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ASYMMETRIC CYCLIZATION REACTIONS OF *N*-BENZOYL-α-DEHYDROARYLALANINE ALKYL ESTERS VIA PHOTOINDUCED ELECTRON TRANSFER FROM ACHIRAL AND CHIRAL AMINES

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Abstract– Irradiation of the title compounds [(*Z*)-**1**] having (*S*)-(+)-*sec*-butyl, (–)-menthyl, and related chiral auxiliaries in methanol and 1,2-dichloroethane containing 2-(diethylamino)ethanol afforded chiral auxiliary-substituted (4*S*,5*S*)-, (4*R*,5*R*)-, (4*R*,5*S*)-, and (4*S*,5*R*)-4,5-dihydrooxazole derivatives (**2**) along with (*E*)-**1**. It was found that the photoinduced electron transfer-initiated cyclization of (*Z*)-**1** gives either of the two diastereomers for *cis*-**2** and *trans*-**2** in diastereomeric excess whose value varies from 8 to 81% depending on the property of solvent as well as on the steric bulkiness of chiral auxiliary. On the other hand, the asymmetric photocyclization of chiral auxiliary-unsubstituted (*Z*)-**1** in 1,2-dichloroethane proceeded cleanly in the presence of the chiral amine, (*S*)-(–)-1-methylpyrrolidine-2-methanol, to give (4*R*,5*R*)-**2** and (4*R*,5*S*)-**2** in enantiomeric excess of 17–38% and 20–33%, respectively, depending on the steric bulkiness of the aryl substituent. A mechanistic consideration of these diastereoselective and enantioselective photocyclization reactions enabled us to propose major factors controlling the extent of asymmetric photoinduction.

INTRODUCTION

Excited state chemistry for organic molecules has continued to contribute to the development of novel synthetic methods that enable the construction of pharmaceutically useful hetero atom-containing ring systems.[1] While sophisticated organic photochemistry has also contributed to the enhancement of enantio- and diastereoselectivities in many asymmetric reactions,[2–5] there have been only a few enantio- and diastereodifferentiating photochemical reactions of synthetic utilities, particularly in liquid phase.

Since many photoinduced electron transfer (PET) reactions have been found to produce useful heterocyclic compounds with high efficiencies,[6] we attempted to develop a new type of diastereoselective cyclization of *N*-benzoyl-α-dehydronaphthylalaninamides carrying some chiral auxiliaries, proceeding through PET. This attempt made it possible to find PET-initiated asymmetric cyclization reactions eventually affording the corresponding 3,4-dihydrobenzo[*f*]quinolinone derivatives in high diastereomeric excesses (de).[7] In addition, detailed analysis of the effects of tertiary amine, solvent, chiral auxiliary, and temperature on the magnitude of de demonstrated that diastereoselectivity in this photocyclization strongly depended on the steric and electronic factors of the chiral auxiliary introduced.

On the other hand, it was quite recently found that the PET reaction of *N*-benzoyl-α-dehydroarylalanine alkyl ester derivatives selectively afforded substituted 4,5-dihydrooxazoles even in less polar solvents.[8] Because these products possess two asymmetric carbons in a dihydrooxazole ring, it is possible to develop a novel type of the PET-initiated asymmetric cyclization of *N*-acyl-α-dehydroarylalanine alkyl esters by introducing a chiral auxiliary into the ester moiety. In addition, a mechanistic consideration of the PET reaction of α-dehydroarylalanine alkyl esters strongly suggested that triethylamine (TEA) as an electron donor exists in the vicinity of key reaction intermediates during their cyclization processes eventually affording the dihydrooxazole derivatives. It is, thus, very likely that alkyl ester derivatives of *N*-acyl-α-dehydroamino acids undergo enantioselective photocyclization reactions in the presence of chiral amines.

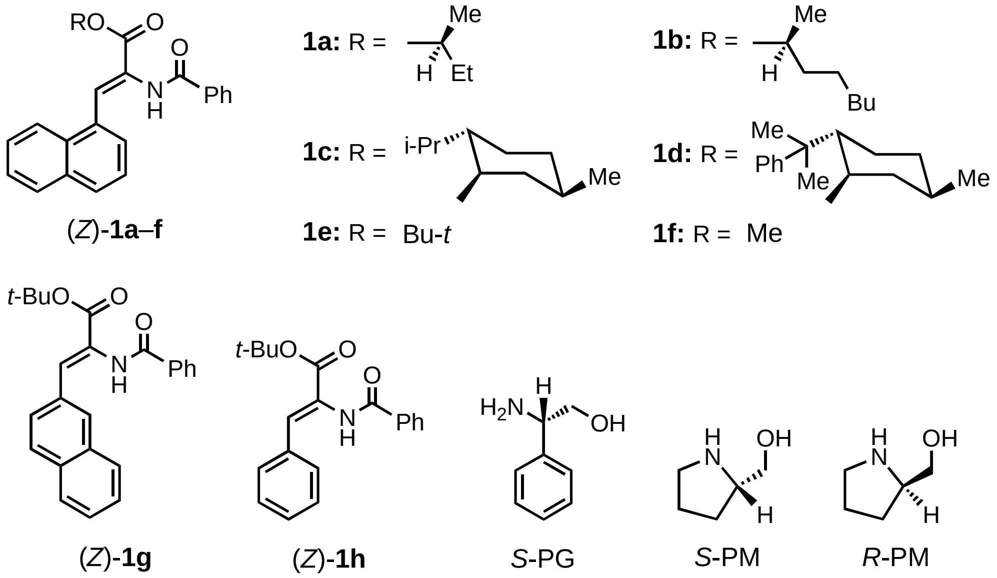


Chart 1

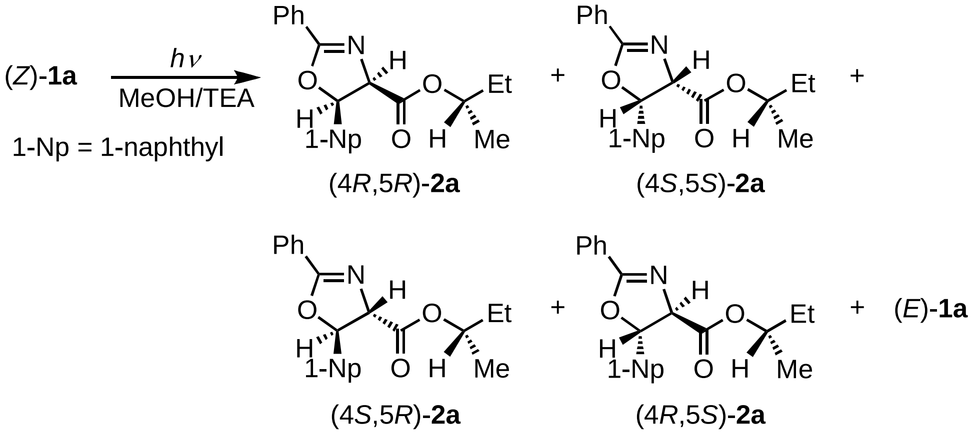
To expand our study on the PET-initiated asymmetric cyclization of *N*-acyl-α-dehydronaphthylalaninamides, we synthesized chiral auxiliary-substituted (*Z*)-*N*-benzoyl-α-dehydro(1-naphthyl)alanine alkyl esters [(*Z*)-**1a**–**d**, Chart 1] and investigated the effects of substituent, solvent, tertiary amine, and temperature on the magnitude of de, hoping to shed much light on the mechanism of asymmetric photoinduction. Since a comprehensive analysis of diastereoselective and enantioselective photocyclization reactions may elucidate not only the major factors governing de but also the mechanism of these asymmetric photoreactions, we explored further the asymmetric photoreactions of chiral auxiliary-unsubstituted (*Z*)-*N*-benzoyl-α-dehydroarylalanine alkyl esters [(*Z*)-**1e**–**h**] in the presence of (*S*)-(+)-2-phenylglycinol (*S*-PG), (*S*)-(+)-pyrrolidine-2-methanol (*S*-PM), (*R*)-(–)-pyrrolidine-2-methanol (*R*-PM) or (*S*)-(–)-1-methylpyrrolidine-2-methanol (*S*-MPM) (Chart 1).

RESULTS AND DISCUSSION

Absolute configuration and composition analysis

After a nitrogen-saturated methanol solution of (*Z*)-**1a** (4.0×10^{-3} mol dm^{-3}, 500 mL) containing TEA

(0.10 mol dm^{-3}) had been irradiated with Pyrex-filtered light (>280 nm) from a 400 W high-pressure Hg lamp for 5 h at room temperature (conversion, ≈100%), the reaction mixture obtained was subjected to preparative thin layer chromatography on silica gel. This chromatography enabled us to isolate *cis*- and *trans*-4-[(*S*)-*sec*-butoxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazoles as their diastereomeric mixtures [*cis*-**2a**: (4*R*,5*R*)-**2a** + (4*S*,5*S*)-**2a**, 78%; *trans*-**2a**: (4*S*,5*R*)-**2a** + (4*R*,5*S*)-**2a**, 8% yield] having the vicinal coupling constants ($J_{4,5}$) of 10.3 Hz and 6.3 Hz in DMSO-d_6, respectively, as shown in Scheme 1. The (*E*)-isomer of **1a** was isolated independently from the reaction mixture, which had been irradiated for 0.5 h under the same conditions (conversion, 20%), by similar workup (Scheme 1). In addition, we were able to separate and isolate four diastereomers derived from *cis*-**2a** and *trans*-**2a** by a combination of preparative thin layer, reversed phase, and normal phase chromatographic techniques. However, any attempts were not fruitful to grow single crystals of these diastereomers. On the other hand, in addition to the previous finding that TEA serves as an electron transfer catalyst for the PET-initiated cyclization reaction of *N*-acetyl-α-dehydronaphthylalaninamides,[6c] negligible formation of the TEA-derived byproducts substantiates the catalytic function of this amine in the above reaction.



Scheme 1

To determine the absolute configuration of four diastereomers isolated, a nitrogen-saturated 1,2-dichloroethane solution of (*Z*)-**1e** (4.0×10^{-3} mol dm^{-3}, 500 mL) containing TEA (0.10 mol dm^{-3}) was irradiated under the same conditions as above for 5 h at room temperature (conversion, ≈100%). The reaction mixture obtained was subjected to preparative thin layer chromatography on silica gel, which afforded *cis*-**2e** and *trans*-**2e** in 56% and 28% yields, respectively. The former *cis*-isomer isolated as an enantiomeric mixture was separated into (4*S*,5*S*)-**2e** and (4*R*,5*R*)-**2e** (showing intense circular dichroism (CD) bands, the signs of which were reversed at 220 nm) by using a HPLC chiral column. Because the observed CD bands are attributable to those of the naphthalene ring and, hence, their sign at 220 nm reflects the absolute configuration of each enantiomer at 5-position on the dihydrooxazole ring, it is possible to unambiguously determine the configuration of a given diastereomer at this position from the sign of its CD band at 220 nm. A single crystal showing the CD band of positive sign ($[\theta]_{220}$ = +1390 deg cm^2 dmol^{-1}) was successfully grown and its structure was analyzed. The ORTEP drawing depicted in Figure 1 established that (4*S*,5*S*)-**2a**,**e** and (4*R*,5*S*)-**2a**,**e** exhibit CD bands of positive sign and those of negative sign are attributed to (4*R*,5*R*)-**2a**,**e** and (4*S*,5*R*)-**2a**,**e**. On the basis of these configurational assignments and diastereomeric composition ratios for *cis*-**2a** (^{1}H NMR spectral analysis) and *trans*-**2a** (^{1}H NMR spectral and/or HPLC analysis), we were able to show that the PET-initiated cyclization of (*Z*)-**1a** affords (4*R*,5*R*)-**2a** (de = 10%) and (4*S*,5*R*)-**2a** (de = 13%) in excess under given conditions. To examine whether the amine-catalyzed isomerization of these two diastereomers takes place, their methanol solutions containing TEA (0.10 mol dm^{-3}) were allowed to stand for 3–4 h at room temperature. ^{1}H NMR spectral analysis revealed only a very little progress of the isomerization (<5%). The de values for *cis*-**2b**–**d** and *trans*-**2b**–**d** were estimated according to the same spectroscopic and chromatographic techniques as above.

