Supporting Information for

Manganese-Catalyzed Asymmetric Hydrosilylation of Aryl Ketones

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1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Tetrahydrofuran (THF) and toluene were distilled from sodium benzenophenone ketyl prior to use.

Spectra were recorded on an Agilent 400 MHz or a Varian Mercury 400 MHz instrument. $^1$H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and $^{13}$C NMR chemical shifts were referenced to the solvent resonance. Data for $^1$H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm). Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) with a Dionex or Agilent chromatography [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), Phenomenex Lux 5u Cellulose-3 (0.46 x 25 cm), Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), Daicel CHIRALPAK AD-H (0.46 x 25 cm), Daicel CHIRALPAK OD-H (0.46 x 25 cm), CHIRALPAK IC (0.46 x 25 cm), and Lux 5u Amylose-2 (0.46 x 25 cm)] in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol I Polarimeter. Elemental analyses and high resolution mass spectrometry (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

X-ray Data Collection and Structure Determinations. Single crystals of complex $(S)$-3d suitable for single crystal X-ray diffraction were grown from the dichloromethane solution of $(S)$-3d. The single crystals of $(S)$-3d were mounted S4 under nitrogen atmosphere on a glass fiber, and data collection was performed on a Bruker APEX DUE diffractometer. The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS. Using Olex2,$^1$ the structures were solved with the ShelXS$^2$ structure
solution program using Direct Methods and refined with the XL\textsuperscript{2} refinement package using Least Squares minimisation.

2. Preparation of Mn complexes

(E)-6-(1-((2,6-diisopropylphenyl)imino)ethyl)picolinonitrile. To a solution of 6-acetylpicolinonitrile (2.00 g, 13.68 mmol) in toluene (35 mL) was added 2,6-diisopropylaniline (2.91 g, 16.42 mmol) and p-toluenesulfonic acid monohydrate (130 mg, 0.68 mmol). The reaction was set to reflux and the water was removed using a Dean-Stark apparatus. After 48 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with EtOAc/petroleum ether 30:1 (v/v) to afford the title compound as a yellow solid (4.05 g, 97%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 8.59\) (dd, \(J = 8.1, 0.9\) Hz, 1H), 7.94 (t, \(J = 7.9\) Hz, 1H), 7.79 (dd, \(J = 7.6, 1.0\) Hz, 1H), 7.19-7.15 (m, 2H), 7.11 (dd, \(J = 8.8, 6.2\) Hz, 1H), 2.71-2.61 (m, 2H), 2.20 (s, 3H), 1.14 (d, \(J = 6.9\) Hz, 6H), 1.13 (d, \(J = 6.8\) Hz, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 165.9, 157.7, 146.0, 137.6, 135.6, 132.8, 129.5, 124.6, 124.2, 123.2, 117.4, 28.4, 23.3, 22.9, 17.2\). These spectroscopic data agree with the reported data.\textsuperscript{3}

(E)-6-(1-((2,6-dibenzhydryl-4-methylphenyl)imino)ethyl)picolinonitrile. To a solution of 6-acetylpicolinonitrile (2.06 g, 14.1 mmol) in toluene (35 mL) was added 2,6-dibenzhydryl-4-methylaniline (6.82 g, 15.5 mmol) and p-toluenesulfonic acid monohydrate (135 mg, 0.71 mmol). The reaction was set to reflux and the water was removed using a Dean-Stark apparatus. After 48 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash
chromatography on silica gel eluting with EtOAc/petroleum ether 30:1 (v/v) to afford the title compound as a yellow solid (6.83 g, 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.0$ Hz, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.30 – 7.13 (m, 12H), 7.04 – 6.95 (m, 8H), 6.67 (s, 2H), 5.18 (s, 2H), 2.17 (s, 3H), 1.09 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.3, 157.3, 145.3, 143.4, 142.2, 137.1, 132.5, 132.1, 131.9, 129.7, 129.4, 129.3, 128.7, 128.4, 128.1, 126.4, 126.1, 124.5, 117.3, 52.2, 21.4, 16.6. These spectroscopic data agree with the reported data.

Preparation of (S)-Bn-IPO [(S)-1a]. To an oven-dried 100 mL two-necked flask fitted with a reflux condenser, (E)-6-(1-((2,6-diisopropylphenyl)imino)ethyl)picolinonitrile (1.20 g, 3.93 mmol) and zinc triflate (360 mg, 3.52 mmol) were added. The system was purged with argon and anhyd toluene (15 mL) was added. The solution was stirred during 5 min and a solution of L-Phenylalaninol (892 mg, 5.90 mmol) in anhydrous toluene (20 mL) was added. The reaction was set to reflux for 48 h. The system was allowed to cool, and the reaction was diluted with 20 mL of EtOAc, then washed with saturated aq. NaHCO$_3$ (3×15 mL) and brine (20 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated under vacuum. The residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:20 → 1:15) to give the title compound [(S)-1a] as a yellow solid (0.857 g, 50 %) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.52 (dd, $J = 7.9$, 1.0Hz, 1H, ary-H), 8.17 (dd, $J = 7.7$, 1.0Hz, 1H, ary-H), 7.91 (t, $J = 7.8$Hz, 1H, ary-H), 7.36-7.23 (m, 5H, ary-H), 7.18-7.15(m, 2H, ary-H), 7.10 (dd, $J=8.6$, 6.5Hz, 1H, ary-H), 4.74-4.65 (m, 1H, NCHCH$_2$O), 4.48 (t, $J = 9.0$Hz, 1H, NCHCH$_2$O), 4.28 (t, $J = 8.1$Hz, 1H, NCHCH$_2$O), 3.33 (dd, $J = 13.8$, 5.0Hz, 1H, PhCH$_2$), 2.82-2.68(m, 3H, PhCH$_2$ and CH(CH$_3$)$_2$), 2.29 (s, 3H, N=CCH$_3$), 1.14 (d, $J = 6.9$Hz, 12H,CH(CH$_3$)$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.8, 163.3, 156.4, 146.4, 146.0, 137.9, 137.2, 135.8, 129.4, 128.8, 126.8, 125.5, 123.8, 123.4, 123.1, 72.7, 68.4, 41.9, 28.4, 23.4, 23.0, 17.4. These spectroscopic data agree with the reported data.
Preparation of (S)-iPr-IPO [(S)-1b]. To an oven-dried 100 mL two-necked flask fitted with a reflux condenser, (E)-6-(1-((2,6-diisopropylphenyl)imino)ethyl)picolinonitrile (1.74 g, 5.70 mmol) and zinc triflate (104 mg, 0.29 mmol) were added. The system was purged with argon and anhyd toluene (30 mL) was added. The solution was stirred during 5 min and a solution of L-Valinol (882 mg, 8.55 mmol) anhydrous toluene (20 mL) was added. The reaction was set to reflux for 48 h. The system was allowed to cool, and the reaction was diluted with 30 mL of EtOAc, then washed with saturated aq. NaHCO₃ (3×15 mL) and brine (30 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:20 → 1:10) to give (S)-iPr-OIP [(S)-1b] (1.22 g, 55%) as pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ = 8.50 (d, J = 7.3 Hz, 1H, ary-H), 8.19 (d, J = 7.0 Hz, 1H, ary-H), 7.89 (t, J = 7.8 Hz, 1H, ary-H), 7.18-7.14 (m, 2H, ary-H), 7.09 (dd, J = 8.6, 6.5 Hz, 1H, ary-H), 4.50 (dd, J = 9.3, 8.2 Hz, 1H, NCH₂), 4.26 (t, J = 8.2 Hz, 1H, NCH₂), 4.23-4.15 (m, 1H, NCH₂), 2.77-2.67 (m, 2H, PhCH(CH₃)₂), 2.28 (s, 3H, N=CH₂), 1.98-1.86 (m, 1H, CH₂), 1.13 (d, J = 6.9 Hz, 12H, PhCH(CH₃)₂), 1.08 (d, J = 6.7 Hz, 3H, CHCH(CH₃)₂), 0.97 (d, J = 6.7 Hz, 3H, CHCH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 162.7, 156.3, 146.4, 146.2, 137.1, 135.8, 135.8, 125.5, 123.8, 123.2, 123.1, 73.0, 71.0, 33.0, 28.3, 23.4, 23.0, 19.3, 18.4, 17.4. These spectroscopic data agree with the reported data.³

