REVISED
Supporting Information

**Asymmetric alkylation of *N*-toluenesulfonylimines with dialkylzinc reagents
catalyzed by copper- chiral amidophosphine**

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General

¹H-NMR (500 MHz), ¹³C-NMR (125 MHz) and ³¹P-NMR (202 MHz) were measured in CDCl₃. Chemical shift values were expressed in ppm downfield from internal tetramethylsilane. Some of the copper salts were prepared or were purified according to the reported procedure. (CuOTf)₂-PhH: Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889-1897. CuTC (copper(I) thiophene-2-carboxylate) and Cu(O₂CCPh₃)₂: Allerd, G. D.; Liebeskind, L. S. *J. Am.*

Chem. Soc. **1996**, *118*, 2748-2749. CuCl-SMe₂, CuBr-SMe₂ and CuI-SMe₂: House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460-1469. Cu(OAc)₂-H₂O, Cu(OTf)₂, CuCN, CuCl and CuI: Armarego, W. L. F.; Chai, C. L. L. in *Purification of Laboratory Chemicals* 5th ed. pp 414-416, Butterworth Heinemann: Amsterdam, 2003. Cu(naphthenate)₂ and Cu₂O were used without purification as obtained commercially.

Synthesis of chiral ligand

(S)-3,3-Bis(2,4,6-trimethylphenylmethyl)-8,8-dimethyl-7-oxa-1-azabicyclo[3.3.0]octane-2-one (7d). A hexane solution of *n*-BuLi (15.8 mL, 24 mmol) was added to a solution of HMDS (5.4 mL, 24 mmol) in 20 mL of THF at -60 °C. After stirring for 1 h at -60 °C, a solution of **6** (3.1 g, 20 mmol) in 8 mL of THF was added at -60 °C. The resulting solution was stirred for 0.5 h at -60 °C, and 2,4,6-trimethylbenzyl bromide (5.1 g, 24 mmol) in 6 mL of THF was added at -60 °C. After stirring for 1 h at room temperature, the mixture of *n*-BuLi (17.2 mL, 26 mmol) and HMDS (5.8 mL, 26 mmol) in 20 mL of THF, and HMPA (4.6 mL, 26 mmol) were added at -60 °C. The whole was stirred for 0.5 h and 2,4,6-trimethylbenzyl bromide (5.6 g, 26 mmol) in 6 mL of THF was added at -60 °C, and the mixture was stirred at room temperature for 3 h. The mixture was quenched with satd NH₄Cl and extracted with benzene. Organic layers were washed with 10% HCl, satd NaHCO₃, and brine, and then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (hexane/EtOAc=10/1) gave **7d** (5.8 g, 69% yield) as a white solid of mp 132 °C and $[\alpha]_D^{25} +138.8$ (*c* 1.01, CHCl₃). ¹H NMR: 1.25-1.30 (1H, m), 1.30 (3H, s), 1.54 (3H, m), 2.04 (1H, dd, *J* = 6.1 Hz, 12.8 Hz), 2.21 (3H, s), 2.22 (3H, s), 2.26 (6 H, s), 2.29 (6H, s), 2.68-2.74 (1H, m), 2.80 (1H, dd, *J* = 7.8 Hz, 9.6 Hz), 2.93 (1H, d, *J* = 14.4 Hz), 2.94 (1H, d, *J* = 14.4 Hz), 3.28 (1H, d, *J* = 14.4 Hz), 3.51 (1H, d, *J* = 14.4 Hz), 3.63 (1H, dd, *J* = 5.5 Hz, 7.8 Hz), 6.77 (2H, s), 6.81 (2H, s). ¹³C NMR: 20.8, 21.2, 23.7, 26.0, 32.2, 37.0, 57.4, 58.1, 70.4, 91.0, 129.1, 132.0, 133.0, 135.6, 135.8, 175.0. IR (nujol): 1660 cm⁻¹. EIMS *m/z*: 419 (M⁺). Anal. Calcd for C₂₈H₃₇NO₂: C, 80.15; H, 8.89; N, 3.34. Found: C, 79.88; H, 8.81; N, 3.27

(S)-3,3-Bis(2,4,6-triisopropylphenylmethyl)-8,8-dimethyl-7-oxa-1-azabicyclo[3.3.0]octane-2-one (7e). A hexane solution of *n*-BuLi (7.8 mL, 12 mmol) was added to a solution of HMDS (2.5 mL, 12 mmol) in 10 mL of THF at -60 °C. After stirring for 1 h at -60 °C, a solution of **6** (1.6 g, 10 mmol) in 3 mL of THF was added at -60 °C. The resulting solution was stirred for 0.5 h at -60 °C, and 2,4,6-triisopropylbenzyl bromide (3.6 g, 12 mmol) in 3 mL of THF was added at -60 °C. After stirring for 1 h at room temperature, the mixture of *n*-BuLi (9.8 mL, 15 mmol) and HMDS (3.2 mL, 15 mmol) in 13 mL of THF, and HMPA (2.3 mL, 15 mmol) were added at -60 °C. The whole was stirred for 0.5 h. 2,4,6-triisopropylbenzyl bromide (3.9 g, 13 mmol) in 3 mL of THF was added at -60 °C, and the mixture was stirred at room temperature for 3 h. The

