w, 2955s, 2925s, 2855s, 1493w, 1459m, 1449m, 1377w, 1343w, 1310w, 1184w, 1169w, 1152w, 1094w, 1054m, 1040m, 1020m, 931w, 897m, 826m, 749m, 700m, 639m, 501w, 424w, 327w cm^{-1}. EIMS: *m/z* (% relative intensity) 342 (M^+, 31), 325 (24), 275 (5), 247 (10), 213 (22), 185 (5), 184 (14), 183 (100), 166 (6), 165 (17), 106 (23), 105 (56), 77 (19), 51 (6). HRMS Calcd for $C_{20}H_{16}F_2OS$ (M^+): 342.0890; found: 342.0892. **4o**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64–7.19 (m, 15H, Ar*H*), −0.05 (s, 9H, OSi(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5 (2×C), 136.7 (2×CH), 131.8 (t, *J*=292.7 Hz, CF_2), 129.4 (CH), 128.8 (2×CH), 128.7 (4×CH), 127.8 (2×CH), 127.6 (4×CH), 127.1 (d, *J*=2.3 Hz, C), 84.5 (t, *J*=23.7 Hz, CF_2), 1.7 (3×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −77.66 (s, 2F). IR (Nujol): ν_{max} 3416br w, 3063w, 2926s, 2855s, 1951w, 1895w, 1808w, 1711w, 1601w, 1581w, 1494w, 1461s, 1447s, 1406w, 1377m, 1307w, 1263m, 1247s, 1217w, 1195m, 1178w, 1163m, 1152m, 1104s, 1076s, 1063s, 1040s, 1021m, 999w, 936m, 912m, 879s, 847s, 825s, 755s, 742s, 697s, 637m, 628m, 536w, 503m, 425w cm^{-1}. EIMS: *m/z* (% relative intensity): 414 (M^+, 0.12), 303 (13), 255 (100), 166 (34), 73 (61). HRMS Calcd for $C_{23}H_{24}F_2OSSi$ (M^+): 414.1285; found: 414.1292.

3.2.16. 1-(Difluoro(phenylsulfanyl)methyl)cyclohexanol (3p).

The reaction of **1** (0.464 g, 2 mmol) with cyclohexanone (0.196 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a white powder of **3p** (0.325 g, 63% yield, mp=55–56 °C). **3p**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.49 (m, 2H, Ar*H*), 7.40–7.24 (m, 3H, Ar*H*), 1.88–1.47 (m, 9H, 8H of (C*H*$_2$)$_4$C*H*H and CO*H*), 1.24–1.04 (m, 1H, (CH$_2$)$_4$CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7 (2×CH), 132.1 (t, *J*=285.5 Hz, CF_2), 129.6 (CH), 128.9 (2×CH), 126.2 (t, J=1.9 Hz, C), 75.9 (t, J=23.0 Hz, C), 31.0 (2×CH_2, t, J=1.6 Hz), 25.3 (2×CH_2), 20.8 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −87.42 (s, 2F). IR (Nujol): ν_{max} 3602w, 3412br m, 2927s, 2855s, 2724w, 1711w, 1583w, 1461s, 1377s, 1267m, 1192m, 1154m, 1078m, 1039m, 989m, 975m, 951m, 906m, 884m, 847w, 811m, 747m, 704w, 690m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 258 (M^+, 100), 241 (28), 221 (13), 191 (14), 160 (38), 110 (12), 109 (10), 99 (34), 81 (99), 80 (31), 77 (8), 65 (5). Anal. Calcd for $C_{13}H_{16}F_2OS$: C, 60.44; H, 6.24. Found: C, 60.60; H, 6.19.

3.2.17. 1-(Difluoro(phenylsulfanyl)methyl)cyclopentanol (3q). The reaction of **1** (0.464 g, 2 mmol) with cyclopentanone (0.168 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a white powder of **3q** (0.219 g, 45% yield, mp=37–38 °C). **3q**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 2H, Ar*H*), 7.47–7.36 (m, 3H, Ar*H*), 2.16–2.05 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 1.8–1.56 and 1.95–1.8 (m, 7H, 6H of $(C\mathit{H}_2)_2CH_2C\mathit{H}_2$ and CO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2 (2×CH), 131.9 (t, J=283.5 Hz, CF_2), 130.3 (CH), 129.6 (2×CH), 126.9 (C), 86.5 (C, t, J=24.7 Hz), 36.5 (2×CH_2), 25.1 (2×CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −84.60 (s, 2F). IR (Nujol): ν_{max} 3335br s, 3064m, 2958s, 2874s, 1951w, 1880w, 1802w, 1582w, 1474s, 1440s, 1396s, 1330m, 1291m, 1265m, 1238m, 1137m, 1052s, 995s, 946s, 920s, 895s, 747s, 690s, 625m, 499s, 418w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 244 (M^+, 100), 227 (12), 207 (10), 205 (8), 160 (7), 110 (6), 109 (3), 85 (4), 77 (1), 68 (26), 65 (3). Anal. Calcd for $C_{12}H_{14}F_2OS$: C, 59.00; H, 5.78. Found: C, 59.33; H, 5.98.