Preparation of dibenzhydryl-(S)-iPr-IPO [(S)-2a]. To an oven-dried 100 mL two-necked flask fitted with a reflux condenser, (E)-6-(1-((2,6-dibenzhydryl-4-methylphenyl)imino)ethyl)picolinonitrile (1.0 g, 1.76
mmol) and zinc triflate (360 mg, 3.52 mmol) were added. The system was purged with argon and anhyd toluene (10 mL) was added. The solution was stirred during 5 min and a solution of L-Valinol (360 mg, 3.52 mmol) in anhydrous toluene (20 mL) was added. The reaction was set to reflux for 48 h. The system was allowed to cool, and the reaction was diluted with 20 mL of EtOAc, then washed with saturated aq. NaHCO₃ (3×15 mL) and brine (20 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:20 → 1:15) to give the title compound as a yellow solid [(S)-3a] (0.66 g, 58%).¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.05 (m, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.25 – 7.12 (m, 12H), 7.01 (d, J = 7.5 Hz, 8H), 6.68 (s, 2H), 5.25 (s, 2H), 4.56 – 4.50 (t, J = 8.2 Hz, 1H), 4.24 (t, J = 8.2 Hz, 1H), 4.21 – 4.14 (m, 1H), 2.17 (s, 3H), 1.43 (s, 3H), 1.09 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 168.97, 162.87, 155.96, 145.97, 145.84, 143.54, 143.51, 142.73, 142.66, 136.57, 132.15, 132.05, 131.65, 129.80, 129.77, 129.46, 128.63, 128.32, 128.29, 127.99, 126.21, 125.98, 125.21, 123.11, 122.85, 70.88, 52.04, 52.00, 32.90, 21.36, 19.14, 18.26, 17.03. Rotation: [α]D²⁸ = -47.33 (c = 0.42, CH₂Cl₂). Anal. Calcd. (C₄₆H₄₃N₃O): C, 84.50; H, 6.63; N, 6.43. Found: C, 84.58; H, 6.60; N, 6.43.

Preparation of dibenzhydryl-(S)-tBu-IPO [(S)-2b]. To an oven-dried 100 mL two-necked flask fitted with a reflux condenser, (E)-6-1-((2,6-dibenzhydryl-4-methylphenyl)imino)ethyl) picolinonitrile (1.0 g, 1.76 mmol) and zinc triflate (32 mg, 0.09 mmol) were added. The system was purged with argon and anhyd toluene (15 mL) was added. The solution was stirred during 5 min and a solution of L-tert-Leucinol (310 mg, 2.64 mmol) in anhydrous toluene (20 mL) was added. The reaction was set to reflux for 48 h. The system was allowed to cool, and the reaction was diluted with 20 mL of EtOAc, then washed with saturated aq.
NaHCO$_3$ (3×15 mL) and brine (20 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated under vacuum. The residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:20 → 1:15) to give the title compound as a yellow solid [(S)-2b] (525 mg, 45%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, $J$ = 7.6 Hz, 1H), 8.09 (d, $J$ = 7.9 Hz, 1H), 7.75 (t, $J$ = 7.8 Hz, 1H), 7.26 – 7.12 (m, 12H), 7.03 (d, $J$ = 6.9 Hz, 8H), 6.70 (s, 2H), 5.27 (s, 2H), 4.47 (t, $J$ = 9.5 Hz, 1H), 4.34 (t, $J$ = 8.4 Hz, 1H), 4.18 – 4.11 (m, 1H), 2.18 (s, 3H), 1.42 (s, 3H), 1.01 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.0, 162.8, 155.9, 145.9, 145.8, 143.5, 143.4, 142.7, 142.5, 136.5, 132.2, 132.0, 131.6, 129.8, 129.7, 129.4, 128.6, 128.3, 128.2, 127.9, 126.1, 125.9, 125.2, 123.0, 76.2, 69.4, 52.0, 51.9, 34.0, 25.9, 21.3, 17.0. These spectroscopic data agree with the reported data.  

