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Chiral binuclear copper(II) catalyzed nitroaldol reaction: scope and mechanism

Suribabu Jammi, Prasenjit Saha, Sridhar Sanyashi, Sekarpandi Sakthivel, Tharmalingam Punniyamurthy *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

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ABSTRACT

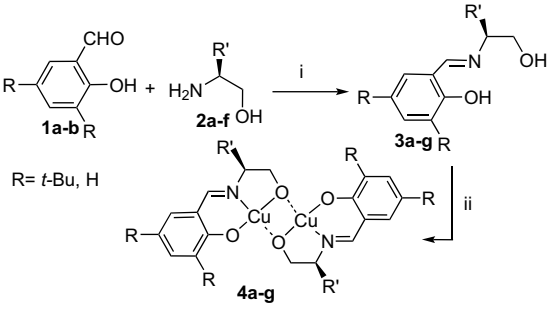
Chiral binuclear copper(II) Schiff base complexes **4a–g** have been prepared from aldehydes **1a**,**b**, (*S*)-amino alcohols **2a–f**, and $Cu(OAc)_2 \cdot 1H_2O$ in high yield. Their catalysis is studied for the addition of nitroalkanes to aldehydes at ambient conditions with 76:24 er.

1. Introduction

Copper is an abundant element in the earth crust. It is also present in proteins such as tyrosinase, hemocyanins, and copper oxidases.[1] Many of these proteins are believed to contain the copper ions in dissymmetric ligand arrangements and therefore modeling the structural aspects of this dissymmetric ligand environment around copper is currently of great interest.[2] Chiral binuclear complexes of copper(II) have received special attention because of their importance in molecular recognition.[3,4] Herein we describe the synthesis and application of a series of chiral binuclear copper(II) complexes **4a–g**, from aldehydes **1a**,**b**, (*S*)-amino alcohols **2a–f**, and $Cu(OAc)_2 \cdot 1H_2O$, for addition of nitroalkanes to aldehydes with upto 76:24 er. The reactions are free from the addition of an additive or base and the complexes **4a–g** act as bifunctional catalysts. Both the aryl and alkyl aldehydes are compatible with this protocol providing the nitroaldol products in high yields. Nitromethane is more reactive compared to nitroethane and nitropropane.

2. Results and discussion

Aldehydes **1a**,**b** were reacted with (*S*)-amino alcohols **2a–f** in EtOH to provide Schiff bases **3a–g** in high yield. The latter were then treated with $Cu(OAc)_2 \cdot 1H_2O$ in EtOH to give the complexes **4a–g** as green colored powder (Scheme 1). During recrystallization in a mixture of MeOH and CH_2Cl_2, the complex **4e** was yielded as single crystals whose X-ray analysis showed as a binuclear complex having Cu–O–Cu bridge with the alkyl OH group (Fig. 1).[5] The copper(II) atoms are tetracoordinated with



4	R	R'	Yield [%]
a	*t*-Bu	Me	76
b	*t*-Bu	*i*-Pr	88
c	*t*-Bu	*s*-Bu	79
d	*t*-Bu	*i*-Bu	90
e	*t*-Bu	*t*-Bu	95
f	*t*-Bu	Bn	82
g	H	*t*-Bu	70

Scheme 1. Synthesis of the binuclear copper(II) complex **4a–g**: (i) EtOH, 25 °C, 24 h; (ii) $Cu(OAc)_2 \cdot 1H_2O$, EtOH, 25 °C, 12 h.

* Corresponding author. Fax: +91 361 2690762.
E-mail address: tpunni@iitg.ernet.in (T. Punniyamurthy).

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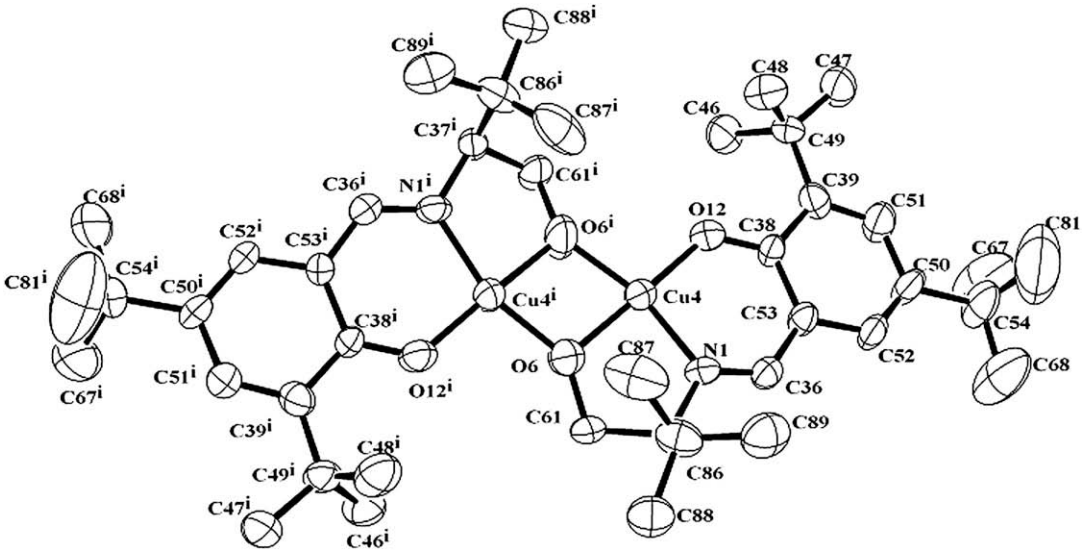


Figure 1. ORTEP diagram of **4e** with thermal ellipsoid set to 50% probability. H-atoms are omitted for clarity.

