Supplementary Information

Enantiodivergent epoxidation of alkenes with a photoswitchable phosphate manganese-salen complex

Xiaofei Chen,¹,⁴ Pieter J. Gilissen,¹,⁴ Paul Tinnemans,¹ Nicolas Vanthuyne,² Floris P. J. T. Rutjes,¹ Ben L. Feringa,³ Johannes A.A.W. Elemans,¹ and Roeland J.M. Nolte¹

¹ Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands. ² Aix Marseille Univ, CNRS, Centrale Marseille, iSm2, Marseille, France. ³ Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. ⁴ These authors contributed equally to this work.

E-mail: r.nolte@science.ru.nl; j.elemans@science.ru.nl; b.l.feringa@rug.nl
Contents
1. Experimental details .................................................................................................................. 1
   1.1 General information ............................................................................................................. 1
   1.2 Synthesis of phosphate photo-switch .................................................................................. 2
   1.3 Synthesis of substrates ......................................................................................................... 15
   1.4 Synthesis of catalysts ........................................................................................................... 17
   1.5 General epoxidation procedure ............................................................................................. 18
   1.6 Epoxide products .................................................................................................................. 19
2. Resolution of enantiomers of phosphoric acid Rac-1 ................................................................. 22
   2.1 Analytical chiral HPLC separation data for compound Rac-1 .................................................. 22
   2.2 Preparative separation data for compound Rac-1 ................................................................. 23
   2.3 Optical rotations ................................................................................................................... 24
   2.4 Electronic Circular Dichroism ............................................................................................... 25
3. Optimized conditions for catalysis ............................................................................................. 26
4. Crystal data ............................................................................................................................... 30
5. UV-Vis and ECD spectra of catalysts ......................................................................................... 46
6. Details of catalytic epoxidation reactions and assignment of absolute configurations of
   enantioenriched epoxides ........................................................................................................... 47
7. Mn2 obtained via different route and the corresponding catalytic results .................................. 49
8. Supporting references ............................................................................................................... 51
9. Copies of NMR spectra of new compounds and chiral HPLC results ...................................... 52
1. Experimental details

1.1 General information

Tetrahydrofuran was distilled from potassium under a nitrogen atmosphere. Chloroform was distilled from phosphorus pentoxide under a nitrogen atmosphere. Benzene was distilled from sodium under an argon atmosphere. n-Heptane was distilled from sodium under an argon atmosphere. Dichloromethane was distilled from calcium hydride under a nitrogen atmosphere. Acetonitrile was distilled from calcium hydride under an argon atmosphere. Other solvents and reagents were obtained from commercial suppliers and used without further purification. Reactions were followed by using thin-layer chromatography (TLC) on silica gel-coated plates (Merck 60 F254). Detection was performed with UV light at 254 nm and/or by charring at 150 °C after dipping in an aqueous solution of potassium permanganate. Column chromatography was performed manually using Acros silica gel, 0.035−0.070 mm, 60A, and Merck silica gel, 60H. Melting points were taken on a polarization microscope with a programmable hot-stage. NMR spectra were recorded at 298 K (unless stated otherwise) on a Bruker Avance III 500 spectrometer (500 MHz) equipped with a Prodigy BB cryoprobe. \(^1\)H NMR chemical shifts (\(\delta\)) are given in parts per million (ppm) and were referenced to tetramethylsilane (0.00 ppm). Coupling constants are reported as \(J\) values in Hertz (Hz). Data for \(^1\)H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration, assignment if applicable). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), m (multiplet), b (broad). Mass spectra were recorded on a JEOL AccuTOF CS JMS-T100CS mass spectrometer. UV-vis spectra and ECD spectra were recorded at 298 K on a JASCO J-815 CD spectrophotometer (1 mm or 2 mm quartz cell). Irradiation experiments were carried out using Thorlabs Fiber-Coupled LEDs (M365FP1 and M470F3). Optical rotationary values are performed by Anton Paar Modular Circular Polarimeter MCP 100.
1.2 Synthesis of phosphate photo-switch
6,8-Dibromo-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (4)

A solution of bromine (4.1 mL, 80 mmol, 3.0 equiv) in dry chloroform (20 mL) was added dropwise over 10 minutes to a solution of 4-(4-methoxyphenyl)butanoic acid 3 (5.2 g, 27 mmol, 1.0 equiv) and iron powder (0.15 g, 2.7 mmol, 10 mol%) in dry chloroform (50 mL). The resulting red-brown solution was stirred at 20 °C for 67 hours under an argon atmosphere. The reaction mixture was carefully poured into aqueous sodium metabisulfite (10% by weight, 400 mL) and the product was extracted with chloroform (3 × 100 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed in vacuo to afford crude 4-(3,5-dibromo-4-methoxyphenyl)butanoic acid (10 g) as a tan solid. This solid was added portion wise over 10 minutes to a preheated 40 °C solution of phosphorus pentoxide in methanesulfonic acid (7.7% by weight, Eaton’s reagent, 125 mL). The resulting red solution was stirred at 40 °C for 4 hours under an argon atmosphere. Upon cooling, the mixture was poured into ice-water (500 mL) and the resulting suspension was stirred vigorously for 1 hour. Then, the product was extracted with chloroform (2 × 250 mL). The combined organic extracts were washed with water (500 mL) and brine (250 mL); then dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified twice by 60A silica gel column chromatography (eluent first column: CHCl₃/n-heptane, 1:1 following 1:0, v/v; eluent second column: EtOAc/n-heptane, 1:20, v/v) to afford ketone 4 (4.4 g, 49% over 2 steps) as a white solid.

m.p. 95–97 °C.

1H NMR (500 MHz, CDCl₃) δ 7.46 (t, J = 0.9 Hz, 1H, H-5), 3.89 (s, 3H, H-11), 2.94–2.89 (m, 2H, H-4), 2.72–2.66 (m, 2H, H-2), 2.13–2.05 (m, 2H, H-3).

13C NMR (126 MHz, CDCl₃) δ 196.28 (C-1), 154.22 (C-7), 143.20 (C-10), 132.56 (C-5), 132.10 (C-9), 123.14 (C-6), 118.72 (C-8), 60.69 (C-11), 39.90 (C-2), 30.30 (C-4), 22.58 (C-3).

HRMS (ESI) calcd. for [C₁₁H₁₀⁷⁹Br₂O₂ + Na]⁺ 354.8945, found 354.8962.
A Schlenk flask was charged with aryl dibromide 4 (3.8 g, 11 mmol, 1.0 equiv), 4-(tert-butyl)phenylboronic acid (2.0 g, 11 mmol, 1.0 equiv), K$_3$PO$_4$ (19 g, 91 mmol, 8.0 equiv), Pd$_2$dba$_3$ (0.21 g, 0.23 mmol, 2.0 mol%) and DPEPhos (0.25 g, 0.46 mmol, 4.0 mol%). The flask was evacuated and refilled with argon (3×). Then, deoxygenated THF/water (110 mL, 4:1, v/v) was added and the resulting mixture was stirred at 50 °C for 46 hours under an argon atmosphere. Upon cooling, the reaction mixture was diluted with water (100 mL) and the product was extracted with EtOAc (2 × 150 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60A silica gel column chromatography (eluent: CH$_2$Cl$_2$/n-heptane, 1:1 → 1:0, v/v). All fractions containing the desired product were combined and the solvent was removed in vacuo. The purified material was dissolved in CH$_2$Cl$_2$/n-heptane (40 mL, 1:1, v/v). Most CH$_2$Cl$_2$ was removed under reduced pressure and the resulting suspension was allowed to settle. The yellow n-heptane layer was decanted and the residual white solid was dried under high vacuum to afford ketone 5 (3.0 g, 68%) as a white solid.

m.p. 168–172 °C.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.56–7.51 (m, 2H, H-13), 7.48–7.43 (m, 2H, H-14), 7.20 (t, J = 0.9 Hz, 1H, H-5), 3.45 (s, 3H, H-11), 2.98–2.94 (m, 2H, H-4), 2.74–2.69 (m, 2H, H-2), 2.15–2.08 (m, 2H, H-3), 1.37 (s, 9H, H-17).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.77 (C-1), 154.46 (C-7), 151.62 (C-15), 142.47 (C-10), 140.15 (C-6), 133.96 (C-12), 131.36 (C-9), 130.31 (C-5), 128.76 (C-14), 125.54 (C-11), 125.54 (C-13), 118.55 (C-8), 60.43 (C-11), 40.16 (C-2), 34.83 (C-16), 31.47 (C-17), 30.64 (C-4), 22.84 (C-3).

HRMS (ESI) calcd. for [C$_{21}$H$_{23}$BrO$_2$ + H]$^+$ 387.0960, found 387.0960; calcd. for [C$_{21}$H$_{23}$BrO$_2$ + Na]$^+$ 409.0779, found 409.0779.
4’-(tert-Butyl)-2-methoxy-1,1’-biphenyl (7)

A Schlenk flask was charged with 2-bromoanisole 6 (16 g, 86 mmol, 1.0 equiv), 4-(tert-butyl)phenylboronic acid (23 g, 0.13 mol, 1.5 equiv), K$_2$CO$_3$ (35 g, 0.26 mol, 3.0 equiv) and Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (0.90 g, 1.1 mmol, 1.3 mol%). The flask was evacuated and refilled with argon (3×). Then, deoxygenated dioxane/water (400 mL, 4:1, v/v) was added and the resulting red mixture was refluxed for 22 hours under an argon atmosphere, quickly turning from red to black. Upon cooling, water (200 mL) was added and the product was extracted with EtOAc (2 × 300 mL). The combined organic extracts were washed with brine (200 mL); then dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60A silica gel column chromatography (eluent: EtOAc/n-heptane, 1:20, v/v). The purified material was recrystallized from methanol (100 mL) to afford biphenyl 7 (15.2 g, 74%) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.50–7.45 (m, 2H, H-9), 7.45–7.40 (m, 2H, H-10), 7.33 (dd, $J$ = 7.5, 1.8 Hz, 1H, H-6), 7.30 (ddd, $J$ = 8.2, 7.4, 1.8 Hz, 1H, H-4), 7.02 (td, $J$ = 7.5, 1.1 Hz, H-5), 6.97 (dd, $J$ = 8.2, 1.1 Hz, H-3), 3.81 (s, 3H, H-7), 1.36 (s, 9H, H-13).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 156.66 (C-2), 149.81 (C-11), 135.64 (C-8), 131.02 (C-6), 130.67 (C-1), 129.27 (C-9), 128.47 (C-4), 125.11 (C-10), 120.94 (C-5), 111.27 (C-3), 55.67 (C-7), 34.67 (C-12), 31.54 (C-13).

Spectral data were in agreement with literature values.$^\text{S1}$
(4’-[ tert-Butyl]-2-methoxy-[1,1’-biphenyl]-3-yl)boronic acid (8)

n-Butyllithium (1.6M in hexanes, 23 mL, 38 mmol, 1.5 equiv) was added at −78 °C to a solution of arene 7 (6.0 g, 25 mmol, 1.0 equiv) and TMEDA (5.6 mL, 38 mmol, 1.5 equiv) in dry diethyl ether (75 mL) and the resulting mixture was stirred at 20 °C for 3 hours under an argon atmosphere. Then, the solution was cooled to −78 °C again and trimethyl borate (28 mL, 0.25 mol, 10 equiv) was added. The resulting mixture was stirred at 20 °C for 19 hours. Then, aqueous NaOH (6M, 125 mL) was added and the biphasic mixture was stirred for 1 hour and then the pH was brought to 1 with aqueous sulfuric acid (4M). The product was extracted with CH2Cl2 (2 × 300 mL). The combined organic extracts were washed with water (200 mL); then dried over sodium sulfate and the solvent was removed in vacuo to afford a yellow oil. The crude product was purified by 60A silica gel column chromatography (eluent: CH2Cl2/MeOH, 1:0 → 99:1). The first eluted fraction contained traces of the starting material. The second eluted fraction contained the desired boronic acid and monomethyl/dimethyl ester derivatives. The latter mixture was dissolved in CH2Cl2 (100 mL) and aqueous sulfuric acid (1M, 100 mL) was added. The biphasic mixture was stirred vigorously for 15 minutes to hydrolyze the boronic esters. Then, the organic layer was separated, dried over sodium sulfate and the solvent was removed in vacuo. Recrystallization from n-heptane (50 mL) afforded boronic acid 8 (4.1 g, 58%) as a white solid.

m.p. 108–110 °C.

1H NMR (500 MHz, CDCl3) δ 7.83 (dd, J = 7.4, 1.9 Hz, 1H, H-4), 7.52–7.48 (m, 2H, H-9), 7.48–7.43 (m, 2H, H-10), 7.46 (dd, J = 7.5, 1.9 Hz, 1H, H-6), 7.24 (t, J = 7.4 Hz, 1H, H-5), 6.33 (s, 2H, H-14), 3.42 (s, 3H, H-7), 1.37 (s, 9H, H-13).

13C NMR (126 MHz, CDCl3) δ 163.44 (C-2), 150.58 (C-11), 135.57 (C-4), 135.34 (C-8), 135.09 (C-6), 134.01 (C-1), 128.66 (C-9), 125.57 (C-10), 124.77 (C-5), 123.10 (C-3), 61.55 (C-7), 34.74 (C-12), 31.53 (C-13). Note: C-3 was detected indirectly through 1H-13C HMBC correlations from H-5 and H-14.

HRMS (ESI) calcd. for [C19H25BO3 + Na]+ 334.1831, found 334.1837; calcd. for [C19H25BO3 + Na]+ 335.1794, found 335.1801. Note: the measurement was performed using methanol as the solvent, therefore, instead of the boronic acid (C19H23BO3), the dimethyl boronate (C19H23BO3) was detected.
A Schlenk flask was charged with the aryl bromide 5 (2.9 g, 7.5 mmol, 1.0 equiv), boronic acid 8 (3.3 g, 12 mmol, 1.5 equiv), K$_2$CO$_3$ (3.1 g, 23 mmol, 3.0 equiv) and Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (0.31 g, 0.38 mmol, 5.0 mol%). The flask was evacuated and refilled with argon (3×). Then, deoxygenated dioxane/water (75 mL, 4:1, v/v) was added and the resulting red mixture was refluxed for 18 hours under an argon atmosphere, quickly turning from red to black. Upon cooling, water (100 mL) was added and the product was extracted with EtOAc (3 × 100 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60A silica gel column chromatography (eluent: CH$_2$Cl$_2$/n-heptane, 3:1, v/v) to afford ketone 9 (3.5 g, 85%) as a white solid.

m.p. 103–107 °C.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.62–7.57 (m, 2H, H-13), 7.57–7.52 (m, 2H, H-26), 7.46–7.42 (m, 2H, H-14), 7.42–7.38 (m, 2H, H-27), 7.33 (dd, J = 7.6, 1.8 Hz, 1H, H-23), 7.29 (s, 1H, H-5), 7.17 (t, J = 7.6 Hz, 1H, H-22), 7.06 (dd, J = 7.5, 1.7 Hz, 1H, H-21), 3.21 (s, 3H, H-24), 3.18 (s, 3H, H-11), 3.01 (t, J = 6.1 Hz, 2H, H-4), 2.61–2.55 (m, 2H, H-2), 2.18–2.10 (m, 2H, H-3), 1.36 (s, 9H, H-17), 1.35 (s, 9H, H-30).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.95 (C-1), 154.95 (C-19), 154.77 (C-7), 151.06 (C-15), 149.73 (C-28), 140.72 (C-10), 139.35 (C-6), 136.52 (C-25), 134.95 (C-12), 134.28 (C-8), 134.23 (C-18), 132.74 (C-20), 131.53 (C-9), 130.89 (C-5), 130.18 (C-23), 129.00 (C-21), 128.89 (C-26), 128.77 (C-13), 125.43 (C-14), 125.13 (C-27), 123.46 (C-22), 60.58 (C-11), 60.31 (C-24), 40.47 (C-2), 34.78 (C-16), 34.66 (C-29), 31.58 (C-17 or C-30)*, 31.51 (C-17 or C-30)*, 30.54 (C-4), 23.33 (C-3). Note: carbon signals marked with an asterisk (*) could not be assigned unambiguously.

