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Facial Diastereoselectivity in the Photocycloaddition of Chiral *N*-Acyl Enamines to Benzaldehyde

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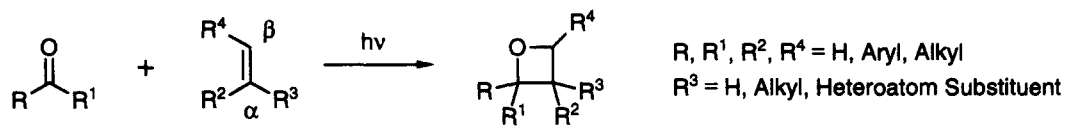
Abstract: The facial diastereoselectivity in the photocycloaddition of the chiral *N*-acyl enamines **5**, **6**, and **7** to benzaldehyde has been studied. The enamide **5** derived from α-phenylethylamine (**8**) gave the corresponding oxetanes in good total yield (74%) but the diastereofacial selection was unsatisfactory (32% *de*). The *N*-vinyl-oxazolidinones **6** and **7** were prepared from the parent chiral 4-phenyl- (**11**) or 4-benzyloxazolidinone (**15**) by vinylation. Their photocycloadditons to benzaldehyde proceeded smoothly and yielded the corresponding oxetanes **12** and **16** (70-80%). A remarkable discrepancy in the course of the reaction was observed. Whereas oxetane formation from **6** proceeded with low diastereoselectivity (30% *de*) the Paternò-Büchi reaction of compound **7** gave predominantly one diastereoisomer **16a** (62% *de*) the relative configuration of which was opposite to the major diastereomer **12a** obtained from oxazolidinone **6**.

INTRODUCTION

The Paternò-Büchi reaction has been developed during the last 30 years into a reliable method for the construction of substituted oxetanes.[3] In the course of the reaction up to three new stereogenic centers are formed. Recently, there has been a continuing interest in the synthesis of diastereomerically pure oxetanes and the search for suitable combinations of carbonyl compounds and alkenes which guarantee high simple diastereoselectivities is a vital area of preparative organic photochemistry.[4] Another stereochemical aspect currently being addressed with regard to oxetane formation deals with the facial diastereoselectivity of the photocycloaddition reaction. Either reaction partner, the carbonyl compound or the alkene, can carry a chiral substituent. From the general picture drawn in scheme 1 three different positions emerge where such a substituent may be placed.



Scheme 1.

The substituent R or R^1 at the carbonyl compound may be chiral. Indeed, a modification at this site has lead to successful control of the facial diastereoselectivity in some cases. Phenylglyoxylates (**1**) which are derived from chiral alcohols were shown to be excellent substrates for the photocycloaddition with a variety of alkenes.[5]

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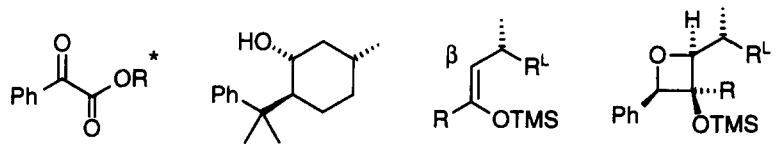
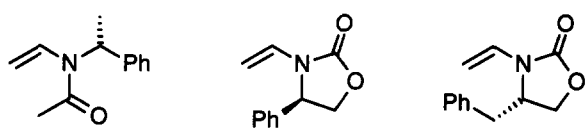
Depending on the facial bias exerted by the auxiliary they yield the corresponding oxetanes with modest to excellent diastereomeric excess. The initial experiments by Gotthardt and Lenz[6] who employed menthol as the chiral alcohol were succeeded by a systematic study carried out by Scharf and co-workers. Their work established concave alcohols such as 8-phenylmenthol (**2**) as superior auxiliaries for the Paternò-Büchi reaction of phenylglyoxlates.[7] Pantolactone frequently used for auxiliary induced diastereoselective transformations[8] proved to be less powerful.[9] Interestingly, chiral glyoxylates and methylglyoxylates underwent oxetane formation with achiral alkenes only in low diastereoselectivities.[7d,10] Attempts by Schreiber et al. to use chiral aliphatic aldehydes in the Paternò-Büchi reaction have encountered no success in terms of facial diastereoselection.[11] A similar lack of face discrimination was observed with chiral acyl cyanides.[12]



1 **2** **3** **4**

Figure 1. Structures of compounds **1-4**

The alkene (scheme 1) offers two positions (α- and β-site) where a chiral substituent can be installed. Provided that R^2 and R^4 are connected the resulting cyclic chiral alkenes exhibit good facial diastereoselectivity as free rotation around single bonds is prohibited. In general, an approach of the achiral carbonyl compound occurs from the less shielded face of the cyclic alkene[13] although an exception has been reported.[14] Attempts to induce a facial diastereoselection in acyclic systems have seen minor success if the α-substituent (R^2 or R^3 in scheme 1) was chosen to be chiral. In some examples the substituents were attached to the alkene via a oxygen[15] or a carbon chain.[16] Even alkenes in which the stereogenic center (R^3) was directly bound to the olefinic α-carbon atom exhibited diastereoselectivites which were not fully satisfactory.[17] The only reported examples in which significant facial diastereoselectivities were achieved are concerned with silyl enol ethers which carry a chiral substituent in β-position (**3**).[18] Due to the 1,3-allylic strain[19] free rotation is apparently restricted in these systems and the approach of the photoexcited carbonyl compound is directed to the less shielded face. With large (R^L = $SiMe_2Ph$, *t*-Bu) and polar (R^L = OAlkyl) substituents at the stereogenic center the face selection is good to excellent and the diastereomerically pure oxetanes **4** are obtained.



5 **6** **7**

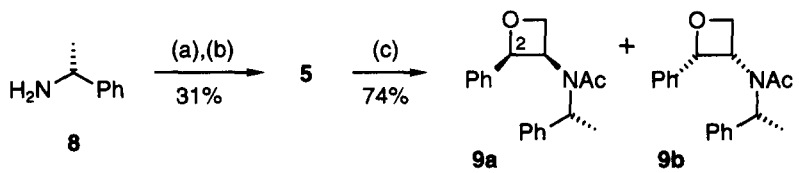
Figure 2. Structures of compounds **5-7**

The study described below has been concerned with the photocycloaddition of chiral *N*-acyl enamines **5**, **6** and **7** to benzaldehyde and the facial diastereoselectivity of this reaction. In earlier experiments we have demonstrated that α-unsubstituted *N*-acyl enamines (enamides) add to aldehydes with good simple diastereoselectivity (d.r. = >85/15).[20] The corresponding *cis*-3-*N*-acylaminooxetanes thus obtained are versatile

starting materials for the synthesis of *syn*- and *anti*-1,2-aminoalcohols.[21] In addition, a naturally occuring *cis*-3-aminooxetane, the antibiotic (±)-oxetin, was prepared in a stereoselective fashion employing this methodology.[22] Based on these results the problem of regio- and simple diastereoselectivity appeared to be solved and the question of facial diastereoselectivity has been addressed.