mixture was quenched with satd NH_4Cl and extracted with benzene. Organic layers were washed with 10% HCl , satd NaHCO_3 , and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/acetone=20/1) gave **7e** (4.4 g, 73% yield) as a white solid of mp 60-61 °C and $[\alpha]^{25}_{\text{D}} +50.9$ (*c* 1.05, CHCl_3). ^1H NMR: 0.96-1.35 (40H, m), 1.59 (3H, s), 2.04 (1H, m), 2.84 (1H, heptet, *J* = 6.4 Hz), 2.85 (1H, heptet, *J* = 6.7 Hz), 2.95-2.98 (1H, m), 2.96 (1H, d, *J* = 15.0 Hz), 3.10 (1H, d, *J* = 14.7 Hz), 3.19-3.40 (5H, m), 3.29 (1H, d, *J* = 14.7 Hz), 3.51 (1H, d, *J* = 15.0 Hz), 3.78 (1H, m), 6.91-6.98 (4H, m). ^{13}C NMR: 14.1, 20.9, 21.8, 22.1, 22.3, 23.0, 23.8, 23.9, 24.0, 24.2, 25.5, 26.1, 26.7, 29.1, 29.3, 29.8, 30.2, 32.2, 32.8, 33.1, 33.9, 34.1, 34.6, 57.7, 58.0, 60.3, 70.3, 91.3, 120.3, 120.5, 120.8, 128.5, 129.9, 146.8, 147.2, 147.9, 148.2, 148.4, 148.6, 175.6. IR (nujol): 1645 cm^{-1} . EIMS *m/z*: 588 (M^+). Anal. Calcd for $\text{C}_{40}\text{H}_{61}\text{NO}_2$: C, 81.72; H, 10.46; N, 2.38. Found: C, 81.65; H, 10.33; N, 2.29.

(S)-3,3-Bis(2,4,6-trimethylphenylmethyl)-5-hydroxymethylpyrrolidine-2-one (8d). A solution of **7d** (2.2 g, 5 mmol) and *p*-TsOH· H_2O (10 mg, 0.05 mmol) in 22 mL of methanol was refluxed for 36 h. Concentration and crystallization from methanol gave **8d** (1.6 g, 79% yield) as colorless plates of mp 198 °C and $[\alpha]^{25}_{\text{D}} -70.0$ (*c* 1.03, CHCl_3). ^1H NMR: 1.27 (1H, dd, *J* = 7.3, 13.4 Hz), 1.69 (1H, brs), 1.95 (1H, dd, *J* = 7.3, 13.4 Hz), 2.21 (6H, s), 2.23 (6H, s), 2.30 (6H, s), 2.72-2.80 (2H, m), 2.90 (1H, d, *J* = 14.4 Hz), 2.91 (1H, d, *J* = 14.4 Hz), 3.21-3.26 (1H, m), 3.34 (1H, d, *J* = 14.6 Hz), 3.47 (1H, d, *J* = 14.6 Hz), 6.14-6.22 (1H, brs), 6.81 (4H, s). ^{13}C NMR: 20.8, 21.1, 29.7, 36.7, 37.3, 49.7, 53.5, 66.7, 129.2, 129.3, 131.9, 132.7, 135.7, 135.8, 137.7, 137.8, 182.7. IR (nujol): 3350, 1685 cm^{-1} . EIMS *m/z*: 379 (M^+). Anal. Calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_2$: C, 79.11; H, 8.76; N, 3.69. Found: C, 78.45; H, 8.66; N, 3.61.

(S)-3,3-Bis(2,4,6-triisopropylphenylmethyl)-5-hydroxymethylpyrrolidine-2-one (8e). A solution of **7e** (3.0 g, 5.1 mmol) and *p*-TsOH· H_2O (97 mg, 0.5 mmol) in 10 mL of methanol was refluxed for 3 h. Concentration and crystallization from methanol gave **8e** (2.6 g, 94% yield) as a white solid of mp 198-199 °C and $[\alpha]^{25}_{\text{D}} -32.7$ (*c* 1.02, CHCl_3). ^1H NMR: 0.88-1.29 (38H, m), 1.88 (1H, dd, *J* = 7.0, 13.5 Hz), 2.49 (1H, brs), 2.80-2.90 (3H, m), 2.90 (1H, d, *J* = 14.7 Hz), 3.01 (1H, d, *J* = 14.7 Hz), 3.24 (1H, d, *J* = 14.4 Hz), 3.09-3.40 (6H, m), 3.52 (1H, d, *J* = 14.7 Hz), 6.88-7.08 (4H, m). ^{13}C NMR: 22.0, 22.2, 23.0, 24.0, 24.1, 24.2, 24.3, 25.4, 26.0, 26.4, 29.1, 29.4, 29.8, 30.4, 32.3, 33.1, 34.0, 34.1, 50.4, 54.0, 66.7, 120.5, 120.8, 121.0, 121.3, 128.2, 129.3, 146.9, 147.2, 148.1, 148.6, 182.6. IR (nujol): 3400, 1670 cm^{-1} . EIMS *m/z*: 548 ($\text{M}^+ + 1$). Anal. Calcd For $\text{C}_{37}\text{H}_{57}\text{NO}_2$: C, 81.12; H, 10.49; N, 2.56. Found: C, 81.14; H, 10.59; N, 2.53.

