Asymmetric Kharasch Reaction: Catalytic Enantioselective Allylic Oxidation of Olefins Using Chiral Pyridine Bis(diphenyloxazoline)−Copper Complexes and *tert*-Butyl Perbenzoate†,‡

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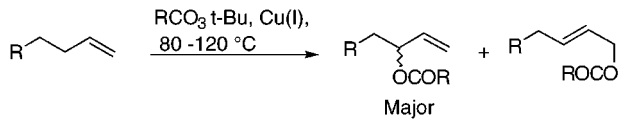
Copper complexes of chiral pyridine bis(diphenyloxazoline)-type ligands have been studied as catalysts for the enantioselective allylic oxidation of olefins. Using 2.5−5 mol % of these chiral catalysts and *tert*-butyl perbenzoate as oxidant, optically active allylic benzoates were obtained in up to 86% ee. A variety of copper salts was studied under different conditions and in different solvents. Acetone was found to be a superior solvent for the reaction. Use of phenylhydrazine in conjunction with the chiral copper complex played a crucial role in increasing the rate of the reaction. Use of 4 Å molecular sieves increased the optical yield of product in almost every case.

Introduction

The allylic oxidation of olefins with peresters in the presence of copper salts to give allylic esters has been previously studied by Kharasch and co-workers.[1] The reaction exploits the special nature of an allylic CH bond and proceeds in a regioselective manner. For example, in case of an acyclic terminal olefin, a mixture of internal secondary ester and a primary ester is formed in which the former one predominates (Scheme 1). Since the allylic ester can easily be converted into allylic alcohol by saponification or reduction method, the Kharasch reaction eventually becomes an allylic alcohol synthesis. Asymmetric version of this reaction will nicely complement other methods to prepare chiral allylic alcohols, which are useful building blocks in organic synthesis.[2,3]

Early attempts for asymmetric version of this reaction using copper complexes of (+)-α-ethyl camphorate,[4a] chiral Schiff bases,[4b] and optically active amino acids[4b] gave a very poor asymmetric induction (5−17% ee) in the allylic oxidation of olefins. The area was dormant for a number of years until 1991, when Muzart studied allylic oxidation of cyclohexene with copper complexes of L-amino acids using acetic acid and *t*-BuOOH, but the asymmetric induction still remained poor (<30% ee).[5a] A few years later, Muzart and Levina[5b,c] and Feringa et al.[6] independently studied the same reaction with copper(I) and -(II) complexes of a variety of optically active amino acids. Under their best conditions using a Cu(II) complex of (*S*)-proline, cyclopentene and cyclohexene gave 54% and 63% ee's, respectively. During the course of our study on enantioselective allylic oxidation of olefins, important contributions were made by several groups.[7,8] Pfaltz et al.[8a] and Andrus et al.[8b,c] independentely reported that chiral copper(I)−bis(oxazoline) complexes would catalyze the allylic oxidation of olefins in a reasonably good enantioselective manner. Around the same time, Katsuki et al.[8d,e] introduced copper(II) complexes of tris(oxazoline) ligand that showed some improvement in the enantioselective allylic oxidation of cyclopentene; but, however, other olefins gave only modest enantioselectivity. Andersson et al.[8f] used a chiral copper complex of a bicyclic amino acid for the same reaction, but the enantioselectivity remained modest. *The universal problem with all the previous reports had been*

Scheme 1



† Dedicated to Professor E. J. Corey on the occasion of his 70th birthday.

‡ Part of the work was presented in the form of an invited lecture at the 48th ACS Southeast Regional Meeting on asymmetric synthesis Nov 10−13, 1996, Greenville, SC.

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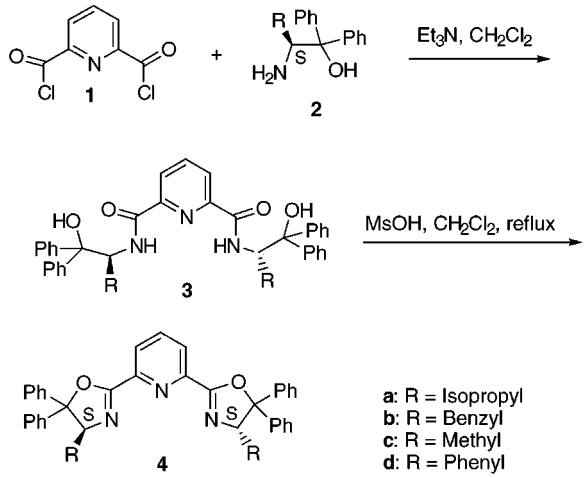
the very slow rate of the reaction, requiring several days for completion, and sometimes close to a month. Besides this, optical and chemical yield for some cycloolefins had been very poor. In this paper, we address some of these issues and delineate full details of our work in this area.

Results and Discussion

Design, synthesis, and tuning of a suitable chiral ligand around a metal center is an important task in asymmetric synthesis.[9] During the past several years, we were involved in designing chiral bases for conversion of epoxides to chiral allylic alcohols.[10] We now report that the same goal of preparing chiral allylic alcohols can be achieved by an enantioselevtive allylic oxidation of olefins using a catalytic amount of copper complex of chiral pyridine bis(diphenyloxazoline) ligand (henceforth we will call it "pybox−diph" ligand). Pyridine bis(oxazoline)type ligand (pybox ligand) was first used by Nishiyama for asymmetric hydrosilylation reactions.[11] Later on, these ligands were used for asymmetric dehydrogenative silylation of ketones,[12] chiral recognition of binaphthol,[13] enantioselective cyclopropanation reactions,[14] aldol reactions,[15] and Diels−Alder reactions.[16] While working on an asymmetric cyclopropanation reaction[17] using an ip−pybox−diph ligand **4a**, we envisioned that its copper complex would be quite suitable as a catalyst for the enantioselective allylic oxidation of olefins with a perester. To carry out the reactions, a variety of pybox−diph ligands were synthesized. The ligands **4a**−**d** were synthesized in two steps, viz., by coupling of 2,6-dipiconyl chloride **1**[18] and (*S*)-diphenylamino alcohol **2**[19] followed by intramolecular condensation of **3** with methanesulfonic acid (Scheme 2).[17,20] Similarly, the ligand **7** was synthesized from isophthalyl chloride **5** (Scheme 3).[21]

