Supporting Information
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Supporting Information

for

Copper-mediated fluoroalkylation reactions with [(Phenylsulfonyl)difluoromethyl]trimethylsilane: synthesis of PhSO₂CF₂-containing allenes and alkynes

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General Remarks…S2
Preparation of PhSO₂CF₂SiMe₃ 1………………………………………………………………………………………………………...S2–S3
Reaction between compound 1 and propargylic derivatives 3…………………………………S3–S5
Reaction between compound 1 and alkynyl halides 5…………………………………………S5–S8
preparation of compound 8…………………………………………………………………………………………………………..S8
preparation of compound 12………………………………………………………………………………………………………S9
References………………………………………………………………………………………………………………………S9
NMR spectra for isolated products……………………………………………………………………………………………………S10–S51
**General Remarks:** Unless otherwise mentioned, all chemicals were purchased from commercial sources. THF was freshly distilled over sodium. Anhydrous DMF (containing molecular sieves) was distilled over CaH$_2$. Silica gel (300–400 mesh) was used for column chromatography. All the melting points were uncorrected. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a 400-MHz or 300-MHz NMR spectrometer. $^1$H NMR chemical shifts were determined relative to internal (CH$_3$)$_4$Si (TMS) at δ 0.0 or to the signal of a residual protonated solvent: CDCl$_3$ δ 7.26. $^{13}$C NMR chemical shifts were determined relative to internal TMS at δ 0.0. $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ at δ 0.0. Chemical shifts are reported in ppm. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI, ESI.

1. **Preparation of PhSO$_2$CF$_2$SiMe$_3$ 1**

Under N$_2$ atmosphere, $n$-butyllithium in hexane (1.6 M, 20.2 mL, 33.1 mmol) was added into the solution of bromodifluoromethyl phenyl sulfone (5.0 g, 18.2 mmol) and chlorotrimethylsilane (3.7 mL, 27.6 mmol) in THF (60 mL) at −78 °C, and the mixture was stirred for 1 h at the same temperature. Then the reaction was quenched with cold 1M HCl aqueous solution, and the reaction mixture was extracted with Et$_2$O (50 mL, 3 times). The combined organic phase was washed with brine, and water, and then dried over anhydrous Na$_2$SO$_4$. After solvent removal, the crude product was fractionally distilled to afford 3.9 g (78% yield) of product 1 as a colorless liquid, b.p. 96–97 °C/1 mmHg. $^1$H NMR (CDCl$_3$): δ 7.96 (d, $J = 8.0$ Hz, 2H); 7.74 (t, $J = 7.5$ Hz, 1H); 7.60 (t, $J = 7.5$ Hz, 2H); 0.42 (s, 9H). $^{19}$F NMR (CDCl$_3$): δ −111.5 (s). The data are consistent with the previous report.$^1$
2. Reaction between compound 1 and propargylic chloride derivatives 3

![Chemical structure of reaction]

Under N₂ atmosphere, into a 10-mL Schlenk flask, was added CuI (48 mg, 0.25 mmol), CsF (36 mg, 0.27 mmol) and DMF (1.5 mL). The reaction mixture was cooled to −30 °C, and PhSO₂CF₂SiMe₃ (67 mg, 0.25 mmol; dissolved in 1 mL of DMF) was added into the solution. After the reaction mixture was stirred at −30 °C for 4 h, 3-chloro-3-methylbut-1-yne (dissolved in 1 mL of DMF) was added into the solution, and then the temperature was raised to 0 °C. The whole reaction mixture was stirred at 0 °C for additional 16 h, and then was quenched by adding H₂O (10 mL) and extracted with Et₂O (10 mL) three times. The combined organic phase was washed with H₂O, and dried over anhydrous Na₂SO₄. After filtration and solvent removal, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate, 30:1 v/v) to give product (1,1-difluoro-4-methylpenta-2,3-dienylsulfonyl)benzene 4a (39 mg, 60% yield) as a yellow liquid. ¹H NMR (CDCl₃, 300 MHz): δ 7.93–7.91 (d, J = 7.8 Hz 2H), 7.69–7.64 (t, J = 7.8 Hz 1H), 7.55–7.53 (t, J = 7.5 Hz 2H), 5.35–5.22 (m, 1H), 1.68–1.67 (d, J = 2.7 Hz 6H); ¹³C NMR (CDCl₃, 75 MHz): δ 207.1, 135.1, 130.7, 129.2, 120.0 (t, J = 217.5 Hz), 103.5, 80.3 (t, J = 20.3 Hz), 19.3; IR (Film): 2917, 1974, 1585, 1450, 1340, 1166, 1097 cm⁻¹; MS (EI, m/z, %) 259 (M+H⁺, 0.85), 77 (100.00), 117 (96.34), 133 (67.98), 97 (59.19); HRMS (EI) calcd. For C₁₂H₁₂F₂O₂S (M⁺) 258.0526; Found: 258.0526.