RESULTS AND DISCUSSION

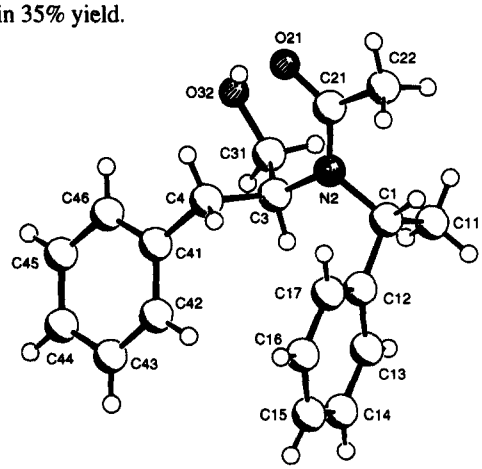
Preparation and Photocycloaddition of Enamide 5. As a cheap source of chiral information (*R*)-(+)-α-phenylethylamine (**8**) was selected. The conventional enamide synthesis[23] we employed started from an amine and, consequently, compound **8** was directly used. After condensation with acetaldehyde the acylation with acetic anhydride led to the desired *N*-acyl enamine **5** in 31% overall yield (scheme 2). The low yield was due to the formation of the corresponding parent acetamide during the acylation which could not be avoided (see experimental).

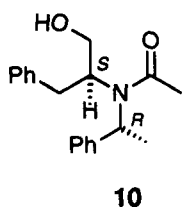


(a) MeCHO, KOH, 5-10 °C; (b) Ac_2O, NEt_3, 10 °C → 80 °C (PhH); (c) PhCHO, hv (MeCN).

Scheme 2.

Upon irradiation of enamide **5** in the presence of benzaldehyde we observed two major diastereoisomeric oxetanes **9a** and **9b** in a ratio of 2/1 (32% *de*) the *cis*-configuration of which was deduced from their ^{1}H-NMR spectra. A minor third isomer presumably with *trans*-configuration was detected by GLC. The complete separation of the two major isomers was not possible but we succeeded in isolating the prevailing diastereoisomer **9a** in 35% yield.

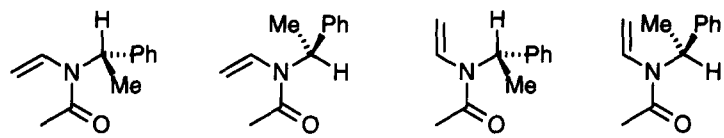




10

Figure 3. A molecule of compound **10** in the crystal[24]

The relative configuration of oxetane **9a** was elucidated after hydrogenolysis.[25] Treatment with hydrogen in the presence of Pd/C (MeOH) led to the selective cleavage of the O-C(2) bond and yielded the protected amino alcohol **10** (85%). Single crystal X-ray analysis revealed the (*R,S*)-stereochemistry of the product as depicted in figure 3. From this data the structure of oxetane **9a** can be deduced as shown in scheme 2. Apparently, the attack of the photoexcited carbonyl compound has occured from the *Si* face of the alkene. Possible conformations of the enamide **5** are shown in figure 4. In order to account for the observed discrimination the two conformations **5'** and **5''''** have to be considered. Both of them lead to the correct product configuration if the aldehyde attack is to occur from the face of the methyl group. Based on force field calculations (PC model)[26] the conformation **5'** appears to be the favored one whereas conformation **5''''** represents an energetically more costly arrangement. Both conformations **5''** and **5'''** are only 2 kJ mol^{-1} remote in energy from conformation **5'**. The low diastereoselectivity of the reaction may therefore be due to the low barrier of free rotations depicted in figure 4.

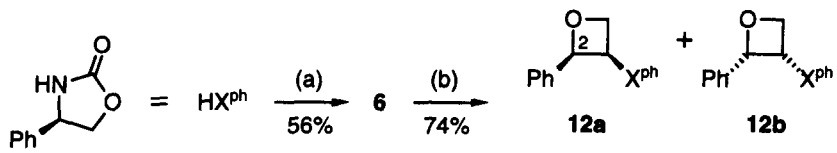


5' **5''** **5'''** **5''''**

Figure 4. Possible Conformations of Enamide **5**

These arguments, however, are valid only if it is assumed that the steric situation in the intermediate 1,4-biradicals resembles the alkene ground state (*vide infra*). Compared to earlier studies on the [2+1]-carbene addition of related *N*-carbamoyl enamines[27] the face selectivity in our case is more pronounced. Still, it is preparatively not satisfactory.

Preparation and Photocycloaddition of Enamide 6. The enamide **6** is derived from oxazolidinone **11** and was prepared by *N*-vinylation of the corresponding heterocycle (scheme 3).[27b] The oxazolidinone in turn was prepared by conventional synthesis from the commercially available (*R*)-phenylglycinol. According to earlier studies[27b] and according to force field calculations[26] the vinyl group attached to the nitrogen atom of the oxazolidinone is preferably in a transoid arrangement as shown in figure 2.



11 **12a** **12b**

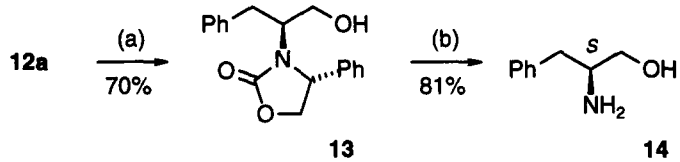
\+ *trans* isomers (**12c, 12d**)

(a) MeCH(OEt)$_2$, CSA, 55 °C; ΔT (200-250 °C). (b) PhCHO, hv, 30 °C (MeCN).

Scheme 3.

Irradiation of *N*-vinyloxazolidinone **6** and benzaldehyde yielded oxetanes in good overall yields (74%). The diastereoselectivity was not equally satisfying. Four products were obtained the separation of which was not fully possible by flash chromatography. Still, we were able to isolate all four diastereoisomers in pure form in yields of

28%, 18%, 6% and 6% for **12a**, **12b**, **12c** and **12d**, respectively. The relative configuration of the stereogenic centers within the ring was elucidated by ^{1}H-NMR NOE studies. Both **12a** and **12b** showed strong contact between the proton at C(2) and the proton at C(3) which is evidence for a *cis*-arrangement. From the ratio of isomers in the crude product mixture which was determined by GLC the diastereomeric ratio (**12a**,**12b**/**12c**,**12d**) which reflects the simple diastereoselectivity is 84/16. The ratio **12a**/**12b** is a measure for the facial diastereoselectivity and amounted to the disappointing value of 65/35 (30% *de*). The configuration of the major product **12a** was further elucidated by degradation studies. To this end, the oxetane ring was opened by hydrogenolysis and the corresponding alcohol **13** was furthed reduced with lithium in liquid ammonia (scheme 4). Based on the specific optical rotation $[\alpha]_D$ the obtained phenylalaninol (**14**) proved to be the (*S*)-enantiomer.