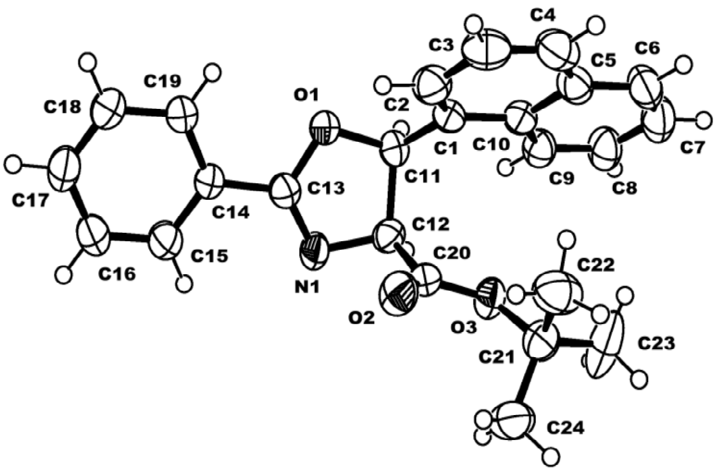
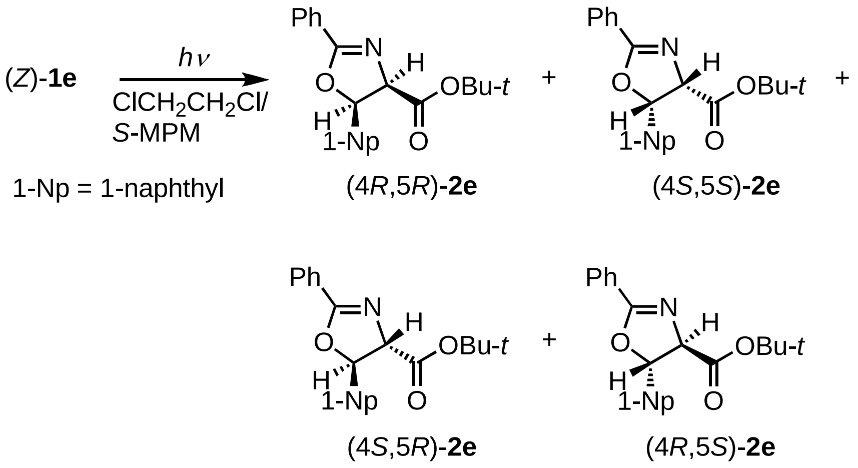


Figure 1. ORTEP drawing of (4*S*,5*S*)-**2e**



Scheme 2

On the other hand, nitrogen-saturated 1,2-dichloroethane solutions of (*Z*)-**1e** (4.0×10^{-3} mol dm^{-3}, 10 mL) containing *S*-MPM (0.10 mol dm^{-3}) were irradiated in parallel for 6 h at room temperature and the resulting solutions were subjected to normal phase HPLC analysis after the chiral amine had been removed by treatment with hydrochloric acid. For the purpose of determining the retention times of HPLC signals and enantiomeric excesses (ee) for the **2e**-derived enantiomers, (4*S*,5*S*)-**2e** ($[\theta]_{220}$ = +1390 deg cm^{2} dmol^{-1}) and (4*R*,5*R*)-**2e** ($[\theta]_{220}$ = –1120 deg cm^{2} dmol^{-1}) were isomerized into (4*R*,5*S*)-**2e** and (4*S*,5*R*)-**2e**, respectively, in methanol containing TEA. The enantiomeric mixtures obtained were subjected to normal phase HPLC analysis, from which the retention times of the (4*S*,5*S*)-, (4*R*,5*R*)-, (4*R*,5*S*)-, and (4*S*,5*R*)-enantiomers were estimated to be 15.4, 12.5, 7.1 and 8.8 min, respectively.[8] Based on the area ratios of HPLC signals for the *cis*-**2e**- and *trans*-**2e**-derived enantiomers, the asymmetric cyclization of (*Z*)-**1e** proceeding by the PET mechanism was found to produce (4*R*,5*R*)-**2e** (ee = 19%) and (4*R*,5*S*)-**2e** (33%) in excess (Scheme 2). Enantiomeric composition analysis of *cis*-**2f**–**h** and *trans*-**2f**–**h** was made in the same manner as described above.

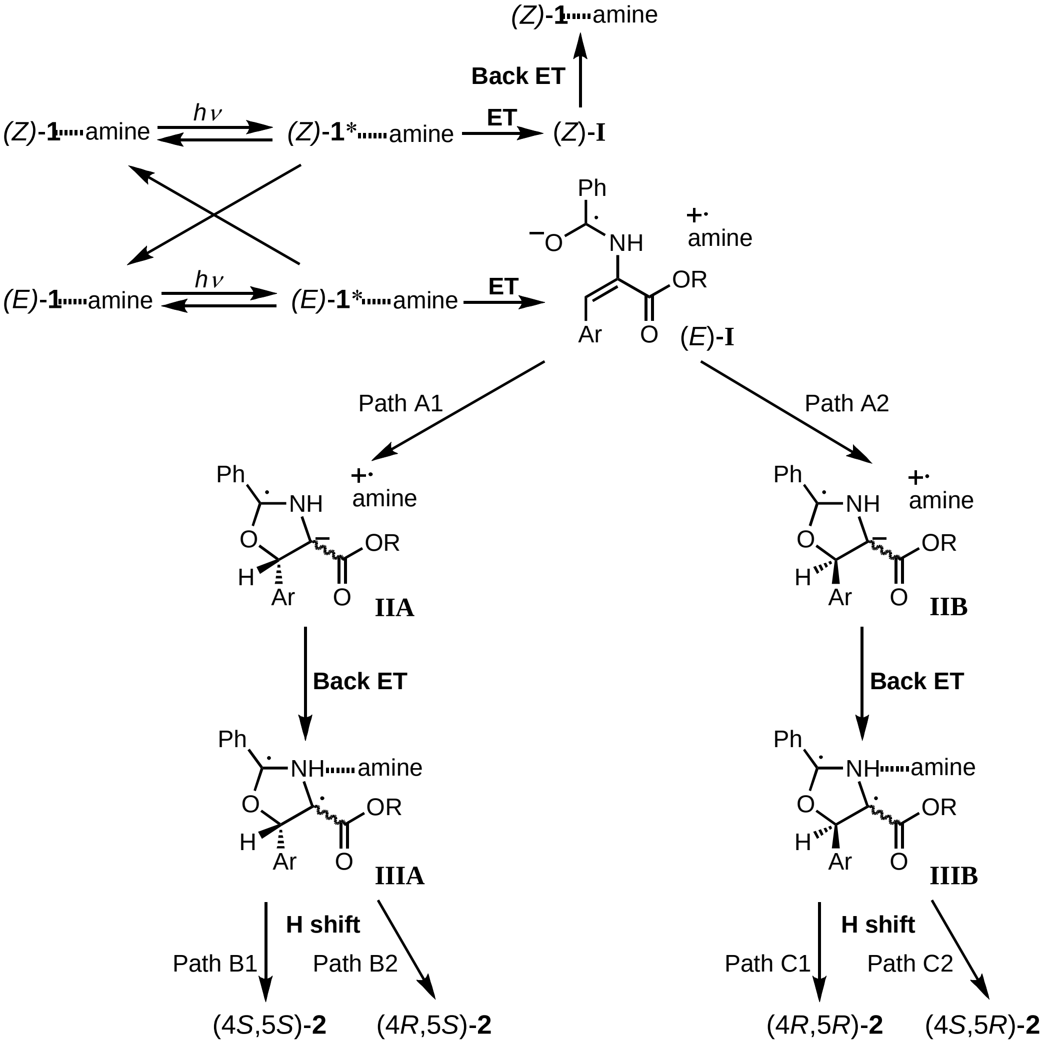
Diastereoselective photocyclization

Table 1. Substituent, solvent, and tertiary amine effects on the photoreactivity of **1** and the de for *cis*-**2** and *trans*-**2**, obtained by the 3 h irradiation of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}) in the presence of TEA or DEAE (0.10 mol dm^{-3}) at room temperature

			Composition and de (%)							
					cis-**2**			*trans*-**2**		
Compound	Solvent	Amine	(*Z*)-**1**	(*E*)-**1**	(4*R*,5*R*)-**2**	(4*S*,5*S*)-**2**	de	(4*S*,5*R*)-**2**	(4*R*,5*S*)-**2**	de
(*Z*)-**1a**	MeOH	TEA	9.3	21.8	29.3	24.0	10	8.8	6.8	13
(*Z*)-**1a**	$ClCH_2CH_2Cl$	TEA	2.5	3.4	26.2	29.1	5	23.1	15.7	19
(*Z*)-**1a**	MeOH	DEAE	10.2	22.8	8.9	6.2	18	30.7	21.2	18
(*Z*)-**1a**	$ClCH_2CH_2Cl$	DEAE	8.3	18.0	18.3	20.6	6	19.8	15.0	14
(*Z*)-**1b**	MeOH	DEAE	12.2	20.5	30.9	24.4	12	7.0	5.0	17
(*Z*)-**1b**	$ClCH_2CH_2Cl$	DEAE	7.6	12.5	24.9	29.0	8	14.0	12.0	8
(*Z*)-**1c**	MeOH	DEAE	11.0	30.5	19.3	28.9	20	3.4	6.9	34
(*Z*)-**1c**	$ClCH_2CH_2Cl$	DEAE	4.5	9.5	33.7	26.0	13	8.5	17.8	35
(*Z*)-**1d**	MeOH	DEAE	20.2	36.1	4.3	20.2	65	2.8	16.4	71
(*Z*)-**1d**	$ClCH_2CH_2Cl$	DEAE	29.2	29.2	5.0	7.0	17	2.8	26.8	81

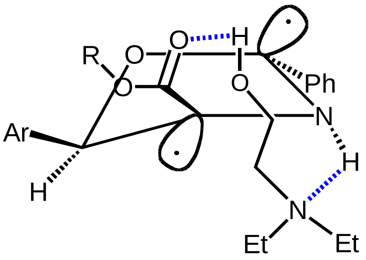
In Table 1 are summarized the effects of substituent (chiral auxiliary), solvent, and tertiary amine on the photoreactivity (conversion) of **1** and the de value of each diastereomer for *cis*-**2** and *trans*-**2**. As can be seen from the data of this Table, 2-(diethylamino)ethanol (DEAE) used instead of TEA showed a tendency to increase both the de values estimated in methanol and 1,2-dichloroethane and, hence, is a better tertiary amine for inducing higher diastereoselectivity, probably through hydrogen-bonding interactions of both the amino nitrogen and hydroxy hydrogen in DEAE with **1** as well as with reaction intermediate(s) involved. Interestingly, a change in solvent from methanol to 1,2-dichloroethane reversed the configuration of major diastereomer for *cis*-**2a** without affecting it for *trans*-**2a**. If we consider the great ability of methanol for hydrogen-bonding solvation, this interesting finding implies that there is a difference in the asymmetric induction mechanism between these two solvents. Similar results were obtained for the asymmetric photocyclization of **1b** bearing an (*S*)-1-methylheptyl auxiliary. In a previous study it has been found that an increase in the steric bulkiness of the alkyl group bonded to the carboxy oxygen in *N*-benzoyl-α-dehydroarylalanine alkyl esters greatly enhances selectivity for the *cis*-dihydrooxazole isomer.[8] Since the PET-initiated cyclization reaction eventually forming *cis*- and *trans*-

4,5-dihydrooxazole derivatives has been shown to be a kinetically-controlled process, this finding stimulated us to introduce a more bulky auxiliary group into the ester moiety of (*Z*)-**1**. (–)-Menthyl and (–)-8-phenylmenthyl groups were chosen as bulky auxiliaries. Careful diastereomer analysis of the isolated products **2c** and **2d** revealed that the menthyl group influenced an asymmetric cyclization process in a manner different from the *sec*-butyl group: In most cases the configuration of diastereomer formed in excess was reversed and the de of this diastereomer was greatly enhanced particularly for the **2d**-derived diastereomers (de = 65% for *cis*-**2d** and 71% for *trans*-**2d** in methanol; de = 17% for *cis*-**2d** and 81% for *trans*-**2d** in 1,2-dichloroethane). In addition, solvent effects on the composition ratio of (*Z*)-**1** to (*E*)-**1** showed that this ratio for **1d** increases by a factor of about 2 on changing solvent from methanol to 1,2-dichloroethane though minor solvent effects were observed for the (*Z*)-**1a**–**c**/(*E*)-**1a**–**c** composition ratios. The presence of the bulky 8-phenylmenthyl group might exert a great effect not only on the relative rates for isomerization of (*Z*)-**1** and (*E*)-**1** but also on the relative rate for the subsequent cyclization reaction.



Scheme 3

Our attention is now directed to a mechanism for the PET-initiated asymmetric cyclization of (*Z*)-**1**. On the basis of *N*-acyl substituent effects on the fluorescence intensity and photoreactivity of *N*-acyl-α-dehydroarylalanine *tert*-butyl esters, we have already proposed the radical ion pair intermediate (*E*)-**I**, as shown in Scheme 3 (Ar = 1-naphthyl).[8] In this Scheme the given chiral amine is considered to form a hydrogen bond to the amide N–H hydrogen in **1**. The occurrence of π-face selective intramolecular cycloaddition in the (*E*)-**1**-derived radical anion (path A) is required for inducing asymmetry at 5-position on the dihydrooxazole ring. This asymmetric cycloaddition can be considered to result in a preferential formation of either the cyclized radical ion pair **IIA** or the **IIB**. There are two possible routes for the subsequent back ET within the radical ion pair **II**. One is the transfer of an unpaired electron from 2-position on the oxazole ring to the amine radical cation, which gives a zwitterion intermediate. The other is the transfer of one of the paired electrons from 4-position on the oxazole ring to the amine radical cation (see Scheme 3). The electron deficient carbon generated at 2-position on the ring of the zwitterion should greatly promote the dissociation of the N–H proton. If so, intramolecular proton shift in this zwitterion intermediate is unlikely to occur depending on the abilities of solvent and tertiary amine to form hydrogen bonds. Thus, solvent and tertiary amine effects on the composition ratio of *cis*-**2** to *trans*-**2** favor the existence of the biradical intermediate **III** (Table 1). While π-face selective cycloaddition in (*E*)-**I** induces asymmetry at 5-position on the oxazole ring of **2**, asymmetric induction at 4-position on this ring is accomplished by preferential hydrogen shift in either the *re* or *si* face of **III** (Paths B and C in Scheme 3). The simultaneous C=N bond formation may provide a driving force for this hydrogen shift eventually leading to *cis*-**2** and *trans*-**2**. The finding that the magnitude of de for **2a** as well as the composition ratio of *cis*-**2a** to *trans*-**2a** depends on the properties of the amine examined suggests that the amino nitrogen and hydroxy hydrogen in DEAE form hydrogen bonds to the N–H hydrogen and ester carbonyl oxygen in **III**, respectively, to exert an effect different from that caused by TEA, as shown in Figure 2.