(1,1-Difluoro-4-methylhexa-2,3-dienylsulfonyl)benzene (4b)

63% yield, liquid. ¹H NMR (CDCl₃, 300 MHz): δ 8.02–8.00 (d, J = 7.8 Hz 2H), 7.75–7.73 (t, J = 7.7 Hz 1H), 7.64–7.62 (t, J = 7.5 Hz 2H), 5.56–5.54 (m, 1H), 2.05–2.04 (d, J = 3.1 Hz 2H), 1.78–1.77 (d, J = 3.2 Hz 3H), 1.06–1.02 (t, J = 12.2 Hz 3H); ¹⁹F NMR (CDCl₃, 270 MHz): δ −99.7 (d, J = 10.7 Hz 2F); ¹³C NMR (CDCl₃, 75 MHz): δ 207.1, 135.1, 130.7, 129.2, 120.0 (t, J = 217.5 Hz), 103.5, 80.3 (t, J = 20.3 Hz), 19.3; IR (Film): 2917, 1974, 1585, 1450, 1340, 1166, 1097 cm⁻¹; MS (EI, m/z, %) 259 (M+H⁺, 0.85), 77 (100.00), 117 (96.34), 133 (67.98), 97 (59.19); HRMS (EI) calcd. For C₁₂H₁₂F₂O₂S (M⁺) 258.0526; Found: 258.0526.
MHz): δ –99.3 (dd, J = 220 Hz, J = 11.1 Hz 1F), –98.1 (dd, J = 220 Hz, J = 12.2 Hz 1F); 13C NMR (CDCl₃, 75 MHz): δ 206.5, 135.1, 133.1, 130.7, 129.1, 117.2 (t, J = 210.2 Hz), 109.7, 82.0 (t, J = 20.3 Hz), 30.3, 17.8, 11.7; IR (Film): 2966, 1971, 1585, 1450, 1346, 1261, 1093 cm⁻¹; MS (EI, m/z, %) 91 (100.00), 147 (54.90), 77 (47.71), 111 (40.21); HRMS (EI) calcd. For C₁₃H₁₄F₂O₂S (M⁺) 272.0683; Found: 272.0683.

(4,4-Difluoro-4-(phenylsulfonyl)buta-1,2-dienyl)benzene (4c)

64% yield, pale yellow liquid. ¹H NMR (CDCl₃, 300 MHz): δ 7.95–7.92 (d, J = 7.7 Hz 2H), 7.67–7.65 (t, J = 7.6 Hz 1H), 7.53–7.50 (t, J = 7.3 Hz 2H), 7.23–7.16 (m, 5H), 6.61–6.58 (m, 1H), 6.02–5.88 (m, 1H); ¹⁹F NMR (CDCl₃, 270 MHz): δ –99.9 (d, J = 216.1 Hz, 1F), –98.7 (d, J = 216.1 Hz, 1F); ¹³C NMR (CDCl₃, 75 MHz): δ 242.1, 167.1, 162.5, 161.1, 160.6, 160.3, 159.5 (t, J = 217.5 Hz), 132.7, 118.1 (t, J = 22.5 Hz); IR (Film): 3065, 1960, 1730, 1448, 1308, 1093 cm⁻¹; MS (EI, m/z, %) 306 (M⁺, 2.76), 181 (100.00), 115 (61.67), 164 (54.97), 165 (42.78); HRMS (EI) calcd. For C₁₆H₁₂F₂O₂S (M⁺) 306.0526; Found: 306.0526.

