Pergamon

Tetrahedron Vol 51, No. 37, pp 10219-10230, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00611-7

Synthesis and Reactions of New 2-Substituted 5-Phenyl-6-oxa-4-azaspiro[2,4]-hepten-7-one Derivatives

Lukas Wick[a], Christoph Tamm[a*], Markus Neuburger[b] and Margareta Zehnder[b]

[a]Institut für Organische Chemie der Universität, St. Johanns-Ring 19, CH-4056 Basel

[b]Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH-4056 Basel

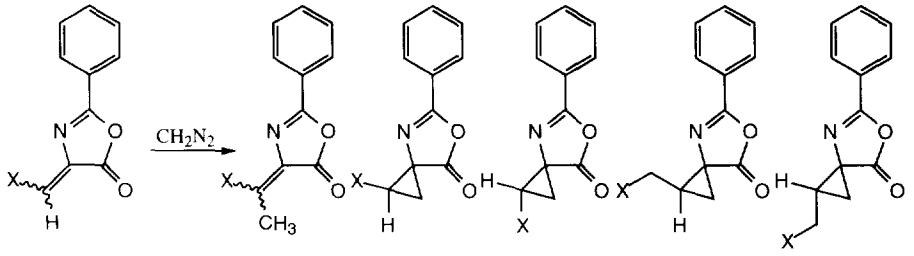
Abstract: Synthesis, reactions and relative configurations of new 2-halogen-, 2-acetyl- and 2-pivaloyl-substituted 5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one derivatives **1a-h** as potential precursors of 1-aminocyclopropanecarboxylic acids are described

1-Aminocyclopropanecarboxylic acid (ACC) is the direct biosynthetic precursor of the important plant growth regulator ethylene [1,2,3,4]. Interested in synthesizing substituted ACC derivatives as potential inhibitors or promoters of the ethylene biosynthesis (cf [5]), we studied the synthesis and reactions of a few new 2-substituted 5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one derivatives, following a well-known procedure for the preparation of ACC analogues (e.g.[6,7]).

As shown in Scheme 1, the (*Z*)-β-hydroxy, (*E*)-β-chloro and the (*E*)-β-bromo compounds **1a**, **1b**, **1c** are prepared using an extension of previously described methods [8,9]. The β-iodo **1d** compound was obtained in nearly quantitative yield by nucleophilic substitution with KI starting either from the (*E*)-β-chloro **1b** or (*E*)-β-bromo compound **1c** presumably under inversion resulting in the (*Z*)-configuration of **1d** (cf [10]). The synthesis of the corresponding β-fluoro compound by the same method using KF or other sources of nucleophilic fluorine failed. The application of diethylaminosulfur trifluoride (DAST) as a fluorinating agent to **1a** led to 4-(*N*,*N*-diethylaminomethylene)-2-phenyl-5(4*H*)-oxazolone (**1g**) as the only product. The β-esters **1e** and **1f** were synthesized starting from **1a** using acetyl chloride and pivaloyl chloride, respectively. The synthesis of the appropriate sulfonyl esters using the same method failed. The relative configuration of the substituent at the double bond of **1e** was confirmed by an X-ray analysis (Figure 1), allowing the conclusion that **1a** and **1f** possess a (*Z*)-configuration.

Treatment of **1b-f** with an excess of diazomethane gave a mixture of compounds **2-6**, which was readily separated by chromatography on silica. The yield and the relative ratios of the products formed are summarized in Table 1. Apart from the expected halogen cyclopropanes **3** and **4**, compounds **2** (as a diastereoisomeric mixture), as well as **5** and **6**, were formed by methyl insertion and vinyl to allyl rearrangement, respectively. While the latter were obtained only in very poor yield in the chloro series, they were formed as the only products in the iodo series. In contrast to chloro compound **1b** the (iodomethylene)oxazolone **1d** experienced exclusively this rearrangement when treated with diazomethane. This is consistent with the lower stability of a chlorine radical vs. an iodine radical (cf [9,11]). Treatment of **1a** with diazomethane formed (*Z*)-4-(methoxymethylene)-2-phenyl-5(4*H*)-oxazolone as the only product. In the ester series no insertion products

were found. The structure and the relative configuration of the products were determined by NMR studies. ^{13}C NMR analyses based on the γ-effect [12] (which was applied to the C(2) of the oxazolone carbonyl group vs. the substituents of the rigid cyclopropane moiety of the spiro system) demonstrated that the *trans*-substitution of the substituent at C-2 position led to *syn*-conformation and consequently to a high field shift of the carbonyl C-atom of the oxazolone. X-ray diffraction of **3f** (Figure 2) and ring closure reactions starting from **5d** and **6d** clearly confirmed the results of the NMR analyses.



Scheme 1

Table 1. Yield and Distribution of Products Formed by CH_2N_2 Addition to **1**

compound	**1** (% yield)	**2** (% yield)	**3** (% yield)	**4** (% yield)	**5** (% yield)	**6** (% yield)
b (X = Cl)	--	1.9	20	53	3.5	3.9
c (X = Br)[1)]	--	3	15	2.5	2	25
d (X = I)	--	--	--	--	34	42
e (X = OAc)	--	--	34	42	--	--
f (X = OPiv)	--	8	43	30	--	--
h ($X = OCH_3$)	93	--	--	--	--	--

1) experimental data are described in detail elsewhere (cf [9])

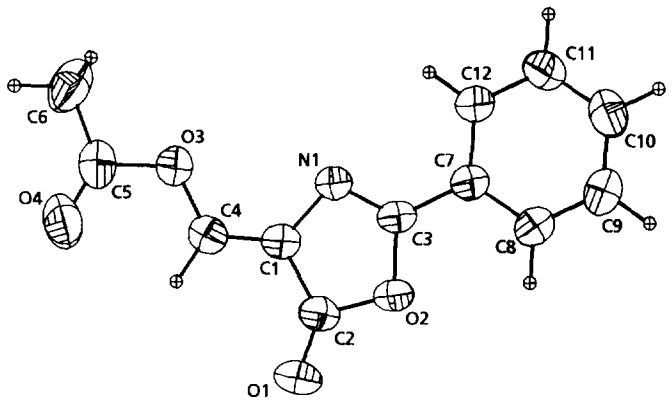
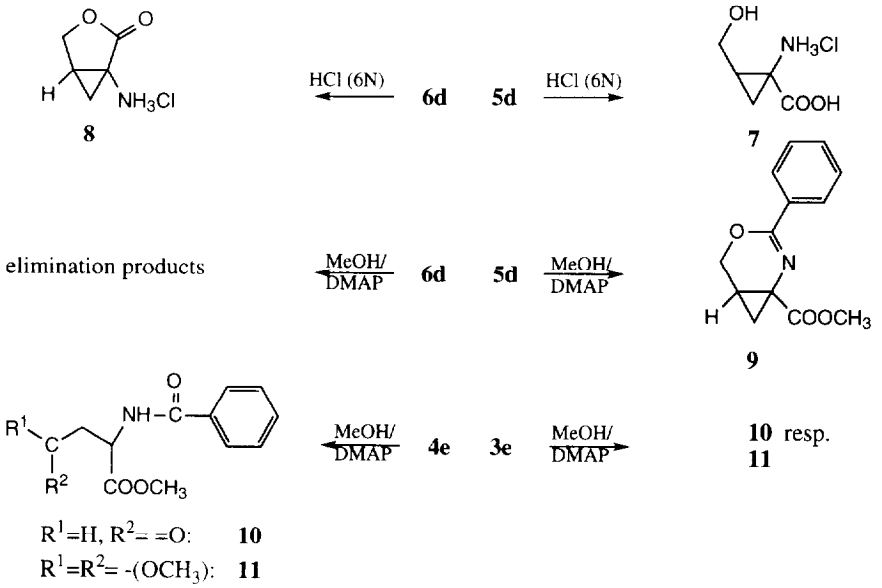


