Supporting Information

Catalytic Asymmetric Conjugate Addition of Dialkylzinc Reagents to β -Aryl- α,β -unsaturated *N*-2,4,6-Triisopropylphenylsulfonylaldimines with use of *N*-Boc-L-Val-Connected Amidophosphane-Copper(I) Catalyst

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General. IR spectra were expressed in cm^{–1}. ¹H, ¹³C, ³¹P and ¹⁹F spectra were taken in CDCl₃ at 500, 125, 202, and 470 MHz, respectively. Chemical shift values are expressed in ppm relative to internal TMS, external 85% H₃PO₄ for ³¹P, and external TFA for ¹⁹F. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Synthesis of *tert*-butyl (*S*)-1-((*S*)-4,4-dibenzyl-2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-3-methyl-1-oxobutan-2-ylcarbamate (6).

Under argon atmosphere, to a solution of (*S*)-*tert*-butyl 4,4-dibenzyl-2-[(diphenylphosphino)methyl]pyrrolidine-1-carboxylate (1.8 mmol) in dioxane (2.2 mL) was added 6.1N HCl-dioxane (4.9 mL, 30 mmol) at 0 °C over 5 min, and then the whole was stirred at room temperature for 1 h. The mixture was concentrated to give a yellow amorphous. To this yellow amorphous in anhydrous DMF (18 mL) and CH₂Cl₂ (18 mL) were added *N*-Boc-L-valine (395 mg, 1.82 mmol), HOObt (314 mg, 1.93 mmol), EDC•HCl (415 mg, 2.16 mmol), and *N*-methylmorpholine (0.8 mL, 7.2 mmol) at –20 °C. The mixture was stirred at –20 °C for 0.5 h, then at 0 °C for 18 h, and at room temperature for 1 h. AcOEt (50 mL), brine (10 mL), and 10% aq citric acid (10 mL) were added. The organic layer was successively washed with 10% aq citric acid (10 mL), saturated aqueous sodium bicarbonate (15mLx2), water (15 mL), and brine (15 mL), and then dried over Na₂SO₄. Concentration and purification through silica gel column chromatography (hexane/ethyl acetate =4/1) gave (–)-**6** (1.06g, 91% yield) as a white amorphous of [α]_D²⁵ –52.0 (*c* 1.07, benzene). ¹H NMR: 0.68+0.82+0.86+0.91 (total 6H, *d*, *J*=6.4 Hz), 1.26 (1H, *m*), 1.42+1.45 (total 9H, *s*), 1.6 (2H, *m*), 1.9 (1H, *m*), 2.1 (1H, *m*), 2.70 (2H, *s*), 3.21 (1H, *m*), 3.22 (1H, *d*, *J*=10 Hz), 3.66 (1H, *d*, *J*=10 Hz), 3.9 (1H, *m*), 4.3 (1H, *m*), 5.23+5.37 (total 1H, *d*, *J*=9.2 Hz), 6.9-7.8 (20H, *m*). ¹³C NMR: 14.1, 17.2, 17.8, 19.3, 19.3, 20.9, 28.2, 28.4, 31.6, 32.4, 32.8 (*d*, *J*=13 Hz), 40.2 (*d*, *J*=8.3 Hz), 41.0 (*d*, *J*=8.5 Hz), 42.3, 42.7, 43.1, 44.9, 46.0, 52.1, 54.9, 55.0 (*d*, *J*=20 Hz), 56.5, 57.1, 57.1, 60.3, 79.2, 126.5 (*d*, *J*=10 Hz), 128.3, 128.6 (*d*, *J*=7.2 Hz), 130.1, 130.5, 132.4 (*d*, *J*=19 Hz), 132.6, 133.3 (*d*, *J*=19 Hz), 137.7 (*d*, *J*=12 Hz), 137.1, 137.3, 139.2 (*d*, *J*=12 Hz), 155.3, 155.8, 170.7. ³¹P NMR: –23.1 (5/6P, *s*), –22.7 (1/6P, *s*). IR (nujol): 3410, 1720, 1640 cm^{–1}. EIMS *m/z*: 648 (M⁺). *Anal.* Calcd for C₄₁H₄₉N₂O₃P: C, 75.90; H, 7.61; N, 4.32. Found: C, 75.87; H, 7.66; N, 4.31.

Imines were synthesized from aldehydes and sulfonylamide by the reported procedure in Love, B. E.; Raja, P. S.; Williams, T. C., II. *Synlett* 1994, 493-494.