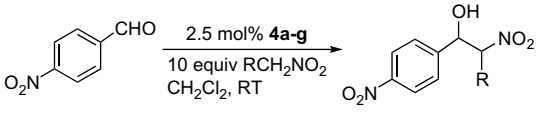
a distorted square planar geometry. The Cu–Cu distances (2.853–2.907 Å), bond lengths of the bridged (1.856–1.939 Å) and terminal (1.8351–1.876 Å) Cu–O, Cu–N (1.886–1.927 Å), and the bond angles of Cu–O–Cu (96.04°–101.50°) agree with the reported data.[6] The five-membered rings, arising from the coordination of the bridged O and imine N of **4e** with Cu(II), exist in envelope conformation.

The catalytic activity of the complexes **4a–g** was then studied for the addition of nitroalkanes to aldehydes.[7–10] The optimization of the reaction conditions was carried out with the addition of nitromethane to *p*-nitrobenzaldehyde as a model substrate (Table 1). The best results observed when substrates were stirred for 24 h in the presence of 2.5 mol % of **4e** at ambient temperature. Of the solvents studied, CH_2Cl_2, toluene, THF, EtOH, CH_3CN, and $CHCl_3$, the former found to be the choice for these reactions (Table 2). The reaction with complex **4e** was superior to that used **4a–d** and **4f**,**-g** as the catalysts.

The reactions of other aldehydes were next studied with nitromethane (Table 3). Benzaldehyde underwent reaction with 92% yield and 60:40 er. Similar results observed with 2-bromo-, 2-methoxy-, 3-bromo-, 3-nitro-, 4-bromo-, 4-chloro-, 4-fluoro-, 4-methoxy-, and 4-methylbenzaldehydes. Likewise, 2-naphthaldehyde, 2-thiophenecarboxaldehyde, 2-furaldehyde, cyclohexanecarboxaldehyde, ethyl glyoxalate, and isobutyraldehyde underwent reaction to give nitroaldol products with upto 89% yield and 68:32 er. In aryl aldehydes, the substrates bearing electron-withdrawing groups exhibited greater reactivity compared to that having electron-donating groups.

The observed experimental results suggest that the complexes **4** act as bifunctional catalysts in these reactions: first, as Brønsted base, and then, as Lewis acid. To reveal, the complex **4e** was titrated with HCl whose electronic spectra showed that the intensity of the bands at 384 nm and 283 nm decreased with respect to the increasing concentration of HCl, and shifted to lower wavelength at 327 nm and 263 nm, respectively (Fig. 2).[11] These studies clearly reveal that the phenolate oxygen is selectively protonated (Fig. 3). Thus, the phenolate oxygen acts as a stronger base compared to

Table 1
Reaction of 4-nitrobenzaldehyde: screening of complexes **4a–g** and nitroalkanes

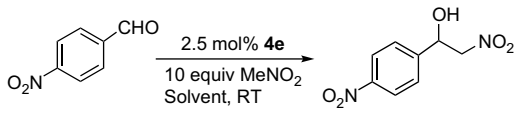


R = H, Et, Me

Entry	Catalyst	RCH_2NO_2	Product		
			Yield[a] (%)	er[d]	Configuration[e]
1	**4a**	$MeNO_2$	55	53:47	*S*
2	**4b**	$MeNO_2$	86	58:42	*S*
3	**4c**	$MeNO_2$	77	57:43	*S*
4	**4d**	$MeNO_2$	75	56:44	*S*
5	**4e**	$MeNO_2$	90	66:34	*S*
6	**4f**	$MeNO_2$	82	53:47	*S*
7	**4g**	$MeNO_2$	75	45:55	*S*
8	**4e**	$EtNO_2$	78 (11:9)[b,c]	56:44, 64:36	nd
9	**4e**	$PrNO_2$	45 (11:9)[b,c]	55:45, 59:41	nd
10	**4e**	*i*-$PrNO_2$	nr[f]	—	—

[a] 4-Nitrobenzaldehyde (0.5 mmol), **4a–g** (2.5 mol %), and nitroalkane (5 mmol) stirred for 24 h in CH_2Cl_2 (1 mL).
[b] *syn*/*anti* ratio.
[c] Reaction time=48 h.
[d] Determined by HPLC with Chiralcel OD-H column using hexane/isopropanol (85:15).
[e] Determined from sign of optical rotation.
[f] nr=no reaction.

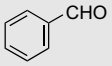
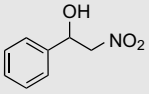
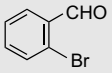
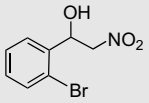
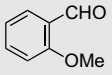
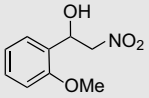
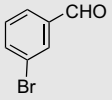
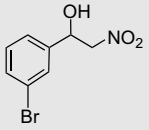
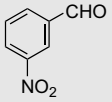
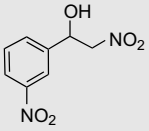
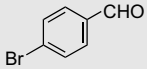
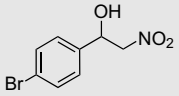
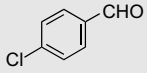
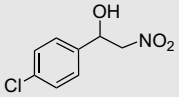
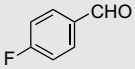
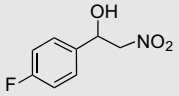
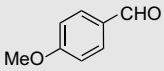
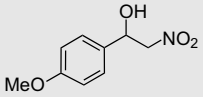
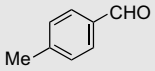
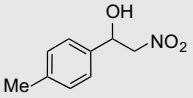
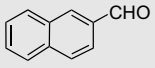
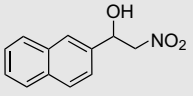
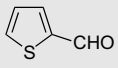
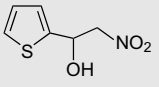
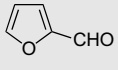
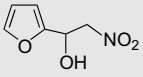
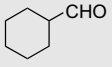
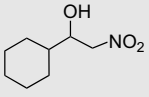
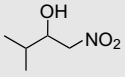
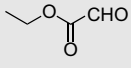
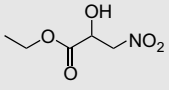
Table 2
Reaction of 4-nitrobenzaldehyde with nitromethane using **4e**: solvent effect



