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Novel N,N-Bidentate Ligands for Enantioselective Copper(I)-Catalyzed Allylic Oxidation of Cyclic Olefins

Qitao Tan[a,b] and Masahiko Hayashi[b,*]

[a] Department of Frontier Research and Technology, Headquarters for Innovative Cooperation and Development, Kobe University, Nada, Kobe 657-8501, Japan
[b] Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan
Fax: (+81)-78-803-5688; e-mail: mhayashi@kobe-u.ac.jp

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Abstract: New N,N-bidentate Schiff base ligands containing the 2-quinolyl moiety proved to be effective in conferring high reactivity and moderate to high enantioselectivity (up to 84% *ee*) to the copper(I)-catalyzed asymmetric allylic oxidation of various cylic olefins with *tert*-butyl perbenzoate. As copper(I) sources, we employed copper(II) triflate/phenylhydrazine [$Cu(OTf)_2$/$PhNHNH_2$] and tetra(acetonitrile)copper hexafluorophosphate [$Cu(CH_3CN)_4PF_6$]. Using the same N,N-bidentate Schiff base ligand, the former showed high reactivity and the latter showed high enantioselectivity.

Keywords: allylic oxidation; bidentate ligands; copper; enantioselectivity

Introduction

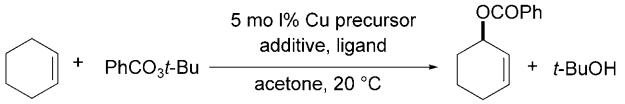
In the late 1950s, Kharasch and Sosnovsky reported for the first time the allylic oxidation of olefins using *tert*-butyl perbenzoate catalyzed by copper bromide.[1] After that report, much effort has been made to improve the copper-catalyzed allylic oxidation of olefins because of its potential utility in organic synthesis.[2] Asymmetric versions of this reaction have been well studied. Initially, the enantiomeric excess (*ee*) of the product was low.[3] However, in the mid 1990s, moderate to high enantioselectivity was realized. Most of the reactions used chiral oxazoline-based ligands.[4] Unfortunately, one problem remains to this day: low reactivity. For example, in Katsuki's system, the $Cu(OTf)_2$-tris(oxazolines) complex required 92 h for the oxidation of cyclopentene (0 °C, 84% *ee*, 44% yield) and 670 h for that of cycloheptene (−20 °C, 69% *ee*, 10% yield).[4c] Singh et al. reported that the addition of phenylhydrazine greatly reduced the reaction time without affecting enantioselectivity,[5] and this method has been used by other researchers.[6] Other non-oxazoline-type ligands, bis(imidazolines)[7] and (iminophosphoranyl)ferrocenes,[8] especially the latter, showed high enantioselectivity. Shul′pin et al. reported a mechanistic study in alkene hydroperoxidation with peroxides catalyzed by copper complexes in the racemic version.[9] We herein disclose a new type of chiral Schiff base ligand that contains a quinoline moiety for asymmetric allylic oxidation. To the best of our knowledge, there is only one report of the use of a Schiff base for asymmetric allylic oxidation. However, in that system, the optical yield of the product was less than 10% *ee*, judging from the optical rotation after derivatization to the corresponding olefinic alcohol.[10]

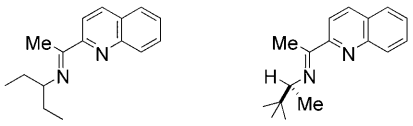
Results and Discussion

We first examined the effect of the addition of our newly designed N,N-bidentate Schiff base ligand containing a quinoline moiety on the reaction of cyclohexene with *tert*-butyl perbenzoate. As shown in Table 1, the addition of phenylhydrazine to $Cu(OTf)_2$ increased the reactivity (entry 3). Further addition of designed N,N-bidentate ligands **1** and **2** to the above system dramatically increased the reaction rate (entries 4 and 5).

It should be mentioned that as for the nature of copper(I) precursor, $(CuOTf)_2{\cdot}C_6H_6$ showed a higher reactivity than $Cu(CH_3CN)_4PF_6$, however, the use of $(CuOTf)_2{\cdot}C_6H_6$ produced undesired products to give a lower yield (20%). In the case of $Cu(CH_3CN)_4PF_6$, the reactivity was lower, but a higher yield of the product was obtained (40% yield).