In our initial study, the complex of **4a**[17] with CuI in acetonitrile was found to catalyze the allylic oxidation of

Scheme 2



Scheme 3

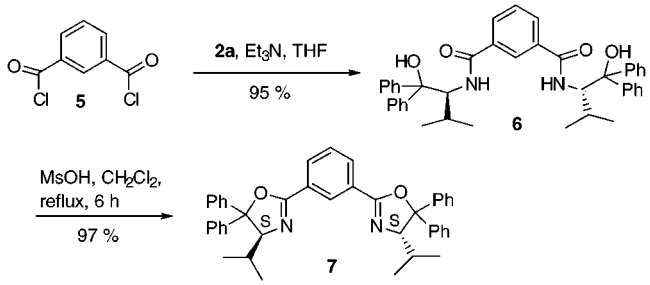
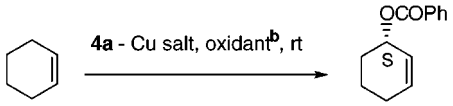


Table 1. Effect of Copper Salt in the Complex with the Ligand 4a on Catalytic Enantioselective Allylic Oxidation of Cyclohexene[a]



entry	Cu salt	solvent	time[c]	% yield[d]	% ee[e]
1	CuI	MeCN	05 d	37	09
2	CuCN	MeCN	05 d	48	42
3	$Cu(OTf)_2$	acetone	28 h	44	26
4	$(CuOTf)_2PhH$	acetone	06 d	87	73
5	[Cu(I)OTf][f]	acetone	24 h	65	71

[a] The reaction was done at rt, which here refers to 30 °C. [b] PhCOOH and *t*-BuOOH were used for entries 1 and 2. $PhCO_3$-*t*-Bu was used for entries 3−5. [c] h for hours and d for days. [d] Isolated yield. [e] Determined by HPLC on chiral columns. [f] Prepared in situ by reducing the Cu(II) OTf complex with $PhNHNH_2$.

cyclohexene with *tert*-butyl hydroperoxide and benzoic acid, but the enantioselectivity was very poor (Table 1, entry 1). We then tried other copper complexes prepared from various copper salts such as CuCN, Cu(II) triflate, and Cu(I) triflate. It was found out that all of them catalyzed the allylic oxidation reaction, but only the **4a**−Cu(I) triflate complex gave reasonably higher asymmetric induction. It was observed that the rate of the reaction depended upon how the **4a**−Cu(I) triflate complex was prepared and used in the reaction (Table 1, entry 4 vs 5). The **4a**−Cu(I) triflate complex was prepared in two ways. In the first way, the ligand **4a** was directly treated with $(CuOTf)_2$·PhH, which is available commercially (Table 1, entry 4). In the second way, the Cu(I) species was prepared in situ by reducing the complex **4a**−Cu-$(OTf)_2$ with phenylhydrazine (Table 1, entry 5).[22] With **4a**-Cu(I) triflate complex prepared in situ by using

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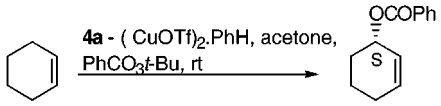
Table 2. Effect of Phenylhydrazine and 4 Å Molecular Sieves on Catalytic Enantioselective Allylic Oxidation of Cyclohexene with Chiral 4a−(CuOTf) Complex[a]



entry	$PhNHNH_2$	4 Å	time[b]	% yield[c]	% ee[d]
1	no	No	06 d	87	73
2	yes	No	05 h	78	70
3	no	Yes	21 d	88	86
4	yes	Yes	10 h	77	67

[a] The reaction was done at rt, which here refers to 18−20 °C. [b] h for hour and d for days. [c] Isolated yield. [d] Determined by HPLC on Chiracel OJ and OD-H columns.

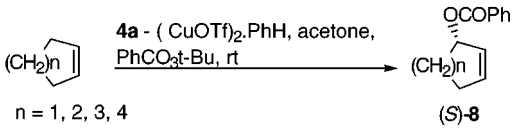
$PhNHNH_2$, the rate of the reaction was fast and it took much less time (6 days vs 1 day) without affecting the enantioselectivity to a great extent (73% ee vs 71% ee). With this exciting result, it was imperative to know the effect of phenylhydrazine on the enantioselective oxidation reaction with a complex prepared from **4a** and commercially available Cu(I) triflate. It was also thought that if the last traces of moisture from the reaction mixture was removed by using 4 Å molecular sieves, the catalytic activity of the copper complex might go up, and in turn, it might increase the enantioselectivity of the reaction. So, the effect of $PhNHNH_2$ and 4 Å molecular sieves was examined on the allylic oxidation of cyclohexene with chiral **4a**-(CuOTf) complex in acetone (Table 2). It was gratifying to note that phenylhydrazine increased the rate of the reaction severalfold without affecting the enantioselectivity too much. For example, when cyclohexene was treated with *tert*-butyl perbenzoate and 5 mol % of the complex **4a**−(CuOTf) in the presence of phenylhydrazine, the reaction time was reduced from 6 days to 5 h (Table 2, entry 1 vs 2). If phenylhydarzine was replaced by 4 Å molecular sieves, the reaction became very sluggish. However, the enantioselectivity increased to 86% (Table 2, entry 3). For cyclohexene, this was the highest enantioselectivity obtained, to date, for this kind of transformation. The presence of phenylhydrazine and 4 Å molecular sieves together with the complex in the reaction mixture was not benificial for asymmetric induction.

