Supporting Information for

Highly Enantioselective Oxidation of Non-activated Aliphatic C-H Bonds with Hydrogen Peroxide Catalyzed by Manganese Complexes

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1. Experimental Section

1.1 Materials

Reagents and solvents used were of commercially available reagent quality unless stated otherwise. Solvents were purchased from SDS and Scharlab. Solvents were purified and dried by passing through an activated alumina purification system (M-Braun SPS-800) or by conventional distillation techniques.

1.2 Instrumentation

Oxidation products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds, and/or by $^1$H and $^{13}$C($^1$H)-NMR analyses. IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer using a MKII Golden Gate single reflection ATR system. Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons. NMR spectra were taken on BrukerDPX300 and DPX400 spectrometers using standard conditions. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer using a 1 mM solution of the analyzed compound. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument with a ESI source at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate. Chromatographic resolution of enantiomers was performed on an AgilentGC-7820-A chromatograph using a CYCLOSIL-B column and HPLC 1200 series Agilent technologies using CHIRALPAK-IA and CHIRALPAK-IC columns. The configuration of the major enantiomer was determined by chemical correlation.
2. Synthesis of the complexes

2.1 Synthesis of the pyridine synthons

Pyridine synthons $\text{TIPS}_2\text{PyCHO}^1$ and $5\{-2,6\text{-bis(trifluoromethyl)phenyl}-2\text{-chloromethyl}\text{pyridine}\}^2$ were synthetized following previously described procedure.

\[
\begin{align*}
\text{TIPS}_2\text{PyCHO} & \quad \text{TIPS}_2\text{PyCH}_2\text{OH}:
\end{align*}
\]

Pyridine synthons $\text{TIPS}_2\text{PyCHO} (5 \text{ g}, 19 \text{ mmol})$ was dissolved in absolute ethanol (45 ml) and NaBH$_4$ (2 eq., 38 mmol) was directly added as a solid in little portions. The reaction mixture was stirred for 4 hours at room temperature and then 10 ml of water were slowly added. After 10 minutes of stirring, the solvent was removed under reduced pressure and 10 ml of water were added. The mixture was extracted with 3 x 20 ml of CH$_2$Cl$_2$, the combined organic phases were dried with anhydrous MgSO$_4$ and the solvent was removed under reduced pressure to yield the desired product, (2.57 g, 9.68 mmol, 51% yield). $^1$H-NMR (400 MHz, CDCl$_3$, 300 K) $\delta$, ppm 8.62 (dd, $J = 1.7$, 1.0 Hz, 1H), 7.78 (dd, $J = 7.7$, 1.8 Hz, 1H), 7.28 (dd, $J = 7.7$, 0.9 Hz, 1H), 4.78 (s, 2H), 1.42 (hept, $J = 7.4$ Hz, 3H), 1.08 (d, $J = 7.5$ Hz, 18H).$^{13}$C($^1$H)-NMR 159.3, 154.1, 143.7, 128.3, 120.1, 64.2, 18.4, 10.9, 10.6. HRMS(ESI-MS) $m/z$ calculated for C$_{15}$H$_{27}$NOSi[M+H]$^+$ 266.1935, found 266.1941.

\[
\begin{align*}
\text{TIPS}_2\text{PyCH}_2\text{OH} & \quad \text{TIPS}_2\text{PyCH}_2\text{Cl}\cdot\text{HCl}:
\end{align*}
\]

Pyridine synthons $\text{TIPS}_2\text{PyCH}_2\text{OH} (2.50 \text{ g}, 9.42 \text{ mmol})$ was dissolved in 167 ml of anhydrous CH$_2$Cl$_2$ and a solution of SOCl$_2$ (5 equiv., 47.1 mmol) in anhydrous CH$_2$Cl$_2$ (20 ml) was slowly added at 0°C under inert atmosphere. The reaction mixture was stirred overnight at room temperature and then the solvent was removed at reduced pressure to yield the desired product, (2.95 g, 9.2 mmol, 98% yield). $^1$H-NMR (400 MHz, CDCl$_3$, 300 K) $\delta$, ppm 8.61 (s, 1H), 8.19 (d, $J = 7.2$ Hz, 1H), 7.82 (d, $J = 7.7$, 0.9 Hz, 1H), 4.78 (s, 2H), 1.42 (hept, $J = 7.4$ Hz, 3H), 1.08 (d, $J = 7.5$ Hz, 18H).$^{13}$C($^1$H)-NMR 152.6,
HRMS(ESI-MS) $m/z$ calculated for $C_{15}H_{26}NO SiCl[M+H]^+ 284.1596$, found 284.1591.

### 2.2 Synthesis of the ligands

$N,N$-$1,2$-cyclohexanediamine derivatives were prepared according to the reported procedures.\(^3\) TIPS\textsubscript{mcp} and TIPS\textsubscript{pdp} ligand was prepared according to the reported procedures.\(^1\)

\[
\begin{align*}
 & \text{R} \rightarrow \text{H} \\
 & (S,S) \text{ or } (R,R) \\
 & \text{R: } -\text{Me} \\
 & \quad -\text{Et} \\
 & \quad -\text{CH}_2\text{c-}(\text{C}_3\text{H}_5) \\
 & \quad -\text{CH}_2\text{c-}(\text{C}_6\text{H}_{11}) \\
 & \quad -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3 \\
 & \text{Na}_2\text{CO}_3, \text{TBABr} \rightarrow \text{CH}_3\text{CN} \text{ahn, } \text{N}_2 \\
 & (S,S) \text{ or } (R,R)
\end{align*}
\]

$\text{(S,S)-TIPS}_{\text{ecp}}: (S,S)$-$N,N$-Diethyl-$1,2$-cyclohexanediamine (0.5 g, 2.9 mmol), TIPS$\text{PyCH}_2\text{Cl}$-$\text{HCl}$ (2.08 g, 6.5 mmol), $\text{Na}_2\text{CO}_3$ (11 g, 104 mmol) and TBABr (10 mg) was dissolved in anhydrous $\text{CH}_3\text{CN}$ (100 ml). The reaction mixture was refluxed overnight under $\text{N}_2$. At this point, the crude reaction was filtered and the solvent was evaporated under reduced pressure. NaOH (50 ml) was added and the organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with $\text{CH}_2\text{Cl}_2$ (3x) and the organic layer were combined and dried over $\text{Na}_2\text{SO}_4$. The obtained brown oil was purified by silica column ($\text{CH}_2\text{Cl}_2$:$\text{MeOH}$:$\text{NH}_3$ 95:4:1) and the collected fractions were removed under reduced pressure to provide 1.1 g (1.65 mmol, yield 57%) of a brown-yellow oil that turns solid after drying under vacuum. $^1\text{H}$-NMR (400 MHz, $\text{CDCl}_3$, 300 K) $\delta$, ppm: 8.45 (t, $J = 1.3$ Hz, 2H),
7.58 (d, \( J = 7.7 \text{ Hz}, 2\text{H})\), 7.52 (dd, \( J = 7.8, 1.8 \text{ Hz}, 2\text{H})\), 3.83 (d, \( J = 15.2 \text{ Hz}, 2\text{H})\), 3.55 (d, \( J = 15.2 \text{ Hz}, 2\text{H})\), 2.65 (d, \( J = 7.3 \text{ Hz}, 2\text{H})\), 2.49 (ddt, \( J = 20.1, 12.8, 6.6 \text{ Hz}, 4\text{H})\), 1.97 (d, \( J = 10.2 \text{ Hz}, 2\text{H})\), 1.67 (m, 3H), 1.59 (m, 2H), 1.37-1.24 (m, 6H), 1.00 (dd, \( J = 7.5, 1.1 \text{ Hz}, 3\text{H})\), 0.92 (t, \( J = 7.1 \text{ Hz}, 6\text{H})\).

\( ^{13}\text{C}\{^1\text{H}\}\)-NMR 165.5, 154.1, 142.83, 142.75, 127.2, 126.7, 122.7, 122.6, 60.8, 56.4, 53.4, 44.1, 26.1, 25.9, 18.4, 14.3, 10.9, 10.6, 10.4. HRMS(ESI-MS) m/z calculated for C\(_{40}\)H\(_{72}\)N\(_4\)Si\(_2\)[M+H]+ 665.5368, found 665.5366.

**{(S,S)-TIPS}cpcp:** Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH\(_2\)Cl\(_2\):MeOH:NH\(_3\) 96:3:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.230 g, 61% yield). \(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3, 300 \text{ K}) \delta, \text{ppm}: 8.49 (d, \( J = 1.6 \text{ Hz}, 2\text{H})\), 7.76 (d, \( J = 7.8 \text{ Hz}, 2\text{H})\), 7.58 (dd, \( J = 7.8, 1.8 \text{ Hz}, 2\text{H})\), 4.05 (d, \( J = 15.1 \text{ Hz}, 2\text{H})\), 3.59 (d, \( J = 15.1 \text{ Hz}, 2\text{H})\), 2.95 (d, \( J = 7.3 \text{ Hz}, 2\text{H})\), 2.63 (dd, \( J = 13.0, 5.4 \text{ Hz}, 2\text{H})\), 2.24 (dd, \( J = 13.0, 7.5 \text{ Hz}, 2\text{H})\), 2.06 (d, \( J = 10.4 \text{ Hz}, 2\text{H})\), 1.75 (d, \( J = 10.4 \text{ Hz}, 2\text{H})\), 1.36 (q, \( J = 7.4 \text{ Hz}, 6\text{H})\), 1.18 (d, \( J = 11.8 \text{ Hz}, 4\text{H})\), 1.05 (d, \( J = 7.8 \text{ Hz}, 36\text{H})\), 0.76 (qd, \( J = 8.0, 6.7, 3.8 \text{ Hz}, 2\text{H})\), 0.36 (tt, \( J = 8.8, 4.6 \text{ Hz}, 2\text{H})\), 0.24 (tt, \( J = 8.9, 4.6 \text{ Hz}, 2\text{H})\), 0.02 (dq, \( J = 9.5, 4.9 \text{ Hz}, 2\text{H})\), 0.09 (dq, \( J = 9.5, 4.9 \text{ Hz}, 2\text{H})\).