**Preparation of [(S)-Bn-IPO]MnCl$_2$ [(S)-3a].** To a yellow solution of (S)-1a (260 mg, 0.66 mmol) in approximately 30 mL of THF, 179 mg (0.66 mmol) of MnCl$_2$(THF)$_2$ was added. The resulting mixture was stirred at 60 °C for 24 h. After that, it was filtered through a plug of Celite and the volatiles were removed in vacuo. The residue was washed with toluene (3 mL*5) to afford product (S)-3a as an orange solid (390 mg, 96 %). Anal. Calcd. for C$_{29}$H$_{33}$Cl$_2$MnN$_3$O: C, 61.60, H, 5.88, N, 7.43; Found: C, 61.72, H, 5.75, N, 7.33.

**Preparation of [(S)-iPr-IPO]MnCl$_2$ [(S)-3b].** This compound was prepared in a manner similar to (S)-3a with 178 mg (0.66 mmol) of (S)-1b, 179 mg of MnCl$_2$(THF)$_2$ (0.66 mmol) and approximately 30 mL of THF. This procedure yielded 330 mg (96%) of a orange solid identified as (S)-3b. Anal. Calcd. for C$_{46}$H$_{43}$Cl$_2$MnN$_3$O: C, 70.86, H, 5.56, N, 5.39; Found: C, 70.82, H, 5.55, N, 5.64.
Preparation of [dibenzydryl-(S)-iPr-IPO]MnCl₂ [(S)-3c]. This compound was prepared in a manner similar to (S)-3a with 430 mg (0.66 mmol) of (S)-2a, 178 mg of MnCl₂(THF)₂ (0.66 mmol) and approximately 20 mL of THF. This procedure yielded 460 mg (90%) of an orange solid identified as (S)-3c. Anal. Calcd. for C₄₇H₄₅Cl₂MnN₃O: C, 71.12, H, 5.71, N, 5.29; Found: C, 70.71, H, 5.56, N, 5.19.

Preparation of [dibenzydryl-(S)-tBu-IPO]MnCl₂ [(S)-3d]. This compound was prepared in a similar manner to (S)-3a with 162 mg (0.24 mmol) of (S)-2a, 65 mg of MnCl₂(THF)₂ (0.24 mmol) and approximately 20 mL of THF. This procedure yielded 178 mg (90%) of an orange solid identified as (S)-3d. Anal. Calcd. for C₄₇H₄₅Cl₂MnN₃O: C, 71.12, H, 5.71, N, 5.29; Found: C, 70.71, H, 5.56, N, 5.19.

3. Procedure for Hydrosilylation of Ketones

3.1 Optimization Studies (Table S1)
In a nitrogen-filled glovebox, to a solution of IPO manganese complex 3 (0.005mmol, 1 mol%) in solvent, a solution (1.0 M in THF) of NaBHEt₃ (10 μL, 0.01 mmol) was slowly added at 25 °C. After stirring for 1 min, silane (0.5 mmol, 1 equiv), ketone 4a or 4b (0.5mmol, 1 equiv) were sequentially added. The reaction mixture was stirred for 3 h at 25 °C and then was quenched by exposing the solution to air. Then MeOH (1.5 mL) and 10 % NaOH (2 mL) were added with vigorous stirring for 10 h. The resulting solution was extracted with EtOAc, washed with brine (15 mL) and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography.
Table S1. Optimization of reaction conditions

| entry | cat. | silane | conc. | solvent | yields (%) | e.r. |
|-------|------|--------|-------|---------|------------|------|
| 1a    | (S)-3a | PhSiH₃ | 0.5   | toluene | 94         | 76.5:23.5 |
| 2a    | (S)-3a | Ph₂SiH₂ | 0.5   | toluene | 91         | 71.5:28.5 |
| 3a    | (S)-3a | (EtO)₂SiH | 0.5 | toluene | 82         | 59.5:40.5 |
| 4a    | (S)-3a | DMF | 0.5 | toluene | /          | /    |
| 5     | (S)-3a | PhSiH₃ | 0.5   | toluene | 89         | 75:25  |
| 6     | (S)-3b | PhSiH₃ | 0.5   | toluene | 89         | 77.5:22.5 |
| 7     | (S)-3c | PhSiH₃ | 0.5   | toluene | 92         | 80.5:19.5 |
| 8     | (S)-3d | PhSiH₃ | 0.5   | Toluene | 98         | 88:12  |
| 9     | (S)-3b | PhSiH₃ | 0.5   | THF     | 60         | 50.5:49.5 |
| 10    | (S)-3b | PhSiH₃ | 0.5   | Ether   | 85         | 59.5:40.5 |
| 11    | (S)-3b | PhSiH₃ | 0.5   | Dioxane | 97         | 66.5:33.5 |
| 12    | (S)-3b | PhSiH₃ | 0.5   | Hexane  | 75         | 78.5:21.5 |
| 13    | (S)-3c | PhSiH₃ | 1.0   | Toluene | 90         | 82.5:17.5 |
| 14    | (S)-3c | PhSiH₃ | 0.5   | Toluene | 93         | 84.5:15.5 |
| 15    | (S)-3c | PhSiH₃ | 0.1   | Toluene | 97         | 88.5:11.5 |
| 16    | (S)-3d | PhSiH₃ | 0.1   | Toluene | 98         | 95.5:4.5 |

aReaction conditions: 4b (0.5 mmol), silane (1 equiv), (S)-3 (1 mol%), NaBHEt₃ (2 mol%) at 25 °C. Yields were determined by ¹H NMR spectroscopy using mesitylene as an internal standard. The e.r. values were determined by HPLC analysis. bThe concentration of ketone substrate 4. c4a was used as the substrate.

3.2 Representative procedure for hydrosilylation of ketones with manganese complex. In a nitrogen-filled glovebox, to a solution of (S)-3d (0.005mmol, 4.0 mg) in 2 mL of toluene, a solution (1.0 M in THF) of NaBHEt₃ (10 μL, 0.01 mmol) was slowly added at 25 °C. After stirring for 1 min, PhSiH₃ (54.1 mg, 0.5 mmol, 1 equiv), 1-(4-isobutylphenyl)ethane 4b (88.0 mg, 0.5mmol) were sequentially added. The reaction mixture stirred for 3 h at 25 °C and then was quenched by exposing the solution to air. Then, MeOH (1.5 mL) and 10 % NaOH (2 mL) were added with vigorous stirring for 10 h. The resulting solution was extracted with EtOAc, washed with brine (15 mL) and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography with
EtOAc/petroleum ether (1:20) to give the title compound 5b (88 mg, 98 %) as colorless oil.

