Studies on enantioselective allylic oxidation of olefins using peresters catalyzed by Cu(I)-complexes of chiral pybox ligands†

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Enantioselective allylic oxidation of olefins with various peresters, using a catalytic amount of Cu(I)-pybox complex, can be tuned to achieve high asymmetric induction (up to 98% ee) by choosing a unique combination of a ligand and a perester at room temperature. The asymmetric induction in the reaction strongly depends on the nature of the substituents attached to the aryl ring of peresters. The presence of a *gem*-diphenyl group at C-5 and secondary or tertiary alkyl substituents at the chiral center (C-4) of the oxazoline rings is crucial for high enantioselectivity. A π–π stacking model has been proposed and discussed to explain the stereochemical outcome of the reaction.

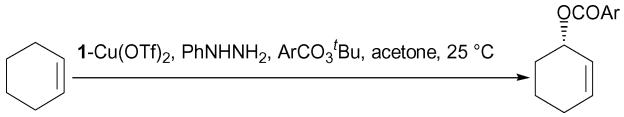
Introduction

Enantioselective allylic oxidation of olefins with peresters to chiral allylic esters catalyzed by chiral copper complexes is an important transformation in organic synthesis.[1,2] Although a reasonable progress has been made in this reaction using copper complexes of a variety of chiral bisoxazoline,[3] trisoxazoline,[4] and pybox ligands,[5] a balance of high enantioselectivity and shorter reaction time still remains a major concern. High enantioselectivity (94–99% ee) has been achieved for this transformation with the use of *tert*-butyl *p*-nitroperbenzoate as an oxidant, but only at the cost of very poor reactivity of catalysts (reaction time 8–17 days).[3f] The reactivity of catalysts prepared from the pybox ligand in our laboratory was enhanced by employing phenylhydrazine in acetone, but the enantioselectivity could not be improved beyond 93% under this condition.[5c] In this paper we demonstrate that by choosing a unique ligand–substrate–reagent combination, one can obtain, for the first time, excellent enantioselectivity (up to 98% ee) without losing the reactivity of the catalysts.

A complex of a chiral ligand, 2,6-pyridine bis(4′-isopropyl-5′,5′-diphenyloxazoline) **1a** (henceforth we will call it 'ip-pybox-diph') with $Cu(OTf)_2$ in conjunction with phenylhydrazine in acetone is known to give 91% ee in the allylic oxidation of cyclohexene with *tert*-butyl perbenzoate.[5c] The reaction was explained using a transition state model based on π-stacking between phenyl groups of the pybox ligand and the perester used in the reaction (*vide infra*). It is logical to think that electron donating and electron withdrawing groups on these phenyl substituents would affect the electron density on the π-face of the aromatic rings, giving useful information about the transition state model. It was easier to see the above effect by having different substituents on the phenyl ring of the peresters. In this paper, we describe our results in a systematic study for enantioselective allylic oxidation of olefins using different substituents on the aryl ring of a perester and the pybox ligand. The results described here would provide an insight into the π–π stacking[6] in the transition state model.

Results and discussion

Since the reaction is supposed to proceed *via* a cleavage of the O–O bond of the perester, it was logical to start with an electron withdrawing group such as nitro at the *para* position of the phenyl ring of the perester which, besides facilitating the cleavage reaction, should give high enantiomeric excess (ee) in the allylic oxidation reaction due to a better π–π stacking. Unfortunately, it was not the case. The reaction was sluggish and the ee was slightly inferior (86% ee; Table 1, entry 2). A nitro group at the *ortho* and *meta* positions of the phenyl ring gave similar results (entries 3 and 4). This led us to examine the influence of other aryl substituents of peroxyesters on enantioselectivity in the allylic oxidation reaction (Scheme 1) and the results are summarized in Table 1. Electron donating groups such as methoxy and alkyl on the phenyl ring of peresters gave similar results as phenyl (entries 5–7 and entry 11). Since the pentafluorophenyl group is known to show strong π–π interactions with phenyl groups, pentafluoro substituted phenyl peroxyester was also used in the allylic oxidation reaction. Unfortunately, the reaction was very sluggish (32 h) and the ee dropped down to 40% (entry 13).