Entry	Solvent	Product		
		Yield[a] (%)	er[b]	Configuration[c]
1	EtOH	40	61:39	*S*
2	THF	53	57:43	*S*
3	CH_3CN	20	56:44	*S*
4	Toluene	49	60:40	*S*
5	$CHCl_3$	84	60:40	*S*
6	CH_2Cl_2	90	66:34	*S*

[a] 4-Nitrobenzaldehyde (0.5 mmol), **4e** (2.5 mol %), and nitromethane (5 mmol) stirred for 24 h in appropriate solvent (1 mL).
[b] Determined by HPLC analysis with Chiralcel OD-H column using hexane/isopropanol (85:15).
[c] Determined from sign of optical rotation.

Table 3
Reaction of alkyl, aryl, and 2-naphthyl aldehydes with nitromethane

Entry	Substrate	Time (h)	Product	Yield[a,b] (%)	er[c]	Configuration[d]
1		28		92	60:40	*S*
2		20		93	55:45	*S*
3		34		89	65:35	*S*
4		30		85	60:40	nd
5		26		90	76:24	*S*
6		24		95	58:42	nd
7		23		90	54:46	*S*
8		22		94	55:45	*S*
9		38		84	66:34	*S*
10		30		90	64:36	*S*
11		36		81	61:39	*S*
12		30		65	54:46	*S*
13		16		74	55:45	*S*
14		24		89	68:32	*S*
15		20		86	64:36	*S*
16		30		55	57:43	nd

[a] Substrate (0.5 mmol), **4e** (2.5 mol %), and nitromethane (5 mmol) stirred in CH_2Cl_2 (1 mL) at ambient temperature.
[b] Isolated yield.
[c] Determined by HPLC analysis using Chiralcel OD-H (for entries 1–12 and 16) and Chiralpak AD-H (for entries 13–15) columns with *n*-hexane/isopropanol.
[d] Determined from sign of optical rotation.

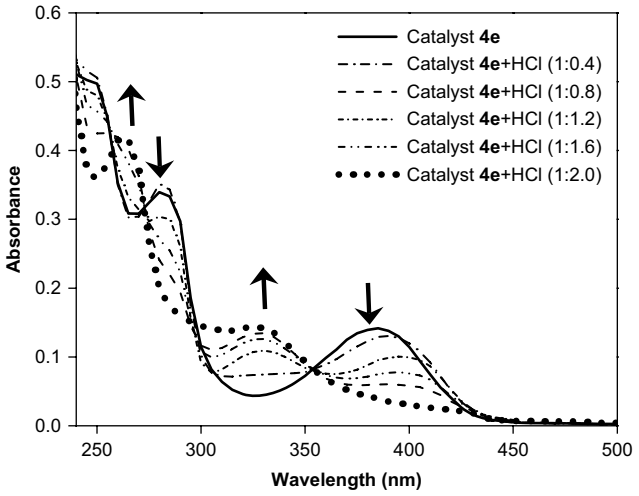


Figure 2. UV–vis spectra of **4e** (3.3×10^{-2} mM) with an increasing concentration of HCl ($0.0–6.6\times10^{-2}$ mM) in CH_2Cl_2.

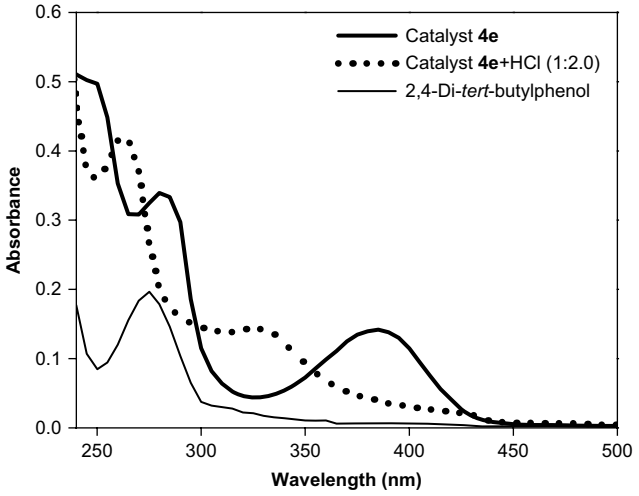


Figure 3. UV–vis spectra of **4e**, **4e**+HCl and 2,4-di-*tert*-butylphenol in CH_2Cl_2.

carboxylate oxygen under these conditions. Hence, the reaction of complex **4** with nitroalkane and aldehyde can generate monomeric complex ***a*** that could transform to intermediate ***c*** via intramolecular addition of nitronate to aldehyde ***b*** followed by reaction with fresh nitroalkane. The intermediate ***c*** can complete the catalytic cycle by reaction with fresh aldehyde (Scheme 2).

