Regioselective Anodic Oxidation of *N*-Acyl, *N*-Alkoxycarbonyl, and *N*-(2-Nitrophenylsulfenyl) Dipeptide Esters[1)]

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The chloride-mediated anodic methoxylation of protected dipeptide esters shows high regioselectivity. It is influenced by the *N*-protecting groups and the amino acid side-chains. The anodic methoxylation may be effectively directed to the selective oxidation of the C-terminal amino acid. Regioselective oxidation of the N-terminal amino acid is obtained by direct electrolysis of *N*-(2-nitrophenylsulfenyl)-protected dipeptides with formation of the sulfenimino dipeptides.

Regioselektive anodische Oxidation von *N*-Acyl-, *N*-Alkoxycarbonyl- und *N*-(2-Nitrophenylsulfenyl)-Dipeptidestern

Die durch Chlorid katalysierte anodische Methoxylierung geschützter Dipeptidester zeigt hohe Regioselektivität. Diese wird sowohl durch die *N*-Schutzgruppen als auch durch die Aminosäure-Seitenketten beeinflußt. Die anodische Methoxylierung läßt sich effektiv in Richtung auf die selektive Oxidation der C-terminalen Aminosäure steuern. Die regioselektive Oxidation der N-terminalen Aminosäuren gelingt, wenn man von *N*-(2-Nitrophenylsulfenyl)-geschützten Dipeptidestern ausgeht. Man erhält auf diese Weise die entsprechenden Sulfenimino-Verbindungen.

Selective oxidation in the α-position of the N- or C-terminal amino acid residue in protected dipeptides is synthetically interesting. It leads to compounds which are potential chiral electrophilic amino acid equivalents. The introduction of nucleophiles into the oxidized α-position with stereochemical control by the second amino acid residue is therefore possible. The α-oxidation of dipeptides would be especially easy to perform using electrochemical methodology. In the case of *N*-acyl and *N*-alkoxycarbonyl amino acid derivatives we have shown that indirect electrochemical oxidation using sodium chloride as redox catalyst is especially successful for α-methoxylation[2)]. On the other hand, *N*-(2-nitrophenylsulfenyl)-(NPS-)protected amino acid esters could be oxidized by direct electrolysis to the corresponding 2-NPS imino acid esters[3)]. In this paper we now report the application of these two methods to the selective oxidation of protected dipeptides.

Indirect Electrochemical Methoxylation in the α-Position to the Nitrogen of Protected Dipeptides with Sodium Chloride as Redox Catalyst

Like *N*-acylamino acid esters[1)], *N*-acyl or *N*-alkoxycarbonyl dipeptides **1** can be anodically oxidized in the α-position to the nitrogen, using NaCl as mediator, by the intermediate formation of the regioisomeric *N*-chloro derivatives **2** and **3** and the imino compounds **4** and **5**. Thus, in the case of the dipeptides, two regioisomeric methoxylated dipeptides **6** and **8** may be obtained by oxidation at the C- or the N-terminal amino acid. The reaction sequence is shown in Scheme 1.

The results summarized in Table 1 show that the oxidation occurs selectively and in high yields at the C-terminal amino acid, if *N*-benzoyl protecting groups without electron-donating substituents are used (**1a**, **b**, **e**, **f**). This leads to the methoxylated products **6**, which may be accompanied by 4-imidazolidinones **7** if an α-branched C-terminal amino acid is employed. With the 4-methoxybenzoyl group (**1c**), methoxylation at the N-terminal amino acid residue dominates although in low yields. The *Z*-protecting group (**1d**, **g**, **h**) predominantly leads to oxidation at the C-terminus, in two cases accompanied by the formation of hydantoins **9** and **10** with a methoxy group in the α-position to the former N-terminus.

The Boc protecting group causes selective methoxylation at the C-terminus if glycine is the C-terminal amino acid (**1k**), whereas in the case of *N*-Boc-glycyl-valine methylester (**1i**) the unsubstituted glycine residue at the N-terminus is predominantly methoxylated, accompanied by oxidation at the C-terminus leading to the imidazolidinone **7i**. In conclusion, it can be said that α-alkylated amino acids are more difficult to oxidize than the glycine residue. Oxidation at the C-terminus usually predominates and in many cases may be performed with total selectivity, leading to the methoxylated dipeptide and/or the 4-imidazolidinone. The latter product can be obtained in high yields if the electrooxidation is run in acetonitrile/5% methanol[4)]. The formation of the 4-imidazolidinone occurs with α-branched amino acids at the C-terminus by oxidation in the α-position to the N of the C-terminal amino acid, followed by intramolecular attack of the N-terminal nitrogen onto the C-terminal imino group. Urethane protecting groups and others with a smaller electron-withdrawing tendency lead to partial methoxylation at the N-terminus. Cyclization to the 4-imidazolidinone can be suppressed by use of the phthaloyl protecting group, leading only to methoxylation at the C-terminus. In the case of

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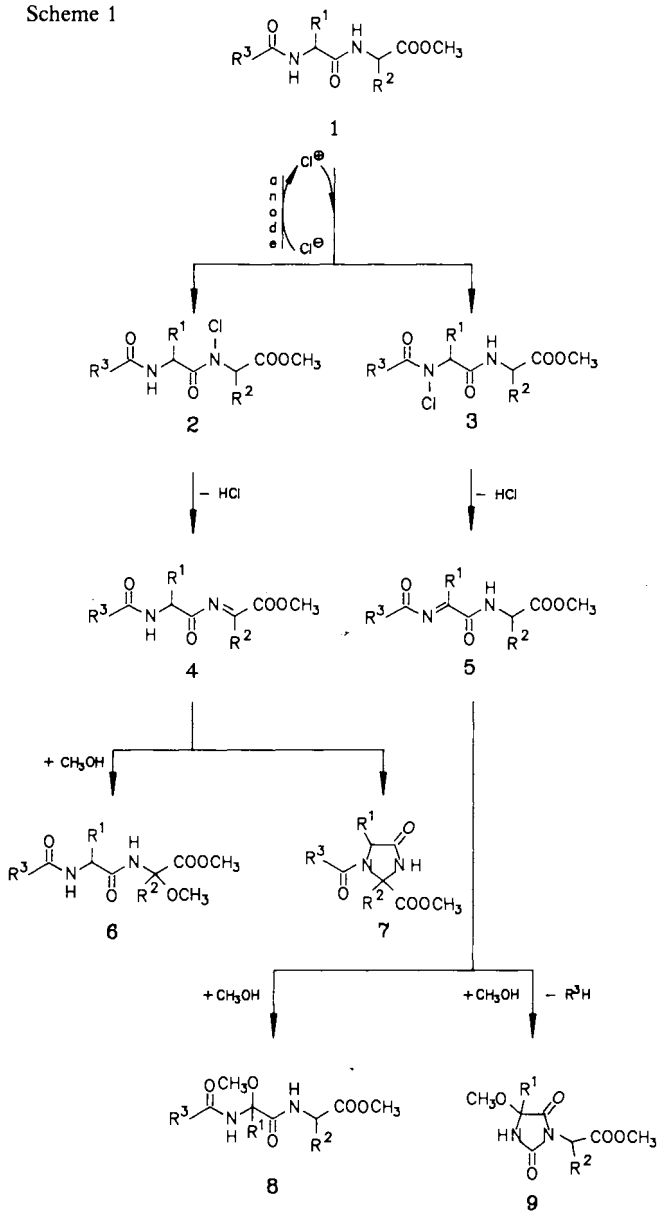
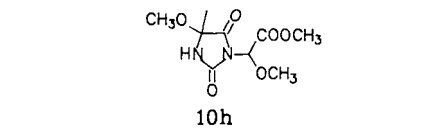
Scheme 1