Scheme 1 Enantioselective allylic oxidation of cyclohexene with different peresters and pybox ligands.

So far we have studied allylic oxidation of cyclohexene with the ip-pybox-diph ligand **1a** using different peresters by changing the electronic environment in the phenyl ring and have achieved a maximum of 93% ee using *tert*-butyl *p*-methoxyperbenzoate (entry 5). In order to gain more information about the reaction, a few more chiral ligands were synthesized where substituents at only two positions (C-4 and C-5) were varied (Fig. 1). A single ligand that produces allyl esters in high selectivity with a wide range of

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Table 1 Enantioselective allylic oxidation of cyclohexene with different peresters and pybox ligands[a] (Scheme 1)

Entry	L*	Ar	Time/h	Yield (%)	ee (%)[b]
1	**1a**	Phenyl	1	67	91[c]
2		*p*-Nitrophenyl	10	65	86
3		*o*-Nitrophenyl	16	43	80
4		*m*-Nitrophenyl	24	56	88
5		*p*-Methoxyphenyl	2	60	93
6		*o*-Methoxyphenyl	5	50	91
7		*m*-Methoxyphenyl	5	57	91
8		*p*-Chlorophenyl	4	72	87
9		*o*-Chlorophenyl	5	61	88
10		*m*-Chlorophenyl	6	44	89
11		4-*i*-Propylphenyl	1	65	91
12		2,6-Difluorophenyl	1	63	72[d]
13		Pentafluorophenyl	32	56	40[d]
14	**1b**	Phenyl	8	57	91
15		*p*-Nitrophenyl	15	49	87
16		*o*-Nitrophenyl	15	65	83
17		*m*-Nitrophenyl	18	63	86
18		*p*-Methoxyphenyl	5	61	92
19		*o*-Methoxyphenyl	2	71	98
20		*m*-Methoxyphenyl	3	63	90
21		*p*-Chlorophenyl	2	69	89
22		*o*-Chlorophenyl	3	68	87
23		*m*-Chlorophenyl	2	55	85
24		4-*i*-Propylphenyl	5	61	89
25		2,6-Difluorophenyl	21	66	79[d]
26		Pentafluorophenyl	56	68	52[d]
27	**1c**	Phenyl	5	77	65
28		*p*-Methoxyphenyl	4	71	67
29		*o*-Methoxyphenyl	7	56	68
30	**1d**	Phenyl	11	70	66
31		*p*-Methoxyphenyl	29	77	63
32		*o*-Methoxyphenyl	8	69	64
33	**1e**	Phenyl	72	74	56
34		*p*-Methoxyphenyl	48	64	58
35		*o*-Methoxyphenyl	55	61	59
36	**1f**	Phenyl	11	40	19
37		*p*-Methoxyphenyl	17	40	10
38		*o*-Methoxyphenyl	7	35	12
39	**1g**	Phenyl	2	59	87
40		*p*-Methoxyphenyl	2	62	89
41		*o*-Methoxyphenyl	7	58	89
42	**1h**	Phenyl	4	74	66
43		*p*-Methoxyphenyl	5	61	71
44		*o*-Methoxyphenyl	2	73	70
45	**1i**	Phenyl	18	85	65[c,e]
46		*p*-Methoxyphenyl	18	73	70
47		*o*-Methoxyphenyl	20	67	70

[a] 5 mol% of the chiral ligand was used. [b] Determined by chiral HPLC columns. [c] See ref. 5*c*. [d] Determined by converting into benzoyl ester. [e] Pfaltz *et al.* have reported 71% ee (ref. 3*a*) under other conditions (**1i**-CuOTf, MeCN, 3 days).

