Supporting Information for:

**Chiral *N*-Acyl-ethylenediamines as New Modular Ligands for the Catalytic Asymmetric
Addition of Alkylzinc Reagents to Aldehydes**

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General Methods. NMR spectra were recorded on a 300 MHz instrument using CDCl₃ as the solvent and TMS as the internal standard. Mass spectra were recorded on an electrospray mass spectrometer. Enantiomeric excess was determined using either HPLC with a Daicel Chiralcel OD (or OD-H) column (0.46 cm i.d. x 25 cm) with UV detection at 219 nm or by ¹⁹F NMR on a 400 MHz NMR spectrometer of the corresponding (*R*)-MTPA ester. Optical rotations were recorded on a polarimeter at ambient temperature and 589 nm (c = g/100 mL). Melting points are uncorrected. Solvents were of reagent grade and used as received. Solvents were removed by rotary evaporation at water aspirator pressure followed by further drying at approximately 1 torr. All reagents were used as received except benzaldehyde, which was distilled from CaH₂ prior to use. Anhydrous procedures were conducted using oven dried glassware and standard syringe and cannula transfer techniques. Reactions were conducted under a N₂ atmosphere. Reactions were monitored using TLC. TLC plates were visualized with either PMA staining solution or UV at 254 nm.

Figure S1. ¹H NMR spectrum for ligand **4a**.

Figure S2. ¹³C NMR spectrum for ligand **4a**.

Figure S3. ¹H NMR spectrum for ligand **4b**.

Figure S4. ¹³C NMR spectrum for ligand **4b**.

Figure S5. ¹H NMR spectrum for ligand **4c**.

Figure S6. ¹³C NMR spectrum for ligand **4c**.

Figure S7. ^1H NMR spectrum for ligand **4d**.

Figure S8. ^{13}C NMR spectrum for ligand **4d**.

Figure S9. ¹H NMR spectrum for ligand **4e**.

Figure S10. ¹³C NMR spectrum for ligand **4e**.

Figure S11. ¹H NMR spectrum for ligand 4f.

Figure S12. ¹³C NMR spectrum for ligand 4f.

Figure S13. ¹H NMR spectrum for ligand **4g**.

Figure S14. ¹³C NMR spectrum for ligand **4g**.

Figure S15. ¹H NMR spectrum for ligand **4h**.

Figure S16. ¹³C NMR spectrum for ligand **4h**.

Figure S19. ¹H NMR spectrum for ligand **4j**.

Figure S20. ¹³C NMR spectrum for ligand **4j**.

Figure S21. ¹H NMR spectrum for ligand **4k**.

Figure S22. ¹³C NMR spectrum for ligand **4k**.

Figure S23. ¹H NMR spectrum for ligand **4l**.

Figure S24. ¹³C NMR spectrum for ligand **4l**.

Figure S25. ¹H NMR spectrum for ligand **4m**.

Figure S26. ¹³C NMR spectrum for ligand **4m**.

Figure S27. ^1H NMR spectrum for ligand **4n**.

Figure S28. ^{13}C NMR spectrum for ligand **4n**.

Figure S29. ¹H NMR spectrum for ligand **4o**.

Figure S30. ¹³C NMR spectrum for ligand **4o**.

Figure S31. ¹H NMR spectrum for ligand **1a**.

Figure S32. ¹³C NMR spectrum for ligand **1a**.

Figure S33. ^1H NMR spectrum for ligand **1d**.

Figure S34. ^{13}C NMR spectrum for ligand **1d**.

Figure S35. ¹³C NMR spectrum for ligand **1i**.

Figure S36. ¹H NMR spectrum for ligand **1i**.

Figure S37. ¹H NMR spectrum for ligand **1b**.

Figure S38. ¹³C NMR spectrum for ligand **1b**.

Figure S39. ¹H NMR spectrum for ligand **1c**.

Figure S40. ¹³C NMR spectrum for ligand **1c**.

Figure S41. ¹H NMR spectrum for ligand **1e**.

Figure S42. ¹³C NMR spectrum for ligand **1e**.

Figure S43. ¹H NMR spectrum for 2-amino-*N*-(2-diethylamino-ethyl)-3-methyl-butamide.

Figure S44. ¹³C NMR spectrum for 2-amino-*N*-(2-diethylamino-ethyl)-3-methyl-butamide.

Figure S45. ^1H NMR spectrum for ligand **1g**.

Figure S46. ^{13}C NMR spectrum for ligand **1g**.

Figure S47. ¹H NMR spectrum for ligand **1h**.

Figure S48. ¹³C NMR spectrum for ligand **1h**.

Figure S49. ¹H NMR spectrum for ligand **1j**.

Figure S50. ¹³C NMR spectrum for ligand **1j**.

Figure S51. ¹H NMR spectrum for ligand **1f**.

Figure S52. ¹³C NMR spectrum for ligand **1f**.