3.2.18. 1,1-Difluoro-2-methyl-1-phenylsulfanylpropan-2-ol (3r). The reaction of **1** (0.464 g, 2 mmol) with acetone (0.116 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a pale yellow liquid of **3r** (0.283 g, 65% yield). **3r**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.69–7.56 (m, 2H, Ar*H*), 7.46–7.31 (m, 3H, Ar*H*), 2.11 (br s, 1H, CO*H*), 1.45 (s, 6H, 2×$C\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.6 (2×CH), 131.6 (t, J=285.3 Hz, CF_2), 129.6 (CH), 128.9 (2×CH), 126.0 (t, J=1.7 Hz, C), 75.0 (t, J=24.1 Hz, C), 24.1 (t, J=1.8 Hz, 2×CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −86.42 (s, 2F). IR (neat): ν_{max} 3419br s, 3064m, 2991s, 2943m, 1956w, 1886w, 1811w, 1636w, 1584s, 1475s, 1442s, 1376s, 1250m, 1200s, 1158m, 1099s, 1054s, 1016s, 979s, 953s, 854m, 833s, 750s, 704m, 691s, 664m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 218 (M^+, 100), 201 (24), 199 (5), 181 (7), 160 (18), 151 (5), 135 (3), 123 (2), 110 (13), 109 (8), 77 (3), 65 (7), 59 (19). Anal. Calcd for $C_{10}H_{12}F_2OS$: C, 55.03; H, 5.54. Found: C, 55.05; H, 5.20.

3.2.19. 1-(Difluoro(phenylsulfanyl)methyl)cyclohex-2-enol (3s). The reaction of **1** (0.464 g, 2 mmol) with 2-cyclohexenone (0.192 g, 2 mmol) and TBAF (0.2 mL, 0.2 mmol, 1 M solution in THF) gave a pale yellow liquid of **3s** (0.307 g, 60% yield). **3s**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.68–7.54 (m, 2H, Ar*H*), 7.47–7.28 (m, 3H, Ar*H*), 6.15 (dq, J=10.1, 2.8 Hz, 1H, C*H*=CHCOH), 5.86 (d, J=10.1 Hz, 1H, CH=C*H*COH), 2.23–2.03 (m, 3H, 2H of $C\mathit{H}_2CH{=}CH$ and CO*H*), 2.02–1.92 (m, 2H, $CH_2C\mathit{H}_2COH$), 1.85–1.71 (m, 2H, $CH_2C\mathit{H}_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.6 (2×CH), 135.4 (CH), 131.3 (t, J=285.8 Hz, CF_2), 129.6 (CH), 128.9 (2×CH), 126.1 (t, J=1.7 Hz, C), 124.53 (dd, J=3.3, 1.3 Hz, CH), 73.6 (t, J=23.4 Hz, C), 30.3 (CH_2), 24.9 (CH_2), 17.7 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −87.3 (d, J=203.0 Hz, 1F), −85.7 (d, J=203.0 Hz, 1F). IR (neat): ν_{max} 3418br s, 3062w, 3035w, 2941s, 2873m, 2834w, 1818w, 1650w, 1583w, 1474s, 1441s, 1397w, 1383w, 1350w, 1324w, 1262w, 1195m, 1161s, 1032s, 996s, 967s, 934s, 895s, 838m, 750s, 735s, 704m, 691s, 650w, 593w, 502m cm^{-1}. EIMS: *m*/*z* (% relative intensity): 256 (M^+, 2), 239 (7), 160 (27), 110 (8), 109 (10), 98 (7), 97 (100), 79 (31), 77 (25), 65 (7), 55 (10). HRMS Calcd for $C_{13}H_{14}F_2OS$ (M^+): 256.0733; found: 256.0733.

3.3. Desilylation of compound 4b to provide compound 3b

A solution of compound **4b** (2.066 g, 5.62 mmol) in CH_2Cl_2 (10 mL) was treated with potassium fluoride (KF) in CH_3CN (10 mL). The reaction mixture was stirred at room temperature overnight and quenched with a saturated NH_4Cl solution and extracted with EtOAc (3×50 mL). The organic phase was washed successively with brine, water and dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified by chromatotron (SiO_2, 5% EtOAc in hexanes) to give a pale yellow liquid of **3b** (1.528 g, 91% yield).