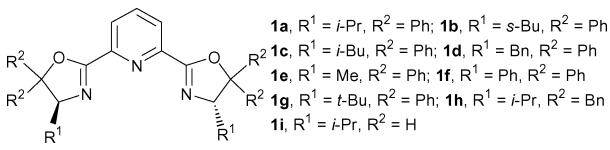


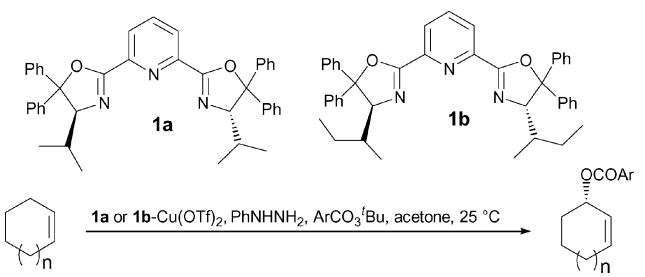
Fig. 1 Chiral pybox ligands.

substrates will most likely never be found. The metal–ligand combination will continue to be fine-tuned for each substrate for both reactivity and selectivity.[1a] This study is important as small changes in conformational, steric, and electronic properties of chiral ligands can often lead to dramatic variation in the enantioselectivity. The ligands **1a–1g** had *gem*-diphenyl groups at the C-5 positions, but the variation was made only at the chiral center, C-4 by having different substituents such as *i*-Pr (**1a**), *s*-Bu (**1b**), *i*-Bu (**1c**), Bn (**1d**), Me (**1e**), Ph (**1f**), *t*-Bu (**1g**). A copper complex of these ligands was tested for the allylic oxidation reaction of cyclohexene under the above conditions using selected peresters. The results are summarized in Table 1. It was observed that the behavior of the ligands, sb-pybox-diph (**1b**) and tb-pybox-diph (**1g**) was similar to that of ip-pybox-diph (**1a**). The ligand **1b**, that had an *s*-butyl group at the chiral center, gave excellent enantioselectivity (98% ee) in the reaction when *tert*-butyl *o*-methoxyperbenzoate was used (entry 19). It was observed that when a bulkier substituent such as a *tert*-butyl group at the chiral center was used as in the ligand **1g**, the enantioselectivity dropped down to 89% (entries 40 and 41). Copper complexes of ligands **1c**, **1d**, and **1e** having other alkyl substituents at the chiral center gave moderate enantioselectivity (entries 27–35). The ligand **1f** having a phenyl group at the chiral center showed poor catalytic activity in the allylic oxidation of cyclohexene (entries 36–38).

In order to find out the role of the *gem*-diphenyl group of the ligands on enantioselectivity, we studied enantioselective allylic oxidation with ligands ip-pybox-bn (**1h**) and ip-pybox (**1i**) where the phenyl groups at C-5 of the oxazoline ring were replaced by benzyl and hydrogen, respectively. From the results in Table 1 (entries 42–47), it was observed that the *gem*-diphenyl group is crucial for getting high enantioselectivity in the allylic oxidation reaction.

Based on the results in Table 1, ligands **1a** and **1b** were chosen for further study of the above reaction on other olefins and the results are summarized in Table 2. It was noticed that an optimal combi-

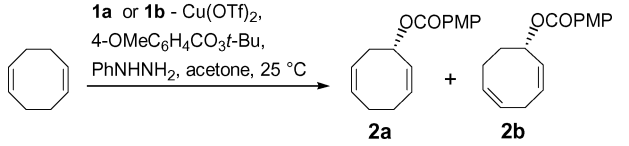
Table 2 Enantioselective allylic oxidation of cyclic olefins with different peresters using ligands **1a** and **1b**[a]



