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Diastereoselective radical addition to dehydroalanine derivatives of pantolactone

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Abstract—The diastereoselective synthesis of α-amino acids by radical addition to dehydroalanine derivatives of pantolactone using the stannane method both in the presence and absence of Lewis acid catalysts is reported. The absolute configuration of the newly-generated stereogenic center is highly dependent on the nature of the added radical. Acid hydrolysis afforded the amino acids with excellent yields and without racemization. This approach constitutes a novel method for the asymmetric synthesis of α-amino acids by a radical pathway. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The purpose of this study was to develop a method for the synthesis of unnatural α-amino acids by radical addition to α,β-dehydroamino acids in homogeneous phase. The use of free radicals to create C–C bonds has aroused considerable interest in this area.[1] Conjugate addition to α,β-unsaturated systems is a fundamental process in organic chemistry, and chiral auxiliary-controlled diastereoselective synthesis based on free-radical additions is emerging as an important route to enantiomerically enriched compounds. However, little has been done concerning the diastereoselective conjugate addition of radicals to acyclic systems in solution.[2] In connection with this, we present herein the results that we have obtained on radical additions to dehydroalanine derivatives of pantolactone.

One advantage of addition to dehydroamino acids is the possibility of adding a sterically hindered alkyl or carbohydrate radical to generate non-proteogenic α-amino acids or glycosyl α-amino acids, respectively. Research into radical additions to chiral dehydroamino acids were originally initiated by Crich.[3]

Diastereoselective radical addition (d.e.: 40–92%) to a chiral nickel(II) complex of a Schiff base derivative of dehydroalanine was achieved by Belokon[4] using the stannane method, indicating the *Re* attack of tributyltin hydride on the intermediate radical. However, the preparation of the chiral substrate is long and tedious. Chai[5] demonstrated that addition to chiral methylenepiperazine-2,5-diones using the organomercury method produces only the disubstituted *cis*-isomer, but with low yields of 46–49%.

Beckwith[6] realized an enantioselective synthesis of *C*-glycosyl amino acids (yields: 67–88%) by radical addition of glycosyl halides to (2*R*)-4-methyleneoxazolidin-5-one (d.e.: 100%). The high stereoselectivity of this addition is due to the double asymmetric induction induced by the chiral auxiliary and anomeric stereoelectronic control[7] from the carbohydrate radical. It was also found that when the reaction was performed using the stannane method, the best diastereoisomeric excesses were obtained, whereas the organomercury method provided the best yields.

Pyne's[8] original approach for preparing optically active homoserine derivatives has been achieved via photoinduced radical additions of alcohols and ethers to the chiral 4-methyleneoxazolidin-5-ones. These reactions proceed with moderate yields (17–48%) and low to excellent diastereoselectivities (d.e.: 10–96%), but the photoadducts are prone to epimerization and fail to release the desired amino acids.

Chiral oxazolidinones prepared from lactamide and 2-bromobenzaldehyde followed by *N*-alkylation with

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ethyl bromoacetate and ethyl 2-propionate are suitable for the generation of glycinyl and alaninyl radicals. The control of the stereochemistry proceeds via a 1,5-hydrogen atom transfer mechanism, and in this work Renaud[9] brilliantly introduced the innovative notion of the PRT (protecting-radical translocating group) where the protecting group plays both the role of a radical precursor and a secondary source of chirality. Allylation of these oxazolidinones proceeds with satisfactory yields (59–85%) and diastereoselectivities (d.e.: 32–96%).

Furthermore Naito[10] demonstrated that it is also possible to realize highly diastereoselective syntheses of α-amino acids by radical addition to the Oppolzer's camphor sultam derivative of glyoxylic oxime ether. High chemical yields (57–86%) and diastereoselectivities (80–96%) were observed in the presence of Lewis acids. Reductive cleavage releases the enantiomerically pure α-amino acid of (*R*)-configuration.

The results of these investigations showed that the diastereoselectivity of the reaction depends both on the nature of the nitrogen protecting group and the hydrogen atom transfer to the α-carbon-centered intermediate radical. The use of sterically hindered secondary or tertiary halides is generally recommended to improve both yields and diastereoisomeric excesses.

2. Results and discussion

We studied the stereoselective radical addition to the chiral *N*-phthaloyl dehydroalanine pantolactonyl ester using the stannane method, both in the presence and absence of Lewis acid catalysts, with a view to its development as a possible synthesis of α-amino acids.

The *N*-phthaloyl group was selected because of its strong electron-withdrawing properties, which counterbalance the deactivating effects of the amino group. This was shown by Renaud[11] in the addition of the *tert*-butyl radical to benzyl 2-*N*-phthaloyl-2-butenoate which gave a 41% yield of a 2.3:1 mixture of *anti*:*syn* isomers. The stereoselectivity of the reaction could be explained by the effect of 1,3-allylic strain.[12] The 1,3-allylic strain model is in complete accordance with the pioneering ESR experiments on ester-substituted radicals of Giese,[13] who showed that allylic strain effects are responsible for the 1,2-stereoinduction in acyclic radicals, where the attack of the entering radical on the preferred conformation of the α-prochiral radical center occurs *anti* to the more sterically hindered group.

The pantolactonyl group was chosen since Helmchen[14] demonstrated that Lewis acids such as $TiCl_4$ induce a stable bidentate coordination complex with pantolactonyl acrylate, which amplifies diastereofacial discrimination in pericyclic reactions. By analogy to these reactions, it is expected that Lewis acids will strongly influence the outcome of radical reactions, both in their reactivity as well as their stereoselectivity.[15–17] These results guided our approach to study the effects of Lewis acids in radical additions to dehydroamino esters.