HRMS (ESI) calcd. for [C$_{38}$H$_{42}$O$_3$ + H]$^+$ 547.3212, found 547.3218; calcd. for [C$_{38}$H$_{42}$O$_3$ + Na]$^+$ 569.3032, found 569.3029.
8-(4′-[tert-Butyl]-2-methoxy-[1,1′-biphenyl]-3-yl)-6-(4-[tert-butyl]phenyl)-7-methoxy-2-methyl-3,4-
dihyronaphthalen-1(2H)-one (10)

n-Butyllithium (1.6M in hexanes, 5.1 mL, 8.1 mmol, 1.3 equiv) was added dropwise at 0 °C to a solution of
diisopropylamine (1.3 mL, 9.3 mmol, 1.5 equiv) in dry THF (20 mL) under an argon atmosphere. The resulting
mixture was stirred at 0 °C for 30 minutes and then it was cooled to −78 °C. Then, a solution of ketone 9 (3.4 g, 6.2
mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise at −78 °C. The resulting pale orange
solution was stirred at −78 °C for 1 hour and then iodomethane (0.67 mL, 11 mmol, 1.7 equiv) was
added. The resulting yellow solution was stirred for 21 hours, while the temperature was gradually
increased from −78 °C to 20 °C. The reaction was quenched by the addition of aqueous NH₄Cl (2M,
50 mL). The product was extracted with EtOAc (3 × 50 mL). The combined organic extracts were
dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by
60A silica gel column chromatography (eluent: EtOAc/Hexane, 1:40, v/v) to afford ketone 10 (3.3
g, 95%) as a white solid. The product was obtained as a >9:1 mixture of conformers.

m.p. 101–104 °C.

1H NMR (500 MHz, CDCl₃, major conformer) δ 7.61–7.57 (m, 2H, H-13), 7.57–7.52 (m, 2H, H-26),
7.46–7.42 (m, 2H, H-14), 7.42–7.38 (m, 2H, H-27), 7.33 (dd, J = 7.5, 1.9 Hz, 1H, H-23), 7.29 (s, 1H,
H-5), 7.20 (t, J = 7.5 Hz, 1H, H-22), 7.15 (dd, J = 7.6, 1.9 Hz, 1H, H-21), 3.17 (s, 6H, H-11 + H-24),
3.09 (ddd, J = 16.6, 11.5, 4.7 Hz, 1H, H-4a), 3.01 (dt, J = 16.6, 4.4 Hz, 1H, H-4b), 2.66–2.56 (m, 1H,
H-2), 2.18 (dq, J = 13.3, 4.5 Hz, 1H, H-3a), 1.88 (dt, J = 13.3, 11.5, 4.9 Hz, 1H, H-3b), 1.36 (s, 9H,
H-17), 1.35 (s, 9H, H-30), 1.16 (d, J = 6.7 Hz, 3H, H-31).

13C NMR (126 MHz, CDCl₃, major conformer) δ 200.82 (C-1), 154.56 (C-7 or C-19)*, 154.48 (C-7 or
C-19)*, 150.86 (C-15), 149.63 (C-28), 139.93 (C-10), 139.00 (C-6), 136.46 (C-25), 134.95 (C-12),
134.06 (C-18), 133.72 (C-8), 132.46 (C-20), 131.80 (C-9), 130.77 (C-5), 130.15 (C-23), 129.48 (C-
21), 128.79 (C-26), 128.72 (C-13), 125.33 (C-14), 125.06 (C-27), 123.43 (C-22), 60.44 (C-11 or C-
24)*, 60.16 (C-11 or C-24)*, 43.50 (C-2), 34.69 (C-16), 34.57 (C-29), 31.57 (C-3), 31.52 (C-17 or C-
30)*, 31.46 (C-17 or C-30)*, 29.31 (C-4), 15.82 (C-31). Note: carbon signals marked with an asterisk
(*) could not be assigned unambiguously.

HRMS (ESI) calcd. for [C₃₉H₄₅O₃ + H]+ 561.3369, found 561.3375; calcd. for [C₃₉H₄₆O₃ + Na]+
583.3188, found 583.3179.
{(E)-8-(4′-[tert-Butyl]-2-methoxy-[1,1′-biphenyl]-3-yl)-6-(4-[tert-butyl]phenyl)-7-methoxy-2-methyl-3,4-dihydranaphthalen-1(2H)-ylidene}hydrazine (11)

Hydrazine monohydrate (55 mL) was added to a solution of ketone 10 (3.1 g, 5.5 mmol, 1.0 equiv) and Sc(OTf)$_3$ (0.27 g, 0.55 mmol, 10 mol%) in n-butanol (55 mL) and the resulting mixture was refluxed for 69 hours. Upon cooling, the mixture was diluted with water (100 mL) and the product was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with brine (50 mL); then dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60A silica gel column chromatography (elucent: CH$_2$Cl$_2$/MeOH, 1:0 → 50:1, v/v) to afford hydrazone 11 (2.9 g, 90%) as a pale-yellow solid. The product was obtained as a 1:1 mixture of conformers. Note: if desired, the conformers could be separated by column chromatography. Note 2: the hydrazone has limited stability in CDCl$_3$ solution.

m.p. 121–123 °C.

$^1$H NMR (500 MHz, CDCl$_3$, first conformer) δ 7.65–7.60 (m, 2H, H-13), 7.60–7.55 (m, 2H, H-26), 7.45–7.38 (m, 4H, H-14 + H-27), 7.26 (dd, $J = 7.6$, 1.8 Hz, 1H, H-23), 7.13 (s, 1H, H-5), 7.04 (t, $J = 7.5$ Hz, 1H, H-22), 6.85 (dd, $J = 7.5$, 1.8 Hz, 1H, H-21), 5.03 (bs, 2H, H-32), 3.44 (s, 3H, H-24), 3.16 (s, 3H, H-11), 2.92 (dp, $J = 8.8$, 6.9 Hz, 1H, H-2), 2.70 (dt, $J = 14.7$, 4.2 Hz, 1H, H-4a), 2.59–2.49 (m, 1H, H-23), 2.13 (s, 1H, H-5), 3.47 (dd, $J = 16.3$, 12.6, 8.9, 3.7 Hz, 1H, H-3b), 1.47 (s, 1H, H-31).

$^1$H NMR (500 MHz, CDCl$_3$, second conformer) δ 7.57–7.53 (m, 2H, H-13), 7.53–7.49 (m, 2H, H-26), 7.44–7.36 (m, 5H, H-14 + H-21 + H-27), 7.27 (dd, $J = 7.6$, 1.8 Hz, 1H, H-23), 7.20 (t, $J = 7.6$ Hz, 1H, H-22), 7.12 (s, 1H, H-5), 5.03 (bs, 2H, H-32), 3.21 (s, 3H, H-11), 3.10 (s, 3H, H-24), 2.97–2.87 (m, 1H, H-2), 2.75–2.65 (m, 1H, H-4a), 2.59–2.49 (m, 1H, H-4b), 2.29–2.19 (m, 1H, H-3a), 1.52–1.42 (m, 1H, H-3b), 1.35 (s, 9H, H-17), 1.35 (s, 9H, H-30), 1.14 (d, $J = 6.9$ Hz, 3H, H-31).

$^{13}$C NMR (126 MHz, CDCl$_3$, 1:1 mixture of conformers) δ 157.20, 154.66, 154.48, 153.65, 150.94, 150.06, 150.01, 149.81, 149.64, 149.59, 136.83, 136.60, 136.40, 136.07, 136.00, 134.97, 134.18, 133.91, 133.74, 133.60, 133.55, 133.70, 132.37, 132.14, 130.48, 129.53, 129.37, 129.16, 128.93, 128.86, 128.80, 128.74, 125.25, 125.21, 125.12, 125.06, 123.26, 122.60, 60.65, 60.50, 60.03, 59.58, 34.68, 34.66, 34.64, 32.51, 32.08, 31.59, 31.57, 31.55, 29.94, 29.03, 28.99, 28.76, 16.90, 16.25. Note: carbon signals could not be assigned unambiguously.

HRMS (ESI) calcd. for [C$_{39}$H$_{48}$N$_2$O$_2$ + H]$^+$ 575.3637, found 575.3625.
9H-Fluorene-9-thione (12)

Lawesson’s reagent (10 g, 25 mmol, 1.0 equiv) was added to a solution of 9H-fluorene-9-one (4.5 g, 25 mmol, 1.0 equiv) in dry toluene (25 mL) and the resulting mixture was stirred at 90 °C for 1 hour under an argon atmosphere. The color of the mixture gradually turned from yellow to dark green. Upon cooling, the mixture was directly loaded onto a 60A silica gel column, eluting with CH₂Cl₂/n-pentane (1:10, v/v). The green fraction was collected and the solvent was removed in vacuo to afford thioketone 12 (2.3 g, 47%) as a dark green solid. Note: The thioketone has limited stability and therefore should be used immediately in the next reaction.

¹H NMR (500 MHz, CDCl₃) δ 7.76 (ddd, J = 7.5, 1.1, 0.7 Hz, 2H), 7.48 (td, J = 7.3, 1.1 Hz, 2H), 7.45 (ddd, J = 7.4, 1.4, 0.7 Hz, 2H), 7.22 (td, J = 7.3, 1.4 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 228.21, 144.02, 141.01, 134.28, 129.06, 124.11, 119.83.
A solution of PIFA (2.3 g, 5.3 mmol, 1.1 equiv) in dry DMF (10 mL) was added at −50 °C to a solution of hydrazone 11 (2.8 g, 4.8 mmol, 1.0 equiv) in dry DMF (40 mL) under an argon atmosphere. The color of the solution quickly turned from yellow to orange-pink. After 1 minute of stirring at −50 °C, a solution of thioketone 12 (1.6 g, 8.2 mmol, 1.7 equiv) in dry DMF (10 mL) was added dropwise at −50 °C. The addition of the thioketone resulted in effervescence. The resulting brown solution was stirred at 20 °C for 4 hours. Then, the mixture was diluted with EtOAc (100 mL) and successively was washed with aqueous NH₄Cl (2M, 100 mL), water (2 × 100 mL) and brine (100 mL); then dried over sodium sulfate and the solvent was removed in vacuo to afford the crude episulfide intermediate. Then, HMPT (5.0 mL, 28 mmol, 5.8 equiv) was added to a solution of the crude episulfide in toluene (50 mL) and the resulting mixture was refluxed for 40 hours under an argon atmosphere. Upon cooling, the solvent was removed in vacuo. The crude product was purified by 60A silica gel column chromatography (eluent: CH₂Cl₂/n-pentane, 1:10 → 1:4, v/v). The yellow fraction was collected and the solvent was removed in vacuo. The resulting yellow solid was dissolved in CH₂Cl₂/EtOH (50 mL, 1:1, v/v). Most CH₂Cl₂ was removed under reduced pressure and the resulting yellow suspension was filtered. The precipitate was washed with EtOH (20 mL) and dried under high vacuum to afford overcrowded alkene 13 (2.4 g, 71% over 3 steps) as a yellow solid. The product was obtained as a >9:1 mixture of conformers. The relative stereochemistry of the major and minor conformers was deduced from 2D NOESY experiments. The initial part of the yellow fraction from the column was enriched in the minor conformer.

m.p. 202–206 °C.

¹H NMR (500 MHz, CDCl₃, major conformer) δ 7.87 (d, J = 7.6 Hz, 1H, H-43), 7.69–7.65 (m, 2H, H-13), 7.59–7.55 (m, 1H, H-40), 7.50 (dt, J = 7.6, 1.0 Hz, 1H, H-37), 7.49–7.45 (m, 2H, H-14), 7.32 (s, 1H, H-5), 7.29–7.24 (m, 3H, H-27 + H-42), 7.21 (td, J = 7.3, 1.1 Hz, 1H, H-41), 7.16–7.11 (m, 3H, H-26 + H-36), 6.96 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H, H-35), 6.88 (dd, J = 7.7, 1.7 Hz, 1H, H-21), 6.86 (dd, J = 7.7, 1.7 Hz, 1H, H-23), 6.85 (dt, J = 7.9, 1.0 Hz, 1H, H-34), 6.51 (t, J = 7.7 Hz, 1H, H-22), 4.08 (sextet, J = 6.9 Hz, 1H, H-2), 3.25 (s, 3H, H-11), 3.11 (s, 3H, H-24), 2.78 (dt, J = 15.0, 5.0 Hz, 1H, H-4a), 2.60–2.52 (m, 1H, H-4b), 2.33 (ddt, J = 12.6, 7.2, 5.3 Hz, 1H, H-3a), 1.55–1.45 (m, 1H, H-3b), 1.49 (d, J = 7.0 Hz, 3H, H-31), 1.38 (s, 9H, H-17), 1.32 (s, 9H, H-30).

¹H NMR (400 MHz, CDCl₃, minor conformer) δ 7.78–7.68 (m, 3H), 7.58–7.52 (m, 1H), 7.50 (dt, J = 7.5, 1.0 Hz, 1H), 7.49–7.45 (m, 2H), 7.35 (s, 1H), 7.28–7.18 (m, 5H), 7.12 (dt, J = 7.9, 0.9 Hz, 1H), 7.09 (dd, J = 7.5, 1.8 Hz, 1H), 7.04  (dd, J = 8.1, 7.2, 1.2 Hz, 1H), 6.84 (dd, J = 7.5, 1.8 Hz, 1H),
6.83–6.78 (m, 2H), 6.74 (t, J = 7.5 Hz, 1H), 4.13 (sextet, J = 7.1 Hz, 1H), 3.26 (s, 3H), 3.08 (s, 3H), 2.70–2.60 (m, 1H), 2.46–2.34 (m, 2H), 1.56–1.46 (m, 1H), 1.52 (d, J = 6.9 Hz, 3H), 1.38 (s, 9H), 1.32 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$, major conformer) $\delta$ 154.86 (C-7), 154.25 (C-19), 150.26 (C-15), 149.41 (C-28), 146.80 (C-1), 140.24 (C-39), 139.82 (C-33), 139.22 (C-38), 138.75 (C-44), 137.90 (C-9), 136.55 (C-10), 136.37 (C-25), 136.03 (C-12), 134.89 (C-6), 133.95 (C-32), 133.88 (C-18), 133.35 (C-8), 132.28 (C-21), 130.34 (C-20), 130.09 (C-23), 129.40 (C-5), 128.91 (C-13), 128.68 (C-26), 126.88 (C-41), 126.63 (C-36), 126.54 (C-42), 126.20 (C-35), 125.33 (C-14), 124.86 (C-27), 124.66 (C-43), 124.23 (C-34), 121.83 (C-22), 119.49 (C-40), 118.89 (C-37), 61.04 (C-11), 59.67 (C-24), 35.91 (C-2), 34.73 (C-16), 34.57 (C-29), 32.08 (C-3), 31.57 (C-17), 31.55 (C-30), 28.23 (C-4), 20.28 (C-31).

