General:

Unless otherwise mentioned, all other chemicals were purchased from commercial sources. Potassium tert-butoxide (95%) was used as received. DMF was distilled over calcium hydride, and stored over activated molecular sieve. Phenyl trifluoromethyl sulfone (1a) or sulfoxide (1b) was prepared by the oxidation of phenyl trifluoromethyl sulfide with hydrogen peroxide or mCPBA.\(^1\,^2\) Methyl trifluoromethyl sulfone (1c) was prepared using known procedures.\(^3\) Most of the trifluorinated products are known, and their characterization results are consistent with the reported data.\(^4\,^8\)

\(^1\)H, \(^13\)C and \(^19\)F NMR spectra were recorded on superconducting NMR spectrometers at either 500 or 360 MHz. \(^1\)H NMR chemical shifts were determined relative to internal (CH\(_3\))\(_4\)Si (TMS) at \(\delta\) 0.0 or to the signal of a residual protonated solvent: CDCl\(_3\) \(\delta\) 7.26. \(^13\)C NMR chemical shifts were determined relative to internal
TMS at δ 0.0 or to the $^{13}$C signal of solvent: CDCl$_3$ δ 77.0. $^{19}$F NMR chemical shifts were determined relative to internal CFCl$_3$ at δ 0.0. The $^{19}$F NMR yields were determined by the integration of the corresponding product peaks with respect to PhOCF$_3$ internal standard. Mass spectra were recorded on GC-MS spectrometer with a mass selective detector at 70 eV.

**Typical procedures for $^1$BuOK induced trifluoromethylation:**

The reaction was commonly carried out in a Schlenk flask under an argon atmosphere. Into 7 ml DMF solution of phenyl trifluoromethyl sulfone ($\text{1a}$, 420 mg, 2 mmol) and 4-methylbenzophenone (196 mg, 1 mmol) at – 50 °C, was added 3 ml DMF solution of $^1$BuOK (280 mg, 2.5 mmol). The reaction flask was then sealed and the reaction mixture was then stirred from – 50 °C for 1h, followed by stirring at – 50 °C to room temperature overnight. The reaction mixture was quenched with 10 ml of ice water, and extracted with ether (20 ml x 3). The combined ether phase was washed with saturated NH$_4$Cl aqueous solution, followed by washing with water. After drying over MgSO$_4$, the ether solvent was removed under vacuum. The crude product was further purified by column chromatography (hexanes/ether = 9/1) to give 225 mg of product, 4-methyl-$\alpha$-phenyl-$\alpha$-(trifluoromethyl)benzenemethanol as a colorless oily liquid, yield 85 %. $^1$H NMR (CDCl$_3$): δ 3.01 (b, 1H); 7.35-7.38 (m, 6H); 7.49-7.52 (m, 4H). $^{19}$F NMR (CDCl$_3$): δ - 74.5. MS: 252 (M$^+$).
Other products:

**1-Phenyl-2,2,2-trifluoroethanol:**\(^4\) yellow oily liquid, 77 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.86 (s, 1H); 5.01 (q, \(^3\)J\(_{H-F}\) = 6.3 Hz, 1H); 7.43 (m, 2H); 7.48 (m, 3H). \(^19\)F (CDCl\(_3\)): \(\delta\) -78.5 (d, \(^3\)J\(_{H-F}\) = 6.2 Hz). MS: 176 (M\(^\text{+}\)).

**1-(2’-Naphthyl)-2,2,2-trifluoroethanol:**\(^4\) yellow solid, 62 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.76 (b, 1H); 5.19 (q, \(^3\)J\(_{H-F}\) = 6.7 Hz, 1H); 7.51-7.96 (m, 7H). \(^19\)F (CDCl\(_3\)): \(\delta\) -78.4 (d, \(^3\)J\(_{H-F}\) = 6.7 Hz). MS: 226 (M\(^\text{+}\)).

**4’-Ethyl-phenyl-2,2,2-trifluoroethanol:**\(^5\) oily liquid, 83 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.25 (t, 3H); 2.60 (b, 1H); 2.67 (q, 2H); 4.99 (m, 1H); 7.25 (d, 2H); 7.38 (d, 2H). \(^19\)F NMR (CDCl\(_3\)): \(\delta\) -78.9 (d, \(^3\)J\(_{H-F}\) = 7.7 Hz). \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 15.4; 28.6; 72.6 (q, J = 31.9 Hz); 124.3 (q, J = 282.5 Hz); 127.4; 128.1; 131.2; 145.8. MS: 204 (M\(^\text{+}\)).

**4’-Biphenyl-2,2,2-trifluoroethanol:**\(^6\) white solid, 76 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.87 (b, 1H); 5.07 (m, 1H); 7.40-7.65 (m, 9 H). \(^19\)F NMR (CDCl\(_3\)): \(\delta\) -78.7 (d, J = 7.6 Hz). \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 72.6 (q, J = 31.6 Hz); 124.3 (q, J = 281.8 Hz); 127.1; 127.3; 127.7; 127.8; 128.8; 132.8; 140.3; 142.5. MS: 252 (M\(^\text{+}\)).

**α-Phenyl-α-(trifluoromethyl)benzenemethanol:**\(^4\) oily liquid, 86 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.36 (s, 3H); 2.89 (s, 1H); 7.17-7.51 (m, 9H). \(^19\)F NMR (CDCl\(_3\)): \(\delta\) -74.4. MS: 266 (M\(^\text{+}\)).

**4,4’-Dichloro-α-phenyl-α-(trifluoromethyl)benzenemethanol:**\(^7\) pale yellow oily liquid, 74 % yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.95 (s, 1H); 7.34 (d, 4H); 7.40 (d, 4H). \(^19\)F NMR (CDCl\(_3\)): \(\delta\) -75.1. MS: 320 (M\(^\text{+}\)).
4-Nitro-α-phenyl-α-(trifluoromethyl)benzenemethanol: pale yellow oily liquid, 83% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 3.15 (s, 1H); 7.37-8.23 (m, 9 H). \(^{19}\)F NMR (CDCl\(_3\)): \(\delta\) -74.7. MS: 297 (M\(^+\)).

4-Methoxy-α-phenyl-α-(trifluoromethyl)benzenemethanol: oily liquid, 73% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.80 (s, 1H); 3.81 (s, 3H); 6.87-7.49 (m, 9 H). \(^{19}\)F NMR (CDCl\(_3\)): \(\delta\) -75.0. MS: 281 (M\(^+\)-1).

2-(Trifluoromethyl)-2-adamantanol: 82 % yield, white solid (sublimed). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.56-2.27 (m, 15H). \(^{19}\)F (CDCl\(_3\)): \(\delta\) -76.1. MS: 220 (M\(^+\)).

2,2,2-Trifluoroacetophenone: 82 % yield, colorless liquid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.53 (t, J = 8.0 Hz, 2H); 7.70 (t, J = 7.5 Hz, 1H); 8.06 (d, J = 8.0 Hz, 2 H). \(^{19}\)F (CDCl\(_3\)): \(\delta\) -71.8. MS: 174 (M\(^+\)).

Phenyl trifluoromethyl sulfide: 87 % yield, colorless liquid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.43 (t, J = 7.5 Hz, 2H); 7.50 (t, J = 7.5 Hz, 1H); 8.67 (d, J = 7.5 Hz, 2 H). \(^{19}\)F (CDCl\(_3\)): \(\delta\) -43.2.