3.3 Characterization of Products 5

(R)-1-(4-chlorophenyl)ethanol (5a). Colorless oil (76 mg, 97%). 93:7 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO₂/MeOH = 98/2, v = 2.5 mL·min⁻¹, λ = 214 nm, t (minor) = 8.661 min, t (major) = 9.190 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.29 (m, 4H), 4.86 (q, J = 6.4 Hz, 1H), 2.06 (br s, 1H), 1.46 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.2, 133.0, 128.6, 126.8, 69.7, 25.2. Rotation: [α]D₂₈ += +22.18 (c = 0.45, CH₂Cl₂). These spectroscopic data correspond to reported data.¹⁰

(R)-1-(4-isobutylphenyl)ethanol (5b). Colorless oil (88 mg, 98%). 95.5:4.5 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO₂/MeOH = 98/2, v = 2.5 mL·min⁻¹, λ = 214 nm, t (minor) = 6.753 min, t (major) = 6.425 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.87 (q, J = 6.4 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.83 (br s, 1H), 1.91 – 1.81 (m, 1H), 1.49 (d, J = 6.5 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 140.9, 129.2, 125.2, 70.2, 45.1, 30.2, 25.0, 22.3. Rotation: [α]D₂₈ += +30.57 (c = 0.63, CH₂Cl₂). These spectroscopic data correspond to reported data.⁵

(R)-1-(4-tertbutylphenyl)ethanol (5c). White solid (83 mg, 93%). 96:4 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), scCO₂/MeOH = 98/2, v = 3.0 mL·min⁻¹, λ = 214 nm, t (minor) = 5.207 min, t (major) = 5.619 min]. ¹H NMR (400 MHz, CDCl₃) δ 1.31 (s, 9H); 1.48 (d, 3H, J = 6.6Hz); 1.77 (br s, 1H); 4.92 (q, 1H, J =
6.6Hz); 7.30 (AA’BB’, 2H, J = 7.5Hz); 7.37 (AA’BB’, 2H, J = 7.5Hz). $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 24.9; 31.3; 34.5; 70.2; 125.2; 125.4; 142.8; 150.5. Rotation: $[\alpha]_D^{28} = +31.97$ (c = 0.62, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.  

(R)-1-(4-cyclohexylphenyl)ethanol (5d). White solid (99 mg, 97%). 94:6 e.r. [Phenomenex Lux 5u Cellulose-3 (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 9.27 min, t (major) = 9.98 min]. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.87 (q, J = 6.4 Hz, 1H), 2.52 – 2.47 (m, 1H), 1.88 – 1.85 (m, 4H), 1.76 (d, J = 12.2 Hz, 1H), 1.66 (br s, 1H), 1.50 (d, J = 6.4 Hz, 3H), 1.44 – 1.35 (m, 4H), 1.31 – 1.22 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.4, 143.2, 126.9, 125.4, 70.3, 44.2, 34.5, 26.9, 26.2, 24.9. Rotation: $[\alpha]_D^{28} = +31.39$ (c = 0.49, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data. 

(R)-1-(4-propylphenyl)ethanol (5e). Colorless oil (79 mg, 96%). 90:10 e.r. [Phenomenex Lux 5u Cellulose-3 (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 9.08 min, t (major) = 9.61 min]. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (br d, J = 8.0 Hz, 2H), 7.17 (br d, J = 8.0 Hz, 2H), 4.86 (q, J = 6.5 Hz, 1H), 2.59 (t, J = 7.5 Hz, 2H), 2.00 (br s, 1H), 1.65 (sex, J = 7.5 Hz, 2H), 1.49 (d, J = 6.5 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.0, 141.9, 128.5, 125.3, 70.2, 37.7, 25.0, 34.5, 13.8. Rotation: $[\alpha]_D^{28} = +32.05$ (c = 0.49, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data. 

(R)-1-(o-tolyl)ethanol (5f). Colorless oil (58 mg, 85%). 94:6 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 9.66 min, t (major) = 9.12 min]. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53
(d, \( J = 7.6 \) Hz, 1H), 7.27 – 7.14 (m, 3H), 5.13 (q, \( J = 6.3 \) Hz, 1H), 2.33 (s, 3H), 2.33 (s, 1H), 1.48 (d, \( J = 6.4 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 143.8, 134.2, 130.3, 127.1, 126.3, 124.4, 66.7, 23.9, 18.9. Rotation: \([\alpha]_D^{28} = +33.92 \) (c = 0.43, CH\(_2\)Cl\(_2\)).

These spectroscopic data correspond to reported data.\(^9\)

**(R)-1-(2,4,6-trimethylphenyl)ethanol (5g).** White solid (79 mg, 96%). 95:5 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), \( n \)-hexane/\( i \)-propanol = 90/10, \( \nu = 0.7 \) mL min\(^{-1}\), \( \lambda = 214 \) nm, t (minor) = 6.87 min, t (major) = 6.13 min]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.85 (s, 2H), 5.36 (q, \( J = 6.7 \) Hz, 1H), 2.44 (s, 6H), 2.29 (s, 3H), 2.00 (br s, 1H), 1.54 (d, \( J = 6.8 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 137.6, 136.4, 135.6, 130.1, 67.4, 21.6, 20.7, 20.5. Rotation: \([\alpha]_D^{28} = +36.13 \) (c = 0.53, CH\(_2\)Cl\(_2\)). These spectroscopic data correspond to reported data.\(^10\)

**(R)-1-(3-chlorophenyl)ethanol (5h).** Colorless oil (76 mg, 97%). 93:7 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO\(_2\) /MeOH = 99/1, \( \nu = 2.5 \) mL min\(^{-1}\), \( \lambda = 214 \) nm, t (minor) = 12.649 min, t (major) = 13.106 min]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.32 – 7.31 (m, 1H), 7.25 – 7.16 (m, 3H), 4.77 (q, \( J = 6.5 \) Hz, 1H), 2.69 (br s, 1H), 1.41 (d, \( J = 6.5 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 147.8, 134.3, 129.8, 127.5, 125.6, 123.5, 69.7, 25.1. Rotation: \([\alpha]_D^{28} = +40.45 \) (c = 0.55, CH\(_2\)Cl\(_2\)). These spectroscopic data correspond to reported data.\(^8\)