Figure 1. X-ray structure of **1e**

The opening of the oxazolone ring (as a functional protection moiety of the amino acid functions) was achieved by hydrolysis. Two types of hydrolyses were performed: Hydrolysis with 6 N aqueous HCl and with 1 eq. DMAP in MeOH. The acid hydrolysis of **3b**, **3c**, **4b** and **4c** led to the corresponding ACC derivatives as was previously described for the chloro compound [8]. The acid hydrolysis for the rearrangement products **5** and **6** led to a mixture of decomposition products except in the iodo series in which the already known hydroxymethyl alcohol and the internal lactone (cf [13]) were formed in a new synthetical approach to **7** and **8**. DMAP catalysed hydrolysis of **5d** gave **9** as the main product, whereas the hydrolysis of **6d** led to a mixture of elimination products. Acid hydrolysis of the esters **3e**, **3f**, **4e** and **4f** yielded the hydrochlorides of a mixture of ring opened amino acids, meanwhile the reaction with DMAP resulted in analogy to the chloro compounds [8] in the formation of the benzamides of the pivaloyl ester. Under the same conditions however the less stable acetyl ester **3e** and **4e** were hydrolized with subsequent cleavage of the cyclopropane ring and oxydation of the alcohol function to the corresponding aldehyde **10** and its dimethylacetal **11**, respectively (Scheme 2).



Scheme 2

This result is consistent with earlier reports which describe the decomposition of 2-amino-cyclopropanecarboxylic acids and esters by release of the ring strain with succeeding hydrolysis leading to keto compounds [14,15]. As was shown in the case of the acid hydrolyses and of the different behavior of the acetates vs. the pivaloates towards methanolysis, the instability of the cyclopropane ring seems to be related to the free alcohol function. To our knowledge this is the first laboratory demonstration of the instability of substituted ACC derivatives towards nucleophiles.

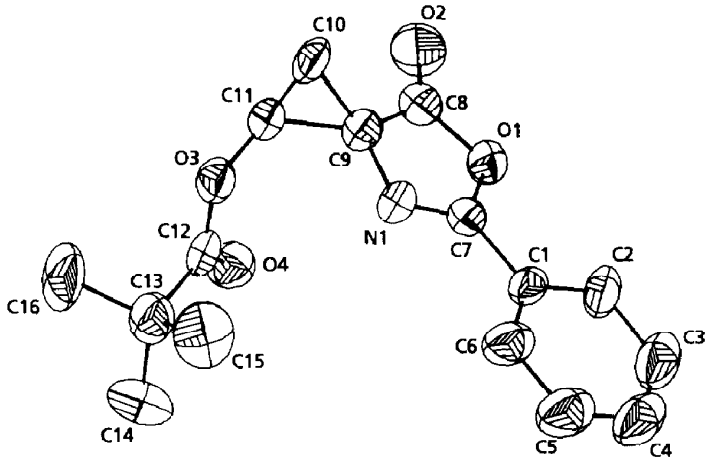


Figure 2. X-ray structure of **3f**

EXPERIMENTAL

All chemicals were purchased from Fluka AG or Merck GmbH in purum or puriss. p. a. quality. Reactions were performed under N_2. Solvents used in reactions were distilled and dried whenever necessary. Solvents (industrial grade) used for column chromatography were distilled once. The org. extracts were dried over Na_2SO_4 and the solvents removed on a rotary evaporator (≤ 40°/≥ 14 Torr) and dried under high vacuum (≥ 0.1 Torr). Solutions of diazomethane in ether were prepared with *N*-methyl-*N*-nitroso-p-toluenesulfonamide (DIAZALD®, Aldrich) using a Diazald-Kit for distillation following a standard method (cf [16]). All reactions with diazomethane were performed in a hood behind a safety shield. TLC: precoated glass plates 0.25 mm silica gel 60 F_{254} (Merck), detection by UV light and/or spraying with a soln. of aq. 2 % $KMnO_4$, 4 % $NaHCO_3$ and a soln. of 3 % ninhydrine in acid *n*-propanol for amino acids, respectively followed by heating. Column chromatography (CC): Merck silica gel 60, 63-200 mm. Flash chromatography (FC): overpressure ca. 0.3 bar; Merck silica gel 60, 40-63 mm. Medium pressure liquid chromatograhpy (MPLC): Büchi 681 pump with a Uvikon 735 LC detector. Anal GC: an HP 5890 A gas chromatograph equipped with a flame ionization detector and a 'fused-silica'-capillary (25 m x 0.2 mm) coated with a 0.33-mm 5 % cross-linked (phenylmethyl)silicone layer was used. M. p. were determined on a Kofler block and are corrected. IR [cm^{-1}]: Perkin-Elmer-781 spectrometer. NMR: Varian Gemini-300 spectrometer (^1H: 300 MHz; ^{13}C: 75 MHz; δ in ppm rel. to internal TMS (= 0 ppm) or sodium 3-(trimethylsilyl)-propionate (^1H: 0.00 ppm; ^{13}C: 1.70 ppm); digital resolution for coupling constants 0.25 Hz/point; MS (m/z (%)): VG-70-250 spectrometer. X-ray structure analysis of **1e** and **3f**. Unit cells parameters were determined by accurate centering of 25 strong independent reflections by the least square method. Reflection intensities were collected at r.t. on a four-circle diffractometer Enraf Nonius CAD 4 equipped with a graphite monochromated MoK_α and a CuK_α radiation,

respectively. The structure was solved by direct methods using SHELXS-86 [17]. Anisotropic least-squares refinement was carried out on all non-H-atoms using the program CRYSTALS [18]. Position of H-atoms were calculated. Scattering factors were taken from International Tables of Crystallography, Vol. IV. Fractional coordinates are deposited in the Cambridge Crystallographic Data Base.

