Supporting Information

Difluorophenylsulfanylmethyl Radical and Difluoromethylene Diradical Synthons: *gem*-Difluoromethylene (CF₂) Building Block

Vichai Reutrakul,* Thanchanok Thongpaisanwong, Patoomratana Tuchinda, Chutima Kuhakarn and Manat Pohmakotr*

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand

scvrt@mahidol.ac.th ; scmpk@mahidol.ac.th

Table of Contents

Preparation of bromodifluorophenylsulfanylmethane (1).....	S2
General procedures for the difluorophenylsulfanylmethane radical (2) addition....	S3-S4
Spectroscopic and analytical data of compounds 4a-4g, 5, 6.....	S4-S9
General procedure for preparation of difluorosulfoxide derivative (8).....	S9-S-10
Spectroscopic and analytical data of compounds 8a-8e.....	S10-S14
General procedure for preparation of gem-difluoroalkene derivative (9).....	S14
Spectroscopic and analytical data of compounds 9a-9e.....	S14-S17
Preparation of 1,1-difluoro-3-phenylpropyl phenyl sulfone (10).....	S17-S18
General procedure for the synthesis of 13.....	S18
Spectroscopic and analytical data of compounds 13a-d.....	S19-S21

General Methods. All reactions were performed under Argon atmosphere unless otherwise noted. Solvents were purified as follows: tetrahydrofuran (THF) and benzene were freshly distilled from sodium-benzophenone ketyl under an Argon atmosphere. Dichloromethane (CH₂Cl₂) and *N,N*-dimethylformamide (DMF) were distilled from CaH₂ under an Argon atmosphere and stored over activated molecular sieve (4A°). Reagents were obtained from commercial sources and used as received. Column chromatography was performed using silica gel 60 (5-40 µm). Radial chromatography on a chromatotron was performed with silica gel 60 PF₂₅₄ containing CuSO₄ (5-40 µm). Analytical TLC was performed with silica gel 60 PF₂₅₄ aluminium sheet with 0.2 mm layer of silica gel. ¹H NMR spectra were recorded at 300, 400 or 500 MHz in CDCl₃ solution with tetramethylsilane as an internal standard. ¹³C NMR spectra were recorded at 75, 100 or 125 MHz with residual non-deuterated solvent peak as an internal standard. ¹⁹F NMR spectra were recorded at 376 MHz with trichlorofluoromethane as an internal standard. 2D NMR experiments, i.e. COSY, HMBC and HMQC, were carried out on some compounds in order to establish signal assignments and atom connectivity. IR spectra were obtained as thin film on NaCl plates.

Preparation of bromodifluorophenylsulfanylmethane (1)

1

To a suspension of sodium hydride (3.6 g, 150.0 mmol) in DMF (200 mL), was slowly added thiophenol (10.2 mL, 100.0 mmol) at room temperature over a period of 30 min. The reaction mixture was cooled to -60 °C for 15 min before dibromodifluoromethane (28.0 mL, 300.0 mmol) was bubbled into the reaction mixture over a period of 30 min. The resulting reaction mixture was maintained at -60 °C for 3 h. The reaction flask was cooled in an ice-water bath and excess sodium hydride was quenched by dropwise addition of water (100 mL). The aqueous phase was extracted with Et₂O (3x100 mL). The combined organic layers were washed with water (3x100 mL),

brine (50 mL), dried (anh. MgSO₄). Filtration and solvent removal (aspirator) afforded a crude product that was purified by flash column chromatography on silica gel using pure hexanes as eluent. Bromodifluorophenylsulfanylmethane (**1**) (16.38 g, 69%) was obtained as a colorless liquid; analytical TLC on silica gel, hexane, R_f 0.6; ¹H NMR (300 MHz, CDCl₃): δ 7.68-7.62 (2H, m), 7.54-7.46 (1H, m), 7.45-7.37 (2H, m); ¹³C NMR (75 MHz, CDCl₃): δ 136.4, 131.1, 129.4, 127.2, 119.2 (t, ¹J_{CF} = 336.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃/CFCl₃): δ -22.49 (2F, s); IR (neat, cm⁻¹): 1062 (C-F); MS: m/z (% relative intensity) 239, 237 (M⁺, 12), 159 (100), 109 (15), 77 (25); HRMS: Molecular ion calcd for C₇H₅BrF₂S: 237.9262; found: 237.9283, error = 8 ppm.

General procedure for the difluorophenylsulfanylmethane radical (**2**) addition.

Method A: Under an argon atmosphere at 0 °C, a solution of bromodifluorophenylsulfanylmethane (**1**) (238 mg, 1.0 mmol), olefin (2.0 mmol) and *i*-PrOH (0.15 mL, 2.0 mmol) in THF (5 mL) was added to a deep blue SmI₂ (1.5 mmol) solution freshly prepared from samarium powder (40 mesh, 380 mg) and diiodomethane (0.12 mL, 1.5 mmol) in THF (20 mL). The reaction mixture was stirred for 15 min at 0 °C and allowed to warm to room temperature for an additional 2 h. The reaction mixture was quenched with saturated NaHCO₃ solution (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were washed with water (3x10 mL), brine (10 mL), dried (anh. MgSO₄) and filtered. The filtrate was evaporated (aspirator) to give the crude product, which was purified by radial chromatography.

Method B: To a refluxing solution of bromodifluorophenylsulfanylmethane (**1**) (238 mg, 1.0 mmol) and olefin (2.0 mmol) in benzene (1 mL), were simultaneously added a solution of *n*-Bu₃SnH (0.53 mL, 2.0 mmol) in benzene (2 mL) and AIBN (164 mg, 1.0 mmol) in benzene (2 mL) via syringe pump (0.06 mL/min). After the addition was completed, the reaction mixture was refluxed for 10 h. After cooling to room temperature, the solution was evaporated, diluted with saturated NaF solution (10 mL) and filtered. The aqueous layer was extracted with EtOAc (3x10 mL). The combined

organic extracts were washed with water (3x10 mL), brine (10 mL), dried (anh. MgSO₄) and filtered. The filtrate was evaporated (aspirator) to give the crude product, which was purified by radial chromatography.

Method C: To a solution of bromodifluorophenylsulfanylmethane (**1**) (238 mg, 1.0 mmol) and olefin (2.0 mmol) in CH₂Cl₂ (5 mL), were added *n*-Bu₃SnH (0.40 mL, 1.5 mmol) and Et₃B (1 M in hexane, 1.2 mL, 1.2 mmol) at room temperature. To this mixture, oxygen gas was bubbled by syringe pump (rate of addition 1.3 mL/min) over 30 min. After being stirred at room temperature overnight (16 h), the reaction mixture was diluted with a saturated solution of NaF (10 mL) and filtered. The aqueous phase was extracted with CH₂Cl₂ (3x10 mL). The combined CH₂Cl₂ extracts were washed with water (3x10 mL), brine (10 mL), dried (anh. MgSO₄), and filtered. Solvent removal (aspirator) yielded the crude product, which was purified by radial chromatography.