(a) H_2, Pd/C, 25 °C (MeOH); (b) Li, -78 °C (NH_3).

Scheme 4.

Additional proof for the relative configuration of alcohol **13** came from single crystal X-ray analysis. The structure obtained is depicted in figure 5 and confirmed the stereochemical assignment.

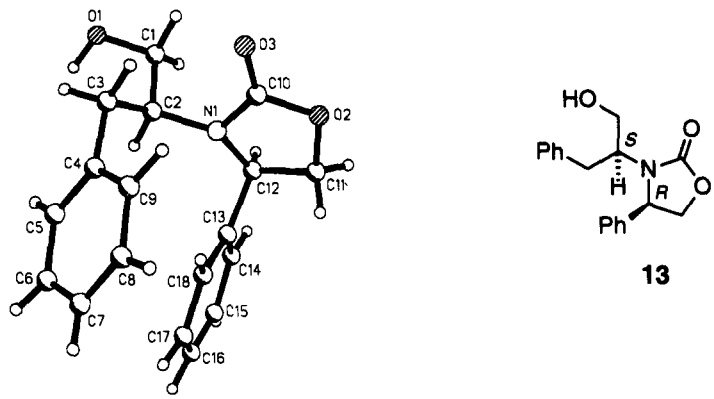
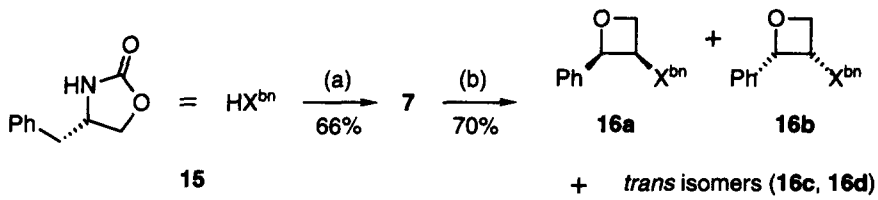


Figure 5. A molecule of compound **13** in the crystal[28]

The formation of the major diastereoisomer in the photocycloaddition of benzaldehyde to alkene **6** can be understood on the basis of the preferred conformation depicted in figure 2. Attack from the *Re*-face predominates as the phenyl group shields the *Si*-face. However, the facial diastereoselectivity is much lower than the one generally observed employing oxazolidinone **11** as auxiliary.[29] In order to find out whether this imbalance is due to steric or electronic factors we studied the Paternò-Büchi reaction of the related enamide **7**. The benzyl group is considered to be smaller than the phenyl group and it was thus expected to exert an even less pronounced steric bias.

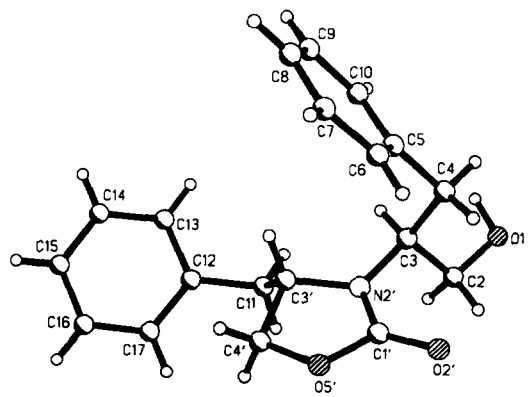
Preparation and Photocycloaddition of Enamide 7. The preparation of enamine **7** started from oxazolidinone **15**[30] and followed the previously outlined vinylation protocol. Upon irradiation in the presence of benzaldehyde oxetanes were formed. To our surprise one isomer strongly prevailed and this isomer (**16a**) could be isolated in 58% yield. The GLC of the crude product mixture exhibited a peak close to the signal which was due to diastereoisomer **16a**. We assigned this peak tentatively to the diastereoisomer **16b** which differs from **16a** in the absolute configuration of the stereogenic centers within the oxetane ring. The isomer **16b** was isolated in 11% yield. This picture is consistent with the ^{1}H-NMR spectrum which revealed the presence of the other two minor diastereoisomers. The diastereomeric ratio **16a/16b** was determined by integration (^{1}H NMR) to be 81/19 (62% *de*). The influence of the temperature on the diastereoselectivity observed in the photocycloaddition reaction was not significant. For preparative purposes an irradiaton at lower temperature proved advantageous.

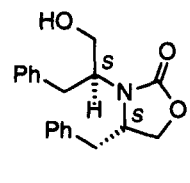


(a) $MeCH(OEt)_2$, CSA, 55 °C; ΔT (200-250 °C). (b) PhCHO, hv, -30 °C (MeCN).

Scheme 5.

The relative configuration of compound **16a** was deduced from degradation by hydrogenolysis as described for the phenyl derivative (78%) and subsequent single crystal X-ray analysis. It came as a big surprise to us that the relative configuration of the alcohol **17** obtained from the major diastereoisomer **16a** was opposite to the one of the analogous alcohol **13** studied in the previous example. In other words, the absolute configuration of the stereogenic centers within the oxetane are identical in the major diastereoisomers **16a** and **12a** despite the fact that the absolute configurations of the auxiliaries **15** and **11** are opposite to each other.





17

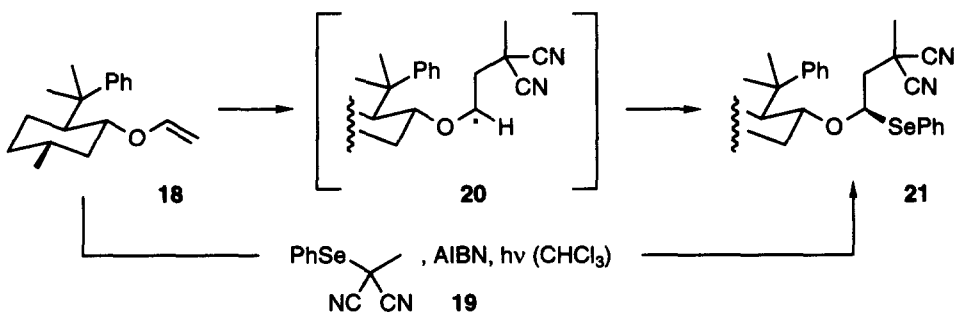
Figure 6. A molecule of compound **17** in the crystal[31]

We secured the identity of the crystal by dissolving it in $CDCl_3$ and running a ^{1}H-NMR spectrum which proved to be completely identical with the spectrum of alcohol **17** obtained from oxetane **16a** in a separate

experiment. We need to conclude that the degree of facial diastereoselectivity in the benzyl case (**7**) is higher than in the phenyl case (**6**) and, more importantly, that the relative direction of the face selectivity induced by oxazolidinone **11** is opposite to the one induced by oxazolidinone **15**.

