Photo aldol reactions with 5-methoxyoxazoles: Highly regio- and diastereoselective synthesis of α-amino β-hydroxy carboxylic acid derivatives

Axel G. Griesbeck and Samir Bondock

Abstract: A versatile route to derivatives of α-amino β-hydroxy carboxylic acids, either with tertiary (from a corresponding glycine equivalent) or a quaternary α-carbon center is described. The key reaction is the cycloaddition of electronically excited carbonyl compounds (aromatic and aliphatic aldehydes, respectively) to oxazoles. To make the products hydrolytically more labile, a methoxy substituent at position C-5 was introduced leading to the formation of cycloadducts with an orthoester substructure. The photocycloaddition, either with triplet excited (aromatic) carbonyls or with singlet excited (aliphatic) carbonyls, led to the formation of mixtures of *endo*- and *exo*-diastereoisomers with moderate to very high *exo*-selectivities. The 4-unsubstituted 5-methoxyoxazole **1** (glycine equivalent) gave the [2 + 2]-adducts **3a**–**3f** with aldehydes **2a**–**2f** in high yields and excellent diastereoselectivities. Hydrolysis of these compounds resulted in the α-amino β-hydroxy esters **4a**–**4f** with preferred *erythro* (*S**,*S**) configuration. As an extension of this process, 4-alkylated 5-methoxyoxazoles **5a**–**5f** were applied as alkene components and the corresponding cycloadducts with benzaldehyde **6a**–**6f** were obtained. Again, the *exo*-diastereoisomers were formed as the major products in diastereoselectivities from 73:27 (*exo*:*endo*) up to >95:5. Hydrolysis of these adducts resulted in the formation of α-amino β-hydroxy esters **7a**–**7f** with *like* (*S**,*S**) configuration of the major diastereoisomers.

Key words: photo aldol reaction, oxazoles, oxetanes, photocycloaddition, amino acids, hydroxy acids.

Résumé : On décrit une voie versatile pour obtenir des acides α-amino-β-hydroxycarboxyliques portant des centres α-carbonés tertiaire (à partir de la glycine équivalente correspondante) ou quaternaire. La réaction clé est une cycloaddition de composés carbonylés électroniquement excités (aldéhydes aromatiques et aliphatiques respectivement) à des oxazoles. Afin de que les produits soient plus facilement hydrolysables, on a introduit un substituant méthoxyle en position C-5 afin d'obtenir des cycloadduits comportant une structure orthoester. La photocycloaddition, avec des carbonyles (aromatiques) excités à l'état triplet ou avec des carbonyles (aliphatiques) excités à l'état singulet, conduit à la formation de mélanges de diastéréomères *endo*- et *exo*- dans lesquels la sélectivité en faveur de l'*exo*- est de modérée à très élevée. La réaction du 5-méthoxyoxazole non substitué en position 4 (**1**) (équivalent de la glycine) avec les aldéhydes **2a**–**2f** donne les adduits [2 + 2] **3a**–**3f** avec des rendements élevés et d'excellentes diastéréosélectivités. L'hydrolyse de ces composés conduit aux α-amino-β-hydroxyesters **4a**–**4f** avec la configuration *érythro* (*S**,*S**) préférée. Comme extension de ce procédé, on a utilisé les 5-méthoxyoxazoles alkylées en position 4 (**5a**–**5f**) comme composants alcéniques et, par réaction avec les benzaldéhyde, on a obtenu les cycloadduits correspondants **6a**–**6f**. Une fois de plus, les diastéréoisomères se forment comme produits majeurs, avec des diastéréosélectivités allant de 73:27 (*exo*:*endo*) jusqu'à >95:5. L'hydrolyse de ces produits conduit à la formation des α-amino-β-hydroxyesters **7a**–**7f** dans lesquels les diastéomères de configuration apparentée à (*S**,*S**) sont prépondérants.

Mots clés : réaction photoaldolique, oxazoles, oxétanes, photocycloaddition, acides aminés, hydroxyacides.

[Traduit par la Rédaction]

Introduction

The photochemical aldol addition route has been developed by Schreiber (1) as a powerful photochemical tool for the synthesis of β-hydroxy carbonyl compounds. This concept is surprising because electronic excitation leads, in most cases, to an *umpolung* effect, i.e., the regioselectivity of the carbonyl addition to enolate analogues is expected to be reversed. This is in fact the case for monoalkenes such as 2,3-dihydrofuran (2). The Paternò–Büchi reaction of furan and furan derivatives, however, with electronically excited aliphatic as well as aromatic aldehydes proceeds highly regioselective to give the 2,7-dioxabicyclo[3.2.0]hept-3-enes with the substituent at C-6 preferentially in the *exo*-position.