\( ^{13}\text{C}\{^1\text{H}\}\)-NMR 162.4, 154.1, 142.6, 126.6, 122.9, 61.2, 56.3, 55.6, 26.1, 25.5, 18.5, 10.6, 5.5, 2.8. HRMS(ESI-MS) m/z calculated for C\(_{40}\)H\(_{76}\)N\(_4\)Si\(_2\)[M+H]+ 717.5681, found 717.5676.

**{(S,S)-TIPS}chcp:** Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH\(_2\)Cl\(_2\):MeOH:NH\(_3\) 95:4:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.130 g, 41% yield). \(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3, 300 \text{ K}) \delta, \text{ppm}: 8.49 (d, \( J = 1.6 \text{ Hz}, 2\text{H})\), 7.76 (d, \( J = 7.8 \text{ Hz}, 2\text{H})\), 7.58 (dd, \( J = 7.8, 1.8 \text{ Hz}, 2\text{H})\), 4.05 (d, \( J = 15.1 \text{ Hz}, 2\text{H})\), 3.59 (d, \( J = 15.1 \text{ Hz}, 2\text{H})\), 2.95 (d, \( J = 7.3 \text{ Hz}, 2\text{H})\), 2.63 (dd, \( J = 13.0, 5.4 \text{ Hz}, 2\text{H})\), 2.24 (dd, \( J = 13.0, 7.5 \text{ Hz}, 2\text{H})\), 2.06 (d, \( J = 10.4 \text{ Hz}, 2\text{H})\), 1.75 (d, \( J = 10.4 \text{ Hz}, 2\text{H})\), 1.36 (q, \( J = 7.4 \text{ Hz}, 6\text{H})\), 1.18 (d, \( J = 11.8 \text{ Hz}, 4\text{H})\), 1.05 (d, \( J = 7.8 \text{ Hz}, 36\text{H})\), 0.76 (qd, \( J = 8.0, 6.7, 3.8 \text{ Hz}, 2\text{H})\), 0.36 (tt, \( J = 8.8, 4.6 \text{ Hz}, 2\text{H})\), 0.24 (tt, \( J = 8.9, 4.6 \text{ Hz}, 2\text{H})\), 0.02 (dq, \( J = 9.5, 4.9 \text{ Hz}, 2\text{H})\), 0.09 (dq, \( J = 9.5, 4.9 \text{ Hz}, 2\text{H})\).

\( ^{13}\text{C}\{^1\text{H}\}\)-NMR 162.4, 154.1, 142.6, 126.6, 122.9, 61.2, 56.3, 55.6, 26.1, 25.5, 18.5, 10.6, 5.5, 2.8. HRMS(ESI-MS) m/z calculated for C\(_{40}\)H\(_{76}\)N\(_4\)Si\(_2\)[M+H]+ 717.5681, found 717.5676.
300 K) $\delta$, ppm: 8.53 (s, 2H), 7.67 (d, $J = 1.5$ Hz, 4H), 4.03 (d, $J = 15.2$ Hz, 2H), 3.63 (d, $J = 15.2$ Hz, 2H), 2.85 – 2.72 (m, 2H), 2.42 (dd, $J = 6.8$, 3.2 Hz, 4H), 2.14 – 2.05 (m, 2H), 1.76 (m, 4H), 1.65 – 1.48 (m, 8H), 1.40 (p, $J = 7.5$ Hz, 6H), 1.34 – 1.21 (m, 6H), 1.08 (d, $J = 7.4$ Hz, 36H), 1.04 – 0.95 (m, 6H), 0.66 (ddt, $J = 23.5$, 11.8, 8.6 Hz, 4H). $^{13}$C($^1$H)-NMR 162.4, 154.2, 142.7, 126.6, 122.6, 61.9, 58.9, 36.3, 32.14, 32.09, 26.7, 26.3, 26.2, 26.0, 18.4, 10.6. HRMS(ESI-MS) $m/z$ calculated for C$_{50}$H$_{88}$N$_4$Si$_2$[M+H]+ 801.6620, found 801.6605.

(5S,5S)-TIPS$tBucp$: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH$_2$Cl$_2$:MeOH:NH$_3$ 95:4:1 and the product was concentrated to dryness. The product was isolated as a brown-yellow oil (0.170 g, 23% yield). $^1$H-NMR (400 MHz, CDCl$_3$, 300 K) $\delta$, ppm: 8.53 (s, 2H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.60 (dd, $J = 7.8$, 1.8 Hz, 2H), 3.96 (d, $J = 15.2$ Hz, 2H), 3.64 (d, $J = 15.2$ Hz, 2H), 2.76 (d, $J = 7.7$ Hz, 2H), 2.61 – 2.44 (m, 4H), 2.15 – 2.00 (m, 2H), 1.80 – 1.77 (m, 2H) 1.46 – 1.38 (m, 6H), 1.36 – 1.22 (m, 4H), 1.07 (d, $J = 7.4$ Hz, 36H), 1.02 – 0.94 (m, 4H), 0.74 (s, 18H). $^{13}$C($^1$H)-NMR 162.4, 154.1, 142.7, 126.7, 122.7, 61.3, 56.5, 46.8, 42.8, 29.8, 29.4, 26.3, 26.2, 18.4, 10.6. HRMS(ESI-MS) $m/z$ calculated for C$_{48}$H$_{88}$N$_4$Si$_2$[M+H]+ 777.6620, found 777.6603.

(5S,5S)-CF$_3$mc$p$: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH$_2$Cl$_2$:MeOH:NH$_3$ 97:2:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.210 g, 44% yield). $^1$H-NMR (400 MHz, CDCl$_3$, 300 K) $\delta$, ppm: 8.39 (s, 2H), 7.99 (dd, $J = 8.1$, 3.7 Hz, 4H), 7.68 (q, $J = 7.9$ Hz, 4H), 7.55 – 7.45 (m,
2.3 Synthesis of the complexes

[(Fe(CF₃SO₃))₂(mcp)],⁴ [Fe(CF₃SO₃)]₂(pdp)),⁵ [Fe(CF₃SO₃)]₂(TIPS mcp)],¹ [Fe(CF₃SO₃)]₂(TIPS pdp)],¹ [Mn(CF₃SO₃)]₂(mcp)],⁶ [Mn(CF₃SO₃)]₂(pdp)],⁷ [Mn(CF₃SO₃)]₂(2,6-Me₂N pdp)],⁸ and [Mn(CF₃SO₃)]₂(BzIm pdp)]⁹ complexes were prepared according to the reported procedures.

(R,R)-[Mn(CF₃SO₃)]₂(TIPS mcp)]: Under N₂ atmosphere, a suspension of Mn(CF₃SO₃)₂ (83.1 mg, 0.24 mmol) in anhydrous THF (1 mL) was added drop-wise to a vigorously stirred solution of (R,R)-TIPS mcp (150 mg, 0.24 mmol) in THF (1 mL). After a few seconds the solution became cloudy and a white precipitate appeared. After stirring for 4 hours the solution was filtered off and the resultant white solid dried under vacuum. This solid was dissolved in

\[\text{R} \quad -\text{Si}((\text{Pr})₃\\ -\text{Ph(CF}_3)_2\]
CH$_2$Cl$_2$ (3 mL) and the solution filtered off through Celite®. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, white crystals (158 mg, 0.16 mmol, 67% yield). Anal. Calcd for C$_{40}$H$_{68}$F$_6$MnN$_4$O$_6$S$_2$Si$_2$: C, 48.52; H, 6.92; N, 5.66 Found: C, 48.65; H, 6.95; N, 5.76 %. FT-IR (ATR) ν, cm$^{-1}$: 2943 – 2866 (C-H)$_{sp}$, 1572, 1459, 1311, 1233, 1121, 1026, 882, 701, 635, 567, 514. ESI-HRMS calcd. for C$_{38}$H$_{32}$F$_{18}$MnF$_3$SO$_3$ [M-OTf$^+$]: 840.3878, found: 840.3888.

(S,S)-[Mn(CF$_3$SO$_3$)$_2$(CF$_3$mcp)]: Following the previous conditions, white crystals were obtained after slow diethyl ether diffusion in CH$_2$Cl$_2$. (286 mg, 0.26 mmol, 68% yield). Anal. Calcd for C$_{38}$H$_{32}$F$_{18}$MnN$_4$O$_6$S$_2$: C, 41.43 H, 2.93; N, 5.09 Found: C, 41.20; H, 2.91; N, 4.84 %. FT-IR (ATR) ν, cm$^{-1}$: 3458 – 2945 (C-H)$_{sp}$, 1612, 1459, 1293, 1127, 1067, 1030, 822, 761, 677, 635, 513. ESI-HRMS calcd. for C$_{36}$H$_{32}$N$_4$F$_{12}$MnCF$_3$SO$_3$ [M-OTf$^+$]: 952.1331, found: 952.1346.