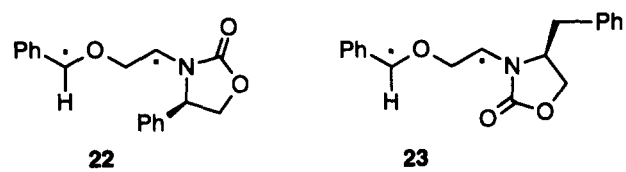
Experiments with other Aldehydes. In earlier studies it was shown that other aromatic aldehydes may be employed in the photocycloaddition to *N*-acyl enamines and related electronrich alkenes.[3,4,22] Aliphatic aldehydes, however, appear unsuited for these reactions. Attempts to react acetaldehyde and other aliphatic carbonyl compounds in a fashion analogous to that described for benzaldehyde remained unsuccessful and gave only low yields of the corresponding oxetane. It can be assumed that the singlet state is not quenched efficiently because the concentration of the alkene is comparably low. In the triplet manifold the well-documented reactions of aliphatic aldehydes[4d] (Norrish type cleavage, hydrogen abstraction) take over and inhibit oxetane formation.

Discussion of Results and Conclusion. It has been noted in previous studies that the conformations of an alkene from which a radical is formed are not neccesarily directly related for the observed facial diastereoselectivity. An example can be found in the reaction of chiral α-alkoxy radicals.[32] The enol ether **18** derived from 8-phenylmenthol exists as a mixture of *s-trans* and *s-cis* isomers. Although there is a ground state preference for the *s-trans* isomer the reaction with the selenomalonitrile **19** gave predominantly product **21** the formation of which can be best understood as if it is derived of an intermediate *s-cis* radical **20**. The authors concluded that a more product like model may prove useful to explain the facial diastereoselectivity.



Scheme 6.

Based on related arguments it is likely that the predominant conformations from which oxetane ring closure occurs differ for the apparently similar 1,4-biradicals[33] **22** and **23** (scheme 7).



Scheme 7.

To the best of our knowledge there are no data available as to the structure of chiral α-amino radicals and we therefore do not want to speculate at present about possible reasons for the face discrimination. Still, it is

important to note that the model applied earlier to predict favored radical conformations may be successfully applied to the reactions of vinyl oxazolidinone **6** and *N*-acyl enamine **5**. It fails, however, completely for the case of vinyl oxazolidinone **7**. Further studies with regard to the facial diastereoselectivity of chiral α-amino radicals in addition reaction and of chiral enamides in Paternò-Büchi reactions are in progress in our laboratory.

EXPERIMENTAL

General. All reactions involving water sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. Irradiation experiments were performed in degassed solvents under Ar. Acetonitrile, triethylamine and dichloromethane were distilled from calcium hydride. Benzene was distilled from sodium/benzophenone. Common solvents (pentane, *t*-butylmethylether) used for chromatography were distilled prior to use. All other reagents and solvents were used as received. - Melting points: Reichert hot bench (uncorrected). - Specific rotations $[\alpha]_D$ were determined at room temperature (25 °C) on a Perkin-Elmer 241 polarimeter. - IR: Bruker IFS 88 FT-IR. - MS: Varian CH7 (EI), Varian Saturn II ion trap instrument (GC/MS). - ^1H and ^{13}C NMR: Bruker AC-300, and Bruker AM-400. Chemical shifts are reported relative to tetramethylsilane as an internal reference. $CDCl_3$ was used as solvent unless noted otherwise. The multiplicities of the ^{13}C-NMR signals were determined with APT puls sequences. - Elemental analyses: Varian Elementar vario EL. - TLC: glass-backed plates (Merck 0.25 mm silica gel 60-F); eluent given in brackets, a pentane (PE) / *t*-butylmethylether (TBME) mixture was used unless stated otherwise; detection by UV or by coloration with ceric ammonium molybdate (CAM). - Flash chromatography[34] (FC): Merck silica gel 60 (230-400 mesh) (50 g for 1 g of material to be separated).

(R)-(+)-N-(1-Phenylethyl)-N-vinylacetamide (5). To a solution of 125 mmol (*R*)-(+)-*N*-(1-phenylethyl)ethylidene amine[27a] (18.4 g) and 125 mmol triethylamine (12.7 g, 17.4 mL) in 50 mL dry benzene 125 mmol of acetic anhydride (12.8 g, 11.7 mL) were added at 5-8 °C. After the addition was complete the mixture was stirred for another hour at ambient temperature. The solvent was removed under atmospheric pressure and the crude product was distilled in vacuo (120-130 °C, 0.3 mmbar). The distilled product was further purified by flash chromatography with PE/TBME (90/10). Yield: 7.3 g (31%). R_f = 0.60 (40/60). $[\alpha]_D$ = 55.4 (c = 2.5, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w, $C_{ar}H$), 3005 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2920 (w, $C_{al}H$), 1660 (vs, C=O), 1630 (vs, C=C), 1470 (m), 1440 (m), 1415 (m), 1365 (s), 1310 (s), 1220 (m), 1195 (m), 1080 (m), 1050 (m), 1020 (m), 780 (m), 760 (m), 705 (m), 690 (s). - ^1H NMR (300 MHz): δ = 1.40 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 2.23 (s, 3 H, $COCH_3$), 4.53 (d, ^3J = 15.8 Hz, 1 H, *CH*HCHN), 4.56 (d, ^3J = 9.1 Hz, 1 H, CH*H*CHN), 6.12-6.18 (m, 1 H, *CH*Me), 6.22-6.43 (m, 1 H, *CH*CH_2), 7.15-7.41 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 15.7 (q, $CHCH_3$), 22.9 (q, $COCH_3$), 50.2 (d, *C*HMe), 104.2 (t, $CHCH_2$), 126.4 (d, $C_{ar}H$), 126.8 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 131.7 (d, *C*HCH_2), 140.6 (s, C_{ar}), 169.7 (s, *C*OMe). - MS (IT), *m/z* (%): 189 (43) [M^+], 146 (22) [M^+ - Ac], 130 (12), 105 (100) [$C_7H_6Me^+$], 86 (18), 77 (12), 43 (29). - Anal. Calcd. for $C_{12}H_{15}NO$ (189.3): C, 76.16; H, 7.99; N, 7.40; found: C, 75.95; H, 7.89; N, 7.61.

As major product the corresponding *N*-(1-Phenylethyl)acetamide was identified. The compound is significantly more polar [R_f = 0.26 (40/60)] than the desired product and, consequently, the separation by flash chromatography was facile.