Entry	Olefin	Ar	Time/h		Yield (%)		ee (%)[b]	
			1a	**1b**	**1a**	**1b**	**1a**	**1b**
1		Phenyl	3	20	76	75	70[c]	65
2		*p*-Nitrophenyl	13	6	47	42	62	58
3		*p*-Methoxyphenyl	3	3	55	57	77	72
4		*o*-Methoxyphenyl	4	4	71	74	80	80
5		Phenyl	6	—	47	—	86[c]	—
6		*p*-Nitrophenyl	64	72	36	40	85	90
7		*p*-Methoxyphenyl	96	18	45	45	91	94
8		*o*-Methoxyphenyl	13	16	42	39	91	87
9		Phenyl	6	24	34	34	94[c]	95
10		*p*-Nitrophenyl	36	72	28	39	91	88
11		*p*-Methoxyphenyl	21	19	31	42	96	90
12		*o*-Methoxyphenyl	33	48	38	43	91	92
13		Phenyl	120	—	31	—	80[c]	—
14		*p*-Nitrophenyl	48	72	42	45	66	65
15		*p*-Methoxyphenyl	29	15	49	50	95	96
16		*o*-Methoxyphenyl	10	16	62	52	86	82

[a] 5 mol% of the chiral ligand was used. [b] Determined by HPLC chiral columns. [c] See ref. 5*c*.

Table 3 Enantioselective allylic oxidation of 1,5-cyclooctadine using ligands **1a** and **1b**[a]



			Ratio			ee (%)[b]	
Entry	L*	Time/h	**2a**	**2b**	Yield (%)	**2a**	**2b**
1	**1a**	12	3	2	68	93	94
2	**1b**	5	1	1	70	93	93

[a] 5 mol% of the chiral ligand was used. [b] Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column.

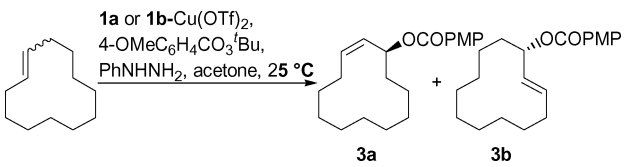
nation of chiral ligands and peresters was desired in order to get high enantioselectivity. In the case of cyclopentene, a combination of either **1a** or **1b** and *tert*-butyl *o*-methoxyperbenzoate was more compatible (80% ee; entry 4). For cycloheptene, a combination of **1b** and *tert*-butyl *p*-methoxyperbenzoate was quite suitable (94% ee) in the allylic oxidation reaction (entry 7). Cyclooctene gave the highest enantioselectivity (96% ee) with a combination of **1a** and *tert*-butyl *p*-methoxyperbenzoate (entry 11). Similarly, high enantioselectivity (95–96% ee) was obtained in the allylic oxidation of 1,3-cyclooctadiene with a combination of the chiral ligand **1a** or **1b** and *tert*-butyl *p*-methoxyperbenzoate (entry 15).[7]

The allylic oxidation of 1,5-cyclooctadiene with *tert*-butyl-*p*-methoxyperbenzoate, under the above conditions, using catalyst **1a** and **1b** gave a mixture of products **2a** and **2b**. The optical purity of these products was 93–94% (Table 3).[7]

The allylic oxidation of *cis* and *trans* mixture of Cyclododecene was also studied with the catalyst **1a** and **1b** using *tert*-butyl-*p*-methoxyperbenzoate and a mixture of *cis* (**3a**) and *trans* (**3b**) allylic oxidation products was obtained. Under the optimal condition, **3b** was obtained with maximum of 57% ee using the chiral ligand **1b** (Table 4).[7]

Although high enantioselectivities were obtained for most of the cyclic olefins, the reaction was not effective for acyclic olefins. As summarized in Table 5, 1-octene under optimal conditions with *tert*-butyl-*p*-methoxyperbenzoate gave an inseparable mixture of **4a** and **4b** with poor enantioselectivity (31% ee).

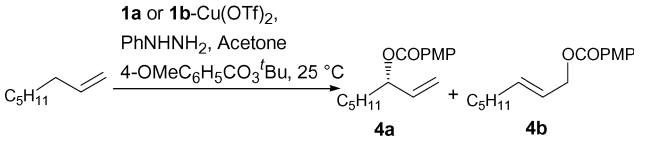
Table 4 Enantioselective allylic oxidation of a *cis* and *trans* mixture of cyclododecene using ligands **1a** and **1b**[a]



			Yield (%)		ee (%)[b]	
Entry	L*	Time/h	**3a**	**3b**	**3a**	**3b**
1	**1a**	12	13	37	17	56
2	**1b**	5	14	40	06	57

[a] 5 mol% of the chiral ligand was used. [b] Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column.