(*R*)-1-Phenyl-1-propanol

68% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 12.2$ min for (*R*) and $t_R = 13.9$ min for (*S*).¹

Figure S53. HPLC trace of 1-phenyl-1-propanol.

(*R*)-1-Phenyl-1-ethanol

86% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 13.0$ min for (*R*) and $t_R = 16.5$ min for (*S*).² $t_R = 6.9$ min for benzaldehyde and $t_R = 22.0$ min for benzylalcohol.

Figure S54. HPLC trace of 1-phenyl-1-ethanol.

(*R*)-1-(1'-Naphthyl)-1-propanol

23% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 23.3$ min for (*S*) and $t_R = 49.2$ min for (*R*).¹

Figure S55. HPLC trace of 1- (1'-naphthyl)-1-propanol.

(*R*)-1-(1'-Naphthyl)-1-ethanol

78% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 27.5$ min for (*S*) and $t_R = 44.0$ min for (*R*).²

Figure S56. HPLC trace of 1- (1'-naphthyl)-1-ethanol.

(*R*)-1-(2'-Naphthyl)-1-propanol

74% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 23.2$ min for (*S*) and $t_R = 25.9$ min for (*R*).¹ $t_R = 34.5$ min for 2-naphthalenemethanol.

Figure S57. HPLC trace of 1-(2'-naphthyl)-1-propanol.

(*R*)-1-(2'-Naphthyl)-1-ethanol

85% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:ethanol (95.0:5.0) at 1.0 mL/min and detected at 219 nm), $t_R = 26.5$ min for (*S*) and $t_R = 28.7$ min for (*R*).² $t_R = 13.8$ min for 2-naphthylaldehyde and $t_R = 36.5$ min for 2-naphthalenemethanol.

Figure S58. HPLC trace of 1-(2'-naphthyl)-1-ethanol.

(R)-1-Phenyl-pent-1-(E)-en-3-ol

63% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 21.4$ min for (*R*) and $t_R = 39.5$ min for (*S*).¹ $t_R = 14.1$ min for *trans*-cinnamaldehyde.

Figure S59. HPLC trace of 1-phenyl-pent-1-(*E*)-en-3-ol.

(R)-4-Phenyl-4-but-3-(E)-en-2-ol

26% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 24.9$ min for (*R*) and $t_R = 44.2$ min for (*S*).³ $t_R = 13.8$ min for *trans*-cinnamaldehyde.

Figure S60. HPLC trace of 4-phenyl-4-but-3-(*E*)-en-2-ol.

(*R*)-1-Phenyl-3-pentanol

0% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 15.8$ min for (*R*) and $t_R = 24.8$ min for (*S*).⁴

Figure S61. HPLC trace of 1-phenyl-3-pentanol.

(*R*)-1-Cyclohexyl-1-propanol

26% ee by ¹⁹F NMR analysis of the (*R*)-MTPA ester; $[\alpha]_D^{23} = +1.5$ (c = 1.84, CHCl₃) {lit.¹ $[\alpha]_D^{24} = -6.39$ (c = 1.05, CHCl₃) for 97% ee (*S*)}.⁴

Figure S62. ¹⁹F NMR spectrum of the (*R*)-MTPA ester derivative of 1-cyclohexyl-1-propanol.

(*R*)-1-(4'-Methoxyphenyl)-1-propanol

40% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 16.7$ min for (*R*) and $t_R = 19.7$ min for (*S*).¹ $t_R = 10.7$ min for 4-MeO-benzaldehyde.

Figure S63. HPLC trace of 1-(4'-methoxyphenyl)-1-propanol.

(*R*)-1-(4'-Chlorophenyl)-1-propanol

76% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 11.1$ min for (*S*) and $t_R = 12.0$ min for (*R*).¹

Figure S64. HPLC trace of 1-(4'-chlorophenyl)-1-propanol.

(*R*)-1-(4'-Chlorophenyl)-1-ethanol

82% ee by HPLC analysis (Chiralcel OD-H column eluted with hexanes:2-propanol (97.5:2.5) at 1.0 mL/min and detected at 219 nm), $t_R = 12.1$ min for (*S*) and $t_R = 13.2$ min for (*R*).⁵ $t_R = 7.2$ min for 4-Cl-benzaldehyde.

Figure S65. HPLC trace of 1-(4'-chlorophenyl)-1-ethanol.

(*R*)-2,2-Diethyl-pentan-3-ol

53% ee by ^{19}F NMR analysis of the (*R*)-MTPA ester; $[\alpha]_D^{23} = +1.2$ ($c = 5.35$, CHCl_3) {lit.⁶ $[\alpha]_D^{22} = -32.6$ ($c = 2.38$, CHCl_3) for 98% ee (*S*)}.

Figure S66. ^{19}F NMR spectrum of the (*R*)-MTPA ester derivative of 2,2-Diethyl-pentan-3-ol.

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