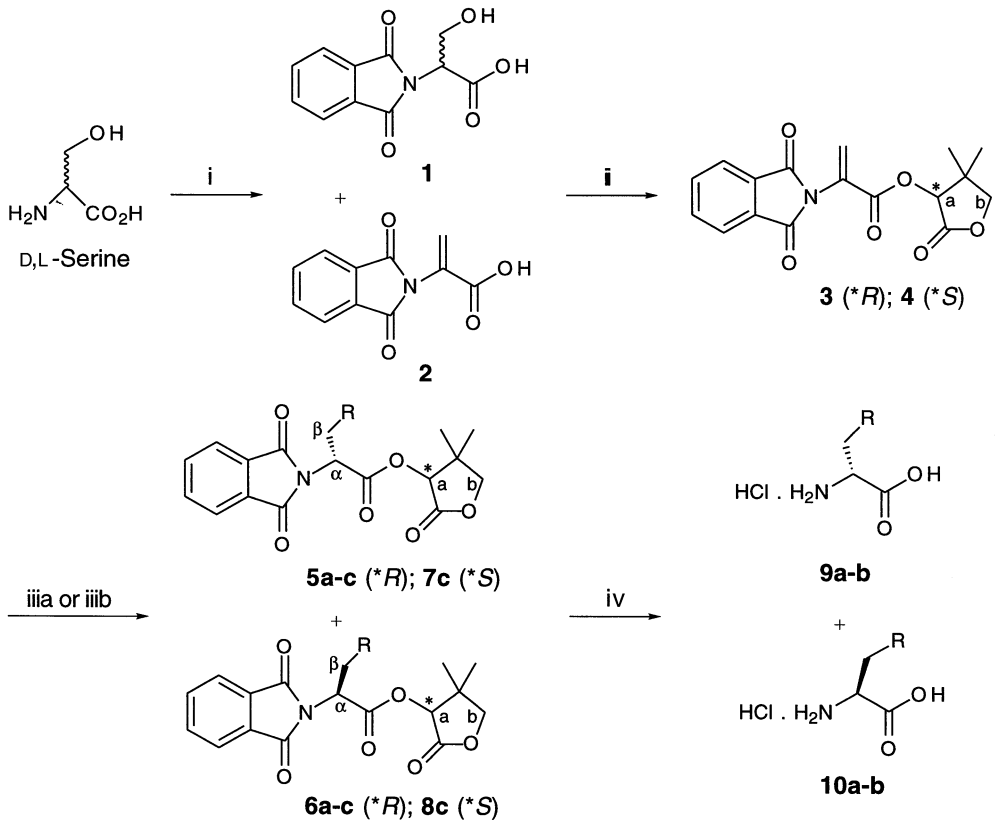
The *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester **3** was easily prepared in two steps from DL-serine. A mixture of DL-serine, phthalic anhydride and triethylamine[18] heated in refluxing toluene with azeotropic elimination of water yielded a mixture of *N*-phthaloyl serine **1** (16%) and *N*-phthaloyl dehydroalanine **2** (50%). Esterification of the mixture of **1** and **2** with (*R*)-pantolactone using DCC/DMAP produced the desired product **3** (61%). During the esterification step, spontaneous dehydration of **2** into **3** occurred (Scheme 1).

In a typical experiment, a solution of the chiral dehydroamino acid **3**, Bu_3SnH and AIBN in benzene was slowly added (90 min) to a refluxing solution of the alkyl halide or glycosyl halide, following the conditions of Vogel and co-workers,[19] according to Scheme 1. After disappearance of the starting material as shown by TLC analysis (1–4 h), chromatography of the crude product, free from organotin residues after treatment with acetonitrile/hexane, yielded a mixture of the diastereoisomeric adducts **5a**–**c** and **6a**–**c**.

The compounds **5a**,**6a**, **5b**,**6b** and **5c**,**6c**, resulting from addition of *tert*-butyl iodide **11**, cyclohexyl iodide **12** and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **13** (TA-glc-Br) onto *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester **3**, respectively, were isolated as colorless powders in 54–60% yields (Table 1; entries 1–3). In all cases, the mixtures of these diastereoisomers were separated, but only by analytical HPLC on a chiral reverse-phase column, as the usual methods failed.

Spectral and chemical analysis of the compounds enabled their structural characterization. COSY $^1H/^1H$ and $^1H/^{13}C$ correlation experiments were required for the assignments of the protons and the carbons in the adducts. Diastereoisomeric excesses were determined via the 250 MHz ^1H NMR spectrum (C_6D_6) of the crude products (Table 1). For **5a**,**6a** (R: *tert*-Bu), the integration of the *tert*-Bu singlet found at 0.95 ppm for the major diastereoisomer was compared to the signal of the minor diastereoisomer at 1.00 ppm, and gave a ratio of 78:22 (entry 1). Integration of the protons of the pantolactonyl moiety for **5b**,**6b** and **5c**,**6c** resulted in a ratio major/minor of 68:32 with cyclohexyl iodide **12** and only of 52:48 in the case of glycosyl bromide **13**, respectively (entries 2 and 3).

To confirm the hypothesis of a mismatched addition in this last reaction, where the configuration of the chiral auxiliary of the (*R*)-pantolactone was counterbalanced by the induction from the carbohydrate radical, we carried out the radical addition of **13** to *N*-phthaloyl dehydroalanine (*S*)-pantolactonyl ester **4**, using the same protocol as for **3**, but from DL-serine and (*S*)-pantolactone (60% yield). The yields of the radical addition to **4** (63%) and **3** were comparable (60%), in contrast the ratio was successfully improved to 78:22, as expected (entries 3 and 4).