III

Figure 2. Schematic illustration for typical hydrogen-bonding interactions between the biradical **III** and DEAE

Since hydrogen-bonding interaction of the intermediates (*E*)-**I** and **III** with methanol or DEAE plays a key role in the control of de, temperature effects on the de value can be predicted to provide additional information regarding our asymmetric induction mechanism. Inspection of the data collected in Table 2 confirmed that the de values of *cis*-**2c** and *trans*-**2c** in 1,2-dichloroethane were both increased with a lowering of temperature whereas there was a sudden decrease in de (for these two dihydrooxazole isomers) estimated in methanol at –78 °C. The former finding is consistent with the participation of

Table 2. Temperature effects on the photoreactivity of **1c** and the de values for *cis*-**2c** and *trans*-**2c**, obtained by the 3 h or 1 h (–78 °C) irradiation of (*Z*)-**1c** (4.0×10^{-3} mol dm^{-3}) in methanol and 1,2-dichloroethane containing DEAE (0.10 mol dm^{-3})

		Composition and de (%)							
				cis-**2c**			*trans*-**2c**		
Solvent	Temperature (°C)	(*Z*)-**1c**	(*E*)-**1c**	(4*R*,5*R*)-**2c**	(4*S*,5*S*)-**2c**	de	(4*S*,5*R*)-**2c**	(4*R*,5*S*)-**2c**	de
MeOH	50	11.2	27.8	17.2	33.6	32	3.4	6.8	33
MeOH	rt	11.0	30.5	19.3	28.9	20	3.4	6.9	34
MeOH	–78	13.0	77.3	4.4	4.4	0	0.4	0.5	11
$ClCH_2CH_2Cl$	50	12.7	22.9	23.5	19.5	9	8.3	13.1	22
$ClCH_2CH_2Cl$	rt	4.5	9.5	33.7	26.0	13	8.5	17.8	35
CH_2Cl_2[a]	–78	2.0	4.9	42.5	22.8	30	7.3	20.5	47

[a] Since 1,2-dichloroethane is solidified at –78 °C, dichloromethane was used instead.

Table 3. Substituent and solvent effects on the composition of **III** and the rate ratio (*R*r) of given two competitive paths, obtained by the 3 h irradiation of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}) in the presence of DEAE (0.10 mol dm^{-3})

			Composition of **III** (%) and *R*r				
Compound	Solvent	Temperature (°C)	**IIIA**	**IIIB**	*R*r (A1/A2)	*R*r (B1/B2)	*R*r (C1/C2)
(*Z*)-**1a**	MeOH	rt	27.4	39.6	0.7	0.3	0.3
	$ClCH_2CH_2Cl$	rt	35.6	38.1	0.9	1.4	0.9
(*Z*)-**1b**	MeOH	rt	29.4	37.9	0.8	4.9	4.4
	$ClCH_2CH_2Cl$	rt	41.0	38.9	1.1	2.4	1.8
(*Z*)-**1c**	MeOH	50	40.4	20.6	2.0	4.9	5.1
	MeOH	rt	35.8	22.7	1.6	4.2	5.7
	MeOH	–78	4.9	4.8	1.0	8.8	11.0
	$ClCH_2CH_2Cl$	50	32.6	31.8	1.0	1.5	2.8
	$ClCH_2CH_2Cl$	rt	43.8	42.2	1.0	1.5	4.0
	CH_2Cl_2	–78	43.3	49.8	0.9	1.1	5.8
(*Z*)-**1d**	MeOH	rt	36.6	7.1	5.2	1.2	1.5
	$ClCH_2CH_2Cl$	rt	33.8	7.8	4.3	0.3	1.8

hydrogen-bonding interaction between DEAE and **III** while the latter finding suggests that hydrogen-bonding interaction of methanol with (*E*)-**I** is a factor controlling de in this protic solvent. The intermediate (*Z*)-**I** should also be formed by ET from DEAE to (*Z*)-**1*** but its cyclization is unable to proceed from the (*Z*)-configuration to afford the corresponding intermediate **II** (Scheme 3). Thus, we are able to speculate that (*Z*)-**I** undergoes an exclusive back ET to regenerate (*Z*)-**1** and DEAE. In addition to mechanistic information obtained from a previous study,[8] these considerations render the asymmetric induction mechanism shown in Scheme 3 reasonable further, in which asymmetry at 5- and 4-positions on the dihydrooxazole ring is induced at the stages of the **II**-forming cycloaddition and the hydrogen shift in **III**, respectively.

It is possible to estimate the compositions of **IIIA** and **IIIB** (or **IIA** and **IIB**), as well as the rate ratios of paths A, B, and C, on the basis of the composition of each diastereomer for *cis*-**2** and *trans*-**2** collected in Table 1, because configurational interconversion between **IIIA** and **IIIB** or between **IIA** and **IIB** is very unlikely to occur during irradiation (Table 3). A comparison between the compositions of **IIIA** and **IIIB** thus estimated shows that asymmetric induction for **1a**–**c** in 1,2-dichloroethane is achieved at the stage of hydrogen shift in the biradical **III** while a difference in the radical ion pair **II**-forming cyclization rate is mainly responsible for the asymmetric induction in methanol. Since rate ratios for paths B and C depend on chiral auxiliary and temperature in any solvents, hydrogen-bonding and steric interactions of DEAE with **IIIA** and **IIIB** may change the relative rates of paths B1 and C1 and paths B2 and C2 (to a different extent) in the process of hydrogen shift in **III**. In the π-face selective intramolecular cycloaddition, both the steric bulkiness of chiral auxiliary and the hydrogen-bonding solvation of the radical ion pair (*E*)-**I** by methanol are considered to cause the difference in rate for paths A1 and A2. Surprisingly, the introduction of a (–)-8-phenylmenthyl auxiliary group resulted in a considerable increase in the relative composition of **IIIA** in any solvents examined. This suggests that steric repulsion between the bulky chiral auxiliary and the *N*-benzoyl carbonyl oxygen in the radical ion pair intermediate (*E*)-**I** is a dominant factor controlling the relative rate of path A, irrespective of the solvent properties. The fact that the cyclized radical ion pair **IIA** is formed in excess proves that the bulky phenylmenthyl group exists preferentially in the *si* face of the intermediate (*E*)-**I** to cause cycloaddition in the *re* face of this intermediate. On the other hand, the observation of much lower de (than expected) for *cis*-**2d** in 1,2-dichloroethane must be related to the greatly diminished relative rate of path B1. In this aprotic solvent the presence of the bulky phenylmenthyl group may slow down the rate of hydrogen shift in the *re* face of the biradical intermediate **IIIA**.

Enantioselective photocyclization

In the preceding section we demonstrated that asymmetric induction in the PET-initiated cyclization of (*Z*)-**1a**–**d** eventually affording the corresponding 3,4-dihydrooxazole derivatives was achieved at the stages of the **II**-forming intramolecular cycloaddition as well as the hydrogen shift in **III**. At the former stage the steric bulkiness of a given chiral auxiliary group played a great role in the control of de, whereas hydrogen-bonding interaction between **III** and DEAE was a major factor governing the magnitude of de at the latter stage. As already described, aliphatic amines such as DEAE and TEA may interact directly with this biradical intermediate, so that the presence of a chiral amine is supposed to bring about the asymmetric cyclization of (*Z*)-**1** having no chiral auxiliary and also to unravel the role of the amine-derived radical cation intermediate in the **II**-forming cyclization process.

While irradiation of a nitrogen-saturated 1,2-dichloroethane solution of (*Z*)-**1e** containing each chiral amine afforded quantitatively the corresponding dihydrooxazole derivative **2e**, a small amount of this derivative was only detected on irradiating its methanol solution under the same conditions (Scheme 2). Much higher photoreactivity of *N*-benzoyl-α-dehydroarylalanine alkyl esters in 1,2-dichloroethane than in methanol indicates that chiral amines given in Chart 1 have lower electron donating abilities and also are subject to stronger hydrogen-bonding solvation in methanol, as compared to TEA.[8] In Table 4 are summarized the effects of substituent and chiral amine on the magnitude of ee for *cis*-**2e** and *trans*-**2e** formed in 1,2-dichloroethane. Examination of the amine effects on the ee confirmed that the ability to induce the asymmetric cyclization was lowered in the order of *S*-MPM ≥ *S*-PM > *S*-PG and *R*-PM used instead of *S*-PM gave enantiomers having inverse configurations, namely (4*R*,5*R*)-**2e** and (4*R*,5*S*)-**2e** in excess. Since this order mainly reflects the difference in basicity among these chiral amines, *S*-MPM was chosen as a chiral amine for investigating the substituent and temperature effects on the ee value. The replacement of an 1-naphthyl group by a phenyl or a 2-naphthyl enhanced the ee value for *cis*-**2** with a decrease in this value for the *trans*-isomer, whereas the introduction of a less bulky methoxycarbonyl group into the *tert*-butoxycarbonyl moiety of (*Z*)-**1e** exerted a minor steric effect on the ee for both the *cis*- and *trans*-dihydrooxazole isomers. As described above, we proposed steric interaction between the chiral auxiliary groups and the *N*-benzoyl carbonyl oxygen in the cycloaddition process of **II** as well as hydrogen-bonding interaction between **III** and the tertiary amines, as control factors of de (Scheme 3). Thus, the slight steric effect of the alkoxycarbonyl group suggests that *π*-face selective cycloaddition in (*E*)-**I** takes place to only a minor extent and also the *S*-MPM-derived radical

Table 4. Substituent and chiral amine effects on the selectivity of each enantiomer and the ee values for *cis*-**2** and *trans*-**2**, obtained by the 6 h irradiation of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}) in 1,2-dichloroethane containing chiral amine (0.10 mol dm^{-3}) at room temperature

			Composition[b] and ee (%)					
			cis-**2**			*trans*-**2**		
Compound	Chiral amine	Conversion (%)[a]	(4*R*,5*R*)-**2**	(4*S*,5*S*)-**2**	ee	(4*S*,5*R*)-**2**	(4*R*,5*S*)-**2**	ee
(*Z*)-**1e**	*S*-PG	95	18.6	23.4	11	30.7	27.3	6
(*Z*)-**1e**	*S*-PM	97	13.0	23.6	29	37.1	26.3	17
(*Z*)-**1e**	*R*-PM	97	23.8	12.8	30	26.3	37.1	17
(*Z*)-**1e**	*S*-MPM	100	36.6	24.8	19	12.9	25.7	33
(*Z*)-**1f**	*S*-MPM	100	33.4	23.6	17	16.0	27.0	26
(*Z*)-**1g**	*S*-MPM	100	26.6	12.5	36	24.4	36.5	20
(*Z*)-**1h**	*S*-MPM	100	24.2	10.8	38	26.0	39.0	20

[a] Conversion was estimated by dividing the sum of compositions for *cis*-**2** and *trans*-**2** by the sum of compositions for (*Z*)-**1**, (*E*)-**1**, *cis*-**2**, and *trans*-**2**.

[b] Composition of each enantiomer for *cis*-**2** and *trans*-**2** was evaluated by dividing the composition for each enantiomer by the sum of compositions for *cis*-**2** and *trans*-**2**.

cation is not actively involved in this **II**-forming cycloaddition process. Moreover, the aryl substituent effect on the ee value provides additional evidence for the PET-initiated asymmetric cyclization mechanism shown in Scheme 3 (Ar = 1-naphthyl, 2-naphthyl or phenyl), where the steric bulkiness of an aryl group attached to 5-position on the dihydrooxazole ring affects hydrogen shifts in the *re* and *si* faces of the biradical intermediate **III** to a different extent. It is likely that this intermediate (hydrogen bonded to a given chiral amine) adopts different conformations depending on steric and electronic interactions among unpaired electrons, heteroatoms, and alkoxycarbonyl and aryl groups.

Since hydrogen-bonding interaction between the intermediate **III** and the chiral amine was shown to be one of the factors controlling the magnitude of ee for the cyclized product **2**, it is expected that ee for *cis*-**2e** and *trans*-**2e** estimated in 1,2-dichloroethane containing *S*-MPM is increased as temperature is lowered and also increased with an increase in the *S*-MPM concentration. Contrary to our expectation, ee for *trans*-**2e**, i.e., (4*R*,5*S*)-**2e** exhibited a very small temperature dependence while ee for *cis*-**2e**, i.e., (4*R*,5*R*)-**2e** had a tendency to decrease with a drop in temperature ([(*Z*)-**1e**] = 4.0×10^{-3} mol dm^{-3}, [*S*-MPM] = 0.10 mol dm^{-3}): ee for (4*R*,5*R*)-**2e** = 21% (50 °C), 19% (room temperature, Table 4), 10% (–78 °C, CH_2Cl_2) and ee for (4*R*,5*S*)-**2e** = 30% (50 °C), 33% (room temperature, Table 4), and 28% (–78 °C). On the basis of these temperature effects on the ee value, we propose that the hydrogen-bonded biradical intermediate adopts a temperature-dependent conformation. A drop in temperature is very likely to affect hydrogen shifts in the *re* and *si* faces of **III** to a similar extent. On the other hand, an increase in the concentration of *S*-MPM enhanced not only the conversion of **1e** but also the magnitude of ee for both the enantiomers (Table 5). These findings are consistent with our expectation and, hence, provide evidence supporting not only the involvement of the hydrogen-bonding interaction as a control factor of ee, but also the participation of a PET mechanism.

