Supporting Information

A New Zinc(II)-Based Catalyst for Enantioselective Azomethine Ylide Cycloadditions

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I. General Methods

Reactions were performed in flame-dried glassware under an atmosphere of argon. Dichloromethane (DCM) was dried and distilled over calcium hydride prior to use. Commercial $\text{Zn}(\text{OTf})_2$ was benzene-azeotroped, placed under vacuum for about 1 h and stored under Ar in a desiccator. Chiral Fam (ferrocenyl substituted aziridinyl methanol) ligands **7**, **7a**, **7b**, and **7c** were benzene-azeotroped and dissolved in dry DCM before transferring into the reaction flask. Liquid dipolarophiles were distilled and kept under Ar prior to use. Stock solutions of the solid N-methyl maleimide and solid dimethyl fumarate in dry DCM were transferred *via* syringe. Et_3N was distilled and kept over NaOH pellets under Ar. Products were purified by flash column chromatography on silica gel 60 (Merck, 230–400 mesh ASTM). TLC analyses were performed on 250 μm Silica Gel 60 F254 plates and visualized by quenching of the UV fluorescence at 254 nm. All melting points were taken in open-end capillary tubes and are uncorrected. IR spectra are reported in reciprocal centimeters (cm^{-1}). Unless indicated otherwise, ^1H -NMR and ^{13}C -NMR samples were prepared in 1:1 $\text{CDCl}_3\text{-CCl}_4$ and recorded at 400 MHz and 100 MHz, respectively. ^1H -NMR data are reported as chemical shifts (δ , ppm) relative to tetramethylsilane (δ 0.00), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad singlet), coupling constant (Hz) and integration. Proton decoupled ^{13}C -NMR data are reported as chemical shifts. High resolution MS data were obtained using electron impact (EI) ionization. Enantiomeric excess (ee) was determined by chiral HPLC analysis using a chiral stationary phase (Daicel Chiralcel OD or Chiralpak AS), eluting with *i*-PrOH-hexanes, and using UV detection at 210 nm or 230 nm.

II. Characterization Data

Synthesis of Aziridino Ketones 5 and 6: Br_2 (4.57 mmol in 9.0 mL DCM) was added to a stirred solution of **4** (1.00 g, 4.17 mmol) in DCM at $-78\text{ }^\circ\text{C}$ over 5 minutes, at which point the reaction was judged to be complete by TLC. The crude mixture was filtered

through a short plug of silica gel using CHCl_3 as the eluent. Evaporation of the solvent gave pure 1,2-dibromopronionylferrocene (1.63 g, 98% yield). To a stirred solution of this material (1.0 g, 2.5 mmol) in CHCl_3 (0.1 M) was added Et_3N (0.592 mL, 4.25 mmol). After 4-5 h at rt, TLC analysis signified complete conversion to α -bromoacryloylferrocene. To this solution was added D-(+)- α -methylbenzylamine (0.574 mL, 4.45 mmol) and the mixture was stirred at rt overnight. The solvent was removed by rotary evaporation and the crude reaction mixture was flash chromatographed on silica gel (3:1 hexanes-EtOAc) to afford aziridine **5** (54% yield) and **6** (42%).

Aziridino Ketone 5: R_f = 0.17, 3:1 hexanes-EtOAc; mp 123-125 °C; $[\alpha]_D^{25}$ = 74.9 (*c* 0.5, DCM); ^1H NMR δ 7.42 (d, J = 7.4 Hz, 2H, Ph), 7.34 (t, J = 7.4 Hz, 2H, Ph), 7.26 (t, J = 7.2 Hz, 1H, Ph), 5.03 (br, 1H, ferrocene), 4.94 (br, 1H, ferrocene), 4.52 (br, 2H, ferrocene), 4.23 (s, 5H, ferrocene), 2.62 (q, J = 6.5 Hz, 1H), 2.57 (dd, J = 6.5 & 3.0 Hz, 1H), 2.26 (br, 1H), 1.66 (d, J = 6.5 Hz, 1H), 1.55 (d, J = 6.5 Hz, 3H); ^{13}C NMR δ 199.8, 143.8, 128.4, 127.3, 126.9, 78.07, 72.32, 72.21, 70.36, 69.88, 69.82, 43.50, 35.64, 23.72; IR (neat) 2939, 1660, 1450, 1251, 818, 796, 701. HRMS (EI) for $\text{C}_{21}\text{H}_{21}\text{FeNO}$ calculated 359.0973, found 359.0971.