HRMS (ESI) calcld. for [C$_{52}$H$_{52}$O$_2$ + Na]$^+$ 731.3865, found 731.3864.
1-(4'-[tert-Butyl]-2-hydroxy-[1,1'-biphenyl]-3-yl)-3-(4-[tert-butyl]phenyl)-8-(9H-fluoren-9-ylidene)-7-methyl-5,6,7,8-tetrahydroanaphthalen-2-ol (14)

MeMgI (3M in Et₂O, 6.7 mL, 20 mmol, 10 equiv) was added to methyl aryl ether 13 (1.4 g, 2.0 mmol, 1.0 equiv) under an argon atmosphere. The resulting yellow slurry was stirred at 20 °C for 5 minutes. Then, the mixture was heated to 80 °C under a positive argon pressure with continuous outflow. After 1 hour of gentle evaporation of the diethyl ether, the solid mixture was heated to 160 °C for and it was kept at this temperature for 1 hour. Upon cooling, the reaction was quenched with ice-water (100 mL) and then aqueous NH₄Cl (1M, 100 mL). The product was extracted with CH₂Cl₂ (2 × 100 mL). The combined organic extracts were washed with brine (100 mL); then dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60H silica gel column chromatography (eluent: Et₂O/\(\text{n-heptane, 1:25, v/v}\)) to afford diol 14 (1.28 g, 95%) as a yellow solid. The product was obtained as a 2:1 mixture of conformers. The relative stereochemistry of the major and minor conformers was deduced from 2D NOESY experiments. Note: longer reaction times resulted in substantial decomposition of the overcrowded alkenyl moiety.

m.p. 155–160 °C.

\(^1\)H NMR (500 MHz, CDCl₃, major conformer) δ 7.86–7.80 (m, 1H, H-43), 7.68–7.64 (m, 2H, H-13), 7.58–7.53 (m, 1H, H-40), 7.53–7.47 (m, 3H, H-14 + H-37), 7.35 (s, 1H, H-5), 7.35–7.31 (m, 2H, H-27), 7.28–7.22 (m, 2H, H-41 + H-42), 7.20 (dd, \(J = 7.7, 1.8\) Hz, 1H, H-21), 7.20–7.16 (m, 1H, H-36), 7.08 (dt, \(J = 7.8, 0.9\) Hz, 1H, H-34), 6.96 (ddd, \(J = 8.1, 7.3, 1.2\) Hz, 1H, H-35), 6.83–6.79 (m, 2H, H-26), 6.78 (dd, \(J = 7.5, 1.7\) Hz, 1H, H-23), 6.63 (t, \(J = 7.6\) Hz, 1H, H-22), 5.97 (s, 1H, H-11), 5.38 (s, 1H, H-24), 4.14 (sextet, \(J = 7.1\) Hz, 1H, H-2), 2.75–2.67 (m, 1H, H-4a), 2.52–2.39 (m, 2H, H-3a + H-4b), 1.59 (d, \(J = 6.9\) Hz, 3H, H-31), 1.50–1.40 (m, 1H, H-3b), 1.38 (s, 9H, H-17), 1.32 (s, 9H, H-30).

\(^1\)H NMR (500 MHz, CDCl₃, minor conformer) δ 7.81–7.77 (m, 1H, H-43), 7.70–7.66 (m, 2H, H-13), 7.64–7.60 (m, 1H, H-40), 7.60–7.55 (m, 1H, H-40), 7.57–7.52 (m, 1H, H-37), 7.52–7.48 (m, 2H, H-14), 7.37 (s, 1H, H-5), 7.37–7.33 (m, 2H, H-27), 7.28–7.22 (m, 2H, H-41 + H-42), 7.18 (td, \(J = 7.3, 1.1\) Hz, 1H, H-36), 7.09–7.05 (m, 2H, H-26), 7.00 (ddd, \(J = 8.4, 7.3, 1.2\) Hz, 1H, H-35), 6.89 (dd, \(J = 7.6, 1.7\) Hz, 1H, H-23), 6.84 (dt, \(J = 7.9, 0.9\) Hz, 1H, H-34), 6.79 (dd, \(J = 7.7, 1.7\) Hz, 1H, H-21), 6.43 (t, \(J = 7.6\) Hz, 1H, H-22), 5.22 (s, 1H, H-11), 4.97 (s, 1H, H-24), 4.05 (sextet, \(J = 6.9\) Hz, 1H, H-2), 2.76 (dt, \(J = 14.5, 4.7\) Hz, 1H, H-4a), 2.61–2.52 (m, 1H, H-4b), 2.37–2.29 (m, 1H, H-3a), 1.50–1.40 (m, 1H, H-3b), 1.40 (d, \(J = 6.9\) Hz, 3H, H-31), 1.38 (s, 9H, H-17), 1.33 (s, 9H, H-30).

\(^1\)C NMR (126 MHz, CDCl₃, major conformer) δ 150.63 (C-28), 150.37 (C-15), 149.22 (C-7), 149.06 (C-19), 144.56 (C-1), 140.51 (C-39), 139.16 (C-38), 138.48 (C-44), 138.24 (C-33), 137.44 (C-9),
135.33 (C-12), 135.21 (C-10), 135.00 (C-32), 134.04 (C-25), 132.84 (C-21), 130.03 (C-6), 129.71 (C-23), 129.62 (C-18), 129.36 (C-13), 129.01 (C-26), 128.99 (C-5), 127.02 (C-8 + C-41), 126.89 (C-36), 126.71 (C-42), 126.59 (C-35), 125.83 (C-27), 125.51 (C-14), 124.90 (C-34), 124.63 (C-43), 123.13 (C-20), 120.15 (C-22), 119.49 (C-40), 118.69 (C-37), 35.04 (C-2), 34.76 (C-16), 34.71 (C-29), 31.66 (C-3), 31.53 (C-17), 31.46 (C-30), 28.94 (C-4), 21.87 (C-31).

\(^{13}\text{C} \text{NMR (126 MHz, CDCl}_3, \text{minor conformer)} \delta 150.50 (C-15), 150.45 (C-28), 149.68 (C-7), 149.64 (C-19), 145.74 (C-1), 140.44 (C-39), 139.71 (C-33), 139.34 (C-38), 138.61 (C-44), 137.10 (C-9), 135.01 (C-12), 134.47 (C-32), 134.46 (C-25), 133.57 (C-10), 131.23 (C-21), 130.75 (C-23), 129.69 (C-5), 129.21 (C-13), 128.97 (C-6), 128.84 (C-26), 128.65 (C-18), 127.14 (C-41), 126.98 (C-36), 126.67 (C-42) 126.64 (C-35), 125.70 (C-27), 125.51 (C-14), 124.53 (C-43), 124.34 (C-34), 122.99 (C-8), 120.42 (C-20), 119.99 (C-22), 119.59 (C-40), 119.08 (C-37), 35.59 (C-2), 34.77 (C-16), 34.70 (C-29), 32.00 (C-3), 31.53 (C-17), 31.46 (C-30), 27.86 (C-4), 20.36 (C-31).

HRMS (ESI) calcd. for \([C_{50}H_{48}O_2 + Na]^+\) 703.3552, found 703.3541.
4,8-Bis(4-[tert-butyl]phenyl)-13-(9H-fluoren-9-ylidene)-6-hydroxy-12-methyl-10,11,12,13-tetrahydrobenzo[d]naptho[1,2-f][1,3,2]dioxaphosphepine 6-oxide (I)

POCl₃ (0.74 mL, 7.9 mmol, 3.0 equiv) was added dropwise to a solution of diol 14 (1.8 g, 2.6 mmol, 1.0 equiv) in dry pyridine (40 mL) under an argon atmosphere. The resulting mixture was heated to 70 °C and stirred for 2 hours. Then, the solution was cooled to 20 °C and water (8 mL) was added. The resulting mixture was heated to 70 °C and stirred for another hour. Upon cooling, the reaction mixture was poured into aqueous HCl (1M, 600 mL). The product was extracted with CHCl₃ (2 × 150 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by 60H silica gel column chromatography (CH₂Cl₂/MeOH, 1:0 → 19:1, v/v). The yellow fraction was collected and the solvent was removed in vacuo.

The resulting yellow solid was dissolved in CHCl₃ (100 mL) and washed with aqueous HCl (1M, 3 × 100 mL); then dried over sodium sulfate and the solvent was removed in vacuo to afford phosphoric acid Rac-I (1.8 g, 92%) as a yellow solid. Each enantiomer was present as a single conformer.

m.p. 255–257 °C.

1H NMR (500 MHz, c = 4 × 10⁻² M in TFA/CDCl₃, 1:24, v/v) δ 7.93–7.87 (m, 1H, H-43), 7.61–7.57 (m, 2H, H-13), 7.56–7.50 (m, 1H, H-40), 7.50–7.46 (m, 2H, H-14), 7.48 (s, 1H, H-5), 7.42 (dt, J = 7.5, 1.0 Hz, 1H, H-37), 7.39 (dd, J = 7.8, 1.7 Hz, 1H, H-21), 7.34–7.30 (m, 2H, H-27), 7.30–7.25 (m, 2H, H-41 + H-42), 7.18 (td, J = 7.4, 1.0 Hz, 1H, H-36), 7.04 (td, J = 7.6, 1.2 Hz, 1H, H-35), 7.02–6.98 (m, 2H, H-26), 6.95 (ddd, J = 7.5, 1.6, 0.9 Hz, 1H, H-23), 6.90 (dt, J = 7.9, 0.9 Hz, 1H, H-34), 6.84 (td, J = 7.7, 1.2 Hz, 1H, H-22), 4.23 (sextet, J = 7.0 Hz, 1H, H-2), 2.86–2.77 (m, 1H, H-4a), 2.63–2.48 (m, 2H, H-3a + H-4b), 1.64 (d, J = 6.9 Hz, 3H, H-31), 1.46–1.38 (m, 1H, H-3b), 1.36 (s, 9H, H-17), 1.31 (s, 9H, H-30).

13C NMR (126 MHz, c = 4 × 10⁻² M in TFA/CDCl₃, 1:24, v/v) δ 151.32 (C-15), 150.69 (C-28), 144.10 (d, 2J_C,P = 8.9 Hz, C-19), 143.17 (d, 2J_C,P = 9.2 Hz, C-7), 141.48 (d, 2J_C,P = 1.8 Hz, C-10), 141.41 (C-1), 140.84 (C-39), 139.21 (C-38), 137.99 (C-44), 137.64 (C-33), 136.71 (d, 4J_C,P = 1.3 Hz, C-9), 136.06 (C-32), 134.52 (d, 3J_C,P = 1.6 Hz, C-6), 134.49 (d, 3J_C,P = 1.7 Hz, C-18), 133.58 (C-12 + C-25), 131.04 (d, 4J_C,P = 1.3 Hz, C-21 or C-23)*, 131.02 (d, 4J_C,P = 1.3 Hz, C-21 or C-23)*, 130.46 (d, 4J_C,P = 1.3 Hz, C-5), 129.66 (d, 3J_C,P = 1.9 Hz, C-8), 129.32 (C-13), 129.24 (C-26), 127.71 (C-41), 127.62 (C-36), 127.30 (d, 3J_C,P = 1.7 Hz, C-20), 127.15 (C-35), 126.95 (C-42), 125.47 (C-14), 125.02 (C-27), 124.95 (C-43), 124.78 (d, 3J_C,P = 1.9 Hz, C-22), 124.26 (C-34), 119.61 (C-40), 118.89 (C-37), 34.77 (C-16), 34.65 (C-29), 34.56 (C-2), 31.47 (C-3), 31.34 (C-17), 31.32 (C-30), 29.46 (C-4), 21.35 (C-31). Note: carbon signals marked with an asterisk (*) could not be assigned unambiguously.

31P NMR (202 MHz, c = 4 × 10⁻² M in TFA/CDCl₃, 1:24, v/v) δ 2.20.

HRMS (ESI) calcd. for [C₉H₄O,P + Na]⁺ 765.3110, found 765.3131.
1.3 Synthesis of substrates$^{2}$

2,2-Dimethyl-6-nitro-2H-chromene (17a)$^{82}$

This compound was purchased from Sigma-Aldrich and purified further by silica gel column chromatography (elucent: ethyl acetate/n-pentane, 1:4, v/v) to give light-yellow solid 17a as a white solid.

2,2-Dimethyl-2H-chromene-6-carbonitrile (18a)$^{84}$

Titanium tetraethoxide (1.14 g, 5 mmol) and 1.7 g (10 mmol) of [1,1’-biphenyl]-4-ol were added to a three-neck flask and diluted with dry toluene until a final volume of 16 mL was reached. The mixture was heated to 90 °C and kept at this temperature for 50 minutes, after which distilled ethanol was carefully added under argon. Thereafter, a solution of 2.52 g (30 mmol) of 3-methylbut-2-enal dissolved in 50 mL dry toluene was added to the flask. The mixture was refluxed for 6 hours and an aqueous saturated solution of ammonium chloride was added. The mixture was extracted with diethyl ether, the combined fractions concentrated and the obtained product purified by silica gel chromatography (elucent: ethyl acetate/ pentane, 1:5, v/v) to give a light-yellow solid in 48% yield (2.4 mmol, 0.57 g).

