Supporting Information

Nucleophilic perfluoroalkylation of aldehydes, ketones, imines, disulfides and diselenides

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Table of Contents

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General Experimental Methods

NMR spectra were recorded at 300 MHz for ^{1}H, at 75 MHz for ^{13}C, and at 282 MHz for ^{19}F NMR spectra, respectively. All spectra were obtained at room temperature in $CDCl_3$ using tetramethylsilane (TMS), $CFCl_3$ and TMS as internal standards, ^{1}H, ^{19}F, and ^{13}C NMR spectra, respectively. TDAE was prepared by a published procedure (with some modification),[1] *N*-tosyl aldimines were prepared according to the previous literature.[2]

Characterization data for other products from aldehyde or ketone addition

1,1,1,2,2-Pentafluoro-5-(2-methoxy-phenyl)-pent-4-en-3-ol (2c): ^{1}H NMR, δ 7.45 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.31 (m, 1H), 7.25 (d, J = 16.2 Hz, 1H), 6.95 (m, 1H), 6.87 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 6.27 (dd, J_1 = 16.2, Hz, J_2 = 7.1 Hz, 1H), 4.66 (m, 1H), 3.87 (s, 3H), 2.26 (s, 1H); ^{19}F NMR, δ -81.40 (m, 3F), -122.25 (AB, dd, J_1 = 291 Hz, J_2 = 9.9 Hz, 1F), -129.12 (dd, J_1 = 291 Hz, J_2 = 9.9 Hz, 1F); Anal. Calcd for $C_{12}H_{10}F_5O_2$: C, 51.25; H, 3.56; N, 0.0. Found: C, 51.18; H, 3.51; N, 0.0.

1,1-Diphenyl-2,2,3,3,3-pentafluoropropan-1-ol (2e):[3] ^{19}F NMR, δ -84.65 (s, 3F), -115.97 (s, 2F).

Pentafluoroethyl cyclohexan-1-ol (2f):[4] ^{19}F NMR, δ -78.17 (s, 3F), -126.25 (s, 2F).

1,1,1,2,2-Pentafluorohexan-3-ol (2g):[5,6] ^{19}F NMR, δ -81.57 (m, 3F), -122.75 (m, 1F), -131.40 (m, 1F).

Characterization data for other products from imine addition

4-Methyl-*N*-[3,3,3,2,2-pentafluoro-(4-fluoro-phenyl)-propyl]-benzenesulfonamide (5d): White solid (72 % yield); mp 151-152 ^{o}C; ^{1}H NMR, δ 7.52 (d, J = 8.4 Hz, 2H), 7.12 (m, 4H), 6.92 (t, J = 8.4 Hz, 2H), 5.37 (d, J = 9.3 Hz, 1H), 4.98 (m, 1H); 2.36 (s, 3H); ^{19}F NMR, δ -81.39 (s, 3F), -111.84 (m, 1F), -120.60 (dd, J_1 = 291.3 Hz, J_2 = 11.1 Hz, 1F), -123.19 (dd, J_1 = 293.7 Hz, J_2 = 13.5 Hz, 1F); Anal. Calcd for $C_{16}H_{13}F_6NO_2S$: C, 48.36; H, 3.27; N, 3.53. Found: C, 48.26; H, 3.27; N, 3.33.

4-Methyl-*N*-[3,3,3,2,2-pentafluoro-(4-trifluoromethyl-phenyl)-propyl]-benzenesulfonamide (5e): White solid (68 % yield); mp 155-156 ^{o}C; ^{1}H NMR, δ 7.47 (d, J = 6.1 Hz, 2H), 7.45 (d, J = 6.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 5.65 (d, J = 9.9 Hz, 1H), 5.05 (m, 1H), 2.31 (s, 3H); ^{19}F NMR, δ -63.54 (s, 3F), -81.41 (s, 3H), -119.54 (dd, J_1 = 292.5 Hz, J_2 = 14.4 Hz, 1F), -123.91 (dd, J_1 = 292.5 Hz, J_2 = 14.4 Hz, 1F); Anal. Calcd for $C_{17}H_{13}F_8NO_2S$: C, 45.64; H, 2.91; N, 3.13. Found: C, 45.34; H, 2.83; N, 3.01.