Aziridino Ketone 6. R_f = 0.1, 3:1 hexanes-EtOAc; mp: 114-116 °C; $[\alpha]_D^{25}$ = 185.9 (*c* 0.4, DCM); ^1H NMR δ 7.37 (d, J = 7.3 Hz, 2H, Ph), 7.25 (t, J = 7.6 Hz, 2H, Ph), 7.14 (t, J = 7.3 Hz, 1H, Ph), 4.59 (br, 2H, ferrocene), 4.32 (br, 2H, ferrocene), 3.81 (s, 5H, ferrocene), 2.51 (q, J = 6.5 Hz, 1H), 2.44 (dd, J = 6.5 & 3.1 Hz, 1H), 2.33 (dd, J = 2.6 & 1.5 Hz, 1H), 1.74 (dd, J = 6.5 & 1.3 Hz, 1H), 1.45 (d, J = 6.6 Hz, 3H); ^{13}C NMR δ 199.1, 144.3, 137.3, 128.7, 127.6, 126.9, 78.60, 72.28, 72.11, 71.12, 69.72, 69.49, 69.37, 41.51, 37.07, 23.58; IR(neat) 2969, 1660, 1455, 1251, 823, 755, 696. HRMS (EI) for $\text{C}_{21}\text{H}_{21}\text{FeNO}$ calculated 359.0973, found 359.0971.

Synthesis of Chiral Ligand Fam-7: Aziridino ketone **5** (1.34 g, 3.73 mmol) was dissolved in MeOH (0.1 M) and cooled to $-78\text{ }^{\circ}\text{C}$. To this stirred solution was added ZnCl_2 (762 mg, 5.59 mmol). After 1 h, NaBH_4 (282 mg, 7.46 mmol) was added and stirring continued at $-78\text{ }^{\circ}\text{C}$ for 2 hours when TLC analysis showed the reaction to be complete. The reaction mixture was partitioned between DCM (2 x 25 mL) and water (25 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated to give crude **7**. Purification by flash column chromatography on silica gel eluting with 4:1 hexane-EtOAc gave pure **7** (1.29g) in 96% yield. $R_f = 0.5$, 2:1 hexanes-EtOAc; mp: $83\text{--}85\text{ }^{\circ}\text{C}$; $[\alpha]_D^{25} = 77.4$ (c 1.3, DCM); ^1H NMR δ 7.33-7.19 (m, 5H, Ph), 4.47 (d, $J = 3.8$ Hz, 1H), 4.26 (br, 1H, ferrocene), 4.23 (br, 1H, ferrocene), 4.17 (s, 5H, ferrocene), 4.13 (br, 2H, ferrocene), 2.61 (br, 1H, OH), 2.57 (q, $J = 6.5$ Hz, 1H), 1.83-1.80 (m, 1H), 1.80 (d, $J = 2.8$ Hz, 1H), 1.31 (d, $J = 6.6$ Hz, 3H), 1.29 (d, $J = 7.0$ Hz); ^{13}C NMR δ 144.2, 128.2, 126.9, 126.5, 89.7, 68.8, 68.4, 68.2, 67.8, 67.6, 67.0, 65.7, 43.8, 30.0, 23.5; IR (neat) 3431, 3100, 2969, 1494, 1445, 1221, 1100, 812, 759, 691, 481; HRMS (EI) for $\text{C}_{21}\text{H}_{23}\text{FeNO}$ calculated 361.1129, found 361.1123.