Table 5. Concentration effects of *S*-MPM on the conversion of **1e** and the ee values for *cis*-**2e** and *trans*-**2e**, obtained by the 6 h irradiation of (*Z*)-**1e** (4.0×10^{-3} mol dm^{-3}) in 1,2-dichloroethane containing this chiral amine at room temperature

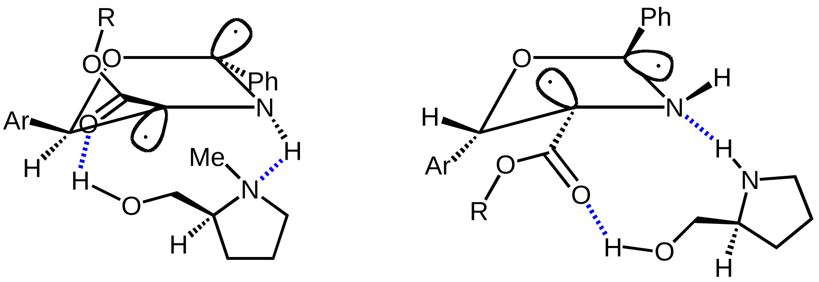
[*S*-MPM] (mol dm^{-3})	Conversion (%)	Composition and ee (%)							
		(*Z*)-**1e**	(*E*)-**1e**	*cis*-**2e**			*trans*-**2e**		
				(4*R*,5*R*)-**2e**	(4*S*,5*S*)-**2e**	ee	(4*S*,5*R*)-**2e**	(4*R*,5*S*)-**2e**	ee
0.010	43	24.7	32.0	8.1	6.8	9	12.5	15.9	12
0.050	58	18.1	24.4	13.7	10.1	15	12.5	21.2	26
0.10	100	0	0	36.6	24.8	19	12.9	25.7	33

According to the same procedures as those employed in the preceding section, both the compositions of **IIIA** and **IIIB** (or **IIA** and **IIB**) and the rate ratios of paths A, B and C were estimated from the composition of each enantiomer for *cis*-**2e**–**h** and *trans*-**2e**–**h** collected in Table 4 (Table 6). As already predicted, rate ratios for the **IIA**- and **IIB**-forming cyclization processes, paths A1 and A2, were unity irrespective of α-dehydroarylalanine alkyl esters and reaction temperatures tested, thus allowing us to conclude that asymmetry at 4-position on the 4,5-dihydrooxazole ring is induced at the stage of hydrogen shifts within the hydrogen-bonded biradical intermediates **IIIA** and **IIIB**. The chiral amine-derived radical cation is considered to play only a minor role in inducing asymmetry at 5-position on the ring, namely, in inducing π-face selective cycloaddition within the radical ion pair intermediate (*E*)-**I**. In addition, analysis of the substituent effects on the *R*r (B1/B2) and *R*r (C1/C2) values led us to assume that

Table 6. Substituent, chiral amine and temperature effects on the composition of **III** and the rate ratio (*R*r) of given two competitive paths, obtained by the irradiation of (*Z*)-**1** in the presence of the amine

			Composition of **III** (%) and *R*r				
Compound	Chiral amine	Temperature (°C)	**IIIA**	**IIIB**	*R*r (A1/A2)	*R*r (B1/B2)	*R*r (C1/C2)
(*Z*)-**1e**	*S*-MPM	rt	50.5	49.5	1.0	1.0	2.8
(*Z*)-**1f**	*S*-MPM	rt	50.6	49.4	1.0	0.9	2.1
(*Z*)-**1g**	*S*-MPM	rt	49.0	51.0	1.0	0.3	1.1
(*Z*)-**1h**	*S*-MPM	rt	49.8	50.2	1.0	0.3	0.9
(*Z*)-**1e**	*S*-MPM	50	49.3	50.7	1.0	1.0	2.8
(*Z*)-**1e**	*S*-MPM	–78	50.7	49.3	1.0	1.6	3.5
(*Z*)-**1e**	*S*-PG	rt	50.7	49.3	1.0	0.9	0.6
(*Z*)-**1e**	*S*-PM	rt	49.9	50.1	1.0	0.9	0.4

both the alkoxycarbonyl groups in **IIIA** and **IIIB** exist preferentially in the *re* face and exert steric effects on the hydrogen shift in this face resulting in an excess of (4*R*,5*R*)-**2** and (4*R*,5*S*)-**2**. It is quite likely that steric and electronic interactions among unpaired electrons, heteroatoms, and alkoxycarbonyl and aryl groups in these two biradical intermediates determine their most stable conformations. Interestingly, when the primary and secondary chiral amines *S*-PG and *S*-PM were used instead of the tertiary amine *S*-MPM, the *cis*- and *trans*-enantiomers formed in excess changed from (4*R*,5*R*)-**2e** and (4*R*,5*S*)-**2e** to (4*S*,5*S*)-**2e** and (4*S*,5*R*)-**2e**, respectively (Table 4). The fact that all of the *R*r (A1/A2) values for *S*-PG, *S*-PM and *S*-MPM are unity substantiates an alteration in the mode of hydrogen-bonding interaction



III

Figure 3. Schematic illustration for typical hydrogen-bonding interactions of the biradical **III** with *S*-MPM and *S*-PM

between **III** and these chiral amines (Table 6). As typically depicted in Figure 3, we propose that while *S*-MPM assists hydrogen shift in the *si* face (through hydrogen bonds formed between the amine N–Me nitrogen and the N–H hydrogen in **III** as well as between the amine O–H hydrogen and the ester carbonyl oxygen in **III**), *S*-PG and *S*-PM partially block this face through similar type of hydrogen bonds to promote hydrogen shift in the *re* face.

CONCLUSION

The steric effects of chiral auxiliary and 1-naphthyl groups on the hydrogen-bonding interaction between DEAE and the biradical intermediate **III** as well as on the hydrogen-bonding solvation and π-face selective intramolecular cycloaddition of the radical ion pair intermediate (*E*)-**I** were shown to be major controlling factors of de for the PET-initiated asymmetric cyclization of (*Z*)-**1a**–**d**. In addition, the introduction of a (–)-8-phenylmenthyl auxiliary group induced a large asymmetry at the stage of the **II**-forming cyclization process, irrespective of the solvation ability of the solvent tested. A large steric repulsion between the chiral auxiliary group introduced and the *N*-benzoyl carbonyl oxygen in the radical ion pair intermediate (*E*)-**I** was proposed in order to explain the π-face selective cycloaddition of this carbonyl oxygen to the olefinic carbon of (*E*)-**I**. On the other hand, the chiral auxiliary-unsubstituted derivatives (*Z*)-**1e**–**h** were found to undergo enantioselective photocyclization reactions in the presence of chiral aliphatic amines such as *S*-PM and *S*-MPM. On the basis of the substituent, chiral amine, and temperature effects on the ee values for *cis*-**2e** and *trans*-**2e**, we were led to conclude that while the chiral amine-derived radical cation plays only a minor role in the **II**-forming cycloaddition process, hydrogen-bonding interactions between the biradical intermediate **III** and the chiral amine enables asymmetric hydrogen shift within this intermediate.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were taken with a JEOL JNM-ECA500 or a JEOL JNM-ECA600 spectrometer. Chemical shifts were determined using tetramethylsilane as an internal standard. IR spectra were recorded on a SHIMADZU IRPrestige-21 infrared spectrophotometer. HPLC analysis was performed on a SHIMADZU LC-10AT (for separation and quantification) or a SHIMADZU LC-8A (for separation and isolation) high-performance liquid chromatography system equipped with a 4.6×150-mm Daicel Chiralcel OD-RH column (for quantification of *trans*-diastereomer), a 4.6×250-mm Daicel Chiralpak IA column (for quantification of enantiomer) or a 10×250-mm Daicel Chiralcel OJ column (for isolation of enantiomer) and a SHIMADZU SPD-10A UV detector [detection wavelength = 250 nm; mobile phase, MeCN:H_2O = 3:1 v/v (for quantification of diastereomer), *i*-PrOH:$CHCl_3$:*n*-C_6H_{12} = 1:1:18 v/v (for quantification of enantiomer) or *i*-PrOH:*n*-C_6H_{12} = 1:5 v/v (for isolation of enantiomer)]. UV absorption spectra were recorded on a HITACHI U-3300 spectrophotometer. A cell with a 10-mm pathlength was used. Circular dichroism spectra were recorded on a NIHONBUNKO J-600 spectropolarimeter. Optical rotations were measured with a NIHONBUNKO P-1020 polarimeter. Elemental analyses were performed on a PERKIN-ELMER PE2400 series II CHNS/O analyzer. Mass spectra were taken with a

JEOL JMS-01 SG-2 spectrometer. MeOH was purified according to the standard procedure and freshly distilled prior to use.[9] 1,2-Dichloroethane and dichloromethane were of spectroscopic grade and used as received. TEA and DEAE were fractionally distilled from sodium hydroxide. All other reagents including chiral amines were obtained from commercial sources and were of the highest grade available.

General procedure for the synthesis of (*Z*)-4-(1-naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone, (*Z*)-4-(2-naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone and (*Z*)-4-benzylidene-2-phenyl-5(4*H*)-oxazolone

N-Benzoylglycine (50 mmol), 1-naphthaldehyde, 2-naphthaldehyde or benzaldehyde (50 mmol), and sodium acetate (20 mmol) were added to acetic anhydride (10–30 mL) and the resulting mixture was heated at 65–75 °C for 1–2 h with stirring. The mixture was cooled with ice and the solid separated out was collected by filtration with suction and washed with water, a small amount of cold EtOH, and then with dry hexane. After the crude product had been air-dried at room temperature, it was recrystallized from hexane-$CHCl_3$ to give yellow crystals (61–74%).

(*Z*)-4-(1-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone: mp 166.0–167.0 °C; IR (KBr) ν/cm^{-1} = 1797, 1647, 1167; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.54 (2H, dd, *J* = 7.3, 7.6 Hz), 7.55 (1H, dd, *J* = 8.6, 8.6 Hz), 7.62 (1H, dd, *J* = 7.3, 7.3 Hz), 7.63 (1H, dd, *J* = 8.6, 8.6 Hz), 7.64 (1H, dd, *J* = 6.7, 8.6 Hz), 7.90 (1H, d, *J* = 8.6 Hz), 7.97 (1H, d, *J* = 8.6 Hz), 8.13 (1H, s), 8.21 (2H, d, *J* = 7.6 Hz), 8.31 (1H, d, *J* = 8.6 Hz), 9.03 (1H, d, *J* = 6.7 Hz).

(*Z*)-4-(2-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone: mp 142.0–143.0 °C; IR (KBr) ν/cm^{-1} = 1797, 1626, 1167; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (1H, dd, *J* = 7.9, 7.9 Hz), 7.54 (1H, dd, *J* = 7.9, 7.9 Hz), 7.54 (2H, dd, *J* = 7.9, 7.9 Hz), 7.61 (1H, dd, *J* = 7.9, 7.9 Hz), 7.83 (1H, d, *J* = 7.9 Hz), 7.89 (1H, d, *J* = 8.5 Hz), 7.91 (1H, d, *J* = 7.9 Hz), 8.19 (2H, d, *J* = 7.9 Hz), 8.43 (1H, s), 8.49 (1H, d, *J* = 8.5 Hz).

(*Z*)-4-Benzylidene-2-phenyl-5(4*H*)-oxazolone: mp 162.0–163.0 °C; IR (KBr) ν/cm^{-1} = 1779, 1659, 1266; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.25 (1H, s), 7.47 (2H, dd, *J* = 7.4, 8.0 Hz), 7.49 (1H, dd, *J* = 7.4, 7.4 Hz), 7.54 (2H, dd, *J* = 7.2, 7.4 Hz), 7.62 (1H, dd, *J* = 7.4, 7.4 Hz), 8.19 (2H, d, *J* = 8.0 Hz), 8.21 (2H, d, *J* = 7.2 Hz).

General procedure for the synthesis of alkyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoates and *tert*-butyl (*Z*)-3-aryl-2-benzoylamino-2-propenoates

(*Z*)-4-(1-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone (for **1a**–**f**, 10 mmol), (*Z*)-4-(2-naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone (for **1g**, 10 mmol) or (*Z*)-4-benzylidene-2-phenyl-5(4*H*)-oxazolone (for **1h**, 10 mmol) was added to an 1,2-dichloroethane solution (60 mL) containing a given chiral alcohol (for **1a**–**d**, 30 mmol) and 4-(dimethylamino)pyridine (20 mmol) or to an achiral alcohol solution (for **1e**–**h**, 60 mL) containing 4-(dimethylamino)pyridine (20 mmol), and the resulting mixture was refluxed for 1–2 h. After removal of the solvent under reduced pressure, the residual solid obtained was dissolved in $CHCl_3$ (50–100 mL) and then washed twice with hydrochloric acid (0.5 mol dm^{-3}, 50 mL) and finally dried over sodium sulfate. Evaporation of chloroform in vacuo gave the crystalline solid which was recrystallized from EtOAc–hexane affording colorless crystals (47–92%). In order to purify the crude products, column chromatography on silica gel was also used.