The drastic effect of phenylhydrazine on the rate of the reaction in the allylic oxidation of cyclohexene prompted us to examine its effect on other substrates. We extended the reaction to several cycloolefins and found out the similar effects (Table 3). In every case, the reaction time was reduced from several days to few hours. Besides this, the enantioselectivity was also high.

Since we had achieved the highest asymmetric induction (86% ee) in the allylic oxidation of cyclohexene with the complex **4a**−(CuOTf) in the presence of 4 Å molecular sieves, we subjected other olefins to this condition, and it was found out that the reaction was very slow in all the cases (Table 4). Unlike cyclohexene, other olefins did not give high asymmetric induction in the allylic oxidation reaction.

(22) (a) We have confirmed by UV−vis and EPR methods that **4a**−Cu(II) triflate complex gets reduced to Cu(I) species in the presence of phenylhydrazine. For details, see ref 17. (b) For reduction of Cu(II) species to Cu(I) with phenylhydrazine, also see: Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193. (c) For use of the same reduction method in the cyclopropanation reaction, see: Kanemasa, S.; Hamura, S.; Harada, E.; Yamamoto, H. *Tetrahedron Lett.* **1994**, *35*, 7985.

Table 3. Effect of Phenylhydrazine on Catalytic Enantioselective Allylic Oxidation of Olefins with Chiral 4a−(CuOTf) Complex[a]

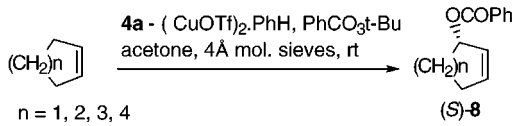


n = 1, 2, 3, 4 (*S*)-**8**

Entry	Olefins	$PhNHNH_2$	Time[b]	% Yield[c]	% ee[d]
1.		No	48 h	90	51
2.		Yes	03 h	62	54
3.		No	06 d	87	73
4.		Yes	05 h	78	70
5.		No	6.5 d	63	71
6.		Yes	06 h	35	72
7.		No	30 d	28	80
8.		Yes	24 h	26	81

[a] The reaction was done at rt, which here refers to 18−20 °C. [b] h for hours and d for days. [c] Isolated yield. [d] Determined by HPLC on chiral columns and by 400 MHz ^{1}H NMR spectrum of a Mosher ester of the corresponding alochol.

Table 4. Catalytic Enantioselective Allylic Oxidation of Olefins with Chiral 4a−(CuOTf) Complex in the Presence of 4 Å Molecular Sieves[a]



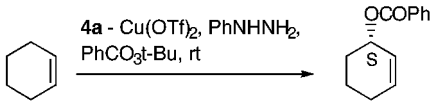
n = 1, 2, 3, 4 (*S*)-**8**

Entry	Olefins	Time[b]	% Yield[c]	% ee[d]
1.		09 d	85	51
2.		21 d	88	86
3.		60 d	47	66
4.		75 d	20	70

[a] The reaction was done at rt, which here refers to 18−20 °C. [b] d for days. [c] Isolated yield. [d] Determined by HPLC on chiral columbs and by 400 MHz ^{1}H NMR spectrum of a Mosher ester of the corresponding alcohol.

It was clear from the Table 3 that the use of phenylhydrazine was highly benificial for the enantioselective allylic oxidation of olefins with a complex **4a**−(CuOTf). In view of the high cost and handling problem of (CuOTf) due to its unstability, it was thought to prepare the same species in situ by reducing a **4a**−$Cu(OTf)_2$ complex with $PhNHNH_2$. Since our initial study on allylic oxidation of cyclohexene with **4a**−Cu(I) triflate prepared in this manner in acetone was highly encouraging (vide supra), we examined the effect of other factors such as solvent, temperature, and additives on the reaction. Solvent study indicated that acetone and acetonitile were better than benzene. The rate of the reaction was faster in acetone in comparison to acetonitile, and the enantioselectivty was comparable (Table 5). Lowering the temperature did improve the enantioselectivity to some

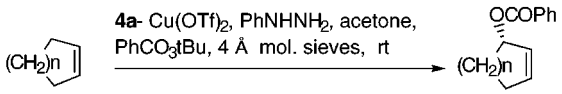
Table 5. Effect of Solvent and 4 Å Molecular Sieves on Catalytic Enantioselective Allylic Oxidation of Cyclohexene with Chiral 4a−Cu(I) Complex Reduced in Situ from 4a−Cu(OTf)$_2$ by Phenylhydrazine[a]



entry	solvent	4 Å	time[b]	% yield[c]	% ee[d]
1	benzene	no	24 h	55	28
2	benzene	yes	72 h	70	35
3	acetonitrile	no	10 d	43	70
4	acetonitrile	yes	15 d	58	80
5	acetone	no	24 h	65	71
6	acetone	yes	24 h	73	75
7	acetone	yes	30 d	78	79

[a] All the reactions, except entry 7, was done at rt, which here refers to 27−30 °C. The entry 7 was done at 10 °C. [b] h for hours and d for days. [c] Isolated yield. [d] Determined by HPLC on chiral columns.

