Supporting Information

for

Benzothiazolium salts as reagents for the deoxygenative perfluoroalkylthiolation of alcohols

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Experimental section
Contents

1 General Information S2
2 Synthesis of BT-SR F Reagents S3
  2.1 Perfluoroalkylation of MBT with Perfluoroalkyl Iodides S3
  2.2 N-Methylation of 2-((Perfluoroalkyl)thio)benzo[d]thiazoles 1 S6
3 Scope and Limitations of the Deoxyperfluoroalkylthiolation of Alcohols S9
  3.1 Deoxyperfluoroalkylation of 4-Nitrobenzyl alcohol (2a) with Different BT-SR F Reagents S9
  3.2 Deoxypentafluoroethylation of Alcohols 2 with BT-SC2F5 S16
  3.3 Deoxyheptafluoropropylation of Alcohols 2 with BT-SC3F7 S21
4 NMR Spectra of Novel Compounds S22
1 General Information

Solvents were purified either with the solvent purification system MB-SPS-800 (Braun) or by manual distillation over standard drying agents. The dried solvents were then stored over molecular sieves or transferred under argon. UVA light irradiation for the synthesis of the reagents was provided by a LED lamp ($\lambda_{\text{max}} = 365 \text{ nm}$, IP65). All compounds employed were purchased from commercial suppliers and used as received. The deoxygenative perfluoroalkylthiolation reactions were performed in round-bottom flasks under an atmosphere of air. Flash chromatography was performed using silica gel.

NMR spectra were acquired on a JEOL ECX 400 (400 MHz), JEOL ECP 500/ Bruker Avance 500 (500 MHz), Varian INOVA 600 (600 MHz) or a Bruker Avance 700 (700 MHz) in CDCl$_3$ or CD$_3$CN as a solvent. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra. $^{19}$F NMR spectra are not calibrated by an internal reference and coupling constants ($J_{F-H}$) where reported were determined from proton coupled $^{19}$F NMR studies. Coupling constants ($J$) are quoted in Hz. $^1$H NMR yields where reported were measured using CH$_2$Br$_2$ as an internal standard.

Mass spectra were obtained on a ESI-FTICR-MS: Ionspec QFT-7 (Agilent/Varian) or on a HR-EI-MS: Waters Autospec Premier with Agilent 7890B GC. Infrared spectra were measured on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. Characteristic absorption bands are displayed in wavelengths $\tilde{\nu}$ in cm$^{-1}$ and were analyzed with the software Spectral Manager from JASCO.
2 Synthesis of BT-SR\textsubscript{F} Reagents

2.1 Perfluoroalkylation of MBT with Perfluoroalkyl Iodides

**General Procedure A:**\(^1\) Mercaptobenzothiazole (1.0 equiv) was dissolved in DMF (0.16-0.25 M) under argon. Sodium hydride (60 wt % in mineral oil, 1.1 equiv) was added and the mixture was stirred at rt for 30 min. The perfluoroalkyl iodide (1.2 or 2 equiv) was then added (condensed in for I\textsubscript{2}C\textsubscript{2}F\textsubscript{5}) and the mixture was stirred under irradiation from UVA LEDS (\(\lambda_{\text{max}} = 365\) nm) overnight. Water was added and the crude product was extracted with EtOAc (3×). The combined organic fractions were washed with water (3×), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. Purification by column chromatography over silica gel afforded the 2-((perfluoroalkyl)thio)benzo[d]thiazole intermediate 1.

2-((Perfluoroethyl)thio)benzo[d]thiazole (1a)

\[
\text{SCF}_2\text{CF}_3
\]

Prepared using General Procedure A with 2 equiv of I\textsubscript{2}C\textsubscript{2}F\textsubscript{5} on a 29.9 mmol scale. Pale yellow oil (5.21 g, 18.2 mmol, 61%).

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 8.16\) (dm, \(J = 8.1\) Hz, 1H), 7.90 (dm, \(J = 8.1\) Hz, 1H), 7.56 (ddd, \(J = 8.3, 7.2, 1.4\) Hz, 1H), 7.50 (t, \(J = 8.5, 7.2, 1.3\) Hz, 1H). \(^19\)F NMR (376 MHz, Chloroform-d) \(\delta = -82.5\) (t, \(J = 3\) Hz, 3F), -90.1 (q, \(J = 3\) Hz, 2F). \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta = 153.3\) (C\textsubscript{q}), 150.0 (C\textsubscript{q}), 138.6 (C\textsubscript{q}), 127.2 (CH), 127.0 (CH), 124.5 (CH), 121.4 (CH), 119.7 (tq, \(J = 294, 42\) Hz, CF\textsubscript{3}), 118.4 (qt, \(J = 287, 36\) Hz, SCF\textsubscript{2}). HRMS (ESI): m/z calculated for [C\textsubscript{9}H\textsubscript{5}F\textsubscript{5}NS\textsubscript{2}]\(^+\) ([M+H])\(^+\): 285.9778, measured: 285.9793. IR (ATR): \(\nu\) (cm\(^{-1}\)): 3071, 2927, 1592, 1556, 1456, 1410, 1329, 1312, 1206, 1103, 1016, 994, 949, 853, 757, 751, 727, 708, 676, 651, 629, 608, 597, 550.

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\(^1\) Procedure adapted from: A. Harsányi, É. Dorkó, Á. Csapó, T. Bakó, C. Peltz, J. Rábai, *J. Fluorine Chem.* 2011, 132, 1241-1246.
2-((Perfluoropropyl)thio)benzo[d]thiazole (1b)

![Chemical Structure](image)

1b

Prepared using General Procedure A with 2 equiv of I-C\(_3\)F\(_7\) on a 10.0 mmol scale. Pale yellow oil (2.64 g, 7.87 mmol, 79%).