Scheme 1. *Reagents and conditions*: (i) phthalic anhydride, Et_3N, toluene, 5 h/Δ; (ii) (*R*)- or (*S*)-2-hydroxy-3,3-dimethyl-γ-butyrolactone (pantolactone), DCC/DMAP, CH_2Cl_2, 15 h, rt; (iiia) RX (*tert*-BuI **11**, *c*-$C_6H_{11}I$ **12**, TA-glc-Br **13**), Bu_3SnH, AIBN, C_6H_6, 1–4 h, 80°C; (iiib) RX (*tert*-BuI **11**), Bu_3SnH (2.0 equiv.), Et_3B (2.0 equiv.), CH_2Cl_2/THF (4/1), 5.5 h, −78 to −20°C; Lewis acids (1.1–2.1 equiv.): $TiCl_4$, $Sm(OTf)_3$, $MgI_2{\cdot}Et_2O$; (iv) HCl (6 M)/glacial acetic acid, 5 h/Δ.

Table 1. Radical additions to dehydroalanine derivatives of pantolactone

Entry	Substrate	RX	Lewis acids (equiv.)	Yield of the diastereoisomers (%)	Maj./min.[c]
1[a]	**3**	**11**	–	**5a**,**6a** (54)	78:22
2[a]	**3**	**12**	–	**5b**,**6b** (60)	68:32
3[a]	**3**	**13**	–	**5c**,**6c** (60)	52:48
4[a]	**4**	**13**	–	**7c**,**8c** (63)	78:22
5[b]	**3**	**11**	$TiCl_4$ (2.2)	**5a**,**6a** (65)	68:32
6[b]	**3**	**11**	$TiCl_4$ (1.1)	**5a**,**6a** (71)	75:25
7[b]	**3**	**11**	$Sm(OTf)_3$ (1.1)	**5a**,**6a** (70)	83:17
8[b]	**3**	**11**	$MgI_2{\cdot}Et_2O$ (1.1)	**5a**,**6a** (48)	79:21

[a] See (iiia) and (iiib) in Scheme 1.
[b] See (iiia) and (iiib) in Scheme 1.
[c] Determined by ^1H NMR (250 MHz).

Next, to determine the configuration of the predominant newly-generated stereogenic center, we simultaneously deprotected the amino and acid functions. Non-racemizing acid hydrolysis[20] of compounds **5a**,**6a** and **5b**,**6b** in refluxing HCl/glacial acetic acid quantitatively released the mixtures of enantiomers **9a**,**10a** and **9b**,**10b** in 90 and 86% yields, respectively. The hydrochlorides **9a**,**10a** were converted into amino acids **9a′**,**10a′** using propylene oxide. Comparison of the specific rotation of the product mixture to the value for the pure enantiomer from the literature, allowed the deduction of the configuration of the predominant product enantiomer and thereby the corresponding predominant diastereoisomer (Table 2). Enantiomeric excesses measured agreed with diastereoisomeric excesses established by NMR before deprotection.

Surprisingly, the additions with *tert*-butyl iodide and cyclohexyl iodide led to opposite configurations of the major isomers, (*S*) and (*R*), respectively. It appeared that the radical hydrogen is added to the conformation which minimized 1,3-allylic strain effects[12] of the first radical obtained by addition of the alkyl group. This particular conformation was dependent upon the bulkiness of the alkyl group introduced and was different for the cyclohexyl and *tert*-butyl groups.

Table 2. Deprotected amino acids

Entry	RX	Yield (%)	$[\alpha]_D^{20}$ lit.	$[\alpha]_D^{20}$ exp.	Configuration of the major enantiomer	Enantiomers Maj./min.[a]	Diastereoisomers Maj./min.[b]
1	*tert*-BuI	**9a′**,**10a′** (90)	(*S*): −12.6[21]	−5.0	(*S*)	**10a′**:**9a′** 70:30	**6a**:**5a** 78:22
2	*c*-$C_6H_{11}I$	**9b**,**10b** (86)	(*R*): −11[22]	−3.8	(*R*)	**9b**:**10b** 68:32	**5b**:**6b** 68:32

[a] Enantiomeric excesses determined by measurement of the specific rotation, $[\alpha]_D^{20}$.
[b] Diastereoisomeric excesses determined by ^1H NMR (250 MHz).

Hydrolysis of the diastereoisomers **5c**,**6c** and **7c**,**8c** resulting from the addition of carbohydrate radical were not performed because of the thermal sensitivity of these compounds, and therefore the configurations of the major diastereoisomers were not established.

Lewis acids were then used in an attempt to increase the diastereoselectivity in these radical additions. Among the variety of Lewis acids evaluated: titanium tetrachloride ($TiCl_4$), samarium triflate ($Sm(OTf)_3$) and magnesium iodide–diethylether ($MgI_2{\cdot}Et_2O$), which have been reported to give the best results,[16,25] were preferred.

In a standard procedure,[26] *tert*-butyl iodide, tributyltin hydride and triethylboron were successively added to a solution containing the chiral dehydroamino ester **3** and a Lewis acid, at low temperature and under a saturated atmosphere of oxygen (Scheme 1). In this reaction, the tandem triethylboron/oxygen plays acts as the radical initiator.[23,24] After purification of the residue, the diastereoisomers **5a**,**6a** were isolated with acceptable yields (48–71%; Table 1, entries 5–8).

Moderate increases in the yields (54–71%; Table 1, entries 1 and 6) and diastereoselectivities (78:22–83:17; entries 1 and 7) were observed. Furthermore, these results suggested, that it was preferable to use 1.1 equiv. instead of 2.2 equiv. of Lewis acid for optimization of the reaction conditions (entries 5 and 6). Moreover, we can report that the best result was obtained in the presence of $Sm(OTf_3)$ (yield: 70%; ratio: 83:17).

3. Conclusion

In conclusion, Lewis acid-catalyzed diastereoselective radical additions onto dehydroamino acid pantolactonic esters were carried out and gave satisfactory diastereoisomeric excesses. The absolute configuration of the predominant product isomer depended greatly on the nature of the entering alkyl radical. Acid hydrolysis released the amino acids in high yields and without racemization.

