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Chiral bipyridine–copper(I) complex-catalyzed enantioselective allylic oxidation of cyclic alkenes†

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Abstract—Chiral copper(I)–bipyridine complexes were prepared and used as catalysts in the enantioselective allylic oxidation of cyclic alkenes with *tert*-butyl perbenzoate. The yields ranged from moderate to good and enantioselectivities up to 70% were observed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The copper-catalyzed allylic oxidation of olefins with peresters has been the subject of numerous synthetic and mechanistic investigations.[1–7] Through this useful reaction, unactivated olefins can be functionalized into chiral allylic carboxylates, which are important intermediates in the synthesis of biologically active compounds. Early attempts toward asymmetric allylic oxidation using Cu complexes of (+)-α-ethyl camphorate,[8] chiral Schiff bases[9] and optically active amino acids[9] gave poor enantioselectivities. In the last decade better results have started to appear. Several groups have reported the use of oxazoline-containing ligands in the Cu-catalyzed allylic oxidation of alkenes, which gave good enantioselectivity.[10–19] However, a universal problem that still remains is the very poor reaction rate. The reactions sometimes require close to a month to reach completion. Also, some ligands are not stable enough to withstand the harsh oxidizing environment of the reaction. It is therefore a challenge to develop new ligand systems for this reaction.

Chiral bipyridine ligands have received extensive attention in asymmetric catalysis in the past 10 years. They were reported to have applications in several asymmetric reactions, such as Cu-catalyzed cyclopropanation,[20–26] Zn-catalyzed allylic alkylation,[27] and Pd-catalyzed allylic substitution.[28,29] Very good results for Cu-catalyzed allylic oxidations have also been obtained recently by Kočovský et al.[30] We recently reported the synthesis of chiral bipyridine alcohols **1**–**6** and their use in the asymmetric diethylzinc addition reaction, in which excellent enantioselectivities were obtained.[31] In an extension of the synthetic scope of this class of ligand, we report herein the use of bipyridine alcohols **1**–**8** in the copper-catalyzed asymmetric allylic oxidation of olefins with *tert*-butyl perbenzoate (Scheme 1).

2. Results and discussion

Ligands **1**–**6** were prepared in good yields according to the previously reported procedures.[31] Ligands **7** and **8** were prepared by cross coupling of bromopyridyl alcohols **9** and **10** with 2-pyridylzinc chloride using catalytic amounts of tetrakis(triphenylphosphine)palladium(0) catalyst (Scheme 2).[31,32] Ligands **7** and **8** were isolated in 73 and 75% yield, respectively.

Having prepared these C_1- and C_2-symmetric bipyridine ligands, they were tested in the Cu-catalyzed allylic oxidations of cyclohexene. The reactions were carried out with 6 mol% of **1**–**8** and 5 mol% of $[Cu(CH_3CN)_4]PF_6$ as catalyst at room temperature in acetonitrile. All reactions were allowed to proceed until the catalyst turnover slowed or stopped. The results are summarized in Table 1. Ligand **1**–$CuPF_6$ complex gave cyclohex-2-enyl benzoate as the product with 57% isolated yield and 93% conversion after 48 h (entry 1). The enantiomeric excess (e.e.) of the product was 52%. The other ligand–$CuPF_6$ complexes were found to be active catalysts (entries 6–9 and 14–16). Isolated yields were from moderate to good and the enantioselectivities were varied with product e.e.s ranging between 0 and 65%. In general, reactions with C_2-symmetric ligands

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† Dedicated to Professor K. Barry Sharpless for the occasion of his 60th birthday.

