Supporting Information for

Highly Active Chiral Phosphoramide-Zn(II) Complexes as Conjugate Acid–Base Catalysts for Enantioselective Organozinc Addition to Ketones

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1. General methods: $^1$H NMR spectra were measured on a Varian Mercury-300 (300 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the TM scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. $^{13}$C NMR spectra were measured on Varian Mercury-300 (75 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.10 ppm). $^{31}$P NMR spectra were measured on a Varian Mercury-300 (121 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($\text{H}_3\text{PO}_4$ at 0 ppm). IR spectra were determined by a FT-IR spectrometer. All experiments were carried out under an atmosphere of dry nitrogen. For thin-layer chromatography (TLC) analysis throughout this work, Merck TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. 37560). Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO$_4$ and phosphomolybdic acid. All dry solvents and reagents were obtained from commercial source and were distilled before use.

2. Representative procedure for preparing chiral ligand (1b)

\[
\begin{align*}
\text{HO} & \text{HN-Boc} \\
\text{O} & \text{CH}_2\text{Cl}_2, \text{rt, 24 h} \\
& \text{DCC (1.1 equiv)} \\
& \text{HOBt (1.1 equiv)} \\
& \text{pyrrolidine (2.1 equiv)} \\
& \text{S1} \\
& \rightarrow \\
\text{HN-Boc} & \text{O} \\
\text{CH}_2\text{Cl}_2, \text{rt, 24 h} \\
& \text{AcCl, MeOH, 0 °C, 5 h} \\
& \rightarrow \\
& \text{LiAlH}_4 (10 \text{ equiv}) \\
& \text{THF, reflux, 48 h} \\
\text{S2} & \rightarrow \\
\text{NH}_2 & \text{NH} \\
\text{O} & \text{CH}_2\text{Cl}_2, \text{rt, 3 h} \\
& \text{Ph}_2\text{P(=O)Cl (1.1 equiv)} \\
& \text{Et}_3\text{N (2.1 equiv)} \\
& \text{S3} \\
& \rightarrow \\
& \text{HN-} \text{PPh}_2 \\
\text{1b} & \text{rt} \\
\end{align*}
\]

The 1st. step of Eq. 1: To a solution of S1 (20 mmol) in dry CH$_2$Cl$_2$ (100 mL) was added...
N,N'-dicyclohexylcarbodiimide (DCC) (4.54 g, 22 mmol) and 1-hydroxybenzotriazole (HOBt) (2.97g, 22 mmol) and pyrrolidine (2.99 g, 42 mmol) at 0 °C. After being stirred for 15 min at the same temperature, the reaction mixture was allowed to warm to ambient temperature and was stirred for 24 h. The reaction was quenched with 10 % citric acid (20 mL). The mixture was stirred for 10 min with a formation of white solid. The white solid was filtered and the filtrate was extracted with CHCl₃. The combined organics were washed with 10 % citric acid, saturated NaHCO₃, and brine. The organic layers were dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was purified by neutral column chromatography on silica gel using hexane–EtOAc (v/v = 3/1–1/1) as eluent to give S2 (82% yield, 4.43 g).

\[
(\text{S)-tert]-butyl~3\text{-methyl-1-oxo-1-(pyrrolidin-1-yl)butan-2-ylcarbamate}\ (\text{S2}):}\ 
\]

\[
\text{1H NMR (300 MHz, CDCl}_3) \delta 0.93 (d, J = 10.5 Hz, 3H), 0.96 (d, J = 10.8 Hz, 3H), 1.43 (s, 9H), 1.80-2.04 (m, 5H), 3.10-3.60 (m, 3H), 3.68 (m, 1H), 4.25 (t, J = 8.7 Hz, 1H), 5.27 (d, J = 8.7 Hz, 1H).
\]

\[
\text{13C NMR (75 MHz, CDCl}_3) \delta 17.5, 19.5, 24.2, 26.0, 28.4, 31.5, 45.8, 46.7, 57.0, 79.3, 155.9, 170.7.
\]

IR (KBr) 3291, 2971, 2874, 1708, 1637, 1499, 1443, 1250, 1171 cm⁻¹. HRMS calcd for C₁₄H₂₇N₂O₃ [M+H]⁺ 271.2022, found 271.2024.