(6,6-Difluoro-3-methyl-6-(phenylsulfonyl)hexa-3,4-dienyl)benzene (4d)

56% yield, colourless liquid. ¹H NMR (CDCl₃, 300 MHz): δ 7.92–7.90 (d, J = 7.8 Hz 2H), 7.64–7.61 (t, J = 7.7 Hz 1H), 7.53–7.51 (t, J = 7.5 Hz 2H), 7.22–7.09 (m, 5H), 5.39–5.33 (m, 1H), 2.28–2.25 (t, J = 9.3 Hz 2H), 1.71–1.70 (d, J = 2.4 Hz 3H); ¹⁹F NMR (CDCl₃, 270 MHz): δ –99.5 (dd, J = 221.2 Hz, J = 11.2 Hz 1F), –98.5 (dd, J = 221.2 Hz, J = 10.7 Hz 1F); ¹³C NMR (CDCl₃, 75 MHz): δ 206.6, 141.1, 135.0, 132.9, 130.6, 129.1, 128.2, 122.7 (t, J = 240.1 Hz), 107.5, 82.0 (t, J = 21.5 Hz), 33.3, 30.2, 17.9; IR (Film): 3029, 1971, 1585, 1497, 1449, 1344, 1166 cm⁻¹; MS (ESI, m/z) 366 (M+NH₄⁺); HRMS (ESI) calcd. For C₁₉H₁₈F₂O₂SNa (M+Na⁺) 371.0893; Found: 371.0888.
(3-Cyclohexylidene-1,1-difluoroallylsulfonyl)benzene (4e)

42% yield, pale yellow liquid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.01–7.99 (d, $J =$ 7.7 Hz 2H), 7.74–7.72 (t, $J =$ 7.6 Hz 1H), 7.63–7.58 (t, $J =$ 7.2 Hz 2H), 5.46–5.37 (m, 1H), 2.17–2.13 (m, 4H), 1.61–1.52 (m, 6H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –99.6 (d, $J =$ 7.4 Hz, 2F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 134.8, 133.1, 131.2, 129.5, 119.9, 109.8, 79.8 (t, $J =$ 20.1 Hz), 29.9, 26.6, 25.4; IR (Film): 2935, 1971, 1585, 1497, 1449, 1346, 1163 cm$^{-1}$; MS (ESI, m/z) 316 (M+NH$_4^+$); HRMS (ESI) calcd. For C$_{15}$H$_{16}$F$_2$O$_2$SNa (M+Na$^+$) 321.0737; Found: 321.0731.

3. Reaction between compound 1 and alkynyl halides 6

Under N$_2$ atmosphere, into a 10-mL Schlenk flask, was added CuI (48 mg, 0.25 mmol), CsF (36 mg, 0.27 mmol) and DMF (1.5 mL). The reaction mixture was cooled to –30 °C, and PhSO$_2$CF$_2$SiMe$_3$ (67 mg, 0.25 mmol; dissolved in 1 mL of DMF) was added into the solution. The solution was stirred at –30 °C for 4 h, and (iodoethyl)benzene (dissolved in 1 mL of DMF) was added into the solution. Then the temperature was raised to 0 °C, and the reaction mixture was stirred for additional 16 h. Thereafter, the reaction mixture was quenched by adding H$_2$O (10 mL) and extracted with Et$_2$O (10 mL) three times. The combined organic phase was washed with H$_2$O, and dried over anhydrous Na$_2$SO$_4$. After filtration and solvent removal, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate, 20:1 v/v) to give product (3,3-difluoro-3-(phenylsulfonyl)prop-1-ynyl)benzene 6a (79% yield) as a colorless liquid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.99–7.29 (m, 10H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –88.8 (s, 2F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 135.8, 132.6, 132.1, 131.1, 129.5, 128.6, 113.7 (t, $J =$ 195.5 Hz), 94.7, 77.0 (t, $J =$ 24.1 Hz); IR (Film): 3069, 2231, 1583, 1448, 1351, 1298, 1171 cm$^{-1}$; MS (EI, m/z, %) 151 (100.00), 77 (34.63), 141 (13.51), 51 (12.99); HRMS (EI) calcd. For C$_{15}$H$_{10}$F$_2$O$_2$S (M$^+$) 292.0370; Found: 292.0370.
1-(3,3-Difluoro-3-(phenylsulfonyl)prop-1-ynyl)-4-fluorobenzene (6b)

58%, white solid. M.P. 56-58°C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.99–7.97 (d, $J = 7.7$ Hz 2H), 7.74–7.72 (t, $J = 7.6$ Hz 1H), 7.59–6.99 (m, 6H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –88.6 (s, 2F), –105.1 (d, $J = 3.9$ Hz 1F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 162.9 (d, $J = 195$ Hz), 135.8, 135.1, 131.1, 129.6, 116.1, 93.5, 74.1 (t, $J = 26.3$ Hz); IR (Film): 2236, 1600, 1507, 1451, 1347, 1235, 1149 cm$^{-1}$; MS (ESI, $m/z$) 333 (M+Na$^+$); HRMS (ESI) calcd. For C$_{15}$H$_9$F$_3$O$_2$SNa (M+Na$^+$) 333.0173; Found: 333.0168.