3.4. Preparation of sulfoxide 5

3.4.1. 2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylsulfinylethanol (5b). *General procedure*: A solution of compound **3b** (269.7 mg, 0.9 mmol) in THF (15 mL) at −78 °C was treated with a solution of 70% *m*-chloroperbenzoic acid (MCPBA) (235.3 mg, 0.94 mmol) in THF (5 mL). The reaction mixture was stirred at −78 °C and slowly warmed to room temperature overnight. The reaction was quenched with a saturated $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined extracts were dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified by column chromatography (SiO_2, 20% EtOAc in hexanes and then 2% MeOH in hexanes) to give a white powder of **5b** as a mixture (62:38) of two diastereomers (210.5 mg, 74% yield, mp=111–115 °C). ^1H NMR (500 MHz, $CDCl_3$/MeOD): δ 7.67 and 7.63 (d each, J=7.0 and 6.8 Hz, respectively, 2H, Ar*H*), 7.59–7.46 (m, 3H, Ar*H*), 7.4–7.3 (m, 2H, Ar*H*), 6.87 and 6.83 (d each, J=7.9 and 8.0 Hz, respectively, 2H, Ar*H*), 5.23 (d, J=23.5 Hz) and 4.90 (t, J=12.7 Hz) (1H, C*H*OH), 3.74 and 3.72 (s each, 3H, O$C\mathit{H}_3$), 3.35 (br s, 1H, CHO*H*). ^{13}C NMR (125 MHz, $CDCl_3$/MeOD): δ 159.9 and 159.8 (C), 136.0 and 135.3 (C), 132.4 and 132.2 (CH), 129.1 and 128.8 (2×CH), 129.7 (2×CH), 126.8 and 126.6 (C), 126.3 and 126.2 (CH), 113.6 and 113.4 (2×CH), 71.5 (t, J=21.9 Hz) and 68.9 (dd, J=29.1, 19.1 Hz) (CH), 55.0 and 54.9 (CH_3). ^{19}F NMR (470 MHz, $CDCl_3$/MeOD/$CFCl_3$): δ −117.92 and −117.66 (d each, J=213.4 and 220.0 Hz, 1F), −114.14 and −112.58 (d each, J=213.8 and 220.0 Hz, 1F). IR (KBr): ν_{max} 3266s, 3068w, 2998w, 2954m, 2929m, 2908m, 2835w, 2679w, 2551w, 2055w, 1735w, 1719w, 1609s, 1587w, 1509s, 1459m, 1445s, 1420w, 1350w, 1330w, 1304m, 1294m, 1250s, 1202s, 1175s, 1110s, 1085s, 1041s, 975s, 846m, 824w, 793s, 785s, 754s, 748s, 699m, 688m, 626w, 5814m, 568s, 529s, 481m, 450m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 312 (M^+, 9), 295 (42), 187 (13), 186 (93), 170 (22), 167 (38), 139 (100), 137 (33), 135 (12), 127 (19), 126 (95), 109 (36), 108 (13), 97 (10), 94 (18), 79 (13), 78 (89), 77 (27). HRMS Calcd for $C_{15}H_{14}F_2O_3S$ (M^+): 312.0632; found: 312.0628.

3.4.2. 2,2-Difluoro-1-(2,4-dimethoxyphenyl)-2-phenylsulfinylethanol (5c). Treatment of compound **3c** (451.6 mg, 1.38 mmol) in THF (20 mL) with a solution of 70% MCPBA (358 mg, 1.45 mmol) in THF (8 mL) afforded a white powder of **5c** as a mixture (54:46) of two diastereomers (324.4 mg, 69% yield, mp=108–111 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.71 (m, 2H, Ar*H*), 7.64–7.50 (m, 3H, Ar*H*), 7.36 and 7.31 (d each, *J*=8.4 and 8.4 Hz, respectively, 1H, Ar*H*), 6.55–6.40 (m, 2H, Ar*H*), 5.65 (d, *J*=24 Hz) and 5.42 (dd, *J*=17.4, 8.6 Hz) (1H, C*H*OH), 4.12 (br s, 1H, CHO*H*), 3.86 and 3.80 (s each, 3H, OC*H*$_3$), 3.82 and 3.76 (s each, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 and 162.1 (C), 159.5 and 159.4 (C), 137.5 and 137.0 (C), 133.2 and 133.0 (CH), 131.2 and 131.1 (CH), 129.7 and 129.6 (2×CH), 127.1 and 127.0 (2×CH), 125.7 and 125.1 (CF_2, dd each, *J*=305.1, 295.3 and 306.0, 295.0 Hz, respectively), 115.2 and 115.0 (C), 105.6 and 105.4 (CH), 99.6 and 99.4 (CH), 70.5 and 67.8 (CH, dd each, *J*=22.7, 22.7 and 29.0, 19.6 Hz, respectively), 56.4 and 56.1 (2×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −119.48 and −117.49 (dd each, *J*=216.8, 17.2 and 223.0, 24.0 Hz, respectively, 1F), −111.41 (d, *J*=223.0 Hz) and −109.49 (dd, *J*=216.4, 8.0 Hz), (1F). IR ($CHCl_3$): ν_{max} 3674w, 3598w, 3495br m, 3066w, 3013m, 2964m, 2941m, 2841w, 2455w, 1888w, 1719w, 1614s, 1589s, 1509s, 1466s, 1446s, 1439m, 1422m, 1296s, 1269m, 1185m, 1160s, 1128s, 1086s, 1039s, 999w, 974m, 936w, 922m, 839m, 825m, 638w, 593w, 566m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 342 (M^+, 0.27), 217 (35), 216 (41), 198 (13), 197 (100), 187 (18), 169 (28), 167 (50), 165 (23), 151 (17), 149 (12), 139 (64), 137 (32), 126 (39), 121 (72), 109 (21), 91 (38), 78 (40), 77 (36). HRMS Calcd for $C_{16}H_{16}F_2O_4S$ (M^+): 342.0737; found: 342.0732.