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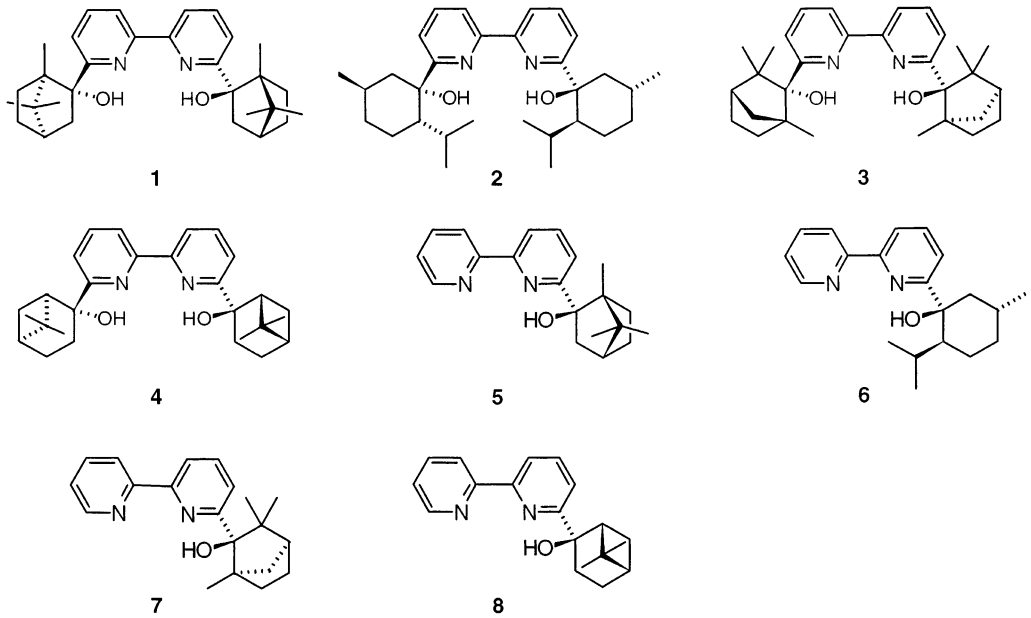
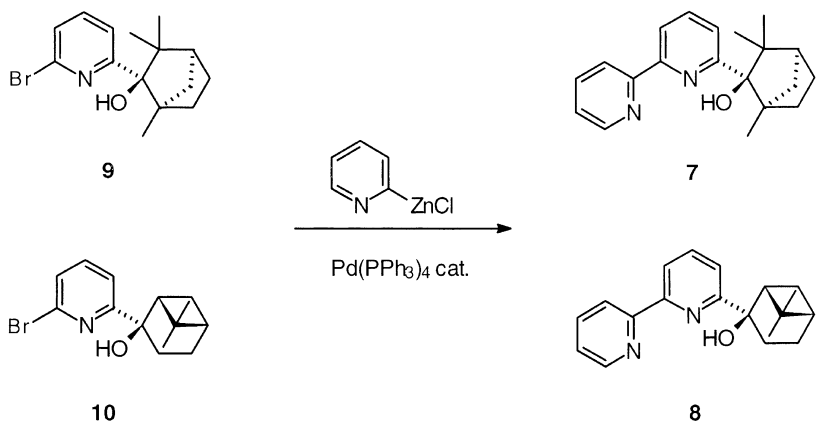


Scheme 1.

were slightly faster than those with C_1-symmetric ligands. The C_2-ligands gave (*R*)-allylic benzoates as the major product. Interestingly, the absolute configurations of the major products obtained for the C_1-symmetric ligands **5** and **7** were opposite to their corresponding C_2-symmetric ligands **1** and **3**. This suggests that the transition states of the reactions promoted by complexes of **1** and **3** may be different from those of the reactions promoted by complexes of **5** and **7**. Similar observations were also reported in the literature.[17] Of the four C_1-symmetric ligands, the best result was achieved with **5**. It gave 65% e.e. and 65% conversion after 48 h (entry 9). In contrast, **6** and **8** gave no asymmetric induction (entries 14 and 16).