$^{2}$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.84 (m, 2H), 7.40 (m, 2H), 7.34 (dd, $J = 8.4$, 2.3 Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.20 (d, $J = 2.3$ Hz, 1H), 6.84 (d, $J = 8.3$, 1H), 6.38 (dd, $J = 9.8$, 0.7 Hz, 1H), 5.65 (d, $J = 9.8$ Hz, 1H), 1.46 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 152.55, 140.86, 133.84, 131.07, 128.67, 127.72, 126.62, 124.96, 122.31, 121.39, 116.57, 76.43, 28.10. GC-MS (C$_{17}$H$_{14}$O): Calculated 236.1201, Found 236.1290.
6-Bromospiro[chromene-2,1'-cyclohexane] (20a)\textsuperscript{S2}

Ammonium chloride (1.5 g, 27.5 mmol), copper(I) chloride (290 mg, 3.0 mmol), and aqueous 37.5% hydrochloric acid (15.0 mL) were added to a three-neck flask and the mixture was cooled with an ice bath. After 15 minutes, 3-ethylpent-1-yn-3-ol (1.72 g, 15.6 mmol) was slowly added to the flask and the mixture was stirred for 2 hours. Subsequently, it was extracted with diethyl ether and the combined organic layers were concentrated under vacuum. Dichloromethane was added and the product was filtrated. The compound 1-ethynyl-1-chlorocyclohexane was obtained as a light-yellow oily solid and directly used for next step\textsuperscript{S3} in which 4-bromo-phenol (173 mg, 1 mmol) was used as the starting material. All further procedures were the same as described for the synthesis of 17. After reaction, the product was purified by silica gel column chromatography (eluent: CH2Cl2/n-pentane, 1:1, v/v) to give 20a as a pale-yellow solid with 65% yield (0.65 mmol, 0.18 g).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.17 (dd, \(J = 8.5, 2.4\) Hz, 1H), 7.07 (d, \(J = 2.4\) Hz, 1H), 6.69 (dd, \(J = 8.5, 0.7\) Hz, 1H), 6.25 (dd, \(J = 9.9, 0.7\) Hz, 1H), 5.67 (d, \(J = 9.8\) Hz, 1H), 1.32 - 1.93 (m, 10H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 151.93, 131.76, 131.41, 128.71, 124.05, 121.74, 118.17, 112.58, 77.15, 35.86, 25.24, 21.28. GC-MS (C\textsubscript{14}H\textsubscript{15}BrO): Calculated 278.0306, Found 278.0392.
1.4 Synthesis of catalysts

The synthetic procedure was based on a previously reported protocol.\textsuperscript{52}

**Rac-Mn2.**

Manganese(III) salen complex Mn15 (29.0 mg, 50 µmol, 1.0 equiv) and phosphoric acid Rac-1 (37.8 mg, 51 µmol, 1.02 equiv) were dissolved in acetone (0.40 mL). Then, aqueous 2.5M NaOH (20.4 µL, 51 µmol, 1.02 equiv) was added and the resulting mixture was stirred for 4 hours in the dark. The solvent was removed in vacuo to afford a brown solid. This brown solid was dissolved in dry CH\textsubscript{2}Cl\textsubscript{2} (6 mL) leaving behind a white precipitate of NaCl. The solution was separated from the precipitate, and the solvent was removed in vacuo to afford again a brown solid. This dissolution, separation, and evaporation process was repeated two more times to ensure complete removal of NaCl. The thus obtained brown material was dried under high vacuum (<1 mbar) for 2 days to afford the racemic catalyst Rac-Mn2 (61.8 mg, 48 μmol, 96%) as a brown solid.

M.p. 264–266 °C. HRMS (ESI) Calcd. for [C\textsubscript{82}H\textsubscript{92}MnN\textsubscript{2}O\textsubscript{6}P + H]\textsuperscript{+} 1287.6152, Found 1287.6224.

Anal. Calcd. for C\textsubscript{82}H\textsubscript{92}MnN\textsubscript{2}O\textsubscript{6}P + H\textsubscript{2}O: C, 75.44; H, 7.26; N, 2.15. Found: C, 74.70; H, 7.34; N, 2.11. UV-Vis (CH\textsubscript{2}Cl\textsubscript{2}) λ/\text{nm} (log(ε/M\textsubscript{−1}\cdot cm\textsuperscript{−1})) 335 (4.46), 353 (4.46).

(R,S,M)-Mn2.

According to the procedure for Rac-Mn2, the reaction of Mn15 (29.0 mg, 50 µmol, 1.0 equiv), enantiopure (S,M,R)-1 (37.8 mg, 51 µmol, 1.02 equiv), and aqueous 2.5M NaOH (20.4 µL, 51 µmol, 1.02 equiv) in acetone (0.40 mL) afforded (S,M,R)-Mn2 (63.1 mg, 49 µmol, 98%) as a brown solid.

M.p. 258–260 °C. UV-Vis (CH\textsubscript{2}Cl\textsubscript{2}) λ/\text{nm} (log(ε/M\textsubscript{−1}\cdot cm\textsuperscript{−1})) 335 (4.44), 353 (4.45). ECD (CH\textsubscript{2}Cl\textsubscript{2}) λ/\text{nm} (Δε/M\textsubscript{−1}\cdot cm\textsuperscript{−1}) 257 (+7.4), 279 (−56.5), 322 (+9.1), 433 (+5.2).

(R,P,Sa)-Mn2.

According to the procedure for Rac-Mn2, the reaction of Mn15 (29.0 mg, 50 µmol, 1.0 equiv), enantiopure (R,P,Sa)-1 (37.8 mg, 51 µmol, 1.02 equiv), and aqueous 2.5M NaOH (20.4 µL, 51 µmol, 1.02 equiv) in acetone (0.40 mL) afforded (R,P,Sa)-Mn2 (61.8 mg, 48 µmol, 96%) as a brown solid.

M.p. 267–269 °C. UV-Vis (CH\textsubscript{2}Cl\textsubscript{2}) λ/\text{nm} (log(ε/M\textsubscript{−1}\cdot cm\textsuperscript{−1})) 335 (4.44), 353 (4.45). ECD (CH\textsubscript{2}Cl\textsubscript{2}) λ/\text{nm} (Δε/M\textsubscript{−1}\cdot cm\textsuperscript{−1}) 257 (+7.4), 279 (−56.5), 322 (+9.1), 433 (+5.2).
1.5 General epoxidation procedure
A pre-dried Schlenk finger was charged with racemic or enantiopure catalyst Mn2 (3.2 mg, 2.5 mol%). The Schlenk finger was evacuated and backfilled with argon (3×). Then, olefin substrate (0.10 mmol, 1.0 equiv) and dry benzene (1.9 mL) were added and the resulting brown solution was stirred at 20 °C for 5 minutes. Subsequently, iodosylbenzene (26.4 mg, 0.12 mmol, 1.2 equiv) was added in one portion. The resulting mixture was stirred for 16 hours in the dark under an argon atmosphere. Thereafter, the solvent was removed in vacuo and the crude product was purified by preparative TLC (eluent: EtOAc/n-heptane, 1:3, v/v) to afford the isolated epoxide product. Enantiomeric excess values were determined by chiral HPLC analysis.
1.6 Epoxide products
2,2-Dimethyl-6-nitro-1a,7b-dihydro-2H-oxireno[2,3-c]chromene (17b)

Compound 17b (19.7 mg, 89 µmol, yield 89%) was obtained from compound 17a (20.5 mg, 0.10 mmol) with (S,M,Rα)-Mn2 according to the general epoxidation procedure.1H NMR (500 MHz, CDCl3) δ 8.30 (d, J = 2.7 Hz, 1H), 8.15 (dd, J = 9.0, 2.8 Hz, 1H), 6.89 (d, J = 9.0 Hz, 1H), 3.99 (d, J = 4.3 Hz, 1H), 3.56 (d, J = 4.4 Hz, 1H), 1.62 (s, 3H), 1.32 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 158.28, 141.46, 126.30, 125.80, 120.26, 118.48, 75.19, 62.08, 50.04, 25.47, 23.15. GC-MS (C11H11NO3): Calculated 221.0688, Found 221.0743. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 9:1, v/v, flow rate 0.8 mL/min, detection at λ 215 nm, 35 °C, eluted enantiomers at 26.5 and 28.3 min.). [α]D20 = +104.895° (c = 0.257 g/100 mL in ethyl acetate) obtained by (S,M,Rα)-Mn2. [α]D20 = -45.752° (c = 0.153 g/100 mL in ethyl acetate) obtained by (S,P,Sα)-Mn2. [α]D20 = -128.384° (c = 0.358 g/100 mL in ethyl acetate) obtained by (R,P,Sα)-Mn2. [α]D20 = +55.306° (c = 0.217 g/100 mL in ethylacetate) obtained by (R,M,Rα)-Mn2.

2,2-Dimethyl-1a,7b-dihydro-2H-oxireno[2,3-c]chromene-6-carbonitrile (18b)

Compound 18b (17.1 mg, 85 µmol, yield 85%) was obtained from compound 18a (18.5 mg, 0.10 mmol) with (S,M,Rα)-Mn2 according to the general epoxidation procedure.1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 2.1 Hz, 1H), 7.55 (dd, J = 8.5, 2.1 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 3.93 (dd, J = 4.4, 0.6 Hz, 1H), 3.56 (d, J = 4.4 Hz, 1H), 1.62 (s, 3H), 1.32 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 156.49, 134.41, 133.80, 121.09, 119.03, 118.42, 104.33, 74.67, 62.30, 49.88, 25.50, 23.04. GC-MS (C12H11NO2): Calculated 201.0790, Found 201.0786. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 7:3, v/v, flow rate 0.5 mL/min, detection at λ 215 nm, 35 °C, eluted enantiomers at 22.2 and 23.1 min.). [α]D20 = +79.470° (c = 0.151 g/100 mL in ethyl acetate) obtained by (S,M,Rα)-Mn2. [α]D20 = -42.373° (c = 0.118 g/100 mL in ethylacetate) obtained by (S,P,Sα)-Mn2. [α]D20 = -0.151 g/100 mL in ethyl acetate) obtained by (S,P,Sα)-Mn2.

2,2-Dimethyl-6-phenyl-1a,7b-dihydro-2H-oxireno[2,3-c]chromene (19b)

Compound 19b (18.9 mg, 75 µmol, yield 75%) was obtained from compound 19a (23.6 mg, 0.10 mmol) with (S,M,Rα)-Mn2 according to the general epoxidation procedure.1H NMR (400 MHz, CDCl3) δ 7.58 (dt, J = 8.1, 1.6 Hz, 3H), 7.50 (dd, J = 8.4, 2.3 Hz, 1H), 7.45 (m, 2H), 7.34 (m, 1H), 6.91 (d, J = 8.4 Hz, 1H), 4.00 (dd, J = 4.4 Hz, 1H), 3.55 (d, J = 4.4 Hz, 1H), 1.64 (s, 3H), 1.33 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.12, 140.45, 134.31, 129.00, 128.77, 128.30, 126.89, 126.72, 120.16, 118.36, 73.27, 62.78, 51.11, 25.71, 22.73. GC-MS (C11H16O2): Calculated 252.1150, Found 252.1125. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 98:2, v/v, flow rate 0.5 mL/min, detection at λ 215 nm, 35 °C, eluted enantiomers 16.3 and 23.3 min.). [α]D20 = +43.410° (c = 0.253 g/100 mL in ethyl acetate) obtained by (S,M,Rα)-Mn2. [α]D20 = -22.099° (c = 0.362 g/100 mL in ethyl acetate) obtained by (S,P,Sα)-Mn2.

6'-Bromo-1a',7b'-dihydrospiro[cyclohexane-1,2'-oxireno[2,3-c]chromene] (20b)
Compound 20b (23.9 mg, 81 µmol, yield 81%) was obtained from compound 20a (27.9 mg, 0.10 mmol) with \((S,M,R_\alpha)-\text{Mn2}\) according to the general epoxidation procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 2.4$ Hz, 1H), 7.35 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.77 (dd, $J = 8.6, 0.6$ Hz, 1H), 3.83 (dd, $J = 4.4, 0.6$ Hz, 1H), 3.50 (d, $J = 4.4$ Hz, 1H), 2.09 (m, 1H), 1.94 (m, 1H), 1.62 (m, 4H), 1.45 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.44, 133.00, 132.09, 122.92, 119.94, 112.74, 74.00, 62.23, 49.83, 34.03, 30.22, 25.33, 21.11, 20.85. GC-MS \((C_{10}H_{13}BrO_2)\): Calculated 294.0255, Found 294.0341. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, v/v, 98:2, flow rate 0.5 mL/min, detection at $\lambda$ 215 nm, 35 °C, eluted enantiomers at 13.7 and 14.7 min.). $[\alpha]^{20}_D = +20.661^\circ$ (c = 0.387 g/100 mL in ethyl acetate) obtained by \((S,M,R_\alpha)-\text{Mn2}\). $[\alpha]^{20}_D = -7.160^\circ$ (c = 0.419 g/100 mL in ethyl acetate) obtained by \((S,P,S_\alpha)-\text{Mn2}\).

Styrene oxide (21b)

Compound 21b (7.9 mg, 66 µmol, yield 66%) was obtained from compound 21a (10.4 mg, 0.10 mmol) with \((S,M,R_\alpha)-\text{Mn2}\) according to the general epoxidation procedure. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.35 (m, 5H), 3.87 (dd, $J = 4.1, 2.5$ Hz, 1H), 3.15 (dd, $J = 5.5, 4.1$ Hz, 1H), 2.82 (dd, $J = 5.5, 2.6$ Hz, 1H). GC-MS \((C_8H_{18}O)\): Calculated 120.0575, Found 120.0583. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 98:2, v/v, flow rate 0.5 mL/min, detection at $\lambda$ 215 nm, 35 °C, eluted enantiomers at 12.6 and 13.5 min).

2-(4-Chlorophenyl)oxirane (22b)

Compound 22b (13.6 mg, 88 µmol, yield 88%) was obtained from compound 22a (13.8 mg, 0.10 mmol) with \((S,M,R_\alpha)-\text{Mn2}\) according to the general epoxidation procedure. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.35 (m, 2H), 7.24 (m, 2H), 3.86 (dd, $J = 4.1, 2.5$ Hz, 1H), 3.17 (dd, $J = 5.4, 4.0$ Hz, 1H), 2.78 (dd, $J = 5.4, 2.5$ Hz, 1H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 136.18, 133.95, 129.00, 128.72, 126.84, 51.80, 51.25. GC-MS \((C_9H_{16}ClO)\): Calculated 154.0185, Found 154.0189. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 98:2, v/v, flow rate 0.5 mL/min, detection at $\lambda$ 215 nm, 35 °C, eluted enantiomers at 11.2 and 11.9 min.).

4-(Oxiran-2-yl)phenyl acetate (23b)

Compound 23b (15.8 mg, 89 µmol, yield 89%) was obtained from compound 23a (16.2 mg, 0.10 mmol) with \((S,M,R_\alpha)-\text{Mn2}\) according to the general epoxidation procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (m, 2H), 7.10 (m, 2H), 3.89 (dd, $J = 4.1, 2.6$ Hz, 1H), 3.16 (dd, $J = 5.5, 4.0$ Hz, 1H), 2.79 (dd, $J = 5.5, 2.6$ Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.42, 150.54, 135.23, 126.56, 121.72, 51.92, 51.22, 21.11. GC-MS \((C_{10}H_{14}O_2)\): Calculated 178.0630, Found 178.0562. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 98:2, v/v, flow rate 0.5 mL/min, detection at $\lambda$ 215 nm, 35 °C, eluted enantiomers at 36.4 and 40.9 min.).

1-Phenyl-7-oxabicyclo[4.1.0]heptane (24b)
Compound 24b (11.9 mg, 68 µmol, yield 68%) was obtained from compound 24a (15.8 mg, 0.10 mmol) with \((S,M,R)_2\)-Mn2 according to the general epoxidation procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.38 (m, 4H), 7.27 (d, \(J = 7.0\) Hz, 1H), 3.10 (dt, \(J = 3.6, 1.1\) Hz, 1H), 2.31 (ddd, \(J = 14.9, 8.5, 5.4\) Hz, 1H), 2.15 (m, 1H), 2.01 (m, 2H), 1.62 (m, 2H), 1.49 (m, 1H), 1.38 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 142.53, 128.25, 127.16, 125.31, 61.92, 60.23, 28.86, 24.73, 20.13, 19.81. GC-MS (C\(_{15}\)H\(_{22}\)O\(_2\)): Calculated 174.1045, Found 174.1062. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 98:2, v/v, flow rate 0.5 mL/min, detection at \(\lambda = 215\) nm, 35 °C, eluted enantiomers at 8.9 and 9.9 min.).