\(^1\)H NMR (600 MHz, Chloroform-d) \(\delta = 8.16\) (dd, \(J = 8.2, 0.8\) Hz, 1H), 7.90 (d, \(J = 8.2, 0.9\) Hz, 1H), 7.55 (ddd, \(J = 8.3, 7.2, 1.3\) Hz, 1H), 7.50 (ddd, \(J = 8.3, 7.2, 1.3\) Hz, 1H). \(^{19}\)F NMR (565 MHz, Chloroform-d) \(\delta = -78.8\) (t, \(J = 9\) Hz, 3F), -85.8 (q, \(J = 9\) Hz, 2F), -123.3 (m, 2F). \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta = 153.3\) (C\(_q\)), 149.9 (C\(_q\)), 138.6 (C\(_q\)), 127.2 (CH), 127.0 (CH), 124.5 (CH), 121.4 (CH), 122.1 (tt, \(J = 295, 34\) Hz, SCF\(_2\)), 117.6 (qt, \(J = 288, 34\) Hz, CF\(_3\)), 108.7 (tm, \(J = 266\) Hz, CF\(_2\)). HRMS (EI): m/z calculated for [C\(_{10}\)H\(_4\)F\(_7\)NS\(_2\)]\(^+\) ([M]\(^+\)): 334.9668, measured: 334.9644. IR (ATR): \(\nu\) (cm\(^{-1}\)): 3068, 2927, 2854, 1556, 1456, 1410, 1335, 1313, 1208, 1185, 1115, 1091, 1040, 1016, 916, 846, 757, 741, 727, 708, 687, 674, 598.

2-((Perfluoropentyl)thio)benzo[d]thiazole (1c)

![Chemical Structure](image)

1c

Prepared using General Procedure A with 2 equiv of I-C\(_5\)F\(_{11}\) on a 6.0 mmol scale. Pale yellow oil (1.79 g, 4.11 mmol, 69%).

\(^1\)H NMR (600 MHz, Chloroform-d) \(\delta = 8.16\) (dm, \(J = 8.3\) Hz, 1H), 7.90 (dm, \(J = 8.0\) Hz, 1H), 7.56 (ddm, \(J = 8.3, 7.1\) Hz, 1H), 7.50 (ddm, \(J = 8.1, 7.1\) Hz, 1H). \(^{19}\)F NMR (565 MHz, Chloroform-d) \(\delta = -80.8\) (m, 3F), -84.9 (m, 2F), -119.0 (m, 2F), -122.2 (m, 2F), -126.1 (m, 2F). \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta = 153.3\) (C\(_q\)), 150.0 (C\(_q\)), 138.7 (C\(_q\)), 127.2 (CH), 127.1 (CH), 124.5 (CH), 121.4 (CH), 122.8 (tt, \(J = 297, 35\) Hz, SCF\(_2\)), 117.3 (qt, \(J = 286, 33\) Hz, CF\(_3\)), 110.7 (tm, \(J = 270\) Hz, CF\(_2\)). Note: Two perfluoroalkyl \(^{13}\)C peaks could not be observed. HRMS (EI): m/z calculated for [C\(_{12}\)H\(_4\)F\(_{11}\)NS\(_2\)]\(^+\) ([M]\(^+\)): 434.9604, measured: 434.9620. IR (ATR): \(\nu\) (cm\(^{-1}\)): 3065, 3046, 1552, 1456, 1410, 1357, 1314, 1271, 1232, 1199, 1136, 1111, 1086, 1075, 1017, 999, 941, 854, 813, 767, 761, 745, 722, 696, 682, 659, 619, 594, 570.

S4
2-((Perfluorooctyl)thio)benzo[d]thiazole (1d)\(^2\)

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{SCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3
\end{array}
\]

1d

Prepared using General Procedure A with 1.2 equiv of I-C\(_8\)F\(_{17}\) on a 3.0 mmol scale. White solid (1.67 g, 2,85 mmol, 95%).

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 8.17\) (dm, \(J = 8.3\) Hz, 1H), 7.92 (dm, \(J = 8.1\) Hz, 1H), 7.57 (m, 1H), 7.52 (m, 1H). \(^{19}\)F NMR (376 MHz, Chloroform-d) \(\delta = -80.6\) (t, \(J = 11\) Hz, 3F), -84.8 (t, \(J = 15\) Hz, 2F), -118.7 (m, 2F), -121.0 (m, 2F), -121.6 (m, 2F), -121.8 (m, 2F), -122.6 (m, 2F), -126.0 (m, 2F).

The data agree with literature precedents.\(^2\)

2-((Perfluoropropan-2-yl)thio)benzo[d]thiazole (1e)

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{CF}_3\text{F} \\
\text{SCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3
\end{array}
\]

1e

Prepared using General Procedure A with 1.2 equiv of I-CF\(_3\)\(_2\) on a 14.1 mmol scale. Pale yellow oil (4.30 g, 12.8 mmol, 91%).

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 8.16\) (dm, \(J = 8.2\) Hz, 1H), 7.88 (dm, \(J = 7.9\) Hz, 1H), 7.54 (ddd, \(J = 8.2, 7.3, 1.4\) Hz, 1H), 7.48 (ddd, \(J = 8.0, 7.2, 1.3\) Hz, 1H). \(^{19}\)F NMR (376 MHz, Chloroform-d) \(\delta = -73.9\) (d, \(J = 10\) Hz, 6F), -155.6 (sept, \(J = 11\) Hz, 1F). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta = 153.2\) (C\(_q\)), 149.9 (C\(_o\)), 138.8 (C\(_o\)), 127.1 (CH), 127.1 (CH, two overlapping peaks), 124.6 (CH), 121.4 (CH), 120.1 (qd, \(J = 288, 29\) Hz, CF\(_3\)), 98.1 (d(sept), \(J = 255, 35\) Hz, CF). HRMS (EI): m/z calculated for [C\(_{10}\)H\(_4\)F\(_7\)NS\(_2\)]\(^+\) ([M]\(^+\)): 334.9668, measured: 334.9688. IR (ATR): ν (cm\(^{-1}\)): 3068, 2927, 2854, 1555, 1456, 1409, 1281, 1263, 1219, 1170, 1134, 1092, 992, 959, 934, 853, 755, 728, 717, 676, 619, 589, 602, 551.

\(^2\) D. E. Yerien, S. Barata-Vallejo, B. Camps, A. E. Cristófalo, M. E. Cano, M. L. Uhrig, A. Postigo, Catal. Sci. Technol. 2017, 7, 2274-2282.
2.2  N-Methylation of 2-((Perfluoroalkyl)thio)benzo[d]thiazoles 1

![Chemical Structure](image.png)

**General Procedure B**: 2-Substituted benzothiazoles (1.0 equiv) were dissolved in dry CH₂Cl₂ (0.10 M) and methyl trifluoromethanesulfonate (2.2-3.0 equiv) was added. The reaction mixture was stirred at rt for 48 h and the product was precipitated with diethyl ether. The suspension was then filtered, and the residue washed with diethyl ether (3×). After drying in vacuo, BT-SRᵣ salts were obtained as off-white solids.