Table 1. Rate enhancement by the addition of bidentate nitrogen ligands in $Cu(OTf)_2/PhNHNH_2$ system.[a]



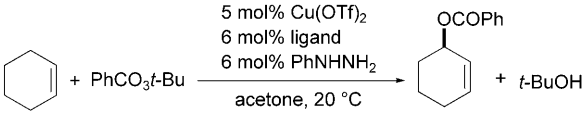


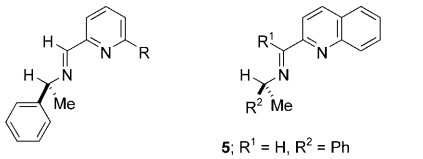
1 2

Entry	Cu precursor	Additive	Ligand	Time	Yield [%][b]
1	$Cu(OTf)_2$	—	—	24 h	0
2	$CuOTf{\cdot}0.5\ C_6H_6$	—	—	24 h	20
3	$Cu(OTf)_2$	$PhNHNH_2$	—	3 h	50
4	$Cu(OTf)_2$	$PhNHNH_2$	**1**	< 30 min	87
5	$Cu(OTf)_2$	$PhNHNH_2$	**2**	< 30 min	88[c]

[a] Cyclohexene:$PhCO_3t$-Bu = 5:1. Six mol% of additive and/or ligands were added.
[b] Isolated yield.
[c] 46% *ee* (*R*). Determined by HPLC (CHIRALCEL OD-H column).

Table 2. Enantioselective allylic oxidation of cyclohexene using $Cu(OTf)_2/PhNHNH_2$ system.[a]





3; R = H
4; R = Me

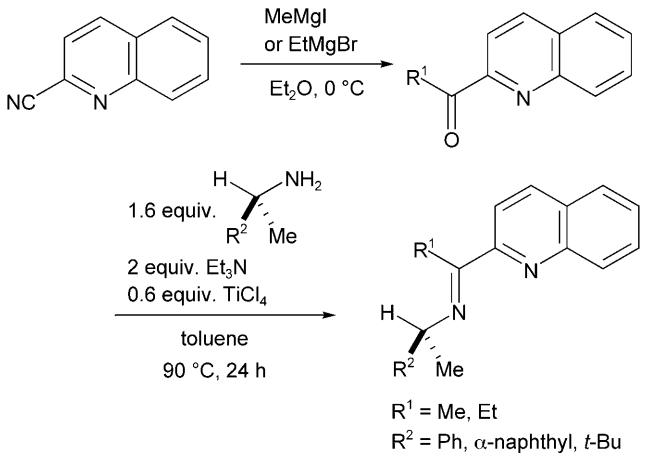
5; R^1 = H, R^2 = Ph
6; R^1 = H, R^2 = α-naphthyl
7; R^1 = Me, R^2 = α-naphthyl
8; R^1 = H, R^2 = *t*-Bu
9; R^1 = Et, R^2 = *t*-Bu

Entry	Ligand	Time [h]	Yield [%][b]	*ee* [%][c]
1	**3**	72	28	9 (*R*)
2	**4**	8	42	9 (*R*)
3	**5**	<0.5	85	11 (*R*)
4	**6**	<0.5	70	10 (*R*)
5	**7**	<0.5	80	20 (*R*)
6	**8**	<0.5	85	19 (*R*)
7	**2**	<0.5	88	46 (*R*)
8	**9**	<0.5	80	44 (*R*)

[a] Cyclohexene:$PhCO_3t$-Bu = 5:1.
[b] Isolated yield.
[c] Determined by HPLC analysis (CHIRALCEL OD-H).

Then, chiral Schiff base ligands **3**–**9** were prepared. Aldimines were readily prepared by simple condensation of 2-pyridylaldehyde or 2-quinolylaldehyde with chiral amines. For the synthesis of ketoimine ligands, the reaction of 2-quinolyl nitrile with Grignard reagents gave the corresponding ketones, which were reacted with chiral amines in the presence of $TiCl_4$ and Et_3N to give the desired ketoimines (Scheme 1).