6a-Methyl-1a,6a-dihydro-6H-indeno[1,2-b]oxirene (25b)

Compound 25b (5.1 mg, 35 µmol, yield 35%) was obtained from compound 25a (13.1 mg, 0.10 mmol) with \((S,M,R)_2\)-Mn2 according to the general epoxidation procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.48 (dt, \(J = 7.2, 1.0\) Hz, 1H), 7.21 (m, 3H), 4.07 (d, \(J = 1.3\) Hz, 1H), 3.19 (d, \(J = 17.7\) Hz, 1H), 2.94 (dd, \(J = 17.8, 1.1\) Hz, 1H), 1.73 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 144.52, 141.77, 128.25, 126.07, 125.79, 124.88, 65.36, 65.05, 38.73, 18.57. GC-MS (C\(_{10}\)H\(_{10}\)O): Calculated 146.0732, Found 146.0711. The enantiomeric purity was determined by chiral HPLC (Lux 3u Cellulose II, eluent heptane/isopropanol, 99:2:0.8, v/v, flow rate 0.5 mL/min, detection at \(\lambda = 215\) nm, 35 °C, eluted enantiomers at 22.5 and 23.5 min.).
2. Resolution of enantiomers of phosphoric acid Rac-1

2.1 Analytical chiral HPLC separation data for compound *Rac-1*

The sample was dissolved in dichloromethane, injected onto the chiral column, and detected with an UV detector at 254 nm and with a circular dichroism detector at 254 nm. The flow-rate was 1 mL/min.

| Column         | Mobile Phase                                | t1   | k1  | t2   | k2  | α   | Rs  |
|----------------|---------------------------------------------|------|-----|------|-----|-----|-----|
| Chiralpak IE   | Ethanol with 0.1% of trifluoroacetic acid / dichloromethane (50/50, v/v) | 3.54 (+) | 0.20 | 4.43 (-) | 0.50 | 2.52 | 3.72 |

Supplementary Figure 1. Chiral HPLC chromatogram of Rac-1.

| RT [min] | Area  | Area % | Capacity Factor | Enantioselectivity | Resolution (USP) |
|----------|-------|--------|-----------------|-------------------|------------------|
| 3.54     | 3896  | 50.72  | 0.20            |                   |                  |
| 4.43     | 3786  | 49.28  | 0.50            | 2.52              | 3.72             |
| Sum      | 7682  | 100.00 |                 |                   |                  |
2.2 Preparative separation data for compound *Rac-1*

- **Sample preparation:** circa 1.5 g of *Rac-1* was dissolved in 60 mL of dichloromethane / ethanol (50/50, v/v).

- **Chromatographic conditions:** Chiralpak IE (250 x 10 mm), eluent ethanol with 0.1% of trifluoroacetic / dichloromethane (50/50 v/v) as mobile phase, flow-rate 5 mL/min, UV detection at 290 nm.

- **Injections (stacked):** 430 times 140 µL, every 2.9 min.

- **First fraction:** 720 mg of the first eluted enantiomer with ee > 99 %.

  ![Supplementary Figure 2. Chiral HPLC chromatogram of the first eluted enantiomer of compound 1.](image)

| RT [min] | Area | Area% |
|----------|------|-------|
| 3.53     | 4718 | 99.60 |
| 4.46     | 19   | 0.40  |
| Sum      | 4737 | 100.00|

- **Second fraction:** 680 mg of the second eluted enantiomer with e.e. > 99 %.

  ![Supplementary Figure 3. Chiral HPLC chromatogram of the second eluted enantiomer of compound 1.](image)

| RT [min] | Area  | Area% |
|----------|-------|-------|
| 3.54     | 51    | 0.40  |
| 4.42     | 12588 | 99.60 |
| Sum      | 12639 | 100.00|
2.3 Optical rotations
Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578 and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

Supplementary Table S1. Optical rotations of the enantiomers of compound 1.

| λ (nm) | Compound 1 First eluted enantiomer on Chiralpak IE \([\alpha]_{25}^{CH_2Cl_2, c = 0.22}\) | Compound 1 Second eluted enantiomer on Chiralpak IE \([\alpha]_{25}^{CH_2Cl_2, c = 0.19}\) |
|--------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| 589    | + 570                                                                            | - 570                                                                            |
| 578    | + 610                                                                            | - 610                                                                            |
| 546    | + 760                                                                            | - 760                                                                            |
2.4 Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

First eluted enantiomer: green solid line, concentration 0.21 mmol.L\(^{-1}\) in acetonitrile.

Second eluted enantiomer: red dotted line, concentration 0.21 mmol.L\(^{-1}\) in acetonitrile.

Supplementary Figure 4. ECD (top) and UV-vis (bottom) spectra of the two enantiomers of compound 1.
3. Optimized conditions for catalysis

![Catalysis reaction diagram]

Supplementary Table 2. Optimizing the conditions for catalysis. Effect of solvent

| Entry | Solvent       | Conversion/% | Catalyst concentration/% | Yield/% b |
|-------|---------------|--------------|--------------------------|-----------|
| 1     | Benzene       | 99           | 5                        | 85        |
| 2     | Benzene       | 96           | 2.5                      | 84        |
| 3     | Dry benzene   | 99           | 2.5                      | 89        |
| 4     | Dry dichloromethane | 20      | 2.5                      | 11        |
| 5     | Dry acetonitrile | 82         | 2.5                      | 70        |
| 6     | Dry toluene   | 28           | 2.5                      | 19        |
| 7     | Dry chloroform| 31           | 2.5                      | 18        |
| 8     | Dry methanol  | 39           | 2.5                      | 28        |
| 9     | Dry DMF       | 20           | 2.5                      | 7         |

a Reaction time 6 h. b Isolated yield of epoxide. c The enantiomeric excess result data is shown in Supplementary Figure 59.
Supplementary Table 3. Optimizing the conditions for catalysis. Effect of water

| Entry | Solvent               | Catalyst       | Conversion/ % | Yield/ % | e.r.  | e.e. | Figure |
|-------|-----------------------|----------------|---------------|----------|-------|------|--------|
| 1     | Benzene (S,M,Ra)-Mn2  | 96             | 85            | 23:77    | 54    |      | S60    |
| 2     | Benzene (S,P,Sa)-Mn2  | 95             | 84            | 64:36    | 28    |      | S61    |
| 3     | Dry benzene (S,M,Ra)-Mn2 | 99        | 89            | 13:87    | 74    |      | S62    |
| 4     | Dry benzene (S,P,Sa)-Mn2 | 90          | 73            | 71:29    | 42    |      | S63    |
| 5     | Benzene with 5% water (S,M,Ra)-Mn2 | 96      | 75            | 36:64    | 28    |      | S64    |
Supplementary Table 4. Optimizing the conditions for catalysis. Effect of solvent polarity

| Entry | Solvent                   | Catalyst          | Conversion/\% | Yield/\% | e.r. | e.e. | Figure |
|-------|---------------------------|-------------------|---------------|----------|------|------|--------|
| 1     | 50% Benzene, 50% heptane  | (S,M,R<sub>a</sub>)-Mn2 | 92            | 76       | 16:84| 68   | S65    |
| 2     | 10% Benzene, 90% heptane  | (S,M,R<sub>a</sub>)-Mn2 | 68            | 54       | 18:82| 64   | S66    |
| 3     | Dry acetonitrile          | (S,M,R<sub>a</sub>)-Mn2 | 85            | 70       | 40:60| 20   | S67    |
Supplementary Table 5. Optimizing the conditions for catalysis. Effect of temperature

| Entry | Solvent                        | Catalyst               | Conversion/\% | Yield/\% | e.r. | e.e. | Figure |
|-------|--------------------------------|------------------------|---------------|----------|------|------|--------|
| 1     | Dry benzene 20 °C              | (S,M,R<sub>a</sub>)-Mn2 | 99            | 89       | 13:87| 74   | S62    |
| 2<sup>a</sup> | Dry benzene 10 °C              | (S,M,R<sub>a</sub>)-Mn2 | 98            | 79       | 17:83| 66   | S68    |
| 3     | Dry benzene 30 °C              | (S,M,R<sub>a</sub>)-Mn2 | 99            | 85       | 16:84| 68   | S69    |
| 4<sup>a</sup> | Dry benzene (50%) dry heptane (50%) 0 °C | (S,M,R<sub>a</sub>)-Mn2 | 59            | 50       | 22:78| 56   | S70    |

<sup>a</sup>Reaction time 8 h.
4. Crystal data

Supplementary Figure 5. Structures and corresponding schematic top-down views of the two enantiomers present in the X-ray crystal structure of Rac-Mn2. a Capped stick style view of the X-ray structure of the \((S,M,R_a)\)-Mn2 enantiomer. b Capped stick style view of the X-ray structure of the \((R,P,S_a)\)-Mn2 enantiomer. Color coding: blue: fluorenyl group; dark green: tBu-phenyl; light green: methyl group attached to the stereogenic center; orange: phosphorus atom; red: oxygen atoms of the phosphate moiety; purple: manganese center; hydrogen atoms have been omitted for clarity.

Deposition Number 2125340

-------------------------------------------------------------------------------
Summary of Data - Deposition Number 2125340
-------------------------------------------------------------------------------

Compound Name: \((S,M,R_a)\text{-Mn2}/(R,P,S_a)\text{-Mn2}\) racemate

Data Block Name: data_p2125b

Unit Cell Parameters: a 14.7197(9) b 25.5687(16) c 21.0556(13) P21/c

-------------------------------------------------------------------------------
CheckCIF/PLATON report

Structure factors have been supplied for datablock(s) p2125b

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: p2125b

| Bond precision: | C-C = 0.0043 Å | Wavelength=0.71073 |
|-----------------|----------------|--------------------|

| Cell: | a=14.7197(9) | b=25.5687(16) | c=21.0556(13) |
|-------|--------------|---------------|---------------|
|       | alpha=90     | beta=105.779(2) | gamma=90     |
| Temperature: | 150 K     |                |               |

| Volume | Calculated    | Reported       |
|--------|---------------|----------------|
|        | 7626.0(8)     | 7625.9(8)      |

| Space group | P 21/c     | P 21/c     |
|-------------|------------|------------|
| Hall group  | -P 2ybc    | -P 2ybc    |

| Moiety formula | C82 H92 Mn N2 O6 P, C7 H8 | C82 H92 Mn N2 O6 P, C7 H8 |
|----------------|--------------------------|--------------------------|
| Sum formula    | C89 H100 Mn N2 O6 P      | C89 H100 Mn N2 O6 P      |
| Mr             | 1379.63                  | 1379.61                  |
| Dx, g cm⁻³     | 1.202                    | 1.202                    |
| Z               | 4                        | 4                        |
| Mu (mm⁻¹)      | 0.249                    | 0.249                    |
| F000           | 2944.0                   | 2944.0                   |
| F000'          | 2946.84                  |                          |
| h,k,lmax       | 19,34,28                 | 19,34,28                 |
| Nref           | 19089                    | 18937                    |
| Tmin,Tmax      | 0.950,0.993              | 0.624,0.746              |
| Tmin’          | 0.931                    |                          |

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.746AbsCorr = MULTI-SCAN

Data completeness= 0.992

\[ R(\text{reflections}) = 0.0613(12949) \]

\[ \text{wr}R^2(\text{reflections}) = 0.1626(18937) \]
$S = 1.039 \quad \text{Npar} = 965$
The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Level B
PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 12 Note

Author Response: OMIT due to beamstop or rejected as (Iobs-Icalc)/SigmaW > 10 Outlier

Level C
PLAT213_ALERT_2_C Atom C94 has ADP max/min Ratio ...... 3.3 prolat
PLAT213_ALERT_2_C Atom C95 has ADP max/min Ratio ...... 3.1 prolat
PLAT213_ALERT_2_C Atom C96 has ADP max/min Ratio ...... 4.0 prolat
PLAT220_ALERT_2_C NonSolvent Resid 1 C Ueq(max)/Ueq(min) Range 5.9 Ratio
PLAT222_ALERT_3_C NonSolvent Resid 1 H Uiso(max)/Uiso(min) Range 6.2 Ratio
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C70 Check
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C74 Check
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C85 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including C100 0.107 Check
PLAT331_ALERT_2_C Small Aver Phenyl C-C Dist C88 --C90 . 1.37 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ...... 2.904 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thm & STh/L= 0.600 6 Report

Level G
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 14 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 106 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGT Unusually Large 8.49 Why ?
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records 1 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) C88 --C89 . 5.4 s.u.
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2 ) 100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 3 ) 100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... (Resd 2 ) 11.58 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... (Resd 3 ) 3.42 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ........... 8 Note
PLAT793_ALERT_4_G Model has Chirality at C59 (Centro SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............. 1770 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 135 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT933_ALERT_2_G Number of HKL-Omit Records in Embedded .res File 4 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity .............. 4.4 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 5 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by 2 Check

0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully

S33
12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
22 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
15 ALERT type 2 Indicator that the structure model may be wrong or deficient
 7 ALERT type 3 Indicator that the structure quality may be low
12 ALERT type 4 Improvement, methodology, query or suggestion
 1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation); however, if you intend to submit to Acta Crystallographica Section C or E or IUCrData, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the Notes for Authors of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/05/2022; check.def file version of 17/05/2022
ORTEP-style illustration p2125b_ORTEP_50 (for Rac-Mn2)
Supplementary Figure 6. Structures of the stable and metastable (obtained after irradiation) isomers present in the X-ray crystal structure of Mn2. a Capped stick style view of the X-ray structure of the stable $\left(R,P,S_a\right)$-Mn2 isomer. b Capped stick style view of the X-ray structure of the metastable $\left(R,M,R_a\right)$-Mn2 isomer. Color coding: dark blue: phosphate ligand 1, red: salen ligand; magenta: ethylene bridge of salen. green: manganese center; hydrogen atoms have been omitted for clarity.

The crystal structures of $\left(S,M,R_a\right)$-Mn2 in Fig. 3a and $\left(R,P,S_a\right)$-Mn2 in the Supplementary Figure 6a were selected from the stable rac-Mn2 crystal. The crystal structures of $\left(S,P,S_a\right)$-Mn2 in Fig. 3b and $\left(R,M,R_a\right)$-Mn2 in the Supplementary Figure 6b were selected from the metastable rac-Mn2 crystal.

$(S,M,Ra)$-Mn2 (stable)

Supplementary Table 6: Crystal structure and structure refinement for $(S,M,Ra)$-Mn2

| Crystal structure and structure refinement |
|-------------------------------------------|
| General information                       |
| Identification code RU/paper              | p2125b / $(R,P,S_a)$-Mn2 |
| CCDC Deposition Number                    | 2125340 |
| Crystal colour                            | brown |
| Crystal dimensions [mm] / shape            | 0.03 x 0.17 x 0.29 / needle |
| Crystallization solvent                    | toluene-n-heptane (1:8, v/v) |
| Empirical formula                         | $C_{82}H_{92}MnN_2O_6P$, $C_{7}H_{8}$ |
| Formula weight [g/mol]                     | 1379.61 |

| Crystal Data                                |
|---------------------------------------------|
| Crystal system                              | Monoclinic |
| Space group                                 | $P2_1/c$ (#14) |
| Unit cell dimensions                        |
| $a$, $b$, $c$ [Å]                           | 14.7197(9), 25.5687(16), 21.0556(13) |
| $\alpha$, $\beta$, $\gamma$ [°]            | 90, 105.779(2), 90 |
| Volume [Å$^3$]                              | 7626.0(8) |
| Z                                           | 4 |
| Density (calculated) [g/cm$^3$]             | 1.202 |
| Absorption coefficient (MoKα) [ mm$^{-1}$ ] | 0.249 |
| F(000)                                      | 2944 |

| Data Collection                             |
|---------------------------------------------|
| Temperature during experiment [K]           | 150 |
| Wavelength [Å]                              | 0.71073 |
Reflections were measured on a Bruker D8 Quest diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073\AA$). The software package used for the intensity integration was Saint (v8.40a). Absorption correction was performed with SADABS. The structures were solved with direct methods using SHELXT-2014/5. Least-squares refinement was performed with SHELXL-2018/3 against $|F_o|^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were placed on calculated positions or located in difference Fourier maps. All calculated hydrogen atoms were refined with a riding model.