(S,S)-[Mn(CF$_3$SO$_3$)$_2$(TIPS)pdp]: Under N$_2$ atmosphere, a suspension of Mn(CF$_3$SO$_3$)$_2$ (86.5 mg, 0.25 mmol) in anhydrous THF (1 mL) was added drop-wise to a vigorously stirred solution of (S,S)-TIPSdp (159 mg, 0.25 mmol) in THF (1 mL). After a few seconds the solution became cloudy and a white precipitate appeared. After stirring for 4 hours the solution was filtered off and the resultant white solid dried under vacuum. This solid was dissolved in CH$_2$Cl$_2$ (3 mL) and the solution filtered off through Celite®. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, white crystals (155 mg, 0.16 mmol, 64% yield). Anal. Calcd for C$_{40}$H$_{68}$F$_6$MnN$_4$O$_6$S$_2$Si$_2$: C, 48.62;
H, 6.73; N, 5.67 Found: C, 48.83; H, 7.05; N, 5.81 %. FT-IR (ATR) ν, cm⁻¹: 2944 – 2866 (C-H)sp³, 1593, 1463, 1307, 1229, 1030, 983, 882, 760, 682, 636, 514. ESI-HRMS calcd. for C₃₉H₆₆N₄Si₂MnCF₃SO₃ [M-OTf]⁺: 838.3721, found: 838.3723.

(S,S) or (R,R)

R: -CH₂CH₃
-CH₂-(C₃H₆)
-CH₂-(C₆H₁₁)
-CH₂CH₂Bu

(S,S)-[Mn(CF₃SO₃)₂(TIPS)ecp]: Under N₂ atmosphere, a suspension of MnCl₂ (30.5 mg, 0.24 mmol) in anhydrous CH₃CN (1 mL) was added drop-wise to a vigorously stirred solution of (S,S)-TIPS ecp (161 mg, 0.24 mmol) in CH₃CN (1 mL). After 4 hours 2 equiv. of AgCF₃SO₃ (123.3 mg, 0.48 mmol) were added to the solution. After 2 hours, the reaction mixture was filtered through Celite® and dried under vacuum. The solid was crystallized by layering CH₂Cl₂ solution of the complex with hexane to yield the desired white/brown complex (163 mg, 0.16 mmol, 68% yield). Anal. Calcd for C₄₀H₇₂F₆MnN₄O₆S₂Si₂: C, 49.54; H, 7.13; N, 5.5 %. Found: C, 49.71; H, 7.35; N, 5.80 %. FT-IR (ATR) ν, cm⁻¹: 2944 – 2866 (C-H)sp³, 1592, 1462, 1309, 1211, 1163, 1111, 1028, 882, 683, 636, 568, 514. ESI-HRMS calcd. for C₄₀H₇₂N₄Si₂MnCF₃SO₃ [M-OTf]⁺: 868.4191, found: 868.4200.
(S,S)-[Mn(CF$_3$SO$_3$)$_2$]$_2$(TIPSchcp)]: Following the previous conditions, white crystals were obtained by layering CH$_2$Cl$_2$ solution of the complex with hexane. (153 mg, 0.14 mmol, 48% yield). Anal. Calcd for C$_{46}$H$_{76}$F$_6$MnN$_4$O$_6$S$_2$Si$_2$: C, 51.62; H, 7.16; N, 5.23 %. Found: C, 51.32; H, 7.06; N, 5.29 %. FT-IR (ATR) $\nu$, cm$^{-1}$: 2944 – 2866 (C-H)sp$^3$, 1592, 1462, 1311, 1233, 1210, 1163, 1025, 882, 704, 682, 634, 569, 513. ESI-HRMS calcd. for C$_{46}$H$_{76}$N$_4$Si$_2$MnCF$_3$SO$_3$ [M-OTf]+: 920.4504, found: 920.4482.

(S,S)-[Mn(CF$_3$SO$_3$)$_2$](TIPSchcp)]: Following the previous conditions, white crystals were obtained by layering CH$_2$Cl$_2$ solution of the complex with hexane. (127 mg, 0.11 mmol, 51% yield). Anal. Calcd for C$_{52}$H$_{88}$F$_6$MnN$_4$O$_6$S$_2$Si$_2$: C, 54.10; H, 7.68; N, 4.85 %. Found: C, 49.71; H, 7.50; N, 4.98 %. FT-IR (ATR) $\nu$, cm$^{-1}$: 2944 – 2866 (C-H)sp$^3$, 1592, 1462, 1311, 1233, 1210, 1163, 1025, 882, 704, 682, 634, 569, 513. ESI-HRMS calcd. for C$_{52}$H$_{88}$N$_4$Si$_2$MnCF$_3$SO$_3$ [M-OTf]+: 1004.5443, found: 1004.5470.
(S,S)-[Mn(CF₃SO₃)₂(TIPS:Bucp)]: Following the previous conditions, white/brown crystals were obtained by layering CH₂Cl₂ solution of the complex with hexane. (98 mg, 0.087 mmol, 41% yield). Anal. Calcd for C₅₀H₈₈F₆MnN₄O₆S₂Si₂: C, 53.12; H, 7.85; N, 4.96%. Found: C, 53.50; H, 8.05; N, 4.91%. FT-IR (ATR) ν, cm⁻¹: 2944 – 2866 (C-H)sp³, 1592, 1463, 1311, 1209, 1165, 1025, 881, 682, 635, 569, 514. ESI-HRMS calcd. for C₄₉H₈₈N₄Si₂MnCF₃SO₃ [M-OTf]+: 980.5448, found: 980.5451.
3. Synthesis of the substrates

The following substrates were prepared according to the reported procedures. All the remaining ones are commercially available.

S2, S3, S8, S9, S10, S11, S12, S13, S15

S18, S19

S20, S21, S22

A round-bottom flask equipped with a septum and kept under nitrogen was charged with a 0.20 M solution of the amine (1.1 equiv) in dichloromethane and cooled to 0 °C. Triethylamine (1.1 equiv) was added to the reaction flask. The acyl chloride (1.0 equiv) was added dropwise and the reaction was stirred overnight at room temperature. At this point, a saturated aqueous Na₂CO₃ solution was added until pH~10-11 and then diluted with dichloromethane. The organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with dichloromethane (2x) and the organic layers were combined. The organic layer was washed with 1N HCl and dried over anhydrous sodium sulfate (Na₂SO₄). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel.

N-Cyclohexylpivalamide (S8): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.38 g, 79% yield).

$^1$H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 5.46 (bs, 1H), 3.75 - 3.73 (m, 1H), 1.92 - 1.86 (m, 2H), 1.73 - 1.57 (m, 3H), 1.44 - 1.30 (m, 3H), 1.18 (s, 9H), 1.14 – 1.04 (m, 2H). $^{13}$C-NMR 177.4, 47.9, 38.5, 33.1, 27.6, 25.6, 24.9 HRMS(ESI+) m/z calculated for C₁₁H₂₁NO [M+Na]+ 206.1515, found 206.1512.
**N-Cyclohexylisobutyramide (S9):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.43 g, 83% yield).

$^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.34 (bs, 1H), 3.82 - 3.70 (m, 1H), 2.35 - 2.28 (q, 1H), 1.94 - 1.88 (m, 2H), 1.74 - 1.60 (m, 3H), 1.43 – 1.31 (m, 2H), 1.23 – 1.21 (m, 1H), 1.15 (d, 6H), 1.10 - 1.0 (m, 2H). $^{13}$C-NMR 176.0, 47.8, 35.8, 33.2, 25.6, 24.9, 19.7. HRMS(ESI+) $m/z$ calculated for C$_{10}$H$_{19}$NO [M+Na]$^+$ 192.1359, found 192.1358.

**N-(cyclohexyl)-2,2-dimethylbutanamide (S10):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.56 g, 97% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.45 (bs, 1H), 3.86 – 3.66 (m, 1H), 1.96 – 1.80 (m, 2H), 1.75 – 1.55 (m, 4H), 1.51 (q, $J = 7.5$ Hz, 2H), 1.44 – 1.27 (m, 2H), 1.22 – 1.14 (m, 1H), 1.12 (s, 6H), 1.10 – 1.02 (m, 1H), 0.82 (t, $J = 7.5$ Hz, 3H). $^{13}$C-NMR 176.6, 47.9, 42.1, 33.9, 33.2, 25.6, 25.0, 24.9, 9.1. HRMS(ESI+) $m/z$ calculated for C$_{12}$H$_{23}$NO [M+Na]$^+$ 220.1672, found 220.1673.

