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Axially dissymmetric binaphthyldiimine chiral salen-type ligands for copper-catalyzed asymmetric aziridination

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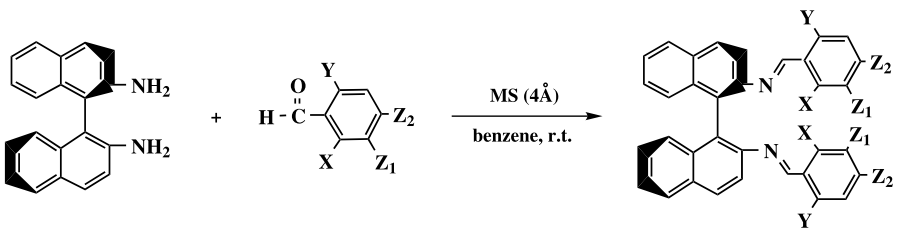
Abstract—Axially dissymmetric chiral salen-type ligands **1**–**4** and **7** were prepared from the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 2,6-dichlorobenzaldehyde, 2,3-dichlorobenzaldehyde, 3,4-dichlorobenzaldehyde or salicylaldehyde in high yields, respectively. The catalytic asymmetric aziridination of alkenes has been examined using these novel chiral ligands. Excellent enantioselectivity in the aziridination of cinnamates has been achieved using the C_2-symmetric chiral ligand **1**.

1. Introduction

Aziridines are versatile intermediates for the synthesis of compounds bearing nitrogen functionalities.[1] In 1991, Evans et al. reported that cationic Cu(I) complexes catalyzed the nitrene-transfer reaction [*N*-(*p*-tolylsulfonyl)imino]phenyliodane (PhI=NTs) smoothly.[1] Since then, many studies on asymmetric aziridination have been carried out with chiral copper(I) complexes as catalysts. Evans et al. were the first to report that 4,4′-disubstuituted bisoxazolines are excellent chiral ligands for enantioselective aziridination.[2a,b] Lowenthal and Masamune[3] also reported that the copper complex bearing a bisoxazoline ligand was an effective catalyst for the aziridination of styrene. Jacobsen et al. utilized their own chiral diimine to serve as an effective chiral auxiliary for the copper-catalyzed aziridination of aryl-substituted (*Z*)-olefins.[4] In addition, Aggarwal disclosed catalytic asymmetric aziridination catalyzed by $Rh_2(OAc)_4$ and mediated by chiral sulfur ylides,[5a] and Burrows and Katsuki employed chiral Mn–salen complexes as catalyst for enantioselective epoxidation and aziridination.[5b,c] On the other hand, axially dissymmetric 1,1′-binaphthyl and 1,1′-biphenyl ligands bearing two identical groups in the 2- and 2′-positions have proved remarkably useful in



Ligand 1: X=Y= Cl, Z_1=Z_2= H; 92%.
Ligand 2: X=Z_1= Cl, Y=Z_2= H; 90%.
Ligand 3: X=Y= H, Z_1=Z_2= Cl; 89%.
Ligand 4: X= OH, Y=Z_1=Z_2= H; 92%.

Scheme 1.

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enantioselective catalysis, with enantioselectivities close to 100% enantiomeric excess (e.e.) being obtained in several preparatively important reactions.[6] Very recently, Scott disclosed that the highly enantioselective aziridination of alkenes could be achieved using the [(biaryldiimine)Cu^{I}] catalyst system.[7] Herein, we wish to report the synthesis of axially dissymmetric binaphthyldiimine chiral salen-type ligands **1**–**4** and **7** from C_2-symmetric (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine and the results from the catalytic asymmetric aziridination of alkenes using these novel chiral ligands.[8]

2. Results and discussion

The axially chiral salen-type ligands **1**–**4** were prepared by the reaction of C_2-symmetric (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine as a chiral scaffold with the corresponding arylaldehydes in anhydrous benzene in the presence of 4 Å molecular sieve (MS) (Scheme 1). After the usual work-up and purification by silica gel column chromatography or recrystallization, ligands **1**–**4** were obtained as yellow solids in ca. 90% yields.