3-Methyl-2-((perfluoroethyl)thio)benzo[d]thiazol-3-i um trifluoromethanesulfonate (BT-SC₂F₃)

Prepared from 1a using General Procedure B with 2.2 equiv of MeOTf on a 16.3 mmol scale. Off-white solid (6.70 g, 14.9 mmol, 91%).

¹H NMR (400 MHz, Acetonitrile-d₃) δ = 8.40 (dm, J = 8.3 Hz, 1H), 8.29 (dm, J = 8.8 Hz, 1H), 8.07 (ddm, J = 8.6, 7.2 Hz, 1H), 7.99 (ddm, J = 8.4, 7.2 Hz, 1H), 4.47 (s, 3H). ¹⁹F NMR (565 MHz, Acetonitrile-d₃) δ = -78.5 (3F), -82.0 (t, J = 3 Hz, 3F), -87.8 (q, J = 3 Hz, 2F). ¹³C NMR (151 MHz, Acetonitrile-d₃) δ = 158.6 (Cₛ), 143.9 (Cₐ), 134.6 (Cₐ), 132.5 (CH), 131.7 (CH), 125.3 (CH), 122.0 (q, J = 322 Hz, SO₂CF₃), 119.9 (tq, J = 299 Hz, 42, CF₃), 119.6 (CH), 118.7 (qt, J = 286 Hz, 35, SCF₂), 40.2 (CH₃). HRMS (ESI): m/z calculated for [C₁₀H₇F₅NS₂]+= (M−OTf+): 299.9935, measured: 299.9948. IR (ATR): ν (cm⁻¹): 3092, 3028, 1578, 1491, 1463, 1433, 1383, 1330, 1278, 1267, 1241, 1211, 1160, 1337, 1111, 1207, 955, 815, 160, 150, 722, 714, 658, 638, 602, 573.

3-Methyl-2-((perfluoropropyl)thio)benzo[d]thiazol-3-i um trifluoromethanesulfonate (BT-SC₃F₇)

Prepared from 1b using General Procedure B with 3.0 equiv of MeOTf on a 5.25 mmol scale. Off-white solid (2.46 g, 4.92 mmol, 94%).
\( ^1H \text{ NMR} \ (400 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 8.39 \ (d, J = 8.5 \text{ Hz, 1H}), \ 8.27 \ (d, J = 8.8 \text{ Hz, 1H}), \ 8.04 \ (t, J = 8.0 \text{ Hz, 1H}), \ 7.96 \ (t, J = 7.8 \text{ Hz, 1H}), \ 4.45 \ (s, 3H). \ \ ^{19}F \text{ NMR} \ (376 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = -79.2 \ (3F), \ -80.5 \ (t, J = 9 \text{ Hz, 3F}), \ -83.8 \ (q, J = 9 \text{ Hz, 2F}), \ -123.2 \ (m, 2F). \ \ ^{13}C \text{ NMR} \ (176 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 158.7 \ (C_6), \ 144.1 \ (C_6), \ 134.7 \ (C_6), \ 132.6 \ (CH), \ 131.8 \ (CH), \ 125.3 \ (CH), \ 122.5 \ (t, J = 299, 35 \text{ Hz, SCF}_2), \ 122.0 \ (q, J = 320 \text{ Hz, SO}_2\text{CF}_3), \ 118.3 \ (q, t, J = 288, 34 \text{ Hz, CF}_3), \ 119.7 \ (CH), \ 109.4 \ (t, m, J = 267 \text{ Hz, CF}_2), \ 40.3 \ (CH_3). \ \text{HRMS (ESI)}: \ m/z \text{ calculated for } [\text{C}_{13}\text{H}_3\text{F}_5\text{NS}_2]^+ \ ([\text{M+OTf}]^+): \ 439.9903, \ \text{measured:} \ 439.9922. \ \text{IR (ATR): } \nu \ (\text{cm}^{-1}): \ 3089, \ 3031, \ 1578, \ 1490, \ 1463, \ 1433, \ 1382, \ 1340, \ 1277, \ 1239, \ 1266, \ 1218, \ 1189, \ 1163, \ 1163, \ 1121, \ 1054, \ 1027, \ 914, \ 848, \ 815, \ 761, \ 751, \ 743, \ 723, \ 714, \ 687, \ 639, \ 574.

3-Methyl-2-((perfluoropentyl)thio)benzo[d]thiazol-3-ium trifluoromethanesulfonate (BT-\(SC_5F_{11} \))

![Diagram of the molecule](attachment:image)

Prepared from 1c using General Procedure B with 2.5 equiv of MeOTf on a 3.68 mmol scale. Off-white solid (2.07 g, 3.45 mmol, 94%).

\( ^1H \text{ NMR} \ (400 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 8.42 \ (d, J = 8.3 \text{ Hz, 1H}), \ 8.31 \ (d, J = 8.6 \text{ Hz, 1H}), \ 8.07 \ (t, J = 8.0 \text{ Hz, 1H}), \ 8.00 \ (t, J = 7.8 \text{ Hz, 1H}), \ 4.48 \ (s, 3H). \ \ ^{19}F \text{ NMR} \ (376 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = -79.2 \ (3F), \ -81.4 \ (t, J = 10 \text{ Hz, 3F}), \ -82.7 \ (t, J = 14 \text{ Hz, 2F}), \ -118.8 \ (m, 2F), \ -122.5 \ (m, 2F), \ -126.5 \ (m, 2F). \ \ ^{13}C \text{ NMR} \ (151 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 159.6 \ (C_6), \ 144.0 \ (C_6), \ 134.7 \ (C_6), \ 132.6 \ (CH), \ 131.8 \ (CH), \ 125.3 \ (CH), \ 123.1 \ (t, J = 300, 35 \text{ Hz, SCF}_2), \ 122.0 \ (q, J = 320 \text{ Hz, SO}_2\text{CF}_3), \ 119.6 \ (CH), \ 118.0 \ (t, m, J = 289, 33 \text{ Hz, CF}_3), \ 111.3 \ (t, m, J = 267 \text{ Hz, CF}_2), \ 40.2 \ (CH_3) \ \text{Note: Two perfluoroalkyl } ^{13}C \text{ peaks could not be observed. HRMS (ESI)}: \ m/z \text{ calculated for } [\text{C}_{13}\text{H}_3\text{F}_5\text{NS}_2]^+ \ ([\text{M+OTf}]^+): \ 449.9839, \ \text{measured:} \ 449.9843. \ \text{IR (ATR): } \nu \ (\text{cm}^{-1}): \ 3101, \ 3031, \ 1577, \ 1490, \ 1462, \ 1433, \ 1357, \ 1277, \ 1266, \ 1241, \ 1224, \ 1201, \ 1163, \ 1142, \ 1081, \ 1028, \ 941, \ 863, \ 847, \ 815, \ 762, \ 737, \ 722, \ 697, \ 664, \ 639, \ 597, \ 572.