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Dedicated to Don Arnold on the occasion of his 65th birthday in recognition of his remarkable and influential contributions to organic photochemistry.

A.G. Griesbeck[1] and S. Bondock. University of Cologne, Institute of Organic Chemistry, Greinstr. 4, D-50939 Köln, Germany.

[1]Corresponding author (e-mail: griesbeck@uni-koeln.de).

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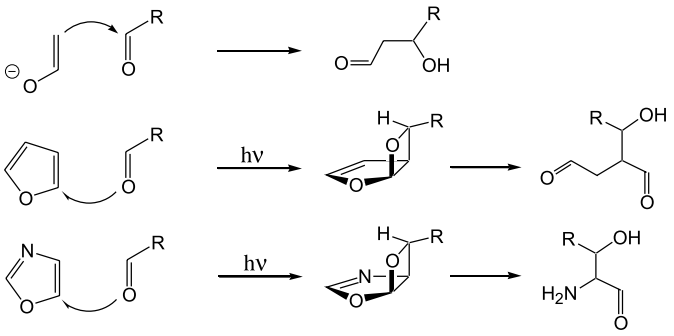
In these cases, the heteroaromatic dienes operate as vinylogue enolate equivalents. The *exo–endo* selectivity is unusually high (e.g., 212:1 for the benzaldehyde–furan case) for a *two-step triplet* photocycloaddition (2). Aliphatic aldehydes react with slightly lower *exo*-selectivity and a weak spin-selectivity effect (3) was determined; singlets favor the formation of the *exo*-diastereoisomer less pronounced than the corresponding triplets (4).[2] These photocycloadditions have been extensively used for synthetic applications especially because of the extraordinarily high degree of diastereocontrol (5–12). Several other five-membered aromatic heterocycles were used as alkene components in the Paternò–Büchi photocycloaddition (13–19) and recently the oxazole-based route to α-amino β-hydroxy ketones was added by us (20). As substrate, the commercially available 2,4,5-trimethyloxazole was used and excellent (*exo*-)diastereoselectivities were observed for the photocycloaddition with aldehydes. An attractive family of target compounds, which might be available by this route, consists of derivatives of α-amino β-hydroxy carboxylic acids (21–26), either with tertiary (from a corresponding glycine equivalent) or quaternary α-carbon centers (Fig. 1).

Fig. 1. The aldol and photo aldol route to β-hydroxy carbonyl compounds.



Results and discussion

To investigate this concept, we first applied the 4-unsubstituted 5-methoxyoxazole **1** (27) as a diene and as the glycine equivalent in the photocycloaddition with aldehydes **2a**–**2f**. In all cases only one regioisomeric bicyclic oxetane (**3a**–**3f**) was detected in the crude photolysis mixture and, in most cases, only one diastereoisomer (Scheme 1). From the comparison with the results from the trimethyloxazole experiment (20) and NMR comparison with the hydrolysis products, the *exo*-configuration of the cycloadducts could be determined. Especially, the strong ring-current-induced upfield shift for the phenylated product **3a** is indicative of the *exo*-configuration of the aryl substituent; for **3a**: ^{1}H NMR (H-1) δ: 4.58 ppm; for **3d**: ^{1}H NMR (H-1) δ: 5.04 ppm. The ring-current effects detected for the phenylated compound **3a** were analogous in size to effects detected in β-lactams which resulted from the Yang cyclization of amino-acid-derived chiral butyrophenone derivatives (28). The primary photoproducts (**3a**–**3f**) were hydrolytically unstable and underwent twofold ring opening to give the β-hydroxy amino acid esters **4a**–**4f** (Table 1). In most cases, the diastereoisomeric ratio (d.r.) of the ring-opened products matched the d.r. of the oxetane precursors.

The relative configuration of the methyl esters of phenylserine (**4a**) (29) and β-hydroxyleucine (**4e**) (30) were already elucidated in the literature and by comparison with our data, the *erythro* (*S**,*S**) configuration for the major diastereoisomers of **4a**–**4f** was established, e.g., for the β-hydroxyleucine derivative **4e**: ^{13}C NMR for the β-carbon δ: 77.2 ppm for *R**,*S** (29); 69.8 ppm for the major diastereoisomer (*S**,*S**) obtained via the photo aldol route.