(+)-N-(1-Phenylethyl)-N-(2-phenyloxetan-3-yl)acetamide (9a). (General Procedure A) A quartz tube was charged with 1.5 mmol of benzaldehyde (159 mg, 152 μL), 3 mmol of enamide **5** (570 mg) and 10 mL of

acetonitrile. The sample was irradiated at 300 nm (RPR 3000 Å) in an air-cooled merry-go-round unit (temperature: ca. 30 °C). The reaction was monitored by TLC and GC. After complete consumption of the aldehyde (24 h) the irradiation was stopped. The diastereomeric ratio was determined by ^{1}H-NMR analysis of the crude product mixture. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography with PE/TBME (90/10 → 70/30). The total yield of oxetanes **9** a complete separation of which was not possible amounted to 74%. Collection of the fractions which contained only the major diastereoisomer and evaporation in vacuo yielded 155 mg (35%) of compound **9a**. R_f = 0.41 (40/60). $[\alpha]_D$ = 90.0 (c = 1.1, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w, $C_{ar}H$), 3010 (m, $C_{ar}H$), 2950 (w, $C_{al}H$), 2900 (s, $C_{al}H$), 2830 (w), 1640 (vs, C=O), 1480 (m), 1435 (s), 1305 (s), 1280 (m), 1225 (m), 1030 (m), 980 (s, COC), 740 (s), 695 (vs). - ^{1}H NMR (300 MHz): δ = 1.14 (d, ^3J = 6.7 Hz, 3 H, CHC*H*$_3$), 1.98 (s, 3 H, COC*H*$_3$), 3.71 (virt. t, $^2J \cong {}^3J$ = 7.6 Hz, 1 H, OC*H*H), 4.60 (virt. t, $^2J \cong {}^3J$ = 8.1 Hz, 1 H, OCH*H*), 4.82 (q, ^3J = 6.7 Hz, 1 H, C*H*CH$_3$), 5.37 (virt. q, $^3J \cong$ 8.3 Hz, 1 H, CHN), 5.90 (d, ^3J = 7.4 Hz, 1 H, C*H*Ph), 6.98-7.09 (m, 2 H, arom. H), 7.19-7.46 (m, 8 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 18.7 (q, CH*C*H$_3$), 22.2 (q, CO*C*H$_3$), 54.5 (d, *C*HMePh), 54.5 (d, CHN), 71.6 (t, OCH$_2$), 87.9 (d, *C*HPh), 126.0 (d, $C_{ar}H$), 126.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 138.1 (s, C_{ar}), 139.6 (s, C_{ar}), 171.2 (s, CO). - MS (EI, 70eV), *m/z* (%): 295 (12) [M$^+$], 265 (20) [M$^+$ - CH_2O], 252 (18) [M$^+$ - COMe], 235 (21), 220 (19), 204 (28), 189 (51) [M$^+$ - PhCHO], 160 (51), 149 (60), 119 (80), 105 (100) [$C_7H_6Me^+$], 85 (99), 84 (97), 77 (14), 57 (84), 51 (92). - Anal. Calcd. for $C_{19}H_{21}NO_2$ (295.384): C, 77.26; H, 7.17; N, 4.74; found: C, 77.04; H, 7.41; N, 4.70.

(+)-N-(1-Hydroxymethyl-2-phenylethyl)-N-(1-phenylethyl)acetamide (10). (General Procedure B) 0.5 mmol oxetane **9a** (148 mg) was dissolved in 5 ml of methanol and 50 mg Pd/C [10% w/w] was added to the solution. The hydrogenolysis was carried out in a conventional hydrogenation apparatus at ambient temperature and atmospheric pressure. The progression of the reaction was indicated by the volume of consumed hydrogen and was further monitored by TLC. After the reaction was complete the mixture was filtered and the solvent removed in vacuo. The residue was purified by flash chromatography with PE/TBME (70/30). Yield: 104 mg (70%). R_f = 0.15 (40/60). $[\alpha]_D$ = 27.0 (c = 0.8, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3420 cm^{-1} (s, OH), 3060 (w, $C_{ar}H$), 3025 (m, $C_{ar}H$), 2980 (m, $C_{al}H$), 2940 (s, $C_{al}H$), 2855 (w, $C_{al}H$), 1620 (vs, C=O), 1455 (s), 1380 (m), 1240 (w), 1150 (w), 1145 (m), 765 (m), 715 (s). - ^{1}H NMR (300 MHz): δ = 1.56 (d, ^3J = 7.0 Hz, 3 H, CHC*H*$_3$), 2.01 (dd, ^2J = 12.9 Hz, ^3J = 3.2 Hz, 1 H, C*H*HPh), 2.41 (s, 3 H, COCH$_3$), 3.01-3.03 [m, 1H, (CH$_2$)$_2$C*H*], 3.55-3.64 (m, 3H, C*H*$_2$OH, CH*H*Ph), 5.18 (q, ^3J = 7.0 Hz, 1 H, C*H*CH$_3$), 6.56-6.58 (m, 2 H, arom. H), 7.07-7.09 (m, 3 H, arom. H), 7.40-7.50 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 17.2 (q, CH*C*H$_3$), 23.4 (q, CO*C*H$_3$), 34.5 (t, *C*H$_2$Ph), 57.4 (d, *C*HMePh), 60.4 (d, CHN), 63.9 (t, CH$_2$OH), 126.0 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 128.8 (d, $C_{ar}H$), 129.9 (d, $C_{ar}H$), 138.7 (s, C_{ar}), 138.9 (s, C_{ar}), 172.2 (s, CO). - MS (EI, 70eV), *m/z* (%): 296 (2) [M$^+$ - 1], 224 (3), 206 (3) [M$^+$ - C_7H_7], 164 (26), 105 (100) [$C_7H_6Me^+$], 91 (27) [$C_7H_7^+$], 77 (24), 43 (29). - Anal. Calcd. for $C_{19}H_{23}NO_2$ (297.400): C, 76.73; H, 7.80; N, 4.71; found: C, 76.50; H, 7.79; N, 4.86.

4-Phenyl-3-(2-phenyloxetan-3-yl)oxazolidin-2-one (12). The reaction was carried out as above (General Procedure A) employing 3 mmol of *N*-vinyloxazolidinone **11**[27b] (570 mg). The total yield of oxetane **12** after flash chromatography with PE/TBME (90/10 → 70/30) amounted to 327 mg (74%). The separation remained incomplete, but it was possible to obtain fractions which contained diastereomerically pure material.