Synthesis of (S,R,R) Fam-7a: Ketone **5** (1.00 g, 2.78 mmol) was dissolved in THF (16 mL, distilled over Na-benzophenone) in a reaction flask. The flask was cooled to $-78\text{ }^{\circ}\text{C}$ and L-Selectride (4 mL, from 1M THF solution) was added slowly over 30 min. After stirring about 1h, TLC showed no starting material. To the reaction flask was added 10% NaOH solution (15 mL) followed by EtOAc (20 mL) and the two layers were separated. The aqueous layer was extracted one more time with EtOAc (25 mL). The combined organic layers were dried over MgSO_4 , concentrated and purified by flash chromatography on silica gel using 3:1 hexane/EtOAc. Ligand **7a** was obtained in 90% yield as yellow oil. ^1H NMR δ 7.34-7.27 (m, 3H, Ph), 7.24-7.19 (m, 2H, Ph), 4.30 (br,

1H), 4.18 (s, 5H, ferrocene), 4.13-4.10 (m, 4H, ferrocene), 2.70 (br, 1H, OH), 2.49 (q, $J = 6.5$ Hz, 1H), 1.79-1.76 (m, 1H), 1.72 (d, $J = 3.4$ Hz, 1H), 1.37 (d, $J = 6.6$ Hz, 3H) 1.34 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR δ 144.4, 128.3, 127.0, 126.7, 90.9, 70.2, 69.2, 68.6, 67.8, 67.7, 66.3, 65.8, 45.5, 31.5, 23.8. HRMS (EI) for $\text{C}_{21}\text{H}_{23}\text{FeNO}$ calculated 361.1129, found 361.1123.

Synthesis of (*S,S,R*) Fam-7b: Ketone **6** (1.34 g, 3.73 mmol) was dissolved in THF (37 mL) in a reaction flask (100 mL). Reaction flask was then cooled to $-78\text{ }^{\circ}\text{C}$ and ZnCl_2 (762 mg, 5.59 mmol) was added and the reaction mixture was stirred for 1 h at this temperature. Then LiAlH_4 (282 mg, 7.46 mmol) was added and stirring continued for about 2 h at which point TLC showed that no starting material was left. The contents of the reaction flask was hydrolyzed with distilled water and then extracted with DCM (25 mL). The aqueous layer was extracted one more time with DCM (25 mL). the combined organic layers were dried over MgSO_4 , concentrated and purified by flash chromatography on silica gel using 4:1 hexane/EtOAc. Alcohol **7b** was obtained in 82% yield as light yellow yellow oil. ^1H NMR δ 7.30-7.27 (m, 3H, Ph), 7.25-7.21 (m, 2H, Ph), 4.30 (d, $J = 3.4$ Hz, 1H), 4.07 (s, 5H, ferrocene), 4.05-4.04 (m, 2H, ferrocene), 4.03-4.02 (m, 2H, ferrocene), 2.64 (br, 1H, OH), 2.59 (q, $J = 6.5$ Hz, 1H), 2.02 (d, $J = 3.4$ Hz, 1H), 1.77-1.73 (m, 1H), 1.42 (d, $J = 6.7$ Hz, 1H), 1.40 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR δ 145.0, 129.2, 127.9, 127.3, 90.0, 70.1, 69.1, 68.5, 68.3, 67.5, 67.4, 67.0, 43.1, 30.6, 23.0. HRMS (EI) for $\text{C}_{21}\text{H}_{23}\text{FeNO}$ calculated 361.1129, found 361.1127.

Synthesis of (*R,S,R*) Fam-7c: Ketone **6** (1.00 g, 2.78 mmol) was dissolved in dry THF (0.17 M) under Ar and cooled to $-78\text{ }^{\circ}\text{C}$. L-Selectride (4 mL, 1 M in THF) was added slowly over 30 min. After stirring about 1h, TLC analysis indicated no starting material.

The reaction was partitioned between 10% NaOH solution (15 mL) was and EtOAc (2 x 25 mL). The combined organic layers were dried over MgSO₄, concentrated and purified by flash chromatography on silica gel (3:1 hexanes-EtOAc). Ligand **7c** was obtained as a yellow oil in 67% yield along with 25% of the *S,S,R*-diastereomer **7b**. *R_f* = 0.29, 2:1 hexanes-EtOAc; [α]_D²⁵ = 8.67 (*c* 1.30, DCM); ¹H NMR δ 7.34-7.23 (m, 5H, Ph), 4.05 (s, 5H, ferrocene), 4.03 (br, 1H, ferrocene), 3.97 (br, 1H, ferrocene), 3.94 (br, 2H, ferrocene) 3.76 (br, 1H), 2.50(q, *J* = 6.5 Hz, 1H), 1.98 (d, *J* = 4.0 Hz, 1H), 1.90 (d, *J* = 3.4 Hz, 1H), 1.77-1.73 (m, 1H), 1.5 (d, *J* = 6.5 Hz, 1H) 1.44 (d, *J* = 6.5 Hz, 3H); ¹³C NMR δ 144.4, 128.7, 127.6, 127.0, 90.0, 70.5, 69.8, 68.5, 67.6, 66.3, 66.1, 43.9, 32.0, 29.8, 22.8. IR (neat) 3412, 3086, 2960, 1489, 1455, 1378, 1280, 1105, 817, 754, 696, 482; HRMS (EI) for C₂₁H₂₃FeNO calculated 361.1129, found 361.1135.