(*E*)-4-(Chloromethylene)-2-phenyl-5(4*H*)-oxazolone (1b)

To a suspension of 18.3 g (0.097 mol) of the hydroxy compound **1a** in 100 ml dry toluene 25 ml (0.291 mol) of oxalyl chloride was added during 10 min and stirred for 3 h at r.t.. After concentration in vacuo a brown red solid was achieved which was crystallized from toluene to afford 18.6 g (93%) of light pink needles. M.p.: 134-135.5°. TLC: R_f 0.53 (EtOAc/pentane (1:5)). IR (KBr): 3070, 1800 (CO), 1650. ^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (*m*, 2H, arom. H_o); 7.59 (*m*, 3H, arom. $H_{m,p}$); 7.19 (*s*, 1H, H-C(1')). ^{13}C NMR (75 MHz, $CDCl_3$): 165.42 (CO); 164.14 (C(2)); 137.84 (C(4)); 134.32 (C_p, Ar); 129.29, 128.96 ($C_{o,m}$, Ar); 126.49 (C(1')); 124.92 (C_{ipso}, Ar). MS (EI, 70 eV): 209 (6.4, M^+); 207 (M^+, 20.5); 105 (100), 77 (56.9), 51 (21.0), 50 (7.2).

(*Z*)-4-(Iodomethylene)-2-phenyl-5(4*H*)-oxazolone (1d)

To 100 mg (0.482 mmol) **1b** in 10 ml acetone 144 mg (0.964 mmol) KI were added and stirred for 24 h. After evaporation of the solvent the remaining red brown residue was dissolved in 20 ml CH_2Cl_2 and washed with H_2O and brine (2 x 10 ml). After drying the soln. over Na_2SO_4 the solvent was removed in vacuo to afford 144 mg of pure brown crystals (97%). M.p.: 125-128°; TLC: R_f 0.80 (CH_2Cl_2). IR (KBr): 3040, 1780 (CO), 1620, 1535, 1260, 1130, 685. ^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (*m*, 2H, arom. H); 7.85 (*s*, 1H, H-C(1')), 7.57 (*m*, 3H, arom. $H_{m,p}$). ^{13}C NMR (75 MHz, $CDCl_3$): 165.42 (CO); 160.45 (C(2)); 144.97 (C(4)); 134.06 (C_p, Ar); 129.00, 128.70 ($C_{o,m}$, Ar); 124.83 (C_{ipso}, Ar); 91.44 (C(1')). MS (EI, 70 eV): 299 (M^+, 24.6); 166 (3.4), 127 (3.9), 105 (100), 77 (59.5), 51 (24.8).

(*Z*)-4-(Acetoxymethylene)-2-phenyl-5(4*H*)-oxazolone (1e)

To a suspension of 50 mg (0.264 mmol) of **1a** in 5 ml dry CH_2Cl_2 25 µl (2.64 mmol) of acetyl chloride was added and stirred for 20 h at r.t.. The resulting brown red soln. was washed with H_2O and brine (3 x 10 ml). The combined organic extracts were dried and evaporated to dryness in vacuo. The crude brown red product was purified by FC (acetone/Et_2O, (1:1)) to afford 52 mg (84%) of pure solid which was crystallized from CH_2Cl_2/pentane. M.p.: 143-146°. TLC R_f 0.55 (acetone). IR (KBr): 3060, 2980, 1775 (CO), 1755 (CO), 1670, 1140, 860, 690. ^{1}H NMR (300 MHz, $CDCl_3$): 8.22 (*s*, 1H, H-C(1')); 7.62 (*m*, 2H, arom. H_o; 7.56 (*m*, 3H, arom. $H_{m,p}$); 2.41 (*s*, 3H, $COOCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 167.04 (CO); 165.88 (C(5)=O); 162.54 (C(2)); 137.37 (C(1')); 133.45 (C_p, Ar); 128.91; 128.32; ($C_{o,m}$, Ar); 125.12 (C_{ipso}, Ar); 122.31 (C(4)); 20.52 (CH_3-O). MS (EI, 70 eV): 231 (M^+, 1.4); 189 (55.4), 105 (100), 77 (49.4), 51 (18.6); 43 (88.7). X-Ray Data: cf Table 2.

Table 2. Crystal Data and Parameters of Data Collection for **1e**

Molecular formula	$C_{12}H_9NO_4$	Crystal dimensions [mm]	0.3 x 0.5 x 0.6
Crystal system	monokline	Temperature [K]	298
Space group	P 21/c	Q max [°]	74.33
a [Å]	10.012(1)	Radiation	Cu $K(\alpha)$, l=1.54178 Å
b [Å]	8.900(1)	Scan type	w/2Q
c[Å]	12.460(1)	No. of independent refl.	2236
a [°]	90(0)	No. of refl. in refinement	2030
b [°]	97.942(5)	No. of variables	154
g [°]	90(0)	Final R	6.38
V [Å^3]	671.01(19)	Final R_W	6.45
Z	4	Weighting scheme	weight·[1-(ΔF/6 σF)^2]^2

(*Z*)-4-(pivaloyloxymethylene)-2-phenyl-5(4*H*)-oxazolone (1f)

To a suspension of 200 mg (1.058 mmol) of **1a** in 5 ml dry CH_2Cl_2 156 µl (2.64 mmol) of acetyl chloride was added and stirred for 14 h at r.t.. The resulting brown red soln. was washed with H_2O and brine (3 x 10 ml). The organic extract was dried and evaporated to dryness in vacuo. The crude brown red product was purified by FC (CH_2Cl_2) to afford 224 mg (78 %) of pure solid. M.p.: 116-119°. TLC: Rf 0.49 (Et_2O/pentane). IR (KBr): 3080, 2980, 2920, 2850, 1800 (CO), 1730 (CO), 1680, 1170, 1060, 870, 700. ^{1}H NMR (300 MHz, $CDCl_3$): 8.24 (*s*, 1H, H-C(1')); 8.12 (*m*, 2H, arom. H_o); 7.56 (*m*, 3H, arom. $H_{m,p}$); 1.40 (*s*, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 173.58 (CO); 167.58 (C(5)=O); 162.12 (C(2)); 138.49 (C(1')); 133.23 (C_p, Ar); 128.86; 128.28 ($C_{o,m}$, Ar); 125.35 (C_{ipso}, Ar); 122.41 (C(4)); 39.30 ($C(CH_3)_3$); 26.73 ($C(CH_3)_3$). MS (CI, NH_3): 274 ([M+H]$^+$, 100); 189 (4.5), 174 (11.8), 122 (3.8), 105 (4.0).