(*S*)-*sec*-Butyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1a]: mp 113.5–114.5 °C; IR (KBr) ν/cm^{-1} = 3336, 1654, 1577; $[\alpha]_D^{25}$ +20.2° (*c* = 0.5, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.89 (3H, t, *J* = 7.6 Hz), 1.24 (3H, d, *J* = 6.2 Hz), 1.59 (2H, dq, *J* = 6.9, 7.6 Hz), 4.90 (1H, tq, *J* = 6.2, 6.9 Hz), 7.45 (2H, dd, *J* = 7.6, 8.3 Hz), 7.50 (1H, dd, *J* = 6.9, 8.3 Hz), 7.53 (1H, dd, *J* = 7.6, 7.6 Hz), 7.55–7.59 (2H, m), 7.70 (1H, d, *J* = 6.9 Hz), 7.81 (2H, d, *J* = 7.6 Hz), 7.87 (1H, s), 7.92 (1H, d, *J* = 8.3 Hz), 7.95 (1H, d, *J* = 8.3 Hz), 7.99 (1H, d, *J* = 8.3 Hz), 9.95 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 9.4, 19.1, 28.2, 72.9, 124.0, 125.4, 126.2, 126.6, 126.7, 127.6 (2C), 128.3 (2C), 128.5, 129.1, 129.2, 129.7, 130.5, 130.9, 131.7, 133.2, 133.5, 166.4, 166.5. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.18; H, 6.23; N, 3.46.

(*S*)-2-Octyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1b]: mp 104.0–105.0 °C; IR (KBr) ν/cm^{-1} = 3398, 1666; $[\alpha]_D^{25}$ +58.1 (*c* 0.5, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.82 (3H, t, *J* = 6.9 Hz), 1.14–1.35 (8H, m), 1.25 (3H, d, *J* = 6.2 Hz), 1.49–1.60 (2H, m), 4.94 (1H, tq, *J* = 6.2, 6.2 Hz), 7.44 (2H, dd, *J* = 7.6, 7.6 Hz), 7.49 (1H, dd, *J* = 6.9, 8.3 Hz), 7.53 (1H, dd, *J* = 7.6, 7.6 Hz), 7.54–7.59 (2H, m), 7.70 (1H, d, *J* = 6.9 Hz), 7.81 (2H, d, *J* = 7.6 Hz), 7.87 (1H, s), 7.92 (1H, d, *J* = 8.3 Hz), 7.94–7.96 (1H, m), 7.99 (1H, d, *J* = 6.9 Hz), 9.96 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 13.9, 19.6, 22.0, 24.5, 28.5, 31.1, 35.3, 71.7, 123.9, 125.4, 126.1, 126.6, 126.7, 127.6 (2C), 128.3 (2C), 128.6, 129.1, 129.2, 129.7, 130.5, 131.0, 131.7, 133.2, 133.4, 164.5, 166.5. Anal. Calcd for $C_{28}H_{31}NO_3$: C, 78.29; H, 7.27; N, 3.26. Found: C, 78.62; H, 7.20; N, 3.47.

(1*R*,2*S*,5*R*)-(–)-Menthyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1c]: mp 126.0–127.0 °C; IR (KBr) ν/cm^{-1} = 3350, 1672, 1639; $[\alpha]_D^{25}$ –32.2 (*c* 0.5, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.78 (3H, d, *J* = 6.9 Hz), 0.81 (3H, d, *J* = 6.9 Hz), 0.82–2.06 (9H, m), 0.90 (3H, d, *J* = 6.9 Hz), 4.71 (1H, ddd, *J* = 6.9, 6.9, 6.9 Hz), 7.45 (2H, dd, *J* = 7.5, 7.5 Hz), 7.50 (1H, dd, *J* = 7.5, 7.5 Hz), 7.53–7.60 (3H, m), 7.71 (1H, d, *J* = 7.5 Hz), 7.79 (2H, d, *J* = 7.5 Hz), 7.89 (1H, s), 7.93 (1H, d, *J* = 8.6 Hz), 7.95–7.98 (2H, m), 9.94 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 16.3, 20.6, 21.9 (2C), 23.0, 25.6, 30.9, 33.7, 40.0, 40.4, 46.6, 74.7, 123.9, 125.5, 126.2, 126.7, 127.6 (2C), 128.3 (2C), 128.6, 129.2, 129.6, 130.4, 130.9, 131.7, 133.2, 133.5, 164.4, 166.6. Anal. Calcd for $C_{30}H_{33}NO_3$: C, 79.09; H, 7.30; N, 3.03. Found: C, 79.48; H, 7.35; N, 3.07.

(1*R*,2*S*,5*R*)-(–)-8-Phenylmenthyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1d]: mp 135.0–135.5 °C; IR (KBr) ν/cm^{-1} = 3311, 1701, 1657; $[\alpha]_D^{25}$ +169.5 (*c* 0.1, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.81–0.84 (1H, m), 0.87 (3H, d, *J* = 6.3 Hz), 1.03–1.16 (2H, m), 1.26 (3H, s), 1.39 (3H, s), 1.41–1.44 (2H, m), 1.53–1.55 (1H, m), 1.96–1.98 (1H, m), 2.07–2.10 (1H, m), 4.83 (1H, ddd, *J* = 6.9, 6.9, 6.9 Hz), 6.91 (1H, dd, *J* = 7.5, 7.5 Hz), 7.20 (2H, dd, *J* = 7.5, 7.5 Hz), 7.33 (2H, d, *J* = 7.5 Hz), 7.45 (2H, dd, *J* = 7.5, 7.5 Hz), 7.47 (1H, dd, *J* = 7.5, 7.5 Hz), 7.50 (1H, s), 7.51–7.60 (3H, m), 7.65 (1H, d, *J* = 7.5 Hz), 7.80 (2H, d, *J* = 7.5 Hz), 7.86 (1H, d, *J* = 8.0 Hz), 7.90 (1H, d, *J* = 7.5 Hz), 7.94 (1H, d, *J* = 8.0 Hz), 9.76 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 20.7 (2C), 20.9, 22.2 (2C), 24.8, 26.1, 28.5, 34.3, 38.6, 46.2, 71.6, 123.9, 124.2, 125.5, 126.3, 126.86, 126.89, 127.61 (2C), 128.0, 128.4 (2C), 128.7, 129.4, 129.6, 130.2, 130.41, 130.43, 131.0, 131.8, 132.2, 132.6, 133.6, 164.3, 166.8. Anal. Calcd for $C_{36}H_{37}NO_3$: C, 81.32; H, 7.01; N, 2.63. Found: C, 81.50; H, 6.98; N, 2.51.

***tert*-Butyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1e]:** mp 120.0–121.0 °C; IR (KBr) ν/cm^{-1} = 3289, 1709, 1638; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.50 (9H, s), 7.45 (2H, dd, *J* = 7.6, 8.2 Hz), 7.50 (1H, dd, *J* = 6.9, 8.2 Hz), 7.54 (1H, dd, *J* = 7.6, 7.6 Hz), 7.58 (1H, dd, *J* = 6.9, 8.2 Hz), 7.59 (1H, dd, *J* = 6.9, 7.6 Hz), 7.68 (1H, d, *J* = 6.9 Hz), 7.81 (2H, d, *J* = 8.2 Hz), 7.82 (1H, s), 7.92 (1H, d, *J* = 8.2 Hz), 7.96 (1H, d, *J* = 7.6 Hz), 8.01 (1H, d, *J* = 8.2 Hz), 9.88 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 27.6 (3C), 80.7, 124.0, 125.4, 126.0, 126.5 (2C), 127.5 (2C), 128.2 (2C), 128.4, 128.6, 128.9, 130.4, 130.7, 130.9, 131.5, 133.1, 133.6, 163.7, 166.5. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.35; H, 6.29; N, 3.74.

Methyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1f]: mp 118.0–118.5 °C; IR (KBr) ν/cm^{-1} = 3200, 1732, 1632; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 3.80 (3H, s), 7.46 (2H, dd, *J* = 7.6, 7.6 Hz), 7.51 (1H, dd, *J* = 7.6, 8.9 Hz), 7.55 (1H, dd, *J* = 7.6, 7.6 Hz), 7.58 (1H, dd, *J* = 6.9, 6.9 Hz), 7.59 (1H, dd, *J* = 6.9, 7.6 Hz), 7.69 (1H, d, *J* = 7.6 Hz), 7.84 (2H, d, *J* = 7.6 Hz), 7.90 (1H, s), 7.94 (1H, d, *J* = 8.9 Hz), 7.97 (1H, d, *J* = 6.9 Hz), 8.05 (1H, d, *J* = 7.6 Hz), 10.0 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 52.3, 124.1, 125.4, 126.2, 126.62, 126.65, 127.6 (2C), 128.3 (2C), 128.5, 128.9, 129.2, 129.9, 130.5, 131.0, 131.8, 133.15, 133.22, 165.3, 166.4. Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 75.88; H, 4.98; N, 4.19.

***tert*-Butyl (*Z*)-2-benzoylamino-3-(2-naphthyl)-2-propenoate [(*Z*)-1g]:** mp 169.0–170.0 °C; IR (KBr) ν/cm^{-1} = 3323, 1707, 1660; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.48 (9H, s), 7.49 (1H, s), 7.51–7.56 (4H, m), 7.61 (1H, dd, *J* = 7.4, 7.4 Hz), 7.82 (1H, d, *J* = 8.6 Hz), 7.86-7.91 (3H, m), 7.98 (2H, d, *J* = 7.4 Hz), 8.19 (1H, s), 10.1 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 28.5 (3C), 81.5, 126.9, 127.4, 127.9, 128.3, 128.4 (2C), 128.7, 129.1, 129.2, 129.3 (2C), 131.1, 132.2, 132.6, 132.7, 133.5, 133.8, 134.5, 164.9, 167.2. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.02; H, 6.19; N, 3.70.

***tert*-Butyl (*Z*)-2-benzoylamino-3-phenyl-2-propenoate [(*Z*)-1h]:** mp 144.0–145.0 °C; IR (KBr) ν/cm^{-1} = 3248, 1709, 1641; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.44 (9H, s), 7.31 (1H, s), 7.34 (1H, dd, *J* = 7.5, 7.5 Hz), 7.40 (2H, dd, *J* = 7.5, 7.5 Hz), 7.51 (2H, dd, *J* = 7.5, 7.5 Hz), 7.60 (1H, dd, *J* = 7.5, 7.5 Hz), 7.65 (2H, d, *J* = 7.5 Hz), 7.95 (2H, d, *J* = 7.5 Hz), 9.98 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 27.1 (3C), 80.1, 127.1 (2C), 127.7, 127.9 (2C), 128.1 (2C), 128.7, 129.2 (2C), 131.2, 131.4, 133.15, 133.19, 163.5, 165.8. Anal. Calcd (found) for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.11; H, 6.21; N, 4.43.

General procedure for the irradiation of (*Z*)-1a–h

For the purpose of analyzing the effects of chiral auxiliary, substituent, aliphatic amine, and solvent on the magnitude of de or ee, nitrogen-saturated MeOH or 1,2-dichloroethane solutions (10 mL) of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}) containing a given aliphatic amine (0.10 mol dm^{-3}), placed in a sealed tube, were irradiated in parallel for a given period of time with a 400 W high-pressure Hg lamp set in a Pyrex cooling jacket. Parallel irradiation of the solutions was done on a merry-go-round apparatus (RIKO model RH400-10W) immersed into a water bath. After the irradiation, each solution was concentrated to dryness in vacuo. The resulting residue was dissolved in DMSO-d_6 and n-C_6H_{12}-$CHCl_3$ (95:5 v/v) and subjected to ^{1}H NMR spectral and HPLC analyses, respectively. The aliphatic amine of high boiling point was removed by treating it with diluted hydrochloric acid before these spectral and chromatographic analyses. Temperature effects on the de and ee values were accomplished by irradiating a nitrogen-saturated MeOH or CH_2Cl_2 solution (4.0×10^{-3} mol dm^{-3}, 50 mL), placed in a Pyrex vessel thermostated at 50 or –78 °C, with a 400 W high-pressure Hg lamp.

On the other hand, a nitrogen-saturated MeOH or 1,2-dichloroethane solution of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}, 500 mL) containing achiral or chiral amine (0.10 mol dm^{-3}), placed in a Pyrex vessel, was irradiated for a given period of time with Pyrex-filtered light from a 400 W high-pressure Hg lamp at room temperature. After the irradiation, an aliquot (5 mL) of the solution was pipetted off and concentrated to dryness in vacuo. The resulting residue was dissolved in DMSO-d_6 and subjected to ^{1}H NMR spectral analysis. The composition was estimated from the area ratio of a given ^{1}H NMR signal for each compound. The remaining solution was concentrated to dryness under reduced pressure and the resulting residue was subjected to column chromatography on silica gel (230 mesh, Merck) eluting with $CHCl_3$-EtOAc or hexane-EtOAc. For the purpose of isolating the photoproducts, preparative TLC plate (silica gel) and HPLC chiral column were also used. Physical and spectroscopic data of (*E*)-**1a** and diastereomers derived from *cis*- and *trans*-4,5-dihydrooxazoles (*cis*- and *trans*-**2a**–**d**) are as follows. In addition, the dihydrooxazole isomers *cis*- and *trans*-**2e**–**h** were isolated and characterized as enantiomeric mixtures. To determine the absolute configuration of each enantiomer and the retention time of its HPLC signal, *cis*-**2e** (30 mg) was dissolved in 2-propanol (10 mL) and separated into (4*S*,5*S*)-**2e** and (4*R*,5*R*)-**2e** by normal-phase HPLC using 2-propanol-hexane (1:5 v/v) as a mobile phase. The isomerization of (4*S*,5*S*)-**2e** and (4*R*,5*R*)-**2e** into the corresponding (4*R*,5*S*)- and (4*S*,5*R*)-enantiomers was accomplished by allowing a methanol solution of the former *cis*-enantiomer containing TEA (0.10 mol dm^{-3}) to stand for 10 days at room temperature. The latter *trans*-enantiomer formed was separated and purified by preparative thin-layer chromatography over silica gel (eluent: EtOAc-hexane).