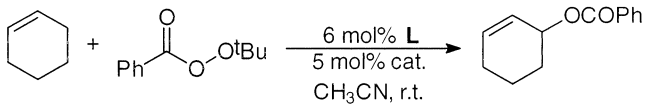
With **1** and **5** being the best ligands, reaction conditions were optimized by varying the Cu salts (entries 2–5 and 10–13). Variation of Cu salts had a great effect on both the enantioselectivity and reactivity. For **1**, the best result was achieved with Cu(OTf) as the copper source. The reaction took 48 h and gave product with 95% conversion and 58% e.e. (entry 3). $[Cu(CH_3CN)_4]ClO_4$ gave slightly lower conversion and e.e. By using either CuBr or CuCl as the metal precursor, the reaction occurred slowly and no enantioselectivity was induced by the catalyst (entries 4 and 5).

For **5**, different trends were observed. The highest enantioselectivity (65% e.e.) was still obtained with $[Cu(CH_3CN)_4]PF_6$ (entry 9). The highest reaction rate was observed with $[Cu(CH_3CN)_4]ClO_4$ (entry 10), which gave 74% conversion after 48 h. However, CuOTf, CuBr or CuCl as the precursor gave very poor product e.e.s and/or conversions (entries 11–13). Preliminary rate studies indicated that the rate of the



Scheme 2.

Table 1. Asymmetric allylic oxidation of cyclohexene promoted by chiral bipyridine copper(I) complexes



Entry	Ligand **L**	Catalyst	Time (h)	Conversion (%)[a]	Yield (%)[b]	E.e. (%)[c]
1	**1**	$[Cu(CH_3CN)_4]PF_6$	48	93	57	52 (*R*)
2	**1**	$[Cu(CH_3CN)_4]ClO_4$	48	81	70	47 (*R*)
3	**1**	CuOTf	48	95	63	58 (*R*)
4	**1**	CuCl	48	73	78	0
5	**1**	CuBr	60	63	71	0
6	**2**	$[Cu(CH_3CN)_4]PF_6$	60	63	79	22 (*R*)
7	**3**	$[Cu(CH_3CN)_4]PF_6$	48	59	44	31 (*R*)
8	**4**	$[Cu(CH_3CN)_4]PF_6$	48	57	47	30 (*R*)
9	**5**	$[Cu(CH_3CN)_4]PF_6$	48	65	43	65 (*S*)
10	**5**	$[Cu(CH_3CN)_4]ClO_4$	48	74	38	64 (*S*)
11	**5**	CuOTf	72	54	77	16 (*S*)
12	**5**	CuCl	48	14	N.D.[d]	N.D.[d]
13	**5**	CuBr	48	0	N.D.[d]	N.D.[d]
14	**6**	$[Cu(CH_3CN)_4]PF_6$	72	42	66	0
15	**7**	$[Cu(CH_3CN)_4]PF_6$	96	73	80	8 (*S*)
16	**8**	$[Cu(CH_3CN)_4]PF_6$	72	40	68	0

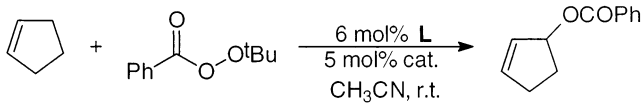
[a] Conversions were calculated based on the ratio of *tert*-butyl perbenzoate and product obtained from GC.
[b] Yields were isolated and were calculated based on conversion.
[c] Determined by HPLC analysis using a chiral OD column (hexane/propan-2-ol = 1000/1). Absolute configuration was determined by comparing the order of elution with samples of known configurations.[17]
[d] Not determined.

reaction is affected by the concentration of the copper catalyst but not the alkene or *tert*-butyl perbenzoate concentration. Work is in progress to understand the kinetics and mechanism of the reaction.

Ligands **1** and **5** were also found to catalyze the allylic oxidation of cyclopentene. The results of this study are summarized in Table 2. For the ligand **1**, the best enantioselectivity of 61% was achieved with CuBr (entry 4), which is in sharp contrast to the equivalent reaction with cyclohexene. The reactions with different copper salts proceeded at comparable rates (entries 1–4). Similar rates and enantioselectivities were observed for ligand **5** using either $[Cu(CH_3CN)_4]PF_6$ or $[Cu(CH_3CN)_4]ClO_4$, (entries 5 and 6). However, using CuOTf or CuBr as the metal source gave poorer results in terms of enantioselectivity or conversion (entries 7 and 8).