**N-(cyclohexyl)-2-ethylbutanamide (S11):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.65 g, 84% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.62 (bs, 1H), 3.78 (tdt, $J = 10.7, 8.1, 3.9$ Hz, 1H), 1.87 (dd, $J = 12.5, 3.8$ Hz, 2H), 1.79 (tt, $J = 9.3, 5.1$ Hz, 1H), 1.67 (dt, $J = 13.2, 3.6$ Hz, 2H), 1.62 – 1.50 (m, 3H), 1.46 – 1.26 (m, 4H), 1.18 – 1.05 (m, 3H), 0.88 – 0.80 (t, $J = 7.4$ Hz, 6H). $^{13}$C-NMR 174.6, 51.4, 47.8, 33.3, 25.8, 25.5, 24.9, 12.0. HRMS(ESI+) $m/z$ calculated for C$_{12}$H$_{23}$NO [M+Na]$^+$ 220.1672, found 220.1673.
**N-(cyclohexyl)-2-propylbutanamide (S12):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.53 g, 80% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) δ, ppm: 5.39 (bs, 1H), 3.90 – 3.70, (m, 1H), 2.04 – 1.81 (m, 3H), 1.76 – 1.51 (m, 5H), 1.45 – 1.19 (m, 8H), 1.12 (ddd, $J = 23.0, 12.1, 3.4$ Hz, 3H), 0.88 (t, $J = 7.1$ Hz, 6H). $^{13}$C-NMR 174.9, 47.9, 47.8, 35.4, 33.4, 25.6, 24.9, 20.8, 14.1 HRMS(ESI+) m/z calculated for C$_{14}$H$_{27}$NO [M+Na]$^+$ 248.1985, found 248.1981.

$\text{N-(cyclohexyl)-3,3-dimethylbutanamide (S13):}$ Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.75 g, 85% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) δ, ppm: 5.26 (bs, 1H), 3.84 - 3.77 (m, 1H), 2.02 (s, 2H), 1.99 - 1.86 (m, 2H), 1.77 - 1.55 (m, 3H), 1.47 - 1.28 (m, 2H), 1.25 – 1.07 (m, 3H), 1.04 (s, 9H). $^{13}$C-NMR 170.6, 50.9, 48.0, 33.3, 30.8, 29.8, 25.6, 24.9 HRMS(ESI+) m/z calculated for C$_{12}$H$_{23}$NO [M+Na]$^+$ 220.1672, found 220.1667.

$\text{N-Cyclohexylcyclohexanecarboxamide (S15):}$ Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.32 g, 53% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) δ, ppm: 5.34 (bs, 1H), 3.85 - 3.64 (m, 1H), 2.02 (tt, $J = 11.7, 3.4$ Hz 1H), 1.93 - 1.58 (m, 10H), 1.47 - 1.03 (m, 10H). $^{13}$C-NMR 175.1, 47.7, 45.7, 33.3, 30.9, 29.7, 26.5, 25.8, 24.9 HRMS(ESI+) m/z calculated for C$_{13}$H$_{23}$NO [M+Na]$^+$ 232.1672, found 232.1678.
N-(cyclohexyl)-(S)-(+-2-methylbutanamide (S14): Following the traditional methodology used for peptide synthesis, the product was isolated as a white solid (0.85 g, 85% yield).

\[ \text{H-NMR (CDCl}_3, 400 \text{ MHz, 300K)} \delta, \text{ppm: } 5.41 (\text{bs, 1H}), 3.79 (\text{tdt, } J = 12.2, 8.1, 3.9 \text{ Hz, 1H}), 2.02 (\text{dq, } J = 13.5, 6.8 \text{ Hz, 1H}), 1.92-1.88 (m, 2H), 1.73 - 1.56 (m, 4H), 1.49 - 1.28 (m, 4H), 1.21-1.17 (m, 2H), 1.12 (dd, } J = 12.4, 7.9 \text{ Hz, 3H}), 0.89 (t, } J = 7.4 \text{ Hz, 3H}). \]

\[ ^{13}\text{C-NMR 175.4, 47.8, 43.3, 33.4, 27.4, 25.6, 24.9, 17.6, 11.9. HRMS(ESI+) } m/z \text{ calculated for C}_{11}\text{H}_{21}\text{NO } [\text{M+Na}]+ 206.1515, \text{found 206.1517.} \]

N-Cyclohexyltrifluoroacetamide (S17): A round-bottom flask equipped with a septum and kept under nitrogen was charged with cyclohexylamine (1.0 equiv, 0.24 g, 2.4 mmol) and solubilized in diethylether (1.4 M). Triethylamine (0.7 equiv) was added to the reaction flask. Trifluoroacetic anhydride (1.0 equiv, 0.5 g, 2.4 mmol) in diethylether (1.4 M) was added dropwise and the reaction was stirred for 2 hours at room temperature. At this point H\textsubscript{2}O was added and the basic aqueous layer was separated. The organic layer was extracted with NaHCO\textsubscript{3}, saturated with NH\textsubscript{4}Cl and dried over anhydrous sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.25 g, 1.3 mmol 54% yield). \[ ^{1}\text{H-NMR (CDCl}_3, 400 \text{ MHz, 300K)} \delta, \text{ppm: } 6.24 (\text{bs, 1H}), 3.94 - 3.69 (m, 1H), 2.08 - 1.88 (m, 2H), 1.87 - 1.59 (m, 3H), 1.52 - 1.08 (m, 5H). \]

\[ ^{13}\text{C-NMR 156.5, 117.8, 113.9, 100.0, 49.2, 32.4, 25.2, 24.6 HRMS(ESI+) } m/z \text{ calculated for C}_{8}\text{H}_{12}\text{F}_{3}\text{NO } [\text{M+Na}]+ 218.0763, \text{found 218.0762.} \]
**N-Cyclohexyltetrafluorophthalimide (S19)**: Tetrafluorophthalic anhydride (0.5 g, 2.3 mmol, 1.2 eq.) was added to a solution of cyclohexylamine (0.19 g, 1.9 mmol, 1.0 eq.) in glacial acetic acid and refluxed overnight. The solvent was removed under reduced pressure and the reaction mixture was refluxed in acetic anhydride for 12 h. The solvent was evaporated and the crude amide was purified by flash chromatography over silica gel with hexane:ethyl acetate 3:1 and the product was concentrated to dryness. The product was isolated as a yellow solid (0.24 g, 82% yield). \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 4.08 (t, \(J = 12.4\) Hz, 1H), 2.26 – 2.06 (m, 2H), 1.87 (d, \(J = 13.0\) Hz, 2H), 1.70 (d, \(J = 12.0\) Hz, 3H), 1.47 – 1.13 (m, 3H). \(^13\)C-NMR 162.5, 146.2, 144.5, 143.5, 141.9, 113.8, 51.9, 29.6, 25.9, 24.9. HRMS(ESI+) \(m/z\) calculated for C\(_{14}\)H\(_{11}\)F\(_4\)NO\(_2\)\[(CH\(_3\)OH)]\([M+Na]\)\(^+\) 356.0880, found 356.0885.

Hydroxylamine hydrochloride (1.2 equiv) followed by pyridine (3.0 equiv) was added to a solution of ketone (a) (1.0 equiv) in absolute ethanol and the reaction mixture was heated to reflux temperature under stirring for 5 hours. The reaction was then quenched with water and the product extracted with ethyl acetate (2 x 50 mL). The organic fractions were washed with water and dried over anhydrous MgSO\(_4\). The solvent was removed under vacuum to obtain the oxime (b) that was used in the next step without further purification. To a stirred solution of lithium aluminium hydride (0.5 equiv) in anhydrous THF under \(N_2\), was added a solution of intermediate b drop wise. The reaction was slowly heated to reflux temperature for 3 hours. After this, the reaction mixture was quenched with 1M NaOH solution at 5°C. After filtration through Celite© and extraction with ethyl acetate (2 x 50 mL) the organic fractions were dried over anhydrous MgSO\(_4\), the solvent removed under vacuum and the obtained intermediate c was used in the next acylation step without further purification to give the corresponding amide.
**N-(4,4-dimethylcyclohexyl)pivalamide (S20):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.39 g, 94% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.49 (s, 1H), 3.68 (tt, $J = 9.2$, 4.8 Hz, 1H), 1.75-1.72 (m, 2H), 1.38 – 1.17 (m, 6H), 1.17 (s, 9H), 0.91 (s, 6H). $^{13}$C-NMR 177.6, 48.1, 38.5, 37.6, 31.5, 29.5, 28.7, 27.6, 25.1. HRMS(ESI+) $m/z$ calculated for $\text{C}_{13}\text{H}_{25}\text{NO}$ [M+Na]$^+$ 234.1828, found 234.1822.

**N-(3,3-dimethylcyclohexyl)pivalamide (S21):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.38 g, 70% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.32 (d, $J = 7.0$ Hz, 1H), 3.88 (tdt, $J = 12.0$, 8.0, 4.1 Hz, 1H), 1.95 – 1.92 (m, 1H), 1.64 – 1.46 (m, 4H), 1.35 – 1.31 (m, 1H), 1.15 (s, 9H), 1.09 – 0.99 (m, 2H), 0.94 (s, 3H), 0.91 (s, 3H), 0.88-0.84 (m, 1H). $^{13}$C-NMR 177.5, 46.0, 45.2, 38.53, 38.46, 33.3, 33.0, 31.7, 27.6, 24.7, 21.3. HRMS(ESI+) $m/z$ calculated for $\text{C}_{13}\text{H}_{25}\text{NO}$ [M+Na]$^+$ 234.1828, found 234.1826.