Table 6. Catalytic Enantioselective Allylic Oxidation of Olefins with Chiral 4a−Cu(I) Complex Reduced in Situ from 4a−Cu(OTf)$_2$ by Phenylhydrazine[a]



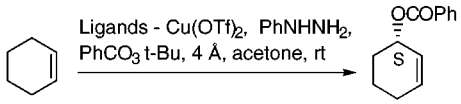
Entry	Olefins	Time[b]	% Yield[c]	% ee[d]
1.		04 h	80	60
2.		24 h	73	75
3.		24 h	42	82
4.		72 h	28	81

[a] The reaction was done at rt, which here refers to 28−30 °C. [b] h for hour. [c] Isolated yield. [d] Determined by HPLC on chiral columns and by 400 MHz ^{1}H NMR spectrum of a Mosher ester of the corresponding alochol.

extent, but the longer reaction time discouraged us to do the reaction at lower temperature (Table 5, entry 7). Molecular sieves (4 Å) helped to improve the enantioselectivity to some extent in all the solvents. This prompted us to examine allylic oxidation of other olefins with **4a**−Cu(I) triflate species prepared in situ by phenylhydrazine in acetone in the presence of 4 Å molecular sieves. The results are summarized in Table 6. In the case of cyclopentene, the reaction was complete in just 4 h and the asymmetric induction was 60%. Cyclohexene and cycloheptene took 24 h for completion of the reaction, and the asymmetric induction was 75% and 82%, respectively. In the case of cyclooctene, the reaction was a bit slow and it took 3 days for completion. However, the enantioselectivity was 81%. It is worthy of note that the asymmetric induction obtained in the cases of cycloheptene and cyclooctene is the highest, to date, for the asymmetric Kharasch reaction.

Next, to study the effect of different substituents at the chiral center in the pybox−diph ligand on the allylic oxidation reaction, we carried out the reactions with

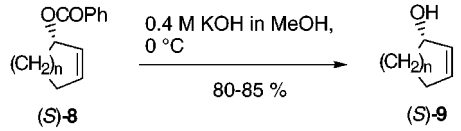
Table 7. Enantioselective Allylic Oxidation of Cyclohexene with Copper Complexes of Different Ligands[a]



entry	ligand	time[b]	% yield[c]	% ee[d]
1	**4a**	24 h	73	75
2	**4b**	24 h	79	62
3	**4c**	02 d	69	23
4	**4d**	36 h	57	11
5	**7**	24 h	62	00

[a] The reaction was done at rt, which here refers to 18−20 °C. [b] h for hour and d for days. [c] Isolated yield. [d] Determined by HPLC on chiral columns.

Scheme 4



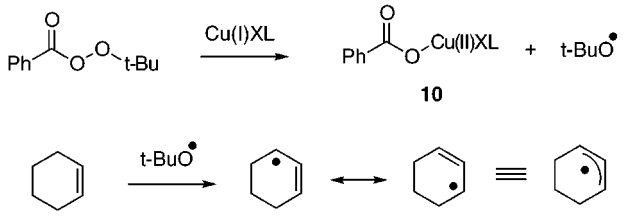
different ligands under the best conditions we had for **4a**. When the isopropyl of the ligand **4a** was replaced by methyl, benzyl, or phenyl, the asymmetric induction in the allylic oxidation reaction was poor (Table 7). The absence of any asymmetric induction with ligand **7** indicated that the pyridine N was essential for chirality transfer in the catalytic allylic oxidation reaction of olefins.

It was observed that in all the cases (*S*)-pybox−diph ligand gave (*S*)-allylic benzoates. The enantiomeric excess in the reactions was determined by HPLC on chiral columns and by 400 MHz ^{1}H NMR spectrum of a Mosher ester[23] of the corresponding allylic alcohol obtained by hydrolysis of benzoates. To see whether there is any racemization during the hydrolysis of allylic benzoates, we hydrolyzed 2-cyclohexenyl benzoate **8** (n = 2) with known optical purity (86% ee, chiralcel OD-H column) into allylic alcohol **9** (n = 2), and then converted back to the benzoate **8** (n = 2). The analysis of this allylic benzoate sample by HPLC on a Chiralcel OD-H column indicated its optical purity to be 85.6% ee. Thus, there is no racemization during the hydrolysis of allylic benzoates under the reported conditions (Scheme 4).

The mechanism of the Kharasch reaction has been very well studied. There is enough evidence in the literature that the reaction proceeds via a radical intermediate. The Cu(I) species cleaves the perester to give Cu(II) benzoate **10** and *tert*-butoxy radical.[24] The *tert*-butoxy radical abstracts an allylic hydrogen to give *tert*-butyl alcohol and allylic radical (Scheme 5).[25] It has been proposed in the literature that there are two possibilities for the reaction of allylic radical with Cu(II) benzoate (Figure 1). The Cu(II) benzoate may add to the allylic radical to generate Cu(III) benzoate **11** which can rearrange via a six-membered cyclic transition state to give allylic benzoate.[26] The other possibility could be that there is a bonding

(23) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.
(24) (a) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 774. (b) Kochi, J. K.; Bemis, A. *Tetrahedron* **1968**, *24*, 5099.
(25) (a) Walling, C.; Zavitsas, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 2084. (b) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877.
(26) Beckwith, A. L. J.; Zavitas, A. A. *J. Am. Chem. Soc.* **1986**, *108*, 8230 and references therein.

Scheme 5



between an incipient double bond of the allylic radical and the Cu(II) benzoate as designated in **12**.[27] In literature, the former possibility has been favored as the Cu(III) intermediate has been detected spectroscopically.[26] In view of ours and others finding that Cu(II) complexes also catalyze the reaction equally well, the mechanism of the reaction becomes even more complicated. In that case, it can be assumed that the reaction proceeds via **12**, and based on this we propose a transition state model **13a** to account for the obtained asymmetric induction in the reaction.[28] Knowing the complex nature of redox chemistry of copper, the possibility of an intermediate of the type **11** can also not be ignored. And if this is the case, a transition state of the type **13b** can explain the enantioselectivity in the reaction.

In these favorable transition state assemblies, copper benzoate may attain an orientation to provide a π-stacking of the two aromatic rings.[29] Since the distance between both the rings is approximately 3.5 Å, there might be some attractive interaction which would stabilize the drawn conformation. In that case, the allylic radical will approach the Cu species from the less hindered side as shown in Figure 2. The benzoate oxygen attacks the allylic carbon, which is electrophilic in nature due to coordination of incipient double bond with the copper species. This follows reduction of the Cu species into its original oxidation state. Thus, the catalytic cycle of the allylic oxidation of olefins continues.