3-Methyl-2-((perfluoroctyl)thio)benzo[d]thiazol-3-ium trifluoromethanesulfonate (BT-\(SC_8F_{17} \))

![Diagram of the molecule](attachment:image)

Prepared from 1d using General Procedure B with 3.0 equiv of MeOTf on a 1.57 mmol scale. Off-white solid (1.08 g, 1.44 mmol, 92%).

\( ^1H \text{ NMR} \ (400 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 8.40 \ (d, J = 8.4 \text{ Hz, 1H}), \ 8.29 \ (d, J = 8.7 \text{ Hz, 1H}), \ 8.07 \ (t, J = 7.6 \text{ Hz, 1H}), \ 7.99 \ (t, J = 7.8 \text{ Hz, 1H}), \ 4.47 \ (s, 3H). \ \ ^{19}F \text{ NMR} \ (376 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = -79.3 \ (3F), \ -81.4 \ (t, J = 10 \text{ Hz, 3F}), \ -82.5 \ (t, J = 14 \text{ Hz, 2F}), \ -118.5 \ (m, 2F), \ -121.4 \ (m, 2F), \ -121.5 \ (m, 2F), \ -122.2 \ (m, 2F), \ -123.0 \ (m, 2F), \ -126.5 \ (m, 2F). \ \ ^{13}C \text{ NMR} \ (176 \text{ MHz, Acetonitrile-\(d_2 \)}) \ \delta = 158.5 \ (C_6), \ 143.9 \ (C_6), \ 134.7
(C₂), 132.6 (CH), 131.8 (CH), 125.3 (CH), 123.1 (tt, J = 300, 35 Hz, SCF₂), 122.0 (q, J = 318 Hz, SO₂CF₃), 119.6 (CH), 118.0 (qt, J = 288, 32 Hz, CF₃), 111.6 (m, several overlapping peaks, CF₂), 40.2 (CH₃) Note: Several perfluoroalkyl ¹³C peaks could not be assigned. HRMS (ESI): m/z calculated for [C₁₆H₇F₁₇NS₂]⁺ ([M-OTf]⁺): 599.9743, measured: 599.9730. IR (ATR): ν (cm⁻¹): 3101, 2361, 1576, 1490, 1461, 1435, 1370, 1328, 1281, 1251, 1200, 1149, 1134, 1097, 1054, 1031, 958, 930, 849, 816, 798, 768, 756, 741, 723, 714, 707, 655.

3-Methyl-2-((perfluoroisopropyl)thio)benzo[d]thiazol-3-ium trifluoromethanesulfonate (BT-SCF(CF₃)₂)

Prepared from 1e using General Procedure B with 3.0 equiv of MeOTf on a 12.8 mmol scale. Off-white solid (3.73 g, 10.7 mmol, 83%).

¹H NMR (700 MHz, Acetonitrile-d₃) δ = 8.43 (ddd, J = 8.4, 1.2, 0.7 Hz, 1H), 8.33 (dt, J = 8.7, 0.9 Hz, 1H), 8.07 (ddd, J = 8.6, 7.2, 1.2 Hz, 1H), 7.99 (ddd, J = 8.3, 7.2, 1.0 Hz, 1H), 4.51 (s, 3H). ¹⁹F NMR (376 MHz, Acetone-d₆) δ = -74.7 (d, J = 11 Hz, 6F), -78.9 (3F), -154.7 (sept, J = 11 Hz, 1F). ¹³C NMR (177 MHz, Acetonitrile-d₃) δ = 158.3 (C₉), 143.8 (C₉), 134.8 (C₉), 132.7 (CH), 132.0 (CH), 125.4 (CH), 122.0 (q, J = 321 Hz, SO₂CF₃), 120.4 (qd, J = 289, 28 Hz, CF₃), 119.7 (CH), 98.4 (d(sept), J = 260, 36 Hz, CF), 40.4 (CH₃). HRMS (ESI): m/z calculated for [C₁₆H₁₇F₁₇NS₂]⁺ ([M-OTf]⁺): 349.9903, measured: 349.9923. IR (ATR): ν (cm⁻¹): 3086, 3031, 1579, 1491, 1463, 1432, 1382, 1276, 1240, 1221, 1178, 1159, 1139, 1099, 1027, 965, 937, 814, 755, 720, 638, 572, 540.
3 Scope and Limitations of the Deoxyperfluoroalkylthiolation of Alcohols

$$\text{R}^-\text{OH} \xrightarrow{\text{BT-SR}_F (1.25 \text{ equiv})} \xrightarrow{\text{DIPEA (2 equiv)}} \text{R}^-\text{SR}_F$$

**MeCN, −40 °C, 2 h**

**General Procedure C:** The alcohol (0.50 mmol, 1.0 equiv) was dissolved in MeCN (0.17 M), **BT-SR$_F$** (0.625 mmol, 1.25 equiv) was added and the reaction mixture was cooled to −40 °C. NEt(iPr)$_2$ (174 μL, 1.0 mmol, 2.0 equiv) was then added dropwise and the reaction mixture was stirred for 1-2 h at −40 °C. The reaction mixture was concentrated in vacuo and purified by column chromatography over silica gel.