4-(*N*,*N*-Diethylaminomethylene)-2-phenyl-5(4*H*)-oxazolone (1g)

To a soln. of 34 µl (0.265 mmol) diethylaminosulfur trifluoride (DAST) in 2 ml dry acetone a soln. of 50 mg (0.265 mmol) **1a** in 1.5 ml THF was dropped at -78° and stirred for 18 h without further cooling. The resulting brown red soln. was diluted with 15 ml of CH_2Cl_2 and washed with H_2O and brine (3 x 10 ml). The organic extract was dried and evaporated to dryness in vacuo. The crude brown red product was purified by FC (gradient: CH_2Cl_2 to acetone) to afford 33 mg (52 %) of a pure oil. TLC: Rf 0.15 (CH_2Cl_2). IR (film): 3060; 2980; 2920; 2880; 1720 (CO); 1630; 1590; 1430; 1370; 1260; 1090; 890; 840; 690. ^{1}H NMR (300 MHz, $CDCl_3$): 7.95 (*m*, 2H, arom. H_o); 7.41 (*m*, 3H, arom. $H_{m,p}$); 7.15 (*s*, 1H, H-C(1')); 4.03 (*q*, *J* = 7.1, 2H, N-CH_2); 3.42 (*q*, *J* = 7.2, 1H, N-CH_2); 1.34 (*t*, *J* = 7.1, 3H, -CH_3); 1.33 (*t*, *J* = 7.2, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) : 170.36 (CO); 153.30 (C(2)); 141.28 (C(1')); 130.29 (C_p, Ar); 128.50 ($C_{o,m}$, Ar); 127.53 (C_{ipso}); 126.25 ($C_{o,m}$, Ar); 107.57 (C(4)); 51.62 (N-CH_2); 44.56 (N-CH_2); 14.61 (CH_3); 13.10 (CH_3). MS (EI, 70 eV): 244 (64.1, M$^+$); 229 (7.8), 139 (6.0), 111 (100), 105 (94.1), 95 (7.8), 83 (7.2), 77 (49.8), 56 (24.4), 52 (15.5).

(*Z*)-4-(Methoxymethylene)-2-phenyl-5(4*H*)-oxazolone (1h)

To a suspension of 50 mg (0.264) **1a** in 20 ml of CH_2Cl_2 an excess of ethereal diazomethane soln. (0.3 N) was dropped at r.t. during 5 min and stirred for 30 min at r.t.. Anhydrous $CaCl_2$ was then added. After gas evolution ceased the reaction mixture was filtered, and the solid was washed with CH_2Cl_2. The filtrate was concentrated to afford 50 mg of a pale brown solid (93 %). M.p.: 93.5-95°. TLC: R_f 0.21 (Et_2O/pentane (1:1)). IR (KBr): 3060, 2995, 2940, 2845, 1740 (CO), 1680, 1275, 995, 815. ^1H NMR (300 MHz, $CDCl_3$): 8.06 (*m*, 2H, arom. H_o); 7.49 (*m*, 3H, arom. $H_{m,p}$); 7.29 (*s*, 1H, H-C(1')); 4.19 (*s*, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 168.21 (CO); 159.46 (C(2)); 153.32 (C(1')); 132.39 (C_p, Ar); 128.71; 127.63 ($C_{o,m}$, Ar); 125.77 (C_{ipso}, Ar); 117.98 (C(4)); 63.37 (CH_3O). MS (EI, 70 eV): 203 (M^+, 19.8); 105 (100), 77 (61.4), 51 (25.1).

General Procedure for Reactions with Diazomethane:

To a soln. of the methylene compound (**1b, 1d, 1e, 1f**) in 20 ml of CH_2Cl_2 excess of ethereal diazomethane soln. (0.3 N) was dropped at 0° during 5 minutes and stirred for 2 h at r.t. controlling the reaction with TLC. Anhydrous $CaCl_2$ was added. After gas evolution ceased the reaction mixture was filtered, and the solid was washed with CH_2Cl_2. The filtrate was concentrated and purified on silica either by MPLC or FC.

Addition of Diazomethane to (*E*)-4-(Chloromethylene)-2-phenyl-5(4*H*)-oxazolone (1b)

1 g of **1b** (4.82 mmol) was used to afford a mixture of crude products which was further separated by MPLC (Et_2O/Pentane, (1:5)):

*4-(2'-Chloroethylidene)-2-phenyl-5(4*H*)-oxazolone (**2b**).* According to the results of GC analysis and the ratio of singlets of the methoxy group at 2.79 ppm and 2.70 ppm resp in ^1H NMR-spectrum (300 MHz, $CDCl_3$) a diastereoisomeric ratio of 9:1 was found. Yield: 20.3 mg (2%). M.p.: 119-122°. TLC: R_f 0.55 (Et_2O/pentane, (1:5)). IR (KBr): 3020, 2910, 1770 (CO), 1640, 1320, 1290, 1220, 960, 880, 690. ^1H NMR (300 MHz, $CDCl_3$): 8.11 (*m*, 2H, arom. H_o); 7.54 (*m*, 3H, arom. $H_{m,p}$); 2.79 (*s*, 3H, H-C(1'), (88%); 2.70 (*s*, 3H, H-C(1'), (12%). ^{13}C NMR (75 MHz, $CDCl_3$) : 163.71 (CO); 161.66 (C(2)); 146.22 (C(1')); 133.40 (C_p, Ar); 128.92, 128.31 ($C_{o,m}$, Ar); 127.42 (C(4)); 125.10 (C_{ipso}, Ar); 22.59 (C(2')). MS (EI, 70 eV, GC-MS): 221 (M^+, 15.5); 142 (0.9), 106 (8.9), 105 (100), 77 (50.4), 51 (18.1).

*(2RS,3RS)-2-Chloro-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**3b**).* Yield: 216 mg (20%). M.p.: 104-106°. TLC : R_f 0.39 (Et_2O/pentane, (1:5)). IR (KBr): 3400 (NH), 3050, 2960, 1790 (CO), 1610, 1470, 1430, 1310, 1280, 1210, 980. ^1H NMR (300 MHz, $CDCl_3$): 8.05 (*m*, 2H, arom. H_o); 7.53 (*m*, 3H, arom. $H_{m,p}$); 3.87 (*dd*, *J* = 6.7, 7.9, 1H, H-C(2)); 2.26 (*m*, 2H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$) : 176.00 (CO); 163.62 (C(5)); 132.90 (C_p, Ar); 128.85, 127.74 ($C_{o,m}$, Ar); 127.49 (C_{ipso}, Ar); 51.78 (C(1)); 41.22 (C(2)); 27.05 (C(3)).