**The 2nd. step Eq. 1:** To a solution of S2 (1.35 g, 5 mmol) in MeOH (50 mL) was added dropwise acetyl chloride (5 mL) at 0 °C. After being stirred at 0 °C for 5 h, the reaction mixture was allowed to warm to ambient temperature, and was stirred for 1 h, and then the solution was concentrated in vacuo. Resultant product in THF (10 mL) was added via cannula to the 25 mL of THF solution with lithium aluminum hydride (1.89 g, 50 mmol) at 0 °C. After being stirred at the same temperature for 30 min, the reaction mixture was allowed to reflux and was stirred at that temperature for 48 h. Then, the reaction was quenched with Na₂SO₄ (2.5 g) and water (4 mL) with vigorous stirring at 0 °C for 30 min. The white–pale gray suspension was filtered and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on Cromatorex® NH-DM1020 using hexane–EtOAc (v/v = 3/1–1/1) as eluent to give the S3 (61% yield, 0.476 g).

\[
(\text{S)-3-methyl-1-(pyrrolidin-1-yl)butan-2-amine}\ (\text{S3}):}\ 
\]

\[
\text{1H NMR (300 MHz, CDCl}_3) \delta 0.90 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 1.30-1.70 (br, 2H), 1.56 (m, 1H), 1.70-1.80 (m, 4H), 2.23 (dd, J = 11.4, 3.3 Hz, 1H), 2.30-2.52 (m, 3H), 2.52-2.63 (m, 2H), 2.67 (m, 1H).
\]

\[
\text{13C}
\]
NMR (75 MHz, CDCl$_3$) $\delta$ 17.8, 19.4, 23.5, 32.2, 54.4, 55.0, 61.0. IR (film) 3303, 2958, 2928, 2786, 1714, 1463 cm$^{-1}$. HRMS calcd for C$_9$H$_{21}$N$_2$ [M+H]$^+$ 157.1705, found 157.1706.

The 3rd. step Eq. 1: To a solution of S$_3$ (312 mg, 2 mmol) in THF (5 mL) was added Et$_3$N (0.59 mL, 4.2 mmol) at room temperature. Diphenylphosphinic chloride (520 mg, 2.2 mmol) in THF (5 mL) was added via cannula to the solution at 0 °C. After being stirred for 15 min at 0 °C, the reaction mixture was allowed to warm to ambient temperature and stirred for 3 h. The resulting mixture was cooled in ice bath, and diluted with CHCl$_3$ and water. The product was extracted with CHCl$_3$ and combined organic layer was washed by brine. The combined extracts were dried over MgSO$_4$ and filtered and concentrated in vacuo. The crude product was purified by column chromatography on Cromatorex® NH-DM1020 using hexane–EtOAc as eluent (v/v = 3/1–1/1) to give the corresponding phosphoramide 1b (72% yield, 0.513 g).

![Diagram of (S)-N-(1-(Dimethylamino)-3-methylbutan-2-yl) diphenylphosphinic amide (1a):](image)

1H NMR (300 MHz, CDCl$_3$) $\delta$ 0.82 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.9$ Hz, 3H), 1.98 (m, 1H), 2.15 (s, 6H), 2.27 (m, 1H), 2.38 (m, 1H), 3.14 (m, 1H), 3.28 (m, 1H), 7.35–7.54 (m, 6H), 7.80–8.20 (m, 4H).