N-phthaloyl-glycyl-alanine methyl ester (**11**), 40 to 50% of *N*-phthaloyl-glycyl-α-methoxyalanine methyl ester (**6l**) is formed. The low yield is due to partial anodic ring opening of the protecting group. Therefore, it should be better to use *N*-(Boc)$_2$-protected dipeptides[5].

The electrochemical introduction of the methoxy group into glycine residues of dipeptides with C- or N-terminal alanine or valine residues shows almost no diastereoselectivity. However, after deprotection of **6k** (98% HCOOH; quantitative) and instantaneous cyclization to the corresponding (3*S*,6*RS*)-3-isopropyl-6-methoxy-2,5-piperazinedione (**11**), the methoxy group can be exchanged by nucleophiles. The stereochemistry is controlled by the α-C-atom of the L-valine residue with high diastereoselectivity. With dibenzoylmethane, under the catalytic influence of trifluoroacetic acid, the substitution product can be obtained in 64% yield with 82% diastereomeric excess in favour of the *anti*-form. This reaction sequence, using **11** as an electrophilic chiral glycine equivalent, is currently being investigated for the synthesis of optically active substituted amino acids[6].



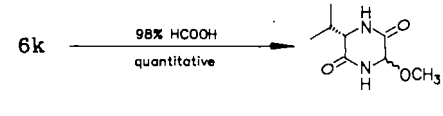


Table 1. Results of the chloride-mediated electrochemical oxidation of differently substituted dipeptides **1** in methanol[a]

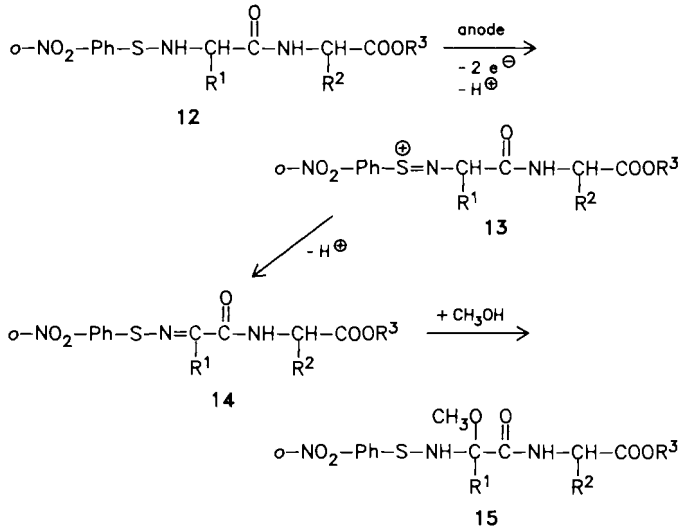
starting material **1**			products (% yield)[b]			
	R^1	R^2	R^3	**6**	**7**	**8**	**9**
a:	H	H	Ph	56.6(81)	–	–	–
b:	H	H	4-Cl-Ph	49.4(83)	–	–	–
c:	H	H	4-MeO-Ph	6.4(10)	–	13(21)	–
d:	H	H	$PhCH_2O$	51.2(73)	–	–	–
d: (at Pt-anode)	H	H	$PhCH_2O$	32.3(53)	–	–	4.0(6.5)
e:	H	CH_3	Ph	14.5(24)	40.2(66)	–	–
f:	CH_3	H	Ph	51.6(85)	–	–	–
g:	H	CH_3	$PhCH_2O$	30(43)	14(19)	–	–
g: (at Pt anode)	H	CH_3	$PhCH_2O$	14(19)	43(60)	–	–
h: (at Pt anode)	CH_3	H	$PhCH_2O$	20.1(21)	–	–	18.2(19)[c]
i:	H	iPr	$(CH_3)_3CO$	–	13.1	40	–
k:	iPr	H	$(CH_3)_3CO$	69	–	–	–
l:	H	CH_3	[d]	50	–	–	–

[a] Undivided cell; anode material: graphite foil (Sigraflex®, 25 cm^2) with the three indicated exceptions; galvanostatic control (200 mA); electrolyte: 35 ml MeOH/0.2 M $LiClO_4$/200 mg NaCl; yields determined after consumption of 2–3 F/mol at 11–14°C. – [b] Yields in parentheses with regard to consumed starting material. – [c] Accompanied by 11.4% (12%) of the dimethoxylated hydantoin **10h** (second methoxy group in α-position to the nitrogen of the C-terminal amino acid). – [d] R^3CONH replaced by phthalimido.

Direct Electrochemical Oxidation of *N*-(2-Nitrophenylsulfenyl)-Protected Dipeptides

2-NPS-protected amines and amino acids may be oxidized in the α-position to the nitrogen by direct electrolysis in the presence of 2,6-dimethylpyridine as base and dichloromethane as solvent (divided cell). Thus, 2-NPS-imines are formed[3]. Application of this method to 2-NPS-protected dipeptides **12a** (R^1=H; R^2=CH_3; R^3=CH_3; cyclovoltammogram: first irreversible anodic peak potential 980 mV vs. Ag/$AgNO_3$) and **12b** [R^1=CH_2Ph; R^2=H; R^3=CH_2(3,4-MeO)Ph; cyclovoltammogram: first irreversible anodic peak potential 870 mV vs. Ag/$AgNO_3$] leads to the formation of (2-nitrophenylthio)imines by oxidation in the α-position to the nitrogen of the N-terminal amino acid according to Scheme 2.