The absolute configurations of the products obtained for C_2-bipyridine **1** (*R*) and C_1-bipyridine **5** (*S*) were again opposite. From the above results, it seems that the effect of the copper salt is strongly dependent on the substrate and the specific ligand. The reactions promoted with $[Cu(CH_3CN)_4]PF_6$ were generally faster than those with other Cu salts.

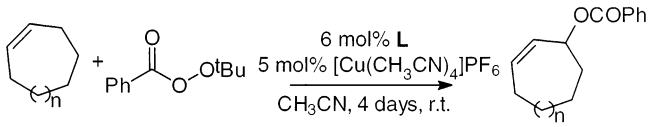
Table 2. Asymmetric allylic oxidation of cyclopentene promoted by copper(I) complexes of chiral bipyridine ligands **1** and **5**



Entry	Ligand **L**	Catalyst	Time (h)	Conversion (%)[a]	Yield (%)[b]	E.e. (%)[c]
1	**1**	$[Cu(CH_3CN)_4]PF_6$	48	88	64	26 (*R*)
2	**1**	$[Cu(CH_3CN)_4]ClO_4$	48	81	70	38 (*R*)
3	**1**	CuOTf	48	90	88	32 (*R*)
4	**1**	CuBr	48	81	59	61 (*R*)
5	**5**	$[Cu(CH_3CN)_4]PF_6$	48	78	83	56 (*S*)
6	**5**	$[Cu(CH_3CN)_4]ClO_4$	48	84	87	55 (*S*)
7	**5**	CuOTf	48	81	82	29 (*S*)
8	**5**	CuBr	144	37	53	54 (*S*)

[a] Percent conversions were calculated based on the ratio of *tert*-butyl perbenzoate and product obtained from GC.
[b] Yields were isolated and were calculated based on conversion.
[c] Determined by HPLC analysis using a chiral OD column (hexane/propan-2-ol = 1000/1). Absolute configuration was determined by comparing the order of elution with samples of known configurations.[17]

Table 3. Asymmetric allylic oxidation of cycloheptene and cyclooctene promoted by copper(I) complexes of chiral bipyridine ligands **1** and **5**



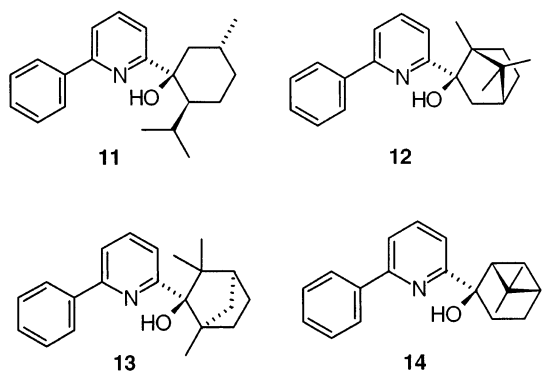
Entry	Ligand **L**	Substrate	Conversion (%)[a]	Yield (%)[b]	E.e. (%)
1	1	$n=1$	79	62	61 (*R*)[c]
2	1	$n=2$	35	72	70 (*R*)[d]
3	5	$n=1$	71	69	21 (*S*)[c]
4	5	$n=2$	31	81	12 (*S*)[d]

[a] Percent conversions were calculated based on the ratio of *tert*-butyl perbenzoate and product obtained from GC.
[b] Yields were isolated and were calculated based on conversion.
[c] Determined by HPLC analysis using a chiral OJ column (hexane/propan-2-ol = 1000/1). Absolute configuration was determined by comparing the order of elution with samples of known configurations.[30]
[d] Determined by HPLC analysis using a chiral OD column (hexane/propan-2-ol = 1000/1). Absolute configuration was determined by comparing the order of elution with that of products from cyclohexene and cyclopentene.