**N-(3,3,5,5-tetramethylcyclohexyl)pivalamide (S22):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.41 g, 55% yield). $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 5.35 (d, $J = 7.5$ Hz, 1H), 4.07 (ddt, $J = 12.0$, 8.2, 3.9 Hz, 1H), 1.70 (dddd, $J = 11.4$, 3.7, 2.2, 1.3 Hz, 2H), 1.36 – 1.19 (m, 2H), 1.18 (s, 9H), 1.07 (s, 6H), 0.91 (s, 6H), 0.84 (d, $J = 12.0$ Hz, 2H). $^{13}$C-NMR 177.6, 51.7, 46.1, 43.3, 38.5, 35.1, 32.2, 27.6, 27.3. HRMS(ESI+) $m/z$ calculated for $\text{C}_{15}\text{H}_{29}\text{NO}$ [M+Na]$^+$ 262.2141, found 262.2139.
4. Oxidation reactions

Hydrogen peroxide solutions employed in the oxidation reactions were prepared by diluting commercially available hydrogen peroxide (30% \( \text{H}_2\text{O}_2 \) solution in water, Aldrich) in acetonitrile to achieve a 1.5 M. Commercially available glacial acetic acid (99-100%) purchased from Riedel-de-Haën was employed. The purity of the amide substrates synthetized as described above was in all cases >99%. Carboxylic acids were purchased from Acros and Aldrich.

4.1 Reaction protocol for catalysis

An acetonitrile solution (400 \( \mu \text{L} \)) of the substrate (0.25 M) and the corresponding complex (2.5 mM) was prepared in a vial (10 mL) equipped with a stir bar cooled at -40 °C, in a \( \text{CH}_3\text{CN}/\text{N}_2(\text{liq}) \) bath. 98 \( \mu \text{L} \) (neat, 17 equiv.) of acetic acid were added directly to the solution. Then, 236 \( \mu \text{L} \) of a 1.5 M hydrogen peroxide solution in \( \text{CH}_3\text{CN} \) (3.5 equiv.) were added by syringe pump over a period of 30 min. At this point, an internal standard (biphenyl) was added and the solution was quickly filtered through a basic alumina plug, which was subsequently rinsed with 2 x 1 mL AcOEt. GC analysis of the solution provided substrate conversions and product yields relative to the internal standard integration. Isomer ratio was determined by GC or \(^1\text{H}-\text{NMR}. \) Commercially unavailable products were identified by a combination of \(^1\text{H}, \) \(^{13}\text{C}\left({^1\text{H}}\right)-\text{NMR} \) analysis, and HRMS. The oxidized products were identified by comparison to the GC retention time of racemate products.

Attempts to trap the alcohol product were performed by carrying out catalytic reactions in the presence of acetic anhydride or trifluoroacetic anhydride. Unfortunately, under these conditions oxidation did not take place. Reactions performed using substoichiometric amounts of oxidant, providing low conversion of the substrate did not result in the accumulation of the alcohol, indicating that this initial product is much more reactive against oxidation than the starting material, and can not accumulate in solution.
Table S1. Oxidation of N-(cyclohexyl)pivalamide (S8) with (S,S)-[Mn(CF₃SO₃)₂(TIPS cpcp)], (S,S)-[Mn(CF₃SO₃)₂(TIPS chcp)] and (S,S)-[Mn(CF₃SO₃)₂(TIPS tBucp)]

| Entry | Cat.          | Conv (%)<sup>a</sup> | Yield (%)<sup>a</sup> | Ee % |
|-------|---------------|-----------------------|------------------------|------|
| 1     | Mn<sup>TIPS</sup>cpcp | 85                    | 60                     | 80   |
| 2     | Mn<sup>TIPS</sup>chcp | 22                    | 10                     | 86   |
| 3     | Mn<sup>TIPS</sup>tBucp | 31                    | 20                     | 56   |

<sup>a</sup>Conversions and yields determined from crude reaction mixtures by GC.
Ee’s determined by GC with chiral stationary phase.

Table S2. Oxidation of N-(cyclohexyl)pivalamide (S8) with (R,R)-[Mn(CF₃SO₃)₂(TIPS mcp)] using different equivalents of acetic acid

| Entry | x (equiv) | Conv (%)<sup>a</sup> | Yield K₃ (%)<sup>a</sup> | Ee % |
|-------|-----------|-----------------------|--------------------------|------|
| 1     | 50        | >99                   | 90                       | 72   |
| 2     | 25        | >99                   | 90                       | 73   |
| 3     | 17        | >99                   | 90                       | 79   |
| 4     | 13        | >99                   | 84                       | 79   |
| 5     | 10        | 80                    | 74                       | 74   |
| 6     | 8         | 86                    | 74                       | 78   |
| 7     | 5         | 33                    | 28                       | 75   |

<sup>a</sup>Conversions and yields determined from crude reaction mixtures by GC.
Ee’s determined by GC with chiral stationary phase.
4.2 General Procedure for product isolation

A 25 mL round bottom flask was charged with: catalyst (6 μmol, 1.0 mol%), substrate (1 equiv.), CH₃CN (3.3 mL) and a magnetic stir bar. The carboxylic acid of choice was the added (17 equiv.) and the mixture was cooled at -40 ºC in an CH₃CN/N₂(liq) bath under magnetic stirring. Then, 1.4 mL of a 1.5 M hydrogen peroxide solution in CH₃CN (3.5 equiv.) were added by syringe pump over a period of 30 min at -40 ºC. At this point, 15 mL of an aqueous NaHCO₃ saturated solution were added to the mixture. The resultant solution was extracted with CH₂Cl₂ (3 x 10 mL). Organic fractions were combined, dried over MgSO₄, and the solvent was removed under reduced pressure to afford the oxidized product. This residue was filtered by silica gel column to obtain the pure product.

5. Characterization of the isolated products

The oxidation products obtained after oxidation of substrates S1, S3, S4, S5, S6, S18 and S19 (P1, P3, P4, P5, P6, P18, P19, respectively) were collected as mixtures of C3 and C4 oxidation products.

**3-tert-butylcyclohexanone (P1 (K₃), Scheme 4)** purification by flash chromatography (SiO₂; hexane:AcOEt 5:1) gave the product as a white solid (50% total yield (K₃+K₄), 64% ee K₃); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 2.45-2.43 (m, 1H), 2.37-2.35 (m, 1H), 2.23 (dt, J = 6.0, 13.5 Hz, 1H), 2.12-2.08 (m, 1H), 2.04 (t, J = 12.0 Hz, 1H), 1.96-1.91 (m, 1H), 1.59-1.45 (m, 2H), 1.32 (qd, J = 3.6, 12.8 Hz, 1H), 0.89 (s, 9H). HRMS(ESI+) m/z calculated for C₁₀H₁₈O [M+Na]+ 177.1250, found 177.1250. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.¹⁶

**4-tert-butylcyclohexanone (P1 (K₄))** ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 2.41-2.39 (m, 1H), 2.33-2.31 (m, 1H), 2.23 (dt, J = 6.0, 13.5 Hz, 1H), 2.12-2.08 (m, 1H), 2.04 (t, J = 12.0 Hz, 1H), 1.96-1.91 (m, 1H), 1.59-1.45 (m, 2H), 1.32 (qd, J = 3.6, 12.8 Hz, 1H), 0.89 (s, 9H). ¹³C-NMR 212.9, 49.4, 43.6, 41.3, 32.7, 27.2, 26.2, 25.6. Spectroscopic data are in agreement with a previous literature report.¹⁶
3-oxocyclohexylpivalate (P2 (K₃), Scheme 4) purification by flash chromatography (SiO₂; hexane:AcOEt 5:1) gave the product as a white solid (36% yield, 61% ee); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 5.18 (tt, J = 5.7, 3.0 Hz, 1H), 2.57 (ddd, J = 15.8, 10.2, 6.1 Hz, 2H), 2.42 – 2.36 (m, 2H), 2.19 – 2.02 (m, 4H), 1.26 (s, 9H). ¹³C-NMR 209.9, 177.8, 68.0, 39.0, 37.2, 30.4, 27.2. HRMS(ESI+) m/z calculated for C₁₁H₁₈O₃ [M+Na]+ 221.1148, found 221.1146. [α]D²⁴ +9.3 (CHCl₃, c 0.333). Chiral GC analysis with CYCLOSIL-B.

4-oxocyclohexylpivalate (P2 (K₄)) white solid product (9% yield); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 5.28 (tt, J = 5.5, 2.8 Hz, 1H), 2.64 (dd, J = 14.8, 4.2 Hz, 1H), 2.56 – 2.35 (m, 4H), 2.07 (dd, J = 11.3, 4.6 Hz, 1H), 1.98 (d, J = 7.9 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.20 (s, 9H). ¹³C-NMR 208.3, 177.5, 71.2, 46.4. HRMS(ESI+) m/z calculated for C₁₁H₁₈O₃ [M+Na]+ 221.1148, found 221.1140.