13C NMR (75 MHz, CDCl$_3$) $\delta$ 17.0, 18.1, 29.7, 45.7, 61.3 (d, $J = 5.7$ Hz), 128.2 (d, $J = 12.6$ Hz), 128.3 (d, $J = 12.0$ Hz), 131.5 (d, $J = 2.8$ Hz), 132.0 (d, $J = 9.8$ Hz), 132.1 (d, $J = 9.2$ Hz), 133.3 (d, $J = 126.1$ Hz), 133.4 (d, $J = 130.1$ Hz). 31P NMR (121 MHz, CDCl$_3$) $\delta$ 22.7. IR (KBr) 3208, 3056, 2959, 2216, 1737, 1462, 1438, 1193, 1121, 1044 cm$^{-1}$. [$_{\alpha}$]$_D^{20}$ = −6.0 (c 1.00, CHCl$_3$). HRMS calcd for C$_{19}$H$_{28}$N$_2$OP [M+H]$^+$ 331.1939, found 331.1937.

![Diagram of (S)-N-(3-Methyl-1-(1-pyrrolidinyl)-2-butanyl) diphenylphosphinic amide (1b):](image)

1H NMR (300 MHz, CDCl$_3$) $\delta$ 0.84 (d, $J = 6.3$ Hz, 3H), 0.91 (d, $J = 6.3$ Hz, 3H), 1.69 (m, 4H), 1.99 (m, 1H), 2.30–2.55 (m, 5H), 2.59 (dd, $J = 12.6$, 7.8 Hz, 1H), 3.15 (m, 1H), 3.27 (m, 1H), 7.38–7.50 (m, 6H), 7.85–7.95 (m, 4H). 13C NMR (75 MHz, CDCl$_3$) $\delta$ 17.5, 18.1, 23.6, 30.3, 54.3, 55.3, 57.9 (d, $J = 5.7$ Hz), 128.3 (d, $J = 12.0$ Hz), 131.5 (d, $J = 2.8$ Hz), 131.6 (d, $J = 2.3$ Hz), 132.1 (d, $J = 9.8$ Hz), 132.2 (d, $J = 9.2$ Hz), 133.6 (d, $J = 124.3$ Hz), 133.7 (d, $J = 129.5$ Hz). 31P NMR (121 MHz, CDCl$_3$) $\delta$ 22.8. IR (KBr) 3158, 2957, 2777, 1590, 1458, 1354, 1283, 1179, 1107, 1049 cm$^{-1}$. [$_{\alpha}$]$_D^{20}$ = −9.2 (c 1.00, THF). HRMS calcd for C$_{21}$H$_{36}$N$_2$OP [M+H]$^+$ 357.2096, found 357.2095.
was determined by GC or HPLC on chiral column. The combined extracts were dried over MgSO₄. The mixture was diluted pyrex Schlenk tube was charged with diphenylzinc (0.40 mmol) was added. The resulting mixture was stirred for 30 min, and then keto (2) (0.20 mmol) was added. The resulting mixture was stirred at room temperature for 8–24 h by monitoring with TLC. After hydrolysis with 10 mL of sat. NH₄Cl aqueous solution, the product was extracted with ether (10 mL × 3) and washed by brine (10 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the crude product was purified by neutral silica gel column chromatography (eluent: hexane/ EtOAc = 20/1 to 1/2), to give the desired products (3). The enantiomeric purity was determined by GC or HPLC on chiral column.

(S)-N-(3-Methyl-1-(1-piperidinyl)2-butyl) diphenylphosphinic amide (1c): ¹H NMR (300 MHz, CDCl₃) δ 0.81 (d, J = 6.3 Hz, 3H), 0.88 (d, J = 6.3 Hz, 3H), 1.37–1.43 (m, 2H), 1.46–1.55 (m, 4H), 1.97 (m, 1H), 2.20–2.50 (m, 6H), 3.20 (m, 1H), 3.50 (m, 1H), 7.38–7.52 (m, 6H), 7.84–8.00 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 17.5, 17.7, 24.4, 26.1, 30.4, 53.4, 54.9, 60.2 (d, J = 6.9 Hz), 128.2 (d, J = 12.7 Hz), 128.3 (d, J = 12.6 Hz), 131.4 (d, J = 2.2 Hz), 131.5 (d, J = 2.8 Hz), 132.0 (d, J = 9.1 Hz), 132.1 (d, J = 8.6 Hz), 133.5 (d, J = 125.5 Hz), 133.8 (d, J = 130.1 Hz). ³¹P NMR (121 MHz, CDCl₃) δ 22.8. IR (KBr) 3159, 2938, 2851, 1591, 1536, 1382, 1281, 1181, 1108, 1036 cm⁻¹. [α]D²⁰ = +18.0 (c 1.00, CHCl₃). HRMS calcd for C₂₂H₃₂N₂OP [M+H]⁺ 371.2252, found 371.2252.