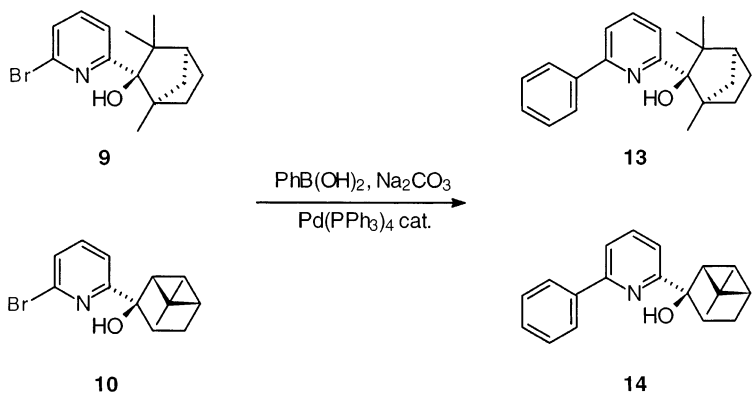
With the use of **1** or **5** and $[Cu(CH_3CN)_4]PF_6$ as catalyst under the optimized reaction conditions as cyclohexene, we also examined the oxidation of cycloheptene and cyclooctene (Table 3). In the case of cycloheptene, conversions between 79 and 71% for **1** and **5**, respectively, were obtained after 4 days (entries 1 and 3). However, reaction promoted by **1** gave higher enantioselectivity than **5** (61 and 21% e.e. for **1** and **5**, respectively). In the case of cyclooctene, the reaction proceeded at a much lower rate than other substrates. Ligands **1** and **5** only gave 35 and 31% conversion, respectively, after 4 days (entries 2 and 4). The enantioselectivity obtained with **1** was again markedly greater than **5** (70 and 12% e.e. for **1** and **5**, respectively). Additionally, the absolute configurations of the products achieved with **1** and **5** were opposite to each other.

Although bipyridine ligands **1**–**8** can function as *N*,*N*-bidentate ligands, they could also function as *N*,*O*-bidentate ligands. A previous study using **1**–**6** showed that they probably function as *N*,*O*-ligands in the alkylation of aldehydes.[31] In order to reveal more details of the nature of the active catalytic species, we prepared the phenyl substituted pyridylalcohols **11**–**14** and compared their reactivity with **1**–**8**, respectively (Scheme 3). The synthesis of **11** and **12** were reported previously and **13** and **14** were prepared by similar methods using palladium(0)-catalyzed cross coupling of bromopyridyl alcohols **9** and **10** with phenylboronic acid (Scheme 4).[31,32] Ligands **11**–**14** were all active in catalyzing allylic oxidation. However, all of them gave very low product e.e.s of <5%. The results seem to suggest that **1**–**8** are not functioning as *N*,*O*-ligands.

With these observations and the absolute configurations of the products formed by the C_1- and C_2-symmetric ligands, we proposed the models shown in



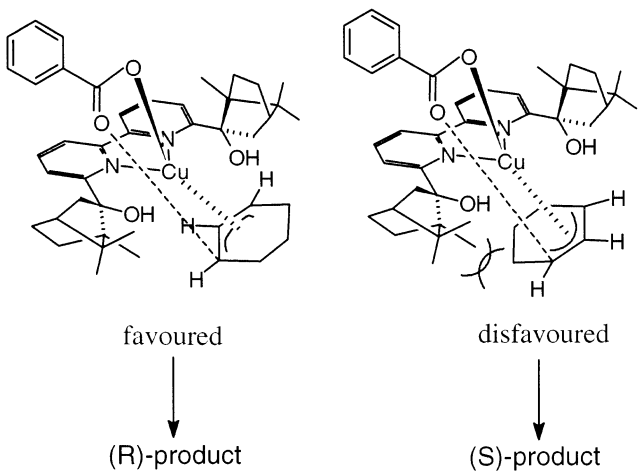
Scheme 3.