**(R)-1-(2-chlorophenyl)ethanol (5i).** Colorless oil (68 mg, 87%). 92:8 e.r. [Lux 5u Amylose-2 (0.46 x 25 cm), \( n \)-hexane/\( i \)-propanol = 98.5/1.5, \( \nu = 0.7 \) mL min\(^{-1}\), \( \lambda = 214 \) nm, t (minor) = 14.81 min, t (major) = 13.93 min]. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (d, \( J = 7.6 \) Hz, 1H), 7.32 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 5.28 (q, \( J = 6.4 \) Hz, 1H), 2.78 (br s, 1H), 1.47 (d, \( J = 6.4 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 143.0,
131.6, 129.4, 128.4, 127.2, 126.4, 67.0, 23.5. Rotation: $[\alpha]_D^{28} = +38.36$ (c = 0.58, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^8$

(R)-1-(4-methoxyphenyl)ethanol (5j). Colorless oil (75 mg, 99%). 90.5:9.5 e.r. [Daicel Chiralpak OD-H (0.46 x 25 cm), n-hexane/i-propanol = 95/5, $\nu$ = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 17.81 min, t (major) = 16.05 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.24 (m, 2H), 6.87 – 6.84 (m, 2H), 4.79 (q, $J$ = 6.4 Hz, 1H), 3.77 (s, 3H), 2.89 (br s, 1H), 1.43 (d, $J$ = 6.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.9, 138.0, 126.6, 113.8, 69.9, 55.3, 25.0. Rotation: $[\alpha]_D^{28} = +35.02$ (c = 0.45, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^8$

(R)-1-(3-methoxyphenyl)ethanol (5k). Colorless oil (74 mg, 98%). 96.5:3.5 e.r. [Daicel Chiralpak OD-H (0.46 x 25 cm), n-hexane/i-propanol = 95/5, $\nu$ = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 20.79 min, t (major) = 18.01 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.21 (m, 1H), 6.92 – 6.90 (m, 2H), 6.78 (ddd, $J$ = 8.2, 2.5, 1.0 Hz, 1H), 4.82 (q, $J$ = 6.4 Hz, 1H), 3.78 (s, 3H), 2.46 (br s, 1H), 1.45 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.7, 147.6, 129.5, 117.7, 112.9, 110.9, 70.2, 55.2, 25.1. Rotation: $[\alpha]_D^{28} = +32.84$ (c = 0.49, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^{14}$

(R)-1-(3-methoxyphenyl)ethanol (5l). Colorless oil (70 mg, 92%). 91.5:8.5 e.r. [Daicel Chiralpak OD-H (0.46 x 25 cm), n-hexane/i-propanol = 95/5, $\nu$ = 0.7 mL·min$^{-1}$, $\lambda$ = 214 nm, t (minor) = 13.89 min, t (major) = 14.82 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J$ = 7.2 Hz, 1H), 7.25 (t, $J$ = 7.8 Hz, 1H), 6.97 (t, $J$ = 7.4 Hz, 1H), 6.88 (d, $J$ = 8.2 Hz, 1H), 5.12 (q, $J$ = 6.5 Hz, 1H), 3.82 (s, 3H), 3.19 (br s, 1H), 1.49 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.5, 133.3, 128.2, 126.0,
120.7, 110.3, 66.9, 55.2, 23.1. Rotation: $[\alpha]_D^{28} = +17.93$ (c = 0.48, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^8$

(R)-1-(4-bromophenyl)ethanol (5m). Colorless oil (99 mg, 98%). 92.5:7.5 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO$_2$ /MeOH = 98/2, v = 3.0 mL·min$^{-1}$, $\lambda = 214$ nm, t (minor) = 9.422 min, t (major) = 10.011 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 4.76 (q, $J = 6.5$ Hz, 1H), 2.61 (s, 1H), 1.40 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.6, 131.4, 127.1, 120.9, 69.5, 25.1. Rotation: $[\alpha]_D^{28} = +27.19$ (c = 0.47, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^8$

(R)-1-(4-iodophenyl)ethanol (5n). White solid (120 mg, 97%). 90.5:9.5 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), scCO$_2$ /MeOH = 80/20, v = 0.7 mL·min$^{-1}$, $\lambda = 214$ nm, t (minor) = 6.57 min, t (major) = 6.14 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.3$ Hz, 2H), 7.11–7.06 (m, 2H), 4.80 (q, $J = 6.4$ Hz, 1H), 2.71 (br s, 1H), 1.34 (d, $J = 6.4$, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.4, 137.4, 127.4, 92.7, 69.7, 25.2. Rotation: $[\alpha]_D^{28} = +21.78$ (c = 0.69, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^8$

(R)-1-(benzo[d][1,3]dioxol-5-yl)ethanol (5o). Colorless oil (82 mg, 99%). 93:7 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), n-hexane/i-propanol = 80/20, v = 0.7 mL·min$^{-1}$, $\lambda = 214$ nm, t (minor) = 9.38 min, t (major) = 8.43 min]. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.81 (d, $J = 1.4$ Hz, 1H), 6.81–6.69 (m, 2H), 5.87 (s, 2H), 4.71 (q, $J = 6.4$ Hz, 1H), 3.00 (br s, 1H), 1.38 (d, $J = 6.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.6, 146.7, 140.1, 118.7, 108.0, 106.1, 100.9, 70.0, 25.1. Rotation: $[\alpha]_D^{28} = +32.35$ (c = 0.67, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^9$
(R)-1-phenylethanol (5p). Colorless oil (42 mg, 68%). 94:6 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL·min⁻¹, λ = 214 nm, t (minor) = 10.15 min, t (major) = 11.03 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.28 (m, 5H), 4.86 (q, J = 6.4 Hz, 1H), 2.39 (br s, 1H), 1.49 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 128.5, 127.4, 125.4, 70.3, 25.1. Rotation: [α]D²⁸ = +34.31 (c = 0.78, CH₂Cl₂). These spectroscopic data correspond to reported data.

