Supporting Information
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Supporting Information for:

Asymmetric Mukaiyama Aldol Reaction Catalyzed by $C_2$–Symmetric $N,N'$-Dioxide–Ni(II) Complex

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(A) General

1H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. 13C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on DAICEL CHIRALCEL AD-H/OJ-H/IB in comparison with the authentic racemates. Optical rotations were reported as follows: \([\alpha]_D^T\) (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. Glyoxal derivatives 1a-1k were synthesized according to the previously reported method.[1] Enolsilane 3a and 3b were prepared in accordance with literature methods.[2]

(B) General procedure for chiral N,N'-dioxide preparation

The N,N'-dioxide ligands L1-L7 were synthesized by the same procedure in the literature.[3] Ligand L5: white solid; \([\alpha]^{26}_D = -50.0\) (c 0.26 in CH2Cl2). 1H NMR (400 MHz, CDCl3): 1.19 (t, \(J = 7.6\) Hz, 12 H), 1.41-1.51 (m, 2 H), 1.69-1.73 (m, 2 H), 1.92-1.95 (m, 2 H), 2.14-2.18 (m, 4 H), 2.40-2.43 (m, 2 H), 2.54-2.60 (m, 8 H), 2.75-2.79 (m, 2 H), 2.95-3.01 (m, 2 H), 3.42-3.47 (m, 2 H), 3.59-3.68 (m, 6 H), 7.09-7.12 (m, ArH, 4 H), 7.18-7.20 (m, ArH, 2 H), 11.93 (s, NH, 2 H) ppm. 13C NMR (100 MHz, CDCl3): 14.8, 16.3, 20.3,
22.4, 25.3, 26.6, 64.8, 66.1, 76.4, 126.5, 127.6, 132.3, 140.5, 167.3 ppm. ESI-HRMS: calcd for C$_{35}$H$_{52}$N$_4$O$_4$ [M+Cl] 627.3677, found 627.3625.

Ligand L7: white solid; [α]$_{26}^D$ = -35.2 (c 0.29 in CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$): 1.17 (t, 12 H, $J = 7.6$ Hz), 2.49-2.70 (m, 16H), 2.82-2.86 (m, 2H), 3.39-3.42 (m, 2 H), 3.63-3.70 (m, 6 H), 3.82-3.87 (m, 2 H), 7.09-7.12 (m, ArH, 4 H), 7.17-7.21 (m, ArH, 2 H), 12.47 (s, NH, 2 H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 14.7, 20.2, 20.3, 25.3, 27.7, 64.6, 67.9, 77.2, 126.5, 127.5, 132.3, 140.5, 165.9 ppm. ESI-HRMS: calcd for C$_{33}$H$_{48}$N$_4$O$_4$ [M+H$^+$] 565.3754, found 565.3763.

(C) General procedure for the catalytic enantioselective Mukaiyama aldol reaction

Ligand L7 (0.01 mmol) and Ni(BF$_4$)$_2$·6H$_2$O (0.01 mmol) were dissolved in 0.5 mL of CH$_2$Cl$_2$ and stirred at 30 °C for 1 h. Then the solvent was removed and glyoxal derivative 1 (0.1 mmol) was added. After adding CH$_2$Cl$_2$ (1.0 mL) and enolsilane 3 (0.15 mmol), the mixture was stirred at 30 °C for 24 h under N$_2$ atmosphere. Then, THF (2.0 mL) and 1 N HCl (1.0 mL) were added to the reaction mixture. After stirring at room temperature for 30 min, this solution was poured into a separatory funnel and diluted with Et$_2$O (5.0 mL) and H$_2$O (1.0 mL). After mixing, the aqueous layer was discarded and the ether layer was washed with saturated aqueous NaHCO$_3$ (5.0 mL) and brine (5.0 mL). The resulting ether layer was dried over anhydrous MgSO$_4$, and concentrated in vacuo. The crude product was chromatographed on silica gel to give the desired adduct.
(D) The analytical and spectral characterization data of aldol reaction products

2-hydroxy-1,4-diphenylbutane-1,4-dione (5a)

(C\textsubscript{16}H\textsubscript{14}O\textsubscript{3}) a white solid; 94% yield, 92% ee. \(\alpha_D^{25} = +11.9\) (c 0.454 in CH\textsubscript{2}Cl\textsubscript{2}) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/\(n\)-hexane = 20/80, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: 18.6 min (minor) and 20.5 min (major); \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) 3.37-3.49 (m, 2H), 4.04 (d, \(J = 6.0\) Hz, 1H), 5.68-5.73 (m, 1H), 7.46-7.55 (m, 4H), 7.58-7.66 (m, 2H), 7.95-8.01 (m, 4H) ppm.
2-hydroxy-4-phenyl-1-o-tolylbutane-1,4-dione (5b)