(S)-N-(3-methyl-1-(pyrrolidin-1-yl)butan-2-yl)-P₂P-di(naphthalen-1-yl)phosphinic amide (1d): ¹H NMR (300 MHz, CDCl₃) δ 0.87 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 1.63 (m, 4H), 2.20–2.65 (m, 7H), 3.40–3.60 (m, 2H), 7.36–7.56 (m, 6H), 7.80–8.02 (m, 5H), 8.21 (dd, J = 15.9, 7.2 Hz, 1H), 8.87 (m, 1H), 8.99 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 16.9, 18.6, 23.6, 31.1, 54.3, 55.6, 57.1 (d, J = 5.7 Hz), 124.4 (d, J = 14.4 Hz), 124.5 (d, J = 14.4 Hz), 126.2 (d, J = 4.6 Hz), 127.0, 127.6 (d, J = 2.8 Hz), 128.7, 130.4 (d, J = 121.5 Hz), 130.6 (d, J = 124.3 Hz), 132.7 (d, J = 2.8 Hz), 132.8 (d, J = 2.8 Hz), 133.4 (d, J = 11.5 Hz), 133.5 (d, J = 9.8 Hz), 133.7 (d, J = 5.8 Hz), 133.8 (d, J = 5.8 Hz), 133.9 (d, J = 9.7 Hz), 134.0 (d, J = 7.5 Hz). ³¹P NMR (121 MHz, CDCl₃) δ 28.7. IR (KBr) 3210, 2958, 2782, 1457, 1175, 1158 cm⁻¹. HRMS calcd for C₂₉H₃₄N₂OP [M+H]⁺ 457.2409, found 457.2405.

3. Typical procedure for the catalytic enantioselective addition of Ph₂Zn to ketones

A well-dried pyrex Schlenk tube was charged with diphenylzinc (43.9 mg, 0.20 mmol) and Et₂Zn (0.40 mL of 1.0 M solution in heptane, 0.40 mmol) at the room temperature under nitrogen atmosphere. The mixture was stirred for 30 min, and then poured into another well-dried pyrex Schlenk tube with (S)-1d (9.1 mg, 0.020 mmol) via cannula. This solution was stirred for 30 min, and then ketone (2) (0.20 mmol) was added. The resulting mixture was stirred at room temperature for 8–24 h by monitoring with TLC. After hydrolysis with 10 mL of sat. NH₄Cl aqueous solution, the product was extracted with ether (10 mL × 3) and washed by brine (10 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the crude product was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc = 20/1 to 1/2), to give the desired products (3). The enantiomeric purity was determined by GC or HPLC on chiral column.
1-(4-chlorophenyl)-1-phenylethanol (3a): \(^{3}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.87 (s, 3H), 2.38 (br, 1H), 7.18-7.40 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 30.7, 75.8, 125.8, 127.2, 127.3, 128.2, 128.3, 132.7, 146.6, 147.5. IR (film) 3419, 2979, 1489, 1446, 1093, 1013 cm\(^{-1}\). HRMS calc'd for C\(_{14}\)H\(_{12}\)Cl [M–OH]\(^+\) 215.0628, found 215.0626. Chiral GC \(\beta\)-DM [150 °C, \(t_1\) = 30.6 min, \(t_2\) = 31.9 min].