Scheme 2



Thus, compound **14a** ($R^1 = H$; $R^2 = CH_3$; $R^3 = CH_3$) was formed in 66% yield. The yield of **14b** [$R^1 = CH_2Ph$; $R^2 = H$; $R^3 = CH_2(3,4\text{-MeO})Ph$], however, was only 13%, due to the lability of the 3,4-dimethoxybenzyl ester group towards oxidation. If **12b** [$R^1 = CH_2Ph$; $R^2 = H$; $R^3 = CH_2(3,4\text{-MeO})Ph$] is oxidized by the selective oxidizing agent tris(4-bromophenyl)ammoniumyl hexachloroantimonate, **14b** is obtained in 63% yield[3]. Direct electrochemical oxidation of dipeptide methyl esters should occur without problems. In methanol solution at room temperature **14a** undergoes methanol addition to the imino group to provide the α-methoxy-NPS-glycyl-alaninemethyl ester (**15a**) in 93% yield. This reaction is reversible, since **15a** eliminates methanol even during drying under vacuum. Introduction of other nucleophiles by addition to the imine double bond should be possible.

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Experimental

^{1}H-NMR spectra: Bruker WH-90 and Bruker AC-200 (δ values, TMS internal standard). – ^{13}C-NMR spectra: Bruker WH-90 and Bruker AC-200 (δ values, TMS internal standard). – IR spectra: Pye-Unicam SP 1100. – Mass spectra: A.E.I. MS-9, MS-30, and MS-50. – Melting points (uncorrected): Kofler micro heating plate (Reichert). – Microanalyses: Perkin-Elmer CH-Analyser 240 and Heraeus CHNO-Rapid. – TLC Analyses: TLC aluminum sheets, silica gel 60 F_{254} (Merck, Riedel-de Haën). – Preparative LC Separations: Silica gel for flash chromatography 30–60 μm (Baker). – Preparative HPLC Separations: Steel column, 25 × 2.5 cm (Knauer Vertex), LiChrosorb Si 60 (Merck), 7 μm in combination with a Waters high-pressure pump, model 590 with U6K injection system, a Knauer UV photometer, a Gilson fraction collector model 201, and a Hewlett-Packard integrator, model 3390A.

Cyclohexane, ethyl acetate, triethylamine, and 2,6-dimethylpyridine were purified by distillation. Methanol (Merck, p.a., stored over 4 Å molecular sieve), acetonitrile (Merck, Aldrich, p.a), dichloromethane (Baker, p.a.), glycine, L-alanine, glycylglycine, *N*-benzoylglycine methyl ester, Z chloride, BOC-ON, HOBT, DCC, benzoyl chloride, *N*-methyl-*N*-nitrosotoluene sulfonamide (Diazald), carbitol (all from Janssen Chimica), *o*-nitrophenylsulfenyl chloride (Ega, Sigma) were used as obtained.

N-Acyl- and *N*-alkoxycarbonyl protected dipeptides were prepared by standard procedures, either starting from glycylglycine with *N*-protection under Schotten-Baumann conditions and esterification by diazomethane (**1a–d**) or by the DCC/HOBT method[7] (**1e–l**). The NPS-protected dipeptides **12a** and **12b** were prepared by the DCC/HOBT method[3,7] from the NPS-amino acid and the corresponding amino acid hydrochloride. All starting materials were characterized by correct ^{1}H-NMR and ^{13}C-NMR spectra and elemental analyses.

Preparative Electrolysis: A FuG (Rosenheim) stabilized current source, modified as potentiostat, NTN 700–200 M, was used in combination with a digital coulombmeter based on voltage-to-frequency conversion.

Cells: Undivided beaker-type glass cell with cooling mantle (50 ml, cell 1), equipped with a cylindrical Pt-foil (25 cm^2) or Sigraflex® foil (Sigri Elektrographit, Meitingen; 25 cm^2) anode, a coaxial Pt-wire cathode, and a magnetic stirrer.
Divided beaker-type glass cell with cooling mantle (100 ml, cell 2), equipped with a graphite disc anode (8 cm^2), an $Ag/AgNO_3$ (0.1 M CH_3CN) reference electrode (570 mV vs. NHE), and a magnetic stirrer. The cathode compartment was formed by a glass cylinder closed by a G-4 glass frit and was equipped with a carbon felt cathode (6 cm^2 × 0.5 cm).

General Procedure for the Electrolysis of N-Acyl and N-Alkoxycarbonyl Protected Dipeptide Esters in the Presence of NaCl: Electrolysis of **1a–l** (3–4 mmol) was performed between 11 and 17°C in cell 1 in 35 ml of methanol (0.2 M $LiClO_4$) containing 200 mg of NaCl. Under controlled current conditions (200 mA) it was electrolyzed until 3 F/mol were consumed. For workup, the solvent was partially evaporated at temperatures below 40°C. After addition of 35 ml of water, the organic phase was extracted with 4 × 80 ml of chloroform, dried with $MgSO_4$, and filtered and the solvent evaporated. The products were separated by flash chromatography or HPLC with ethyl acetate/cyclohexane mixtures as eluents.

General Procedure for the Electrolysis of NPS-Protected Dipeptide Esters: Electrolysis in cell 2 containing 40 ml of CH_2Cl_2 (0.1 M tetra-*n*-butylammonium perchlorate was started at a potential of 430 (**12a**) or 650 (**12b**) mV vs. $Ag/AgNO_3$, and the substrate (1 mmol) and 2,6-dimethylpyridine (1 ml) were added, resulting in a strong increase in current. After the theoretical amount of charge for the oxidation had passed (193 As), or the current had decreased to a value below 1 mA, the yellow or yellow-brown solution was worked up. For the separation of the conducting salt, the solvent was evaporated in the presence of silica gel, and the residue was extracted with ether. After evaporation of the solvent, the crude product was purified by flash chromatagraphy or HPLC.

N-Benzoylglycyl-α-methoxyglycine Methyl Ester [Methyl 2-(N-benzoylglycyl)amino-2-methoxyacetate] (**6a**): 297 mg (57%). – IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1} (m, N–H), 1770 (s, C=O), 1690 (s, C=O, amide I), 1650 (s, amide II), 1123 (s, C–O–C), 700 (m, C–H aromat.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 3.6 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 4.3 (d, J = 5 Hz, 2H, CH_2), 5.6 (d, J = 9 Hz, 1H, CH), 7.5–7.8 (m, 5H, aromat. H), 7.5–7.8 (2H, 2NH). – MS (70 eV): m/z (%) = 281 (0.25) [M^+ + H], 248 (0.5) [M^+ –

CH_3OH], 221 (27), 162 (48), 135 (46), 134 (80), 106 (21), 105 (100), 103 (9), 77 (72), 60 (97), 51 (18).