3.4.3. 2,2-Difluoro-1-(3,4-dimethoxyphenyl)-2-phenylsulfinylethanol (5d). Treatment of compound **3d** (372.3 mg, 1.14 mmol) in THF (18 mL) with a solution of 70% MCPBA (294 mg, 1.19 mmol) in THF (6 mL) afforded a white powder of **5d** as a mixture (51:49) of diastereomers (275 mg, 70% yield, mp=121–125 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.69 (m, 2H, Ar*H*), 7.66–7.51 (m, 3H, Ar*H*), 7.11–6.95 (m, 2H, Ar*H*), 6.89 and 6.85 (d each, *J*=8.8 and 8.4 Hz, respectively, 1H, Ar*H*), 5.43–5.31 (m, 1H, C*H*OH), 4.22 (br s, 1H, CHO*H*), 3.90 and 3.88 (s each, 6H, 2×C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6 and 150.4 (C), 149.8 and 149.6 (C), 136.6 (d, *J*=3.5 Hz) and 136.3 (CH), 133.4 and 133.2 (CH), 129.8 and 127.0 (2×CH), 127.5 and 127.1 (C), 127.0 (2×CH), 124.9 and 124.2 (CF_2, dd each, *J*=303.0, 295.6 and 309.8, 291.4 Hz, respectively), 121.6 and 121.1 (CH), 111.4 (2×CH), 73.9 and 71.3 (CH, dd each, *J*=21.7, 21.7 and 28.9, 19.5 Hz, respectively), 56.5 (2×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −119.81 and −117.39 (dd each, *J*=218.2, 14.2 and 224.4, 22.1 Hz, respectively, 1F), −110.75 (d, *J*=224.4 Hz) and −109.86 (dd, *J*=218.2, 9.6 Hz), (1F). IR ($CHCl_3$): ν_{max} 3673w, 3597w, 3392br m, 3066w, 3019s, 2963m, 2938m, 2840m, 1960w, 1608m, 1596m, 1519s, 1465s, 1446s, 1423m, 1344w, 1309w, 1267s, 1188m, 1158s, 1143s, 1108s, 1087s, 1026s, 984m, 909m, 867w, 646w, 625w, 590w, 566w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 342 (M^+, 1), 324 (4), 216 (100), 187 (51), 169 (38), 139 (41), 126 (38), 78 (42), 77 (24). Anal. Calcd for $C_{16}H_{16}F_2O_3S$: C, 56.13; H, 4.71. Found: C, 56.22; H, 4.30.

3.4.4. 1,1-Difluoro-4-phenyl-1-phenylsulfinyl-3-buten-2-ol (5e). Treatment of compound **3e** (369.5 mg, 1.26 mmol) in THF (21 mL) with a solution of 70% MCPBA (320 mg, 1.32 mmol) in THF (6 mL) afforded a white powder of **5e** as a mixture (60:40) of two diastereomers (212 mg, 50% yield, mp=110–114 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.71 (m, 2H, Ar*H*), 7.67–7.53 (m, 3H, Ar*H*), 7.47–7.38 (m, 2H, Ar*H*), 7.38–7.24 (m, 3H, Ar*H*), 6.88 (d, *J*=16 Hz, 1H, PhC*H*═CH), 6.34 and 6.27 (dd each, *J*=15.6, 7.0 and 16.0, 6.0 Hz, respectively, 1H, PhCH═C*H*), 5.05 (dd, *J*=21.0, 5.0 Hz) and 4.98–4.86 (m), (1H, C*H*OH), 4.11 and 3.40 (br s each, 1H, CHO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 and 136.6 (CH), 136.4 and 136.2 (2×C), 133.4 (CH), 129.9 (2×CH), 129.3 (2×CH), 129.1 and 127.6 (CH), 127.5 (2×CH), 127.1 (2×CH), 121.9 and 121.8 (CH), 73.4 and 70.9 (CH, t each, *J*=22.8 and 27.4 Hz, respectively). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −118.49 and −116.78 (dd each, *J*=220.6, 11.8 and 224.8, 20.7 Hz, respectively, 1F), −112.62 (d, *J*=224.7 Hz) and −109.98 (dd, *J*=220.6, 10.9 Hz), (1F). IR (KBr): ν_{max} 3285br s, 3058m, 3027m, 2897w, 2688w, 2364w, 2345w, 1891w, 1813w, 1648w, 1496m, 1475m, 1446s, 1424m, 1358w, 1331w, 1306w, 1282w, 1262w, 1192s, 1115s, 1085s, 1062s, 1034s, 1020s, 998s, 970s, 950s, 869w, 850w, 804w, 767s, 748s, 728m, 689s, 669w, 605w, 547m, 521s, 488m, 444m cm^{-1}. EIMS: *m*/*z* (% relative intensity) 308 (46), 291 (100), 233 (31), 186 (21), 182 (76), 146 (26), 133 (32), 126 (62), 115 (50), 78 (64), 77 (20). HRMS Calcd for $C_{16}H_{14}F_2O_2S$ (M^+): 308.0683; found: 308.0678.

3.4.5. 1,1-Difluoro-4-(2-methoxyphenyl)-1-phenylsulfinyl-3-buten-2-ol (5f). Treatment of compound **3f** (190 mg, 0.59 mmol) in THF (9 mL) with a solution of 70% MCPBA (149 mg, 0.62 mmol) in THF (3 mL) afforded a white powder of **5f** as a mixture (65:35) of two diastereomers (118.9 mg, 60% yield, mp=127–130 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 and 7.77 (d each, *J*=8.0 and 7.6 Hz, respectively, 1H, Ar*H*), 7.65–7.53 (m, 3H, Ar*H*), 7.47 (dd, *J*=7.6, 1.6 Hz, 1H, Ar*H*), 7.32–7.23 (m, 1H, Ar*H*), 7.18 and 7.17 (d each, *J*=16.0 and 16.0 Hz, respectively, 1H, Ar*H*), 6.97–6.84 (m, 2H, 1H of Ar*H* and 1H of PhC*H*═CH), 6.38 and 6.31 (dd each, *J*=16.0, 7.2 and 16.0, 6.8 Hz, respectively, 1H, PhCH═C*H*), 5.09–5.00 and 4.90–4.80 (m each, 1H, C*H*OH), 3.84 and 3.83 (s each, 3H, C*H*$_3$), 3.10 (br s, 1H, CHO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8 and 157.7 (C), 137.1 and 136.3 (C), 133.2 (CH), 132.5 and 131.9 (CH), 130.4 and 130.2 (CH), 129.7 (2×CH), 128.2 and 128.1 (CH), 127.1 (2×CH), 125.4 and 125.2 (C), 122.4 and 122.3 (CH), 121.3 (CH), 111.6 (CH), 73.8 and 71.4 (CH, dd each, *J*=22.9, 22.9 and 28.5, 20.6 Hz, respectively), 56.10 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −118.4 and −117.1 (dd each, *J*=219.8, 12.4 and 223.5, 21.0 Hz, respectively, 1F), −112.4 (d, J=223.5 Hz) and −110.4 (dd, J=219.8, 10.3 Hz), (1F). IR (neat): ν_{max} 3354br s, 3063w, 3003w, 2939w, 2839w, 1897w, 1732m, 1714m, 1650m, 1599s, 1579m, 1489s, 1464s, 1446s, 1374w, 1357w, 1293s, 1247s, 1194s, 1163m, 1104s, 1049s, 998m, 977s, 951s, 867m, 751s, 688s, 606w, 583w, 526m, 489m, 433w, 417w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 338 (M$^+$, 1.22), 212 (100), 192 (63), 164 (41), 126 (44), 115 (33), 91 (48), 78 (66). HRMS Calcd for $C_{17}H_{16}F_2O_3S$ (M+): 338.0788; found: 338.0788.