Table 5 Enantioselective allylic oxidation of 1-octene using ligands **1a** and **1b**[a]



			Ratio			ee (%)[b]
Entry	L*	Time/h	**4a**	**4b**	Yield (%)	**4a**
1	**1a**	39	7	3	39	31
2	**1b**	39	6	4	35	28

[a] 5 mol% of the chiral ligand was used. [b] Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column.

The above results have been rationalized by a transition state model shown in Fig. 2.[1a,5a] The initial attack of copper(II) benzoate on the allylic radical can produce two diastereomeric allyl adducts. In a favorable transition state assembly, copper benzoate may attain an orientation to provide a π-stacking of the two aromatic rings. Since the distance between both the rings is approximately 3.5 Å,[5a] there might be some attractive interaction which would stabilize the drawn conformation. In this case, the allylic radical will approach the Cu species from the less hindered side as shown. The benzoate oxygen attacks the allylic carbon, which is electrophilic in nature due to coordination of the incipient double bond with the copper species leading to the (*S*)-enantiomer as the major product. If the olefin approaches the Cu(II) benzoate ester in an alternative way (unfavored), severe non-bonding interactions of the aryl group and the olefin with substituents at the chiral centers make it difficult. Some support for our assumption of π-stacking of the two aromatic rings in the transition state comes from the results of chiral ligands **1h** and **1i**, which lacked *gem*-diphenyl rings. We observed that either by increasing the distance of phenyl ring by one carbon or removing it from the C-5 carbon of the oxazoline ring, π-stacking gets disturbed and hence enantioselectivity drops down (Table 1, entries 42–47).

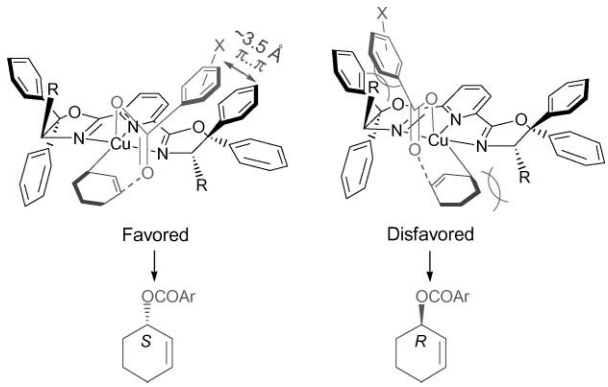


Fig. 2 Transition state models.

If the π–π stacking is involved in the reaction, we should have got better results when X was nitro or halo. But, it was not the case. In fact, we got better results when X was a methoxy group. It was also surprising that pentafluoro groups on the phenyl ring gave very poor results. These anomalies can be rationalized using the same

models (Fig. 2). When X is such a group which provides better π–π stacking, it can also move to some extent towards the left side and show attractive interaction with the phenyl group on the left hand side of the ligand. This attractive interaction outweighs the steric repulsion caused by the alkyl group on the chiral carbon. Under this arrangement, the 'O' of the peroxy group would attack the other face of the olefin giving rise to the (*R*)-enantiomer, resulting in lowering of the ee of the (*S*)-enantiomer. This is the reason the pentafluoro substituted phenyl ring is not effective in giving a high ee in the reaction. Electron donating groups such as alkyl and methoxy behave like a simple phenyl group that provides optimum stacking which is not strong enough to outweigh steric repulsion with the alkyl group at the chiral center. This is the reason it orients only in the right hand side giving products in high ee's. The model also fits well for the effect of substituents on chiral centers. When R is *i*-Pr (**1a**), *s*-Bu (**1b**), and *t*-Bu (**1g**), we get high enantioselectivity. However, substituents such as *i*-Bu (**1c**), Bn (**1d**), and Me (**1e**), gave poor results because the steric repulsion shown in Fig. 2 is not enough to outweigh the π-stacking. It is very surprising that the ligands having R as a phenyl group gave very poor enantioselectivity (<20% ee). This could be because of the planarity of the ring, it orients in a manner to provide less steric repulsion in the transition state.