Subsequently, we investigated a series of 5-methoxy oxazoles (**5a**–**5f**) as substrates with an additional substituent at C-4. These substrates were easily available from the amino acids alanine, α-amino butyric acid, valine, norvaline, leucine, and isoleucine (31–33). The photocycloadditions of **5a**–**5f** with benzaldehyde were performed using equimolar amounts of the substrates in benzene. The primary photoadducts (**6a**–**6f**) were formed with excellent diastereoselectivities except for additions to oxazole substrates with bulky substituents R^2. Again, the strong ring-current-induced upfield shifts for the phenylated products were indicative of the *exo*-configuration of the aryl substituent. Because of the less-pronounced diastereoselectivities of the benzaldehyde additions in these cases, both *endo*- and *exo*-isomers could be compared. The isopropyl-substituted oxazole **5d** gave in 80% yield a mixture of diastereoisomers (regioisomeric purity >98% in all cases) (**6d**). The ^{1}H NMR chemical shifts of the methyl groups for *i*-Pr in *exo*-**6d** were 0.52 and 0.73 ppm, and in *endo*-**6d** were 0.93 and 0.98 ppm, again analogous to effects detected for photochemically synthesized β-lactams (28).

Upon chromatography, most of the products were hydrolyzed to give the (*S**,*S**) α-acylamino β-hydroxy carboxylic acid esters **7a**–**7f** (Scheme 2, Table 2). The relative configuration of the oxetanes (**6**) was confirmed by NMR spectroscopy and spectral comparison with representative literature-known products (*anti*-**7**) (34–37).

Whereas the high *exo*-selectivity of the photocycloaddition of electronically excited aldehydes to the C4-unsubstituted oxazole **1** is analogous to the furan case, the high diastereoselectivity for the trisubstituted oxazoles **5a**–**5f** deserves a comment. In the triplet photocycloaddition to cycloalkenes (38), ring alkylation leads to a *decrease* in selectivity and, in some cases, to selectivity inversion because of interference with the spin-orbit-coupling geometries (39). This is obviously not the case for the oxazoles **5a**–**5f** which indicates that the secondary orbital interaction model originally applied for the benzaldehyde–furan reaction is operating (2). Figure 2 shows the triplet 1,4-biradical conformers **A**–**C** with reactive spin-orbit-coupling geometries (40). If most of the spin inversion process is directed through the channel **C**, high *exo*-selectivity is expected. The *endo*-contribution from **A** becomes only relevant for bulky groups R^2 (as for **5d**–**5f**).

An alternative interpretation, proposed by Abe, for the high *exo*-selectivities observed in triplet photocycloadditions

[2] A.G. Griesbeck, M. Fiege, and S. Bondock. Unpublished results.

Scheme 1. Photo aldol reaction with oxazole **1**.

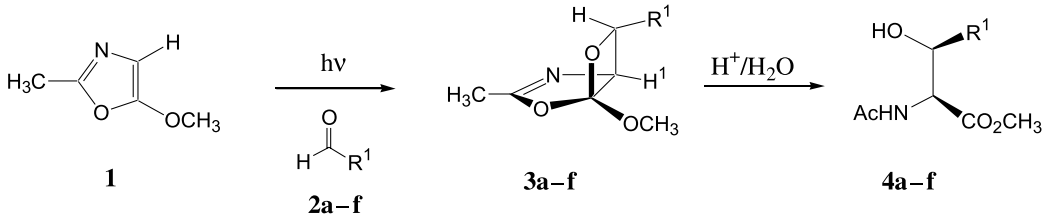


Table 1. Photocycloaddition of aldehydes (**2**) with 5-methoxyoxazole (**1**) and subsequent ring opening.