*(2RS,3SR)-2-Chloro-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**4b**).* Yield: 568 mg (53%). M.p.: 140-142°. TLC: R_f 0.72 (Et_2O/pentane (1:5)). ^1H NMR (300 MHz, $CDCl_3$): 7.98 (*m*, 2H, arom. H_o); 7.55 (*m*, 3H, arom. $H_{m,p}$); 4.02 (*t (dd)*, *J* = 7.5, 1H, H-C(2)); 2.41 (*t (dd)*, *J* = 7.5, 1H, H-C(3)); 2.14 (*t (dd)*, *J* = 6.9, 1H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$) : 172.71 (CO); 163.03 (C(5)); 132.72 (C_p, Ar); 128.77, 127.35 ($C_{o,m}$, Ar); 127.13 (C_{ipso}, Ar); 51.76 (C(1)); 40.32 (C(2)); 27.27 (C(3)).

*(2RS,3SR)-2-(Chloromethyl)-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**5b**).* Yield: 40mg (3.5%). M.p.: 59-61°. TLC: R_f 0.33 (Et_2O/pentane (1:5)). IR (CCl_4, 0.2 mm): 3040, 2940, 1800 (CO), 1620, 980, 690. ^1H NMR (300 MHz, $CDCl_3$): 8.01 (*m*, 2H, arom. H_o); 7.53 (*m*, 3H, arom. $H_{m,p}$); 3.90 (*dd*, J = 7.0, 11.5, 1H, H-C(1')); 3.78 (*dd*, J = 8.0, 11.5, 1H, H-C(1')); 2.46 (*m*,, 1H, H-C(2)); 2.02 (*dd*, J = 5.5, 9.5, 1H, H-C(3)); 1.87 (*dd*, J = 5.5, 7.8, 1H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 177.15 (CO); 162.55 (C(5)); 132.56 (C_p, Ar); 128.84, 127.46 ($C_{o,m}$, Ar); 125.99 (C_{ipso}, Ar); 52.59 (C(1)); 40.07 (C(1')); 33.50 (C(2)); 24.65 (C(3)). MS (EI, 70 eV): 237 (M^+, 1.4); 235 (M^+, 4.3); 200 ([M^+-Cl], 8.9); 173 (2.7), 154 (2.5), 105 (100), 77 (46.1), 51 (17.8), 41 (2.3).

*(2RS,3RS)-2-(Chloromethyl)-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**6b**).* Yield: 44 mg (3.9%). M.p.: 82-85°. TLC : R_f 0.24 (Et_2O/pentane (1:5)). IR (CCl_4, 0.2 mm): 3040, 2940, 1800 (CO), 1620, 1000; 970, 860; 700. ^1H NMR (300 MHz, $CDCl_3$): 7.99 (*m*, 2H, arom. H_o); 7.54 (*m*, 3H, arom. $H_{m,p}$); 3.98 (*dd*, J = 6.7, 11.7, 1H, H-C(1')); 3.86 (*dd*, J = 8.9, 11.8, 1H, H-C(1')); 2.66 (*m*, 1H, H-C(2)); 2.20 (*dd*, J = 5.5, 9.5, 1H, H-C(3)); 1.83 (*dd*, J = 5.5, 8.3, 1H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 176.19 (CO); 162.11 (C(5)); 132.58 (C_p, Ar); 128.85, 127.41 ($C_{o,m}$, Ar); 125.88 (C_{ipso}, Ar); 52.02 (C(1)); 40.59 (C(1')); 34.03 (C(2)); 25.78 (C(3)). MS (EI, 70 eV, GC-MS): 237 (M^+, 1.8); 235 (M^+, 4.6); 200 ([M^+-Cl], 10.1); 173 (2.8), 154 (2.6), 105 (100), 77 (42.5), 51 (18.1), 41 (2.2).

Addition of Diazomethane to 4-(Iodomethylene)-2-phenyl-5(4*H*)-oxazolone (1d)

150 mg of **1d** (0.50 mmol) was used to afford a mixture of crude products which was further separated with FC (Et_2O/pentane, (1:19)):

*(2RS,3SR)-2-(Iodomethyl)-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**5d**).* Yield: 56 mg (34%). M.p.: 56.5-58.5°. TLC: R_f 0.35 (Et_2O/pentane (1:5)). IR (CCl_4, 0.2 mm): 3040 , 2900, 1800 (CO), 1630, 1520, 1340, 1220, 980. ^1H NMR (300 MHz, $CDCl_3$): 8.01 (*m*, 2H, arom. H_o); 7.53 (*m*, 3H, arom. $H_{m,p}$); 3.90 (*dd*, J = 7.0, 11.5, 1H, H-C(1')); 3.78 (*dd*, J = 8.0, 11.5, 1H, H-C(1')); 2.46 (*m*, 1H, H-C(2)); 2.02 (*dd*, J = 5.5, 9.5, 1H, H-C(3)); 1.87 (*dd*, J = 5.5, 7.8, 1H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 176.81 (CO); 162.52 (C(5)); 132.52 (C_p, Ar); 128.81, 127.44 ($C_{o,m}$, Ar); 126.06 (C_{ipso}, Ar); 55.67 (C(1)); 35.37 (C(2)); 27.89 (C(3)); 1.94 (C(1')). MS (CI, NH_3): m/z 328 ([M+H]$^+$, 12.7); 222 (0.3), 202 ([(M-J)+H]$^+$, 100); 188 (0.2), 139 (2.1).

*(2RS,3RS)-2-(Iodomethyl)-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**6d**).* Yield: 69 mg (42%). M.p. 57-59°. TLC: R_f 0.24 (Et_2O/pentane (1:5)). IR (CCl_4, 0.2 mm): 2900, 2840, 1790 (CO), 1620, 1530, 1240, 990. ^1H NMR (300 MHz, $CDCl_3$): 7.97 (*m*, 2H, arom. H_o); 7.53 (*m*, 3H, arom. $H_{m,p}$); 3.64 (*dd*, J = 8.1, 10.3, 1H, H-C(1')); 3.49 (*dd*, J = 8.1, 10.3, 1H, H-C(1')); 2.77 (*m*, 1H, H-C(2)); 2.25 (*dd*, J = 5.4, 9.1, 1H, H-C(3)); 1.76 (*dd*, J = 5.4, 8.4, 1H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 175.83 (CO); 161.85 (C(5)); 132.54 (C_p, Ar); 128.85, 127.38 ($C_{o,m}$, Ar); 125.86 (C_{ipso}, Ar); 55.85 (C(1)); 35.80 (C(2)); 29.10 (C(3)); -0.04 (C(1')). MS (CI, NH_3): 328 ([M+1]$^+$, 12.7); 222 (14.6), 202 ([(M-I)+1]$^+$, 100); 188 (3.9), 162 (3.2), 139 (5.9), 122 (3.9), 105 (3.5). MS (FAB, NBA): 328 ([M+1]$^+$, 100); 222 (4.6), 201 (8.4), 200 (9.3), 149 (3.8), 122 (8.1), 105 (100), 89 (12.0), 77 (24.1).