(R)-1-([1,1'-biphenyl]-4-yl)ethanol (5q). White solid (97 mg, 98%). 94:6 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO₂ /MeOH = 96/4, v = 3.0 mL·min⁻¹, λ = 214 nm, t (minor) = 14.148 min, t (major) = 17.028 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.59 (m, 4H), 7.48 – 7.47 (m, 4H), 7.47 – 7.37 (m, 1H), 4.95 (q, J = 6.4, 1H), 2.14 (br s, 1H), 1.55 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 140.9, 140.4, 128.8, 127.3, 127.2, 125.9, 70.1, 25.2. Rotation: [α]D²⁸ = +34.42 (c = 0.50, CH₂Cl₂). These spectroscopic data correspond to reported data.

(R)-4-(1-hydroxyethyl)benzonitrile (5r). clear oil (57 mg, 76%). 66:34 e.r. [Daicel Chiralpak AD-H (0.46 x 25 cm), n-hexane/i-propanol = 98/2, v = 0.7 mL·min⁻¹, λ = 214 nm, t (minor) = 88.69 min, t (major) = 84.57 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 4.92 (q, J = 6.6 Hz, 1H), 2.53 (br, 1H), 1.46 (d, J = 6.6Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.5, 132.2, 126.1, 118.9, 110.5, 69.4, 25.3. Rotation: [α]D²⁸ = +21.27 (c = 0.2, CH₂Cl₂). These spectroscopic data correspond to reported data.
(R)-1-(naphthalen-2-yl)ethanol (5s). White solid (85 mg, 99%). 89.5:10.5 e.r. [Phenomenex Lux 5u Cellulose-3 (0.46 x 25 cm), n-hexane/i-propanol = 90/10, v = 0.7 mL·min⁻¹, λ = 214 nm, t (minor) = 17.06 min, t (major) = 21.16 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.82–7.76 (m, 4H), 7.50–7.47 (m, 3H), 5.00 (q, J = 6.3 Hz, 1H), 2.56 (br s, 1H), 1.56 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 133.3, 132.9, 128.3, 127.9, 127.7, 126.1, 125.8, 123.9, 123.8, 70.4, 25.1. Rotation: [α]D²⁸ = +31.39 (c = 0.46, CH₂Cl₂). These spectroscopic data correspond to reported data.⁸

(R)-1-phenylpropan-1-ol (5t). Colorless oil (34 mg, 50%). 94:6 e.r. [Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO₂ /MeOH = 98/2, v = 0.7 mL·min⁻¹, λ = 214 nm, t (minor) = 6.396 min, t (major) = 5.623 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.31 (m, 5H), 4.60 (t, J = 6.5 Hz, 1H), 3.22 (br s, 1H), 1.84–1.67 (m, 2H), 1.84 – 1.67 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.1, 128.4, 127.4, 126.0, 74.3, 41.3, 19.1, 14.0. Rotation: [α]D²⁸ = +27.53 (c = 0.70, CH₂Cl₂). These spectroscopic data correspond to reported data.⁸

(R)-1,2-diphenylethanol (5u). White solid (48 mg, 48%). 69.5:30.5 e.r. [Phenomenex Lux 5u Cellulose-4 (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL·min⁻¹, λ = 214 nm, t (minor) = 11.16 min, t (major) = 13.10 min]. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.20 (m, 10H), 4.90 – 4.87 (m, 1H), 3.05 – 3.02 (m, 2H), 2.20 (br s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.9, 138.1, 129.6, 128.5, 128.4, 127.6, 126.6, 125.9, 102.4, 75.3, 46.1. Rotation: [α]D²⁸ = +2.59 (c = 0.47, CH₂Cl₂). These spectroscopic data correspond to reported data.⁸

(R)-phenyl(cyclopropyl)methanol (5v). Colorless oil (132 mg, 89%). 71.5:28.5 e.r. [Phenomenex Lux 5u Cellulose-3 (0.46 x 25 cm), n-hexane/i-propanol = 90/10, v =
0.7 mL-min⁻¹, λ = 214 nm, t (minor) = 12.13 min, t (major) = 13.28 min. \(^1\)H NMR (400 MHz, CDCl₃) δ 0.36-0.70 (m, 4H), 1.18-1.30 (m, 1H), 3.20 (s, 1H), 3.96 (d, J = 8.4 Hz, 1H), 7.27-7.45 (m, 5H). \(^1\)C NMR (101 MHz, CDCl₃) δ 2.9, 3.8, 19.1, 78.2, 126.2, 127.4, 128.3, 144.1. Rotation: \([\alpha]_{D}^{28} = -12.89\) (c = 0.57, CH₂Cl₂). These spectroscopic data correspond to reported data.\(^{11}\)

\((R)-2,3\text{-dihydro-1H-inden-1-ol}\) (5w). White solid (62 mg, 93%). 84:16 e.r.

[CHIRALPAK IC (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL-min⁻¹, λ = 214 nm, t (minor) = 11.12 min, t (major) = 11.85 min]. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 6.2 Hz, 1H), 7.30 – 7.24 (m, 3H), 5.25 (t, J = 6.0 Hz, 1H), 3.13 – 3.01 (m, 1H), 2.89 – 2.78 (m, 1H), 2.57 – 2.44 (m, 1H), 1.96 – 1.88 (m, 1H). \(^1\)C NMR (101 MHz, CDCl₃) δ 144.8, 143.7, 128.1, 126.6, 124.7, 124.3, 76.3, 35.8, 29.6. Rotation: \([\alpha]_{D}^{28} = -12.83\) (c = 0.62, CH₂Cl₂). These spectroscopic data correspond to reported data.\(^{12}\)

\((R)-2,3,4\text{-trihydro-1H-quinoline-1-ol}\) (5x). White solid (68 mg, 92%). 86.5:13.5 e.r.

[CHIRALPAK IC (0.46 x 25 cm), n-hexane/i-propanol = 95/5, v = 0.7 mL-min⁻¹, λ = 214 nm, t (minor) = 10.75 min, t (major) = 11.86 min]. \(^1\)H NMR (400 MHz, CDCl₃) δ 1.74-2.06 (m, 5H), 2.56 (br s, 1H), 2.68-2.89 (m, 2H), 4.78 (t, J = 4.5 Hz, 1H), 7.10-7.14 (m, 1H), 7.18-7.24 (m, 2H), 7.41-7.46 (m, 5H). \(^1\)C NMR (101 MHz, CDCl₃) δ 18.9, 29.3, 32.4, 67.9, 125.8, 127.3, 128.4, 128.8, 137.0, 138.9. Rotation: \([\alpha]_{D}^{28} = -18.80\) (c = 0.46, CH₂Cl₂). These spectroscopic data correspond to reported data.\(^{11}\)

\((R)\)-phenyl(o-tolyl)methanol (5y). White solid (98 mg, 99%). 51.5:48.5 e.r.