$C_{13}H_{16}O_5N_2$ (280.28) Calcd. C 55.71 H 5.75 N 9.99
Found C 55.35 H 5.84 N 9.51

$C_{13}H_{17}O_5N_2$ (M^+ + H) Calcd. 281.1138 Found 281.1138 (MS)

N-(o-Chlorobenzoyl)glycyl-α-methoxyglycine Methyl Ester ⟨Methyl 2-[N-(o-Chlorobenzoyl)glycyl]amino-2-methoxyacetate⟩ (**6b**): 540 mg (49%). – IR (KBr): $\tilde{\nu}$ = 3390, 3330 cm^{-1} (m, N–H), 1762 (s, CO, ester), 1650 (s, CO, amide), 1540 (m, N–H), 1109 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): δ = 3.4 (s, 3H, OCH_3), 3.7 (s, 3H, OCH_3), 4.2 (d, *J* = 5 Hz, 2H, CH_2), 5.5 (d, *J* = 9 Hz, 1H, CH), 7.3–7.6 (m, 4H, aromat. H), 7.1–7.6 (2H, 2 NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 43.4 (1 CH_2), 52.7 (1 $COOCH_3$), 56.7 (1 OCH_3), 78.3 (1 CH), 126.9 (1 aromat. CH), 129.7 (1 aromat. CH), 130.8 (1 aromat. C), 131.4 (1 aromat. CH), 134.2 (1 aromat. C), 167.0, 168.0, 169.5 (3 C=O). – MS (70 eV): *m/z* (%) = 315 (0.06) [M^+ + H], 255 (7), 198 (11), 196 (30), 171 (5), 170 (15), 169 (18), 168 (40), 141 (58), 140 (17), 139 (99), 111 (42), 75 (23), 60 (100).

$C_{13}H_{15}ClN_2O_5$ (314.72) Calcd. C 49.61 H 4.80 N 8.90
Found C 49.35 H 4.88 N 8.81

$C_{13}H_{16}ClN_2O_5$ (M^+ + H) Calcd. 315.0748 Found 315.0751 (MS)

Mixture of N-(p-Methoxybenzoyl)glycyl-α-methoxyglycine Methyl Ester ⟨Methyl 2-[N-(p-Methoxybenzoyl)glycyl]amino-2-methoxyacetate⟩ (**6c**) *and N-(p-Methoxybenzoyl)-α-methoxyglycylglycine Methyl Ester* ⟨Methyl 2-[N-(p-Methoxybenzoyl)-α-methoxyglycyl]aminoacetate⟩ (**8c**): 223 mg (31%). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (m, N–H), 1770 (s, CO, ester), 1680 (s, CO, amide), 1110 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): **6c:** δ = 3.5 (s, 3H, OCH_3), 3.7 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 4.1 (d, *J* = 5.8 Hz, 2H, CH_2), 5.73 (d, *J* = 8 Hz, 1H, CH), 6.8 (d, *J* = 9 Hz, 2H, aromat. H), 7.7 (d, *J* = 9 Hz, 2H, aromat. H), 6.8–7.7 (2H, 2 NH); **7c**: 3.4 (s, 3H, OCH_3), 3.7 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 4.2 (d, *J* = 6 Hz, 2H, CH_2), 5.74 (d, *J* = 8 Hz, 1H, CH), 6.8 (d, *J* = 9 Hz, 2H, aromat. H), 7.7 (d, *J* = 9 Hz, 2H, aromat. H), 6.8–7.7 (2H, 2 NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 52.0, 52.1 (2 $COOCH_3$), 55.2, 55.6 (2 OCH_3), 55.7, 56.1 (2 aromat. OCH_3), 41.0 (2 CH_2), 79.2, 79.3 (2 CH), 111.1, 113.5, 129.2, 129.6 (aromat. CH), 125.0, 125.8 (2 aromat. C), 157.7, 162.5, (2 aromat. C), 166.5, 167.6, 168.6, 168.7, 169.8 (6 C=O). – MS (70 eV): *m/z* (%) = 310 (0.15) [M^+], 228 (19), 222 (2), 207 (1), 203 (10), 194 (26), 192 (8), 164 (2), 136 (11) 135 (100).

$C_{14}H_{18}N_2O_6$ (M^+) Calcd. 310.1165 Found 310.1144 (MS)

N-Benzyloxycarbonylglycyl-α-methoxyglycine Methyl Ester [Methyl 2-(N-Benzyloxycarbonylglycyl)amino-2-methoxyacetate] (**6d**): 567 mg (51%). – IR (KBr): $\tilde{\nu}$ = 3430, 3365 cm^{-1} (m, N–H), 3000 (m, CH), 1750 (s, CO, ester), 1684 (s, CO, amide), 1560 (m, N–H), 1074 (s, C–O–C, ether), 800 (s, aromat. CH). – ^1H NMR (90 MHz, $CDCl_3$): δ = 3.4 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 3.9 (d, *J* = 5 Hz, 2H, CH_2), 5.1 (s, 2H, CH_2O), 5.5 (d, *J* = 9 Hz, 1H, CH), 5.6 (t, *J* = 5 Hz, 1H, NH), 7.2 (d, *J* = 9 Hz, 1H, NH), 7.3 (s, 5H, aromat. H). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 44.4 (1 CH_2), 52.8 (1 $COOCH_3$), 56.5 (1 OCH_3), 67.2 (1 OCH_2), 78.2 (1 CH), 128.0 (2 aromat. CH), 128.2 (1 aromat. CH), 128.5 (2 aromat. CH), 136.1 (1 aromat. C), 156.6 [1 $CH_2O(NH)C=O$], 168.3 (1 $CH_3OC=O$), 170.1 [1 $CH_2(NH)C=O$]. – MS (70 eV): *m/z* (%) = 279 (0.06) [M^+ – OCH_3], 251 (4), 192 (4), 172 (23), 150 (11), 92 (10), 91 (100), 60 (17).

$C_{14}H_{18}N_2O_6$ (310.30) Calcd. C 54.17 H 5.85 N 9.03
Found C 54.11 H 5.44 N 8.31

Methyl 2-(5-Methoxy-2,4-dioxoimidazolidin-3-yl)acetate (**9d**): ^1H NMR (90 MHz, $CDCl_3$): δ = 3.4 (s, 3H, OCH_3), 3.7 (s, 3H, $COOCH_3$), 4.2 (s, 2H, CH_2), 6.4 (br., 1H, NH), 5.2 (d, *J* = 2 Hz, 1H, CH). – MS (70 eV): *m/z* (%) = 202 (0.3) [M^+], 174 (28), 172 (74), 171 (25), 143 (28), 115 (100), 88 (38), 56 (51).

$C_7H_{10}N_2O_5$ (M^+) Calcd. 202.0590 Found 202.0596 (MS)

N-Benzoylglycyl-α-methoxyalanine Methyl Ester [Methyl 2-(N-Benzoylglycyl)amino-2-methoxypropionate] (**6e**): 159 mg (15%). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (m, N–H), 1760 (s, CO, ester), 1742 (s, CO, amide), 1550 (m, N–H), 1170 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.6 (s, 3H, CH_3), 3.2 (s, 3H, OCH_3), 3.7 (s, 3H, OCH_3), 4.2 (d, *J* = 5 Hz, 2H, CH_2), 7.4–7.8 (m, 5H, aromat. H), 7.4–7.8 (br., 2H, 2 NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 23.1 (1 CH_3), 43.9 (1 CH_2), 51.2 (1 OCH_3), 52.9 (1 $COOCH_3$), 84.4 (1 C), 127.2–127.3 (2 aromat. CH), 128.5–128.7 (2 aromat. CH), 131.9 (1 aromat. CH), 133.2 (1 aromat. C), 168.1, 169.1, 170.8 (3 C=O). – MS (70 eV): *m/z* (%) = 294 (0.09) [M^+], 281 (0.1), 235 (12), 162 (38), 135 (74), 134 (83), 105 (100), 77 (60), 74 (69).