(*E*)-2,4,6-triisopropyl-*N*-[(*E*)-3-phenylallylidene]benzenesulfonamide (1d). Recrystallization from hexane/AcOEt (12/1) gave **1d** in 75% as colorless needles of mp 166-167 °C. ¹H NMR: 1.26 (6H, *d*, *J*=6.4 Hz), 1.27 (12H, *d*, *J*=6.4 Hz), 2.91 (1H, septet, *J*=6.4 Hz), 4.24 (2H, septet, *J*=6.4 Hz), 7.00 (1H, *dd*, *J*=9.5, 15.5 Hz), 7.19-7.57 (8H, *m*), 8.75 (1H, *d*, *J*=9.5 Hz). ¹³C NMR: 23.5, 24.7, 29.7, 34.2, 123.8, 125.1, 128.6, 129.2, 131.2, 131.4, 134.3, 151.1, 152.9, 153.6, 169.4. IR (nujol): 1580, 1370, 1150 cm^{–1}. EIMS *m/z*: 397 (M⁺). *Anal.* Calcd for C₂₄H₃₁NO₂S: C, 72.50;

H, 7.86; N, 3.52. Found: C, 72.38; H, 7.70; N, 3.55.

(E)-2,4,6-triisopropyl-N-[(E)-3-*o*-tolylallylidene]benzenesulfonamide (9e). Recrystallization from hexane/AcOEt (9/1) gave **9e** in 60% as a colorless needles of mp 129-130 °C. ¹H NMR: 1.25 (6H, d, *J*=7.0 Hz), 1.27 (12H, d, *J*=7.0 Hz), 2.38 (3H, s), 2.91 (1H, septet, 7.0 Hz), 4.25 (2H, septet, 7.0 Hz), 6.99 (1H, dd, *J*=9.5, 15.9 Hz), 7.19-7.44 (7H, m), 8.74 (1H, d, *J*=9.5 Hz). ¹³C NMR: 21.2, 23.5, 24.7, 29.7, 34.2, 123.8, 124.9, 125.8, 129.1, 129.2, 131.2, 132.4, 134.3, 138.9, 151.2, 153.2, 153.6, 169.5. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 411 (M⁺). *Anal.* Calcd for C₂₅H₃₃NO₂S: C, 72.95; H, 8.08; N, 3.40. Found: C, 72.78; H, 7.88; N, 3.39.

(E)-2,4,6-triisopropyl-N-[(E)-3-*m*-tolylallylidene]benzenesulfonamide (9f). Recrystallization from hexane/AcOEt (4/1) gave **9f** in 64% as colorless needles of mp 150.5-151 °C. ¹H NMR: 1.25 (6H, d, *J* = 7.1 Hz), 1.28 (12H, d, *J*=7.1 Hz), 2.45 (3H, s), 2.91 (1H, septet, *J*=7.1 Hz), 4.26 (2H, septet, 7.1 Hz), 6.94 (1H, dd, *J*=9.2, 15.6 Hz), 7.19-7.34 (5H, m), 7.61 (1H, d, *J*=7.6 Hz), 7.74 (1H, d, *J*=15.6 Hz), 8.79 (1H, d, *J*=9.2 Hz). ¹³C NMR: 19.7, 23.5, 24.7, 29.7, 34.2, 123.9, 125.9, 126.7, 126.8, 131.1, 131.2, 131.3, 133.2, 138.2, 150.5, 151.1, 153.6, 169.6. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 411 (M⁺). *Anal.* Calcd for C₂₅H₃₃NO₂S: C, 72.92; H, 8.03; N, 3.44. Found: C, 72.78; H, 7.88; N, 3.39.

(E)-2,4,6-triisopropyl-N-[(E)-3-(2-methoxyphenyl)allylidene]benzenesulfonamide (9g). Recrystallization from hexane/AcOEt (2/1) gave **9g** in 82% as colorless needles of mp 165-166 °C. ¹H NMR: 1.25 (6H, d, *J*=6.8 Hz), 1.27 (12H, d, *J*=6.8 Hz), 2.90 (1H, septet, 6.8 Hz), 3.86 (3H, s), 4.24 (2H, septet, *J*=6.8 Hz), 6.94 (1H, m), 7.01-7.03 (1H, m), 7.07 (1H, dd, *J*=9.2, 15.6 Hz), 7.18 (2H, m), 7.39-7.42 (1H, m), 7.55 (1H, d, *J*=7.6 Hz), 7.80 (1H, d, *J*=15.6 Hz), 8.72 (1H, d, *J*=9.2 Hz). ¹³C NMR: 23.5, 24.7, 29.7, 34.2, 55.6, 111.4, 120.9, 123.4, 123.8, 125.4, 128.9, 131.5, 132.9, 148.4, 151.1, 153.4, 158.6, 170.3. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 427 (M⁺). *Anal.* Calcd for C₂₅H₃₃NO₃S: C, 70.22; H, 7.78; N, 3.28. Found: C, 70.22; H, 7.69; N, 3.22.

(E)-2,4,6-triisopropyl-N-[(E)-3-(4-methoxyphenyl)allylidene]benzenesulfonamide (9h). Recrystallization from hexane/AcOEt (2/1) gave **9h** in 82% as a colorless needles of mp 172-173 °C. ¹H NMR: 1.25 (6H, d, *J*=7.0 Hz), 1.27 (12H, d, *J*=7.0 Hz), 2.90 (1H, septet, 7.0 Hz), 3.86 (3H, s), 4.25 (2H, septet, 7.0 Hz), 6.87 (1H, dd, *J*=9.2, 15.6 Hz), 6.93 (1H, d, *J*=8.6 Hz), 7.18 (2H, s), 7.39 (2H, d, *J*=15.6 Hz), 7.52 (2H, d, *J*=8.6 Hz), 8.70 (1H, d, *J*=9.2 Hz). ¹³C NMR: 21.2, 23.5, 24.7, 29.7, 34.2, 123.9, 124.9, 125.8, 129.1, 129.2, 131.2, 132.4, 134.3, 138.9, 151.1, 153.2, 153.6, 169.4. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 427 (M⁺). *Anal.* Calcd for

C₂₅H₃₃NO₃S: C, 70.22; H, 7.78; N, 3.28. Found: C, 70.24; H, 7.78; N, 3.28.

