Supporting Information

Solvent-dependent strong asymmetric amplification in catalytic enantioselective Henry reaction using *trans-N,N'*-bis-biphenyl-4-ylmethyl-cyclohexane-1,2-diamine-$CuCl_2$ complex

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General

^{1}H-NMR spectra were recorded on JEOL JNM-GSX 400 spectrometer with tetramethylsilane (TMS) as the internal standard. Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) on Chiralcel OD column (Daisel).

General procedure for catalytic Henry reaction

(*R,R*)-**1a** (0.05 mmol) and $CuCl_2$ (0.05 mmol) were treated with AcOEt (1.0 mL) and the resulted blue solution was stirred for 30 sec at 60 °C then for 1 h at 25 °C. Then a solution of benzaldehyde (0.5 mmol) and CH_3NO_2 (5.0 mmol) in AcOEt was added, followed by addition of Et_3N (0.05 mmol) via syringe. The reaction mixture was stirred at 0 °C. After 24 h, the cold reaction mixture was put into a plug of silica gel (*n*-hexane/AcOEt 1:1, v/v) and afforded the desired (*S*)-1-phenyl-2-nitroethane-1-ol **2a** of 91% ee in 87% yield. Product was analyzed by ^{1}H NMR spectra and enantiomeric excess (ee) was determined using HPLC on Chiralcel OD column (Daisel) (Eluent: *n*-hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, λ = 254 nm, t_{minor} = 14.35 min, t_{major} = 17.91 min).

X-Ray structure determination

Single crystals of compounds **3**, **4**, and **5** from each bulk sample were isolated, checked under polarized microscope and mounted into a loop. Intensity data for the single crystals of compounds **3** and **5** was obtained by collecting reflections, respectively at 150 and 296 K using 0.5° ω scans on a Bruker X8 diffractometer furnished with an APEX II CCD detector using CuKα radiation (λ = 1.54178 Å).1 Integration was done using the SAINT software that is a part of the APEX II software suite and absorption corrections were introduced using SADABS.[1] For compound 4 MoKα radiation (λ = 0.71073 Å) and CrystalClear software for data collection at 100 K, cell refinement and data reduction was used.[2]

Structures were solved via direct methods and refined using SHELXLTL software suite.[3] In each structure, all non-hydrogen atoms were located via difference Fourier maps and refined anisotropically. Aromatic and methyl groups hydrogen atom positions were placed at their idealized positions and allowed to ride on the coordinates of the parent atom with isotropic thermal parameters (Uiso) fixed at 1.2 Ueq of the carbon atom to which they are attached. Nitrogen H-atoms were found from Δρ maps and their positions were refined in isotropic mode.

1 Bruker (2005). APEX2, SAINT and SADABS Bruker AXS Inc., Madison, Wisconsin, USA.
2 Rigaku (2011). CrystalClear. Rigaku/MSC, 2006, Tokyo, Japan.
3 G. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.

Table S1 Catalytic asymmetric Henry reaction of benzaldehyde with nitromethane in the presence of various ee (%) of (*R,R*)-**1a**-$CuCl_2$ complex in AcOEt.

Entry	ee (%) of **1a**	yield (%) of **2a**	ee (%) of **2a**
1	100	87	91
2	80	83	91
3	60	83	90
4	40	80	89
5	20	69	87
6	10	44	82
7	5	47	64
8	0	23	0

Table S2 Catalytic asymmetric Henry reaction of benzaldehyde with nitromethane in the presence of various ee (%) of (*R,R*)-

1a-$CuCl_2$ complex in MeOH.

Entry	ee (%) of **1a**	yield (%) of **2a**	ee (%) of **2a**
1	100	73	77
2	80	82	75
3	60	78	67
4	40	67	39
5	20	80	29
6	10	75	15
7	5	75	3
8	0	79	0

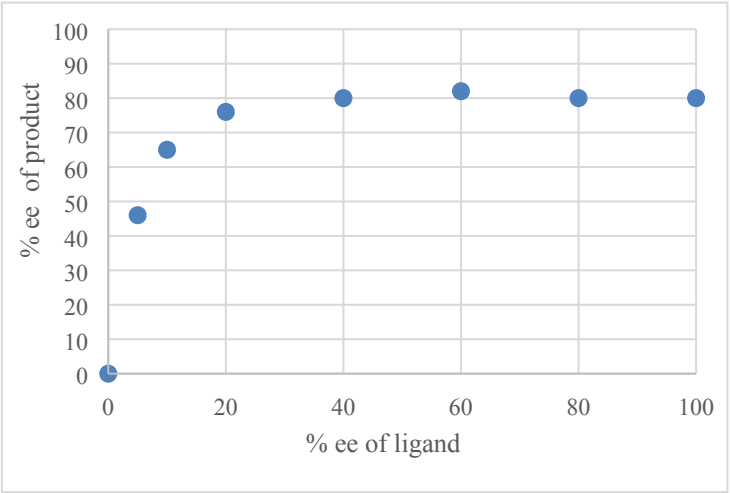

Fig. S1 Relation between the enantiomeric excess (ee) of ligand (*R,R*)-**1a**-$CuCl_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in MeCN.