[Phenomenex Lux 5u Cellulose-1 (0.46 x 25 cm), scCO₂ /MeOH = 96/4, v = 3.0 mL-min⁻¹, λ = 214 nm, t (minor) = 11.716 min, t (major) = 11.099 min]. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.53 (dd, J = 7.6, 1.4 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.30 – 7.20 (m, 3H), 7.16 (d, J = 7.3 Hz, 1H), 6.00 (d, J = 3.4 Hz, 1H), 2.29 (br s, 1H), 2.26 (s,
$^1$H NMR (101 MHz, CDCl$_3$) δ 142.8, 141.4, 135.3, 130.5, 128.5, 127.5, 127.1, 126.2, 126.1, 73.3, 19.5. Rotation: $[\alpha]_D^{28} = +0.29$ (c = 0.54, CH$_2$Cl$_2$). These spectroscopic data correspond to reported data.$^{12}$

4. Plausible Mechanism

A plausible mechanism is proposed based on our previous work and a precedent of Mn-catalyzed ketone hydrosilylation described by Trovitch and co-workers (Scheme S1).$^{[14,15]}$ Initially, the active catalytic species [IPO]MnH is generated in situ upon the addition of NaBHEt$_3$ to the precatalyst [IPO]MnCl$_2$. The resulting manganese hydride species is coordinated by a ketone. Subsequently, migratory insertion of ketone into Mn-H bond forms the alkoxide manganese complex, which undergoes $\sigma$-bond metathesis with silane to produce silyl ether and regenerate the [IPO]MnH species.

![Scheme 1S. Proposed Mechanism](image)

The insertion step is proposed to be the enantio-determing step (Scheme 2S). The ketone will approach Mn center from the face away from the bulky $^t$Bu group in the IPO ligand. Meanwhile, the large substituent of ketone will be oriented away from the sterically hindered imino aryl ring of the ligand, favoring the Si-face attack over Re-face attack. As a consequence, the secondary alcohol with $R$-configuration will be produced as the major stereoisomer, which is in accordance with the experimental
results. Considering the enantioselectivity is significantly affected by using different silane source, silane might be involved in the enantio-determining transition state by coordination with ketone.

Scheme 2S. Plausible Enantio-determining Transition States
5. Crystallographic Data of Complexes 3d

| Identification code             | mo_dm15549_0m  |
| Empirical formula              | C49 H49 Cl6 Mn N3 O |
| Formula weight                 | 963.55          |
| Temperature                    | 130 K           |
| Wavelength                     | 0.71073 Å       |
| Crystal system                 | Monoclinic      |
| Space group                    | P 1 2 1 1       |
| Unit cell dimensions           |                |
| a = 12.6498(7) Å              | a = 90°         |
| b = 21.1935(12) Å             | b = 108.4260(10)° |
| c = 18.1029(11) Å             | g = 90°         |
| Volume                         | 4604.5(5) Å³    |
| Z                              | 4               |
| Density (calculated)           | 1.390 Mg/m³     |
| Absorption coefficient         | 0.675 mm⁻¹      |
| F(000)                         | 1996            |
| Crystal size                   | 0.25 x 0.2 x 0.15 mm³ |
| Theta range for data collection| 1.697 to 30.582° |
| Index ranges                   | -18<=h<=18, -30<=k<=26, -25<=l<=25 |
| Reflections collected          | 46905           |
| Independent reflections        | 22883 [R(int) = 0.0360] |
| Completeness to theta = 26.000° | 100.0 %        |
| Absorption correction          | Semi-empirical from equivalents |
| Max. and min. transmission     | 0.7461 and 0.6355 |
| Refinement method              | Full-matrix least-squares on F² |
| Data / restraints / parameters  | 22883 / 8 / 1109 |
| Goodness-of-fit on F²          | 1.026           |
| Final R indices [I>2sigma(I)]  | R1 = 0.0462, wR2 = 0.0985 |
| R indices (all data)           | R1 = 0.0695, wR2 = 0.1096 |
| Absolute structure parameter   | 0.024(14)       |
| Extinction coefficient         | n/a             |
| Largest diff. peak and hole    | 0.565 and -0.603 e.Å⁻³ |
Selected Bond Length for Complex (S)-3d

| Selected Bond Length | Distance(Å) |
|----------------------|-------------|
| Mn1-N1               | 2.304(4)    |
| Mn1-N2               | 2.175(3)    |
| Mn1-N3               | 2.384(4)    |
| Mn1-Cl1              | 2.3148(14)  |
| Mn1-Cl2              | 2.3578(15)  |

Selected Bond Angles for Complex (S)-3d

| Selected Bond Angles | (deg)       |
|----------------------|-------------|
| N1-Mn1-N2            | 74.07(14)   |
| N2-Mn1-N3            | 69.49(13)   |
| N1-Mn1-N3            | 141.16(13)  |
| N2-Mn1-Cl1           | 136.66(12)  |
| N2-Mn1-Cl2           | 100.90(11)  |
| Cl1-Mn1-Cl2          | 121.94(6)   |
6. References

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7. NMR Spectra

Figure S1. $^1$H & $^{13}$C NMR spectrum of 5a
Figure S2. $^1$H & $^{13}$C NMR spectrum of 5b
Figure S3. $^1$H & $^{13}$C NMR spectrum of 5c
Figure S4. $^1$H & $^{13}$C NMR spectrum of 5d
Figure S5. $^1$H & $^{13}$C NMR spectrum of 5e
Figure S6. $^1$H & $^{13}$C NMR spectrum of 5f.
Figure S7. $^1$H & $^{13}$C NMR spectrum of 5g
Figure S8. $^1$H & $^{13}$C NMR spectrum of 5h
Figure S9. $^1$H & $^{13}$C NMR spectrum of 5i
Figure S10. $^{1}H$ & $^{13}C$ NMR spectrum of 5j
Figure S11. $^1$H & $^{13}$C NMR spectrum of 5k