4. Experimental

Solvents were purified in the usual way. Pantolactone was purchased from Fluka Chemical Co. All other chemicals were commercially pure compounds and were used as received. Thin-layer chromatography was carried out on silica gel 60 F_{254} Merck aluminum sheets. Column chromatography was performed using silica gel Geduran Si 60 (0.63–0.200 mm) supplied by Merck. Capillary melting points were determined with an Electrothermal 9200 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-250 or AC-400 machines. Data are reported as follow: chemical shifts (δ) in ppm with respect to TMS, multiplicity (s: singlet, d: doublet, t: triplet, m: multiplet, br: broad), coupling constants (J) in Hz. Diastereoisomeric excesses were determined on the crude products. IR spectra were recorded with a Perkin–Elmer paragon 1000. Optical rotations were measured for the sodium D line (589 nm) at 20°C with a Perkin–Elmer 141 polarimeter. Mass spectra were recorded on a SX 102 or DX 3200 type spectrometer (JEOL). The matrices used were glycerol or *meta*-nitrobenzyl alcohol. Reverse-phase analytical and preparative HPLC was carried out with a Nucleosil C18 column; HPLC: (fast gradient H_2O/ACN (CH_3CN): 10–100% ACN in 30 min), (Nucleosil column 5 C 18; 250×4.6 mm; flow: 1 mL/min, T column: 30°C). Reverse phase chiral analytical HPLC was carried out with a Nucleosil C18 column (column Chiracel OD, 250×4.6 mm, flow: 1 mL/min, detector 484 Waters, $\lambda = 214$ nm, hexane/isopropanol). A flow rate of 1 mL/min of the solvent, using ACN/H_2O/TFA as eluent, was applied with a Waters Associates pump (Model 510). Elemental analyses were performed by the Service Central d'Analyse, Département Analyse Elémentaire de Vernaison (CNRS-Lyon).

4.1. Preparation of *N*-phthaloyl serine 1 and *N*-phthaloyl dehydroalanine 2

A mixture of DL-serine (5 g, 47.61 mmol), phthalic anhydride (7 g, 47.29 mmol) and triethylamine (0.7 mL) in toluene (250 mL) was heated under reflux under nitrogen atmosphere for 4 h with azeotropic elimination of water with a Dean–Stark apparatus.[18] After removal of the solvent under reduced pressure, ethyl acetate was added and the organic phase was washed with dilute HCl (1 M) to eliminate the unreacted serine, then dried over $MgSO_4$ and filtered and concentrated to give a yellow oil. This oil was purified by column chromatography and the elution with petroleum ether/EtOAc (7/3) afforded *N*-phthaloyl serine **1** and *N*-phthaloyl dehydroalanine **2** as colorless powders.

4.2. *N*-Phthaloyl serine 1

1.78 g (colorless powder); 16% yield; $R_f = 0.1$ (CH_2Cl_2/EtOAc: 1/1+ε AcOH); mp 70–72°C; MS (FAB): $[M+H]^+ = 236$; HPLC (isocratic, H_2O/ACN: 52/48) $t_R = 9.47$ min; ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 4.90 (dd, $J = 11.6$ Hz, $J = 9.2$ Hz, 1H, H_β); 5.14 (dd, $J = 11.6$ Hz, $J = 4.7$ Hz, 2H, $H_{\beta'}$); 5.38 (dd, $J = 9.2$ Hz, $J = 4.7$ Hz, 1H, H_α); 7.72 (m, 2H, ArH); 7.86 (m, 2H, ArH); 8.05 (br s, 1H, OH).

4.3. *N*-Phthaloyl dehydroalanine 2

5.13 g (colorless powder); 50% yield; $R_f = 0.26$ (CH_2Cl_2/EtOAc: 1/1+ ε AcOH); mp 74–75°C (EtOAc); MS (FAB): $[M+H]^+ = 218$; HPLC (isocratic, H_2O/ACN: 52/48) $t_R = 8.47$ min; IR (KBr) ν (cm^{-1}): 1739 (C=O, imide), 1712 (C=O, acid); ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 6.03 (s, 1H, C=C-H); 6.74 (s, 1H, C=C-H); 7.70 (m, 2H, ArH); 7.81 (m, 2H, ArH); 8.60 (br s, 1H, CO_2H). Anal. calcd for $C_{11}H_{17}NO_4$ (217): C, 60.80; H, 3.28; N, 6.44; O, 29.47; found: C, 60.63; H, 3.43; N, 6.37; O, 29.45.

4.4. Preparation of *N*-phthaloyl dehydroalanine (*R*)- or (*S*)-pantolactonyl esters 3 or 4: general procedure

To a mixture of *N*-phthaloyl dehydroalanine **2** (1 mmol), (*R*)- or (*S*)-pantolactone (1.1 mmol) and 4-dimethylaminopyridine (0.1 mmol) in CH_2Cl_2 (6 mL) was added dicyclohexylcarbodiimide (1.2 mmol) at 0°C. The mixture was stirred at room temperature for 12 h. Dicyclohexylurea was removed by filtration and the solution was concentrated under vacuum. The residue was diluted into ethyl acetate (5 mL) and allowed to stand for 1 h at −15°C and again, the remaining dicyclohexylurea was filtered off. The solution was dried over $MgSO_4$ and evaporated under vacuum. The crude oil was purified by column chromatography (petroleum ether/EtOAc: 7/3).