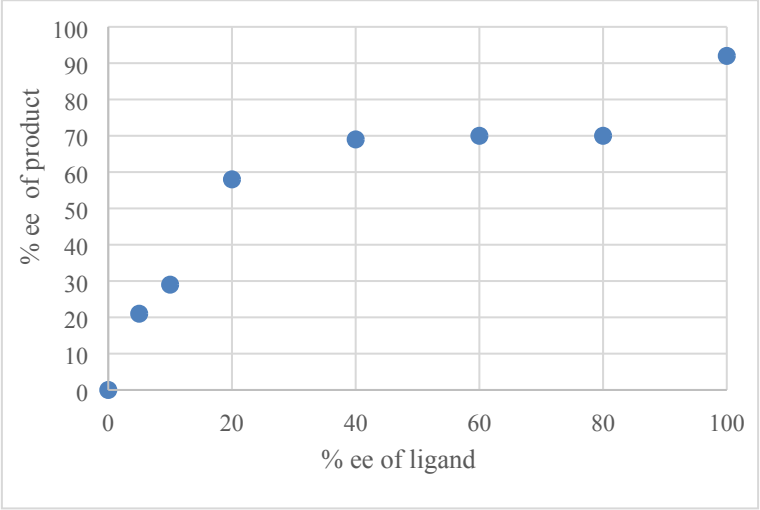

Fig. S2 Relation between the enantiomeric excess (ee) of ligand (*R,R*)-**1a**-$CuCl_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in THF.

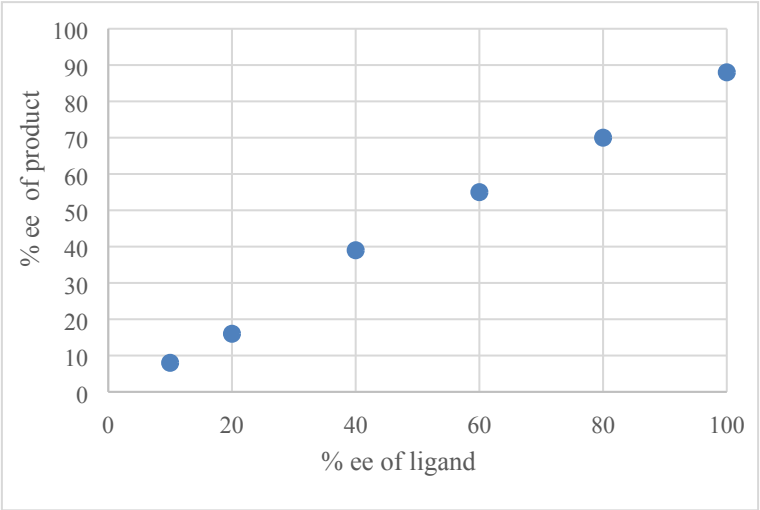

Fig. S3 Relation between the enantiomeric excess (ee) of ligand (*R*,*R*)-**1a**-$Cu(OAc)_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in AcOEt.

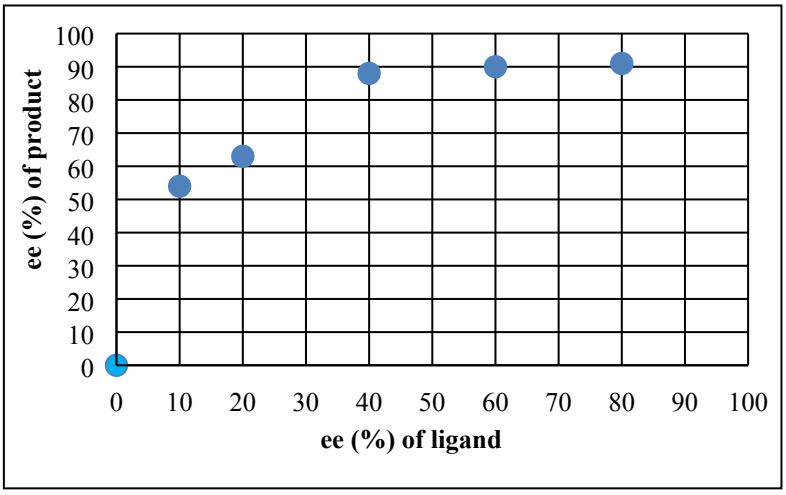

Fig. S4 Relation between the enantiomeric excess (ee) of ligand (*R*,*R*)-**1b**-$CuCl_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in AcOEt.