No.	R^1 =	d.r. (**3**)[a]	Yield (**3**)[b]	d.r. (**4**)[a]	Yield (**4**)[c]
a	Ph	>98:2	87	>98:2	70
b	β-Naph	>98:2	85	>98:2	75
c	$BnCH_2$	>98:2	87	>98:2	65
d	Et	>98:2	90	95:5	72
e	*i*-Pr	>98:2	86	>98:2	78
f	*i*-Bu	>98:2	88	>98:2	74

[a]Based on the integration of characteristic signals in the ^{1}H NMR spectrum of the crude product mixture (±2%).
[b]Yield (%) based on converted oxazole of the isolated mixture of diastereoisomers **3**.
[c]Yield (%) of the isolated mixture of diastereoisomers.

of aldehydes to heterocyclic dienes was recently proposed by Abe.[3] It is also based on the comparison of the intermediate 1,4-triplet biradical conformers as depicted in Fig. 2, however, with emphasis on the additional anomeric stabilization in structure **C** and **B** that is not present in **A** (no lone pair at oxygen antiperiplanar to the ring oxygen). This small difference in energy is sufficient to explain the high *exo*-selectivities and the cleavage competition as expressed in the quantum yields (3).

Conclusions

In summary, an efficient stereoselective photochemical protocol for the synthesis of α-amino β-hydroxy carboxylic acid derivatives was developed. The major advantage of these light-induced reactions in comparison with classical thermal aldol processes is the high diastereocontrol in the (triplet as well as singlet) photocycloaddition. As a plausible explanation for the high *exo*-selectivity, secondary orbital effects are postulated at the stage of the ISC (intersystem crossing)-active triplet-1,4-biradical conformers. The adducts of the Paternò–Büchi reactions were hydrolytically unstable and ring-opened to give α-*N*-acylamino β-hydroxy carboxylic acid methyl esters. As major diastereoisomers, the *erythro*-products with tertiary α-carbon centers and the *like* (*S**,*S**) products with quaternary α-carbon centers were formed.

Experimental

General remarks

All reactions were carried out in oven-dried glassware (100°C). All solvents were dried before use. Ether was distilled from sodium–benzophenone, chloroform, and dichloromethane from calcium hydride. Aldehydes were purchased from Aldrich and were distilled before use. Mixtures of ethyl acetate and *n*-hexane were used as eluents. TLC: commercially precoated polygram© SIL-G/UV 254 plates (Macherey–Nagel). Spots were detected with UV light in an iodine chamber. ^{1}H NMR: Bruker AC 300 (300 MHz). ^{13}C NMR: Bruker AC 300 (75.5 MHz), carbon multiplicities were determined by DEPT. UV–vis: Hitachi U-3200. Mass spectroscopy (EI or CI): Finnigan Incos 500; *m*/*z* (rel. %). HR-MS (FAB): Finnigan MAT H-SQ 30. Preparative TLC: silica gel (2–25 μm) on TLC plates (Fluka) (layer thickness 0.25 mm, medium pour diameter 60 Å, 20 × 20 on glass plates). All melting points were determined with a Büchi melting point apparatus (type Nr. 535) and are uncorrected. Combustion analyses: Elementar Vario EL. Rayonet® chamber photoreactors RPR-208 (8 × 3000 Å lamps, ca. 800 W, λ = 300 ± 10 nm) were used for irradiation.

Synthesis of 5-methoxyoxazoles

General procedure

N-Acetyl-L-amino acid methyl ester (0.1 mol) was dissolved in 20 mL of chloroform in a 250 mL flask; 20.8 g (0.1 mol) of phosphorous pentachloride were added and the flask was fitted with a calcium chloride tube. The solution was gently warmed by means of a water bath (ca. 60°C) with stirring until the HCl gas evolution ceased and the solution became an intense yellow. Then, the flask was cooled by an ice–salt bath and 50 mL of absolute ether were added. To the cooled mixture, 20% aq KOH was added dropwise with vigorous stirring until neutralization. The mixture was stirred at room temperature for 30 min. The organic layer was subsequently separated and the aqueous layer was extracted with 2 × 200 mL of ether. The combined organic extracts were washed with water and brine and dried over anhyd $MgSO_4$. After removal of the solvents under vacuum, the remaining oil was distilled by a Büchi Kugelrohr apparatus to give the product.

[3] M. Abe. Personal communication and poster contribution at the XIXth IUPAC Symposium on Photochemistry, Budapest, 14–19 August 2002.

Scheme 2. Photo aldol reaction with 5-methoxyoxazoles **5a**–**5f**.

