1) Experimental Procedures and Spectroscopic Data for Compounds 4, 7, 8, 9, 11, and 12.

2) $^1$H NMR and $^{19}$F NMR Spectra for Compounds 4, 7, 8, 9, 11, and 12

**General.** Unless otherwise indicated, all compounds and reagents were purchased from commercial suppliers and used without further purification. Proton and fluorine nuclear magnetic resonance spectra are recorded at either 300 or 400 MHz. Fluorine NMR spectra are internally referenced relative to 2,2,2-trifluoroethanol and proton NMR spectra to CDCl$_3$. All chemical shifts ($\delta$) are given in ppm and coupling constants ($J$) are given in Hz. Electrospray mass spectrometry was obtained from the Scripps Research Institute Mass Spectrometry Facility. Optical rotations were measured using a 1.00 dm path length cell. Crystal structure determination was performed at the UCSD Department of Chemistry and Biochemistry Small Molecule X-Ray facility (Dr. Peter Gantzel) on a Bruker SMART APEX CCD X-ray Diffractometer.

**N-Boc-4(S)-hydroxy-4-trifluoromethyl-L-proline methyl ester (4).** A solution of prolinone 3 (215 mg, 884 $\mu$mol) in 4 ml of dry THF was cooled to 0$^\circ$C and treated with 261 $\mu$L (1.77 mmol) of CF$_3$TMS. A catalytic amount of TBAF $\cdot$ 3 x H$_2$O (20 mg, 88 $\mu$mol) was added and the amber-colored solution was allowed to warm gradually to rt. After 8 h, 2 eq. of TBAF $\cdot$ 3 x H$_2$O (462 mg, 1.77 mmol) was added and the reaction stirred at rt for 2h. The solution was concentrated in vacuo to a brown oil, taken up in 20 ml of water and extracted with DCM (3 x 20 mL). The organic layers were dried over MgSO$_4$ and evaporated to give 265 mg of a viscous brown liquor. Careful column chromatography over silica gel (3:1
Hex:EtOAc) yielded 155 mg of N-Boc-4(S)-hydroxy-4-trifluoromethyl-L-proline methyl ester (4) as an off-white sticky foam (56%). Molecular formula C_{12}H_{18}O_{5}NF_{3}. Molecular weight 313.11 g/mol; $R_f$ =0.24 (30% EtOAc/Hex). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.58-4.40 (2d, $J_{\beta}$=9.6 Hz, 1H, rotamers), 3.80-3.75 (2s, $J_3$=3.9 Hz, 3H, rotamers), 3.74-3.65 (m, 2H), 2.53 (m, 1H), 2.18 (m, 1H), 1.45-1.41 (2s, 9H, rotamers); $^{19}$F NMR (300 MHz, CF$_3$CH$_2$OH) $\delta$ -81.46 and -81.62 (2s, 3F, rotamers); EI-MS [MH+] calc for 4 314, found 314, 336 [MNa+]; $[\alpha]_D^{20}$ = -31.2° ($c$ = 1.0, MeOH).

**N-Boc-2(S)-tert-butyldimethylsilyloxymethyl-4-trifluoromethyl-4,5-pyrroline (7).**

A solution of compound 6 (1.00 g, 2.50 mmol) in dry THF (30 mL) was treated with NaH (170 mg, 4.26 mmol) at 0°C under Ar. After stirring 15 min, tolenesulfonyl chloride (716 mg, 3.75 mmol) was added and the mixture allowed to warm to rt. After TLC showed complete disappearance of the starting material (2 h), the reaction mixture was cooled to –78°C and t-BuOK (562 mg, 5.00 mmol) was added in one portion. The reaction was removed from the cooling bath and became bright yellow after 20 min. After 2 h of stirring at rt the mixture was poured into 100 mL of water and extracted with EtOAc (5 x 40 mL). The combined organic layers were dried over MgSO$_4$ and concentrated to give a 1.10 g of a yellow oil. Purification by silica gel flash chromatography (19:1 Hex:EtOAc) gave 725 mg (1.90 mmol) of pure N-Boc-2(S)-tert-butyldimethylsilyloxymethyl-4-trifluoromethyl-4,5-pyrroline (7) as a colorless oil (76%). Molecular formula C$_{17}$H$_{30}$O$_3$NF$_3$Si, Molecular weight 381.51 g/mol; $R_f$=0.54 (10% EtOAc/Hex). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.04 and 6.85 (2s, 1H, rotamers), 4.38-4.17 (m, 1H), 3.63 (m, 1H), 2.98-2.71 (complex, 2H), 1.47 (s, 9H), 0.82 (s, 9H), 0.02 and 0.09 (2s, 6H, rotamers); $^{19}$F NMR (300 MHz, CF$_3$CH$_2$OH) $\delta$ -64.77 (s, 3F); EI-MS [MH+] calc for 4 383, found 383, 405 [MNa+]; $[\alpha]_D^{20}$ = -71.8° ($c$ = 1.0, MeOH).