$C_{14}H_{18}N_2O_5$ (294.30) Calcd. C 57.13 H 6.17 N 9.52
Found C 56.88 H 6.32 N 10.29

$C_{14}H_{18}N_2O_5$ (M^+) Calcd. 294.1216 Found 294.1236 (MS)

Methyl 1-Benzoyl-2-methyl-4-oxoimidazolidin-2-carboxylate (**7e**): 380 mg (40%). – IR (KBr): $\tilde{\nu}$ = 3240, 3160 cm^{-1} (s, N–H), 2815 (s, CH), 1750 (s, CO, ester), 1710, 1630 (s, CO, amide), 1605, 1575 (m, aromat. C=C), 1445, 1415 (s, CH_3, CH_2), 1270, 1239 (s, C–O, ester). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.7 (s, 3H, CH_3), 3.6 (s, 3H, $COOCH_3$), 3.7 and 4.2 (2 d, *J* = 15 Hz, 2H, CH_2), 7.5 (m, 5H, aromat. H), 9.4 (br. s, 1H, NH). – ^{13}C NMR (90 MHz, DMSO): δ = 21.8 (1 CH_3), 50.1 (1 CH_2), 52.6 (1 $COOCH_3$), 75.9 (1 C), 127.1 (2 aromat. CH), 128.2 (2 aromat. CH), 130.9 (1 aromat. CH), 134.6 (1 aromat. C), 168.4 (Ar–C=O, amide), 168.6 (C=O, ester), 170.2 (C=O, amide). – MS (70 eV): *m/z* (%) = 263 (0.09) [M^+ + H], 224 (8), 204 (15), 164 (21), 105 (100), 77 (30), 51 (6), 42 (4).

$C_{13}H_{14}N_2O_4$ (262.26) Calcd. C 59.53 H 5.38 N 10.68
Found C 59.68 H 5.42 N 10.77

$C_{13}H_{15}N_2O_4$ (M^+ + H) Calcd. 263.1032 Found 263.1039 (MS)

N-Benzoylalanyl-α-methoxyglycine Methyl Ester [Methyl 2-(N-Benzoylalanyl)amino-2-methoxyacetate] (**6f**) *(1:1 mixture of 2 diastereomers):* 565 mg (52%). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (m, N–H), 1770 (s, CO, ester), 1664 (s, CO, amide), 1550 (m, N–H), 1115 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.4, 1.42 (2 d, *J* = 7 Hz, 3H, CH_3), 3.31, 3.35 (2s, 3H, OCH_3), 3.62, 3.69 (2s, 3H, $COOCH_3$), 4.8 (quint, *J* = 7 Hz, 1H, CH), 5.5 (d, *J* = 9 Hz, 1H, CH), 7.4–7.7 (m, 6H, aromat. CH, 1 NH), 8.0 (d, *J* = 9 Hz, 1H, 1 NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 18.3, 18.5 (1 CH_3, 2 diastereomers), 49.3 (1 CH), 52.8 (1 $COOCH_3$), 56.2 (1 OCH_3), 78.4 (1 CH), 127.2 (2 aromat. CH), 128.5 (2 aromat. CH), 131.8 (1 aromat. CH), 133.5 (1 aromat. C), 167.3, 168.2, 173.6 (3 C=O). – MS (70 eV): *m/z* (%) = 295 (0.29) [M^+ + H], 281 (0.5), 263 (0.2), 235 (12), 176 (42), 149 (69), 148 (96), 106 (27), 105 (100), 77 (69), 60 (46).

$C_{14}H_{18}N_2O_5$ (294.30) Calcd. C 57.13 H 6.17 N 9.52
Found C 56.86 H 6.09 N 8.89

N-Benzyloxycarbonylglycyl-α-methoxyalanine Methyl Ester [Methyl 2-(N-benzyloxycarbonylglycyl)amino-2-methoxypropionate] (**6g**): 324 mg (30%). – IR (KBr): $\tilde{\nu}$ = 3329 cm^{-1} (m, N–H), 1738 (s, CO, ester), 1700 (s, CO, amide), 1550 (m, N–H), 1157 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.6 (s, 3H, CH_3), 3.2 (s, 3H, OCH_3), 3.7 (s, 3H, $COOCH_3$), 3.8 (d, *J* = 6 Hz, 2H, CH_2), 5.1 (s, 2H, Ar-CH_2), 5.7 (br., 1H, NH), 7.3 (s, 6H, 5 aromat. CH, 1 NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 22.7 (1 CH_3), 43.7 (1 CH_2), 50.6 (1 OCH_3), 52.2 (1 $COOCH_3$), 66.1 (1 $ArCH_2$), 83.4 (1 C), 127.4 (2 aromat. CH), 127.5 (1 aromat. CH, 127.9 (2 aromat. CH), 136.0 (1 aromat. C), 156.2 (1 C=O), 168.6,

170.2 (2 C=O). – MS (70 eV): *m/z* (%) = 294 (8) [$M^+ - CH_2O$], 265 (7), 192 (2.5), 91 (100).

$C_{15}H_{20}N_2O_6$ (324.33) Calcd. C 55.55 H 6.21 N 8.64
Found C 55.26 H 6.27 N 8.53

Methyl 1-Benzyloxycarbonyl-2-methyl-4-oxoimidazolidin-2-carboxylate (**7g**): 432 mg (43%). – IR (KBr): $\tilde{\nu}$ = 3250, 3138 cm^{-1} (m, N–H), 1735 (s, CO, ester), 1645 (s, CO, amide). – ^1H NMR (90 MHz, $CDCl_3$, double signals because of hindered rotation around the exocyclic amide bond): δ = 1.84, 1.88 (2 s, 3H, CH_3), 3.5, 3.7 (2 s, 3H, $COOCH_3$), 4.09, 4.1 (2 s, 2H, CH_2), 5.2 (s, 2H, $ArCH_2$), 7.2 (s, 5H, aromat. H), 7.6 (s, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$, double signals because of hindered rotation around the exocyclic amide bond): δ = 22.6, 22.8 (1 CH_3), 48.5, 48.9 (1 CH_2), 53.1 (1 $COOCH_3$), 67.4, 67.8 (1 $ArCH_2$), 75.8, 76.2 (1 C), 127.9 (2 aromat. CH), 128.0 (1 aromat. CH), 128.5 (2 aromat. CH), 135.8 (1 aromat. C), 153.3 (1 OCON), 170.0, 170.3 (2 C=O). – MS (70 eV): *m/z* (%) = 292 (0.005) [M^+], 264 (0.2), 263 (1.5), 234 (2.7), 129 (2.8), 92 (10), 91 (100).