3.4.6. 1-(Difluoro(phenylsulfinyl)methyl)-1,2,3,4-tetrahydronapthalen-1-ol (5l). Treatment of compound **3l** (309.0 mg, 1.00 mmol) in THF (15 mL) with a solution of 70% MCPBA (273 mg, 1.10 mmol) in THF (4 mL) afforded a diastereomeric mixture of **5l**, which was separated by radial chromatography (20% EtOAc in hexanes) to give 123 mg (38% yield, mp=139–142 °C) of diastereomer **A** and 97 mg (30% yield, mp=115–118 °C) of diastereomer **B**. Diastereomer **A**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.81 (m, 1H, Ar*H*), 7.70 (d, J=8.0 Hz, 2H, Ar*H*), 7.63–7.47 (m, 3H, Ar*H*), 7.36–7.23 (m, 2H, Ar*H*), 7.22–7.12 (m, 1H, Ar*H*), 2.92–2.77 (m, 2H, PhCH_2), 2.77–2.64 (m, 1H, C*H*HOH), 2.45 (br s, 1H, CO*H*), 2.13–1.94 (m, 2H, 1H of CH*H*OH and 1H of CH_2C*H*HCH_2), 1.93–1.75 (m, 1H, CH_2CH*H*CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7 (C), 137.1 (C), 134.9 (C), 133.2 (CH), 129.9 (CH), 129.6 (2×CH), 129.5 (CH), 128.3 (d, J=2.7 Hz, CH), 127.5 (2×CH), 126.8 (CH), 124.6 (dd, J=317.0, 300.0 Hz, CF_2), 76.7 (t, J=19.3 Hz, C), 34.0 (CH_2), 29.4 (CH_2), 19.2 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −115.73 (d, J=219.5 Hz, 1F), −99.57 (d, J=219.6 Hz, 1F). Diastereomer **B**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J=7.6, 3H, Ar*H*), 7.69–7.57 (m, 3H, Ar*H*), 7.33–7.16 (m, 3H, Ar*H*), 4.10 (br s, 1H, CO*H*), 2.97–2.86 (m, 2H, PhCH_2), 2.86–2.77 (m, 1H, C*H*HCOH), 2.52–2.40 (m, 1H, C*H*HCOH), 2.18–2.00 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4 (C), 136.2 (C), 133.8 (C), 133.4 (CH), 129.8 (2×CH), 129.6 (CH), 129.5 (CH), 129.2 (d, J=4.3 Hz, CH), 127.2 (2×CH), 126.9 (CH), 124.1 (dd, J=319.1, 295.3 Hz, CF_2), 76.7 (t, J=3 Hz, C), 35.4 (CH_2), 29.9 (CH_2), 19.4 (d, J=2.6 Hz, CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −115.31 (d, J=220.9 Hz, 1F), −100.50 (d, J=221.5 Hz, 1F). IR (KBr): ν_{max} 3238s, 3081w, 3014w, 2959m, 2919m, 2887w, 2837w, 2817w, 2613w, 2489w, 1655w, 1601w, 1486m, 1477m, 1456m, 1448m, 1431m, 1414w, 1353w, 1341m, 1292w, 1232w, 1200m, 1184w, 1166m, 1149s, 1131s, 1078s, 1065m, 1030s, 1021s, 980s, 959m, 910w, 891m, 874s, 807w, 766s, 752s, 686s, 659m, 623m, 582m, 518m, 495m, 466m, 436m, 897w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 177 (14), 164 (5), 159 (10), 149 (23), 147 (31), 130 (12), 129 (100), 128 (32), 127 (18), 126 (73), 91 (21), 78 (48), 77 (10), 73 (2), 65 (5). Anal. Calcd for $C_{17}H_{16}F_2O_2S$: C, 63.34; H, 5.00. Found: C, 63.34; H, 5.16.