(R,P,S$_{a}$)-Mn2 (metastable) single crystal preparation procedure:

Irradiation of a solution of stable Rac-Mn2 (c = 1 mg/mL in CH$_2$Cl$_2$) for 30 minutes with $\lambda = 365$ nm light furnished a solution of metastable Rac-Mn2. Evaporation of the solvent followed by crystallization from toluene/n-heptane (1:8, v/v) furnished metastable Rac-Mn2 in the crystalline state. The crystal of metastable Rac-Mn2 was dark-brownish colored and had a needle shape. Unfortunately, due to the small size of the crystal, only a partial diffraction data set with low resolution could be obtained. With this limited dataset the non-hydrogen atoms could only be refined isotopically and no hydrogens could be placed via a difference map. The crystallographic information of the tentative metastable structure is given below in the form of a .res file.

```
TITL p2150a_a.res in P-1
CELL  0.71073  14.1195  22.8027  26.3963  91.5433  97.9836  103.6320
ZERR  1.000  0.0029  0.0051  0.0058  0.0068  0.0122  0.0084
LATT  1
SFAC C H P O MN N
UNIT  1 1 1 1 1 1
L.S.  20
BOND $H
CONF
ACTA
rem ANIS
TEMP -150
```
| NAME | NR | X    | Y    | Z    | WT    | FWT |
|------|----|------|------|------|-------|-----|
| MN01 | 5  | 0.586623 | 0.198990 | 0.478301 | 11.00000 | 0.02611 |
| MN02 | 5  | -0.145768 | 0.347334 | 0.888462 | 11.00000 | 0.03136 |
| P003 | 3  | 0.357978 | 0.116355 | 0.487731 | 11.00000 | 0.02562 |
| P004 | 3  | 0.097863 | 0.392911 | 0.932561 | 11.00000 | 0.03001 |
| O005 | 4  | 0.349715 | 0.051672 | 0.479114 | 11.00000 | 0.02621 |
| O006 | 4  | 0.119256 | 0.455780 | 0.956626 | 11.00000 | 0.03301 |
| O007 | 4  | -0.160629 | 0.262734 | 0.877606 | 11.00000 | 0.02661 |
| O008 | 4  | 0.090730 | 0.342231 | 0.974122 | 11.00000 | 0.03066 |
| O009 | 4  | 0.368842 | 0.137414 | 0.548658 | 11.00000 | 0.02549 |
| O010 | 4  | 0.434188 | 0.161467 | 0.468587 | 11.00000 | 0.03114 |
| O011 | 4  | 0.250339 | 0.127130 | 0.466814 | 11.00000 | 0.02035 |
| O012 | 4  | 0.191781 | 0.388611 | 0.906940 | 11.00000 | 0.02955 |
| O013 | 4  | -0.179510 | 0.363923 | 0.819236 | 11.00000 | 0.02944 |
| O014 | 4  | 0.583734 | 0.271366 | 0.514066 | 11.00000 | 0.02485 |
| O015 | 4  | 0.005181 | 0.369812 | 0.895229 | 11.00000 | 0.03962 |
| O016 | 4  | 0.600507 | 0.231150 | 0.414396 | 11.00000 | 0.02900 |
| N017 | 6  | 0.626901 | 0.167412 | 0.546548 | 11.00000 | 0.02776 |
| N018 | 6  | 0.627644 | 0.125704 | 0.454513 | 11.00000 | 0.02923 |
| O019 | 4  | 0.167507 | -0.033232 | 0.448308 | 11.00000 | 0.08232 |
| C020 | 1  | 0.146219 | 0.092186 | 0.637479 | 11.00000 | 0.02096 |
| C021 | 1  | 0.209777 | 0.218582 | 0.438573 | 11.00000 | 0.02149 |
| C022 | 1  | 0.047223 | 0.414065 | 1.065832 | 11.00000 | 0.02916 |
| C023 | 1  | -0.125776 | 0.227798 | 0.908552 | 11.00000 | 0.04843 |
| C024 | 1  | 0.398268 | 0.060111 | 0.632283 | 11.00000 | 0.01986 |
| C025 | 1  | 0.215477 | 0.146417 | 0.566570 | 11.00000 | 0.01711 |
| C026 | 1  | 0.444920 | 0.035154 | 0.597052 | 11.00000 | 0.02158 |
| Column | Row | X     | Y     | Z     | E    | Sigma |
|--------|-----|-------|-------|-------|------|-------|
|        | 27  | 0.67838 | 0.118092 | 0.545604 | 11.00000 | 0.02145 |
|        | 28  | -0.173649 | 0.424851 | 0.907967 | 11.00000 | 0.03200 |
|        | 29  | 0.596215 | 0.182044 | 0.591021 | 11.00000 | 0.03307 |
|        | 30  | 0.228020 | 0.068497 | 0.648135 | 11.00000 | 0.02553 |
|        | 31  | 0.509770 | 0.032179 | 0.701760 | 11.00000 | 0.02465 |
|        | 32  | 0.138134 | 0.130967 | 0.597534 | 11.00000 | 0.01601 |
|        | 33  | 0.258893 | 0.440669 | 0.756002 | 11.00000 | 0.02063 |
|        | 34  | -0.099140 | 0.240708 | 0.961936 | 11.00000 | 0.03291 |
|        | 35  | -0.221422 | 0.455652 | 0.823623 | 11.00000 | 0.01800 |
|        | 36  | 0.084043 | 0.365395 | 1.083409 | 11.00000 | 0.03664 |
|        | 37  | 0.293146 | 0.120639 | 0.576904 | 11.00000 | 0.01978 |
|        | 38  | 0.157203 | 0.331472 | 0.960591 | 11.00000 | 0.02799 |
|        | 39  | 0.203658 | 0.199919 | 0.383751 | 11.00000 | 0.02815 |
|        | 40  | 0.508703 | 0.235288 | 0.640220 | 11.00000 | 0.01999 |
|        | 41  | 0.190115 | 0.416103 | 0.709627 | 11.00000 | 0.02273 |
|        | 42  | -0.045083 | 0.144214 | 0.921111 | 11.00000 | 0.03173 |
|        | 43  | 0.654202 | 0.116360 | 0.412329 | 11.00000 | 0.02440 |
|        | 44  | 0.630752 | 0.081683 | 0.494603 | 11.00000 | 0.01261 |
|        | 45  | -0.008690 | 0.131117 | 0.497281 | 11.00000 | 0.02629 |
|        | 46  | 0.522909 | 0.010507 | 0.614441 | 11.00000 | 0.02119 |
|        | 47  | 0.652291 | 0.155202 | 0.369250 | 11.00000 | 0.03143 |
|        | 48  | 0.255171 | 0.323454 | 0.992095 | 11.00000 | 0.02562 |
|        | 49  | 0.305016 | 0.081432 | 0.618276 | 11.00000 | 0.02885 |
|        | 50  | -0.215549 | 0.441561 | 1.130250 | 11.00000 | 0.04624 |
|        | 51  | -0.122319 | 0.429350 | 1.165525 | 11.00000 | 0.03742 |
|        | 52  | 0.461805 | 0.282359 | 0.649221 | 11.00000 | 0.04316 |
|        | 53  | 0.341514 | 0.323014 | 1.027912 | 11.00000 | 0.03923 |
|        | 54  | 0.639185 | -0.022664 | 0.686145 | 11.00000 | 0.03405 |
|        | 55  | -0.273370 | 0.446920 | 0.718485 | 11.00000 | 0.03300 |
|        | 56  | 0.456213 | 0.325533 | 0.610614 | 11.00000 | 0.03471 |
|        | 57  | -0.236851 | 0.402760 | 0.742994 | 11.00000 | 0.03315 |
|        | 58  | -0.289236 | 0.495906 | 0.747214 | 11.00000 | 0.03308 |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C059 | 1 | -0.262393 | 0.499933 | 0.800049 | 11.00000 | 0.03887 |   |   |   |   |   |   |   |   |
| C060 | 1 | 0.175514  | 0.341318 | 1.010267 | 11.00000 | 0.02299 |   |   |   |   |   |   |   |   |
| C061 | 1 | 0.677118  | 0.131769 | 0.323295 | 11.00000 | 0.03308 |   |   |   |   |   |   |   |   |
| C062 | 1 | 0.169475  | 0.350239 | 1.062748 | 11.00000 | 0.02742 |   |   |   |   |   |   |   |   |
| C063 | 1 | 0.624728  | 0.247244 | 0.329093 | 11.00000 | 0.03392 |   |   |   |   |   |   |   |   |
| C064 | 1 | -0.016000 | 0.160501 | 0.974712 | 11.00000 | 0.03648 |   |   |   |   |   |   |   |   |
| C065 | 1 | 0.549559  | 0.234325 | 0.593282 | 11.00000 | 0.02318 |   |   |   |   |   |   |   |   |
| C066 | 1 | 0.464085  | 0.333935 | 0.971371 | 11.00000 | 0.03222 |   |   |   |   |   |   |   |   |
| C067 | 1 | 0.229193  | 0.179552 | 0.477702 | 11.00000 | 0.02956 |   |   |   |   |   |   |   |   |
| C068 | 1 | 0.024737  | 0.080920 | 0.488730 | 11.00000 | 0.02965 |   |   |   |   |   |   |   |   |
| C069 | 1 | -0.061047 | 0.212269 | 0.538306 | 11.00000 | 0.03638 |   |   |   |   |   |   |   |   |
| C070 | 1 | 0.432750  | 0.057638 | 0.685894 | 11.00000 | 0.04956 |   |   |   |   |   |   |   |   |
| C071 | 1 | 0.418492  | 0.285143 | 0.694655 | 11.00000 | 0.02795 |   |   |   |   |   |   |   |   |
| C072 | 1 | 0.498138  | 0.373285 | 0.527903 | 11.00000 | 0.02970 |   |   |   |   |   |   |   |   |
| C073 | 1 | -0.020812 | 0.435585 | 1.092276 | 11.00000 | 0.02239 |   |   |   |   |   |   |   |   |
| C074 | 1 | -0.058370 | 0.210640 | 0.799142 | 11.00000 | 0.03523 |   |   |   |   |   |   |   |   |
| C075 | 1 | -0.052875 | 0.209556 | 0.996359 | 11.00000 | 0.03959 |   |   |   |   |   |   |   |   |
| C076 | 1 | 0.192239  | 0.449459 | 0.662517 | 11.00000 | 0.03677 |   |   |   |   |   |   |   |   |
| C077 | 1 | 0.556127  | 0.007593 | 0.667981 | 11.00000 | 0.03576 |   |   |   |   |   |   |   |   |
| C078 | 1 | 0.073519  | 0.083657 | 0.674273 | 11.00000 | 0.04071 |   |   |   |   |   |   |   |   |
| C079 | 1 | -0.090654 | 0.178094 | 0.889591 | 11.00000 | 0.01849 |   |   |   |   |   |   |   |   |
| C080 | 1 | -0.008304 | 0.050458 | 0.437612 | 11.00000 | 0.03288 |   |   |   |   |   |   |   |   |
| C081 | 1 | 0.191493  | 0.273651 | 0.452213 | 11.00000 | 0.04362 |   |   |   |   |   |   |   |   |
| C082 | 1 | -0.052032 | 0.404935 | 1.135296 | 11.00000 | 0.04152 |   |   |   |   |   |   |   |   |
| C083 | 1 | 0.154608  | 0.145701 | 0.364771 | 11.00000 | 0.02865 |   |   |   |   |   |   |   |   |
| C084 | 1 | 0.444510  | 0.343715 | 0.472642 | 11.00000 | 0.03022 |   |   |   |   |   |   |   |   |
| C085 | 1 | 0.213437  | 0.193294 | 0.527228 | 11.00000 | 0.02805 |   |   |   |   |   |   |   |   |
| C086 | 1 | 0.610011  | 0.409184 | 0.523856 | 11.00000 | 0.04821 |   |   |   |   |   |   |   |   |
| C087 | 1 | 0.190380  | 0.247287 | 0.545319 | 11.00000 | 0.03511 |   |   |   |   |   |   |   |   |
| C088 | 1 | -0.085723 | 0.098860 | 0.816795 | 11.00000 | 0.04182 |   |   |   |   |   |   |   |   |
| C089 | 1 | 0.540959  | 0.351203 | 0.899664 | 11.00000 | 0.03274 |   |   |   |   |   |   |   |   |
| C090 | 1 | -0.246439 | 0.355619 | 0.652126 | 11.00000 | 0.03027 |   |   |   |   |   |   |   |   |
| C091 | 0.039420 | 0.125325 | 1.010847 | 11.00000 | 0.05777 |
| C092 | -0.096940 | 0.355233 | 0.715486 | 11.00000 | 0.03662 |
| C093 | 0.596507 | 0.307361 | 0.331529 | 11.00000 | 0.04985 |
| C094 | -0.000531 | 0.168171 | 0.547436 | 11.00000 | 0.03836 |
| C095 | 0.241443 | 0.247697 | 0.353915 | 11.00000 | 0.03172 |
| C096 | -0.211117 | 0.406273 | 0.798336 | 11.00000 | 0.02640 |
| C097 | -0.268871 | 0.284508 | 0.724490 | 11.00000 | 0.04429 |
| C098 | -0.075205 | 0.156367 | 0.462816 | 11.00000 | 0.03768 |
| C099 | -0.337780 | 0.543847 | 0.719825 | 11.00000 | 0.04773 |
| C100 | 0.182668 | 0.290419 | 0.505016 | 11.00000 | 0.04228 |
| C101 | 0.669797 | 0.169533 | 0.281740 | 11.00000 | 0.04181 |
| C102 | -0.208055 | 0.461923 | 0.879424 | 11.00000 | 0.03987 |
| C103 | -0.209393 | 0.349719 | 0.707250 | 11.00000 | 0.03095 |
| C104 | 0.230450 | 0.256754 | 0.834539 | 11.00000 | 0.04066 |
| C105 | 0.020682 | 0.176551 | 0.644244 | 11.00000 | 0.05492 |
| C106 | -0.158985 | 0.388319 | 1.206793 | 11.00000 | 0.06462 |
| C107 | 0.477794 | 0.266686 | 1.045424 | 11.00000 | 0.04203 |
| C108 | 0.734740 | 0.008295 | 0.662947 | 11.00000 | 0.04806 |
| C109 | 0.251059 | 0.341531 | 1.098487 | 11.00000 | 0.03116 |
| C110 | 0.250866 | 0.221645 | 0.876872 | 11.00000 | 0.04259 |
| C111 | 0.624741 | 0.211549 | 0.371761 | 11.00000 | 0.04349 |
| C112 | 0.298646 | 0.464826 | 0.645795 | 11.00000 | 0.05497 |
| C113 | 0.241423 | 0.299141 | 0.936626 | 11.00000 | 0.03442 |
| C114 | 0.211730 | 0.310313 | 0.845189 | 11.00000 | 0.04051 |
| C115 | 0.539245 | 0.274672 | 0.555510 | 11.00000 | 0.02278 |
| C116 | 0.501445 | 0.322861 | 0.563754 | 11.00000 | 0.03518 |
| C117 | 0.461011 | 0.350290 | 0.725213 | 11.00000 | 0.04560 |
| C118 | 0.406305 | 0.435877 | 0.966363 | 11.00000 | 0.04615 |
| C119 | -0.063215 | 0.493475 | 1.190731 | 11.00000 | 0.04411 |
| C120 | 0.201511 | 0.352196 | 0.801322 | 11.00000 | 0.03768 |
| C121 | -0.100684 | 0.126358 | 0.410020 | 11.00000 | 0.03904 |
| C122 | 0.302355 | 0.279324 | 0.679687 | 11.00000 | 0.03370 |
|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| C123| 1   | 0.259924 | 0.410286 | 0.798366 | 11.00000 | 0.03577 |
| C124| 1   | 0.650728 | 0.224855 | 0.283842 | 11.00000 | 0.03362 |
| C125| 1   | 0.134112 | 0.358291 | 0.712229 | 11.00000 | 0.03671 |
| C126| 1   | 0.138886 | 0.130533 | 0.309565 | 11.00000 | 0.03269 |
| C127| 1   | -0.067946 | 0.076289 | 0.402089 | 11.00000 | 0.04125 |
| C128| 1   | 0.046622 | 0.156147 | 0.595154 | 11.00000 | 0.04064 |
| C129| 1   | 0.667606 | -0.024029 | 0.742368 | 11.00000 | 0.05156 |
| C130| 1   | -0.229199 | 0.150072 | 0.811571 | 11.00000 | 0.03772 |
| C131| 1   | 0.426989 | 0.308047 | 1.010515 | 11.00000 | 0.03504 |
| C132| 1   | 0.427871 | 0.236541 | 0.733330 | 11.00000 | 0.05060 |
| C133| 1   | -0.204264 | 0.376874 | 0.989478 | 11.00000 | 0.04465 |
| C134| 1   | -0.125648 | 0.288290 | 0.985121 | 11.00000 | 0.04105 |
| C135| 1   | 0.168500 | 0.176903 | 0.279048 | 11.00000 | 0.04764 |
| C136| 1   | -0.114677 | 0.301865 | 0.546562 | 11.00000 | 0.04862 |
| C137| 1   | -0.152914 | 0.245664 | 0.462307 | 11.00000 | 0.04110 |
| C138| 1   | 0.050148 | 0.333828 | 1.124062 | 11.00000 | 0.03935 |
| C139| 1   | 0.159780 | 0.509791 | 0.669900 | 11.00000 | 0.05030 |
| C140| 1   | -0.063914 | 0.261996 | 0.567699 | 11.00000 | 0.03824 |
| C141| 1   | 0.450351 | 0.391428 | 0.948215 | 11.00000 | 0.04827 |
| C142| 1   | 0.116493 | 0.409384 | 0.613919 | 11.00000 | 0.05057 |
| C143| 1   | 0.412588 | 0.314647 | 1.119184 | 11.00000 | 0.05488 |
| C144| 1   | 0.135390 | 0.324490 | 0.755080 | 11.00000 | 0.03813 |
| C145| 1   | -0.020640 | 0.356569 | 1.149641 | 11.00000 | 0.05123 |
| C146| 1   | 0.607973 | -0.091345 | 0.664189 | 11.00000 | 0.03684 |
| C147| 1   | 0.666841 | 0.352503 | 0.375299 | 11.00000 | 0.05148 |
| C148| 1   | -0.094066 | 0.159361 | 0.645692 | 11.00000 | 0.06178 |
| C149| 1   | 0.127478 | 0.172630 | 1.045991 | 11.00000 | 0.04426 |
| C150| 1   | -0.094927 | 0.206610 | 0.483017 | 11.00000 | 0.04003 |
| C151| 1   | 0.503344 | 0.455239 | 0.879363 | 11.00000 | 0.05484 |
| C152| 1   | 0.527024 | 0.311125 | 0.937488 | 11.00000 | 0.04275 |
| C153| 1   | 0.331194 | 0.330884 | 1.081492 | 11.00000 | 0.03837 |
| C154| 1   | 0.216237 | 0.334890 | 0.896454 | 11.00000 | 0.04037 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C155 | 1 | 0.438600 | 0.418557 | 0.542443 | 11.00000 | 0.05464 |
| C156 | 1 | 0.590245 | 0.297434 | 1.065670 | 11.00000 | 0.07500 |
| C157 | 1 | 0.595290 | 0.331493 | 0.857617 | 11.00000 | 0.06117 |
| C158 | 1 | 0.620454 | 0.281689 | 0.859319 | 11.00000 | 0.08068 |
| C159 | 1 | -0.153156 | 0.437888 | 0.966587 | 11.00000 | 0.05748 |
| C160 | 1 | 0.609336 | 0.342167 | 0.279392 | 11.00000 | 0.05547 |
| C161 | 1 | 0.260833 | 0.243989 | 0.928275 | 11.00000 | 0.04288 |
| C162 | 1 | 0.861075 | 0.469474 | 0.510352 | 11.00000 | 0.07007 |
| C163 | 1 | 0.220249 | 0.236187 | 0.299121 | 11.00000 | 0.04869 |
| C164 | 1 | -0.162473 | 0.294561 | 0.490071 | 11.00000 | 0.04763 |
| C165 | 1 | 0.066051 | 0.148655 | 0.696356 | 11.00000 | 0.06479 |
| C166 | 1 | 0.489543 | 0.296062 | 0.336877 | 11.00000 | 0.04445 |
| C167 | 1 | 0.149385 | 0.163397 | 0.219085 | 11.00000 | 0.09836 |
| C168 | 1 | 0.554527 | 0.259843 | 0.938672 | 11.00000 | 0.07777 |
| C169 | 1 | -0.117065 | 0.156972 | 0.829026 | 11.00000 | 0.05705 |
| C170 | 1 | 0.504625 | 0.402145 | 0.904669 | 11.00000 | 0.04569 |
| C171 | 1 | 0.428864 | 0.253348 | 1.094341 | 11.00000 | 0.04836 |
| C172 | 1 | 0.079594 | 0.080627 | 0.981136 | 11.00000 | 0.07714 |
| C173 | 1 | 0.473669 | 0.494664 | 0.894745 | 11.00000 | 0.06615 |
| C174 | 1 | 0.412449 | 0.491953 | 0.936815 | 11.00000 | 0.05236 |
| C175 | 1 | 1.041640 | 0.743551 | 0.663328 | 11.00000 | 0.09542 |
| C176 | 1 | 0.942016 | 0.615999 | 0.607845 | 11.00000 | 0.07279 |
| C177 | 1 | -0.328315 | 0.598772 | 0.750733 | 11.00000 | 0.09227 |
| C178 | 1 | 0.708825 | 0.146592 | 0.230756 | 11.00000 | 0.07923 |
| C179 | 1 | 0.767757 | 0.199049 | 0.204121 | 11.00000 | 0.08534 |
| C180 | 1 | -0.031190 | 0.090141 | 1.048233 | 11.00000 | 0.06454 |
| C181 | 1 | 0.931155 | 0.550743 | 0.587380 | 11.00000 | 0.09221 |
| C182 | 1 | 0.995063 | 0.690651 | 0.685823 | 11.00000 | 0.09594 |
| C183 | 1 | 1.005804 | 0.630957 | 0.659736 | 11.00000 | 0.11131 |
| C184 | 1 | 0.861026 | 0.534705 | 0.536706 | 11.00000 | 0.07664 |
| C185 | 1 | -0.267978 | 0.572476 | 0.679218 | 11.00000 | 0.13255 |
| C186 | 1 | -0.429891 | 0.516283 | 0.690680 | 11.00000 | 0.09941 |
C187  1    0.097550    0.097054    0.200408    11.00000    0.06567
C188  1    0.066045    0.201809    0.195052    11.00000    0.08632
C189  1    0.246505    0.179036    0.196653    11.00000    0.10690
C190  1    0.610613    0.122707    0.191934    11.00000    0.13158
C191  1    0.761500    0.096203    0.239044    11.00000    0.12207
O192  4    0.359008    0.074861    0.841907    11.00000    0.34588
C193  1    0.607297    0.240203    0.896940    11.00000    0.07765