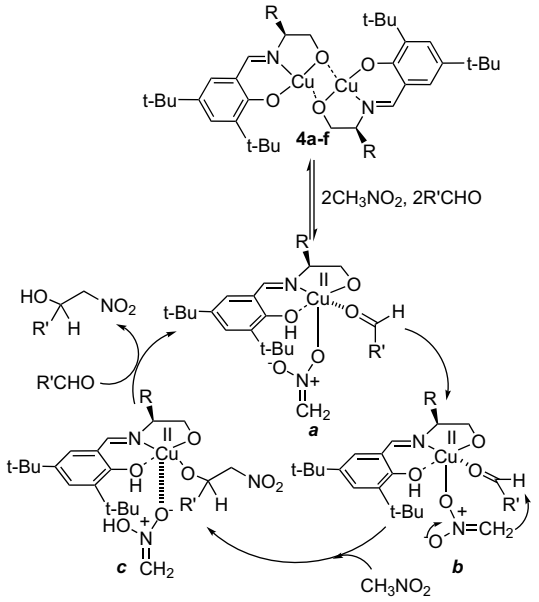
3. Conclusions

In summary, the synthesis of chiral copper(II) Schiff base complexes **4a**–**g** has been accomplished in high yield. They have been studied for the addition of nitroalkanes to aldehydes as bifunctional catalysts with 76:24 er.

4. Experimental section

4.1. General

L-Amino acids, 2,4-di-*tert*-butylphenol (98%), aldehydes, nitroalkanes, and $Cu(OAc)_2\cdot1H_2O$ (>99%) purchased from Aldrich. (*S*)-Amino alcohols obtained by reduction of amino acids according to the literature.[12a] 3,5-Di-*tert*-butylsalicylaldehyde prepared from 2,4-di-*tert*-butylphenol.[12b] NMR spectra recorded using Varian-400



Scheme 2. Proposed catalytic cycle.

spectrometer. FTIR spectra obtained from Nicolet-410 spectrometer. HPLC analysis was carried out on Waters-2478 with chiral stationary phase columns (chiralcel OD-H and chiralpak AD-H). UV–vis spectra obtained from Perkin–Elmer Lambda-25 spectrophotometer. Thermogravimetric analysis recorded using TGA/SDTA-851 Mettler Toledo analyzer. EPR spectra recorded using JES-FA-200 spectrometer. X-ray data collected on Bruker SMART APEX equipped with CCD area detector using Mo Kα radiation. The structure solved using SHELXL-97 Göttingen, Germany. Column chromatography performed on 60–120 mesh silica gel. Elemental analysis carried out in this department using Perkin–Elmer-2400 CHNS analyzer.

4.2. General procedure for the preparation of 3a–g

Aldehydes **1a**,**b** (5 mmol) and (*S*)-amino alcohols **2a**–**f** (5 mmol) was stirred in EtOH (10 mL) for 24 h at ambient temperature. Removal of the solvent provided a residue, which was purified on silica gel column chromatography using ethyl acetate and hexane (1:19) to give **3a**–**g** as yellow compounds.

The ligands 2,4-bis(1,1-dimethylethyl)-6-[[[(1*S*)-1-hydroxymethyl-2-methylpropyl]imino]methyl]-phenol **3b**,[13a] 2,4-bis(1,-1-dimethylethyl)-6-[[[(1*S*,2*S*)-1-(hydroxymethyl)-2-methylbutyl]imino]methyl]-phenol **3c**,[13b] 2,4-bis(1,1-dimethylethyl)-6-[[[(1*S*)-1-(hydroxymethyl)-2,2-dimethylpropyl]imino]methyl]-phenol **3e**[13a] are known and spectral data are consistent with those reported in the literature. The ligands **3a**, **3d**, **3f**, and **3g** are known in the literature but their data are not reported.

4.2.1. 2,4-Bis(1,1-dimethylethyl)-6-[[[(1S)-2-hydroxy-1-methylethyl]imino]methyl]-phenol ***3a***[13c]

A mixture of 3,5-di-*tert*-butylsalicylaldehyde (1.17 g, 5 mmol) and (*S*)-alaninol (0.375 g, 5 mmol) in EtOH (10 mL) was stirred for 24 h. Evaporation of the solvent gave a residue that was purified on column chromatography (5% hexane/ethyl acetate) to give the title compound **3a** (1.19 g, 82%) as yellow liquid; [found: C, 74.28; H, 10.10; N, 4.88. $C_{18}H_{29}NO_2$ requires: C, 74.18; H, 10.03; N, 4.81%]; R_f (5% hexane/ethyl acetate) 0.40; $[\alpha]_D^{25}$ −37.6 (*c* 0.516, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (1H, s, CHN), 7.30 (1H, d, J=2.0 Hz, CH), 7.02 (1H, d, J=2.4 Hz, CH), 3.55 (2H, d, J=6.8 Hz, CH_2OH), 3.33 (1H, m, $CHCH_3$), 1.35 (9H, s, $(CH_3)_3C$), 1.26 (9H, s, $(CH_3)_3C$), 1.13 (3H, d, J=6.4 Hz, CH_3CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 158.3, 140.4, 136.9, 127.3, 126.3, 117.9, 67.4, 66.8, 35.2, 34.3, 31.8, 29.6,

18.5; IR (neat) 3391, 2966, 2879, 1634, 1470, 1373, 1271, 1102, 1035 cm^{-1}.