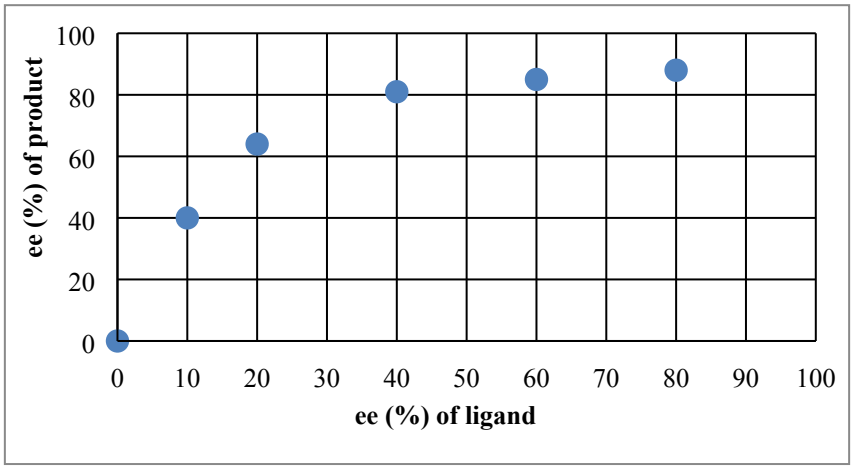

Fig. S5 Relation between the enantiomeric excess (ee) of ligand (*R,R*)-**1c**-$CuCl_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in AcOEt.

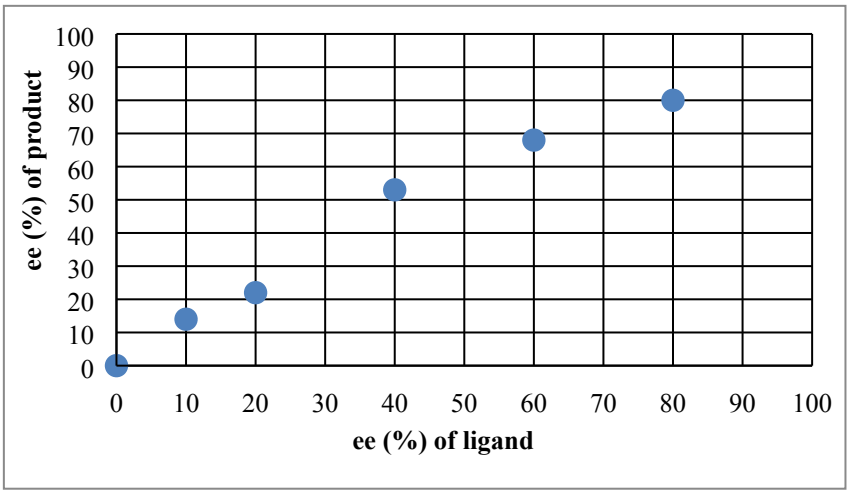

Fig. S6 Relation between the enantiomeric excess (ee) of ligand (*R,R*)-**1d**-$CuCl_2$ complex and that of product (*S*)-**2a** in the catalytic reaction in AcOEt.

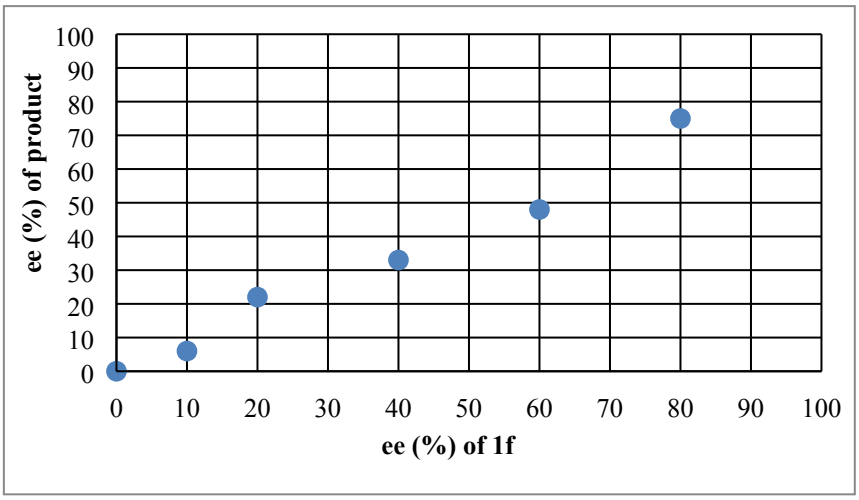

Fig. S7 Relation between the enantiomeric excess (ee) of ligand (*R,R*)-**1e**-$CuCl_2$ complex and that of product (*S*)-2**a** in the catalytic reaction in AcOEt.