1,1-Difluoro-3-phenylpropyl phenyl sulfide (**4a**)

4a

Purified by radial chromatography (hexanes eluent); a colorless liquid; analytical TLC on silica gel, hexane, R_f 0.27; ¹H NMR (300 MHz, CDCl₃): δ 7.65-7.60 (2H, m, ArH), 7.45-7.32 (3H, m, ArH), 7.31-7.24 (2H, m, ArH), 7.23-7.13 (3H, m, ArH), 2.94-2.85 (2H, m, CH₂Ph), 2.47-2.30 (2H, m, CF₂CH₂); ¹³C NMR (75 MHz, CDCl₃): 139.8, 136.1, 129.8, 129.5 (t, ¹J_{CF} = 277.1 Hz, CF₂), 129.1, 128.6, 128.3, 126.9, 126.3, 40.4 (t, ²J_{CF} = 23.5 Hz, CF₂CH₂), 29.3 (t, ³J_{CF} = 3.6 Hz, CF₂CH₂CH₂); ¹⁹F NMR (376 MHz, CDCl₃/CFCl₃): δ -73.54 (2F, t, ³J_{FH} = 14.5 Hz, CF₂CH₂); IR (neat, cm⁻¹): 1167 (C-F); MS: m/z (% relative intensity) 264 (M⁺, 20), 244 (0.43), 159 (2), 110 (69), 91 (100), 77 (13); Anal. calcd for C₁₅H₁₄F₂S: C, 68.16; H, 5.34; found: C, 67.97; H, 5.74.

4,4-Difluoro-2-methyl-4-phenylsulfanylbutanenitrile (4b)

4b

Purified by radial chromatography (1:50 EtOAc/hexane eluent); a colorless liquid; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.27; ^1H NMR (300 MHz, CDCl_3): δ 7.65-7.55 (2H, m), 7.50-7.35 (3H, m), 3.10-3.03 (1H, m), 2.60 (1H, tdd, $J = 14.7, 13.3, 8.1$ Hz), 2.26 (1H, tdd, $J = 14.7, 13.3, 5.7$ Hz), 1.41 (3H, d, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 136.2, 130.2, 129.3, 127.9 (t, $^1J_{\text{CF}} = 277.4$ Hz), 125.9 (t, $^3J_{\text{CF}} = 2.4$ Hz), 121.4, 42.1 (t, $^2J_{\text{CF}} = 24.4$ Hz), 20.5 (t, $^3J_{\text{CF}} = 3.2$ Hz), 18.5; ^{19}F (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -72.99 (1F, dt, $^2J_{\text{FF}} = 203.4$ Hz, $^3J_{\text{FH}} = 14.0$ Hz), -73.68 (1F, dt, $^2J_{\text{FF}} = 203.4$ Hz, $^3J_{\text{FH}} = 14.0$ Hz); IR (neat, cm^{-1}): 2245 (CN), 1171 (C-F); MS: m/z (% relative intensity) 227 (M^+ , 56), 118 (13), 110 (100), 109 (37), 77 (11); Anal. calcd for $\text{C}_{11}\text{H}_{11}\text{F}_2\text{NS}$: C, 58.13; H, 4.88; N, 6.16; found: C, 58.15; H, 4.29; N, 6.09.

Allyl 4,4-difluoro-2-methyl-4-phenylsulfanylbutanoate (4c)

4c

Purified by radial chromatography (1:20 EtOAc/hexane eluent); a pale yellow liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.43; ^1H NMR (500 MHz, CDCl_3): δ 7.62-7.58 (2H, m, ArH), 7.42-7.38 (1H, m, ArH), 7.35-7.31 (2H, m, ArH), 5.95-5.90 (m, 1H, H'), 5.32 (1H, ddd, $J = 17.5, 2.7, 1.4$ Hz, H''), 5.24 (1H, ddd, $J = 10.4, 2.7, 1.4$ Hz, H'''), 4.59 (2H, dt, $J = 6.5$ Hz, 1.4 Hz, CO_2CH_2), 3.00-2.85 (1H, m, CH_3CHCO_2), 2.73 (1H, dddd, $J = 17.7, 15.1, 13.0, 7.7$ Hz, CF_2CH_2), 2.15 (1H, dddd, $J = 17.7, 15.1, 13.0, 5.3$ Hz, CF_2CH_2), 1.27 (3H, d, $J = 7.3$ Hz, CH_3); ^{13}C NMR (125 MHz, CDCl_3): δ 174.7,

136.2, 132.0, 129.8, 129.0, 129.0 (t, $^1J_{\text{CF}} = 277.2$ Hz, CF_2), 126.7, 118.2, 65.4, 41.8 (t, $^2J_{\text{CF}} = 23.5$ Hz, CF_2CH_2), 34.9 (t, $^3J_{\text{CF}} = 2.8$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$), 18.1; ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -72.33 (1F, ddd, $^2J_{\text{FF}} = 207.0$ Hz, $^3J_{\text{FH}} = 17.7$, 13.0 Hz, CF_2CH_2), -73.19 (1F, ddd, $^2J_{\text{FF}} = 207.0$ Hz, $^3J_{\text{FH}} = 17.7$, 13.0 Hz, CF_2CH_2); IR (neat, cm^{-1}): 1739 (C=O), 1647 (C=C), 1250 (C-O), 1177 (C-F); MS: m/z (% relative intensity) 286 (M^+ , 26), 229 (54), 177 (24), 110 (10), 109 (10); Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_2\text{S}$: C, 58.73; H, 5.63; found: C, 58.78; H, 5.77.

1,1-Difluoro-3-phenylsulfonylpropyl phenyl sulfide (4d)

4d

Purified by radial chromatography (1:20 EtOAc/hexane eluent); a white solid, m.p. = 78.6-78.8 °C; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.19; ^1H NMR (300 MHz, CDCl_3): δ 7.89 (2H, d, $J = 6.8$ Hz, ArH), 7.73-7.65 (1H, m, ArH), 7.63-7.49 (4H, m, ArH), 7.48-7.29 (3H, m, ArH), 3.40-3.30 (2H, m, $\text{CH}_2\text{SO}_2\text{Ph}$), 2.60-2.42 (2H, m, CF_2CH_2); ^{13}C NMR (75 MHz, CDCl_3): δ 138.4, 136.2, 134.1, 130.2, 129.5, 129.3, 128.0, 128.0 (t, $^1J_{\text{CF}} = 277.5$ Hz, CF_2), 125.8, 50.4 (t, $^3J_{\text{CF}} = 3.0$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$), 32.1 (t, $^2J_{\text{CF}} = 25.9$ Hz, CF_2CH_2); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -74.07 (2F, t, $^3J_{\text{FH}} = 13.8$ Hz, CF_2CH_2); IR (neat, cm^{-1}): 1322 (SO_2), 1147 (C-F); MS: m/z (% relative intensity) 328 (M^+ , 30), 219 (85), 125 (92), 110 (34), 109 (22), 77 (100); HRMS: Molecular ion calcd for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{O}_2\text{S}_2$: 328.0400; found: 328.0383, error = 5 ppm.