Major cis isomer (–)-12a. Yield: 124 mg (28%). R_f = 0.70 (40/60). $[\alpha]_D$ = –74.1 (c = 6.5, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2900 (m, $C_{al}H$), 1745 (vs, C=O), 1455 (w), 1415 (m), 1245 (sh), 1230 (m), 1035 (m), 1030 (m), 960 (m, COC), 745 (m), 715 (m). - ^{1}H NMR (300 MHz): δ = 3.77 (dd, ^2J = 3.8 Hz, ^3J = 8.4 Hz, 1 H, C*H*HCHPh), 3.83 (virt. t, $^2J \cong {}^3J$ = 8.4 Hz, 1 H, CH_2C*H*Ph), 4.13 (dd, ^2J = 3.8 Hz, ^3J = 8.4 Hz, 1 H, CH*H*CHPh), 4.34 (virt. t, $^2J \cong {}^3J$ = 7.4 Hz, 1 H, C*H*HO), 4.60 (dd, ^2J = 7.4 Hz, ^3J = 8.4 Hz, 1 H, CH*H*O), 5.47 (virt. q, $^3J \cong {}^3J$ = 7.4 Hz, ^3J = 8.4 Hz, 1 H, CHN), 6.00 (d, ^3J = 7.4 Hz, 1 H, C*H*Ph), 7.02-7.05 (m, 2 H, arom. H), 7.32-7.50 (m, 8 H, arom. H). - NOE (400 MHz): H (5.47): $H_{4.60}$ [8 %], $H_{6.00}$ [14 %]; H (6.00): $H_{5.47}$ [16 %]. - ^{13}C NMR (75.5 MHz): δ = 51.0 (d, *C*HPh_{ox}), 58.3 (d, CHN), 70.5 (t, *C*H_2CHPh_{ox}), 71.6 (t, CH_2O), 87.2 (d, *C*HPh), 124.7 (d, $C_{ar}H$), 125.3 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 129.4 (d, $C_{ar}H$), 138.0 (s, C_{ar}), 140.5 (s, C_{ar}), 157.8 (s, CO). - MS (EI, 70eV), *m/z* (%): 266 (0.5) [M^+ + 1 - CH_2O], 265 (3) [M^+ - CH_2O], 189 (78), 130 (22), 104 (44), 92 (40), 54 (100), 28 (7). - Anal. Calcd. for $C_{18}H_{17}NO_3$ (295.341): C, 73.20; H, 5.80; N, 4.74; found: C, 72.90; H, 5.46; N, 4.70.

Minor cis isomer (–)-12b. Yield: 77 mg (18%). R_f = 0.35 (40/60). $[\alpha]_D$ = –17.0 (c = 5.6, CH_2Cl_2) - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2965 (m, $C_{al}H$), 2895 (m, $C_{al}H$), 1735 (vs, C=O), 1455 (w), 1430 (m), 1240 (m), 1240 (m), 1045 (m), 1000 (m), 965 (m, COC), 740 (m), 700 (m). - ^{1}H NMR (300 MHz): δ = 3.81 (dd, ^2J = 4.3 Hz, ^3J = 8.5 Hz, 1 H, C*H*HCHPh), 3.90 (dd, ^2J = 4.3 Hz, ^3J = 8.5 Hz, 1 H, CH*H*CHPh), 4.08 (virt. t, $^2J \cong {}^3J$ = 8.5 Hz, 1 H, CH_2C*H*Ph), 4.50 (virt. q, $^3J \cong {}^3J$ = 6.8 Hz, ^3J = 8.0 Hz, 1 H, CHN), 4.92 (dd, ^2J = 7.5 Hz, ^3J = 8.0 Hz, 1 H, C*H*HO), 5.68 (m, 2 H, CH*H*O, C*H*Ph), 7.00-7.03 (m, 2 H, arom. H), 7.26-7.53 (m, 8 H, arom. H). - NOE (400 MHz): H (4.50): $H_{4.92}$ [9 %], $H_{5.68}$ [14 %]; H (5.68): $H_{4.92}$ [30 %], $H_{4.50}$ [10 %]. - ^{13}C NMR (75.5 MHz): δ = 51.9 (d, *C*HPh_{ox}), 59.5 (d, CHN), 69.6 *C*H_2CHPh_{ox}), 70.9 (t, CH_2O), 86.3 (d, *C*HPh), 126.7 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 137.4 (s, C_{ar}), 137.7 (s, C_{ar}), 157.9 (s, CO). - MS (EI, 70eV), *m/z* (%): 265 (4) [M^+ - CH_2O], 189 (100), 130 (20), 104 (40), 92 (55), 54 (81), 28 (28).

Major trans isomer. Yield: 28 mg (6%). R_f = 0.18 (40/60). $[\alpha]_D$ = –24.0 (c = 3.2, CH_2Cl_2) - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2970 (m, $C_{al}H$), 2925 (m, $C_{al}H$), 1730 (vs, C=O), 1455 (w), 1430 (m), 1230 (m), 1045 (m), 965 (m, COC), 755 (m), 715 (m). - ^{1}H NMR (300 MHz): δ = 4.19 (dd, ^2J = 5.4 Hz, ^3J = 8.8 Hz, 1 H, C*H*HCHPh), 4.52-4.76 (m, 3 H, CH_2C*H*Ph, CH*H*CHPh, CHN), 4.92-5.03 (m, 2 H, CH_2O), 5.63 (d, ^3J = 6.7 Hz, 1 H, C*H*Ph), 7.10-7.14 (m, 2 H, arom. H), 7.25-7.40 (m, 8 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 56.2 (d, *C*HPh_{ox}), 59.5 (d, CHN), 70.1 (t, *C*H_2CHPh_{ox}), 70.2 (t, CH_2O), 85.7 (d, *C*HPh), 125.7 (d, $C_{ar}H$), 126.6 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 129.3 (d, $C_{ar}H$), 138.9 (s, C_{ar}), 139.6 (s, C_{ar}), 159.5 (s, CO). - MS (EI, 70eV), *m/z* (%): 266 (5) [M^+ + 1 - CH_2O], 265 (34) [M^+ - CH_2O], 189 (100), 130 (25), 104 (53), 92 (38), 77 (16), 54 (81), 28 (68).

Minor trans isomer. Yield: 24 mg (6%). R_f = 0.25 (40/60). $[\alpha]_D$ = –34.3 (c = 0.9, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2970 (m, $C_{al}H$), 2925 (m, $C_{al}H$), 1730 (vs, C=O), 1455 (w), 1430 (m), 1230 (m), 1045 (m), 965 (m, COC), 755 (m), 715 (m). - ^{1}H NMR (300 MHz): δ = 4.18 (dd, ^2J = 5.9 Hz, ^3J = 8.7 Hz, 1 H, C*H*HCHPh), 4.49 (m, 1 H, CH_2C*H*Ph), 4.65-4.76 (m, 2 H, CH*H*CHPh, C*H*HO), 4.93 (dd, ^2J = 5.7 Hz, ^3J = 8.7 Hz, 1 H, CH*H*O), 5.29 (m, 1 H, CHN), 5.96 (d, ^3J = 5.8 Hz, 1 H, C*H*Ph), 7.24-7.37 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 56.2 (d, *C*HPh_{ox}), 60.2 (d, CHN), 70.3 (t, *C*H_2CHPh_{ox}), 70.4 (t, CH_2O), 86.0 (d, *C*HPh), 125.9 (d, $C_{ar}H$), 126.6 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 129.2 (d, $C_{ar}H$), 129.5 (d,

$C_{ar}H$), 138.7 (s, C_{ar}), 139.7 (s, C_{ar}), 157.6 (s, CO). - MS (EI, 70eV), *m/z* (%): 265 (18) [M^+ - CH_2O], 189 (68), 133 (38), 130 (32), 105 (100), 91 (33), 77 (44), 54 (86), 28 (33).

