

Supporting information belonging to the paper:

CsF Catalyzed Nucleophilic Trifluoromethylation of *trans*-Enones with Trimethyl(trifluoromethyl)silane: A Facile Synthesis of *trans*- α -Trifluoromethyl Allylic Alcohols

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General Trifluoromethylation Procedure. In a typical reaction, *trans*-enones (5 mM) and trimethyl(trifluoromethyl)silane (5.25.0 mM) were dissolved in 5 mL ethylene glycol dimethyl ether and cesium fluoride (15.0 mg, 0.1 mM) was added directly at room temperature. The reaction was exothermic and the solution changed from colorless to yellowish brown. It was stirred at 25 °C for 3h, diluted with dry pentane (25 mL) and filtered. Removal of solvent at reduced pressure yielded *trans*- α -trifluoromethyl silyl ethers in >95% yield. *trans*- α -Trifluoromethyl silyl ethers were dissolved in THF (15 mL) and treated with 6N HCl slowly. It was stirred for 3 h at room temperature and diluted with water (50 mL). The products were extracted with diethyl ether (50 mL). The ether extract was dried over anhydrous MgSO₄ and filtered. Removal of ether at reduced pressure gave *trans*- α -Trifluoromethyl allylic alcohols in >90% isolated yields.

***trans*-1,1,1-Trifluoro-4-phenyl-3-buten-2-trimethylsilyl ether (2b)**: IR (neat) 1649 (s, C=C) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.2 (s, 9H), 1.6 (s, 3H), 6.2 (d, 1H, $J = 16$ Hz), 6.7 (d, 1H, $J = 16$ Hz), 7.4 (m, 5H); ^{13}C NMR (CDCl_3) δ 2, 22, 76 (q, $J_{\text{C-C-F}} = 30$ Hz), 125 (q, $J_{\text{C-F}} = 283$ Hz), 126, 127, 128., 19, 133, 136; ^{19}F NMR (CDCl_3) δ -82 (s); MS (EI) m/z (species, rel int) 288 (M^+ , 7), 219 ($\text{M}^+ - \text{CF}_3$, 100), 73 (SiMe_3^+ , 37).

***trans*-1,1,1-Trifluoro-4-phenyl-3-buten-2-ol (3b)**: IR (neat) 3433 (b, OH), 1655 (s, C=C) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.2 (s, 3H), 2.1 (s, broad, 1H), 6.2 (d, 1H, $J = 16$ Hz), 6.9 (d, 1H, $J = 16$ Hz), 7.4 (m, 5H); ^{13}C NMR (CDCl_3) δ 22, 74 (q, $J_{\text{C-C-F}} = 29$ Hz), 125 (q, $J_{\text{C-F}} = 283$ Hz), 126, 127, 129, 132, 136; ^{19}F NMR (CDCl_3) δ -83 (s); MS (EI) m/z (species, rel int) 216 (M^+ , 41), 199 ($\text{M}^+ - \text{OH}$, 6), 183 [$\text{M}^+ - (\text{CH}_3 + \text{H}_2\text{O})$, 7], 147 ($\text{M}^+ - \text{CF}_3$, 100), 129 [$\text{M}^+ - (\text{CF}_3 + \text{H}_2\text{O})$, 19], HRMS calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}$: 216.0762. Found 216.0757.

***trans*-2,2-Trifluoromethyl-4-phenyl-3-buten-2-trimethylsilyl ether (2c)**. IR (neat) 1658 (s, C=C) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.23 (s, 9H), 6.19 (d, 1H, $J = 16$ Hz), 6.99 (d, 1H, $J = 16$ Hz), 7.33 (m, 5H); ^{13}C NMR (CDCl_3) δ 1.35 78.3 (q, $J_{\text{C-C-F}} = 39$ Hz), 118.20, 122.5 (q, $J_{\text{C-F}} = 289$ Hz), 127.1, 128.8, 129.1, 134.9, 137.3; ^{19}F NMR (CDCl_3) δ -75.95 (s); MS (EI) m/z (species, rel int) 342 (M^+ , 30), 273 ($\text{M}^+ - \text{CF}_3$, 100), 183 [$\text{M}^+ - (\text{CF}_3 + \text{OSiMe}_3 + \text{H})$, 49], 131 [$\text{M}^+ - (2 \times \text{CF}_3 + \text{SiMe}_3)$, 83], 77 (Ph, 4).

***trans*-2,2-Trifluoromethyl-4-phenyl-3-buten-2-ol (3c)**. IR (neat) 3537 (b, OH), 1657 (s, C=C) cm^{-1} ; ^1H NMR (CDCl_3) δ 4.06 (s, broad, 1H), 6.21 (d, 1H, $J = 16$ Hz), 7.04 (d, 1H, $J = 16$ Hz), 7.32 (m, 5H); ^{13}C NMR (CDCl_3) δ 78.0 (q, $J_{\text{C-C-F}} = 29$ Hz), 118.3, 125.2 (q, $J_{\text{C-F}} = 282$ Hz), 127.2, 128.8, 129.3, 133.2, 136.0; ^{19}F NMR (CDCl_3) δ -

77.52 (s); MS (EI) m/z (species, rel int) 270 (M^+ , 46), 201 ($M^+ - CF_3$, 100), 183 [$M^+ - (CF_3 + H_2O)$, 43]; HRMS calcd. for $C_{11}H_8F_6O$ 270.0479. Found 270.0466.