General Procedure for Catalytic Asymmetric Cycloaddition: Dry Zn(OTf)₂ (10 or 5 mol%) was weighed in a glove bag into a pre-dried reaction flask under Ar. (Commercial Zn(OTf)₂ was dried by azeotroping with benzene under Ar and then removing the residual solvent under vacuum). The reaction flask was then connected to a vacuum line and heated with a heat gun for 10-15 minutes. Benzene-azeotroped chiral ligand (11.5 or 5.8 mol%) dissolved in freshly distilled DCM (1.8 mL per mmole of imine) was added to the reaction flask at rt. The homogeneous mixture was stirred at this temperature for about 1 h and then cooled to -20 °C. To this mixture was added sequentially, the imine (1 equiv), dry Et₃N (10 mol%) and the dipolarophile (1.1 equiv). The resulting mixture was stirred overnight at -20 °C under Ar, at which point the solvent was removed under reduced pressure and the crude product isolated by flash column chromatography on silica gel. The reaction can be performed on up to 500 mg of imine.

(2*S*,3*R*,4*S*,5*R*) 2,3,4-Tricarbomethoxy-5-phenylpyrrolidine (8). 90% ee as determined by HPLC, Chiralpak AS column, 7:3 hexanes-*i*-PrOH, *t_R*(major) = 6.9 min, *t_R*(minor) = 15.7 min; [α]_D²⁵ = 61.9 (*c* 1.44, DCM); ¹H NMR (CDCl₃, 400 MHz) δ 7.25-7.24 (m, 4H,

Ph), 7.20-7.17 (m, 1H, Ph), 4.38 (d, J = 6.7 Hz, 1H, H-5), 4.05 (d, J = 8.9 Hz, 1H, H-2), 3.74 (s, 3H, 2-CO₂Me), 3.62 (s, 3H, 3-CO₂Me), 3.61 (t, J = 8.4 Hz, 1H, H-3), 3.46 (t, J = 7.4 Hz, 1H, H-4), 3.28 (br, 1H, N-H), 3.16 (s, 3H, 4-CO₂Me); ¹³C NMR δ 170.8 170.6, 170.5, 137.2, 128.3, 127.6, 126.7, 65.47, 62.18, 52.49, 52.24, 51.92, 51.16, 51.04.

(2R,3R,4R,5S) 2,3,4-Tricarbomethoxy-5-phenylpyrrolidine (9): 68% ee as determined by HPLC, Chiralcel OD column, 9:1 hexanes-*i*-PrOH, t_R (minor) = 25.4 min, t_R (major) = 50.7 min; $[\alpha]_D^{25}$ = -11.5 (c 1.49 g/100mL, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.30-7.28 (m, 4H, Ph), 7.26-7.24(m, 1H, Ph), 4.62 (t, J = 6.8 Hz, 1H, H-5), 4.15 (t, J = 6.0 Hz, 1H, H-2), 3.84 (s, 3H, 2-CO₂Me), 3.77 (s, 3H, 3-CO₂Me), 3.61 (t, J = 6.6 Hz, 1H, H-3), 3.53 (t, J = 6.8 Hz, 1H, H-4), 3.19 (s, 3H, 4- CO₂Me), 2.76 (br, 1H, N-H); ¹³C NMR δ 172.4, 171.8, 171.3, 138.2, 137.2, 128.2, 127.8, 126.9, 65.48, 63.33, 53.81, 52.38, 52.34, 51.37, 50.68.