(–)-3-[2-(1-Hydroxy-3-phenylpropyl)]-4-phenyloxazolidin-2-one (13). The hydrogenolysis of 0.5 mmol of oxetane **12a** (148 mg) was conducted as described above (General Procedure B). Purification by flash chromatography with PE/TBME (70/30) as eluent yielded 105 mg (70%) of the desired compound. R_f = 0.24 (10/90). $[\alpha]_D$ = –35.4 (c = 0.9, CH_2Cl_2). m.p.: 135-136 °C. - IR (KBr): $\tilde{\nu}$ = 3390 cm^{-1} (s, OH), 3085 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2970 (w, $C_{al}H$), 2875 (w, $C_{al}H$), 1715 (vs, C=O), 1475 (w), 1460 (m), 1350 (m), 1265 (w), 1235 (m), 1100 (m), 1080 (m), 760 (m), 705 (s). - ^1H NMR (300 MHz): δ = 2.99 (d, ^3J = 7.8 Hz, 2 H, CH_2Ph), 3.52-3.65 (m, 2H, $CHCH_2Ph$, CHPh), 3.76 (dd, ^2J = 7.7 Hz, ^3J = 11.1 Hz, 1 H, CHHCHPh), 4.09 (dd, ^2J = 7.7 Hz, ^3J = 8.7 Hz, 1 H, CHHCHPh), 4.52 (virt. t, $^2J \cong {}^3J$ = 8.8 Hz, 1 H, CHHOH), 4.87 (virt. t, $^2J \cong {}^3J$ = 8.8 Hz, 1 H, CHHOH), 7.01-7.33 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 34.5 (t, CH_2Ph), 57.9 (d, CHN), 61.7 (d, CH_2CHPh), 63.2 (t, CH_2CHPh), 70.4 (t, CH_2OH), 126.5 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 129.2 (d, $C_{ar}H$), 137.8 (s, C_{ar}), 138.0 (s, C_{ar}), 149.0 (s, CO). - MS (EI, 70eV), *m/z* (%): 297 (43) [M^+], 266 (67) [M^+ - CH_2OH], 206 (100) [M^+ - $C_7H_7^+$], 164 (30), 130(18), 91 (64) [$C_7H_7^+$]. - Anal. Calcd. for $C_{18}H_{19}NO_3$ (297.353): C, 72.71; H, 6.44; N, 4.71; found: C, 72.47; H, 6.22; N, 4.59. Treatment of 0.27 mmol of compound **13** (80 mg) with 1.6 mmol lithium (11 mg) in 5 mL liquid ammonia at -78 °C for 5 min gave after removal of the solvent (NH_4Cl quench) and work-up (aqueous, CH_2Cl_2 extraction) 33 mg of phenylalaninol **14** (81%) the specific rotation of which was determined. $[\alpha]_D$ = –18.0 (c = 3.3, EtOH) [Lit.[35]: $[\alpha]_D$ = –24.9 (c = 3.0, EtOH)].

(+)-(S)-4-Phenylmethyl-3-vinyl-2-oxazolidin-2-one (7). A mixture of 30 mmol oxazolidinone **15**[30] (5.3 g) and 6 mmol *dl*-camphor-10-sulfonic acid (1.4 g) in 50 mL 1,1-diethoxyethane was kept at 55 °C for 24 h. After cooling, the solution was washed with water and brine and dried over $MgSO_4$. The excess of 1,1-diethoxyethane was subsequently removed under reduced pressure. The crude product was heated to 230 °C for 2 h. Distillation (230 °C, 2 mbar) yielded an oil which was further purified by flash chromatography with PE/TBME (90/10) as eluent. Yield: 4.0 g (66%). R_f = 0.58 (40/60). $[\alpha]_D$ = 96.5 (c = 1.1, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2975 (m, $C_{al}H$), 2925 (m, $C_{al}H$), 1760 (vs, C=O), 1740 (vs, C=C), 1430 (vs), 1400 (vs), 1240 (s), 1085 (s), 1005 (m), 850 (m), 705 (m). - ^1H NMR (300 MHz): δ = 2.79 (dd, ^2J = 13.9 Hz, ^3J = 8.5 Hz, 1 H, CHHPh), 3.22 (dd, ^2J = 13.9 Hz, ^3J = 2.7 Hz, 1 H, CHHPh), 4.13-4.34 (m, 3 H, CHBn, $NCHCH_2$), 4.54 (dd, ^2J = 3.7 Hz, ^3J = 1.1 Hz, 1 H, $CHBnCHHO$), 4.59 (dd, ^2J = 3.7 Hz, ^3J = 1.3 Hz, 1 H, $CHBnCHHO$), 6.83 (dd, ^3J = 9.0 Hz, ^3J = 16.4 Hz, 1 H, $NCHCH_2$), 7.12-7.39 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 35.8 (t, CH_2Ph), 54.3 (d, CHBn), 66.4 (t, $CHBnCH_2O$), 94.0 (t, $NCHCH_2$), 127.2 (d, $C_{ar}H$), 126.8 (d, $C_{ar}H$), 128.8 (d, $NCHCH_2$), 129.2 (d, $C_{ar}H$), 135.1 (s, C_{ar}), 154.9 (s, CO). - MS (EI, 70eV), *m/z* (%): 203 (12) [M^+], 188 (24), 175 (14) [M^+ - CO], 112 (100) [M^+ - C_7H_7], 91 (50), 68 (77). - Anal. Calcd. for $C_{12}H_{13}NO_2$ (203.243): C, 70.91; H, 6.45; N, 6.89; found: C, 70.66; H, 6.35; N, 6.76.

4-Phenylmethyl-3-(2-phenyloxetan-3-yl)oxazolidin-2-one (16). A Duran glass jacket directly attached to a liquid cooled immersion lamp (Orginal Hanau TQ 150) and equipped with a septum-capped joint was charged with 10 ml of acetonitrile and 6.0 mmol of oxazolidinone **7** (1.24 g). The mixture was stirred by a continuous Ar stream which was introduced through a bent gas inlet on the bottom of the glass jacket. After cooling to -25 °C irradiation was started and 3.0 mmol of benzaldehyde (318 mg, 305 µl) dissolved in 10 ml of acetonnitrile was slowly added via syringe. The reaction was subsequently monitored by TLC. After complete consumption of

benzaldehyde (8 h) the mixture was filtered and the solvent was evaporated *in vacuo*. Flash chromatography with PE/TBME (70/30 → 60/40) as the eluent yielded the diastereoisomers **16a** and **16b**.