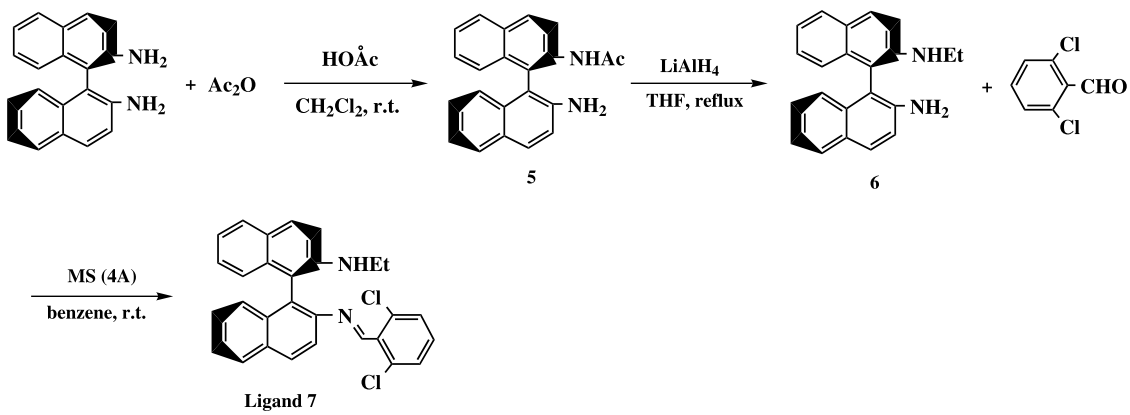
The C_1-symmetric chiral salen-type ligand **7** was prepared in high yield by acylation of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with acetic anhydride/acetic acid in dichloromethane, reduction with $LiAlH_4$ and subsequent reaction with 1,6-dichlorobenzaldehyde under the same conditions as for **1**–**4** (Scheme 2).

Catalytic asymmetric aziridination of the alkenes was carried out in dichloromethane, THF or acetonitrile with a molar ratio of copper:ligand:PhI = NTs:alkene of 0.05:0.055:1:5. The e.e. of the product was determined by HPLC analysis using a chiral stationary phase column (CHIRALCEL OD, OJ or AB). The absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

Using styrene as the substrate, we examined the chiral induction abilities of chiral ligands **1**–**4** in catalytic asymmetric aziridination. The results are summarized in Table 1. We found that C_2-symmetric ligand **1**, derived from the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 2,6-dichlorobenzaldehyde, gave the highest e.e. (Table 1, entries 1–4) and the best result (e.e. of 25%) was obtained with ligand **1** in the presence of $Cu(MeCN)_4ClO_4$ in dichloromethane with 4 Å MS at −20°C (Table 1, entry 12). The solvent also played a very important role in this reaction. Using benzene or neat styrene as the solvents, the products were obtained with lower e.e. (Table 1, entries 9–11). Especially when the reaction was carried out in acetonitrile, no chiral induction was observed (Table 1, entry 8). A copper(II) catalyst such as $Cu(OTf)_2$ showed no chiral induction ability for this reaction (Table 1, entry 6) and CuOTf gave only 11% e.e. (Table 1, entry 7).

In order to reach higher enantioselectivity in the asymmetric aziridination using chiral ligand **1**, we next examined the aziridination of other alkenes under the optimized conditions. We were delighted to find that in the asymmetric aziridination of indene, e.e. of 74% could be achieved although the yield was only 22% (Table 2, entry 3). In the presence of 4 Å MS at −20°C, the yield improved from 22 to 47% with 62% e.e. (Table 2, entry 5). Reducing the temperature led to a slight improvement of e.e. in the aziridination of indene (Table 2, entries 1–5). Excellent results were obtained in the asymmetric aziridination of *trans*-cinnamates (Table 2, entries 6–16). In the aziridination of methyl cinnamate, e.e. of 69% was obtained at 20°C (reaction time = 4 h) and 75% e.e. was obtained at −20°C (reaction time = 24 h) with yields of over 90% in both cases (Table 2, entries 6 and 8). In acetonitrile, e.e. of only 11% was achieved under the same conditions (Table 2, entry 7). Moreover, using phenyl or *tert*-butyl cinnamate as the substrates under the same conditions, we found that e.e.s of 88 and 97%, respectively, could be achieved at −20°C with excellent yields (Table 2, entries 9 and 10).