(2R,4R,5S) 2,4-Dicarbomethoxy-5-phenylpyrrolidine (10). 46% ee as determined by HPLC, Chiralcel OD column, 9:1 hexanes-*i*-PrOH, t_R (minor) = 14.2 and t_R (major) = 29.7 min; $[\alpha]_D^{25}$ = -20.9 (c 0.46, DCM); ¹H NMR (CDCl₃, 400 MHz) δ 7.27-7.22 (m, 5H, Ph), 4.51 (d, J = 7.8 Hz, 1H, H-5), 3.94 (t, J = 8.1 Hz, 1H, H-2), 3.82 (s, 3H, 2-CO₂Me), 3.28 (q, J = 7.2 Hz, 1H, H-4), 3.20 (s, 3H, 4-CO₂Me), 2.74 (br, 1H, NH), 2.42 (t, J = 7.3 Hz, 2H, H-3); ¹³C NMR δ 173.8, 173.0, 139.6, 128.8 (2xC), 127.8, 127.1 (2xC), 66.12, 60.13, 52.43, 51.38, 49.98, 33. 59.

(2R,4R,5S)-2-Carbomethoxy-4-carbo-tert-butoxy-5-phenylpyrrolidine (11). 88% ee as determined by HPLC, Chiralpak AS + guard column, 95:5 hexanes-*i*-PrOH, $t_R(\text{minor}) = 13$ min, $t_R(\text{major}) = 24.8$ min; $[\alpha]_D^{25} = -28.6$ (c 1.36, DCM); ^1H NMR (CDCl_3 , 400 MHz) δ 7.30 (d, $J = 7.3$ Hz, 2H, Ph) 7.23 (t, $J = 7.5$ Hz, 2H, Ph), 7.15 (t, $J = 7.1$ Hz, 1H, Ph), 4.38 (d, $J = 7.8$ Hz, 1H, H-5), 3.84 (t, $J = 8.3$ Hz, 1H, H-2), 3.74 (s, 3H, 2-CO₂Me), 3.16 (q, $J = 7.7$ Hz, 1H, H-4), 2.55 (br, 1H, NH), 2.38-2.31 (m, 1H, H-3), 2.27-2.20 (m, 1H, H-3), 0.95 (s, 9H, *t*-Bu); ^{13}C NMR δ 173.4, 171.5, 139.4, 128.1, 127.3, 80.3, 65.67, 59.88, 52.04, 50.17, 34.17, 30.75, 27.53.

(1S,2R,4S,5R)-Methyl-4-phenyl-7-methyl-6, 8-dioxo-3,7-diazabicyclo[3.3.0]octane-2-carboxylate (12). 70% ee as determined by HPLC, Chiralpak AS column + guard column, 4:1 *i*-PrOH-hexanes, $t_R(\text{minor}) = 7.3$ min, $t_R(\text{major}) = 16.5$ min; $[\alpha]_D^{25} = -61.9$ (c 1.24, DCM); ^1H -NMR (CDCl_3 , 400 MHz) δ 7.25-7.19 (m, 5H), 4.40 (dd, $J = 8.5$ and 5.8 Hz, 1H, H-4), 3.95 (t, $J = 6.1$ Hz, 1H, H-2), 3.80 (s, 3H, CO₂Me), 3.45 (t, $J = 7.2$ Hz, 1H, H-1), 3.32 (t, $J = 8.1$ Hz, 1H, H-5), 2.79 (s, 3H, N-Me), 2.30 (t, $J = 5.2$ Hz, 1H, N-H); ^{13}C NMR δ 175.7, 174.5, 169.9, 136.6, 128.4, 128.3, 127.0, 64.12, 61.69, 52.23, 49.54, 48.25, 24.94.

(1*R*,2*S*,4*R*,5*S*)-Methyl-4-phenyl-7-methyl-6, 8-dioxo-3,7-diazabicyclo[3.3.0]octane-2-carboxylate (ent-12). 76% ee as determined by HPLC, Chiralpak AS column + guard column, 4:1 *i*-PrOH-hexanes, $t_R(\text{minor}) = 7.3$ min, $t_R(\text{major}) = 16.7$ min; $[\alpha]_D^{25} = 63.3$ (c 1.29, DCM).