Methyl 4,4-difluoro-4-phenylsulfanyl-2-tributylstannylmethylbutanoate (4e)

4e

Purified by radial chromatography (hexane eluent); a colorless liquid; analytical TLC on silica gel, 1:20 EtOAc/hexane, R_f 0.41; ^1H NMR (300 MHz, CDCl_3): δ 7.65-7.55 (2H, m), 7.45-7.30 (3H, m), 3.69 (3H, s), 3.10-2.90 (1H, m), 2.85-2.70 (1H, m), 2.20-2.05 (1H, m), 1.65-1.20 (12H, m), 1.15-1.00 (2H, m), 0.93-0.70 (15H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 176.3, 136.2, 129.8, 129.1, 128.8 (t, $^1J_{\text{CF}} = 277.7$ Hz), 126.8, 52.0, 44.4 (t, $^2J_{\text{CF}} = 23.2$ Hz), 38.1, 29.1 (this resonance shows tin isotropomer satellites $^3J_{\text{Sn}} = 20.2$ Hz), 27.4 (this resonance shows tin isotropomer satellites $^2J_{\text{Sn}} = 55.3$ Hz), 13.7, 13.2, 9.3 (this resonance shows tin isotropomer satellites $^1J_{\text{Sn}} = 325.6$ Hz and 311.3 Hz); ^{19}F NMR (MHz, $\text{CDCl}_3/\text{CFCl}_3$): -72.76 (1F, ddd, $^2J_{\text{FF}} = 206.5$ Hz, $^3J_{\text{FH}} = 17.8, 12.4$ Hz), -73.52 (1F, ddd, $^2J_{\text{FF}} = 206.5$ Hz, $^3J_{\text{FH}} = 18.1, 11.7$ Hz); IR (neat, cm^{-1}): 1740 (CO), 1173 (C-F); MS: m/z (% relative intensity) 493 ($\text{M}^+ - \text{C}_4\text{H}_9$, 24), 492 (24), 491 (24), 473 (100), 448(75), 442 (41), 439 (32), 220 (44); HRMS: Molecular ion calcd for $\text{C}_{24}\text{H}_{40}\text{F}_2\text{O}_2\text{SSnNa}$: 573.1637; found: 573.1637, error = 0 ppm.

Methyl 2-(2',2'-difluoro-2'-phenylsulfanylethyl)propenoate (5)

5

Purified by radial chromatography (1:20 EtOAc/hexane eluent); a colorless liquid; analytical TLC on silica gel, 1:20 EtOAc/hexane, R_f 0.37; ^1H NMR (300 MHz, CDCl_3): δ 7.55-7.45 (2H, m), 7.40-7.20 (3H, m), 6.40 (1H, s), 5.81 (1H, s), 3.72 (3H, s), 3.16 (2H, t, $J = 14.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 166.6, 136.2, 131.7 (t, $^3J_{\text{CF}} = 3.1$ Hz), 131.2, 129.8, 129.0, 128.0 (t, $^1J_{\text{CF}} = 278.4$ Hz), 126.6, 52.2, 39.9 (t, $^2J_{\text{CF}} = 24.7$ Hz); ^{19}F NMR (MHz, $\text{CDCl}_3/\text{CFCl}_3$): -72.89 (2F, t, $^3J_{\text{FH}} = 14.4$ Hz); IR (neat, cm^{-1}): 1726 (C=O), 1635 (C=C), 1240, (C-O), 1157 (C-F); MS: m/z (% relative intensity) 257 ($\text{M}^+ - \text{H}$, 100), 238 (42), 227 (91), 211 (32), 207 (58), 200 (41); Anal. calcd for $\text{C}_{12}\text{H}_{12}\text{F}_2\text{O}_2\text{S}$: C, 55.80; H, 4.68; found: C, 55.88; H, 5.20.

1,1-Difluoro-3-butenyl phenyl sulfide (6)

6

Purified by radial chromatography (hexane eluent); a colorless liquid; analytical TLC on silica gel, hexane, R_f 0.37; ^1H NMR (300 MHz, CDCl_3): δ 7.65-7.55 (2H, m), 7.45-7.30 (3H, m), 5.86 (1H, ddt, $J = 16.9, 10.3, 7.0$ Hz), 5.32-5.18 (2H, m), 2.87 (2H, td, $J = 14.0$ Hz, 7.0 Hz, 1.4 Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 136.2, 129.8, 129.0, 128.8 (t, $^1J_{\text{CF}} = 277.5$ Hz), 128.5 (t, $^3J_{\text{CF}} = 4.3$ Hz), 126.9 (t, $^3J_{\text{CF}} = 2.1$ Hz), 120.9, 43.2 (t, $^2J_{\text{CF}} = 24.3$ Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -73.00 (2F, t, $^3J_{\text{FH}} = 14.0$ Hz); IR (neat, cm^{-1}): 1645 (C=C), 1164 (C-F); MS: m/z (% relative intensity) 296(M^+ , 32), 159 (9), 110 (100), 109 (16), 91 (21), 77 (12); HRMS: Molecular ion calcd for $\text{C}_{10}\text{H}_{10}\text{F}_2\text{S}$: 200.0469; found: 200.0477, error = 3 ppm.

1,1-Difluoro-4-(3,4'-dimethoxyphenyl)butyl phenyl sulfide (4f)

4f

Purified by radial chromatography (3:20 EtOAc/hexane eluent); a pale yellow liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.20; ^1H NMR (300 MHz, CDCl_3): δ 7.62-7.52 (2H, m, ArH), 7.44-7.30 (3H, m, ArH), 6.79 (1H, d, $J = 8.1$ Hz, ArH), 6.70 (1H, d, $J = 8.1$ Hz, ArH), 6.68 (1H, s, ArH), 3.87 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 2.60 (2H, t, $J = 7.5$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.20-2.00 (2H, m, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.00-1.85 (2H, m, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): δ 148.9, 147.4, 136.1, 133.7, 130.0 (t, $^1J_{\text{CF}} = 277.5$ Hz, CF_2), 129.6, 128.9, 127.0, 120.2, 111.7, 111.3, 55.9, 55.8, 37.9 (t, $^2J_{\text{CF}} = 23.4$ Hz, CF_2CH_2), 34.5, 24.9 (t, $^3J_{\text{CF}} = 3.0$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$); ^{19}F NMR (376

MHz, CDCl₃/CFCl₃): δ -72.64 (2F, t, $^3J_{\text{FH}} = 14.6$ Hz, CF₂); IR (neat, cm⁻¹): 1261 (C-O), 1156 (C-F), 1029 (C-O-C); MS: m/z (% relative intensity) 338 (M⁺, 79), 229 (4), 151 (100), 110 (4), 109 (4), 77(6); Anal. calcd for C₁₈H₂₀F₂O₂S: C, 63.89; H, 5.96; found: C, 64.14; H, 5.63.