The substituents on the phenyl ring can also affect the enantioselectivity of the aziridination of cinnamates. For example, it was found that, using methyl, phenyl or *tert*-butyl *p*-chlorocinnamate as substrates (Cl can be seen as an electron-withdrawing group) 85%, 84% and 90% e.e., respectively, were achieved under the same conditions (Table 2, entries 11, 12, and 13). The results



Scheme 2.

Table 1. Catalytic asymmetric aziridination of styrene

Entry	Copper	Ligand	Solvent	Temp. [°C]	Time [h.]	Yield[a] [%]	E.e.[b] [%]	Config.[c]
1	$Cu(MeCN)_4ClO_4$	1	CH_2Cl_2	20	4	92	22	*S*
2	$Cu(MeCN)_4ClO_4$	2	CH_2Cl_2	20	4	77	2	*S*
3	$Cu(MeCN)_4ClO_4$	3	CH_2Cl_2	20	4	87	1	*S*
4	$Cu(MeCN)_4ClO_4$	4	CH_2Cl_2	20	4	40	0	*S*
5	$Cu(MeCN)_4BF_4$	1	CH_2Cl_2	20	4	90	20	*S*
6	$Cu(OTf)_2$	1	CH_2Cl_2	20	4	31	0	*S*
7	CuOTf	1	CH_2Cl_2	20	4	89	11	*S*
8	$Cu(MeCN)_4ClO_4$	1	MeCN	20	4	85	0	*S*
9	$Cu(MeCN)_4ClO_4$	1	C_6H_6	20	4	92	12	*S*
10	$Cu(MeCN)_4ClO_4$	1	C_6H_6 + MS(4Å)	20	4	91	14	*S*
11	$Cu(MeCN)_4ClO_4$	1	Styrene	20	4	95	20	*S*
12	$Cu(MeCN)_4ClO_4$	1	CH_2Cl_2 + MS(4Å)	-20	24	93	25	*S*
13	$Cu(MeCN)_4ClO_4$	1	CH_2Cl_2	-20	24	93	21	*S*

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Determined by the sign of the specific rotation.

are very similar to those of cinnamates. However, using methyl, phenyl or *tert*-butyl *p*-methoxycinnamate (MeO is a typical electron-donating group) as substrate, the aziridinations were relatively slow and these reactions required 36 h to give the corresponding products in yields of ca. 60%. The achieved e.e.s and chemical yields are also lower than those observed for cinnamates (Table 2, entries 14, 15, and 16).

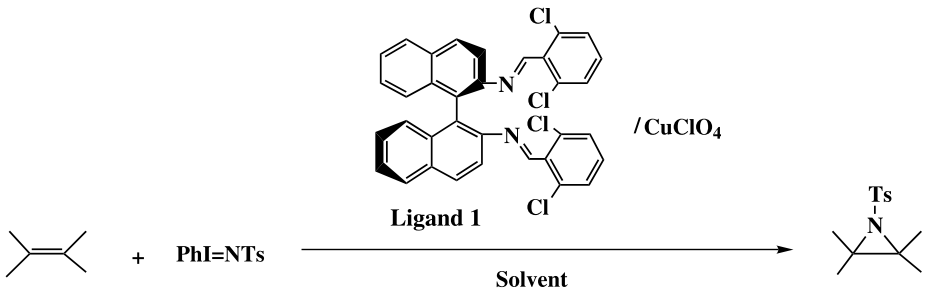
On the other hand, using C_1-symmetric chiral ligand **7** in the aziridination of cinnamates under the same conditions we found that the achieved e.e.s were in general lower than those for C_2-symmetric chiral ligand **1**, although the chemical yields were very similar (Table 3, entries 1–3). This result suggests that a C_2-symmetric ligand must be used in order to attain high e.e. in the asymmetric aziridination reaction.