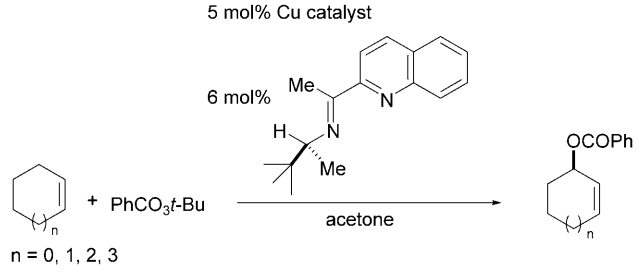
Then, we carried out the asymmetric allylic oxidation of cyclohexene with *tert*-butyl perbenzoate in the presence of 5 mol% $Cu(OTf)_2$, 6 mol% $PhNHNH_2$, and 6 mol% chiral ligands **2**–**9** (Table 2) When Schiff bases **3** and **4** containing the 2-pyridyl moiety were used, the reaction was sluggish and yield and *ee* were low. However, when the 2-quinolyl moiety was introduced instead of the 2-pyridyl moiety, the reaction rate was enhanced dramatically: within 30 min, the reactions were completed to give the product in 70–88% yield. As for *ee*, ketoimine-type N,N-bidentate ligands (R^1 = Me, Et) gave higher *ee* than the corresponding aldimine-type N,N-bidentate ligands (R^1 = H). For example, in the reaction using ketoimine-type N,N-bidentate ligands **2** and **9**, products with 46% *ee* and 44% *ee* were obtained, respectively, whereas aldimine-type N,N-bidentate ligand **8** gave a product having only 19% *ee*. Among the N,N-bidentate ligands examined, ligand **2** gave the best result (88% yield, 46% *ee*). As for the nature of copper precursor, we examined this aspect as follows.



Scheme 1. Preparation of ketoimine-type N,N-bidentate ligands.

Based on the above results, we examined the asymmetric allylic oxidation of various cyclic olefins using the $Cu(OTf)_2/PhNHNH_2$ or the $Cu(CH_3CN)_4PF_6$ system. The results when chiral N,N-bidentate ligand **2** was employed are summarized in Table 3. Among the cyclic olefins, the reaction of cycloheptene with *t*-butyl perbenzoate in the presence of the $Cu(CH_3CN)_4PF_6$/ligand **2** catalyst system afforded the oxidation product in 84% *ee* (0 °C, 48 h, 51% yield). Generally, the $Cu(CH_3CN)_4PF_6$ system (B) gave

Table 3. Enantioselective allylic oxidation of various cyclic olefins.[a]

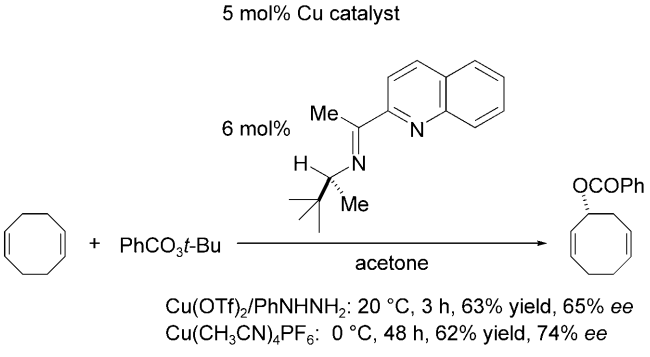


Entry	Cycloalkene	Cu catalyst[b]	Temp [°C]	Time [h]	Yield [%][c]	*ee* [%][d]
1		A	20	< 0.5	80	42 (*R*)
2		B	0	48	70	51 (*R*)
3		A	20	< 0.5	88	46 (*R*)
4		B	0	48	89	51 (*R*)
5		A	20	20	52	70 (*R*)
6		B	0	48	51	84 (*R*)
7		A	20	72	31	65 (*R*)
8		B	20	72	41	70 (*R*)

[a] Cyclic olefins:$PhCO_3t$-Bu = 5:1.
[b] A: $Cu(OTf)_2/PhNHNH_2$; B: $Cu(CH_3CN)_4PF_6$
[c] Isolated yield.
[d] The *ee* values were determined on a chiral HPLC column (CHIRALCEL OD-H for entries 1–4, 7 and 8, CHIRALPAK AD-H for entries 5 and 6).

higher *ee*, although the reactivity was slightly lower than that of the $Cu(OTf)_2/PhNHNH_2$ system (A).

Finally, we examined the asymmetric allylic oxidation of 1,5-cyclooctadiene. As shown in Scheme 2, the $Cu(OTf)_2/PhNHNH_2$/ligand **2** system and the $Cu(CH_3CN)_4PF_6$/ligand **2** system afforded a product with 65% *ee* (20 °C, 3 h, 63% yield) and 74% *ee* (0 °C, 48 h, 62% yield), respectively. The second oxidation did not take place under the present reaction conditions.