12,12-Difluoro-12-phenylsulfanyldodecan-1-ol (**4g**)

4g

Purified by radial chromatography (3:20 EtOAc/hexane eluent); analytical TLC on silica gel, 3:10 EtOAc/hexane, R_f 0.28; ¹H NMR (300 MHz, CDCl₃): δ 7.64-7.56 (2H, m, ArH), 7.45-7.32 (3H, m, ArH), 3.60 (2H, t, $J = 6.6$ Hz, CH₂OH), 2.48 (1H, br s, OH), 2.20-1.98 (2H, m, CF₂CH₂), 1.65-1.50 (4H, m, CF₂CH₂CH₂ and CH₂CH₂OH), 1.42-1.30 (14H, m, CF₂CH₂CH₂(CH₂)₇); ¹³C NMR (75 MHz, CDCl₃): δ 136.1, 130.1 (t, $^1J_{\text{CF}} = 276.6$ Hz, CF₂), 129.6, 129.0, 127.2, 63.0, 38.7 (t, $^2J_{\text{CF}} = 23.3$ Hz, CF₂CH₂), 32.8, 29.53, 29.50, 29.38, 29.36, 29.2, 29.0, 25.7, 23.0 (t, $^3J_{\text{CF}} = 3.1$ Hz, CF₂CH₂CH₂); ¹⁹F NMR (376 MHz, CDCl₃/CFCl₃): δ -76.84 (2F, t, $^3J_{\text{FH}} = 11.8$ Hz, CF₂CH₂); IR (neat, cm⁻¹): 3343 (O-H), 1171 (C-F); MS: m/z (% relative intensity) 330 (M⁺, 50), 313 (0.2), 311 (0.3), 292 (0.7), 187 (1), 110 (100), 109 (16), 77 (7); Anal. calcd for C₁₈H₂₈F₂OS: C, 65.42; H, 8.54; found: C, 65.15; H 8.14.

Preparation of difluorosulfoxide derivative (**8**)

General procedure D

To a solution of **4a**, **4c**, **4d**, **4f** or **4g** in CH₂Cl₂ at 0 °C (ice-water bath), was added a solution of *m*-CPBA in CH₂Cl₂. The reaction mixture was maintained at 0 °C for 15 min and then at room temperature for 2 h. The reaction mixture was poured into a saturated sodium bicarbonate solution (50 mL). The aqueous layer was separated and

extracted with CH₂Cl₂ (3x50 mL). The combined organic extracts were washed with water (3x50 mL), brine (50 mL), dried (anh. MgSO₄) and filtered. The filtrate was evaporated (aspirator) to give the crude product.

1,1-Difluoro-3-phenylpropyl phenyl sulfoxide (8a)

Following the general procedure D, 1,1-difluoro-3-phenylpropyl phenyl sulfide (**4a**) (0.1320 g, 0.5 mmol) in CH₂Cl₂ (2 mL) and *m*-CPBA (0.1122 g, 0.65 mmol) in CH₂Cl₂ (3 mL) were employed. Purification by radial chromatography (1:20 EtOAc/hexane eluent) afforded **8a** (0.1286 g, 92%), a pale yellow liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.34; ¹H NMR (300 MHz, CDCl₃): δ 7.74-7.68 (2H, m, ArH), 7.62-7.50 (3H, m, ArH), 7.34-7.11 (5H, m), 3.00-2.75 (2H, m, CH₂Ph), 2.70-2.45 (1H, m, CF₂CH₂), 2.30-2.08 (1H, m, CF₂CH₂); ¹³C NMR (125 MHz, CDCl₃): δ 139.2, 136.9 (t, ³J_{CF} = 2.6 Hz, C_q of Ar), 132.3, 129.1, 128.6, 128.2, 127.9 (dd, ¹J_{CF} = 295.2, 284.4 Hz, CF₂), 126.5, 125.8, 31.8 (t, ²J_{CF} = 20.1 Hz, CF₂CH₂), 27.2 (t, ³J_{CF} = 4.0 Hz, CF₂CH₂CH₂); ¹⁹F NMR (376 MHz, CDCl₃/CFCl₃): δ -102.42 (1F, ddd, ²J_{FF} = 223.6 Hz, ³J_{FH} = 26.5, 11.2 Hz, CF₂CH₂), -104.78 (1F, ddd, ²J_{FF} = 223.6 Hz, ³J_{FH} = 26.5, 7.7 Hz, CF₂CH₂); IR (neat, cm⁻¹): 1189 (C-F), 1096 (S=O); MS: m/z (% relative intensity) 280 (M⁺, 3), 264 (0.51), 154 (1), 126 (84), 110 (3), 109 (6), 91 (100), 77 (22); Anal. calcd for C₁₅H₁₄F₂OS: C, 64.27; H, 5.03; found: C, 64.35; H, 4.98.

Allyl 4,4-difluoro-2-methyl-4-phenylsulfinylbutanoate (8b)