**N-Boc-2(S)-hydroxymethyl-4(S)-trifluoromethyl pyrrolidine (8).**

Pyrroline 7 (135 mg, 354 µmol) was dissolved in 3 mL of EtOAc and treated with 142 mg of 5% Pd/C. The stirring solution was put under H$_2$ (1 atm) and stirred at rt for 8 h. The reaction mixture was filtered through a pad of celite and the pad was rinsed 3 times with DCM. The filtrate was concentrated in vacuo to give 115 mg of a colorless oil. Analysis of the $^{19}$F NMR spectrum showed a 94:6 ratio of compounds 8:10. Purification by silica gel flash chromatography (4:1 Hex:EtOAc) yielded 78 mg (290 µmol) of pure N-Boc-2(S)-hydroxymethyl-4(S)-trifluoromethyl pyrrolidine (8) as a colorless oil (78%). Molecular formula C$_{11}$H$_{18}$O$_3$NF$_3$, Molecular weight 269.26 g/mol; $R_f$=0.16 (25% EtOAc/Hex). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$
4.92 (bs, 1H), 3.95 (m, 1H), 3.76 (t, \(J=6.2\) Hz, 1H), 3.71-3.60 (m, 2H), 3.29 (t, \(J=16.5\) Hz, 1H), 2.81 (m, 1H), 2.25 (ddd, \(J_a=12.9\) Hz, \(J_b=J_c=7.5\) Hz), 1.67-1.57 (m, 1H), 1.44 (s, 9H); \(^{19}\)F NMR (300 MHz, CF\(_3\)CH\(_2\)OH) \(\delta\) -72.02 (d, \(J=4.8\) Hz, 3F); EI-MS [MH+] calc for 4 269, found 269; \([\alpha]_D^{20}\) = -56.6° (c = 1.0, MeOH).

**N-Boc-2(\(R\))-hydroxymethyl-4(\(S\))-trifluoromethyl pyrrolidine (11).** A solution of pyrrole 10 (200 mg, 748 \(\mu\)mol) in 2 mL of dry DCM at rt was treated with 12 mg (15 \(\mu\)mol) of [Ir(COD)PyPCy\(_3\)] and promptly put under H\(_2\) atmosphere (1 atm). The orange reaction solution became colorless within 10 min, after which the color gradually returned over 20 min. After 30 min, TLC indicated complete consumption of the starting material and the solvent was removed in vacuo to yield 210 mg of a crude orange oil. Analysis of the \(^{19}\)F NMR spectrum showed a 99.4:0.6 ratio of compounds 10:8. Purification through a plug of silica gel (eluted with 3:1 EtOAc/Hex) yielded 183 mg of pure N-Boc-2(\(R\))-hydroxymethyl-4(\(S\))-trifluoromethyl pyrrolidine (11) as a colorless oil (91%). Molecular formula C\(_{11}\)H\(_{18}\)O\(_3\)NF\(_3\), Molecular weight 269.26 g/mol; \(R_f\) =0.17 (30% EtOAc/Hex). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.08 (bs, 1H), 3.82 (bs, 1H), 3.68 (m, 1H), 3.59-3.52 (m, 2H), 2.95 (m, 1H), 2.16 (m, 1H), 1.88 (m, 1H), 1.44 (s, 9H); \(^{19}\)F NMR (300 MHz, CF\(_3\)CH\(_2\)OH) \(\delta\) -72.78 (d, \(J=7.5\) Hz, 3F); EI-MS (MH+) calc for 4 270, found 270, 292 (MNa+), 268 (M-H); \([\alpha]_D^{20}\) = -31.9° (c = 1.0, MeOH).