Scheme 2. Asymmetric allylic oxidation of 1,5-cyclooctadiene.

Conclusions

In summary, the copper complex of ketoimine **2** possessing the 2-quinoline moiety was proven to catalyze the asymmetric allylic oxidation of various cycloolefins and cyclooctadienes with high efficiency and in moderate to high enantioselectivity (up to 84% *ee*). In view of the high reactivity compared with those of previously reported catalyst systems and the ready modification of these ligands, we plan to conduct more studies in this field.

Experimental Section

General Remarks

All reactions were performed under an argon atmosphere using Schlenk tube techniques and freshly distilled solvents. All melting points were measured on a Yanaco MP-500D and were uncorrected. ^1H and ^{13}C NMR spectra (400 and 100.6 MHz, respectively) were recorded on a JEOL JNM-LA 400 using Me_4Si as the internal standard (0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were measured with a Perkin–Elmer FT-IR spectrometer Spectrum 1000. Elemental analyses were performed with a Yanaco CHN Corder MT-5. Mass spectra were measured on a Thermo Quest LCQ DECA plus. Optical rotations were measured on a Horiba Sepa-300 Polarimeter for solutions in a 1 dm cell. Preparative column chromatography was carried out on Fuji Silysia BW-820MH or YMC*GEL silica (6 nm I-40–63 μm). Thin layer chromatography (TLC) was carried out on Merck 25 TLC aluminum sheets of silica gel 60 F_{254}. Chiral HPLC was performed on a Hitachi L-2000 series instrument equipped with an L-2455 diode array detector.

General Procedure for the Synthesis of Aldimine Ligands (3–6 and 8)

A mixture of chiral amines (1.10 mmol) and corresponding aldehydes (1.00 mmol) was dissolved in toluene (5 mL). Na_2SO_4 (1.0 g) was added and the mixture was heated to 110 °C for 12 h. After filtration, the solvent was evaporated in vacuum to give the desired compounds. The sample for analysis was obtained by silica gel (pre-neutralized with Et_3N) chromatography or recrystallization.

(*S*)-1-Phenyl-*N*-(pyridin-2-ylmethylene)ethylamine (3):[11] Yield: 85%; light yellow oil; $[\alpha]_D^{24}$: +38 (*c* 1.0, $CHCl_3$); IR (thin film): ν_{max} = 3060, 2971, 1645, 1586, 1493, 1467, 1436, 1371, 1080, 762, 700, 612 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.61 (d, J = 6.8 Hz, 3H), 4.65 (q, J = 6.8 Hz, 1H), 7.2–7.4 (m, 6H), 7.72 (dt, J = 7.2 Hz, 1.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.46 (s, 1H), 8.63 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.5, 69.5, 121.4, 124.6, 126.6, 126.9, 128.5, 136.4, 144.5, 149.3, 154.8, 160.4.

(*S*)-*N*-[(6-Methylpyridin-2-yl)methylene]-1-phenylethylamine (4):[12] Yield: 83%; light yellow oil; $[\alpha]_D^{25}$: +5.6 (*c* 1.0, $CHCl_3$); IR (thin film): ν_{max} = 2971, 2862, 1646, 1591, 1456, 1369, 1085, 792, 764, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, J = 6.8 Hz, 3H), 2.58 (s, 3H), 4.62 (q, J = 6.8 Hz,

1H), 7.16 (d, $J=7.2$ Hz, 1H), 7.23 (d, $J=6.8$ Hz, 1H), 7.34 (t, $J=7.2$ Hz, 2H), 7.4–7.5 (m, 2H), 7.61 (t, $J=7.8$ Hz, 1H), 7.92 (d, $J=7.8$ Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=24.3$, 24.5, 69.5, 118.4, 124.3, 126.7, 126.9, 128.5, 136.7, 144.6, 154.3, 158.0, 160.8.