Addition of Diazomethane to (*Z*)-4-(Acetoxymethylene)-2-phenyl-5(4*H*)-oxazolone (1e)

300 mg of **1d** (1.30 mmol) was used to afford a mixture of crude products which was difficult to separate properly (FC (Et_2O/pentane, (1:5))):

*(2RS,3SR)-2-Acetoxy-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**3e**).* Yield: 128 mg (40 %). TLC: R_f 0.28 (Et_2O/pentane (1:5)). ^1H NMR (300 MHz, $CDCl_3$): 7.96 (*m*, 2H, arom. H_o); 7.50 (*m*, 3H, arom. $H_{m,p}$); 4.68 (*dd*, *J* = 5.9, 7.3, 1H, H-C(2)); 2.26 (*m*, overlapped, 2H, H-C(3)); 2.12 (*s*, 3H, CH_3CO). ^{13}C NMR (75 MHz, $CDCl_3$): 175.84 (CO); 170.14 (CO); 163.01 (C(5)); 132.48 (C_p, Ar); 128.65, 127.38 ($C_{o,m}$, Ar); 125.84 (C_{ipso}, Ar); 59.89 (C(2)); 50.97 (C(1)); 22.37 (C(3)); 20.19 (CH_3CO). MS (CI, NH_3): 246 ($[M+H]^+$, 100); 204 (23.1), 188 (10.7), 174 (5.5), 122 (3.3), 105 (7.4).

*(2RS,3RS)-2-Acetoxy-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**4e**).* Yield: 64 mg (20 %). TLC: R_f 0.27 (Et_2O/pentane (1:5)). ^1H NMR (300 MHz, $CDCl_3$): 7.96 (*m*, 2H, arom. H_o); 7.50 (*m*, 3H, arom. $H_{m,p}$); 4.72 (*t(dd)*, *J* = 6.7, 1H, H-C(2)); 2.27 (*m*, 1H, H-C(3)); 2.13 (*m*, overlapped, 1H, H-C(3)); 2.12 (*s*, 3H, CH_3CO). ^{13}C NMR (75 MHz, $CDCl_3$): 173.70 (CO); 170.65 (CO); 162.43 (C(5)); 132.43 (C_p, Ar); 128.65, 127.38 ($C_{o,m}$, Ar); 125.73 (C_{ipso}, Ar); 60.04 (C(2)); 51.49 (C(1)); 23.38 (C(3)); 20.19 (CH_3CO).

Addition of Diazomethane to (*Z*)-4-(Pivaloyloxymethylene)-2-phenyl-5(4*H*)-oxazolone (1e)

79 mg of **1e** (0.289 mmol) was used to afford a mixture of crude products which was further separated with FC and MPLC (Et_2O/pentane, (1:5)):

*2-Phenyl-4-[(2')-(pivaloyloxyethylidene)]-5(4H)-oxazolone (**2f**).* According to the results of GC analysis and the ratio of both singlets of the methyl and the pivaloyloxy group at 2.79 ppm and 2.70 ppm in ^1H NMR-spectrum (300 MHz, $CDCl_3$) a diastereoisomeric ratio of 9:1 was found. Yield: 7 mg (8.5%) (oil) TLC: R_f 0.52 (Et_2O/pentane (1:5)). IR (KBr): 3020, 2960, 2940, 1770, 1740 (CO), 1660, 1310, 1170, 1070. ^1H NMR (300 MHz, $CDCl_3$): 8.00 (*m*, 2H, arom. H_o); 7.50 (*m*, 3H, arom. $H_{m,p}$); 2.53 (*s*, 3H, H-C(2)) (90%); 2.46 (*s*, 3H, H-C(2)) (10%); 1.40 (*s*, 9H, $C(CH_3)_3$) (90%); 1.37 (*s* , 9H, $C(CH_3)_3$) (10%). ^{13}C NMR (75 MHz, $CDCl_3$): 175.03 (CO); 166.50 (C(5)=O); 159.01 (C(2)); 157.66 (C(1')); 132.87 (C_p, Ar); 128.81, 127.97 ($C_{o,m}$, Ar); 125.59 (C_{ipso}, Ar); 111.70 (C(4)); 39.47 ($C(CH_3)_3$); 27.07 ($C(CH_3)_3$); (17.53 (C(2')). MS (CI, NH_3): 288 ($[M+H]^+$, 100); 220 (1.2), 204 (5.9), 188 (15.3), 184 (5.3), 168 (4.8), 122 (3.6), 105 (6.2), 102 (3.9).

*(2RS,3SR)-2-Pivaloyloxy-5-phenyl-6-oxa-4-azaspiro[2.4]hepten-7-one (**3f**).* The purified solid was crystallized from CH_2Cl_2 to afford suitable crystals for X-ray analysis. Yield: 36 mg (43%). M.p. 91-94°. TLC: R_f 0.39 (Et_2O/pentane (1:4)). IR (CCl_4, 0.2 mm): 3050, 2950, 2840, 1775 (CO), 1740 (CO), 1660, 1310, 1180, 1070, 870, 690. ^1H NMR (300 MHz, $CDCl_3$): 7.94 (*m*, 2H, arom. H_o); 7.49 (*m*, 3H, arom. $H_{m,p}$); 4.65 (*dd*, *J* = 5.9, 7.1, 1H, H-C(2)); 2.32 (*dd*, *J* = 5.9, 7.1, 1H, H-C(3)); 2.15 (*t(dd)*, J = 7.1, 1H, H-C(3)); 1.23 (*s*, 9H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$): 178.05 (CO); 176.11 (C(7)=O); 162.53 (C(5)); 132.45 (C_p, Ar); 128.75, 127.31 ($C_{o,m}$, Ar); 126.10 (C_{ipso}, Ar); 60.04 (C(2)); 51.16 (C(1)); 38.65 ($C(CH_3)_3$; 26.97 ($C(CH_3)_3$); 22.50 (C(3)). MS (CI, NH_3): 288 ($[M+H]^+$, 100); 204 (9.1), 188 (37.3), 162 (13.8), 139 (7.1), 122 (7.7), 105 (1.8), 102 (3.7), 58 (4.2), 46 (5.8). X-Ray data: cf Table 3.