(*E*)-*N*-[(*E*)-3-(2-chlorophenyl)allylidene]-2,4,6-triisopropylbenzenesulfonamide (9i).

Recrystallization from hexane/AcOEt (3/1) gave **9i** in 76% as colorless needles of mp 144-145 °C. ¹H NMR: 1.25 (6H, d, *J*=6.7 Hz), 1.27 (12H, d, *J*=6.7 Hz), 2.91 (1H, septet, 6.7 Hz), 4.25 (2H, septet, *J*=6.7 Hz), 6.99 (1H, dd, *J*=9.5, 15.9 Hz), 7.19 (1H, s), 7.31-7.40 (3H, m), 7.45 (1H, d, *J*=7.6 Hz), 7.69 (1H, d, *J*=7.6 Hz), 7.91 (1H, d, *J*=15.9 Hz), 8.80 (1H, d, *J*=9.5 Hz). ¹³C NMR: 23.4, 24.7, 29.7, 34.2, 123.9, 127.2, 127.4, 127.8, 130.4, 130.9, 132.1, 132.4, 135.3, 147.9, 151.2, 153.7, 169.1. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 432 (M⁺). *Anal.* Calcd for C₂₄H₃₀ClNO₂S: C, 68.72; H, 7.00; N, 3.24. Found: C, 68.56; H, 6.91; N, 3.25.

(*E*)-2,4,6-triisopropyl-*N*-[(*E*)-3-(4-chlorophenyl)allylidene]benzenesulfonamide (9j).

Recrystallization from hexane/AcOEt (3/1) gave **9j** in 83% as colorless needles of mp 192-193 °C. ¹H NMR: 1.25 (6H, d, *J*=7.0 Hz), 1.27 (12H, d, *J*=7.0 Hz), 2.90 (1H, septet, *J*=7.0 Hz), 4.23 (2H, septet, *J*=7.0 Hz), 6.96 (1H, dd, *J*=9.5, 15.9 Hz), 7.19-7.50 (7H, m), 8.74 (1H, d, *J*=9.5 Hz). ¹³C NMR: 23.5, 24.7, 29.7, 34.2, 123.9, 125.6, 129.5, 129.6, 131.1, 132.8, 137.5, 151.0, 151.1, 153.7, 168.9. IR (nujor): 1580, 1380, 1150 cm⁻¹. EIMS *m/z*: 432 (M⁺). *Anal.* Calcd for C₂₄H₃₀ClNO₂S: C, 68.72; H, 7.00; N, 3.24. Found: C, 68.56; H, 6.91; N, 3.25.

(*E*)-2,4,6-triisopropyl-*N*-[(*E*)-3-(naphthalen-1-yl)allylidene]benzenesulfonamide (9k).

Recrystallization from hexane/AcOEt (5/1) gave **9k** in 71% as brown needles of mp 161-162 °C. ¹H NMR: 1.26 (6H, d, *J*=6.7 Hz), 1.28 (12H, d, *J*=6.7 Hz), 2.92 (1H, septet, *J*=6.7 Hz), 4.29 (2H, septet, *J*=6.7 Hz), 7.12 (1H, dd, *J*=9.5, 15.3 Hz), 7.21 (2H, s), 7.51-7.64 (3H, m), 7.85 (1H, d, *J*=7.9 Hz), 7.90 (1H, d, *J*=7.9 Hz), 7.95 (1H, d, *J*=7.9 Hz), 8.15 (1H, d, *J*=8.9 Hz), 8.31 (1H, d, *J*=15.3 Hz), 8.90 (1H, d, *J*=9.5 Hz). ¹³C NMR: 23.4, 24.7, 29.7, 34.2, 122.7, 123.9, 125.5, 125.9, 126.5, 127.3, 127.4, 128.9, 129.0, 131.2, 131.3, 131.9, 133.8, 149.4, 151.1, 153.6, 169.4. IR (nujor): 1560, 1380, 1150 cm⁻¹. EIMS *m/z*: 447 (M⁺). *Anal.* Calcd for C₂₈H₃₃NO₂S: C, 75.13; H, 7.43; N, 3.22. Found: C, 74.89; H, 7.30; N, 3.22.

(*E*)-2,4,6-triisopropyl-*N*-[(*E*)-3-(naphthalen-2-yl)allylidene]benzenesulfonamide (9l).