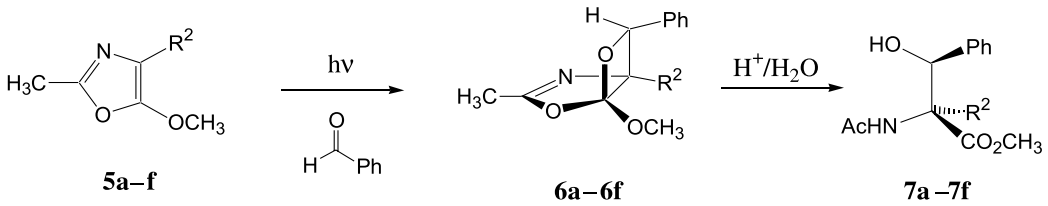
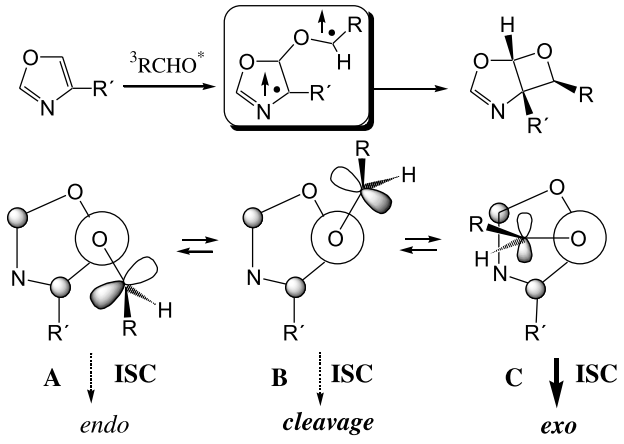


Fig. 2. 1,4-Biradical geometries in oxazole – triplet carbonyl photocycloadditions.



Photolyses of 5-methoxyoxazoles with aldehydes

General procedure

A mixture of the 5-methoxyoxazole (5 mmol) and the aldehyde (5 mmol) was dissolved in 50 mL benzene, the solution transferred to a vacuum jacket quartz tube, and degassed with a steady stream of N_2 gas. The reaction mixture was irradiated at 10°C in a Rayonet photoreactor (RPR-208, λ = 300 ± 10 nm) for 24 h. The solvent was evaporated (40°C, 20 torr (1 torr = 133.322 Pa)) and the residue was purified by preparative thick layer chromatography (EA = ethyl acetate, H = hexane).

exo-*5-Methoxy-3-methyl-7-phenyl-4,6-dioxa-2-aza-bicyclo[3.2.0]heptene-2-ene* (exo-*3a)*

A solution of benzaldehyde (0.53 g, 5 mmol) and 2-methyl-5-methoxyoxazole (0.57 g, 5 mmol) in 50 mL of benzene was irradiated for 24 h according to the general procedure. The crude product was purified by preparative thick layer chromatography (EA:H = 1:4) to give 0.55 g (65%) of the oxetane as a colorless oil. R_f = 0.43 (EA:H = 1:4). IR (film) (cm^{-1}): 2987 (C-H), 1635 (C=N), 1600 (Ph), 1440 (CH), 1012 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.11 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 4.58 (d, J = 7.7 Hz, 1H, 1-H), 5.68 (d, J = 7.7 Hz, 1H, 7-H), 7.26–7.31 (m, 5H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 15.9 (q), 52.8 (q), 76.2 (d, C-1), 83.0 (d, C-7), 122.9 (s, C-5), 125.4 (d), 126.2 (d), 128.1 (d), 134.3 (s), 167.7 (s, C-3). HR-MS calcd. ($C_{12}H_{13}NO_3$): 219.0892; found: 219.0886.

Table 2. Diastereoselective photocycloaddition of benzaldehyde with 5-methoxyoxazoles **5a**–**5f** and subsequent ring opening.

No.	R^2 =	d.r. (**6**)[a]	Yield (**6**)[b]	d.r. (**7**)[a]	Yield (**7**)[c]
a	Me	>98:2	85	>98:2	65
b	Et	>98:2	84	93:7	73
c	*n*-Pr	>98:2	86	90:10	58
d	*i*-Pr	73:27	80	90:10	48
e	*i*-Bu	87:13	78	90:10	57
f	*sec*-Bu	85:15	81	92:8	58

[a]Based on the integration of characteristic signals in the ^{1}H NMR spectrum of the crude product mixture (±2%).
[b]Yield (%) based on converted oxazole of the isolated mixture of diastereoisomers **6**.
[c]Yield (%) of the isolated mixture of diastereoisomers **7**.

exo-*5-Methoxy-1,3-dimethyl-7-phenyl-4,6-dioxa-2-aza-bicyclo[3.2.0]heptene-2-ene* (exo-*6a)*