Conclusions

We have investigated enantioselective allylic oxidation of a variety of cyclic olefins with copper complexes of different pybox ligands with various peresters. We have shown that high enantioselectivity (98% ee for cyclohexene; 96% ee for cyclooctene and 1,3-cyclooctadiene; 94% ee for cycloheptene and 1,5-cyclooctadiene; 80% ee for cyclopentene) can be achieved in the allylic oxidation of cyclic olefins to allylic esters by choosing a unique combination of a chiral ligand and a perester at room temperature. The presence of a *gem*-diphenyl group at C-5 and a secondary or tertiary alkyl substituent at the chiral center at C-4 of the oxazoline rings is crucial for high enantioselectivity. A stereochemical outcome of the reaction is also discussed with the help of a transition state model.

Experimental

General methods

Chemicals were purchased and used without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer. All chemical shifts are quoted on the δ scale, with TMS as internal standard, and coupling constants are reported in Hz. Routine monitoring of reactions was performed by TLC, using 0.2 mm Kieselgel 60 F_{254} precoated aluminium sheets, commercially available from Merck. Visualization was done by fluorescence quenching at 254 nm, or by exposure to iodine vapor. All the column chromatographic separations were done by using silica gel (Acme's, 60–120 mesh). HPLC was done on a Daicel chiral column having 0.46 cm internal diameter × 25 cm length. Petroleum ether used was of boiling range 60–80 °C. Reactions that needed anhydrous conditions were run under an atmosphere of nitrogen or argon using flame-dried glassware. The organic extracts were dried over *anhydrous* sodium sulfate. Evaporations of solvents were performed at reduced pressure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from CaH_2 and acetone was distilled from anhydrous potassium carbonate under nitrogen.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-*sec*-butyloxazolin-2′-yl] pyridine (1b). This was prepared as per the general procedure[5c] from pyridine dicarboxylic acid and (*S*)-isoleucine to afford the product **1b** as a white amorphous solid; yield 70%; mp 77–79 °C; R_f 0.52 (1 : 2, EtOAc in petroleum ether); $[\alpha]_D^{25}$ −337.3 (*c* 1.2, $CHCl_3$); ν_{max}/cm^{-1} (solid) 3060, 3028, 2961, 1656, 1454, 1372, 1129, 956 and 755; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.48 (6H, t, $J = 7.3$ Hz, 2 × CH_2CH_3), 1.07 (6H, d, $J = 6.6$ Hz, 2 × $CHCH_3$), 1.23–1.30 (4H, m, 2 × CH_3CH_2CH), 1.56–1.64 (2H, m, 2 × CH_3CHCH_2), 4.94 (2H, d, $J = 4.4$ Hz, 2 × NCHCH), 7.21–7.38 (16H, m, Ar), 7.60 (4H, d, $J = 7.6$ Hz, Ar), 7.96 (1H, t, $J = 7.8$ Hz, Ar), 8.21 (2H, d, $J = 7.8$ Hz, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 11.4, 18.0, 23.9, 36.7, 80.4, 93.6, 125.4, 126.2, 126.9, 127.2, 127.6, 127.8, 128.3, 137.5, 140.3, 145.1, 146.9, 160.2. Anal. calcd for $C_{43}H_{43}N_3O_2$: C, 81.48; H, 6.84; N, 6.63. Found: C, 81.23; H, 7.02; N, 6.70%.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-isobutyloxazolin-2′-yl] pyridine (1c). This was prepared as per our general procedure[5c] from pyridine dicarboxylic acid and (*S*)-leucine to afford the product **1c** as a white amorphous solid; yield 72%; mp 80–82 °C; R_f 0.61 (1 : 2, EtOAc in petroleum ether); $[\alpha]_D^{25}$ −372.7 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} (solid) 3060, 3030, 2955, 1658, 1455, 1373, 1131, 966 and 751; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.86 (6H, d, $J = 5.6$ Hz, 2 × $CHCH_3$), 1.01 (6H, d, $J = 5.6$ Hz, 2 × $CHCH_3$), 1.04–1.16 (4H, m, 2 × $CHCH_2CH$), 1.99–2.09 (2H, m, 2 × CH_3CHCH_3), 5.03 (2H, dd, $J = 11.2$ and 3.4 Hz, $NCHCH_2$), 7.18–7.34 (12H, m, Ar), 7.39 (4H, t, $J = 7.6$ Hz, Ar), 7.57 (4H, d, $J = 8.0$ Hz, Ar), 7.95 (1H, t, $J = 7.6$ Hz, Ar), 8.21 (2H, dd, $J = 7.8$ and 1.3 Hz, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 21.6, 23.9, 25.3, 43.1, 73.4, 93.6, 125.6, 126.4, 126.8, 127.4, 127.8, 127.9, 128.4, 137.6, 140.6, 144.2, 147.3, 160.5. Anal. calcd for $C_{43}H_{43}N_3O_2$: C, 81.48; H, 6.84; N, 6.63. Found: C, 81.63; H, 6.99; N, 6.75%.