4.2.2. 2,4-Bis(1,1-dimethylethyl)-6-[[[(1S)-1-(hydroxymethyl)-3-methylbutyl]imino]methyl]-phenol **3d**[13c]

A mixture of 3,5-di-*tert*-butylsalicylaldehyde (1.17 g, 5 mmol) and (*S*)-isoleucinol (0.585 g, 5 mmol) in EtOH (10 mL) was stirred for 24 h. Evaporation of the solvent afforded a residue that was purified on column chromatography (5% hexane/ethyl acetate) to give the title compound **3d** (1.53 g, 92%) as yellow liquid; [found: C, 75.73; H, 10.60; N, 4.31. $C_{21}H_{35}NO_2$ requires: C, 75.63; H, 10.58; N, 4.20%]; R_f (5% hexane/ethyl acetate) 0.33; $[\alpha]_D^{25}$ −23.3 (*c* 0.316, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (1H, s, CHN), 7.40 (1H, d, *J*=2.4 Hz, CH), 7.13 (1H, d, *J*=2.4 Hz, CH), 3.72–3.64 (2H, m, CH_2OH), 3.40–3.36 (1H, m, $CHCH_2OH$), 1.63–1.53 (3H, m, CH_2CHCH_3), 1.44 (9H, s), 1.28 (9H, s), 0.91–0.99 (6H, m, $(CH_3)_2C$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.3, 140.4, 136.9, 127.3, 126.3, 117.8, 70.2, 66.8, 41.1, 35.2, 34.4, 31.7, 29.6, 24.6, 23.8, 21.7; IR (neat) 3412, 2960, 2868, 1633, 1457, 1396, 1360, 1251, 1171, 1097, 1045, 1017 cm^{-1}.

4.2.3. β-[[[3,5-Bis(1,1-dimethylethyl)-2-hydroxyphenyl]-methylene]amino]-(βS)-benzenepropanol **3f**[13d]

A mixture of 3,5-di-*tert*-butylsalicylaldehyde (1.17 g, 5 mmol) and (*S*)-phenylalaninol (0.756 g, 5 mmol) in EtOH (10 mL) was stirred for 24 h. Evaporation of the solvent provided a residue that was purified by column chromatography (5% hexane/ethyl acetate) to give the title compound **3f** (1.47 g, 80%) as yellow liquid; [found: C, 78.58; H, 9.10; N, 3.79. $C_{18}H_{29}NO_2$ requires: C, 78.43; H, 9.05; N, 3.81%]; R_f (5% hexane/ethyl acetate) 0.38; $[\alpha]_D^{25}$ −17.2 (*c* 0.28, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, s, CHN), 7.40 (1H, s, CH), 7.29–7.25 (2H, m, CH), 7.21–7.16 (3H, m, CH), 7.01 (1H, s, CH), 3.81–3.75 (2H, m, CH_2OH), 3.53–3.50 (1H, m, $CHCH_2OH$), 2.97–2.89 (2H, m, CH_2Ph), 1.46 (9H, s, $(CH_3)_3C$), 1.28 (9H, s, $(CH_3)_3C$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 158.2, 140.4, 138.2, 136.8, 129.7, 128.7, 127.4, 126.6, 126.4, 117.8, 73.4, 66.1, 39.4, 35.3, 34.3, 31.7, 29.6; IR (neat) 3395, 3055, 2960, 2875, 1644, 1503, 1475, 1386, 1275, 1245, 1165, 1053, 1028 cm^{-1}.

4.2.4. 2-[[[(1S)-1-(Hydroxymethyl)-2,2-dimethylpropyl]-imino]methyl]-phenol **3g**[13e]

A mixture of salicylaldehyde (0.610 g, 5 mmol) and (*S*)-*tert*-leucinol (0.585 g, 5 mmol) in EtOH (10 mL) was stirred for 24 h. Evaporation of the solvent gave a residue that was purified by column chromatography (5% hexane/ethyl acetate) to give the title compound **3g** (1.02 g, 92%) as yellow liquid; [found: C, 70.63; H, 8.69; N, 6.35. $C_{13}H_{19}NO_2$ requires: C, 70.56; H, 8.65; N, 6.33%]; R_f (5% hexane/ethyl acetate) 0.32; $[\alpha]_D^{25}$ −22 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, s, CHN), 7.33–7.26 (2H, m, CH), 6.96–6.87 (2H, CH), 3.94 (1H, d, *J*=10.8 Hz, CHOH), 3.72 (1H, t, *J*=9.6 Hz, $CHCH_2OH$), 2.95 (1H, d, *J*=9.2 Hz, CHOH), 0.97 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 166.1, 161.6, 132.6, 131.7, 118.8, 117.2, 81.2, 62.5, 33.3, 27.2; IR (neat) 3365, 2958, 2871, 1633, 1469, 1390, 1361, 1274, 1252, 1173, 1062, 1047 cm^{-1}.

4.3. General procedure for the preparation of 4a–g

The ligands **3a–g** (3 mmol) reacted with $Cu(OAc)_2 \cdot 1H_2O$ (0.597 g, 3 mmol) in EtOH (10 mL) for 12 h at ambient temperature. The solvent was evaporated under reduced pressure, and the residue purified on silica gel column chromatography using ethyl acetate and hexane as eluent to give **4a–g** as a green colored powder.

4.3.1. Complex **4a**

A mixture of **3a** (0.874 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent yielded a residue that was purified by column chromatography (10% hexane/ethyl acetate) to give the title compound **4a** (1.61 g, 76%) as green powder; [found: C, 61.36; H, 7.72; N, 4.01. $C_{36}H_{54}N_2O_4Cu_2$ requires: C, 61.25; H, 7.71; N, 3.97%]; R_f (10% hexane/ethyl acetate) 0.41; $[\alpha]_D^{25}$ +520 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2957, 1627, 1530, 1433, 1325, 1255, 1167, 1054, 874, 690, 626, 520 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 610 (7931), 388 nm (14,981 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.12, $g_{\perp}$=2.03, $A_{\|}$=320 mT.