1,1-Difluorohept-2-ynylsulfonyl)benzene (6c)

82%, Colourless liquid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.94–7.54 (m, 5H), 2.11–0.81 (m, 9H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –87.5 (s, 2F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 136.1, 133.1, 129.6, 113.0 (t, $J = 202.5$ Hz), 98.1, 66.5, 29.6, 21.8, 18.5, 13.4; IR (Film): 2936, 2244, 1585, 1450, 1352, 1243, 1172 cm$^{-1}$; MS (ESI, $m/z$) 295 (M+Na$^+$); HRMS (ESI) calcd. For C$_{13}$H$_{14}$F$_2$O$_2$SNa (M+Na$^+$) 295.0580; Found: 295.0575.

1,1-Difluoroundec-2-ynylsulfonyl)benzene (6d)

59%, Colourless liquid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.95–7.93 (d, $J = 7.7$ Hz 2H), 7.69–7.67 (t, $J = 7.6$ Hz 1H), 7.56–7.52 (t, $J = 7.2$ Hz 2H), 2.31–2.28 (t, $J = 5.4$ Hz 2H), 1.53–0.81 (m, 15H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –87.5 (t, $J = 6.1$ Hz 2F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 135.5, 132.1, 131.0, 129.3, 113.0 (t, $J = 204.1$ Hz), 98.1, 66.5 (t, $J = 27.1$ Hz).
Hz), 31.7, 28.9, 28.7, 27.2, 22.6, 18.8, 14.1; IR (Film): 2926, 2242, 1584, 1449, 1352, 1288, 1171 cm⁻¹; MS (ESI, m/z) 346 (M+NH₄⁺); HRMS (ESI) calcd. For C₁₇H₂₂F₂O₃Na (M+Na⁺) 351.1206; Found: 351.1201.

![Chemical structure of 3-Cyclohexyl-1,1-difluoroprop-2-ynylsulfonyl]benzene (6e)

67%, Colourless liquid. ¹H NMR (CDCl₃, 300 MHz): δ 7.95–7.93 (d, J = 7.8 Hz 2H), 7.73–7.67 (t, J = 7.5 Hz 1H), 7.60–7.54 (t, J = 7.4 Hz 2H), 2.53–2.51 (m, 1H), 1.74–1.27 (m, 10H); ¹⁹F NMR (CDCl₃, 270 MHz): δ –87.6 (s, 2F); ¹³C NMR (CDCl₃, 75 MHz): δ 136.1, 131.0, 129.2, 113.1 (t, J = 204.8 Hz), 101.4, 66.7 (t, J = 26.3 Hz); IR (Film): 2934, 2858, 2239, 1583, 1478, 1350, 1242 cm⁻¹; MS (ESI, m/z) 321 (M+Na⁺); HRMS (ESI) calcd. For C₁₅H₁₆F₂O₂SNa (M+Na⁺) 321.0737; Found: 321.0731.

![Chemical structure of 4-(Benzyloxy)-1,1-difluorobut-2-ynylsulfonyl]benzene (6f)

45%, pale yellow liquid. ¹H NMR (CDCl₃, 300 MHz): δ 8.04–8.01 (d, J = 7.8 Hz 2H), 7.80–7.76 (t, J = 7.5 Hz 1H), 7.64–7.59 (t, J = 7.4 Hz 2H), 7.37–7.36 (m, 5H), 4.63–4.62 (d, J = 2.4 Hz 2H), 4.63–4.62 (t, J = 3.6 Hz 2H); ¹⁹F NMR (CDCl₃, 270 MHz): δ –99.6 (d, J = 7.4 Hz, 2F); ¹³C NMR (CDCl₃, 75 MHz): δ 136.3, 131.7, 131.1, 129.4, 128.2, 112.8 (t, J = 210 Hz), 91.8, 72.2, 56.5; IR (Film): 3066, 2237, 1583, 1449, 1352, 1229, 1171 cm⁻¹; MS (ESI, m/z) 354 (M+NH₄⁺); HRMS (ESI) calcd. For C₁₇H₁₄F₂O₃Na (M+Na⁺) 359.0529; Found: 359.0524.
(4,4-Difluoro-4-(phenylsulfonyl)but-2-ynyl)benzene (6g)