### 3.1 Deoxyperfluoroalkylation of 4-Nitrobenzyl alcohol (2a) with Different BT-SR$_F$ Reagents

#### 3.1.1 With BT-SC$_2$F$_5$

**a) At rt** (DIPEA added at 0 °C then reaction warmed to rt over 2 h)

$$\text{O}_2\text{N} -\text{OH} \xrightarrow{\text{BT-SC}_2\text{F}_5 (1.25 \text{ equiv})} \xrightarrow{\text{DIPEA (2 equiv)}} \text{O}_2\text{N} -\text{SCF}_2\text{CF}_3 \quad 3a \quad (78\% \text{ NMR})$$

$$\text{O}_2\text{N} -\text{OH} \xrightarrow{\text{BT-SC}_2\text{F}_5 (1.25 \text{ equiv})} \xrightarrow{\text{DIPEA (2 equiv)}} \text{O}_2\text{N} -\text{OCF}_3 \quad 4a \quad (7\% \text{ NMR})$$

**Crude $^1$H NMR Spectrum:** 0.5 mmol scale, CH$_2$Br$_2$ (0.1 mmol) as internal reference
b) At $-40 \, ^\circ\text{C}$ (General Procedure C)

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{BT-SC}_2\text{F}_5 \, (1.25 \text{ equiv}) \quad \text{DIPEA} \, (2 \text{ equiv}) \quad \text{MeCN} \\
\begin{array}{c}
\quad \text{meCN} \quad -40 \, {^\circ}\text{C}, 2 \text{ h} \\
\end{array} & \quad \text{O}_2\text{N} \quad \text{SCF}_2\text{CF}_3 \\
\text{S}_{\text{a}} & \quad \text{O}_2\text{N} \quad \text{SCF}_2\text{CF}_3 + \quad \text{O}_2\text{N} \quad \text{SCF}_2\text{CF}_3
\end{align*}
\]

Crude $^1\text{H NMR Spectrum}$: 0.5 mmol scale, CH$_2$Br$_2$ (0.1 mmol) as internal reference
(4-Nitrobenzyl)(perfluoroethyl)sulfane (3a)

Prepared from 4-nitrobenzyl alcohol (2a) and BT-SC₂F₅ using General Procedure C. Yellow liquid (131 mg, 0.46 mmol, 91%).

¹H NMR (600 MHz, Chloroform-d) δ = 8.20 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 4.21 (s, 2H). ¹⁹F NMR (565 MHz, Chloroform-d) δ = -83.3 (m, 3F), -92.0 (m, 2F). ¹³C NMR (151 MHz, Chloroform-d) δ = 147.8 (C₉), 142.7 (C₉), 130.0 (CH), 124.2 (CH), 121.3 (tq, J = 289, 41 Hz, CF₂), 118.5 (qt, J = 286, 36 Hz, CF₃), 32.2 (t, J = 4 Hz, CH₂). HRMS (ESI): m/z calculated for [C₉H₅F₅NO₂S]⁻ ([M-H]⁻): 285.9967, measured: 285.9967. IR (ATR): ν (cm⁻¹): 3117, 3093, 2952, 2860, 1602, 1521, 1346, 1323, 1254, 1205, 1095, 1016, 966, 889, 858, 819, 802, 750, 706, 642, 624, 590, 551.
3.1.2 With BT-SC$_3$F$_7$

\[
\text{O}_2\text{N} \quad \text{MeCN} \quad -40^\circ\text{C}, 2\text{ h} \quad \text{O}_2\text{N}
\]

Crude $^1$H NMR Spectrum: 0.5 mmol scale, CH$_2$Br$_2$ (0.5 mmol) as internal reference

(4-Nitrobenzyl)(perfluoropropyl)sulfane (5a)

Prepared from 4-nitrobenzyl alcohol (2a) and BT-SC$_3$F$_7$ using General Procedure C. Yellow solid (139 mg, 0.412 mmol, 82%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 8.21 (dm, $J = 8.7$ Hz, 2H), 7.55 (dm, $J = 8.7$ Hz, 2H), 4.24 (s, 2H).

$^{19}$F NMR (377 MHz, Chloroform-d) $\delta$ = -80.0 (t, $J = 10$ Hz, 3F), -88.0 (qt, $J = 9$, 4 Hz, 2F), -124.0 (t, $J = 4$ Hz, 2F).

$^{13}$C NMR (177 MHz, Chloroform-d) $\delta$ = 147.8 (Cq), 142.8 (Cq), 130.1 (CH), 124.3 (CH), 123.8 (tt, $J = 290, 34$ Hz, SCF$_2$), 117.7 (qt, $J = 288, 34$ Hz, CF$_3$), 108.6 (tm, $J = 265$ Hz, CF$_2$), 32.3 (t, $J = 4$ Hz, CH$_2$).

HRMS (EI): m/z calculated for [C$_{10}$H$_{14}$F$_3$NO$_2$S]$^+$ ([M]$^+$): 337.0002, measured: 337.0004.

IR (ATR): v (cm$^{-1}$): 3083, 2929, 2857, 1931, 1726, 1602, 1522, 1494, 1424, 1346, 1208, 1182, 1109, 1087, 1038, 1017, 926, 890, 855, 801, 751, 742, 717, 706, 678, 653, 631, 622, 606.
3.1.3 With BT-SC₅F₁₁

\[
\begin{align*}
\text{2a} & \xrightarrow{\text{BT-SC₅F₁₁ (1.25 equiv)}} \text{7a (74% NMR)} + \text{8a (28% NMR)} \\
\text{OH} & \text{SCF₂(CF₂)₃CF₃} \quad \text{O₂N} \\
\text{MeCN} & \\
-40 \degree C, 2 h
\end{align*}
\]

Crude \(^1\)H NMR Spectrum: 0.5 mmol scale, CH₂Br₂ (0.5 mmol) as internal reference
3.1.4 With BT-SC$_8$F$_{17}$

\[
\text{O}_2\text{N} \xrightarrow{\text{MeCN} \quad -40 \degree C, 2 h} \text{Br}_2 \quad \text{DIPEA (2 equiv)} \quad \text{BT-SC$_8$F$_{17}$ (1.25 equiv)} \quad \text{O}_2\text{N}
\]

2a \quad SC\text{F}_2(\text{CF}_2)_2\text{CF}_3 \quad + \quad \text{SC}\text{F}_2(\text{CF}_2)_2\text{CF}_3 \quad 9a (46\% \text{ NMR}) \quad + \quad 10a (47\% \text{ NMR})

**Crude $^1$H NMR Spectrum:** 0.5 mmol scale, CH$_2$Br$_2$ (0.5 mmol) as internal reference
3.1.5 With BT-SCF(CF$_3$)$_2$

\[ \text{O}_2\text{N} \quad \text{O}_2\text{N} \]

\[ \text{H} \quad \text{H} \]

\[ 2\text{a} \quad 11\text{a (trace)} \]

**Crude $^1$H NMR Spectrum**: 0.5 mmol scale, CH$_2$Br$_2$ (0.5 mmol) as internal reference
3.2 Deoxypentafluoroethylation of Alcohols 2 with BT-SC$_2$F$_5$

(Benzyl)(perfluoroethyl)sulfane (3b)$^3$

\[
\text{SCF}_2\text{CF}_3
\]

3b

Prepared from benzyl alcohol (2b) and BT-SC$_2$F$_5$ using General Procedure C. Pale yellow liquid (88 mg, 0.36 mmol, 73%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta = 7.29 – 7.38$ (m, 5H), 4.17 (s, 2H). $^{19}$F NMR (377 MHz, Chloroform-d) $\delta = -83.3$ (t, $J = 4$ Hz, 3F), -92.3 (t, $J = 4$ Hz, 2F).