*(2RS,3RS)-2-Pivaloyloxy-5-phenyl-6-oxa-4-azaspiro[2,4]hepten-7-one (**4f**).* Yield: 25 mg (30%). M.p.: 97-100°. TLC: R_f 0.26 (Et_2O/pentane (1:4)). IR (CCl_4, 0.2 mm): 3020, 2950, 2840 , 1785 (CO), 1750 (CO), 1660, 1150, 1060, 1000, 860, 690. ^1H NMR (300 MHz, $CDCl_3$): 7.97 (*m*, 2H, arom. H_o); 7.50 (*m*, 3H, arom. $H_{m,p}$); 4.69 (*dd*, *J* = 6.1, 7.0, 1H, H-C(2)); 2.26 (*m*, 2H, H-C(3)); 1.23 (*s* , 9H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$): 178.55 (CO); 173.43 (C(7)=O); 162.53 (C(5)); 132.51 (C_p, Ar); 128.75, 127.48 ($C_{o,m}$, Ar); 125.91 (C_{ipso}, Ar); 60.06 (C(2)); 51.67 (C(1)); 38.65 ($C(CH_3)_3$; 27.01 ($C(CH_3)_3$); 23.42 (C(3)). MS

(CI, NH_3): 288 ([M+H]$^+$, 100); 204 (8.2), 188 (33.3), 162 (11.0), 139 (7.2), 122 (10.7), 105 (3.2), 58 (3.2), 46 (3.1).

Table 3. Crystal Data and Parameters of Data Collection for **3f**

Molecular formula	$C_{16}H_{17}NO_4$	Crystal dimensions [mm]	0.23 x 0.43 x 0.50
Crystal system	trikline	Temperature [K]	298
Space group	P 1-	*Q* max [°]	26.32
a [Å]	7.259(1)	Radiation	Mo*K*(α), *l*=0.71069 Å
b [Å]	10.454(1)	Scan type	w/2Q
c[Å]	10.576(1)	No. of independent refl.	3065
a [°]	75.974(7)	No. of refl. in refinement	1957
b [°]	83.068(7)	No. of variables	194
g [°]	78.826(5)	Final *R*	3.59
V [Å3]	671.01(11)	Final R_W	2.71
Z	2	Weighting scheme	weight·[1-(ΔF/6 σF)^2]^2

(1*RS*,2*SR*)-1-Amino-2-(hydroxymethyl)cyclopropane-1-carboxylic Acid Hydrochloride (7)

Under protection from light a suspension of 50 mg **5d** (0.153 mmol) 4 ml aqueous HCl (6 N) was heated under reflux for 5 h. To the yellow soln. 10 ml H_2O were added and extracted with Et_2O (3 x 8 ml). The aqueous layer was lyophilized to afford 25 mg product which was futher crystallized from EtOH/acetonitrile/Et_2O. Yield: 20 mg (78%). IR (KBr): 3600-2600 (NH, OH), 1700 (CO), 1600, 1420, 1200, 1010, 870. ^{1}H NMR (300 MHz, D_2O): 4.06 (*dd*, *J* = 4.1, 12.4; 1H, H-C(1')); 3.86 (*dd*, *J* = 6.2, 12.4; 1H, H-C(1')); 2.12 (*m*, 1H, H-C(2)); 1.76 (*dd*, *J* = 6.5, 10.2; 1H, H-C(3)); 1.48 (*t (dd)*, *J* = 7.5, 1H, H-C(3)). ^{13}C NMR (75 MHz, D_2O): 177.08 (CO); 61.87 (C(1')); 42.38 (C(1)); 30.22 (C(2)); 20.16 (C(3)). MS (FAB, NBA): 132 ([M+H]$^+$, 100); 114 (11.31), 68 (4.16).

(1*RS*,5*RS*)-1-Amino-2-oxo-3-oxabicyclo[3.1.0]hexane Hydrochloride (8)

Under protection from light a suspension of 61 mg **6d** (0.187 mmol) 4 ml aqueous HCl (6 N) was heated under reflux for 6 h. To the yellow soln. 10 ml H_2O were added and extracted with Et_2O (3 x 8 ml). The aqueous layer was lyophilized to afford 25 mg product which was not further purified. ^{1}H NMR (300 MHz, D_2O): 4.60 (*dd*, *J* = 4.8, 9.8, 1H, H-C(4)), 4.38 (*d*, *J* = 9.8, 1H, H-C(4)); 2.98 (*m*, 1H, H-C(5)); 1.89 (*dd*, *J* = 6.5, 8.9, 1H, H-C(6)); 1.53 (*t(dd)*, *J* = 5.6, 1H, H-C(6)). ^{13}C NMR (75 MHz, D_2O): 173.08 (CO); 69.87 (C(4)); 37.38 (C(1)); 21.22 (C(5)); 15.16 (C(6)).

(1*RS*,6*SR*)-1-Methoxycarbonyl-3-phenyl-2-aza-4-oxa-bicyclo[4.1.0]hept-2-ene (9)

Under protection from light a soln. of 53 mg (0.164 mmol) **5d** and 20 mg (0.164 mmol) dimethylaminopyridine (DMAP) in 5 ml dry methanol was stirred for 36 h at r.t.. The reaction was controlled with TLC. The resulting brown soln. was diluted with 15 ml of CH_2Cl_2 and washed with 10% citric acid and

brine (3 x 10 ml). The organic extract was dried and evaporated to dryness in vacuo to afford a yellow oil which was further purified by FC (Et_2O/pentane, (3:7)). Yield: 5.5 mg (66 %). TLC: Rf 0.32 (Et_2O/pentane (1:4)). IR (CCl_4, 0.2 mm): 3060; 2960; 2880; 1720 (CO); 1640; 1430; 1320; 1270; 1160; 1110; 690. ^1H NMR (300 MHz, $CDCl_3$): 7.94 (*m*, 2H, arom. H_o); 7.38 (*m*, 3H, arom. $H_{m,p}$); 4.49 (*d*, *J* = 10.5, 1H, H-C(5)); 4.23 (*dd*, *J* = 1.5, 10.5, 1H, H-C(5)); 3.85 (*s*, 3H, OCH_3); 2.37 (*m*, 1H, H-C(6)); 1.94 (*dd*, *J* = 4.5, 9.0, 1H, H-C(7)); 1.59 (*dd*, *J* = 4.5, 7.0, 1H, H-C(7)). ^{13}C NMR (75 MHz, $CDCl_3$) : 173.08 (CO); 153.11 (C(3)); 132.92 (C_{ipso}, Ar); 130.80 (C_p, Ar); 128.06, 127.22 ($C_{o,m}$, Ar); 60.75 (C(5)); 52.54 (O-CH_3); 37.45 (C(1)); 26.79 (C(6)); 24.67 (C(7)). MS (EI, 70 eV): 232 (4.2, M^+); 199 (2.0), 105 (100), 85 (3.7), 77 (35.2), 71 (5.9), 57 (10.2), 51 (10.2), 43 (9.3).