(S)-5-((Diphenylphosphino)methyl)-3,3-bis[1-(2,4,6-trimethylphenyl)methyl]pyrrolidin-2-one (10d). Small pieces of sodium (0.3 g, 15 mmol) were added at 0 °C to a solution of Ph_2PCl (0.6 mL, 3.5 mmol) in 16 mL of 1,4-dioxane and the mixture was stirred under reflux for 15 h. A

solution of **21** (1.1 g, 2.0 mmol) in 6 mL of THF was added at 0 °C. After stirring for 1 h at rt, the mixture was filtered through celite to afford a pale yellow amorphous (4.6 g). Silica gel column chromatography (hexane/acetone = 5/1) gave **10d** (0.5 g, 46% yield) as a white amorphous of mp 80-81 °C and $[\alpha]^{25}_D +55.0$ (c 1.04, CHCl₃). ¹H NMR: 1.38 (1H, dd, *J* = 6.7, 13.3 Hz), 1.61 (1H, dd, *J* = 6.7, 13.3 Hz), 1.68 (1H, dd, *J* = 7.3, 13.4 Hz), 2.69 (1H, dd, *J* = 6.7, 13.3 Hz), 2.85 (1H, d, *J* = 14.7 Hz), 2.89 (1H, d, *J* = 14.7 Hz), 3.27 (1H, d, *J* = 14.4 Hz), 3.44 (1H, d, *J* = 14.4 Hz), 6.03 (1H, brs), 6.73 (2H, s), 6.81 (2H, s), 7.12-7.32 (10H, m). ¹³C NMR: 20.8, 21.1, 36.1, 36.5, 37.0, 37.2, 49.3, 50.0, 128.4, 128.5, 128.7, 128.8, 129.2, 132.0, 132.4, 132.6, 132.8, 135.5, 137.4, 137.5, 137.9, 181.8. ³¹P NMR: -22.6. IR (nujol): 1690 cm⁻¹. MS *m/z*: 547 (M⁺). Anal. Calcd for C₃₇H₄₂NOP: C, 81.14; H, 7.73; N, 2.56. Found: C, 80.94; H, 7.77; N, 2.52.

(S)-1-[4,4-Bis(2,4,6-trimethylphenylmethyl)-2-hydroxymethylpyrrolidin-1-yl]-2,2-dimethylpropan-1-one (11d). A BH₃-THF solution (2.5 mL, 2.5 mmol) was added to a solution of **8d** (0.4 g, 1.0 mmol) in 2.5 mL of THF. The mixture was stirred under reflux for 2.5 d. The mixture was cooled to 0 °C, and was added with 5 mL of methanol and concentrated to remove THF and methanol. After addition of 2 mL of 5 N NaOH, the whole was refluxed for 2 h, and extracted with benzene. Combined organic layers were washed with brine, and dried over K₂SO₄, and then concentrated to give a white gum. (0.4 g). A solution of the white gum (0.26 g, 0.72 mmol), Et₃N (0.30 mL, 2.16 mmol), and pivaloyl chloride (0.09 mL, 0.72 mmol) in 1.5 mL of EtOAc was stirred at -20 °C for 5 h. After addition of 20 mL of EtOAc, the solution was washed with 10% HCl, satd NaHCO₃, and brine, and then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (hexane/EtOAc=10/1) gave **11d** (0.23 g, 73% yield) as a white amorphous of mp 75-77 °C and $[\alpha]^{25}_D +54.4$ (c 1.04, CHCl₃). ¹H NMR: 0.87 (1H, m), 1.33 (9H, s), 2.01-2.03 (1H, m), 2.21 (3H, s), 2.25 (3H, s), 2.37 (12H, s), 2.48 (1H, d, *J* = 14.6 Hz), 2.57 (1H, d, *J* = 14.6 Hz), 2.78 (1H, d, *J* = 14.6 Hz), 2.91 (1H, d, *J* = 14.6 Hz), 3.15 (1H, d, *J* = 10.1 Hz), 3.31 (1H, dd, *J* = 7.6, 11.8 Hz), 3.48 (1H, d, *J* = 11.8 Hz), 3.84 (1H, d, *J* = 10.1 Hz), 4.39-4.44 (1H, m), 5.34 (1H, brs), 6.76 (2H, s), 6.88 (2H, s). ¹³C NMR: 20.7, 20.8, 21.9, 27.1, 27.8, 31.9, 35.8, 36.6, 39.0, 47.1, 58.5, 62.0, 68.2, 129.4, 129.5, 130.9, 132.5, 135.6, 137.2, 179.4. IR (nujol): 3360, 1600 cm⁻¹. EIMS *m/z*: 449 (M⁺). Anal. Calcd for C₃₀H₄₃NO₂: C, 80.13; H, 9.64; N, 3.11. Found: C, 80.20; H, 9.72; N, 2.95.