The data agree with literature precedents.$^3$

(4-Iodobenzyl)(perfluoroethyl)sulfane (3c)

\[
\text{SCF}_2\text{CF}_3
\]

3c

Prepared from 4-iodobenzyl alcohol (2c) and BT-SC$_2$F$_5$ using General Procedure C. Yellow liquid (140 mg, 0.38 mmol, 76%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta = 7.69$ (dm, $J = 8.5$ Hz, 2H), 7.10 (dm, $J = 8.5$ Hz, 2H), 7.30 (m, 1H), 4.09 (s, 2H). $^{19}$F NMR (376 MHz, Chloroform-d) $\delta = -83.2$ (t, $J = 4$ Hz, 3F), -92.2 (q, $J = 4$ Hz, 2F).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta = 138.2$ (CH), 134.6 (C$_q$), 131.0 (CH), 121.4 (tq, $J = 288, 41$ Hz, CF$_2$), 118.7 (qt, $J = 286, 37$ Hz, CF$_3$), 92.8 (C$_q$), 32.6 (t, $J = 4$ Hz, CH$_2$). HRMS (EI): m/z calculated for [C$_9$H$_6$F$_5$IS]$^+$ ([M]$^+$): 367.9150, measured: 367.9176. IR (ATR): $\nu$ (cm$^{-1}$): 3040, 2946, 1906, 1588, 1485, 1400, 1322, 1205, 1094, 1060, 1008, 966, 878, 827, 809, 750, 736, 676, 642, 624, 598, 551.

$^3$ Q. Glenadel, M. Bordy, S. Alazet, A. Tiili, T. Billard, Asian J. Org. Chem. 2016, 5, 428-433.
(Perfluoroethyl)(2,4,6-trichlorobenzyl)sulfane (3d)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{SCF}_2	ext{CF}_3 \\
\end{array}
\]

3d

Prepared from 2,4,6-trichlorobenzyl alcohol (2d) and BT-SC\(_2\)F\(_5\) using General Procedure C. Colourless liquid (166 mg, 0.48 mmol, 96%).

\(^1\text{H} \text{NMR (400 MHz, Chloroform-d)} \delta = 7.37 \text{ (s, 2H), 4.44 \text{ (s, 2H).}}\)

\(^{19}\text{F} \text{NMR (376 MHz, Chloroform-d)} \delta = -83.1 \text{ (t, } J = 4 \text{ Hz, 3F), -92.2 \text{ (q, } J = 4 \text{ Hz, 2F).}\)

\(^{13}\text{C} \text{NMR (101 MHz, Chloroform-d)} \delta = 136.6 \text{ (C}_q\), 135.3 \text{ (C}_q\), 130.1 \text{ (C}_q\), 128.8 \text{ (CH), 121.5 \text{ (tq, } J = 288, 41 \text{ Hz, CF}_2\), 118.7 \text{ (qt, } J = 286, 37 \text{ Hz, CF}_3\), 28.2 \text{ (t, } J = 4 \text{ Hz, CH}_2\).}\)

HRMS (EI): m/z calculated for [C\(_9\)H\(_4\)Cl\(_3\)F\(_5\)S]\(^+\) ([M]\(^+\): 343.9014, measured: 343.9037. IR (ATR): ν (cm\(^{-1}\)): 3089, 2933, 2857, 1726, 1581, 1550, 1441, 1420, 1376, 1321, 1254, 1208, 1135, 1094, 967, 897, 857, 786, 750, 679, 656, 640, 625, 590, 563, 551.

([1,1'-Biphenyl]-4-ylmethyl)(perfluoroethyl)sulfane (3e)

\[
\begin{array}{c}
\text{SCF}_2	ext{CF}_3 \\
\text{CH} \\
\text{CH} \\
\text{CH} \\
\text{CH} \\
\end{array}
\]

3e

Prepared from biphenyl-4-methanol (2e) and BT-SC\(_2\)F\(_5\) using General Procedure C. Colourless solid (144 mg, 0.45 mmol, 90%).

\(^1\text{H} \text{NMR (400 MHz, Chloroform-d)} \delta = 7.68 - 7.59 \text{ (m, 4H), 7.56 - 7.37 \text{ (m, 5H), 4.25 \text{ (s, 2H).}}\)

\(^{19}\text{F} \text{NMR (376 MHz, Chloroform-d)} \delta = -83.2 \text{ (t, } J = 4 \text{ Hz, 3F), -92.1 \text{ (q, } J = 4 \text{ Hz, 2F).}\)

\(^{13}\text{C} \text{NMR (101 MHz, Chloroform-d)} \delta = 141.3 \text{ (C}_q\), 140.5 \text{ (C}_q\), 133.7 \text{ (C}_q\), 129.7 \text{ (CH), 129.0 \text{ (CH), 127.8 \text{ (CH), 127.7 \text{ (CH), 127.2 \text{ (CH), 121.6 \text{ (tq, } J = 288, 41 \text{ Hz, CF}_2\), 118.8 \text{ (qt, } J = 286, 37 \text{ Hz, CF}_3\), 32.8 \text{ (t, } J = 4 \text{ Hz, CH}_2\).}\)

HRMS (EI): m/z calculated for [C\(_{15}\)H\(_{11}\)F\(_5\)S]\(^+\) ([M]\(^+\): 318.0496, measured: 318.0509. IR (ATR): ν (cm\(^{-1}\)): 3083, 3033, 2939, 2860, 1977, 1919, 1796, 1683, 1598, 1565, 1522, 1488, 1443, 1408, 1324, 1248, 1199, 1129, 1096, 1007, 966, 843, 751, 769, 735, 714, 690, 638, 625, 593, 540.
((4-tert-Butyl)benzyl)(perfluoroethyl)sulfane (3f)

Prepared from 4-tert-butylbenzyl alcohol (2f) and BT-SC₂F₅ using General Procedure C. Yellow liquid (119 mg, 0.40 mmol, 80%).

¹H NMR (600 MHz, Chloroform-d) δ = 7.39 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 4.15 (s, 2H), 1.33 (s, 9H).