1-(4-bromophenyl)-1-phenylethanol (3b): \(^{4,5}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.88 (s, 3H), 2.38 (br, 1H), 7.18-7.45 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 30.7, 75.9, 120.9, 125.8, 127.2, 127.7, 128.3, 131.1, 147.1, 147.3. IR (film) 3420, 2978, 1485, 1446, 1394, 1077, 1027 cm\(^{-1}\). HRMS calc'd for C\(_{14}\)H\(_{12}\)Br [M–OH]\(^+\) 259.0122, found 259.0123. Chiral HPLC (OD-H; hexane/IPA = 99/1, 1.0 mL/min) \(t_1\) = 41.8 min, \(t_2\) = 49.9 min.

1-(4-methoxyphenyl)-1-phenylethanol (3c): \(^{3,6}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.91 (s, 3H), 2.21 (br, 1H), 3.77 (s, 3H), 6.78-6.87 (m, 2H), 7.18-7.44 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 31.0, 55.2, 75.9, 113.4, 125.8, 126.8, 127.2, 128.1, 140.3, 148.3, 158.5. IR (film) 3464, 2974, 1610, 1509, 1446, 1394, 1077, 1027 cm\(^{-1}\). HRMS calc'd for C\(_{15}\)H\(_{15}\)O \([M–OH]\(^+\) \(193.1128\), found 193.1128. Chiral HPLC (OJ-H; hexane/IPA = 9/1, 1.0 mL/min) \(t_1\) = 39.8 min, \(t_2\) = 51.2 min.

1-phenyl-2,3-dihydro-1H-inden-1-ol (3d): \(^{8-10}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.11 (br, 1H), 2.40-2.56 (m, 2H), 2.94 (m, 1H), 3.16 (m, 1H), 7.08 (d, \(J = 7.5\) Hz, 1H), 7.16-7.44 (m, 8H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 29.9, 44.9, 85.5, 124.0, 125.0, 125.7, 126.9, 127.1, 128.1, 128.5, 144.2, 146.4, 148.0. IR (film) 3397, 3023, 2938, 1446, 1050 cm\(^{-1}\). HRMS calc'd for C\(_{13}\)H\(_{13}\) [M–OH]\(^+\) 193.1017, found 193.1019. Chiral GC \(\beta\)-DM [160 °C, \(t_1\) = 12.6 min, \(t_2\) = 13.3 min].

1-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (3e): \(^{8,9}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)
1.78 (m, 1H), 1.90-2.20 (m, 3H), 2.16 (s, 1H), 2.80-2.96 (m, 2H), 7.00-7.40 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 19.7, 29.9, 41.5, 75.4, 126.4, 126.5, 126.6, 127.5, 127.8, 128.9, 129.0, 137.7, 142.1, 149.0. IR (film) 3444, 2936, 1488, 1445, 1324, 1068 cm\(^{-1}\). HRMS calcd for C\(_{16}\)H\(_{15}\) [M–OH]\(^{+}\) 207.1174, found 207.1171. Chiral GC β-DM [170 °C, \(t_1 = 12.4\) min, \(t_2 = 13.1\) min].

\[\text{HO Ph} \]

5-phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (3f)\(^8\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.49 (m, 1H), 1.60-1.82 (m, 2H), 1.90 (m, 1H), 2.12 (m, 1H), 2.26 (br, 1H), 2.52 (m, 1H), 2.60-2.76 (m, 2H), 7.10 (m, 1H), 7.15-7.35 (m, 7H), 7.62 (m, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 26.1, 27.4, 36.3, 41.0, 79.9, 126.2, 126.9, 127.0, 127.4, 127.5, 128.5, 130.5, 141.0, 145.2, 145.3. IR (film) 3420, 2929, 2857, 1485, 1447, 1317, 1011 cm\(^{-1}\). HRMS calcd for C\(_{17}\)H\(_{17}\) [M–OH]\(^{+}\) 221.1130, found 221.1129. Chiral GC β-DM [170 °C, \(t_1 = 18.7\) min, \(t_2 = 19.9\) min].