(*S*)-1-Phenyl-*N*-(quinolin-2-ylmethylene)ethylamine (5):[13] Yield: 82%; yellow solid (from CH_3CN); mp 90–92 °C; $[\alpha]_D^{26}$: −54 (*c* 1.0, $CHCl_3$); IR (KBr): $\nu_{max}=2966$, 2860, 1633, 1596, 1504, 1452, 1367, 1086, 835, 774, 759, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.65$ (d, $J=7.2$ Hz, 3H), 4.72 (q, $J=7.2$ Hz, 1H), 7.2–7.3 (m, 1H), 7.3–7.4 (m, 2H), 7.48 (d, $J=7.2$ Hz, 2H), 7.5–7.6 (m, 1H), 7.7–7.8 (m, 1H), 7.83 (d, $J=10.4$ Hz, 1H), 8.13 (d, 8.4 Hz, 1H), 8.17 (d, $J=8.4$ Hz, 1H), 8.26 (d, $J=8.4$ Hz, 1H), 8.64 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=24.6$, 69.6, 118.6, 126.7, 127.0, 127.4, 127.7, 128.5, 128.8, 129.6, 129.7, 136.4, 144.5, 147.8, 155.1, 160.9.

(*S*)-1-(Naphthalen-1-yl)-*N*-(quinolin-2-ylmethylene)ethylamine (6):[14] Yield: 84%; yellow oil; $[\alpha]_D^{26}$: +152 (*c* 1.0, $CHCl_3$) [lit.[14] −130.6 (*c* 0.83, $CHCl_3$) (*R*)]; IR (thin film): $\nu_{max}=2977$, 2864, 1649, 1595, 1502, 1429, 1369, 1304, 1119, 959, 837, 778, 753, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.79$ (d, $J=6.8$ Hz, 3H), 5.54 (q, $J=6.8$ Hz, 1H), 7.5–7.6 (m, 4H), 7.7–7.9 (m, 5H), 8.10 (d, $J=8.4$ Hz, 1H), 8.18 (d, $J=8.4$ Hz, 1H), 8.27 (d, $J=8.4$ Hz, 1H), 8.31 (d, $J=8.4$ Hz, 1H), 8.68 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=24.1$, 65.3, 118.6, 123.6, 124.1, 125.4, 125.6, 125.9, 127.3, 127.6, 127.7, 128.8, 128.9, 129.5, 129.7, 130.7, 134.0, 136.4, 140.3, 147.7, 155.1, 161.2.

(*S*)-3,3-Dimethyl-*N*-(quinolin-2-ylmethylene)butan-2-amine (8): Yield: 81%; light yellow oil; $[\alpha]_D^{25}$: +73 (*c* 1.0, $CHCl_3$); IR (thin film): $\nu_{max}=2958$, 2866, 1646, 1595, 1502, 1458, 1393, 1364, 1204, 1121, 961, 834, 750, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.98$ (s, 9H), 1.20 (d, $J=6.4$ Hz, 3H), 3.15 (q, $J=6.4$ Hz, 1H), 7.5–7.6 (m, 1H), 7.7–7.8 (m, 1H), 7.83 (d, $J=8.4$ Hz, 1H), 8.1–8.2 (m, 3H), 8.50 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=17.3$, 26.6, 34.3, 75.3, 118.6, 127.2, 127.7, 128.7, 129.5, 129.6, 136.3, 147.8, 155.3, 160.0; MS (ESI): $m/z=241.4$ $(M+H)^+$, 263.3 $(M+Na)^+$; anal. calcd. for $C_{16}H_{20}N_2$: C 79.96, H 8.39, N 11.66; found: C 79.89, H 8.33, N 11.40.

Synthesis of Methyl 2-Quinolyl Ketone

To a solution of 2-quinolinecarbonitrile (2.0 g, 13.0 mmol) in anhydrous Et_2O (50 mL) cooled to 0 °C was added dropwise a solution of MeMgI in Et_2O (30 mL) [prepared from Mg (0.343 g, 14.3 mmol) and MeI (2.05 g, 14.3 mmol)]. After addition, the mixture was allowed to warm to room temperature and stirred overnight. After cooling to 0 °C, the mixture was quenched by adding ice water and 2M H_2SO_4 (25.0 mL, 50.0 mmol) successively. The mixture was stirred at room temperature for 5 h and washed with aqueous NaOH solution. The organic layer was separated and the aqueous layer was extracted with Et_2O (3×30 mL). The combined organic phase was washed with brine twice and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by silica gel chromatography (hexane:EtOAc=20:1) to give the desired compound as a colorless solid; yield: 1.25 g (56%); mp 50–51 °C (lit.[15] 50–52 °C); IR (KBr): $\nu_{max}=3012$, 1691, 1592, 1504, 1355, 1306, 1287, 1123, 942, 838, 756, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.88$ (s, 3H), 7.65 (td, $J=8.0$ Hz, 1.2 Hz, 1H), 7.79 (td, $J=6.8$ Hz, 1.2 Hz, 1H), 7.87 (d, $J=8.0$ Hz, 1H), 8.13 (d, $J=8.8$ Hz, 1H), 8.20 (d, $J=8.8$ Hz, 1H), 8.27 (d, $J=8.0$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=25.5$, 117.9, 127.6, 128.5, 129.5, 130.0, 130.6, 136.8, 147.3, 153.3, 200.7.