¹³C NMR (151 MHz, Chloroform-d) δ = 151.4 (C₆), 131.4 (C₆), 128.9 (CH), 126.0 (CH), 123.4 (tq, J = 288, 40 Hz, CF₂), 118.7 (qt, J = 286, 36 Hz, CF₃), 34.7 (C₆), 32.6 (t, J = 4 Hz, CH₂), 31.3 (CH₃). HRMS (EI): m/z calculated for [C₁₃H₁₅F₅S]⁺ ([M⁺]): 298.0815, measured: 298.0840. IR (ATR): ν (cm⁻¹): 3028, 2965, 2909, 2869, 1517, 1465, 1414, 1365, 1322, 1269, 1252, 1209, 1095, 1019, 986, 836, 750, 590, 559.

Methyl 4-(((perfluoroethyl)thio)methyl)benzoate (3g)

Prepared from methyl 4-(hydroxymethyl)benzoate (2g) and BT-SC₂F₅ using General Procedure C. Yellow liquid (128 mg, 0.43 mmol, 85%).

¹H NMR (600 MHz, Chloroform-d) δ = 8.02 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 4.17 (s, 2H), 3.91 (s, 3H). ¹⁹F NMR (565 MHz, Chloroform-d) δ = -83.3 (m, 3F), -92.2 (m, 2F). ¹³C NMR (151 MHz, Chloroform-d) δ = 167.3 (C₆), 138.8 (C₆), 130.3 (CH), 130.0 (C₆), 129.1 (CH), 120.5 (tq, J = 289, 41 Hz, CF₂), 118.6 (qt, J = 286, 36 Hz, CF₃), 52.3 (CH₃), 32.6 (t, J = 4 Hz, CH₂). HRMS (EI): m/z calculated for [C₁₁H₉F₅O₂S]⁺ ([M⁺]): 300.0243, measured: 300.0254. IR (ATR): ν (cm⁻¹): 3007, 2956, 2848, 1720, 1613, 1578, 1437, 1415, 1323, 1279, 1206, 1180, 1095, 1021, 966, 861, 839, 797, 775, 750, 723, 711, 624, 590, 552.
(3-Bromobenzyl)(perfluoroethyl)sulfane (3h)

Prepared from methyl 3-bromobenzyl alcohol (2h) and BT-SC\textsubscript{2}F\textsubscript{5} using General Procedure C. Pale red liquid (126 mg, 0.39 mmol, 78%).

\( ^{1}H \text{ NMR (400 MHz, Chloroform-d)} \delta = 7.52 (t, J = 1.8 \text{ Hz}, 1H), 7.45 (ddd, J = 7.8, 2.0, 1.2 \text{ Hz}, 1H), 7.30 (m, 1H), 7.23 (t, J = 7.8 \text{ Hz}, 1H), 4.11 (s, 2H). \)

\( ^{19}F \text{ NMR (376 MHz, Chloroform-d)} \delta = -83.3 (t, J = 4 \text{ Hz}, 3F), -92.2 (q, J = 4 \text{ Hz}, 2F). \)

\( ^{13}C \text{ NMR (101 MHz, Chloroform-d)} \delta = 137.2 (C\text{q}), 132.2 (CH), 131.5 (CH), 130.6 (CH), 127.4 (CH), 122.9 (C\text{q}), 121.4 (tq, J = 288, 41 \text{ Hz}, CF\textsubscript{2}), 118.7 (qt, J = 286, 37 \text{ Hz}, CF\textsubscript{3}), 32.4 (t, J = 4 \text{ Hz}, CH\textsubscript{2}). \)

HRMS (EI): m/z calculated for [C\textsubscript{9}H\textsubscript{6}BrF\textsubscript{5}S]\textsuperscript{+} ([M]\textsuperscript{+}): 319.9288, measured: 319.9280.

IR (ATR): \( \nu (\text{cm}^{-1}) \): 3071, 2949, 1601, 1571, 1476, 1429, 1322, 1206, 1095, 1072, 998, 966, 888, 848, 787, 750, 730, 681, 668, 625, 591, 577, 550.

(Perfluoroethyl)(3-phenylprop-2-yn-1-yl)sulfane (3i)

Prepared from 3-phenylprop-2-yn-1-ol (2i) and BT-SC\textsubscript{2}F\textsubscript{5} using General Procedure C. Yellow liquid (108 mg, 0.41 mmol, 81%).

\( ^{1}H \text{ NMR (600 MHz, Chloroform-d)} \delta = 7.44 (dd, J = 7.7, 1.8 \text{ Hz}, 2H), 7.37 – 7.30 (m, 3H), 7.30 (m, 1H), 3.94 (s, 2H). \)

\( ^{19}F \text{ NMR (565 MHz, Chloroform-d)} \delta = -83.3 (t, J = 4 \text{ Hz}, 3F), -93.2 (q, J = 4 \text{ Hz}, 2F). \)

\( ^{13}C \text{ NMR (151 MHz, Chloroform-d)} \delta = 131.9 (CH), 128.9 (CH), 128.5 (CH), 122.3 (C\text{q}), 121.3 (tq, J = 289, 41 \text{ Hz}, CF\textsubscript{2}), 118.7 (qt, J = 286, 36 \text{ Hz}, CF\textsubscript{3}), 84.9 (C\text{q}), 82.2 (C\text{q}), 18.5 (t, J = 6 \text{ Hz}, CH\textsubscript{2}). \)

HRMS (EI): m/z calculated for [C\textsubscript{11}H\textsubscript{7}F\textsubscript{5}S]\textsuperscript{+} ([M]\textsuperscript{+}): 266.0183, measured: 266.0193. IR (ATR): \( \nu (\text{cm}^{-1}) \): 3059, 2928, 2854, 2224, 1729, 1599, 1492, 1443, 1410, 1312, 1271, 1207, 1131, 1095, 1029, 964, 916, 860, 751, 726, 689, 640 625, 551.
(Cinnamyl)(perfluoroethyl)sulfane (3j)³

\[
\begin{array}{c}
\text{SCF}_2\text{CF}_3 \\
\end{array}
\]

3j

Prepared from cinnamyl alcohol (2j) and BT-SC₂F₅ using General Procedure C. Pale yellow liquid (17 mg, 0.063 mmol, 13%).