4.5. *N*-Phthaloyl dehydroalanine (*R*)-pantolactonyl ester 3

Following the general procedure, from *N*-phthaloyl dehydroalanine **2** (4.06 g, 18.7 mmol), **3** (3.74 g, 61% yield) was obtained as a colorless solid; $R_f = 0.54$ (petroleum ether/EtOAc: 5/5); mp 122°C (EtOAc/CH_2Cl_2: 5/5); MS (FAB): $[M+H]^+ = 330$; $[\alpha]_D^{20} = -20$ ($c = 1$, $CHCl_3$); HPLC (isocratic, H_2O/ACN: 52/48) $t_R = 21.64$ min; IR (KBr) ν (cm^{-1}): 1793 (C=O, lactone), 1739 (C=O, imide), 1726 (C=O, ester), 1638 (C=C); ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.05 (s, 3H, Me); 1.21 (s, 3H, Me); 4.01 (s, 2H, H_b+$H_{b'}$); 5.40 (s, 1H, H_a); 6.08 (d, $J_{\beta\beta'} = 0.8$ Hz, 1H, H_β); 6.72 (d, $J_{\beta\beta'} = 0.8$ Hz, 1H, $H_{\beta'}$); 7.75–7.88 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.92, 23.05, 40.96, 76.86, 77.04, 124.05, 128.43, 129.56, 132.30, 134.47, 161.71, 166.51, 171.99. Anal. calcd for $C_{17}H_{15}NO_6$ (329): C, 62.00; H, 4.59; N, 4.25; O, 29.15; found: C, 62.00; H, 4.41; N, 4.12; O, 29.47%.

4.6. *N*-Phthaloyl dehydroalanine (*S*)-pantolactonyl ester 4

Following the general procedure, from *N*-phthaloyl dehydroalanine **2** (1.51 g, 6.96 mmol), **4** (1.37 g, 60% yield) was obtained as a colorless solid; $R_f = 0.54$ (petroleum ether/EtOAc: 5/5); mp 122°C (EtOAc/CH_2Cl_2: 5/5); MS (FAB): $[M+H]^+ = 330$; HRMS (FAB) calcd for $C_{17}H_{16}NO_6$ $[M+H]^+ = 330.0978$, found: 330.1024; $[\alpha]_D^{20} = +20$ ($c = 1$; $CHCl_3$); HPLC (isocratic, H_2O/ACN: 55/45) $t_R = 13.51$ min; IR (KBr) ν (cm^{-1}): 1793 (C=O, lactone), 1739 (C=O, imide), 1726 (C=O, ester),1637 (C=C); ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.10 (s, 3H, Me); 1.27 (s, 3H, Me); 4.05 (s, 2H, H_b+$H_{b'}$); 5.45 (s, 1H, H_a); 6.13 (d, $J_{\beta\beta'} = 0.8$ Hz, 1H, H_β); 6.78 (d, $J_{\beta\beta'} = 0.8$ Hz, 1H, $H_{\beta'}$); 7.79–7.94 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.21, 23.40, 41.04, 76.47, 76.63, 124.12, 124.22, 128.47, 129.49, 132.08, 134.81, 135.10, 161.75, 166.55, 171.99.

4.7. Radical addition onto *N*-phthaloyl dehydroalanine (*R*)- and (*S*)-pantolactonyl esters 3 and 4: general procedure

A 0.5 M solution of alkyl iodide **11** or **12** (1.50 mmol) or 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **13** (1.50 mmol) in anhydrous benzene was heated under reflux. Chiral dehydroamino ester **3** or **4** (0.75 mmol), Bu_3SnH (0.97 mmol) and AIBN (0.06 mmol) in anhydrous benzene (5 mL) was added through an automatic syringe in 90 min.[19] The mixture was then heated under reflux for between 1 and 4 h and allowed to cool to 20°C. The solvent was evaporated under vacuum. The residue was dissolved in acetonitrile (10 mL) and washed with hexane (5×5 mL). The acetonitrile phase was dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by column chromatography and the elution with petroleum ether/EtOAc (8/2) afforded a mixture of two diastereoisomers **5a–c**, **6a–c** or **7c**,**8c** which were separated on an analytical HPLC equipped with a chiral reverse-phase column (column Chirasphere Merck, 25 cm×4 mn, flow: 1 mL/min, hexane/isopropanol: 85/15).

4.8. *N*-Phthaloyl (*R*)- and (*S*)-γ-methylleucine (*R*)-pantolactonyl esters 5a,6a

Following the general procedure ($t = 1$ h), from *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester **3** (250 mg, 0.75 mmol), a mixture of **5a**,**6a** (157 mg, 54% yield) was obtained as a colorless solid; $R_f = 0.60$ (petroleum ether/EtOAc: 6/4); mp 144°C (benzene/heptane: 1/9); MS (FAB): $[M+H]^+ = 388$; HRMS (FAB) calcd for $C_{21}H_{26}NO_6$ $[M+H]^+ = 388{,}1760$, found: 388,1777; chiral HPLC (isocratic, hexane/iPrOH: 85/15) $t_{R1} = 10.88$ min, $t_{R2} = 13.83$ min; IR (KBr) ν (cm^{-1}): 1788 (C=O, lactone), 1759 (C=O, imide), 1712 (C=O, ester); ^1H NMR (250 MHz, C_6D_6) δ (ppm): 0.6 (s, 3H, Me min.); 0.65 (s, 3H, Me maj.); 0.70 (s, 3H, Me min.); 0.95 (s, 9H, *tert*-Bu maj.); 1.00 (s, 9H, *tert*-Bu min.); 2.55–2.70 (m, $J_{\beta\beta'} = 7.5$ Hz maj., $J_{\beta\beta'} = 7.0$ Hz min., $J_{\alpha\beta} = 3.8$ Hz, 4H, H_β+$H_{\beta'}$ maj. and H_β+$H_{\beta'}$ min.); 2.90–3.11 (AB syst., $J_{bb'} = 8.9$ Hz, 2H, H_b+$H_{b'}$ maj.); 2.92–

3.15 (AB syst., $J_{bb'}=8.7$ Hz, 2H, $H_b+H_{b'}$ min.); 5.11 (s, 1H, H_a min.); 5.26 (s, 1H, H_a maj.); 5.51 (dd, $J_{\alpha\beta}=8.8$ Hz, $J_{\alpha\beta'}=3.8$ Hz, 2H, H_α maj.+ H_α min.); 6.87 (m, 2H, ArH min.); 6.92 (m, 2H, ArH maj.); 7.56 (m, 2H, ArH maj.); 7.66 (m, 2H, ArH min.); ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 19.91, 20.23, 23.44, 23.05, 29.53, 29.58, 30.78, 30.82, 41.62, 42.02, 49.62, 49.93, 76.43, 76.45, 76.52, 76.70, 123.97, 132.06, 132.15, 134.65, 134.78, 167.94, 169.06, 171.80. Anal. calcd for $C_{21}H_{25}NO_6$ (387): C, 65.17; H, 6.51; N, 3.51; O, 24.81; found: C, 64.93; H, 6.56; N, 3.97; O, 24.54%.