(C$_{17}$H$_{16}$O$_{3}$) a colourless viscous liquid; 88% yield, 92% ee. $[\alpha]_D^{25} = +6.7$ (c 0.420 in CH$_2$Cl$_2$) HPLC DAICEL CHIRALCEL OJ-H 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, $\lambda$ = 254 nm, retention time: 23.1 min (minor) and 24.8 min (major); $^1$H NMR (400 MHz, CDCl$_3$) 2.42 (s, 3H), 3.37-3.40 (m, 2H), 4.02 (d, $J = 6.0$ Hz, 1H), 5.65-5.69 (m, 1H), 7.36-7.47 (m, 4H), 7.55-7.59 (m, 1H), 7.50-7.80 (m, 2H), 7.93-7.95 (m, 2H) ppm.
2-hydroxy-4-phenyl-1-m-tolylbutane-1,4-dione (5c)

\[(\text{C}_{17}\text{H}_{16}\text{O}_3)\] a colourless viscous liquid; 95% yield, 93% ee. \( [\alpha]_D^{25} = +10.5 \) (c 0.420 in \( \text{CH}_2\text{Cl}_2 \))

HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, \( \lambda = 254 \text{ nm} \), retention time: 13.9 min (minor) and 14.9 min (major);

\(^1\)H NMR (400 MHz, CDCl\(_3\))

2.57 (s, 3H), 3.30-3.50 (m, 2H), 4.06 (d, \( J = 8.0 \text{ Hz} \), 1H), 5.45-5.49 (m, 1H), 7.25-7.31 (m, 2H), 7.39-7.45 (m, 1H), 7.54-7.61 (m, 2H), 7.91-7.95 (m, 2H) ppm.
2-hydroxy-4-phenyl-1-p-tolylbutane-1,4-dione (5d)

(C_{17}H_{16}O_3) a white solid; 65% yield, 90% ee. [\alpha]_D^{25} = +2.9 (c 0.348 in CH_2Cl_2) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, \lambda = 254 nm, retention time: 26.2 min (minor) and 27.8 min (major); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) 2.42 (s, 3H), 3.31-3.44 (m, 2H), 4.03 (d, J = 6.0 Hz, 1H), 5.65-5.69 (m, 1H), 7.26-7.30 (m, 2H), 7.43-7.47 (m, 2H), 7.55-7.59 (m, 1H), 7.88-7.95 (m, 4H) ppm.

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2-hydroxy-1-(3-methoxyphenyl)-4-phenylbutane-1,4-dione (5e)

\((\text{C}_{17}\text{H}_{16}\text{O}_4)\) a colourless viscous liquid; 74% yield, 93% ee. \([\alpha]_D^{25} = +24.3\ (c\ 0.230\ \text{in CH}_2\text{Cl}_2)\) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, \(\lambda = 254\ \text{nm},\) retention time: 22.8 min (minor) and 25.5 min (major); \(^1\)H NMR (400 MHz, CDCl\(_3\)) 3.40-3.44 (m, 2H), 3.86 (s, 3H), 4.01 (d, \(J = 6.0\ \text{Hz},\) 1H), 5.63-5.68 (m, 1H), 7.14-7.17 (m, 1H), 7.14-7.17 (m, 1H), 7.38-7.47 (m, 3H), 7.52-7.59 (m, 3H), 7.91-7.94 (m, 2H) ppm.

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1-(3-chlorophenyl)-2-hydroxy-4-phenylbutane-1,4-dione (5f)

(C_{16}H_{13}ClO_{3}) a white solid; 74% yield, 93% ee. [\alpha]_{D}^{25} = +13.7 (c 0.280 in CH_{2}Cl_{2}) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, \lambda = 254 nm, retention time: 15.4 min (minor) and 16.9 min (major); H NMR (400 MHz, CDCl_{3}) 3.39-3.50 (m, 2H), 4.01 (d, J = 5.2 Hz, 1H), 5.54-5.57 (m, 1H), 7.41-7.51 (m, 3H), 7.56-7.61 (m, 2H), 7.86-7.89 (m, 1H), 7.93-8.00 (m, 3H) ppm.
1-(4-chlorophenyl)-2-hydroxy-4-phenylbutane-1,4-dione (5g)

\((\text{C}_{16}\text{H}_{13}\text{ClO}_3)\) a white solid; 70% yield, 91% ee. \(\left[\alpha\right]_D^{25} = +2.0\) (c 0.300 in CH₂Cl₂) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: 15.4 min (minor) and 17.2 min (major); \(^1\)H NMR (400 MHz, CDCl₃) 3.35-3.49 (m, 2H), 4.02 (d, \(J = 6.0\) Hz, 1H), 5.57-5.60 (m, 1H), 7.42-7.53 (m, 4H), 7.56-7.61 (m, 1H), 7.93-8.03 (m, 4H) ppm.