Following the general procedure D, allyl 4,4-difluoro-2-methyl-4-phenylsulfinylbutanoate (**4c**) (0.5955 g, 2.08 mmol) in CH_2Cl_2 (10 mL) and *m*-CPBA (0.5144 g, 2.29 mmol) in CH_2Cl_2 (10 mL) were employed. Purification by radial chromatography (3:20 EtOAc/hexane eluent) gave **8b** (0.4969 g, 79%) as a mixture of two diastereomers (1:1); a pale yellow liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.26; ^1H NMR (500 MHz, CDCl_3 , 1:1 of two diastereomers): δ 7.66-7.61 (2H, m), 7.56-7.47 (3H, m), 5.85-5.74 (1H, m), 5.25-5.13 (2H, m), 4.54-4.45 (2H, m), 2.85-2.68 (2H, m), 2.43-2.18 (1H, m), 1.21 (1.5H, d, $J = 7.1$ Hz), 1.18 (1.5H, d, $J = 6.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3 , 1:1 of two diastereomers): δ 174.14, 174.12, 136.8, 132.5, 131.80, 131.78, 129.14, 129.13, 127.7 (dd, $^1J_{\text{CF}} = 287.1$, 285.1 Hz), 127.6 (dd, $^1J_{\text{CF}} = 305.5$, 284.9 Hz), 125.8, 118.34, 118.30, 65.5, 65.4, 33.4, 32.97 (t, $^2J_{\text{CF}} = 19.5$ Hz), 32.93 (t, $^2J_{\text{CF}} = 19.9$ Hz), 18.1, 17.8; ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -101.08 (0.5F, ddd, $^2J_{\text{FF}} = 225.4$ Hz, $^3J_{\text{FH}} = 27.5$, 11.3 Hz), -101.73 (0.5F, ddd, $^2J_{\text{FF}} = 224.7$ Hz, $^3J_{\text{FH}} = 28.5$, 7.3 Hz, CF_2CH_2), -103.50 (0.5F, ddd, $^2J_{\text{FF}} = 224.7$ Hz, $^3J_{\text{FH}} = 30.8$, 8.1 Hz), -103.85 (0.5F, ddd, $^2J_{\text{FF}} = 225.4$ Hz, $^3J_{\text{FH}} = 27.1$, 8.1 Hz); IR (neat, cm^{-1}): 1739 (C=O), 1646 (C=C), 1192s (C-O), 1140 (C-F), 1095 (S=O); MS: m/z (% relative intensity) 303 ($\text{M}^+ + \text{H}$, 100), 245 (16), 177 (38), 125 (11); Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_3\text{S}$: C, 55.62; H, 5.33; found: C, 55.97; H, 5.86.

1,1-Difluoro-3-phenylsulfonylpropyl phenyl sulfoxide (8c)

8c

Following the general procedure D, 1,1-difluoro-3-phenylsulfonylpropyl phenyl sulfide (**4d**) (0.0835 g, 0.25 mmol) in CH₂Cl₂ (1 mL) and *m*-CPBA (0.0629 g, 0.28 mmol) in CH₂Cl₂ (2 mL) were employed. Purification by radial chromatography (1:5 EtOAc/hexane eluent) yielded **8c** (0.0672 g, 77%); a colorless liquid; analytical TLC on silica gel, R_f 0.17; ¹H NMR (500 MHz, CDCl₃): δ 7.90-7.80 (2H, m), 7.73-7.68 (1H, m), 7.67-7.55 (7H, m), 3.37 (1H, ddd, *J* = 14.0, 12.4, 4.4 Hz), 3.23 (1H, ddd, *J* = 14.0, 12.4, 4.4 Hz), 2.74-2.58 (1H, m), 2.42-2.28 (1H, m); ¹³C NMR (125 MHz, CDCl₃): δ 138.3, 136.4, 134.2, 132.8, 129.53, 129.50, 128.0, 126.6 (dd, ¹*J*_{CF} = 297.0, 284.5 Hz), 125.6, 48.6 (t, ³*J*_{CF} = 3.4 Hz), 24.4 (t, ²*J*_{CF} = 21.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃/CFC₃): δ -105.53 (1F, ddd, ²*J*_{FF} = 218.2 Hz, ³*J*_{FH} = 23.9, 13.9 Hz), -106.82 (1F, ddd, ²*J*_{FF} = 218.2 Hz, ³*J*_{FH} = 23.2, 7.4 Hz); IR (neat, cm⁻¹): 1322 (SO₂), 1149 (C-F), 1093 (S=O); MS: *m/z* (% relative intensity) 345 (M⁺+H, 6), 219 (100), 125 (40), 77 (10); Anal. calcd for C₁₅H₁₄F₂O₃S₂: C, 52.31; H, 4.10; found: C, 52.44; H, 4.42.

1,1-Difluoro-4-(3',4'-dimethoxyphenyl)butyl phenyl sulfoxide (8d)

8d

Following the general procedure D, 1,1-difluoro-4-(3',4'-dimethoxyphenyl)butyl phenyl sulfide (**4f**) (0.3184 g, 0.94 mmol) in CH₂Cl₂ (4 mL) and *m*-CPBA (0.2327 g, 1.06 mmol) in CH₂Cl₂ (6 mL) were employed. Purification of the crude product by radial

chromatography (1:5 EtOAc/hexane eluent) gave **8d** (0.2517 g, 75%); a pale yellow liquid; analytical TLC on silica gel, 2:5 EtOAc/hexane, R_f 0.24; ^1H NMR (500 MHz, CDCl_3): δ 7.63-7.58 (2H, m, ArH), 7.54-7.41 (3H, m, ArH), 6.70 (1H, d, $J = 8.0$ Hz, ArH), 6.59 (1H, d, $J = 8.0$ Hz, ArH), 6.57 (1H, s, ArH), 2.53 (2H, t, $J = 7.0$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.25-2.10 (1H, m, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.90-1.70 (3H, m, $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$ and $\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (125 MHz, CDCl_3): δ 149.0, 147.5, 136.9, 133.3, 132.2, 129.0, 128.3 (dd, $^1J_{\text{CF}} = 296.2, 284.2$ Hz, CF_2), 125.8, 120.2, 111.7, 111.5, 55.9, 55.8, 34.6, 29.5 (t, $^2J_{\text{CF}} = 20.4$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$), 22.9 (t, $^3J_{\text{CF}} = 3.3$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -102.11 (1F, ddd, $^2J_{\text{FF}} = 222.1$ Hz, $^3J_{\text{FH}} = 25.7, 13.0$ Hz, CF_2CH_2), -104.42 (1F, ddd, $^2J_{\text{FF}} = 222.1$ Hz, $^3J_{\text{FH}} = 25.7, 6.8$ Hz); IR (neat, cm^{-1}): 1261 (C-O-C), 1156 (C-F), 1029 (C-O); MS: m/z (% relative intensity) 355 ($\text{M}^+ + \text{H}$, 4), 354 (M^+ , 14), 289 (88), 209 (100), 151 (54); Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{O}_3\text{S}$: C, 61.00; H, 5.69. Found: C, 60.94; H, 5.75.