The reason for the increase in the rate of the reaction on use of phenylhydrazine is not very clear to us. In a preliminary study, we observed that phenylhydrazone increased the rate of the reaction as well. In view of this, it is proposed that phenylhydrazine reacts with acetone to form phenylhydrazone, which increases the rate of the reaction.[30] The similar rate enhancement in the allylic oxidation reaction could not be obtained by replacing it by amine bases such as pyridine, DBN, or DBU.[31] The role of molecular sieves could be that it removes the last traces of moisture from the reaction mixture.

In conclusion, we have studied enantioselective allylic oxidation of olefins with a copper complex of pybox−diph ligands. We have shown for the first time that the rate of the reaction can be increased severalfold by using phenylhydrazine. Under the best conditions, we were able to convert cyclic olefins to (*S*)-allylic benzoates in up to 86% ee. Although there is some limitaion[32] with this reaction, the methodology will be highly useful in near future once it gets wide attention from organic chemists across the world.

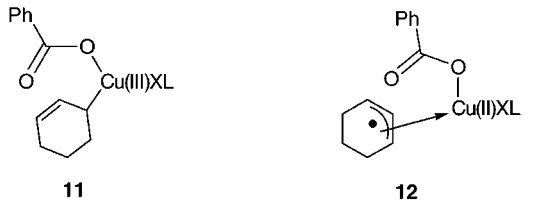


Figure 1.

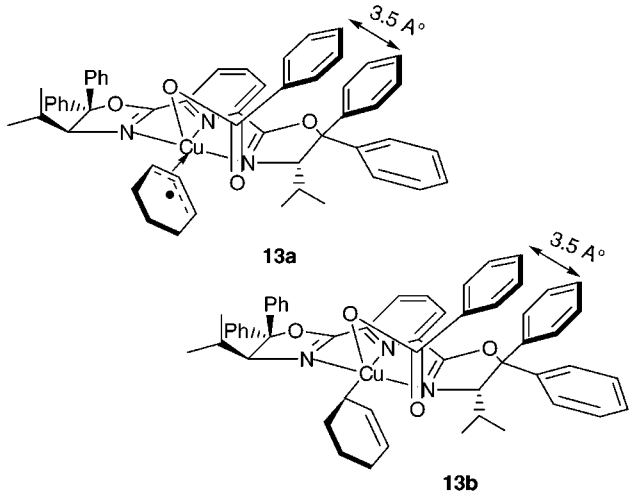


Figure 2.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on 60, 300, and 400 MHz spectrometers. Chemical shifts are expressed in ppm downfield from TMS as internal standard, and coupling constants are reported in hertz. Routine monitoring of reactions was performed using silica gel-G obtained from Acme. All the column chromatographic separations were done by using silica gel (Acme's, 60−120 mesh). Petroleum ether used was of boiling range 60−80 °C. Reactions that needed anhydrous conditions were run under an atmosphere of dry nitrogen or argon using flame-dried glassware. The organic extracts were dried over *anhydrous* sodium sulfate. Evaporation of solvents was performed at reduced pressure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Benzene, dichloromethane, acetonitrile, and acetone were distilled from CaH_2.

General Procedure for Synthesis of Amido Alcohols (3). To a stirred solution of (*S*)-diphenylamino alcohol (10 mmol) and Et_3N (25 mmol) in CH_2Cl_2 (30 mL) was added dropwise a solution of dipicolinyl chloride **1** (5 mmol) in 5 mL of CH_2Cl_2 at 0 °C, and the mixture was stirred for 16 h (0 °C to rt). The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous $NaHCO_3$, water, and brine. The organic layer was dried, and the solvent was evaporated in vacuo. Purification by column chromatography over silica gel gave pure coupled product **3**.

***N,N′*-Bis[1′-(*S*)-isopropyl-2′,2′-diphenyl-2′-hydroxyethyl]-2,6-pyridinedicarboxamide (3a).**[17] This was prepared as per our own procedure: yield 90%; mp 110−111 °C; R_f 0.22 (1:4, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −46.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.83 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 6.8 Hz, 6H), 1.81 (m, 2H), 5.02 (d, J = 11.2 Hz, 2H), 6.06 (s, 2H, O*H*)), 7.02 (m, 2H), 7.15 (m, 6H), 7.32 (t, J = 7.2

(27) Kochi, J. K.; Mains, H. E. *J. Org. Chem.* **1965**, *30*, 1862.
(28) Professor Muzart is also quite apprehensive about the traditional mechanism. For details, see ref 5d.
(29) For a review on the π stacking effect in asymmetric synthesis, see: Jones, G. B.; Chapman, B. J. *Synthesis* **1995**, 475.
(30) We have observed that Cu(II) species can be reduced to Cu(I) using phenylhydrazone.
(31) For allylic oxidation of olefins using a complex of DBN/DBU−$Cu(OTf)_2$, see: Sekar, G.; DattaGupta, A.; Singh, V. K. *Tetrahedron Lett.* **1996**, *37*, 8435.
(32) The drawback of the reaction is that acyclic olefins reacted very slowly and gave very poor asymmetric induction. For example, 1-octene gave 11% ee in the allylic oxidation reaction with the ligand **4a** under the best conditions.

Hz, 4H), 7.53 (m, 8H), 8.0 (bs, 2H, N*H*), 8.06 (dd, J = 8.0, 6.0 Hz, 1H), 8.26 (d, J = 10.8 Hz, 2H).