HKLF 4

REM  p2150a_a.res in P-1
REM wR2 = 0.3863, GooF = S = 1.311, Restrained GooF = 1.311 for all data
REM R1 = 0.1626 for 4074 Fo > 4sig(Fo) and 0.3004 for all 10515 data
REM 773 parameters refined using 0 restraints

END
5. UV-Vis and ECD spectra of catalysts

Supplementary Figure 7. UV-Vis spectra of the racemic and enantiopure Mn2 catalysts (c = 5×10^{-5} M, CH2Cl2, l = 2 mm). The solutions of the metastable isomers were obtained by irradiating the solutions of the stable isomers with λ = 365 nm for 2 minutes.

Supplementary Figure 8. ECD spectra of the racemic and enantiopure Mn2 catalysts (c = 5×10^{-5} M, CH2Cl2, l = 2 mm). The solutions of the metastable isomers were obtained by irradiating the solutions of the stable isomers with λ = 365 nm for 2 minutes.
6. Details of catalytic epoxidation reactions and assignment of absolute configurations of enantioenriched epoxides.

Supplementary Table 7. Enantio-divergent epoxidation of alkenes using Mn2 as the catalyst.

| Entry | Substrate | Product | Catalyst | Conversion (%) | Yield (%) | e.e. (%) | Figure |
|-------|-----------|---------|----------|---------------|-----------|----------|--------|
| 1     |           |         | (S,M,R)-Mn2 | 99 | 89 | 74 (1aR,7bR) | S62   |
| 2     |           |         | (S,M,R)-Mn2 | 97 | 90 | 74 (1aR,7bR) | S73   |
| 3     |           |         | (S,M,R)-Mn2 | 99 | 86 | 70 (1aR,7bR) | S74   |
| 4<sup>a</sup> |       |     | (S,P,S)-Mn2 | 90 | 73 | 42 (1aS,7bS) | S63   |
| 5<sup>a</sup> |       |     | (S,P,S)-Mn2 | 93 | 79 | 44 (1aS,7bS) | S75   |
| 6     |           |         | (R,P,S)-Mn2 | 92 | 77 | 68 (1aS,7bS) | S71   |
| 7     |           |         | (R,P,S)-Mn2 | 93 | 79 | 70 (1aS,7bS) | S76   |
| 8     |           |         | (R,P,S)-Mn2 | 95 | 75 | 68 (1aS,7bS) | S77   |
| 9<sup>b</sup> |         |     | (R,M,R)-Mn2 | 96 | 85 | 42 (1aR,7bR) | S72   |
| 10<sup>b</sup> |       |     | (R,M,R)-Mn2 | 95 | 82 | 44 (1aR,7bR) | S78   |
| 11    |           |         | (S,M,R)-Mn2 | 95 | 85 | 74 (1aR,7bR) | S79   |
| 12    |           |         | (S,M,R)-Mn2 | 98 | 90 | 78 (1aR,7bR) | S79   |
| 13<sup>a</sup> |     |     | (S,P,S)-Mn2 | 92 | 74 | 20 (1aS,7bS) | S79   |
| 14<sup>a</sup> |     |     | (S,P,S)-Mn2 | 90 | 76 | 16 (1aS,7bS) | S79   |
| 15    |           |         | (S,M,R)-Mn2 | 89 | 75 | 56 (1aR,7bR) | S80   |
| 16    |           |         | (S,M,R)-Mn2 | 90 | 80 | 52 (1aR,7bR) | S80   |
| 17<sup>a</sup> |   |     | (S,P,S)-Mn2 | 85 | 67 | 40 (1aS,7bS) | S80   |
| 18<sup>a</sup> |   |     | (S,P,S)-Mn2 | 82 | 62 | 42 (1aS,7bS) | S80   |
| 19    |           |         | (S,M,R)-Mn2 | 95 | 81 | 50 (1aR,7b'R) | S81   |
| 20<sup>a</sup> |     |     | (S,M,R)-Mn2 | 96 | 85 | 52 (1aR,7b'R) | S81   |
| 21<sup>a</sup> |     |     | (S,P,S)-Mn2 | 95 | 83 | 32 (1aS,7b'S) | S81   |
| 22<sup>a</sup> |     |     | (S,P,S)-Mn2 | 98 | 85 | 30 (1aS,7b'S) | S81   |
| 23    |           |         | (S,M,R)-Mn2 | 85 | 66 | 24 (R) | S82   |
| 24    |           |         | (S,M,R)-Mn2 | 90 | 63 | 22 (R) | S82   |
| 25<sup>a</sup> |   |     | (S,P,S)-Mn2 | 78 | 62 | 12 (S) | S82   |
| 26<sup>a</sup> |   |     | (S,P,S)-Mn2 | 74 | 53 | 16 (S) | S82   |
| 27    |           |         | (S,M,R)-Mn2 | 96 | 88 | 16 (R) | S83   |
| 28    |           |         | (S,M,R)-Mn2 | 90 | 83 | 12 (R) | S83   |
| 29<sup>a</sup> |     |     | (S,P,S)-Mn2 | 95 | 83 | 12 (S) | S83   |
| 30<sup>a</sup> |     |     | (S,P,S)-Mn2 | 98 | 85 | 10 (S) | S83   |
| 31    |           |         | (S,M,R)-Mn2 | 96 | 89 | 20 (R) | S84   |
| 32    |           |         | (S,M,R)-Mn2 | 97 | 91 | 16 (R) | S84   |
| 33<sup>a</sup> |     |     | (S,P,S)-Mn2 | 97 | 85 | 16 (S) | S84   |
| 34<sup>a</sup> |     |     | (S,P,S)-Mn2 | 96 | 88 | 10 (S) | S84   |
| 35    |           |         | (S,M,R)-Mn2 | 76 | 68 | 14 (1S,6S) | S85   |
| 36    |           |         | (S,M,R)-Mn2 | 72 | 60 | 12 (1S,6S) | S85   |
| 37<sup>a</sup> |     |     | (S,P,S)-Mn2 | 70 | 51 | 12 (1R,6R) | S85   |
| 38<sup>a</sup> |     |     | (S,P,S)-Mn2 | 68 | 50 | 6 (1R,6R) | S85   |
| 39    |           |         | (S,M,R)-Mn2 | 68 | 35 | 30 (1R,6aS) | S86   |
| 40    |           |         | (S,M,R)-Mn2 | 59 | 27 | 22 (1R,6aS) | S86   |
| 41<sup>a</sup> |     |     | (S,P,S)-Mn2 | 60 | 39 | 12 (1aS,6aR) | S86   |
| 42<sup>a</sup> |     |     | (S,P,S)-Mn2 | 51 | 30 | 10 (1aS,6aR) | S86   |

<sup>a</sup>Conversion was calculated based on the recovered substrate. <sup>b</sup>Isolated yield. <sup>c</sup>Enantiomeric excess values (e.e.) were determined by chiral HPLC. See the next section for the assignment of the absolute configurations of the enantioenriched epoxides. <sup>d</sup>Catalyst (S,P,S)-Mn2 was obtained by irradiation of (S,M,R)-Mn2 (c = 1 mg/mL in CH2Cl2) for 30 min with λ =
365 nm light, followed by evaporation of the solvent. Catalyst $(R,M,R_\alpha)$-Mn$_2$ was obtained by irradiation of $(R,P,S_\alpha)$-Mn$_2$ (c = 1 mg/mL in CH$_2$Cl$_2$) for 30 min with $\lambda = 365$ nm light, followed by evaporation of the solvent.