12,12-Difluoro-12-phenylsulfanyldodecan-1-ol (**8e**)

Following the general procedure D, 12,12-difluoro-12-phenylsulfanyldodecan-1-ol (**4g**) (0.0895 g, 0.27 mmol) in CH_2Cl_2 (1 mL) and *m*-CPBA (0.0670 g, 0.30 mmol) in CH_2Cl_2 (2 mL) were employed. Purification by radial chromatography (1:5 EtOAc/hexane eluent) afforded **8e** (0.0763 g, 81%); a colorless liquid; analytical TLC on silica gel, 2:5 EtOAc/hexane, R_f 0.22: ^1H NMR (500 MHz, CDCl_3): δ 7.63-7.58 (2H, m, ArH), 7.54-7.41 (3H, m, ArH), 3.55 (2H, t, $J = 6.7$ Hz, CH_2OH), 2.25-2.10 (1H, m, CF_2CH_2), 1.90-1.70 (3H, m, CF_2CH_2 and OH), 1.60-1.40 (4H, m, $\text{CF}_2\text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{CH}_2\text{OH}$), 1.30-1.20 (14H, m, $(\text{CH}_2)_7$); ^{13}C NMR (125 MHz, CDCl_3): δ 136.9, 132.2, 129.0, 128.3 (dd, $^1J_{\text{CF}} = 296.4, 284.0$ Hz, CF_2), 125.9, 30.0 (t, $^2J_{\text{CF}} = 20.3$ Hz, CF_2CH_2), 29.4, 29.37, 29.30, 29.2, 29.1, 29.0, 25.7, 21.0 (t, $^3J_{\text{CF}} = 3.2$ Hz, $\text{CF}_2\text{CH}_2\text{CH}_2$); ^{19}F NMR

(376 MHz, CDCl₃/CFCl₃): δ -102.48 (1F, ddd, $^2J_{\text{FF}} = 221.6$ Hz, $^3J_{\text{FH}} = 26.1, 12.9$ Hz, CF₂CH₂), -104.56 (1F, ddd, $^2J_{\text{FF}} = 221.6$ Hz, $^3J_{\text{FH}} = 26.1, 8.0$ Hz, CF₂CH₂); IR (neat, cm⁻¹): 3539 (O-H), 1194 (C-F), 1054 (S=O); MS: m/z (% relative intensity) 347 (M⁺+H, 5), 126 (100), 78 (52); Anal. calcd for C₁₈H₂₈F₂O₂S: C, 62.40; H, 8.14; found: C, 62.53; H, 8.20.

Preparation of *gem*-difluoroalkene derivative (**9**)

General procedure E

Difluorosulfoxide derivatives **8a**, **8b**, **8c**, **8d** or **8e** was heated at 150-160 °C *in vacuo* (0.05 mmHg) for 6 h. The alkene formed was trapped by a U-tube cooled at -78 °C (solid CO₂/acetone).

1,1-Difluoro-3-phenyl-1-propene (**9a**)

9a

According to the general procedure E, 1,1-difluoro-3-phenylpropyl phenyl sulfoxide (**8a**) (0.0700 g, 0.25 mmol) was employed to produce analytically pure **9a** (0.0294 g, 81%); a colorless liquid; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.56; ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.25 (2H, m), 7.25-7.15 (3H, m), 4.40 (1H, dtd, $J = 24.8, 8.0, 2.4$ Hz), 3.33 (2H, d, $J = 8.0$ Hz); ¹³C NMR (75 MHz, CDCl₃): δ 156.6 (dd, $^1J_{\text{CF}} = 285.8, 284.1$ Hz), 139.4, 128.6, 128.0, 126.4, 77.7 (dd, $^2J_{\text{CF}} = 23.0, 20.2$ Hz), 28.4 (d, $^3J_{\text{CF}} = 4.7$ Hz); ¹⁹F NMR (376 MHz, CDCl₃/CFCl₃): δ -89.31 (1F, d, $^2J_{\text{FF}} = 45.5$ Hz), -92.18 (1F, dd, $^2J_{\text{FF}} = 45.5$ Hz, $^3J_{\text{FH}} = 24.8$ Hz); IR (neat, cm⁻¹): 1747 (F₂C=CH); MS: m/z (% relative intensity) 154 (M⁺, 64), 135 (5), 134 (12), 91 (7), 77 (18); HRMS: Molecular ion calcd for C₉H₈F₂Na: 177.0492; found: 177.0492, error = 0 ppm.

Allyl 4,4-difluoro-2-methyl-3-butenolate (**9b**)

According to the general procedure E, allyl 4,4-difluoro-2-methyl-4-phenylsulfenylbutanoate (**8b**) (0.0755 g, 0.25 mmol) was employed to give **9b** (0.0313 g, 71%); a pale yellow liquid; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.34; ^1H NMR (300 MHz, CDCl_3): δ 5.85 (1H, ddt, $J = 17.3, 10.5, 5.6$ Hz), 5.25 (1H, ddt, $J = 17.3, 1.4, 0.8$ Hz), 5.18 (1H, ddt, $J = 10.5, 1.4, 0.8$ Hz), 4.52 (2H, dt, $J = 5.6$ Hz, 1.4 Hz), 4.32 (1H, ddd, $J = 24.5, 10.0, 2.1$ Hz), 3.30-3.20 (1H, m), 1.25 (3H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 174.0, 156.9 (dd, $^1J_{\text{CF}} = 287.4, 285.5$ Hz), 132.5, 119.0, 79.6 (dd, $^2J_{\text{CF}} = 25.4, 18.9$ Hz), 66.2, 35.0 (d, $^3J_{\text{CF}} = 5.0$ Hz), 18.7 (t, $4J_{\text{CF}} = 2.1$ Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -88.06 (1F, d, $^2J_{\text{FF}} = 42.1$ Hz), -89.17 (1F, dd, $^2J_{\text{FF}} = 42.1$ Hz, $^3J_{\text{FH}} = 24.5$ Hz); IR (neat, cm^{-1}): 1747 ($\text{F}_2\text{C}=\text{CH}$, $\text{C}=\text{O}$), 1172 ($\text{C}-\text{O}$).

1,1-Difluoro-3-phenylsulfonyl-1-propene (**9c**)

According to the general procedure E, 1,1-difluoro-3-phenylsulfonylpropyl phenyl sulfoxide (**8c**) (0.0560 g, 0.16 mmol) was employed to produce analytically pure **9c** (0.0243 g, 68%); a colorless liquid; 1:10 EtOAc/hexane, R_f 0.10; ^1H NMR (500 MHz, CDCl_3): δ 7.92 (2H, dd, $J = 7.7, 0.7$ Hz), 7.70 (1H, dd, $J = 7.7, 0.7$ Hz), 7.59 (2H, t, $J = 7.7$ Hz), 4.41 (1H, dtd, $J = 24.5, 8.3, 0.6$ Hz), 3.74 (2H, dd, $J = 8.3, 0.6$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 158.5 (t, $^1J_{\text{CF}} = 291.3$ Hz), 138.0, 134.1, 129.3, 128.4, 68.8 (dd,

$^2J_{\text{CF}} = 30.8, 18.4 \text{ Hz}$), $51.3 \text{ (t, } ^3J_{\text{CF}} = 5.8 \text{ Hz)}$; ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -81.06 (1F, d, $^2J_{\text{FF}} = 24.5 \text{ Hz}$), -84.74 (1F, t, $^2J_{\text{FF}} = 24.5 \text{ Hz}$, $^3J_{\text{FH}} = 24.5 \text{ Hz}$); IR (neat, cm^{-1}): 1746 ($\text{F}_2\text{C}=\text{CH}$), 1311 (SO_2); MS: m/z (% relative intensity) 218 (M^+ , 100), 125 (29), 77 (4); HRMS: Molecular ion calcd for $\text{C}_9\text{H}_8\text{F}_2\text{O}_2\text{SNa}$: 241.0111; found: 241.0118, error = 3 ppm.