(*S*)-*sec*-Butyl (*E*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*E*)-1a]: mp 118.5–119.0 °C; IR (KBr) ν/cm^{-1} = 3454, 1654, 1560; $[\alpha]_D^{25}$ –1.6 (*c* 0.5, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.50 (3H, t, *J* =7.6 Hz), 0.83 (3H, d, *J* = 5.2 Hz), 1.19 (2H, dq, *J* = 6.3, 7.6 Hz), 4.60 (1H, tq, *J* = 5.2, 6.3 Hz), 7.27 (1H, s), 7.33 (1H, d, *J* = 6.9 Hz), 7.47 (1H, dd, *J* = 7.5, 7.5 Hz), 7.56 (2H, dd, *J* = 7.5, 8.0 Hz), 7.54–7.58 (2H, m), 7.63 (1H, dd, *J* = 6.9, 7.5 Hz), 7.88 (1H, d, *J* = 7.6 Hz), 7.99 (2H, d, *J* = 8.0 Hz), 8.00 (1H, dd, *J* = 6.9, 6.9 Hz), 8.02 (1H, d. *J* = 8.0 Hz), 10.6 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 8.9, 18.2, 27.6, 72.3, 120.0, 122.2, 124.6, 125.3, 125.9, 126.1, 126.3, 127.7 (2C), 127.9, 128.3, 128.5 (2C), 131.2, 131.9, 132.0, 132.1, 133.0, 164.0, 165.0. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.34; H, 6.25; N, 3.61.

(4*R*,5*R*)-4-[(*S*)-*sec*-Butoxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*R*,5*R*)-2a]: mp 111.0–111.5 °C; IR (KBr) ν/cm^{-1} = 1734, 1653; $[\alpha]_D^{25}$ –460.7 (*c* 0.5, MeOH); $[\theta]_{220}$ –420 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = –0.33 (3H, d, *J* = 6.3 Hz), 0.54 (3H, t, *J* = 7.5 Hz), 1.02 (2H, dq, *J* = 7.5, 7.5 Hz), 4.01 (1H, tq, *J* = 7.5, 7.5 Hz), 5.57 (1H, d, *J* = 10.3 Hz), 6.83 (1H, d, *J* = 10.3 Hz), 7.48 (1H, dd, *J* = 7.5, 7.5 Hz), 7.51 (1H, d, *J* = 7.5 Hz), 7.56–7.60 (2H, m), 7.57 (2H, dd, *J* = 7.5, 8.0 Hz), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.89 (1H, d, *J* = 7.5 Hz), 7.95 (1H, d, *J* = 8.0 Hz), 8.06 (2H, d, *J* = 8.0 Hz), 8.10 (1H, d, *J* = 8.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 8.9, 16.7. 27.6, 71.7, 72.1, 80.2, 123.1, 123.8, 125.1, 125.9, 126.2, 126.8, 128.2 (2C), 128.3, 128.4, 128.9 (2C), 130.1, 132.0, 132.2, 133.0, 165.0, 168.3. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.96; H, 5.99; N, 3.67.

(4*S*,5*S*)-4-[(*S*)-*sec*-Butoxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*S*,5*S*)-2a]: mp 90.5–91.0 °C; IR (KBr) ν/cm^{-1} = 1734, 1653; $[\alpha]_D^{25}$ +365.5 (*c* 0.5, MeOH); $[\theta]_{220}$ +300 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.12 (3H, t, *J* = 7.5 Hz), 0.39 (2H, dq, *J* = 7.5, 7.5 Hz), 0.60 (3H, d, *J* = 6.3 Hz), 3.96 (1H, tq, *J* = 7.5, 7.5 Hz), 5.53 (1H, d, *J* = 10.3 Hz), 6.81 (1H, d, *J* = 10.3 Hz), 7.50 (1H, dd, *J* = 7.5, 8.0 Hz), 7.55–7.56 (2H, m), 7.56 (2H, dd, *J* = 6.9, 7.5 Hz), 7.59 (1H, d, *J* = 7.5 Hz), 7.65 (1H, dd, *J* =7.5, 7.5 Hz), 7.89 (1H, d, *J* = 8.0 Hz), 7.95 (1H, d, *J* = 8.0 Hz), 8.05 (2H, d, *J* = 6.9 Hz), 8.08 (1H, d, *J* = 8.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 8.3, 18.1, 26.7, 71.9, 72.6, 80.3, 123.2, 123.6, 125.1, 125.9, 126.3, 126.8, 128.1 (2C), 128.3, 128.4, 128.8 (2C), 129.9, 131.9, 132.2, 133.0, 165.1, 168.1. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.87; H, 6.12; N, 3.61.

(4*R*,5*S*)-4-[(*S*)-*sec*-Butoxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*R*,5*S*)-2a]: oily liquid; IR (neat) ν/cm^{-1} = 1734, 1653, 1560; $[\alpha]_D^{25}$ +108.9 (*c* 0.5, MeOH); $[\theta]_{220}$ +150 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.87 (3H, t, *J*= 7.5 Hz), 1.28 (3H, d, *J* = 6.3 Hz), 1.59 (2H, dq, *J* = 7.5 Hz), 4.78 (1H, d, *J* = 6.3 Hz), 4.95 (1H, tq, *J* = 7.5, 7.5 Hz), 6.66 (1H, d, *J* = 6.3 Hz), 7.51 (1H, d, *J* = 8.0 Hz), 7.54 (1H, dd, *J* = 7.5, 8.0 Hz), 7.58 (2H, dd, *J* = 7.5, 7.5 Hz), 7.60–7.62 (2H, m), 7.67 (1H, dd, *J* = 6.3, 7.5 Hz), 7.96–7.98 (2H, m), 8.02–8.04 (1H, m), 8.05 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 9.3, 19.1, 28.1, 73.4, 75.7, 78.5, 80.7, 122.6, 122.9, 125.5, 126.3, 126.4, 126.7, 128.3 (2C), 129.0 (2C), 129.1, 129.2, 132.4, 133.5, 134.6, 164.5, 170.2. HR EI-MS *m*/*z* calcd for $C_{24}H_{23}NO_3$: 373.1678. Found: 373.1678.

(4*S*,5*R*)-4-[(*S*)-*sec*-Butoxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*S*,5*R*)-2a]: oily liquid; IR (neat) ν/cm^{-1} = 1734, 1639, 1577; $[\alpha]_D^{25}$ +73.7 (*c* 0.5, MeOH); $[\theta]_{220}$ –50 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.88 (3H, t, *J* = 7.5 Hz), 1.24 (3H, d, *J*

= 6.3 Hz), 1.62 (2H, dq, *J* = 7.5, 7.5 Hz), 4.76 (1H, d, *J* = 6.3 Hz), 4.95 (1H, tq, *J* = 7.5, 7.5 Hz), 6.65 (1H, d, *J* = 6.3 Hz), 7.52–7.54 (2H, m), 7.58 (2H, dd, *J* = 7.5, 7.5 Hz), 7.59–7.61 (2H, m), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.92–7.93 (1H, m), 7.97 (1H, d, *J* = 8.0 Hz), 8.04 (1H, d, *J* = 7.5 Hz), 8.05 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 9.4, 19.1, 28.0, 71.9, 73.6, 75.7, 80.8, 122.5, 122.8, 125.5, 126.3, 126.4, 126.7, 128.3 (2C), 129.0 (2C), 129.1, 129.2, 132.4, 133.5, 134.6, 164.6, 170.2. HR EI-MS *m*/*z* calcd for $C_{24}H_{23}NO_3$: 373.1678. Found: 373.1678.

(4*R*,5*R*)-5-(1-Naphthyl)-4-[(*S*)-2-octyloxycarbonyl]-2-phenyl-4,5-dihydrooxazole [(4*R*,5*R*)-2b]: oily liquid; IR (neat) ν/cm^{-1} = 1742, 1655; $[\alpha]_D^{25}$ –370.5 (*c* 0.5, MeOH); $[\theta]_{220}$ –1040 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = –0.29 (3H, d, *J* = 6.3 Hz), 0.81 (3H, t, *J* = 7.5 Hz), 0.80–1.13 (8H, m), 1.19 (1H, tq, *J* = 7.5, 7.5 Hz), 4.07 (1H, tq, *J* = 5.2, 6.3 Hz), 5.56 (1H, d, *J* = 10.9 Hz), 6.82 (1H, d, *J* = 10.9 Hz), 7.48 (1H, dd, *J* = 6.9, 8.0 Hz), 7.52 (1H, d, *J* = 8.0 Hz), 7.54–7.58 (2H, m), 7.60 (2H, dd, *J* = 6.9, 7.5 Hz), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.88 (1H, d, *J* = 6.9 Hz), 7.94 (1H, d, *J* = 7.5 Hz), 8.04 (2H, d, *J* = 6.9 Hz), 8.10 (1H, d, *J* = 8.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 13.9, 17.3, 21.9, 24.2, 28.3, 31.0, 34.6, 70.6, 72.1, 80.1, 123.1, 123.8, 125.1, 125.9, 126.1, 126.7, 128.2 (2C), 128.3, 128.4, 128.8 (2C), 130.1, 132.0, 132.2, 133.0, 165.0, 168.2. Anal. Calcd for $C_{28}H_{31}NO_3$: C, 78.29; H, 7.27; N, 3.26. Found: C, 77.88; H, 7.20; N, 3.25.

(4*S*,5*S*)-5-(1-Naphthyl)-4-[(*S*)-2-octyloxycarbonyl]-2-phenyl-4,5-dihydrooxazole [(4*S*,5*S*)-2b]: oily liquid; IR (neat) ν/cm^{-1} = 1742, 1655; $[\alpha]_D^{25}$ +224.2 (*c* 0.5, MeOH); $[\theta]_{220}$ +850 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.53 (2H, m), 0.78 (3H, d, *J* = 6.3 Hz), 0.76–0.96 (8H, m), 0.84 (3H, t, *J* = 6.3 Hz), 4.00 (1H, tq, *J* = 6.3, 6.3 Hz), 5.53 (1H, d, *J* = 10.3 Hz), 6.80 (1H, d, *J* = 10.3 Hz), 7.49 (1H, dd, *J* = 7.5, 7.5 Hz), 7.53–7.58 (3H, m), 7.57 (2H, dd, *J* = 7.5, 8.0 Hz), 7.65 (1H, dd, *J* = 8.0, 8.0 Hz), 7.88 (1H, d, *J* = 8.0 Hz), 7.93 (1H, d, *J* = 7.5 Hz), 8.05 (2H, d, *J* = 8.0 Hz), 8.08 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 14.0, 18.7, 22.0, 23.8, 28.2, 30.8, 33.8, 71.0, 72.6, 80.4, 123.3, 123.7, 125.2, 125.9, 127.3, 126.3, 126.8, 128.2 (2C), 128.4, 128.9 (2C), 130.0, 132.0, 132.3, 133.0, 165.0, 168.2. Anal. Calcd for $C_{28}H_{31}NO_3$: C, 78.29; H, 7.27; N, 3.26. Found: C, 77.96; H, 7.30; N, 3.25.

(4*R*,5*S*)-5-(1-Naphthyl)-4-[(*S*)-2-octyloxycarbonyl]-2-phenyl-4,5-dihydrooxazole [(4*R*,5*S*)-2b]: oily liquid; $[\alpha]_D^{25}$ +98.4 (*c* 0.5, MeOH); $[\theta]_{220}$ +720 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.79 (3H, t, *J* = 6.9 Hz), 1.18–1.28 (8H, m), 1.27 (3H, d, *J* = 6.3 Hz), 1.52–1.57 (2H, m), 4.76 (1H, d, *J* = 6.3 Hz), 5.01 (1H, tq, *J* = 6.3, 6.3 Hz), 6.65 (1H, d, *J* = 6.3 Hz), 7.49 (1H, dd, *J* = 7.5, 7.5 Hz), 7.54 (1H, dd, *J* = 7.5, 7.5 Hz), 7.56 (2H, dd, *J* = 6.9, 7.5 Hz), 7.58–7.60 (2H, m), 7.65 (1H, dd, *J* = 8.0, 8.0 Hz), 7.94–7.98 (2H, m), 8.02 (1H, d, *J* = 8.0 Hz), 8.03 (2H, d, *J* = 6.9 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 14.6, 20.4, 22.6, 25.3, 29.1, 31.9, 35.9, 73.0, 76.4, 81.3, 123.3, 123.6, 126.3, 126.9, 127.1, 127.4, 129.0 (2C), 129.66 (2C), 129.72, 129.8, 129.9, 133.2, 134.3, 135.3, 165.2, 170.9. HR FAB-MS *m*/*z* calcd for $C_{28}H_{32}NO_3$: 430.2382 $[M + H]^+$. Found: 430.2384.

