Experimental Details: Racemic epoxides were prepared from the corresponding styrene derivative according to the Sharpless procedure (MTO/pyrdine/H_2O_2 ; *J. Am. Chem. Soc*. **1997**, *119*, 6189) or from the corresponding aldehyde with dimethylsulfonium methylide. Racemic diols were prepared either from the epoxide derivative via ceric ammonium-catalyzed hydrolysis (Tetrahedron **1991**, *47*, 9861) or from the styrene derivative with ultrasound-accelerated permanganate oxidation (*Tet. Letters* **1998**, 7463). Tricyclohexylphosphine was obtained from Strem Chemicals, Inc. Anhydrous THF was obtained from Aldrich. Optical rotation data was obtained on a Perkin Elmer 241 polarimeter.

Representative Example: Synthesis of Diol 4a

Potassium osmate dihydrate (185 mg; 0.50 mmols) was combined with t-butanol (75 ml) and water (70 ml) at RT and stirred for 10 min, followed by the addition of N-methylmorpholine N-oxide (11.15 g; 95.2 mmols), and $(DHQ)_2PHAL$ (440 mg; 0.56 mmols). After stirring at RT for 15 min., the solution was cooled to 20 ^{o}C and 3,5-bis(trifluormethyl)styrene (**5a**)(14.9 g; 62.1 mmols) was added via syringe pump over 4 h, followed by aging at 20 ^{o}C for 2 h. The reaction was quenched by adding 10 % aq sodium sulfite (100 ml) slowly, followed by addition of EtOAc (100 ml). The layers were separated and the aq layer extracted with EtOAc (2 x 60 ml). The combined organic layers were washed with 0.4 M sulfuric acid in saturated sodium sulfate (1 x 75 ml) followed by drying over sodium sulfate. The volatiles were removed in vacuo to give 16.9 g of crude diol as an oil (80% assay yield; 92% ee). The crude diol was crystallized by dissolution in refluxing hexanes (85 ml) and EtOAc (12 ml), followed by cooling to RT over 2 h, then to 5 ^{o}C and aging for 1 h. The solids were isolated by filtration and washed with chilled hexanes (2 x 25 ml) to give 12.7 g (75% yield) of (S)-diol **4a** as a colorless solid (>98 A%; 97% ee). mp 142-144 ^{o}C. $[\alpha]^{25}_{D} = 19.85$ (*c* 2.8 MeOH); ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 8.02 (s, 2H), 7.94 (s, 1H), 5.69 (d, *J* = 4.8, 1H), 4.84 (t, *J* = 5.6, 1H), 4.77 (q, *J* = 5.3, 1H), 3.59 (m, 1H), 3.50 (m, 1H); ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 147.7, 130.1 (q, *J* = 32.8), 127.5 (q, *J* = 3.2), 123.9 (q, *J* = 273.1), 120.8

(septet, *J* = 4.0), 72.6, 66.8; Anal. Calcd for $C_{10}H_8F_6O_2$ C 43.81; H, 2.94; F, 41.58. Found: C, 43.45; H, 2.77; F, 41.93.

GC Chiral assay: Chiraldex gamma-cyclodextrin column (G-TA) 20 m x 0.25 mm

Temp 130 ^{o}C-hold 10 min – ramp to 150 ^{o}C at 1 ^{o}C/min; total flow: 160 ml/min. Retention times:

R- isomer 9.55 min
S-isomer 9.88 min

Representative Example: Synthesis of Epoxide 2a

Tricyclohexylphosphine (900 mg; 3.2 mmol) was dissolved in anhydrous THF (3 mL) at rt, followed by cooling to 5 ^{o}C and the addition of diisopropylazodicarboxylate (0.60 mL; 3.1 mmol) dropwise over 5 min. The solution was warmed to 15 ^{o}C during which time the reaction mixture thickened. After aging for 10 min, (S)-diol **4a** (600 mg; 2.2 mmols) dissolved in THF (2 mL) was added dropwise followed by warming to 22 ^{o}C and aging for 2 h. LC analysis of the reaction mixture indicated 519 mg of epoxide **2a** (92% yield). A portion was bulb-to-bulb distilled (120 ^{o}C oven temp; 4 torr) to provide pure material for chiral assay (96.4 % ee). Alternatively, pure material was obtained by chromatography (SiO_2; 7/1 hexanes/EtOAc). $[\alpha]_D^{20}$ –5.7 (*c* 0.17, $CHCl_3$). ^{1}H NMR (400.25 MHz; $CDCl_3$): δ 2.79 (dd, 1H, $H_{2\mathit{cis}}$, J_{gem} = 5.4 Hz, $J_{1\text{-}2\mathit{cis}}$ = 2.4 Hz); 3.23 (dd, 1H, $H_{2\mathit{trans}}$, J_{gem} = 5.2 Hz, $J_{1\text{-}2\mathit{trans}}$ = 4.0 Hz); 4.00 (dd, 1H, H_1 $J_{1\text{-}2\mathit{cis}}$ 2.4 Hz, $J_{1\text{-}2\mathit{trans}}$ =4.0 Hz). ^{13}C NMR (100.65 MHz; $CDCl_3$): δ 140.69 (s, C1), 132.06 (septet, $C_{3,5}$, J = 33.7 Hz), 125.69 (m, $C_{2,6}$), 123.18 (q, CF_3, J = 273 Hz), 122.04 (apparent septet, C_4, J = 3.7 Hz).

Chiral GC assay: column as above; Initial temp = 100 °C-hold 4 min and then ramp to 200 °C at 15 °C/min. Retention times:

R-isomer: 6.01 min
S-isomer: 6.38 min

<u>Pertinent Optical Rotation Values:</u>

Compound **2g** : $[\alpha]_D^{20}$ -12.1 ° (c 0.02 $CHCl_3$)