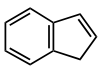
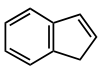
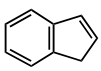
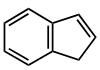
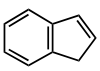
Previously, we reported a very similar axially dissymmetric chiral(diimine) ligand **8** and $Cu(OTf)_2$-catalyzed asymmetric aziridination of alkenes (Scheme 3).[9] But only very poor enantioselectivities have been achieved. We believe that this is because the catalytic site in ligand **8** is relatively remote from the stereogenic center in comparison with the best chiral ligand **1**.

3. Conclusions

In conclusion, the chiral C_2-symmetric axially dissymmetric chiral salen-type ligands **1**–**4** and C_1-symmetric salen-type ligand **7** were successfully synthesized. We found that C_2-symmetric ligand **1**, derived from the reaction of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 2,6-dichlorobenzaldehyde, gave excellent results in the enantioselective aziridination of *trans*-cinnamate derivatives. Although the achieved results are very similar to those reported by Scott,[7] this is the first application of ligand **1** in the asymmetric aziridination. Efforts

Table 2. Catalytic asymmetric aziridination of alkenes



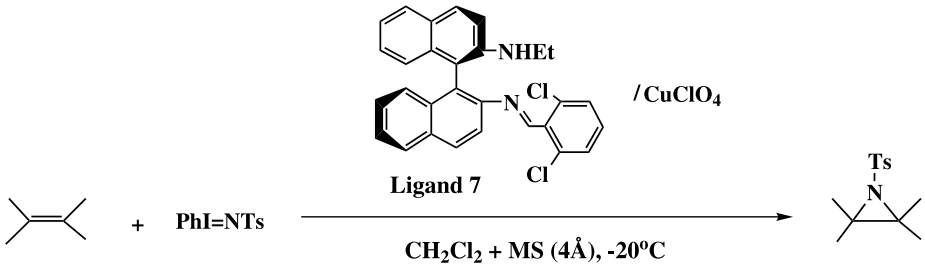
Entry	Alkene	Solvent	Temp. [°C]	Time [h.]	Yield[a] [%]	E.e.[b] [%]	Config.[d]
1		CH_2Cl_2	20	4	25	64	1*S*,2*R*
2		CH_2Cl_2	-20	24	25	73	1*S*,2*R*
3		CH_2Cl_2	-20	24	22	74[c]	1*S*,2*R*
4		CH_2Cl_2 + MS (4Å)	20	4	25	50	1*S*,2*R*
5		CH_2Cl_2 + MS (4Å)	-20	24	47	62	1*S*,2*R*
6	Ph·CH=CH·CO_2Me	CH_2Cl_2 + MS (4Å)	20	4	90	69	2*S*,3*R*
7	Ph·CH=CH·CO_2Me	MeCN + MS (4Å)	20	4	71	11	2*S*,3*R*
8	Ph·CH=CH·CO_2Me	CH_2Cl_2 + MS (4Å)	-20	24	92	75	2*S*,3*R*
9	Ph·CH=CH·CO_2Ph	CH_2Cl_2 + MS (4Å)	-20	24	90	88	2*S*,3*R*
10	Ph·CH=CH·CO_2Bu^t	CH_2Cl_2 + MS (4Å)	-20	24	91	97	2*S*,3*R*
11	*p*-ClPh·CH=CH·CO_2Me	CH_2Cl_2 + MS (4Å)	-20	24	90	85	2*S*,3*R*
12	*p*-ClPh·CH=CH·CO_2Ph	CH_2Cl_2 + MS (4Å)	-20	24	86	84	2*S*,3*R*
13	*p*-ClPh·CH=CH·CO_2Bu^t	CH_2Cl_2 + MS (4Å)	-20	24	85	90	2*S*,3*R*
14	*p*-MeOPhCH=CH·CO_2Me	CH_2Cl_2 + MS (4Å)	-20	36	65	53	2*S*,3*R*
15	*p*-MeOPh·CH=CH·CO_2Ph	CH_2Cl_2 + MS (4Å)	-20	36	60	64	2*S*,3*R*
16	*p*-MeOPh·CH=CH·CO_2Bu^t	CH_2Cl_2 + MS (4Å)	-20	36	60	88	2*S*,3*R*

[a] Isolated yield. [b] Determined by chiral HPLC. [c] Using $Cu(MeCN)_4BF_4$ as a catalyst.