$C_{14}H_{16}N_2O_5$ (292.29) Calcd. C 57.5 H 5.5 N 9.6
Found C 57.5 H 5.5 N 9.4

$C_{13}H_{16}N_2O_5$ (M^+) Calcd. 292.1059 Found 292.1098 (MS)

N-Benzyloxycarbonylalanyl-α-methoxyglycine Methyl Ester [Methyl 2-(N-Benzyloxycarbonylalanyl)amino-2-methoxyacetate] (**6h**): 220 mg (20%). – IR (KBr): $\tilde{\nu}$ = 3360 cm^{-1} (m, N–H), 1760 (s, CO, ester), 1675 (s, CO, amide), 1550 (m, N–H), 1130 (s, C–O–C, ether). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.3 (d, *J* = 7 Hz, 3H, CH_3), 3.4 (s, 3H, OCH_3), 3.7 (s, 3H, $COOCH_3$), 4.3 (quint, *J* = 7 Hz, 1H, CH), 5.1 (s, 2H, $ArCH_2$), 5.2 (d, *J* = 7 Hz, 1H, NH), 5.5 (d, *J* = 9 Hz, 1H, CH), 7.1 (br., d, *J* = 9 Hz, 1H, NH), 7.2 (s, 5H, aromat. H). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 18.4 (1 CH_3), 50.7 (1 CH), 52.6 (1 $COOCH_3$), 56.4 (1 OCH_3), 67.1 (1 $ArCH_2$), 78.5 (1 CH), 128.0 (2 aromat. CH), 128.2 (1 aromat. CH), 128.5 (2 aromat. CH), 136.1 (aromat. C), 156.0 (1 O–CO–N), 168.2, 173.4 (2 C=O). – MS (70 eV): *m/z* (%) = 325 (0.05) [M^+ + H], 265 (24), 206 (20), 186 (23), 178 (48), 135 (10), 134 (63), 103 (24), 92 (23), 91 (100), 88 (41).

$C_{15}H_{20}N_2O_6$ (324.09) Calcd. C 55.55 H 6.21 N 8.63
Found C 55.53 H 6.19 N 9.07

$C_{15}H_{21}N_2O_6$ (M^+ + H) Calcd. 325.1400 Found 325.1402 (MS)

Methyl 2-(5-Methoxy-5-methyl-2,4-dioxoimidazolidin-3-yl)acetate (**9h**): 134 mg (18%). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.5 (s, 3H, CH_3), 3.3 (s, 3H, OCH_3), 3.7 (s, 3H, $COOCH_3$), 4.3 (s, 2H, CH_2), 6.5 (s, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 23.2 (1 CH_3), 39.1 (1 CH_2), 51.6 (1 OCH_3), 52.7 (1 $COOCH_3$), 87.6 (1 C), 155.0, 167.4, 171.8 (3 C=O). – MS (70 eV): *m/z* (%) = 216 (0.5) [M^+], 188 (44), 186 (57), 185 (51), 173 (6), 157 (21), 129 (100), 126 (18), 125 (21), 114 (18), 100 (71), 88 (28), 86 (54), 74 (27), 73 (29), 56 (27).

$C_8H_{12}N_2O_5$ (M^+) Calcd. 216.0746 Found 216.0743 (MS)

Methyl 2-Methoxy-2-(5-methoxy-5-methyl-2,4-dioxoimidazolidin-3-yl)acetate (**10h**): ^1H NMR (90 MHz, $CDCl_3$): δ = 1.6 (s, 3H, CH_3), 3.24 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.84 (s, 3H, $COOCH_3$), 5.5 (s, 1H, CH), 6.5 (s, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$, mixture of 2 diastereomers): δ = 23.0, 23.2 (1 CH_3), 51.3, 51.4 (1 OCH_3), 53.3, 53.4, (1 $COOCH_3$), 57.4 (1 OCH_3), 77.6 (1 CH), 87.1, 87.2 (1 C), 154.1, 166.0, 171.2 (3 C=O). – MS (70 eV): *m/z* (%) = 246 (0.014) [M^+], 215 (4), 187 (100), 159 (66), 155 (17), 144 (56), 143 (26), 103 (26), 100 (23), 86 (88), 75 (25).

$C_9H_{14}N_2O_6$ (M^+) Calcd. 246.0852 Found 246.0826 (MS)

Methyl 1-tert-Butoxycarbonyl-2-isopropyl-4-oxoimidazolidin-2-carboxylate (**7i**): 130 mg (13%). – M.p. 101°C. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (m, NH), 2960 (m, CH), 1760, 1730 (s, 2 CO), 1045 (m, C–O–C). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.77, 1.02 (d, *J* = 7 Hz, 6H, 2 CH_3), 1.37 (s, 9H, 3 CH_3), 2.86 (br. m, 1H, CH), 3.62 (d, *J* = 7.6 Hz, 1H, CH_2), 3.68 (s, 3H, OCH_3), 3.91 (d, *J* = 7.6 Hz, 1H, CH_2), 7.93 (br. s, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 15.89 (1 CH_3), 17.36 (1 CH_3), 28.06 (3 CH_3), 31.07 (1 CH), 49.03 (1 CH_2), 52.62 (1 OCH_3), 81.21 (1 C), 82.05 (1 C), 152.16 (1 CO), 171.93 (1 CO), 169.73 (1 CO). – MS (90 eV): *m/z* (%) = 287 (0.05) [M^+ + H], 227 (11), 172 (8), 171 (62), 158 (8), 143 (15), 130 (10), 127 (32), 125 (16), 57 (100).