(S)-1-[4,4-Bis(2,4,6-triisopropylphenylmethyl)-2-hydroxymethylpyrrolidin-1-yl]-2,2-dimethylpropan-1-one (11e). A BH₃-THF solution (11.1 mL, 11.1 mmol) was added to a solution of **8e** (2.4 g, 4.4 mmol) in 11 mL of THF. The mixture was stirred under reflux for 1 d. The mixture was cooled to 0 °C, and was added with 40 mL of methanol and concentrated to remove THF and methanol. After addition of 10 mL of 5 N NaOH, the whole was refluxed for 2 h, and extracted with benzene. Combined organic layers were washed with brine, and then dried

over K_2SO_4 , and then concentrated to give a white solid. A solution of this white solid (2.7 g), Et_3N (1.8 mL, 13.2 mmol), and pivaloyl chloride (0.6 mL, 4.8 mmol) in 4.5 mL of EtOAc was stirred at $-50\text{ }^\circ\text{C}$ for 10 h. After addition of 30 mL of EtOAc, the solution was washed with 10% HCl, satd NaHCO_3 , and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave **11e** (1.9 g, 69% yield) as a white amorphous of mp $87\text{--}89\text{ }^\circ\text{C}$ and $[\alpha]^{25}_{\text{D}} +43.5$ (c 1.02, CHCl_3). ^1H NMR: 0.74-1.45 (46H, m), 1.85-2.03 (1H, m), 2.45 (1H, d, $J = 15.0$ Hz), 2.5 (1H, m), 2.56 (1H, d, $J = 15.0$ Hz), 2.76-2.90 (3H, m), 2.86 (1H, d, $J = 14.4$ Hz), 2.99 (1H, d, $J = 14.4$ Hz), 3.19-3.47 (5H, m), 3.93 (1H, d, $J = 10.1$ Hz), 2.92 (1H, brs), 4.39-4.44 (1H, m), 6.87-6.91 (m, 4H). ^{13}C NMR: 22.0, 22.6, 23.8, 23.9, 24.0, 24.1, 25.5, 26.2, 27.8, 29.2, 29.5, 30.1, 30.8, 33.3, 33.9, 34.0, 35.1, 38.9, 45.6, 58.5, 61.2, 68.5, 120.9, 127.4, 129.0, 147.0, 147.1, 147.3, 147.9, 148.5, 179.5. IR (nujol): $3400, 1608\text{ cm}^{-1}$. EIMS m/z : 617 (M^+). Anal. Calcd for $\text{C}_{42}\text{H}_{67}\text{NO}_2$: C, 81.63; H, 10.93; N, 2.27. Found: C, 81.38; H, 10.87; N, 2.18.

(S)-1-[4,4-Bis(2,4,6-trimethylphenylmethyl)-2-chloromethylpyrrolidin-1-yl]-2,2-dimethylpropane-1-one (12d). A solution of **11d** (135 mg, 0.3 mmol) and MsCl (0.03 mL, 0.4 mmol) in 0.5 mL of 2,4,6-collidine was stirred at $0\text{ }^\circ\text{C}$ for 2.5 h. After dilution with benzene, the whole was washed with 10% HCl, 10% CuSO_4 , brine, satd NaHCO_3 , and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/EtOAc=20/1) gave **12d** (137 mg, 99% yield) as a white amorphous of mp $59\text{--}60\text{ }^\circ\text{C}$ and $[\alpha]^{25}_{\text{D}} +29.1$ (c 1.00, CHCl_3). ^1H NMR: 1.29 (9H, s), 1.55 (1H, dd, $J = 9.8, 12.4$ Hz), 2.0-2.2 (7H, m), 2.22 (3H, s), 2.26 (3H, s), 2.38 (6H, s), 2.55 (1H, d, $J = 14.6$ Hz), 2.62 (1H, d, $J = 14.6$ Hz), 2.79 (1H, d, $J = 14.1$ Hz), 2.90 (1H, d, $J = 14.1$ Hz), 3.23 (1H, d, $J = 9.8$ Hz), 3.62-3.70 (2H, m), 3.81 (1H, d, $J = 9.8$ Hz), 4.47-4.48 (1H, m), 6.80 (2H, s), 6.89 (2H, s). ^{13}C NMR: 20.7, 20.9, 22.0, 27.7, 32.1, 35.5, 37.2, 39.0, 46.1, 48.0, 57.8, 59.1, 129.3, 129.4, 131.1, 132.7, 135.5, 137.3, 177.0. IR (nujol): 1630 cm^{-1} . EIMS m/z : 469 ($\text{M}^+ + 2$). Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{ClNO}$: C, 76.97; H, 9.04; N, 2.99. Found: C, 77.15; H, 9.18; N, 2.84.