A solution of benzaldehyde (0.53 g, 5 mmol) and 2,4-dimethyl-5-methoxyoxazole (0.64 g, 5 mmol) in 50 mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative thick layer chromatography (EA:H = 1:4) to give 0.59 g (72%) of the oxetane as a colorless oil. R_f = 0.51 (EA:H = 1:4). IR (film) (cm^{-1}): 2987, 2894 (C-H), 1615 (C=N), 1605 (Ph), 1445 (CH), 1008 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.79 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 3.52 (s, 3H, OCH_3), 5.19 (s, 1H, 7-H), 7.21–7.25 (m, 5H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 13.4 (q), 14.8 (q), 51.2 (q), 75.8 (s, C-1), 89.3 (d, C-7), 124.9 (s, C-5), 125.7 (d), 128.2 (d), 129.1 (d), 136.3 (s), 164.9 (s, C-3). HR-MS calcd. ($C_{13}H_{15}NO_3$): 233.0762; found: 233.0758.

Synthesis of *erythro* (2*S**,3*S**)-α-acetamido-β-hydroxy esters

General procedure

To a solution of bicyclic oxetanes (2 mmol) in 20 mL methylene chloride, 0.5 mL of concd HCl was added. The mixture was stirred in an open flask at room temperature for 2 h and the reaction was controlled by TLC. The reaction mixture was quenched by being poured into water and extracted with methylene chloride (3 × 20 mL). The organic layer was washed with 5% $NaHCO_3$ and brine and dried over anhyd $MgSO_4$. The solvent was removed in vacuo and the residual oil was purified by preparative thick layer chromatography.

Methyl (2S*,3S*) 2-(N-acetylamino)-3-hydroxy-3-phenylpropionate (erythro-4a)

According to the above general procedure, bicyclic oxetane **3a** (0.44 g, 2 mmol) was cleaved hydrolytically in 3 h. Preparative chromatography yielded 0.33 g (70%) of the product as a colorless oil. R_f = 0.34 (EA:H = 1:4). IR (film) (cm^{-1}): 3500 (OH), 3370 (NH), 2983, 2894 (C-H), 1725 (COO), 1675 (CON), 1605 (Ph), 1445 (CH), 1018 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.07 (s, 3H, CH_3CO), 3.97 (s, 3H, OCH_3), 4.45 (d, *J* = 9.7 Hz, 1H, CHN), 5.85 (d, *J* = 9.7 Hz, 1H, CHOH), 6.37 (bs, 1H, NH), 7.28–7.35 (m, 5H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 23.7 (q), 52.4 (q), 75.4 (d, C-2), 81.6 (d, C-3), 126.2 (s, C-5), 128.9 (d), 129.6 (d), 134.3 (s), 169.3 (s, CON), 170.3 (s, COO). Anal. calcd. ($C_{12}H_{15}NO_4$): C 60.75, H 6.37, N 5.90; found: C 60.65, H 6.42, N 5.85.

Methyl (2S*,3S*) 2-(N-acetylamino)-3-hydroxy-3-phenylpropionate (erythro-7a)

According to the above general procedure, bicyclic oxetane **6a** (0.47 g, 2 mmol) was cleaved hydrolytically in 4 h. Preparative chromatography yielded 0.32 g (65%) of the product as a colorless oil. R_f = 0.33 (EA:H = 1:4). MS (EI, 70 eV) *m*/*z* (%): 249 ($M^+ - H_2$, 4), 236 (M^+ – Me, 8), 202 (8), 192 ($M^+ - CO_2Me$, 15), 191 (78), 160 (10), 131 (100), 105 (50), 91 (20), 77 (30), 51 (10). IR (film) (cm^{-1}): 3500 (OH), 3320 (NH), 2988 (C-H), 1720 (COO), 1680 (CON), 1580 (Ph), 1440 (CH), 1025 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23 (s, 3H, CH_3), 2.12 (s, 3H, CH_3CO), 3.79 (s, 3H, OCH_3), 4.06 (s, 1H, CHOH), 7.28–7.35 (m, 5H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 13.5 (q), 21.4 (q), 21.4 (q), 23.4 (q), 47.7 (s, C-2), 49.1 (d, C-3), 52.9 (q), 127.6 (s, C-5), 128.4 (d), 129.6 (d), 133.5 (s), 169.9 (s, CON), 179.4 (s, COO). HR-MS calcd. ($C_{13}H_{17}NO_4$): 251.1254; found: 251.1249.

Acknowledgements

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