62%, pale yellow liquid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.91–7.24 (m, 10H), 3.73–3.70 (s, 2H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –88.4 (d, $J = 3.6$ Hz, 2F); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 135.8, 133.1, 132.1, 130.6, 128.8, 128.0, 127.4, 115.7 (td, $J = 210.5$ Hz, $J = 76.1$ Hz), 95.1, 68.8 (t, $J = 26.3$ Hz), 25.1; IR (Film): 3441, 3067, 2917, 2245, 1602, 1496, 1449 cm$^{-1}$; MS (ESI, m/z) 329 (M+Na$^+$); HRMS (ESI) calcd. For C$_{16}$H$_{12}$F$_2$O$_2$SNa (M+Na$^+$) 329.0424; Found: 329.0418.

4. Preparation of compound 8

Under N$_2$ atmosphere, into a 10-mL Schlenk flask, was added Mg (6 mg, 0.25 mmol), HgCl$_2$ (3 mg, 0.01 mmol) and DMF (1.5 mL) at rt. The mixture was stirred at rt for 20 min, then cooled to –10 °C. 4-MeOPhCH=O (68 mg, 0.5 mmol) and 6a (58 mg, 0.2 mmol) were dissolved in DMF (1.0 mL) and added into the above solution. The temperature was raised to rt in a period of 3 h. The reaction mixture was quenched by adding HCl (1M, 2 mL) and extracted with Et$_2$O (10 mL) three times. The combined organic phase was washed with H$_2$O, and dried over anhydrous Na$_2$SO$_4$. After filtration and solvent removal, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate, 10:1 v/v) to give product 2,2-difluoro-1-(4-methoxyphenyl)-4-phenylbut-3-yn-1-ol 8 (37 mg; 65% yield) as a white solid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.52–7.29 (m, 7H), 6.94–6.91 (d, $J = 9.1$ Hz 2H), 5.05–4.95 (m, 1H), 3.83 (s, 3H), 2.68–2.61 (m, 1H); $^{19}$F NMR (CDCl$_3$, 270 MHz): $\delta$ –93.6 (dd, $J = 267.1$ Hz, $J = 7.2$ Hz 1F), –92.1 (dd, $J = 267.1$ Hz, $J = 7.5$ Hz 1F). The data are consistent with the previous report.$^2$
5. Preparation of compound 12

Under N₂ atmosphere, into a 10-mL Schlenk flask was added CuCl₂ (26 mg, 0.25 mmol), CsF (36 mg, 0.27 mmol) and DMF (1.5 mL). The reaction mixture was cooled to −30 °C, and PhSO₂CF₂SiMe₃ [67 mg, 0.25 mmol; dissolved in DMF (1.0 mL)] was added into the solution. The reaction mixture was kept at −30 °C for 4 h, followed by stirring at 0 °C for additional 16 h. The reaction mixture was quenched by adding H₂O (10 mL), and extracted with Et₂O (10 mL) three times. The combined organic phase was washed with H₂O, and dried over anhydrous MgSO₄. After filtration and solvent removal, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate, 40:1 v/v) to give product (chlorodifluoromethylsulfonyl)benzene 12 (34 mg, 60% yield). ¹H NMR (CDCl₃): δ 7.98 (d, J = 7.2 Hz, 2H); 7.77 (t, J = 7.1 Hz, 1H); 7.61 (t, J = 7.5 Hz, 2H). ¹⁹F NMR (CDCl₃): δ −63.4 (s). The data are consistent with the previous report.³

References

NMR spectra for isolated products

\[
\text{SO} \quad \text{CF}_2 \text{TMS}
\]

\( ^1\text{H MNR CDCl}_3 \)
$\text{SO}_2\text{CF}_2\text{TMS}$

( $^{19}$F NMR CDCl$_3$)
\[ \text{\textsuperscript{1}H NMR (CDCl	extsubscript{3})} \]
(19F NMR CDCl3)
$^{1}H$ NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)