[d] Determined by the sign of the specific rotation.

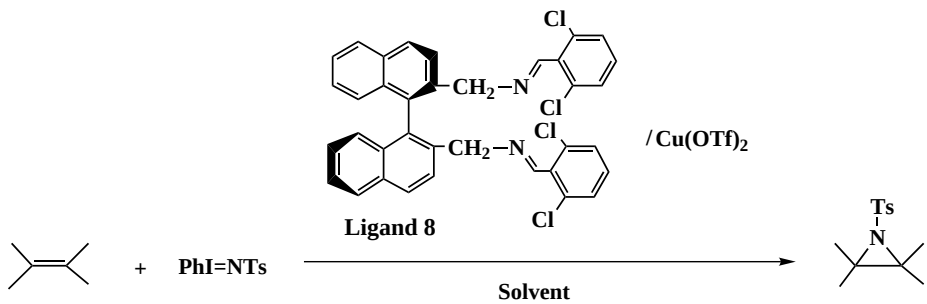
are underway to elucidate the mechanistic details of this reaction and to disclose the exact structure of the active species. Moreover, we are planning to synthesize more bidentate C_2-symmetric chiral binaphthyldiimine ligands in order to seek out more effective and stereoselective ligands, which can be utilized in other catalytic

Table 3. Catalytic asymmetric aziridination of alkenes in the presence of ligand **7**



Entry	Alkene	Temp. [°C]	Time [h.]	Yield[a)] [%]	E.e.[b)] [%]	Config.[c)]
1	Ph·CH=CH·CO_2Me	-20	24	92	51	2*S*,3*R*
2	Ph·CH=CH·CO_2Ph	-20	24	80	54	2*S*,3*R*
3	Ph·CH=CH·CO_2Bu^t	-20	24	81	72	2*S*,3*R*

[a)] **Isolated yield.** [b)] **Determined by chiral HPLC.** [c)]**Determined by the sign of the specific rotation.**



Scheme 3.

asymmetric reactions. Work along this line is currently in progress.

4. Experimental

4.1. General

MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Optical rotations were determined in a solution of $CHCl_3$ at 20°C by using a Perkin–Elmer-241 MC polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ or C_6D_6 with tetramethylsilane (TMS) as internal standard; coupling constant (J) values are reported in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured using a Finnigan MA+mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All aziridination experiments were performed under argon using standard Schlenk techniques. Dichloromethane and acetonitrile were distilled from calcium hydride under nitrogen. $CuClO_4$ and CuOTf were handled in the drybox under an argon atmosphere. All olefins were distilled prior to use. The enantiomeric purities of aziridines were determined by HPLC analyses using a chiral stationary phase column (column, Daicel Co. Chiralcel OD, AB, and OJ; eluent, 100:0.5–2 hexane–2-propanol mixture; flow rate, 1.0 mL min^{-1}; detection, 254 nm light) and the absolute configuration of the major enantiomer was

assigned according to the sign of the specific rotation. (*R*)-(+)-1,1′-Binaphthyl-2,2′-diamine was purchased from Aldrich Co.

4.2. Representative experimental details for the synthesis of ligands 1–4

(*R*)-(+)-1,1′-Binaphthyl-2,2′-diamine (0.2 mmol), arylaldehyde (0.56 mmol) and MS (4 Å, ca. 0.2 g) were stirred in anhydrous benzene (5.0 mL) at room temperature for 10 h. After filtration, the solvent was removed under reduced pressure and the corresponding Schiff base was separated by flash chromatography on silica gel (eluent: hexane:EtOAc:Et_3N = 250:10:1). The yields of **1**–**4** were about 90%.