Recrystallization from hexane/AcOEt (7/1) gave **9l** in 81% as brown needles of mp 180-181 °C. ¹H NMR: 1.26 (6H, d, *J*=7.0 Hz), 1.28 (12H, d, *J*=7.0 Hz), 2.91 (1H, septet, *J*=7.0 Hz), 4.27 (2H, septet, *J*=7.0 Hz), 7.11 (1H, dd, *J*=9.2, 15.6 Hz), 7.20 (2H, s), 7.54-7.97 (8H, m), 8.80 (1H, d, *J*=9.2 Hz). ¹³C NMR: 23.5, 24.7, 29.7, 34.2, 123.4, 123.9, 125.2, 127.1, 127.9, 128.0, 128.9,

129.1, 131.1, 131.3, 131.9, 133.2, 134.7, 151.1, 152.9, 153.6, 169.4. IR (nujor): 1560, 1380, 1150 cm^{-1} . EIMS m/z : 447 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{S}$: C, 75.13; H, 7.43; N, 3.22. Found: C, 75.13; H, 7.36; N, 3.11.

(*E*)-*N*-[(*E*)-3-(furan-2-yl)allylidene]-2,4,6-triisopropylbenzenesulfonamide (9m).

Recrystallization from hexane/AcOEt (3/1) gave **9m** in 53% as colorless needles of mp 160.5–161 °C. ^1H NMR: 1.26 (6H, d, $J=7.1$ Hz), 1.28 (12H, d, $J=7.1$ Hz), 2.90 (1H, septet, $J=7.1$ Hz), 4.24 (2H, septet, $J=7.1$ Hz), 6.53–6.64 (1H, m), 6.74–6.75 (1H, m), 6.85 (1H, dd, $J=9.8, 15.6$ Hz), 7.17 (3H, s), 7.56 (1H, s), 8.66 (1H, d, $J=9.8$ Hz). ^{13}C NMR: 23.4, 24.7, 29.7, 34.2, 113.0, 117.1, 122.7, 123.6, 123.8, 131.3, 137.7, 146.3, 151.0, 153.5, 168.7. IR (nujor): 1580, 1380, 1150 cm^{-1} . EIMS m/z : 387 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_3\text{S}$: C, 68.18; H, 7.54; N, 3.61. Found: C, 68.09; H, 7.51; N, 3.61.

Table 1, entry 1: Asymmetric ethylation of cinnamaldehyde 1 catalyzed by 4c-copper(I). (–)-(*R*)-3-phenylpentan-1-ol 2 and (*S,E*)-1-phenylpent-1-en-3-ol 3a. Under Ar atmosphere, a solution of amidophosphine **4c** (40.1 mg, 0.065 mmol) in 4 mL of toluene was added to a suspension of $\text{Cu}(\text{OTf})_2$ (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 cinnamaldehyde **1** (132 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 satd NH_4Cl , 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 NaHCO_3 and brine, and then dried over Na_2SO_4 . Concentration gave a pale yellow oil, which was treated with NaBH_4 (37 mg, 1.0 mmol) in methanol (4 mL) for 0.5 h under ice bath cooling. After addition of water and ethyl acetate, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO_3 and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/ethyl acetate = 50/1) gave (–)-*R*-**2** (41 mg, 25% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -1.48$ (c 0.99, benzene) and (–)-*S*-**3a** (48 mg, 30% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -0.26$ (c 1.13, CHCl_3).

(–)-*R*-**2**: The ee was determined to be 7% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 16.0 min and minor 20.4 min). The absolute

configuration was determined to be *R* by the specific rotation (Pridgen, N.; Mokhallalati, M. K.; Wu, M.-J. *J. Org. Chem.* **1992**, *57*, 1237–1241). ¹H NMR: 0.78 (3H, t, *J*=7.4 Hz), 1.11 (1H, brs), 1.56–2.00 (4H, m), 2.59 (1H, tt, *J*=4.7, 4.7 Hz), 3.45–3.56 (2H, m), 7.15–7.3 (5H, m). ¹³C NMR: 12.1, 29.7, 39.1, 44.2, 61.0, 126.0, 127.6, 128.3, 144.9. IR (neat): 3350 cm⁻¹. EIMS *m/z*: 164 (*M*⁺).

(–)-*S*-**3a**: The ee was determined to be 13% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 1.0 mL/min, 254 nm, major 14.0 min and minor 21.7 min). The absolute configuration was determined to be *S* by the specific rotation in Okamoto, T.; Oka, S. *J. Org. Chem.* **1983**, *49*, 1589–1594. ¹H NMR: 0.97 (3H, t, *J*=7.3 Hz), 1.26 (1H, brs), 1.59–1.73 (2H, m), 4.20–4.23 (1H, m), 6.22 (1H, dd, *J*=7.3, 15.9 Hz), 6.58 (1H, d, *J*=15.9 Hz), 7.04–7.53 (5H, m). ¹³C NMR: 9.7, 30.8, 74.3, 125.6, 126.4, 127.5, 127.9, 128.5, 130.3, 132.2. IR (neat): 3550, 3100 cm⁻¹. EIMS *m/z*: 162 (*M*⁺).