Ethyl 2-Quinolyl Ketone

The preparation is the same as that of methyl 2-quinolyl ketone except that EtMgBr (1.0M in THF) was used; yield: 62%; colorless solid; mp 56–57 °C (lit.[15] 59–60 °C); IR (KBr): $\nu_{max}=2977$, 1692, 1560, 1460, 1399, 1358, 1115, 968, 935, 806, 789, 753, 621 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.28$ (t, $J=7.6$ Hz, 3H), 3.43 (q, $J=7.6$ Hz, 2H), 7.64 (td, $J=8.0$ Hz, 0.8 Hz, 1H), 7.78 (td, $J=6.8$ Hz, 1.2 Hz, 1H), 7.87 (d, $J=8.4$ Hz, 1H), 8.14 (d, $J=8.4$ Hz, 1H), 8.20 (d, $J=8.4$ Hz, 1H), 8.26 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=8.1$, 30.9, 118.2, 127.7, 128.4, 129.6, 129.9, 130.5, 136.9, 147.2, 153.1, 203.2.

General Procedure for the Synthesis of Ketoimine Ligands (1, 2, 7, and 9)

To the corresponding ketone (2.0 mmol), chiral amine (3.2 mmol), and Et_3N (4.0 mmol) in toluene (20 mL) was added dropwise $TiCl_4$ (135 μL, 1.2 mmol) in toluene (3 mL). After stirring for an additional hour at room temperature, the mixture was heated to 90 °C for 24 h. The mixture was then cooled to 0 °C, quenched with 1M NaOH (10 mL), and extracted with EtOAc (3×20 mL). The combined organic layer was washed with 1M NaOH (10 mL) and brine (3×10 mL), and dried (Na_2SO_4). After removal of the solvent, the solid sample for analysis was obtained by recrystallization from solvent.

***N*-[1-(Quinolin-2-yl)ethylidene]pentan-3-amine (1):** Yield: 95%; light yellow oil; IR (thin film): $\nu_{max}=2965$, 1697, 1640, 1597, 1502, 1358, 1123, 837, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.87$ (t, $J=7.2$ Hz, 6H), 1.6–1.7 (m, 4H), 2.52 (s, 3H), 3.5–3.6 (m, 1H), 7.52 (td, $J=8.0$ Hz, 1.2 Hz, 1H), 7.71 (td, $J=8.8$ Hz, 1.2 Hz, 1H), 7.80 (d, $J=8.0$ Hz, 1H), 8.1–9.1 (m, 2H), 8.28 (d, $J=8.8$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=11.0$, 14.0, 28.9, 64.2, 119.1, 126.7, 127.5, 128.3, 129.1, 129.8, 135.7, 147.2, 158.2, 164.7; MS (ESI): $m/z=241.3$ $(M+H)^+$; anal. calcd. for $C_{16}H_{20}N_2$: C 79.96, H 8.39, N 11.66; found: C 79.79, H 8.40, N 11.85.

(*S*)-3,3-Dimethyl-*N*-[1-(quinolin-2-yl)ethylidene]butan-2-amine (2): Yield: 92% (from CH_3CN); colorless needles; mp 97–99 °C; $[\alpha]_D^{27}$: +105 (*c* 1.0, $CHCl_3$); IR (KBr): $\nu_{max}=2970$, 2867, 1633, 1596, 1558, 1499, 1366, 1127, 842, 763, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.98$ (s, 9H), 1.08 (d, $J=6.4$ Hz, 3H), 2.49 (s, 3H), 3.50 (q, $J=6.4$ Hz, 1H), 7.52 (td, $J=8.4$ Hz, 0.8 Hz, 1H), 7.68 (td, $J=8.4$ Hz, 0.8 Hz, 1H), 7.80 (d, $J=8.4$ Hz, 1H), 8.0–8.1 (m, 2H), 8.33 (d, $J=8.8$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=12.9$, 15.5, 26.5, 34.8, 65.0, 119.0, 126.7, 127.5, 128.3, 129.1, 129.8, 135.7, 147.2, 158.2, 163.4; MS (ESI): $m/z=255.3$ $(M+H)^+$, 277.3 $(M+Na)^+$; anal. calcd. for $C_{17}H_{22}N_2$: C 80.27, H 8.72, N 11.01; found: C 79.97, H 8.89, N 11.01.