(2*R*,4*R*,5*S*)-5-Naphthalen-2'-yl-pyrrolidine-2,4-dicarboxylic acid dimethyl ester (13). 37% ee as determined by HPLC, Chiralpak AS column, 9:1 hexanes-*i*-PrOH, $t_R(\text{minor}) = 12.4$ min, $t_R(\text{major}) = 25.3$ min; $[\alpha]_D = -15.2$ (c 1.04 g/100mL, DCM); ^1H NMR (CDCl_3 , 400 MHz) δ 7.82-7.74 (m, 4H), 7.45-7.38 (m, 3H), 4.65 (d, $J = 7.7$ Hz; 1H), 3.99 (t, $J = 8.1$ Hz; 1H), 3.85 (s, 3H), 3.36 (dd, $J = 14.0$ & 7.1 Hz; 1H), 3.11 (s, 3H), 2.50-2.39 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 172.7, 136.6, 133.2, 132.9, 128.0, 127.7, 127.5, 126.0, 125.8, 125.5, 125.1, 66.0, 59.9, 52.1, 51.1, 49.6, 33.4.

***tert*-Butyl-(2*R*,4*R*,5*S*)-2-methoxycarbonyl-5-(2-naphthyl)pyrrolidin-4-carboxylate (14).** 78% ee as determined by HPLC, Chiralpak AS column 95:5 hexanes-*i*-PrOH, $t_R(\text{minor}) = 9.3$ min, $t_R(\text{major}) = 17.3$ min; $[\alpha]_D = -21.4$ (c 0.73 g/100mL, CH_2Cl_2). ^1H -NMR and ^{13}C -NMR data were consistent with previously reported values.³

(2*S*,3*R*,4*R*,5*R*)-2,3,4-tricarbomethoxy-5-(4-methoxyphenyl)pyrrolidine (15). 95% ee as determined by HPLC, Chiralpak AS column 85:15 hexanes-*i*-PrOH, $t_R(\text{major}) = 15.7$ min, $t_R(\text{minor}) = 30.5$ min; $[\alpha]_D = +72.6$ (c 0.74 g/100mL, CH_2Cl_2); ^1H NMR (CDCl_3 ,

400 MHz) δ 7.23 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.40 (d, J = 6.9 Hz, 1H), 4.09 (d, J = 8.8 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.64 (t, J = 8.4 Hz, 1H), 3.48 (t, J = 7.4 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 170.7, 170.6, 159.1, 129.2, 127.9, 113.7, 65.0, 62.2, 55.0, 52.5, 52.2, 51.9, 51.2, 50.9.

***tert*-Butyl-(2*R*,4*R*,5*S*)-2-methoxycarbonyl-5-(4-methoxyphenyl)pyrrolidin-4-carboxylate (16).** 84% ee as determined by HPLC, Chiralpak AS column 9:1 hexanes-*i*-PrOH, t_{R} (minor) = 6.6 min, t_{R} (major) = 9.6 min; $[\alpha]_{\text{D}} = -22.9$ (c 0.96 g/100mL, CH_2Cl_2). ^1H -NMR and ^{13}C -NMR data were consistent with previously reported values.³

(2*S*,3*S*,4*R*,5*S*)-2,3,4-Tricarbomethoxy-5-phenylpyrrolidine (18). $[\alpha]_{\text{D}}^{25} = -21.3$ (c 1.00, DCM); ^1H NMR (CDCl_3 , 400 MHz) δ 7.32-7.26 (m, 5H, Ph), 4.67 (d, J = 8.0 Hz, 1H, H-5), 4.22 (d, J = 7.6 Hz, 1H, H-2), 3.84 (s, 3H, 2- CO_2Me), 3.78 (s, 3H, 3- CO_2Me), 3.66 (dd, J = 7.6, 5.7 Hz, 1H, H-3), 3.58 (dd, J = 8.0, 5.7 Hz, 1H, H-4), 3.21 (s, 3H, 4- CO_2Me).

(2*R*,3*R*,4*S*,5*R*)-2,3,4-Tricarbomethoxy-5-phenylpyrrolidine (ent-18). $[\alpha]_{\text{D}}^{25} = 9.7$ (c 0.51, DCM).

Table 1. Results of Catalytic Asymmetric Cycloaddition Reactions with the Diastereomers (7a, 7b, and 7c) of Chiral Ligand 7.