Asymmetric ethylation of *N*-sulfonylimine **1b with diethylzinc catalyzed by amidophosphane (**4c**)-copper (Table 1).** Under Ar atmosphere, a solution of amidophosphine **4c** (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 α,β-unsaturated imine (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 hexane solution of diethylzinc (2.0 mL, 2.0 mmol) was added at 0 °C and the whole was stirred at 0 °C for the indicated time. The reaction was quenched with satd NH₄Cl 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 gave a pale yellow oil which was dissolved in 4.4 mL of THF/10% aq HCl (10/1) and the whole was stirred at room temperature for 1 h. Ethyl acetate (10 mL) and water (5 mL) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO₃ and brine, and then dried over Na₂SO₄. Concentration gave a pale yellow oil, which was treated with NaBH₄ (37 mg, 1.0 mmol) in methanol (4 mL) for 0.5 h under ice bath cooling. After addition of water and ethyl acetate, 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 gave **2**

and **3**.

Table 1, entry 2: From 1b to 2 and (-)-(E)-N-(1-phenylpent-1-en-3-yl)methanesulfonamide (3b). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave (-)-**R-2** (32% ee, 68 mg, 41% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -5.00$ (*c* 1.34, benzene) and **3b** (76 mg, 32% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -47.8$ (*c* 0.50, ethanol).

3b: The ee was determined to be 68% by ^1H NMR using $\text{Eu}(\text{hfc})_3$ (methyl proton, major peak at 3.55 ppm, minor peak at 3.41 ppm). ^1H NMR: 1.00 (3H, t, $J=7.7$ Hz), 1.6-1.8 (2H, m), 2.94 (3H, s), 3.95-4.05 (1H, m), 4.42 (1H, d, $J=7.4$ Hz), 6.05 (1H, dd, $J=7.9, 15.9$ Hz), 6.60 (1H, d, $J=15.9$ Hz), 7.12-7.43 (5H, m). ^{13}C NMR: 10.2, 29.1, 42.2, 57.9, 126.4, 128.0, 128.6, 129.2, 132.1, 136.1. IR (neat): 3250, 1600, 1490, 1310, 1150 cm^{-1} . EIMS m/z : 239 (M^+). HRMS-FAB (m/z): Calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}-\text{H}]^-$: 238.0902. Found: 238.0894.

Table 2, entry 1: 2 and (-)-(E)-N-(1-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3c). Silica gel column chromatography (hexane/ethyl acetate =20/1) gave (-)-**R-2** (16% ee, 65 mg, 40% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -2.00$ (*c* 0.60, benzene) and **3c** (117 mg, 37% yield) as a colorless solid of $[\alpha]^{25}_{\text{D}} -82.4$ (*c* 0.93, ethanol).

3c: The ee was determined to be 83% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=10/1, 0.6 mL/min, 254 nm, major 19.6 min and minor 22.3 min). ^1H NMR: 0.89 (3H, t, $J=7.3$ Hz), 1.52-1.65 (2H, m), 2.31 (3H, s), 3.82-3.88 (1H, m), 4.65 (1H, d, $J=7.6$ Hz), 5.71 (1H, dd, $J=7.6, 15.9$ Hz), 6.21 (1H, d, $J=15.9$ Hz), 7.01-7.76 (9H, m). ^{13}C NMR: 9.93, 21.4, 28.9, 57.7, 126.3, 127.3, 127.6, 128.4, 128.6, 129.5, 131.6, 136.3, 138.1, 143.2. IR (neat): 3250, 1600, 1490, 1310, 1150 cm^{-1} . EIMS m/z : 315 (M^+). *Anal.* Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.35; H, 6.71; N, 4.26.

Table 2, entry 2: 2 and (-)-(E)-2,4,6-triisopropyl-N-(1-phenylpent-1-en-3-yl)benzene-sulfonamide (3d). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave (-)-**R-2** (16% ee, 94 mg, 57% yield) of $[\alpha]^{25}_{\text{D}} -1.97$ (*c* 0.96, benzene) as a colorless oil and **3d** (77 mg, 18% yield) as a colorless solid of $[\alpha]^{25}_{\text{D}} -25.1$ (*c* 0.82, ethanol).

3d: The ee was determined to be 67% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 16.4 min and minor 9.88 min). ^1H NMR: 0.92 (3H, t, $J=7.4$ Hz), 1.21 (6H, d, $J=6.7$ Hz), 1.25 (12H, d, $J=6.7$ Hz), 1.57 (2H, m), 2.82 (1H, septet, $J=6.7$ Hz), 3.98 (1H,

m), 4.13 (2H, septet, $J=6.7$ Hz), 4.40 (1H, d, $J=6.4$ Hz), 5.71 (1H, dd, $J=7.7, 15.9$ Hz), 6.21 (1H, d, $J=15.9$ Hz), 7.03-7.27 (7H, m). ^{13}C NMR: 9.90, 23.4, 24.5, 24.8, 29.6, 33.9, 57.5, 123.6, 126.2, 127.6, 128.3, 128.8, 131.7, 134.2, 136.2, 149.7, 152.4. IR (neat): 3250, 1600, 1490, 1310, 1150 cm^{-1} . EIMS m/z : 427 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{37}\text{NO}_2\text{S}$: C, 73.02; H, 8.72; N, 3.28. Found: C, 72.73; H, 8.59; N, 3.53