(2*RS*)-1-Methyl-1-benzoylamino-4-oxobutanoic Acid (10)

A mixture of 40 mg (0.156 mmol) **3e/4e** and 19.1 mg DMAP (0.187 mmol) in 10 ml dry methanol was stirred at r.t. for 36 h. The reaction was controlled with TLC. The resulting soln. was diluted with 15 ml of CH_2Cl_2 and washed with 10 % citric acid and brine (3 x 10 ml). The organic extract was dried and evaporated to dryness in vacuo to afford a yellow oil which was further purified by FC (Et_2O/pentane, (8:2)). Yield: 27.3 mg (76 %). TLC: Rf 0.42 (Et_2O). IR (film): 3340 (NH), 3050, 2940 , 2840, 2730, 1720 (CO_{ester}), 1630 (CO_{amide}), 1520, 1330, 1220, 1100, 920, 800, 710. ^1H NMR (300 MHz, $CDCl_3$): 9.76 (*s*; 1H, CHO); 7.78 (*m*, 2H, arom. H_o); 7.48 (*m*, 3H, arom. $H_{m,p}$); 7.14 (*br d*, *J* = 6.7, 1H, NH); 5.05 (*m*, 1H, H-C(2)); 3.78 (*s*, 3H, O-CH_3); 3.24 (*dd*, *J* = 4.7, 7.4, 2H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 199.56 ($CO_{aldehyde}$); 171.20 (CO_{ester}); 167.00 (CO_{amide}); 133.41 (C_{ipso}, Ar); 131.97 (C_p, Ar); 128.63, 127.09 ($C_{o,m}$, Ar); 52.93 (O-CH_3); 47.77 (C(3)); 45.57 (C(2)). MS (EI, 70 eV): 235 (0.1, M^+); 207 (1.2), 190 (0.2), 176 (10.1), 162 (0.3), 148 (17.9), 130 (5.4), 121 (0.7), 105 (100), 77 (41.3), 75 (0.1), 51 (13.9), 42 (0.2).

(2*RS*)-1-Methyl-1-benzoylamino-4-dimethoxybutanoic Acid (11)

The experiment was performed in an analogous way as described before. The amount of DMAP added was increased continuosly for 96 h from 0.1 mol-% to 1 mol-% until from TLC a reaction could be seen. Yield : 24 mg (77%). TLC: Rf 0.66 (Et_2O). IR (film): 3300 (NH), 3040, 2920, 2820, 1730 (CO_{ester}), 1630 (CO_{amide}), 1520, 1430, 1200, 1120, 1050, 700, 680. ^1H NMR (300 MHz, $CDCl_3$): 7.81 (*m*, 2H, arom. H_o); 7.47 (*m*, 3H, arom. $H_{m,p}$); 7.26 partially overlapped with $CDCl_3$-signal (*br s*, 1H, NH); 4.86 (*m*, 1H, H-C(2)); 4.51 (*t*, *J* = 5.3, 1H, H-C(4)); 3.78 (*s*, 3H, $COOCH_3$); 3.39 (s, 3H, OCH_3); 3.36 (s, 3H, OCH_3); 2.25 (*m*, 2H, H-C(3)). ^{13}C NMR (75 MHz, $CDCl_3$): 172.83 (CO_{ester}); 166.91 (CO_{amide}); 133.80 (C_{ipso}, Ar); 131.74 (C_p, Ar); 128.59, 127.03 ($C_{o,m}$, Ar); 102.69 (C(4)); 54.05; 53.62 (O-CH_3); 52.51 (OCH_3); 49.74 (C(2)); 34.45 (C(3)). MS (EI, 70 eV): 235 (0.1, M^+); 207 (1.2), 190 (0.2), 176 (10.1), 162 (0.3), 148 (17.9), 130 (5.4), 121 (0.7), 105 (100), 77 (41.3), 75 (0.1), 51 (13.9), 42 (0.2).

Acknowledgement: We are grateful to the Swiss National Science Foundation for the financial support of these investigations.

REFERENCES

1. Abeles, F. B.; Morgan, P. W.; J. M. Saltveit, *Ethylene in Plant Physiology;* second ed.; Academic Press: San Diego, New York, Boston, Sydney, Tokyo, Toronto, 1992.
2. Adams, D. O.; Yang, S. F. *Proc. Nat. Acad. Sci. USA* **1979**, *76*, 170-174.
3. Kende, H. *Ann. Rev. Plant Physiol. Plant Mol. Biol.* **1993**, *44*, 283-307.
4. Ecker, J. R. *Science* **1995**, *268*, 667-675.
5. Wick, L.; Tamm, C.; Boller, T. *Helv. Chim. Acta* **1995**, *78*, 403-410.
6. Arenal, I.; Bernabé, M.; Alvarez, E. F.; Izquierdo, M. L.; Penadés, S. *J. Heterocycl. Chem.* **1983**, *20*, 607-613.
7. Srivastava, P.; Roberts, M.; Holmes, T.; Stammer, C. H. *J. Org. Chem.* **1989**, *54*, 5866-5870.
8. Bland, J. M.; Varughese, K. I.; Stammer, C. H. *J. Org. Chem.* **1984**, *49*, 1634-1636.
9. Bland, J.; Shah, A.; Bortolussi, A.; Stammer, C. H. *J. Org. Chem.* **1988**, *53*, 992-995.
10. Turchi, I. J. In *Oxazoles*; Y. S. Rao, Ed.; Interscience: New York, 1986; *45*, 362-690
11. Engel, P. S. *Chem. Rev.* **1980**, *80*, 118-123.
12. Kalinowski, H. O.; Berger, S.; Braun, S. Georg Thieme Verlag: Stuttgart, New York, 1984; pp 88-96.
13. Koskinen, A. M.; Muñoz, L. *J. Org. Chem.* **1993**, *58*, 879-886.
14. Cannon, J. G.; Garst, J. E. *J. Org. Chem.* **1975**, *40*, 182-184.
15. Shroff, C. C.; Stewart, W. S.; Uhm, S. J.; Wheeler, J. W. *J. Org. Chem.* **1971**, *36*, 3356-3361.
16. *Aldrchimica Acta* **1983**, *16*, 3.
17. SHELXS-86: Sheldrick, G. M. University of Goettingen **1983**.
18. CRYSTALS, Issue 9: Watkin, D. Chemical Crystallography Laboratory, Oxford **1983**.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

(*Received in Germany* 2 *June* 1995; *accepted* 21 *July* 1995)