***N,N′*-Bis[1′-(*S*)-benzyl-2′,2′-diphenyl-2′-hydroxyethyl]-2,6-pyridinedicarboxamide (3b).** This was prepared following the general procedure mentioned above: yield 85%; mp 114−116 °C; R_f 0.24 (1:4, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −115.2° (*c* 1.25, $CHCl_3$); IR (KBr) 3400, 3040, 1660 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.78 (d, J = 12.4 Hz, 2H), 2.93 (dd, J = 14.0, 3.6 Hz, 2H), 5.39 (dt, J = 10.4. 1.4 Hz, 2H), 6.42 (s, O*H*), 7.05 (m, 8H), 7.15 (m, 8H), 7.23 (m, 2H), 7.39 (t, J = 8 Hz, 4H), 7.65 (m, 8H), 7.78 (bs, N*H*), 7.89 (dd, J = 8.0, 7.0 Hz, 1H), 8.33 (d, J = 10.4 Hz, 2H); LCMS (APCI, *m*/*z*) 737 ($M^+ + 1$). Anal. Calcd for $C_{49}H_{43}N_3O_4$: C, 79.76; H, 5.87; N, 5.69. Found: C, 79.18; H, 5.73; N, 5.72.

***N,N′*-Bis[1′-(*S*)-methyl-2′,2′-diphenyl-2′-hydroxyethyl]-2,6-pyridinedicarboxamide (3c):** yield 90%; mp 98−100 °C; R_f 0.71 (1:1, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −9.0° (*c* 1.0, $CHCl_3$); IR (KBr) 3390, 3040, 1660 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, J = 6.8 Hz, 6H), 2.9 (bs, 2H, O*H*), 5.22 (m, 2H), 7.13 (m, 2H), 7.26 (m, 6H), 7.38 (t, J = 7.6 Hz, 4H), 7.56 (m, 8H), 7.91 (dd, J = 7.6 Hz, 1H), 8.09 (d, J = 9 Hz, 2H, N*H*), 8.18 (d, J = 8 Hz, 2H); LCMS (APCI, *m*/*z*) 586 ($M^+ + 1$). Anal. Calcd for $C_{37}H_{35}N_3O_4$: C, 75.87; H, 6.02; N, 7.17; Found: C, 75.41; H, 6.12; N, 7.06.

***N,N′*-Bis[1′-(*S*)-phenyl-2′,2′-diphenyl-2′-hydroxyethyl]-2,6-pyridinedicarboxamide (3d):** yield 94%; mp 158−160 °C; R_f 0.36 (1:3, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −341° (*c* 1.0, $CHCl_3$); IR (KBr) 3390, 3030, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.25 (s, 2H, O*H*), 6.09 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8 Hz, 4H), 7.05−7.42 (m, 22H), 7.73 (d, J = 8 Hz, 4H), 7.88 (dd, J = 8.0 Hz, 1H), 8.91 (d, J = 9.2 Hz, 2H). Anal. Calcd for $C_{47}H_{39}N_3O_4$: C, 79.53; H, 5.54; N, 5.52. Found: C, 79.32; H, 5.47; N, 5.38.

General Procedure for Cyclization of Amido Alcohols (3) to Pyridine Bis(diphenyloxazolines) (4). A solution of amido alcohol **3** (1.1 mmol) and methanesulfonic acid (6.6 mmol) in CH_2Cl_2 (20 mL) was refluxed for 6 h while keeping CaH_2 in an addition funnel for removing the water generated during the reaction. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with aqueous $NaHCO_3$, water, and brine, and dried. Solvent removal gave a solid mass that was chromatographed over silica gel to provide pure cyclized product **4**.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-isopropyloxazolin-2′-yl]pyridine (4a):[17] yield 85%; mp 65−66 °C; R_f 0.55 (1:4, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −233.2° (*c* 2.7, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.68 (d, J = 6.4 Hz, 6H), 1.06 (d, J = 6.8 Hz, 6H), 1.95 (m, 2H), 4.89 (d, J = 4.8 Hz, 2H), 7.28 (m, 8H), 7.36 (m, 8H), 7.6 (d, J = 8 Hz, 4H), 7.96 (t, J = 7.2 Hz, 1H), 8.21 (d, J = 8 Hz, 2H).

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-benzyloxazolin-2′-yl]pyridine (4b): yield 85%; mp 101−102 °C; R_f 0.48 (1:4, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −328.0° (*c* 1, $CHCl_3$); IR (KBr) 3000, 1620 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 2.8 (d, J = 7.5 Hz, 4H), 5.15 (t, J = 7.5 Hz, 2H), 6.8−7.7 (m, 30H), 7.98 (dd, J = 7.0, 6.0 Hz, 1H), 8.18 (d, J = 8 Hz, 2H); MS (FAB, *m*/*z*) 702 ($M^+ + 1$, base peak). Anal. Calcd for $C_{49}H_{39}N_3O_2$: C, 83.85; H, 5.60; N, 5.98. Found: C, 83.52; H, 5.80; N, 5.73.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-methyloxazolin-2′-yl]pyridine (4c). This was prepared as per the general procedure mentioned above: yield 45% as a sticky material; R_f 0.37 (1:3, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −112.1° (*c* 2.5, $CHCl_3$); IR (film) 3000, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.4 (d, 6H), 5.12 (m, 2H), 6.75−7.5 (m, 20H), 7.99 (t, J = 8 Hz, 1H), 8.27 (d, J = 9 Hz, 1H), 8.37 (d, J = 9 Hz, 1H); MS (FAB, *m*/*z*) 550 ($M^+ + 1$, base peak). Anal. Calcd for $C_{37}H_{31}N_3O_2$: C, 80.84; H, 5.68; N, 7.64. Found: C, 80.52; H, 5.35; N, 7.35.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-phenyloxazolin-2′-yl]pyridine (4d). This was prepared as per the general procedure mentioned above: yield 67%; mp 99−101 °C; R_f 0.27 (1:4, EtOAc in petroleum ether); $[\alpha]^{25}_D$ −152.0° (*c* 1.0, $CHCl_3$); IR (film) 3040, 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.12 (s, 1H), 6.8−7.21 (m, 20H), 7.28−7.45 (m, 8H), 7.6 (m, 2H), 7.97 (dd, J = 8.0 Hz, 1H), 8.31 (m, 2H), 9.88 (s, 1H); LCMS (APCI, *m*/*z*) 674 ($M^+ + 1$). Anal. Calcd for $C_{47}H_{35}N_3O_2$: C, 83.78; H, 5.24; N, 6.24. Found: C, 83.52; H, 5.12; N, 6.11.