![NMR Spectrum Image]

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Figure S12. $^1$H & $^{13}$C NMR spectrum of 51
Figure S13. $^1$H & $^{13}$C NMR spectrum of 5m
Figure S14. $^1$H & $^{13}$C NMR spectrum of 5n
Figure S15. $^1$H & $^{13}$C NMR spectrum of 50
Figure S16. $^1$H & $^{13}$C NMR spectrum of 5p
Figure S17. $^1$H & $^{13}$C NMR spectrum of 5q
Figure S18. $^{1}$H & $^{13}$C NMR spectrum of 5r
Figure S19. $^1$H & $^{13}$C NMR spectrum of 5s
Figure S20. $^1$H & $^{13}$C NMR spectrum of 5t
Figure S21. $^1$H & $^{13}$C NMR spectrum of 5u
Figure S22. $^1$H & $^{13}$C NMR spectrum of 5v
Figure S23. $^1$H & $^{13}$C NMR spectrum of 5w
Figure S24. $^1$H & $^{13}$C NMR spectrum of 5x
Figure S25. $^1$H & $^{13}$C NMR spectrum of 5y
6. HPLC and GC chromatographs

Figure S26. HPLC traces of racemic and enantioenriched 5a
Figure S27. HPLC traces of racemic and enantioenriched 5b
Figure S28. HPLC traces of racemic and enantioenriched 5c

Peak Results

| RT  | Area  | Height | % Area |
|-----|-------|--------|--------|
| 1   | 5.202 | 2342260| 325183 | 49.87  |
| 2   | 5.636 | 2354765| 321014 | 50.13  |

Peak Results

| RT  | Area  | Height | % Area |
|-----|-------|--------|--------|
| 1   | 5.207 | 191710 | 25076  | 4.13   |
| 2   | 5.619 | 4449294| 813232 | 95.87  |
Figure S29. HPLC traces of racemic and enantioenriched 5d
Figure S30. HPLC traces of racemic and enantioenriched 5e
Figure S31. HPLC traces of racemic and enantioenriched 5f

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 9.13 n.a.     |           | 443.555      | 76.793         | 49.79        | n.a.   | BM*  |
| 2   | 9.66 n.a.     |           | 418.115      | 77.396         | 50.21        | n.a.   | M*   |
|     |               |           |              | 154.159        | 100.00       | 0.000  |      |

Total:

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 9.12 n.a.     |           | 814.320      | 145.528        | 93.85        | n.a.   | BM*  |
| 2   | 9.66 n.a.     |           | 50.351       | 9.538          | 6.15         | n.a.   | M*   |
|     |               |           |              | 155.068        | 100.00       | 0.000  |      |

Total:
Figure S32. HPLC traces of racemic and enantioenriched 5g
Figure S33. HPLC traces of racemic and enantioenriched 5h
Figure S34. HPLC traces of racemic and enantioenriched 5i

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|-------------|------------|--------|------|
| 1   | 14.04        | n.a.      | 649.397    | 170.293     | 49.76      | n.a.   | BM   |
| 2   | 14.94        | n.a.      | 605.599    | 171.964     | 50.24      | n.a.   | M    |
| Total|              |           | 1254.966   | 342.257     | 100.00     | 0.000  |      |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|-------------|------------|--------|------|
| 1   | 13.93        | n.a.      | 529.007    | 137.469     | 91.81      | n.a.   | BM   |
| 2   | 14.81        | n.a.      | 43.139     | 12.258      | 8.19       | n.a.   | M    |
| Total|              |           | 572.146    | 149.727     | 100.00     | 0.000  |      |
Figure S35. HPLC traces of racemic and enantioenriched 5j
Figure S36. HPLC traces of racemic and enantioenriched 5k
**Figure S37.** HPLC traces of racemic and enantioenriched 5I

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 13.89        | n.a.      | 355.456    | 99.910       | 49.27      | n.a.   | BM * |
| 2   | 14.83        | n.a.      | 332.308    | 102.868      | 50.73      | n.a.   | M *  |
| **Total:** |             |           | 687.825    | 202.779      | 100.00     | 0.000  |      |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 13.89        | n.a.      | 43.770     | 12.520       | 8.57       | n.a.   | BM * |
| 2   | 14.82        | n.a.      | 425.730    | 134.557      | 91.43      | n.a.   | M *  |
| **Total:** |             |           | 469.500    | 147.167      | 100.00     | 0.000  |      |
Figure S38. HPLC traces of racemic and enantioenriched 5m
Figure S39. HPLC traces of racemic and enantioenriched 5n
Figure S40. HPLC traces of racemic and enantioenriched 5o
Figure S41. HPLC traces of racemic and enantioenriched 5p
Figure S42. HPLC traces of racemic and enantioenriched 5q
Figure S43. HPLC traces of racemic and enantioenriched 5r
Figure S44. HPLC traces of racemic and enantioenriched 5s
Figure S45. HPLC traces of racemic and enantioenriched 5t
Figure S46. HPLC traces of racemic and enantioenriched 5u

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type  |
|-----|--------------|-----------|------------|--------------|------------|--------|-------|
| 1   | 11.16        | n.a.      | 135.748    | 29.303       | 50.00      | n.a.   | BMB*  |
| 2   | 13.11        | n.a.      | 113.457    | 29.395       | 50.00      | n.a.   | BMB*  |
|     | **Total:**    |           | 249.206    | 58.798       | 100.00     | 0.000  |       |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type  |
|-----|--------------|-----------|------------|--------------|------------|--------|-------|
| 1   | 11.16        | n.a.      | 61.486     | 13.337       | 30.36      | n.a.   | MB*   |
| 2   | 13.10        | n.a.      | 118.057    | 30.598       | 69.64      | n.a.   | BMB*  |
|     | **Total:**    |           | 179.542    | 43.935       | 100.00     | 0.000  |       |
Figure S47. HPLC traces of racemic and enantioenriched 5v
Figure S48. HPLC traces of racemic and enantioenriched 5w
Figure S49. HPLC traces of racemic and enantioenriched 5x
Figure S50. HPLC traces of racemic and enantioenriched 5y