(4*S*,5*R*)-5-(1-Naphthyl)-4-[(*S*)-2-octyloxycarbonyl]-2-phenyl-4,5-dihydrooxazole [(4*S*,5*R*)-2b]: oily liquid; $[\alpha]_D^{25}$ –23.2 (*c* 0.5, MeOH); $[\theta]_{220}$ –860 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.80 (3H, t, *J* = 6.9 Hz), 1.01 (3H, d, *J* = 6.3 Hz), 1.17–1.27 (8H, m), 1.52–1.59 (2H, m), 4.75 (1H, d, *J* = 6.3 Hz), 4.98 (1H, tq, *J* = 6.3, 6.3 Hz), 6.62 (1H, d, *J* = 6.3 Hz), 7.51 (1H, dd, *J* = 7.5, 7.5 Hz), 7.53–7.60 (3H, m), 7.56 (2H, dd, *J* = 7.5, 7.5 Hz), 7.65 (1H, dd, *J* = 8.0, 8.0 Hz), 7.91 (1H, d, *J* = 8.0 Hz), 7.96 (1H, d, *J* = 7.5 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 8.04 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 13.9, 19.6, 21.9, 22.5, 24.6, 28.4, 31.1, 35.1, 39.1, 72.4, 75.7, 80.7, 122.5, 122.9, 125.5, 126.1, 126.3, 126.7, 128.3 (2C), 128.7, 128.9, 129.0, 129.1, 132.4, 133.5, 164.5, 170.1. HR FAB-MS *m*/*z* calcd for $C_{28}H_{32}NO_3$: 430.2382 [M + H]$^+$. Found: 430.2384.

(4*R*,5*R*)-4-[(1*R*,2*S*,5*R*)-(–)-Menthyloxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*R*,5*R*)-2c]: oily liquid; IR (neat) ν/cm^{-1} = 1734, 1654; $[\alpha]_D^{25}$ –193.8 (*c* 0.5, MeOH); $[\theta]_{220}$ –1020 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.01 (3H, d, *J* = 6.9 Hz), 0.35 (3H, d, *J* = 6.9 Hz), 0.67 (3H, d, *J* = 6.9 Hz), 0.35–1.59 (9H, m), 3.95 (1H, ddd, *J* = 6.9, 6.9, 6.9 Hz), 5.54 (1H, d, *J* = 10.3 Hz), 6.77 (1H, d, *J* = 10.3 Hz), 7.43 (1H, dd, *J* = 8.0, 8.0 Hz), 7.47 (1H, d, *J* = 8.0 Hz), 7.56–7.61 (4H, m), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.76 (1H, d, *J* = 8.0 Hz), 7.89 (1H, d, *J* = 8.0 Hz), 7.95 (1H, d, *J* = 8.0 Hz), 8.04 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 15.4, 20.2, 20.5, 21.8, 22.4, 24.6, 30.6, 45.5, 72.8, 80.5, 123.3, 123.5, 125.1, 125.8, 126.3, 126.7, 127.2, 127.4, 128.1 (2C), 128.2, 128.4, 128.5, 128.8 (2C), 129.6, 131.6, 132.2, 165.2, 168.1. Anal. Calcd for $C_{30}H_{33}NO_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 78.81; H, 6.91; N, 3.33.

(4*S*,5*S*)-4-[(1*R*,2*S*,5*R*)-(–)-Menthyloxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*S*,5*S*)-2c]: oily liquid; IR (neat) ν/cm^{-1} = 1739, 1653; $[\alpha]_D^{25}$ +173.7 (*c* 0.5, MeOH); $[\theta]_{220}$ +1090 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = –0.30 (1H, m), 0.27–0.29 (1H, m), 0.42 (3H, d, *J* = 6.3 Hz), 0.54 (3H, d, *J* = 6.9 Hz), 0.68–0.84 (7H, m), 0.73 (3H, d, *J* = 6.9 Hz), 3.96 (1H, ddd, *J* = 6.3, 6.3, 6.3 Hz), 5.58 (1H, d, *J* = 10.9 Hz), 6.83 (1H, d, *J* = 10.9 Hz), 7.49–7.61 (6H, m), 7.66 (1H, dd, *J* = 6.9, 6.9 Hz), 7.88–7.90 (1H, m), 7.94 (1H, d, *J* = 8.0 Hz), 8.05 (2H, d, *J* = 6.9 Hz), 8.10 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 16.3, 20.6, 21.6, 25.8, 30.2, 33.5, 37.9, 46.1, 72.3, 80.4, 123.6, 124.1, 125.5, 126.1, 126.5, 127.0, 127.6, 128.5 (2C), 128.7, 128.8, 129.1 (2C), 130.7, 131.5, 132.2, 132.5, 133.6, 165.4, 168.5. Anal. Calcd for $C_{30}H_{33}NO_3$: C, 79.09; H, 7.30; N, 3.07. Found: C, 78.80; H, 6.96; N, 2.95.

(4*R*,5*S*)-4-[(1*R*,2*S*,5*R*)-(–)-Menthyloxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*R*,5*S*)-2c]: oily liquid; $[\alpha]_D^{25}$ +48.9 (*c* 0.5, MeOH); $[\theta]_{220}$ +900 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.76 (3H, d, *J* = 6.9 Hz), 0.78 (3H, d, *J* = 6.9 Hz), 0.89 (3H, d, *J* = 6.9 Hz), 1.06–1.10 (2H, m), 1.35–1.40 (2H, m), 1.46–1.48 (1H, m), 1.60–1.63 (2H, m), 1.78–1.80 (1H, m), 1.95–1.98 (1H, m), 4.74 (1H, d, *J* = 6.9 Hz), 4.76 (1H, ddd, *J* = 4.8, 4.8, 5.5 Hz), 6.61 (1H, d, *J* = 6.9 Hz), 7.51 (1H, d, *J* = 7.5 Hz), 7.53 (1H, dd, *J* = 7.5, 7.5 Hz), 7.53–7.56 (1H, m), 7.56 (2H, dd, *J* = 7.5, 7.5 Hz), 7.60 (1H, dd, *J* = 7.5, 7.5 Hz), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.82 (1H, d, *J* = 7.5 Hz), 7.97 (1H, d, *J* = 7.5 Hz), 8.03 (1H, d, *J* = 8.3 Hz), 8.04 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6)

δ = 16.3 (2C), 20.5 (2C), 21.9, 23.0, 25.9, 30.9, 33.6, 40.3, 46.4, 64.4, 75.4, 76.6, 82.3, 109.0, 110.2, 118.1, 125.7, 126.4 (2C), 126.8, 128.4, 129.1 (2C), 129.2, 133.7, 134.4, 165.2, 170.2. HR FAB-MS *m*/*z* calcd for $C_{30}H_{34}NO_3$: 456.2539 $[M + H]^+$. Found: 456.2538.

(4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-(–)-Menthyloxycarbonyl]-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole [(4*S*,5*R*)-2c]: oily liquid; $[\alpha]_D^{25}$ –199.6 (*c* 0.5, MeOH); $[\theta]_{220}$ –910 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.72 (3H, d, *J* = 6.9 Hz), 0.83 (3H, d, *J* = 6.9 Hz), 0.86–0.87 (1H, m), 0.92 (3H, d, *J* = 6.9 Hz), 1.05–1.08 (2H, m), 1.37–1.39 (1H, m), 1.50–1.52 (1H, m), 1.63–1.67 (2H, m), 1.88–1.89 (1H, m), 2.07–2.09 (1H, m), 4.77 (1H, ddd, *J* = 4.1, 4.5, 5.5 Hz), 4.78 (1H, d, *J* = 6.9 Hz), 6.64 (1H, d, *J* = 6.9 Hz), 7.49 (1H, d, *J* = 7.5 Hz), 7.53 (1H, dd, *J* = 7.5, 7.5 Hz), 7.57 (2H, dd, *J* = 7.5, 7.5 Hz), 7.59–7.61 (2H, m), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.94 (1H, d, *J* = 8.0 Hz), 7.98 (1H, d, *J* = 7.5 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 8.04 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 16.6 (2C), 20.6 (2C), 22.1, 23.4, 26.1, 31.1, 33.8, 40.5, 46.7, 75.6, 76.0, 81.0, 122.8, 123.1, 125.9, 126.5, 127.0, 128.5, 129.3 (2C), 129.36, 129.39 (2C), 132.8, 133.8 (2C), 164.9, 170.4. HR FAB-MS *m*/*z* calcd for $C_{30}H_{34}NO_3$: 456.2539 $[M + H]^+$. Found: 456.2548.

(4*R*,5*R*)-5-(1-Naphthyl)-2-phenyl-4-[(1*R*,2*S*,5*R*)-(–)-8-phenylmenthyloxycarbonyl]-4,5-dihydro-oxazole [(4*R*,5*R*)-2d]: oily liquid; $[\alpha]_D^{25}$ –115.2 (*c* 0.1, MeOH); $[\theta]_{220}$ –230 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = – 0.37–0.34 (1H, m), 0.35–0.37 (1H, m), 0.43 (3H, d, *J* = 6.3 Hz), 0.70–0.82 (3H, m), 1.00 (3H, s), 1.08 (3H, s), 1.22–1.30 (3H, m), 3.86 (1H, ddd, *J* = 4.1, 5.0, 5.0 Hz), 5.62 (1H, d, *J* = 10.3 Hz), 6.84 (1H, d, *J* = 10.3 Hz), 7.08 (1H, dd, *J* = 7.5, 7.5 Hz), 7.10 (2H, d, *J* = 7.5 Hz), 7.18 (2H, dd, *J* = 7.5, 7.5 Hz), 7.52–7.58 (3H, m), 7.57 (2H, dd, *J* = 7.5, 8.0 Hz), 7.63 (1H, d, *J* = 7.5 Hz), 7.65 (1H, dd, *J* = 7.5, 7.5 Hz), 7.89 (1H, d, *J* = 8.0 Hz), 7.92 (1H, d, *J* = 7.5 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 8.07 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 21.3, 26.8, 27.5, 30.3, 31.4, 33.8, 41.6, 49.9, 50.2, 57.0, 80.8, 91.9, 93.0, 98.9, 99.3, 120.2, 123.6, 124.3, 125.5 (2C), 125.9 (2C), 126.1, 127.9, 129.0 (2C), 130.1 (2C), 132.9, 133.9, 135.6, 140.6, 147.2, 159.6, 160.0, 163.9. Anal. Calcd for $C_{36}H_{37}NO_3$: C, 81.32; H, 7.01; N, 2.63. Found: C, 81.02; H, 7.30; N, 2.28.

(4*S*,5*S*)-5-(1-Naphthyl)-2-phenyl-4-[(1*R*,2*S*,5*R*)-(–)-8-phenylmenthyloxycarbonyl]-4,5-dihydro-oxazole [(4*S*,5*S*)-2d]: oily liquid; $[\alpha]_D^{25}$ +294.4 (*c* 0.1, MeOH); $[\theta]_{220}$ +840 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = – 0.42–0.40 (1H, m), 0.19–0.20 (1H, m), 0.36 (3H, d, *J* = 6.3 Hz), 0.70–0.80 (3H, m), 1.03 (3H, s), 1.13 (3H, s), 1.22–1.30 (3H, m), 4.02 (1H, ddd, *J* = 4.1, 5.0, 5.0 Hz), 4.69 (1H, d, *J* = 10.3 Hz), 6.60 (1H, d, *J* = 10.3 Hz), 7.19 (2H, d, *J* = 7.5 Hz), 7.20 (1H, dd, *J* = 7.5, 7.5 Hz), 7.35 (2H, dd, *J* = 7.5, 7.5 Hz), 7.40 (1H, d, *J* = 7.5 Hz), 7.45 (1H, dd, *J* = 7.5, 7.5 Hz), 7.55 (2H, dd, *J* = 7.5, 7.5 Hz), 7.59 (1H, dd, *J* = 7.5, 7.5 Hz), 7.60–7.67 (2H, m), 7.79 (1H, d, *J* = 8.0 Hz), 7.85 (1H, d, *J* = 7.5 Hz), 7.92 (1H, d, *J* = 8.0 Hz), 8.03 (2H, d, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 21.4, 25.3, 25.8, 27.5, 30.1, 33.9, 38.3, 49.6, 72.0, 74.1, 80.0, 123.5, 124.2, 125.36, 125.40, 125.5 (2C), 126.2, 126.5, 126.8, 128.2 (2C), 128.5 (2C), 128.7, 128.9, 129.2 (2C), 130.7, 132.2, 132.6, 133.6, 135.2, 152.3, 165.3, 168.0. Anal. Calcd for $C_{36}H_{37}NO_3$: C, 81.32; H, 7.01; N, 2.63. Found: C, 81.59; H, 7.40; N, 2.33.