Major syn isomer (+)-16a. Yield: 534 mg (58%). R_f = 0.27 (40/60). $[\alpha]_D$ = 16.5 (c = 1.0, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w, $C_{ar}H$), 3010 (w, $C_{ar}H$), 2950 (m, $C_{al}H$), 2880 (m, $C_{al}H$), 1730 (vs, C=O), 1590 (w), 1480 (m), 1465 (m), 1405 (s), 1225 (s), 1105 (s), 1065 (m), 1020 (m), 970 (s, COC), 730 (s), 695 (vs). - ^{1}H NMR (300 MHz): δ = 2.13 (dd, ^2J = 13.6 Hz, ^3J = 9.8 Hz, 1 H, C*H*HPh), 2.82 (dd, ^2J = 13.6 Hz, ^3J = 4.6 Hz, 1 H, CH*H*Ph), 3.20 (dddd, ^3J = 9.8 Hz, ^3J = 8.0 Hz, ^3J = 4.6 Hz, ^3J = 3.3 Hz, 1 H, C*H*Bn), 3.56 (virt. t, $^2J \cong {}^3J$ = 8.4 Hz, 1 H, CHBnC*H*HO), 3.69 (dd, ^3J = 8.8 Hz, ^3J = 3.3 Hz, 1 H, CHBnCH*H*O), 4.81-4.92 (m, 1 H, CHN), 5.01 (virt. t, $^3J \cong$ 7.6 Hz, 1 H, C*H*HO), 5.45 (virt. t, $^3J \cong$ 6.8 Hz, 1 H, CH*H*O), 5.82 (d, ^3J = 7.1 Hz, 1 H, C*H*Ph), 6.89-6.95 (m, 2 H, arom. H), 7.14-7.55 (m, 8 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 37.5 (t, *C*H_2Ph), 51.8 (d, CHN), 55.5 (d, *C*HBn), 66.0 (t, CHBn*C*H_2O), 70.9 (t, CH_2O), 85.8 (d, *C*HPh), 126.2 (d, $C_{ar}H$), 126.8 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 135.3 (s, C_{ar}), 137.5 (s, C_{ar}), 157.4 (s, CO). - MS (EI, 70eV), *m/z* (%): 279 (1) [M^+ - CH_2O], 203 (15), 188 (7), 158 (6) 144 (4), 133 (5), 117 (6), 112 (100), 105 (16) [$C_7H_6Me^+$], 91 (66). - HRMS Calcd. for $C_{19}H_{18}NO_3$: 308.1287; found: 308.1277.

Minor syn isomer (+)-16b. Yield: 111 mg (11%). R_f = 0.46 (40/60). $[\alpha]_D$ = 57.7 (c = 0.9, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2930 (m, $C_{al}H$), 1750 (vs, C=O), 1560 (w), 1260 (m), 1050 (m), 1025 (m), 980 (s, COC), 740 (m), 700 (s). - ^{1}H NMR (400 MHz): δ = 2.47 (dd, ^2J = 13.6 Hz, ^3J = 8.6 Hz, 1 H, C*H*HPh), 2.63 (dd, ^2J = 13.6 Hz, ^3J = 4.9 Hz, 1 H, CH*H*Ph), 3.09 (virt. t, ^2J = 8.4 Hz, ^3J = 7.7 Hz, 1 H, CHBnC*H*HO), 3.41-3.45 (m, 1 H, C*H*Bn), 3.68 (virt. d, ^2J = 8.5 Hz, 1 H, CHBnCH*H*O), 4.66 (virt. t, ^2J = 7.4 Hz, ^3J = 7.3 Hz 1 H, C*H*HO), 4.72 (virt. t, ^2J = 7.4 Hz, ^3J = 8.1 Hz, 1 H, CH*H*O), 5.23-5.29 (m, 1 H, CHN), 5.88 (d, ^3J = 7.3 Hz, 1 H, C*H*Ph), 6.94-6.96 (m, 2 H, arom. H), 7.18-7.35 (m, 8 H, arom. H). - ^{13}C NMR (100 MHz): δ = 40.8 (t, *C*H_2Ph), 51.0 (d, CHN), 55.8 (d, *C*HBn), 67.3 (t, CHBn*C*H_2O), 71.9 (t, CH_2O), 87.6 (d, *C*HPh), 127.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 134.2 (s, C_{ar}), 135.4 (s, C_{ar}), 157.3 (s, CO). - MS (EI, 70eV), *m/z* (%): 279 (2) [M^+ - CH_2O], 203 (11), 188 (9), 144 (4), 133 (3), 117 (4), 112 (100), 105 (8) [$C_7H_6Me^+$], 97 (5).

(–)-3-[2-(1-Hydroxy-3-phenylpropyl)]-4-phenylmethyloxazolidin-2-one (17). The hydrogenolysis of 0.5 mmol of oxetane **16a** (155 mg) was conducted as described above (General Procedure B). Purification by flash chromatography with PE/TBME (70/30) as eluent yielded 122 mg (78%) of the desired compound. R_f = 0.26 (40/60). $[\alpha]_D$ = -21.1 (c = 1.0, CH_2Cl_2). - IR (film): $\tilde{\nu}$ = 3338 cm^{-1} (s, OH), 3085 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 2945 (w, $C_{al}H$), 2875 (w, $C_{al}H$), 1725 (vs, C=O), 1495 (w), 1455 (m), 1435 (m), 1390 (w), 1245 (w), 1095 (m), 1030 (m), 765 (m), 705 (m). - ^{1}H NMR (300 MHz): δ = 2.57 (dd, ^2J = 13.5 Hz, ^3J = 9.1 Hz, 1 H, C*H*HPh$_{ox}$), 2.93 (dd, ^2J = 13.5 Hz, ^3J = 5.3 Hz, 1 H, CH*H*Ph$_{ox}$), 3.00 (dd, ^2J = 13.5 Hz, ^3J = 5.0 Hz, 1 H, C*H*HPh), 3.05-3.15 (m, 1 H, CHN$_{ox}$), 3.22 (dd, ^2J = 13.5 Hz, ^3J = 10.2 Hz, 1 H, CH*H*Ph), 3.37-3.45 (m, 1 H, CHN), 3.88-3.96 (m, 4 H, CH_2O,C*H*$_2$OH), 6.97-6.99 (m, 2 H, arom. H), 7.22-7.32 (m, 8 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 37.5 (t, *C*H_2Ph$_{ox}$), 39.7 (t, *C*H_2Ph), 59.0 (d, CHN), 59.6 (d, CHN$_{ox}$), 64.0 (t, CH_2O), 67.6 (t, CH_2OH), 126.8 (d, $C_{ar}H$), 127.0 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 128.9 (d, $C_{ar}H$), 129.1 (d, $C_{ar}H$), 135.5 (s, C_{ar}), 138.6 (s, C_{ar}), 158.7 (s, CO). - MS (EI, 70eV), *m/z* (%): 311 (1) [M^+], 280 (16) [M^+ - CH_2OH], 221 (18), 220 (100) [M^+ - $C_7H_7^+$], 117 (23), 105 (13), 91 (64) [$C_7H_7^+$], 86 (8).- HRMS Calcd. for $C_{19}H_{18}NO_3$: 311.1521; found: 311.1519.

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