$C_{13}H_{22}N_2O_5$ (286.30) Calcd. C 54.54 H 7.74 N 9.78
Found C 54.51 H 7.73 N 9.50

$C_{13}H_{23}N_2O_5$ (M^+ + H) Calcd. 287.1607 Found 287.1582 (MS)

N-tert-Butoxycarbonyl-α-methoxyglycyl-L-valine Methyl Ester, [Methyl (2S)-2-[(2RS)-N-tert-Butoxycarbonyl-2-methoxyglycyl]-amino-2-isopropylacetate] (**8i**) *(1:1 mixture of 2 diastereomers)*: 436 mg (40%). – M.p. 105°C. – IR (KBr): $\tilde{\nu}$ = 3300 (s, NH), 2960 (s, CH), 1718 (s, CO, ester), 1680 (s, amide I), 1500 (s, amide II), 1150 (s, C–O–C, ether), 1080 (m, C–O). – ^1H NMR (90 MHz, $CDCl_3$, double signals because of diastereomers): δ = 0.84, 0.93 (2 d, *J* = 6 Hz, 6H, 2 CH_3), 1.2 (s, 9H, 3 CH_3), 2.13 [m, *J* = 6 Hz, 1H, $(CH_3)_2CH$], 3.4, 3.41 (2 s, 3H, OCH_3), 3.71 (s, 3H, $COOCH_3$), 4.9 (dd, *J* = 8 Hz, 6 Hz, 1H, CH), 5.2, 5.3 (2 d, *J* = 8 Hz, 1H, $CHOCH_3$), 5.5 (d, *J* = 8 Hz, 1H, NH), 7.0 (d, *J* = 8 Hz, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$, double signals because of diastereomers): δ = 17.6 (1 CH_3), 18.7 (1 CH_3), 27.9 (3 CH_3), 30.97, 31.04 (1 CH), 51.9 (1 $COOCH_3$), 54.75, 55.08 (1 $CHOCH_3$), 57.12 (1 CH), 80.2 [1 $(CH_3)_3C$], 80.7, 81.04 (1 CH), 155.5 (1 O–CO–N), 167.6, 167.8 (1 CO), 171.8 (1 CO). – MS (90 eV): *m/z* (%) = 319 (0.36) [M^+ + 1], 318 (0.23) [M^+], 245 (8), 160 (67), 130 (12), 127 (19), 104 (81), 72 (18), 60 (100), 57 (96), 41 (20).

$C_{14}H_{26}N_2O_6$ (318.342) Calcd. C 52.82 H 8.22 N 8.80
Found C 52.58 H 8.39 N 8.60

$C_{14}H_{27}N_2O_6$ (M^+ + H) Calcd. 319.1869 Found 319.1858 (MS)

N-tert-Butoxycarbonyl-L-valyl-D,L-α-methoxyglycine Methyl Ester [Methyl (2RS)-2-(N-tert-Butoxycarbonyl-L-valyl)amino-2-methoxyacetate] (**6k**) *(1:1 mixture of 2 diastereomers)*: 6.04 g (70%). – M.p. 74–75°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (s, N–H), 2960 (m, CH), 1760 (s, CO, ester), 1660 (s, amide I), 1530 (s, amide II), 1170 (m, C–O–C, ether), 1080 (m, C–O–C). – ^1H NMR (90 MHz, $CDCl_3$, double signals because of diastereomers): δ = 0.86, 0.95 (2 d, *J* = 6 Hz, 6H, 2 CH_3), 1.4 [s, 9H, $(CH_3)_3C$], 2.35 (m, *J* = 6 Hz, 1H, CH), 3.42 (s, 3H, OCH_3), 3.75 (s, 3H, $COOCH_3$), 4.0 (dd, *J* = 9 and 6 Hz, 1H, $NHCH$), 5.08 (br. d, *J* = 9 Hz, 1H, NH), 5.52, 5.54 (2 d, *J* = 9 Hz, 1H, $CHOCH_3$), 7.1 (br. d, *J* = 9 Hz, 1H, NH). – ^{13}C NMR (90 MHz, $CDCl_3$, double signals because of diastereomers): δ = 17.4, 17.7 (1 CH_3), 19.12, 19.29 (1 CH_3), 28.22 [3 CH_3, $(CH_3)_3C$], 30.71 [1 $CH(CH_3)_2$], 52.82 (1 $COOCH_3$), 56.44 (1 $CHOCH_3$), 59.97 (1 CH), 78.52, 78.29 (1 $CHOCH_3$), 80.04 [1 $(CH_3)_3C$], 155.85 (O–CO–N), 168.28 (1 CO), 172.61, 172.74 (1 CO). – MS (70 eV): *m/z* (%) = 319 (0.27) [M^+ + 1], 172 (41), 116 (83), 103 (10), 98 (8), 88 (12), 72 (100), 60 (30), 57 (79).

$C_{14}H_{26}N_2O_6$ (318.34) Calcd. C 52.82 H 8.22 N 8.80
Found C 52.91 H 8.31 N 8.71

$C_{14}H_{27}N_2O_6$ (M^+ + H) Calcd. 319.1869 Found 319.1887 (MS)

α-Methoxy-N-(phthaloylglycyl)alanine Methyl Ester [Methyl 2-Methoxy-2-(N-phthaloylglycyl)aminopropionate] (**6l**): M.p. 171–172°C. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (m, NH), 3060 (aromat. CH), 2940 (aliphat. CH), 1720 (s, CO), 1420 (s, NH), 1160 (s, C–O–C). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.71 (s, 3H, CH_3), 3.21 (s, 3H, OCH_3), 3.75 (s, 3H, $COOCH_3$), 4.35 (s, 2H, CH_2), 6.92

(s, 1H, NH), 7.57–8.0 (m, 4H, aromat. CH). – ^{13}C NMR (90 MHz, $CDCl_3$): δ = 22.68 (1 CH_3), 39.00 (1 CH_2), 50.20 (1 OCH_3), 51.43 (1 $COOCH_3$), 82.66 (1 C), 122.28 (2 aromat. CH), 131.05 (2 aromat. C), 133.22 (2 aromat. CH), 165.36, 166.56, 169.38 (4 CO). – MS (70 eV): *m/z* (%) = 262 (11), 261 (63) [$M^+ - COOCH_3$], 188 (14), 161 (28), 160 (100), 117 (28), 74 (44).

$C_{15}H_{16}N_2O_6$ (320.28) Calcd. C 56.25 H 5.03 N 8.75
Found C 55.95 H 4.86 N 8.64

$C_{15}H_{16}N_2O_6$ (M^+) Calcd. 320.1009 Found 320.1000

(3S,6RS)-3-Isopropyl-6-methoxy-2,5-piperazinedione [cyclo(-L-Val-Gly-OMe)] (**11**): 900 mg (90%). – 2 diastereoisomers in a ratio of 2:1 were separated by flash chromatography [ethyl acetate/methanol (19:1)].

Minor Isomer: R_f = 0.28 [ethyl acetate/methanol (19:1)]. – M.p. 215°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (CH), 1650 (s, CO), 1078 (m, C–O–C). – ^{1}H NMR (90 MHz, $CDCl_3$/TFA): δ = 0.84 (d, *J* = 6.4 Hz, 3H, CH_3), 1.04 (d, *J* = 6.4 Hz, 3H, CH_3), 2.46 (qd, *J* = 6.4, 3.0 Hz, 1H, CH), 3.46 (s, 3H, OCH_3), 4.11 (d, *J* = 3 Hz, 1H, CH), 5.02 (s, 1H, CH). – ^{13}C NMR (90 MHz, $CDCl_3$/CD_3OD): δ = 16.08 (1 CH_3), 18.37 (1 CH_3), 30.81 (1 CH), 55.31 (1 OCH_3), 59.58 (1 CH), 81.96 (1 CH), 166.26 (1 CO), 170.18 (1 CO). – MS (90 eV): *m/z* (%) = 187 (0.04) [M^+ + 1], 186 (0.74) [M^+], 185 (1), 156 (12), 144 (7), 143 (78), 128 (8), 115 (20), 111 (9), 72 (54), 69 (19), 60 (100).