(4*R*,5*S*)-5-(1-Naphthyl)-2-phenyl-4-[(1*R*,2*S*,5*R*)-(–)-8-phenylmenthyloxycarbonyl]-4,5-dihydrooxazole [(4*R*,5*S*)-2d]: oily liquid; $[\alpha]_D^{25}$ +31.8 (*c* 0.5, MeOH); $[\theta]_{220}$ +320 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.86 (3H, d, *J* = 6.3 Hz), 0.89–0.90 (1H, m), 1.07 (3H, s), 1.11 (3H, s), 1.03–1.17 (2H, m), 1.45–1.48 (1H, m), 1.61–1.63 (1H, m), 1.67–1.70 (1H, m), 1.79–1.80 (1H, m), 2.08–2.11 (1H, m), 3.78 (1H, d, *J* = 7.6 Hz), 4.79 (1H, ddd, *J* = 6.9, 6.9, 6.9 Hz), 6.41–6.45 (3H, m), 6.48 (1H, d, *J* = 7.6 Hz), 6.91–6.95 (2H, m), 7.46 (1H, d, *J* = 7.6 Hz), 7.52 (2H, dd, *J* = 7.6, 8.0 Hz), 7.54 (1H, dd, *J* = 7.6, 7.6 Hz), 7.60 (1H, dd, *J* = 7.6, 7.6 Hz), 7.62–7.67 (2H, m), 7.76–7.78 (1H, m), 7.95 (2H, d, *J* = 8.0 Hz), 8.03 (1H, d, *J* = 7.6 Hz), 8.09–8.10 (1H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 21.6, 23.8, 25.9, 28.5, 30.7, 33.9, 39.1, 40.7, 49.3, 75.6, 75.7, 79.2, 80.2, 122.6, 123.5, 124.3, 124.9 (2C), 125.6, 126.24, 126.27, 126.8, 127.3 (2C), 128.2 (2C), 128.9 (2C), 129.1, 129.5, 132.4, 133.6, 134.4, 151.1, 164.0, 169.1. HR FAB-MS *m*/*z* calcd for $C_{36}H_{38}NO_3$: 532.2852 $[M + H]^+$. Found: 532.2847.

(4*S*,5*R*)-5-(1-Naphthyl)-2-phenyl-4-[(1*R*,2*S*,5*R*)-(–)-8-phenylmenthyloxycarbonyl]-4,5-dihydrooxazole [(4*S*,5*R*)-2d]: oily liquid; $[\alpha]_D^{25}$ –18.7 (*c* 0.5, MeOH); $[\theta]_{220}$ –280 deg cm^2 dmol^{-1} (2.0×10^{-5} mol dm^{-3}, MeOH); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 0.83–0.85 (1H, m), 0.88 (3H, d, *J* = 6.2 Hz), 1.04–1.08 (2H, m), 1.17 (3H, s), 1.22 (3H, s), 1.48–1.50 (1H, m), 1.92–1.95 (1H, m), 1.97–2.02 (3H, m), 4.22 (1H, d, *J* = 6.2 Hz), 4.73 (1H, ddd, *J* = 6.8, 6.8, 6.8 Hz), 6.39 (1H, d, *J* = 6.2 Hz), 6.79 (1H, dd, *J* = 7.5, 7.5 Hz), 6.95 (2H, dd, *J* = 7.5, 7.5 Hz), 7.15 (2H, dd, *J* = 7.5, 7.5 Hz), 7.38 (1H, d, *J* = 7.5 Hz), 7.53 (1H, dd, *J* = 7.5, 7.5 Hz), 7.56 (2H, dd, *J* = 7.5, 7.5 Hz), 7.61–7.63 (3H, m), 7.88 (1H, d, *J* = 8.3 Hz), 7.97 (1H, d, *J* = 7.5 Hz), 8.02 (2H, d, *J* = 6.9 Hz), 8.04 (1H, d, *J* = 8.3 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 22.4, 27.0, 27.3, 27.5, 31.5, 34.6, 41.8, 50.4, 75.9, 76.3, 81.4, 123.6, 124.3, 125.5, 126.0 (2C), 126.2, 126.9, 127.1, 127.3, 128.3 (2C), 128.5, 129.0 (2C), 129.66 (2C), 129.69, 129.8, 130.0, 133.1, 134.3, 135.2, 150.9, 165.1, 170.4. HR FAB-MS *m*/*z* calcd for $C_{36}H_{38}NO_3$: 532.2852 $[M + H]^+$. Found: 532.2849.

***cis*-4-*tert*-Butoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2e):** mp 144.0–145.0 °C; IR (KBr) ν/cm^{-1} = 1737, 1649; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.50 (9H, s), 5.48 (1H, d, *J* = 10.3 Hz), 6.81 (1H, d, *J* = 10.3 Hz), 7.51 (1H, d, *J* = 8.2 Hz), 7.54 (1H, dd, *J* = 7.6, 8.2 Hz), 7.58 (1H, dd, *J* = 7.6, 7.6 Hz), 7.58 (2H, dd, *J* = 6.9, 7.6 Hz), 7.62 (1H, dd, *J* = 7.6, 8.2 Hz), 7.66 (1H, dd, *J* = 7.6, 7.6 Hz), 7.93 (1H, d, *J* = 7.6 Hz), 7.98 (1H, d, *J* = 7.6 Hz), 8.07 (2H, d, *J* = 6.9 Hz), 8.11 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 26.4 (3C), 72.5, 80.0, 80.2, 123.1, 124.0, 125.2, 125.9, 126.1, 126.8, 128.1 (2C), 128.31, 128.33, 128.8 (2C), 130.2, 132.1, 132.3, 133.0, 164.8, 167.6. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.30; H, 6.03; N, 3.65.

***trans*-4-*tert*-Butoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2e):** oily liquid; IR (neat) ν/cm^{-1} = 1728, 1647; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.51 (9H, s), 4.65 (1H, d, *J* = 6.2 Hz), 6.61 (1H, d, *J* = 6.2 Hz), 7.50 (1H, d, *J* = 6.9 Hz), 7.54 (1H, dd, *J* = 6.9, 6.9 Hz), 7.58 (2H, dd, *J* = 7.6, 7.6 Hz), 7.60–7.63 (2H, m), 7.67 (1H, dd, *J* = 7.6, 7.6 Hz), 7.97 (1H, d, *J* = 6.9 Hz), 7.97 (1H, d, *J* = 6.9

Hz), 8.03–8.06 (1H, m), 8.06 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ = 27.6 (3C), 76.4, 80.8, 82.1, 122.7, 122.8, 125.5, 126.2, 126.4, 126.6, 128.3 (2C), 128.92, 128.94 (2C), 129.0, 129.1, 132.4, 133.5, 134.7, 164.4, 169.6. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.94; H, 5.96; N, 3.57.

***cis*-4-Methoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2f):** mp 133.0–134.0 °C; IR (KBr) ν/cm^{-1} = 1742, 1646; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ = 2.72 (3H, s), 5.62 (1H, d, *J* = 10.3 Hz), 6.88 (1H, d, *J* = 10.3 Hz), 7.51–7.52 (2H, m), 7.57 (1H, dd, *J* = 7.4, 7.4 Hz), 7.59 (2H, dd, *J* = 7.4, 7.7 Hz), 7.60 (1H, dd, *J* = 7.4, 8.7 Hz), 7.67 (1H, dd, *J* = 7.4, 7.4 Hz), 7.90–7.92 (1H, m), 7.96 (1H, d, *J* = 7.4 Hz), 8.08 (2H, d, *J* = 7.7 Hz), 8.10 (1H, d, *J* = 8.7 Hz); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ = 50.7, 72.7, 80.0, 122.9, 123.6, 125.1, 125.9, 126.2, 126.4, 128.2 (2C), 128.3, 128.4, 128.9 (2C), 129.7, 132.0, 132.3, 132.8, 165.2, 169.0. Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 75.89; H, 5.20; N, 4.48.

***trans*-4-Methoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2f):** mp 108.0–109.0 °C; IR (KBr) ν/cm^{-1} = 1742, 1640; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ = 3.81 (3H, s), 4.89 (1H, d, *J* = 6.9 Hz), 6.70 (1H, d, *J* = 6.9 Hz), 7.52 (1H, d, *J* = 7.4 Hz), 7.54 (1H, dd, *J* = 6.9, 7.4 Hz), 7.57 (2H, dd, *J* = 7.4, 7.4 Hz), 7.62 (1H, dd, *J* = 8.6, 9.2 Hz), 7.62 (1H, dd, *J* = 6.3, 9.2 Hz), 7.67 (1H, dd, *J* = 7.4, 7.4 Hz), 7.98 (1H, d, *J* = 6.9 Hz), 8.00 (1H, d, *J* = 8.6 Hz), 8.04 (1H, d, *J* = 6.3 Hz), 8.05 (2H, d, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ = 53.3, 75.8, 81.2, 123.3, 123.7, 126.1, 126.8, 126.9, 127.4, 128.9 (2C), 129.5 (2C), 129.6, 129.7, 130.0, 133.0, 134.1, 135.0, 165.1, 171.5. Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.14; H, 5.21; N, 4.09.

***cis*-4-*tert*-Butoxycarbonyl-5-(2-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2g):** mp 142.0–143.0 °C; IR (KBr) ν/cm^{-1} = 1736, 1655; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ = 0.77 (9H, s), 5.29 (1H, d, *J* = 11.0 Hz), 6.24 (1H, d, *J* = 11.0 Hz), 7.38 (1H, d, *J* = 8.2 Hz), 7.50–7.53 (2H, m), 7.55 (2H, dd, *J* = 7.6, 7.6 Hz), 7.64 (1H, dd, *J* = 7.6, 7.6 Hz), 7.87 (1H, s), 7.89–7.93 (3H, m), 8.02 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ = 26.8 (3C), 73.3, 80.4, 82.4, 124.4, 125.7, 126.3, 126.5, 126.8, 127.5, 127.7, 127.8, 128.2 (2C), 128.8 (2C), 132.1, 132.4, 132.8, 133.9, 164.7, 167.7. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.83; H, 6.40; N, 3.76.

***trans*-4-*tert*-Butoxycarbonyl-5-(2-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2g):** mp 103.0–104.0 °C; IR (KBr) ν/cm^{-1} = 1730, 1638; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ = 1.47 (9H, s), 4.77 (1H, d, *J* = 7.6 Hz), 5.97 (1H, d, *J* = 7.6 Hz), 7.47 (1H, d, *J* = 8.2 Hz), 7.52–7.55 (4H, m), 7.62 (1H, dd, *J* = 7.6, 7.6 Hz), 7.92–8.01 (6H, m); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ = 27.6 (3C), 76.7, 81.7, 83.2, 123.3, 125.0, 126.57 (2C), 126.64, 127.6, 128.0, 128.2 (2C), 128.8 (2C), 128.9, 132.2, 132.6, 132.8, 136.8, 164.0, 169.5. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.19; H, 6.43; N, 3.87.

***cis*-4-*tert*-Butoxycarbonyl-2,5-diphenyl-4,5-dihydrooxazole (*cis*-2h):** mp 108.0–109.0 °C; IR (KBr)

ν/cm^{-1} = 1748, 1653; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.95 (9H, s), 5.22 (1H, d, J = 10.9 Hz), 6.06 (1H, d, J = 10.9 Hz), 7.29 (2H, d, J = 6.9 Hz), 7.33 (1H, dd, J = 6.9, 6.9 Hz), 7.38 (2H, dd, J = 6.9, 6.9 Hz), 7.54 (2H, dd, J = 7.4, 7.4 Hz), 7.63 (1H, dd, J = 7.4, 7.4 Hz), 7.98 (2H, d, J= 7.4 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 26.9 (3C), 73.1, 80.4, 82.2, 126.7 (2C), 126.8, 128.07 (2C), 128.10 (2C), 128.3, 128.8 (2C), 132.1, 136.5, 164.6, 167.6. Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 73.94; H, 6.21; N, 4.39.

***trans*-4-*tert*-Butoxycarbonyl-2,5-diphenyl-4,5-dihydrooxazole (*trans*-2h):** mp 89.0–90.0 °C; IR (KBr) ν/cm^{-1} = 1734, 1643; ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.47 (9H, s), 4.66 (1H, d, J = 7.4 Hz), 5.88 (1H, d, J = 7.4 Hz), 7.38-7.40 (3H, m), 7.44 (2H, dd, J = 6.9, 7.6 Hz), 7.53 (2H, dd, J = 7.4, 7.4 Hz), 7.62 (1H, dd, J = 7.4, 7.4 Hz), 7.97 (2H, d, J = 7.4 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 27.6 (3C), 76.8, 81.7, 82.9, 125.7 (2C), 126.5, 128.2 (2C), 128.6, 128.8 (2C), 128.9 (2C), 132.2, 139.6, 164.0, 169.4. Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.23; H, 6.25; N, 4.46.

X-Ray crystallographic analysis of (4*S*,5*S*)-2e

A colourless prism (of the molecular formula $C_{24}H_{23}NO_3$) having approximate dimensions of 0.35×0.15×0.10 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation (λ= 0.71069 Å) on a Rigaku RAXIS-RAPID equipped with an imaging plate. Data collection and cell refinement: MSC/AFC diffractometer control. Data reduction: ‘teXsan for windows version 1.06’;[10] ‘Structure solution, SIR92’;[11] ‘Refinement, SHELXL97’.[12]

Crystal data for (4*S*,5*S*)-2e: $C_{24}H_{23}NO_3$, *f*w = 373.45; orthorhombic, space group $P2_12_12_1$ (#19); a = 8.239(3) Å, b = 10.024(4) Å, c = 24.467(9) Å, V = 2020.6(12) Å^3; Z = 4; D_{calc} = 1.228 g cm^{-3}; R = 0.0634, $wR2$ = 0.0582. Crystallographic data (excluding these structure factors) for (4*S*,5*S*)-**2e** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 636944. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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