\(^1\)H NMR (400 MHz, Chloroform-d) δ = 7.30 – 7.48 (m, 4H), 7.28 (m, 1H), 6.63 (d, J = 15.5 Hz, 1H), 6.22 (d, J = 15.5, 7.4 Hz, 1H), 3.77 (d, J = 7.4 Hz, 2H). \(^{19}\)F NMR (377 MHz, Chloroform-d) δ = -83.3 (t, J = 4 Hz, 3F), -91.9 (t, J = 4 Hz, 2F).

The data agree with literature precedents.³

(Perfluoroethyl)(3-phenylpropyl)sulfane (3k) + O-(3-Phenylpropyl) 2,2,2-trifluoroethanethioate (4k)

\[
\begin{array}{c}
\text{SCF}_2\text{CF}_3 \\
\end{array}
\]

3k + 4k

Prepared from 3-phenylprop-2-yn-1-ol (2k) and BT-SC₂F₅ using General Procedure C. Thioether 3k and thionoester 4k were isolated as a partially separable mixture. Yellow liquid (76 mg, ratio 3k:4k = 64:36, calculated yield: 3k = 37%, 4m = 21%).

3k: \(^1\)H NMR (600 MHz, Chloroform-d) δ = 7.28 – 7.34 (m, 2H), 7.18 – 7.25 (m, 3H), 2.93 (t, J = 7.3 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.04 (pent, J = 7.4 Hz, 2H). \(^{19}\)F NMR (565 MHz, Chloroform-d) δ = -83.4 (t, J = 4 Hz, 3F), -91.9 (q, J = 4 Hz, 2F).

4k: \(^1\)H NMR (600 MHz, Chloroform-d) δ = 7.28 – 7.34 (m, 2H), 7.18 – 7.25 (m, 3H), 4.57 (t, J = 6.4 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.21 (m, 2H). \(^{19}\)F NMR (565 MHz, Chloroform-d) δ = -71.0 (3F).

Mixture (definitive assignment of all peaks to 3k or 4k was not possible): \(^{13}\)C NMR (151 MHz, Chloroform-d) δ = 196.4 (q, J = 39 Hz, C₈), 140.5 (C₈), 140.4 (C₈) 128.8 (CH), 128.7 (CH), 128.57 (CH), 128.56 (CH), 126.5 (CH), 126.4 (CH), 122.0 (tq, J = 288, 39 Hz, CF₂), 118.7 (qt, J = 286, 37 Hz, CF₃), 115.9 (q, J = 280 Hz, CF₃), 73.3 (CH₂), 34.5 (CH₂), 31.9 (CH₂), 31.3 (CH₂), 29.3 (CH₂), 28.0 (t, J = 4 Hz, CH₂). \(\text{HRMS (EI)}\): m/z calculated for [C₁₁H₁₁F₅S]⁺ ([M⁺] for 3k): 270.0496, measured: 270.0514. \(\text{Note: A molecular ion peak for 4k could not be found, however, a possible fragmentation product was identified: m/z calculated for [C₁₁H₁₀F₃O]⁺ ([M−SH]⁺ for 4k): 215.0678, measured: 215.0676. IR (ATR, mixture): v (cm⁻¹): 3089, 3068, 3029, 2928, 2859, 1604, 1497, 1455, 1391, 1321, 1289, 1209, 1152, 1097, 1069, 1030, 911, 749, 698, 669, 625, 639, 590, 567, 550.}

S20
3.3 Deoxyheptafluoropropylation of Alcohols 2 with BT-SC$_3$F$_7$

(Perfluoropropyl)(2,4,6-trichlorobenzyl)sulfane (5d)

![Structure of 5d]

Prepared from 2,4,6-trichlorobenzyl alcohol (2d) and BT-SC$_3$F$_7$ using General Procedure C. Colourless liquid (196 mg, 0.49 mmol, 98%).

$^1$H NMR (600 MHz, Chloroform-d) $\delta = 7.38$ (s, 2H), 4.44 (s, 2H). $^{19}$F NMR (565 MHz, Chloroform-d) $\delta = -80.0$ (t, $J = 9$ Hz, 3F), -88.3 (m, 2F). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta = 136.6$ (C$_q$), 135.2 (C$_q$), 130.1 (C$_q$), 128.8 (CH), 123.8 (tt, $J = 290$, 34 Hz, SCF$_2$), 117.8 (qt, $J = 287$, 35 Hz, CF$_3$), 108.7 (tm, $J = 265$ Hz, CF$_2$), 28.2 (t, $J = 5$ Hz, CH$_2$). HRMS (EI): m/z calculated for [C$_{10}$H$_4$Cl$_3$F$_7$S]$^+$ ([M]$^+$): 393.8982, measured: 393.8983. IR (ATR): $\nu$ (cm$^{-1}$): 3083, 2928, 2851, 1726, 1581, 1550, 1528, 1441, 1420, 1376, 1336, 1207, 1184, 1110, 1088, 1072, 1037, 925, 852, 802, 786, 751, 742, 679, 654, 608, 563.

([1,1'-Biphenyl]-4-ylmethyl)(perfluoropropyl)sulfane (5e)

![Structure of 5e]

Prepared from biphenyl-4-methanol (2e) and BT-SC$_3$F$_7$ using General Procedure C. Pale yellow solid (145 mg, 0.394 mmol, 79%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta = 7.59 - 7.65$ (m, 4H), 7.44 - 7.52 (m, 4H), 7.41 (m, 1H), 4.25 (s, 2H). $^{19}$F NMR (376 MHz, Chloroform-d) $\delta = -80.0$ (t, $J = 9$ Hz, 3F), -88.2 (m, 2F), -124.0 (t, $J = 4$ Hz, 2F). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta = 141.3$ (C$_q$), 140.6 (C$_q$), 133.6 (C$_q$), 129.7 (CH), 129.0 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 123.9 (tt, $J = 289$, 34 Hz, SCF$_2$), 117.9 (qt, $J = 288$, 34 Hz, CF$_3$), 108.9 (tm, $J = 265$ Hz, CF$_2$), 32.8 (t, $J = 4$ Hz, CH$_2$). HRMS (EI): m/z calculated for [C$_{16}$H$_{11}$F$_7$S]$^+$ ([M]$^+$): 368.0464, measured: 368.0476. IR (ATR): $\nu$ (cm$^{-1}$): 3074, 3032, 1520, 1488, 1445, 1407, 1335, 1207, 1183, 1112, 1089, 1037, 1007, 924, 857, 769, 740, 717, 695, 673, 610.
4 NMR Spectra of Novel Compounds