4.3.2. Complex **4b**

A mixture of **3b** (0.958 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent gave a residue, which was purified on column chromatography (15% hexane/ethyl acetate) to give the title compound **4b** (2.01 g, 88%) as green powder; [found: C, 63.12; H, 8.22; N, 3.75. $C_{40}H_{62}N_2O_4Cu_2$ requires: C, 63.05; H, 8.20; N, 3.68%]; R_f (15% hexane/ethyl acetate) 0.60; $[\alpha]_D^{25}$ +492 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2958, 1626, 1528, 1433, 1323, 1255, 1164, 1054, 837, 525 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 597 (3352), 382 nm (25,832 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.05, $g_{\perp}$=2.01, $A_{\|}$=317 mT.

4.3.3. Complex **4c**

A mixture of **3c** (1.0 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent provided a residue, which was purified by column chromatography (5% hexane/ethyl acetate) to yield the title compound **4c** (1.87 g, 79%) as green powder; [found: C, 63.80; H, 8.50; N, 3.59. $C_{42}H_{66}N_2O_4Cu_2$ requires: C, 63.85; H, 8.42; N, 3.55%]; R_f (5% hexane/ethyl acetate) 0.83; $[\alpha]_D^{25}$ +476 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2959, 1625, 1528, 1459, 1432, 1324, 1255, 1166, 1057, 837, 526 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 605 (9282), 382 nm (29,270 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.13, $g_{\perp}$=2.04, $A_{\|}$=320 mT.

4.3.4. Complex **4d**

A mixture of **3d** (1.0 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent provided a residue, which was purified by column chromatography (10% hexane/ethyl acetate) to give the title compound **4d** (2.13 g, 90%) as green powder; [found: C, 63.79; H, 8.45; N, 3.59. $C_{42}H_{66}N_2O_4Cu_2$ requires: C, 63.85; H, 8.42; N, 3.55%]; R_f (10% hexane/ethyl acetate) 0.50; $[\alpha]_D^{25}$ +395 (*c* 0.02, CH_2Cl_2); IR (KBr) ν 2959, 1625, 1528, 1459, 1432, 1324, 1255, 1164, 1057, 837, 526 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 613 (8492), 384 nm (18,723 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.10, $g_{\perp}$=2.02, $A_{\|}$=313 mT.

4.3.5. Complex **4e**

A mixture of **3e** (1.0 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent afforded a residue, which was purified by column chromatography (5% hexane/ethyl acetate) to give the title compound **4e** (2.25 g, 95%) as green powder; [found: C, 63.75; H, 8.53; N, 3.68. $C_{42}H_{66}N_2O_4Cu_2$ requires: C, 63.85; H, 8.42; N, 3.55%]; R_f (5% hexane/ethyl acetate) 0.53; $[\alpha]_D^{25}$ +400 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2960, 1619, 1537, 1260, 1163, 1076, 840, 554, 426 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 385 (4272), 281 nm (10,303 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.28, $g_{\perp}$=2.02, $A_{\|}$=317 mT; μ_{eff}(powder, 298 K): 1.58 μ_B/Cu.

4.3.6. Complex **4f**

A mixture of **3f** (1.10 g, 3 mmol) and $Cu(OAc)_2 \cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (5% hexane/ethyl acetate) to afford the title compound **4f** (2.11 g, 82%) as green powder; [found: C, 67.30; H, 7.35; N, 3.29. $C_{48}H_{62}N_2O_4Cu_2$ requires: C, 67.18; H, 7.28; N, 3.26%]; R_f (5% hexane/ethyl acetate) 0.63; $[\alpha]_D^{25}$ +320 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2966, 1635, 1540, 1441, 1322, 1266, 1178, 1076, 890, 855, 564,

446 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 615 (9137), 390 nm (12,526 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.13, $g_{\perp}$=2.06, $A_{\|}$=314 mT.

4.3.7. Complex ***4g***

A mixture of **3g** (0.664 g, 3 mmol) and $Cu(OAc)_2\cdot 1H_2O$ (0.598 g, 3 mmol) in EtOH (10 mL) was stirred for 12 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (5% hexane/ethyl acetate) to provide the title compound **4g** (1.18 g, 70%) as green powder; [found: C, 55.32; H, 6.09; N, 5.07. $C_{26}H_{34}N_2O_4Cu_2$ requires: C, 55.21; H, 6.06; N, 4.95%]; R_f (5% hexane/ethyl acetate) 0.44; $[\alpha]_D^{25}$ +430 (*c* 0.02, CH_2Cl_2); IR (KBr): ν 2961, 1631, 1536, 1447, 1348, 1194, 1072, 1016, 902, 852, 760, 671, 582, 544, 461 cm^{-1}; UV–vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 614 (4943), 385 nm (9859 $mol^{-1}\,dm^3\,cm^{-1}$); EPR (MeOH): liquid N_2 temp; $g_{\|}$=2.14, $g_{\perp}$=2.05, $A_{\|}$=315 mT.

4.4. General procedure for nitroaldol reaction

Aldehyde (0.5 mmol), nitroalkane (5 mmol), and complex **4a**–**g** (2.5 mol %) were stirred in appropriate solvent (1 mL) at ambient temperature. The progress of the reaction was monitored by TLC. After completion, the solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as eluent.

4.4.1. (S)-(+)-2-Nitro-1-(4-nitrophenyl)ethanol (Table 1, entry 5)[14a]

A mixture of 4-nitrobenzaldehyde (75.5 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 24 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (95.6 mg, 90%) as colorless solid; R_f (20% hexane/ethyl acetate) 0.43; mp 84–85 °C; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 14.7 min, 18.1 min; 66:34 er; $[\alpha]_D^{20}$ +8.4 (*c* 1, CH_2Cl_2).