4.2.1. Ligand 1: (*R*)-(+)-*N*,*N*′-Bis(2,6-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine. $[\alpha]_D^{20}$ −88 (*c* 0.089, acetone); mp: 180–181°C; IR (CH_2Cl_2) *v* 1615 cm^{-1} (C=N); ^1H NMR (C_6D_6, TMS, 300 MHz) δ 6.22 (m, 2H), 6.64 (d, J = 8.0 Hz, 4H), 7.12 (m, 2H), 7.23 (m, 2H), 7.47 (d, J = 8.67 Hz, 2H), 7.60 (d, J = 8.58 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 8.73 (s, 2H, imino-H); MS (EI) m/e 598 (M^+, 6.09), 441 (M^+−158, 100), 424 (M^+−174, 29.8); anal. calcd for $C_{34}H_{20}Cl_4N_2$ requires C, 68.23; H, 3.34; N, 4.68; found: C, 68.53; H, 3.47; N, 4.32%.

4.2.2. Ligand 2: (*R*)-(+)-*N*,*N*′-Bis-(2,3-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine. $[\alpha]_D^{20}$ +282 (*c* 0.13, acetone); mp: 130–131°C; IR (CH_2Cl_2) *v* 1607 cm^{-1} (C=N); ^1H NMR (C_6D_6, TMS, 300 MHz) δ 6.29 (m, 2H), 6.80–6.83 (m, 2H), 7.05–7.10 (m, 2H), 7.18–7.27 (m, 4H), 7.55–7.64 (m, 4H), 7.71–7.78 (m, 4H), 8.77 (s, 2H, imino-H); MS (EI) m/e 598 (M^+, 27.42), 561 (M^+−37, 1.01), 424 (M^+−174, 100); anal. calcd for $C_{34}H_{20}Cl_4N_2$ requires C, 68.23; H, 3.34; N, 4.68; found: C, 68.11; H, 3.37; N, 4.58%.

4.2.3. Ligand 3: (*R*)-(+)-*N*,*N*′-Bis-(3,4-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine. $[\alpha]_D^{20}$ +15 (*c* 0.1, acetone); mp: 162–163°C; IR (CH_2Cl_2) *v* 1614 cm^{-1} (C=N); ^1H NMR (C_6D_6, TMS, 300 MHz) δ 6.71 (d, J = 8.3 Hz, 2H), 6.90 (m, 2H), 7.04–7.12 (m, 2H), 7.18–7.26 (m, 6H), 7.55–7.64 (m, 4H), 7.58 (d, J = 8.7 Hz, 2H), 7.75–7.82 (m, 4H), 7.84 (s, 2H, imino-H); MS (EI) m/e 598 (M^+, 6.11), 561 (M^+−37, 1.60), 424 (M^+−174, 100); anal. calcd for $C_{34}H_{20}Cl_4N_2$ requires C, 68.23; H, 3.34; N, 4.68; found: C, 68.14; H, 3.31; N, 4.52%.

4.2.4. Ligand 4: (*R*)-(+)-*N*,*N*′-Bis-(2-hydroxylbenzylidene)-1,1′-binaphthyl-2,2′-diamine. $[\alpha]_D^{20}$ −655 (*c* 0.12, acetone); ^1H NMR (C_6D_6, TMS, 300 MHz) δ 6.61 (d, J = 7.9 Hz, 2H), 6.82 (t, J = 7.2, 6.5 Hz, 2H), 7.20–7.34 (m, 6H), 7.42–7.49 (m, 4H), 7.90 (d, J = 8.9 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H), 8.22 (d, J = 8.9 Hz, 2H), 8.98 (s, 2H, imino-H). This is a known compound. The physical data are inconsistent with those reported.[10]

4.3. (*R*)-(+)-*N*-Acetyl-1,1′-binaphthyl-2,2′-diamine 5

Acetic anhydride (52 μL, 0.55 mmol) was added to a mixture of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (142 mg, 0.5 mmol), acetic acid (0.3 mL, 5.0 mmol) and dichloromethane (5.0 mL) with ice-cooling. The mixture was stirred at room temperature overnight, and saturated $NaHCO_3$ (5.0 mL) was added. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography on Al_2O_3 (eluent: hexane:ethyl acetate = 3:1) to afford **5** as a colorless solid (90 mg, 55%). ^1H NMR ($CHCl_3$, TMS, 300 MHz) δ 1.83 (s, 3H, Me), 3.60 (br, 3H, amino-H), 6.85–7.44 (m, 7H, Ar H), 7.79–8.03 (m, 4H, Ar), 8.40 (d, J = 8.9 Hz, 2H, Ar). This compound was used for the next reaction.