(S)-1-[4,4-Bis(2,4,6-triisopropylphenylmethyl)-2-chloromethylpyrrolidin-1-yl]-2,2-dimethylpropane-1-one (12e). A solution of **11e** (1.8 g, 2.9 mmol) and MsCl (0.3 mL, 3.4 mmol) in 3 mL of 2,4,6-collidine was stirred at $0\text{ }^\circ\text{C}$ for 3 h. After dilution with benzene, the whole was washed with 10% HCl, 10% CuSO_4 , brine, satd NaHCO_3 , and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/EtOAc=10/1) gave **12e** (1.4 g, 79% yield) as a white amorphous of mp $120\text{--}121\text{ }^\circ\text{C}$ and $[\alpha]^{25}_{\text{D}} +18.3$ (c 1.02, CHCl_3). ^1H NMR: 0.71-1.46 (46H, m), 1.99-2.03 (1H, m), 2.37 (1H, brs), 2.54 (1H, d, $J = 15.0$ Hz), 2.64 (1H, d, $J = 15.0$ Hz), 2.77-2.99 (3H, m), 2.84 (1H, d, $J = 14.7$ Hz), 2.98 (1H, d, $J = 14.7$ Hz), 3.26-3.31 (2H, m), 3.30 (1H, d, $J = 9.7$ Hz), 3.62 (2H, brs), 3.86 (1H, d, $J = 9.7$ Hz),

4.45-4.47 (1H, m), 6.88-7.01 (4H, m). ^{13}C NMR: 14.2, 20.9, 21.8, 22.5, 23.9, 23.9, 23.9, 24.0, 25.5, 26.2, 27.7, 28.9, 29.5, 30.0, 30.6, 33.7, 34.0, 34.1, 34.4, 38.9, 46.1, 46.6, 57.8, 59.0, 60.3, 120.6, 120.8, 127.6, 128.9, 146.9, 147.0, 148.0, 148.6, 177.0. IR (nujol): 1620 cm^{-1} . EIMS m/z : 635 (M^+). Anal. Calcd for $\text{C}_{42}\text{H}_{66}\text{ClNO}$: C, 79.26; H, 10.45; N, 2.20. Found: C, 79.15; H, 10.28; N, 2.24.

(S)-1-[2-Diphenylphosphinomethyl-4,4-bis(2,4,6-trimethylphenylmethyl)pyrrolidin-1-yl]-2,2-dimethylpropan-1-one (5d). Small pieces of sodium (3.9 g, 171 mmol) were added at $0\text{ }^{\circ}\text{C}$ to a solution of Ph_2PCl (7.7 mL, 43 mmol) in 84 mL of 1,4-dioxane and the whole was stirred under reflux for 16 h. A solution of **12d** (10.0 g, 21 mmol) in 27 mL of THF was added at $0\text{ }^{\circ}\text{C}$. After stirring at room temperature for 6 h, the mixture was filtered through celite and silica gel. Concentration and purification by silica gel column chromatography (hexane/EtOAc=10/1) gave **5d** (10.8 g, 83% yield) as a white amorphous of mp $79\text{--}80\text{ }^{\circ}\text{C}$ and $[\alpha]_D^{25} -35.5$ ($c\ 1.00$, CHCl_3). ^1H NMR: 1.71 (1H, dd, $J = 10.1, 12.5\text{ Hz}$), 2.07- 2.12 (1H, m), 2.24 (3H, s), 2.25 (3H, s), 2.26 (12H, s), 2.46 (1H, d, $J = 14.7\text{ Hz}$), 2.58 (1H, d, $J = 14.7\text{ Hz}$), 2.70 (1H, d, $J = 14.6\text{ Hz}$), 2.80 (1H, d, $J = 14.6\text{ Hz}$), 3.02 (1H, td, $J = 4.6, 13.4\text{ Hz}$), 3.21 (1H, d, $J = 10.1\text{ Hz}$), 3.78 (1H, d, $J = 9.8\text{ Hz}$), 4.35-4.39 (1H, m), 6.79 (2H, s), 6.83 (2H, s), 7.22-7.53 (10H, m). ^{13}C NMR: 20.7, 20.8, 20.9, 21.8, 27.9, 32.1, 33.2, 36.8, 39.0, 39.1, 48.2, 55.9, 56.0, 58.3, 60.4, 128.2, 128.2, 128.3, 128.4, 128.5, 128.6, 129.3, 131.4, 132.4, 132.6, 132.9, 133.0, 133.2, 135.3, 135.4, 137.3, 176.5. IR (nujol): 1625 cm^{-1} . EIMS m/z : 632 (M^+). Anal. Calcd for $\text{C}_{42}\text{H}_{50}\text{NOP}$: C, 81.65; H, 8.48; N, 2.27. Found: C, 81.65; H, 8.59; N, 2.27.