The absolute configurations of the enantioenriched epoxides 17b–20b were assigned on the basis of the sign of the optical rotation as reported by Jacobsen et al.$^{55}$ Epoxides 17b–20b generated with catalysts $(S,M,R_\alpha)$-Mn$_2$ or $(R,M,R_\alpha)$-Mn$_2$ displayed positive optical rotations corresponding to the $(1aR,7bR)$-configuration.$^{55}$ Those produced by $(R,P,S_\alpha)$-Mn$_2$ or $(S,P,S_\alpha)$-Mn$_2$ displayed negative optical rotations corresponding to the $(1aS,7bS)$-configuration.$^{55}$ The correlation between the $(R_\alpha)$ axial chirality of the phosphate ligand and the $(1aR,7bR)$ absolute configuration of the enantioenriched epoxide was also observed by List et al.$^{82,86}$

For the styrene oxide series (epoxides 21b–23b), which displayed low enantioselectivities (e.e. $< 25\%$), optical rotation measurements did not prove reproducible: while a first measurement of a sample could give a positive optical rotation, a second or third measurement could suddenly give a negative optical rotation. We attribute this inaccuracy to the low level of enantioenrichment for these compounds. Nonetheless, the absolute configurations of the styrene oxides were determined by comparing the HPLC elution orders to authentic samples (i.e. $(R)$- and $(S)$-phenyloxirane/styrene oxide 21b) that were obtained from commercial suppliers (See Supplementary Figure 82). The chiral HPLC elution order for the enantiomers of the related epoxides on the same chiral column is assumed to be the same, i.e. $(R)$-22b and $(R)$-23b are the first eluted enantiomers, and $(S)$-22b and $(S)$-23b are the second eluted enantiomers.

Finally, the absolute configurations of the enantioenriched epoxides 24b and 25b were determined by comparison of the HPLC traces of these epoxides produced by Mn$_2$ to those produced by Jacobsen’s catalyst $(R,R)$-Mn$_{16}$. The latter catalyst has been reported to produce enantioenriched epoxides $(1S,6S)$-24b$^{57}$ and $(1aR,6aS)$-25b,$^{58}$ both of which were the second eluted enantiomers.
7. **Mn2** obtained via different route and the corresponding catalytic results

Supplementary Table 8. Catalytic results of **Mn2**, obtained via different synthesis routes, and enantioselective effects (See also Supplementary Figure 9 and 10).

| Entry | Catalyst                  | Conversion (%) | Yield (%) | e.r. (%:%) | e.e. (%) | Figure |
|-------|---------------------------|----------------|-----------|------------|----------|--------|
| 1a    | (S,P,Sa)-Mn2             | 97             | 84        | 73:27      | 46 (1aS,7bS) | S87 |
| 2b    | (S,M,Ra)-Mn2             | 95             | 89        | 16:84      | 68 (1aR,7bR) | S88 |
| 3c    | (R,M,Ra)-Mn2             | 98             | 89        | 28:72      | 44 (1aR,7bR) | S89 |
| 4d    | (R,P,Sa)-Mn2             | 93             | 81        | 82:18      | 64 (1aS,7bS) | S90 |

*S,(S,P,Sa)-Mn2 prepared via route c-d) in Supplementary Figure 9. b,(S,M,Ra)-Mn2 prepared via route c-d-e) in Supplementary Figure 9. c,(R,M,Ra)-Mn2 prepared via route h-i) in Supplementary Figure 10. d,(R,P,Sa)-Mn2 prepared via route h-i-j) in Supplementary Figure 10.*

Supplementary Figure 9. Preparation routes towards (S,M,Ra)-Mn2 and (S,P,Sa)-Mn2. Included are the catalytic performance of the isomeric catalysts prepared via different routes in the epoxidation of substrate 17a. Details of the catalytic results in blue are presented in Supplementary Table 7 and those in red are presented in Supplementary Table 8.
Supplementary Figure 10. Preparation routes towards \((R,P,S_a)-\text{Mn}_2\) and \((R,M,R_a)-\text{Mn}_2\). Included are the catalytic performance of the isomeric catalysts prepared via different routes in the epoxidation of substrate 17a. Details of the catalytic results in blue are presented in Supplementary Table 7 and those in red are presented in Supplementary Table 8.
8. Supporting references
S1. Shen, A. et al. Supporting ligand-assisted N-heterocyclic carbene palladium complexes: characterization, computation, and catalytic activity in Suzuki-Miyaura cross coupling between aryl and heteroaromatic chlorides and various boronic acids. *Tetrahedron Lett.* **57**, 2055–2058 (2016).

S2. Liao, S. & List, B. Asymmetric counteranion-directed transition-metal catalysis: enantioselective epoxidation of alkenes with manganese (III) salen phosphate complexes. *Angew. Chem. Int. Ed.* **49**, 628–631 (2010).

S3. Lu, B.-L. & Shi, M. Synthesis of functionalized polycyclic compounds: rhodium(I)-catalyzed intramolecular cycloaddition of yne and ene vinylidencyclopropanes. *Angew. Chem. Int. Ed.* **50**, 12027–12031 (2011).

S4. Dai, W. et al. Asymmetric epoxidation of alkenes catalyzed by a porphyrin-inspired manganese complex. *Org. Lett.* **15**, 4138-4141 (2013).

S5. Lee N. H., Muci, A. R. & Jacobsen E. N. Enantiomerically pure epoxychromans via asymmetric catalysis. *Tetrahedron Lett.* **32**, 5055–5058 (1991).

S6. Merten, C., Pollok, C. H., Liao, S. & List, B. Stereochemical communication within a chiral ion pair catalyst. *Angew. Chem. Int. Ed.* **54**, 8841–8845 (2015).

S7. Brandes, B. D. & Jacobsen, E. N. Highly enantioselective, catalytic epoxidation of trisubstituted olefins. *J. Org. Chem.* **59**, 4378–4380 (1994).

S8. Kürti, L., Blewett, M. M. & Corey, E. J. Origin of enantioselectivity in the Jacobsen epoxidation of olefins. *Org. Lett.* **11**, 4592–4595 (2009).
9. Copies of NMR spectra of new compounds and chiral HPLC results

Supplementary Figure 11. $^1$H NMR spectrum of compound 4 (500 MHz, CDCl$_3$, 298 K).

Supplementary Figure 12. $^{13}$C NMR spectrum of compound 4 (126 MHz, CDCl$_3$, 298 K).
Supplementary Figure 13. $^1$H NMR spectrum of compound 5 (500 MHz, CDCl$_3$, 298 K).

Supplementary Figure 14. $^{13}$C NMR spectrum of compound 5 (126 MHz, CDCl$_3$, 298 K).
Supplementary Figure 15. $^1$H NMR spectrum of compound 8 (500 MHz, CDCl$_3$, 298 K).

Supplementary Figure 16. $^{13}$C NMR spectrum of compound 8 (126 MHz, CDCl$_3$, 298 K).
Supplementary Figure 17. $^1$H NMR spectrum of compound 9 (500 MHz, CDCl$_3$, 298 K).

Supplementary Figure 18. $^{13}$C NMR spectrum of compound 9 (126 MHz, CDCl$_3$, 298 K).
Supplementary Figure 19. $^1$H NMR spectrum of compound 10 (500 MHz, CDCl$_3$, 298 K, >9:1 mixture of conformers).

Supplementary Figure 20. $^{13}$C NMR spectrum of compound 10 (126 MHz, CDCl$_3$, 298 K, >9:1 mixture of conformers).
Supplementary Figure 21. $^1$H NMR spectrum of compound 11 (500 MHz, CDCl$_3$, 298 K, 1:1 mixture of conformers).

Supplementary Figure 22. $^{13}$C NMR spectrum of compound 11 (126 MHz, CDCl$_3$, 298 K, 1:1 mixture of conformers).
Supplementary Figure 23. $^1$H NMR spectrum of compound 13 (500 MHz, CDCl$_3$, 298 K, >9:1 mixture of conformers).

Supplementary Figure 24. $^{13}$C NMR spectrum of compound 13 (126 MHz, CDCl$_3$, 298 K, >9:1 mixture of conformers).
Supplementary Figure 25. $^1$H NMR spectrum of compound 14 (500 MHz, CDCl$_3$, 298 K, 2:1 mixture of conformers).

Supplementary Figure 26. $^{13}$C NMR spectrum of compound 14 (126 MHz, CDCl$_3$, 298 K, 2:1 mixture of conformers).
Supplementary Figure 27. $^1$H NMR spectrum of compound 1 (500 MHz, $4 \times 10^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).

Supplementary Figure 28. $^{13}$C NMR spectrum of compound 1 (126 MHz, $4 \times 10^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).
Supplementary Figure 29. $^{31}$P NMR spectrum of compound 1 (202 MHz, 4 x 10$^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).

Supplementary Figure 30. $^1$H-$^1$H COSY NMR spectrum of compound 1 (500 MHz, 4 x 10$^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).
Supplementary Figure 31. $^1$H-$^1$H NOESY NMR spectrum of compound 1 (500 MHz, $4 \times 10^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).

Supplementary Figure 32. $^1$H-$^{13}$C HSQC NMR spectrum of compound 1 (500/126 MHz, $4 \times 10^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).
Supplementary Figure 33. $^1$H-$^{13}$C HMBC NMR spectrum of compound 1 (500/126 MHz, $4 \times 10^{-2}$ M in TFA/CDCl$_3$, 1:24, v/v, 298 K).
Supplementary Figure 34. $^1$H NMR spectrum of compound 17a.

Supplementary Figure 35. $^{13}$C NMR spectrum of compound 17a.
Supplementary Figure 36. $^1$H NMR spectrum of compound 18a.

Supplementary Figure 37. $^{13}$C NMR spectrum of compound 18a.
Supplementary Figure 38. $^1$H NMR spectrum of compound 19a.

Supplementary Figure 39. $^{13}$C NMR spectrum of compound 19a.
Supplementary Figure 40. $^1$H NMR spectrum of compound 20a.

Supplementary Figure 41. $^{13}$C NMR spectrum of compound 20a.
Supplementary Figure 42. $^1$H NMR spectrum of compound 17b.

Supplementary Figure 43. $^{13}$C NMR spectrum of compound 17b.
Supplementary Figure 44. $^1$H NMR spectrum of compound 18b.

Supplementary Figure 45. $^{13}$C NMR spectrum of compound 18b.
Supplementary Figure 46. $^1$H NMR spectrum of compound 19b.

Supplementary Figure 47. $^{13}$C NMR spectrum of compound 19b.
Supplementary Figure 48. $^1$H NMR spectrum of compound 20b.

Supplementary Figure 49. $^{13}$C NMR spectrum of compound 20b.
Supplementary Figure 50. $^1$H NMR spectrum of compound 21b.

Supplementary Figure 51. $^1$H NMR spectrum of compound 22b.
Supplementary Figure 52. $^{13}$C NMR spectrum of compound 22b.

Supplementary Figure 53. $^1$H NMR spectrum of compound 23b.
Supplementary Figure 54. $^{13}$C NMR spectrum of compound 23b.

Supplementary Figure 55. $^1$H NMR spectrum of compound 24b.
Supplementary Figure 56. $^{13}$C NMR spectrum of compound 24b.

Supplementary Figure 57. $^1$H NMR spectrum of compound 25b.
Supplementary Figure 58. $^{13}$C NMR spectrum of compound 25b.

Supplementary Figure 59. Chiral HPLC result of Table S2 Entry 2.
Supplementary Figure 60. Chiral HPLC result of Table S3 Entry 1.

Supplementary Figure 61. Chiral HPLC result of Table S3 Entry 2.
Supplementary Figure 62. Chiral HPLC result of Table S3 Entry 3.

Supplementary Figure 63. Chiral HPLC result of Table S3 Entry 4.
Supplementary Figure 64. Chiral HPLC result of Table S3 Entry 5.

Supplementary Figure 65. Chiral HPLC result of Table S4 Entry 1.
Supplementary Figure 66. Chiral HPLC result of Table S4 Entry 2.

Supplementary Figure 67. Chiral HPLC result of Table S4 Entry 3.
Supplementary Figure 68. Chiral HPLC result of Table S5 Entry 2.

Supplementary Figure 69. Chiral HPLC result of Table S5 Entry 3.
Supplementary Figure 70. Chiral HPLC result of Table S5 Entry 4.

Supplementary Figure 71. Chiral HPLC result of Table S7 Entry 6.
Supplementary Figure 72. Chiral HPLC result of Table S7 Entry 9.

Supplementary Figure 73. Chiral HPLC duplicated experiment result of Table S7, entry 2.
Supplementary Figure 74. Chiral HPLC triplicated experiment result of Table S7, entry 3.

Supplementary Figure 75. Chiral HPLC duplicated experiment result of Table S7, entry 5.
Supplementary Figure 76. Chiral HPLC duplicated experiment result of Table S7, entry 7.

Supplementary Figure 77. Chiral HPLC triplicated experiment result of Table S7, entry 8.
Supplementary Figure 7. Chiral HPLC duplicated experiment result of Table S7, entry 10.

| peak# | Ret. Time | Area     | Height | Area% | Height% |
|-------|-----------|----------|--------|-------|---------|
| 1     | 26.769    | 5663294  | 162831 | 27.508| 29.989  |
| 2     | 28.587    | 14924239 | 380136 | 72.492| 70.011  |
| Total |           | 20587533 | 542967 | 100.000| 100.000 |

Detector A Channel 2 215nm

![Graph of peak retention times and areas](image-url)
Supplementary Figure 79. Chiral HPLC catalytic result for 18a as substrate.
Supplementary Figure 80. Chiral HPLC catalytic result for 19a as substrate.
Supplementary Figure 81. Chiral HPLC catalytic result for 20a as substrate.
Supplementary Figure 82. Chiral HPLC catalytic result for 21a as substrate.
Supplementary Figure 83. Chiral HPLC catalytic result for 22a as substrate.
Supplementary Figure 84. Chiral HPLC catalytic result for 23a as substrate.
Supplementary Figure 85. Chiral HPLC catalytic result for 24a as substrate.
Supplementary Figure 86. Chiral HPLC catalytic result for 25a as substrate.
Supplementary Figure 87. Chiral HPLC catalytic result for Supplementary table 8 entry 1 with (S,P,S)-Mn2.

Supplementary Figure 88. Chiral HPLC catalytic result for Supplementary table 8 entry 2 with (S,M,R)-Mn2.

Supplementary Figure 89. Chiral HPLC catalytic result for Supplementary table 8 entry 3 with (R,M,R)-Mn2.
Supplementary Figure 90. Chiral HPLC catalytic result for Supplementary table 8 entry 4 with \((R,P,S)_2\)-Mn2.