(*S*)-1-(Naphthalen-1-yl)-*N*-[1-(quinolin-2-yl)ethylidene]-ethylamine (7): Yield: 80%; yellow needles (from MeOH); mp 111–112 °C; $[\alpha]_D^{26}$: +215.4 (*c* 1.0, $CHCl_3$); IR (KBr): $\nu_{max}=2971$, 1640, 1593, 1559, 1501, 1445, 1353, 1129, 837, 800, 781, 758, 736, 624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.76$ (d, $J=6.4$ Hz, 3H), 2.53 (s, 3H), 5.70 (q, $J=6.4$ Hz,

1H), 7.5–7.6 (m, 4H), 7.70 (qt, $J=6.8$ Hz, 1H), 7.75 (d, $J=8.0$ Hz, 1H), 7.82 (d, $J=8.0$ Hz, 1H), 7.8–7.9 (m, 2H), 8.11 (d, $J=8.4$ Hz, 1H), 8.16 (d, $J=8.8$ Hz, 1H), 8.34 (d, $J=8.0$ Hz, 1H), 8.49 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=14.0$, 24.3, 57.3, 119.1, 123.6, 124.1, 125.3, 125.8, 126.9, 127.2, 127.5, 128.5, 129.0, 129.2, 129.9, 134.1, 135.9, 142.0, 147.2, 165.9; MS (ESI): $m/z=325.3$ $(M+H)^+$, 347.3 $(M+Na)^+$; anal. calcd. for $C_{23}H_{20}N_2$: C 85.15, H 6.21, N 8.63; found: C 84.87, H 6.23, N 8.77.

(*S*)-3,3-Dimethyl-*N*-[1-(quinolin-2-yl)propylidene]butan-2-amine (9): Yield: 89%; colorless needles (from CH_3CN); mp 63–64 °C; $[\alpha]_D^{21}$: +108 (*c* 1.0, $CHCl_3$); IR (KBr): $\nu_{max}=$ 2967, 2866, 1630, 1558, 1500, 1455, 1361, 1130, 835, 761, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.99$ (s, 9H), 1.10 (d, $J=6.8$ Hz, 3H), 1.15 (t, $J=7.2$ Hz, 3H), 2.9–3.0 (m, 1H), 3.2–3.3 (m, 1H), 3.54 (q, $J=6.8$ Hz, 1H), 7.52 (td, $J=8.4$ Hz, 0.8 Hz, 1H), 7.69 (td, $J=6.8$ Hz, 1.2 Hz, 1H), 7.80 (dd, $J=8.4$ Hz, 0.8 Hz, 1H), 8.10 (d, $J=8.4$ Hz, 2H), 8.28 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=12.4$, 16.5, 19.6, 26.5, 34.6, 64.2, 119.6, 126.6, 127.4, 128.3, 129.0, 129.9, 135.6, 147.3, 157.3, 168.2; MS (ESI): $m/z=269.4$ $(M+H)^+$, 291.3 $(M+Na)^+$; anal. calcd. for $C_{18}H_{24}N_2$: C 80.55, H 9.01, N 10.44; found: C 80.23, H 9.00, N 10.64.

General Procedure for Asymmetric Allylic Oxidation of Cycloolefins in the Presence of $Cu(OTf)_2$/$PhNHNH_2$/Ligand Complexes

A solution of chiral Schiff base ligand (0.06 mmol) and $Cu(OTf)_2$ (0.05 mmol) in acetone (3 mL) was stirred at 20 °C for 1 h. To this dark red solution was added phenylhydrazine (6.5 mg, 0.06 mmol), and the mixture was stirred for 30 min during which the solution became clear red. Then, an olefin (5.0 mmol) was added, followed by dropwise addition of *tert*-butyl perbenzoate (1.0 mmol) under an argon atmosphere. For the most reactive cycloolefins (cyclopentene and cyclohexene), the reaction was completed immediately after the addition of *tert*-butyl perbenzoate and the heat released could be detected even by hand. For the relatively less reactive cycloolefins, the color changed to green after several minutes and the reaction was left to proceed at 20 °C until it was completed (determined by the disappearance of perester from TLC or the change of color to red). The solvent was then removed and the residue was purified by silica gel chromatography using hexane:EtOAc (100:1) as eluent to give the product as a light yellow liquid.