2,6-Bis[5′,5′-diphenyl-4′-(*S*)-*tert*-butyloxazolin-2′-yl] pyridine (1g). This was prepared as per our general procedure[5c] from pyridine dicarboxylic acid and (*S*)-*tert*-leucine to afford the product **1g** as a white amorphous solid; yield 80%; mp 221–223 °C; R_f 0.58 (1 : 2, EtOAc in petroleum ether); $[\alpha]_D^{25}$ −347.2 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} (solid) 3057, 3027, 2944, 1656, 1566, 1446, 1226, 1158, 964 and 748; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.90 (18H, s, 6 × CCH_3), 4.90 (2H, s, NCHC), 7.25 (9H, m, Ar), 7.36 (3H, t, $J = 7.3$ Hz, Ar), 7.40–7.43 (4H, m, Ar), 7.69 (4H, d, $J = 7.3$ Hz, Ar), 7.95 (1H, t, $J = 7.8$ Hz, Ar), 8.23 (2H, d, $J = 7.8$ Hz, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 28.0, 35.5, 83.1, 93.9, 125.5, 126.5, 127.2, 127.5, 127.8, 128.2, 128.7, 137.5, 140.0, 146.1, 147.0, 160.2; Anal. calcd for $C_{43}H_{43}N_3O_2$: C, 81.48; H, 6.84; N, 6.63. Found: C, 81.55; H, 6.96; N, 6.55%.

2,6-Bis[5′,5′-dibenzyl-4′-(*S*)-isopropyloxazolin-2′-yl] pyridine (1h). This was prepared as per our general procedure[5c] from pyridine dicarboxylic acid and (*S*)-valine to afford the product **1h** as a white amorphous solid; yield 85%; mp 80–82 °C; R_f 0.45 (1 : 2, EtOAc in petroleum ether); $[\alpha]_D^{25}$ +227.9 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} (solid) 3060, 3026, 2922, 1664, 1571, 1490, 1443, 1168, 1138, 979 and 759; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.19 (6H, d, $J =$

6.6 Hz, 2 × CHCH_3), 1.26 (6H, d, J = 6.6 Hz, 2 × CHCH_3), 2.13 (2H, m, 2 × CH_3CHCH_3), 2.77 (2H, d, J = 14.6 Hz, CH_2Ph), 2.88 (2H, d, J = 14.1 Hz, CH_2Ph), 3.32 (4H, m, 2 × CH_2Ph), 3.66 (2H, d, J = 10 Hz, NCHCH), 7.10–7.20 (8H, m, Ar), 7.22–7.35 (12H, m, Ar), 7.92–8.02 (3H, m, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 21.2, 21.8, 28.2, 39.7, 42.2, 76.3, 90.7, 124.9, 126.5, 128.0, 128.2, 131.0, 131.1, 136.2, 136.6, 137.5, 147.2, 159.6; Anal. calcd for $C_{45}H_{47}N_3O_2$: C, 81.66; H, 7.16; N, 6.35. Found: C, 81.79; H, 7.05; N, 6.41%.