1,1-Difluoro-4-(3',4'-dimethoxyphenyl)-1-butene (9d)

According to the general procedure E, 1,1-difluoro-4-(3',4'-dimethoxyphenyl)butyl phenyl sulfoxide (**8d**) (0.0480 g, 0.14 mmol) was employed to produce analytically pure **9d** (0.0248 g, 80%); a pale yellow liquid; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.29; ^1H NMR (400 MHz, CDCl_3): δ 6.81 (1H, d, $J = 8.0 \text{ Hz}$), 6.72 (1H, dd, $J = 8.0, 1.8 \text{ Hz}$), 6.71 (1H, d, $J = 1.8 \text{ Hz}$), 4.16 (1H, dtd, $J = 25.5, 7.7, 2.5 \text{ Hz}$), 3.89 (3H, s), 3.87 (3H, s), 2.64 (2H, t, $J = 7.7 \text{ Hz}$), 2.29 (2H, dtd, $J = 7.7, 7.7, 1.8 \text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3): δ 159.9 (t, $^1J_{\text{CF}} = 284.4 \text{ Hz}$), 149.5, 148.0, 134.2, 120.9, 112.3, 111.9, 77.9 (t, $^2J_{\text{CF}} = 21.3 \text{ Hz}$), 56.55, 56.50, 35.9 (t, $^4J_{\text{CF}} = 2.3 \text{ Hz}$), 24.8 (d, $^3J_{\text{CF}} = 4.2 \text{ Hz}$); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -89.46 (1F, d, $^2J_{\text{FF}} = 47.7 \text{ Hz}$), -91.56 (1F, dd, $^2J_{\text{FF}} = 47.7 \text{ Hz}$, $^3J_{\text{FH}} = 25.5 \text{ Hz}$); IR (neat, cm^{-1}): 1747 ($\text{F}_2\text{C}=\text{CH}$), 1261 (C-O-C), 1030 (C-O); MS: m/z (% relative intensity) 228 (M^+ , 41), 151 (100); HRMS: Molecular ion calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}_2\text{Na}$: 251.0860; found: 251.0857, error = 1 ppm.

12,12-Difluoro-11-dodecene-1-ol (**9e**)

9e

According to the general procedure E, 12,12-difluoro-12-phenylsulfinyl-1-dodecan-1-ol (**8e**) (0.0865 g, 0.25 mmol) was employed to provide analytically pure **9e** (0.0342 g, 62%); a colorless liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.34; ^1H NMR (500 MHz, CDCl_3): δ 4.12 (1H, dtd, $J = 25.7, 7.9, 2.6$ Hz), 3.64 (2H, t, $J = 6.7$ Hz), 1.99-1.91 (2H, m), 1.57 (3H, m), 1.40-1.25 (14H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 156.3 (t, $^1J_{\text{CF}} = 283.8$ Hz), 78.0 (t, $^2J_{\text{CF}} = 21.0$ Hz), 63.1, 32.8, 29.53, 29.50, 29.4, 29.3, 28.9, 25.7, 22.1 (d, $^3J_{\text{CF}} = 4.4$ Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -90.28 (1F, d, $^2J_{\text{FF}} = 49.5$ Hz), -92.69 (1F, dd, $^2J_{\text{FF}} = 49.5$ Hz, $^3J_{\text{FH}} = 25.7$ Hz); IR (neat, cm^{-1}): 3353 (O-H), 1747 ($\text{F}_2\text{C}=\text{CH}$), 1057 (C-O); MS: m/z (% relative intensity) 220 (M^+ , 6), 219 (18), 218 (100), 91 (20), 77 (10).

Preparation of 1,1-difluoro-3-phenylpropyl phenyl sulfone (**10**)

10

To a solution of 1,1-difluoro-3-(phenyl)propyl phenyl sulfide (**4a**) (0.2640 g, 1.0 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C, was added a solution of *m*-CPBA (0.5177 g, 2.1 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature overnight (16 h). The reaction mixture was poured into a saturated sodium bicarbonate solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x10 mL). The combined organic extracts were washed with water (3x10 mL), brine (10 mL), dried (anh. MgSO_4) and filtered. The filtrate was evaporated (aspirator) to

give the crude product which was purified by radial chromatography (3:20 EtOAc/hexane eluent) to produce **10** (0.2461 g, 83%); a white solid, m.p. = 84.3-84.5 °C; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.23; ^1H NMR (300 MHz, CDCl_3): δ 8.00 (2H, d, J = 7.8 Hz), 7.77 (1H, t, J = 7.8 Hz), 7.63 (2H, d, J = 7.8 Hz), 7.34-7.11 (5H, m), 2.99-2.93 (2H, m), 2.74-2.57 (2H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 139.1, 135.3, 132.4, 130.7, 129.3, 128.7, 128.3, 126.6, 124.1 (t, $^1J_{\text{CF}}$ = 284.4 Hz), 31.2 (t, $^2J_{\text{CF}}$ = 19.9 Hz), 27.1 (t, $^3J_{\text{CF}}$ = 3.8 Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -104.22 (2F, t, $^3J_{\text{FH}}$ = 18.1 Hz); IR (neat, cm^{-1}): 1189 (C-F), 1096 (S=O); MS: m/z (%relative intensity) 280 (M^+ , 3), 264 (0.51), 154 (1), 126 (84), 110 (3), 109 (6), 91 (100), 77 (22); HRMS: Molecular ion calcd for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{O}_2\text{S}$: 296.0679; found: 296.0686, error = 2 ppm.