Chiral Ligand	Dipolarophile	Yield(%)	ee(%)	cycloadduct
7a	Dimethyl maleate	60	18	8
“	N-methylmaleimide	81	12	12
“	Methyl acrylate	54	34	ent-10
7b	Dimethyl maleate	80	48	ent-8
“	N-methylmaleimide	84	46	ent-12
“	<i>tert</i> -Butyl acrylate	80	44	ent-11
7c	N-methylmaleimide	93	76	ent-12
“	Dimethyl maleate	70	22	8

III. Assignment of Absolute Configuration

Below are compiled the previously published data that was used to assign the absolute configuration of the cycloadducts reported in this work.

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	8	64.7 (<i>c</i> 1.07, DCM)	87	-	OR analogy with ref. 2
2	8	18.2 (<i>c</i> 0.60, DCM)	-	-	correlation with X-ray of auxiliary conjugate
3	ent-8	-	60	major>minor	X-ray of close derivative
4	8	100 (<i>c</i> 0.05, DCM)	94	minor>major	OR analogy with ref. 1
5	8	71.7 (<i>c</i> 1.00, DCM)	97	?	OR analogy with ref. 1
this work	8	61.9 (<i>c</i> 1.44, DCM)	90	minor>major	correlation with X-ray of auxiliary conjugate

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	ent-9	9.04 (<i>c</i> 1.54, DCM)	52	?	analogy with related structure
4	ent-9	43 (<i>c</i> 0.10, DCM)	>99	minor>major	OR analogy with ref. 1
5	ent-9	19.2 (<i>c</i> 1.00, DCM)	89	?	OR analogy with ref. 1
6	ent-9	20 (<i>c</i> 0.35, DCM)	76	minor>major	analogy with X-ray of close derivative
7	9	16.7 (<i>c</i> 0.45, DCM)	76	?	OR analogy with ref. 1
this work	9	-11.5 (<i>c</i> 1.49, DCM)	68	major>minor	OR analogy with ref. 1

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	ent-10	33.1 (<i>c</i> 1.11, DCM)	60	?	analogy with related structure
4	ent-10	36 (<i>c</i> 0.08, DCM)	95	minor>major	OR analogy with ref. 6
7	ent-10	38 (<i>c</i> 0.10, DCM)	88	major>minor	OR analogy with ref. 1
this work	10	-20.9 (<i>c</i> 0.46, DCM)	46	major>minor	OR analogy with ref. 1

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	ent-11	33.1 (<i>c</i> 1.11, DCM)	93	?	analogy with related structure
3	11	-30.8 (<i>c</i> 1.15, DCM)	91	major>minor	analogy with X-ray of close derivative
5	ent-11	26 (<i>c</i> 1.00, DCM)	88	?	OR analogy with ref. 1
this work	11	-28.6 (<i>c</i> 1.36, DCM)	88	major>minor	OR analogy with ref. 3

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	ent-12	61 (<i>c</i> 1.18, DCM)	79	?	analogy with related structure
4	ent-12	51 (<i>c</i> 0.14, DCM)	>99	minor>major	OR analogy with ref. 1
7	12	34.3 (<i>c</i> 45, DCM)	25	?	?
this work	12	-61.9 (<i>c</i> 1.24, DCM)	70	major>minor	OR analogy with ref. 1
this work	ent-12	63.3 (<i>c</i> 1.29, DCM)	76	minor>major	OR analogy with ref. 1

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
6	ent-13	34 (<i>c</i> 0.10, DCM)	91	minor>major	analogy with related structure
8	ent-13	17.3 (<i>c</i> 0.61, CHCl ₃)	62	major>minor	OR analogy with ref. 3
this work	13	-15.2 (<i>c</i> 1.04, DCM)	38	major>minor	analogy with related structure

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
3	14	-26.8 (<i>c</i> 1.29, DCM)	94	major>minor	analogy with X-ray of close derivative
6	ent-14	not given	3	minor>major	analogy with related structure
9	ent-14	17 (<i>c</i> 0.45, DCM)	62	minor>major	presumably by analogy with X-ray in ref. 6
this work	14	-21.4 (<i>c</i> 0.73, DCM)	82	major>minor	OR analogy with ref. 3