\[\text{HO Ph} \]

1-(2-naphthalenyl)-1-phenylethanol (3g)\(^{4,7}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.98 (s, 3H), 2.42 (br, 1H), 7.15-7.48 (m, 8H), 7.66-7.84 (m, 3H), 7.93 (m, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 30.7, 76.3, 123.7, 125.0, 125.9, 126.0, 126.1, 127.0, 127.9, 128.2, 128.3, 132.3, 133.0, 145.3, 147.7. IR (film) 3433, 3056, 1493, 1446, 1373, 1126, 1065 cm\(^{-1}\). HRMS calcd for C\(_{18}\)H\(_{15}\) [M–OH]\(^{+}\) 231.1174, found 231.1174. Chiral HPLC (OD-H; hexane/IPA = 20/1, 0.5 mL/min) \([t_1 = 34.2\) min, \(t_2 = 39.8\) min].

\[\text{HO Ph} \]

1-phenyl-1-(2-thiophenyl)ethanol (3h)\(^{11}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.01 (s, 3H), 2.42 (br, 1H), 6.86-6.96 (m, 2H), 7.20-7.38 (m, 4H), 7.46-7.53 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 32.2, 74.8, 124.2, 125.0, 125.3, 126.6, 127.3, 128.2, 147.2, 153.4. IR (film) 3420, 2979, 1445, 1233, 1063 cm\(^{-1}\). HRMS calcd for C\(_{12}\)H\(_{11}\)S [M–OH]\(^{+}\) 187.0581, found 187.0583. Chiral GC β-DM [140 °C, \(t_1 = 16.4\) min, \(t_2 = 17.1\) min].

\[\text{HO Ph} \]

1-phenyl-1-(3-thiophenyl)ethanol (3i)\(^{12}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.92 (s, 3H), 2.28 (br, 1H), 6.97 (dd, \(J = 5.1, 1.5\) Hz, 1H), 7.17 (dd, \(J = 3.0, 1.5\) Hz, 1H), 7.20-7.36 (m, 4H), 7.38-7.46 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 31.1, 74.6, 120.8, 125.4, 126.0, 126.7, 127.0, 128.2, 147.4, 149.7. IR (film) 3418, 2978, 1492, 1446, 1370, 1231, 1069 cm\(^{-1}\). HRMS calcd for C\(_{12}\)H\(_{11}\)S [M–OH]\(^{+}\) 187.0581, found 187.0584. Chiral GC β-DM [140 °C, \(t_1 = 18.3\) min, \(t_2 = 19.1\) min].
(E)-2,4-diphenyl-3-buten-2-ol (3j):\(^7\) \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 1.78 (s, 3H), 1.98 (br, 1H), 6.51 (d, \(J = 16.2\) Hz, 1H), 6.66 (d, \(J = 16.2\) Hz, 1H), 7.15-7.55 (m, 10H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) δ 29.7, 74.7, 125.3, 126.6, 127.1, 127.6, 127.7, 128.3, 128.5, 136.3, 136.7, 146.6. IR (film) 3397, 3025, 1598, 1492, 1446, 1369, 1067 cm\(^{-1}\). HRMS calcd for C\(_{16}\)H\(_{15}\)[M–OH]\(^+\) 207.1174, found 207.1172. Chiral GC β-DM [170 °C, \(t_1 = 15.8\) min, \(t_2 = 16.3\) min].