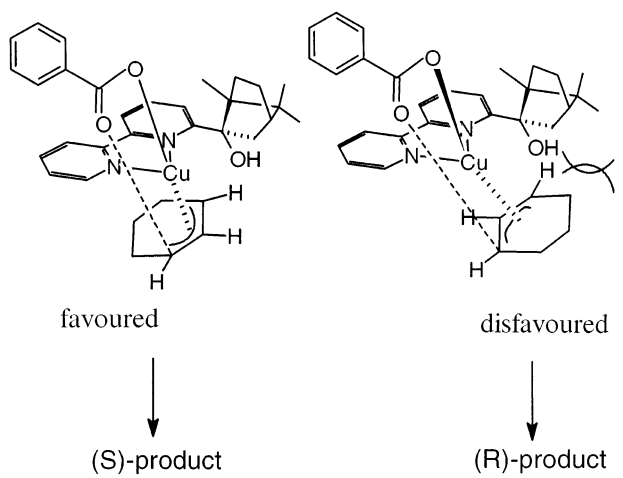
Scheme 4.

Schemes 5 and 6, in which ligands **1** and **5**, respectively, were used with cyclohexene, to explain the results here. The first set of models for **1** (Scheme 5) was similar to those proposed based on chiral C_2-symmetric *N*,*N*-bidentate[11] and *N*,*N*,*N*-tridentate ligand–copper complex catalysts.[12] In these models, the favored transition states are depicted with the cyclohexenyl and benzoate groups positioned to minimize interaction with the bulky pendant group of the bipyridine ligand. In the second set of models, for **5** (Scheme 6), we proposed that the removal of a bulky pendant group from one side of the ligand leads to the change in the coordination of the cyclohexenyl group. In order to further minimize interaction with the pendant group of the ligand, the opposite prochiral face then coordinates to the metal center.

In conclusion, we have successfully demonstrated that **1**–**8** are good catalytic ligands for the copper-catalyzed allylic oxidation of olefins. In the case of cyclooctene, we achieved an e.e. of 70%. Comparison of the enantioselectivity of the reactions of **11**–**14** with those of **1**–**8**, indicates that **1**–**8** do not function as *N*,*O*-bidentate ligands in the allylic oxidation reaction. However, the exact nature of the coordination of these ligands still needs further investigation and we are continuing our efforts to find other, better catalysts for this reaction.



Scheme 5.



Scheme 6.

3. Experimental

3.1. General methods

Acetonitrile was distilled under N_2 over calcium hydride. Chemicals were of reagent-grade quality and were obtained commercially. Ligands **1**–**6** and **9**–**12** were prepared according to the literature.[31] Infrared spectra, in the range 500–4000 cm^{-1}, were recorded as KBr plates on a Perkin–Elmer model 1600 FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz Mercury instrument. Positive-ion FAB mass spectra were recorded on a Finnagin MAT 95 spectrometer as 3-nitrobenzylalcohol matrices. Electron-ionization mass spectra were recorded on a Hewlett–Packard 5890II GC instrument coupled with a 5970 mass selective detector. Elemental analyses were performed on a Vario EL elemental analyzer. Optical rotation was measured by a JASCO DIP-370 digital polarimeter. Melting points were measured by an electrothermal digital melting point apparatus. Reactions were monitored by GC using a Hewlett–Packard 5890II GC instrument with an Ultra 2-crosslinked 5% PhMesilcone (25 m×0.2 mm×0.33 μm) column.