4.9. *N*-Phthaloyl (*R*)- and (*S*)-cyclohexylalanine (*R*)-pantolactonyl esters 5b,6b

Following the general procedure ($t=1$ h), from *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester **3** (250 mg, 0.75 mmol), a mixture of **5b**,**6b** (182 mg, 59% yield) was obtained as a colorless solid; $R_f=0.67$ (petroleum ether/EtOAc: 6/4); mp 61°C (benzene/heptane: 1/9); MS (FAB): $[M+H]^+=414$; HRMS (FAB) calcd for $C_{23}H_{28}NO_6$ $[M+H]^+=414.1917$, found: 414.1866; chiral HPLC (isocratic, hexane/iPrOH: 85/15) $t_{R1}=11.78$ min, $t_{R2}=13.95$ min; IR (KBr) ν (cm^{-1}): 1792 (C=O, lactone), 1730 (C=O, imide), 1717 (C=O, ester); ^{1}H NMR (250 MHz, C_6D_6) δ (ppm): 0.62 (s, 3H, Me maj.); 0.73 (s, 3H, Me maj.); 0.79 (s, 3H, Me min.); 0.86 (s, 3H, Me min.); 0.90–1.20 (m, 12H, Chx maj.+ Chx min.); 1.30–1.50 (m, 2H, H_γ maj.+H_γ min.); 1.50–1.75 (m, 8H, Chx maj.+ Chx min.); 2.26–2.36 (ddd, $J_{\beta\beta'}=14.2$ Hz, $J_{\beta\gamma}=9.5$ Hz, $J_{\alpha\beta}=4.8$ Hz, 1H, H_β min); 2.36–2.45 (ddd, $J_{\beta\beta'}=14.9$ Hz, $J_{\beta\gamma}=9.5$ Hz, $J_{\alpha\beta}=4.8$ Hz, 1H, H_β maj.); 2.55–2.66 (m, 2H, $H_{\beta'}$ maj.+$H_{\beta'}$ min.); 3.09 (d, $J_{bb'}=8.8$ Hz, 1H, H_b min.); 3.11 (d, $J_{bb'}=8.8$ Hz, H_b maj.); 3.20 (d, $J_{bb'}=8.8$ Hz, 1H, $H_{b'}$ maj.); 3.30 (d, $J_{bb'}=8.8$ Hz, 1H, $H_{b'}$ min.); 5.21 (s, 1H, H_a maj.); 5.33 (s, 1H, H_a min.); 5.49 (dd, $J_{\alpha\beta}=10.6$ Hz, $J_{\alpha\beta'}=4.8$ Hz, 1H, H_α maj.); 5.50 (dd, $J_{\alpha\beta}=11.0$ Hz, $J_{\alpha\beta'}=4.8$ Hz, 1H, H_α min.); 6.90 (m, 2H, ArH min.); 6.93 (m, 2H, ArH maj.); 7.54 (m, 2H, ArH maj.); 7.55 (m, 2H, ArH min.); ^{13}C NMR (100 MHz, C_6D_6) δ (ppm):19.47, 19.70, 22.27, 22.66, 26.36, 26.74, 26.57, 26.59, 32.14, 32.18, 33.88, 34.01, 34.86, 34.98, 36.73, 37.01, 39.86, 40.28, 50.38, 50.60, 75.26, 76.34, 76.65, 123.57, 123.63, 132.25, 132.33, 134.08, 134.23, 167.80, 167.91, 169.48, 167.91, 171.22, 171.28. Anal. calcd for $C_{23}H_{27}NO_6$ (413): C, 66.81; H, 6.58; N, 3.38; O, 23.21; found: C, 66.95; H, 6.60; N, 3.51; O, 22.94%.

4.10. (2*R*)- and (2*S*)-(*R*)-Pantolactonyl 2-*N*-phthaloyl-3-(2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranosyl propanoate 5c,6c