4-Methyl-*N*-[3,3,3,2,2-pentafluoro-(2-thiophenyl)-propyl]-benzenesulfonamide (5f): 55 % yield; ^{1}H NMR, δ 7.58 (d, J = 8.4 Hz, 2H), 7.25 (m, 1H), 7.17 (d, J = 8.4 Hz, 2H), 6.88 (m, 2H), 5.34 (m, 1H), 5.02 (m, 1H) 2.38 (s, 3H); ^{19}F NMR, δ -82.3 (s, 3F), -120.7 (dd, J_1 = 289.2 Hz, J_2 = 11.1 Hz, 1F), -123.4 (dd, J_1 = 289.2 Hz, J_2 = 11.1 Hz, 1F); Anal. Calcd for $C_{14}H_{12}F_5NO_2S_2$: C, 43.64; H, 3.12; N, 3.64. Found: C, 43.58; H, 3.10; N, 3.62.

4-Methyl-*N*-[3,3,3,2,2-pentafluoro-(2-furanyl)-propyl]-benzenesulfonamide (5g): Light brown solid (60 % yield); mp 150-151 ^{o}C; ^{1}H NMR, δ 7.60 (d, J = 8.4 Hz, 2H), 7.19 (m, 3H), 6.21 (m, 2H), 5.33 (d, J = 10.2 Hz, 1H), 5.11 (m, 1H), 2.38 (s, 3H); ^{19}F NMR, δ -82.0 (s, 3F), -120.7 (dd, J_1 = 291.3 Hz, J_2 = 13.2 Hz, 1F), -122.3 (dd, J_1 = 289.2

Hz, J_2 = 13.1 Hz, 1F); Anal. Calcd for $C_{14}H_{12}F_5NO_3S$: C, 45.53; H, 3.25; N, 3.79. Found: C, 45.25; H, 3.26; N, 3.75.

4-Methyl-*N*-[5,5,5,4,4,3,3,2,2-nonafluoro-(4-fluorophenyl)-propyl]-benzenesulfonamide (6c): White solid (70% yield); mp 143-144 ^oC; ^1H NMR, δ 7.49 (d, J = 8.4 Hz, 2H), 7.09 (m, 4H), 6.89 (m, 2H), 5.40 (d, J = 9.3 Hz, 1H), 5.07 (m, 1H), 2.33 (s, 3H); ^{19}F NMR, δ -81.4 (t, J = 9 Hz, 3F), -111.9 (m, 1F), -116.7 (dm, J_1 = 297.9 Hz, 1F), -119.3 (d, J_1 = 297.9 Hz, 1F), -121.4 (m, 2F), 126.5 (m, 2F); Anal. Calcd for $C_{18}H_{13}F_{10}NO_2S$: C, 43.46; H, 2.62; N, 2.82. Found: C, 43.67; H, 2.54; N, 2.72.

4-Methyl-*N*-[5,5,5,4,4,3,3,2,2-nonafluoro-(4-trifluoromethylphenyl)-propyl]-benzenesulfonamide (6d): White solid (75 % yield); mp 157-158 ^oC; ^1H NMR, δ 7.47 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 5.99 (d, J = 10.2 Hz, 1H), 5.16 (m, 1H); 2.31 (s, 3H); ^{19}F NMR, δ -63.6 (s, 3F), -81.4 (t, J = 11.1 Hz, 3F), -115.8 (dm, J = 304.5 Hz, 1F), -119.8 (dm, J = 304.5 Hz, 1F), -121.3 (m, 2F), 126.5 (m, 2F); Anal. Calcd for $C_{19}H_{13}F_{12}NO_2S$: C, 41.65; H, 2.38; N, 2.56. Found: C, 41.75; H, 2.30; N, 2.55.

4-Methyl-*N*-[5,5,5,4,4,3,3,2,2-nonafluoro-(2-thiophenylphenyl)-propyl]-benzenesulfonamide (6e): 45 % yield; ^1H NMR, δ 7.57 (d, J = 8.1 Hz, 2H), 7.23 (m, 1H), 7.14 (d, J = 8.1 Hz, 2H), 6.90 (m, 1H), 6.83 (m, 1H), 5.42 (m, 2H), 2.36 (s, 3H); ^{19}F NMR, δ -81.4 (t, J = 11.1 Hz, 3F), -116.7 (dm, J = 297.9 Hz, 1F), -119.2 (dm, J = 297.9 Hz, 1F, -121.5 (m, 2F), 126.5 (m, 2F); Anal. Calcd for $C_{16}H_{12}F_9NO_2S_2$: C, 39.56; H, 2.47; N, 2.88. Found: C, 39.57; H, 2.42; N, 2.78.