4.4.2. 2-Nitro-1-(4-nitrophenyl)propanol (Table 1, entry 8)[14a]

A mixture of 4-nitrobenzaldehyde (75.5 mg, 0.5 mmol), nitroethane (375.3 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 48 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to provide the title compound (88.2 mg, 78%) as colorless solid; R_f (20% hexane/ethyl acetate) 0.52; *syn*/*anti* ratio 55:45; mp 92–94 °C; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.3 mL/min, retention time: 32.6 min, 38.2 min, 41.0 min, 42.5 min; 56:44, 64:36 er; $[\alpha]_D^{20}$ −0.3 (*c* 0.4, CH_2Cl_2).

4.4.3. 2-Nitro-1-(4-nitrophenyl)butanol (Table 1, entry 9)

A mixture of 4-nitrobenzaldehyde (75.5 mg, 0.5 mmol), 1-nitropropane (445.4 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 48 h. Evaporation of the solvent provided a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (54.0 mg, 45%) as colorless solid; R_f (20% hexane/ethyl acetate) 0.51; *syn*/*anti* ratio 55:45; mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (2H, d, *J*=8.8 Hz, CH), 7.57 (2H, d, *J*=8.8 Hz, CH), 5.17–5.13 (1H, m, $CHNO_2$), 4.61–4.56 (1H, m, CHOH), 2.96 (1H, d, *J*=0.8 Hz, OH), 1.94–1.84 (1H, m, CH_2CH_3), 1.50–1.41 (1H, m, CH_2CH_3), 0.90 (3H, t, *J*=0.8 Hz, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 145.9, 145.8, 128.0, 127.5, 124.3, 128.1, 94.8, 94.3, 74.5, 73.4, 24.0, 21.4, 10.5, 10.2; IR (KBr) ν 3460, 1557, 1520, 1345 cm^{-1}; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.3 mL/min, retention time: 29.6 min, 32.2 min, 33.5 min, 35.2 min; 55:45, 59:41 er; *syn*/*anti* ratio 55:45; $[\alpha]_D^{20}$ −0.2 (*c* 0.28, CH_2Cl_2). Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N 11.66. Found: C, 50.03; H, 5.05; N, 11.70.

4.4.4. (S)-(+)-2-Nitro-1-phenylethanol (Table 3, entry 1)[14a]

A mixture of benzaldehyde (53.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 28 h. Evaporation of the solvent afforded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to yield the title compound (76.8 mg, 92%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.60; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.6 mL/min, retention time: 34.1 min, 39.5 min; 60:40 er; $[\alpha]_D^{20}$ +10 (*c* 0.1, CH_2Cl_2).

4.4.5. (S)-(+)-2-Nitro-1-(2-bromophenyl)ethanol (Table 3, entry 2)[14b,c]

A mixture of 2-bromobenzaldehyde (92.5 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 20 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to provide the title compound (144.4 mg, 93%) as colorless oil; R_f (20% hexane/ethyl acetate) 0.58; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 11.43 min, 12.14 min; 55:45 er; $[\alpha]_D^{20}$ +3.5 (*c* 1, $CHCl_3$).

4.4.6. (S)-(+)-2-Nitro-1-(2-methoxyphenyl)ethanol (Table 3, entry 3)[14c]

A mixture of 2-methoxybenzaldehyde (68.07 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 34 h. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to afford the title compound (87.7 mg, 89%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.56; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 12.5 min, 14.3 min; 65:35 er; $[\alpha]_D^{20}$ +12 (*c* 1.06, CH_2Cl_2).

4.4.7. (+)-2-Nitro-1-(3-bromophenyl)ethanol (Table 3, entry 4)[14d]

A mixture of 3-bromobenzaldehyde (92.5 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 30 h. Evaporation of the solvent provided a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (104.5 mg, 85%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.66; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 17.45 min, 23.1 min; 60:40 er; $[\alpha]_D^{20}$ +2 (*c* 1, CH_2Cl_2).

4.4.8. (S)-(+)-2-Nitro-1-(3-nitrophenyl)ethanol (Table 3, entry 5)[14a]

A mixture of 3-nitrobenzaldehyde (75.5 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 26 h at ambient temperature. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (94.5 mg, 90%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.45; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 21.8 min, 24.4 min; 76:24 er; $[\alpha]_D^{20}$ +14 (*c* 0.4, CH_2Cl_2).

4.4.9. (+)-2-Nitro-1-(4-bromophenyl)ethanol (Table 3, entry 6)[14e]

A mixture of 4-bromobenzaldehyde (92.5 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 24 h at ambient temperature.

Evaporation of the solvent afforded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (116.8 mg, 95%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.51; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 15.7 min, 18.9 min; 58:42 er; $[\alpha]_D^{20}$ +1.5 (*c* 0.5, CH_2Cl_2).

4.4.10. (S)-(+)-2-Nitro-1-(4-chlorophenyl)ethanol (Table 3, entry 7)[14a]

A mixture of 4-chlorobenzaldehyde (70.2 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 23 h at ambient temperature. Evaporation of the solvent provided a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (90.7 mg, 90%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.64; HPLC Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 12.8 min, 16.09 min; 54:46 er; $[\alpha]_D^{20}$ +2 (c 0.5, CH_2Cl_2).

4.4.11. (S)-(+)-2-Nitro-1-(4-fluorophenyl)ethanol (Table 3, entry 8)[14f]

A mixture of 4-fluorobenzaldehyde (62.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 22 h. Evaporation of the solvent afforded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (87.0 mg, 94%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.56; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 12.1 min, 14.0 min; 55:45 er; $[\alpha]_D^{20}$ +1.7 (*c* 0.8, CH_2Cl_2).