***N,N′*-Bis[1′-(*S*)-isopropyl-2′,2′-diphenyl-2′-hydroxyethyl]-1,3-benzenedicarboxamide (6).** To a stirred solution of (*S*)-diphenylamino alcohol **2a** (1.92 g, 7.5 mmol) and Et_3N (2.1 mL, 15 mmol) in THF (10 mL) was added dropwise a solution of isophthalyl chloride **5** (505 mg, 2.5 mmol) in 60 mL of THF at room temperature, and the reaction mixture was stirred for 6 h. The resulting white solid was filtered and washed with water and methanol. It was dried to give 1.51 g of product (95% yield): mp 182−184 °C; $[\alpha]^{25}_D$ −100.5° (*c* 2.0, DMSO); IR (film) 3400, 3050, 1620 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 0.73 (d, J = 6.8 Hz, 6H), 0.96 (d, J = 6.8 Hz, 6H), 1.8 (m, 2H), 3.3 (s, O*H*), 5.12 (d, J = 10 Hz, 2H), 5.86 (s, 2H, N*H*), 7.0−7.38 (m, 12H), 7.4−7.6 (m, 8H), 7.68 (dd, J = 8.0, 2.0 Hz, 1H), 7.89 (dd, J = 8.0, 2.0 Hz, 2H), 7.99 (s, 1H); LCMS (APCI, *m*/*z*) 641 ($M^+ + 1$). Anal. Calcd for $C_{42}H_{44}N_2O_4$: C, 78.72; H, 6.92; N, 4.37. Found: C, 78.31; H, 6.72; N, 4.31.

1,3-Bis[5′,5′-diphenyl-4′-(*S*)-isopropyloxazolin-2′-yl] benzene (7). A solution of amido alcohol **6** (704 mg, 1.1 mmol) and methanesulfonic acid (425 μL, 6.6 mmol) in CH_2Cl_2 (20 mL) was refluxed for 6 h while keeping CaH_2 in an addition funnel for removing the water generated during the reaction. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with aqueous $NaHCO_3$, water, and brine, and dried. Solvent removal gave a solid mass that was chromatographed over silica gel to provide pure product **7** (646 mg, yield 97%): mp 177−180 °C; $[\alpha]^{25}_D$ −345.0° (*c* 1, acetone); IR (KBr) 3060, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.64 (d, J = 6.8 Hz, 6H), 1.06 (d, J = 6.8 Hz, 6H), 1.88 (m, 2H), 4.91 (d, J = 5.6 Hz, 2H), 7.2−7.6 (m, 21H), 8.26 (dd, J = 8.0, 1.6 Hz, 2H), 8.80 (s, 1H); MS (FAB, *m*/*z*) 606 ($M^+ + 1$), 605 (M^+, base peak). Anal. Calcd for $C_{42}H_{40}N_2O_2$: C, 83.39; H, 6.66; N, 4.65. Found: C, 82.98; H, 6.52; N, 4.51.

General Procedure for Enantioselective Allylic Oxidation of Cyclohexene Using PhCOOH and *t*-BuOOH. A solution of the ligand **4a** (0.06 mmol) and copper salt (CuI or CuCN, 0.05 mmol) in CH_3CN (4 mL) was stirred at room temperature for 1 h. To this red-colored solution were added benzoic acid (2.5 mmol) and cyclohexene (10 mmol). Then, 70% *t*-BuOOH in water (1 mmol) was added dropwise, and during this time the color of the mixture slowly changed from red to blue green. The reaction mixture was left at room temperature for 5 days. After the reaction was over, most of the acetonitrile was removed in vacuo, and the crude was taken in EtOAc. It was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. After drying, solvent removal, and purification over silica gel, the allylic benzoate **8** (n = 2) was obtained in a pure form.

General Procedure for Enantioselective Allylic Oxidation of Cyclohexene with *tert*-Butyl Perbenzoate in the Presence of 4a−Cu(OTf)$_2$. A solution of the ligand **4a** (0.06 mmol) and $Cu(OTf)_2$ (0.05 mmol) in an appropriate solvent was stirred at room temperature for 1 h. To this blue-green solution was added cyclohexene (10 mmol). Then, *tert*-butyl perbenzoate (1 mmol) was added dropwise under N_2 atmosphere, and the reaction mixture was left at room temperature until the reaction was complete (disappearnce of *tert*-butyl perbenzoate by TLC). Workup and purification were done as above.

General Procedure for Enantioselective Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the Presence of 4a−(CuOTf)$_2$·PhH. A solution of the ligand **4a** (36.3 mg, 0.06 mmol) and $(CuOTf)_2$·PhH (12.6 mg, 0.025 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this red solution was added an olefin (10 mmol). Then, *tert*-butyl perbenzoate (190 μL, 1 mmol) was added dropwise under N_2 atmosphere, and during this time the color of the solution changed from red to blue-green. The reaction mixture was left at room temperature until the reaction was complete (disappearnce of *tert*-butyl perbenzoate by TLC). During this time the color of the reaction mixture changed back to red. Workup and purification were done as above.

General Procedure for Enantioselective Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the

Presence of 4a−Cu(OTf)$_2$ and PhNHNH$_2$. A blue-green solution of the ligand **4a** (36 mg, 0.06 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. Phenylhydrazine (6μL, 0.06 mmol) was added, and the color of the solution changed from blue-green to red (an indication of reduction of Cu(II) to Cu(I)). After 5 min, an olefin (10 mmol) was added. Then, *tert*-butyl perbenzoate (1 mmol) was added dropwise under N_2 atmosphere and the reaction mixture was left at room temperature until the reaction was complete (disappearance of *tert*-butyl perbenzoate by TLC). Workup and purification were done as above.