(S)-1-[2-Diphenylphosphinomethyl-4,4-bis(2,4,6-triisopropylphenylmethyl)pyrrolidin-1-yl]-2,2-dimethylpropan-1-one (5e). Small pieces of sodium (0.4 g, 16 mmol) were added at $0\text{ }^{\circ}\text{C}$ to a solution of Ph_2PCl (0.7 mL, 4 mmol) in 8 mL of 1,4-dioxane and the whole was stirred under reflux for 12 h. A solution of **12e** (1.3 g, 2 mmol) in 3.5 mL of THF was added at $0\text{ }^{\circ}\text{C}$. After stirring at room temperature for 2 h, the mixture was filtered through celite and silica gel. Concentration and purification by silica gel column chromatography (PhH/EtOAc=100/1) gave **5e** (1.30 g, 82% yield) as a white amorphous of mp $96\text{--}97\text{ }^{\circ}\text{C}$ and $[\alpha]_D^{25} -32.0$ ($c\ 1.00$, CHCl_3). ^1H NMR: 0.71-1.21 (45H, m), 1.49 (1H, m), 1.66 (1H, m), 2.18 (1H, m), 2.50 (1H, d, $J = 15.0\text{ Hz}$), 2.50 (1H, brs), 2.62 (1H, d, $J = 15.0\text{ Hz}$), 2.77 (1H, d, $J = 15.0\text{ Hz}$), 2.87 (1H, d, $J = 15.0\text{ Hz}$), 2.80-3.10 (6H, m), 3.29 (1H, d, $J = 9.8\text{ Hz}$), 3.82 (1H, d, $J = 9.8\text{ Hz}$), 4.35-4.38 (1H, m), 6.93-7.57 (14H, m). ^{13}C NMR: 22.2, 22.6, 24.0, 25.6, 26.3, 27.8, 29.1, 29.7, 30.1, 33.4, 33.6, 33.7, 34.1, 37.8, 37.9, 38.9, 46.9, 55.6, 55.7, 58.3, 128.0, 128.1, 128.5, 129.1, 132.4, 133.1, 146.8, 147.3, 148.0, 148.9, 176.5. ^{31}P NMR: -23.4 . IR (nujol): 1620 cm^{-1} . EIMS m/z : 786 (M^+). Anal. Calcd for $\text{C}_{54}\text{H}_{76}\text{NOP}$: C, 82.50; H, 9.74; N, 1.78; Found: C, 82.22; H, 9.89; N, 1.89.

Asymmetric alkylation

The absolute configuration was determined by its sign of specific rotation. **3aE**: (a) Raban, M.; Moulin, C. P.; Lauderback, S. K.; Swilley, B. *Tetrahedron Lett.* **1984**, 25, 3419-3422. (b) Fujihara, H.; Nagai, K.; Tomioka, K. *J. Am. Chem. Soc.* **2000**, 122, 12055-12056. **3aM** and **3aP**: Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 339-343. Those of other **3** were assigned by the reaction analogy.

N-[(1*S*)-1-Phenylpropan-1-yl]-4-methylbenzenesulfonamide (3aE) (Table 1, Entry 5). Under Ar atmosphere, a solution of amidophosphine **5d** (40.1 mg, 0.065 mmol) in 4 mL of toluene was added to a suspension of Cu(OTf)₂ (18.1 mg, 0.050 mmol) in 14.5 mL toluene. The resulting yellow solution was stirred for 1 h at room temperature. A solution of imine **1a** (259 mg, 1.0 mmol) in 13 mL of toluene was added at room temperature. After stirring at room temperature for 10 min, at 0 °C for 15 min, a hexane solution of diethylzinc (2.0 mL, 2.0 mmol) was added at 0 °C and the whole was stirred at 0 °C for 5 h. The reaction was quenched with 10% HCl and stirred at room temperature for another 0.5 h. The organic layer was separated and the water layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO₃ and brine, and then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (hexane/acetone=10/1) gave (*S*)-(-)-**3aE** (280 mg, 97 % yield) as a white solid of mp 106-107.5 °C and [α]_D²⁵ -49.3 (c 0.89, EtOH). The ee was determined to be 96 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 0.6 mL/min, 254 nm, major 15.1 min and minor 20.3 min). ¹H NMR: 0.78 (3H, t, *J* = 7.4 Hz), 1.70 (1H, m), 1.82 (1H, m), 4.18 (1H, ddd, *J* = 7.3, 7.3, 7.1 Hz), 5.03 (1H, d, *J* = 7.3 Hz), 6.95- 7.80 (9H, m). ¹³C NMR: 10.4, 21.4, 30.6, 59.8, 126.5, 127.0, 127.3, 128.4, 129.3, 137.7, 140.6, 142.9. IR (nujol): 3250, 1600, 1320, 1160 cm⁻¹. EIMS *m/z*: 289 (M⁺), 260 (M-Et).

N-[(1*S*)-1-Phenylethan-1-yl]-4-methylbenzenesulfonamide (3aM) (Table 1, Entry 13). Under Ar atmosphere, a solution of amidophosphine **5e** (40.1 mg, 0.065 mmol) in 4 mL of toluene was added to a suspension of Cu(OTf)₂ (18.1 mg, 0.050 mmol) in 14.5 mL toluene. The resulting yellow solution was stirred for 1 h at room temperature. A solution of **1a** (259 mg, 1.0 mmol) in 13 mL of toluene was added at room temperature. After stirring at room temperature for 10 min, and at 0 °C for 15 min, a toluene solution of dimethylzinc (4.0 mL, 8.0 mmol) was added at 0 °C and stirred at room temperature for 20 h. The reaction was quenched with 10 % HCl and stirred at room temperature for another 0.5 h. The organic layer was separated and the water layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO₃ and brine, and then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (hexane/acetone=20/1) gave (*S*)-(-)-**3aM** (267 mg, 97 % yield) as a white solid of mp 86-87 °C, [α]_D²⁵ -64.4 (c 1.07, EtOH) and [α]_D²⁵ -64.0 (c 0.82, PhH). The ee was

determined to be 87 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 0.6 mL/min, 254 nm, major 14.5 min and minor 11.8 min). ¹H NMR: 1.43 (3H, t, *J* = 7.3 Hz), 2.39 (3H, s), 4.43-4.48 (1H, m), 4.78 (1H, brs), 7.09- 7.28 (7H, m), 7.61- 7.63 (2H, m). ¹³C NMR: 24.0, 41.6, 53.8, 126.3, 127.9, 128.9, 129.2, 129.3, 131.9, 132.7, 135.7. IR (nujol): 1300 cm⁻¹. EIMS *m/z*: 275 (M⁺).