$C_8H_{14}N_2O_3$ (186.20) Calcd. C 51.61 H 7.57 N 15.04
Found C 52.05 H 7.48 N 14.58

$C_8H_{14}N_2O_3$ (M^+) Calcd. 186.1005 Found 186.1005 (MS)

Major Isomer: R_f = 0.20 [ethyl acetate/methanol (19:1)]. – M.p. 220–221°C. – ^{1}H NMR (90 MHz, $CDCl_3$/TFA): δ = 0.91 (d, *J* = 6.4 Hz, 3H, CH_3), 1.0 (d, *J* = 6.4 Hz, 3H, CH_3), 2.24 (qd, *J* = 6.4, 4.2 Hz, 1H, CH), 3.48 (s, 3H, OCH_3), 3.93 (d, *J* = 4.2 Hz, 1H, CH), 4.95 (s, 1H, CH). – ^{13}C NMR (90 MHz, $CDCl_3$/CD_3OD): δ = 18.25 (1 CH_3), 19.35 (1 CH_3), 33.72 (1 CH), 56.5 (1 OCH_3), 61.91 (1 CH), 82.27 (1 CH), 166.01 (1 CO), 170.99 (1 CO).

$C_8H_{14}N_2O_3$ (186.20) Calcd. C 51.61 H 7.57 N 15.04
Found C 51.59 H 7.55 N 14.70

N-(o-Nitrophenylthio)iminoglycyl-L-alanine Methyl Ester ⟨Methyl (2S)-2-[N-(o-nitrophenylthio)iminoacetyl]aminopropionate⟩ (**14a**): 204 mg (66%). – IR (film): $\tilde{\nu}$ = 3300 (m, NH, br.), 2940 (m, CH), 1750 (s, CO), 1660 (s, CO–NH), 1990, 1560 (s, m, aromat. C=C), 1510, 1330 (s, N=O), 730 (s, aromat. CH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 7.5 Hz, 3H, CH_3), 3.76 (s, 3H, OCH_3), 4.63 (quint, *J* = 7.5 Hz, 1H, CH), 7.36 (ddd, *J* = 8.2, 7.0, and 1.5 Hz, 1H, CH), 7.73 (ddd, *J* = 8.2, 7.0, and 1.5 Hz, 1H, CH), 8.14 (s, 1H, CH), 8.29–8.22 (m, 2H, 2 CH). – ^{13}C NMR (200 MHz, $CDCl_3$): δ = 18.3 (1 CH_3), 48.0 (1 CH), 52.7 (1 CH_3), 125.5 (1 aromat. CH), 125.9 (1 aromat. CH), 126.2 (1 aromat. CH), 134.5 (1 aromat. CH), 137.7 (1 aromat. C), 142.5 (1 aromat. C), 153.6 (1 CH=N), 160.9 (1 CO), 173.0 (1 CO). – MS (70 eV): *m/z* (%) = 311 (21) [M^+], 280 (7), 186 (10), 160 (64), 154 (100), 138 (40), 106 (95), 102 (83), 96 (76), 95 (82), 70 (65).

$C_{17}H_{18}N_2O_2S$ (M^+) Calcd. 311.0576 Found 311.0571 (MS)

α-Methoxy-N-(o-nitrophenylthio)glycyl-L-alanine Methyl Ester ⟨Methyl (2S)-2-[N-(o-nitrophenylthio)-α-methoxyglycyl]aminopropionate⟩ (**15a**): 209 mg (93%). – Because **15a** eliminates methanol during drying in vacuo, thereby partially forming **14a**, the NMR data are extracted from a mixture of **15a** and **14a** (2:1). **15a** is formed as two diastereoisomers (1:1). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43, 1.38 (2 d, *J* = 7 Hz, 3H, CH_3), 3.49 (2 s, 3H, OCH_3), 3.75, 3.73 (2 s, 3H, OCH_3), 4.60–4.47 (m, 2H, 2 CH), 7.13 (br. d, *J* = 7.5 Hz, 1H, NH), 7.30–7.21 (m, 1H, aromat. CH), 7.70–7.62 (m, 1H, aromat. CH), 8.37–8.20 (m, 2H, aromat. CH). – ^{13}C NMR (200 MHz, $CDCl_3$): δ = 18.2, 18.5 (1 CH_3), 52.7 (1 CH), 50.9 (1 CH_3), 55.5, 55.9 (1 CH_3), 91.6, 91.8 (1 CH), 125.1 (1 aromat. CH), 125.2 (1 aromat. CH), 125.6 (1 aromat. CH), 134.2 (1 aromat. CH), 142.4, 142.7 (1 aromat. C), 145.1, 145.3 (1 aromat. C), 167.7, 167.9 (1 CO), 172.8, 172.9 (1 CO).

CAS Registry Numbers

1a: 51514-00-2 / **1b**: 122092-69-7 / **1c**: 57463-87-3 / **1d**: 13437-63-3 / **1e**: 63203-22-5 / **1f**: 79113-32-9 / **1g**: 16816-28-7 / **1h**: 4840-29-3 / **1i**: 58871-93-5 / **1k**: 51803-69-1 / **1l**: 122092-70-0 / **6a**: 122092-71-1 / **6b**: 122092-72-2 / **6c**: 122092-73-3 / **6d**: 122092-74-4 / **6e**: 122092-75-5 / **6f**: 122092-76-6 / **6g**: 122092-77-7 / **6h**: 122092-78-8 / **6k**: 122092-79-9 / **6l**: 122092-80-2 / **7e**: 122092-81-3 / **7g**: 122092-82-4 / **7i**: 122092-83-5 / **8c**: 122092-84-6 / **8i**: 122092-85-7 / **9d**: 122092-86-8 / **9h**: 122092-87-9 / **10h**: 122092-88-0 / **11** (isomer 1): 122092-89-1 / **11** (isomer 2): 122170-10-9 / **12a**: 30907-99-4 / **12b**: 114675-81-9 / **14a**: 122092-90-4 / **14b**: 114675-98-8 / **15a**: 122092-91-5 / glycylglycine: 556-50-3

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[1] In part presented at the „Tagung der Fachgruppe Angewandte Elektrochemie der GDCh", Frankfurt/Main, October 14–16, 1987; the „Chemiedozenten-Tagung", Mainz, March 13–16, 1988, and the "20th European Peptide Symposium", Tübingen, September 4–9, 1988.

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[142/89]