3.2. General procedures for the synthesis of bipyridine ligands 7 and 8

A solution of 2-bromopyridine (1.1 g, 7 mmol) in THF (30 mL) was cooled to −78°C and treated slowly with a solution of *n*-butyllithium in hexanes (2.5 M, 2.8 mL, 7 mmol). The resulting red–brown solution was stirred at this temperature for 30 min and was then transferred by cannula into a cold (−78°C) solution of dry $ZnCl_2$ (0.96 g) in THF (20 mL) ($ZnCl_2$ was used after fusion by flame-drying under reduced pressure). The color of the solution remained at this temperature. After warming to rt, the mixture was stirred until the color changed to yellow–brown. This mixture was transferred into a stirred solution of bromopyridyl alcohol **9** or **10** (3.5 mmol) and of tetrakis(triphenylphosphine)palladium(0) (0.4 mmol, 0.4 g) in THF (20 mL). After stirring for 16 h at rt, saturated aqueous $NaHCO_3$ (100 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3×50 mL) and the combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give crude product, which was purified by column chromatography. The product was then characterized by IR, ^1H NMR, ^{13}C NMR, CHN and MS analysis.

3.2.1. Bipyridine ligand 7. The above general procedure was followed. Usual work-up gave 0.79 g (73%) of **7**: mp 76.5–78.5°C; $[\alpha]_D^{25} = -60.0$ (*c* 0.52, CCl_4); IR (KBr): 3355.3 s, 1572.1 s, 1559.6 s; ^1H NMR (300 MHz,

$CDCl_3$): δ 0.50 (s, 3H), 1.03 (s, 3H), 1.04 (s, 3H), 1.19 (m, 1H), 1.39 (m, 1H), 1.52 (m, 1H), 1.80–1.95 (m, 2H), 2.26–2.44 (m, 2H), 6.10 (s, 1H), 7.32 (m, 1H), 7.56 (d, 1H, $J=7.7$ Hz), 7.70–7.80 (m, 2H), 8.20–8.40 (d, 2H), 8.68 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.18, 22.25, 24.39, 29.30, 32.50, 41.97, 46.00, 48.79, 51.93, 83.72, 118.58, 120.66, 122.99, 123.53, 136.08, 136.67, 148.90, 152.80, 155.42, 161.46; MS (EI) m/z (rel. int.): 308 (M^+, 7), 280 (32), 227 (88), 211 (base), 170 (30), 155 (99). Anal. calcd for $C_{20}H_{24}N_2O$: C, 77.92; H, 7.79; N, 9.09. Found: C, 77.67; H, 7.84; N, 9.27%.

3.2.2. Bipyridine ligand 8. The above procedure was followed. Usual work-up gave 0.77 g (75%) of **8**: mp 89.5–91.5°C; $[\alpha]_D^{25}=-19.4$ (c 0.51, CCl_4); IR (KBr): 3355.3 s, 1572.1 s, 1559.8 s; ^{1}H NMR (300 MHz, $CDCl_3$): 1.27 (s, 3H), 1.31 (s, 3H), 1.20–1.40 (m, 1H), 1.90–2.30 (m, 6H), 2.60–2.75 (m, 1H), 4.75 (s, 1H), 7.32 (m, 1H), 7.50, (d, 1H, $J=7.7$ Hz), 7.70–7.90 (m, 2H), 8.30 (d, 1H, $J=7$ Hz), 8.41 (d, 1H, $J=7.7$ Hz), 8.67 (d, 1H, $J=4.4$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 23.52, 25.06, 27.78, 29.90, 38.92, 40.11, 53.55, 78.85, 118.91, 119.74, 120.80, 123.56, 136.62, 137.30, 148.86, 153.83, 155.51, 165.63; MS (EI) m/z (rel. int.): 294 (M^+, 21), 211 (69), 183 (51), 170 (43), 155 (base). Anal. calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.67; H, 7.84; N, 9.27%.

3.3. General procedure for the synthesis of pyridyl alcohols 13 and 14

A solution of bromopyridyl alcohol **9** or **10** (5.76 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.17 mmol, 0.2 g) in toluene (12 mL) was treated with a solution of Na_2CO_3 (11.53 mmol, 1.22 g) in H_2O (6 mL), followed by a solution of phenylboronic acid (6.92 mmol, 0.84 g) in MeOH (3 mL). The mixture was stirred at 85°C for 4 h under N_2. After cooling to rt, a solution of concentrated aqueous NH_3 (2.9 mL) in saturated aqueous Na_2CO_3 (29 mL) was added and the mixture was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and filtered. Evaporation of the filtrate under reduced pressure gave crude product, which was purified by chromatography (25:1 petroleum ether–ethyl acetate). The product was characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and CHN.