Table 2, entry 12 (Table 3, entry 1): Asymmetric ethylation of **1d with diethylzinc catalyzed by **5a-copper(I)** giving **2**.** Under Ar atmosphere, a solution of amidophosphine **5a** (30.5 mg, 0.065 mmol) in 4 mL of toluene was added to a suspension of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ (15.1 mg, 0.050 mmol) and MS4A (750 mg) in 14.5 mL toluene. The resulting solution was stirred for 1 h at room temperature. A solution of unsaturated imine **1d** (1.0 mmol) in 13 mL of toluene was added at room temperature. After stirring at room temperature for 10 min, the reaction mixture was cooled to -40 $^\circ\text{C}$ over 40 min, and then stirred at -40 $^\circ\text{C}$ for 0.5 h. A hexane solution of diethylzinc (1.2 mL, 1.2 mmol) was added at -40 $^\circ\text{C}$ and the whole was stirred at -40 $^\circ\text{C}$ for 2 h. Then, a hexane solution of diethylzinc (1.2 mL, 1.2 mmol) was added and the whole was stirred at -40 $^\circ\text{C}$ for further 3 h. The reaction was quenched with satd NH_4Cl and stirred at room temperature for 0.5 h. After filtration through celite, the organic layer was separated and the water layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO_3 and brine, and then dried over Na_2SO_4 . Concentration gave a pale yellow oil, which was filtered through aluminium oxide 90 standardized (Merck, 20 g) using ethyl acetate (300 mL) as an eluate. Concentration gave a pale yellow oil, which was treated with NaBH_4 (37 mg, 1.0 mmol) in methanol (4.0 mL) for 0.5 h under ice bath cooling. After addition of water and ethyl acetate, the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with satd NaHCO_3 and brine, and then dried over Na_2SO_4 . Concentration and purification by silica gel column chromatography (hexane/ethyl acetate = 20/1) gave (–)-**R-2** (127 mg, 77% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -5.62$ (c 1.12, CHCl_3). The ee was determined to be 80% by HPLC (Daicel Chiralcel OD-H, hexane/ i -PrOH=50/1, 1.0 mL/min, 254 nm, major 15.7 min and minor 19.4 min).

(–)-3-*o*-tolylpentan-1-ol (10e) (Table 3, Entry 2). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10e** (151 mg, 84% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -5.47$ (c 1.06, CHCl_3). The ee was determined to be 83% by HPLC (Daicel Chiralcel OD-H, hexane/ i -

PrOH=50/1, 1.0 mL/min, 254 nm, major 14.6 min and minor 16.1 min). ¹H NMR: 0.78 (3H, t, *J* = 6.4 Hz), 1.16 (1H, brs), 1.53-1.99 (4H, m), 2.33 (3H, s), 2.95-2.99 (1H, m), 3.43-3.56 (2H, m), 7.06-7.17 (4H, m). ¹³C NMR: 11.7, 19.2, 29.6, 38.0, 39.0, 61.0, 125.5, 125.7, 126.2, 130.1, 136.4, 143.3. IR (neat): 3360 cm⁻¹. EIMS *m/z*: 178 (M⁺). HRMS (EI⁺) Calcd for C₁₂H₁₈O: 178.1358. Found: 178.1362.

(-)-3-*m*-tolylpentan-1-ol (10f) (Table 3, Entry 3). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10f** (151 mg, 81% yield) as a colorless oil of [α]_D²² -3.21 (*c* 1.09, CHCl₃). The ee was determined to be 80% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 50/1, 1.0 mL/min, 254 nm, major 13.5 min and minor 15.2 min). ¹H NMR: 0.78 (3H, t, *J* = 6.4 Hz), 1.16 (1H, brs), 1.53-1.99 (4H, m), 2.33 (3H, s), 2.95-2.99 (1H, m), 3.43-3.56 (2H, m), 7.06-7.17 (4H, m). ¹³C NMR: 11.9, 19.2, 29.6, 38.3, 39.6, 61.3, 125.5, 126.2, 130.4, 135.9, 144.5. IR (neat): 3360 cm⁻¹. EIMS *m/z*: 178 (M⁺). *Anal.* Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.16.

(-)-3-(2-methoxyphenyl)pentan-1-ol (10g) (Table 3, Entry 4). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10g** (146 mg, 75% yield) as a colorless oil of [α]_D²⁵ -3.58 (*c* 1.31, CHCl₃). The ee was determined to be 75 % by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 15.0 min and minor 23.1 min). ¹H NMR: 0.81 (3H, t, *J*=7.4 Hz), 1.54-1.70 (3H, m), 1.97-2.17 (2H, m), 3.10-3.19 (1H, m), 3.30-3.35 (1H, m), 3.45-3.50 (1H, brs), 3.79 (3H, s), 6.87-6.89 (m, 1H), 6.95-6.97 (1H, m), 7.14-7.18 (2H, m). ¹³C NMR: 12.0, 28.3, 34.9, 38.9, 55.5, 60.8, 110.6, 121.1, 126.8, 127.3, 132.8, 157.5. IR (neat): 3350 cm⁻¹. EIMS *m/z*: 194 (M⁺). *Anal.* Calcd for C₁₂H₁₈O₂: C, 74.19; H, 9.34. Found: C, 73.91; H, 9.35.