3-methyl-2-phenylbutan-2-ol (3k):\(^4,7\) \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 0.79 (d, \(J = 6.9\) Hz, 3H), 0.87 (d, \(J = 6.9\) Hz, 3H), 1.50 (s, 3H), 1.80 (br, 1H), 2.00 (m, 1H), 7.20 (t, \(J = 7.2\) Hz, 1H), 7.30 (t, \(J = 8.1\) Hz, 2H), 7.40 (d, \(J = 8.1\) Hz, 2H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) δ 17.2, 17.4, 26.6, 38.6, 76.6, 125.2, 126.3, 127.8, 147.8. IR (film) 3464, 2971, 1446, 1372, 1090, 1029 cm\(^{-1}\). HRMS calcd for C\(_{11}\)H\(_{15}\)[M–OH]\(^+\) 147.1174, found 147.1172. Chiral GC β-DM [110 °C, \(t_1 = 7.7\) min, \(t_2 = 8.3\) min].

1-cyclohexyl-1-phenylethanol (3l):\(^4,7\) \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 0.88-1.30 (m, 5H), 1.50 (s, 3H), 1.54-1.86 (m, 7H), 7.20 (t, \(J = 6.6\) Hz, 1H), 7.30 (t, \(J = 8.1\) Hz, 2H), 7.39 (d, \(J = 7.2\) Hz, 2H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) δ 26.4, 26.6, 26.6, 26.7, 27.2, 27.3, 49.0, 76.6, 125.3, 126.3, 127.8, 147.8. IR (film) 3464, 2929, 2852, 1446, 1372, 1090, 1029 cm\(^{-1}\). HRMS calcd for C\(_{14}\)H\(_{19}\)[M–OH]\(^+\) 187.1487, found 187.1491. Chiral HPLC (OD-H; hexane/IPA = 20/1, 0.5 mL/min) [\(t_1 = 12.5\) min, \(t_2 = 15.3\) min].

4. Typical procedure for the catalytic enantioselective addition of Et\(_2\)Zn to ketones

A well-dried pyrex Schlenk tube was charged with (S)-1d (45.6 mg, 0.10 mmol) under nitrogen atmosphere. Then, Et\(_2\)Zn (3.0 mL of 1.0 M solution in heptane, 3.0 mmol) was added at −78 °C. This solution was stirred at −78 °C for 30 min, and ketone (2) (1.0 mmol) was added. The mixture was then gradually warmed to room temperature, and stirred for 16–24 h by monitoring with TLC. After hydrolysis with 10 mL of sat. NH\(_4\)Cl aqueous solution, the product was extracted with ether (10 mL × 3) and washed by brine (10 mL). The combined extracts were dried over MgSO\(_4\). The organic phase was concentrated under reduced pressure and the crude product was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc or pentane/ether), to give the desired products (S). The enantiomeric purity was determined by chiral GC.
2-Phenyl-2-butanol (5a):\textsuperscript{5,13-15} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 0.75 (t, \( J = 7.5 \) Hz, 3H), 1.48 (s, 3H), 1.73-1.81 (m, 2H), 2.16 (br, 1H), 7.25-7.38 (m, 5H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 8.3, 29.7, 36.7, 74.9, 124.9, 126.5, 128.1, 147.8. IR (film) 3407, 2970, 1446, 1374, 1029 cm\textsuperscript{-1}. HRMS calcd for C\textsubscript{10}H\textsubscript{13} [M–OH]\textsuperscript{+} 133.1017, found 133.1020. Chiral GC β-DM [100 °C, \( t_1 = 9.1 \) min, \( t_2 = 9.7 \) min].

2-(3-chlorophenyl)butan-2-ol (5b):\textsuperscript{14,16} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 0.78 (t, \( J = 7.5 \) Hz, 3H), 1.51 (s, 3H), 1.79 (q, \( J = 7.5 \) Hz, 1H), 1.80 (q, \( J = 7.5 \) Hz, 1H), 1.95 (br, 1H), 7.16-7.31 (m, 3H), 7.43 (m, 1H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 8.2, 29.6, 36.6, 74.7, 123.2, 125.4, 126.6, 129.4, 134.1, 149.9. IR (film) 3408, 2972, 2935, 1683, 1473, 1419 cm\textsuperscript{-1}. HRMS calcd for C\textsubscript{10}H\textsubscript{12}Cl [M–OH]\textsuperscript{+} 167.0628, found 167.0626. Chiral HPLC (OD-H; hexane/IPA = 99/1, 0.3 mL/min) \([t_1 = 48.9 \) min, \( t_2 = 58.1 \) min].