3-oxocyclohexylpivalate (P2 (K₃), Scheme 4) purification by flash chromatography (SiO₂; hexane:AcOEt 5:1) gave the product as a white solid (36% yield, 61% ee); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 5.18 (tt, J = 5.7, 3.0 Hz, 1H), 2.57 (ddd, J = 15.8, 10.2, 6.1 Hz, 2H), 2.42 – 2.36 (m, 2H), 2.19 – 2.02 (m, 4H), 1.26 (s, 9H). ¹³C-NMR 209.9, 177.8, 68.0, 39.0, 37.2, 30.4, 27.2. HRMS(ESI+) m/z calculated for C₁₁H₁₈O₃ [M+Na]+ 221.1148, found 221.1146. [α]D²⁴ +9.3 (CHCl₃, c 0.333). Chiral GC analysis with CYCLOSIL-B.

methyl-3-oxocyclohexanecarboxylate (P4 (K₃) Table 2, entry 4) purification by flash chromatography (SiO₂; hexane:AcOEt 4:1) gave the product as a white solid (52% total yield (K₃+K₄), 11% ee K₃); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 3.69 (s, 3H), 2.84-2.75 (m, 1H), 2.55 (d, J = 8.0 Hz, 2H), 2.40-2.29 (m, 2H), 2.13-2.02 (m, 2H), 1.87-1.81 (m, 1H), 1.77-1.69 (m, 1H). HRMS(ESI+) m/z calculated for C₈H₁₂O₃ [M+Na]+ 179.0679, found 179.0680. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.¹⁷
methyl-4-oxocyclohexanecarboxylate (P4 (K₄)) ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, 3.71 (s, 3H), 2.83-2.75 (m, 1H), 2.50-2.46 (m, 2H), 2.40-2.29 (m, 2H), 2.23-2.19 (m, 2H), 2.13-2.02 (m, 2H). Spectroscopic data are in agreement with a previous literature report.¹⁸

[P5 (K₃)] HO₂C

[P5 (K₄)] HO₂C

(P5 (K₃+K₄), Table 2, entry 5) purification by flash chromatography (SiO₂; hexane:AcOEt 2:1) gave the product as a white solid (30% total yield, 9% ee K₃); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 2.93-2.80 (m, 2H), 2.61-2.58 (m, 2H), 2.56-2.50 (m, 2H), 2.44-2.36 (m, 4H), 2.30-2.23 (m, 2H), 2.22-2.16 (m, 1H), 2.14-2.03 (m, 3H), 1.96-1.87 (m, 1H), 1.84-1.74 (m, 1H).¹³C-NMR 209.9, 209.0, 180.4, 179.4, 42.9, 42.7, 40.9, 40.3, 39.6, 29.7, 28.2, 27.5, 24.3. HRMS(ESI+) m/z calculated for C₇H₉O₃ [M] 141.0546, found 141.0563. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.¹⁹ The ee was determined after esterification following a reported procedure.¹⁹

[H₃CO] CO

(P6 (K₃+K₄), Table 2, entry 6) purification by flash chromatography (SiO₂; hexane:AcOEt 4:1) gave the product as a white solid (66% total yield, 8% ee K₃); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 2.90 – 2.80 (m, 1H), 2.79 – 2.72 (m, 1H), 2.47-2.36 (m, 3H), 2.34 – 2.22 (m, 4H), 2.17 (s, 3H), 2.14 (s, 3H), 2.07-1.97 (m, 3H), 1.89-1.79 (m, 1H), 1.75-1.59 (m, 2H).¹³C-NMR 210.0, 209.8, 209.7, 208.5, 50.8, 48.4, 42.3, 40.8, 39.7, 28.17, 28.15, 27.8, 27.1, 24.7. HRMS(ESI+) m/z calculated for C₈H₁₂O₂ [M+Na]+ 163.0730, found 163.0738. Chiral GC analysis with CYCLOSIL-B.

[H₃CO] CO

N-[(3-oxocyclohexyl)acetamide (P7, Table 4, entry 1), purification by flash chromatography (SiO₂; hexane:AcOEt 1:1) gave the product as a white solid; (61% yield, 78% ee); ¹H-NMR (CDCl₃, 400 MHz, 300K) δ, ppm: 5.79 (bs, 1H), 4.30 - 4.25 (m, 1H), 2.72-2.68 (m, 1H), 2.47-2.38 (m, 2H), 2.28 (m, 2H), 2.09 (m, 1H), 1.98 (s, 3H), 1.78 – 1.69 (m, 2H).¹³C-NMR 209.0, 169.4,
48.5, 47.6, 41.0, 30.8, 23.4, 22.1. HRMS(ESI+) m/z calculated for C₈H₁₃NO₂ [M+Na]+ 178.0838, found 178.0839. [α]$_D$^{24} -6.1 (CHCl₃, c 0.312). Chiral GC analysis with CYCLOSIL-B.

\[ \text{N-(3-oxocyclohexyl)pivalamide (P8, Table 4, entry 3), purification by flash chromatography (SiO}_2; \text{ hexane:AcOEt 1:1) gave the product as a white solid (84% yield, 91% ee);} \]
\[ ^1\text{H-NMR (CDCl}_3, 400 MHz, 300K) \delta, \text{ppm}: 5.60 (bs, 1H), 4.33 - 4.15 (m, 1H), 2.69 (ddt, } J = 13.9, 4.8, 1.5 \text{ Hz, 1H), 2.49 - 2.20 (m, 3H), 2.14 - 1.97 (m, 1H), 1.99 - 1.59 (m, 3H), 1.18 (s, 6H).} \]
\[ ^13\text{C-NMR 209.0, 177.7, 48.4, 47.6, 41.0, 38.6, 30.7, 27.5, 22.2. HRMS(ESI+) m/z calculated for C}_{11}\text{H}_{19}\text{NO}_2 [M+Na]+ 220.1308, found 220.1307. [α]$_D$^{24} -2.9 (CHCl₃, c 0.272). Chiral GC analysis with CYCLOSIL-B.} \]

\[ \text{N-(3-oxocyclohexyl)isobutyramide (P9, Table 4, entry 2), purification by flash chromatography (SiO}_2; \text{ hexane:AcOEt 1:1) gave the product as a white solid (60% yield, 88% ee);} \]
\[ ^1\text{H-NMR (CDCl}_3, 400 MHz, 300K) \delta, \text{ppm}: 5.57 (bs, 1H), 4.35 - 4.17 (m, 1H), 2.69 (ddt, } J = 13.9, 4.8, 1.4 \text{ Hz, 1H), 2.48 - 2.18 (m, 4H), 2.14 - 1.92 (m, 2H), 1.86 - 1.62 (m, 2H), 1.14 (dd, } J = 6.9, 1.0 \text{ Hz, 6H).} \]
\[ ^13\text{C-NMR 209.0, 176.3, 48.2, 47.6, 41.0, 35.6, 30.7, 22.1, 19.6, 19.5 \text{ HRMS(ESI+) m/z calculated for C}_{10}\text{H}_{17}\text{NO}_2 [M+Na]+ 206.1151, found 206.1152. [α]$_D$^{24} -6.5 (CHCl₃, c 0.232). Chiral GC analysis with CYCLOSIL-B.} \]

\[ \text{(S)-N-(3-oxocyclohexyl)-2,2-dimethylbutanamide (P10, Table 4, entry 4), purification by flash chromatography (SiO}_2; \text{ hexane:AcOEt 1:1) gave the product as a white solid; (85% yield, 94% ee);} \]
\[ ^1\text{H-NMR (CDCl}_3, 400 MHz, 300K) \delta, \text{ppm}: 5.81 (d, } J = 6.3 \text{ Hz, 1H), 4.25 - 4.08 (m, 1H), 2.60 (d, } J = 13.6 \text{ Hz, 1H), 2.38 - 2.26 (m, 1H), 2.26 - 2.13 (m, 2H), 2.00 - 1.90 (m, 1H), 1.65 (q, } J = 12.0, 10.7 \text{ Hz, 2H), 1.46 (q, } J = 7.3 \text{ Hz, 2H), 1.07 (s, 6H), 0.76 (t, } J = 7.3 \text{ Hz, 3H).} \]
\[ ^13\text{C-NMR 208.9, 176.9, 48.3, 47.6, 42.2, 40.8, 33.8, 30.8, 24.84, 24.82, 22.2, 9.1. HRMS(ESI+) m/z calculated for C}_{12}\text{H}_{23}\text{NO}_2 [M+H]+ 234.1465, found 234.1464. [α]$_D$^{24} -5.2 (CHCl₃, c 0.302). Chiral GC analysis with CYCLOSIL-B. Structure was confirmed by X-Ray diffraction analysis.} \]
**N-(3-oxocyclohexyl)-2-ethylbutanamide (P11, Table 4, entry 5),** purification by flash chromatography (SiO$_2$; hexane:AcOEt 1:1) gave the product as a white solid; (45% yield, 96% ee); $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.71 (d, $J = 6.9$ Hz, 1H), 4.31 (qt, $J = 8.8$, 4.4 Hz, 1H), 2.69 (dd, $J = 14.1$, 4.9 Hz, 1H), 2.45 - 2.22 (m, 2H), 2.12 – 1.93 (m, 2H), 1.83 (ddd, $J = 14.1$, 9.1, 5.1 Hz, 1H), 1.79 – 1.60 (m, 2H), 1.62 – 1.53 (m, 2H), 1.52 – 1.40 (m, 2H), 0.87 (td, $J = 7.4$, 3.4 Hz, 6H). $^{13}$C-NMR 209.0, 175.0, 48.3, 47.8, 40.9, 30.9, 25.8, 25.7, 22.1, 12.05, 12.02. HRMS(ESI+) m/z calculated for C$_{12}$H$_{21}$NO$_2$ [M+Na]+ 234.1465, found 234.1459. $\lbrack \alpha \rbrack_D^{24}$-5.17 (CHCl$_3$, c 0.6). Chiral GC analysis with CYCLOSIL-B.