Following the general procedure ($t=4$ h), from *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester **3** (250 mg, 0.75 mmol), a mixture of **5c**,**6c** (298 mg, 60% yield) was obtained as a colorless solid; $R_f=0.10$ (petroleum ether/EtOAc: 5/5); mp 95–97°C (petroleum ether); MS (FAB): $[M+H]^+=662$; HRMS (FAB) calcd for $C_{31}H_{36}NO_{15}$ $[M+H]^+=662.2085$, found: 662.2033; chiral HPLC (isocratic, hexane/iPrOH: 85/15) $t_{R1}=$ 16.89 min, $t_{R2}=20.65$ min; IR (KBr) ν (cm^{-1}): 1782 (C=O, lactone), 1743 (C=O, imide), 1723 (C=O, ester); ^{1}H NMR (250 MHz, C_6D_6) δ (ppm): 0.40 (s, 6H, 2Me, Me maj.+Me min.); 0.55 (s, 3H, Me min.); 0.66 (s, 3H, Me maj.); 1.71 (s, 6H, OAc maj.+OAc min.); 1.76 (s, 6H, OAc maj.+OAc min.); 1.78 (s, 6H, OAc maj.+OAc min.); 1.99 (s, 6H, OAc maj.+OAc min.); 3.10 (AB syst., $J_{bb'}=8.8$ Hz, 4H, $H_b+H_{b'}$ maj. and $H_b+H_{b'}$ min.); 3.01–3.22 (m, $J_{\beta\beta'}=15.7$ Hz; $J_{\alpha\beta'}=11.4$ Hz; $J_{\alpha\beta}=3.4$ Hz, 4H, $H_\beta+H_{\beta'}$ maj. and $H_\beta+H_{\beta'}$ min.); 3.86–3.92 (m, $J_{4\text{-}5}=9.1$ Hz, $J_{5\text{-}6'}=5.1$ Hz, $J_{5\text{-}6}=2.4$ Hz, 2H, H_5 maj.+ H_5 min.); 4.20 (dd, $J_{6\text{-}6'}=12.2$ Hz, $J_{5\text{-}6}=2.4$ Hz, 2H, H_6 maj.+H_6 min.); 4.42–4.48 (m, $J_{1\text{-}2}=5.7$ Hz, 2H, H_1 maj.+H_1 min.); 4.50 (dd, $J_{6\text{-}6'}=12.2$ Hz, $J_{5\text{-}6'}=5.1$ Hz, 2H, $H_{6'}$ maj.+$H_{6'}$ min.); 5.25 (s, 2H, H_a maj.+H_a min.); 5.30 (dd, $J_{2\text{-}3}=9.0$ Hz; $J_{1\text{-}2}=5.7$ Hz, 2H, H_2 maj.+H_2 min.); 5.31 (t, $J_{4\text{-}5}=9.1$ Hz; $J_{3\text{-}4}=9.0$ Hz, 2H, H_4 maj.+H_4 min.); 5.61 (dd, $J_{\alpha\beta'}=11.4$ Hz; $J_{\alpha\beta}=3.4$ Hz, 2H, H_α maj.+H_α min.); 5.73 (t, $J_{2\text{-}3}=J_{3\text{-}4}=$ 9.0 Hz, 2H, H_3 maj.+H_3 min.); 6.90 (m, 2H, ArH); 7.48 (m, 2H, ArH); ^{13}C NMR (100 MHz, C_6D_6): 17.81, 18.03, 18.61, 18.68, 18.75, 18.81, 18.86, 19.03, 19.73, 20.63, 21.03, 23.78, 47.17, 60.69, 67.32, 67.65, 68.67, 68.87, 69.20, 73.66,75.25, 122.12, 122.16, 130.51, 130.83, 132.57, 132.74, 166.19, 167.58, 167.78, 167.83, 167.97, 168.09, 168.17, 168.52, 165.98, 168.80, 1693. Anal. calcd for $C_{31}H_{35}NO_{15}$ (661): C, 56.28; H, 5.29; N, 2.92; O, 35.05; found: C, 56.28; H, 5.29; N, 2.13; O, 36.30%.

4.11. (2*R*)- and (2*S*)-(*S*)-Pantolactonyl 2-*N*-phthaloyl-3-(2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranosyl propanoate 7c,8c

Following the general procedure ($t=4$ h), from *N*-phthaloyl dehydroalanine (*S*)-pantolactonyl ester **4** (250 mg, 0.75 mmol), a mixture of **7c**,**8c** (312 mg, 63% yield) was obtained as a colorless solid; $R_f=0.10$ (petroleum ether/EtOAc: 5/5); mp 92°C (petroleum ether); MS (FAB): $[M+H]^+=662$; HRMS (FAB) calcd for $C_{31}H_{36}NO_{15}$ $[M+H]^+=662.2085$, found: 662.2033; chiral HPLC (isocratic, hexane/iPrOH: 15/85) $t_{R1}=7.61$ min, $t_{R2}=20.65$ min; IR (KBr) ν (cm^{-1}): 1794 (C=O, lactone), 1752 (C=O, imide), 1721 (C=O, ester); ^{1}H NMR (250 MHz, C_6D_6) δ (ppm): 0.71 (s, 3H, Me); 0.76 (s, 3H, Me); 1.77 (s, 3H, OAc); 1.79 (s, 6H, 2OAc); 1.99 (s, 3H, OAc); 3.16 (ddd, $J=7.0$ Hz, $J=4.1$ Hz, $J=12.1$ Hz, 1H, H_β); 3.18 (AB syst., $J=8.9$ Hz, 2H, $H_b+H_{b'}$); 3.25 (ddd, $J=12.1$ Hz, $J=11.4$ Hz, $J=7.3$ Hz, 1H, $H_{\beta'}$); 4.09 (ddd, $J=8.6$ Hz, $J=5.2$ Hz, $J=2.6$ Hz, 1H, H_5); 4.24 (dd, $J=12.1$ Hz, $J=2.6$ Hz, 1H, H_6); 4.47 (dd, $J=12.1$ Hz, $J=5.2$ Hz, 1H, $H_{6'}$); 4.42–4.51 (m, 1H, H_1); 5.17 (s, 1H, Ha); 5.30 (t, 1H, H_4, $J=8.8$ Hz); 5.32 (dd, $J=5.7$ Hz, $J=8.8$ Hz, 1H, H_2); 5.66 (dd, $J=11.4$ Hz, $J=4.0$ Hz, 1H, H_α); 5.74 (t, $J=8.8$ Hz, 1H, H_3); 6.94 (m, 2H, ArH); 7.53 (m, 2H, ArH); ^{13}C NMR (100 MHz, C_6D_6): 19.57, 20.25, 20.37, 20.41, 20.57, 22.47, 25.36, 40.02, 49.02, 62.56, 68.96, 69.30, 70.40, 70.70, 70.94, 75.39, 76.94, 123.78, 132.40, 134.28, 168.04, 169.05, 169.60, 169.68, 169.95, 170.81, 171.28.