3.4.7. 2,2-Difluoro-1,1-diphenyl-2-phenylsulfinylethanol (5o). Treatment of compound **3o** (662.6 mg, 1.93 mmol) in THF (20 mL) with a solution of 70% MCPBA (496 mg, 2.02 mmol) in THF (10 mL) afforded a white powder of **5o** (493.1 mg, 71% yield, mp=158–161 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.78 (m, 2H, Ar*H*), 7.77–7.67 (m, 2H, Ar*H*), 7.67–7.38 (m, 8H, Ar*H*), 7.37–7.24 (m, 3H, Ar*H*), 5.18 (br s, 1H, CO*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4 (C), 139.5 (C), 136.3 (C), 133.5 (CH), 129.8 (2×CH), 129.4 (CH), 129.3 (2×CH), 129.0 (CH), 128.6 (2×CH), 128.4 (2×CH), 128.0 (CH), 127.9 (CH), 127.1 (2×CH), 123.0 (dd, J=318.7, 299.9 Hz, CF_2), 82.5 (t, J=19.9, 19.8 Hz, C). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −112.44 (d, J=220.2 Hz, 1F), −98.60 (d, J=220.2 Hz, 1F). IR (KBr): ν_{max} 3255s, 3053m, 1491m, 1450s, 1411m, 1289w, 1261w, 1172m, 1120s, 1083s, 1063s, 1039s, 1021s, 998m, 905m, 821m, 749s, 706s, 698s, 687s, 659m, 618m, 572m, 512m, 483m, 437m, 397w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 359 (M$^+$+1, 3.32), 213 (62), 185 (40), 183 (19), 166 (17), 165 (100), 127 (12), 126 (33), 106 (5), 105 (35), 78 (37), 77 (45), 50 (15). Anal. Calcd for $C_{20}H_{16}F_2O_2S$: C, 67.02; H, 4.50. Found: C, 67.10; H, 4.08.

3.5. Preparation of 1,1-difluoroalkene 6

3.5.1. 1,1-Difluoro-2-(4-methoxyphenyl)ethene (6b).[12] *General procedure A*: Sulfoxide **5b** (110 mg, 0.35 mmol) was heated at 170–200 °C (0.05 mmHg) to give a pure oil of **6b** (47.1 mg, 79% yield), which was trapped at −78 °C (see Fig. 1).

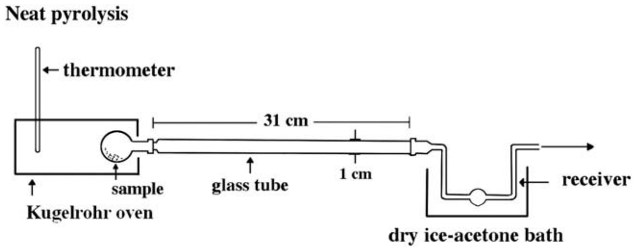


Figure 1.

General procedure B: Flash vacuum pyrolysis of sulfoxide **5b** (105.2 mg, 0.34 mmol) (conditions: oven temperature 120 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a pure oil of **6b** (46.4 mg, 82% yield), which was trapped at −78 °C (see Fig. 2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, J=8.4 Hz, 2H, Ar*H*), 6.87 (d, J=8.7 Hz, 2H, Ar*H*), 5.20 (dd, J=26.4, 3.8 Hz, 1H, C*H*=CF_2), 3.79 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6 (t, J=2.1 Hz, C), 155.8 (dd, J=294.8, 284.9 Hz, CF_2), 128.8 (2×CH, dd, J=6.3, 3.4 Hz), 122.7 (t, J=6.1 Hz, C), 114.1 (2×CH), 81.5 (dd, J=29.0, 14.1 Hz, CH), 55.2 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −86.86 (d, J=36.9 Hz, 1F), −85.04 (dd, J=43.8, 36.7 Hz, 1F). IR (neat): ν_{max} 3450w, 3038m, 3006m, 2959m, 2938m, 2912m, 2839m, 2666w, 2550w, 2066w, 2024w, 1886w, 1733s, 1613s, 1578m, 1515s, 1466m, 1443m, 1421m, 1351s, 1317w, 1299s, 1248s, 1182s, 1166s, 1113w, 551s, 523s, 475w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 170 (M$^+$, 100), 139 (9), 127 (10), 107 (3), 77 (1).

3.5.2. 1,1-Difluoro-2-(2,4-methoxyphenyl)ethene (6c). According to *general procedure A*, neat pyrolysis of sulfoxide **5c** (104.2 mg, 0.30 mmol) at 170–200 °C (0.05 mmHg) gave a pure oil of **6c** (44.5 mg, 74% yield). According to

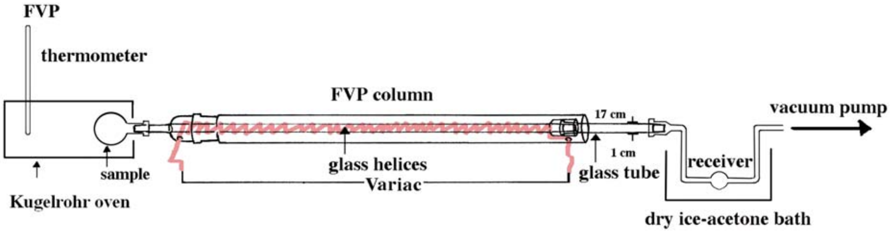


Figure 2.