**N-(3-oxocyclohexyl)-2-ethylbutanamide (P12, Table 4, entry 6),** purification by flash chromatography (SiO$_2$; hexane:AcOEt 1:1) gave the product as a white solid; (8% yield, 90% ee); $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 5.46 (d, $J = 7.3$ Hz, 1H), 4.32 (qt, $J = 8.5$, 4.3 Hz, 1H), 2.71 (dd, $J = 14.1$, 4.9 Hz, 1H), 2.46 - 2.37 (m, 1H), 2.30 (dt, $J = 14.2$, 7.9 Hz, 2H), 2.09 (dd, $J = 12.8$, 3.4, Hz, 1H), 1.98 (ddd, $J = 12.7$, 8.7, 5.1 Hz, 2H), 1.86 – 1.66 (m, 3H), 1.65 – 1.54 (m, 2H), 1.43 – 1.29 (m, 6H), 0.94 – 0.89 (m, 6H). $^{13}$C-NMR 208.9, 175.3, 48.3, 47.77, 47.76, 41.0, 35.3, 35.2, 30.9, 29.7, 22.2, 20.8, 20.7, 14.1. HRMS(ESI+) m/z calculated for C$_{14}$H$_{25}$NO$_2$ [M+Na]+ 262.1778, found 262.1781. $\lbrack \alpha \rbrack_D^{24}$-2.0 (CHCl$_3$, c 0.204). Chiral GC analysis with CYCLOSIL-B.

**N-(3-oxocyclohexyl)-3,3-dimethylbutanamide (P13, Table 4, entry 7),** purification by flash chromatography (SiO$_2$; hexane:AcOEt 1:2) gave the product as a white solid (69% yield, 94% ee); $^1$H-NMR (CDCl$_3$, 400 MHz, 300K) $\delta$, ppm: 6.18 (d, $J = 7.7$ Hz, 1H), 4.21 – 4.12 (m, 1H), 2.59 (dd, $J = 14.0$, 4.8 Hz, 1H), 2.39 - 2.16 (m, 3H), 1.97 (s, 4H), 1.74 – 1.56 (m, 2H), 0.96 (s, 9H). $^{13}$C-NMR 209.1, 171.0, 50.2, 48.2, 47.7, 40.8, 30.9, 30.8, 29.8, 22.1. HRMS(ESI+) m/z calculated for C$_{12}$H$_{22}$NO$_2$ [M+Na]+ 234.1465, found 234.1472. $\lbrack \alpha \rbrack_D^{24}$-7.3 (CHCl$_3$, c 0.94). Chiral GC analysis with CYCLOSIL-B.
**N-(3-oxocyclohexyl)-(S)-(+)2-methylbutanamide** (P14, Table 4, entry 8), purification by flash chromatography (SiO2; hexane:AcOEt 1:1) gave the product as a white solid; (50% yield, 91% ee); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 5.97 (d, \(J = 7.2\) Hz, 1H), 4.28 - 4.15 (m, 1H), 2.65 (dd, \(J = 14.1, 4.8\) Hz, 1H), 2.36 (d, \(J = 14.6\) Hz, 1H), 2.30 - 2.20 (m, 2H), 2.05 (dt, \(J = 16.4, 8.2\) Hz, 2H), 1.97 - 1.94 (m, 1H), 1.74 - 1.67 (m, 2H), 1.65 - 1.58 (m, 1H), 1.43 - 1.36 (m, 1H), 1.08 (d, \(J = 6.9\) Hz, 3H), 0.85 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C-NMR 209.0, 175.8, 48.2, 47.8, 43.0, 40.9, 30.8, 27.3, 22.1, 17.5. 11.8. HRMS(ESI+) \(m/z\) calculated for C\(_{11}\)H\(_{19}\)NO\(_2\) [M+Na]+ 220.1308, found 220.1303. \([\alpha]_D^{24}\) +9.5 (CHCl\(_3\), c 0.508). Chiral GC analysis with CYCLOSIL-B.

**N-(3-oxocyclohexyl)cyclohexanecarboxamide** (P15, Table 4, entry 9), purification by flash chromatography (SiO\(_2\); hexane:AcOEt 1:1) gave the product as a white solid (75% yield, 91% ee); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 5.55 (d, \(J = 6.6\) Hz, 1H), 4.31 - 4.23 (m, 1H), 2.69 (dd, \(J = 14.0, 4.8\) Hz, 1H), 2.46 - 2.35 (m, 1H), 2.30 - 2.24 (m, 2H), 2.04 (t, \(J = 11.7\) Hz, 2H), 1.79 (d, \(J = 13.8\) Hz, 4H), 1.72 - 1.63 (m, 2H), 1.42 (dd, \(J = 22.9, 12.4\) Hz, 2H), 1.25 (dd, \(J = 17.2, 10.9\) Hz, 5H). \(^{13}\)C-NMR 209.0, 175.4, 48.2, 47.7, 45.5, 41.0, 30.7, 29.7, 29.6, 25.68, 25.66, 22.16. HRMS(ESI+) \(m/z\) calculated for C\(_{13}\)H\(_{21}\)NO\(_2\) [M+Na]+ 246.1465, found 246.1473. \([\alpha]_D^{24}\) -2.7 (CHCl\(_3\), c 0.412). Chiral GC analysis with CYCLOSIL-B.

**N-(3-oxocyclohexyl)trifluoroacetamide** (P17, Table 4, entry 11), purification by flash chromatography (SiO\(_2\); hexane:AcOEt 1:1) gave the product as a white solid (65% yield, 65% ee); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 7.19 (s, 1H), 4.21 (s, 1H), 2.69 (dd, \(J = 14.3, 4.9\) Hz, 1H), 2.50 - 2.35 (m, 2H), 2.35 - 2.19 (m, 1H), 2.19 - 1.98 (m, 2H), 1.88 - 1.67 (m, 2H). \(^{13}\)C-NMR 207.9, 156.8, 49.2, 46.5, 40.5, 38.8, 30.0, 21.8. HRMS(ESI+) \(m/z\) calculated for C\(_{10}\)H\(_8\)F\(_3\)NO\(_2\) [M+H]+ 232.0580, found 232.0560. \([\alpha]_D^{24}\) -5.6 (CHCl\(_3\), c 0.54). Chiral GC analysis with CYCLOSIL-B.
N-(3-oxocyclohexyl)phthalimide (P18 \((K_3+K_4)\), Table 4, entry 12), purification by flash chromatography (SiO\(_2\); hexane:AcOEt 3:1) gave the product as a white solid; (37% total yield, 62% ee \(K_3\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 7.90 – 7.80 (m, 3H), 7.78 – 7.67 (m, 3H), 4.64 (tt, \(J = 12.1, 4.1\) Hz, 1H), 4.57 – 4.43 (m, 1H), 3.41 – 3.27 (m, 1H), 2.83 – 2.63 (m, 1H), 2.58 – 2.49 (m, 5H), 2.20 – 2.11 (m, 2H), 2.09 – 2.05 (m, 1H), 1.99 – 1.95 (m, 1H), 1.69 (ddddd, \(J = 17.5, 12.7, 10.4, 6.6, 3.5\) Hz, 1H). \(^{13}\)C-NMR 208.8, 207.8, 168.1, 167.9, 134.2, 134.1, 131.8, 131.7, 123.34, 123.26, 49.0, 48.3, 44.8, 40.4, 39.8, 28.6, 22.4. HRMS(ESI+) \(m/z\) calculated for C\(_{14}\)H\(_{13}\)NO\(_3\) [M+Na]+ 266.0788, found 266.0783. HPLC analysis. Spectroscopic data are in agreement with a previous literature report.\(^{20}\)

N-(3-oxocyclohexyl)tetrafluorophthalimide (P19 \((K_3+K_4)\), Table 4, entry 13) purification by flash chromatography (SiO\(_2\); hexane:AcOEt 3:1) gave the product as a white solid; (40% total yield); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 4.62 (tt, \(J = 12.1, 4.1\) Hz, 1H), 4.53 – 4.44 (m, 1H), 3.28 (ddd, \(J = 13.5, 12.4, 0.9\) Hz, 1H), 2.68 (qd, \(J = 12.7, 5.5\) Hz, 2H), 2.57 – 2.37 (m, 8H), 2.20 – 2.00 (m, 1H), 2.13 – 2.03 (m, 2H), 1.96 (dtt, \(J = 12.9, 3.9, 2.2\) Hz, 1H), 1.78 – 1.65 (m, 1H). \(^{13}\)C-NMR 146.4, 144.8, 143.8, 142.1, 113.5, 49.8, 49.2, 44.4, 40.3, 39.6, 28.3, 22.2. HRMS(ESI+) \(m/z\) calculated for C\(_{14}\)H\(_9\)F\(_4\)NO\(_3\) [M+Na]+ 338.0411, found 338.0417. HPLC analysis.