4.12. Hydrolysis of *N*-phthaloyl pantolactonyl esters 5a,6a or 5b,6b: general procedure

A mixture of *N*-phthaloyl pantolactonyl esters **5a**,**6a** or **5b**,**6b** (0.5 mmol), acetic acid (1.4 mL) and 6 M aqueous

HCl solution (14 mL) was heated under reflux until completion of the hydrolysis[20] (6 h). The reaction was monitored by TLC (hexane/EtOAc 5/5). The solution was allowed to cool to room temperature and the volatile products were eliminated under reduced pressure. Water (15 mL) was added to the residue and the aqueous phase was washed with EtOAc (3×15 mL). Evaporation under vacuum of the aqueous layer gave the free amino acids as enantiomers **9a**,**10a** or **9b**,**10b**.

4.13. (*S*)- and (*R*)-γ-Methylleucine hydrochlorides 9a,10a

Following the general procedure, from *N*-phthaloyl pantolactonyl esters **5a**,**6a** (427 mg, 1.10 mmol), **9a**,**10a** (180 mg, 90% yield) were obtained as colorless solids; mp (scalemic 70/30) >300°C (petroleum ether); MS (ESI): $[M+H]^+=146$; HPLC (fast gradient) $t_R=4.11$ min; IR (KBr) ν (cm^{-1}): 3348 (NH_3^+); 3204–2636 (OH, acid); 1743 (C=O); ^1H NMR (250 MHz, D_2O) δ (ppm): 0.99 (s, 9H, *tert*-Bu); 1.68 (dd, $J=14.9$ Hz, $J=6.3$ Hz, 1H, H_β); 2.20 (dd, $J=14.9$ Hz, $J=5.3$ Hz, 1H, $H_{\beta'}$); 4.41 (dd, $J=6.3$ Hz, $J=5.3$ Hz, 1H, H_α).

4.14. (*S*)- and (*R*)-γ-Methylleucine 9a′,10a′

To the hydrochlorides **9a**,**10a** (60 mg, 0.33 mmol) in anhydrous ethanol (5 mL) was added a large excess of propylene oxide[27] (0.20 mL, 2.35 mmol). The mixture was heated under reflux for 20 min then concentrated under vacuum to quantitatively afford the amino acids **9a′**,**10a′** (48 mg); mp (scalemic 70/30) 234–235°C (H_2O); ESI-MS: $[M+H]^+=146$; $[\alpha]_D^{20}=-5.00$ ($c=1$, H_2O), ($[\alpha]_D^{20}$ lit.[21] $=-12.6$ ($c=1$, H_2O), (*S*) config.); HPLC (isocratic, H_2O/MeOH: 95/5) $t_R=4.00$ min; IR (KBr) ν (cm^{-1}): 3136–2500 (OH acid), 1744 (C=O, acid); ^1H NMR (250 MHz, D_2O) δ (ppm): 1.10 (s, 9H, *tert*-Bu); 1.71 (dd, $J=14.8$ Hz, $J=7.3$ Hz, 1H, H_β); 2.01 (dd, $J=14.8$ Hz, $J=4.8$ Hz, 1H, $H_{\beta'}$); 4.41 (dd, $J=7.3$ Hz, $J=4.8$ Hz, 1H, H_α).

4.15. (*S*)- and (*R*)-Cyclohexylalanine hydrochlorides 9b,10b

Following the general procedure, from *N*-phthaloyl pantolactonyl esters **5b**,**6b** (500 mg, 1.21 mmol), **9b**,**10b** (179 mg, 86% yield) were obtained as colorless solids; $R_f=0.76$ (*n*-BuOH/AcOH/H_2O: 4/4/1); mp (scalemic 70/30) 298°C (petroleum ether/EtOAC 5/5); MS (FAB): $[M+H]^+=172$; MS (ESI): $[M+H]^+=172$; HRMS (FAB) calcd for $C_{31}H_{36}NO_{15}$ $[M+H]^+=172.1338$, found: 172.1291; $[\alpha]_D^{20}=-3.8$ ($c=0.53$, H_2O) ($[\alpha]_D^{20}$ lit.[24] $=-11$+or -1 ($c=1$, HCl), (*R*) config.); HPLC (fast gradient) $t_R=3.71$ min; IR (KBr) ν (cm^{-1}): 3386 (NH_3^+); 3640–2542 (OH, acid), 1747 (C=O, acid); ^1H NMR (250 MHz, D_2O) δ (ppm): 0.97–1.09 (m, 2H, Chx); 1.26–1.34 (m, 3H, Chx); 1.42–1.58 (m, 1H, H_γ of Chx); 1.70–1.92 (m, 6 H, 5H of Chx+H_β); 1.92 (ddd, $J=14.2$ Hz, $J=8.5$ Hz, $J=5.5$ Hz, 1H, $H_{\beta'}$); 4.07 (dd, $J=8.5$ Hz, $J=5.5$ Hz, 1H, H_α).

4.16. Radical addition of *tert*-butyl iodide to *N*-phthaloyl dehydroalanine (*R*)-pantolactonyl ester 3 catalyzed by Lewis acids: general procedure

To a 0.04 M solution of **3** (250 mg, 0.75 mmol) in CH_2Cl_2/THF (4/1) at −78°C under a blanket of oxygen was added the Lewis acid[†] (1.1–2.2 equiv.). *tert*-Butyl iodide (0.45 mL, 3.75 mmol), Bu_3SnH (0.4 mL, 1.50 mmol) and triethylborane (1 M in hexane, 1.5 mL, 1.5 mmol) were successively added dropwise to the solution.[26] The reaction mixture was stirred at −78°C for 5.5 h. After completion of the reaction, the crude residue was diluted with Et_2O (30 mL), washed with 10% HCl (2×15 mL) and brine. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/EtOAc: 4/1) and gave a mixture of the diastereoisomers **5a**,**6a** (Table 1, entries 5–8) whose characteristics were previously given.

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[†] $MgI_2{\cdot}Et_2O$ was freshly prepared.[28]

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