general procedure B, flash vacuum pyrolysis of sulfoxide **5c** (103.0 mg, 0.30 mmol) (conditions: oven temperature 120 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a pure oil of **6c** (42.1 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, J=8.4, 1.2 Hz, 1H, Ar*H*), 6.51 (dd, J=8.4, 2.4 Hz, 1H, Ar*H*), 6.46 (d, J=25.6, 5.6 Hz, 1H, Ar*H*), 5.56 (dd, J=25.8, 5.5 Hz, 1H, C*H*=CF_2), 3.82 (s, 6H, 2×CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9 (C), 157.2 (dd, J=4.1, 1.5 Hz, C), 155.9 (dd, J=292.8, 284.8 Hz, CF_2), 128.8 (dd, J=8.8, 2.2 Hz, CH), 111.8 (t, J=5.0 Hz, C), 104.7 (CH), 98.4 (CH), 75.8 (dd, J=29.7, 14.6 Hz, CH), 55.5 (CH_3), 55.4 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −86.31 (dd, J=36.6, 25.6 Hz, 1F), −86.11 (dd, J=36.6, 6.4 Hz, 1F). IR (neat): ν_{max} 3446w, 3005w, 2942w, 2840w, 1868w, 1732s, 1614s, 1582s, 1508s, 1465s, 1439m, 1420m, 1346m, 1312s, 1291s, 1236s, 1210s, 1169s, 1115m, 1036s, 993w, 942s, 836m, 792w, 753w, 688w, 630w, 588w, 547w, 466w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 200 (M$^+$, 100), 185 (22), 157 (10), 149 (5), 121 (5). HRMS Calcd for $C_{10}H_{10}F_2O_2$ (M$^+$): 200.0649; found: 200.0653.

3.5.3. 1,1-Difluoro-2-(3,4-methoxyphenyl)ethene (6d).

According to *general procedure A*, neat pyrolysis of sulfoxide **5d** (101.3 mg, 0.29 mmol) at 170–200 °C (0.05 mmHg) gave a pure oil of **6d** (40.9 mg, 71% yield). According to *general procedure B*, flash vacuum pyrolysis of sulfoxide **5d** (117.0 mg, 0.34 mmol) (conditions: oven temperature 120 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a pure oil of **6d** (46.0 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91–6.80 (m, 3H, Ar*H*), 5.21 (dd, J=26.4, 3.9 Hz, 1H, C*H*=CF_2), 3.89 (s, 3H, CH_3), 3.88 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5 (dd, J=294.7, 285.1 Hz, CF_2), 149.6 (C), 148.8 (C), 123.6 (t, J=6.0 Hz, C), 121.0 (t, J=4.4 Hz, CH), 111.9 (CH), 111.1 (d, J=4.4 Hz, CH), 82.5 (dd, J=15.5, 13.7 Hz, CH), 56.5 (2×CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −86.54 (dd, J=36.5, 3.8 Hz, 1F), −84.81 (dd, J=36.7, 25.4 Hz, 1F). IR (neat): ν_{max} 3546w, 3004m, 2959m, 2939m, 2912m, 2838m, 2592w, 2018w, 1836w, 1731s, 1607m, 1585m, 1519s, 1466s, 1418s, 1345s, 1322s, 1293s, 1269s, 1246s, 1212s, 1178s, 1157s, 1145s, 1028s, 978m, 918s, 892m, 857s, 826m, 805m, 764m, 746m, 638m, 596w, 562m, 405w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 200 (M$^+$, 100), 185 (25), 157 (14), 139 (5), 127 (6), 110 (11), 109 (51), 107 (19), 77 (3). HRMS Calcd for $C_{10}H_{10}F_2O_2$ (M$^+$): 200.0649; found: 200.0655.

3.5.4. (*E*)-1-(4,4-Difluoro-1,3-butadienyl)benzene (6e).[11b]

According to *general procedure A*, neat pyrolysis of sulfoxide **5e** (120.5 mg, 0.39 mmol) at 170–200 °C (0.05 mmHg) gave a pure oil of **6e** (45.1 mg, 70% yield). According to *general procedure B*, flash vacuum pyrolysis of sulfoxide **5e** (168.5 mg, 0.547 mmol) (conditions: oven temperature 120 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a crude pyrolyzate, which was purified by chromatotron (SiO_2, hexanes) to give a pale yellow oil **6e** (54.8 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.35 (m, 2H, Ar*H*), 7.35–7.29 (m, 2H, Ar*H*), 7.29–7.21 (m, 1H, Ar*H*), 6.68 (ddd, 1H, J=15.8, 10.8, 1.2 Hz, 1H, PhCH=C*H*), 6.48 (d, J=15.8 Hz, 1H, PhC*H*=CH), 5.14 (dddd, J=24.1, 10.8, 1.5, 0.6 Hz, 1H, C*H*=CF_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (dd, J=295.4, 289.8 Hz, CF_2), 137.5 (C), 131.7 (dd, J=11.4, 3.3 Hz, CH), 129.3 (2×CH), 128.3 (CH), 126.8 (2×CH), 118.5 (CH), 83.5 (dd, J=27.6, 16.8 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −87.46 (d, J=26.4 Hz, 1F), −85.74 (t, J=25.4 Hz, 1F). IR (neat): ν_{max} 3447br m, 3084w, 3062w, 3028w, 2960m, 2926m, 2853m, 2646w, 2363w, 1812m, 1717s, 1648w, 1630w, 1597w, 1578w, 1519w, 1498w, 1451w, 1418w, 1353m, 1329m, 1295m, 1276s, 1210w, 1184s, 1116w, 1073w, 1028w, 962m, 934s, 851w, 828m, 747m, 692m, 605w, 563w, 516w, 505w cm^{-1}. EIMS: m/*z* (% relative intensity) 166 (M$^+$, 28), 149 (100), 115 (54), 105 (46), 95 (35), 91 (35), 77 (50).