4.4.12. (S)-(+)-2-Nitro-1-(4-methoxyphenyl)ethanol (Table 3, entry 9)[14c]

A mixture of 4-methoxybenzaldehyde (68.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 38 h. Evaporation of the solvent afforded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (82.8 mg, 84%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.53; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 16.9 min, 21.7 min; 66:34 er; $[\alpha]_D^{20}$ +10 (*c* 1.4, CH_2Cl_2).

4.4.13. (S)-(+)-2-Nitro-1-(4-methylphenyl)ethanol (Table 3, entry 10)[14g]

A mixture of 4-methylbenzaldehyde (60.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 30 h at ambient temperature. Evaporation of the solvent provided a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (81.5 mg, 90%) as colorless oil; R_f (20% hexane/ethyl acetate) 0.66; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (90:10), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 16.5 min, 21.2 min; 64:36 er; $[\alpha]_D^{20}$ +8 (*c* 1, CH_2Cl_2).

4.4.14. (S)-(+)-2-Nitro-1-naphthylethanol (Table 3, entry 11)[14g]

A mixture of naphthaldehyde (78.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 36 h at ambient temperature. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to yield the title compound (87.9 mg, 81%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.58; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, retention time: 34.4 min, 49.7 min; flow rate: 0.8 mL/min, 61:39 er; $[\alpha]_D^{20}$ +10 (*c* 1, CH_2Cl_2).

4.4.15. (S)-(−)-2-Nitro-1-(2-thiophenyl)ethanol (Table 3, entry 12)[14h]

A mixture of 2-thiophenecarboxaldehyde (56.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 30 h at ambient temperature. Evaporation of the solvent afforded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (56.28 mg, 65%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.58; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 9.6 min, 10.4 min; 54:46 er; $[\alpha]_D^{20}$ −2.5 (*c* 0.2, CH_2Cl_2).

4.4.16. (S)-(−)-2-Nitro-1-(2-furanyl)ethanol (Table 3, entry 13)[14h]

A mixture of 2-furaldehyde (48.01 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 16 h at ambient temperature. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to provide the title compound (58.1 mg, 74%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.53; HPLC: Chiralpak AD-H column, *n*-hexane/isopropanol (95:5), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 26.6 min, 28.1 min; 55:45 er; $[\alpha]_D^{20}$ −7 (*c* 0.5, CH_2Cl_2).

4.4.17. (S)-(+)-2-Nitro-1-cyclohexylethanol (Table 3, entry 14)[14f]

A mixture of cyclohexanecarboxaldehyde (56.08 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 24 h. Evaporation of the solvent provided a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (77.0 mg, 89%) as yellow oil; R_f (20% hexane/ethyl acetate) 0.72; HPLC: Chiralpak AD-H column, *n*-hexane/isopropanol (97:3), wavelength: 215 nm, flow rate: 0.8 mL/min, retention time: 33.2 min, 35.8 min; 68:32 er; $[\alpha]_D^{20}$ +3.5 (*c* 2, CH_2Cl_2).

4.4.18. (S)-(+)-3-Methyl-1-nitro-2-butanol (Table 3, entry 15)[14a]

A mixture of isobutyraldehyde (36.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 20 h. Evaporation of the solvent yielded a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to give the title compound (57.2 mg, 86%) as colorless oil; R_f (20% hexane/ethyl acetate) 0.66; HPLC: Chiralpak AD-H column, *n*-hexane/isopropanol (95:5), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 11.5 min, 15.6 min; 64:36 er; $[\alpha]_D^{20}$ +1.2 (*c* 0.45, CH_2Cl_2).

4.4.19. (−)-2-Hydroxy-3-nitropropanoic acid ethyl ester (Table 3, entry 16)[14i]

A mixture of ethyl glyoxalate (51.0 mg, 0.5 mmol), nitromethane (305.2 mg, 5 mmol), and catalyst **4e** (9.8 mg, 2.5 mol %) in CH_2Cl_2 (1 mL) was stirred for 30 h at ambient temperature. Evaporation of the solvent gave a residue, which was purified by column chromatography (20% hexane/ethyl acetate) to afford the title compound (4.8 mg, 55%) as colorless solid; R_f (20% hexane/ethyl acetate) 0.41; HPLC: Chiralcel OD-H column, *n*-hexane/isopropanol (85:15), wavelength: 215 nm, flow rate: 1 mL/min, retention time: 8.1 min, 8.6 min; 57:43 er; $[\alpha]_D^{20}$ −0.5 (*c* 0.38, CH_2Cl_2).

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Supplementary data

Crystal data, EPR, TGA and UV–vis of **4e**, and NMR (^{1}H and ^{13}C) spectra of the ligands **3a**–**g** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.10.009.

References and notes

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5. The single crystal X-ray analysis of $C_{42}H_{66}Cu_2N_2O_4$ **4e** showed M_r=790.05, deep green crystal 0.51×0.20×0.11 mm^3, monoclinic, space group=C_2, a=31.67(5), b=10.5061(16), c=28.397(4) Å; α=90, β=112.432(9), γ=90°, V=8734(2) Å^3, Z=8, ρ_{calcd}=1.202 mg/m^3, Mo Kα radiation, λ=0.71073 Å; measured reflection=24,401, unique reflections=14,178, temperature=296(2) K, data were collected on a Bruker smart CCD area detector system with graphite monochromator. The structure was solved by direct methods and refined on F^2 by full-matrix-block least squares (G. M. Sheldrick. *SHELXL-97 Program of the Solution of Crystal Structure*. University of Göttingen: Göttingen, Germany, 1997). In refinement, data/restraints/parameters are 14,718/1/938. The final R_1=0.0646, wR_2=0.1608 ($I>2\sigma(I)$); R_1=0.1107, wR_2=0.1858 (all data), GOF on F^2=0.864. CCDC-291783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).
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