N-(4,4-dimethyl-3-oxocyclohexyl)pivalamide (P20, Scheme 4), purification by flash chromatography (SiO\(_2\); hexane:AcOEt 1:1) gave the product as a white solid; (52% yield, 76% ee); \(^1\)H-NMR (CDCl\(_3\), 400 MHz, 300K) \(\delta\), ppm: 5.57 (s, 1H), 4.22 – 4.13 (m, 1H), 2.70 (ddd, \(J =
14.1, 4.9, 1.5 Hz, 1H), 2.43 (dd, J = 14.1, 9.6 Hz, 1H), 2.03 (ddtd, J = 13.4, 8.0, 4.0, 2.0 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.74 – 1.61 (m, 2H), 1.20 (s, 9H), 1.15 (d, J = 9.9 Hz, 6H). $^{13}$C-NMR 213.0, 177.7, 49.0, 44.5, 43.9, 38.7, 36.6, 27.5, 27.3, 25.0, 24.7. HRMS(ESI+) m/z calculated for C$_{13}$H$_{23}$NO$_{2}$ [M+Na]+ 248.1621, found 248.1621. $[^\alpha]_{D}^{24}$ +19.5 (CHCl$_{3}$, c 0.574). Chiral GC analysis with CYCLOSIL-B.

\[
\text{N-}(\text{5,5-dimethyl-3-oxocyclohexyl})\text{pivalamide (P21, Scheme 4), purification}
\]

by flash chromatography (SiO$_{2}$; hexane:AcOEt 1:1) gave the product as a white solid; (39% yield, 55% ee); $^{1}$H-NMR (CDCl$_{3}$, 400 MHz, 300K) δ, ppm: 5.47 (d, J = 7.6 Hz, 1H), 4.28 (tddd, J = 12.0, 7.8, 5.0, 4.3 Hz, 1H), 2.69 (ddt, J = 13.7, 5.1, 1.8 Hz, 1H), 2.36 – 2.07 (m, 3H), 1.90 (ddt, J = 12.9, 4.0, 1.9 Hz, 1H), 1.59 – 1.42 (m, 1H), 1.19 (s, 9H), 1.09 (s, 3H), 0.95 (s, 3H). $^{13}$C-NMR 208.1, 177.7, 54.1, 47.1, 45.2, 44.7, 38.6, 33.5, 31.7, 27.5, 25.9. HRMS(ESI+) m/z calculated for C$_{13}$H$_{23}$NO$_{2}$ [M+Na]+ 248.1621, found 248.1627. $[^\alpha]_{D}^{24}$ -12.0 (CHCl$_{3}$, c 0.366). Chiral GC analysis with CYCLOSIL-B.
A1 $^1$H and $^{13}$C{$^1$H} NMR spectra of ligands

$^1$H-NMR of TIPS$_2$PyOH in CDCl$_3$

$^{13}$C{$^1$H}-NMR of TIPS$_2$PyOH in CDCl$_3$
$^{13}$C-$^1$H-NMR of TIPS\textsubscript{PyCl} in CDCl$_3$
\[ ^{13}\text{C}(^{1}\text{H})\text{-NMR of CF}_3\text{mcp in CDCl}_3 \]
$^1$H-NMR of TIPS\textsubscript{ecp} in CDCl\textsubscript{3}

$^{13}$C\textsubscript{($^1$H)}-NMR of TIPS\textsubscript{ecp} in CDCl\textsubscript{3}
$^1$H-NMR of TIPS cpcp in CDCl$_3$
$^{13}$C($^1$H)-NMR of TIPS$_2$cp in CDCl$_3$

$^1$H-NMR of TIPS$_2$chp in CDCl$_3$

$^{13}$C($^1$H)-NMR of TIPS$_2$chp in CDCl$_3$
$^1$H-NMR of TIPS$_2$Bu$_2$ in CDCl$_3$

$^{13}$C($^1$H)-NMR of TIPS$_2$Bu$_2$ in CDCl$_3$
A2 $^1\text{H}$ and $^{13}\text{C}^{(1)}\text{H}$ NMR spectra of substrates

$^1\text{H}$-NMR of $\text{S}8$ in CDCl$_3$

$^{13}\text{C}^{(1)}\text{H}$-NMR of $\text{S}8$ in CDCl$_3$
$^1$H-NMR of S9 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S9 in CDCl$_3$
$^1$H-NMR of S10 in CDCl$_3$
$^{13}$C($^1$H)-NMR of S10 in CDCl$_3$

$^1$H-NMR of S11 in CDCl$_3$
$^{13}$C{H}_NMR of S1 in CDCl$_3$
$^1$H-NMR of S12 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S12 in CDCl$_3$

$^1$H-NMR of S13 in CDCl$_3$
$^{13}\text{C}^{[\text{H}]}$-NMR of S13 in CDCl$_3$

$^1\text{H}$-NMR of S14 in CDCl$_3$
$^{13}C$-$^{1}H$-NMR of S14 in CDCl$_3$
$^1$H-NMR of S15 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S15 in CDCl$_3$

$^1$H-NMR of S17 in CDCl$_3$
$^{13}$C$^1$H-NMR of S17 in CDCl_3
$^{1}$H-NMR of S19 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S19 in CDCl$_3$
$^1$H-NMR of S20 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S20 in CDCl$_3$
$^{1}$H-NMR of $S21$ in CDCl$_3$

$^{13}$C($^1$H)-NMR of $S21$ in CDCl$_3$
$^1$H-NMR of S22 in CDCl$_3$

$^{13}$C($^1$H)-NMR of S22 in CDCl$_3$
A3 $^1$H and $^{13}$C($^1$H) NMR spectra of isolated products

$^1$H-NMR of P1 ($K_3+K_4$) in CDCl$_3$

$^{13}$C($^1$H)-NMR of P1 ($K_3+K_4$) in CDCl$_3$
$^1$H-NMR of P2 ($K_3$) in CDCl$_3$

$^{13}$C($^1$H)-NMR of P2 ($K_3$) in CDCl$_3$
$^1$H-NMR of $\text{P}_2 (\text{K}_4)$ in CDCl$_3$

$^{13}$C($^1$H)-NMR of $\text{P}_2 (\text{K}_4)$ in CDCl$_3$
H-NMR of P3 (K₃+K₄) in CDCl₃

\[ ^{13}C\{^1H\}-NMR of P3 (K₃+K₄) in CDCl₃ \]
$^{1}H$-NMR of $P_4 (K_3+K_4)$ in CDCl$_3$

$^{13}C(^1H)$-NMR of $P_4 (K_3+K_4)$ in CDCl$_3$
$^1$H-NMR of P5 ($K_3+K_4$) in CDCl$_3$

$^{13}$C($^1$H)-NMR of P5 ($K_3+K_4$) in CDCl$_3$
$^1$H-NMR of $\textbf{P6 (K}_3\text{+K}_4\text{)}$ in CDCl$_3$

$^{13}$C($^1$H)-NMR of $\textbf{P6 (K}_3\text{+K}_4\text{)}$ in CDCl$_3$
$^1$H-NMR of P7 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P7 in CDCl$_3$
$^1$H-NMR of P8 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P8 in CDCl$_3$
$^1$H-NMR of P9 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P9 in CDCl$_3$
$^{1}H$-NMR of P10 in CDCl$_3$

$^{13}C(^1H)$-NMR of P10 in CDCl$_3$
$^1$H-NMR of P11 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P11 in CDCl$_3$
$^1$H-NMR of P12 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P12 in CDCl$_3$
$^1$H-NMR of P13 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P13 in CDCl$_3$
$^{1}$H-NMR of P14 in CDCl$_3$

$^{13}$C$^{(1)}$H-NMR of P14 in CDCl$_3$
$^{1}$H-NMR of P15 in CDCl$_3$

$^{13}$C$[^1]$H-NMR of P15 in CDCl$_3$
$^1$H-NMR of P17 in CDCl$_3$

$^{13}$C($^1$H)-NMR of P17 in CDCl$_3$
$^1$H-NMR of P18 ($K_3+K_4$) in CDCl$_3$

$^{13}$C($^1$H)-NMR of P18 ($K_3+K_4$) in CDCl$_3$
$^1$H-NMR of P19 (K$_3$+K$_4$) in CDCl$_3$

$^{13}$C($^1$H)-NMR of P19 (K$_3$+K$_4$) in CDCl$_3$
$^1$H-NMR of P20 in CDCl$_3$
$^1$H-NMR of P21 in CDCl$_3$

$^{13}$C$^{[1]}$H-NMR of P21 in CDCl$_3$
A4 HPLC and GC spectra of products
The racemic products were obtained by using the racemic $[\text{Mn(CF}_3\text{SO}_3)_2(\text{TIPS mcp})]$ complex.
![Chemical Structure](Rac)

**Rac**

**P2 (K3)**
Rac

\[
\text{P5 (K3) after esterification}
\]
Rac

P11
HPLC-separation conditions: Chiralpack IA 25°C, 240.8 nm, 88/12 hexane/i-PrOH, 1.0 mL/min; r.t.(minor) = 26.166 min, r.t.(major) = 27.910 min.

Rac

| Peak | RetTime | Sig Type | Area [mAU*s] | Height [mAU] | Area % |
|------|---------|----------|--------------|--------------|--------|
| 1    | 26.674  | BV       | 6397.72949   | 131.63432    | 46.6248|
| 2    | 28.318  | VB       | 7323.99268   | 131.42468    | 53.3752|

P18 (K₃)

| Peak | RetTime | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|------|---------|------|-------------|--------------|--------------|--------|
| 1    | 26.166  | BV   | 0.5937      | 1895.62903   | 47.48789     | 19.1476|
| 2    | 27.910  | VB   | 0.7504      | 8004.47949   | 158.72383    | 80.8524|
Rac

P20
Chiral resolution of S21:

![Rac S21 Graph]

![S21 Graph]
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