General procedure for the synthesis of peresters

Caution! Peroxy compounds present a serious detonation hazard. While peresters are not nearly as reactive as peracids, use of a teflon coated spatula for solid material is recommended.

Ethyl chloroformate (0.4 mL, 5 mmol) was added dropwise to a solution of an acid (5 mmol) and triethylamine (0.7 mL, 5 mmol) in CH_2Cl_2 (15 mL) at 0 °C under N_2 atmosphere. After stirring the reaction mixture for 30 min, triethylamine (0.7 mL, 5 mmol) was again added. Then, *tert*-butyl hydroperoxide (5–6 M in nonane, 1.1 mL, 6 mmol) was added dropwise to the solution while maintaining the same temperature. The reaction was warmed to room temperature and then stirred for 12 h. It was diluted with some CH_2Cl_2 and washed with aqueous $NaHCO_3$, water, and brine. The organic layer was dried (Na_2SO_4) and the solvent was evaporated on a rotary evaporator to get a crude yellow liquid, which was purified over silica gel by column chromatography (65–85% yield).

***tert*-Butyl 2,6-difluoroperbenzoate.** This compound was prepared following the general procedure described above using 2,6-difluorobenzoyl chloride; yield 80%; ν_{max}/cm^{-1} (film) 3105, 3071, 2984, 1775, 1469, 1242, 1080, 1010, 795; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.40 (9H, s, 3 × CCH_3), 7.00 (2H, t, J = 8.6 Hz, Ar), 7.46–7.50 (1H, m, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.8, 84.4, 111.8, 112.0, 133.6, 159.0, 161.6.

***tert*-Butyl pentafluoroperbenzoate.** This compound was prepared following the general procedure described above using 2,3,4,5,6-pentafluorobenzoyl chloride; yield 82%; ν_{max}/cm^{-1} (film) 2987, 1778, 1502, 1323, 1178, 1000, 774; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.40 (9H, s, 3 × CCH_3); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.8, 85.1, 156.5; δ_F (376 MHz; $CDCl_3$; Me_4Si) −156.82 to −156.93 (2F, m), −166.95 to −167.1 (1F, m), −179.79 to −179.45 (2F, m).

General procedure for enantioselective allylic oxidation of olefins with peresters in the presence of $PhNHNH_2$ using a complex of chiral ligands and $Cu(OTf)_2$

A solution of a chiral ligand (0.06 mmol) and $Cu(OTf)_2$ (18.1 mg, 0.05 mmol) in acetone (4 mL) was stirred at room temperature for 1 h. To this colored (green for **1a**, **1b**, **1d**, **1f**, **1g** and **1h**; blue for **1c**, **1e** and **1i**) solution was added phenylhydrazine (6 μL, 0.06 mmol), and the mixture was stirred for 30 min. During this time, the color of the solution changed to dark brown, giving an indication for the reduction of Cu(II) to Cu(I) species. Then, an olefin (10 mmol) was added followed by a dropwise addition of a perester (1 mmol) under N_2 atmosphere. After few minutes, the color of the solution changed to green. The reaction mixture was left at room temperature until the reaction was complete (disappearance of the perester by TLC) during which time the color of the reaction mixture again changed to dark brown. After the reaction was over, the solvent was removed *in vacuo* and the crude product was purified by column chromatography using silica gel.

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7 The absolute stereochemistry is temporarily assigned based on other cyclic olefins.