The reaction of 1,1-difluoro-3-phenyl propylphenyl sulfone (10**) with samarium (II) iodide in the presence of various olefins**

General procedure F

In an ALDRICH AtmosBag charged with argon gas, samarium (40 mesh, 0.32 g, 2.08 mmol) was weighed into a round-bottom flask. After the flask was evacuated and flushed with argon gas (three times), anhydrous THF (3 mL) was added. The slurry of samarium powder in THF was cooled to 0 °C and CH_2I_2 (0.10 mL, 1.25 mmol) was added to give a deep blue-green solution. The mixture was stirred at 0 °C for 15 min and allowed to warm to room temperature for an additional 2 h. To a deep blue-green SmI_2 solution at 0 °C, were added a solution of 1,1-difluoro-3-phenylpropyl phenyl sulfone (**10**) (0.0740 g, 0.25 mmol), olefin (1.25 mmol), isopropanol (0.10 mL, 1.25 mmol) in THF (2 mL), followed by HMPA (1.0 mL). The reaction mixture was stirred at 0 °C for 20 min then at room temperature for an additional 2 h. Saturated sodium bicarbonate solution (10 mL) was added and organic layer was separated. The aqueous layer was extracted with EtOAc (3x20 mL). The combined EtOAc extracts were washed with water (3x20 mL), brine (20 mL), dried (anh. MgSO_4) and filtered. The filtrate was evaporated (aspirator) to give the crude product, which was purified by radial chromatography.

3,3-Difluoro-1,5-diphenylpentane (13a)

13a

According to the general procedure F, styrene (0.14 mL, 1.25 mmol) was employed to produce **13a**. Analytically pure compound **13a** (0.0483 g, 74%) was obtained from PLC (hexane eluent, 2 elutions); a colorless liquid; analytical TLC on silica gel, hexane, R_f 0.12; ^1H NMR (300 MHz, CDCl_3): δ 7.25-7.18 (4H, m), 7.17-7.07 (6H, m), 2.80-2.70 (4H, m), 2.20-2.00 (4H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 140.6, 128.6, 128.3, 126.2, 124.1 (t, $^1J_{\text{CF}} = 239.9$ Hz), 38.5 (t, $^2J_{\text{CF}} = 25.2$ Hz), 28.5 (t, $^3J_{\text{CF}} = 5.1$ Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFC}_3$): δ -99.70 (2F, quin, $^3J_{\text{FH}} = 16.0$ Hz); IR (neat, cm^{-1}): 1193 (C-F); MS: m/z (% relative intensity) 260 (M^+ , 51), 105 (15), 91 (100), 77 (11); HRMS: Molecular ion calcd for $\text{C}_{17}\text{H}_{18}\text{F}_2$: 260.1372; found: 260.1390, error = 6 ppm.

4,4-Difluoro-2-methyl-6-phenylhexanenitrile (13b)

13b

According to the general procedure F, methacrylonitrile (0.10 mL, 1.25 mmol) was employed to produce **13b**. Analytically pure compound **13b** (0.0330 g, 59%) was obtained from radial chromatography (1:50 hexane/EtOAc eluent); a colorless liquid; analytical TLC on silica gel, 1:5 EtOAc/hexane, R_f 0.42; ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.26 (2H, m), 7.25-7.15 (3H, m), 2.97-2.90 (1H, m), 2.86-2.78 (2H, m), 2.43-1.85 (4H, m), 1.41 (3H, d, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 140.0, 128.6, 128.2,

126.4, 122.7 (t, $^1J_{\text{CF}} = 241.3$ Hz), 122.1, 40.5 (t, $^2J_{\text{CF}} = 25.4$ Hz), 38.7 (t, $^2J_{\text{CF}} = 24.6$ Hz), 28.2 (t, $^3J_{\text{CF}} = 5.1$ Hz), 19.5 (t, $^3J_{\text{CF}} = 4.4$ Hz), 18.8; ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -98.59 (1F, m), -99.72 (1F, m); IR (neat, cm^{-1}): 2244 (CN), 1179 (C-F); MS: m/z (% relative intensity) 223 (M^+ , 41), 222 (35), 208 (8), 105 (10), 91 (100), 77 (7); HRMS: Molecular ion calcd for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{N}$: 223.1169; found: 223.1166, error = 1 ppm.

Methyl 4,4-difluoro-2-methyl-6-phenylhexanoate (13c)

According to the general procedure F, methyl methacrylate (0.13 mL, 1.25 mmol) was employed to produce **13c**. Analytically pure compound **13c** (0.0345 g, 54%) was obtained from radial chromatography (1:20 hexane/EtOAc eluent); a colorless liquid; analytical TLC on silica gel, 1:10 EtOAc/hexane, R_f 0.48; ^1H NMR (300 MHz, CDCl_3): δ 7.40-7.15 (5H, m), 3.70 (3H, s), 2.86-2.77 (3H, m), 2.55-2.36 (1H, m), 2.21-2.04 (2H, m), 1.97-1.79 (1H, m), 1.25 (3H, d, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 176.3, 140.5, 128.5, 128.2, 126.2, 123.8 (t, $^1J_{\text{CF}} = 240.3$ Hz), 51.9, 40.0 (t, $^2J_{\text{CF}} = 24.8$ Hz), 38.8 (t, $^2J_{\text{CF}} = 25.0$ Hz), 33.9 (t, $^3J_{\text{CF}} = 3.1$ Hz), 28.3 (t, $^3J_{\text{CF}} = 5.1$ Hz), 18.4; ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -88.92 (1F, m), -100.27 (1F, m); IR (neat, cm^{-1}): 1738 (C=O), 1166 (C-F); MS: m/z (% relative intensity) 256 (M^+ , 0.32), 236 (31), 205 (7), 154 (6), 91 (100), 77 (6); HRMS: Molecular ion calcd for $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}_2 + \text{NH}_4$: 274.1619; found: 274.1616, error = 1 ppm.

3,3-Difluoro-1,6-diphenylhexane (**13d**)

13d

According to the general procedure F, allyl benzene (0.16 mL, 1.25 mmol) was employed to produce **13d**. Analytically pure compound **13d** (0.0147 g, 21%) was obtained from radial chromatography (hexane eluent); a colorless liquid; analytical TLC on silica gel, hexane, R_f 0.21; ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.13 (10H, m), 2.80-2.74 (2H, m), 2.65 (2H, t, $J = 7.1$ Hz), 2.20-2.07 (2H, m), 1.90-1.81 (4H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 141.4, 140.7, 128.5, 128.41, 128.40, 128.3, 126.2, 126.0, 124.6 (t, $^1J_{\text{CF}} = 239.7$ Hz), 38.3 (t, $^2J_{\text{CF}} = 25.4$ Hz), 36.0 (t, $^2J_{\text{CF}} = 25.2$ Hz), 35.4, 28.4 (t, $^3J_{\text{CF}} = 5.1$ Hz), 24.0 (t, $^3J_{\text{CF}} = 4.6$ Hz); ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -99.10 (2F, quin, $^3J_{\text{FH}} = 15.9$ Hz); IR (neat, cm^{-1}): 1154 (C-F); MS: m/z (% relative intensity) 274 (M^+ , 28), 254 (2), 105 (10), 104 (57), 91 (100), 77 (4); HRMS: Molecular ion calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2$: 274.1528; found: 274.1520, error = 2 ppm.