General Procedure for Asymmetric Allylic Oxidation of Cycloolefins in the Presence of $Cu(CH_3CN)_4PF_6$/Ligand Complexes

A solution of chiral Schiff base ligand (0.06 mmol) and $Cu(CH_3CN)_4PF_6$ (0.05 mmol) in acetone (3 mL) was stirred at 20 °C for 1 h. After cooling to the temperature indicated in Table 3, an olefin (5.0 mmol) was added to this dark red solution, followed by dropwise addition of *tert*-butyl perbenzoate (1.0 mmol). After the addition of perester, the color changed to green and the reaction was left at the indicated temperature for the time listed in Table 3. The solvent was then removed and the residue was purified by silica gel chromatography using hexane:EtOAc (100:1) as eluent to give the product as a colorless liquid.

(*R*)-2-Cyclopentenyl 1-benzoate (Table 3, entry 2):[41] The *ee* was determined as 51% *ee* by HPLC on a CHIRALCEL OD-H (DAICEL) column [hexane:2-propanol = 99.9:0.1]; 0.5 mL min^{-1}; t_R of *S*-isomer = 24.6 min, t_R of *R*-isomer = 29.5 min; $[\alpha]_D^{26}$: +101.2 (*c* 1.0, $CHCl_3$) {lit.[41] $[\alpha]_D^{25}$: −136.2 (*c* 0.9, $CHCl_3$) for 70% *ee* (*S*)}.

(*R*)-2-Cyclohexenyl 1-benzoate (Table 3, entry 4):[41] The *ee* was determined as 51% *ee* by HPLC on a CHIRALCEL OD-H (DAICEL) column [hexane:2-propanol = 99.9:0.1]; 0.5 mL min^{-1}; t_R of *S*-isomer = 25.6 min, t_R of *R*-isomer = 27.0 min; $[\alpha]_D^{24}$: +96.6 (*c* 1.0, $CHCl_3$) {lit.[41] $[\alpha]_D^{25}$: −167.2 (*c* 4.4, $CHCl_3$) for 93% *ee* (*S*)}.

(*R*)-2-Cycloheptenyl 1-benzoate (Table 3, entry 6):[5] The *ee* was determined as 84% *ee* by HPLC on a CHIRALPAK AD-H (DAICEL) column [hexane:2-propanol = 99.7:0.3]; 0.5 mL min^{-1}; t_R of *R*-isomer = 18.4 min, t_R of *S*-isomer = 19.8 min; $[\alpha]_D^{24}$: +40.5 (*c* 1.0, $CHCl_3$) {lit.[5] $[\alpha]_D^{25}$: −38.2 (*c* 4.4, $CHCl_3$) for 82% *ee* (*S*)].

(*R*)-2-Cyclooctenyl 1-benzoate (Table 3, entry 8):[41] The *ee* was determined as 70% *ee* by HPLC on a CHIRALCEL OD-H (DAICEL) column [hexane:2-propanol = 99.9:0.1]; 0.5 mL min^{-1}; t_R of *R*-isomer = 27.1 min, t_R of *S*-isomer = 29.4 min; $[\alpha]_D^{25}$: −58.0 (*c* 1.0, $CHCl_3$) {lit.[41] $[\alpha]_D^{25}$: +86.5 (*c* 1.2, $CHCl_3$) for 94% *ee* (*S*)}.

(*R*)-2,6-Cyclooctadienyl 1-benzoate (Scheme 2): The *ee* was determined as 74% *ee* by HPLC on a CHIRALCEL OB (DAICEL) column [hexane:2-propanol = 99.7:0.3]; 0.75 mL min^{-1}; t_R of minor isomer = 11.9 min, t_R of major isomer = 16.1 min; $[\alpha]_D^{28}$: −33.3 (*c* 1.0, $CHCl_3$).

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