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
1	15	60.6 (<i>c</i> 1.03, DCM)	92	?	analogy with related structure
2	15	71.4 (<i>c</i> 2.25, DCM)	?	?	correlation with X-ray of auxiliary conjugate
5	15	76.7 (<i>c</i> 1.0, DCM)	98	?	OR analogy with ref. 1
this work	15	72.6 (<i>c</i> 0.74 DCM)	96	minor>major	OR analogy with ref. 1 and 5

reference	structure	$[\alpha]_D$ (conc., solv.)	reported ee (%)	relative t_R	assignment basis
3	16	-29.2(c 1.23, DCM)	95	major>minor	analogy with X-ray of close derivative
9	ent-16	19 (c 2.1, DCM)	56	minor>major	presumably by analogy with X-ray in ref. 6
this work	16	-22.9(c 0.96 DCM)	83	major>minor	OR analogy with ref. 3

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IV. ^1H and ^{13}C Spectra

f DKHDB.001

f DKHDB.002

f DKH-164D2.01q(2)

f DKH-164D2.02q

f AB-62.001

f AB-62.002

h DKH-132F.001 (2)

f DKH-132F.002

f DKH-174C.01q(2)

f DKH-174C.02q

f DKH-266CD.001

f DKH-266CD.002

f DKH-268pr.001

f DKH-268pr.002

d DKH-235F.01q

d DKH-235F.002

f DKH-280C.001

f DKH-280C.002

f DKH-281D.001(2)

f DKH-281D.002

k DKH-362B.001

F DKH-372A.001

F DKH-372A.002

V. Representative HPLC Traces

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.94	n.a.	253,365	381,646	94,43	n.a.	BMB*
2	15.73	n.a.	12,786	22,523	5,57	n.a.	BMB*
Total:			266,151	404,169	100,00	0,000	

HPLC trace of *racemic 8 + ent-8*:

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.71	n.a.	489,233	663,006	49,21	n.a.	BMB*
2	14.21	n.a.	262,278	684,202	50,79	n.a.	BMB*
Total:			751,511	1347,208	100,00	0,000

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	25,36	n.a.	143,307	306,484	15,80	n.a.	MB*
2	50,73	n.a.	472,401	1633,011	84,20	n.a.	BMB*
Total:			615,708	1939,495	100,00	0,000	

HPLC trace of *racemic 9 + ent-9*:

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23,26	n.a.	698,190	1956,426	49,91	n.a.	BMB*
2	51,16	n.a.	491,976	1963,405	50,09	n.a.	BMB*
Total:			1190,165	3919,832	100,00	0,000

HPLC trace of *racemic 10* + *ent-10*:

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,09	n.a.	52,840	175,845	5,66	n.a.	BMB*
2	24,82	n.a.	488,235	2933,124	94,34	n.a.	BMB*
Total:			541,076	3108,969	100,00	0,000	

HPLC trace of *racemic 11* + *ent-11*:

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,54	n.a.	458,211	1561,514	50,26	n.a.	BMB*
2	25,17	n.a.	260,501	1545,320	49,74	n.a.	BMB*
Total:			718,712	3106,834	100,00	0,000

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,33	n.a.	96,634	202,066	14,30	n.a.	MB*
2	16,46	n.a.	290,169	1210,597	85,70	n.a.	BM *
Total:			386,803	1412,662	100,00	0,000

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,31	n.a.	1580,896	3495,635	87,60	n.a.	MB*
2	16,73	n.a.	130,833	494,910	12,40	n.a.	BMB*
Total:			1711,729	3990,545	100,00	0,000	

HPLC trace of *racemic 12* + *ent-12*:

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7,42	n.a.	1382,056	2981,798	51,40	n.a.	M *
2	16,65	n.a.	631,836	2819,539	48,60	n.a.	BMB*
Total:			2013,892	5801,337	100,00	0,000

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,38	n.a.	486,457	1575,325	31,55	n.a.	BMB*
2	25,33	n.a.	555,038	3417,460	68,45	n.a.	BM *
Total:			1021,494	4992,785	100,00	0,000

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,57	n.a.	172,667	284,786	8,23	n.a.	BM *
2	9,61	n.a.	1222,447	3173,671	91,77	n.a.	MB*
Total:			1395,113	3458,457	100,00	0,000	