(-)-3-(4-methoxyphenyl)pentan-1-ol (10h) (Table 3, Entry 5). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10h** (151 mg, 78% yield) as a colorless oil of [α]_D²⁵ -5.83 (*c* 1.08, CHCl₃). The ee was determined to be 79% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 22.1 min and minor 24.4 min). ¹H NMR: 0.77 (3H, t, *J* = 7.4 Hz), 1.11 (1H, brs), 1.54-2.04 (4H, m), 2.55 (1H, m), 3.45-3.56 (2H, m), 3.83 (3H, s), 6.83-6.85 (2H, m), 7.07-7.08 (2H, m). ¹³C NMR: 11.9, 29.8, 39.3, 43.2, 55.1, 61.0, 113.7, 128.5, 136.9, 157.9. IR (neat): 3350 cm⁻¹. EIMS *m/z*: 194 (M⁺). *Anal.* Calcd for C₁₂H₁₈O₂: C, 74.19; H, 9.34. Found: C, 74.33; H, 9.34.

(–)-3-(2-chlorophenyl)pentan-1-ol (10i) (Table 3, Entry 6). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10i** (156 mg, 79% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -3.58$ (c 1.31, CHCl_3). The ee was determined to be 82% by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 15.7 min and minor 18.2 min). ^1H NMR: 0.80 (3H, t, J = 7.4 Hz), 1.54-1.70 (3H, m), 1.97-2.17 (2H, m), 3.10-3.19 (1H, m), 3.30-3.35 (1H, m), 3.45-3.50 (1H, brs), 6.87-6.97 (2H, m), 7.14-7.18 (2H, m). ^{13}C NMR: 11.6, 29.0, 38.8, 39.9, 60.9, 127.1, 127.8, 129.5, 134.6, 142.3, 157.5. IR (neat): 3340 cm^{-1} . EIMS m/z : 198 (M^+). *Anal.* Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}$: C, 66.49; H, 7.61. Found: C, 66.54; H, 7.71.

(–)-3-(4-chlorophenyl)pentan-1-ol (10j) (Table 3, Entry 7). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10j** (154 mg, 78% yield) as a colorless oil of $[\alpha]^{25}_{\text{D}} -4.55$ (c 1.34, CHCl_3). The ee was determined to be 78% by HPLC (Daicel Chiralcel AS-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 20.3 min and minor 16.1 min). ^1H NMR: 0.80 (3H, t, J = 7.4 Hz), 1.25 (1H, brs), 1.50-1.58 (2H, m), 1.63-1.79 (2H, m), 1.90-1.98 (1H, m), 3.37 (1H, m), 3.45-3.53 (1H, m), 7.11-7.36 (4H, m). ^{13}C NMR: 11.9, 29.6, 39.1, 43.5, 60.9, 128.6, 129.0, 131.8, 143.5, . IR (neat): 3350 cm^{-1} . EIMS m/z : 198 (M^+). *Anal.* Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}$: C, 66.49; H, 7.61. Found: C, 66.77; H, 7.71.

(–)-3-(naphthalen-1-yl)pentan-1-ol (10k) (Table 3, Entry 8). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10k** (175 mg, 82% yield) as a pale yellow oil of $[\alpha]^{25}_{\text{D}} -4.01$ (c 1.27, CHCl_3). The ee was determined to be 91% by HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 19.9 min and minor 21.9 min). ^1H NMR: 0.82 (3H, t, J =7.3 Hz), 1.14 (1H, brs), 1.85 (2H, m), 2.01-2.13 (2H, m), 3.45-3.63 (3H, m), 7.41-8.23 (7H, m). ^{13}C NMR: 11.8, 29.4, 38.7, 44.1, 60.9, 123.1, 123.2, 125.3, 125.5, 125.7, 126.4, 128.9, 132.6, 133.9, 141.3. IR (neat): 3350 cm^{-1} . EIMS m/z : 214 (M^+). HRMS (EI^+) Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: 214.1357. Found: 214.1352.

(–)-3-(naphthalen-2-yl)pentan-1-ol (10l) (Table 3, Entry 9). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10l** (182 mg, 85% yield) as a colorless oil of $[\alpha]^{22}_{\text{D}} -2.41$ (c 1.11, CHCl_3). The ee was determined to be 75% by HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 23.6 min and minor 22.3 min). ^1H NMR: 0.80 (3H, t, J = 7.4 Hz), 1.13 (1H, brs), 1.76 (2H, m), 1.89-2.05 (2H, m), 2.78 (1H, m), 3.46-3.58 (3H, m), 7.4-8.2 (7H, m). ^{13}C NMR: 12.0, 29.5, 38.9, 44.2, 60.9, 125.1, 125.6, 125.8, 126.4,

127.4, 127.5, 128.1, 132.3, 133.4, 142.4. IR (neat): 3350 cm^{-1} . EIMS m/z : 214 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.07; H, 8.47. Found: C, 83.91; H, 8.51.