3.5.5. (*E*)-1-(4,4-Difluoro-1,3-butadienyl)-2-methoxybenzene (6f).

According to *general procedure A*, neat pyrolysis of sulfoxide **5f** (107.5 mg, 0.32 mmol) at 170–200 °C (0.05 mmHg) gave a pure oil of **6f** (48.7 mg, 78% yield). According to *general procedure B*, flash vacuum pyrolysis of sulfoxide **5f** (104.0 mg, 0.31 mmol) (conditions: oven temperature 120 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a pure oil of **6f** (43.5 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J=7.3, 1.6 Hz, 1H, Ar*H*), 7.25–7.20 (m, 1H, Ar*H*), 6.98–6.91 (m, 1H, Ar*H*), 6.88 (dd, J=8.3, 1.0 Hz, 1H, Ar*H*), 6.82 (d, J=16.1 Hz, 1H, PhC*H*=CH), 6.70 (ddd, J=16.0, 10.7, 1.2 Hz, 1H, PhCH=C*H*), 5.17 (ddd, J=23.7, 10.7, 0.3 Hz, 1H, C*H*=CF_2), 3.87 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3 (dd, J=295.1, 289.3 Hz, CF_2), 157.2 (C), 131.3 (C), 129.2 (CH), 127.2 (CH), 126.6 (dd, J=11.3, 3.2 Hz, CH), 121.4 (CH), 119.1 (dd, J=4.1, 2.2 Hz, CH), 111.5 (CH), 84.1 (dd, J=17.2, 16.8 Hz, CH), 56.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −88.17 (d, J=27.8 Hz, 1F), −86.40 (dd, J=27.7, 23.7 Hz, 1F). IR (neat): ν_{max} 3415w, 3004w, 2927m, 2839w, 2644w, 1812w, 1716s, 1625w, 1597m, 1578w, 1489s, 1465m, 1438m, 1354s, 1295m, 1279m, 1246s, 1180s, 1104w, 1052w, 1030m, 970m, 934s, 854w, 841w, 821w, 775w, 749s, 731w, 607w, 578w, 508w cm^{-1}. EIMS: *m*/*z* (% relative intensity) 196 (M$^+$, 14), 165 (43), 118 (61), 77 (24), 63 (75), 50 (100). HRMS Calcd for $C_{11}H_{10}F_2O$ (M$^+$): 196.0700; found: 196.0699.

3.5.6. 1-(Difluoromethylene-1,2,3,4-tetrahydronapthalene (6l).[11b] According to *general procedure B*, flash vacuum pyrolysis of sulfoxide **5l** (110.1 mg, 0.34 mmol) (conditions: oven temperature 205 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a crude pyrolyzate, which was purified by chromatotron (SiO_2, hexanes) to give a colourless oil of **6l** (25.0 mg, 41% yield); ^1H NMR (300 MHz, $CDCl_3$): δ 7.5 (d, J=7.4 Hz, 1H, ArH), 7.17–6.98 (m, 3H, ArH), 2.72 (t, J=6.2 Hz, 2H, PhCH_2), 2.47–2.33 (m, 2H, $CH_2CH_2CH_2$), 1.84–1.70 (m, 2H, CH_2COH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (dd, J=294.3, 282.7 Hz, CF_2), 137.6 (d, J=6.0 Hz, C), 129.0 (CH), 127.3 (d, J=1.5 Hz, C), 127.1 (d, J=1.6 Hz, C), 126.6 (CH), 126.1 (CH), 88.2 (dd, J=23.6, 8.6 Hz, C), 30.4 (CH_2), 23.3 (t, J=2.1 Hz, CH_2), 22.2 (t, J=1.4 Hz, CH_2). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −88.5 (d, J=42.1 Hz, 1F), −88.1 (d, J=43.7 Hz, 1F). IR (neat): ν_{max} 3065w, 3025w, 2931s, 2857m, 1855m, 1713s, 1602w, 1488m, 1453m, 1350w, 1323m, 1270w, 1231s, 1160w, 1119m, 1071w, 989s, 945w, 909w, 878w, 784w, 759s, 727w, 688w cm^{-1}. EIMS: m/z (% relative intensity) 180 (M^+, 39), 159 (21), 147 (100), 129 (72), 91 (25), 77 (6).

3.5.7. 1,1-Difluoro-2,2-diphenylethene (6n).[11b] According to *general procedure B*, flash vacuum pyrolysis of sulfoxide **5n** (110.8 mg, 0.31 mmol) (conditions: oven temperature 205 °C, column temperature 425 °C; pressure 0.05 mmHg) gave a crude pyrolyzate, which was purified by chromatotron (SiO_2, hexanes) to give a colourless oil **6n** (53.6 mg, 80% yield); ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.12 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8 (t, J=291.5 Hz, CF_2), 134.3 (2×C), 129.6 (3×CH, t, J=3.3 Hz), 128.4 (4×CH), 127.5 (3×CH), 96.2 (t, J=18.0 Hz, C). ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ −88.27 (s, 2F). IR (neat): ν_{max} 3086w, 3061w, 3027w, 2927w, 2484w, 1952w, 1879w, 1810w, 1707s, 1599w, 1578w, 1541w, 1498m, 1446s, 1338w, 1323w, 1245s, 1211s, 1158w, 1075w, 1035w, 1001m, 985s, 933w, 912m, 844w, 761s, 732w, 696s, 636m, 600m, 515m cm^{-1}. EIMS: m/z (% relative intensity) 216 (100), 197 (13), 195 (11), 165 (86).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.04.015.

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