3.3.1. Pyridyl alcohol 13. Following the above procedure, using bromopyridyl alcohol **9** and usual work-up gave 0.78 g (44%) of **13**: mp 107–109°C; $[\alpha]_D^{25}=-71.2$ (c 0.51, CCl_4); IR (KBr): 3359.8 s, 1570.1 s; ^{1}H NMR ($CDCl_3$): δ 0.49 (s, 3H), 1.03 (s, 3H), 1.04 (s, 3H), 1.17 (m, 1H), 1.38 (d, 2H, $J=10$ Hz), 1.51 (m, 1H), 1.84 (m, 2H), 2.38 (m, 2H), 6.25 (s, 1H), 7.35–7.50 (m, 4H), 7.59 (d, 1H, $J=7.7$ Hz), 7.70 (t, 1H, $J=7.7$ Hz), 7.99 (d, 2H, $J=7.7$ Hz); ^{13}C NMR ($CDCl_3$): δ 17.21, 22.31, 24.40, 29.29, 32.49, 41.94, 45.95, 48.78, 51.81, 83.66, 117.71, 121.36, 126.48, 128.46, 128.79, 136.79, 138.51, 153.79, 161.72; MS (EI) m/z (rel. int.): 307 (M^+, 6), 279 (28), 226 (74), 210 (base), 169 (31), 154 (99). Anal. calcd for $C_{21}H_{24}NO$: C, 82.35; H, 7.84; N, 4.58. Found: C, 82.05; H, 7.88; N, 4.33%.

3.3.2. Pyridyl alcohol 14. Following the above procedure, using bromopyridyl alcohol **10** and usual work-up gave 0.74 g (44%) of **14**: mp 58–60°C; $[\alpha]_D^{25}=-35.4$ (c 0.52, CCl_4); IR (KBr): 3422.2 s, 1566.7 s; ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 3H), 1.30 (s, 3H), 1.20–1.40 (m, 1H), 1.90–2.25 (m, 6H), 2.50–2.70 (m, 1H), 4.98 (s, 1H), 7.35–7.50 (m, 4H), 7.62 (d, 1H, $J=7.7$ Hz), 7.75 (t, 1H, $J=7.7$ Hz), 8.01 (d, 2H, $J=6.9$ Hz); ^{13}C NMR ($CDCl_3$): δ 23.52, 25.05, 25.77, 27.80, 29.87, 38.95, 40.13, 53.54, 78.74, 118.01, 118.17, 126.63, 128.44, 128.83, 137.06, 138.64, 154.96, 165.97; MS (EI) m/z (rel. int.): 293 (M^+, 29), 265 (52), 210 (70), 182 (64), 169 (65), 154 (base). Anal. calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 82.35; H, 8.25; N, 4.26%.

3.4. General procedure for copper-catalyzed allylic oxidation Cu(I) complexes of ligands 1–8 as catalyst

The copper catalyst was generated by stirring **1**–**8** (0.06 mmol) with copper(I) salt (0.05 mmol) in CH_3CN (3 mL) under nitrogen. Alkene (4 mmol) was added, followed by the slow addition of *tert*-butyl perbenzoate (1 mmol, 190 μL) over a 1 min period. The reaction was monitored by GLC and was quenched by adding a saturated solution of $NaHCO_3$. The mixture was extracted with diethyl ether and evaporated. The product was purified by column chromatography (petroleum ether/EtOAc) and was then characterized by ^{1}H NMR, ^{13}C NMR, IR, and GC–MS. The enantiomeric excess of the product was determined by HPLC with a Daicel Chiralcel OD or OJ column, using hexane/propan-2-ol = 1000/1 as the eluent.

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