**Representative Procedure for Oxidation of Alcohols 8 and 11.** Two oxidant solutions were prepared prior to carrying out the reaction. The first consisted of 84 mg (742 \(\mu\)mol) of 80% NaClO\(_2\) dissolved in 0.4 ml water (~2 M). The second was comprised of 22 \(\mu\)L of bleach diluted with 0.4 mL water. The desired alcohol (100 mg, 371 \(\mu\)mol) was dissolved in a 3:2 mixture of MeCN:NaH\(_2\)PO\(_4\) buffer (pH = 6.6, 0.67M) and warmed to 45°C. The reaction mixture was treated with 6 mg (37 \(\mu\)mol) of TEMPO followed by the dropwise, simultaneous addition (over 1 h) of the two oxidant solutions described above. Stirring was maintained at 45°C until TLC showed complete consumption of starting material (usually 24 h). The reaction was cooled to rt and a saturated Na\(_2\)SO\(_3\) solution was added dropwise until the reaction mixture became colorless. The solution was carefully acidified with 1M HCl to pH<3 and extracted 6 times with EtOAc. The organic layers were dried over Na\(_2\)SO\(_4\) and concentrated in vacuo to give a white solid which was sufficiently pure by NMR and TLC. The products could be further purified by crystalization out of DCM:hexanes.
**N-Boc-(2S,4S)-trifluoromethylproline (9).** 94% yield. Molecular formula C\textsubscript{11}H\textsubscript{16}O\textsubscript{4}NF\textsubscript{3}, Molecular weight 283.25 g/mol; \( R_f \) =0.53 (50% EtOAc/Hex). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 4.43-4.33 (2dd, \( J_a=J_b=7.8 \) Hz, 1H, rotamers), 3.84 (m, 1H), 3.46 (m, 1H), 2.94 (m, 1H), 2.68-2.35 (complex m, 2H), 1.47-1.40 (2s, 9H, rotamers); \(^{19}\)F NMR (300 MHz, CF\textsubscript{3}CH\textsubscript{2}OH) \( \delta \) -71.98 (d, \( J=8.1 \) Hz, 3F); EI-MS [M-H] calc for 11 282, found 282, 306 [MNa\textsuperscript{+}]; MADLI-FTMS [MNa\textsuperscript{+}] calc for 11 306.0924, found 306.0926; \([\alpha]_D^{20}= -59.2^o \) (\( c = 1.0, \text{MeOH} \)).

**N-Boc-(2S,4R)-trifluoromethylproline (12).** 96% yield. Molecular formula C\textsubscript{11}H\textsubscript{16}O\textsubscript{4}NF\textsubscript{3}, Molecular weight 283.25 g/mol; \( R_f \)=0.49 (50% EtOAc/Hex). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 4.47-4.36 (2d, \( J=6.3 \) Hz, 1H, rotamers), 3.79-3.68 (2dd, \( J_a=J_b=11.1 \) Hz, 1H, rotamers), 3.52 (m, 1H), 3.06 (m, 1H), 2.48-2.20 (complex m, 2H), 1.46-1.40 (2s, 9H, rotamers); \(^{19}\)F NMR (300 MHz, CF\textsubscript{3}CH\textsubscript{2}OH) \( \delta \) -72.51 and –72.62 (2d, \( J=8.7 \) Hz, 3F, rotamers); EI-MS [M-H] calc for 12 282, found 282, 306 [MNa\textsuperscript{+}]; MADLI-FTMS [MNa\textsuperscript{+}] calc for 12 306.0924, found 306.0926; \([\alpha]_D^{20}= -30.1^o \) (\( c = 1.0, \text{MeOH} \)).