***trans*-1,1,1-trifluoro-2-ethyl-2-methyl-3-buten-2-trimethylsilyl ether (2d)**. IR (neat) 1678 (s, C=C) cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.85 (t, 3H, $J = 7$ Hz), 1.6 (q and d, overlapped, 5H), 5.37 (d, 1H, $J = 16$ Hz), 5.82 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.5, 6.8, 17.4, 27.1, 78.5 (q, $J_{C-C-F} = 28$ Hz), 125.6 (q, $J_{C-F} = 287.0$ Hz), 127.5, 129.2; ^{19}F NMR ($CDCl_3$) δ -79.4 (s); MS (EI) m/z (species, rel int) 240 (M^+ , 3), 211 ($M^+ - CF_3$, 100), 171 ($M^+ - CF_3$, 37), 73 ($SiMe_3$, 72), 69 (CF_3 , 80).

***trans*-1,1,1-trifluoro-2-ethyl-2-methyl-3-buten-2-ol (3d)**. IR (neat) 3464 (b, OH), 1680 (s, C=C) cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.89 (t, 3H), 1.74 (overlapped doublet and quartet, 5H), 4.17 (s, broad, 1H), 5.43 (d, 1H, $J = 15$ Hz), 5.85 (q, 1H); ^{19}F NMR ($CDCl_3$) δ -81.7 (s); MS (EI) m/z (species, rel int) 151 ($M^+ - OH$, 8), 139 ($M^+ - C_2H_5$, 70), 99 ($M^+ - CF_3$, 60), 69 (CF_3 , 100).

***trans*-1,1,1-Trifluoro-4-(-2-thienyl)-3-buten-2-methyl-2-ol (2e)** IR (neat) 1649 (s, C=C) cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 1.59 (s, 3H), 6.12 (d, 1H, $J = 15.8$ Hz), 6.91 (d, 1H, $J = 15.8$ Hz), 7.0 (m, 2H), 7.21 (d, 1H, $J = 5$ Hz); ^{13}C NMR ($CDCl_3$) δ 2.0, 21.5, 75.8 (q, $J_{C-C-F} = 28.5$ Hz), 124.9 (q, $J_{C-F} = 255.6$ Hz), 125.2, 125.8, 126.9, 127.5, 140.9, 124.9 (q, $J_{C-F} = 283.0$ Hz), 126.8, 127.6, 128.2, 128.6, 132.6, 135.9; ^{19}F NMR ($CDCl_3$) δ -82.2 (s); MS (EI) m/z (species, rel int) 294 (M^+ , 38), 225 ($M^+ - CF_3$, 100), 73 ($SiMe_3$, 24); HRMS calcd. for $C_{12}H_{17}F_3OSiS$ 294.0722. Found 294.0735.

***trans*-1,1,1-Trifluoro-4-(-2-thienyl)-3-buten-2-methyl-2-ol (3e)** IR (neat) 3508 (b, OH), 16554 (s, C=C) cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.54 (s, 3H), 2.25 (s, broad, 1H), 6.10 (d, 1H, $J = 16.9$ Hz), 6.96 (d, 1H, $J = 16.9$ Hz), 7.01 (m, 2H), 7.21 (d, 1H, $J = 5$ Hz); ^{13}C

NMR (CDCl₃) δ 22.1, 73.7 (q, J_{C-C-F} = 29.4 Hz), 125.6 (q, J_{C-F} = 283 Hz), 125.3, 125.4, 127.1, 127.5, 140.5; ¹⁹F NMR (CDCl₃) δ -82.4 (s); MS (EI) m/z (species, rel int) 222 (M⁺, 70), 205 (M⁺ - OH, 2), 153 (M⁺ - CF₃, 100); HRMS calcd. for C₁₉H₉F₃OS (M⁺) 222.0326. Found 222.0311.

2-Cyclohexen-1-trifluoromethyl-1-trimethylsilyl ether (2f). IR (neat) 1655 (s, C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 0.11 (s, 9H), 1.73 (m, 4H), 2.05 (m, 2H), 5.77 (d, 1H, J = 9 Hz), 6.08 (d of q, 1H), ¹³C NMR (CDCl₃) δ 1.8, 17.0, 24.6, 30.3, 72.5 (q, J_{C-C-F} = 29 Hz), 125.9 (q, J_{C-F} = 284.0 Hz), 123.9, 135.3; ¹⁹F NMR (CDCl₃) δ -82.6 (s); MS (EI) m/z (species, rel int) 238 (M⁺, 57), 223 (M⁺ - CH₃, 16), 169 (M⁺ - CF₃, 100), 73 (SiMe₃, 37).

2-Cyclohexen-1-trifluoromethyl-1-ol (3f). IR (neat) 3495 (b, OH), 1660 (s, C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 1.69 (s, H), 1.79 (m, 4H), 2.05 (m, 2H), 5.70 (d, 1H, J = 10 Hz), 6.12 (d of q, 1H); ¹³C NMR (CDCl₃) δ 17.17, 24.7, 28.8, 72.0 (q, J_{C-C-F} = 29 Hz), 125.2 (q, J_{C-F} = 282 Hz), 127.0, 136.3; ¹⁹F NMR (CDCl₃) δ -83.0 (s); MS (EI) m/z (species, rel int) 149 (M⁺ - OH, 44), 97 (M⁺ - CF₃, 100), 69 (CF₃, 19).