4.4. (*R*)-(+)-*N*-Ethyl-1,1′-binaphthyl-2,2′-diamine 6

To a stirred suspension of $LiAlH_4$ (93 mg, 2.65 mmol) in anhydrous THF (20 mL) was added dropwise a solution of **5** (170 mg, 0.53 mmol) in THF (2 mL). The mixture was heated under reflux for 4 h. The reaction mixture was cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water (1.0 mL) and then 10% NaOH (1.0 mL). A white precipitate was filtered off and thoroughly washed with ether. The combined filtrate and ether washings were washed with brine and dried over $MgSO_4$. After the solvents were evaporated under reduced pressure, the product was purified by flash chromatography (Al_2O_3, EtOAc:petroleum ether = 1:6) affording **6** (130 mg, 91%) as a colorless solid. ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.92 (t, J = 6.7 Hz, 3H, Me), 3.14 (q, J = 6.7 Hz, 2H, CH_2), 3.48 (br, 3H, amino-H), 6.84–7.20 (m, 8H, Ar), 7.65–7.82 (m, 4H, Ar). This compound was used in the next reaction.

4.5. Chiral ligand 7: (*R*)-(+)-*N*-ethyl-*N*′-(2,6-dichlorobenzylidene)-1,1′-binaphthyl-2,2′-diamine

Compound **6** (63 mg, 0.2 mmol), 2,6-dichlorobenzaldehyde (49 mg, 0.28 mmol), and MS (4 Å, ca. 0.2 g) were stirred in anhydrous benzene (5.0 mL) at room temperature for 10 h. After filtration, the solvent was removed under reduced pressure and the corresponding Schiff base was separated by flash chromatography on silica gel (eluent: hexane:EtOAc:Et_3N = 300:10:1) to afford a yellowish viscous compound **7**: 78 mg, 83%; $[\alpha]_D^{20}$ −60.5 (*c* 0.13, acetone); IR (CH_2Cl_2) *v* 1615 cm^{-1} (C=N); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.64 (t, J = 6.7 Hz, 3H, Me), 2.78 (q, J = 6.7 Hz, 2H, CH_2), 3.59 (br, 1H, amino-H), 6.18 (t, J = 8.5 Hz, 1H), 6.61 (d, J = 8.5 Hz, 2H), 6.98–7.23 (m, 4H), 7.44–7.60 (m, 2H), 7.70–7.83 (m, 6H), 8.44 (s, 1H, imino-H); MS (EI) m/e 468 (M^+, 63.64), 424 (M^+−44, 14.61), 309 (M^+−159, 57.73), 280 (M^+−188, 100); anal. calcd for $C_{29}H_{22}Cl_2N_2$ requires C, 74.36; H, 4.70; N, 5.98; found: C, 74.01; H, 4.41; N, 5.73%.

4.6. Typical reaction procedure for the aziridination reaction catalyzed by $[Cu(CH_3CN)_4]ClO_4$

To a schlenk tube placed with chiral ligand **1** (9.0 mg, 0.014 mmol), molecular sieve (MS) (4 Å, ca. 40 mg) and anhydrous dichloromethane (2 mL) were added

$[Cu(CH_3CN)_4]ClO_4$ (4.0 mg, 0.013 mmol) under an argon atmosphere. The reaction mixture was stirred for 2 h at room temperature. Methyl cinnamate (202 mg, 1.23 mmol) was added and the solution was stirred for a further 30 min. The solution was then cooled to −20°C and solid PhI=NTs (94 mg, 0.25 mmol) was added against a positive argon counterflow. The heterogeneous mixture was stirred at −20°C for 1 h. After the specified time interval the solution was filtered through a plug of silica gel, and the product was separated by flash chromatography on silica gel (eluent: EtOAc:hexane=1:6). Enantiomeric excess (e.e.) was readily determined using Chiral HPLC.

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