***N*-[(*S*)-2-Methyl-1-phenylpropan-1-yl]-4-methylbenzenesulfonamide (3aP) (Table 1, Entry 16).** Under Ar atmosphere, a solution of amidophosphine **5e** (40.1 mg, 0.065 mmol) in 4 mL of toluene was added to a suspension of Cu(OTf)₂ (18.1 mg, 0.050 mmol) in 14.5 mL toluene. The resulting yellow solution was stirred for 1 h at room temperature. A solution of **1a** (259 mg, 1.0 mmol) in 13 mL of toluene was added at room temperature. After stirring at room temperature for 10 min, at 0 °C for 15 min, a hexane solution of diisopropylzinc (2.0 mL, 2.0 mmol) was added at 0 °C and the whole was stirred at 0 °C for 2 h. The reaction was quenched with 10 % HCl and the whole was stirred at room temperature for another 0.5 h. The organic layer was separated and the water layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO₃ and brine, and then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (hexane/acetone=20/1) gave (*S*)-(-)-**3aP** (278 mg, 92 % yield) as a white solid of mp 141 °C and [α]_D²⁵ -22.8 (c 0.95, EtOH). The ee was determined to be 78 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 1.0 mL/min, 254 nm, major 12.4 min and minor 8.89 min). ¹H NMR: 0.73 (3H, d, *J* = 6.7 Hz), 0.94 (3H, d, *J* = 6.7 Hz), 1.92 (1H, m), 2.32 (3H, s), 4.02 (1H, m), 4.78 (1H, dq, *J* = 6.7, 15.0 Hz), 5.04 (1H, d, *J* = 8.3 Hz), 6.91- 7.49 (9H, m). ¹³C NMR: 18.8, 19.3, 21.4, 34.4, 64.1, 126.9, 127.0, 128.1, 129.1, 137.6, 139.9, 142.8. IR (nujol): 1300 cm⁻¹. EIMS *m/z*: 303 (M⁺).

***N*-[(1*S*)-1-(4-Methoxyphenyl)propan-1-yl]-4-methylbenzenesulfonamide (3bE) (Table 4, Entry 2).** Silica gel column chromatography (hexane/acetone=20/1) gave (-)-**3bE** as a white solid of mp 108 °C and [α]_D²⁵ -41.9 (c 1.00, EtOH). The ee was determined to be 86 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 0.6 mL/min, 254 nm, major 27.2 min and minor 23.6 min). ¹H NMR: 0.77 (3H, t, *J* = 7.3 Hz), 1.64- 1.85 (2H, m), 2.37 (3H, s), 3.75 (3H, s), 4.12 (1H, ddd, *J* = 7.3, 7.3, 7.1 Hz), 4.85 (1H, brs), 6.69 (2H, d, *J* = 8.3 Hz), 6.92 (2H, d, *J* = 7.3 Hz), 7.14 (2H, d, *J* = 7.9 Hz), 7.54 (2H, d, *J* = 7.9 Hz). ¹³C NMR: 10.4, 21.4, 30.5, 55.2, 59.3, 113.7, 127.1, 127.7, 129.2, 132.8, 137.8, 142.8, 158.8. IR (nujol): 3200, 1390, 1170 cm⁻¹. EIMS *m/z*: 319 (M⁺), 290 (M-Et). Anal. Calcd for C₁₇H₂₁NO₃S: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.62; H, 6.58; N, 4.37.

***N*-[(1*S*)-1-(Furan-2-yl)propan-1-yl]-4-methylbenzenesulfonamide (3cE) (Table 4, Entry 3).** Silica gel column chromatography (hexane/acetone=20/1) gave (-)-**3cE** as a white solid of mp 96 °C and [α]_D²⁵ -68.3 (c 1.00, EtOH). The ee was determined to be 91 % by HPLC (Daicel

Chiralcel OD-H, hexane/*i*-PrOH=10/1, 0.6 mL/min, 254 nm, major 15.2 min and minor 13.1 min). ¹H NMR: 0.84 (3H, t, *J* = 7.3 Hz), 1.77- 1.83 (2H, m), 2.38 (3H, s), 4.32 (1H, ddd, *J* = 7.3, 7.3, 7.9 Hz), 4.82 (1H, m), 5.90 (1H, m), 6.11 (1H, d, *J* = 1.8 Hz), 7.14 (1H, m), 7.19 (1H, d, *J* = 7.9 Hz), 7.61 (2H, d, *J* = 7.9 Hz). ¹³C NMR: 10.0, 21.3, 27.9, 53.1, 106.8, 109.9, 126.9, 129.3, 137.8, 141.7, 142.9, 152.9. IR (nujol): 3200, 1590, 1300, 1170 cm⁻¹. EIMS *m/z*: 279 (M⁺).