2-(4-chlorophenyl)butan-2-ol (5c):\textsuperscript{15} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 0.77 (t, \( J = 7.5 \) Hz, 3H), 1.53 (s, 3H), 1.77-1.83 (m, 2H), 1.82 (br, 1H), 7.28 (d, \( J = 8.7 \) Hz, 2H), 7.35 (d, \( J = 9.0 \) Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 8.3, 29.6, 36.7, 74.7, 126.6, 128.2, 132.3, 146.4. IR (film) 3419, 2971, 2934, 1489, 1094 cm\textsuperscript{-1}. HRMS calcd for C\textsubscript{10}H\textsubscript{12}Cl [M–OH]\textsuperscript{+} 167.0628, found 167.0630. Chiral HPLC (OD-H; hexane/IPA = 99/1, 0.3 mL/min) \([t_1 = 55.5 \) min, \( t_2 = 66.2 \) min].

2-(naphthalen-2-yl)butan-2-ol (5d):\textsuperscript{14,15,17} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 0.79 (t, \( J = 7.5 \) Hz, 3H), 1.61 (s, 3H), 1.80-2.05 (m, 3H), 1.92 (br, 1H), 7.38-7.55 (m, 3H), 7.76-7.86 (m, 3H), 7.89 (m, 1H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 8.3, 29.7, 36.4, 75.1, 123.2, 123.8, 125.6, 126.0, 127.5, 127.8, 128.1, 132.2, 133.2, 145.1. IR (film) 3420, 2970, 2932, 1457, 1375, 1130 cm\textsuperscript{-1}. HRMS calcd for C\textsubscript{14}H\textsubscript{15} [M–OH]\textsuperscript{+} 183.1174, found 183.1173. Chiral HPLC (OD-H; hexane/IPA = 98/2, 0.4 mL/min) \([t_1 = 52.1 \) min, \( t_2 = 61.9 \) min].

2-(thiophen-2-yl)butan-2-ol (5e):\textsuperscript{14,15,17} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 0.87 (t, \( J =
7.5 Hz, 3H), 1.60 (s, 3H), 1.88 (q, J = 7.5 Hz, 2H), 2.18 (br, 1H), 6.89 (dd, J = 3.6, 1.5 Hz, 1H), 6.93 (dd, J = 4.8, 3.6 Hz, 1H), 7.17 (dd, J = 4.8, 1.2 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ 8.5, 29.6, 37.4, 74.0, 122.3, 123.6, 126.5, 153.2. IR (film) 3408, 2971, 2932, 1457, 1375, 1235, 1125 cm⁻¹. HRMS calcld for C8H11S [M–OH]⁺ 139.0581, found 139.0580. Chiral HPLC (OD-H; hexane/IPA = 98/2, 0.4 mL/min) [t1 = 26.6 min, t2 = 29.4 min].

2-(thiophen-3-yl)butan-2-ol (5f):¹⁴,¹⁸ ¹H NMR (300 MHz, CDCl3) δ 0.81 (t, J = 7.5 Hz, 3H), 1.52 (s, 3H), 1.80 (q, J = 7.5 Hz, 2H), 2.01 (br, 1H), 7.03 (dd, J = 4.8, 1.2 Hz, 1H), 7.12 (dd, J = 3.0, 1.5 Hz, 1H), 7.25 (dd, J = 4.8, 3.0 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ 8.4, 29.0, 36.4, 73.8, 119.4, 125.6, 125.8, 149.8. IR (film) 3397, 2970, 2932, 1456, 1373 cm⁻¹. HRMS calcld for C8H11S [M+H]⁺ 139.0581, found 139.0579. Chiral HPLC (OD-H; hexane/IPA = 98/2, 0.4 mL/min) [t1 = 27.6 min, t2 = 31.5 min].

5. References