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1-(4-fluorophenyl)-2-hydroxy-4-phenylbutane-1,4-dione (5h)

(C_{16}H_{13}FO_3) a white solid; 85% yield, 92% ee. [α]_{D}^{25} = +20.2 (c 0.386 in CH_{2}Cl_{2}) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.8 min (minor) and 17.5 min (major); ^1H NMR (400 MHz, CDCl_{3}) 3.34-3.49 (m, 2H), 4.02 (d, J = 6.0 Hz, 1H), 5.60-5.63 (m, 1H), 7.15-7.26 (m, 2H), 7.45-7.49 (m, 2H), 7.53-7.59 (m, 1H), 7.93-7.96 (m, 2H), 8.04-8.08 (m, 2H) ppm.

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1-(4-bromophenyl)-2-hydroxy-4-phenylbutane-1,4-dione (5i)

(C\textsubscript{16}H\textsubscript{13}BrO\textsubscript{3}) a white solid; 77% yield, 95% ee. [\alpha]\textsubscript{D}\textsuperscript{25} = -1.7 (c 0.460 in CH\textsubscript{2}Cl\textsubscript{2}) HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 20/80, flow rate = 1.0 mL/min, \(\lambda = 254\) nm, retention time: 17.2 min (minor) and 19.4 min (major); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) 3.35-3.50 (m, 2H), 4.01 (d, \(J = 6.0\) Hz, 1H), 5.54-5.59 (m, 1H), 7.44-7.48 (m, 2H), 7.56-7.58 (m, 1H), 7.59-7.61 (m, 2H), 7.86-7.89 (m, 2H), 7.90-7.95 (m, 2H) ppm.

The absolute configuration was determined by the comparison of HPLC retention time and the optical rotation.\textsuperscript{[4]}
1-(furan-2-yl)-2-hydroxy-4-phenylbutane-1,4-dione (5j)

\[
\text{(C}_{14}\text{H}_{12}\text{O}_{4}) \quad \text{a white solid; 63% yield, 91% ee. } [\alpha]_D^{29} = +2.7 \ (c \ 0.146 \text{ in CH}_2\text{Cl}_2) \\
\text{HPLC DAICEL CHIRALCEL OJ-H, 2-propanol/n-hexane = 15/85, flow rate = 1.0 mL/min, } \lambda = 254 \text{ nm, retention time: } 36.1 \text{ min (minor) and 39.7 min (major); } ^1\text{H NMR (400 MHz, CDCl}_3\text{) 3.46-3.60 (m, 2H), 3.90 (d, } J = 6.0 \text{ Hz, 1H), 5.30-5.34 (m, 1H), 6.59-6.60 (m, 1H), 7.45-7.50 (m, 3H), 7.56-7.63 (m, 2H), 7.96-7.98 (m, 2H) ppm.}
\]
(S) 2-Hydroxy-4-oxo-4-phenyl-butyric acid ethyl ester (5k)

(C_{12}H_{14}O_4) a slightly yellow liquid; 93% yield, 94% ee. [α]_D^{29} = +5.3 (c 0.412 in CH_2Cl_2), [α]_D^{29} = -7.3 (c 0.289 in EtOH) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/n-hexane = 20/80, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 19.3 min (major) and 21.4 min (minor); ^1H NMR (400 MHz, CDCl_3) 1.25-1.31 (m, 3H), 3.36 (s, 1H), 3.43-3.50 (dd, J = 17.6, 4.0Hz, 1H), 3.50-3.57 (dd, J = 17.6, 6.0 Hz, 1H), 4.24-4.30 (m, 2H), 4.65-4.67 (m, 1H), 7.46-7.50 (m, 2H), 7.57-7.60 (m, 1H), 7.94-7.97 (m, 2H) ppm.

The absolute configuration was determined by the comparison of HPLC retention time and the optical rotation.\[^{[5]}\]
4-(4-chlorophenyl)-2-hydroxy-1-phenylbutane-1,4-dione (5l)

(C_{16}H_{13}ClO_3) a white solid; 67% yield, 92% ee. [α]_D^{25} = +2.4 (c 0.340 in CHCl_3). HPLC DAICEL CHIRALCEL IB, 2-propanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.1 min (minor) and 15.2 min (major); ^1H NMR (400 MHz, CDCl_3) 3.32-3.44 (m, 2H), 4.03 (d, J = 6.0 Hz, 1H), 5.66-5.70 (m, 1H), 7.44-7.46 (m, 2H), 7.52-7.56 (m, 2H), 7.62-7.68 (m, 1H), 7.89-7.92 (m, 2H), 8.00-8.02 (m, 2H) ppm.
(E) Copies of NMR spectra for the catalysts.
(F) References