4-Methyl-*N*-[5,5,5,4,4,3,3,2,2-nonafluoro-(2-furanyl-phenyl)-propyl]-benzenesulfonamide (6f): Brown solid (40 % yield); mp 121-122 ^oC; ^1H NMR, δ 7.59

(d, J = 8.4 Hz, 2H), 7.26 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.21 (m, 2H), 5.42 (m, 2H), 2.38 (s, 3H); ^{19}F NMR, δ -81.4 (t, J = 11.1 Hz, 3F), -116.7 (dm, J = 297.9 Hz, 1F), -119.2 (dm, J = 297.9 Hz, 1F), -121.5 (m, 2F), 126.5 (m, 2F); Anal. Calcd for $C_{16}H_{12}F_9NO_3S$: C, 40.91; H, 2.56; N, 2.98. Found: C, 40.73; H, 2.45; N, 2.91.

Characterization data for other perfluoroalkyl sulfides and selenides

Ethyl trifluoromethyl sulfide (7c):[7,8] ^{1}H NMR, δ 2.70 (q, J = 7.4 Hz, 2H), 1.32 (t, J = 7.4 Hz, 3H); ^{19}F NMR, δ -41.45 (s, 3F).

2-Pyridyl Trifluoromethyl Sulfide (7d):[7,9] ^{1}H NMR, δ 8.49-7.11 (m, 4H); ^{19}F NMR, δ -40.45 (s, 3F).

4-Pyridyl Trifluoromethyl Sulfide (7e):[7] ^{1}H NMR, AB system, δ 8.52 (dd, J = 4.8, 2.0 Hz, 2H), &.7.37 (dd, J = 4.7, 1.75 Hz, 2H); ^{19}F NMR, δ -40.97 (s, 3F).

Ethyl Pentafluoroethyl Sulfide (9b):[10] ^{1}H NMR, δ 2.70 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{19}F NMR, δ -83.0 (t, J_{FF} = 3.2 Hz ,3F), -92.32 (q, J_{FF} = 3.2 Hz, 2F).

Butyl Pentafluoroethyl Sulfide (9c):[10] ^{1}H NMR, δ 2.69 (t, J = 7.3 Hz, 2H), 1.66 (quintet, J = 7.6 Hz, 2H), 1.42 (sextuplet, J = 7.6 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{19}F NMR, δ -82.95 (t, J_{FF} = 3.2 Hz ,3F), -92.55 (q, J_{FF} = 3.2 Hz, 2F).

2-Pyridyl Pentafluoroethyl Sulfide (9d):[11] ^{1}H NMR, δ 8.47 (m, 1H), 7.62 (m, 2H), 7.11 (m, 1H), ^{19}F NMR, δ -83.2 (t, J_{FF} = 2.01 Hz ,3F), -91.0 (q, J_{FF} = 2.01 Hz ,2F).

Ethyl nonafluorobutyl sulfide (10b):[10] ^{1}H NMR, δ 2.70 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{19}F NMR, δ -81.3 (t, J_{FF} = 8.9 Hz , 3F), -87.8 (m, 2F), -121.05 (m, 2F), -125.6 (m, 2F).

2-Pyridyl nonafluorobutyl sulfide (10d):[12] ^{1}H NMR, δ 8.47 (m, 1H), 7.62 (m, 2H), 7.11 (m, 1H); ^{19}F NMR, δ -81.1 (t, J_{FF} = 10.7 Hz , 3F), -86.1 (m, 2F), -120.35 (m, 2F), -125.7 (m, 2F).

4-Pyridyl nonafluorobutyl sulfide (10e): ^{1}H NMR, δ 8.51 (dd, J_1 = 4.8 Hz, J_2 = 2.0 Hz, 2H), 7.37 (dd, J_1 = 4.7 Hz, J_2 = 1.75 Hz, 2H); ^{19}F NMR, δ -81.2 (t, J_{FF} = 10.5 Hz , 3F), -86.0 (m, 2F), -120.25 (m, 2F), -125.6 (m, 2F); Anal. Calcd for $C_9H_4F_9NS$: C, 32.83; H, 1.22; N, 4.26. Found: C, 32.79; H, 1.22; N, 4.23.

Methyl nonafluorobutyl selenide (12b):[10] ^{1}H NMR, δ 2.30 (s, 3H); ^{19}F NMR, δ -81.5 (t, J_{FF} = 8.5 Hz , 3F), -90.0 (t, J_{FF} = 12.8 Hz, 2F), -119.8 (m, 2F), -126.1 (m, 2F).

Methyl trifluoromethyl selenide (8b):[10] ^{19}F NMR, δ – 37.3 (s).

References and Footnotes

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