1. General methods

**General procedure for the preparation of Mosher’s esters.** To a solution of a chlorohydrine (0.04 mmol) and DMAP (0.2 mmol, 24 mg) in CH$_2$Cl$_2$ (2 mL) (R)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetic chloride (0.04 mmol, 10.1 mg) was added under argon at room temperature and the reaction mixture was stirred overnight. Then the reaction was quenched with a saturated aqueous solution of NH$_4$Cl (5 mL), washed with a saturated aqueous solution of NaHCO$_3$, and extracted by ether (3 × 5 mL). The combined organic fractions were dried over MgSO$_4$ and volatiles were removed under reduced pressure. The crude product was used for determination of the diastereoisomeric ratio without further purification to avoid possible amplification of the ee.
2. Copies of $^1$H or $^{19}$F spectra showing enantiomer ratio

2.1 Opening of 3a to 4a catalyzed by $(R,R_{ax})$-1a or $(R,S_{ax})$-1b

Opening of 3a to 4a catalyzed by $(R,R_{ax})$-1a in CH$_2$Cl$_2$ ($^1$H NMR)

Opening of 3a to 4a catalyzed by $(R,R_{ax})$-1a in MeCN ($^1$H NMR)
Opening of $3a$ to $4a$ catalyzed by $(R,R_{ax})$-$1a$ in THF ($^1$H NMR)

Opening of $3a$ to $4a$ catalyzed by $(R,R_{ax})$-$1a$ in toluene ($^1$H NMR)
Opening of 3a to 4a catalyzed by \((R,R_{ax})-1a\) in PhCl \((^1H\text{ NMR})\)

Opening of 3a to 4a catalyzed by \((R,S_{ax})-1b\) in CH\(_2\)Cl\(_2\) \((^1H\text{ NMR})\)
Opening of 3a to 4a catalyzed by (R,S)_ax-1b in MeCN (^1H NMR)

Opening of 3a to 4a catalyzed by (R,S)_ax-1b in THF (^1H NMR)
2.2. Opening of 2a with (R,R<sub>ax</sub>,R)-2a and (R,S<sub>ax</sub>,R)-2b
Opening of 3a to 4a catalyzed by (R,R<sub>ax</sub>,R)-2a in CH<sub>2</sub>Cl<sub>2</sub> (1H NMR)

Opening of 3a to 4a catalyzed by (R,R<sub>ax</sub>,R)-2a in MeCN (1H NMR)
Opening of 3a to 4a catalyzed by (R,Rax,R)-2a in THF ($^1$H NMR)

Opening of 3a to 4a catalyzed by (R,Rax,R)-2a in toluene ($^1$H NMR)
Opening of 3a to 4a catalyzed by \((R,R_{ax},R)\)-2a in PhCl \(\text{^1H NMR}\)

Opening of 3a to 4a catalyzed by \((R,S_{ax},R)\)-2b in CH\(_2\)Cl\(_2\) \(\text{^1H NMR}\)
Opening of 3a to 4a catalyzed by \((R,S_{ax},R,)-2b\) in MeCN (\(^1\)H NMR)

Opening of 3a to 4a catalyzed by \((R,S_{ax},R,)-2b\) in THF (\(^1\)H NMR)
Opening of 3a to 4a catalyzed by (R,S_{ax, R})-2b in toluene (\textsuperscript{1}H NMR)

Opening of 3a to 4a catalyzed by (R,S_{ax, R})-2b in PhCl (\textsuperscript{1}H NMR)
2.3. Opening of 3b-3e with \((R,R)\)-2a and \((R,S)\)-2b

Opening of 3b to 4b catalyzed by \((R,R_{ax})\)-2a in MeCN (\(^{19}\)F NMR)

Opening of 3d to 4d catalyzed by \((R,R_{ax})\)-2a in CH\(_2\)Cl\(_2\) (\(^{19}\)F NMR)
Opening of 3d to 4d catalyzed by (R,Rα)-2a in MeCN (¹⁹F NMR)

Opening of 3e to 4e catalyzed by (R,Rα)-2a in CH₂Cl₂ (¹⁹F NMR)
Opening of \(3e\) to \(4e\) catalyzed by \((R,R_{ax})-2\) in MeCN (\(^{19}\text{F NMR}\))

Opening of \(3b\) to \(4b\) catalyzed by \((R,S_{ax})-2\) in MeCN (\(^{19}\text{F NMR}\))
Opening of 3c to 4c catalyzed by (R,S$_{ax}$)-2b in MeCN ($^{19}$F NMR)

Opening of 3d to 4d catalyzed by (R,S$_{ax}$)-2b in CH$_2$Cl$_2$ ($^{19}$F NMR)
Opening of 3d to 4d catalyzed by (R,S$_{ax}$)-2b in MeCN ($^{19}$F NMR)

Opening of 3e to 4e catalyzed by (R,S$_{ax}$)-2b in CH$_2$Cl$_2$ ($^{19}$F NMR)
Opening of 3e to 4e catalyzed by (R,S$_{ax}$)-2b in MeCN ($^{19}$F NMR)
2.4. Opening of 3b-3e with (R,R<sub>ax</sub>,R)-2a and (R,S<sub>ax</sub>,R)-2b

Opening of 3b to 4b catalyzed by (R,R<sub>ax</sub>,R)-2a in THF (19F NMR)

Opening of 3c to 4c catalyzed by (R,R<sub>ax</sub>,R)-2c in THF (19F NMR)
Opening of 3d to 4d catalyzed by \((R,R_{ax},R)\)-2a in THF \(^{19}\text{F NMR}\)

Opening of 3e to 4e catalyzed by \((R,R_{eq},R)\)-2a in THF \(^{19}\text{F NMR}\)
Opening of 3b to 4b catalyzed by (R,Sax,R)-2b in THF ($^{19}$F NMR)

Opening of 3c to 4c catalyzed by (R,Sax,R)-2b in THF ($^{19}$F NMR)
Opening of 3d to 4d catalyzed by \((R,S_{ax},R)-2b\) in THF (\(^{19}\)F NMR)

Opening of 3e to 4e catalyzed by \((R,S_{ax},R)-2b\) in THF (\(^{19}\)F NMR)