3-(furan-2-yl)pentan-1-ol (10m) (Table 3, Entry 10). Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave **10m** (175 mg, 72% yield) as a colorless oil of $[\alpha]_{\text{D}}^{23} -6.67$ (c 0.63, CHCl_3). The ee was determined to be 67% ee by ^{19}F NMR of the corresponding (*R*)-Mosher ester (trifluoromethyl group, major peak at 3.55 ppm, minor peak at 3.41 ppm). ^1H NMR: 0.84 (3H, d, $J=7.3\text{Hz}$), 1.26 (1H, brs), 1.65 (2H, m), 1.86 (2H, m), 2.78 (1H, m), 3.51-3.64 (2H, m), 6.02 (1H, d, $J=2.3\text{ Hz}$), 6.28 (1H, m), 7.32 (1H, s). ^{13}C NMR: 11.7, 27.2, 36.8, 37.2, 61.0, 105.3, 109.8, 134.8, 140.9. IR (neat): 3340 cm^{-1} . EIMS m/z : 154 (M^+). HRMS (EI) Calcd for $\text{C}_9\text{H}_{14}\text{O}_2$: 154.0989. Found: 154.0990.

(*R*)-MTPA ester was synthesized by the reported way in Meyers, A. I.; Roth, G. P; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611-4624.

To a solution of **10m** (9.4 mg, 0.061 mmol) in CHCl_3 (1 mL), (*R*)-MTPA-Cl (50.9 mg, 0.201 mmol) and Et_3N (10 μL) were added at room temperature and the whole was stirred for 18 h. After addition of ether (5 mL) and 3-(dimethylamino)propylamine (1.0 mL) the whole was washed with 1N aq HCl, satd NaHCO_3 , and brine (10 mL), and then dried over Na_2SO_4 . Concentration gave MTPA ester (22.3 mg). ^1H NMR: 0.79 (3H, t, $J=7.7\text{ Hz}$), 0.82 (1H, m), 1.63 (2H, m), 1.98 (1H, m), 2.65 (1H, m), 3.55 (3H, d, $J=5.5\text{ Hz}$), 4.15-4.27 (2H, m), 5.95 (1H, m), 6.28 (1H, brs), 7.30-7.59 (6H, m). ^{13}C NMR: 11.6, 27.0, 29.7, 32.3, 37.2, 64.8, 109.9, 127.5, 128.5, 128.8, 129.7, 129.9, 141.4. IR (neat): 1750 cm^{-1} . EIMS m/z : 370 (M^+). HRMS (EI^+) Calcd for $\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_4$: 370.1392. Found: 370.1402.

(-)-4-methyl-3-(naphthalen-1-yl)pentan-1-ol (10n) (Table 3, Entry 11). Silica gel column chromatography (hexane/ethyl acetate = 15/1) gave **10n** (176 mg, 77% yield) as a pale yellow oil of $[\alpha]_{\text{D}}^{23} -12.1$ (c 1.19, CHCl_3). The ee was determined to be 78% by HPLC (Daicel Chiralcel OJ and OJ-H were connected, hexane/*i*-PrOH=50/1, 1.0 mL/min, 254 nm, major 24.9 min and minor 29.2 min). ^1H NMR: 0.80 (3H, brs), 1.03 (3H, brs), 1.09 (1H, brs), 1.99 (2H, brs), 2.24 (1H, m), 3.34 (1H, brs), 3.46 (2H, brs), 7.39-8.11 (7H, m). ^{13}C NMR: 20.1, 21.2, 34.0, 35.1, 41.5, 61.4, 123.3, 123.5, 125.3, 125.4, 125.8, 126.4, 129.0, 133.1, 133.9, 140.8. IR (neat): 3340 cm^{-1} . EIMS m/z : 228 (M^+). HRMS (EI^+) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514. Found: 228.1513.

80 % ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 15.8 min, minor 19.5 min

83 % ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 14.0 min, minor 16.1 min

80 % ee(HPLC, Daicel Chiralcel AD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 13.5 min, minor 15.2 min

75 % ee(HPLC, Daicel Chiralcel AD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 15.0 min, minor 23.1 min

79 % ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 22.1 min, minor 24.4 min

82% ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 15.0 min, minor 16.0 min

79 % ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 22.1 min, minor 24.4 min)

91 % ee(HPLC, Daicel Chiralcel AD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 19.9 min, minor 21.9 min)

75 % ee(HPLC, Daicel Chiralcel OD-H, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 14.0 min, minor 16,1 min

78% ee(HPLC, Daicel Chiralcel OJ and OJ-H were connected, Hexane/ i-PrOH=50/1, 1.0 ml/min, 254 nm, major 24.9 min, minor 29.2 min