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***N*-[(1*S*)-1-Cyclohexylpropan-1-yl]-4-methylbenzenesulfonamide (3dE) (Table 4, Entry 4).** Silica gel column chromatography (hexane/acetone=20/1) gave (–)-**3dE** as a white solid of mp 132.5- 133 °C and [α]_D²⁵ –38.3 (c 0.99, EtOH). The ee was determined to be 96 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 1.0 mL/min, 254 nm, major 15.5 min and minor 14.3 min). ¹H NMR: 0.69 (3H, t, *J* = 7.4 Hz), 0.69- 1.68 (13H, m), 2.42 (3H, s), 2.97- 3.05 (1H, m), 4.15 (1H, d, *J* = 8.6 Hz), 7.28 (2H, d, *J* = 8.3 Hz), 7.74 (2H, d, *J* = 8.3 Hz). ¹³C NMR: 9.9, 21.4, 24.6, 26.7, 28.2, 28.9, 40.9, 60.2, 126.9, 129.4, 138.6, 142.9. IR (nujol): 1460, 1380 cm⁻¹. EIMS *m/z*: 295 (M⁺), 266 (M–Et). Anal. Calcd for C₁₆H₂₅NO₂S: C, 65.05; H, 8.53; N, 4.74. Found: C, 64.80; H; 8.28; N; 4.59.

***N*-[(3*S*)-5-Phenylpentan-3-yl]-4-methylbenzenesulfonamide (3eE) (Table 4, Entry 5).** Silica gel column chromatography (hexane/acetone=20/1) gave (–)-**3eE** as a colorless oil of [α]_D²⁵ –32.8 (c 0.88, EtOH). The ee was determined to be 93 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 1.0 mL/min, 254 nm, major 10.8 min and minor 12.3 min). ¹H NMR: 0.78 (3H, t, *J* = 7.3 Hz), 1.35- 1.73 (4H, m), 2.42 (3H, s), 2.43- 2.58 (4H, m), 3.18- 3.25 (1H, m), 4.59 (1H, d, *J* = 8.3 Hz), 7.01- 7.76 (9H, m). ¹³C NMR: 9.4, 21.4, 27.6, 31.6, 36.2, 55.0, 125.9, 127.1, 128.3, 128.4, 129.6, 138.4, 141.5, 143.2. IR (nujol): 3280, 1160 cm⁻¹. EIMS *m/z*: 317 (M⁺), 288 (M–Et). HRMS (*m/z*): Calcd for C₁₈H₂₃NO₂S, 317.1449 (M⁺); Found, 317.1456.

$^1\text{H-NMR}$ of **7d** in CDCl_3

$^{13}\text{C-NMR}$ of **7d** in CDCl_3

¹H-NMR of **8d** in CDCl₃

¹³C-NMR of **8d** in CDCl₃

$^1\text{H-NMR}$ of **10d** in CDCl_3

$^{13}\text{C-NMR}$ of **10d** in CDCl_3

^{31}P -NMR of **10d** in CDCl_3

^1H -NMR of **11d** in CDCl_3

^{13}C -NMR of **12d** in CDCl_3

^1H -NMR of **5d** in CDCl_3

$^1\text{H-NMR}$ of **7e** in CDCl_3

$^{13}\text{C-NMR}$ of **7e** in CDCl_3

$^1\text{H-NMR}$ of **11e** in CDCl_3

$^{13}\text{C-NMR}$ of **11e** in CDCl_3

$^1\text{H-NMR}$ of **12e** in CDCl_3

$^{13}\text{C-NMR}$ of **12e** in CDCl_3

$^1\text{H-NMR}$ of **5e** in CDCl_3

$^{13}\text{C-NMR}$ of **5e** in CDCl_3

^{31}P -NMR of **5e** in CDCl_3

^1H -NMR in CDCl_3

96 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / i-PrOH =10 / 1, 0.6 ml / min, 254 nm
major 19.5 min and minor 14.9 min.

¹H-NMR in CDCl₃

¹³C-NMR in CDCl₃

87 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / *i*-PrOH = 10 / 1, 0.6 ml / min, 254 nm
major 14.5 min and minor 11.8 min.

78 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / *i*-PrOH =10 / 1, 1.0 ml / min, 254 nm
major 12.4 min and minor 8.89min.

$^1\text{H-NMR}$ in CDCl_3

$^{13}\text{C-NMR}$ in CDCl_3

86 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / *i*-PrOH = 10 / 1, 0.6 ml / min, 254 nm
major 27.2 min and minor 23.6 min.

91 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / iPrOH =10 / 1, 0.6 ml / min, 254 nm
major 15.1 min and minor 13.1 min.

96 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / iPrOH =10 / 1, 1.0 ml / min, 254 nm
major 15.5 min and minor 14.3 min.

93 % ee (HPLC, Daicel Chiralpac OD-H, Hexane / *i*-PrOH = 10 / 1, 0.6 ml / min, 254 nm
major 10.8 min and minor 12.3 min.