General Procedure for Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the Presence of 4a−(CuOTf)$_2$·PhH and PhNHNH$_2$. A solution of the ligand **4a** (36.3 mg, 0.06 mmol) and (CuOTf)$_2$·PhH (12.6 mg, 0.025 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this red solution was added phenylhydrazine (6 μL, 0.06 mmol), and the solution was stirred for 10 min. After this, an olefin (10 mmol) was added. Then, *tert*-butyl perbenzoate (1 mmol) was added dropwise under N_2 atmosphere, and during this time the color of the solution changed from red to blue-green. The reaction mixture was left at room temperature until the reaction was complete (disappearnce of *tert*-butyl perbenzoate by TLC). During this time the color of the reaction mixture again changed to red. Workup and purification were done as above.

General Procedure for Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the Presence of 4a−(CuOTf)$_2$·PhH and 4Å Molecular Sieves. A solution of the ligand **4a** (36.3 mg, 0.06 mmol) and (CuOTf)$_2$·PhH (12.6 mg, 0.025 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this red solution were added 10−15 grains of 4 Å molecular sieves and an olefin (10 mmol). Then, *tert*-butyl perbenzoate (190 μL, 1 mmol) was added dropwise under N_2 atmosphere, and during this time the color of the solution changed from red to blue-green. The reaction mixture was left at room temperature until the reaction was complete (disappearance of *tert*-butyl perbenzoate by TLC). After completion of the reaction, the color of the reaction mixture changed back to red. Workup and purification were done as above.

General Procedure for Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the Presence of 4a−(CuOTf)$_2$·PhH, Phenylhydrazine, and 4 Å Molecular Sieves. A solution of the ligand **4a** (36.3 mg, 0.06 mmol) and (CuOTf)$_2$·PhH (12.6 mg, 0.025 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this red solution was added phenylhydrazine (0.06 mmol), and the mixture was stirred for 10 min. Then, 10−15 grains of 4 Å molecular sieves and an olefin (10 mmol) were added. Then, *tert*-butyl perbenzoate (190 μL, 1 mmol) was added dropwise under N_2 atmosphere, and during this time the color of the solution changed from red to blue-green. The reaction mixture was left at room temperature until the reaction was complete (disappearance of *tert*-butyl perbenzoate by TLC). After completion of the reaction, the color of the reaction mixture again changed back to red. Workup and purification were done as above.

General Procedure for Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate in the Presence of 4a−Cu(OTf)$_2$, Phenylhydrazine, and 4 Å Molecular Sieves. A solution of the ligand **4a** (36.3 mg, 0.06 mmol) and Cu(OTf)$_2$ (18 mg, 0.05 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this blue-green solution was added phenylhydrazine (0.06 mmol), and the mixture was stirred for 10 min. During this time, the color of the solution changed from blue-green to red (an indication for reduction of Cu(II) to Cu(I) species). Then, 10−15 grains of 4 Å molecular sieves and an olefin (10 mmol) were added. Then, *tert*-butyl perbenzoate (190 μL, 1 mmol) was added dropwise under N_2 atmosphere, and during this time the color of the solution changed from red to blue-green. The reaction mixture was left at room temperature until the reaction was complete (disappearance of *tert*-butyl perbenzoate by TLC). After completion of the reaction, the color of the reaction mixture again changed back to red. Workup and purification were done as above.

General Procedure for Hydrolysis of (*S*)-Allylic Benzoates. A solution of (*S*)-allylic benzoate (0.5 mmol) in 0.4 M KOH solution in MeOH (4 mL) was kept at 0−3 °C until the TLC showed complete disappearnce of the benzoate (10−30 h). After the reaction was over, methanol was removed in vacuo, and the crude mixture was taken in CH_2Cl_2 (15 mL). It was washed with water and brine and dried. Solvent removal and filtration through a small plug of silica gel gave pure (*S*)-allylic alcohol **9**.[10]

(*S*)-2-Cyclopentenyl-1-benzoate. It was obtained in a maximum of 60% ee. The optical purity was determined by HPLC on chiralcel OD column [hexane/2-propanol 99.95:0.05; flow rate 0.5 mL/min; t_R = 27.48 min (*S*), 34.75 min (*R*)]: $[\alpha]^{25}_D$ −116.8° (*c* 7.5, $CHCl_3$) [lit.[8d,e] (93% ee); $[\alpha]^{25}_D$ −179.0° (*c* 0.37, $CHCl_3$)].

(*S*)-2-Cyclohexenyl-1-benzoate. It was obtained in a maximum of 86% ee. The optical purity was determined by HPLC on chiralcel OD-H column [hexane/2-propanol 99.5:0.5; t_R = 17.26 min (*R*), 18.78 min (*S*)]; $[\alpha]^{25}_D$ −157.0° (*c* 2.8, $CHCl_3$) [lit.[8d,e] (66% ee); $[\alpha]^{25}_D$ −118.0° (*c* 0.45, $CHCl_3$)].

(*S*)-2-Cycloheptenyl-1-benzoate. It was obtained in a maximum of 82% ee, which was determined by HPLC on chiralcel OD-H column [heptane/2-propanol 99.9:0.1; t_R = 22.97 min (*S*), 24.85 min (*R*)]; $[\alpha]^{25}_D$ −38.2° (*c* 1, $CHCl_3$) [lit.[8d,e] (60% ee); $[\alpha]^{25}_D$ −29.0° (*c* 0.24, $CHCl_3$)].

(*S*)-2-Cyclooctenyl-1-benzoate. It was obtained in a maximum of 82% ee, which was determined by Mosher ester[23] of the corresponding alcohol: $[\alpha]^{25}_D$ +72.6° (*c* 1.25, $CHCl_3$) [lit.[8d,e] (64% ee); $[\alpha]^{25}_D$ +55.0° (*c* 0.11, $CHCl_3$)].

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